LIQUID AND VAPOR PHASE GROWTH OF III-V MATERIALS FOR PHOTONIC DEVICES

W. Dexter Johnston, Jr., Michael A. DiGiuseppe, and Daniel P. Wilt

W. Dexter Johnston, Jr., Michael A. DiGiuseppe, *and* ***Daniel P. Wilt*** *are with AT&T Bell Laboratories, Murray Hill, New Jersey. Mr. Johnston is supervisor of the Solid State Materials Group in the Lightwave Devices Laboratory. He is responsible for development of chemical vapor deposition processes for epitaxial growth of laser and light-emitting diode materials. He received a Ph.D. in atomic and molecular physics from Massachusetts Institute of Technology. He joined AT&T in 1966. Mr. DiGiuseppe is a supervisor in the Lightwave Devices and Materials Department. His group works on epitaxial processes for growth of III-V alloys for application in optoelectronic systems. He has a B.S. in chemistry from Brooklyn Polytechnic Institute and a Ph.D. in solid-state chemistry from Brown University. He joined AT&T in* (continued on page 63)

Precisely controlled epitaxial growth of microscopically thin semiconductor layers is essential for lightwave source and detector components. Achieving precise control while simultaneously meeting manufacturing volume and cost requirements is a demanding challenge. We are meeting that challenge with the development of advanced liquid and vapor phase epitaxial growth technologies. In this article we provide a review of the principles, a brief description of the state-of-the-art implementation, and a discussion of the advantages and limitations of the four epitaxial techniques we use—liquid phase epitaxy, trichloride and hydride vapor phase epitaxy, and metal-organic chemical vapor deposition epitaxy.

Introduction

The term *heteroepitaxial growth* refers to the deposition of a crystalline layer of one material on a crystalline (substrate) wafer of another. For photonic devices operating at 1.3 or 1.55 micrometers (μm), the substrate of choice is indium phosphide (InP), which permits heteroepitaxial layers of indium gallium arsenide phosphide, $In_{1-x}Ga_xAs_yP_{1-y}$, to be used. For $0 \leq x \leq 0.47$ and $0 \leq y \leq 1$, compositions of this alloy exist that (1) have the same crystal structure and interatomic spacing (lattice constant) as InP and (2) will emit light at any chosen wavelength between 0.9 and 1.6 mm. It is important that the lattice constants of the epitaxial layers be matched closely to each other and to the substrate (typically within 0.1 percent) to avoid strain at the interfaces between the substrate and the epitaxial layers. Such strain leads to device degradation during operation and reduced operational lifetimes for lasers and light-emitting diodes (LEDs).

J. E Clemans et al. describe the preparation and properties of InP substrates in another paper in this issue.[1] As they indicate, InP and phosphorus-containing semiconductor alloys in general tend to decompose, with loss of phosphorus, at elevated temperatures. This requires that epitaxial growth occur from a medium—either gas or liquid—

Panel 1. Acronyms and Abbreviations in This Paper

As	arsenic
Cl	chlorine
CONCEPS-CC	a process control system
CVD	chemical vapor deposition
Fe	iron
Ga	gallium
H	hydrogen
In	indium
LED	light-emitting diode
LPE	liquid phase epitaxy
MBE	molecular-beam epitaxy
MOCVD	metal-organic chemical vapor deposition
Nd:YAG	neodymium—yttrium aluminum garnet
O	oxygen
P	phosphorus
p-i-n	p-type–intrinsic–n-type semiconductor structure
pn	p-type–n-type semiconductor structure
S	sulfur
Sn	tin
Zn	zinc

containing sufficient phosphorus to prevent decomposition. In liquid phase epitaxy, growth occurs by precipitation from a liquid metal solution saturated in phosphorus (and the other alloy constituents) so that decomposition is prevented. In chemical vapor deposition epitaxy, growth occurs from a gaseous nutrient that can be adjusted to contain a suitable overpressure of phosphorus vapor. Thus, these techniques have found favor and are used extensively for the epitaxial growth of InGaAsP compositions.

Liquid Phase Epitaxy

Liquid phase epitaxial growth systems are designed to deposit precisely controlled single-crystal epitaxial layers from supersaturated metal-rich liquid melts onto single-crystal subtrates. The liquid-solid phase equilibrium between the liquid metal melt with mole fractions X_{In}, X_{Ga}, X_{As}, and X_P and the solid $In_{1-x}Ga_xAs_yP_{1-y}$ at the growth temperature (typically 630°C) is determined by the phase diagram, as shown in Figure 1. For the sake of simplicity, the figure shows the liquid-solid phase equilibrium for the binary alloy InP.

To grow solid InP from the In-rich liquid, a melt is prepared and heated so that its temperature and composition correspond to a point in the phase diagram that is near but below the solid-liquid phase boundary, on the In-rich side of the phase diagram. The difference between the liquid composition and the phase boundary is the supersaturation of the liquid. When this solution is brought into contact with the substrate, the excess solute (in this case P) begins to diffuse to the substrate surface and to deposit as a solid (in this case InP). Similar reactions occur when the solid InGaAsP is grown from liquid, except that the three minority components of the liquid (Ga, As, P) must diffuse to the solid interface to deposit material. For liquid phase epitaxy, it is most common to use group-III-rich liquids, since they have much lower vapor pressure than group-V-rich liquids. It is also true that, for InGaAsP, the dominant component of all liquid melts is In.

As shown in Figure 2, the typical InGaAsP liquid phase growth system consists of:

- A quartz reactor vessel through which an inert or reducing ambient gas (typically H_2) flows
- A surrounding furnace, which provides a growth region of controlled and uniform temperature
- A boat, which holds the liquid melts and has a sliding mechanism for moving the substrate from melt to melt to grow layers in the sequence desired.[2,3]

The high-purity inert or reducing gas ambient ensures an atomically clean surface on the substrate crystal and aids in removing surface oxides and wetting the surface with the liquid melts. Precise temperature measurement and control in the growth region (within 0.1°C) is required to ensure the proper supersaturation of the growth melts

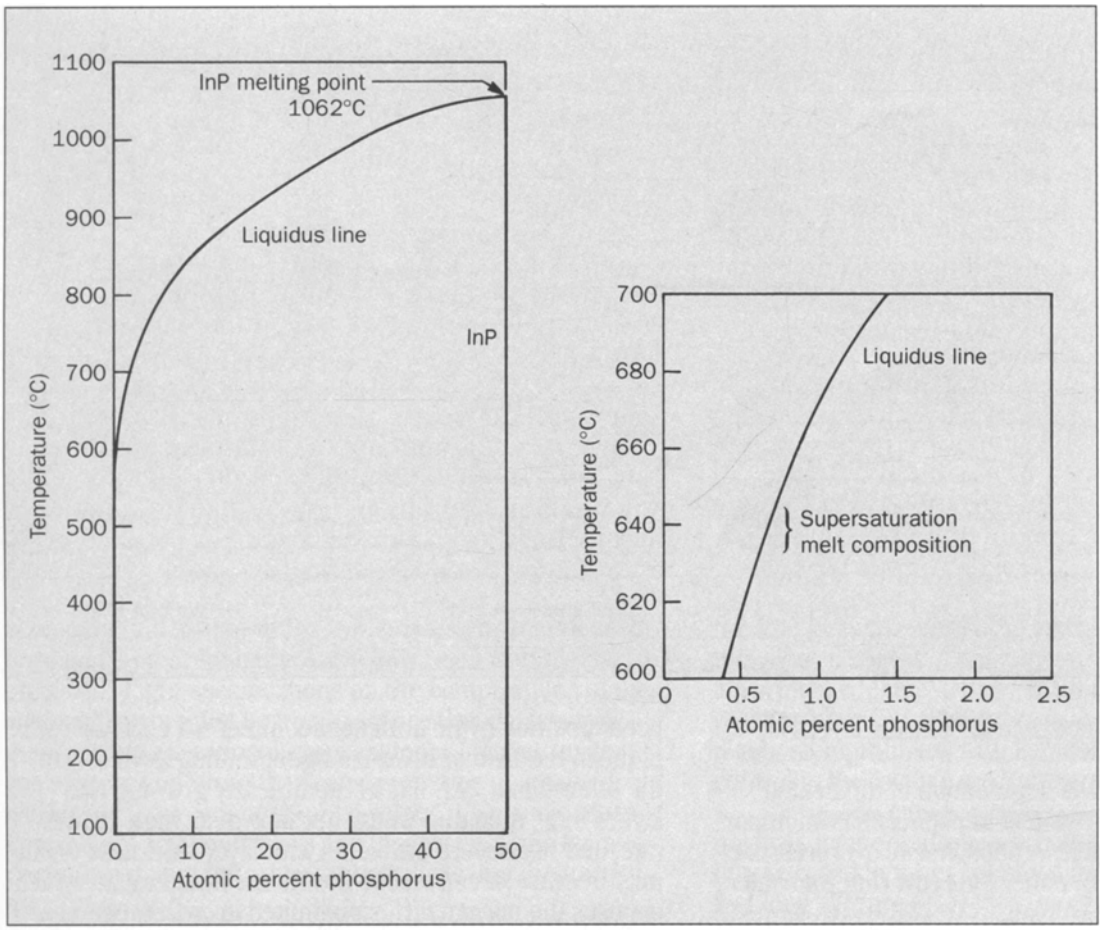

Figure 1. Liquid phase growth of indium phosphide.

and, for lattice matching and emitting the required wavelength, the composition of the grown alloy.

Finally, the sliding mechanism must be able to push the substrate wafer into contact with the liquid melts at precisely the proper times and temperatures to grow the crystal layers with thicknesses and properties appropriate for the desired semiconductor device. For this purpose, we find it advantageous in growing advanced lightwave devices to have computer-automated apparatus to control gas flow, epitaxial cycle times, push speeds and distances, and temperature.

In practice, liquid phase epitaxy (LPE) is usually performed in two cycles. In the first cycle, liquid indium is loaded into the reactor and baked at a high temperature (e.g., 720°C) for several hours to drive off impurities. The other melt components (which have been precisely weighed) and substrate are then loaded and the reactor is maintained at a lower temperature (e.g., 660°C) to homogenize the melts. Finally, the temperature is reduced to the desired growth temperature (e.g.,

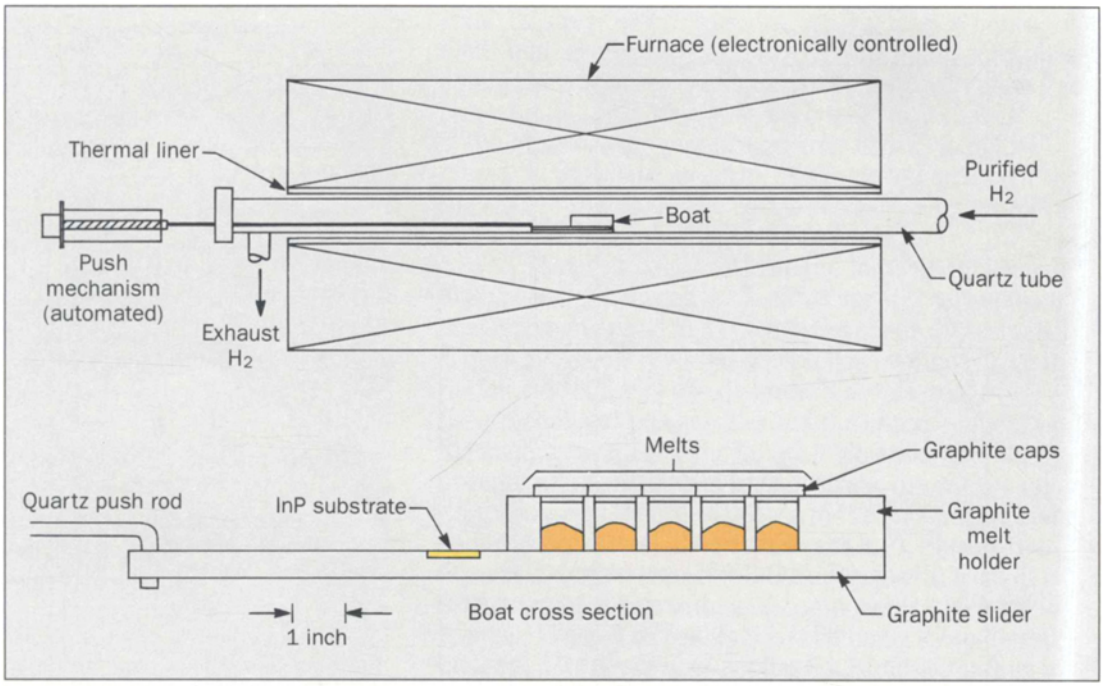

Figure 2. LPE growth furnace and boat schematic.

630°C) and the desired sequence of epitaxial layers is then grown.

Preventing surface degradation of the heated substrate through evaporation of phosphorus is an important aspect of the LPE cycle. A phosphorus overpressure is supplied to prevent this, either by a covering InP wafer or an InP-saturated tin (Sn) melt.

In contrast to vapor phase epitaxial techniques, the liquid phase technique offers some unique advantages and disadvantages to the device designer. An LPE reactor is usually simpler and can easily produce efficient light-emitting material (i.e., material with long minority-carrier lifetime). LPE also has the advantage that the alloy composition is determined by precisely weighing melt components and establishing growth temperature, both highly reproducible tasks, as opposed to precisely controlling the numerous gas flows required for vapor phase processes. For these reasons, LPE has been historically the dominant commercial epitaxial technique in the field of InGaAsP light-emitting devices. On the other hand, LPE has great difficulty growing thin layers (e.g., quantum wells) because of its high growth rate, and has severe problems with layer thickness uniformity because of convective flow in the liquid melts, which opposes the normal diffusion-limited growth processes.

Finally, since the LPE growth technique involves wiping liquids on and off the crystal surface, the morphology of LPE-grown wafers often leaves a great deal to be desired. Surfaces are rarely uniformly flat and smooth. This interferes with subsequent processing and reduces yields to levels that pose serious problems for large-scale production.

Chemical Vapor Deposition Epitaxy

The process variants in the chemical vapor deposition (CVD) category differ in the specifics of their

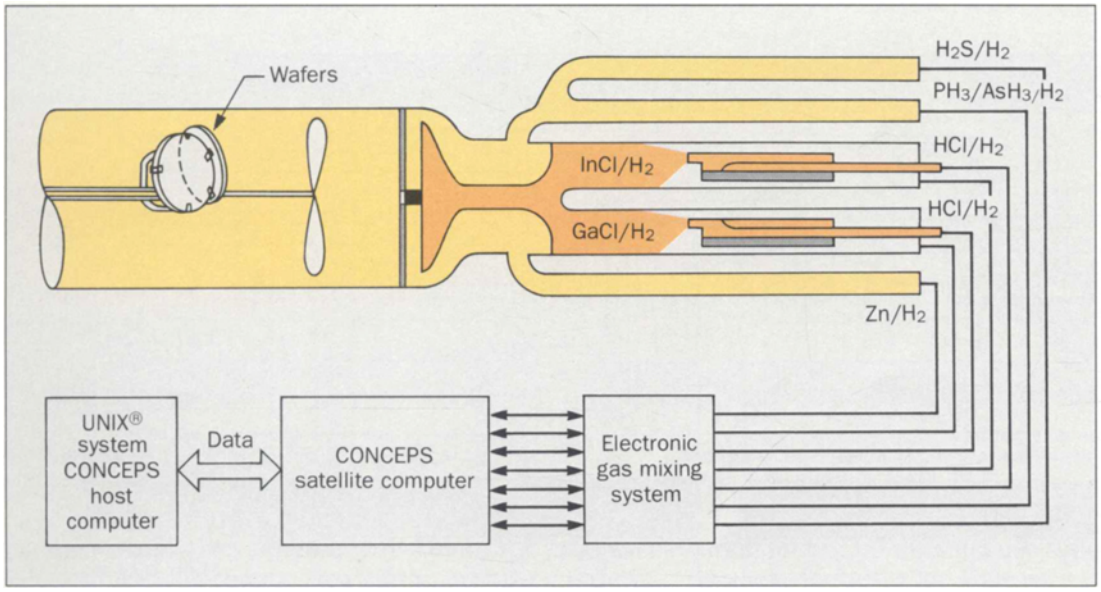

Figure 3. Hydride CVD reactor schematic.

chemistry, but share similar system designs that depend on controlling gas mixtures and flow rates with high precision. Tight specifications on the compositions of the epitaxial layers must be met to assure that devices will meet system operational specifications. This means that gas mixtures entering the reactor must be maintained within 1 to 2 percent of nominal values. Electronic mass-flow meters and controllers and, generally, some form of computer system for process control provide the necessary precision.

We have found CONCEPS-CC, a real-time multitasking host/satellite process control system[4] based on the UNIX® operating system, to be particularly advantageous for the most complicated CVD process development. With it, multiple processes can be controlled "simultaneously" in the satellite computer and an operator can monitor processes and modify recipes in real time from a console.

CVD processes take place in a transparent quartz reactor vessel. Optical techniques therefore can be used to monitor the reactant species and concentrations actually present in the gas phase at the surface of the substrate wafer during growth. A simple ultraviolet absorption scheme[5] yields data for understanding the reaction chemistry, for process development, and for diagnosing problems with technology transfer or quality control in the factory environment.

Hydride Chemical Vapor Deposition. Hydride CVD is a hot-wall, near-equilibrium process that takes place in a quartz reaction tube typically 4 inches in diameter and 5 feet long (Figure 3). Hydrogen chloride (HCl), arsine (AsH_3), and phosphine (PH_3) gases are introduced at low partial pressures in a hydrogen carrier. (The name of the process comes from arsine and phosphine, which are hydrides.) The HCl reacts with metallic Ga and In sources (at about 700°C) to form volatile chlorides. The metal chlorides flow in the vapor phase to a mixing region (at 800°C), where they combine with the arsenic and phosphorus vapors that form when the arsine and phosphine thermally decompose as they pass into the furnace. This mixture flows onto a polished substrate wafer of InP held at 700°C, and a quaternary layer of $In_{1-x}Ga_xAs_yP_{1-y}$ grows.

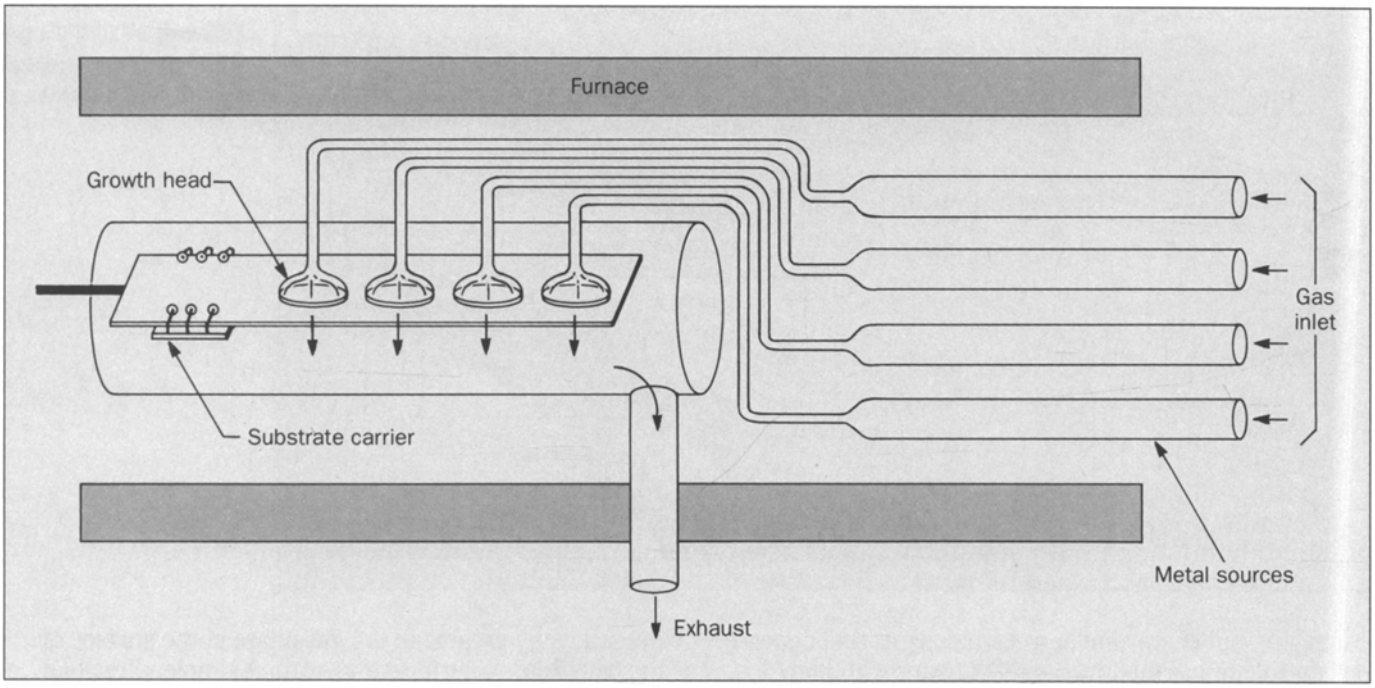

Figure 4. Multichamber hydride reactor schematic.

The mole fraction x of Ga in the epitaxial layer is determined to first order by the ratio of GaCl to InCl in the gas phase. The mole fraction y of As is similarly determined by the ratio of As to P species in the gas phase. The mole partial pressure of reactants affects the growth rate, and the ratio of metal species to group V species affects the surface quality and level of residual electronic donors in the material. The flow velocity of the total gas stream is an important determinant of the uniformity of layer composition and thickness, particularly as substrate size is increased or multiple substrates are introduced.

Because the reactions involved in this growth are reversible, controlled etching as well as growth is possible. Conditions can be continuously varied to yield growth rates ranging from positive to negative, so that small growth rates may be established when very thin layers are required or high rates selected for thick structures.

State-of-the-art hydride reactors of the type shown in Figure 3 are used for laser and LED wafer growth on two 2-inch-diameter wafers per run. The reactors can handle several runs per day. A more complex hydride reactor is shown schematically in Figure 4. This is intended for exploratory development of advanced photonic device structures requiring multiple ultrathin (quantum-well) layers. This multichamber reactor allows alternate layers of differing doping or composition to be grown by translating the substrate from one growth head to another, much as in LPE, instead of by moving the substrate to a holding position, changing the gas flows, and reinserting the substrate into the growth zone. Using a reactor of this type, we have demonstrated atomically per-

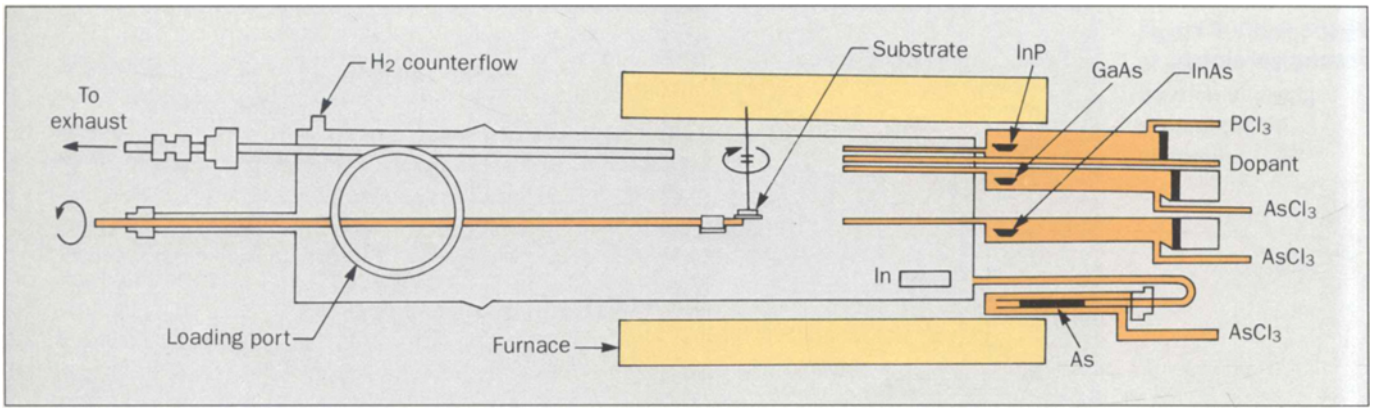

Figure 5. Trichloride chemical vapor deposition system for growing high-purity III-V materials.

fect interfaces comparable to those obtained by molecular-beam epitaxy (MBE) techniques.

In the hydride CVD process, reactant species can be controlled and adjusted in real time. The process therefore offers maximum flexibility in growing a variety of device structures. The principal disadvantage of the process is that it needs toxic and reactive compressed gas sources. The gas cylinders must be made of pressure-tested steel and are a source of contamination. As a result, typically 3 to 5×10^{15} electrically active impurity atoms per cubic centimeter are found in hydride-grown material. HCl gas is highly reactive and corrosive in any but strictly anhydrous environments, and arsine and phosphine are thermally unstable and highly toxic. The need for frequent cylinder changes requires special procedures and monitoring equipment to assure worker safety and process integrity. Accordingly, possible liquid chemical alternatives are being investigated. Candidates include alkyl arsenides, phosphides, and chlorides, which are generally much less toxic and are far more convenient to handle.

Trichloride Chemical Vapor Deposition. The trichloride CVD growth technique is also a hot-wall near-equilibrium process that takes place in a quartz reactor tube of similar dimensions to that used in the hydride process (Figure 5). However, unlike the hydride technique, trichloride CVD does not use arsine and phosphine as sources for the group V elements. Instead, arsenic and phosphorus are introduced into the reactor at low partial pressure in a hydrogen carrier from very high purity liquid arsenic trichloride $AsCl_3$ and phosphorus trichloride PCl_3 sources. High-purity hydrogen chloride is synthesized *in situ* by heating $AsCl_3$ in hydrogen and removing the condensed arsenic solid. The HCl reacts, as in the hydride process, with metallic indium to form the volatile chloride. $AsCl_3$ and PCl_3 react with solid GaAs or InP to produce gallium or indium chloride along with arsenic or phosphorus allotropes.[5] Growth process reactions are reversible, and controlled *in-situ* etching of the substrate plays a major role in the production of high-quality epitaxial layers with abrupt interfaces.

A significant advantage of the trichloride process is its ability to produce routinely high-purity InP and InGaAs epitaxial layers with very low free-carrier concentration and high electron mobilities. Impurity incorporation and growth rate are influenced by the group V trichloride mole fraction, the V to III ratio, and the temperature of the sources. Under ideal reactor conditions, InP layers with residual impurity doping levels below

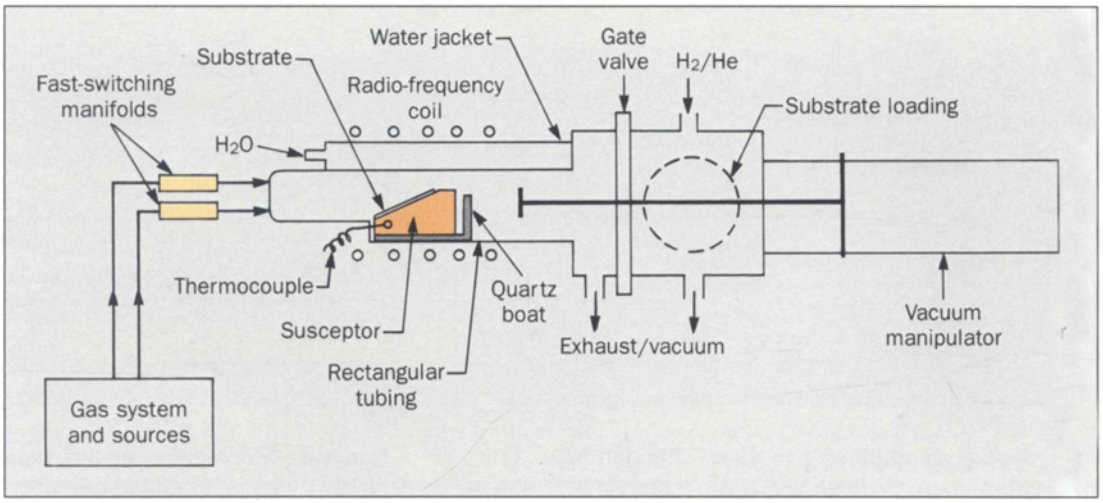

Figure 6. MOCVD reactor schematic.

1×10^{13} cm^{-3} have been produced.[7]

60

Trichloride reactors similar to that illustrated in Figure 5 are used to make heterostructures on 50-millimeter-diameter InP substrates, from which high-performance photodetectors for 1.3- and 1.55-μm optical communications systems are produced. Advanced reactor design is an important aspect of our materials development activities. The ability to grow heterostructures with high-electron-mobility epitaxial layers makes the trichloride process an attractive materials technology for high-speed InP-based electronic devices.[8,9] This ability could yield added performance from InP lightwave devices whose electronic circuits as well as sources and detectors are integrated on one chip.

Metal-Organic Chemical Vapor Deposition. In the metal-organic chemical vapor deposition (MOCVD) technique, metal alkyls are the sources of In and Ga. Although other compounds have been investigated, trimethyl indium [$(CH_3)_3In$] and trimethyl gallium [$(CH_3)_3Ga$] have come to be the preferred choices. The former is a waxy, clear solid at room temperature with a modest vapor pressure (2.0 torr at 22°C), while the latter is a volatile liquid. Trimethyl gallium freezes at –17°C and is usually used just above this point (–14°C, 18 torr) for quaternary growth.

Unlike the hydride and trichloride processes described above, the MOCVD process introduces a mixture of the metal alkyl vapors and arsine and phosphine gas, with a hydrogen carrier, into a cold-wall reactor vessel. The substrate is placed on a susceptor (typically graphite) and heated to the growth temperature—in the 600 to 650°C range—by infrared lamps or radio-frequency induction (see Figure 6). A pyrolytic reaction forms the InGaAsP layer. Since this reaction is nonreversible, control of the growth rate is limited, and *in-situ* etching of the substrate surface is not practical. This makes substrate surface preparation and cleaning particularly critical.

The group III alkyls and the group V hydrides can form undesired reaction compounds of the form $(CH_3)_3In$: AsH_3 in the gas stream. These interfere with the growth of the desired semiconductor alloy and must be avoided by minimizing the reaction time after mixing of the vapor streams. At the same time, mixing must be sufficient to promote uniform growth. The cold-wall/hot-susceptor combination produces convective eddy cells,

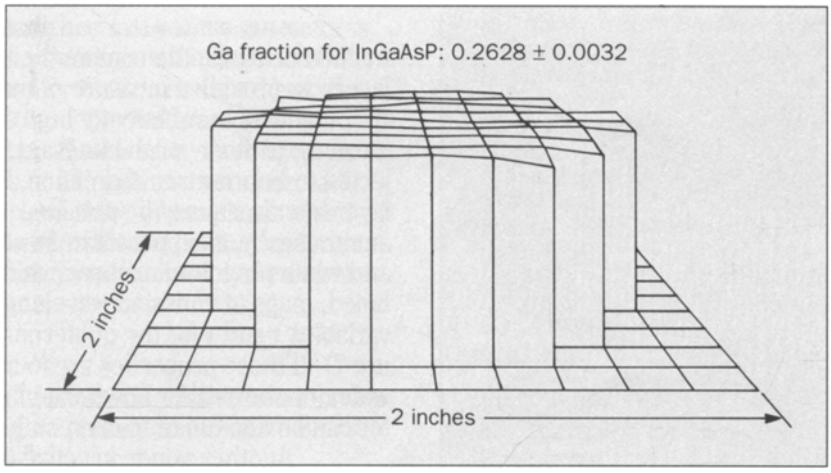

Figure 7. Wafer map of gallium mole fraction showing compositional uniformity.

particularly in vertical-flow reactors, which tend to make layers less uniform and interfaces less abrupt. Low-pressure operation (tens of torr or less) relieves these effects and is being adopted increasingly in spite of the increase in system complexity it necessitates.

A particular advantage of the MOCVD process is the ability to incorporate iron as a dopant in the growth of InP layers by using ferrocene,[10] an organo-iron compound with moderate room-temperature vapor pressure. Layers doped with iron (Fe) have resistivities exceeding 10^8 ohm-centimeters and can provide current isolation between devices or ensure current confinement to the active stripe of laser diodes, as described in the paper by N. K. Dutta in this issue.[11] The high-resistivity layer is an alternative to a reverse-biased pn junction structure for current isolation and has the advantage of lower parasitic capacitance, yielding higher-speed operation. The surface quality and interfacial abruptness of MOCVD-grown structures can be excellent, and, although the process is less well developed than the older hydride and trichloride processes, it is viewed today as holding the most promise for the future. In the low-pressure variation, it offers the versatility of the hydride system with purity levels approaching those obtained with trichloride CVD. Although the reason is not fully understood, the impurities residual in arsine appear to be less efficiently incorporated in the growing layer during low-pressure MOCVD growth than in atmospheric-pressure MOCVD or hydride growth.

Material Characterization and Quality Control

To assure high device yield, it is important to establish that the composition and thickness distributions across a wafer and from wafer to wafer are within specification. Tightening these distributions will increase the yield of satisfactory devices and therefore will reduce cost or enhance performance. We use a combination of photoluminescence spectroscopy and precision x-ray diffraction to determine the compositional uniformity of wafers, and have recently devised procedures to determine layer thicknesses nondestructively using x-ray diffraction as well as infrared reflectivity.

Photoluminescence. The wafer to be evaluated is excited by light from a Nd:YAG laser emitting at 1.06 μm. This wavelength corresponds to a higher photon energy than the bandgap of the active layers in 1.3- or 1.55-μm lightwave sources, but is lower in energy than the bandgap of the InP layers and substrate. Thus, the InP layers are optically transparent, and the active layers ab-

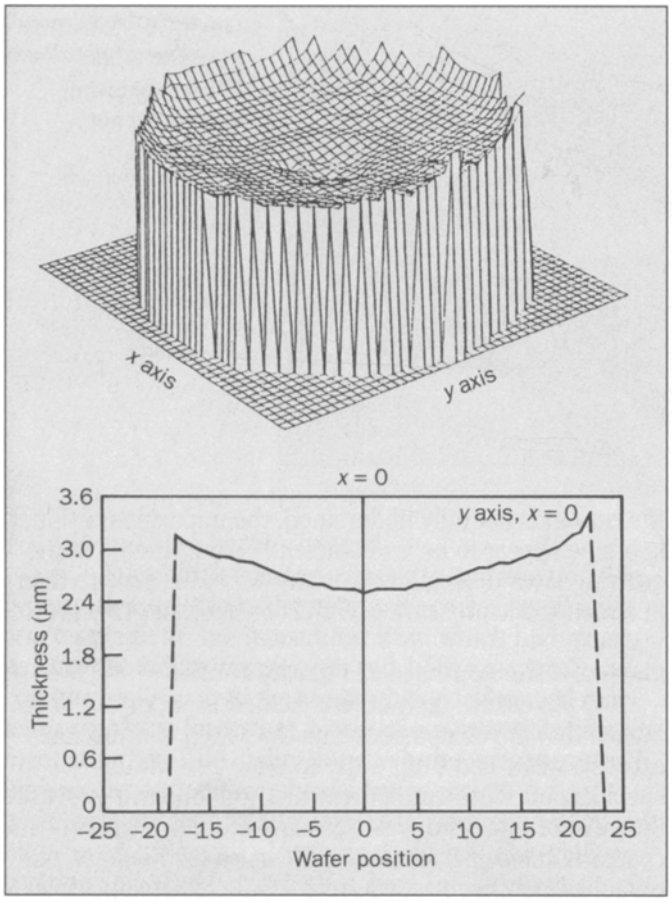

Figure 8. Infrared wafer map showing thickness uniformity.

sorb the 1.06-μm excitation light. Recombination radiation emitted from the active layers is analyzed and recorded with automated spectrometric apparatus. The emission peak provides an accurate measure of the bandgap of the active layer. An automated stepping stage maps the wafer; typically, it measures 65 points on a 2-inch-diameter wafer for characterization purposes, while five points suffice for quality control.

X-Ray Diffraction. Precision double-crystal x-ray diffraction is used to determine the lattice constants of the layers, to provide a measure of the crystalline quality, and (if the quality is sufficiently high) to derive an accurate measure of the layer thicknesses.[12] If the data are subjected to Fourier transformation, the distances between layer interfaces may be obtained. The wafer is scanned automatically, as in photoluminescence measurements, and when photoluminescence and x-ray data are combined, maps of emission wavelength and compositional variables x and y for the quaternaries may be plotted (Figure 7). If these properties are found to "taper" across the wafer, or show other flow-related nonuniformity, the reactor can be fine-tuned to correct the tendency.

Another nondestructive optical technique using near-infrared reflectance spectroscopy has been developed to determine epitaxial layer thickness in complex heterostructures. Multilayer interfaces produce a modulation of the spectrum that, when analyzed, yields layer thickness. The technique is sensitive enough to detect the small reflection at an InP homointerface across which the doping changes. Repeatable thickness measurement, accurate to 1 percent, can be achieved, as can automated wafer mapping (Figure 8).

Future Needs

Liquid phase epitaxy is well established and has provided the bulk of material for development and early manufacture of the source and detector devices used in modern lightwave systems. CVD epitaxial processes offer enhanced throughput, uniformity, (for the trichloride) very high purity, and (for MOVCD) Fe-doped InP confinement structures.

For the future, perhaps what is most needed is a process that reliably grows epitaxial material on nonplanar structures—for example, around mesas or ridges, or in "tubs" or channels. Good results have been obtained with LPE, hydride CVD, and MOCVD for growth over low-relief features, such as the gratings essential for distributed feedback lasers, and hydride and halide

growth in tubs and channels has met with some success. Completely burying mesas becomes difficult when the structural height exceeds 1 or 2 μm, or when dovetail-like, reentrant structures must be overgrown. Full exploitation of the potential predicted for monolithic integrated optical devices or all-photonic switches and logic elements will require mastery of nonplanar epitaxy. This awaits an improved understanding at the research level of the surface chemistry and surface dynamics of epitaxial growth.

Acknowledgment

We thank K. M. Lee and J. N. Hollenhorst for the epitaxial layer thickness data presented in Figure 8.

References

1. J. E Clemans et al., "Bulk III-V Semiconductor Crystal Growth," *AT&T Technical Journal*, Vol. 68, No. 1, January/February 1989, pp. 29-42.
2. K. Nakajima, "The Liquid Phase Epitaxial Growth of InGaAsP," *Semiconductors and Semimetals*, T. Tsang, editor, Vol. 22, Part A, Academic Press, London, 1985.
3. R. A. Logan, "Liquid Phase Epitaxy of Buried Heterostructure Laser Devices," *Progress in Crystal Growth*, Vol. 12, 1986, pp. 215-242.
4. L. G. McKnight, M. E. Terry, and R. F. Karlicek, Jr. "CONCEPS-CC Process Command and Control under the UNIX Operating System," *Proceedings of AIChE Annual Meeting*, November 1988.
5. R. F. Karlicek, B. Hammarlund, and J. Ginnochio, "UV Absorption Spectroscopy for Monitoring Hydride Vapor-phase Epitaxy of InGaAsP Alloys," *Journal of Applied Physics*, Vol. 60, 1986, pp. 794-799.
6. P. Vohl, "Vapor Phase Epitaxy of InGaAsP and InP," *Journal of Crystal Growth*, Vol. 54, 1981, pp. 101-108.
7. R. C. Clark, "Indium Phosphide Vapor Epitaxy: A Review," *Journal of Crystal Growth*, Vol. 54, 1981, pp. 88-100.
8. A. Antreasyan et al., "High Speed Enhancement Mode InP Metal-Insulator-Semiconductor Field Effect Transistors Exhibiting Very High Transconductance," *Applied Physics Letters*, Vol. 49, 1986, pp. 513-515.
9. A. Antreasyan et al., "Gigahertz Logic Based on InP Metal-Insulator-Semiconductor Field Effect Transistors by Vapor Phase Epitaxy," *IEEE Transactions on Electron Devices*, Vol. ED-34, 1987, pp. 1897-1901.
10. J. A. Long, V. G. Riggs, and W. D. Johnston, Jr., "Growth of Fe-doped Semi-insulating InP by MOCVD," *Journal of Crystal Growth*, Vol. 69, 1984, pp. 10-14.
11. N. K. Dutta, "III-V Device Technologies for Lightwave Applications," *AT&T Technical Journal*, Vol. 68, No. 1, January/February 1989, pp. 5-18.
12. A. T. Macrander, "Precision X-ray Techniques for Semiconductors," *Annual Review of Materials Science*, Vol. 18, 1988, pp. 283-302.

Biographies (continued)

1980. Mr. Wilt is supervisor of the Laser Materials and Diagnostics Group in the Semiconductor Laser Development Department, working on epitaxial growth and characterization of long-wavelength laser materials. He has an A.B. in mathematics and physics from the University of Southern California and a Ph.D. in applied physics from California Institute of Technology. He joined AT&T in 1981.

(Manuscript received November 11, 1988)