11 April 1969, Volume 164, Number 3876 SCIENCE

Electronic Materials and Applications

Harry C. Gatos

I attempt here to review the role of materials and materials processing in solid-state electronics with an eye on the future. Semiconductors are given primary emphasis, but much of what pertains to semiconductors can be readily extended to other electronic materials such as superconductors, magnetics, and optical materials.

Electronic materials are not necessarily a distinct class of materials, but they are referred to as such when they are considered in the context of electronic processes in which transport of electrical carriers or quantum transitions of the constituents of the atom are involved. Such a distinction cannot of course be precise, or need it be particularly meaningful. For example, since its discovery, silicon carbide has been known and used as an abrasive or refractory material. It still is; but in recent years it has taken a distinguished place among electronic materials as well. Aluminum oxide is a widely used abrasive, it is a widely used gem (particularly as ruby, which contains small amounts of chromium impurities), and recently (again in the form of ruby) it has become a very important optical material for lasers.

In assessing the present or considering the future of electronic materials, or of any materials, I believe the following question must be asked: Is it the phenomenon and the envisioned application that lead to a search for the material, or is it the material that leads to the discovery of the application? There is no simple answer to this question, but I will attempt to deal with some of its aspects.

An "effective" interplay between material and application requires an understanding of the principles involved in the application, an understanding of the material itself, and control of the material design parameters. Obviously the achievement of such an interplay is not commonplace; in fact, depending on what is meant by "effective," it may never have been fully realized. Yet a truly sound way to look into the future is to extrapolate from the existing material-phenomenon-application relationship. This approach is certainly suitable in the case of electronic materials and solid-state electronics, where fundamental understanding of materials and concepts for new applications are in the lead, and where realization of the concepts requires materials of a chemical and crystalline perfection not yet attainable.

It should be instructive to reflect on some past developments in materials and then, through the present, to attempt to look into the future.

Metals

The class of materials known as metals is an interesting one. Metals have been used from ancient times, occasionally with great proficiency, as in the bronzes of antiquity or the swords of Damascus. Yet, through the centuries, lack of understanding of the nature of metals stood in the way of realizing more of their potential. The search in the Middle Ages for the "philosopher's stone" that would turn base metals into gold may not be a fair reflection of man's understanding of metals at that time, after many centuries of use, but it is a reflection nevertheless.

The use of metals has developed largely through a trial-and-error process. Even today the development of metallic alloys is as much an art as it is a science. For example, the stainless steels were empirically developed half a century ago, yet to this day their unusual properties are not understood. Application has usually preceded understanding; however, every advance in understanding raised the starting level of the trial-and-error exercise. A great impetus to the use of metals and, in fact, to the industrial revolution was the increased understanding of steelmaking processes that was achieved in the mid-19th century. Again, in the 1920's fundamental studies on metal single crystals brought important phenomena like plastic deformation, annealing, hardening, grain growth, and others to a level of understanding which, although not definitive, served as the springboard for a new trial-and-error era and for development of the more complex and subtle alloys of present technology.

Abrasives

Another interesting general class of materials is the class of abrasives. These, like metals, were a part of life from primitive times. Early man shaped his stone tools by rubbing stones against harder stones, which he discovered by trial and error. The trial-and-error process still goes on, for the phenomenon of abrasion is extremely complex and not even today fully understood. Yet the art of abrasion had to, and did, keep pace with the needs of the times. Artisans incredibly skilled in abrasion (makers of jewelry, for example) lived from ancient Egyptian times on. More importantly, as a result of truly heroic engineering and semi-empirical efforts, abrasives and abrasive techniques of extraordinary complexity and precision are available to

The author is professor of electronic materials in the department of metallurgy and materials science and professor of molecular engineering in the department of electrical engineering at the Massachusetts Institute of Technology, Cambridge.

present-day technology. And, as in the case of metals, the development efforts, empirical as they may have been, were enormously aided by every advance in the understanding of fundamental properties such as brittleness, hardness, crystallinity, cohesive forces, and even chemical bonding. In parallel, chemical synthesis has added new dimensions by introducing synthetic abrasives like silicon carbide, boron, carbides, synthetic aluminum oxide, and synthetic diamond.

But the spectrum of applications in abrasives and in metals is much broader than the corresponding spectrum of fundamental understanding. Nevertheless, empirical development and basic understanding have always been, and will continue to be, critically dependent on each other. The remarkable present state of alloy steels could not have been achieved without empiricism on the one hand and, on the other, without understanding of the complex iron-carbon phase equilibrium diagram and its nonequilibrium structural configurations.

Elemental Semiconductors

The class of semiconductors stands in striking contrast to all other classes of materials. In my opinion, the unique position of semiconductors in the world of materials must be explicitly appreciated if an assessment of the present status and future trends is to be meaningful at all.

Semiconductors were launched into prominence with the discovery of the transistor in 1948. In the amazingly short period of 4 to 6 years the elemental semiconductors germanium and silicon became better understood than any other material. Their covalent nature, with the well-defined four-nearest-neighbor coordination and highly directional bonds, made possible truly elegant theoretical studies based, to a large extent, on first principles. Furthermore, due to their unique nature, which is intimately related to their position in the middle of the periodic table (group IV), it was possible to prepare them at purities of the order of 0.1 part per billion, which had not been achieved before and have not been achieved since with any other material. Similarly, nearly theoretical crystalline perfection became attainable in germanium and silicon. Consequently, experimental studies were carried out at extraordinary stages of refinement, so that theory and experiment reinforced each other with an effectiveness hardly approached before. Thus, the detailed structure of the electron energy bands, the effective masses of the electrical carriers, their transport and scattering characteristics, their interaction with impurity atoms or structural defects, and their response to electric and magnetic fields became well-understood realities.

The outcome was (in the early 1950's) a situation rare in the history of science and engineering: theory and basic understanding of materials overtook technology. That is, new phenomena, new devices, and, in general, new aspects of electronic behavior were predicted before the materials themselves could be brought to the necessary level of chemical and structural control. For example, the cyclotron resonance which eventually allowed direct and accurate determination of the effective mass of the electrical carriers was observed, and numerous semiconductor devices (including the field effect transistors) were developed, long after they were theoretically described. In other words, soon after the transistor was discovered, the development of suitable materials, rather than basic understanding or device principles, became the slow step in the progress of solid-state electronics. This exact situation prevails today.

Actually, since the discovery of the transistor, every burst forward in solid-state electronics has sprung from a new advance in materials technology. The large-scale application of zone refining to the purification of germanium and silicon literally opened the gates to modern solid-state electronics. The amazing purity levels referred to above were reproducibly achieved on an industrial basis.

But in the early 1950's transistor technology came to a standstill and in fact was shaken to its foundation because, unexpectedly, the stability, life, and reproducibility of transistor devices could not be controlled in mass production. It was not until the problems of semiconductor surface sensitivity and deterioration were solved that solid-state electronics really took hold.

The next landmark was the development of planar diffusion processes whereby sharp *p-n* junctions could be made with characteristics far superior to those of junctions prepared from the molten state (grown junctions). Diffused junctions opened new vistas for the development of silicon and germanium devices with improved reproducibility, speed, and versatility. Later on came the development of highly controlled vapor-solid reactions (epitaxial and evaporation techniques) which, together with further refinements in planar diffusion processes, led straight to today's amazing integrated circuitry.

The progress in integrated circuitry is indeed awe-inspiring. Tiny silicon chips (3 by 3 millimeters) can now contain a completely integrated circuit with about 250 individual components, including about 50 transistors. Here is an illustration of the impact that integrated circuitry is making. A new integrated-circuit computer has replaced the original transistorized computer in the Minuteman missile. The original computer weighs 70 pounds and has approximately 15,000 individual parts; the new one weighs 36.5 pounds and has 5500 parts. The power requirement for the original computer is 350 watts; for the new one, less than 200 watts. The new computer occupies 40 percent less volume than the original one and has twice the capability. In the new Minuteman computer, 95 percent of the electronic functions are performed by approximately 2000 integrated circuits. The silicon wafers that contain all these circuits, which perform 95 percent of the computer's functions, weigh, in all, 2.5 grams, or less than 0.1 ounce.

Solid-state electronics is still essentially centered about the classical elemental semiconductors germanium and silicon; the end of the potential of these materials in electronics is not in sight. There is still some way to go toward achieving greater chemical purity and structural perfection and toward improving the associated processing techniques.

Compound Semiconductors

In addition to the elemental semiconductors, compound semiconductors have been of considerable interest in the last 10 to 15 years. Potentially, compound semiconductors and their alloys represent an immense extension of the semiconductor properties and applications of germanium and silicon with respect to energy gaps, electrical-carrier characteristics (such as mobility and lifetime), and so on.

The compound semiconductors consist of elements positioned symmetrically about group IV in the periodic table of the elements; it is in group IV that germanium and silicon belong. Gallium arsenide (a group III–V compound), zinc sulfide (a group II–VI compound), and silicon carbide (a group IV–IV compound) are typical semiconductor compounds. As a class they represent phenomena and applications with higher frequencies, higher speeds, higher power, and higher temperatures than those of the group-IV elements. They are also the potential key to optoelectronics, where interaction of light and semiconductivity are involved and where electronic signals are coupled with light energy rather than with electrical charge or magnetic flux.

Progress with semiconductor compounds has been very slow, the main reason being that preparation of these materials with high chemical and structural perfection has not been achieved in a reproducible way. A crystal of high quality is occasionally obtained, but these are rare events, painstakingly planned, and contribute only to our frustrations.

Of all semiconductor compounds, gallium arsenide and indium antimonide, belonging to the group III–V class, have received the greatest overall attention. Some remarkable advances have been made. Gallium arsenide Varactor diodes having cutoff frequencies up to 300 gigacycles have been realized. Equally remarkable are the microwave oscillators of gallium arsenide which are capable of generating at least 25 milliwatts of continuous power, or 350 watts of pulsed power at the amazing frequencies of 10 gigacycles. This type of application implies revolutionary developments in radar technology. Radar for automobiles is certainly one of them. Furthermore, there are indications that gallium arsenide transistors could operate at temperatures up to at least 200°C.

Indium antimonide and indium arsenide have found interesting applications as Hall effect devices, where the voltage output is proportional to the product of the current passing through and the magnetic field perpendicular to the current. These compounds have also found applications in infrared detection, along with the well-known detectors of the group IV–VI compounds (like lead sulfide).

In recent years gallium arsenide, gallium phosphide, and aluminum phosphide have been extensively studied in conjunction with electroluminescence. Respectable efficiencies have been achieved with gallium phosphide diodes, as discussed below. Silicon carbide has also been intensively studied, with impressive results. A silicon carbide diode with a remarkably narrow line light source, well suited for recording voice or other types of information on photographic films, has been developed and marketed.

Compared with germanium and silicon, compound semiconductors have not even begun to enter the arena of solid-state electronics. And yet sound scientific understanding and engineering reasoning suggest that their potential in this field is virtually unlimited. Of the numerous device and system applications already well worked out in principle and well within the limits of the known material parameters, only a small fraction have been realized, and these, in most instances, only in the laboratory.

The reasons are quite simple. In semiconductor compounds the materials problems are far more difficult than they are in germanium and silicon. In each compound one is faced with the problem of the purity of two elements and of course with the equally difficult problem of stoichiometry—that is, the exact ratio of the elements in the compound. Then the detailed control and reproducibility of the level of impurity and of the structural parameters represent some of the most challenging problems that materials science and engineering have ever faced. And all these problems become exponentially more difficult as the temperature for preparation of the material increases. Silicon carbide crystals, for example, are prepared at temperatures in the vicinity of 2500°C.

Difficult as those problems may be, their solution is perhaps not beyond our reach at present and certainly will not be beyond our reach in the near future. The Russians, through intensive work over a number of years, overcame many of the obstacles associated with silicon carbide, one of the most difficult materials to control, with the result that electroluminescent diodes made of silicon carbide are widely used in the Soviet Union and monolithic alpha-numeric devices are being mass-produced.

In reviewing the status of electronic materials in the last 10 to 15 years, it becomes apparent that theoretical concepts and conceptual applications have in many instances come first, ahead of the refinements in materials and processes that have made possible their realization. This pattern will prevail in the next 5 to 10 years—with perhaps a sprinkling of hidden surprises; we simply have not harnessed the potential of the available electronic materials. It is very unlikely that new classes of phenomena will be discovered which will require major deviations from present goals in materials and materials processing.

The potential growth of solid-state electronics through advances in electronic materials technology is indeed overwhelming. One can clearly see strides in electronic processes toward greater compactness (we might say ultramicrominiaturization), greater speeds, greater reliability, higher and lower power controls, higher temperatures, greater versatility, and broader applicability; lowered cost will continue to be a compelling consideration throughout.

Among electronic materials, semiconductors are now the most widely applied, and this trend will continue in the near future. The estimate of $1.2 billion for sales of semiconductor devices in 1968 is about four times the figure for sales of the next most popular class of electronic devices—that is, magnetic devices, including computer cores, transformers, and other ferrite components.

Integrated Circuits

In the next 10 years the greatest thrust in semiconductor electronics, in terms of development effort, achievements, and sales, will be provided by integrated electronics (electronic logic) of the hybrid and monolithic variety. (It is estimated that, within less than 10 years, sales for all semiconductor devices will exceed $3 billion in the United States alone.) A realistic target will be 100 or more integrated circuits (that is, a few thousand individual components) per chip area of approximately 10 square millimeters. Such large-scale integration will grow out of refinements of present-day technology. It will develop along parallel avenues, one utilizing the classical bipolar active electronic devices (based on *p-n* junctions) and the other utilizing structures of the metal-oxide-semiconductor (MOS) type.

Integrated circuitry will find a wide

variety of uses, including application in the entertainment industry. Provided reliability keeps pace with development, large-scale integration will find increasing application in the two giants of the electronic world, communications and computers. High density of information and high speeds will be constantly moving targets in the future. At the same time the electronic systems will be so designed that they can "fail softly"—that is, there will be a high probability that they will operate even with faulty components, of course at lower speeds. Monolithic computer memories (based on bipolar and MOS technology) will find increased uses where permanent storage of information is not necessary; once the power is removed from a monolithic memory, the information is lost.

For all practical purposes only silicon will be exclusively used in integrated electronics in the foreseeable future. Germanium is the only other material that now (and for years to come) meets the requirements, and indeed it even offers a greater carrier mobility than silicon; however, germanium oxide does not have the all-important stability and insulating characteristics of silicon oxide. Among the many refinements expected in monolithic circuitry technology (evaporation, diffusion, surface passivation, electrical contacts, and so on), it is apparent that masking tolerances will decrease to less than 1 micron over an area of 10 square millimeters.

Power Control Devices

On the other side of the spectrum, semiconductor devices for handling high levels of electrical power will continue to be of great importance. In this category belong the high-power rectifiers and the Thyristor switches whose bistable action is based on a *p-n-p-n* type structure. The requirements here are quite similar to those in integrated electronics: well-defined and properly profiled junctions in material of high-crystalline perfection and well-controlled purity.

Semiconductor devices of this type are being used in the automobile industry (solid-state alternators) and in some low-power electric applicances. One can expect, with some certainty, that in the next 5 to 10 years semiconductor devices will find widespread use in motor controls of ordinary appliances. The controlling factor in this case will be economics rather than technology.

However, an increase in the use of semiconductor devices for switching extremely high electrical power, either in conjunction with electrical motors or in power transmission, will require refinements of the present technology. Motors for rolling mills are being designed that will deliver more than 20,000 horsepower. The mechanical switching of large amounts of electrical power is a serious problem. Maximum rating of mechanical circuit breakers is still in the vicinity of 3000 amperes.

In the high-power-handling area, also, silicon will continue to be the principal semiconductor material. Silicon carbide is perhaps a more suitable material for power control, in view of its high-temperature characteristics. However, the needed silicon carbide technology is not likely to be developed in the next 5 years. During that period the sales volume of high power and control semiconductor devices ($5 to $15 million per year in the United States) may not be sufficient to encourage the required development work on silicon carbide. It is more likely that it will be another 10 years before the many potential applications of silicon carbide are realized, unless there is a government crash program.

Electroluminescence

Another area of great scientific and technological significance is that of electroluminescence, whereby electronic energy is converted to light. Electroluminescence was discovered in 1937, 10 years before the transistor, when it was observed that light could be produced by application of an alternating voltage across an insulator containing a luminescent material like zinc sulfide doped with copper. The flat green night-lights are familiar devices based on this phenomenon. This form of electroluminescence has not had wide application and is not likely to have in the future, because of the power requirements (high voltage, high frequency), the low efficiency, and the complexities of the physical processes involved.

In the last 10 years considerable work has been carried out on electroluminescent diodes, where electronic excitation leading to emission of light is brought about across a *p-n* junction. Here again there are the usual materials limitations. In order for the emitted light to be visible, the energy gap of the semiconductor must be greater than 2 electron volts. Germanium and silicon, with energy gaps of 0.6 and 1.1 electron volts, respectively, are disqualified completely. Gallium arsenide diodes can be made to electroluminesce with high efficiencies (greater than 20 percent at room temperature), but their light is in the infrared region (1.45 electron volts). The choice of available materials that have appropriate energy gaps and that can be prepared as *n*- and *p*-type is limited indeed: gallium phosphide (2.24 electron volts), aluminum phosphide (3.1 electron volts), and silicon carbide (2.7 electron volts).

Essentially all of the work on electroluminescence has been concentrated on these three materials, and working electroluminescent diodes have been obtained in all cases. All three semiconductors have indirect energy band gaps, which are less favorable than direct band gaps for achieving high efficiencies. For this reason, extensive work has been done in alloying the gallium phosphide or aluminum phosphide with the direct-gap material gallium arsenide. In this process *direct* band gaps can be achieved that are somewhere between that of gallium phosphide (or aluminum phosphide) and that of gallium arsenide. The external quantum efficiencies attained with such alloys (the light quantum emitted per injected carrier) are greater by about two orders of magnitude than those attained with the pure compounds (1 percent as opposed to 0.01 percent). But this increase in efficiency is achieved at the expense of shifting the light in the red part of the spectrum, where the eye is more than an order of magnitude less sensitive.

The future of electroluminescent diodes is bright indeed. Standing in the way of realization of their vast potential are light efficiency (now too low by one to two orders of magnitude) and cost (now too high by one to two orders of magnitude). Probably in the next 5 to 10 years both obstacles will have been removed. Because of their extremely low power requirements (milliwatts or even less) and their infinite life, these diodes will find broad applications as light bulbs and in all types of instruments and displays, including automobile and airplane dashboards and many others. Gallium phosphide diodes (0.25 centimeter in diameter and consuming 10 milliwatts each) have worked successfully in illuminating the dialing mechanism of touch-tone telephones (one diode in each button). Because of their low power requirements and high speeds, such diodes are compatible with electronic circuitry. Here again the possibilities are virtually unlimited. A significant start has been made in demonstrating that the light of silicon carbide diodes can be modulated electronically and can be employed in recording sound optically on photographic films. Optical recording and retrieving of information is certainly a promising possibility for the near future. In the future, also (perhaps after 5 to 10 years), lies the exciting area of optoelectronics, where light will be an important element of circuitry, offering complete isolation of the input from the output.

Regarding materials for electroluminescent devices, it is not likely that, in the near future, there will be new materials other than the phosphides and silicon carbide, because well-controlled *p-n* junctions will probably not be achieved in other materials (II–VI compounds, for example) with high energy band gap. Silicon carbide, although it presents the most severe problems, will become the dominant material for electroluminescent devices because of its chemical stability and, in general, its refractory nature.

Other Applications

In the mainstreams of solid-state electronics there will continue to be efforts to explore specialized applications of electronic materials, to reexamine past effort that did not meet with complete success, and to probe the potential of new materials.

The work on group III–V compounds will continue, and reliable diodes of gallium arsenide will become more widely available for microwave or other specialized applications. Similarly, an increased number of devices of indium antimonide and indium arsenide will find application in infrared-detection and other high-speed devices. Most likely, compound semiconductors will complement germanium in radiation detection and radiation analysis in the near future. Silicon carbide could be used in this field also, if the need for high-temperature detection becomes compelling. Actually, silicon carbide stands as the most promising material for high-temperature electronics in general. Gallium arsenide is well suited for temperatures up to about 200°C. Beyond these temperatures silicon carbide essentially has no competitor since the other compounds with high-energy band gaps present serious chemical instabilities at high temperatures.

There will be attempts to reexamine thermoelectric energy conversion for broader applications than the now limited ones, in which alloys based on bismuth telluride are used at low temperatures and silicon-germanium alloys, at higher temperatures. Efforts to develop thermoelectric devices have been on the verge of success for a number of years; perhaps the next round of intensive effort will bring successful results. Here again silicon carbide is a promising high-temperature thermoelectric material. There will also be renewed efforts to make semiconductor solar batteries (of silicon or of semiconductor compounds) economically acceptable.

Progress in solid-state electronics must be coupled to advances in various areas of nonelectronic materials technology. A single silicon chip measuring 3 by 3 millimeters and containing a complete integrated circuit imposes a number of requirements with respect to electrical leads, contacts, packing materials, and others. It is quite clear that the passive components of solid-state electronics will continue to present real challenges and sound opportunities of their own, along with challenges in technologies such as vacuum, high-temperature, testing, and instrumentation.

As for electronic materials other than semiconductors, the opportunities for improved magnetics, dielectrics, insulators, superconductors, and optical materials are very broad. Unfortunately progress will be relatively slow because the materials problems here are far more complex than in semiconductors and because the known research and development efforts in the United States are, in most instances, subcritical.

One should note, however, the potential of dielectric materials for electrooptic or elastooptic applications. Lasers have distinct advantages in communications, but utilization of these advantages requires that the laser beams be modulated or in some way affected in a controlled manner. Recent studies have revealed that the electrooptic and elastooptic properties of single-domain ferroelectric lithium niobate ($LiNbO_3$) and lithium tantalate ($LiTaO_3$) make these materials very promising for such devices. An early success will probably trigger extensive research and development on optical materials of this type and usher in a new era of quantum electronics.

Conclusions

Semiconductor electronics more than any other branch of science and technology has brilliantly demonstrated that utilization of the ultimate potential of new electronic phenomena hinges critically on the degree of our understanding of the materials and of our control of their purity and crystalline perfection. This intimate interplay of materials and applications is certainly not limited to electronic phenomena. The electronic behavior is just one manifestation of the material's basic nature. In fact, in covalent materials it is rapidly becoming clear that electrical behavior cannot be divorced from mechanical and other properties. It has been shown, for example, that germanium and other materials undergo significant decreases in hardness upon irradiation with light or upon passage of an electrical current. In the case of cadmium sulfide, a pronounced increase in flow stress has been found upon illumination; the increase is dependent on the intensity of illumination and on the wavelength. There is every reason to believe that these photomechanical and electromechanical effects are just typical instances of fundamental relationships among various properties in well-characterized materials. In fact, it is safe to say that many of our difficulties in understanding the mechanical and chemical behavior of most solids are associated with the fact that we have never examined these solids at levels of chemical and crystalline purity where one deals with the material's basic nature. In many areas of technology—including mechanical and civil engineering, engineering of ceramics and plastics, and others—the detailed understanding of materials and materials control still presents extraordinary complexities.

I conclude with the thought that the future of electronics and, in fact, the future of all technology, not just in the next 10 years but for all times, rests on advances in materials through materials understanding coupled with refinements in purity and purity control, crystalline perfection, and materials processing.