the thickness range from 40 to 260 nm. When anodic oxide films are grown at constant current density, the dependence of L on overpotential can be tested as well. The growth of an anodic oxide film on a valve metal is probably the easiest electrochemical process to study with an ellipsometer because the strong dependence of current density on field serves to keep the film thickness uniform. If growth is continued into the region where breakdown effects become important, the electrochemical process changes and begins to modify the structure of the oxide film.

The data in Table II and plotted in Fig. 4 on the anodic oxidation of titanium in an acetone-based electrolyte are typical of optical measurements in such systems. Titanium is known to exhibit ideal valve-metal behavior over a relatively narrow thickness range before processes begin which eventually lead to film breakdown, and the optical analysis must be able to determine this range as well as the best-fit values of n and k. The optical analysis is simplified somewhat in this case by the knowledge that the oxide film is transparent in the region of ideal behavior.

If we apply the Simplex algorithm to the entire data set the results are not encouraging; we find that the curve that minimizes the response function has a negative extinction coefficient and rather large deviations from the measured points. If we assume that the cause for this lack of fit is that for thicker films the assumption of a single uniform film of constant index is not valid, then we can attempt to analyze the data in subsets. The Simplex algorithm gives $n = 2.479$ for the index of the transparent film which provides the best fit to points A-B in Fig. 4, and the standard deviation calculated for n under the assumption that $k = 0$ is 0.010. Dropping point B from the analysis has no effect on the standard deviation, but adding the next point increases it to 0.018. Beyond point B the values calculated for n under the assumption that $k = 0$ decrease monotonically approximately linearly with film thickness. The curve in region B-C of Fig. 4 is calculated for a model in which n decreases linearly with thickness from a value of 2.479 at B to 2.039 at C.

Electrochemical measurements are particularly useful in ellipsometric studies of anodic oxidation. Direct measurement of bare surface P and A values for titanium are not possible under our experimental conditions, and hence we use extrapolated values calculated using electrochemical parameters which are proportional to film thickness. For valve-metal oxides either the reciprocal capacitance or the Tafel slope (the parameter relating overpotential to the logarithm of the current density) can be used in the extrapolation. The bare surface P and A values in Table II were calculated using Tafel slope and reciprocal capacitance values determined from open-circuit transients. (All of the other entries in Tables I and II are direct measurements.) As expected, the thickness of the titanium oxide film increases linearly with time in the ideal region (the standard deviation is 0.1 nm for thicknesses up to 32 nm). There is electrochemical evidence of a change in the relation between current density and field at the point where n begins to decrease, but that evidence involves too much detail to be included here. It may be that the structural modifications which occur at thicknesses over 32 nm take place sufficiently uniformly for the film to be treated as a homogeneous film with a progressively changing index, but there is little electrochemical evidence to support this view. Without such evidence a homogeneous transformation model cannot be regarded as more than an interesting possibility no matter how elaborate the algorithm used in the optical analysis.

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REFERENCES

1. F. L. McCrackin, E. Passaglia, R. R. Stromberg, and H. L. Steniberg, *J. Research. Nat. Bur. Std. A,* **67A,** 363 (1963).
2. E. Passaglia, R. R. Stromberg, and J. Kruger, Editors, "Ellipsometry in the Measurement of Surfaces and Thin Films," Nat. Bur. Std. Misc. Pub. 256, U.S. Government Printing Office, Washington, DC (1964).
3. N. M. Bashara, A. B. Buckman, and A. C. Hall, Editors, "Recent Developments in Ellipsometry," North-Holland, Amsterdam (1969).
4. N. M. Bashara and R. M. A. Azzam, Editors, "Proceedings of the Third International Conference on Ellipsometry," *Surf. Sci.,* **56** (1976).
5. F. L. McCrackin and J. Colson, NBS Tech. Note 242 (1964).
6. F. L. McCrackin, NBS Tech. Note 479 (1969).
7. M. S. Caceci and W. P. Cacheris, *BYTE,* **9,** 340 (1984).
8. J. A. Nelder and R. Mead, *Computer J.,* **7,** 308 (1965).
9. M. Born and E. Wolf, "Principles of Optics," 3rd ed., pp. 51-70, Pergamon Press, Oxford, London, New York (1964).
10. P. C. S. Hayfield and G. W. T. White, in "Ellipsometry in the Measurement of Surfaces and Thin Films," E. Passaglia, R. R. Stromberg, and J. Kruger, Editors, p. 157, Nat. Bur. Std. Misc. Pub. 256, U.S. Government Printing Office, Washington, DC (1964).

Thermodynamics of Gallium Arsenide Electrodeposition

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ABSTRACT

The gallium arsenide-gallium-arsenic-water electrochemical equilibrium diagram is calculated and compared with some results obtained in electrodeposition experiments of gallium-arsenide.

Although in the past only a few semiconductors have been considered for preparation by electrodeposition techniques, attempts to deposit germanium and silicon have been made as early as the nineteenth century, and several studies have been aimed at the electrosynthesis of II-VI compounds such as cadmium sulfide, selenide, or telluride.

However, electrochemical preparation of III-V compounds like gallium arsenide, did not arouse much interest among scientists until recently. High temperature techniques such as vacuum or plasma deposition yielded thin layers with very well-defined composition and properties but, when concern about the energy consumption and prices of these techniques arise from the energy crisis of the 1970's, new studies to develop thin film electrochemical deposition techniques were started in many countries.

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Table I. Standard free enthalpy of formation of some gallium compounds

	$\Delta G°_f$ (kJ mol^{-1})
Ga^{+3}(aq)	−159.0
$GaOH^{+2}$(aq)	−380
$Ga(OH)_2^+$(aq)	−597.4
$H_2GaO_3^-$(aq)	−745
$HGaO_3^{-2}$(aq)	−686
GaO_3^{-3}(aq)	−619

Electrodeposition of the elements present in the usual binary semiconductors is very difficult, and for many of them not possible, but becomes easier as one considers columns III, IV, V, and VI of the periodic table.

Indeed it is very difficult to electrodeposit silicon. According to literature, it can be achieved only, except for a few reported experiments that need confirmation (1), in organic solvents or molten salts (2), while, although difficulties come from the existence of secondary reactions, the electrodeposition of several II-VI compounds can be achieved [see for instance Ref. (3, 4)].

A few years ago, we began researching electropreparation of III-V compounds, and our attention was mostly focused on gallium arsenide, known for its photoelectrochemical properties (5).

Two mechanisms could be considered for its electrosynthesis: (*i*) Mechanism I: direct electrodeposition from aqueous solutions. (*ii*) Mechanism II: electroprecipitation through two successive reactions: electrochemical reduction of arsenic compound leading to the formation of arsenide AsH_3, followed by chemical reaction between the gallium ions and the hydride.

Equilibrium Diagram

The preliminary experiments we made in aqueous solution gave, in most cases, nonhomogeneous deposits. The composition varied from pure gallium or arsenic to variable proportions of both elements, and we concluded that the recalculation of the thermodynamical stability diagram of gallium arsenide in contact with aqueous solutions containing gallium and arsenic compounds was necessary to explain the results observed experimentally and to select the best possible conditions for its electrosynthesis.

Such calculations have already been used for II-VI systems (4), but, as far as I know, not for GaAs.

For equilibria of gallium arsenide in contact with aqueous solutions, it was necessary, as a preliminary step, to recalculate the arsenic-water and the gallium-water equilibrium diagrams, with consideration of the latest available data for the thermodynamical functions of the various compounds involved in these diagrams, particularly the data published in "oxydation-reduction potentials in aqueous solutions" (6), and in the U.S. National Bureau of Standards tables (7), which gave $\Delta G°_f$: standard free enthalpy, or Gibb's energy, of formation for the various compounds involved.

For each electrochemical equilibria, we have calculated the equilibrium potential, referenced *vs.* the standard hydrogen electrode (SHE) and the slope of its variations with pH: dE/dpH, and for the ionic equilibria, the standard free enthalpy of reaction $\Delta G°$ and the value pH° corresponding to zero value of the concentration term.

Gallium-water-diagram.—Only the monomeric three valent compounds, for which we know values of the standard free enthalpy of formation in aqueous solutions, were considered (Table I). The numerous condensed forms, the existence of which has been proposed in the literature, and the gallium monohydride, which would appear only at very cathodic potentials, are not considered in this study.

We can write the following equilibria

	E_o(SHE)	dE/dpH	
$Ga = Ga^{+3} + 3e^-$	−0.549V	0.0 mV	[1]
$Ga + H_2O = GaOH^{+2} + H^+ + 3e^-$	−0.494V	−19.6 mV	[2]
$Ga + 2H_2O = Ga(OH)_2^+ + 2H^+ + 3e^-$	−0.424V	−39.2 mV	[3]
$Ga + 3H_2O = H_2GaO_3^- + 4H^+ + 3e^-$	−0.115V	−78.5 mV	[4]
$Ga + 3H_2O = HGaO_3^{-2} + 5H^+ + 3e^-$	+0.089V	−98.1 mV	[5]
$Ga + 3H_2O = GaO_3^{-3} + 6H^+ + 3e^-$	+0.320V	−117.8 mV	[6]

$Ga^{+3} + OH^- = GaOH^{+2}$ [7]
$\Delta G° = -64.14$ kJ mol^{-1} pH° = 2.77

$GaOH^{+2} + OH^- = Ga(OH)_2^+$ [8]
$\Delta G° = -60.04$ kJ mol^{-1} pH° = 3.49

$Ga(OH)_2^+ + H_2O = H_2GaO_3^- + 2H^+$ [9]
$\Delta G° = 89.64$ kJ mol^{-1} pH° = 7.85

$H_2GaO_3^- = HGaO_3^{-2} + H^+$ [10]
$\Delta G° = 67$ kJ mol^{-1} pH° = 10.33

$HGaO_3^{-2} = GaO_3^{-3} + H^+$ [11]
$\Delta G° = 59$ kJ mol^{-1} pH° = 11.73

The equilibrium diagram obtained (Fig. 1) shows that the gallium is thermodynamically not stable in contact with aqueous solution but could be electrodeposited at any pH, provided that the hydrogen evolution reaction (HER) overvoltage on the working electrode is high enough, about 500 mV in the pH range 0-14. Experimentally, electrodeposition is easier in alkaline solution.

Arsenic-water diagram.—In this case, we consider only the oxidation states: −3, 0, +3; the pentavalent compounds

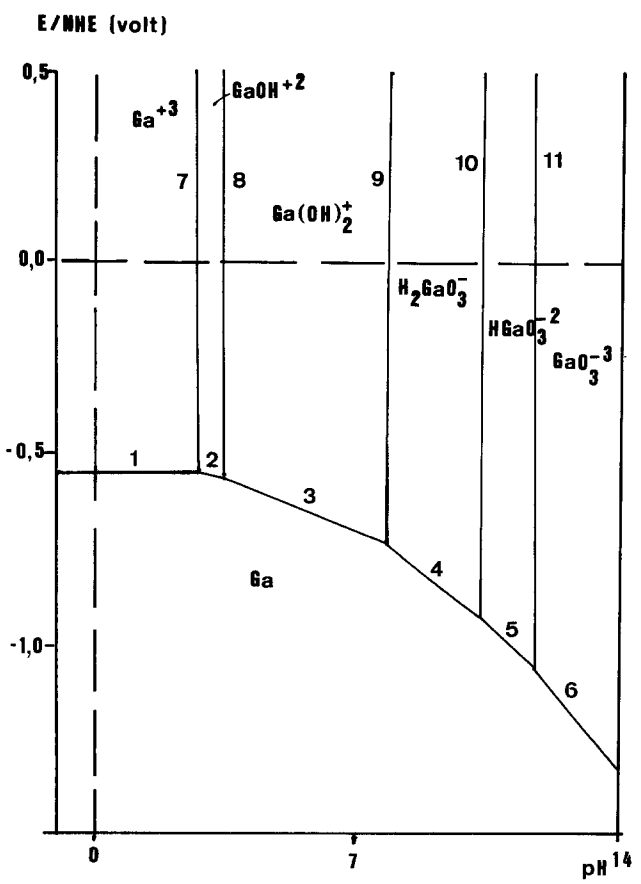

Fig. 1. Gallium-water *E*-pH diagram

Table II. Standard free enthalpy of formation of some arsenic compounds

	$\Delta G°_f$ (kJ mol^{-1})
AsH_3(g)	+ 68.9
AsO^+(aq)	−163.80
$HAsO_2$(aq)	−402.66
AsO_2^-(aq)	−350

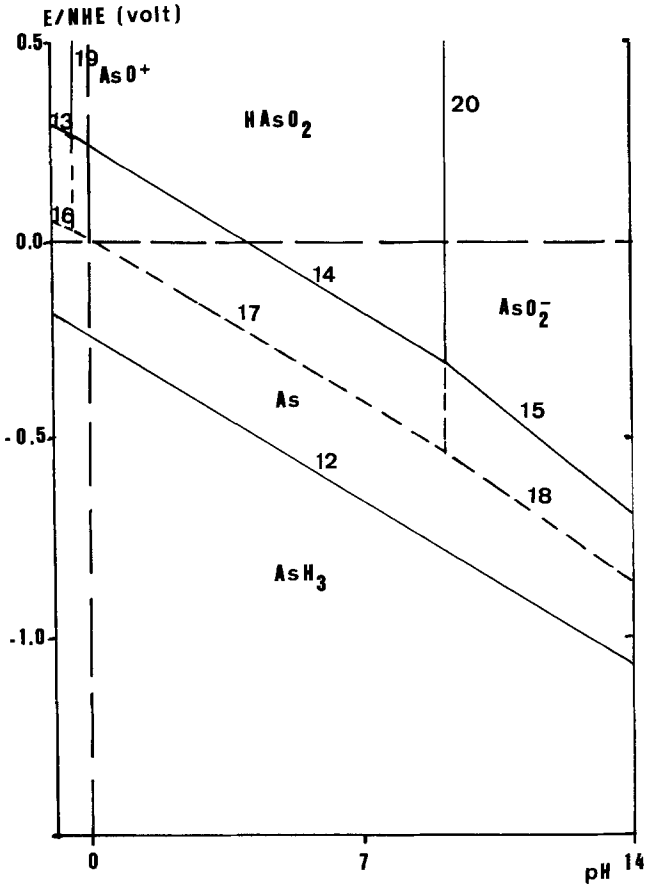

Fig. 2. Arsenic-water *E-pH* diagram

will not be considered since we are looking towards preparation of arsenides. The standard free enthalpy of formation of these compounds are given in Table II, and we can write the following equilibria

	E_o(SHE)	dE/dpH	
$AsH_3 = As + 3H^+ + 3e^-$	−0.237V	−58.9 mV	[12]
$As + H_2O = AsO^+ + 2H^+ + 3e^-$	+0.26V	−39.2 mV	[13]
$As + 2H_2O = HAsO_2 + 3H^+ + 3e^-$	+0.24V	−58.9 mV	[14]
$As + 2H_2O = AsO_2^- + 4H^+ + 3e^-$	+0.430V	−78.5 mV	[15]
$AsH_3 + H_2O = AsO^+ + 5H^+ + 6e^-$	+0.008V	−49.1 mV	[16]
$AsH_3 + 2H_2O = HAsO_2 + 6H^+ + 6e^-$	+0.005V	−58.9 mV	[17]
$AsH_3 + 2H_2O = AsO_2^- + 7H^+ + 6e^-$	+0.096V	−68.7 mV	[18]

$AsO^+ + OH^- = HAsO_2$ [19]
$\Delta G° = -81.80$ kJ mol^{-1} $pH° = 0.32$

$HAsO_2 = AsO_2^- + H^+$ [20]
$\Delta G° = +52.68$ kJ mol^{-1} $pH° = 9.23$

The theoretical equilibrium diagram (Fig. 2) shows the various domains of stability for the arsenic compounds. Arsenic could be deposited from aqueous solutions at any pH value, but experimentally, this can be done easily only in acidic or neutral solutions, and cannot be achieved in alkaline solutions. Arsine can be formed by arsenic reduction provided that the HER overvoltage is high enough, more than 240 mV. However, if we assumed that the overvoltage for the reduction of arsenious compounds into arsenic is high enough, more than the differences between equilibria 14/15 and 12, in average approximately 480 mV, these compounds, which are in a metastable state, could be reduced directly into arsine. This reaction can be observed experimentally, particularly in acid solutions. By rapid bubbling of inert gas through the solution, an As mirror can be obtained by thermal decomposition or oxygen oxidation of AsH_3 outside the solution. The same results can be obtained by chemical reduction of an arsenious solution and has been used for determination of arsenic contents. In our case, arsenic precipitation in the solution or deposition at the electrode could occur through the antidisproportionation reaction.

In acid or in neutral solutions

$AsH_3 + HAsO_2 = 2As + 2H_2O$ [21]
$\Delta G° = -140.72$ kJ mol^{-1}

In alkaline solutions

$AsH_3 + AsO_2^- = 2As + H_2O + OH^-$ [22]
$\Delta G° = -113.2$ kJ mol^{-1}

Indeed, in several experiments, we have observed formation of an arsenic layer onto the cell walls or of very fine powder in the solution.

Gallium arsenide diagram.—Calculation of the complete diagram for the As-Ga-H_2O system requires consideration of the equilibria of gallium arsenide, which has a standard free enthalpy of formation

$$\Delta G°_f = -67.8 \text{ kJ mol}^{-1} \quad (7)$$

with all the compounds involved in the As-H_2O and Ga-H_2O diagrams.

	E_o(SHE)	dE/dpH	
$GaAs = As + Ga^{+3} + 3e^-$	−0.315V	0.0 mV	[23]
$GaAs + H_2O = As + GaOH^{+2} + H^+ + 3e^-$	−0.259V	−19.6 mV	[24]
$GaAs + 2H_2O = As + Ga(OH)_2^+ + 2H^+ + 3e^-$	−0.190V	−39.2 mV	[25]
$GaAs + 3H_2O = As + H_2GaO_3^- + 4H^+ + 3e^-$	0.116V	−78.5 mV	[26]
$GaAs + 3H_2O = As + HGaO_3^{-2} + 5H^+ + 3e^-$	0.319V	−98.1 mV	[27]
$GaAs + 3H_2O = As + GaO_3^{-3} + 6H^+ + 3e^-$	0.551V	−117.8 mV	[28]
$GaAs + 3H^+ + 3e^- = AsH_3 + Ga$	−0.472V	−58.9 mV	[29]
$GaAs + H_2O = AsO^+ + Ga^{+3} + 2H^+ + 6e^-$	−0.030V	−19.6 mV	[30]
$GaAs + 2H_2O = HAsO_2 + Ga^{+3} + 3H^+ + 6e^-$	−0.034V	−29.4 mV	[31]
$GaAs + 3H_2O = HAsO_2 + GaOH^{+2} + 4H^+ + 6e^-$	−0.005V	−39.2 mV	[32]
$GaAs + 4H_2O = HAsO_2 + Ga(OH)_2^+ + 5H^+ + 6e^-$	0.028V	−49.0 mV	[33]
$GaAs + 5H_2O = HAsO_2 + H_2GaO_3^- + 7H^+ + 6e^-$	0.181V	−68.7 mV	[34]
$GaAs + 5H_2O = AsO_2^- + H_2GaO_3^- + 8H^+ + 6e^-$	0.273V	−78.5 mV	[35]
$GaAs + 5H_2O = AsO_2^- + HGaO_3^{-2} + 9H^+ + 6e^-$	0.374V	−88.3 mV	[36]
$GaAs + 5H_2O = AsO_2^- + GaO_3^{-3} + 10\,H^+ + 6e^-$	0.490V	−98.1 mV	[37]

$GaAs + 3H^+ = AsH_3 + Ga^{+3}$ [38]
$\Delta G° = -22.3$ kJ mol^{-1} $pH° = 1.30$

$GaAs + 3H_2O = AsH_3 + GaO_3^{-3} + 3H^+$ [39]
$\Delta G° = -11.12$ kJ mol^{-1} $pH° = 13.3$

The diagram obtained (Fig. 3) shows that there exists an *E-pH* domain between pH 1.3 and 13.3 in which gallium ar-

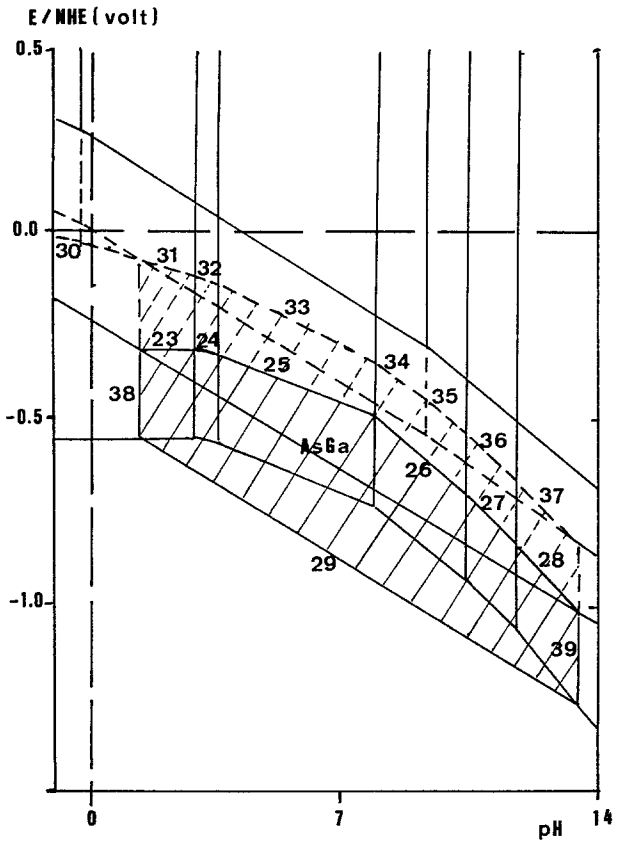

Fig. 3. Gallium arsenide-gallium-arsenic-water *E-pH* diagram

senide could be stable in contact with aqueous solutions containing both arsenious and gallium compounds, provided that the HER overvoltage is high enough for a particular set of experimental conditions (solid lines), and GaAs could be electrodeposited by simultaneous reduction of both arsenic and gallium compounds. This stability domain will be enlarged to less cathodic potentials if we consider the metastable equilibria between arsine and arsenious compounds in aqueous solutions (dotted lines).

Indeed, we have seen above that, if the overpotential for arsenic electrodeposition is high enough, the soluble arsenious compounds, which are in a metastable state, could be reduced directly to arsine, and we can assume that, under the same conditions, GaAs could be electrodeposited directly by simultaneous reduction of both gallium compounds and arsenious compounds, not arsenic.

Experimental Results

We have performed experiments in various ranges of *p*H, with solutions obtained by dissolution of Ga_2O_3 and As_2O_3 in alkaline media. The *p*H was adjusted by addition of either hydrochloric or phosphoric acid. Working electrodes were either pure molybdenum sheets or thin films of SnO_2 vapor deposited onto glass.

We observed that reaction rates show important increase between 25° and 60°C, and most experiments were performed with a water jacketed cell at temperature adjusted between 50° and 60°C. Laboratory built water thermostatic equipment provided a ±0.1°C thermal regulation.

The deposits obtained were studied by electronic microprobe analysis for gallium and arsenic distribution on the surface of the electrode. Unpolarized deposits were not stable in contact with aqueous solutions, and rest potentials could not be obtained. However, instant potential measurements, immediately after switching off the electropolarization current, show values close to the Ga potential in high alkaline solutions while in acidic solutions they could not be correlated with any theoretical potential values.

Alkaline and acid solution experiments were performed prior to the theoretical diagram calculation, neutral solution experiments later.

Alkaline solution.—In highly alkaline solutions, near *p*H 14, we have obtained only gallium depositions. First, there is deposition of a very thin layer of gallium. When the thickness of the deposit increases, the experiments being performed at temperature above the melting point of the metal, we observed formation on the surface of drops of fused metal, easily observed after cooling of the working electrode outside the solution. For the experiments performed below melting point of the metal, deposition could not be achieved. This is probably due to much lower reaction rates.

Only traces of arsenic in the deposit, and very slight modifications of the characteristics of the potential-current and potentiostatic current-time curves for the system can be detected with very high concentrations of arsenic compounds in the solution.

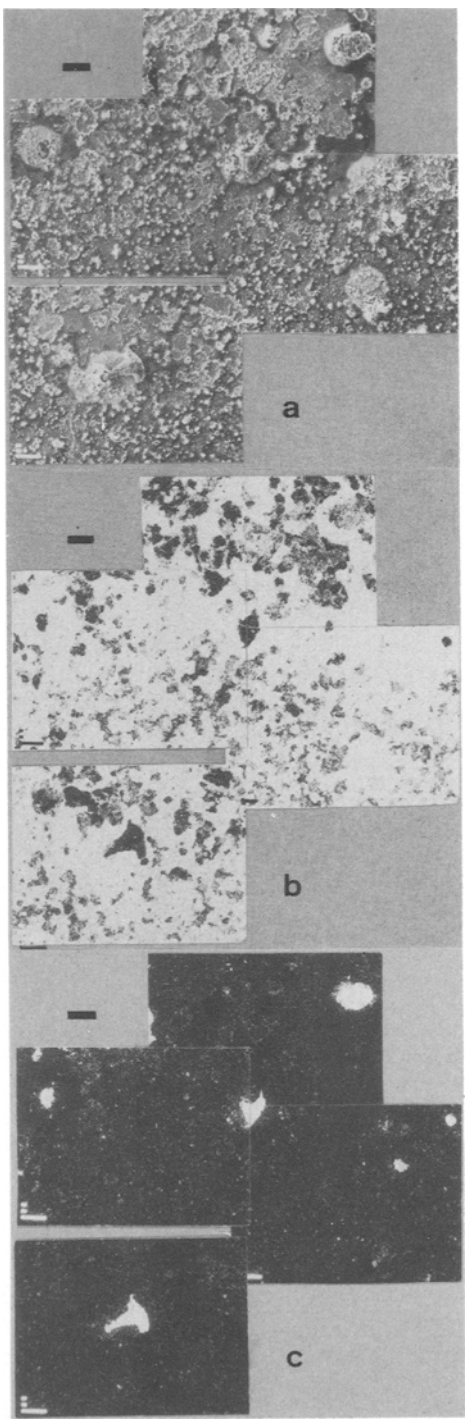

Fig. 4. Deposit in acid solution. a, MEB image; b, As distribution; c, Ga distribution. The black segment in the upper left corner of each composite picture represents a length of 100 μm.

No gallium arsenide formation was observed, as can be explained with the *E*-*p*H diagram calculated above, GaAs being thermodynamically not stable for these *p*H values.

Acid solutions.—In very acid solutions, around *p*H 0 to 1, the deposits we have obtained, exhibit a very uneven texture and contain both gallium and arsenic in various proportions.

In most cases, we observed segregation between gallium and arsenic, the second being largely predominant. It appears that a relatively continuous layer containing mostly arsenic and a very small amount of gallium is formed first. On this layer, small grains with higher proportion of gallium are formed, and almost pure gallium dendrite-like nodules can develop (Fig. 4). However, gallium arsenide formation could not be detected by x-ray analysis.

From the calculated diagram, it can be expected that no direct electrodeposition will occur in this *p*H range, since GaAs is not thermodynamically stable, and we can assume, from our experimental results, that electroprecipitation of GaAs cannot be achieved in these solutions.

Amorphous GaAs might have been formed but, its presence could not be tested by microprobe analysis, the deposits texture being very rough and irregular (Fig. 4a). Moreover no photocurrent could be detected.

Neutral solutions.—With the theoretical diagram, we selected a few particular sets of conditions for which we might expect gallium arsenide formation in the *p*H range 4-11.

For solutions above *p*H 10, the results are comparable with those obtained at *p*H 14, while near *p*H 4 or 5 they are similar to those obtained in very acid solutions.

In neutral solutions, in the *p*H range 6-8, we observed the formation of a very smooth, mirror-like, arsenic deposit, and electrodeposition of GaAs could not be achieved. The arsenic deposition observed can tentatively be explained, at least in part, by the reactions considered in the arsenic diagram. Indeed, it might be inferred that an overpotential for the arsenic deposition exists, allowing the arsine to form first. The hydride reacts with arsenious compounds present in the solution leading to chemical formation of arsenic according to the antidisproportionation reaction [21] (see above).

This reaction might also interfer with mechanism II of the electrosynthesis of GaAs described above. Indeed, reaction [21], according to its standard free enthalpy

$$\Delta G^\circ = -140.72 \text{ kJ mol}^{-1}$$

will be predominant over the various chemical reactions of arsine leading to GaAs formation.

$$AsH_3 + Ga^{+3} = GaAs + 3H^+ \quad [38]$$
$$\Delta G^\circ = +22.3 \text{ kJ mol}^{-1}$$

$$AsH_3 + GaOH^{+2} = GaAs + 2H^+ + H_2O \quad [40]$$
$$\Delta G^\circ = +6.05 \text{ kJ mol}^{-1}$$

$$AsH_3 + Ga(OH)_2^+ = GaAs + H^+ + 2H_2O \quad [41]$$
$$\Delta G^\circ = -13.78 \text{ kJ mol}^{-1}$$

$$AsH_3 + H_2GaO_3^- = GaAs + 2H_2O + OH^- \quad [42]$$
$$\Delta G^\circ = -23.24 \text{ kJ mol}^{-1}$$

$$AsH_3 + HGaO_3^{-2} = GaAs + H_2O + 2\,OH^- \quad [43]$$
$$\Delta G^\circ = -2.06 \text{ kJ mol}^{-1}$$

$$AsH_3 + GaO_3^{-3} = GaAs + 3\,OH^- \quad [39]$$
$$\Delta G^\circ = +11.12 \text{ kJ mol}^{-1}$$

Conclusion

All the results obtained in this study show clearly that the electrosynthesis of gallium arsenide, either by electrodeposition or by electroprecipitation, cannot be achieved in aqueous solutions of arsenious compounds. GaAs electrodeposition will require, either non oxygen containing As-III compounds, or additives which, by complexing the arsenious compounds, could prevent them from reacting with arsine.

Indeed, the hydride, which is very easily obtained by the reduction of As-III compounds, appears to be the probable intermediate in the electrochemical preparation of gallium arsenide, but more experimental work would have to be done to confirm this point.

The same theoretical calculations could be done for other systems, provided that the thermodynamical functions of all compounds involved are known, and particularly the standard free enthalpy of formation of the III-V compound concerned. We have already done the calculation for AlAs, and it appears that this compound has no thermodynamical stability domain in contact with aqueous solutions. Other compounds such as GaSb, InSb, InAs, or InP, for which ΔG°_f are known, will be considered in the future.

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REFERENCES

1. E. Becquerel, in "Traité d'Electricité et de Magnétisme," Vol. II, Electrochimie, Didot, Editor, pp. 93-95, Paris (1855).
2. A. K. Agrawal and A. E. Austin, *This Journal*, **128,** 2292 (1981); C. H. Lee and F. A. Kröger, *ibid.*, **129,** 936 (1982); T. R. Ramamohan and F. A. Kröger, *Electrochim. Acta*, **27,** 371 (1982).
3. M. Tomkiewicz, I. Ling, and W. S. Parsons, *This Journal*, **129,** 2016 (1982); A. S. Baranski and W. R. Fawcett, *ibid.*, **127,** 766 (1980); A. S. Baranski, W. R. Fawcett, A. C. McDonald, R. M. de Nobriga, and J. R. MacDonald, *ibid.*, **128,** 963 (1981); M. P. R. Panicker, M. Knaster, and F. A. Kröger, *ibid.*, **125,** 566 (1978); M. Skyllas-Kazacos and B. Miller, *ibid.*, **127,** 869, 2378 (1980); G. P. Power, D. R. Peggs, and A. J. Parker, *Electrochim. Acta*, **26,** 681 (1981); M. Skyllas-Kazacos, *J. Electroanal. Chem.*, **148,** 233 (1983).
4. C. Sella, These Doctorat 3e Cycle, Paris 15.II (1985).
5. A. Heller, *Acc. Chem. Res.*, **14,** 154 (1981); E. A. Perez-Albuerne and Y. S. Tyan, *Science*, **208,** no. 4446, (May 28, 1980).
6. "Standard Potential in Aqueous Solutions," J. Bard, R. Parsons, and J. Jordan, Editors, Marcel Dekker Inc., New York (1985).
7. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, N. L. Churney, and R. L. Nutall, "The NBS Tables of Chemical Thermodynamic Properties," *J. Phys. Chem. Ref. Data*, **11,** Suppl. no. 2 (1982).