

Vapor Phase Epitaxy of Gallium Arsenide

ARRIGO ADDAMIANO

*Solid State Technology Branch
Electronics Division*

January 26, 1973



NAVAL RESEARCH LABORATORY
Washington, D.C.

ABSTRACT

GaAs epitaxial layers of good semiconductor quality (comparable to bulk GaAs) have been prepared by the arsine method. The preparative technique and improvements are described. Overall, the arsine system has proved not only reliable but simple as well. The growth rates are reasonably high for practical device fabrication.

The epitaxial reactor undergoes continued cleanup during operation. After a few months of operation the residual donor concentration stabilizes at $\sim 10^{15}/\text{cm}^3$. By locating substrates in the As-rich, low-temperature zone, p-type layers can be grown; n-type layers are usually obtained with the substrates at about 725°C .

PROBLEM STATUS

An interim report on the NRL problem.

AUTHORIZATION

NRL Problem R08-44
Project RR 008-03-46-5673

Manuscript submitted November 13, 1972.

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INTRODUCTION

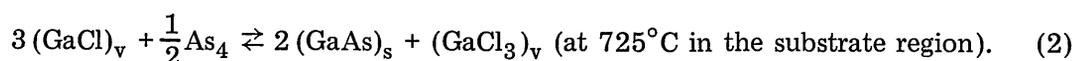
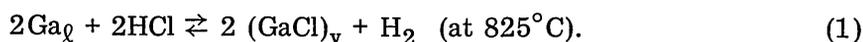
Welker (1) pointed out in 1952 that gallium arsenide and other III-V compounds should be semiconductors similar to silicon and germanium. The work of the past twenty years has confirmed Welker's prediction. Gallium arsenide is now well established among the useful semiconductors, as indicated, for instance, by the recent International Symposia on Gallium Arsenide (2 - 4).

Interest in GaAs in the Solid State Technology Branch of the Electronics Division of NRL focuses mainly on potential applications for a variety of microwave devices. A program was initiated in 1970 to develop an in-house capability for chemical vapor epitaxial growth. At that time a careful survey of the literature yielded wide variations in deposition parameters for any given deposition method. It is the intent of the present work to establish a simple, reproducible technique capable of producing high-quality epitaxial layers with low carrier concentration ($\approx 10^{15}/\text{cm}^3$) and near bulk mobility.

CHOICE OF THE SYSTEM

Different vapor-phase epitaxial techniques are available for GaAs. Among them the most popular methods are the open-flow, "arsine" and "chloride" methods (5 - 8), which use AsH_3 and AsCl_3 , respectively, as the source of arsenic. The arsine method has the following advantages: (a) immediate startup of the system; (b) better control of the arsenic concentration; (c) better control of the thickness of the epitaxial layers in the submicron range. For these reasons this method was preferred for our work.*

The reactions of interest in the arsine method are:



Reaction (1) results in the formation, at relatively high temperature, of a volatile chloride of gallium, GaCl , which is carried downstream. In the deposition zone of the furnace, at about 750°C or slightly less, the GaCl reacts with arsenic vapor from the thermal dissociation of AsH_3 and forms GaAs on the substrates. For reaction (2) to go to the right with deposition of GaAs on the substrates, a temperature gradient must exist in the reactor. A two-zone furnace was used to insure the right temperature profile. Figure 1 shows the operating conditions in the two-zone furnace, which is 80 cm long and has an

*Exploratory work on the chloride method has been published elsewhere (9,10).

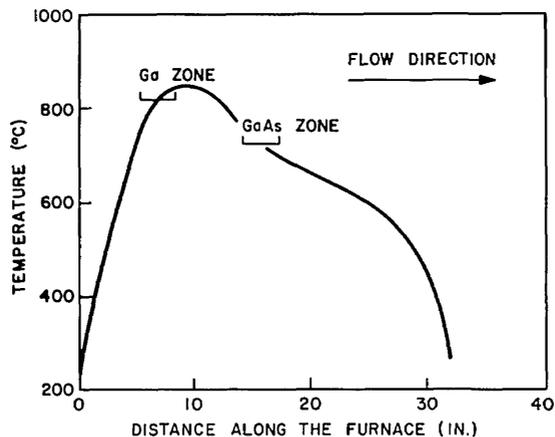


Fig. 1 — Operating conditions in the two-zone furnace

inside diameter of 5 cm. The fused-quartz reactor tube, with an overall length of 95 cm and an inside diameter of 4.5 cm, has separate inlets for the H_2 carrier gas, the HCl, the AsH_3 and the dopant gas (usually H_2Se). All the connections to the reactor tube are made of flexible Swagelock fittings; the mixing bottles used to dilute the HCl and AsH_3 with H_2 are made of stainless steel. The gas lines are made entirely of stainless steel; the introduction of even a short piece of plastic or rubber tubing in the lines results immediately in substantial deterioration of the quality of the epitaxial layers! High-purity H_2 tanks, showing no trace of oxygen or other impurities by mass spectroscopic analysis down to the ppm range, were used to supply the carrier gas and to dilute the AsH_3 and HCl to the levels needed to obtain the low growth rates needed for high-quality growth. Tanks of 10% HCl — 90% H_2 and 15% AsH_3 — 85% H_2 were used as sources of HCl and AsH_3 . The rates of flow of the gases were measured with commercial calibrated flow meters.

SEED PREPARATION

Polished $\langle 100 \rangle$ slices of semi-insulating, Cr-doped, GaAs were generally used as substrates. For more reproducible results the slices were cut 2° off the (100) plane. Immediately before use, the substrates were etched 5 min at room temperature in $5 H_2SO_4 - 1 H_2O_2 - 1 H_2O$. Then they were soaked in NH_4OH for 5 min, rinsed in high-purity deionized water and then in electronic-grade methyl alcohol, and were introduced still wet into the reactor tube on a quartz plate of dimensions 4 in. by 1.25 in. by 0.125 in. The fused-quartz plate itself was placed in a dump tube, which extended through the length of the reactor tube and could conveniently be extracted from it for loading, unloading, and cleaning. It must be stressed that only high-purity water (having a resistivity of 14 megohm cm or more at room temperature) can be used for rinsing the substrates and the quartz ware. Use of relatively impure water results in nonreproducible growth and in less uniform layers.

OPERATING PROCEDURE

The deposition of epitaxial layers of GaAs on GaAs substrates, as practiced by us, requires the following steps.

1. With the furnace at room temperature and the reaction tube filled with flowing H_2 , the dump tube containing the substrates is introduced into the reaction tube.
2. The reaction tube is then sealed, exhausted to less than 10^{-4} torr, and flushed five times with high-purity H_2 .
3. The H_2 pressure is brought to a slightly higher value than the atmospheric pressure, and H_2 is flushed through all the lines and the mixing bottles for 30 min or more.
4. The furnace is energized. When a temperature of $600^\circ C$ is obtained, AsH_3 is added to the H_2 flow and the flow rates checked for deposition conditions.
5. With the gallium boat at $825^\circ C$ and the substrates at about $725^\circ C$, a mixture of $HCl + H_2$ is added to the flowing gases. Reaction with the Ga (Eq. (1)) occurs, and deposition of GaAs takes place on the substrates.
6. After the desired thickness of GaAs is deposited, the HCl flow is interrupted for 10 min, keeping AsH_3 , H_2 , and dopant, if any, flowing at constant temperature.
7. After this period the furnace is switched off and allowed to cool.
8. When the temperature is at $600^\circ C$, the AsH_3 flow is discontinued, the reaction tube is sealed off and overnight cooling in the H_2 atmosphere is allowed.
9. The dump tube is extracted from the furnace and the substrates are recovered and examined.

The conditions which resulted in high-quality growth are:

- Substrates: $\langle 100 \rangle$ GaAs cut 2° off the (100) plane
- AsH_3 flow: 20 ml/min of 15% AsH_3 in H_2
- H_2 added to the AsH_3 : 70 ml/min
- HCl flow: 25 ml/min of 10% HCl in H_2
- H_2 added to the HCl : 70 ml/min
- H_2 carrier gas: 50 ml/min
- Temperature of the Ga boat: $825^\circ C$
- Temperature of the substrates: $725^\circ C$ to $750^\circ C$
- Deposition rate: 0.2-0.3 $\mu m/min$

The deposition, or growth rate was measured by comparing the thickness of the substrates covered by epitaxial layers with that of an adjacent area which was covered by a thin chip of GaAs during growth. Direct measurements and Zeiss interferometric measurements both gave rate values in good agreement with each other and with those reported in the literature, i.e., 0.2 to 0.3 $\mu\text{m}/\text{min}$.

It was observed that the quality of the epitaxial layers changed if the substrates were moved through the hot zone. At about 725°C the undoped layers were routinely n-type and usually smooth, with a bluish tinge. In the region of the furnace exhaust, where a strong excess of As exists, the grown layers, usually of relatively poor quality, are p-type. Similar observations were made by Knappett (11), who reported that both p- and n-type epitaxial GaAs could be obtained by simply changing the Ga to As ratio in a chloride reactor, which usually gave p-type layers. The quality of the epitaxial layers obtained improved constantly in the course of our work. Table 1 compares some typical data obtained at the beginning of the work with data obtained at later dates. In all cases the growth time is about 30 min, which corresponds to layers 6 μm thick.

Table 1
Some Electrical Data for GaAs Epitaxial Layers
Grown on $\langle 100 \rangle$ GaAs

Sample	Resistivity (ohm cm)	Room-Temperature Mobility ($\text{cm}^2/\text{V s}$)	Charge Carriers (cm^{-3})
33	6.6×10^{-3}	511	1.8×10^{18}
34	3.2×10^{-2}	1417	1.4×10^{17}
45	1.8×10^{-2}	1212	2.8×10^{17}
51	6.7×10^{-2}	913	1.0×10^{17}
52	2.6×10^{-2}	1225	2.0×10^{17}
53	2.1×10^{-2}	1940	1.5×10^{17}
55	8.2×10^{-2}	1400	5.4×10^{16}
56	7.2×10^{-2}	2090	4.2×10^{16}
72	2.8×10^{-1}	3400	7.0×10^{15}
75	2.3×10^{-1}	4200	4.1×10^{15}
77	6.0×10^{-1}	4500	2.5×10^{15}

Mobilities in the four-figure range and carrier concentrations in the low 10^{15} range are currently obtained. These values are close to the corresponding values obtained for single-crystal GaAs. Thus the immediate objective of this research has been attained.

DISCUSSION

The arsine method has proved capable of producing epitaxial layers of near-bulk-value qualities; however, it is usually considered to be quite risky because arsine is a very poisonous gas. In the course of our work, however, we experienced no serious difficulty in handling the arsine. Because of its corrosive action, however, the HCl has given occasional troubles, such as leaky valves and flow meters. In one case the pressure gauges and the tanks had to be replaced three times in a row. The use of very dilute HCl might prevent these

inconveniences and the hazards due to relatively concentrated HCl. Since the 10% HCl must be further diluted with H₂ for optimum results, it might be possible to start with tanks of HCl of the right concentration and to eliminate the mixing procedure. Similarly, an arsine concentration lower than 15% might be used without further dilution with H₂. If this is done, the practice of the arsine method can be made very simple indeed.

Overall the arsine method, as used, has proved simple and reliable. The "cleaning up" of the reactor in the course of time, which results in progressively better epitaxial layers, is a feature observed by numerous other workers in the field and may be due to different factors such as (a) cleaning up of the reactor itself, (b) boiling off of impurities from the gallium boat (even though the gallium used is free from metals, ubiquitous impurities such as oxygen, are usually present), and (c) purification of the gas lines and of the gas tanks. Since the flow rates for deposition are quite small, the gas tanks last for a considerable time, and relatively stable growth conditions exist over a long period before new tanks need to be used.

Temperature is undoubtedly the most important physical parameter affecting the rate and quality of growth. This is because a small increase in the substrate temperature (say 20°C) will result in dissociation of the substrates, with losses of As, whereas a small decrease in the temperature results in a noticeable increase in the growth rate and in inferior quality of the epitaxial layers. Optimum conditions exist only in a limited zone of the reactor. Possible improvements which we may suggest include locating the substrates at an angle (say 30°) to the direction of gas flow, rather than parallel to it, possibly with the addition of a slow rotational movement, as is used in practice for the preparation of Ga(As, P) (12). With a stationary substrate, parallel to the gas flow, uniform growth occurs in a zone having a length of 1 in. This limits the useful size of the substrates. Our most uniform layers were obtained on substrates approximately 6 × 6 mm².

ACKNOWLEDGMENTS

I thank J. E. Davey for his continued interest in this research. I am obliged to P. H. Klein of the Central Materials Research Activity (Code 6060) for the donation of a boule of GaAs and to N. Saks, W. Schmidt, and H. Grant for help with the instrumentation and the electrical measurements.

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DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Naval Research Laboratory Washington, D.C. 20375		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE VAPOR PHASE EPITAXY OF GALLIUM ARSENIDE			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Interim report on one phase of the NRL problem.			
5. AUTHOR(S) (First name, middle initial, last name) Arrigo Addamiano			
6. REPORT DATE January 26, 1973		7a. TOTAL NO. OF PAGES 9	7b. NO. OF REFS 12
8a. CONTRACT OR GRANT NO. NRL Problem R08-44		9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 7523	
b. PROJECT NO. RR 008-03-46-5673		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.			
d.			
10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Department of the Navy Office of Naval Research Arlington, Va. 22217	
13. ABSTRACT <p>GaAs epitaxial layers of good semiconductor quality (comparable to bulk GaAs) have been prepared by the arsine method. The preparative technique and improvements are described. Overall, the arsine system has proved not only reliable but simple as well. The growth rates are reasonably high for practical device fabrication.</p> <p>The epitaxial reactor undergoes continued cleanup during operation. After a few months of operation the residual donor concentration stabilizes at $\sim 10^{15}/\text{cm}^3$. By locating substrates in the As-rich, low-temperature zone, p-type layers can be grown; n-type layers are usually obtained with the substrates at about 725°C.</p>			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Gallium arsenide Epitaxy Semiconductor technology Arsine (handling of) Hydrochloric acid (handling of)						