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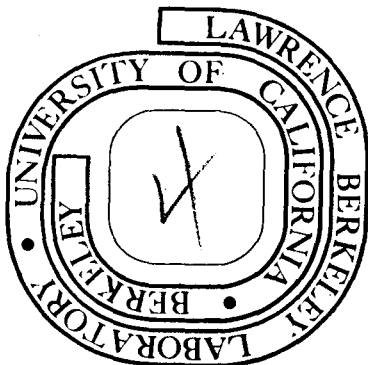
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Reactor Designs for the Chemical Vapor
Deposition of Epitaxial $\text{GaAs}_{1-x}\text{P}_x$

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December, 1973

Abstract

Research and commercial reactor designs for the chemical vapor deposition of $\text{GaAs}_{1-x}\text{P}_x$ alloys are reviewed. Chemical reaction schemes and reactor designs are surveyed for reactor design criteria and limitations for open flow reactors utilizing alternative source chemicals. Commercial reactor design is examined in terms of flow orientation, source chemicals and substrate orientation. The design and operating properties of a cold wall reactor utilizing trimethyl gallium as a source chemical is examined in detail and compared to hot wall reactor properties.

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Introduction

Chemical processes for the growth of epitaxial layers of compound semiconductors have advanced significantly in the last two decades (1,2). Much of the impetus for the research on epitaxial film growth is derived from the development of planar technology for electronic device processing, and the perfection of processes able to attain bulk materials properties in thin films (3).

The chemical vapor deposition process has been primarily responsible for the industrial preparation of electronic materials as thin layers on substrate surfaces. Indeed, this process has become almost commonplace for semiconductor device processing in recent years. This technique has the distinct advantage that high-melting materials can be deposited over selected substrate areas at temperatures far below their melting points. Although epitaxial silicon deposited by the pyrolysis of silane has become the main semiconducting material processed by this method, chemical vapor deposition reactions are currently under study for III-V compound semiconductors and their alloys, such as $\text{GaAs}_{1-x}\text{P}_x$. These materials offer a wide range of electrical and optical properties that make them superior to silicon in many device applications such as light emitters, microwave transistors, high temperature semiconductors and photocathodes (4).

The chemical reactions required for deposition III-V compound alloy are more complex than for elemental semiconductor deposition, because of the high dissociation pressures of the compounds, the

presence of competing gas phase reactions, and the need for hot-wall reactors. The relatively low efficiency of many reaction schemes and the high cost of reagent chemicals has promoted an interest in reactor design for improving the yield and uniformity of the chemical vapor deposition process on an industrial scale. In this study a general survey of research on chemical reactions and reactor designs for research and industry are presented with special emphasis on the light-emitting diode material, $\text{GaAs}_{1-x}\text{P}_x$. Based on the chemical and physical principles involved in the chemical vapor deposition process, design criteria are developed for optimization of various reaction schemes.

Reactions and Thermodynamics

A wide variety of reactions have been successfully used for the deposition of III-V compound films (5). Both closed and open flow systems have been shown to allow growth by chemical transport reactions. The prevailing reaction depends principally on the source chemical, and these are summarized in Table I. The semiconductor compound sources are used principally in closed transport processes while more volatile, component-element compounds are required in open flow processes.

Solid Compound Sources

The compounds GaAs and GaP have been successfully chemically transported with HCl as a transport agent in closed quartz containers at 800°C (6). Gallium monochloride and elemental arsenic or phosphorus

TABLE I

Source Chemicals for Chemical Transport
of GaAs and GaAs_{1-x}P_x Alloys

A. Compound Semiconductor Sources

1. GaAs_(s) , GaP_(s)
2. GaAs_{1-x}P_x

B. Component Element Compound Sources

1. Gallium

- a) GaCl₃(l)
- b) GaCl_(v) , produced with HCl and Ga_(l)
- c) Ga(CH₃)₃(v)

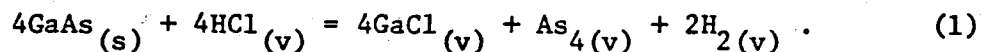
2. Arsenic

- a) As_(s)
- b) AsCl₃(l)
- c) AsH₃(v)

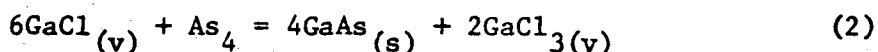
3. Phosphorus

- a) P_(s)
- b) PCl₃(l)
- c) PH₃(v)

are formed by the reaction at the solid source,

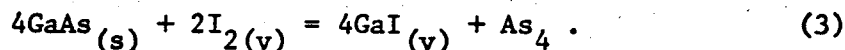


The reverse transport reaction takes place in a zone of lower temperature. The disproportionation reaction



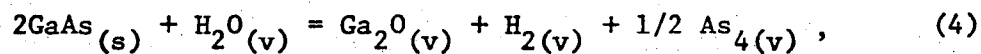
was believed to be the deposition reaction, but recent mass spectrometric studies have failed to detect GaCl_3 in H_2 -rich, open flow reactors⁽⁷⁾.

The compound GaAs can also be chemically transported by other halides such as iodine. In a hydrogen-rich atmosphere, the iodine reaction produces volatile GaI and arsenic by the reaction,



Magomedov^(8,9) applied this reaction in vertical, open flow system, and found it to be more convenient than the closed-tube chloride transport process.

The water vapor reaction with GaAs, InAs or InP produces volatile suboxides, such as Ga_2O , and arsenic, both of which are volatile⁽¹⁰⁻¹³⁾. This reaction,

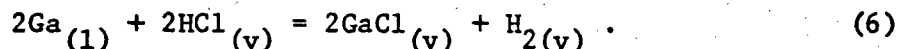


has the disadvantage, however, that high oxygen impurity content is incorporated in the deposited films. In general, transport reactions

utilizing compound semiconductor sources are relatively slow and not easily scaled to large size for industrial applications.

Liquid and Gaseous Sources

Open flow reaction systems offer enhanced simplicity over closed-system transport processes. These processes utilize halides, hydrides or organometallic compounds as source chemicals. The basic method is exemplified by the deposition of GaAs from Ga_(l), AsCl₃ and H₂, which has been well studied^(14,16). Finch and Mehal also introduced PCl₃ with AsCl₃ to deposit GaAs_{1-x}P_x alloys. The reaction proceeds by the saturation of liquid gallium with arsenic and phosphorus produced by the reaction,



The deposition reaction occurs on substrates maintained at a lower temperature by the reverse of the reaction given in Eq. 1.

The only reaction systems which have been used industrially for the deposition of GaAs_{1-x}P_x alloys utilize volatile GaCl as the transported species containing gallium irrespective of the source chemicals. As many of the more important transport processes are carried out with H₂ as a carrier gas, all reactions in the Ga-As-P-Cl-H system become important.

A compilation of possible reactions occurring for the deposition of GaAs_{1-x}P_x in this system is presented in Table II. In addition, the reactions for deposition of GaAs_{1-x}P_x from organometallic gallium sources are also given. The thermodynamic data for these latter

TABLE II

Reaction Equilibria in the Ga-As-P-Cl-H System

Reaction number	Reaction	$\log_{10} K_1$ (atm units)	Zone	Reference
1	$\text{Ga}(\ell) + \frac{1}{2}\text{Cl}_2 \rightarrow \text{GaCl}(\text{g})$	$6.46 + 3.69 \times 10^3/T - 0.47 \ln T$	Saturation	18, 19, 20, 21 (calculated)
2	$\text{Ga}(\ell) + \frac{3}{2}\text{Cl}_2 \rightarrow \text{GaCl}_3(\text{g})$	$-1.96 + 2.25 \times 10^4/T - 0.17 \ln T$	Saturation	17 (calculated)
3	$\text{GaCl} + \text{Cl}_2 \rightarrow \text{GaCl}_3(\text{g})$	$-8.37 + 1.87 \times 10^4/T + 0.30 \ln T$	Saturation	17 (calculated)
4	$\text{GaCl}_3 + 2\text{Ga} \rightarrow 3\text{GaCl}(\text{g})$	$4.87 - 4.66 \times 10^3/T$	Saturation	19 (experimental)
5	$\frac{1}{2}\text{H}_2 + \frac{1}{2}\text{Cl}_2 \rightarrow \text{HCl}(\text{g})$	$2.79 + 4.56 \times 10^3/T - 0.31 \ln T$	Saturation	18 (calculated)
6	$\text{GaCl}_3 + \text{H}_2 \rightarrow \text{GaCl} + 2\text{HCl}$	$13.95 - 9.58 \times 10^3/T - 0.92 \ln T$	Saturation	calc. from reactions 3&5
7	$\text{As}_4(\text{g}) \rightarrow 2\text{As}_2(\text{g})$	$11.6 - 1.36 \times 10^4/T - 0.43 \ln T$	Reaction	19, 21 (calculated)
8	$\frac{1}{4}\text{As}_4 + \frac{3}{2}\text{H}_2 \rightarrow \text{AsH}_3(\text{g})$	$3.65 - 7.52 \times 10^3/T - 1.0 \ln T$ $+ 0.6 \times 10^{-3} T$	Reaction	18, 19, 21 (calculated)
9	$\frac{1}{4}\text{As}_4 + \frac{3}{2}\text{Cl}_2 \rightarrow \text{AsCl}_3$	$-6.18 + 1.76 \times 10^4/T + 0.37 \ln T$	Reaction	18, 19, 21 (calculated)
10	$\text{Ga}(\ell) + \frac{1}{4}\text{As}_4 \rightarrow \text{GaAs}(\text{s})$	$-4.62 + 6.15 \times 10^3/T + 0.35 \times 10^{-3} T$	Deposition	18, 19, 22 (calculated)
11	$2\text{GaCl} + \frac{1}{2}\text{As}_4 \rightarrow 2\text{GaAs}(\text{s}) + \text{Cl}_2$	$-21.64 + 4.86 \times 10^3/T + 1.1 \ln T$	Deposition	18 (calculated)

Table II (continued)

Reaction number	Reaction	$\log_{10} K_1$ (atm units)	Zone	Reference
12	$3\text{GaCl} + \frac{1}{2} \text{As}_4 \rightarrow 2\text{GaAs}_{(s)} + \text{GaCl}_3$	$-30.1 + 2.36 \times 10^4 / T + 1.4 \ln T + 0.7 \times 10^{-3} T$	Deposition	23 (experimental)
13	$\text{GaCl} + \frac{1}{4} \text{As}_4 + \frac{1}{2} \text{H}_2 \rightarrow \text{GaAs} + \text{HCl}$	$-8.04 + 6.99 \times 10^3 / T + 0.22 \ln T + 0.35 \times 10^{-3} T$	Deposition	24 (experimental)
14	$\text{P}_4 \rightarrow 2\text{P}_2$	$11.5 - 1.21 \times 10^4 / T - 0.5 \ln T$	Reaction	19, 25 (calculated)
15	$\frac{1}{4} \text{P}_4 + \frac{3}{2} \text{H}_2 \rightarrow \text{PH}_3$	$4.88 + 1.47 \times 10^3 / T - 1.2 \ln T$	Reaction	19, 25 (calculated)
16	$\frac{1}{4} \text{P}_4 + \frac{3}{2} \text{Cl}_2 \rightarrow \text{PCl}_3$	$-6.21 + 1.79 \times 10^4 / T + 0.25 \ln T$	Reaction	19, 22, 25 (calculated)
17	$\text{Ga} + \frac{1}{2} \text{P}_2 \rightarrow \text{GaP}$	$-5.36 + 9.41 \times 10^3 / T$	Deposition	23 (experimental)
18	$\text{Ga} + \frac{1}{4} \text{P}_4 \rightarrow \text{GaP}$	$-2.46 + 6.38 \times 10^3 / T - 0.13 \ln T$	Deposition	Calculated from reactions 14 & 17
19	$2\text{GaCl} + \frac{1}{2} \text{P}_4 \rightarrow 2\text{GaP} + \text{Cl}_2$	$-18.00 + 5.39 \times 10^3 / T + 0.68 \ln T$	Deposition	Calculated from reactions 18 & 12
20	$3\text{GaCl} + \frac{1}{2} \text{P}_4 \rightarrow 2\text{GaP} + \text{GaCl}_3$	$-26.46 + 2.41 \times 10^4 / T + 0.98 \ln T$	Deposition	Calculated from reactions 19 & 16
21	$\text{GaCl} + \frac{1}{4} \text{P}_4 + \frac{1}{2} \text{H}_2 \rightarrow \text{GaP} + \text{HCl}$	$-6.08 + 7.255 \times 10^3 / T + 0.03 \ln T$	Deposition	Calculated from reactions 18, 14

Table II (continued)

Reaction number	Reaction	$\log_{10} K_1$ (atm units)	Zone	Reference
22	$\text{As}_2 + \text{P}_2 \rightarrow \text{As}_2\text{P}_2$	not determined	Reaction	---
23	$\text{As}_2\text{P}_2 \rightarrow 2\text{AsP}$	not determined	Reaction	---
24	$2\text{As}_2\text{P}_2 \rightarrow \text{As}_3\text{P} + \text{AsP}_3$	not determined	Reaction	---
25	$\text{Ga}(\ell) + \text{HCl} \rightarrow \text{GaCl} + \frac{1}{2}\text{H}_2$	$K_{25} = K_1/K_5$	Saturation	Calculated from reactions 1&5
26	$\text{GaCl} + 2\text{HCl} \rightarrow \text{GaCl}_3 + \text{H}_2$	$K_{26} = K_3/K_5^2$	Saturation	Calculated from reactions 3&5
27	$\text{Ga}(\text{CH}_3)_3 + \frac{3}{2}\text{H}_2 \rightarrow \text{Ga} + 3\text{CH}_4$	not determined	Reaction	---
28	$\text{Ga}(\text{CH}_3)_3 + \frac{3}{2}\text{H}_2 + \frac{1}{4}\text{As}_4 \rightarrow \text{GaAs} + 3\text{CH}_4$	not determined	Deposition	---
29	$\text{Ga}(\text{CH}_3)_3 + \frac{3}{2}\text{H}_2 + \frac{1}{4}\text{P}_4 \rightarrow \text{GaP} + 3\text{CH}_4$	not determined	Deposition	---

reactions has still not been published. However, in a recent study by Saitoh⁽²⁶⁾ it was shown that the reactions are non-equilibrium in that virtually all of the gallium compound dissociates and gallium in turn reacts with P_4 , As_4 or HCl .

A comparison of the equilibrium constants for these reactions indicates that many of the reactions can be neglected for the high temperature growth conditions occurring at the vapor-solid interface.

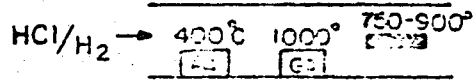
When gallium metal is transported with HCl in H_2 and used with arsenic and phosphorous halides or hydrides, the species present in appreciable quantities at the vapor-solid interface are HCl , $GaCl$, As_4 , As_2 , P_r , P_2 and PH_3 with traces of $GaCl_3$, $AsCl_3$ and PCl_3 .

Similarly for organo gallium and AsH_3 and PH_3 sources, only $Ga(CH_3)_3$, As_4 , As_2 , P_r , P_2 and PH_3 as well as mixed polymers should be present at the vapor-solid interface. By a careful elimination of the unimportant reactions, the number of total species present at equilibrium at the vapor-solid interface can be reduced in phase equilibrium calculations^(27,28). This technique has also been used by the present authors⁽²⁹⁾ for process design of the open flow reactions.

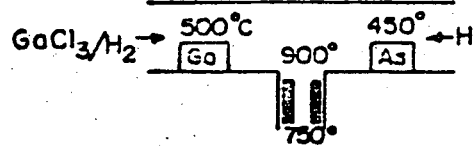
Survey of Research Reactors

Schematic diagrams of open flow reactors which have been proposed for growing $GaAs$, GaP and $GaAs_{1-x}P_x$ are shown in Fig. 1. Early reactors used both arsenic and gallium in the solid form as starting

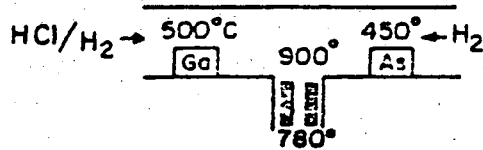
a. Newman⁽³⁾ and Minden⁽⁴⁾



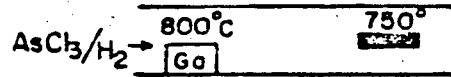
b. Goldsmith⁽⁵⁾



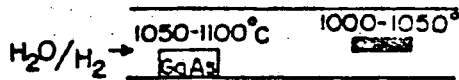
c. Amick⁽⁷⁾ and Michtelsch⁽⁸⁾



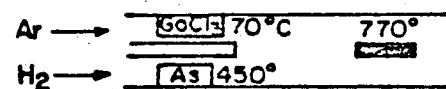
d. Effer⁽⁹⁾



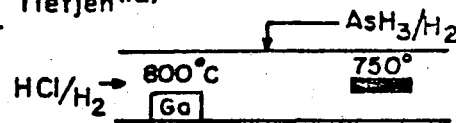
e. Lawly⁽¹⁰⁾



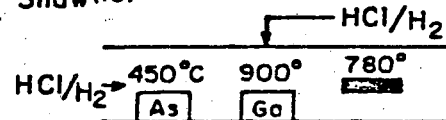
f. Rubenstein⁽¹¹⁾



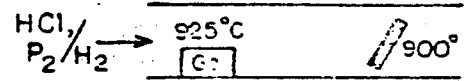
g. Tietjen⁽¹²⁾



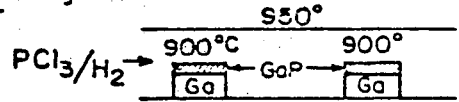
h. Shaw⁽¹³⁾



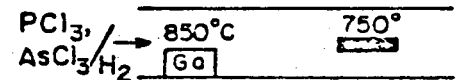
i. Luther⁽¹⁴⁾



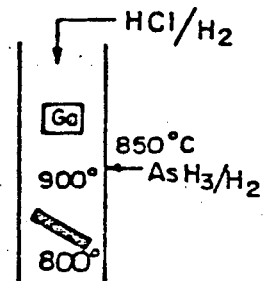
j. Ringel⁽¹⁵⁾



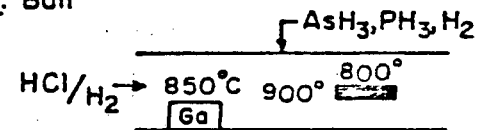
k. Finch and Mehal⁽¹⁶⁾



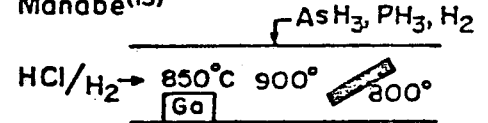
l. Goettler⁽¹⁷⁾



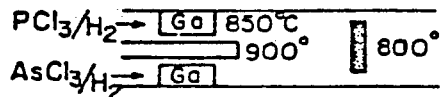
m. Bon⁽¹⁸⁾



n. Manabe⁽¹⁹⁾



o. Bleicher⁽²⁰⁾



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Figure 1. Open flow reactors for the chemical vapor deposition of GaAs, GaP and GaAs_{1-x}P_x solid solutions.

materials but later AsH_3 or AsCl_3 replaced solid arsenic as a transport species. Attempts were then made to use other oxidizing agents besides the halides, and principally chlorides.

Figure 1a shows schematically the flow-through reactor used by Newman⁽³⁰⁾ and by Minden⁽³¹⁾ for GaAs in 1961. They simply chlorinated arsenic and gallium and deposited the solids on a GaAs substrate. The reactor was a horizontal type with three temperature regions. Goldsmith⁽³²⁾ modified this reactor and placed the substrate in the middle of the arsenic and gallium sources, the substrates being placed in a side tube. This design used GaCl_3 as the starting material. The reason why this study used such a low-temperature for the $\text{Ga}(\ell)$ is not apparent. Possibly the GaCl_3 reacted with $\text{Ga}(\ell)$ to form the GaCl transport species. However, according to the data published by Kirwan⁽²³⁾ at a much later date, GaCl_3 is the most stable chloride of gallium at lower temperatures, and only at temperatures of 600°C does GaCl become important. Amick⁽³³⁾ and Michelitsch⁽³⁴⁾ used HCl instead of GaCl_3 in essentially the same process as used by Goldsmith, and the reactor temperatures were also the same. In 1965, Effer⁽¹⁴⁾ modified the Newman-Minden version of the reactor by using AsCl_3 as starting material for arsenic instead of pure arsenic (Fig. 1d). Lawly's reaction scheme utilized the water reaction of Eq. 4⁽³⁵⁾.

The advantages of introducing a gaseous species at the input instead of a solid as a source of arsenic are so great in terms of ease and controllability that few subsequent reactor studies have

used arsenic in the solid form. The liquid reagent AsCl_3 is safer than other arsenic sources, and also the rate of vaporization can be controlled more easily than for solid arsenic. Once the advantages of using a gaseous arsenic source were realized other sources besides AsCl_3 were exploited⁽³⁶⁾. AsCl_3 still had the disadvantage that since it is a liquid; hydrogen has to be bubbled through it with great care to prevent variations in AsCl_3 vapor pressure. However, AsH_3 is a gas at standard temperature and pressure and can be introduced at precise flow rates. Therefore control of the growth process is much easier and precise. Teitjen⁽³⁷⁾ first used AsH_3 as a source of arsenic in 1966 and reacted gallium with HCl to form GaCl and GaCl_3 . Shaw⁽³⁸⁾ in 1968 employed As (solid) again in 1970 but subsequently modified his reactor to the form used earlier by Tietjen and others.

The reactors for GaP are essentially the same as those for the deposition of GaAs . However, because GaP was explored much later as a potential electronic device material, the reactor studies placed more emphasis on deposition uniformity and its dependence on the orientation of the substrate holder. The work of Luther⁽³⁹⁾ is a very good example and the design of the substrate holder is treated in great detail. He showed that if liquid N_2 is passed under the substrate to cool it, the growth is faster and planar because the gradient in temperature on the growing surface does not allow constitutional supercooling which causes the planar growing surface to become unstable with respect to protrusions. In his reactor the

substrate is placed at an angle to the gas flow direction as shown in Fig. 11. Ringel⁽⁴⁰⁾ explored rheotaxy on a $\text{Ga}_{(1)}$ substrate. Goettler⁽⁴¹⁾ designed a vertical reactor in 1970 in which the substrate is again at an angle rather than being parallel to the flow direction. In silicon reactors and later studies of $\text{GaAs}_{1-x}\text{P}_x$ deposition the substrates are usually placed at an angle to, or normal to the flow direction rather than parallel to the flow direction as used by all earlier studies. The reactants for $\text{GaAs}_{1-x}\text{P}_x$ and the reactor itself are essentially the same as for GaAs and GaP . This is apparent from the studies made by Ban⁽⁴²⁾, Manabe⁽²⁷⁾, and Bleicher⁽²⁸⁾.

In a recent paper Saitoh⁽²⁶⁾ examined the characteristics of the $\text{GaAs}_{1-x}\text{P}_x$ epitaxial layers by pyrolytic growth using $\text{Ga}(\text{CH}_3)_3$ as a source of gallium. This method has a potential advantage over the traditional chloride transport methods in that reactions at reactor walls is kinetically hindered. The growth of $\text{GaAs}_{1-x}\text{P}_x$ layers in this case is dynamically controlled rather than controlled by equilibrium reactions. The deposition rate is then less temperature-dependent, and higher growth rates should be achievable. This reaction source is similar to silane, SiH_4 , used in the epitaxial growth of silicon.

The substrate placement in the reactor is an important aspect of the reactor design itself since the velocity distribution for gases flowing over the substrate controls the uniformity of the growth rate, and this is influenced by the direction of flow. The flow properties of the gases and the geometry of the system also affect the growth rate uniformity.

Reactor Design

There are numerous problems associated with an optimal design for $\text{GaAs}_{1-x}\text{P}_x$ chemical vapor deposition reactors. The reactor which is used with the commonly used chloride transport reactor utilizing gallium metal and HCl gas must have (i) an HCl - Ga₍₁₎ contactor, or saturator, where volatile gallium chlorides are generated, (ii) a deposition zone containing the substrates, and (iii) a connecting mixing zone where dissociation reactions can take place.

It has been found that gallium metal is the best starting source for gallium transport since it is available in ultra-high purity grades. Recent works has shown, however, that organometallic compounds such as $\text{Ga}(\text{CH}_3)_3$ are becoming available in high purity grades.

The starting materials most commonly used for arsenic and phosphorus are their hydrides, AsH_3 and PH_3 , or their chlorides, AsCl_3 and PCl_3 which are gases and liquids, respectively, at room temperature.

Horizontal and Vertical Reactors

Both horizontal and vertical reactors have been used in GaAs, GaP, and $\text{GaAs}_{1-x}\text{P}_x$ deposition processes. The vertical reactor was used by Goettler⁽⁴¹⁾ in 1970. It has advantages over the horizontal type in that the gases used in the growth process using group V halides and HCl/H₂ over liquid gallium are carried by hydrogen which is a very light gas. The typical flow regime in the reactor is laminar which means that mixing is slow. The gases which

take part in the deposition equilibrium i.e., GaCl , GaCl_3 , HCl , As_4 , As_2 , P_4 and P_2 in the Ga-As-P-H-Cl system are much heavier. Therefore, in a gravitational field the reactants will tend to concentrate on the bottom wall if the reactor is of a horizontal type. This will give rise to an uneven concentration distribution and poor uniformity of the reaction. In the vertical type reactor, the heavy gases can be more easily directed toward the substrates. Of course, turbulent mixing of transport gases can improve gas uniformity of either type.

Another disadvantage of horizontal flow reactor is that the gases will tend to create backflow due to any difference in temperature between the top wall and substrate whereas in the vertical reactor, this effect is negligible. Therefore it is suggested that a vertical reactor is better than a horizontal type for growth of $\text{GaAs}_{1-x}\text{P}_x$ using metallic gallium as a source.

Source Compounds for Arsenic and Phosphorous

The two preferred source compounds for arsenic (or phosphorous) are AsCl_3 (PCl_3) and AsH_3 (PH_3) . As was seen in the survey of previous reactors the chloride normally is passed over gallium to obtain GaCl and GaCl_3 . The combined gases are then transported to the substrate for deposition. The reaction of the chloride on gallium surfaces is not controllable precisely, because GaAs or GaP is formed on the surface of the liquid gallium. The rate of formation of surface coating is unknown and a good control of deposition reactions is not possible. On the other hand the hydride decomposes to arsenic and

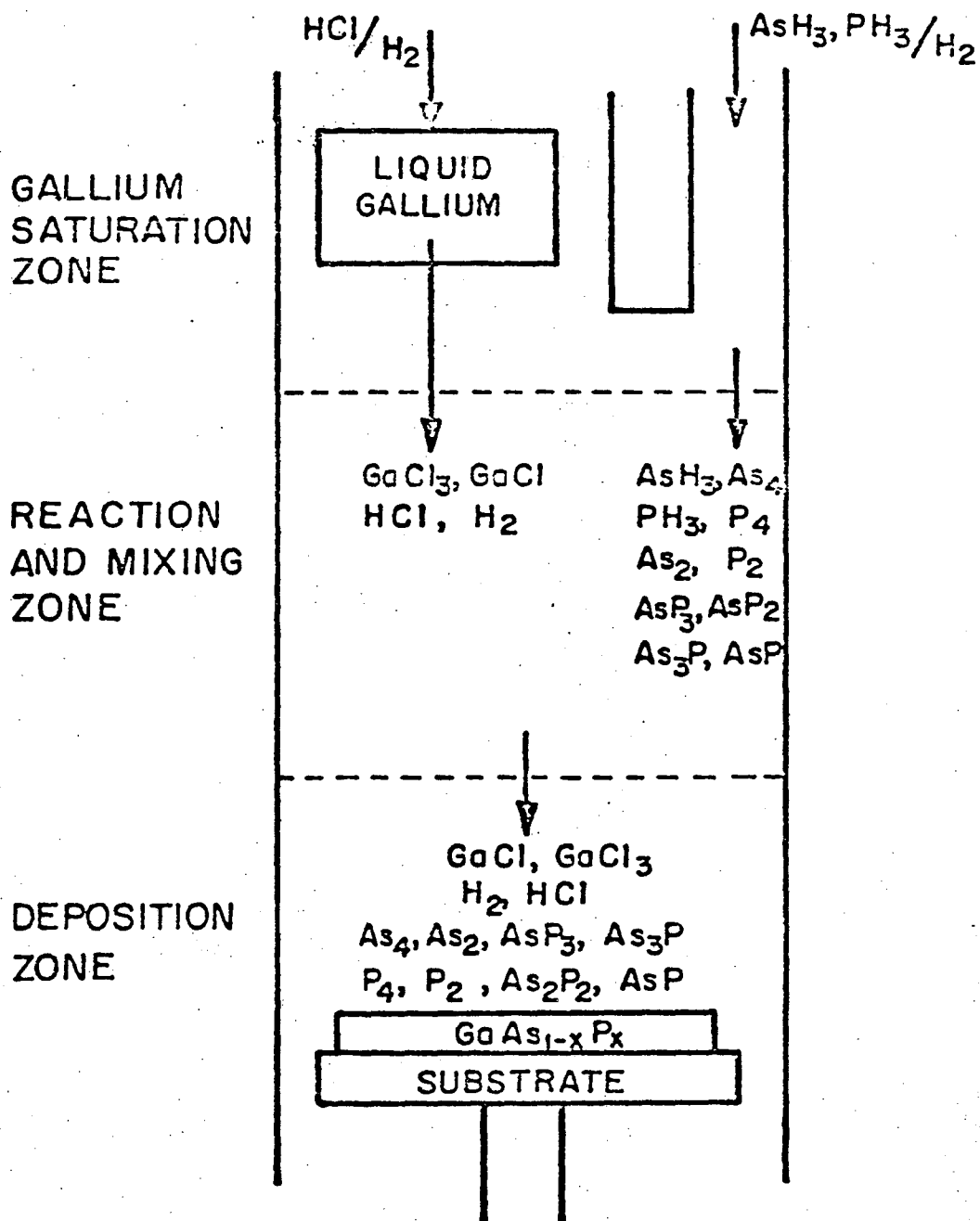
phosphorous and reacts with gallium only on the surface of the substrate. The decomposition of the hydride is almost complete⁽⁴³⁾ at high temperature (~900°C). So the arsenic or phosphorous in the elemental form reacts with the major species, GaCl, on the surface of the substrate.

Another reason for preference for the hydride over the chloride is that the chloride is in liquid form at standard temperature and pressure, and must be volatilized to be introduced into the reactor. For the hydride no such problem exists because it is already in gaseous form and can be easily metered through a metering valve and flowmeter.

Therefore, the hydrides (AsH₃ and PH₃) are preferred as starting materials over other types. This choice is supported by the increased purity and availability of arsine and phosphine for electronics materials applications. The hydride reactor is shown schematically in Fig. 2.

Gallium Saturator

In all of the recent reactor designs, HCl has been used in the chlorination of gallium. This is partially due to the fact that HCl is found in the gaseous form. Another reason is that it reacts almost completely with the gallium to form volatile GaCl. The main problem in design of the saturator is to assure good contact of HCl with gallium to achieve equilibrium in the saturator. Although the problem involves simultaneous mass transfer and chemical reaction, it has not been studied in detail. Ban⁽⁴²⁾ shows that about 80% of HCl is converted to GaCl at 850°C by HCl gas flowing over an open gallium boat. Goettler⁽⁴¹⁾ achieved essentially complete equilibrium in a



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Figure 2. Schematic of the vertical Ga₍₁₎-HCl-AsH₃-PH₃-H₂ reactor showing major chemical species in each reaction zone.

toroidal saturator. Thermodynamic equilibria suggests that 99.9% HCl should be converted to GaCl at 850°C⁽²⁹⁾.

In order to approach equilibrium at the gallium contactor the HCl should have sufficient contact time to equilibrate. The gallium contactor can be of three types:

- (1) HCl/H₂ gas flowing over the liquid gallium in laminar flow,
- (2) gas impinging on liquid gallium in turbulent flow, or
- (3) gas bubbling through liquid gallium.

The third process is the most efficient means of mass transfer of the three types.

For a gas bubbler, the gas bubbles should be reduced to small sizes by passing them through a jet or dispenser to increase the surface area for reaction and hence the conversion efficiently. The reactor designed by Goettler⁽⁴¹⁾ uses such a liquid gallium bubbler.

Mixing of Gases

Before the gases reach the substrate for deposition, they should be well mixed and given a uniform velocity profile. Therefore a mixing region is necessary after the gallium saturator zone where arsenic and phosphorous in the elemental form can mix with the effluent stream from the gallium boat. In this region nearly complete decomposition of AsH₃ and PH₃ also takes place. Therefore the gases should have a sufficient residence time here. These objectives may be achieved by increasing turbulence in a mixing region and by restricting the flow to the deposition zone. Mixing can be done by providing a nozzle or

orifice in the reactor between the gallium saturation and deposition zone. To make the flow of gases over the substrate as uniform as possible, however, the gases should be allowed to flow through a calming length in the reactor.

Substrate Orientation

For a uniform deposition thickness over a substrate which is required for electronic grade materials, the gases should have a uniform composition and they should contact the substrate with uniform velocities. But due to the diffusion controlled kinetics at high temperatures a boundary layer is formed over the substrate by the incoming gases. The thickness of the boundary layer may vary from one part to another; which in turn affects the deposition rate uniformity. This problem can be decreased by a proper positioning of the substrate. For flow parallel to the flow direction of the gases, the laminar boundary layer will increase in thickness from the point where gases first reach the substrate throughout the length of the substrate. Temperature variations along the substrate will also affect the rate of reaction. For flow normal to the substrate, the boundary layer thickness will decrease towards the edges of the substrate, and the nonuniformity of the layer will cause a nonuniform growth. When flow is at an angle to the substrate, the boundary layer will have a structure between the two above cases. This positioning has been used in many recent studies.

In some research reactors and in commercial reactors, the substrate is rotated and because of the slight turbulence caused by the rotation, the boundary layer becomes more uniform. A complete solution of this

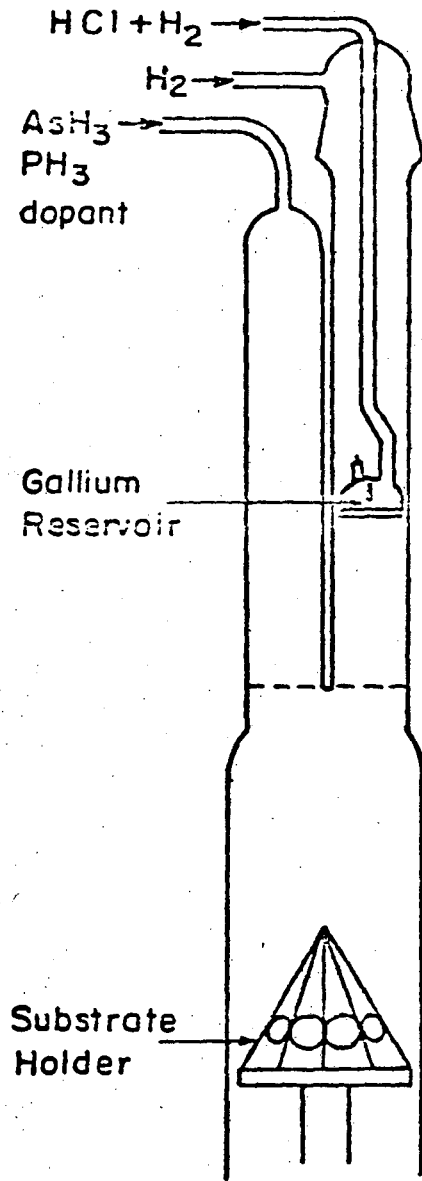
problem is not yet found. The best arrangement seems to be the rotation of the substrate at an angle to the flow of the gases.

Commerical Applications

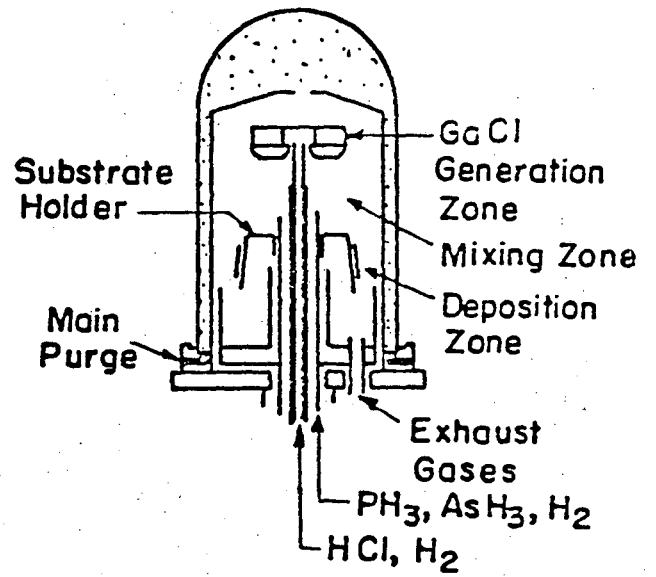
Development of commercial reactors for CVD of $\text{GaAs}_{1-x}\text{P}_x$ has been reported by Ruherwein⁽⁴⁴⁾ and by Pelser and Benzing⁽⁴⁵⁾.

The Monsanto Research Corporation has carried out an extensive study of the manufacturing methods for epitaxial growth of GaAs, GaP and $\text{GaAs}_{1-x}\text{P}_x$, including the study of various reactor designs. They used both horizontal and vertical reactors employing PH_3 , AsH_3 , PCl_3 , AsCl_3 , HCl and Ga(l) in this process. Both turbulent and laminar flows of reactant gases across the substrate were explored. Their study showed that a vertical reactor with laminar gas flow is best suited for the growth of GaAs or GaP (or $\text{GaAs}_{1-x}\text{P}_x$) by chemical vapor deposition.

The Mansanto study included the design of gallium-HCl contactors and substrate holders, employing various designs for flowing HCl - H_2 gases over liquid gallium, gases impinging on gallium through a jet, or bubbling through gallium. They found that a bubbler is best suited for maximum efficiencies of conversion but that a cover over the gallium container is required in order to keep gallium from spilling out of the container. Their design of the gallium saturator is shown in Fig. 3(a). This study concluded that a rotating pyramid substrate holder (5-40 rpm) produces the best boundary layer conditions for a uniform deposition. The gases flow oblique to the substrate and the



a. Monsanto Reactor



b. AMT Reactor

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Figure 3. Industrial reactors for the epitaxial deposition of $GaAs_{1-x}P_x$ layers on GaAs substrates.

boundary layer is compressed in the middle, becoming more uniform. The rotation speed of the substrate holder can be varied according to the deposition desired. The schematic of the pyramidal substrate holder is also shown in Fig. 2(a). The pyramid has eight sides and can hold up to 16 substrates. Additional HCl gas can be introduced to prevent deposition on reactor walls. Extensive data have also been published for diverse conditions of growth. Other commercial reactors which are still proprietary utilize basically the same reactor design with slight variations, mostly in the positioning of the substrates.

The $\text{GaAs}_{1-x}\text{P}_x$ reactor developed by Applied Materials Technology is shown in Fig. 3(b).

The most radical advantage of this reactor over the others is that it utilizes RF induction heating instead of resistance heating. RF induction heating and water cooling allow a reduction in batch cycle time and therefore, handling and operateability becomes much easier. Another big advantage of this reactor is that between the runs only one seal is broken to load and unload the substrates. Other features of the Pelser-Benzing reactor include a purge under the substrate holder and along the reactor walls to prevent undesirable deposition there. Also, the substrate holder rotates at a slow speed which creates a uniform boundary layer over the 32 substrates.

The gallium saturator design is similar to the Monsanto reactor and radial and linear mixing is achieved on the surface of the gallium by restricting the flow radially.

New Developments

Chemical compound reagents which are highly volatile have a definite advantage over liquid and solid sources reagents. In the existing technology both arsenic and phosphene sources are in the vapor form. Saitoh⁽²⁶⁾ has shown that $\text{Ga}(\text{CH}_3)_3$ can be used successfully to deposit epitaxial $\text{GaAs}_{1-x}\text{P}_x$.

Epitaxial growth of GaAs from trimethyl gallium (TMG) using the $\text{TMG-AsH}_3\text{-H}_2$ system on GaAs substrates of (100) orientation and on sapphire of (0001) orientation was recently studied by Manasevit⁽⁴⁶⁾ and Rai-Choudhury^(47,48). Layers were grown at 700°C with TMG and AsH_3 partial pressures of 6.5×10^{-4} and 1.2×10^{-2} , respectively. The growth rate varied from 0.11 to 0.69 $\mu\text{m}/\text{min}$ depending on gas velocities over the substrate. The epitaxial orientation relationship with sapphire substrates were $(111)\text{GaAs} \parallel (0001)\text{H}_2\text{O}_3$ and $[\bar{1}\bar{1}0]\text{GaAs} \parallel [11\bar{2}0]\text{H}_2\text{O}_3$. Transmission electron microscopy examination of the epitaxial layers shown them to be comparable to those grown from the $\text{Ga-HCl-AsCl}_3\text{-H}_2$ system.

The advantage of $\text{Ga}(\text{CH}_3)_3$ over metallic gallium is that it dissociates almost completely on the surface of the substrate. The achievable growth rates are therefore much higher than those using the GaCl transport. Also the effect of temperature on growth rates is almost negligible.

Since $\text{Ga}(\text{CH}_3)_3$ is a liquid at room temperature, H_2 is bubbled thru it, becoming saturated with $\text{Ga}(\text{CH}_3)_3$. Hence the flow of $\text{Ga}(\text{CH}_3)_3$ to the reactor can be easily controlled by changing the bubbler temperature.

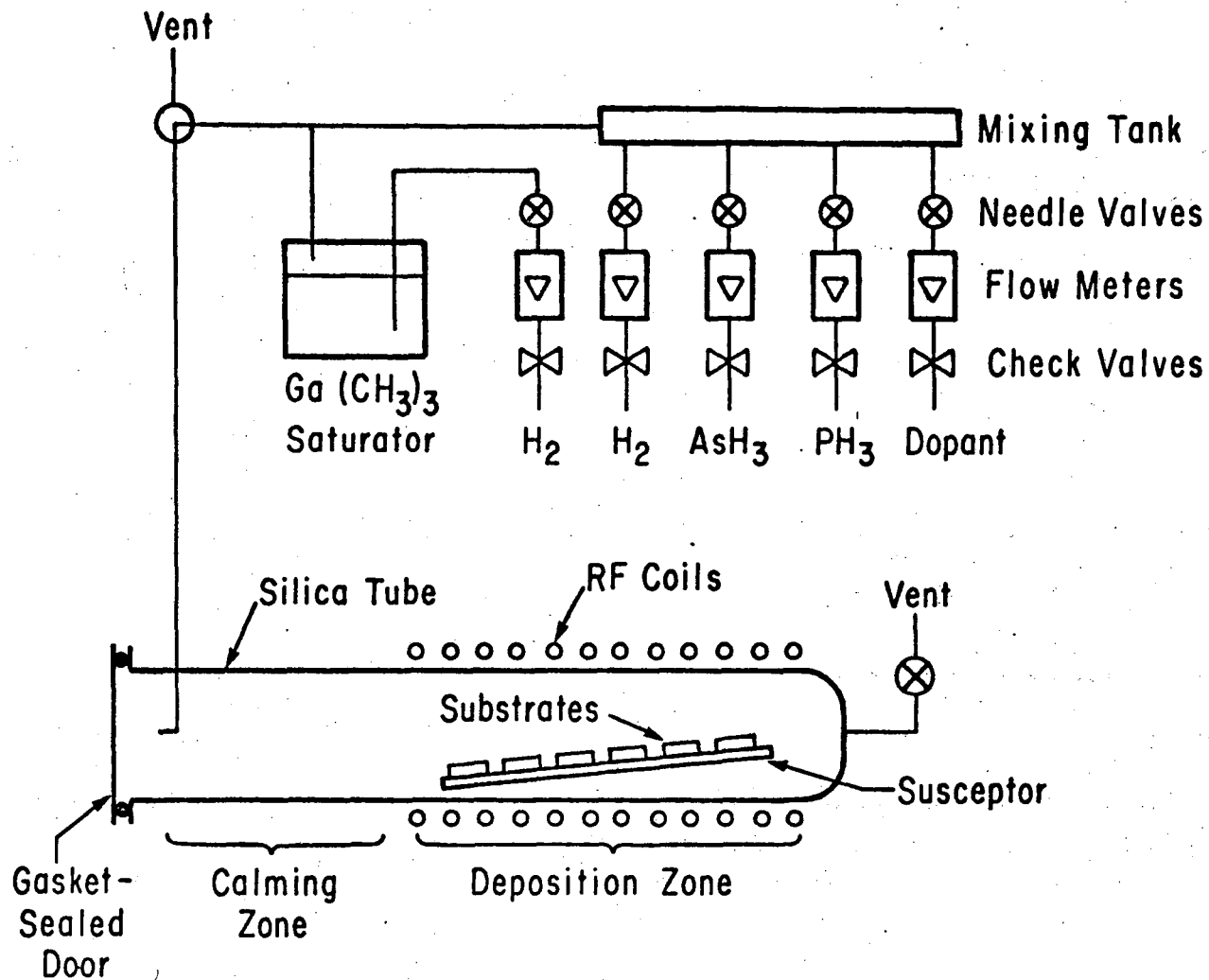
A schematic of the reactor which can be used for $\text{GaAs}_{1-x}\text{P}_x$ epitaxial growth is shown in Figure 4. This reactor is very similar to the existing silicon epitaxy reactors. A graphite susceptor is heated by RF induction heating and substrates are placed on the susceptor. The gases enter at one end of the reactor and the deposition takes place thru a laminar boundary layer which is inclined slightly to flatten the boundary layer profile.

Eversteijn and Peek⁽⁴⁹⁾ have considered the design of a similar reactor for silicon. They found that placing the susceptor at angle ϕ is better than placing it horizontally due to mass transfer limitations. The exact value of ϕ depends on the particulate system. Saitoh⁽²⁾ used a value of $\phi_0 = 20^\circ$. They also showed that the growth rate goes thru a minimum for the maximum free height above the susceptor b and this minimum value increases with a decrease in the value of ϕ .

Since the $\text{GaAs}_{1-x}\text{P}_x$ deposition system is much more complex due to the number of reacting species present and their equilibria, all the assumptions for a silicon reactor may not hold and a further study is needed to investigate this reactor design in detail for $\text{GaAs}_{1-x}\text{P}_x$ deposition.

Conclusion

Reactor designs for chemical vapor deposition of $\text{GaAs}_{1-x}\text{P}_x$ have been explored extensively in recent years. Reactors using chlorine transport method are fairly well understood and their technology is highly developed. Nevertheless, the search is still continuing for



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Figure 4. Cold-wall reactor for epitaxial deposition of $\text{GaAs}_{1-x}\text{P}_x$ from $\text{Ga}(\text{CH}_3)_3$, AsH_3 and PH_3 in H_2 .

better designs in order to achieve better yield and growth rate uniformity, easier handling and operation. Organometallic gallium compounds, mainly $\text{Ga}(\text{CH}_3)_3$ are significantly suitable as gallium source reagents. The reactor design based on these sources is relatively simple. Also, much higher growth rates can be achieved through due consideration of the basic transport principles involved. Some thermodynamic data is still lacking for the organogallium compounds, however, and additional study is needed in that area.

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