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Thermal Oxidation of III-V Compound Semiconductors

O.R. Monteiro (Ph.D. Thesis)

November 1988

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Thermal Oxidation of III-V Compound Semiconductors

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Othon do Rego Monteiro Neto Ph.D. Thesis

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November 1988

Thermal Oxidation of III-V Compound Semiconductors

Othon do Rego Monteiro Neto November 1988

Ph.D.

Materials Science and Mineral Engineering

Abstract

Thermal oxidation of III-V compound semiconductors has been studied in the temperature range of $300^{\circ}C$ to $600^{\circ}C$. Two members of this class of materials, namely InP and GaAs, were the object of the experimental work carried out here. The main analytical tools used were transmission electron microscopy (TEM) and secondary ion mass spectroscopy (SIMS). TEM was employed to access microstructural changes and SIMS to access the composition redistribution that takes place as a consequence of the oxidation reaction.

Below 400° C oxidation of both materials led to the formation of amorphous scales, which consisted of a mixture of gallium and arsenic oxides in the case of GaAs, and indium phosphate and oxide in the case of InP. The oxidation kinetics of InP was found to be slower than that of GaAs.

In the high temperature regime, i.e. above $400^{\circ}C$, the oxidation of both materials resulted in crystalline products. Precipitation of the group V element at the scale/semiconductor interface took place during oxidation. At the GaAs/Ga₂O₃ interface, As precipitates were formed with a truncated square pyramid shape bound by $\{111\}_{GaAs}$ planes. These precipitates are such that $\{0003\}_{As}$ // $\{111\}_{GaAs}$ and $< 11\overline{20} >_{As}$ // $< 110 >_{GaAs}$.

The precipitates found at the $InPO_4/InP$ interface were either a phosphorus rus rich phase or red phosphorus. Strong vaporization under the electron beam

prohibited a more accurate determination. The morphology of those precipitates were very similar to the As ones in GaAs.

Thermal oxidation of GaAs initially led to the formation of an epitaxial film of γ -Ga₂O₃. As the film thickened, it became polycrystalline and finally transformed into β -Ga₂O₃, which is thermodynamically more stable. Some As₂O₃ and As₂O₅ crystallites are also formed as a result of the oxidation reaction, and they were found dispersed in the gallium oxide matrix. The epitaxial γ -Ga₂O₃ and the parent GaAs are oriented relative to each other such that $\{110\}_{GaAs} // \{110\}_{\gamma-Ga_2O_3}$ and $< 001 >_{GaAs} // < 001 >_{\gamma-Ga_2O_3}$.

Thermal oxidation of indium phosphide produced an epitaxial film of InPO₄ and some In₂O₃. The latter is believed to be the result of incongruent vaporization that takes place at temperatures higher than $362^{\circ}C$, and accounts for some loss of phosphorus to the atmosphere. Epitaxial indium phosphate formed with $\{110\}_{InP}$ // $\{110\}_{InPO_4}$ and $< 001 >_{InP}$ // $< 001 >_{InPO_4}$. The symmetries of these phases imply the existence of four twin related variants of this orientation relationship.

Dopants were shown to affect the kinetics of oxide growth in GaAs. Ntype materials produced thicker oxide layers than chromium and undoped materials. Also, arsenous oxide were found more frequently when the latter group of materials were oxidized. A tentative explanation for this effect was provided. It assumes the oxide film to be a n-type semiconductor, and that electron trasnport through the oxide film plays an important role in the reaction kinetics.

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Although the research that leads to a PhD dissertation is sometimes a lonely effort, there are a number of persons that have contributed for the completion of this work. Initially I would like to express my gratitude to Prof. Jim Evans, my research advisor for this work, for his guidance and support. I am also grateful to Prof. Eicke Weber and Prof. Dennis Hess who patiently read this thesis and provided constructive criticisms. I wish to extend my gratitude to Professors T. Devine, R. Gronsky and F. M. Doyle, and Drs. K. Westmacott and U. Dahmen with whom I had enlightening discussions.

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Chapter 1

Introduction

The importance of III-V compound semiconductors has been early recognized [31]. These materials are amenable to forming p-n homo and heterojunctions, and thus have practical use in electronics. III-V compounds and their alloys can be prepared with direct energy gaps ranging from the infrared (InSb) to the yellow-green $(In_{0.27}Ga_{0.73}P)$. This makes these materials useful as lasers and light emitters [16]. In the ternary or quaternary systems, such as $Al_xGa_{1-x}As$, $GaAs_xP_{1-x}$, $In_xGa_{1-x}P$, $Al_xGa_{1-x}P$ and $In_xGa_{1-x}P_xAs_{1-x}$, the band structure can be varied continuously from direct to indirect energy gap. Some III-V compounds have been successful as materials for field effect transistors due to their high carrier drift velocity.

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The synthesis and material technology of such compounds are more complicated than that of elemental semiconductors[32]. Large differences in physical properties of the elements in the group III and those of group V require stricter processing conditions in order to obtain the ideal characteristics of the final device. This, consequently, leads to higher costs.

In device technology, a process of utmost importance is the growth of a dielectric layer over the semiconductor material. Insulating dielectric layers used for III-V compounds can be classified as homomorphic or heteromorphic. Homomorphic dielectric layers are those produced by oxidation or ion implantation, while heteromorphic layers are those which are deposited from a vapor phase by means of pyrolisis reactions or sputtering. In the former, the only extraneous added element

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is oxygen, and the atoms of the substrate take part in the reaction forming the dielectric layer. In the case of heteromorphic layers, the substrate atoms do not participate in any reaction, and the dielectric is entirely made of extraneous atoms. This thesis is concerned with one of the processes used to produce homomorphic layers, namely thermal oxidation.

Research on the oxidation of III-V surfaces and on the properties of the resulting oxide layers has been directed towards two primary objectives [72,37,31]: passivation of the surfaces of discrete devices and ICs, and production of suitable gate insulators for MISFETs (Metal Insulator Semiconductor Field Effect Transistor). The evolution of MISFET technology requires a thorough understanding and precise technological control of the properties of the interface between the semiconductor and the dielectric layer. A comprehensive model of such interfaces is not available yet.

The purpose of this thesis is to study the thermal oxidation of III-V compound semiconductors. The focus was on the characterization of the microstructure developments that take place during the reaction. On the other hand, in order to understand the changes in microstructure during oxidation, it was important to determine which species were moving during the oxide growth. Two particular compounds, namely GaAs and InP, were chosen for the experimental work because of their technological importance and conflicting information on their oxidation available in the literature. The review presented in the next chapter demonstrates that the processes that take place during the reaction are not fully understood, and therefore justified the research work that is described in this thesis.

This thesis is divided in six chapters. In chapter 2, a survey of the most relevant published work on thermal oxidation of GaAs and InP is provided. The disagreement between the referred results, and the inability to identify some important effects demonstrate the lack of understanding of the overall process. Chapter 3 provides a description of the experiments that had been designed to clarify the mechanism of the reaction. In chapter 4, the thermal oxidation of GaAs is first approached on a purely thermodynamic basis, and then the experimental results are described and discussed. After the determination of the moving species, a tentative

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CHAPTER 1. INTRODUCTION

model for the effect of the doping elements on the oxidation kinetics is provided. Chapter 5 contains the results on the thermal oxidation of InP. Finally, chapter 6 summarizes the results, and outlines the common features of the oxidation of the two compounds.

In the study of thermal oxidation of gallium arsenide, transmission electron microscopy was used to observe the reaction in-situ, as it occurs, as well as to analyze the post-oxidation microstructure. An effect of the dopants on the oxidation kinetics, not reported previously, was noticed. Secondary ion mass spectrometry confirmed this dopant effect. Marker experiments [52] were used to determine the species that migrate during the reaction. Finally, a rational for the effect of the dopants on the oxidation kinetics was proposed.

As for the thermal oxidation of indium phosphide, this study focussed on microstructural developments during the oxidation reaction. Precipitation of phosphorus or a phosphorus-rich phase at the InP/scale interface is first reported here. The findings in this research resolve the controversy on the reaction products that has been the subject of many studies summarized in chapter 2.

Finally, the O-lattice theory has been proved to be very successful in describing the scale/semiconductor interface. It was shown that, in the case of the compounds used here, the oxidation initially proceeds so that it minimizes interface energy between parent and product phase. The success of the O-lattice theory to describe interface characteristics allows the prediction of other features that would be otherwise difficult to determine.

Chapter 2

Previous Studies

2.1 Introduction

An important reason for the enormous success of silicon in semiconductor device technology is the ease of growing a native oxide with excelent dielectric properties. Thermally grown silicon dioxide is used in VLSI processing applications for several purposes: masking against ion implantation and diffusion, passivation of silicon surface, isolation of individual devices, use as a gate oxide in MOS devices, and use as a tunneling oxide in electrically alterable ROMs. Therefore it is not surprising that native oxides have been considered for similar use in processing devices of III-V compound semiconductors. This argument has been used by several workers [78,77,24,34,74,69,42,65,73,60,82] as the driving force for an extensive number of studies on methods to produce suitable oxides. Three major processes have been proposed – namely anodic, plasma and thermal oxidation.

Anodic oxidation consists of positively biasing the III-V compound with respect to an oxygen source. This technique has the advantage of flexibility and also results in layers with electrical properties that are generally superior to their thermal counterparts. Wet chemical anodization, involving the transport of oxygen atoms to the semiconductor surface from an electrolyte, is the simplest of all these techniques and has been implemented using a variety of solutions [36].

The anodic oxides and their interfaces have been found to be somewhat different

from the ones produced at high temperatures. Wilmsen [77] suggested three reasons for such differences:

- 1. The anodic oxides are grown near room temperature in a liquid electrolyte which usually contains water.
- 2. The oxides are grown faster than thermal oxides.
- 3. Anodic oxides are grown in a high electric field $(5 \times 10^6 V cm^{-1})$.

Szpak [67] has found some indication of an island growth mechanism for anodic oxides grown on GaAs at constant current in a tartaric acid/propylene glycol electrolyte. Interfaces in anodic oxides contained little or no excess of the group V element, and the bulk oxides were composed of significant concentrations (usually in a 1:1 ratio) of the oxides of both elements. Despite their low resistivity, anodically formed layers have been used to make a variety of device structures in the case of some III-V compounds.

Plasma anodization has also been used with some success to produce insulating layers for electronic devices. In this case the reactivity of the oxidation process is enhanced by locating the sample close to or inside an oxygen plasma discharge. This process is cleaner than the wet chemical anodization but far less simple and more expensive. Both anodization processes utilize low substrate temperatures whereas in thermal oxidation the substrate temperature is high.

Although varying in details, all oxidation methods suffer from the fact that two dissimilar elements with different oxidation rates and vapor pressures are being combined into one dielectric, and that, in general, severe inhomogeneities and nonstoichiometries are likely to result. Since the main subject of this work concerns thermal oxidation of GaAs and InP, detailed literature reviews of such areas are provided in sections 2.2 and 2.3 respectively. It is currently accepted that there is no general mechanism for describing thermal oxidation of the entire class of III-V materials. Moreover, for each particular compound, little is known about the oxidation reaction at high temperatures.

2.2 Thermal Oxidation of Gallium Arsenide

Minden [44] published one of the first articles on the thermal oxidation of GaAs. His work was followed by a series of others, which used a variety of experimental techniques to characterize the phases formed during the reaction [5,6,27,46,47,57,59,61,69,74,80]. Most of those publications are consistent with the following description of the oxidation process.

At low temperatures, i.e. below approximately $400^{\circ}C$, an amorphous phase slowly forms upon oxidation [5,27]. No composition analysis of such a product was provided. Since all the polymorphs of gallium oxides (α , β , γ , δ , ϵ) and arsenic oxides have intense lines with d-spacings lying within the broad amorphous rings found, it was believed that the amorphous layer consisted of a mixture of gallium and arsenic oxides [5].

At intermediate temperatures, i.e. between approximately $400^{\circ}C$ and $700^{\circ}C$, most of the previous work points to β -Ga₂O₃ as the main product [44,27,57]. Bull and Sealy [5] used transmission electron microscopy to characterize the oxidation products on an n-type (110) GaAs surface. The crystallographic relation between GaAs and β -Ga₂O₃ was found to be:

 $< 002 >_{\beta-Ga_2O_3} / / < 002 >_{GaAs}$

 $< 10\overline{2} >_{\beta-Ga_2O_3} / / < 1\overline{1}1 >_{GaAs}$

with some twinning about < 002 > at temperatures of $500^{\circ}C$ and above. This work failed to detect any arsenic containing phase among the products, even when the oxidation was carried out in arsenic saturated atmospheres. A more recent work [57] used lattice imaging to detect the presence of hexagonal arsenic crystallites at the oxide-GaAs interface. Those appeared to have a unique orientation relationship with the GaAs:

 $\{001\}_{As}//\{1\overline{1}1\}_{GaAs}$

 $< 110 >_{As} // < 110 >_{GaAs}$

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This work [57] studied the oxidation of (100) Si-doped GaAs and the major oxidation product found was γ -Ga₂O₃ rather than β -Ga₂O₃, and the oxide formed according to:

$$\{111\}_{\gamma-Ga_2O_3}//\{111\}_{GaAs}$$

$$<110>_{\gamma-Ga_2O_3}//<110>_{GaAs}$$

In-situ electron microscopy carried out by Hall et al. [27] has shown that oxidation of (001) n-type GaAs initially produces γ -Ga₂O₃, with the same crystallographic relation described by Sands et al. [57]. However, after sufficient time the γ phase transformed into β -Ga₂O₃. The latter is the thermodynamically stable form [63]. This work [27], however, failed to detect any arsenic containing phase in the oxide or at the interface.

Surface analytical techniques have been used to obtain concentration profiles of Ga and As [74,80] of oxidized GaAs as a means to characterize the reaction products. Proper interpretation of these results requires great care because the probe size usually employed (in the μ m or mm range) is large compared with interfacial features such as voids or precipitates. Therefore these techniques tend to overlook such microscopic features and provide results that are in fact averages over the probed region. Another source of difficulty is related to the fact that sputtering is carried out at constant bombardment rate , and it is assumed implicitly that this corresponds to a constant sputtering rate, although this is often not true.

Studies of thermal oxidation of gallium arsenide at temperatures higher than $700^{\circ}C$ have been more limited. This is partially due to the inability of GaAs to withstand such high temperatures without degrading. The products of the reaction under these circumstances consist of a combination of β -Ga₂O₃ and GaAsO₄ with increasing amounts of the latter as the temperature increases [69].

A summary of two kinetic studies on the oxidation of GaAs is presented in Figure 1. Murarka [46] has studied the oxidation in air at $350^{\circ}C$, $450^{\circ}C$, and $500^{\circ}C$ using polished (100) GaAs substrates. Measurements of oxide thickness were done by using a Talystep. A linear relation between oxide thickness and time was used to

fit the experimental data, without any consideration to the reaction mechanism. Butcher and Sealy [6] have studied thermal oxidation of (100) and (110) GaAs at temperatures of $450^{\circ}C$ to $760^{\circ}C$ using Rutherford Backscattering Spectroscopy. A parabolic growth law was found for oxide thickness smaller than 100 nm in (110) GaAs. Thicker oxides appeared to follow a linear growth.

Despite the large number of published work on thermal oxidation of GaAs [5,6,27,46,57,59] some fundamental points remain unresolved, thereby making impossible an accurate description of the overall reaction. Some of these points are the determination of the moving species during the oxide growth and the definition of the product phases. The experimental results presented in chapter 4 were obtained with the purpose of clarifying these points.

2.3 Thermal Oxidation of Indium Phosphide

Thermal oxidation of indium phosphide has been the subject of some studies where a number of surface analytical techniques were used to characterize the oxidation products [77,23,78,81,26,82,71,60], and the reaction kinetics [82,73]. Wilmsen [78]has determined the compositional profile of InP oxidized at $450^{\circ}C$ in dry oxygen. Excess phosphorus at the oxide-semiconductor interface was evident, in agreement with the Raman data by Schwartz et al. [60]. Due to the low solubility of P in InP, this excess phosphorous is expected to be accomodated as precipitates or another oxidic layer. However, no direct observation of either one of those has been reported. Recently, lattice imaging [49] has been used to observe the oxidation reaction; it failed to detect any P containing phase other than the InP substrate.

Wager and Wilmsen [73] have studied the growth rate and the chemical composition of thermally grown oxides in dry oxygen. The oxide was found to grow very slowly below $350^{\circ}C$, and rapidly above that temperature. All the oxides produced between $350^{\circ}C$ and $450^{\circ}C$ consisted of approximately 75% In₂O₃ and 25%P₂O₅. Some evidence of low concentration of another bonding state of P was also found [73]. Yamaguchi and Ando [82] studied the thermal oxidation of InP and the properties of the oxide films. They [82] concluded that the process is controlled by

CHAPTER 2. PREVIOUS STUDIES



Figure 1: Oxide thickness during thermal oxidation of gallium arsenide.

diffusion through a polycrystalline film made of In_2O_3 and P_2O_5 . This scale composition has been strongly disputed by Griffiths and co-workers [26], who reanalyzed Yamaguchi and Ando's infrared absorption data [82] to conclude that the dominant product above $620^{\circ}C$ was indium orthophosphate. Resistivities of the oxide films, measured at room temperature, ranged from 10^8 to 10^9 Ω cm, and decreased with increasing oxidation temperature and time. Such a decrease was attributed to the loss of P_2O_5 . A comparison between oxidation kinetics measured by Wager and Wilmsen [73] and Yamaguchi and Ando [82] is given in Figure 2

Simonne [62] has recently indicated that for MOS applications, oxidation temperatures should be kept below $350^{\circ}C$ to minimize substrate degradation. In this temperature range, he found $InPO_4$ and In_2O_3 as the resulting phase with excess phosphorus appearing at the oxide-semiconductor interface. The same reaction products were observed by Fathipour et al. [20] after photoenhanced thermal oxidation of InP between $200^{\circ}C$ and $400^{\circ}C$.

The literature survey summarized in the previous paragraphs indicated that a clear understanding of thermal oxidation of InP is still lacking. In chapter 5 some results of electron microscopy are presented, and should enhance the understanding of this reaction. The main points addressed are:

- Characterization of product phases
- Determination of the spatial distribution of the product phases
- Explanation of the crystallographic relations between the scale and the substrate

Thermal Oxidation of Indium Phosphide. Data from : M. Yamaguchi, J. Appl. Phys., 53(3), 1834(1982) and J. F. Wager and C. W. Wilmsen, J. Appl. Phys., 51(1), 812(1980).



Figure 2: Oxide thickness during thermal oxidation of indium phosphide

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Chapter 3

Experimental

3.1 Materials

The gallium arsenide used throughout this work has been kindly provided by Hewlett-Packard Optoelectronics Division and Morgan Semiconductors. Wafers were cut from crystals grown either by Liquid Encapsulated Czochralski (LEC) or by Horizontal Bridgman (HB) techniques [10,33]. Although the latter technique can produce ingots with very low dislocation densities, LEC has become the most viable growth process for use in GaAs production facilities.

(001) undoped, silicon-doped, tellurium-doped and chromium-doped gallium arsenide were used as starting materials for the oxidation studies. Silicon and tellurium are common doping elements for making n-type gallium arsenide. The former can be intentionally added, or be present due to some dissolution of the silica crucible. Chromium has been used for many years as a midgap electron trap for compensating shallow donors such as silicon [17,18]. Its use, however has recently decreased with the advent of semi-insulating GaAs. The dopant concentration of each kind of GaAs is given in Table 1.

The indium phosphide used in this study was obtained from Crystacom Inc. (Mountain View, CA). It was a (001) wafer from a LEC grown ingot. No intentional dopant was added.

Fable 1: Dopant	concentration	in	GaAs	
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undoped GaAs	$\leq 10^{15} cm^{-3}$
Si-doped GaAs	$2.2 \times 10^{18} cm^{-3}$
Te-doped GaAs	$2.0 imes 10^{18} cm^{-3}$
Cr-doped GaAs	$3.0 imes 10^{15} cm^{-3}$

3.2 Thermal Oxidation

3.2.1 In-situ

In-situ thermal oxidation in this work refers to the oxidation carried out inside a high voltage electron microscope (HVEM). The two microscopes used for this purpose are a HITACHI HU650 and a KRATOS EM1500 available at the National Center for Electron Microscopy, Lawrence Berkeley Laboratory. Both microscopes are equipped with an environmental cell (e-cell) and a single-tilt hot-stage specimen holder. The e-cell allows to produce a controlled atmosphere around the specimen, while the specimen holder brings the sample to the desired temperature. Hence, reactions between gases and solids can be directly observed and continuously followed, with specimen temperature, gas pressure and gas composition as controllable parameters. The e-cell used in this study was designed by Swann and Tighe [66,7] and it is schematically presented in Figure 3. The entire set up for the in-situ oxidation is shown in Figure 4. A detailed description of the e-cell operation wil not be given here since it is available elsewhere [53].

Oxidations were carried out by initially flooding the specimen chamber with the desired gas mixture, and then raising the temperature to its intended value. In the oxidation experiments, pure O_2 and Ar/O_2 mixtures were used. In some instances, the specimen was brought to the oxidation temperature in the presence of pure Ar, and then O_2 allowed in the e-cell. These two procedures yielded indistinguishable results when the time at which the specimen was kept at high temperature and in an inert atmosphere was small. Annealing in inert gas atmosphere was also performed for comparison with the oxidation experiments. The conditions at which in-situ

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Figure 3: Schematic representation of the side-entry environmental cell used in this study



- 1. gas mixture
- 2. transducer
- 3. digital flowmeter
- 4. gate valve
- 5. needle valve
- 6. gate valve

- 7. pressure gauge
- 8. E-cell
- 9. thermocouple
- 10. power supply
- 11. HVEM
- 12. to mechanical pump

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Figure 4: Schematic representation of the set up for in-situ oxidation.

$T(^{\circ}C)$	Atmosphere	Presurre (torr)
300	vacuum	10 ⁻⁵
300	N_2	10
300	O ₂	10
300	O ₂	20
400	vacuum	10 ⁻⁵
400	N_2	10
400	O ₂	10
400	O2	20
500	vacuum	10^{-5}
500	N_2	10
500	O2	10
500	O_2	20
500	O ₂	40
600	vacuum	10 ⁻⁵
600	N_2	10
600	O ₂	10
600	O ₂	20
600	O ₂	40

Table 2: Experimental Conditions of In-situ Oxidation

oxidations were performed are described in Table 2

Temperature measurements during the experiments do not correspond accurately to specimen temperature, since the thermocouple was attached to the specimen holder, and not to the foil itself. The temperature difference between the furnace and the specimen has been measured by connecting a thermocouple to a nickel grid in the furnace under vacuum. The results, shown in Figure 5 from reference [53], indicated a deviation increasing with temperature. No calibration curve was obtained in the case of gas flowing, but it was assumed that the difference between the actual specimen temperature and the temperature reading was about the same as in the case of no gas. The accuracy of these measurements is further hindered because of the specimen heating due to the electron beam [7].

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3.2.2 Ex-situ

In contrast with in-situ oxidation, ex-situ oxidation here refers to the oxidation performed outside the environmental cell, and which produced materials that required further preparation in order to become observable in a TEM. Ex-situ thermal oxidation was carried out in a quartz tubular furnace, with temperature and gas composition as controllable parameters.

The need for performing ex-situ experiments is twofold. It was important to evaluate whether there would be a difference between the results from the two procedures. It has been reported [7] that in some instances artifacts may result when a very thin foil is oxidized. The second reason for conducting ex-situ oxidation was the need for producing samples that could be used for further cross section TEM and in-depth concentration analyses. Transmission electron microscopy of cross sections of oxidized samples provides complementary information to that obtained from planar view TEM. Also, measurements of the oxide layer thickness from cross section samples, although tedious, is very accurate.

The conditions employed for the ex-situ oxidation are listed in Table 3 for both GaAs and InP. Oxygen partial pressures in the in-situ experiments were substantially lower than in the ex-situ. Pressure inside the e-cell could not be raised above 100 Torr because of loss of contrast due to electron scattering in the gas phase. In order to verify whether such a pressure difference had any effect on the product phases two procedures were taken:

- 1. A few thin foils were oxidized ex-situ and then analyzed.
- 2. Some thin foils were oxidized inside the e-cell at atmospheric pressure, but with the high voltage turned off during the oxidation, and analysed a posteriori.

These experiments showed no detectable difference between the products obtained from the in-situ and the ex-situ oxidations.

$T(^{\circ}C)$	Atmosphere	Presurre (torr)
300	N ₂	760
300	O_2	760
300	O_2	152
400	N_2	760
400	O ₂	760
400	O_2	152
500	N_2	760
500	O_2	760
500	O ₂	152
600	N_2	760
600	O2	760
600	O ₂	152

 Table 3: Experimental Conditions of Ex-situ Heat Treatments

3.3 Specimen Preparation for T.E.M.

Transmission electron microscopy is a very powerful technique to analyze transformations in materials. It was used in this thesis to characterize the oxidation reactions of GaAs and InP. Three different ways of sample preparation were used in order to obtain the most information from oxidized samples, as it is shown in Figure 6. The first type of samples, shown in Figure 6a, was used for the in-situ oxidation. They were prepared from unoxidized (001) wafers. The wafers were polished with emery paper, 6μ m and 1μ m diamond paste until a foil 150 μ m thick was obtained. Three millimeters discs were cut from this foil, and a dimple made on one side, so that perforation almost occurred (thinnest region about 20 μ m). Final thinning was carried out in a 2% bromine-methanol solution, until electron transparent regions were produced.

The second type of samples for TEM, shown in Figure 6b, was prepared in a similar way, however the starting material was the oxidized wafer. In order to preserve the oxide layer the final chemical thinning was replaced by ion-milling. During TEM analyses of the samples just described, a and b in Figure 6, the oxide/semiconductor interface is normal to the electron beam. This allows the observation of structural defects at the interface such as misfit dislocations. A difficulty associated with this method is that the oxide and the semiconductor are imaged overlapping each other.

The third type of sample used in the TEM analyses is shown in Figure 6, and is such that the oxide/semiconductor interface is nearly parallel to the electron beam. Therefore, the oxide film can be imaged without benig superimposed on the substrate. This method is commonly referred to as cross-section TEM (XTEM), and is the most appropriate to determine how the interface behaves as the reaction front advances. This method is also useful in studying the nucleation and growth of precipitates at the scale/semiconductor interface.

Specimen for electron microscopy of cross section samples were prepared from wafers that had been oxidized according to the conditions described in Table 3. A procedure similar to that proposed by Bravman and Sinclair [4] was used. Oxidized GaAs and InP wafers were cleaved along {110} planes and the resulting slabs joined by the {001} oxidized surfaces with "M-BOND 610 ADHESIVE" (Measurements Group, Rayleigh, NC 27611). The assembly was then polished from both parallel {110} sides until about 200 μ m thick. At this point the specimen was glued to a grid with an oval opening, which provided mechanical strength to further polishing. Final thinning of the GaAs were performed by Argon ion bombardment at 5 kV for GaAs and 4 kV for InP, while cooling the samples with liquid nitrogen. In the case of InP, ion milling was possible only for very short times (less than 30 min), and this required much thinner specimens. No chemical means was acceptable in the preparation of cross section samples because of the different solubilities of the several phases.

3.4 Marker Experiments

Marker experiments have been successfully used to determine the transport number of species involved in oxidation of metals and semiconductor materials [52]. It consists basically of observing the shift of the oxide/gas and the oxide/substrate interfaces with respect to an immobile plane located inside the oxide film. These




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experiments were used here to determine the moving species during the thermal oxidation of GaAs. This information is necessary in order to postulate a microscopic model for the reaction.

Once the oxidation reaction starts, the oxidizing gas and the GaAs are separated by the oxide layer. In order for the reaction to proceed, either Ga and As, or oxygen, or both must be transported across this oxide film. Five possible mechanisms[52] may, in general, occur:

- 1. The cations migrate alone, and the reaction to form the new oxide occurs at the oxide/oxygen interface.
- 2. The oxygen migrates alone and the reaction occurs at the GaAs/oxide interface.
- 3. Both cations and oxygen migrate simultaneously, and the reaction can take place at the two interfaces.
- 4. Both cations and oxygen migrate simultaneously, and the reaction occurs inside the oxide.
- 5. Both cations and oxygen migrate simultaneously, and the reaction takes place at both interfaces and inside the film.

Figure 7 from reference [52] shows schematically the several possible results in a generic marker experiment. Mechanisms 4 and 5 should result in the broadening of the marker peak, whereas 1 through 3 should not. If mechanism 1 is predominant, the markers should stay at the oxide/GaAs interface, and if mechanism 2 is the predominant, they should stay at the surface.

The choice of suitable markers is very important in this experiments. Ideally, the marker should not interfer with the oxidation process, i.e. it should be inert. Some interference, however, is inevitable, but size and concentration of the markers should be kept small in order to minimize its effects. Also, a marker should be immobile. Xe has been proved to satisfy these requirements to a good extent [21,48], and therefore was used as the marker here.



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Figure 7: Effect of cation and oxygen migration on the position of inert immobile markers in an oxide film. Roman numerals index the five possible mechanisms discussed in the text and the resulting marker profiles are shown at the side of each diagram

¹³¹Xe ions with energy of 40 keV were implanted in undoped GaAs with a dose of 1.1×10^{14} cm⁻². Transmission electron microscopy of cross-section samples of Xe-implanted GaAs was used to verify that no extended defects were produced as a result of the implantation process. The low implantation energy was necessary in order to minimize damage, which could affect the oxidation, and to place the maximun ¹³¹Xe concentration at about 15 nm inside the GaAs with a projected straggle of 5 nm. Implanted samples were oxidized at 400°C and 600°C for up to 4 h and analyzed for Xe and As by SIMS. The As peak was used to show the oxide/GaAs interface.

3.5 Analytical techniques

3.5.1 Transmission electron microscopy

Transmission electron microscopy is a technique whereby thin foils can be imaged by a beam of electrons with energy high enough to cross the foil. Besides images, this technique can provide information on the structure of the material being imaged. Since several books have extensively treated the subject [30,68,55,39], only the pertinent points that can help the interpretation of the results are discussed here.

A transmission electron microscope (TEM) basically consists of an electron source (electron gun) and an assembly of electromagnetic lenses. These lenses shape the electron beam, and magnify the image of the specimen region that has been illuminated. A schematic view of a TEM, borrowed from reference [30], is shown in Figure 8. Ray paths that account for image and diffraction pattern are indicated in this figure.

In conventional electron microscopy, the image is formed by one beam only, which is selected among all the spots in the back focal plane of the objective lens by placing an objective aperture at the appropriate place. This type of imaging is called amplitude contrast image, because it reflects the changes in amplitude of a specific spot. The resulting image is such that the regions that contribute to



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the selected spot appear bright and the other regions dark. Amplitude contrast image can be obtained by selecting the transmitted beam (spot in the objective lens back focal plane) or any of the diffracted beams. The image obtained with the transmitted beam is called bright field image and the one obtained with a diffracted beam is called dark field image.

The interaction between high energy incident electrons and the specimen inside an electron microscope also produces X-rays that are characteristic of the "illuminated" region. Spectrometry of these X-rays provides information of the chemical content within that particular region. This is the basis of Energy Dispersive X-ray analysis (EDS or EDX). Extensive descriptions of this technique are readily available [39,76]. The smaller the size of the incident electron beam (electron probe), the more localized the analysis will be. In today's microscopes, probes with diameter of 10 nm are ordinarily obtained.

Four electron microscopes were used in this study: two with high voltage (HVEM) and two with low voltage. High voltage (500 kV in the HITACHI HU650 and 1500 kV in the KRATOS) is required for the study of gas-solid reactions in-situ to reduce electron scattering by the gas phase. It also allows the use of thicker samples, which are more representative of the bulk phenomena than the ordinary thin foils used in low voltage electron microscopy. The low voltage microscopes (100 kV) were used primarily for cross-section samples (Phillips 301) and for chemical analyses (Phillips 400).

3.5.2 Secondary ion mass spectroscopy

Secondary ion mass spectroscopy (SIMS) has become a powerful and popular technique for impurity analysis in semiconductors. It has high sensitivity, allowing one to measure concentrations of the order of 10^{-14} cm⁻³ (ppb), and ease of obtaining concentration versus depth profiles. Good reviews of SIMS have been published by Deline [14] and Reed [54]. A good review of SIMS applications has been given by Zinner [83].

The method uses low energy ionized atoms to bombard a surface, whose atoms are ionized and ejected (sputtered) from the material. The "secondary ions", as

opposed to the primary ions used for the bombardment, are analyszed by mass spectrometry. The resulting ion intensity (in counts per sampling time, as measured by the mass spectrometer) versus sputtering time data is converted to concentration versus depth data by means of appropriate calibration techniques.

The primary beam is usually Ar^+ , O_2^+ or Cs^- , depending on the electronegativity of the species to be analyzed. The energy of this beam is relatively low (1-15 keV) so that damage to the matrix material is minimized. The complexity of the sputtering process imposes several limitations on the resolution of both concentration and depth determinations. This leads to uncertainties regarding the accuracy of the values and profile shapes measured.

There are a few steps that should be taken in order to minimize the above mentioned problems. An effective way to convert ion intensity to elemental concentration is to use standard samples in which the concentration of a desired element in the matrix material is known, and obtain the conversion factor for that particular system. A standard can be made by implanting a known total dose of the desired element into the matrix material. Then by integrating the SIMS ion intensity time profile and comparing it to the total dose (and knowing the size of the sampled area), one can obtain a counts-to-atom conversion factor. This number is multiplied by the atomic density in the solid of one of the matrix elements (e.g. As in GaAs) and then divided by the ionic intensity of that element for that profile. This takes into account the fact that the ion intensity value - which is in counts per sampling time - depends on the sputtering rate of that particular analysis. Therefore, each time an analysis is made, the same conversion factor is used; one just measures the matrix ion intensity value at the end of the sputtering and uses this and the modified conversion factor to make the conversion from intensity to concentration.

Inaccuracy in depth measurements is another factor to be considered. One problem is a variable sputtering rate, which may be caused by features such as inclusions, precipitates and thin films on the matrix. If, for example there is a region of enhanced sputtering, then the measured depth will be smaller, and the measured concentration will be higher than the actual values. There is no general way to correct for this. Deal [13] suggested that one should be able to say whether

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this effect is occurring by simultaneously profiling a matrix element, and observing whether its concentration changes. In the case studied here, i.e. of oxide films on a substrate, Deal's procedure [13] is not effective, and the use of supplementary analytical techniques, such as TEM, was necessary to interpret SIMS results.

Another source of difficulties in the determination of concentration profiles with SIMS is the crater that is created by the sputtering process. As the crater gets deeper, the primary beam becomes defocussed, and the crater area may change. This may affect the sampling area, and therefore the results. In addition, atoms from the side of the crater may sputtered and counted as coming from much deeper regions. These two effects are minimized by using a laterally controlled beam, which raster out a larger crater, and an aperture that allows sampling only from a small area at the center of the crater.

A CAMECA IMS 3F SIMS system, from Charles Evans and Associates (Redwood City, CA) was used for the analysis of the oxidized GaAs. Oxygen ion bombardment and positive ion mass spectrometry were employed to obtain Cr, O and As distribution profiles in the Cr-doped GaAs. Oxygen ion bombardment was also used for the Xe-implanted samples in the marker experiments. Cesium ion bombardment and negative ion mass spectrometry were used to profile O, As and either Si or Te in the respectively doped samples. The beam size was $75\mu m$ in diameter, and rastered an area of $500\mu m \times 400\mu m$, and the sampling area was $75\mu m^2$. The sputtering time-to-depth calibration was determined by measuring the depth of the SIMS crater after each analysis with a stylus profilometer. A micrograph of the crater, shown in Figure 9, indicates that it is very uniform, as required for reliable analyses.





Chapter 4

Thermal Oxidation of Gallium Arsenide

4.1 Thermodynamic analysis

Table 4 presents the calculated free energies of some relevant reactions that may take place during the thermal oxidation of GaAs. These calculations used literature values of free energy data for each individual species [75]. Table 5 shows the equilibrium oxygen pressure for the corresponding reaction, calculated assuming that that the other species were present at unit activity.

Reaction	no.	$400^{\circ}C$	$500^{\circ}C$	$600^{o}C$
$2 \text{ GaAs} + 4 \text{ O}_2 \rightarrow \text{Ga}_2\text{O}_3 + \text{As}_2\text{O}_5$	(1)	-1325	-1245	-1166
$2 \operatorname{GaAs} + 3 \operatorname{O}_2 \rightarrow \operatorname{Ga}_2\operatorname{O}_3 + \operatorname{As}_2\operatorname{O}_3$	(2)	-1212	-1157	-1103
$2 \text{ GaAs} + 3/2 \text{ O}_2 \rightarrow \text{Ga}_2\text{O}_3 + 2 \text{ As}$	(3)	-735	-702	-672
$2 \ \mathrm{GaAs} + \mathrm{As}_2\mathrm{O}_3 \rightarrow \mathrm{Ga}_2\mathrm{O}_3 + 4 \ \mathrm{As}$	(4)	-259	-246	-242
2 GaAs + $3/5$ As ₂ O ₅ \rightarrow Ga ₂ O ₃ + $16/5$ As	(5)	-382	-377	-377
$2 \text{ GaAs} + 3 \text{ As}_2\text{O}_5 \rightarrow \text{Ga}_2\text{O}_3 + 4 \text{ As}_2\text{O}_3$	(6)	-873	-894	-915

Table 4: Free energy of reaction (kJ)

Reaction no.	400° C	500°C	600° C
(1)	$1.3 imes 10^{-24}$	$6.8 imes 10^{-19}$	$2.3 imes10^{-15}$
(2)	$3.8 imes10^{-29}$	$6.1 imes10^{-24}$	$7.6 imes10^{-20}$
(3)	$6.8 imes10^{-36}$	$1.5 imes10^{-29}$	7.6×10^{-25}

Table 5: Equilibrium partial oxygen pressure (torr)

Based on the values displayed in Table 4, a significant portion of the Ga-As-O ternary phase diagram was deduced, and is shown in Figure 10. Although there are some allotropic variations of the compounds considered, a lack of free energy data made the choice of the species almost straightforward. The phases considered were As_2O_3 (arsenolite), β -Ga₂O₃ and orthorhombic As_2O_5 . It was assumed that, at equilibrium, these condensed phases are essentially pure in all the reactions with the other phases. This assumption results in a ternary diagram that consists entirely of straight lines connecting one phase to another. These lines are called pseudobinary lines.

Figure 10 agrees partially with the phase diagram proposed by Thurmond et al. [69]. It differs only in ignoring the presence of $GaAsO_4$. The following reasons justify the omission of $GaAsO_4$ from the phase diagram:

- 1. No evidence of formation of $GaAsO_4$ has been found in the experiments described in this work, as it is shown later.
- 2. $GaAsO_4$ has been reported to form only at temperatures higher than the ones of interest to this work [69,45].
- 3. There is no accurate data for the free energy of formation of $GaAsO_4$.

Based on Figure 10, the distribution of phases that are present upon different oxidation conditions can be described. Under strong oxidizing conditions, the outermost region of the scale should contain the most oxidized species, i.e. Ga_2O_3 and As_2O_5 ; the central region contain Ga_2O_3 and As_2O_3 ; and the innermost contain Ga_2O_3 and As. Under intermediate oxidizing conditions, the scale should consist of an external



Figure 10: Calculated Ga-As-O phase diagram. It was assumed that the solid phases were totally immiscible in each other.

layer containing Ga_2O_3 and As_2O_3 and an internal layer containing Ga_2O_3 and As. Finally, if the oxidation is carried out in weakly oxidizing conditions, only a layer containing Ga_2O_3 and As should form. In all cases, the high vapor pressure of As and its oxides affects the relative amount of the phases present, and complicate the description of the oxide film.

According to the data presented in Table 5, the experimental conditions used here, and described in Tables 2 and 3, should be considered strong. Therefore a scale consisting of three layers should be expected. Most of the previous studies on thermal oxidation of gallium arsenide described in the previous chapter were also performed under strong oxidizing conditions, although only a few have detected arsenic oxides. This failure should be attributed to either loss during the high temperature reaction or to the post-oxidation treatment to manufacture appropriate samples to be analyzed.

4.2 Electron microscopy results

4.2.1 Low temperature oxidation

At oxidation temperatures lower than $400^{\circ}C$ the primary oxidation product was an amorphous film, in agreement with the results of Bull and Sealy [5]. The nature of the oxide present, however, could not be unambiguously determined. Energy dispersive X-ray analyses have indicated it consists of a mixture of gallium and arsenic oxides. The in-situ experiments did not detect any difference in the behavior of the different types of GaAs oxidized in this temperature range.

Figure 11 shows a sequence of electron micrographs obtained when Si-doped GaAs is annealed at $400^{\circ}C$ and in the microscope vacuum (10^{-5} torr). Reaction times are given at the top right hand side of each micrograph. Diffraction patterns after 30 and 40 minutes indicated the presence of an amorphous film covering the entire surface of GaAs. The dark spots that appear in the micrographs at 30 and 40 minutes are arsenic precipitates, as it was determined later by TEM of cross section samples. These precipitates did not grow much bigger than it is shown even

for long oxidation times. Oxidation at higher pressures showed the same general behavior.

4.2.2 High temperature oxidation

At 500°C and 600°C, in-situ oxidation of undoped, silicon-doped and telluriumdoped gallium arsenide produced mainly Ga_2O_3 with some As_2O_5 . Although elemental As was not detected during in-situ oxidation, cross section samples of oxidized GaAs indicated that As is always present at the interface, as it will be shown later in this thesis. In the case of chromium-doped material, some As_2O_3 was detected in the oxide layer besides As_2O_5 and Ga_2O_3 . These findings suggest that the overall reaction can be written as

$$2GaAs + 4O_2 \Longrightarrow Ga_2O_3 + As_2O_5 + (As_2O_3 + As) \tag{1}$$

but it should be kept in mind that the phenomena involved in the oxidation are more complicated than equation 1 may suggest.

Figure 12 shows the oxidation of an undoped GaAs foil at $500^{\circ}C$ and 10 torr oxygen. Reaction times in minutes are given on the top left hand side of the bright field micrographs. The diffraction patterns shown correspond to the areas indicated by the arrows. The micrograph at time 0, which was taken at $500^{\circ}C$ but prior to starting the flow of oxygen, already shows some arsenic precipitates. Those were formed during the heating period. After 20 minute oxidation, the diffraction pattern indicates the presence of Ga₂O₃.

Gallium oxide initially forms in its cubic form γ -Ga₂O₃ in an unique orientation relationship with respect to GaAs, as Figure 13 indicates:

$$< 001 >_{GaAs} / / < 001 >_{\gamma-Ga_2O_3}$$

 $\{110\}_{GaAs} / / \{110\}_{\gamma-Ga_2O_3}$

This crystallographic orientation agrees with that found by Sands et al. [57] after oxidation of Si-doped GaAs at $500^{\circ}C$, and Hall et al. [27] for oxidation of



Figure 11: Sequence of TEM bright field images obtained during in-situ annealing of a Si-doped GaAs. Times, in minutes, are shown at the top right hand side of each micrograph (XBB 869-7871).



Figure 12: Sequence of TEM images and diffraction patterns obtained during in-situ oxidation of an undoped GaAs at $500^{\circ}C$ and 10 torr O₂. Reaction times in minutes are shown in each micrograph (XBB 869-7870).



Figure 13: Diffraction pattern of a planar view specimen of GaAs oxidized at $500^{\circ}C$ with the electron beam parallel to the $[001]_{GaAs}$. The large numbers correspond to the beams diffracted by the GaAs whereas the small numbers to beams diffracted by γ -Ga₂O₃ (XBB 882-1368).

Te-doped GaAs at $600^{\circ}C$. The sequence of diffraction patterns shown in Figure 14 indicates that the initial epitaxial oxide transforms into polycrystalline γ -Ga₂O₃ and subsequently into β -Ga₂O₃, according to the scheme below:

$$2 \ GaAs + 4 \ O_2 \Longrightarrow polycrystalline \ \beta - Ga_2O_3 + As \ products \tag{2}$$
$$\downarrow \qquad \uparrow$$

 $epitaxial \gamma - Ga_2O_3 \implies polycrystalline \gamma - Ga_2O_3$

According to equation (2), the growth of the oxide film proceeds in three stages, similar to the two stage mechanism proposed by Cathcart et al. for metal oxide films [3,9]. In the first stage, where the film is very thin, the characteristics of the oxide are determined primarily by the interfacial energy. As the oxide film gets thicker, the misfit energy of GaAs/oxide interface becomes less important, and the minimization of the energy per unit volume associated with strain determines the microstructure. This is accomplished initially by the formation of a polycrystalline γ -Ga₂O₃, which subsequently transforms into the more stable β -Ga₂O₃ [56].

 As_2O_5 crystallites dispersed in the gallium oxide layer were found during insitu oxidation at 500°C and 600°C. This is shown in Figure 15, where the As_2O_5 appears as the bright particles in the dark field image. It is worth mentioning that these particles did not last long at the oxidation temperatures under the electron beam because of their high vapor pressure. This may explain the failure to detect As_2O_5 in previous studies [57,6,27].

During the in-situ oxidation of chromium-doped gallium arsenide, formation of the gallium oxides followed equation (2), but As_2O_3 was also found in the oxide layer. This is presented in Figure 16, which shows a GaAs thin-foil oxidized at $500^{\circ}C$ and 2666 Pa (20 torr) of oxygen for 80 minutes. The dark field image (DF) in this figure was obtained using the As_2O_3 reflection indicated in the attached diffraction pattern. Therefore As_2O_3 particles appear bright in the dark field image.

Transmission electron microscopy of cross section samples of oxidized gallium arsenide allowed the characterization of the microstructure that resulted from the



Figure 14: Sequence of diffraction patterns obtained during in-situ oxidation of Te-doped GaAs at $500^{\circ}C$. Reaction times, in minutes, are given at the top right hand side of each pattern (XBB 882-1369).



Figure 15: Te-doped GaAs oxidized in-situ at $500^{\circ}C$ and 20 torr for 30 minutes. Dark field image (DF) was obtained with a As_2O_5 reflection, and shows this phase in bright contrast dispersed in the Ga_2O_3 (XBB 869-7873 A).

CHAPTER 4. THERMAL OXIDATION OF GALLIUM ARSENIDE



Figure 16: Cr-doped GaAs oxidized in-situ at $500^{\circ}C$ and 20 torr for 80 minutes. Dark field image (DF) was obtained with the As₂O₃ reflection indicated in the inserted diffraction pattern (XBB 869-7884).

oxidation reaction, and portrays a clearer picture of the product phases than the insitu observations. A great disadvantage is, however, the likelihood that the specimen preparation procedure may inadvertently alter the phases that one wants to observe. The fact that most of the studies using TEM have failed to detect arsenic oxide in oxidized GaAs [57,27,5] can be attributed to its loss during specimen preparation procedures.

A cross-section view of a Cr-doped GaAs oxidized for 2 hours at $600^{\circ}C$ is shown in Figure 17. A thin but continuous oxide (about 15 nm thick) covers the GaAs, with several voids between the two phases. Elemental As particles were also found at the interface between GaAs and the oxide film. Those particles are easily identified by the Moire fringes that results from the superimposition of As and GaAs cystals, as one can see in Figure 18

Some As loss to the atmosphere contributes to the increase of the void size at the interface. The continuity of the oxide film, as seen in Figure 17 suggests that, contrary to what hase been suggested previously [57], arsenic loss occurs by solid state diffusion through the oxide film. The presence of arsenic oxides dispersed in the film supports the idea that As should diffuse through the oxide film before vaporizing.

Analysis of the interface between As and GaAs using planar view samples for electron microscopy is complicated because it was not possible to remove the oxide film without also dissolving the As precipitates. Therefore one is faced with the problem of observing a stack of three different phases, with two superimposed interfaces. Besides this problem, the presence of voids at the oxide/GaAs interface and the variations in the oxide thickness make image interpretation quite difficult. However, some useful information could still be obtained.

The electron micrograph shown in Figure 19 was taken from an undoped GaAs that had been oxidized for 15 minutes at $600^{\circ}C$. The thin foil was oriented in the TEM so that the electron beam was close to a $\{001\}_{GaAs}$ zone axis, and in a perfect two-beam condition. Moire fringes resulting from interference of beams diffracted by $\{110\}_{As}$ and $\{220\}_{GaAs}$ are evident in the regions marked P. Those regions correspond to precipitates that were formed with a variant of the orientation



Figure 17: XTEM image of a Cr- doped GaAs after ex-situ oxidation for 2 hours at $600^{\circ}C$. Several voids are observable at the interface between GaAs and the oxide XBB 879-7479).



Figure 18: TEM image of a Te-doped GaAs oxidized at $500^{\circ}C$ in 10 torr oxygen for 2 hours. Moire fringes identify the As precipitates at the interface (XBB 889-8876).

relationship described below. The fringe spacing in those regions is 3 nm, which agrees well with the expected value of 3.1 nm of a parallel Moire produced by those two reflections.

The fringe pattern of distinct islands (precipitates) in Figure 19 are not all parallel. Fringes in precipitate A are, for instance, rotated from those in precipitates P, and its spacing is smaller. This effect probably results from the existence of four $\{111\}_{GaAs}$ planes that can give origin to the As precipitation. Precipitates with $(111)_{GaAs} // (0003)_{As}$ and $(11\overline{1})_{GaAs} // (0003)_{As}$, for instance, will produce fringes that are not parallel. The misalignment of epitaxial islands and Moire fringes in electron images of three dimensional islands have received some attention in the past years [43,25], and some general factors have been pointed out to explain the disturbance of Moires regularity. Mathews [43] suggested that misalignment may result from discrete changes in misfit strain that accompany the formation of misfit dislocations. Dislocations also produce distortions of the fringes, usually in the form of terminating fringes [30].

Transmission electron microscopy of cross-section samples have indicated that the As precipitates have facets along $\{111\}_{GaAs}$, as it is shown in Figure 20. Diffraction patterns of As and GaAs showed that these precipitates have a particular orientation relationship with respect to the GaAs substrate (Figure 21):

 $<110>_{GaAs}//<11\overline{2}0>_{As}$ $\{11\overline{1}\}_{GaAs}//\{0003\}_{As}$

This crystallographic relation agrees with the one found by Sands et al. [57] and Lee [35]. The dark contrast at the GaAs/As interface is due to elastic strains that result from the difference in lattice parameters between As and GaAs. The bending of the Moire fringes near the As/GaAs interface, observed in the XTEM micrographs, is another evidence of a strained interface. Lee [35] has suggested that no elastic strain should be present at a GaAs/As interface after As precipitation during annealing of As-rich GaAs. According to him [35], such an interfacial strain could be accomodated by a high concentration of point defects at the interface,



Figure 19: Bright field image of an undoped GaAs oxidized at $600^{\circ}C$ for 15 minutes. The thin foil is oriented with the electron beam near the $[001]_{GaAs}$ zone axis. Moire fringes show the As precipitates at the interface (XBB 889-8878).



Figure 20: Micrograph of a Cr-doped GaAs oxidized at $600^{\circ}C$ in 10 torr for 2 hours. As precipitates have facets along $\{111\}_{GaAs}$ and $\{001\}_{GaAs}$ (XBB 879-7473).



Figure 21: Convergent beam diffraction pattern of oxidized Te-doped GaAs showing the crystallographic relations between As precipitates and GaAs (XBB 889-8881).

namely gallium vacancies. The apparent discrepancy between his results and the ones presented here can be attributed to the size of the precipitates, which are much larger here.

Elastic strain at the GaAs/As interface may lead to the formation of twins during precipitate growth. Such a twin is shown in Figure 22 in the arrowed precipitates. The larger the precipitate, the more twins are expected to growth. Unfortunately the occurrence of such twins were quite rare, which made their complete characterization not possible. The fact that As is continuously lost during the oxidation, prohibited that larger As precipitates could be intentionally grown.

The morphology of the oxide film and of the interface changes with the oxidation temperature. Figures 22 and 23 show a cross-section view of a Te-doped GaAs oxidized for 2 hours in O_2 at $500^{\circ}C$ and $600^{\circ}C$ respectively. It is clear from these figures that the GaAs/oxide interface is flatter when oxidation was performed at the higher temperature. Precipitation of As at the interface is intense in both cases, although vaporization is more intense at higher temperatures.

Another piece of valuable information that could be obtained from the observation of cross-section samples is the thickness of the scale. It is obvious from Figure 22, as well as from the other cross-section results, that thickness measurements that are averaged over large areas contain some inherent inaccuracy due to the interface roughness. This roughness is of the same order of magnitude that the scale thickness itself. This may account, at least partially, for the discrepancy between the results of Murarka [46] and Butcher and Sealy [6],which are shown in Figure 1. According to measurements from micrographs of cross section samples, oxide grown on Crdoped GaAs was the thinnest among all the materials used in this stuty, whereas the ones grown on Te- and Si-doped materials were the thickest. SIMS results presented in the next section support these findings. A tentative explanation for this fact is given in the discussion of oxidation mechanism at the end of this chapter.



Figure 22: Bright field image of a Te-doped GaAs oxidized at $500^{\circ}C$ in 10 torr for 2 hours. The arrowed precipitate consists of two twin related As crystals (XBB 879-7480).



Figure 23: Bright field image of a Te-doped GaAs oxidized at $600^{\circ}C$ in 10 torr for 2 hours (XBB 879-7467).

4.3 Secondary ion mass spectroscopy

SIMS was used to probe the composition of the Cr, Si and Te-doped GaAs after ex-situ oxidation. Since the TEM results have shown a dependence of the oxide film thickness on the dopant type, it became important to determine how the dopant atoms behaved during the reaction. Concentration and ion-counts profiles are shown in Figures 24 through 32. The horizontal axes in these figures are the distance measured from the free surface of the oxide.

Figures 24 and 29 were obtained from samples that had not been oxidized, but contained a thin layer of native oxide (less than 3nm), which grows whenever a fresh surface of GaAs is exposed to air. Figure 24 is from a Si-doped material, and indicates that the Si concentration is fairly uniform, without any fluctuation at the surface. A small variation of the As content was detected near the surface, but that is within the experimental accuracy of the measurement. Cross sectional TEM did not detect any structural defect that could be associated with such a fluctuation.

Thermal oxidation of Si-doped GaAs result in profound changes in the distribution of the species, as Figures 25 and 26 indicates. The silicon content in the oxide layer after oxidation at $500^{\circ}C$ and $600^{\circ}C$ is about one order of magnitude larger than in bulk GaAs. The same is true for the Te-doped GaAs (Figures 27 and 28).

The ion count profiles of all the oxidized samples indicated an increase in As concentration at the GaAs/oxide interface. This increase corresponds to the hexagonal As precipitates shown in section on TEM results. The profile of As also indicates that its concentration within the oxide layer is small, but not negligible, and decreases with increasing temperature (compare Figures 27 and 28 or 25 and 26). This can be explained in terms of the increase of the equilibrium vapor pressure of the arsenic oxides with temperature [75].

The bulk concentration of Cr in the Cr-doped GaAs is at the detection limit of the spectrometer in depth profiling conditions. However, the increase in concentration near the surface is significant, and should not be neglected. An oxidation at extreme conditions, i.e. $600^{\circ}C$ for 24 h, indicated a remarkable increase in Cr concentration near the surface (Figure 32), up to a value above the detection limit



Figure 24: SIMS in-depth concentration profile of Si-doped GaAs



Figure 25: SIMS in-depth concentration profile of Si-doped GaAs oxidized at $600^{\circ}C$ for 2 hours. Two silicon isotopes were probed simultaneously, giving rise to the two Si curves shown. Concentration scale valid for Si and O curves only. As curve shown in arbitrary units.



XBL 8812-4115

Figure 26: SIMS in-depth concentration profile of Si-doped GaAs oxidized at $500^{\circ}C$ for 2 hours. Concentration scale valid for Si and O curves only. As curve shown in arbitrary units.



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Figure 27: SIMS in-depth concentration profile of Te-doped GaAs oxidized at $600^{\circ}C$ for 2 hours. Concentration scale valid for Te and O curves only. As curve shown in arbitrary units.




Figure 28: SIMS in-depth concentration profile of Te-doped GaAs oxidized at $500^{\circ}C$ for 2 hours. Concentration scale valid for Te and O curves only. As curve shown in arbitrary units.



Figure 29: SIMS in-depth concentration profile of Cr-doped GaAs. Concentration scale valid for Cr and ion counts scale valid for O.



Figure 30: SIMS in-depth concentration profile of Cr-doped GaAs oxidized at $500^{\circ}C$ for 20 min. Concentration scale valid for Cr and ion counts scale valid for O and As.



Figure 31: SIMS in-depth concentration profile of Cr-doped GaAs oxidized at $500^{\circ}C$ for 2 hours. Concentration scale valid for Cr and ion count scale valid for O and As.



Figure 32: SIMS in-depth concentration profile of Cr-doped GaAs oxidized at $600^{\circ}C$ for 24 hours. Concentration scale valid for Cr and ion count scale valid for other elements.

of the spectrometer.

In all cases, the dopant concentration showed a substantial increase at the oxide layer. This increase cannot be related to the differences in sputtering rate between the oxide and the GaAs, as discussed in section 5.4.2, because the thicknesses measured from the SIMS profiles are higher than the actual ones determined by TEM. Despite the increase in the concentration of the dopant elements in the oxide layer, no extra phase such as TeO_2 , SiO_2 or Cr_2O_3 was found to exist mixed with the gallium oxide. Therefore the dependence of oxidation rate on the dopants should be related to their effect on the gallium oxide properties.

4.4 The $GaAs/\gamma$ - Ga_2O_3 Interface

4.4.1 Introduction

The usefulness of geometric description of crystalline metal-oxide interfaces has been demonstrated recently [50,51]. It can provide valuable information in the studies of mechanisms governing the growth of an oxide scale or the internal oxidation of alloys. The breadth of use of this technique is extended here to the case of crystalline scales grown on semiconductor compounds.

Several theoretical models dealing with the description of crystalline interfaces have been developed [70,41,1,2]. However, the O-lattice introduced by Bollmann [2] as an extension of the coincidence site lattice has proven successful in describing metal-oxide interfaces [50]. This method leads to the definition of boundary periodicity, and describes the interface in terms of primary and secondary dislocations.

One of the greatest advantages of the O-lattice formalism is that it does not require the knowledge of atomic forces or atomic positions, but only the knowledge of the translation cell parameters for the adjacent phases. However, since it is a geometric description, it does not furnish quantitative values of energy of the boundary. Also, other factors, such as chemical bonding differences in interphase interfaces, may affect the boundary structure and are not taken into consideration by a geometric approach. A brief description of the O-lattice theory is provided in Appendix 1. It will be applied in this and the next chapter to explain some of the experimental results presented here, and be used to predict some features of the reaction.

4.4.2 Interfacial stresses and strains

The elongation of the diffraction spots originated from the γ -Ga₂O₃, and shown in Figure 14, indicates that the epitaxial oxide film is ellastically strained. The origin of stresses and strains in thin films over substrates has been the subject of recent reviews [15], and the ones most relevant for the case of growing oxides will be discussed here. In order to understand the origin of these stresses, the assumptions invoked in each model should be made clear. It is generally assumed that the growing layer is thin with respect to the substrate, and that its lateral dimensions are much bigger than its thickness (thin film approximation). Also the interface is often assumed planar.

There are several distinct sources of stresses in growing oxides. Fromhold [22] has suggested that the drag force that the moving species experience during the migration through the oxide leads to stresses in the oxide. On a microscopic basis, a frictional force can be attributed to the scattering of the moving species by the atomic constituents of the oxide, which constitutes the diffusion medium. The momentum exchange between the diffusing species and the diffusion medium is equivalent to some average force acting on each point of the oxide. The elastic strain that results is primarily parallel to the diffusion currents. Once the reaction is stopped, in principle these stresses should vanish.

Stresses in growing oxides can also result from Coulombic interactions. The substrate/oxide interface is constrained, whereas the oxide/oxygen interface is not. Therefore compressive stresses should exist in the oxide whenever the electrostatic potential difference across the film is non-zero. Such a potential difference may arise from surface charge densities at both interfaces [29,64]. Stresses resulting from Coulombic interactions are also primarily parallel to the diffusion currents.

A third cause for stresses and strains in growing oxide films has been proposed in a series of papers by Cathcart and co-workers [3,8,9]. It results from an uniform expansion of each volume element in the oxide lattice due to the defect concentrations present within the volume element. In the case of cation interstitials, the oxide should expand, and the strain associated with this mechanism is position dependent, since the concentration of moving species depends on the position.

Finally, stresses due to epitaxial effects should also be of concern when treating growing oxides. A thin oxide senses the periodic potential of the crystalline substrate underneath it, and there will be a tendency for it to grow matching this periodicity. Van der Merwe and co-workers have treated the problem of overgrowth very elegantly, and calculated a maximum difference of 9% between the interplanar distances in order for the mismatch to be fully accomodate elastically. The driving force to produce epitaxy result from the periodic potential of the two crystals. Such stresses are primarily lateral, in the sense that changes in the lattice parameters occur parallel to the interface, and therefore normal to the direction that the oxide grows. These stresses are predicted to fall off exponentially with distance from the interface. The existence of a preferred orientation relationship between the oxide and the GaAs strongly suggests an important role of epitaxial forces during oxidation.

4.4.3 O-lattice calculations

Both lattices of GaAs and γ -Ga₂O₃ are cubic with lattice constants equal to 0.5634 nm and 0.822 nm respectively. A homogeneous transformation of the the GaAs lattice into the γ -oxide so that the exact orientation relationship described in Section 4.2.2 is satisfied can be described by:

$$\mathbf{T} = \begin{pmatrix} \frac{0.822}{0.5634} & 0 & 0\\ 0 & \frac{0.822}{0.5634} & 0\\ 0 & 0 & \frac{0.822}{0.5634} \end{pmatrix}$$
$$\mathbf{T} = \begin{pmatrix} 1.454 & 0 & 0\\ 0 & 1.454 & 0\\ 0 & 0 & 1.454 \end{pmatrix}$$

or

Then the O-lattice is determined by solving

$$(\mathbf{I} - \mathbf{T}^{-1})x^{(O)} = b^{(1)}$$

where I is the identity matrix, $b^{(1)}$ a translation vector in the GaAs lattice and $x^{(O)}$ is the vector coordinate of an O-lattice point. Figure 33 shows a (001) projection of the two lattices, and the resulting O-lattice cell walls. The intersection between those cell walls and the interphase boundary are the loci where misfit dislocations are expected to exist. The proximity of such dislocations and the existence of voids at the interface may account for the absence of the ordinary contrast produced by line defects in TEM images. Those misfit dislocations should not act as fast diffusion paths during the oxidation since they are parallel to the interface, i.e. normal to the species flow. Rapp and Pieraggi [51] have proposed that in the case of metal oxidation controlled by cation-vacancy diffusion, those dislocations act as sink to incoming vacancies, and might climb towards the substrate. No dislocations were found at or near the GaAs/oxide interface.

Whereas the growth of oxide films have been the subject of several experimental studies, nucleation of these films have received far less attention because of the difficulties involved. Models for oxide nucleation are therefore fairly limited in number and in the amount of information that can be inferred from. The O-lattice theory is used here to provide some information on the early stages of the oxidation, i.e. before a continuous oxide film is formed.

It is reasonable to assume that in thermal oxidation of gallium arsenide small oxide nuclei are formed at the onset of oxidation. Some indication of a similar mechanism for anodic oxidation has been presented by Szpak [67]. The shape of such nuclei can be inferred, considering the physical idea behind the O-lattice theory (and for that purpose the Coincidence Site Lattice theory).

At the O-points, the match between the two lattices is best. Therefore a nucleus with a high density of O-points at its boundary with the substrate has a good match, and the nucleus shape will be such that it maximizes the number of O-points per unit area of the nucleus/substrate interface. The nuclei of gallium oxide should therefore be pyramids with square base limited by [110] and $[1\overline{11}]$ and with {111}



XBL 8812-4122

Figure 33: (001) projections of GaAs and γ -Ga₂O₃ lattices. The O-lattice cell walls are the continuous lines, and indicate the position where misfit dislocations are expected.

faces.

The diffraction patterns in Figures 13 and 14 have shown that the epitaxial oxide film is somewhat strained, and this strain may result in slight deviations from the exact crystallographic relation determined previously. These deviations will result in an increase of interfacial energy, since the match between the two lattices will not be optimun. As the misorientation between the two crystals increase, the dimension of the O-lattice cell decreases, resulting in a larger density of misfit dislocations. The possible amount of misorientation between the oxide nucleous and the GaAs can therefore be estimated qualitatively from the variation of the determinant of $I - (RT)^{-1}$ as a function of the misorientation. R is any rotation of one lattice with respect to the other, away from the optimum orientation relationship.

For the sake of an example, consider R to the rotation by θ degrees around the common direction (001). In this case:

$$\mathbf{RT} = \begin{pmatrix} 1.454 \cos\theta & -1.454 \sin\theta & 0\\ 1.454 \sin\theta & 1.454 \cos\theta & 0\\ 0 & 0 & 1.454 \end{pmatrix}$$

which results in

$$det(\mathbf{I} - (\mathbf{R}.\mathbf{T})^{-1}) = -1.9824 + 1.5325\cos\theta$$

This expression is plotted in Figure 34, and shows that small changes in the orientation would produce only slight changes in $det(I - (R.T)^{-1})$. This suggests that small misorientations can be tolerated without much expenditure of energy. From the same figure, one can conclude that the orientation relationship found to exist between GaAs and Ga₂O₃ at the early stages of the reaction is the one that provides the best fit between the two lattices, therefore minimizing the interface energy.

4.5 Mechanism of oxide growth

The mechanisms governing thermal oxidation of gallium arsenide are still unclear. Wilmsen [77] has suggested that the reaction at the semiconductor-oxide interface



Figure 34: Determinant of I - $(\mathbf{R}.\mathbf{T})^{-1}$ as a function of the rotation angle θ around the common [001] direction.

2

plays an important role, and the breakage of the GaAs bonds is the rate determining step. Some other workers [46,6] have postulated the reaction to be mass transfer controlled. All these models, as formulated, do not depend strongly on the doping element, and therefore do not explain the results found in this work.

The study of the oxide growth mechanism consists of determining the moving species (cation, oxygen or both), and of elucidating their microscopic transport mechanism. Previous workers have determined the moving species during anodic oxidation [21] and plasma oxidation [48] of GaAs. It was concluded that in both cases cations and oxygen ions take place in the transport, with the latter to a greater extent.

The marker experiments described in chapter 3 were used to determine the moving species during thermal oxidation of gallium arsenide. Concentration profiles of Xe-implanted GaAs oxidized at $400^{\circ}C$ and $600^{\circ}C$ are shown in Figures 35, 36 and 37. The As peak in these experiments was used as the fingerprint of the GaAs/oxide interface. Figure 35 shows Xe profiles after oxidation at $400^{\circ}C$ for 30, 120 and 240 minutes. It is obvious from this figure that the Xe peak moves with time, but does not broaden, since the slopes of the profiles at the descending side are approximately the same. Figure 36 shows Xe profiles after oxidation at $600^{\circ}C$ for 0 and 120 minutes. Figure 37 shows not only the Xe profiles but also the As "bump" at the interface, which moves as the reaction proceeds.

Several factors make an accurate determination of the transport numbers impracticable. Among these one can mention:

- interface roughnesss
- presence of voids at the interface
- loss of one of the elements (As vaporization)
- variable composition of the oxide layer

However the general behavior observed in Figures 35 through 37 is that the Xe peak remains close to the oxide/GaAs interface. This suggests that the primary mechanism for oxide growth is cation diffusion towards the oxide/oxygen interface.



Figure 35: Xe concentration profile in a Xe-implanted GaAs that has been oxidized at $400^{\circ}C$. Reaction times in minutes are shown in the figure for each curve.



Figure 36: Xe concentration profile in a Xe-implanted GaAs that has been oxidized at $600^{\circ}C$. Reaction times in minutes are shown in the figure for each curve.



Figure 37: Xe concentration profile in a Xe-implanted GaAs that has been oxidized at $600^{\circ}C$ for 120 minutes. The As peak, in arbitrary units is also shown, and it is located just ahead the Xe peak.

The uncertainties that arise from the factors mentioned previously still do not completely rule out the possibility of some contribution of oxygen migration towards the GaAs/oxide interface. However, if oxygen does migrate during the oxidation, its contribution to the oxide growth should be much smaller than that of cation migration. This result differs from that found in the case of anodic oxidation [21], where oxygen transport appears to dominate.

 β -Ga₂O₃ has been found to be a n-type oxide [38,19]. Unfortunately no data are available on the semiconducting characteristics of γ -Ga₂O₃. However, on the basis of the findings that:

- the oxide film is predominantly gallium oxide (and therefore assumed n-type)
- the moving species are the cations

the oxidation reaction can be broken into

$$Ga_{i}^{...} + As_{i}^{...} + 3/2 O_{2} + 6e \rightarrow Ga_{Ga}^{\times} + As_{As}^{\times} + 3 O_{O}^{\times}$$
 (3)

at the oxide/oxygen interface, and

$$Null \rightarrow Ga_i^{\dots} + As_i^{\dots} + 6 e \tag{4}$$

at the GaAs/oxide interface. The Kroger-Vink notation is used here. According to that, the symbol A_B^C implies that the element A is located at a lattice site B, which can be either a regular site (B=symbol of element that would occupy that site) or an interstice (B=i). The superscript C stands for the net charge that the element A have when occupies a B site. If such a net charge is negative apostrophes are used; their number being the same as the net charge. If the net charge is positive dots are used in the same way.

In order for the oxide to grow according to reactions 3 and 4, a flux of Ga and As interstitials from the GaAs/oxide interface to the surface should be balanced by a flow of electrons in the same direction. Hartnagel [28] has shown that the cation contribution to oxide thickening approaches zero linearly with increasing ionic radius. Since As ionic radius is greater than Ga ionic radius, As enrichment near the interface is expected on pure kinetics grounds. The scheme given above for describing the oxidation of GaAs can be used to provide a tentative explanation for the observed effect of the doping elements on the oxidation kinetics. Dopants like Si and Te in GaAs are oxidized according to

$$\underline{Si} \to Si_{Ga} + e \tag{5}$$

and

$$\underline{Te} \to Te_{Ga} + e \tag{6}$$

where the underlined species means in the GaAs phase. Lorentz et al. [38] have measured the electron concentration of several β -Ga₂O₃ crystals to be about 10¹⁸ cm⁻³. According to the concentration profiles shown in Section 4.3, Te and Si concentrations on the oxide are also about 10¹⁸ cm⁻³. Based on equations 5 and 6 the resulting increase in electron concentration in the oxide is significant. On the other hand, being a gallium isovalent, chromiun does not provide extra electrons to the oxide layer. This doping of the oxide may account for differences in the oxidation kinetics.

Chapter 5

Thermal Oxidation of Indium Phosphide

This chapter consists of the presentation and discussion of the results on thermal oxidation of indium phosphide. Transmission electron microscopy was the main experimental tool for characterizing the microstructural developments during the reaction. The crystallographic relations between the InP and the product scale are explained in terms of the minimization of the interphase interfacial energy using the O-lattice theory.

5.1 Electron microscopy results

At temperatures below $450^{\circ}C$, oxidation of InP produced an amorphous layer. Below $350^{\circ}C$, the oxide growth is extremely slow, so that any film is barely noticed by electron diffraction. In Figure 38 the microstructure of an InP thin foil that had been oxidized in-situ is shown. Even when the oxidation was carried out for periods of time longer than two hours, no observable change in microstructure could be detected. This agrees with the kinetic data provided by Wager and Wilmsen [73], according to which more than two hours are required to grow a 5 nm thick oxide. The amorphous oxide growth rate increases with temperature. Energy dispersive x-ray analyses have shown that the scale contains both In and P.

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Figure 38: Sequence of electron micrographs taken during the oxidation of InP at $300^{\circ}C$. The morphology remained unaltered even after 2 hours, and the diffraction pattern inserted shows no indication of oxide formation (XBB 862-1334).

At temperatures between $450^{\circ}C$ and $600^{\circ}C$, in-situ oxidation produced orthorhombic InPO₄ and cubic In₂O₃. A sequence of diffraction patterns obtained during the oxidation of a thin foil at $600^{\circ}C$ is shown in Figure 39: pattern A, obtained just prior to the oxidation, indicates that the only phase present is InP; pattern B, obtained after 10 minutes of oxidation, indicates the coexistence of polycrystalline In₂O₃ (ring pattern) with InPO₄ (spot patterns); finally, pattern C, obtained from an area close to the edges of the foil after 30 minutes, indicates the predominance of In₂O₃.

The bright field images in Figure 40 show the complete oxidation of InP into In_2O_3 at the thinnest regions of the foil, i.e. near the edges, when the reaction is carried out at temperature above $450^{\circ}C$. The diffraction pattern in Figure 41, which was taken from the area shown in (a) after 10 minutes of reaction, shows that the only phases present are InP and In_2O_3 . In thicker regions of the foil, the microstructure of the products was quite different, as Figures 42 and 43 show. The predominant phase is $InPO_4$, which is heavily twinned, and some In_2O_3 is also present. One can then conclude that the phosphorus loss is more intense from the thinnest areas of the foil. This can be attributed to the increased surface-to-volume ratio as well as to the higher density of ledges and kinks at the surface in these regions.

The excess indium in the scale with respect to the 1:1 stoichiometry in InP could be the result of two different processes. The first results from preferential vaporization of phosphorus at high temperatures. Lum and Clawson [40] have shown that at temperatures above $362^{\circ}C$, (001) InP surfaces vaporizes incongruently, resulting in pits filled with In. Those pits are truncated rectangular-base pyramids, with sides along {111} and basis along {001} planes. Therefore one could expect that, as temperature is increased during thermal oxidation, and while it is kept high, some amount of phosphorus is lost to the atmosphere.

A second mechanism to account for In-enrichment in the scales relies on the difference in diffusion coefficients of In and P in the oxidic layer, and has been suggested by Wilmsen et al.[79,78]. They have suggested that the oxide grows by out-diffusion of In and P, with the former diffusing faster than the latter, and

CHAPTER 5. THERMAL OXIDATION OF INDIUM PHOSPHIDE



Figure 39: Sequence of diffraction patterns taken during thermal oxidation of InP at $600^{\circ}C$ and 10 torr oxygen. Pattern A was obtained prior to the reaction start, pattern B after 10 minutes of reaction and pattern C from an area near the edge of the foil after 30 minutes (XBB 872-1233).

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Figure 40: Sequence of electron micrographs indicating intense P loss near the edges of a InP foil oxidized at $500^{\circ}C$ and 10 torr oxygen (XBB 872-1234).



Figure 41: Diffraction patterns taken after 10 minutes of reaction from area shown in the previous figure indicating the presence of InP and indium oxide (XBB 879-7478).



Figure 42: Bright field image of InP after 20 minutes of oxidation at $500^{\circ}C$ and 10 torr oxygen of a thick region of an InP foil. The InPO₄ phase is easily recognized because of the twinning (XBB 889-8877).



Figure 43: Diffraction pattern of area shown in the previous figure indicating the presence of $InPO_4$ (XBB 889-8879).

therefore the scale should be In-rich near the surface and P-rich near the interface. The assumption of faster diffusivity of In ions with respect to P ions has not been proven experimentally, and, in fact, does not appear to be correct. Using the formalism proposed by Hartnagel [28] on the dependence of cation diffusivities in a compound scale on the ionic radius, one should expect that phosphorus (r = 0.106 nm) should diffuse faster than indium (r = 0.144 nm). Therefore although Wilmsen's mechanism may explain In-enrichment at the outermost regions of the scale, it does not appear to be for the proper reasons.

The existence, or not, of P-rich phases at the semiconductor/scale interface has been the subject of some studies; but to the best of my knowledge, no conclusive experimental evidence has been published so far [49,20,60]. Electron microscopy of cross-section samples of oxidized InP and energy dispersive X-ray analyses were used here to evaluate the microstructure and composition of phases that may exist at the interface.

Figures 44 and 45 show an InP wafer that has been oxidized at $600^{\circ}C$ for 15 minutes in oxygen. The interface contains some voids and precipitates of a third phase (neither InP nor InPO₄). EDS was used to determine the chemical composition of these precipitates. However, in order to obtain a statistically valid number of counts, it was necessary to focus the converged electron beam onto the precipitate for extended periods of time. Yet, this extensive beam exposure tended to disintegrate the precipitates. An example of this degradation is given in Figure 44, where precipitate marked A was very much like B, before being exposed to the converged electron probe for 100 seconds. Thus, although precipitates such as the one marked C in Figure 44 have indicated a high P content, it was not possible to determine whether it consisted of pure P or a P-rich phase. Figure 44 also shows that, in general, these precipitates and the voids that are present at the interface are bound by $\{111\}_{InP}$ planes.

The voids in Figure 44 are similar to the pits found by Lum and Clawson [40] after annealing of InP, in the sense that they are bound by the same set of crystallographic planes. Figure 46 shows a planar view of an oxidized InP sample, and indicates that those voids have a near rectangular shape (appearing in light



Figure 44: Electron micrograph of a cross section sample of InP oxidized at $600^{\circ}C$ for 15 minutes. Precipitation at the interface is indicated by the arrows (XBB 889-8874).



Figure 45: Electron micrograph of a cross section sample of InP oxidized at $600^{\circ}C$ for 15 minutes (XBB 889-8880).

contrast in the referred figure). Thus, it may be expected that incongruent vaporization plays some role in the formation of In_2O_3 during the oxidation of InP, i.e. phosphorus is lost from the topmost layers and the indium left behind is oxidized to In_2O_3 . As the scale grows thicker, its role should decrease in importance. The imbalance of the oxidation rates of In and P, associated with the low solubility of the latter in the InP, should lead to formation of P-rich precipitates.

5.2 The $InP/InPO_4$ interface

Figure 47 is an enlargement of the diffraction pattern B in Figure 39. It indicates that the $InPO_4$ that results from the oxidation reaction has an unique crystallographic relation with the parent InP:

$$\{110\}_{InP} // \{110\}_{InPO_4}$$

 $<001>_{InP} // <001>_{InPO_4}$

Indium phosphide has a cubic lattice (a=0.5869 nm) and indium phosphate has an orthorhombic lattice (a=0.5320 nm, b=0.7993 nm, c=0.6785 nm). Since [001], i.e. the c-axis, is a four-fold rotation axis for InP and a two-fold rotation axis for InPO₄, the described orientation relationship has a total of four variants. Those account for the multiplicity of spots shown in Figure 47

Geometric considerations provided in the following paragraphs will demonstrate that this crystallographic relation between the two phases is the one that provide the least misfit. A general O-lattice calculation [2] would require to consider all possible rotations between the two lattices. However, since the results described in this thesis showed that InP and InPO₄ have parallel c-axis, only rotations around [001] were considered. Using the lattice constants of the InP and InPO₄, a homogeneous transformation of the former into the latter, followed by a θ -degree rotation around the c-axis can be written in matrix form as:

$$\mathbf{RT} = \begin{pmatrix} \cos\theta & -\sin\theta & 0\\ \sin\theta & \cos\theta & 0\\ 0 & 0 & 1 \end{pmatrix} \times \begin{pmatrix} \frac{0.532}{0.5869} & 0 & 0\\ 0 & \frac{0.7993}{0.5869} & 0\\ 0 & 0 & \frac{0.6785}{0.5689} \end{pmatrix}$$



Figure 46: Bright field image of a planar view sample of InP that had been oxidized at $600^{\circ}C$ for 1 hour. The near rectangular shape regions in light contrast correspond to pits in the InP (XBB 870-10484).



Figure 47: Diffraction pattern indicating the phosphate reflections. Two different variants of the orentation relationship described in the text are shown: one with the subscript a and one without (XBB 870-10485).

Predicted by O-lattice	Measured from Diffraction Pattern
9.94	12
80.06	78
99.94	102
170.06	168

Table 6: Rotation between InP and InPO₄ lattices

According to the O-lattice theory [2], the transformation **RT** resulting in the smallest absolute value of the determinant of $(\mathbf{I} - (\mathbf{RT})^{-1})$ is the one with most significance, i.e. producing the best fit between the two lattices. I is the identity matrix. A plot of determinat of $(\mathbf{I} - (\mathbf{RT})^{-1})$ versus θ , shown in Figure 48, indicates that the angle that produces the best fit is 9.94°. The symmetry of the system results in four possible rotations producing geometrically equivalent interfaces between the two lattices. Those are compared in Table 6 with the angles determined from the diffraction pattern.

The agreement between predicted angles and those found from direct measurements of the diffraction patterns is fair. This indicates that, at least initially, the phosphate grows in such a way that it minimizes the mismatch with the parent InP. Going back to the discussion on stresses in the scale given in Section 4.4.2, this crystallographic relation between the phosphate and the phosphide suggests an important role for epitaxial forces during scale growth. Therefore, at least in principle, by controlling the oxidation conditions, it should be able to produce epitaxial scales on InP.

The above O-lattice calculation is similar to the problem of an invariant line strain as pointed out by Dahmen et al. [12,11]. However in the case of growing scales, the O-lattice approach is more general because it does not impose any constraints to the eingenvalues of the transformation matrix in order to be used. For instance, although both approaches are equivalent in the case of InP oxidation, the same is not true in the case of GaAs oxidation.



XBL 8712-5311

Figure 48: Determinant of I - $(\mathbf{RT})^{-1}$ as a function of the rotation angle θ around the common c-axis.

The possibility of having one lattice translated with respect to the other has been ignored in the previous calculations, and an explanation for this procedure is considered appropriate. It has been demonstrated that if the rank of $(I-A^{-1})$, where A is the total matrix transformation RT, is 3, the effect the translation of one lattice with respect to the other is only a translation of the O-lattice [2]. This does not affect the size of the O-lattice unit cell, which is the important factor in determining the misfit. In the case of InP oxidation, the rank of $(I-T^{-1})$ equals 2 at the rotation angles that provide the best misfit. In this case, translation in the (001) plane purely translates the O-lattice but does not change its configuration. Only a translation with a component normal to (001) would change the O-lattice geometry, and consequently the misfit characteristics.

Chapter 6

Summary and Conclusions

A study of the thermal oxidation of III-V compound semiconductors has been made. Two members of this class of materials, GaAs and InP, were the object of the experimental work described in this thesis. Dynamical experiments inside a transmission electron microscope allowed direct observation of the microstructure evolution as the oxidation reaction takes place. Conventional transmission electron microscopy of planar view and cross-section samples was used to characterize the post-oxidation microstructure. In the case of thermal oxidation of GaAs, secondary ion mass spectrometry was used to assess in-depth composition profiles.

At low temperatures, i.e. below $400^{\circ}C$, oxidation of both GaAs and InP produced amorphous films. These films consisted of a mixture of gallium and arsenic oxides or a mixture of indium phosphate and oxide respectively. Under similar experimental conditions, GaAs was oxidized easier than InP and thicker scales could be grown on GaAs than on InP.

At temperatures above $400^{\circ}C$, remarkable changes in the microstructure of both compounds and corresponding scales started to occur. The scale became crystalline and intense precipitation at the oxide/semiconductor interface began. At the GaAs/Ga₂O₃ interface, hexagonal As precipitates were formed with a truncated square pyramid shape bound by $\{111\}_{GaAs}$ and $\{001\}_{GaAs}$ planes. These precipitates were oriented such that $\{0003\}_{As}$ // $\{111\}_{GaAs}$ and $< 11\overline{2}0 >_{As}$ // $< 110 >_{GaAs}$. As the reaction proceeded, some of this As was oxidized and lost to
the atmosphere, leaving voids at the interface.

In the case of InP, oxidation at temperatures higher than $400^{\circ}C$ also led to precipitation at the InP/scale interface. However the amount of precipitates was smaller than those in oxidized GaAs. It was not possible to fully characterize the precipitates because of its instability under the electron beam. However it was found to be either a phosphorus rich phase or, most likely, red phosphorus. The general morphology of the precipitates is similar to the As precipitates in the oxidation of GaAs.

Overall, thermal oxidation of GaAs at temperatures between $400^{\circ}C$ and $600^{\circ}C$ produced a layer consisting of mixture of gallium and arsenic oxides, and As precipiates at the interface. Thermal oxidation of InP, on the other hand, produced a layer that contained indium phosphate and indium oxide. Incongruent vaporization of InP accounts for some of the In₂O₃ present at the scale. Incongruent vaporization of GaAs only becomes important at temperatures higher than $600^{\circ}C$.

Arsenic precipitation at the GaAs/oxide interface was more intense than that of P at the InP/phosphate interface. This was explained in terms of the differences in diffusivities of As and Ga in Ga_2O_3 , and the reaction products. In the thermal oxidation of GaAs the oxide layer is primarily gallium oxide, and the reaction proceeds by the outdiffusion of cations. Thus since the ionic radius of As is bigger than that of Ga, the latter is expected to diffuse faster, leaving the former behind. The low solubility of As in GaAs and the thermodynamic analysis described in Chapter 4 indicates that under these conditions, arsenic should precipitate. As for the thermal oxidation of InP, the primary product found was InPO₄, which has the same stoichiometric ratio In:P as the substrate InP. Also, the ionic radii of In and P are such that if there is any big difference in diffusivities, P should be the faster diffusing element.

Thermal oxidation of GaAs initially led to the formation of an epitaxial film of γ -Ga₂O₃. As the film thickened, it became polycrystalline and finally transformed into β -Ga₂O₃, which is thermodynamically more stable. Some As₂O₃ and As₂O₅ crystallites were also formed as a result of the oxidation reaction, and they were found dispersed in the gallium oxide matrix. The epitaxial γ -Ga₂O₃ and the parent

GaAs were oriented relative to each other such that $\{110\}_{GaAs} // \{110\}_{\gamma-Ga_2O_3}$ and $<001>_{GaAs} // <001>_{\gamma-Ga_2O_3}$.

Thermal oxidation of indium phosphide produced an epitaxial film of $InPO_4$ and some In_2O_3 . The latter is believed to be the result of incongruent vaporization that takes place at temperatures higher than $362^\circ C$, and accounts for some loss of phosphorus to the atmosphere. Epitaxial indium phosphate formed with $\{110\}_{InP}$ // $\{110\}_{InPO_4}$ and $< 001 >_{InP}$ // $< 001 >_{InPO_4}$. The symmetries of these phases imply the existence of four twin related variants of this orientation relationship.

The fact that, at least at the early stages of the reaction, well defined crystallographic relations between reactants and products existed suggests that epitaxial forces played a very important role in the scale growth. In each case, the O-lattice theory has proved very successful in predicting the orientation relationship of the growing oxide (phosphate) with the parent semiconductor. Such crystallographic relations were the ones that minimizes the mismatch at the interphase interfaces. However differences of interplanar distances in the two phases result in stresses at the interface. In indium phosphide oxidation, these stresses led to the formation of a heavily twinned scale. In gallium arsenide oxidation this was not the case, and although the mismatch might have resulted in the formation of misfit dislocations, these were not detected.

Dopants were observed to have an effect on the kinetics of the oxidation. This effect has not been previously reported for III-V compounds, although dopants are known to affect the kinetics of silicon oxide growth. A tentative model that assumes the oxidation reaction to be controlled by electron flow through the oxide has been proposed. Electron transport control appears to be a reasonable assumption because the electric field in thermal oxidation is low, the electron concentration in the oxide is expected to be low, and diffusion coefficients increase with temperature.

Finally, the understanding of oxidation requires the knowledge of the identity of moving species so that mechanisms can be postulated and results properly interpreted. Marker experiments were used in conjunction with some data available from the literature to conclude that the oxide growth in GaAs occurs primarily by cationic diffusion from the GaAs/oxide interface to the oxide/oxygen interface. This work has provided answers to some questions that have been lasting for some time. It is, however, by no means conclusive. Studies with other III-V compounds are encouraged so that their oxidation behavior can be compared to the ones described here. Verification of the effect that dopants have on the reaction kinetics may be attempted with elements that decrease the electron concentration in the oxide. If the model proposed here is correct, slower rates should result.

Considering the practical uses of thermal oxidation as a process in III-V compounds device technology, this work has shown some of the difficulties that need to be overcome. The excessive precipitation of group V elements at the oxide - semiconductor interface poses a serious problem. Differences in oxidation potentials as well as the ability to withstand high temperatures without loss of stoichiometry are important factors to be considered. The thermal oxidation of GaAs will always lead to high current leakage conditions, as a result of the presence of elemental arsenic at the interface [58]. The use of other oxidants, such as As_2O_3 , As_2O_5 or a mixture of these compounds, will not alleviate the problem of As precipitation, according to the phase diagram deduced. As for InP, the situation is different in the sense that single phase indium orthophosphate layers are in principle obtainable. The difficulty in this case resides in eliminating the In_2O_3 and the excessive pitting that may result from high temperature treatments.

Despite the difficulties involved in thermal oxidation, the ability of growing epitaxial oxide (and phosphate) is something that deserve further attention. One may idealize conditions at which an homomorphic oxide (or phosphate) layer is epitaxially deposited onto a III-V compound. It is expected that this work enlightens the road for someone who decides to travel on it.

Appendix A

The O-lattice Theory

The O-lattice theory is a geometric approach to the structure of crystalline interfaces. It provides a mathematical method for calculating the detailed structure of the interface between crystals at arbitrary relative orientations. Since the interface energy is a function of the boundary structure, among other things, this theory may be used to determine optimum boundaries in some instances.

In order to construct the O-lattice for a particular set of two lattices, one has to imagine the two lattices interpenetrating each other. Any point in space can be represented by coordinates that are the sum of external and internal coordinates. The external locate the unit cell in which the point is placed, and the internal provide the location with respect to the origin of that particular unit cell. O-points are points in space that have common internal coordinates in the two interpenetrating lattices. These points, which are periodically arranged, form the O-lattice. Mathematically one can write:

$$(\mathbf{I} - \mathbf{A}^{-1}) \underline{x}^{(O)} = \underline{b}^{(L)}$$

where I is the identity matrix, A is the matrix representation of the transformation of lattice 1 into lattice 2, $\underline{b}^{(L)}$ is a translation vector in lattice 1 and $\underline{x}^{(O)}$ is the vector coordinates of an O-point. The solution of this equation gives the coordinates of the points in the O-lattice. The boundaries between adjacent Wigner-Seitz (W-S) unit cells of the O-lattice are the locus of worst match between the two original lattices. Therefore misfit, dislocations, if present, are supposed to reside on the intersection of the boundary itself with the W-S cell walls.

Some of the features of the O-lattice that were used in this thesis are explained next. The determinant of $(\mathbf{I} - \mathbf{A}^{-1})$ is the ratio of the volume of the *b*-unit cell to the O-lattice unit cell. Therefore, the smaller this determinant is, the larger becomes the O-lattice unit cell, which implies a smaller msifit dislocation density. If a crystal, at the early stages of growth, tries to orient itself as to minimize the interface energy, it is expected that this orientation will be the one that results in the smallest absolute value of the determinant of $(\mathbf{I} - \mathbf{A}^{-1})$.

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