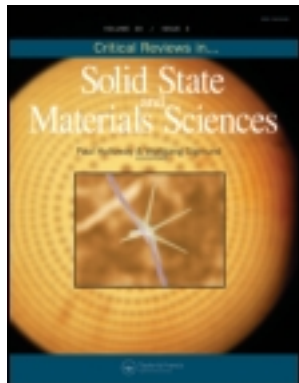


This article was downloaded by: [Weizmann Institute of Science]

On: 09 January 2013, At: 02:17

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



C R C Critical Reviews in Solid State Sciences

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/bsms19>

GaAs surface chemistry - a review

B. Schwartz ^a

^a Bell Laboratories Murray Hill, New Jersey

Version of record first published: 27 Sep 2006.

To cite this article: B. Schwartz (1975): GaAs surface chemistry - a review, C R C Critical Reviews in Solid State Sciences, 5:4, 609-624

To link to this article: <http://dx.doi.org/10.1080/10408437508243518>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

GaAs SURFACE CHEMISTRY – A REVIEW

Author: **B. Schwartz**
Bell Laboratories
Murray Hill, New Jersey

TABLE OF CONTENTS

- I. Introduction
- II. Background Information
 - A. Natural Oxide
 - B. Native Oxides
- III. Experimental Results and Discussion
 - A. Thermal Oxidation
 - B. Chemical and Galvanic Oxidation
 - C. Anodic Oxidation
 - D. Plasma Oxidation
 - E. Chemical Etching Relationships
- IV. Conclusions
- V. Acknowledgments
- VI. References

I. INTRODUCTION

The surfaces of semiconductors are probably the most studied and best understood of all solid surfaces, especially the surface of silicon. Yet today there are still large areas of this field that have eluded complete description (for example, the fundamental nature of fixed oxide charge and

surface states, the basics of surface reconstruction, or even how to relate the chemistry and physics on a semiconductor surface adequately). To circumvent these gaps in our understanding of surfaces, device engineers have resorted to empirical models (e.g., surface recombination velocity) to explain the strong effects of surfaces on device characteristics. To control the properties of silicon

surfaces, they have developed methods for growing and processing silicon dioxide on the surface of silicon. The ability to grow "good" native oxides on the surface of silicon has led to the growth of a major industry in solid-state electronics. But even here, what constitutes a "good" oxide structure is still its empirical behavior, for too little is known about the chemistry of the interface between the oxide and the silicon.

It is not surprising, therefore, that when one considers semiconductor surfaces other than silicon (e.g., GaAs), the complexities introduced by the compound nature of the material result in great difficulties, not the least of which is the lack of knowledge concerning the surface chemistry of these materials. Whereas on silicon the oxidation products of variations of silicon dioxide, the oxidation product of GaAs are confused by the possibly different resulting oxidation states for the gallium and the arsenic (e.g., 0, +1, or +3 or, +5 for the latter), as well as by any compounds formed by the subsequent reaction of these primary oxidation products. The characterization of a GaAs surface is further complicated by the possible decomposition of the GaAs itself when it is heated for some device fabrication reason, or by the possible loss of one of the oxidation reaction products (i.e., As_2O_3) at these elevated temperatures. Finally, since there are numerous potential reaction products, each of which can be separately removed from the surface by some preferential chemistry, it is imperative that some ground rules be established as to what chemical systems are involved on the surface of these materials.

In this paper, we shall attempt to address a part of this problem by discussing information related to the oxidation of GaAs. We shall concentrate primarily on thermal and anodic oxides, but reference will also be made to other systems. Although this review will not be exhaustive, it is hoped that enough information will be given to show the present state of understanding in this area.

II. BACKGROUND INFORMATION

There are two reasons for examining the chemistry of surface oxides on semiconductors:

first, in the dissolution (i.e., chemical etching) of any semiconductor, there is always an oxidation state change involved; and second, the final real surface will always be covered by at least one or two monolayers of a natural oxide (unless very special conditions are utilized, such as cleavage in an ultrahigh vacuum system). Understanding the chemistry of surface oxide formation can give us insight into the nature of the surface about which we are concerned.

A. Natural Oxide

One of the earliest investigations into the "oxidation" of GaAs was done by Rosenberg¹ when he examined the room-temperature oxygen uptake of powdered samples of silicon, germanium, GaAs, and other III-V compounds. He observed that GaAs oxidized very much like silicon and germanium, and about a factor of 2 slower than the antimonides (see Figure 1). Recently, Luke² examined the room-temperature oxidation of cleaved surfaces of silicon and of gallium arsenide (see Figures 2 and 3 respectively), and he also found a very strong similarity in the kinetics of the processes. It appears, then, that the natural oxide present on the surface of any GaAs sample will, like silicon, normally be in the 20- to 30-Å thickness region under standard laboratory conditions.³ Obviously, if special precautions are taken to keep a freshly cleaved surface away from any oxidizing ambient, then a thinner (i.e., zero to one monolayer) natural-oxide film will be present on the surface. It is the latter approach that is usually attempted in controlled surface physics studies. Unfortunately, the real world of semiconductor device surface physics is not nearly so well controlled, and this thin natural oxide is very often ignored. Recent studies, however, have shown the strong influence of a very thin oxide between a metal and a semiconductor⁴⁻⁷ and have caused semiconductor device design and fabrication engineers to be even more careful about surface preparation techniques.

B. Native Oxides^a

It is obvious from Figure 3 that the natural oxide on GaAs is normally quite thin. For technological uses it is considered important that

^aThe term "native oxide" is defined as the residual surface oxide product that is formed when the surface of the host crystal (e.g., GaAs) is consumed in an oxidizing ambient. The differentiation between a natural and a native oxide implies other than simple room-temperature exposure of the surface to air for native oxide formation.

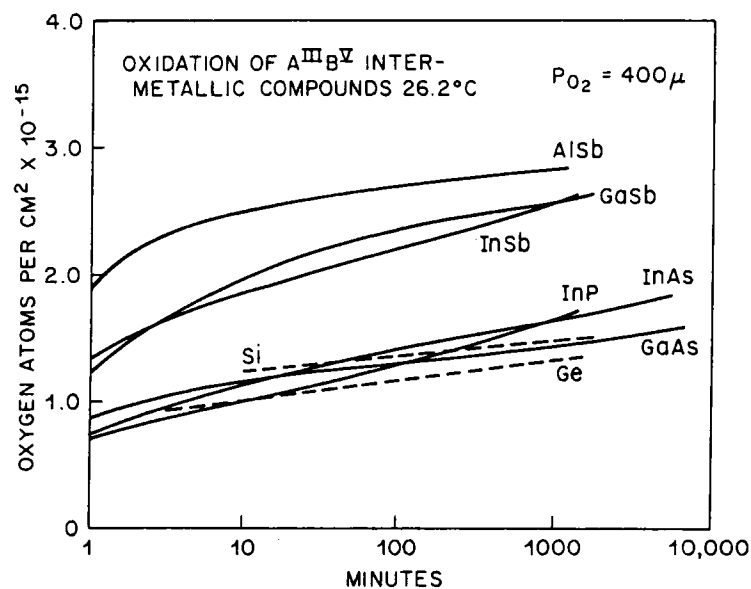


FIGURE 1. Plot of oxygen sorption, normalized to unit surface area, as a function of time for a number of powdered semiconductor samples at 26.2°C and at an oxygen pressure of 0.40 to 0.45 torr. (From Rosenberg, A. J., *J. Phys. Chem. Solids*, 14, 175, 1960. With permission.)

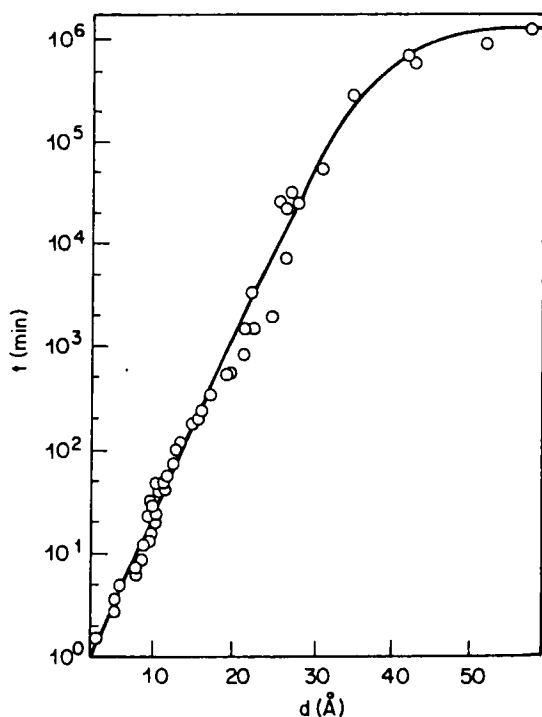


FIGURE 2. Plot of oxide film thickness (obtained by ellipsometry) versus time for cleaved [i.e., (111)] single-crystal silicon surface in air at room temperature. (From Lukeš, F., *Surf. Sci.*, 30, 91, 1972. With permission.)

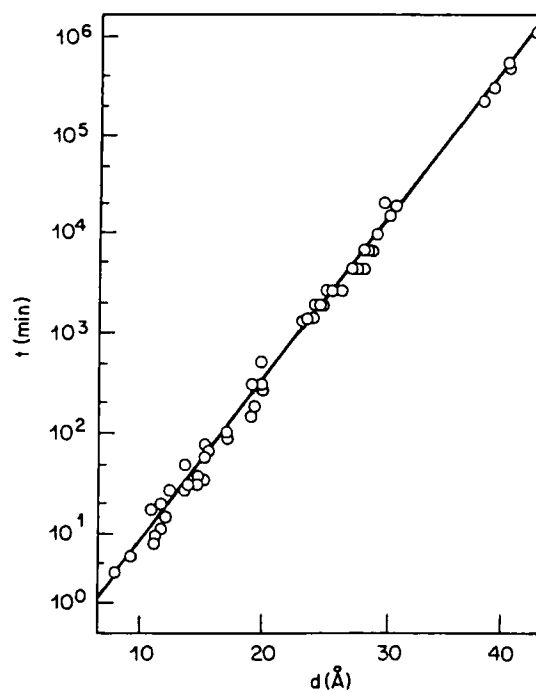


FIGURE 3. Plot of oxide film thickness (obtained by ellipsometry) versus time for a cleaved [i.e., (110)] single-crystal GaAs surface in air at room temperature. (From Lukeš, F., *Surf. Sci.*, 30, 91, 1972. With permission.)

"good", thick native oxides (i.e., greater than 1,000 Å) be preparable. This requirement comes about because of the following types of device needs: (1) the product of dielectric breakdown strength and oxide thickness must be adequate for MOS or dielectric standoff needs (i.e., ~20 V minimum), and (2) the oxide should be thick enough to minimize the permeability of the oxide to unwanted impurities for potential passivation uses; additionally, it is considered very useful for MOS oxides if (3) the Q_{ss} (fixed charge density) and N_{ss} (interface trap density) can be controlled and kept low (less than $10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$), and (4) if the mobile-ion charge density in the oxide can also be kept low ($10^{10}/\text{cm}^2$ range, if possible).

An implied requirement for a "good" and useful native oxide is the structural homogeneity of the oxide film. This means that the film must be a continuous, uniform medium that contains very few grain boundaries. This requirement is met if the film is crystalline and epitaxial to the substrate (i.e., with minimal interfacial strain at the oxide/semiconductor interface), or if the film is completely amorphous.

If one could prepare a native oxide on GaAs that met all of the above mentioned criteria, then, coupling this with the already known properties of GaAs (e.g., high electron mobility), one could fabricate some interesting new and improved MOS-type device structures; even more generally, planar technology similar to that used in silicon might result. It was with these ideas in mind that people began to examine the question of thick native-oxide growth on GaAs surfaces.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Thermal Oxidation

Because of the success achieved in growing thick oxides on silicon by high-temperature processing, oxidation of GaAs was at first approached in a similar manner. In 1962, Minden⁸ examined the thermal oxidation of GaAs in pure oxygen and in water-vapor-containing oxygen, at temperatures between 600°C and 900°C; he stated that at temperatures below 600°C the oxidation was negligible and that above 900°C the sample tended to "burn up." He noted that electron diffraction examination of the grown films yielded "sharp rings which had spots characteristic of partial orientation of the crystallites in the film."

He concluded that the evidence "... showed unequivocally that the film consisted of β -Ga₂O₃ ..."; he found no evidence of an arsenic-containing phase. Later, Rubenstein⁹ examined the thermal oxidation of GaAs and GaP in pure oxygen in the temperature range between 700°C and 1,130°C. He found that primarily β -Ga₂O₃ and a small amount of crystalline GaAsO₄ were observed as the products in the oxidation of GaAs, but when GaP was thermally oxidized, it was primarily GaPO₄ and only a small amount of β -Ga₂O₃ that were observed. Finally, in 1973, Phillips et al.¹⁰ reported on the thermal oxidation of Ga(AsP) (where $P \cong \text{As}$) in dry oxygen in the temperature range between 600°C and 900°C (see Figure 4). Again, they observed that the film consisted of a mixture of crystalline products (i.e., β -Ga₂O₃ and GaPO₄).

In evaluating some of the properties of thermal oxides, Zaininger and Revesz¹¹ found that samples of GaAs oxidized at 660°C in dry oxygen had a granular structure about 0.5 μm in size; their chemical analysis indicated that the films were essentially free of arsenic. From some of their etching and ellipsometric measurements they concluded "... that the film has a composite nature and cannot be completely removed by boiling hydrochloric acid." They suspected that there was a build-up of arsenic at the interface between the semiconductor and the oxide during the oxidation. Recently, Sealy and Hemment¹² examined some thermal oxides grown on GaAs; they also concluded that some form of arsenic was still present in the oxide film grown in an oxygen atmosphere at 610°C, whereas films grown at 680°C contained practically no arsenic. From their data, they deduced that very little arsenic was accumulated at the GaAs/oxide interface.

All of the work noted above described high-temperature growth of oxides on GaAs that resulted in predominantly, if not completely, polycrystalline layers. Navrátil¹³ has reported the results of some of his studies on the oxidation of GaAs in dry oxygen over a much lower temperature range (i.e., 400°C to 530°C) than his predecessors used, and one can infer from his paper that the degree of crystallinity in the grown films was comparatively low. From his data (see Figure 5), one observes that at temperatures below 400°C there was "negligible" native oxide growth, whereas above 530°C there appeared to be a runaway condition. He noted that, for tempera-

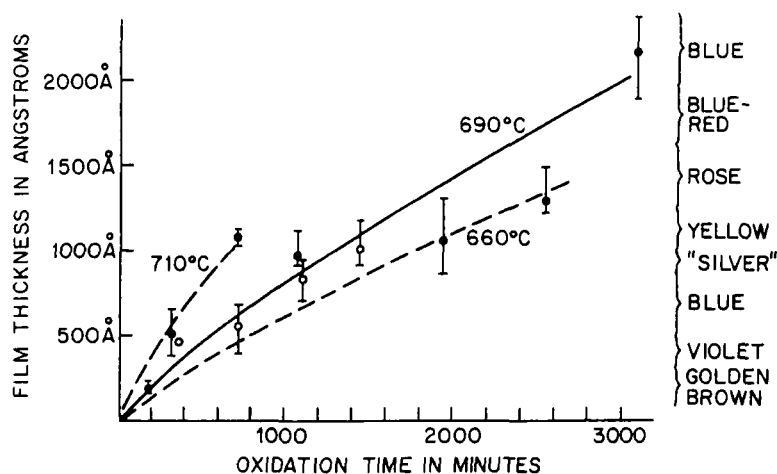


FIGURE 4. Plot of oxide film thickness of (100)-oriented GaAsP ($P = As$) in dry oxygen at atmospheric pressure as a function of temperature: the ordinate to the right indicates the apparent color of the film at the thickness listed on the left ordinate. (From Phillips, D. H. et al., *J. Electrochem. Soc.*, 120, 1087, 1973. With permission.)

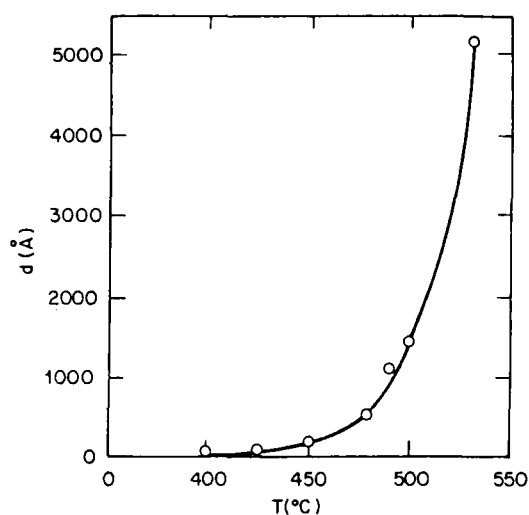


FIGURE 5. Plot of oxide film thickness versus temperature for (111)-oriented GaAs samples exposed to dry oxygen for 2 hours. (From Navrátil, K., *Czech. J. Phys.*, B18, 266, 1968. With permission.)

tures higher than 550°C, “it was not possible to use optical methods for thickness determination,” and for temperatures of 650°C and above, “only a dim and nontransparent layer was formed on the surface.” However, in the temperature range between 400°C and 525°C, what appeared to be reasonable films could be grown. Recently, Murarka¹⁴ did similar experiments and observed that films grown between 450°C and 500°C were,

indeed, amorphous and of good uniformity and electrical quality.

It appears, then, that this low-temperature oxidation technique might meet the needs of device technologists. More important, this result shows that a higher degree of oxidation can take place on GaAs at temperatures relatively low compared to those required for the oxidation of silicon. It should be mentioned, however, that even the smoothest and apparently most uniform films grown at low temperatures showed some “haziness” at the GaAs/oxide interface, indicative of “interface reaction” possibly caused by outdiffusion of either gallium or arsenic from the substrate during the stages of oxidation; this effect becomes even more noticeable as the oxidation time is increased.

Navrátil described the parabolic (diffusion) law for the oxide growth between 400°C and 450°C and a linear-growth law between 480°C and 530°C. It appears, then, that below 450°C his growing oxide was probably a continuous, amorphous material that acted as the diffusion medium through which the oxidant was transported in order to get from the external gas ambient to the GaAs/oxide interface where the actual oxidation took place.¹⁵ Above 480°C the degree of crystallization apparently started to become important enough to cause the uniform diffusion front to break down, and grain boundary mobility of the oxidant (which can be very rapid) took place,

allowing for a much higher oxidation rate and a different kinetic control mechanism.

B. Chemical and Galvanic Oxidation

As stated earlier, chemical etching of semiconductors always involves an oxidation-state change, and, because most GaAs etches are aqueous-based systems, the formation of oxides as intermediates is to be expected. The effects of exposing bromine-methanol polished¹⁶ GaAs surfaces to various "oxidizing" ambients was reported by Schwartz,¹⁷ and his results are shown in Table 1. A number of important points immediately come into focus from these data. The first is that deionized water itself can oxidize GaAs; in fact, not only will water oxidize GaAs, it will then attack the formed oxide to dissolve some of the oxide reaction products and leave the rest behind in crystallized form. From the Pourbaix diagrams¹⁸ on gallium and arsenic (see Figures 6 through 9)^b it is obvious that As_2O_3 will dissolve more readily in water at $\text{pH} = 7$ than it will in acidic water at $\text{pH} \leq 5$, whereas Ga_2O_3 will not

dissolve in water at $\text{pH} = 7$, but will at $\text{pH} = 3$. Therefore, the observation that polycrystalline $\text{Ga}_2\text{O}_3 \cdot \text{H}_2\text{O}$ was observed as the reaction product on the surface of gallium arsenide exposed to pure water is totally consistent with the Pourbaix diagrams.

When acidified water is used as the ambient for the gallium arsenide, it is important to consider the acid anion present in the ambient as well as the hydrogen ion concentration. It can be seen in Table 1 that, when Cl^- was present, the GaAs sample was left basically intact, and only a relatively thin "native oxide" was observed on the surface. When NO_3^- was the acid anion, the GaAs was totally consumed, and only powdered As_2O_3 was observed to be the reaction product.

As for basic aqueous solutions, one can again see in the Pourbaix diagrams (see Figures 6 and 8) that As_2O_3 above $\text{pH} = 9$ becomes quite soluble with increasing pH and that Ga_2O_3 above $\text{pH} \approx 11$ is totally soluble. In addition, it is known that gallium hydroxide is very soluble in ammonia solutions (i.e., NH_4OH)¹⁹ and that the free energy

TABLE 1
Effect of "Oxidants" on GaAs^a

Orientation	Dopant	Oxidant	Time (days)	Results
(100)	Te 10^{18}	—	—	25 Å ^b
(100)	Te 10^{18}	H_2O (room temperature)	6	~850 Å ^b (powdery surface)
(100)	Si 10^{18}	H_2O (warm, 60°C)	6	$\text{Ga}_2\text{O}_3 \cdot \text{H}_2\text{O}^c$ (Ga:O:1:2) ^d
(100)	Te 10^{18}	H_2O_2	6	115 Å
(100)	Te 10^{18}	H_2SO_4^e	6	$\text{Ga}_2(\text{SO}_4)_3^c$
($\bar{1}\bar{1}\bar{1}$)	Semi-insulating	HNO_3	5	As_2O_3 powder ^f
(100)	Te 10^{18}	HCl	5	55 Å ^b
($\bar{1}\bar{1}\bar{1}$)	Semi-insulating	NaOH	5	Na_2CO_3
(100)	Te 10^{18}	NaOCl	6	Dull stained surface

^aAll samples were polished on Pan-W cloth with solutions of 0.075% Br_2 in CH_3OH . Deionized water (10 MΩ-cm resistivity) was used. All oxidant solutions were concentrated reagents, except H_2O_2 , which was 30% by volume.

^bFrom ellipsometric analysis.

^cFrom X-ray analysis.

^dFrom electron microprobe analysis.

^eSample dried at 250°C.

^fThe GaAs was completely converted to a white powder.

^bIn using these diagrams, it is very important to remember that they were derived from a particular set of conditions; modifying these conditions can cause changes in the details of these diagrams. But as a starting point for understanding pH effects, the information as presented is very useful.

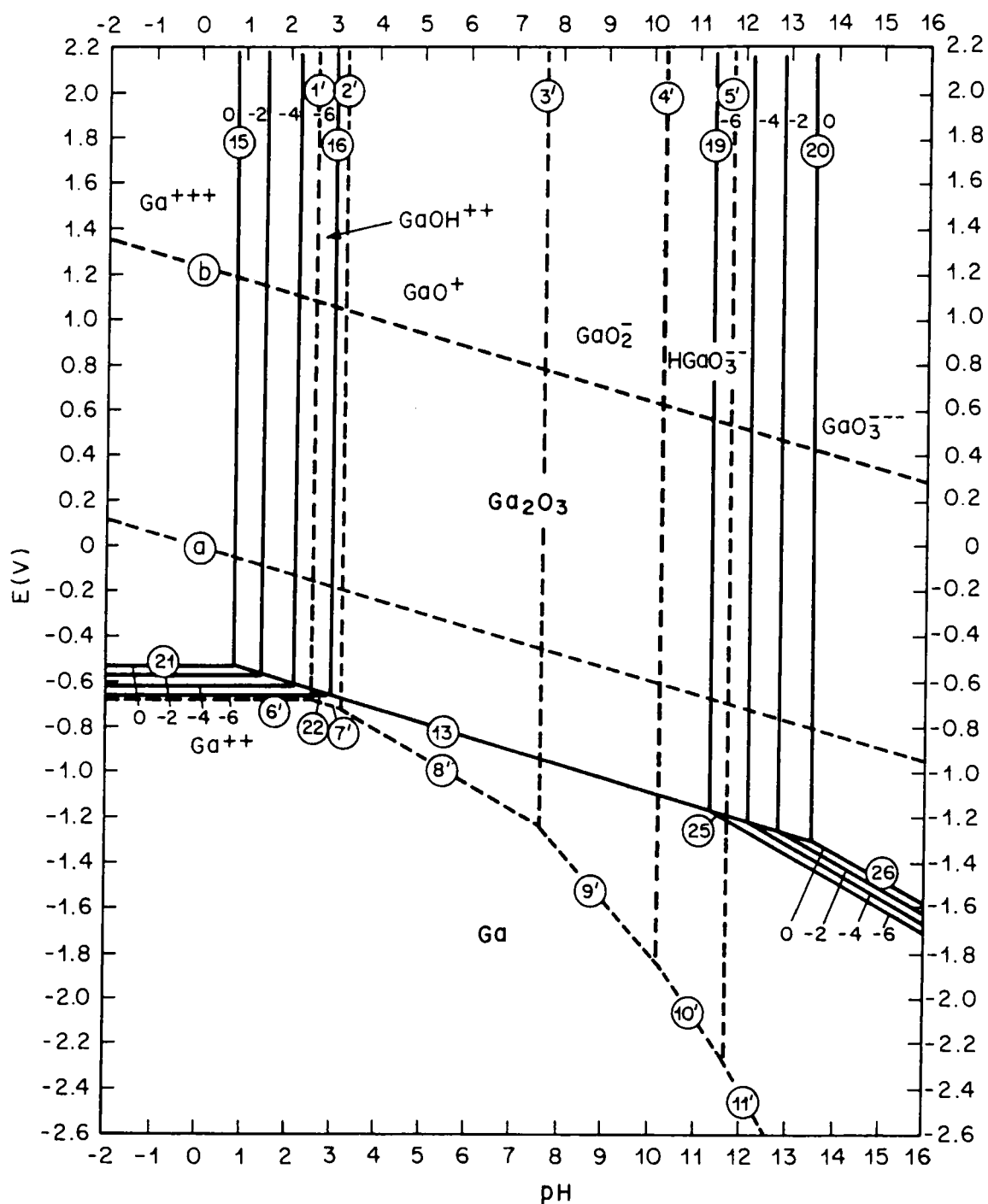


FIGURE 6. Equilibrium potential-pH diagram for the system Ga-H₂O at 25°C. (From Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solution*, Pergamon Press, New York, 1966. With permission.)

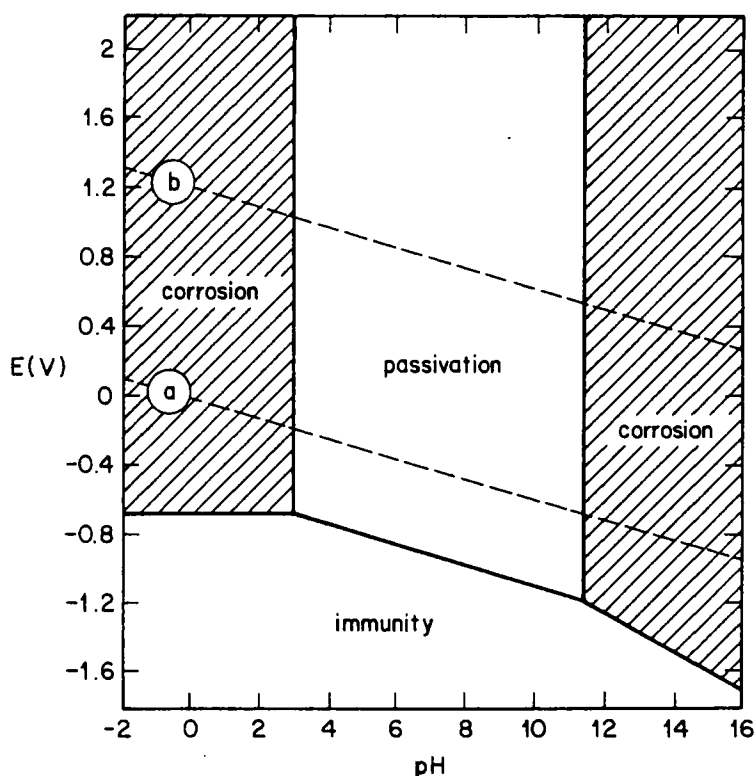
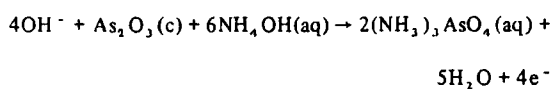


FIGURE 7. Theoretical conditions of corrosion, immunity, and passivation of gallium at 25°C, assuming passivation by a film of $\alpha\text{-Ga}_2\text{O}_3$. (From Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solution*, Pergamon Press, New York, 1966. With permission.)

of formation of $(\text{NH}_4)_3\text{AsO}_4(\text{aq})$ is large,²⁰ so that the reaction



where $\Delta G_{298}^\circ < -100$ kcal, is considered favorable, even at room temperature. Therefore, $\text{NH}_4\text{OH}(\text{aq})$ is to be considered a good solvent for the native oxides grown on GaAs.

It should be pointed out at this time that the Na_2CO_3 observed when GaAs was exposed to NaOH (see Table 1) is really an artifact, because the exposure of any NaOH solution to air will always yield the carbonate, due to CO_2 absorption from the air. In addition, NaOH would also be effective as an etchant for GaAs native oxide, except that Na^+ contamination of the surface is a

possible consequence and the complexing action of NH_4^+ is not available for enhanced dissolution.

Whereas water will oxidize GaAs, albeit slowly, and preferentially dissolve one or another of the reaction products and leave behind a polycrystalline residue, as described above, aqueous H_2O_2 will cause a stable, *amorphous* native oxide to grow, which is thicker than one that can be grown in water at any pH (see Table 1). However, even in boiling H_2O_2 solutions, only relatively thin oxide layers (i.e., approximately 150 Å) can be grown galvanically.^c This effect now can be understood in light of the results of Harvey,²² who found, by potentiostatic examination of a GaAs electrode both in acidic and in basic aqueous solutions, a classic "passivity" in the current-voltage plot (see Figure 10). From his analysis, Harvey determined that the passive film was about 28 atom-layer equivalents, which, when multiplied by a factor of

^cThe terms "galvanic" and "chemical" oxidation are used as defined in the paper by Schwartz and Sundberg.²¹ They refer, respectively, to the presence or absence of a nonreactive ohmic contact on one face of the GaAs while it is exposed to the oxidant solution either allowing or inhibiting, respectively, the cathodic component of the oxidation-reduction reaction.

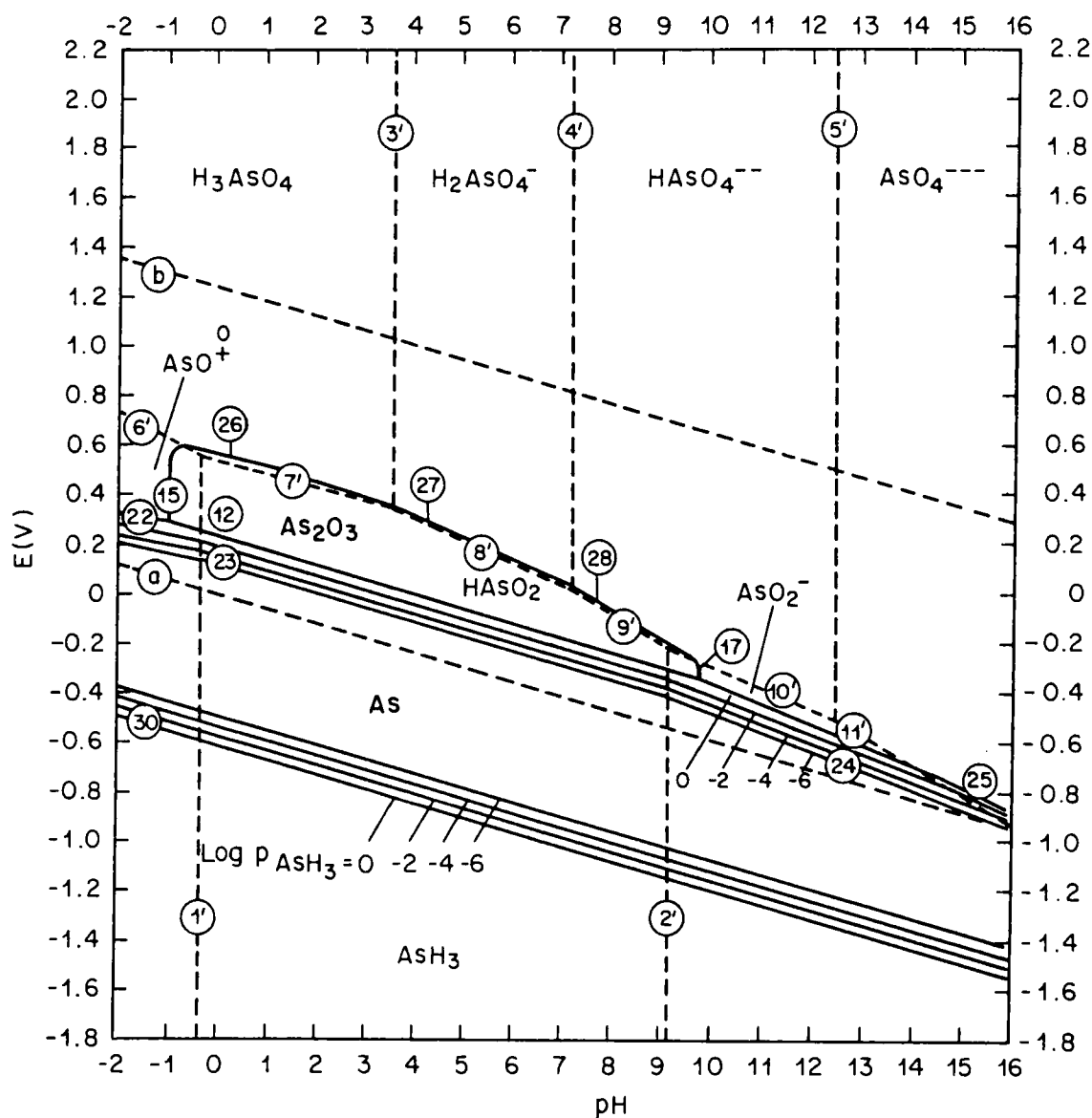


FIGURE 8. Equilibrium potential-pH diagram for the system $\text{As-H}_2\text{O}$ at 25°C . (From Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solution*, Pergamon Press, New York, 1966. With permission.)

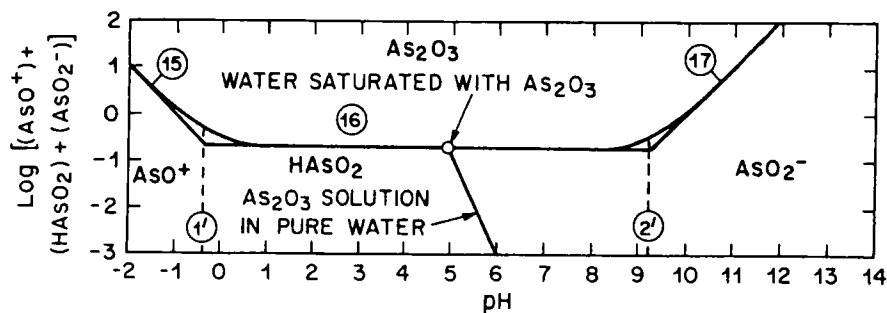


FIGURE 9. Plot of the influence of pH on the solubility of As_2O_3 in H_2O at 25°C . (From Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solution*, Pergamon Press, New York, 1966. With permission.)

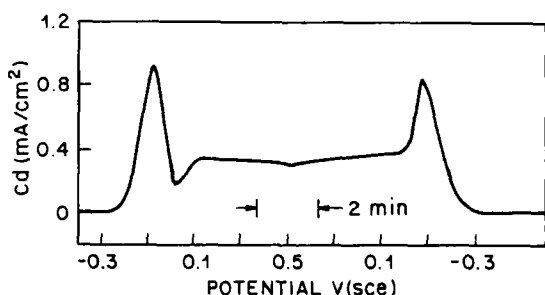


FIGURE 10., Plot of the variation of anodic current density during a slow triangular potential sweep to a low over-potential in a potentiostatic analysis of a GaAs anode in aqueous solution, with pH = 7.4. (From Harvey, W. W. and Kruger, J., *Electrochim. Acta*, 16, 2017, 1971. With permission.)

5 Å per atom-layer, calculates to 140 Å, and this is in excellent agreement with the 150 Å noted above. This thin native oxide growth on GaAs is to be contrasted with the thick galvanic oxide (e.g., 1,300 Å in 14 hr) that can be grown on GaP²¹ in boiling H₂O₂. From the data obtained by Memming and Schwandt,²³ who potentiostatically examined a GaP electrode both in acidic and in basic electrolytes (see Figure 11), no evidence is found of the type of passivity effect seen with GaAs.

The cause of the "passivity" in oxide growth on GaAs is not clearly defined, but it could well be due to the very good diffusion-barrier properties observed for the native oxide on GaAs.²⁴ In galvanic as well as in thermal oxidation of GaAs, diffusion of the oxidant occurs from the external ambient to the semiconductor/oxide interface, where the oxidation actually takes place; therefore, if the oxidant cannot diffuse through the already formed oxide layer, no additional growth will result. It is thus possible that the low and relatively narrow temperature range observed both by Navrátil¹³ and by Murarka¹⁴ for good amorphous thermal oxide growth may be related to the fact that at about 320°C As₂O₃ has a vapor pressure of approximately 1 at. It may well be that the loss of some As₂O₃ is necessary to allow for appreciable diffusion of the oxidant (see Section IV for discussion on film crystallization). In addition, because the formed amorphous oxide is a metastable phase, at higher temperature additional energy is available, resulting in rapid crystallization of the oxidation reaction products, which then causes the entire growth mechanism to shift away from diffusion control.

C. Anodic Oxidation

Although only relatively thin oxides can be grown galvanically on GaAs in H₂O₂ solution, much thicker amorphous oxides have been grown on GaAs by use of anodic techniques, both in H₂O₂ solutions²⁵ and in dilute aqueous solutions of H₃PO₄²⁶ (see Figure 12). In fact, when hot aqueous electrolytic solutions were used, films as thick as 8,000 Å were prepared.²⁷ Under normal room-temperature conditions, films can be grown on GaAs surfaces at about 20 Å of oxide for every volt of working potential available; for each 20 Å of oxide grown, approximately 13 Å of GaAs is consumed.

At this point it is necessary to define the working potential. It was observed that, when n-type GaAs was made the anode either in an aqueous H₂O₂ solution²⁸ or in a very dilute solution of H₃PO₄,²⁹ the semiconductor/electrolyte interface acted as a reverse-biased Schottky diode, and the relationship that governed the working potential was

$$V_{ox} = (V_a - V_b - V_s) (f[r(t)])$$

where V_{ox} = working potential drop across the growing oxide layer, V_a = applied bias, V_b = breakdown voltage of the semiconductor, V_s = electrolyte double-layer voltage, and $f[r(t)]$ = a resistance function dependent on the oxide thickness and resistivity.

For the generation of the data used in Figure 12, an n-type GaAs sample doped with silicon to about $2 \times 10^{18} \text{ cm}^{-3}$ was used as the semiconductor electrode. Because the breakdown voltage for such heavily doped GaAs is low³⁰ (e.g., about 2 to 3 V), and because the solution double-layer voltage is also expected to be low (i.e., about 1 V), the offset from the origin is small and not easily detected in the scale of Figure 12. However, when the doping level of the GaAs is low (e.g., $\sim 10^{16} \text{ cm}^{-3}$), then the V_b will be large (i.e., 70 V), and the voltage offset will also be large; special device geometries have been fabricated by using this effect for controlled electrolytic etching.^{28,29}

D. Plasma Oxidation

A modified form of anodic oxidation of GaAs in a plasma has been demonstrated by Weinreich,³¹ using a system similar to that designed by Ligenza³² for silicon plasma anodization. Weinreich³¹ notes that, using a temperature

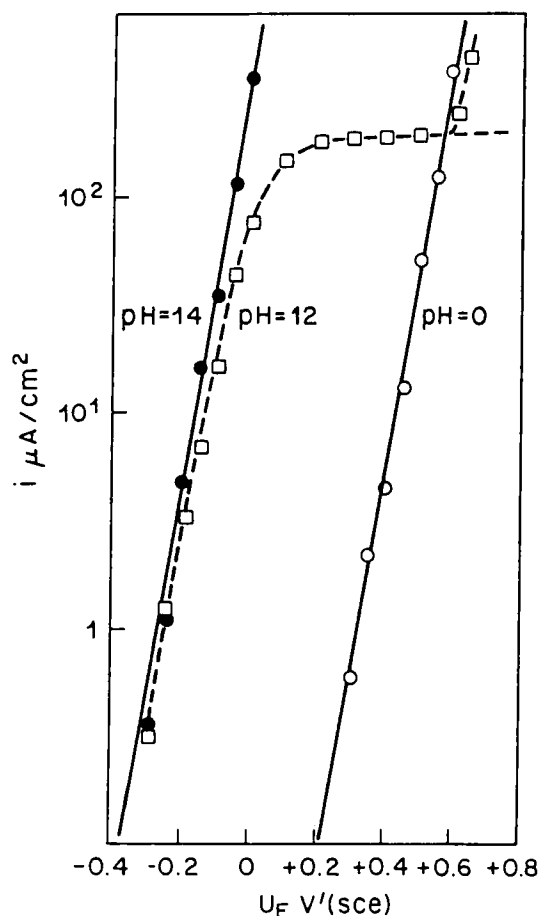


FIGURE 11. Semilogarithmic plot of interfacial current (i) versus electrode potential (U_E) of a GaP anode in aqueous solutions of different pH containing 1N Na_2SO_4 , under potentiostatic analysis. (From Memming, R. and Schwandt, G., *Electrochim. Acta*, 13, 1299, 1968. With permission.)

of 70°C, he was able to grow *amorphous* oxide layers and achieve the thicknesses shown in Figure 13; no additional data have since been published on these layers. However, Sugano and Mori,³³ who have been doing plasma oxidation of GaAs, GaP, and GaAsP in a simple high-frequency oxygen-discharge plasma, report on the growth of primarily *polycrystalline* oxidation products, similar to those reported for high-temperature thermal oxidation. Also reported by them was a very strong orientation dependence as well as pressure and input-power dependence, as shown in Figure 14. Since this is a sparsely reported oxidation technique, it will take some time and

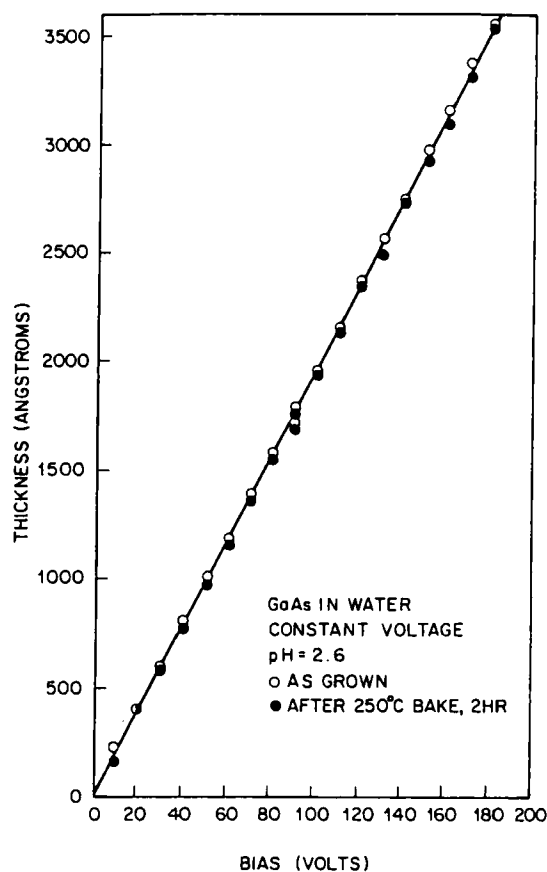


FIGURE 12. Plot of oxide thickness versus applied potential (i.e., at a constant applied bias) for the anodization of GaAs in an aqueous solution of H_3PO_4 at a pH of 2.6, at 25°C. (From Schwartz, B. and Ermanis, F., *J. Electrochem. Soc.*, 121, 206C, 1974. With permission.)

much more work before any conclusive statements on product crystallinity can be made.

E. Chemical Etching Relationships

As mentioned earlier, chemical etching of GaAs always involves an oxidation-state change for both the gallium and the arsenic atoms. Therefore, it seems reasonable to conclude that, since a "redox" reaction will be taking place at the surface of the GaAs during chemical etching, any orientation dependence of oxidation potential should also become evident as differences in etching rates during an etching reaction that is not under diffusion control.^d Straumanis et al.³⁴ observed

^dThat is, neither diffusion of the reagent to the surface nor the reaction products away from the surface of the GaAs into the solution is the rate-controlling step.

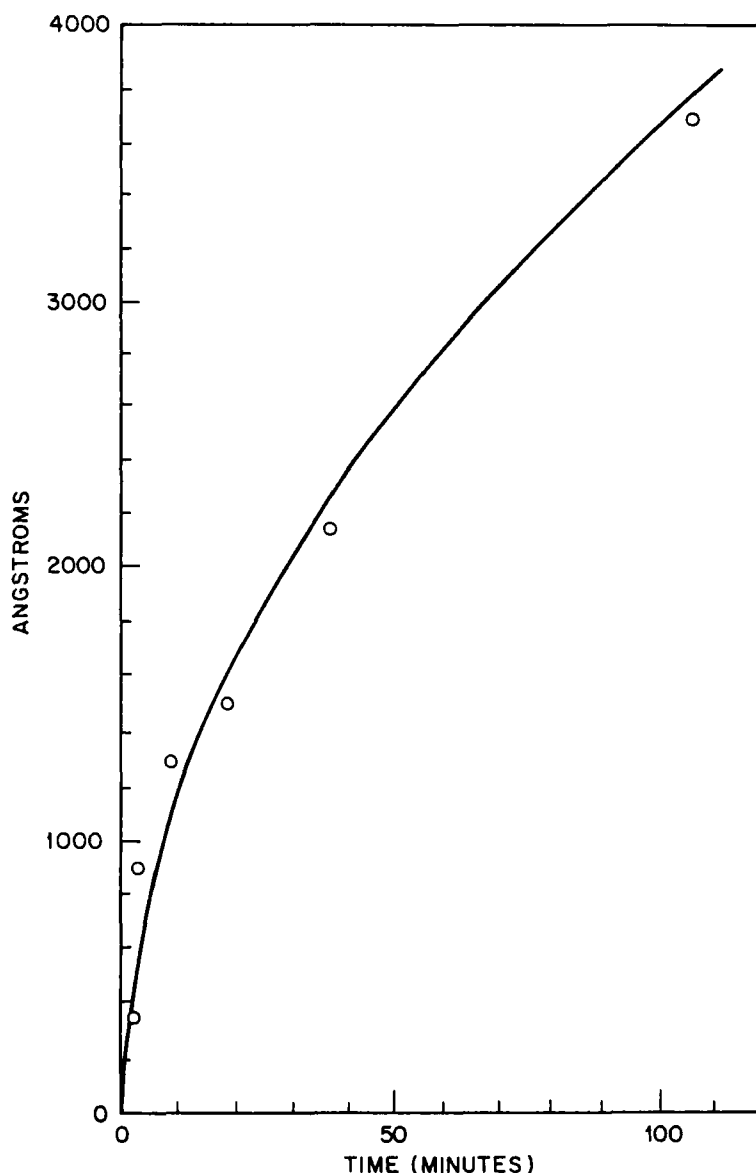


FIGURE 13. Plot of oxide thickness versus time for (111)-oriented GaAs, anodized in an oxygen plasma generated by a 1-kw cw output "Microtron" microwave heater at 0.2 torr and 70°C, with an anodization bias of 50 V. (From Weinreich, O. A., *J. Appl. Phys.*, 37, 2924, 1966. With permission.)

the orientation dependence of the anodic dissolution potentials of GaAs in 1N KOH, as shown in Figure 15; the orientation dependence^e is as follows: $(\bar{1}\bar{1}\bar{1}) > (110) > (100) > (111)$. Considering, also, the observation of MacRae,³⁵ made in some of his LEED experiments, that the sticking probability for oxygen is ten times greater on the $(\bar{1}\bar{1}\bar{1})$ face of GaAs than it is on the (111)

face of GaAs, it seems reasonable to conclude that the $(\bar{1}\bar{1}\bar{1})$ face of GaAs has a higher oxidation potential than the (111) face of this material. It is, therefore, not surprising that in almost all of the reported simple etching systems used on GaAs the $(\bar{1}\bar{1}\bar{1})$ face is faster-etching than the (111) face. In those cases where metal-displacement plating was utilized (e.g., Cr³⁶ or Ag³⁷), or where the

^eThe convention used in this paper is that in GaAs the (111) surface is the gallium-rich surface and the $(\bar{1}\bar{1}\bar{1})$ is the arsenic-rich surface.

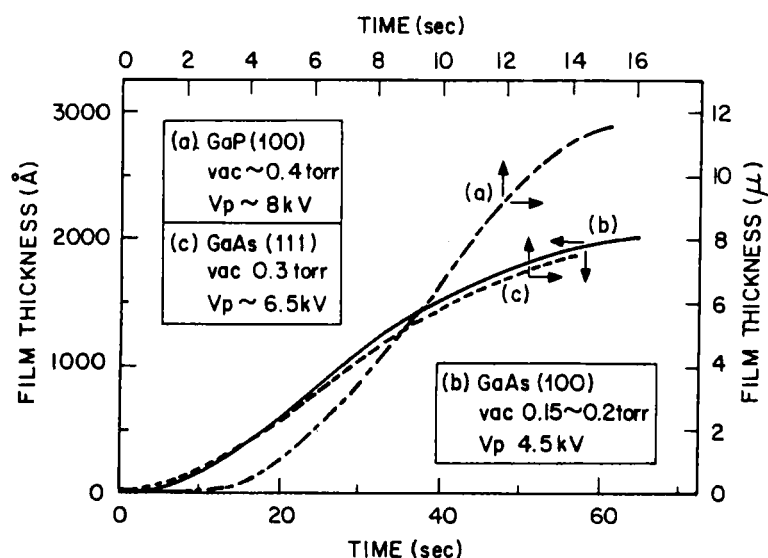


FIGURE 14. Plot of oxide thickness versus time for variously oriented GaAs and GaP samples in an RF-generated oxygen plasma. (From Sugano, T. and Mori, Y., *J. Electrochem. Soc.*, 121, 113, 1974. With permission.)

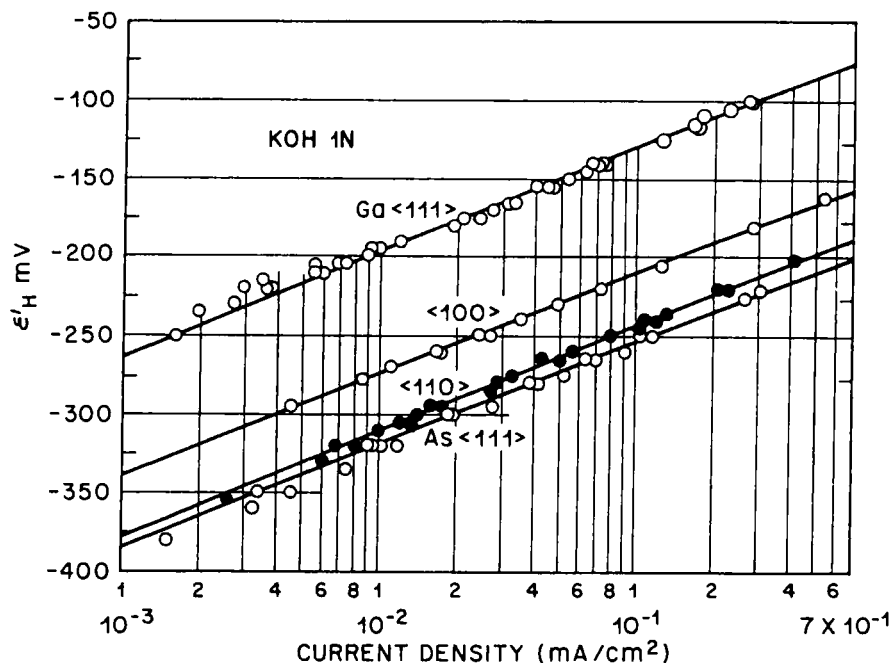


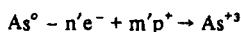
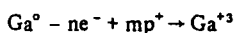
FIGURE 15. Plot of anodic dissolution potentials (E_h) of GaAs versus the logarithm of current density (i) for variously oriented GaAs surfaces. (From Straumanis, M. E., Krumme, J. P., and Jones, W. J., *J. Electrochem. Soc.*, 115, 1050, 1968. With permission.)

oxidation potential of H_2O_2 was drastically modified (i.e., lowered) by adding a strong base to raise the pH of the etching solution,^{38,39} the orientation dependences have been modified enough to allow for the polishing of the (111) face.

If one now considers the nonaqueous Br_2-CH_3OH etching systems¹⁶ acting on GaAs, the bromine is the oxidant and the CH_3OH is the solvent for the formed gallium and arsenic bromides.⁴⁰ Tarui and his co-workers⁴¹ examined the orientation dependence of the etch rate of GaAs in Br_2-CH_3OH solutions and found that $(110) > (\bar{1}\bar{1}\bar{1}) > (100) > (111)$. Although the orientation order is similar to the Straumanis ordering, it should be kept in mind that the (110) is the only nonpolar plane in the listing. Additionally, in the Br_2-MeOH etching system, the oxidant is a molecule, and it "approaches" the surface as such.⁴⁰ (i.e., not as an ion or a dipole, as in many aqueous etching systems).

Another factor that must be considered relates to additives, other than the metal-displacement systems, which result in changes in the dielectric constant of the solvent medium (e.g., acetic acid, glycerine, tartaric acid, etc.). These additives can cause appreciable changes in the ionization constant (i.e., oxidation potential) of the oxidant in the solvent, thereby changing the orientation dependence of the etch rates.

Finally, the question of electron or hole involvement in the actual oxidation step^{40,42} is not to be ignored if one wants to understand the role of conductivity type in oxidation²¹ and preferential etching. This means that, in determining the oxidation reactions for gallium and for arsenic,



where $n + m = 3$ and $n' + m' = 3$, the question of the values of n , n' , m , and m' becomes important. In the case of germanium dissolution, Brattain and Garrett⁴² showed that the reaction was predominantly hole-concentration-dependent. A similar hole-concentration dependence has been observed in the anodic oxidation and dissolution of GaAs;^{22,43} however, the absolute values of these coefficients will depend on the oxidant used.⁴⁰

IV. CONCLUSIONS

From the data shown in Table 1, and from the analyses reported in the high-temperature thermal-oxidation studies, one can infer that both gallium and arsenic occur in the +3 oxidation state when the native oxide is amorphous, and in the +3 and +5 oxidation states, respectively, when the oxide has undergone crystallization. It appears that the amorphous oxide is a metastable phase that is a mixture (solution) of Ga_2O_3 and As_2O_3 (possibly the hydrates thereof), and once crystallization occurs (which is the true stable phase), only the compounds Ga_2O_3 and $GaAsO_4$ are the reaction products; the crystallization reaction is irreversible. The rationale for the argument that the amorphous state is a mixture instead of the compound $GaAsO_3$ (i.e., where both the gallium and the arsenic are also in the +3 oxidation states) is that analysis of the oxide compositions, by combined Rutherford backscattering and He-induced X-ray generation,⁴⁴ has shown a non-uniform Ga/As ratio in depth, from the outer to the inner surfaces of the oxide. In addition, the existence of vitreous As_2O_3 is a very well known and documented system,⁴⁵ but neither amorphous Ga_2O_3 nor amorphous $GaAsO_3$ has ever been reported. It is reasoned, therefore, that the As_2O_3 could be considered the vitreous "solvent" in which the Ga_2O_3 is dissolved. Thus, when the As_2O_3 concentration becomes relatively low, the $\alpha-Ga_2O_3$ begins to precipitate out, and we obtain the results noted in the high-temperature thermal-oxidation studies, where the first crystalline phase determined was always a form of Ga_2O_3 .

It is also obvious that there are many options to be considered when trying to understand the surface chemistry of a specific etching system attacking a GaAs surface. Of those we already know, there are such parameters as the pH and anion effects, as well as the presence of complexing agents (e.g., NH_4^+ ions) or displacement-platable metals that can strongly influence the direction of the reactions. The more subtle factors, such as the requirements of the oxidant for electrons or holes during the actual oxidation step and the role of crystal orientation in oxidation potential, are yet to be unraveled. Most assuredly, this last factor must be related to the polar nature or partial ionic character of the Ga-As bond and the resulting surface-layer dipole.⁴⁶ Unfortunately, we are not yet far enough along in our

understanding of these surface dipoles to be able to attempt a complete model to explain preferential etching; it is hoped that this will be achieved in the not-too-distant future.

As for the utilization of some of these native oxides on GaAs, it has already been demonstrated that under the proper set of conditions they can be used as a zinc diffusion mask,²⁷ as a mesa etching mask,²⁵ as a surface passivation layer (at least for short times) against the attack of water on double-heterostructure mirror faces,⁴⁷ as a material for dielectric and optical isolation in GaAs monolithic integrated circuits,³³ and as a potentially useful material for MIS capacitors.¹⁰ Some of the properties that have been determined for variously grown native oxides are its inertness to organic solvents with solubility in certain mineral acids and bases, thermal stability up to 850°C for very short periods of time,²⁷ and a refractive index of 1.81 ± 0.1 . Unfortunately, most of the oxides grown to date have breakdown

voltages in the 10^5 to 10^6 V/cm range; more work is required before the desired dielectric properties (e.g., 10^6 to 10^7 V/cm breakdown field) will be achieved.

It is obvious that the surface chemistry of semiconductors is very complicated, and as the number of elements involved in the semiconductor (and the dopants) goes up, the problems appear to scale correspondingly in complexity.

V. ACKNOWLEDGMENTS

I would like to thank the many people at Bell Laboratories who have given of their time and efforts in numerous discussions, but I especially wish to thank F. Ermanis, L. Derick, C. D. Thurmond, A. S. Jordan, S. P. Murarka, R. M. Ryder, and Mrs. M. Read for the assistance they gave in various stages of this work, and R. M. Ryder and E. H. Nicollian for their critical reading of this manuscript.

VI. REFERENCES

1. Rosenberg, A. J., The oxidation of intermetallic compounds. III. The room-temperature oxidation of $A^{III}B^V$ compounds, *J. Phys. Chem. Solids* 14, 175, 1960.
2. Lukeš, F., Oxidation of Si and GaAs in air at room temperature, *Surf. Sci.*, 30, 91, 1972.
3. Adams, A. C. and Pruniaux, B., Gallium arsenide surface film evaluation by ellipsometry and its effect on Schottky barriers, *J. Electrochem. Soc.*, 120, 408, 1973.
4. Card, H. C. and Rhoderick, E. H., The effect of an interfacial layer on minority carrier injection in forward-biased silicon Schottky diodes, *Solid State Electron.*, 16, 365, 1973.
5. Green, M. A. and Sewchun, J., Current multiplication in metal/insulator/semiconductor (MIS) tunnel diodes, *Solid State Electron.*, 17, 349, 1974.
6. Haeri, S. Y., GaP electroluminescent memory switch, *Electron. Lett.*, 9, 12, 1973.
7. Nicollian, E. H., Schwartz, B., Ryder, R. M., Brews, J. R., and Coleman, D. J., The influence on Schottky diode characteristics of a thin oxide layer between the metal and the semiconductor, to be published.
8. Minden, H. J., Thermal oxidation of GaAs, *J. Electrochem. Soc.*, 104, 733, 1962.
9. Rubenstein, M., The oxidation of GaP and GaAs, *J. Electrochem. Soc.*, 113, 540, 1966.
10. Phillips, D. H., Grannemann, W. W., Coerver, L. E., and Kuhlmann, G. J., Fabrication of GaAsP MIS capacitors, using a thermal-oxidation dielectric growth process, *J. Electrochem. Soc.*, 120, 1087, 1973.
11. Zaininger, K. H. and Revesz, A. G., Ellipsometric investigations of oxide films on GaAs, *J. Phys. Paris*, 25, 208, 1964.
12. Sealy, B. J. and Hemment, P. L. F., Structure and composition of native oxides on GaAs, *Thin Solid Films*, 22, 539, 1974.
13. Navrátil, K., Thermal oxidation of gallium arsenide, *Czech. J. Phys.*, B18, 266, 1968.
14. Murarka, S. P., Thermal oxidation of GaAs, *Appl. Phys. Lett.*, 26, 180, 1975.
15. Poate, J. M., Buck, T. M., and Schwartz, B., A Rutherford scattering study of the chemical composition of native oxides on GaP, *J. Phys. Chem. Solids*, 34, 779, 1973.
16. Fuller, C. S. and Allison, H. W., A polishing etchant for III-V semiconductors, *J. Electrochem. Soc.*, 109, 880, 1962.
17. Schwartz, B., Preliminary results on the oxidation of GaAs and GaP during chemical etching, *J. Electrochem. Soc.*, 118, 657, 1971.
18. Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solution*, Pergamon Press, New York, 1966.
19. Sidgwick, N. V., *The Chemical Elements and Their Compounds*, Clarendon Press, Oxford, 1962, 467.

20. Wagman, D. D., Evans, W. H., Parker, V. B., Holow, I., Bailey, S. M., and Schumm, R. H., *Selected Values of Chemical Thermodynamic Properties*, Technical Note 270-3, U.S. Bureau of Standards, Washington, D.C., 1968.
21. Schwartz, B. and Sundburg, W. J., Oxidation of GaP in an aqueous H_2O_2 solution, *J. Electrochem. Soc.*, 120, 576, 1973.
22. Harvey, W. W. and Kruger, J., The passivity of gallium arsenide, *Electrochim. Acta*, 16, 1017, 1971.
23. Memming, R. and Schwandt, G., Electrochemical properties of gallium phosphide in aqueous solutions, *Electrochim. Acta*, 13, 1299, 1968.
24. Spitzer, S. M., Schwartz, B., and Weigle, G. D., Native-oxide mask for zinc diffusion in gallium arsenide, *J. Electrochem. Soc.*, 121, 820, 1974.
25. Logan, R. A., Schwartz, B., and Sundburg, W. J., The anodic oxidation of GaAs in aqueous H_2O_2 solution, *J. Electrochem. Soc.*, 120, 1385, 1973.
26. Schwartz, B. and Ermanis, F., The anodization of GaAs and GaP in aqueous solutions: analysis of the anodization process, *J. Electrochem. Soc.*, 121, 206C, 1974.
27. Spitzer, S. M., Schwartz, B., and Weigle, G. D., Preparation and stabilization of anodic oxides on GaAs, *J. Electrochem. Soc.*, 121, 92C, 1974.
28. Rode, D. L., Schwartz, B., and DiLorenzo, J. V., Electrolytic etching and electron mobility of GaAs for FETs, *Solid State Electron.*, 17, 1119, 1974.
29. Niehaus, W. C. and Schwartz, B., A self-limiting anodic etch-to-voltage (AETV) technique for fabrication of modified Read IMPATTs, *J. Electrochem. Soc.*, 121, 207C, 1974.
30. Sze, S. M., *Physics of Semiconductor Devices*, John Wiley & Sons, New York, 1969.
31. Weinreich, O. A., Oxide films grown on GaAs in an oxygen plasma, *J. Appl. Phys.*, 37, 2924, 1966.
32. Ligenza, J. R., Silicon oxidation in an oxygen plasma excited by microwaves, *J. Appl. Phys.*, 36, 2703, 1965.
33. Sugano, T. and Mori, Y., Oxidation of $GaAs_{1-x}P_x$ surface by oxygen plasma and properties of oxide film, *J. Electrochem. Soc.*, 121, 113, 1974.
34. Straumanis, M. E., Krumme, J. P., and Jones, W. J., Current-density–anodic-potential curves of single-crystal GaAs at low currents in KOH, *J. Electrochem. Soc.*, 115, 1050, 1968.
35. MacRae, A. U., Low-energy electron diffraction study of the polar [111] surfaces of GaAs and GaSb, *Surf. Sci.*, 4, 247, 1966.
36. Abrahams, M. S. and Buiocchi, C. J., Etching of dislocations on the low-index faces of GaAs, *J. Appl. Phys.*, 36, 2855, 1965.
37. Richards, J. L. and Crocker, A. J., Etch pits in gallium arsenide, *J. Appl. Phys.*, 31, 611, 1960.
38. Schumb, W. C., Satterfield, C. N., and Wentworth, R. L., *Hydrogen Peroxide*, Reinhold Corp., New York, 1955, 358.
39. Dymant, J. C. and Rozgonyi, G. A., Evaluation of a new polish for gallium arsenide using a peroxide-alkaline solution, *J. Electrochem. Soc.*, 118, 1346, 1971.
40. Gerischer, D. H. and Wallem-Mattes, I., Dissolution mechanism of gallium arsenide due to oxidizing agents, *Z. Phys. Chem.*, 64, 187, 1969.
41. Tarui, Y., Komiya, Y., and Haiada, Y., Preferential etching and etched profile of GaAs, *J. Electrochem. Soc.*, 118, 118, 1971.
42. Brattain, W. H. and Garrett, C. G. B., The interface between germanium and an electrolyte, *Bell Syst. Tech. J.*, 34, 129, 1955.
43. Efimov, E. A. and Erusalimchik, I. G., Anodic dissolution of gallium arsenide, *Elektrokhimiya*, 1, 818, 1965.
44. Feldman, L. C., Poate, J. M., Ermanis, F., and Schwartz, B., The combined use of He backscattering and He-induced X-rays in the study of anodically grown oxide films on GaAs, *Thin Solid Films*, 19, 81, 1973.
45. Rawson, H., *Inorganic Glass Forming System*, Academic Press, New York, 1967.
46. Nosker, R. W., Mark, P., and Levine, J. D., The influence of native oxides on the degradation and passivation of GaAs junction lasers, *Surf. Sci.*, 19, 291, 1970.
47. Schwartz, B., Dymant, J. C., and Haszko, S. E., Polar surfaces of wurtzite and zinc blende lattices, in *Gallium Arsenide and Related Compounds, Proceedings of the Fourth International Symposium, Boulder, Colorado, September 1972*, Conference Series, The Institute of Physics, London, 1973.