Chemistry. Many of the chemicals and process steps used for PCB processing are similar to those used in the POP industry; however, electroless copper is used exclusively.

Application Methods. The three PCB processing techniques may be summarized as:

Subtractive process	Semiadditive process	Additive process
copper-clad board	thin copper-clad board	unclad board
form holes	form holes	adhesive coat
catalyze	catalyze	form holes
accelerate	accelerate	etch surface
electroless copper	electroless copper	catalyze
positive resist coat	negative resist coat	negative resist coat
electrolytic copper	electrolytic copper	accelerate
dissimilar metal electroplate	dissimilar metal electroplate	electroless copper
strip resist	strip resist	
etch copper	etch copper	

Additive and semiadditive processing can give material savings and higher circuit densities, whereas subtractive processing is technologically easier.

Additional steps used for multilayer production include application of black or red oxide to foil; application of photoresist or screened etch resist; imaging and development of photoresist; copper etching; removal of resist; assembling of layers, checking registration and lamination; drilling; and removal of drill smear on copper inner layers. Rinses and additional cleaning, neutralizing, light etching, and developing steps are required.

Electroless Copper. Electroless copper, introduced in the mid-1950s, is available commercially in great variety. Formaldehyde is usually the reducing agent, copper sulfate (occasionally copper nitrate or copper chloride) is the metal salt, and sodium hydroxide is used to control pH. The complexers may be tartrate, ethylenediaminetetraacetic acid (EDTA), tetrakis(2-hydroxypropyl)ethylenediamine, nitrilotriacetic acid (NTA), or some other strong chelate. Numerous proprietary stabilizers, eg, sulfur compounds, nitrogen heterocycles, and cyanides (qv) are used. These formulated baths differ in deposition rate, ease of waste treatment, stability, bath life, copper color and ductility, operating temperature, and component concentration. Most have been developed for specific processes; all deposit nearly pure copper metal.

Printed Circuit Etchants. Two types of etchants are used in printed circuit board processing for entirely different purposes. Etchants used for etchback or desmear attack only organic materials, whereas copper etchants dissolve only copper. Etchback refers to massive removal of the organic board material perpendicular to the drilled hole, to expose annular copper rings from the inner layers of multilayer boards to ensure good conductivity after plating. Desmear is a less aggressive type to roughen drilled hole surfaces and remove organic residues from the drill-exposed copper inner layers. Older chromic acid and sulfuric acid etchants have been replaced by regenerable permanganate systems and by plasma etching. These etchants directly contribute to electroless plating through microroughening the surface and removing loosely bonded debris, thereby improving adhesion and performance.

Emerging Printed Circuit Technologies. Much research has been devoted to developing safer, cheaper, and more reliable alternatives to formaldehyde reduced electroless coppers, and many processes are in the advanced stages of development. These include hypophosphite-reduced electroless coppers; substitution of conductive graphite colloids for electroless coppers; direct electroplating over catalyzed or catalyzed and sulfide treated substrates; and non-noble metal catalysts. Three-dimensional printed circuit boards, usually on engineering quality plastics, are becoming more common (see ENGINEERING PLASTICS). High performance boards of novel types continue to be developed with controlled impedance layers; ultrathin and narrow copper conductors; ceramic substrates; high temperature plastic laminates; and Invar or Kovar inner layers in place of copper or dielectric.

Other Processes

Silver, the first metal used for metallizing nonconductors, is rarely employed because of high cost, low stability, and inability to plate a thick deposit autocatalytically. Formulations typically consist of ammoniacal silver nitrate solutions and a reducing agent of sugar, formaldehyde, hydrazine, or dimethylamineborane. These baths are generally unstable, and are used until exhausted.

Most electroless silver applications are for silvering glass or metallizing record masters. Mirror production is the principal usage for electroless silver. Silver is also used in the jewelry and button industry.

The other important commercial glass-plating application is for production of architectural reflective glasses. Translucent metal films are used for decoration and for reduction of environmental heat gain. Electroless plating is used by one producer for this type of product.

Ceramic plating is similar to glass plating in that a two-step catalyst is used. The surface is often mechanically roughened or chemically etched to improve the metal adhesion.

An electroless nickel matrix can be used to securely bond diamonds to cutting tools, and electroless nickel–diamond composites are also used (see TOOL MATERIALS).

Electroless gold is commercially used on printed circuit boards, flex circuits, ceramics, three-dimensional circuits, metals, and highly specialized substrates. The newest type is extremely stable and cost-effective; older baths were highly unstable. Electroless palladium is also used in specialty applications in the electronics industry where the need for pore-free or discontinuous coatings justifies the high price. Both coatings are normally applied over electroless nickel, Kovar, or other materials, but cannot be used directly on copper.

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ELECTRONIC MATERIALS

Electronic materials are those exquisitely pure crystal structures which form the basis for the information technology of the 1990s. The chemistry and chemical engineering required for making electronic materials, ie, these very specific inorganic chemical bonding structures, have come about by techniques employing chemical vapor deposition to effect material growth and through an increased control over surface and interfacial chemistry.

Semiconductor Energy Levels

Semiconductor materials are rather unique and exceptional substances. The entire semiconductor crystal is one giant covalent molecule. 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. 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, of all the electrons in the material, the possibility exists for two separate quasi-Fermi levels in the same crystal.

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.

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, Si; germanium, Ge; and gallium arsenide, GaAs, have a tendency to reject both extrinsic and intrinsic defects, contributing to their technological success.

Semiconductor Surfaces

Semiconductor surfaces are the most likely location for intrinsic defects such as dangling or weak bonds to occur. 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 form 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 Role of Silicon

The Si–SiO₂ Interface. Beginning in the mid-1950s, thermal oxidation of silicon at high temperatures in oxygen was begun, coating the silicon with a thin layer of silicon dioxide, SiO_2, glass. The thermal oxidation recipe was gradually perfected 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, and the pocket calculator, were developed. In 1992, microchip production was a ~$6 × 10^{10} annual industry worldwide, supporting a ~5 × 10^{11} systems, software, and communications industry, employing millions of highly educated people.

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, $SiHCl_3$, followed by chemical vapor deposition (CVD) of bulk polycrystalline silicon (at 1100°C), $SiHCl_3 + H_2 \rightarrow Si(s) + 3HCl(g)$. 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. Metallurgical-grade silicon is not sufficiently pure for applications in electronics (see SILICON AND SILICON ALLOYS).

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, 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, 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. 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.

Physics and chemistry researchers approach III–V synthesis and epitaxial growth differently. The physics approach, known as molecular beam epitaxy (MBE), is essentially the evaporation of the elements. The chemistry approach, organometallic chemical vapor deposition (OMCVD) is exemplified by the typical chemical reaction: (at 580°C) $Ga(CH_3)_3 + AsH_3 \rightarrow GaAs(s) + 3CH_4(g)$. 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.

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ELECTRONICS, COATINGS

Coating technology can be defined as replacing air at the surface of a substrate to give a film structure having varying layers of different properties. This technology covers a wide range of products and processes (see COATING PROCESSES; COATINGS; PAINT). Electronics coatings refers to the wide variety of coated structures used in electronic devices.

These coatings have some unique aspects of formulation, production, and use. The ability to produce high resolution coatings, at high volume and low cost, has been the driving force for the revolutionary advances in a wide variety of electronic components, integrated circuits (qv), memory chips, magnetic storage devices, cathode ray tubes, optical storage disks, etc (see also ELECTRONIC MATERIALS; INFORMATION STORAGE MATERIALS). Improved functionality of these components has led to advances in a wide range of consumer, industrial, and military products. Typical devices are television sets, video cassette recorders, cameras, fax machines, cellular phones, personal and laptop computers, fly-by-wire control systems for airplanes, and the guidance system for such military ordnance as smart bombs and cruise missiles.

Significant advances have also been made in the more traditional area of wire and cable used to transmit the electricity needed for these devices (see ELECTRICAL CONNECTORS). The optical cables (see FIBER OPTICS; NONLINEAR OPTICAL MATERIALS) that are replacing the traditional copper (qv) cables for telephone usage require very sophisticated coatings to protect cable from light loss and deterioration. The ribbon cable and multiple coaxial cable assemblies used for cable television, stereo systems, and burglar alarms all depend on the cable coatings reducing interference with each other so that signal quality is maintained.

Economic Aspects

Electronic coatings are of significant economic importance, as are the finished products in which they go. The worldwide total value of the resulting products is $500 billion. The annual electronic coatings market value is estimated to be $5 billion. These coatings are manufactured in several countries. Some of the principal manufacturers of electronic coatings are

Company	Products
Minnesota Mining and Manufacturing	conformal coatings
W. R. Grace & Co.	dielectric and conductive adhesives, encapsulants, heat dissipating materials, manufacturing aid coatings
Union Carbide Corp.	Parylene conformal coatings, photoresists, developers, etchants, solder masks, potting compounds
Conap unit of American Cyanamid	potting compounds, conformal coatings
DuPont Co.	conformal coatings, photoresists, manufacturing aids, electronic functional coating compounds
OGG Microelectronic Materials, Olin/CIBA-GEIGY venture	photosensitive polyimides, high performance semiconductors
Dexter	encapsulants
Dow Corning	potting and encapsulating compounds
Asahi	packing materials
Nippon Kayaku	packing materials
General Electric	packaging materials
Unilver	adhesives, dielectric coatings, protective coatings, dielectric interlayers, electronic functional coatings

Functions of Electronics Coatings

Electronics coatings can generally be classified as (*1*) functional, ie, coatings that provide a variety of electrical, magnetic, optical, chemical, mechanical, and/or thermal properties enabling a device to function as prescribed; (*2*) manufacturing aids, ie, coatings that serve as an integral part of the manufacturing process to make a specific component or device; or (*3*) protective/decorative, ie, coatings that protect the component or device from environmental damage during its normal use cycle.

Coatings Properties

Material property specifications must be written by design and material engineers to control engineering requirements and to control incoming raw material quality. Material property requirements depend on various in-use functional needs in terms of electrical, mechanical, thermal, chemical, optical, and magnetic properties.

Electronic coatings can be classified as either organic, inorganic, or metallic. Organic coatings are typically polymeric in nature. A wide variety of polymer types are used. Although polymeric properties vary considerably less over the full range than those of the inorganics and metallics, both chemistry and molecular structure play a role because these dictate properties and coating behavior. A list of polymer uses in electronic coatings follows. More detail can be found in the literature.

Polymer	Uses
alkyd	polyesters for protective and decorative coatings; paints
acrylic	general purpose for molding, casting, and coating formulations; dip and sprayable PC board coatings
epoxy	protective and electrical-grade adhesives, electronic encapsulation, composites, and PC boards; solder masks
fluorocarbons	good chemical and electrical properties, protective coatings, release coatings, barrier coatings
phenolic	work-horse thermoset for adhesives; parts
polyimide	high temperature applications, glass-reinforced PC boards, flexible film and cable, interlayer dielectrics
polyurethane	tough, abrasion resistant for casting, potting, and encapsulation of connectors and modules; conformal coatings for PC assemblies
polyvinyls	chlorides, fluorides, vinylidene chlorides and fluorides, vinyl aldehydes, and polystyrene; used for moisture barriers, primary-wire insulation, corrosion protection, dielectric impregnants, and baking enamels
polyxylylene	conformal coatings for PC assemblies; insulation