KINETIC STUDIES OF THE REACTION OF GALLIUM ARSENIDE
WITH MOLECULAR CHLORINE AND IODINE

BY

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Abstract

The GaAs/Cl₂ reaction has been studied at pressures of Cl₂ between 0.10 and 9.0 Torr, and in the temperature range from 90 to 110°C whereas the GaAs/I₂ reaction has been investigated at four temperatures between 270 and 330°C with the I₂ pressure being varied between 0.10 and 1.25 Torr.

Both reactions show a linear dependence on the etchant gas pressure in the low pressure region, however, the dependence become nonlinear in the high pressure range. In the case of the Cl₂ reaction, the non linearity was found to be due to the occurrence of a reaction that was half order with respect to the pressure of Cl₂. This behavior was found to be consistent with a "reversible dissociative adsorption" mechanism proposed in earlier studies of the Cl₂ and Br₂ etching of silicon. This mechanism involves the physisorption of the halogen molecule on the semiconductor surface followed by the dissociation of the molecule into chemisorbed atoms, and finally the reaction of these atoms with the surface to yield gaseous products.

The first and the half order rate constant for both reactions were determined and represented in the form of the following Arrhenius equations:

First order rate constants,

\[ k_1 \text{ (for Cl}_2\text{)} = 10^{10.4\pm2.3} \mu\text{m min}^{-1} \text{Torr}^{-1} e^{- (76\pm16 \text{kJ mol}^{-1}/\text{RT})} \]

\[ k_3 \text{ (for I}_2\text{)} = 10^{4.7\pm0.2} \mu\text{m min}^{-1} \text{Torr}^{-1} e^{- (55\pm2 \text{kJ mol}^{-1}/\text{RT})} \]

Half order rate constants,

\[ k_{1/2} \text{ (for Cl}_2\text{)} = 10^{13.6\pm2.6} \mu\text{m min}^{-1} \text{Torr}^{-1/2} e^{- (100\pm19 \text{kJ mol}^{-1}/\text{RT})} \]

\[ k_{1/2}^* \text{ (for I}_2\text{)} = 10^{6.5\pm0.9} \mu\text{m min}^{-1} \text{Torr}^{-1/2} e^{- (69\pm10 \text{kJ mol}^{-1}/\text{RT})} \]
The etching profile of GaAs with Cl₂ was found to be "crystallographic" and a relatively smooth etched face resulted after the etching process.

In contrast to the Cl₂ reaction, GaAs etching with I₂ was isotropic and a very rough etched surface was obtained. Mass spectrometry was employed to analyze the reaction products collected in the cold trap after the reaction was completed. GaI₃ and AsI₃ were determined to be the major stable products of the reaction.
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Chapter 1 : Introduction

Germanium was one of the first materials to be used in semiconductor device fabrication, but it was rapidly replaced by silicon during the early 1960's. Silicon emerged as the dominant material because it was found to have many major processing advantages. Silicon and germanium are elemental semiconductors. They can both be subjected to a large variety of processing steps without loss of stoichiometry that is ever present with compound semiconductors. Since silicon has a wider energy gap than germanium, it can be fabricated into microcircuits capable of operation at higher temperatures than the germanium counterparts. The upper operating temperature for silicon integrated circuits is approximately between 125 and 175°C\(^1\) and this is entirely acceptable for a large number of applications. Also, silicon can easily be oxidized to form silicon dioxide. This oxide layer was found to be not only a high quality insulator but also an excellent barrier for the selective diffusion steps needed in integrated circuit fabrication.

The first successful fabrication technique produced single transistors on a silicon die 1 to 2 mm on a side. The early integrated fabricated circuits contained several transistors and resistors to make simple logic gates and amplifier circuits. From this modest beginning, integration levels of several million components on a 7 mm x 7 mm die have been achieved. For example, a one-megabit dynamic random-access memory (DRAM) chip has more than 1,000,000 transistors and more than 1,000,00 capacitors in the memory array, as well as tens of thousands of transistors in the access and decoding circuits. The level of integration has been doubling every one to two years since the early 1960's\(^2\).

However, silicon is not perfect in every sense. For instance, since silicon is an indirect bandgap semiconductor, many important electrooptical applications
are not possible with silicon devices or microcircuits. The industry therefore turned to group III-V semiconductors which turned out to be complementary to silicon in these applications.

1.1 Gallium Arsenide (GaAs)

1.1.1 Overview

Among the many compound semiconductors currently under investigation, gallium arsenide is the most technological advanced. Its most promising property is the great electron mobility in this material. As a result, gallium arsenide circuits are faster at equal or lower power than the silicon circuits\(^3\). As gallium arsenide consumes less power, it produces less waste heat that must be drawn from the circuit. This quality is particularly valuable since there is a trade-off between a semiconductor's speed and power. Also the high electron mobility in gallium arsenide enables this material to be used in high frequency, low-noise operation which is particularly valuable for the detection of television and microwave signals.

A second advantage of gallium arsenide over silicon lies in the much greater ease with which the separation between its valence and its conduction band, or bandgap, can be engineered. The bandgap is larger in gallium arsenide than in silicon, but it can be narrowed or widened by judicious substitution with other atoms such as aluminium, indium or phosphorus.

In addition to the electron mobility and bandgap flexibility, gallium arsenide's third most dramatic advantage over silicon is its capacity to radiate and detect near-infrared radiation. This makes this material extremely useful in optoelectronic applications. Furthermore, the wide range of operating temperatures and great resistance to high energy radiation render it invaluable for automotive and military applications respectively.
Moreover, the gallium arsenide's speed advantage has been exploited in some advanced digital applications in mainframe computer and supercomputer which emphasize performance more than cost. Recently, the first commercial supercomputer with its processor entirely made with gallium arsenide became available\textsuperscript{4}. This supercomputer is capable of performing two billion mathematical operations per second but has a comparatively modest maximum power requirement of 40 kW.

1.1.2 Crystal Structure of Gallium Arsenide

Gallium arsenide crystallizes in a zincblende structure and the unit cell of the lattice is depicted in Figure 1.1. Black spheres represent Ga and the white ones represent As atoms. Solid lines are used to show bonds between atoms whereas the dashed lines outline the cubic unit cell. The structure can be visualized as a face centred cubic arrangement of As atoms with Ga atoms filling half the tetrahedral holes. The lattice constant for the GaAs structure is 5.6534 Å.

The bonding in this structure consists of sp\textsuperscript{3} hybrid orbitals on both Ga and As atoms. In contrast to the purely covalent Group IV semiconductor, there is a charge transfer between the Group III and V atoms contributing to the ionic character of Ga-As bond. The bonding has been shown to be polar covalent\textsuperscript{5}, having 32% ionic character. This polar property of the Ga-As bond affects the cleavage of this crystal making it different from that of the Group IV crystals.

To explain the cleaving property of GaAs, let's first examine some of its low index surface planes. Figure 1.2a shows the top view of the first 3 layers of an ideal GaAs(100) face. The topmost layer of the structure contains only As atoms each with 2 dangling bonds projecting out of the paper and with the other 2 bonds receding behind the plane of the paper. The second layer is found to be containing only Ga atoms adopting the same tetrahedral bonding structure as the
Figure 1.1 The unit cell of gallium arsenide.
Figure 1.2  Top view of some ideal low index surfaces of GaAs  (a) (100) face,  (b) (111)B face and  (c) (110) face.
first one with 2 bonds extended to the upper layer atoms and 2 others to the lower ones. Similarly, the third layer resembles the first one with only As atoms again. This layer pattern continues along the [100] direction throughout the structure and thus the (100) plane of GaAs can be considered as being composed of alternate layers of sp$^3$ hybridized Ga and As atoms. Therefore when a GaAs crystal is cut to expose its (100) plane, the face will consist of only one kind of species, either Ga or As atoms. Since both types of faces (Ga rich or As rich) can be obtained by breaking the same number of Ga-As bonds (2 bonds per atom), there is an equal probability that a cleaved face will contained only Ga or As atoms. The (100) face therefore alternatively exposes Ga and As layers to the etchant gas during the etching reaction.

In Figure 1.2c, the first 2 layers of atoms of an ideal GaAs(110) face is shown. This plane lies on an array of chains, made up of alternate Ga and As atoms running from the top to the bottom of the paper. This layer has equal numbers of Ga and As atoms, as do the underlying ones. Each atom in the topmost layer has 2 bonds in the plane and 1 behind the plane. This leaves 1 dangling bond extending out of the paper, i.e. there is 1 dangling bond per surface atom. The (110) plane has the same number of Ga and As atoms. Furthermore every (110) plane along the [110] direction is identical. Due to this non-polar nature of the \{110\} plane and of its small number of bonds to be broken per atom during the cleavage, this plane is the preferred cleavage plane for GaAs in contrast to a Group IV semiconductor which has the \{111\} plane as the cleavage plane. The (110) face meets other \{110\} planes at right angles and thus cleavage along \{110\} plane allows the fabrication of a precisely rectangular GaAs chip. This is vital to laser diode applications.

Some interesting things happen in the GaAs (111) plane. The disparity between Ga and As atoms gives rise to 2 kinds of (111) faces, one gallium rich and one arsenic rich. Usually they are referred to as (111)A and (111)B faces.
respectively. In Figure 1.2b, the (111)B face is illustrated. The topmost layer contains only As atoms whereas the next underlying layer is composed of only Ga. Every As atom has 3 obliquely angled bonds extending into the gallium layer only a short distance behind the plane of the paper, and has 1 dangling bond projecting directly out of the paper. Therefore, in moving along the [111] direction, we will pass pairs of planes closed together, and each adjacent pair of planes are separated from the next pair by a full bond distance. If a crystal of GaAs having an exposed (111)B surface is cut parallel to the previous face and when it is viewed along the same [111] direction, the cleavage can occur either between adjacent pairs of planes by breaking 1 Ga-As bond per atom to give an all As surface i.e. (111)B surface, or between the 2 planes within the same pair by breaking 3 bonds per atom which in turn generates an all Ga surface. However, the latter case is energetically highly unfavourable and in fact never happens. As a consequence, only (111)B surfaces can be obtained by cutting a GaAs single crystal parallel to the previously exposed (111)B face.

The (111)A structure is exactly the same as the (111)B except that all the Ga and As atoms in Figure 1.2b are interchanged. They are of course the same layers of atoms, but viewed from the opposite direction. Suppose we have a wafer with a (111)B face on the front side, then the surface on the back side will be (111)A. However, their reactivities are different because the (111)A face has all Ga atoms on the surface layer whereas (111)B is all As. The difference in chemical reactivities between the Ga and As atoms determine the activities of the corresponding surfaces.

The gallium atom has 3 valence electrons and on the (111)A surface they are all used to bond to the As atoms behind the surface, leaving an empty sp\(^3\) hybrid orbital projecting out of the surface. It is often referred to as dangling bond because of the potential that it has for bonding to an electron pair of some donor species. On the (111)B face, 3 out of the 5 valence electrons on the As
atom are employed in the bonding to the bulk. This leaves 2 non-bonding electrons in its dangling bond which makes the As atom more susceptible than the Ga atom to be attacked by an electrophile. Although this may be an oversimplified picture with the assumption that the Ga and As atoms in the structure are neutral, the result makes the right prediction that the (111)B face is more reactive towards etching and oxidation by electrophiles. The inertness of (111)A face causes some fascinating preferential etching profiles which is referred to as crystallographic etching and will be discussed later in section 1.2.1.

1.1.3 Electronic Structure of Gallium Arsenide

Figure 1.3 shows a simplified version of the band structure diagram of silicon and gallium arsenide in which the energy is plotted against the momentum of the electron in the crystal (denoted by wave vector k). In the band diagram, the upper curve is called the conduction band and the lower curve is called the valence band. The separation between the bottom of the conduction band and the top of the valence band is called the bandgap $E_g$ of that material. For silicon, Figure 1.3a, the conduction band minimum and the valence band maximum occur at different k values. Consequently, when an electron is excited from the valence band to the conduction band, it requires not only a change in its energy but also a large change in its momentum. This kind of transition is optically forbidden. Silicon is thus called an indirect bandgap semiconductor because a change of momentum is required in the electron transition between the top of the valence band and the bottom of the conduction band.

However, in gallium arsenide, Figure 1.3b, the maximum of valence band and the minimum of the conduction band lie at the same k value. Therefore, an electron making a transition from the valence band to the conduction band can do so without a change in momentum and this kind of transition is optically allowed. For this reason, gallium arsenide is called a direct bandgap semiconductor. This
Figure 1.3 Band structure diagram of (a) silicon and (b) gallium arsenide.
property makes gallium arsenide capable of generating photons with energy equal to the bandgap. It can therefore be used to fabricate light emitting diodes and semiconductor lasers.

The effective mass of the electron ($m^*$) in the crystal is related to the second derivative of energy ($E$) with respect to the wave vector ($k$) as follows:

$$m^* \propto \left(\frac{d^2E}{dk^2}\right)^{-1}$$  \hspace{1cm} (1.1)

Therefore, the greater the curvature of the conduction band is, the smaller the effective mass will be. For example, gallium arsenide has a narrow conduction band parabola and so the effective mass of the electron is only 0.07 $m_0$ (where $m_0$ is the mass of the free electron) whereas silicon, with a wider conduction band parabola, has an effective electron mass of 0.19 $m_0$. Since the mobility of electrons in the material is inversely proportional to the effective mass of the electrons, the electrons in gallium arsenide have a higher mobility than in silicon. This property makes it possible for GaAs circuits to work faster than those fabricated out of silicon.

1.2 Etching

In the fabrication of microelectronics devices, etching is one of the essential steps in which the exposed part of the material is removed by a chemical or physical process. Figure 1.4a, shows the procedures used to open a window on the layer A to expose part of the semiconductor substrate B. The part which is to remain intact is firstly covered with a mask (usually a silicon oxide, silicon nitride layer or organic polymer) which is more inert to the etching process as illustrated in Figure 1.4b. The whole wafer is put in an etching medium which is reactive only to the layer A. The region of layer A not covered by the mask is gradually removed in the etching medium and it will stop when it reaches the substrate B (Figure 1.4c). After the removal of the mask, it leaves on
Figure 1.4  Steps involved in opening a window on the layer A.
the layer A a particular pattern determined by the structural features of the mask as in Figure 1.4d. Etching can generally be classified into two categories: wet etching and dry etching.

1.2.1 Wet Chemical Etching

Wet chemical etching is performed by putting the wafer to be etched into a chemical solution. The chemicals react with the exposed part of the semiconductor material removing a certain thickness of the material determined by the exposure time. This wet process has been used extensively in semiconductor processing. It can be used to delineate patterns and to open windows in insulating material. The agitation and temperature of the etchant solution can affect the etch rate. Usually, the reaction process involves the dissolution of the material or the conversion of it into other substances which are soluble in the etching medium.

Wet chemical etching tends to be an isotropic process, etching equally in all directions. Figure 1.5a shows the result of isotropic etching of a semiconductor. This etching process will etch under the mask to a distance equal to the vertical etched depth. This could cause serious problems in microelectronic processing which requires a linewidth with dimensions similar to the vertical etched depth.

However, of the various wet etching methods for GaAs, very few are truly isotropic. This is because the surface activity of the GaAs(111)A and (111)B faces are very different. The (111)A face tends to be etched much more slowly than the other planes; this results in orientation-dependent etching called crystallographic etching. A commonly used orientation dependent etching solution for GaAs consists of a 1% solution of bromine in methanol. The etch rates at room temperature are approximately 0.7 \( \mu \text{m min}^{-1} \) for the (100) plane, 1.0 \( \mu \text{m min}^{-1} \) for the (110) plane, 0.9 \( \mu \text{m min}^{-1} \) for the (111)B and only 0.15 \( \mu \text{m min}^{-1} \) for the (111)A plane. As a result, when the (100) face is etched with the
Figure 1.5 Etching profiles obtained with (a) isotropic wet etching and (b) dry anisotropic etching.
mask window aligned with the $\langle 0 1 1 \rangle$ direction, the etch profile will be a reverse mesa shaped with the $\{111\}$A faces exposed as in Figure 1.6a. However, if the mask is running along $\langle 011 \rangle$ direction, the exposed planes are also $\{111\}$A plane but the etch profile now is V-shaped as presented in Figure 1.6b.

1.2.2 Dry Etching

Instead of using liquid etchants as in wet etching, dry etching employs gaseous etchants in the etching process. The advantage of dry etching is that a highly anisotropic etching profile can usually be obtained as shown in Figure 1.5b, avoiding the undercutting problem of Figure 1.5a which is characteristic of wet processes. This highly anisotropic profile in dry etching can be achieved by constant vertical bombardment of the surface to be etched with ions during the etching process. This makes the vertical etch rate much higher than the lateral one. As a result, the etched profile will have a vertical wall instead of a curved one.

The second advantage of dry processes is that they only need a small amount of etchant gas whereas wet etching requires the disposal of large amounts of liquid chemical waste. For these reasons, dry etching has been widely used in Very Large Scale Integration (VLSI) fabrication.

In gallium arsenide etchings, a number of dry etching techniques have been developed to achieve highly anisotropic, fast and damage free processes, notably chemical etching\(^8\), plasma etching\(^9\), reactive ion etching\(^10\), radical beam etching\(^11\), reactive ion beam etching\(^12\) and laser induced etching\(^13\). Almost all the methods mentioned above employ chlorine or chlorine containing etchants directly, or used them to generate a plasma which can etch gallium arsenide.

In view of the topic of this thesis, only purely chemical dry etching, which involves a gaseous etchant and a solid gallium arsenide substrate, will be discussed in detail.
Figure 1.6  Crystallographic etching of gallium arsenide. (a) with mask running in \(\langle 0\overline{1}1\rangle\) direction. (b) with the mask running in \(\langle 01\overline{1}\rangle\) direction.
The chemical dry etching process can be viewed as occurring through five elementary steps as illustrated in Figure 1.7. (1) The process begins with the diffusion of etchant gas to the reactive surface. (2) The reactant is adsorbed on the surface. (3) This is followed by chemical reaction on the surface to form products which are volatile. (4) These compounds are desorbed from the surface. (5) The products diffuse away from the surface into the bulk gas and are pumped out by the vacuum system.

These are consecutive steps. If any one of them is slower than the others, it will become the rate determining step. In the etching system, it is possible to ensure that step 1 and step 5 are not rate controlling by having a sufficiently fast gas flow rate over the sample to be etched and by choosing an appropriate temperature and pressure range. The remaining steps: adsorption, reaction and desorption, can be rate determining in the kinetics of the etching process, and therefore will be discussed in the following sections.

1.2.3 Adsorption

There are two ways molecule can stick on a surface. In physisorption, the force between the surface and the adsorbed molecules is the long range and relatively weak Van der Waal force. Therefore, the enthalpy change in the physisorption process is of the order of the heat of condensation. The heat of physisorption is seldom more negative than about -25 kJ mol\(^{-1}\). These energies are insufficient to lead to bond breaking and so in physisorption, the adsorbed molecule retains its identity, although it may be stretched or bent because of the proximity of the surface.

In chemisorption, the adsorbed molecule sticks on the surface as a result of bond formation between the adsorbed molecule and the surface. The bond is usually covalent in nature. Therefore, the enthalpy change in this type of adsorption is much higher (usually more negative than -40 kJ mol\(^{-1}\)). A
Figure 1.7  Steps in dry etching process.
molecule under chemisorption may be torn apart by the unsatisfied valencies of the surface atoms and so it may lose its identity.

Figure 1.8 shows the potential energy curve for adsorption of a molecule on a substrate surface. As the molecule approaches the surface, its energy will decrease to the first minimum as it becomes physisorbed. Dissociation into fragments often takes place as the molecules moves into its chemisorbed state. The energy of the molecule rises as the bond is stretched and then drops sharply into chemisorption state. It moves to the second minimum when the surface-adsorbate bond(s) reach their full strengths. The energy barrier between physisorption and chemisorption might lie below the energy of the free molecule as in Figure 1.8a. In this case, it is called an non-activated process and it is expected to proceed quickly. In other cases as in Figure 1.8b, the transition state between physisorption and chemisorption lies above that of the free molecule and therefore it generally proceeds more slowly than non-activated chemisorption.

Using absolute-rate theory, the typical values of pre-exponential factors for the various rate-limiting steps have been calculated and are presented in Table 1.1. By comparing these theoretical values with the experimental values, it is sometimes possible to identify the rate controlling steps in the gas-solid reaction. Surface reactions that are controlled by slow adsorption or slow surface reaction steps have pre-exponential factors in the range $10^2$ to $10^4$ s$^{-1}$. For surface-diffusion-controlled reactions, the pre-exponential factor varies from $10^7$ to $10^{12}$ s$^{-1}$, depending upon the density of active sites. Desorption or unimolecular reaction-controlled surface reactions have factors typically greater than $10^{12}$ s$^{-1}$, in the range of $10^{13}$ to $10^{17}$ s$^{-1}$.

1.2.4 Langmuir Adsorption Isotherm

The first quantitative theory for the adsorption of a gas on a surface was formulated by Irving Langmuir in 1916. It based on the assumptions that (1)
Figure 1.8  Potential energy curve for physisorption and chemisorption.  
\( \Delta H_{\text{phys}} \) is the enthalpy of physisorption, \( \Delta H_{\text{chem}} \) is the enthalpy of chemisorption and \( E_a \) is the activation for chemisorption.
Table 1.1  Typical values of pre-exponential factors\textsuperscript{15}.

<table>
<thead>
<tr>
<th>Rate determining step</th>
<th>Typical pre-exponential factor (s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>$10^2 - 10^4$</td>
</tr>
<tr>
<td>Desorption</td>
<td>$10^{13}$</td>
</tr>
<tr>
<td>Surface diffusion</td>
<td>$10^7 - 10^{12}$</td>
</tr>
<tr>
<td>First order surface reaction</td>
<td>$10^{13}$</td>
</tr>
</tbody>
</table>
there is a fixed number of adsorption sites on the surface. At any pressure and temperature, a fraction ($\theta$) of the sites are occupied. (2) Each site can hold one adsorbed molecule. (3) The ability of a gas to adsorb on a surface site is independent of whether or not the neighbouring sites are occupied. (4) The adsorbed molecule is in dynamic equilibrium with free molecules. This equilibrium can be described by the following equation in which $k_a$ is the adsorption rate constant and $k_d$ is the desorption rate constant.

\[
A(g) + M_{\text{surface}} \xrightleftharpoons[k_d]{k_a} AM
\]  \hspace{1cm} (1.2)

The adsorption rate is proportional to the pressure of $A$ and the number of unoccupied sites available on the surface i.e. $N(1-\theta)$ where $N$ is the total number of sites on the surface. Therefore,

\[
\text{rate of adsorption} = k_a P_A N(1-\theta) \hspace{1cm} (1.3)
\]

The rate of desorption is proportional to the number of adsorbed species on the surface which is equal to $N\theta$:

\[
\text{rate of desorption} = k_d N\theta \hspace{1cm} (1.4)
\]

At equilibrium, the adsorption and desorption rates are equal and solving for $\theta$ will give the Langmuir isotherm:

\[
\theta = \frac{KP_A}{(1 + KP_A)} \hspace{1cm} \text{where } K = \frac{k_a}{k_d} \hspace{1cm} (1.5)
\]

The whole adsorption curve is presented in Figure 1.9. Two limiting cases of this isotherm are of particular interests. When $KP_A << 1$, i.e. if the pressure of the gas is low or the adsorption equilibrium constant is small,

\[
\theta \approx KP_A \hspace{1cm} (1.6)
\]

This indicates that the coverage of the surface is linearly dependent on the pressure in the low pressure range of the adsorption curve. When $KP_A >> 1$, i.e.
Figure 1.9  A typical Langmuir isotherm.
at high pressures or for a particularly strong adsorption between the surface and adsorbate, the isotherm reduces to,

\[ \theta \approx 1 - \frac{1}{K_P A} \]  

(1.7)

The isotherm will reach a plateau in the high pressure region.

1.3 Purpose of Study

The etching of gallium arsenide by halogen atoms and molecules is central to the processes commonly used in the fabrication of microelectronic circuits with this material. However, the mechanisms of these reactions and the rate constants for the elementary steps in the processes remain largely undetermined. In 1988, Ha et al.\(^{17}\) reported a kinetic study of the etching of GaAs by molecular chlorine in which they found that the etch rate was not a linear function of the chlorine pressure. From the form of the pressure dependence which they observed, they concluded that the etch rate reached a plateau at high pressures because of the "saturation" of sites for reaction on the surface. Such interpretation of the non-linear kinetics was reinforced by similar observations and interpretations in the reactions of Br\(_2\)\(^{18}\) and Cl\(_2\)\(^{19}\) with silicon. However, more recently, it has been shown that neither of these latter reactions reached a plateau at high pressures, and that at high pressures they both simply became half order with respect to the partial pressure of the molecular halogen\(^{20,21}\). We therefore decided to reinvestigate the GaAs/Cl\(_2\) reaction to see if any systematic errors occurred in the earlier work which prevented this reaction from being recognized as half order.

Due to the high volatility of the chlorides of gallium and arsenic, Cl\(_2\) and chlorine containing gases are commonly used in these etching techniques. However, Cl\(_2\) is a very corrosive gas to handle, and it shows a relatively low selectivity for semiconductors over commonly used masking materials such as
photoresists. Consequently other etchant gases such as Br₂ have been investigated as alternatives. Although the reactions of GaAs with Cl₂ and with Br₂ have been examined by a number of laboratories to investigate the mechanisms and to determine their rate constants, there have been no similar study on the etching by I₂. In 1976 Jacobi et al. reported a study of the interaction of a molecular beam of I₂ molecules with a GaAs (111)As surface. Gallium and arsenic compounds were found to be desorbed continuously from the surface at room temperatures. This suggests that a continuous reaction between GaAs and I₂ can occur at relatively low temperatures despite the low volatility of the stable iodides of gallium and arsenic. Consequently, we have undertaken a quantitative study on this GaAs/I₂ system to determine the experimental conditions (pressure and temperature range) in which practical etch rates can be achieved, and to determine the order and activation energy of the reaction.
Chapter 2 : Experimental

2.1 Apparatus

The etching systems used for both Cl₂ and I₂ etchants were the same except for some minor modifications. Due to the highly corrosive nature of these etchant gases, the apparatus was mainly constructed of Pyrex and only glass and Teflon parts were used in the system whenever possible. Most of the valves used were made with Teflon moving parts and different parts of the glassware were joined by Viton O-ring seal joints. However, in some components such as pressure gauges, Cajon fittings and needle valves where metals had to be used, only stainless steel and monel, were used. Despite the high inertness of stainless steel, it was found that the steel would be corroded by the etchant gas after a period of time. Since the heterogeneous reaction is extremely sensitive to the impurities such as water present in the system, cleaning the metal parts exposed to the etchant from time to time was done to decrease the corrosion rate.

2.1.1 Etching Reactor

A schematic diagram of the whole reactor design used in the studies is depicted in Figure 2.1. The etching reactor was constructed from a Pyrex tube 2 cm in diameter and 17 cm long. A 7 cm length of this tube that surrounded the sample holder was wrapped with heating tape, which allowed the temperature of the walls, the etchant gas and the substrate to be maintained at any temperature between 25 and 500°C. The temperature of the sample was controlled by using a Variac transformer to adjust the current flowing through the heating tape. A 20 cm length of tubing installed before the reactor was separately wrapped with heating tape to preheat the gas stream to the desired temperature before the gas entered the reactor. Another side-arm extending from the reactor was connected to a pressure gauge to measure the pressure of etchant gas in the
Figure 2.1  Apparatus for chlorine and iodine etching of gallium arsenide.
system. For I\(_2\) etching, the pressure gauge had to be warmed to 45°C to prevent any condensation of I\(_2\) on its diaphragm.

### 2.1.2 Sample Holder

The sample holder assembly used in etching experiments is shown in Figure 2.2. It was made of a 1.5 x 1 x 1 cm\(^3\) single-crystal silicon block with smoothly polished faces to ensure good thermal contact with the sample. The relatively big mass of the silicon block can be used as a heat sink to conduct away the heat generated on the sample surface by the etching reaction. We will therefore assume that the measured temperature on the block was the actual temperature of the sample. The surface of the silicon block was thermally oxidized by a hot flame in air to form a protective layer of SiO\(_2\) and hence prevent any reaction with the halogen gas. The whole block was supported by a glass tube which penetrated the block. A thermocouple probe passing through this tube into the centre of the silicon block was used to measure the substrate temperature. A glass spring was employed to hold the sample in place and to ensure good thermal contact with the sample holder.

The sample holder was connected to the system by an O-ring seal joint which could maintain the system in vacuum and enable fast loading and unloading of the sample.

### 2.1.3 Gas Handling System

For Cl\(_2\) etching, a monel and stainless steel pressure regulator was used for the connection with the gas cylinder. The Cl\(_2\) gas was delivered from the regulator to the system by a \(\frac{1}{4}\) inch Teflon FEP tubing (by Cole-Parmer). The gas flow was controlled with a monel Nupro needle valve. A Swagelok fitting
Figure 2.2 Sample holder used in the chlorine and iodine etching of gallium arsenide.
with a Teflon ferrule was used for the metal-to-Teflon joint, and both the metal-to-glass and glass-to-glass connections were made with Cajon fittings.

When working with I\textsubscript{2}, because of the corrosive nature of I\textsubscript{2} towards metal parts, particularly in the presence of water, metals were avoided particularly in the I\textsubscript{2} reservoir. With this in mind, the reservoir designed was made of glass and was equipped with Teflon-glass control valves with maximum orifices of 4 mm. The 300 cm\textsuperscript{3} reservoir was firstly loaded with solid I\textsubscript{2} and then evacuated at room temperature to remove any gases and moisture adsorbed on the solid I\textsubscript{2}. To ensure rapid vaporization, the I\textsubscript{2} reservoir was heated to 80°C with a heating tape. The connecting glass tubing and control valves were also heated to avoid I\textsubscript{2} condensation. With the pumping speed kept constant, the partial pressure of I\textsubscript{2} in the reactor was regulated by adjusting the Teflon stopcock on the I\textsubscript{2} vessel to change the flow of I\textsubscript{2} vapor in the system. The I\textsubscript{2} flow rate was varied between 4 and 85 sccm whereas the Cl\textsubscript{2} gas flow rate was ranging from 4 to 800 sccm. It ensured that the supply of the halogen gases exceeded the consumption rate by at least a factor of 5000. Under these conditions, there would not be any dilution of the reactant stream by the gaseous reaction products and therefore no reactant concentration gradients established above the substrate surface.

In addition to the etchant gas lines, a helium line was also installed to purge the system during the loading and unloading of the sample in order to prevent any moisture from getting into the reactor. It was also used to restore the system to atmospheric pressure after the completion of etching so that the whole system was stored in this inert atmosphere when not in use.

The flow system was evacuated with a 77 K cryostatic pump backed by a rotary pump (Sargent Welch Model No. 1400) allowing the system to be pumped down to a base pressure of about 10 milliTorr before etching of the sample. The U-tube cold trap not only served as a cryostatic pump but also prevented the halogen gas from entering the rotary pump and avoided any diffusion of
hydrocarbons from the pump back to the system. The system and the pump were separated by a Teflon throttle valve and this valve was fully opened to achieve the flow rate used in the etching experiments.

2.1.4 Sample Preparation

Before the GaAs(100) wafer was used in the etching experiment, the (100) face of the wafer was covered with 0.05 μm thick silicon nitride (Si₃N₄) stripes 50 μm wide and 50 μm apart, running in the 〈0 1 1〉 direction in some regions and in the 〈011〉 direction in others. This Si₃N₄ mask was deposited by Hiroshi Kato of the UBC Centre for Advanced Technology in Microelectronics. The following procedure was used:

Firstly, the wafer on which the mask would be deposited was degreased and cleaned in hot trichloroethylene, acetone and then isopropyl alcohol for 10 min in each solvent. Then a layer of Si₃N₄ was deposited on the wafer by plasma enhanced chemical vapor deposition under the following condition: SiH₄ flow = 380 sccm, NH₃ flow = 42.5 sccm, H₂ flow = 500 sccm, temperature = 300°C, RF power = 100 watts and deposition time = 2.5 min. A photoresist was spin-deposited on the wafer with a speed of 4700 rpm for 35 s. After that, the photoresist was baked at 95°C for 25 min and was then exposed for 27 s to UV light from a mercury lamp source (i.e. 320 nm) through a striped mask. The photoresist was baked at 95°C for 25 min and the pattern developed in 50% MF-312 developer. A buffered HF solution was used to etch the Si₃N₄ not covered by the photoresist and then it was rinsed with deionized water. Finally the photoresist was removed with a hot
acetone, isopropyl alcohol wash, and the wafer was blown dry by nitrogen gas.

In order to ensure that the residual photoresist was completely removed, the wafer was washed with a hot commercially available liquid called "Resist Stripper" and then with deionized water before it was used in the etching study.

2.2 Chemicals

2.2.1 Single Crystal Gallium Arsenide (100)

The single crystal GaAs (100) wafers we used in this study were supplied by Crystar (nee Johnson Matthey, nee Cominco). The size of the wafer was 0.5 mm thick and 7.5 cm in diameter and it was "undoped semi-insulating". No other information such as purity and background carrier concentration was available for these wafers.

2.2.2 Chlorine

Commercially available Cl₂ gas from Mattheson was used in all Cl₂ etching experiments without further purification. The quoted purity of the Cl₂ is at least 99.99 %.

2.2.3 Iodine

The I₂ used in all the experiments was B.D.H analytical reagent grade, purified by resublimation with a quoted purity of 99.8 %. This I₂ solid was used directly without further purification.

2.3 Experimental Procedure

2.3.1 Temperature and Pressure Measurement
The temperature of the sample during etching conditions was measured with a thermocouple embedded inside the silicon sample holder. The thermocouple was a Chromel-Alumel type with a working range from 0 to 1260°C and it was used with an Omega readout device (Model 115 KC). The temperature variation was about ±1°C throughout all the etching experiments.

Gas pressure was measured with an MKS Baratron pressure gauge (Type 122A) with a working range from 0 to 100 Torr. This device was calibrated with a cold cathode pressure gauge before used. The base pressure of the etching system measured was approximately 10 milliTorr. However, it should be noted that all residual gases are quickly flushed out of the system when the I₂ flow is started. The pressure and temperature was chosen such that the etching rate of GaAs was between 0.05 and 2.0 μm min⁻¹ because these were most easily measured by our monitoring method.

### 2.3.2 Determination of the Volume of the System

To determine the volume of the system (Vₛ), helium gas at a known pressure (Pᵥ) in a glass vessel of known volume (Vᵥ) was allowed to expand into the evacuated reactor system with a base pressure of Pᵇ. With the final pressure after expansion being Pᶠ, Vₛ can be calculated with the ideal gas law relationship:

\[
Vₛ = \frac{Pᵥ - Pᶠ}{Pᶠ - Pᵇ} Vᵥ \tag{2.1}
\]

From several trials with different Pᵥ values, Vₛ can be found by plotting (Pᵥ - Pᶠ)Vᵥ vs (Pᶠ - Pᵇ) as shown in Figure 2.3. The slope of the straight line which equals Vₛ is calculated by linear regression to be 227 cm³.
Figure 2.3 Determination of the system volume.
2.3.3 Flow Calibration

In the GaAs/I₂ etching experiment, a flowmeter was not used to measure the gas flow through the system because of I₂ condensation inside the flow tube. Therefore an indirect way was designed to determine the gas flow in the system. It was worthwhile to note that all the experiments were performed at a constant pumping speed and the gas pressure over the substrate was regulated by adjusting the flow rate of the etchant gas into the system with a control valve located upstream from the reactor. This ensured that the residence time of the gas over the etching sample was relatively constant at all pressures. For this reason, under a fixed pumping speed, when the pressure of the gas inside the system is at some value, it will correspond to a particular constant gas flow rate. At a certain temperature, if the evacuation is suddenly shut off, the pressure will increase with a rate of \( \frac{dP}{dt} \) and this rate can be determined by measuring the pressure change as a function of time. Since the volume of the system \( (V_s) \) remains constant. The gas flow \( (F) \) will be given by:

\[
F = V_s \frac{dP}{dt} / (12.67 \text{ Torr cm}^3 \text{s}^{-1} \text{ sccm}^{-1})
\]

(2.2)

where \( F \) is the flow in sccm, \( P \) is the pressure in the system in Torr and \( t \) is the time in second. The flows at room temperature determined in this way at different etchant gas pressures are presented in Figure 2.4.

2.3.4 Etching Procedure

Before the etching experiment was performed, the system was heated up to the desired temperature and it was left for about 1 h to allow all parts of the reactor to come to thermal equilibrium. At the same time, the system was evacuated for at least 1 h to degas all the surfaces inside the system. Then, the evacuation was shut off to check the leakage of the system.
Figure 2.4 Calibration of the etchant gas flow at various gas pressures.
The patterned GaAs (100) wafer was cut into ca. 0.04 cm$^2$ chips. Prior to etching, a chip was dipped in concentrated hydrochloric acid (38%) for 30 s to remove the native oxide layer. It was then washed with distilled water and dried under nitrogen gas. The system was restored to atmospheric pressure by helium gas and the sample was loaded into the reactor while the system was being purged with helium gas. The sample was left in the system under a helium atmosphere for 4 min so that the sample could be in thermal equilibrium with its surrounding. Then, the system was evacuated by fully opening the pump throttle valves to ensure maximum pumping speed. After aligning the laser beam with the sample to be etched and the photodetector, the etchant gas flow was turned on and quickly adjusted to produce the desired pressure of etchant gas. On completion of the etching, the etchant flow was stopped and the system was restored to atmospheric pressure with helium gas.

2.4 Etch Rate Measurement

2.4.1 Laser Interference Method

The etch rates were measured in situ by laser interferometry. A 1 mW HeNe cw laser of wavelength 632.8 nm was reflected off the surface of the GaAs sample. As shown in Figure 2.5, part of the light was reflected from the silicon nitride surface (beam A) while part was from the GaAs face (beam B). There would be interference between these two beams and the intensity change was monitored by the silicon photodetector connected to a chart recorder. The exposed GaAs surface recedes as it is being etched, therefore there will be an increase in the path difference ($\Delta$) between the beam A and B where,

$$\Delta = 2d \cos \theta$$  

(2.3)

This gives rise to a sinusoidal reflected light intensity as a function of time. Constructive interference occurs when the path difference between the 2 beam is:

$$\Delta = n \lambda$$  

(2.4)
Figure 2.5 Laser interferometry method for etch rate determination.
where $\Delta$ is the path difference, $\lambda$ is the wavelength of the laser used and $n$ is any positive integer. Assuming that the incident laser beam is perpendicular to the surface i.e. $\theta \approx 0^\circ$, then $\Delta = 2d$ and equation (2.4) will become:

$$d \approx n \frac{\lambda}{2}$$

(2.5)

Similarly, for destructive interference,

$$d \approx n \frac{\lambda}{2} + \frac{\lambda}{2}$$

(2.6)

The etch rate (ER) is then given by,

$$ER = \frac{\lambda}{2t}$$

(2.7)

where ER is the etch rate in $\mu m \ min^{-1}$ and $t$ is time in min measured on the chart recorder between 2 adjacent maxima or minima. Figure 2.6. shows a typical interferogram obtained in an etching experiment. The etch rate was found to vary about 5 to 10% during the course of an experiment.

2.4.2 Profilometry Method

The etch rate determined by laser interferometry was occasionally verified with a Tencor surface profilometer which measured directly the etched depth relative to the silicon nitride masked surface. The device was operated with a fine stylus moving across the surface. The step heights are measured, producing a profile as shown in Figure 2.7. By knowing the total etched depth and the total etching time, the etch rate can then be calculated. It was also useful as a check of the uniformity of the etch. In general, a typical variation of ca. $\pm 5\%$ of the total etched depth was observed. The etch rates determined by these two methods are compared in Figure 2.8. They were found to be consistent within $\pm 10\%$. 

38
Figure 2.6 Typical interferogram obtained in the etching of GaAs with Cl₂ at 110°C and with gas pressure of 0.10 Torr.
Figure 2.7 Profile of the etched gallium arsenide surface measured by profilometer.
Figure 2.8 Comparison between the etch rate results obtained by interferometry and profilometry.
2.5 Data Calculations

2.5.1 Etch Rate Calculation Method

Five modulations in the interferogram were usually obtained for every set of conditions. The etch rate as a function of time was then determined by measuring the peak-to-peak and minimum-to-minimum separations in Figure 2.6 for the first five modulations and the results are presented in Figure 2.9. The average etch rate was calculated by numerical integration of the curve in Figure 2.9.

2.5.2 Curve Fitting and Plotting

All the plotting and curve fitting were performed on an Apple Macintosh personal computer using the software "Igor" by WaveMetrics.
Figure 2.9 The etch rate as a function of time for iodine etching of gallium arsenide sample at $T = 310^\circ C$ and $P = 1.25$ Torr.
Chapter 3 : Results

3.1 Data for the Etching of GaAs(100) with Chlorine

The quantitative experiments were carried out at 90, 100, and 110°C with the Cl₂ pressure ranging from 0.10 to 9.0 Torr to determine the order of reaction with respect to the Cl₂ pressure and its activation energy. The pressure dependence of the etch rate is shown in Figure 3.1. It can be seen that the etch rate continues to increase as the pressure of the Cl₂ increases and no saturation of reaction rate is observed in the working pressure range.

It is conceivable that a plateau is not observed at high pressures because of a temperature rise on the sample due to the greater amount of heat released during the reaction at higher Cl₂ pressure. In order to check such a possibility, another run was carried out at 110°C and 1.00 torr of Cl₂, with a small drop of gallium metal put between the sample and the silicon sample holder to ensure a maximum rate of heat dissipation to the heat sink (sample holder). The result obtained for this sample was indistinguishable from those obtained in the absence of gallium metal. Therefore, the continuously increasing etch rate with increasing pressure appears to be real rather than an experimental artifact.

3.1.1 Kinetic Analysis of the GaAs/Cl₂ System

Assuming that the etch rate (ER) of the reaction depends on the pressure of chlorine (P_{Cl₂}) in the following way :

\[ \text{ER} = k \ (P_{Cl₂})^n \]  \hspace{1cm} (3.1)

where \( k \) is the rate constant and \( n \) is the order of the reaction with respect to the chlorine pressure, the order \( n \) can be determined by plotting the ln (ER) vs ln (P_{Cl₂}). Such a plot is presented in Figure 3.2 and the linear regressions yield slopes of approximately 0.5. This suggests a simple half order dependence on the
Figure 3.1  The GaAs(100) etch rate as a function of the pressure of Cl₂ at 90° (○), 100° (△) and 110°C (□).
Figure 3.2 A plot of $\ln (ER)$ versus $\ln (P_{Cl_2})$ at $90^\circ$ (○), $100^\circ$ (△) and $110^\circ$C (□).
Cl₂ pressure. This was verified by making an ER vs √P₁ Cl₂ plot as shown in Figure 3.3. Interestingly, instead of passing through the origin, the best fit straight lines intersect the y-axis at slightly negative values. The magnitude of this negative y-intercept shows a systematic increase with increasing temperature. Similar results have been reported for the etching of Si by the halogens. ²⁰,²¹
Thus, an empirical equation (3.2) can be used to represent the pressure dependence of the etch rate.

\[
ER = C₁ \sqrt{P_{Cl₂}} - C₂
\]

(3.2)

where \(C₁\) are the slopes and \(C₂\) are the y-intercepts of the straight lines in Figure 3.3. at the temperatures indicated. The calculated values of \(C₁\) and \(C₂\) at various temperatures are listed in Table 3.1.

Assuming that \(C₁\) and \(C₂\) exhibit Arrhenius temperature dependence, i.e.

\[
k = A e^{-\frac{Eₐ}{RT}}
\]

(3.3)

where \(k\) is the rate constant of reaction, \(A\) is the pre-exponential factor, \(Eₐ\) is the activation energy of the reaction, \(R\) is the gas constant and \(T\) is the temperature in Kelvin. The Arrhenius parameters of \(C₁\) and \(C₂\) can be obtained by plotting \(\ln (C₁)\) and \(\ln (C₂)\) vs \(\frac{1}{T}\) as shown in Figure 3.4. A least squares fit of the data points yields activation energies and pre-exponential factors which are presented in Table 3.2.

3.1.2 Surface Morphology and Etched Profiles

A typical interferogram for Cl₂ etching of GaAs (100) is depicted in Figure 3.5. In the figure, 4 modulations which correspond to 1.2656 μm of etched depth, are shown. Comparing the reflected light intensity of the maxima of those peaks, it can be seen that they show only a small decrease during the reaction. This indicates that the smoothness of the etched face is not much
Figure 3.3 A plot of the etch rate versus \( \sqrt{P_{\text{Cl}_2}} \) at 90° (\( \circ \)), 100° (\( \triangle \)) and 110°C (\( \square \)).
Table 3.1  $C_1$ and $C_2$ obtained at three temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$C_1$ (µm min$^{-1}$ Torr$^{-1/2}$)</th>
<th>$C_2$ (µm min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.591</td>
<td>1.75</td>
</tr>
<tr>
<td>100</td>
<td>0.527</td>
<td>1.12</td>
</tr>
<tr>
<td>110</td>
<td>0.683</td>
<td>0.0953</td>
</tr>
</tbody>
</table>
Figure 3.4 A plot of \( \ln C_1 (\bigcirc) \) and \( \ln C_2 (\bullet) \) versus \( \frac{1}{T} \).
Table 3.2  Pre-exponential factor (A) and activation energy (E_a) of C_1 and C_2.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>E_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_1</td>
<td>10^{13.6} \mu \text{m min}^{-1} \text{Torr}^{-1}</td>
<td>100 \text{ kJ mol}^{-1}</td>
</tr>
<tr>
<td>C_2</td>
<td>10^{16.4} \mu \text{m min}^{-1}</td>
<td>75 \text{ kJ mol}^{-1}</td>
</tr>
</tbody>
</table>
Figure 3.5 Interferogram result from Cl₂ etching of GaAs.
changed by the etching process. The smoothness of the GaAs face is further verified by the profile scan with the Tencor profilometer in Figure 3.6. The bottom of the trough is the etched surface and it can be seen that the bottom is extremely flat. Another piece of evidence for this smoothness comes from the scanning electron microscopy (SEM) photograph of the etched face of the same sample as in Figure 3.7. Our finding therefore confirms the earlier report that the etching of GaAs with Cl\textsubscript{2} can achieve an atomically flat surface under suitable conditions\textsuperscript{24}.

Figure 3.8 shows the SEM photographs of the cross-sections for a (100) substrate after it is etched at a temperature of 110°C and at a Cl\textsubscript{2} pressure of 0.10 Torr. In Figure 3.8a, the substrate has the mask stripes running parallel to \langle01\overline{1}\rangle direction, the etched region has outward sloping walls or V-shape grooves. However, in Figure 3.8b, where the stripes are running in the \langle0\overline{1}1\rangle direction, the etch profile is reverse mesa shaped with inward sloping walls.

On close examination, the outward sloping and the inward sloping walls make angles with the Si\textsubscript{3}N\textsubscript{4} mask at approximately 54° and 125° respectively. In accordance with the crystal structure of GaAs, when the crystal is viewed along the \langle011\rangle direction, the \{111\}A planes intersect the (100) face at 54°44' as shown in Figure 3.9a. On the other hand, when it is viewed along \langle0\overline{1}1\rangle direction as presented in Figure 3.9b, the \{111\}A planes intersect the (100) faces at 125°16'. Therefore, both the inward sloping and the outward sloping planes observed in Figure 3.8 are probably the \{111\}A planes. The formation of these exposed \{111\}A planes can be explained by considering that etching of the \{111\}B, \{110\} and \{100\} planes are much faster than the \{111\}A plane. As a result, the etching proceeds rapidly until it reaches the \{111\}A face. Eventually, only these faces are exposed and become the walls of the etched grooves.
Figure 3.6 Etch profile of GaAs surface after etching with Cl$_2$ measured by profilometer.
Figure 3.7 SEM photographs of the etched GaAs surface by Cl\textsubscript{2}. 
Figure 3.8 SEM photograph of the etching profile by Cl\textsubscript{2}. 
Figure 3.9  Schematic diagram of cross sections etched in \{100\} planes of GaAs by drawing through \{110\} planes and of relation between \{100\} and \{111\} plane (●) Ga atoms, (○) As atoms. (a) cross section of a channel etched parallel to \langle 01\bar{1} \rangle direction in (100), (b) cross section of a channel etched parallel to \langle 0 \bar{1} 1 \rangle direction in (100).
3.2 Data for the Etching of GaAs(100) with Iodine

The GaAs (100) face was found to be etched at a measurable rate by gaseous I\(_2\) at temperatures above 260°C. The variation of the etch depth across the surface measured by profilometry was found to be about ±5% of the etched depth. The dependence of the etch rate on the pressure of I\(_2\) and temperature was determined at pressures ranging from 0.10 to 1.25 Torr and, at four temperatures between 270 and 330°C. The results are summarized in Figure 3.10.

3.2.1 Kinetic Analysis of the GaAs/I\(_2\) System

In all cases, the etch rates (ER) appeared to increase linearly with increasing pressure of I\(_2\) (P\(_{I_2}\)) in the low pressure region and became non-linear above 0.4 Torr. The order of reaction in the nonlinear region was determined by plotting ln (ER) vs ln (P\(_{I_2}\)) as shown in Figure 3.11. The least squares lines through these points gave slopes ranging from 0.78 to 0.87, which meant that the order was between first and half with respect to the I\(_2\) pressure. Such behavior is similar to those observed earlier in the studies of the etching of GaAs and Si by Cl\(_2\) \(^{21}\) and Br\(_2\) \(^{20,23}\). In all those cases, the ER is first order at low pressures but changes to half order at high pressures. The apparent order of 0.8 for our GaAs/I\(_2\) reaction is probably due to the fact that our working pressure range from 0.4 to 1.25 Torr is right in the intermediate range in which the pressure dependence changes from first to half order. Since the pressure range of our experiment does not cover any half order region, we cannot simply plot ER vs \(\sqrt{P_{I_2}}\) to determine the rate constants as we did in section 3.1.1 for the Cl\(_2\) etching results. The kinetic analysis will be performed in section 4.2 after the full ER expression for the proposed mechanism has been established.
Figure 3.10 Etch rate of GaAs(100) as a function of the iodine pressure at 270 (□), 290 (○), 310 (△) and 330 °C (○).
Figure 3.11  A plot of ln (ER) versus ln (P₁₂) at 270 (□), 290 (○), 310 (△) and 330 °C (○).
3.2.2 Surface Morphology and Etched Profiles

A typical interferogram obtained for the etching of GaAs with I\textsubscript{2} is shown in Figure 3.12. The intensity of the reflected laser light drops rapidly during the first 5 modulations. This indicates that the GaAs surface changes from the original smooth surface to a very rough one during the etching process. The bottom of the etched GaAs face, measured with a profilometer, is shown in Figure 3.13. The bottom face can be seen to be quite rough and irregular. This is consistent with the conclusion drawn from the laser interferogram. Under the electron microscopy, these irregular bumps appear as 'scratches' on the etched surface and they seem to be 'directional'. In Figure 3.14a, which has the stripes running in \langle 0\bar{1}1 \rangle, the scratches extend perpendicular to the mask, i.e. in the \langle 0\bar{1}1 \rangle direction. Similarly in Figure 3.14b, which has the stripes running in the \langle 0\bar{1}1 \rangle direction, the scratches are parallel to the mask i.e. also in the \langle 0\bar{1}1 \rangle direction. The directionality of these features suggest that the etching by I\textsubscript{2} is somehow sensitive to the defects in the crystal structure of GaAs. However, further investigation will be required to find out the reason for this phenomenon.

In contrast to the result of GaAs/Cl\textsubscript{2} reaction, both samples, the one with mask stripes running in \langle 0\bar{1}1 \rangle and the other with stripes in \langle 0\bar{1}1 \rangle directions formed a U-shape grooves with outward slopes. The SEM pictures of these grooves are shown in Figure 3.15a and 3.15b respectively. They indicate that the etching of GaAs by I\textsubscript{2} is probably isotropic.

3.2.3 Etch Product Analysis

The products of the GaAs/I\textsubscript{2} reaction are easily condensed in the cool region of the system. After the etching reaction, a brown solid residue appeared on the cool walls downstream of the sample and also in the cold trap. Mass
Figure 3.12 Interferogram result from I$_2$ etching of GaAs.
Figure 3.13 Etch profile of GaAs surface after etching with I₂ measured by profilometer.
Figure 3.14 SEM photographs of the etched GaAs surface by I$_2$. 

(a) 

(b)
Figure 3.15  SEM photograph of the etching profile by \textit{l}_2.
spectrometry (MS) was used to analyze this residue in the range of 1-550 mass units (m/e). The natural abundance of isotopes of Ga, As and I are shown in Table 3.3. Since the natural abundances of Ga$^{69}$ and Ga$^{71}$ are 60.4 and 39.6% respectively, any species containing one Ga atom will appear as a doublet with mass peak-height ratio of 1.525:1. The doublet is separated by two mass units. This helps in identifying the peaks corresponding to gallium containing species.

The MS spectrum in Figure 3.16 shows major peaks corresponding to GaI$_x^+$ and AsI$_x^+$ species where $x$ is a number from 1 to 3 and there is no significant peak with m/e higher than 456 which corresponds to AsI$_3$. The assignment of the major peaks is indicated in Table 3.4 and it is further confirmed by high resolution MS. The highest m/e peaks for Ga and As correspond to GaI$_3$ and AsI$_3$ respectively. This suggests that GaI$_3$ and AsI$_3$ are the major stable products of the reaction. Also GaI$_3$ is described in the literature as a brown solid$^{26}$. However, we cannot simply conclude that GaI$_3$ and AsI$_3$ were indeed the species leaving the semiconductor surface because they could have been formed subsequently from other less stable species that desorbed from the surface. To analyze the desorption products directly without additional reactive collisions, a more extensive study with in situ monitoring of desorbed species with an MS positioned very near to the surface will be required.

The GaI$^+$, AsI$^+$, GaI$_2^+$ and AsI$_2^+$ signals observed in the MS spectrum can be either due to the presence of the corresponding neutral species in the product residue or to the fragmentation of GaI$_3$ and AsI$_3$. Even if their presence in the residue can be confirmed, as we have mentioned before, it still can not give much information on what kind of species are actually desorbing from the surface during the reaction. Therefore, we can only conclude that GaI$_3$ and AsI$_3$ are one of the major ‘final’ products of the GaAs/I$_2$ reaction.
Table 3.3 Natural abundance of isotopes

<table>
<thead>
<tr>
<th></th>
<th>Natural Abundance (%)</th>
<th>Relative Atomic Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga(^{69})</td>
<td>60.4</td>
<td>68.9257</td>
</tr>
<tr>
<td>Ga(^{71})</td>
<td>39.6</td>
<td>70.9249</td>
</tr>
<tr>
<td>As(^{75})</td>
<td>100</td>
<td>74.9216</td>
</tr>
<tr>
<td>I(^{127})</td>
<td>100</td>
<td>126.9004</td>
</tr>
</tbody>
</table>
Figure 3.16 Mass spectrum of the reaction product residue.
**Table 3.4** Assignment of peaks in low resolution MS spectrum

<table>
<thead>
<tr>
<th>Mass Unit Measured by Low Resolution MS</th>
<th>Mass Unit Measured by High Resolution MS</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>456</td>
<td>455.6362</td>
<td>AsI$_3^+$</td>
</tr>
<tr>
<td>452</td>
<td>451.6887</td>
<td>Ga$^{69}$I$_3^+$</td>
</tr>
<tr>
<td>450</td>
<td>449.6404</td>
<td>Ga$^{71}$I$_3^+$</td>
</tr>
<tr>
<td>329</td>
<td>328.7287</td>
<td>AsI$_2^+$</td>
</tr>
<tr>
<td>325</td>
<td>324.7349</td>
<td>Ga$^{69}$I$_2^+$</td>
</tr>
<tr>
<td>323</td>
<td>322.7344</td>
<td>Ga$^{71}$I$_2^+$</td>
</tr>
<tr>
<td>254</td>
<td>253.8084</td>
<td>I$_2^+$</td>
</tr>
<tr>
<td>202</td>
<td>201.8238</td>
<td>AsI$^+$</td>
</tr>
<tr>
<td>128</td>
<td>127.9119</td>
<td>HI$^+$</td>
</tr>
<tr>
<td>127</td>
<td>126.9042</td>
<td>I$^+$</td>
</tr>
<tr>
<td>75</td>
<td>74.9222</td>
<td>As$^+$</td>
</tr>
</tbody>
</table>
4.1 Cl₂ Etching of GaAs

The GaAs/Cl₂ reaction was previously studied by Ha\textsuperscript{27}. Saturation of etch rate was observed at pressures above 15 Torr. It was explained by as the "saturation of sites" for reaction on the surface. However, recent studies of the etching of silicon by Cl₂ and Br₂ found that the etch rates were half order with respect to the partial pressure of the halogen gas instead of reaching a plateau.

Considering that, in Ha's study, the pressure of the etchant gas was changed by adjusting the throttle valve (to change the pumping speed), this meant that the total gas flow through the system was unchanged as the pressure was increased. Therefore, the residence time of the gas over the sample would increase with increasing pressure. Under these circumstances, the reaction became increasingly diffusion controlled at high pressures because the products were not swept away as quickly as they might be if the pressure were increased by increasing the total gas flow rather than by throttling the flow.

With this in mind, the same GaAs/Cl₂ reaction was reinvestigated with the pressure being regulated only by adjusting the gas flow into the system. This ensured that the residence time of the gas over the etching sample was relatively constant at all pressures.

Instead of reaching a plateau, it was found that as in silicon etching studies, the ER displayed a simple half order dependence on the Cl₂ pressure. It is quite probable that the small but significant difference between the data obtained in this work and the earlier study can be attributed to the difference in the two flow control techniques. The experimental results suggest that the reaction proceed through a reversible dissociation mechanism, proposed later in the Si etching with Cl₂\textsuperscript{21} and Br₂\textsuperscript{20}, rather than the "Surface Site Saturation" mechanism proposed by Ha\textsuperscript{27}. The mechanism which we propose to explain this change in order from
first to half involves the reversible dissociative adsorption of the halogen molecule on the semiconductor surface.

4.1.1 The Reversible Dissociative Adsorption (RDA) Mechanism

The half order dependence of the ER on \( \text{Cl}_2 \) pressure and the negative y-intercepts of the ER vs \( P_{\text{Cl}_2} \) plot in Figure 3.3 mentioned in section 3.1.1 can be explained by the "reversible dissociative adsorption" mechanism proposed earlier\(^\text{20,21}\). In this mechanism, the \( \text{Cl}_2 \) molecule first dissociatively adsorbs on the already halogenated GaAs surface to form two chemisorbed chlorine atoms (\( \text{Cl}(\text{ads}) \)) as represented by equations (4.1, -4.1). In the second step (equation (4.2)), this \( \text{Cl}(\text{ads}) \) species reacts with the surface to form reaction products or some intermediates which yield reaction products in a subsequent non rate-controlling process.

\[
\begin{align*}
\text{Cl}_2(g) & \xrightleftharpoons[k_1]{k_2} 2 \text{Cl}(\text{ads}) \\
\text{Cl}(\text{ads}) & \xrightarrow[k_2]{k_2} \text{Product}
\end{align*}
\]  

(4.1, -4.1)

(4.2)

The rate law for such a reaction mechanism has been derived previously\(^\text{20}\). Once a steady state is established, the rate law takes the form:

\[
\text{ER} = \frac{k_2^2}{4k_1} \sqrt{1 + \frac{16k_1k_2}{k_2^2} P_{\text{Cl}_2}} - \frac{k_2^2}{4k_1}
\]

(4.3)

At low pressure, equation (4.3) reduces to:

\[
\text{ER} = 2k_1 P_{\text{Cl}_2}
\]

(4.4)

i.e. reaction (4.1) is rate controlling and so the etch rate exhibits a first order dependence on \( P_{\text{Cl}_2} \). On the other hand, at high pressures, equation (4.3) reduces to:
\[ ER = k_2 \sqrt{\frac{k_2}{k_1}} \sqrt{P_{\text{Cl}_2}} - \frac{k_2^2}{4k_1} \]  

(4.5)

e.g. the reaction approaches half order kinetics with respect to \( \text{Cl}_2 \) because reaction (4.2) now becomes rate controlling and an equilibrium concentration of \( \text{Cl}_{(\text{ads})} \) is maintained by reactions (4.1-4.1). We will refer to \( (k_2 \sqrt{\frac{k_1}{k_1}}) \) as the "composite half order rate constant" and abbreviate it as \( k_{1/2} \).

According to equation (4.5), in the high pressure regime, the plot of \( ER \) vs \( \sqrt{P_{\text{Cl}_2}} \) will result in a straight line with a negative y-intercept. This is consistent with the data shown in Figure 3.3 where the slopes and intercepts are equal to \( (k_2 \sqrt{\frac{k_1}{k_1}}) \) and \( (-\frac{k_2^2}{4k_1}) \) respectively and the first order rate constant \( k_1 \) can subsequently be determined from the relationship:

\[
k_1 = \frac{-\text{slope}^2}{4 \times \text{y-intercept}}
\]

(4.6)

The rate constants calculated in this way are presented in Table 4.1. Assuming that both \( k_1 \) and \( k_{1/2} \) exhibit Arrhenius temperature dependence as in equation (3.3), \( E_a \) and \( A \) for \( k_1 \) and \( k_{1/2} \) can be determined by plotting \( \ln(k) \) vs \( \frac{1}{T} \). Such plots are shown in Figure 4.1, and the following expressions for \( k_1 \) and \( k_{1/2} \) are obtained.

\[
k_1 = 10^{10.4 \pm 2.3} \mu \text{m} \text{ min}^{-1} \text{ Torr}^{-1} \ e^{-(76 \pm 16 \text{ kJ mol}^{-1}/\text{RT})}
\]

(4.7)

\[
k_{1/2} = 10^{13.6 \pm 2.6} \mu \text{m} \text{ min}^{-1} \text{ Torr}^{-1/2} \ e^{-(100 \pm 19 \text{ kJ mol}^{-1}/\text{RT})}
\]

(4.8)
Table 4.1  Experimental values of the first and the half order rate constants for the GaAs/Cl\textsubscript{2} reaction.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(k_1) ((\mu\text{m min}^{-1}\text{ Torr}^{-1}))</th>
<th>(k_{1/2}) ((\mu\text{m min}^{-1}\text{ Torr}^{-1/2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.40</td>
<td>0.21</td>
</tr>
<tr>
<td>100</td>
<td>0.60</td>
<td>0.39</td>
</tr>
<tr>
<td>110</td>
<td>1.47</td>
<td>1.20</td>
</tr>
</tbody>
</table>
Figure 4.1 Arrhenius plot for $k_1$ (○) and $k_{1/2}$ (●).
4.1.2 The Gas Phase Dissociation Mechanism

Although the above mechanism can provide an explanation for the observed half order kinetics, alternative mechanisms have been considered\(^\text{20}\). In these mechanisms, the Cl\(_2\) molecule is thermally dissociated into gas phase Cl atoms either through collisions with other molecules in the gas phase or by collisions with the walls of the reaction vessel. Provided the gas phase atom concentration is in equilibrium with molecular chlorine, this mechanism is equally capable of explaining the change from first to half order kinetics. However, using thermodynamic data for this equilibrium at 100°C\(^\text{28}\), the degree of dissociation of Cl\(_2\) is found to be only 7.4x10\(^{-12}\)%.

Under a Cl\(_2\) pressure of 2.0 Torr, if an equilibrium concentration of atoms is established, the partial pressure of Cl atom would be 2.96x10\(^{-13}\) Torr. Assuming that all the Cl atoms react with GaAs with zero activation energy, the predicted etch rate would be 1.73x10\(^{-9}\) µm min\(^{-1}\). This is only 4.33x10\(^{-7}\)% of the observed etch rate (0.40 µm min\(^{-1}\)). The above analysis shows that the thermal dissociation of Cl\(_2\) in the gas phase is insufficient to explain the observed kinetics, even if the dissociation can be made to occur rapidly enough in the short heated region immediately before the gas strikes the GaAs surface.

4.1.3 Potential Energy Curve for RDA Mechanism

For the RDA mechanism, the activation energy for \(k_1\) (i.e. for the dissociative adsorption) is 76 kJ mole\(^{-1}\). This is 166.6 kJ mole\(^{-1}\) below the bond dissociative energy of Cl\(_2\). Although it represents a large reduction in the dissociation energy, the value is not unreasonable. The potential energy curve for the reaction is shown schematically in Figure 4.2. The dissociative adsorption
Figure 4.2 Potential energy curve for the rate determining steps in the etching of gallium arsenide by molecular chlorine gas.
of Cl$_2$(g) on the GaAs surface to form 2 Cl$_{(ads)}$ is represented by movement over the first energy barrier of 76 kJ mole$^{-1}$ on the left hand side of the diagram. Although Cl$_{(ads)}$ must lie below the first transition state, its position in the figure is undetermined and it is therefore represented by a dotted line on the diagram. This Cl$_{(ads)}$ species then reacts to yield reaction products through a second transition state. Although the activation energy for the second step is also undetermined, the energy of the second transition state relative to the initial reactants is 100 kJ mol$^{-1}$ (i.e. the activation energy obtained for $k_{1/2}$).

As in the case of the reaction of silicon with halogen molecules, the pre-exponential factor belonging to $k_1$ is several orders of magnitude larger than collision frequency. The collision frequency for Cl$_2$ molecules on a surface under our experimental conditions is 2.16x10$^{24}$ collision m$^{-2}$ s$^{-1}$ Torr$^{-1}$ which, expressed in the same units as the etch rate, equals 5860 μm min$^{-1}$ Torr$^{-1}$. However, the experimental pre-exponential factor is 10$^{10.4}$, i.e. 2.51x10$^{10}$ μm min$^{-1}$ Torr$^{-1}$, which is more than 6 orders of magnitude larger than collision frequency. Such "large" pre-exponential factors have also been observed in silicon etching by Br$_2$ and Cl$_2^{20,21}$. They have been elucidated in the earlier work by proposing the occurrence of a reversible physisorption step (with a zero or very small activation energy) prior to the dissociative chemisorption. The experimental rate constant ($k_1$) then represents a composite rate constant which can have a pre-exponential factor not directly related to the Cl$_2$ collision frequency. Such a reaction sequence is illustrated in equation (4.9),

$$\text{Cl}_2(g) \rightleftharpoons \text{Cl}_2(ads) \rightleftharpoons 2 \text{Cl}(ads) \quad (4.9)$$
4.1.4 Etch Product Analysis

There have been several studies for the reaction products of the GaAs/Cl\(_2\) system. However, there is little agreement among them and it still remains controversial.

McNevin\(^{29}\) reported a theoretical studies of the GaAs/Cl\(_2\) system and the thermodynamic calculation predicted that the products should be GaCl\(_3\) and AsCl\(_3\). However, an investigation of the mechanism for ion-assisted etching of GaAs in Cl\(_2\) using a modulated Ar\(^+\) ion beam by McNevin and Becker\(^{30}\) found that GaCl, GaCl\(_2\) and AsCl\(_3\) were the major products in the temperature range from 300 to 500 K. On the other hand, Balooch and Olander\(^{31}\) concluded from their study of the GaAs/Cl\(_2\) system with and without simultaneous bombardment by energetic ions that GaCl\(_3\) and AsCl\(_3\) were the main products at temperatures up to 550 K but only monochlorides were observed as major products at above 550 K. Recently, Hou \textit{et al.}\(^{32}\) performed a molecular beam study of the Cl\(_2\) + GaAs reaction at surface temperatures in the range 300-500 K. They observed that GaCl\(_3\) and AsCl\(_3\) were the major products below 400 K. At higher temperatures, GaCl\(_3\) and As\(_4\) were obtained as the main products.

Although the results of the above studies are divergent, there is one thing in common among them. Most of them found GaCl\(_3\) and AsCl\(_3\) to be the main products at our working temperature (i.e. ~373 K). The available evidence indicates that the major products of the GaAs/Cl\(_2\) thermal reaction are probably GaCl\(_3\) and AsCl\(_3\).

4.2 I\(_2\) Etching of GaAs

Since the etch rate data for the I\(_2\) reaction are qualitatively similar to those obtained for the Cl\(_2\) reaction, the data are therefore analyzed with the assumption that it occurs by the same mechanism.
4.2.1 The Reversible Dissociative Adsorption (RDA) Mechanism

By analogy with the RDA mechanism for the Cl\textsubscript{2} reaction described in section 4.1.1, we can write the RDA mechanism as it would apply to the I\textsubscript{2} reaction.

\[
\begin{align*}
\text{I}_2(\text{g}) & \underset{k_3}{\overset{k_4}{\rightleftharpoons}} 2\text{I(ads)} \\
\text{I(ads)} & \rightarrow \text{Product}
\end{align*}
\]

where all the symbols carry the same meanings as described in section 4.1.1. The rate law is given by:

\[
ER = \frac{k_4^2}{4k_3} \sqrt{1 + \frac{16k_3k_4}{k_4^2} P_{I_2}} - \frac{k_4^2}{4k_3}
\]

in the low pressure limit,

\[
ER = 2k_3 P_{I_2}
\]

and at high pressure, equation (4.12) becomes,

\[
ER = k_4 \sqrt{\frac{k_3}{k_4} P_{I_2}} - \frac{k_4^2}{4k_3}
\]

Again, we define \( k_3 \) as the first order rate constant and \( k_4 \sqrt{\frac{k_3}{k_4}} = k_{1/2}^* \) as the half order rate constant.

Since the data points, shown in Figure 3.10, fall into the intermediate range between purely first and purely half order, they cannot be simply analyzed by either equation (4.13) or equation (4.14). Therefore the full expression (4.12) was used as an empirical equation and curve fitting methods were employed to find the optimal values of \( k_3, k_4 \) which give the best fit to the data points. On first sight, equation (4.12) seems to have three independent variables i.e. \( k_3, \)
k_3 and k_4. However through substituting k_{1/2}^* into equation (4.12), the number of variables in the equation can be reduced to two and it thus becomes:

\[
ER = \frac{(k_{1/2}^*)^2}{4k_3} \sqrt{1+16 \left(\frac{k_3}{k_{1/2}^*}\right)^2 P_{I_2}} - \frac{(k_{1/2}^*)^2}{4k_3}
\]  
\[ (4.15) \]

The "best fitting" lines are shown as solid lines in Figure 3.10 and the optimal values of k_3 and k_{1/2}^* obtained are listed as a function of temperature in Table 4.2.

Arrhenius plots for the first and the half order rate constants of the reaction are shown in Figure 4.3. A least squares linear regression on those points yields the following results.

\[
k_3 = 10^{4.7\pm0.2} \text{ \mu m min}^{-1} \text{ Torr}^{-1} e^{-\left(55\pm2 \text{ kJ mol}^{-1}/\text{RT}\right)}
\]  
\[ (4.16) \]

\[
k_{1/2}^* = 10^{6.5\pm0.9} \text{ \mu m min}^{-1} \text{ Torr}^{-1/2} e^{-\left(69\pm10 \text{ kJ mol}^{-1}/\text{RT}\right)}
\]  
\[ (4.17) \]

4.2.2 The Gas Phase Dissociation Mechanism

Since the dissociation energy of I_2 is much lower than it is for Cl_2, we have to consider more carefully the possibility that gas phase dissociation of I_2 can account for the fractional order of this reaction. For this reason, two alternative mechanisms, one involving I_2 dissociation in the gas phase and the other on the reactor walls, will be considered.

It is known that I_2 molecules can be thermally dissociated in a bimolecular collision to give two gas phase I atoms. This reaction is reversible and is represented by,

\[
I_2(g) + I_2(g) \xrightleftharpoons[k_5]{k_5} 2 I(g) + I_2(g)
\]  
\[ (+4.18, -4.18) \]
Table 4.2  Experimental values of the first and the half rate constants obtained at various temperatures for the GaAs/I_2 reaction.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>k_3 (μm min^{-1} Torr^{-1})</th>
<th>k_{1/2}^* (μm min^{-1} Torr^{-1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>0.957</td>
<td>2.58</td>
</tr>
<tr>
<td>310</td>
<td>0.606</td>
<td>2.10</td>
</tr>
<tr>
<td>290</td>
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<td>1.03</td>
</tr>
<tr>
<td>270</td>
<td>0.283</td>
<td>0.602</td>
</tr>
</tbody>
</table>
Figure 4.3  Arrhenius plot for the rate constants $k_3$ (O) and $k_{1/2}^*$ (●).
We will further assume that the next step is the reaction of the I atom with GaAs to form products:

\[ \text{I}_{(\text{ads})} \xrightarrow{k_6} \text{Product} \]  

(4.19)

Literature values of the equilibrium constant \( K_p (=k_5/k_5) \) for the thermal dissociation of \( I_2 \) and of the recombination rate constant for I atoms \( (k_{-5}) \) at 300 °C are 7.87x10^{-9} \text{ mol m}^{-3} \text{ and } 5.1300 \text{ m}^{-6} \text{ mol}^{-2} \text{ s}^{-1} \) respectively. From these values, a value of 4.04x10^{-4} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} for the rate constant \( k_5 \) is then obtained. Under an \( I_2 \) partial pressure of 0.50 Torr, the rate of I atom generation is 1.58x10^{-7} \text{ mol m}^{-3} \text{ s}^{-1}. Since the volume of the system is 2.27x10^{-4} \text{ m}^3, under a volume flow of 7.565x10^{-4} \text{ m}^3 \text{ s}^{-1}, the residence time will be about 0.3 s. The concentration of I atoms when it reach the sample holder will equal 4.74x10^{-8} \text{ mol m}^{-3} which corresponds to 1.69x10^{-6} \text{ Torr} \text{ in pressure units. Assuming that all the I atoms react with GaAs with a 1:1 stoichiometry at collision frequency, the predicted ER would be 0.0042 \text{ µm min}^{-1}. This upper limit is only 1% of the observed ER which is about 0.40 \text{ µm min}^{-1}. Keeping in mind that (a) we have ignored the recombination of I atoms in the gas phase which must be occurring if less than first order kinetics is to be observed, (b) it is unlikely that \( k_6 \) has zero activation energy and (c) a period of about 33 s is required for an equilibrium concentration of \( I_2 \) to be established, therefore the gas phase \( I_2 \) dissociation mechanism is too slow to explain the experimental result.

However, dissociation on the walls of the reactor can be much more rapid. Such a mechanism can be written as:

\[ \text{I}_2(\text{g}) + \text{wall} \xleftrightarrow{k_7} 2 \text{I}_2(\text{g}) \xrightarrow{k_7} \text{Product} \]  

\[ +4.20, -4.20 \]  

(4.20)

\[ \text{I}_{(\text{ads})} \xrightarrow{k_8} \text{Product} \]  

(4.21)
Step (4.20) represents the dissociation of $I_2$ on the hot walls of the reactor to give gas phase $I$ atoms. Assuming that the dissociation reaction is fast enough to bring about the equilibrium concentration of $I$ atoms, then the partial pressure of $I$ atom would be $3.75 \times 10^{-4}$ Torr when the pressure of $I_2$ and temperature are $0.50$ Torr and $300^\circ$C respectively. If all the $I$ atoms produced react with GaAs with zero activation energy, then the predicted ER would be $0.936$ $\mu$m $\text{min}^{-1}$. In comparison with the observed ER (i.e. $0.40$ $\mu$m $\text{min}^{-1}$), this wall reaction mechanism is fast enough to explain the observed kinetics. However, the activation energy of $k_7$ which governs the dissociation must be at least equal to the bond energy of $I_2$ molecule (i.e. $152.53$ kJ mole$^{-1}$), the experimental value of this activation energy is only $55$ kJ mole$^{-1}$. Since the experimental value of $E_a$ for $k_7$ is only $\frac{1}{3}$ of the bond dissociation energy, the discrepancy is beyond experimental error, and therefore we reject this wall catalyzed mechanism for the GaAs/$I_2$ etching reaction.

4.2.3 Potential Energy Curve for the RDA mechanism

From equation (4.16), the activation energy of $k_3$ for dissociative adsorption is $55$ kJ mole$^{-1}$. This is $98$ kJ mole$^{-1}$ below the bond dissociative energy of $I_2$ which is $152.53$ kJ mole$^{-1}$. Since the bonds being formed may be stronger than those being broken, this value is not unreasonable. If this mechanism is valid, a potential energy curve for the reaction can be sketched as in Figure 4.4. The reactants are arbitrarily set at zero on the energy scale. The energy barrier for the dissociative adsorption of $I_2(g)$ on the surface is described by the peak on the left hand side in the graph. The gaseous $I_2$ at zero potential interacts with the GaAs surface to give $I_{(ads)}$ through a transition state that lies $55$ kJ mole$^{-1}$ above the reactants. The potential energy of $I_{(ads)}$ relative to the
Figure 4.4 Potential energy curve for the reversible dissociative adsorption mechanism.
reactants is undetermined, although it must lie below the transition state. It is therefore represented by a dotted line in the graph. The second reaction step starts with $I_{(ads)}$ and proceeds through another transition state to form the products. Although the $E_a$ for $k_4$ is also undetermined, the energy of the second transition state relative to $I_{2(g)}$ is given by the $E_a$ of the half order rate constant i.e. 69 kJ mole$^{-1}$.

As in the GaAs/Cl$_2$ reaction mentioned in section 4.1.3, the only apparent problem associated with the rate constants in RDA mechanism is the pre-exponential factor of $k_3$. The collision frequency of I$_2$ molecule on a surface under our experimental condition is calculated to be only $9.21 \times 10^{23}$ collision m$^{-2}$ s$^{-1}$ Torr$^{-1}$ which equals 2500 μm min$^{-1}$ Torr$^{-1}$ after conversion to etch rate units. However, the pre-exponential factor for $k_3$ is found to be $10^{4.69}$ i.e 50,000 μm min$^{-1}$Torr$^{-1}$, which is 20 times the collision frequency. Again it can be explained by considering that the reversible dissociative adsorption step is not an elementary steps but rather composed of at least 2 elementary steps with the first one being the physisorption of gaseous I$_2$ on the GaAs surface followed by dissociative chemisorption as described in equation 4.22.

$$I_2 \leftrightarrow I_{2(ads)} \leftrightarrow 2I_{(ads)} \quad (4.22)$$

The activation energy for the half order rate constant in the RDA mechanism (i.e. 69 kJ mole$^{-1}$) is close to the heat of vaporization of GaI$_3$ which equals 64.43 kJ mole$^{-1}$ 34. This might suggest that the vaporization of this species from the surface could be the rate determining step of the reaction. However, the calculated rate of free vaporization$^{35}$ of GaI$_3$ under the experimental conditions is $6 \times 10^5$ μm min$^{-1}$. This value exceeds the observed etch rate, which is only 1.0 μm min$^{-1}$, by six orders of magnitude. Although some studies of GaAs/Cl$_2$ considered the desorption of GaCl$_3$ from the reacting surface to be the rate
controlling step, we reject this possibility in the $I_2$ etching reaction due to the great discrepancy between the predicted and observed ER.

4.2.4 The Surface Site Saturation (SSS) Mechanism

An alternative explanation for the deviation of the reaction kinetics from first order kinetics at high pressures lies in the fact that there must be a limited number of reaction sites on the semiconductor surface. If a significant fraction of these sites are covered by physisorbed halogen molecules, then a non linear dependence of the etch rate on the pressure of $I_2$ could result. A mechanism based on such an assumption was used by Repinskii and coworkers to explain their observations on the etching of Si and Ge by $Br_2^{18,37}$. If we assume that the adsorption step is reversible then the complete mechanism takes the form:

$$I_{2(g)} + S_f \xrightleftharpoons{k_9}{k_9} I_{2(ads)} \quad (4.23)$$

$$I_{2(ads)} \xrightarrow{k_{10}} \text{Product} + S_f \quad (4.24)$$

In the proposed mechanism the gaseous $I_2$ molecule first reversibly physisorbs on a GaAs surface site ($S_f$) to give the $I_{2(ads)}$ species as depicted in equation (4.23). This adsorbed species can then react with the surface in the reaction represented by equation (4.24) to form gaseous products which free the surface site. Assuming that the physisorption steps ($k_9, k_9$) are fast compared with the surface reaction step ($k_{10}$), an equilibrium concentration of $I_{2(ads)}$ is maintained and the rate law governing the reaction is:

$$ER = \frac{K P_{I_2}}{1 + K P_{I_2} k_{10}} \quad \text{where } K = \frac{k_9}{k_9} \quad (4.25)$$

Taking the reciprocal of both sides:

$$\frac{1}{ER} = \frac{1}{k_{10}K P} + \frac{1}{k_{10}} \quad (4.26)$$
i.e. a plot of $1/ER$ vs $1/P_{I_2}$ will be a straight line with the slope and intercept equal to $1/k_{10}K$ and $1/k_{10}$ respectively. Such a plot is presented in Figure 4.5 for data obtained at four temperatures. The solid lines are "weighted least squares straight lines" through the points. The fit is not unreasonable, and therefore the values of $K$ and $k_{10}$ obtained from these lines are listed in Table 4.3, and presented in Figure 4.6 as an Arrhenius plot. The Arrhenius plots are reasonably linear and the data can be represented by the following two equations:

$$K = 10^{-4.8 \pm 0.7} \text{ Torr}^{-1} e^{(49 \pm 7 \text{ kJ mol}^{-1}/RT)} \quad (4.27)$$

$$k_{10} = 10^{0.2 \pm 0.4} \mu \text{m min}^{-1} e^{-(96 \pm 5 \text{ kJ mol}^{-1}/RT)} \quad (4.28)$$

Equation (4.27) is consistent with the SSS mechanism which requires the physisorption step to be exothermic. The heat of adsorption is determined to be -49 kJ mole$^{-1}$. The value of -49 kJ mol$^{-1}$ is larger than the typical value of the heat of physisorption (i.e. -25 kJ mole$^{-1}$), however, it is not totally unreasonable in view of the large polarizability of $I_2$ molecule.

For the rate constant $k_{10}$, the activation energy and the pre-exponential factors are 96 kJ mol$^{-1}$ and $10^{9.2} \mu \text{m min}^{-1}$ (or $8.19 \times 10^{10} \text{ s}^{-1}$) respectively. The pre-exponential factor does not depart far from the calculated value for a first order surface reactions based on absolute rate theory (i.e. $10^{13} \text{ s}^{-1}$) $^{15}$. 

### 4.2.5 Potential Energy Curve for the SSS mechanism

The potential energy curve depicting this mechanism is shown in Figure 4.7. The $I_2(g)$ molecule of zero potential energy reversibly adsorbs on the surface to form a physisorbed species $I_2(ads)$. The heat of adsorption is -49 kJ mol$^{-1}$. The $I_2(ads)$ species then pass through an energy barrier of 96 kJ mol$^{-1}$ to form reaction products. It follows that when the adsorbed molecules are present in their equilibrium concentrations, the activation energy of the overall forward reaction will be 96 - 49 or 47 kJ mol$^{-1}$. 

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Figure 4.5 A plot of the reciprocal of the GaAs(100) etch rate against the reciprocal of the $I_2$ pressure at 270 (□), 290 (◊), 310 (Δ) and 330 °C (◯).
Table 4.3  Experimental values of the K and $k_{10}$ obtained at various temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>K (Torr⁻¹)</th>
<th>$k_{10}$ (µm min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>0.282</td>
<td>6.46</td>
</tr>
<tr>
<td>310</td>
<td>0.331</td>
<td>3.66</td>
</tr>
<tr>
<td>290</td>
<td>0.591</td>
<td>1.56</td>
</tr>
<tr>
<td>270</td>
<td>0.770</td>
<td>0.815</td>
</tr>
</tbody>
</table>
Figure 4.6 Arrhenius plot for $K$ (○) and $k_{10}$ (●).
Figure 4.7 Potential energy curve for the reaction if it proceeds through the surface site saturation mechanism.
4.3 Comparison of I₂ and Cl₂ Etching Results

In order to make any comparison between the Cl₂ and I₂ reactions with GaAs, we will have to assume that both of these reactions proceed through the RDA mechanism.

Although the Cl₂ and I₂ reactions were studied in two different temperature ranges, it is not difficult to show by extrapolation that at 100°C the Cl₂ reaction is 10000 faster than the I₂ reaction at the same pressure range. It is quite remarkable that this difference occurs despite the fact that the activation energies for the Cl₂ reaction are slightly larger than those for the I₂ reaction. This increase is entirely due to the much larger pre-exponential factors for the Cl₂ reaction.

Comparing the activation energies of the first order rate constants for the Cl₂ (k₁) and I₂ (k₃) reactions, k₁ has an \( E_a \) of 76±16 kJ mole\(^{-1}\) which is almost within experimental error of k₃ (i.e. 55±2 kJ mole\(^{-1}\)). On the other hand, the pre-exponential factor of k₁ is more than 5 orders of magnitude greater than that of k₃. If the first step in the proposed mechanism is really composed of a physisorption step followed by the dissociation of the halogen molecule on the surface, both the pre-exponential factors of k₁ and k₃ contain the collision frequencies of the etchant gas molecules on the surface to be etched. The collision frequency (\( Z_w \)) is given by the following expression:

\[
Z_w = \frac{p}{\sqrt{2\pi mkT}} \tag{5.1}
\]

where \( p \) is the gas pressure, \( m \) is the mass of the gas molecule, \( k \) is the Boltzmann constant and \( T \) is the temperature in Kelvin. Since I₂ has a larger molecular weight than Cl₂, under experimental conditions, the collision frequency of Cl₂ is 2.5 times that of I₂. Therefore, k₁ for Cl₂ reaction is expected to have larger pre-exponential factor in comparison with k₃ for I₂ and which is consistent with
our experimental results. However the difference in collision frequencies is not sufficient to explain the 5 orders of magnitude difference which is observed.

A second source of this difference in pre-exponential factors between $k_1$ and $k_3$ could be a steric factor. Since the size of the $I_2$ molecule is much larger than $Cl_2$, it might experience a larger steric hindrance from other surface $I$ species during the physisorption step. This would result in a somewhat smaller pre-exponential factor in $k_3$ than in $k_1$ but it is difficult to estimate how significant such a factor would be.

Similarly, it is also possible to compare the half order rate constants $k_{1/2}$ and $k_{1/2}^*$ for the $Cl_2$ and $I_2$ reactions respectively. The activation energy for $k_{1/2}$ is $100\pm19$ kJ mole$^{-1}$ whereas that for $k_{1/2}^*$ is $69\pm10$ kJ mole$^{-1}$. The activation energy of $k_{1/2}$ is slightly larger than that of $k_{1/2}^*$. However, as in the case of the comparison between $k_1$ and $k_3$, the pre-exponential factor of $k_{1/2}$ is considerably larger than that of $k_{1/2}^*$. Unfortunately there is no obvious explanation for this big difference but it might also be attributed to the discrepancies in steric factor between $Cl_2$ and $I_2$ in the reactions.
Chapter 5: Summary and Conclusion

5.1 Cl₂ Etching of GaAs

The reaction of molecular chlorine with the (100) face of a gallium arsenide crystal has been reinvestigated at pressures of Cl₂ between 0.10 and 9.0 Torr and in the temperature range from 90 to 110°C. Instead of reaching a plateau in the high pressure region as reported in an earlier study, the etch rate was found to be half order with respect to Cl₂ at high pressures. The similarity of these results to those recently obtained for the reaction of molecular chlorine and bromine with silicon points to a mechanism in which the gaseous halogen molecule is first physisorbed on the semiconductor surface and then dissociates into chemisorbed atoms. The data indicate that both steps occur reversibly at higher pressures, where the composite half order rate constant can be represented by the Arrhenius equation:

\[
\frac{k_{1/2}}{P_{\text{min}}} = 10^{13.6\pm2.6} \mu\text{m min}^{-1} \text{Torr}^{-1/2} \text{ e}^{-\left(100\pm19 \text{ kJ mol}^{-1}/\text{RT}\right)}
\]

At low pressures the first order rate constant is given by the equation:

\[
k_1 = 10^{10.4\pm2.3} \mu\text{m min}^{-1} \text{Torr}^{-1} \text{ e}^{-\left(76\pm16 \text{ kJ mol}^{-1}/\text{RT}\right)}
\]

The etching profile is crystallographic (orientation dependent) and a relatively flat etched face, which is comparable to the unetched one, is obtained.

5.2 I₂ Etching of GaAs

For the GaAs(100)/I₂ reaction, the chemical etching has been studied at I₂ pressures between 0.10 and 1.25 Torr and in the temperature range from 270 to 330°C. GaAs was found to be etched continuously at rates between 0.05 and 1.70 \(\mu\text{m min}^{-1}\) under these conditions. Although the etch rate appeared to be first order with respect to I₂ at pressures below 0.3 Torr, the order decreased at higher pressures. The results have been analyzed in terms of two mechanisms.
which have been proposed for the etching of semiconductors by halogen molecules. These are the "reversible dissociative adsorption" (RDA) mechanism and the "surface site saturation" (SSS) mechanism. The RDA mechanism uses the reversibility of the dissociative adsorption to explain the non linear pressure dependence. The adsorption steps occur irreversibly at low pressure giving rise to first order kinetics with the first order rate constant ($k_3$) which can be expressed in the form of the following Arrhenius equation:

$$k_3 = 10^{4.7\pm0.2} \text{ µm min}^{-1} \text{ Torr}^{-1} \ e^{- (55\pm2 \text{ kJ mol}^{-1}/\text{RT})}$$

At higher pressures, the dependence on $I_2$ changes to half order and the composite half order rate constant ($k_{1/2}^*$) can be represented by the equation:

$$k_{1/2}^* = 10^{6.5\pm0.9} \text{ µm min}^{-1} \text{ Torr}^{-1/2} \ e^{- (69\pm10 \text{ kJ mol}^{-1}/\text{RT})}$$

On the other hand, the SSS mechanism involves the reversible physisorption of $I_2$ on the GaAs surface (governed by an equilibrium constant $K$) followed by a rate controlling reaction of this physisorbed species to form the volatile products (governed by the rate constant $k_{10}$). The calculated values for these two parameters are:

$$K = 10^{-4.8\pm0.7} \text{ Torr}^{-1} \ e^{- (49\pm7 \text{ kJ mol}^{-1}/\text{RT})}$$

$$k_{10} = 10^{9.2\pm0.4} \text{ µm min}^{-1} \ e^{- (96\pm5 \text{ kJ mol}^{-1}/\text{RT})}$$

Unfortunately our data do not allow us to choose between these two mechanisms. The etching of GaAs by $I_2$ was found to be isotropic and a very rough surface resulted after etching. Analysis of the reaction product residue collected in the cold trap by mass spectrometry showed that GaI$_3$ and AsI$_3$ were the products of the reaction.
REFERENCES