FACTORS AFFECTING THE PROPERTIES OF THERMALLY GROWN OXIDES ON GALLIUM ARSENIDE.

by

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SUMMARY

This thesis concerns the growth mechanisms and the physical and electrical properties of dielectric films grown on gallium arsenide in dry oxygen between 350°C and 760°C for times up to 3 hours.

Rutherford backscattering of 1.5 MeV helium ions was used to measure the thickness and composition of the films and to ascertain and compare their growth mechanisms on (110) and (100) surfaces of n and p-type bulk and epitaxial material.

Metal-oxide-semiconductor (MOS) devices were fabricated from oxidised n-type bulk material and their a.c. and d.c. electrical characteristics were measured at room temperature by capacitance-voltage, capacitance-frequency and voltage-current techniques.

Investigations were carried out, also, into the effect on the oxidation rate of implanting foreign ions into the surfaces prior to oxidation. Thirteen species of ions were implanted and, as a result, significant increases and probable reductions in the oxidation rate were obtained.

It is shown by the results that native oxides formed thermally on gallium arsenide appear to grow because of indiffusing oxygen reacting with gallium at the substrate-oxide interface. The resulting films consist essentially of Ga₂O₃, but they contain small quantities of arsenic when grown at high temperatures. The growth characteristics of bulk and epitaxial material are similar and do not appear to be
affected by the dopant species at the concentrations used in conventional semiconducting material. However, differences between the oxidation rate on (110) and (100) surfaces were observed and are attributed to arsenic outdiffusion and to strains within the films caused by mismatch between the oxide and substrate lattices.

The electrical measurements show that the MOS devices possess field induced hysteresis and small flat band voltages. Their oxide films have breakdown field strengths and dielectric constants which are lower than those of films grown by other methods and which render them unsuitable for use as gate insulators of MOS devices.
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Chapter 1.

INTRODUCTION

This thesis presents the results of research carried out in the Department of Electronic and Electrical Engineering at the University of Surrey from October 1974 to October 1976 into the factors affecting the properties of oxides grown thermally on gallium arsenide.

Gallium arsenide (GaAs) is a compound semiconductor. It has a high electron mobility and, therefore, the possibility exists of producing field effect devices which have a frequency performance superior to those manufactured from silicon. Consequently, there is a requirement for a suitable dielectric to form the insulator of an insulated gate device and which can be used, possibly, for encapsulation and passivation purposes. But no satisfactory dielectric had been produced for gallium arsenide - a situation which contrasts with that for silicon where suitable native oxide insulators are formed by a thermal oxidation process.

A limited amount of information was available at the beginning of this project and showed that native oxide films had been grown on gallium arsenide by thermal (1-6), chemical (6-9), plasma (10,11) and anodic (12-16) techniques.

The growth of thermally grown films was shown to be influenced by surface orientation and by the humidity and temperature of the oxidising gas (4), but, in common with films grown by the other methods, no detailed accounts of their properties were recorded. No gallium
arsenide field effect transistors having native oxide gate dielectrics had been produced, but insulators formed by the chemical vapour deposition of SiO₂, Si₃N₄ and Al₂O₃ (17), had been used in experimental GaAs MISFETs. However, these devices had gate capacitances with large frequency dispersions and exhibited field induced hysteresis. Also, they possessed high interfacial state densities. Although these characteristics were improved by Ito et al (18), who used a dielectric consisting of a double layer of SiO₂ and Al₂O₃, they are not good enough for device applications.

More recent work has shown that native oxide films formed by plasma or anodic methods may be suitable as dielectrics for devices. This, together with the earlier data, is detailed in a later chapter, but, the foregoing brief review of the situation in the autumn of 1974 shows that a detailed study of the properties of native oxides formed on gallium arsenide might lead to films suitable for device applications being produced. This was true particularly for thermally grown native oxides as, from the evidence of silicon technology, they should possess better properties than those grown by other methods. Also, they should have advantages from a production point of view. Consequently, this project was concerned with the growth mechanism, composition and electrical characteristics of native oxides thermally grown on gallium arsenide with the aim of obtaining an understanding of the factors affecting their properties.

Films were analysed by the Rutherford backscattering technique and the mechanisms operating during the oxidation of various types of material at temperatures between 350°C and 760°C have been identified.
Their electrical characteristics, which show correlations with certain physical properties, were obtained from current-voltage, capacitance-voltage and capacitance-frequency measurements.

The conclusions from the results were that native oxides suitable for device applications could not be grown under the conditions employed in these investigations, and that modifications to the technique are necessary before good oxides can be produced. Because of this, the scope of the project was extended to include a preliminary study of the effects of implanted ions on the oxidation behaviour.

Ion implantation is a well established method whereby ions of a foreign element are introduced into a surface to controlled depths and concentrations, leaving the bulk of the material unaffected. These specific attributes have resulted in its application to semiconductor device manufacture (19-21) and to wear and corrosion studies of materials (22-29).

It is the ability of implanted ions to affect the corrosion rate of surfaces which suggests that the technique might have a beneficial effect on the properties of thermally grown oxides. However, although there was considerable data on this topic for metals (22, 25-28) and alloys (22, 26), there was little for semiconductors (29). Moreover, there was no general theory from which it was possible to predict the effect of any particular implanted species on the oxidation rate. It appeared that the electronegativity and ionic radius were influential in the case of some metals but not in others, and, therefore, there was no guidance as to which ions would be suitable for implanting into gallium arsenide. However, a series of 13 species, covering a wide range of electronegativity values and including a set having a common value, was implanted into epitaxial material and the effect of each type of ion on the oxidation rate was measured.
The results from this investigation show that ion implantation does alter the oxidation rate. Significant increases were obtained by the implantation of potassium, nitrogen and fluorine ions, whilst calcium, aluminium and nickel ions might have caused small reductions. These variations in the oxidation rate may be due to the electronegativities and ionic radii of the implanted species, rather than because of implantation damage which was minimised by implanting and annealing at elevated temperatures.
2.1. Introduction.

During this project, oxides were grown on surfaces of different orientations and on different types of gallium arsenide material. This chapter explains those differences in terms of the structure of gallium arsenide and includes relevant data on its properties and its use in electronic devices.

2.2. The structure of gallium arsenide.

Gallium arsenide is one of 25 possible IIIb-Vb binary compounds and one of the twelve phosphides, antimonides and arsenides of boron, aluminium, gallium and indium which crystallise in the zinc blende structure (\(\text{ZnS}\)). The arsenic atoms lie on a face-centered cubic lattice which penetrates a similar lattice of gallium (figure 2.1.). Each arsenic atom is separated from four nearest neighbour gallium atoms, which lie at the corners of a tetrahedron, by a distance equal to the sum of the covalent radii of the two types of elements. The binding between atoms, each of which has four bonds, is primarily the homopolar (covalent) bonding of two electrons with opposite spins, but a small amount of heteropolar (ionic) bonding exists between 'closed shell' ions of gallium (cations of charge +3) and arsenic (anions of charge -3).
Fig. 2.1 The GaAs (zinc-blende) lattice.

Fig. 2.2 The (100) surface of GaAs.
Of the possible surface structures, the most important are those of surfaces perpendicular to the \(<100>\), \(<110>\), \(<111>\) and \(<\overline{111}>\) directions. The ideal structures of these surfaces are explained below.

The (100) surface (figure 2.2.) is formed by cubically arranged Ga or As atoms, each of which is bound by two bonds to atoms of the other type lying in the plane immediately below. The other two bonds are unattached (or dangling). This structure is independent of the type of atom in the topmost layer.

The (110) surface (figure 2.3.*) consists of an equal number of Ga and As atoms, each being connected by one bond to an atom in the next layer, and by two bonds to the next nearest neighbours lying in the surface plane. The fourth bond is dangling.

The (111) surface (figure 2.4.*) consists of Ga atoms, each of which is bonded to three As atoms lying in the next lower layer and has the remaining bond dangling. This second layer is bound to Ga atoms in the third plane by the fourth bond of its As atoms. As a consequence of this bonding configuration the distance between the first and second planes is smaller than that between the second and third. Therefore, the \(<111>\) and \(<\overline{111}>\) directions are not equivalent. (\(\overline{111}\)) surfaces contain As atoms which are bonded to the next lower lying plane of Ga atoms in the same way as for (111) surfaces.

A possible alternative arrangement for (111) and (\(\overline{111}\)) surfaces is for the topmost atoms to be linked by one bond to the next lower plane and have three dangling bonds - but such an arrangement is not as stable
Fig. 2.3  The (110) surface of GaAs.

Fig. 2.4  The (111) surface of GaAs.
as the above possibility and does not appear to exist. Both crystal
growth and etching in the $<111>$ and $<\overline{1}\overline{1}\overline{1}>$ directions always seem
to take place in double layers. Consequently, the top and bottom surfaces
of a parallel slice of (111) material contain different types of atoms.

2.3. Types of material.

Semiconducting material can be grouped into four main categories
depending on (a) the method by which it is grown and (b) the type of
dopant used to provide electrical conduction.

Bulk material is grown as large single crystal ingots from a
stoichiometric melt of gallium and arsenic (e.g. by the Czochralski
process) whereas epitaxial material consists of thin layers which have
been deposited on the surfaces of substrate wafers cut from bulk grown
ingots. Either liquid, vapour phase or molecular beam epitaxy
can be used for this process which produces a layer structure the same
as that of the supporting slice but of lower defect density.

The material is made conducting by introducing dopant atoms which
render it 'n' or 'p' type. Usually sulphur, selenium or tellurium are
used for the former and zinc or cadmium for the latter at carrier
concentrations of between $10^{15}$ and $10^{18}$ cm$^{-3}$. Semi-insulating material
is doped with chromium.
2.4. Properties of gallium arsenide.

Gallium arsenide is greyish in colour and has a density of 5.32 gms.cm$^{-3}$. It decomposes at temperatures above 640°C in ultra high vacuum due to the preferential evaporation of arsenic \(^{(33)}\).

It is a semiconductor with a direct band gap of energy 1.4 eV (figure 2.5.) and has electron and hole mobilities of 7000 and 400 cm$^2$.V$^{-1}$.sec$^{-1}$ respectively for carrier concentrations of less than about $10^{15}$cm$^{-3}$ \(^{(34)}\). The dielectric constant is 12.5. \(^{(35)}\). Other properties are \(^{(34)}\):

\begin{align*}
\text{Atoms cm}^{-3} & \quad 2.21 \times 10^{22} \\
\text{Atomic weight} & \quad 144.63 \\
\text{Breakdown field} & \quad 4 \times 10^5 \text{ V cm}^{-1} \\
\text{Electron affinity} & \quad 4.07 \text{ volts} \\
\text{Melting point} & \quad 1238 \text{ °C} \\
\text{Work function} & \quad 4.7 \text{ volts} \\
\text{Minority carrier lifetime} & \quad 10^{-8} \text{ secs.} \\
\text{Intrinsic carrier concentration} & \quad 1.1 \times 10^7 \text{ cm}^{-3}
\end{align*}

2.5. GaAs devices.

Two of the properties of the semiconductor - the direct band gap and the high electron mobility - focussed attention on its use for electronic device fabrication. Its superiority at high frequencies over other materials, especially silicon, is shown in table 2.1, but, also, it can emit radiation in the infra-red region of the spectrum.
Electron energy $E = 0.35$ eV
$E_0 = 1.4$ eV (direct gap)
$\Delta E = 0.05$ eV

Hole energy

Fig. 2.5 The Energy Band structure of GaAs.
(From: Prew - Physics Bulletin Sept. 1975 (399))
<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Lattice constant at 300°K (Å)</th>
<th>Band gap at 300°K (eV)</th>
<th>Mobility at 300°K (cm²/volt sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>3.57</td>
<td>5.47</td>
<td>1800 1600</td>
</tr>
<tr>
<td>Ge</td>
<td>5.66</td>
<td>0.66</td>
<td>3900 1900</td>
</tr>
<tr>
<td>Si</td>
<td>5.43</td>
<td>1.12</td>
<td>1500 600</td>
</tr>
<tr>
<td>AlSb</td>
<td>6.12</td>
<td>1.63</td>
<td>200 420</td>
</tr>
<tr>
<td>GaSb</td>
<td>6.10</td>
<td>0.67</td>
<td>4000 1400</td>
</tr>
<tr>
<td>GaAs</td>
<td>5.65</td>
<td>1.43</td>
<td>8500 400</td>
</tr>
<tr>
<td>GaP</td>
<td>5.45</td>
<td>2.24</td>
<td>110 75</td>
</tr>
<tr>
<td>InSb</td>
<td>6.48</td>
<td>0.16</td>
<td>78000 750</td>
</tr>
<tr>
<td>InAs</td>
<td>6.06</td>
<td>0.33</td>
<td>33000 460</td>
</tr>
<tr>
<td>InP</td>
<td>5.87</td>
<td>1.29</td>
<td>4600 150</td>
</tr>
</tbody>
</table>

Several types of GaAs devices have been made. Schottky barrier field effect transistors (FETs) with properties superior to similar silicon devices (36), Impatt diodes (37), and Gunn diodes (38) are in production. Experimental IGFETS with various gate insulators (17,18,39), Trapatt diodes (40) and, recently, MOSFETS with anodic oxide gates (41,42) have been produced. Radiation emission at a wavelength of about 9000 Å has been obtained from Light Emitting Diodes (LEDs) (43) and Injection Lasers (44). Improvements in device technology continue to be made and it is expected that "it will not be long before the 40 GHz low-noise FET amplifier and an X-band low power FET are developed" (45).
The applications for GaAs devices are in the field of high frequency circuitry for computers where they can replace the existing silicon technology, and in radar where their power conversion efficiency, gain and noise factor are superior to the silicon equivalents. Furthermore, GaAs impatt diodes are replacing klystron valves in low power systems.
Chapter 3.

OXIDES

3.1. Introduction.

The general aspects of oxides are covered in this chapter. Oxide classification, growth mechanisms and their structure are included along with an account of the growth methods and properties of oxides grown on gallium arsenide.

3.2. Oxide classification.

An oxide is a chemical compound, formed by the combination of cations and anions, in which oxygen (the anion) is bonded to one or more types of cation to form either single oxides, in which there is only one type of cation, or complex oxides. The latter consist of at least two different cations and form from either mutually soluble single oxides or insoluble islands of one oxide within another (46,47).

The bonding requirements mean necessarily that anions and cations should combine in a definite ratio and form 'stoichiometric' compounds, but it is possible for there to be an excess of either cations or anions. Hence interstitial positions within the crystal lattice can be occupied by excess ions or lattice sites may be vacant due to a deficiency. Both a cation excess and an oxygen deficit results in the oxide having free unbound electrons, whereas an oxygen excess or a cation deficit produces free unbound holes. Accordingly, these 'non-stoichiometric' oxides behave as n and p-type semiconductors respectively. In addition, oxide films can be either porous or compact.

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3.3. Defects in oxides.

3.3.1. General defects.

Interstitials and vacancies are but two of the possible defects occurring in oxide films and are amongst the following imperfections which can exist (48).

(i) phonons
(ii) electrons
(iii) holes
(iv) vacancies
(v) interstitials
(vi) foreign atoms - either interstitial or substitutional
(vii) dislocations
(ix) grain boundaries
(x) external surfaces
(xi) internal surfaces

Non-stoichiometric films can have any of the above defects, but only those which maintain the cation-anion ratio can be present in stoichiometric films. Consequently, the formation of interstitial and vacancy defects in such oxides is limited to certain defined types such as the Schottky-Wagner defect, the Frenkel defect and anti-structure disorder.
3.3.2. Surface states.

These are defects located at the surface of a material where their density is of the same order as that of the surface atoms (34). However, at the interface of the oxide and substrate, their number decreases to about $10^{11}$ cm$^{-2}$. They have electronic energy levels within the forbidden gap of the semiconductor and act as fast surface recombination centres. Consequently, they modify the energy band structure and the charge density at the interface.

3.3.3. Fixed charges.

These are defects located in the oxide within not more than 200Å from the interface and are due, apparently, to an excess of cations introduced from the substrate into the oxide during the oxidation process (34). Their density is independent of oxide thickness and impurity dopant, but is influenced by the orientation of the surface and the oxidation conditions.

As these defects are positively charged they induce a negative charge within the substrate.

3.3.4. Ionic space charges.

These are defects of density about $10^{12} - 10^{13}$ cm$^{-2}$ within the oxide located at a relatively large distance from the interface. They exist as either traps induced by ionising radiation or as mobile foreign ions (34).
3.4. Oxidation mechanisms (46,47).

Oxide growth begins by oxygen atoms or ions being adsorbed onto the surface of a material. After a short time this process is superseded by the diffusion of ions through the oxide film and growth is governed by the rate of diffusion via defects within the oxide. Consequently, the defect structure dominates the rate of oxide formation and the type of oxide formed.

At low temperatures growth is at a logarithmic or inverse logarithmic rate i.e. \(x \propto \log t\) or \(1/x \propto \log t\) respectively, where \(x =\) film thickness and \(t = \) time. However, the mechanism responsible for this form of growth is not understood. Several theories have been proposed to explain it in which a decrease of the sticking coefficient with time, electron tunnelling and ion transport under the action of a potential gradient have been considered. Other possible explanations which have been put forward are diffusion along pores or low resistant paths, the formation of cavities and oxide nucleation.

A similar situation exists in the case of growth at higher temperatures where the rate may be linear, cubic or parabolic with only the latter being explained by a theory which has general acceptance.

Linear growth \((x \propto t)\) is attributed to a constant sticking coefficient and a cubic growth rate \((x \propto t^3)\) to a field induced transport of metal ions in a p-type film.
According to Wagner, ion and vacancy diffusion caused by concentration gradients within the oxide leads to a parabolic growth rate \( (x^2 \propto t) \). As the mobilities of anions, cations and electrons are different, a separation of charge occurs which produces an electric field. Once established, the field opposes any further separation of charge and a stationary state is reached for which no net electric current flows. Diffusion then proceeds at a constant rate producing a compact film.

In contrast to the compact films grown by the Wagner mechanism, porous scales may form as a result of stresses within such an oxide causing it to rupture. This is most likely to occur when oxygen indiffuses and the metal-oxide volume ratio is greater than one, but it can be due also to the collection of vacancies at the oxide-substrate interface, as well as to the formation of a film having a low melting point. The latter process results in 'catastrophic oxidation' due to excessively fast oxidation producing films which are spongoid or loosely adherent to the surface.

When foreign atoms are introduced into a material, by way of alloying or implantation, the oxidation mechanism and properties of the oxide films should be altered in accordance with the Wagner-Hauffe semiconductor valence rules. These state that the introduction of foreign atoms of a valence higher (lower) than that of the host material will increase the oxidation rate when either electron (hole) flow, cation (anion) diffusion via vacancies or anion (cation) diffusion via interstitials is the rate controlling factor, whereas if either hole (electron) flow, anion (cation) diffusion via vacancies or cation (anion) diffusion via interstitials is the rate controlling factor, the oxidation rate will be reduced.
The above rules are limited to the case where the foreign ions dissolve substitutionally in the oxide under minor alloying conditions and apply only occasionally to implanted material for which, up until now, no general rules have emerged.

An important phenomenon which occurs for alloys is the selective oxidation of the least noble element of the constituents when the concentration is great enough and the temperature is high enough. Most alloys exhibit this behaviour, amongst them FeCrAl alloy which forms $\text{Al}_2\text{O}_3$ when it is oxidised above about $800^\circ\text{C}$ (49) and GaAlAs which produces the same aluminium oxide (50). These films form on the surface, but selective oxidation can take place below the parent oxide when oxygen dissolves in the alloy and its rate of indiffusion is greater than the rate of outdiffusion of the least noble component. If, under these circumstances, the internal film is subject to catastrophic oxidation due to the process of internal oxidation or subscale formation, the parent oxide may lift from the surface.

3.5. Growth methods of native oxides.

3.5.1. Introduction.

Four basic methods exist for growing native oxides and all have been used for gallium arsenide. These are reviewed below whilst the properties of the resulting films are considered in later sections.

3.5.2. Chemical and galvanic oxidation.

Although these two methods differ in detail, they can be coupled together as one as far as the process is concerned (9).
The samples to be oxidised are immersed in water or a dilute acid and left for several days at room temperature to form films of from tens of angstroms to up to about 1000Å thick. The process can be accelerated by increasing the temperature.

In the galvanic process a non-reactive ohmic contact is made to one face of the sample to allow the cathodic component of the reaction to take part in the oxidation process. No such contact is applied for chemical oxidation and, consequently, the cathodic component is inhibited.

3.5.3. Plasma oxidation.

As the name indicates, this technique produces oxides in an ionised atmosphere of low pressure oxygen. It was used first for the oxidation of silicon and a similar system was used later for gallium arsenide (10).

The plasma is formed by an r.f. field generated by an oscillator supplying hundreds of watts of power.

3.5.4. Anodic oxidation.

In this process a surface is oxidised in an electrolyte in which dissociated oxygen anions migrate under the influence of a d.c. field applied externally between a negative electrode and the positively biased sample (12-16). The voltage bias is from either a stabilised voltage supply or a constant current source.
3.5.5. Thermal oxidation.

Thermally grown oxides are produced in a furnace through which oxygen, air or steam flows at a predetermined rate. This method has been used successfully for silicon oxides and is the method of oxide growth used throughout this project on gallium arsenide.

3.6. Growth mechanisms and properties of native oxides formed on GaAs.

3.6.1. Introduction.

The first report concerning gallium arsenide native oxides was by Haisty (7) in 1961 who formed $\beta$-Ga$_2$O$_3$ during anodic etching experiments. The following year Minden (1) used the thermal technique to grow films at high temperatures for masking purposes, but his results were discouraging and he concluded that the method was unsuitable. This led Revesz and Zaininger (12) to investigate further the composition of anodically grown oxides and, later, that of thermally grown films (2). They made no comment on the suitability of their films as oxide masks, but Rubenstein (3) came to the same conclusion as Minden after thermally oxidising gallium arsenide and gallium phosphide although the latter compound did form films suitable for passivation. However, Weinreich (10) appears to have had better success by growing films in an oxygen plasma but although these were produced in 1966, it was not until 1974 that further films were grown by this method by Sugano and Mori (11).

In the meantime, Navratil (4) set out to find the law governing the formation of oxide layers grown in oxygen and air. Whereas the earlier work had used temperatures above 600°C, Navratil concentrated on the range
400°C to 530°C and found that, contrary to Minden's findings, thermally grown films of significant thickness can be grown below 600°C.

From 1971 interest in the oxides of gallium arsenide increased. In that year Dell'Oca et al. (13) published their results on anodically grown films and Schwartz (8) those on oxidation during chemical etching. In the following year Lukes (5) published data for films grown in air at room temperature. A further study of anodic oxides was made later by Logan et al. (14) and by Spitzer et al. (15), whilst Sealy and Hemment (6) grew both aqueous and thermal oxides and compared their compositions and electrical properties. Stoneham (16) grew uniform anodic layers in a non-aqueous electrolyte and further results were published by Spitzer et al. (51) which included the effect of heat treatment on films grown in a hot electrolyte. They investigated also the etch rate of their films.

Despite the above efforts, no films suitable for devices had been grown until Hasegawa et al. (52) discovered, in 1975, an electrolyte which has been used subsequently to grow films suitable for use as the gate insulator of experimental MOS devices (41,42,53). At about the same time Murarka (60) renewed efforts on the thermal oxidation in air at low temperatures and formed oxides mechanically more stable than those grown by Navratil. Schwartz et al. (54) reported, also, on their investigations into the growth and solubility of anodic oxides in water. Finally, in 1976, Chang and Sinha (55) published information on films grown by a new plasma oxidation process. From their data it appears that the films possess good electrical properties which may make them suitable for device fabrication.

The details of the above investigations are given in the following sections.
3.6.2. Chemically grown oxides.

Hasty (7) showed first that \( \text{Ga}_2\text{O}_3 \) was formed during chemical etching in dilute \( \text{KCl} \) solution and this has been confirmed by Schwartz (8) who investigated the surface product on (110) and (111) orientated surfaces of tellurium doped gallium arsenide which had been immersed in a number of oxidising reagents. He found that a residual film of thickness between 25Å and 50Å was present after the surface had been etched in a bromine/methanol solution and, further, that deionised water is an important oxidant which produces \( \text{Ga}_2\text{O}_3\cdot\text{H}_2\text{O} \). At room temperature it takes six days for such a film, 850Å thick, to form. For the same time in \( \text{H}_2\text{O}_2 \) the resulting film is about only one-seventh as thick and less than one-twentieth as thick when the oxidant is \( \text{CH}_3\text{OH} \). A 55Å thick film is formed in \( \text{HCl} \) in five days.

X-ray or electron diffraction appears to show that for thicknesses up to a few hundred angstroms the films are amorphous.

The absence of arsenic in the oxide layer is attributed to the solubility of \( \text{As}_2\text{O}_3 \) which, according to a later review paper by Schwartz (9), dissolves more readily in water at \( \text{pH} = 7 \) than in acidic water at \( \text{pH} = 5 \). In contrast, \( \text{Ga}_2\text{O}_3 \) will not dissolve in water at \( \text{pH} = 7 \), but it will when \( \text{pH} = 3 \) and when the \( \text{pH} \) is greater than about 11. Consequently, gallium arsenide is converted to a white powder composed of \( \text{As}_2\text{O}_3 \) when immersed in nitric acid for five days.

Chemically grown oxides were produced also by Sealy and Hemment (6) in dilute (40%) \( \text{H}_2\text{O}_2 \). After seven days the films were about 1000Å thick which suggests, by comparing them with those grown by Schwartz in water.
and in H$_2$O$_2$, that they were formed mainly by the water content of the oxidant. The films were patchy and poor in uniformity of thickness, but better films were produced when fresh boiling H$_2$O and diluted (40%) H$_2$O were used to grow them for 4 hours. These were analysed by electron spectroscopy for chemical analysis (ESCA), transmission electron diffraction (TED) and Rutherford backscattering (RBS) and showed that the films, which were about 1000Å thick, appeared to have compositions which were non-uniform and which were a mixture of Ga$_2$O$_3$ polymorphs. Traces of As$_2$O$_3$, As$_2$O$_5$ and GaAsO$_4$ appeared to be present as well, but the arsenic content was lost during a 15 minute anneal at 750°C which left the films consisting mostly of β-Ga$_2$O$_3$. Electrical measurements showed there were short circuit paths through parts of the films.

3.6.3. Plasma grown films.

Oxides have been grown in plasmas of temperatures ranging from 1150°C to about 40°C at respective pressures of from about 0.6 torr to 0.002 torr.

Sugano and Mori (11) oxidised (111) surfaces at an ambient temperature of 1150°C and produced stable films up to 8μm thick in less than 16 seconds, whilst at the slightly lower temperature of 950°C similar films on (100) surfaces were grown in about 70 seconds. These oxides grew, apparently, according to a parabolic growth law. They were initially composed of β-Ga$_2$O$_3$ but an increasing amount of arsenic in the form of GaAsO$_4$ and As$_2$O$_3$ was incorporated as they grew in thickness. When the films were at least 5000Å thick elemental arsenic built up at the oxide-substrate interface and from these observations, it was concluded
that arsenic evaporates from the surface during the initial stages of growth. When thicker than about 1µm the oxides consisted substantially of orientated polycrystalline GaAsO₄.

A parabolic growth law was obtained also by Weinreich (10) for the growth of amorphous films on surfaces having (110) and (111) orientations. These were grown at the much lower temperatures of 70°C and 130°C where, at the lower temperature, 100 minutes was needed to grow oxides 4000Å thick.

Films similar in composition to those grown by Sugano and Mori were obtained by Chang and Sinha (55) who used the apparatus shown in figure 3.1. The plasma had a pressure of 0.002 torr and a temperature of about 40°C. From ion backscattering and x-ray measurements they showed that the films grown on (100) orientated surfaces possess approximately equal amounts of gallium and arsenic. This, together with measurements of the oxygen content led them to conclude that the films consist of Ga₂O₃, As₂O₅ and As₂O₃.

The growth curves for the above films grown at 40°C are reproduced in figure 3.2 which shows also the effect of bias voltage on the growth rate.

From Talystep measurements of the oxide thickness, Chang and Sinha conclude that the growth rate obeys initially an approximate t³/₄ law (t = time), but after a few minutes it slows down so that thickness is proportional approximately to t¹/₃. This they believe is due to oxygen
Fig. 3.1 Apparatus for plasma oxidation of GaAs.
(From: Chang & Sinha - App. Phys. Lett. 22 1 76)

Fig. 3.2 Growth rate of plasma oxides on GaAs.
(From: Chang & Sinha - App. Phys. Lett. 22 1 76)
molecules interacting with plasma electrons at the substrate surface and forming negatively charged oxygen anions (e.g. $\overline{O}$, $O_2^-$ and $O^-_3$) which then diffuse through the oxide at a rate controlled by the electric field strength and the charged particle flux at the oxide surface. That the anions were not extracted mainly from the bulk of the plasma was shown by the drastically reduced growth which occurred when the substrate was orientated parallel to the external magnetic field lines.

The oxides grown by the above plasma techniques appear to be smooth, uniform and stable, but they dissolve in hot water and HCl although they are not easily soluble in alkalis or other acids. Their breakdown field strengths can be as high as $5 \times 10^6$ V/cm and the dielectric constant 6.4. at 1MHz (55). The value of the refractive index depends on the composition of the film and is in the range from a maximum of about 2.5 for films with equal amounts of $\beta$-Ga$_2$O$_3$ and GaAsO$_4$, to a minimum of less than 1.5 (11).

3.6.4. Anodically grown films.

By oxidising gallium arsenide in various electrolytes at room temperature it has been established that, providing the pH of the solution is within the range 1.0 to 6.5, uniform smooth films can be grown at a rate which is linear with the applied voltage. This has been shown by Logan et al (14) who oxidised the (110) surfaces of both n and p-type material in aqueous H$_2$O$_2$ and by Hasegawa et al (56) who formed films on (100) surfaces of both types of material in a solution of tartaric or citric acid mixed with ethylene or propylene glycol. Such a law has been confirmed by Spitzer et al (57) for (100) and (111) surfaces in H$_2$O$_2$, but they showed also that when the electrolyte is boiling at about 106°C the law is contravened and the surfaces oxidise at an enhanced
rate (figure 3.3). Schwartz et al (54) observe the same phenomenon when oxidation takes place in acidic water at 100°C.

A similar growth law occurs when films are grown under constant current conditions. Both Dell'oca et al (13), who grew films at 25°C in aqueous ammonium pentaborate and used a constant current of 1 mA/cm², and Schwartz et al (54), who used water of various pH values and current densities between 10 - 20 mA/cm², obtained a relationship in which the developed voltage was linear with either thickness or time. However, when Revesz and Zaininger (12) used a current density of 10 mA/cm² to grow films at room temperature in a KNO₃ saturated acetic anhydride electrolyte, the result was severely pitted films whose thicknesses were impossible to measure. Non-uniform films were formed also in acetone-KMnO₃ solution by Stoneham (16) when the anodising current dropped below a critical value.

Non uniform films are the result, also, of a high anodising voltage. Depending on the condition of the electrolyte, grey and granular films are formed in hot aqueous H₂O₂ at voltages as low as 140 volts (57), but at room temperature the same solution does not produce such films until the voltage is in excess of 225 volts (14).

Films grown by the anodic process are composed of the oxides of gallium and arsenic, although the amount of gallium and arsenic present appears to be dependant on the forming electrolyte. An oxide grown in aqueous H₂O₂ was analysed by Feldman et al (58) using Rutherford backscattering and x-ray techniques and found to consist of gallium, arsenic and oxygen in the ratio 1:1:2. However, no arsenic was present in the outer surface of the film, which, to a depth of less than 200Å,
Fig. 3.3  Thickness of oxides grown in $\text{H}_2\text{O}_2$ vs. anodization potential and temperature.
(From: Spitzer et al. J. Electrochem. Soc. 122 3 75 (399))
consisted of Ga$_2$O$_3$. This composition contrasts with the films grown by Logan et al \(^{(14)}\), who assumed them to be the hydrated forms of Ga$_2$O$_3$$\cdot$$n$H$_2$O and As$_2$O$_3$$\cdot$$n$H$_2$O, and also with those grown in acetic anhydride/KNO$_3$ solution. Revesz and Zaininger \(^{(12)}\) showed, using reflection electron diffraction, that the latter consist of amorphous Ga$_2$O$_3$ and As$_2$O$_5$ (perhaps combined as the silica-like compound GaAsO$_4$). The gallium to arsenic ratio was shown, by chemical analysis, to be 1.3.

The oxides grown in hot aqueous H$_2$O$_2$ by Spitzer et al \(^{(57)}\) are amorphous, but after being annealed at a temperature in excess of 800°C, they consist of small quantities of $\beta$-Ga$_2$O$_3$ within a glassy structure (presumably GaAsO$_4$). After four hours of such annealing the films crystallise and flake off, although they are fully stable at temperatures up to at least 700°C.

Annealing has an effect, also, on the thickness of the films. Reductions up to 50% can occur at an annealing temperature which depends on the conditions under which a film is grown. Those formed in cold H$_2$O$_2$ start reducing at temperatures as low as 250°C \(^{(14)}\), whereas when grown in hot H$_2$O$_2$ no reduction takes place until the temperature is 450°C \(^{(57)}\). For acid/glycol grown oxides no thinning of the film is noticed if the temperature is less than 300°C.

As well as its effect on thickness, the annealing temperature affects the solubility of anodic oxides. Water will dissolve films grown in hot aqueous H$_2$O$_2$ \(^{(57)}\) and in ammonium pentaborate \(^{(13)}\), but the former are insoluble after being annealed at above 400°C. Neither are they attacked substantially by acids or alkalis, with the exception of hot concentrated H$_3$PO$_4$, after an anneal above 600°C. However, most bases and acids, except HNO$_3$ \(^{(57)}\), will dissolve films annealed at less than 250°C.
The preparation of a surface is an important factor in the oxidation process, as abraded surfaces produce films which are about 10% thicker than those formed on chemically polished surfaces (14), but neither surface orientation nor material type have any apparent effect on growth rate (57,14). However, it has been shown recently that ambient light affects the growth rate of n-type material, whereas no appreciable effect occurs for p-type material with either low or high doping levels (59).

The refractive indices of anodic oxides are about 1.8 (13,14,15,52,57).

The maximum values of dielectric constant and breakdown field strength have been obtained for films grown in acid/glycol. For such oxides grown between 1800° and 2000° thick, the dielectric constant is between 7 and 8 at 1MHz, and the breakdown field strength between 4 and 5.10^6 Vcm^-1 (52).

3.6.5. Thermally grown films.

Native oxides of gallium arsenide have been grown thermally in air or oxygen at temperatures from 350°C to above 1000°C, whilst growth for up to about two years in air at 25°C has produced thin natural oxides.

The natural oxides were grown in air at room temperature on cleaved (110) surfaces by Lukes (5) who obtained a logarithmic growth for films up to about 40Å thick. At higher temperatures, between 350°C and 500°C, Murarka (60) claims that air oxidation of (110) and (100) surfaces produces a linear growth rate but that no law can be established between thickness and times of less than four hours at 500°C. However, a least squares fit of the data for 450°C (figure 3.4) for times up to 6 hours gives 0.92 and
**Fig. 3.4** Growth rate in air at 350°C & 450°C of oxides formed on gallium arsenide.

*(From: Murarka - App. Phys. Letters. 26 4 75)*

**Fig. 3.5** Murarka's results (fig. 3.4) replotted to show parabolic growth for periods up to six hours at 450°C.
1.00 as the coefficients of determination for a linear law and parabolic law respectively. Thus, by reploting the data as thickness$^2$ against time (figure 3.5) it can be seen that Murarka's results are consistent with a parabolic growth law for oxides grown at 450°C for times up to at least six hours. However, as is indicated by the parabolic curve in figure 3.4, such a law appears not to apply for longer periods.

The data is insufficient for any conclusion to be reached for growth at 350°C, but at 500°C it is apparent that linear growth does occur when the oxidation time is in excess of four hours. Consequently, the above results are consistent with those obtained by Navratil (4) for (111) surfaces oxidised in air and oxygen between 400°C and 530°C. Navratil found that oxidation at 400°C and 450°C resulted in parabolic growth for up to at least 16 hours with an activation energy of about 1.0 eV. However, at 480°C and 530°C the rate was linear with an activation energy of about 2.0 eV. Moreover, he showed that at temperatures below about 495°C the oxidation rate was greater in oxygen than in air, but above this temperature the position was reversed. The growth rate on (111) Ga faces was seen to be 13% faster than on (111) As faces and, from a comparison with Murarka's results, both appear to oxidise more rapidly than either (110) or (100) surfaces. Murarka was unable to measure any effect on the oxidation rate due to surface orientation but the difference between that on (110) and (111) surfaces is consistent with the results of Minden (1) for films grown between 600°C and 900°C. Also within this temperature range Minden found that n and p-type material oxidised at the same rate.

It has been shown that the composition of thermally grown films depends on the temperature of growth. Thin films between 200Å and 500Å thick, grown in dry oxygen at 450°C by Wilmsen (61) and analysed by Auger spectroscopy, have gallium, arsenic and oxygen profiles as given by figure 3.6. Sealy and Hemment (6) have shown by transmission electron
**Fig. 3.6** Composition profile of thermal oxide grown on gallium arsenide at 450°C.

(From: Wilmsen - Thin Solid Films 39 (1976) 113)
diffraction analysis that oxides about 2500Å thick grown for one hour at 600°C, contain arsenic. This element was detected also, in the form of 
$\text{As}_2\text{O}_3$, by Zaininger and Revesz (2) using reflection electron diffraction, in films grown at 660°C on (110) and (111) surfaces. It was suspected
that the latter films contained elemental arsenic at the interfaces, but this was not confirmed by chemical analysis. Also, arsenic, in the form of 
$\text{GaAsO}_4$, was detected by x-ray diffraction in films grown at greater than 700°C by Rubenstein (3). Up to 10% of the oxide consists of this compound
when grown between 850°C and 965°C, but above 1000°C the arsenic constituent, with, he suspects, some $\text{GaAs}$ and $\text{Ga}_2\text{O}_3$, evaporates so leaving the films composed solely of $\text{Ga}_2\text{O}_3$.

The above results are at variance, however, with those of Minden who found no significant growth at temperatures below 600°C and detected
no arsenic by T.E.M. in films between 1000Å and 6000Å thick grown between 600°C and 900°C on (110) and (111) surfaces. Films grown at 900°C were
white, crystalline and waxy in texture.

The arsenic content of oxides has been found to evaporate also during annealing. This has been seen to occur in nitrogen at 680°C which leaves the films composed of polycrystalline $\beta$-$\text{Ga}_2\text{O}_3$. At 700°C and above
the polycrystalline structure becomes more granular with a preferred orientation (6). Similar granular structures form also during the oxidation of (111) surfaces at temperatures as low as 400°C, but these can be rubbed off easily, although on other surfaces they are adherent and mechanically stable (4).
At 800°C, water vapour has been shown to cause oxide flaking after producing hard white crystalline spots at the oxide-substrate interface, but no such effect is observed when water vapour is introduced deliberately into the system at lower temperatures (1). However, (111) surfaces become pitted during growth in dry atmospheres as low as 600°C, whilst (110) surfaces, which remain smooth at this temperature, become so only after more than ½ hours growth at 700°C (1).

Thermally grown oxides are porous (1,2,3) and dissolve in HF and HCl (1,4,60), but they are insoluble in bromine-methanol solutions and HNO₃ (60). They have refractive index values between 1.57 (4) and 2.0 (60), but no further data concerning their electrical properties has been published.

Certain tentative conclusions regarding the oxidation mechanism and composition of thermal oxides can be obtained from the above data.

The growth of thin films at about room temperature is logarithmic whereas it is parabolic at temperatures from below 400°C to about 500°C at which it transforms to a linear rate. However, the temperature at which such a change takes place depends on the growth time and this is influenced by certain other factors. Among these could be thermal stresses and surface preparation which may account for the enhanced growth rate of thick films grown at 450°C and the inability to grow films at a constant rate at 500°C for times of less than four hours.

During parabolic growth, the oxidation rate is greater in oxygen than it is in air, but during linear growth the opposite occurs. In the former case the phenomenon could be due to the availability of oxygen whereas during linear growth cracks or pores within the oxide may permit the indiffusion of water vapour which could form a subscale hydride at
the interface. Possible support for this contention is the observation that films flake from the surface after being grown in a humid atmosphere at 800°C.

Because the oxide growth rate is greater on (111) surfaces than it is on those with (111) orientation, it must be concluded that, in agreement with Miller et al. (62), films evaporate during oxidation as, from surface bonding considerations, (111) surfaces should be the more readily oxidisable of the two (31). As native oxides consist essentially of polycrystalline Ga$_2$O$_3$, it follows that although oxidation is faster on (111) surfaces the arsenic oxide evaporates. This is supported by the fact that arsenic oxides have a lower melting point and lower heat of formation than gallium oxides. Consequently they are less stable and evaporate at lower temperatures.

The arsenic oxide is incorporated in films grown at temperatures up to about 700°C as As$_2$O$_3$, but above this temperature it is in the form of GaAsO$_4$. This glassy silica-like compound, whose appearance seems to coincide with the coalescence and orientation in a preferred direction of the polycrystalline film, evaporates at temperatures above 1000°C.

3.6.6. Application of native oxides to GaAs devices.

Oxides can perform three functions relating to the fabrication of GaAs devices.

First, they can be used as an encapsulant for the annealing process necessary after ion implantation. In this role their function is
to inhibit decomposition while the ions are made electrically active. Hemment et al. (63) used this technique after discovering that $\beta$-$\text{Ga}_2\text{O}_3$ formed under a deposited layer of $\text{SiO}_2$ during an anneal in nitrogen at between 600°C and 700°C. Also, Sealy and D'Cruz (64) found that native gallium arsenide oxides, grown for 15 or 30 minutes at between 500°C and 600°C can be used for encapsulation purposes at 700°C. However, in some instances, arsenic builds up at the oxide-substrate interface during the annealing stage and this arsenic then controls the electrical properties of the substrate. Moreover, in most cases, the electrical activity is low compared with samples coated with $\text{Si}_3\text{N}_4$ or aluminium, and, although $\text{Ga}_2\text{O}_3$ can give good results, they are not very reproducible. They achieved significant improvements, however, by evaporating an aluminium layer on the oxide surface which increased the post annealing activity by a factor of approximately two. D'Cruz (65) took this work further and found that thermal oxides reduce the indiffusion of aluminium into GaAs but that even at 700°C there is an outdiffusion of gallium and arsenic into the aluminium through the oxide. Nevertheless, as an encapsulant, the oxide-aluminium system works effectively at 800°C for an anneal time of five minutes, and in all cases it is superior to aluminium alone.

It is only recently that native oxides have been used in their second role - that of the gate insulator of MOS transistors. The oxides were produced by the anodic method using the electrolyte developed by Hasegawa et al. (52). This enabled Bayraktaroglu et al. (41) to fabricate GaAs inversion mode MOSFETs from p-type material, and Lile et al. (42) to produce a depletion mode device from n-type epitaxial layers deposited on (100) semi-insulating substrates.
Insufficient information on their properties has been given to allow an assessment of their suitability as circuit components to be made. The p-type devices exhibit no hysteresis in their current-voltage characteristics and the inversion charge mobility is about $2350 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ (41). The n-type device has a mobility of about half this value. Although these mobilities are a lot lower than the feasible value for gallium arsenide, the conclusion of Weiss et al (66) that "there is a good chance to make GaAs MOSFETs as successful in the microwave field as Schottky gate transistors" appears to be justified.

No use has been made of native oxides for passivation.
Chapter 4.

EXPERIMENTAL EQUIPMENT, THEORY AND PROCEDURE

4.1. Introduction.

The investigation into the properties of native oxides formed on gallium arsenide was carried out on small samples of bulk and epitaxial material. The films were grown thermally in oxygen and analysed subsequently by Rutherford backscattering. MOS devices were fabricated from n-type bulk samples and their electrical properties obtained from current - voltage (I-V), capacitance - frequency (C-f) and capacitance - voltage (C-V) measurements.

This chapter describes the methods and apparatus used for the production of films and their analysis.

4.2. Preparation of samples.

4.2.1. Slicing and polishing of bulk material.

Single crystal ingots of bulk n and p-type gallium arsenide were cut parallel to an end face into slices approximately 1.5 mm thick by a lubricated diamond impregnated wheel saw.

The next step was to clean the slices in warm trichloroethelene and then chemically polish them in a 4% bromine/methanol solution in order to remove the surface damage resulting from the cutting process.
First, a slice was glued with wax to a quartz disc and the height of the surface was measured by the micrometer head of a Talystep. Then it was polished by gliding it lightly on a 'Hyprocel Pellon Fan - W' abrasive pad immersed in the etching solution. From time to time the slice was removed from the etch, immediately rinsed in methanol, dried and remeasured until 250μm had been removed from the surface. Finally the slice was placed in a rotating beaker containing 1/2% bromine/methanol solution for 5 minutes to free etch a further 10μm of damaged surface left by the polishing process, rinsed again in methanol and removed from the disc with trichloroethelene.

4.2.2. Dicing of slices.

Slices of both the bulk and epitaxial material were mounted face downwards onto glass slides with wax and cut into approximately square samples of 20 mm² with a lubricated diamond impregnated wire saw. The samples were removed from the slides by warm trichloroethelene, cleaned in methanol and dried with a moistened spill made from filter paper or cotton wool.

4.2.3. Final preparation of samples.

Immediately before it was used, each sample was immersed for two or three minutes in hot concentrated HCl, rinsed in de-ionised water and then methanol, then dried. This process removed any surface oxide which may have formed during etching. A final examination was made under the optical microscope to check that the surface was smooth and unblemished.
4.3. The oxidation and annealing process.

4.3.1. Equipment.

The growth and annealing of oxide films were carried out in a thermostatically controlled furnace through which gas flowed at atmospheric pressure at a monitored rate. The gas, from a cylinder, entered the sealed inlet end of the furnace tube after passing through a drying agent (silica gel) and flowmeter and was expelled to the outside atmosphere via a flexible tube connected to the sealed end of the outlet.

The hot zone temperature could be set to within ±5°C of the required value with the aid of a calibration chart, and to ±2°C by using thermocouples attached to the sample holder. Steady state conditions were attained within one hour of the furnace and gas supply being switched on. However, due to a lack of sensitivity in the control mechanism which monitored the temperature at the centre of the tube and not that of the hot zone, fluctuations of up to ±5°C occurred throughout the 'on' period.

Two sample holders were used during the course of the experiments, one was a gallium arsenide boat on which the samples were placed and pushed to the hot zone by a stainless steel rod, and the other was a quartz holder connected to a quartz rod. Thermocouples were attached to the latter holder thereby permitting the temperature to be monitored continually by a digital voltmeter.
4.3.2. Method.

A gas flow of 5 ft$^3$/hour was passed through the furnace which was set to the required temperature. After steady conditions had been reached samples were placed on the holder at the gas inlet end of the tube.

In early experiments samples were oxidised by pushing them quickly into the hot zone, leaving them for the required time then pushing them to the outlet where they cooled before being removed. This method produced films which possessed low breakdown characteristics which were attributed to pin holes or cracks. Consequently, an improved technique was devised to obtain films of a better quality. This was used throughout the present investigations for both the oxidation and annealing processes and was carried out as below.

Whilst oxygen, for oxidation, or nitrogen, for annealing, flowed through the tube, the samples were pushed towards the hot zone at a rate of 2 cms every 2 minutes over a period of $\frac{1}{2}$ hour. They remained in the hot zone for the required oxidation or annealing time, at the end of which, and after oxygen had been switched to nitrogen, they were pushed to the outlet over a further $\frac{1}{2}$ hour period of 2 minute intervals.

4.4. Oxide analysis.

4.4.1. Introduction.

After growing an oxide, the next step was to determine its thickness and composition. This was achieved by using the relatively
new method of Rutherford backscattering which is being applied increasingly
to surface analysis in such fields as metallurgy and semiconductors. Its
particular advantage over other more established methods is its ability
to probe to depths of several microns beneath a surface without the need
to remove successively the topmost layer.

The principle behind the technique is that energetic charged
particles will undergo a loss of energy due to interactions with the
nuclei and electrons of atoms within a material. Moreover, the probability
of a collision is proportional to the cross-section and area density of
the atoms. Consequently, from a knowledge of the yield and energy spectrum
of particles re-emitted from a material, the depth distribution and
identity of surface constituents can be established.

The equipment required is an accelerator to generate a stable
collimated beam of high energy ions and a data acquisition system with
which to analyse the backscattered particles.

Several excellent publications have been written concerning
Rutherford backscattering (67-69) and, therefore, only those aspects which
are relevant to these investigations are included in this chapter. These
together with an account of the equipment and analytical procedure used
are covered in the following sections.

4.4.2. Rutherford backscattering theory.

The fraction $Y$ of particles of mass $M_o$ elastically (Rutherford)
scattered through an angle $\Theta$ by impact with particles of mass $M_1$ is
proportional to the differential cross-section of \( M_1 \) and is given by:

\[
Y \propto \left[ \frac{Z_0 \cdot Z_1}{E} \right]^2 \left( \text{Cosec}^4(\theta/2) - 2M_0^2/M_1^2 \right)
\]  

(1)

where:

\( Z_0 \) and \( Z_1 \) are the atomic numbers of masses \( M_0 \) and \( M_1 \) respectively, and \( E \) is the energy of \( M_0 \) immediately before impact.

For large values of \( \Theta \), equation (1) reduces to:

\[
Y \propto \left[ \frac{Z_0 \cdot Z_1}{E} \right]^2 \cdot \frac{M_1^2 - 2M_0^2}{2 M_1^2}
\]

(2)

and, also, when \( M_1 \gg M_0 \)

\[
Y \propto \left[ \frac{Z_0 \cdot Z_1}{E} \right]^2
\]

(3)

The energy \( E \) is a function of the distance \( x \) from the surface and is given by:

\[
E = E_0 - xS
\]

(4)

where \( S \) (\( = \text{d}E/\text{d}x \)) is the stopping power of the medium and \( E_0 \) is the initial energy of \( M_0 \).
Due to the impact, $M_0$ is deflected through an angle $\Theta$, and immediately after impact has an energy $E'$ given by:

$$E' = k^2 \cdot E$$  \hfill (5)

The constant $k^2$, the kinematic factor, is obtained from simple energy-momentum calculations, and is given by:

$$k = \frac{M_0 \cos \Theta}{M_o + M_1} + \left[ \frac{M_1^2 - M_0^2 \sin^2 \Theta}{(M_0 + M_1)^2} \right]^{1/2}$$  \hfill (6)

On returning to the surface, $M_0$ will suffer a further energy loss of $S^+ \cdot \sec \Theta$, and emerge from the medium with a final energy $E_f$ given by:

$$E_f = E' + xS^+ \sec \Theta$$  \hfill (7)

For an amorphous material the stopping power is non-directional and $S^+ = S$. Therefore,

$$E_f = E' + xS \sec \Theta$$  \hfill (8)

By substituting for $E'$ and $xS$ from equations (5) and (4) respectively, equation (8) becomes:

$$E_f = E(k^2 - \sec \Theta) + E_o \sec \Theta$$  \hfill (9)

and equation (2) becomes, in terms of $E_f$:

$$Y \propto \left[ \frac{Z_0 \cdot Z_1 \cdot (k^2 - \sec \Theta)^2}{E_f - E_o \sec \Theta} \right] \cdot \frac{M_1^2 - 2M_0^2}{M_1^2}$$  \hfill (10)
Equation (10) shows that $Y$ is inversely proportional to $(E_f - E_0 \sec \theta)^2$ and has maximum and minimum values for $E_f = 0$ and $E_f = k^2 E_0$ respectively. Therefore the shape of the $Y$ vs $E_f$ curve is as shown in figure 4.1.

The energy ordinate $E_f$ can be expressed also in terms of distance $x$ from equations (8), (5) and (4) which give:

$$x = \frac{E_f - k^2 E_0}{(k^2 - \sec \theta)S} \quad (11)$$

Therefore,

$$\Delta x = \frac{\Delta E_f}{(k^2 - \sec \theta)S} \quad (12)$$

Equation (12) has important implications for compounds because of the dependence of $\Delta x$ on $k$. For example, an oxide on the surface of a single element material will produce a yield-energy curve having the form shown in figure 4.2. The denoted energy values $k_1^2 E_0$ and $k_2^2 E_0$ are the respective energies of ions backscattered from the atoms of the material and oxygen at the surface of the oxide (at $x = 0$) in accordance with equation (11). For an oxide of thickness $\Delta x$ the values of $\Delta E_f$ are given by equation (12) for the corresponding values of $k$. As, for figure 4.2, $k_2$ is less than $k_1$ then $\Delta E_{f2}$ is less than $\Delta E_{f1}$.

The composition of the oxide is denoted by the hatched areas of figure 4.2, which give the relative amount of each type of atom present. However, because of the dependence of $Y$ on equation (2), the relative concentrations of the two types of atoms within the oxide is given by:

- 47 -
**Fig. 4.1** Yield vs Energy spectrum of single element material

**Fig. 4.2** Yield vs Energy spectrum of oxide.
\[
\frac{N_2}{N_1} = \frac{\text{Area 2}}{\text{Area 1}} \left[\frac{Z_1}{Z_2}\right]^2 \left[\frac{M_2}{M_1}\right]^2 \frac{M_1^2 - 2M_0^2}{M_2^2 - 2M_0^2} \tag{13}
\]

If \( Y \) is the yield at the surface, the area is \( Y \cdot \Delta E_f \). Therefore,

\[
\frac{\text{Area 2}}{\text{Area 1}} = \frac{Y_2}{Y_1} \frac{\Delta E_{f2}}{\Delta E_{f1}} \tag{14}
\]

where \( Y_2 \) and \( Y_1 \) are the respective yields at \( k_2^2 E_0 \) and \( k_1^2 E_0 \).

If \( \Delta E_f \) cannot be measured, then recourse can be made to equation (12), (from \( \Delta E_f = \Delta x \cdot (k^2 - \sec \theta)S \)), to obtain:

\[
\frac{\text{Area 2}}{\text{Area 1}} = \frac{Y_2(k_2^2 - \sec \theta)}{Y_1(k_1^2 - \sec \theta)} \tag{15}
\]

Consequently, from equations (13) and (15),

\[
\frac{N_2}{N_1} = \frac{Y_2(k_2^2 - \sec \theta)(Z_1 \cdot M_2)^2(M_1^2 - 2M_0^2)}{Y_1(k_1^2 - \sec \theta)(Z_2 \cdot M_1)^2(M_2^2 - 2M_0^2)} = \frac{Y_2 \cdot U_2}{Y_1 \cdot U_1} \tag{16}
\]

where:

\[
U = (k^2 - \sec \theta)M^2 / Z^2(M^2 - 2M_0^2) \tag{17}
\]

The constant '\( U \)' has been calculated for oxygen, gallium and arsenic with \( \theta = 150^\circ \) and \( M_0 = 4 \) (helium). The resulting values are listed in table 4.1.
Table 4.1. Calculated values of 'U' for oxygen, gallium and arsenic.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Z</th>
<th>M</th>
<th>k²</th>
<th>k²·secθ (m)</th>
<th>M²/Z²(M²−2M₀²) (n)</th>
<th>U (m²n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>8</td>
<td>16</td>
<td>0.385</td>
<td>1.450</td>
<td>0.01786</td>
<td>0.0275</td>
</tr>
<tr>
<td>Ga</td>
<td>31</td>
<td>69.72</td>
<td>0.808</td>
<td>1.962</td>
<td>0.00147</td>
<td>0.0021</td>
</tr>
<tr>
<td>As</td>
<td>33</td>
<td>74.92</td>
<td>0.819</td>
<td>1.974</td>
<td>0.00092</td>
<td>0.0018</td>
</tr>
</tbody>
</table>

The above review of backscattering theory has dealt with single element materials and surface oxides formed on them. In the case of a compound material composed of two types of atoms, A and B, the spectrum is more complicated than that shown in figure 4.1. It has the form shown in figure 4.3 where the total yield $Y$ is the sum of the yields $Y_A$ and $Y_B$ from atoms A and B respectively. $Y_A$ and $Y_B$ are each given by equation (10) in which $k_1$, $Z_1$ and $M_1$ have the appropriate values for atoms A and B.

The yield-energy curve from an oxide film formed on a two element material has the form given in figure 4.4. The relative numbers of each type of atom in the oxide are given again by the hatched areas so that:

$$\frac{\text{No. anions}}{\text{No. cations}} = \frac{N_2}{(N_A + N_B)}$$

$$= \frac{1}{(N_A/N_2 + N_B/N_2)} \quad \text{(18)}$$

- 50 -
Fig. 4.3 Yield vs Energy spectrum of double element material

Fig. 4.4 Yield vs Energy spectrum of oxide.
The system employed at Surrey\textsuperscript{(70)} is shown diagrammatically in figure 4.5. The accelerator is a standard 2 MeV Van de Graaff machine which produces helium ions from an r.f. source. These are deflected through $172^\circ$ by a 1.7 tesla electromagnet of mass energy product $24$ a.m.u. - MeV and then collimated by a series of adjustable apertures to a beam of about 1 mm cross-sectional diameter. The magnet current, which is used also as the reference energy for the ions, is constant to 1 in $10^6$, whilst the potential of the high voltage terminal is stabilised by feedback signals generated from a pair of water cooled slits situated on the exit side of the magnet. The beam line is sectioned by valves and both it and the target chamber are evacuated by a series of oil diffusion pumps which maintain the pressure at about $1.10^{-6}$ torr.

Within the target chamber is a remotely controlled goniometer whose movement, in increments of 0.1° about each of three axes, is monitored by three external dials. Screwed into the goniometer is a removable insulated sample holder which consists of a cylindrical PTFE insert onto which is fixed an aluminium base plate carrying a spring clip. Contact to the plate is made by a terminal through the holder to a flying lead connecting with an external current meter. This meter serves two functions - it measures the beam current flowing to earth and outputs pulses to a digital counter. A second flying lead connects an aluminium annulus, located 5 mm in front of and isolated from the base plate, to an external power unit to provide a negative voltage for secondary electron suppression.

Mounted on the inside periphery of the chamber is a silicon surface
Fig. 4.5 The Surrey Rutherford backscattering system.
(Van de Graaff diagram from: Cracknell et al. Fuel Inst. & Meth. 92 (1971) 468.)
barrier detector aligned to receive ions backscattered through 150° with respect to the beam line. This device, which has a resolution of about 15 keV FWHM, provides input pulses via low noise high gain amplifiers to a rate-meter in parallel with a pulse height analyser (a Didac 800). The latter, which is the analytical part of the system, routes each incoming pulse to one of 800 digital channels set to receive pulses between defined voltage limits. At the same time the channels are scanned and their count displayed in analogue form on the C.R.O. The data held in the P.H.A. can be fed to an X-Y plotter to give a yield-energy spectrum of the backscattered ions and, in binary form, to a Teletypewriter which prints out the count in each channel. In addition, the typewriter can punch the data onto paper tape. The output of the ratemeter feeds into a chart recorder thereby enabling the samples to be orientated into channelled or random directions with respect to the helium beam line.

4.4.4. Backscattering procedure.

In order to obtain its backscattered spectrum, each sample was placed in the holder of the goniometer, the current and suppressor leads were connected and the target chamber pumped down to below 5.10⁻⁶ torr. Then the required voltages were applied to the suppressor (-300 volts) and slowly to the detector (+75 volts). The current integrator was switched on and the valves in the beam line opened to allow a 1 mm² 1.5 MeV helium ion beam to fall onto the sample at a predetermined current.

When a channelled spectrum was required, the beam current was set to 5 nA and the output from the ratemeter was plotted by the pen recorder as the sample was rotated slowly about a vertical axis for various angles of rotation about the horizontal axis. When a position was obtained at which the backscattered pulse rate was a minimum the energies of the backscattered
ions were recorded by the pulse height analyser (set to receive inputs on all 800 channels at 100 channels per volt) during a count of 50,000 pulses registered from the current integrator. This count represented a beam charge of 5 μ coulombs.

When a random spectrum was required the sample was positioned so that the rate of backscattering was maximum. Also the beam current was reduced to 2.5 nA and the spectrum obtained whilst the current integrator emitted 100,000 pulses.

The data held in the pulse height analyser was fed in analogue form to the X-Y plotter and in digital form to the typewriter.

4.4.5. Backscattering analysis.

The data on the printouts from the typewriter were plotted to obtain the backscattered spectrum for each sample. These were similar in form to the spectrum in figure 4.2.

The oxygen profiles (as indicated by area 2 in figure 4.2) were extracted from the spectra by extrapolating the background contours of the gallium arsenide yields (indicated by the broken line in figure 4.2) and measuring the oxygen yield at each channel number. These yields were replotted and resulted in profiles similar to figure 4.6.

The widths of the oxygen profiles were obtained by measuring the difference between the channel number of the surface $N_o$ and interface $N_i$ at which the backscattered yield was half the maximum value ($Y_o$).
Generally, \( N_0 \) could be identified to within 1 channel whereas this was doubled in the case of \( N_1 \) for thin films (where \( N_0 - N_1 \) is less than about 30 channels). For thick films the uncertainty in the value of \( N_1 \) resulted in an error of about \( \pm 10\% \) in the profile width.

The interface portions of the oxygen spectra indicated that the concentration of oxygen in the oxide-substrate regions decreased with depth. In order to measure the widths of these regions an assumed profile of an abrupt edge was superimposed on each spectrum at the position where the interface profile reduced to zero. This is shown by the dotted curve in figure 4.6 where the interface width is given by the difference in channel numbers \( (N_1 - N_a) \) of the half height points of the two edges.

Owing to the imprecision in positioning the abrupt edges, the measurements of the interface widths \( (N_1 - N_a) \) have an error of about \( \pm 3 \) channels.

![Fig. 4.6. Backscattered spectrum of oxygen profile.](image)

Identification of the constituents of the oxides was carried out by first obtaining the channel numbers representing surface gallium \( (N_{Ga}) \) and arsenic \( (N_{As}) \) from the spectrum of a clean gallium arsenide calibration
sample which was backscattered during the course of each day's run. The spectrum was similar to that of figure 4.3 with $k_{\text{E}}^{2}E_{\text{O}}$ representing the arsenic edge at channel $N_{\text{As}}$ and $k_{\text{E}}^{2}E_{\text{O}}$ representing the gallium edge at $N_{\text{Ga}}$. The two channel numbers were obtained to within ± 1 channel from the half height points of the edges in a manner similar to that used for identifying the oxygen edge (figure 4.6).

The heights of the steps at the gallium and arsenic edges of the spectra from the oxidised samples were measured to give the yields, $Y_{\text{Ga}}$ and $Y_{\text{As}}$, of gallium and arsenic respectively, from the atoms at the surfaces of the oxide films. Together with similar measurements of the oxygen yields ($Y_{\text{O}}$), these values were inserted into equations (16) and (17) (section 4.4.2) to obtain the relative concentration of oxygen atoms (anions) and cations (gallium and arsenic) and of gallium and arsenic atoms at the surfaces of the films.

The yields $Y_{\text{O}}$, $Y_{\text{Ga}}$, and $Y_{\text{As}}$ could be measured with estimated errors of ± 10%, ± 5% and ± 20% respectively, the large error in $Y_{\text{As}}$ being due to the small quantity of arsenic.

4.4.6. Calibration measurements.

The channel axes of the oxygen spectra were calibrated in terms of thickness by removing parts of the oxides and measuring the step heights with a Rank-Taylor-Hobson Talystep.

Parts of the oxides of several samples oxidised at $510^\circ$C were covered with wax and the samples dipped in cold HCl to remove the exposed parts of the films. Several talystep traces were obtained from each sample
as listed in table 4.1 and their mean value and standard deviation calculated. The formulae used in these calculations are given in section 4.7.

<table>
<thead>
<tr>
<th>Channels (N)</th>
<th>$\lambda$ (10^{-8} cm)</th>
<th>$\lambda / N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.5 ± 10%</td>
<td>900 ± 200</td>
<td>28.6 ± 7.0</td>
</tr>
<tr>
<td>n</td>
<td>1100 ± 200</td>
<td>35.0 ± 7.3</td>
</tr>
<tr>
<td>n</td>
<td>800 ± 200</td>
<td>25.4 ± 6.8</td>
</tr>
<tr>
<td>n</td>
<td>1000 ± 200</td>
<td>31.7 ± 7.1</td>
</tr>
<tr>
<td>47.5 ± 10%</td>
<td>1200 ± 200</td>
<td>25.3 ± 4.9</td>
</tr>
<tr>
<td>n</td>
<td>1200 ± 200</td>
<td>25.3 ± 4.9</td>
</tr>
<tr>
<td>n</td>
<td>1300 ± 200</td>
<td>27.4 ± 5.0</td>
</tr>
<tr>
<td>65.0 ± 10%</td>
<td>2000 ± 200</td>
<td>30.8 ± 4.4</td>
</tr>
<tr>
<td>n</td>
<td>1600 ± 200</td>
<td>24.6 ± 4.1</td>
</tr>
<tr>
<td>Mean value (M)</td>
<td></td>
<td>28.0 ± 2.0</td>
</tr>
<tr>
<td>Standard deviation (d)</td>
<td></td>
<td>3.4</td>
</tr>
</tbody>
</table>

4.5. MOS devices.

4.5.1. Introduction.

Before the electrical properties of a film can be measured, an ohmic contact has to be made to the substrate and contact electrodes deposited
onto the oxide. This results in a metal-oxide-semiconductor (MOS) device which, for ease of handling, is fixed to a flat metal base.

The theory of MOS devices, on which the properties of films grown on n-type bulk material were measured, and the procedure used for their construction, are detailed below.

4.5.2. MOS theory.

A detailed analysis of the operation of MOS devices is given in S.M. Sze - "Physics of Semiconductor Devices". The following is a simplified account of their operation which is sufficient to explain their general behaviour under the conditions used in this project. Only devices with n-type semiconductors are considered. P-type devices behave similarly and differ only by the energy of the Fermi level and the need to reverse the polarity of the applied voltage.

(a) The ideal MOS device.

An ideal MOS device has no charges - ions, traps or fixed charges - within the insulating oxide, or surface states at the oxide-substrate interface (section 3.3). In addition, the work functions of the metal and semiconductor are the same.

The energy band structure of a device under four conditions of bias voltage applied to the metal electrode with the semiconductor contact at earth potential is shown in figure 4.7.

With zero bias the energy bands are flat throughout the semiconductor and free electrons reside in the conduction band.
Fig. 4.7 Energy band diagrams of ideal MOS structures for n-type semiconductors (34).
When the applied voltage is positive the conduction band, the valence band and the intrinsic Fermi level are bent at the interface whilst the Fermi level is moved nearer to the conduction band. Consequently, the free electron concentration in the conduction band is increased and electrons accumulate in the region behind the oxide.

When accumulation conditions exist the availability of free electrons in the conduction band renders the device conducting and the whole of the applied voltage is dropped across the oxide.

Negative voltages bend the energy bands in a way which causes the electron concentration to be reduced. As the bias increases from zero the Fermi level at the interface moves nearer to the intrinsic Fermi level and the electron concentration is reduced to below the flat band concentration for a depth in which the energy bands are bent. This region of the semiconductor is the depletion region. The width of the depletion region increases with increasing negative voltage to a maximum when the Fermi level meets the intrinsic Fermi level midway in the energy gap. Thereafter, the Fermi level moves closer to the valence band and holes accumulate in the inversion region at the interface between the oxide and the depletion region deeper within the semiconductor.

The depletion region forms a barrier to electron flow between the metal contact and the semiconductor and, therefore, it is capacitive. Consequently, the voltage applied to the device is divided between the oxide and the depletion region in inverse proportion to their capacitances.

The capacitances of the oxide and the depletion region are in series and together constitute a device capacitance which varies with applied voltage owing to changes in the depletion width. The relationship between
applied voltage and device capacitance is derived in a later section.

(b) The practical device.

Deviations from the ideal device occur in practical devices owing to the charged defects mentioned previously and to the differences between work functions of the metal and the semiconductor. These cause the energy bands at the interface to be bent at zero bias and the device to be set into either the accumulation or depletion mode. Consequently a bias, the flat band voltage \( V_{PB} \), has to be applied across the device to obtain the flat band condition.

(c) The relationship between device capacitance and applied voltage.

The following derivation applies to an ideal device operating in the depletion mode. It assumes an abrupt junction exists at the interface and the donor density within the semiconductor is constant.

If: 
\[ V = \text{applied voltage across device} \]

then, 
\[ V = V_O + V_D \]  \hspace{1cm} (1)

where \( V_O \) and \( V_D \) are the voltages developed across the oxide and depletion region.

The relationship between device capacitance \( C \), oxide capacitance \( C_O \) and depletion capacitance \( C_D \) is given by:

\[ \frac{1}{C} = \frac{1}{C_O} + \frac{1}{C_D} \]  \hspace{1cm} (2)

A change \( dV \) in applied voltage results in changes in the voltages.
across the oxide and depletion regions which are related by the differential of equation (1), i.e.:

\[ dV = dV_0 + dV_D \]  (3)

\( dV \) changes the thickness \((x)\) of the depletion region which results in a change \(dC_D\) in the depletion capacitance. The oxide capacitance \(C_o\) is unaffected by voltage changes and, hence, \(dC_o = 0\). Consequently, the differential of equation (2) is:

\[ d(1/C) = d(1/C_D) \]  (4)

The relationship between voltage and capacitance of the depletion region is given by:

\[ dV_D = dQ/C_D \]  (5)

where \(dQ\) is the change in the charge \((Q)\) due to the voltage change \(dV_D\).

\(Q\) is related to \(V_D\) by Maxwell's equation:

\[ \text{Div } \varepsilon \cdot E_D = ne \]  (6)

where:

\(ne\) = charge density
\(n\) = donor density within the semiconductor
\(e\) = electronic charge
\(E_D\) = electric field within depletion region of width \(x\)
\(\varepsilon\) = permittivity of semiconductor
Rewriting equation (6) as:

\[
d^2V_D/dx^2 = ne/\varepsilon
\]  

(7)

and solving equation (7) for \(V_D\), gives:

\[
V_D = ne(x^2/2 + ax + b)/\varepsilon
\]  

(8)

where \(a\) and \(b\) are integration constants.

Both \(a\) and \(b\) are zero as \(V_D\) and \(E_D\) are zero when \(x\) is zero. Therefore:

\[
V_D = nex^2/2\varepsilon
\]  

(9)

and

\[
dV_D = nexdx/\varepsilon
\]  

(10)

As the depletion capacitance \(C_D\) is given by:

\[
C_D = A\varepsilon/x
\]  

(11)

where \(A\) is the contact area,

\[
dx = A\varepsilon d(1/C_D)
\]  

(12)

From equations (10), (11) and (12),

\[
dV_D = neA^2\varepsilon (1/C_D)d(1/C_D)
\]  

(13)
From equations (5) and (13):

\[ dQ = neA^2 \varepsilon d(1/C_D) \]  \hspace{1cm} (14)

Therefore, from equations (2), (3), (4) and (14):

\[ dV = neA^2 \varepsilon (1/C) d(1/C) \]  \hspace{1cm} (15)

At flat band voltage \( V_{FB} \) the device capacitance is that of the oxide \( (C_O) \). Therefore, equation (15) can be integrated between voltage limits \( V_{FB} \) and \( V \), and between capacitance limits \( C_O \) and \( C \). This gives:

\[ \int_{V_{FB}}^{V} dV = neA^2 \varepsilon \int_{C_O}^{C} (1/C) d(1/C) \]  \hspace{1cm} (16)

Integration of equation (16) and a rearrangement of terms gives:

\[ 2(V - V_{FB})(C_O/A)^2/ne \varepsilon = (C_O/C)^2 - 1 \]  \hspace{1cm} (17)

Equation (17) agrees with that derived by Goetzberger and Nicollian (71) and by Grove et al (72). Furthermore, by substituting

\[ (1/C) d(1/C) = d(1/2C^2) \]  \hspace{1cm} (18)

equation (15) results in:

\[ n = 2 \left[ eA^2 \varepsilon (1/C^2)/dV \right]^{-1} \]  \hspace{1cm} (19)

which has been derived by Gelder and Nicollian (73).
Equation (17) shows that a plot of \((\frac{C_o}{C})^2 - 1\) versus \(V\) will yield a straight line which cuts the voltage axis at the flat band voltage \(V_{FB}\) and that the line has a slope from which the donor density \(n\) can be evaluated. Such a plot is shown in figure 4.8 where values of \((\frac{C_o}{C})^2 - 1\) between 1.0 and zero are plotted linearly against arbitrary values of negative voltage \(V\).

![Graph showing \((\frac{C_o}{C})^2 - 1\) versus voltage \(V\).]

Fig. 4.8. \((\frac{C_o}{C})^2 - 1\) versus arbitrary values of voltage \(V\).

The theoretical C-V characteristic can be plotted as shown in figure 4.9 where \(C_o/C\) has been calculated from the values of \((\frac{C_o}{C})^2 - 1\) at corresponding values of \(V\) in figure 4.8.

The C-V characteristic of a practical device differs from the theoretical curve in ways which are pointed out in the following section.
The variation of capacitance (C) with applied voltage (V) of a practical device is shown in figure 4.10 in which the three modes of operation are indicated.

**Fig. 4.9.** Theoretical C-V curve of MOS device.

**Fig. 4.10.** The practical C-V curve for a MOS device.
The constant capacitance in the accumulation region is that of the oxide \((C_o)\) which is assumed to be independent of frequency. The curve in the depletion region corresponds to that in figure 4-9, and in the inversion region to \(C_o C_D/(C_o + C_D)\), where \(C_D\), the capacitance of the depletion region, is constant at high frequencies.

A noticeable difference between the practical and theoretical curves is seen in the region of the flat band voltage (determined as in section (g) below) where, in the former, the device capacitance is less than that of the oxide. It is probable that this is due to surface states or to an increase in donor density at the semiconductor surface. This last phenomenon may be caused by the "snow-plough" effect whereby surface donors are pushed into the substrate by the growing oxide (74).

It should be noted that charge exchange can occur between the inversion and depletion regions at low frequencies. This reduces the depletion width causing the device capacitance to increase with increasing reverse bias towards the value of the oxide.

An inversion region will not form under high frequency pulse bias conditions owing to the long generation time of minority carriers (holes) and the device capacitance continues to decrease with bias until breakdown of the semiconductor occurs.

The above effects are shown by the broken lines in figure 4-10.

(f) Field induced hysteresis.

Charges within the oxide insulator affect the position of the flat band voltage. In the absence of any charges the device capacitance at high frequencies follows the curve in figure 4-10 when the voltage is cycled.
between a high positive potential and a high negative potential. But when positively charged ions or electron traps are present, the curve is shifted to the left or right respectively as shown in figure 4.l1.

![Diagram](image)

**Fig. 4.l1** Effect of ions and traps on C-V curve of n-type MOS device.

Positively charged ions are repelled to the interface by a positive potential on the metal electrode. These induce negative charges within the depletion region of the semiconductor. Consequently the depletion layer capacitance is increased. A negative bias has the opposite effect.

When electron traps are present in the oxide, a positive bias causes them to be filled by electrons transferred across the interface from the depletion region. A negative bias causes trapped electrons to be injected into the depletion region, thereby increasing its capacitance.

It follows from above that when a bias cycle is applied between positive and negative potentials the C-V curves of MOS devices may exhibit hysteresis induced by the negative applied field due to:

(a) mobile ions being neutralised, or
(b) electron traps being emptied.

Consequently the C-V hysteresis indicates which type of defect is present.
within an oxide.

There is no accepted method which can be used to compare the amount of hysteresis of MOS devices. However, a figure of merit for a device can be defined by:

\[ H = \left( \frac{\Delta V}{V_{FB}} \right) \times 100 \% \quad (20) \]

where \( \Delta V \) is the voltage shift of the C-V curve at constant capacitance as indicated in figure 4.11.

(g) Flat band voltage.

The value of the flat band voltage \( V_{FB} \) of a device is obtainable from the intercept with the voltage axis of the line of a plot of \( (C_0/C)^2 - 1 \) versus \( V \) where the device capacitance \( C \) is measured under depletion mode conditions (figure 4.8).

(h) Donor density \( n \).

Differentiation of equation (17) shows that:

\[ \frac{dV}{d} \left( (C_0/C)^2 - 1 \right) = n\text{se} / 2(C_0/A)^2 \quad (21) \]

Therefore, the density of donors \( n \) in the semiconductor is obtainable from the slope of the line in figure 4.8.
4.5.3. Device construction.

(a) Ohmic contacting.

Ohmic contacts were made to the surfaces with tin. However, before this was possible, the underside oxides had to be scraped away to expose the substrates. This was achieved by laying the samples face down on filter paper and using a scalpel.

After the debris had been removed with a methanol moistened spill, the samples were placed face down on a clean gallium arsenide slice resting on the hot plate of a small annealing furnace. Segments of tin wire were placed on the samples and the cover of the furnace replaced.

An inert $10^5$ Hz/N gas mixture was passed through the furnace, the heater switched on and the voltage raised slowly until the cover felt warm. At that point part of the gas flow was diverted through concentrated HCl to introduce acid vapour into the mixture to prevent the tin from oxidising. The voltage was increased further until, at $230^\circ$C, the tin melted into spherical globules. After one minute the power supply voltage was reduced to zero slowly and the acid vapour flow turned off. The samples were allowed to cool in the gas flow before being removed.

(b) Electrode deposition and area measurement.

The electrodes on the oxide of the devices are 1 mm diameter aluminium contacts deposited through masks in a standard Edwards evaporator. The vacuum pressure during this process was about $2 \times 10^{-6}$ torr.

Four such contacts, about 2000 $\AA$ thick, were made on each sample.
whenever possible. Their diameters \((d_1\) and \(d_2\)) were measured in two orthogonal directions by a travelling microscope and their areas \((A)\) were calculated from:

\[
A = \pi d_1 d_2 / 4
\]  

(1)

The edges of the circular contacts are not smooth, which in conjunction with the resolution of the measuring instrument, results in errors in the values of the diameters of about ± 5% and in area of about ± 7%.

(c) Base attachment.

The final stages in the fabrication process was the fixing of the contacted samples with silver dag onto metal bases. These were cut from thin duralloy sheeting and a hole was drilled into each to locate the tin contacts.

4.6. Electrical measurements.

4.6.1. Introduction.

Electrical measurements were made whilst the devices were held between the contacts of a spring loaded probe. Subsequent measurements gave values of the following parameters:

i. Breakdown field strength.

ii. Resistivity.

iii. Dielectric loss factor \((\tan \delta)\) at 1 MHz.

iv. Dielectric constant (relative permittivity) at 1 MHz.
v. Dielectric frequency dispersion.
vi. Flat band voltage
vii. Field induced hysteresis.
viii. Donor density.

Values of the above parameters were obtained from current-voltage, capacitance-frequency and capacitance-voltage measurements in association with thickness measurements from backscattering. The experimental methods and the calculations used to obtain these parameters are detailed below.

4.6.2. Current-voltage (I-V) measurements.

A Telequipment curve tracer (Type CT 71) was used to show that each device possessed MOS diode characteristics and had a forward breakdown voltage close to the voltage \( V_B \) at which a current of 50 \( \mu A \) flowed. Accurate values of voltage were measured with an error of \( \pm 0.5\% \) by a digital voltmeter connected across the diode and a current reading electrometer (Keithley Instruments Type 602).

The voltage \( V \), from a stabilised d.c. unit, was increased slowly and incrementally until the current \( I \) through the device was 50 \( \mu A \). Voltage and current readings were noted at each step, the current readings having an error of \( \pm 2\% \).

Two parameters of the oxides were calculated from the above measurements, - breakdown field strength and resistivity.

(a) Breakdown field strength \( E_B \).

Breakdown field strength is defined as breakdown voltage \( V_B \) per
unit thickness \((t)\) i.e.:

\[ E_B = \frac{V_B}{t} \]  

As mentioned above, \(V_B\) is specified as the forward voltage across the device when a current of 50 \(\mu A\) flows. This is not the actual breakdown voltage of the oxide. Several measurements showed that the current could be increased to about 100 \(\mu A\) before the oxides broke down and became short circuits. However, the voltages at which this occurred were less than 10\% greater than those when currents of 50 \(\mu A\) flowed. Consequently, the value of the voltage at this latter current was chosen in order to retain the diodes for further measurements.

The errors involved in the calculation of \(E_B\) are due mainly to the uncertainty in the value of oxide thickness \((t)\) – the error in the measurement of voltage \((V)\) being negligible. The mean value \((M)\) of the calibration factor (28.0 \(\text{\AA}\)) was used to convert thickness in terms of channel numbers \((N)\) to angstrom units \((\text{\AA})\). Consequently the error in the value of \(t\) is taken to be due solely to the error in \(N\). This method was adopted as relative values of thickness were required in most cases. Absolute values of thickness have an additional error given by the error \((\pm 6\%)\) of the calibration factor.

(b) Resistivity \((\rho)\)

The resistivities \((\rho)\) of the films were obtained by plotting the forward \(I-V\) characteristics of the devices and calculating the ohmic resistances \((dV/dI)\) from the slopes of the linear portions of the curves in the low current regions. A typical \(I-V\) curve depicting the linear ohmic
region is shown in figure 4.12.

\[ \frac{dV}{dI} \text{ was substituted in the formula:} \]

\[ \rho' = \frac{(dV/dI)A}{t} \quad (2) \]

where \( A \), the area of the electrode, was calculated from equation (1), section 4.5.3 and \( t \) is the oxide thickness as calculated in (a) above.

The errors associated with the calculated values of resistivity are due to that of the oxide thickness (\( t \)) (as detailed in (a) above) and to
inaccuracies in the measurement of contact area (A) (section 4.5.3(b)).
The error in $dV/dl$ is small, being about $\pm 2\%$.

4.6.3. Capacitance-frequency (C-f) measurements.

Measurements of oxide capacitance were made at zero d.c. bias over
a range of frequencies from 100 Hz to 1 MHz by using two sets of equipment
which, except where stated below, were manufactured by Wayne Kerr.

At frequencies below 1 MHz an a.f. bridge (Type B221) with an
external signal generator (Type S121) and a selective null detector (STC
type B601) were used. Measurements taken at 1 MHz were made on an r.f.
bridge (Type B601) to which a combined oscillator and detector unit (Type
SR268) was connected.

All measurements were made with a peak to peak a.c. signal of
300 mV.

The sensitivity of the bridge at 100 Hz made it difficult to obtain
capacitance readings with an error of less than $\pm 5\%$, but this figure
dropped to less than $\pm 1\%$ at the higher frequencies of 1 KHz to 1 MHz.

At 1 MHz resistance measurements were made simultaneously with those
of capacitance. The former have an error of about $\pm 5\%$ due to the difficulty
in reading accurately the logarithmic calibration dial of the bridge.
Frequency could be set to within $\pm 1\%$ of the required value.

Three parameters of the oxide films were obtained from these
measurements - the dielectric loss factor ($\tan \delta$) at 1 MHz, the dielectric
constant ($\epsilon_{1\text{MHz}}$) at 1 MHz and the frequency dispersion of capacitance.

(a) Dielectric loss factor (tan $\delta$) at 1 MHz.

The loss factors were calculated from:

$$\tan \delta = (2\pi fRC)^{-1}$$

(3)

where $f$ is the frequency (1 MHz) at which resistance ($R$) and capacitance ($C$) are measured and where $(2\pi fC)^{-1}$ is the impedance of the oxide capacitance.

The uncertainty in the values of tan $\delta$ are due only to the small errors involved in the measurement of capacitance ($\pm 1\%$), resistance ($\pm 5\%$) and the setting of the frequency ($\pm 1\%$). Calculations using equation (4) section 4.7 show that the error in tan $\delta$ is less than $\pm 5\%$.

(b) Dielectric constant ($\epsilon_{1\text{MHz}}$).

The dielectric constants at 1 MHz were calculated from:

$$\epsilon = \frac{Ct}{A\epsilon_0}$$

(4)

where $C$, $t$ and $A$ are the capacitance, oxide thickness and the area of the device respectively. $\epsilon_0$ is the permittivity of free space ($8.85 \times 10^{-14}$ F cm$^{-1}$).

The error in the calculated value of dielectric constant is due mainly to the errors involved in thickness ($t$) and area ($A$). These are larger than the error in the capacitance measurement which becomes negligible. These errors have been dealt with previously (e.g. section 4.6.2(b)).
(c) Frequency dispersion of capacitance.

The variation of oxide capacitance with frequency was shown by a simple plot of these two parameters.

In order to compare the relative merits of devices a value for frequency dispersion has been defined as the ratio of the capacitance at a low (L) and a high (H) frequency, i.e. $C_L/C_H$. Two such values were calculated for each oxide,

(a) the capacitance ratio at 100 Hz and 10 KHz

and

(b) the capacitance ratio at 10 KHz and 1 MHz.

The largest errors involved in the above capacitance ratios occur for those measured at low frequencies due to the ± 5% error in the value of capacitance measured at 100 Hz (section 4.6.3). At higher frequencies the error is ± 1%. Consequently, using equation (4) section 4.7, the error in case (a) is ± 5% and in case (b) it is ± 1.4%.

4.6.4. Capacitance-voltage (C-V) measurements.

The variation of the capacitance of each device was plotted automatically at 1 MHz by the equipment shown schematically in figure 4.13. The principle of the system is that the resistive component of the signal emanating from the bridge is suppressed whilst the capacitive component is given as a d.c. output which is proportional to capacitance. A setting up procedure is necessary to obtain this condition and that adopted in this investigation was as follows:

Before a device was connected a suitable capacitance was inserted by the bridge into the system and the 'phase sensitive detector' (p.s.d.)
set to zero. Variations were made alternately to the bridge resistance and the 'phase shifter' until the output of the p.s.d. was unaffected by any further changes in the resistance. The output of the p.s.d. was reset to zero, the bridge capacitance returned to zero and the p.s.d. gain adjusted to give full scale deflection on the output meter. Then the bridge capacitance was returned to its former value and the controls of the X-Y plotter were adjusted to give a calibrated output.

After the system had been set up, it was checked for linearity of output voltage with capacitance and then a device was inserted with the oxide electrode connected to the output of the power supply unit.

A voltage ramp of 0.1 V/sec. was applied across the device in the
forward direction and reversed when it reached the breakdown voltage. It was reversed again when the reverse breakdown voltage was reached, and returned to zero.

The C-V curves resulting from the above procedure were analysed as outlined in section 4.5.2 to obtain the flat band voltage, hysteresis and donor density of each device. The errors involved in the measurement of these parameters are as below.

(a) Flat band voltage $V_{FB}$.

The point at which the line cut the voltage axis to give the flat band voltage could be measured to within $\pm 0.1$ volt.

(b) Donor density ($n$).

It was possible to measure the slopes of the lines with an estimated error of less than $\pm 5\%$. $C_0$ and $A$ have measurement errors of $\pm 1\%$ and $\pm 7\%$ respectively which result in an error in the value of $(C_0/A)^2$ of $\pm 15\%$. Thus the error in the calculated values of $'n'$ is about $\pm 16\%$ (section 4.7).

(c) Hysteresis ($H$).

The voltage shift in the C-V curves, measured at the capacitance at the flat band voltage, was measured with an error of less than $\pm 0.2$ volt.

The direction of the voltage shift indicated the cause of the field induced hysteresis as shown in figure 4.11.
4.7. Measurement errors.

Reference has been made in previous sections to the errors in the measurements and in the values of parameters calculated from those measurements. The formulae used in calculating errors are given below. They have been taken from "Errors of observation and their treatment". (75).

(a) Mean value (M).

The arithmetic mean (M) of a set of N values (a, b, c, ..., n) is given by:

\[ M = \frac{a + b + c + ... + n}{N} \]  

\[ (1) \]

(b) Error (e).

The error (e) of each value in a set is given by:

\[ e = M - a, \text{ etc.} \]  

\[ (2) \]

(c) Standard deviation (\( \sigma \))

The standard deviation (\( \sigma \)) of a set of N values is given by:

\[ \sigma = \left( N^{-1} \sum \epsilon^2 \right)^{\frac{1}{2}} \]  

\[ (3) \]

(d) Mean error (\( e_m \))

The mean error (\( e_m \)) of a value \( V \) given by the sum, difference, quotient or product of N values a, b, c, ..., n, having respective errors \( \delta a, \delta b, \text{ etc.} \) is given by:

\[ e_m = \left( N^{-1} \sum \delta a^2 \right)^{\frac{1}{2}} \]  

\[ (4) \]
The error of the mean of a set of $N$ values each having a mean error $e_m$ is given by:

$$E_M = N^{-\frac{1}{2}} \left( N^{-1} \sum e_m^2 \right)^\frac{1}{2}$$  \hspace{1cm} (5)

In most cases an insufficient number of values of a parameter was measured for the standard deviation to have any meaning. For example, two identical values, each having a measurement error ($e$) of $\pm 10\%$, have a standard deviation ($\sigma$) of zero (equation (3) above). However, equation (5) shows that the mean ($M$) of the values has an error ($E_M$) given by:

$$E_M = 2^{-\frac{1}{2}} \left( 2^{-1} \cdot 2 \cdot 10^2 \right)^\frac{1}{2} \% = 7\%.$$ 

Therefore the errors given in plots of the results in the next chapter are the errors of the means ($E_M$) calculated from equation (5).

4.8. Summary.

This chapter has detailed the procedures which were used to form native oxides on gallium arsenide, the methods and equipment used to measure their properties and the theory behind the measurements.

The next chapter deals with the results and their analyses.
Chapter 5.

RESULTS

5.1. Introduction.

The following sections present the results of investigations into the properties of native oxides grown thermally on gallium arsenide.

Most of this work was concerned with the growth, composition and electrical properties of films grown between 350°C and 760°C on < 110 > orientated tellurium doped \( n \sim 1.2 \times 10^{17} \text{ cm}^{-3} \) samples of bulk material, but a number of experiments were performed in order to assess the effect of different types of material on oxide growth and composition. To this end (110) and (100) surfaces of zinc doped \( (p \sim 3.7 \times 10^{17} \text{ cm}^{-3}) \) bulk and (100) surfaces of \( n/n^+ (n \sim 2 \times 10^{15} \text{ cm}^{-3}) \) epitaxial material were included.

The first part of this chapter deals with the physical properties of oxides grown on all the types of material mentioned above. The electrical properties, which were measured only for films grown on (110) n-type bulk material, are given in the latter sections.

5.2. Rutherford backscattering analysis.

(a) Unoxidised gallium arsenide.

The random spectra obtained from calibration samples of unoxidised gallium arsenide are similar to that reproduced in figure 5.1 which shows the channel positions for surface gallium \( (N_{\text{Ga}}) \) at number 599 and for surface arsenic \( (N_{\text{As}}) \) at number 609.
Fig. 5.1 Typical RBS spectrum from gallium arsenide.
The curve is similar to that in figure 4.3, but the small width \((N_{As} - N_{Ga})\) is due to the small difference in the kinematic factors \(k^2\) of arsenic (0.819) and gallium (0.808) as given by equation (6) section 4.4.2. Also, the yields of arsenic \(Y_{As}\) and gallium \(Y_{Ga}\) are approximately the same due to the dependence of \(Y\) on the square of the atomic number \(Z\) (equation (3), section 4.4.2). \(Z_{As}\) (33) and \(Z_{Ga}\) (31) would indicate a difference of 12\% between the yields from arsenic and gallium.

(b) Oxides grown below 550\(^\circ\)C.

The backscattered spectra from oxides grown below 550\(^\circ\)C are similar to that shown in figure 5.2 which is the random spectrum from a sample oxidised for 2\(\frac{1}{4}\) hours at 510\(^\circ\)C. The front edge at channel number 599 corresponds to the backscattered yield from gallium atoms at the surface of the oxide (figure 5.1) and no yield can be detected at channel 609. Consequently no arsenic appears to be present at the surface of the film. This situation occurs in the spectra of all films grown below 550\(^\circ\)C.

The inset in figure 5.2 is that of the oxygen profile of the spectrum replotted as explained in section 4.4.5. The thickness of the oxide \((N_{o} - N_{a})\) is 38 channels wide, and the width of the 'tail' of the profile, which indicates a gradual decrease in oxygen concentration in the interface region \((N_{l} - N_{a})\), is 5 channels. Both widths have been determined as explained in section 4.4.5.

(c) Oxides grown above 550\(^\circ\)C.

The spectra from oxides grown above 550\(^\circ\)C are similar to those from films grown at lower temperatures, but, as indicated in figure 5.3, a small
Fig. 5.2 Typical RBS spectrum from gallium arsenide oxidised below 550°C.

Fig. 5.3 Typical RBS spectrum from gallium arsenide oxidised above 550°C.
yield \( (Y_{AS}) \) from surface arsenic atoms occurs at channel 609.

5.3. Physical properties of oxides grown for \( 1\frac{1}{2} \) hours between 350°C and 760°C.

5.3.1. Oxidation rate between 350°C and 760°C.

No films were detected on samples oxidised at 350°C, neither visually nor by Rutherford backscattering, and, consequently, if any films were present they were too thin to be analysed by backscattering. The limit of detection is about 5 channels of the spectrum and, therefore, from the calibration factor of 28.0 Å per channel (table 4.1), the films are estimated to have been less than about 150 Å thick.

The thicknesses of films grown for \( 1\frac{1}{2} \) hours between 465°C and 760°C are given in table 5.1 which lists the values measured for n and p-type samples having (110) and (100) orientations. No differences can be seen between the oxidation rates of n and p-type material, or between those of (100) bulk and (100) epitaxial samples.

Because of the above observations it is considered justified to plot the mean value and error of the thicknesses of oxides grown at each temperature on surfaces having the same orientation. These values are plotted in figures 5.4 and 5.5 for oxides on (110) and (100) surfaces respectively. Best fit curves have been drawn through the points.

The outstanding features of figures 5.4 and 5.5 are the shapes of the curves and the difference between them. Both sets of results show that the oxidation rate increased with increasing temperature up to a limiting temperature and then decreased to a minimum before it increased again.
<table>
<thead>
<tr>
<th>T °C</th>
<th>655</th>
<th>665</th>
<th>675</th>
<th>685</th>
<th>695</th>
<th>705</th>
<th>715</th>
<th>725</th>
<th>735</th>
<th>745</th>
<th>755</th>
<th>765</th>
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</thead>
<tbody>
<tr>
<td>10⁻³/°</td>
<td>1.255</td>
<td>1.255</td>
<td>1.255</td>
<td>1.253</td>
<td>1.215</td>
<td>1.180</td>
<td>1.132</td>
<td>1.095</td>
<td>1.055</td>
<td>1.020</td>
<td>0.978</td>
<td>0.968</td>
</tr>
<tr>
<td>n</td>
<td>10 ± 3</td>
<td>23 ± 3</td>
<td>31 ± 3</td>
<td>34 ± 3</td>
<td>36 ± 3.6</td>
<td>110 ± 11</td>
<td>-</td>
<td>38 ± 8.5</td>
<td>70 ± 7</td>
<td>65 ± 6.5</td>
<td>32 ± 3</td>
<td>41 ± 4</td>
</tr>
<tr>
<td>p</td>
<td>9 ± 3</td>
<td>21 ± 3</td>
<td>32 ± 3</td>
<td>-</td>
<td>42 ± 4</td>
<td>95 ± 9.2</td>
<td>85 ± 8.5</td>
<td>-</td>
<td>62 ± 6</td>
<td>-</td>
<td>34 ± 3.4</td>
<td>25 ± 3</td>
</tr>
<tr>
<td>σ</td>
<td>0.5</td>
<td>1.0</td>
<td>1.25</td>
<td>-</td>
<td>3.0</td>
<td>10.3</td>
<td>-</td>
<td>16.0</td>
<td>-</td>
<td>3.5</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>(b)</td>
<td>9.5</td>
<td>± 2.1</td>
<td>22</td>
<td>± 2.1</td>
<td>± 1.6</td>
<td>-</td>
<td>39</td>
<td>± 2.7</td>
<td>96.7</td>
<td>± 5.6</td>
<td>-</td>
<td>67.4</td>
</tr>
<tr>
<td>q</td>
<td>270</td>
<td>± 80</td>
<td>620</td>
<td>± 60</td>
<td>± 50</td>
<td>-</td>
<td>110 ± 75</td>
<td>2730</td>
<td>-</td>
<td>1900</td>
<td>± 85</td>
<td>± 85</td>
</tr>
<tr>
<td>Mean</td>
<td>12 ± 3</td>
<td>19 ± 3</td>
<td>± 6 ± 4.5</td>
<td>39 ± 3</td>
<td>11 ± 3</td>
<td>-</td>
<td>10 ± 3</td>
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<td>20 ± 3</td>
<td>24 ± 3</td>
<td>18 ± 3</td>
<td>55 ± 5.5</td>
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<tr>
<td>p</td>
<td>11 ± 3</td>
<td>25 ± 3</td>
<td>75 ± 3.5</td>
<td>32 ± 3</td>
<td>27 ± 3</td>
<td>-</td>
<td>20 ± 3</td>
<td>22 ± 3</td>
<td>12 ± 3</td>
<td>26 ± 3</td>
<td>21 ± 3</td>
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<td>5.0</td>
<td>-</td>
<td>3.0</td>
<td>4.5</td>
<td>-</td>
<td>5.0</td>
<td>1.0</td>
<td>3.0</td>
<td>1.0</td>
<td>3.0</td>
</tr>
<tr>
<td>(c)</td>
<td>11.5</td>
<td>± 2.1</td>
<td>22</td>
<td>± 2.1</td>
<td>± 2.1</td>
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<td>25</td>
</tr>
<tr>
<td>q</td>
<td>270</td>
<td>± 80</td>
<td>620</td>
<td>± 60</td>
<td>± 50</td>
<td>-</td>
<td>110 ± 75</td>
<td>2730</td>
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<td>± 6 ± 4.5</td>
<td>39 ± 3</td>
<td>11 ± 3</td>
<td>-</td>
<td>10 ± 3</td>
<td>20 ± 3</td>
<td>20 ± 3</td>
<td>24 ± 3</td>
<td>18 ± 3</td>
<td>55 ± 5.5</td>
</tr>
</tbody>
</table>

| (H)    | 1.2 | 2.2 | - | - | - | - | - | - | - | - | - | - |
| Mean   | 15.5 | 22 | ± 1.5 | ± 1.5 | - | - | - | - | - | - | - | - |
|          | 300 | 620 | ± 40 | ± 40 | - | - | - | - | - | - | - | - |

**TABLE 5.1.** Oxide thickness of films grown for 1½ hours between 65° and 765° C.
Fig. 5.4  Thickness - temperature characteristic of films grown for $1\frac{1}{2}$ hours on (110) surfaces of GaAs.
Fig. 5.5 Thickness - temperature characteristic of films grown for 1½ hours on (100) surfaces of GaAs.
Furthermore, up to a growth temperature of about 510°C and above about 700°C it appears that no differences were measured which can be attributed to surface orientation. (This point is seen, also, in table 5.1 where the mean values of oxide thicknesses on (100) and (110) surfaces agree within the limits of their errors). However between these temperatures the effect of surface orientation was considerable. Whereas the rate of growth of the oxides on (100) surfaces reached a maximum at about 515°C and thereafter decreased rapidly to a minimum at about 525°C, that of (100) surfaces reached a maximum at about 550°C and then decreased slowly to a minimum at about 700°C.

5.3.2. Activation energy.

Further analysis of the data in figures 5.4 and 5.5 has been carried out by plotting in figure 5.6 the mean values and errors (table 5.1) on an Arrhenius diagram of oxide thickness against reciprocal growth temperature. The thicknesses were converted to angstrom units by the factor of 28.0 Å per channel (table 4.1). The results plotted at 465°C, 505°C and 750°C are the mean values for n and p-type (100) and (110) material (table 5.1). The justification for this procedure is given in the above section. For temperatures between 510°C and 710°C inclusive the mean values for (110) and (100) surfaces are plotted separately. Included on the diagram are results obtained by Navratil and Murarka.

The results for (110) surfaces oxidised at temperatures up to 550°C and for (100) surfaces oxidised at temperatures up to 510°C are seen to agree closely with the data of Navratil and Murarka. The method of least squares has been used to fit a line to the results and from it an activation energy of $1.25 \pm 0.15$ eV has been calculated for oxide growth in the above temperature ranges. This is close to the value of $1.0 \pm 0.07$ eV which
Fig. 5.6. Thickness - temperature characteristic of oxides grown on GaAs for 1½ hours.
Navratil obtained for films growing parabolically with time on (111) surfaces between 400°C and 450°C. Therefore it is probable that the films grew in accordance with a parabolic law. Results for isothermal growth at 510°C on (110) surfaces, which are dealt with in section 5.4.1, appear to support this.

Outside the above temperature ranges the growth mechanism obeys a different law. However the spread in the results does not allow precise values of activation energies to be calculated or possible growth mechanisms to be deduced.

The activation energies associated with the regions where increasing temperature reduces the growth rate of oxides are 0.83 ± 0.32 eV and 3.6 ± 1.8 eV respectively for (110) surfaces (between about 575°C and 700°C) and (100) surfaces (between about 510°C and 525°C). A later discussion in section 6.3.2 suggests the possibility that several factors such as oxide evaporation and structural changes are involved which may account for the reduction in film thickness with increasing growth temperature.

The slow increase with increasing temperature of the growth rates of oxides on (100) surfaces between about 525°C and 700°C results in a value of 0.17 ± 0.15 eV for the activation energy.

Oxide growth at temperatures above about 700°C appears to be independent of surface orientation and is seen to increase with increasing temperature. The activation energy is 1.7 ± 0.8 eV. Navratil measured 2.2 ± 0.1 eV for the activation energy for linear growth between 480°C and 530°C. Consequently the value 1.7 ± 0.8 eV is consistent with such a growth mechanism. However, as the structures and compositions of films on gallium arsenide are different when grown at high and low temperatures,
the activation energies associated with a particular growth mechanism may be different over different temperature ranges. Therefore it is not possible to deduce the likely mechanism involved in the oxidation for 1½ hours of samples above 700°C.

The activation energies and the temperature ranges over which they apply are summarised in table 5.2 below.

Table 5.2. Activation energies of oxides grown for 1½ hours on GaAs.

<table>
<thead>
<tr>
<th>Approximate temperature (°C)</th>
<th>Activation energy (eV)</th>
<th>Surface orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>450 - 510</td>
<td>1.25 ± 0.15</td>
<td>1.25 ± 0.15</td>
</tr>
<tr>
<td>510 - 525</td>
<td>1.25 ± 0.15</td>
<td>-3.6 ± 1.8</td>
</tr>
<tr>
<td>525 - 550</td>
<td>1.25 ± 0.15</td>
<td>0.17 ± 0.15</td>
</tr>
<tr>
<td>550 - 700</td>
<td>-0.83 ± 0.32</td>
<td>0.17 ± 0.15</td>
</tr>
<tr>
<td>700 - 760</td>
<td>1.7 ± 0.8</td>
<td>1.7 ± 0.8</td>
</tr>
</tbody>
</table>

5.3.3 Variation of oxide composition with growth temperature.

The backscattered spectra show that the surfaces of films grown below about 575°C were composed of gallium and oxygen (figure 5.2) whilst those grown at higher temperatures appear to contain small quantities of arsenic (figure 5.3) in addition to gallium and oxygen.
The ratios of the backscattered yields from surface oxygen and gallium \( \frac{Y_O}{Y_{Ga}} \) are listed in table 5.3. Similar ratios from arsenic and gallium \( \frac{Y_{As}}{Y_{Ga}} \) are listed in table 5.4.

The mean values and errors of the above ratios have been corrected to give the ratios of the numbers of atoms \( \frac{N_O}{N_{Ga}} \) and \( \frac{N_{As}}{N_{Ga}} \) respectively) by using equation (16) section 4.4.2. This gives 13.4 and 0.87 for the multiplication factors involved.

(a) Oxygen to gallium ratio (Table 5.3).

By comparing the values of \( \frac{Y_O}{Y_{Ga}} \) for oxides on (110) surfaces of n and p-type samples it is seen that, generally, the values for each temperature agree within the limits defined by the errors. Only in two cases is this not so - at 505°C and 610°C. However the disagreement at 505°C is small and may be due to one or other of the results having an error greater than ±11%. The worst case error is the sum of the errors in the measurements of \( Y_O \) (±10%) and \( Y_{Ga} \) (±5%), i.e. ±15%, (section 4.4.5) and the two results at 505°C agree to within this figure.

The maximum and minimum results for \( \frac{Y_O}{Y_{Ga}} \) measured for n-type (110) samples oxidised at 610°C are not consistent unless the maximum value has an error of ±14%. Although this is possible (for the reason given above) there is disagreement still between it and the result for the p-type sample. In fact, the latter agrees only with the lowest value measured on n-type samples. This could be due to a difference in the oxygen content of films on n and p-type material, but this is not confirmed by the results for films grown at higher temperatures.

The results for films grown on (100) surfaces of n and p-type samples
<table>
<thead>
<tr>
<th>Oxidation temperature (°C)</th>
<th>455</th>
<th>505</th>
<th>510</th>
<th>518</th>
<th>525</th>
<th>550</th>
<th>575</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>4.0 ± 0.4</td>
<td>11.0 ± 1.2</td>
<td>12.3 ± 1.4</td>
<td>-</td>
<td>9.0 ± 1.0</td>
<td>12.3 ± 1.4</td>
<td>-</td>
</tr>
<tr>
<td>p</td>
<td>4.7 ± 0.5</td>
<td>8.3 ± 0.9</td>
<td>12.3 ± 1.4</td>
<td>-</td>
<td>9.3 ± 1.0</td>
<td>11.0 ± 1.2</td>
<td>-</td>
</tr>
<tr>
<td>n</td>
<td>7.3 ± 0.8</td>
<td>10.7 ± 1.2</td>
<td>11.0 ± 1.2</td>
<td>10.3 ± 1.1</td>
<td>4.7 ± 0.5</td>
<td>-</td>
<td>11.0 ± 1.2</td>
</tr>
<tr>
<td>p</td>
<td>6.0 ± 0.7</td>
<td>10.0 ± 1.1</td>
<td>11.3 ± 1.3</td>
<td>10.7 ± 1.2</td>
<td>11.7 ± 1.3</td>
<td>-</td>
<td>10.7 ± 1.2</td>
</tr>
<tr>
<td>100xMean Y_o/Y_Ga</td>
<td>5.5 ± 0.3</td>
<td>10.0 ± 0.6</td>
<td>11.7 ± 0.7</td>
<td>10.5 ± 0.8</td>
<td>8.7 ± 0.5</td>
<td>11.7 ± 0.9</td>
<td>10.9 ± 0.8</td>
</tr>
<tr>
<td>100xMean N_o/N_Ga</td>
<td>7.4 ± 0.4</td>
<td>13.4 ± 0.7</td>
<td>15.7 ± 0.9</td>
<td>14.0 ± 1.1</td>
<td>11.6 ± 0.7</td>
<td>15.7 ± 1.2</td>
<td>14.6 ± 1.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oxidation temperature (°C)</th>
<th>610</th>
<th>640</th>
<th>675</th>
<th>710</th>
<th>750</th>
<th>760</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>15.0 ± 1.7</td>
<td>13.0 ± 1.5</td>
<td>12.0 ± 1.3</td>
<td>11.6 ± 1.3</td>
<td>13.0 ± 1.5</td>
<td>13.7 ± 1.5</td>
</tr>
<tr>
<td>p</td>
<td>9.3 ± 1.0</td>
<td>-</td>
<td>11.0 ± 1.2</td>
<td>14.0 ± 1.6</td>
<td>14.7 ± 1.6</td>
<td>-</td>
</tr>
<tr>
<td>n</td>
<td>11.7 ± 1.2</td>
<td>12.0 ± 1.3</td>
<td>12.0 ± 1.3</td>
<td>15.0 ± 1.5</td>
<td>16.0 ± 1.8</td>
<td>-</td>
</tr>
<tr>
<td>p</td>
<td>9.3 ± 1.0</td>
<td>13.7 ± 1.5</td>
<td>11.0 ± 1.2</td>
<td>13.0 ± 1.5</td>
<td>14.3 ± 1.6</td>
<td>-</td>
</tr>
<tr>
<td>100xMean Y_o/Y_Ga</td>
<td>11.7 ± 0.5</td>
<td>13.0 ± 0.8</td>
<td>11.3 ± 0.6</td>
<td>13.4 ± 0.7</td>
<td>14.9 ± 1.0</td>
<td>15.0 ± 1.7</td>
</tr>
<tr>
<td>100xMean N_o/N_Ga</td>
<td>15.7 ± 0.7</td>
<td>17.4 ± 1.1</td>
<td>15.2 ± 0.8</td>
<td>17.9 ± 1.0</td>
<td>19.9 ± 1.3</td>
<td>20.0 ± 2.3</td>
</tr>
</tbody>
</table>

\[ Y = \text{backscatter yield.} \quad N = \text{no. atoms.} \]

**Table 5.3.** Oxygen to gallium ratios at surfaces of films grown for 1.5 hours on gallium arsenide.
<table>
<thead>
<tr>
<th>Oxidation temperature (°C)</th>
<th>575</th>
<th>610</th>
<th>640</th>
<th>675</th>
<th>710</th>
<th>750</th>
<th>760</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110) surfaces n %</td>
<td>5.0 ± 1.0</td>
<td>11.7 ± 2.4</td>
<td>13.4 ± 2.7</td>
<td>15.7 ± 3.1</td>
<td>16.5 ± 3.4</td>
<td>9.2 ± 1.9</td>
<td>2.6 ± 0.5</td>
</tr>
<tr>
<td>p</td>
<td>4.7 ± 0.9</td>
<td>19.4 ± 4.0</td>
<td>-</td>
<td>8.8 ± 1.8</td>
<td>2.6 ± 0.5</td>
<td>6.3 ± 1.3</td>
<td>-</td>
</tr>
<tr>
<td>Mean n &amp; p %</td>
<td>4.8 ± 0.7</td>
<td>15.5 ± 1.5</td>
<td>16.5 ± 3.4</td>
<td>9.0 ± 1.3</td>
<td>2.6 ± 0.4</td>
<td>6.3 ± 1.3</td>
<td>15.0 ± 3.1</td>
</tr>
<tr>
<td>(100) surfaces n %</td>
<td>6.3 ± 1.3</td>
<td>9.7 ± 2.0</td>
<td>12.3 ± 2.5</td>
<td>2.5 ± 0.5</td>
<td>4.2 ± 0.9</td>
<td>7.2 ± 1.5</td>
<td>-</td>
</tr>
<tr>
<td>p</td>
<td>5.5 ± 1.1</td>
<td>11.2 ± 2.3</td>
<td>6.5 ± 1.4</td>
<td>2.8 ± 0.6</td>
<td>3.2 ± 0.7</td>
<td>6.8 ± 1.4</td>
<td>-</td>
</tr>
<tr>
<td>Mean n &amp; p %</td>
<td>6.0 ± 0.9</td>
<td>10.5 ± 1.5</td>
<td>9.5 ± 1.5</td>
<td>2.5 ± 0.5</td>
<td>3.5 ± 0.5</td>
<td>7.0 ± 1.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5.4. Arseneic - Gallium ratios at surfaces of oxides grown for 11/2 hours on GaAs.
show complete agreement except for films grown at 525°C. In this case the maximum value of $Y_0/Y_{Ga}$ for the n-type sample is half that of the p-type sample. Moreover, it disagrees substantially with all other results for (100) surfaces and appears to be an anomaly. However, it is a thin film comparable to those grown at 465°C (figure 5.5) and may be discontinuous.

It is apparent from the above analysis of the results that there is no evidence which suggests that the oxygen to gallium ratio of the oxides is influenced by the type of doping of the semiconductor. A similar comparison of the results for films grown on (110) and (100) surfaces suggests, also, that surface orientation has no effect. However, there is a discrepancy in the results for oxides grown at 465°C and 525°C on n-type samples. Films grown at the latter temperature have an anomalously low value of 0.047, as pointed out above, whilst the differences in the results for the films grown at 465°C may be due also to the films being discontinuous.

In view of the fact that the results show no measurable differences in the values of $Y_0/Y_{Ga}$ for films grown at a particular temperature, the atom ratios ($N_0/N_{Ga}$) have been calculated from the mean values of $Y_0/Y_{Ga}$ and plotted in figure 5.7.

The curve in figure 5.7 is the best fit through the points and shows the variation of the oxygen to gallium ratios with temperature.

The result for 525°C has been regarded as anomalous and has been neglected. Its low value is accounted for partly by the result for the film grown on the n-type sample, but the results for films on (110) surfaces are low also - by about 22%. This is outside the limits of experimental error and cannot be explained.
Fig. 5.7: Variation with temperature of oxygen to gallium ratio at surfaces of oxides grown for 1½ hours on GaAs.
It is seen from figure 5.7 that the ratio of oxygen to gallium at the surfaces of oxides grown at temperatures between about 505°C and 675°C is 1.3 ± 0.1. This indicates that the films are substantially Ga₂O₃ although as is shown in figure 5.8, those grown at 575°C and above contain small quantities of arsenic. But when grown below 505°C and above 675°C the films have a deficit and an excess, respectively, of oxygen. The low amount of oxygen may be due to surface films of Ga₂O₃ being discontinuous or, alternatively, to the formation of Ga₂O in addition to Ga₂O₃. The excess oxygen in films grown above about 675°C may be associated with the occurrence of grain growth and trapping of oxygen in grain boundaries.

(b) Arsenic to gallium ratio (Table 5.4).

The proportion of arsenic measured as a percentage of the gallium at the film surface is listed in table 5.4.

It is seen for both (110) and (100) surfaces that, generally, no differences were measured between the arsenic content of oxides grown on n and p-type material. Exceptions to this generality are the measurements for films grown at 610°C on (110) surfaces and at 640°C on (100) surfaces. However, the former are consistent when the maximum possible measurement error of ±25% is taken into account, but the disagreement in the values for films grown on (100) surfaces at 640°C cannot be explained in the same way. It is probable in this case the difference is due to slight variations in the orientations of the surfaces - it being noted from the results for oxides grown at 610°C and 675°C that the arsenic content of films varies significantly with surface orientation when oxidation takes place at elevated temperatures.

No differences in the arsenic to gallium ratios which can be
attributed to surface orientation can be seen for films grown at \(575^\circ C\), \(710^\circ C\) and \(750^\circ C\).

The mean values of the ratios of arsenic to gallium atoms at the surfaces of the films are plotted in figure 5.8. It shows that the quantity of arsenic in films grown between \(575^\circ C\) and about \(700^\circ C\) on (110) surfaces appears to be up to approximately 50% greater than that in films grown on (100) surfaces at the same temperature. The arsenic content reaches a maximum within the above temperature range at about \(625^\circ C\) and increases, also, with increasing temperature from a minimum at about \(700^\circ C\).

The different behaviour of arsenic in films grown on (110) and (100) surfaces may be due to the formation of different polymorphs of \(Ga_2O_3\) as discussed later in section 6.2.

5.3.4. The interface regions between substrates and oxides.

Estimates of the widths \((\bar{\alpha}_1-N_a)\) of the interface regions, as indicated by the tails in the oxygen spectra (figure 4.6), are given as ratios of the thicknesses of the oxides in table 5.5. This ratio should be zero for ideal substrate-oxide interfaces.

Within the accuracy determined by the large experimental errors, no differences were measured between films grown at temperatures up to \(510^\circ C\). However, the interface ratios for films on (100) surfaces are approximately twice those for films on (110) surfaces when oxides are grown at higher temperatures up to about \(750^\circ C\). No effects were measured which can be explained by differences in the type of dopant in the material.

The mean values of the results are plotted in figure 5.9. The curves
Fig. 5.8 Arsenic to gallium ratio at surfaces of films grown for 1½ hours on GaAs.
<table>
<thead>
<tr>
<th>Oxidation temp. (°C)</th>
<th>465</th>
<th>505</th>
<th>510</th>
<th>518</th>
<th>525</th>
<th>550</th>
<th>575</th>
<th>610</th>
<th>642</th>
<th>675</th>
<th>712</th>
<th>750</th>
<th>760</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110) n surfaces</td>
<td>55.0</td>
<td>25.0</td>
<td>9.0</td>
<td></td>
<td>14.0</td>
<td>10.0</td>
<td></td>
<td>11.0</td>
<td>10.0</td>
<td>9.5</td>
<td>9.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>37.5</td>
<td>24.5</td>
<td>14.0</td>
<td></td>
<td>16.0</td>
<td>7.0</td>
<td></td>
<td>7.0</td>
<td></td>
<td>12.5</td>
<td>18.0</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>Mean (110) surfaces</td>
<td>46.25</td>
<td>25.0</td>
<td>11.0</td>
<td></td>
<td>15.0</td>
<td>8.0</td>
<td></td>
<td>9.5</td>
<td></td>
<td>13.0</td>
<td>12.0</td>
<td>15.0</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>± 8.0</td>
<td>± 4.0</td>
<td>± 2.0</td>
<td></td>
<td>± 2.5</td>
<td>± 1.5</td>
<td></td>
<td>± 1.5</td>
<td>± 3.0</td>
<td>± 2.0</td>
<td>± 2.5</td>
<td>± 2.5</td>
<td>± 4.0</td>
</tr>
<tr>
<td>(100) n surfaces</td>
<td>52.0</td>
<td>34.0</td>
<td>16.0</td>
<td>20.0</td>
<td>25.0</td>
<td></td>
<td>22.0</td>
<td>20.0</td>
<td>26.0</td>
<td>23.0</td>
<td>25.0</td>
<td>13.0</td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>32.0</td>
<td>29.0</td>
<td>8.5</td>
<td>24.0</td>
<td>16.0</td>
<td></td>
<td>26.0</td>
<td>25.0</td>
<td>28.5</td>
<td>17.0</td>
<td>23.0</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>Mean (100) surfaces</td>
<td>42.0</td>
<td>32.0</td>
<td>12.0</td>
<td>22.0</td>
<td>21.0</td>
<td></td>
<td>24.0</td>
<td>23.0</td>
<td>27.0</td>
<td>20.0</td>
<td>24.0</td>
<td>13.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>± 7.0</td>
<td>± 5.0</td>
<td>± 2.0</td>
<td>± 4.0</td>
<td>± 4.0</td>
<td></td>
<td>± 4.0</td>
<td>± 5.0</td>
<td>± 4.0</td>
<td>± 4.0</td>
<td>± 2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean (110) &amp; (110)</td>
<td>44.0</td>
<td>28.0</td>
<td>12.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>± 5.5</td>
<td>± 3.5</td>
<td>± 1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.5. Interface widths as percentages of oxide thicknesses of films grown for 1.5 hours on gallium arsenide.
Fig. 5.9  Interface width as a percentage of oxide thickness of films grown for $1\frac{1}{2}$ hours on GaAs.
through the points are those considered to be the best fit, although it may
appear that other curves are possible - particularly through the (100)
points. However, the similarity between figure 5.9 and figure 5.6 suggests
that the dips in the (100) curve of figure 5.9 at about 525°C and 750°C are
significant. Furthermore, the curves appear to show that the interfaces of
films thicker than about 700 Å are approximately a constant percentage
(10%) of oxide thickness and, also, are independent of growth temperature.
However, the relative widths of the interfaces of thinner films appear to
increase as oxide thickness decreases. Again, this seems to be independent
of growth temperature.

5.4. Physical properties of oxides grown at 510°C on n-type (100) bulk
material.

5.4.1. Oxidation rate at 510°C.

The widths of the oxygen profiles (N) in the spectra (figure 5.2)
obtained by Rutherford backscattering from oxide films grown for a time
(t) at 510°C are given in figure 5.10.

Seven of the points can be related by a straight line as shown, but
the results for films grown for 1.5 and 2.5 hours are anomalous. The latter
points appear to be related to each other by a line parallel to that linking
the former results which suggests that, although the growth mechanism of all
the films may have been the same, the films grown for 1.5 and 2.5 hours may
have done so at a higher temperature. However, extrapolation of the upper
line in figure 5.10 indicates that 1.5 hours growth would result in a film
of thickness equivalent to 51 channels, i.e. about 1450 Å. To grow such a
film in 1.5 hours requires a temperature of about 535°C (figure 5.6). This
is 20°C greater than the maximum temperature at which growth is believed
Fig. 5.10 Thickness-time characteristic of oxides grown on n-type (110) GaAs at 510°C.
to have occurred and, consequently, some factor other than temperature appears to have been responsible for the enhanced growth rate.

In addition to temperature, surface orientation and surface damage can affect the rate of oxidation. Therefore it may be that the surfaces of the two samples which oxidised at an enhanced rate were orientated at a small angle to the <110> direction or, alternatively, were not free of damage.

Although the lower straight line in figure 5.10 suggests that the oxides grew linearly with time, its extrapolation below a thickness of 10 channels indicates that growth commenced at 510°C about 1 hour before the samples entered the hot zone of the furnace. This is a physical impossibility as growth must have commenced only when the temperature was at least 450°C and, therefore, just a few minutes prior to the samples reaching the hot zone. Consequently, it is unlikely that the oxides grown for short periods obeyed the linear growth law. Moreover, a least squares fit of the data gives coefficients of determination of 0.98 and 1.00 for a linear law and parabolic law respectively. Therefore, the parabolic curve in figure 5.10 appears to fit the results better than the straight line. Furthermore, a plot of $N^2$ versus $t$ (figure 5.11) shows that the results are consistent with the parabolic growth law mechanism for times up to 3 hours and that growth started approximately five minutes before the samples reached the hot zone of the furnace.

5.4.2. Composition.

In common with films grown below 575°C for 1½ hours (section 5.3.3), no arsenic was detected by backscattering at the surfaces of films grown for up to 3 hours at 510°C.

The ratio of oxygen to gallium atoms at the surfaces of the oxides are plotted in figure 5.12 and the best fit line drawn through the points.
Fig. 5.11 Plot of thickness$^2$ vs time for oxides grown on n-type (110) GaAs at 510°C.
The ratios were calculated from the backscattered yields in the same way as those for films grown for 1\frac{1}{2} hours.

Figure 5.12 shows that only films of thickness equivalent to about 25 to 45 channels (i.e. 700Å to 1250Å) are stoichiometric Ga₂O₃. Thinner films appear to be deficient in oxygen whilst thicker films appear to contain an excess.

The curve in figure 5.12 is similar to that in figure 5.7 which shows that films grown for 1\frac{1}{2} hours at temperatures below 510°C are deficient in

Fig. 5.12  Variation with thickness of oxygen to gallium ratio at surfaces of oxides grown on n-type (110) GaAs at 510°C.
Consequently the results for both sets of measurements taken on thin films are in agreement and, therefore, the reasons advanced in section 5.3.3(a) for the oxygen deficit, i.e. discontinuous oxides or Ga₂O₃, may apply also to the results for thin films grown for up to $\frac{3}{2}$ hour at 510°C.

The explanation given in section 5.3.3(a) for the excess of oxygen in films grown above about 600°C - i.e. that oxygen is trapped in grain boundaries - may be valid also for films grown at 510°C. However, an alternative explanation is that oxygen is held in cracks which develop when films become a certain thickness, as suggested in section 6.3.5. It is noticeable that those films which possess excess oxygen are thicker than about 45 channels (approximately 1250Å). Two of these films grew at an enhanced rate but the third film (which is 47 channels thick) appears not to have done so. However, when the maximum measurement error of ±15% is taken into account, the result for the latter film indicates that the excess of oxygen may be small and insufficient to induce excessive growth.

5.4.3. The interface regions between substrates and oxides.

The widths of the interface regions ($W_1 - W_a$) of films grown at 510°C are relatively large compared to the thicknesses ($N$) of the films. The results have errors which are too large to allow the variation of interface width with film thickness to be determined, but, as plotted in figure 5.13 as a percentage of film thickness, they show a reduction from more than about 30% when films are thin (15 channels) to less than about 10% when films are thick (greater than 40 channels). This suggests that whilst the interfaces may not remain constant, they did not increase at the same rate as the thicknesses of the films.
Fig. 5.13 Interface width as a percentage of oxide thickness of films grown on n-type (110) GaAs at 510°C.
5.5. Miscellaneous properties of oxide films.

5.5.1. Appearance.

The majority of the films appear uniformly coloured in daylight, although several look patchy - particularly those which have a reddish coloration.

When viewed under a microscope the thinnest films appear to contain discontinuous dark and light brown patchy areas whilst thicker films grown below 550°C have an appearance described best as resembling a flat surface of well mixed two coloured sand. The surfaces of films grown at higher temperatures are not as uniform and seem to consist of discontinuous areas surrounding multicoloured circular ring patterns.

The patchy areas of the thin films supports the idea that parts of the substrate surfaces may be unoxidised or that parts of the oxides contain Ga₂O (section 5.3.3).

The ring patterns in films grown above 550°C coincide with the appearance of arsenic at their surfaces (figure 5.8) and this suggests that the arsenic is not distributed uniformly.

5.5.2. Smoothness.

The talystep traces from several samples, made after portions of their oxides had been removed, show that the surfaces of the films are comparatively smooth whilst the interfaces are rough.

A typical result (from a sample oxidised for 3 hours at 510°C) is
Fig. 5.14 Talystep trace of oxide and interface region of GaAs oxidised for 3 hours at 510°C.
given in figure 5.14. It shows less than 100 Å peak to peak variation across the oxide surface and 600 Å peak to peak across the interface. The large variation at the oxide surface near the step of the trace is believed to be caused by acid creeping beneath the protective layer of wax.

5.5.3. Adhesion and solubility.

All films adhered well to the substrates and none showed signs of flaking. They could be removed with warm concentrated HCl fairly rapidly, but it took 30 minutes for cold acid to remove a film grown to about 1100 Å at 510°C. Most of the oxide was removed within the first two minutes, but the remaining 500 Å dissolved slowly.

5.6. Electrical properties of oxides grown on (110) n-type material.

5.6.1. Introduction.

The electrical parameters obtained from MOS devices fabricated from oxidised samples of (110) n-type gallium arsenide are given below.

There are two sets of results for each parameter. One set is for oxides grown at 510°C and the other is for films grown at various temperatures for 1½ hours. In the latter case more than one oxide was grown at each temperature and used for constructing devices. Measurements were made on up to four capacitors on each device. These measurements have been tabulated and their mean values and errors, calculated as in section 4.7, plotted.

Measurements on devices having oxides grown at 510°C were made only
on those capacitors having the highest breakdown field strength per device. These results are plotted directly.

The two sets of data carry the same figure number but they are distinguished by letters (a) and (b) for films grown at 510°C and for films grown for 1½ hours respectively. Best fit curves have been drawn through the points.

5.6.2. Electrical results.

(1). Breakdown field strength \( E_b \).

The results of calculations of the breakdown field strength \( E_b \) (section 4.6.2a) are given in figures 5.15(a) and 5.15(b).

Figure 5.15(a) shows the variation with film thickness of the highest values measured on each device having oxides grown at 510°C.

Large variations in breakdown field strength were recorded for films thinner than about 30 channels (850Å) in thickness, whilst those of thicker films appear to be independent of the thickness of the oxide and to be approximately \( 2.5 \times 10^5 \) V.cm\(^{-1}\). Increasingly higher values were measured as the films decreased in thickness over a narrow range from 30 to 20 channels for which the maximum breakdown field strength of \( 1.5 \pm 0.25 \times 10^{-6} \) volts per cm. was measured. However, no consistency was obtained in the measurements for films of thicknesses equivalent to 15 and 10 channels which have breakdown field strengths of \( 0.25 \pm 0.05 \times 10^6 \) V.cm\(^{-1}\) and \( 0.75 \pm 0.25 \times 10^6 \) V.cm\(^{-1}\) respectively.

The trend in the variation of breakdown field strength with oxide
Fig. 5.15(a) Breakdown field strengths of films grown on n-type (110) GaAs at 510°C.
thickness indicated in figure 5.15(a) suggests that the measurements for the two thinnest films should have been about an order of magnitude greater. However, although the low values may be due in part to rough interfaces (figure 5.14) producing regions of thin oxide having low breakdown voltages, they could be due to variations in the compositions of the films. This possibility is supported by the measurements for their dielectric constants (section (4) below). Therefore the results have been neglected in fitting the curve through the points in figure 5.15(a).

The breakdown field strengths of oxides grown at 510°C were shown to be susceptible to annealing. Moreover the effect produced depended on the time and temperature of the anneal and whether or not the electrode contacts were made before or after annealing the oxides.

After being annealed in nitrogen at 300°C for three successive periods of $\frac{1}{2}$ hour the breakdown voltage of the 20 channels thick contacted film decreased by nearly 80% whilst that of the similarly contacted 40 channels thick film decreased by less than 10%. Most of the degradation occurred during the first $\frac{1}{2}$ hour period of the anneal. However, after being annealed for 3 hours at 300°C prior to the electrodes being deposited, the breakdown voltage of a 27 channels thick film grown for 1 hour was about 80% greater than that measured for an unannealed oxide. Similar treatment of two other films grown at the same time but annealed at 250°C and 400°C, caused apparent decreases of about 20% in the values of breakdown field strength.

The changes in the breakdown field strengths are too small for any reliance to be placed on the results owing to the spread in values obtained from different areas of the same film as discussed below. Nevertheless the variations in the values recorded for those films which were contacted before being annealed are valid to within 2% as measurements were taken.
on the same areas each time. Therefore the changes observed must be the direct result of the annealing process causing changes in the compositions and/or the thicknesses of the films.

The variation of the breakdown field strength across the surface of an oxide is shown by the results for films grown between 465°C and 760°C. These are listed in table 5.6 which records the measurements made on up to three different points on the surface of each film.

In general, the variations in these three results are less than about three to one. However, in the case of the film grown at 750°C the spread is about ten to one. In the cases where comparisons can be made between the breakdown field strengths of films grown at the same temperature, i.e. 465°C, 510°C, 610°C and 675°C, the results show that significant differences were measured only for films grown at the latter two temperatures. But the variation from film to film in the results for oxides grown at 675°C are within the spread measured across the surface of the film grown at 750°C. Consequently they do not appear to be spurious. Only in the case of films grown at 610°C is there a difference in the values which suggests that reproducible results were not obtained.

The general trend in the results, as shown by their mean values, indicates that the breakdown field strength decreases as the oxidation temperature increases. Consequently the high values for the film grown at 610°C appear to be anomalies. Also, no spread in values was measured and this casts further doubt on the validity of the results. Other properties of this film are anomalous also (e.g. dielectric constant – section (4) below) and the suspicion exists that the measurements are in error owing to a high impedance between the substrate and the metal base of the device. Either the oxide on the rear side of the sample was not removed completely
<table>
<thead>
<tr>
<th>Oxidation temp. (°C)</th>
<th>465</th>
<th>505</th>
<th>510</th>
<th>550</th>
<th>610</th>
<th>675</th>
<th>750</th>
<th>760</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_B \times 10^5 \text{ V cm}^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$18.0 \pm 6.0$</td>
<td>$8.2 \pm 1.1$</td>
<td>$4.3 \pm 0.43$</td>
<td>$5.4 \pm 0.54$</td>
<td>$25.0 \pm 2.5$</td>
<td>$7.0 \pm 0.7$</td>
<td>$4.5 \pm 0.45$</td>
<td>$1.5 \pm 0.15$</td>
</tr>
<tr>
<td></td>
<td>$13.5 \pm 4.5$</td>
<td>$8.5 \pm 1.2$</td>
<td>$2.4 \pm 0.24$</td>
<td>$3.3 \pm 0.33$</td>
<td>$25.0 \pm 2.5$</td>
<td>$6.0 \pm 0.6$</td>
<td>$3.8 \pm 0.38$</td>
<td>$0.6 \pm 0.06$</td>
</tr>
<tr>
<td></td>
<td>$6.8 \pm 2.25$</td>
<td>$5.8 \pm 0.8$</td>
<td>$2.5 \pm 0.25$</td>
<td>$25.0 \pm 2.5$</td>
<td>$4.0 \pm 0.4$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>$12.8 \pm 4.3$</td>
<td>$7.5 \pm 1.0$</td>
<td>$3.4 \pm 0.34$</td>
<td>$3.7 \pm 0.37$</td>
<td></td>
<td>$5.7 \pm 0.57$</td>
<td>$2.9 \pm 0.29$</td>
<td>$1.05 \pm 0.10$</td>
</tr>
<tr>
<td></td>
<td>$14.5 \pm 4.8$</td>
<td></td>
<td>$2.7 \pm 0.27$</td>
<td>$4.5 \pm 0.45$</td>
<td>$1.5 \pm 0.15$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$9.5 \pm 3.2$</td>
<td></td>
<td></td>
<td>$2.8 \pm 0.28$</td>
<td>$1.2 \pm 0.12$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$6.8 \pm 2.25$</td>
<td></td>
<td></td>
<td></td>
<td>$2.0 \pm 0.20$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>$10.3 \pm 3.4$</td>
<td></td>
<td>$2.7 \pm 0.27$</td>
<td>$3.1 \pm 0.31$</td>
<td>$1.35 \pm 0.14$</td>
<td>$1.0 \pm 0.1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$11.5 \pm 2.7$</td>
<td></td>
<td>$3.1 \pm 0.22$</td>
<td>$3.4 \pm 0.24$</td>
<td>$1.35 \pm 0.14$</td>
<td></td>
<td>$4.5 \pm 0.3$</td>
<td>$2.9 \pm 0.29$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$1.05 \pm 0.10$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>$4.15$</td>
<td>$1.20$</td>
<td>$0.84$</td>
<td>$1.18$</td>
<td>$0.17$</td>
<td>$1.18$</td>
<td>$1.80$</td>
<td>$0.45$</td>
</tr>
</tbody>
</table>

* Results believed to be erroneous. See text for details.

Errors in $E_B$ are due solely to errors in 'N'. Absolute values are above values ±6%.

Table 5.6. Breakdown field strengths of films grown for 1½ hours on gallium arsenide.
and the tin dot failed to alloy with the gallium arsenide or the contact broke away while being fixed to the base. Because of these possibilities the value of $25 \times 10^5 \text{V.cm}^{-1}$ has been omitted from the calculations of the mean values of breakdown field strengths given in table 5.6 and from the plot in figure 5.15(b).

It is not possible to draw a smooth curve through the points in figure 5.15(b) and that shown is indicative only of the trend in the results which may be susceptible to pinholes or cracks within the films or to variations in thicknesses of the oxides due to rough interface regions. Nevertheless, the measurements appear to show that breakdown field strengths of films grown for $1\frac{1}{2}$ hours decrease with increasing temperatures below about $525^\circ \text{C}$. At higher temperatures the breakdown field strengths remain constant at a value of about $2.5 \times 10^5 \text{V.cm}^{-1}$. This is identical to the values measured for films grown at $510^\circ \text{C}$ and thicker than about 40 channels (figure 5.15(a)).

(2). Resistivity ($\rho$) of films grown at $510^\circ \text{C}$.

The resistivities of oxides grown at $510^\circ \text{C}$ are plotted in figure 5.16 which shows the results varying by two orders of magnitude, i.e. between $10^9$ and $10^{11} \Omega \text{cm}$.

The values show a logarithmic increase in resistivity with film thicknesses between about 20 and 55 channels with thinner films having resistivities about an order of magnitude greater than the minimum value, and thicker films having an apparent constant value of about $10^{11} \Omega \text{cm}$.

The relatively high values of resistivity of the two thinnest films may have been influenced by the same factors affecting their breakdown
Fig. 5.15(b) Breakdown field strengths of films grown for $1\frac{1}{2}$ hours on n-type (110) GaAs.
Fig. 5.16 Resistivities of films grown on n-type (110) GaAs at 510°C.
field strengths (see (1) above). But as the measurements of dielectric constants (section (4) below) suggest that the estimated thicknesses of the oxides are not substantially in error, the values of resistivity of the two thinnest films appear to be correct. Thus the results point to the resistivity being minimum when films are about 20 channels (560°) thick.

(3). Dielectric loss factor (tan δ) at 1 MHz.

The results of calculations of tan δ (section 4.6.3a), measured at 1 MHz, are given in figure 5.17(a) for films grown at 510°C for different times and in table 5.7 for films grown for 1½ hours at different temperatures. Table 5.7 includes, also the mean values and their errors. These are plotted in figure 5.17(b).

The measurements taken on oxides thicker than 30 channels (850°) and grown at 510°C indicate that tan δ decreases with increasing film thickness until the a.c. resistance of the device capacitance is about two orders of magnitude greater than the capacitance impedance (i.e. tan δ = 0.01). This occurs, apparently, when films are thicker than about 55 channels (1500°). However, no consistent results were obtained for films less than 30 channels in thickness, as shown by figure 5.15(a). The values of tan δ are in error by less than ± 5° (section 4.6.3) and are the most accurate of the electrical measurements by being independent of errors in thickness and area measurements. Therefore the results show that no direct relationship between tan δ and film thickness was obtained for oxides grown at 510°C. However they do show that low dielectric losses of tan δ ~ 0.01 are obtainable.

Large variations of tan δ were measured between different areas of a particular film grown between 465°C and 760°C and between different films.
Fig. 5.17(a) Dielectric loss factor (tan δ) at 1 MHz of oxides grown on n-type (110) GaAs at 510°C.
<table>
<thead>
<tr>
<th>Oxidation temp. (°C)</th>
<th>465</th>
<th>505</th>
<th>510</th>
<th>550</th>
<th>610</th>
<th>675</th>
<th>750</th>
<th>760</th>
</tr>
</thead>
<tbody>
<tr>
<td>tan δ</td>
<td>0.078</td>
<td>0.054</td>
<td>0.037</td>
<td>0.050</td>
<td>0.012</td>
<td>0.035</td>
<td>0.045</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>0.065</td>
<td>0.050</td>
<td>0.023</td>
<td>0.038</td>
<td>0.010</td>
<td>0.020</td>
<td>0.035</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>0.063</td>
<td>0.045</td>
<td></td>
<td>0.025</td>
<td>0.008</td>
<td>0.015</td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.069</td>
<td>0.050</td>
<td>0.030</td>
<td>0.038</td>
<td></td>
<td>0.023</td>
<td>0.033</td>
<td>0.016</td>
</tr>
<tr>
<td>± 0.002</td>
<td>± 0.002</td>
<td>± 0.001</td>
<td>± 0.001</td>
<td>± 0.0007</td>
<td>± 0.001</td>
<td>± 0.0006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tan δ</td>
<td>0.071</td>
<td></td>
<td>0.079</td>
<td>0.040</td>
<td>0.032</td>
<td>0.044</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.060</td>
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</tr>
<tr>
<td></td>
<td>0.038</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.056</td>
<td></td>
<td>0.079</td>
<td>0.034</td>
<td>0.026</td>
<td>0.034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>± 0.002</td>
<td>± 0.004</td>
<td>± 0.001</td>
<td>± 0.001</td>
<td>± 0.001</td>
<td>± 0.001</td>
<td>± 0.0006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.062</td>
<td>0.050</td>
<td>0.046</td>
<td>0.036</td>
<td>0.026</td>
<td>0.028</td>
<td>0.033</td>
<td>0.016</td>
</tr>
<tr>
<td>± 0.0013</td>
<td>± 0.0013</td>
<td>± 0.0007</td>
<td>± 0.001</td>
<td>± 0.0007</td>
<td>± 0.001</td>
<td>± 0.0006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>σ</td>
<td>0.0125</td>
<td>0.0037</td>
<td>0.024</td>
<td>0.0115</td>
<td>0.006</td>
<td>0.016</td>
<td>0.016</td>
<td>0.0105</td>
</tr>
</tbody>
</table>

* - Results believed to be erroneous. See text for details.

Table 5.7. tan δ at 1MHz for films grown for 1½ hours.
Fig. 5.17(b)  Dielectric loss factor (tan δ) at 1 MHz of oxides grown on n-type (110) GaAs for 1 1/2 hours.
grown for $1\frac{1}{2}$ hours at the same temperature (table 5.7). The variation is about five to one in the case of the oxide grown at $760^\circ C$ but, in general, the spread in values is approximately two to one.

Some of the lowest values of $\tan \delta$ (0.008 to 0.012) were obtained from one of the films grown at $610^\circ C$, but the device of which this film formed a part is believed to have been faulty for the reason given in section (1) above. Consequently these measurements are suspect and have been neglected in the calculations of the mean values in table 5.7.

The curve in figure 5.17(b) indicates that the dielectric losses of oxides grown on gallium arsenide decrease as growth temperature increases. However, this may be true only for growth temperatures up to about $600^\circ C$ above which $\tan \delta$ may then increase. This is shown by the results from three or four measurements made on films grown at $675^\circ C$ and $750^\circ C$.

(4). Dielectric constant ($\epsilon$) at 1 MHz.

The dielectric constants of the oxides were measured at 1 MHz as explained in section 4.6.3(b) and by using equation (4) of that section.

The values for films grown at $510^\circ C$ are given in figure 5.18(a). Those for films grown for $1\frac{1}{2}$ hours at different temperatures are listed in table 5.8 and their mean values and errors are plotted in figure 5.18(b).

Measurements from the oxides grown at $510^\circ C$ gave values of dielectric constants at 1 MHz between 2.6 and 4.6 (figure 5.18(a)).

The large errors involved in the measurements do not permit the variation of dielectric constant with film thickness to be determined with
Fig. 5.18(a) Dielectric constant at 1 MHz ($\varepsilon_{1MHz}$) of oxides grown on n-type (110) GaAs at 510°C.
<table>
<thead>
<tr>
<th>Growth temp. (°C)</th>
<th>465</th>
<th>505</th>
<th>510</th>
<th>550</th>
<th>610</th>
<th>675</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{1MHz}$</td>
<td>4.6 ± 1.6</td>
<td>3.3 ± 0.5</td>
<td>3.4 ± 0.4</td>
<td>5.0 ± 0.6</td>
<td>1.0 ± 0.1</td>
<td>5.3 ± 0.8</td>
<td>5.5 ± 0.8</td>
</tr>
<tr>
<td>Mean</td>
<td>3.6 ± 1.2</td>
<td>2.9 ± 0.4</td>
<td>3.4 ± 0.4</td>
<td>4.3 ± 0.5</td>
<td>-</td>
<td>5.0 ± 0.6</td>
<td>5.3 ± 0.6</td>
</tr>
<tr>
<td>$E_{1MHz}$</td>
<td>2.1 ± 0.7</td>
<td>3.25 ± 0.4</td>
<td>5.8 ± 0.7</td>
<td>4.0 ± 0.5</td>
<td>5.6 ± 0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>-</td>
<td>3.1 ± 0.37</td>
<td>4.1 ± 0.49</td>
<td>4.0 ± 0.48</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>3.6 ± 1.2</td>
<td>2.9 ± 0.4</td>
<td>3.2 ± 0.27</td>
<td>4.0 ± 0.34</td>
<td>5.2 ± 0.44</td>
<td>5.3 ± 0.64</td>
<td></td>
</tr>
<tr>
<td>$\sigma$</td>
<td>1.46</td>
<td>0.3</td>
<td>0.2</td>
<td>1.15</td>
<td>-</td>
<td>0.32</td>
<td>0.22</td>
</tr>
</tbody>
</table>

* - Results believed to be erroneous. See text for details.

Table 5.8. Dielectric constants at 1MHz of films grown for 1½ hours on gallium arsenide.
Fig. 5.18(b)  Dielectric constant at 1 MHz ($\varepsilon_{1\text{MHz}}$) of oxides grown on n-type (110) GaAs for 1½ hours.
any certainty. The results suggest that the dielectric constant may increase from about 2.8 for films 30 channels (850Å) thick to about 4.0 as films increase or decrease in thickness. However, the results are consistent also with the dielectric constant increasing linearly with oxide thickness. Thus the results for films thinner than 30 channels in thickness are inconclusive.

The curves in figures 5.15(a) and 5.16 point to the possibility that the values calculated for the breakdown field strengths and resistivities of the two thinnest films are an order of magnitude too low and too high respectively. If this were correct then the errors must be due to the effective thicknesses of the films being about one tenth of the measured values. But if the films were thinner by this amount their dielectric constants would be about 0.35. As no material has a dielectric constant of less than 1.0 the effective thicknesses of the films cannot differ from the measured values by more than - 60%. In fact the dielectric constants of solids are usually greater than 3.0(76). Therefore the values plotted in figure 5.18(a) are unlikely to be too low and the thicknesses used in calculating the dielectric constants of the two thinnest films are unlikely to be too large.

Measurements of capacitance made on those devices which had been subjected to the anneal procedure detailed in (1) above showed that the dielectric constants of the 20 and 40 channels thick films grown at 510°C were increased by nearly 60% and decreased by about 30% respectively by the 300°C anneal in nitrogen. A 60% increase was obtained also by the annealing at 400°C of the 27 channel thick film prior to the deposition of the electrodes. No significant differences were measured after the anneals at 250°C and 300°C.

The results for oxides grown at temperatures from 465°C to 760°C
(table 5.8) show that in five cases the dielectric constant was calculated to be about 1.0 or less (i.e. oxides grown at 610°C and 465°C). These results have been disregarded in the calculations of the mean values plotted in figure 5.16(b) for the reasons given above and in section (1).

The spread in the results from any one film is greater than the differences measured between oxides grown at the same temperature (e.g. at 510°C, 550°C and 675°C).

The plot in figure 5.18(b) suggests that the dielectric constant increases linearly with increasing growth temperature and may reach a value of about 6.0 for films grown at 750°C. However it is not possible to be specific in the case of films grown below 450°C and above 750°C and the apparent trend may apply only for films grown between these temperatures for 11/2 hours.

(5). Dielectric dispersion.

Capacitance measurements made between 100 Hz and 1 MHz showed that the dielectric constants of the films decreased with increasing frequency. The variation shown in figure 5.19 is typical of those of oxides grown at 510°C. Films grown at higher temperatures show similar variations for frequencies between 100 Hz and 10 KHz, but the high frequency dispersion \( \frac{C_{10 KHz}}{C_{1 MHz}} \) increases from 1.0 to nearly 3.0 as the growth temperature of the films is increased from 510°C to 760°C. This increase in the dispersion can be seen in figure 5.20 for a few oxides grown for 1½ hours in the above temperature range.
Fig. 5.19  Typical variation of capacitance with frequency at zero bias of oxides grown at 510°C.
Fig. 5.20 Dispersion of dielectric constant between 10KHz and 1MHz of films grown for 1½ hours on gallium arsenide.
Variation of capacitance with voltage.

The variation of the capacitance of the MOS devices under forward and reverse bias was obtained as explained in section 4.6.4. The resulting C-V curves were similar to that in figure 5.21.

Under zero and forward bias the capacitances remained constant at the values of the oxides \( (C_o) \) and the semiconductors were in accumulation. Under reverse (negative) bias the semiconductors were in the depletion mode and the decreasing capacitances tended towards a plateau value before the breakdown points of the oxides were reached. Therefore the semiconductors appeared to go into inversion.

Field induced hysteresis was present in most of the devices.

\[
\frac{(C_o/C)^2 - 1}{V} \text{ curves.}
\]

The variation of \( (C_o/C)^2 - 1 \) with reverse bias voltage was plotted from the C-V curves in the manner described in section 4.6.4. An example of this procedure is given in figure 5.22 in which capacitance and voltage values were taken from figure 5.21.

The linear portion of the curve (between -4 volts and -2 volts) is consistent with equation (17) derived in section 4.5.2(c) for an ideal uniformly doped MOS device operating in the depletion mode. But at large reverse bias voltages, where inversion tends to occur, the equation does not hold. This is indicated by the curve between the points at -4 volts and -8 volts. Measurements beyond the latter voltage could not be made owing to breakdown of the oxide.
1 hr at 510°C.
f = 1 MHz
(110) n-type GaAs

\[ (C_0/C)^2 - 1 \text{ vs } V \text{ for values in fig. 5.21} \]
Values of flat band voltages \( V_{FB} \) and donor densities \( n \) of the MOS devices, from curves similar to that in figure 5.22, are listed in the following sections.

(8). Flat band voltage \( V_{FB} \).

The applied voltage biases \( V_{FB} \) needed to obtain flat energy bands at the oxide-semiconductor interfaces were always negative and between \(-0.5 \pm 0.1 \) volts and \(-2.8 \pm 0.1 \) volts for oxides grown at \( \text{510}^\circ \text{C} \). These voltages, which were measured as indicated in section 4.6.4(a), are given in table 5.9.

There are no signs that the flat band voltage increases linearly with film thickness, as would be expected if film thickness is the only factor affecting \( V_{FB} \). Therefore it is probable that defects at the interfaces and/or within the films vary in density from film to film in a non-uniform way.

Devices which have oxide insulators grown for \( 1\frac{1}{2} \) hours at \( \text{610}^\circ \text{C} \) and \( \text{760}^\circ \text{C} \) have flat band voltages of \(-0.3 \pm 0.1 \) volts and \(-1.0 \pm 0.1 \) volts respectively.

(9). Field induced hysteresis \( \mathcal{H} \).

The shifts in the voltages \( \Delta V \) at the flat band voltages, induced by reverse bias cycling and exhibited in C-V curves such as in figure 5.21, are tabulated in table 5.9 for devices having films grown at \( \text{510}^\circ \text{C} \). Included in the table are measurements of the hystereses \( \mathcal{H} \) as defined by equation (20) section 4.5.2(f).
<table>
<thead>
<tr>
<th>N</th>
<th>$V_{FB}$</th>
<th>$\Delta V$</th>
<th>H (%)</th>
<th>n</th>
<th>$n_{nom}$</th>
<th>$n/n_{nom}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-1.3</td>
<td>0.15</td>
<td>+8</td>
<td>5.7</td>
<td>1.2</td>
<td>4.0</td>
</tr>
<tr>
<td>15</td>
<td>-0.5</td>
<td>0.10</td>
<td>-20</td>
<td>2.1</td>
<td>&quot;</td>
<td>1.8</td>
</tr>
<tr>
<td>20</td>
<td>-1.5</td>
<td>0.60</td>
<td>-40</td>
<td>0.7</td>
<td>&quot;</td>
<td>0.5</td>
</tr>
<tr>
<td>27</td>
<td>-2.3</td>
<td>1.25</td>
<td>-54</td>
<td>0.8</td>
<td>&quot;</td>
<td>0.7</td>
</tr>
<tr>
<td>32</td>
<td>-1.8</td>
<td>1.0</td>
<td>-54</td>
<td>0.3</td>
<td>&quot;</td>
<td>0.3</td>
</tr>
<tr>
<td>40</td>
<td>-1.4</td>
<td>0.60</td>
<td>-44</td>
<td>1.2</td>
<td>&quot;</td>
<td>1.0</td>
</tr>
<tr>
<td>47</td>
<td>-2.3</td>
<td>0.90</td>
<td>-40</td>
<td>2.8</td>
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<td>2.4</td>
</tr>
<tr>
<td>54</td>
<td>-1.6</td>
<td>0.55</td>
<td>-35</td>
<td>0.8</td>
<td>1.9</td>
<td>0.4</td>
</tr>
<tr>
<td>65</td>
<td>-2.8</td>
<td>1.10</td>
<td>-38</td>
<td>0.8</td>
<td>&quot;</td>
<td>0.4</td>
</tr>
</tbody>
</table>

$N$ = Oxide thickness (no. oxide channels)

$V_{FB}$ = Flat band voltage (volts)

$\Delta V$ = Voltage shift (volts)

$H$ = Hysteresis (|$\Delta V$| .100/$V_{FB}$) (\%)

n = Measured donor density ($10^{17}$ cm$^{-3}$)

$n_{nom}$ = Manufacturer's value of donor density ($10^{17}$ cm$^{-3}$)

Table 5.9. MOS device parameters - Gate oxides grown at 510°C.
Except for the case of the 10 channel thick film, the C-V characteristics are consistent with the presence of mobile ions within the oxides. This is seen by the shifts to less negative voltages of the curves. The shift of 0.1 volt towards a more negative voltage of the C-V curve of the 10 channel thick film indicates the presence of traps.

The hysteresis induced in films thicker than about 15 channels is between approximately 35% and 55%, whereas devices having thin oxides have low hysteresis.

Devices with oxides of comparable thicknesses but grown at different temperatures showed completely different C-V characteristics. Whereas the hysteresis of the device with the 65 channel thick film grown at 510°C is 38%, devices with oxides grown for 1½ hours at 610°C and 760°C gave values of H of virtually zero and about 10% respectively. The direction of the shift of ΔV in the latter case was to a more negative voltage. This is indicative of electron trapping.

An insufficient number of measurements were made on oxides grown at high temperatures for any definite conclusions to be drawn about the hysteresis induced in such films. However the results point to the possibility that mobile ions reside in oxides grown below about 600°C whereas traps are present in oxides grown at higher temperatures.

(10). Donor density (n).

The donor densities in the tellurium doped gallium arsenide beneath the oxide layers, together with the nominal values (n_{nom}) stated by the manufacturer of the material and the ratios n/n_{nom}, are listed in table 5.9.
Because the dopant ions in the material can vary in density from slice to slice and from part to part of a slice, the values of $n_{\text{nom}}$ are uncertain. However, in general, the measurements show that the donor densities at the semiconductor-oxide interfaces of the devices are within about 50% of the manufacturer's figure. Therefore thermal oxidation does not appear to alter the level by any significant amount. But, the result for the thinnest (10 channel thick) film indicates that up to about four times the nominal amount of tellurium ions can exist.

If the results are taken at face value, they suggest that tellurium builds up at the semiconductor surface either during the polishing process or during the initial stages of oxidation. As oxidation progresses, the tellurium is consumed by the oxide as it advances into the semiconductor. This lowers the donor density to the nominal value. Thereafter it appears that either tellurium diffuses into the oxide at a rate which is faster than that at which gallium arsenide is consumed or, alternatively, oxygen diffuses into the substrate and compensates up to 50% of the dopant ions within the region in the semiconductor behind the interface.

5.7. Summary.

The above sections have dealt with the measurements from oxides grown thermally on gallium arsenide. The next chapter discusses these results in more detail and relates the physical properties of the films to their electrical characteristics. Also it compares their properties with those of films grown by the plasma and anodic methods.
Chapter 6.

DISCUSSION

6.1. Introduction.

This is the final chapter dealing with native oxides. The results from the work carried out on this project and presented in the preceding chapter are discussed and conclusions drawn from them.

The effect of the physical properties of the oxides on their electrical characteristics are considered, and comparisons are made between the properties of these oxides and those grown by other methods.

6.2. Composition of native oxides.

The measurements given in figures 5.7 and 5.12 show that the composition of oxides thermally grown between 465°C and 760°C on gallium arsenide is essentially Ga₂O₃ although films thinner than about 500 Å may contain Ga₂O and those thicker than about 1000 Å may possess an excess of oxygen. However, the thin films may be discontinuous (section 5.5.1) and parts of their analysing beams be backscattered from unoxidised portions of the surfaces. This would explain the low backscattered yield from the oxygen in such films even if the oxides are Ga₂O₃. Oxygen trapped in cracks or grain boundaries may be the cause of the measured excess in thick films.

The absence of arsenic at the surfaces of films grown below about 550°C (section 5.3.3), and its presence in small quantities in films grown at higher temperatures (figure 5.8), is consistent with, and confirms, the results of most other workers (section 3.6.5) except those of Minden.
Consequently, it is assumed that the films consist essentially of Ga$_2$O$_3$ with those grown between about 550°C and 700°C containing As$_2$O$_3$ and those grown at higher temperatures containing GaAsO$_4$.

It is shown by the reasonably flat profiles of both the oxygen and GaAs backscattered spectra (e.g. figure 5.2) that the composition throughout the films is fairly constant, except at the interfaces between the oxides and the substrates. These regions are large compared to the thicknesses of the films (figures 5.9 and 5.13) and although the backscattered spectra indicate that the concentrations of oxygen within the interface regions diminishes with depth, the rough substrate surfaces exposed after the oxides have been removed (figure 5.14) point to the possibility that the interface regions consist of numerous cone-like structures of stoichiometric Ga$_2$O$_3$ extending deep into the substrates. Such structures could explain the 'tails' in the oxygen spectra (figure 5.2) and, also, the multicoloured effects seen under the microscope (section 5.5.1).

Although Rutherford backscattering has been satisfactory for determining the chemical compositions of the films, it is not able to analyse their physical structure. Several polymorphs of Ga$_2$O$_3$ exist (α, β, γ, δ and ε) but, while the temperature of transition from one phase to another is documented (77), their temperatures of formation are not. It is clear that the δ-form cannot exist above 550°C (it transforms to ε-Ga$_2$O$_3$ between 525°C and 550°C) whilst the α, β and ε structures transform to the β-polymorph at 600°C, 650°C and 870°C respectively. β-Ga$_2$O$_3$ has been identified in films annealed at 680°C (6) and grown at 700°C (6), and δ-Ga$_2$O$_3$ is believed to be the composition of a 9000 Å thick film grown in air at 500°C (60). Also, the δ-polymorph might have grown chemically in H$_2$O$_2$/H$_2$O solution (78).

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The above data shows that there is insufficient information from which the structures of the films can be determined, but it does suggest that different polymorphs might have grown at different temperatures. Nevertheless, there is the strong possibility that oxides grown at the higher temperatures are $\beta\text{-Ga}_2\text{O}_3$ whilst the others consist of one or more of the possible polymorphs. In addition, the structures may be dependent on the orientation of the substrate surface (79).

6.3. The characteristics of native oxide growth.

6.3.1. The effect of temperature on growth rate.

Both (110) and (100) surfaces (figures 5.4 and 5.5 respectively) possess thickness-temperature characteristics which indicate that several distinct mechanisms operate within the temperature range of 350°C to 760°C. It appears that the oxidation rate increases rapidly up to a certain temperature above which it decreases to a minimum before it increases again. The temperatures at which maximum and minimum growth occur depend on the orientation of the substrate surface. Possible explanations for this phenomenon are discussed in the following section.

The form of the characteristics shown in figures 5.4 and 5.5 has not been observed previously, although Navratil (4) reported that a rapid increase in the oxidation rate of (111) surfaces occurs at temperatures in excess of about 480°C and Minden (1) found an insignificant growth of oxide on (100) surfaces oxidised below 600°C.

The results within the lower temperature range (figure 5.6) are seen to agree well with those of Navratil and Murarka up to about 500°C and it
is concluded that the growth mechanism up to this temperature is the same for (100), (110) and (111) surfaces. As Navratil \(^4\) has shown that an activation energy of about 1.0 eV corresponds to a parabolic growth mechanism, whilst 2.2 eV is the activation energy for linear growth, the value of 1.25 ± 0.15 eV listed in table 5.2 for the activation energy of films grown for 1½ hours points to the oxides having grown in accordance with the parabolic law. This contention is supported by the results for isothermal growth at 510°C (figure 5.11) and by the reanalysed data of Murarka (figure 3.5). Consequently, there is agreement between the various sets of data. However, breakdown of the parabolic mechanism has been observed for oxide growth on (100) surfaces at 450°C (figure 3.5) and, possibly, on (110) surfaces at 510°C (figure 5.11). It is probable that this is due to films becoming unstable at a certain thickness owing to strain caused by mismatch between the lattices of the substrates and the oxides. If this does occur, then the orientation of the surface would be expected to influence the strain within the film and breakdown of the parabolic growth mechanism to take place when oxides on (100) and (110) surfaces were at different thicknesses. A similar effect could be caused by differences in the preparations of substrate surfaces and this may explain Murarka's inability to establish any growth law at 300°C for times less than 4 hours.

The diminution with increasing temperature of the oxide thickness, as seen for both (110) and (100) surfaces in figure 5.6, may be due to either or both of the following phenomena:

(1) Films grown at different temperatures may have different structures as suggested in section 6.2 above. As a consequence the rate of diffusion of ions through a film may be reduced and the oxidation rate be affected.

(2) As the oxidation increases arsenic may diffuse through the film at an increasing rate and reduce the formation of gallium oxide at
the interface by forming As$_2$O$_3$ which then evaporates. Support for this is
given possibly by the identification of arsenic at the surfaces of films
grown above about 575°C (figure 5.8) and of As$_2$O$_3$ in films grown at 600°C (2).
Probably the arsenic becomes trapped in the films during the cooling period.

Above about 700°C, where a further increase in the oxidation rate
occurs and the activation energy is about 1.7 ± 0.8 eV (table 5.2), the
growth mechanism cannot be determined. However, the results are consistent
with the oxide structures being different from those formed at lower
temperatures. It is known that grain growth and reorientation of the oxide
crystallites occur at about these temperatures (6) and, also, that GaAsO$_4$
is a constituent of oxides grown above about 800°C. Therefore, it is
apparent that these films have structures which inhibit the diffusion of
arsenic. As is stated in the preceding section (6.2), films grown at these
temperatures cannot be α, β, or γ polymorphs of gallium oxide. Of the
remaining two possibilities only β-Ga$_2$O$_3$ has been identified.

The slow growth rate between about 550°C and 700°C on (100) surfaces
appears to be consistent with Minden's findings (1). The activation energy
of 0.17 ± 0.15 eV (table 5.2) gives no clue to the growth mechanism involved
but the thinness of the films suggests that the growth is unlikely to be
linear with time.

6.3.2. The effect of surface orientation on growth rate.

Figure 5.6 shows clearly that the oxidation rate is dependent on the
orientation of the surface of the substrate, particularly at growth
temperatures between about 515°C and 700°C where (110) surfaces oxidise at
a rate much greater than that of (100) surfaces. However this may be a
delusion. If there is a mismatch between oxide and substrate, then
differences in the degree of mismatch with (110) and (100) surfaces would
be expected to result in differences in the mechanical properties of the films grown on these surfaces and/or the growth of different polymorphs. Consequently the susceptibility of the oxides to arsenic outdiffusion may be different. It is this possibility which could cause the results to be misinterpreted. The reason for this contention is given below.

If arsenic can diffuse easily through a film during oxidation then it may form arsenic oxide which evaporates. Although this would reduce the thickness of the film, an oxide of gallium would still be formed. This appears to happen on (110) surfaces oxidised above about 550°C. However, if arsenic cannot diffuse through the film then it could build up at the interface and form a low melting point oxide \( (As_2O_3) \) by reacting with indiffusing oxygen. As mentioned in section 3.4, catastrophic oxidation could then take place causing the film to lift from the surface. Presumably, further oxidation of gallium would occur after the arsenic oxide had evaporated and a thin film would be obtained at the end of the oxidation period. This mechanism may be the reason for the thinness of oxides formed on (100) surfaces above about 525°C and, also, be the reason for Navratil's films being loosely adherent to their substrates (4).

6.3.3. The effect of impurity dopants on growth rate.

The results from n-type and p-type material (section 5.3.1) indicate that there is no difference in oxidation rate due to carrier type. This is in accord with the conclusion of Minden (1). But dopant ions do affect the oxidation rate of gallium arsenide, as is shown in chapter 7. The absence of any such effect could be attributed to the low level of tellurium (n-type) and zinc (p-type) doping or to these elements having an equal effect.
6.3.4. The effect of bulk and epitaxial material on growth rate.

In general, the results do not show any measurable differences between the oxidation rates of bulk and epitaxial gallium arsenide. This implies that the preparation of samples cut from bulk material was satisfactory and the surfaces were free of gross defects.

6.3.5. The isothermal growth of native oxides at 510°C.

It is concluded from section 5.4.1 that, generally, for periods up to 3 hours at 510°C, oxides on the (110) surfaces of n-type bulk material grew in accordance with a parabolic law. This differs substantially from the linear law obtained by Navratil \(^{(4)}\) at temperatures greater than about 495°C and by Murarka \(^{(60)}\) at 500°C for times in excess of 4 hours, but it does agree with their results for the growth of thin films at lower temperatures. However, Murarka's results for growth at 450°C (figure 3.5) show that films thicker than about 700 Å grow at a rate which his data for growth at 500°C indicates is linear.

A linear law can be the result of oxygen indiffusing through cracks within a film. Consequently, the enhanced growth of the films grown for 1\(\frac{1}{2}\) and 2\(\frac{1}{2}\) hours (figure 5.11) might have been due to this phenomenon or, alternatively, to diffusion via grain boundaries. Neither of these possibilities can be substantiated, but backscattering shows that these two oxides appear to possess excess oxygen (figure 5.12). Reasons have been advanced in section 5.4.1 why these samples behaved differently from the others - they may have slightly different orientations or residual damage was not removed from their surfaces during the preparation stage.

The conclusions reached in preceding sections are that the growth

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characteristics are independent of material type and dopant species at all temperatures. Also, it appears that below about 505°C the growth of oxides on (110) and (100) surfaces is identical and parabolic with time for film thicknesses up to about 700 Å. At this thickness the growth mechanism of oxides on (100) surfaces changes to one obeying a linear law, whilst the changeover for films on (110) surfaces may not occur until a thickness in excess of 1100 Å is reached.

It is not possible to deduce from the results the isothermal growth characteristics at higher temperatures.

6.3.6. Growth mechanism.

The establishment of the parabolic growth law implies that Wagner's theory of oxidation applies (section 3.4), and consequently that film growth was due to the diffusion of ions through compact layers. However, either gallium or oxygen could be the diffusant thereby causing oxidation to take place at the oxide surface or interface respectively. Wilmsen (61) believes that the former process takes place, but the tails in the oxygen spectra and the lack of any perceivable gallium deficiency behind the interfaces in figures 3.6 and 5.2 suggest this is not so but, instead, support the view of Schwartz (9) that oxidation occurs at the interface.

The linear growth mechanism has been mentioned previously in section 6.3.5 and attributed to a rapid influx of oxygen to the interface via cracks or grain boundaries. With these defects a film would not be compact and no concentration gradient of oxygen would occur. It seems likely that under these conditions oxygen would reach the oxide-substrate interface at a constant rate, with the result that the sticking coefficient of oxygen would be constant. This condition is believed to lead to a linear
relationship between film thickness and growth time (section 3.4).

It appears to have been established that the parabolic mechanism of oxide growth precedes the linear mechanism and that the point at which the change from one to the other takes place is determined by the thickness of the oxide. This is consistent with Murarka's and Navratil's data although their results seem to show that the growth mechanism is controlled by temperature. However, before the parabolic growth mechanism is established, it is probable that arsenic evaporates from the surface and oxide nucleation takes place during the initial stages of growth.

The suggestion is made in section 6.2 that, as thin films may be discontinuous, portions of the substrate surfaces are unoxidised. But no arsenic was detected from the backscattered spectra of such films (sections 5.3.3 and 5.4.2). Consequently arsenic might have evaporated from the surfaces of the substrates either prior to or during the formation of discontinuous islands of Ga$_2$O$_3$. This is compatible with arsenic oxide having a low evaporation temperature as mentioned at the end of section 3.6.5.

During the formation of discontinuous films the growth law may be logarithmic (section 3.4). This is a possibility which appears to be supported by the results obtained by Lukes (5) for the oxidation of gallium arsenide at room temperature.

6.3.7. The stability and solubility of oxides.

The fact that oxides grown on (100) and (110) surfaces are stable mechanically, unlike those formed on (111) surfaces (4), tends to support the suggestion made in section 6.3.2 that different polymorphs of Ga$_2$O$_3$ grow on surfaces of different orientations and/or that film instability
is caused by mismatch between oxide and substrate. Figures 2.3 to 2.4 show the atomic configurations at the (100), (110) and (111) surfaces of gallium arsenide. One of the noticeable differences is the rhombus-like positioning of gallium atoms in (111) surfaces and the square-like arrangement of gallium atoms in (100) and (110) surfaces.

Although no serious attempts were made to investigate the solubility properties of thermal oxides, the result mentioned in section 5.5.3 confirms that they dissolve in hydrochloric acid. However, the difficulty experienced in removing the last few hundred angstroms of the film points to the interface region being reasonably thick and of different composition to the bulk of the film. This corroborates the conclusions reached from back-scattering (figure 5.2) that the interfaces between substrates and oxides are regions in which oxygen diminishes with depth.

6.3.8. Summary of the physical properties of oxides.

The foregoing discussion of the physical properties of native oxides grown thermally on gallium arsenide is complex, and it seems advantageous to summarise the main points made before the electrical properties are considered. Briefly, it appears that:

(a) During the initial stages of oxidation arsenic is lost from the surface either prior to or during the formation of discontinuous films of Ga$_2$O$_3$ and/or Ga$_2$O.

(b) Following, and maybe during, the above growth stage, the oxidation continues via the parabolic mechanism of oxygen indiffusion up to film thicknesses of about 700 Å on (100) surfaces and about 1500 Å on (110) surfaces.
(c) Thicker films grow linearly with time owing to a rapid indiffusion of oxygen via cracks or grain boundaries. These films may possess an excess of oxygen.

(d) The films are mainly Ga$_2$O$_3$ but those grown above about 525°C contain small quantities of arsenic. This is in the form of As$_2$O$_3$ in films grown below about 700°C and may be GaAsO$_4$ in films grown above about 700°C.

(e) Different polymorphs of Ga$_2$O$_3$ may grow within the various temperature ranges, but the high temperature form is $\beta$-Ga$_2$O$_3$.

(f) The oxidation rate for 1½ hours growth up to about 505°C and above about 700°C is independent of the orientation of the surface. Between these temperatures the rate on (100) surfaces decreases rapidly to a minimum at about 525°C whilst that on (110) surfaces increases to a maximum at about 550°C and then decreases slowly to a minimum at about 700°C.

(g) Differences in the oxidation rate of (100) and (110) surfaces may be due to arsenic outdiffusion through films of different structures. Catastrophic oxidation may occur on (100) surfaces.

(h) The films have smooth surfaces but do not possess abrupt interfaces.

(i) The films are stable but dissolve in HCl.

(j) The above characteristics are independent of dopant species and of the type (i.e. bulk or epitaxial) of substrate material.
6.4. Electrical properties.

6.4.1. General appraisal of the electrical measurements.

The most obvious feature of the electrical parameters is the large spread of values which were recorded between both the measurements taken on any one device and those taken on devices possessing oxides grown at the same temperature. Obviously, measurement inaccuracies, particularly those associated with contact area and film thickness, account for much of this spread. However, measurements of dielectric loss factor (tan \( \delta \)) involve only capacitance and resistance whose product has an error of less than \( \pm 6\% \). This is insufficient to account for the large spread in the values of tan \( \delta \), and, consequently, other factors appear to have influenced the results.

It seems probable that lateral variations in the compositions of the films, particularly at the interfaces, had a marked effect on the values which were obtained. This contention appears to be supported by the evidence of the rough interface region shown in figure 5.14. Moreover, the measurements of the interface widths suggest that the films can be considered to be double layer dielectrics whose individual characteristics cannot be determined. Nevertheless, the effect of the interface region would seem to be less marked for a thick film.

Although the above has pointed out the difficulties involved in interpreting the results, the figures show certain trends which point to there being correlations between variations in the electrical parameters and variations in the compositions of the films. These are considered in the following sections.
By comparison with oxides grown on gallium arsenide by anodic and plasma techniques, the breakdown field strengths of thermally grown films are low. In general, their average value of about $2.5 \times 10^5 \text{ V.cm}^{-1}$ is an order of magnitude lower than the typical value of anodic films (52) and even lower than the value of $5 \times 10^6 \text{ V.cm}^{-1}$ of plasma grown films.

One essential difference between the oxides is the low quantity of arsenic in those grown thermally - as shown in figure 5.8. However, although films grown at temperatures greater than $550^\circ\text{C}$ contain measurable amounts of arsenic, the breakdown field strengths of these films are lower than the values of approximately $1 \times 10^6 \text{ V.cm}^{-1}$ of films grown at $465^\circ\text{C}$. Obviously another factor must be important.

It is noticeable in figure 5.15(b) that the breakdown field strength is a minimum for films grown at temperatures where the oxidation rate is a maximum, i.e. between about $550^\circ\text{C}$ and $610^\circ\text{C}$. Films grown at lower temperatures appear to have no arsenic at their surfaces, but they contain an increasing quantity of oxygen as the growth temperature is increased (figure 5.7). It is inferred from this that the reduction in breakdown field strength may be due to an excess of oxygen within the films. But although the oxygen content increases as the growth temperature increases, the presence of arsenic in oxides grown at high temperatures seems to inhibit the effect of oxygen. Therefore it is likely that two competitive breakdown mechanisms operate in films grown thermally on gallium arsenide.

If arsenic is necessary for high breakdown field strengths, then it follows that the breakdown field strength of pure gallium oxide is low
and less than $2.5 \times 10^5 \text{ V} \cdot \text{cm}^{-1}$. Accordingly, the relatively high values measured for thin films grown at $510^\circ \text{C}$ (figure 5.15a) and at $465^\circ \text{C}$ (figure 5.15b) indicate that arsenic is present, possibly in the interface regions, and that it contributes towards the measured breakdown field strengths.

6.4.3. Resistivity.

Because resistivity measurements were made only on oxides grown at $510^\circ \text{C}$, any conclusions which are drawn from the results are limited and unsupported by evidence from films grown at other temperatures. Nevertheless, the calculated resistivities of the films are much lower, at $10^9 - 10^{11} \ \Omega \ \text{cm}$, than the values of $10^{14} - 10^{16} \ \Omega \ \text{cm}$ of anodic oxides. This implies, again, that lack of arsenic contributes to poor electrical properties, but as $10^9 - 10^{11} \ \Omega \ \text{cm}$ is similar in magnitude to that of oxides grown in high temperature plasmas, this explanation cannot be substantiated. However oxides grown at high temperatures on gallium arsenide have a different structure to those grown below about $700^\circ \text{C}$ and may contain GaAsO$_4$. Also, the resistivity of pure Ga$_2$O$_3$ is around $10^7 \ \Omega \ \text{cm}$, i.e. lower than the above values. Consequently, even though films grown at $510^\circ \text{C}$ are predominantly Ga$_2$O$_3$, they appear to contain sufficient quantities of impurities which increase their resistivities by up to four orders of magnitude.

If the assumption that any arsenic in films grown at $510^\circ \text{C}$ resides at the oxide-substrate interfaces is correct, then the resistivity would be expected to decrease towards the value for pure oxide as the contribution of the interface region diminishes. Figure 5.14 shows that this may occur in the case of thin films, but as the oxygen content of thick films increases the resistivity follows suit.
6.4.4. Dielectric loss factor.

Differences between the compositions of oxides grown on gallium arsenide are believed to be responsible for dissimilar measurements of the electrical properties of the films. This view is confirmed by the spread in values of the dielectric loss factors (tan δ) which were obtained from individual films and from films grown at the same temperature, (table 5.7). Measurement errors, which are less than ± 6%, are insufficient to account for these variations.

There is a correspondence between the values of tan δ (figure 5.17b) and the relative widths of the oxide-substrate interface regions (figure 5.9). Both parameters decrease as the growth temperature of the films increases. Consequently the interface regions may be the lossy parts of the system. This possibility is supported by the results from oxides grown at 510°C which show a similar correlation between variations of tan δ (figure 5.17a) and variations in the relative widths of the interfaces (figure 5.13).

It is intimated in the discussions on the breakdown field strengths (section 6.4.2) and resistivities (section 6.4.3) of the films that arsenic resides at the interfaces and affects the electrical parameters. The above comparisons between tan δ and relative interface width substantiate this view and suggest further that the arsenic ions are mobile. Therefore, when arsenic ions are immobilised the dielectric losses decrease. If this is correct, the relatively low dielectric loss of the 20 channel thick film grown at 510°C (figure 5.17a) can be explained on the basis of it having a low concentration of mobile arsenic ions.
6.4.5. Dielectric constant.

Although the values of dielectric constant are the most inaccurate of the electrical parameters, the trend indicated by the average values for films grown for $1 \frac{1}{2}$ hours (figure 5.18b) demonstrates that they increase with growth temperature and reach a value of about 5.5. This increase shows that the dielectric constants are related inversely to both the dielectric loss factors (figure 5.17b) and the relative interface widths (figure 5.9) of the films. The latter is further evidence that the interface regions of the oxides affect the electrical measurements significantly.

If the films are regarded as double layer dielectrics - of oxides and interface regions - then the measured value of the dielectric constant would be expected to increase and approach the true value of the oxide as the relative width of the interface decreases.

Notwithstanding the large errors involved in the measurement of dielectric constant, there are inverse correlations also between variations in the dielectric constant and variations in the breakdown field strength, both for films grown for $1 \frac{1}{2}$ hours and for those grown at 510°C. The relationship between these parameters is strengthened by the changes which occurred as a result of annealing. Whenever capacitance increased, breakdown voltage decreased. However, the opposite did not always occur and further discussion on this point is made later in section 6.4.12.

The values of the dielectric constants given in figures 5.18(a) and 5.18(b) tend to be lower than the maximum value of 7 to 8 of anodic films\textsuperscript{12} but some are close to the figure of 6.4 for plasma films\textsuperscript{55}. But anodic oxides can have dielectric constants as low as 3.9\textsuperscript{9}. Therefore the lack of arsenic may not be the reason for the low values of films grown thermally.
6.4.6. Dielectric dispersion.

The variation of dielectric constant with frequency, as measured by the changes in capacitance (figure 5.19), lends support to the belief that mobile ions, which respond to low frequency a.c. signals, are present within the films.

The higher dispersion above 10 KHz for films grown above 510°C (figure 5.20) may be due to the charging and discharging of fast traps.

Both of the above observations and explanations are consistent with the results from C-V measurements which are considered in the section below.

6.4.7. Variation of capacitance with voltage.

The variation of device capacitance with applied voltage, as shown in figure 5.21, is typical of MOS devices (34). However, the inability of the devices to go into deep inversion appears to be due to the oxides breaking down at relatively low voltages, notwithstanding the fact that most of the applied voltages are taken up across the semiconductors.

6.4.8. Field induced hysteresis.

The suggestion made previously that mobile ions exist within the films grown at 510°C whilst their numbers reduce and trap density increases as the growth temperature increases, appears to be supported by the measurements of field induced hysteresis.

The calculations are only qualitative indications of the hysteresis
shown by films grown at 510°C (table 5.9), but they can be used to compare the suitability of oxides for device applications. In this respect the results point to there being an optimum temperature of about 610°C for the production of films having no hysteresis (section 5.6.2(9)).

The origin of the mobile ions and traps within the films seems to be associated with the growth mechanism. This aspect is considered later in section 6.4.11.

6.4.9. Flat band voltage.

The flat band voltages of between about zero and -2.5 volts of those devices which were measured (table 5.9), are much lower than the value of about +15 volts of anodic oxide devices (81). This is a major difference between native oxides grown by the thermal and anodic methods which may signify that the net defect density caused by surface states (section 3.3.2) fixed charges (section 3.3.3) and space charges (section 3.3.4) is significantly less in thermal oxides than in anodic oxides.

6.4.10. Donor density.

The differences between the measured densities of the donors in the gallium arsenide beneath the oxides and the nominal donor density stated by the manufacturer of the material may be due to oxygen, which induces deep level traps 0.4 eV below the conduction band and 0.65 eV above the valence band (34). Such traps would capture donated carriers thereby reducing the concentration of electrons available for conduction. However, the density of donors in bulk material can vary throughout an ingot and
across the surface of a slice. Therefore the results can be taken only as a guide to the mechanism involved. Moreover, there are indications that surface preparation affects the density of the donors.

6.4.11. The origin of mobile ions and traps.

The presence of mobile ions and traps within the films is believed to be responsible for much of the electrical phenomena of thermally grown oxides. If this is true, then the formation of these defects must be associated with the growth mechanism of the films and the electrical measurements should be consistent with the growth mechanism. This does appear to be the case.

Because gallium has both a higher oxidation potential (section 3.6.5) and a lower electronegativity (66) than arsenic, oxygen combines selectively with gallium leaving arsenic as unbonded ions. If oxidation takes place at the interface (section 6.3.6) then the arsenic would remain within the vicinity at low temperatures. However, as the growth temperature increases it would diffuse away from the interface and through the film. Whilst travelling towards the surface it is able to combine with indiffusing oxygen owing to the absence of unbonded gallium. On reaching the surface the arsenic oxide would evaporate. Consequently at this stage, the growth rate of gallium oxide would be reduced owing to less oxygen reaching the interface. Therefore, reductions in the oxide growth rate and concentration of mobile arsenic ions would occur simultaneously. Further increases in temperature cause arsenic to dissociate at the interface and diffuse away more rapidly than oxygen indiffuses - thereby creating vacancies which act as electron traps.

The effect that annealing has on the electrical parameters appears to be complicated and difficult to explain. Some annealing after growth is necessary in order to avoid short circuits which may be due to pin holes in the films. The slow cooling method used in this investigation seems to have overcome this problem although the initial slow formation of the films might have been responsible.

It is seen from the measurements made on films before and after annealing that, at a suitable temperature, the breakdown field strength of a particular film may be improved. However, this is accompanied by a reduction in its value of dielectric constant. Likewise, an improvement in the dielectric constant is accompanied by a degradation of the breakdown field strength. This is consistent with the general trend which shows an inverse correlation between variations in these two parameters, as mentioned in section 6.4.5. It was not possible to increase both of these parameters, but they could be reduced simultaneously.

The annealing effects seem to be associated with changes in the composition of the oxides and interface regions of films annealed both before and after the deposition of electrodes. In the latter case some effects may be due to migration of metal ions (aluminium) into the oxide and, or alternatively, to the electrodes inhibiting any evaporation of arsenic.

Although only a few experiments were performed, they appear to show that it is unlikely that any low temperature anneal procedure will improve the electrical properties of the films sufficiently to make them suitable for use as device dielectrics.
6.4.13. Summary of the electrical properties of oxides.

The discussion on the electrical results has covered a wide range of parameters. Below is a summary of the electrical properties of the oxides and the factors which influence them.

The results appear to show that:

(a) The electrical properties vary due to variations in the compositions of the films.
(b) The interface regions between the substrates and oxides influence the measured values.
(c) The breakdown field strength is about \(2.5 \times 10^5\) V.cm\(^{-1}\). Immobile arsenic within the interface region may increase this value by a factor of about five.
(d) The resistivities of the films are higher than that of pure \(\text{Ga}_2\text{O}_3\). This may be due to excess oxygen within the films and, or alternatively, to small amounts of arsenic within the interface regions.
(e) Variations in the dielectric loss factor show some correlation with variations in the oxygen content of the films, but, in addition, there are indications that the interface regions are the lossy parts of the system.
(f) Generally, the dielectric constant is low. The average value is about 2.5, but rises to about 5.5 when the film contains an excess of oxygen and, or alternatively, immobile arsenic.
(g) The dielectric constant is high when breakdown field strength is low and vice versa.
(h) The dielectric dispersion is high at low frequencies owing to mobile ions. It is negligible at high frequencies for films grown at 510°C, but it increases with growth temperature due to the formation of traps.
Mobile ions cause field induced hysteresis in films grown below about 600°C whilst at higher temperatures it is due to the formation of traps.

The flat band voltages of MOS devices are low and negative (between approximately zero and -2.5 volts).

Oxygen causes trapping in the semiconductor beneath the interface and may compensate up to about 50% of the impurity donors.

Gallium arsenide MOS devices with thermally grown oxide dielectrics are in accumulation under zero and forward bias and in depletion under reverse bias up to about half of the reverse breakdown voltage. They do not go into a deep inversion condition owing to the low breakdown voltages of the oxides.

Mobile ions and traps are the result of unbonded arsenic which builds up at the interface at low temperatures and diffuses away at high temperatures.

Low temperature annealing fails to improve the electrical properties.

6.5. Conclusions from the investigations into native oxides.

The investigations into the characteristics of native oxides grown thermally on gallium arsenide have shown that the growth mechanism is complex and the electrical properties appear to be influenced by the interface regions and compositions of the oxides.

Arsenic seems to play an important role in the oxidation process, particularly in the initial stages and at temperatures above about 515°C when it may evaporate and cause the oxidation rate to reduce. Also, its presence in the form of mobile ions is almost certainly responsible for high dielectric losses, frequency dispersion and field induced hysteresis, but its low concentration within the films is the reason for their low
breakdown field strengths.

In general, it has been shown that the electrical properties are not as good as those of films grown either by anodic or plasma oxidation techniques and, mainly because of their low breakdown field strengths, they appear to be unsuitable as gate dielectrics of field effect devices.

The oxides grown below 500°C were thin and, consequently, their electrical properties were influenced by relatively wide interface regions. It is probable that thicker films grown at low temperatures have different properties, but longer growth times would be necessary to form films of a reasonable thickness.

Ion implantation prior to oxidation is a known technique which can influence the growth rate of oxide films on materials and it was thought that it could have benefits in the case of gallium arsenide. Moreover, it may be possible to produce foreign or mixed oxides which possess good dielectric properties.

The following chapter deals with the preliminary investigations which were made into implanted gallium arsenide and the results obtained therefrom.
Chapter 7.

THE EFFECT OF IMPLANTATION ON THE THERMAL OXIDATION OF GaAs.

7.1. Introduction.

7.1.1. General.

The conclusions reached from the discussion in the previous chapter show that native oxides suitable for GaAs devices cannot be grown by the thermal technique used in these investigations. As a consequence of this, experiments were carried out in order to establish if any improvements can be obtained from ion implantation.

This chapter covers those aspects of implantation which are relevant to this study.

7.1.2. Oxidation of implanted materials.

Many examples are available to show that ion implantation is an effective means of changing the oxidation rate of materials. However, most of the work in this field has been concerned with the corrosion of metals and alloys and has shown that, in general, the oxidation mechanism of implanted material is different from that of conventional alloys.

With the possible exception of anodically and thermally oxidised aluminium, and thermally oxidised FeCrAl alloy, the Wagner-Hauffe rules (section 3.4) are not obeyed by implanted materials, but, prior to this investigation of gallium arsenide, there was no general theory explaining
the oxidation behaviour of different materials after the implantation of a particular ion species. In the case of aluminium, Towler et al (28) found a correlation between the rate of anodic oxidation and the valence of the ion species, and Butcher (26) came across a similar relationship when aluminium and FeCrAl alloy were oxidised thermally. However, when the concentration of the impurity ions exceeded about 10% of the aluminium content of the alloy the ionic radii of the ions appeared to be the important parameter affecting the oxidation rate.

In contrast to the behaviour of implanted aluminium, no relationship between the valence of implanted ions and their effect on oxidation rate seems to exist when other materials are oxidised thermally. From investigations into the manner in which ions affect titanium and stainless steel, Dearnaley et al (82) have found a possible relationship between the electronegativity of the implanted species and oxidation rate, but more recent measurements by Benjamin and Dearnaley (83) point to the oxidation of titanium being related more accurately to the heat of formation of impurity oxides with ion size being a further contributory factor. Moreover, although the oxidation rate of copper was found by Morris (30) to be influenced by electronegativity, the size of the implanted ions is believed, again, to have an effect.

It is possible that ion size is responsible for surface strains and changes in surface topography which Goode (84) suggests influence the oxidation behaviour of nickel. A similar effect is attributed by Weidman (25) to the creation of cracks and pores within an oxide film grown on Zirconium. Although Nomura and Hirose (29) have shown that this is not so in the case of silicon, Muhl et al (85) believe that implantation damage is the dominant factor in the oxidation of chromium but suspect that the oxidation potential of the ions may be important.
7.1.3. Factors affecting the implantation of gallium arsenide.

The species of ions selected for this investigation have atomic masses ranging from 7 to 82. Consequently the common projected range to which the ions could be implanted into gallium arsenide was about 750 Å. This arises from the limit of the mass-energy product of 45 a.m.u.-MeV and instability below energies of 40 KeV of the Surrey University 600 KeV heavy ion accelerator (70).

During implantation the ions create lattice damage within the material which is decreased when the implantation is carried out at an elevated temperature. Subsequent annealing of the material for a short time at a higher temperature minimises the effects of residual lattice damage and a high percentage of the implanted ions are activated electrically.

By implanting each species of ion at the same dose level, differences in the oxide growth rates cannot be due to variations in the numbers of ions of the various species, providing the encapsulating oxides (ref. section 7.3) grow to the projected range of the ions and remove half of the ions. This ideal situation is not achieved unless the effects of implantation on the growth of the encapsulants are known. Therefore any preliminary results are influenced by variations in the concentrations of the ions. Nevertheless, providing the encapsulating oxides do not remove all of the ions, the results will indicate which ion species affect the oxidation rate.
7.2. Implantation of ions.

7.2.1. Ion species.

The series of ion species selected for implantation are shown in table 7.1 together with their relevant parameters (86). The five species having an electronegativity of 1.8 are part of the largest series in the periodic table, whilst the other eight have electronegativities ranging from 0.8 to 4.0. The cation radii of the ions range from 1.13 to 0.07 Å.

7.2.2. Ion energy.

The energy required to implant ions to the projected range is governed by the theory of Lindhard, Scharff and Schiott (the LSS theory), an outline of which is given in several publications concerned with ion implantation (67,68,69). Energy-range values based on LSS theory have been computed by Johnson and Gibbons (87) and the energies necessary to implant the ions to the desired projected range in gallium arsenide were obtained from their tables.

7.2.3. Experimental procedure.

Doses of $1.10^{15}$ ions cm$^{-2}$ of the species listed in table 7.1 were implanted into the (100) surfaces of $n/n^+$ epitaxial samples of gallium arsenide to a projected range of approximately 750 Å by the Surrey 600 KeV accelerator.

Implantation of the most abundant isotope of each species took place at the energies listed in table 7.2 with the samples at 200°C in a vacuum of about $5.10^{-7}$ torr. The normals of the samples were orientated at 8° to
the beam line to minimise channeling and the currents employed were between 0.04 and 0.4 μA cm\(^{-2}\).

Table 7.1. Ion parameters (86).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ni</th>
<th>Tl</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
<th>F</th>
<th>N</th>
<th>Se</th>
<th>Te</th>
<th>Mn</th>
<th>Al</th>
<th>Ca</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_i )</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>4.0</td>
<td>3.0</td>
<td>2.4</td>
<td>2.1</td>
<td>1.5</td>
<td>1.5</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>( r_i (\AA) )</td>
<td>0.62</td>
<td>0.95</td>
<td>0.93</td>
<td>1.12</td>
<td>0.84</td>
<td>0.07</td>
<td>0.11</td>
<td>0.42</td>
<td>0.56</td>
<td>0.80</td>
<td>0.50</td>
<td>0.99</td>
<td>1.33</td>
</tr>
<tr>
<td>( r_n (\AA) )</td>
<td>0.72</td>
<td>1.40</td>
<td>0.53</td>
<td>0.71</td>
<td>1.20</td>
<td>1.36</td>
<td>1.71</td>
<td>1.98</td>
<td>2.21</td>
<td>0.46</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( r_c (\AA) )</td>
<td>1.15</td>
<td>1.48</td>
<td>1.22</td>
<td>1.01</td>
<td>1.47</td>
<td>0.72</td>
<td>0.75</td>
<td>1.16</td>
<td>1.36</td>
<td>1.17</td>
<td>1.18</td>
<td>1.74</td>
<td>2.03</td>
</tr>
<tr>
<td>( r_a (\AA) )</td>
<td>1.24</td>
<td>1.71</td>
<td>1.37</td>
<td>1.62</td>
<td>1.75</td>
<td>-</td>
<td>0.92</td>
<td>1.40</td>
<td>1.60</td>
<td>1.35</td>
<td>1.43</td>
<td>1.97</td>
<td>2.35</td>
</tr>
<tr>
<td>Z, M</td>
<td>28</td>
<td>81</td>
<td>32</td>
<td>50</td>
<td>82</td>
<td>9</td>
<td>7</td>
<td>34</td>
<td>52</td>
<td>25</td>
<td>13</td>
<td>20</td>
<td>19</td>
</tr>
</tbody>
</table>

\( E_i = \) electronegativity \( r_i = \) ionic radius \( r_c = \) covalent radius
\( r_a = \) atomic radius \( Z = \) atomic number \( M = \) atomic weight

Table 7.2. Implant energy of ions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>( \text{Ni}^+ )</th>
<th>( \text{Tl}^{2+} )</th>
<th>( \text{Ge}^+ )</th>
<th>( \text{Sn}^+ )</th>
<th>( \text{Pb}^{2+} )</th>
<th>( \text{F}^+ )</th>
<th>( \text{N}^+ )</th>
<th>( \text{Se}^+ )</th>
<th>( \text{Te}^+ )</th>
<th>( \text{Mn}^+ )</th>
<th>( \text{Al}^+ )</th>
<th>( \text{Ca}^+ )</th>
<th>( \text{K}^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (KeV)</td>
<td>165</td>
<td>207</td>
<td>190</td>
<td>280</td>
<td>207</td>
<td>55</td>
<td>40</td>
<td>200</td>
<td>300</td>
<td>160</td>
<td>80</td>
<td>120</td>
<td>115</td>
</tr>
<tr>
<td>Isotope mass</td>
<td>58</td>
<td>205</td>
<td>72</td>
<td>120</td>
<td>208</td>
<td>19</td>
<td>14</td>
<td>78</td>
<td>128</td>
<td>55</td>
<td>27</td>
<td>40</td>
<td>39</td>
</tr>
</tbody>
</table>
7.3. Post implantation processing.

It is mentioned in section 7.1.3 that post implantation annealing is required to activate electrically the implanted ions. But in order to prevent the surfaces of the samples dissociating at high temperatures it is necessary to cover the surfaces with a suitable encapsulant. D'Cruz (65) has shown that an efficient encapsulant for gallium arsenide is a native oxide film covered with evaporated aluminium. After annealing in nitrogen at 700°C for 4 hour the film is removed with hot dilute HF.

The native oxide encapsulants used in these experiments were grown in dry flowing oxygen at 510°C for 26 hours by the method given in section 4.3.2. The films were nominally 1125 Å thick (figure 5.10) and extended approximately to the projected range of the implanted ions.

Following their growth, the films were covered with evaporated aluminium and then annealed.

After the encapsulants had been removed the samples were cleaned in deionised water and dried with a spill moistened with methanol.

The encapsulating procedure left about half of the implanted ions within the gallium arsenide. The quantity of ions remaining depended on the influence they had on the growth rates of the encapsulating oxides and on their behaviour during oxide growth and annealing. However, only in the case when the ions cause a large increase in the oxidation rate would all the ions be consumed and removed by the encapsulating oxide thus leaving the samples devoid of implanted ions.
7.4. Oxidation procedure.

The processed samples were oxidised again for 2½ hours at 510°C. Three samples were oxidised at a time, together with an n-type (110) bulk sample which was used for calibration purposes. In one case an unimplanted (100) epitaxial sample, which had been processed as in section 7.3, was included so that a comparison could be made between implanted and unimplanted samples of the same surface orientation and material.

7.5. Oxide thickness measurements.

The oxides formed on the samples were analysed by Rutherford back-scattering (section 4.4) and their thicknesses calculated in terms of the channel numbers of the interface and surface edges of the gallium arsenide spectra. This method introduces a possible error of ±10 channels in the thickness measurement due to the uncertainty in identifying the element of the interface edge. However, as it is the ratio of two such measurements which is required, the overall error is reduced to a maximum of ±15%.

7.6. Results and analysis.

7.6.1. Ratio of oxide thicknesses formed on implanted and unimplanted gallium arsenide.

The ratios (R) of the thicknesses of the oxides formed on implanted and unimplanted (100) epitaxial samples were calculated. The resulting values are given in table 7.3.
Table 7.3. Ratio (R) of oxide thickness formed on annealed implanted and unimplanted n/n+ (100) epitaxial GaAs oxidised for 2½ hours at 510°C. Implanted dose = $1.10^{15}$ ions cm$^{-2}$.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ni</th>
<th>Tl</th>
<th>Ge</th>
<th>Sn</th>
<th>Pb</th>
<th>F</th>
<th>N</th>
<th>Se</th>
<th>Te</th>
<th>Mn</th>
<th>Al</th>
<th>Ca</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>0.86</td>
<td>1.19</td>
<td>1.05</td>
<td>1.28</td>
<td>1.10</td>
<td>1.38</td>
<td>1.38</td>
<td>1.18</td>
<td>1.12</td>
<td>0.97</td>
<td>0.84</td>
<td>0.87</td>
<td>1.38</td>
</tr>
</tbody>
</table>

7.6.2. Analysis of results.

(a) Introduction.

The results have been analysed by comparing the oxide thickness ratios (R) with certain parameters of the ions. The parameters are those which other workers have considered in attempts to relate them with the effects induced by ions on the oxidation rates of various materials.

(b) Comparison of results with ion parameters.

Table 7.4 lists the parameters and their values for each species of ion implanted into gallium arsenide. Column 2 of the table gives the ions in the order of their effect on the oxidation rate.

No correlations between variations in the oxidation rate and variations in the parameters of the ions are apparent from table 7.4. This may be because of variations in the concentrations of the species present in the samples after the encapsulation procedure (section 7.3) and/or possible errors of $\pm 15\%$ in the calculated values of the oxide ratios.
<table>
<thead>
<tr>
<th>(1) Oxide Ratio (A)</th>
<th>(2) Ion</th>
<th>(3) Valence</th>
<th>(4) Atomic mass</th>
<th>(5) Atomic radius (Å)</th>
<th>(6) Covalent radius (Å)</th>
<th>(7) 1st ionisation energy (V)</th>
<th>(8) Heat of formation of oxide (Kcal/Mol)</th>
<th>(9) Standard oxidation potential (V)</th>
<th>(10) Electronegativity</th>
<th>(11) PE work function (eV)</th>
<th>(12) Ionic radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.43</td>
<td>F</td>
<td>+7</td>
<td>19</td>
<td>-</td>
<td>0.72</td>
<td>4.02</td>
<td>5.5</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>1.76</td>
</tr>
<tr>
<td>1.38</td>
<td>K</td>
<td>+1</td>
<td>39</td>
<td>2.35</td>
<td>2.03</td>
<td>1.00</td>
<td>86</td>
<td>2.92</td>
<td>0.8</td>
<td>2.15</td>
<td>1.33</td>
</tr>
<tr>
<td>1.38</td>
<td>N</td>
<td>-3,+5</td>
<td>14</td>
<td>0.92</td>
<td>0.75</td>
<td>3.66</td>
<td>14.6</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>1.71</td>
</tr>
<tr>
<td>1.28</td>
<td>Sn</td>
<td>+2,+4</td>
<td>119</td>
<td>1.62</td>
<td>1.41</td>
<td>1.69</td>
<td>138</td>
<td>0.14</td>
<td>1.8</td>
<td>4</td>
<td>1.11</td>
</tr>
<tr>
<td>1.19</td>
<td>Ti</td>
<td>+1,+3</td>
<td>204</td>
<td>1.71</td>
<td>1.48</td>
<td>1.41</td>
<td>42</td>
<td>0.34</td>
<td>1.8</td>
<td>3.7</td>
<td>1.05</td>
</tr>
<tr>
<td>1.18</td>
<td>Se</td>
<td>-2,+6</td>
<td>79</td>
<td>1.4</td>
<td>1.16</td>
<td>2.23</td>
<td>1.56</td>
<td>0.78</td>
<td>2.4</td>
<td>5.0</td>
<td>1.08</td>
</tr>
<tr>
<td>1.12</td>
<td>Te</td>
<td>-2,+6</td>
<td>128</td>
<td>1.6</td>
<td>1.36</td>
<td>2.03</td>
<td>0.51</td>
<td>2.1</td>
<td>4.4</td>
<td>-</td>
<td>2.21</td>
</tr>
<tr>
<td>1.10</td>
<td>Pb</td>
<td>+2,+4</td>
<td>195</td>
<td>1.75</td>
<td>1.47</td>
<td>1.71</td>
<td>0.13</td>
<td>1.8</td>
<td>4.1</td>
<td>-</td>
<td>0.84</td>
</tr>
<tr>
<td>1.05</td>
<td>Ge</td>
<td>+2,+4</td>
<td>72</td>
<td>1.17</td>
<td>1.22</td>
<td>1.27</td>
<td>23</td>
<td>1.28</td>
<td>-</td>
<td>1.8</td>
<td>4.5</td>
</tr>
<tr>
<td>0.97</td>
<td>Mn</td>
<td>+2,+7</td>
<td>55</td>
<td>1.35</td>
<td>1.17</td>
<td>1.71</td>
<td>90 to 0.27</td>
<td>1.18</td>
<td>1.5</td>
<td>3.7</td>
<td>0.93</td>
</tr>
<tr>
<td>0.87</td>
<td>Ca</td>
<td>+2</td>
<td>40</td>
<td>1.97</td>
<td>1.74</td>
<td>1.41</td>
<td>152</td>
<td>2.87</td>
<td>1.0</td>
<td>2.8</td>
<td>0.99</td>
</tr>
<tr>
<td>0.86</td>
<td>Ni</td>
<td>+2,+3</td>
<td>59</td>
<td>1.24</td>
<td>1.15</td>
<td>1.76</td>
<td>58</td>
<td>0.25</td>
<td>1.8</td>
<td>4.5</td>
<td>0.72</td>
</tr>
<tr>
<td>0.84</td>
<td>Al</td>
<td>+3</td>
<td>27</td>
<td>1.43</td>
<td>1.18</td>
<td>1.33</td>
<td>399</td>
<td>1.66</td>
<td>1.0</td>
<td>3.7</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Table 7.4: Comparison between ion parameters and oxidation rate.
Nevertheless, the results appear to confirm the conclusion which can be deduced from the published data (section 7.1.2) that no single ion parameter is responsible for changing the oxidation rate of implanted materials.

Only in the cases where the oxide ratio is greater than 1.15 or less than 0.85 (i.e. when the results are outside the experimental errors) is it certain that implantation had an effect on the oxidation rate. Consequently, of the 13 species of ions implanted, only fluorine, potassium, nitrogen, tin, thallium and selenium ions have been shown to affect the oxidation rate, and these ions caused an increase. However, the order of their effects cannot be established and, indeed, the results may be distorted owing to variations in the concentrations of the ions due to the encapsulating oxides.

None of the results prove that the oxidation rate was reduced by ion implantation. But it is statistically unlikely that the results for implanted calcium, nickel and aluminium ions all have the maximum error and, therefore, probably at least one of these species caused the oxidation rate to reduce.

Notwithstanding the errors involved in the results, they appear to show a trend which suggests that both electronegativity and ionic radius are the parameters of the implanted species which influence the oxidation rate. This trend is seen in figure 7.1 where a plot of oxide ratio (R) against electronegativity (E) indicates that the results lie approximately on parallel lines of constant ionic radius.

If the ionic radii of the ions are identified correctly, then figure 7.1 suggests (a) that \( R' \) increases as the electronegativity of ions of constant radius increases, and (b) that \( R' \) increases as the ionic radius of ions of
constant electronegativity increases. This apparent dependence of the oxidation rate on these two parameters may account for the high rates of oxide growth caused by potassium (which has a low electronegativity and large cation radius) and by nitrogen and fluorine (which have large electronegativities and small cation radii) whilst calcium, aluminium and nickel (which have relatively low ionic radii and electronegativities) cause only small changes in the oxidation rate.

![Diagram](image)

**Fig. 7.1** Effect of electronegativity of implanted ions on the oxidation rate of gallium arsenide.
The results obtained by oxidising implanted gallium arsenide have shown that the oxidation rate can be changed by ion implantation. It is certain that the rate can be increased and probable that the rate can be reduced. This may lead to the quality of oxide films being improved if suitable ions are implanted prior to oxidation and the oxidation temperature reduced (e.g. for nitrogen - when a nitride compound may form) or the temperature increased (e.g. possibly for aluminium - when an aluminium oxide may form).

When the results are taken at their face values they point to the probability that the ionic radius and electronegativity of the implanted species are responsible for changing the oxide growth rate. However, no definitive relationship between these factors can be deduced owing to doubts about the valence states and the concentrations of the ions. These doubts could be eliminated by repeating the experiments using multi-energy implantations so that the concentrations of the ions are constant with depth, and using a better method of encapsulation (e.g. deposited Si$_3$N$_4$) during annealing so that an oxide encapsulant need not be grown. Also, analyses of the oxides by methods other than Rutherford backscattering (e.g. T.E.M.) may indicate the valence states, and hence the ionic radii, of the ions. In addition, an increase in the implanted doses by a factor of ten, i.e. to $10^{16}$ ions cm$^{-2}$, would affect the oxidation rates to a greater extent and permit the relative thicknesses of the films to be measured with greater accuracy.
Conclusions.

The rate at which gallium arsenide oxidises is affected by implantation of foreign ions. Whilst it has been shown that certain ions enhance the oxidation rate, e.g. potassium, nitrogen and fluorine, others – e.g. calcium, nickel and aluminium – may cause a reduction. These effects may be due to the electronegativities and ionic radii of the implanted species.
Chapter 8.

CONCLUSIONS.


The properties of native oxides grown thermally on gallium arsenide for 1 hour at temperatures between 350°C and 760°C and at 510°C for periods up to 3 hours have been investigated using Rutherford back-scattering analysis and electrical measurements. In addition, the effect of ion implantation on oxidation at 510°C has been studied and the ion parameters responsible for changes in the oxide growth rate appear to have been identified.

It has been shown that the oxide growth mechanism over the range of temperature used is complex and is associated probably with the formation of different polymorphs of Ga₂O₃. Although no differences were measured between the oxidation rates of conventionally doped 'n' and 'p' type materials (in which the carrier concentrations are about 10¹⁷ to 10¹⁸ cm⁻³), a significant difference exists between those of (100) and (110) surfaces when the growth temperature is between about 515°C and 700°C. This is one of three temperature ranges between 350°C and 760°C which have been identified as being significant in the oxidation mechanism.

Measurements from native oxides grown for 1½ hours have shown that growth is exponential with temperature up to about 520°C and that the activation energy of formation is 1.25 ± 0.15 eV. The amount of oxidation taking place at 350°C is negligible whereas growth at 450°C appears to commence by the evaporation of arsenic from the surface and the creation
of islands of gallium oxide. Oxide growth at 510°C is parabolic for film thicknesses up to about 1000 Å and it is concluded from the evidence of diffusion 'tails' in the backscattered spectra of the oxygen that growth occurs owing to the indiffusion of oxygen. However, films about 1000 Å thick grew sometimes at enhanced rates and contain excess oxygen. This is believed to be due to cracks, which occur because of strains within the films, or to grain boundaries permitting a rapid indiffusion of oxygen. In such cases the oxides grew at a linear rate.

The maximum growth rate of native oxides occurs at temperatures of about 550°C for (110) surfaces and of about 515°C for (100) surfaces. Small quantities of arsenic are detectable at the surfaces of films grown at and above 525°C and the growth rate diminishes to a minimum at about 550°C and 675°C on (100) and (110) surfaces respectively. These two phenomena appear to be linked to the formation of different polymorphs of Ga₂O₃ and to the diffusion and evaporation of arsenic.

The main constituent of oxides grown at temperatures above about 700°C appears to be orientated polycrystalline β-Ga₂O₃. This oxide may be less susceptible than other possible polymorphs to arsenic indiffusion.

Thermally grown native oxides have electrical properties which are influenced by the interface regions between oxides and substrates as well as by the composition. In general, their properties are inferior to those of anodically and plasma grown films.

The results indicate that a high concentration of arsenic is necessary for oxides to have high breakdown field strengths.

All thermally grown films show a high dispersion with frequency
in their capacitances at low frequency while at high frequencies the
dispersion is negligible for films grown at 510°G, but it increases as the
growth temperature increases. Their dielectric constants at 1 MHz are low,
being on average about 3.5 but ranging up to about 5.5. Also, their
resistivities, which are between 10^9 and 10^{11} Ω cm, are low.

Generally, MOS devices having thermally grown oxides were found to
possess field induced hysteresis. This is due to mobile ions in the films
grown below about 600°G and to traps in the films grown at higher
temperatures. The flat band voltages of the devices were always negative
and between about zero and -3 volts. Under larger negative bias potentials
the devices were in the depletion mode but did not go into deep inversion
owing to breakdown of the oxides. Under forward bias they were in the
accumulation mode.

Two further important facts which have emerged from the electrical
measurements are that low temperature annealing of the films seems unlikely
to improve their characteristics sufficiently for them to be used as the
dielectrics of electronic devices, and the thermal oxidation technique does
not appear to affect seriously the carrier concentration in the gallium
arsenide beneath the oxides.

Because the electrical characteristics of thermally grown native
oxides render them unsuitable for device fabrication, a preliminary
investigation was made into implanted material.

A series of ion species was implanted into n-type epitaxial gallium
arsenide and the effects on the growth of surface oxide films were measured.
The results from this investigation show that ion implantation does alter the oxidation rate. Significant increases were obtained by the implantation of potassium, nitrogen and fluorine ions, whilst calcium, aluminium and nickel ions might have caused small reductions. These variations in the oxidation rate may be due to the electronegativities and ionic radii of the implanted species, rather than because of implantation damage which was minimised by implanting and annealing at elevated temperatures.

8.2. Future work.

Although this project has resulted in a clearer understanding of the factors involved in the properties of oxides grown thermally on gallium arsenide, the picture is far from complete. None of the problems associated with the formation of thermal oxides suitable for use in devices have been solved. Consequently much work still needs to be done. Below are a few suggestions for future work into aspects of thermal oxidation which seem to need investigating.

The isothermal growth mechanism of oxides on (110) and (100) surfaces at temperatures lower and higher than $510^\circ$C needs to be established, in particular that at low temperatures where films with better electrical properties may be grown.

A more detailed analysis of the composition and structure of thermally grown films ought to be made so as to clarify the reasons for different growth mechanisms operating over (a) different temperature ranges, (b) different oxide thicknesses and (c) surfaces of differing orientations.
In the field of implanted gallium arsenide, further measurements of the oxidation rate of the material implanted with doses of about $10^{16}$ ions cm$^{-2}$ are necessary before the parameters responsible for changing the oxidation rate can be identified positively. Although there appears to be a trend in the results which suggests that electronegativity and ionic radius are influential, the ionic radius of the implanted species needs to be determined by techniques such as transmission electron microscopy. Investigations into the electrical properties of the oxides may provide information as to their suitability as gate dielectrics of devices.

A further line of research which may have practical implications is into films produced by ion bombardment with large doses of oxygen. Such films should be amorphous and contain equal quantities of gallium and arsenic. Consequently their electrical properties should be inherently superior to those grown thermally at high temperatures.

The End.
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