**Title:** Growth Mechanisms and Properties of the Thermal and Anodic Oxides of the III-V Compound Semiconductors

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**Abstract:** The mechanisms of oxide growth on InP, GaP, GaAs and InGaAs were investigated and their electrical properties measured. Islands were observed as the initial stage of anodization of InP and GaAs but the details of the growth on the two materials are different. The thermal oxides of InP and GaP also differ in composition and surface topography. InP forms bubbles and GaP has pits under the oxide. Traps at the deposited insulator/InP interface were also investigated.
Growth Mechanisms and Properties of the Thermal
and Amodic Oxides of the III-V Compound Semiconductors

Final Report

By

C.W. Wilmsen

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I. Statement Of The Research Problem

Discrete and integrated device structures on the III-V compounds require dielectric films for gate and field oxides, annealing caps and for passivation. Deposited insulators, such as \( \text{SiO}_2 \) and \( \text{Al}_2\text{O}_3 \), have an inherent mismatch with the substrate, can damage the surface during deposition and can dope the substrate during heat treatment. The grown oxides more naturally accommodate the surface defects and thus have a strong appeal.

This research program sought to determine many of the mechanisms involved in III-V growth, the changes which occur during heat treatment and to investigate the causes of electrical instabilities at the interface. Understanding these fundamentals has lead to better application of oxidation and how to control the interface. Four substrate materials were investigated: InP, GaAs, GaP and InGaAs with primary emphasis placed on InP.

Most of the experimental research utilized surface analysis techniques such as x-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS) and secondary electron microscopy (SEM).

II. Summary Of The Most Important Results

The results given below are organized by process technique with substrate materials as sub-topics.

A. Thermal Oxidation

InP

The thermal oxides of InP were investigated to determine the chemical composition as a function of depth, the surface morphology, the crystalline structure and the direction of oxide growth. It was determined that the compositional profiles and surface topography changed dramatically above a growth temperature of 620°C in 1 atm dry oxygen. Below this temperature the surface is relatively smooth and the interface has deposits of elemental phosphorous. The
oxide is composed of a mixture of \( \text{In}_2\text{O}_3 \) and \( \text{InPO}_4 \) with no detectable elemental phosphorus at the interface. This behavior was believed to occur by the softening of the oxide layer due to the rapid release of energy from the exothermic oxidation. Any elemental phosphorus creates a pressure beneath the soft oxide. This causes bubbles to form. The diffusion rate of P in the soft oxide is much greater than before and thus the oxide film becomes predominately \( \text{InPO}_4 \).

The above data argues in favor of growth by the out diffusion of In and a slower out diffusion of P. \( \text{O}_2 \) is thought to diffuses only slowly. In order to test this hypothesis and to alter the growth kinetics, oxides were grown in high pressure atmospheres. Oxide films grown in a high pressure (500 atm) ambient were found to contain no elemental P but rather \( \text{P}_2\text{O}_5 \). This is evidence that the \( \text{O}_2 \) is driven into the film where it oxidizes the elemental P. The oxide film thus becomes layered. Oxidation in high pressure steam in \( \text{H}_3\text{PO}_4 \) yields different results indicating that the diffusing oxidant molecules changes the reaction kinetics. No difference was observed for growth at 1 atm in these ambients. Models for this oxide growth have not been worked out at present.

**GaP**

In principle the thermal oxidation of GaP should be very similar to that of InP. However, this was not found to be the case, e.g. the GaP oxide composition was found to be uniformly \( \text{GaPO}_4 \) for all growth temperatures and the growth rate in steam is 10 times that in dry \( \text{O}_2 \). In addition, no bubbles were observed on the GaP oxides but rather large pits framed under the oxides grown in dry \( \text{O}_2 \) but none for the steam grown.

A detailed study of the pits revealed a progression of shapes and sizes starting with small vertical wall pits aligned with the substrate crystalline planes. These change to rounded channels which winded around under the oxide (Figure 1).
**InGaAs**

The composition of these oxides follow from that previously observed on GaAs and InAs. The oxide bulk is a mixture of \( \text{Ga}_2\text{O}_3 \) and \( \text{In}_2\text{O}_3 \) with very little arsenic oxide. The As collects at the interface in elemental form. The growth rate fall midway between that of InAs and GaAs thus the out diffusion of In and Ga probably controls the growth.

**B. Anodic Oxidation**

**GaAs**

When GaAs is anodized at constant current it is convenient to record the cell voltage versus time. After an initial step in voltage there is a relatively flat portion of the curve which had been thought to be caused by island formation. We investigated this island formation by studying transmission electron micrographs of carbon replicas of the surface. These produced fine details of the islands and the nuclei as seen in Figure 2. The following observations were made.

- The nucleation process does not occur only in the initial stage but continued until the entire surface was covered with oxide.
- The islands grow to a thickness of \( \sim 200\AA \) which occurs when the individual island area \( \sim 0.1\mu^2 \)
- When the islands touched, they grew together and did not have a liquid like coalescence.
- The edges of the islands were very rough but clearly identifiable.

The above data shows that continuous oxide layers less than \( 200\AA \) thickness cannot be formed, at least by the standard process.

**InP**

The island growth of InP anodic oxides was found to be different from that of GaAs in that they had very smooth edges and tended to form in lines. All the islands were the same size and no small islands or nuclei were observed. This indicates that all the nuclei form at one time during an initial stage. While the
islands as InP appear to grow to approximately the same height as GaAs the islands were difficult to observe in the microscope since the edges were not abrupt.

The composition of the thicker InP anodic oxides were determined by x-ray photoelectron emission profiling to be a mixture of P₂O₅ and In₂O₃, which is different from the thermal oxides. The P₂O₅/In₂O₃ ratio could be varied in a controlled manner by adjusting the pH and the electrolyte composition. The composition ratio was correlated to electrical measures which strongly suggested the oxide was composed of small islands of one compound imbedded in a matrix of the other. since the In₂O₃ is a conductor and the P₂O₅ is an insulator, varying the ratio caused a very large change in the electrical resistance. For a small P₂O₅/In₂O₃ ratio, the current was carried by electron percolation through the maze of islands but for longer ratios the electrons must tunnel from island to island.

While the "as grown" anodic oxide can have a very high resistivity, ~10¹⁶ ohm-cm, the P₂O₅ in the films readily absorb water which greatly reduces the resistivity. Annealing the as grown films partial converts the mixed oxide to InPO₄ but annealing at 650°C cause the film to peel away from the substrate, rendering it useless as a protective coating.

Another type of anodization holds more promise. This technique forms a double layer anodic oxide film by anodizing a previously deposited aluminum film and the underlying InP substrate. While the same anodic process is followed the routine oxide has been found to be InPO₄ and not a mixture of P₂O₅ and In₂O₃. This oxide yields a high quality interface which may be suitable for device applications since it is stable in air and has a low interface state density. The resistivity of the double layer was found to be lower than the same single layers. This appears to be due, at least in part, to the migration of In through the outer layer of Al₂O₃.
C. Plasma Oxidation

InP

When SiO₂ is deposited on InP by the plasma enhanced CVD process, the excited O₂/N₂O may enhance the InP oxidation rate. Thus, this process could lead to a thicker interfacial oxide. This enhancement was characterized by comparing the oxide thickness resulting from the exposure of plasma to that of a normal thermal oxide. For these tests a plasma enhanced CVD chamber was used but no SiH₄ was introduced into the chamber. Placing an InP wafer at the mouth of the plasma tube resulted in a rapid growth of oxide above 150°C while placing the wafer well away from the plasma tube yielded little change from the normal thermal oxidation but increases rapidly above 350°C. There was, however, an initial fast rise in growth rate which saturated at ~10Å thicker than without the plasma. The composition of the plasma enhanced film was very similar to that of the thermally grown oxide.

D. Interfacial Trapping

InP MOSFETs fabricated with a deposited gate dielectric have a drift in the drain current. The magnitude of the drift varies from very fast (seconds) to very slow (hours). It is thought that the drift is caused by traps in either the deposited dielectric or in the interfacial native oxide. We have investigated traps in both of these.

The XPS compositional profiles of thin native oxides on InP indicate that the inner most layer is primarily InPO₄ and the outer layer is a mixture of InPO₄ and In₂O₃. We have used surface analytical techniques to measure the band gap and electron affinity of InPO₄ and In₂O₃ in relation to the InP substrate. The band gap of InPO₄ was determined to be 4.5eV with the conduction band edge ~ 1.2eV above that of InP. The conduction band of In₂O₃ is only slightly above the conduction band of InP. Thus, the In₂O₃ can act as a trap for inversion layer electrons in InP. Using this as a model, calculations were made and compared to
published electrical data. A very close fit could be obtained by adjusting the oxide layer thickness. Electron loss spectra (ELS) from the native oxide indicated the presence of the $\text{In}_2\text{O}_3$ trap but no other intrinsic level. Thus, we concluded that there are no traps in the native oxide other than $\text{In}_2\text{O}_3$.

ELS and ultraviolet photoelectron spectroscopy (UPS) were used to identify traps in deposited $\text{SiO}_2$. Traps associated with Si-Si and Si-O bands were observed but these were too low in the band to yield the drain current drift. The study of impurity traps are presently being pursued.
III. List of Publications Resulting from this Contract


IV. Personnel Supported by the Project

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<td>Y. D. Lin</td>
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Figure 1. Pits under the thermal oxide of GaP.
Figure 2. Anodic oxide islands on GaAs grown in tartaric acid electrolyte, pH = 7 with strong light.

Figure 3. Anodic oxide islands on InP formed by dipping the InP substrate in tartaric acid electrolyte, pH = 7.
Figure 4. An energy band diagram for the SiO$_2$/InP system depicting possible trap sites in the SiO$_2$, and In$_2$O$_3$ intermediate layer, and in the bulk native oxide. The width of the native oxide is exaggerated for clarity.
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