THE CLEANING OF InP SUBSTRATES FOR GROWTH BY MBE

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ABSTRACT

A novel technique of using an in-situ ECR generated H-plasma to produce high quality surfaces on InP substrates, for growth of n- and p-type InP layers by GSMBE, has been investigated. The initial substrate surface quality determines the quality of the subsequently grown layers and therefore, the cleaning procedure is of critical importance. The standard approach entails a thermal desorption of a passivating oxide; however, this technique leaves carbon on the surface and, because oxides may vary in composition depending on the growth conditions, a consistent temperature for desorption may not be obtained. The desorption process is also dependent on the atmosphere in which it is carried out; i.e. whether an overpressure of $P_2$ or $As_2$ is used. Thermal desorption of oxides from InP requires the substrate to reach temperatures higher than normal GSMBE growth temperatures which can lead to substrate decomposition and, for regrowth applications, can alter dopant profiles and layer composition in ternary and quaternary layer growths. As an alternative, H-plasmas in separate vacuum chambers have been used to remove oxides from InP but this typically produces highly defective substrates due to a loss of phosphorus from the substrate. In this work the combination of an in-situ H-plasma with a stabilizing atmosphere of $P_2$ is used for the removal of oxides at temperatures equal to growth temperature and below.
The mechanism involved in the thermal desorption of an oxide is first clarified and this procedure is compared with oxide removal by H-plasma etch in a phosphorus atmosphere. The ECR source can produce various plasma modes which have been thoroughly characterized. The effect of the different plasma conditions on clean InP is determined. These modes have different properties which result in different oxide etch rates. Various modes are compared and the mechanism of oxide removal is documented. As an alternative to oxide growth S-passivation has recently received attention as a surface passivation technique. Application of this surface, with and without H-plasma cleaning, has been investigated. The above treatments and other wet chemical surface treatments are compared to determine the optimal surface cleaning technique.

The results indicate that thermal desorptions are driven by reaction with phosphorus from the substrate and therefore require high temperatures to promote significant phosphorus evaporation from the substrate. A H-plasma etch of the oxide is driven by the presence of atomic H in the plasma and results in the formation of water. Oxide removal rates were determined at various temperatures from 250°C - 490°C. The plasma etch was found to remove carbon contamination from the surface whereas, thermal desorptions do not. Defect levels in the underlying InP are sensitive to the plasma properties but with careful choice of plasma conditions defect states can be minimized. An optimal surface cleaning procedure has been developed which involves a UV-ozone treatment and H-plasma cleaning, resulting in interfaces free of electrically active defects in n-type material and a defect concentration of $8 \times 10^{11}$ cm$^{-2}$.
in p-type material.
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CHAPTER I

INTRODUCTION

It became apparent, in the mid 1970's, that the InGaAsP/InP system was going to be an important contributor to fibre optic communications. As is illustrated in figure I.1 the InGaAsP alloys are direct gap materials and can be formulated to emit light at 1.3 or 1.55 µm which is optimal for transmission in fused silica glass fibres. There are also possible high speed device applications for this family of alloys due to their high electron mobility and high saturation velocity. The alloys can be grown

![Figure I.1. Energy gap vs. Lattice constant[1.1].](image-url)
lattice matched to InP substrates and thereby, multi-layer heterostructures can be produced without material strain due to lattice mismatch.

The realization of multi-layer heterostructures, with Angstrom level dimensions, for opto-electronic applications became possible with the development of sophisticated growth techniques such as molecular beam epitaxy (MBE) and metal-organic chemical vapour deposition. Both growth techniques involve the deposition of the semiconductor material on a crystalline substrate such that the growing material will mimic the structure of the substrate. Thus, for these, or any epitaxial technique, the substrate surface quality will determine the quality of the subsequently grown layers.

In order to produce a high quality surface, substrates are generally protected from contaminants in the atmosphere by a covering of a protective oxide which is removed immediately prior to crystal growth. Due to the importance of the substrate surface to the growth process much effort, in recent years, has been devoted to the study of oxide formation and removal[1.2-18]. A typical procedure would involve the growth of an oxide by either a wet chemical or UV-ozone treatment, then the oxide would be thermally desorbed in the deposition chamber immediately prior to growth. However, there are complications to this procedure particularly for InP. The temperature required to remove oxides from InP depends on the oxide composition and the overpressure present during desorption and, regardless of the oxide composition, the required temperature for thermal desorption is well above the congruent sublimation temperature for InP (365 °C[I.19]). Therefore, an overpressure of either As₂ or P₂ must be maintained to prevent decomposition of the substrate. At
the McMaster MBE facility substrates are mounted In-free, as this eliminates any ex-vacuo heating and is more convenient for post-growth handling; however, this can introduce an additional risk of thermal decomposition since the back surface of the substrate is exposed to the heater filaments. Thus, for semi-insulating substrates, there is a large temperature gradient from the back of the sample to the front and back-side decomposition can occur. This results in a change in the radiative coupling into the substrate and consequently, poor epitaxial growth. Even under the appropriate conditions where thermal desorptions are effective at removing oxides from InP, the process is reported to leave carbon on the substrate surface[I.11, 20, 21].

As an alternative to thermal desorption, hydrogen plasmas have been used to remove oxides at temperatures much lower than thermal desorption temperatures[I.20-32]. Being able to perform a low temperature cleaning of InP has various advantages; as well as reducing the risk of substrate thermal decomposition, low temperature cleaning can improve the production of some modern opto-electronic devices which require ex-vacuo processing prior to the completion of the growth.

When the sample is re-introduced into the deposition chamber the sample surface will contain impurities and have a protective oxide coating that must be removed. The high temperature associated with thermal desorption tends to result in rough surfaces with significant impurity accumulation and may alter the dopant and/or compositional profile of the structure[I.20]. Thus, a surface cleaning at or below growth temperature should be beneficial to the regrowth of sophisticated structures for opto-electronic devices.
Atomic hydrogen will react with carbon and oxygen to form volatile species; however, H-plasmas have not been extensively used with InP because the etch process depletes the surface of phosphorus resulting in an In-rich surface with poor electronic qualities[I.23, 32, 33]. The solution to this problem is, as with thermal desorptions, to simultaneously supply the surface with excess phosphorus. There are two conceivable approaches to accomplish this. One is to adapt a plasma chamber to accommodate a phosphorus source, as was done by Aller et al.[I.20], where they maintained a phosphorus overpressure with an rf-excited H-plasma and had limited success in etching oxides from InP at 310 °C. The other approach is to put a plasma source in-situ on a growth chamber. In this way no transfer is required, that can result in surface contamination, after completion of surface cleaning. An electron cyclotron resonance (ECR) plasma source is ideal for this application. The ECR source is an electrodeless plasma source with remote plasma generation and extraction by a magnetic field. The apparatus used for this investigation has an ECR source built onto the source flange of a gas source MBE (GSMBE) chamber[I.34].

In general, the plasmas generated by ECR sources are not well characterized or understood despite being extensively used for reactive ion etching of semiconductors and for the deposition of insulators. The plasma characteristics exhibit multimodal behaviour and hysteresis[I.35] and small amounts of contaminants can dramatically affect plasma properties[I.36]. Using an ECR source to generate a H-plasma in an MBE chamber is even more complicated because the gas throughput is designed for crystal growth and not to optimize the plasma characteristics, which for the system
used here means gas pressures 1-2 orders of magnitude lower than in a typical ECR plasma process chamber. The sample position is also limited by that required for crystal growth. An ECR process chamber typically has the substrate anywhere from inside the plasma source to 10 - 20 cm downstream. For the MBE chamber, the substrate stage at full forward is ~70 cm downstream from the plasma source.

The present study is focussed on developing an understanding of the operation of an in-situ ECR source for the production of a H-plasma to etch oxides from InP. This technique is an alternate approach to thermally desorbing the oxide and therefore the mechanism of thermal desorptions is investigated for comparison. Since ECR sources are not well understood, particulary in MBE chamber environments, the plasma is thoroughly characterized, including its multimodal behaviour, by a Langmuir probe and optical emission spectroscopy. The magnetic field profile produced by the ECR source is calculated and the effect the magnetic field profile has on determining plasma properties, of stable modes, is explained.

Using Auger electron spectroscopy (AES) and reflection high energy electron diffraction (RHEED), the etching characteristics of the plasma are determined and the important plasma properties for optimal etching are resolved. The effect the plasma has on clean InP is also determined by CV-profiles and secondary ion mass spectrometry (SIMS) analysis of samples where the H-plasma has been applied to growth interrupted interfaces. Also, sulfur-passivated InP surfaces have been demonstrated to be thermally and chemically stable[1,37, 38] and are therefore an alternative to oxide growth for the passivation of the surfaces. In this investigation
different sulfur treatments are compared in terms of surface composition and stability. The applicability of the technique, with and without H-plasma cleaning, as a surface preparation procedure for InP is assessed. In order to determine an optimal surface cleaning procedure, various surface cleaning procedures including; thermal desorption of an oxide, H-plasma etch of an oxide, S-passivation, with and without H-plasma cleaning, and an acid etch of the InP surface are compared in terms of the defect states produced, as measured by CV-profiling and SIMS analysis.

In chapter II, the necessary background is presented on the apparatus used for this study, including the GSBME chamber, the RHEED apparatus, the AES chamber and the ECR source. In the ECR section, particular attention is paid to the effect the magnetic field gradient has on plasma properties as this phenomenon is critical to the understanding of plasma behaviour. Chapter III is a discussion of what is currently known about oxide growth and both thermal desorption of oxides and H-plasma etching. A brief review of thermodynamics is given as a thermodynamic model will be applied to the oxide desorption results. The chapter concludes with a discussion of S-passivation. In chapter IV, the experimental apparatus and the methods used are presented. In Chapter V, the experimental results are presented and discussed. Results of experiments aimed at resolving the mechanism of thermal desorptions are first presented and these results are explained by a thermodynamic model. The H-plasma characterization results are then presented, followed by the measurements of the defects produced in clean InP and the etching experiments. Mechanisms for both thermal desorptions and H-plasma etching are presented. The results of using a sulfur
treatment to passivate the surface of InP are then given and discussed. Various surface treatments are then compared to determine an optimal treatment. Finally, in chapter VII conclusions are given.
CHAPTER II

SYSTEM THEORY

II.1 INTRODUCTION

A schematic of the McMaster MBE system is shown in figure II.1. The MBE chamber is equipped with a RHEED gun and an ECR source. The chamber is vacuum linked to an Auger spectrometer. What follows is a discussion of the principles of each of these sub-systems with emphasis placed on details that are important to the current investigation.

II.2 GAS SOURCE MOLECULAR BEAM EPITAXY

GSMBE is one of several epitaxial techniques that employs vapour transport to carry material from a source to a crystal surface where epitaxial growth will occur. In figure II.2 the various techniques are categorized according to their respective pressure regimes. There exist several texts that review the epitaxial techniques. For a detailed presentation of GSMBE as it applies to the growth of InGaAsP/InP alloys see the review by Panish et al.[II.1] Parker has assembled a more general review of MBE[II.2] and Matthews has edited a text covering various epitaxial techniques[II.3].

The apparatus used in this study is a hydride source MBE. The working
1. Load Lock  
2. Trolley Line  
3. Auger Spectrometer  
4. MBE Chamber  
5. Sample Stage  
6. ECR Source  
   a. Magnets  
   b. Microwave source  
7. Gas Cabinet  
8. Hot Cracker  
9. Effusion Cell  
10. RHEED Gun  
11. RHEED Screen

Figure II.1. Schematic of McMaster MBE system
pressure is such that the mean free path of the source materials is greater than the
growth chamber dimensions. The system contains solid sources of In and Ga and of
the dopant species Si (n-type) and Be (p-type). The solids are contained in effusion
cells such that the flux is controlled by regulation of the source vapour pressure by
precise heating of the cell. The group V species, P\textsubscript{2} and As\textsubscript{2}, are supplied as PH\textsubscript{3} and
AsH\textsubscript{3} to a hot gas cracker where the molecules decompose primarily into their dimeric

\[ MBE \]

\[ \text{GAS SOURCE MBE (GSMBE)} \]

\[ \text{ELEMENTAL SOURCE MBE} \]

\[ (\text{ESMBE}) \]

\[ \text{HYDRIDE SOURCE MBE} \]

\[ (\text{HSMBE}) \]

\[ \text{METAL ORGANIC MBE} \]

\[ (\text{MOMBE}) \]

\[ \text{LOW PRESSURE MOCVD} \]

\[ \text{ATM. PRESSURE MOCVD} \]

\[ \text{ELEMENTS} \]

\[ \text{ELEMENTS (III)} \]

\[ \text{HYDRIDES (V)} \]

\[ R_5 \text{III} \]

\[ H_3V \]

\[ \text{OR} \]

\[ R_3V \]

\[ \text{MOLECULAR FLOW} \]

\[ \text{MFP} \geq D_{s-s} \]

\[ \text{VISCOUS FLOW} \]

**Figure II.2.** Various epitaxial techniques categorized according to
pressure regime. MFP is mean free path and \( D_{s-s} \) is the source-substrate
distance[II.1].

forms (P\textsubscript{2}, As\textsubscript{2}, H\textsubscript{2}). Figure II.3 shows the relative abundances of the various forms of
phosphorus and arsenic coming from a hot tantalum cracker. The important
observation is that over the temperature range of 900 - 1150 °C the dimer species
dominate.

High quality epitaxial crystal growth on a single crystal substrate is only
possible if stoichiometric amounts of the source atoms are incorporated into the growing crystal and bond to the appropriate crystal site.

In the late sixties, Arthur[II.4] observed that, over a certain temperature range where the Ga sticking coefficient is unity, the sticking probability of As is 0 on an As-terminated surface and 1 on a Ga-terminated surface. Therefore, precise control of the source fluxes is not required to grow stoichiometric films. Generally, the growth of III-V semiconductor films employs an overpressure of the group V element since none will stick to the crystal surface unless the group III atom is present, so that the growth rate is easily controlled by the group III flux. With the McMaster system the crystal growth rate is typically 0.75 µm/hr. or ~1 monolayer/s and all the solid sources are individually shuttered, thus abrupt interfaces and precise control of the layer composition are possible.

The growth of InP is somewhat more delicate than the growth of GaAs as the temperature required for stoichiometric growth (~470 °C) is above the congruent
sublimation point (~365 °C[II.5]). Figure II.4 shows the flux ratio of \( P_2/In \) for a (100) InP surface. Thus, the overpressure of the group V element, normally employed during any III-V crystal growth, is not just a luxury allowed by the chemistry of the system but, in the case of InP, is critically important to replenish any phosphorus lost by evaporation from the substrate surface and supply that necessary for crystal growth. With the system used here the \( P_2 \) overpressure supplies more than 10 times the flux lost from the surface at the growth temperature.

With source conditions set appropriately and the substrate temperature within the correct range, crystal growth will proceed by source atoms occupying minimum energy sites on the crystal surface. The quality of the initial surface will determine the quality of the grown layers therefore, pre-growth preparation of this surface is critical. Substrate surface preparation can be considered in two phases. The first is the polishing done by the manufacturer and is beyond the control of the crystal grower. The second is the surface treatment used immediately

![Figure II.4. Temperature dependence of \( P_2/In \) flux ratio][II.1].
prior to growth. This step is the final opportunity to prepare the foundation for the subsequent growth and is critical in the production of high quality material. It is therefore the focus of this investigation.

II.3 REFLECTION HIGH ENERGY ELECTRON DIFFRACTION

RHEED is one of several electron diffraction techniques that is useful in determining the structure of surfaces and thin films. RHEED is a non-destructive technique that allows for in-situ surface diagnostics of a static or growing structure[II.6, 7].

The geometry of the RHEED apparatus, as used in these GSMBE studies, is shown in figure II.1. The RHEED gun contains a hot filament held at high negative potential. Electrons are emitted from the filament and are accelerated toward an anode at ground potential. The beam is then focused and steered by two separate electrostatic lenses. The wavelength of the electrons is determined by the accelerating potential through the relation:

\[
\lambda_{DB} = \frac{12.25}{(V + 10^{-6}V^2)^{1/2}}
\]  

(1)

Where \(\lambda_{DB}\) is the deBroglie wavelength (in Angstroms) and \(V\) is the accelerating potential (in volts). Typical energies range from 20 - 100 keV. For this system a voltage of 27 kV is usually used giving an electron wavelength of 0.075 Å which is
less than the atomic spacing of InP. The beam is incident on the sample surface at glancing angle (−2°) and therefore only penetrates the top few atomic layers making it sensitive to only the surface structure. The beam is diffracted by the sample and strikes a phosphor screen producing an image yielding information on the surface structure and lattice spacing.

A diffraction pattern is produced because the electron wavelength is less than the atomic spacing and therefore the beam is deflected by individual atomic planes. Incident electrons that satisfy the Bragg condition (stated in equation (2)) experience constructive interference with electrons from a neighbouring atomic plane and produce bright streaks on the phosphor screen. The Bragg condition can be expressed as:

\[ \sin \theta = \frac{n\lambda}{2d} \]  

(2)

where θ is the angle of incidence of the beam to the atomic plane, \( \lambda \) is the electron wavelength, \( d \) is the atomic spacing and \( n \) is an integer. A typical pattern from a clean surface of InP or GaAs will appear as a series of bright streaks, known as primary streaks which correspond to the interatomic spacing. Between the primary streaks a series of streaks with narrower spacing, known as intermediates, appear which are a reflection of longer range symmetry. The RHEED pattern from the surface of an InP substrate is shown in figure II.5. RHEED images are labelled according to the size of the surface unit mesh relative to the underlying bulk structure.
Thus, a surface structure denoted by InP(100)-2x4 indicates that the (100) surface of InP has a unit mesh 2 and 4 times the bulk unit cell in mutually perpendicular directions on the surface. The full theory of RHEED patterns is highly complex and not necessary for the present study. The reader is referred to the text edited by Larsen et al.[II.6] for a detailed explanation of RHEED patterns.

As mentioned above, the RHEED measurements give information on the surface structure. If the surface is covered with an amorphous oxide thicker than ~10 Å then no diffraction pattern is observed, only a diffuse glow from scattered electrons appears on the RHEED screen. For thinner oxides the electron beam is able to sample the underlying crystal structure. However, the diffracted electron intensity will be low and thus, only the first order diffraction streak is observed. As the oxide continues to thin the intensity of the first order diffraction streak will increase as more incident electrons experience diffraction. For a very thin oxide the higher order diffraction streaks will appear, these are the primary RHEED streaks. Finally, when the surface is atomically clean the intermediate streaks may appear, depending on the temperature.
Therefore, with careful calibration against oxides of known thickness it is possible to use the in-situ RHEED to obtain information on the thickness of the oxide layer covering the substrate surface.

For this investigation RHEED measurements were employed for two purposes. First, the intensity of the specular streak was measured and correlated with oxide thicknesses, as measured by Auger electron spectroscopy (see below). This allowed for in-situ measurement of the oxide thickness. Second, the RHEED pattern was used to indicate the completion of a desorption procedure, either thermal or by H-plasma, through the appearance of the well known 2x4 surface reconstruction that occurs above 450\(^\circ\)C for a clean P-terminated InP surface\[II.8]\.

II.4 AUGER ELECTRON SPECTROSCOPY

Auger electron spectroscopy (AES) is based on the process of Auger electron emission\[II.9]\. This process is illustrated in figure II.6. An energetic electron beam, typically 3-5 keV, is incident on a sample causing the ejection of a core level electron. A higher orbital electron will decay into the lower vacant orbital emitting an x-ray photon. The photon can be emitted or can be absorbed by a second electron causing the emission of this electron. This is called the Auger electron. The energy of the Auger electron is independent of the incident beam energy and is dependent only on the difference between the energy released in the decay of the first electron and the binding energy of the Auger electron. Thus,
\[ E_k = (E_o - E_b) - E_b' \]

where \( E_k \) is the kinetic energy of the Auger electron and the other terms are the binding energies of the respective electrons.

The kinetic energy of the Auger electron is due to transitions within an atom and therefore the energy is unique to that atom. Thus, AES provides a method to fingerprint the elements and is useful for identifying various elements present in a sample. Figure II.7 shows the energy of Auger electrons from various elements. The processes are labelled according to the orbitals involved. An Auger spectrum is generated by sweeping the bias on an electron energy analyzer called a cylindrical mirror analyzer (CMA) and thereby, analyzing the kinetic energies of the emitted electrons. The actual spectrum is a plot of electron counts, \( N(E) \) vs. energy, \( E \). Because the characteristic Auger electrons appear as small peaks on a large continuous background of secondary electrons, it is common to plot the derivative \( dN(E)/dE \) vs. \( E \). For a constant background the contribution to \( dN(E)/dE \) is zero which improves the detection of small peaks. An example of an Auger spectrum of an oxidized surface of InP is
shown in Figure II.8. Generally, the elemental composition of the surface is quantified by determining the relative peak-to-valley height of the differentiated peaks as this height is reflective of the amount of the given element in the sample. However, the intensity of an Auger peak is difficult to correlate exactly with an atomic concentration. A model for quantitative analysis is as follows[II.12].

If \( n_A \) is the concentration of an element in a solid, \( I_o \) is the incident electron flux, and \( \sigma \) is the Auger ionization cross section, then the number of electrons ejected for a given volume is \( N_o = \sigma n_A I_o \). Since the detector has a specific solid angle for acceptance of the ejected electrons, many ejected electrons are not collected and not all collected electrons are counted, leading to a detector collection efficiency, \( S \).
Detection of an Auger electron also requires that the electron have no energy loss due to inelastic scattering prior to reaching the detector.

The probability of an electron escaping from a solid can be treated as follows\[\text{II.12}\]: The number of electrons originating from a vertical line segment $dx$ located at a depth, $x$, below the surface is:

$$dN = N_0 S e^{-x/\lambda} dx$$

(3)

where $\lambda$ is the inelastic mean free path. For most materials $\lambda$ is in the range of 3 - 25 Å making Auger measurements sensitive to only the near surface region of a solid. The total signal intensity from an element in a layer much thicker than $\lambda$ is obtained by integrating the above equation to infinite depth:
\[ N_A = \int_0^\infty N_o S e^{-x/\lambda} dx = N_o S \lambda = \sigma n_A I_o S \lambda \quad (4) \]

The incident electron flux, \( I_o \), will be the same for all elements in the solid, \( \sigma \), \( S \) and \( \lambda \) can be combined into a single sensitivity coefficient, \( S_A \), that is unique to each element. These sensitivity coefficients have been tabulated and are transferable to different machines as only \( S \) is machine specific but it cancels out in the determination of relative concentrations. The relative concentration of an element in a solid is then given by:

\[ [A] = \frac{N_A/S_A}{\sum_i N_i/S_i} \quad (5) \]

In this study, the principal material investigated is InP with a thin oxide on the surface. The oxide thickness was typically close to or less than \( \lambda \) for oxygen, therefore, integrating equation (3) to infinite depth is not valid. The oxygen peak is instead calculated by integrating from 0 to the oxide thickness \( W \):
\[ N_A = \int_0^w N_0 Se^{-\alpha d} dx = N_0 S \lambda (1 - e^{-\alpha w}) \]  \hspace{1cm} (6)

\(N_0 S \lambda\) is the signal intensity that would be measured for a very thick oxide, therefore, the measured oxygen peak can be written as:

\[ O = O_o (1 - e^{-\alpha w_o}) \]  \hspace{1cm} (7)

This expression can be rearranged to calculate the oxide thickness:

\[ W = -\frac{\lambda_o \ln(1 - \frac{O}{O_o})}{O_o} \]  \hspace{1cm} (8)

\(O\) is the measured peak-to-valley value in the differentiated signal and \(O_o\) is the peak to peak value from an oxide much thicker than \(\lambda_o\).

A similar treatment can be done for the In and P peaks; however, the energy of Auger electrons from In in InP is very similar to that of In in InP-oxides and thus, the peaks overlap making thickness calculations impossible. Even with phosphorus there is slight overlap but the peaks are distinguishable. Oxidized-P has a low Auger electron yield making reliable thickness calculation difficult; however, a strong peak is produced by P in InP allowing for a second estimate of the oxide thickness. Because
the P signal is from the substrate, equation (3) is integrated from \( W \) to \( \infty \). After rearrangement for calculation of the oxide thickness the equation becomes:

\[
W = -\lambda_p \ln \left( \frac{P}{P_\infty} \right)
\]  

(9)

In this case \( P_\infty \) is the phosphorus peak-to-valley value from a clean surface of thick InP.

Equations (8) and (9) are used to determine and verify the oxide thickness. For both equations knowledge of the mean free paths is required. Various theories have been proposed to calculate \( \lambda \)'s achieving only moderate agreement with experimental values[II.13, 14]. Thus, for this work, equations (8) and (9) were used to get an accurate estimate of the mean free paths. This was done iteratively by substituting values for \( \lambda_o \) and \( \lambda_p \) in the two equations until the respective values for \( W \) were in good agreement. It was determined that for the material system of an InP-oxide on InP, \( \lambda_o = 14.5 \pm 0.5 \) Å and \( \lambda_p = 6.9 \pm 0.3 \) Å. These values are in close agreement with the theory proposed by Ballard[II.13]. Because \( \lambda_o \) is larger than \( \lambda_p \), thicker oxides can be measured from the O signal. Also, because the O peak does not overlap with any peak from the substrate the O peak-to-valley value was used to calculate the oxide thicknesses and the P peak-to-valley value was used to verify the result, particularly for thinner oxides.

Application of equations (8) and (9) to different samples on different days requires that there be no drift in the machine sensitivity otherwise the values of \( O_\infty \)
and $P_\omega$ will drift. This, unfortunately, was not the case and in general is not the case for most Auger systems. Some of the instrumental difficulties encountered with quantitative Auger analysis are reported by Smith[II.15]. Factors such as sample position, proper operating voltage of the electron multiplier, the transmission function of the energy analyzer and stray magnetic and electrostatic fields can all affect the recorded Auger signal.

When measurements were done for this study, precautions were taken to ensure the same instrumental parameters were used for all measurements; however, drift in the peak amplitudes was still observed. Two methods were considered to compensate for the drift. The first method involved measurement of the peak generated by the elastically scattered electrons, since it should be the same for every sample, prior to recording the sample spectrum. A standard elastic peak-to-valley value could then be selected and for each sample the measured elastic peak-to-valley value would be compared to the standard value and a normalizing factor calculated. This factor would then be used to adjust the peak-to-valley values of the sample spectra. It was observed that instrumental drifts occurred between measuring the elastic signal and recording the sample spectra possibly because both the sensitivity and the energy scale required adjusting between the two measurements. Regardless, the drift was present and this technique could not be used.

The second method employed to compensate for drift proved to be successful. It involved calculating a standardizing factor from the recorded spectrum itself. It was assumed that for a given oxide thickness the ratio of two peaks, say O/In, would be
Figure II.9. Standardizing plot for the oxygen (O) and phosphorus (P) peaks.

the same regardless of the instrumental conditions since both the O and In signals would experience the same shifts. There could also exist energy dependent shifts in the CMA but this effect is assumed to be small[II.12], especially since the Auger electron energy of O (503 eV) is close to that of In (405 eV). The P electron energy is 120 eV. Figure II.9 is a plot of the P and O peak-to-valley values vs. the O/In ratio for various samples analyzed on different days. The shape of the curves produced by each sample is similar but there are intensity shifts from sample to sample. From the data a standard curve was selected for all samples. Then the O/In ratio, which is independent of the instrumental sensitivity, is used to determine the O
and P peak-to-valley values for use in equation (8) and (9). The standardizing expressions are written below:

\[ O = 39.2(\pm 0.8)(\frac{O}{In})^{0.73(\pm 0.02)} \]  

\[ P = 68(\pm 7)e^{-3.1(\pm 0.3)(O/In)} \]

These equations are generated by determining the best curve fit to the data in figure II.9. By growing a thick oxide and adjusting the O signal according to equation (10) it was determined that \( O_\infty = 50\pm 5 \) mm. Measurement of a clean InP sample gave \( P_- = 68\pm 7 \) mm. A summary of the relevant information for quantitative Auger analysis is presented in table II.1.

A final comment on the Auger analysis needs to be made. For the calculated oxide thicknesses to be accurate the oxide must have a uniform composition with depth and this may not be the case; however, in this work, the thickness calculations are used for

<table>
<thead>
<tr>
<th>Table II.1 Summary of equations and parameters for AES measurements.</th>
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<tr>
<td><strong>Equations</strong></td>
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<tr>
<td>( O = 39.2(O/In)^{0.73} )</td>
</tr>
<tr>
<td>( P = P_-\exp[-3.1(O/In)] )</td>
</tr>
<tr>
<td>( W = -\lambda_0\ln(1-O/O_\infty) )</td>
</tr>
<tr>
<td>( W = -\lambda_P\ln(P/P_-) )</td>
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comparison purposes and great care was taken to ensure that oxides were generated under identical conditions. Therefore, any non-uniformities will be present in all samples and the use of the calculated thickness is valid.

II.5 ELECTRON CYCLOTRON RESONANCE HYDROGEN PLASMA

II.5.1 INTRODUCTION

The plasma generated by an electron cyclotron resonance (ECR) source involves the resonant absorption of microwave energy by electrons in a magnetic field. The resulting plasma is a complex arrangement of neutral and charged molecules, atoms, and free electrons. The description of this plasma state is a complicated subject, which involves the physics of single particle motion as well as a treatment of the collective motion of the particles. Recently, a review was written Boudreau on the application of plasma physics to an ECR system[II.16]. Included in that review are discussions on microwave propagation, plasma generation, mirror field confinement and the theory of plasma analysis by a Langmuir probe and optical emission spectroscopy. For other reviews of plasma physics see references[II.17] and [II.18].

This section will briefly review the physics of plasma generation and maintenance, then present a more detailed description of the characteristics of an ECR plasma and how the ECR source configuration (magnetic field profile and microwave power) affects the characteristics of the plasma. Included in the section will be some of the recent experimental findings and theoretical discussions presented in the literature on ECR plasma operation, particularly as they pertain to H-plasmas.
II.5.2 PLASMA GENERATION

A schematic of the ECR source used for this study is shown in figure II.10. This system was initially developed and characterized by Popov[II.19, 20]. In an ECR source, microwave energy is delivered to a neutral gas in a magnetic field. If a molecule of the gas becomes ionized, possibly by a cosmic ray, the electron and the

![Figure II.10. ECR Plasma Source[II.19].](image)

charged molecule will experience motion as described by the Lorentz force law:

\[
F = \frac{mdv}{dt} = q(E + vxB)
\]  

(12)

where \( m \) is the mass of the particle, \( q \) its charge, \( v \) its velocity and E and B are the
applied electric and magnetic fields, respectively. The applied magnetic field will only affect charged particles with a velocity component perpendicular to the field. A particle initially moving perpendicularly to the field will have a circular trajectory while a particle initially moving at an angle to the applied field will have its motion turned into a corkscrew or helical motion. The circular motion will have a characteristic radius, called the Larmor radius:

\[ r_L = \frac{mv_\perp}{qB} \]  \hspace{1cm} (13)

where \( v_\perp \) is the perpendicular velocity component, and a characteristic frequency called the Larmor- or cyclotron-frequency:

\[ \omega_c = \frac{qB}{m} \]  \hspace{1cm} (14)

The applied electric field will accelerate the charged particle parallel to the field direction regardless of the particle's initial motion. With an ECR source, microwave energy is delivered at a frequency of 2.45 GHz and with the field direction perpendicular to the direction of the magnetic field. At microwave frequencies the motion of the ions in the plasma is largely unaffected due to their large mass and
therefore, only electron motion needs to be considered. A frequency of 2.45 GHz gives an angular frequency of 15.4 rad./s (ω = 2πν). Using this frequency in equation (14), and the charge and mass of an electron the corresponding magnetic field is seen to be 0.0875 Tesla or 875 Gauss. Thus, for electrons at 875 G the cyclotron frequency will match the microwave frequency, and resonant absorption of the microwave energy by free electrons will occur.

The ECR source used in this study has a resonant cavity with a diameter smaller than the cutoff for the applied microwaves, therefore microwave propagation will not occur into the cavity. However, resonant absorption of the microwave energy will still occur if the resonant magnetic field is generated near the vacuum window where microwaves are introduced[II.21].

Generally, ECR sources are operated at low gas pressures (10⁻¹ - 10⁻² torr) such that a given electron can absorb significant microwave energy prior to collisions with other molecules. Also, energy transfer from the electrons to the gas molecules is inefficient due to the large mass difference. These factors allow the free electrons to reach very high effective temperatures (>10,000 K higher than the neutral gas temperature). A high energy electron will eventually collide with a gas molecule possibly causing ionization. Ionization processes result in an increasing number of free electrons, which can absorb the microwave energy and in turn collide with other molecules resulting in further ionization. It is this process that results in the generation of the plasma. A steady state is achieved when the rate of charged species
generated equals the rate at which charged species are lost from the resonant cavity
due to recombination in the plasma volume, diffusion along the magnetic field
gradient, and recombination at the chamber walls.

The efficient absorption of microwave energy in the resonant zone makes ECR
sources an effective way to generate an electrodeless low pressure plasma with high
ionization efficiencies compared to other plasma sources[II.22].

II.5.3 DIFFUSION AND RECOMBINATION

Mechanisms of plasma decay are very important to ECR plasma sources. For
many other plasma sources the target material is placed within the plasma source
itself, between two electrodes for example. With ECR sources, the plasma is typically
extracted from the source by a magnetic field gradient and delivered to a target
downstream and hence, significant plasma decay can occur between the plasma source
and the target. Loss of plasma species occurs by diffusion and recombination which is
difficult to quantify. The exact process of decay is dependent on the plasma species,
the density, the energy and the spatial distribution of the plasma. For detailed reviews
of diffusion and recombination see references [II.16] and [II.18]

In general, for high plasma densities recombination, which is proportional to $n^2$,
where $n$ is the plasma density, is the dominant mechanism of plasma decay. Once the
density has reached a low value diffusion becomes the dominant mechanism. It can
be shown that for decay by recombination the plasma density decreases reciprocally
with time,

\[ n \propto 1/\alpha t \]

where \( \alpha \) is called the recombination coefficient. With diffusion the decay is exponential,

\[ n \propto e^{-\nu t} \]

where \( \tau \) is the time constant. This behaviour of plasma decay is seen in figure II.11 which shows the results of measurements of the density decay in the afterglow of a weakly ionized H-plasma.

### II.5.4 Description of the Plasma State

The plasma state is described by several parameters. Again the reader is referred to the review by Boudreau[II.16] or the plasma texts[II.17, 18] for a detailed description of these parameters. One important parameter is the species temperature. The velocity distribution of particles in the plasma can be described by a Maxwell
Boltzmann distribution:

\[ f(v) = A \exp\left(-\frac{mv^2}{2kT}\right) \]  \hspace{1cm} (15)

where \( v \) is the velocity, \( m \) is the mass, \( A \) is a normalizing constant, \( k \) is the Boltzmann constant and \( T \) is the temperature. The temperature is related to the average energy of the particles by

\[ E_{av} = \frac{3}{2} kT \]  \hspace{1cm} (16)

Therefore the energy of a species in the plasma can be described by a temperature. As mentioned previously the electron temperature is much higher than the ion or neutral gas temperature. The temperature of a given species will vary with position in the plasma.

The thermal motion of particles allows electrons and ions to separate creating a localized region of unbalanced charge. The charge separation creates an electric field or a restoring force. The greater the thermal energy, as defined in equation (16), the greater the maximum distance of separation. This maximum distance is called the Debye length and is expressed as follows:
\[ \lambda_D = \left( \frac{e_0 k T_e}{n e^2} \right)^{1/2} \]  

where \( T_e \) is the electron temperature and \( n \) is the plasma density. As expected, the Debye length increases with increasing temperature, and decreases with increasing density due to the greater number of collisions occurring, causing neutralization.

The final parameter to be presented is the plasma frequency. The plasma frequency also arises from areas of unbalanced charge. Restoring forces are present due to the electric field which causes electrons to rearrange their positions establishing an internal oscillation at a frequency called the plasma frequency. The frequency is expressed as:

\[ \omega_p = \left( \frac{n e^2}{\varepsilon_0 m} \right)^{1/2} \]  

The plasma frequency is an important concept in determining the response of the plasma to an applied electromagnetic wave. It is the lowest frequency oscillation that can propagate in the plasma in the absence of a magnetic field. The expression can be rearranged to express the maximum plasma density that will allow an applied wave to propagate:
\[ n_c = \frac{\varepsilon_0 m \omega^2}{e^2} \]  

(19)

For plasma densities greater than \( n_c \) a wave of frequency \( \omega \) will not propagate.

Maximum absorption of microwave energy in an ECR source occurs when the plasma density equals \( n_c[I.I.19, 21] \) thus for a microwave frequency of 2.45 GHz the critical density is \( 7.4 \times 10^{10} \) cm\(^{-3} \).

**II.5.5 EFFECT OF THE MAGNETIC FIELD GRADIENT**

In an ECR source high energy electrons in circular motion are accelerated from the ECR source by the magnetic field gradient. The accelerated electrons cause a negative potential toward the substrate. Therefore, an electric field will be generated which accelerates the ions and decelerates the electrons such that charge balance is maintained. This technique of extracting ions from the plasma source is known as divergent magnetic field plasma extraction.

The theory of magnetic field extraction is given by Matsuo[I.I.23] and is summarized here. Under plasma conditions the ions and electrons must have the same acceleration to maintain charge balance:
\[
\frac{F_i}{m_i} = \frac{F_e}{m_e}
\]  

(20)

where \( F \) is the force and \( m \) is the mass. The force on the ions results from the electric field generated by the negative potential towards the substrate, while the force on the electrons originates from the divergent magnetic field and the resulting electric field.

The forces can be expressed as follows:

\[
F_i = qE
\]  

(21)

\[
F_e = -\mu \frac{dB}{dz} - qE
\]  

(22)

where \( \mu \) is the magnetic moment of the electron circular motion, \( B \) is the strength of the magnetic field and \( E \) is the generated electric field. The magnetic moment can be expressed in terms of the kinetic energy, \( \varepsilon \), of the electron and the magnetic field strength.

\[
\mu = \frac{\varepsilon}{B}
\]  

(23)
The magnetic moment is an adiabatic invariant, meaning it is constant as long as changes in \( E \) and \( B \) occur slowly compared to the cyclotron frequency. From equations (20) - (23) it can be shown that the generated electric field is given by:

\[
E = \frac{(e \cdot jB_y)(-dB/dz)}{(1+m_e/m_i)}
\]  

(24)

Where \( e_o \) and \( B_o \) are the initial kinetic energy and magnetic field experienced by the electron. Assuming \((1+m_e/m_i)=1\), integration of equation (24) gives the ion potential, \( \phi \), as:

\[
\phi = -\frac{e_o}{q}(1-\frac{B}{B_o})
\]  

(25)

This equation states that the ion energy at the substrate is a function of the electron initial kinetic energy and the ratio of the initial magnetic field to the magnetic field at the substrate. The divergent magnetic field converts the circular energy of the electron into ion energy along the magnetic field and therefore has a crucial role in determining the plasma energy at the substrate.

The invariance of the electron magnetic moment means that the electron will lose transverse energy and gain axial energy as it travels along the axis of the resonant
cavity to a region of lower magnetic field. The reverse happens as the electron travels to a region of higher field. The experimental apparatus has two magnets surrounding the resonant cavity (see figure II.10). The magnetic field profile can be configured such that the magnet farthest from the microwave window generates a field strong enough to convert all the axial energy of the electron into transverse energy. At this point the gradient of the field may cause the electron to be reflected. This is known as mirror field confinement and results in additional containment of electrons in the resonant zone where further absorption of microwave energy can occur. Generally, this leads to an increase in the plasma density and is therefore an important consideration in the configuration of the plasma.

Recently, there have been several investigations into the effect the magnetic field gradient has on ECR plasma characteristics[II.24-28]. The various groups report that a shallower gradient results in higher plasma densities with greater uniformity in the radial direction. Samukawa et al.[II.25] investigated the effect that the magnetic field profile at the resonance zone has on a Cl₂ plasma. They explained that the higher plasma densities and greater uniformity could be attributed to the applied microwave energy having a distribution around 2.45 GHz and that a shallower field gradient will create a larger ECR zone where efficient absorption of the microwaves can occur. Fujiwara et al.[II.26], also using a Cl₂ plasma, found that a shallower magnetic field gradient between the ECR zone and a Si substrate increased the etch rate and improved the etch uniformity of the Si. Holber et al.[II.27] and Matsuoka et
al.[II.28] found, using an argon plasma, that a shallower gradient between the ECR source and the substrate results in lower ion energies with a narrower distribution compared to plasmas generated with steeper gradients.

II.5.6 PLASMA DIAGNOSTICS

To determine the properties of the plasmas generated for this work two non-intrusive techniques were used. A Langmuir probe was used to measure the ion current, plasma density, electron temperature, ion temperature, floating potential and plasma potential. Optical emission spectroscopy was used to measure the relative abundances of neutral excited species.

II.5.6.1 LANGMUIR PROBE

An electrostatic Langmuir probe is a conducting wire placed within the plasma stream with a sweeping bias applied to the probe such that the electrical characteristics of the plasma are measured[II.16, 29]. When the probe is biased it is isolated from the plasma by Debye shielding and therefore, the effects of the probe on the plasma only occur over this shielded region or sheath which is approximately a Debye length in thickness. The Debye length for a typical plasma in this system is ~4\(\mu\)m and therefore, the probe is considered non-intrusive.

An idealized Langmuir scan for a single probe in a plasma with no magnetic field is shown in figure II.12. At high negative bias the electrons of the plasma are
repelled while the ions are collected. This gives the ion saturation current. The ion saturation current can be approximated by [II.18]:

\[ I = n_e q A (kT_e/M)^{1/2} \]  

(26)

where \( n_e \) is the plasma density, \( A \) is the probe area, \( T_e \) is the electron temperature and \( M \) is the mass of the ions. The plasma density is easily calculated from the ion saturation current once \( T_e \) is known. With increasing positive voltage electrons at the high energy end of the distribution can reach the probe giving a decrease in current until the electron current exactly equals the ion current. At this point the net current is zero and the voltage at which this occurs is the floating potential, \( V_f \). This is the same potential that an insulating wall in the plasma would reach. With further positive bias lower energy electrons are collected and the plasma
potential, \( V_p \) is reached. At this point there is no sheath and the current is given by the random thermal currents of the ions and electrons. The electrons produce the dominant current since they are much lighter and faster. The difference between \( V_f \) and \( V_p \) is the energy of the fastest moving electrons and is approximately equal to the ion energy[II.30]. In the region between \( V_f \) and \( V_p \) the increasing current is a reflection of the electron energy distribution and is described as[II.29]:

\[
I_e = I_e^{sat} \exp\left(\frac{-e(V_p-V)}{kT_e}\right)
\]

(27)

where \( I_e^{sat} \) is the electron current at high positive bias. From the log of the current in the region between \( V_f \) and \( V_p \) the electron temperature is calculated.

The above Langmuir probe theory assumes that the probe radius (0.5mm for the system used here) is much greater than the Debye length and that the electron temperature is much greater than the ion temperature. Both are reasonable assumptions for the system used in this investigation. However, the above theory also assumes that there is no magnetic field at the probe position. In our experimental set-up, however, we have calculated that, during plasma operation, there is a field of 20 Gauss at the probe position. This has two effects. First, the electron current is reduced, because only electrons on a flux line intersecting the probe will be collected, and second, the electron current will not saturate[II.16], which will affect the
calculation of the electron temperature and plasma density. In interpreting the experimental Langmuir scan this effect will be ignored because the emphasis is on determining the difference between different plasma conditions as opposed to measuring absolute values of the plasma properties.

II.5.6.2 OPTICAL EMISSION SPECTROSCOPY

Collisions in the plasma can result in energy transfer such that an atom or molecule in the plasma is left in an excited state. The return of the excited electron to its ground state, or lower energy state, can result in the emission of a photon. The wavelength of the photon from the most prominent transition will give the plasma a characteristic colour. To characterize the H-plasmas used in this study, the emitted photons were collected by a fibre optic cable, passed through a monochromator and collected by a photo multiplier allowing the optical spectra to be recorded. The wavelength region scanned ranged from 400 - 850 nm. Beyond this range the quartz window becomes absorbing. The peaks in the recorded spectra are correlated with reference values to determine what species are present. By monitoring the change in intensity, at a given wavelength with different plasma conditions, relative amounts of certain species present under different plasma conditions are determined.

II.5.7 ECR HYDROGEN-PLASMAS

ECR H-plasmas have recently received attention due to their applications for
impurity removal[II.31-43] and defect passivation[II.44-53]. Most studies have focused on the technological development of optimal plasma treatments without characterizing the plasma. Generally, plasmas generated from molecular species are more difficult to generate and maintain than plasmas from atomic species because there are many mechanisms for energy transfer that do not result in ionization. The various reactions that can occur in a H-plasma are given below:

i) ion and electron formation

\[ e + \text{H}_2 \rightarrow \text{H}_2^+ + 2e \quad (a) \]

or

\[ e + \text{H} \rightarrow \text{H}^+ + 2e \quad (b) \]

ii) atom and radical formation

\[ e + \text{H}_2 \rightarrow \text{H} + \text{H} + e \]

iii) generation of light

\[ e + \text{H}_2 \rightarrow \text{H}_2^+ + e \quad \text{then} \quad \text{H}_2^+ \rightarrow \text{H}_2 + \text{h}v \quad (a) \]

or

\[ e + \text{H} \rightarrow \text{H}^+ + e \quad \text{then} \quad \text{H}^+ \rightarrow \text{H} + \text{h}v \quad (b) \]

The major recombination reactions are as follows:

v) electron-ion recombination

\[ e + \text{H}_2^+ \rightarrow \text{H}_2^{(*)} \quad (a) \]
or

\[ e + H^+ \rightarrow H^{(*)} \]  \hspace{1cm} (b)

vi) dissociative recombination

\[ e + H_2^+ \rightarrow H^{(*)} + H'' \]

where \((*)\) indicates the species may be in an excited state. For molecules this includes excited vibrational and rotational states. With atomic plasmas only reactions i)(b), iii)(b) and v)(b) are possible and thus, it is apparent that molecular plasmas are significantly more complex than atomic plasmas. Often with plasmas generated from diatomic molecules dissociative recombination is the most prevalent source of the atomic radicals[II.29].

Outten et al.[II.30] have studied the characterization of ECR H-plasmas. They measured the plasma density and the electron temperature near the ECR zone and 17 cm downstream. They found that near the ECR zone, \(T_e\) varies from 15 - 30 eV and the plasma density varies from 1 - 18x10^8 cm\(^{-3}\). At 17 cm downstream, \(T_e\) varies from 5 - 7 eV and the density varies from 1 - 5x10^8 cm\(^{-3}\). Both \(T_e\) and the density were dependent on the input microwave power. Higher densities result in lower temperatures as more collisions occur distributing the electron energy. This group also measured the ion energy downstream and found that it was 30±5 eV in good agreement with the theory given by Matsuo[II.23] that has been summarized previously.
For the ECR system used in this study the chamber diameter is about half that of Outten’s system and the gas flows used are typically 10 times less. Therefore, lower plasma densities are expected and possibly higher electron temperatures. Two magnetic field profiles for the ECR source (see appendix A for calculation of the field profile) are shown in figure II.13 along with the positions of the source magnets, the Langmuir probe and the sample stage. It is evident that the Langmuir probe and sample stage are much further downstream than would normally be the case in an ECR system. Significant plasma decay will occur between the ECR source and the substrate and electron temperatures measured by the Langmuir probe are expected to

![Figure II.13. Magnetic field profile of ECR source.](image)
be low, as the field strength has dropped to low values. The fact that the magnetic field has dropped to fairly low values at the sample stage also suggests that most of the initial electron kinetic energy will have been converted to ion energy. However, in the presence of a magnetic field the mean free path is the electron Larmor radius, therefore collisions will occur within the plasma resulting in loss of energy. Therefore the ion energy in the system used here is expected to be less than that observed by Outten et al.[II.30]

The density and energy of the neutral species is the most difficult to quantify. First of all, in most plasmas there is one charged species to every 100,000 to 1,000,000 neutral species and most of the neutral species will be unaffected by the plasma[II.29]. Some neutral species will be generated by collisions and recombination and the exact energy of these neutrals will depend on the specifics of the collision or where in the plasma stream recombination occurred.

The transfer of energy from the plasma to the sample surface is another important factor to consider. It can be assumed that the ion energy in the H-plasma will be >10 eV. An InP substrate at growth temperature (470 °C) has an associated thermal energy of 0.06 eV and thus, energy will be imparted to the sample by the plasma. Plasma species impinging on the sample surface can collide with surface atoms and transfer energy which enhances surface reactions or, can penetrate into the sample losing energy through inelastic collisions with the sample atoms. It can be shown that the average transfer of energy from a particle with high kinetic energy to
one with low energy is most efficient when the two species are of similar mass,

$$e_{\text{coll}} = \frac{2mM}{(m+M)^2}\Delta\varepsilon$$

(28)

where $e_{\text{coll}}$ is the average energy transfer to the lower energy particle, $m$ is the mass of the lighter particle and $\Delta\varepsilon$ is the initial energy difference. The maximum energy a H ion would transfer to a surface atom in an InP-oxide would be in the range of 0.1 - 1 eV depending on which surface atom was involved. The implantation of H into the sample is expected to be significant as hydrogen has a small radius. Indeed, passivation studies have shown that InP exposed to a H-plasma can have H implanted up to 1 $\mu$m deep\cite{II46}.

It is clearly evident that the effective use of an ECR plasma is not simply a matter of generating a resonant magnetic field of 875 G to absorb the 2.45 GHz microwave energy. The actual plasma properties are a complicated function determined by both the magnetic field profile in the ECR region and by the downstream gradient. Part of this work is devoted to understanding plasma behaviour based on the applied magnetic field profile.

II.5.8 OTHER IMPORTANT CONSIDERATIONS

In the successful operation of an ECR source there are several factors other
than the configuration of the magnetic field that must be considered. The most obvious is the input microwave power. Other factors, which are difficult to quantify, are the appearance and effect of multiple steady states, hysteresis and abrupt transitions as well as the effect of contaminants.

II.5.8.1 INPUT MICROWAVE POWER

The applied microwave power delivers energy to electrons in cyclotron orbits and therefore, an increase in microwave power should increase the electron density. Both Outten et al.[II.30] and Holber et al.[II.27] observed that this is the case; however, the electron density quickly saturates with increasing microwave power. This is attributed to the plasma becoming over dense (see equation (19)) such that the applied microwave frequency is effectively cut off. Basically, the plasma has saturated its ability to absorb the microwave power.

Popov observed[II.21, 54], using an ECR chamber with a diameter smaller than the microwave cutoff, that as long as the resonant magnetic field is close to the microwave window greater than 95% of the incident microwave energy can be absorbed with no observed saturation up to 1000 W of incident power. The generation of plasmas with densities greater than 10 times the critical density were reported.

The discrepancy between these results is probably due to several factors. The particulars of the source configuration will obviously be important, the gas used as well as the gas pressure will also be important. For a given gas, a plasma can only
support a limited ionization ratio before recombination dominates, thereby saturating the plasma density.

II.5.8.2 MULTIPLE STEADY STATES AND HYSTERESIS

Various groups have observed that ECR plasmas can be unstable and exhibit hysteresis and multimodal behaviour in some regions of their operation[II.54-57]. The net effect is that a plasma can have an abrupt change in properties with no accompanying change in the equipment settings, or a plasma with specific properties may not be reproducible on different days. Although this effect is not well understood, Aydil et al.[II.55] suggest that it is due to a non-linear feedback mechanism between the neutral and plasma densities. The local neutral density will of course affect the ionization rate which will affect the plasma density. The plasma density in turn, affects the rate at which ions are extracted from the source which will then determine the neutral density profile. Such non-linear feedback mechanism can lead to the observed steady state multiplicity and to complex dynamic behaviour. Conventionally, these regions of instability have been avoided in setting up the plasma. However, this can limit the functionality of the plasma if one of the modes has desirable properties. Experimentally, it is important to be aware of plasma hysteresis and multimodal behaviour and to not assume that reproducing equipment settings will necessarily produce a plasma with the expected properties.
II.5.8.3 EFFECT OF CONTAMINANTS

Another important consideration in the operation of an ECR system is the recent history of the apparatus. Trace amount of impurities from past operation can affect the plasma properties. This has been observed by Goeckner et al[II.58]. They suggest several phenomena that could occur including: the contaminants producing ions of different mass, and possibly charge, from the bulk of the ions, and the energy used to ionize and/or dissociate the contaminants altering the energy distribution of the high temperature electrons. In addition, I also suggest that the ionization energy of the contaminants will affect the initial start-up of the plasma which will change the possible hysteresis experienced as well as the modal behaviour. The overall effect of contaminants is a highly complex phenomenon which can, as Goeckner et al.[II.58] showed, significantly affect the plasma properties.

II.5.9 SUMMARY

ECR plasma generation occurs as the result of a free electron in a cyclotron orbit resonantly absorbing microwave energy at the same frequency as the cyclotron orbit. The exact magnetic field profile through the ECR zone and the field gradient beyond the ECR source will largely determine the plasma properties. Other effects which will alter the plasma properties, and are not well characterized or understood, are the magnitude of the input microwave power, the hysteresis and multimodal behaviour exhibited by plasmas and the role of contaminants. The actual plasma
properties are the result of a highly complex interaction between these various factors.

In a discussion of the effects a plasma will have on a substrate it is evident that the results must be correlated with the plasma properties and the instrumental settings.
CHAPTER III

SURFACE TREATMENTS

III.1 INTRODUCTION

This section is a review of the more recent oxide characterization studies along with discussions of oxide removal procedures including both thermal desorption techniques and H-plasma etching. Also included is a discussion on the techniques and applications of sulfur passivation. The chapter begins with a review of thermodynamic principles as thermodynamic models will be used, with the experimental results, to describe the formation and removal of oxides from InP. The thermodynamic calculations are completed using a program called "F*A*C*T", an acronym for Facility for the Analysis of Chemical Thermodynamics. The review of thermodynamics will include the principles that are necessary to comprehend the method of the computer calculations.

III.2 REVIEW OF THERMODYNAMICS

The objective of thermodynamics is to establish criteria for determining the feasibility or spontaneity of physical or chemical transformations[III.1]. The principles are most rigorously applied to systems at, or close to, equilibrium. For reactions far
from equilibrium, kinetic effects can have a large influence on the reaction pathway
and products; however, thermodynamic calculations still provide insight into what
products are most likely and which will be most prevalent. Also, a comparison of
thermodynamic predictions with experimental results provides a method for
determining the influence of kinetic effects. For a thorough discussion of the
principles and applications of thermodynamics see references [III.1] and [III.2].

The central thermodynamic parameter for determining reaction spontaneity is
the Gibb's free energy which, for a reaction run at a constant temperature, is defined
as:

\[ \Delta G = \Delta H - T\Delta S \]  

where \( \Delta H \) is the enthalpy and \( \Delta S \) is the entropy. Notice that all three of the above
thermodynamic variables have an associated \( \Delta \) indicating that only changes in these
properties can be determined. To calculate absolute values a reference state for each
variable must be defined. The third law of thermodynamics, which states:

The entropy of each pure element or pure compound in its stable molecular
configuration may be taken to be zero at zero Kelvin.

allows absolute values of the entropy to be calculated. For the enthalpy and the
Gibb's free energy a reference state has been agreed upon, called the standard state,
which is the most stable form of a species at 1 atm. and a specified temperature. The
most stable form is the form of lowest free energy. Generally, the specified
temperature is 298.15 °K. Using this reference point, a standard free energy of
formation \( \Delta G^\circ \) can be determined for any compound. \( \Delta G^\circ \) for a compound is the
energy of reaction for the formation of one mole of the compound in its standard state
from its elements in their standard state. It is a requirement of this definition that \( \Delta G^\circ \)
for any element be zero. \( \Delta H^\circ \) and \( \Delta S^\circ \) can be determined for any compound by the
same principle as \( \Delta G^\circ \) and \( S^\circ_{\text{abs}} \) can be determined for a compound based on the 3rd
law.

\( \Delta G \) for a reaction, \( \Delta G_{\text{rxn}} \), is the critical parameter in determining reaction
spontaneity. For a given reaction such as:

\[
A + B \rightarrow C + D
\]  

(2)

\( \Delta G_{\text{rxn}} \) can be calculated from the \( \Delta G^\circ \)'s of the various species, as a consequence of
Hess' law (stated below),

\[
\Delta G_{\text{rxn}} = \sum \Delta G^\circ_{\text{products}} - \sum \Delta G^\circ_{\text{reactants}}
\]  

(3)

A negative \( \Delta G \) for the reaction indicates that the elements arranged as the product
species C+D are in a lower energy state than the same elements arranged as A+B and
therefore, C+D is the more stable configuration and the reaction will proceed
spontaneously. A positive \( \Delta G \) indicates that the reactant mixture (A+B) is more stable
and the reaction will not proceed unless energy is added by an external agent.
Hess' law states that for a given chemical reaction the heat evolved or absorbed is the same whether the reaction occurs in one step or many steps. The law can also be stated as: the enthalpy changes for chemical reactions are additive. Consequently, the same heat is evolved if a reaction occurs at 20 °C or if the reaction mixture is first heated to 100 °C then allowed to react and then cooled to 20 °C again.

$\Delta G_{rn}$ for any reaction is the energy released (or required) in the complete transformation of the reactants into products. Most chemical reactions, if allowed to proceed to equilibrium, do not go to completion. If the above reaction is at equilibrium a constant, called the equilibrium constant, can be defined as:

$$k = \frac{[C][D]}{[A][B]}$$  \hspace{1cm} (4)

where the square brackets indicate the concentrations of the species, or the partial pressures of gaseous species. $k$ will be constant for any reactant-product mixture at a given temperature, and can be related to $\Delta G_{rn}$ according to the expression:

$$\Delta G_{rn} = -RT\ln k$$  \hspace{1cm} (5)

Thus, for a given temperature, if $\Delta G_{rn}$ is known, $k$ can be calculated and vice versa.

Another thermodynamic parameter used in the F*A*C*T program is the heat capacity of a compound. The heat absorbed by a body (not undergoing a phase
transformation) is proportional to the change in temperature:

\[ Q = C(T_2 - T_1) \]  \hspace{1cm} (6)

\( C \) is the proportionality constant and is called the heat capacity. For the reactions examined in this study a constant pressure is assumed, hence the relevant heat capacity is expressed as:

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_p \]  \hspace{1cm} (7)

The heat capacity allows for the calculation of thermodynamic properties at any temperature provided the properties are known at a single temperature.

Numerical values for the heat capacities cannot be calculated from classical thermodynamics alone and therefore, empirical relations have been developed that are valid over certain temperature ranges as long as no phase transformations occur. Two expressions commonly used to calculate heat capacities are:

\[ C_p = a + bT + cT^2 + dT^3 \]  \hspace{1cm} (8)

and

\[ C_p = a + bT + cT^2 \]  \hspace{1cm} (9)
Based on the thermodynamic principles presented here, if the $\Delta H^o$, $\Delta S^o$ (or $S^o_{\text{abs}}$) and the expression for $C_p$ for a compound are known, the compound can be combined with any other compound(s), with known thermodynamic properties, and reaction energies and equilibrium mixtures can be calculated at any temperature and pressure (as long as the pressure can be considered constant during the reaction). The F*A*C*T program contains the above thermodynamic properties for a tremendous number of compounds and therefore, can perform the aforementioned calculations for any combination of these compounds.

In chapter V, two programs within F*A*C*T are used to model the thermal desorption and the H-plasma etch of oxides from InP. One program is called "equilibrium" which allows the user to enter any reactants at any temperature and pressure and the program calculates the equilibrium mixture for the reaction. To calculate the equilibrium mixture the program has two constraints. It must maintain the reaction stoichiometry and must maximize the decrease in $\Delta G_{\text{mix}}$. This is done iteratively using equation (3) and the thermodynamic properties of compounds contained within the program's database. As an example consider the reactants AB and CD; the products of these two reactants must contain one or several of the elements A, B, C, and D and no other elements can be included. There must also be the same amount of each element in the products as there are in the reactants. The program selects possible products from its database of known compounds, possible products include the reactants, and calculates the amount of each compound that will be produced to maximize the decrease in $\Delta G_{\text{mix}}$. The calculations are based on
determining the $\Delta G_r^\circ$ for each compound from $\Delta H_r^\circ$, $\Delta S_r^\circ$ (or $S^\circ_{\text{abs}}$) and using equation (3). The expression for $C_p$ is used to determine the energy change associated with any temperature changes. The user may add compounds to the database if the thermodynamic properties are known or can be estimated. Also, the user may select which of the possible reaction products may be included in the equilibrium mixture. This program is used to determine the most probable reaction products for a given set of reactants.

Another program called "reaction" enables the user to enter a complete reaction pathway, reactants and products, at any temperature and pressure and the program will determine the thermodynamic properties, such as $\Delta G_{\text{rxn}}$, $\Delta H_{\text{rxn}}$ and $\Delta S_{\text{rxn}}$ for the reaction going to completion. $\Delta H_{\text{rxn}}$ and $\Delta S_{\text{rxn}}$ can be calculated by the same format as equation (3). Again, for this program, the $C_p$ expressions are used to determine the energy change associated with a change in temperature. This program is used to compare the $\Delta G_{\text{rxn}}$'s for various oxide desorption pathways to determine the most likely pathway.

III.3 REVIEW OF OXIDATION TECHNIQUES

Application of oxides on InP with properties appropriate for the fabrication of integrated circuits has led to the development of various techniques for producing such oxides. These techniques include; various chemical and thermal methods as well as anodic oxidation, and a UV/ozone treatment of the surface. The UV/ozone treatment appears to give results most appropriate for surface passivation prior to epitaxial growth. The oxides produced by the other techniques have been compared and the
references are given here. Shibata et al.[III.3] have characterized oxides produced chemically (in boiling water), thermally (in dry oxygen) and chemically under illumination, by XPS. Hollinger et al.[III.4] have used XPS to characterize oxides produced by various chemical treatments, as well as anodic oxides and thermal oxides. Anodic oxidation of InP has also been investigated by Al-Refaie[III.5]. Mittova et al.[III.6] thoroughly investigated the growth of thermal oxides. Ingrey[III.7] has recently written a review on the various techniques used to produce clean surfaces for epitaxial growth.

Wet chemical[III.8, 9] and thermal oxides[III.10] have also been used to protect substrates prior to epitaxial growth. Typically, wet chemical oxides contain impurities and require higher temperatures for thermal desorption than UV/ozone oxides[III.10], and thermal oxides give results very similar to those of UV/ozone oxides but are not as convenient to produce and often contain impurities; therefore, the focus of this study will be on oxides produced by a UV/ozone treatment.

The procedure for producing oxides on InP by a UV/ozone treatment involves placing an InP substrate under UV lamps, in air or an oxygen atmosphere. The UV light produces O_3 from O_2 molecules. The O_3 reacts with the substrate to form an InP-oxide. Besland et al.[III.11] give a more detailed description of the oxide growth by UV/ozone treatments. The UV/ozone oxides can be used in device structures but are of particular importance for forming a protective oxide on InP substrates. The UV/ozone treatment eliminates carbon compounds from the surface of the InP, by forming CO, CO_2 and H_2O which are eliminated in the gas phase as the oxide
grows[III.11]. Then, when the oxide is removed immediately prior to epitaxial growth, the remaining surface should be impurity free.

There have been various reports on the composition and the temperature required for thermal desorption of oxides produced by UV/ozone[III.10, 12-15]. The discrepancies in the various results probably arise from the difficulties in making accurate remote temperature measurements, difficulties in interpretation of XPS spectra, and the fact that UV/ozone oxidation is very sensitive to the initial surface conditions of the substrate. In a recent study by Hollinger et al.[III.12] it was determined, using XPS, that the UV/ozone oxide is an In-rich oxide with a chemical structure similar to that of InPO₄. The oxide will be either inhomogeneous or homogeneous with depth depending on the oxidation time[III.11].

Oxide growth by UV/ozone can be considered to occur in two regions, linear and parabolic with time. Initially, the oxide thickness increases linearly with time then, as the growth becomes diffusion limited, the growth rate becomes parabolic with time. In the linear region the oxides formed are inhomogeneous, probably due to the loss of volatile oxidized phosphorus from the surface. In the parabolic region the oxide becomes homogeneous due to both the rearrangement of bonds and the fact that the thicker oxide hinders the diffusion of volatile phosphorus compounds from the oxide/substrate interface. It is apparent that the specifics of the oxide growth will determine the exact composition.
III.4 THERMODYNAMICS OF OXIDE FORMATION

Various InP-oxides have been reported to exist such as: \( \text{P}_2\text{O}_3 \), \( \text{P}_2\text{O}_5 \), \( \text{In}_2\text{O}_3 \), \( \text{InPO}_4 \), \( \text{In(PO}_3)_3 \) and others that may exist as decomposition products of these oxides. The formation of a particular oxide will depend on the oxidizing conditions and may be a single or multi-phase oxide. Understanding which oxides form under certain conditions is important for the development of a reproducible insulator on InP and is also necessary for producing a reliable passivating oxide, that can easily be removed prior to epitaxial growth.

Schwartz et al.[III.16] have completed a thorough investigation to determine which InP-oxides form under different conditions and they have presented a phase diagram (figure III.1) of the oxides.

The phase diagram is a thermodynamic map of the stable oxides that can form on InP. The map is based on the

![Figure III.1. In-P-O Phase Diagram][III.16].
Gibb's free energy of formation of each of the oxides and whenever possible the thermodynamic predictions are confirmed by experiment. The lines connecting the elements In, P and O are the axes which represent mole fractions of the elements, for example, InP is half-way between In and P. The lines connecting the elements to oxides, or oxides to oxides represent stable mixtures. For example, since there is a straight line connecting In to InPO₄, a mixture of In and InPO₄ will not react. The diagram can also be used to determine what products will form from an unstable mixture. For example, there is no line connecting InP with In₂O₃ and therefore, this is an unstable mixture and will react. The reaction products are determined by drawing an imaginary line between the two reagents and finding any intersection points. There is an intersection with the line joining In with InPO₄ and therefore, In and InPO₄ will be the products of a mixture of InP and In₂O₃, given that the reaction has sufficient energy to proceed.

During a UV/ozone treatment of the surface of an InP substrate the only oxidizing species present is the oxygen derivative, O₃, so according to the phase diagram the oxide that forms is a single phase oxide with the composition InPO₄. This oxide is stable on InP, that is, there are no further reactions with the substrate to form other oxides. Schwartz et al. [III.16] determined that InPO₄ alone is stable to 900 °C. Besland et al. [III.11] prepared oxides on InP by UV/ozone treatments and determined, by comparing the XPS spectrum to that of known samples, that the peaks in the spectrum have similar energy positions and widths to that of InPO₄ oxides, formed by thermal oxidation and therefore, the bonding structure and chemical
behaviour will be that of InPO₄. The exact composition they measured was InP₀.₃O₂.₇₅ and this was attributed to excess In in the oxide due to the loss of volatile phosphorus products. Composition is a bulk property and not reflective of the chemical structure thus, the chemical behaviour of the UV/ozone oxide can be considered to be that of InPO₄. They also determined that the oxide is stable to at least 500 °C thus, the chemical structure and thermal behaviour is in agreement with that predicted by the phase diagram. XPS results obtained on UV/ozone treated substrates from this lab have the same chemical structure and composition as that given above and therefore, all modelling of reactions involving an oxide will only consider InPO₄.

III.5 REVIEW OF OXIDE REMOVAL

III.5.1 THERMAL DESORPTION

The removal of oxides from InP is more complicated than for other III-V materials due to the fact that the temperature required to remove the oxide is higher than the congruent sublimation temperature for InP (365 °C[III.17]). The ensuing excess loss of phosphorus results in a highly defective surface. For GaAs, the UV/ozone oxide desorption temperature is below congruent sublimation. Also, the oxide on GaAs decomposes into the sub-oxides of As₂O₃ and Ga₂O₃ which desorb at different temperatures[III.18]. With InP, the oxide maintains its original composition to at least 500 °C[III.12] and most likely throughout the desorption process[III.19].

During the desorption process the excess loss of phosphorus from the surface can be compensated for by maintaining an overpressure of P₂ or As₂. The gas used
will affect the desorption process. It has been determined, for a wet chemical oxide, that an As$_2$ overpressure stabilizes the sample surface, thereby reducing the risk of thermal decomposition due to phosphorus loss[III.9], but the more stable surface requires higher temperatures to completely remove the oxide than a surface that is P$_2$ stabilized[III.8]. The result is attributed to the As bonding with In from the oxide creating a more stable surface whereas, with the P$_2$ overpressure the P has a shorter surface lifetime and does not bond with the free In. Genova et al.[III.20] also observed that desorption under As$_2$ results in the formation of InAs crystallites and these may result in the formation of oval defects in a grown layer.

It has been determined in this lab that a temperature of 525-530 °C[III.21] is required for oxide removal under P$_2$ and Gallet et al.[III.10] determined that a brief anneal to 560 °C is required to completely remove the oxide under As$_2$. This result is explored further in this study.

### III.5.2 Oxide Removal with a Hydrogen Plasma

The basic principle behind H-plasma etching is that the plasma will generate reactive atomic hydrogen which will react with an oxide or semiconductor to form stable hydrides which are volatile and evaporate from the sample surface. Using an H-plasma to clean the surface of semiconductors offers several advantages. It has been reported that with a H-plasma, some semiconductors can be cleaned at temperatures lower than required for thermal desorptions[III.22, 23, 24], thereby reducing the diffusion of dopants and, for III-V materials, minimizing the risk of
thermal decomposition, as well as the risk of phase separation in ternary and quaternary alloys such as InGaAsP. A H-plasma will also remove carbon from the surface of semiconductors whereas a thermal desorption will not[III.22, 23].

The application of a hydrogen plasma to etch various semiconductors and their oxides was demonstrated in 1982 by Chang et al.[III.24] who measured the etch rate of a H-plasma, generated in a rf discharge, on Si, GaAs, GaSb, InP and their oxides. The etch rates varied by orders of magnitude depending on the material. Generally, the etch rate of the oxide was faster than the etch rate of the bulk semiconductor. A problem encountered with the III-V compounds was the preferential loss of the group V element with prolonged etch times. More recently, the use of a H-plasma has been optimized for the cleaning of Si prior to thin film deposition[III.25] and has been successfully applied to the cleaning of GaAs[III.26-32] and AlGaAs[III.32, 33], producing surfaces that are suitable for device processing or thin film deposition.

The cleaning of InP, which is the focus of this study, is somewhat more challenging than other III-V semiconductors due to the relative thermal instability of InP and the ease at which phosphorus in the top few monolayers will react with atomic hydrogen to form volatile PH3, which results in a defective, In-rich surface[III.23, 24, 34-38]. The applicability of any cleaning procedure is evaluated by the ability to recover a high quality, smooth, crystalline surface and therefore, the cleaning of InP surfaces with pure atomic hydrogen is not an acceptable procedure. Efforts have been made to improve the quality of the InP surface following oxide removal by including a phosphorus overpressure during the H-plasma exposure[III.39,
40]. Schutz et al. [III.40] reported that atomic hydrogen, created in an rf plasma, will create phosphorus vacancies only in the top few atomic layers and that these vacancies can diffuse into the bulk which would be detrimental to device performance. However, if a sufficient flux of phosphorus is maintained to the surface the vacancies that form are quickly filled with incoming P and the source of vacancies will be eliminated. Using a H-plasma and a phosphorus overpressure, at a substrate temperature of 350 °C they were able to produce atomically smooth InP, from chemically etched substrates, with no excess P-vacancies, as determined by photoluminescence measurements. Aller et al. [III.39] used an rf plasma to clean chemically etched InP substrates and could control the bias on the substrate stage. They found that at a substrate temperature of 310 °C, with a phosphorus overpressure, optimization of the substrate bias is required to produce acceptable quality surfaces.

It is apparent that the use of a H-plasma to clean the surface of InP has the potential to be a tool to produce high quality reproducible surfaces for growth or regrowth of epitaxial InP but, it is also apparent that this technique is far from optimized, in terms of plasma characteristics, gas flows (H₂:P₂), and substrate temperature. To this point rf plasma sources have been modified to include phosphorus sources. In this investigation we report on the optimal plasma conditions for removing oxide from InP substrates with an ECR source that is in-situ on an MBE chamber and the chemical mechanism by which the oxide is removed. Having an in-situ plasma source means no transfer is necessary after the surface cleaning. With vacuum linked plasma chambers a transfer is required through vacuum of usually
lower quality than is normally associated with an MBE chamber. Even MBE environments have low levels of C and O emanating from hot surfaces (eg. effusion cells and RHEED gun filament) it is therefore not only advantageous for the sample to remain in the MBE chamber but also to be able to initiate crystal growth immediately after the cleaning step.

III.6 SULFUR PASSIVATION

As an alternative to oxidation, sulfur passivation has recently received considerable attention as a surface passivation technique for III-V semiconductors. There has been extensive theoretical work devoted to deducing the optimal preparation procedure for this surface as well as, the structure of the surface and the bonding configuration[III.41-74]. Most preparation procedures result in a surface that consists of a monolayer of sulfur with low or undetectable amounts of oxygen present. This S-passivated surface has application in device structures. For structures that have been exposed to air, prior to the final deposition step, the S-passivation has been found to improve interface properties including; epi-layer/insulator interfaces in both GaAs and InP[III.75-83], epi-layer/metal interfaces in GaAs[III.53, 84-86], and epi-layer/epi-layer interfaces in GaAs and AlGaAs[III.87-89]. The S-treated interfaces show reduced carrier recombination compared to interfaces that did not receive the treatment. The improvement is attributed to the S-passivation resulting in a lower oxygen content at the interfaces.

A majority of the recent studies of the S-passivated surface has been done on
GaAs[III.41-62]. Several surface treatment procedures have been used such as; exposure of a clean surface of GaAs to an atmosphere of pure H₂S or a plasma discharge of H₂S, immersing a GaAs sample in a Na₂S solution or immersing GaAs in an (NH₄)₂Sₓ solution. Similar results are obtained for all preparation procedures where the reaction of a GaAs surface with S results in the formation of both S-As and S-Ga bonds, the exact amount of sulfur incorporated will depend on the preparation procedure. With annealing above ~200 °C the S-As bonds are no longer observed, only S-Ga bonds, resulting in a sulfur terminated surface of ~1 monolayer with no dangling bonds. The procedure most commonly used to prepare the S-passivated surface involves immersion in an (NH₄)₂Sₓ solution as this treatment produces surfaces with less oxygen then a treatment with a Na₂S solution[III.59] and does not require the equipment associated with obtaining an atmosphere of pure H₂S or a plasma discharge of H₂S; however, there is considerable variation in the methods that involve the (NH₄)₂Sₓ solution. Different concentrations and temperatures have been used and it has not been determined whether a pre-cleaning in HF or HCl is required to remove oxides prior to the deposition of sulfur on the surface. In this study two different, recently developed procedures, are compared in terms of the amount of S, C and O deposited on the surface. Also, the importance of a pre-treatment to remove oxides is investigated.

The application of S-passivation as a surface preparation treatment, on GaAs, prior to insulator or metal deposition does not require that the sulfur be removed only that the surface not oxidize prior to deposition. The resistance of the S-passivated
surface to oxidation has been investigated by Oshima et al.[III.42] and by Kawanishi et al.[III.51]. Both groups determined that the oxidation rate of a S-passivated surface is much less than that of an As-terminated GaAs surface. Crystal growth on a S-passivated surface may require that the sulfur be removed. Kawanishi et al.[III.52] determined that the sulfur desorbs from the GaAs surface at 590 °C. However, Melloch et al.[III.89] found that growth of GaAs on a S-passivated surface results in sulfur being incorporated at the interface as an n-type dopant even when the growth temperature is as high as 600 °C. Guel et al.[III.88] achieved minimal success removing the sulfur layer with an in-situ HCl etch prior to crystal growth. It is evident that, for GaAs, S-passivation is an interesting surface with device applications but, that the treatment requires further investigation to determine if it is applicable as a surface preparation technique for epitaxial growth.

The S-passivation of InP[III.63-70] has not been studied as rigorously as that of GaAs. However, the available information indicates that the behaviour of the S/InP system is very similar to that of S/GaAs. Maeda et al.[III.64] determined that the sulfur surface prepared using an \((\text{NH}_4)_2\text{S}_x\) solution initially contains S-P and S-In bonds as well as polysulfide bonds. However, Gallet et al.[III.63] Lu et al.[III.66] and Tao et al.[III.67] all determined that the sulfur surface prepared from an \((\text{NH}_4)_2\text{S}_x\) solution contains only S-In bonds. The major difference in the respective preparation procedures was that Maeda et al. did not include a water rinse after the \((\text{NH}_4)_2\text{S}_x\) treatment thus, it is proposed that the water rinse dissolves the P-S compounds and the polysulfides. Gallet et al.[III.63] also report that not all the In-S bonds are at the
surface but the sulfur penetrates to the fifth atom plane and resides on P sites.

RHEED measurements of S-passivated InP produce a 1x1 pattern at low temperature (below -200 °C)[III.66, 74] and a 2x1 pattern at higher temperatures (above -350 °C)[III.63, 74]. Gallet et al.[III.63] have shown that the S-passivated 2x1 surface is stable to 560 °C and at 570 °C the surface degrades due to loss of phosphorus. This is the same temperature at which an InP substrate would degrade under an As₂ overpressure. They propose that the thermal and chemical stability of the S-passivated surface is attributed to the stability of the In-S bonds and the formation of S-S dimers on the surface but they speculate that the surface will oxidize with prolonged air exposure based on the higher bond strength of the In-O bond compared to the In-S bond.

Similar to GaAs, the application of S-passivation on InP has been shown to improve interface qualities at epi-layer/insulator interfaces compared to air exposed surfaces[III.75, 78, 81, 82]. However, there are no reported studies of the application of sulfur treatments for preparing surfaces for use in epitaxial growth. In this study the resistance of the S-passivated surface to oxidation will be investigated as well as the possibility of using an (NH₄)₂S₄ treatment as a surface preparation procedure prior to epitaxial growth. The use of a H-plasma to remove the sulfur layer will also be reported.
CHAPTER IV

EXPERIMENTAL

IV.1 INTRODUCTION

The purpose of this study is to investigate the effectiveness of an in-situ H-plasma in the cleaning of surfaces of InP prior to crystal growth by MBE and to compare the removal of oxides from InP by thermal desorption to H-plasma etch of the oxide. This chapter describes the experimental apparatus and all procedures used in the investigation. The relevance of each procedure to the central purpose of the investigation is also stated. Figure IV.1, similar to figure II.1, illustrates the MBE system which was built by UHV instruments. This figure is intended to highlight the equipment central to the measurements taken for this study. The MBE chamber is equipped with a RHEED gun, and a retractable Langmuir probe. An optical fibre can be mounted on a view port for optical emission spectroscopy (OES) measurements. The chamber is vacuum linked to an Auger spectrometer.

IV.2 OXIDE GROWTH

To obtain reliable H-plasma etch rate data of oxides on InP a consistent oxide of reliable thickness must be produced. It is known that the compositions and
structures of oxides produced on InP are the result of the oxidation process and the initial surface condition of the InP[IV.1]. Therefore, to ensure a consistent oxide, substrates were either rinsed in HF to remove the manufacturer's oxide or, epi-layers were grown prior to a UV/ozone treatment. Thus, oxides were grown on essentially clean InP surfaces. Oxides were grown by placing the InP samples 1 cm from UV-lamps in a closed container. The oxidation time could be varied to produce oxides of varying thicknesses. Figure IV.2 shows the oxide thickness, as determined by AES measurements, as a function of the UV/ozone time. For the H-plasma etch studies the oxidation time was 20 min. producing oxides 20-25 Å thick.

IV.3 THERMAL DESORPTION PROCEDURES

Thermal desorption of oxides from InP was investigated to resolve the details of the desorption mechanism, which are not reported in the literature, and to establish a basis for the comparison with the H-plasma etch of the oxides. Characterization of
the thermal desorption process was done at two different facilities. Auger measurements were done at the McMaster MBE facility which has both P$_2$ and As$_2$ sources. X-ray photoelectron spectroscopy (XPS) studies were performed at the MBE facility at the Ecole Centrale de Lyon in France. Their system has an elemental arsenic source, a RHEED gun and is vacuum linked to an XPS chamber.

At McMaster, AES measurements were taken of two substrates before and after they were thermally treated by an identical thermal cycle, the first under P$_2$ and the second under As$_2$. The desorption process was done in the MBE chamber and was conducted as follows. Initially the samples were ramped at 2 °C/min. to 510 °C, then a ramp rate of 1 °C/min. was used to a temperature of 532 °C (the temperature required for complete desorption under P$_2$), then the samples were cooled. The RHEED patterns were monitored throughout the process. All temperatures were measured by a pyrometer.

At Ecole Centrale de Lyon XPS data were recorded of an InP substrate that had received a UV/ozone treatment after being rinsed in HF to remove any initial
oxides. The oxide was partially desorbed and XPS spectra were recorded. XPS spectra were recorded after heating the substrate for 3 minutes at 525 °C under As₂ and again after 12 minutes at 525 °C under As₂. The composition of the oxides was determined by comparing the spectral peak shifts and shapes to that of oxides of known composition.

**IV.4 H-PLASMA GENERATION AND CHARACTERIZATION**

It is important to note that the motivation for investigating and characterizing the behaviour of the H-plasma is to obtain the most suitable plasma for the cleaning of InP substrates. Therefore, the plasma parameters such as: gas flows, microwave power and the magnetic field profile are adjusted to obtain a variety of plasma properties in anticipation of allowing the cleaning properties to determine which configuration is most useful. H-plasmas were generated in the ECR source and extracted into the MBE chamber. The ECR system has two independently adjustable magnets mounted around a 7.6 cm diameter resonant cavity. Microwave energy, at 2.45 GHz, is delivered to the resonant cavity through a waveguide equipped with a directional coupler for measuring forward and reflected power. Plasmas are delivered from the resonant cavity into the MBE chamber through a 5.1 cm diameter tube that is 30.5 cm long.

The ECR chamber is directly connected to the MBE chamber, which is not designed for the high gas throughput normally associated with ECR operation, and the maximum gas flow is limited by the pumping capacity of the system. With these
constraints \( \text{H}_2 \) gas flow of 1.7 - 3.7 sccm, fed directly into the resonant cavity, were used to generate the H-plasmas. Because of the need for a simultaneous \( \text{P}_2 \) flux on the substrate during the etching (in order to eliminate any surface dissociation) the H-plasmas were generated with a \( \text{PH}_3 \) flow of 0 - 6.5 sccm through an EPI-cracker at 1000 °C to produce the necessary \( \text{P}_2 \) flux. Plasma modes were obtained by first starting the gas flow and then, turning the magnet current settings to initial values close to that required to produce a plasma, then the microwave power was applied. The current settings were then adjusted until a significant decrease in the reflected power was observed. The currents were then fine tuned until the plasma was stable as judged by a stable reflected power and Langmuir scan.

Plasma modes where the magnetic field at the microwave window was equal to the resonant field of 875 G are called resonant modes and generally, these modes produce the lowest reflected power. Stable plasmas could also be produced without the resonance condition being satisfied at the microwave window and these modes, which had higher reflected power compared to resonant modes, are called non-resonant modes. The adjustable parameters of the plasma are the microwave power, the magnetic field profile and the gas flows. The measurable properties are the microwave reflected power, the properties obtained from a Langmuir probe and the emission intensity of excited plasma species. To characterize the various plasma modes, resonant and non-resonant, in an organized manner the modes were grouped into "families" of modes; where a family would be a series of modes with the same current applied to magnet 1 and the current to magnet 2 would be varied. The current
to magnet 1 could then be changed and a new family of modes generated and characterized.

Langmuir probe scans were taken by inserting the probe into the plasma, then sweeping the bias on the probe from -100 V to 100 V with a total scan time of 2000 ms. An example Langmuir probe scan is shown in Figure IV.3. It is noted that the experimental Langmuir scan is significantly different from the theoretical scan presented in section II.5.6.1. The most notable differences are the noise on the scan and that the electron current of the experimental scan does not saturate. The noise is attributed to the low plasma density and the lack of saturation is attributed to the presence of a magnetic field at the Langmuir probe (see section II.5.6.1). However, the Langmuir scan was still used to calculate the following properties: ion current, floating potential, plasma potential, electron temperature, and the plasma density according to the procedures given for the Langmuir probe data acquisition software[IV.2]. The ion current is obtained by performing a linear regression of the scan in the region of negative potential, then the ion current is specified as the current at -100 V. The floating potential is the potential at zero current. The plasma potential

Figure IV.3. Langmuir probe scan of H-plasma.
and the electron temperature are both obtained by calculating the natural log (ln) of
the scan, then the electron temperature is given by the slope of the curve near I=0
and the plasma potential is the potential at the point where the ln of the electron
current begins to saturate. The plasma density is calculated from the ion current and
the electron temperature according to the following equation:

\[ n = \frac{I_{ion}}{qA(kT_e/M)^{1/2}} \]

where \( q \) is the electron charge, \( A \) is the probe area in m\(^2\), \( k \) is Boltzmann's constant
and \( M \) is the mass of the ions in kg. In section II.5.4 it was stated that the critical
density, that is the density at which maximum absorption of microwave power occurs,
is \(7.4 \times 10^{10}\) cm\(^{-3}\) for a microwave frequency of 2.45 GHz. The densities measured for
the system used in this work are in the range 1-7 \times 10^7 \text{ cm}^{-3}. The lower than critical
density is attributed to the low gas pressure used compared to typical ECR systems.

Optical emission measurements were used to obtain a measure of the relative
intensities from excited species present in the plasma. The configuration of the
chamber view ports is such that the optical emission measurements are reflective of
the excited species that are in the MBE chamber, near the sample surface, and not the
ECR source. Figure IV.4 is a typical optical emission scan, from 400 nm to 850 nm,
of a H-plasma. All observed peaks are attributable to electron transitions within
atomic H\(^+\). The most prominent line at 656 nm is the H\(_a\) line corresponding to a 3d-
2p transition[IV.3]. The peak at 486 nm is due to a 4d to 2p transition and the peak at 434 nm is due to a 5d to 2p transition[IV.3]. Other hydrogen species may exist in the plasma, such as \( \text{H}_2^+ \) and \( \text{H}_2^{++} \), but these were not observed in the scan. Typically, optical transitions for molecular species yield much lower intensities due to spreading of the transitions by vibrational levels. Excited phosphorus may also exist in the plasma; however, the most prominent line in the atomic spectra is expected to be at 255.3 nm which cannot be observed through the quartz window. The transitions in molecular phosphorus would not be observed for the same reasons given for molecular hydrogen.

The intensity of the hydrogen peak at 656 nm was used to compare the relative abundances of atomic hydrogen in the different plasma modes. The measured intensity is sensitive to the exact placement of the fibre probe on the viewport and therefore, to achieve an accurate comparison between modes all modes were generated with an identical experimental setup. Initially, measurements were done from two different view ports (see figure IV.1). The results proved to be independent of the window used so a majority of the plasma modes were characterized using only view port 1, as greater intensities were achieved with this view port. To verify the H-peak
intensity associated with
different plasma
conditions time lapse
spectra were recorded by
observing the intensity at
one wavelength (656 nm)
and recording data every
second, see figure IV.5.

Using this technique, the
H⁺ intensity of various modes could be obtained on one plot. For both methods the
monochromator slit width was set at 2 mm. For the wavelength scans, intensity
measurements were taken every 0.1 nm with a 0.1 s integration time at each
increment.

IV.5 EFFECT OF H-PLASMA ON InP

To evaluate how the plasma affects the surface morphology, Nomarski
photographs were taken of a grown layer on an H-plasma cleaned substrate and of a
grown layer on a thermally desorbed substrate. Growth of InP was carried out with a
substrate temperature of 465 °C, a PH₃ flow rate of 5 sccm and a growth rate of 0.75
µm/hr.

To estimate the concentration of any defects produced by the H-plasma, growth
interrupted samples were produced where ~0.5 µm of material would be deposited and
then, the In shutter would be closed. A plasma treatment would be applied to this surface then crystal growth was resumed. Using this procedure several interfaces (typically, 2 or 3) could be produced on one sample. Two techniques were used to evaluate the samples: CV-profiling and secondary ion mass spectrometry (SIMS). The CV-profiles were taken at McMaster University with a polaron PN2400 semiconductor profiler. Defect concentrations were determined by integration of the peaks in the CV-profiles. Often small doping steps, before and after the interfaces, would be included in samples to evaluate the reliability of the CV-profile. SIMS analysis was done at Bell Northern Research with a Cameca IMS secondary mass spectrometer utilizing a 10 keV Cs+ primary beam of 60 nA focused to a 20 μm spot. Where possible the SIMS measurements were calibrated to standard samples allowing impurity concentrations to be calculated.

IV.6 H-PLASMA ETCH OF InP

To measure the rate at which the H-plasma etches clean InP, a substrate was prepared with a mask over the surface similar to that seen in figure IV.6. The sample was heated to 465 °C and the H-plasma applied to the surface for 4 hrs. Multiple alpha-step scans were taken at various positions on the

Figure IV.6. Mask for H-plasma etch of InP.
surface and an average etch rate was calculated.

IV.7 PROCEDURE FOR PERFORMING H-PLASMA ETCH MEASUREMENTS

To determine the plasma properties that are most effective at removing oxides from InP two plasma modes were selected for detailed study of their oxide etching efficiencies. One mode, with current settings of 210A/190A, had a high ion current and a low optical intensity, the other mode, with current settings of 190A/130A, had a low ion current and high optical intensity. For both modes the PH$_3$:H$_2$ fluxes were 6.5 sccm:2.1 sccm. This is the lowest H$_2$ flow that would produce a reliable stable plasma and the highest PH$_3$ flow that could be used within the safety constraints of the MBE chamber. Both modes were used to obtain etch rate measurements at various temperatures such that the overall reaction kinetics could be determined.

To ensure a consistent oxide all etch experiments were carried out on samples that had an epi-layer of InP deposited on the substrate prior to the UV/ozone treatment. Within minutes of the UV/ozone treatment the samples would be introduced into the vacuum system. After an appropriate pump-down time, the samples were transferred to the Auger chamber where they were degassed at 350 °C for 15 min. A minimum of three Auger spectra from different spots on the sample surface would then be recorded. Samples were then transferred to the MBE chamber for H-plasma exposures.

Once on the substrate stage, samples were heated to the desired temperature for the plasma etch, under an overpressure of P$_2$. The ECR source would then be
configured in the appropriate mode according to the procedure outline above. The ECR shutter would then be opened for the designated amount of time and on closure of the shutter the microwave power, magnet currents and hydrogen flux were shut down. To determine the amount of oxide removed two techniques were used: One, where repeated plasma exposures and Auger measurements were taken, and the other where RHEED measurements were combined with the repeated plasma exposures.

Auger measurements involved cooling the sample to ~300 °C (the P₂ overpressure was removed at 350 °C) then, a transfer to the Auger chamber where several spectra were recorded. Figure IV.7 shows an oxidized InP surface and the same surface after exposure to the H-plasma. Auger spectra were used to determine the oxide thickness according to the equations presented in section II.4. Rate information is easily obtained by determining the change in oxide thickness for a given timed exposure to the H-plasma. This technique was used to determine the overall reaction kinetics and correlate RHEED intensity measurements with oxide thicknesses.

Figure IV.7. Auger spectrum of an oxidized surface of InP (a) before and (b) after H-plasma exposure.
Using the RHEED intensity to determine oxide thickness allowed for the sample to remain in the MBE chamber for the entire etch process. For this method a RHEED image was produced after each plasma exposure and the image recorded by a screen grabber which digitizes the image. The digitized image was used to accurately determine the RHEED intensity. Figure IV.8 shows how the intensity of the specular RHEED streak changes with sequential plasma exposures. The oxide etch rate is calculated by measuring the initial oxide thickness, by AES, and then the sample would be repeatedly exposed to the H-plasma, and RHEED images recorded, until the plateau was observed.

For three samples etched at different temperatures it was observed that the plateau in the RHEED intensity always occurred at the same oxide thickness of 3±0.5 Å. The etch rate is therefore given by the difference between the initial thickness and the thickness at the plateau (3±0.5 Å) divided by the total time of plasma exposures to reach the plateau.

To confirm the reliability of this technique, the same mode was used at the same...
temperature on three different occasions and the measured etch rates proved to be reproducible to within 10%. Modes, other than the two being studied, were used to etch the oxide at a single temperature to obtain a comparison between various modes.

**IV.8 H-PLASMA ETCH IN THE REACTIVE ION ETCH CHAMBER**

The MBE chamber has limited capability for determining the product species of the reaction of the H-plasma with the surface oxides. Thus, to aid in the determination of the reaction mechanism the etching of oxides was also performed in a reactive ion etch (RIE) chamber. The RIE system uses an ECR source built by Wavemat. For a detailed description of the system see reference [IV.4]. The etch chamber is equipped with a secondary ion mass spectrometer located close to the sample surface allowing for direct measurement of the oxide etch products. On several samples a thick oxide was grown by a 30 min. UV/ozone treatment. A sample would be loaded into the RIE chamber and then, with the shutter closed, a H- or D-plasma would be generated. Argon was introduced into the plasma chamber in order to generate a plasma. Once generated, the Ar flow was reduced to 2.8 sccm while the \( H_2 \) (\( D_2 \)) flow was 15.6 sccm, this is the lowest Ar flow that could be used to maintain a stable plasma. The background levels of all relevant masses were determined then the sample shutter was opened and the intensity from various masses recorded. During the etch the intensities from the following species were determined: \( H_2O \), \( P \), \( P_2 \), \( P_4 \), \( PH \), \( PH_2 \), \( PH_3 \), \( P_2O_3 \), \( P_2O_5 \), \( In \), \( InH \), \( InO \), and \( In_2O_3 \).
IV.9 SULFUR PASSIVATION

Sulfur passivation, of the surface of InP, has recently emerged as a potential surface preparation technique for InP. The sulfur surface is very stable and cannot be removed by a thermal desorption process that involves temperatures which will maintain the InP surface integrity. In this study S-passivated surfaces are prepared and characterized then exposed to a H-plasma to determine if the sulfur can be chemically removed by the H-plasma and the resulting surface is compared to that prepared by oxidation of the InP surface and H-plasma removal.

Various preparation procedures for the S-passivation of InP have been reported in the literature. Two recently reported techniques that result in very low oxygen content at the surface were chosen for investigation. The first recipe used is similar to that reported by Lu et al.[IV.5] The samples were initially UV/ozone for 5 min, then placed in 10:1 H₂O:HF to remove the oxide, then thoroughly rinsed in deionized water. Samples were then placed directly into a (NH₄)₂Sₙ solution at 60 °C under 200 W illumination for 15 min. Samples were then thoroughly rinsed with deionized water and dried with N₂.

The second recipe is similar to that reported by Gallet et al.[IV.6] Here the samples are given the same UV/ozone treatment and HF rinse as in the previous procedure. They are then immersed in a solution composed of 1:1 H₂O:(NH₄)₂Sₙ with a few drops of HNO₃. The solution is held at 60 °C and the sample is left in the solution for 10 min. after which it is thoroughly rinsed in deionized water and dried with N₂.
IV.10 COMPARISON OF SURFACE CLEANING TECHNIQUES

To complete a proper evaluation of the surfaces prepared by an H-plasma etch the surface had to be compared in quality to surfaces prepared by other standard surface cleaning procedures. To evaluate a surface cleaning technique the technique would be used to prepare an interface between two epi-layers then post-growth analysis of the interface would be done by CV-profiling and/or SIMS analysis to determine the concentration of electrically active defects and the identity of impurities. Interface state concentrations were determined by integrating the peaks in the CV-profile. A typical sample growth would involve the growth of an initial layer on a substrate then the sample would be brought out to air, where any ex-vacuo treatments would be applied, then re-introduction into vacuum, where any in-vacuo treatments would occur, such as H-plasma cleaning or thermal desorption. Then, further growth of InP would be carried out. Samples generally contained two or three interfaces, each prepared using a different cleaning procedure. Both n- and p-type material was investigated.

The ex-vacuo treatments used are outlined below:

1. Air Exposure: Samples were brought into the loadlock and exposed to atmosphere for 5 min. with the loadlock lid open and the N₂ leak valve shut.

2. UV-Ozone Treatment: Samples were placed in the UV-ozone chamber for 5 min. producing an oxide 7 - 10 Å thick.

3. Acid Etch: Samples were placed in concentrated H₂SO₄ for 5 min. then rinsed
thoroughly with deionized water, and dried with N₂. This is a similar
procedure to that used by Gallet et al.[IV.7].


The in-vacuo treatments are outlined below:

1. **H-plasma Treatment:** The gas flows were 6.5 sccm for the PH₃ and 2 sccm for
the H₂. The current settings for the magnets were 190 A and 130 A for magnet
1 and 2 respectively (this mode has high H⁺ intensity and low ion current).
Microwave power was set at 300 W. The time used for the plasma exposures
varied with different samples and is included with the results.

2. **Thermal Desorption:** Samples were heated under a P₂ overpressure (PH₃ flow
set at 5 sccm) at a rate of 10 °C/min to 500 °C then at 3 °C/min until RHEED
streaks emerged, typically at 525 - 530 °C. The sample was held at this
temperature until a sharp 2x4 RHEED pattern was observed, typically 10 min.
The samples were then cooled to growth temperature.

**IV.11 SUMMARY**

The above procedures were used to determine the usefulness of an ECR
generated H-plasma for the surface cleaning of InP and to compare the technique to
other surface cleaning techniques. Also, the procedures were used to develop an
understanding of the mechanisms involved in H-plasma etching such that the operation
of ECR sources can be better predicted and controlled.
CHAPTER V

RESULTS AND DISCUSSION

V.1 INTRODUCTION

The thermal desorption of UV-ozone oxides from InP is investigated and a thermodynamic model is developed to determine the reaction mechanism and establish a basis for comparison with oxide removal by H-plasma cleaning. The H-plasma is investigated by first measuring the characteristics of the plasma modes to determine how the magnetic field profile affects the plasma characteristics. Then, defect creation on the InP surface by the H-plasma is measured and any dependence of defect level on plasma mode is established. To resolve which plasma properties influence the etch rate of the oxide, a detailed etch study of the H-plasma on the oxides is performed. Experimental results are compared to a thermodynamic model and a mechanism is given. To further explore the use of a H-plasma to produce a clean surface of InP the results of applying a S-passivated surface in conjunction with an H-plasma etch is presented and finally the various surface cleaning procedures are compared and evaluated for possible use as regrowth techniques.
V.2 THERMAL DESORPTION

Figure V.1. Nomarski photographs of the back surfaces of InP substrates. (a) showing thermal decomposition. (b) polished back-side.

The thermal desorption of oxides from InP is a standard part of the surface preparation procedure for most MBE groups; however, there are difficulties associated with thermal desorptions particularly for In-free mounted samples. Depending on the back-side polish, the high temperatures required for thermal desorption can result in thermal decomposition of the back-side. Figure V.1(a) shows a Nomarski photograph of the back-side of a semi-insulating substrate that has thermally decomposed during a thermal desorption. For comparison, a photograph of the polished back-side of a substrate is given in fig. V.1(b). The decomposed back-side will have very different radiative coupling to the heater filaments and generally results in poor quality crystal growth. This problem with In-free mounted semi-insulating substrates provided motivation to fully explore the possibilities of removing the surface oxides at much
lower temperatures using a H-plasma.

V.2.1 THERMODYNAMIC MODEL OF THERMAL DESORPTION

Despite the described difficulties thermal desorptions are commonly used; however, a mechanism for the desorption has not been reported in the literature. The thermal desorption process is a near equilibrium process since the oxide is slowly heated while in constant contact with the substrate and thus, a thermodynamic model should be a reasonably accurate description of the actual process. In the following section the thermodynamic model is based on calculations done using the computer modelling program F*A*C*T. As mentioned in section III.2, to include a compound in a calculation, the F*A*C*T program requires knowledge of $\Delta H_f^o$, $S_{trs}^o$ (can be calculated from $\Delta S_f^o$) and the coefficients of the expression for $C_p$. For the modelling of a UV-ozone oxide on InP, the oxide is assumed to be an InPO$_4$ like oxide, based on the work presented by Besland et al.[V.1]. Although the F*A*C*T program contains thermodynamic data on a tremendous number of compounds, the compound InPO$_4$ is only now being investigated and the thermodynamic properties are not completely known and must be estimated.

In the paper by Schwartz et al.[V.2] the authors estimate the free energy of formation ($\Delta G_f^o$) of InPO$_4$ to be $-287$ kcal/mol. Their estimation is based on the following chemical equation:

$$\frac{1}{2}\text{In}_2\text{O}_3 + \frac{1}{2}\text{P}_2\text{O}_5 \rightarrow \text{InPO}_4$$

(1)
The $\Delta G^\circ_r$ for In$_2$O$_3$ is -198.6 kcal. and for P$_2$O$_5$ is -322.4 kcal.\cite{V.2}. Equation (3) in section III.2 states that:

$$\Delta G_{\text{rx}} = \Sigma \Delta G^\circ_r(\text{products}) - \Sigma \Delta G^\circ_r(\text{reactants}) \quad (2)$$

Neglecting the energy of reaction, that is setting $\Delta G_{\text{rx}} = 0$, the $\Delta G^\circ_r$ for InPO$_4$ can be estimated by performing a mole weighted sum based on equation (1) to give a value of -261 kcal/mol. The extra stabilizing energy of reaction can then be estimated by examining known data from AlPO$_4$ and GaPO$_4$. For example, the formation of AlPO$_4$ can be expressed similar to equation (1):

$$\frac{1}{2}\text{Al}_2\text{O}_3 + \frac{1}{2}\text{P}_2\text{O}_5 \rightarrow \text{AlPO}_4 \quad (3)$$

The F*A*C*T program contains the thermodynamic data for all compounds in equation (3). The $\Delta G^\circ_r$ of Al$_2$O$_3$ is -373.8 kcal. and for P$_2$O$_5$ is -322.4 kcal. combining these values, using a mole weighted sum, gives an estimated value of $\Delta G^\circ_r$ for AlPO$_4$ of -348.1 kcal. However, the actual $\Delta G^\circ_r$ for AlPO$_4$ is -386.5 kcal. the difference between the actual and the estimated is -38.4 kcal. which is the energy of reaction ($\Delta G_{\text{rx}}$). Therefore, for AlPO$_4$ the energy of reaction is $\sim 10\%$ of the estimated value for $\Delta G^\circ_r$. Assuming an energy of reaction that is 10% of the estimated $\Delta G^\circ_r$ for InPO$_4$ gives and improved estimate of -287 kcal/mol. instead of -261 kcal/mol.

Having estimated $\Delta G^\circ_r$ for InPO$_4$ the enthalpy and entropy terms must now be
calculated as it is these terms that are required by the F*A*C*T program. These terms are not currently available in the literature and are estimated here by using a similar procedure to that of Schwartz[V.2]. Both the enthalpy and entropy are estimated by completing a mole weighted sum based on equation (1), then the $\Delta H^o_f$ and $\Delta S^o_f$ can be determined by again examining the data available on AlPO$_4$ and GaPO$_4$ giving a final thermodynamic equation for InPO$_4$ of:

$$\Delta G_f = -315000 + 94.0T \text{ (gives } -287 \text{ kcal @298 °C})$$

All terms are expressed in calories.

The F*A*C*T program also requires the density and the specific heat equation. Both of these can be determined by performing a mole weighted sum based on known values of the reactants in equation (1). The density is calculated to be 4.187 g/cm$^3$.

The general form of the specific heat equation is:

$$C_P = \sum_{n=1}^{a} A_n T^{\beta_n}$$

Only the first three terms are important and the calculated values for InPO$_4$ are obtained by performing a mole weighted sum from the terms for In$_2$O$_3$ and P$_2$O$_5$.

Estimating the heat capacity coefficients based on data from other compounds is known as Kopp's theorem[V.3]. The thermodynamic properties for InPO$_4$ are shown.
Table V.1. Summary of thermodynamic properties of InPO$_4$.

<table>
<thead>
<tr>
<th>Free Energy Terms @ 298 °C (cal.)</th>
<th>Dens. (g/cm$^3$)</th>
<th>Specific Heat Terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G_r$</td>
<td>-287000</td>
<td></td>
</tr>
<tr>
<td>$\Delta H_r$</td>
<td>-315000</td>
<td></td>
</tr>
<tr>
<td>$\Delta S_r$</td>
<td>-94.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.187</td>
<td>n 1 18.985 0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>n 2 2.795$x10^2$ 1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>n 3 -2.755$x10^5$ -2</td>
</tr>
</tbody>
</table>

in table V.1. Having entered the thermodynamic data into the F*A*C*T program it is possible to obtain a variety of thermodynamic information on reactions involving InPO$_4$.

The F*A*C*T program "equilibrium", permits the user to enter any group of reactants and the program calculates the equilibrium mixture for those reactants. The compound InPO$_4$ was entered into this program as the only reactant and various reaction temperatures were specified from 100 °C to 800 °C (see section III.2 for the principles used for the calculations). This calculation was performed to determine the decomposition temperature of the oxide. No restrictions were placed on the possible products and therefore, the product list would include the various forms and states of In and P as well as the sub-oxides of In and P and the compound InP. The program determines which, of all possible mixtures of the various compounds, has the lowest Gibb's free energy and is therefore the most stable. At all temperatures the equilibrium mixture was calculated to be composed entirely of InPO$_4$, indicating that, based on thermodynamic considerations, the compound is stable well beyond
temperatures normally associated with the thermal desorption of the oxide (525-565 °C). This is in agreement with the results presented by Schwartz[V.2] who reported that InPO₄ is stable to 900 °C. Therefore, InPO₄ alone is thermally very stable and some other mechanism must cause the desorption of the oxide other than simple decomposition.

Having determined that InPO₄ is a stable compound, the reactants InPO₄ and InP were entered into the "equilibrium" program to resolve whether a reaction of the oxide with InP could cause the decomposition of the oxide. Again, the equilibrium mixture was calculated at various temperatures. At low temperatures (<450 °C) the calculated mixture was composed entirely of the reactants indicating no reaction will occur. At temperatures close to experimental thermal desorption temperatures, the equilibrium mixture was calculated to be composed of volatile P₂O₃, some In gas and In liquid; therefore, since InPO₄ alone did not decompose at these temperatures, the presence of InP is causing the decomposition of the oxide. This is an encouraging result as the thermodynamic properties of InPO₄ were estimated yet the calculated thermal desorption temperature is close to what is observed experimentally.

To further resolve the desorption mechanism, the program was used to react InPO₄ with pure In. Throughout the temperature range of 100 °C to 800 °C the equilibrium mixture for these two reactants was composed entirely of the two reactants therefore, the In does not affect the thermal stability of the oxide. InPO₄ was then combined with atomic P, and this reaction resulted in the same products forming at the same temperature as the previously calculated reaction of InPO₄ with InP. Thus, based
on these various calculations, the following reaction is proposed as the reaction
causing the thermal desorption of InPO$_4$ from InP at 525 °C:

$$3\text{InPO}_4 + 5\text{P} \rightarrow 4\text{P}_2\text{O}_3(\text{g}) + 3\text{In(\text{g/l})}$$ (6)

For this reaction the phosphorus is driving the desorption of the oxide thus, to
complete the description of the actual mechanism the source of atomic phosphorus
must be known.

During thermal desorption, the substrate is heated under an overpressure of $P_2$.
Thus, the source of atomic P could be supplied from the overpressure by $P_2$ molecules
cracking on the surface of the oxide. The F*A*C*T program "reaction" was used to
determine the reaction free energy change for the reaction of InPO$_4$ with $P_2$. The $\Delta G_{\text{ran}}$
for the reaction is -24 kcal/mol of InPO$_4$ compared to -166 kcal/mol of InPO$_4$ for
reaction of InPO$_4$ with atomic P. Both reactions have a negative $\Delta G_{\text{ran}}$, indicating that
the reactions are favourable and, as would be expected, the reaction with atomic P has
a much larger negative $\Delta G_{\text{ran}}$ since the reaction with $P_2$ would require the breaking of
the P-P bond which requires additional energy. The reaction with atomic P is
expected to be favourable kinetically again, because the breaking of the P-P bond is
not required.

Atomic phosphorus could originate from two sources, it could be produced
along with $P_2$ by the cracking of PH$_3$ in the gas cracker also, the temperature required
for thermal desorption is above the congruent sublimation temperature and therefore,
there is a preferential loss of phosphorus from the substrate that could diffuse into the oxide layer. If either of these sources is supplying significant amounts of atomic P to the oxide then this would provide the driving force for the desorption.

V.2.2 EXPERIMENTAL RESULTS OF THERMAL DESORPTION

To determine if the cracking of \( P_2 \) on the oxide surface is required for the desorption reaction to proceed the first series of experiments involved replacing the \( P_2 \) overpressure with \( As_2 \). This should result in a different reaction rate as the bond dissociation energy for P-P is 117.0 kcal/mol. and for As-As is 91.3 kcal/mol.[V.4] In general, the equation governing the kinetics of a reaction can be written as follows:

\[
K = A e^{\frac{E_a}{kT}}
\]

(7)

where \( K \) is the rate constant, \( A \) is a constant, \( E_a \) is the activation energy, \( k \) is Boltzmann's constant and \( T \) is the temperature. If dissociation of the diatomic species is required for oxide desorption then the bond dissociation energy will determine the activation energy for the desorption reaction and a significant difference in the reaction rate, between \( As_2 \) and \( P_2 \) overpressures would be expected with the reaction with \( As_2 \) being more rapid due to the lower bond energy. The McMaster MBE chamber is equipped with both \( P_2 \) and \( As_2 \) sources thus, there is a unique opportunity to investigate the desorption reaction under both overpressures. Figure V.2 shows the
Figure V.2. AES spectrum of an oxidized InP surface (a) before and (b) after thermal desorption under a $P_2$ overpressure.

Auger spectra of an oxidized layer of InP and the same surface after it has been subjected to the thermal desorption cycle outlined in the experimental section. From the height of the oxygen peak, the oxide was calculated to be initially 20 Å thick. The thermal cycle used is generous for the desorption under $P_2$ as the sample was being ramped at 1 °C/min. and the 2x4 RHEED pattern, which indicates a clean surface, was observed at 528 °C and yet sample heating continued to 532 °C. The Auger spectrum of the thermally desorbed surface indicates that no detectable oxide is present.

The same thermal cycle that was used with the $P_2$ overpressure was applied to an oxidized layer under an $As_2$ overpressure. The 2x4 RHEED pattern was not observed during the thermal cycle. In figure V.3 the Auger spectrum of the oxidized
Figure V.3. AES spectrum of an oxidized InP surface (a) before and (b) after thermal desorption under an As$_2$ overpressure.

layer, also calculated to be initially 20 Å thick, is shown along with the same surface after the thermal cycle. It is evident that significant oxide is still present at the surface after the thermal cycle. Spectra taken from different positions on the substrate surface indicate that the oxide is somewhat non-uniform. The calculated average thickness is 2±1 Å. Arsenic, which has a Auger electron yield approximately 8 times less than phosphorus, was also detected at the sample surface. A comparison of figures V.2 and V.3 demonstrates that the overpressure species used during the desorption does affect the removal of the oxide.

To further resolve the thermal desorption mechanism, XPS measurements were taken of an oxidized substrate after varying degrees of desorption under an As$_2$
Figure V.4. XPS spectrum of an oxidized surface of InP showing various stages of thermal desorption under an As$_2$ overpressure.

overpressure. The XPS spectrum of the initial surface is shown in figure V.4(a).

Using the procedure presented by Hollinger et al.[V.5], the oxide was calculated to be
initially 19 Å thick. The energy position and widths of the O1s, In3d and P2p peaks are characteristic of InPO₄-like oxides, that form by thermal oxidation[1]. Figure V.4(b) shows the same surface after the sample had been heated to 525 °C for 3 minutes. At this point the oxide was calculated to be 13 Å thick. The positions of the various peaks are the same as that in figure V.4(a) indicating that the oxide has retained its initial chemical structure. Also, very weak arsenic peaks are detected and RHEED measurements revealed a faint 2x1 surface reconstruction. The energy shift of the As peaks are indicative of As bound to In. Figure V.4(c) is the same surface after the sample had been heated to 525 °C for 12 minutes. From this XPS spectrum the oxide is calculated to be 3 Å thick. RHEED measurements revealed a 2x4 surface reconstruction with very faint intermediates in the x4 pattern. Arsenic is detected at the surface and again, the energy shift of the As peaks is indicative of As bound to In. No As bound to O is observed in any of the spectra. Incoming As is therefore bonding to either free In, that is produced as the oxide desorbs, or to In in the substrate as holes appear in the oxide. The 2x1 RHEED pattern observed after 3 min. of desorption along with the XPS spectra (figure V.4(b)) indicates that the oxide has desorbed inhomogeneously and that oxide free regions with the surface composition InAs have formed.

It is evident, from the experimental results, that the overpressure species influences the thermal desorption process and it appears, at least in the case of an As₂ overpressure, that As does not bond to O but, only to In in the substrate once holes in the oxide have formed. The fact that no As is observed to be bound to the oxide
could indicate that the overpressure does not significantly react with the oxide itself. It was observed here, as it was by Averbeck et al.[V.7], that the bulk of the oxide desorbs at a similar rate regardless of the overpressure, only the last few Angstroms require a higher temperature with an As$_2$ overpressure. This confirms that the diatomic overpressure species, As$_2$ or P$_2$, does not significantly contribute to the desorption for the bulk of the oxide.

It is possible that the gas cracker could provide small amounts of atomic phosphorus, from the cracking of PH$_3$, which would lead to desorption. To resolve whether the source of atomic P which gives rise to the desorption reaction is from the gas cracker, and therefore the overpressure, or the substrate, is difficult since it is likely both the substrate and the overpressure contribute to the desorption reaction. However, several observations imply that the contribution from the overpressure is minimal. The XPS results indicate that desorption in an As$_2$ overpressure does not result in any oxidized arsenic on the surface, only arsenic bound to In. According to equation (6) the oxygen from the oxide is removed as P$_2$O$_3$ and the oxide has the approximate composition InPO$_4$. Thus, for the volatile species to form, additional phosphorus or arsenic must bond to oxygen. If arsenic from the overpressure is driving the reaction then the oxygen would be lost as As$_2$O$_3$ or PAsO$_3$ and one would expect to observe oxidized arsenic in the x-ray spectra but, this is not observed. Also, Comedi et al.[V.6] observed that the phosphorus content in the oxide increases with increasing temperature prior to any thinning of the oxide (their measurements were done without any overpressure). Therefore, it is evident that atomic P does diffuse
from the substrate into the oxide and must provide the dominant driving force for the desorption reaction.

It was observed, from the AES results, that the final monolayer or less of the oxide is more difficult to remove in an As$_2$ overpressure than in a P$_2$ overpressure. This is explained by the observations that the thinning of the oxide is non-uniform and that As is bound to In as the oxide is thinning. The non-uniform thinning implies that holes in the oxide form during the desorption and these holes increase in diameter until desorption is complete. Since InAs is more stable than InP, the InAs that forms in exposed regions of the substrate would reduce the reaction rate at the dangling bonds that are at the edge of the holes in the oxide also, the desorption rate would be slowed by As diffusing through the oxide to occupy a P vacancy, which would slow the desorption of the group V atom from the substrate. This is the mechanism that results in the slower desorption of the oxide carried out under an As$_2$ overpressure.

The conclusion that the reaction of phosphorus with the oxide is driving the desorption is in slight disagreement with the phase diagram presented by Schwartz et al.[V.2] (figure III.1). In their diagram the mixture of solid phosphorus with InPO$_4$ is considered a stable mixture. This discrepancy is easily explained. In the paper by Schwartz they report the $\Delta G_{\text{mix}}$ for the reaction of P with InPO$_4$ to be 102 $\pm$ 121 kcal at 298 °C. This is in agreement with calculations using the F*A*C*T program which also indicates that at room temperature there is minimal reaction between P and InPO$_4$, only at higher temperatures does the reaction proceed. Schwartz et al.[V.2] placed solid phosphorus in a sealed tube with InPO$_4$ and heated it to 900 °C for several days
then washed the products in HNO₃, which dissolves all products except In₂O₃, InPO₄ and In(PO₃)₂. They observed that InPO₄ remained and concluded that the mixture of P and InPO₄ is stable.

With the F*A*C*T program calculations atomic P was reacted with InPO₄, instead of solid phosphorus, because this is closer to the experimental situation. The reaction with atomic P is more thermodynamically favourable than with solid P as no bonds need to be broken for a reaction with the atomic species. It should also be noted that an equilibrium mixture of phosphorus and InPO₄ may contain both InPO₄ and P₂O₅. In a vacuum system, such as an MBE chamber, the volatile product P₂O₅ would be pumped away and the reaction would proceed to replace the removed product and in this way, the reaction can be driven to completion. Also, in vacuum environments, metastable species could form that would normally react further to form the thermodynamically favoured products; however, since there are virtually no collisions with other species the metastable species could exist until they are effectively pumped away. However, equation (6) will still represent the major products responsible for the desorption of the oxide. Based on the above discussion, the phase diagram in figure V.5

![Figure V.5. Proposed phase diagram of the In-P-O system.](image-url)
represents the In-P-O system when the volatile P₂O₅ is included. This diagram was suggested by Schwartz[V.2] but, was ruled out for the condensed phase diagram based on the evidence given above. Note that in figure V.5 the reaction of InPO₄ with P is expected to produce P₂O₅ and InP; however, for the phase diagram the equilibrium mixtures are assumed to be at room temperature whereas, equation (6) represents the reaction of InPO₄ with P above the congruent sublimation temperature of InP such that InP is not considered stable.

In equation (6) above, the P from the oxide is lost as a volatile product but, the question remains as to what happens to the In from the oxide. The following calculation was done to determine if free In, that may result from the oxide desorption, remains at the surface or has sufficient vapour pressure to evaporate. The vapour pressure of In on InP was taken from a paper by Farrow[V.8] and the following equation was used to determine the rate of evaporation:

\[
Rate = 3.51 \times 10^{22} \left( \frac{P_{\text{torr}}}{\sqrt{MT}} \right) \text{ molecules/cm}^2\text{s}
\] (8)

where T is the temperature and M is the molar mass of In. It was determined that the amount of free In that would result from the decomposition of 10 Å of oxide would evaporate in 2.6 minutes at a temperature of 530°C. This calculation is in agreement with what was observed by Comedi et al[V.6]. Therefore, it is possible that the In from the oxide will evaporate as opposed to remaining on the surface to form In-balls.
or combine with incoming P or As to form InP or InAs.

On the basis of the above discussion, it is concluded that the most likely reaction pathway for the thermal desorption of InPO$_4$ from the surface of InP is via equation (6) where phosphorus from the substrate reacts with the oxide to form volatile P$_2$O$_3$ and the remaining In is volatile enough that it will evaporate from the surface. Desorption under a P$_2$ or As$_2$ overpressure is equivalent for the bulk of the oxide but, once regions of the substrate are exposed As will replace P in the substrate making removal of the final few Angstroms of oxide more difficult.

V.3 CHARACTERIZATION OF THE H-PLASMA

Before the in-situ H-plasma was used to remove oxides from InP the various operating conditions of the H-plasma were thoroughly characterized such that the etching behaviour of different plasma modes could be correlated to the properties of the mode. The initial operation of the ECR source revealed some interesting features of this system. It was observed that when the microwave power is applied the reflected power is approximately equal to the forward power until the magnetic field is strong enough to create a resonant condition. This would indicate that the microwave power cannot initially propagate into the resonant cavity. This is expected since the cavity diameter is smaller than the cutoff diameter for the applied frequency (see section II.5.2) but it is an important point in the discussion of plasma generation.

Also, it was observed that the ECR apparatus exhibits hysteresis and multimodal behaviour. However, we have found experimentally that the same mode
can be reproduced if care is taken in configuring the magnetic field while monitoring the microwave reflected power and ion current. Occasionally, it would be necessary to pursue certain modes where these modes could only be produced by approaching them from a region of higher magnetic field and then slowly reducing the field or by slowly decreasing the microwave power, as opposed to increasing it. Generally, it is important to be aware of the hysteresis and multimodal behaviour and let the plasma properties determine the operating conditions.

V.3.1 LANGMUIR PROBE RESULTS

Several different plasma modes were characterized by Langmuir probe scans, using different gas flows and magnetic field profiles. Figure IV.3 is an example Langmuir scan of a H-plasma. The methods for determining various plasma properties are described in section IV.4. A summary of the measured and calculated plasma properties are presented in table V.2 where $N_e$ is the plasma density, $T_e$ is the electron temperature, $V_f$ is the floating potential, $V_p$ is the plasma potential, $T_i$ is the ion temperature, and $I_i$ is the ion current.

The measured

<table>
<thead>
<tr>
<th>Property</th>
<th>Range</th>
<th>Typical Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_e$ (cm$^3$)</td>
<td>1 - 7\times10^7</td>
<td>4\times10^7</td>
</tr>
<tr>
<td>$T_e$ (eV)</td>
<td>3 - 10</td>
<td>5</td>
</tr>
<tr>
<td>$V_f$ (V)</td>
<td>(-3) - (-45)</td>
<td>-15</td>
</tr>
<tr>
<td>$V_p$ (V)</td>
<td>(-10) - 12</td>
<td>4</td>
</tr>
<tr>
<td>$T_i$ (eV)</td>
<td>10 - 30</td>
<td>19</td>
</tr>
<tr>
<td>$I_i$ (\muA)</td>
<td>0.3 - 3</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table V.2. Summary of plasma properties measured by a Langmuir probe.
plasma properties, as determined by the Langmuir probe, were found to be insensitive to the PH$_3$ gas flow as long as a H$_2$ flow of 2 sccm or greater was maintained into the resonant cavity. Lower H$_2$ flow led to unstable plasmas.

For all plasma modes the plasma density is very low, it is much lower than the critical density of 7.4x10$^{10}$ cm$^{-3}$ where maximum microwave power absorption would occur (see section II.5.2). This is expected due to the low hydrogen pressure in the resonance cavity and the fact that the Langmuir probe is so far downstream that recombination and diffusion will result in significant decay of the plasma. The low plasma density results in significant noise on the Langmuir probe scans. However, several plasma modes were observed to be stable, more specifically, the Langmuir probe scan was stable with time and virtually the same scan characteristics could be generated with the same experimental settings on different days. It was observed that the ion current, at -100 V, was the most consistent property and the least susceptible to noise and therefore, it became one of the benchmark properties used in characterization of the plasma modes (see following results).

The plasma potential and the electron temperature measured for the various plasmas all fell within a relatively small range and essentially within the experimental error of the Langmuir probe measurements. This small variation in these parameters is expected as both are dependent on the electron kinetic energy in the resonance zone and the magnetic field gradient from the resonance zone to the Langmuir probe. The electron kinetic energy will depend on the amount of absorbed microwave power. The Langmuir probe position is far enough away from the resonant cavity that the field
strength at the Langmuir probe is fairly weak and remains approximately constant regardless of the field strength in the resonant cavity. Due to the large distance between the resonant zone and the Langmuir probe both the electron temperature and the ion temperature are expected to be low, as is observed. Recall from section II.5.7 that in the presence of a magnetic field, the mean free path within the plasma is the electron orbital radius and that at 875 G the electron radius is \( \sim 1 \) mm and at 25 G the radius \( \sim 35 \) mm. Therefore, since these dimensions are less than the chamber dimensions, collisions will occur in the plasma stream that reduce the average energy of ions and electrons reducing in turn the temperature of these species.

V.3.2 OPTICAL EMISSION MEASUREMENTS

For examples of optical emission spectra and a description of the techniques used to obtain the spectra see section IV.4. For all optical emission measurements the configuration of the measuring fibre on the chamber view ports was such that the optical emission measurements are reflective of the excited species that are in the MBE chamber and not the ECR source. The intensity of the hydrogen peak at 656 nm was used to compare the relative abundances of atomic hydrogen in the different plasma modes.

V.3.3 EFFECT OF MICROWAVE INPUT POWER

Figure V.6 shows the change in ion current and H* intensity with increasing microwave power for one plasma mode. The H* intensity saturates above \( \sim 300 \) W
whereas, the ion current continues to increase to \( \sim 450 \) W. The fact that both saturate indicates that the plasma density limits the amount of microwave power that can be absorbed by the plasma. Similar results have been obtained with other modes. Typically, the reflected power is 0.3 - 0.5 times the input power and thus, higher input power results in greater heating of the water cooled block that absorbs the reflected power, known as the dummy load, which can result in the melting of the cooling lines. For this reason and the fact that the production of atomic H saturates at \( \sim 300 \) W, the remainder of the plasma characterization was done with the input power set at 300 W.

**V.3.4 CHARACTERIZATION OF PLASMA MODES**

To characterize plasma modes with the same gas flows and different magnetic field profiles, narrow region OES scans, from 645 nm to 665 nm, of the H\(^+\) peak at 656 nm were recorded. The measured intensity of the hydrogen peak along with the ion current, measured at -100 V, and the reflected power for all families of plasma
modes are presented in figures V.7 - V.11. The measured plasma properties are plotted against $I_2$, the current to magnet 2. The graphs represent the full range of plasma conditions possible for this ECR system as higher current settings are not possible and lower current settings do not result in plasma generation.

It is evident that for every grouping of modes there is a distinct current setting where the reflected power reaches a minimum. The magnetic field profiles for the current settings that produce this maximum power absorption are shown in figure V.12. The maximum microwave power absorption occurs when the resonant field (875 G) is at the plasma window and therefore, these are labelled the "true" resonant modes. Modes where the resonant field was not at the microwave window but, plasma generation still occurred are considered non-resonant modes.

![Graph](image)

**Figure V.7.** Properties of family of modes with $I_1=160$A.
Figure V.8. Properties of family of modes with I1=170A.

Figure V.9. Properties of family of modes with I1=180A.
Figure V.10. Properties of family of modes with I1=190A.

Figure V.11. Properties of family of modes with I1=210A.
It is also observed in figures V.7 - V.11 that modes with maximum microwave power absorption (minimum reflected power), the true resonant modes, correlate with the maximum production of H⁺. There are two reasons why the maximum microwave power absorption corresponds to the maximum production of atomic H. First, the dissociation energy of H₂ (4.5 eV) is less than the ionization energy of H or H₂ (13.6 eV and 15.4 eV[V.11] respectively). Therefore, dissociation will be an efficient way for the electrons to distribute energy to the plasma gas since, dissociation requires a smaller fraction of the electron energy. Secondly, low reflected power, which corresponds to high microwave power absorption, implies a high ionization efficiency. It was stated in section II.5.3 that the extent of plasma decay through recombination is greater with higher ionization yield and thus, more recombination of H⁺ and e⁻ and

Figure V.12. Magnetic field profiles of the "true" resonant modes. The magnet current settings (I1/I2) are indicated.
dissociative recombination of H$_2^+$ and e$^-$ is expected when low reflected power is observed.

Further examination of the field profiles for the resonant modes (fig. V.12) reveals that modes with a field greater than 875 G, at magnet two, results in an overlap of maximum ion current and maximum H$^+$ (modes with current settings 160A/190A, fig. V.7 and 170A/170A, fig. V.8). Having a magnetic field strength greater than 875 G at the down stream magnet is known as mirror field confinement (see section II.5.5) and results in containment of electrons in the resonant zone leading to greater ionization efficiency and therefore, higher ion currents. When the current to magnet two decreases below the mirror field condition the maxima in the ion current and the H$^+$ intensity, for a family of modes, occur at different current settings, such as is the case when I$_1$ = 190 A (fig. V.10) or 210 A (fig. V.11).

A comparison of the properties of the true resonant modes further reveals the effect the magnetic field profile has on the plasma properties. Table V.3 is a summary of the true resonant mode properties. The field profile can be considered in two regions; through the resonant zone and from the resonant zone to the substrate. It was stated in section II.5.5 that a shallow magnetic field gradient at the ECR zone produces a larger resonant zone and therefore, higher microwave power absorption. The resonant mode with current settings 160A/190A has the most shallow gradient through the ECR zone and the lowest reflected power, as expected. Modes with a steeper gradient through the ECR zone (higher current setting at magnet 1) have reduced microwave power absorption and therefore, lower plasma densities.
Table V.3. Summary of plasma properties for the true resonant modes.

<table>
<thead>
<tr>
<th>Current Settings (I₁/I₂ Amps)</th>
<th>Reflected Power (W)</th>
<th>Ion Current (µA)</th>
<th>H⁺ Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>160/190</td>
<td>83</td>
<td>1.5</td>
<td>2.1</td>
</tr>
<tr>
<td>170/170</td>
<td>110</td>
<td>2.0</td>
<td>2.7</td>
</tr>
<tr>
<td>180/145</td>
<td>122</td>
<td>1.7</td>
<td>3.0</td>
</tr>
<tr>
<td>190/130</td>
<td>126</td>
<td>1.0</td>
<td>2.6</td>
</tr>
<tr>
<td>210/105</td>
<td>153</td>
<td>1.8</td>
<td>2.2</td>
</tr>
</tbody>
</table>

It was also stated in section II.5.5 that a shallower gradient between the ECR source and the substrate delivers a higher density plasma downstream. For the ECR system used for this study a low current at magnet 2 is required to produce a shallow gradient from the ECR zone to the substrate. However, the magnetic field from each magnet is additive thus, a low current at magnet 2 requires a high current at magnet 1, and therefore a steep gradient, in order to achieve the resonant condition. A steep gradient through the ECR zone will result in reduced absorption of microwave power and therefore, a lower plasma density as is observed for the mode with current settings 210A/105A. Thus, for this system, the resonant mode properties at the substrate are a compromise. The system configuration is such that there must be either efficient generation of the plasma and poor delivery to the substrate or lower initial density and more efficient delivery of the plasma to the substrate. A mode such as the one with current settings of 180A/145A will have a lower plasma density at the resonant zone.
than the mode with current settings of 160A/190A, as evidenced by the reflected power but, a greater amount of H\textsuperscript+ is achieved at the substrate due to the shallower gradient between the resonant zone and the substrate.

The effect of the magnetic field profile between the ECR zone and the substrate can be understood by considering Matsuo's formulation (equation (25), section II.5.5). It was stated there that the magnetic field gradient accelerates the electrons causing separation of the ions and electrons which generates an electric field that accelerates the ions. Thus, the steeper the field gradient away from the resonant source, the greater the separation of ions and electrons which results in higher ion energies and less recombination will occur in the plasma stream. This is consistent with the results of Fujiwara et al.[V.12] where they found that the Cl\textsubscript{2} plasma etch rate of Si improved in magnitude and uniformity with a shallower gradient between the ECR source and the substrate. The higher rate can be attributed to the higher production of atomic neutral species with a shallow gradient and the greater uniformity is attributed to the narrower energy distribution obtained. Etching with a H\textsubscript{2} plasma is expected to be similar to etching with a Cl\textsubscript{2} plasma as both involve a diatomic species for generation of the plasma and both will have a reactive atomic neutral species in the plasma stream.

Mirror field confinement must also be considered in discussing the response of the plasma to the magnetic field. As discussed above, mirror field confinement results in higher ion currents than when the mirror field is not present. However, it appears that mirror field confinement is a minor effect compared to the magnetic field gradient
at the ECR zone and between the ECR zone and the substrate.

It is evident that the ECR source can produce a variety of plasma modes with different properties which undoubtedly makes the operation of the ECR source complicated but, more importantly, enables the operator to generate plasmas with specific, desirable properties.

V.4 EFFECT OF THE H-PLASMA ON InP

It is known that the application of a H-plasma to InP can deplete the substrate of phosphorus[V.13-15] and passivate dopants[V.16-25]. Therefore, having determined that the H-plasma can be configured with various properties it is necessary to determine what detrimental effects the H-plasma may have on InP and whether any defects produced can be minimized by an appropriate selection of the plasma mode.

To determine the effect different H-plasma modes have on InP, several samples were prepared. Of the first two samples one was p-type, doped $5 \times 10^{17}$ cm$^{-3}$, and the other n-type, doped $2 \times 10^{17}$ cm$^{-3}$. Both samples, containing 3 different interfaces, each separated by 0.5 μm of material, were grown by MBE. At each interface a different plasma mode was used. All plasma treatments were done for the same amount of time at the same temperature. The samples were characterized using electrochemical etching and CV profiling to determine the dopant concentration as a function of depth. The profile of the p-type sample is seen in figure V.13 and the n-type profile in figure V.14. The ion current of the plasma and the optical intensity of the atomic H transition are indicated in the figure captions. The defect concentration at each
interface is indicated in $\text{cm}^2$. It is evident that different modes will produce different defect levels in the InP. Generally, it was observed that the higher the ion current the greater the number of defects produced. These defects appear to be donor-like in behaviour.

It is interesting that the same number of defects are not produced in p-type material as in n-type material. This observation is at least partially attributable to an instrumental effect. The CV-profiler requires illumination to etch n-type material such that when the illumination is removed, and the CV measurements made, no residual etching of the material can occur. This process results in well defined profiles and accurate CV measurements. With p-type material the illumination is not required for
Figure V.14. CV-profile of n-type material. $I_i$ in $\mu A$, and the $H^*$ intensity at each interface was: 1: $I_i=2.5$, $H^*$=background, 2: $I_i=1.7$, $H^*$=2.7, 3: $I_i=0.8$, $H^*$=2.6.

etching only an applied bias; however, when the bias is removed, and the CV measurements made, some residual etching can still occur. Consequently, this results in a lower quality profile and thereby lower resolution of the interface measurements. To check the quality of the profiles intentional doping steps were included in the material; one between the surface and the first interface and the other between the final interface and the substrate. The two dopant steps in the n-type material (figure V.14) are both well defined but, with the p-type material(figure V.13) the step near to the substrate is not well defined.

To determine the effect the gas flow ratio ($PH_3/H_2$) has on the plasma treatments, n- and p-type InP samples were grown containing three interfaces each and
Figure V.15. CV-profile of p-type material. The PH$_3$/H$_2$ ratio at each interface was: Interface 1-1.5/1, interface 2-2.5/1 and at interface 3-3.2/1. Defect concentrations are indicated in cm$^{-2}$.

again each interface was separated by 0.5 μm of material. At each interface the same plasma mode was applied but, the gas flows were varied. The H-plasma mode used was one with low ion current and high H$^+$ optical intensity. Figures V.15 and V.16 are CV profiles of the two samples. The defect concentration at each interface is indicated in cm$^{-2}$. It is clearly evident, particularly with the n-type sample, that a high PH$_3$/H$_2$ ratio is required to minimize the number of electrically active defects. It appears that phosphorus etching from the substrate does occur and must be compensated for with excess P$_2$. Also, in an independent experiment, RGA analysis of the gases in the plasma stream indicated that the plasma converts some P$_3$ into a hydride species, which has a low incorporation rate into InP, and this is an additional
Figure V.16. CV-profile of n-type material. The \( \text{PH}_3/\text{H}_2 \) ratio at each interface was: Interface 1-1.5/1, interface 2-2.5/1 and at interface 3-3.2/1. Defect concentrations are indicated in \( \text{cm}^2 \).

reason to ensure a large excess of \( \text{P}_2 \) is flowing into the MBE chamber.

It is also evident from figures V.13 - V.16 that the plasma will produce a significant number of electrically active defects if it is not properly configured. Even with the appropriate plasma properties and gas flows some compensation is evident in p-type material. This is probably due to the formation of P-vacancies from the etching of phosphorus from the InP. P-vacancies are reported to be deep donors producing a donor level 0.35 eV from the conduction band[V.26]. A deep donor would explain the depletion of carriers in p-type material but does not explain the carrier increase in n-type material. The P-vacancy is also reported to create energy levels close to and within the conduction band [V.26] but the charge state of these levels is unknown. It
is possible that with higher defect concentrations the energy levels close to the conduction band will behave as shallow donors and create the spike of n-type carriers observed in the n-type material. The important observation is that the H-plasma can be configured to minimize the number of defects produced. In n-type material electrically active defects can be virtually eliminated; however, the same gas flow result in a small amount of defects still present in p-type material which could indicate that the formation of P-vacancies cannot be entirely prevented with the range of gas flows possible with MBE system used here.

Figure V.17 is a SIMS profile of a p-type sample containing a single, plasma exposed interface, showing a small silicon peak at the interface. The presence of silicon would explain the effects seen in figures V.15 and V.16; however, the silicon level does not appear high enough to produce all the defect levels seen in either the n-
type or p-type material and therefore, P-vacancies may still be present even at the highest PH$_3$/H$_2$ ratio. The highest PH$_3$/H$_2$ ratio used is essentially the functional limit of the apparatus for maintaining a stable plasma. The large quantity of silicon observed at the substrate interface is possibly introduced by the manufacturer during the polishing of the substrates.

It has been observed on other samples that, for a given plasma mode, the longer the exposure time to the plasma, the greater the number of defects, as would be expected. In addition, for plasma exposures at 250°C the surface of a subsequently grown layer will have a high concentration of defect clusters, as observed under an optical microscope. These clusters are not observed when plasma exposures are carried out at temperatures greater than 400°C. This observation is attributable to free indium, from the oxide, that may bond together forming defect clusters at low temperature whereas, at high temperatures the indium has sufficient mobility to bond with incoming phosphorus at a crystal site or be removed by the H-plasma.

Hydrogen is known to passivate dopants in InP[V.16-25]. The effect is more pronounced in p-type material than in n-type[V.16]. Generally, the electrical activity of passivated dopants is recovered with anneals of 400-450°C, which is below the InP growth temperature. Also, the hydrogen passivation of Be specifically, in InP, is thought to be of minor significance[V.17]; however, it has been observed that hydrogen remains present in Be-doped samples, even after anneals to 850°C but, it does not appear to affect the electrical activity[V.17]. No significant passivation effects were observed with any of the MBE samples grown here probably because the
growth temperature is higher than the re-activation temperature for most dopants. Therefore, the hydrogen should readily diffuse throughout the samples even though the H-plasma is only applied at static surfaces.

To determine the distribution of hydrogen in the samples, a deuterium plasma was used since hydrogen levels are very difficult to quantify by SIMS. Two Be-doped samples were produced on Zn-doped substrates. The first was grown to determine if longer exposures to the plasma leads to greater accumulation of hydrogen and the second was grown to assess whether the hydrogen level showed any correlation to the doping level. Neither sample was removed from the MBE chamber until after completion of the full structure. The first sample had a constant doping level of \(5 \times 10^{17} \text{ cm}^{-3}\) throughout and contained two interfaces. At the first interface the plasma was applied for 5 minutes and at the second for 2 minutes. The SIMS analysis of the Si, Be and D content is shown in figure V.18. Again, silicon is observed at the interfaces indicating that this will contribute to the interface depletion observed in p-type material. There is a greater amount of silicon observed here than with the H-plasma because the higher mass D will have a higher sputtering yield of the impurity source which may be the quartz microwave window, although this would imply that the BN coating on the window is depleted, or Si which is present on the chamber walls. Again, the Si at the substrate is attributed to the manufacturer's polish. The larger Si peak at interface 2 is due to the longer plasma exposure. Other than the two doping steps the Be doping level is constant throughout the grown layer. The substrate is Zn-doped to \(1-2 \times 10^{18} \text{ cm}^{-3}\) (not shown in the figure). The deuterium
Figure V.18. SIMS profile of a p-type sample with two D-plasma treated interfaces. Plasma exposures were for 1.2 min. and 2.5 min.

The D profile is accurate to within a factor of 2 and the level is greater than an order of magnitude lower than all the doping levels.

The second Be-doped sample contained three interfaces. At each interface the D-plasma treatment was exactly the same but, the Be-doping level was different. The sample was produced with three ~0.5 μm thick layers, each with a different doping level. At the mid-way point in each layer, growth was interrupted and the surface was exposed to the D-plasma for 2 minutes. The SIMS analysis of this sample is seen in figure V.19. The Be profile reveals important information on the behaviour of Be in
InP. The Be in the layer with the highest doping has diffused well into the adjacent layer and into the substrate. This indicates that this doping level is close to the solid solubility limit of Be in InP. The Be peaks in the centre of this layer (where the D-plasma exposure occurred) and at the substrate are probably due to the diffusing Be accumulating at defect states at the two interfaces or, for the peak in the centre of the layer, it could be that during growth there is surface segregation of Be that must be maintained to achieve high doping and at the growth interrupted interface the high surface concentration of Be becomes trapped.

The Si profile exhibits peaks that are at approximately the same level at each interface and there is a much higher peak at the substrate. From the D profile in
figure V.19 and figure V.18 it is evident that at growth temperature the deuterium (or hydrogen) will incorporate into the sample during growth and have sufficient energy to diffuse throughout the sample and become trapped at dopant sites. The actual deuterium (or hydrogen) profile can then be described by thermodynamics. If X is the dopant atom than the reaction with H can simply be written as follows:

\[ X + H = XH \] (9)

The reaction with have an equilibrium constant expressed as:

\[ K = \frac{[XH]}{[X] [H]} \] (10)

Since \( k \) is constant at a given temperature, a greater amount of \( X \) would require a greater amount of \( XH \) and therefore, in regions where the doping is higher, a larger amount of hydrogen will remain bound. In figure V.18 the ratio of the D to Si level is higher than the D to Be level indicating the \( k \) for the D-Si reaction is higher than for the D-Be reaction. The equilibrium constant for the D-Zn reaction is also higher than for the D-Be reaction as evidenced in figure V.19 where the D level is higher in the substrate than in layer 2. The substrate for this sample is Zn-doped \(~1 \times 10^{18} \text{ cm}^{-3}\) and layer 2 is Be-doped \(1 \times 10^{18} \text{ cm}^{-3}\).

The thermodynamic equilibrium constant requires that the Be level and D level
be at a constant ratio regardless of the Be doping level, assuming the D uniformly
diffuses throughout the sample. This is not the case in figure V.19. At higher doping
levels there is a higher D to Be ratio than at lower Be levels. This can be explained
by the observation that at the highest doping level the Be is approaching, or is above,
the solid solubility limit and heavy diffusion has resulted. This indicates that
significant Be is not bound to a crystal site but is either transiently or permanently
positioned interstitially. It is probable that D will have a different equilibrium
constant for Be in a crystal site than Be that is interstitial thus, the high D to Be ratio
with high Be levels is attributed to D bonding to interstitial Be.

From the above discussions it is evident that the dominant defects produced by
the H-plasma are the result of phosphorus being etched from the InP and Si impurities
that are introduced during plasma exposure. Defects can be minimized by providing
the InP surface with a sufficient overpressure of $P_2$ and minimizing the plasma ion
current. After the plasma exposure the hydrogen will diffuse throughout the structure
and bond to dopant atoms; however, no effect on the carrier concentration has been
observed due to the H-dopant complex existing at very low levels and/or the H-dopant
complex does not change the electrical activity of the dopant. Hydrogen passivation is
therefore a negligible effect.

V.5 H-PLASMA ETCH OF OXIDES-REACTION KINETICS

To determine which plasma modes are best suited for the removal of the
surface oxide on InP, in terms of the plasma properties, two modes were selected for
Figure V.20: Plot to show the constant etch rate until the oxide is very thin.

detailed study. One mode had high ion current and low optical intensity with the current settings of I1 = 210 A and I2 = 190 A (see figure V.11 for properties) referred to as mode A and the other had low ion current and high optical intensity and thus congruently, high atomic H with current settings of I1 = 190 A and I2 = 130 A (see figure V.10 for properties) referred to as mode B.

To determine the overall reaction kinetics and to optimize the procedure of using RHEED intensity measurements for determining the oxide thickness, two experiments were completed. By consecutively applying mode B to an oxidized substrate at 460 °C and taking AES measurements, the dependence of the oxide thickness on plasma exposure time was determined. As is seen in figure V.20, the
thinning of the oxide is linear with time exposed to the H-plasma that is, the oxide is removed at a constant rate, until the oxide is very thin then, there is a notable change in the removal rate. The constant rate when the oxide is thick is understood as a uniform surface reaction, where the reaction rate is a constant that does not depend on the oxide thickness but only on the plasma mode and substrate temperature. Because the reaction is a surface reaction the amount of oxygen can be considered constant even though the oxide is thinning as long as there is a complete surface of oxide. At a given temperature the reaction will depend only on the incoming flux of the reactive species in the plasma.

When there is less than a complete surface of oxide the reaction rate is proportional to the amount of oxygen left on the surface. That is:

\[ \text{Rate} = K[O] \]  

(11)

where \( K \) is a proportionality constant. In this first order reaction the rate limiting step is the hydrogen flux reacting with the residual oxygen coverage at the surface thus, as the amount of oxygen decreases the rate decreases. To determine experimentally if a reaction is first order, the above equation is written in derivative form:

\[ \text{Rate} = \frac{d[O]}{dt} = K[O] \]  

(12)

then is integrated:
\[ \ln[O_e] - \ln[O] = Kt \]  

(13)

where \( t \) is the time and \( O_e \) is the oxide thickness at \( t = 0 \). The rate constant can be calculated from a plot of \( \ln[O] \) vs. time. This first order behaviour was observed when less than complete surface coverage of the oxide occurred. Therefore, the complete removal of the oxide needs to be expressed in two equations as follows:

For thick oxides: 
\[ \text{Rate} = K_1 \]  
(14)

For thin oxides: 
\[ \text{Rate} = K_2[O] \]  
(15)

where \( K_1 \) and \( K_2 \) are the rate constants and a thin oxide constitutes one with less than complete surface coverage. The above two rate expressions could describe sputtering or chemical etching; however, sputtering would be temperature independent thus, the rate constant as a function of temperature needs to be determined.

The constant rate when the oxide is thick allowed for RHEED intensity measurements to be used to determine oxide etch rates. For a complete discussion on how the RHEED intensity measurements are used to obtain oxide removal rates see section IV.7. A series of oxide etch rates were determined for the two modes at various temperatures. The results are plotted in the form of an Arrhenius plot shown in figure V.21. Assuming the etch process follows a thermally activated rate equation of the form:
\[ K = Ae^{-\frac{E_a}{kT}} \]  

where \( K \) is the rate constant, \( A \) is a constant, \( E_a \) is the activation energy for the reaction, \( k \) is the Boltzmann constant and \( T \) is the temperature. A plot of \( \ln K \) vs. \( 1/T \) should produce a straight line with a slope of \( E_a/k \). This is seen to be the case in figure V.21.

It is evident from the curves that the rate of oxide removal with mode B is greater than that of mode A. For mode A, at temperatures \( >425 \, ^\circ C \) the rate plateaus until \( 490 \, ^\circ C \) and then increases again. Mode A had no measurable optical output and thus, a low level of atomic H in the plasma. The plateau at \( 425 \, ^\circ C \) is therefore due to atomic H flux incident on the sample surface being the rate limiting species. At \( 490 \, ^\circ C \), the rate increases due to the contribution from the thermal desorption of the oxide. Thermal desorption data is included in figure V.21. The data was first acquired by Comedi et al.[V.6] at this lab, and the results were reproduced for this experiment.

At lower temperatures \( (<250 \, ^\circ C) \) the oxide removal rate for mode A exceeds the extrapolated level in the Arrhenius plot (fig. V.21). This is probably due to oxide being physically removed due to sputtering by the plasma with a removal rate greater than the chemical etch rate at that temperature. The sputtering effect is expected to be greater for mode A than mode B, since the current of the energetic ions is higher. In the mid-temperature range, both curves are linear and have approximately the same slope. This slope gives an activation energy, for the chemical removal, of \( 0.45 \pm 0.05 \)
Figure V.21. Arrhenius plot for two ECR modes.

cV. The equivalent slope for both modes indicates that the same reaction is causing
the removal of oxide with both modes; however, mode A has a smaller pre-
exponential factor (see equation (16)). The pre-exponential factor is interpreted as the
attempt frequency for the reaction therefore, mode A must contain less of the active
ingredient in the plasma resulting in the etching reaction occurring with reduced
frequency, compared to mode B. Examining the properties of mode A (fig. V.11) and
mode B (fig. V.10) it is evident that mode B contains significantly more H⁺ therefore,
the neutral atomic species must dominate the etching reaction through the mid-
temperature range

Also, at temperatures above 300°C the ionized species appear to have little
affect on the etch rate of the oxide since mode A, which has the higher ion current, has the lower etch rate. Mode B had a smaller ion current and a greater amount of H* compared to mode A therefore, it is evident that the optimal plasma mode for removing oxide from InP is one that has the maximum amount of neutral atomic H present. Etch rate measurements of the various resonant modes confirm this assessment since, all the resonant modes had similar atomic H content and etch rates of 2 ± 0.5 Å/s and no dependence on the ion current was apparent. Other modes with no measurable atomic H present had etch rates of -0.2 ± 0.1 Å/s regardless of the ion current. The overall oxide removal rate can be expressed as a sum of the contributions from thermal desorption, hydrogen etch and sputtering:

\[
\text{Rate} = A_{th}e^{-\frac{3.9\pm0.4}{kT}} + A_{H}e^{-\frac{0.45\pm0.05}{kT}} + S
\]

where 3.9 ± 0.4 is the activation energy for thermal desorption, in eV, 0.45 ± 0.05 is the activation energy for the hydrogen etch of the oxide, in eV, S is the temperature independent sputtering rate, measured to be -0.03 ± 0.02 Å/s for mode A, and \( A_{th} \) and \( A_{H} \) are the reaction attempt frequencies. S and \( A_{H} \) will depend on the plasma mode.

The above determination of H-plasma etch kinetics was completed for the case of a thick oxide (greater than a monolayer). For thin oxides the first order rate constants (\( K_2 \) in equation (15)) were also measured at different temperatures and were used to generate an Arrhenius plot (figure V.22). The activation energy obtained from this plot is 1.0 ± 0.3 eV. In general, the activation energy depends on what bonds
need to be broken in order for the reaction to proceed. The difference in activation energy from the thick oxide reaction and the thin oxide reaction is an indication that the final layer, or less, of oxide is bound in a different configuration than the bulk of the oxide. There are several situations that would result in a different bonding configuration; possibly the interface between the oxide and substrate is not abrupt but rather, some oxygen can diffuse deeper into the substrate and will be more difficult to remove, or the residual O must be considered part of the InP surface and not an InPO₄ species, or the O is bound to an impurity species. It is possible that all three situations are present and this is investigated later in this chapter (section V.7).

V.6.1 OXIDE ETCH MECHANISM - THERMODYNAMIC MODEL

It has been determined that atomic H is the active species for removing the oxide and that the reaction rate is constant until a thin oxide is obtained; however, the products of the reaction need to be determined. The conclusion that atomic H is the active species in the plasma is a good assumption thermodynamically, as it can be
shown that reactions of H\textsubscript{2} with the oxide are not favourable (a positive \(\Delta G_{\text{rea}}\)) whereas the reaction with atomic H is favourable (a negative \(\Delta G_{\text{rea}}\)). Also, other groups use H\textsubscript{2} cracked over a heated filament, to produce atomic H, to etch oxides[\textsuperscript{2}, \textsuperscript{8}].

The process of etching the InPO\textsubscript{4} from the surface of InP using a H-plasma must be considered as farther from an equilibrium process than the thermal desorption of the oxide. The species in the H-plasma are at much higher effective temperatures than the substrate and will quickly react to form stable or unstable species that can be pumped away in vacuum and thus, not react further to form the most thermodynamically stable species. Nevertheless, the thermodynamic modelling will provide insight into the possible reaction products and pathways.

The sub-program "equilibrium" in F*\textsuperscript{*}A*C*T was used to determine the thermodynamic products of the reaction of atomic H with InPO\textsubscript{4} at the MBE growth temperature (470 °C). The calculated equilibrium mixture contained virtually no InPO\textsubscript{4} and had a large negative \(\Delta G_{\text{rea}}\). The most prevalent product was water, followed by volatile P\textsubscript{2}O\textsubscript{3}, In, InH, and some In liquid. The surprising initial result is that no phosphorus hydrides were reported to form. However, the program will only form products to maximize the change in free energy indicating that losing the phosphorus from the oxide as P\textsubscript{2}O\textsubscript{3} results in a combination of products with a lower \(\Delta G\) than would be the case with hydride species as products. This is expected as the P-O bond energy is 142 kcal/mol and the P-H bond energy is 82 kcal/mol[\textsuperscript{4}]. The program does allow the user to suppress the formation of certain species so the equilibrium calculation was repeated and P\textsubscript{2}O\textsubscript{3} was removed from the possible list of products.
With these constraints, $P_2$, $PH_2$ and $PH_3$ were all reported to form and the reaction still had a large negative $\Delta G_{\text{rxn}}$, although reduced from the reaction including $P_2O_3$.

The thermodynamic model shows that $\text{InH}$ forms in significant amounts at temperatures close to growth temperature for $\text{InP}$. The formation of this product is the most likely pathway for removing $\text{In}$ from the surface though the program also indicates that Indium evaporating from the surface would contribute to a lesser extent.

V.6.2 OXIDE ETCH MECHANISM - EXPERIMENTAL RESULTS

The MBE system itself has very limited capabilities for determining the species that form at the substrate surface. Therefore, an ECR-based reactive ion etch (RIE) system, equipped with a SIMS - quadrupole mass analyzer that can be placed close to the sample surface, was used to determine the product species of a hydrogen plasma reaction with an $\text{InP}$-oxide.

A significant difference between the RIE and the MBE is that the RIE system does not have a phosphorus source and therefore, the temperature of the reaction must be kept below the congruent sublimation point for $\text{InP}$. The substrate temperature was 350 °C and both hydrogen and deuterium plasmas were run on different samples. The deuterium plasma was employed to distinguish certain etch products from the background of the system such as water and phosphine. The following products were scanned for with the quadrupole: $D_2O$, $P$, $P_2$, $PD$, $PD_2$, $PD_3$, $P_2O_3$, $P_2O_5$, $\text{In}$, $\text{InD}$, $\text{InD}_2$, $\text{InD}_3$, and $\text{In}_2O_3$. The results indicated that water is the dominant product of the reaction, no $P$ or $P_2$ is observed to form, nor are any of the oxidized phosphorus
Figure V.23. RGA analysis of reaction products of D-plasma on an InP-oxide.

The initial sharp increase in the levels at $t = 170s$ corresponds to the opening of the shutter that protects the sample. Beyond this point the $D_2O$ signal slowly decays then, as the signal becomes constant, the $PD_2$ and $PD_3$ signals increase dramatically. This suggests that the surface oxide is gradually removed followed by the plasma etching the substrate. It would appear that the oxide etch products are water and various deuterated phosphorus species.

In the RIE chamber, neither In or In products were observed with the quadrupole. Visual inspection of the surface after the plasma etch revealed a surface
covered with In-clusters and thus, the In from the oxide and possibly some from the 
substrate has remained at the surface of the substrate and bonded together to form 
clusters. This is the same result as was observed by other groups preforming oxide 
etching at temperatures below congruent sublimation[V.13-15]. The reaction 
temperature in the RIE was 350°C whereas typical temperatures for oxide removal in 
the MBE are at least 100 degrees higher. Oxide removal at this higher temperature 
does not result in the formation of In-clusters.

It was observed, during the rate constant measurements, that the In-clusters do 
not form in the MBE chamber if the substrate temperature is above ~400°C and a 
coincident P₂ flux is present. Vapour pressure calculations show that at 470°C the In 
has a surface lifetime of ~9 minutes whereas typical plasma treatments are 2 minutes. 
This indicates that at higher temperatures the remaining In has sufficient mobility to 
find crystal sites and bond with incoming phosphorus or the In is removed from the 
surface during the plasma etch.

To determine the fate of the In a series of experiments were conducted using 
an As₂ flux with the H-plasma on an oxidized substrate of InP with characterization 
carried out using AES. As the oxide is etched by this plasma at 460°C, any In that 
stays at the surface should bond with the incoming As forming InAs and the As Auger 
peak should be readily detectable. If the In does not remain at the surface then no As 
peak should be observed. The results clearly indicated that no As remains at the 
surface with the removal of the oxide and therefore, the In from the oxide does not 
remain at the surface during the plasma etch of the oxide. Only, after the oxide has
been completely removed, is an As peak observed and this is attributed to the exchange of As with P in the substrate.

To further resolve if the H-plasma does remove In from the surface, a substrate was subjected to 4 hrs of etching through a shadow mask at growth temperature (470°C). The depth profile of the masked substrate is shown in figure V.24. The deep pit on one side of the groove is attributed to the mask scratching the sample surface causing preferential etching along the scratch. Based on the measurements of the etch groove depth at various places on the sample, the average etch rate was calculated to be 1.2 Å/min. This etch rate is higher than the evaporation rate of In which confirms that the plasma does react to produce a volatile In species in agreement with what was predicted thermodynamically.

The experimental observations indicate that the H-plasma etch of the InP-oxide results in the formation of water and the hydrogenated species of phosphorus. The In from the oxide is removed from the surface during the etch process. This is in agreement with the thermodynamic model if certain kinetic constraints are considered. The reaction is driven by atomic hydrogen, from the plasma, which forms water with
oxygen from the oxide and phosphorus hydrides. An approximation to the actual reaction can be written as follows:

\[ \text{InPO}_4 + 7.3\text{H} \rightarrow 2\text{H}_2\text{O} + 0.5\text{PH}_2 + 0.5\text{PH}_3 + 0.8\text{InH} + 0.2\text{In} \]  

(14)

For the proposed etching reaction it is assumed that all oxygen is removed as water since, both thermodynamic calculations and etching studies indicate this to be the case. The coefficients on the phosphine products are estimated by comparing the thermodynamic predictions to the etch study results taking into account the cracking pattern of phosphine in a quadrupole mass spectrometer. The In product coefficients are estimated based on the thermodynamic prediction that both InH and In will exist as product species and by assuming that all In from the oxide will be removed. The contribution from evaporation is determined by calculating the In evaporation rate at the oxide removal temperature and the remaining In is assumed to be removed as InH. The equation and the coefficients are approximations and should reflect the most dominant products for the reaction. Thermodynamically, the dominant phosphorus product was initially predicted to be P$_2$O$_3$; however, suppression of this product in the model resulted in the formation of PH$_2$ and PH$_3$ which agrees with the observed results. This would suggest that the surface is overwhelmed with H such that, the oxide is entirely converted to water and the hydrogenated species of P. The reaction to form water and hydrogenated phosphorus was shown to be a thermodynamically favourable one and is the pathway observed in this study.
V.7 OPTIMIZATION OF H-PLASMA TREATMENT

It has already been determined that the optimal H-plasma treatment, to clean an InP surface of oxide leaving a high quality, low defect concentration surface for MBE growth, involves a plasma mode with high neutral atomic H content and low ion current, also, a significant overpressure of P₂ is required. To determine if there is an optimal H-plasma exposure time for oxide removal a sample was prepared with 3 interfaces. At each interface the sample received a UV-ozone treatment and then was H-plasma etched in the MBE chamber at 465 °C. The plasma treatments were done for different times at each interface. Figure V.25 is the SIMS depth profile of the C and O content in the sample. The CV-profile (not shown) of the sample indicated a

![SIMS profile](image)

**Figure V.25.** SIMS profile of p-type material; time of plasma treatments: Interface 1: 30 s, interface 2: 240 s, interface 3: 60 s.
Figure V.26. CV-profile of p-type material; temperature of plasma treatment of each interface is: interface 1: 470 °C, interface 2: 425 °C, interface 3: 450 °C.

highly defective 1st interface such that the etch profile could not be completed, and this is confirmed by the SIMS analysis. It is evident that 30 s is insufficient time to remove the oxide. A 60 s plasma treatment further reduces the oxygen level but, 240 s does not reduce the level further. This suggests there is no advantage to prolonged etch times and that the oxide remaining is more stable than the bulk of the oxide.

To determine if there is an optimal temperature for oxide removal by the H-plasma a p-type sample was prepared with 3 interfaces. At each interface the sample received a UV-ozone treatment and a H-plasma cleaning. A different temperature was used for the plasma cleaning at each interface. All temperatures were within a range that does not result in In-clusters (>400 °C) or where thermal desorption of the oxide is
not significant (<490°C), and, using the rate data presented earlier is this chapter, the H-plasma etch time was adjusted to give an equivalent etch at each surface. Figure V.26 is the CV-profile of the sample. The concentration of interface states is indicated in cm². It is apparent that there is no advantage to removing the oxide at a temperature different from growth temperature based on the interface states that remain at the interface. It is however, advantageous to be above the 2x1 to 2x4 transition temperature (450°C[V.29]) for at these temperatures the RHEED reconstructions are more sensitive to impurities and therefore RHEED measurements can be used to determine a clean surface.

In order to identify the remaining defects that arise from a UV-ozone treatment
combined with an H-plasma desorption, SIMS analysis was preformed on interfaces treated with this procedure. It was speculated that the possible impurities would be carbon, oxygen or silicon. Also, for Be doped InP it is possible that BeO could be formed by the ozone treatment and this is a very stable oxide and removal would be very difficult. If BeO is produced then the oxygen level at the interface should increase with higher Be-doping. Figure V.27 shows the SIMS analysis of a sample that contains two interfaces. The first interface is in a Be-doped \(5\times10^{17}\ \text{cm}^{-3}\) layer and the second in an undoped layer. The oxygen level is the same for both interfaces therefore, the oxygen impurity is not associated with the Be. Silicon is observed at the interface but, there is no carbon present. Oxygen is also present and is probably associated with the Si as SiO\(_2\) which, like BeO, is significantly more stable than the InP-oxides [V.4] thus, if SiO\(_2\) is present this would explain why longer plasma exposures did not significantly reduce the amount of oxygen present.

Based on the presented results it is evident that the optimal plasma treatment for removal of a UV-ozone generated oxide is a 2 minute exposure to a H-plasma with a high neutral atomic H content and low ion current. The exposure should be completed in an overpressure of \(P_2\) to prevent damage to the substrate. The treatment can be done at MBE growth temperature such that the RHEED reconstructions can be used to verify an atomically clean surface.

V.8 COMPARISON OF THERMAL DESORPTION AND H-PLASMA ETCH

Having characterized and optimized the use of a H-plasma it is necessary to
compare the results of using a H-plasma to that of a thermal desorption. The H-plasma and thermal desorptions were used to remove oxides from the surface of InP and AES measurements were carried out on the desorbed surfaces. It was observed that the H-plasma successfully removes surface carbon whereas the thermal desorption does not. Also, MBE grown layers on H-plasma cleaned substrates had the same surface morphology as layers grown on thermally desorbed substrates; i.e. there was an equal number of macroscopic surface defects observed for each case.

The quality of the resulting interfaces produced by further growth on the oxide desorbed surfaces were also compared using CV-profiling measurements. Figure V.28 shows the profile of an n-type sample with three interfaces. At each interface the

![Figure V.28. CV-profile of n-type InP. Interface 1. Air exposure and H-plasma etch. Interface 2. UV-ozone treatment and thermal desorption. Interface 3. UV-ozone treatment and H-plasma etch.](image)
sample was removed from vacuum and exposed to air and/or a UV-ozone treatment. It was then re-introduced into the MBE chamber and subjected to either a H-plasma etch or a thermal desorption prior to resumption of growth. At interface 1 the treatment involved air exposure and a H-plasma cleaning. Interface 2 received a UV-ozone treatment and thermal desorption while interface 3 was H-plasma etched after a UV-ozone treatment. It is evident that for the n-type sample the combination of a UV-ozone oxide and a H-plasma etch results in a interface virtually free of electrically active defects. Figure V.29 shows the CV-profile of a p-type sample which contains identical interface treatments as for the above described n-type sample. For this sample the thermal desorption and the H-plasma etch of the oxide produce a similar

![Figure V.29. CV-profile of n-type InP. Interface 1. Air exposure and H-plasma etch. Interface 2. UV-ozone treatment and thermal desorption. Interface 3. UV-ozone treatment and H-plasma etch.](image-url)
defect level of $-8.0 \times 10^{11}$ cm$^2$. This is higher than the defect level produced in the n-type material indicating that the predominant defect is a deep donor or, if it is a shallow donor, such as Si, it must be present at a concentration close to the n-type doping level such that no effect is observed with n-type material and a depletion layer is observed in p-type material. The defect level observed in p-type material is close to the lowest value given in the literature, of $5 \times 10^{11}$ cm$^2$[V.30].

The "reaction" program was used to compare the free energies of reactions for the thermal desorption process with the H-plasma etch of the oxide. It was determined that throughout the temperature range of room temperature to beyond thermal desorption temperatures, the reaction with atomic H has a much larger negative $\Delta G_{\text{ran}}$ than the thermal desorption reaction. Also, it was shown that the thermal desorption reaction was dependent on the migration of P from the substrate into the oxide and therefore required higher temperatures than the reaction with atomic H.

For the thermal desorption of the oxide the loss of phosphorus from the substrate, which is a destructive process, is critical to the removal of the oxide. The phosphorus loss must be replaced by a P-overpressure to prevent the formation of defects. The removal of the oxide with the H-plasma is not inherently destructive but, phosphorus loss from the substrate can occur due to the formation of phosphine and therefore, a P-overpressure should also be maintained during plasma etching to preserve the quality of the substrate.
V.9 SULFUR PASSIVATION

V.9.1 INTRODUCTION

The pre-growth treatments discussed previously and others that are commonly used require the removal of an oxide prior to initiation of deposition and generally result in some residual impurities at the surface. Recently, as an alternative to oxidation, the use of ammonium sulfide to produce a sulfur passivated surface on III-V semiconductors has received considerable attention[V.31-53]. This surface is interesting from a theoretical perspective as it is speculated that the sulfur forms a single monolayer on the semiconductor surface resulting in no dangling bonds. The surface also has applications in device structures, as it has been found to reduce carrier recombination at interfaces and air exposed surfaces[V.54-59]. Melloch et al.[V.60] investigated the use of S-passivation in the regrowth of GaAs and found that sulfur is incorporated at the interface as an n-type dopant even when the growth temperature was as high as 600°C. Similar thermal stability of the S-surface on InP was observed by Gallet et al[V.32]. They observed little deterioration with annealing up to 560°C.

Sulfur passivated surfaces have been used to improve the interface properties of epitaxial grown structures based on GaAs and InP (see section III.6 for a full discussion). The improvement in interface properties is attributed to a reduced amount of oxygen at air exposed interfaces which thereby reduces carrier recombination. The S-passivated surface could be an alternative to oxidation as a pre-treatment prior to epitaxial growth; however, for InP, the thermal stability of the surface is such that the InP substrate will decompose before the sulfur desorbs from the surface[V.32].
Because the MBE system used in this study is equipped with an in-situ H-plasma source it has the capability of chemically removing the sulfur surface immediately prior to crystal growth.

The more recently reported methods used to produce the S-passivated surface often involve the use of an ammonium sulfide solution. Generally, all procedures using this solution report a uniform sulfur surface approximately a monolayer thick (Gallet et al.[V.32] report small amounts of sulfur up to five atomic rows deep) with little or no measurable oxygen. In this section two S-passivation procedures, involving ammonium sulfide, were employed and the surfaces produced are characterized by Auger spectroscopy. The surfaces produced are further evaluated by RHEED measurements to determine the thermal stability of the S-passivated surface. Also, for the first time, the usefulness of the S-passivation, in combination with an H-plasma cleaning, is assessed as a surface preparation technique.

V.9.2 RESULTS

The two different procedures used to prepare the S-passivated surfaces are described in the experimental section. One reported by Gallet et al.[V.32] (procedure A) and the other by Lu et al.[V.35] (procedure B). The surfaces prepared by these two different procedures have been characterized by AES and the spectra are shown in figure V.30. The two spectra are very similar. The surface prepared according to procedure A contains slightly more oxygen. The oxygen on the surface partially desorbs with subsequent annealing at 350°C. Generally, it was observed that the
Figure V.30. Auger spectra of S-passivated surfaces of InP. (a) Prepared by procedure A. (b) Prepared by procedure B.

resulting surfaces from the two preparation procedures are essentially equivalent in terms of surface composition.
In both of the above mentioned procedures there is an acid pre-treatment to remove any native oxides from the InP surface. It is unknown whether this pre-treatment is necessary since the sulfur from the reactive solution may replace surface oxygen. Therefore, to assess the requirement of an acid pre-treatment, two samples were prepared. Both were initially oxidized by an ozone treatment and then one sample had the oxide removed by placing the substrate in an HF solution while the other did not have the oxide removed. Both samples were then S-passivated using procedure B. Auger spectra were recorded and the surface concentrations of the various elements are shown in table V.4. The concentrations were calculated by the method outlined in section II.4. Also, included in the table are the AES results from several other samples. Two samples that were prepared using a procedure similar to procedure B except that instead of maintaining the ammonium sulfide solution at 65°C for 15 minutes the solution was maintained at 40°C for 1 hour. One sample had an oxidized layer removed prior to S-passivation, the other did not. The motivation for lowering the temperature is based on the fact that the ammonium sulfide solution is close to its decomposition temperature at 65°C and it evaporates fairly quickly. The other samples included in the table are a test of the S-passivated surface's air stability.

It is evident from the AES results presented in table V.4 that the acid-treatment is not required because the S-passivation of an oxidized surface results in the same sulfur and oxygen levels as the pre-treated samples. It is an advantage to eliminate the acid pre-treatment from the procedure since this step could potentially introduce chemical impurities into the InP surface. It is also noted that the procedure
Table V.4. Summary of AES measurements of S-passivated surface.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>%P ±2%</th>
<th>%S ±2%</th>
<th>%C±25%</th>
<th>%In±1%</th>
<th>%O±10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Procedure B on oxidized InP</td>
<td>52.4</td>
<td>19.8</td>
<td>1.2</td>
<td>24.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Procedure B with oxide removed</td>
<td>48.5</td>
<td>18.7</td>
<td>4.4</td>
<td>26.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Procedure B with (NH₄)₂S solution at 40 °C - on oxidized InP</td>
<td>30.4</td>
<td>24.5</td>
<td>4.7</td>
<td>37.0</td>
<td>3.4</td>
</tr>
<tr>
<td>Above surface after 1 week in air</td>
<td>27.7</td>
<td>16.1</td>
<td>6.4</td>
<td>36.7</td>
<td>13.1</td>
</tr>
<tr>
<td>Procedure B with (NH₄)₂S solution at 40 °C - oxide removed</td>
<td>30.6</td>
<td>25.5</td>
<td>2.5</td>
<td>38.1</td>
<td>3.3</td>
</tr>
<tr>
<td>Above surface after 1 week in air</td>
<td>26.0</td>
<td>16.1</td>
<td>7.6</td>
<td>37.0</td>
<td>13.3</td>
</tr>
</tbody>
</table>

Involving the lower temperature ammonium sulfide solution results in a surface with higher sulfur content.

From Table V.4 it is clear that the sulfur passivated surface is susceptible to oxidation when exposed to air for prolonged periods of time. It has been observed in this lab that a S-passivated surface is easily oxidized with a brief UV-ozone treatment. The observed lack of stability in an oxidizing environment is attributed to In-O having a stronger bonding energy than In-S, so that the oxidized surface is more thermodynamically stable and will gradually convert the sulfur surface.

The thermal stability of the sulfur surface in vacuum was evaluated using RHEED measurements. A S-passivated substrate was heated in the MBE chamber, in a phosphorus atmosphere, to 535 °C, which is the decomposition temperature of In-free mounted samples. Figure V.31 shows a series of RHEED photographs taken at
various temperatures and the final photograph is the same surface after exposure to a H-plasma for 10 s at InP growth temperature (470 °C). As discussed in section II.3 a 2x4 surface reconstruction indicates a clean P-terminated InP surface. It is evident from figures 31 (a) and (b) that the sulfur terminated surface results in only primary RHEED streaks and that this surface is stable beyond the temperatures associated with the desorption of an oxide from InP; however, the sulfur is easily removed by the H-plasma leaving the phosphorus stabilized 2x4 RHEED reconstruction. This behaviour is understood through thermodynamic considerations. The S-passivated surface on (100) InP is reported to consist of a monolayer of S with each sulfur atom bonded to an In atom in the underlying layer. The In-S bond energy is 69

Figure V.31. (a) S-passivated surface at 450 °C. (b) S-passivated surface at 535 °C. (c) S-passivated surface after 10 s H-plasma.
kcal/mol and the surface is further stabilized by the formation of S-S dimers. The bond energy of S-H in H₂S, which is a well known stable molecule, is 90 kcal/mol and the plasma contains highly reactive atomic H; therefore, the atomically clean 2x4 surface is produced by the H-plasma removing the sulfur from the surface through the formation of volatile H₂S.

To further assess the possibility of using the S-passivation as a pre-growth or regrowth treatment a sample was produced that contained two sulfur passivated interfaces separated by 0.5 μm of n-type InP. At one interface material was deposited onto the S-passivated surface and at the other interface, the sulfur was removed by the H-plasma prior to initiation of deposition. The CV-profile of the sample is seen in figure V.32 and the SIMS profile is shown in figure V.33. It is clear that if the sulfur

![Graph showing CV-profile and SIMS profile of n-type InP with interfaces labeled 1 and 2 with counts of 17e14 and 4.3e12 respectively.]

**Figure V.32.** CV-profile of n-type InP. Interface (1) S-passivated surface. Interface (2) S-passivated surface removed by H-plasma.
is not removed from the InP surface that, as the growth proceeds, this S is incorporated as a dopant sheet at the growth interface. However, subjecting the S-passivated surface to a H-plasma for 10 s at 465 °C removes most of the sulfur leaving the dopant sheet at the interface greatly reduced. The H-plasma removes sulfur to the extent that it is no longer the predominant defect at the interface rather, Si, C and O are present in larger quantities. Typically, wet chemical treatments result in a greater number of impurities compared to dry processes, such as UV ozone treatment, and this is what is observed here. The remaining amount of sulfur are probably atoms that have bonded several atomic rows into the crystal, consistent with the structure reported by Gallet et al. [V.32], and is therefore more difficult to remove than the surface sulfur.

Figure V.33. SIMS profile of n-type InP. Interface (1) S-passivated surface. Interface (2) S-passivated surface removed by H-plasma.
V.10 COMPARISON OF SURFACE TREATMENTS

The surface treatments investigated in this study are not only applicable to the initial substrate cleaning, which will determine the quality of subsequent growth but, are also applicable to regrowth where a sample is removed from vacuum prior to completion of a structure and subject to external processing. This surface will require cleaning prior to resumption of crystal growth. A successful regrowth technique offers an additional degree of freedom for the design of heterostructure devices. It makes possible the growth of highly doped layers and abrupt profiles while maintaining underlying or adjacent structures. A low temperature regrowth technique has additional advantages in that it will not promote phase separation of alloys or the smearing of dopant profiles. Regrowth has been successfully employed in the production of buried heterostructure lasers[V.56, 61], distributed feedback lasers[V.62] and in surface tunnelling transistors[V.63]. The traditional method for preparing surfaces for regrowth has involved wet chemical treatments[V.56, 60, 62, 64-66] and more recently, plasma etching has emerged as an effective tool for preparing surfaces in vacuum[V.61, 63, 67]. Baba et al.[V.63] investigated the use of an in-situ hydrogen plasma to clean GaAs and GaSb surfaces for regrowth and found that hydrogen cleaning was more effective than thermal treatments.

Throughout this study C-V profiles were used to determine the number of defect states at interfaces that had been subjected to oxidation and S-passivation treatments. Such techniques can be viewed as potential regrowth techniques whereby, samples need ex-vacuo treatments partway through the growth of device structures.
The results of this work are therefore, the first measurements of the effectiveness of a H-plasma cleaning for regrowth of InP. Table V.5 is a summary of all potential regrowth treatments investigated in this study. Also, for a more complete comparison, included in the table are results from using H$_2$SO$_4$ to etch an oxide from InP since this technique is reported in the literature to give good results.

It is evident from the table that the combination of a UV-ozone treatment and an in-situ H-plasma etch give the best combined result on n- and p-type InP. The results are similar to that obtained using a thermal desorption but the H-plasma etch

<table>
<thead>
<tr>
<th>Regrowth Treatments</th>
<th>Material type</th>
<th>Defect Concentration (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex-vacuo</td>
<td>none</td>
<td>p</td>
</tr>
<tr>
<td>In MBE</td>
<td></td>
<td>2.8x10$^{12}$</td>
</tr>
<tr>
<td>Air Exposure</td>
<td>none</td>
<td>p</td>
</tr>
<tr>
<td></td>
<td>2 min. plasma</td>
<td>1.3x10$^{12}$</td>
</tr>
<tr>
<td>Air Exposure</td>
<td>2 min. plasma</td>
<td>n</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.2x10$^{10}$</td>
</tr>
<tr>
<td>UV-ozone + H$_2$SO$_4$ etch</td>
<td>n</td>
<td>1.6x10$^{12}$</td>
</tr>
<tr>
<td>S-passivation</td>
<td>none</td>
<td>n</td>
</tr>
<tr>
<td></td>
<td>10 s plasma</td>
<td>1.7x10$^{14}$</td>
</tr>
<tr>
<td>S-passivation</td>
<td>30 s plasma</td>
<td>n</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.3x10$^{12}$</td>
</tr>
<tr>
<td>UV-ozone</td>
<td>Thermal Desorb.</td>
<td>p</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.0x10$^{11}$</td>
</tr>
<tr>
<td>UV-ozone</td>
<td>Thermal Desorb.</td>
<td>n</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.6x10$^{11}$</td>
</tr>
<tr>
<td>UV-ozone</td>
<td>2 min. plasma</td>
<td>p</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.3x10$^{11}$</td>
</tr>
<tr>
<td>UV-ozone</td>
<td>2 min. plasma</td>
<td>n</td>
</tr>
<tr>
<td></td>
<td></td>
<td>undetectable</td>
</tr>
</tbody>
</table>

Table V.5. Summary of regrowth treatments.
offers the advantage of removing the oxide at growth temperature such that a partially completed structure is not exposed to excess temperatures.

SIMS analysis of the various samples (some SIMS profiles are shown on previous pages) indicated that Si impurities are common to all samples and sometimes as the dominant impurity. The source of the observed silicon could be the ambient air or the UV-ozone treatment, as the UV lamps are made of quartz. In order to determine the silicon source, samples were grown that contained air exposed interfaces that received no UV-ozone treatment. These samples contained the equivalent amount of silicon as those that received the UV-ozone treatment; therefore, oxide growth by UV-ozone is not the dominant source of the silicon observed at the interfaces.

Ishikawa et al.[V.68] also observed that Si impurities result at air exposed interfaces and proposed the hepa filters, containing silica fibres, may be the cause of the ambient silicon. With the experimental apparatus used for this study there is a hepa filter directly over the load lock where samples are introduced into the vacuum system. The fan in the filter blows air down toward the loadlock to keep dust away. To see if this is contributing to the observed silicon levels, a sample was produced containing two interfaces. At both interfaces the samples were exposed to air. At one interface the fan in the hepa filter was turned off several hours prior to the sample being exposed to air and at the other interface the fan was left on. Figure V.34 is the SIMS analysis of the sample showing that virtually the same silicon levels are produced at the interfaces; therefore, the hepa filter is not the dominant source of silicon but rather, the silicon levels present in air are sufficient to produce the observed silicon spikes at the
Figure V.34. SIMS profile: Hepa fans were turned off at one interface.

A final comment needs to be made with regard to the removal of oxides, by any technique, from the surface of III-V semiconductors. It has been observed in this lab, and reported by Ingrey et al.[V.69] that the formation and removal of oxides from the surface of semiconductor materials is sensitive to the initial surface conditions of the semiconductor. The type of oxide that forms, by a UV-ozone treatment for example, will be influenced, in terms of structure and composition, by any residual oxide or impurities that are on the surface of the semiconductor. Therefore, the removal of the grown oxides, by thermal desorption or H-plasma etch, may not be consistent from substrate to substrate particularly if various manufacturers are
involved. The removal rates given for an H-plasma etch in this study are from UV-ozone oxides grown on clean InP surfaces and this rate will not be the same for all oxides. However, the mechanisms presented for oxide removal are applicable to all circumstances and the plasma configuration required for optimal removal of oxides with minimal substrate damage is applicable to any circumstance.
CHAPTER VI

CONCLUSIONS

In this investigation a mechanism for the thermal desorption of oxides from InP has been developed. This technique was compared to cleaning by an ECR generated H-plasma. It was found that the ECR source needs to be configured such that the resulting plasma will be stable and have the highest level possible of atomic hydrogen and a low ion current. Applying a plasma with these properties to the surface of oxidized InP, at MBE growth temperature, in a background of P$_2$, will efficiently remove the oxide from the surface leaving a high quality surface suitable for epitaxial growth. The H-plasma can also be used to clean a sulfur passivated surface which cannot be thermally desorbed from InP without causing decomposition of the substrate. The possibility of using the H-plasma in combination with an ex-vacuo treatment as a regrowth procedure was investigated and it was found that a UV-ozone treatment in combination with a H-plasma cleaning results in an interface that is free of electrically active defects in n-type material and produces 8x10$^{11}$ defects/cm$^2$ in p-type material.

Based on a thermodynamic model and experimental results, it is concluded that the thermal desorption of an oxide from the surface of InP proceeds by atomic phosphorus from the substrate diffusing into the oxide and reacting to form the volatile
species $P_2O_3$. The substrate temperature must be high enough for there to be significant diffusion of atomic P from the substrate. For typical, desorption temperatures, 525 - 560 °C depending on the overpressure, the surface In has sufficient vapour pressure to evaporate during the process. Differences in the desorption temperature, with different overpressures, is attributed to As exchanging with P in the substrate which reduces the diffusion of P into the oxide.

An ECR generated H-plasma can be configured in various modes with each plasma mode having different properties. The highest plasma densities are obtained when the resonant field is at the microwave window. The properties of the plasma are controlled by the magnetic field profile. For the ECR/MBE system the electron and ion temperatures are relatively low at the substrate. This is due to the fact that for this system the distance from the ECR source to the substrate is much greater than would normally be the configuration in an ECR chamber. This results in significant plasma decay and a shallow field gradient at the substrate.

The optimal H-plasma mode for etching oxides from InP is one with high neutral atomic H content, which is the active species, and low ion current, since a high ion current will cause damage to the substrate surface. Initially, the oxide etches at a constant rate with an activation energy of ~0.45 eV. Once there is less than a monolayer of oxide, the etch rate follows first order behaviour in the oxygen level with an activation energy of ~1.0 eV. The dominant product of the oxide etch is water. $PH_2$ and $PH_3$ are also observed to form and InH is expected to form based on thermodynamic calculations. The etch mechanism agrees well with thermodynamic
predictions as long as certain constraints are recognized.

Desorption of the oxide with the H-plasma results in surfaces that are free of carbon whereas, thermal desorptions do not remove carbon. Grown layers on H-plasma cleaned substrates have equivalent surface morphology to layers grown on thermally desorbed substrates. The use of the H-plasma does require a \( P_2 \) overpressure to maintain the surface quality and thus, use of a H-plasma demands careful selection of plasma mode and gas flows. The H-plasma will etch the oxide at a rate of 2 Å/s and will etch InP at a rate of 1.2 Å/minute.

It was determined that the H-plasma could be used in conjunction with a S-passivated surface to produce a clean surface since the plasma can remove the sulfur whereas thermal desorptions cannot; however, this treatment appears to be limited by high impurity levels resulting from the use of chemical solutions. The best results for regrowth were obtained by combining the H-plasma cleaning with an ex-vacuo ozone treatment. No electrically active defects were observed with n-type material and p-type material contained a defect concentration of \( 8 \times 10^{11} \text{ cm}^{-2} \). The residual impurities were determined to be Si from the air.
APPENDIX A

MEASUREMENT AND CALCULATION OF THE MAGNETIC FIELD PROFILE

The magnetic field strength was measured by removing the magnets from the resonant cavity and placing them in what would normally be the functional configuration but with the inner diameters accessible. Current was then applied to the magnets and a gaussometer was used to measure the field at four different positions along a line through the center of the magnets (see figure A.1). This procedure was repeated for several different current settings.

Figure A.1. Experimental configuration of ECR magnets, dimensions in mm. The four positions for field strength measurements are shown.
The Biot-Savart law can be used to determine the magnetic field strength along the axis of a solenoid:

\[ B = \frac{1}{2} \mu_0 n I (\cos \beta - \cos a) \]  

(1)

Where \( \mu_0 \) is the permeability constant, \( n \) is the number of turns of the conducting coil, \( I \) is the current applied to the coil, \( \beta \) is the angle from the axis to the furthest edge of the coil and \( a \) is the angle from the axis to the closest edge of the coil. The angles, \( a \) and \( \beta \), can also be expressed in length parameters according to figure A.2. Then, making \( \frac{1}{2} \mu_0 n \) a single constant \( k \), the field strength at point P, according to equation (1) becomes:

\[ B = kI \left( \frac{d_1}{(x^2 + d_1^2)^{1/2}} - \frac{d_2}{(x^2 + d_2^2)^{1/2}} \right) \]  

(2)

where \( r \) is the radius and \( d_1 \) and \( d_2 \) are measurable distances. For the magnets of the ECR apparatus the number of turns \( n \), and therefore the constant \( k \), is unknown and the thickness, and therefore the radius, of the coil is unknown. To calculate the magnetic field profiles these unknowns must be determined. This was accomplished by measuring the field strength generated by each magnet separately. It was assumed that the coil thickness could be represented by a single radius \( r \). The measured field
strength for two different positions (see figure A.1) for a given current setting was put into equation (2). This gives a solvable set of two equations with two unknowns. This procedure yielded values for magnet 1 of: \(k = 4.87\) and \(r = 81.8\text{mm}\) and for magnet 2: \(k = 5.18\) and \(r = 123.8\text{mm}\). The values of \(r\) are within the physical dimensions of the magnet and therefore acceptable.

Knowing the values of the constants for each magnet, the field from each magnet could be determined at any position with the total field being the sum of the two. The calculated values were compared with measured values, at different positions others than those indicated in figure A.1, and were in good agreement for all current settings. In this manner the magnetic field profile throughout the ECR cavity and the MBE chamber was determined.
REFERENCES


