Metalorganic Chemical Vapor Deposition of III-V Semiconductors

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Summary. Metalorganic chemical vapor deposition (MOCVD) is a process in which two or more metalorganic chemicals (for instance, trimethylgallium) or one or more metalorganic sources and one or more hydride sources (for instance, arsine, AsH_3) are used to form the corresponding intermetallic crystalline solid solution. MOCVD materials technology is a vapor-phase growth process that is becoming widely used to study the basic physics of novel materials and to grow complex semiconductor device structures for new optoelectronic and photonic systems. The MOCVD process is described and some of the device applications and results that have been realized with it are reviewed, with particular emphasis on the III-V compound semiconductors.

The monopoly that the semiconductor silicon has enjoyed for the past 30 years in the area of large-scale electronic device applications will soon be broken by the advent of several compound semiconductor materials composed of crystalline solid solutions of elements from columns IIIa and Va of the periodic table. These III-V compound semiconductor materials have many unique electronic and optical properties that distinguish them from the column IVa semiconductor silicon. For example, many of these alloy semiconductors have a direct band structure; that is, the minimum of the energy for electrons in the "conduction band" and the minimum of the energy for holes in the "valence band" are at the center of the Brillouin zone, where the crystal momentum k is zero. In the case of silicon, the minimum energy in the condition band and the minimum energy in the valence band occur at different points in the Brillouin zone; thus silicon has an indirect band structure.

As a result of the details of their band structure, the alloy semiconductors that have a direct band gap, such as GaAs, are very efficient emitters of photons, while semiconductors having indirect band structures, such as Si, are inefficient sources of light. The use of such direct-band-gap semiconductors for visible light-emitting diode applications is familiar to everyone. An increasingly important application for such light-emitting materials is in the construction of semiconductor lasers that emit coherent light in the infrared portion of the spectrum. Such lasers are in great demand for use in optical data storage and playback applications (for instance, videodisc systems) and for high-speed optical communications systems that use low-optical-loss glass fibers to transmit information coded in a pulsed light beam (for instance, in an undersea communications link across the Atlantic Ocean).

Several materials technologies have been developed for growth of the thin-film epitaxial structures that are required for the realization of such III-V compound semiconductor optoelectronic devices. In general, these growth techniques can be classified in three categories: (i) liquid-phase epitaxy (LPE), (ii) molecular-beam epitaxy (MBE), and (iii) vapor-phase epitaxy (VPE). The LPE process uses heated liquid solutions of the IIIa and Va elements to produce a epitaxial thin crystalline film of the corresponding alloy semiconductor on an appropriate single-crystal substrate or host crystal. This is accomplished by cooling the liquid solution below the saturation temperature while it is in contact with the substrate. The MBE technology employs ultrahigh-vacuum systems in which elemental atomic or molecular beams are produced for each elemental species of the desired III-V compound semiconductor thin film. These molecular beams are formed by heating the corresponding elemental source to a high temperature in vacuum, producing a molecular beam, which then impinges on a heated substrate. Under the proper conditions, an epitaxial layer of the corresponding III-V alloy semiconductor is grown on the substrate (*1*). The VPE growth technique utilizes chemical reactions that occur between the vapors of certain chemical compounds of the IIIa and Va elements when they are heated together. These reactions produce chemically active species that interact in the vapor phase or at the surface of the substrate to produce the corresponding III-V semiconductor thin film. The particular VPE process that is the subject of this article employs metalorganic compounds as sources of the IIIa elements; the sources of the Va elements are either Va hydrides or mixtures of the Va hydrides and Va metalorganics. This metalorganic chemical vapor deposition (MOCVD) process is becoming widely used in the growth of many important III-V compound semiconductors.

Development of the MOCVD Process

In this article, the term metalorganic denotes the broad class of compounds that contain metal-carbon bonds (known as organometallic compounds), as well as those with metal-oxygen-carbon bonds (the alkoxides) and the coordination compounds of metals and organic molecules. Metalorganic compounds were first identified by Robert Bunsen in 1839 (*2*). Since that time, there have been extensive studies of their chemical and physical properties as well as their reactions with other compounds, giving rise to a vast area of chemical research, development, and production. In the past 30 years many of these compounds have become of great practical interest. The first American Chemical Society symposium devoted entirely to metalorganics was held in 1957 (*3*), and numerous international conferences on the chemistry of these compounds have been held since.

Although many of the chemical and physical properties of a large number of metalorganics were established in the 1950's, it was not until 1968 that any work was reported on the growth of epitaxial semiconductor thin films with metalorganic sources (*4*). In this work, actually begun in 1967, Manasevit (*4*) showed that vapor-phase mixtures of the metalorganic compound trimethylgallium $(CH_3)_3Ga$, and the hydride arsine, AsH_3, when pyrolized at 600° to 700°C in an H_2 atmosphere, could be used to grow

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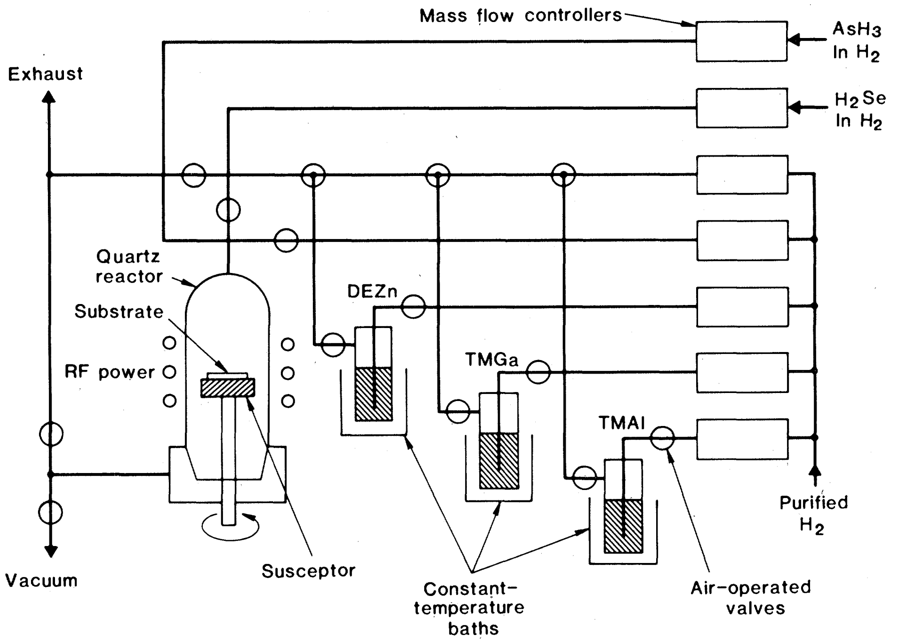

Fig. 1. Schematic diagram of a vertical atmospheric-pressure MOCVD reactor.

thin single-crystal epitaxial films of GaAs in an open-tube reactor. Manasevit used this MOCVD process to grow heteroepitaxial (*5*) single-crystal films of GaAs on single-crystal insulating substrates such as sapphire (Al_2O_3), spinel ($MgAl_2O_4$), and beryllium oxide (BeO) (*4*). His interest in the heteroepitaxial growth of III-V compound semiconductor thin films on insulating substrates the growth of III-V compound semiconductor thin films on insulating substrates such as sapphire (*6*). This silicon-on-sapphire (SOS) materials technology is applied in certain important specialized device areas.

Other laboratories were also interested in semiconductor-on-insulator epitaxial growth, and much of the early literature on MOCVD research in the growth of compound semiconductors was devoted to the study of heteroepitaxial films on insulating oxide substrates. This work has been reviewed (*7–9*) and will not be discussed here.

At this same time, research was being done on the application of MOCVD to the growth of homoepitaxial semiconductor thin films and on the growth of heteroepitaxial semiconductor thin films on other semiconductor substrates. However, because of the availability of other, more advanced technologies for the growth of III-V compound semiconductor thin films, such as the LPE process and the halide-transport VPE processes, the MOCVD technology was not extensively used for this purpose.

In the past 5 years, there has been increasing interest throughout the world in MOCVD growth of semiconductors. This is the result of interest in the potential large-scale use of certain compound semiconductor devices based on submicrometer-thick layers [for instance, field-effect transistors (FET's)] and high-quality heterojunctions between two different semiconductor materials (heterojunction solar cells, and heterojunction lasers and light-emitting diodes). The MOCVD materials technology is well-suited to the fulfillment of these requirements and has some advantages over alternative materials technologies. As a result of this interest in device applications, much of the MOCVD materials research is device-oriented, and virtually every major corporation with an interest in compound semiconductor devices has a research program in the MOCVD growth of these materials.

Table 1. Metalorganics for semiconductor thin film deposition.

Group of metal in periodic table	Compound	Symbol
IIa	Biscyclopentadienyl-magnesium	Cp_2Mg
IIb	Dimethylzinc	DMZn
	Diethylzinc	DEZn
	Dimethylcadmium	DMCd
	Dimethylmercury	DMHg
	Diethylmercury	DEHg
IIIa	Trimethylaluminum	TMAl
	Trimethylgallium	TMGa
	Triethylgallium	TEGa
	Diethylgallium chloride	DEGaCl
	Trimethylindium	TMIn
	Triethylindium	TEIn
IVa	Tetramethyltin	TMSn
	Tetraethyltin	TESn
	Tetramethyllead	TMPb
	Tetraethyllead	TEPb
Va	Triethylphosphine	TEP
	Trimethylantimony	TMSb
	Trimethylarsine	TMAs
VIa	Dimethyltelluride	DMTe
	Diethyltelluride	DETe

The MOCVD Process

The metalorganic chemical vapor deposition process involves the pyrolysis (*10*) of vapor-phase mixtures of two or more metalorganic sources, one or more metalorganic compounds, and one or more hydride compounds. Many other names have been used for this process, including "organometallic CVD" (OMCVD), "metal alkyl vapor-phase epitaxy" (MAVPE), "metalorganic VPE" (MOVPE), and "organometallic VPE" (OMVPE). The term "metalorganic chemical vapor deposition" is used here since it is a more general description of the process, encompassing the use of any of the metalorganic compounds (not just the organometallics) and the growth of nonepitaxial (polycrystalline or amorphous) films.

The metalorganics of interest for the growth of semiconductor films are typically liquids at room temperature, although some of the useful metalorganic compounds are solids at room temperature and above. These metalorganics generally have relatively high vapor pressures and can be readily transported into the reaction zone by passing a carrier gas, such as H_2, through the liquid sources or over the solid sources. The hydrides of interest for semiconductor thin-film growth are gases at room temperature and are generally used as dilute mixtures in an H_2 matrix and are contained in high-pressure cylinders. These metalorganic and hydride compounds are mixed in the vapor phase and are usually pyrolyzed in a flowing H_2 atmosphere in a open-tube reactor operating at atmospheric pressure or at a reduced pressure of about 70 torr (0.1 atm). Pyrolysis temperatures typically in the range 600° to 800°C are employed. Energy for heating the gaseous source mixtures is usually provided by a high-power radio-frequency (RF) generator operating at about 450 kHz. This RF generator heats a graphite "susceptor" on which the single crystal substrate is placed. The gas mixture at or near the substrate surface is thus heated to high temperatures while the walls of the reactor chamber remain relatively cool, leading to deposition of the semiconductor thin film on the substrate crystal and not much loss of reactants to the surfaces of the reactor chamber. A typical atmospheric-pressure MOCVD reactor is shown schematically in Fig. 1.

The net chemical reaction for the specific case of the MOCVD growth of the semiconductor GaAs from the metalorganic trimethylgallium $(CH_3)_3Ga$ (TMGa), and the hydride arsine, AsH_3, is

$$(CH_3)_3Ga + AsH_3 \xrightarrow[700°C]{H_2} GaAs + 3CH_4 \qquad (1)$$

Similar reactions are employed for the growth of other semiconductor binary, ternary, and quaternary compound semiconductor thin films. For example, for the technologically important ternary alloy semiconductor $Al_xGa_{1-x}As$, the following process is typically employed:

$$(1 - x)[(CH_3)_3Ga] + x[(CH_3)_3Al] + AsH_3 \xrightarrow[\sim 700°C]{H_2} Ga_{1-x}Al_xAs + 3CH_4 \qquad (2)$$

In this case, the alloy composition of the epitaxial thin film is directly related to the relative initial partial pressures of the trimethylgallium and trimethylaluminum (TMAl) in the vapor phase. Unfortunately, this simple relation between the composition of the sources in the vapor phase and the composition of the resulting thin solid film is not always true for the growth of compound semiconductors by MOCVD.

Most of the research on MOCVD growth of compound semiconductors has employed the methyl and ethyl metalorganics. These compounds are relatively simple to prepare and can be readily pyrolyzed in a hydrogen atmosphere to yield the corresponding metal atoms, with methane or ethane produced as a by-product. Table 1 lists the principal metalorganics that have been utilized in the growth of compound semiconductor thin films. All of these compounds are now commercially available in "electronic grade" purity, typically more than 99.9995 percent pure. However, most applications of high-purity semiconductor materials require epitaxial layers with total impurity levels of less than 0.1 part per million. Thus, reliable methods for producing metalorganics with improved purity are essential in the future large-scale application of MOCVD for the growth of high-purity semiconductors. However, many semiconductor device structures that are being studied today employ "doped" layers, that is, layers in which impurities have been intentionally added to levels of about 100 ppm. Thus, the currently available metalorganic sources are quite useful in the realization of many practical semiconductor devices.

The large variety of metalorganic sources that are listed in Table 1 implies that a wide variety of compound semiconductor materials have been grown by MOCVD. In fact, binary compound semiconductors have been grown in the III-V, II-VI, and IV-VI semiconductor materials families. Also, many of the important ternary and quaternary III-V compound semiconductors have been grown by MOCVD. Table 2 shows the binary and ternary III-V semiconductors that have been produced by MOCVD and the reactants employed. The greatest amount of attention has been devoted to the technologically important alloy $Al_xGa_{1-x}As$, which is of interest for many practical semiconductor devices including solar cells and semiconductor lasers. In addition, a few of the quaternary alloy semiconductors have been grown by MOCVD. The quaternary alloy $In_xGa_{1-x}As_{1-y}P_y$ has been grown with great success by MOCVD and will be discussed below.

Thin films of many of the II-VI and IV-VI compound semiconductors have also been deposited by MOCVD, as indicated in Table 3. Although research in this area has not been as extensive as that on the III-V semiconductors, recent results (*11*, *12*) have shown that high-quality films of ZnSe and $ZnSe_{1-x}S_x$ can be produced by MOCVD, indicating that it should be possible to produce similarly high-quality films of other II-VI materials. In addition, the important II-VI ternary alloy $Hg_{1-x}Cd_xTe$ has been produced by MOCVD (*13*), as have thin films of some of the important IV-VI compound semiconductors, including $Pb_{1-x}Sn_xTe$.

Table 2. Binary and ternary III-V compound semiconductors formed by MOCVD.

Compound	Reactants
Binary	
AlAs	TMAl-AsH_3
AlN	TMAl-NH_3
GaAs	TMGa-AsH_3
	TEGa-AsH_3
	DEGaCl-AsH_3
GaN	TMGa-NH_3
GaP	TMGa-PH_3
	TMP-PH_3
	TEGa-PH_3
GaSb	TEGa-TMSb
InAs	TEIn-AsH_3
InP	TEIn-PH_3
	TMIn-PH_3
	TMIn-TMP
InSb	TMIn-TMSb
Ternary	
$GaAs_{1-x}P_x$ (x = 0.0–1.0)	TMGa-AsH_3-PH_3
$GaAs_{1-x}Sb_x$	TMGa-AsH_3-SbH_3
(x = 0.0–3, 0.6–1.0)	TMGa-TMSb-AsH_3
	TMGa-TMSb-TMAs
$Ga_{1-x}Al_xAs$	TMGa-TMAl-AsH_3
(x = 0.0–1.0)	TEGa-TMAl-AsH_3
$Ga_{1-x}In_xAs$	TMGa-TEIn-AsH_3
(x = 0.0–1.0)	TMGa-TMIn-AsH_3
	TMGa-TMIn-TMAs
$InAs_{1-x}P_x$ (x = 0.0–0.6)	TEIn-AsH_3-PH_3
$InAs_{1-x}Sb_x$ (x = 0.0–1.0)	TEIn-TESb-AsH_3

It is evident that the MOCVD materials technology can be used to produce thin films of many compound semiconductors that are of interest today for the fabrication of technologically important semiconductor devices. There are, however, additional features of the MOCVD process that make it attractive for the growth of such semiconductor thin-film structures. These features are described below.

Process control is inherent. The deposition process occurs by passing a homogeneous gas-phase mixture of reactants and carrier gases over a heated substrate. Only the temperature of the substrate need be carefully controlled. Most of the properties of films grown by MOCVD are only weakly dependent on temperature, so that slight variations in substrate temperature are inconsequential. The partial pressure of the various gaseous constituents can be controlled by electronic mass flow control of the source flow rates. These features allow all of the critical variables in the growth process to be controlled with extremely high accuracy, ensuring reproducibility.

Multilayer, multicomponent epitaxial structures can be deposited in a single growth sequence. The reactors typically used for MOCVD growth have facilities for several metalorganic and hydride sources. In addition, process involves no etching species, so that abrupt interfaces between various materials can be formed. The absence of an etching species also helps to achieve the growth of films with uniform thickness and composition, since the growth process is not the result of competing deposition and etching reactions, as is the case for some other vapor-phase epitaxy processes. Such reactions could lead to the introduction into the gas phase of uncontrollable amounts of III-V compound substrate components, which would subsequently upset the desired film stoichiometry and impurity level.

The process is scalable to high volume. Large-area uniform growth of epitaxial structures can be achieved by MOCVD with equipment similar to that

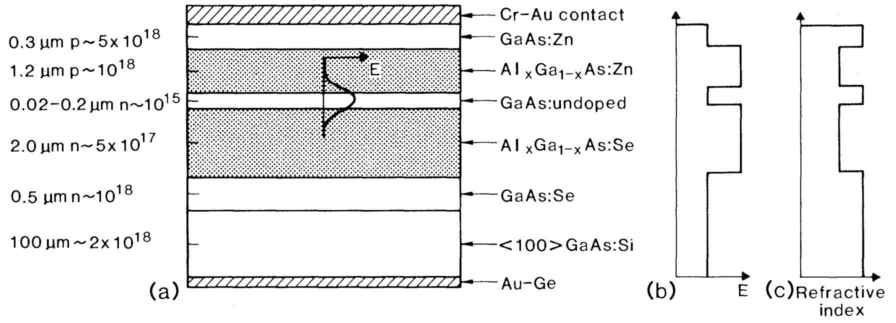

Fig. 2. (a) Schematic cross section of a conventional $Al_xGa_{1-x}As$-GaAs double-heterojunction laser. (b) Variation of the energy gap, E_g, in the structure. (c) Variation of the index of refraction.

currently used in large-scale commercial epitaxial growth of semiconductor silicon. MOCVD systems are available with the capacity for growing simultaneously on 20 substrates that are 2 inches in diameter. While this is still far from the capacity of large silicon epitaxy reactors, it is much larger than the capacity of growth systems based on other III-V materials technologies such as LPE and MBE. In addition, when desirable, high growth rates compatible with production applications are achievable.

Materials Properties of MOCVD Semiconductors

The materials properties of III-V compound semiconductors are of great concern for all device applications. Many applications for high-speed electronic information systems require the growth of epitaxial layers of binary and ternary compound semiconductor thin films with extremely low concentrations of unwanted chemical impurities. The goal is to achieve the highest possible speed for electrons in these devices, and additional impurities can slow the electrons through scattering interactions, thus reducing the speed of response of the device to the electrical signal applied to it.

The purity of a semiconductor material can be determined by measuring the mobility of the electrons and holes through the crystal lattice of the epitaxial layer. High mobilities indicate that the number of impurities in the semiconductor crystal is low, since the electrons are not slowed down by scattering from impurity atoms. Because most useful devices are made from *n*-type material in which the number of electrons *n* is greater than the number of holes *p*, the important measurement is the mobility of the electrons, which is dependent on the total number of impurity atoms in the epitaxial layer. Theoretically, a high-quality GaAs thin film will have an electron mobility of about 125,000 cm^2/V-sec at 77 K when the total impurity concentration is 5×10^{14} cm^{-3}. For lower concentrations of impurities the mobility is higher, and an epitaxial layer having a mobility of 200,000 cm^2/V-sec at 77 K is considered excellent since the impurity concentration should be below 1×10^{14} cm^{-3}.

The effects of metalorganic and hydride source purity, growth temperature, and reactor pressure on residual impurity incorporation have been shown to be important in determining the purity of epitaxial GaAs layers grown by MOCVD (*14, 15*). In this work, far-infrared photoconductivity measurements and low-temperature photoluminescence measurements showed that C, Si, and Zn are the dominant residual impurities in unintentionally doped MOCVD GaAs films. The highest mobilities were obtained for films grown in the temperature range 600° to 625°C. Mobilities in these undoped GaAs films varied greatly with the trimethylgallium and arsine sources used, as routinely observed by other workers. Purification of the trimethylgallium by redistillation resulted in GaAs films with improved mobilities and fewer unwanted impurities. Also, higher mobilities could be obtained with a given set of sources if the reactor pressure during growth was lowered from about 760 torr to about 70 torr (*14, 16*). Total impurity concentrations as low as 5×10^{14} cm^{-3} were measured for films with mobilities as high as 125,000 cm^2/V-sec at 77 K. As noted above, this is about the theoretical maximum for GaAs films with this impurity concentration. Other workers (*17*) have also reported growth of high-purity GaAs films by MOCVD. The films were grown at atmospheric pressure by using specially refined trimethylgallium with mobilities as high as 139,000 cm^2/V-sec. The total impurity concentration was about 4×10^{14} cm^{-3}. More recently, mobilities as high as 150,000 cm^2/V-sec have been reported for MOCVD GaAs epitaxial layers (*18*).

Table 3. II-VI and IV-VI semiconductors formed by MOCVD.

Compound	Reactants
	II-VI
ZnS	DEZn-H_2S
ZnSe	DEZn-H_2Se
ZnTe	DEZn-DMTe
CdS	DMCd-H_2S
CdSe	DMCd-H_2Se
CdTe	DMCd-DMTe
$Hg_{1-x}Cd_xTe$	Hg-DMCd-DETe
ZnS_xSe_{1-x}	DEZn-H_2S-H_2Se
	IV-VI
SnTe	TESn-DMTe
PbTe	TMPb-DMTe TEPb-DMTe
$Pb_{1-x}Sn_xTe$	TMPb-TESn-DMTe
PbS	TMPb-H_2S
PbSe	TMPb-H_2Se

For comparison, other materials technologies such as VPE and MBE have produced GaAs films with electron mobilities greater than 200,000 cm^2/V-sec and total impurity levels less than 7×10^{13} cm^{-3}. These results indicate that the metalorganic and hdyride sources still need some improvement before MOCVD reaches the level of purity achieved by some of the other III-V materials technologies. However, most devices of interest do not require GaAs of this purity and consequently MOCVD can meet the needs of most device applications.

Another III-V semiconductor that is of great interest is the ternary alloy $Al_xGa_{1-x}As$, which is a solid solution of the two binary compounds GaAs and AlAs. Application of MOCVD for the growth of epitaxial films of this ternary alloy is currently of great interest because of the increasing commercial importance of a wide variety of devices that employ thin layers of this material. One of the unique features of the MOCVD process is that it is the only vapor-phase epitaxy process capable of easily handling the growth of compounds containing aluminum.

Because of the extreme reactivity of aluminum, care must be taken to ensure that the reactor system is leak-tight. It is also critically important that the hydride gas sources be free of even small concentrations (less than 1 ppm) of water vapor. Because of problems with arsine sources and also because reactor systems were not constructed as carefully as they are today, early reports of the properties of MOCVD $Al_xGa_{1-x}As$ indicated excessive incorporation of oxygen. However, results published in 1977 and 1978 (*19, 20*) showed that high-quality $Al_xGa_{1-x}As$ films and $Al_xGa_{1-x}As$-GaAs heterojunctions could be grown by this process.

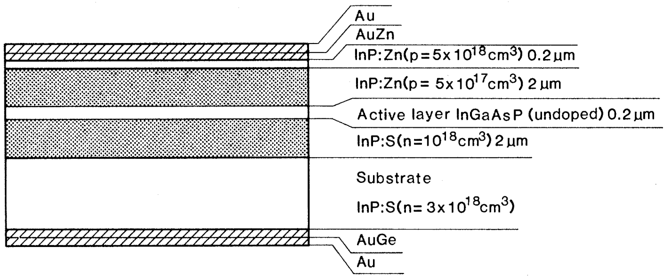

Fig. 3. Schematic cross section of a typical conventional $In_{1-x}Ga_xAs_yP_{1-y}$-InP double-heterostructure laser. The "active layer" is made of the quaternary $In_{1-x}Ga_xAs_yP_{1-y}$.

The optical properties of this material are of interest since $Al_xGa_{1-x}As$ thin films are widely used in semiconductor laser structures. These devices, which are described below in more detail, are becoming extremely important in optical communications and information transmission systems.

At present, GaAs and $Al_xGa_{1-x}As$ are the principal III-V compounds grown by MOCVD. However, there is great interest in the application of this materials technology to the growth of other important compound semiconductors, for instance, InP and $In_{1-x}Ga_xAs_yP_{1-y}$ epitaxial thin films. A number of different MOCVD processes are being studied for this purpose. Trimethylindium and triethylindium are primarily used for the indium sources. The phosphorus sources are phosphine, triethylphosphine, and trimethylphosphine. One approach that is being extensively studied is the use of adduct compounds that are formed by reacting a metalorganic containing indium with another metalorganic containing phosphorus, for instance, the trimethylindium-trimethylphosphine adduct (*21*). This compound is stable near room temperature and can be handled with somewhat greater safety than the simple metalorganics since the adduct is much less reactive and is not pyrophoric. One of the attractive features of this approach is that it should be possible to grow the quaternary solid $In_{1-x}Ga_xAs_yP_{1-y}$ with a given composition from a single metalorganic adduct source containing the right amounts of In, Ga, As, and P. These III-V semicondcutor materials containing indium are of increasing importance in a variety of device application areas. One specific application to an injection laser device structure is discussed further below.

Heterojunction Structures and Devices

In many of the important semiconductor device structures being developed today, it is critically important that highly perfect interfaces be made between two different single-crystal semiconductor materials. Such an interface between two materials having different chemical compositions is called a heterojunction or heterostructure. If the two different crystalline materials have the same spacing between corresponding planes of atoms, the heterojunction is called a lattice-matched heterojunction.

One of the most important device structures of this class is the semiconductor double-heterojunction (DH) injection laser. These devices were first grown by LPE (*22, 23*) and are the light sources used in most high-speed optical communications systems today (*24*). Typically, these devices have five separate layers of different materials, with the layers being as thin as 0.1 µm or less. The chemical composition of these layers must be carefully controlled in order to achieve the desired device performance. A schematic diagram of a standard DH laser made in the GaAs-$Al_xGa_{1-x}As$ materials system is shown in Fig. 2a. The epitaxial structure consists of five layers, which are, in order of growth, (i) an *n*-type GaAs layer doped with Se having a carrier concentration $n = 1 \times 10^{18}$ cm^{-3} and a thickness of 0.5 µm; (ii) an *n*-type $Al_xGa_{1-x}As$ layer doped with Se having $n = 5 \times 10^{17}$ cm^{-3} and 2.0 µm thick; (iii) an undoped GaAs layer (the active region) 0.02 to 0.2 µm thick having a background carrier concentration $n = 1 \times 10^{15}$ cm^{-3}; (iv) a *p*-type $Al_xGa_{1-x}As$ layer doped with Zn to a level of $p = 1 \times 10^{18}$ cm^{-3} and 1.2 µm thick; and (v) a *p*-type GaAs layer doped with Zn having $p = 5 \times 10^{18}$ cm^{-3}. The epitaxial layers are grown on an *n*-type GaAs substrate that is doped with silicon. This single-crystal substrate is sawed from a large ingot and is polished and etched before epitaxial crystal growth.

As discussed above, the MOCVD process has many inherent features that permit precise control of the growth of laser structures such as that shown in Fig. 2a. The first room-temperature operation of a semiconductor laser grown by MOCVD was reproted in 1977 (*19*), and since that time the application of MOCVD to the growth of such device structures has become a subject of intense study, in particular for lasers made of materials in the $Al_xGa_{1-x}As$-GaAs system (*25, 26*).

Another III-V compound semiconductor system that is of great importance for the fabrication of semiconductor lasers is $In_{1-x}Ga_xAs_yP_{1-y}$-InP (*27, 28*). A typical laser structure composed of materials in this system is shown in Fig. 3. Note that in this case all but one of the layers is composed of InP. The active region is made of $In_{1-x}Ga_xAs_yP_{1-y}$. The alloy composition of this layer determines the energy of the photons that the laser will emit. This quaternary system is important because the energies of the photons that are emitted cover the range where the optical losses in silica-based optical fibers reach a minimum (0.8 to 0.9 eV, photon wavelengths of 1.33 to 1.55 µm). Lasers in this III-V system were first reported in 1976 (*27*) and were grown by LPE. The first $In_{1-x}Ga_xAs_yP_{1-y}$-InP lasers grown by MOCVD were reported in 1980 (*29*). Since then, great progress has been made in the MOCVD growth of these materials (*30, 31*) and the performance characteristics of these lasers are equal to those of the best comparable devices grown by LPE and of similar lasers grown recently by MBE (*32*).

Compared to the more conventional LPE process for growth of these device structures, MOCVD offers a higher degree of uniformity of devices fabricated from a wafer (*33, 34*) and also a much greater production capacity because of the much larger substrates that can be utilized in an MOCVD reactor. In addition, MOCVD has some advantages over the MBE materials technology in scale-up to large-area device production and in total system cost.

Quantum Well Structures

The operating characteristics of most conventional double-heterostructure devices are determined by the bulk properties of the materials that form their structure. However, if the active region of the device has a thickness less than about 500 Å, the device characteristics are influenced by quantum mechanical effects in addition to the properties of the materials themselves. These "quantum size effects" (*35*) result from the confinement of electrons and holes to the extremely thin active region of such a "quantum well" double-heterostructure device. The energy levels of these electrons and holes are quantized, in much the same way as the classical "particle in a box." As a result of this quantization of the electron and hole energy levels, the electronic properties of the active region of the device are modified. The effect of this quantization on the density of states for electrons in the conduction band and holes in the valence band is shown schematically in Fig. 4. The dashed curves show the density of states, $g(E)$, as a function of energy for electrons, E_n, and holes, E_h, in bulk GaAs. The solid "stair-step" curves are the new densities of states for a quantum well made of GaAs and bounded on both sides by layers of $Al_xGa_{1-x}As$. Because of quantum mechanical effects, radiative recombination of electrons and holes can occur only between electron and hole states having the same quantum number (that is, $\Delta n = 0$); thus the luminescence spectra of such a structure will consist of emission peaks characteristic of the quantum well energy levels of the electrons and holes. The electronic conduction characteristics of thin quantum well layers are also very different from those of "bulk" layers. Quantum effects have been used to produce extremely high mobility thin GaAs layers in $Al_xGa_{1-x}As$-GaAs double heterostructures (*36, 37*).

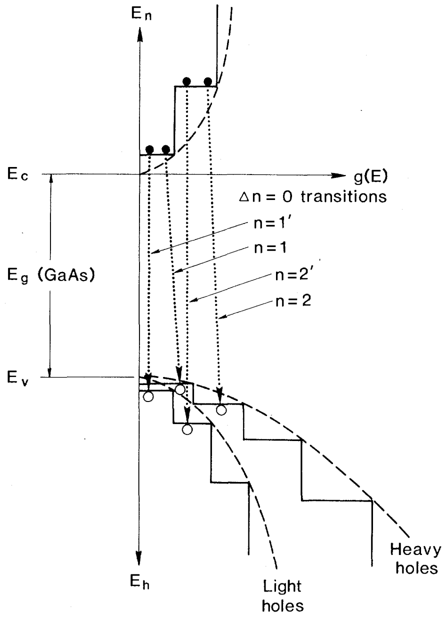

Fig. 4. Density of states $g(E)$ as a function of energy for electrons, E_n, and holes, E_h, in an $Al_xGa_{1-x}As$-GaAs quantum well double heterostructure. The stair-step solid lines show the density of states for the quantum well. The dashed curves show the corresponding density of states for thick layers of GaAs (thickness greater than 500 Å).

The first room-temperature operation of a quantum well semiconductor laser was reported in 1976 for epitaxial $Al_xGa_{1-x}As$-GaAs quantum well structures grown by MBE (*38*), but these lasers were optically pumped and had relatively high thresholds for laser operation. In 1977 quantum well lasers were grown by LPE in the $In_{1-x}Ga_xAs_yP_{1-y}$-InP system (*39*). These lasers were also optically pumped and exhibited a relatively high threshold for laser operation. The first quantum well lasers grown by MOCVD were reported in 1978 (*40*). They were made in the $Al_xGa_{1-x}As$-GaAs materials system and were the first injection-pumped quantum well lasers; they were also the first that were capable of operation at low thresholds at room temperature. These lasers show pronounced quantum effects in their spectral output and other operating characteristics. Extensive studies of optically pumped and injection quantum well MOCVD lasers have shown that high-performance (that is, low-threshold, high-quantum efficiency, and long life) quantum well lasers can be grown by MOCVD (*33, 34, 41*).

Quantum well lasers are unique in many respects and typically have low thresholds, high-energy spectral emission (greater than the energy gap of the material), and high external differential quantum efficiencies. These features have been utilized to achieve levels of performance that far exceed those of semiconductor lasers with a more conventional double-heterostructure geometry. In 1983, MOCVD quantum well lasers were reported in the $Al_xGa_{1-x}As$ system that operate in the visible portion of the spectrum at about 7200 Å (*42*). These were the first low-threshold semiconductor injection lasers that emitted visible light. In addition, such MOCVD quantum well structures have been used to fabricate visible semiconductor lasers emitting 100 mW of optical power at about 7300 Å (*43*) at a drive current of only 180 mA. They are very much more efficient than the He-Ne gas laser and will probably replace it in many applications, since they require much less space and less power to operate.

Another recent development in the area of MOCVD quantum well lasers is the use of monolithic arrays of such lasers to make a structure capable of emitting greater optical powers than previously reported for any semiconductor laser structure. Optical powers greater than 2.5 W have been reported for continuously operating arrays of 40 individual lasers (*44*). These high optical powers are emitted from a laser device that is only 400 μm wide; 250 μm long, and 100 μm thick, and they are achievable only because of the high efficiency of the quantum well laser structure and the quality of MOCVD $Al_xGa_{1-x}As$. It is possible that such arrays could replace much larger krypton and argon gas lasers (which require water cooling) in some high-power laser applications requiring high efficiency and small weight, as in certain space-based laser communication systems.

Other Device Structures and Recent Developments

Several other III-V compound semiconductor device structures have been grown by MOCVD. Many of them are heterojunction devices consisting of $Al_xGa_{1-x}As$ and GaAs. Among these are heterojunction solar cells (*45*), heterojunction phototransistors (*46*), heterojunction field-effect transistors (*47*), and heterojunction photocathodes (*48*).

As the requirements for heterojunction devices increase MOCVD will become more widely used for a variety of compound semiconductor materials and devices. For example, the MOCVD process has been used to make device structures in the $In_{1-x}Ga_xAs_yP_{1-y}$-InP system. Most of this work has been in the growth of laser structures. However, selectively doped heterojunction structures in the $In_{1-x}Ga_xAs_yP_{1-y}$-InP system have been reported recently (*49*).

MOCVD has also been used in novel ways to produce thin films of several metals and some of the III-V semiconductors by using laser excitation to either thermally or photolytically decompose the metalorganics. Thin films of such metals as aluminum and cadmium have been produced by laser enhancement of the chemical decomposition reactions, using metalorganic sources (*50, 51*). Thin epitaxial films of GaAs have been produced by laser-induced pyrolysis of mixtures of $(CH_3)_3Ga$ and AsH_3 (*52*). More recently, InP epitaxial films have been deposited by photolytic dissociation of In- and P-containing metalorganic compounds (*53*). The use of laser-induced chemistry in the MOCVD growth of semiconductor films and for the deposition of metals opens vast new areas of research, since this process permits selective growth of thin films, potentially with very high resolution. It may be possible to use the laser light to "write" epitaxial structures on substrates and thus to build complex electronic and optical circuits with this technology. Such integrated circuits are the next step in the application of III-V compound semiconductors to high-speed information processing.

Conclusions

The metalorganic chemical vapor deposition process has been used to grow a wide variety of III-V, II-IV, and IV-VI compound semiconductors. Much research on the application of the MOCVD materials technology has concentrated on the epitaxial growth of III-V compound semiconductor heterojunction structures in the $Al_xGa_{1-x}As$-GaAs and the $In_{1-x}Ga_xAs_yP_{1-y}$-InP systems. The rather brief description has presented some of the results on the application of the MOCVD process to the growth of injection lasers in these two materials systems.

In the future, MOCVD will be used to grow films of other compound semiconductors, and novel approaches to the growth of complex three-dimensional integrated circuits will be developed. MOCVD promises to be an extremely important research tool as well as an important commercial process for the production of compound semiconductor materials and devices.

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