ELECTRONIC MATERIALS

1. Introduction

Electronic materials are those exquisitely pure crystal structures which form the basis for the information technology of the 1990s. Since the original theoretical understanding, the progress of solid-state electronics has been paced by the ability to control chemical bonding structures, particularly at surfaces and interfaces

(1). A series of chemical discoveries and insights in Ge, Si, and the Group 13–15 (III–V) semiconductors is responsible for the solid-state electronics revolution. Every new device and capability can be identified with a particular chemical breakthrough. The chemistry and chemical engineering required for making electronic materials, ie, these very specific inorganic chemical bonding structures, has come about by techniques employing chemical vapor deposition to effect materials growth and through an increased control over surface and interfacial chemistry (see ELECTRONIC COATINGS; SURFACE AND INTERFACE ANALYSIS; THIN FILMS).

2. Semiconductor Energy Levels

Semiconductor materials are rather unique and exceptional substances (see SEMICONDUCTORS). The entire semiconductor crystal is one giant covalent molecule. In benzene molecules, the electron wave functions that describe probability density are spread over the six ring-carbon atoms; in a large dye molecule, an electron might be delocalized over a series of rings, but in semiconductors, the electron wave-functions are delocalized, in principle, over an entire macroscopic crystal. Because of the size of these wave functions, no single atom can have much effect on the electron energies, ie, the electronic excitations in semiconductors are delocalized.

Good semiconductors are drawn from the central columns, Groups 13, 14, and 15 (III,IV, and V), of the Periodic Table, where the atoms tend to be nonpolar. For this reason, and because of the giant size of the wave functions, the electron–atom interaction is very weak. The electrons move as if in free space, colliding with the atomic lattice rather infrequently.

In a semiconductor the available energy levels are the valence and conduction bands, which are generally filled and empty, bonding and antibonding, respectively, separated by a forbidden gap as shown in Figure 1. The electrons in the conduction and valence bands act as two separate subsystems. Not only do the electrons ignore the crystallographic lattice of atoms, the electrons in one band tend to ignore those in the other subsystem. This property is unique to electronic materials.

Electrons excited into the conduction band tend to stay in the conduction band, returning only slowly to the valence band. The corresponding missing electrons in the valence band are called holes. Holes tend to remain in the valence band. The conduction band electrons can establish an equilibrium at a defined chemical potential, and electrons in the valence band can have an equilibrium at a second, different chemical potential. Chemical potential can be regarded as a sort of available voltage from that subsystem. Instead of having one single chemical potential, ie, a Fermi level, for all the electrons in the material, the possibility exists for two separate quasi-Fermi levels in the same crystal.

The idea of having two distinct quasi-Fermi levels or chemical potentials within the same volume of material, first emphasized by Shockley (1), has deeper implications than the somewhat similar concept of two distinct effective temperatures in the same block of material. The latter can occur, for example, when nuclear spins are weakly coupled to atomic motion (see MAGNETIC SPIN RESONANCE).

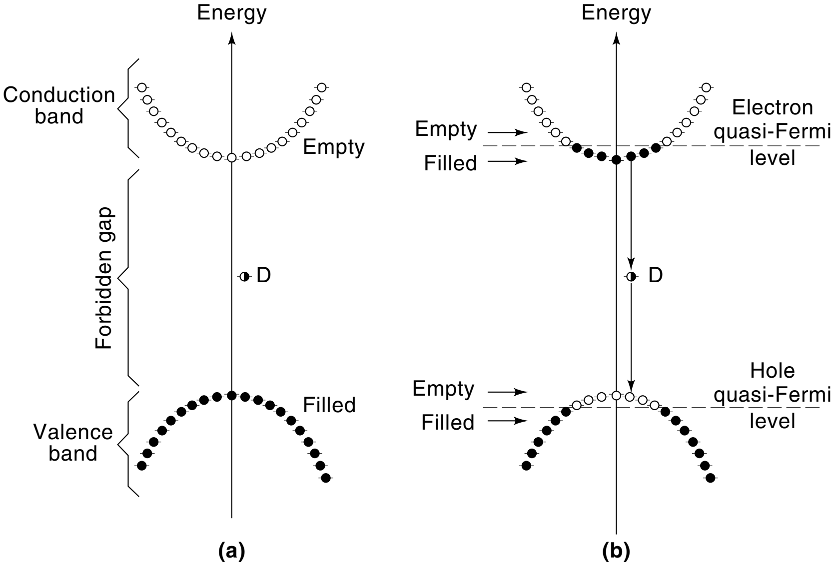

Fig. 1. The energy levels in a semiconductor. Shown are the valence and conduction bands and the forbidden gap in between where –•– represents an occupied level, ie, electrons are present; –○–, an unoccupied level; and ◑ an energy level arising from a chemical defect D and occurring within the forbidden gap. The electrons in each band are somewhat independent. (**a**) A cold semiconductor in pitch darkness where the valence band levels are filled and conduction band levels are empty. (**b**) The same semiconductor exposed to intense light or some other form of excitation showing the quasi-Fermi level for each band. The energy levels are occupied up to the available voltage for that band. There is a population inversion between conduction and valence bands which can lead to optical gain and possible lasing. Conversely, the chemical potential difference between the quasi-Fermi levels can be connected as the output voltage of a solar cell. Equilibrium is reestablished by stepwise recombination at the defect levels D within the forbidden gap.

Quasi-Fermi level separations are often labeled as $\mathrm{Im}_{\mathrm{ref}}$, Fermi's name spelled backwards.

In the quantum level structures illustrated in Figure 1**b**, electrons in each band fill up the energy levels, up to the available chemical potential. From Figure 1**b** two critical optoelectronic devices can be explained.

1. Solar cells: the difference between conduction and valence band chemical potentials is the available output voltage of a solar cell. Light creates the chemical potential difference simply by boosting a population of electrons from the valence band into the conduction band (see PHOTOVOLTAIC CELLS; SOLAR ENERGY).
2. Lasers (qv): levels just above the valence band chemical potential are essentially (2) empty and unfilled, but levels just below the conduction band chemical potential are filled, permitting a population inversion. Filled levels above, empty levels below, is the principle by which lasers operate (see also LIGHT GENERATION, SEMICONDUCTOR LASERS).

These two devices are the inverse of one another: the semiconductor laser converts electricity into light; the solar cell converts light into electricity.

The possibility of two separate electronic equilibria, ie, the establishment of two quasi-Fermi levels or two different chemical potentials, requires a very slow decay of electrons from the conduction band back into the valence band. The very weak electron–atom coupling, resulting from the large delocalized wave functions in nonpolar materials, permits the slow decay. Electron-hole recombination requires getting rid of the electronic band gap energy, which is usually around one volt, and dumping it off as heat of atomic motion. In relation to characteristic energies of atomic motion, one volt is a huge amount of energy to dissipate in a single step. The weak electron–atom coupling makes nonradiative decay an extremely unlikely event and the low probability for semiconductor materials to dissipate electronic energy as heat is probably their most unique property. By contrast, in organic molecules, decay by nonradiative recombination is sufficiently likely to occur that it is given the name internal conversion.

In fact, nonradiative recombination does occur in semiconductors, but primarily as a result of chemical defects that introduce new energy levels into the forbidden gap. These defect levels act as stepping stones, permitting conduction electrons to cascade down to the valence band in two smaller steps rather than one improbable leap. An energy level within the forbidden gap owing to a defect D is shown in Figure 1. The defects act as electron–hole recombination catalysts, promoting recombination without being consumed themselves. This model of stepwise nonradiative recombination through impurities or other defects is associated with the names of Hall (3) and Shockley and Read (4).

Thus a principal goal of semiconductor materials science has been to create chemically perfect semiconductor structures. Any defects that disturb the perfect valence bonding structure, allowing energy levels in the forbidden gap, must be eliminated as far as possible. Even the utmost extrinsic chemical purity is insufficient, however, because intrinsic defects such as broken bonds, self-interstitials, and vacancies are also proscribed. In particular, unsaturated chemical bonds on the material surface, or in the bulk, contribute nonbonding orbitals having unwanted energy levels in the forbidden gap. The rigid, tetrahedrally coordinated semiconductor crystal structures of silicon [7440-21-3], Si; germanium [7440-56-4], Ge; and gallium arsenide [1303-00-0], GaAs, have a tendency to reject both extrinsic and intrinsic defects, contributing to their technological success.

3. Semiconductor Surfaces

Semiconductor surfaces are the most likely location for intrinsic defects such as dangling or weak bonds to occur. The need for surfaces of extremely high chemical quality can be appreciated from examination of Figure 2 showing the point contact germanium transistor. The emitter point contact emits a cloud of minority carriers (Fig. 2**a**), which by definition are the least dense of the two types of carriers, either electrons or holes. As indicated in Figure 2**b**, these minority carriers undergo a random walk to find the small-area collector point contact. If the transistor is to have any significant gain, almost all the minority carriers must be

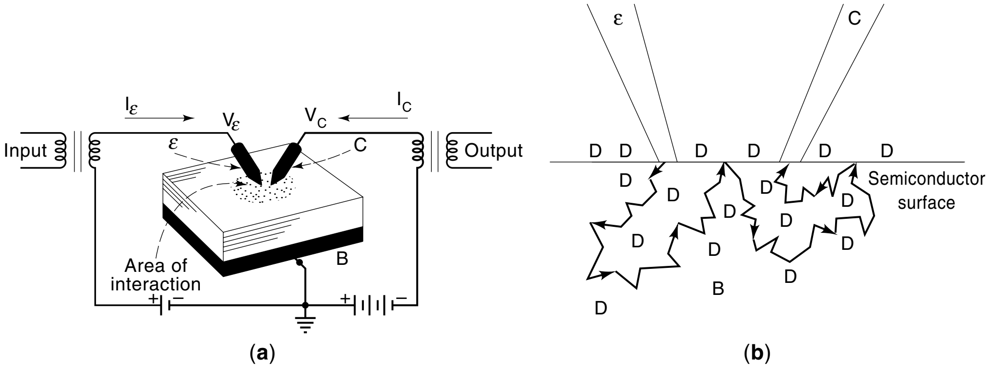

Fig. 2. A germanium transistor where B is the base, C, the collector, and ε, the emitter. (**a**) The external transistor circuit showing the diffusion cloud of minority carriers around the emitter point contact; I_C and $I_ε$, and V_C and $V_ε$, are the current and the voltage of the collector and emitter, respectively. (**b**) The area of interaction showing a typical random walk the minority carriers must undergo, passing a gauntlet of defects D in order to find the collector point contact. In practice, the surface concentration of defective chemical bonds must be less than 1 per 10,000 surface bonds for the carriers to have any significant probability of finding the collector before recombining. Defects are usually less than 1 in 10^4 to 1 in 10^7 at the surface and less than 1 in 10^6 to 1 in 10^{11} in the bulk material. For the transistor to have any significant gain, almost all the carriers must find the collector.

collected. During the random walk these carriers must pass a gauntlet of defects any one of which could catalyze recombination (see INTEGRATED CIRCUITS).

On average, a carrier scatters off the surface thousands of times before it finally stumbles its way into the collector. If even a tiny fraction of the surface were covered with defects, the carriers would never make it to the collector. A germanium surface covered with a natural air-grown oxide has less than 1 part per 10,000 of defective chemical bonds on the surface. The discovery of the Ge point-contact transistor was therefore critically dependent on this chemical property. Indeed the point-contact transistor is not possible using silicon or any of the other semiconductor compounds known as of this writing. The density of chemical defects at interfaces having air-grown oxides is generally too high.

The bulk chemical defect densities that can be tolerated in solid-state electronics range from 1 in 10^6 to 1 in 10^{11}, depending on the specific application. Corresponding surface defect densities that can be tolerated range from 1 in 10^4 to 1 in 10^7, ie, nearly all of the semiconductor surface atoms must be cleanly saturated with strong covalent bonds, because defects introduce energy levels into the forbidden gap. These requirements for semiconductor surfaces and interfaces give rise to a chemical figure of merit, ie, equivalent to a surface chemical reaction having a 99.99% to 99.99999% yield. The surface of germanium minimally satisfies this requirement in air, permitting the discovery of the first transistor, but the germanium surface cannot be further improved.

4. The Role of Silicon

4.1. The Si–SiO$_2$ Interface. Beginning in the mid-1950s (5), thermal oxidation of silicon at high temperatures in oxygen was begun, coating the silicon with a thin layer of silicon dioxide [7631-86-9], SiO_2, glass. The thermal oxidation recipe was gradually perfected (6,7) and by the late 1960s the figure of merit for the $Si{-}SiO_2$ interface had been improved to 1 defective chemical bond in 10^6. The $Si{-}SiO_2$ interface is an amorphous crystalline heterojunction. The interfacial bonds can be 99.9999% saturated. Thus, in short order the microprocessor (1969), the memory chip (1971), and the pocket calculator (1972), were developed. In 1975 *Time* magazine declared the microcomputer to be the Man-of-the-Year. In 1992, microchip production was a $\sim\$6 \times 10^{10}$ annual industry worldwide, supporting a $\sim\$5 \times 10^{11}$ systems, software, and communications industry and millions of highly educated people.

4.2. Purification of Silicon. Chemical purity plays an equally important role in the bulk of materials as on the surface. To approach the goal of absolute structural perfection and chemical purity, semiconductor Si is purified by the distillation of trichlorosilane [10025-78-2], $SiHCl_3$, followed by chemical vapor deposition (CVD) of bulk polycrystalline silicon.

$$SiHCl_3 + H_2 \xrightarrow{1100^\circ C} Si\ (s) + 3\ HCl\ (g) \tag{1}$$

Purified polycrystalline CVD silicon from this reaction is then melted and a single-crystal boule weighing as much or more than 50 kg, and having a diameter up to 20 cm, is pulled from the melt by Czochralski growth (8). Metallurgical-grade silicon is not sufficiently pure for applications in electronics (see SILICON AND SILICON ALLOYS).

The distillation of $SiHCl_3$ is a relatively straightforward and low cost purification method. On the other hand, the reprecipitation of elemental silicon by CVD is expensive and complicated because of the need to maintain the utmost purity at highly elevated temperatures. Long narrow rods of polycrystalline silicon are heated by an electric current to ~1100°C providing the thermodynamic conditions for silicon precipitation. Because the yield in equation 1 is only ~10%, there is considerable recycling of chlorosilane reagents. In this respect, the semiconductor silicon factory is typical of most chemical plants. The growth of the polycrystalline silicon rod is diffusion rate limited, ~1 μm/min, taking as long as two weeks to grow out to a 10-cm diameter. Therefore the process is very slow, very capital intensive, and because heat is continually radiated away at 1100°C during the long growth period, very energy intensive as well. Heat radiation reflectors are employed to reduce energy cost, as well as clusters of rods which intercept one another's thermal radiation. Owing to the electrical energy cost component, semiconductor silicon plants are frequently located in regions having low cost hydroelectric power, such as the Pacific Northwest of the United States. To further reduce the energy cost, silane [7803-62-5], SiH_4, gas decomposition is being used in at least one large plant to produce semiconductor silicon in large volumes. The advantage of using silane is that decomposition takes place at a diminished temperature, ~800°C.

Semiconductor-grade polycrystalline silicon costs about $40/kg. Of the two high temperature processing steps, CVD and crystal growth, the CVD process is more responsible for the high monocrystalline silicon boule costs. The single-crystal boule that finally results from CVD and crystal growth can have a bulk purity of 1 part in 10^{11}, not counting oxygen and carbon impurities which are relatively benign. Normally the entire boule is structurally perfect, ie, there are no dislocations. Worldwide, around 40,000 metric tons of electronically pure silicon are produced per year and the cost is less than \$10 per 10-cm diameter wafer.

5. III–V Semiconductors

For optoelectronics the binary compound semiconductors drawn from Groups 13 and 15 (III and V) of the Periodic Table are essential. These often have direct rather than indirect band gaps, which means that, unlike Si and Ge, the lowest lying absorption levels interact strongly with light. The basic devices of optical communications, light-emitting diodes (LEDs) (see LIGHT GENERATION, LIGHT-EMITTING DIODES) and semiconductor lasers, are made of these III–V semiconductors. Aluminum arsenide [22831-42-1], AlAs, GaAs, and the alloys of these compounds have historically been the most important III–V material system. The reason once again derives from the need to control interfacial chemical bonding structures.

The double heterostructure, invented in the early 1960s (9), is shown schematically in Figure 3. It is essentially a crystalline sandwich: the bread is made of AlAs and the filling of GaAs. Because the band gaps of AlAs and GaAs are 2.2 eV and 1.4 eV, respectively, the GaAs wave functions are sandwiched in by the 2.2 eV potential barriers, as shown. Although the electrons and holes are prevented from seeing any external surface, they do see the AlAs–GaAs interface. However, the cubic unit cell dimensions of GaAs and AlAs are 0.56533 nm and 0.56605 nm, respectively. Thus the mismatch at the interface is less than 0.1% meaning that the crystal structures can match up nearly perfectly, leaving only a few unsaturated chemical bonds at the interface. Generally, the interfacial bonds in the $Ga_{1-x}Al_xAs$ system are 99.999% saturated. Although this is not as good as the best $Si-SiO_2$ interfaces, it is excellent nonetheless. The growth of successive atomic layers of semiconductor material, in perfect registry with atoms in the underlying crystal, is called epitaxy; the perfect atomic registry between layers of differing composition is called heteroepitaxy.

When the sandwich in Figure 3 is made very narrow, quantum confinement influences the wave functions in the GaAs. Excellent control is possible because the layers can be grown one atomic monolayer at a time (10). The wave functions can also be modified by alloying aluminum [7429-90-5], Al, or indium [7440-74-6], In, into the GaAs. Moreover, arsenic [7440-38-2], As, can be replaced by phosphorus [7723-14-0], P, or antimony [7440-36-0], Sb. Furthermore, lattice matching can be accomplished by intentionally straining mismatched systems (11). Much research is oriented toward extending these artificial structures into the third dimension (12).

Inorganic semiconductor crystals have innumerable possible arrangements. Whereas there has been a long-standing call (13) for a molecular electronics based on organic molecular structures, inorganic quantum structures are already being made and there is a well-developed inorganic electronics. Hydrocarbon-based molecules do not satisfy the requirements of wave function

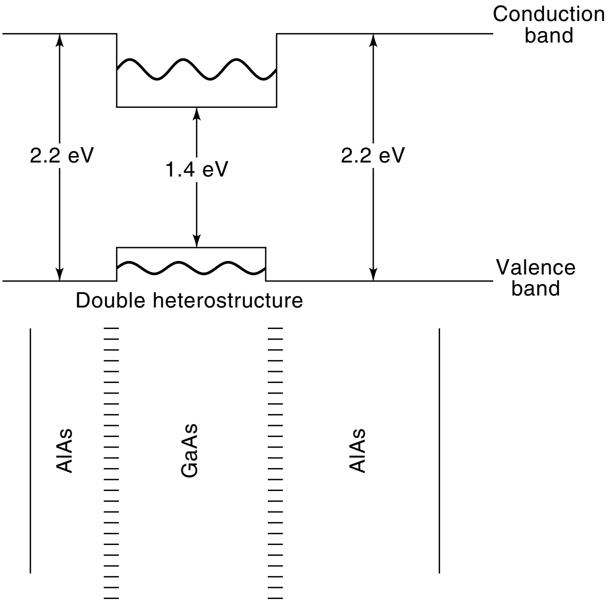

Fig. 3. The lattice-matched double heterostructure, where the waves shown in the conduction band and the valence band are wave functions, (x), representing probability density distributions of carriers confined by the barriers. The chemical bonds, shown as short horizontal stripes at the AlAs–GaAs interfaces, match up almost perfectly. The wave functions, sandwiched in by the 2.2 eV potential barrier of AlAs, never see the defective bonds of an external surface. When the GaAs layer is made so narrow that a single wave barely fits into the allotted space, the potential well is called a quantum well. Because of the match in the atomic spacings between GaAs and AlAs, 99.999% of the interfacial chemical bonds are saturated.

delocalization, weak electron–atom coupling, and structural perfection to the same degree that the successful inorganic semiconductors do.

Physics and chemistry researchers approach III–V synthesis and epitaxial growth, ie, growth in perfect registry with the atoms of an underlying crystal, differently. The physics approach, known as molecular beam epitaxy(MBE), is essentially the evaporation (14–16) of the elements, as illustrated in Figure 4. The chemistry approach, organometallic chemical vapor deposition (OMCVD) (17) is exemplified by the typical chemical reaction:

$$\mathrm{Ga(CH_3)_3 + AsH_3 \xrightarrow{580^\circ C} GaAs\ (s) + 3\ CH_4\ (g)}$$

Thin-film epitaxy by OMCVD is generally more flexible, faster, lower in cost, and more suited for industrial production than MBE. An OMCVD system usually consists of two principal components, a gas manifold for blending the gas composition, and a graphite substrate holder which is usually inductively heated. A schematic diagram of an OMCVD system is shown in Figure 5.

The development of double-heterostructure III–V semiconductor lasers (18) together with the demonstration of low loss SiO_2 glass fibers (19) which both

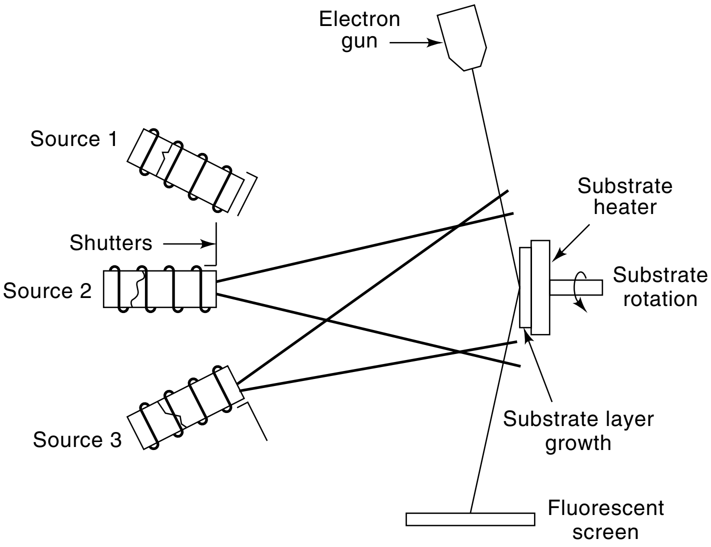

Fig. 4. Schematic of an ultrahigh vacuum molecular beam epitaxy (MBE) growth chamber, showing the source ovens from which the Group III–V elements are evaporated; the shutters corresponding to the required elements, such as that in front of Source 1, which control the composition of the grown layer; an electron gun which produces a beam for reflection high energy electron diffraction (rheed) and monitors the crystal structure of the growing layer; and the substrate holder which rotates to provide more uniformity in the deposited film. After Ref. 14, see text.

occurred coincidentally in 1969, gave birth to optical communications. Optical fibers are the technology of choice in newer trunk and long-distance communications installations, and optical fibers are expected to connect to individual telephone subscribers soon, making unprecedented bandwidth available for revolutionary new services (see Fiber optics). The materials for these fibers are prepared by these thin-film crystal growth processes, MBE and OMCVD.

In an MBE growth reactor, the Group III–V elements are evaporated from source ovens in a growth chamber having background pressure in the $10^{-9} - 10^{-8}$ Pa ($10^{-11} - 10^{-10}$ torr) range. The crucible holding the Group III–V elements is usually made of boron nitride [10043-11-5], BN, or alumina [1344-28-1], Al_2O_3, which is radiatively heated by a refractory metal filament (see Refractories). The composition of the growing layer is controlled by shutters, which correspond to the respective elements and source ovens. The crystal structure of the growing layer is monitored by reflection high energy electron diffraction (rheed).

In contrast to MBE, OMCVD can be carried out either at atmospheric or at low pressures. A critical role is played by ultrapure hydrogen [1333-74-0], H_2, which is produced by diffusion through a metal filter made of a heated palladium [7440-05-3], Pd, membrane. Only hydrogen gas can diffuse through such a membrane; thus, chemical purity is maintained even at high pressures. Substrates are placed on a graphite susceptor and heated by either radio frequency induction or infrared radiation. The gas manifold shown in Figure 5 is designed to

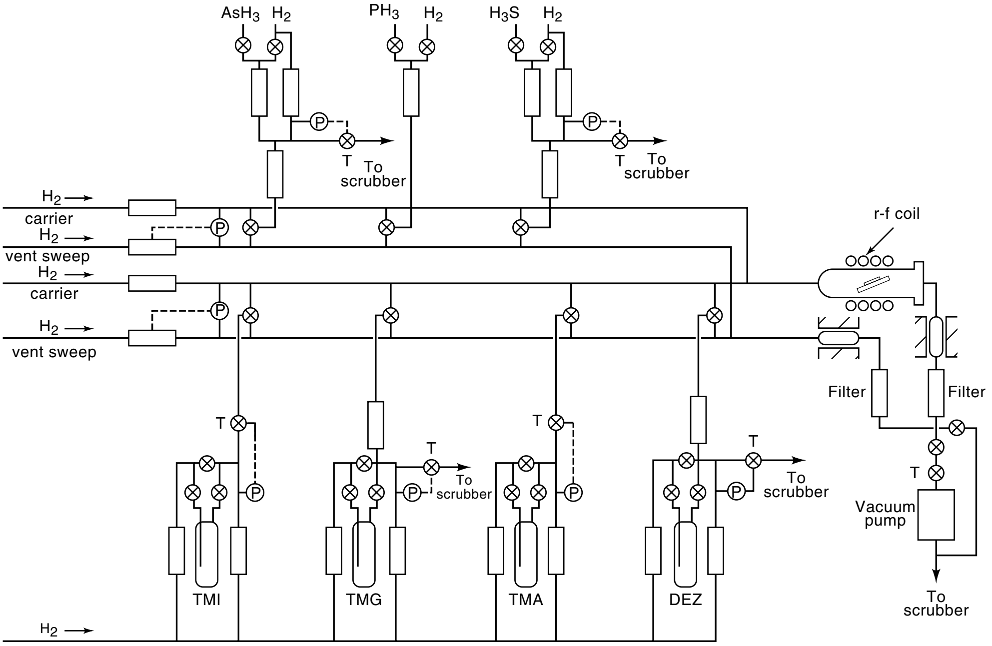

Fig. 5. A gas manifold for the production of epitaxial layers of Group III–V semiconductors by OMCVD where ▭ represents a mass flow controller; ⊗, a pneumatic valve; $\overset{T}{\otimes}$, a throttle valve; Ⓟ, pressure sensor and controller; and –⊂⊃–, a pyrolysis oven. Reactive gases are swept along by ultrapure hydrogen gas. Gases are trimethylindium [3385-78-2] (TMI); trimethylgallium [1445-79-0] (TMG); trimethylaluminum [75-24-1] (TMA); and diethylzinc [557-20-0] (DEZ). The semiconductor wafer is on a graphite susceptor inside the radio frequency (r-f) coil (17).

allow abrupt changes in gas composition, corresponding to abrupt interfaces between layers of different composition in the growing material. The ability to select various precursor gases (20) provides considerable flexibility for optimizing the reactor conditions. For example, some gases are considerably less toxic than the arsine [7784-42-1], AsH_3, and phosphine [7803-51-2], PH_3, which have traditionally been used for OMCVD. Other gases can produce less carbon contamination, or conversely can produce more efficient doping by carbon, etc. The gas composition parameters are likely to be an important engineering variable as OMCVD develops in the future.

Control over the inorganic chemistry of semiconductor crystals, surfaces, and interfaces has determined the rate of progress in solid-state electronics. Whereas inorganic electronic materials have been emphasized herein, organic materials are also important to the electronics revolution, not as the active electronic material, but as enabling components. For example, photoresists are photographic materials that allow the patterning of microcircuits (see LITHOGRAPHY; PHOTOCONDUCTIVE POLYMERS), and insulators, such as the polyimides (qv), are helpful in microcircuit fabrication and packaging (see INSULATION, ELECTRIC; PACKAGING, SEMICONDUCTOR AND ELECTRONIC MATERIALS).

BIBLIOGRAPHY

"Electronic Materials", in *ECT* 4th ed., Vol. 9, pp. 219–229, by Eli Yablonovitch, University of California at Los Angeles; "Electronic Materials" in *ECT* (online), posting date December 4, 2000, by Eli Yablonovitch, University of California at Los Angeles.

CITED PUBLICATIONS

1. W. Shockley, *Electrons and Holes in Semiconductors*, Van Nostrand, New York, 1950.
2. E. Yablonovitch and E. O. Kane, *J. Lightwave Tech.* **LT-4**, 504 (1986). In present-day semiconductor lasers, E_{Fv} does not extend all the way down into the valence band as shown in Figure 1, penalizing efficiency.
3. R. N. Hall, *Phys. Rev.* **87**, 387 (1952).
4. W. Shockley and W. T. Read, *Phys. Rev.* **87**, 835 (1952).
5. M. M. Atalla, E. Tannenbaum, and E. J. Scheibner, *Bell Syst. Tech. J.* **38**, 749 (1959).
6. B. E. Deal, E. H. Snow, and A. S. Grove, *Semicond. Prod. Solid-State Technol.* **9**, 25 (1966).
7. A. S. Grove, *Physics and Technology of Semiconductor Devices*, John Wiley & Sons, Inc., New York, 1967.
8. K. E. Benson in S. Mahajan and L. C. Kimerling eds., *Encyclopedia of Semiconducting Materials and Related Technologies*, Pergamon Press, Oxford, UK, 1992, p. 467.
9. H. Kroemer, *Proc. IEEE* **51**, 1782 (1963); USSR Pat. 181737 (1963). Z. I. Alferov and R. F. Kazarinov.
10. M. A. Tischler, N. G. Anderson, and S. M. Bedair, *Appl. Phys. Lett.* **49**, 1199 (1986).
11. G. C. Osbourn, R. M. Biefeld, and P. L. Gourley, *Appl. Phys. Lett.* **41**, 172 (1982).
12. M. Tsuchiya and co-workers, *Phys. Rev. Lett.* **62**, 466 (1989).
13. F. L. Carter, ed., *Molecular Electronic Devices*, Marcel Dekker, Inc., New York, 1982.
14. J. P. Harbison in Ref. 8, p. 306.
15. L. L. Chang and K. Ploog, eds., *Molecular Beam Epitaxy and Heterostructures*, Martinys Nijhoff, Dordrecht, The Netherlands, 1985.
16. M. A. Herman and H. Sitter, *Molecular Beam Epitaxy: Fundamentals and Current Status*, Springer-Verlag, Berlin, 1989.
17. R. Bhat and S. Mahajan in Ref. 8, p. 349.
18. M. B. Panish and I. Hayashi, *Appl. Phys. Lett.* **16**, 326 (1970).
19. R. D. Mauer, *Proc. IEEE* **61**, 452 (1973).
20. G. B. Stringfellow, *OMVPE: Theory and Practice*, Academic Press, Boston, Mass., 1989

ELI YABLONOVITCH
University of California at Los Angeles