

ELEMENTARY PROCESSES IN ALKANE-BASED
REACTIVE ION ETCHING OF III-V SEMICONDUCTORS

By

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Abstract

Reactive ion etching (RIE) is a process used extensively in the microelectronics industry. Recently, the use of alkane-based plasmas has been developed for the etching of compound semiconductors. However, due to the complex nature of the plasma environment, relatively little is known about the etching mechanisms involved. To gain some understanding of the elementary processes involved in this technology, the interactions of some relevant ions and free radicals with these semiconductors were examined.

To simulate the low energy ion bombardment that occurs in RIE using alkanes, GaAs and InP were exposed to 20-500 eV carbon ions, using a mass-separated carbon ion beam in an ultrahigh vacuum chamber. The changes induced by ion bombardment and the effects of subsequent damage-removal treatments were determined by angle-dependent X-ray photoelectron spectroscopy (XPS). To enable the effects of sputtering and ion penetration to be quantified with XPS, an InP wafer consisting of an ultrathin (4 nm) epitaxial InP layer on InGaAs was used. Initially, carbon ion irradiation caused minor sputtering of the semiconductors and preferential removal of the group V constituents, with concurrent formation of carbon-semiconductor phases. The extent of the interaction increased with increasing bombardment energy. A chemically resistant, amorphous carbon residue formed after further bombardment. Whereas heating or ultraviolet light/ozone oxidation did not remove the damage, removal was effected by exposure to hydrogen ions.

Similar results were observed when these semiconductors were exposed to low energy methyl ions (<100 eV), except that the deposited amorphous hydrocarbon was readily removed by ozone oxidation treatments. Methyl radicals are suspected as likely etchant species. The methyl ion impact energy

was therefore lowered to 3 eV, an energy where the CH_3^+ species should remain intact on the surface. No sputtering or etching was observed at room temperature. However, when the surface was heated to 350 °C during the bombardment with 3 eV methyl ions, etching of InP was observed.

In addition to methyl radicals, hydrogen atoms are believed to be the major etchant species in alkane plasmas. Therefore, GaAs samples were exposed to thermalised hydrogen atoms produced in a remote microwave-driven molecular hydrogen discharge. The absolute atom pressures were measured by a calorimetric technique, and varied from 20 to 50 mTorr. GaAs was found to etch continuously with etch rates between 10 and 40 nm min⁻¹ and at temperatures ranging from 180 to 375 °C. An Arrhenius activation energy of 20.2 ± 3.9 kJ mol⁻¹ was determined. The resultant surfaces were rough, exhibited crystallographic features, and were arsenic deficient.

Addition of methane into the hydrogen atom stream increased the etch rate of GaAs by up to an order of magnitude. Using the well established rate constants for the reactions of hydrogen atoms and methane and the flow parameters of the apparatus, a model was developed to calculate the concentration of methyl radicals at the etching surface. The etch rates obeyed a first order dependence on the calculated methyl radical concentration. The first order rate constants were large ($\approx 5 \times 10^5$ nm min⁻¹ Torr⁻¹) but were limited by the diffusion of the methyl radicals to the surface. The resultant surface morphology was rough and crystallographic etch features were always observed. Arsenic deficient surfaces also resulted, but were less depleted than hydrogen atom etched surfaces. Gallium-containing residues were deposited on the reactor surfaces.

The implications of these results for alkane-based RIE are discussed.

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1. Nothing is as easy as it looks.
2. Everything takes longer than you think
3. In any field of scientific endeavour, anything that can go wrong will go wrong.

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For my grandparents, Sandy and Maggie.

Semiconductor devices have rapidly increased in complexity and capability since the first germanium-based transistor was developed in 1948. Since then, silicon has become the most commonly used semiconductor material, primarily due to its natural abundance, excellent material properties and ability to form stable oxides. Silicon-based technology has developed to the point where today, more than one million transistors can be accommodated on a square centimetre of silicon wafer, and chips containing 16 million devices are widely available.

In 1952, Welker's studies on GaAs and related compounds suggested that they might be useful semiconductors¹. However, early difficulties in producing high quality wafers and the lack of a good native oxide on these materials retarded progress for many years, thus allowing silicon to become the dominant technology. In recent years, however, III-V semiconductor processing has advanced tremendously, and instead of supplanting silicon technology, GaAs, InP and related materials are used for specialised and unique applications. To illustrate this statement, the properties and applications of III-V semiconductors will be reviewed.

1.1 III-V SEMICONDUCTOR PROPERTIES AND APPLICATIONS

In a crystalline material, the linear combination of a vast number of atomic orbitals leads to the formation of broad bands of states. Partial energy band structures for GaAs and Si are shown in Figure 1.1, where the electron energy is plotted against the momentum vector (k) of the electron in the crystal² (the band structure for InP is qualitatively similar to that of GaAs). Several important applications of these semiconductors are determined by three features on these diagrams: the positions of the conduction band minimum (upper curve) and the

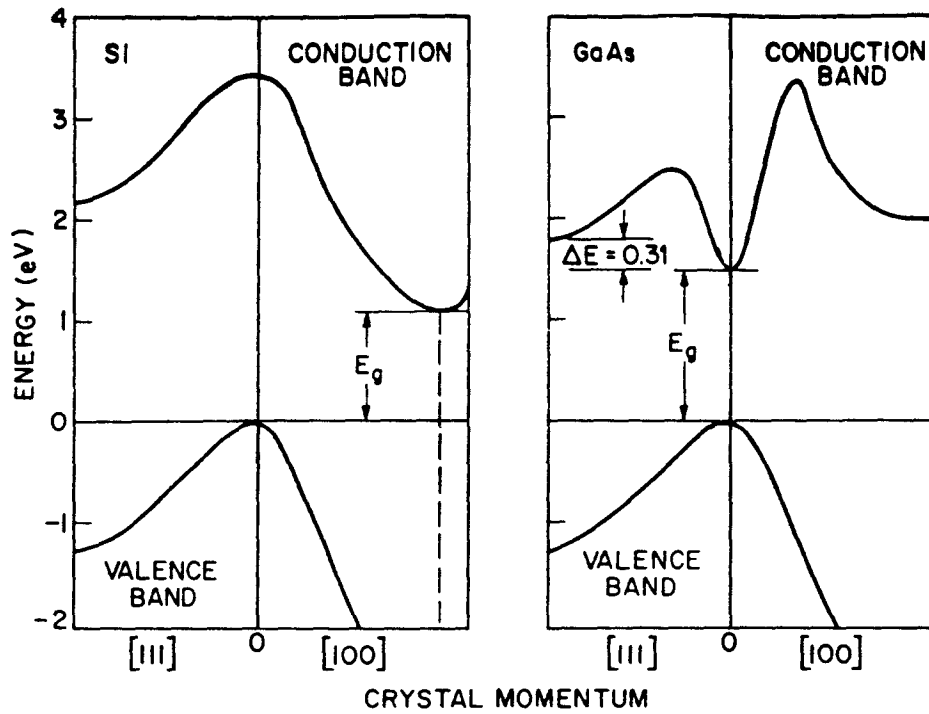


Figure 1.1 Partial band structures of Si and GaAs showing the valence band maximum and the conduction band minimum along two of the principle directions in the crystals (from Sze²)..... 2

valence band maximum (lower curve), the curvature of the band edges, and the minimum separation between the bands (the band-gap).

In GaAs and InP, the extrema of the valence and conduction bands occur at the same momentum vector. Therefore, an electron transition between the valence band maximum and the conduction band minimum can occur without a change in momentum. GaAs and InP are thus called direct band-gap semiconductors. A transition from the valence band into the conduction band can be achieved by irradiation with light of energy greater than the band-gap. Conversely, a transition from the conduction band into the valence band can occur with emission of a photon with energy E_g . In contrast, because its valence band maximum and conduction band minimum occur at different k values, silicon is called an indirect band gap semiconductor. Therefore, a transition between the bands also requires a change of momentum. As photons have negligible momentum, an interaction with a lattice vibration or other momentum source is necessary for an electron transition to occur. Because such three-body interactions are inherently improbable, GaAs and InP have a unique advantage over silicon in that they can effectively convert electrical energy into light. They are used to fabricate photodetectors and light emitting diodes. Alloys such as InGaAs and InGaAsP are widely used to produce diode lasers and detectors with various emission and absorption wavelengths, for optical fibre based communications.

Another important advantage that GaAs and InP have over silicon stems from the shape of the conduction band edges. The effective mass of the electron, m^* , in the crystal is related to the energy and magnitude of the momentum vector by the following expression³:

$$\frac{\delta^2 E}{\delta k^2} = \frac{\hbar^2}{m^*}$$

Thus, the curvature of $E(k)$ for a band will determine m^* . Both the III-V materials have narrower conduction bands than silicon, and electrons in those bands will

therefore have smaller effective masses. If m_0 is the mass of the free electron, the effective electron masses for GaAs, InP and Si are 0.067, 0.075 and 0.19 m_0 , respectively. This directly affects the velocity of the electrons and therefore the potential speed of semiconductor devices fabricated from these materials.

The velocity which electrons acquire when they are accelerated by an electric field, F , depends on their effective mass and the average time, τ , between collisions. The drift velocity, V_D , is given by,

$$V_D = e\tau F/m^*$$

Figure 1.2 shows the electron drift velocity in GaAs, InP and Si as a function of applied electric field. Whereas the drift velocity in silicon slowly reaches a plateau, in GaAs and InP it peaks at electric fields of about 3000 and 10,000 $V\text{ cm}^{-1}$, respectively, and then decreases. This behaviour in GaAs and InP arises from the presence of a second conduction band minimum, 0.31 and 0.27 eV higher than the direct band gap. From Figure 1.1(b), we can see that because this band edge has a smaller curvature (also in InP), the electron has a greater effective mass. Therefore at higher fields, an electron may be excited into this sub-band where it will move more slowly. Under low field operation (below 3000 $V\text{ cm}^{-1}$ for GaAs and 10,000 $V\text{ cm}^{-1}$ for InP) the smaller effective masses of the electrons in the conduction bands of GaAs and InP result in drift velocities that are about two to five times greater than it is in silicon. However, typical III-V devices operate at higher applied fields than silicon devices ($> 10,000\text{ V cm}^{-1}$), so the speed advantage of GaAs over silicon is about a factor of two, while InP has a greater advantage. This property can be exploited for the production of high speed integrated circuits used in digital computing. For example, the first commercial supercomputer using GaAs for its processor chips recently became available, and can perform 2×10^9 operations per second⁴.

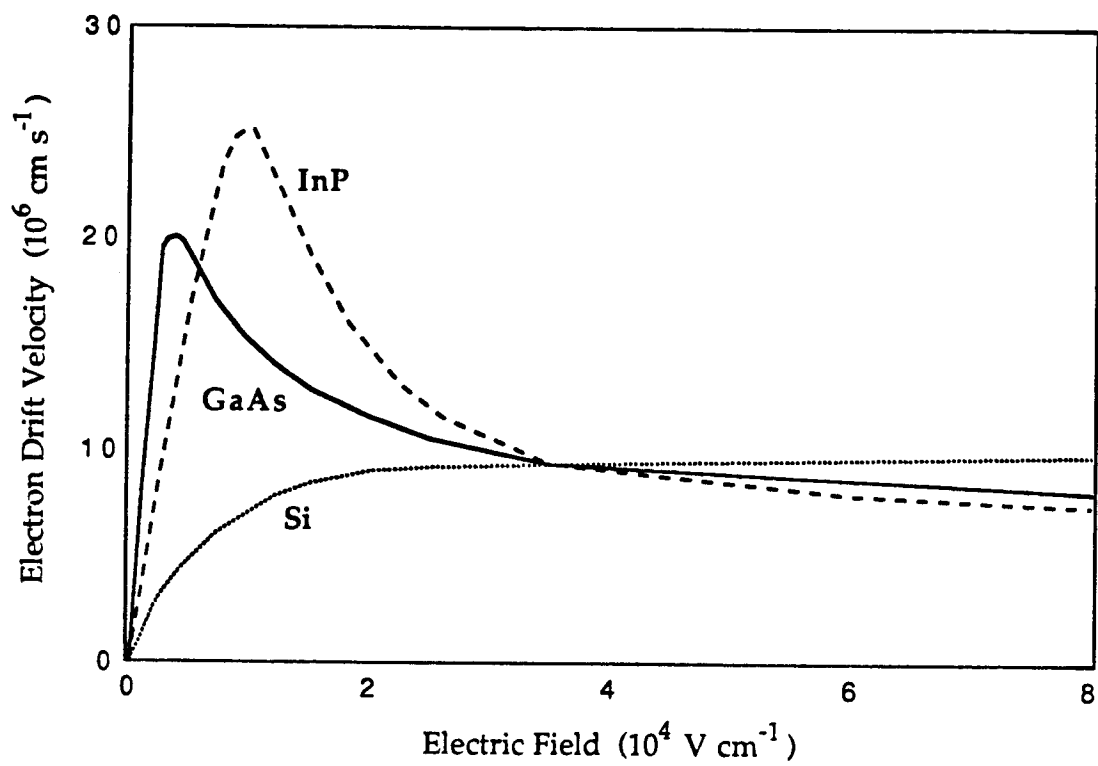


Figure 1.2 Plot of electron drift velocity versus electric field for Si, GaAs and InP

High drift velocities are also important for low-noise operation. The weakest usable signal is determined by random fluctuations in voltage. This noise can be minimized at high frequencies by maximizing the electron velocities in the transistor and in its connections to the rest of the circuit. The speed and lower noise operation of GaAs circuits is used extensively in satellite communications, where transistors operating at frequencies of up to 12 GHz enable microwave wavelengths to be converted and amplified to clear, almost noiseless electrical signals.

The third important aspect of Figure 1.1 is the energy separation between the valence band maximum and the conduction band minimum, or the band-gap E_g . The size of the band-gap determines the maximum temperature at which a semiconductor can operate. Therefore, integrated circuits based on GaAs and InP, which have E_g values at 300 K of 1.42 eV and 1.35 eV, respectively, can function at higher temperatures than Si with a band gap of 1.12 eV.

The width of the band-gap can be readily altered in III-V compounds by forming alloys of these materials. For example, aluminium arsenide has direct band gap of 2.16 eV at room temperature, which is considerably higher than that for GaAs. Substitution of gallium by aluminium to form $\text{Al}_x\text{Ga}_{1-x}\text{As}$, produces compounds with band gaps which are proportional to the mole fraction, x , of aluminium up to a fraction $x = 0.45$, when it becomes an indirect gap material⁵:

$$E_g = 1.424 + 1.087x + 0.438x^2$$

Adjustable band gap semiconductors such as $\text{In}_{1-x}\text{Ga}_x\text{As}$ and $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ are used for optoelectronic applications.

As mentioned previously, III-V semiconductors have several conduction band minima. Electron transitions into these bands limits the semiconductor electron drift velocity under typical operating conditions. However, the separation between the direct conduction band minimum and the next lowest energy

minimum are also affected by changing the composition of the semiconductor. For example, for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ compounds, the indirect energy gaps between the valence band maximum and the subsidiary conduction band minima as a function of the mole fraction, x , of aluminium are:

$$E_g = 1.905 + 0.10x + 0.16x^2, \text{ and } 1.705 + 0.695x$$

It is thus possible to increase the speed of devices by choosing a suitable composition for the alloy.

Two other material properties of GaAs and InP also give them a technological advantage over silicon. First, GaAs and particularly InP are significantly more resistant to high energy radiation than silicon, which is important for satellite and military applications. Second, GaAs wafers can be produced with a resistivity several orders of magnitude higher than silicon. These semi-insulating crystals have had a major impact on circuit design, practically eliminating current leakage between devices. However, as the level of circuit miniaturisation increases, this advantage will diminish.

Although GaAs and InP have several advantages over silicon, there are many problems associated with processing these III-V semiconductors. Briefly, the difficulties stem from their low-quality native oxides, the high density of surface defect states, large recombination velocities, and the appreciable vapour pressures of the group V constituents at elevated temperatures. This latter characteristic limits the temperatures used to activate ion-implanted dopants and anneal the ion-induced damage. Consequently, complete activation of the dopants is difficult, which leads to variations in device performance across the chip. This has been a factor in limiting the level of miniaturisation on GaAs chips. For example, a "state-of-the-art" gallium arsenide chip contains only tens of thousands of components per square centimetre, whereas a similar silicon chip has over one million. Also, the natural abundance and robust material characteristics of silicon coupled with

the advanced state of its processing technology means that production costs for silicon-based devices are significantly lower than those for production of III-V based devices. However, the potential advantages of compound semiconductors have led to the development of many ingenious solutions to these processing problems. Although silicon will probably remain the material of choice for most digital processing applications, the use of III-V materials in optoelectronic devices and high speed applications will ensure their place in the semiconductor industry.

Finally in this section, Table 1 lists several important properties of silicon, gallium arsenide and indium phosphide.

1.2 CRYSTAL STRUCTURE

The crystal structure of a semiconductor can determine the etch rates and surface morphology in many etch processes. Therefore a brief review of this subject will prepare the reader for discussions later in this thesis.

III-V semiconductors such as gallium arsenide and indium phosphide have a zincblende (or sphalerite) structure at atmospheric pressure. This consists of two interpenetrating face centred cubic lattices with one of the cubes displaced one quarter of the way along the main diagonal of the other. The unit cell is illustrated in Figure 1.3(a). This structure is identical to that of diamond and silicon, except that one of the face centred cube lattices consists of group III atoms and the other of group V atoms. The zincblende unit cell contains 8 atoms. Each group III atom is surrounded by four group V atoms and vice versa, in a tetrahedral arrangement, with the bond angles being $109^{\circ}28'$. Figure 1.3(b) illustrates how a zincblende lattice is constructed from such tetrahedral units. This spatial arrangement is characteristic of sp^3 hybridised covalent bonding, but the bonds are somewhat polar. The negative charge is distributed towards the group V element, with the fractional ionic character of the Ga-As and In-P bonds being 0.31 and 0.42, respectively⁵.

Table 1.1 Selected properties of Si, GaAs and InP at 300 K

Property	Si	GaAs	InP
Band gap (eV)	1.12	1.42	1.35
Electron mobility (cm ² V ⁻¹ s ⁻¹)	1500	8500	4500
Hole mobility (cm ² V ⁻¹ s ⁻¹)	450	300	100
Crystal structure	diamond	zincblende	zincblende
Lattice constant (Å)	5.43	5.65	5.87
Molecular or atomic weight (g)	28.09	144.64	145.79
Density (g cm ⁻³)	2.33	5.32	4.79
Melting point (°C)	1142	1238	1062
Heat of formation (from atoms) (kJ mol ⁻¹)	324	535	560
Maximum resistivity (Ω cm)	10 ⁵	10 ⁹	–
Dielectric constant	11.9	12.9	12.6
Thermal conductivity (W cm ⁻¹ K ⁻¹)	1.5	0.46	0.68
Linear coefficient of thermal expansion(°C ⁻¹)	2.6x10 ⁻⁶	6.86x10 ⁻⁶	4.75x10 ⁻⁶

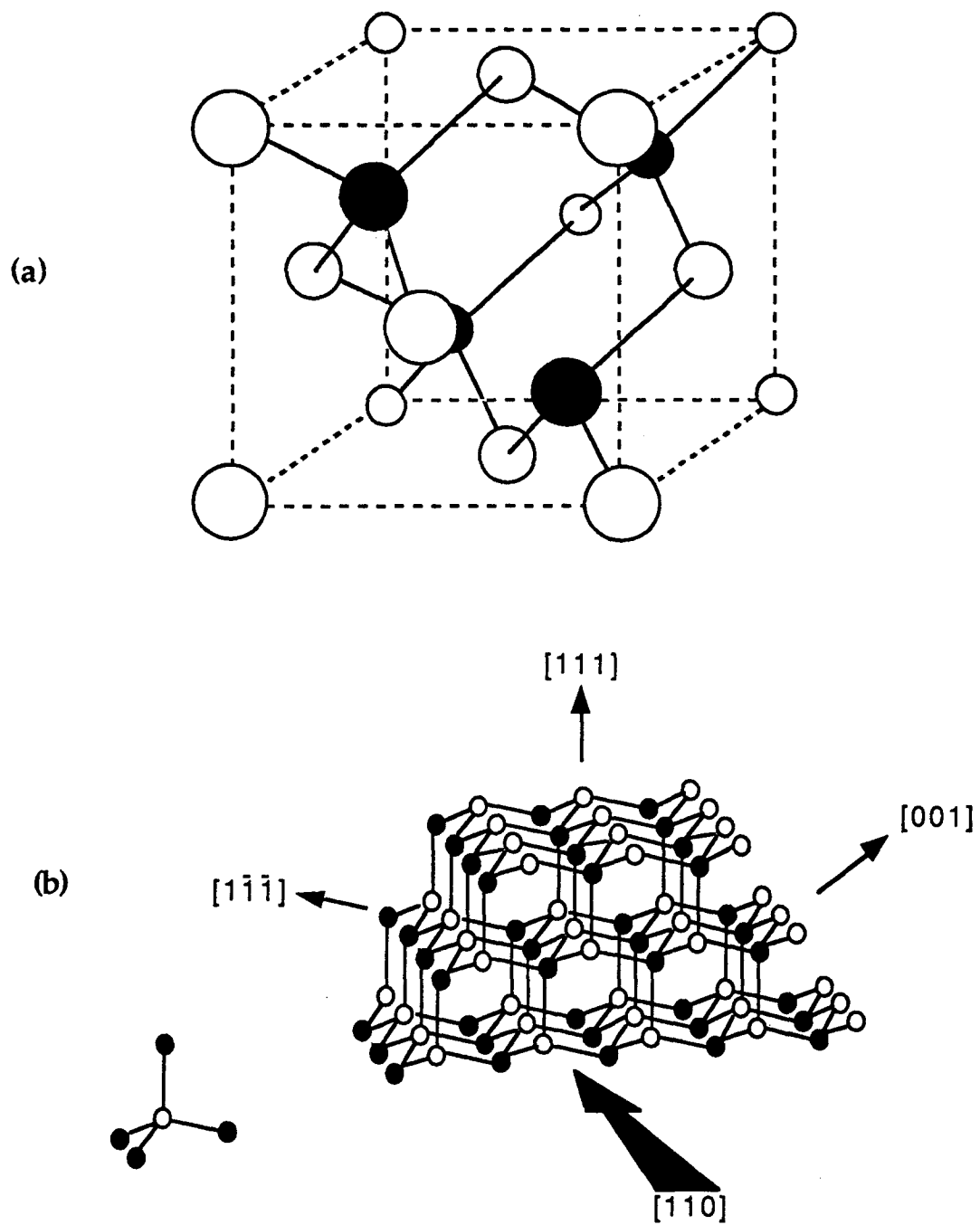


Figure 1.3 (a) zincblende unit cell and (b) tetrahedral arrangement of atoms in a zincblende lattice.

This ionic character affects the way these crystals cleave, and also their chemical properties.

Atomic planes are conveniently described using Miller indices. A specific plane within a unit cell, which intersects the x-y-z axes at distances a , b and c , respectively, from the origin, is described by the notation (hkl) , where h , k , and l are the smallest set of integers for the ratio of $1/a$ to $1/b$ to $1/c$. The notation $[hkl]$ is commonly used to indicate a crystallographic direction, and $\{hkl\}$ refers to a family of planes. Examples of low index planes are shown in Figure 1.4.

Figure 1.5 shows the views obtained when looking along the $[100]$, $[110]$ and $[111]$ directions of the zincblende crystal. The $\{100\}$ planes are composed of alternate layers of group III and group V atoms. Each surface atom has two bonds leading to atoms in the next layer, and two sp^3 orbitals projecting out of the surface. These orbitals are called "dangling bonds" in semiconductor terminology, to indicate their potential for forming a bond. The (100) surfaces of GaAs and InP are the most often used for device fabrication.

Figure 1.5(c) shows that the GaAs $\{110\}$ planes consist of an array of 'W'-shaped chains, made up of an equal number of alternating Ga and As atoms. Each Ga (or As) atom in the top layer has two bonds to As (or Ga) atoms in the same layer and one bond to an As atom in the next layer. This leaves one "dangling bond". This plane is the preferred cleavage plane in these crystals, due to its non-polar nature and small number of bonds to be broken per atom. The $\{110\}$ planes intersect at right angles and thus rectangular chips can be formed from a wafer with a (100) surface by cleavage along $\{110\}$ planes. This is a very useful property, and is exploited for laser diode applications.

Figure 1.5(c)) also indicates the orientations of the $\{111\}$ planes. These consist of an alternating sequence of two closely spaced planes, separated by a larger distance. In the closely spaced planes, one layer consists only of group III atoms and

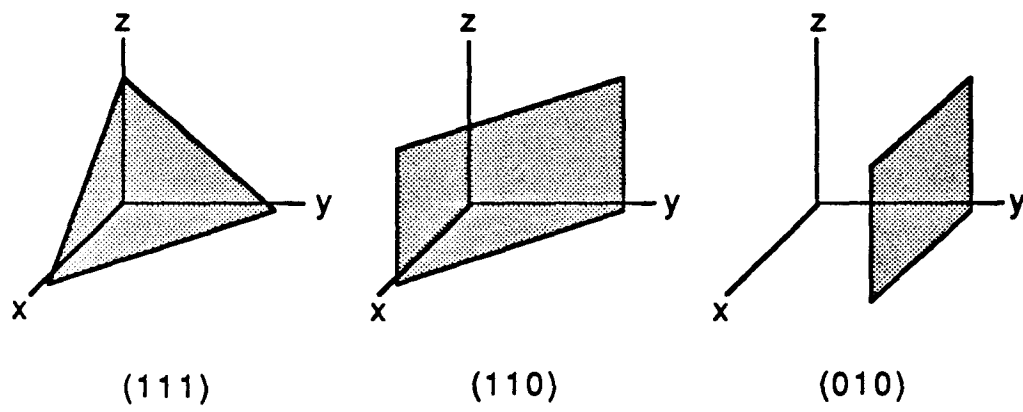


Figure 1.4 Examples of low index Miller planes

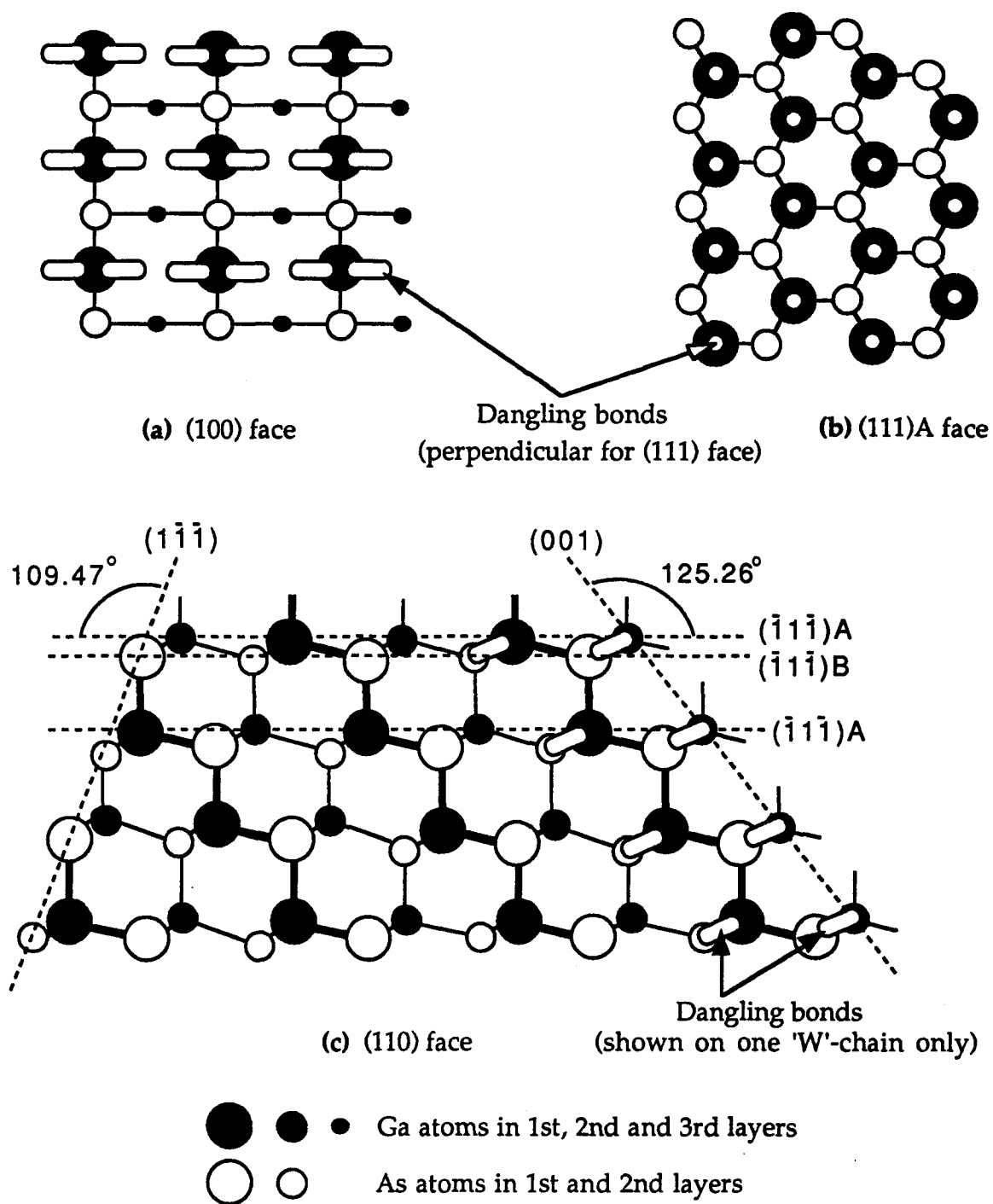


Figure 1.5 (a) (100), (b) (111) and (c) (110) faces of a zincblende crystal, viewed perpendicularly to each surface .

the other of only group V atoms. This is also shown in Figure 1.5(b), which indicates that the non-bonding orbitals have a normal projection to the surface. Cleavage cannot occur between the planes of the closely spaced double layer because three bonds would have to be broken between each atom. Thus, one surface of a GaAs (111) wafer will consist entirely of gallium atoms (called (111)A) while the backside surface will be entirely comprised of arsenic (called (111)B). This property, combined with the polar bonds in III-V semiconductors gives rise to variations in chemical reactivity, depending on the direction that the plane is approached. For example, {100} planes are found to etch more slowly than As {111} planes and faster than Ga {111} planes⁶. This type of disparity in etch rates causes the phenomenon of crystallographic etching. Thus, when a masked (100) surface is etched, a 'V'-shaped (Figure 1.6(a)) groove with exposed {111}A faces may form when the mask window is aligned with the $[01\bar{1}]$ direction. When the mask is aligned with the $[0\bar{1}1]$ direction, a reverse-mesa shaped groove forms (Figure 1.6(b))⁷.

1.2.1 Defects

The performance of semiconductor devices is greatly affected by the crystal quality of the material. Extensive research effort has therefore been applied to this branch of solid-state science. Deviations from the ideal crystalline structure arise because of a large range of defects. These include point defects, dislocations, stacking faults and grain boundaries. Such imperfections are incorporated into the crystal during the growth stage and also during the many subsequent processing steps.

Point defects are classified into three categories: vacancies, where an atom is absent from a lattice site; interstitials, which are atoms in sites where they should not be; misplaced atoms or antisite defects, for example, where a gallium lattice site is occupied by an arsenic atom or an impurity atom. A large percentage of the point

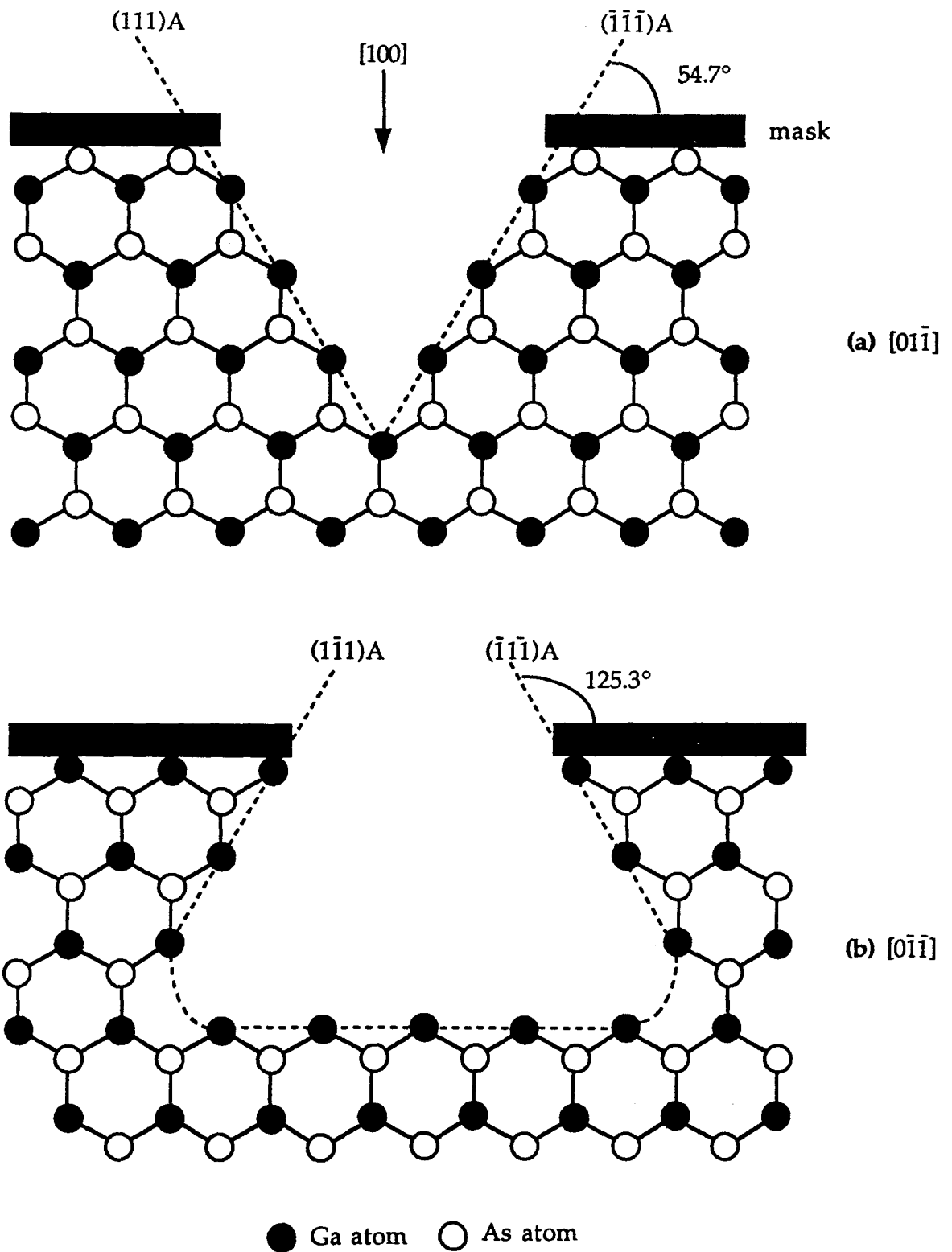


Figure 1.6 Crystallographic etch profiles of (100) GaAs resulting from mask aligned with (a) $[0\bar{1}1]$ direction and (b) $[0\bar{1}\bar{1}]$ direction.

defects in a semiconductor arise from the addition of foreign impurities during crystal growth. These may be intentionally added to obtain particular electrical characteristics or be impurities such as C, Si, O and S, which are present in the vessels used for crystal growth.

Dislocations are line defects and can be caused by several factors including thermal stress during growth, precipitation of excess point defects, ion implantation and diffusion. Edge dislocations, which are similar to stacking faults, arise when an additional plane of atoms is incorporated into the crystal lattice. Screw dislocations occur when one atom plane partially slips over another. Growth in this vicinity propagates in a spiral manner through the crystal. Dislocations can be a serious hindrance to device performance and therefore, growth and processing steps are carefully controlled in order to minimise their density. For a detailed discussion of III-V semiconductor crystal defects, see for example "Materials Aspects of GaAs and InP Based Structures"⁵.

1.2.2 Reconstruction

Atoms in a surface layer experience different forces than those in the bulk of the crystal and are thus subject to displacements from the sites they would occupy in an ideal surface. The driving force is the minimisation of the surface free energy. Such displacements can alter the electronic structure of the semiconductor. The non-polar (110) surfaces of III-V semiconductors have received the most attention since they can be prepared in ultrahigh vacuum by crystal cleavage. The reconstructions of GaAs (110) are well characterised. The less-studied, polar (100) and (111) surfaces of GaAs have been found to undergo many types of reconstruction, depending on their method of preparation. For example, there are 11 different structures known for the GaAs (100) surface⁸. At present, there is still

no clear understanding of the relationships and transitions between any two reconstructed surfaces of the same material⁹.

The study of surface reconstruction is restricted to ultrahigh vacuum conditions, and contamination can alter the surface structure extensively. In a conventional semiconductor etching process, the operating pressures range from atmospheric down to tenths of a milli Torr. For typical etch rates, approximately 5 to 100 atomic layers are removed from the crystal every second and each surface atom may be struck by many thousands of reactant species per second. The surface is continually covered by at least one monolayer of etchant. Reconstruction does occur, and may strongly influence the etch process, but *in situ*, "real time" observation of the atomic structure of these etching surfaces is not yet possible. Thus, aside from extrapolating the initial surface reconstruction to the high pressure regime, determining the role of reconstruction in the etch process is almost impossible.

1.3 ETCHING IN THE FABRICATION OF III-V INTEGRATED CIRCUITS

Creating a microelectronic device, such as a transistor, is a complex process. Commencing with the production of ultra-pure, defect free semiconductor crystals, a device is formed by a sequence of patterning, deposition (or implantation) and etching steps. As this thesis is a study on certain aspects of a developing etch process, a description of the fabrication sequence for a typical III-V semiconductor device will serve to illustrate the essential role of etching in the microelectronics industry.

The device considered is a metal-semiconductor field effect transistor (MESFET), which is the primary active component in microwave integrated circuits. Figure 1.7 shows the basic structure of a MESFET. Current flow between the source and the drain occurs through the n -doped channel and is controlled by

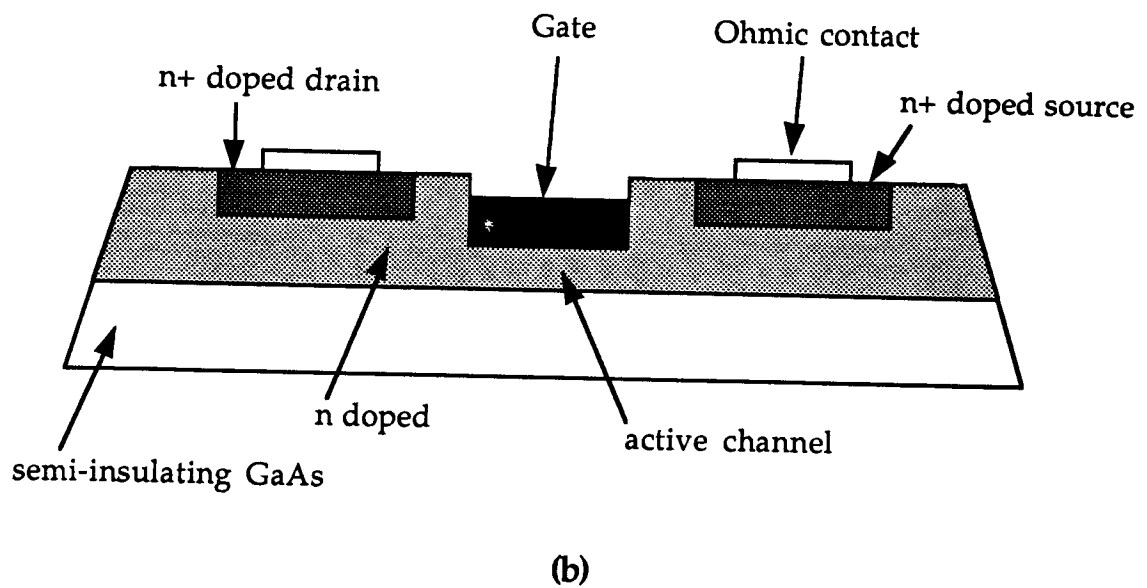
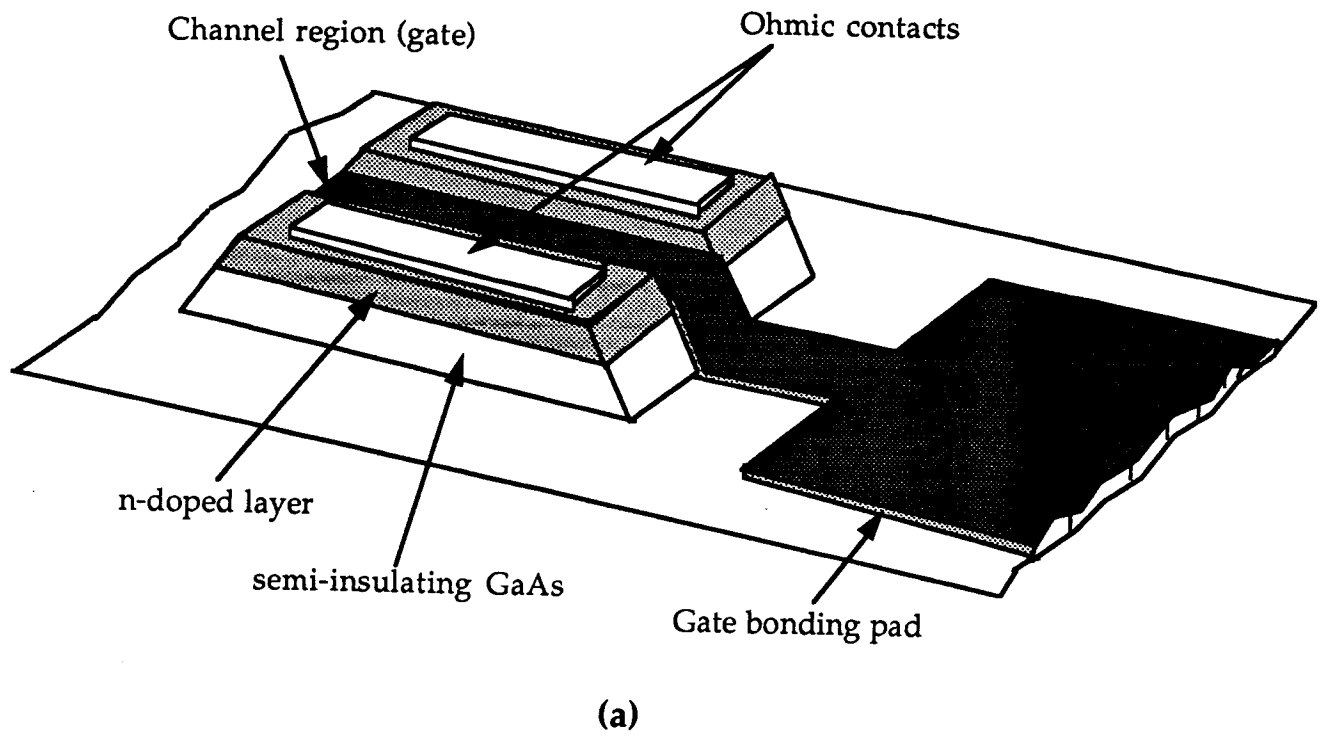


Figure 1.7 (a) Drawing of a GaAs MESFET and (b) cross-section through device.

the application of a voltage to the gate – a metal/semiconductor interface (a Schottky barrier). The source and drain are heavily doped (n^+) to reduce contact resistance.

Figure 1.8 is a schematic of the fabrication process. The starting material is high quality, semi-insulating (100) GaAs, which has been cut into wafers from a large single-crystal ingot, and polished. The first step is the deposition of a layer of silicon nitride on both sides of the wafer, by exposing it to a plasma containing ammonia, hydrogen and silane. This coating prevents out-diffusion of arsenic from the substrate during subsequent high temperature treatments. Silicon is implanted into the substrate by ion bombardment and forms a layer of n -doped material, which serves as the active channel for the MESFET. An alternative approach is to grow a perfectly crystalline n -doped layer from the gas phase using processes called vapour phase epitaxy and molecular beam epitaxy.

The source and drain are regions of highly doped material, and are formed by implantation of a second dose of silicon. The areas to be n^+ -doped are determined by depositing a mask on the surface. Mask deposition is part of the process of lithography. Essentially, a thin layer of light sensitive material called "photoresist" is "spin-coated" onto a wafer and exposed to UV light (or X-rays, electrons) through a photographic mask (a greatly reduced circuit diagram). Interaction with the light alters the solubility of the photoresist, which is then "developed" in a suitable solution, leaving an image of the mask on the surface. Subsequent ion bombardment leads to silicon being implanted only in the regions with no photoresist.

Following the implantation steps, the photoresist is removed and the implanted silicon is activated either by annealing slowly in a high temperature furnace or by very rapid, "flash" annealing. The protective layer of silicon nitride is then removed either by a wet etch or by plasma etching. These processes will be

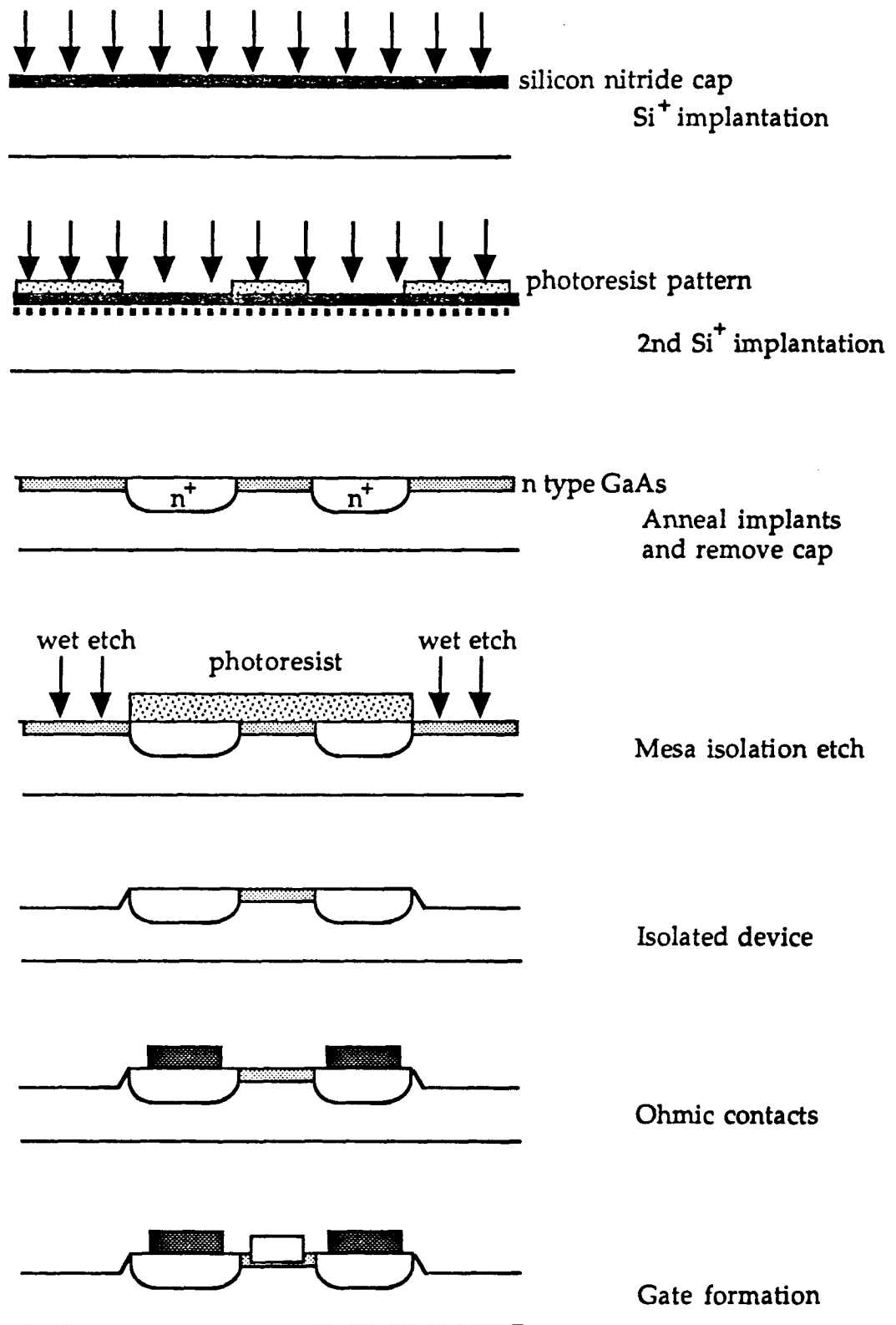


Figure 1.8 Fabrication sequence for a GaAs MESFET.

described in further detail later. The MESFET is then isolated from other devices on the wafer by etching the implanted layer around the device area. This is achieved by photoresist masking and wet etching. The photoresist is subsequently removed.

The next stage is the formation of metallic connections to the source and drain. Once again, the wafer is coated with photoresist and patterned to expose the GaAs in areas where the contacts are required. A thin layer of germanium/gold alloy is then evaporated onto the wafer, followed by a layer of nickel or indium and a thicker layer of the germanium/gold alloy. The unwanted metal is removed along with the photoresist. The metal-semiconductor connection is improved by diffusing some of the metal into the substrate with a rapid anneal.

The speed of the transistor is primarily determined by its gate length *i.e.* the linear dimension of the gate between the source and drain. Thus, for sub-micron gate lengths, a high degree of control is required for both the photolithography and etching steps. As before, the wafer is coated with a layer of photoresist, which is patterned to leave exposed GaAs in the gate region. A narrow trench is then etched into the GaAs, leaving a thin, n -doped layer which serves as the current channel. Metal is then evaporated into this recess, forming the gate and gate connection.

Integration of the transistor with other components is achieved by a series of insulator-deposition, masking, etching, and metallisation steps. The thickness of the wafer is then reduced by mechanically polishing the backside, and connections made to the integrated circuits by depositing metal in holes (or "vias") etched into this side. Cleavage of the wafer yields up to several hundred chips.

1.4 ETCHING OF SEMICONDUCTORS

The term "etching" was used several times in the previous section to describe a process where a solid material was removed. Etching can be a chemical

or physical process, and the species which does the etching can be in any state of matter. In the semiconductor industry, etching is usually classified as a wet or dry process. Wet etching is the simplest technique, where the material to be etched is immersed in an "aggressive" liquid. For example, GaAs is often etched in a solution of ammonia and hydrogen peroxide. If the wafer is masked with a material that is quite inert to the etchant, only the exposed material will be removed. However, there is very little directional control with these purely chemical etches, and the resultant etch profiles are either anisotropic (crystallographic, as discussed above) or isotropic, with undercutting of the mask (see Figure 1.9). The degree of undercutting depends on the etch depth and this limits the minimum lateral dimensions achievable with wet etching. For features which are greater than approximately 3 μm wide, the profiles obtained with wet etching are acceptable. As device dimensions have decreased, however, processes in which the downward etch rate is greater than the lateral etch rate are required to produce vertical sidewalls and thereby enable accurate pattern transfer (Figure 1.9). Such anisotropic etching is essential if greater levels of miniaturisation are to be achieved, and device performance is to be optimised. For example, as mentioned above, the gate length of a MESFET largely determines its speed.

1.4.1 Dry etching

Several dry etching techniques are suitable for generating vertical, anisotropic etch profiles. As the name implies, these processes involve the interactions of gas phase species with the surface. The reactants can be ions, free radicals and atoms generated in a low pressure discharge, or molecular gases. Another important advantage of a dry process is the compatibility with vacuum production-line fabrication, *i.e.* the majority of the processing steps can be performed under vacuum.

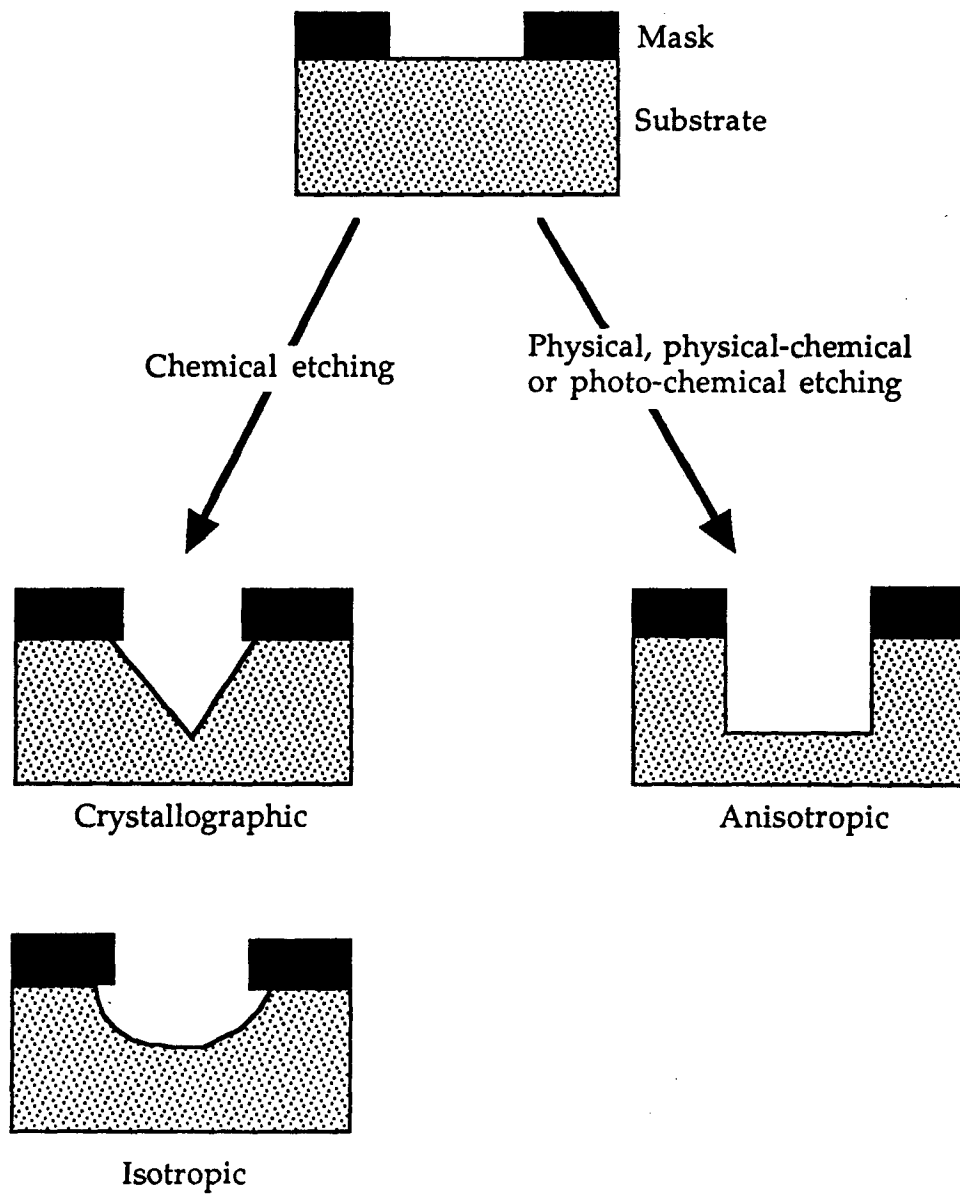


Figure 1.9 Etch profiles of masked semiconductors, resulting from four types of etch process.

There are several approaches to dry etching, which can be classified according to the etching mechanism involved¹⁰: physical, chemical, chemical-physical, and photo-chemical etching. Of these, purely chemical etching, while enjoying some of the advantages afforded by a dry process, suffers from the same limitation inherent in a wet process - isotropic or crystallographic etching. However, some discussion of chemical etching will be useful, since it is an essential part in chemical-physical and photo-chemical etching.

1.4.1.1 Chemical etching processes

Chemical etching occurs via a sequence of steps, any one of which may be rate controlling:

- (1) Etchant formation and diffusion to surface, *e.g.* atom and radical production in a plasma.
- (2) Adsorption and/or reaction of etchant with surface.
- (3) Formation of volatile product molecule.
- (4) Desorption of product.

These etch processes can be highly selective, *i.e.* various materials etch at different rates. This is a useful feature, allowing surfaces to be patterned accurately without excessive mask loss, or enabling a thin film to be etched down to its interface with a substrate of different affinity to the etchant, *e.g.* the selective etching of GaAs layers on AlGaAs can be achieved by using fluorine-containing etchants due to the relative involatility of aluminium fluorides. Another example of a dry, purely chemical etch is the reaction of molecular chlorine with GaAs (100) at 100 °C¹¹.

1.4.1.2 Physical etching processes

Physical etching methods are, in principle, less complex than chemical ones. Ions are accelerated towards a substrate and their impact with the surface causes

material to be ejected from it. This process is known as sputtering. There is extensive literature on this topic¹², so only a brief discussion of the processes involved will be given here.

As ions approach the surface, most of them are neutralised by Auger or resonance processes in about 10^{-15} seconds. The momentum of these neutral particles carries them into the solid with several consequences. When the ion energy is below 100 keV (typically 30 eV to 3 keV for ions in physical etching), its energy is lost by a series of elastic collisions with the substrate atoms. This leads to the creation of fast recoil particles, which in turn slow down by setting other atoms in motion. The number of progressively slower moving particles increases until, after about 10^{-13} s, the transferable energy is lower than the lattice-atom displacement energy of 5-20 eV. This volume of moving substrate atoms is called the collision cascade, and is a localised "hot" region in the substrate. After about 10^{-12} s, various interactions with the lattice begin to dissipate the energy of the cascade, and about 10^{-11} to 10^{-10} s are needed to "thermalise" the atoms in this region. If a surface atom receives an impulse with an energy greater than that binding it to the surface, it will be ejected from the substrate. Meanwhile, the incident particle will become implanted in the lattice. The sputter yield is defined as the number of atoms that are ejected from the surface by one incoming particle. The yield is a function of the ion's energy, mass and angle of incidence, as well as the type of target material and its morphology.

In purely physical etching processes, inert ions are extracted from plasmas of noble gases, such as argon and are directed towards the surface to be etched. Even though the resultant etch profiles are anisotropic, ions are non-selective, so unless a focused ion-beam is used, there is little control over what gets sputtered. Other problems with this approach are the redeposition of non-volatile sputtered material onto the surface, and the extensive damage introduced into the

semiconductor by the high energy ions required to achieve reasonable etch rates. Consequently, these techniques are not widely employed in the semiconductor industry.

The remaining two dry etching processes, chemical-physical and photo-chemical, are synergistic in nature *i.e.* the vertical etching rate of a chemical process is enhanced by a concomitant physical process, with the combined rate being greater than the individual rates. In practice, highly anisotropic etching can be achieved this way. Photo-chemical etching is still a largely undeveloped field. This can be a wet or dry process in which photons enhance a surface chemical reaction by excitation of either the gas phase reactants, adsorbed reactants or products, or the solid. The remainder of this section will be devoted to the description of physically enhanced chemical etching.

1.4.1.3 Chemical-physical etching processes

When semiconductors were first etched in plasma reactors, it was observed that anisotropic etching could be achieved by exposing the wafers directly to the electric field¹³. The implication was that sputtering by ions from the plasma increased the reactive-neutral etch rate in the vertical direction. A few years later, Coburn and Winters¹⁴ examined the etching of silicon with combinations of xenon difluoride molecular beams and argon ion bombardment, and effectively demonstrated that a synergistic effect could exist in such processes. The etch rate when both species were incident on the surface was over ten times higher than the rates for the individual species. This is illustrated in Figure 1.10. Rate enhancement due to localised heating and electronic excitation was ruled out, and the effect was only observed for substrates which formed volatile halides.

A vast quantity of research by many workers has since been carried out to determine the mechanism by which the etch rate is enhanced. Much controversy

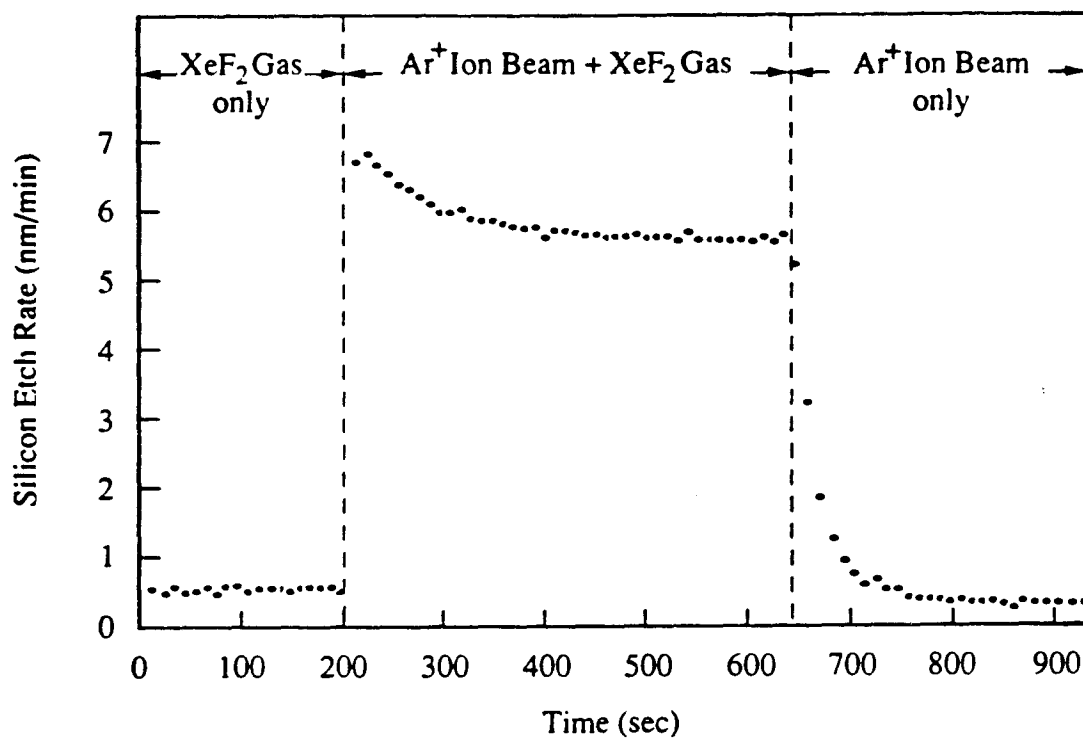


Figure 1.10 Etch rate of Si with separate and combined beams of XeF_2 and Ar^+ demonstrating synergistic etching (from Coburn and Winters¹⁴).

still exists, even for the extensively studied case of ion-assisted xenon difluoride etching of silicon¹⁵.

However, it is believed that the ion enhancement of an etch may occur in a number of ways:

(1) Ion impact will disrupt the surface bonding and alter its composition, possibly accelerating subsequent chemical reactions with the substrate.

(2) Ion bombardment may keep a horizontal etching surface clear of a relatively involatile layer that forms (usually a polymer) but the etching of vertical sidewalls is inhibited by this coating. There is strong evidence to suggest that such a mechanism is responsible for the anisotropic etching of SiO₂ on Si, in CF₄/H₂ plasmas¹⁶.

(3) Ion bombardment provides energy to the surface species, thus increasing the rate of the chemical reaction leading to formation of volatile products, which subsequently desorb (sometimes called "chemical sputtering"). Chemical sputtering can also occur when a surface is exposed solely to ions – provided that they are not inert. In addition to the bond-breaking and disorder induced by the impact of the ions, bonds between the implanted and substrate atoms can form, which may alter the surface binding energy. The resultant alloy may be more, or less resistant to sputtering than the pure substrate *e.g.* N⁺ bombardment on silicon forms silicon nitride, which is more resistant to sputtering than pure silicon¹⁷. Further bombardment with "reactive" ions may even generate volatile species, thereby enhancing the sputter yield.

(4) A chemical reaction forms weakly bound species that are more readily ejected from the surface by an impulse from the collision cascade. Without the ion bombardment, the etch rate is limited by product desorption. This is called "chemically-enhanced physical sputtering". In practice, all of these processes probably contribute to the enhancement of the etch rate, and for a particular etching

system, a large number of operating parameters will determine the dominant mechanism.

There are many variations of reactor configurations available to achieve ion-assisted etching. Several use a gas in the form of a plasma to provide a continuous supply of ions, free radicals and atoms. Others employ a more controlled approach, exposing a surface to a flux of reactive neutrals with simultaneous bombardment by a separately produced ion beam. One extensively used process is called reactive ion etching (hereafter RIE).

A RIE reactor consists of two parallel electrodes in a high-vacuum chamber (Figure 1.11). The top electrode and the chamber walls are electrically grounded, while the lower electrode and the substrate holder are connected through a dc-blocking capacitor and matching network to a radio frequency generator typically operating at 13.56 MHz. The resulting negative bias on the sample electrode, accelerates positive ions from the plasma towards the substrate, enhancing the etch rate in the vertical direction.

The term "reactive ion etching" is a confusing misnomer, implying that reactive ions are responsible for the etch. At the pressures normally used in a RIE reactor (10-200 mTorr) the flux of ions at the surface is typically 3 orders of magnitude lower than the neutrals flux. This is illustrated in Figure 1.12, which also shows the removal rate of Ga and As atoms corresponding to a GaAs etch rate of 100 nm/min (3.7×10^{15} atoms $\text{cm}^{-2} \text{s}^{-1}$)¹⁸. Thus, the ion flux alone cannot account for the "observed etch rate", even if the sputter yield was increased by the formation of more volatile surface species. Also, with ion bombardment perpendicular to the surface, it is unlikely that the sputter yield per ion would be greater than unity. However, the use of "reactive ion etching" to describe such an experimental configuration is prevalent in the semiconductor industry, and will therefore be used in this thesis.

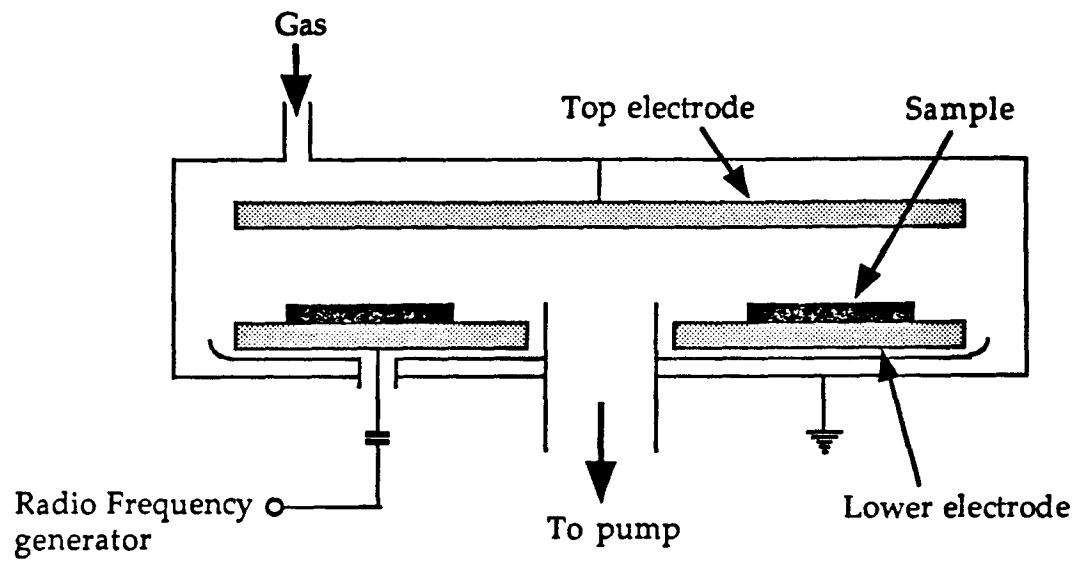


Figure 1.11 Schematic of a RIE reactor.

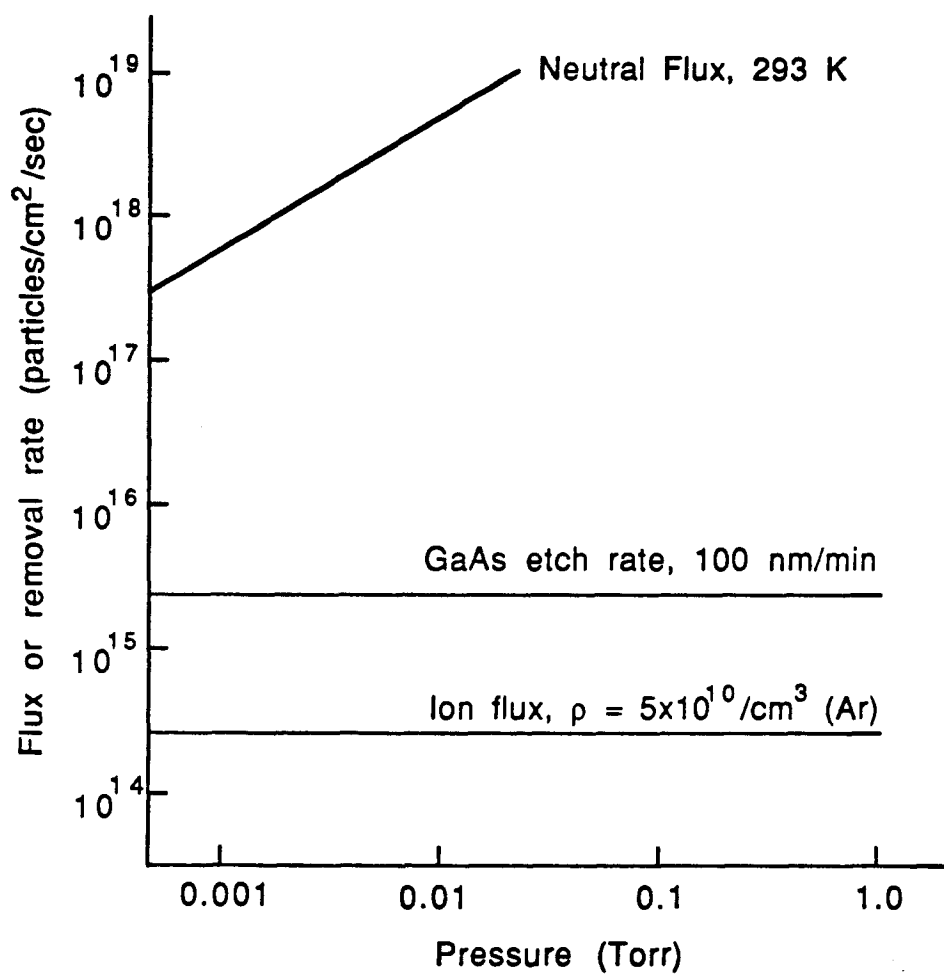


Figure 1.12 Plot of ion and neutral fluxes on a surface in a plasma, and flux of As and Ga atoms leaving the surface corresponding to an etch rate of 100 nm min^{-1} (from ref. 18).

The advantages of RIE, aside from its highly anisotropic etching characteristics, are that, compared to a purely sputtering process, lower ion energies are usually sufficient to maintain reasonable etch rates, and the reactive chemical species can be quite selective in their etch rates with various materials (*e.g.* photoresist, oxides, semiconductors).

1.4.2 Advances in reactive ion etching

Conventionally, a chlorine or fluorine containing gas is used as the source of the reactive species in the RIE of III-V materials¹⁹. The etching process is strongly dependent on the volatility of the etch products, and in the RIE of GaAs, the high vapour pressure of the gallium and arsenic chlorides enables efficient etching of the semiconductor. However, for the RIE of indium based semiconductors, the relative involatility of the indium chlorides and fluorides has resulted in problems such as low etch rates, poor surface morphology, low selectivity between the mask and surface, and post-etch halogenated surfaces²⁰. Conversely, for GaAs, the high etch rates can be a problem for the fabrication of devices when precise control of the etch depth is critical. Coupled with the growing concern about atmospheric contamination by chlorofluorocarbons, these problems have resulted in the development of a new etch process using alkane/hydrogen or alkane/inert-gas plasmas.

In 1985, Niggebrugge *et al.*²¹ reported the successful RIE of InP using a methane/hydrogen gas mixture. Since then, many workers have studied this new process²². As with other ion assisted processes, the etch rates are found to increase with increasing plasma power density and substrate bias, as is the amount of damage induced in the near-surface. The greatest etch rates are observed when the gas mixture is composed of approximately 10% methane in hydrogen or an inert gas, although more stoichiometric surfaces are obtained with higher fractions of

methane. There is also negligible etching of mask materials, which is essential for accurate pattern transfer – a necessity for the fabrication of sub-micron devices.

Despite the improved etch characteristics, alkane-based etching is not without its own difficulties. For both GaAs and InP, etching in these alkane-based plasmas produces surfaces that are depleted in the group V constituent. Also, excessive polymer deposition on the reactor walls may lead to particulate contamination, and "pre-conditioning" of the plasma reactor is often necessary to ensure reproducible etching behaviour. Etching at high methane concentrations causes polymer residues to accumulate on the semiconductor surface, retarding the etch rate and leaving a surface that may require subsequent cleaning treatments before further processing is possible. Furthermore, the exposure to a hydrogen containing plasma is likely to alter the electrical characteristics of the semiconductor, for example by passivating donors in GaAs and acceptors in InP²³.

Although there have been many recent publications on alkane-based plasma etching of GaAs, InP and related compounds²², these have been predominantly of an empirical nature *i.e.* etch rate and morphology optimization via macroscopic parameters such as plasma power density, gas flow rates and composition, and total pressure. This can be attributed to the complexity of the plasma environment, where the determination of even the major etching species is difficult. In the most comprehensive study to date, Hayes *et al.*²⁴ confirmed previous findings²⁵ that for the etching of InP, the primary phosphorus containing product in the discharge is phosphine. They did not observe any volatile indium products. Under etching conditions of high anisotropy, no polymeric deposits were found on the trench sidewalls, thus ruling out the possibility that the vertical etch rate was favoured because of a sidewall passivation mechanism (mechanism 2, in Section 1.4.1.3). Pearton *et al.*²⁶ examined alkane/hydrogen reactively ion etched GaAs surfaces

with X-ray photoelectron spectroscopy, Auger and electrical characterisation, but no further insight into the mechanism of the process was gained.

Thus, there is still relatively little known about the actual etching mechanisms that occur in the reactive ion etching of III-V semiconductors with methane-containing plasmas. However, the success of this process is believed to be due to the reaction of methyl radicals with the metallic components of the semiconductors to form volatile organometallic compounds, and reaction of the group V constituents with hydrogen atoms to form hydride species. A review of the literature will show that there is substantial evidence for this belief.

1.4.3 Interactions of hydrogen with III-V semiconductors

Hydrogen atoms have long been known to react with many elements. In 1924, Bonhoeffer²⁷ found that hydrogen atoms reacted with phosphorus, sulphur, arsenic and antimony to give the volatile hydrides of these elements. Pearson *et al.*²⁸ observed that hydrogen atoms also removed thin films ("mirrors") of germanium, tin and tellurium, but detected no reaction with lead or bismuth. Pietsch²⁹ found that when the metals silver, beryllium, gallium, indium and tantalum were exposed to hydrogen atoms, they became covered with surface films of substances which, when treated with water, evolved hydrogen leaving metallic hydroxides. These films that he considered to be metallic hydrides, have salt-like characteristics analogous to LiH. Table 1.2 lists the melting and boiling points of some group III and V hydrides. Thus, hydrogen atoms are known to react with the group V constituents of GaAs and InP, and also to some extent with the metal components. The interaction of these materials in plasmas of hydrogen would be expected to be more facile considering the energetic nature of the discharge.

As alternatives were being sought for halogen-based etching of III-V semiconductors, interest in discharged hydrogen as a possible etchant for these

Table 1.2 Melting and boiling point data for some group III and V hydrides

	m.p. (°C)	b.p. (°C)
Ga_2H_6	≈ -50	*0
AsH_3	-116	-55
PH_3	-133	-87
InH_x	?	?

*decomposes³⁰

materials grew. For example, Chang *et al.*³¹ etched GaAs, GaSb and InP and their oxides in an RF hydrogen discharge and observed etch rates of up to 50 nm min⁻¹ for GaAs. They reported that the GaAs surfaces were stoichiometric, whereas the etched InP surfaces showed phosphorus depletion and indium segregation into globules. While this behaviour for InP had been observed previously by Clark *et al.*³², and has been confirmed by many subsequent studies³³, a later report on the interaction of a hydrogen plasma with GaAs (100) indicated a slight depletion of arsenic³⁴.

The behaviour of these materials towards thermal H atoms has also been investigated. The etching of GaAs oxides has been examined in several studies using hydrogen atoms in high vacuum systems³⁵, although no continuous etching of GaAs has been reported. Aston³⁶ studied the etching of InP with H atoms produced in a remote microwave discharge at pressures below 1 Torr. He found that at temperatures above the melting point of indium (156 °C), extensive phosphorus depletion occurred, leaving the surface completely covered with globules of indium. No etching was observed beyond this point. Obviously, such interactions are a serious problem for device fabrication, particularly when processing steps involve hydrogen containing plasmas.

There have also been a considerable number of high vacuum surface studies of GaAs and InP exposed to hydrogen atoms and ions. Analysis techniques used include X-ray and synchrotron ultraviolet photoelectron spectroscopies (XPS, UPS), Auger electron spectroscopy (AES), high resolution electron energy loss spectroscopy (HREELS), low energy electron diffraction (LEED) and reflection high energy electron diffraction (RHEED), infrared spectroscopy (IR), and temperature programmed desorption (TPD). As the reactive hydrogen fluxes are very low, etching is generally not observed. Nonetheless, a review of this previous work may shed light on the mechanism of hydrogen atom etching of GaAs and InP.

The surface most extensively studied has been the non-polar (110) face of GaAs. However, the few reports on the interaction of hydrogen with (100) faces of III-V semiconductors have shown that the interactions are qualitatively similar to those on the (110) surface. GaAs and InP surfaces are quite inert to molecular hydrogen, and chemisorption only occurs at elevated temperatures³⁷. However, annealing GaAs at 600 °C in a stream of H₂ at atmospheric pressure has been used to remove surface oxides and other carbonaceous contamination, leaving stoichiometric surfaces³⁸. In the studies of the hydrogen-semiconductor surface interaction under vacuum, the surfaces are normally exposed to "activated hydrogen" *i.e.* hydrogen atoms produced by the dissociation of molecular hydrogen on a hot (2200 K) tungsten filament, or ions and atoms from beam sources. Exposures are determined indirectly from surface coverage measurements.

The interaction of III-V surfaces with hydrogen atoms has been shown to occur in two stages³⁹: an initial chemisorption step, followed by decomposition at higher exposures. For atom exposures leading to coverages of up to a monolayer, bonds with both constituents of the semiconductors are formed, leading to a saturation of the surface atom "dangling bonds". This removes the surface reconstruction of the bare surface. For example, a c(8x2) (or (4x2)) reconstructed (100) GaAs surface was found to change to a 4x1, then a 1x1 and finally to a 1x2 reconstruction with increasing hydrogen atom exposure⁴⁰. This is illustrated in Figure 1.13. Thus, the (100) surface returns to a dimerised structure, where two dangling bonds between neighbouring surface arsenic or gallium atoms form a σ bond, with hydrogens attached via the other two surface bonds.

Once the surface bonds are completely saturated, further exposure leads to bond cleavage between the substrate atoms and to the formation of volatile products. For GaAs (100), the HREELS data of Schaefer *et al.*⁴⁰ shows that the intensity of the As-H vibration signal increases strongly with increasing hydrogen

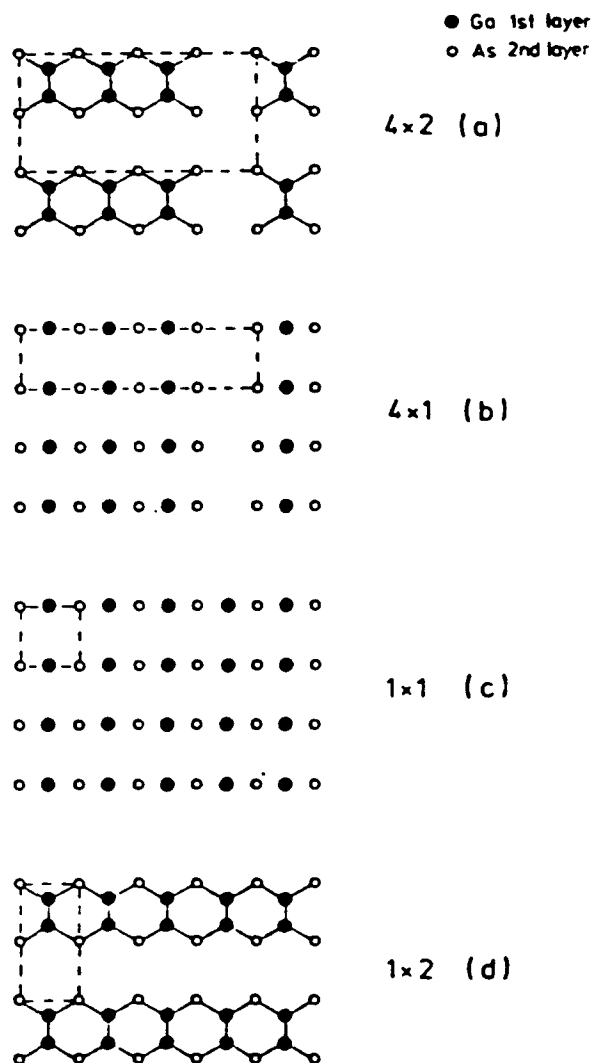


Figure 1.13 Models of surface reconstruction from LEED patterns on GaAs (100) caused by increasing exposure to atomic hydrogen. (a) Unexposed c(8x2) and exposed to (b) 10^2 (c) 10^3 and (d) 10^4 L H_2 . (1L = 10^{-6} Torr s; dissociation occurs on a hot tungsten foil) (from Schaefer *et al.*⁴⁰).

atom exposure and then attenuates rapidly, whereas the Ga-H signal intensity always increases. This suggests that arsenic hydrides are readily formed and desorb from the surface even at low hydrogen doses. This seems quite probable considering the TPD results of Mokwa *et al.*⁴¹. After high hydrogen exposures, they observed an arsine desorption peak (plus AsH₂ and AsH) for surface temperatures of 250 K to 450 K. The increase in the Ga-H stretching frequency and the observation of a new line in the HREELS spectra are interpreted as being due to the formation of a gallium dihydride species⁴⁰. (This is supported by the observation of a LEED 1x1 surface reconstruction, where Ga-H and Ga-H₂ species are possible). Further hydrogenation causes a reduction of the dihydride signals and the concomitant desorption of molecular hydrogen. This implies that an interaction between the gallium hydrides and/or adsorbed hydrogen is occurring, but this does not appear to etch the unheated surface. It is also possible that some gallium trihydride forms and could lead to etching at higher temperatures. However, no one has yet directly detected any gas phase hydrogenated gallium species, but such species should exist since continuous etches of GaAs have been observed. In the TPD experiments⁴¹, no gallium was detected until the surface temperature was above 680 K, at which point both arsine and molecular hydrogen had already desorbed. In a more recent TPD study, Creighton⁴² detected no gallium hydrides from (100) GaAs surfaces exposed to hydrogen atoms, and attributed this to surface hydride decomposition resulting in molecular hydrogen formation. The presence of a gallium rich layer is also supported by photoemission yield spectroscopy, UPS, and AES data³⁹.

InP is more extreme than GaAs in its response to hydrogenation *i.e.* the evidence for a layer of indium on the surface following phosphorus depletion, presumably as phosphine, is substantial. Similar to GaAs, no metal-hydrides have been detected, although the formation of In droplets in the etching of InP and the

cessation of etching upon complete surface coverage with indium imply that stable or volatile hydrides of indium do not form under these conditions.

In higher pressure etching situations, further evidence for the formation of a group V hydride with exposure to reactive hydrogen has been reported by Schmid *et al.*²⁶. In the reactive ion etching of InP with CH₄/H₂ mixtures, they could readily detect PH₄⁺ ($m/z = 35$). A similar result was obtained by Hayes *et al.*²⁵, who determined phosphine to be the primary volatile phosphorus containing species in CH₄/H₂ plasma etching of InP. Other evidence of hydride formation, which is also related to the RIE process is given by Chuang and Coburn⁴³. When an unheated GaAs (100) sample was simultaneously exposed to fluxes of hydrogen atoms and argon ions at 2 keV, several AsH_x⁺ peaks attributable to arsine desorption were observed. No gallium peaks were detected. No AsH_x⁺ peaks were observed when the sample was exposed to a flux of hydrogen atoms alone. However, this may be due to the arsenic deficiency on the surface caused by prior bombardment with 2 keV argon ions for 1 hr. These results imply that the rate limiting steps for the etching of GaAs and InP are the removal of gallium and indium, respectively, while the formation of volatile arsenic and phosphorus hydrides is facile.

1.4.4 Methyl radicals as possible etchants of III-V semiconductors

Early reports on hydrogen plasma etching of III-V semiconductors led to the work of Niggebrugge *et al.*²¹ who found that continuous etching of InP could be achieved in a hydrogen plasma containing approximately 10% methane. This process has since been shown to etch several III-V materials and even II-VI compounds⁴⁴. The success of this process is attributed to the reaction of methyl radicals with the "metallic" components of these semiconductors, leading to the formation of volatile organometallic products.

However, methane plasmas are complex, and may contain over 200 different neutral and charged species⁴⁵. The review by Drabner *et al.*⁴⁶ lists 125 positive ions and their relative abundances in five different methane plasmas. The major positive ions for one of these plasmas (electron energy = 100 eV, 0.165 Torr) are listed in Table 1.3. Since carbon-hydrogen bond dissociation energies are of the order of 4-5 eV, whereas ion bombardment energies in a reactive ion etcher may reach 800 eV, most alkyl ions striking the surface will be dissociated into atomic fragments. Thus, ion bombardment in these plasmas will effectively be by carbon and hydrogen. Negative ions constitute only a very small percentage of the CH₄ plasma – approximately 10⁻⁴%.

In a typical radio-frequency plasma used for semiconductor processing (13.56 MHz, 0.1 Torr), the concentration of neutral particles may exceed that of the ions by about 4–6 orders of magnitude⁴⁷. They are formed by the electron impact dissociation of CH₄, by ion/molecule reactions, by neutralisation of ions on the walls of the ion source, and also by dissociative recombination of positive ions and electrons. Methyl radicals and hydrogen atoms are the most abundant species in a methane plasma⁴⁸, although in a hydrogen/methane plasma, the concentration of hydrogen atoms would be expected to be significantly larger.

Methane-containing plasmas are also widely used for the deposition of amorphous carbon and diamond-like films, and have therefore been frequently studied to determine the most likely growth precursor species. Numerous experimental⁴⁹ and modelling⁵⁰ studies suggest that the methyl radical is the dominant growth species. In the RIE process, the deposition of polymers on most surfaces also occurs. It therefore seems surprising that etching occurs at all.

It has long been known that methyl radicals can form volatile compounds with some elements. In the classic experiments by Paneth⁵¹, methyl radicals were found to remove "mirrors" of lead and antimony. Subsequent work

Table 1.3 Major ion species in a methane plasma

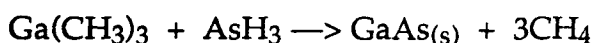
(electron energy ≈ 100 eV, pressure 0.165 Torr) (from ref. 46)

Positive Ions	Relative %
CH_5^+	43
C_2H_5^+	38
C_3H_5^+	7
C_2H_3^+	1
CH_4^+	1
CH_3^+	1

by Rice and others⁵² showed that mirrors of lithium, sodium, potassium, calcium, cadmium, mercury, lanthanum, thallium, tin, arsenic, bismuth, selenium and tellurium could also be removed by methyl radicals, although negative results were obtained for magnesium, copper, silver, gold and cerium. The reactions of the CH₂ diradical were also studied during this early period of research⁵³. Methylene was found to remove mirrors of tellurium, antimony, selenium and arsenic, but not those of zinc, cadmium, bismuth, thallium or lead, all of which are readily removed by methyl radicals.

In an attempt to achieve continuous etching of InP downstream from the plasma, Aston³⁶ produced methyl radicals by the abstraction of iodine from iodomethane with hydrogen atoms. When a flow of iodomethane, which was sufficient to remove all the hydrogen atoms from an atomic/molecular hydrogen stream, was introduced, the indium globules initially formed by a hydrogen atom etch were removed, leaving a stoichiometric surface. However, continuous etching was difficult to achieve. This suggests that methyl radicals do react with indium.

Both trimethyl gallium (b.p. 55.7 °C) and trimethyl indium (b.p. 133.8 °C) are well known compounds, and are used as precursors for the growth of GaAs and InP. For example, trimethyl gallium and arsine at 500 °C form GaAs on GaAs surfaces,



Consequently, methyl radicals and hydrogen atoms are believed to be the major etching species in methane-based etching plasmas – essentially the reverse of the deposition process. However, because of the complexity of the plasma environment, there is as yet no definite experimental evidence to support this belief. The strongest evidence stems from non-plasma assisted work carried out by Spencer *et al.*⁵⁴ (published during the course of this thesis) where several compound semiconductors were successfully etched in the products of the reaction

of F atoms with a mixture of CH₄ and H₂ (a mixture of methyl radicals and hydrogen atoms).

1.5 OBJECTIVES OF PRESENT RESEARCH

As we have seen, relatively little is known about the fundamental chemical aspects of this alkane-based etching process. There are several questions that need to be addressed:

1. What are the roles of ions and neutrals in the etching process?
2. Do reactive ions such as CH₃⁺ sputter, react with or deposit on the surface without the assistance of the neutrals?
3. Do neutrals react with the ion damaged surface, the deposited material, or the sputtered material?
4. Do neutrals like H and CH₃ react more rapidly with one of the two components of the semiconductor?

In the work described in this thesis, we examine the reactions of GaAs with suspected primary neutral etchant species – hydrogen atoms (produced in a remote plasma) and methyl radicals (produced downstream from the plasma).

In alkane based RIE, the majority of hydrocarbon ions striking the surface will be dissociated into atomic fragments. Therefore, a study of the ion-surface interactions can be simplified by examining the effects of carbon ion bombardment on semiconductor surfaces. Thus we have studied the interactions of low energy carbon and hydrogen ions with GaAs and InP using angle-dependent X-ray photoelectron spectroscopy (XPS).

For alkyl ions of lower energy, one might expect a decrease in the fraction of ions dissociated by impact with the surface, and consequently, different reactions

with the semiconductors. Therefore, we also studied the interactions of 3-100 eV methyl ions with GaAs and InP surfaces.

CHAPTER 2 INTRODUCTION (II): METHODS FOR FUNDAMENTAL STUDIES

In this chapter, some background information will be given on two central techniques used in this work: X-ray photoelectron spectroscopy, and the generation and detection of gas phase atoms and radicals.

2.1 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

X-ray photoelectron spectroscopy (XPS), often called electron spectroscopy for chemical analysis (ESCA), is a widely used technique for surface analysis. It has the ability to provide the elemental composition of the near-surface region of a solid and also qualitative information on surface chemistry and interactions.

The basis of photoelectron spectroscopy is described by the Einstein equation. When an atom absorbs a photon of sufficient energy, an electron is ejected from one of the core electronic levels with a kinetic energy KE given by,

$$KE = h\nu - BE + \Phi$$

where $h\nu$ is the energy of the exciting radiation, BE is the binding energy of the emitted electron (the difference between the total energies of the initial and final states of the atom following photoemission), and Φ is the spectrometer work function. After an electron is ejected, the core hole is filled by an electron from an outer shell. Conservation of energy is maintained by the emission of either a photon, or a secondary Auger electron. These processes are illustrated in Figure 2.1. Therefore, if a material is excited by monoenergetic photons and the kinetic energy of the ejected photoelectrons analysed, the binding energies with which the electrons are bound to the atom can be obtained. Binding energies are normally referenced to the Fermi level of the spectrometer. By measuring the number of electrons ejected while scanning the kinetic energy, a photoelectron spectrum is

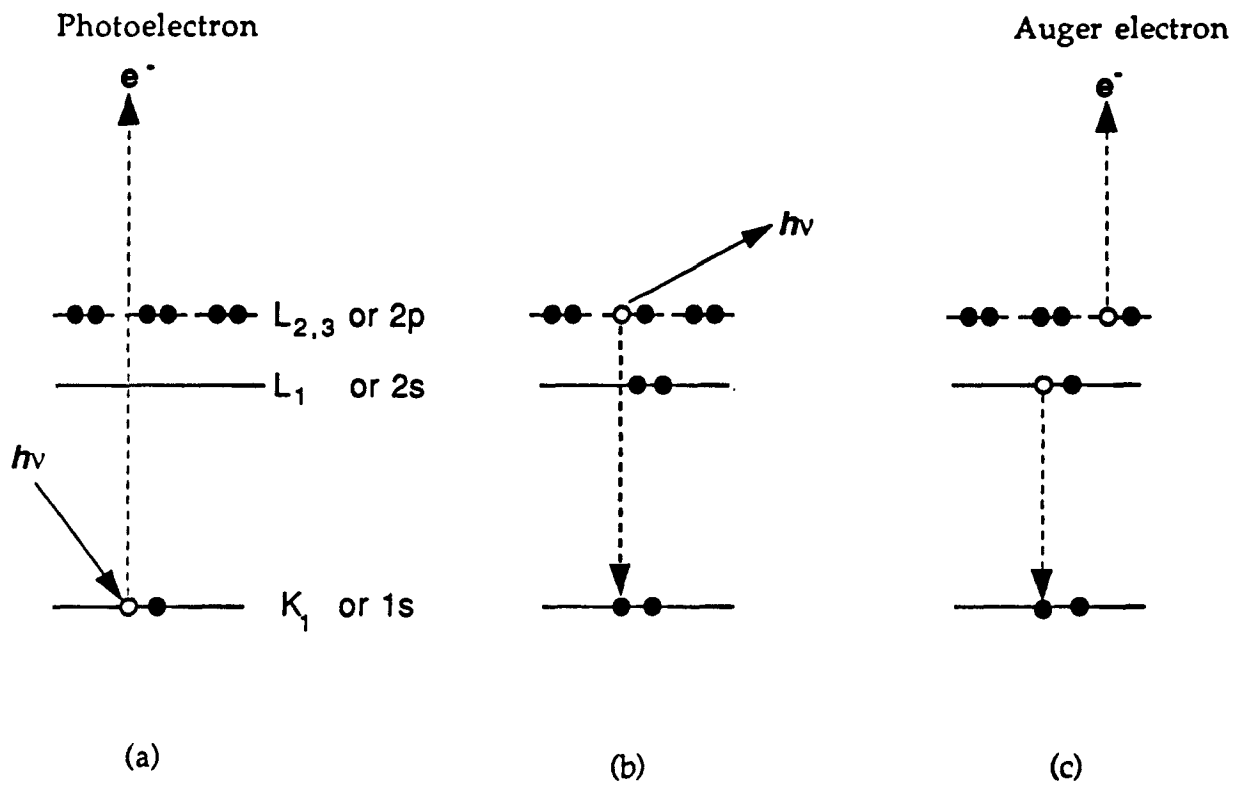


Figure 2.1 Illustration of electron transitions that can occur when a photon interacts with an atom: (a) photoemission and (b) X-ray emission or (c) Auger effect.

obtained. Since each atom has a unique electronic structure, photoelectron spectra will also be unique for each atom.

Since photoelectrons emitted by common photon sources have relatively low kinetic energies (50 to 2000 eV), they will have a high probability of undergoing an inelastic collision with a lattice atom if they travel very far before leaving the surface. Thus, only those electrons originating from the surface layer or a few atomic layers below the surface will contribute to an XPS peak. The XPS analysing depth therefore depends on the electron inelastic mean free path (IMFP, λ) of the electron in the sample. At any given detection angle, the number of electrons (I) exiting the surface without having undergone any inelastic scattering, from a depth d in the sample is given by the Beer-Lambert relationship:

$$I = I_0 \exp(-d/\lambda)$$

where I_0 is the number emitted from an infinitely thick, clean substrate. Figure 2.2 shows the experimentally obtained IMFPs (called attenuation lengths) in monolayers versus the photoelectron kinetic energy for a range of elements. Most data points lie on the so-called "universal curve" from which an empirical value of the IMFP has been obtained⁵⁵:

$$\lambda = \frac{538}{E^2} + 0.41(aE)^{0.5} \text{ monolayers}$$

where E is the electron energy in eV above the Fermi level, and a is the monolayer thickness in nanometres, defined in terms of the density, ρ , Avogadro's number, N , and the atomic weight, A , by:

$$a^3 = 10^{24}A/\rho N \text{ nm}$$

For inorganic compounds, the relationship is,

$$\lambda = \frac{2170}{E^2} + 0.72(aE)^{0.5} \text{ monolayers}$$

Other, more theoretical methods for obtaining the IMFP have been developed⁵⁶.

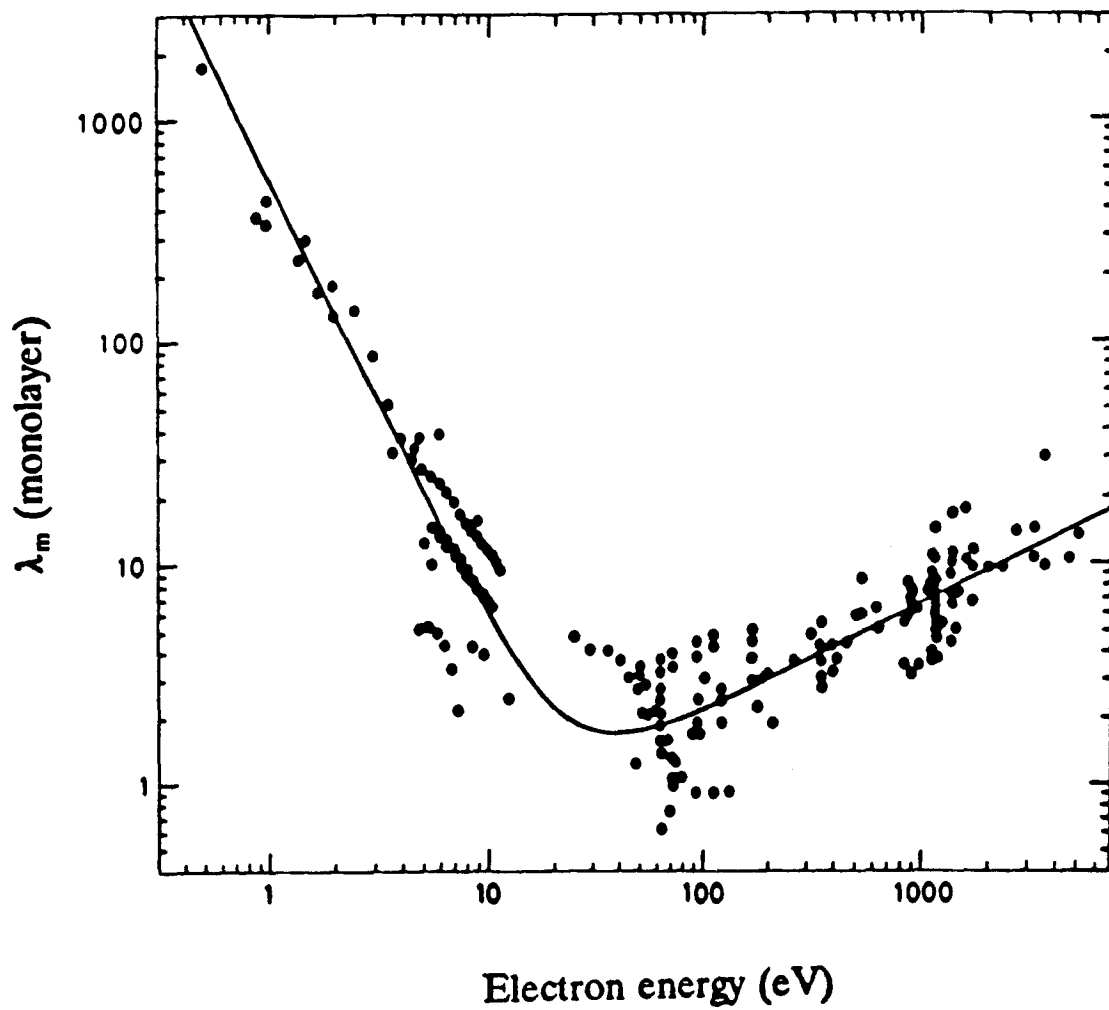


Figure 2.2 The dependence of the attenuation length, λ , on the emitted electron energy for elements (after Seah and Dench⁵⁵).

2.1.1 Instrumentation

An X-ray photoelectron spectrometer consists of an X-ray source, an electron energy analyser and detector, and a sample holder for positioning the sample, all of which are housed in an ultrahigh vacuum (UHV) chamber. Data recording and analysis are usually facilitated by an integrated computer system. A schematic⁵⁷ of the SSX-XPS used in this work is shown in Figure 2.3. UHV (pressures below 10^{-8} Torr) is a requirement for reliable surface analysis. It ensures that photoelectrons emitted from the surface do not undergo collisions with residual gas molecules present in the analysis chamber, thereby allowing the maximum spectral intensity. Such low pressures also enable the preservation of a "clean" surface and thus prevent unwanted reactions from interfering with the analysis at hand.

The kinetic energy of the photoelectrons depends on the energy of the incident radiation. Therefore a monochromatic X-ray source is necessary for high resolution in an XPS spectrum. Most commercial spectrometers use the characteristic $K\alpha$ X-ray lines of aluminium or magnesium, which are generated by bombarding the metal anodes with 10-15 keV electrons. These metals are widely used because they emit X-rays with sufficient energy to access core levels and also have low bremsstrahlung backgrounds. The magnesium and aluminium $K\alpha_{1,2}$ lines at 1253.6 eV and 1486.6 eV, respectively, are unresolved doublets with linewidths of 0.70 and 0.85 eV. By using a monochromator and removing the bremsstrahlung, the source linewidth can be narrowed considerably. However, this has the disadvantage of reducing the photon flux and making analysis more time consuming. Other radiation sources are also used in photoelectron spectroscopy. When photons from low energy ultra-violet sources, such as helium discharge lamps are used, only electrons from valence shells are removed. This approach is called ultraviolet photoelectron spectroscopy (UPS). Nowadays, the availability of

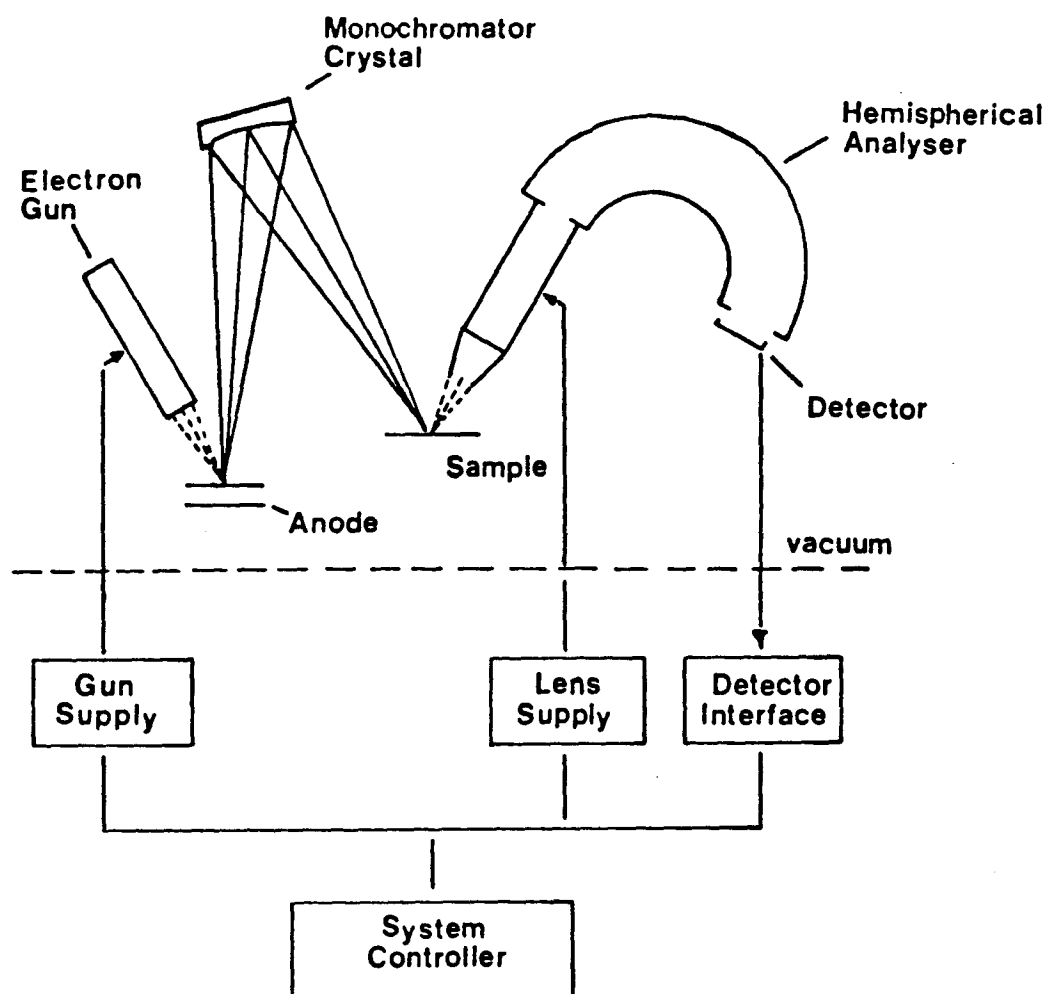


Figure 2.3 Schematic of the SSX-100 X-ray photoelectron spectrometer used in this work (from Wagner and Joshi⁵⁷).

tunable synchrotron radiation sources allows electrons to be removed from levels ranging from valence shells up to 1s core levels, and effectively bridges the gap between UPS and XPS.

Electron energy analysers are generally of two types: the cylindrical mirror analyser or the concentric hemispherical analyser. Both operate by electrostatic dispersion, although the latter is used predominantly in XPS instruments because of its higher inherent resolution. Two hemispherical sectors are placed concentrically, and a negative potential (relative to that applied on the inner sphere) is applied to the outer sector. Thus for a given potential difference between the two cylinders, only electrons with a very narrow velocity range (or "pass" energy $E + \Delta E$) will follow a trajectory that takes them from the entrance slit through the analyser and out of the exit aperture to the detector. By changing the potential across the analyser and recording the electron detection rate, an energy spectrum of intensity versus electron kinetic energy can be obtained. However, analysis is normally performed in the constant analyser energy mode. Here, the electrons are electrostatically retarded by a lens or grid before entering the analyser. Only those electrons with energies that match the preset analyser pass energy can be transmitted and detected. A spectrum is obtained by ramping the retarding field potential and plotting electron energy versus electron counts. The advantages of this approach are the increased resolution of the analyser⁵⁸ and constant resolution for all lines in the spectrum⁵⁹.

An electron multiplier or a channel plate multiplier is often used to count the photoelectrons passing the energy analyser. A channel plate multiplier also detects the arrival position of the electrons at the exit slit (corresponding to their kinetic energy). Usually, the signal-to-noise ratio is improved by the use of a multi-channel analyser or a computer, which allow multiple scans to be made.

2.1.2 Spectral interpretation

2.1.2.1 Spectra

Figure 2.4 is an XPS "survey" or "broad scan" spectrum of a clean (100) GaAs sample, with a higher resolution spectrum of the As 3d line superimposed. The incident photons were Al K α X-rays and the pass energy of the analyser for the survey spectrum was 150 eV. Since each atom has a unique electronic structure, its photoelectron spectrum will also be distinct. Therefore, XPS can identify the chemical constitution of a surface. The spectrum includes several peaks superimposed on a background that increases with binding energy. The peaks are labelled on the spectrum, indicating the core level from which the photoelectron originated. The peaks have variable intensities and several core levels are split into doublets. The arsenic and gallium LMM Auger lines are also present in the spectrum. The general increase of the background signal is due to primary and secondary electrons that have undergone inelastic collisions. One important electronic energy loss process is the inelastic interaction of the photoelectron with the valence electron cloud of the solid. This process is called plasmon loss and usually results in the formation of small, broad peaks on the high binding energy side of the core level peaks.

Other peaks may occur in an XPS spectrum. For example, "shake-up satellites" are caused by the simultaneous excitation of a valence electron to a higher, unoccupied orbital as a result of the initial photoionisation process. This reduces the energy of the photoemitted electron and it therefore appears at a higher binding energy than the primary line. "Ghosts" and X-ray satellites caused by multi-band emission from a non-monochromatised X-ray source may also appear.

The full width of a peak at half maximum, ΔE is a convolution of contributions from the inherent width of the core level ΔE_n , the width of the X-ray source ΔE_p , and the analyser resolution ΔE_a :
$$\Delta E = (\Delta E_n^2 + \Delta E_p^2 + \Delta E_a^2)^{1/2}$$

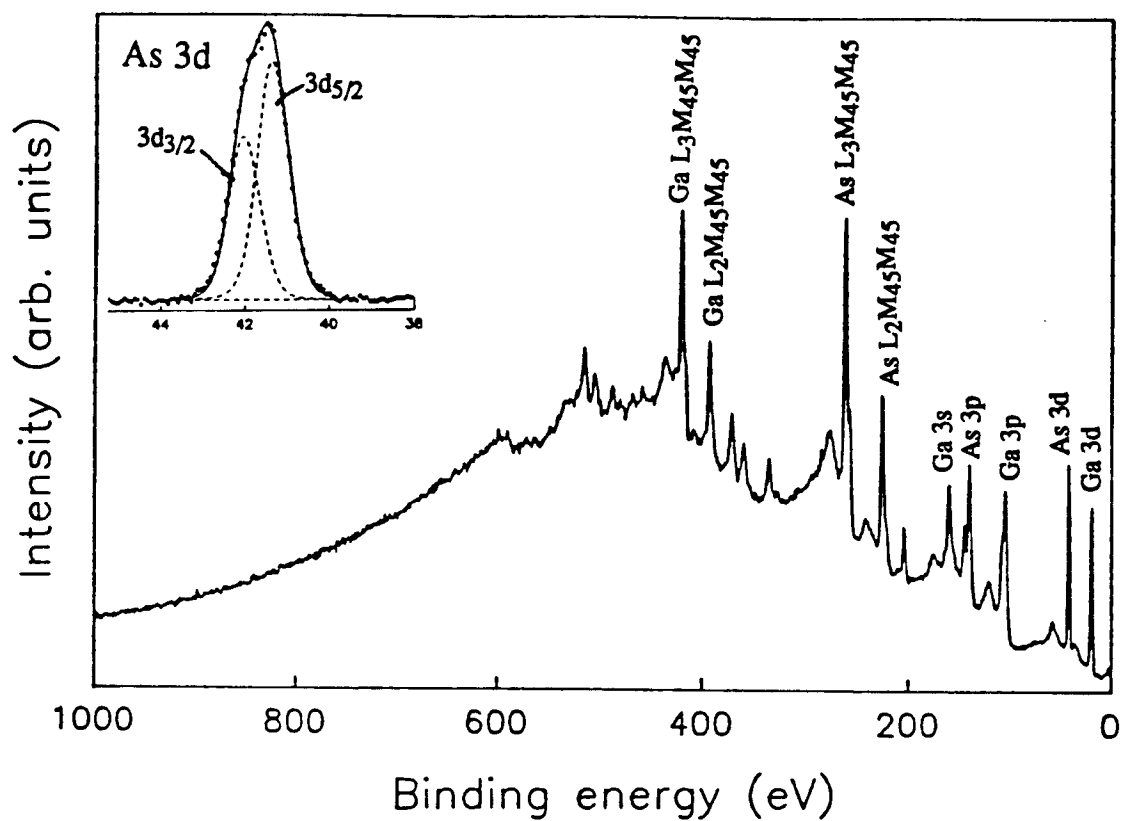


Figure 2.4 XPS survey spectrum of a clean GaAs surface, with higher resolution spectrum of As 3d peak inset.

2.1.2.2 Chemical shifts

The ability to measure shifts in the binding energy of core electrons resulting from a change in the chemical environment is one of the most important capabilities of XPS. Such changes in binding energy, termed chemical shifts, can result from a change in the oxidation state of atoms in a material, formation of new bonds, or even from modification of the crystal structure. Hence the acronym ESCA, meaning electron spectroscopy for chemical analysis, commonly used when referring to XPS.

Chemical shifts are caused by changes in the electron density of the valence shell of an atom. The valence shell electrons exert a repulsive force on the core electrons that effectively screens these electrons from the nuclear charge, reducing the nuclear attractive force. The addition of electron density into the valence shell increases the screening effect and therefore reduces the binding energy of the core electrons. The reverse is true if electron density is removed from the valence shell. As an example of chemical environment causing a core level shift, Figure 2.5 shows the As 3d peak of a GaAs sample which has been exposed to ozone for 15 minutes. The As 3d peak now occurs at 3 other higher binding energy positions (compare with Figure 2.4). This is a result of arsenic being bonded to 1, 2 and 3 oxygen atoms instead of gallium.

For some elements, identification of its chemical state is difficult because the chemical shifts are small, thus resulting in broad peaks. Such spectral envelopes may be deconvoluted with peak fitting software, but these are approximations and require chemical "intuition" and experience from the operator. They should be used judiciously. For example, the As 3d spectrum shown in Figure 2.5 has been fitted to show the presence of the different oxidation states of arsenic. The binding energies and peak widths have been obtained from extensive research⁶⁰. Ideally, reference spectra for the element in each chemical state should be used.

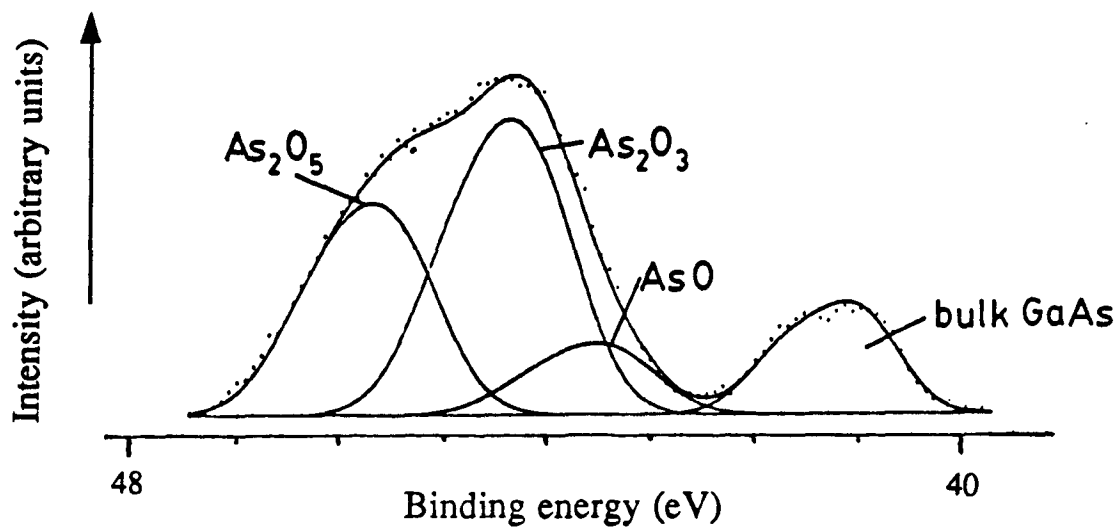


Figure 2.5 High resolution XPS spectrum of As 3d peak for a GaAs sample exposed to ultraviolet light/ozone for 15 minutes.

It is often essential to be able to measure binding energies to ± 0.1 eV for proper interpretation of spectra. XPS measured binding energies from a calibrated instrument are usually referenced to the Au 4f_{7/2} peak at 83.93 eV.

2.1.2.3 Peak intensity

The probability of a photoelectron being ejected by the absorption of an incident X-ray photon will determine the relative intensity of a core level peak. This probability is called the photoionisation cross section, σ , and is required to calculate the concentrations of chemical species in the near-surface region of a sample. The cross sections for the core levels of the elements have been calculated by Scofield⁶¹.

2.1.2.4 Multiplet splitting

When photoionisation occurs in an atom with one or more unpaired electrons in the valence shell, spin-orbit coupling between the two orbitals with unpaired electrons causes a splitting in the energy levels of the core level. For example, as already shown, in the high resolution spectrum of a clean GaAs surface (Figure 2.4) the components of the As 3d peak is split into a doublet with an energy separation of 0.68 eV. The peaks shown in Figure 2.5 are also composed of the 3d doublets, but have been combined for clarity. The extent of multiplet splitting depends on the core level being accessed, and is greatest when the unpaired electrons are in orbitals of the same principal quantum number. The area ratio of the two peaks in a doublet is given by $(l+1)/l$ where l is the orbital angular momentum quantum number.

2.1.3 Quantitative analysis:

2.1.3.1 Composition

The penetration depth of an X-ray photon is much larger than the inelastic mean free path (IMFP) of a photoelectron. Therefore the sampling depth in XPS is dependent on the IMFP of the photoelectron and the sine of the angle that the detector makes with the surface: escape depth = $\lambda \sin \theta$. The atomic composition in the volume contained within the sampling depth and the area illuminated by the X-ray spot can be calculated from the relative peak intensities. For a homogeneous material, the concentration (c) of an atomic species is related to the measured intensity (I) of a specific peak by the following relation:

$$I = c J \sigma D T \lambda$$

where J is the X-ray flux, σ is the photoelectric cross section for the orbital of interest, D is an angular efficiency factor depending on the angle between the paths of the X-rays and detected electrons, T is the analyser detection efficiency, and λ is the photoelectron inelastic mean free path. Data for many of these parameters is unavailable, so instead they are incorporated into a set of sensitivity factors specific to a particular instrument.

$$S = \sigma D T \lambda$$

If the X-ray flux remains constant, the atomic percentage of an element i can be obtained by dividing the intensity (normally the peak area, with a linear or non-linear (Shirley) background subtraction) by the sensitivity factor and expressing it as a fraction of the summation of all normalised intensities:

$$C_i \text{ (atomic \%)} = \frac{c_i}{\sum_k c_k} = \frac{I_i/S_i}{\sum_k I_k/S_k} \times 100\%$$

Accuracies to within 10-20% are possible with this semiquantitative approach, provided the sample is homogeneous over the sampling volume, surface

roughness is minimal and contributions from contamination layers are insignificant.

Software supplied with the spectrometer enable composition tables to be automatically calculated by measuring the relative peak areas of the constituent elements.

2.1.3.2 Depth analysis (angle-dependent)

If a photoelectron is emitted at a depth x below the surface and in a direction that makes an angle θ with the surface plane, the distance it must travel before it can exit the sample is given by $x/\sin\theta$. As θ gets smaller, the path length increases and consequently, only electrons generated closer to the surface will escape without any inelastic scattering, *i.e.* the probability of escape will decrease as $e^{(-x/\sin\theta)}$. Thus, tilting the sample to reduce the "take-off" angle between the surface plane and the electron analyser will increase the intensity of the signal arising from electrons that have escaped from the uppermost layers of the sample. This is illustrated in Figure 2.6 which shows how a reduction of the take-off angle increases the detected signal from a thin (1.0 nm) overlayer, while the signal from the underlying substrate is correspondingly diminished. That is, surface sensitivity is enhanced as the take-off angle decreases. This extremely useful feature of XPS allows composition depth profiles to be calculated from angle-dependent spectra. Consider the simple example of a thin overlayer of uniform composition on an "infinitely" thick substrate. The thickness of the overlayer can be obtained from the ratio of the intensities of the overlayer (o) and substrate (s) peaks:

The peak intensity from an element i from a layer (o) of thickness d is given by,

$$I_o^i = c_o^i S_i (1 - e^{-d/\lambda_i \sin\theta}) J$$

where S_i is the instrument sensitivity factor for the element i , and J is the X-ray

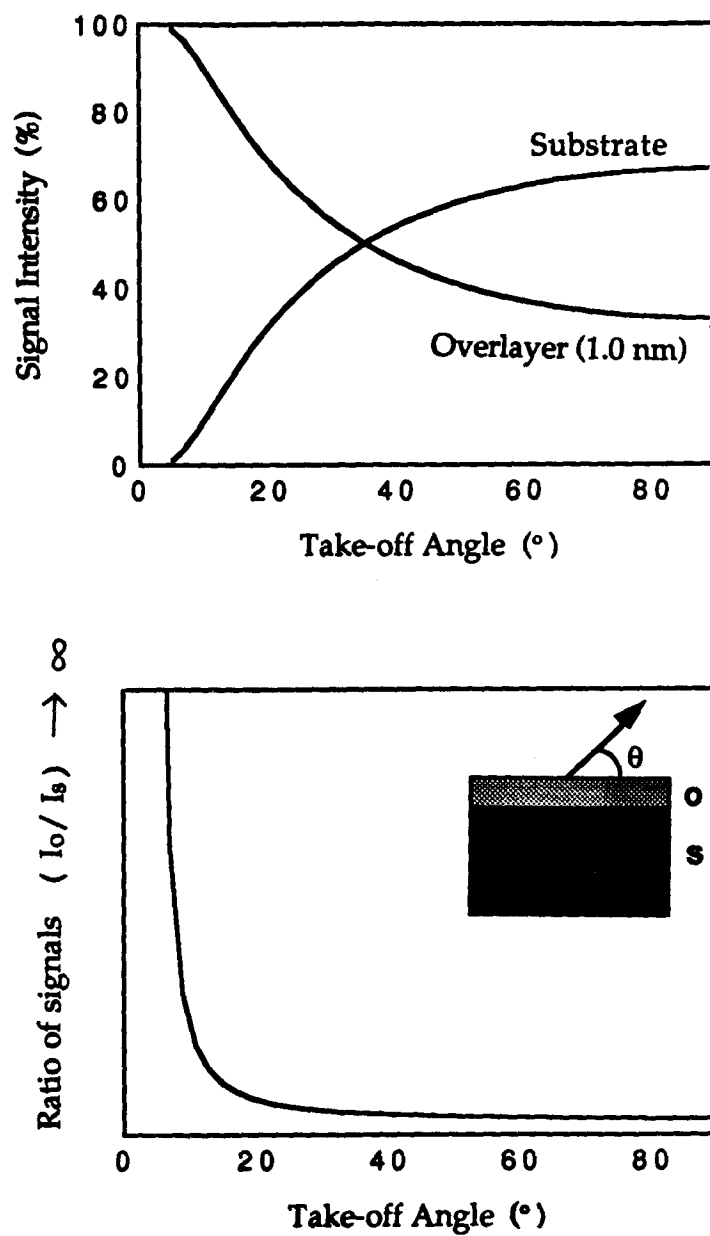


Figure 2.6 Plots showing variation of the XPS signal intensity as a function of the photoelectron take-off angle, for a 1 nm overlayer on an infinitely thick substrate.

photon flux, as described above. The peak intensity from an element k in the substrate is,

$$I_s^k = c_s^k S_k e^{-d/\lambda_k \sin\theta}$$

The ratio of the overlayer to substrate peaks is then,

$$\frac{I_o^i}{I_s^k} = \left[\frac{c_o^i S_i}{c_s^k S_k} \right] \{ e^{d/\lambda_k \sin\theta} - e^{(-d/\lambda_i \sin\theta + d/\lambda_k \sin\theta)} \}$$

This expression can be simplified by assuming that the inelastic mean free paths for the overlayer and substrate photoelectrons are the same, *i.e.* independent of both kinetic energy and matrix effects. In most cases, this is a gross approximation, but for photoelectrons with similar kinetic energies and materials with similar average-atom sizes, it does not increase the error significantly. Taking natural logarithms gives,

$$d = \lambda \sin\theta \ln \left[\frac{I_o^i c_s^k S_k}{I_s^k c_o^i S_i} + 1 \right]$$

or more simply,

$$d = \lambda \sin\theta \ln \left[\frac{C_i}{C_k} + 1 \right]$$

where C_i and C_k are the normalised atomic concentrations obtained as above.

Flat surfaces are a necessity for the enhancement of surface sensitivity, as surface roughness leads to an averaging of electron take-off angles and also to shadowing effects. Also, the finite size of the detector entrance slit means that electrons are collected with a range of take-off angles. The signal measured will therefore be a weighted sum of the number of electrons leaving the surface across this range of take-off angles. Thus, depth composition profiles and overlayer thickness calculations obtained from "conventional" instruments and using the

simple relations described above are, at best, rough approximations. Greater accuracy can be achieved by reducing the acceptance angle of the detector and by accounting for the angular variation⁶². More detailed treatments of depth composition profiling can be found elsewhere⁶³.

The "escape depth" (ED) is a term commonly used to describe the sampling range in an XPS experiment. This is defined as the distance from the surface at which the probability of an electron escaping without significant energy loss due to inelastic scattering is $1/e$ of its original value. Since the ED is a function of the inelastic mean free path of the photoelectron in the medium and the angle of detection, then,

$$ED = \lambda \sin\theta.$$

Another term used to describe the sampling range is the "information depth". This is the distance below the surface over which a specific percentage of the detected electrons are generated. For example 63.2% of the detected electrons from a homogeneous material are generated from within a distance equal to the escape depth from the surface and 99.3% of the electrons come from within a depth of 5 times the escape depth.

2.2 ATOM AND RADICAL PRODUCTION AND MEASUREMENT

Hydrogen atoms and methyl radicals are believed to be the major etchant species in the methane/hydrogen plasma. Part of this thesis is a study of the reactions of these neutral species with GaAs, so some background pertaining to their nature, generation and measurement will be presented.

Although the occurrence of gas phase iodine atoms, sodium atoms, and certain other elements was known before the turn of the century, the idea that free

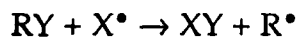
atoms were involved in a number of chemical reactions arose in photochemistry. In 1918, Nernst⁶⁴ proposed that the absorption of a photon by a chlorine molecule could explain the very large quantum yield in the photochemical synthesis of hydrogen chloride from hydrogen and chlorine. Many other examples of such chain reactions involving atoms quickly became evident. In 1920, Wood⁶⁵ showed that hydrogen atoms produced in a discharge tube (later known as the Wood's tube) could be pumped out of the discharge in large quantities and carried along for some distance before recombination was complete. Four years later, Bonhoeffer²⁸ adapted Wood's method to investigate several reactions of hydrogen atoms. In 1925, Taylor⁶⁶ suggested that atoms could convert organic molecules into free radicals, which could also lead to chain reactions.

In 1929 Paneth⁵¹ demonstrated how methyl radicals could be detected and that they could exist for several milliseconds, albeit at low pressure. In this classic work, methyl radicals were formed by the thermal decomposition of tetramethyl lead, resulting in the deposition of a lead "mirror" on the walls of the reaction tube. These radicals were then carried downstream in a fast stream of hydrogen, where they removed previously deposited antimony, lead or zinc mirrors. This method of detection was subsequently employed to detect free radicals produced in the thermal decomposition of many organic compounds⁵².

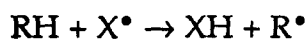
Thus, the field of gas-phase atom and radical chemistry was born. There has since been a vast body of published work characterising the reactions of these "odd-electron" species. A large portion of this work has been devoted to the reactions of two elementary species - hydrogen atoms and methyl radicals, and comprehensive reviews have been published on the reaction kinetics of both^{67,68}.

These species generally exhibit three types of elementary gas phase bimolecular reactions:

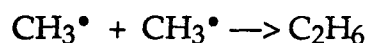
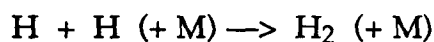
(1) a metathesis (or abstraction) reaction of an atom or radical with a molecule to form a molecule and another radical, *viz.*,



or more commonly, when Y is a hydrogen atom,

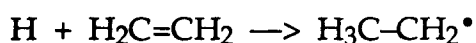


(2) The recombination of two atoms or radicals to form a stable molecule, e.g.,



The recombination of two atoms to form a stable molecule requires a simultaneous collision by a third body M to remove part of the bond energy, as there are no internal degrees of freedom to extend the lifetime of a colliding pair beyond approximately 10^{-13} seconds after collision. Termolecular reactions are not very probable at low pressures, and for hydrogen atoms, the third body normally takes the form of the vessel wall. As the pressure is increased, the stabilisation of the collision complex by molecular hydrogen becomes more important. Wall losses can be greatly reduced by treatment with several acids and other materials. Thus, under the right conditions (walls poisoned with acids) hydrogen atoms can have a long lifetime. However, this is not the case for methyl radicals, which normally recombine in a bimolecular collision at pressures above about 1 Torr; the additional degrees of freedom in the collision complex give it a much longer lifetime, during which a stabilising collision with a third body can occur.

(3) Additions to unsaturated compounds, particularly unsaturated organic molecules, *e.g.*



which normally does not require a third body at pressures near and above 1 Torr, and produces a new free radical.

2.2.1 Generation of atoms and radicals

2.2.1.1 Hydrogen atom production

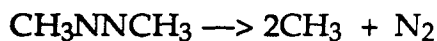
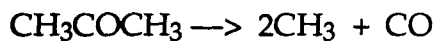
Many methods of producing hydrogen atoms are available. Among these are thermal decomposition, electrical discharges (including electrodeless, high-frequency discharges), mercury-photosensitised decomposition of molecular hydrogen and hydrocarbons⁶⁹, direct photolysis⁷⁰, radiolysis of paraffins⁷¹, certain flame reactions⁷², and shock tubes⁷³. However, not all of these are suited for the production of a pure, constant flux of atoms.

The earliest experiments used hot tungsten filaments⁷⁴, and this approach is still in common use today⁴⁰, along with high temperature ovens to "crack" molecular species. The most convenient method is the use of "discharge tubes" (Wood's tubes), where a low pressure flow of molecular hydrogen passes over metallic electrodes held at relatively high voltages. However, contamination from the electrodes is a major limitation. This problem has been eliminated by the use of electrodeless radiofrequency and microwave discharges, which can cause up to 90% dissociation of molecular hydrogen. With efficient poisoning, 20-50% yields of hydrogen atoms can be obtained from a microwave plasma⁷⁵. Therefore, a microwave discharge was used as the source of hydrogen atoms in this work.

2.2.1.2 Methyl radical production

There are several alternatives for the generation of methyl radicals⁷⁶. As previously mentioned, methyl radicals were first studied by Paneth⁵¹, who used the thermal instability of tetramethyl lead to generate them. Subsequent work showed that methyl radicals are produced by thermal decomposition of the methyl

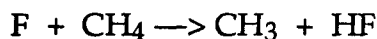
derivatives of many metals⁵². Thermal decomposition of acetone and azomethane can also yield these radicals⁷⁶,



Although methyl radicals are present in the plasmas of many organic materials, this method of preparation is quite unsuitable because of the complications that arise from the large number of neutral and charged species that are also present.

The photolysis of the halomethanes, CH_3X , where $\text{X} = \text{Cl}, \text{Br}$ or I has been a widely used source of methyl radicals. Iodomethane has strong absorption band centred at 194 nm, where C-I bond fission occurs with unit efficiency⁷⁷. Cleaner sources are achieved by the photodissociation of acetone, azomethane and nitromethane, which also occur with high efficiency in the UV.

Finally, chemical reactions are an important source of alkyl radicals. Methyl radicals can be formed by the abstraction of hydrogen from methane, or by the abstraction of a halogen from a halomethane. For example, the reaction of fluorine atoms with methane,



has a rate constant of $5 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at room temperature, which is close to collision frequency. The bond strength of the resultant HF molecule renders it essentially "inert" to further reactions. This reaction was used by Spencer *et al.*⁵⁴ to generate H atoms from H_2 and CH_3 radicals from CH_4 for the etching of III-V semiconductors. However, the main drawback with this reaction is the difficulty in determining the concentrations of fluorine atoms and consequently, the methyl flux on the sample cannot be calculated. This problem can be circumvented by using hydrogen atoms whose absolute concentrations can readily be measured. The reaction with iodomethane to form HI and CH_3 is fast ($k = 5.8 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, 25 °C), although subsequent reactions of hydrogen atoms with HI are also rapid.

Hydrogen atoms also react with methane to form H_2 and CH_3 . This reaction is relatively slow so that complete removal of the hydrogen atoms is possible only at elevated temperatures.

Three methods of methyl radical production were employed in this work for the etching of GaAs.

- (1) The photolysis of acetone was potentially the cleanest source of methyl radicals but this approach was unsuccessful.
- (2) The reaction of hydrogen atoms with iodomethane was found to work, but was complicated by the presence of iodine atoms.
- (3) The reaction of hydrogen atoms with methane was effective although complex.

2.2.2 Measuring the absolute concentrations of atoms and radicals

There are a number of techniques that have been used to detect atoms and radicals. These methods rely on both chemical and physical properties.

2.2.2.1 Detection of hydrogen atoms

One of the simplest methods developed for estimating the concentration of hydrogen atoms in a gas containing only H and H_2 was designed by Wrede⁷⁸ and Harteck⁷⁹. A bulb is attached to the main flow system by a capillary or narrow slit, with the size of the opening being less than the mean free path of the gas (approximately 0.1 mm for hydrogen at 1 Torr). Atoms and molecules diffuse into the capillary, but H atoms recombine on the walls or on a catalyst, so that only molecules are present in the bulb. Measurement of the small pressure difference across the orifice enables the volume percent of atoms in the flow system to be calculated.

Hydrogen atom concentrations have been determined by measuring their absorption of the Lyman α line (121.578 nm) emitted from a hydrogen discharge

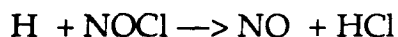
lamp, or by measuring the resonance fluorescence of the excited hydrogen ($2P$) produced by this Lyman α radiation^{80,81}.

Electron spin resonance is a sensitive technique for the measurement of atoms and radicals. The spectrum for the hydrogen atom consists of a widely spaced doublet and has often been used to obtain absolute concentrations of this species^{82,83}.

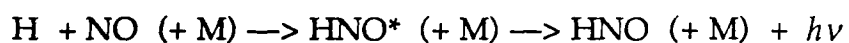
Hydrogen atom concentrations can also be determined by mass spectrometry. In this method, the ions pass through a pinhole into the ionising chamber of the spectrometer⁸⁴. The problem with this technique is the large peak at the atom mass that comes from the parent molecule. Time-of-flight mass spectrometry has also been used for H atom detection⁸⁵.

In 1924, Bonhoeffer²⁸ used thermometer bulbs coated with metals to catalyse the recombination of hydrogen atoms and measured the temperature rise. Since then, calorimetric methods have been widely used for the detection and estimation of atoms^{86,87}. Hydrogen atoms are particularly well suited to quantification by this technique, since they recombine very efficiently on metal surfaces and the temperature rise can be directly related to the number of atoms recombining on the surface. Further discussion of the calorimetric technique will be given in the next chapter.

A chemical technique for H atom detection involves measuring the chemiluminescence from excited HNO^* (500-800 nm) generated by the reaction of hydrogen atoms with NO, NO_2 or NOCl ^{88,89}. With NOCl , the initial step is believed to be,



followed by,



When the concentration of NOCl is equal to that of the H atoms, the HNO* emission is extinguished, yielding the concentration of H atoms.

There are several other methods for H atom detection, but these are generally non-quantitative. For example, molybdenum oxide films change colour from pale yellow to blue when exposed to H atoms⁹⁰, and the removal of mirrors, *e.g.* arsenic and antimony was once a popular technique⁵².

In this work, we use the simple but effective method of isothermal calorimetry to detect the hydrogen atoms produced in a remote microwave discharge.

2.2.2.3 Detection of methyl radicals

The earliest use of a "detector" for methyl radicals also stems from the pioneering work of Paneth, *ie.* the removal of metallic mirrors. A large volume of the early research was performed using this method⁹¹. It is, however, not very quantitative. A few of the techniques already mentioned for the detection of atomic hydrogen also apply to the detection of methyl radicals, particularly time-of-flight mass spectrometry, electron spin resonance, and spectroscopic methods. Most of the recent determinations of this species have been spectroscopic. These include infrared absorption⁹², flash photolysis⁹³, and most recently by resonance enhanced multiphoton ionisation spectroscopy⁹⁴. This latter technique involves collecting the photoelectrons generated by laser ionisation of gas phase species. A peak in the collected photoelectron signal occurs when the laser wavelength is 333.5 nm due to the two-photon resonant, three-photon ionisation of CH₃. Photoionisation mass spectrometry⁹⁵ has also been successfully used for kinetic studies on methyl radicals. In this process, methyl radicals are ionised with radiation from a low-pressure krypton resonance lamp, mass selected with a quadrupole mass filter, and counted with a Daly detector.

In the absence of a dedicated photoionisation mass spectrometer no reliable method was found for measuring the methyl concentration in our system. Fortunately, the reactions of H with CH_4 and CH_3I and the many subsequent reactions are well characterised. Therefore, with a knowledge of the flow system characteristics and the rate constants for the reactions of H atoms with methane and subsequent reactions, the concentrations of methyl radicals at the semiconductor surface were calculated.

3.1. LOW ENERGY ION BOMBARDMENT

3.1.1 Samples and preparation

Bombardment by ions with energies lower than about 50 eV was only expected to generate damage within the first few atomic layers of the substrate, whereas damage created by higher energies should reach greater depths. Therefore, a special InP structure was prepared to assist the analysis by angle dependent XPS. The InP samples were supplied by Bell-Northern Research and consisted of a 4 nm *p*-InP layer epitaxially grown on a 0.1 mm layer of *p*-InGaAs; the support substrate was InP. Both the InP and InGaAs layers were doped with zinc to a concentration of $5 \times 10^{17} \text{ cm}^{-3}$. This sample structure was designed because of the following three considerations. Firstly, high resolution XPS analysis of the In and P in the first layer will show the damage in this layer, while analysis of the As and Ga of the underlying layer will show if the damage has propagated through the first layer. Secondly, by obtaining the ratio of the phosphorus to arsenic signal intensities as a function of the photoelectron take-off angle, the thickness of the remaining InP layer, and thereby the sputtering yield, can be calculated. Finally, exposure to the equivalent of a few monolayers of ions should be sufficient to demonstrate the bombardment effects.

The GaAs samples were *n*-type, Bridgman grown (100), with a silicon dopant concentration of $1 \times 10^{18} \text{ cm}^{-3}$. Both the GaAs and InP wafers were cut into chips approximately 8 mm x 8 mm in size.

Prior to introduction into the low energy ion beam system, the samples were oxidized by ultraviolet light generated ozone (UV/ozone) for 20 minutes in a UVOCS Inc. reactor (Montgomeryville, Pennsylvania), followed by a 30 second HF etch and methanol rinse. This ozone treatment is known⁹⁶ to efficiently remove

hydrocarbon contamination from semiconductor surfaces and forms an oxide, approximately 1.5 nm thick. By removing the sacrificial oxide with a subsequent wet etch, clean stoichiometric, oxide-free surfaces can be obtained⁹⁷. Although we found that the GaAs surfaces etched with HF were slightly arsenic rich, the UV/ozone/HF treatment was used in the present study for the preparation of a reproducible starting surface. The UV/ozone treatment was also tried as a possible carbon residue removal procedure on the samples bombarded with carbon and hydrocarbon ions.

3.1.2 Low Energy Ion Beam system

A diagram of the low energy ion beam system at the University of Western Ontario is shown in Figure 3.1 and a schematic of the beam electrode configuration given in Figure 3.2. Its design is based on the Colutron G-2 Ion Gun, with the ion source, focusing lens and mass filter supplied by the Colutron Research Corporation (Boulder, Colorado). The ion source is a hot filament DC plasma contained in a graphite or quartz chamber. Positively charged ions are extracted from the chamber through a small, approx. 1 mm diameter hole in the anode. After being focused by two einzel lenses, the extracted 3 keV beam is mass filtered using a Wien filter. A bend in the ion column in combination with electrostatic deflection plates, separates neutrals from the ion beam. Finally, the ion beam is focused and decelerated by a series of electrostatic lenses, onto the sample. Details of the design and construction of the deceleration lens can be found elsewhere⁹⁸. The ion source, the beam-extraction/focusing chamber and the Wien filter chamber are collectively pumped by a Balzers TPU-510 plasma turbomolecular pump unit backed by a Leybold D65BCS rotary pump unit. This allows for an operating pressure of 1×10^{-5} Torr with the ion source at $3-5 \times 10^{-2}$ Torr. The base pressure is 5×10^{-8} Torr. The second focusing chamber and the target chamber are

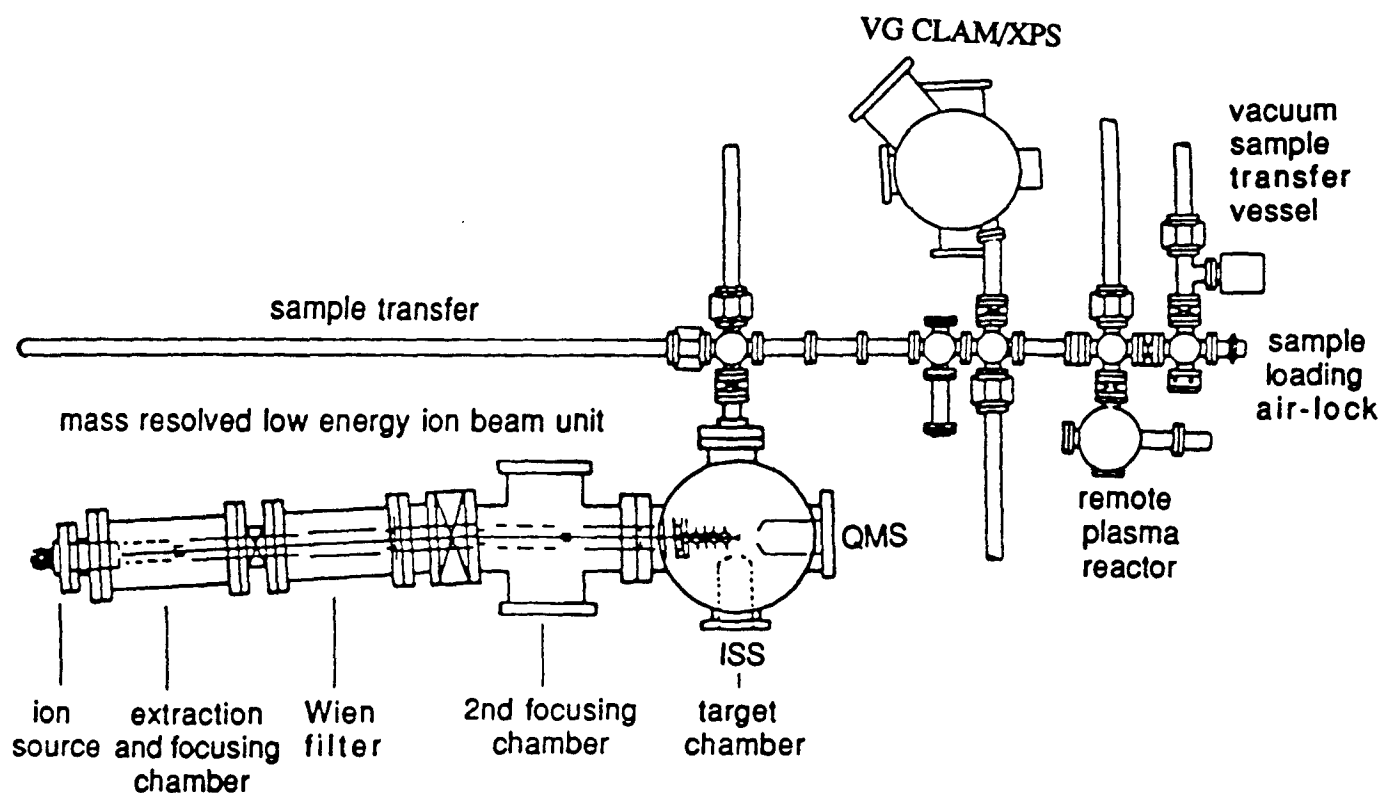


Figure 3.1 Diagram illustrating the layout of the low energy ion beam system used in this work. Samples were transferred *in vacuo* to a remote SSX-100 XPS.

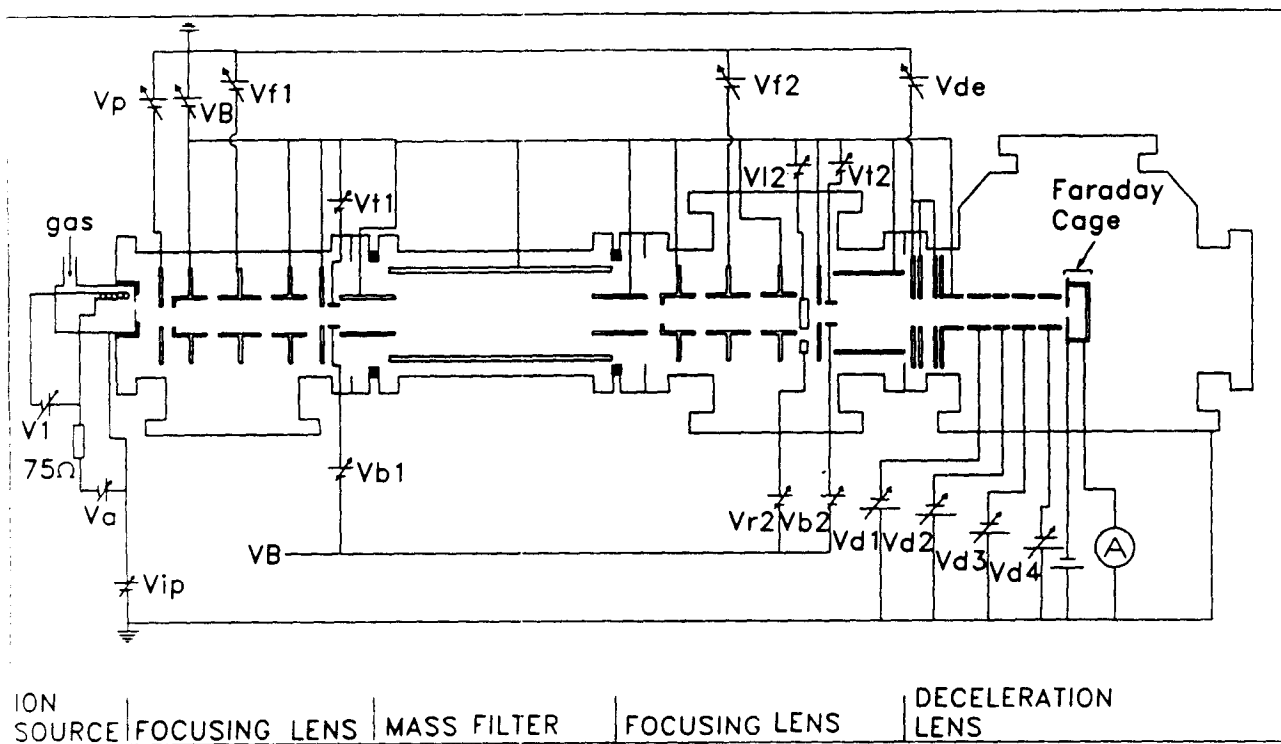


Figure 3.2 Electrode configuration in the low energy ion beam.

each pumped by CTI CRYOTORR-8 cryopumps, which enable a base pressure of 1×10^{-9} Torr to be maintained. During bombardment, the operating pressure in the target chamber increases to 5×10^{-9} Torr.

A VG SPX300 quadrupole mass spectrometer is attached to the target chamber. It is equipped with a VG CMX500 cylinder mirror energy analyser mounted along the beam axis and enables the energy and mass of the decelerated beam to be measured. A set of ion entrance electrodes is housed in front of the spectrometer for directing a portion of the ion beam into the analyser.

The sample is affixed to a holder by two spring-metal clamps and then inserted into the sample load-lock chamber. After evacuation to below 1×10^{-7} Torr, the sample is transferred via a UHV transport corridor into the target chamber by a magnetically coupled transfer rod. The sample is mounted on a movable and rotatable platform where it can also be heated. The surface temperature during the heating experiments was monitored with a calibrated pyrometer. The sample surfaces were always perpendicular to the beam axis.

Below the sample position are two Faraday cages (grounded through an external ammeter), with 1.3 and 10 mm diameter screening holes. These enable characterisation of the beam current. The larger cage allows total-current measurements to be made and the smaller one is used for beam profiling and hence determination of the optimum focusing parameters. The beam current cross section was typically of Gaussian distribution. For example, a previously measured 100 eV Ar^+ beam profile is shown in Figure 3.3

The normal set-up procedure was as follows: by adjusting the focusing voltages at all stages of the beam, the beam current in the small hole of the Faraday cup was maximised. The Faraday cup was then raised, allowing the beam to reach the entrance of the mass spectrometer. The Wien filter was switched on and the magnetic field swept to select the desired mass. The filtering was optimised with

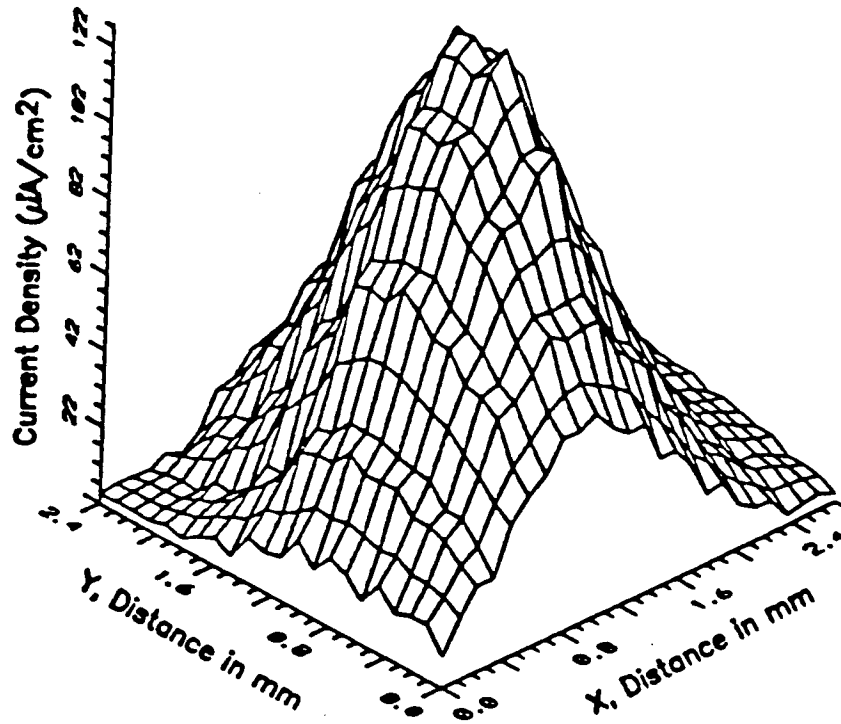


Figure 3.3 Ion density profile of a 100 eV argon ion beam.

the aid of the mass spectrometer. The Faraday cup was then lowered again, and the single species ion beam current maximised by making slight focusing adjustments. The ion flux inside the small 1.3 mm diameter hole was calculated, and the time required to achieve the required dose determined, *i.e.*,

$$\text{time (s)} = \frac{\text{dose (ions cm}^{-2}\text{)} \times 1.602 \times 10^{-19} \text{ (C ion}^{-1}\text{)}}{0.7 \times \text{max. ion flux (C s}^{-1} \text{ cm}^{-2}\text{)}}$$

For carbon ion bombardment, doses of $2\text{--}5 \times 10^{16}$ ions cm^{-2} were normally used.

The gate-valve between the target and focusing chambers was then closed and the platform lowered 31.0 mm (the separation between the centre of the small hole in and the centre of the sample holder). Bombardment was commenced by re-opening the gate valve. CO_2 was used as the source gas for C^+ ions, while CH_3^+ ions were extracted from an argon-stabilised methane plasma. Typically, ion currents of *ca.* $0.2 \mu\text{A cm}^{-2}$ were delivered to the unheated samples at impact energies of 20 to 500 eV. The beam spot diameter was normally ≈ 2 mm. Figure 3.4 shows the mass spectra of a beam extracted from a carbon dioxide plasma before and after mass selection for carbon, mass 12. The Wien filter can separate species of masses within ± 1 amu of each other. The beam has been focused and decelerated to an energy of 143.5 eV, and this is shown by the energy spectrum for mass 12 in Figure 3.4(c). The energy spectrum also shows that the energy spread of the decelerated beam is 2.7 eV. With all of the beam parameters fully optimised, an energy spread of ± 0.6 eV has been achieved for argon ions at 21 eV.

Hydrogen ion bombardment using a 100 eV H_2^+ ion beam was also used for the removal of the damage induced by carbon ion bombardment on GaAs. To ensure adequate hydrogen ion exposure on the spot previously bombarded with carbon ions, the beam was defocused by moving the target platform further from the exit of the final decelerating lens. This resulted in a beam diameter at the surface of *ca.* 5 mm, but with a significantly reduced ion current density. Several hours of exposure were therefore required to attain the necessary dose.

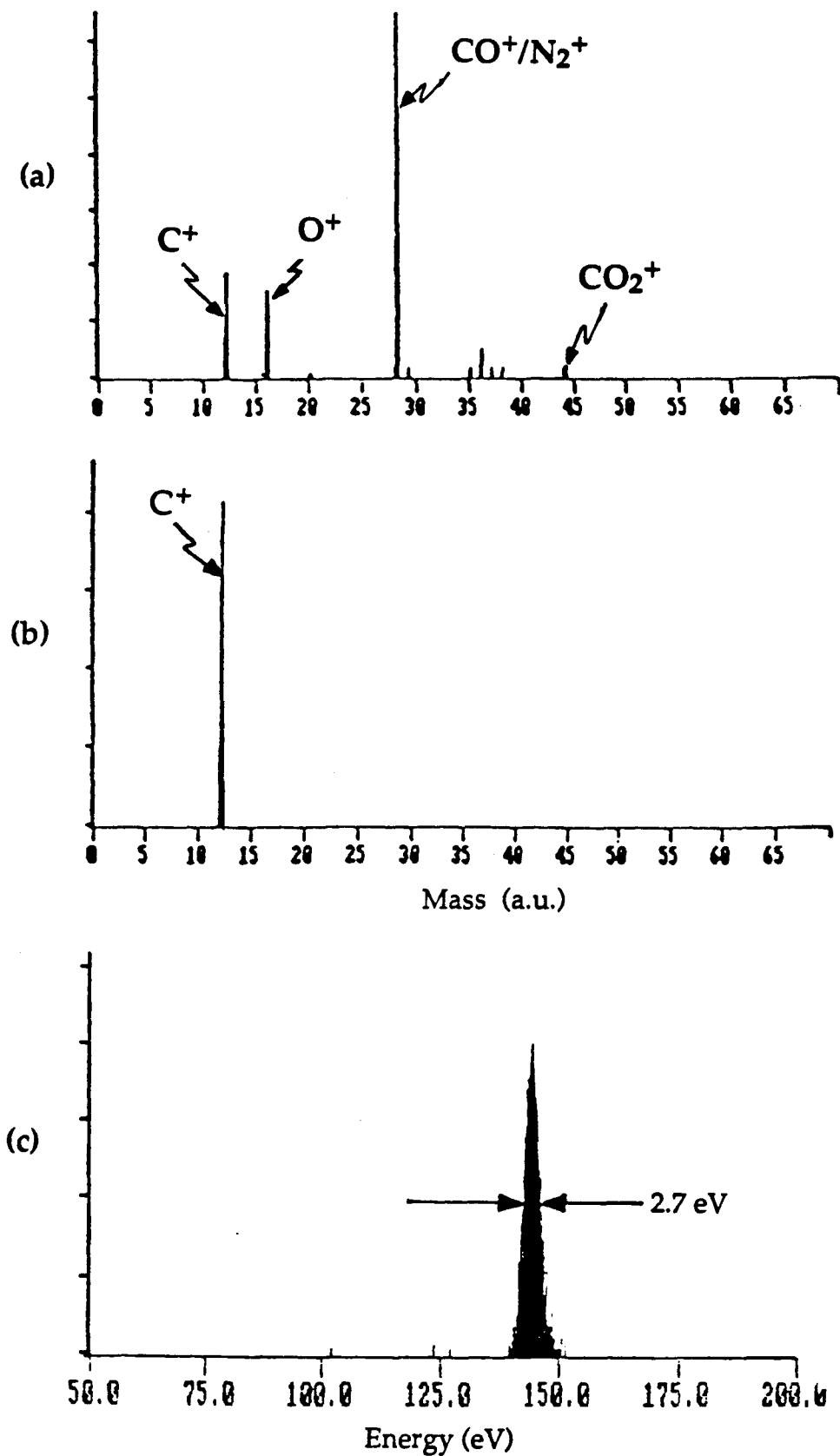


Figure 3.4 Mass spectra of a beam extracted from a CO_2 plasma in a quartz chamber, (b) after mass selection for ^{12}C , and (c) energy spectrum for mass 12.

Also integrated with the ion beam system is an X-ray photoelectron spectrometer based on a VG CLAM-2 analyser. However, because the irradiated areas on the samples were small (approx. 2 mm or less), the microscopic analysis features of a remote Surface Science Laboratory SSX-100 spectrometer were utilised instead of the VG spectrometer. This necessitated intersystem transfer in a battery operated, ion-pumped transfer unit which could be attached to the introduction ports of both systems. The pressure during transfer was kept below 1×10^{-7} Torr.

3.1.3 XPS analysis

Angle dependent XPS is an appropriate technique for monitoring the effects of low energy ion bombardment because it provides depth distributions of the chemical species from the surface to a depth of about 10 nm. Furthermore, the analysis is non-destructive and does not perturb the distribution of the species during sampling. After exposure to the low energy ion beam, the samples were transferred *in vacuo* from the beam system to a Surface Science Laboratory SSX-100 spectrometer. This system features a separate sample introduction chamber, an isolated sample preparation chamber and the analysis chamber housing the X-ray spectrometer. A schematic of the spectrometer can be found in the previous chapter (Figure 2.3).

The spectrometer uses monochromatic Al $K\alpha$ X-rays, generated by bombarding an Al anode with 10 keV electrons. The $K\alpha_{1,2}$ doublet has a linewidth of ≈ 0.85 eV, but use of a toroidal quartz crystal to select the $K\alpha_1$ line at 1486.6 eV gives a monochromatised linewidth of 0.2-0.3 eV. The size of the X-ray spot on the sample is determined by the size of the electron beam at the Al anode. For the SSX-100, ellipse shaped spots with short axes of 150, 300, 600 or 1000 μm may be used. While the use of a larger spot size will increase the intensity of the photoelectron signal from the sample and thereby reduce the time required for data acquisition, it

will also increase the energy spread of the X-rays arriving at the sample and degrade the final resolution. Table 3.1 lists the relevant parameters obtained by selecting a particular resolution setting on the spectrometer. In this work, atomic compositions were obtained with a spot size of 1000 μm , whereas high resolution spectral analysis was performed with resolution setting 2.

Photoelectrons emitted from the sample with trajectories within a 30° cone are collected, focused and retarded to a constant energy by a lens system before arriving at the entrance slit of a concentric hemispherical energy-dispersive analyser (CHA). A potential is applied between two concentric hemispherical sectors, so that the photoelectrons follow a path through the analyser determined by their kinetic energy and the voltage across the spheres. The voltage across the spheres is kept constant, giving a constant analyser resolution and the photoelectron kinetic energy is scanned by changing the retarding voltage in the lens system. The resolution is changed by adjusting the pass energy. Table 3.1 also lists the pass energies obtained from the four resolution settings on the SSX-100.

An electron reaching the analyser exit slit strikes a channel plate electron multiplier and its arrival position along the exit slit (corresponding to its kinetic energy) is determined by a resistive anode encoder. The result is a plot of electrons detected per unit time versus the kinetic or binding energy.

Ultra-high vacuum is maintained in the analysis and preparation chambers by turbomolecular and ion pumps. Vacuum in the introduction chamber is achieved by a turbomolecular pump backed with a rotary pump, which initially reduce the chamber pressure from ambient to below 10^{-7} Torr. Once the pressure in the introduction chamber drops below 10^{-7} Torr, a gate valve separating the introduction and analysis chambers is opened and the sample and holder are transferred with a long feed-through rod onto a rotatable carousel in the analysis chamber. The rod is then withdrawn and the gate valve closed. Analysis was

Table 3.1 Parameters of SSX-100 XPS

Resolution setting	X-ray spot size (μm)	Analyser pass energy (eV)
1	150	25
2	300	50
3	600	100
4	1000	150

usually commenced when the pressure in the analytical chamber was below 5×10^{-9} Torr. The sample holder carousel can be moved in the x, y, z directions and has 360° rotational freedom. When samples are mounted in the normal horizontal position, the detector is at an angle of 35° with respect to the surface. However, the use of other holders incline the sample, so that the detector is normal to the surface. When such holders are placed in the centre position of the carousel, the angle between the surface and the detector can be varied from 0 to 90° by rotation of the stage. As discussed earlier, this effectively changes the sampling depth, and enables angle dependent data to be obtained (escape depth = $\lambda \sin \theta$). For most of this work, the sample holders had an inclination of only 15° because of the clearance requirements in the ion beam system. Thus, analysis angles between 20° and 50° were accessible. Analysis was carried out only at those two angles (20° and 50°) since the photoelectron "take-off cone" of the spectrometer is approximately 30°.

The spectrometer functions are controlled by a Hewlett-Packard Model 9836 microcomputer, which is also equipped with the SSL software used for data analysis. Surface compositions were calculated from the integrated peak intensities using the photoionization cross sections derived by Scofield⁶⁰. The high resolution spectra were peak-fitted using 80% Gaussian-20% Lorentzian peaks in an iterative chi-squared fitting program. The background subtraction was performed using Shirley functions. Binding energies were calibrated to the 83.93 eV, Au 4f_{7/2} peak of sputtered gold foil always present in the chamber. Inelastic mean free paths were calculated using an expression given by Tanuma *et al.*⁵⁶. Other peak fitting constraints are listed in Table 3.2.

3.1.3 Other surface analyses

Raman spectroscopy was performed with a Dilor Omars 89 spectrometer equipped with an Olympus BH2 optical microscope and an image intensified array

Table 3.2 Peak fitting constraints used in this work

Element and core level	Spin orbit splitting	Peak separation	Area ratio of doublet $n/2 + (n/2+1)$
As 3d	$3d_{3/2}3d_{5/2}$	0.69 eV	1.5
Ga 3d	"	0.48 eV	1.5
In 4d	"	7.60 eV	1.5
P 2p	$2p_{1/2}, 2p_{3/2}$	0.86 eV	2

detector. The spectra were obtained in the microscopic mode. The 487.98 nm line of a Coherent Radiation argon ion laser was used as the incident photon source.

Scanning electron microscopy of samples bombarded with carbon ions was also performed using an ISI DS-130 SEM.

3.2 HYDROGEN ATOM AND METHYL RADICAL ETCHING OF GaAs

3.2.1 Samples

The GaAs samples were cut from single crystal, semi-insulating (100) wafers supplied by Johnson Matthey (Trail, B.C.). To enable etch rates to be determined by laser interferometry, the (100) faces of the wafers were masked with 0.05 μm thick silicon nitride (Si_3N_4) stripes. The stripes were oriented in the $[01\bar{1}]$ and $[0\bar{1}1]$ directions and were 15 μm wide with a spacing of 15 μm . The masks were deposited in the UBC Centre for Advanced Technology in Microelectronics, using the following procedure:

The wafer was degreased in sequential washes of hot trichloroethylene, acetone and finally in isopropyl alcohol. A layer of Si_3N_4 was deposited on the wafer in a plasma enhanced chemical vapour deposition chamber using ammonia, hydrogen and silane. The flows were 43, 500 and 380 sccm, respectively. The RF power was 100 Watts and the deposition time was 2.5 minutes. A thin layer of photoresist was spin-deposited on the Si_3N_4 covered wafer (speed 4700 rpm, time 35 seconds), and then baked at 95 $^{\circ}\text{C}$ for 25 minutes. The mask image was imprinted into the photoresist with 320 nm light from a mercury lamp, and then developed in a 50% solution of MF-312 developer. A buffered solution of hydrofluoric acid was used to etch the silicon nitride not covered by the photoresist. The wafer was

then rinsed in distilled water, before the photoresist was removed with a hot acetone/isopropyl alcohol wash.

Small chips, approximately 2mm x 3mm in size, were cut from these wafers. Before being etched, the native GaAs oxide on the chips was removed by a 30 second wash in concentrated HCl, followed by a rinse in distilled water and blown dry with a fast stream of nitrogen. The samples were attached to the sample holder and inserted into the hot reactor which was backfilled with an overpressure of helium.

3.2.2 Gases

Prepurified hydrogen supplied by Linde was used. The purity was quoted as 99.99%, with the major contaminants being oxygen (5 ppm) and water (5 ppm). The methane used was Ultra-pure with a quoted purity of 99.97% and was supplied by Matheson Gas products. Iodomethane was obtained from BDH Chemicals (99.5% purity) and stored in a flask wrapped with black PVC tape to prevent photodecomposition. Prior to a series of experiments, the liquid was degassed by several freeze, pump, thaw cycles. The vapour pressure of CH₃I was sufficiently high at room temperature to allow reasonable flows. Spectroscopic grade acetone (99.5% purity) supplied by BDH was used in the laser photodissociation experiments.

Hydrogen iodide was prepared by the following synthesis⁹⁹: A "slip" of 2.5g of red phosphorus in 5g H₂O was added to 50g I₂ and 5g H₂O in a 3-necked, round bottomed flask. The reaction can be quite vigorous, and care is needed to prevent iodine from being carried over with the HI. The flask was therefore cooled in a salt/ice-water mixture, and attached to a reflux condenser in series with an ice-water cooled U-trap and a liquid nitrogen cooled U-trap. The atmosphere above the reaction was purged with dry nitrogen. One end of the U-trap containing the

frozen HI was sealed and the other attached via a 3 way valve to a vacuum line and an evacuated bulb. The residual gas in the U-trap was pumped away and the HI evaporated into the bulb. The HI in the bulb was then further purified with a series of freeze, pump, thaw cycles. HI is readily decomposed by light, organic compounds such as greases, and by extensive glass surfaces (particularly in the presence of water)¹⁰⁰. Therefore the bulb was washed with hot KOH and thoroughly evacuated and baked. No grease was used on the O-rings of the Teflon stopcock. The bulb was covered with black PVC tape. The gas was used within two days of preparation.

3.2.3 Etch rate measurement

The etch rates were measured by laser interferometry. This is a simple, non-destructive method for obtaining accurate, *ex situ* measurements¹⁰¹. The principle of interferometry is illustrated for a masked GaAs sample in Figure 3.5. A laser beam is reflected at an angle, θ , from the silicon nitride mask and GaAs surfaces, which are separated by a height, d . The light reflected off the semiconductor will have travelled a distance $2d\sin\theta$ further than that reflected from the mask, so the intensity of the combined beam will depend on the extent of the interference between its constituent reflected beams. Constructive interference between two identical waves occurs when they are separated by a distance equal to an integral number of wavelengths, $n\lambda$. Therefore, if the height difference between the mask and GaAs surfaces is such that $2d\sin\theta = n\lambda$, then the intensity of the reflected light will be a maximum. For simplicity, the laser beam is incident perpendicular to the surface ($\theta \approx 90^\circ$) so the condition for maximum reflected intensity is just $d = n\lambda/2$. During an etch, d will increase as the GaAs is eroded (silicon nitride is unreactive towards many chemicals), and the reflected light intensity will vary sinusoidally with time. The resulting output on a chart recorder is called an interferogram. For the HeNe laser, reflected light intensity maxima occur every time 316.4 nm

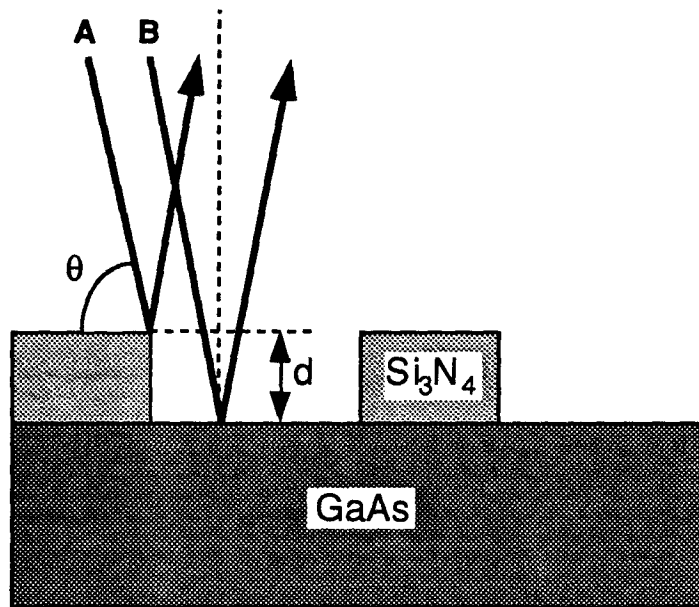


Figure 3.5 Principle of laser interferometry for monitoring the etch rate of GaAs masked with silicon nitride.

of material has been etched away. Thus, the etch rate is equal to $(316.4 \text{ nm})/t$, where t is the time between two adjacent maxima or minima, measured from the chart recorder. By using a suitable chart speed, the error associated with determining this time can be minimised, and an error of less than $\pm 5\%$ can be achieved¹⁰¹. A typical interferogram is shown in Figure 3.6.

In this work, a 10 mW HeNe beam was further reduced in intensity with a blue filter, and a silicon photoconductor was used for detection of the reflected light. The sensitivity of the detector was enhanced by filtering out background light and using a voltage offset for the chart recorder.

From Figure 3.6, we can see that the distance between successive maxima increases, indicating that the etch rate is decreasing with time. This illustrates the inherent advantage of using laser interferometry as an etch rate monitor, as opposed to other commonly used measurement techniques; a "real time" measurement yields information on how the etch proceeds. The interferogram also shows a gradual reduction of the reflected light intensity. This is caused by a roughening of the semiconductor surface during the etch. Thus, interferometry is also a useful indicator of the surface morphology during an etch.

During the initial experiments, a Tencor alpha-step 200 profilometer was used to measure etch rates. In this technique, the trench depth relative to the mask surface is measured by a fine metal stylus which traverses the sample. After accounting for the mask thickness, the etch rate can be obtained by dividing the etch depth by the total etch time. However, as shown above, the etch rates varied with time and there was often a lengthy induction period. Therefore, profilometry was much less reliable than interferometry for this particular etching system. Etch depths, albeit with limited accuracy, can also be estimated from SEM images.

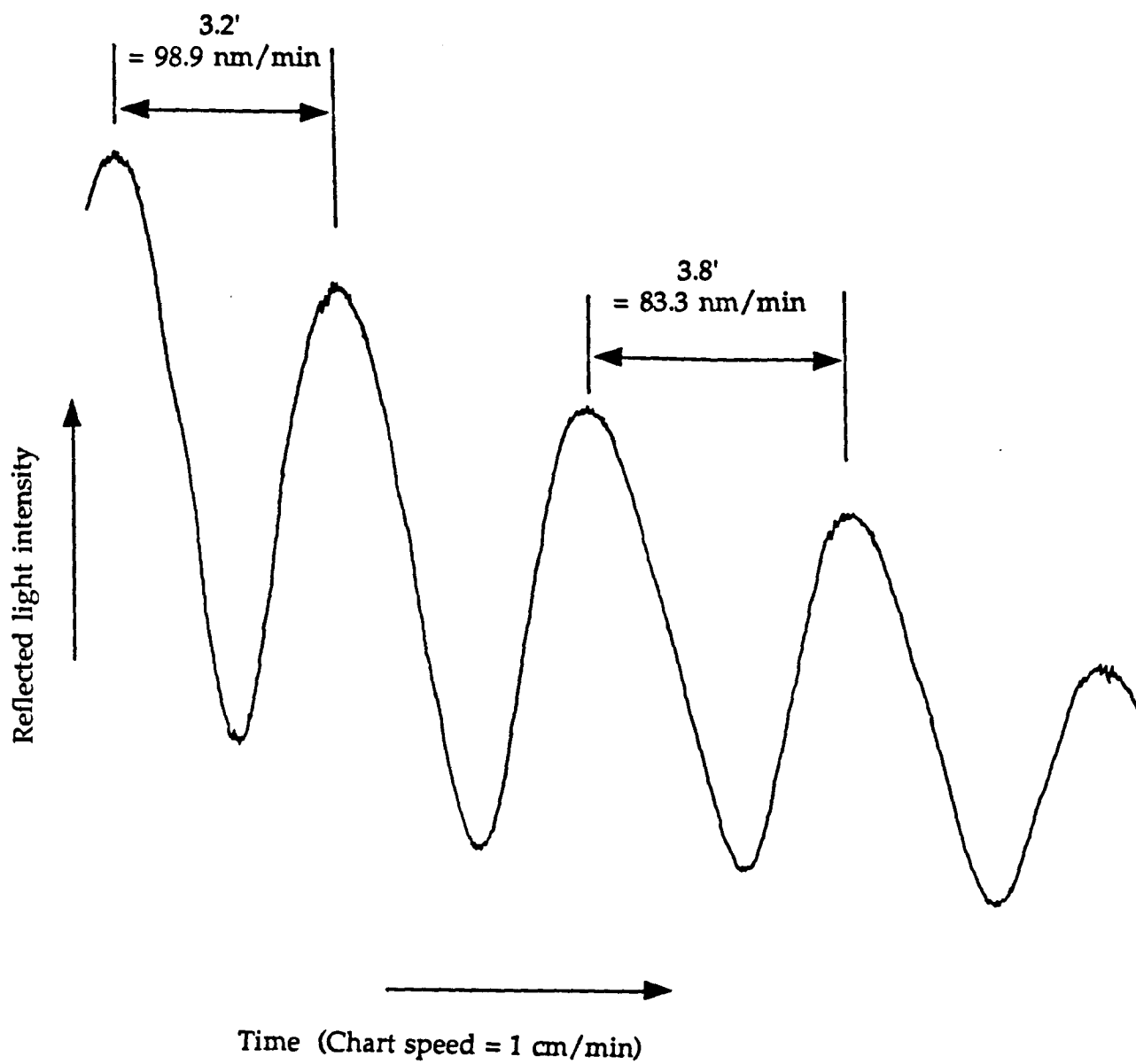


Figure 3.6 Interferogram obtained from etching of a masked GaAs sample with H/CH₃/I

3.2.4 Hydrogen atom etching of GaAs

3.2.4.1 Equipment

A schematic of the system used for hydrogen atom etching is shown in Figure 3.7. For etching experiments with other reactive species (generated by abstraction reactions with hydrogen atoms) the system was modified by the addition of a secondary gas inlet, which consisted of a 6 mm diameter Pyrex tube with four small (approx 2mm diameter) radially oriented holes bored into it (see Figure 3.8).

The system was constructed entirely from Pyrex. A light trap was added to the end of the discharge region to keep the discharge radiation from impinging on the substrate and the interferometer photodetector. The system was separated from the rotary pump (Sargent-Welch model No. 1402, 160 l/min pumping speed) by a butterfly valve. To minimise vibrations from the pump which would also affect the interferometer, a short length of thick walled rubber tubing connected the pump to the valve. The system base pressure was typically a few milliTorr. To prevent backstreaming of hydrocarbon vapours from the pump oil when no gases were flowing, the valve was closed, isolating the system from the pump. After extensive flushing with hydrogen and a lengthy evacuation, normal leak/degas rates were in the order of 0.1 to 0.5 mTorr min⁻¹. The sample holder and atom detector were attached with concentric, Cajon type, O-ring fittings, so that by slightly loosening one O-ring, they could be easily moved inside the apparatus while maintaining vacuum.

Gas lines were either 1/4 inch copper or polyethylene tubing. They were attached to needle valves with Parker fittings. Hydrogen flow rates were measured with a calibrated Sierra TopTrak flowmeter. Secondary gas flows were regulated with a Granville-Phillips series 203 variable leak valve. The valve was calibrated for each gas by pumping at various flows, isolating the system from the pump and

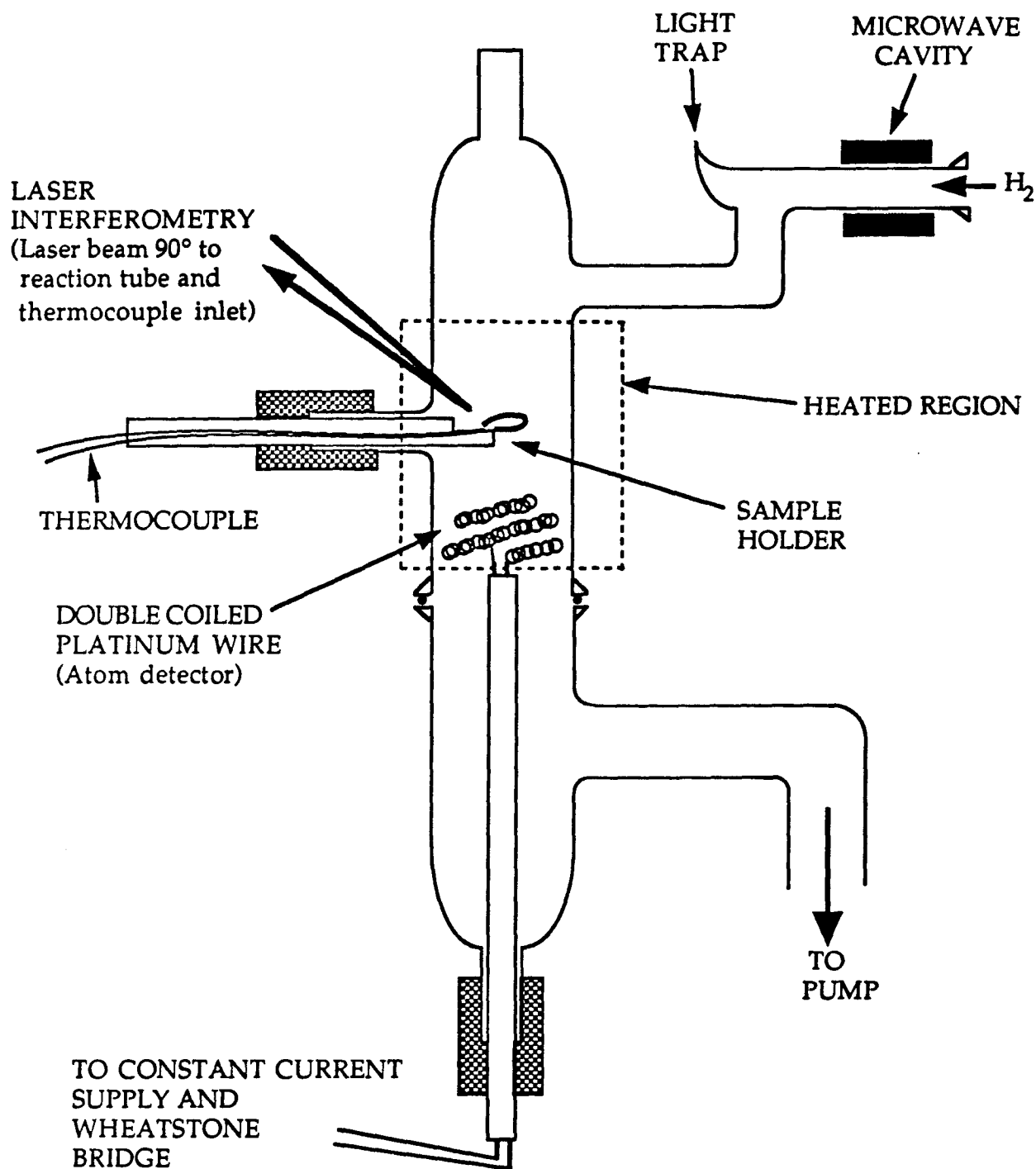


Figure 3.7 Schematic of apparatus used for etching GaAs with H atoms.

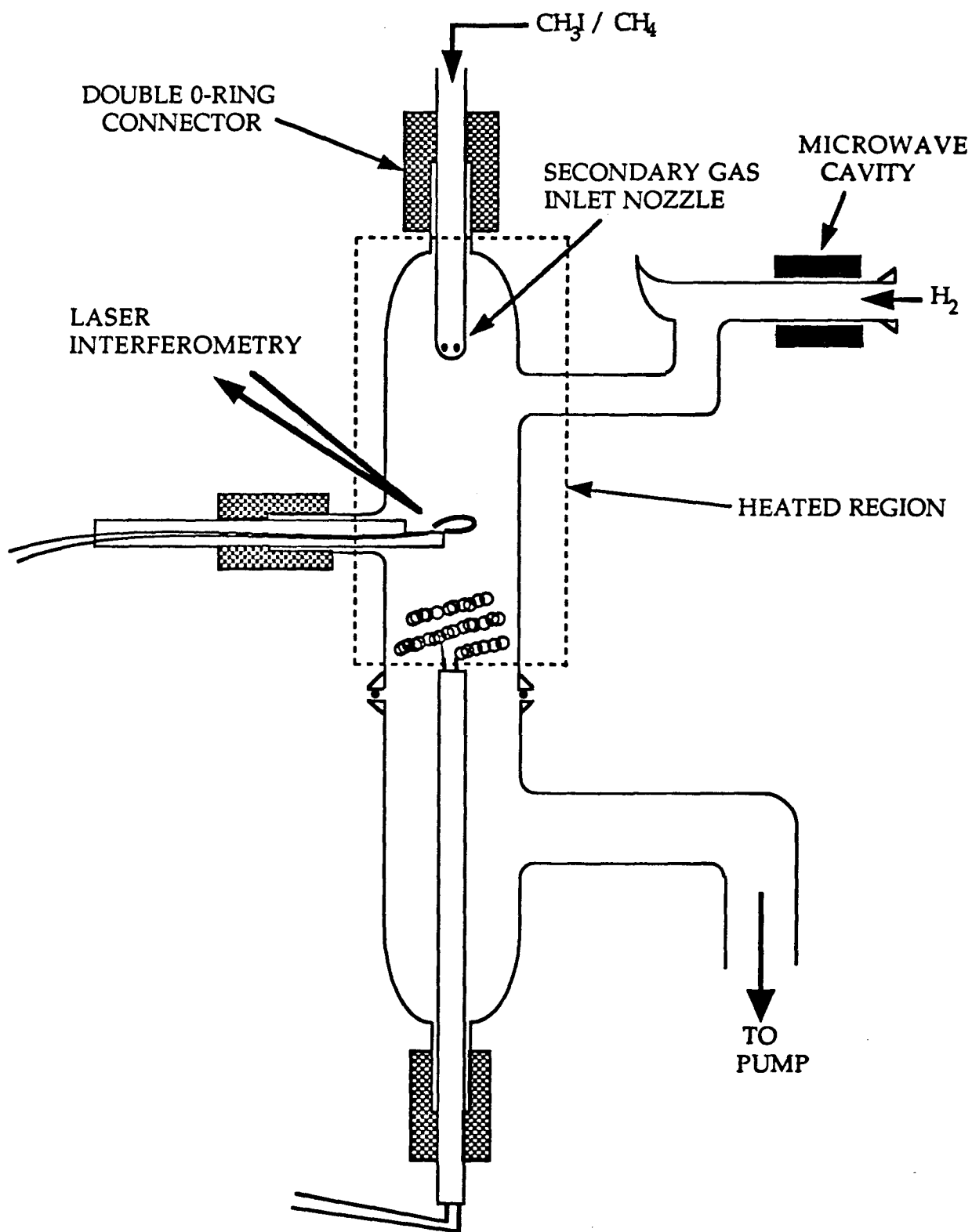


Figure 3.8 Schematic of apparatus for the production of methyl radicals to etch GaAs (modified version of Figure 2.7).

measuring the rate of pressure increase in the closed system. The system volume was obtained by measuring the pressure change upon expansion of a fixed pressure of gas into a large, known volume. The total gas pressure was measured with an MKS pressure transducer (type 122A).

An E.M.I. Microtron 200 microwave source (2.45 GHz) attached to a quarter wave cavity was used to create a hydrogen plasma inside a 13 mm diameter Pyrex tube. The discharge region was cooled with compressed air to prevent overheating and to reduce H atom losses to the hot walls. The microwave was operated at 50–100 watts.

Hydrogen atoms recombine rapidly on many surfaces. The largest flows of atoms could be obtained by degreasing the walls of the system with hot KOH and then rinsing with a dilute solution of ortho-phosphoric acid and finally distilled water. A few drops of concentrated acid were smeared on the walls of the discharge region and heated to dryness in a flame. Phosphoric acid has been found⁷⁵ to be effective for reducing the wall recombination rate of H atoms. Teflon coatings also have this property, but are difficult to apply and are easily damaged in the vicinity of the discharge. Although concentrated phosphoric acid in the discharge area enables large concentrations of atoms to leave the discharge, it requires a long "burn-in" period during which the atom flow continually decreases towards a stable value. This problem arises from water absorption by the dried acid, and occurs every time the system is opened to air (even with an overpressure of helium). The presence of dried acid in the discharge region also introduces the possibility that contamination could interfere with the etching process. The most reproducible performance was obtained from a newly constructed system which was washed and rinsed as above, but did not have any phosphoric acid in the discharge area. The atom flows were lower, but became quite reproducible after several hours exposure to hydrogen atoms. With this treatment, the atom flows

measured between the secondary gas inlet and the sample region were found to be constant, within experimental error. This shows that the walls were effectively poisoned and that wall losses were insignificant over the length of the titration with the secondary gas. The lower part of the apparatus was not rinsed in dilute phosphoric acid, and the wall losses were large.

The sample was heated by wrapping a heating tape around the region of the apparatus indicated in Figure 3.8. When methane was added to the hydrogen streams, kinetic modelling required that the gas and wall temperatures be constant over the length of the titration. A movable, shielded (from radiation) thermocouple was employed to determine the heating uniformity in the system. It was found that simple wrapping of the heating tape around the reaction region resulted in large temperature gradients. This problem was exacerbated at higher temperatures where radiation effects become increasingly important. The region was therefore covered with aluminium foil and wrapped uniformly with a narrow heat tape. After an extensive period of trial and error, the uniformity of the gas temperature along the reaction tube was improved to within $\pm 3\text{ }^{\circ}\text{C}$ at $325\text{ }^{\circ}\text{C}$, by adding insulation to particular areas of the heating tape.

3.2.4.2 Sample holder and temperature measurement

Temperature measurement has always been problematic in the study of the reactions of atoms with surfaces, due to the heat of recombination on the surface of the material being monitored. Once the discharge is ignited and atoms flow, the temperature measured at the sample is always found to increase. For this reason the surface temperature of a sample could be much higher than the temperature recorded through the glass wall of a sample holder. Various attempts to solve this problem have been tried in this laboratory. One approach involves mounting the samples on large heat sinks such as blocks of silicon. This assumes that perfect

thermal contact exists between the backside of the sample and the sink, that a thermal gradient does not exist between the wafer surface and the backside of the sink, and that there is perfect contact between the thermocouple leads and the sink. Another simpler approach was to mount the sample on a glass tube which was drawn out to a very thin diameter. This was an attempt to minimise the amount of Pyrex between the sample and the thermocouple because the thermal conductivity of Pyrex is very poor. The approach that was finally employed in this work is illustrated in Figure 3.9, where the thermocouple is in direct contact with the sample. A small hole was blown into a piece of 3 mm diameter quartz tubing, and a "crater" rim fashioned into it. The end of the tubing was softened and drawn out to form a spring, which would hold the sample in place. A 0.25 mm diameter alumel /chromel thermocouple was fixed into the tube with "TorrSeal" epoxy, so that the tip protruded slightly from the hole. The curvature of the leads as they approached the hole also resulted in a spring action. The samples were then squeezed tightly between the thermocouple lead and the quartz spring. The sample was also in contact with the rim of the hole, effectively covering the thermocouple and thus preventing atoms from directly recombining on it. The thermal contact between the sample backside and the thermocouple is expected to be good, and no gradient should exist across the wafer (thickness = 0.5 mm). This sample holder was found to be very sensitive to changes in temperature and our confidence in the accuracy of the measured temperatures correspondingly high.

3.2.4.3 Hydrogen atom measurement

Hydrogen atoms were measured by a calorimetric technique first used in 1948 by LeRoy⁸⁶. The method is based on the energy released by atom recombination on a heated wire under isothermal conditions. A double-coiled platinum wire of known resistance is inserted into the system and heated by passing a constant

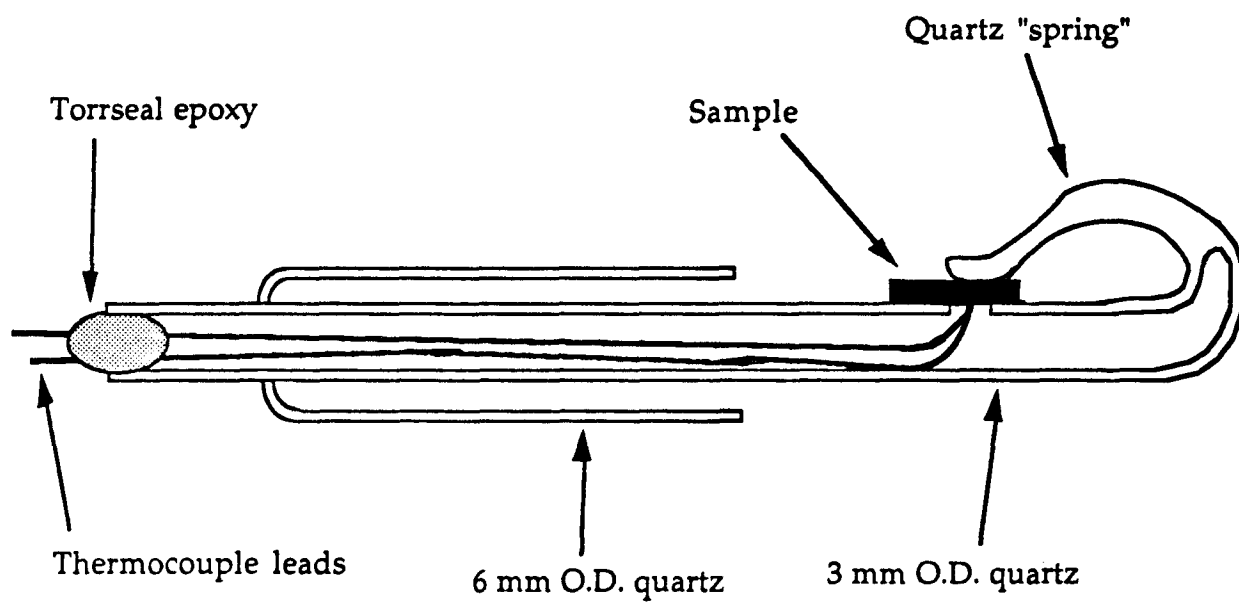


Figure 3.9 Schematic of holder used to accurately monitor sample temperature during etching experiments with H atoms.

current through it. The coil is one arm of a Wheatstone bridge (For details of constant current bridge design, see Appendix A). The current is measured across a 1 Ohm precision resistor. Hydrogen atoms produced by the microwave discharge flow downstream and recombine with unit efficiency on the hot wire, thus heating it further. Once the coil reaches a steady temperature, the bridge is then balanced. The discharge is then switched off. The bridge goes out of balance as the coil cools and its resistance decreases. To compensate for this, the current passing through the wire is manually increased until the bridge is rebalanced *i.e.* the coil is now at the same temperature as before. From the difference in current required to keep the coil at the same temperature, and the resistance of the coil at that temperature, we can calculate the power (or energy/second) released into the coil by the recombination of the atoms. If we then divide this value by the known heat of recombination of hydrogen atoms (half of the H-H bond energy), the flow of atoms over the coil can be calculated:

$$\text{Atom flow (mole s}^{-1}\text{)} = \frac{(i_x^2 - i_o^2) R}{\Delta H}$$

where i_x is the current passing through the coil with the discharge off and i_o is the current when the atoms are flowing. ΔH is the heat of atom recombination and is 217.97 kJ mol⁻¹ for hydrogen. R is the resistance of the platinum coil.

The validity of this technique depends on the complete removal of all the atoms from the gas stream and upon the isothermal conditions under which the measurements are taken. To ensure quantitative atom collection, the platinum coil is wound so as to occupy as much volume as possible without actually touching the walls of the vessel. The best arrangement was achieved by winding 50 cm of wire into a tight coil and then forming a spiral with the coil. The temperature of the wire is also important since the efficiency of recombination increases as the coil is heated (electrically or externally). A plot of calculated

hydrogen atom flow versus current passed through the coil is shown for two external temperatures in Figure 3.10. From the plot obtained at room temperature, we can see that above a coil temperature of approximately 120 °C, there appears to be no increase in the efficiency of atom recombination, and from the data obtained with external heating to 200 °C, the maximum efficiency for atom recombination is reached with lower currents flowing through the coil. However, we cannot simply assume that the plateau in the atom flow measurements means that all the atoms are being removed from the stream. Therefore, a second similarly coiled platinum wire placed a few centimetres downstream from the primary detector was used to measure any atoms that might pass through the first (see Figure 3.11). When the first coil was unheated, the measured atom flow obtained from the lower coil operating at its optimum temperature, decreased by about 30% showing that significant losses occur on an unheated platinum wire. Current was then passed through the upper coil and the atom flow measured by this coil reached a plateau beyond a temperature of 120 °C, as in Figure 3.10, indicating its maximum efficiency had been reached. Meanwhile, the flow measured by the lower detector decreased to zero. The discrepancy between the point where the efficiency began to plateau and the temperature required to remove all the atoms is within experimental error, and could also be due to diffusion effects. There was also the possibility that heat from the upper coil was affecting the lower detector. However, this was eliminated by balancing the lower coil in the absence of atoms (with the upper coil unheated), and then raising the temperature of the upper coil to 175 °C. The bridge for the lower coil did not move out of balance. When the system was heated to 200 °C, there were no atoms measured by the lower coil, even when no current was passed through the upper coil.

This two-coil arrangement is therefore a good test of a detector's ability to quantitatively remove atoms. It confirms the optimum operating temperature

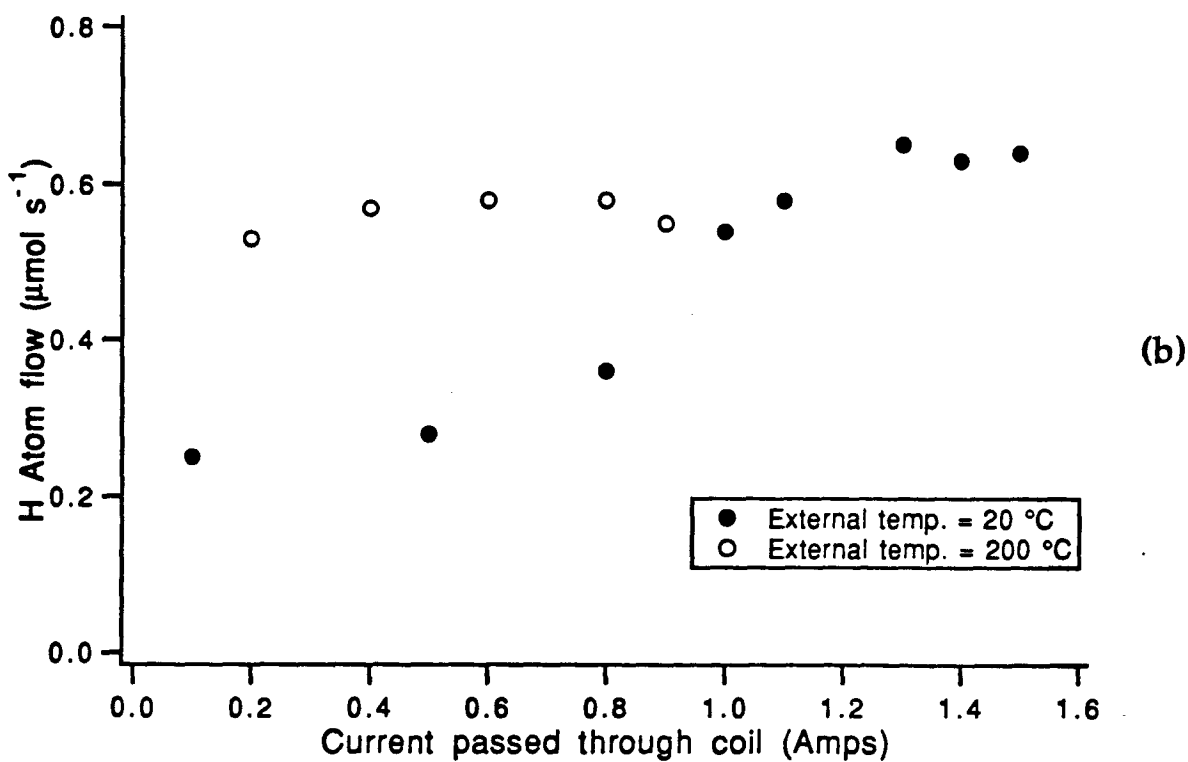
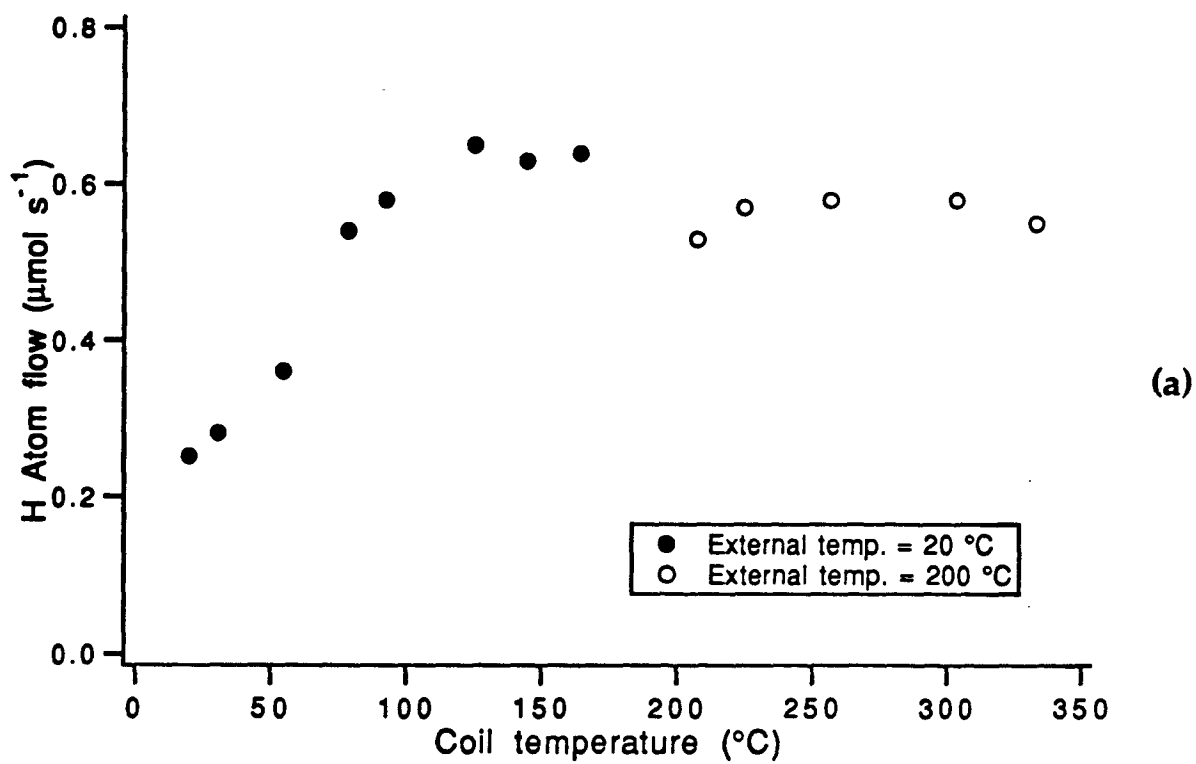


Figure 3.10 Plots of H atom flow versus (a) coil temperature and (b) current passed through coil for two external temperatures.

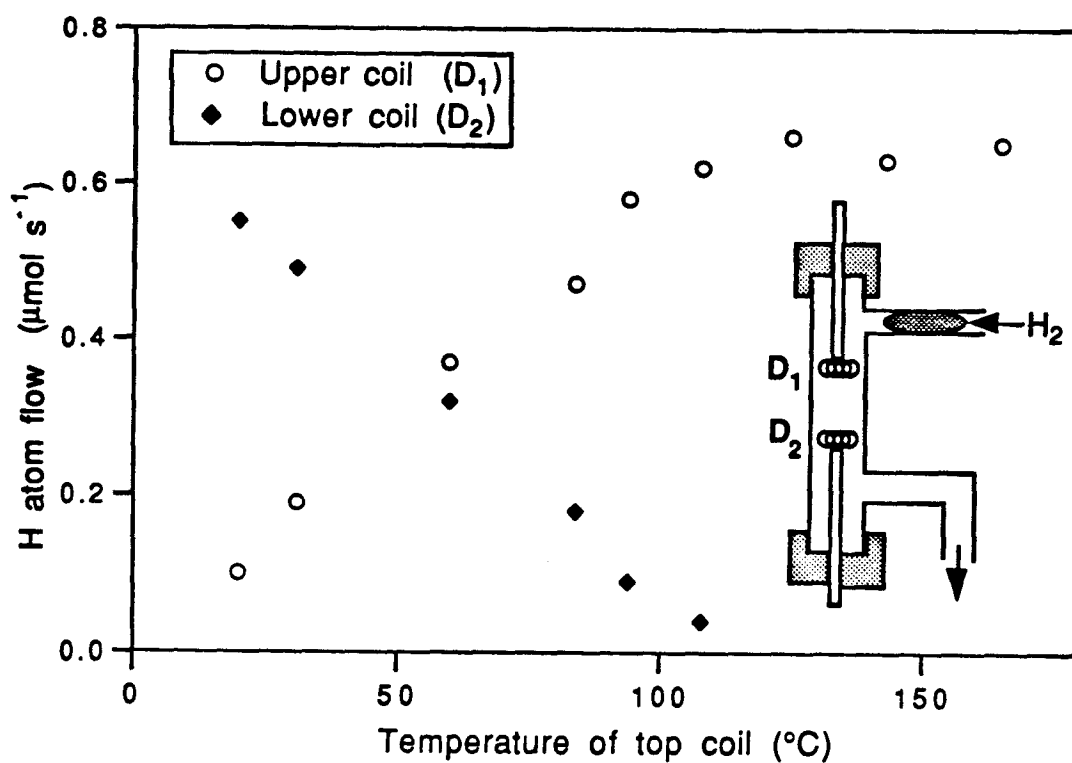


Figure 3.11 Plot of H atoms measured by two detectors in series as a function of the upper detector (D_1) temperature *i.e.* showing the atom removal efficiency of the upper coil.

of a coil and also if its structure is ideal. For example, in another experiment, the upper coil was not wound effectively. Although a plateau in its calculated atoms-versus-temperature behaviour was observed, atoms were detected by the lower coil even when the upper coil was operating at "maximum efficiency".

Another important requirement for atom measurement is operation under isothermal conditions *i.e.* the rate of heat loss from the detector when the discharge is on and off should be identical. Therefore, the gas stream temperatures were measured with a thermocouple wrapped with Teflon tape (negligible H atom recombination), which was placed in the sample position. With external temperatures above 200 °C, there was no change (within ± 1 °C) in the measured gas temperature when the discharge was switched on or off. Therefore, the slight change in the gas thermal conductivity caused by the presence of hydrogen atoms would appear to have a negligible effect on the heat loss of the detector.

Another requirement is that the energy accommodation of the detector is unity, *i.e.* that all of the energy released by the atom recombination is transferred into the wire and not released into the gas. Other workers⁸⁷ using platinum wire calorimetric detectors have compared their measured atom concentrations with values obtained from titrations with NOCl, and have shown that the results are in almost complete agreement. Thus, a platinum coil operating at an elevated temperature is deemed to be an accurate detector of hydrogen atoms.

From a series of experiments carried out under stable conditions (*i.e.* running the discharge for several hours and continually flushing the system with H₂), the measured hydrogen atom flows were found to differ by less than $\pm 10\%$.

3.2.2.5 Typical procedure

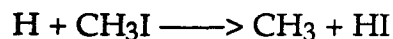
Experiments were carried out in the following manner. Hydrogen was flowed through the system for several minutes to allow the flow to stabilize and to

flush any impurities from the walls. The apparatus was brought up to the desired operating temperature with a heating tape connected to a Variac. The discharge was ignited with a Tesla coil and the atoms flowed for several minutes. The platinum detector was moved into the position normally occupied by the sample and the atom concentration measured in the usual manner. The detector was then moved back to below the sample position. The discharge was shut off and the hydrogen flow stopped (without adjusting the valve setting). The system was then isolated from the pump and filled with an over-pressure of helium. The sample holder was removed by loosening an O-ring fitting. A sample, which was washed for 30 seconds in concentrated hydrochloric acid, rinsed in distilled water and blown dry with nitrogen, was placed under the spring on the holder. This was then inserted into the hot, helium filled system and the O-ring fitting tightened. The helium was shut off and the system was evacuated. The hydrogen flow was then started, and the sample quickly brought up to temperature. Meanwhile, the rotation of the sample holder and the position of the photodetector were adjusted so that the reflected laser light was maximised (as observed from the signal on the chart recorder). The discharge was started and the etch parameters recorded at regular intervals. For etches with species other than hydrogen atoms, the secondary gas was then introduced into the hydrogen atom stream at a precalibrated flow rate. After a sufficient period of etching, the sample was withdrawn from the etching gas stream into an arm of the apparatus, and the platinum detector again moved into that position to record the atom flow.

3.2.3 Methyl radical production

As we have seen in Chapter 1, there are several potential methods of generating methyl radicals. Two different techniques were used in this work: photodissociation of acetone and the reaction of hydrogen atoms with CH_3I or CH_4 .

Our initial work used well characterised flows of hydrogen atoms to abstract iodine from iodomethane thus producing methyl radicals and hydrogen iodide:



This is a fast reaction, facilitated by a C-I bond energy of only 234 kJ mol⁻¹ (*cf.* H-I bond energy of 297 kJ mol⁻¹). The second order rate constant is 5.8x10¹² cm³ mol⁻¹ s⁻¹ at 300 K.

A schematic of the apparatus used was shown previously (Figure 3.8). When small flows of iodomethane were introduced into a flow of hydrogen atoms, GaAs was found to etch quite rapidly at elevated temperatures. However, subsequent investigation showed that iodine atoms formed by the fast consecutive reaction of unreacted hydrogen atoms with hydrogen iodide were responsible for a significant fraction of the etch:



Therefore, a "cleaner" supply of methyl radicals was sought.

The photodissociation of acetone has often been used as a source of methyl radicals in gas phase kinetic studies. Preliminary calculations suggested that enough methyls could be produced by the dissociation of acetone with a pulsed argon fluoride excimer laser to give a measurable etch rate. A system to facilitate such a process was therefore constructed. This is illustrated in Figure 3.12. The system was designed with a small reaction volume to enable the maximum interaction of the acetone vapour with the laser beam. The unfocused beam dimensions are approximately 12x20 mm, so a 25 mm diameter Suprasil window was used. The remainder of the system was constructed from Pyrex, which effectively blocks the escape of scattered radiation with damaging wavelengths. Since surface oxides and contamination are believed to be etch inhibitors, the apparatus also had the capacity for *in situ* hydrogen plasma cleaning and downstream hydrogen atom etching/cleaning. The samples were placed on a

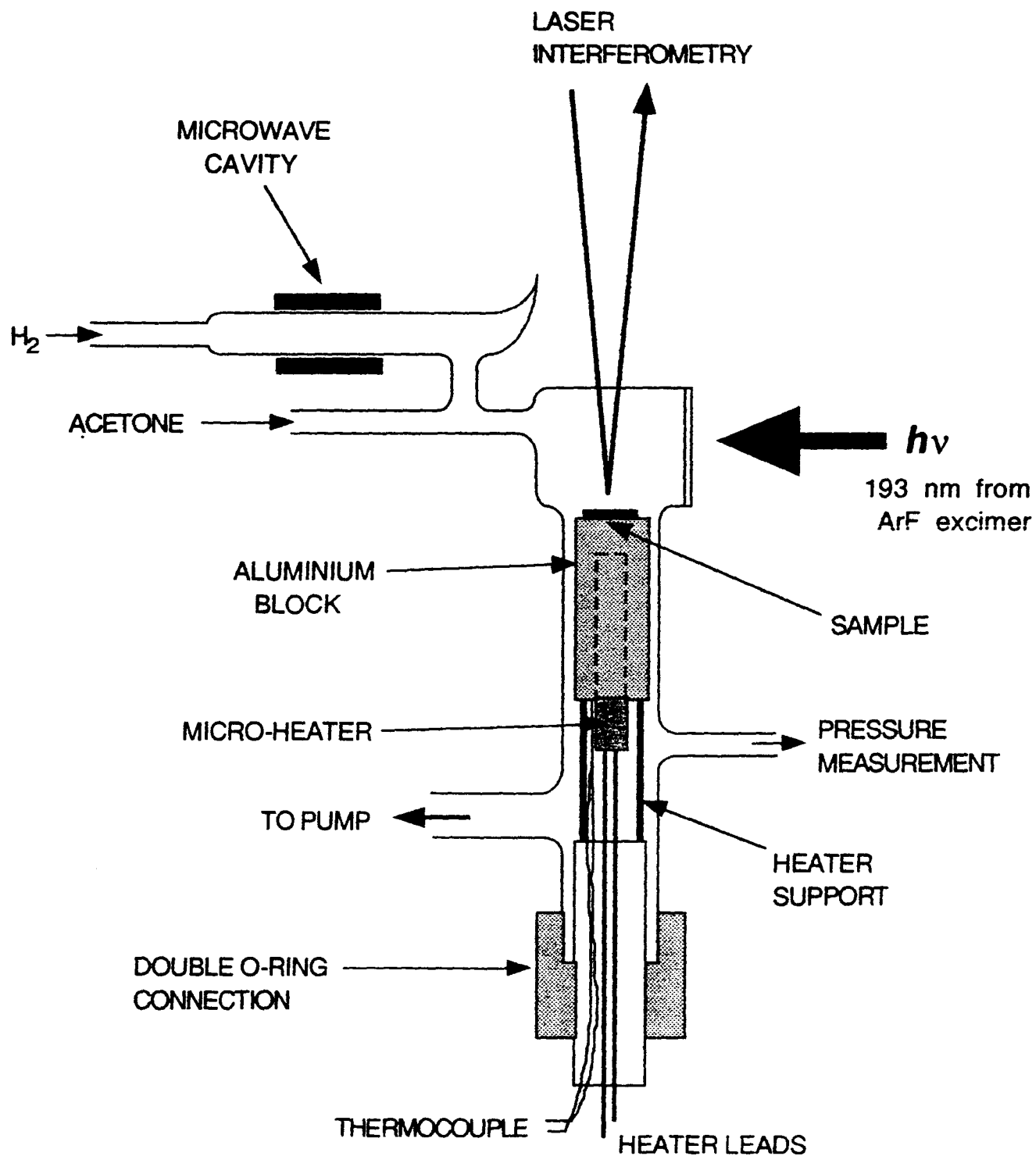


Figure 3.12 Schematic of apparatus used to etch GaAs with methyl radicals produced by the photo-dissociation of acetone.

machined aluminium block, which could be heated internally with a 1/4" diameter Omegalux cartridge heater. Thermal contact between the sample and the block was improved by attaching the wafer with a small quantity of melted indium. The etch rate could be measured with HeNe laser interferometry. The 193 nm line of a Lumonics Model TE 860-2 pulsed excimer laser with an argon/fluorine/helium gas mixture was used as the source of dissociating radiation. The maximum usable pulse rate was 10 Hz.

However, as discussed in greater detail later, etching was not observed with this experimental configuration. Therefore, we returned to a chemical titration to provide a steady flux of etchant species. The reaction chosen was the abstraction of a hydrogen atom from methane:



Although the rate constant is several orders of magnitude lower at room temperature than the rates of the subsequent methyl radical loss reactions, computer modelling indicated that a steady flux of methyls could be attained at higher temperatures. Etching was observed, so this source of methyl radicals was used to obtain the quantitative data reported in this thesis. The apparatus was the same as that used for the iodomethane titrations (Figure 3.8).

3.2.4 Surface analysis

3.2.4.1 SEM/EDX

Scanning electron microscopy was performed on the etched samples using an Hitachi Model S-2300 SEM. Electrons generated at a hot tungsten filament are accelerated with a 20 kV voltage bias, and focused into an approximately 4 nm diameter beam on the sample surface. In the interaction volume, secondary, backscattered and Auger electrons as well as X-rays are produced. The low energy secondary electrons are collected by an electron detector, biased at 200 V. The

primary electron beam is rastered over the sample and the signal from the photomultiplier synchronously scanned onto a cathode ray tube. An image of the surface results from this process. The detector is configured to minimise collection of high energy backscattered electrons, which reduce the achievable resolution.

A Kevex 8000 energy dispersive X-ray spectrometer attached to an older SEM (Hitachi Model S-570) was used to determine the elemental constitution of the etch deposits found on several glass surfaces of the apparatus.

3.2.4.2 XPS

The samples etched with hydrogen atoms and/or methyl radicals were analysed in a Surface Science Laboratory SSX-100 X-ray photoelectron spectrometer. The details of this system have already been described (section 3.1).

3.2.5 Concentrations of methyl radicals from computer modelling

The partial pressures of the methyl radicals generated by the reactions of hydrogen atoms with iodomethane and methane were calculated from the well documented rate constants for these processes and from a knowledge of the hydrogen atom and secondary gas concentrations at the initial point of titration.

Second order rate equations can be solved quite simply by direct integration. When two second order reactions occur consecutively, obtaining integrated rate expressions becomes complex and analytical solutions for the coupled differential equations can be found for only a few special cases. When more than two reactions occur consecutively, obtaining an analytical solution is impossible. However, solutions for such systems of differential equations can be achieved by using numerical techniques.

The rate equation for any second order reaction between reactants A and B can be written as:

$$-\frac{d[A]}{dt} = k[A][B]$$

where k is the second order rate constant and $[]$ denotes concentration. This differential equation describes the slope of the tangent to the curve at the point $([A], t)$ when dt is infinitesimally small. The tangent to the curve is therefore a good approximation of the actual slope over a small range close to that point. Thus, when dt is a small, finite time interval Δt , the slope is also close to the correct value and this continuous function can be approximated by using small, discrete values for $d[A]$ and dt , *i.e.*

$$-\frac{\Delta[A]}{\Delta t} = k[A][B]$$

The accuracy of $\frac{\Delta[A]}{\Delta t}$ is limited by the size of Δt . Therefore, a very good approximation of the rate equation can be obtained by using a sufficiently small time interval, Δt . Although smaller increments require more computing time, erroneous behaviour may be observed with larger time intervals. Detailed discussions of numerical techniques can be found in many texts¹⁰².

The abstraction reaction of hydrogen atoms with methane and the subsequent series of reactions were modelled by such a numerical technique. The most important reactions that occur and their rate constants at 25 °C and 325 °C are given below (the units are $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$) (* At 0.8 Torr¹⁰³).

		k (25 °C)	k (325 °C)
1.	$\text{CH}_4 + \text{H}^\bullet \rightarrow \text{CH}_3 + \text{H}_2$	2.5×10^5	3.1×10^9
2.	$\text{CH}_3^\bullet + \text{H}^\bullet (+\text{M}) \rightarrow \text{CH}_4 (+\text{M})$	$*1.1 \times 10^{12}$	$*1.2 \times 10^{12}$
3.	$\text{CH}_3^\bullet + \text{CH}_3^\bullet \rightarrow \text{C}_2\text{H}_6$	2.6×10^{13}	1.7×10^{13}
4.	$\text{CH}_3^\bullet + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}^\bullet$	7.7×10^3	9.0×10^7
5.	$\text{C}_2\text{H}_6 + \text{H}^\bullet \rightarrow \text{C}_2\text{H}_5^\bullet + \text{H}_2$	4.5×10^7	3.8×10^{10}
6.	$\text{H}^\bullet + \text{H}^\bullet \rightarrow \text{H}_2 (\text{wall})$		$< 1 \text{ s}^{-1}$

The expressions used to calculate the rate constants are given below. Several equations are from the compilation by Tsang and Hampson¹⁰⁴ (the units are cm³ mol⁻¹ s⁻¹).

	uncertainty ($\pm$ %)	reference
$k_1 = 7.48 \times 10^{13} \exp(-49900/RT)$	20	104
$k_2 = 1.50 \times 10^{12} \exp(-25/T) \times P(\text{Torr})$	≈ 30	103, 105
$k_3 = 1.01 \times 10^{15} \times T^{-0.64}$	10–15	104
$k_4 = 2.9 \times T^{3.12} \exp(-4384/T)$	≈ 50	104
$k_5 = 5.5 \times 10^2 \times T^{3.5} \exp(-2600/T)$	≈ 50	104

The rate of recombination of hydrogen atoms is very small on phosphoric acid coated glass surfaces⁷⁵, and the measured flows of hydrogen atoms did not decrease within experimental error over the length of the reaction zone. Therefore, reaction 6 was not included in the model. Also, reaction 4 (the reverse of the initial abstraction reaction) is extremely slow, even at elevated temperatures, and so the loss of methyl radicals by this process will be insignificant. Reaction 5 should not diminish the hydrogen atom concentration significantly, as the concentration of ethane will be small. Subsequent reactions with the products of the processes listed above were also omitted from the model since the concentrations of the species produced are negligible under the conditions present in our flow system, *e.g.* $\text{CH}_3^\bullet + \text{C}_2\text{H}_5^\bullet \rightarrow \text{C}_3\text{H}_8^\bullet$.

Reaction 2 follows third order kinetics below pressures of about 50 Torr, and reaches the second order limit at around 150 Torr¹⁰⁶. Therefore, a pressure dependent expression for k_2 was used in this model, based on the results of Michael *et al.*¹⁰⁵ and Teng *et al.*¹⁰³. The recombination of methyl radicals (reaction 3) is at the second order limit at pressures nearing 1 Torr.

The concentration of methyl radicals will be largely determined by reactions 1, 2 and 3. The rate equation for the change in $\text{CH}_3^\bullet$ concentration with time can therefore be written as,

$$\frac{d[\text{CH}_3^\bullet]}{dt} = k_1[\text{CH}_4][\text{H}^\bullet] - k_2[\text{CH}_3^\bullet][\text{H}^\bullet] - k_3[\text{CH}_3^\bullet]^2$$

and can be approximated by,

$$\frac{\Delta[\text{CH}_3^\bullet]}{\Delta t} = k_1[\text{CH}_4][\text{H}^\bullet] - k_2[\text{CH}_3^\bullet][\text{H}^\bullet] - k_3[\text{CH}_3^\bullet]^2$$

or
$$[\text{CH}_3^\bullet]_{t+\Delta t} = [\text{CH}_3^\bullet]_t - \Delta t \{ k_1[\text{CH}_4][\text{H}^\bullet] - k_2[\text{CH}_3^\bullet][\text{H}^\bullet] - k_3[\text{CH}_3^\bullet]^2 \}$$

Expressions for the above equations were input into a spreadsheet program (Microsoft Excel 3.0a) on an Apple Macintosh Plus computer. This enabled concentration versus time profiles to be calculated for the major species present in such a reaction system, with various initial concentrations, pressures and temperatures. A typical plot is shown in Figure 3.13. Thus, from a knowledge of the residence times in the system and the distance from the methane inlet to the sample position, the partial pressure of methyl radicals at the sample could be determined.

The uncertainty in the concentration of $\text{CH}_3^\bullet$ at any reaction time can be determined by inserting the error limits for the initial parameters into the program. For uncertainties in the temperature and pressure of $\pm 3\%$, $k_1 \pm 20\%$, $k_2 \pm 30\%$, $k_3 \pm 15\%$, $[\text{H}] \pm 15\%$ and $[\text{CH}_4] \pm 5\%$, the error in $[\text{CH}_3^\bullet]$ at the sample position (≈ 11 ms) varies from $\approx \pm 70\%$ at the lowest pressures and temperatures to $\approx \pm 30\%$ for high temperatures and pressures. The gas temperature has the greatest influence on the uncertainty of $[\text{CH}_3^\bullet]$. Negligible error in the modelling program was achieved by reducing the time increment until the calculated concentration of $\text{CH}_3^\bullet$

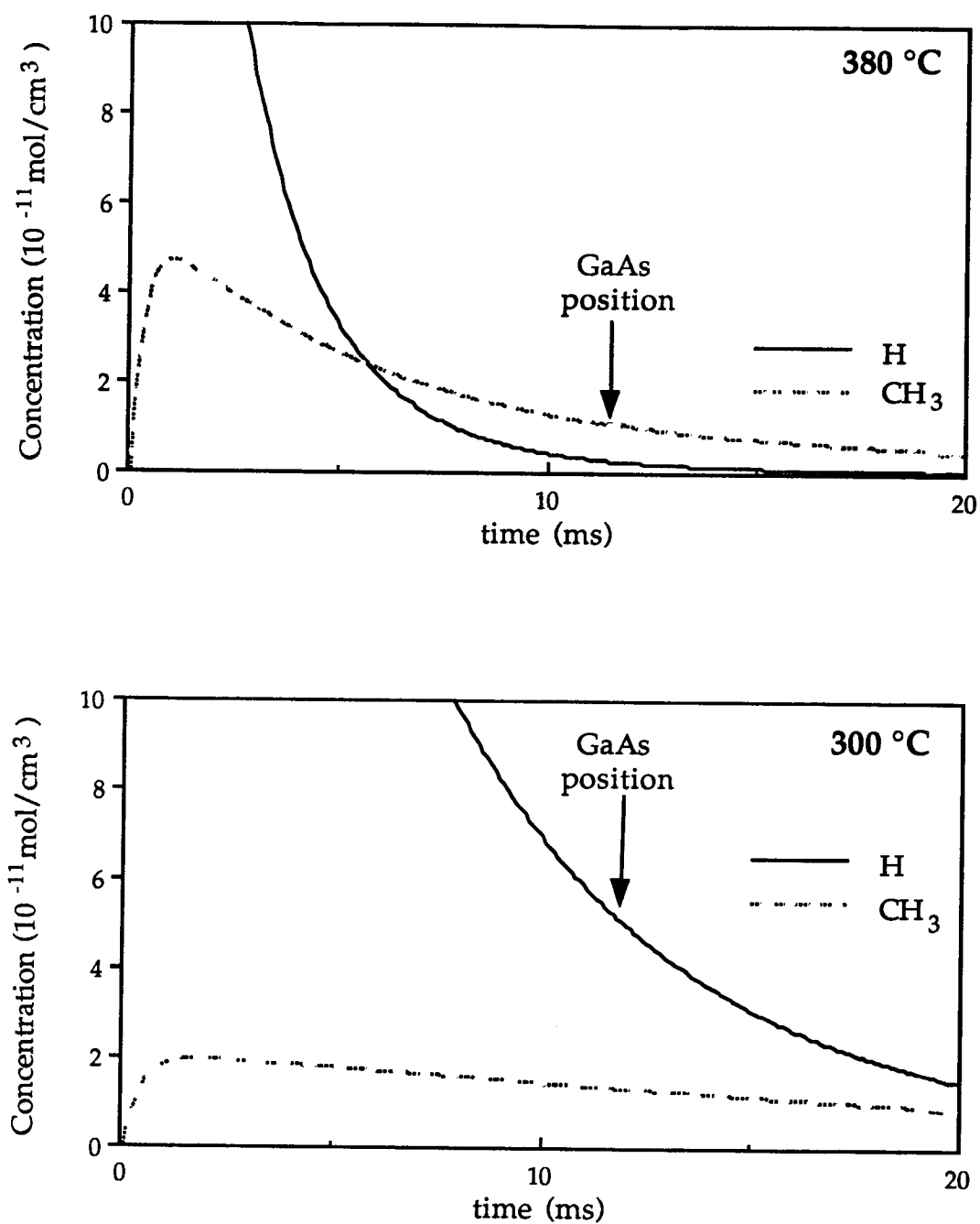


Figure 3.13 Typical concentration versus time plots obtained from a numerical modelling program for H atoms and CH₃ radicals produced by the reaction H + CH₄.

did not change by ± 1 in the fourth decimal place ($\approx \pm 0.005\%$). The assumption that "plug flow" conditions are adhered to will also introduce some uncertainty into the calculated concentration of CH_3^* , but this should be small compared to the error from the rate constants. This will be discussed further in the next section.

3.2.5.1 Validity of modelling

The expression for the concentration of methyl radicals as a function of time (or distance along the reaction tube) assumes that "plug-flow" conditions prevail in this system *i.e.* we are considering a "chunk" of gas with a uniform radial composition and a volume determined by the inner diameter of the flow tube, which is moving with constant velocity along the reaction tube. In this system, the inside diameter of the reaction tube is 2.50 cm and a plug 1 cm long therefore has a volume of 4.91 cm^3 . One residence time is assumed for this plug.

Under the conditions typically used in these experiments (0.8 to 2 Torr) and with the dimensions of the reaction tube (diameter = 2.5 cm), the gas flow is considered to be viscous, *i.e.* the diameter of the tube is much greater than the mean free path of the gas molecules and the flow is determined by collisions between molecules. Viscous flow is characterised by a Knudsen number < 0.01 (the ratio of the mean free path of the molecules to the dimension of the channel through which the gas flows). Thus, the flow is expected to be laminar and can be approximately described by the Poiseuille equation. Laminar flow has a maximum velocity in the centre of the tube, but is slower near the walls because of frictional forces imposed on the gas. However, such flow characteristics only occur when the flow is fully developed *i.e.* when the velocity profile is not position-dependent and there is no turbulent motion of the gas. In the system used here, neither of these criteria are valid. The main flow of gas ($\text{H}_2 + \text{H}$) enters the reaction tube through a 7 mm inner diameter tube at an angle of 90° to the larger tube. With this geometry,

turbulence will persist for some distance along the reaction tube before laminar flow becomes fully developed. In addition, the inlet for the secondary gas is positioned just below the H_2 inlet, and will introduce further turbulence to the gas flow. Turbulence will effectively reduce the parabolic profile of laminar flow, producing a profile with a "flatter" distribution of velocities. To prevent streaming of the secondary gas at higher pressures (*i.e.* longitudinal flow with no radial diffusion) and to improve the mixing (increase the turbulence) of the reacting gases, the secondary gas inlet has four 2 mm radial holes bored into a 6 mm Pyrex tube with a closed end.

The flow characteristics were also examined visually by utilising the characteristic greenish-yellow afterglow of discharged air¹⁰⁷. The hydrogen flow was replaced with air, and the afterglow filled the entire system. Helium was used as the secondary gas, and the effect on the afterglow examined. The pressures of both gases were varied to simulate the range of experimental conditions used in this work. No streaming was observed when the total pressure was kept below approximately 3 Torr. Further confirmation of the efficiency of the mixing was obtained by using discharged air as the secondary gas and helium as the primary flow. The afterglow had disappeared within a few millimetres of entering the main gas flow, indicating that complete mixing had occurred.

Therefore, in this system, the high mixing efficiency and turbulence means that the flow profile will be "flat" and the assumption of plug flow would appear to be justified¹⁰⁸. Calculation of the concentrations of reaction products then simply requires a knowledge of the gas flow velocity and residence time. However, these calculations will only be valid over a distance of a few centimetres from the initial point of mixing. Beyond this, the transition to laminar flow will vitiate the model, and the characteristics of the flow will have to be incorporated into the model. For

a detailed discussion on reaction kinetics for fast flows in long tubes (laminar flow), the reader is referred to Kaufman¹⁰⁹.

CHAPTER 4 RESULTS AND DISCUSSION (I): LOW ENERGY ION BOMBARDMENT

4.1 CARBON ION BOMBARDMENT

4.1.1 Effects of carbon ion bombardment on gallium arsenide

Figure 4.1 shows the XPS survey spectra obtained from a GaAs sample before and after bombardment with a dose of $3 \times 10^{16} \text{ cm}^{-2}$ carbon ions at 100 eV impact energy. The take-off angle was 50° (with respect to the surface). Ion bombardment has reduced the intensity of the semiconductor signals. In addition, there is also a reduction of the oxygen signal, which suggests that the amount of native GaAs oxides on the surface was reduced by the carbon ion bombardment. However, the most significant result of the bombardment is the large increase of the C 1s peak intensity. The normalised surface composition showed that the volume analysed was approximately 70% carbon. A similar composition was observed after exposure to an identical dose of 20 eV carbon ions. The observed reduction of the As and Ga signals implies that the majority of the carbon is deposited on the GaAs surface. Although we expect some incorporation of carbon to have occurred for the higher energy ions, we can make a rough estimate of the overlayer thickness by assuming that the carbon is entirely on the surface. The thickness, t , of the deposited layer is then related to the the ratio of the normalised fractional compositions for carbon and the underlying substrate, $I_{\text{overlayer}}$ and $I_{\text{substrate}}$ by the following expression,

$$t \text{ (nm)} = \lambda \sin \theta \ln(I_{\text{overlayer}} / I_{\text{substrate}} + 1)$$

where θ is the photoelectron take-off angle. This crude approximation assumes that the inelastic mean free paths (λ) of the As and Ga 3d photoelectrons in the carbon overlayer are the same as that of the C 1s photoelectron. Using a value⁵⁵ of 2.8 nm for λ , and correcting for the residual carbon contamination, the thickness of the carbon layer deposited on the GaAs surface is estimated to be approximately

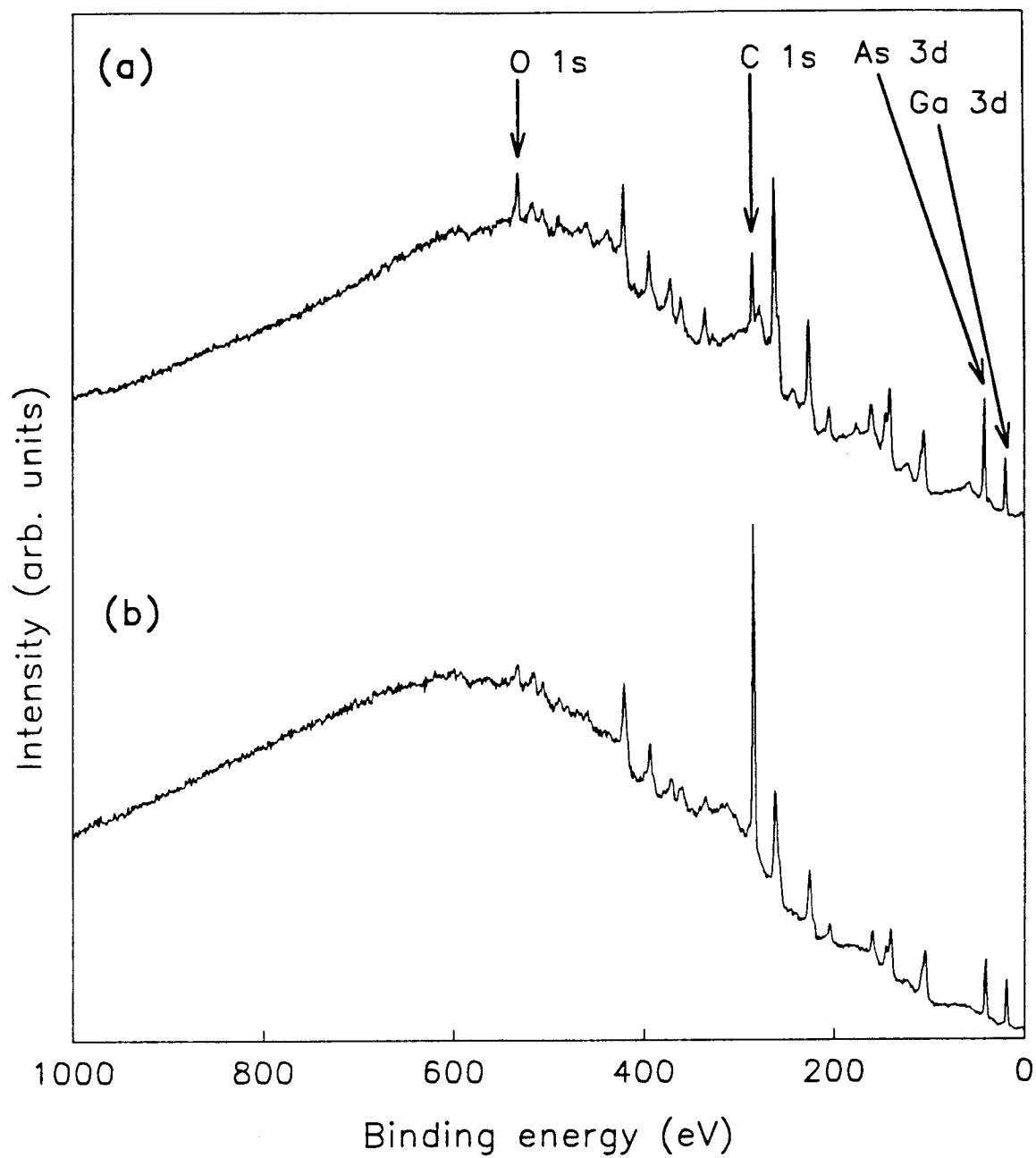


Figure 4.1 XPS survey spectra obtained from a GaAs sample (a) after an HF etch and (b) after bombardment with a dose of $3 \times 10^{16} \text{ cm}^{-2}$, 100 eV C^+ ions.

2.0 nm. For a sticking coefficient of 1.0, a dose of $3 \times 10^{16} \text{ cm}^{-2}$ carbon ions should produce a layer 2.8 nm thick (assuming the density of carbon to be 2.1 g cm^{-3}). Therefore, the sticking coefficient of the carbon ions is quite high (approximately 0.7) and the self-sputter yield is low in this energy range *i.e.* deposition is the dominant process. This is what would be expected from such low energy reactive-ion bombardment, where the energy of the collision cascade generated by the impact will generally be insufficient to cause ejection of material from the surface¹¹. For bombardment with 500 eV carbon ions (dose = $3 \times 10^{16} \text{ cm}^{-2}$), the deposited carbon layer was estimated to be only about 1.5 nm thick. Although the self-sputtering yield increases with bombardment energy, the sputter yields of carbon by Ne^+ , Ar^+ , Kr^+ and Xe^+ at 400 eV are only about 0.1¹³. Therefore, such a process is unlikely to contribute significantly to the reduction of the deposited layer thickness. However, the 500 eV ions are expected to have a greater penetration range into the semiconductor. Since the probability of a photoelectron escaping from the surface without having undergone an inelastic collision decreases exponentially with increasing depth below the surface, a larger fraction of sub-surface carbon would reduce the measured C 1s XPS signal. It is also possible that at these higher energies, the consumption of carbon atoms by a "chemical sputtering" process could be increased, *i.e.* the formation of carbon-semiconductor bonds may enhance the sputter rate relative to the bare GaAs surface, prior to the accumulation of a carbon overlayer.

Figure 4.2 shows the plasmon energy loss spectrum for the C 1s photoelectrons (same sample as in Figure 4.1). This spectrum is qualitatively similar to that reported by Kasi *et al.*¹¹⁴ in a study of low energy ion deposition of diamond-like carbon films. There have been a considerable number of reports on the characterisation of these films by XPS and other photoemission techniques¹¹⁵. Also shown for comparison in Figure 4.2 are the electron energy loss spectra of

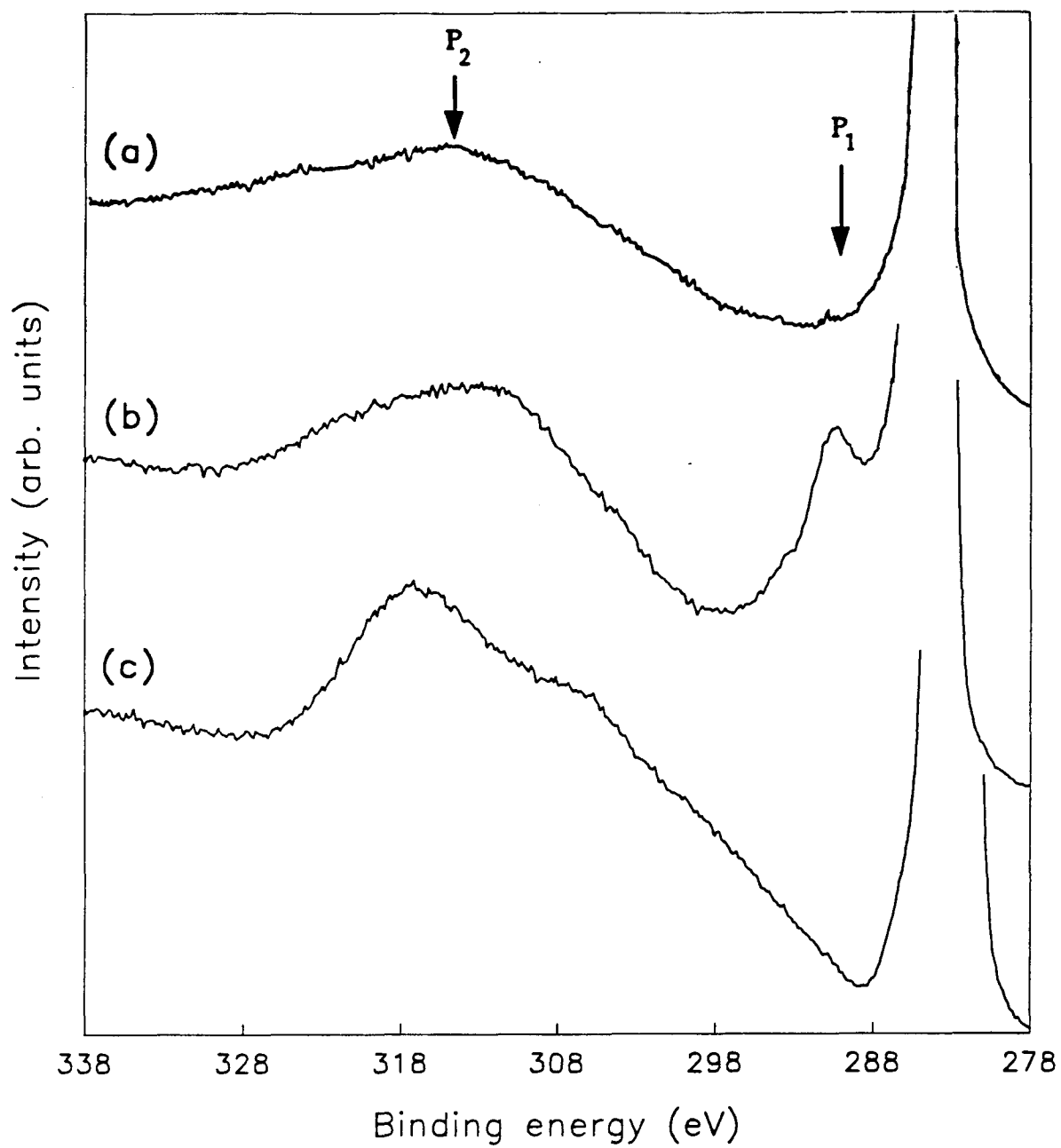


Figure 4.2 C 1s plasmon loss structures for (a) carbon deposited on GaAs from a dose of $3 \times 10^{16} \text{ cm}^{-2}$, 100 eV C^+ ions, (b) graphite and (c) diamond (111)A.

graphite and diamond ((111), type IIa) previously obtained in this laboratory. The small peak labelled P₁, which is present in the spectrum for graphite, is caused by the interactions of the photoelectron with π electrons (π plasmon) in the solid. Since diamond has no π -type electrons (sp^3 versus sp^2 hybridised), this peak is absent in its spectrum. Thus, the deposited carbon appears to be predominantly sp^3 hybridised. The broader peak (P₂) on all three spectra is due to bulk plasmon losses, and its energy (relative to the C 1s peak position) is determined by the electron density in the solid. The energy, E, is given by¹¹⁶,

$$E = \hbar\omega_p/2\pi = \hbar/2\pi \times \sqrt{4\pi e^2 n / m^*}$$

where $\hbar$ is Planck's constant, e is the electron charge, n is the electron density, and m^* is the effective electron mass, which can be approximated by the free-electron mass. The bulk plasmon energy is 31 eV for the ion-deposited carbon, which gives an electron density of $6.8 \times 10^{23} \text{ cm}^{-3}$. There are 4 valence electrons per carbon atom, so the density of the film is estimated to be 3.4 g cm^{-3} , which is close to that of diamond (3.53 g cm^{-3}). This value brings our estimation of the sticking coefficient closer to unity. Although the plasmon loss spectra indicate that the deposited carbon is diamond-like (in terms of density and bonding), the broad, featureless Raman scattering peak centered at 1580 cm^{-1} in Figure 4.3 is consistent with an amorphous film¹¹⁷. Work in other laboratories^{111,118} has shown that carbon films produced by low energy carbon ion deposition are also hard and chemically inert.

High resolution XPS spectra of the As and Ga 3d regions of GaAs samples after bombardment with 20, 100 and 500 eV carbon ions are shown in Figure 4.4. Even at impact energies as low as 20 eV, it is evident from the significant broadening of the peaks that the incident carbon ions interacted extensively with the GaAs surface.

As discussed in Chapter 1, accurately resolving the individual chemical contributions of a peak is extremely difficult when the chemical shifts and spin-

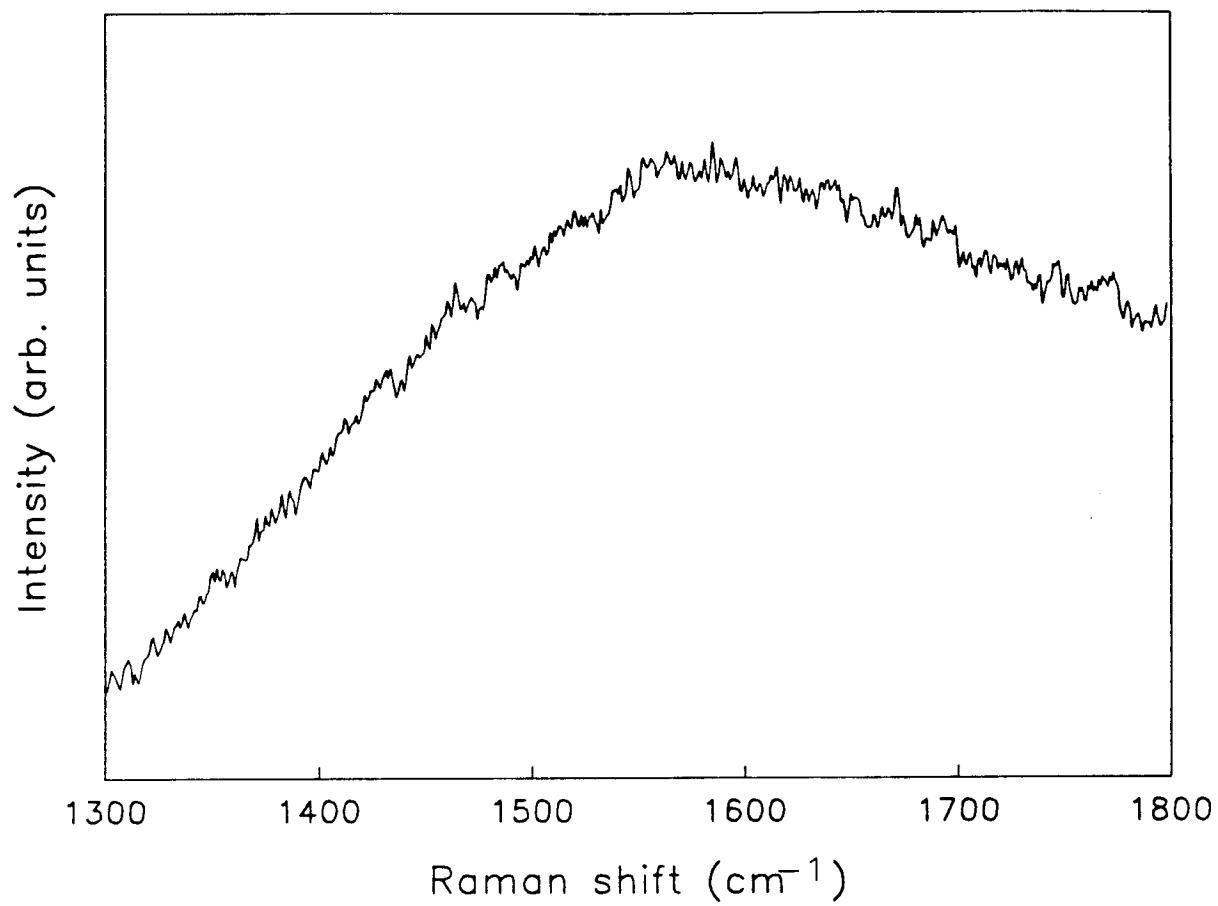


Figure 4.3 Raman scattering spectrum from carbon residue deposited on GaAs by a dose of $5 \times 10^{16} \text{ cm}^{-2}$, 150 eV C^+ ions.

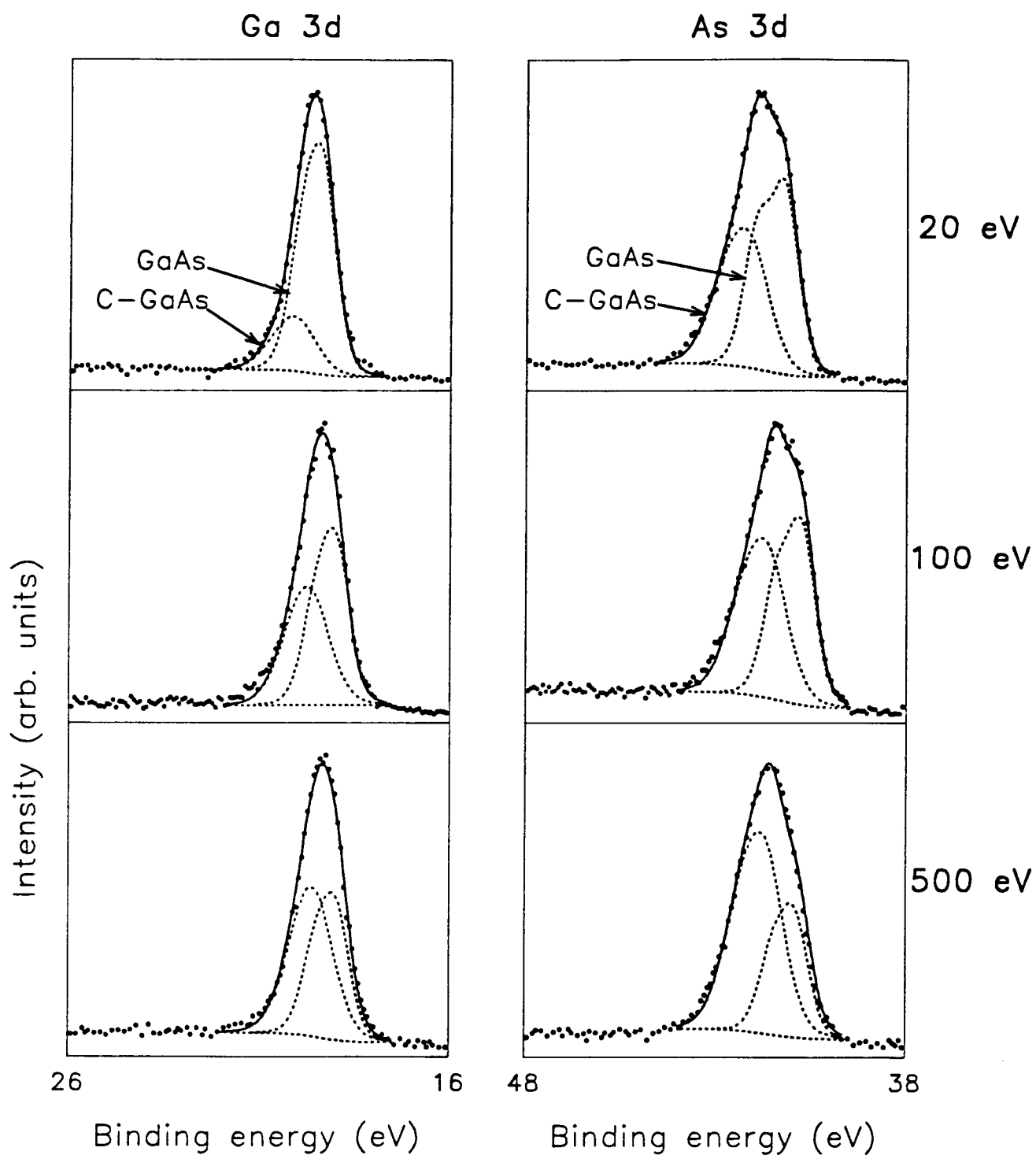


Figure 4.4 High resolution As and Ga 3d spectra from GaAs samples exposed to 20, 100 and 500 eV C^+ ions (all doses = $3 \times 10^{16} \text{ cm}^{-2}$, take-off angle = 50°). The data has been fitted to show the contributions of C-GaAs species to the spectral envelopes. The 3d doublets have been combined for clarity.

orbit splittings are small. Such is the case for the As and Ga 3d peaks where the spin-orbit splittings are 0.69 and 0.48 eV, respectively. Ideally, the spectra are compared to known standards, but in the present situation no reference data on arsenic or gallium carbides was available. An attempt was made to obtain such data by bombarding elemental arsenic and gallium samples with carbon ions. Even after prolonged cleaning by argon ion bombardment, the presence of native oxides rendered the spectra useless. Therefore, the spectral envelopes were fitted by assuming that they were composed of a bulk GaAs phase with a fixed peak width, with the remainder attributable to a higher binding energy carbon-GaAs phase. Based on the peak widths (FWHM) of the As 3d doublet at this spectrometer resolution, the doublet peaks for the bulk-GaAs component were held at 0.8 eV. For consistency and to enable the effects of different ion energies to be usefully compared, the widths for the C-GaAs peaks were kept at 1.20 eV and the chemical shifts unchanged from sample to sample. These broad peaks probably encompass several chemical states plus contributions from the damaged semiconductor. However, in this work, these could not be meaningfully resolved. For the remainder of this thesis, these peaks will often be referred to as arising from "carbides".

As can be seen from Figure 4.4, bombardment with 100 and 500 eV ions increased the contribution these C-GaAs species made to the overall peak, *i.e.* these higher energy carbon ions cause greater damage in the near-surface region of the semiconductor. Such damage includes Ga-As bond cleavage with the displacement of As and Ga atoms from their lattice positions, implantation of carbon atoms in interstitial sites and lattice vacancies, and the formation of C-GaAs bonds. The percentage of the XPS signal derived from the C-GaAs and GaAs species as a function of ion energy is summarised in Table 4.1.

Table 4.1 Percentage of components from peak-fitting of As and Ga 3d spectra as a function of ion impact energy (50° take-off angle).

Peak	Species	20 eV	100 eV	500 eV
Ga 3d	C-GaAs	22	46	55
"	GaAs	78	54	45
As 3d	C-GaAs	44	55	66
"	GaAs	56	45	34

As the bombarded areas were much smaller than the sample size, exposed samples were transferred *in vacuo* to a remote spectrometer with microanalysis capabilities. While the pressures at all stages of the transfer procedure were kept below 1×10^{-7} Torr, the accumulation of 1–2 monolayers of carbonaceous contamination normally occurred. Therefore, determination of the beam-spot location above the background signal was difficult when the ion doses were below approximately 2×10^{16} ions cm^{-2} . For this reason, we were unable to investigate the initial stages of the ion bombardment ($1\text{--}9 \times 10^{15}$ ions cm^{-2}) where most of the interaction with the semiconductor will occur. Figure 4.5 shows the effect of increasing the dose of bombarding ions from 2×10^{16} to 3×10^{16} ions cm^{-2} on the As and Ga 3d peak widths. Above about 2×10^{16} ions cm^{-2} only a slight increase in peak broadening was observed, which is consistent with the formation of a "protective" overlayer of carbon on the surface.

The survey spectrum in Figure 4.1 also shows that the stoichiometry of the semiconductor has been altered: the intensity of the arsenic signal is reduced in relation to the gallium signal. Gallium enrichment of the GaAs surfaces was also observed after bombardment with 20 and 500 eV carbon ions. As expected, the extent of the arsenic depletion increased with increasing ion energy. The As/Ga ratios as a function of ion energy are shown in Table 4.2. The experimental error is approximately 10%.

Since the accumulation of carbon on the surface should ultimately block the interaction between the ions and the underlying semiconductor, most of the arsenic depletion (particularly for the lower energy ion bombardment) probably occurred during the initial stages of the bombardment. Preferential removal of arsenic from GaAs caused by low energy ion bombardment has also been observed by other workers¹¹⁹. Arsenic depletion by up to 50% in the near surface region of GaAs exposed to 100 eV N_2^+ ion bombardment was also observed¹²⁰.

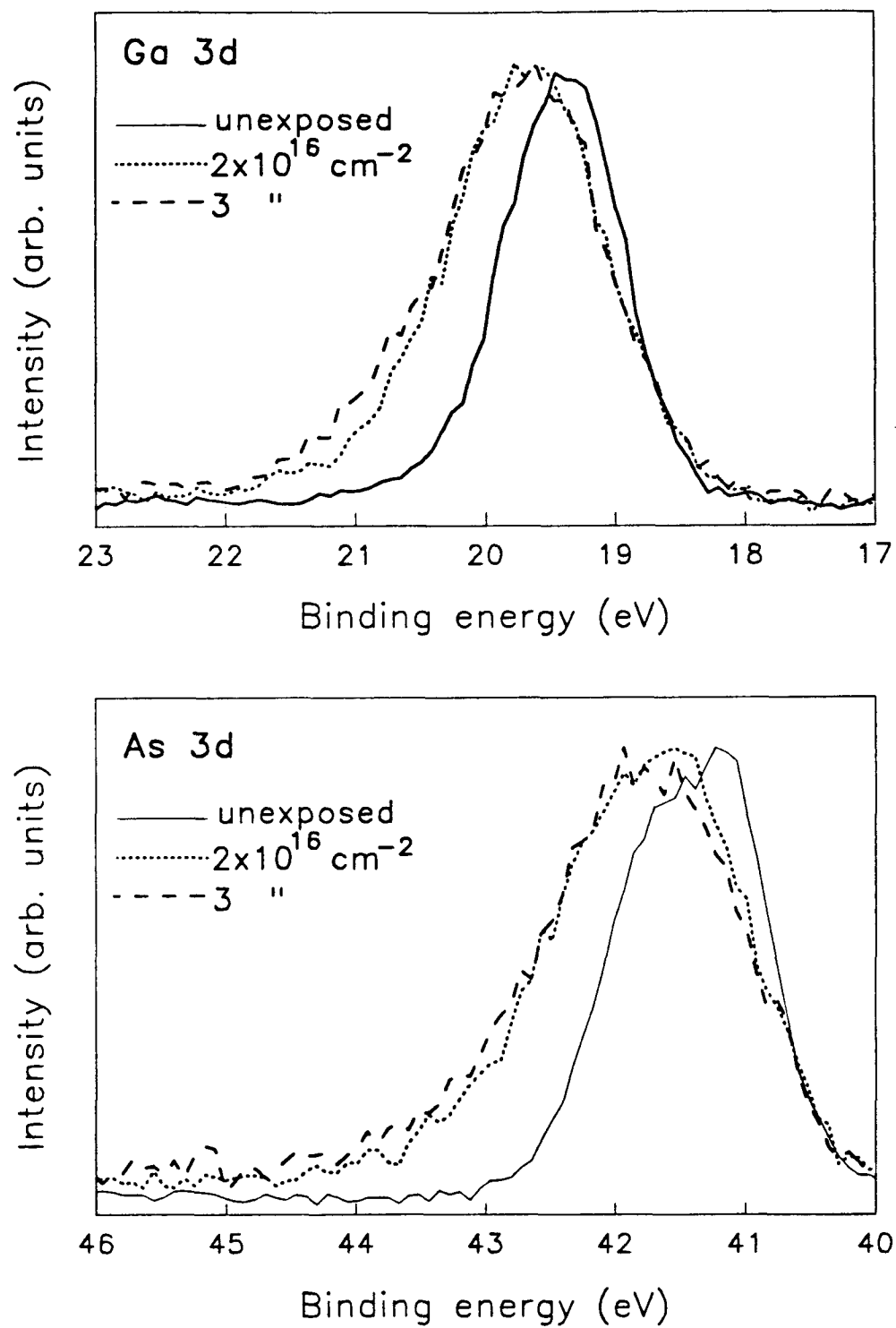


Figure 4.5 As and Ga 3d spectra showing the effect of increasing the dose of 100 eV C^+ ions on the peak broadening.

Table 4.2 As/Ga ratios of carbon ion bombarded GaAs surfaces as a function of ion impact energy (Take-off angle = 50°, dose = $3 \times 10^{16} \text{ cm}^{-2}$) (* the initial ozone/HF prepared GaAs surfaces were arsenic rich).

	unexposed	20 eV	100 eV	500 eV
As/Ga ratio	1.12*	1.00	0.77	0.63

There are several processes which lead to ion bombardment induced changes in the surface composition of multicomponent solids¹²¹. Preferential sputtering occurs when the constituents of an alloy or compound have different ejection probabilities. Based on simple momentum and energy transfer, one would intuitively expect that preferential sputtering of the lighter component in a compound would occur, but there are as many examples known where alloys lose a heavier mass constituent as where they lose a lighter component. Such is the case for GaAs. However, when the surface binding energies of the constituents are considered, a good correlation with the known data is found. The binding energy of a surface atom in a material depends on its position and bonding to neighbouring atoms, and can be reasonably approximated by the heat of vaporisation of the elements. When surfaces are bombarded with "reactive" ions, the situation is complicated further by the formation of chemical species (*e.g.* carbides), which are also likely to have different binding energies. From the data presented here, it is not possible to say whether carbide formation has enhanced the depletion of arsenic relative to a purely physical interaction.

Composition changes resulting from ion bombardment are also significantly influenced by transport processes, such as thermal diffusion, radiation enhanced diffusion, recoil implantation or cascade mixing, thermal surface segregation, and radiation induced segregation. Although it is possible to say qualitatively which component will be enriched at the surface as a result of ion bombardment, the extent of this enrichment cannot yet be predicted. Detailed discussions on this phenomenon have been given by Kelly¹²².

Since the arsenic depletion is quite severe for samples bombarded with 100 and 500 eV ions, it is probable that the lower binding energy, "bulk" GaAs peaks in Figure 4.4 also contain contributions from a non-stoichiometric, damaged GaAs layer. However, the signals from this gallium rich, damaged layer could not be

distinguished from the bulk GaAs signals by peak-fitting the XPS data, and there was no strong evidence for a lower binding energy shoulder on the Ga 3d peaks that would be attributable to metallic gallium. On the other hand, samples bombarded with 20 eV ions showed minimal arsenic depletion, and since the ion induced damage should also be small, we expect the bulk GaAs substrate to be the major contribution to the lower binding energy peaks shown in Figure 4.4.

Figure 4.6 is a comparison of the As and Ga 3d spectra obtained from a 20 eV irradiated sample at photoelectron take-off angles of 50° and 20°. The percentage of the C-GaAs component is significantly larger at the shallower sampling depth, implying that the carbon-GaAs interaction region is near the surface as expected. If we suppose that for this sample, there is a C-GaAs layer of uniform composition on an undamaged GaAs substrate, and use the equation and assumptions described above (with a value of 2.8 nm for the IMFP⁵⁵), calculation of the thickness of this interaction layer for both angles gives a value of about 0.8 nm. However, for the 100 eV and 500 eV bombarded samples, the spectra obtained at both take-off angles were essentially identical. This implies that the damaged, C-GaAs surface layer is fairly uniform to a depth, which combined with the carbon overlayer, is greater than the sampling range of the XPS technique. For example, at a take-off angle of 50°, 95% of the XPS signal would come from a surface layer 6.4 nm thick. Table 4.3 summarises the percentage contribution of the "bulk" and C-GaAs components from fitting the XPS peaks obtained at a take-off angle of 20°. Comparison with Table 4.1 shows the similarity for 100 and 500 eV bombardment.

These results are in reasonable agreement with previous reports on the depths of damage caused by low energy ion bombardment. For example, a medium energy ion scattering study¹²³ of the depth distribution of bombardment induced defects in crystalline silicon found that with 510 eV argon ions, the top 4.3 nm of

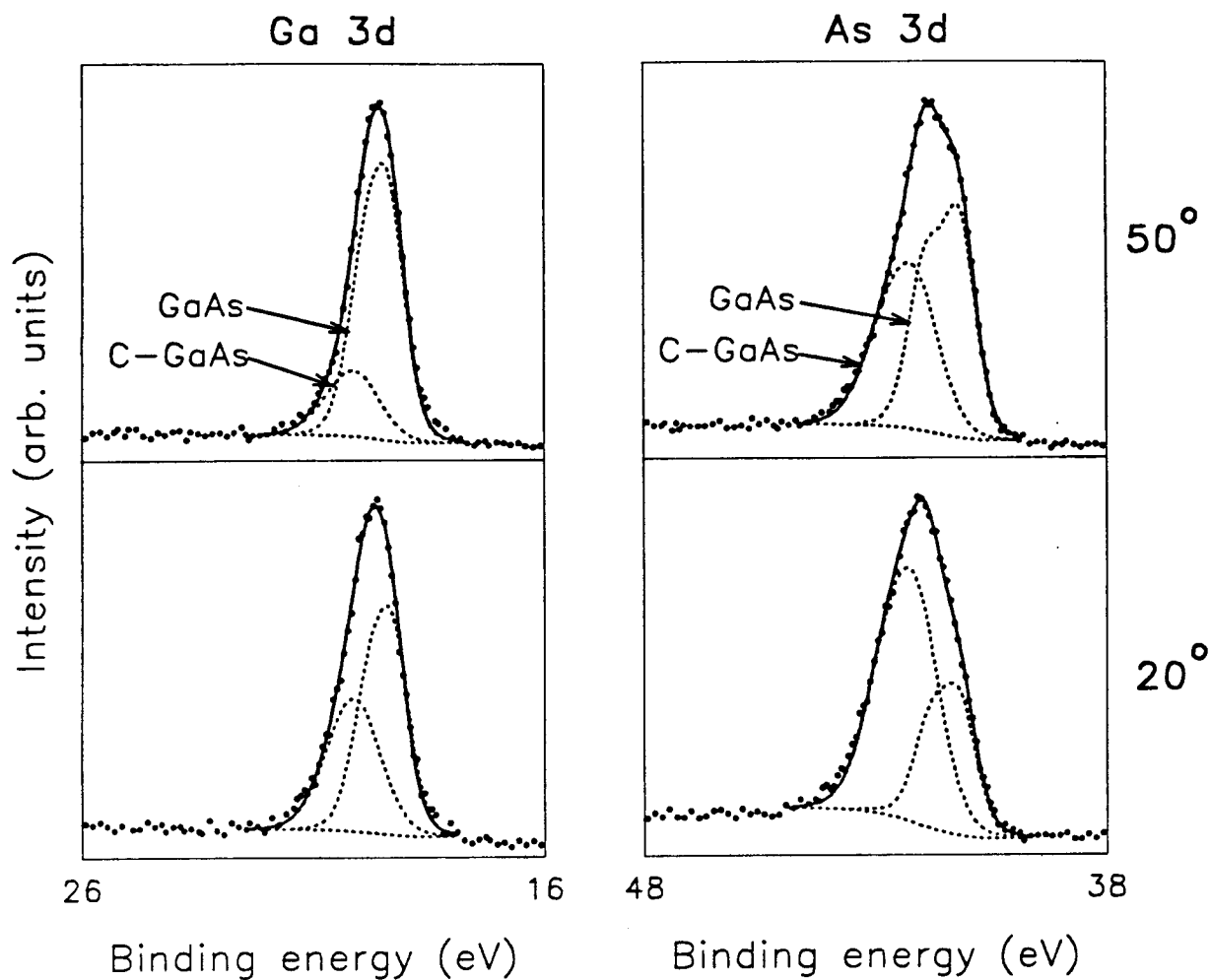


Figure 4.6 Comparison of As and Ga 3d spectra obtained at two take-off angles, for a GaAs sample exposed to a dose of $3 \times 10^{16} \text{ cm}^{-2}$, 20 eV C^+ ions. (take-off angles = 20 and 50°).

Table 4.3 Percentage of components from peak-fitting of As and Ga 3d spectra as a function of ion impact energy (20° take-off angle).

Peaks	Species	20 eV	100 eV	500 eV
Ga 3d	C-GaAs	59	45	55
"	GaAs	41	55	45
As 3d	C-GaAs	67	43	64
"	GaAs	33	59	36

the silicon was amorphised after exposure to a dose of $1 \times 10^{16} \text{ cm}^{-2}$. With the same dose of 60 eV ions, the depth of the amorphous layer was 2.0 nm.

Surface Fermi level shifts towards the valence band maximum (VBM), were also observed with XPS. For 20, 100 and 500 eV bombardments, both the As and Ga 3d bulk GaAs component peaks were shifted by *ca.* 0.1, 0.3 and 0.4 eV, respectively, closer to the VBM. Although it is possible that these shifts were caused by charging on the thin dielectric carbon deposit, this was ruled out by two pieces of evidence. Firstly, charging causes shifts away from the VBM *i.e.* the escape velocity of the photoelectrons is reduced by the positive surface charge and they therefore appear to have a higher binding energy. Secondly, the C 1s peak occurred at the standard reference position of 284.6 eV indicating a lack of surface charging. However, only the shifts measured for the 20 eV irradiated samples are meaningful, since the amount of damage caused by this low energy ion bombardment was small, and the arsenic depletion was not extensive. At higher energies, the shifts may also be caused by a damaged, gallium rich layer. Lowering of the Fermi level can be attributed to the creation of *p*-type defects at the surface. In the present case, this could be a result of carbon atoms occupying the near surface arsenic lattice vacancies, and acting as acceptors.

4.1.2 Effects of carbon ion bombardment on indium phosphide

An ultrathin (4 nm) InP/InGaAs sample structure was used in this study to take advantage of the angle dependent surface sensitivity of XPS. As described in Chapter 2 (section 2.1.1), high resolution XPS analysis of the In and P in the first layer will show the interaction of the ions with this layer, while analysis of the As and Ga of the underlying layer will show if damage has propagated through the first layer. Also, the thickness of the InP layer can be calculated from the phosphorus to arsenic signal intensity ratios as a function of the photoelectron

take-off angle. From the change in thickness caused by bombardment, the sputtering yield can also be estimated.

Prior to the ion bombardment experiments, the InP/InGaAs sample structure was characterised with XPS to determine its suitability for this work. A chip of the wafer was cleaned (Section 3.1.1) and analysed by angle dependent XPS. The P 2p and As 3d XPS spectra obtained at take-off angles of 30° and 90° are shown in Figure 4.7. All spectra were accumulated for the same acquisition time and with the same spectrometer settings. The increase of the P/As ratio when the sampling depth was decreased (by decreasing the take-off angle from 90° to 30°) is consistent with the presence of an InP layer on top of an InGaAs layer.

It is possible to estimate the thickness (t) of the overlayer from the following equation:

$$t = \lambda \sin\theta \ln(I_P / I_{As} + 1)$$

where I_P and I_{As} are the normalised element fractions in the analysis volume. This simplified calculation assumes that the inelastic mean free path of the As 3d photoelectron is the same in both layers and is the same as that for the P 2p electrons. Detailed calculations show that this assumption is not unreasonable⁵⁵. A value of $\lambda = 2.8$ nm was used. The average thickness of the InP overlayer was calculated to be *ca.* 4.5 nm. This agrees well with the original estimate of the BNR-fabrication laboratory.

Figure 4.7 also shows that the constituent peak widths of the two semiconductors in the ultrathin layer structure are similar to those of normal, bulk semiconductors. Furthermore, negligible quantities of surface native oxides were observed on the HF etched surface. The InP layer was, however, found to be indium rich (average P/In ratio = 0.73), even when the indium contribution from the InGaAs layer was taken into account.

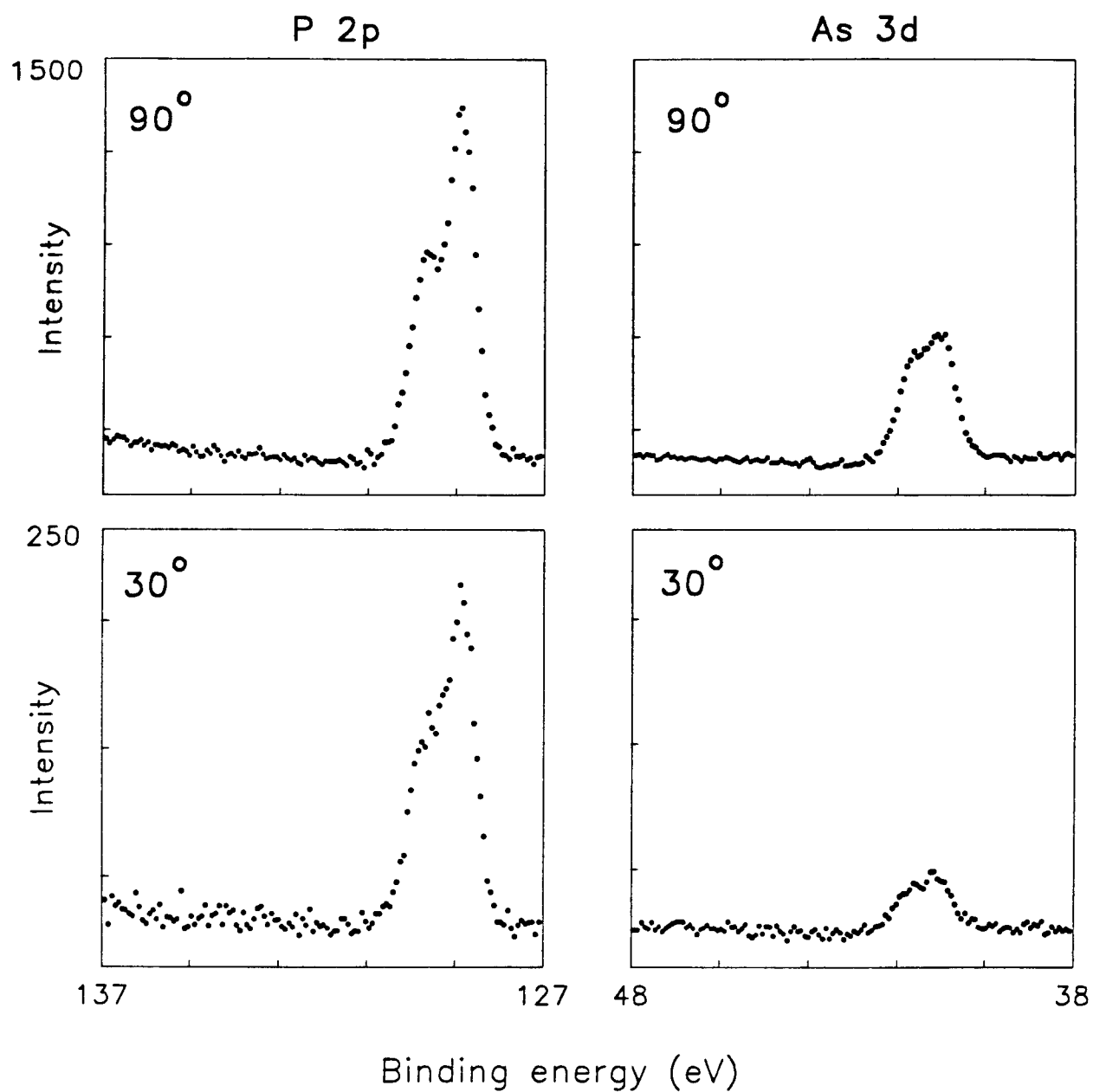


Figure 4.7 P 2p and As 3d spectra from a clean InP/InGaAs sample showing the effect of decreasing the take-off angle on the relative P and As intensities.

Figure 4.8 shows the survey spectra obtained from an InP/InGaAs sample before and after bombardment with a dose of $3 \times 10^{16} \text{ cm}^{-2}$ carbon ions at 100 eV impact energy. As with the bombardment on GaAs, the most obvious difference is the drastic increase of the C 1s peak intensity and the reduction of the semiconductor signals. The thickness and nature of the deposited carbon were essentially identical to the carbon layers on GaAs (same dose).

High resolution XPS spectra of the P 2p and In 3d_{5/2} regions from a sample before and after bombardment with 20 eV carbon ions are shown in Figure 4.9. Similar to the bombardment on GaAs, the substantial peak broadening indicates that extensive interaction with the surface occurred, even at this low energy. The width of the spectral peaks suggest the presence of many different chemical environments for the phosphorus and indium in the near surface region of the bombarded sample. For GaAs, the peak broadening could be easily fitted with the addition of a moderately broad, higher binding energy peak, which encompassed all of the possible contributing species. However, because the ion induced broadening of the P 2p peaks was so extreme, several additional peaks would be needed to fit the spectral envelope. Since the number of fitting parameters would also increase dramatically, development of a consistent fitting procedure is difficult and potentially meaningless without standard reference spectra. For the remainder of this thesis, this peak broadening will be attributed to an In-P-C alloy structure, and will be shown by simply overlaying the peaks from unexposed samples. For comparison, the P 2p spectra of InP subjected to 3 keV Ar⁺ bombardment at an incident angle of 30° is included in Figure 4.9. Although the carbon ion energy was almost two orders of magnitude lower than that of the argon ions, the peak broadening observed from the C⁺ bombarded surface was much larger than that from the Ar⁺ bombarded surface. This shows that in addition to the changes induced in the semiconductor by collision and related energy transfers,

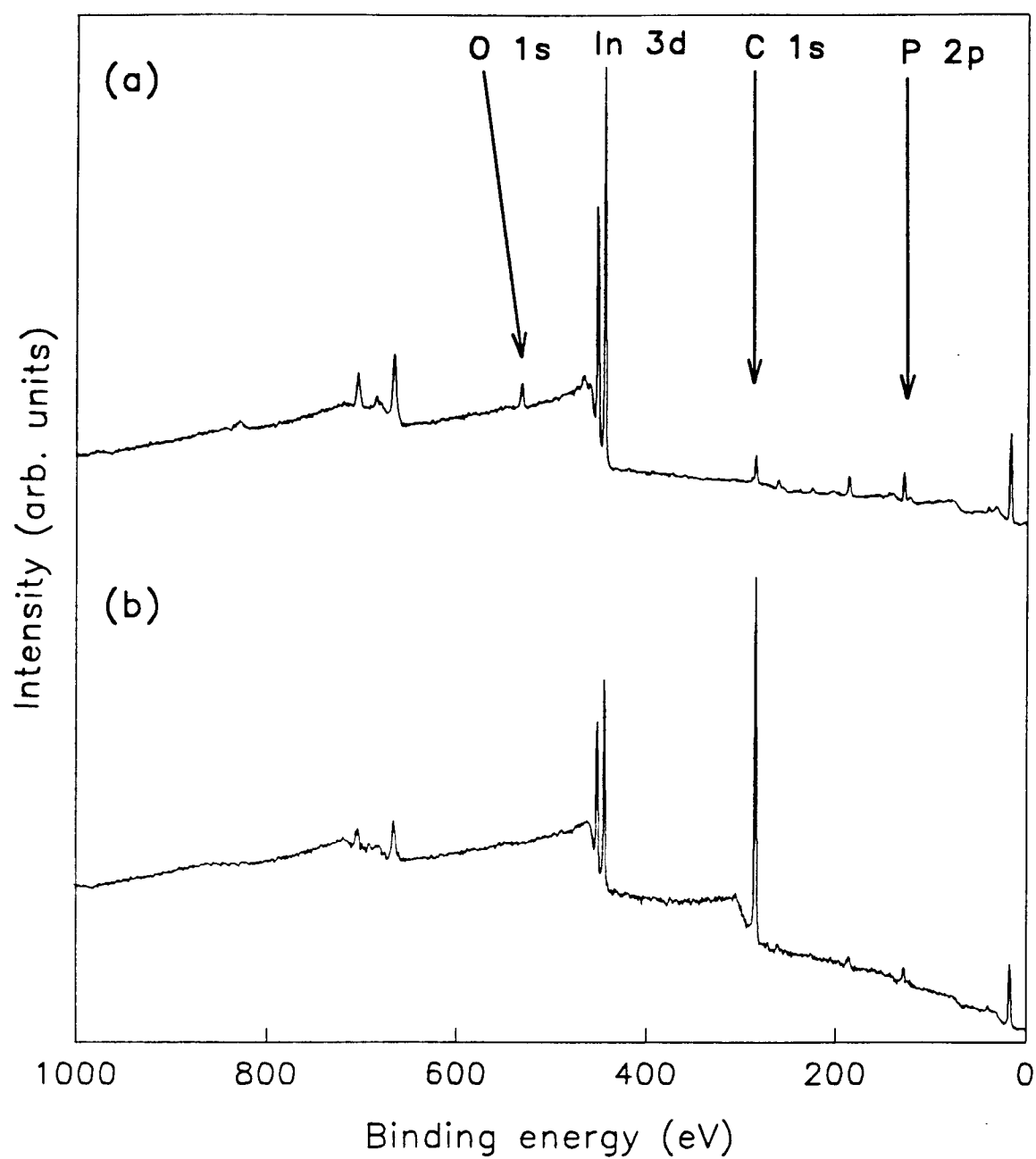


Figure 4.8 Survey spectra of an InP/InGaAs sample (a) before and (b) after bombardment with a dose of $3 \times 10^{16} \text{ cm}^{-2}$, 100 eV C^+ ions.

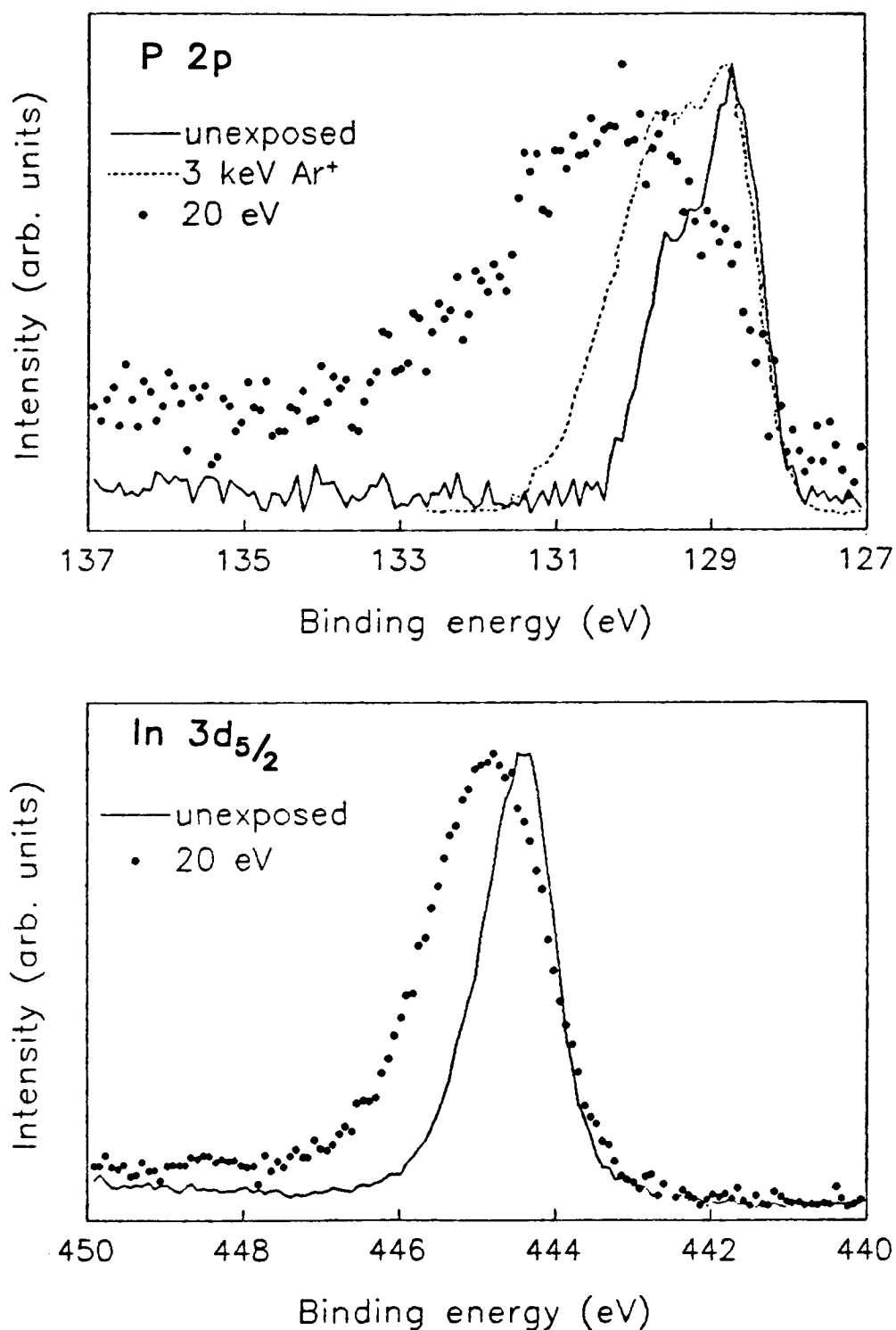


Figure 4.9 P 2p and In 3d_{5/2} spectra showing the effect of bombardment with 20 eV C⁺ ions on an InP/InGaAs sample (dose = $3 \times 10^{16} \text{ cm}^{-2}$, take-off angle = 20°). Also shown is the P 2p spectrum from an InP sample bombarded with 3 keV Ar⁺ ions (incident angle 30° $\approx$ 1.5 keV).

such as the collapse of the InP crystal and the formation of In-In and P-P bonds¹²⁴, the incorporation of carbon in the damaged InP led to the formation of In-C and P-C bonds.

As expected, the degree of damage induced by ion bombardment increases with the impact energy. Figure 4.10 shows the P 2p and In 3d_{5/2} spectra obtained from samples bombarded with 20 eV and 100 eV carbon ions. The angle of analysis was 50°, and the dose was 3x10¹⁶ cm⁻² for both samples. After bombardment with the higher energy ions, the amount of the In-P-C alloy components has increased while the peak attributable to phosphorus bonded to indium in an InP environment has diminished. Thus, the amount of damage generated by the incident carbon ions is severe.

XPS compositional analysis also indicates that the bombardment caused some sputtering of the InP. The P/As and P/In ratios are listed in Table 4.4. An accurate measurement of sputter yields is difficult because the accumulation of carbon on the surface may reduce the ability of C⁺ ions to sputter InP. Furthermore, preferential sputtering of phosphorus over indium was also observed which makes the estimation of the InP sputter yield even more complicated. The In content in the InP overlayer can be determined from the relative amounts of In, Ga, and As, by assuming that the composition of the InGaAs layer was not changed by the bombardment. The composition of the underlying layer is In_{0.53}Ga_{0.47}As, so the percentage of In in the InP layer is given by:

$$\% \text{In(InP)} = \% \text{In(total)} - \% \text{As} \times 0.53$$

In the present study, we estimated that with a carbon ion dose of 3x10¹⁶ cm⁻², bombardment with 20, 100 and 500 eV C⁺ ions removed approximately 0.3, 0.9 and 3.3 nm, respectively, from the InP layer. Compared to the P/In ratio of the InP overlayer for the unexposed sample (normalised to 1.0), the ratios are 0.87, 0.68, and

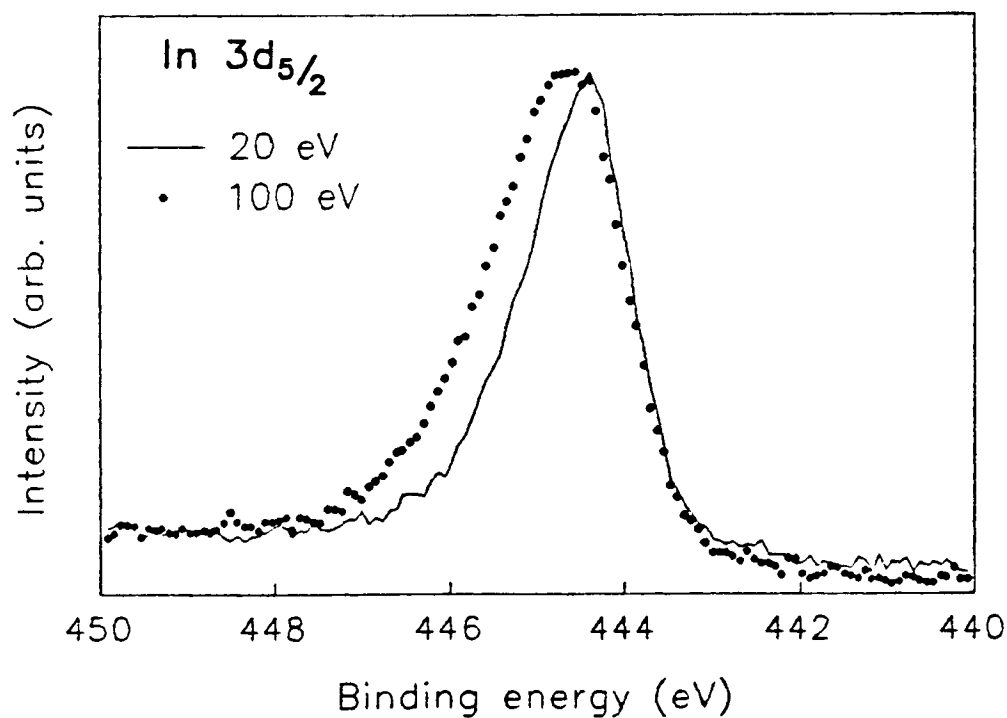
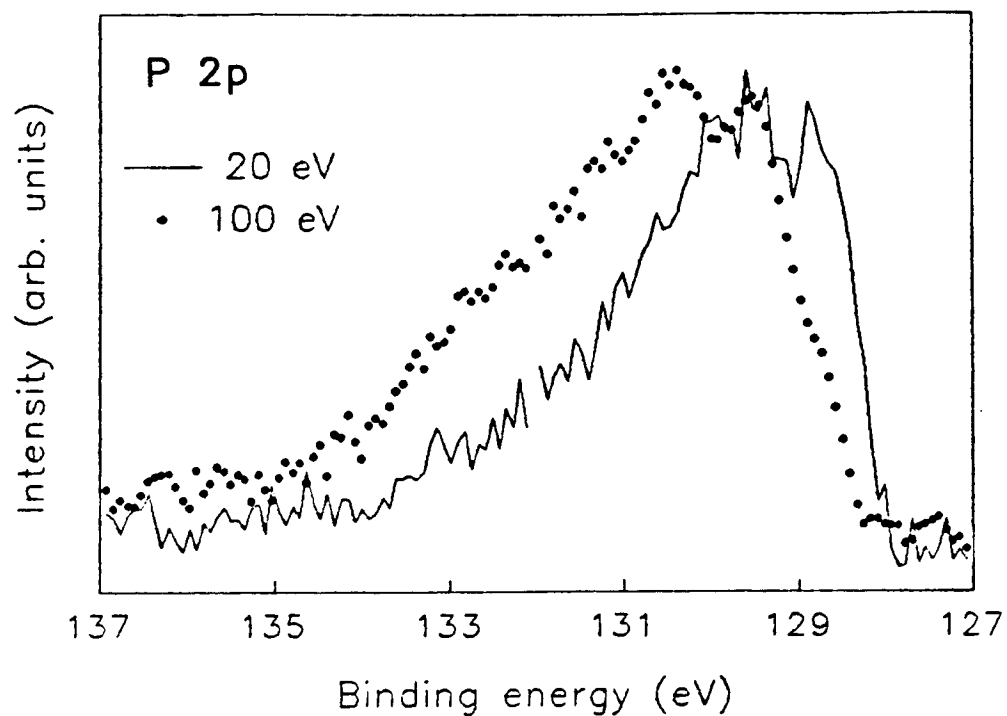


Figure 4.10 Effect of increasing C^+ kinetic energy from 20 to 100 eV on the P 2p and In 3d_{5/2} peak widths of InP/InGaAs samples (dose = $3 \times 10^{16} \text{ cm}^{-2}$, take-off angle = 50°).

Table 4.4 P/As and P/In ratios of InP/InGaAs samples exposed to carbon ions as a function of ion impact energy (take-off angle = 50°, dose = $3 \times 10^{16} \text{ cm}^{-2}$) (* the initial surfaces were indium rich and the indium signal from both layers lowers the P/In ratio).

Ratio	Unexposed	20 eV	100 eV	500 eV
P/In	0.72*	0.61	0.50	0.23
P/As	8.5	5.8	3.7	0.46
In/As	11.8	9.5	7.4	2.0

0.40 for the samples bombarded with carbon ions at 20, 100, and 500 eV, respectively. Thus, the extent of the phosphorus depletion increases strongly with increasing impact energy. There have been several reports in the literature which also show this preferential removal of P from InP surfaces after ion bombardment¹²⁵.

As mentioned above, high resolution XPS analysis of the As 3d and Ga 3p peaks of the InGaAs layer can yield information on any damage propagation through the InP overlayer, as a result of the bombardment. However, the stoichiometry of the InGaAs layer necessitated overly long accumulation times for the Ga 3p region, so that only the As 3d region was used as a monitor of damage in this layer. After 20 eV carbon ion bombardment, no broadening of the As 3d peak was observed. This implies that the damage was confined to the 4 nm thick, InP overlayer. On the other hand, Figure 4.11 shows that after exposure to 100 eV carbon ions, some damage was created in the lower layer suggesting that the range of these ions can extend beyond 4 nm. From Figure 4.11, it would appear that a large amount of damage has been propagated into the InGaAs layer by 500 eV ion bombardment. However, since approximately 80% of the InP layer was removed during the initial stages of the bombardment, only about 1 nm of InP remained and the ions could penetrate into the InGaAs layer more easily. It is therefore impossible to estimate the damaging range of these 500 eV ions, although it would be expected to be much larger than the range of 100 eV ions.

Despite the extensive interaction with the InGaAs layer, the As/Ga ratio was not changed significantly by carbon ion bombardment at 500 eV. In comparison, the As/Ga ratio decreased from 1.1 to 0.6 after carbon ion bombardment at 500 eV on GaAs, with the same dose. These results show that momentum transfer and mixing caused by collisional cascades do not change the As/Ga ratio at the InP/InGaAs boundary, and that the preferential sputtering of As over Ga observed on bare GaAs is due to the difference between these two elements,

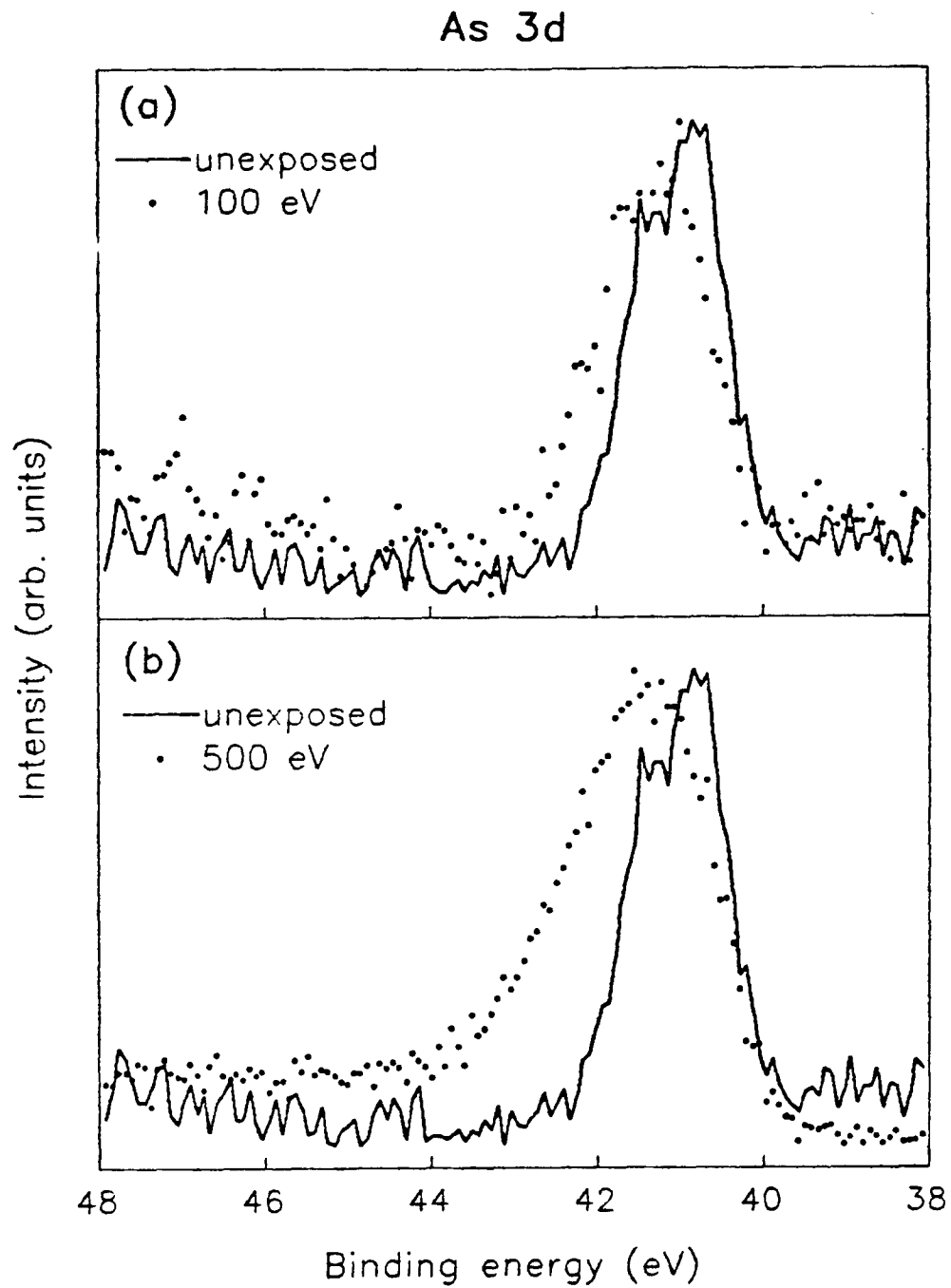


Figure 4.11 As 3d spectra from InP/InGaAs samples exposed to 100 and 500 eV C^+ ions (dose = $3 \times 10^{16} \text{ cm}^{-2}$, take-off angle = 50°).

or their carbides, in surface bond breaking and in desorption processes.

4.1.3 Damage removal treatments on bombarded surfaces

4.1.3.1 Thermal annealing

In an attempt to determine more about the nature of the carbide species and to see whether the effects of the ion bombardment could be removed by annealing, the samples were subsequently heated *in vacuo* to 350 °C (and also to 520 °C for the GaAs samples) and reanalysed with XPS. No significant reduction in peak broadening (no desorption of the carbon-semiconductor phases) was observed for either semiconductor. For the GaAs samples, the As/Ga ratios and percentage of surface carbon remained essentially unchanged. This data is given in Table 4.5. However, it seems probable that the presence of an overlayer of carbon may have prevented desorption of any volatile, underlying carbon-semiconductor species.

For the InP samples that were indium rich after bombardment (exposed to 100 and 500 eV ions), heating caused the P/In ratios to increase slightly, which suggests a loss of indium from the surface. However, scanning electron microscopy showed that aggregation of dispersed indium into indium droplets had occurred on these surfaces.

Annealing also led to changes of the surface Fermi level. For a GaAs sample previously exposed to 20 eV ions, a Fermi level shift of 0.33 eV (in addition to the 0.10 eV shift caused by ion bombardment) closer to the VBM was measured after heating to 350 °C, with a further 0.14 eV shift after heating to 520 °C (total shift from unexposed samples = 0.55 eV). Unlike the GaAs sample, the surface Fermi level position of the InP sample did not change significantly upon exposure to 20 eV carbon ions. However, heating of the bombarded sample at 350 °C caused a 0.2 eV decrease of the surface Fermi level position, from 0.95 eV to 0.75 eV relative to the valence band maximum. These results suggests that annealing may have increased

Table 4.5 Effect of heating on the percentage of C–GaAs species for GaAs samples previously exposed to carbon ions (50° take-off angle).

Ion energy (eV)	Peak	C–GaAs contribution to 3d peaks (%)		
		unheated	350 °C	520 °C
20	Ga 3d	22	26	21
	As 3d	44	49	38
100	Ga 3d	46	43	44
	As 3d	55	50	44
500	Ga 3d	55	58	51
	As 3d	66	59	49

the recombination of the implanted carbon with lattice vacancies in the semiconductors, thereby enabling the carbon to behave as acceptors.

4.1.3.2 Ultraviolet light/ozone oxidation

The effectiveness of UV light/ozone oxidation treatments in the removal of surface carbon contamination was mentioned in Chapter 3. The samples bombarded with carbon ions were therefore exposed to UV light/ozone for various times and reanalysed with XPS. There were no significant changes in the C 1s peak profiles and compositional analysis also showed no loss of the carbon overlayers. Even after 45 minutes of UV light/ozone exposure, the carbon depletion was minimal. Thus, unlike most hydrocarbons which are readily removed by the UV light/ozone treatment, the amorphous carbon layer formed by carbon ion bombardment is resistant to this treatment. Even after subsequent etching of the oxide in hydrofluoric acid, the carbon remained on the surface, further confirming the chemical inactivity of these deposits.

4.1.3.3 Hydrogen ion bombardment

In the alkane based RIE process, the presence of reactive hydrogen species may be important for the removal of carbon and hydrocarbon deposits from the surface. Hydrogen atoms and ions are common etchants for graphite, and are increasingly used in semiconductor surface cleaning processes. Therefore, we bombarded a GaAs sample previously exposed to a dose of $2 \times 10^{16} \text{ cm}^{-2}$ (20 eV) carbon ions with 100 eV hydrogen ions. The predominant species in the beam was H_2^+ , but neutralization and impact with the surface should effectively convert most of the reactants into hydrogen atoms. Figure 4.12 shows the survey spectrum and high resolution As and Ga 3d spectra of the sample after the hydrogen ion bombardment with a dose of $2 \times 10^{18} \text{ cm}^{-2}$ ions. In agreement with other reports on

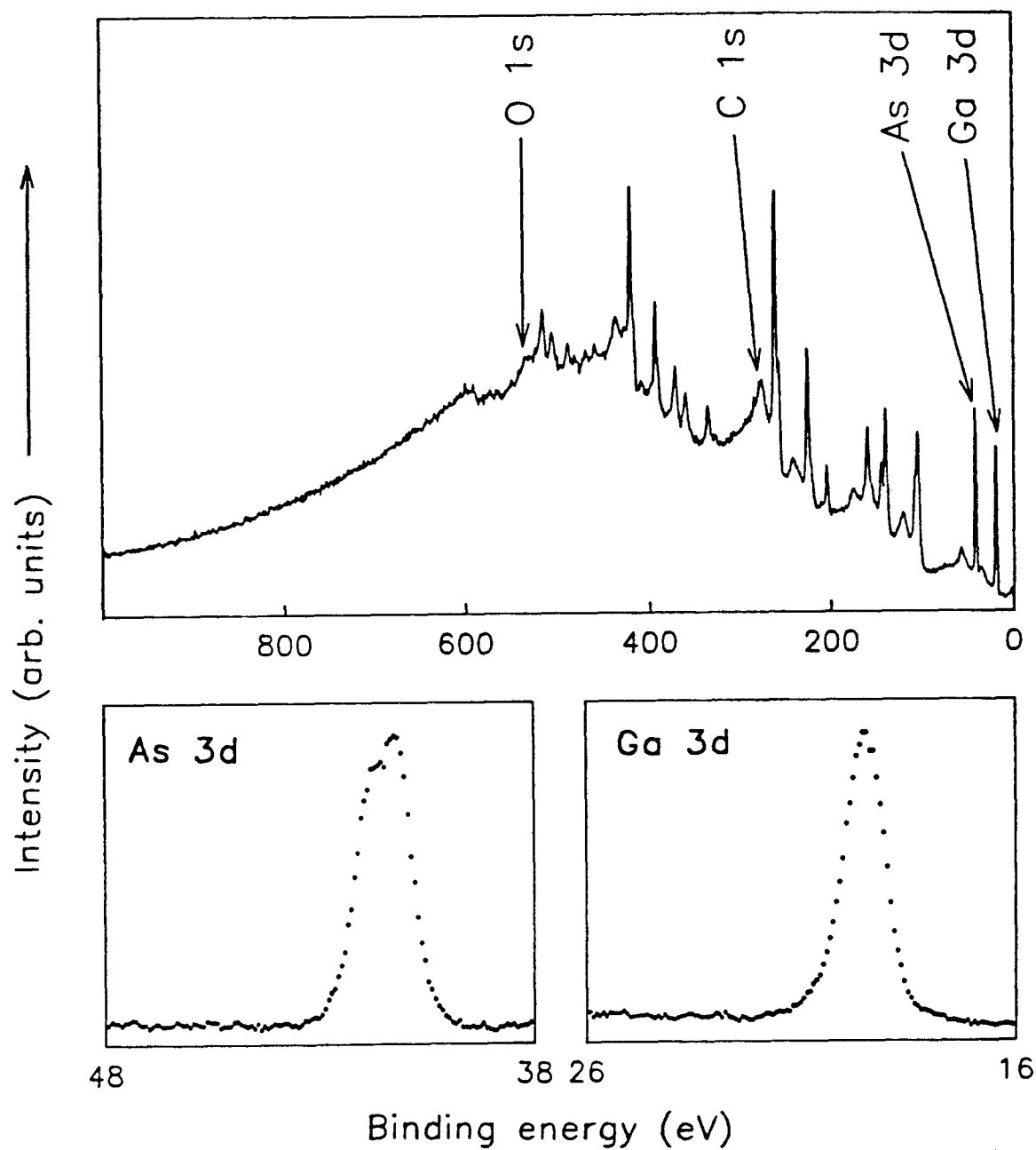


Figure 4.12 Survey, and As and Ga 3d spectra from a GaAs sample previously exposed to carbon ions, after bombardment with $2 \times 10^{18} \text{ cm}^{-2}$, 100 eV H_2^+ ions.

GaAs surfaces exposed to hydrogen ions and plasmas^{31,34}, the resultant surface was arsenic deficient. However, it was also free from all carbon deposits and any carbon-containing phases formed by the carbon ion bombardment. The exact dose of hydrogen ions required to remove the carbon deposited from a $2 \times 10^{16} \text{ cm}^{-2}$ dose of 20 eV carbon ions on GaAs is not known, although we can make a rough estimate. Since the sticking coefficient for the 20 eV carbon ions was determined to be close to unity, approximately $2 \times 10^{16} \text{ cm}^{-2}$ carbon atoms were removed by the hydrogen bombardment. Therefore, with a dose of $2 \times 10^{18} \text{ cm}^{-2} \text{ H}_2^+$ ions ($= 4 \times 10^{18} \text{ cm}^{-2}$, H atoms), the minimum etch/sputter yield must be *ca.* 0.005. The etch/sputter yield for $\approx 110 \text{ eV}$ hydrogen ions on graphite has been reported to be approximately 0.009¹²⁶.

4.2 METHYL ION BOMBARDMENT

4.2.1 GaAs and InP bombarded with 20 and 100 eV CH_3^+ ions

The most significant feature of the GaAs and InP surfaces exposed to 20 and 100 eV methyl ions was the accumulation of an amorphous carbon film on the surface. The survey spectra are indistinguishable from those already shown for carbon ion bombardment on these surfaces (Figures 4.1 and 4.8). However, unlike the deposits resulting from carbon ion bombardment, the layers produced by methyl ions were readily removed by ultraviolet light/ozone treatments. This suggests that incorporation of hydrogen into the deposited material significantly altered its chemical reactivity. However, this was not obvious from the C 1s peak position and shape, and the plasmon loss peak was not significantly different from the spectrum shown previously in Figure 4.2. Despite the reactivity towards UV/ozone, annealing *in vacuo* was ineffective in removing the deposited layer.

Table 4.6 lists the constituent ratios for GaAs and InP/InGaAs surfaces after exposure to 20 and 100 eV CH_3^+ ions. Once again, bombardment with ions in this energy range appears to cause slight sputtering of the semiconductors, along with preferential removal of the group V constituents. In comparison to the samples exposed to carbon ions, a greater depletion of arsenic from GaAs and phosphorus from InP appears to have occurred. This may be due to reaction with the energetic hydrogen species created by fragmentation of the methyl ions upon impact with the surface. As discussed in Chapter 1, hydrogen atoms have a strong affinity for these elements and formation of volatile hydrides is therefore facile.

Figures 4.13 and 4.14 show the high resolution XPS spectra obtained from GaAs and InP/InGaAs samples before and after bombardment with 20 and 100 eV methyl ions (doses were $3 \times 10^{16} \text{ cm}^{-2}$). Again, broadening of the constituent peaks has occurred, due to disruption of the semiconductor bonding environment and the formation of semiconductor-carbon/hydrogen bonds. Also shown for comparison are the As and Ga 3d peak profiles for GaAs samples bombarded with C^+ ions (to compensate for doping effects, these profiles are referenced to the Fermi level of the unexposed surface). For InP, the P 2p peak appears to be unshifted (similar to Figures 4.9 and 4.10), whereas there is a significant difference between the In 3d_{5/2} peaks for surfaces bombarded with these ions. The broadening on the low binding energy side of the bulk InP component suggests the presence of metallic indium on the surface¹²⁷, or at the carbon-semiconductor "interface". InP is known to be more susceptible to loss of P and formation of In droplets upon exposure to H plasmas and atoms (and ion beams)³¹⁻³⁴, so it would seem that such an interaction has occurred here. The P/In ratios in Table 4.6 further confirm the indium enrichment upon exposure to CH_3^+ ions.

Some broadening of the As 3d peak for the underlying InGaAs layer was also evident after the InP heterostructure was bombarded with 100 eV methyl ions

Table 4.6 Constituent ratios for GaAs and InP/InGaAs samples exposed to 20 and 100 eV CH₃⁺ ions.

	Ratio	Unexposed	20 eV	100 eV
GaAs	As/Ga	1.04	0.80	0.63
InP/InGaAs	P/In	0.73	0.51	0.41
	P/As	8.2	3.1	2.0
	In/As	11.2	6.1	4.9

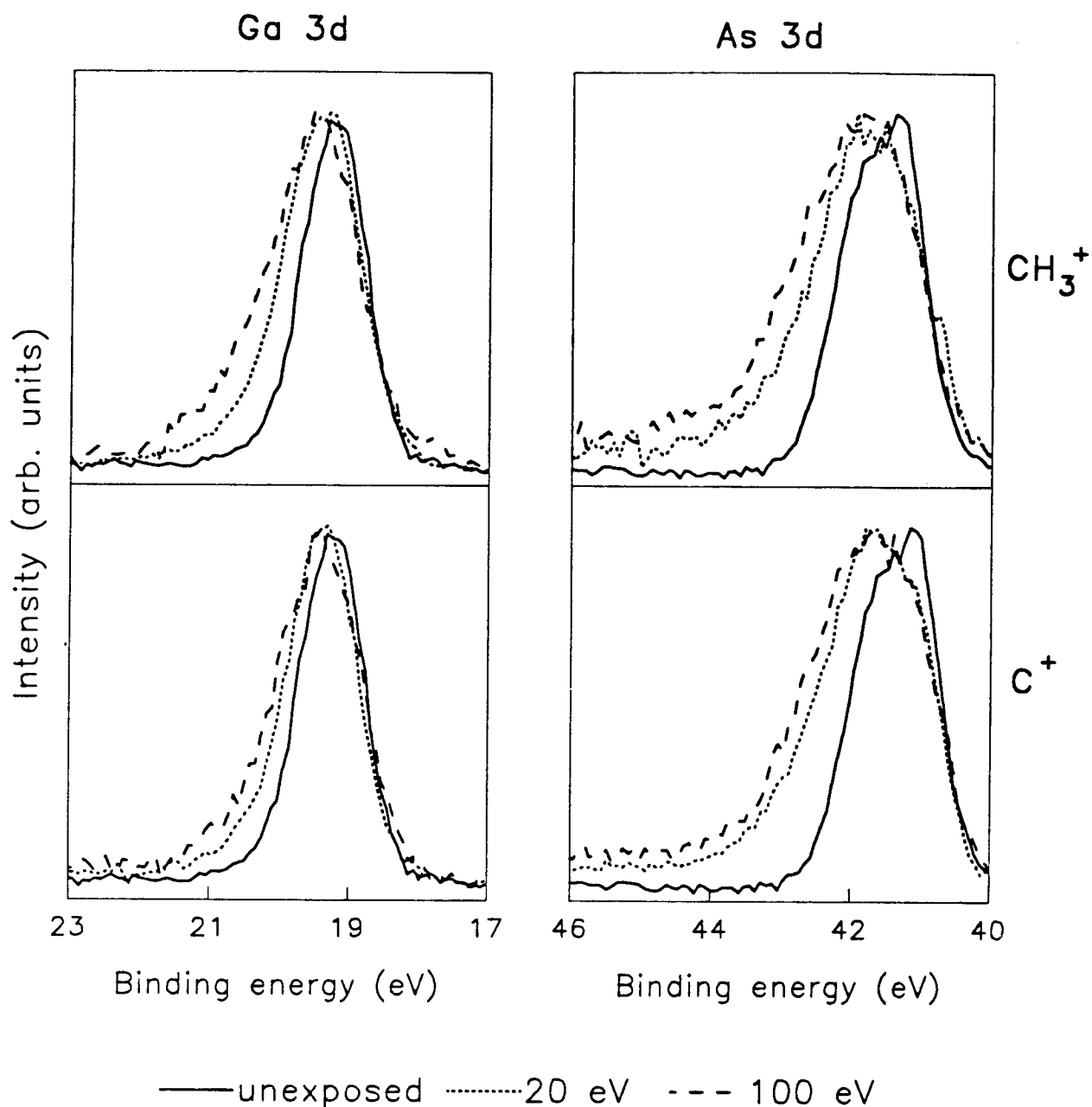


Figure 4.13 As and Ga 3d spectra from GaAs samples exposed to 20 and 100 eV CH_3^+ ions. Also shown for comparison are the peak profiles from samples exposed to 20 and 100 eV C^+ ions. To compensate for doping effects, all peaks have been referenced to the Fermi levels of the unexposed samples (all doses = $3 \times 10^{16} \text{ cm}^{-2}$, take-off angle = 50°).

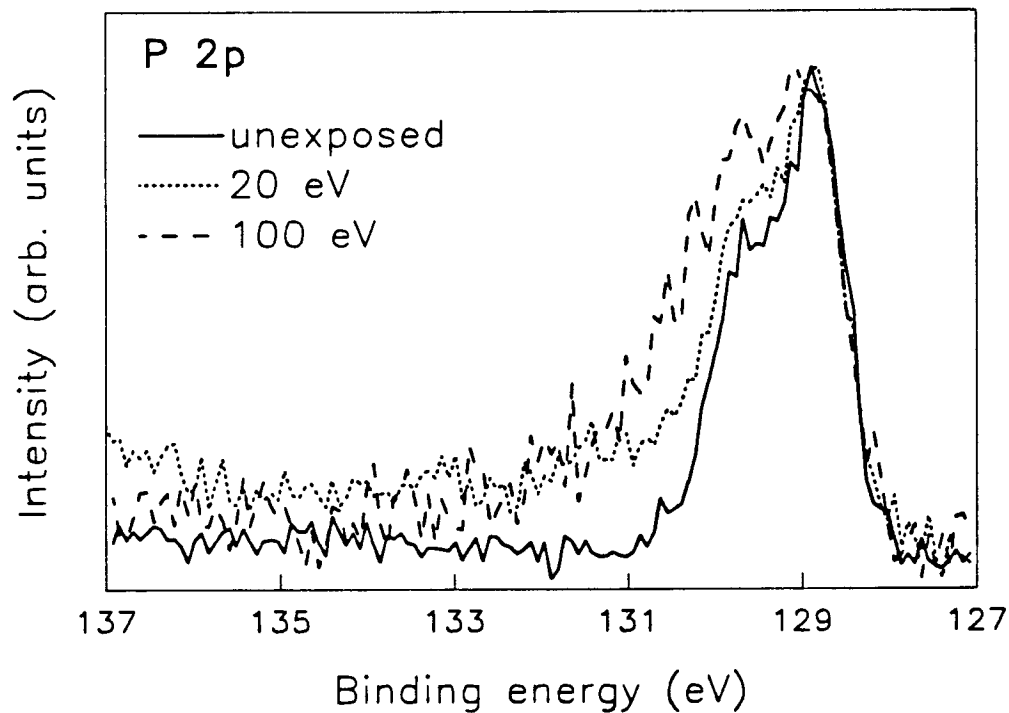
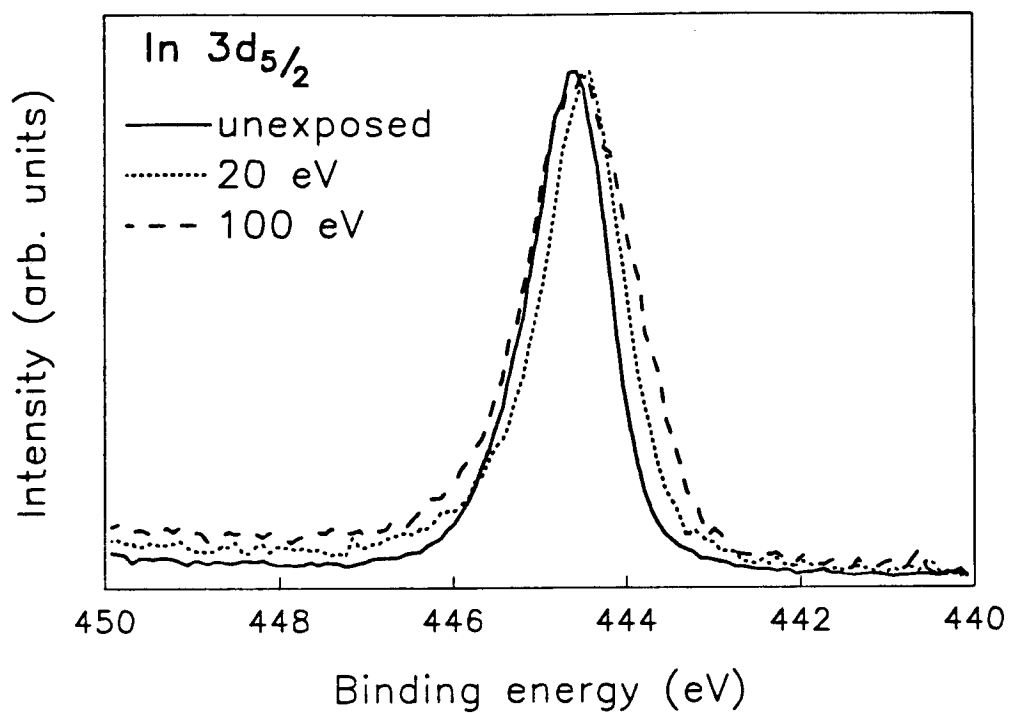


Figure 4.14 P 2p and In 3d_{5/2} spectra from InP/InGaAs samples before and after exposure to 20 and 100 eV CH₃⁺ ions (dose = 3×10¹⁶ cm⁻², take-off angle = 50°).

(Figure 4.15). This is similar to the interaction observed previously with 100 eV C^+ ions (Figure 4.11).

4.2.2 GaAs and InP bombarded with 3 and 9 eV CH_3^+ ions

Since the interactions of 20 and 100 eV methyl ions with GaAs and InP were qualitatively similar to those with carbon ions, we lowered the CH_3^+ impact energies to see if different interactions with the semiconductor surfaces would occur. Initially, the ions were decelerated to 9 eV (± 1.5 eV). This is sufficient energy to cleave two C-H bonds and form two H atoms and a CH species on the surface.

The In 3d_{5/2} and P 2p spectra measured on an InP sample after exposure to $3 \times 10^{16} \text{ cm}^{-2}$ CH_3^+ ions at 9 eV are shown in Figure 4.16. Bombardment with methyl ions has resulted in a slight broadening of the semiconductor peaks. In comparison to the spectra obtained for bombardment with 20 and 100 eV ions (Figure 4.14), the interaction is less extensive. This was also reflected in the P/In and P/As ratios, which were unchanged (within experimental error) from those of the clean surface. This is intuitively what one would expect from bombardment with such low energy ions. However, once again a layer of amorphous hydrocarbon was deposited on the surface, whose thickness was consistent with an ion sticking coefficient approaching unity.

When the impact energy was lowered to 3 eV – an energy where the methyl species is expected to remain intact on the surface, no broadening of the semiconductor peaks was observed and a layer of amorphous hydrocarbon on the surface was the only observable result.

These latter results were somewhat disappointing because in light of the etching behaviour of methyl radicals with GaAs and InP, we anticipated that etching of the InP by the "hot" methyl species might occur. However, the formation of a hydrocarbon layer suggests that the reaction with the surface is

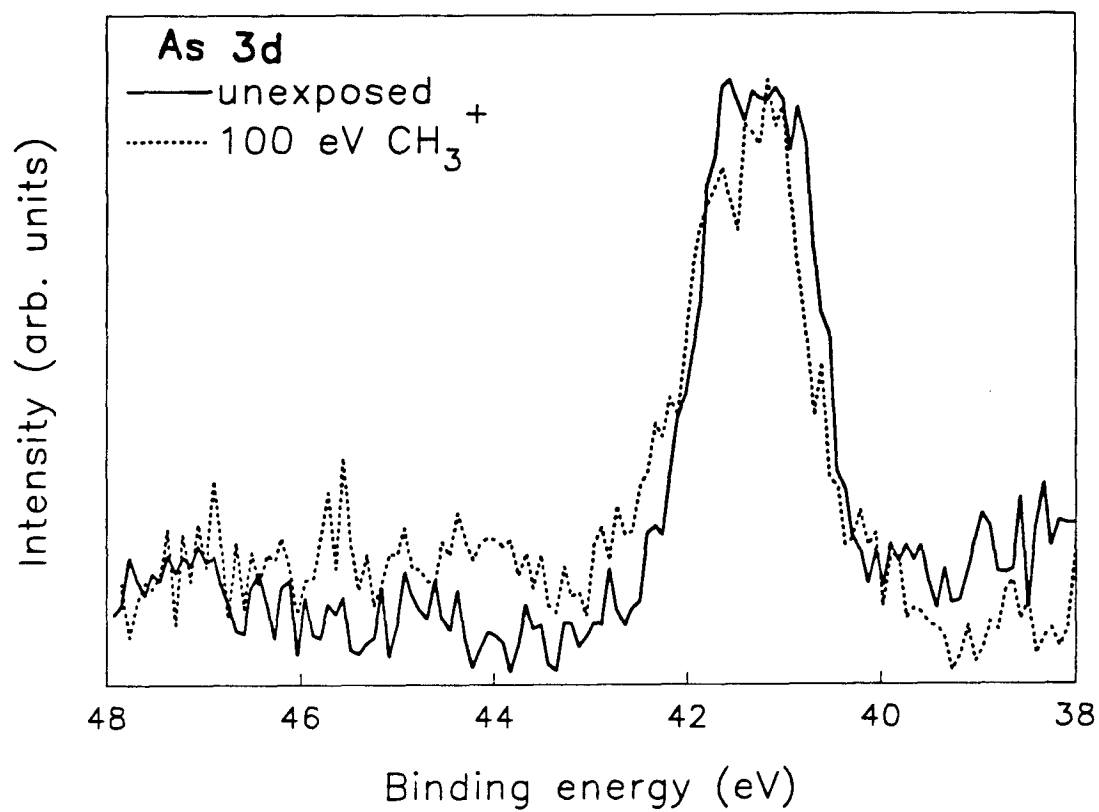


Figure 4.15 As 3d spectra from InP/InGaAs samples before and after exposure to 100 eV CH₃⁺ ions (dose = $3 \times 10^{16} \text{ cm}^{-2}$, take-off angle = 50°).

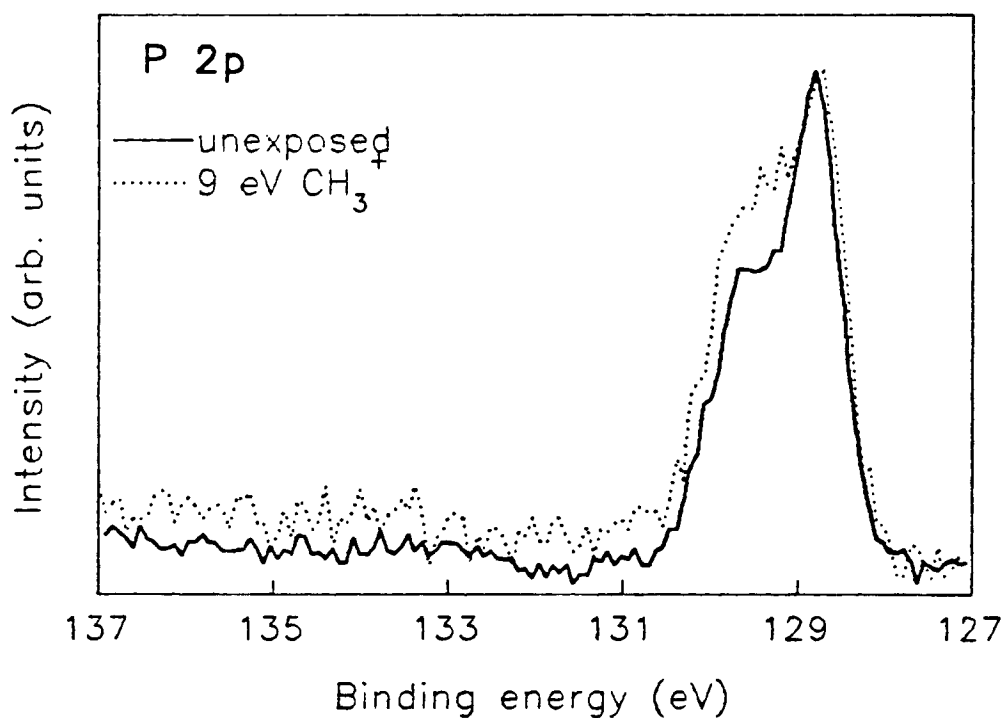
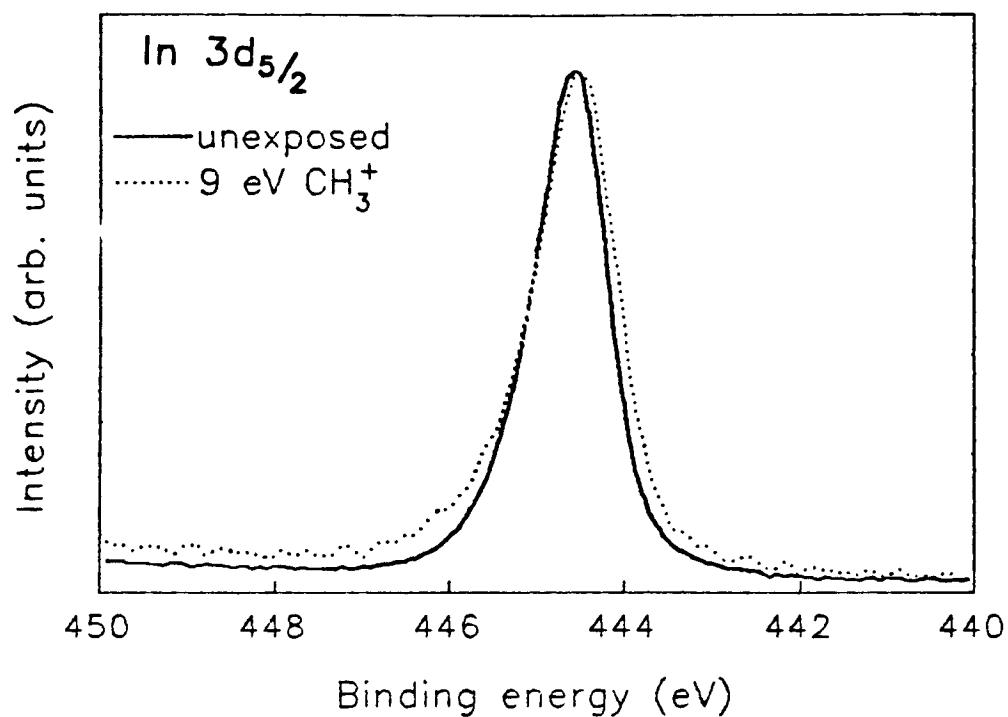


Figure 4.16 P 2p and In 3d_{5/2} spectra from InP/InGaAs samples before and after exposure to 9 eV CH₃⁺ ions (dose = 3×10^{16} cm⁻², take-off angle = 50°).

negligible compared to the formation of C–C bonds. In an attempt to enhance the surface reaction, we repeated the experiments with 3 eV CH_3^+ ions, but with the sample surfaces heated to 350 °C.

Figure 4.17 shows the high resolution XPS spectra obtained from GaAs and InP surfaces before and after exposure to 3 eV CH_3^+ ions, at 350 °C. No broadening of the peaks is evident, which suggests that negligible quantities of carbides were formed and that the surface damage was minimal. However, all the peaks are shifted towards the VBM by approximately 0.25 eV, most likely as a result of surface band bending caused by incorporation of carbon atoms. Although exposure to hydrogen plasmas is known to passivate *n*-type dopants in GaAs and *p*-type dopants in InP, this behaviour can be annealed out by heating at 300 – 500 °C.

The exposed surfaces were also non-stoichiometric *i.e.* preferential removal of the group V constituents had occurred. The InP/InGaAs sample also showed a reduction of its P/As (0.48) and In/As (0.92) ratios, which is consistent with the removal of some of the InP overlayer. From these ratios, we estimate that the thickness of the InP layer decreased by approximately 3.0 nm because of the exposure to the methyl ions.

Accumulation of amorphous hydrocarbon still occurred on both the GaAs and InP surfaces, but to a significantly lesser degree than was observed on the unheated samples. Whereas the thickness of the layer deposited by 3 eV ions on the unheated samples was approximately 2.0 nm, it was estimated as only *ca.* 1.0 nm when the samples were heated. However, the reduction of the P/As and P/In ratios for the InP/InGaAs sample suggests that etching of the InP surface occurred. Thus, assuming that the sticking coefficient of the ions was still unity, about half of the methyls appear to have been consumed by the etching process. By measuring the P/As ratio across the bombarded area of the sample, the beam interaction diameter was found to be approximately 3 mm. If the maximum etch

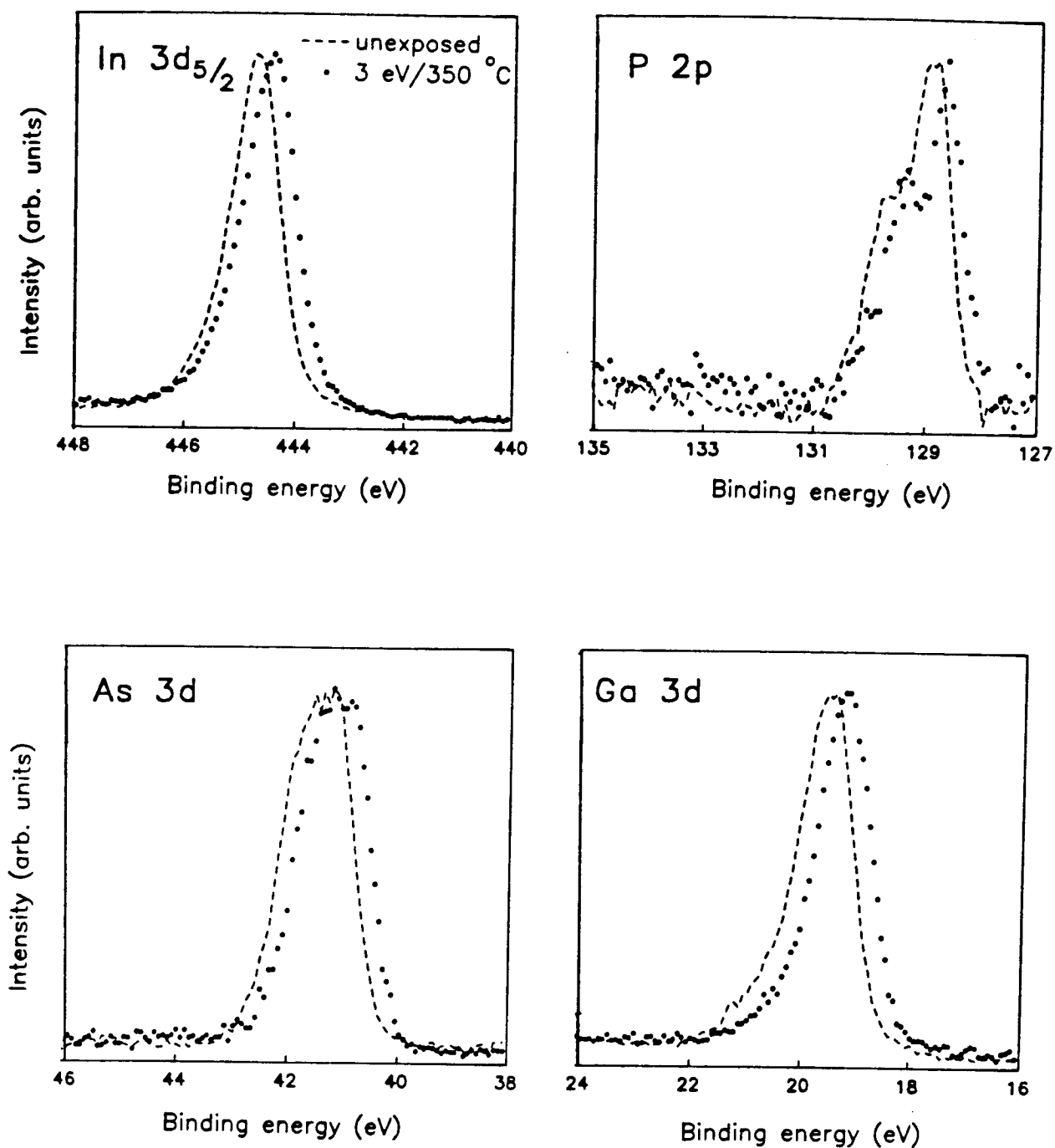


Figure 4.17 Spectra from GaAs and InP/InGaAs samples before and after bombardment with 3 eV CH_3^+ ions. During bombardment, the samples were heated to 350 °C (dose = $3 \times 10^{16} \text{ cm}^{-2}$).

depth was 3.0 nm, then the volume of InP removed by the ions is roughly 10^{14} nm^3 . Since this volume contains approximately 2×10^{15} In and P atoms, we get an etch yield of ≈ 0.1 . However, as discussed earlier, most of this etching probably occurred during the initial stages of the bombardment, prior to the accumulation of an amorphous carbon layer. Nonetheless, these results do suggest that bombardment of a heated InP surface with 3 eV CH_3^+ ions could give a practical etch rate and a substrate surface with minimal residual damage. Further research in this direction may lead to some novel RIE processes.

CHAPTER 5 RESULTS AND DISCUSSION (II): ATOM AND RADICAL ETCHING OF GaAs

5.1 HYDROGEN ATOM ETCHING OF GaAs

5.1.1 Etch inhibition

At surface temperatures above *ca.* 200 °C, GaAs (100) samples were found to etch continuously in a stream of hydrogen atoms produced in a remote microwave discharge. However, the etches were very sensitive to the preparation of the sample *i.e.* if the time between blow-drying the sample (after an HCl wash and distilled H₂O rinse) and evacuating the helium back-filled system was greater than about 30 seconds, etching frequently would not start. This problem was particularly significant at temperatures below approximately 250 °C. Such etch inhibition is most likely caused by a thin oxide layer, formed upon inserting the sample into a hot system. The thickness of the oxide is minimised by reducing the time the sample is exposed to air.

In an attempt to avoid the problem of etch inhibition, the samples were transferred into a cold system and heated in a stream of hydrogen at a pressure of 1 Torr. This technique resulted in no significant improvement in the ability to initiate an etch. Because the time required to reach the desired temperature increased, for the majority of this work the sample was introduced into an already heated tube.

There are several conflicting reports in the literature on the ability of reactive hydrogen species to remove GaAs native oxides. Mikhailov *et al.*¹²⁵ studied the hydrogen plasma cleaning of GaAs with XPS, and found that stable Ga-oxides could not be removed when surface temperatures were below 150 °C. In contrast, Lu *et al.*¹²⁶ reported that exposure to a hydrogen electron cyclotron resonance plasma "de-oxidised" an unheated GaAs surface. Ingrey and co-workers¹²⁷ found that all traces of In_{0.53}Ga_{0.47}As oxides grown by exposure to

ultraviolet light and ozone were removed by hydrogen atoms when the substrate was heated to 192 °C. However, Schaefer *et al.*¹²⁸ reported that both arsenic and gallium oxides were absent on "unheated" GaAs surfaces after exposure to atomic hydrogen in an ultra-high vacuum system. The H was generated by dissociation of H₂ on a hot (2200 K) tungsten filament, which was positioned 5 cm above the sample (an identical arrangement was used by Creighton⁴² to expose GaAs to atomic hydrogen for a temperature programmed desorption study, but he reported that radiation from the filament raised the temperature of the GaAs sample by ≈ 60 °C!). In the most recent study, Petit and co-workers¹²⁹ reported that heating to 300 °C was necessary for the removal of GaAs "hydroxides" by atomic hydrogen generated in the same manner as Schaefer *et al.*¹²⁸.

Our observations suggest that hydrogen atoms are incapable of removing the native oxides on GaAs, or that the etch rates are very low. Even at temperatures above 300 °C, we could not initiate etches on oxidised GaAs samples. However, it is also possible that reoxidation of the surface is occurring in our system. This stems from the fact that the base pressure in our system was about 10^{-3} Torr, and that traces of atomic oxygen are produced in glass discharge tubes. Thus, our minimum etch temperature could be the point where the etch rate is faster than oxidation. Such reoxidation should not be as prevalent when atomic hydrogen is produced in a high-vacuum chamber by dissociation of H₂ on a hot filament^{128,129}, but would depend on the oxygen impurity level in the molecular hydrogen. The conflict in the results reported in the literature may stem from differences in experimental conditions. Further investigation is necessary to rationalise this behaviour.

5.1.2 Temperature dependence of H atom etching

The partial pressures of hydrogen atoms could not be changed appreciably (and still remain measurable) by varying the discharge power or hydrogen flow.

Consequently, the pressure dependence of the etch rates and hence the order of the reaction could not be determined. We assumed a first order dependence of the etch rate on the partial pressure of hydrogen atoms, P_H . This is consistent with all previous etching reactions of atomic species such as F, Cl and Br¹³⁰. For each etch, the partial pressure of the H atoms was calculated from the measured atom flows, F_H , and total hydrogen flow, F_{total} , with the relationship:

$$P_H(\pm 15\%) = \frac{F_H(\pm 10\%)}{F_{total}(\pm 3\%)} \times P_{total}(\pm 2\%)$$

Table 5.1 lists the etch rates, partial pressures of H atoms and the calculated first order rate constants, k_H , for etches at several temperatures. Table 5.1 shows that the rate constants increase when the temperature is raised. Figure 5.1 is a plot of $\ln(k_H)$ against $1/T$. By fitting the data (k_H vs T) to the Arrhenius equation with a weighted, non-linear curve fitting routine, an activation energy of 20.2 ± 3.9 kJ mol⁻¹ and pre-exponential factor of $10^{4.8 \pm 0.4}$ nm min⁻¹ Torr⁻¹ were calculated (1 standard deviation). The straight line fit to the data shown in Figure 5.1 is consistent with these values and corresponds to the equation,

$$k_H = 10^{4.8} \text{ nm min}^{-1} \text{ Torr}^{-1} \exp(-20.2 \text{ kJ mol}^{-1} / RT)$$

Error bars are included for the y-axis only, since the error in the temperature readings can be considered negligible compared to the uncertainty in the rate constants. The error in the rate constants was estimated to be $\pm 20\%$, which is close to the value needed to bring all the points on to a straight line fit.

Our activation energy is very close to the value of 19 kJ mol⁻¹ reported by Kishimoto and co-workers¹³¹ for the etching/cleaning of (100) GaAs in a hydrogen plasma. Their etch rate data were obtained at three substrate temperatures between 300-500 °C and although the H atom concentrations were not measured, they were probably lower than ours.

Table 5.1 Data for H atom etching of GaAs.

Temp (°C)	Etch Rate (nm/min)	P _H (Torr)	k _H (nm/min/Torr)
201	22.6	0.0504	448
218	10.5	0.0288	365
245	26.4	0.0510	518
276	15.1	0.0266	568
282	21.7	0.0267	813
300	39.5	0.0513	770
351	34.3	0.0233	1470

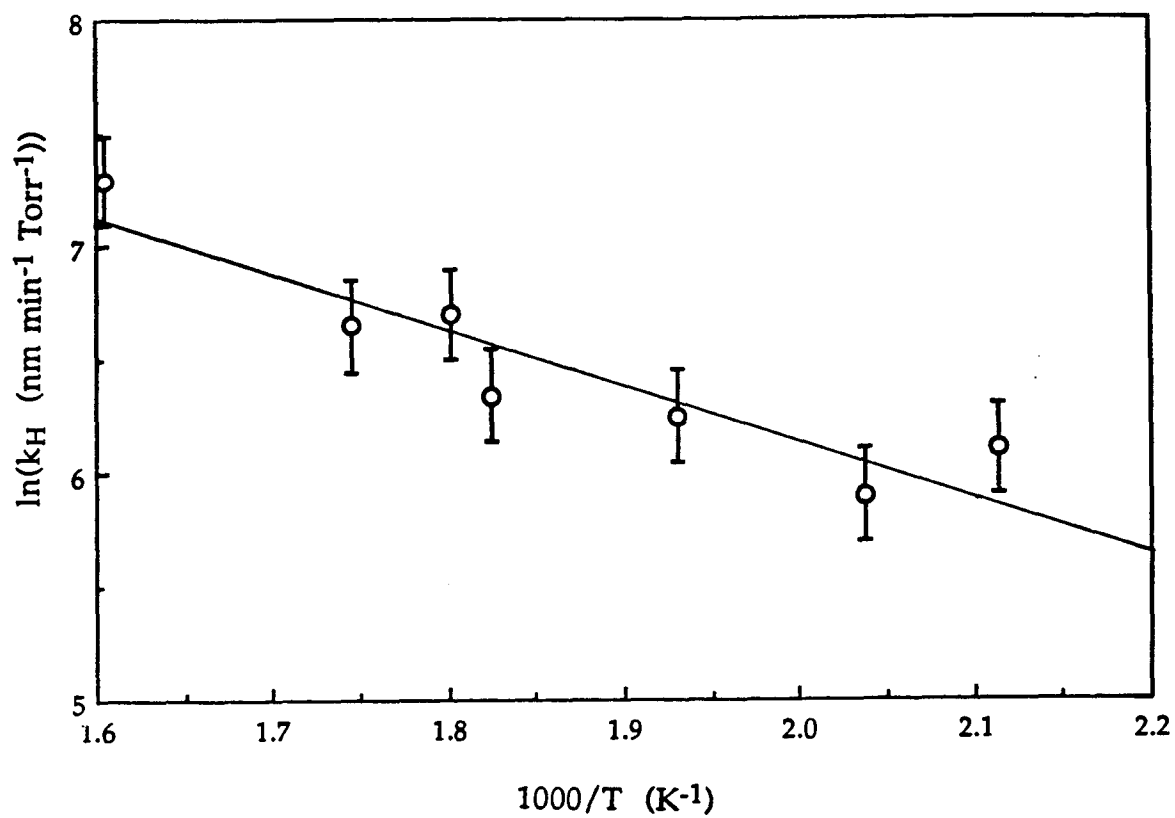


Figure 5.1 Plot of $\ln(k_H)$ versus $1/T$ for H atom etching of GaAs.

From the density of GaAs (5.32 g cm^{-3}), the pre-exponential factor can be converted to units of molecule $\text{cm}^{-2} \text{ s}^{-1} \text{ Torr}^{-1}$, which represents the flux of Ga and As product molecules leaving the surface per unit time and per unit etchant pressure. This yields $A = 2.2 \times 10^{18} \text{ molecule cm}^{-2} \text{ s}^{-1} \text{ Torr}^{-1}$. If k_H is the rate constant for an elementary rate controlling step, then according to kinetic theory, A is the frequency factor and should be less than or equal to the collision frequency, Z , of reactant on the surface. Z is given by¹³²,

$$Z = 3.513 \times 10^{22} \frac{P}{\sqrt{MT}} \text{ cm}^{-2} \text{ s}^{-1}$$

where P is the pressure in Torr, M is the atomic or molecular mass in grams per mole, and T is the absolute temperature (K). For hydrogen atoms at 300°C , this is calculated to be $1.46 \times 10^{21} \text{ collisions cm}^{-2} \text{ s}^{-1} \text{ Torr}^{-1}$. Thus A is less than the collision frequency and the process could be an elementary reaction step.

It is easy to show that the reaction rate was not limited by the arrival rate of reactants on the surface. For a hydrogen atom partial pressure of 0.0513 Torr at 300°C , an etch rate of 39.5 nm min^{-1} was obtained. The flux of hydrogen atoms striking the surface under these conditions is calculated to be $7.50 \times 10^{19} \text{ H atoms cm}^{-2} \text{ s}^{-1}$. For this etch rate, the flux of Ga and As atoms leaving the surface is $1.46 \times 10^{15} \text{ atoms cm}^{-2} \text{ s}^{-1}$. Therefore, more than 10^4 H atoms collide with the surface for every Ga or As atom leaving the surface.

5.1.3 Surface morphology

The interferograms recorded during the etching experiments always showed a continual reduction of the reflected light intensity as the etch progressed (as illustrated in Figure 5.2). This suggests that the surfaces become increasingly rough during the etch.

To determine the morphology of the etched surfaces, scanning electron microscopy of several samples was carried out. Figure 5.3(a) is the

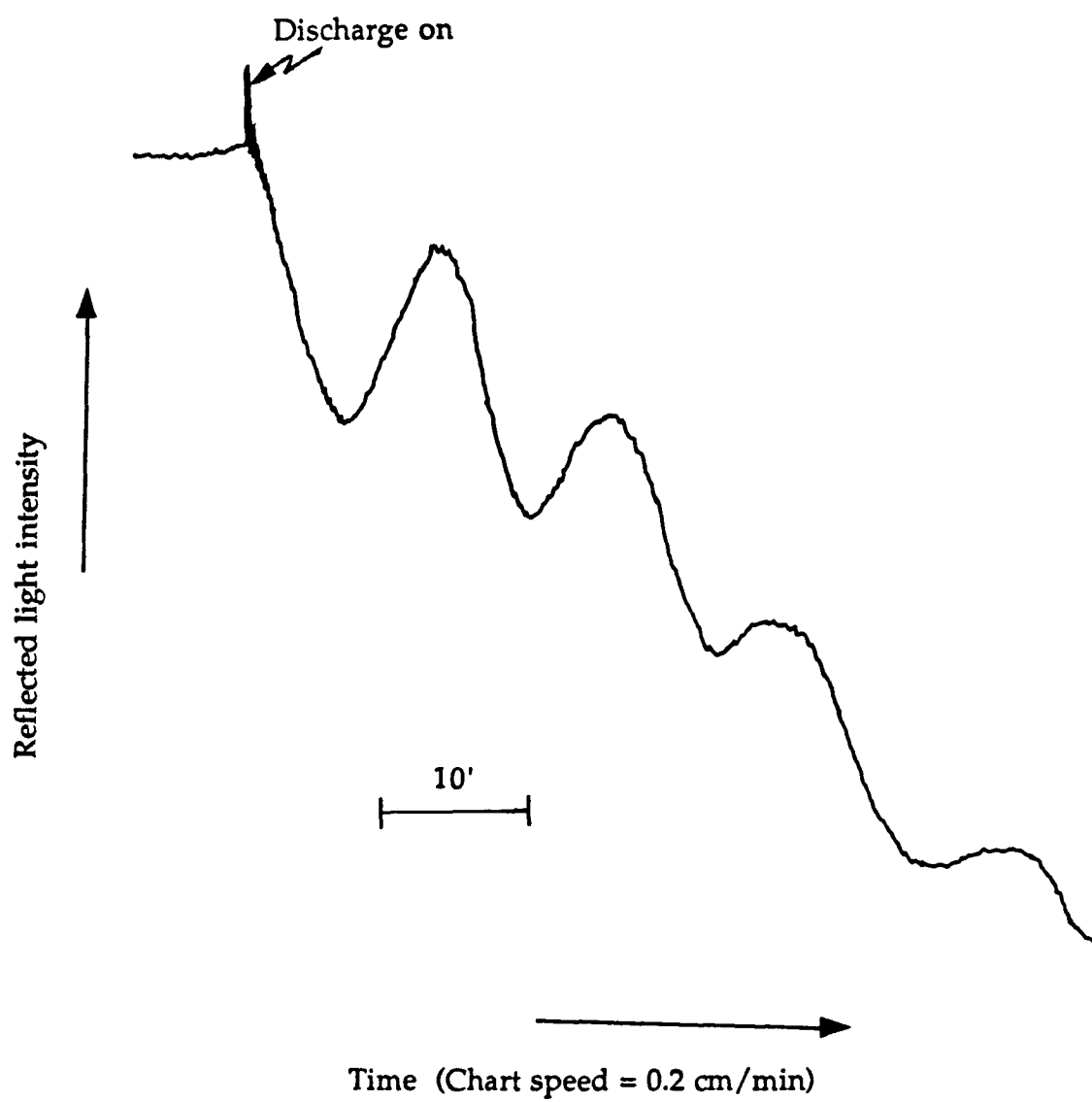
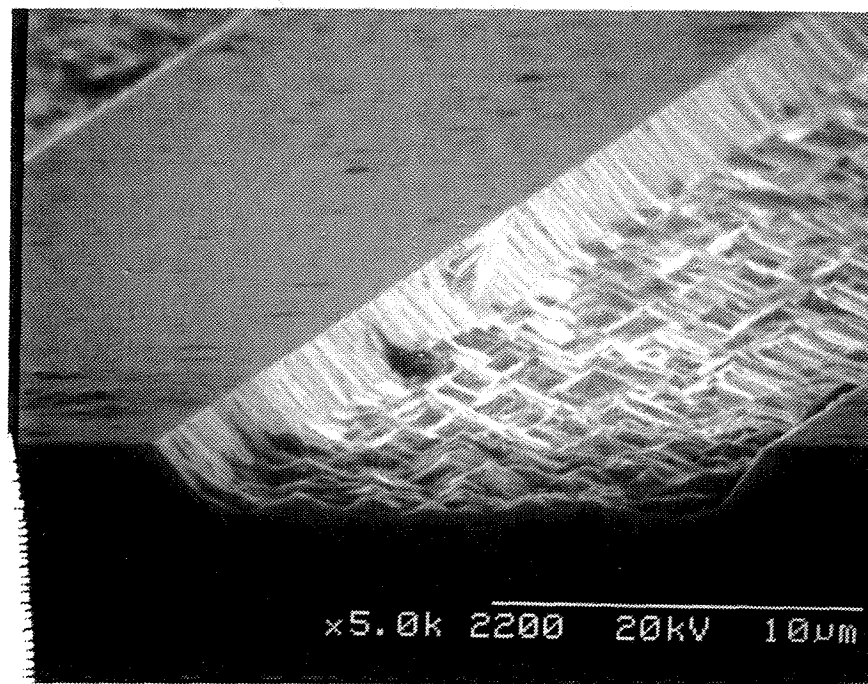


Figure 5.2 Interferogram obtained from the etching of GaAs with H atoms at 245 °C.

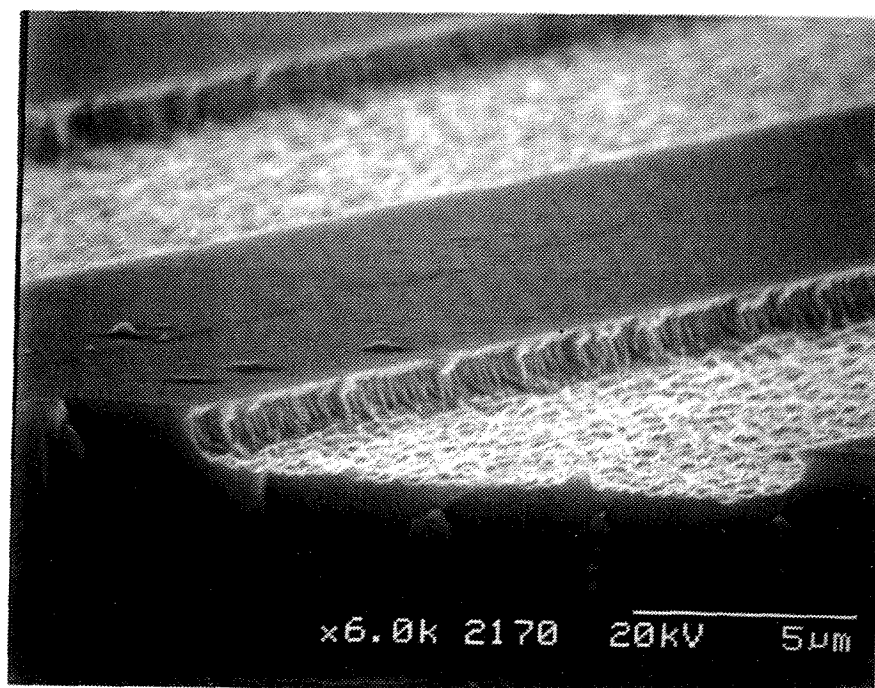
photomicrograph obtained for a sample etched at a temperature of 205 °C. The surface is extremely rough, which explains the reduction of the reflected light intensity observed with interferometry. The features on the surfaces show many crystallographic planes. The sidewall is oriented at an angle to the (100) surface in Figure 5.3(a) that suggests it is a (111) plane ($\approx 55^\circ$ angle of incidence to the surface). In addition, the surface features appear to be "pyramidal", and could be composed of 4 intersecting {111} planes. As discussed in Chapter 1, crystallographic etching is commonly observed with purely chemical etching (not ion assisted), and is the result of differential etch rates for various crystal planes. Normally, the gallium {111}A planes have the lowest etch rates because the surface atoms have three bonds to the next layer and the number of these atoms per unit area is the highest for the low index planes. The sidewall angle and surface features observed here are consistent with this behaviour.

Figure 5.3(b) shows that the surface features are less distinct for a sample etched at a higher temperature (280 °C). Whereas the sidewall observed in Figure 5.3(a) resulted from a sample with the mask aligned with the $[01\bar{1}]$ direction, the mask in Figure 5.3(b) is oriented with the $[0\bar{1}\bar{1}]$ axis. However, the complexity of this sidewall is far removed from the undercut expected from a simple crystallographic etch (see Figure 1.6(b)).

As the etch temperature is increased further, the surfaces become less rough. The micrographs in Figure 5.4 were obtained from a sample etched at 308 °C. The pyramidal features observed at lower temperatures have given way to striations on the surface, which are perpendicular to the mask, *i.e.* aligned with the $[0\bar{1}\bar{1}]$ direction. Figure 5.4(b) is a higher magnification image of Figure 5.4(a), and was taken with the sample rotated towards the $[0\bar{1}\bar{1}]$ direction. It seems reasonable that this directional or "ocean waves" effect could be "extrapolated" to produce the surface in Figure 5.3(a), with the crests of each wave increasing in amplitude to give

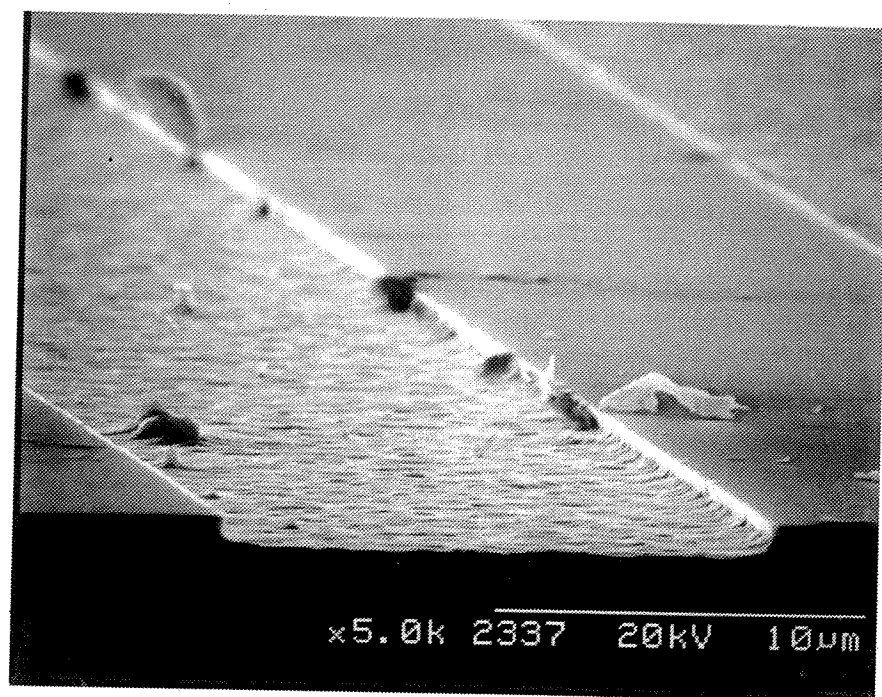


(a)

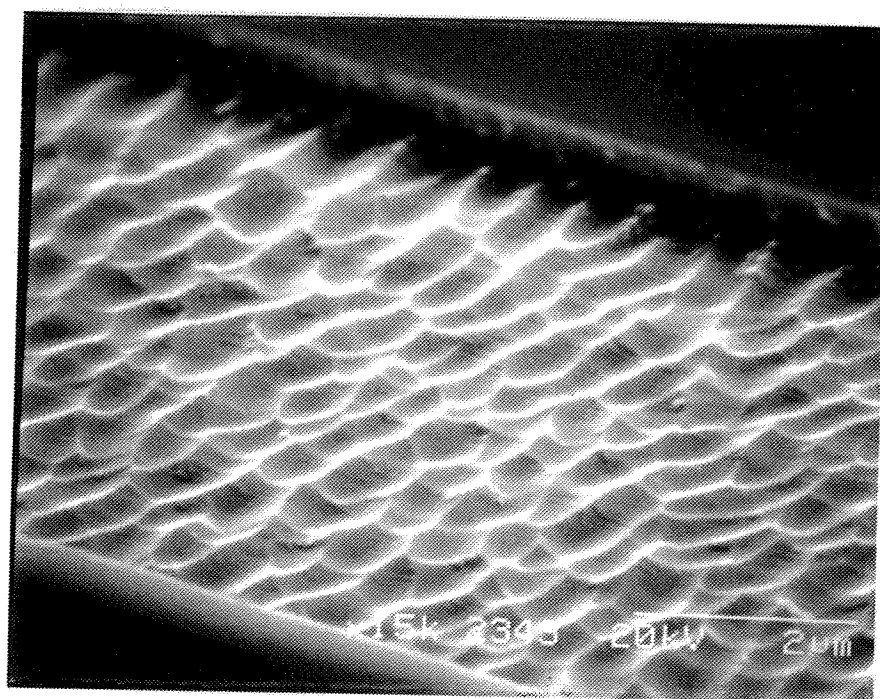


(b)

Figure 5.3 Scanning electron micrographs from (100) GaAs surfaces etched with H atoms at (a) 205 °C and (b) 280 °C. The masks are aligned with (a) the $[01\bar{1}]$ direction and (b) $[0\bar{1}\bar{1}]$ direction.



(a)



(b)

Figure 5.4 Scanning electron micrographs from a (100) GaAs surface etched with H atoms at 308 °C. (a) looking along the $[01\bar{1}]$ direction and (b) x3 magnification of (a) and rotated $\approx 60^\circ$.

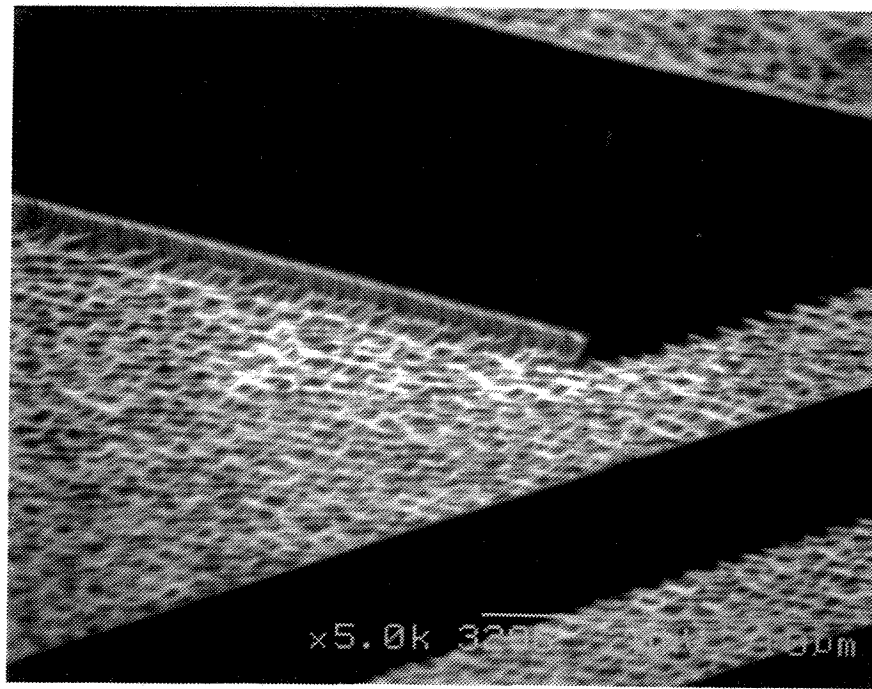
pyramidal features. It is difficult to determine which crystal planes are contributing to this effect. This may be due to a transition from crystallographic towards isotropic etching, since the higher temperatures should increase the reactivity of the hydrogen atoms with the slow etching {111} planes.

Finally, the photomicrographs from a sample with mask stripes oriented in both directions are shown in Figure 5.5. This sample was etched at 325 °C. Figure 5.5(a) shows the region where the two stripe orientations meet. The surface is still rough and has directional striations. The $[0\bar{1}\bar{1}]$ sidewall appears to be less complex than in Figure 5.3(b), but looks qualitatively similar. Closer examination of the $[01\bar{1}]$ sidewall (Figure 5.5(b)), shows that it is slightly rough, but is now vertical or even negatively inclined to the surface. The reason for the transition from a $\approx 55^\circ$ inclined (111) sidewall (Figure 5.3(a)) to a wall with an angle greater than 90° is unclear. However, it may be associated with an increased reactivity towards gallium {111}-type planes at higher temperatures.

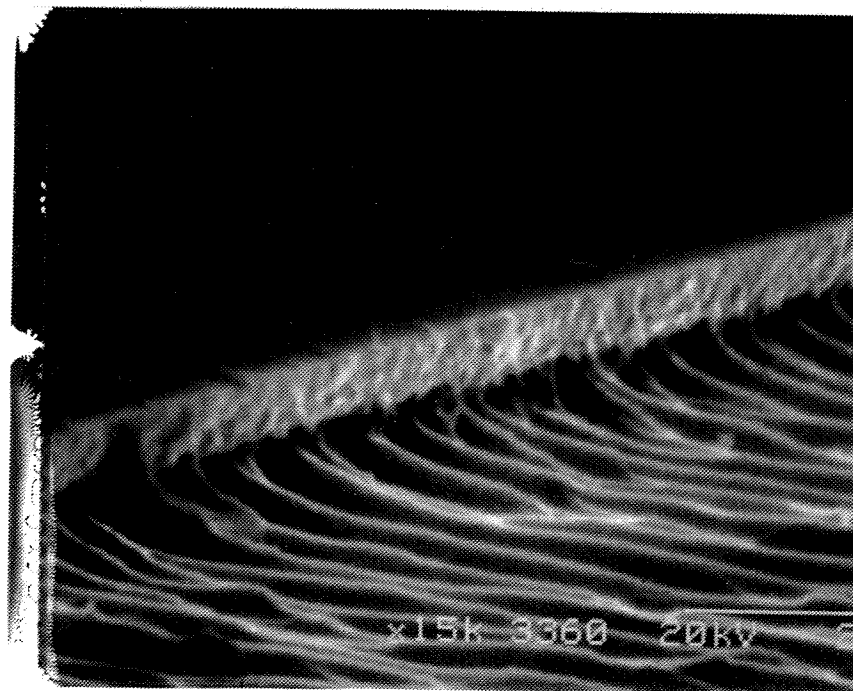
5.1.4 XPS analysis of etched surfaces

The surface compositions of etched samples were determined by XPS. The take-off angle was 35° (with respect to the surface). As the samples had been exposed to the atmosphere and consequently oxidised, no attempt was made to obtain high resolution spectra. However, there have been several reports of high resolution XPS analysis on GaAs surfaces exposed to atomic hydrogen¹³³ which have shown that formation of both Ga-H and As-H bonds does occur.

For samples etched at 200 and 275 °C, the ratios of the As 3d to Ga 3d integrated peak intensities (average of measurements for 3 spots) were 0.31 and 0.41, respectively, which are significantly less than the stoichiometric value of 1.00. Thus, the etched surfaces are very arsenic deficient. This is in agreement with



(a)



(b)

Figure 5.5 Scanning electron micrographs from a (100) GaAs surface etched with H atoms at 325 °C. (a) looking at the intersection of two mask directions, towards the sidewall of the $[0\bar{1}1]$ mask and (b) x15 k magnification of the $[01\bar{1}]$ direction sidewall.

many of the reports in the literature (see Chapter 1), and is strong evidence that the removal of gallium is the slower, rate controlling process in these etches.

If the surfaces were flat, it would be possible to estimate the thickness of the arsenic depletion layer (see Appendix B). However, such a condition is far removed from the surfaces shown in Figures 5.3–5.5, and consequently, simple interpretation of the XPS ratios is impossible. To illustrate the effect of crystallographic surface features on measured As/Ga ratios, consider the simple case where the etching of a masked (100) wafer (mask aligned with $[01\bar{1}]$ direction) produces "V"-shaped trenches composed of Ga {111} planes oriented at $\approx 55^\circ$ to the surface (as in Figure 1.6(a)). If the spectrometer has a single take-off angle of 35° and the sample is oriented such that the detector is aligned with the $[01\bar{1}]$ direction (*i.e.* looking across the mask), then the analysis angle would effectively be 90° . Only half of the planes would contribute to the measured signal (planes directly facing detector). This is identical to the analysis of a perfectly flat Ga {111} surface, with a take-off angle of 90° . The separation between Ga and As {111} planes in GaAs is 0.326 nm, so compared to the initial (100) surface with an As/Ga ratio of 1.0, the ratio would decrease to 0.80 (Appendix B). However, if the sample was rotated by 90° , so that the detector was "looking" along the "V"-shaped trenches, both sides of the "V" would contribute equally to the signal, but the effective take-off angle would decrease to 22° *i.e.* the experiment would become more surface sensitive, and the measured As/Ga ratio would decrease to 0.58.

The features present on our samples are much more complex than the simple examples just described, showing features which are indicative of {111}A (Ga) planes. In addition, the take-off angle for the SSX-100 spectrometer is a 30° cone of angles centred around 35° . Therefore, the measured As/Ga 3d ratios are an average of many take-off angles (probably on Ga {111} planes), and the differences observed between the samples etched at 200 and 275 °C may be a function of their

surface morphology and not of a decrease in the arsenic depletion at higher temperatures. It is impossible to say if the arsenic depletion extends into the surface (*i.e.* more than just a monolayer of Ga from a {111} plane), in the way that phosphorus is stripped from InP surfaces which are exposed to atomic hydrogen. Such interactions lead to the formation of indium globules on the surface. There is no evidence of gallium droplets on our surfaces.

5.1.5 Mechanisms for H atom etching of GaAs

The present study appears to be the first report of continuous etching of GaAs by hydrogen atoms in the absence of ion bombardment from a plasma. Our XPS data indicates that the etching surfaces are gallium rich and is consistent with the large body of literature on the interaction of hydrogen plasmas and atoms with GaAs surfaces. This suggests that the rate limiting process for the hydrogen atom etching of GaAs is the removal of gallium, whereas the removal of the arsenic as hydrides is much faster. The activation energy determined in this work must therefore be associated with the gallium removal process. Whether this rate limiting step is the formation or desorption of a surface hydride species is still unknown. As gallane (GaH_3) is expected to have a low boiling point, its desorption should occur readily and the activation energy of the process would then be related to a bond formation step. However, since digallane decomposes³⁰ into gallium and hydrogen above 0 °C, and etching occurred only above 180 °C, it seems probable that the desorbing species could be an unsaturated molecule. For example, work on fluorine etching of silicon¹³⁴ has shown that unsaturated silicon fluoride species such as SiF_2 are desorbed from the surface. In our etch process, such a molecule could be GaH (GaH and GaH_3 are much more stable than GaH_2 because of their closed electron shells¹³⁵). Listed in Table 5.2 are the bond energies for GaAs, H_2 , and the gallium and arsenic hydrides. As discussed in Chapter 1,

Table 5.2 Bond energies of GaAs, H₂, and Ga and As hydrides

Bond	Energy (kJ mol ⁻¹)	Reference
Ga—As	586	136
H—H	436	137
Ga—H	271	138
HGa—H	172	135
H ₂ Ga—H	317	135
As—H	268	139
HAs—H	286	139
H ₂ As—H	310	139

no gallium hydrides have been detected from GaAs surfaces exposed to hydrogen atoms, although the continuous exposure to hydrogen atoms in our work may be sufficient to produce and desorb such a species.

5.1.5.1 Absorption of H by GaAs

Bulk hydrogen can play an important role in surface reactions. For example, a recent report by Johnson and co-workers¹⁴⁰ has shown that absorbed deuterium atoms in nickel were responsible for the hydrogenation of CH₃ adsorbed on the surface, whereas no CH₃D was produced when the deuterium was co-adsorbed. They attributed this to the direct recombination of an interstitial D atom with a CH₃ species directly above in a threefold hollow surface site.

Hydrogen is known to diffuse readily in GaAs¹⁴¹. Although the absorbed hydrogen in most studies was introduced into the semiconductor by exposure to hydrogen plasmas, where the high energies of the ions drive them into the lattice, incorporation can also be achieved by exposure to atoms¹⁴². Therefore, it seems likely that our samples are acting as sinks for the incoming hydrogen atoms. The important question is whether this absorbed hydrogen is in any way involved in the etching process. For example, dissolved hydrogen could be a source of H atoms for the formation of volatile arsenic and gallium species.

There is very little quantitative data on the diffusion and solubility of hydrogen in GaAs. The expression given by Omeljanovsky *et al.*¹⁴³ yields a diffusion coefficient of $2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for hydrogen in semi-insulating GaAs at 600 K. Normal diffusion of hydrogen in GaAs (*i.e.* the diffusion coefficient, D , is independent of concentration) satisfies Fick's diffusion equation (in one dimension),

$$\frac{\partial[H]}{\partial t} = D \frac{\partial^2 [H]}{\partial x^2}$$

In our etching experiments, the supply of atoms to the surface is constant and at time $t = 0$, the concentration of H at a distance, x , beneath the surface is $[H](x, 0) = 0$. The boundary conditions for this equation are $[H](0, t) = H_s$ and $[H](\infty, t) = 0$. The solution to the diffusion equation is then,

$$[H](x, t) = H_s \operatorname{erfc}\left(\frac{x}{\sqrt{4Dt}}\right)$$

At small depths, $x/\sqrt{4Dt} \ll 1$, and this equation simplifies to,

$$[H](x, t) \approx H_s \left(1 - \frac{2x}{\sqrt{4Dt\pi}}\right)$$

After about 10^{-3} s, the concentration of H a few layers below the surface (≈ 1 nm) is only 4% lower than the surface concentration, and after 1 s, the concentration at 1 nm is only 0.12% less than H_s . Thus, the concentration of H atoms below the surface increases rapidly, and if the solubility of H in GaAs is sufficiently large, this subsurface hydrogen could be contributing significantly to the etching process. The highest measured concentrations are $\approx 10^{21} \text{ cm}^{-3}$, but may be significantly higher during the exposure¹⁴¹. One might also expect to see a continuation of the etch when the discharge is shut-off. In our experiments, interferometry indicated that etching ceased immediately when the atom supply was stopped. However, the boundary conditions for the diffusion equation also change and the subsurface concentration of hydrogen will rapidly decrease as the atoms continue to diffuse towards the low-concentration region of the sample (the loss of hydrogen out of the solid surface would depend on the nature of the surface *e.g.* an oxide layer could prevent recombination and desorption of H_2 ¹⁴⁴). The drop-off rate would not be detectable with our interferometry technique.

Experimental evidence for muonium in GaAs¹⁴⁵, and several theoretical studies¹⁴⁶ indicate that the most energetically favourable position for an absorbed hydrogen atom is in a Ga-As bond *i.e.* in a so-called 3 centre bond rather than an interstitial site. Although such a position does require an increase in the bond

length, it is favoured by the increased strength of the resulting Ga-H-As bond. However, hydrogen is more likely to be found in interstitial sites when the semiconductor has a large supply of extra electrons, *i.e.* heavily n-doped, so that formation of H^- reduces the hydrogen interaction with the semiconductor orbitals.

The activation energy given for the diffusion of H in semi-insulating GaAs is therefore most likely to be the energy needed to hop from one three-centre bond into another one. However, the value of 80 kJ mol^{-1} for diffusion in semi-insulating GaAs given by Omeljanovsky *et al.*¹³⁹, is approximately four times larger than the activation energy we obtained for the etching of GaAs. It is thus unlikely that diffusion of hydrogen in the bulk will contribute significantly to the etch process.

However, it is possible that the entrance of hydrogen atoms into the GaAs bonds in the surface region has a relatively low activation energy. The rate controlling step in the process would then be either the formation of the 3 centre bond or the breaking of the As-HGaH_x bond (to form gaseous GaH_{x+1}). Since the etching appears to be crystallographic, it is probably not the "addition step" that is rate controlling but the "leaving step". This follows from the fact that leaving certain faces could be easier since there are fewer bonds to be broken in the formation of GaH_x. For example, the surface atom densities on {100}, {110} and {111} faces are 6.26 , 4.42 and $7.23 \times 10^{14} \text{ atoms cm}^{-2}$, respectively, and the atoms in each face have 2, 1 and 3 bonds to the next layer, respectively. Thus, a {111} face would have almost 5 times more bonds to break per cm^2 than a {110} face. We earlier eliminated the possibility that the formation of AsH_x could be rate controlling from the observation that the surface was always arsenic deficient.

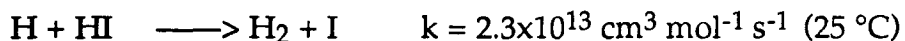
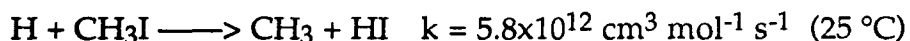
5.2 ETCHING OF GaAs BY METHYL RADICALS

As described in Chapter 1, three methods were employed to generate methyl radicals for the etching of GaAs. The results will be presented chronologically.

5.2.1 CH₃ generated from CH₃I + H

When iodomethane was introduced into a 0.400 Torr stream of H₂ and H atoms, GaAs was observed to etch continuously and much more rapidly than with hydrogen atoms alone. Etch rates of up to 90 nm min⁻¹ were obtained at temperatures of 300 °C. Figure 5.6 shows the interferograms recorded for two different flows of iodomethane. With a larger flow of iodomethane, the etch rate decreases with time. This may be due to the gradual accumulation of iodine on the reactor walls, which could reduce the hydrogen atom concentration necessary for the titration. The constancy of the reflected light intensity in the interferograms also indicates that the etching surfaces are reasonably smooth. Rougher surfaces resulted from etches at lower temperatures.

Iodomethane was chosen as a hydrogen atom titrant because the C-I bond energy is low (234 kJ mol⁻¹) and consequently the abstraction is fast. However, HI is a primary product of this reaction, and a faster secondary reaction with a hydrogen atom will also occur, *viz.*



Computer modelling indicated that after a few milliseconds, the concentration of iodine atoms would be at least as high as the methyl radical concentration. Thus, iodine atoms could also be responsible for the etching of GaAs. In order to ascertain the contribution of iodine atoms to the etch, hydrogen iodide was titrated with hydrogen atoms.

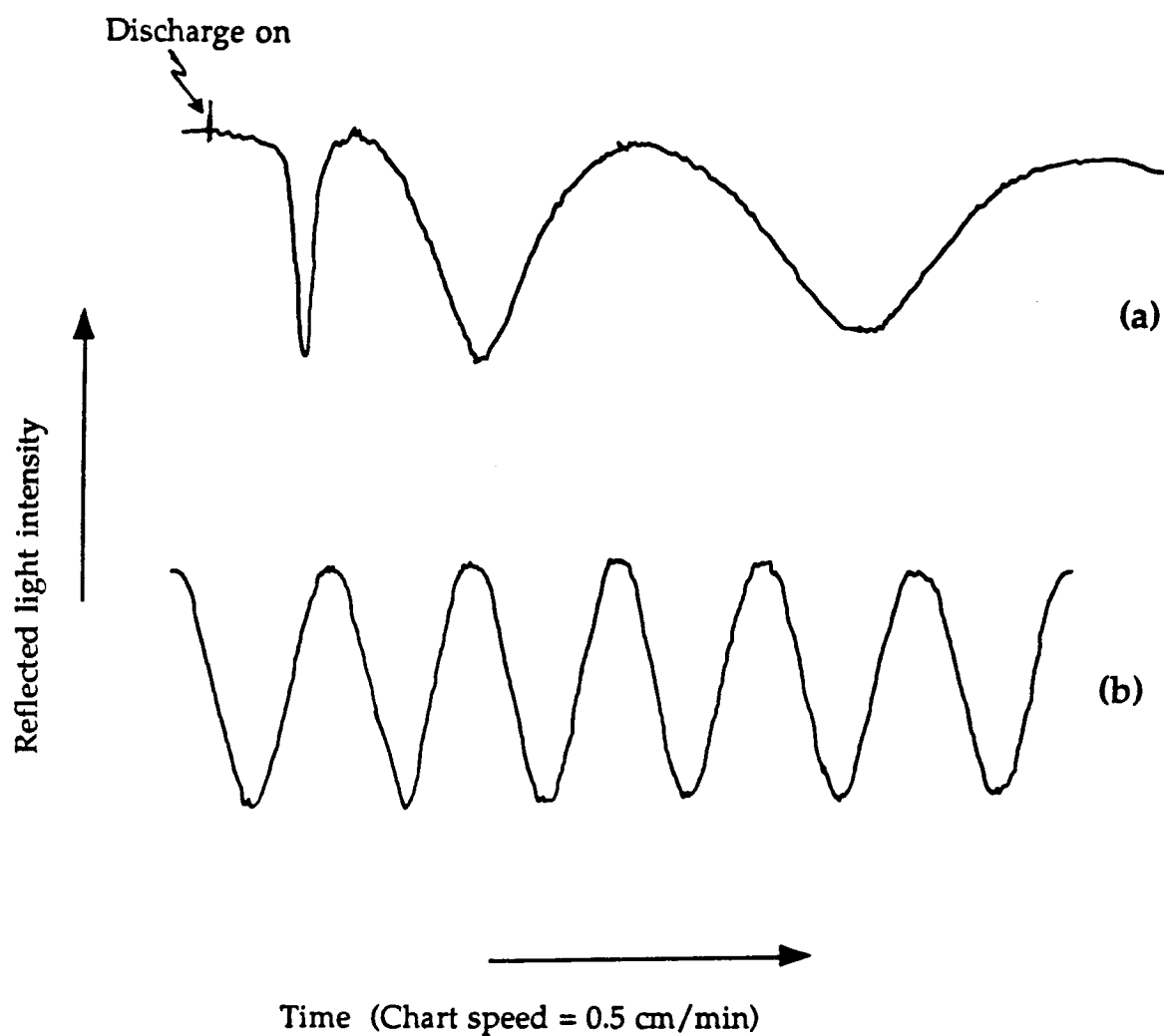


Figure 5.6 Interferograms showing the etching of GaAs for two ratios of the CH_3I to H flows (a) 2:1 and (b) 1:7 at 195 °C.

For conditions where hydrogen atoms were etching GaAs at 10 nm min^{-1} , the introduction of 0.200 Torr of HI increased the etch rate by almost a factor of 35. This is shown in Figure 5.7. No etching was observed with HI alone. The decrease of the reflected light intensity in Figure 5.7 is a result of increasing surface roughness during the etch.

If we assume that all of the H atoms react with the HI to form iodine atoms, then the partial pressure of I atoms, P_I , will be equal to that of the initial H atom pressure, P_H . Thus, the rate constants, k_I , for I atom etching of GaAs can be calculated. The rate constants and other data are given in Table 5.3

A plot of $\ln(k_I)$ versus $1/T$ shows an Arrhenius behaviour for the etching with I atoms (Figure 5.8). A linear least squares fit of the data gives an Arrhenius activation energy of $26.2 \pm 5.1 \text{ kJ mol}^{-1}$ and a pre-exponential factor of $10^{6.9 \pm 0.5} \text{ nm min}^{-1} \text{ Torr}^{-1}$. The line in Figure 5.8 is given by,

$$k_I = 10^{6.9} \text{ nm min}^{-1} \text{ Torr}^{-1} \exp(-26.2 \text{ kJ mol}^{-1}/RT).$$

The error in the rate constants is expected to be largely derived from the uncertainty in the constants for H etching, but we are also assuming complete "conversion" of the H atoms to I atoms. Thus, the error in the activation energy was determined from the extrema in the Arrhenius plot.

The pre-exponential term is equivalent to $2.9 \times 10^{20} \text{ atoms cm}^{-2} \text{ sec}^{-1} \text{ Torr}^{-1}$. This is quite reasonable since the collision frequency of iodine atoms on the surface decreases from 1.4 to $1.3 \times 10^{20} \text{ collisions cm}^{-2} \text{ sec}^{-1} \text{ Torr}^{-1}$ over this temperature range.

As the etch rates are large, the possibility that the reactions were limited by the supply of iodine atoms to the surface needs to be considered. For example, at 498 K, the etch rate was 351 nm min^{-1} , which is equivalent to the removal of $1.3 \times 10^{16} \text{ atoms cm}^{-2} \text{ sec}^{-1}$. The partial pressure of iodine atoms was 0.020 Torr, which corresponds to a flux on the surface of $2.8 \times 10^{18} \text{ atoms cm}^{-2} \text{ sec}^{-1}$. There are

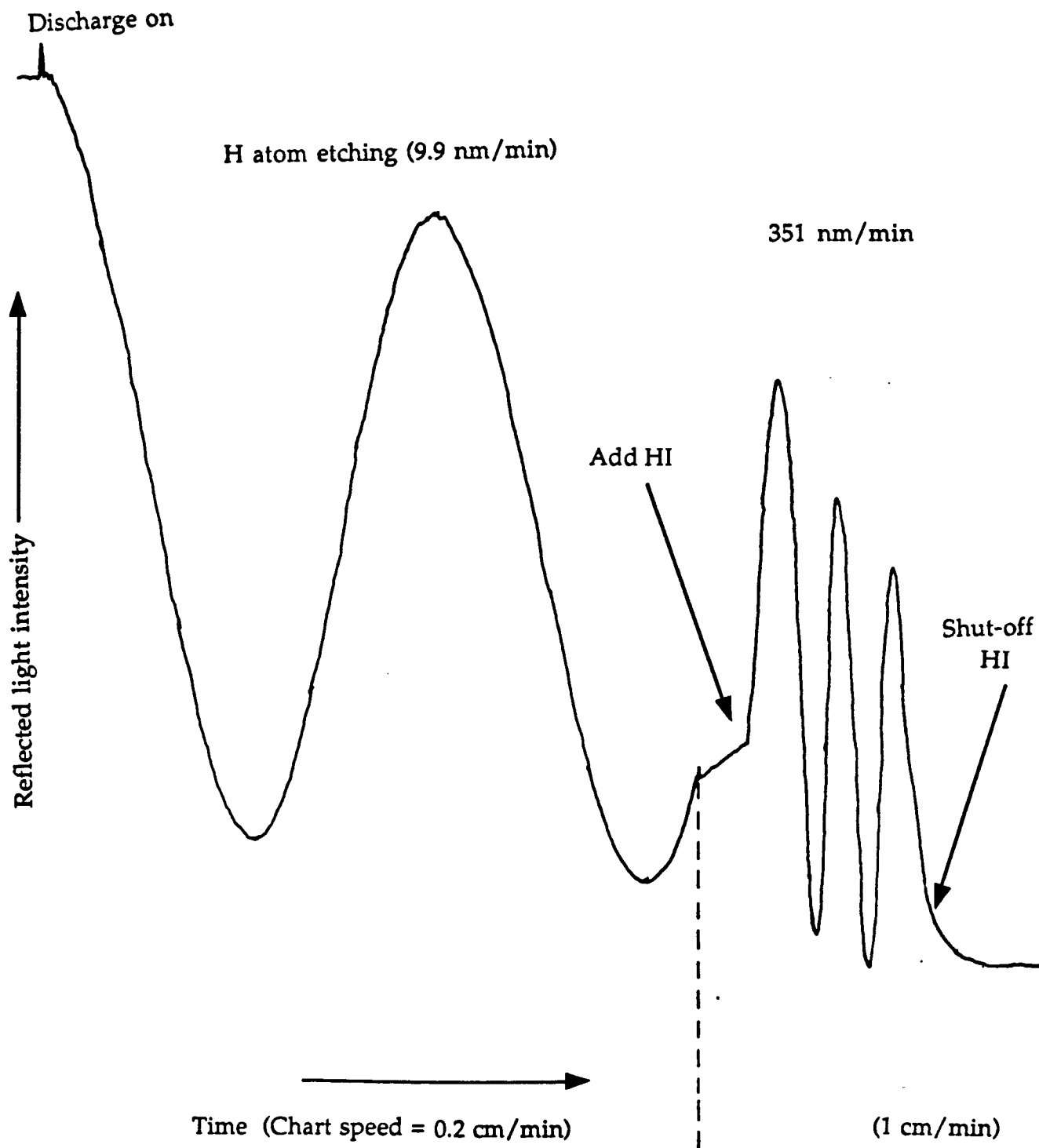


Figure 5.7 Interferogram showing the effect of adding HI to the H flow on the etch rate of a GaAs sample (225 °C).

Table 5.3 Rate constants and pertinent data for H and I etching of GaAs.

Temp. (°C)	H atom etch rate (nm/min)	I atom etch rate (nm/min)	$P_H = P_I$ (Torr)	k_I (nm/min/Torr)	$\ln(k_I)$	k_H (nm/min/Torr)
199	6.0	158.2	0.0161	9826	9.19	372
225	9.9	351.5	0.0204	17189	9.75	484
294	9.7	379.7	0.0121	31421	10.36	803

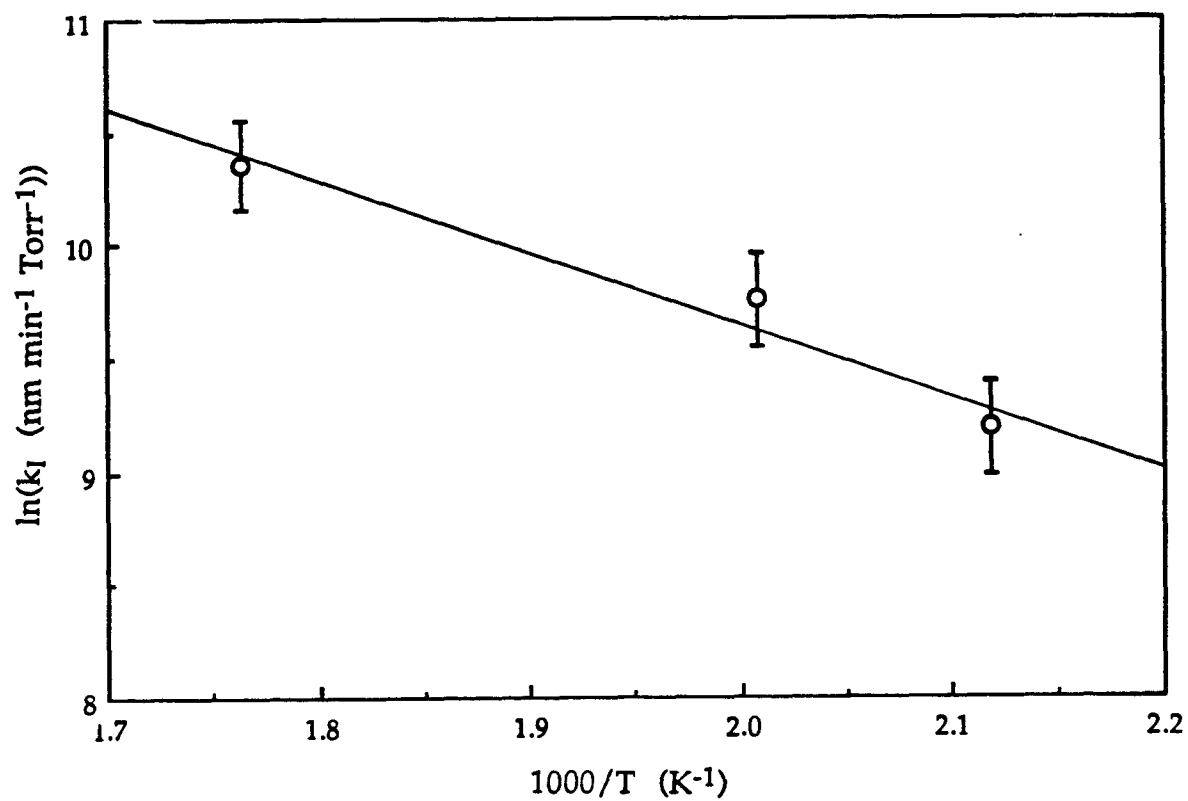


Figure 5.8 Plot of $\ln(k_I)$ versus $1/T$ for iodine atom etching of GaAs.

therefore approximately 215 iodine atoms available for each arsenic or gallium atom removed. If the desorbing products were GaI_3 and AsI_3 (products trapped in $\text{N}_2(\text{l})$ trap from I_2 etching of GaAs^{147}), then 3 iodine atoms would be required to remove each surface atom and the minimum reactive sticking coefficient would be 0.014. This is not unreasonable, but suggests that the etch rates could easily approach the limit of reactant transport at higher temperatures.

Etching of GaAs with molecular iodine was observed in separate work carried out in this laboratory¹⁴⁷. The activation energy for this process was determined to be $69 \pm 10 \text{ kJ mol}^{-1}$, which is considerably higher than the 26 kJ mol^{-1} we obtained for the etching by atoms. Rough surfaces were also observed to form in the I_2 etching.

From the results of the $\text{HI} + \text{H}$ experiments, we can conclude that in the iodomethane/hydrogen atom system, the etchants are hydrogen atoms and iodine atoms. The contribution of methyl radicals was not established by this study. Since the primary concern of this work was to determine kinetic parameters for the neutral etchants in alkane-based RIE, a cleaner supply of methyl radicals was sought.

5.2.2 Photodissociation of acetone

The feasibility of using the photolysis of acetone as a source of methyl radicals for the etching of GaAs was determined from the following calculation. An ArF excimer laser operating at 193 nm under optimum conditions can produce a flux of 10^{17} photons per pulse. If all of the photons are absorbed by acetone and the laser pulse rate is 10 Hz, then 2×10^{18} methyl radicals would be produced each second. Assuming that half of these could be made to react with the GaAs , and that three methyl radicals are needed to remove each surface atom (as GaMe_3 and AsMe_3), an etch rate of $\approx 10^5 \text{ nm min}^{-1}$ on a typical sample ($3 \text{ mm} \times 3 \text{ mm}$) would

be observed. However, if we limit the acetone pressure to 2 Torr and the path length is only 2 cm, then approximately 10% of the photons will be absorbed per pulse¹⁴⁸ and the etch rate will reduce to $\approx 10^4$ nm min⁻¹.

Thus, it would seem that reasonable etch rates are possible. However, the loss of CH₃ due to recombination will be significant at these pressures. The question is how the loss by recombination compares to the loss due to reaction. To maximise the reaction rate, the substrate temperature should be as high as possible. Also, by keeping the pressure low and generating the radicals near the surface, losses from recombination should be reduced.

Although we optimised all the above parameters, etching was never observed in this system, even when the surface was cleaned in an *in situ* hydrogen plasma and substrate temperatures were above 350 °C.

The lack of etching may be attributed to several possible factors.

- (1) The loss of CH₃ by recombination is very high, and despite production just above the surface, insufficient radicals were available for etching.
- (2) The presence of oxygen impurities may have oxidised the hot surface, thus inhibiting the etch.
- (3) Methyl radicals may not etch GaAs without the presence of H atoms or ion bombardment (methyl radicals may be more reactive towards elemental Ga and As (mirrors) than to a GaAs surface).

We therefore returned to a chemical method of producing methyl radicals, *i.e.* the titration of methane with hydrogen atoms.

5.2.3 CH₃ generated from H + CH₄

5.2.3.1 Etching of GaAs

When methane was introduced into a flow of molecular and atomic hydrogen, substantial increases in the etch rate of GaAs were observed. Whereas H

atom etches would not commence when the surface temperature was below approximately 200 °C, etching could be achieved at temperatures as low as 100 °C in H + CH₄ mixtures. In addition, etch rate initiation was also significantly improved with methane present. However, etches in the temperature range 100 – 200 °C, were not very reproducible, so the results presented here were obtained at 200 – 380 °C.

Table 5.4 summarises the data for the etching of GaAs in H/CH₄ mixtures. The etch rates for P_{CH₄} = 0 *i.e.* no added methane (marked with an asterisk), were calculated from the initial H atom flows and the previously determined Arrhenius expression for H atom etching.

Figures 5.8 - 5.10 are the plots of GaAs etch rate versus the partial pressure of added methane at several temperatures. Despite the scatter in these plots, it appears that for temperatures below 350 °C, the etch rates increase linearly with increasing pressure of added methane, but begin to plateau at higher pressures. However, at 374 and 380 °C the etch rates are highest at very low pressures of methane and then decrease as more CH₄ is added.

The increase in the etch rate with addition of methane can only be attributed to the presence of methyl radicals, since apart from H atoms, no other reactive species should be present in significant concentrations (*e.g.* C₂H₅•). Therefore, the partial pressures of methyl radicals at the sample position were calculated for each etch by modelling the gas compositions as discussed in Chapter 3. Figures 5.11–5.13 are the plots of etch rate versus the calculated partial pressures of methyl radicals. Also shown are the weighted linear least squares fits to each set of data.

The linear dependence of the etch rate on the partial pressure of methyl radicals suggests a process which is first order in CH₃. The slopes of the lines in Figures 5.11 – 5.13 thus correspond to the first order rate constants for this process. This data is summarised in Table 5.5 and is shown as an Arrhenius plot in

Table 4.4 Data for H + CH₄ etching of GaAs

$\bar{T}_{\text{sample}}$ (°C)	$\bar{T}_{\text{gas}}$ (°C)	$\bar{F}_{\text{H}_2}$ ($\mu\text{mol/s}$)	$\bar{F}_{\text{H}}$ ($\mu\text{mol/s}$)	F_{CH_4} ($\mu\text{mol/s}$)	Etch rate (nm/min)
232	211	67	0.71	0	4.1*
				9	18.8
				17	29.6
				23	28.6
				32	32.5
				34	39.0
				48	34.0
259	236	67	0.70	0	5.2*
				13	41.8
				14	46.5
				18	53.5
				22	53.5
				51	59.4
				51	66.8
285	268	67	0.62	0	5.6*
				6	79.4
				8	35.7
				8	49.5
				14	33.4
				14	45.8
				22	33.4
				26	80.0
				26	96.9
				34	93.5
310	297	67	0.60	0	6.6*
				3	28.2
				6	41.1
				10	62.9
				14	106.3
				17	82.3
				29	158.1
				29	141.4
				37	163.2
				46	161.3

Table 4.4 Data for H + CH₄ etching of GaAs (continued)...

$\bar{T}_{\text{sample}}$ (°C)	$\bar{T}_{\text{gas}}$ (°C)	$\bar{F}_{\text{H}_2}$ ($\mu\text{mol/s}$)	$\bar{F}_{\text{H}}$ ($\mu\text{mol/s}$)	F_{CH_4} ($\mu\text{mol/s}$)	Etch rate (nm/min)
310	300	82	0.60	0	6.7*
				14	87.0
				31	182.0
				47	211.2
				80	217.4
				113	196.5
348	333	67	0.61	0	8.7*
				2	50.9
				2	56.3
				6	118.9
				6	107.0
				13	167.0
				22	152.9
				27	178.3
				39	212.8
374	370	113	0.69	0	9.6*
				10	169.0
				14	208.7
				29	186.8
				31	187.0
				47	211.5
				62	172.2
				80	186.9
				113	148.8
380	370	14 + 162(He)	0.84	0	15.0*
				2	157.3
				14	164.8
				22	178.5
				31	214.6
				39	202.2
				43	217.1
				64	201.2
				113	162.6
				146	158.6

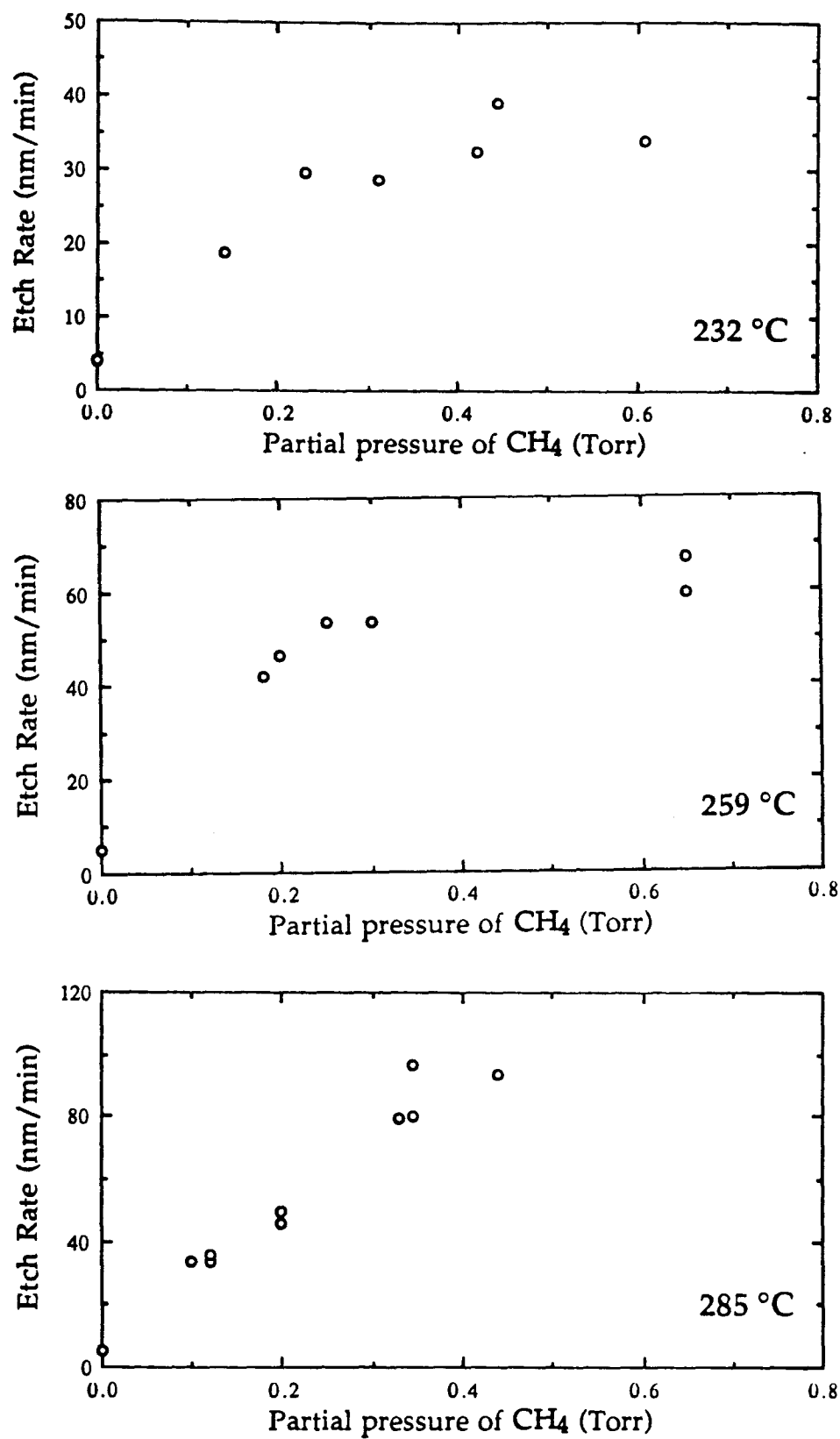


Figure 5.9 Plots of GaAs etch rate versus partial pressure of CH₄ added to a stream of H atoms and H₂ at sample temperatures of 232, 259 and 285 °C.

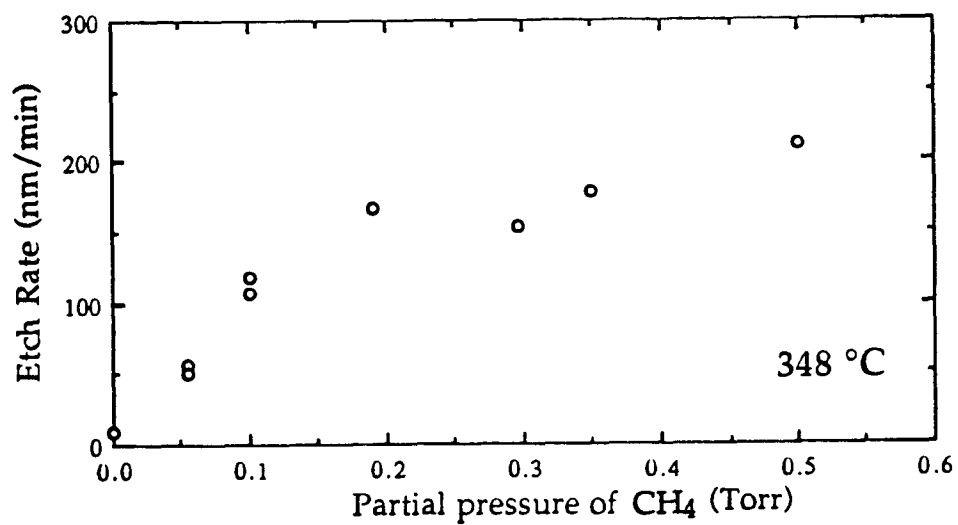
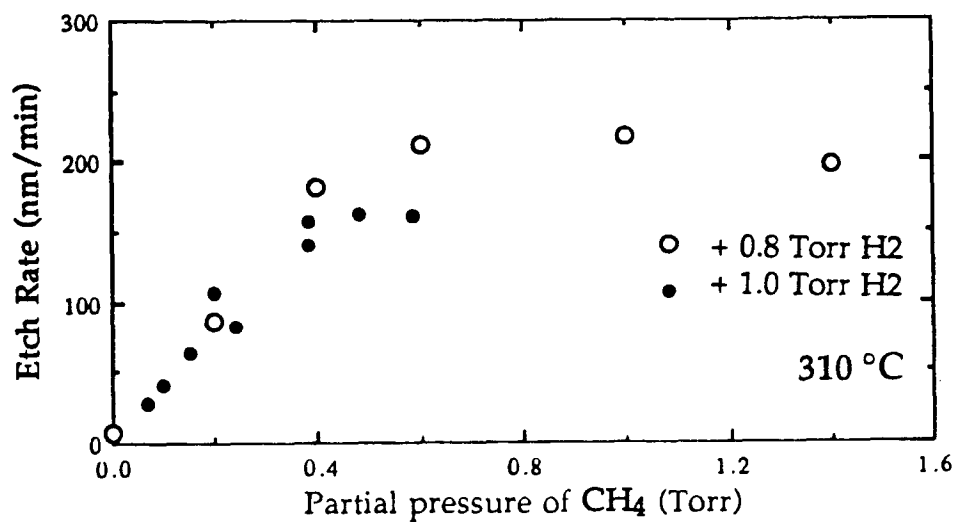


Figure 5.10 Plots of GaAs etch rate versus partial pressure of CH₄ added to a stream of H atoms and H₂ at sample temperatures of 310 and 348 °C (two pressures of H₂ at 310 °C).

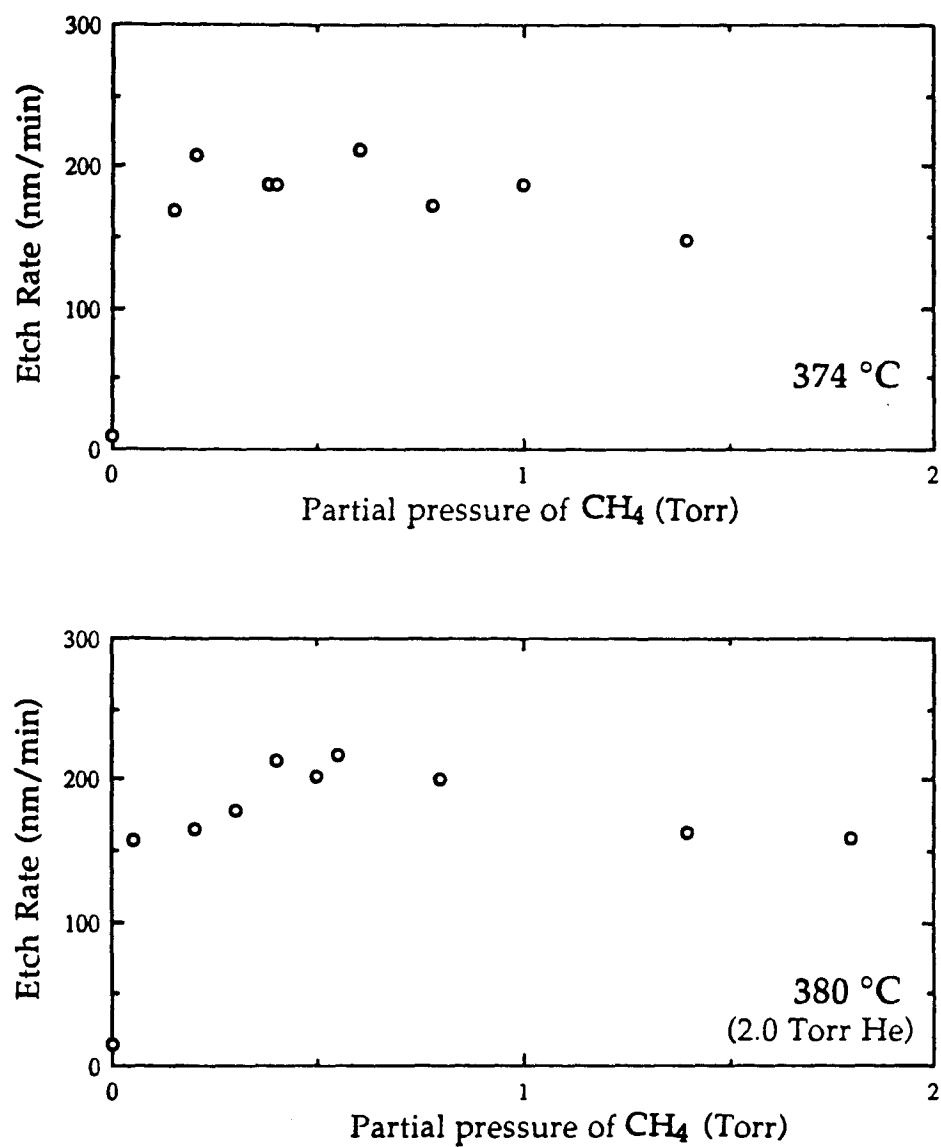


Figure 5.11 Plots of GaAs etch rate versus partial pressure of CH₄ added to a stream of H atoms and H₂ at sample temperatures of 374 and 380 °C.

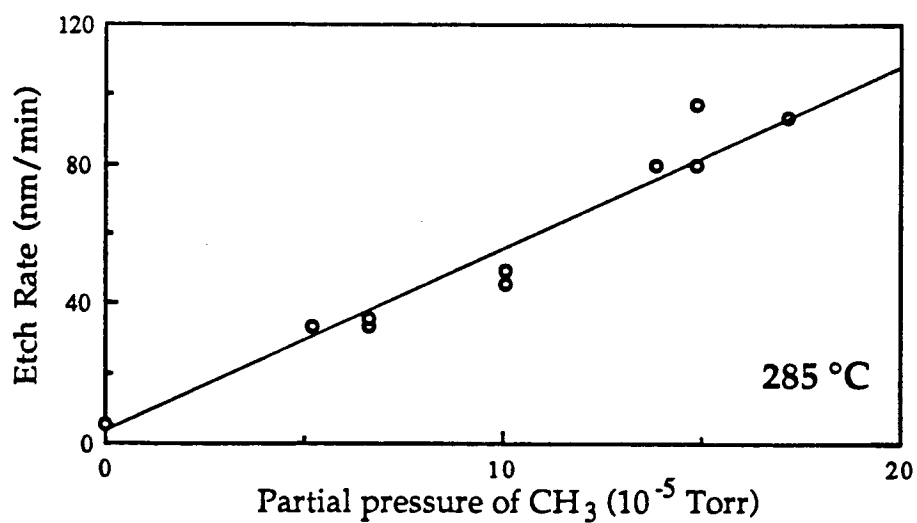
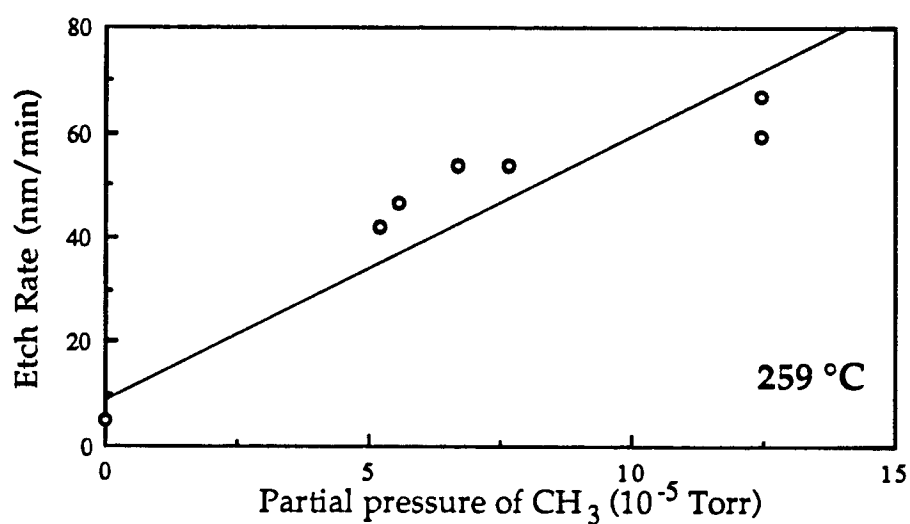
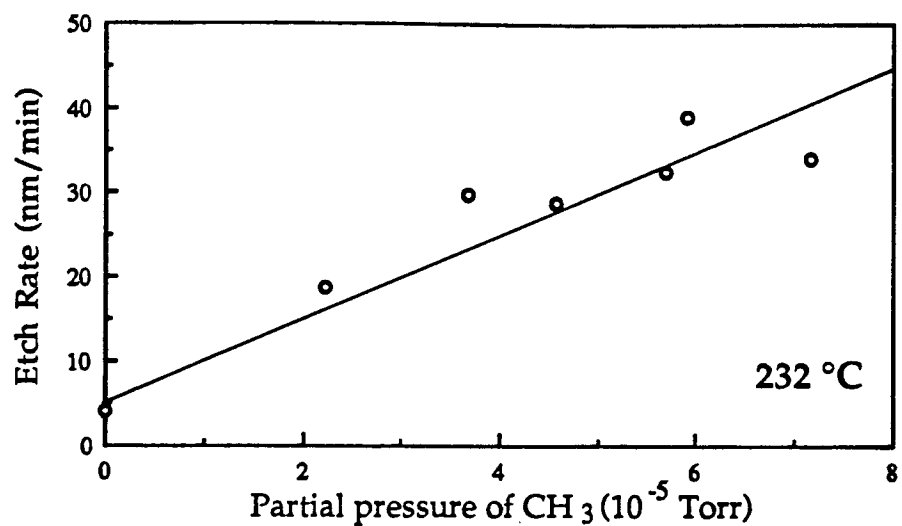


Figure 5.12 Plots of GaAs etch rate versus calculated pressure of CH_3 (from the reaction of H with CH_4) at sample temperatures of 232, 259 and 285 °C.

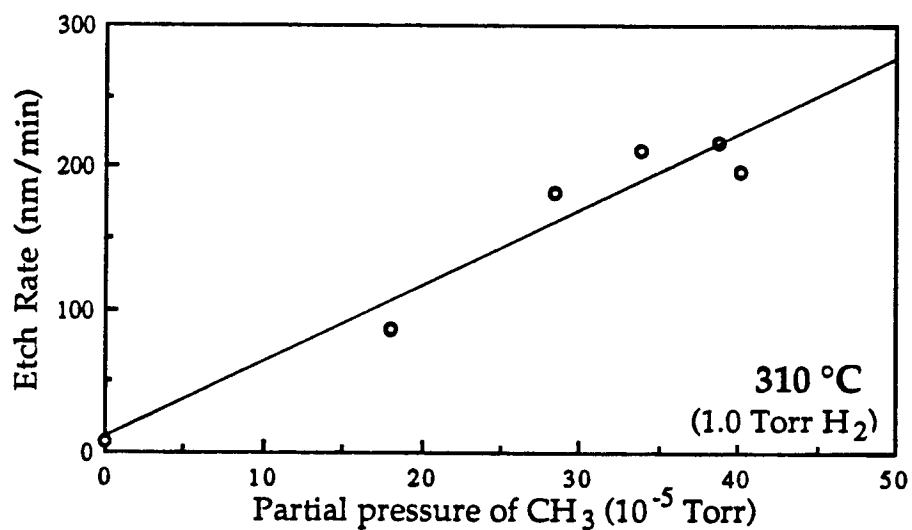
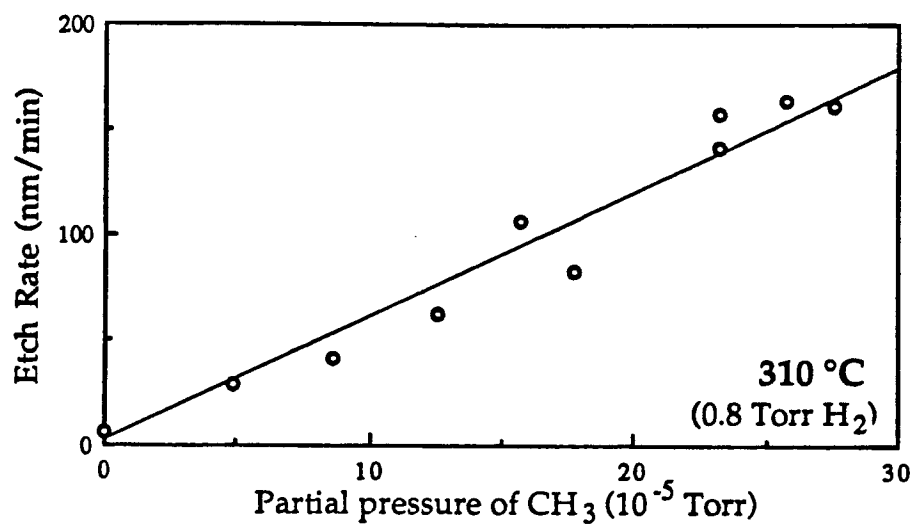


Figure 5.13 Plots of GaAs etch rate versus calculated pressure of CH_3 at a sample temperatures of 310°C (for two pressures of H_2).

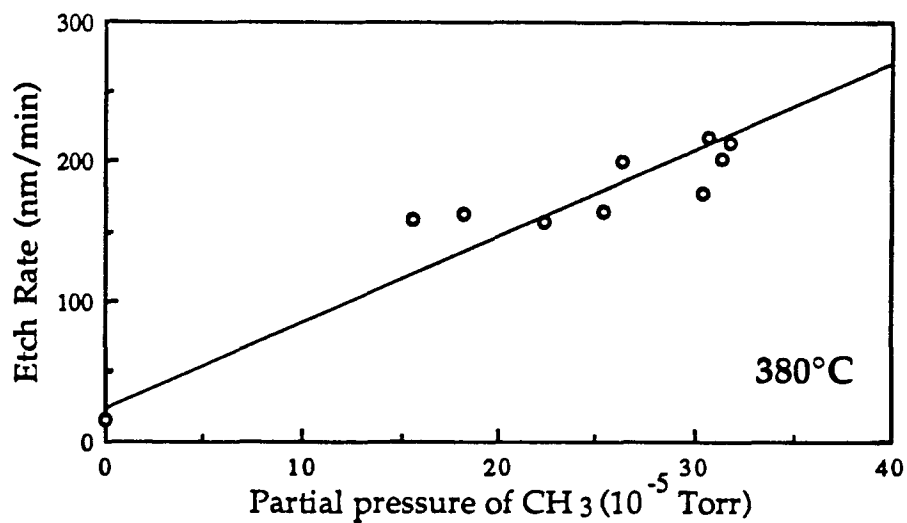
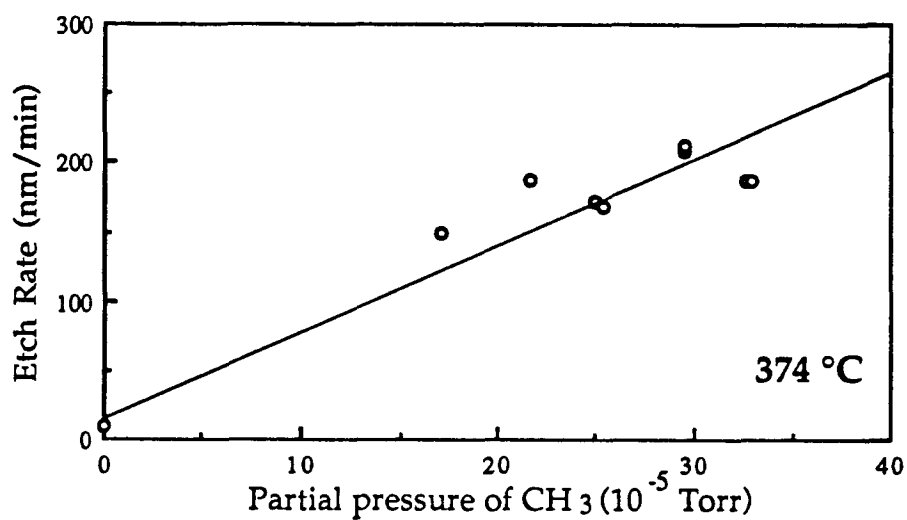
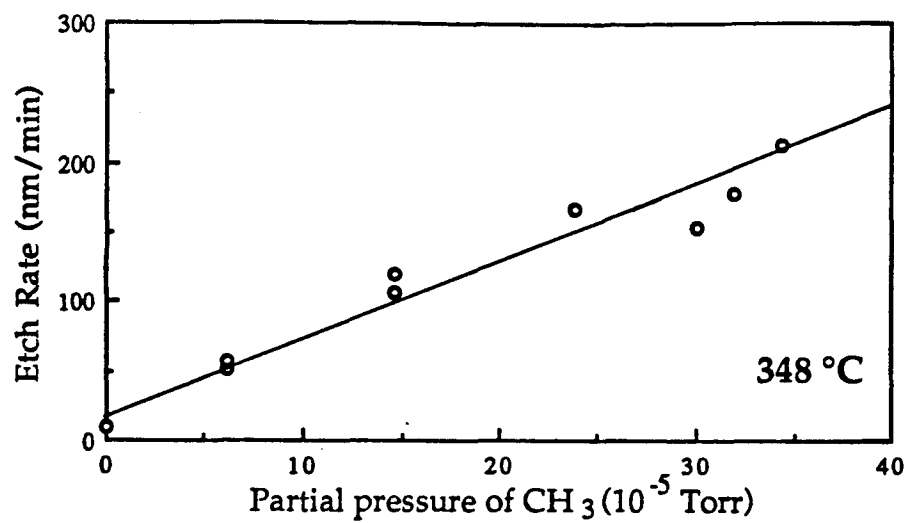


Figure 5.14 Plots of GaAs etch rate versus calculated pressure of CH₃ at sample temperatures of 348, 374 and 380 °C.

Table 5.5 Rate constants as a function of temperature for CH₃ etching of GaAs.

T _{surface} (°C)	k (x10 ⁻⁵) (nm/min/Torr)
232	4.99
259	5.06
285	5.26
310	5.82
310	5.40
348	5.63
374	6.31
380	6.30

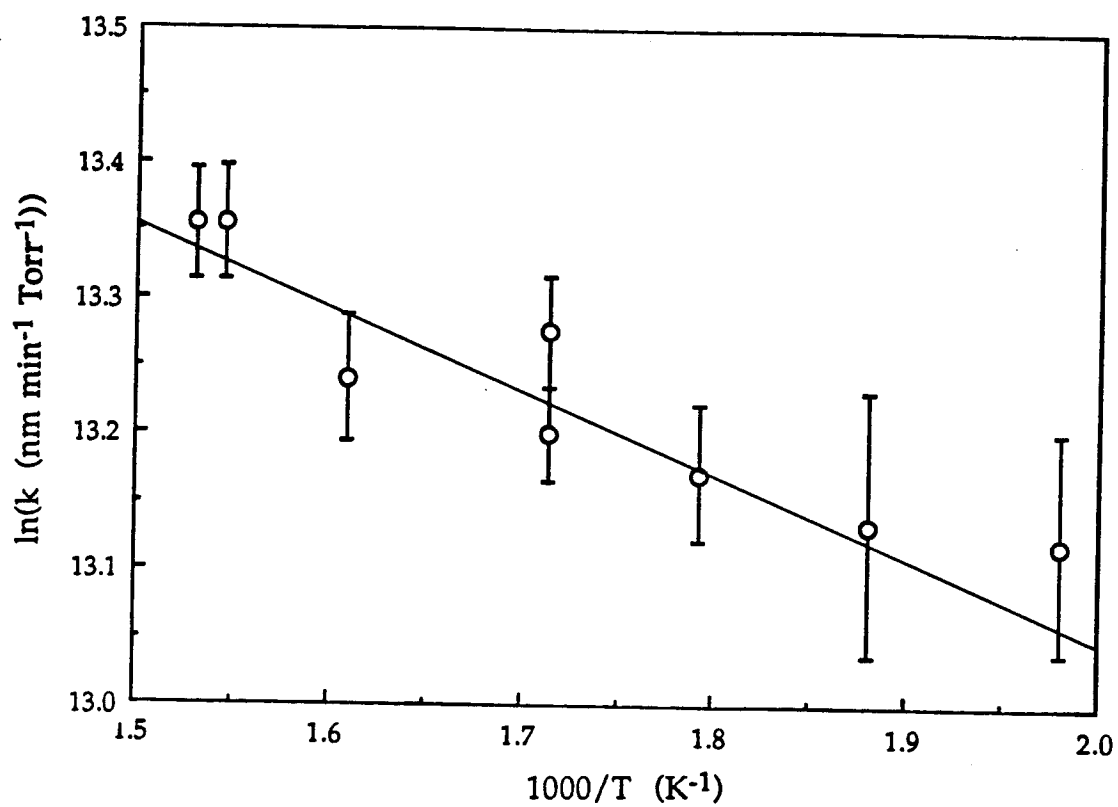


Figure 5.15 Plot of $\ln(k)$ versus $1/T$ for the rate constants obtained from the slopes of Figures 5.12 – 5.14 (H/CH₃ etching of GaAs).

Figure 5.15. A weighted least squares fit of the data gives an activation energy of $5.1 \pm 1.2 \text{ kJ mol}^{-1}$ and a pre-exponential value of $10^{6.1 \pm 0.4} \text{ nm min}^{-1} \text{ Torr}^{-1}$.

The rate constants are very large ($5.0 - 6.3 \times 10^5 \text{ nm min}^{-1} \text{ Torr}^{-1} = 1.8 - 2.3 \times 10^{19} \text{ molecules cm}^{-2} \text{ s}^{-1} \text{ Torr}^{-1}$). Over this temperature range ($232 - 380 \text{ }^\circ\text{C}$), the surface collision frequency of methyl radicals decreases from 4.0 to $3.5 \times 10^{20} \text{ collisions cm}^{-2} \text{ s}^{-1} \text{ Torr}^{-1}$. Thus, the flux of CH_3 radicals on the surface is only an order of magnitude greater than the number of As and Ga atoms removed per unit area per second. Table 5.6 lists the ratio of incident methyl radicals to the number of As and Ga atoms removed for each gas temperature. Depending on the stoichiometry of the etch products (e.g. $\text{Ga}(\text{CH}_3)_3$), the reactive sticking coefficients could be as high as 0.2. The etch rates could therefore be limited by the supply of methyl radicals to the surface, and raises the possibility that the process could be diffusion controlled *i.e.* the reaction with the surface is so rapid that a concentration gradient is set up, across which the methyl radicals must diffuse. Thus, the actual concentration of CH_3 at the surface would be smaller than our calculated values. This would mean that both the rate constants and the reactive sticking coefficients would be higher *i.e.* almost every incident methyl radical would have to react with the surface.

Let us consider the effect of diffusion on a reaction that is occurring at collision frequency. If we assume a simple concentration gradient (neglecting turbulence), then the flux of methyl radicals, J , on the GaAs surface is given by,

$$J = (C_B - C_S)D/d$$

where d is the distance from the surface at which the concentration of radicals is equal to the bulk value, C_B (called the boundary layer thickness). C_S is the concentration of radicals at the surface and D is a proportionality constant called the diffusion coefficient. The diffusion coefficient for methyl radicals in hydrogen (neglecting added methane, for simplicity) can be determined from¹⁴⁹,

Table 5.6 Ratio of incident CH₃ flux on surface to flux of As and Ga atoms removed from the surface, as a function of temperature.

T _{gas} (°C)	CH ₃ /atom
201	21.8
236	20.3
268	20.4
297	17.8
300	18.9
333	17.4
370	15.4
370	15.1

$$D_{1,2} = \frac{\sqrt{(V_1^2 + V_2^2)}}{3\pi (N_1 + N_2) \sigma_{12}^2}$$

where 1 and 2 represent H₂ and CH₃, N is the number of molecules/cm³, V is the molecular velocity in cm/s, and σ_{12} is the average molecular diameter in cm (= 3.26x10⁻⁸ cm). The pressure and temperature dependence of D is approximately given by¹⁴⁹,

$$D = D^\circ \times (T/273)^{1.75} \times (P^\circ/P)$$

At 1 Torr and 325 °C, D = 1660 cm² s⁻¹, so diffusion is about an order of magnitude faster than the gas flow velocity (mean diffusion length, $x^2 = 2Dt$ and $V_{\text{gas}} \approx 300$ cm s⁻¹). If we assume that reaction at the surface is occurring with unit efficiency (reactive sticking coefficient = 1), then the concentration of radicals at the surface is effectively zero (rapidly converted to product) and the flux on the surface is simply,

$$J = C_B D / d$$

Now we can estimate a boundary layer thickness by equating the etch rates (E.R.) to the flux of radicals on the surface, J, *i.e.*

$$\text{E.R.} = J = C_B D / d$$

Since by definition E.R. = kP_{CH_3} , then at a radical pressure of 1 Torr,

$$\text{E.R.} = k = C_B D / d$$

$$\Rightarrow k = C_B D^\circ (P^\circ/P) (T/273)^{1.75} / d$$

At 1 Torr and 273 K, D[°] is calculated to be 510 cm² s⁻¹, and C_B = 9.66x10¹⁸/T radicals/cm³. Therefore, for any temperature, and at 1 Torr,

$$k = 2.69 \times 10^{17} \times T^{0.75} / d \text{ (molecules cm}^{-2} \text{ s}^{-1}\text{)}$$

As before, we can use the density of GaAs to convert our rate constants in units of nm/min/Torr to units of product molecule flux leaving the surface (molecule cm⁻² s⁻¹ Torr⁻¹). A plot of our values of k versus T^{0.75} gives d = 1.50 cm. This is

close to the radius of the reaction tube (1.25 cm). Figure 5.16 is our Arrhenius plot (Figure 5.15) with the addition of a line showing the temperature dependence of the rate constants for a reaction occurring at collision frequency, but limited by diffusion of reactant across a depleted layer 1.50 cm thick. The slope of this line is very similar to that for the "best fit" of our rate constants. Thus, it would appear that our etch rates are diffusion controlled and the activation energy may be associated with the small temperature dependence of the diffusion coefficient.

During the course of this work, Spencer *et al.*⁵⁴ reported an activation energy of 30.1 kJ mol⁻¹ for the etching of GaAs with CH₃ and H, produced by the reaction of a mixture of CH₄ and H₂ with F atoms. This value was obtained from three etches (each at a different temperature) over the temperature range of 100 – 195 °C. The maximum etch rate was 10 nm min⁻¹ at 195 °C. However, in this study they did not measure the concentrations of the reactive species and therefore did not determine the order of the reaction or report any rate constants. In a subsequent paper, Spencer¹⁵⁰ shows an example of a concentration versus time profile for CH₃ and H, calculated from initial conditions of approximately 8 mTorr of F, 30 mTorr H₂ and 6 mTorr CH₄ at a total pressure of 1 Torr in argon. He estimated that 0.2 mTorr of H and 0.1 mTorr of CH₃ would rapidly be produced by the abstraction reactions of F ($F + H_2 \rightarrow HF + H$ and $F + CH_4 \rightarrow HF + CH_3$), and the CH₃ would decay by $CH_3 + CH_3 \rightarrow C_2H_6$. He did not consider the H + CH₃ reaction. The sample was close to the titration point and approximately 5 ms would elapse before the reactants reached the surface. With our modelling program, we can use this data to estimate the concentration of methyl radicals at his surfaces. After 5 ms, the initial concentrations of H and CH₃ would have decreased by 3 and 47%, respectively. If we now assume that 0.047 mTorr of methyl radicals was available for all his etching experiments and use his activation energy of 30.1 kJ mol⁻¹, then we can calculate the rate constants. Table 5.7 lists the etch rates and temperatures

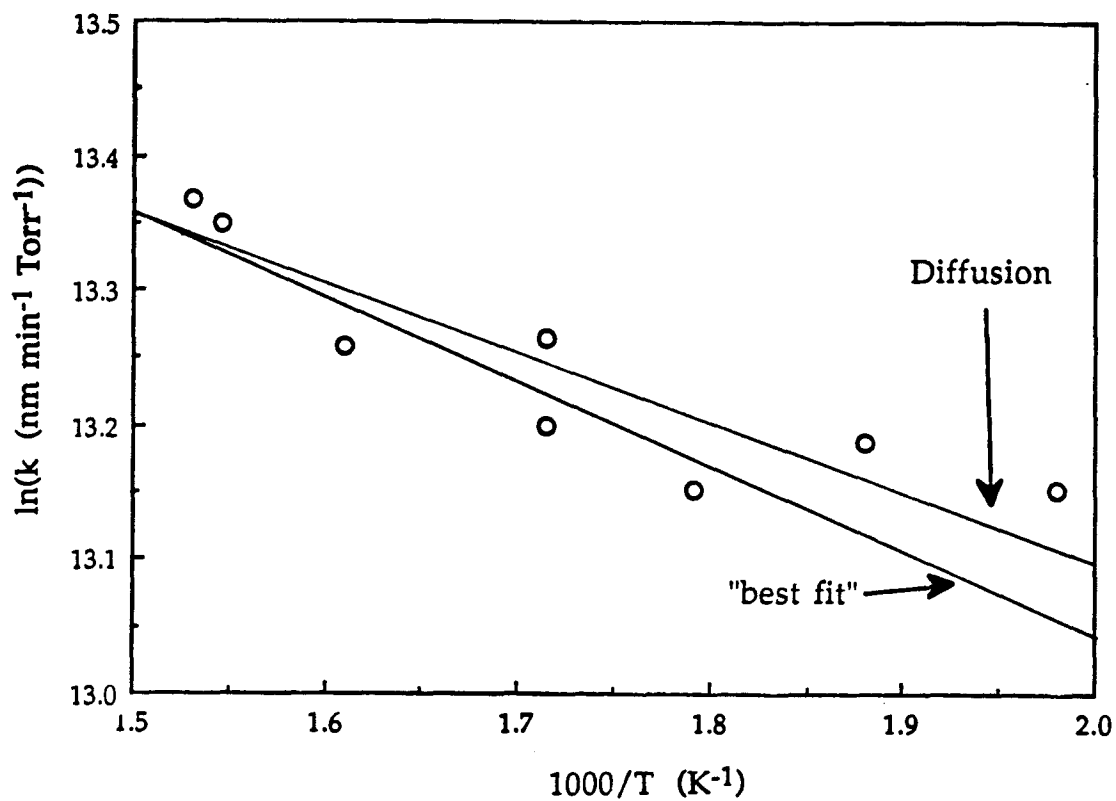


Figure 5.16 Comparison of our Arrhenius plot (Figure 5.15) with the temperature dependence of the rate constants for a process occurring at collision frequency but limited by diffusion across a boundary layer 1.5 cm thick.

for the results reported by Spencer *et al.*⁵⁴ and the rate constants which we calculated from their data, with the assumption that the rate controlling step is the reaction with CH₃.

Figure 5.17 is a combination of our rate constants with those estimated from the results of Spencer *et al.*⁵⁴. Also shown is the line for a process occurring at collision frequency but not limited by diffusion, and our calculated line for the diffusion controlled rate. The change in the temperature dependence of the etch rates with increasing temperatures indicate that our etch rates are in a region where they are diffusion controlled. Although there is considerable uncertainty in our estimation of Spencer's rate constants, his two highest values of k may be approaching the limit of diffusion control. It is also possible that his etch rates were reduced by the consumption of radicals on large samples (no information on sample size was given). However, Figure 5.17 does suggest that the real activation energy for this etching process may be close to 30 kJ mol⁻¹.

5.2.3.2 Morphology of etched surfaces

As was the case for hydrogen atom etching (section 5.1.4), the intensity of the reflected light during interferometric monitoring of methyl radical and hydrogen atom etches also decreased as the etch progressed. However, the amplitude reduction occurred over several periods of the interferogram, whereas this was more rapid for etches with hydrogen atoms alone. Thus, the CH₃/H combination seems to produce a somewhat smoother surface. The etched surface morphologies were examined by scanning electron microscopy.

Figure 5.18(a) is the photo-micrograph obtained from a GaAs sample etched at 267 °C, with a CH₃:H ratio of 1:47. The surface is still rough, but compared to Figure 5.5, is less extreme than observed for H atom etched surfaces. This is in agreement with the interferometry results. The directional "ocean waves" effect

Table 5.7 Etch rate data reported by Spencer *et al.*⁵⁴ and rate constants which we have calculated from this data.

T _{surface} (°C)	Etch Rate (nm/min)	k(x10 ⁻⁵) (nm/min/Torr)	ln(k)
100	10	0.30	10.31
185	8	1.60	11.98
192	1.5	2.28	12.34

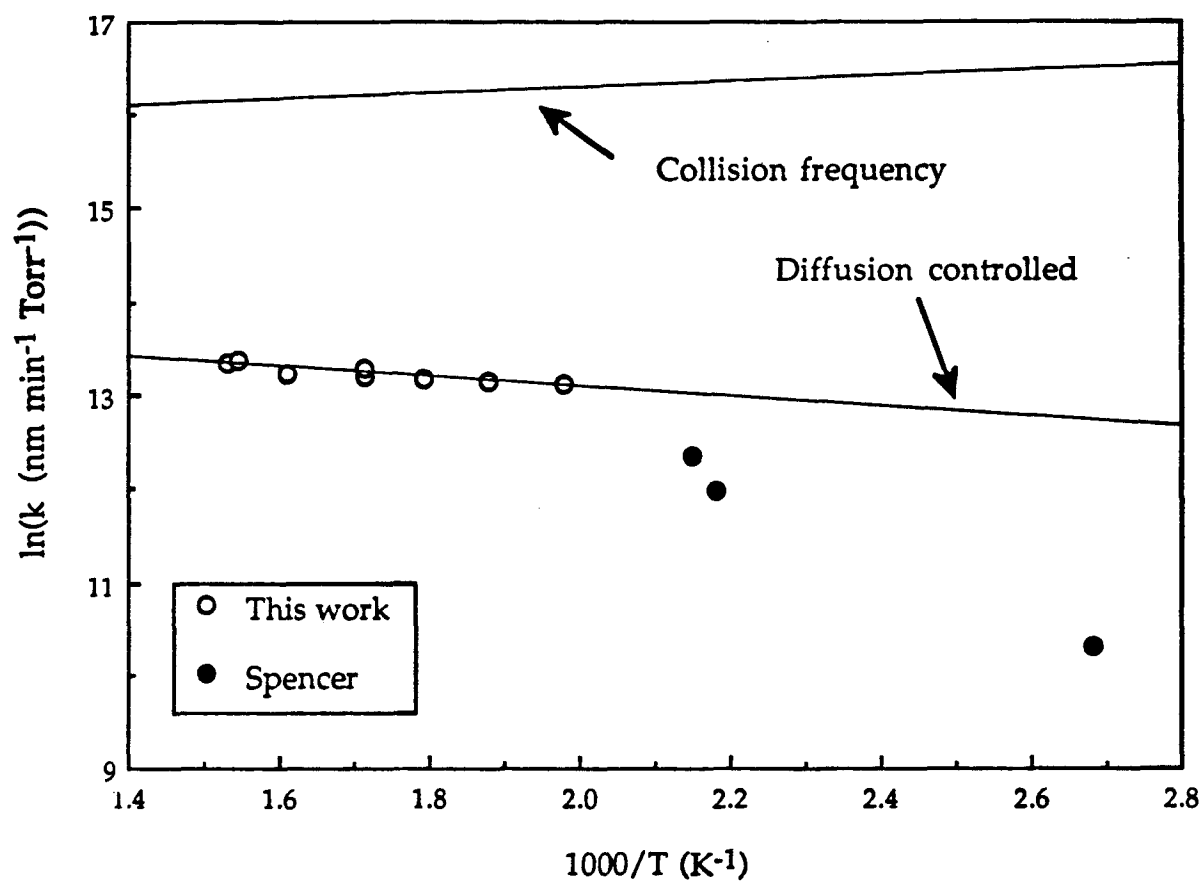
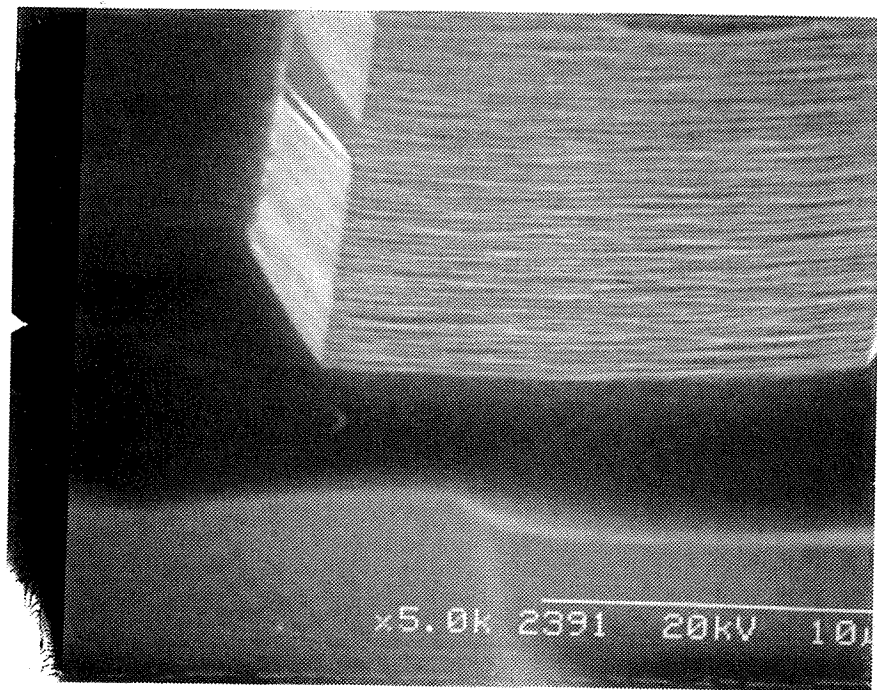
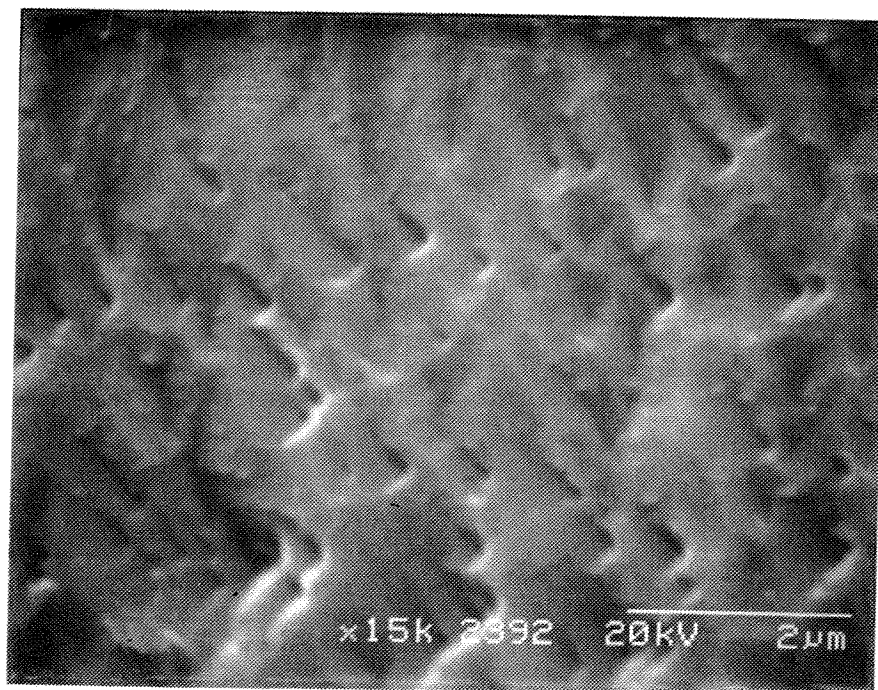


Figure 5.17 Temperature dependence of our rate constants and those we estimated from the results of Spencer *et al.*⁵⁴ (large uncertainty). Also shown are the lines corresponding to collision frequency and to a diffusion controlled process.



(a)



(b)

Figure 5.18 Scanning electron micrographs of a (100) GaAs surface etched with H atoms and CH_3 radicals ($\text{CH}_3:\text{H}$ ratio = 1:47) at 267 °C. (a) looking along the $[01\bar{1}]$ direction ($\approx 10^\circ$ tilt) and (b) looking at (a) rotated by 90° and with a tilt of 35° (x3 higher magnification).

apparent on the surfaces of the micrographs obtained for the etches with H atoms (Figures 5.3–5.5) is also evident in Figure 5.18(a) *i.e.* the striations are aligned with the $[0\bar{1}1]$ direction. Figure 5.18(b) is a magnified image of Figure 5.18(a), but looking at the surface perpendicular to the direction in that micrograph. The viewing angle is also steeper (35° – looking along the striations). The surface features are similar to those observed when Si (111) surfaces are etched in certain chemicals to reveal defects *i.e.* the defective material is removed until slow etching {111} planes are encountered, producing triangular pits¹⁵¹. The angular nature of the pits in Figure 5.18(b) are also consistent with the exposure of {111} type planes, and suggests that a large number of defects of dislocations may be present on this surface. When the depth of these pits is large, the raised areas may appear as the larger "waves" and even "pyramids" observed on the H-etched surfaces.

To investigate the possibility that this surface morphology is caused by an excessive number of defects in the wafers, an unmasked sample was cut from a different wafer (different supplier) and etched under the same conditions. Figure 5.19 shows the micrographs obtained from this sample. Figures (a) and (b) were taken at the same observation angle (12°), but the rotation of the sample differed by 90° . Figure 5.19(c) was taken from the same direction as (b) *i.e.* along the "ripples", but at an inclination of 50° . These surfaces are essentially identical to those for the masked sample. Although this sample was expected to be of higher quality than the masked samples, the etched surfaces do not show significant differences, implying that this surface may also have a high defect density. A similar directional surface morphology was also observed on etched (111)A and (111)B samples (not shown). Such surface roughness is commonly reported in the literature, but remains poorly understood⁵⁴.

Since the etch rates with H/CH₃ were routinely 10–30 times faster than etches with H atoms, several microns of material could be removed in a reasonable

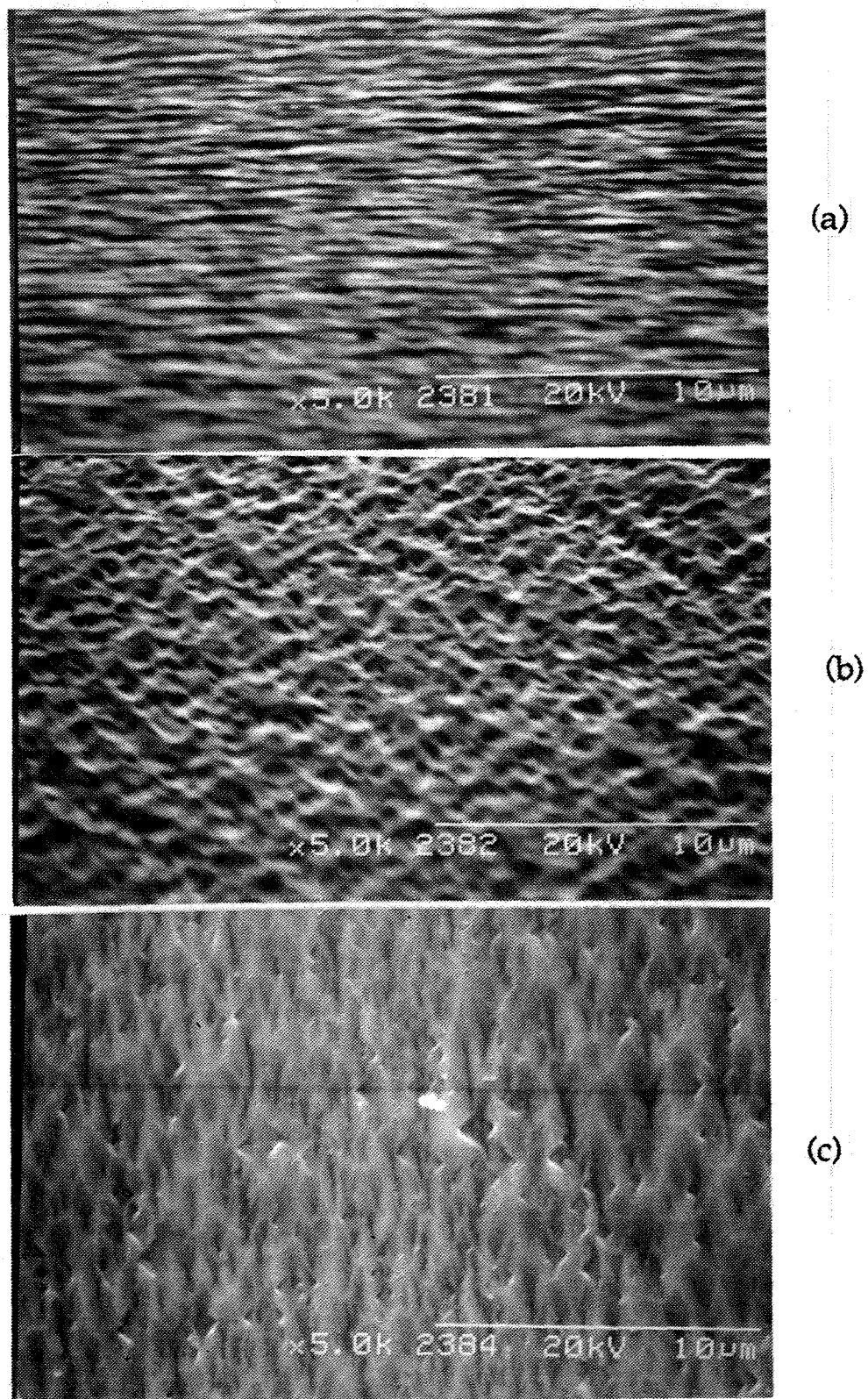
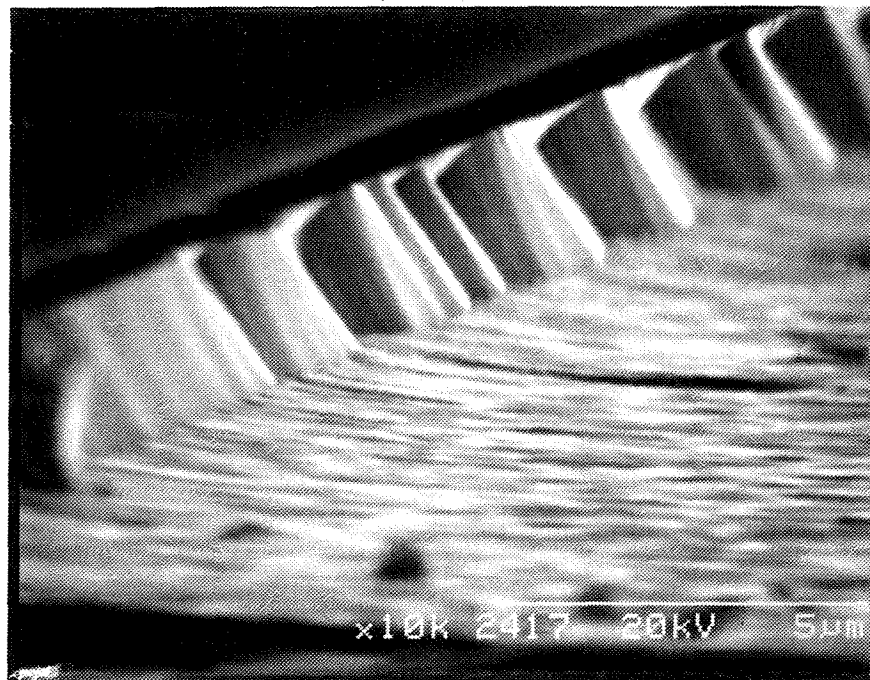


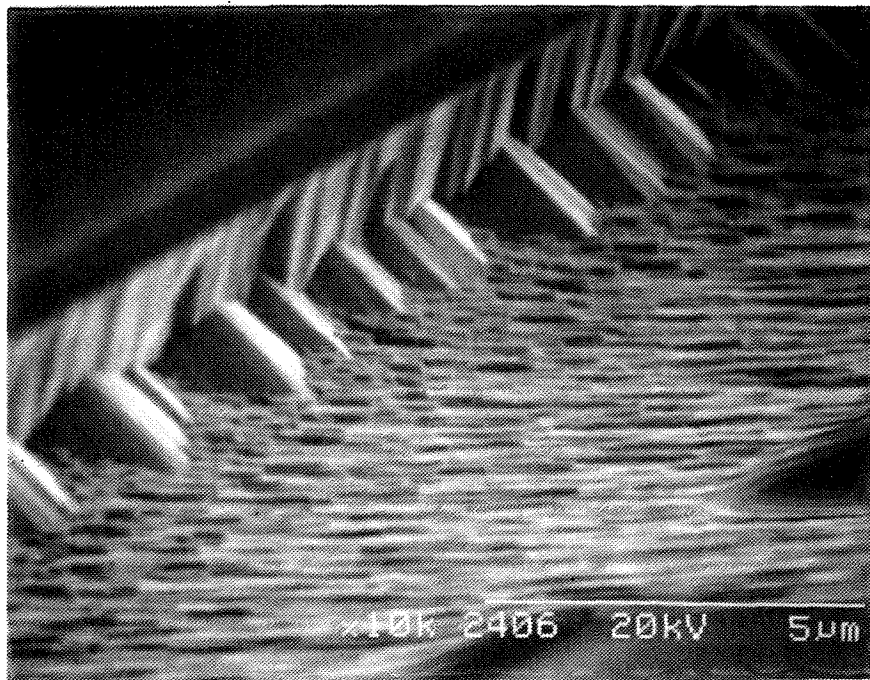
Figure 5.19 Scanning electron micrographs of an unmasked (100) GaAs surface (different supplier) etched under the same conditions as the sample in Figure 5.18. Viewed along (a) $[01\bar{1}]$ and (b) $[0\bar{1}1]$ directions with a 12° tilt, and (c) same as (b) but 50° tilt.

time (≈ 1 hour). Therefore, the sidewalls of these samples were easily observed. The angle of the sidewall in Figure 5.18(a) appears to be close to 55° , with respect to the surface, and can therefore be identified as a (111) plane. This is consistent with an etching mechanism where {111} gallium planes are most resistant to removal, and correlates well with our observation that removal of Ga by H (and CH_3) are rate controlling process.

Closer examination of the sidewall in Figure 5.18(a) shows the presence of a "notch" approximately half-way down its length. Figure 5.20(a) was obtained from a sample etched under the same conditions, but the etch depth was slightly greater ($\approx 3.5 \mu\text{m}$). The observation point is also shallower and rotated to facilitate examination of the sidewall. We can see that several notches have been cut into the (111) plane, resulting in "buttress"-like features. For a sample etched at a slightly higher temperature (285°C , $\text{CH}_3:\text{H} = 1:69$) and to a depth of $4.0 \mu\text{m}$, the resultant sidewall profile was more extreme (see Figure 5.20(b)). From this micrograph, it is evident that the buttresses have diminished considerably, exposing a back-wall which appears to have a negative angle. An "end-on" shot of this sidewall is shown in Figure 5.21(a). Measurement of the angles suggests that the exposed back-wall ($\approx 70^\circ$ to the mask surface) is a higher index ($11\bar{3}$) plane, while the buttresses are inclined at $\approx 55^\circ$ to the surface (see schematic Figure 5.21(b)). Although an angle of 55° is typical of a (111) plane, it is obvious from Figure 5.20 that several crystal faces are present on these features. Their identification is extremely difficult. MacFadyen¹⁵² observed similar features on GaAs samples etched in solutions of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}$, and correlated the sidewall angles (Figure 5.21(b)) with the solution temperature and composition. Although it was clearly evident from his micrograph that the lower sidewall was not continuous *i.e.* composed of "buttresses", he did not investigate these features. His surfaces were

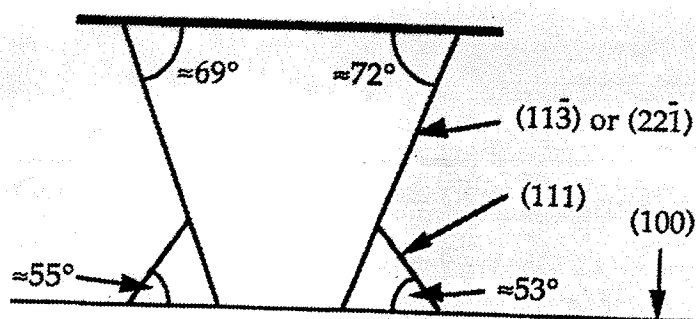
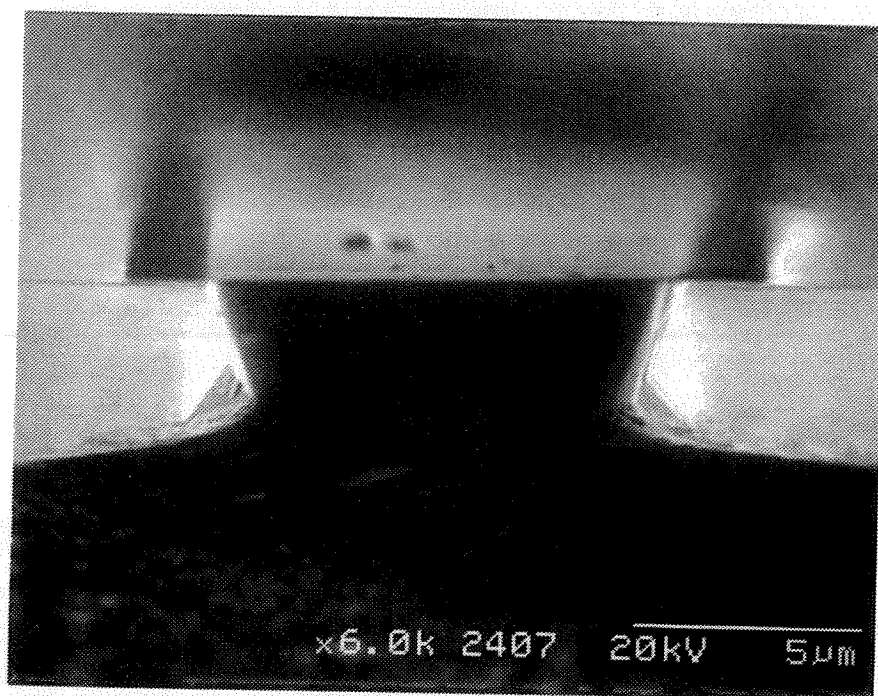


(a)



(b)

Figure 5.20 Scanning electron micrographs of (a) sidewall in Figure 5.18(a) (x10 k) and (b) same view of another sample etched under the same conditions ($\text{CH}_3\text{:H}$ ratio = 1:47, 267°C), but a deeper etch.



MEASURED ANGLES

Viewed along $[01\bar{1}]$ direction

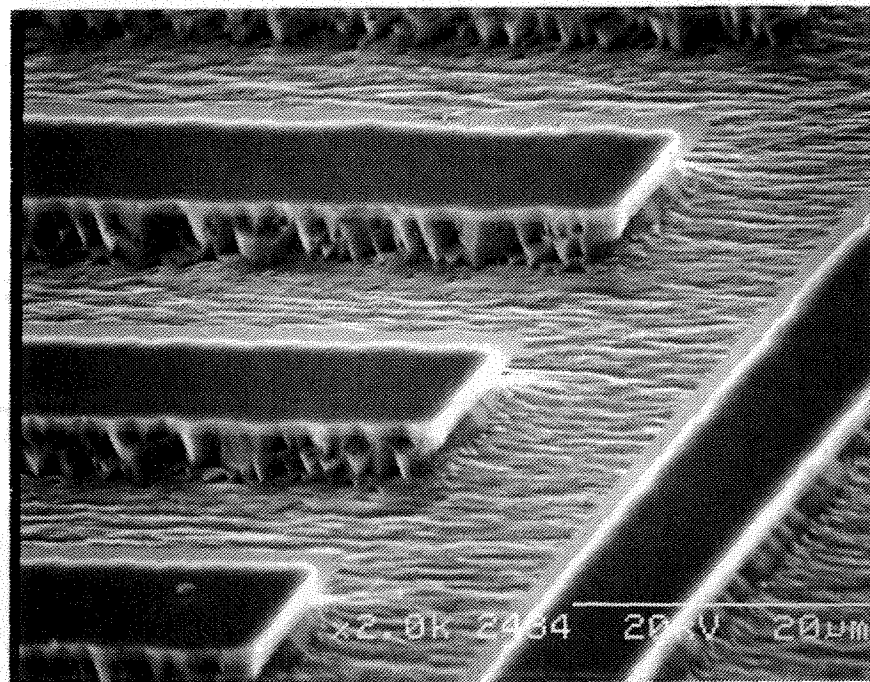
Figure 5.21 Scanning electron micrograph of sample shown in previous Figure (5.20(b)), but viewing the cleaved mask edge at 3° . The sidewall angles are shown in the drawing of this micrograph.

also extremely rough, and exhibited the directional morphology observed on our samples.

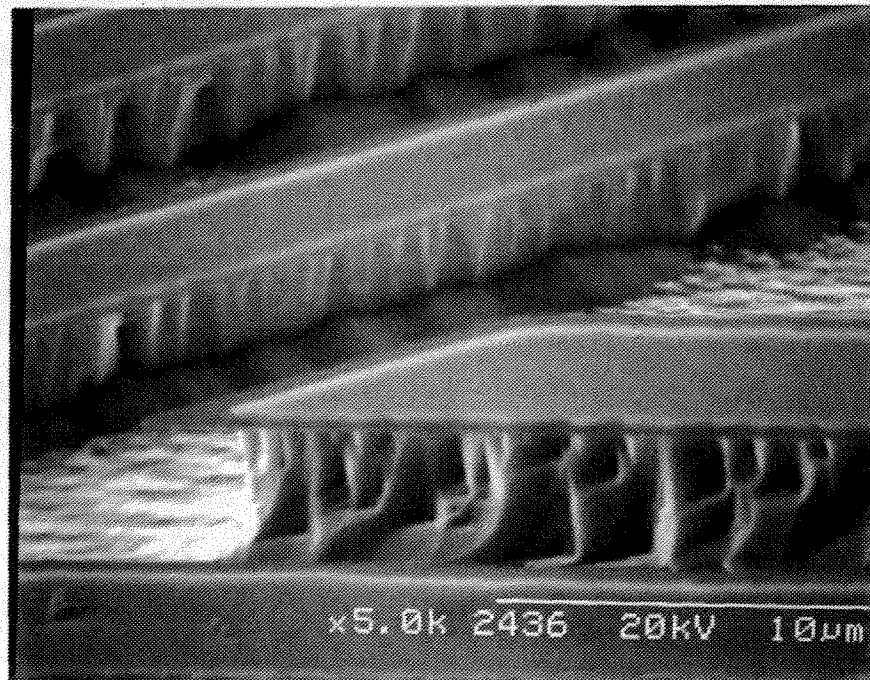
So far, we have only examined the sidewalls produced when the mask is oriented in the $[01\bar{1}]$ direction. Figure 5.22(a) was obtained from a sample with both mask orientations (same conditions as samples shown in Figures 5.18–5.21(a)), and is viewed at the intersection of the two directions. The sidewalls oriented along the $[0\bar{1}1]$ direction are quite different from the walls described above. Instead of the buttresses observed on the $[01\bar{1}]$ direction, many angular features have been exposed. Figure 5.22(b) is a view of the same intersection, but from the opposite direction. Because the viewing angle is more oblique, the buttresses on the far wall appear to be "flatter" than those described above. However, the appearance is still consistent with the under-cut back-wall shown in Figure 5.22. The complexity of the face in the foreground (Figure 5.22(b)) is apparent. With our present data, we are unable to propose a process which would satisfactorily explain these complex etch features, and be consistent for both mask directions.

As the surface temperature was increased, the complexity of the $[0\bar{1}1]$ oriented sidewalls increased, at least in the presence of hydrogen atoms (Figure 5.23(a)). This surface was etched at 380 °C with a $\text{CH}_3\text{:H}$ ratio of 1:1. At the same temperature, but with a $\text{CH}_3\text{:H}$ ratio of 80:1, the trench floors were relatively smooth (Figure 5.23(b)). The small pits apparent on the surface indicate that defects are exposed by these etchants. The features in Figure 5.18(b) could propagate from pits similar to those on this surface.

Figure 5.23(b) suggests that the crystallographic features observed on all the surfaces may be caused by the presence of hydrogen atoms, whereas methyl radicals are quite reactive to all crystal planes. For most temperatures and pressures used, H was the predominant species, while the flux of methyl radicals on the surfaces was relatively small. Therefore, most of the CH_3 would be consumed on

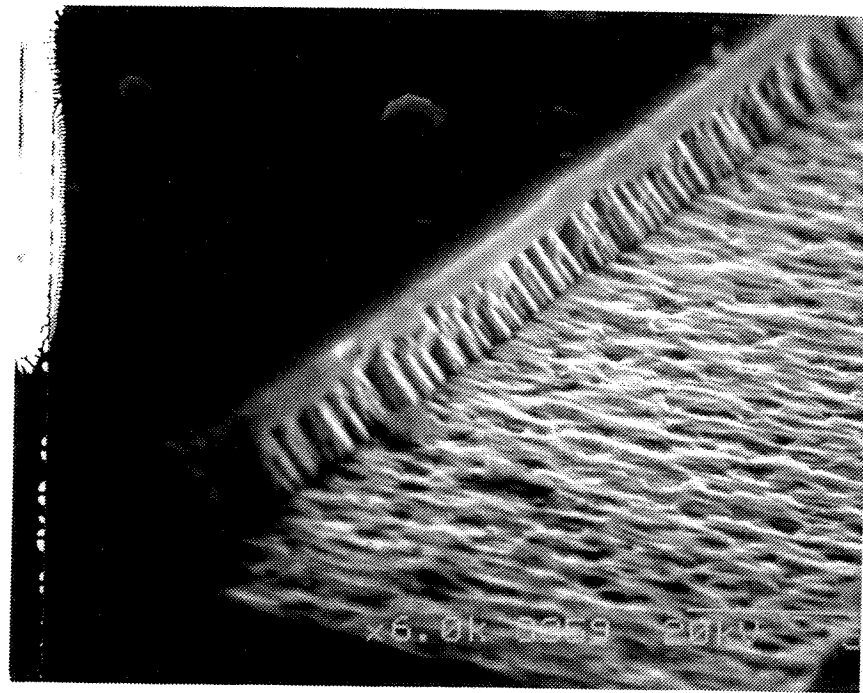


(a)

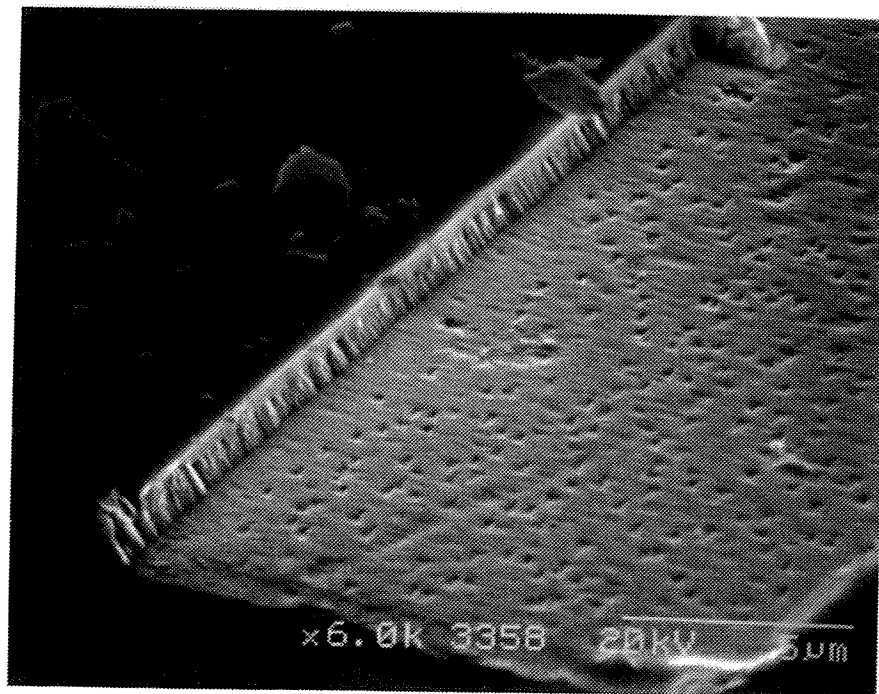


(b)

Figure 5.22 Scanning electron micrographs of a (100) GaAs sample with mask oriented in both directions ($\text{CH}_3\text{:H}$ ratio = 1:47, 267 °C). (a) looking at the intersection of the two mask directions (x2 k, $[0\bar{1}\bar{1}]$ mask parallel to top of the page) and (b) x5 k view in opposite direction of (a), so that $[01\bar{1}]$ sidewall is also visible.



(a)



(b)

Figure 5.23 Scanning electron micrographs of a (100) GaAs samples etched with different $\text{CH}_3:\text{H}$ ratios at 380°C – (a) $\text{CH}_3:\text{H} = 1:1$ and (b) $\text{CH}_3:\text{H} = 80:1$. Mask is aligned with $[0\bar{1}\bar{1}]$ direction for both.

the trench floors, giving surfaces that are somewhat less rough than those produced by hydrogen atoms alone. Thus, while the vertical etch rate is enhanced by the faster reaction with methyl radicals, the complex sidewall features evolve, as hydrogen atoms slowly etch {111}A type crystal planes.

5.2.3.3 XPS analysis of etched surfaces

The As/Ga ratios determined by XPS analysis of samples etched under various conditions are given in Table 5.8. Atmospheric oxidation of the samples precluded any useful measurement of high resolution spectra. Table 5.8 shows that compared to the stoichiometric As/Ga ratio of 1.0 for a (100) surface, all the surfaces etched with methyl radicals and hydrogen atoms were gallium rich. However, compared to the ratios for H atom etched surfaces, the extent of the depletion appears to be less extreme, particularly at the higher temperatures. As we discussed earlier, this trend may not necessarily be directly related to a decrease in the arsenic depletion, but may be influenced by the surface morphology. As shown in the previous section, the surface roughness with CH₃/H etches was significantly less than that observed on H atom etched surfaces. Nonetheless, the ratios imply that the surface may be covered with at least one monolayer of gallium.

Modelling results indicate that consumption of the hydrogen atoms by methane is incomplete below temperatures of ≈ 400 °C (for reasonable pressures of added methane). Thus, while the enhanced etch rates (compared to H atom etches) can be attributed to the presence of methyl radicals, significant pressures of hydrogen atoms were also present. Also listed in Table 5.8 are the ratios for the calculated partial pressures of methyl radicals and hydrogen atoms at the surface for each etch. For experiments performed at temperatures below approximately 350 °C, relatively large pressures of hydrogen atoms were also available for etching.

Table 5.8 XPS As/Ga 3d ratios for H/CH₃ etched GaAs surfaces as a function of CH₃:H ratio and temperature (As/Ga = 1.0 for unetched (100) surface).

Temperature during etch (°C)	Average As/Ga 3d ratio	Calculated CH ₃ : H ratio
380	0.56	80.4
374	0.51	11.3
374	0.62	3.8
311	0.53	0.22
310	0.49	0.06
232	0.30	0.01

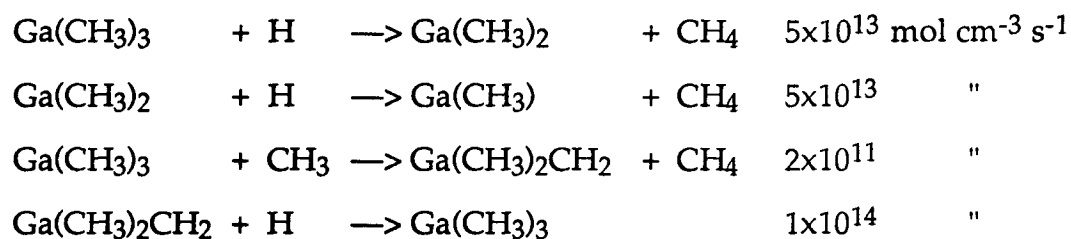
From Table 5.8, it would appear that the correlation between the arsenic depletion and the relative amounts of CH_3 and H is rather poor. This may be due to variations in surface roughness. For the highest CH_3/H ratio used (80: 1), SEM showed that the surface was relatively smooth (Figure 5.23(b)). The As/Ga ratio is therefore a better reflection of the surface stoichiometry. Even with this large pressure of methyl radicals, the surface is still gallium rich. If the reaction of hydrogen atoms with arsenic was much faster than the removal of gallium by methyl radicals, then the presence of very small amounts of H atoms could lead to this depletion. Therefore, we cannot say whether methyl radicals alone produce a gallium rich surface *i.e.* the relative reaction rates of methyl radicals with As and Ga are unknown. However, for $\text{CH}_3 + \text{H}$ mixtures, the H reaction appears to be more rapid and the removal of gallium should be the rate controlling step in this process.

5.2.3.4 Deposition of etch products

Another feature of this etching process was the formation of a deposit on the sample holder and surrounding areas of the reactor. The location and appearance of this deposit varied, depending on the temperature of the walls. When etching GaAs at lower temperatures, a brownish ring formed just below the heated region of the apparatus. At higher temperatures, this colouration was observed further downstream from the heated region, with a silvery coloured deposit closer to the hot walls and on the sample holder. Energy dispersive X-ray analysis of deposits on the Pyrex surfaces showed only the presence of gallium, with no traces of arsenic. XPS analysis of both the brown and silvery deposits also showed that they contained only gallium. Although carbon was also detected, little can be inferred from its presence, since the samples were exposed to the atmosphere. Consequently, the high resolution spectra of the Ga 3d region showed only a broad

peak, with the major contributions probably arising from oxides. Any peaks attributable to methyl-gallium species are likely to be cloaked by the broad oxide peak, and would not be resolvable from these spectra. Similarly, any carbon-gallium species could not be distinguished from the large C 1s signal due to atmospheric carbon contamination.

The deposition of gallium on the cooler parts of the reactor in the CH₃/H etches suggests that the desorbing species is less volatile than trimethyl gallium, which is a gas above 56 °C and does not decompose appreciably below 400 °C¹⁵³. Table 5.9 lists the Ga-C bond energies for mono-, di- and trimethyl gallium¹⁵⁴. The etch products could be dimethyl gallium, or possibly GaH_x(CH₃)_{3-x} species¹⁵⁵. However, it is also quite probable that a gas phase reaction occurs between hydrogen atoms or methyl radicals and the desorbed etch product, to form a less volatile gallium species that deposits on cooler surfaces. Listed below are some possible gas phase reactions of trimethyl gallium and their rate constants¹⁵⁶:

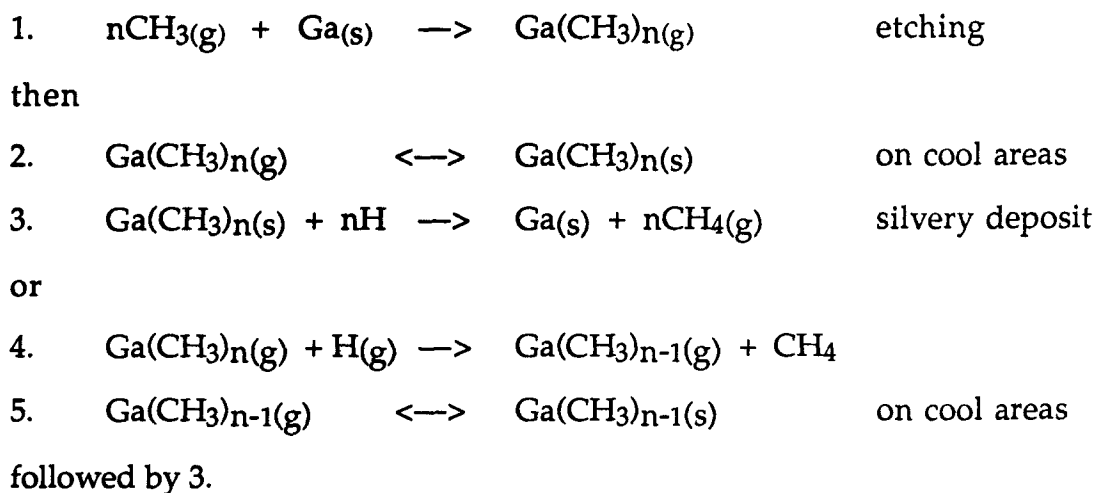


Thus, the reaction of hydrogen atoms with trimethyl gallium to form methane and dimethyl gallium is very rapid, and the removal of another methyl to form monomethyl gallium is equally facile. The reactions of methyl radicals with these methylated gallium species are about two orders of magnitude slower than the hydrogen atom reactions (reaction 3), and consequently the reformation of trimethyl gallium via reaction 4 will not be significant, even though it could occur at collision frequency. GaCH₃ is believed to be responsible for black polymer

Table 5.9 Gallium–carbon bond energies in methyl gallium species (from ref 154).

Bond	Bond energy (kJ/mol)
$(\text{CH}_3)_2\text{Ga}-\text{CH}_3$	248.9
$(\text{CH}_3)\text{Ga}-\text{CH}_3$	148.1
$\text{Ga}-\text{CH}_3$	324.3

formations observed on surfaces when $\text{Ga}(\text{CH}_3)_3$ is pyrolysed¹⁵⁴ and could be the species deposited on our reactor surfaces. However, further reactions of H atoms with such deposits are likely to reduce them to elemental gallium, although the stronger Ga–C bond (Table 5.9) could give this process a higher activation energy. Thus, the brown coloured deposits, which were observed on relatively cool areas, may only be partially reduced. A reaction scheme which could account for the observed behaviour can be written as:

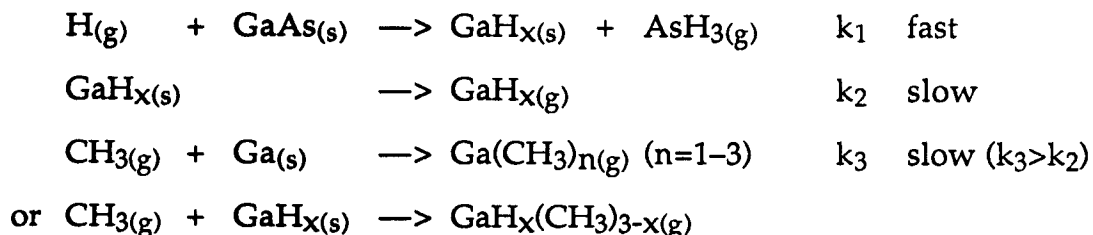


Unfortunately, the large oxide peaks in the high resolution Ga 3d spectra make it impossible to determine if any gallium-methyl species are present in the deposits. Ideally, the samples and deposits should be analysed with *in situ* XPS. Although no other workers have detected any gas phase gallium containing products with mass spectrometry, it may be possible to detect such species in a system of our type, since this is the first report of continuous etching of GaAs with hydrogen atoms.

5.3 MECHANISMS OF ETCHING WITH CH_3 RADICALS AND H ATOMS

Since we expect the removal of gallium to be the rate limiting step for the etching of GaAs with hydrogen atoms, then a reasonable assumption is that methyl

radicals increase the etch rate by forming methyl-gallium or hydrogen/methyl-gallium species. The rate constants obtained are therefore for the reaction of methyl radicals with the gallium component of GaAs. With these assumptions, the following mechanism for the methyl radical/hydrogen atom etching of GaAs is consistent with our observations:



Although methyl radicals are shown reacting with the gallium component of the GaAs in the above scheme, they may also be able to remove arsenic as $\text{As(CH}_3)_n$, (e.g. trimethyl arsenic, b.p. 50.5 °C). However, we have no direct evidence that methyl radicals can etch GaAs in the absence of hydrogen atoms. Even at the highest temperatures (and pressures of methane) used in these experiments, the calculated concentration of hydrogen atoms was only about 80 times lower than the CH_3 concentration. As our XPS results have indicated, reaction of H with As is significantly faster than their reaction with Ga or even the reaction of CH_3 with Ga. Therefore, the hydrogen present in an 80:1 CH_3 :H mixture may be more than adequate to strip the arsenic from the surface. Thus, our etch rates may reflect a synergistic etching process, where the hydrogen atoms continually remove arsenic, leaving methyl radicals to "mop-up" the gallium. Spencer *et al.*⁵⁴ etched GaAs with a combination of H atoms and CH_3 radicals (obtained in the reactions $\text{F} + \text{H}_2$ and $\text{F} + \text{CH}_4$). Although in principle, he could also produce methyl radicals alone ($\text{F} + \text{CH}_4$), no results were given for methyl-only etching. However, in a later review of atom/radical etch processes, he said

that "the addition of hydrogen to the methane was found to improve the etch rate". No data was provided to substantiate this statement. Methyl radicals are known to react with elemental arsenic⁵², so it seems quite possible that they can also etch the As in GaAs.

We noted earlier that methyl radicals enable etches to occur at much lower temperatures than are possible for etches with hydrogen atoms alone, and that etch rate initiation was significantly improved. The work of Spencer *et al.*⁵⁴ also shows that etching occurs at $\approx 100^\circ\text{C}$, and in a subsequent review article¹⁵⁰, he states that etch initiation was improved with methyl radicals. We previously attributed the etch inhibition observed with H atoms to the presence of a native gallium oxide on the surface. Thus, it appears that the reactions of methyl radicals with both Ga and GaO_x are faster than the corresponding reactions with hydrogen atoms.

CHAPTER 6 RESULTS AND DISCUSSION (III): IMPLICATIONS FOR ALKANE-BASED RIE OF GaAs AND InP

From our experiments with C^+ and CH_3^+ ions, it is evident that carbon or methyl ion bombardment alone is not sufficient for etching GaAs or InP. However, bombardment at energies as low as 20 eV does cause significant damage to the near-surface region of the semiconductors. This damage is manifest as sputtering and preferential removal of arsenic from GaAs and phosphorus from InP, and also in the formation of carbon-semiconductor bonds. The degree and depth of the interaction are found to increase at higher bombardment energies. These results emphasize the importance of minimizing the impact energy during the etching process, as such damage is likely to impair the device performance, and may even require subsequent wet etch treatments before further fabrication steps are performed.

Obviously, the substrate biasing or ion impact energy should be as low as possible. However, it has been well established that the etch rate is directly proportional to the ion impact energy^{21,22}, and thus, the substrate biasing used in most RIE processes will be a compromise between achieving reasonable etch rates with anisotropic profiles and keeping the near-surface damage at an acceptable level. Already, etching has been demonstrated with ion impact energies as low as 15 eV, by using electron cyclotron resonance (ECR) discharges¹⁵⁷ instead of conventional microwave or radio-frequency plasmas. Although the plasma density is very high, ECR etching is carried out at low pressures *i.e.* 10^{-4} to 10^{-5} Torr, and the concentrations of neutral atoms and radicals are correspondingly small. The etch rates are therefore quite low, so this type of etch configuration is unlikely

to find widespread use in the semiconductor industry, but may be utilised for the fabrication of specialised devices.

Our results on the etching of GaAs with hydrogen atoms and methyl radicals provides strong evidence that these species are the primary etchants in alkane-containing plasmas. From this work and previous reports on the etching of InP with hydrogen atoms and methyl radicals³⁶, it would appear that for the etching of III-V semiconductors, the rate determining step for both etchants is the removal of the metallic constituent from a group V depleted surface. However, the reaction of methyl radicals with the metals is much more rapid than the reaction with hydrogen atoms, particularly for InP, where continuous etching with hydrogen atoms was not observed³⁶. Although ion bombardment is generally believed to be the cause of the group V depletion in RIE processes, our work shows that the reaction of the neutral etchants with GaAs produces very gallium rich surfaces. In addition, Aston³⁶ showed that InP surfaces are extremely prone to P depletion. Non-stoichiometric surfaces can present problems for semiconductor device fabrication. However, there have been several reports of devices fabricated directly on H₂/CH₄ reactively ion etched surfaces¹⁵⁸.

In a plasma assisted etching process, the etch rate due to neutral reactants is enhanced in the vertical direction by ion bombardment on the surface. The ion trajectories are perpendicular to the surface, and anisotropic etch profiles result. From our work on ion bombardment, it appears that hydrocarbon ions are more likely to deposit a layer of amorphous, chemically "inert" carbon on the surface than they are to form volatile products with the semiconductor constituents. Depositions on the semiconductor would be a serious problem in the RIE process, since they would inhibit the etching reactions with the surface and reduce the anisotropy. However, since the ion to neutral ratio in these plasmas is small, the accumulation from ion bombardment may not be significant. Additionally, we

have shown that hydrogen ions can remove such etch-inhibiting deposits. Although the etch/sputter yield is low, hydrogen ions are one of the most abundant ion species in an alkane/hydrogen plasma, and concomitant H^+ bombardment could prevent the formation of carbon residues. Conversely, no polymers were observed in the reactions of H atoms and CH_3 radicals with GaAs. The polymer depositions in alkane-based RIE must therefore be associated with the complex gas phase reactions in such plasmas. Although we found that atomic hydrogen was very unreactive towards surface oxides, H atoms could easily keep the carbon in a volatile form.

As device dimensions move towards the sub-micron range, the need to avoid the crystallographic etch features we observed with H/ CH_3 etching becomes critical. Thus, an understanding of the synergistic mechanisms in ion-plus-neutral etch processes is necessary. Despite the apparent tendency towards deposition, (in the absence of neutrals?) hydrocarbon ion bombardment must enhance the etch rate and anisotropy in an alkane-containing plasma of a reactive ion etcher. As we have shown, the ion bombardment does sputter the semiconductors, preferentially removing the group V constituents, and generating carbon-semiconductor bonds. We do not have enough evidence to determine the synergistic mechanism of chemical etching and ion bombardment in alkane RIE, but we can speculate on such processes based on our observations:

(1) The neutral etch rates appear to be limited by the formation or desorption of metal- CH_x species. Therefore, the formation of carbon-semiconductor bonds and in particular metal-C or $-CH_x$ bonds by bombardment with alkyl ions could enhance the etch rate. This enhancement would be in the vertical direction only, as the ions cannot interact with the sidewalls. Alternatively, this surface damage may enable neutral etchants to stick with greater efficiency.

(2) The ion bombardment may provide energy to an adsorbed surface species, thus increasing the chemical reaction rate leading to formation of volatile products, which subsequently desorb. For example, an As–Ga(CH₃)_x bond could be broken, allowing an adjacently physisorbed methyl radical to form a bond with the new precursor, creating a volatile species.

(3) A chemical reaction may form a weakly bound species that is more readily ejected from the surface by an impulse from the collision cascade. Without the ion bombardment, the etch rate is limited by product desorption. For example, Ga(CH₃) and Ga(CH₃)₂ are known¹⁵⁶ to be less volatile than trimethyl gallium, but could well be the product of the etching process. If the removal of one of these species was the rate controlling process in the thermal reaction, then ion-induced desorption could enhance the etch rate.

(4) Ion bombardment may keep a horizontal etching surface clear of a relatively involatile layer that forms (usually a polymer) but not the vertical sidewalls, which would inhibit lateral etching. As alkane plasmas usually result in the deposition of polymers on surfaces, this mechanism is widely believed to be responsible for the etch characteristics in the RIE process. However, a study by Hayes *et al.*²⁴ showed that under conditions of maximum anisotropy (low fraction of methane), there were no significant polymeric deposits on the sidewalls, vitiating the above mechanism.

Although the RIE of III-V semiconductors in alkane/hydrogen plasmas has been shown to be an effective method of etching these materials, most recent reports have used methane diluted in inert gases instead of hydrogen^{159,160}. This trend is driven by the need to reduce problems associated with exposure to hydrogen-containing plasmas *i.e.* modification of the semiconductor electrical properties due to dopant passivation. In these alkane/inert-gas plasmas there is still an abundance of reactive hydrogen species, and their contribution to the etch

will be maintained. However, if inert-gas ion bombardment is responsible for keeping the surface free from carbon accumulation, higher energies would be required to achieve the equivalent cleaning effect of hydrogen, and consequently, the physical damage imparted to the surface is likely to be greater than with an alkane/hydrogen based process. Hydrogen bombardment induced problems such as dopant passivation can be resolved by post-etch annealing but damage induced by physical sputtering is more difficult to remove. Consequently, an alkane/hydrogen based process would appear to be more favourable than an alkane/inert-gas process.

Finally, it is interesting to note that there have been a few recent reports on the use of iodine-containing gases for the etching of GaAs and InP. Flanders *et al.*¹⁶¹ used RIE to etch InP, InGaAs and InGaAsP with Ar/I₂ and Ar/HI/CH₄ gas mixtures, and observed high etch rates and extremely anisotropic etch profiles. Pearton *et al.*¹⁶² etched InP in an HI/H₂/Ar electron cyclotron resonance plasma and obtained etch rates that were 8-10 times faster than those obtained in CH₄/H₂ plasmas. The resultant surfaces were also smooth and residue free. The high etch rates reported by these workers are consistent with our findings on the etching of GaAs with the products formed by the reactions of hydrogen atoms with iodomethane and hydrogen iodide. Also, the surfaces produced with H + CH₃I did not exhibit the roughness found with all the other etchants used. Thus, iodomethane could be a promising source of reactive species (I and CH₃) for the RIE of III-V materials. However, while such a process would eliminate some of the problems associated with etching in alkane-based plasmas, the corrosive nature of iodine is a major limitation for practical systems.

CHAPTER 7 CONCLUSION

To better understand the elementary processes involved in the etching of III-V semiconductors with alkane-containing plasmas, the interactions of GaAs and InP with low energy carbon and methyl ions, and the reactions of GaAs with hydrogen atoms and methyl radicals were examined.

The effects of low energy carbon ion bombardment (20-500 eV) on GaAs and an ultrathin InP/InGaAs heterostructure were studied with angle-dependent XPS. Slight sputtering occurred with preferential loss of the group V components, along with the deposition of an amorphous, chemically "inert", carbon overlayer. Even at 20 eV ion impact energies, the semiconductors were damaged, resulting in significant peak broadening as carbon-semiconductor phases were formed. Analysis of the angle-dependent data for GaAs showed that the thickness of the damaged, carbon-GaAs layer was about 0.8 nm after a dose of $3 \times 10^{16} \text{ cm}^{-2}$. No broadening of the As 3d peak of the underlying InGaAs layer of the InP/InGaAs heterostructure was observed, indicating that the ion induced damage was confined to the 4 nm InP overlayer, but approximately 0.3 nm of the InP surface was removed. At 100 and 500 eV bombarding energies, the extent of the group V constituent depletion increased, as did the amount of the carbon-semiconductor phases. The depth of the interaction also increased at these higher impact energies. For the GaAs samples, the composition of the carbon-GaAs phases extended almost uniformly beyond the XPS sampling range, while, for the InP/InGaAs structure, significant amounts of the InP layer were removed and the underlying InGaAs layer was damaged. Surface Fermi level *p*-shifts were attributed to implanted carbon atoms recombining with lattice vacancies in the damaged semiconductors and creating acceptor sites. Various treatments were used for possible removal of the ion bombardment induced damage. Heating *in vacuo* at 350 °C (and also at

520 °C for GaAs) did not desorb the carbon overlayer or the carbon-semiconductor species, and UV/ozone treatments were also found to be ineffective in removing the products of carbon ion bombardment. However, the carbon overlayer, carbon-semiconductor species and damage were removed by bombardment with 100 eV hydrogen ions.

Similar results were observed when these semiconductors were exposed to 20 and 100 eV methyl ions, except that the deposited amorphous hydrocarbon was readily removed by ozone oxidation treatments. In addition, the depletion of the group V constituents was more extensive, possibly as a result of the interaction with hydrogen produced by fragmentation of the ions at the surface.

The methyl ion impact energy was lowered to 9 eV and finally to 3 eV, to reduce the fragmentation of the CH_3^+ species on the surface. Slight interaction with the 9 eV ions was observed, but the formation of an amorphous layer on the surface was the only observable result with 3 eV ions. However, etching of InP was observed with 3 eV methyl ions when the surface temperature was at 350 °C.

Continuous etching of GaAs was achieved by exposing samples to thermalised hydrogen atoms produced in a remote molecular hydrogen discharge. The absolute H concentrations were determined by measuring the heat of atom recombination on a hot platinum wire, under isothermal conditions. For H atom partial pressures, P_{H} , ranging from 20 to 50 mTorr, and with surface temperatures between 180 to 375 °C, etch rates up to 40 nm min⁻¹ were measured and absolute rate constants were determined in this temperature range. The rate constants can be described by the Arrhenius equation,

$$k = 10^{4.8 \pm 0.4} \text{ nm min}^{-1} \text{ Torr}^{-1} \exp(-20.2 \pm 3.9 \text{ kJ mol}^{-1} / RT)$$

where the etch rate = kP_{H} . The etched surfaces were rough and exhibited many crystallographic planes. A transition from anisotropic etching (cystallographic) towards isotropic etching behaviour was observed as the substrate temperature was

increased. The post-etch surfaces were also very gallium rich, indicating that the limiting process for H atom etching of GaAs is the removal of gallium.

Addition of methane into the hydrogen atom stream increased the etch rate of GaAs by up to an order of magnitude. From the known rate constants for the reactions of hydrogen atoms and methane and the flow parameters of the apparatus, a model was developed to calculate time-concentration profiles for methyl radicals. The etch rates showed a linear dependence on the calculated methyl radical concentration, implying a first order process. The rate constants for this process are given by the Arrhenius equation,

$$k = 106.1 \pm 0.4 \text{ nm min}^{-1} \text{ Torr}^{-1} \exp(-5.1 \pm 1.2 \text{ kJ mol}^{-1} / RT).$$

The magnitude of these rate constants and their temperature dependence are consistent with a diffusion controlled process.

Crystallographic etch features were always observed. The resultant surface morphologies exhibited similar features to those produced by hydrogen atom etching, but the trench floors were smoother, particularly when methyl radicals were the dominant species. The crystallographic sidewalls are therefore attributed to the reactions of H atoms, whereas the limited supplies of CH₃ are consumed on the trench floors. XPS analysis of the etched surfaces showed that they were also arsenic deficient, even when methyl radicals were the most abundant species. Another significant feature of this process was the deposition of gallium-containing material on the walls of the reaction tube. This is probably due to the gas phase reaction of gallium etch products with hydrogen atoms to produce less volatile species that condense on cooler surfaces.

The etching of GaAs with hydrogen atoms and methyl radicals that we observed provides strong evidence that these species are the primary etchants in alkane-containing plasmas. In light of previous reports on the interactions of these species with InP, and the results presented here, we believe that the rate limiting

step for the etching of III-V materials is the removal of the metallic constituents, whereas formation and desorption of group V hydrides is facile. In the RIE process, ion enhancement of the neutral etch rate in the vertical direction occurs, producing anisotropic etch profiles. Although our work on ion bombardment shows that hydrocarbon ions readily form carbon deposits on the semiconductor surfaces, bombardment with ions of energies as low as 20 eV does cause sputtering of these semiconductors with preferential removal of the group V constituents, and also results in the formation of a significant number of carbon-semiconductor bonds.

As the neutral etch rates are limited by the formation or desorption of metal-CH_x species, etch rate enhancement by ion bombardment may occur by one or a combination of the following processes: (1) the formation of metal-carbon bonds (carbides), (2) the ejection of less volatile surface species (3) energy deposition (*i.e.* bond cleavage and localised heating). Such processes are consistent with the observations of Hayes *et al.*²⁴, who showed that despite the polymer deposits associated with methane-containing plasmas, a sidewall passivation mechanism was not responsible for the anisotropic etching. However, much work is still needed to elucidate the mechanism of ion assisted etching in alkane-based plasmas. In addition, the complementary roles of methyl radicals and hydrogen atoms in these etching processes needs to be unravelled.

Suggestions for further work

1. The nature of the desorbing products from H and H/CH₃ etching could possibly be identified by mass spectrometry if the gas was sampled with a pinhole probe very close to the sample.
2. An *in situ* XPS study of GaAs surfaces etched with methyl radicals may clarify the nature of the radical-surface interaction.
3. The validity of the modelling used in this work could be ascertained by directly measuring the methyl radical concentration. In particular, photoionisation mass-spectrometry has been shown to be an effective technique for obtaining the concentration of methyl radicals.
4. The use of F + CH₄ would help determine if methyl radicals can etch these semiconductors in the absence of hydrogen.
5. The temperature dependence for the etching of GaAs with methyl radicals requires further investigation, *i.e.* outside the diffusion controlled region. This could be achieved with F + CH₄, or by using the H + CH₄ reaction, but at a much higher gas temperature and with the sample temperature independently controlled. The former would be more effective if absolute CH₃ concentrations could be determined.
6. Since the reactions of CH₃ with GaAs occur with a surface that is Ga rich, a study of the reactions of methyl radicals with gallium metal could be valuable.

7. The effect of doping and defects on the etch rate of GaAs with H, CH₃ and H/CH₃ warrants further investigation.
8. Ascertain the influence of hydrogen absorption on etch rates. For example, the use of very thin GaAs samples would allow H to reach its solubility limit in the crystal and potentially enable etching to occur in the absence of surface hydrogen.
9. Measure the rate of hydrogen atom and H/CH₃ etching of GaAs with simultaneous bombardment of the surface by inert ions. A similar experiment was carried out by Chuang and Coburn⁴³, but because they did not heat the substrates and used low pressures, continuous etching was not observed. This would help determine if ion bombardment in the RIE process enhances the etch rate by keeping the surface clear of etch-stopping residues or polymers (no polymers are present with H/CH₃ etching).
10. By employing a system similar to that used by Winters *et al.*¹³⁴ for investigations of the plasma assisted etching of silicon with fluorine, it should be possible to gain significant insight into the mechanisms of alkane-based RIE of III-V semiconductors. Such a system would be compatible with ultrahigh vacuum and could produce separate beams of hydrogen atoms, methyl radicals and inert ions, each of which could be modulated. Etch rates and products would be determined by *in situ* mass spectrometry, and the surfaces could be analysed by XPS or Auger spectroscopy.

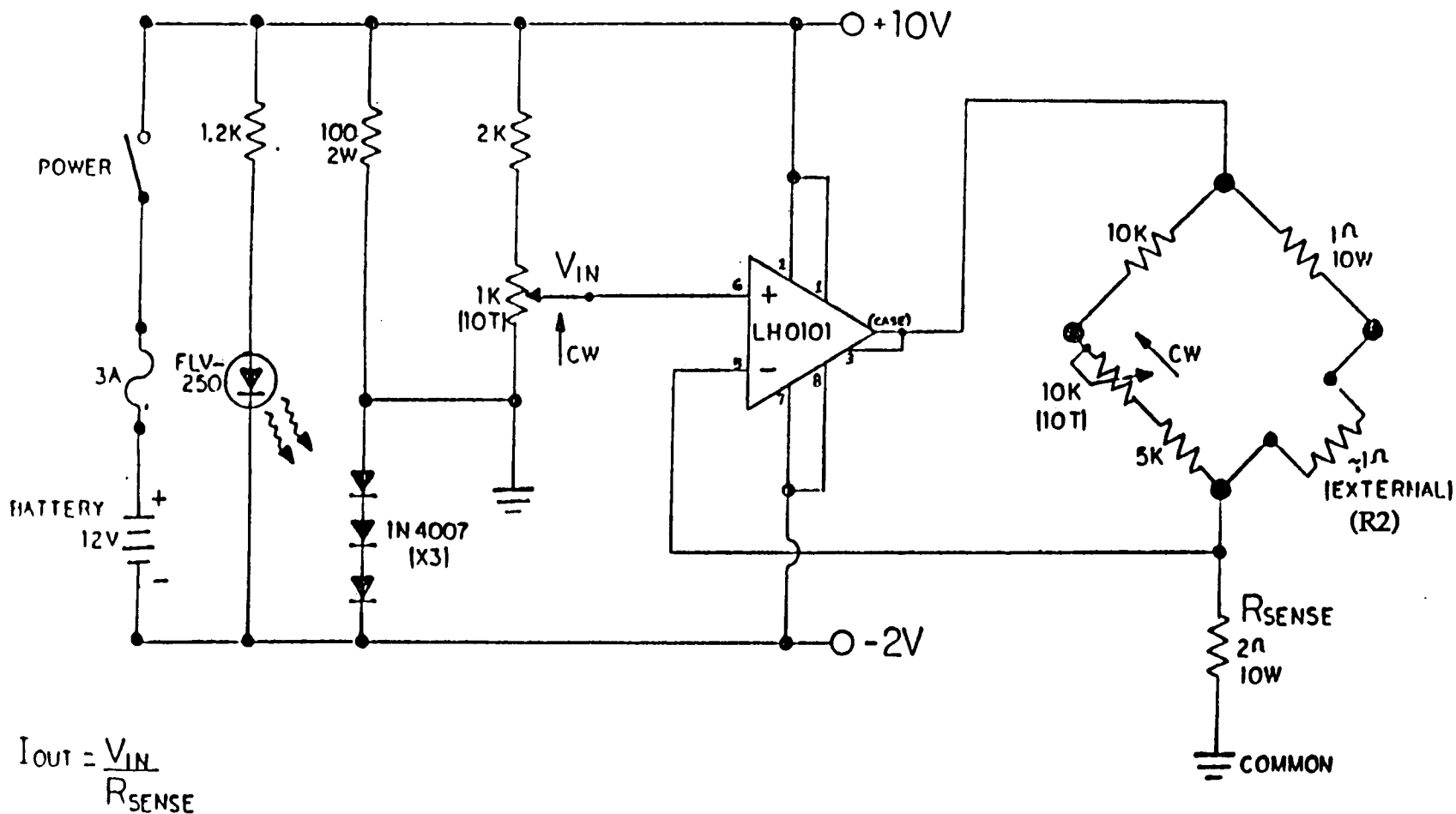


Figure A1 Circuit design for the constant current bridge used to determine heat of H atoms recombining on a platinum wire (R2).

Appendix B

Estimation of arsenic depletion layer thickness from XPS measurements

From an As/Ga 3d ratio, the depth of the arsenic depletion can be estimated. To do this, we assume that there is a gallium rich layer with a uniform composition, $\text{Ga}_{n\text{x}}\text{As}_x$, on a stoichiometric substrate, $\text{Ga}_{1.0}\text{As}_{1.0}$. This model is illustrated in Figure B1. The As/Ga ratio in the top layer is simply $1/n$, and the measured XPS ratio, R , is derived from the As and Ga 3d intensities of both layers, *viz.*

$$R = (x + 1)/(nx + 1)$$

The amount of As in the upper layer, x , is then,

$$x = (1-R)/(nR-1)$$

As we showed in Chapter 1, the thickness, t , of a layer (of uniform composition) on an infinitely thick substrate can be determined from the ratio of measured XPS intensities from both layers, $I_{\text{overlayer}}$ and $I_{\text{substrate}}$, by the following expression:

$$t = \lambda \sin \theta \times \ln \left\{ \frac{I_o}{I_s} + 1 \right\}$$

where λ is the inelastic mean free path of the photoelectrons in the overlayer, and θ is the take-off angle for the spectrometer. Inserting the ratios for both layers in our model, we get,

$$t = \lambda \sin \theta \times \ln \left\{ \frac{nx+x}{1+1} + 1 \right\}$$

Putting $x = (1-R)/(nR-1)$ into this expression and rearranging, we have,

$$t = \lambda \sin \theta \times \ln \left\{ \frac{(R+1)(n-1)}{2(nR-1)} \right\}$$

Thus, if we knew the stoichiometry ratio, n , in the top layer, we could calculate the thickness of that layer. Alternatively, if the As/Ga 3d ratio, R , was measured at two or more take-off angles, solving the resulting simultaneous equations would enable both n and t to be determined.

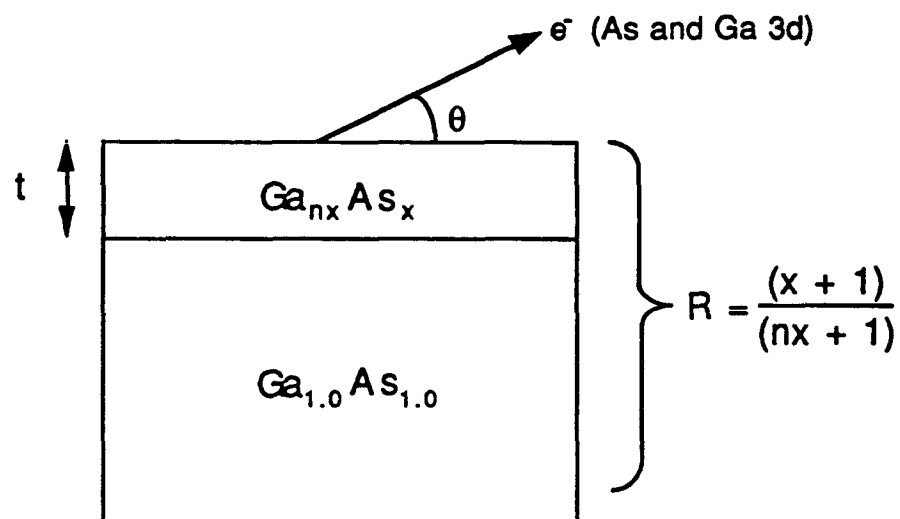


Figure B1 Model used to estimate the thickness of a gallium rich layer on GaAs from XPS As/Ga composition ratios.

Since only one angle was used for the analysis of our samples, we must assume that the top layer of the surface consists only of gallium *i.e.* $n \rightarrow \infty$. Using $\lambda = 2.8 \text{ nm}$ and $\theta = 35^\circ$ for these experiments, then,

$$t = 1.61 \times \ln\left\{\frac{(R+1)}{2R}\right\}$$

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