An important aspect in device technology is the processing of GaAs to produce highly-resolved etch patterns on the substrate. This is done typically on the GaAs(100) surface. Recently, a number of methods, all using chlorinated vapor reactants, have been applied to fabrication of GaAs devices. In spite of these technological advances, the understanding of the chemistry of the surface reaction on a fundamental level is still rudimentary. Practical etching involves a combination of chemical phenomenon and physical sputtering, in the presence of a mixture of chlorine containing gases to achieve material removal. The complexity of these processes precludes them as experiments for understanding the mechanisms responsible for etching. A simpler approach, used here, involves
thermal etching and electron-induced desorption processes to study the material removed after a GaAs(100) surface is exposed to molecular chlorine.

Another important aspect of device technology involves the atomic level interactions between metals and semiconductors as they are brought into contact. In this vein it has been found that sulfur containing compounds tend to lower the Schottky barrier height at the GaAs(100) surface, and thereby produce ohmic contacts at the metal-semiconductor interface. As with the GaAs/chlorine system, information on the GaAs/sulfur system is by no means conclusive. Molecular sulfur, hydrogen sulfide, as well as alkaline sulfides have all been used to deposit sulfur on the surface. This study concentrates on molecular sulfur and H$_2$S and the very different behavior between the two upon adsorption and subsequent desorption from the GaAs(100) surface.

These experiments on clean, chlorine and sulfur covered surfaces were all performed on well characterized GaAs(100) substrates either cleaned in situ by ion bombardment and annealing (IBA) techniques or grown in situ by molecular beam epitaxy (MBE). The information was gathered using standard surface science techniques under ultra-high vacuum (UHV) conditions. These techniques allow investigation of structure, composition and reaction present at the surface of materials.
GaAs(100) Surface Chemistry: Interactions
with Molecular Chlorine and Sulfur Compounds

by

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Date thesis is presented April 20, 1990

Typed for Scott M. Mokler by Scott M. Mokler
This work is dedicated to my brother

J. Matthew Mokler

May 27, 1959 - Dec. 6, 1986
ACKNOWLEDGEMENT

This work would have never begun, let alone be completed, without the careful guidance of Philip Watson, advisor, colleague, and friend. Thank-you, Phil.

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# TABLE OF CONTENTS

I. Introduction ........................................... 1

II. Experimental Techniques ................................. 6
   A. Ultra-High Vacuum (UHV) .......................... 6
   B. Auger Electron Spectroscopy (AES) ................. 12
   C. Low Energy Electron Diffraction (LEED) .......... 24
   D. Desorption Spectroscopy ............................ 37
      1. Thermal Desorption Spectroscopy (TDS) ....... 42
      2. Electron Stimulated Desorption (ESD) ....... 49

III. Background ............................................. 58

IV. Experiments ............................................. 70
   A. Adsorption and Thermal Desorption of Chlorine from GaAs(100) Surfaces .......... 71
      1. Introduction .................................... 71
      2. Experimental ................................... 72
      3. Results ....................................... 75
      4. Discussion .................................... 92
      5. Conclusions .................................. 104
   B. Electron Stimulated Desorption of Chlorine from GaAs(100) Surfaces .......... 106
      1. Introduction .................................... 106
      2. Results ....................................... 107
      3. Discussion .................................... 115
      4. Conclusions .................................. 119
   C. Interactions of $S_2$ and $H_2S$ with the GaAs(100) Surface:
      An Adsorption/Desorption Study ....................... 121
      1. Introduction .................................... 121
      2. Results ....................................... 124
      3. Discussion .................................... 139
      4. Conclusions .................................. 147

V. Conclusions ............................................. 149

VI. Bibliography ........................................... 152

VII. Appendix ............................................. 158
     Laboratory Procedures ................................. 158
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>II.1</td>
<td>15</td>
</tr>
<tr>
<td>II.2</td>
<td>18</td>
</tr>
<tr>
<td>II.3</td>
<td>21</td>
</tr>
<tr>
<td>II.4</td>
<td>22</td>
</tr>
<tr>
<td>II.5</td>
<td>28</td>
</tr>
<tr>
<td>II.6</td>
<td>38</td>
</tr>
<tr>
<td>II.7</td>
<td>41</td>
</tr>
<tr>
<td>II.8</td>
<td>44</td>
</tr>
<tr>
<td>II.9</td>
<td>47</td>
</tr>
<tr>
<td>II.10</td>
<td>53</td>
</tr>
<tr>
<td>II.11</td>
<td>55</td>
</tr>
<tr>
<td>III.1</td>
<td>59</td>
</tr>
<tr>
<td>III.2</td>
<td>61</td>
</tr>
</tbody>
</table>

II.1 Energy level diagram for KL₂L₃ Auger electron.

II.2 Schematic diagram for retarding field analyzer (RFA) detection system.

II.3 Electron intensity signal vs. retarding field with first and second derivative.

II.4 Schematic diagram for cylindrical mirror analyzer (CMA) detections system.

II.5 One dimensional plane wave scattering from evenly spaced scattering centers.

II.6 Lennard-Jones potential used to describe adsorbate-substrate interaction during physisorption.

II.7 Adsorption potential between adsorbate and surface. Positive $E_A$ describes activated process.

II.8 Shape of first and second order desorption curves. Second order is nearly symmetric while first order is skewed.

II.9 Desorption maximum vs. temperature at different surface coverages. $\beta_1$ and $\beta_2$ result from two different adsorption sites.

II.10 Menzel-Gomer-Redhead potential curves used to describe electron stimulated desorption (ESD).

II.11 Knotek-Fiebelman (KF) model for EDS from maximal valency compounds.

III.1 Crystal structure for zinc-blende compounds.

III.2 Low-index faces of ideally terminated GaAs surfaces.
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>III.3</td>
<td>GaAs(100) $c(2\times8)$ and $(2\times4)$ reconstructions from scanning tunneling microscopy (STM) data of Pashley.</td>
<td>69</td>
</tr>
<tr>
<td>IV.A.1</td>
<td>Chlorine uptake on GaAs(100) as measured by Auger spectroscopy for As (squares) vs. Ga (circles) stabilized reconstructions. The slope of the initial uptake results in a ratio of the initial sticking coefficients of $S_{As}/S_{Ga}=0.72$.</td>
<td>76</td>
</tr>
<tr>
<td>IV.A.2</td>
<td>Auger intensity of As and Ga during chlorine adsorption on Ga and As stabilized surfaces. The Ga intensity has been doubled in order to plot it on the same scale as As.</td>
<td>79</td>
</tr>
<tr>
<td>IV.A.3</td>
<td>Chlorine Auger (183 eV) signal during adsorption on GaAs(100) on MBE $c(2\times8)$ and sputter damaged surface. The Cl gun was operated at one-half the operating current used in Figure 1, hence the difference in exposure time.</td>
<td>82</td>
</tr>
<tr>
<td>IV.A.4</td>
<td>Ga(55 eV) and As(31 eV) Auger signals during TDS from a Cl covered Ga-stabilized surface. Similar behavior is seen on the As-stabilized surface.</td>
<td>84</td>
</tr>
<tr>
<td>IV.A.5</td>
<td>Arsenic dimer desorption from clean GaAs(100) surface reconstructions. Region A shows (1x1) and $c(2\times8)$ LEED patterns. Region B shows (1x6) and $(4\times6)$ diffraction patterns. Region C is the Ga-rich surface and shows a $(4\times1)$ or $c(8\times2)$ reconstruction. Starting a TDS scan with an already As depleted surface, i.e. the $c(8\times2)$, results in no dimer desorption below 625 °C.</td>
<td>88</td>
</tr>
<tr>
<td>IV.A.6</td>
<td>TDS of the chlorine saturated GaAs(100)-(1x1) surface. No higher chlorides of either Ga or As desorb.</td>
<td>89</td>
</tr>
</tbody>
</table>
LIST OF FIGURES (cont'd)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV.A.7.</td>
<td>TDS of the chlorine saturated GaAs(100)-c(8x2) surface. No higher chlorides of either Ga of As desorb.</td>
<td>91</td>
</tr>
<tr>
<td>IV.A.8</td>
<td>As₂ dimer desorption from the clean and Cl covered c(8x2) surface.</td>
<td>93</td>
</tr>
<tr>
<td>IV.B.1</td>
<td>The uptake of chlorine on an As-rich(1x1) GaAs(100) surface monitored with the Cl(183 eV) Auger signal. The chlorine exposure is the time for which the electrochemical Chlorine source was turned on at a current of 150 μA.</td>
<td>108</td>
</tr>
<tr>
<td>IV.B.2</td>
<td>The effect of a 1000 eV electron beam used for Auger analysis, at 26.0 and 15.0 μA beam currents, on the Cl (183 eV) Auger signal from chlorine adsorbed on GaAs(100). The solid lines are bi-exponential decay best fits for the two ESD processes with cross-sections of approximately $1 \times 10^{-18}$ cm² and $2 \times 10^{-19}$ cm².</td>
<td>110</td>
</tr>
<tr>
<td>IV.B.3</td>
<td>A comparison of the rate of removal of surface chlorine from GaAs(100) as monitored by the decay of the Cl (183 eV) Auger signal (solid line), and the appearance of Cl atoms in the gas phase, measured by the 35 AMU mass spectrometer signal (filled circles).</td>
<td>111</td>
</tr>
<tr>
<td>IV.B.4</td>
<td>An experiment to create a &quot;hole&quot; in a chlorine adlayer on GaAs(100) and observe any migration of chlorine into the depleted region from its surroundings. The chlorine adsorption was monitored with a rastered beam to avoid ESD. The chlorine source was then turned off and the beam kept stationary to create a Cl-deficient region by ESD. The electron beam was then turned off completely except for very short measurement of the Cl Auger intensity at 183 eV at 5 minute intervals.</td>
<td>114</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES (cont'd)

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV.C.1</td>
<td>The uptake of sulfur on a Ga-rich c(8x2) GaAs(100) surface monitored with the S(152 eV) Auger signal. The sulfur exposure is the time for which the electrochemical sulfur source was turned on at a current of 500 mA.</td>
<td>125</td>
</tr>
<tr>
<td>IV.C.2</td>
<td>Thermal desorption of GaS₂ and AsS₂ from a Ga-rich c(8x2) GaAs(100) surface which has been saturated with S₂. The products are monitored by mass spectrometry.</td>
<td>126</td>
</tr>
<tr>
<td>IV.C.3</td>
<td>Thermal desorption of GaS and AsS from a Ga-rich c(8x2) GaAs(100) surface after S₂ saturation, presumably due to cracking of the disulfides.</td>
<td>127</td>
</tr>
<tr>
<td>IV.C.4</td>
<td>Thermal desorption of GaS and AsS after fractional coverage of the GaAs(100) surface by S₂. No disulfides or low temperature monosulfides are seen.</td>
<td>128</td>
</tr>
<tr>
<td>IV.C.5</td>
<td>The uptake of H₂S on a Ga-rich c(8x2) GaAs(100) surface monitored with the S(152 eV) Auger signal. The uptake is initially rapid, and slows after 100 Langmuirs of exposure. The x-axis is plotted in log scale.</td>
<td>130</td>
</tr>
<tr>
<td>IV.C.6</td>
<td>Thermal desorption from an H₂S saturated Ga-rich GaAs(100)-c(8x2) surface. No disulfides or low temperature monosulfides are seen.</td>
<td>131</td>
</tr>
<tr>
<td>IV.C.7</td>
<td>Sulfur 152 eV Auger signal during thermal treatment of H₂S saturated GaAs(100) Ga-stabilized surface. Essentially all sulfur is removed by heating to 625°C.</td>
<td>133</td>
</tr>
<tr>
<td>IV.C.8</td>
<td>Desorption of GaH and AsH₃ after H₂S saturation of GaAs(100)-c(8x2) surface.</td>
<td>134</td>
</tr>
<tr>
<td>IV.C.9</td>
<td>Etching of GaS and AsS from Ga-stabilized surface as a function of temperature while in an ambient of H₂S gas.</td>
<td>135</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>----------</td>
<td>------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>IV.C.10</td>
<td>Etching of Ga and As hydrides at 200°C when the GaAs(100) surface is exposed to H\textsubscript{2}S gas.</td>
<td>136</td>
</tr>
<tr>
<td>IV.C.11</td>
<td>LEED (1,1) beam profile at 120 eV as a function of surface preparation. A surface treated with H\textsubscript{2}S shows a beam profile with a FWHM which is 60% of that which is simply annealed at the same temperature.</td>
<td>138</td>
</tr>
<tr>
<td>IV.C.12</td>
<td>No Ga or As hydride etching is seen to occur at 200°C in an H\textsubscript{2} ambient. GaAs has been found to be inert to molecular hydrogen.</td>
<td>140</td>
</tr>
<tr>
<td>IV.C.13</td>
<td>Schematic representation of the interaction of H\textsubscript{2}S with the GaAs(100) surface. This mechanism results in the formation of surface hydrides and sulfides and is presumed to occur at surface defect locations.</td>
<td>145</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>III.1</td>
<td>General physical properties of gallium arsenide.</td>
<td>60</td>
</tr>
<tr>
<td>III.2</td>
<td>Gallium arsenide reconstructions with measured arsenic coverages in surface layer.</td>
<td>65</td>
</tr>
<tr>
<td>IV.A.1</td>
<td>Desorption products from clean and chlorine covered GaAs(100) surfaces.</td>
<td>86</td>
</tr>
<tr>
<td>IV.A.2</td>
<td>Bond strengths of diatomic molecules relevent to Cl adsorption on GaAs.</td>
<td>101</td>
</tr>
<tr>
<td>IV.B.1</td>
<td>Calculated cross-sections for electron stimulated desorption of chlorine from GaAs(100).</td>
<td>117</td>
</tr>
<tr>
<td>IV.C.1</td>
<td>Bond strengths of diatomic molecules relevant to sulfur adsorption on GaAs.</td>
<td>144</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

Recent advances in development and application of semiconducting devices have been revolutionary. In highly technological applications and in every day life, the use of these devices has changed the way we think and the way we live. A computing machine which just ten years ago filled an entire room, now rests on a table top in nearly every office or home. Although this recent progress is astounding, projections indicate that the applications for the existing devices and the development of better and faster devices is just beginning to be exploited. This technological explosion, however, has come at the expense of a detailed understanding of the processes which occur both during operation, and in the production of these devices.

In modern semiconductor device technology speed and precision are of utmost importance. The fastest devices in existing computers can switch a current on or off in about a billionth of a second [1]. However, faster
devices are still desired. One way to speed the operation of semiconductor devices is to make them smaller, thereby reducing the distance electrons carrying the signal must travel. This increases the surface/bulk ratio, making surface contributions to the device very important. Another way to speed the operation is to increase the velocity of the electrons that flow through it. Technologies adopting this approach are based not on silicon, but on the semiconducting compound gallium arsenide, GaAs. The result of these two factors is that controlling the properties of GaAs surfaces is a very important aspect of the production of faster and better quality semiconducting devices.

Crystalline GaAs consists of the group III Ga and group V As atoms. Hence, it is part of the family of semiconducting compounds known as III-V materials. GaAs shares a number of properties with other III-V compounds which will be discussed in detail in section 3.

GaAs(110) is the natural cleavage plane and therefore (110) surfaces can be easily generated by simply cleaving the crystal in vacuum. Therefore, it has received the most attention of the various GaAs faces [2-10]. The GaAs(100) surfaces, on the other hand, is not so easily prepared and not nearly as well understood. It is the (100) surface, however, which is technologically the most
important. Recent progress in gas-phase epitaxial growth of GaAs, in particular molecular beam epitaxy (MBE), has allowed for growth of semiconducting layers separated by conducting or insulating layers to be prepared on a microscopic level. This progress has led to the development of GaAs based lasers and diodes which otherwise would be difficult to produce. Predominantly, studies of epitaxial growth processes have occurred on the (100) surface of GaAs.

Although there has been much development in the understanding of growth kinetics, the actual surface structure of GaAs(100) has received relatively little attention. This is due in part to the various reconstructions that occur on the GaAs(100) surface. These reconstructions, which can be investigated by diffraction techniques, result in large and complex unit cells. Structure determination is further complicated since GaAs is a compound rather than an elemental semiconductor. Until recently most structure determinations were performed on elemental substrates.

An important aspect in device technology is processing the GaAs to produce highly-resolved etch patterns on the substrate. Again, this is predominantly done on the (100) surface. Recently, various forms of etching such as reactive ion-etching [11], reactive ion
beam etching [12], and ion beam assisted etching [13] all using chlorinated vapor reactants have been applied to fabrication of GaAs devices. In spite of these technological advances, understanding of the etching process on a fundamental level is still rudimentary. This is mainly due to the fact that practical etching involves a combination of chemical phenomenon and physical sputtering, or damage production, in the presence of a mixture of chlorine containing gases to achieve material removal. The complexity of these processes precludes them as experiments for understanding the mechanisms responsible for etching. A simpler approach used here, involves thermal etching and electron-induced desorption processes to study the material removed after a GaAs(100) surface is exposed to molecular chlorine.

Another important aspect of device technology involves the atomic level interactions between metals and semiconductors as they are brought into contact. Recently there have been a number of studies [14-19] concerning GaAs(100) contacts made to such metals as Al, Au and Ag. In this vein it has been found [20] that sulfur containing compounds, when adsorbed onto the semiconductor surface, tend to lower the Schottky barrier height and thereby produce ohmic contacts at the metal-
semiconductor interface. As with the GaAs/chlorine system, information on the GaAs/sulfur system is by no means conclusive. Molecular sulfur, hydrogen sulfide $\text{H}_2\text{S}$, as well as alkaline sulfides have all been used to deposit sulfur on the surface. This study concentrates on molecular sulfur and $\text{H}_2\text{S}$ and the very different behavior between the two upon adsorption and subsequent thermal desorption from the GaAs(100) surface.

These experiments on clean, chlorine and sulfur covered surfaces were all performed on well characterized GaAs(100) substrates either cleaned in situ by ion bombardment and annealing (IBA) techniques or grown in situ by molecular beam epitaxy (MBE). The information was gathered using standard surface science techniques under ultra-high vacuum (UHV) conditions. These techniques allow investigation of surface structure, composition and reaction, and will be described fully in section II.
II. EXPERIMENTAL TECHNIQUES

A. Ultra-High Vacuum (UHV)

One of the most important aspects of studying the surface of any material is that the surface be clean. This is achieved by studying surfaces under the special condition of ultra-high vacuum (UHV). A major reason, in fact, for the development of modern surface science has been the commercial availability and subsequent development of convenient UHV components since the early 1960's. Early work, prior to this time, was carried out in glass vacuum systems using liquid N\textsubscript{2} trapped Hg diffusion pumps [21]. The surface science instrumentation had to be incorporated into these sealed glass vessels with electrical connections made through glass-to-metal seals in the containment vessel. Modern surface science involves the use of many different techniques in the same vessel by mounting each on a stainless steel flange which is sealed to a stainless steel chamber using copper gasket seals. In addition to the development of these demountable metal flanges, great use is also made of ion pumps which require only electrical power to operate and do not require liquid N\textsubscript{2}
and the regular attention that this implies.

In order to study the properties of a surface, it is clear that the composition of the surface must remain essentially constant throughout the duration of the experiment. This means that the rate of arrival of reactive species from the surrounding gas phase must be as low as possible. A reasonable criterion would be that no more than a few percent of an atomic layer of atoms should attach themselves to the surface throughout the duration of a typical experiment.

From the simple kinetic theory of gases the rate of arrival of atoms or molecules from a gas of number density \( n \) per unit volume and with an average velocity \( c \), is

\[
 r = \frac{1}{4} nc_a \quad \text{(II.1)}
\]

Equating the kinetic energy of the particle of mass \( m \) with a root mean square velocity \( c_{\text{rms}} \) to their thermal energy determined by the absolute temperature \( T \) and Boltzmann's constant \( k_b \), gives

\[
 c_{\text{rms}}^2 = \frac{3k_bT}{m} \quad \text{(II.2)}
\]

Finally, using the relationship between the two velocities

\[
 c_a = \left( \frac{8}{3\pi} \right)^{1/2} c_{\text{rms}} \quad \text{(II.3)}
\]

and defining the pressure as

\[
 P = nk_bT \quad \text{(II.4)}
\]
leads an expression relating the rate of arrival to the pressure

\[ r = P \left( 2\pi k_b T m \right)^{-1/2} \]  \hspace{1cm} (II.5)

A convenient form of the expression in which \( P \) is expressed in torr, \( T \) in Kelvin and \( m \) is substituted by molecular weight \( M \) multiplied by the atomic mass unit is

\[ r = 3.5 \times 10^{22} \frac{P}{(TM)^{1/2}} \]  \hspace{1cm} (II.6)

For example, \( N_2 \) molecules at room temperature and one torr have an arrival rate of \( 3.9 \times 10^{20} \) molecules cm\(^{-2}\) s\(^{-1}\).

Although the arrival rate is dependant upon temperature, atomic mass and pressure, for experimental work it is convenient to define coverage simply in terms of pressure. In doing so an assumption is made that a single complete atomic layer consists of about \( 1 \times 10^{15} \) atoms (or molecules) cm\(^{-2}\); and that all atoms or molecules arriving at the surface stick to and are incorporated into this monolayer. Thus, a Langmuir is defined as

\[ L = 1 \times 10^{-6} \text{ torr-sec} \]

For the example of \( N_2 \) then, at a pressure of one torr, monolayer coverage occurs in about \( 2.5 \times 10^{-6} \) sec. If the pressure were \( 10^{-6} \) torr however, a monolayer coverage would require 3 seconds of exposure to the \( N_2 \). At \( 10^{-9} \) torr, exposure time is on the order of an hour. This means that if all gas atoms or molecules did indeed stick to the surface, pressures of \( 10^{-10} \) torr or better are
required to insure that contamination of the surface does not occur in the time frame of a typical experiment.

A major disadvantage of the Langmuir unit of measure is that the actual number of atoms or molecules arriving at the surface in one Langmuir of exposure depends upon the molecular weight of the gaseous species and its temperature. Despite this disadvantage, and the fact it is not an SI unit, the Langmuir is widely used. It has a great advantage in that most surface related experiments are monitored with pressure gauges which measure in torr and a stopwatch to measure exposure times. It provides a convenient unit for characterizing the exposure needed to produce certain adsorption states on a surface and allows some transferability between experimenters working on the same adsorption system.

Although vacuum pumps are capable of operation in the \(10^{-10}\) torr region, an important procedure required to obtain UHV is to "bake" the whole system. In absence of leaks and with suitable pumps, vacua are limited by the outgassing of the inner walls and instrument surfaces within the chamber due mainly to the desorption of adsorbed gases from these surfaces. By heating all of these surfaces, the rate of desorption is increased, the surface coverage decreased and thus, the rate of desorption upon subsequent cooling to room temperature is
reduced. This reduces the gas load on the pumps and allows lower pressures to be achieved. Typically, a vacuum chamber is baked at 100°C-150°C for approximately 72 hours.

Although UHV guarantees that a surface will not be influenced by ambient gas molecules on the time scale of an hour, a further requirement to be able to study surface features is to be able to clean the surface in situ. That is, we must be able to produce a surface which contains no more than a few percent of atomic layer species other than those which comprise the underlying bulk material. Although there are many methods for cleaning, the important procedures used in this study are 1) ion bombardment (Ar⁺ ions), 2) heating and, although it is not cleaning per se, 3) MBE.

The use of Ar ion bombardment of a surface to remove layers of the surface by sputtering is the most widely used method of surface cleaning. The technique is effective in the removal of many atomic layers of a surface and even if an impurity is less effectively sputtered than the substrate it can be removed eventually [22]. The main disadvantage of ion bombardment, which is typically at energies of 0.5-5.0 KeV, is that the surface is left in a heavily damaged state, usually with embedded Ar atoms. In order to restore order to the surface it
must then be annealed. This process is known as ion 
bombardment and anneal (IBA) and usually many cycles are 
required to produce a clean well ordered surface.

Heating a surface, like baking the walls of the 
chamber, can lead to desorption of adsorbed species. 
Many impurities however are too strongly bound and will 
not desorb below the melting point of the substrate 
material. On the other hand, once these impurities have 
been removed, for example by ion bombardment, heating 
alone may be sufficient to regenerate a clean surface 
following an adsorption experiment using more weakly 
bound adsorbate species. This surface regeneration by 
heating is applicable to many materials for which heating 
alone is totally ineffective in the initial cleaning 
process.

The third method, MBE, produces the cleanest and most 
well ordered surfaces. Analysis chambers equipped with 
MBE capabilities can simply shuttle a contaminated 
sample, under vacuum, from analysis to growth chamber 
where the sample is usually annealed and new layers of 
pristine material are deposited onto the existing 
surface. Enough layers can be deposited to completely 
bury any impurities present on the dirty surface.
B. Auger Electron Spectroscopy (AES)

Essentially all practical surface elemental analysis employ electron spectroscopy in one form or another. The reason for this derives itself from three experimental facts. First, electrons with kinetic energy in the range 15-1000 eV have a very short mean free path in matter (<10 Å). Second, the wavelength of these electrons is of the same order as atomic spacings, making diffraction possible in crystalline materials. Finally, the binding energy of a core electron is a sensitive function of atomic identity and chemical environment. Therefore, measurement of the kinetic energy of electrons ejected from a solid after photon or electron bombardment can provide surface specific elemental information. This third fact leads to what is perhaps the most common electron based elemental analysis technique, Auger electron spectroscopy (AES) [23].

If an atom is ionized in an inner shell by electron or photon bombardment, the atom may return to a less energetic state either by an internal reorganization involving the emission of characteristic x-rays or through a radiationless process in which outer shell electrons are ejected with energies characteristic of the atom. These electrons are known as Auger electrons,
named after Pierre Auger who in 1925 first described the process to interpret cloud chamber experiments involving ionization of inert gases by x-rays [24]. Since that time there has been a considerable amount of experimental and theoretical study of the process to further its understanding.

The technique of using electron excited Auger electrons to identify surface impurities was first suggested by Lander [25] in 1953. The high sensitivity of the technique was not realized, however, until 1968 when Harris demonstrated [26] the use of electronic differentiation of the energy distribution, \( N(E) \) vs. \( E \) curves, to obtain Auger spectra in its present familiar form. The technique became very popular as a surface science tool, when it was shown [27,28] that the already available electron optics used for LEED (see section II.3) could be used as a retarding field analyzer to detect Auger electrons.

If a neutral atom of atomic number \( Z \) is ionized in an inner shell, by electron bombardment or photon irradiation for example, the ionized atom may return to a less energetic state through filling the inner shell vacancy by an electron from a higher, less tightly bound level. The excess energy may appear as an x-ray (this is the principle behind the x-ray microprobe and x-ray
emission spectroscopy), or alternatively there may be a radiationless process which reorganizes the ion. In such a case the excess energy is given to another electron in the ion. This electron, which is ejected from the ion, is known as the Auger electron. This electron will leave the now doubly ionized atom with a discrete kinetic energy. If the ionized inner level is the K shell of an isolated atom which is filled by an electron from the L₂ level with the ejection of an Auger electron from the L₃ level, this ejected electron is referred to as the KL₂L₃ Auger electron. This process is illustrated in Figure II.1.

The kinetic energy of the Auger electron is given by

\[ E = E_K(Z) - E_{L2}(Z) - E_{L3}'(Z) \] (II.7)

where \( E_K(Z) - E_{L2}(Z) \) is the difference in the ionization energies of the K and L₂ levels. \( E_{L3}'(Z) \) is the ionization energy of the atom missing an L₂ electron. If \( E_{L3}(Z) \) is the ionization energy of the L₃ level of the neutral atom, then \( E_{L3}'(Z) > E_{L3}(Z) \). In fact,

\[ E_{L3}'(Z) \approx E_{L3}(Z+1) \] (II.8)

where \( E_{L3}(Z+1) \) is the ionization energy of the L₃ level of an atom of atomic number \( Z+1 \). This somewhat empirical procedure is justified since, with a vacancy in the inner shell the outer electron will move in a field which is now effectively equivalent to that corresponding to
Figure II.1  Energy level diagram for a KL$_2$L$_3$ Auger electron
atomic number $Z+1$.

Due to the short mean free path of low energy electrons, AES is a very surface sensitive technique. As the incident electron beam interacts with the sample atoms it loses energy and direction, mainly through outer shell ionization processes, but also through the ionization of the inner shell. Other loss processes involving collective excitations also occur, as well as elastic processes in which the initial direction of the beam may undergo marked change in direction either through a large single scattering or through a series of smaller angle scattering. At some depth within the sample, therefore, the initial direction is lost and the electron motion becomes a random diffusion process. This continuous slowing down of the electron beam gives rise to an envelope beyond which there are no electrons of energy greater than the ionization energy of an inner shell of the sample atoms, which leads to a deexcitation and ejection of an Auger electron. These particular Auger electrons can be produced anywhere within this envelope. However, the same type scattering processes affecting the incident beam also affects the path of the Auger electrons. Therefore, only the Auger electrons in the region very near the surface are able to exit the material. For example, a 2.5 KeV electron beam incident
on a Ag sample can penetrate to a depth of 350 Å and still possess enough energy to ionize the Ag M₄ level, 373 eV. The mean escape depth of the 362 eV Auger electron associated with this ionization, however, has been found [29] to have an escape depth of only 8 Å, about four atomic layers.

Experimentally, Auger electron spectrometers are generally one of two type, Cylindrical Mirror Analyzers (CMA) and Retarding Field Analyzers (RFA).

The RFA is primarily used in systems equipped with LEED optics, since the same geometry will accommodate both experiments. Simply changing potentials on the various grids allows the switch from LEED to AES mode of operation. A schematic diagram of the RFA is shown in Figure II.2. The incident beam can either pass along the axis of the optics, striking the sample at normal incidence, or enter from a direction outside the angle of the optics, striking the sample at a glancing angle. The grid arrangement and modulation are a key factor in detection the Auger electron signal. The grid nearest to the sample is grounded as are the sample and all neighboring components to give, in the absence of stray magnetic fields, a field free region between the grid and sample. This ensures that secondary electrons produced at the center of curvature of the optics will travel in
Figure II.2 Schematic diagram for a retarding field analyzer (RFA) detection system.
radial paths toward the first grid. The next two grids have the retarding voltage applied to them, thus preventing those electrons that have an energy less than that corresponding to this voltage from passing the grids. Two grids are used in order to sharply define the radial retarding field, which is a necessary requirement for high resolution. To these grids is also applied an ac modulation voltage, which together with the dc retarding field enables energy analysis to be carried out. Typical modulation frequencies range from 100 cycles/sec to several thousand cycles/sec. The fourth grid is held at ground potential and serves primarily as an ac shield to reduce the capacitive coupling to the collector of the ac voltages applied to the retarding grids. Typically, the collector is a phosphor coated fluorescent screen biased a few hundred volts positive with respect to ground. This bias voltage ensures that most of the secondary electrons produced at the collector are returned to the collector and also, by increasing the energy of electrons striking the collector ensures stable collection through adequate bombardment-induced conductivity of the phosphor. Although the phosphor is not necessary for Auger electron spectrometers, it is essential when the system is used for LEED analysis.

If the sample is now excited by electrons of energy
eV₀ and the current to the collector is recorded as a function of the retarding field voltage sweeping from ground potential to -V₀, a retarding field plot, as a function of V is obtained. To obtain the energy distribution it is necessary to differentiate this curve with respect to retarding voltage, that is, to determine dI(V)/dV as a function of V. This is very effectively accomplished by applying the small ac modulation voltage to the retarding grids and tuning the detector to the frequency of the modulation. The Auger spectrum detectability is enhanced, and the background slope reduced, when the derivative of the energy distribution is displayed. In order to obtain the derivative of the energy distribution curve, that is, d²I(V)/dV², as a function of V, the detector is tuned to the second harmonic of the modulation frequency [28]. Figure II.3 is a schematic diagram showing the collector currents in the RFA in different modes of operation.

The Cylindrical Mirror Analyzer (CMA), from a structural and performance standpoint appears to be the best suited electrostatic analyzer for AES. However, its geometry is incompatible with LEED optics and therefore requirements for the additional mounting in the vacuum chamber are needed. Shown schematically in Figure II.4, this analyzer consists of two coaxial cylinders, the
Figure II.3  Electron intensity signal vs. retarding field with first and second derivative.
Figure II.4  Schematic diagram for a cylindrical mirror analyzer (CMA) detection system.
inner which is grounded and has two cylindrical gridded apertures properly positioned along its length. The outer cylinder has a negative voltage applied to it such that secondary electrons leaving a suitable located grounded sample from a small region intersecting the axis of the cylinders and entering the first of the apertures tend to be reflected towards the second aperture. For a particular voltage $V_b$ applied to the analyzer, electrons of energy $eV_e$ will pass through the second gridded aperture and come to a focus in a small annular region close to the axis. Here an annular slit is located, allowing only those electrons of energy in the vicinity of $eV_e$ to reach the collector or the first dynode of an electron multiplier. If $V_b$ is swept from ground potential in a negative direction the current to the collector as a function of voltage is recorded. As in the case of the RFA, in order to emphasize the Auger peaks the energy distribution curve is electrically differentiated. This is done by applying a small sinusoidal modulation voltage to the outer cylinder in addition to the ramp voltage and tuning the detector to the frequency of the applied voltage.
C. Low-energy electron diffraction (LEED)

Perhaps the most important consideration after determining atomic species is determining their geometric orientation at the crystal surface. It is the orientation of these atoms which gives rise to many of the unique chemical and physical surface properties. One method, used to determine atomic location at crystal surfaces, exploits the fact that low energy electrons will diffract from crystalline surfaces. This technique is known as low energy electron diffraction, or LEED.

In their famous 1927 experiment Davisson and Germer discovered, by firing electrons with energies between 15 and 200 electron volts at a crystal of nickel, angular variations in the reflected flux were produced which were consistent with electron diffraction [21]. This investigation, along with the independent work of Thompson [30], clearly demonstrated the wave-like nature of electrons proposed earlier by deBroglie. Thus, LEED was born. The difficulties with this early work should not be underestimated, however. High vacuum, essential for crystal surface cleanliness and electron beam propagation was rarely attained at the time. It was, in fact, an accident in Davisson and Germer's laboratory which led to the discovery of electron diffraction. The
glass vacuum system which contained a polycrystalline nickel sample cracked while the sample was being heated, resulting in severe oxidation of the Ni. After repairing the apparatus, the sample was cleaned by high-temperature chemical reduction with hydrogen. This severe oxidation-reduction cycle resulted in an extensive recrystallization of the polycrystalline Ni into (111) microfacets, simulating a single crystal.

Although the discovery of LEED was over sixty years ago very little experimental work was carried out until the mid 1960's. This was presumably due both to the technological complexity of the measurement and the lack of an adequate theory. During the 1960's the commercial availability of vacuum systems, and LEED optics which were compatible with the UHV systems, led to renewed interest in LEED. This renewed experimental interest, in turn, rekindled the interest in developing a successful theory of LEED. It had been known since the 1930's that the single scattering (kinematic) theory would not explain electron diffraction features. The complexities of a multiple scattering (dynamical) theory required computing capabilities which were not available until the early 1970's. Since then, the advances in both experimental technology and theoretical calculations have resulted in a technique that can determine atomic
positions at the surface to within 0.05 Å.

Diffraction results from the interaction between the periodic oscillations of a wavefield and a periodic array of scattering centers. Scattering from individual centers may be very small, but if the scattered waves from successive centers are in phase, then the net result may be significant. The periodicity of the waves and scatterers will normally provide a number of different possible conditions at which strong in-phase scattering may occur. This accounts for the production of a whole series of diffracted beams, rather than a single specular reflection.

When considering diffraction from surfaces, the assumption of infinite periodicity in two dimensions is usually well approximated, but clearly not in the third dimension, which is truncated by the presence of the surface itself. Moreover, low energy electrons penetrate only a short distance, and so the periodicity beyond the top few layers is relatively weakly explored in the direction normal to the surface. The crystal structure actually examined in a typical LEED study may therefore be considered to be a slab, infinitely periodic in two dimensions, but comprising only a limited number of layers in the third dimension.

The surface periodicity is described in terms of a
lattice, which is defined as the simplest arrangement of points which are arranged in space with the fundamental periodicity of the crystal. These lattice points need not correspond to actual atomic centers, however. The arrangement between the lattice and the physical arrangement of atoms is provided by the unit cell, which specifies the repeat unit of the physical structure.

At the surface, the diffraction structure can be described by the lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ subtended by an angle $\alpha$. A plane wave incident on an atom or atoms within the unit cell will be scattered in all directions, but interference between waves scattered from neighboring unit cells will restrict the net flux of scattered electrons to those directions in which the unit cells are in phase. This requires that the scattered waves from neighboring cells differs only by an integral number of wavelengths $\lambda$. For example, the scattering of a plane wave incident at an angle $\theta_o$ with respect to a one dimensional lattice is shown in Figure II.5. The in-phase condition is met for all integers $n$ which satisfy the condition

$$a(\sin \theta_n - \sin \theta_o) = n\lambda \quad (II.9)$$

where $a$ is the separation between scatterers and $\lambda$ is the wavelength of the incident electron beam. This is known as the Laué condition. If the incident and emergent
Figure II.5  One-dimensional plane wave scattering from evenly spaced scattering centers.
beams are described by the unit vectors \( \mathbf{s}_0 \) and \( \mathbf{s}'_0 \) respectively, then this may be written in vector form as

\[
\mathbf{a} \cdot (\mathbf{s}'_0 - \mathbf{s}_0) = n\lambda \quad \text{(II.10)}
\]

or

\[
\mathbf{a} \cdot \Delta \mathbf{s}_n = n\lambda \quad \text{(II.11)}
\]

where

\[
\Delta \mathbf{s}_n = (\mathbf{s}'_0 - \mathbf{s}_0) \quad \text{(II.12)}
\]

The diffracted beams are determined by \( \Delta \mathbf{s} \) and, in the one dimensional case, it is clear that the are given by integral multiples of the basic unit \((\lambda / |\mathbf{a}|)\). From this it can be seen that a reciprocal of the real space lattice vector \( \mathbf{a} \) is involved. Thus, the reciprocal lattice vector \( \mathbf{a}^* \) can be defined as

\[
\mathbf{a}^* = (1/\mathbf{a}) \quad \text{(II.13)}
\]

In two dimensions, the real-space lattice is described by the two lattice vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \), and a corresponding reciprocal lattice can be constructed from the basis vectors \( \mathbf{a}_1^* \) and \( \mathbf{a}_2^* \) defined in the following relations

\[
\mathbf{a}_1 \cdot \mathbf{a}_1^* = \mathbf{a}_2 \cdot \mathbf{a}_2^* = 1 \quad \text{(II.14)}
\]

and

\[
\mathbf{a}_1 \cdot \mathbf{a}_2^* = \mathbf{a}_1^* \cdot \mathbf{a}_2 = 0 \quad \text{(II.15)}
\]

The second relation requires that \( \mathbf{a}_2^* \) be perpendicular to \( \mathbf{a}_1 \) and \( \mathbf{a}_1^* \) be perpendicular to \( \mathbf{a}_2 \). Any vector relating two reciprocal lattice points take the form
\[ g_{hk} = h\mathbf{a}_1^* + k\mathbf{a}_2^* \]  (II.16)

where \( h \) and \( k \) are integers and \( g_{hk} \) is known as a reciprocal lattice vector.

Diffraction from the two dimensional lattice must satisfy the two Laué conditions

\[ \mathbf{a}_1 \cdot \Delta \mathbf{g} = h\lambda \]  (II.17)  
\[ \mathbf{a}_2 \cdot \Delta \mathbf{g} = k\lambda \]  (II.18)

and these can be solved whenever

\[ \Delta \mathbf{g} = \lambda (h\mathbf{a}_1^* + k\mathbf{a}_2^*) = \lambda g_{hk} \]  (II.19)

This means that there is a direct correspondence between the observed diffraction pattern and the reciprocal lattice of the surface. As a result, if the lattice vector in any direction is increased, the corresponding reciprocal lattice vector, that which is observed in the diffraction pattern, will be seen to decrease. This relationship between the observed reciprocal lattice and the real-space lattice allows for a relatively easy method of identification of the lattice present at the surface.

Creation of a surface generally results in the reorganization of those atoms at and near the surface edge. If this reorganization is severe enough, or if adsorbate atoms are present, there may be a reconstruction of the surface which changes the
periodicity from that expected for the ideal case of a simple truncation of the bulk. If these reconstructions occur in a periodic fashion, then the new surface unit vectors \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \) can be described as multiples of the ideal surface unit vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \), i.e.,

\[ |\mathbf{b}_1| = m |\mathbf{a}_1| \quad (II.20) \]

and

\[ |\mathbf{b}_2| = n |\mathbf{a}_2| \quad (II.21) \]

where \( m \) and \( n \) are integers. From this, Wood [31] has developed a shorthand method to describe these surface reconstructions. If the angle which subtends \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \) is identical to that which subtends \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) then the reconstruction may be described as \( p(mxn) \), where \( p \) indicates a primitive unit cell. Unless otherwise noted it is usually understood that the cell is primitive, and the \( p \) therefore, is usually omitted. The unreconstructed surface, then, would be described as a \((1x1)\) unit cell.

If the new lattice vectors are subtended by the same angle as the ideal surface vectors but the whole lattice is rotated through an angle \( \beta \) with respect to \( \mathbf{a}_1 \), the lattice may be described as \((mxn)R\beta\), where \( R \) means "rotated". If the sides of the unit cell are greater than the ideal cell by an even number of lattice spacings, then it is possible for an additional atom to be placed at the center of the cell with bonding symmetry.
identical to that of the corner atoms. This creates a special symmetry and in Wood's notation takes the form c(mxn) where the c stands for centered. The translational symmetry of this type of structure results in destructive interference which causes alternate diffraction beams to disappear. The resulting diffraction pattern can then be seen to be similar to a p(mxn) cell without these diffraction features. This allows for the identification of large unit cells which otherwise would require complicated symmetry notation to describe.

This notation is limited to reconstructions which can only be directly related to the ideal surface vectors and breaks down if more complicated structure appears. For example, if the angle between $b_1$ and $b_2$ differs from the angle between $a_1$ and $a_2$ the Wood notation cannot be used to describe the reconstruction. This scheme, however, allows for the quick classification of surface structures and therefore is widely used in surface crystallography.

Analysis of surfaces using LEED generally proceeds at two levels of sophistication. The first level uses the principle which has been described, that diffraction provides information about the periodicity of the crystal. From simple symmetry related arguments many structures may be inferred from the observed diffraction
pattern. Although this method does not present conclusive evidence for any one particular structure, it can eliminate many structures which do not fit the symmetry of the diffraction pattern. It can also be very useful when adsorbates cause the initial LEED pattern to change. For example, if the diffraction pattern resulting from adsorbing a species on an clean unreconstructed square mesh doubles the area of that mesh, i.e., changing a (1x1) pattern to a c(2x2) pattern, a reasonable guess would be that the structure involves one-half monolayer of adsorbate species, each atom or molecule occupying a symmetrically identical site. This alone is inconclusive evidence, but in conjunction with an independent determination of surface coverage, Auger data for example, a reasonably accurate determination of the surface structure can be made. Accurate enough, at least, as starting point for the next level of sophistication, the analysis of the diffracted beam intensities.

The electron diffraction beam intensities, much like x-ray diffraction intensities, may be interrogated to determine the actual geometric structure of the surface. However, it is not straightforward to determine atom positions from LEED. In x-ray scattering the intensity of each Laué spot is determined by the product of an
atomic scattering factor and a simple geometrical structure factor. The positions of atoms within the cell are varied until the geometrical factors predict the correct intensity for each beam. This simplicity occurs because x-rays interact very weakly with matter; each photon is backscattered after a single encounter with a lattice ion. Another consequence of this kinematic scattering is that spot intensities are independent of both the incident beam energy and the azimuthal angle of incidence. Neither is true in LEED.

Structure determination from LEED is complicated by the fact that every electron undergoes multiple elastic scattering collisions within the first few layers of the crystal. Unlike x-rays, the elastic scattering cross section for electrons is very large (\(-A^2\)) and comparable to the inelastic cross section which makes LEED surface sensitive in the first place. The probability is great that a second or third diffraction event will scatter an electron away from its original diffracting direction.

The energy dependence of LEED beam intensities, the so-called I(V) curves, are used in an iterative procedure to determine the geometrical arrangement of surface atoms [32]. First, an arrangement of atoms is postulated that is consistent with the symmetry of the LEED pattern. Second, the intensities of a number of diffracted beams
are calculated as a function of incident electron energy by solving the equation for the electron wavefunction of the first few atomic layers. Third, the resulting $I(V)$ curves are compared to experiment and the process is continued with a refined geometry until satisfactory agreement with experiment is obtained. This procedure is by no means trivial and involves significant computational effort. The results, however, can predict the atomic arrangement at the surface within 0.05 Å.

Additional information can be gained by probing the variation in diffracted intensity across the width of a single diffracted beam, the so-called spot profile [33]. Any deviation from perfect two-dimensional periodicity will destroy the delta function character of the diffracted beam. Surface steps, defects and islands can all cause broadening or even splitting of the LEED spots. Therefore, the spot profile may be used as a monitor of surface order. This, however, is limited by the resolution of the instrument.

A schematic diagram of a typical modern LEED optics reveals that it is identical to that used for Auger analysis as seen in Figure II.2. Generally, the electron gun is aligned at the center of the grids, but may also be aligned off axis for taking off normal LEED data. The electron gun delivers a beam of typically 1 μA at
energies in the 20-300 eV range to the target sample. The energy spread of this beam is usually about 0.5 eV. Electrons scattered or emitted from the sample travel in straight lines in the field free region to the spherical sector grids as the first of these grids is set to the same potential, usually ground, as the sample. The next two grids are set to retard all electrons other than those which have been elastically scattered by using a potential close to that of the original electron source filament. The elastically scattered, diffracted electrons passing through are then reaccelerated onto the fluorescent screen by applying about 5 kV to the screen. This ensures that they will produce a fluorescent image of the diffraction pattern which may be viewed through the grids from behind the sample.

The display nature of this instrument makes it ideal for easy assessment of the translational symmetry of the surface although less well suited to quantitative beam intensity measurements. This may be achieved in a number of ways. Some systems employ a movable Faraday cup detector to directly measure the electron current of a particular beam. This is a very accurate method of measurement although it is also very tedious. Alternatively, the brightness of a diffracted beam on the phosphor screen may be measured with a spot photometer.
Another method, which is employed in our own laboratory, consists of recording on video tape the LEED patterns at different energies with a TV camera that is equipped for low-light intensities. The whole system can be interfaced to a personal computer which can be used to digitize and integrate the LEED spot intensities. The advantage of this system is that the actual experiment may be carried out quickly, before surface contamination becomes a problem, see section II.1. The recorded data can then be analyzed at a more leisurely pace.

D. Desorption Spectroscopy

The general methods of desorption are by thermal processes and by electronic stimulation. Any species on a surface must be bound to the surface with some specific amount of energy and will desorb at a rate determined by a Boltzmann factor. Heating the surface will increase this desorption rate, and the desorbing species may be detected in the gas phase by a conventional mass spectrometer. Alternatively, incident electrons or photons may lead to excitation of the adsorbed species to a new electronic state in which the adsorbed species find themselves in a repulsive potential and are desorbed.
Figure II.6  Lennard-Jones potential used to describe adsorbate-substrate interaction during physisorption.
In order to fully understand the desorption process, an understanding of the adsorption process is needed. As gas atoms or molecules approach a surface, they are affected by a change in potential. This potential is due to van der Waals attraction between the gas and the surface. As the molecules or atoms approach more closely, forces of repulsion between the electron clouds become dominant. These forces can be conveniently described by the so-called Lennard-Jones, or 6-12 potential

\[ E = 4\Delta H_p \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right] \]  

(II.22)

where \( \Delta H_p \) is the heat of physisorption and \( \sigma \) is as shown in Figure II.6. These interactions result in a weakly bound adsorbate; this is known as physisorption. Typically, binding energies of 0.1-0.2 eV (2-5 kcal) are characteristic of physisorption.

When an adsorbate is more strongly bound to the surface it is said to be chemisorbed. The heat of chemisorption, \( \Delta H_c \), can approach the heat of compound formation, \( \approx 10 \) kcal, and is therefore considered to be much like a chemical bond. By analogy with potential energy curves used widely in molecular spectroscopy to discuss the bonding in diatomic molecules, the chemical bond between the adsorbate and substrate can be represented by a Morse potential curve.
$E = D_e (1 - \exp[-a(R - R_e)])^2$ \hspace{1cm} (II.23)

where $D_e$ is the depth of the potential, and describes a diatomic molecule at infinite separation from the surface. $R$ is the interatomic distance, $R_e$ is the equilibrium distance and $a$ is a constant. In Figure II.7 it can be seen that a gas molecule approaching this surface is first attracted into a physisorbed state. If trapped in this well the adsorbate is said to be in a precursor state. Usually these states are short lived. As the adsorbate approaches closer to the surface it may find itself in the much more strongly bound chemisorption potential well. Of importance is the cross-over point between the physisorption and chemisorption potential curves. If these curves cross above the zero line of the potential energy diagram, then the process of chemisorption is an activated process. That is, there is an energy barrier which the adsorbate must overcome in order to reach the chemisorption well. This energy barrier is labeled as $\Delta E_A$ in Figure II.7. From this it follows that an increase in adsorption with a corresponding increase in temperature is characteristic of an activated process.

For an adsorbed atom or molecule to desorb from a chemisorption site, it must have enough energy to overcome the chemisorption energy, $\Delta H_e$, as well as the
Figure 11.7 Adsorption potential between adsorbate and surface. Positive $E_A$ describes activated process.
activation energy, $\Delta E_A$. The sum of these is known as the desorption energy $E_d$.

1) **Thermal Desorption Spectroscopy (TDS)**

When a sample is heated rapidly in a vacuum the adsorbed species is desorbed from the surface as a gas. Experimentally, it is observed that the rate of gas evolution changes markedly with temperature and in addition there may be several temperatures for which the evolution rate goes through a relative maxima. As the temperature of the surface increases, the rate of evolution of gas increases as well, resulting in a rise of the instantaneous gas density. From this increase it is possible to derive information on the nature and number of adsorbed species as well as on the kinetics of their evolution.

In general, the rate of desorption from a surface layer can be described by the Arrhenius equation, in the form

$$-\frac{dn}{dt} = v n^a \exp(-E_d/RT) \quad \text{(II.24)}$$

where $n$ is the surface coverage, per cm$^2$, $a$ is the kinetic order, $E_d$ is the energy for desorption and $v$ is the frequency factor (typically taken from transition state theory as $\sim 10^{13}$ s$^{-1}$ [34]). If the temperature is
increased in a linear fashion ie,

\[ T = T_0 + \beta t \]  \hspace{1cm} (II.25)

then

\[ \frac{dT}{dt} = \beta \]  \hspace{1cm} (II.26)

and

\[ \frac{dn}{dt} = \beta \left( \frac{dn}{dT} \right) \]  \hspace{1cm} (II.27)

and by substitution, the rate equation, II.24, may be written solely in terms of temperature

\[ -\frac{dn}{dT} = n^8 \left( \frac{v}{\beta} \right) \exp\left(-\frac{E_a}{RT}\right) \]  \hspace{1cm} (II.28)

If the vacuum system is being continuously pumped at a much greater rate than evolution of gas from the surface, then the desorbed species will appear as a pressure transient and a record of the pressure vs. temperature will appear as a peak. The shape of this peak will depend on the kinetics of desorption, and in principle, may be used to determine the order of the reaction. Redhead [35] has shown that a second order reaction will result in a symmetrical peak, while a first order reaction will result in the high temperature half of the peak being narrower than the low temperature half, Figure II.8. This method of analysis, however, can only be used on well resolved peaks which are undistorted by experimental artifacts such as uneven temperature distributions across the sample or inadequate pumping speeds. Therefore, caution must be used when
Figure 11.8  
Shape of first and second order desorption curves. Second order is nearly symmetric while first order is skewed.
interpreting these results.

The maximum rate of desorption, i.e., the peak of the desorption curve, may also be used to infer about the kinetic processes of desorption. When the maximum desorption rate has been reached \( \frac{d^2n}{dT^2} \) is zero. Thus, the general equation II.28 may be differentiated and set equal to zero.

\[
-d^2n/dT^2 = \\
v/\beta(\alpha n^{-1}(dn/dt)\exp(-E_d/RT)+(n^\alpha E_d/RT^2)\exp(-E_d/RT)) \quad (\text{II.29})
\]

Setting this equation equal to zero and the temperature equal to \( T_p \), the peak temperature, and rearranging gives

\[
\alpha n^{-1}(dn/dT) = n^\alpha E_d/RT_p^2 \quad (\text{II.30})
\]

Substituting for \( dn/dT \) from equation II.28 gives

\[
(v\alpha n^{-1}/\beta)\exp(-E_d/RT_p)=E_d/RT_p^2 \quad (\text{II.31})
\]

For first-order desorption \( \alpha=1 \) and

\[
E_d/RT_p^2=(v/\beta)\exp(-E_d/RT) \quad (\text{II.32})
\]

which reveals that the peak desorption temperature, \( T_p \), is independent of the initial coverage, \( n_0 \), in a first-order desorption process. Therefore, a series of desorption peaks at increasing coverage whose position does not change is indicative of first-order desorption kinetics.

For second-order desorption \( \alpha=2 \) and

\[
E_d/RT_p^2=(2vn_p/\beta)\exp(-E_d/RT) \quad (\text{II.33})
\]

where \( n_p \) is the coverage at \( T_p \). Rearranging gives
\[ \ln(\beta E_d/2Rv_{n_p}) = 2 \cdot \ln T_p - (E_d/RT_p) \] (11.34)

As mentioned above, Redhead [35] has shown that second-order desorption curves are symmetrical. It follows then, that \( n_p = n_o/2 \) where \( n_o \) is the initial coverage. Thus, a series of desorption peaks at increasing coverage will have maxima which shift to lower temperature. This is indicative of second-order kinetics.

Although desorption kinetics are easily shown theoretically, in practice these measurements are difficult to make. For instance, a not infrequent complexity which arises is that many first-order desorption processes have an activation energy which decreases with increasing coverage. When this happens the desorption peak shifts to lower temperature at higher coverage, making it appear as a second-order process. Therefore, a great deal of care must be taken when interpreting kinetic processes from desorption spectra.

A much more easily accessible parameter obtained from thermal desorption spectra arises when multiple binding sites, with different binding energies, are present on the surface. Different binding energies will require different heat energies to desorb, ie, \( T_p \) will be a function of \( E_d \). This can be used to probe how different binding sites are filled as the surface coverage changes.
Figure II.9  Desorption maximum vs. temperature at different surface coverage. $\beta_1$ and $\beta_2$ result from two different adsorption sites.
For instance, Figure II.9 shows two desorption peaks, resulting from two different binding sites, as the adsorbate coverage is increased. The first peak, $\beta_2$, is a high energy (temperature) peak which results from a strong binding site and is filled upon initial adsorption. As adsorption increases the less strongly held adsorption site, $\beta_1$, is filled. This is seen in the desorption spectra as a low temperature peak which does not arise until high coverage. This technique is very powerful when used in conjunction with LEED analysis. LEED patterns which change with coverage can be compared with the onset of new desorption peaks at the same coverage. Only binding sites that fit both the LEED symmetry and the energy of thermal desorption will be possible candidates for determining the actual site. Although this procedure is not foolproof, there are usually only a limited number of possibilities that fit both criteria.

Another important measurement made by TDS is to monitor the reaction products between an adsorbate and substrate. Although these products can only be confirmed at the desorption temperature, their presence is indicative of the surface reaction. For instance, if molecule AB is adsorbed onto substrate C, the proportion of products AC vs. BC may be monitored. Alternatively,
when the desorption temperature is known the reaction may be carried out at that temperature. This results in a steady state reaction at the surface which can be followed by monitoring the gas phase products. Generally, these type of reactions are important in catalysis systems, but they also find application in thermal etching reactions of semiconductor device materials.

2) **Electron Stimulated Desorption (ESD)**

When a surface containing an adsorbed layer is bombarded by electrons or photons at energies greater than some threshold energy, usually above 10 eV, electronic excitations in the adsorbed layer may result in the desorption of ion and neutral fragments. Historically, electrons, due to their ease of production, have been used in this process. In general, for electrons in the range of 10-1000 eV, the experimental observations of desorption are as follows:

(1) The cross-section for most ESD processes are smaller than comparable gas-phase processes involving electron induced dissociation and ionization of molecules. This is largely due to the fact that excited species may be recaptured by the surface before entering
the gas phase. Typical gas-phase dissociative-ionization cross-sections for small molecules are $\sim 10^{-16}$ cm$^2$. Cross-sections for ESD of most adsorbates lie in the range $10^{-18}-10^{-23}$ cm$^2$. Also, the cross-sections for neutral desorption are typically larger than cross-sections for ion desorption. However, due to the ease of experimentally detecting ions, it is their characteristics which are most frequently studied.

(2) Mostly positive atomic ions are seen, with $\text{H}^+$, $\text{O}^+$, $\text{F}^+$, and $\text{Cl}^+$ being the most abundant.

(3) Cross-sections for ESD are very sensitive to the mode of bonding between the adsorbate and substrate.

(4) The binding energies for most adsorbates are sufficiently large that direct momentum transfer between the electron and adsorbate does not provide sufficient energy to cause desorption. For example, the energy transfer between a 100 eV electron and an adsorbed $\text{H}_2$ molecule is only 0.11 eV. The binding energy of the $\text{H}_2$ is 2.3 eV and will remain virtually unaffected by the momentum transfer.

(5) All ESD effects are observed to occur at low electron power density, typically 0.1-10 W/m$^2$, so that surface heating effects are both too low to be measurable or to cause thermal desorption.

ESD ion current is observed experimentally to be a
linear function of the incident electron current. It is postulated then, that ESD results can be analyzed in terms of isolated desorption processes; i.e., the ESD ion yield from a surface monolayer at a fixed electron energy can be written as a first-order rate equation [36-42]

\[ i^+ = I_e Q^+ N \]  

(II.35)

where \( i^+ \) is the ion current in amperes, \( I_e \) the electron bombardment current in amperes, \( Q^+ \) the cross-section for desorption of ions in cm\(^2\), and \( N \) the surface coverage in the particular binding state which is affected by ESD.

The time rate of change of coverage \( N \) under electron bombardment can be written as

\[ -\frac{dN(t)}{dt} = n_0 Q N \]  

(II.36)

where \( Q \) is now the total cross-section and can include one or more processes that result in a decrease in population of those species affected by ESD, including desorption of ions, ground state neutrals and metastables. The electron bombardment flux, \( n_0 \), is given by

\[ n_0 = \frac{I_e}{A \epsilon} \]  

(II.37)

where \( A \) is the sample area in cm\(^2\) bombarded by the electron beam of current \( I_e \) and \( \epsilon \) is the charge on the electron in coulombs. Substituting this and integrating equation II.36 gives

\[ \frac{N(t)}{N_0} = \exp\left(-\frac{I_e Q t}{A \epsilon}\right) \]  

(II.38)
All quantities, except for the cross-section, $Q$, are easily determined from the experiment. The cross-section, then, is easily calculated from the equation.

For a simple ESD process a plot of $\ln[N(t)/N_0]$ vs. $t$ will yield a straight line whose slope varies directly with $I_e$. If competing processes occur, for instance thermal desorption, then such plots may exhibit curvature. Likewise, if a distinct change in the slope of $\ln[N(t)/N_0]$ vs. $t$ occurs as a function of time, although remaining linear, there is most likely multiple ESD processes occurring.

Electron stimulated desorption is usually discussed in terms of specific models, but all are consistent with the general description of ESD occurring as a three step process:

1) A fast initial electronic excitation ($\sim 10^{-16}$ sec) leading to a repulsive excited state.

2) Decay of the excited state by conversion of electronic energy to nuclear motion, but in competition with other decay mechanisms that redistribute the energy ($10^{-15}$-$10^{-14}$ sec).

3) A modification of the desorbing species as it recedes from the surface ($10^{-14}$-$10^{-13}$ sec)

The first model developed to explain ESD phenomenon was constructed by Menzel and Gomer in 1964 [43] and
Figure II.10  Menzel-Gomer-Redhead potential curve use to describe ESD.
independently by Redhead, also in 1964 [44], and has subsequently become known as the Menzel-Gomer-Redhead or MGR model of electron stimulated desorption. In this model the primary process is a Frank-Condon excitation or ionization to a repulsive neutral or ionic state, as shown in Figure II.10. Although the actual nature of the repulsive state is not usually specified, the initial proposal was in the context of valence excitation followed by reneutralization. As such, this view is supported by desorption thresholds corresponding to valence electron excitations and by the dominance of neutral yield over ion yield. Since the detailed nature of the electronic excitations is not specified, this model does not have predictive capabilities concerning the initial excited state or about the surface atomic arrangements required for desorption to occur [45]. A variation of the MGR model has been proposed by Antoniwicz [46] where the excited ion begins its trajectory by moving toward the surface where it is neutralized. Evidence for this mechanism has been found in the ESD of rare gases from metals [47].

Another basic model for desorption has been formulated by Michael Knotek and Peter Fiebelman in 1978 [48]. The Knotek-Fiebelman (KF) model was developed to explain ESD of positive ions from maximal valency transition metal
Figure II.11 Knotek-Fiebelman (KF) model for ESD from maximal valency compounds.
oxides, i.e., oxides in which the transition metal cation is oxidized to the rare gas configuration, for example Ti$^{4+}$ in TiO$_2$. The model is based on the ionization of a metal core level as the primary process, Figure II.11. Since the transition metal is in its maximum oxidation state a relaxation of the system may occur via an interatomic Auger transition. The interatomic Auger decay of the core hole creates a positive anion at the initially negative ion site. The expulsion of the positive ion results from the reversal of the Madelung potential. This mechanism explains thresholds observed in many ESD experiments, as well as the large charge transfer occurring in these processes.

The Auger process has been demonstrated to be of importance in desorption of ions from both covalent systems and non-maximal valency systems, but its role is somewhat different from the KF model. In covalent systems the expulsion of the positive ion still results from the unshielded nuclear-nuclear repulsion (also known as hole-hole repulsion), but an additional condition must be met. The holes must remain localized for a sufficiently long time (~10$^{-14}$ sec) in the bonding orbital that initially held the atom to the surface so that electronic energy can be converted into nuclear motion. This mechanism is appropriately called the Auger
Stimulated Desorption (ASD) model [49]. It has been shown to describe desorption from non-maximal valency surface oxides and well as molecular adsorbates on covalent systems.

Both ESD and TDS qualitative experiments are easy to perform, relying on mass analysis. Most vacuum systems are equipped with quadrupole mass analyzers for leak detection. These instruments can operate either by ionizing an incoming gas, or detecting an already ionized species, and applying an RF field to the charged species. By properly tuning the RF field, the ionic species may be mass selected as they move toward the detector. Difficulties arise if the sample is positioned too far from the mass spectrometer that wall effects, such as adsorption, become appreciable. To overcome this problem the sample is placed as close as physically possible to the analyzer of the mass spectrometer. Although background effects such as desorption from the vessel walls and even outgassing of the ion pumps will always be present to some extent, they can usually be assumed to be negligible, or at any rate, constant, if careful experimental procedures are followed.
III. BACKGROUND

Gallium arsenide is a compound semiconductor consisting of group III Ga atoms and group V As atoms. This class of compounds is commonly referred to as III-V compounds, III-V semiconductors or simply as III-V's. As with most III-V compounds, GaAs crystallizes in a zinc-blend structure. This structure, illustrated in Figure III.1, can be considered as two interpenetrating face-centered cubic lattices with group III and group V atoms on different sublattices. The lattice constant along with other general physical properties of GaAs are given in Table III.1. The bonding in the zinc-blend compounds consists of sp³ hybrid orbitals and, in contrast to the purely covalent group IV semiconductors, there is some charge transfer between the two elements and thus, an ionic contribution to the bonding. This may readily be seen in the cleavage behavior of III-V compounds. III-V crystals cleave along the nonpolar (110) plane although the least number of bonds would be broken by cleavage along the (111) plane, which is the natural cleavage plane for Si and Ge. The (110) surface of GaAs is easily produced by cleavage in vacuum. The (100) surface, however must be cut and polished and then cleaned in situ or grown by MBE.
Figure III.1  Crystal structure for zinc-blende compounds.
Table III.1  General physical properties of gallium arsenide.

<table>
<thead>
<tr>
<th>Structure</th>
<th>zinc-blende</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant</td>
<td>5.65359(6) Å</td>
</tr>
<tr>
<td>Band Gap</td>
<td>1.43 eV (300 K)</td>
</tr>
<tr>
<td>Density</td>
<td>5.3165(15) g/cm³</td>
</tr>
<tr>
<td>Melting Point</td>
<td>1513 K</td>
</tr>
</tbody>
</table>
Figure III.2  Low-index faces of ideally terminated GaAs surfaces.
The (100) surface differs substantially from the (110) plane. As shown in Figure III.2, both the (100) and the (111) (the other low index plane) surfaces are polar due to the alternate arrangement of the anion and cation layers parallel to the surface, so that the ideal surface may consist of all anions or all cations. In practice these surfaces are rarely ideal and display numerous reconstructed forms which are dependent upon the method of preparation and the chemical composition of the surface. The surface stoichiometry may range from a pure anion or cation termination to a final layer which may consist of varying amounts of each.

The first LEED patterns of the GaAs(100) surface were published by Jona [50] in 1965. He found initially, the (1x6) and c(8x2) reconstructed surfaces. Subsequently, the (1x1), c(4x4), c(2x8), c(6x4), (3x1), and (4x1) reconstructions have all been seen on this surface [51].

The large number of reconstructions and the considerable size of the unit cell of these reconstructions have made structure determination difficult. Furthermore, it has been found that reconstructions are dependent upon the history of a particular sample.

Typically, GaAs(100) surfaces are generated by either ion-bombardment and annealing (IBA) of a bulk grown
crystal, or by gas phase deposition, usually molecular beam epitaxy (MBE). In either case the surface reconstruction shows a definite temperature dependence. This dependence is a result of the preferential evaporation of the more volatile group V atom, As, from the surface as the temperature is increased. This leaves the surface in a non-stoichiometric state. The reconstructions, then, can be used to monitor the relative amount of Ga or As present in the surface layer. Although this is qualitatively true, precise measurements reveal that there can be a great deal of variation in the Ga/As ratio for any particular reconstruction [52,53]. As mentioned above, the surface composition is very sensitive to the history and treatment of the sample. For instance, an IBA prepared sample which is annealed at 500°C, then quenched after 5 minutes will display a (1x6) LEED pattern. If the sample is then reheated, again to 500°C, this time for 60 minutes, it will still show a (1x6) LEED pattern when quenched. The ratio of Ga/As, however, will be much smaller in this case as the longer annealing time allows for the evaporation of more arsenic. In contrast, if a sample is annealed at 600°C for 5 minutes it will reveal a (4x1) LEED pattern upon quenching. If the sample is annealed for 45 minutes at 600°C, the LEED pattern becomes a c(8x2) reconstruction.
The Ga/As ratio of these two reconstructions are relatively similar. It becomes apparent that it is not simply the evaporation of arsenic from the surface which completely dictates the reconstruction of the surface, but other factors must also be considered. Ga evaporation to some extent occurs at elevated temperatures, and the diffusion rate from bulk to surface of the two constituents must also be considered. The combination of these factors lead to a system which, at present, can only be qualitatively understood. The generally accepted trend in reconstructions, along with the relative amount of arsenic present in the surface layer is shown in Table III.2.

It has been found [54] that a (1x1) surface is one which is completely terminated in As. This surface is typically generated by cooling to room temperature an MBE grown c(2x8) surface in an arsenic ambient. From this surface, all other reconstructions can be generated by simply annealing the sample to the appropriate temperature, according to Table III.2 [52]. The reconstruction associated with the highest temperature before the sample shows signs of decomposition is the c(8x2) reconstruction. This surface has been found to have the least amount of As present in the surface layer and is described as a Ga-stabilized surface. It should
Table III.2  Gallium arsenide reconstructions with measured arsenic coverages in surface layer.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Preparation</th>
<th>As Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>c(8x2)</td>
<td>IBA, 500-620°C</td>
<td>0.22</td>
</tr>
<tr>
<td>(4x1)</td>
<td>IBA, 500-620°C</td>
<td></td>
</tr>
<tr>
<td>(4x6)</td>
<td>IBA, 400-500°C</td>
<td>0.27</td>
</tr>
<tr>
<td>(1x6)</td>
<td>IBA, 350-450°C</td>
<td>0.52</td>
</tr>
<tr>
<td>c(2x8)</td>
<td>MBE</td>
<td>0.61</td>
</tr>
<tr>
<td>c(4x4)</td>
<td>MBE</td>
<td>0.86</td>
</tr>
<tr>
<td>(1x1)</td>
<td>IBA, 150-350°C, MBE</td>
<td>&gt;1.0</td>
</tr>
</tbody>
</table>
be noted, however, that this surface does contain some As in the surface layer and is therefore not a Ga terminated surface.

Virtually all structural studies have centered on the c(2x8) reconstruction. This reconstruction is the predominant surface which results from optimal MBE growth conditions.

In 1976 it was demonstrated by Cho [55] that the two-fold direction in the c(2x8) As-rich structure was parallel to the [-110] plane containing the surface As dangling bonds. This result gave rise to the idea of As atoms dimerizing in the two-fold direction of the As-rich surface. This dimerization reduced the number of surface states and lowered the energy of the system by reducing the number of surface dangling bonds. The occurrence of dimerized arsenic on a GaAs surface was reinforced when Arthur [56] showed that arsenic stabilized c(2x8) surfaces lose about 0.5 monolayer of arsenic as As$_2$ in the gas phase when heated to 500°C. In their evaporation studies of GaAs, Foxon et al. [57] have also shown that arsenic leaves the surface as a dimer.

Recently, concern has arisen over the determination of the four-fold periodicity often observed along the [110] direction. Early models consisted of a complete layer of dimerized As$_2$ which were tilted [58] and twisted
so that one atom moves up and the other down, and arranged so as to give a four-fold periodicity in the [110] direction. These models, however, were inconsistent with diffraction features of RHEED, and cannot fully explain photoemission data, and hydrogen adsorption [60]. Tight binding total-energy calculations by Chadi et al. [61], on various GaAs(100) reconstructed surfaces found that the most likely surface structures contain dimerized arsenic, and that reconstructions result from so-called missing dimer structures. Hydrogen adsorption HREELS studies performed by Frankel et al. [62] showed a ratio of AsH/GaH of 1.5 on the supposedly As-rich c(2x8) surface. Given a unit cell of eight sites per layer they proposed a possible structure with three As dimers and one dimer vacancy. The vacancy would expose four second layer Ga atoms and result in the 1.5 ratio seen. Their model is very similar to that of Chadi.

More recently, Pashley [63] et al. have used the scanning tunneling microscope (STM) to study the MBE grown (2x4) and c(2x8) reconstructions of the As-rich GaAs(100) surface. Their images have confirmed the missing dimer models proposed by both Chadi and Frankel. Furthermore, they found that the (2x4) and c(2x8) reconstructions are essentially identical, the only
difference being the orientation of the dimers at surface kinks, Figure III.3. The lack of As at these sites serve as defects in an otherwise completely As terminated surface.
Figure III.3 GaAs(100) c(2x8) and (2x4) reconstructions from scanning tunneling microscopy (STM) data of Pashley.
IV. EXPERIMENTS

Three separate experiments were carried out on the GaAs(100) surface, each probing a different aspect of the nature and interaction of this surface under controlled conditions. A slightly different experimental setup and technique was used in each case, and therefore it is necessary to treat each individually. The experiments, then, will be described as separate and complete entities, each with its own results and conclusion. A final conclusion of all work completed on this surface will be given in section V.
A. The Adsorption and Thermal Desorption of Chlorine from GaAs(100) Surfaces

1. INTRODUCTION

Here is reported the interaction of chlorine gas with ion-bombarded and annealed (IBA) and epitaxially grown (MBE) GaAs(100) surfaces. Using Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS), low-energy and reflection high-energy electron diffraction (LEED and RHEED), a characterization of the uptake of chlorine on As-rich and Ga-rich GaAs(100) surfaces and its removal by thermal desorption is made. The adsorption of chlorine proceeds only to the extent of about 25% of a monolayer coverage, and it is inferred that the Cl is preferentially bonded to Ga atoms. On heating, only GaCl and As₂ desorb from the surface. A model involving a arsenic-dimer/replacement at defect sites is postulated to account for these observations.
2. EXPERIMENTAL

The experiments were performed in a standard ion-pumped vacuum system fitted with LEED/Auger optics and an in-situ electrochemical source of chlorine that allows dosing of the surface without any appreciable rise in the background chlorine pressure [64]. The system also contains a quadrupole mass spectrometer used to monitor the desorption products. The sample was a Si-doped (4.7×10^{18} \text{ cm}^{-3}) semiconducting GaAs(100) (± 1/4°) surface. It was cleaned with a choline wet-etch prior to mounting on the manipulator, and underwent a series of ion bombardment and anneal (IBA) cycles to produce a clean, well-ordered surface. The manipulator contained an electrically isolated filament for heating, and liquid nitrogen cooling, with a thermocouple in contact with the sample surface to monitor temperature. Specific details concerning the vacuum apparatus and operation of the various spectrometers are given in Appendix A.

In order to identify any differences between IBA and MBE prepared surfaces we performed a series of experiments on MBE grown c(2x8)-As and c(8x2)-Ga surfaces. Here we used a PHI model 425B Molecular Beam Epitaxy growth chamber attached to an analysis chamber.
where we performed Auger analysis during adsorption and desorption of chlorine. The growth chamber contained a RHEED apparatus which was used to insure the crystallinity and orientation of the grown surfaces. The in-situ electrochemical chlorine cell described above was also employed in this system.

One problem faced in using two systems was that of accurate measurement of the surface temperature. The thermocouple for the IBA samples was positioned between the sample surface and the mounting clips of the manipulator, while the MBE thermocouple was located in the area directly behind the sample, between the sample and the heater (both systems used radiant heating elements). Consequently, TDS experiments on the MBE samples gave rise to desorption products at higher temperatures than did the IBA experiments. To overcome this problem we monitored the desorption of gallium oxide which we knew occurred at 580°C from infrared pyrometry measurements made during MBE growth. This provided us with a similar occurrence by which we could calibrate our temperature readings in both systems.

Depending on the history of the sample we could produce the large number of surface structures found by others [52]. Our IBA experiments concentrated on the "low-temperature" (1x1)-As surface, and the "high-
temperature" c(8x2)-Ga surface. These surfaces, along with the c(2x8)-As reconstruction could also be prepared by MBE. The range of intermediate structures found between 25°C and 625°C are shown in Table III.2. It has been established [53] that the reconstructions are due to a decreasing As concentration with a corresponding increase in substrate temperature.

Preparing the IBA sample by annealing at low temperature (350°C) resulted in a (1x1) surface. These (1x1) surface LEED patterns were rather diffuse leading us to believe that there was still some disorder present. This is not unusual considering the low annealing temperatures, and subsequently longer annealing times required to obtain this surface.

The (1x1) surface could also be generated by MBE by allowing the sample to cool in an arsenic ambient. Monitoring the low energy Auger Ga and As transitions on the MBE sample resulted in a As/Ga ratio of 3.12. Others [52,54] have also observed a (1x1) on MBE grown surfaces and have determined that it was As-rich, containing as much as a full monolayer of As. Although this does not guarantee that the IBA prepared (1x1) was indeed arsenic rich, there has yet to be any experimental confirmation of a Ga-rich (1x1) surface. Furthermore, thermal desorption spectra, detailed in section IV.A.3, from the
IBA samples reveal a large flux of arsenic leaving this surface upon heating, which is in good quantitative agreement with previous work by Arthur [56] on the c(2x8)-As surface.

3. RESULTS

a) Auger electron spectroscopy

i) adsorption

The uptake of chlorine was monitored on both Ga-rich and As-rich surfaces. As Cl is rapidly desorbed by the electron beam (see section IV.B), we paid careful attention when taking Auger spectra to avoid Cl-loss by electron-stimulated processes. By taking spectra quickly, keeping the beam energy as low as possible, and rastering the electron beam, we were able to obtain stable Auger spectra which did not vary with time.

Figure IV.A.1 shows typical uptake curves for the c(8x2)-Ga stabilized and the c(2x8)-As stabilized surfaces. Details of the Cl gun performance are given elsewhere [65], but calculations indicate that enough chlorine to completely cover the surface is produced after 200 sec of exposure. From the initial slopes of the curves, the sticking coefficient for the As-
Figure IV.A.1 Chlorine uptake on GaAs(100) as measured by Auger spectroscopy for As(squares) vs. Ga (circles) stabilized reconstructions. The slope of the initial uptake results in a ratio of the initial sticking coefficients of $S_{\text{As}}/S_{\text{Ga}}=0.72$. 

\[ \frac{S_{\text{As}}}{S_{\text{Ga}}} = 0.72 \]
stabilized surface can be calculated as 72% of that for the Ga-stabilized surface,

\[ S_{As}/S_{Ga} = 0.72 \]

indicating that Cl has a preference for Ga. Such a preference for adsorption onto Ga was also seen in unusual effects in the high energy Auger signals [66]. Further evidence of preferential Ga-Cl bonding came from another experiment performed on an "As-capped" surface. In this experiment, approximately 50 Å of As were deposited on an MBE-grown c(2x8) surface - we were unable to measure any Cl adsorption.

Using Auger data to calculate surface coverage information is a difficult task when adsorption occurs on compound materials, especially when the surface structure of the substrate is still in question. More so when surface rearrangements occur upon adsorption which may change the composition of the surface (see section IV.A.4). Considering this, we have taken two approaches to determine the surface chlorine coverage at saturation.

Although the initial rates of Cl uptake are different, both curves level off at the same saturation level. Using existing Auger sensitivity factors [67] we determined that saturation chlorine coverage gave both a Cl/Ga and a Cl/As ratio of 0.15. Although the sensitivity factors were made under different
experimental conditions, they do enable us to make this initial estimate of the amount of adsorbed chlorine. Difficulties arise however, since GaAs is a compound semiconductor, and the composition of these reconstructions varies widely from the As-rich c(2x8) to the Ga-rich c(8x2).

Alternatively, we can monitor the change in the As and Ga Auger signals upon adsorption. The low energy peaks of arsenic (31 eV) and gallium (55 eV) are very surface sensitive, their escape depths having been determined as only 6 Å and 4.8 Å respectively [68]. These can be exploited to reveal the composition of the surface when chlorine is introduced to the system. From the zero-coverage data in Figure IV.A.2 we estimate the initial atomic ratios of As/Ga to be 2.4 for the As-rich c(2x8) surface, while the Ga-stabilized c(8x2) surface has a much lower ratio of 1.6. These peak-to-peak ratios are in good agreement with those determined by Drathen et al [52]. Monitoring the As(31) and the Ga(55) transitions during chlorine adsorption shows that the As signal decreases by 10% on both the As-stabilized and the Ga-stabilized surfaces. The Ga signal, on the other hand, shows a small but measurable decrease of intensity on the Ga-stabilized, but not the As-stabilized surface. Using the layer model proposed by Ranke et al. [68], we
Figure IV.A.2 Auger intensity of As and Ga during chlorine adsorption on Ga and As stabilized surfaces. The Ga intensity has been doubled in order to plot it on the same scale as As.
may determine the surface coverage. Following this model, the thickness of an adsorbed layer is given by

\[ z = -\lambda \ln(J_s(z)/J_{so}) \]  

(eqn. IV.A.1)

where \( \lambda \) is the escape depth of the Auger electron for a transition occurring on the substrate atoms and \( J_{so} \) and \( J_s(z) \) are the intensities of this transition for surfaces respectively clean and covered by the adsorbed layer.

The relationship between coverage, \( \theta \), and thickness of the adsorbed layer was taken as \( z = \theta d \), where \( d \) is the thickness of a monolayer. Assuming a value for \( d \) of 2.16 Å from AsCl₃ bond lengths [69] and assuming reasonable substrate compositions, as given in Table III.2, for the c(8x2) and c(2x8) surfaces, we have calculated, using equation IV.A.1, the amount of coverage to be 24% and 22% respectively for these two reconstructions. These values are similar to one another and also quite similar to that obtained previously. Caution must be used, however, when interpreting this adsorption data, since the amount of surface Ga and As for a particular reconstruction may vary depending upon preparation conditions. Further complications arise if preferential adsorption, reactive chemisorption or surface reconstructions (see section IV.A.4) are occurring during the adsorption. Therefore, these values should be considered as a general guide rather than an absolute
estimate of the surface coverage.

To investigate the role of defects in Cl adsorption, we deliberately damaged an MBE c(2×8) sample, with an As/Ga ratio of 2.4, by sputtering with 3 kV argon ions, followed by a 30 minute anneal at 350°C. The low energy Auger intensities reveal that the sputtering results in an increased amount of surface Ga, giving an As(31eV)/Ga(55eV) Auger ratio of 1.4. This represents even more surface Ga than the c(8×2)-Ga rich surface. Figure IV.A.3 shows the Cl uptake on a MBE-grown c(2×8) well ordered surface and on an MBE sample which was sputter damaged. The ratio of the initial sticking coefficient now becomes

\[ \frac{S_{\text{MBE}}}{S_{\text{damag.}}} = 0.56 \]

where \( S_{\text{MBE}} \) is the sticking coefficient for an As-stabilized MBE grown sample. From this we can say

\[ S_{\text{As,MBE}} < S_{\text{Ga,MBE}} < S_{\text{damag.}} \]

It can also be seen from the figure that the Cl Auger signal on the damaged surface stabilizes with an intensity which is 20% greater than on the ordered surface.

ii) desorption

Monitoring the high energy Ga(1070) and As(1228)
Figure IV.A.3 Chlorine Auger (183 eV) signal during adsorption on GaAs(100) on MBE c(2x8) and sputter damaged surface. The Cl gun was operated at one-half the operating current used in Figure 1, hence the difference in exposure time.
Auger peaks showed no marked change in the ratio of these two signals during desorption, probably due to the large sampling depths corresponding to these transitions. This is in agreement with the Auger studies of Proix et al. [70] on the (110) surface, who found a constant Ga/As ratio until 800°C when the Ga signal rose to approximately four times the size of the As peak.

However, the Cl and low energy Ga and As Auger peaks show marked changes during TDS cycles of Cl saturated samples. Figure IV.A.4 reveals a very sharp drop in the Cl signal at 500°C on both Ga and As-stabilized surfaces. The As(31) peak shows a small rise during Cl desorption followed by a drop in intensity while the Ga(55) peak stays constant during Cl desorption and then rises rapidly above 600°C. These intensities remain constant until the sample is cooled to room temperature. The Ga signal now remains at the same level while the As signal rises about 10-12%.

b) Diffraction

LEED patterns observed during thermal treatments of IBA prepared samples reveal the reconstructive changes which occur by varying the temperature of the substrate. When annealing at temperatures below 400°C we observe a
Figure IV.A.4 Ga(55 eV) and As(31 eV) Auger signals during TDS from a Cl covered Ga-stabilized surface. Similar behavior is seen on the As-stabilized surface.
(1x1) symmetry. Heating at 400°C to 500°C gives rise to either the (1x6) or (4x6) pattern. Finally, heating the sample above 600°C, leads to the (4x1) or c(8x2) reconstruction, depending on the annealing time.

We monitored LEED patterns during adsorption and desorption on the IBA samples. On both As-stabilized and Ga-stabilized surfaces we detected no significant change, other than an increase in the background signal. Likewise, RHEED patterns of chlorine covered As and Ga stabilized MBE grown surfaces revealed no apparent changes in the surface symmetry from that of the clean surfaces.

RHEED patterns taken on sputter damaged then annealed surfaces typically display no ordered patterns. However, RHEED measurements taken after a chlorine adsorption/desorption cycle on a sputter damaged surface, revealed an appreciable degree of surface ordering.

c) Thermal desorption

i) clean surfaces

Thermal desorption experiments were performed on clean and chlorine covered "As-rich" (1x1) and "Ga-rich" c(8x2) surfaces (see Table IV.A.1). Clean GaAs(100) (1x1)-As surfaces display arsenic dimer desorption
Table IV.A.1  Desorption products from clean and chlorine covered GaAs(100) surfaces.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Species</th>
<th>Clean Surface</th>
<th>Cl-sat'd Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T_{\text{max}}$ (°C)</td>
<td>$\theta$ (%)</td>
</tr>
<tr>
<td>(1x1)-As</td>
<td>As$_2$</td>
<td>500</td>
<td>40-50</td>
</tr>
<tr>
<td></td>
<td>GaCl</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>AsCl</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>As$_2$</td>
<td>&gt;600</td>
<td>-</td>
</tr>
<tr>
<td>c(8x2)-Ga</td>
<td>GaCl</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>AsCl</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
starting at 475°C (Figure IV.A.5). Both types of surfaces show a large \( \text{As}_2 \) desorption beginning at 625°C. A rise in the Ga signal accompanies the As signal at 625°C and is attributed to the bulk evaporation of GaAs. In common with others [70] we have observed, using scanning Auger microscopy, the formation of Ga "droplets" on samples heated above 650°C degrees. The samples were never heated above 650°C to insure that the formation of such droplets on the surface would not occur.

The \( \text{As}_2 \) desorption signal at 475°C coincides with the changes noted earlier in the diffraction patterns. The (100) surface changes from a (1x1) symmetry to (1x6) - (4x6) at 400°C to 500°C and finally at 600°C to the (4x1) or c(8x2) structure, depending on annealing time. Integrating the area under the 475°C TDS peak indicates approximately 40%-50% of a monolayer of As desorbing, in agreement with the work of Arthur [56]. When the TDS experiment is now repeated on the c(8x2) surface that forms after heating the As-rich (1x1) structure to 625°C, there is no arsenic dimer peak seen at 475°C.

ii) chlorinated surfaces

A clean (1x1) surface was dosed with chlorine to saturation and the temperature ramped from 0°C to 625°C. The spectrum in Figure IV.A.6 shows a prominent peak due
Figure IV.A.5  Arsenic dimer desorption from clean GaAs(100) surface reconstructions. Region A shows (1x1) and c(2x8) LEED patterns. Region B shows (1x6) and (4x6) diffraction patterns. Region C is the Ga-rich surface and shows a (4x1) or c(8x2) reconstruction. Starting a TDS scan with an already As depleted surface, i.e. the c(8x2), results in no dimer desorption below 625 °C.
Figure IV.A.6  TDS of the chlorine saturated GaAs(100)-(1x1) surface. No higher chlorides of either Ga or As desorb.
to GaCl centering at 375°C with a shoulder at 450-500°C. Integration of these peaks gives approximately 15% of a monolayer of GaCl (Table IV.A.1). Curiously, there is no corresponding AsCl signal. A similar experiment in which Cl was adsorbed on the GaAs sample at -88°C also showed no sign of arsenic chloride desorption, indicating that the more volatile arsenic chlorides were not evaporating during adsorption, before the TDS ramp had begun. There was also no evidence of di-or trichlorides of gallium.

The TDS data of Figure IV.A.6 also shows an arsenic dimer peak slowly rising at 300°C with a sharp increase at 475°C, similar to the sharp rise observed on the clean surface.

A similar experiment on the c(8x2) surface, produced by annealing at 600-625°C, was performed by cooling to 25°C and dosing with Cl₂. At saturation coverage the GaCl TDS trace of Figure IV.A.7 shows, as in the (1x1) case, a prominent peak at 350°C-375°C. It also shows, but to a much lesser extent than the (1X1) surface, a small shoulder at 450-500°C. Integrating the total desorption signal, as for the (1x1) surface, also gives about 15% of a GaCl monolayer.

An interesting aspect of the c(8x2) Cl covered surface is the appearance of arsenic dimer desorption around 550°C from a Cl saturated surface. These dimers
Figure IV.A.7  TDS of the chlorine saturated GaAs(100)-c(8x2) surface. No higher chlorides of either Ga or As desorb.
are not seen below about 600°C when thermal desorption experiments are carried out on the clean c(8X2) surface — as can be seen more clearly in Figure IV.A.8.

We also observe a large Cl desorption signal during TDS from both Ga and As stabilized surfaces. It is somewhat difficult to clearly define the source of this chlorine. From recent mass spectroscopy studies [71], however, it appears that not all Cl which is entering the mass spectrometer is due simply to the cracking of gallium chlorides. The excess amount may be due to desorption of weakly bound Cl from the surface and chlorine which has adsorbed onto other surfaces of the manipulator.

4. DISCUSSION

a) clean surfaces

A significant feature of our desorption results from clean GaAs surfaces is the observation of the desorption of As dimers at about 475°C, followed by evaporation of Ga and As at temperatures in excess of 650°C. These results are consistent with earlier studies. Evaporation studies by Foxon et al. [57], using a modulated beam technique, indicate that arsenic desorbs in a dimer form. The desorption of arsenic dimers from a GaAs surface was
Figure IV.A.8  As$_2$ dimer desorption from the clean and Cl covered c(8x2) surface.
observed earlier by Arthur [56], who showed that arsenic stabilized surfaces lose about 0.5 monolayer of arsenic as As₂ when heated to 500°C. Our integrated mass spectrometric data from an (IBA) prepared sample, indicate about 40%-50% monolayer desorption of arsenic as As₂, in good quantitative agreement with that work. The appearance of As₂ in the gas phase upon desorption does not necessarily imply that dimers were present upon the surface prior to desorption. The As₂ desorption signal could be due to a recombination of As atoms on the surface during the TDS ramp. Unfortunately, the quality of our TDS data do not permit a ready distinction between first and second order desorption processes.

However, there is a wealth of independent evidence that suggests that As dimers are an integral component of the GaAs(100) reconstructions. Cho [55] demonstrated that the two-fold direction in the c(2x8) As-rich structure was parallel to the [1 10] plane containing the surface As dangling bonds, suggesting the existence of As-As bonding. Since then a number of structural studies have been carried out which reasonably demonstrate the existence of arsenic dimers on the (100) surface [58-60]. Recent studies [61-63,72] suggest that the various reconstructions observed result from missing rows of As dimers at the surface. These missing rows serve as
defects in an otherwise completely As terminated surface and give rise to the superstructure diffraction patterns such as the c(2x8) and the (2x4).

Hence, although we cannot definitely associate the observation of As dimers in the gas phase during thermal desorption with the prior existence of the same species on the surface, it seems likely that the observed desorbing dimers do indeed probably originate from pairs of As atoms already partially bonded on the surface prior to desorption.

Figure IV.A.5 shows there are three general regions in the TDS spectra seen upon heating the clean substrate. Region A, from room temperature to 450°C, is the region where we see the (1x1) LEED pattern, and the MBE grown c(2x8) structure. In Region B, where the temperature is increased from 450°C-550°C, desorption of the As dimer is seen in the mass spectrometer and the intermediate (1x6) and (4x6) LEED patterns develop. These patterns we might attribute to the loss of As₂. As the sample is heated further into region C, the loss of more As₂ and of Ga gives rise to the (4x1) and the c(8x2) structures. These structures appear very similar and others [54] have noted similar behavior between the two. Both structures appear at 625°C and the difference between them seems to be attributed to different annealing times. The (4x1)
appears after short anneals (<5 min.), and hence must be a "frozen out" or non-equilibrium structure. The c(8x2) surface appears after annealing the sample for 20-30 min.

b) Chlorinated surfaces

We can summarize the Auger and TDS data from chlorinated GaAs(100) surfaces as follows:

- chlorine does not adsorb on an As-capped surface
- adsorption proceeds to about 25% of a monolayer on a Ga-rich c(8x2) and a As-rich c(2x8) surface
- a sputter-damaged surface adsorbs more chlorine than either the c(8x2)-Ga or c(2x8)-As surfaces
- the sticking coefficient for chlorine varies as $S_{\text{As-rich}} < S_{\text{Ga-rich}} < S_{\text{damaged}}$
- the only chloride observed in TDS is GaCl

Clearly, the sticking coefficient data, and the observation of solely GaCl desorption during TDS, indicate that Cl preferentially adsorbs on exposed Ga at the GaAs(100) surface. The desorption of only GaCl may seem contradictory in view of the higher volatility of the arsenic chlorides. However, we note that this is consistent with the results of Balooch et al [73]. During ion assisted etching reactions on the GaAs(100)
surface they found that at low Cl coverages the mono
chlorides of gallium are initially formed, and that at
room temperature, a non-volatile GaCl "scale" builds up
while the ion beam is turned off. Only under higher Cl
flux did they observe the formation of arsenic chlorides,
mainly as AsCl₂; also at these higher Cl pressures Ga
became fully chlorinated as GaCl₃. Hence, our
experiments are in agreement with their low coverage
experiments.

Other evidence for preferential Ga-Cl bonding on GaAs
comes from the electron energy loss work of Troost et al
[74] on the (110) surface, although contradictory results
were obtained by Margaritondo et al [75]. There is also
evidence of a general trend for preferential bonding of
halides to the group III element in III-V semiconductors.

Jacobi et al [76] have demonstrated the build up of GaIₓ
(x=1,2,3) after a GaAs(111) surface has been exposed
to iodine. Their thermal desorption results, like ours,
shown no indication of the formation of arsenic halides.
Further evidence comes from the XPS analysis of InSb(100)
by Vasquez [77], which showed layers of InCl at the
surface with no detectable bonding between Cl and the
group V element.

The area of an undamaged surface that adsorbs
chlorine is relatively small. This suggests that we are
observing defect chemistry at exposed Ga atoms at the GaAs(100) surface. These results echo the \( \text{H}_2\text{S} \) adsorption work of Massies et al [20]. They observed that the differences in sticking coefficients could be attributed to differences in point defect concentration at the surface.

This scenario can account for many of our observations. Thus, an As-capped surface, with no exposed Ga, is inactive for Cl chemisorption. Sputter damaged surfaces, with more defects that expose Ga, both adsorb chlorine more quickly, and to a greater extent, than do undamaged surfaces. Further support of defect sites as chlorine chemisorption centers comes from the well ordered RHEED patterns seen following chlorine adsorption/desorption cycles on sputter damaged surfaces. RHEED patterns are qualitatively much sharper following these cycles than those from a sputter damaged surface that has not been chlorinated. This is probably due to the removal of the defect sites during the chlorine adsorption/desorption cycle, resulting in a better ordered surface.

It is difficult at this stage to precisely locate these chlorine adsorption sites. We should remember that even a Ga-rich surface still contains a large surface concentration of As. Estimates for the amount of Ga in
the c(8x2)-Ga reconstructed surface vary from as high as 78\% [52] to as low as 48\% on the same surface [78]. We suggest that there are two possible sources of exposed Ga atoms in these surfaces. One type are "missing As dimer" defects that expose underlying Ga atoms, and that are responsible for the many reconstructions. The second are what Massies et al [20] have termed "free" defects that expose Ga at the surface; these are not associated with surface reconstructions, but are still active chemisorption sites, steps for example.

Assuming that the TDS data is accurately reflecting the surface structure, it appears that when chlorine is adsorbed on a GaAs(100) surface it is mobile enough on the surface to find a Ga binding site even on As-rich surfaces. We note here the same ability of H to locate Ga atoms on As-rich surfaces seen by Frankel et al [62]. Not only can Cl apparently efficiently locate Ga atoms even on an As-rich surface, but the total amount of chlorine adsorbed and the amount of GaCl that desorbs upon heating are closely similar between the two surfaces.

This similarity in chlorine adsorption/desorption behavior between what are nominally two rather different starting surfaces leads us to propose that the adsorption process itself changes the nature of an As-rich surface,
the end product closely resembling that of a Ga-rich surface, at least as far as Cl chemisorption sites are concerned.

On an As-rich surface the arsenic atoms have used their dangling bonds to form the dimers. There are few available single As bonding sites to attract the chlorine, without disrupting As dimers. The As cap experiment shows that elemental As itself does not react with chlorine. As the dimers form, they do expose second layer gallium atoms which can act as Cl chemisorption sites.

An inspection of the dissociation energies given in Table IV.A.2 reveals that although both AsCl and GaCl have strong binding energies, it is the comparable strength of the As-As bond which prevents the formation of AsCl, i.e. AsCl will not form at the expense of breaking an As-As bond. Furthermore, assuming that the TDS results truly reflect the surface reactions, it appears that the addition of Cl to a Ga-stabilized surface aids in the formation of As₂ which did not previously exist, as witnessed by the increased 550°C As₂ TDS peak in the chlorinated data in Figure IV.A.8. Apparently it is more energetically favorable to form GaCl and As-As bonds than AsCl.

We find GaCl formation on both As-stabilized and Ga-
Table IV.A.2  Bond strengths of diatomic molecules relevant to Cl adsorption on GaAs.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga-Cl</td>
<td>4.99</td>
</tr>
<tr>
<td>As-Cl</td>
<td>4.64</td>
</tr>
<tr>
<td>As-As</td>
<td>3.96</td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>2.52</td>
</tr>
<tr>
<td>Ga-As</td>
<td>2.17</td>
</tr>
<tr>
<td>Ga-Ga</td>
<td>1.43</td>
</tr>
</tbody>
</table>
stabilized surfaces. On the As-stabilized surface it is possibly the presence of arsenic dimers that results in Cl bonding to second layer gallium which is somewhat exposed [62]. On the Ga-stabilized surface, Cl binds to top-layer Ga, and the formation of the Ga-Cl bond promotes the formation of previously absent arsenic dimers which desorb at 550°C.

On both the As-stabilized and Ga-stabilized surface, during Cl adsorption, there is a noticeable reduction seen in the As(31) Auger peak, while the Ga(55) peak decreases slightly only on the Ga-stabilized surface. This may be indicative of a replacement reaction between Cl and As. A similar replacement reaction is seen between Al and Ga when Al is adsorbed on GaAs(110) [79]. There, it was found by LEED intensity analysis, that upon annealing, Al replaces Ga in the second atomic layer after 0.5 monolayers of Al were adsorbed.

The replacement reaction may occur in a number of ways. One possibility is that the Cl actually removes the As from the surface as a volatile chloride during adsorption. However, our low temperature adsorption/desorption data show no sign of As chloride formation. Alternatively the Cl may initiate the formation of antisite defects, resulting in Ga-Cl bonds and As in Ga sites, thus producing a GaCl surface layer, similar to
that found by Balooch et al [73]. If As atoms move
towards the bulk we might expect to see its Auger signal
to decrease as was observed. The Ga atoms that move
towards the surface are also being covered by Cl, result-
ing in at most a very small change in its Auger signal.
On either surface there is never a change of Auger
intensity of the Ga or As signal of more than 10%. This
indicates that these replacement reactions are occurring
to a small extent, consistent with the proposal that
reactions are occurring mostly at surface defect sites.
5. CONCLUSIONS

We have found, by LEED and RHEED measurements, that chlorine adsorption on the GaAs(100) surface causes no noticeable change in the surface symmetry on both the As and Ga stabilized surfaces. Thermal desorption spectra of clean GaAs shows direct evidence of the loss of As\textsubscript{2} on IBA prepared samples which can be correlated to surface reconstructions. Although IBA samples show a larger degree of damage than MBE prepared samples, they seem to be quite similar in composition, and show similar behavior when exposed to chlorine.

Auger data indicate that Cl bonds preferentially to Ga and covers less than 25\% of the surface at saturation. Ion bombardment results in the adsorption of more chlorine onto the surface with a higher sticking coefficient. This evidence is consistent with chlorination occurring at defect sites. RHEED measurements suggest that surface defects are being removed following chlorine adsorption/desorption cycles.

The desorption of AsCl\textsubscript{x} is never observed, while GaCl is seen to desorb from both As-stabilized and Ga-stabilized surfaces. Adsorption and subsequent desorption appears to occur at missing As dimer defects.
or free defect sites which are not involved in reconstructions, both of which expose second layer Ga atoms. Changes in the Auger signal of the substrate atom may be indicative of a replacement reaction of chlorine for arsenic at defect sites.
B. Electron Stimulated Desorption of Chlorine from GaAs(100) Surfaces

1. INTRODUCTION

For III-V materials, the etching reactions used to form device grade material typically exploit the volatility of the chlorides under the influence of an energetic beam of ions [66]. However, the external energy source in assisted chemical etching of this sort is not limited to ions. Thus, Ashby [80] has shown that incident photons, in the presence of chlorine, will also promote the etching of gallium arsenide. As electron beams are less damaging to the surface, and easier to produce than ion beams, it is of interest to explore their potential as the driving force in the etching of GaAs. In another context, Coburn [81] has shown that the etch rate of silicon dioxide with XeF₂ proceeds at a rate of 200 Å/min in the presence of an incident electron beam. Although others [82,83] have noted removal of surface chlorine by an incident electron beam, the process has received little attention as a possible alternative to ion beam etching for GaAs. This study characterizes the removal of chlorine adsorbed on GaAs(100) surfaces by electron-stimulated desorption.
Such processes may form the basis for the use of electron beams as a focused energy source for high-definition assisted etching. It is found that chlorine adsorbed on a GaAs(100) surface is sensitive to ESD and that loss of chlorine proceeds via two processes on different time scales. Furthermore, chlorine adsorbed on areas of the surface that have not been under the influence of the electron beam does not diffuse at a detectable rate into areas stripped of chlorine by ESD. Using mass spectroscopy, it was determined that, under low chlorine coverage conditions, ESD products consist solely of chlorine atoms, although it is possible that under a high chlorine flux etching may occur.

The experiments were performed in the standard ion-pumped vacuum system and MBE system which were described in section IV.A.2.

2. RESULTS

All ESD experiments were performed on As-stabilized surfaces. After a clean surface was obtained, it was dosed until saturated with chlorine. Figure IV.B.1 is a typical uptake curve as measured by the Cl Auger peak at 183 eV for the As-stabilized surface. Previous work in this laboratory, see section IV.A, has shown that chlorine adsorbs preferentially to Ga atoms at defect
Figure IV.B.1  The uptake of chlorine on an As-rich(1x1) GaAs(100) surface monitored with the Cl(183 eV) Auger signal. The chlorine exposure is the time for which the electrochemical Chlorine source was turned on at a current of 150 μA.
sites in this As-rich surface. In the absence of an incident electron beam, this overlayer is very stable. However, as Figure IV.B.2 shows, the adsorbed Cl is very sensitive to ESD by the electron gun used for the Auger analysis. The incident electron beam energy was varied in the range of 500 - 2000 eV, but typically a beam energy of 1000 eV, and an electron current of 15 microamps, was used. The decay of this signal with time is best fitted by a bi-exponential function, the solid line in the figure, implying at least one fast and one slow route for desorption.

Positioning the sample in front of the mass spectrometer and turning on the electron gun results in the atomic chlorine (AMU 35) signal seen in Figure IV.B.3. The mass spectrometer signal shows a sharp rise initially, followed by an exponential decay of the chlorine signal.

The rate of removal of chlorine is a function of the amount of chlorine present at the surface. As the amount of chlorine at the surface becomes smaller so will the flux of chlorine from the surface become smaller, resulting in the decay seen in the mass spectrometer - this instrument measures flux rather than concentration. Since the Auger signal ($I_{Cl}$) measures the concentration of Cl remaining on the surface, then $(1-I_{Cl})$ represents
Figure IV.B.2 The effect of a 1000 eV electron beam used for Auger analysis, at 26.0 and 15.0 μA beam currents, on the Cl (183 eV) Auger signal from chlorine adsorbed on GaAs(100). The solid lines are bi-exponential decay best fits for the two ESD processes with cross-sections of approximately $1 \times 10^{-18}$ cm$^2$ and $2 \times 10^{-19}$ cm$^2$. 
Figure IV.B.3  A comparison of the rate of removal of surface chlorine from GaAs(100) as monitored by the decay of the Cl (183 eV) Auger signal (solid line), and the appearance of Cl atoms in the gas phase, measured by the 35 AMU mass spectrometer signal (filled circles).
the amount of Cl lost by electron induced processes. The
time derivative of this Auger function, \( \frac{d(1-I_{Cl})}{dt} \),
should closely follow the mass spectrometer decay signal.
The solid line in Figure IV.B.3 is the slope of the
function corresponding to the decay of the Auger signal,
and clearly follows the mass spectrometer decay curve.
The time lag for the mass spectrometer signal to coincide
with the Auger decay curve is presumably due to facile
adsorption of the initially desorbing Cl on the chamber
walls and other surfaces. The large amount of scatter
seen in the mass spectrometer signal is also probably due
primarily to residual chlorine adsorbing and desorbing
from exposed components and the vessel walls.

We scanned all other relevant masses in the
spectrometer for desorption products, especially the
arsenic and gallium chlorides, but saw no other signals
above the noise level of our instrument. We also
searched for positive ion desorption thresholds in the
low energy region (50-250 eV). Again, we detected no
signals above the noise level.

Further confirmation of Cl atoms as the predominant
desorption product comes from comparing the integrated
chlorine signal from the mass spectrometer to that of the
Auger decay signal. If Cl atoms are the only desorption
product, then these two quantities should be identical.
After ten minutes of exposure to the electron beam the Auger chlorine signal has decayed to roughly 25% of its saturation value. Using reasonable values for experimental parameters, we can estimate the amount of chlorine detected by the mass spectrometer during the same time period, as approximately 25%-50% of a monolayer of Cl. This estimate may be somewhat high, primarily due to residual Cl present in the chamber, but is clearly of the same order as that derived from the Auger data.

Figure IV.B.4 shows details of an experiment intended to determine if surface migration of Cl played a role in the observed ESD effect. We monitored the uptake of chlorine on an MBE-grown As-rich surface up to saturation with a rastered Auger beam, to avoid creating ESD damage during adsorption. The raster was then turned off, and a "hole" created in the chlorine adlayer via electron induced desorption of chlorine. After creation of this Cl- deficient region, the electron beam was turned off to allow any Cl to refill the hole by diffusion. The beam was then turned on occasionally for just long enough to sample the Cl (183 eV) transition, and this process repeated over a period of 35 minutes. Figure IV.B.4 shows that there is no appreciable migration of Cl back into the hole once it has been formed. Even if the electron beam was moved one beam diameter away to provide
Figure IV.B.4 An experiment to create a "hole" in a chlorine adlayer and observe any migration of chlorine into the depleted region from its surroundings. Chlorine desorption was monitored with a rastered beam to avoid ESD. The chlorine source was turned off and the beam kept stationary to create a Cl-deficient region by ESD. The electron beam was then turned off completely except for very short measurement of the Cl Auger intensity at 183 eV at 5 minute intervals.
an extra source of energy in the area neighboring the hole, no chlorine was seen to return to the original Cl-depleted region.

3. DISCUSSION

Electron induced changes in the coverage of chlorine on GaAs has been noted by other authors [82,83]. However, these studies were limited to noting the occurrence and did not probe the effect in any detail - for instance, no attempt was made to ascertain the nature of the desorbing species.

Using a mass spectrometer to monitor the desorption products, we find that Cl atoms are the only species being desorbed from the surface in measurable quantities. The rate of appearance of Cl in the gas phase appears to match the disappearance of Cl from the surface, as monitored by Auger spectroscopy. Furthermore, the integrated total losses seen by both techniques are comparable. Thus, it is likely that the surface Cl is being removed by a true electron stimulated desorption process, rather than some other electron induced process, such as diffusion into the bulk of the specimen.

We found that the ESD-induced depletion of the Cl did not fit a single exponential decay, but better a bi-
exponential function, implying two removal routes. The cross-sections for these two processes were calculated using equation II.38 and were found to differ by a factor of 5, being $1 \times 10^{-18}$ cm$^2$ for the fast, and $2 \times 10^{-19}$ cm$^2$ for the slow removal route. Table IV.B.1 is a listing of the cross-sections calculated at different electron current densities, along with the average cross-sections for the fast and slow processes. In addition, the data indicates that both the long and short time constant Cl loss processes are due to desorption. Presumably, chlorine is being desorbed from two different types of adsorption sites with very different activation energies.

Furthermore, as can be seen from Figure IV.B.2, even after long exposures to the electron beam as much as 25% of the original Cl remains. Other work in this laboratory (see section IV.A) has shown that chlorine adsorption on GaAs surfaces is dominated by defect chemistry. Chlorine adsorbs only to a relatively small extent, of the order of 25% of a monolayer, initially at defects in an As-rich GaAs surface. Others have described these defect sites as anything from a missing arsenic dimer which exposes second layer Ga [83] to "free" As or Ga on the surface which is not involved in the surface reconstruction [20]. In either case, these sites appear to be reaction centers where initial
Table IV.B.1  Calculated cross-sections for electron stimulated desorption of chlorine from GaAs(100).

<table>
<thead>
<tr>
<th>Current (µA)</th>
<th>Fast process</th>
<th>Slow process</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.0</td>
<td>6.7 X 10^{-19} cm²</td>
<td>1.2 X 10^{-19} cm²</td>
</tr>
<tr>
<td>22.4</td>
<td>4.5 X 10^{-19} cm²</td>
<td>1.5 X 10^{-19} cm²</td>
</tr>
<tr>
<td>15.0</td>
<td>1.1 X 10^{-18} cm²</td>
<td>2.2 X 10^{-19} cm²</td>
</tr>
<tr>
<td>10.0</td>
<td>1.3 X 10^{-18} cm²</td>
<td>2.9 X 10^{-19} cm²</td>
</tr>
<tr>
<td>5.0</td>
<td>2.0 X 10^{-18} cm²</td>
<td>1.3 X 10^{-19} cm²</td>
</tr>
</tbody>
</table>

ave. 1.0(6)X10^{-18} cm²  1.9(7)X10^{-19} cm²
adsorption occurs. Apparently, it is the most weakly bound Cl which is removed during ESD; at this time it is not possible to associate a particular type of site with this ESD-labile form of adsorbed chlorine. Unfortunately, our experiments were not sensitive enough to detect any desorption thresholds that would correspond to the known core levels of Ga or As. These results could be valuable in identifying the two Cl-loss pathways.

If any products other than Cl atoms are being desorbed under our experimental conditions, their quantities are too low to be detected. Although the lack of an arsenic or gallium chloride signal due to ESD is disappointing, the use of electron beams as the driving force in the GaAs/Cl etching reaction need not be entirely ruled out as an alternative to ion or photon assisted etching. Our experimental arrangement is such that we were only able to provide relatively low chlorine coverage of the sample surface. The ion-assisted etching experiments of Balooch and Olander [73] have shown that very different chemistry can occur at high chlorine fluxes. In particular, they found that true etching only occurred under quite Cl-rich conditions. It is possible that under the proper conditions, electron induced etching of the substrate may be feasible.

We have found by examining the area depleted of Cl by
the electron beam, that Cl diffusion back into the depleted area does not occur at room temperature. Even when neighboring regions are excited by electron bombardment, the Cl desorbs directly into the gas phase and does not migrate back into the original "hole". The low rate of back-diffusion imply that if the conditions were correct for electron induced etching, then well-defined anisotropic etch features may well result.

4. CONCLUSIONS

We find that chlorine adsorbed on a GaAs(100) surface is sensitive to electron stimulated desorption by electrons in the range of 500-2000 eV. Chlorine loss proceeds via two processes on different time scales that are probably associated with different types of exposed Ga atoms at defects in an As-rich surface. Chlorine that is adsorbed on areas of the surface that have not been under the influence of the electron beam does not diffuse at a detectable rate into a hole created in the chlorine adlayer by ESD.

We find that under our experimental conditions of relatively low chlorine surface coverage, ESD products consist solely of chlorine atoms. However, it is possible that under more severe conditions etching may
occur.
C. Interactions of $S_2$ and $H_2S$ with the GaAs(100) Surface; An Adsorption/Desorption Study

1. INTRODUCTION

Adsorption of sulfur on GaAs(100) substrates is of potential interest for the growth and processing of this semiconductor. Incorporation of sulfur as a dopant has been practiced during vapor phase epitaxy (VPE) growth of the material and is found to be strongly orientation dependant. Using cylindrical GaAs samples, Ranke et al [84] found preferential sulfur adsorption on certain terraces as well as enhanced edge adsorption with maximum sulfur incorporation onto (110) orientations. Also a number of other studies [85-88] describe the surface passivation of GaAs(100). Adsorbed sulfur saturates the large number of surface states which are present on this surface, resulting in a lowering of the Shottky barrier height. This barrier lowering may be used to obtain low resistance ohmic contacts at the metal/semiconductor interface.

Commonly, $H_2S$ is used as the source of sulfur in these studies [20,80,90]. However, elemental sulfur [91], $S_2$ produced from an electrochemical source [92],
and alkaline sulfides such as (NH₄)₂S [93] have all been employed. We have studied the adsorption and thermal desorption (TDS) of H₂S and electrochemically produced S₂ on the GaAs(100) surface, and have determined a number of differences between the two sources. S₂ adsorption produces mono and disulfides during desorption while H₂S adsorption results in only monosulfide desorption. Furthermore, monitoring the S(151) AES peak during adsorption indicates that S₂ adsorption saturates at a level five times that of H₂S saturation. We have also found that in the case of H₂S, hydrogen plays an important role in the process and that both Ga and As hydrides are formed.

We have found, further, that H₂S adsorption/desorption cycles tend to reduce the number of defect sites on this surface. Specifically, As and Ga hydride desorption at 100°C leads to a much sharper LEED pattern. Adsorption at these high energy defect sites would result in a lowering of the Schottky barrier, as seen by Massies [94], and supports the defect titration work of Ranke et al [95], who found that adsorption of comparable MBE grown and IBA prepared surfaces resulted in stronger adsorption for all orientations on the IBA surfaces. This was attributed to the additional defects which are a result of this preparation method. Finally,
a mechanism is proposed for H$_2$S adsorption on this surface.

The experiments were performed in a standard ion-pumped vacuum system fitted with LEED/Auger optics as has been described in Section IV.A.2. In addition, this system also contains an in-situ electrochemical source of sulfur as S$_2$, modeled after the source built by Spencer et al [64]. The source allows dosing of the surface without any appreciable rise in the background sulfur pressure. The sample again, was a Si-doped (4.7 X 10$^{18}$ cm$^{-3}$) semiconducting GaAs(100) (+/- 1/4°) surface. It was cleaned with a choline wet-etch prior to mounting on the manipulator, and underwent a series of ion bombardment and anneal (IBA) cycles to produce a clean, well-ordered surface.

As mentioned previously, we could produce the large number of surface structures found by others, and shown in Table III.2. It has been established [64] that the reconstructions are due to a decreasing As concentration with a corresponding increase in substrate temperature. Ion bombarded and annealed (IBA) As-rich surfaces show a diffuse (1X1) LEED pattern leading us to believe that there was still some disorder present. This is not unusual considering the low annealing temperatures, and subsequently longer annealing times
required to obtain this surface. To avoid this problem this study concentrated on only the "high temperature" c(8X2)-Ga structure. It was easy to produce this Ga-rich surface by initially annealing a sputtered surface at 600°-625° C for several hours, and subsequently by simply flashing to 625° C for several minutes.

2. RESULTS

a) S₂ adsorption/desorption

Molecular sulfur was produced by applying a current through a AgS₂ electrochemical cell. The principal component being emitted from the cell is S₂ and we assumed that it is S₂ which dominates the adsorption behavior. Figure IV.C.1 is a typical uptake of sulfur on the GaAs(100) surface at room temperature as monitored by the S(152) Auger intensity.

Figure IV.C.2, shows thermal desorption (TDS) data for an S₂ saturated surface. We can see peaks due to AsS₂ and GaS₂ centered at 150°C. Monitoring the monosulfides during a similar TDS, Figure IV.C.3, also shows a peak at 150°C and to a much lesser extent the beginning of a peak at 550°C. After the adsorption of only 20% of saturation of S₂, the desorption spectrum in Figure IV.C.4 reveals only the monosulfide peaks at
Figure IV.C.1 The uptake of sulfur on a Ga-rich c(8x2) GaAs(100) surface monitored with the S(152 eV) Auger signal. The sulfur exposure is the time for which the electrochemical sulfur source was turned on at a current of 500 mA.
Figure IV.C.2 Thermal desorption of GaS$_2$ and AsS$_2$ from a Ga-rich c(8x2) GaAs(100) surface which has been saturated with S$_2$. The products are monitored by mass spectrometry.
Figure IV.C.3 Thermal desorption of GaS and AsS from a Ga-rich c(8x2) GaAs(100) surface after S\textsubscript{2} saturation, presumably due to cracking of the disulfides.
Figure IV.C.4  Thermal desorption of GaS and AsS after fractional coverage of the GaAs(100) surface by S₂. No disulfides or low temperature monosulfides are seen.
550°C. The origin of the 150°C monosulfide peak seen in Figure IV.C.3, then, may be attributed to the cracking of the disulfides which appear at the same temperature. The ratio of the AsS to GaS peak intensities at 550°C is about 3 to 1. Unfortunately we could only heat the sample to 625°C and therefore only follow the front half of the monosulfide desorption peak. Heating the sample to temperatures of 650° or above results in the formation of Ga "droplets" , which ruin the crystallinity of the surface [70]. Monitoring the Auger S(152) signal during TDS confirms that all sulfur is removed from the surface after heating to 625°C.

b) H$_2$S adsorption/desorption

As monitored by Auger spectroscopy, the adsorption of H$_2$S is initially rapid, but saturates at about 1/5 the intensity as the S$_2$ adsorbed on the same surface. Full coverage is achieved after 3000 L of exposure. Plotting the uptake curve on a log scale as in Figure IV.C.5, results in a shape which is identical to that found by Massies et al [20] on the (4X1)-Ga surface.

The TDS, shown in Figure IV.C.6, from this system reveals only the monosulfides of both As and Ga, desorbing from this system. As in the case of low
Figure IV.C.5 The uptake of H$_2$S on a Ga-rich c(8x2) GaAs(100) surface monitored with the S(152 eV) Auger signal. The uptake is initially rapid, and slows after 100 Langmuirs of exposure. The x-axis is plotted in log scale.
Figure IV.C.6 Thermal desorption from an H$_2$S saturated Ga-rich GaAs(100)-c(8x2) surface. No disulfides or low temperature monosulfides are seen.
coverage, $S_2$ desorption, $H_2S$ desorption shows a ratio of AsS to GaS of 3 to 1. Again, monitoring the S(152) Auger signal, Figure IV.C.7, confirms that the surface is free of sulfur after heating to 625°C.

Monitoring the Ga and As hydrides during desorption reveals that both do desorb from the $H_2S$ saturated surface. Figure IV.C.8 shows that arsine, $AsH_3$, and GaH desorb from the surface at 100°C. Mokwa [96] has also found that $AsH_3$ desorbs from the (110) surface at nearly the same temperature (70°C), after exposure to atomic hydrogen.

c) $H_2S$ thermal etching

In view of the thermal desorption results described above for $H_2S$, we attempted a number of thermal etching experiments to probe the feasibility of using this gas as a potential etchant material. Figure IV.C.9 shows that both Ga and As sulfides are produced at 550°C under a constant flux of $H_2S$. Figure IV.C.10 shows that the hydrides of As and Ga can be continuously produced at a temperature of 200°C. From the intensities of the etch products seen in the mass spectrometer, and the TDS results of Figure IV.C.8, it can be determined that the hydrides represent only small fractions of a monolayer.
Figure IV.C.7  Sulfur 152 eV Auger signal during thermal treatment of $H_2S$ saturated GaAs(100) Ga-stabilized surface. Essentially all sulfur is removed by heating to 625°C.
Figure IV.C.8 Desorption of GaH and AsH$_3$ after H$_2$S saturation of GaAs(100)\text{-}c(8\times2) surface.
Figure IV.C.9  Etching of GaS and AsS from Ga-stabilized surface as a function of temperature while in an ambient of H₂S gas.
Figure IV.C.10 Etching of Ga and As hydrides at 200°C when the GaAs(100) surface is exposed to H$_2$S gas.
These products, therefore, are most likely due to adsorption at defect sites at the surface.

It appears that the process of hydride desorption actually lowers the defect density subsequent to an adsorption/desorption cycle, relative to the total density. A confirmation of this can be seen by measuring LEED beam profiles. It has been determined that the distribution of a LEED beam intensity can be related to the amount of order present at the surface [97]. Figure IV.C.11 shows the succession of LEED beam profiles during the different stages of adsorption and desorption of H₂S. In this case, desorption cycles were ramped to 400°C to 1) insure complete hydride removal 2) for comparison with one of our typical IBA procedures and 3) for comparison with the results of Massies et al [20]. From the figure it can be seen that a surface saturated with H₂S and heated to 400°C actually has a sharper beam profile than either a sample prepared by IBA and annealed at 400°C or a sample annealed at 600°C. Although this H₂S treated surface still contains adsorbed S, which does not thermally desorb until 550°C, the LEED beam profile is sharper than the IBA prepared clean surfaces. This is probably due to As and Ga hydride desorption removing defect sites, which existed on the clean surface.

To further explore the phenomenon of hydride etching
Figure IV.C.11 LEED (1,1) beam profile at 120 eV as a function of surface preparation. A surface treated with H$_2$S shows a beam profile with a FWHM which is 60% of that which is simply annealed at the same temperature.
we used molecular hydrogen as an etchant. Figure IV.C.12 shows that no etch products were ever produced. As has been seen by others [96], this surface is inert to H₂ at these temperatures.

3. DISCUSSION

Although sulfur adsorption on GaAs surfaces has received much attention recently, there is a lack of information concerning the comparative behavior of different sulfur containing compounds as they interact with the substrate. We have studied two such cases; H₂S and S₂. We have found a number of differences in adsorption and desorption behavior of these two species.

a) adsorption/desorption

The adsorption and desorption spectra for S₂ and H₂S reveal that S₂ adsorption, as monitored by AES, proceeds to an extent of nearly five times more than that of H₂S. Assessing absolute coverage values for this surface, however, is difficult. The c(8x2)-Ga rich structure, on which all experiments were performed, has been reported to contain as much as 78% [52] and as little as 48% [98]
Figure IV.C.12 No Ga or As hydride etching is seen to occur at 200°C in an H₂ ambient. GaAs has been found to be inert to molecular hydrogen.
surface Ga. This broad range of surface Ga values results in a quantitative evaluation of the adsorbate coverage with a similarly large distribution. Furthermore, our AES experiments monitored the Ga(1070) and As(1228) transitions of the substrate. These core levels are rather deep and have been reported [68] to have electron escape depths of 19.0 Å and 20.5 Å respectively; not very surface sensitive. We may, however, rely on the H₂S adsorption work by Massies [20] to obtain an estimate of the surface coverage. They found, for H₂S adsorption on the (4x1) reconstructed surface at room temperature, between 0.7 and 1.0 monolayer of sulfur coverage. Although there is no guarantee that our Ga-rich surfaces are identical to theirs, the c(8x2) and (4x1) reconstructions are considered to be quite similar in composition and structure [54]. This, along with the fact that the shape of our uptake curve is essentially identical to theirs, does give us some confidence that we are most likely within that 30% spread and may consider these estimates valid for our own surfaces. This being the case, we must consider that S₂ adsorption results in a multi-layer formation.

This observation is echoed in the TDS which shows the formation of at least disulfides of both Ga and As during
thermal desorption following \( S_2 \) adsorption. Formation of compounds such as \( \text{As}_2\text{S}_3 \) and \( \text{Ga}_2\text{S}_3 \) on the surface during \( S_2 \) adsorption would account for the fact that more than a single monolayer is formed. Waldrop [91], using XPS, proposed the following chemical reaction: 
\[
S + \text{GaAs} = \text{As}_2\text{S}_3 + \text{Ga sulfide},
\]
during the adsorption of elemental sulfur on the (100) surface. He was unable, however, to specify which Ga sulfide was formed. Unfortunately these compounds, \( \text{As}_2\text{S}_3 \) and \( \text{Ga}_2\text{S}_3 \), are not within the detection range of our mass spectrometer.

Another possibility, considering the inclination for sulfur to form compounds such as \( S_4 \) and \( S_8 \), is that these compounds are also forming on top of the surface. However, observing desorption of such species with the mass spectrometer is a difficult task since the desorption of these species may occur from any sulfur exposed areas on the manipulator.

By comparing the sulfide desorption data from \( S_2 \) (Figure IV.C.2) and \( \text{H}_2\text{S} \) (Figure IV.C.6) it is obvious that saturating a surface with \( S_2 \) results in the desorption of at least disulfides while \( \text{H}_2\text{S} \) forms only the monosulfides of Ga and As. In fact, the TDS from saturated \( \text{H}_2\text{S} \) samples are very similar to low coverage \( S_2 \) TDS. Apparently, there are two very different mechanisms of sulfur incorporation onto the surface from these
different sources.

An obvious reason for this is that the hydrogen from the H₂S is filling Ga and As surface sites which results in less availability for further incorporation of sulfur onto the surface. Comparing the appropriate bond strengths, found in Table IV.C.1, leads to a plausible explanation for this occurrence. As-S, S-S, Ga-S, H-SH as well as H-H interactions are all relatively strong compared to the Ga-H and As-H bond strengths. It is likely then, that H₂S must be oriented properly as it approaches the surface so that S··Ga and S··As, rather than HS-H··As or HS-H··Ga interactions will occur, presumably at the high energy defect sites. The formation of S-Ga and S-As surface bonds results in the weakening of the S-H bond, thereby generating a source of free hydrogen near the surface. Others [96] have shown that atomic hydrogen bonds readily to GaAs surfaces. The formation of surface hydrides of Ga and As and atomic hydrogen competes with the formation of surface sulfides. This accounts for the small amount of sulfur incorporation, as compared to S₂, that is seen by AES. Increasing the temperature above 100° C results in the desorption of these hydrides. Figure IV.C.13 is a schematic representation of how this process may occur.

The H-H bond strength is much greater than Ga-H or As-
<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-S</td>
<td>4.95</td>
</tr>
<tr>
<td>Ga-S</td>
<td>N/A</td>
</tr>
<tr>
<td>H-H</td>
<td>4.52</td>
</tr>
<tr>
<td>S-S</td>
<td>4.41</td>
</tr>
<tr>
<td>SH-S</td>
<td>3.93</td>
</tr>
<tr>
<td>As-H</td>
<td>3.64</td>
</tr>
<tr>
<td>Ga-H</td>
<td>&lt;2.82</td>
</tr>
</tbody>
</table>

Table IV.C.1  Bond strengths of diatomic molecules relevent to sulfur adsorption on GaAs.
HYDROGEN SULFIDE INTERACTION WITH GaAs(100)

Figure IV.C.13 Schematic representation of the interaction of H₂S with the GaAs(100) surface. This mechanism results in the formation of surface hydrides and sulfides and is presumed to occur at surface defect locations.
H and it would not be energetically favorable for \( \text{H}_2 \) to form hydrides at the surface. Indeed, this is exactly what we and other workers [96] have observed.

b) thermal etching

It has been found that etching of Ga and As sulfides did occur above 550° C. This temperature, however, may be too close to the congruent evaporation temperature of GaAs to be of practical use. Hydride etching, on the other hand, occurs at the much lower temperature of 200° C. This type of etching appears to help order the IBA prepared surface by removing defect sites. This is seen in the increased quality of the LEED pattern after heating an \( \text{H}_2\text{S} \) saturated sample to 400° C, insuring the removal of all hydrides, but leaving the sulfides. It may in fact be this process which causes a lowering of the Schottky barrier as seen by Massies et al [20].

Spicer et al [99] initially found that a fixation of the Fermi level, and hence the Shottky barrier height, was due to defects induced by metal condensation at the metal/semiconductor interface. It was subsequently shown that defects, and consequently band bending, are present at the free surface before metal deposition [100]. Furthermore, Massies et al [94] found that adsorption of
H₂S at 400° C reduced the Schottky barrier by a factor of two. They attributed this effect to saturation of the defect sites upon adsorption of sulfur. Based on the unusual sharpness of the LEED patterns obtained after H₂S adsorption/desorption cycles at 400° C, we propose that these sites may actually be removed as hydrides during H₂S adsorption at temperatures above 200° C. Since defect sites are known to be active centers, where initial adsorption takes place, it is very likely that during exposure to H₂S, a combination of defect site saturation by S and removal as hydrides is occurring.

4. CONCLUSIONS

We have found the adsorption and desorption behavior of S₂ and H₂S on a GaAs(100) surface to be very different. S₂ forms multilayers at the surface and the formation of at least disulfides of Ga and As are seen in TDS. Compound structures such as As₂S₃ and Ga₂S₃ would account for these observations but experimental constraints limit our ability to detect them. H₂S adsorption leads to a much smaller incorporation of sulfur onto the surface and it is postulated that S-As
and S-Ga bonds are initially created upon adsorption, resulting in a weakening of the S-H bonds, leaving atomic H in close proximity to the surface. This H then, competes with H₂S for the remaining adsorption sites. Heating the H₂S saturated surface to 100° C results in the removal of Ga and As hydrides and improves the quality of the LEED pattern. We attribute this phenomenon to the removal of defect sites which are created by the IBA process.
V. CONCLUSIONS

The interaction of the GaAs(100) surface with chlorine and sulfur containing compounds has been studied. The chemistry of this surface appears to be dominated by the reconstructions which are ubiquitous on this surface. Even clean, carefully grown surfaces under ideal MBE conditions result in reconstructed surfaces. The ideal (1x1) surface is very unstable and rarely seen. Ion bombardment and annealing result in conditions under which the (1x1) surface is even more rarely seen. This is apparently due to the volatility of the group V arsenic atom, although other factors such a sample history play an important role. These factors have made characterization of this surface difficult at best.

The adsorption of chlorine, when interpreted as a result of defect chemistry, reveals a great deal about the nature of this surface. The adsorption proceeds to only 25% of a monolayer which reflects the degree to which defects are considered to dominate the chemistry of this surface. Furthermore, desorption of GaCl from this surface, along with the noticeable absence of any AsCl$_x$ species, is in line with the general belief that surface defects result in exposure of second layer Ga atoms which would otherwise be buried under surface As. Chlorine
data also indicate that although Ga-stabilized surfaces are initially more receptive to chlorine adsorption, when saturated with chlorine, the As-stabilized and Ga-stabilized surfaces may appear quite similar, indicative of a Cl-As replacement reaction occurring at the surface.

It has also been found that adsorbed Cl is very sensitive to desorption due to incident electrons. Careful measurements show that the ESD curve is not a function of a single exponential decay, but is best fitted by a bi-exponential function, indicating at least two desorption sites with two different desorption cross-sections. The implications of this Cl sensitivity are two-fold. 1) Under the proper conditions electron beam etching of this material may be a viable alternative to the present, more severe methods employing ion beams, and 2) a great deal of care must be taken when using electron beams to probe this system; 2000 eV electron beams can reduce by 50% the amount of adsorbed chlorine in less than five minutes.

Finally, the adsorption of sulfur on this surface reveals that different sources of sulfur result in different chemistry at the surface. Although this is quite intuitive, there is very little consistency in the literature as to the type of sulfur containing compounds which are used to supply sulfur to this surface.
Molecular sulfur, $S_2$, appears to form multilayers while $H_2S$ results in only a fraction of a monolayer of surface coverage. Subsequent to $H_2S$ adsorption, however, Ga and As hydrides are seen to desorb at 100° C, and it is believed that the formation of these hydrides may play an important role in the chemistry of $H_2S$ adsorption on this surface. Monitoring LEED intensity profiles during these adsorption/desorption cycles reveals that the profiles become narrower upon hydride desorption, indicative of surface ordering.

GaAs holds great promise for future high-speed opto-electronic devices. Before the properties of this material may be fully exploited, however, it is essential to investigate its fundamental physical and chemical properties, especially those associated with the (100) surface, the primary surface used in epitaxial growth of this semiconductor. This study has been an initial step in the investigation of the interaction of this surface with chlorine, an established etchant, and sulfur a potential surface passivator. Although a great deal of work is yet required before a full understanding of this surface is established, this study will serve as groundwork for future investigations.
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APPENDIX
VII. APPENDIX

LABORATORY PROCEDURES

The following is a detailed description of the operation and maintenance specific to the equipment found in the Surface and Catalysis laboratory in the Department of Chemistry at O.S.U. These procedures are not simply the reiterations of those found in the manuals which accompany the equipment, but rather a set of instructions which may be used to accompany those manuals. These instructions reflect the fact that most equipment does not usually operate in the exact manner as described in owner's manuals.

1) CHAMBER AND PUMPS

The vacuum chamber is a stainless steel vessel designed to operate in the ultra-high vacuum (UHV) region. The lower portion of the chamber is a standard stack piece containing twelve ports. Nine ion pumps are located at the bottom of the vessel and are connected via a high voltage feedthrough to a Perkin-Elmer 5 kilovolt power supply. Also located at the bottom of the vessel is a titanium sublimation pump (TSP), a getter pump which
operates by applying a high current through a Ti filament. This results in evaporation of the titanium which reacts with any gas phase species by adsorption onto the newly formed and very reactive surface. The gas is then bound to the metal and the overall pressure in the vessel reduced. The TSP is operated by the same power supply which is used for the ion pumps. One problem faced when operating the TSP is the build-up of Ti metal flakes in the bottom of the vessel. If the chamber is not carefully brought to atmospheric pressure, these flake may become airborne and become lodged in the ion pumps, rendering them inoperable. The possibility of this occurring, however, is reduced by the presence of the liquid nitrogen trap, a stainless steel cylinder located between the TSP and the ion pumps. If, however, arcing of the ion pumps does occur, the ion pumps may be removed and cleaned. The cleaning procedure is as follows: 1) The top of the vessel must be removed with the hand operated hydraulic lift or "cherry picker". Once removed, the ion pumps are easily accessible. When removing the pumps, a good portion of the upper body may come into contact with the inner walls of the vessel. It is therefore required to properly cover exposed areas of the body in order to prevent skin oils from being deposited on the vessel walls. A hair net is also
recommended. 2) The ion pumps should be removed one by one, taken apart and sand blasted using the sand blaster in the mechanical shop. After blasting, the parts should be cleaned with acetone, hot air dried, and reassembled. 3) Replace the pump and continue this procedure until all pumps have been cleaned.

After cleaning the pumps the continuity should be checked. Since the pumps operate at 5 kV, it is best to use the high voltage tester which is the property of the Agricultural Chemistry department, and is located in the Hi Res. Mass Spec. room in Weiniger Hall.

The following procedures should also be carried out every time the top portion of the chamber is removed. 1) The bottom of the chamber should be inspected for any miscellaneous valuable material (eg. Ti single crystals) and Ti flakes from the TSP should be vacuumed using the shop vacuum. 2) TSP filaments should be checked and replaced if needed. It may seem easier to work on the bottom of the vessel if the liquid nitrogen trap is removed. This, however is not advised. The feedthrough connector is located on a 1" flange inside the chamber. This connector is hard to reach and even harder to properly seal. The nuts are allen head on a mini-flange and are sandwiched between the trap and the flange itself. The area is quite small and difficult to work
in. To further complicate matters, the nuts cannot be seen by direct line-of-site, when one is in the position to tighten them. For these reasons, unless it is absolutely necessary, it is recommended that the liquid nitrogen trap not be removed.

Finally, working on the lower half of the chamber is akin to having a car overhauled. It is usually an unpleasant experience. It is suggested, then, that the work be carried out meticulously and methodically in order that these procedures need not be unnecessarily repeated.

The top portion of the chamber is a custom designed vessel for the specific surface related experiments which are conducted in this laboratory. It contains 17 ports ranging from 2.75" to 10" in diameter. The manipulator is mounted vertically form the top of the system, while the spectrometers mount horizontally. The whole system is connected to a "roughing line" through the main valve. This line is used to "rough pump" the system, that is to pump the system from atmospheric pressure to a pressure where the ion pumps will operate, $10^{-5}$ torr.

Once the ion pumps are started, they should be allowed to pump for a minimum of 12 hours before beginning to bake the system. The bake-out ovens are in two halves. The lower section, which is permanently
fixed around the lower portion of the chamber, and the upper half, itself in two sections, which must be mounted over the chamber during the bake-out. Before mounting the ovens all electrical connections must be disconnected. It must also be confirmed that all apparatus undergoing the bake will be able to sustain the elevated temperatures, especially seals and feedthroughs. The ovens are connected to the oven control unit. The unit allows for baking the chamber for up to 24 hours. If longer bakes are required (typical bakes should last 72-96 hours), the clock must be reset accordingly. The temperature should be ramped up slowly insuring that the pressure stay below $5 \times 10^{-6}$ torr. Pressures above this may cause the ion pumps to automatically shut down.

Typical maximum bake-out temperatures range from 130°C-150°C. Following bake-out, a degas of all filaments should be performed before the chamber cools. All filaments should be operated in their degas mode (see manuals) for 3-5 minutes, with the exception of the Dycor mass spectrometer, for which degassing time should not exceed 3 minutes or damage will result. After degassing the chamber should be allowed to cool until a reasonable background pressure in the low $10^{-10}$ torr range is achieved, typically this requires approximately 12 hours.
2) ION GAUGE

The lower half of the vessel contains an ionization gauge to monitor the chamber pressure, displayed in torr. Generally, the gauge is run continuously, unless the spectrometers are in use. Operation of the gauge is accomplished through the ionization of any gases which may be present near the gauge. To achieve this, a heated filament thermally ejects electrons which are accelerated toward a grid which is held at a positive potential 150 volts above the filament potential. As the electrons traverse the space to the grid they may ionize any gases which are present in that space. These ions, then, are accelerated toward the collector where they generate a current. This current is then converted into units of torr. The gauge is factory calibrated using nitrogen gas as the standard. Tables are given in the manual to convert other gas pressures as referred to the nitrogen standard. This, however, is usually unnecessary since many of the common gases which contribute to the background pressure (H₂O, CO, CO₂), have conversion coefficients which are very near unity when compared to nitrogen.

A problem arises when connecting the gauge since the feedthrough pins are not labeled. The Granville-Philips
manual has a diagram of the pin arrangement on the feedthrough connector. An easy method for remembering the arrangement is to recognize that the filament connections are in line (this becomes more apparent when one thinks of the filament arrangement on the gauge), with the ground connection between the two hot connections (there are two filaments on the same ground). The collector is in the center of the gauge and the grid is opposite the filaments. Furthermore, the grid and collector connections are of different size; the collector has more insulation on the connecting wire and is larger than all other connectors.

3) MANIPULATOR

The manipulator is mounted vertically from the top of the chamber. The sample is mounted off-axis of the vertical centerline of the chamber and may be translated in the x, y, z, and vertical directions. Rotation of the sample may be made in either the horizontal or azimuthal directions. The 6" manipulator flange contains several mini flanges which may be used as feedthroughs. Typically, sample heating and cooling as well as thermocouple connections are made through these mini flanges. Heating is achieved electrically, while cooling
is accomplished by pumping liquid nitrogen through a cooling block which is thermally connected to the sample. Precautions must be taken to insure that the heating and cooling systems are electrically isolated, as heating generally requires high currents or voltages and can be dangerous. Another concern when cooling with liquid nitrogen is the formation of condensation at the feedthrough. Lengthy cooling period may result in a build up of frost around the whole manipulator flange. Measures should be taken to remove this frost to avoid possible rust formation on certain parts of the manipulator. It is suggested that compressed air be used to remove the frost and a rag or hot air gun if the frost has melted.

4) LEED/AUGER

The LEED and Auger spectrometers use the same optics as well as the same power supply. Interchanging the two spectrometers simply requires changing the connections to the optics unit, and switching the power supply between LEED and Auger mode. The optics consist of four hemispherical grids and a phosphor coated collector. In the Auger mode grids 1 and 4 are at ground potential while a retarding voltage is applied to grids 2 and 3.
The collector is biased at 900 volts (+), to aid in the collection of electrons, and the signal is fed into a lock-in amplifier. The output of the lock-in amplifier is sent to an x-y plotter where the differential spectrum is recorded. In the LEED mode grids 1 and 4 are also held at ground potential. Applied to grids 2 and 3 is a potential slightly less than that of the incident electron beam energy, which allows only elastically scattered electrons to pass through the grids to the collector. Both grids 2 and 3 are used to sharply define the cutoff voltage. Here the collector is biased at 3-5 kV to insure proper excitation of the phosphor when the diffracted electrons are incident. The diffracted image is then viewed and recorded through the view port located opposite to the optics. Located at the center of the optics is the electron gun which is controlled by the same control unit as the grids. LEED images may be recorded with a 35mm camera or with a light sensitive video camera. In either case the images are digitized using the oculus-200 frame grabber (see oculus-200 manuals) located in the IBM PC 286. The intensity information can then be analyzed at leisure. The frame grabber is also useful for many applications such as preparing slides and overheads for presentations. The gray library routines are very powerful and should be
exploited to this end. Refer to the manuals for details.

The order of events when operating the LEED/Auger unit is as follows: 1) With the power supply OFF, switch between the LEED and Auger modes. 2) Turn ON power supply (the lock-in, Auger R.F. power supply, and function generator may be left on continuously). 3) Turn ON beam voltage; use the potentiometer to set (Auger, 1000-2000 eV; LEED, 100-300 eV). 4) Turn ON filament (Auger, 10-20 μA; LEED, 0.5-2.0 μA). After Auger spectrum or LEED data have been taken, turn the system off by reversing the above sequence.

5) ION GUN

The ion gun is used for in-situ cleaning of sample surfaces. The gun is operated at an emission current of 15-20 milliamperes and 0.5-5.0 kV. Typically, the voltage is kept at or below 1 kV to reduce surface damage produced by energetic ions. Argon is the usual sputter gas and is admitted to the chamber through a leak valve. With the pumps off, the Ar gas pressure should not be allowed above $5 \times 10^{-5}$ torr. Typically, $2 \times 10^{-5} - 3 \times 10^{-5}$ torr Ar pressure is used. Monitoring the sample current with an ammeter insures proper operation and orientation of the sputtering system.
To operate the gun, 1) turn ON the power supply. 2) Turn up the emission current (15-20 mA), wait five minutes for the filament to warm up. 3) Turn OFF ion pumps and allow Ar gas into chamber monitoring the pressure with the ion gauge. 4) Turn ON high voltage. Following a sputtering cycle (5-60 minutes), reverse the sequence to turn off the sputter system.

6) Mass Spectrometer

The mass spectrometer is a quadrupole type which operates by ionizing any gas species which enter the ionizer of the spectrometer. These ions are then accelerated through a set of four poles (quadrupoles) to a collector. By properly adjusting the frequency of the electric field applied to the poles, the ions may be mass selected \((e/m)\) before they reach the collector. The collector, then, records an ion current for a particular charge-to-mass ratio. The control unit can display these currents, but usually they are converted into pressure units (torr). The mass spectrometer has four modes of operation. Analog and Bar modes are used when monitoring residual gases, or when looking for a cracking pattern of a particular species. Tabular mode is used for leak checking and Pressure-Time mode is used for thermal
desorption spectroscopy (TDS). Here, up to five masses may be selected and monitored as a function of time.

The order of operation of the mass spectrometer is as follows: 1) Turn power ON. 2) Turn filament ON. 3) Turn multiplier ON (if needed). 4) Select mode of operation. As always, when shutting down the equipment, reverse the order of the starting procedure. The spectrometer may be left on (with filament and multiplier OFF) for long periods of time, days or weeks, without any damage resulting. It is advised that the spectrometer be allowed to warm up (filament and multiplier ON) for at least 30 minutes to insure stability. Three cautions while operating the mass spectrometer: 1) Never turn the multiplier ON when the pressure is above $10^{-5}$ torr. 2) Never degas longer that three minutes and 3) never turn the main power OFF without first turning OFF the filament and multiplier. These will all result in damage to the spectrometer.