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Electrodeposition of GaAs from Aqueous Electrolytes

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ABSTRACT

Gallium arsenide films were electrodeposited from both alkaline and acid aqueous electrolytes. Compared to other conventional methods of preparing gallium arsenide films, electrodeposition from aqueous solution has the advantages of low operating and equipment costs, relatively easy control of film properties, and no toxic volatile raw material. The cathodic deposits from an alkaline electrolyte generally were thick, porous, and powdery. With an acid electrolyte, the deposits were thinner and more compact and adherent. The effects of the following operating parameters have been characterized: applied potential, current density, electrolyte composition, cathode material, deposition temperature, pH, additives, and agitation. Secondary ion mass spectroscopy confirmed oxidation states and x-ray diffraction patterns indicated that the as-deposited films were microcrystalline GaAs which became more crystalline on annealing. Mixtures of the deposited elements of gallium and arsenic yielded crystalline gallium arsenide after annealing. Energy dispersive spectroscopy and Auger electron spectroscopy showed that the deposited films contained some oxygen. The source of the oxygen, particularly in the acid electrolytes, is discussed. A mechanistic study confirmed conditions under which arsine is formed and reacts with gallate in the alkaline solution.

GaAs is a prime candidate material for optoelectronic devices. Electrodeposition offers several attractive features in preparation of thin film semiconductor compounds from aqueous solution. The film properties such as film thickness, morphology, composition, etc., are easily controlled by voltage and current density. Use of ambient temperature, atmospheric pressure, and aqueous solution reduces equipment and operating costs. Additionally, raw materials are better conserved. From a safety standpoint, there is no toxic or volatile raw material, such as AsH_3, $AsCl_3$ or organometallics.

Compared with work on other semiconductors, such as CdTe and InSb, relatively little has been done on gallium arsenide electrodeposition. DeMattei and coworkers[1] deposited GaAs from a molten salt containing 67.4% B_2O_3, 20.3% NaF, 4.2% Ga_2O_3, and 8.1% $NaAsO_2$ by weight at 720-760°C. Deposition at 300°C from $GaCl_3$-KCl melt also was reported by Tremillon and coworkers.[2] Wicelinski and Gale[3,4] described gallium arsenide film formation from room temperature chloroaluminate melts ($AlCl_3$:1-butylpyridinium chloride or $AlCl_3$:1-methyl-3-ethylimidazolium chloride). Verbrugge and Carpenter[5,6] also used a room temperature melt of $GaCl_3$ and 1-methyl-3-ethylimidazolium chloride and an $AsCl_3$ solute.

For non-molten salt systems Astier[7] and his coworkers claimed electrodeposition from aqueous solution containing $Ga_2(SO_4)_3$, As_2O_3, and H_2SO_4. Murali and coworkers[8] electrodeposited gallium on copper foil from sodium gallate solution, then arsenic from arsenite solution. The sample was then annealed in a high vacuum at temperatures in the range 520-800°K. No characterization of the film was reported. Based on thermodynamic calculations and some experiments in aqueous solution, Perrault[9] concluded that GaAs cannot be electrosynthesized from a simple aqueous solution. However, Chandra and Khare[10-12] reported the electrodeposition of GaAs using various deposition conditions in acid and depicted the film current-voltage characteristics under illumination for a photoelectrochemical solar cell. This work did not mention the use of additive or complexing agents and could not be duplicated in our laboratory.

Potential-pH equilibrium diagrams for Ga-water and As-water systems show that both gallium and arsenic can be electrodeposited from both high and low pH electrolyte. Although the equilibrium potentials of gallium and arsenic are separated by as much as 0.6 V, kinetic behavior may change the required potential for the codeposition. If the elements gallium and arsenic are codeposited, the mixture is expected to be thermodynamically unstable due to the negative Gibbs free-energy of formation of $GaAs_{(s)}$ [13]

$$Ga_{(s)} + As_{(s)} \rightarrow GaAs_{(s)} \qquad \Delta G^{\circ}_{298} = -83.67 \text{ kJ/mol} \qquad [1]$$

According to the phase diagram of gallium arsenide,[14] a mixture of gallium and arsenic is not thermodynamically stable and should convert to gallium arsenide with either excess gallium or arsenic.

Based on the advantages of electrodeposition and the thermodynamic stability of gallium arsenide film, the goals of this research are: (*i*) an investigation of electrodepositing layers of gallium arsenide from an aqueous solution; (*ii*) a description of the dependence of the properties of deposited films on the operating parameters, and (*iii*) an investigation of possible electroplating mechanisms.

Experimental Features

Figure 1 shows a schematic of a typical experimental setup. The working electrode, a rotating disk electrode, was machined from titanium rod, 0.5 in. in diameter and was imbedded in a rod of Teflon, 1 in. in diameter. This electrode was driven by a Pine Instrument Co. ASR rotator and controller. The counterelectrode was made of platinum. In

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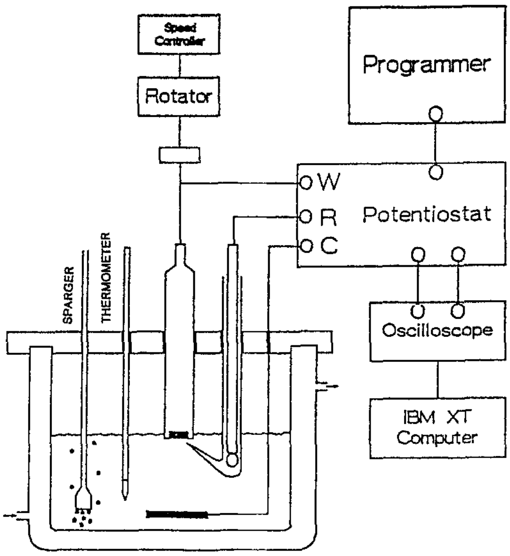

Fig. 1. Schematic diagram of the experimental apparatus and associated equipment.

some cases, the working electrodes were metal foils facing the counterelectrodes vertically, with a magnetic stirrer in the cell bottom. In all cases, the reference electrode was put in a glass tube with a capillary tip close to the working electrode. Three types of reference electrodes were used: Ag/AgCl in saturated KCl (0.197 V *vs.* NHE), Hg/HgO in 0.1*M* NaOH (0.157 V *vs.* NHE), and saturated calomel (0.241 V *vs.* NHE). The cell was contained in a jacketed beaker covered with a polypropylene lid to control the cell temperature.

Since gallium oxides and hydroxides have minimum solubility at a pH value of about 8, we experimented with either acid (pH $\leq$ 3) or basic (pH $\geq$ 12) electrolytes. In preparing the acid electrolyte, 1*M* $GaCl_3$ was mixed in appropriate ratio with 1*M* As_2O_3 solution (in concentrated HCl) in de-ionized water. Reagent grade ammonium hydroxide or KOH solution was used then to adjust the pH. The solution was colorless at pH < 2.7. At higher pH (2.7 < pH $\leq$ 10), $Ga(OH)_3$ or Ga_2O_3 precipitated. For investigating electrolytes in the soluble alkaline range (pH $\geq$ 12), As_2O_3 was added to the Ga_2O_3 solution. The pH was adjusted with concentrated KOH solution. After electrochemical deposition, some of the samples were annealed under nitrogen atmosphere in Pyrex tubing in a small oven monitored by a thermocouple.

A Stonehart Associates BC 1200 Potentiostat and an EG&G PAR Model 175 Programmer were coupled for potential or current control. Current and potential were recorded with a Nicolet 3091 digital oscilloscope and transferred to an IBM XT computer for storage.

An SX-30 Scanning Electron Microscope (SEM) from International Scientific Instruments was used for micrographs. A Princeton Gamma-Tech System IV Energy Dispersive Spectrometer (EDS), with windowless detector was used for element analysis. Quantitative analysis of the sample composition was also made. GaAs of 99.999% purity from Alfa was used as a standard in calculating the atomic concentrations in the sample. Samples were tested directly on substrates or as scraped films. Although some elements might be detected, the reported atomic concentrations of gallium and arsenic in the deposit will be based on [Ga] + [As] = 100%.

Films on substrates were analyzed with a Perkin-Elmer Auger Electron Spectrometer (PHI Model 660). This unit also has capability of depth profiling of the composition with a sputter ion gun. A Philips Electronics X-ray Diffractometer (APD 3520) was used to investigate sample crystallinity. A Model 520B secondary ion mass spectrometer (3M Analytical System) was used to investigate samples without crystalline features. Samples on titanium substrates were sputtered with argon ion at 1.5 keV under 5.50×10^{-5} Torr. The spectra were compared with that from standard GaAs under the same test conditions.

Electrodeposition in Alkaline Solutions

The deposits from solutions containing arsenic (III) and gallium (III) became black or dark brown, with fine dark brown particles near the cathode which also gave off numerous bubbles. Higher concentrations of arsenic in the deposit always made the deposit darker. Generally speaking, the deposits from electrolytes containing gallium and arsenic did not have good adhesion and were powdery. During the deposition, the current density decreased in the first 1 or 2 min, then increased, probably due to increasing surface area. Part of the deposit could be removed by water rinsing. The brown suspension occurring near the cathode was collected and found to be arsenic. This suspension changed the solution from colorless to brown, and dissolved in the solution after 1 to 2 h standing, depending on the electrodeposition time. The deposit also dissolved in the electrolyte, and the gallium in the deposit disappeared much more quickly than the arsenic.

Effect of deposition potential.—The composition of the deposit depends strongly on the potential applied to the working electrode. Figure 2 shows this dependence in the electrolyte at pH 13, containing 0.1*M* [Ga(III)] and 0.02*M* [As(III)], with vertical and parallel cathodes and anodes. Generally speaking, more negative potentials gave more gallium in the deposit. At potentials between −1.65 and −1.73 V *vs.* Hg/HgO, the deposit has relatively constant composition, around 62% of gallium. At even more negative potential, the concentration of gallium increased gradually. At potentials more negative than −1.95 V *vs.* Hg/HgO, only traces of arsenic could be found in the center part of the deposition area.

Arsenic is reduced to arsine at a potential more negative than gallium deposition by only 0.13 V; that is, gallium might be produced while arsenic is reduced to arsine. Arsine is a gas and may co-evolve with H_2. The production of arsine may explain why arsenic did not exist in the deposit at very negative potential.

Effect of deposition temperature.—At room temperature, 25°C, the composition of the deposit was rather constant with depth and will be discussed later. However, at elevated temperature, 77°C, the distribution of the composition in the deposit was very non-uniform. For example, a deposit was obtained from −2.0 V *vs.* SCE and 77°C in the electrolyte of pH 13, containing 0.177*M* Ga(III) and 0.044*M* As(III). The deposit was a gray powder similar to that obtained at 25°C. After it was scraped from the substrate, a bright and silvery liquid film was found on the titanium cathode. The removed powder contained 32.5% gallium, and the silvery film was essentially gallium. This silvery film was not observed beneath any powder film which was obtained at room temperature.

Figure 3 shows the dependence of the gallium content in the removed powdery sample on electrolyte temperature.

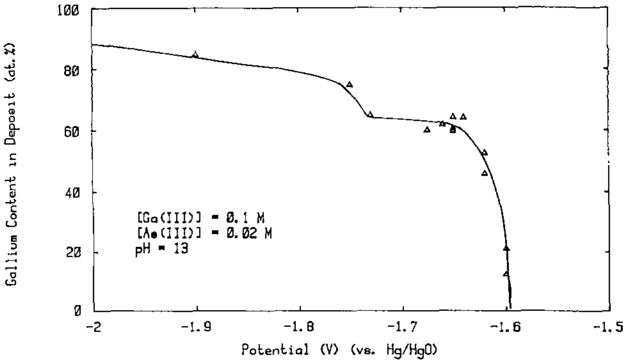

Fig. 2. Relationship between potential and gallium content in Ga/As films from electrolyte at pH 13 containing 0.1*M* Ga(III) and 0.02*M* As(III).

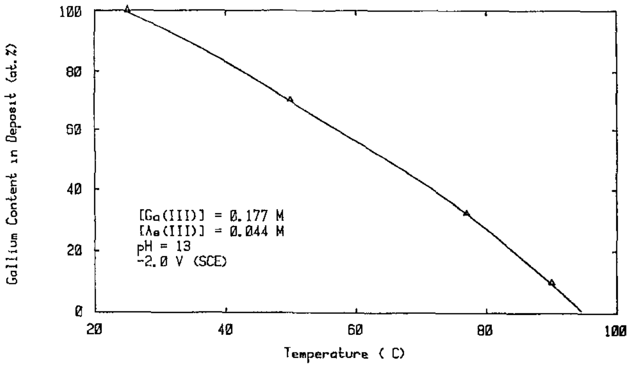

Fig. 3. Relationship between temperature and gallium content in Ga/As films electrodeposited at −2.0 V *vs.* SCE from electrolyte at pH 13 containing 0.177*M* Ga(III) and 0.044*M* As(III).

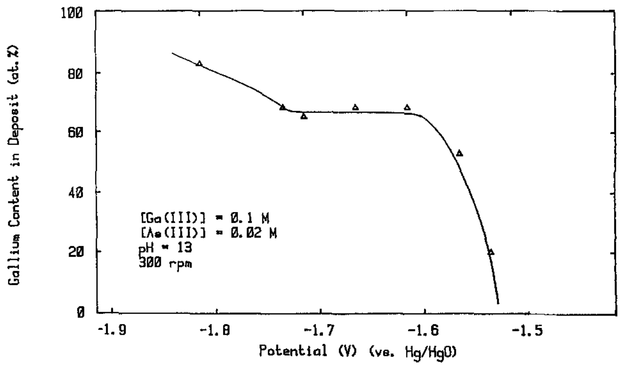

Fig. 4. Relationship between potential and gallium content in Ga/As films electrodeposited at 300 rpm from electrolyte at pH 13 containing 0.1*M* Ga(III) and 0.02*M* As(III).

In this figure, higher temperature corresponds to less gallium content in the sample.

It was believed that part of the gallium penetrates through the gray porous deposit and deposits directly on the surface of the titanium cathode. The penetration behavior was confirmed by the following experiment at 90°C with electrolyte of pH 13, containing 0.177*M* Ga(III) and 0.044*M* As(III). A black deposit was first obtained at −1.80 V *vs.* SCE without a silvery film beneath this black powder. Then, on the areas with and without the as-deposited film removed, rougher deposited films were obtained at −1.9 V *vs.* SCE with a silvery film beneath the rough films. Obviously, the silvery film appeared beneath the powder deposition at potentials more negative than −1.9 V *vs.* SCE at 90°C. Low temperature is necessary to obtain a uniform composition in the deposit.

Effect of electrolyte composition.—It is found that lower concentration of arsenic in the electrolyte gives lower arsenic content in the deposit. This result is also shown in the first four lines of Table I. The last four lines show that a higher content of gallium in the deposit is obtained from higher concentration of gallium in the electrolyte. Furthermore, with the same concentration ratio of gallium to arsenic (lines 3 and 5), the gallium contents are closer to each other.

Effect of agitation.—A rotating disk electrode supplies vigorous agitation. Figure 4 shows the relationship between the gallium content in the deposit and potential on the cathode at 300 rpm in an electrolyte that was the same as that in Fig. 2. After a conversion of the potential into the same reference electrode scale, gallium starts to deposit at −1.5 V *vs.* Hg/HgO, which was a less negative potential than that shown in Fig. 2. This was possibly due to the enhanced agitation which reduces the cathodic mass transfer and gas-induced polarization. At a given applied potential, this depolarization effect will lead to a higher current density and an apparent shift of the polarization curve to less negative potential values. Furthermore, there is a wide range of potentials, from −1.70 to 1-1.81 V *vs.* SCE (or from −1.62 to −1.73 V *vs.* Hg/HgO), for obtaining a constant gallium content of 66% in the deposit. The gallium content increases at even more negative potential. The latter phenomenon was also observed in Fig. 2. It is believed that reduction potential of solid arsenic to arsine was not affected by agitation. The arsenic reduction occurs in a potential region which is more negative than −1.73 V *vs.* Hg/HgO as noted also in Fig. 2. Since no arsenic is consumed at potentials more positive than −1.73 V *vs.* Hg/HgO, and the deposition rates of gallium and arsenic are maintained at the same ratio, the gallium content in the deposit remains constant at potentials between −1.62 and −1.73 V *vs.* Hg/HgO.

Table I. Gallium contents in Ga/As films from various electrolyte compositions and applied potentials.

[Ga] (*M*)	[As] (*M*)	pH	Potential (V)	Ga (%)
0.182	0.230	13	−1.80 (SCE)	1.1
0.182	0.044	13	−1.80 (SCE)	76.2
0.100	0.020	13	−1.70 (Ag/AgCl)	63.0
0.100	0.004	13	−1.70 (Ag/AgCl)	89.1
0.020	0.004	13	−1.70 (Ag/AgCl)	66.6
1.260	0.101	14	−1.67 (Ag/AgCl)	12.4
0.505	0.101	14	−1.67 (Ag/AgCl)	3.1

Substrate effect.—Titanium was the major substrate for the cathodes in the investigation. Since the potential applied to the cathode in the investigation was typically very negative, it was necessary to use a substrate with a high hydrogen overpotential[26] to decrease the hydrogen evolution during the deposition. Another advantage of titanium over other metals is that it does not form alloys with gallium, which may alloy with many metals, for example, copper (which has a hydrogen overpotential as high as titanium). Table II lists the deposition conditions and the gallium content in the deposit on the other four materials. According to Table II, 50% gallium content in the deposit can be obtained by adjusting the potential and electrolyte composition on these substrates just as with titanium. The deposition on silicon required significantly higher potential than that on titanium because of low conductivity in bulk silicon. The deposit was not of better quality than that on titanium.

Annealing effects and x-ray diffraction analysis.—Like many other compound semiconductors,[15,16] the as-deposited film was amorphous or microcrystalline and became fully crystalline after annealing. Figures 5 and 6 show the x-ray diffraction patterns of the deposit before and after annealing in N_2 atmosphere at 300°C for 12 h. The sample was removed from the titanium cathode by scrap-

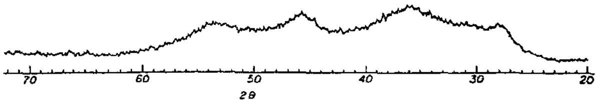

Fig. 5. X-ray diffraction pattern of a Ga/As film electrodeposited at −1.7 V *vs.* SCE from electrolyte at pH 13 containing 0.177*M* Ga(III) and 0.044*M* As(III), [Ga]/[As] = 39.2/60.8 in the film.

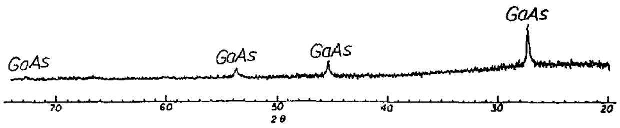

Fig. 6. X-ray diffraction pattern of a Ga/As film electrodeposited at −1.7 V *vs.* SCE from electrolyte at pH 13 containing 0.177*M* Ga(III) and 0.044*M* As(III), and annealed in nitrogen atmosphere at 300°C for 12 h. [Ga]/[As] = 64.1/35.9 in the film.

Table II. Gallium contents in Ga/As films on various substrates and various electrolyte compositions.

Substrate	[Ga(III)] (*M*)	[As(III)] (*M*)	pH	Potential (V)	Ga (%)
Silicon	0.251	0.051	14	−2.99 (Ag/AgCl)	100
	0.251	0.051	14	−2.90 (Ag/AgCl)	77.8
	0.251	0.051	14	−2.80 (Ag/AgCl)	53.9
Lead	0.251	0.051	14	−1.73 (Ag/AgCl)	100
	0.251	0.051	14	−1.71 (Ag/AgCl)	55.6
	0.251	0.051	14	−1.70 (Ag/AgCl)	37.3
	0.251	0.051	14	−1.65 (Ag/AgCl)	29.0
	0.251	0.051	14	−1.60 (Ag/AgCl)	19.9
Tin	0.100	0.020	13	−1.845 (SCE)	49.8
	0.020	0.020	13	−1.73 (Hg/HgO)	32.0
Graphite	0.177	0.044	13	−1.70 (SCE)	68.7
	0.202	0.077	13	−1.70 (SCE)	48.0

ing before annealing. The gallium contents in Fig. 5 and 6 were 39.2% and 64.1%, respectively. The arsenic content decreased after annealing due to the volatility of arsenic. The humps in Fig. 5 indicate that the as-deposited film was microcrystalline. Figure 6 shows that the heat-treated deposit includes crystalline gallium arsenide with sharp peaks at 2θ corresponding to those from standard gallium arsenide. Table III lists the d-value of heat-treated deposit and the standard d-values of gallium arsenide from the Powder Diffraction File.[17] The peak at 2θ = 66.1° (d-value = 1.41 Å) is too weak to be clearly identified. The relative intensities of the peaks in Fig. 6 are on the same order with those listed in Table III. The grain size can be estimated to be at least 300 Å, from the Scherrer equation.[18] With more careful examination of Fig. 5, the humps are observed around 2θ = 27.35°, 45.34°, and 53.97°. This observation suggests that the deposit includes gallium arsenide with some degree of crystallinity. If the heat-treated deposit has more arsenic than gallium, the diffraction pattern shows crystalline arsenic as well as gallium arsenide. Figure 7 shows the x-ray diffraction pattern of another sample with 61.0% arsenic content after annealing. There are two extra peaks for arsenic at 2θ = 28.0° and 32.4° (d-value = 3.18 and 2.77 Å).

For the sample annealed and examined on titanium cathode, the x-ray diffraction patterns only include the peaks for titanium and gallium arsenide as shown in Fig. 8. No extra peak appears. The sample was deposited at −1.67 V *vs.* Ag/AgCl in solution containing 0.25*M* Ga(III), 0.05*M* As(III), and 2*M* KOH. Figure 8 is the spectrum from the sample with 68.1% gallium, after the as-deposited film was annealed at 240°C and 21 h.

Deposition of arsenic on gallium.—One experiment has been done to investigate whether the crystalline gallium arsenide can be produced by annealing mixed gallium and arsenide. In this experiment, arsenic was electrodeposited on gallium which had been previously deposited on titanium cathode. The electrolytes were 0.75*M* Ga(III)/6*M* KOH, and 0.06*M* As(III)/0.3*M* KOH. Before annealing, the arsenic was so thick that only a little gallium beneath it could be detected by EDS. The x-ray diffraction pattern indicates no crystalline gallium, arsenic, or gallium arsenide in the as-deposited film. After annealing at 300°C for 10 h, the diffraction pattern indicates crystalline gallium arsenide in the deposit as shown in Fig. 9. The EDS spectrum showed 49% gallium content.

Table III. Comparison of x-ray diffraction data of gallium arsenide in ASTM card with electrodeposited sample giving the pattern in Fig. 6.

	Standard GaAs		Heat-treated sample	
hkl	Relative intensity	d-value (Å)	d-value (Å)	2θ (degree)
111	100	3.260	3.25	27.4
200	<1	2.832	—	—
220	35	1.999	1.99	45.5
311	35	1.704	1.70	53.9
400	6	1.413	(1.41)	(66.1)
331	8	1.297	1.30	72.9

An attempt has been made to electrodeposit a gallium film on a predeposited arsenic film. During this experiment, probably due to bubble evolution, the arsenic film lifted and fell onto the cell bottom. Two of the possible reasons

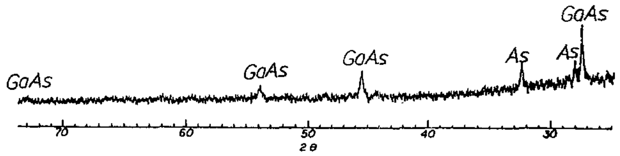

Fig. 7. X-ray diffraction pattern of a Ga/As film electrodeposited at −1.8 V *vs.* SCE from electrolyte at pH 13 containing 0.177*M* Ga(III) and 0.044*M* As(III), and annealed in nitrogen atmosphere at 300°C for 12 h. [Ga]/[As] = 39.0/61.0 in the film.

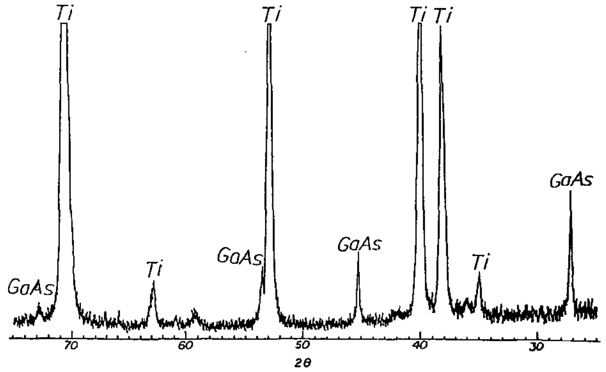

Fig. 8. X-ray diffraction pattern of Ga/As film on titanium substrate, electrodeposited at −1.67 V *vs.* Ag/AgCl from electrolyte containing 0.25*M* Ga(III), 0.05*M* As(III), and 2*M* KOH, and annealed in N_2 at 240°C for 21 h, [Ga]/[As] = 68.1/31.9 in the film.

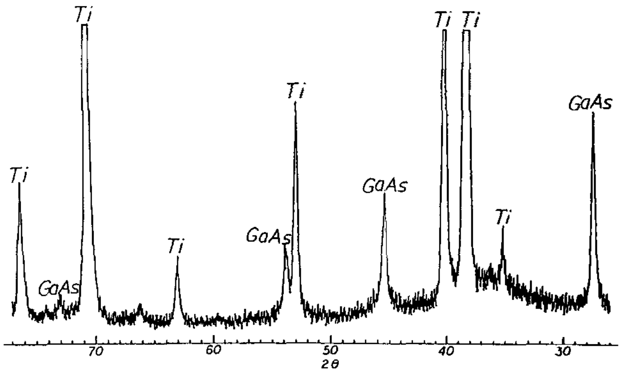

Fig. 9. X-ray diffraction pattern of an arsenic film on a gallium film electrodeposited on titanium substrate and annealed in N_2 at 300°C for 10 h. [Ga]/[As] = 49/51.

Table IV. Comparison of x-ray diffraction data of $CuGa_2$ in ASTM card with electrodeposited film on copper with 15 mA/cm^2 from electrolyte at pH 13.2, containing 0.36*M* Ga(III) and 0.12*M* As(III).

	Standard φ-CuGa ($CuGa_2$)		As-deposited	
hkl	Relative intensity	d-value (Å)	d-value (Å)	2θ (degree)
001	55	5.87	—	—
002	30	2.93	2.93	30.65*
100	65	2.84	2.83	31.55*
101	90	2.56	2.55	35.20*
102	100	2.03	2.05	44.55*
110	90$^+$	2.00	2.00	45.30*
003	65	1.95	1.95	46.70*
111	20	1.90	—	—
112	40	1.65	—	—
004	40	1.46	1.46	63.75*
200	65	1.42	1.42	65.95*
113	65	1.39	—	—
201	10	1.38	—	—
202	20	1.28	—	—
210	40	1.27	1.27	75.00*

are that (*i*) arsenic is reduced to arsine and loses adhesion, and (*ii*) gallium penetrates through arsenic film and destroys its adhesion. This phenomenon makes multilayer deposition of gallium and arsenic difficult.

Deposition on copper cathode.—The deposition on a copper cathode was done at 15 mA/cm^2 from electrolyte at pH 13.2, containing 0.36*M* Ga(III) and 0.12*M* As(III). The as-deposited film had 43.2% gallium content and was analyzed with an x-ray diffractometer. Table IV lists the d-values of this deposit, and the standard d-values of $CuGa_2$ from the Powder Diffraction File.[19] This result is confirmed by other researchers who deposited gallium on copper in alkaline solution.[20] It is believed that gallium reacted more easily with copper than with arsenic. This fact made it difficult to electrodeposit gallium arsenide on a copper cathode.

Mechanistic study of arsine involvement.—Among many analytical methods for the detection of arsenic and arsine,[21,22] the Gutzeit method was used to test for arsine in this research. In this method, 1×10^{-4} mg of arsenic is determinable. First, a strip of filter paper was soaked for $1\frac{1}{2}$ h in a fresh 5% solution of mercuric bromide in 95% methanol. After drying in air, the strip was white and was put into a piece of glass tubing which was connected to the gas outlet of the electrochemical cell, which contained a solution of 0.1*M* Ga(III), 0.02*M* As(III) at pH 13. During the experiment, nitrogen was passed through the cell and carried out the produced gases. Three minutes after the experiment started at −1.85 V *vs.* Hg/HgO, the paper strip became stained. This meant that mercuric bromide was reduced by arsine on the strip. After nitrogen was passed for 30 min with no potential applied, a new paper strip was used and remained white for another 30 min. That is, arsine was produced only during electrodeposition of gallium/arsenic.

To investigate the reaction of arsine with gallate in the solution, a series of 250 ml flasks were set up as shown in Fig. 10. Arsine was produced in beaker (A) by the reaction of 11.8 g of zinc with 0.126*M* arsenite in 14*M* HCl. Beakers (B) and (C) had 0.15*M* KOH and 0.15*M* GaO_3^{-3}/0.1*M* KOH. Each of beakers (D) and (E) had a 5% solution of mercuric bromide in 95% methanol. The purpose of these two beakers was to absorb all of the toxic arsine. The filter paper strips (F1) and (F2) were prepared as described in the last paragraph. Before the experiment, all of the solutions were colorless. Immediately after zinc metal was dropped into beaker (A), black powder and vigorous bubbling was produced. One hour after the start of the experiment, no bubbles evolved in beaker (A), the tissue paper in tubing (T) had trapped fine particles of arsenic, and the solutions in other beakers were as follows: (B), colorless; (C), pale brown; (D), black; (E), orange; and (F), colorless. Paper strips (F1) and (F2) were black and white, respectively. The conclusions are that (*i*) arsine can react with gallate, and (*ii*) all of arsine was absorbed in either beaker (D) or (E). After electrodeposition of gallium and arsenic on the titanium cathode, arsenic may follow one of four routes: (*i*) stay on the cathode with gallium, (*ii*) leave the cathode and form black powder in the solution, (*iii*) be reduced to arsine and evolve into the air, and (*iv*) be reduced to arsine and react with gallate to form very fine arsenic or gallium arsenide. The deposition at the potential range for obtaining constant gallium content is the combination of routes (*i*) and (*ii*). At more negative potential, routes (*iii*) and (*iv*) prevail and give high gallium content in the deposited films.

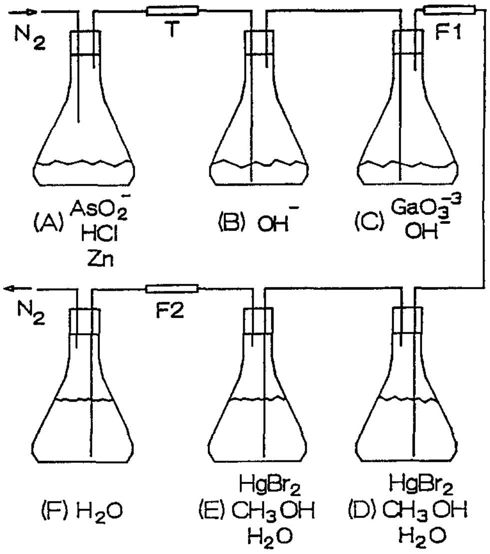

Fig. 10. Schematic diagram of the experiment on arsine reaction.

Secondary ion mass spectroscopy analysis.—Figures 11 and 12 show the spectra from a gallium arsenide wafer from Nippon Mining Company and an as-deposited film,

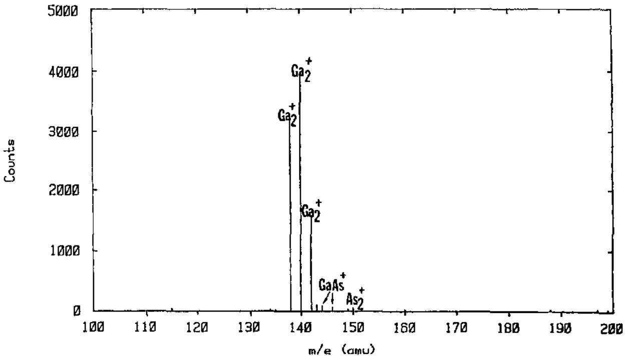

Fig. 11. SIMS spectrum of standard gallium arsenide wafer.

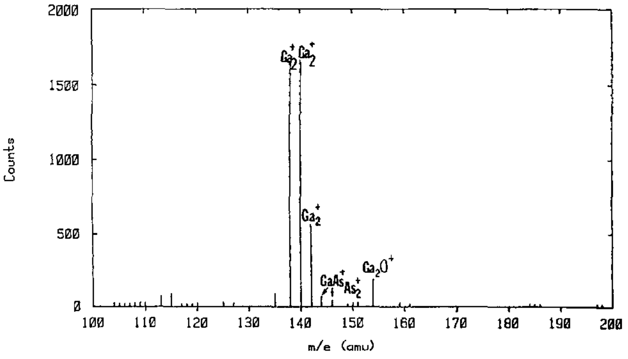

Fig. 12. SIMS spectrum of a GaAs film electrodeposited at −1.67 V *vs.* Hg/HgO from electrolyte at pH 13 containing 0.1*M* Ga(III) and 0.02*M* As(III).

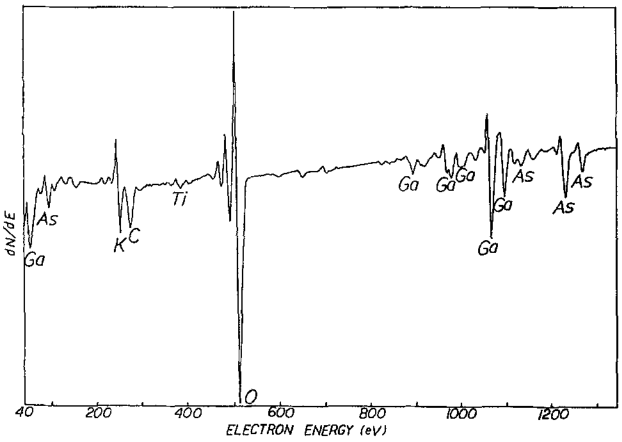

Fig. 13. Auger electron spectrum of a Ga/As film, on titanium cathode, electrodeposited at −1.62 V vs. Hg/HgO from electrolyte at pH 13 containing 0.1*M* Ga(III) and 0.02*M* As(III).

respectively, between m/e = 100 and 200 amu with resolution of 1 amu. The lines at m/e = 138, 140, and 142 amu represent Ga_{2+} arising from the three combinations of isotopes Ga^{69} and Ga^{71}. Arsenic has only one isotope, As^{75}, and is much less sensitive to secondary ion mass spectroscopy (SIMS) in comparison with gallium. The only line for As_{2+} is at m/e = 150 amu. Gallium arsenide shows two lines at m/e = 144 and 146 amu with intensities between Ga_{2+} and As_{2+}. Compared with the spectrum of standard gallium arsenide in Fig. 11, the as-deposited film in Fig. 12 has more lines. The major extra line is at m/e = 154 amu, corresponding to Ga_2O^+.

Auger electron spectroscopy and oxygen content analysis.—Figure 13 is an Auger electron spectroscopy (AES) spectrum of as-deposited film. In addition to the peaks due to gallium (51, 888, 974, 993, 1060, and 1087 eV) and arsenic (91, 1121, 1220, and 1256 eV), those due to potassium (248 eV), carbon (269 eV), titanium (381 eV) and oxygen (508 eV) are observed. The source of potassium was the electrolyte which was prepared from KOH solution. Organic contaminants from the air during the transfer of the sample from the electrochemical cell to the Auger electron spectrometer gave a peak. The sample was powdery, and small holes may expose the titanium substrate to the surface; hence the titanium peak appears in the spectrum. After Ar^+ sputtering for 1.7 min, the spectrum indicates that contents of oxygen, carbon, and potassium decrease.

The content of these elements on the surface before sputtering are K, 5%; C, 10%; Ti, 1%; O, 17%; Ga, 31%; and As, 34%. After sputtering for 1.7 min, about 0.1 μm deep, these are K, 1%; C, 3%; Ti, 1%; O, 12%; Ga, 43%, and As, 41%.

Depth profiles of carbon, oxygen, titanium, gallium, and arsenic are shown in Fig. 14. The sputtering rate was estimated as 0.06 μm/min. The concentrations of gallium, carbon, and oxygen change mainly in the first minute, or within 0.06 μm from the surface. During the rest of time (or at large depth), the concentrations of all elements remain about constant except that of titanium which increases slightly. The higher concentration of oxygen near the surface was probably due to the oxygen in the air reacting with, or absorbed on, the as-deposited film. The oxygen at the deeper location in the film must have come mainly from the electrolyte during electrodeposition of Ga/As. The lower concentration of gallium on the surface was believed due to the dissolution of gallium in the electrolyte a few seconds before the sample was removed from the cell. According to this profile, the concentrations of gallium and arsenic in the deposit are 47% and 38%, respectively. Disregarding other elements, these are 55% gallium and 45% arsenic, in good agreement with the 53% gallium determined with EDS.

Furthermore, after Ar^+ sputtering, the peaks due to gallium shift from 51 to 53 eV, from 974 to 977 eV, from 993 to 996 eV, from 1060 to 1062 eV, and from 1087 to 1089 eV; and the peaks due to arsenic remain unchanged in energy. The shift of the gallium peaks to higher energy and the decrease of oxygen content by sputtering suggest that some of the gallium at the surface is combined with oxygen. These peak shifts were also noted in the CdTe film electrodeposited from aqueous solution.[23] This suggestion does not exclude the possibility that gallium is combined with oxygen in the bulk sample.

Electrodeposition in Acid Solutions

Gallium has a low solubility in neutral solution. Precipitation of gallium oxide or gallium hydroxide was avoided by using pH values between 0.7 and 3.0. During the deposition, the current density dropped abruptly in the first minute, and gradually decreased in the next 20 min, possibly due to the formation of a resistive film. In every deposition from acid solution, the film thickness only increased in the first 20 min.

Unlike the potentiostatic method, a galvanostatic technique produces a large number of fragmented small pieces of smooth foils on the micron scale. Since the galvanostatic deposit was black and more compact, with better adhesion to the cathode than deposits obtained using the potentiostatic method, most of the experiments were done with the former method, though only thinner films can be formed. In some cases at the lowest pH, only a thin yellow or brown layer was produced.

Effect of deposition potential.—Figure 15 shows the dependence of gallium content in the deposit on the potential at 500 rpm from the solution of pH 2.85, containing 0.11*M* Ga(III) and 0.08*M* As(III). Gallium was deposited at potentials more negative than −1.2 V *vs.* Ag/AgCl. Gallium increased in content when potentials were more negative. The gallium content holds at about 65% at potentials between −1.5 and −1.6 V *vs.* Ag/AgCl and a white precipitation occurs on the black deposit. The precipitate could be

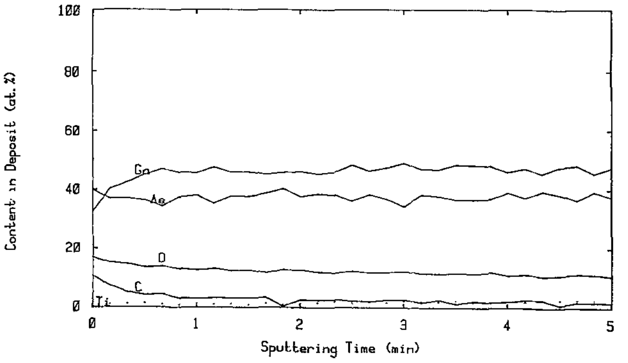

Fig. 14. Auger depth profile for a Ga/As film electrodeposited at −1.62 V vs. Hg/HgO from electrolyte at pH 13 containing 0.1*M* Ga(III) and 0.02*M* As(III).

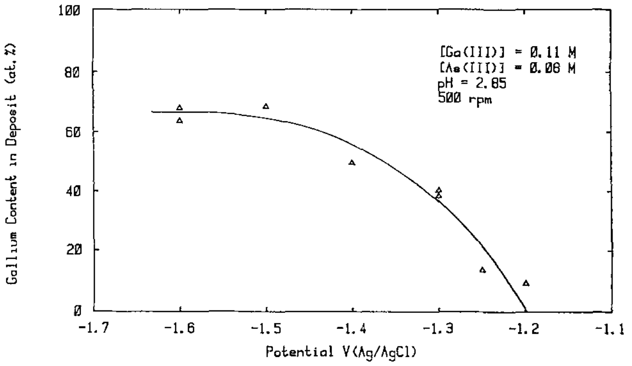

Fig. 15. Relationship between potential and gallium content in Ga/As films from electrolyte at pH 2.85 containing 0.11*M* Ga(III) and 0.08*M* As(III).

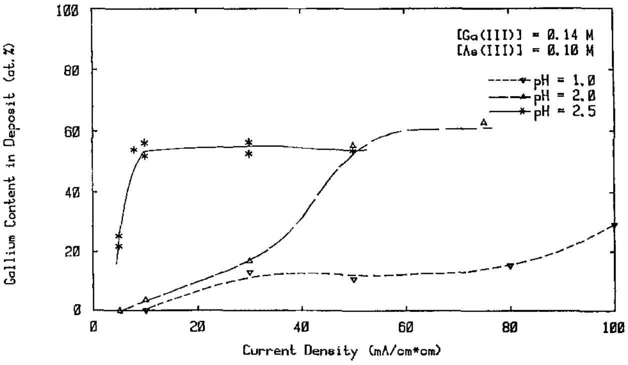

Fig. 16. Relationship between current density and gallium content in Ga/As films from electrolyte at 0.14*M* Ga(III) and 0.10*M* As(III) at pH 1.0, 2.0, and 2.5.

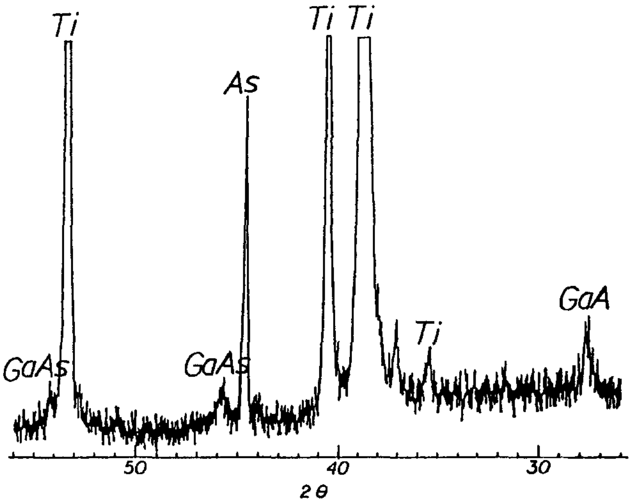

Fig. 17. X-ray diffraction pattern of a Ga/As film on titanium substrate, electrodeposited at 10 mA/cm^2 from electrolyte at pH 2.5 containing 0.14*M* Ga(III) and 0.10*M* As(III), and annealed at 260°C for 8 h.

removed and was found to include gallium and oxygen. It is believed that, at very negative potentials and reduction of hydrogen ion, the pH increased on the cathode surface and decreased the solubility of gallium.

Effect of pH.—pH plays an important role in the electrodeposition of gallium/arsenic from acid solution. At higher pH, *i.e.*, from 2.5 to 3.0, gallium hydroxide readily precipitates on the cathode, particularly at high current density or very negative potential. At lower pH, high current density or very negative potential is necessary to obtain a thick deposit with 50% gallium content. Figure 16 shows the relationship between the gallium content and current density at three different pH values. Generally speaking, higher current density, accompanied with more bubbles on the cathode, produced more gallium in the deposit for a specific pH. For each pH value, there was a range of current density which gave constant gallium content in the deposit. A white precipitate was observed at current densities greater than 60 and 80 mA/cm^2 for pH 2.5 and 2.0, respectively, after 10 min of deposition. At pH 1.0 the gallium content in the thin deposit reached 74.19% at 120 mA/cm^2 with no white precipitate on the cathode. The best deposits were obtained at pH 2.5 and current density between 10 and 50 mA/cm^2. The deposits were dark gray and not removable by a soft material, such as Teflon rod. After scraping with a stainless steel blade, the sample became shiny black on the Ti substrate. This adhesion was significantly different than that of the deposit from alkaline solution, which could be completely removed by wiping with paper to show the original titanium substrate.

Obtaining a deposit containing gallium at pH 0.7 requires a much higher current density; 50% gallium content required 350 mA/cm^2. At lower than 100 mA/cm^2, the deposit was either very thin or absent. A white precipitate was found on the gray deposit at 500 mA/cm^2. From Fig. 16, a deposit with a given composition, e.g. 50% gallium, was obtained at lower current density, with fewer bubbles, from a higher pH. On the other hand, at the same current density, the deposit generally exhibited a higher gallium content from a higher pH.

Effect of complexing agents.—Complexing agents are often used in electrodeposition, particularly in alloy deposition, for example, citric/sodium citrate in indium/antimony electrodeposition.[15] In the gallium/arsenic system, gallium is more difficult to reduce than arsenic by at least 0.65 V. A complexing agent for arsenic that does not complex gallium is desired, though not found.[24,25] In aqueous solution, oxygen has such a strong bond with both gallium and arsenic that few chemical species, other than hydroxide, can form complexes with them. Furthermore, no free arsenic ion exists in any solution, but free gallium ions are present at low pH. This comparison suggests that oxygen has a stronger bond with arsenic than with gallium in an aqueous solution. Therefore, a complexing agent may have less ability to replace oxygen and be less likely to form a complex with arsenic than with gallium. This judgment is confirmed by the stability constants of complexes, such as with citric acid, nitrilotriacetic acid, EDTA, chloride, fluoride, and 1,2-dihydroxybenzene-3,5-disulfonic acid.

Experimentally, citric acid sodium citrate solution has been used in a variety of compositions: 0.057*M* Ga(III)/0.02*M* As(III), 0.263*M* Ga(III)/0.017*M* As(III), and 0.14*M* Ga(III)/0.10*M* As(III), at pH values between 0.7 and 3.0. The total concentrations of citric acid and citrate were at least equal to the sum of [Ga(III)] and [As(III)]. When the current density ranged from 2.5 to 100 mA/cm^2, the solution became brown, and no visible deposit formed on the cathode. The added citric acid or citrate worked as an inhibitor to prevent gallium and arsenic from depositing on the cathode. Acetic acid, tartrate, and succinate were also tested in some of the solutions. The deposits were either of poorer quality (rougher and more porous) or exhibited no improvement over those in noncomplexed systems.

Annealing effect and x-ray diffraction analysis.—The as-deposited film from acid solution did not show any peaks of crystalline GaAs in the x-ray diffraction pattern. Unlike deposits from alkaline solution, the sample prepared from acid electrolyte was so thin (estimated at 0.3 μm) that some samples only showed peaks of the titanium substrate in the diffraction pattern. Figure 17 shows a diffraction pattern of a heat-treated sample prepared on a titanium cathode at 10 mA/cm^2 from a solution at pH 2.5, containing 0.14*M* Ga(III) and 0.10*M* As(III). The as-deposited film was annealed at 260°C for 8 h. The pattern indicates that the sample included gallium arsenide crystals with peaks at 2θ = 27.6°, 45.7° and 54.2° The grain sizes were estimated from the Sherrer equation to be at least 300 Å.

Auger electron spectroscopy and oxygen content analysis.—As for deposits from alkaline solution, a sample prepared at 30 mA/cm^2 from acid solution of pH 2.5, containing 0.14*M* Ga(III) and 0.10*M* As(III), has been tested by Auger electron spectroscopy (AES). Figure 18 shows the depth profile of gallium, arsenic, oxygen, and titanium with a 10 kV incident electron beam. The depth was estimated from the Ar$^+$ sputter time. The steep slope of the curve for titanium between 3000 and 3500 Å indicates that the deposit thickness was about 3000 Å. The oxygen content was as high as 30% in the deposit. Generally speaking, arsenic content increased slightly with depth, then decreased strongly after 3000 Å depth. However, gallium and oxygen contents monotonically decrease with depth. Therefore, the presence of oxygen in the deposit was more likely related to gallium than arsenic. The significant increase in gallium content at 3500 Å depth was not observed in other samples and could be attributed to noise or the rough surface texture of titanium substrate.

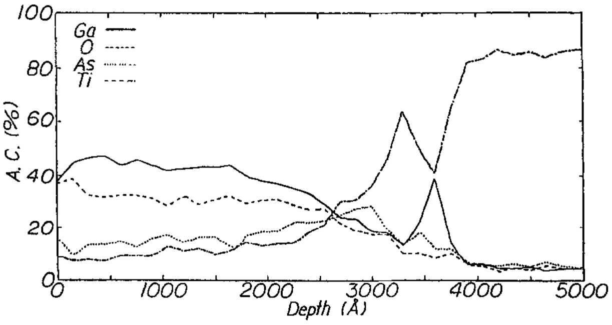

Fig. 18. Auger depth profile for a Ga/As film electrodeposited at 30 mA/cm^2 from electrolyte at pH 2.5 containing 0.14*M* Ga(III) and 0.10*M* As(III).

In a deposit of gallium/arsenic from solution of pH 2.5, containing 0.14M Ga(III) and 0.10M As(III), a large gallium content in the deposit was always accompanied with a large amount of oxygen, as depicted by EDS spectra in Fig. 19 and 20 with gallium contents of 18.6% and 44.1%, respectively. In both figures, titanium shows a peak at 0.452 keV. However, Fig. 20 depicts an additional peak at 0.525 keV for oxygen. This result confirms the hypothesis based on the AES spectrum that oxygen in the deposit is associated with gallium.

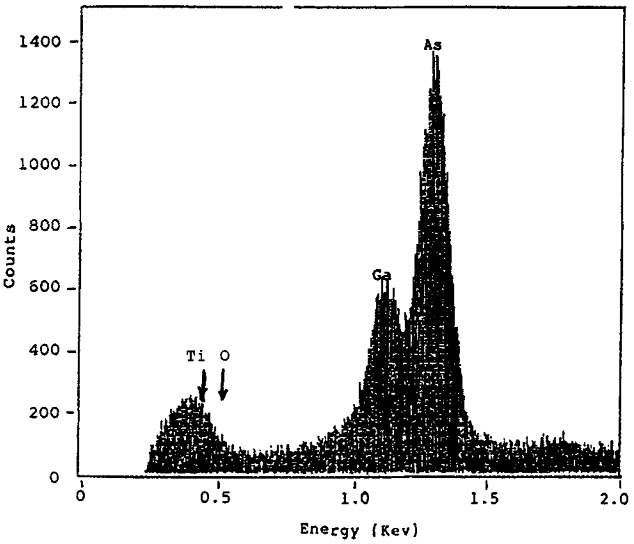

Fig. 19. EDS spectrum of a Ga/As film on titanium cathode, electrodeposited from electrolyte at pH 2.5 containing 0.14*M* Ga(III) and 0.10*M* As(III). [Ga]/[As] = 18.6/81.4 in the film.

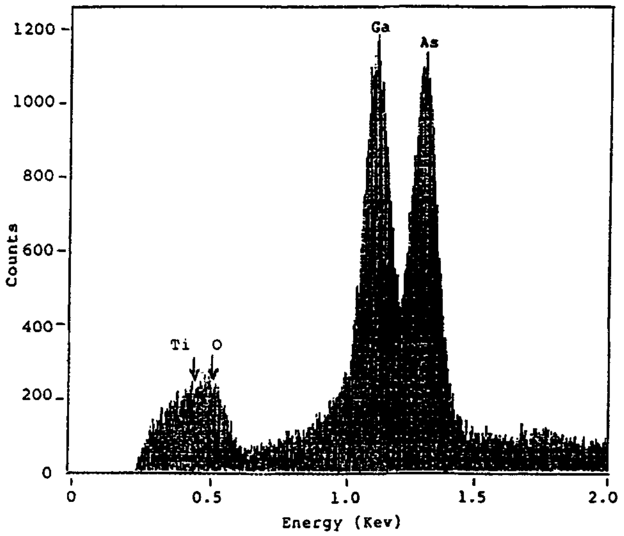

Fig. 20. EDS spectrum of a Ga/As film on titanium cathode, electrodeposited from electrolyte at pH 2.5 containing 0.14*M* Ga(III) and 0.10*M* As(III). [Ga]/[As] = 44.1/55.9 in the film.

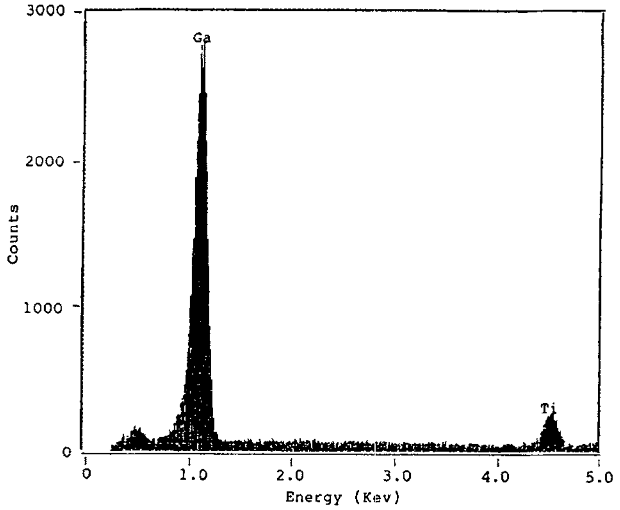

Fig. 21. EDS spectrum of Ga deposit with 30 mA/cm^2 from electrolyte at pH 2.5 containing 0.14*M* Ga(III).

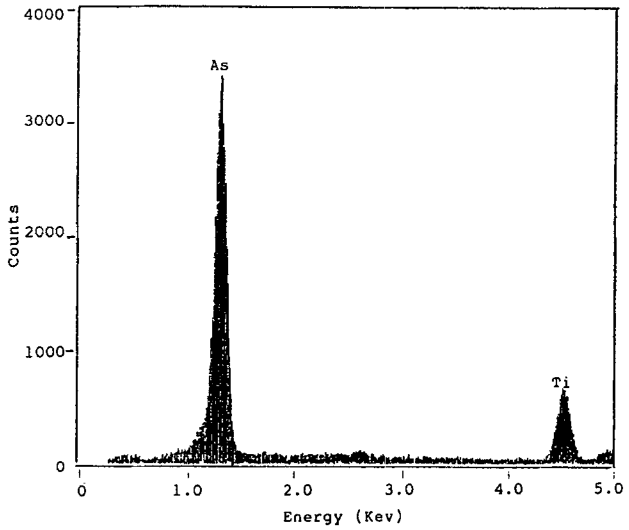

Fig. 22. EDS spectrum of As deposit with 30 mA/cm^2 from electrolyte at pH 2.5 containing 0.10*M* As(III).

To ascertain whether oxygen also incorporates with gallium and arsenic in elemental (single component) electrodeposition, gallium and arsenic were deposited from solutions of pH 2.5 containing 0.14M Ga(III) and 0.10M As(III), respectively. Figures 21 and 22 show the EDS spectra of the deposits with a windowless detector. Figure 21 shows the peaks of gallium and titanium substrate at 1.098 and 4.508 keV, respectively. The small peak at 0.525 keV is due to oxygen which always forms a protective oxide film on the surface of gallium in air or in aqueous solutions. On the other hand, Fig. 22 only shows the peaks of arsenic and titanium substrate at 1.282 and 4.508 keV, respectively. Obviously, only a small amount of oxygen is incorporated in gallium or arsenic elemental electrodeposition.

One possible mechanism for oxygen incorporation in the deposit is the partial reduction of gallium(III) to Ga_2O. The other possibility involves the high pH on the cathode surface, which gives low gallium solubility and coprecipitates some oxygen containing gallium species in the solution into the deposit. The latter may also explain the white precipitate observed at long deposition time or at high current density. The third possibility is that the arsenic might promote the reaction of oxygen with gallium. The presence of arsenic may prevent gallium from forming a continuous phase, and the separated gallium particles or gallium/arsenic particles offer enormous surface for reaction with oxygen.

Conclusions

Gallium arsenide films have been produced by electrodeposition from both acid and alkaline aqueous solutions. X-ray diffraction patterns showed that the as-deposited films on titanium cathodes were microcrystalline GaAs. The films transformed to crystalline gallium arsenide, with some loss of arsenic content, after annealing at 250-300°C for as little as 6 h in a nitrogen atmosphere. Secondary ion mass spectroscopy analysis also confirmed the existence of gallium arsenide in the as-deposited film obtained from an alkaline electrolyte. Auger energy spectroscopy revealed that the composition of the film deposited from alkaline solution was reasonably uniform along its depth. However, the film deposited from acid solution had a relatively nonuniform composition with depth. This analysis also showed that the electrodeposited gallium arsenide films contained oxygen which was probably associated with gallium.

The deposits from alkaline solution were thick and powdery with relatively poor adhesion to the cathode. During potentiostatic deposition, the current density increased with time. The composition of the film can be controlled by the applied potential, temperature, electrolyte composition, and agitation. The gallium content, relative to the arsenic content, was higher at more negative potentials and approaches a constant value over a range before arsine production. This constant composition was not affected by agitation. Higher deposition temperature produced a film with less gallium content and nonuniform composition with depth. Higher concentrations of gallium or arsenic in the electrolyte produced more gallium or arsenic in the film, respectively. The film with 50% gallium content can be obtained on silicon, lead, tin, and graphite, as well as on titanium.

The deposit from acid solution was thin and had good adhesion to the cathode, especially at pH 2.5. The current density decreased during potentiostatic deposition. The composition of the film can be controlled by the applied potential, current density, and pH. Higher current density produced higher gallium content in the deposit, eventually reaching a constant value. At very high current density, or with prolonged deposition time, a white deposit formed on a gray film. An electrolyte with low pH required higher current density to produce a specific gallium content in comparison to an electrolyte at high pH. It is very difficult to obtain good films from solution with pH 0.7. The complexing agents investigated did not improve the film structure.

Arsine was produced during deposition from alkaline solution. This behavior made it possible to obtain deposits with nearly 100% gallium content. Arsine also can react with gallium ion, GaO_3^{-3}, in the electrolyte. Separately deposited films of gallium on arsenic can be converted to crystalline gallium arsenide through annealing. However, arsenic films were destroyed during subsequent gallium deposition. The oxygen found in deposits obtained from acid solution was found to be associated with gallium. Gallium has lower solubility at high pH, as obtained at the cathode surface during high rate deposition.

Acknowledgments

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