A thesis submitted for the degree of PhD

by

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An examination of the damage
cau sed by the reactive ion etching
of gallium arsenide

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ABSTRACT

The reactive ion etch (RIE) process, and its applications in gallium arsenide (GaAs) device fabrication, have been examined. The types of damage caused by RIE, and its effect on electronic and optoelectronic devices have been assessed.

A reactive ion etcher was built to prepare GaAs samples under controlled etch conditions. Three methods were then used to measure and compare the resultant damage. These methods have been examined in detail, both from theoretical and practical viewpoints.

Electrical damage has been measured by probing Schottky diodes fabricated on the etched surfaces. Schottky ideality factors and barrier heights have been obtained for these devices and have been used as figures of merit for the comparison of different RIE gases.

Optical damage has been assessed using two novel methods. A photothermal radiometric microscope has been used to compare surface recombination velocities at etched and unetched surfaces. The second experiment involved firing a five picosecond duration laser pulse at an Auston switch fabricated on the etched surface. The laser pulse generates electron-hole pairs in the GaAs surface and their recombination time is measured electrically using the switch. This recombination time is of the order of 100 picoseconds, and so several ultra-fast measurement techniques have been exploited.

Experimental results from these three methods are presented, and further data obtained from Auger chemical analysis, scanning electron microscopy and mechanical surface probing is used to reinforce the arguments. These results indicate that optical and electrical damage measurements show different trends after reactive ion etching, and the measurements are used together to build up a picture of the damage caused to GaAs surfaces by RIE.
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The baseline value of the Schottky barrier height for the unetched Au/GaAs diode used in this work was 0.89±0.02 eV. In chapter 7, Spicer's model for Schottky barriers was used to explain the experimental results of chapter 6. This model was deduced from experimental results obtained by cleaving a GaAs wafer in UHV, and evaporating the gold Schottky contact 'in situ'. Under these conditions, 0.92±0.01 eV Au/GaAs Schottky barrier heights were obtained. The experimental results obtained in this work are therefore consistent with those used to derive the model, within the estimated errors of the two methods.

Figure 6.5 shows that the Schottky ideality factor does not change significantly with the etch gas composition, whilst the barrier height increases steadily with an increasing Freon-12/Argon percentage. The increase in barrier height with increasing reactive gas composition has been explained in chapter 7 in terms of the improved stoichiometry of the Freon-12 etch process. The lack of change in the ideality factor suggests that there are two competing processes acting in opposite directions as the etch gas composition is varied. The first is that as the argon composition is increased, the ion bombardment damage effect is increased. However, increasing the percentage of Freon-12 in the etch gas mixture increases the amount of polymer deposition on the etched surface, as the electron microscope photographs of figures 6.4 and 6.6 show.

Spicer's model does not attempt to predict the Au/GaAs Schottky barrier height from the energy levels of the As_{Ga} and Ga_{As} antisites. Instead, he uses the model to explain changes in the measured barrier height when the contact is annealed, and surface As is driven off in reference 4 of chapter 7. The value of the Au/GaAs barrier height before annealing is reported to be 0.92 eV, in this paper.
CHAPTER ONE
Introduction

Reactive ion etching uses the energetic gas ion bombardment of a surface in a vacuum to assist in chemically reactive etch processes. It can reproducibly achieve highly selective, anisotropic etching of metallic, semiconductor or insulator layers, and this makes it suitable for automated, high-volume production, for example, in the semiconductor industry. However, the energetic ion bombardment, coupled with UV and x-ray photons emitted from the plasma, can cause radiation damage to semiconductors. Non-annealable structural defects such as interface states, deep level traps and dislocation loops can occur, reducing minority carrier lifetimes. Impurities may penetrate and implant into the damaged surface and the surface may become contaminated or oxidised. In the etching of III-V materials in particular, the stoichiometry of the etched surface may be changed. In order to devise a set of etch parameters for GaAs which minimise the etch damage and contamination it is necessary to prepare sets of samples in which these parameters are systematically varied, and to compare the resultant damage.

The objective of this work was to investigate several methods of GaAs reactive ion etch damage measurement and to assess their potential application in low damage process development. In order to prepare test samples, a GaAs reactive ion etcher was set up so that the etch parameters could be measured and controlled as accurately as possible. The etched samples were then examined using mechanical, optical and electrical methods. The depth of the etch and the morphology of the surface were examined using the department's 'Talystep' mechanical surface probe and scanning electron microscope. Electrical damage to the GaAs was checked by evaporating a thin metal film to form a Schottky diode on the surface and then measuring its ideality factor. This is the most popular method of evaluating etch damage at present and it was compared with new optical methods of assessment developed in this work. These were photothermal radiometric
microscopy and the direct measurement of carrier lifetimes near an etched surface using an Auston switch. Auger analysis was used to check the chemical composition of the etched surface.

1) Description of reactive ion etching

A schematic of a reactive ion etcher is shown in figure 1.1. The equipment consists of a vacuum chamber into which process gases are bled, vacuum pumps which control the pressure in the chamber, and two planar electrodes, one earthed and one r.f. driven. The reactive ion etch configuration is characterised by a low operating pressure (10-150 mTorr) and the position of the sample on the r.f. driven electrode.

A 13.56 MHz rf glow discharge is initiated across the electrodes and the sample is etched by the highly reactive ions and free radicals generated in the discharge. A potential difference (the d.c. bias) develops across the dark space between the plasma and electrode. Ions are accelerated across it and bombard the substrate directionally, contributing to an anisotropic etch profile. This is useful, since it avoids the undercutting problems so prevalent in wet etching, which is usually isotropic. This suggests that RIE can be used to generate high aspect ratio structures, such as rib waveguides, and sub-micron linewidth metal interconnections in semiconductor devices.

Industrial reactive ion etchers often have cassette to cassette loading systems which allow a cassette of 40 or so wafers to be etched in series without letting the chamber up to air in between, thus reducing contamination. The order in which process gases are let into the chamber and the length of time for which each discharge is struck, can be programmed by the process engineer, leaving little scope for operator error. These advantages have allowed reactive ion etchers to replace wet benches in the silicon industry and development work is underway to introduce them into GaAs clean rooms too.
1.1. Schematic of GaAs reactive ion etcher
The development of new processes for reactive ion etching can be difficult, because several etch parameters are inter-related [1]. For example, the d.c. bias determines the kinetic energy with which the reactive ions strike the substrate. This potential difference depends on the rf power density coupled into the plasma, which in turn affects the number density of the ions. Thus it is impossible to control the ion density and kinetic energy independently in a conventional reactive ion etcher.

The other major problem with reactive ion etching is etch damage. The ion bombardment that gives a desired anisotropic etch profile can also cause substrate damage [2]. The advantages of this type of processing are such that it seems worthwhile trying to find ways of minimising the damage, so that the process engineer can have the advantages of both low damage and anisotropy in the future.

2) Applications of GaAs reactive ion etching

The principal uses of GaAs are in microwave and optical devices and circuits. In the former, its high electron mobility is utilised to make fast switching field effect transistors, and its direct energy band gap is useful in optical applications. Reactive ion etching is either in use, or being developed for use, in the manufacture of these devices and the processes required are described below.

i) GaAs monolithic microwave integrated circuits (MMICs)

MMICs using metal-semiconductor field-effect transistors (MESFETs) as their active elements were first developed in the mid-1970s, when it was realised that semi-insulating GaAs substrates could be used to construct low-loss microwave components such as resistors, inductors and capacitors, as well as active devices. Epitaxial active layers are used for the MESFETs and diodes, and all the circuitry necessary for a particular microwave function is
contained within the same batch-produced circuit chip, usually on 3" diameter wafers.

The fabrication of an MMIC involves about a dozen steps which pattern the wafer surface in sequence, building up the device structures. Uniform processing must be achieved over the full 3" diameter of the substrates substrates with very high yields at each step. For example, if each process in a series of 11 steps had a 90% yield, only 31% of the devices would be functional at the end of fabrication. Process steps must be reproducible from wafer to wafer and run to run to achieve desired r.f. performance yields. Reactive ion etching is used in two of these process steps in particular, etching the MESFET gate region and via hole etching.

With the exception of planar devices formed by direct ion implantation into the semi-insulating substrate, MESFETs require precise control of the active layer thickness, particularly under the gate. This thickness is usually less than 0.5 microns. Conventional wet etching is difficult to use satisfactorily because of problems controlling the etch rate and etch uniformity both vertically and laterally. RIE produces the desired etch profile, wafer uniformity and run to run reproducibility, but the damage introduced by the physical bombardment of the surface results in increased ideality factors and reduced Schottky barrier heights in the resulting Schottky gate diodes [3]. These effects are discussed in more detail in chapter 3.

Via hole etching is an area where dry etching has already replaced wet etching in GaAs MMIC fabrication [4]. A cross-section of a via hole is shown in figure 1.2. Via holes are etched from the back of the wafer to the via hole pads on the front face of the chip. When the ground plane metallisation is deposited on the back side, the via holes are also coated, providing a low inductance ground to the selected areas of the circuit. Since the substrates are about 150 microns thick at this stage, isotropic wet etching is inadequate, because the degree of mask undercut limits the separation between
1.2. Cross-section of via hole etched through GaAs MMIC
vias. Instead, very fast, anisotropic reactive ion etching with Freon-12 is currently used. The Freon-12 provides the chlorine ions to etch the bottom of the hole, and it also polymerises on the sidewalls, protecting them and preventing sideways etching. Any polymer which forms on the bottom is sputtered off by the directional bombardment of the ions, so the etch is not halted. Reproducible etch rates of about one micron/minute can be achieved, with acceptable undercut. Etch damage is not a problem in via hole etching, but care must be taken to ensure that the sidewalls of the hole are smooth, otherwise the following metallisation will not stick properly.

ii) GaAs optoelectronic devices

GaAs was first created by Goldschmidt in the 1920s, and the first published article on the semiconductor properties of III-V compounds appeared in 1952 [5]. However, the exploitation of GaAs as an electronic material was hindered until the 1970s by the difficulty in growing the material, so that only small, poor quality wafers were available. The incentive for the development of the material came when it was realised that the direct band gap of GaAs would be useful in photodetectors and efficient light-emitting devices [6].

Photodetectors have hitherto been dominated by discrete devices of silicon and germanium, because near the band-edge energy photons will penetrate about 20 microns into Si, but only one micron into GaAs. Even so, the prospect of monolithic optoelectronic integrated circuits (OEICs) has resulted in the development of low doped GaAs and InGaAs photodetectors. The passive optical devices needed for OEICs, such as stripe waveguides and couplers operating at near infra-red wavelengths, can also be made from GaAs. GaAs solar cells are being developed for use on satellites, to replace silicon devices. The greater radiation hardness of GaAs should mean that their efficiency will stay high for longer and so fewer solar cells are needed, reducing the satellite's weight.
Reactive ion etching has been used to some extent in the manufacture of all these devices. In laser fabrication, it has been important in the formation of the laser facet. This needs an anisotropic etch, leaving a smooth, partially reflecting mirror surface and no undercut at the boundaries of the different AlGaAs and GaAs layers. A mixture of chlorine and oxygen [7] has been used to reactively ion etch laser facets successfully. RIE is also ideally suited to the manufacture of rib waveguides, since the guide profile requires anisotropic etching. In order to minimise the light attenuation, the etched surface must be smooth, and topographic crystal damage of the guide walls must be minimised. Mixtures of freon-12 and argon or oxygen, and silicon tetrachloride have been used for waveguide etching [8,9].

3) Established methods of RIE damage assessment

In the literature, papers have been published describing how the chemical composition of a reactive ion etched surface can be examined using X-ray photoelectron spectroscopy (XPS) [10] and secondary ion mass spectrometry (SIMS) [11]. In XPS analysis, the sample is bombarded with monochromatic x-rays in a vacuum, stimulating the emission of core-level electrons. The inelastic mean free path of photoelectrons generated in a solid is typically 2-5 nm, and so only those photoelectrons emitted from the outermost atomic layer of the sample are collected and energy analysed to give an energy spectrum. The kinetic energy of a photoelectron depends on the binding energy of the core levels from which it was emitted, and so each element gives rise to a set of characteristic peaks in the spectrum. Measurement of these energies allows the elements present on the surface to be identified. The relative intensities of the photoelectron peaks can then be compared to give a quantitative analysis.

In SIMS, the sample is again mounted in a vacuum, and an ion beam sputters material off its surface. The sputtered ions are collected and mass analysed, and the mass spectrum shows which elements were
present on the surface. A quantitative result can be obtained by comparing the relative areas under the mass spectrum peaks. The technique can be developed further to give the depth variation of the chemical composition by repeating the mass spectrum measurement as the ion beam sputters further and further into the sample.

In this work, Auger electron spectroscopy has been used to measure the chemical composition of the etched surface. Auger electrons are produced when the surface of a material in a vacuum is irradiated with a beam of electrons. The primary beam can ionise a surface atom leaving a hole in a core electronic shell which is then filled by an electron from an outer shell. In a similar manner to that described for optical excitation in chapter five, the excess energy of the atom can be lost either by the emission of a photon or by the emission of an electron from an outer shell, the Auger electron. The energy of the Auger electron is determined by the difference in energy of the levels taking part in the process and is characteristic of the parent atom. Auger electrons typically have energies in the range 0 to 2 keV. The escape depths of electrons of this energy are of the order of nanometers and so only electrons from the top one or two atomic layers can escape from the surface without losing energy. The technique therefore has great surface sensitivity, similar to XPS. Auger analysis was chosen for this work because the reactive ion etched samples provided for analysis were small, and the Auger system at Loughborough Consultants Ltd. has better spatial resolution than the XPS system. SIMS was not used because the technique is more complex, and hence more expensive.

Crystallographic disorder in low energy reactive ion bombarded GaAs surfaces has been detected using medium energy ion scattering [12]. In this paper, the sample was mounted on a three axis goniometer in a vacuum chamber, and a 50 keV ion beam fired at the crystal, the goniometer accurately orientating the sample with respect to the beam. The energy of the scattered ions was measured at a fixed angle with respect to the sample, and the width of the energy distribution was
used to calculate the number of displaced atoms in the top 50 Angstroms of the surface.

Lasers can also be used to excite the crystalline lattice, and the scattered light forms a Raman spectrum. Variations in the intensity, or shifts in the position of the scattered peaks of light have been interpreted in terms of the lattice damage sustained by RIE [13].

In the literature, the photoluminescence intensity of an etched versus an unetched surface has been used to assess RIE damage [14]. Photoluminescence experiments were performed at low temperatures (about 10K), and the samples were optically excited by a laser. The resulting luminescence was analysed using a grating monochromator, and the relative intensity of the luminescence peaks were compared to assess variations in lattice damage from sample to sample.

The work described above has demonstrated that reactive ion etching changes the surface stoichiometry of GaAs, and that lattice damage can be detected and compared after different reactive ion etch processes. However, these type of measurements do not indicate how such damage affects devices fabricated subsequently on the etched GaAs surface. The electronic effect of RIE surface damage has often been investigated by the fabrication and testing of Schottky diodes on etched surfaces [2,16,17,18,19]. However, the effect of RIE on optical devices has no firmly established method of damage assessment in the literature. Methods of reactive ion etching laser facets [7] and optical waveguides [8,9] have been described before, but the resultant devices have not been used as a tool for examining the properties of the etch process.

In this thesis, two novel techniques have been developed for the investigation of the optical damage sustained by reactive ion etched surface. A photothermal radiometric microscope has been used to measure RIE damage across GaAs samples and reactive ion etched Auston
switches have had their temporal responses measured and compared. The Schottky diode process was selected as a standard damage measurement technique for comparison, and this process is discussed in detail in chapter three. The photothermal microscope is described in chapter four and the Auston switch measurement technique is explained in chapter five. The photothermal radiometric microscope and Auston switch measurements will be shown in chapters six and seven to contribute new data on the relative surface recombination velocities and recombination decay times of reactive ion etched surfaces compared with unetched surfaces.

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CHAPTER TWO
Reactive ion etch system design

At the start of this project, an r.f sputter coater was converted into a GaAs reactive ion etcher, which was then used to prepare etched specimens for physical damage analysis. Particular attention was paid to the instrumentation required to accurately measure, and if possible control, the etch parameters, since it was essential to be able to repeat sample preparation processes in order to compare the methods of damage measurement.

Figure 2.1 is a photograph of the resultant GaAs etching system, and a schematic of the same system was given in figure 1.1. It can be split into three sections, according to function:

1) vacuum pumps and pressure measurement
2) gas lines
3) r.f power generation and matching

When a reactive ion etch run was performed, the GaAs sample was placed on the r.f. driven electrode, then the vacuum pumps used to pump the chamber down from atmospheric pressure to a base pressure of about $10^{-6}$ Torr. The mass spectrometer could be used to check the gases left in the base vacuum. The chamber was then back filled with the reactive gases via the gas lines, and the pumps throttled back until the chamber pressure increased to about $10^{-1}$ Torr. The r.f. power generator was then turned on and matched into the vacuum chamber, resulting in a glow discharge. The etch process started at this point, and timed with a stopwatch. The d.c. bias voltage which built up between the plasma and the sample was monitored during the run.

1) Vacuum pumps and pressure measurement

An Edwards two stage gas ballasted rotary pump was used to pump the vacuum chamber from atmospheric pressure to $10^{-1}$ Torr. The gas ballast device allows most condensable vapours, in particular water
2.1 Photograph of GaAs reactive ion etcher
vapour, to be pumped directly to the atmosphere. The corrosive gases used for GaAs reactive ion etching attack many of the conventional rotary pump oils and so the rotary pump was filled with a corrosion resistant oil. A Varian diffusion pump was used to pump the vacuum chamber down from \(10^{-1}\) Torr to a base pressure of about \(5 \times 10^{-6}\) Torr. A liquid nitrogen trap between chamber and pump was used to prevent oil back-streaming into the chamber. A mass spectrum taken at this stage in the pump down showed that the dominant peak was at mass 18, indicating water vapour. Attempts were made to reduce this peak by baking the chamber out, but these gave only small improvements because the chamber has many ports, and cold spots were hard to avoid. However, since most of the RIE runs described in this work were carried out at about 100 mTorr pressure, water vapour only makes up 0.005% of the gases present in the chamber during etching.

The pressure in the roughing and backing lines was measured using a Pirani gauge (range \(50-10^{-3}\) Torr). The pressure in the vacuum chamber was measured using a Baratron (range \(10^{5}-10^{-3}\) Torr), a thermopile (range \(10^{-5}-10^{-8}\) Torr), and an ionisation gauge (range \(10^{-8}-10^{-11}\) Torr).

After the pumps had been used to evacuate the chamber from atmospheric pressure to the base pressure of the system, their role changed into one of maintaining an equilibrium pressure in the chamber. The chamber was continuously filled with the reactive process gases via the gas lines and the pumps maintained the pressure by constantly evacuating the spent etch gases. This pumping rate was critical in determining the residence time in the chamber (the mean time that a gas molecule remains in the chamber before being pumped away). In order to estimate it, it was necessary to measure the volume of the vacuum chamber, and this was done by expanding a small known volume of air at atmospheric pressure into the evacuated chamber, measuring the pressure change, and applying Boyle's law. The volume was calculated to be 34.6 Litres and the pumping speed was assumed to be the same as the mass flow rate of the inlet gas when equilibrium is
reached. This was typically 20 sccm, which gave a residence time of about 21 seconds.

The type of gas flow through the chamber was also important and it could have been either viscous or molecular, depending on the pressure. In viscous flow, the gas atoms drag each other along by their internal friction, forming a stream. At very low pressures, when the mean free path becomes very large, collisions with other molecules become rare, and so take place mainly with the walls of the vessel. This is molecular flow [1]. Taking the characteristic dimension of the vacuum chamber as its radius, d, and \( \lambda \) as the mean free path of the gas, then for

\[
\begin{align*}
\text{viscous flow, } & \lambda \ll d \\
\text{molecular flow, } & \lambda > d.
\end{align*}
\]

At a pressure of 10 mTorr, the mean free path of a gas molecule is about 0.5 cm, whilst the radius of the chamber is 10 cm. The flow across the sample in the reactive ion etch chamber was clearly slow and viscous. In order to get uniform etching across a group of samples it was therefore necessary to design the gas inlet to the reaction chamber to give an even flow across the sample. The gas inlets consisted of perforated tubes in this RIE system, and these are discussed in more detail in the next section.

2) Gas lines

The gas lines were used to introduce the process gases from their cylinders to the vacuum chamber. It was vital that they:

(a) did not leak,
(b) did not introduce contamination,
(c) measured and controlled flow rates accurately
and (d) satisfied the safety requirements for poisonous, corrosive and flammable gases.
The components of the gas lines installed in the system are shown in figure 2.2. The gas cylinders were kept in an evacuated cupboard and a stainless steel regulator was used for corrosive gases. The regulators were purged with nitrogen after use, both for safety and to prevent cross-contamination of gases. Stainless steel Swagelok fittings and tubing were used to connect the regulators with the gas control panel. All the filters, switches and needle valves used in the gas control panel were also of stainless steel, but only one mass flow meter was made of steel and therefore suitable for corrosive gases. The most important use of the flow meters was to set up the ratios of mixtures gases accurately.

Etch uniformity across the sample electrode was initially poor with this RIE system, as shown in figure 2.3. The situation was improved by covering the sample electrode with a heavily oxidised silicon wafer, and placing the GaAs samples on this, shown in figure 2.4. The silicon wafer was chosen because it was thought that the sputter yield of SiO₂ would be low enough not to contaminate the etched GaAs surfaces. The electrode was in effect permanently heavily electrically loaded, and so etch rates measured on small samples placed in the centre could be reproduced on larger ones. The etch rate was still considerably reduced: previously maximum etch rates of 1.9 microns/min. could be obtained with Freon-12, but when heavily loaded the system only etched at one micron/min. under similar conditions. This was because the supply of etching species was limited by the gas flow rate and r.f. power matched into the chamber, regardless of the area of material presented to be etched [1].

To improve etch rate uniformity further, a gas ring, a perforated tube and a plain gas inlet have been compared under identical etch conditions. The results are shown in figure 2.5. The etch rate figures have been normalised to 0.3 microns/min. in each diagram, since this was the lowest etch rate obtained for two of the three configurations.
2.2. Components making up a gas line

Gas cylinder

Regulator

0.5 micron filter

ON/OFF switch

Needle valve

Mass flow meter

Mass flow read-out

Perforated tube

Vacuum chamber
2.3. Diagram showing etch uniformity across unloaded sample electrode

Figures given in diagrams are normalised etch rates for small GaAs samples using Freon-12 at 100 mTorr pressure, 6 W/cm r.f power for 30 mins.
2.4. Diagram showing etch uniformity across Si loaded sample electrode
2.5. Diagrams showing the effect of different gas lines on etch uniformity

Figures in diagrams are normalised etch rates for small GaAs samples using Freon 12 at 50 mTorr pressure, 56 sccm flow rate, and 1.2 W/sq cm power. An oxidised Si wafer was used to load the sample electrode in all experiments.
Table 2a: Etch uniformities obtained with different gas inlets

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<th>Mean etch rate (µm/min.)</th>
<th>Standard deviation (µm)</th>
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<tr>
<td>Gas ring</td>
<td>0.57</td>
<td>0.17</td>
</tr>
<tr>
<td>Perforated tube</td>
<td>0.39</td>
<td>0.31</td>
</tr>
<tr>
<td>Inlet</td>
<td>0.54</td>
<td>0.22</td>
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As the table above shows, the circular gas ring not only gives the highest mean etch rate for these conditions, it also gives the smallest standard deviation across the substrate table.

The circular gas ring and the oxidised silicon loading wafer were used for the preliminary experiments, until the Auger analysis shown in the table below was received. This clearly indicated that silicon was contaminating the etched surfaces prepared in the chamber. Such contamination was completely unacceptable, since silicon dopes GaAs, and some of the samples subsequently would be electronically tested for etch damage. The silicon was removed from the sample electrode, the chamber cleaned with an SF₆ plasma, and two 2" undoped GaAs wafers used to load the sample electrode instead. The second set of Auger results showed that the contamination had been reduced, and then completely removed after a second run eliminated chamber memory effects. All the experiments described in chapter 6 of this work were then conducted with a 'clean' chamber, although a prior sequence of experiments had been conducted before the silicon contamination problem was identified.
Table 2b: Sample surface composition before and after silicon decontamination of RIE chamber

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<tr>
<th>Sample preparation</th>
<th>Surface composition (Atom % measured by Auger spectroscopy)</th>
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<tr>
<td></td>
<td>F</td>
</tr>
<tr>
<td>Control (unprocessed wafer)</td>
<td>0.0</td>
</tr>
<tr>
<td>30 min. Ar etch with Si loaded electrode</td>
<td>0.0</td>
</tr>
<tr>
<td>30 min. Ar etch after Si wafer removed, and chamber cleaned</td>
<td>2.6</td>
</tr>
<tr>
<td>30 min. O&lt;sub&gt;2&lt;/sub&gt; etch after Si wafer removed, and chamber cleaned</td>
<td>2.2</td>
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3) R.f. power generation and matching

The power supply used with the GaAs reactive ion etcher was an R.D. Mathis r.f. power supply, built about 20 years ago. Its maximum output is 1250W, although in practice it is difficult to match more than about 500W into the etcher. Since the system is located on the ninth floor of a high-rise building, the r.f. earth is poor (it consists of a copper rod running down through the building, which effectively acts as an aerial), and consequently good matching between power supply and etcher is very difficult to achieve.

The system was used with a Plasma Technology matching network between the power supply and insulating oxidised aluminium sample electrode. The upper electrode was earthed, putting the system in a conventional reactive ion etch configuration. A major feature of this configuration is that the r.f. driven sample electrode rapidly acquires a large negative bias with respect to the plasma. This d.c. bias occurs because the positively charged reactive ions have a much
lower mobility than the negatively charged electrons. The electrons are accelerated more by a given electric field and consequently a larger electron current flows to the insulated electrode during the positive phase of the r.f. cycle. The electrode acquires a negative charge and the positive ions accelerated towards the electrode during the following negative phase are insufficient to discharge it. The resultant negative offset added to the r.f. voltage means that the electrode is negatively biased throughout most of the r.f. cycle [1]. The sample is bombarded almost continuously by positively charged reactive ions, whose kinetic energy is indicated by the d.c. bias.

The Plasma Technology matching network measures the d.c. bias voltage between the r.f. driven electrode and the system ground. The latter is not quite the same as the plasma potential: typical Langmuir probe measurements show that the plasma floats about 25V above the earthed chamber. However, when d.c. sample biases are measured of the order of several hundreds of volts, the error is reasonable. Experiments described in chapter six show that the variation in d.c. bias between sample and plasma can indeed be several hundred volts when different etch gases are used, even if other etch parameters are kept the same. A conventional reactive ion etch configuration cannot independently control this parameter (although it was noted that the new reactive ion beam and electron cyclotron resonance systems would be able to give independent control of ion kinetic energy) and so it was decided to allow this parameter to vary, to note it, and to take it into account when discussing results.

4) Etch parameters used in sample preparation

The same reactive ion etch parameters were used for all samples prepared for etch damage analysis in this work. These parameters were:
Table 2c: Standard etch parameters used in sample preparation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chamber pressure</td>
<td>100 mTorr</td>
</tr>
<tr>
<td>Gas mass flow rate (sum of mass flow rates for mixtures of gases)</td>
<td>20 sccm</td>
</tr>
<tr>
<td>R.F. power matched into chamber</td>
<td>100 W (1.3 W/cm²)</td>
</tr>
<tr>
<td>Etch duration</td>
<td>30 mins.</td>
</tr>
</tbody>
</table>

The chamber pressure chosen was high compared with typical GaAs RIE processes (see references listed after appendix 1). This was because one pressure had to be used for the multitude of different gases tested in this work, some of which could not be r.f. matched at lower pressures. The gas mass flow rate was typical when compared with the literature.

The power matched into the chamber was chosen to ensure that fairly high etch rates could be achieved when reactive gases were used, yet the power was low enough for the matching network to give negligible reflected power back to the r.f. generator for most gases. It was important that the power matched into the etch chamber was kept as similar from run to run as possible, since the plasma power affects not only the ion flux, but also the temperature of the substrate. This parameter is notoriously difficult to measure since considerable thermal gradients can arise between the surface of the substrate and the bulk, and also between the substrate and the electrode, where the thermocouple is usually embedded. In this system, the electrode was water cooled and the temperature of the water leaving the electrode was noted during each run. The maximum value allowed was 27°C, and so this gives a lower limit on the sample temperature. An upper limit was estimated to be 96°C, by assuming that the r.f. power matched into the chamber was entirely dissipated by thermal conductivity through the sample, GaAs loading wafer and electrode, to the cooling water.
The etch duration was 30 minutes for most experiments. This was chosen so that even the slowest etching inert gases would give etch steps which could be measured. Occasionally, when fast reactive gases were used to prepare samples where a deep etch step would affect the damage measurement a shorter etch time of six minutes was used, and this is discussed in more detail in chapters five and six.

The etch gases themselves were chosen after carrying out a literature review. This review is given in appendix one, and it concludes that the Freon-12 and methane/hydrogen processes are the most useful. Freon-12 was chosen to be the reactive gas examined, since it causes considerably more etch damage than the methane/hydrogen mixture and so would be less likely to stretch the sensitivity of the new measurement techniques. Inert gases were also examined for comparison, and finally hydrogen and ammonia reactive ion passivation treatments were investigated.

REFERENCE

Schottky diodes are frequently used to characterise the electronic damage sustained by reactive ion etched semiconductors. References 1 to 5 are a selection of the papers which have assessed GaAs RIE damage by measuring Schottky diode parameters. The popularity of the technique indicated that it should be investigated in this work, and used for comparison with the novel optical methods of etch damage assessment discussed in later chapters.

The fabrication of a test Schottky diode involves making an Ohmic contact on the back surface of the GaAs sample, reactive ion etching the front, then evaporating a Schottky contact on top of the etched front surface. The Ohmic contact is used to introduce current into the semiconductor side of the junction, and a probe placed on the Schottky metallisation allows the current-voltage characteristic of the junction to be plotted. In order to relate these characteristics to the electronic damage sustained by the etched surface, it is necessary to consider:

1. the theory of metal-semiconductor contacts,
2. the effect of RIE damage on such contacts,
3. the setting of a practical minimum damage baseline for comparison with RIE surfaces.

These will be discussed in the following sections of this chapter.

1) Review of the theory of metal-semiconductor contacts

Schottky's theory for rectification in metal-semiconductor contacts postulates that when a metal contacts a semiconductor in thermal equilibrium, charge transfer occurs until the two Fermi levels are the same. As shown in figure 3.1, if an n-type semiconductor is used with a suitable metal, a space charge region depleted in
3.1. Schottky model – band diagrams for n-type semiconductor

Separate metal and semiconductor

\[ E_{\text{vac}} \]

\[ E_{F} \]

\[ E_C \]

\[ E_v \]

\[ X \]

\[ \phi_m \]

\[ w \]

\[ \phi_b \]

- \( E_{\text{vac}} \) = vacuum energy
- \( E_C \) = bottom of conduction band
- \( E_F \) = Fermi level
- \( E_v \) = top of valence band
- \( X \) = semiconductor electron affinity
- \( \phi_m \) = metal work function
- \( w \) = width of space charge region
- \( \phi_b \) = built in potential barrier

Schottky contact

\[ E_{\text{vac}} \]

\[ E_C \]

\[ E_F \]

\[ E_v \]

\[ X \]

\[ \phi_m \]

\[ \phi_b \]

- \( E_{\text{vac}} \) = vacuum energy
- \( E_C \) = bottom of conduction band
- \( E_F \) = Fermi level
- \( E_v \) = top of valence band
- \( X \) = semiconductor electron affinity
- \( \phi_m \) = metal work function
- \( \phi_b \) = built in potential barrier

Static dipole layer formed at boundary
electrons builds up on the semiconductor side of the interface. To maintain charge neutrality, a thin layer of negative charge builds up at the metal surface. This dipole layer creates a potential barrier to the motion of electrons from the semiconductor to the metal [6]. Assuming a uniform distribution of ionised impurities across the depletion region of the semiconductor, Poisson's equation gives the one dimensional parabolic barrier shown in figure 3.1 and described by

\[
\phi(x) = \frac{q N_D x^2}{2 \varepsilon \varepsilon_0} \quad \text{...............(3.i)}
\]

for \( 0 \leq x \leq w \),

where \( q \) = electronic charge
\( N_D \) = ionised donor concentration
\( \varepsilon \) = static dielectric constant
\( \varepsilon_0 \) = permittivity of free space
\( w \) = depletion layer width

i) Barrier heights

To a first approximation, the barrier height is a fixed constant of the two contact materials and is given by

\[
\phi_b = q(\phi_m - X) \quad \text{...............(3.ii)}
\]

where \( \phi_b \) = barrier height
\( \phi_m \) = metal work function
\( X \) = semiconductor electron affinity

It has been observed experimentally that for highly covalent semiconductors such as GaAs, the barrier height is independent of the metal used [7]. It was first proposed by Bardeen that a high density of Tamm or Shockley surface states would pin the Fermi level at the interface, thus fixing the barrier height [8]. Such localised surface states have been shown to originate from the termination of the crystal lattice at the surface of a semiconductor [9]. Their energies can be distributed in the "forbidden" band between the valence band and the conduction band. When these surface states are at equilibrium with the bulk of the semiconductor, the "absolute zero approximation" assumes that they are occupied to the Fermi level \( E_F \) (see figure 3.2)
3.2. Bardeen model - surface state pinning of Fermi level

Separate metal and semiconductor

\[ E_{\text{vac}} \]

\[ q \phi_m \]

\[ \phi_{Bn} \]

\[ E_F \]

\[ \text{Metal} \]

\[ \text{Vacuum} \]

\[ \text{Energy} \]

\[ \text{Distance} \ x \]

\[ \phi_{Bn} = \text{potential barrier at semiconductor surface} \]

Schottky contact

\[ E_{\text{vac}} \]

\[ q \phi_m \]

\[ q \phi_{Bn} \]

\[ q \times E_c \]

\[ E_F \]

\[ \text{Metal} \]

\[ \text{n-type semiconductor} \]

\[ \text{Energy} \]

\[ \text{Distance} \ x \]
3.3. Parabolic depletion layer potential barrier for an n-type semiconductor

\[ E_b = \text{energy band bending in depletion region} \]
and reference 10). However, as the metal makes contact with the semiconductor, charge transfer occurs between the metal and semiconductor in order to bring the two Fermi levels into equilibrium. If the density of surface states is sufficient to accommodate these additional surface charges without appreciably increasing the occupation level $E_F$, the space charge layer in the semiconductor, and hence the barrier height, will remain unaffected [11]. Typical values for the density of surface states between GaAs and its oxide and nitride are given on pages 129 and 130 of chapter 7. The barrier height is therefore determined by the surface state density of the semiconductor surface. In reactive ion etching, further surface states are generated in the GaAs band gap by the impact of the ions on the crystal [3], and so these states will also determine the Schottky barrier height of an etched surface.

ii) Current transport

Three modes of current transport across the potential barrier will be considered here: thermionic, thermionic-field, and field emission, shown in figure 3.3.

Thermionic emission relies on the carriers having sufficient energy to pass over the Schottky barrier. The effect on the potential barrier of forward and reverse biasing the diode is shown by the band diagrams in figure 3.4. Forward bias reduces the band bending, whilst under reverse bias the energy barrier for electrons passing from the metal to the semiconductor is unchanged.

The assumptions made in the thermionic emission theory are as follows:

i) the barrier height, $e\phi >> kT$,

ii) thermal equilibrium is established at the plane which determines emission,

iii) the existence of a current flow does not affect this equilibrium, so that the two current fluxes, the tunneling current from the metal to the semiconductor, and the thermionic current from the semiconductor to the metal, can be superimposed.
3.4. Band diagrams showing effect of bias on potential barrier

Forward bias

Zero bias

Reverse bias

\[ E_F' = \text{quasi Fermi level} \]

\[ J_r \quad J_f \]

\[ J_r \quad J_f \]

\[ J_r \quad J_f \]
These assumptions suggest that the shape of the barrier is relatively unimportant, so that the current flow depends solely on the barrier height. The forward current-voltage curve for electrons travelling from the semiconductor to the metal is calculated using Maxwell-Boltzmann statistics to describe the distributions of carriers with sufficient kinetic energy to overcome the potential barrier. The details of this calculation are given in reference 10, and the resulting current equation is:

\[ J_r = \frac{A^* T e^{(-q\phi_e)} \exp(qV)}{kT} \] ...........(3.iii)

where \( J_r \) = forward current density
\( A^* \) = Richardson constant
\( T \) = absolute temperature
\( k \) = Boltzmann constant
\( V \) = applied voltage

Since the barrier height for electrons moving from the metal into the semiconductor remains the same, the current flowing into the semiconductor is unaffected by the applied voltage. It is equal to the current flowing from the semiconductor to the metal when \( V = 0 \), and in the opposite direction. The total current density is therefore

\[ J = \frac{A^* T e^{(-q\phi_e)} \{\exp(qV) - 1\}}{kT} \] ...........(3.iv)

For moderately doped semiconductors, the current-voltage characteristics for the forward direction are given by (3.iii) when \( V \gg 3kT/q \) and this equation can be used to calculate the barrier height. By extrapolating back the current-voltage plot to \( V = 0 \), and calling the current intercept \( J_0 \), the Schottky barrier height is given by

\[ \phi_e = \frac{kT \ln \left( \frac{A^* T e}{J_0} \right)}{q} \] ...........(3.v)

A correction can be introduced to equation (3.i) to allow for image force lowering of the Schottky barrier. When an electron is a distance \( x \) from the metal, a positive charge will be induced on the metal surface. The electrostatic attraction between these two charges...
lowers the parabolic energy distribution of (3.i) by

$$
\Delta \phi(x) = \left( \frac{c F E^* N_d}{8n^* \varepsilon \varepsilon_0^3} \right)^4 \text{(ref. 6)} \ldots (3.\text{vi})
$$

where $E_0 = \text{energy band bending in depletion region}$

$\varepsilon_0 = \text{dynamic dielectric constant}$

**Thermionic field emission** initially takes over from thermionic emission as the donor concentration is increased and the barrier becomes thin enough for thermally excited carriers to tunnel through the top of the barrier. In reference 6, a measure of the importance of thermionic field emission relative to thermionic emission is shown to be proportional to

$$\frac{\sqrt{N_0}}{T} \ldots \ldots \ldots (3.\text{vii})$$

As temperature increases, the fraction of current transported due to thermionic emission increases, but when doping increases, the barrier width is reduced and thermionic field emission tunneling is enhanced. The relative contribution of thermionic field emission to conduction can be allowed for in the diode equation (3.iv) by incorporating an ideality factor, $n$, into the equation thus:

$$J = J_0 T^e \exp(-qE_0) \exp\left(\frac{-qV}{kT}\right) \left[ 1 - \exp\left(\frac{-qV}{nkT}\right) \right] \ldots (3.\text{viii})$$

When $n$ equals one, equation (3.viii) reduces to equation (3.iv). The value of $n$ for non-ideal diodes can be determined by taking natural logarithms of this equation. A plot of $\ln(J/[1 - \exp(-qV/kT)])$ against $V$ will give a straight line graph of slope $q/nkT$ from which $n$ can be calculated.

**Field emission** tunneling occurs as the doping increases still further. The barrier eventually becomes so thin that significant numbers of carriers can tunnel through the base of the potential barrier, and the current becomes temperature independent. This mode of current transport is highly doping dependent, and is non-rectifying.
Heavy doping is therefore used to make Ohmic contacts to most semiconductor materials, including GaAs.

2. The effect of RIE damage on metal-semiconductor contacts

The theoretical work described in section 1 suggests that any process which changes the density of a semiconductor's surface states will also change the Schottky barrier height of a diode evaporated on that surface. A preliminary experiment on a helium ion etched GaAs surface resulted in a barrier height of 0.64 V, whilst the corresponding unetched surface had a barrier height of 0.89 V. This confirmed that the barrier height is a sensitive measure of the change in surface state density caused by different reactive ion etch processes.

Helium ion etching also increased the ideality factor of the Schottky contact from 1.3 to 1.9. The proportion of thermionic field emission to thermionic emission therefore increases with RIE damage. Equation (3.vii) shows that this ratio depends upon temperature and doping. The etched and unetched diodes were tested at the same ambient temperature with the same current flowing through the contact at each point in the I-V plot, and so the difference cannot be accounted for by temperature variation. Data has been published indicating that ion sputtering can cause a surface damage layer, related to As depletion [12] in n-type GaAs which reduces the depletion layer width, increases the degree of thermionic field emission, and hence increases the ideality factor [12,13]. It seems likely that the physical ion bombardment associated with reactive ion etching would have a similar effect. Thus, the ideality factor increase indicates that RIE has increased the concentration of donor-like states at the GaAs surface.

To summarise, the Schottky barrier height indicates changes in the surface state distribution caused by reactive ion etching. An increased ideality factor shows that the concentration of donor-like surface states has been increased by the RIE process. These
measurements are only useful, however, if we define a practical "minimum damage" baseline for comparison with the etched surfaces, and this is discussed in the following section.

3. Setting a practical minimum damage baseline

The Schottky diodes used in this work were made from silicon doped bulk GaAs, doping concentration $3.3 \times 10^{17} \leq N_0 \text{cm}^{-3} \leq 7.4 \times 10^{17}$, (110) orientation, and gold. It is important to establish here what mode of current transport is expected to predominate in such diodes at room temperature in order to establish an acceptable ideality factor for the unetched baseline. Also, the Schottky barrier height consistent with a minimal initial surface state concentration should be calculated.

In order to establish the mode of current transport, diodes were prepared using GaAs of the following doping concentrations:

1. $2 \times 10^{18}$ cm$^{-3}$, Si doped, 3 μm thick epitaxial GaAs,
2. $3.3 \times 10^{17} \leq N_0 \text{cm}^{-3} \leq 7.4 \times 10^{17}$, Si doped, bulk GaAs,
3. $2.1 \times 10^{18} \leq N_0 \text{cm}^{-3} \leq 7.5 \times 10^{18}$, Si doped, bulk GaAs.

Four diodes were prepared on each GaAs sample, and the mean ideality factors obtained from these sets of diodes are plotted in figure 3.5. The variation of ideality factor with doping agrees with equation (3.vii), indicating that the conduction consists of a mixture of thermionic and thermionic field emission. Reference 14 describes a theoretical method of predicting the ideality factors for mixed thermionic and thermionic field emission, and predicts an ideality factor range of $1.14 \leq n \leq 1.28$ for a gold contact made at room temperature to n-type GaAs of doping concentration range $2 \times 10^{17} \leq N_0 \text{cm}^{-3} \leq 7.5 \times 10^{17}$.

The surface state density, and hence barrier height, depends on the crystal orientation [10,16], the method of growth [15], and the
3.5. Graph of ideality factor against square root of doping concentration
surface finish [16]. For wet etched, (110) 5x10^{16} \text{ cm}^{-3} doped n-type GaAs, contacted with gold, the barrier height has been measured to be 0.94eV [16]. Using equation (3.vi), the image force lowering for 1eV band bending at this concentration is 0.04eV, and so the "ideal" barrier height with no image force lowering should be 0.98eV. For the approximately 5x10^{17} \text{ cm}^{-3} doped material used to prepare the baseline in this work, the image force lowering of the barrier height should be 0.07eV. The expected Schottky barrier height is therefore about 0.91eV.

The baseline diode should therefore have an ideality factor between 1.14 and 1.28 and a barrier height of about 0.91eV. Bearing this in mind, a reproducible process for diode manufacture and testing was developed as follows. Bulk, Si-doped, n-type GaAs was used so that the Ohmic contact could be evaporated on the back surface, the sample annealed and the front surface reactively ion etched without having to protect the Ohmic contact from the etch. An array of Schottky contacts could then be evaporated onto the etched front, again without any masking to protect the Ohmic contact. A cross-section of such a sample is shown in figure 3.6. The most lightly doped bulk GaAs that could be obtained for this experiment was 3.3x10^{17} \leq N_D \leq 7.4x10^{17}. Both sides had been lapped and then the front surface chemically polished.

The first samples were made by evaporating Au/Sn Ohmic contacts on the lapped back surface of the GaAs, annealing at 420°C for 90s to diffuse the tin into the surface (thus heavily doping it and encouraging tunneling through the surface potential barrier), and dipping in 10% ammonia solution for 5 minutes to remove any native oxide immediately before Schottky diode evaporation. An array of gold Schottky diodes was then evaporated on the polished front surface. The I-V characteristics were measured in darkness using a Wentworth prober and Tektronix curve-tracer (see figure 3.7). The voltage was measured at known currents in the range 10^{-9} to 10^{-4} Amps. A graph whose slope gives the diode's ideality factor was then plotted from the I-V.
3.6. Cross-section of test Schottky diode
3.7. Photograph of Schottky probe station
characteristics using a short Pascal program and "Energraphics" software package.

A set of 21 diodes made in this way was found to have a mean ideality factor of 1.26 and a standard deviation of 0.05. The corresponding barrier height was 0.87 ±0.02eV. The high ideality factor and low barrier height indicated that some surface damage remained after the manufacturer's polishing process. In order to obtain further evidence that the surface finish was the factor leading to the poor Schottky characteristics, a set of 28 diodes were made with the Ohmic contact evaporated on the polished surface and the Schottky contacts on the lapped surface. The mean ideality factor for the lapped surface was found to be 9, with a standard deviation of 3. The corresponding barrier height was 0.74 ±0.02eV. This indicated that polishing removes the majority of the lapping damage, and that perhaps a further process was required to remove the polishing damage.

Gentle bubble etching in one part ammonia to four parts hydrogen peroxide to forty parts water was used to remove the top 30 microns of the polished surface. The 30 diodes tested on this surface had a mean ideality factor of 1.16 and a standard deviation of 0.02. The corresponding barrier height was 0.89 ±0.02eV. A set of barcharts showing the number of diodes measured with each ideality factor for lapped, polished and bubble etched polished surfaces is shown in figure 3.8. They show the ideality factor decreasing towards its predicted value as the GaAs surface is processed. Also, a decrease in the standard deviation of the measurements is noted. The standard deviation decreases by an order of magnitude when the lapped surface is polished, and a further factor of 2.5 is lost when the polished surface is bubble etched.

The mean ideality factor of the bubble etched, polished surface lies within the predicted range of ideality factors and the standard deviation is small. The Schottky barrier height is also acceptable, taking the error estimate into account, so the bubble etched, polished
3.8. Bar charts showing distribution of diode ideality factor with surface treatment

![Bar charts showing distribution of diode ideality factor with surface treatment](image)
surface has been used as the baseline for all subsequent Schottky diode measurements in this work. Samples were prepared by evaporating Ohmic contacts on the lapped back surface, annealing them, then bubble etching the polished front surface as described above. The samples were then placed bubble etched side up in the reactive ion etcher and partly shadow masked with another piece of GaAs. Shadow masking was found to give better protection to the reference unetched surface than resist masking. After reactive ion etching, the sample was dipped in dilute ammonia to remove the native oxide layer, and gold Schottky contacts were evaporated on both etched and unetched regions. The mean ideality factors and barrier heights of these regions were then compared as a measure of the reactive ion etch damage.
REFERENCES


CHAPTER FOUR

Analytical methods 2: Photothermal radiometric microscope

The photothermal radiometric microscope [1] is shown schematically in figure 4.1. It uses an intensity modulated, 15mW, 860 nm semiconductor laser to optically pump the sample's surface. The collimated beam is reflected off the germanium filter at 45° into the aperture of an infra-red reflecting objective. The beam is focused onto the surface of the sample with a spot diameter of about 2 μm. Absorption of the modulated laser beam generates both a thermal wave and an electron-hole pair plasma in a semiconductor sample, leading to the modulated emission of black body radiation. Both the reflected laser light and the black body radiation are collected with the same objective and re-collimated. At the germanium filter the black body radiation (wavelength centred around 10 μm) and the laser light are separated. A second reflecting objective is used to focus the black body radiation onto a CMT infra-red detector, whilst the laser light is focused onto a photodiode. An IBM XT computer is used to control the scanning of the sample and to display linescans. Complete colour images can be obtained, but these were found to take far too long with GaAs samples since the integration time for each pixel needs to be at least half a second. Figure 4.2 shows a typical linescan across a partially masked argon ion etched GaAs sample. The mechanism causing the contrast shown will now be discussed.

1) Radiometric imaging of semiconductors

The exciting laser has sufficient photon energy to stimulate an electron-hole plasma in the semiconductor, which temporarily stores the energy until the electrons and holes recombine, giving up their energy to the lattice. Before recombination, the photogenerated carriers increase the emissivity of the semiconductor surface, and so the magnitude of the black body radiation varies with the lifetime of the carriers. When recombination occurs, a thermal wave is generated in the lattice, and the corresponding surface temperature fluctuations...
4.1. Schematic of photothermal radiometric microscope
4.2. Typical photothermal microscope linescan of RIE GaAs
also give rise to black body radiation. There are therefore two
effects, one a function of the electronic structure and the other a
function of the lattice properties of the semiconductor. To determine
the dominant mechanism in each experiment in order to interpret the
image contrast, it is necessary to study thermal wave and free carrier
emission more closely.

2) Thermal wave emission

A thermal wave is a continuously stimulated temperature wave
propagating in a lossy material, generated by the periodic absorption
of the heating beam [1]. The corresponding surface temperature
fluctuations are detected via the black-body radiation emitted by the
surface. For an opaque material, the change in radiated power, $\Delta Q$
corresponding to a small change in surface temperature, $\Delta T$ is given by
[1]

$$\Delta Q = 4\alpha e T^3 \Delta T A \ldots \ldots \ldots \ldots \ldots (4.i)$$

where $\alpha$ = Stefan-Boltzmann constant
$\epsilon$ = material emissivity
$T$ = ambient temperature
and $A$ = emitting surface area

Thermal wave propagation is characterized by a slow response to the
driving square wave, shown in figure 4.3. When the laser turns on, the
surface temperature increases slowly. When the laser turns off, the
temperature slowly decays to its original value. Also, as the
modulation frequency of the laser beam is increased, the magnitude of
the thermal wave signal decreases. This is shown in figure 4.5.

3) Free carrier emission

The generation of an electron-hole pair plasma in a semiconductor
can be used to modulate the infra-red emissivity of the sample. The
change in radiated power is given by [1]

$$\Delta Q = \Delta \epsilon \sigma T^3 A \ldots \ldots \ldots \ldots \ldots (4.ii)$$

where $\Delta \epsilon$ = periodic change in laser induced emissivity
4.3. Thermal response to square wave modulation

5 mV

Driving laser signal

200 mV

Thermal response (rubber sample)

200 μS

4.4. Free carrier response to square wave modulation

5 mV

Driving laser signal

10 mV

Free carrier response GaAs sample

200 μS
4.5. Variation of signal amplitude with frequency

![Graph showing variation of signal amplitude with frequency with free carrier and thermal response areas.](image.png)
Free carrier response is characterised by a relatively short time delay between the laser switching on and off and the radiated signal falling, shown in figure 4.4. This occurs because equilibrium is quickly reached between the photogeneration of carriers by the laser and their recombination. When the laser turns off, the free carrier density decays exponentially due to recombination, but still in a time period much shorter than the laser period. As shown in figure 4.5, the magnitude of the plasma signal is unchanged by increasing the modulation frequency of the laser, until a frequency of $1/\tau$ is reached, where $\tau$ is the carrier lifetime of the sample.

4) Experimental methods of differentiating between the two effects

In order to ensure that the free carrier response of the sample is the predominant form of image contrast, it is first necessary to use near intrinsic samples, since otherwise the contrast between the photogenerated electron-hole pairs and the doped carrier density may be insufficient. Secondly, since the free carrier response has a $T^\alpha$ dependence, whilst the thermal wave signal varies as $T^3$, heating the sample forces the former to predominate. The samples were heated to $100^\circ$C in the free carrier measurements. Finally, the free carrier signal can be identified by checking that the time delay between the modulated laser power and the infra-red signal is negligible, and also by increasing the modulation frequency. If the signal amplitude drops, thermal effects predominate, whilst if it stays constant, free carrier effects dominate.

Thermal wave imaging was observed to predominate when semi-insulating samples were scanned with the 515nm line of the Ar$^+$ ion laser. This can be explained by considering how the photon energy $h\nu$, is distributed between the electron-hole plasma and the lattice when it is absorbed. Let the band gap energy be $E_g$. When the photon is absorbed, an electron is promoted into the conduction band. Part of that energy, $h\nu - E_g$, is transferred to the lattice thermal wave within a picosecond of absorption as the electron relaxes to the band edge.
Thus if a photon with an energy much greater than the band gap is used to probe a semi-insulating sample, the excess energy goes into the thermal wave. A mainly thermal wave signal can be confirmed by checking that there is a slow response to the driving laser and by increasing the modulation frequency to ensure that the signal amplitude drops.

5) Physical interpretation of free carrier contrast

The signal derived from free carrier infra-red emission will vary proportionally with free carrier lifetime. Theoretical analysis given in reference 2 shows that the change in radiated power can be expressed in terms of the material parameters by

\[
\Delta q = \int_{\lambda_1}^{\lambda_2} \frac{\Sigma(\lambda)6(1-R)I_o L_o}{hv(D+L_o s)} Q_a(\lambda,\Theta_s) d\lambda \ldots \ldots \ldots \ldots \ldots \ldots (4.i i i)
\]

where

- \( \lambda_1, \lambda_2 \) = spectral limits of infra-red detector
- \( \Sigma(\lambda) \) = free carrier absorption constant
- \( \delta \) = carrier generation quantum efficiency
- \( R \) = surface reflection coefficient
- \( I_o \) = peak intensity of laser
- \( L_o \) = diffusion length of free carriers, \( L_o = (Dt)^{1/2} \)
- \( Q_a(\lambda,\Theta_s) \) = Planck's radiation function
- \( h \) = Planck's constant
- \( v \) = photon frequency
- \( D \) = carrier diffusion coefficient
- \( s \) = surface recombination velocity

The parameters in this equation which could vary with sample surface treatment are \( L_o, R \) and \( s \).

The variation of reflectance spectra with ion bombardment damage has been investigated in the literature. Reference 3 shows that for 75 keV Ar⁺ ion implantation, the curvature of the reflectance spectrum is related to the damage, not the absolute value of the reflection coefficient at a given energy. The wavelength derivative of the reflectance was also used in reference 4 to detect 800 eV Ar sputtering damage, and no mention was made of the absolute value of \( R \).
Although the ion bombardment energies are higher than those used in RIE, these results suggest that the reflection coefficient at one wavelength will not vary significantly with low energy RIE damage, and so \( R \) is taken to be a constant in this work.

The electrical assessment of semi-insulating bulk GaAs is still in its infancy, and techniques for measuring these parameters in this material have yet to be developed. The mobilities of electrons and holes have been measured in undoped semi-insulating GaAs in reference 8, and from these values the diffusion coefficients have been calculated using the following equation

\[
D = \frac{\mu kT}{q}
\]

where \( \mu = \text{mobility (m}^2\text{V}^{-1}\text{s}^{-1}) \)

The other parameters have been noted for lightly doped n and p type GaAs, to indicate the order of magnitude that may be found in semi-insulating material.

Table 4a: Transport parameters for electrons in lightly doped p-type or S.I. GaAs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Doping</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_e )</td>
<td>140x10^{-6} m</td>
<td>1.9x10^{15} cm^{-3}</td>
<td>7</td>
</tr>
<tr>
<td>( S )</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( D )</td>
<td>9.5x10^{-4} m^2 s^{-1}</td>
<td>Undoped S.I.</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 4b: Transport parameters for holes in lightly doped n-type or S.I. GaAs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Doping</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_h )</td>
<td>&gt;2.5x10^{-6} m</td>
<td>2.0x10^{16} cm^{-3}</td>
<td>5</td>
</tr>
<tr>
<td>( S )</td>
<td>3000 ms^{-1}</td>
<td>5.1x10^{16} cm^{-3}</td>
<td>6</td>
</tr>
<tr>
<td>( D )</td>
<td>5.8x10^{-4} m^2 s^{-1}</td>
<td>Undoped S.I.</td>
<td>8</td>
</tr>
</tbody>
</table>

Using the value of \( s \) obtained for n-type GaAs for both types of material, \( L_e s \) is at least an order of magnitude greater than \( D \), for
holes or electrons. We can therefore assume $L_s s \gg D$ and approximate equation (4.iii) as

$$\Delta Q = \frac{\delta (1-R) L_s L_n}{h v s} \int \frac{\lambda^e}{\lambda} \Sigma(\lambda) Q_e (\lambda, \theta_s) d\lambda \ldots \ldots (4.v)$$

This suggests that for a GaAs/air interface, the free carrier emission is inversely proportional to the surface recombination velocity, and directly proportional to the diffusion length. If the bulk diffusion length is assumed to be largely unaffected by reactive ion etching, the technique is useful for examining the damage caused to the semi-insulating GaAs samples. This assumption is justified in chapter eight, when the estimated penetration of RIE etch damage is shown in figure 8.1. The maximum damage depth is estimated to be 500 Angstroms, which is fifty times smaller than the hole diffusion length and three orders of magnitude smaller than the electron diffusion length tabulated above. It is therefore unlikely that RIE will affect this parameter, and we can say that the PRM measured variations in the surface recombination velocity only. The contrast is good, and a semi-quantitative method of comparing etch damage from sample to sample has been used. Each sample had a shadow masked area which is unaffected by the reactive ion etch. After processing, the masked area was used as the unetched reference. This proved to be a good reference: the average value of the infra-red signal had a standard deviation of 23% in a set of 21 samples from the same wafer, analysed in the same batch. A typical photothermal microscope linescan across such a sample is shown in figure 4.2. The ratio of $A/B$ (as shown in the figure), and henceforth called the photothermal radiometric microscope ratio (PRM ratio), gives the factor by which $s$ is changed by the etch process, and this gives a measure of the damage sustained by the sample's surface.

A physical limitation of the microscope was discovered in this work. The depth of field of the microscope has been estimated to be one micron [9], but even though the Freon-12 reactive ion etched
samples were only etched for 6 minutes in the experiments described in chapter six, the resultant etch steps were deeper than this. The area from which the infra-red signal was collected was therefore larger on the etched side than the focused spot on the unetched control side of the sample, and these results were not valid measurements of etch damage. Fortunately, all the inert etches and passivation treatments described in this work did not remove sufficient material for the depth of field of the microscope to affect their etch damage assessment.

REFERENCES


3 D.D. Sell and A.U. MacRae, "Optical detection of surface damage in GaAs induced by argon ion implantation", J. Appl. Phys. 41, 1970, p.4929.


CHAPTER FIVE

Analytical methods 3: Auston switches

Auston switches are high speed photoconductive switches, used to generate electronic waveforms with picosecond precision for the characterisation of high-speed materials and devices [1,2]. They have not been used to evaluate the effects of semiconductor processing before.

A typical Auston switch consists of a photoconducting film on an insulating substrate on which electrodes have been deposited to form a microstrip transmission line with a gap in it. Since GaAs is available in a photoconductive, semi-insulating form, the simpler structure shown in fig. 5.1 has been used in this work. A small gap of about 40 microns is left in the top microstrip electrode, and this is the active region of the device. When a picosecond pulse of light is focused on the gap, electron-hole pairs are generated, if the photon energy is equal to or greater than the semiconductor band gap. The photogenerated free carriers temporarily short out the switch gap, allowing an electrical pulse to be transferred from one electrode to the other. The rise time of the photoconductivity pulse is limited by the uncertainty principle to $1/v$, where $v$ is the frequency of the photon. This can be as short as $10^{-13}$ s and consequently does not impose an effective limit on the rise time of the detected photocurrent. The quantum efficiency of the initial photocurrent yield is determined by the probability that the electrons and holes will escape the electron-hole pair mutual electrostatic field. In a high mobility semiconductor such as GaAs, this probability is practically 100%.

Although the generation of a photocurrent in the semiconductor is very rapid, the recombination time, which determines the decay time of the photoconductivity pulse, is comparatively slow (and is thus a major problem for picosecond device applications). For damage measurement purposes, this is not a problem, rather an advantage,
5.1. Cross-section of Auston switch

850 nm, 5 ps laser pulse

Photogenerated electron hole pairs

- 200 nm Au
- 20 nm Cr
- 500 microns GaAs
- 20 nm Cr
- 200 nm Au
since the switch is to be used to compare the recombination time at etched and unetched GaAs surfaces. In fast switching devices, the recombination time has been reduced by introducing defects, or mid band energy levels into the semiconductor which act as traps and/or recombination centres. Fast switching may be achieved by radiation damage, impurity addition, or the use of amorphous semiconductors. In reference 2, a dose of $3 \times 10^{15}$ ions cm$^{-2}$ of 400 keV O$^+$ ions reduced the relaxation time of a silicon on sapphire switch from 750 ps to 8 ps.

The rise and decay times of the electrical pulse generated by the switch are not identical to those of the photoconductivity pulse. The photoconductor is incorporated into a transmission line, and the circuit time constant of the transmission line network introduces a delay [1]. Reflections can occur if matching between the microstrip and its external connectors is poor. The electrical bias signal will affect the output pulse and the device used to measure the electrical pulse may distort it further by convoluting the signal with its own impulse response. Despite this, the resultant electrical pulse is still very fast, of the order of 100 ps, and high speed sampling techniques were used. The design and manufacture of the microstrip circuit, the design of the sample mount and the quality of the connections between the microstrip and the coaxial cables are all critical if a reliable pulse period measurement is desired. These topics will be discussed in further detail under the following headings:

1) Design, fabrication and testing of Auston switch circuit and mount
2) High speed sampling techniques
3) Deconvolution of the photoconductivity pulse response from the measured electrical response.

Finally, the physical interpretation of the photoconductivity decay in the switch gap will be considered.
The microstrip used in the Auston switch chip was fabricated on a 500 μm thick undoped S.I. GaAs wafer, and was designed to have a 50Ω characteristic impedance. Using Wheeler’s approximation [3], the ratio of the top electrode width to the thickness of the insulating substrate should be 0.88 for 50 Ohm ± 1 Ohm impedance, and so the electrodes were made 440 microns wide. The configuration of the top electrodes is shown in figure 5.2, and was taken from Auston’s paper on correlation measurements [4]. A mask set was designed using the GAELIC CAD software available on the Rutherford-Appleton Laboratory’s (RAL’s) Prime computer, and the masks were then fabricated by the SERC electron-beam lithography facility at the RAL. The mask set consisted of a pair of negative masks. The first defined the pattern of the top electrodes and the second mask was used to produce a protective coating of resist over the electrodes in order to protect them whilst the Auston switch gaps were being reactively ion-etched. A series of devices were available on each mask, allowing a range of switch gaps from 10μm to 80μm to be fabricated and tested.

The fabrication procedure outlined in figure 5.3 was developed in the device fabrication clean room. A series of switches were made with different switch gap widths, and the amplitudes of the switches’ responses were compared to indicate the efficiency of the electrodes in collecting the photo-generated charge. A trend was noted showing an increase in efficiency as the switch gaps became smaller and the carrier-generating laser beam covered the gap area more efficiently. However, the smallest (10 micron) switch gap was not used because the lift-off process was unreliable when used for switch gaps of less than 20 micron. Instead, as a compromise, a 40 micron gap was used for subsequent experiments.

Both sides of the semi-insulating wafer were polished, and the damage introduced by the polishing process was to prove useful. It is important that the top electrodes of the stripline make good Ohmic
5.2. Switch configuration used for sampling oscilloscope measurements
5.3. Fabrication procedure for Auston switches (details given in appendix II)

(100) cut, undoped S.I. GaAs wafer

**Evaporator** - 20 nm Cr, then 200 nm Au evaporated on wafer back

**Diamond saw** - Wafer cut up into 9.8 mm squares

**Resist spinner** - Samples cleaned, then spun in negative resist to give a 200 nm thick film

**UV mask aligner** - Electrode pattern exposed, soaked in chlorobenzene to harden the surface, and developed

**Evaporator** - 20 nm Cr, then 200 nm Au evaporated on top of resist.

**Wet bench** - 'Lift off' completed by soaking in acetone. Resist dissolves and takes unwanted Au with it

**Resist spinner and mask aligner** - Second layer of resist spun, second mask exposed and developed, to leave switch gaps exposed

**Reactive ion etcher** - Switch gaps reactive ion etched and resist removed with acetone

Sample ready for mounting and testing
contacts to the switch gap so that they efficiently collect any photo-generated charge. A Schottky barrier would normally form between the metal and a semi-insulating semiconductor, but the GaAs polished surface had such a high defect density that the surface depletion layer was sufficiently narrow for tunneling currents to pass through it to the contacts. A current-voltage graph for the electrodes across the switch gap was obtained by probing the Auston switch using the Schottky diode test equipment described in chapter 3. The graph was firstly plotted for the dark current, and then the microscope light attached to the Schottky probe station was switched on to check that the trace remained Ohmic when illuminated. The dark condition graph in figure 5.4 shows that the switch remained linear up to 45V and that low power optical illumination increased the conductance of the gap but the contacts remained Ohmic up to 30V. The dark conductance was noted to be $28 \times 10^{-7}$ Siemens.

The quality of the Ohmic contacts was found to depend on the polished surface damage, and so the top surface of the sample could not be wet etched in order to set a "low damage" baseline similar to that used for the Schottky measurements. An attempt to wet etch the switch gap alone, using the protective resist mask designed for the reactive ion etcher, proved unsuccessful. It is necessary to etch down 30μm to clear the surface damage (this was deduced in chapter 3 from the Schottky ideality factors of devices fabricated after a range of wet etch depths). The switch gaps were 40 microns wide, and so the surface area was more than doubled when compared with a switch gap of the same width, but negligible etch depth. This increased the surface recombination velocity and hence reduced the decay time of the carriers in the switch gap. It was therefore decided to use the as-received, polished surface as the low-damage baseline for the optical experiments. Also, it was noted that care would have to be taken to ensure that the reactive ion etching did not produce a trench more than four microns deep, so that the surface area was not increased by more than 20% for a 40 micron switch.
5.4. I–V characteristic of Auston switch gap
The sample was then mounted so that the back metal plane was earthed, the front electrodes were connected to SMA tab connectors and the laser beam could still illuminate the switch gap. The tab connectors are designed to make a flat contact onto the top electrode of the microstrip and transform the strip geometry to the circular cross-section pin of the central electrode of the 50 Ohm SMA coaxial connector. The earthed outer conductor of the coaxial connector was contacted to the same earth as the earth plane of the microstrip. The connectors and mating semi-rigid coaxial cables allow operation at frequencies from a few MHz through to 25 GHz, according to the manufacturer's literature. It was not feasible to mount each Auston switch in its own package, because the connectors were too expensive, and machining the mounts required expensive precision machining. Instead, four re-usable mounts were made. Each mount consisted of a cube of brass, into which a locating recess was milled. The Auston switch sample was placed in this recess, and a frame containing the four connectors was attached - see photograph 5.5. The connectors and locating recess were positioned so that the tabs were always aligned with the switch electrodes.

The tab connectors proved unreliable initially, and experiments were carried out to check the electrical effect of a spot of conducting epoxy between the tab and the electrode. A Hewlett Packard 25GHz network analyser was used to test the transmission and reflection s-parameters of the unbroken electrode in the centre of the Auston switch sample. The scans showed that the pressure tab contact caused the worst attenuation at higher frequencies, even though the d.c. resistance of the contact was the same as the glued contacts. Silver loaded epoxy resin between tab and microstrip improved the contact a little, but a marked improvement was observed when silver dag was used. A sample was prepared with the microstrip electrolytically plated up to 2 micron of gold, to see whether the skin effect was reducing transmission at higher frequencies, but this did not improve the electrical characteristics of the circuit.
5.5. Photograph of mounted Auston switch sample
The samples were therefore manufactured with 40 micron polished GaAs switch gaps and unplated 200nm thick electrodes. They were contacted using tab connectors with a spot of silver dag between the electrode and the connector, and d.c. tested for good contacts between sample and coaxial connection and short circuits. The interconnected device was then tested optically.

2) Picosecond sampling techniques

Two methods for testing the optical performance of the Auston switch were used:

i) High speed sampling oscilloscope

ii) Electro-optic sampling

i) Sampling oscilloscope

Some preliminary measurements were made with a Tektronix S4 sampling head and a 200 MHz 7704A Tektronix oscilloscope mainframe. The sampling head upper 3dB roll off was at 14 GHz. The switch electrode configuration is shown in figure 5.2. The input electrode was d.c. biased at 17V and a matched 50 Ohm load was placed at the other end of the electrode. Two output electrodes, at right angles to the input electrode, with 40 micron wide switch gaps were used for testing. Fifty Ohm semi-rigid coaxial cable was used to connect the output electrode to the sampling head. A Polaroid photograph of the oscilloscope trace of the response of a Freon-12 etched Auston switch is shown in figure 5.6. The photograph shows that there are reflections of about 200ps period on the line. The geometry of the stripline was such that this would be the round trip time for a reflection from the bias connection to the 50 Ohm matched load. The photograph indicates that the photoconductive decay curve only becomes exponential after an initial, faster part. The first part of the transient depends on the duration and shape of the optical pulse used, and the initial rate of decay approximates to the steady-state lifetime under optical illumination [5]. Care must be taken to ensure that the true exponential decay transient \( t \to \infty \) is measured.
5.6. Polaroid photograph of sampling oscilloscope response to a Freon-12 etched Auston switch
The sampling head proved to be a useful device to check that the switch gap was aligned to the switching laser beam and that the switch was working. However, a photograph of an oscilloscope trace was unsuitable for further data analysis and so another measurement technique was developed. The sampling head was still used in parallel with the other measurements, since it immediately confirmed that the switch was working and that the position of the laser beam was optimised in the switch gap to produce the largest amplitude electrical signal pulse. The electro-optic correlation measurement, which took several minutes to complete a scan, could then be started with confidence.

ii) Electro-optic sampling

The Pockels or electro-optic effect is the principle of this measurement technique. An electric field applied to an electro-optic crystal can change the birefringence properties and hence rotates the polarisation of light that passes through it. By placing the crystal between crossed polarisers, the transmitted light intensity changes as a function of the electric field.

GaAs is an electro-optic material, and so an electric field present in a GaAs substrate can be detected using this effect. A stripline transmission line fabricated on a GaAs substrate can be used as an electro-optic modulator [8]. As shown in figure 5.7, the electrode structure has a fringing field adjacent to the electrodes. A polarised sampling laser beam with a photon energy less than the GaAs band gap (1.06 µm) enters the substrate in the fringing field region from above and is reflected back up from the ground plane electrode. The optical beam travels parallel to the electric field in the crystal and so experiences a longitudinal electro-optic effect.

When the output of an Auston switch is connected to such an electro-optic modulator, the electric fields caused by the pulse propagating along the microstrip are detected by the change in polarisation of the reflected sampling beam. If the time delay between
5.7. GaAs microstrip used as an electro-optic modulator (depicted with electric field lines)

1.06 micron, 5 ps laser pulse
the 850 nm laser beam firing the Auston switch and the 1.06 μm sampling beam is varied, a trace of the Auston switch response is obtained.

The temporal resolution of an electro-optic sampler is limited by three factors: the optical pulse width of the sampling beam, the transit time through the electric field present in the GaAs substrate, and the timing jitter between the optical pulse repetition rate and the signal on the Auston switch [9]. In this experiment, the same Nd YAG laser was used to pump the Styryl9-M dye laser which fired the Auston switch as was used to sample the electro-optic line (see figure 5.8). Timing jitter between the two pulse trains therefore did not occur. Using the approximation of a rectangular optical pulse and a constant electric field between the interaction region, the frequency response of the electro-optic sampler is given by [9]

\[ E(f) = E_c \cdot \text{sinc} \left( \frac{w \Delta T}{2} \right) \cdot \text{sinc} \left( \frac{w \Delta P}{2} \right) \ldots (5.1) \]

where \( \Delta P \) = pulse width
\( \Delta T \) = transit time through the interaction region

In this work, the 100 ps Nd YAG pulse was passed through a grating pulse compressor to shorten it to 5ps before reaching the electro-optic sampling line. The transit time through a 500 μm thick GaAs substrate is 12 ps. The resulting bandwidth is about 35 GHz.

3) Deconvolution of the photoconductivity pulse from the measured electrical response.

The electrical response measured by the electro-optic sampling line is a function of the:
- microstrip circuit response function, \( k(t) \),
- bandwidth of the connectors, \( c(t) \),
- electro-optic sampling line response, \( e(t) \),
- photoconductivity pulse, \( g(t) \).

In this section, the mathematical modelling of the measured electrical response of the switch, as developed by Auston in reference 1, is
5.8. Electro-optic sampling system used in Auston switch experiment

CHART RECORDER

LOCK-IN AMPLIFIER

PHOTODIODE

REFLECTED BEAM

ELECTRO-OPTIC MODULATOR

GRATING PULSE COMPRESSOR (5 PS)

OPTICAL DELAY LINE

Nd YAG LASER
1.06 um, 100 ps, 76 MHz

KTP frequency doubler

STYRYL 9-M LASER
850 nm, 4 ps, 76 MHz

Mechanical chopper
133 MHz ref. signal for lock-in amplifier

AUSTON SWITCH

50 OHM, 18 GHz, COAXIAL CABLE
described. The relative importance of the first three effects listed above are considered, and the deconvolution used to separate the photoconductivity pulse from the experimental measurement is described.

i) Mathematical modelling of Auston switch circuit

The equivalent circuit for a single Auston switch was devised by neglecting retardation effects and representing the photoconductor by time-varying lumped circuit elements. These are a conductance, $g(t)$, and a capacitor with a charge $q(t)$ in parallel, as shown in figure 5.9. This approximation is only valid if the dimensions of the gap and the transmission line cross-section are small relative to the distance an electro-magnetic signal would travel in the shortest time interval of interest. To check this, in 30 ps, an electromagnetic wave will travel 2.6mm in a GaAs substrate. The width of the sample electrode is 0.44 mm, the substrate thickness is 0.5 mm and the switch gap is 0.04 mm, and so the approximation is valid. The charge generated in the sampling transmission line by this circuit can then be written:

\[ Q_m(t) = Q_\infty + \int_{-\infty}^{+\infty} dt' f_m(t' - \tau)V_{D1}\delta(t') \ldots (5.ii) \]

where

\[ f_m(t) = \frac{2}{3ZC_m (1+3ZCG_\infty)} \int_{-\infty}^{+\infty} dt' g(t) \exp\left[-\Gamma(t' - t)\right] \]

\[ \Gamma = \frac{2}{3ZC_m C_\infty} + \frac{G_\infty}{3ZC_m} \text{, the circuit damping factor} \]

\[ C_m = \text{capacitance of switch gap} \]

\[ G_\infty = \text{dark conductance} \]

Let

\[ k(t) = \frac{2}{3ZC_m (1+3ZCG_\infty)} g(t) \exp\left[-\Gamma t\right] \ldots (5.iii) \]

then (5.iii) can be written as the convolution of three terms

\[ Q_m(t) = Q_\infty + V_{D1}\delta(t) * k(t) \]

where * = convolution integral
5.9. a) Microstrip circuit showing incident, reflected, sampled and transmitted waves
b) Equivalent lumped circuit
In Auston's work, the average current for a repetitive train of pulses is measured instead of the total sampled charge $Q$. When using the electro-optic sampling line, the average voltage at a point on the transmission line is measured for a repetitive train of pulses. Since the current and voltage at a given point on a transmission line are related by characteristic impedance of the line, $Z_0$

$$Z_0 = \frac{V(x,t)}{I(x,t)} \quad (5.iv)$$

the voltage measured in this work is directly proportional to the current for which Auston's expression is derived.

$$v(t) = B \cdot \varepsilon \cdot g(t) \cdot k(t) \quad (5.v)$$

where $B$ is a constant of proportionality.

Before reaching the electro-optic sampling line, the signal has to pass through the SMA connectors and a semi-rigid coaxial cable. Both of these act as low-pass filters, and their effect can be accounted for by another convolution [6]. The transmission line voltage is convolved with the connector's time response thus

$$v'(t) = B \cdot \varepsilon \cdot g(t) \cdot k(t) \cdot c(t) \quad (5.vi)$$

by the time it reaches the electro-optic sampling line.

The sampling line performs a cross-correlation measurement of the signal $v'(t)$, as the optical delay line scans the time delay between the Auston switch laser pulse and the electro-optic sampling pulse. The final measurement can therefore be written

$$m(t) = B \cdot \text{Corr}(v'(t), e(t))$$

$$m(t) = B \cdot \text{Corr}(\varepsilon \cdot g(t) \cdot k(t) \cdot c(t), e(t)) \quad (5.vii)$$

ii) Deconvolution of photoconductivity pulse

Splitting equation (5.vii) to deduce $g(t)$ in the time domain would be very complicated. Fourier transforms can be used to simplify the equation using the convolution law [6]:

page 82
Fourier

\[
\text{if } a(t) \leftrightarrow A(f) \\
\text{transform} \\
\text{and } b(t) \leftrightarrow B(f) \\
\text{then } a(t) * b(t) \leftrightarrow A(f) . B(f)
\]

and the correlation law:

\[
\text{Corr}(a(t), b(t)) \leftrightarrow A(f) . B(f)^* \\
\text{where } B(f)^* = \text{complex conjugate of } B(f).
\]

Thus taking the Fourier transform of (5.vii),

\[
M(f) = B . v_{o1..} . G(f) . K(f) . C(f) . E(f)^*. \ldots \ldots \ldots (5.viii)
\]

Since \( v_{o1..} \) is constant for the time-scale of interest, it can be included in the constant term. \( G(f) \) is the recombination term that we want to separate out. \( K(f) \) is the Fourier transform of \( k(t) \), the circuit response. From equation (5.ii) we can see that \( k(t) \) is a one-sided exponential decay pulse of time constant \( 1/\Gamma \), where

\[
\Gamma = \frac{2}{3Z_o C_o} + \frac{G_o}{C_w}
\]

In section 1 of this chapter, it was noted that the dark conductivity, \( G_o \), was 28nS. The capacitances of gaps in microstrip transmission lines have been calculated in reference 10, and reading off the graphs published in this work, the capacitance of a 40 \( \mu \)m gap in \( Z_o = 50\Omega \) microstrip fabricated on 0.5mm thick GaAs is approximately 0.03pF. Using this as the value of \( C_w \), the exponential decay time constant can be estimated to be 2.25 ps. This is practically a delta function relative to the decay pulse that we are trying to measure, and the corresponding Fourier transform will have a bandwidth of about 400 GHz.

\( C(f) \) is the frequency response of the connectors. In section two of this chapter it was mentioned that the frequency response of the SMA connectors and unbroken microstrip was measured in order to compare different methods of contacting. It was noticed at the time that the spectrum crossed -3dB at only 10 GHz, and this indicated that
the connectors could seriously reduce the bandwidth of the electrical signal. In order to measure the effect of the microstrip and the connectors in the experimental electrode configuration, a special test sample was made as shown in figure 5.10. This sample is identical to those used in the experiment, except that it has no switch gap. It's frequency spectrum is shown in figure 5.11 and this shows that the bandwidth of the experiment is indeed impaired. The bandwidth of the semi-rigid coaxial lines used to connect the SMA connectors to the electro-optic sampling line was specified by the manufacturers to be 25.0 GHz, and so these would not significantly affect the signal.

$E(f)$ is the frequency response of the electro-optic sampling line. An expression for $E(f)$ has been given in equation (5.1), and the resultant bandwidth was estimated to be 35 GHz.

<table>
<thead>
<tr>
<th>Term in equation (5.viii)</th>
<th>Bandwidth (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K(f)$</td>
<td>400</td>
</tr>
<tr>
<td>$C(f)$</td>
<td>&lt;20</td>
</tr>
<tr>
<td>$E(f)$</td>
<td>35</td>
</tr>
</tbody>
</table>

Table 5a: Summary of bandwidths of components of Auston switch experiment

The wider the bandwidth of a term, the less its effect in the multiplication in the frequency domain. It is clear from this summary that the connector term will most severely affect the measurement. Since the frequency spectrum $C(f)$ of the connectors had been measured using the spectrum analyser, their distortion could be deconvolved by a point-by-point division of the Fourier transform of the experimental data by the connector frequency response. The connectors did not introduce significant phase distortion, and so only the magnitude of the Fourier transform of the experimental data was corrected. The Fourier transform was performed using a fast Fourier transform algorithm copied from reference 7, then a short 'C' program completed the deconvolution.
5.10. Test sample for connector frequency response measurement

Network analyser
port one

Network analyser
port two

50 Ohm
matched load
5.11. Network analyser graph of connector frequency response

log MAG $S_{21}$

START 0.045 GHz, STOP 26.500 GHz
A plot of an experimental Auston switch response is shown in figure 5.12, and the same response after deconvolution is shown in figure 5.13. The deconvolution certainly sharpens up the decay trace, but it also sharpens up the reflections, first noticed in the sampling oscilloscope photographs of section 2.i) of this chapter. The frequency response of the deconvolved signal (figure 5.14) shows a very large peak in the range 4 to 10 GHz. Filtering out this peak from the frequency spectrum smooths the reflections when the result is inverse Fourier transformed into the time domain (figure 5.15). It was decided to leave the deconvolution and filtering of the experimental data at this point, and to note that the measurement is still band-limited to 25GHz by the coaxial cables. To compare the decay constant in a sensible way from sample to sample, however, it is still necessary to make some physical interpretation of the photoconductivity decay.

4) Physical interpretation of photoconductivity decay

Following the photoexcitation of free charge carriers in the switch gap, recombinations occur through both bulk and surface effects. The bulk recombinations can be divided into two categories:

a) Direct recombination, where electrons and holes recombine by band-to-band transitions.
b) Indirect recombination via intermediate localised energy levels in the forbidden gap (Shockley-Read recombination)

The energy liberated by a direct or indirect transition can be dissipated by one of the following mechanisms:
i) Phonon emission
ii) Photon emission (radiative recombination)
iii) Energy transfer to another free carrier (Auger recombination)

Direct recombination is very slow in GaAs. For example, the band-to-band Auger lifetime for intensely illuminated, lightly doped
5.12. Auston switch response: experimental results

5.13. Auston switch response: connectors deconvolved

Fourier spectrum of deconvolved results
5.15. Auston switch response: deconvolved, filtered results

5.16. Trace of 5.15 with exponential decay fit, 20 ps and 45 ps time constants
p-type GaAs is estimated to be 300 ns [11]. Bulk, direct recombination is therefore not the limiting factor in the lifetimes measured by the Auston switch.

Indirect recombinations both via the GaAs surface states and other localised energy levels within the bulk play an important part in determining photoconductivity pulse shape. At high carrier densities (>10^{19} cm^{-3}) Auger recombination dominates [12]. In this work, the carrier densities generated by the laser can be estimated as follows:

Average optical power, P = 30 mW
Pulse width, t = 5 ps
Pulse repetition rate, 1/T = 76 MHz
Spot size, A = \pi (40 \times 10^{-6}) cm^2.
For red dye laser, \lambda = 600 nm, h\nu = 2.07 eV
Absorption coefficient, \alpha = 5 \times 10^{-4} \text{ cm}^{-1}

No. of photons in each laser pulse = \frac{P \times T}{h\nu} = 1.2 \times 10^8
Volume occupied by these photons = A \times 1/\alpha = 1.0 \times 10^{-7} \text{ cm}^3

Therefore number density of carriers generated (assuming 100% efficiency) = 1.2 \times 10^{19} \text{ cm}^{-3}

This suggests that Auger recombination is insignificant and the energy is liberated either by photon or phonon emission, the process dependent upon which recombination centre is being used. Papers on luminescence measurements of GaAs label various defects such as V_{e} and V_{a} as deep radiative centres, and identify photoluminescence energy bands with them [13]. Deep level transient spectroscopy has been used to identify further defects whose capture cross-sections can be interpreted by phonon emission [14]. Since the recombination centres generated by the reactive ion etched samples have not been identified, further comment on the predominant recombination mechanism is fruitless. However, if radiative recombination is significant, at the high excitation levels present at the start of the decay transient, further electron-hole pairs may be generated by the radiation emitted by the recombination of another pair. The initial photoconductivity transient is not then the anticipated exponential.
In addition to indirect recombination through surface states and bulk defects, photogenerated carriers can be lost by diffusion deep into the semiconductor bulk. The interplay of these effects can be modelled by the continuity equation

\[
\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau} + g(t,x)
\]

Surface recombination is taken into account by the following boundary condition:

\[n(0,t) = D \frac{\partial n}{\partial x} \]

where \(S\) is the surface recombination velocity.

Other boundary conditions are:

\[n(x,0) = 0\]

\[n(\infty,t) = 0\), (if the sample is thick compared to the diffusion length and absorption coefficient).

Numerical methods have been used to solve the continuity equation subject to these boundary conditions, and the results discussed in references 12, 15 and 16. The solutions are summarised in figure 5.17.

This work shows that because of surface recombination, the decay of free carriers is not exponential, but faster at the beginning and slower at the end. A further effect of surface recombinations is that the optical absorption depth should play a significant part in the output pulse width. The computer calculations of reference 12 predict that the smaller the absorption depth, the greater the number of carriers that will be recombed at the surface, and hence the shorter the observed pulse width. This has been confirmed experimentally in the following preliminary results obtained by measuring a set of Auston switches using R6G dye in the dye laser, then repeating the measurements using Styryl-9 dye. R6G lases in the infra-red, whilst Styryl-9 lases in the visible red, and so the two experiments had greatly differing absorption depths.
5.17. Solutions of continuity equation for laser excitation of Auston switch

If constant carrier mobilities are assumed, the conductance depends on the total number of carriers, which is represented by the total area under the curve above. If the excitation is low level, the output voltage is proportional to the conductance and the voltage time response shown below can be predicted.

b) Typical output pulse with surface recombinations included
Table 5b: Comparison of Auston switch measurements taken with different laser wavelengths

<table>
<thead>
<tr>
<th>Dye</th>
<th>Wavelength (nm)</th>
<th>Absorption depth in GaAs (microns)</th>
<th>Auston switch recombination time constant (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Unetched</td>
</tr>
<tr>
<td>R6G</td>
<td>850</td>
<td>1.1</td>
<td>125 ± 40</td>
</tr>
<tr>
<td>Styryl-9</td>
<td>600</td>
<td>0.2</td>
<td>65 ± 20</td>
</tr>
</tbody>
</table>

The red dye consistently gives shorter recombination times when compared with the infra-red, as expected. There is also a measurable difference between the reactive ion etched and unetched switches' recombination time constants. These results indicate that that the pulse recombination time measured by the red laser depends largely upon the surface recombination velocity in this experiment, and that Shockley-Read recombination in the bulk is less significant. Also, provided that the absorption depth is kept constant by keeping the laser wavelength the same, diffusion away from the surface will have the same effect from sample to sample, and these measurements really will compare surface recombination velocity from sample to sample.

The other problem to be considered is how to measure the pulse width. The decay is not the exponential predicted by Schockley-Read recombination. Instead, a sum of two exponentials were used, one with a fast recombination time that modelled the original part of the pulse, and the second a slow decay that fitted the second part. The initial exponential decay time was approximately 30ps in duration for all etched samples, and indicated the non-equilibrium effects at the start of the decay. A graph of such an exponential curve fitted to a set of filtered, deconvolved results is shown in figure 5.16. The slower exponential varied according to surface treatment and was taken to indicate the surface recombination velocity.

To test the deconvolution, filtering and curve-fitting programs, a preliminary experiment checking the variation of the Auston switch
recombination time with the optical power incident upon the switch was performed. The results are plotted in figure 5.18, and show that some variation in the measured recombination time with laser power occurs. This indicates that the recombination mechanism changes with laser power, as discussed earlier in this section, and that care should be taken to compare reactive ion etched switch gaps at the same power. All measurements given in chapter 6 were taken with 40 ± 5 mW Styryl-9 laser power incident upon the switches.
5.18. Plot of exponential decay times versus optical power exciting Auston switch
REFERENCES


CHAPTER SIX

Experimental results

A series of experiments were performed to examine the damage caused by reactive ion etching GaAs, and to determine the sensitivity of the three methods of etch damage measurement described in the preceding chapters. Samples were reactive ion etched in helium, argon, krypton, Freon-12, mixtures of Freon-12 and argon, oxygen, hydrogen and ammonia. All the etch runs were carried out under the standard conditions described in chapter two, section four, and were of 30 minutes duration, except when Freon-12 was used, when the etch was stopped after 6 minutes. Freon-12's fast etch rate meant that even after this short time, an etch step of 4.2 microns could be measured by the Talystep. A deeper etch would not have affected the Schottky diode measurements, but the Auston switch measurement would be severely affected by the increased surface area of the switch gap.

Several samples were placed in the reactive ion etch chamber during each run. A gently bubble-etched rectangle of lightly doped n-type GaAs was prepared for Schottky diode measurements and a polished rectangle of undoped GaAs was etched for photothermal microscope measurements. Both of these samples were partially shadow masked by a third piece of undoped GaAs, which protected part of the samples from the etch for later comparison, and provided an edge for etch depth measurement using the Talystep. Auston switch samples used up more material, and took a long time in preparation and testing, and so they were only included in selected experiments. These samples were also made of polished, undoped GaAs, and the gold electrodes were masked with hardened negative resist. For reasons outlined in chapter five, section one, the Auston switches had to be fabricated on polished, instead of bubble-etched surfaces, and it was decided to use a polished GaAs surface as the baseline for the photothermal radiometric microscope measurement too, in order that the two optical methods should have the same baseline. It is important to note that not only were two different surface finishes used for the electronic
and optical etch damage measurements, but the n-type material used for the electronic tests had to be replaced by semi-insulating, undoped material for the optical testing, to reduce the dark current.

Further polished, undoped GaAs samples were included in some etch runs and sent off to Loughborough Consultants Ltd. for Auger surface analysis. This gave useful information on the chemical composition of the etched surfaces.

The Talystep, Schottky, photothermal radiometric microscope and Auston switch measurements for the reactive ion etch runs discussed below are tabulated in appendix three. These results have been put into an appendix because the clearest way of showing the trends in the measurements described in this chapter is to plot them as bar-charts. However, error estimates cannot be included in bar-charts, and these have been given with the data in the appendix. The Auger results have been tabulated and commented upon at the end of this chapter. The experimental results will be presented under the following sub-headings:

1) Sputtering with inert gases of different atomic masses.
2) Inert gas sputtering compared with Freon-12 RIE.
3) Mixtures of argon and Freon-12 - effect of etch gas composition.
4) Post-etch passivation with oxygen, hydrogen and ammonia.
5) Auger chemical surface analysis.

1) Sputtering with inert gases of different atomic masses.

Helium, argon and krypton were used in this experiment. As explained in chapter two, section three, the d.c. bias which appears between the plasma and sample electrode in the RIE configuration depends upon the magnitude of the ionic current towards the sample electrode. The harder an atom is to ionise, the smaller this current is likely to be, and the greater the d.c. bias. Inert gases, with their high ionisation energies, tend to produce large d.c. biases, and
the magnitude of the bias voltage noted in this experiment varied in the same way as the ionisation energies:

<table>
<thead>
<tr>
<th>Table 6a: Variation of d.c. bias with ionisation energy of etch gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>He</td>
</tr>
<tr>
<td>Ar</td>
</tr>
<tr>
<td>Kr</td>
</tr>
</tbody>
</table>

The etch step height can also be seen to vary with d.c. bias, and hence the kinetic energy of the bombarding ion, in this table.

The first table of appendix three gives the experimental results obtained for damage measurement of inert gas etching. The Schottky diode parameters, plotted in figure 6.1, show a trend of increasing etch damage with decreasing atomic mass of the etch gas. Helium, the lightest ion, accelerated through the largest bias voltage, produces a large ideality factor, and has reduced the potential barrier height greatly compared to the bubble-etched control: it has caused much electronic damage to the GaAs surface. Argon has caused significantly less damage, and krypton, the heaviest atom, least damage of all.

Figure 6.2 shows how the etch depth and photothermal microscope ratios vary with inert gas. The etch depth is very small, and varies very little with etch gas. The PRM ratio does not vary significantly with etch gas either, but it is interesting to compare the ratio for an inert gas etched surface with that of the polished surface. The PRM ratio of a polished surface is, by definition, 1. The PRM ratio of all the sputtered surfaces is, surprisingly, greater than 1, which implies that the surface recombination velocity of photogenerated free carriers at the sputtered surface is slower than that of the control polished surface, that is, their lifetime has been increased.
6.1. Schottky diode test parameters
- variation with etch gas

[Diagram showing idenity factor vs barrier height for different etched surfaces: Bubble etched, He ion etched surface, Bubble etched, Ar ion etched surface, Bubble etched, Kr ion etched surface, Bubble etched, Freon12 RIE'd surface.]
6.2. Talystep etch heights and PRM ratios - variation with etch gas
Auston switches were used to examine helium and argon inert etching. Table one in appendix three shows that the fast exponential decay constant was not significantly affected by the etch process. The slower decay constant was increased by the etching, and the helium etch increased the recombination time more than the argon etch, confirming the unexpected results obtained using the PRM. A bar chart of the second Auston switch decay time is given in figure 6.3.

2) Inert gas sputtering compared with Freon-12 RIE.

Figures 6.1, 6.2 and 6.3 also show the Schottky, Talystep, PRM and Auston switch parameters for a Freon-12 etched surface. The d.c. bias generated during the Freon-12 run was negligible and the sample was etched for one fifth of the time, yet the etch step was two orders of magnitude higher than those observed with inert sputtering. The Schottky parameters show that the ideality factor degradation was similar to that observed with argon sputtering, but the barrier height is actually increased by the RIE process. The Auston switch measurement shows that the photogenerated recombination time is reduced by Freon-12 etching. The PRM ratio indicates the converse, that the surface recombination is reduced, and hence that the recombination time is increased by Freon-12 reactive etching. This apparent contradiction can be explained by considering the limitations of the photothermal microscope. The depth of field of this microscope is only one micron, and samples with etch steps deeper than this will yield inconsistent results, as discussed in chapter four. For this reason, the PRM results obtained for Freon-12 and Freon-12/Argon mixtures with etch steps greater than one micron have had to be discounted.

An argon etched sample and a Freon-12 etched sample were examined in a scanning electron microscope. The microscope photographs in figure 6.4 show that both surfaces are roughened by etching, but the Freon-12 sample also shows evidence of a polymeric web being deposited on the surface during the etch. Underneath the polymer, micromasking can be seen to have roughened the surface even further.
6.3. Auston switch recombination time - variation with etch gas

![Bar chart showing recombination time for different etch conditions.

- Polished, He ion etched surface: 250 ps
- Polished, Ar ion etched surface: 200 ps
- Polished, unetched surface: 150 ps
- Polished, Freon12 RIE'd surface: 100 ps]
6.4 Scanning electron microscope photographs of reactive ion etched GaAs samples

i) Argon etched sample
   15 microns

ii) Freon-12 etched sample
   30 microns
3) Mixtures of argon and Freon-12 - effect of etch gas composition.

Polymer deposition in Freon-12 etching has been observed before in reference 2. The usual solution to this problem is to mix the Freon-12 with an inert gas in order to sputter off any polymer layers as soon as they are formed [3]. It was therefore decided to investigate the variation in etch damage with Freon-12/Ar composition as a next step in this work.

The ratios of argon to Freon-12 in the etch gas mixture were set up using the mass flow meters, the total flow being kept a constant 20 sccm. The d.c. bias decreased steadily with increasing Freon-12 concentration, and the etch rate increased steadily with increasing Freon-12 concentration, as shown in table 6b below. This shows that the chemical component of the etch process is more significant in determining the etch rate of such mixtures than the physical, ion bombardment component.

Table 6b: Variation of d.c. bias with gas composition

<table>
<thead>
<tr>
<th>Gas composition</th>
<th>D.C. bias (V)</th>
<th>Etch step (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 % Freon-12</td>
<td>Negligible</td>
<td>4.20</td>
</tr>
<tr>
<td>67 % Freon-12 / 33 % Ar</td>
<td>10</td>
<td>1.40</td>
</tr>
<tr>
<td>33 % Freon-12 / 67 % Ar</td>
<td>20</td>
<td>0.75</td>
</tr>
<tr>
<td>100 % Ar</td>
<td>190</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The Schottky parameters for the series of etch gas mixtures are shown in figure 6.5. The Schottky ideality factor for 33% Freon-12 concentration appears to be an anomalous result. Ignoring this point, the Schottky ideality factor does not change significantly with etch gas composition, whilst the barrier height increases steadily with increasing Freon-12 composition.

The Freon-12/Ar etched surfaces were examined under the scanning electron microscope, and the polymer layer was reduced by the Ar inclusion, as shown in the photograph in figure 6.6.
6.5. Schottky diode parameters
- variation with Freon-12 concentration

![Graph showing variation of Schottky diode parameters with Freon-12 concentration. The x-axis represents % Freon-12 (diluted in Ar), and the y-axis represents the ideality factor and barrier height (V).]
6.6 Scanning electron microscope photograph of 2:1 Ar/Freon-12 reactive ion etched sample
4) Post-etch passivation with oxygen, hydrogen and ammonia.

The passivation effects of 30 minutes hydrogen RIE or 30 minutes ammonia RIE were tested on a bubble etched GaAs surface, a bubble etched, Freon-12 reactive ion etched surface and a bubble etched, argon ion etched surface. Hydrogen has been shown to etch native GaAs oxide effectively [4], and is thought to passivate surface donor states. A mechanism has been postulated for the ammonia passivation in which the hydrogen in the compound is thought to remove the oxide and arsenic from the surface, then the nitrogen forms a thin layer of passivating GaN [5]. The oxide removal stage of these postulated mechanisms was investigated further by oxidising some bubble etched and dry etched surfaces in an oxygen plasma for 30 minutes, then testing the hydrogen and ammonia passivation again.

The d.c. biases observed when the passivation experiments were performed were high, but there seems to be no correlation with the etch rate, as shown in the table below.

Table 6c: Variation of d.c. bias with passivation gas

<table>
<thead>
<tr>
<th>Passivation gas</th>
<th>D.C. bias (V)</th>
<th>Etch height (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>160</td>
<td>0.02</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>210</td>
<td>0.11</td>
</tr>
<tr>
<td>Ammonia</td>
<td>240</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The Schottky parameters for bubble etched and Freon-12 etched surfaces after passivation or oxidation and passivation are given in figures 6.7 and 6.8. These two bar charts show similar results, and the argon etched surfaces show the same trends again, so the argon results have not been plotted. The PRM ratios for polished surfaces after passivation are plotted in figure 6.9. The Auston switch measurements did not show a clear trend in the passivation experiments. The full set of results is given in the second, third and fourth tables of appendix three.
6.7. Schottky diode test parameters – $O_2$, $H_2$ and $NH_3$ RIE treatment of bubble etched surfaces
6.8. Schottky diode test parameters, $O_2$, $H_2$, and $NH_3$ RIE treatment of bubble-etched, Freon-12 etched surface (attempts to passivate Ar etched surfaces show same trends)
6.9. PRM ratios of $O_2$, $H_2$ and $NH_3$, passivation of polished surface
The bar chart in figure 6.7 shows that none of the processes tested improves the unetched, polished surface. Ammonia reactive ion etching causes the smallest increase in Schottky ideality factor, and oxidation gives the smallest decrease in barrier height. Figure 6.8 shows that ammonia RIE does improve the Schottky ideality factor of the Freon-12 etched surface. Reference to the fourth table in appendix three shows that the ammonia treatment also improves the ideality factor of the argon etched GaAs surface.

Hydrogen RIE always increases ideality factors and reduces Schottky barrier heights. Hydrogen RIE does not appear to passivate any of the GaAs surfaces tested at all.

In all cases, oxidation significantly worsens the Schottky ideality factor, but gives the highest barrier height for an etched sample. Hydrogen treatment of the oxidised surface significantly worsens the electrical characteristics: the barrier height is reduced and the ideality factor is greatly increased. Ammonia treatment of oxidised surfaces has a beneficial effect on the ideality factor, but greatly reduces the barrier height.

The PRM ratios given in figure 6.9 show that surface recombination velocities are increased by the passivation techniques tested, and the Auston switch measurements in table two of appendix three confirm this.

5) Auger chemical surface analysis.

Table 6d is copied from a report produced by Loughborough Consultants Ltd. on the Auger analysis of a set of five samples prepared in the reactive ion etcher. Surface compositions were obtained in two areas per sample, and were shown to be reproducible. The compositions are given in atom percent and these were calculated using experimentally determined relative sensitivity factors. This means that the absolute values are only approximate, but accurate comparisons can be made between these similar samples.
The surface composition for the wet etched surface was omitted in this series of measurements, but in reference 6, an undoped, polished, (100) GaAs wafer was wet etched in 5 H$_2$SO$_4$: 1 H$_2$O$_2$: 1 H$_2$O to remove 10 microns of material, then XPS analysed. The Ga/As ratio for this surface is found to be about 0.53, with a high surface carbon impurity level, and the authors comment that this is typical of their results for a variety of wet chemical treatments of GaAs. These results have been included in table 6d for completeness, and are marked with an asterisk.

Table 6d: Auger analysis of chemical surface composition for different RIE treatments

<table>
<thead>
<tr>
<th>Sample preparation</th>
<th>Surface composition (Atom % measured by Auger spectroscopy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (unprocessed, polished, wafer)</td>
<td>F  Si  Cl  C  N  O  Ar  Ga  As</td>
</tr>
<tr>
<td></td>
<td>0.0  0.0  0.0  22.3  0.4  36.4  0.0  20.5  20.5</td>
</tr>
<tr>
<td>Wet etched surface (XPS measurement)*</td>
<td>0.0  -  0.0  34.4  -  36.5  -  15.4  13.7</td>
</tr>
<tr>
<td>30 min. Ar RIE</td>
<td>2.6  16.1  0.2  10.0  0.3  54.3  0.6  15.8  0.0</td>
</tr>
<tr>
<td>6 min. Freon12 RIE</td>
<td>2.7  0.0  13.6  38.5  0.0  19.2  0.0  11.9  14.0</td>
</tr>
<tr>
<td>30 min. Q$_2$ RIE</td>
<td>2.7  0.0  0.4  8.5  0.0  53.1  0.0  26.6  8.8</td>
</tr>
<tr>
<td>30 min. NH$_3$ RIE</td>
<td>0.0  0.0  0.4  7.4  1.2  53.0  0.0  24.3  13.7</td>
</tr>
</tbody>
</table>

The unetched, polished, control shows good stoichiometry, evidence of a surface oxide layer and typical carbon contamination.

The argon etched sample is still showing traces of the silicon contamination that had been cleaned from the chamber before this set of experiments was started. The silicon had disappeared by the next Freon-12 run. Similarly, the traces of chlorine and fluorine present in the argon etched surface must be caused by chamber memory effects from previous Freon-12 etch runs. The carbon contamination has been reduced when compared with the control. All the etch gases succeeded
in reducing the surface carbon, except for Freon-12. The surface of the argon etched sample has been heavily oxidised, and shows some traces of argon adsorption. The surface stoichiometry has been greatly affected, the arsenic concentration being below the detection limit of the Auger experiment.

The Freon-12 etched sample has the least affected surface stoichiometry of the etched surfaces. This is to be expected, because the chlorine in the compound reacts with the gallium to form a volatile chloride, allowing its rate of removal to catch up with the already volatile arsenic. The surface oxidation is very low, but this is compensated by a very high percentage of carbon. This confirms that the surface 'web' observed in the scanning electron microscope photograph of figure 6.4 is an organic polymer.

The oxygen etched sample shows traces of chlorine and fluorine contamination from the previous etch run. However, the relative concentrations of oxygen and carbon are reversed between the two samples. Oxygen would be expected to clean carbon from the sample surface, however, the percentage of oxygen detected on the surface is no higher than that observed with argon or nitrogen etching. This indicates that oxygen RIE treatment does not thicken the oxide layer on the GaAs surface, and the stoichiometry is unchanged from that of the native oxide.

The ammonia etched sample shows the lowest surface carbon concentration, and the highest nitrogen concentration. The stoichiometry of the etched surface is better than those surfaces etched by argon or oxygen.
6) Summary

The following conclusions can be drawn about the experimental techniques used to assess the RIE etch damage sustained by the GaAs samples:

1) Schottky diode ideality factors are generally a useful, sensitive measure of physical etch damage. However, chemical surface contamination by oxide or polymer layers may also affect the results.

2) Schottky diode barrier heights give complementary information to the ideality factors. They are particularly sensitive to oxide layers left behind on the etched surface.

3) The photothermal microscope ratios give the surprising result that RIE damage reduces the surface recombination velocity of photogenerated free carriers. The Auston switch measurements confirm this. Neither optical technique is as sensitive to etch damage as the Schottky method of assessment.

The Schottky and Auger measurements indicate that:

1) when inert gases are used to etch GaAs, the lighter the ion, the greater the electronic damage.

2) all the inert ion etches caused arsenic depletion of the etched surface

3) of the reactive etch gases tested, only Freon-12 left the etched surface arsenic enriched

4) reactive ion etching, as demonstrated by the Freon-12 etch, greatly increases the etch rate, and causes less electronic damage, when compared with inert sputtering.
5) mixtures of Freon-12 and Ar succeed in reducing polymer deposition, but 100% Freon-12 is still the optimal composition in terms of etch rate and electronic damage measurement.

6) oxygen and hydrogen both worsen the electronic damage sustained by an etched GaAs surface.

7) ammonia has some electronic etch damage passivation properties.

The optical measurements suggest that:

1) inert etching increases the free carrier recombination time when compared with an unetched surface.

2) The PRM indicates that Freon-12 etching causes a greater reduction in surface recombination velocity than argon etching, whilst the Auston switch measurement shows that Freon-12 etching reduces the recombination time.

3) both the PRM and the Auston switch measurements indicated that all the passivation techniques investigated increase the surface recombination time. Both methods showed that ammonia RIE increased the surface recombination time the least.
REFERENCES


5 "A proposed hydrogenation/ nitridization passivation mechanism for GaAs and other III-V semiconductor devices, including InGaAs long wavelength photodetectors", F. Capasso and G.F. Williams, J. Electrochem. Soc. vol. 129, no. 4, 1982, p.821.

CHAPTER SEVEN
Analysis of experimental results

1) Schottky measurements

In all the experiments (except for Freon-12 RIE) described in chapter six, the Schottky barrier height of a gold diode fabricated on a reactive ion etched surface was lower than the barrier height of the control diode fabricated on a bubble etched, control surface, and the ideality factor was increased. Similar results have been observed for reactive ion etching [1] and ion sputtering [2,3], and several explanations have been proposed for these phenomena.

In S.W. Pang's work [1], GaAs surface damage induced by RIE is compared with sputter etching using inert gases. Her results show that sputter etching using Ne, Ar or Xe introduces substantial electronic surface damage, as measured by Schottky diode parameters, and that this damage varies inversely with ionic mass. The results given in chapter six, part one, confirm this trend using He, Ar and Kr. Reactive ion etching, using a variety of chlorine containing gases, was shown in reference 1 to cause considerably reduced damage, and again, the Freon-12 etch measurements given in this work confirm this. The increase in electronic damage with reduced ionic mass was attributed to the increased ion penetration distance of lighter ions, whilst the reactive gas was thought to change the surface structure in some way and make it less susceptible to ion-bombardment induced damage. The results given in chapter six show a trend of increased ion penetration distance causing increasing electronic surface damage even more clearly, since the d.c. bias, and hence the bombardment energy was also higher for the lighter ions.

In order to consider the changes in surface structure that may be caused by reactive ion etching, as Pang suggests, it is necessary to base the argument on a model for an unetched GaAs surface. The surface structure of GaAs has been investigated for many years by W.E. Spicer
at Stanford University, and his "Advanced unified defect model" or AUDM, published in reference 4, will be the basis for the discussion that follows.

In reference 5, Spicer summarised information published by himself and other authors on photoemission studies of clean, stoichiometric, (110) GaAs surfaces. In photoemission spectroscopy, photons supply the energy to excite electrons out of a solid, and the energy distribution of the ejected electrons is analysed. From this energy distribution, it is possible to determine the position of the surface Fermi level, the electronic structure of the valence band (including filled surface states, particularly if they lie in the semiconductor band gap) as well as the electronic structure of the core levels of the atoms making up the semiconductor. In his summary, Spicer established that the band gap of a clean (110) GaAs surface, cleaved in vacuo has no intrinsic filled or empty surface states, as shown in figure 7.1. He also referred to LEED data which indicated that on the (110) surface, the Ga atoms move outwards and the As atoms move inwards, relative to their normal position in the GaAs lattice. This surface reconstruction is thought to be driven by the need to minimise the covalent bond energies, and its effect is to move the intrinsic surface states out of the band gap. The empty surface states lie above the conduction band minimum and the filled states below the valence band maximum.

However, the Fermi level does become pinned when foreign atoms (such as oxygen, or the metallisation for a Schottky contact) are deposited on the GaAs (110) surface. The Fermi level is always pinned at 0.5 and 0.75 eV above the valence band maximum, for p-type and n-type material respectively, regardless of the atom causing the effect, and Spicer concluded in reference 6 that the states causing the pinning are native defect states induced by the foreign atoms. This model was called the unified defect model (UDM), because it applied to both metal-insulator and insulator-semiconductor interfaces, unifying the behaviour of MOS, MIS and Schottky gate FETs.
7.1. Clean (110) GaAs surface in vacuo

Filled surface states (As)       Empty surface states (Ga)

* = empty surface state
A flaw in the UDM was that it did not identify the defects causing the Fermi level pinning and it was not until nearly ten years later, in reference 4, that Spicer attempted to do this. In his paper on the advanced unified defect model, he noted that the 0.5 and 0.75 eV energy levels coincide with those measured for the As_{Ga} antisite (an As atom sitting on a Ga site in the GaAs lattice). This antisite also seems to be the defect central to the EL-2 centre measured by deep level transient spectroscopy (DLTS) [7], and it is measured in high concentration in all as-grown bulk GaAs. However, the As_{Ga} antisite is a double donor, and another compensating minority acceptor defect was needed to explain both the properties of the EL-2 centre and the Fermi level pinning observed in n-type GaAs. This was postulated to be the Ga_{As} antisite (a Ga atom sitting on an arsenic site in the GaAs lattice), shown in figure 7.2.

From computer modelling of the Fermi level position at the surface, Spicer concluded that the number of As_{Ga} antisites must be about double the number of Ga_{As} antisites and other acceptors. Therefore As rich surfaces are expected to be pinned at about the middle of the band gap, and for a gold Schottky contact made to such a surface the expected barrier height is 0.92 eV. Arsenic depleted surfaces should exhibit pinning at a lower level in the band gap, and should form lower Schottky barriers. Arsenic rich surfaces prepared by molecular beam epitaxy (MBE) have been tested and have been shown to fit the model, by producing higher Schottky barrier heights with increasing arsenic enrichment. Further confirmation of these ideas has been given in reference 8, where the DLTS signal of the EL-2 level was shown to decrease in accordance with decreasing gold Schottky barrier heights prepared by oxidising undoped conductive GaAs.

To summarise, there are no intrinsic surface states in the band gap of clean (110) GaAs. When such a surface is exposed to air, or a metal layer is evaporated upon it, the foreign atoms induce native defect states in the GaAs band gap. These defects have been deduced to be As_{Ga} and Ga_{As} antisites, and for a typical surface there are about
7.2. Mid band defects used in Spicer's AUDM for Schottky barrier formation

\[ E_c = 1.4 \text{ eV} \]

\[ E_g = 1.4 \text{ eV} \]

- \( \text{As}_{Ga} \) antisite
- Double donor \( 0.5 \text{ eV} \)
- Double acceptor \( 0.75 \text{ eV} \)
- Probable \( Ga_{As} \) antisite

\( E_c \) = bottom of conduction band
\( E_V \) = top of valence band
twice as many As₅₈ defects as Ga₃₈. Air exposure or metallisation therefore causes surface rearrangement and arsenic enrichment. These band gap defects pin the surface Fermi level and thus determine height of Schottky barriers made to the surface. An gold Schottky diode fabricated on an arsenic rich surface should have a 0.92 eV barrier height and reducing the arsenic concentration results in a lower Schottky barrier.

It is important to relate these ideas to the Schottky barrier heights and ideality factors measured on the control and reactive ion etched surfaces in this work. Spicer's model explains the Fermi level pinning and hence Schottky barrier height observed when a GaAs wafer is cleaved in the [110] direction in a vacuum and various atoms are evaporated onto the surface. (110) GaAs was used for the Schottky diodes results given in chapter six, and so Spicer's description of the band gap defects generated by an oxide layer or gold metallisation is applicable to the control diodes. The energy levels associated with the defects, and the concentration of the defect states relative to each other are important in determining the Schottky barrier height. The Schottky barrier height of an etched surface therefore shows how the distribution of the defect states in the GaAs band-gap is affected by the etch process.

The ideality factor increases with increasing surface donor concentration, as discussed in chapter three. This suggests that the ideality factor is a measure of the concentration of donor defect states in an n-type GaAs surface, but that it will be less sensitive than the Schottky barrier height to the defect states' energy distribution.

A practical baseline has been set in chapter three for assessing the quality of a GaAs surface. The baseline Schottky barrier height is 0.89 eV and baseline ideality factor is 1.2. For some device applications, it may be necessary to "tailor" the Schottky barrier height to lower values [9], or a high ideality factor may be desired.
in order to approximate to an Ohmic contact. In this work, however, a reduction in the Schottky barrier height and an increase in the ideality factor are taken to indicate that the physical quality of the surface has been degraded by the etch process.

The Auger measurements made on reactive ion etched surfaces in this work show that all the etched surfaces except Freon-12 are depleted in arsenic. The graph in figure 7.3 shows the variation in Au Schottky barrier height with As/Ga ratio. Even the Freon-12 etched surface fits in with the trend that the lower the arsenic concentration left on the etched surface, the lower the Schottky barrier height, as predicted by Spicer's model. The oxidised surface does not fit this trend, and the increase in barrier height of gold GaAs Schottky diodes with increasing surface oxide thickness has been noted before in reference 10 and explained in terms of trapped charge at the same interface [11]. This is discussed in more detail later in this chapter when the oxidation and surface passivation experiments are analysed.

The conclusion that can be drawn from these results is that the surface stoichiometry of an etched surface is of critical importance to its electrical quality. Reactive etch gases not only greatly increase the etch rate, but they maintain the stoichiometry of the etched surface because their chemistry increases the rate of gallium removal during etching. By ensuring that the final surface is not excessively arsenic depleted, the surface Fermi level is still pinned by the As\(_{\infty}\) and Ga\(_{\infty}\) antisites, and the Schottky barrier height is maintained at about 0.89 eV.

A small fraction of reactive gas diluted in an inert gas has also been shown to be highly effective at improving the electronic etched surface quality. Even with 33% Freon-12 diluted in argon, a considerable increase in Schottky barrier height can be seen over the pure argon etched surface. The ideality factor can be seen to increase slightly with increasing Freon-12 concentration, however, which
7.3. Graph showing variation in gold Schottky barrier height with surface stoichiometry

Schottky barrier height (V)

0.9

0.8

0.7

0.6

0.5

0
0.25 0.5 0.75 1.0 1.25

% As/%Ga

(Bubble etched control)

(Oxygen RIE)

(Freon-12 RIE)

(Ammonia RIE)

(Argon ion etching)

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suggests an increase in the surface donor defect concentration. Perhaps the increasing polymer deposition observed using the SEM increases the concentration of donor defect states without changing the GaAs surface stoichiometry and hence without changing the surface Fermi level pinning. The carbon contamination and the surface roughness caused by the polymers are also undesirable because they could affect subsequent processing steps. These results indicate that an optimum process could be found where a mixture of Freon-12 and argon prevents polymer deposition, yet maintains surface stoichiometry.

The surface passivation experiments can also be interpreted in terms of Spicer's work [5]. Starting from the empty band gap of a (110) GaAs surface in vacuo, less than 1/100 of a monolayer of oxygen can change the band structure. At first, electrons can be transferred from the dangling bonds of the surface arsenic atoms to the chemisorbed oxygen atoms. For the oxidation to proceed further, and for gallium oxide to form, electrons must be removed from Ga-As bonds, too, increasing the number of mid-band interface states. Photoemission energy distribution curves were used in this paper to monitor the chemical progress of the surface oxidation. These showed that the peaks associated with arsenic bonded with gallium and gallium bonded with arsenic on the clean surface gradually shift to arsenic bonded with oxygen, elemental arsenic, and gallium bonded with oxygen. The total area under the arsenic peaks after oxidation is a small fraction of that observed under the arsenic peaks of clean GaAs, and this is due to the volatility of arsenic oxide. The surface oxide layer will be arsenic depleted, and a complex interface of broken bonds will be formed between the gallium arsenide and the oxide layer.

The Schottky barrier height of a thickly oxidised GaAs surface appears to be higher than a surface covered by native oxide firstly because of the voltage drop across the insulating oxide layer. Also, charge trapped at the oxide-semiconductor interface can also create an image charge in the semiconductor bulk, shifting the
Schottky barrier height further upwards [11]. In order to recover the electrical characteristics of an oxidised surface, first the oxide layer and the charge trapped in the broken bonds of the interface must be removed. This will greatly reduce the Schottky barrier height, and so, in order to move the barrier height back up to the baseline 0.89 eV, the arsenic depletion of the surface must be corrected.

In the experiments presented in chapter six, hydrogen RIE of any oxidised surface, even the native oxide present after bubble etching, reduced the Schottky barrier height and increased the ideality factor. Hydrogen has been shown in reference 12 to selectively etch GaAs oxide over GaAs by a factor of two, and so the reduction in Schottky barrier height could be caused a reduction in the oxide layer thickness. Also, hydrogen plasma treatment would tend to deplete the surface of arsenic by forming highly volatile arsine, which would further reduce the Schottky barrier height.

Several papers have recently been published showing that shallow donors such as silicon in GaAs are passivated by hydrogen RIE [13,14]. However, the increase in ideality factor noticed in this work implies that the total number of donor states has been increased by hydrogen RIE. This suggests that the donor defects generated by reactive ion etching are not shallow donors, and that the mechanism of hydrogen passivation does not work for such defects.

After oxidation, argon etching or Freon-12 RIE, ammonia RIE reduces the ideality factor of a Schottky diode fabricated on the etched surface, but also greatly reduces the Schottky barrier height. The Auger results do not show any reduction in the oxygen percentage of the ammonia treated surface, and so it seems unlikely that the hydrogen in the compound reacts independently with the oxide. However, some degree of nitridisation is indicated by the Auger measurements. Gallium nitride is a wide band gap semiconductor [15,16], and the interface state density between gallium nitride and GaAs has been measured to be $7.6 \times 10^{11} \text{cm}^{-2}\text{eV}^{-1}$ [17], a considerable improvement on
the $10^{13}\text{cm}^{-2}\text{eV}^{-1}$ measured between GaAs and its native oxide [18]. The reduction in interface state density may account for the decrease in ideality factor. The ammonia treatment could also improve the stoichiometry of an etched GaAs surface by consuming any excess gallium into the nitride layer. The Schottky barrier height does not return to the level predicted by Spicer, though, because we are now dealing with a gallium nitride/gold, insulator/metal interface instead of a gallium arsenide/gold, semiconductor/metal interface.

2) Optical measurements

The material used for the optical measurements of etch damage was undoped, semi-insulating, liquid encapsulated Czochralski (LEC) GaAs. The major chemical contaminant in this material is carbon, which is a shallow acceptor in GaAs. As its concentration is usually greater than the total concentrations of chemical donor impurities in LEC GaAs, there must be a native compensating defect which produces semi-insulating behaviour and which is not associated with an impurity. The compensating defect is the EL-2 centre [19], and so the relative amounts of carbon and EL-2 control the position of the Fermi level and thus the resistivity of the material. The highly resistive, undoped material used in these experiments therefore contained large concentrations of the EL-2 centre. We know from the discussion of the electronic measurements, that the energy levels associated with the EL-2 centre are situated in the middle of the GaAs band gap at 0.5eV and 0.75eV above the valence maximum, and that the As$_{Ga}$ antisite is thought to be the physical defect that accounts for these energy levels.

In chapter five, it was decided that despite the high optical power of the dye laser pulses used to fire the Auston switches, the predominant recombination mechanism was indirect recombination via mid-band energy levels, with the energy being liberated via photon or phonon emission. The semiconductor laser used to excite the GaAs
surface for the photothermal microscope measurement also provides "low level excitation", and the recombination mechanisms are expected to be the same. When the recombination and generation of free carriers through recombination centres is considered [20], the position of a recombination centre in the band gap becomes of critical importance. The optimum position for a recombination centre is in the middle of the band gap, and so the EL2 defects which are so important in semi-insulating GaAs are also highly efficient recombination centres. The optically generated free carrier lifetimes can be expected to be short, and the surface recombination velocity to be fast, in such material.

The reactive ion etching of GaAs depleted the surface arsenic concentration in every etch process tested, apart from the Freon-12 RIE. The Auston switch measurements showed that the surface free carrier recombination time was increased by such processing. The Freon-12 etched surface has been slightly enriched in arsenic, and the free carrier recombination time measured by the Auston switch is reduced. This is further evidence for Spicer's AUDM. If surface arsenic depletion does result in a decrease in the EL2 concentration in the band gap, the concentration of recombination centres in semi-insulating GaAs will be reduced by the reactive ion etch process.

The photothermal radiometric microscope measurements broadly agree with the trends noted in the Auston switch work: all the etch processes investigated reduced the surface recombination velocity of the optically generated free carriers, with the exception of the Freon-12 results discussed in chapter six.

The PRM measurements of oxidised, hydrogen and ammonia reactive ion etched surfaces do show the trends expected. Oxygen RIE reduces the surface recombination velocity the most, then hydrogen, then ammonia, and the polished surface has the fastest surface recombination velocity. The Auger measurements show that the oxygen etched surface is the most arsenic depleted, then the ammonia etched
surface, and finally the polished surface, which is not arsenic depleted at all. Unfortunately the hydrogen etched surface was not Auger analysed, but it is clear that the PRM detects the degree of arsenic depletion of the treated surfaces in terms of a reduced surface recombination velocity.

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1) Summary of achievements

In this work, progress has been achieved by building up reactive ion etching equipment, reproducing one method of etch damage assessment that has been published before, and trying out two new methods of etch damage measurement. Information has been obtained on the measurement techniques themselves, and on the reactive ion etching of gallium arsenide. The critical components of the etch damage have been identified for electronic and optical devices, and a possible surface passivation technique has been discovered.

The reactive ion etcher was the first piece of apparatus to be designed and built. Etch parameters could be monitored accurately, and most parameters could be controlled independently of one another. The silicon contamination introduced by the wafer used to load the sample electrode was discovered and cleaned away in time for the final set of experiments described and analysed in chapters six and seven of this thesis.

The Schottky diode method of surface damage assessment was devised by following the many papers published on the subject. A reproducible method of preparing and testing the diodes was developed, and the results justified the popularity of the technique. The diodes were sensitive to all the different etch conditions tried, and some useful conclusions were reached by comparing the trends in the diode parameters with the variations in surface chemistry noted in the Auger analysis.

A new application was found for the photothermal radiometric microscope. Previously, its main use was to map defects on silicon wafers. This work showed that GaAs samples could also be examined by
the microscope, despite the reduced signal levels when compared with silicon, and that it can be sensitive to different types of surface processing. The technique yields complementary information to that obtained with a Schottky diode because the free carrier recombination velocity measured by the microscope is sensitive to different defect levels in the GaAs band-gap. The microscope's use is limited, however, to samples whose surfaces do not vary in height by an amount greater than the depth of focus.

Auston switches have been investigated as material property measurement devices for the first time. The usual priority in the fabrication of these switches is to produce very fast recombination times, using any material or process necessary. The decay transients of the switches have been recorded and analysed for different RIE processes, and variations in the surface recombination times have been detected. More importantly, the results obtained with the Auston switches are consistent with those obtained with the photothermal radiometric microscope, and these results show that the surface free carrier recombination time is not necessarily reduced by RIE damage. However, of the two optical techniques examined, the photothermal microscope is probably more useful, since samples are easier to prepare, and its readings are easier to interpret.

All of the results put together give some indication of the damage processes sustained by a reactive ion etched GaAs surface. The cross-section of such a surface is shown in figure 8.1. The damage processes identified are:

i) surface polymer deposition when Freon-12 is used. This can cause considerable surface roughening by micromasking. This roughness has been estimated to have a root mean squared value of 100 Angstroms using the Talystep.

ii) surface oxidation. The depth of the native oxide on GaAs has been measured by others to be about 30 Angstrom thick after
8.1. Reactive ion etched GaAs surface
(Not to scale)

- Micromasking
- Gallium oxide
- GaAs oxide
- Interface of broken bonds
- Ion implantation
- Dislocations
- Bulk GaAs

100 Å
30 Å
20 Å
450 Å
a few days in air [1], but reactive ion etching in an oxygen containing plasma can increase this thickness with detrimental consequences for the electrical quality of the surface, as shown in this work.

iii) arsenic depletion of the etched surface. This has been demonstrated in this work to be the key problem in GaAs RIE, because the arsenic concentration is related to the EL2 centre concentration. This defect is important determining the electrical properties of the material, because it pins the surface Fermi level, and it affects the material's optical properties by being an efficient recombination centre.

iv) ion implantation. For example, the ion implantation range for argon has been measured to be about 50 Angstroms for a 500V d.c. bias in reference 2.

v) lattice defects such as dislocations. These can extend much further than the ion implantation range. For example, in reference 2, 500 Angstroms of 500V argon etched material had to be removed by wet etching before the I-V characteristics of the control sample were reached. In this reference, ion-enhanced diffusion and channeling were suggested to be mechanisms to account for this extension of the damage depth.

2) Suggestions for further experiments

Further improvements could be made to the reactive ion etcher before preparing samples for further testing. A power splitter could be installed between the r.f. power supply and the electrodes, in order to control the d.c. bias between the plasma and the sample independently of the power matched into the plasma. Also, the
chamber's chemical "memory" effect, discovered when the Auger analysis of the final set of samples arrived, should be taken into account. It would be better practice to clear the chamber of any chemical contamination by routinely striking an argon plasma between each etch run, for example.

A set of photothermal radiometric microscope samples should be Freon-12 etched for a very short duration, 30 seconds, for example, to ensure that the etched step is not deeper than the depth of focus of the microscope. The change in surface recombination velocity caused by Freon-12 etching could then be double-checked.

In this work, the only etch parameter that has been systematically varied is the etch gas. A whole set of experiments could be devised to test the damage effect of varying the gas flow rate, the r.f. power, the d.c. bias, the etch pressure and the substrate temperature.

The Auston switch experiment could be developed considerably. On-chip electro-optic sampling would eliminate the need to pass the signal through the band-limiting connectors. Ion implantation underneath the Auston switch electrodes would allow Ohmic contacts to be made to bubble etched material, so that a similar low-damage baseline could be established to that of the Schottky measurements. Both optical experiments could be repeated with chromium doped semi-insulating GaAs. In this material, the chromium doping provides the mid-band donors required to compensate the carbon acceptors and pin the Fermi level in the middle of the band gap. Variations in the EL2 concentration caused by arsenic depletion should therefore have less effect on the optical recombination time, since the chromium levels would still be available to act as recombination centres.
REFERENCES


APPENDIX I
A literature review of GaAs reactive ion etch processes

Halogen containing gases are usually used to reactive ion etch semiconductors and so it was this group of gases that was examined first for GaAs etching. Although fluorine generating plasmas are often used to etch silicon, it was soon realised that they cannot be used to etch III-V semiconductors, since group III fluorides are involatile at temperatures below 300°C [1]. Bromide etch products are more volatile, and a high etch rate of 70 microns/min. has been reported [2]. Bromine has been neglected as a GaAs etchant though, because it is difficult to handle and tends to block gas lines. Chlorine is a poor etch gas on its own, since it is generally an isotropic etchant, except at very low pressures. Also, it etches native oxides very slowly from the GaAs surface and so a pre-etch treatment such as hydrogen RIE is always needed [3,4]. Adding argon increases anisotropy owing to the increased sputtering element of the etch, and an etch rate of 2 microns/min. can be achieved [5]. Adding oxygen can increase the etch rate to 7 microns/min., but it does not improve the anisotropy significantly [6].

Chlorine containing gases have been thoroughly investigated. Inorganic gases such as boron trichloride and hydrogen chloride etch remarkably anisotropically, but their etch rates are very slow at 17 nm/min. [7], and 60 nm/min. [4] respectively. Silicon tetrachloride shows etch ratios of GaAs relative to masking materials such as Si$_3$N$_4$ and NiCr greater than 10 to 1, but the etch rate is still slow, at about 100 nm/min. [8].

Organic chlorides have been used with success. Carbon tetrachloride can etch at 2 microns/min. [9] and adding oxygen to the feed gas mixture increases the etch rate to 2.5 microns/min. [6]. The oxygen has been shown to increase Cl radical production by scavenging the carbon, and the etch rate increases accordingly. The addition of oxygen seriously roughens the etched surface though, and hydrogen has
been mixed with CCl₄ to give a smooth, anisotropic surface, but a reduced etch rate of 1 micron/min. [10].

Freon-12 (CCl₂F₂) is probably the most frequently used gas in commercial GaAs reactive ion etching. It is highly anisotropic, since the sidewalls are protected by carbon, chlorine and fluorine containing polymers during etching, whilst the same polymers formed on the bottom of the etched region should be sputtered off by the ions accelerated through the d.c. bias. Etch rates of 2 microns/min. can be achieved and can be sustained for several hours in order to etch via holes through 200 micron thick GaAs substrates [11]. Sometimes there can be problems with carbon and polymer deposition on the etched surface, and this can be counteracted by mixing oxygen with the Freon-12 [14]. However, resist etch masks cannot be used, since these are attacked by the oxygen. Mixing argon with the Freon-12 has been shown to increase the etch rate [12], since it sputters off the polymers.

Freon-12 also has the property of etching GaAs selectively over AlGaAs [13]. Non-volatile reaction products such as aluminium fluoride are formed on the surface when the AlGaAs layer is reached and a selectivity (GaAs to AlGaAs) of 300 to 1 can be obtained, depending on the percentage of Al in the AlGaAs.

A departure from chlorinated gases was made in 1987, when a new process using a mixture of methane and hydrogen was published [15]. The fastest etch rate reported to date for this mixture is only 38 nm/min. [16], but there is great interest in the process, since it leaves very little electronic surface damage. More recently, mixtures of ethane and hydrogen have also been found to be effective GaAs etchants, with etch rates of 18 nm/min. [17]. Hydrogen has been found to etch the mixed oxide present on the GaAs surface twice as fast as the etch rate of 60 nm/min. for GaAs itself, and it leaves the stoichiometry of the etched then air exposed surface unchanged from that obtained by cleaving the GaAs surface in air [18]. Nitridization
of the GaAs surface using a hydrogen and nitrogen plasma, or ammonia reactive ion processing has been shown to passivate the GaAs surface successfully [19]. The hydrogen is thought to remove the oxide and arsenic from the surface, then the nitrogen forms a thin layer of the wide band gap semiconductor GaN, which passivates the surface [20]. No etch rate has been published for these processes.

To summarise, the main difficulty in choosing a gas for the reactive ion etching of GaAs is finding one which forms a volatile compound with gallium. Conversely, arsenic and its compounds are highly volatile, and reactive ion etched surfaces are frequently found to be arsenic depleted [21]. Organic, chlorine containing compounds such as Freon-12 have proved most effective when fast anisotropic etching is needed, since gallium chloride has a high vapour pressure, and the organic polymers deposited during etching protect the sidewalls. When a slow etch rate can be tolerated in favour of reduced etch damage, a mixture of methane and hydrogen has yielded the best results. The etch products in this case have been speculated to be trimethyl gallium and arsine [15]. Another approach to the etch damage problem is to passivate the etched surface using a hydrogen or ammonia plasma.
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APPENDIX 2
Details of Auston switch fabrication procedure

1) The whole (100) cut, undoped, S.I. GaAs wafer had 20nm Cr followed by 200nm Au evaporated on its back in an Edwards 12E evaporator. This metallisation formed the earth plane of the switch.

2) The wafer was cut up into 9.8mm squares using a diamond saw, the edges of the squares aligned with the flats of the wafer.

3) The roughened edges on the front of the squares were smoothed by dragging the edge across a glass slide with a slurry of aluminium oxide in water on its surface.

4) The samples were cleaned by dipping in trichloroethylene, ethanol, then de-ionised water.

5) The water vapour was driven off the samples by heating them at 120°C for 5 minutes.

6) Each sample was mounted front uppermost in the resist spinner, spun in primer for 20s, and then spun in Hoechst AZ4110 negative resist for 20s at 4000 rpm. This gives a resist film 200nm thick.

7) The sample was baked at 85°C for 15 minutes to harden the resist.

8) The first mask was exposed for 8s in a Karl Suss UV mask aligner.

9) The sample was soaked in chlorobenzene for one minute. The chlorobenzene soaks into the surface of the non-exposed regions of the resist, hardening the surface further, and giving a better resist profile for the lift-off process used later.
10) The resist was developed in 8 parts Shipley 351 developer to 30 parts de-ionised water for about 2 minutes, then rinsed in de-ionised water.

11) The resist pattern was baked again for 15 minutes at 85°C to harden it further.

12) The sample was returned to the evaporator and 20nm Cr followed by 200nm Au was evaporated on the resist-patterned front surface.

13) The lift-off process was completed by putting the samples into a petri dish of acetone. The acetone dissolves the resist, and any Cr/Au on top of the resist should be lifted off at the same time, leaving the electrode pattern in Cr/Au on the GaAs surface.

14) The sample was prepared for its second mask by repeating steps 4) to 7). The second mask was then exposed to the resist using UV light for 8s.

15) The second resist pattern was hardened and developed by repeating steps 9) to 11). The switch should now be protected by a 200nm layer of hardened negative resist, with only the switch gaps exposed.

16) The Auston switch was removed from the clean room and etched in the reactive ion etcher.

17) The protective layer of resist was removed from the electrodes, and the Auston switch mounted for testing.
## APPENDIX THREE

**First table of experimental results**

<table>
<thead>
<tr>
<th>Processing</th>
<th>Talystep etch height (microns)</th>
<th>Schottky ideality factor</th>
<th>Schottky barrier height (V)</th>
<th>PRM ratio</th>
<th>Auston switch decay (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polished control</td>
<td>0.00</td>
<td>1.25±0.05</td>
<td>0.87±0.02</td>
<td>1.00</td>
<td>25 110±5</td>
</tr>
<tr>
<td>Bubble etched control</td>
<td>2.80</td>
<td>1.15±0.02</td>
<td>0.87±0.09</td>
<td>1.4±0.1</td>
<td>20 65±5</td>
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<tr>
<td>30 mins. He ion etch</td>
<td>0.07</td>
<td>3.80±0.2</td>
<td>0.54±0.00</td>
<td>1.4±0.1</td>
<td>25 215±15</td>
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<tr>
<td>30 mins. Ar ion etch</td>
<td>0.06</td>
<td>1.60±0.2</td>
<td>0.60±0.01</td>
<td>1.4±0.1</td>
<td>45 130±5</td>
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<tr>
<td>30 mins. Kr ion etch</td>
<td>0.01</td>
<td>1.18±0.05</td>
<td>0.68±0.01</td>
<td>1.5±0.1</td>
<td>-</td>
</tr>
<tr>
<td>6 mins. Freon12 RIE</td>
<td>4.20</td>
<td>1.60±0.03</td>
<td>0.89±0.05</td>
<td>1.9±0.1</td>
<td>20 85±5</td>
</tr>
<tr>
<td>6 mins. 2:1 Freon12/Ar RIE</td>
<td>1.40</td>
<td>1.60±0.1</td>
<td>0.84±0.03</td>
<td>1.9±0.2</td>
<td>40 135±5</td>
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<tr>
<td>6 mins. 1:2 Freon12/Ar RIE</td>
<td>0.75</td>
<td>2.20±0.15</td>
<td>0.81±0.02</td>
<td>1.6±0.1</td>
<td>-</td>
</tr>
<tr>
<td>6 mins. Ar ion etch</td>
<td>0.00</td>
<td>1.55±0.00</td>
<td>0.63±0.00</td>
<td>1.3±0.2</td>
<td>50 125±5</td>
</tr>
</tbody>
</table>

*Polished control* and *Bubble etched control* refer to baseline measurements.

*30 mins.* and *6 mins.* denote the duration of the etching process.

*Ar ion etch* stands for Argon ion etching process.

*Kr ion etch* stands for Krypton ion etching process.

*Freon12 RIE* denotes the use of Freon12 RIE (Reactive Ion Etching) process.

*Freon12/Ar RIE* indicates a mixture of Freon12 and Argon in the RIE process.
### Second table of experimental results

<table>
<thead>
<tr>
<th>Processing</th>
<th>Talystep etch height (microns)</th>
<th>Schottky ideality factor</th>
<th>Schottky barrier height (V)</th>
<th>PRM ratio</th>
<th>Auston switch decay (ps)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.00</td>
<td>1.25 ± 0.05</td>
<td>0.87 ± 0.02</td>
<td>1.00</td>
<td>25 110 ± 5</td>
</tr>
<tr>
<td>Bubble etched control</td>
<td>2.80</td>
<td>1.15 ± 0.02</td>
<td>0.87 ± 0.09</td>
<td>1.4 ± 0.1</td>
<td>20 65 ± 5</td>
</tr>
<tr>
<td>30 mins. O₂ RIE</td>
<td>0.02</td>
<td>3.90 ± 0.7</td>
<td>0.80 ± 0.03</td>
<td>1.7 ± 0.1</td>
<td>40 140 ± 5</td>
</tr>
<tr>
<td>30 mins. H₂ RIE</td>
<td>0.11</td>
<td>1.77 ± 0.04</td>
<td>0.64 ± 0.003</td>
<td>1.6 ± 0.1</td>
<td>55 145 ± 5</td>
</tr>
<tr>
<td>30 mins. NH₃ RIE</td>
<td>0.03</td>
<td>1.40 ± 0.1</td>
<td>0.68 ± 0.004</td>
<td>1.3 ± 0.1</td>
<td>40 115 ± 5</td>
</tr>
<tr>
<td>30 mins. O₂ RIE + H₂ RIE</td>
<td>0.12</td>
<td>5.71 ± 0.04</td>
<td>0.72 ± 0.04</td>
<td>1.5 ± 0.1</td>
<td>-</td>
</tr>
<tr>
<td>30 mins. O₂ RIE + NH₃ RIE</td>
<td>0.14</td>
<td>2.02 ± 0.04</td>
<td>0.60 ± 0.00</td>
<td>1.4 ± 0.1</td>
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</table>
### Third table of experimental results

<table>
<thead>
<tr>
<th>Processing</th>
<th>Talystep etch height (microns)</th>
<th>Schottky ideality factor</th>
<th>Schottky barrier height(V)</th>
<th>PRM ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 mins. Freon12 RIE</td>
<td>4.2</td>
<td>1.60±0.03</td>
<td>0.89±0.05</td>
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<tr>
<td>6 mins. Freon12 + 30 mins. O₂ RIE</td>
<td>4.1</td>
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<td>1.53±0.02</td>
<td>0.63±0.00</td>
<td>1.5±0.1</td>
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<tr>
<td>6 mins. Freon12 + 30 mins. NH₃ RIE</td>
<td>3.7</td>
<td>1.45±0.03</td>
<td>0.68±0.01</td>
<td>1.6±0.1</td>
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<tr>
<td>6 mins. Freon12 + 30 mins. O₂ + 30 mins. H₂ RIE</td>
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<td>4.30±0.4</td>
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<td>6 mins. Freon12 + 30 mins. O₂ + 30 mins. NH₃ RIE</td>
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<td>2.60±0.4</td>
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</tr>
<tr>
<td>Processing</td>
<td>Talystep etch height (microns)</td>
<td>Schottky ideality factor</td>
<td>Schottky barrier height (V)</td>
<td>PRM ratio</td>
</tr>
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</tr>
<tr>
<td>30 mins. Ar ion etch</td>
<td>0.06</td>
<td>1.6±0.2</td>
<td>0.600±0.05</td>
<td>1.4±0.1</td>
</tr>
<tr>
<td>30 mins. Ar ion etch + 30 mins. O₂ RIE</td>
<td>0.04</td>
<td>6.0±0.7</td>
<td>0.72±0.01</td>
<td>1.31±0.05</td>
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<tr>
<td>30 mins. Ar ion etch + 30 mins. H₂ RIE</td>
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<td>1.5±0.1</td>
<td>0.65±0.01</td>
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<td>30 mins. Ar ion etch + 30 mins. NH₃ RIE</td>
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<td>1.42±0.04</td>
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<td>30 mins. Ar ion etch + 30 mins. O₂ + 30 mins. H₂ RIE</td>
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<td>5.8±0.1</td>
<td>0.72±0.005</td>
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<td>2.3±0.1</td>
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</tbody>
</table>
ACKNOWLEDGEMENTS

The funding for this research has come from an SERC award and an Industrial Studentship with EEV Ltd. Chris Pitt has helped throughout as my academic supervisor and Gill Burrage from EEV has been my industrial supervisor.

The photothermal radiometric microscope described in chapter four was built by Stephen Sheard for his PhD at UCL. He taught me how to use the microscope and to interpret the results obtained with it. Tom Hiller helped me use the microscope in the later stages of the project.

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