Critical Review

Chemical composition and formation of thermal and anodic oxide/III–V compound semiconductor interfaces

C. W. Wilmens

Electrical Engineering Department, Colorado State University, Fort Collins, Colorado 80523

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The literature on the chemical composition and growth of thermal and anodic oxides of the Ga and In III–V compounds is reviewed and discussed. Emphasis is placed on the questions “what is the chemical composition of the oxide/III–V interface” and “how and why did it get that way”. It is apparent that much is known about these interfaces but knowledge of a number of important growth, thermodynamic, and structural parameters is lacking.

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I. INTRODUCTION

It has been a number of years since the published works on GaAs oxides were reviewed by Bert Schwartz. His paper continues to provide useful insight into oxide growth and interface formation and should be considered required reading for all workers in the III–V oxide field. Also two bibliographies and a special issue of Thin Solid Films on III–V MIS topics have been published. However a considerable number of papers on GaAs oxides and their interfaces have appeared since Schwartz’s review and the importance of other III–V materials has been recognized.

The present paper reviews the thermal and anodic oxides of the Ga and In III–V compounds but does not include the room temperature air-grown oxides, the plasma grown oxides and the oxides grown on Al, ternary, and quaternary compounds. While these latter oxides are important, it was felt that the scope of the paper had to be limited. For information on room temperature oxides the reader is referred to papers by Chang, Sugano, Bertrand, Clark, Wager and their co-workers; and for plasma grown oxides, papers by Chang and Sugano, and co-workers are useful.

The present paper provides the reader with an overview of what is known about the chemical composition of the III–V oxides and their interfaces. It is intended to help answer the questions: What is the chemical composition and structure of oxide/III–V interfaces and how and why did they form that way?

Good progress has been made in answering these questions although some important information is still lacking. Following a statement of general concepts the paper is organized into three sections. The first two review the thermal and anodic oxides respectively by substrate material with some comments and comparisons. The last section attempts to summarize and tie together the present understanding of the interfaces.

II. OXIDE/SEMICONDUCTOR INTERFACE CONCEPTS

Oxide/semiconductor interface formation begins with the interaction of a gaseous or liquid oxidant with the clean semiconductor surface. The oxidant may first physisorb or chemisorb on the surface before breaking back bonds to form the initial oxide layer. When the semiconductor is composed of more than one element, there may be preferential oxidation of one element over the other and there may also be selective evaporation or dissolution of the initial or subsequent oxide layers. In this regard, the column V elements and their oxides are much more volatile than the column III elements, and the column V oxides are usually more water soluble. However solution pH and the type of anion can change the solubility significantly. In addition, the oxidation may proceed through a nucleation and island growth process. Thus, the initial oxide layer and possibly the resultant thick oxide/III–V semiconductor interface may be nonuniform in both chemical composition and thickness.

After the initial oxide layer is formed, diffusion of either the oxidant or the substrate species (or possibly both) must take place in order to grow additional oxide. This growth may change the chemistry and structure of the initial interface or the interface may remain essentially unperturbed. The amount of change which occurs in the interface is determined by kinetic and thermodynamic factors. Understanding these factors provides the key to understanding oxide/III–V interfaces and how they evolve with increasing oxide thickness, growth method, and postoxidation treatment. Equilibrium thermodynamics indicates which is the favored final state for the interface composition, while the kinetic factors determine if this state will be reached during a given set of growth conditions.

III. THERMAL OXIDES AND INTERFACES

The composition, bonding, crystallinity, etc. of thermal oxides grown on III–V compounds change with growth temperature and to some extent with the ambient gases. It is difficult to generalize about the oxide compositions because there appear to be exceptions to all of the general trends. For instance, excess B element in AB compounds is often observed at the oxide/III–V interface, (for convenience the terms A and B elements and A and B oxides are used, A referring to Ga and/or In, and B to P, As and/or Sb) however this is not the case for oxides grown on InP at temperatures above
600°C, for oxides grown on several compounds at low temperatures, or for oxides grown on GaP at any temperature. There appear to be both thermodynamic and kinetic reasons for these differences.

The oxides often contain only a low concentration of B oxide. This is apparently due to the evaporation of the B oxide, but slow transport of the B element through the growing oxide could also be a factor. The thermal oxides of GaP and InAs are exceptions. On GaP the oxide layer appears to be GaPO₄ and on InAs the oxide is a mixture of In₂O₃ and As₂O₅, at least for the growth temperatures reported to date. On InAs there is also elemental As. As the growth temperature decreases, the concentration of B oxide tends to increase. At high temperatures the oxide on InP changes to InPO₄ but on GaAs much of the As is lost and only a fraction of the oxide converts to GaAsO₄. At lower temperatures the oxides are primarily amorphous but begin to crystallize as the growth temperature increases.

Unlike Si, the III–V compounds generally exhibit only a 10% to 20% difference between the oxidation rate in dry and wet oxygen. This may be an indication that the oxidant is not the dominant diffusing species, however this has not yet been demonstrated.

Thermal oxide growth and interface formation on the III–V compounds appears varied and complex. The following section reviews and discusses the published data on these oxides.

A. InSb

Rosenberg and Lavine were the first to observe elemental Sb at the interface of thermally oxidized InSb. To determine the oxide composition profile, they observed electron diffraction patterns from an oxide cross section and chemically analyzed dissolved oxide layers. These indicated little or no Sb in the oxide bulk but a pile-up of elemental Sb at the interface. These results were confirmed some years later by etching, Auger, and XPS profiling and Raman scattering. The Auger profiles of Wilmsen indicated that the concentration of Sb at the interface decreased as the growth temperature was decreased but that elemental Sb was still weakly detected at the interface of oxides grown at 250°C, the lowest growth temperature reported. This growth temperature corresponds (perhaps fortuitously) to the lowest annealing temperature reported by Nakagawa, et al., at which Raman scattering from anodic oxide layers indicated the presence of elemental Sb. Thus, there may be an activation energy associated with the Sb pile-up which has a characteristic temperature of ~250°C. Both Raman and electron diffraction measurements indicate that the Sb is crystalline, even for the oxides grown at 250°C. Korwin-Pawlowski reported that etching the surface oxide grown at 450°C or 500°C revealed a rough interface, apparently composed of In₂O₃ dendrites and elemental Sb. Hillocks also appeared at the interface. It was thought that this roughness gave rise to the observed matte appearance of these oxides.

Rosenberg and Lavine suggested that the presence of elemental Sb at the interface is caused by its slow diffusion through the In₂O₃ layer. This was based on an independent experiment of interrupted oxide growth. Subsequent Auger profiles of thermal oxides which had been anodized after thermal growth by Wilmsen seemed to verify this kinetic model since the anodization removed the elemental interfacial Sb. It was reasoned that the high electric field during the anodization process had lowered the diffusion barrier to Sb and thus allowed it to move through the oxide. However, later thermodynamic analysis by Nakagawa and Smirnova and their co-workers indicated that the thermodynamic instability of Sb₂O₅ at the InSb interface leads to elemental Sb at the interface. Hence, the thermodynamics of the interface appear to be able to account for the Sb pile-up, independent of the kinetics. This is in agreement with the work of Thurmond and co-workers on GaAs and GaSb which is discussed later. Kinetic factors may, however, contribute to or modify the Sb deposits.

While the Auger profiles show that the elemental Sb is localized at the interface and that there is very little Sb oxide in the bulk oxide film, results of Belozerskii et al. and some recent work by Smirnova et al. indicate that the oxide structure is more complex and contains Sb₂O₅ and InSbO₄. Both of these researchers report that the film composition changes with the total time of oxidation. Belozerskii et al. used x-ray diffraction on oxides grown in air at 400°C and therefore could not determine the compositional profile; however, Smirnova et al. used a lapping and voltammetric technique on oxides grown at 350°C. The data indicated the presence of both Sb₂O₅ and elemental Sb at the interface and InSbO₄, Sb₂O₃, Sb₄O₉ and InSbO₃ in the oxide bulk which was distributed in a complex depth profile. They constructed a ternary phase diagram and concluded that the distribution of oxides grown for a prolonged length of time was in agreement with their diagram. They also conclude that the elemental Sb at the interface is due to thermodynamic stability considerations and not growth kinetics.

For oxide films grown at 250°C the XPS results of Iwasaki et al. indicated very little Sb in oxide films. The peak shifts were interpreted to indicate the presence of In₂O₃ and Sb₂O₅. However, there appears to be some doubt about the Sb₂O₅ since the difference between the peak shift for Sb₂O₅ and Sb₂O₃ is not large and standards have not been sufficiently investigated.

Thus, Sb deposits are definitely found at the interface of oxides grown in the range of 250°C to 500°C. There appears, however, to be uncertainty concerning the composition of the oxide film and perhaps the existence of Sb oxides at the interface.

B. InP

Auger XPS and Raman analysis have been used to detect elemental P in the thermal oxides of InP, and the P has been shown to be localized at the interface. The Raman measurements of Schwartz et al. indicate that the P is amorphous for a growth temperature of ~400°C, but as the growth temperature increases above 400°C the P becomes more crystalline. When the growth temperature increases above 650°C the elemental P at the interface is no longer present and the oxide layer appears to be composed of InPO₄.

with some In$_2$O$_3$. Below 550°C the XPS results show that the oxide layer is composed primarily of In$_2$O$_3$ with some P in the form of a phosphate.\textsuperscript{25,27} On InP the changes which occur as a result of high temperature oxidation are dramatic, in that the oxide layer changes from a low concentration of P to one equal to that of In. In addition, at high temperature ($T \geq 600^\circ$C) there is no evidence for pile-up of elemental P at the interface.\textsuperscript{26,28} One report\textsuperscript{29} on IR adsorption and electron diffraction of thermal oxides on InP states that InPO$_4$ is formed at low temperatures and that In$_2$O$_3$ and suboxides are formed during high temperature growth. The presence of InPO$_4$ is in agreement with XPS which indicates\textsuperscript{28,27} that the P is bonded as a phosphate although there is more In than P. The dominance of In$_2$O$_3$ at higher temperatures is also in agreement with recent XPS results from our lab that indicate oxide grown at 700°C or above contain a lower concentration of phosphate. However, the presence of the suboxides is suspect and may be due to an error in the interpretation of the multiplex IR spectrum.\textsuperscript{30}

Kazmerski et al.\textsuperscript{31} have investigated low temperature oxidation of polycrystalline InP using XPS and SIMS. The oxides were grown at 200°C in dry O$_2$ for 1 to 2 h and in wet O$_2$ at 100°C for 24 h. The oxides contained only low concentrations of P except at the interface where the concentration increased. For dry O$_2$ grown films, the interfacial P appeared in an elemental form, but with wet oxidation the interfacial P appeared to be bonded to oxygen in the form of a phosphate as seen by the $\approx 5$ eV shift of the P(2p) line. The fact that a phosphate and not elemental P is found for the wet oxidation is interesting and deserves further study.

XPS profiles from our laboratory on very thin oxides (20–50 Å) grown in the range 340° to 400°C indicate significant concentrations of both P and In oxides with little indication of elemental P at the interface.\textsuperscript{32} For longer oxidation times and thicker films, the P oxide concentration is greatly reduced and elemental P appears at the interface. For all the thermal oxides that we have investigated, (340° to 650°C), the P(2p) line is found to shift $\sim 4$ to $\sim 5$ eV, indicating that the P is bonded as a phosphate and not as P$_2$O$_5$ as we had originally thought.\textsuperscript{27}

For oxides grown at high temperatures, the above XPS results agree with the previous Raman scattering of Schwartz et al.\textsuperscript{26} and the x-ray analysis of Vereikina.\textsuperscript{33}

To date, no phase diagram for the In–P–O system has been reported, (although G. Schwartz has privately discussed his progress in constructing such a diagram). However simple reaction equations using published heats of formation indicate that both P$_2$O$_5$ and In$_2$O$_3$ are not reduced by InP\textsuperscript{34} although the thermodynamic data is not known with high accuracy. It is possible that P$_2$O$_5$ + In$_2$O$_3$ can convert to InPO$_4$ (with the aid of H$_2$O) but the heat of formation for InPO$_4$ is not presently available. It is interesting to note that elemental P collects at the oxide/InP interface during thermal oxidation. This appears to be contrary to the thermodynamic stability arguments given above since the equilibrium interface composition would appear to be either In$_2$O$_3$ + P$_2$O$_5$/InP or InPO$_4$/InP not In$_2$O$_3$ + P/InP. This suggests that considerations such as diffusion, evaporation or reaction barriers may be important in determining the concentration of P at the interface.

C. InAs

There have been only two reports on the composition of the thermal oxides of InAs. Farrow et al.\textsuperscript{16} using Raman scattering found evidence for elemental As in films grown in air at 450°C. Later, Laughlin and Wilmsen\textsuperscript{35} reported XPS profiles of oxides grown in the range 350° to 475°C. Oxides grown at 350°C reached a maximum thickness of only 26 Å and contained approximately equal parts of As$_2$O$_3$ and In$_2$O$_3$. Oxides grown at higher temperatures also contained significant concentrations of As$_2$O$_3$ but also contained elemental As. The presence of the As$_2$O$_3$ is surprising since it does not appear in the thermal oxides of GaAs from which it is thought to evaporate. The elemental As was also found not to be localized at the interface as is the B element in the thermal oxides of InSb, InP, GaAs, and GaSb (discussed elsewhere in this paper).

Also, As$_2$O$_3$ appears at the interface, even though the reaction As$_2$O$_3$ + 2InAs $\rightarrow$ In$_2$O$_3$ + 4As is favorable. Thus, the thermal oxide/InAs interface appears more complex than some of the other III–V. At a growth temperature of $\leq 450^\circ$C the oxides appear amorphous. Above this temperature, both crystalline In$_2$O$_3$ and As$_2$O$_3$ appear in the grown layers.

D. GaAs

The thermal oxides of GaAs have been extensively investigated beginning with Minden's\textsuperscript{36} paper in 1962. Detection of elemental As at the oxide/GaAs interface was first reported as a result of ellipsometric analysis by Zaininger and Revesz.\textsuperscript{57} Subsequent XPS profiles of Sealy and Hemment\textsuperscript{38} indicated little or no As pile-up at the interface. However, later XPS profiles of Mizokawa et al.\textsuperscript{39} and Raman scattering measurements by Cape,\textsuperscript{40} Farrow,\textsuperscript{16} Schwartz\textsuperscript{20,41} and their co-workers and the work of others\textsuperscript{15,42–44} clearly show the presence of interfacial As. Shiota et al.\textsuperscript{44} state that their Auger profiles indicate an orientation dependence of the As pile-up with much less As found on the (111)B face compared to the (111)A. However, Kec\textsuperscript{45} pointed out that there was a misinterpretation of the Ga LMM line and that there were possible erater effects which were not considered. Loschke et al.\textsuperscript{46} found that the (111)A and (111)B faces collected the same amount of As but the (110) face had less. A survey of the substrate orientations used by other authors indicates that there is probably no strong orientation dependence but the data is not sufficient to resolve this issue with complete certainty.

The oxides appear to be amorphous Ga$_2$O$_3$ up to a growth temperature of $\approx 500^\circ$C. Above this temperature they become crystalline $\beta$Ga$_2$O$_3$ as shown by Muraka,\textsuperscript{47} Koshiba and Sugano,\textsuperscript{48} and Sealy and co-workers.\textsuperscript{38,49,50} For even higher temperatures or with an As$_2$O$_3$/Ga$_2$O$_3$ oxidation ambient, amorphous and crystalline forms of GaAs$_x$O$_{4-x}$ appear in the oxide films.\textsuperscript{19,42,52,53}

For oxides grown at high temperatures, the concentration of elemental As at the interface appears to be reduced and some GaAs$_x$O$_{4-x}$ may be formed. There are also some indications that the As diffuses out, perhaps through the grain boundaries. However, at a growth temperature of 620°C, Watanabe et al.\textsuperscript{43} still found a large elemental of As. When As$_2$O$_3$/O$_2$ is...
used as the oxidant, the amount of $\text{As}_2\text{O}_3$ incorporated into the films is greatly increased. With regard to interface composition, some authors have reported that the inner layer of the grown film was difficult to etch off. This film probably is elemental As.

Most of the thermal oxides grown on GaAs are reported to be grown in dry $\text{O}_2$, air or wet $\text{O}_3$. But there are also reports of oxides grown in $\text{As}_2\text{O}_3$ and $\text{As}_2\text{O}_5$ mixtures. The various oxidizing atmospheres yield similar interfaces except that the $\text{As}_2\text{O}_5$ grown oxides have a considerably increased $\text{As}_2\text{O}_3$ concentration in the bulk of the oxide film.

Phases diagrams and interfacial reactions for GaAs oxides have been reported by Thurmond and co-workers. These indicate that the reaction $\text{As}_2\text{O}_3 + 2\text{GaAs} \rightarrow \text{Ga}_2\text{O}_3 + 4\text{As}$ is thermodynamically favorable and readily occurs. The instability of $\text{As}_2\text{O}_3$ in the presence of GaAs and the stability of $\text{Ga}_2\text{O}_3$ are thought to be the cause of the pile-up of elemental As at the interface during thermal oxidation. Previous to the thermodynamic stability studies, discussed above, we reported XPS profiles of very thin thermal oxides grown on GaAs at 450°C. It was proposed that the low diffusion rate of As through the $\text{Ga}_2\text{O}_3$ layer caused the pile-up of As at the interface by a model patterned after that of Rosenberg and Lavine. It is now clear that the reaction of $\text{As}_2\text{O}_3$ with the substrate is an important consideration, however since the diffusing species (O, Ga, As) are not known, the complete model for growth remains clouded. At growth temperatures below 620°C the As does not readily diffuse through the oxide layer, otherwise it would not remain at the interface as seen in many experiments. Whether the slow diffusion of As is really important or not is not clear at this time.

The rough appearance of thermal oxide layers on GaAs was noted in the earliest work on this oxide and by a number of others since then. Observation of an orientation dependence of the film roughness which appeared to be correlated to the growth rate has also been reported. With regard to interface roughness, Navratil and co-workers have done the most extensive work using optical, stylus, and TEM techniques. They report that the interface rms roughness increases with oxidation temperature in the range 400°C to 500°C with a possible decrease at higher temperatures. The roughness was found to begin with the initial stages of oxidation and to saturate after a short time. The height of the roughness was as much as 200 Å and had surface features of $\approx 2500$ Å in diameter. It would seem possible that the roughness may be caused by the nonuniform distribution of As islands like those which are found in annealed plasma grown oxides or by nonuniform evaporation during the initial stage of growth.

E. GaP

XPS profiles of oxides grown on GaP in the temperature range 185°C to 950°C indicate no accumulation of elemental P at the thermal oxide/GaP interface. Iwasaki and co-workers investigated thermal oxides grown at 185°C and 320°C with XPS and estimated near equal concentration of Ga and P in the oxide layer. They suggested that a $\text{GaPO}_x$ compound is formed which changes to $\text{GaPO}_4$ at higher temperatures. Loschke et al. report XPS results on oxides grown at 300°C which indicate a similar uniform distribution of Ga and P oxide up to the interface. These results on low temperature oxides are similar to those reported by Nishitani et al. for XPS profiles of oxides grown in air in the range 600°C to 950°C. They note that the interface width increases significantly with growth temperature and that the chemical shift of the P(2p) line increases near the interface. The apparent increase in interface width could be an artifact caused by the increased crystallinity or surface roughness of the films. The XPS results indicate that the P is bonded as a phosphate, independent of growth temperature. This is in agreement with the x-ray analysis of Rubinstein on oxides grown above 1100°C and that of Vereikina on oxides grown up to 900°C using x-ray and chemical analysis. Recall that the thermal oxides of InP grown above 600°C were also a phosphate but below this temperature the oxide was an $\text{In}_2\text{O}_3$-phosphate mixture with an accumulation of P at the interface.

The above experimental observations on GaP appear to be in agreement with the phase diagram of Schwartz et al. although they were not able to completely pin down the final tie lines of the diagram. $\text{GaPO}_4$ was, however, a leading candidate.

F. GaSb

The thermal oxide/GaSb interface appears similar to that described above for GaAs, i.e. there is elemental Sb at the interface and little $\text{Sb}_2\text{O}_3$ in the oxide film. The elemental Sb was observed with Raman scattering by Farrow et al. and with XPS profiles by Loschke et al. These films were grown in air at 255°C and 300°C respectively. We have observed similar results on oxides grown at 500°C. Again the thermodynamic analysis of Schwartz and co-workers indicates that $\text{Sb}_2\text{O}_3$ will react with GaSb to yield elemental Sb. The presence of $\text{Sb}_2\text{O}_4$ or $\text{GaSbO}_3$ in parallel with the work on InSb oxides has not been reported; however, the apparent low concentration of Sb oxide in the film reduces the importance of this question.

IV. ANODIC OXIDES AND INTERFACES

The anodic oxides and their interfaces have been found to be somewhat different from thermal oxide interfaces. This is probably in part due to the facts that (1) the anodic oxides are grown near room temperature in a liquid electrolyte which usually contains water, (2) the oxides are grown faster than the thermal oxides, and (3) anodic oxides are grown in a high electric field ($\approx 5 \times 10^6$ V/cm). Like the thermal oxides, the anodic oxides on the different III–V compounds have some commonality but there are also some notable exceptions, and one should always keep in mind that the electrolyte and growth condition may strongly effect the resulting anodic oxide and the interface. In some cases it appears to be clear why these differences exist, but in others the reasons are unknown or may even be the result of measurement artifact or error.

Anodic oxidation appears to be initiated by a nucleation and
island growth process. This was discussed at length by Szpak for anodic oxides grown on GaAs at constant current in a tartaric acid/proplylene glycol electrolyte. His potential vs time of growth curves followed a characteristic shape which indicated that an incubation (passivation) time was required before a continuous oxide film covered the GaAs surface. Subsequently, we have observed this incubation characteristic in the growth curves of anodic oxides on InP, InAs, and InSb. It probably also occurs with GaSb and GaP but these have not been investigated.

Szpak directly observed the oxide islands on GaAs with an SEM. We have studied the islands via transmission electron micrographs of surface replicas. Our results verify that the islands do indeed exist and that this initial growth is an important step in the oxidation process. There is also evidence and the islands may be highly dependent upon growth conditions. Further work on the island growth is needed since the interface does not appear to change after this initial oxidation step is complete.

Unlike the thermal oxide/III–V interface, little or no excess B element is found at the anodic oxide interface. This has led some researchers to conclude that anodic oxides are grown far from thermodynamic equilibrium. If this is so, then the kinetics of the growth must be controlling the resulting oxide and interface. Unfortunately, the kinetics of III–V compound anodization has not received much attention. In addition the bulk oxides are composed of significant concentrations (often in a 1:1 ratio) of both the A and B oxides.

During anodization, dissolution of the growth products may occur, and in fact there are indications that dissolution during the island growth phase may be very large compared to that which occurs after a continuous layer is formed. Dissolution in the electrolyte is affected by the water/glycol ratio, pH, temperature, the electrolyte constituents, and current density.

A. InSb

Dewald was the first to report on the chemical composition of an anodic oxide on a III–V compound. He used a microtechnique to chemically analyze anodic oxides of InSb grown in a 0.1 N KOH electrolyte. Sb was found to be deficient at the surface but the Sb:In ratio was ≈1 throughout the oxide bulk and at the interface. This was independent of growth rate. Dewald applied his previously developed model to explain the kinetics of the anodic growth on InSb. This model assumed that the oxide grew by the outward movement of cations and was limited by either the ion space charge current within the oxide or the entrance of the ions into the film at the film/InSb interface. Since pure Sb oxides readily dissolve in KOH, the presence of a large concentration of Sb oxide in the anodic film suggested that a simple interstitial ion transport model was not sufficient to explain the observed growth.

Later sputter-Auger profiles of Wilmsen agreed with the chemical profiles of Dewald. The Auger results indicated a low Sb concentration at the surface, uniform Sb concentration in the oxide bulk, and no Sb pile-up at the interface. Some of the “as grown” anodic layers were subsequently heated to 400°C in O₂ or vacuum and then were Auger profiled. The vacuum annealed samples had essentially no Sb in the oxide film, and no detectable elemental Sb at the interface. The Auger profiles of the O₂ annealed samples were very similar to those of thermally grown oxides, namely some Sb in the film and excess Sb at the interface. Nakagawa et al. pursued the annealing of the InSb anodic oxide using Raman scattering. Anodic layers before annealing indicated little or no elemental Sb. However, after heating in air, Raman scattering indicated the presence of elemental Sb which begins to appear above a temperature between 240°C and 260°C. They suggest that the formation of elemental Sb during annealing is not caused by O₂ in the air but rather by the decomposition of Sb oxide through a reduction reaction such as

\[
\text{InSb + Sb oxide} \rightarrow \text{InSbO}_3 + \text{Sb}.
\]

It would seem that if this were the case the Sb should pile up at the interface during both O₂ and vacuum annealing. This however is contrary to the Auger profiles discussed above. Nevertheless the Sb oxides are extensively evaporated from the film in both vacuum and O₂; the vacuum anneal may allow for a faster out diffusion and evaporation of the Sb.

Very recently Smirnova and co-workers have reported a study of the compositional profile of InSb anodized in KOH using a cyclic voltametric technique. Profiles were obtained by sequential mechanical polishing with a fine SiO₂ powder and analyzing the film after each polish. They do not report a complete profile but state that the Sb:In ratio in the oxide bulk is approximately unity, in agreement with the above discussion. However, the oxide was found to be layered and to contain Sb and Sb₂O₃ at the interface and In₂SbSb₅O₁₃ and Sb₂O₃ in the oxide bulk. They report that the oxide should convert to In₂SbO₄ after a period of time. The authors conclude that these oxides are grown far from equilibrium.

The above results of Smirnova on the bulk oxides are not strictly in disagreement with the other work discussed so far since the previous authors did not identify the Sb oxides present in the film. The detection of elemental Sb at the interface, however, appears at variance with the results of others. XPS studies of Bilz et al. on oxides formed in K MnO₄ solutions indicate a composition profile similar to that obtained by Auger on KOH grown oxides except for an Sb oxide inner layer. This is in partial agreement with Smirnova, who also found elemental Sb, but not with the other reports. Bilz lists a 2.7 to 2.4 eV shift of the Sb(4d) line but he does not state which oxide of Sb this represents. It would appear that the observed shift would indicate an oxide closer to Sb₂O₃ than Sb₂O₅, but this is not well established. The apparent complexity of the InSb anodic oxides is intriguing and warrants further investigation.

B. InP

The composition of anodic oxides of InP were examined with Auger profiling by Wilmsen and soon thereafter by Lile and Collins. These initial investigations indicated that the layers contained a low concentration of P oxide. Lile and Collins also found a large concentration of carbon in the surface layer of their oxide. Apparently this was introduced.
by the electrolyte. In a series of papers reporting Auger and XPS profiles the importance of pH and electrolyte in determining the P$_2$O$_5$ concentration in the oxide and the uniformity of the composition has been demonstrated. However, the anodic oxide interface for all the growth conditions appears to have P$_2$O$_5$ at the interface with a constant P$_2$O$_5$/In$_2$O$_3$ ratio, independent of the bulk oxide layer composition. The difference in the bulk oxide composition appears to be due to selective dissolution of either the In$_2$O$_3$ or the P$_2$O$_5$. It should be noted that the XPS results show that the P(2p) line in the oxide is shifted by 6.1 eV, which corresponds to P$_2$O$_5$. This differs from the P-O bonding in the thermal oxide and air grown, room temperature oxides in which a phosphate is suggested by the 4 to 5 eV shift.

In studying the insulating characteristics of the anodic oxides of InP, we have found that there is a very sharp rise in the resistivity at a P$_2$O$_5$/In$_2$O$_3$ ratio of $\approx$1.3. One model which explains these current-voltage measurements suggests that the In$_2$O$_3$ and P$_2$O$_5$ are separated into islands. If this is a valid model extending to the interface, the islands could cause interface roughness scattering of inversion layer electrons. This model is still in the formative stage and requires considerably more study. Also, the extent of the phase separation envisioned by the model implies a complex growth morphology.

C. InAs

Chemical analyses of InAs anodic oxides have been reported by Baglee et al. using XPS sputter profiling. Unlike the InP anodic oxides, it appears that relatively small changes occur in the InAs anodic oxide profiles with various electrolytes and pH values. The profiles indicate a uniform distribution of In$_2$O$_3$ and As$_2$O$_5$ oxides with the possibility of a small concentration of elemental As in the oxide and at the interface. However, the latter could be due to reduction of the As$_2$O$_5$ caused by the ion milling. There is also an apparent change in interface width with electrolyte.

D. GaAs

Feldman and his co-workers at Bell Labs appear to be the first to have investigated the composition of anodic oxides on GaAs. Using He back scattering and He induced x-rays, they determined that the oxide bulk was composed of a Ga:As ratio of $\approx$1 while the surface was depleted of As. Upon heating the oxide, As in some form was found to diffuse out of the layer at a temperature of 450°C. This also caused the oxide layer to become thinner. Follow-up work by Spitzer et al. showed that baking in N$_2$ caused evaporation of water from the anodic oxide but also showed that there was no apparent reduction in oxide thickness for baking temperatures $\leq$400°C. Etching away an oxide layer baked at 400°C exposed a granular interface material which did not readily etch. Baking at 600°C greatly increased the etch resistance of the entire film. It was also reported that the interface became rough after anodizing to high voltage. Ishii and Jeppson used RBS and mass analysis of the species evaporating from the surface to investigate the effects of annealing on the composition of GaAs anodic oxides. Up to 300°C no changes were observed. Above 300°C, both H$_2$O and As oxide began to evaporate. At 450°C the evaporation was rapid and essentially complete within 15 min. Etching an oxide annealed to 650°C exposed an interfacial layer which they identified as Ga rich, possibly containing droplets of Ga. However, from the work of Thurmond and co-workers it would appear that this interfacial layer was As. Using Raman scattering they clearly identified elemental As formation as a result of annealing. It was shown that the reaction

$$\text{As}_2\text{O}_5 + 2 \text{GaAs} \rightarrow \text{Ga}_2\text{O}_3 + 4\text{As}$$

was thermodynamically favorable and readily occurred.

Weiss et al. also reported As evaporation from anodic films at 400°C and showed that the evaporation was accompanied by the appearance of $\beta$Ga$_2$O$_3$ crystallites. The rate of crystallization was found to be a function of the current density used to grow the oxides, i.e., the higher the current density the more readily did the oxide layer crystallize when heated. This is reminiscent of the observations of Szpak et al. who found that the interface of oxides grown at higher current density was more orderly than when grown at low current density. There may, however, be no correlation between the two observations.

The initial anodic growth and interface composition of GaAs has received significant attention. Szpak proposed a nucleation and island growth model for the initial anodic growth. Supporting evidence was later reported by Matsushita and Geib and Wilmsen. Based on the amount of charge passed during the island growth phase, Szpak estimates that many atomic layers were dissolved before a complete surface covering occurred. Matsushita came to a similar conclusion based on calculations of an effective bulk oxide dissolution current and suggested that an intermediate, more soluble product is formed during the initial stages of growth. It is also possible that a nonoxidative charge transfer could occur in the areas between the islands, and hence the calculation of the amount of dissolved oxide may be overestimated by the above techniques. However, from private discussions with Szpak, this appears unlikely. If there is a large volume of surface dissolution then one would expect that the interface would be nonuniform and possibly quite rough since the dissolution would probably occur between the islands. The ellipsometry work of Aspnes et al. does not indicate a rough interface. However, unpublished TEM results of our laboratory suggest that there is roughness in between the islands, at least close to the islands. Spitzer does report a rough interface for oxides grown at high voltage but this does not appear to relate to roughness caused by island growth. Verplanken and Tijburg used radioactive tracers to determine the amount of dissolution taking place during the anodization of thick films on GaAs in a glycol based electrolyte. For their growth conditions it was found that 25% of the Ga$_2$O$_3$ and 5% of the As$_2$O$_5$ dissolved out of the growing films. These dissolution amounts appear to be too large when compared to the bulk oxide dissolution rates reported by Matsushita for a very similar electrolyte. Perhaps the Verplanken and Tijburg measurement reflects a large dissolution during the island stage. This, however, does not appear to be the case since they measured...
both the electrolyte and the oxide etching solution. The interface roughness/dissolution requires further study and should provide added insight into the initial growth and interface formation process.

Wilsen and co-workers\textsuperscript{55,71} have reported XPS sputter profiles of oxides stopped at different times during and after the island growth stage. These indicate a progression of growth starting with a nucleation which appears to be initiated by merely placing the GaAs wafer in the electrolyte. The XPS results suggest that the initial islands are composed of Ga$_2$O$_3$. Profiles obtained on samples grown for increased periods of time, show that the outer surface of the islands is composed of a mixed As$_2$O$_3$–Ga$_2$O$_3$ layer while the layer next to the substrate is Ga$_2$O$_3$. The profiles were interpreted in terms of a simple island growth model without considering the possibility of large amounts of dissolution. The inner layer of Ga$_2$O$_3$ was found to persist even after a 1000 Å of oxide had been grown in a number of electrolytes, at different growth rates. This has also been seen in the XPS profiles of Mizokawa \textit{et al.}\textsuperscript{81} and Breeze \textit{et al.}\textsuperscript{82} on thick oxides. Optical techniques have not detected this Ga$_2$O$_3$ inner layer\textsuperscript{20,79} in the thick anodic films.

However from their ellipsometric data on thin oxides Harvey and Kruger\textsuperscript{51} suggest that there is an inner layer of \(\sim 25 \text{ Å}\) which is optically more dense than the bulk film and has a much higher conductivity. The high conductivity of this inner layer could be due to either the island stage of the growth or to a Ga$_2$O$_3$ layer which could have a higher conductivity than the mixed oxide. It appears that Harvey and Kruger did not realize that the initial anodic growth on GaAs was an island growth. Thus, their interpretations of the inner layer is probably incorrect; however, in light of the XPS data, their conclusions are intriguing.

The profiles of thin oxides by Geib and Wilsen\textsuperscript{71} also indicate the presence of a low concentration of elemental As. This was also reported by Mizokawa,\textsuperscript{81} Breeze,\textsuperscript{82} and Chang\textsuperscript{83} and co-workers for thick oxides. In the latter case the reported large concentration of elemental As may be an artifact of the method used to reduce the Auger data. The existence of elemental As at the interface as well as the Ga$_2$O$_3$ layer are somewhat controversial. No elemental arsenic was found by Schwartz \textit{et al.}\textsuperscript{20} using Raman scattering or by Aspnes \textit{et al.}\textsuperscript{79} with spectroscopic ellipsometry. The ellipsometric technique appears very sensitive to interfacial composition and roughness, and Aspnes found the interface on the (111)B surface to be exceedingly sharp. On the (100) surface the interface was less well defined but still very thin. Thus, differences may occur with various surfaces and growth procedures as was also observed by Croset.\textsuperscript{84} This variation with growth condition could account for the differences observed by different authors. It is possible that the concentration of elemental As could change as the oxides grow thicker since the high electric field may cause the elemental As to diffuse out of the film. The As could also be an artifact of the sputter profiling technique, or it may be that the optical techniques are not sensitive enough to detect the As. However, recent RBS channeling measurements of Maggiore \textit{et al.}\textsuperscript{85} on GaAs surfaces after chemical etch removal of the anodic layers similarly indicated no elemental As.

Thus, from the substantial evidence of a variety of techniques one is led to conclude, for the moment anyway, that no elemental As exists at the anodic oxide interface. Schwartz \textit{et al.} point out that the absence of As and the As$_2$O$_3$/Ga$_2$O$_3$ mixture at the interface indicates that the anodic oxide is grown far from equilibrium since the As$_2$O$_3$ is not stable in the presence of the GaAs substrate. The instability of the As$_2$O$_3$–GaAs couple, as discussed above, causes a reduction of As$_2$O$_3$ at the interface when the sample is annealed above 300°C.

The only investigation of the diffusing species during anodic growth was reported by Coleman \textit{et al.}\textsuperscript{86} who grew alternate anodic layers in O$^{18}$ and O$^{16}$ water electrolytes. From these experiments they found that the water does not diffuse interstitially. Unfortunately, the experiments did not rule out substitutional diffusion. Hence, only a part of the question has been answered.

While much has been done to determine the chemical composition of the oxide, very little has been published on the bonding structure of these mixed oxides. Palik and co-workers\textsuperscript{87} investigated the anodic oxides of GaAs with optical reflectance and transmission. While their results were not conclusive, they did suggest that the basic As$_2$O$_3$ and Ga$_2$O$_3$ structures are preserved with some interaction between the As$_2$O$_3$ and Ga$_2$O$_3$ molecular groups. Lucovsky and Bauer\textsuperscript{88} examined model structures for the III–V oxides. They conclude that these are probably not diatomic isostuctural analogs of a-SiO$_2$. It is suggested that homogeneous amorphous oxide phases are more probable for GaP and InP than either arsenides or antimonides. Experiments are lacking in this important area of research.

\subsection*{E. GaP}

The anodic oxides of GaP appear similar to those of InP in that the composition of the oxide bulk is strongly dependent on the pH of the electrolyte and is nonuniform except when the pH is small. Poate \textit{et al.}\textsuperscript{89,91} showed this to be the case using RBS. XPS and RBS profiles show that the interface is composed of both Ga and P oxides with no apparent elemental P. Bilz \textit{et al.}\textsuperscript{92} report a 5.8 to 6.5 eV shift of the P(2p) binding energy which indicates that the P is probably in the form of P$_2$O$_5$ and not a phosphate whereas just the opposite was found by others\textsuperscript{22,33,59} for the thermal oxides. This binding energy shift of the P(2p) line is similar to what has been reported on the thermal and anodic oxides of InP and suggests that the oxidation of P is possibly the dominant factor in determining the oxide structure for GaP and InP.

Raman scattering from anodic layers by Schwartz \textit{et al.}\textsuperscript{20} indicated that no elemental P was contained in the "as grown" oxide or after annealing at 650°C for 1 h. They suggest that a number of kinetic factors, such as evaporation of P$_2$O$_5$ or the formation of GaPO$_4$ on Ga(P$_2$O$_5$)$_3$, may prevent the reduction of P$_2$O$_5$ by the GaP substrate. They also report progress toward the formation of a Ga–P–O ternary phase diagram. A number of uncertainties and possible kinetic factors prevented completion of the diagram.

Verplanke and Tijburg\textsuperscript{90} report that 40% of the Ga$_2$O$_3$ and 1.5% of the P$_2$O$_5$ dissolved during anodic growth on GaP. This
TABLE I. Summary of the oxide and interface composition for the thermal oxides of the III–V compound semiconductors.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Bulk oxide composition</th>
<th>Interface composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>InSb</td>
<td>In$_2$O$_3$</td>
<td>In$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>Sb$_2$O$_3$ (low conc.)</td>
<td>Sb$_2$O$_3$, InSbO$_4$</td>
</tr>
<tr>
<td>InAs</td>
<td>In$_2$O$_3$, As$_2$O$_3$</td>
<td>In$_2$O$_3$, As$_2$O$_3$, As</td>
</tr>
<tr>
<td>InP</td>
<td>In$_2$O$_3$, phosphate$^d$</td>
<td>In$_2$O$_3$, phosphate$^d$</td>
</tr>
<tr>
<td>GaSb</td>
<td>Ga$_2$O$_3$, Sb$_2$O$_3$ (low conc.)</td>
<td>Ga$_2$O$_3$, unknown</td>
</tr>
<tr>
<td></td>
<td>O$_2$, Air</td>
<td>Ga$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>H$_2$O, As$_2$O$_3$</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>O$_2$/As$_2$O$_3$</td>
<td>Ga$_2$O$_3$, As$_2$O$_3$, As</td>
</tr>
<tr>
<td>GaP</td>
<td>GaPO$_4$</td>
<td>GaPO$_4$, Ga$_2$O$_3$</td>
</tr>
</tbody>
</table>

$^a$The temperature ranges are different for each III–V material.
$^b$Oxides are assumed to be grown in O$_2$, air or H$_2$O/O$_2$ unless stated otherwise.
$^c$At low temperatures the oxide layers are often very thin and thus no real interface exists.
$^d$Probably InPO$_4$.

large solubility of Ga$_2$O$_3$ at a pH = 6 appears consistent with the results of Poate et al.$^{90}$ who investigated the oxide composition as a function of pH and electrolyte composition. They found a large dissolution of Ga at any value of pH which increased significantly under certain conditions. RBS measurements indicated two different composition depth profiles could be obtained: (1) a uniform distribution of P$_2$O$_5$ and Ga$_2$O$_3$ with a Ga:P:O ratio of $\approx$1:2.5:8.5, or (2) a distribution with a Ga$_2$O$_3$ rich outer layer and a P$_2$O$_5$ rich inner layer. The integrated Ga:P:O ratio was $\approx$1:1.6:5. The RBS does not directly identify chemical bonding, thus the assignment of P$_2$O$_5$ and Ga$_2$O$_3$ had to be deduced by the authors.

The RBS measurements had only a 150 Å depth resolution and thus precise interface composition determination was not possible. However, comparing the RBS results with the XPS profiles of Bilz et al.$^{88}$ indicate that the interface is relatively sharp and contains both Ga$_2$O$_3$ and P$_2$O$_5$. Poate et al.$^{90}$ propose a growth model which assumes Ga diffusion (which is assumed to be much faster than P), Ga dissolution and the possibility of the inward diffusion of the oxidant. While their model is plausible, there is no direct evidence to confirm the assumptions concerning the Ga and P diffusion.

**F. GaSb**

Bilz and co-workers$^{88}$ have reported the composition of anodic oxides on GaSb. Their XPS profiles of oxides grown in three different electrolytes (0.1N KMnO$_4$, 0.1N KOH, and 30% H$_2$O$_2$) indicated large differences in the composition between the KMnO$_4$ grown oxide and the other two. In the oxide grown in KMnO$_4$ the Sb oxide greatly exceeds that of the Ga oxide and appears to form a Sb oxide rich layer at the interface. They also report a Sb oxide rich interfacial layer for the anodic oxide grown on InSb in the same electrolyte. The oxides grown in the other two electrolytes appear to have an Sb oxide/Ga oxide ratio of $\approx$1, except at the surface where some Sb oxide is lost.

Schwartz et al.$^{90}$ examined the anodic oxides of GaSb with Raman scattering before and after annealing. They found no evidence for elemental Sb in the “as grown films” but after annealing at $T \approx 300^\circ$C, the presence of Sb was clearly seen in the spectra. At an annealing temperature of 300°C, the Sb appeared to be amorphous. At 350°C or above, the Sb deposits were crystalline. Coupled with pseudobinary reaction experiments they conclude that the oxide are not grown near equilibrium conditions and that the Sb$_2$O$_3$ reacts with the substrate during annealing.

**V. SUMMARY**

The oxide and interface compositions for the thermal and anodic oxides are summarized in Tables I and II respectively. Since there is not complete knowledge of these compositions or complete agreement between researchers, I have attempted to list the present consensus opinion and in some cases, an alternate opinion. Remarks and footnotes are used to help clarify uncertainty. The tables are given without references since these are all given in the discussion section. It can be seen that the chemical composition of the oxides and interfaces for all of the III–V thermal and anodic oxides has been investigated with varying degrees of completeness. GaAs oxides have received the most attention whereas InP has been neglected, even though it appears to be an important substrate material. The oxides of InAs and GaSb have been investigated the least.

Having all of this compositional data, it is appropriate to ask, “What does it all mean?” First, it appears that the oxide III–V interface, like other chemical systems, attempts to reach thermodynamic equilibrium, and it has been found that the thermal oxides appear to grow closer to equilibrium than do
TABLE II. Summary of the oxide and interface composition for anodic oxides of the III–V compound semiconductors.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Oxide Composition</th>
<th>Interface Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&quot;As grown&quot;</td>
<td>After annealing</td>
</tr>
</tbody>
</table>
| InSb      | In$_2$O$_3$, Sb$_2$O$_4$  
In$_2$O$_3$, Sb$_2$O$_5$, Sb$_2$O$_3$ | In$_2$O$_3$           | In$_2$O$_3$, Sb$_2$O$_5$ (Sb$_2$O$_3$ rich inner layer possible)  
(Also Sb has been observed). | O$_2$, T $>$ 240°C—Sb  
Vac, T $=$ 400°C—In$_2$O$_3$ |
| InAs      | In$_2$O$_3$, As$_2$O$_3$  
unknown | unknown               | In$_2$O$_3$, As$_2$O$_3$ (Possibly As) | unknown |
| InP       | In$_2$O$_3$, P$_2$O$_5$  
unknown | unknown               | In$_2$O$_3$, P$_2$O$_5$ | unknown, but apparently no elemental P |
| GaSb      | Ga$_2$O$_3$, Sb$_2$O$_5$  
unknown, probably Ga$_2$O$_3$ | Ga$_2$O$_3$, Sb$_2$O$_5$ (Sb$_2$O$_3$ rich inner layer possible) | Ga$_2$O$_3$, As$_2$O$_3$  
Ga$_2$O$_3$ (possibly As) | T $>$ 300°C  
Sb |
| GaAs      | Ga$_2$O$_3$, As$_2$O$_3$  
T $\geq$ 450°C  
Ga$_2$O$_3$ | Ga$_2$O$_3$, As$_2$O$_3$  
Ga$_2$O$_3$ (possibly As) | T $>$ 300°C  
As |
| GaP       | Ga$_2$O$_3$, P$_2$O$_5$  
unknown, probably GaPO$_4$  
or Ga$_2$O$_3$ + P$_2$O$_5$ | Ga$_2$O$_3$, P$_2$O$_5$ | T $\geq$ 650°C  
No elemental P, could be GaPO$_4$ or Ga$_2$O$_3$ + P$_2$O$_5$ |

* Sb$_2$O$_3$ has not been definitely identified as the Sb oxide.
* The detail composition of the interfaces after annealing has not been investigated.

The anodic oxides. GaAs and GaSb follow this trend since the thermal oxides of these compounds have large deposits of the B element while the anodic oxides have little or no such deposits. There is some disagreement in the literature on this latter point for GaAs. Annealing the anodic oxides of GaAs and GaSb leads to evaporation of the B oxide and to a decomposition of the B oxides at the interface through the reaction

$$\text{B}_2\text{O}_3 + 2\text{A}_2\text{O}_3 \rightarrow \text{A}_2\text{O}_3 + 4\text{B}(\text{interface deposit})$$

However, the kinetics of the oxide and interface changes with annealing have not been investigated in detail.

The oxides of InSb appear to follow a pattern similar to GaAs and GaSb but the reported phase diagram and measured bulk oxide composition indicate that these oxides may be more complex than those of GaAs and GaSb. The thermal oxide composition of InSb has been reported to change with time. This may also be the case with thermal oxides of InP since thin layers grown at 400°C are composed of approximately equal parts of P and In oxides but this interface changes to In$_2$O$_3$ + elemental P for thicker oxides grown at the same temperature. This time dependence suggests kinetic factors or an activation process is involved in establishing the interface composition.

The oxide/semiconductor interface for InAs, InP, and GaP appear not to fit simple models, and satisfactory thermodynamic explanations have not yet been reported.

While some oxides are grown near thermodynamic equilibrium, the anodic oxides and possibly some thermal oxides are not. In addition some of the oxides may not reach equilibrium even after annealing. Thus, there appear to be reaction paths and various kinetic processes which lead to or prevent equilibrium from occurring during the oxide growth or post oxidation annealing. Unfortunately there is much less known about these processes, e.g., the diffusing species during oxide growth is not known with certainty for any of the oxides, grown by any method on any of the III–V materials (the thermal oxidation of InSb is a possible exception). This lack of knowledge greatly hinders the formulation of growth models.

The kinetics of oxide growth may play a role in the collection of the B element at the thermal oxide interface, although the thermodynamics of the GaAs and GaSb oxides do not require kinetics to explain the observed results. However, on other substrates the picture is not as clear cut, as seen in the following examples. First, elemental P deposits are found at the thermal oxide/InP interface even though it appears that P$_2$O$_5$ and P$_4$O$_{10}$ are not reduced by InP, and InP$_4$O$_{10}$ may be the most stable compound. The Gibbs free energy of InP$_4$O$_{10}$ is not presently known and thus no firm statement can be made on which is the most stable reaction product.

The presence of As$_2$O$_3$ at the interface of the thermal oxide of InAs is a second example where kinetics may be a controlling factor in the interface formation. The changes in composition with time for the thermal oxides of InSb and InP discussed above also suggest kinetic factors must be considered. The lack of change in the interfaces of the anodic oxides of InP and GaP after annealing are other possible examples.

While the above examples are suggestive of kinetic factors, it must be remembered that there is presently only limited understanding of the equilibrium thermodynamics of the In compounds and that some of above observations have not been carefully examined. Thus, more information is required before complete models can be formulated. In particular a list of topics in special need of further work is given below. With such additional data, the answers to the "whys and hows" of oxide growth and interface formation would be significantly advanced.

(1) Determination of the species which diffuse during oxide growth.

(2) Details of the nucleation and island growth phase of anodic oxidation.
(3) Ternary phase diagrams for InP and InAs, as well as further work on those for InSb and GaP.
(4) Morphology of the compositional changes with thermal annealing.
(5) The bonding structure of the mixed oxides.
(6) Accurate measurement of the Gibbs free energy of the Ga and In phosphates.
(7) Composition of the room temperature air grown oxides and how this oxide affects the interface of anodic and thermal oxides.
(8) Crystallinity of the oxides.

From a technology standpoint, deposited insulators appear more important than grown oxides. However, the knowledge gained from the thicker oxides appears very useful in understanding the thin oxides grown by exposure to air or water at room temperature or in a reaction chamber at elevated temperatures. Thus, further work on the oxides is an essential part of the development of III-V technologies.

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