

Materials physics

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Extraordinary advances in materials physics have occurred over the last century. These advances have influenced almost every aspect of human endeavor. In this note, the authors sketch some of these exciting developments in structural, polymeric, and electronic materials. [S0034-6861(99)01502-0]

I. INTRODUCTION

Over the last one hundred years there have been stunning advances in materials research. At the turn of the last century we did not know what the atomic structure of a material was. Today, not only do we know the structure, but we routinely make artificial structures that require placement of atoms at specified locations, that mix atoms to create properties not found in naturally occurring materials, that have the functionality needed by today's technology, and that adjust their properties to a changing environment (smart materials). Over the last few years we have begun to manipulate individual atoms to form structures that enable us to explore scientific issues, but that will surely lead to profound technological and social consequences; for example, the manipulation of nucleotides in a DNA molecule, which is then correlated with the functioning of, say, a gene and with its expression in the control of disease.

A hundred years ago there were no electronic devices, and today there is hardly any electrical appliance without them. It is anticipated that in the near future there will be a microprocessor embedded in almost all electrical appliances and not just in those used for computation or information storage. These devices, inconceivable a century ago, could without exception not be made without the knowledge gained from materials research on insulators, semiconductors, metals, ceramics, and polymers. At the end of this century, we have begun a debate on how far the present devices can continue to develop, given the limits imposed by the speed of light and the discrete nature of atoms, a debate that would have been incomprehensible to scientists and technologists of a century ago and a debate in which we now discuss the possibilities of using single electrons to switch a device on or off.

Our ability to measure temporal phenomena was limited to fractions-of-a-second resolution a hundred years ago. Today we can measure changes in properties with a few femtoseconds' resolution. Strobelike probes enable us to measure phenomena ranging over time scales covering more than ten orders of magnitude. We can, for example, study the relaxation of electrons in a semiconductor on a femtosecond time scale, the visible motion of bacteria in a petri dish, or the slow motion of a sand dollar on a beach.

Materials research spans the range from basic science, through engineering, to the factory floor. This has not

changed over the last hundred years or, for that matter, throughout the history of human civilization. Materials research came out of the practical needs of mankind. Eras of civilization were named after materials, so central has been their role in achieving mankind's mastery over nature. The field of materials research can trace its roots to alchemy, metallurgy, natural philosophy, and even art, as practiced over many centuries. However, the field of modern materials research, as represented by materials physics, is only about sixty years old.

Shifts in materials usage from one type to another are usually gradual. This is due to the very large investments associated with products in the materials-related industries, complex relationships between reliability and functionality, environmental issues, and energy demands. However, measured over time, these shifts become quite perceptible. For example, in automobiles the ratio of plastic components to iron-based alloys has changed from less than 3% to more than 15% over the last two decades. Although the percentage change appears to be modest, the actual volume of material is large; over 40 million tons of structural materials are used annually in cars.

The advances of materials research in this century, which far exceed those of all prior centuries put together, can be illustrated by three examples: structural, polymeric, and electronic materials. Our choice of these three is somewhat, but not completely, arbitrary. It is out of structural materials, particularly from the fields of metallurgy and metal physics, that modern materials physics has evolved. From the crude weaponry of our forefathers to our mastery of air travel, space flight, surface transportation, and housing, structural materials play a role that is unequivocally important. Nature uses the second category of materials, polymers, in amazing ways, to perform very complex functions. We humans are an example of that. Over the last hundred years, we have begun to understand and develop polymers for uses in food packaging, fabrics, and structural applications. We anticipate that polymer research will play an increasingly important role in biomaterials of the future. The third category, electronic materials, were not conceived until quantum mechanics was discovered in this century. Today we cannot imagine a world without telecommunication, computers, radio, and television. These and future devices that will make information available

instantly are only possible because of advances in the control of materials structure and processing to achieve a desired functionality.

II. STRUCTURAL MATERIALS

At the turn of the last century, mankind's use of structural materials was limited primarily to metals, particularly iron and its alloys, ceramics (most notably Portland cement), and polymers, which were limited to naturally occurring rubbers, glues, and fibers. Composites, as a concept were nonexistent even though wood and animals, each composed of different materials, were used in a variety of ways. However, the uses of alloying to enhance the strength of lightweight materials, such as pewter, or copper additions to aluminum, were established techniques, known well before this century. This knowledge was used to build the first dirigibles. The useful nature of a material was often understood through serendipity and not through an understanding of its structure or the relation between structure and properties. We still cannot predict in any quantitative way the evolution of structure with deformation or processing of a material. However, we have come a very long way from the situation that existed a hundred years ago, thanks to the contributions of twentieth century science to our understanding of atomic arrangement and its determination in a material. Our classification of materials by symmetry considerations came into existence once atomic arrangement became known. To the seven crystal systems and amorphous structures, typified by the glasses and liquids, we can now add quasicrystals and molecular phases, such as fullerenes and nanotubes, in a crystalline solid.

The crystal systems define perfect crystals. At finite temperatures, the crystals are no longer perfect but contain defects. It is now understood that these defects are responsible for atomic transport in solids. In fact, the structural properties of materials are not only a function of the inherent strength of a material but also of the defects that may be present. We know that aluminum is soft because crystallographic defects, called dislocations, can be readily generated and moved in this metal. In contrast, in alumina (Al_2O_3), dislocation generation and motion are difficult; hence alumina can be strong but brittle at room temperature. The addition of copper or manganese to aluminum creates second-phase precipitates, which inhibit the motion of dislocations, thus enhancing its strength-to-weight ratio. Our ability to improve the strength-to-weight ratio in materials has increased more than tenfold during the twentieth century. This is to be compared with a change of less than ten over the last twenty centuries. Much of the increase in this century has come from an understanding of the relationship between the processing of materials and their structure. The highest strength-to-weight ratios have been achieved in materials in the form of fibers and nanotubes. In these structures, dislocations either do not exist or do not move.

Most structural materials are not single crystals. In fact, they consist of a large number of crystals joined at interfaces, which in single-phase materials are called grain boundaries. These interfaces can, for example, influence the mechanical and electrical properties of materials. At temperatures where the grain boundary diffusion rate is low, a small grain size enhances the strength of a material. However, when the grain boundary diffusion rate is high, the material can exhibit very large elongation under a tensile load (superplastic behavior), or can exhibit high creep rates under moderate or small conditions of loading. In demanding high-temperature environments, such as the engine of a modern aircraft, grain boundaries are eliminated so that a complex part, such as a turbine blade, made of a nickel alloy, is a single crystal. Thus the use of materials for structural purposes requires an understanding of the behavior of defects in solids. This is true for metallic, ceramic, and glassy materials.

Both ceramics and glasses were known to ancient civilizations. Ceramics were used extensively in pottery and art. The widespread use of ceramics for structural purposes is largely limited by their brittle behavior. This is now well understood, and schemes have been proposed to overcome brittleness by controlling the propagation of cracks. In metals, dislocations provide the microscopic mechanism that carries energy away from the tip of a crack, thereby blunting it. In ceramics, the use of phase transformations induced at the tip of a propagating crack is one analog of dislocations in metals. Other schemes involve the use of bridging elements across cracks so as to inhibit their opening and hence their propagation. Still another scheme is to use the frictional dissipation of a sliding fiber embedded in a matrix not only to dissipate the energy of crack propagation, but also, if the crack propagates through the material, to provide structural integrity. Use of these so-called fault-tolerant materials requires both an understanding of mechanical properties and control over the properties of interfaces to enable some sliding between the fiber and the matrix without loss of adhesion between them. Such schemes rely either on composite materials or on microstructures that are very well controlled.

The widespread use of silicate glasses, ranging from windows to laptop displays, is only possible through the elimination of flaws, which are introduced, for example, by inhomogeneous cooling. These flaws, which are minute cracks, are eliminated during processing by controlling the cooling conditions, as in a tempered glass, and also by introducing compressive strains through composition modulations.

There are a number of fibers that are available for use with ceramics, polymers, and metals to form composite materials with specific applications; these include carbon fibers, well known for their use in golf clubs and fishing rods, and silicon carbide or nitride fibers. Optical fibers, which are replacing copper wires in communication technologies, owe their widespread use not only to their optical transparency, but also to improvements in their

structural properties. Fibers must withstand mechanical strains introduced during their installation and operation.

The use of composite materials in today's civilization is quite widespread, and we expect it to continue as new applications and "smart" materials are developed. An outstanding example of a functional composite product comes from the electronics industry. This is a substrate, called a package, which carries electronic devices. Substrates are complicated three-dimensionally designed structures, consisting of ceramics, polymers, metals, semiconductors, and insulators. These packages must satisfy not only structural needs but also electrical requirements.

Although we have made great progress over the last hundred years in materials physics, our microscopic understanding of the physics of deformation (particularly in noncrystalline solids), fracture, wear, and the role of internal interfaces is still far from complete. There has been considerable progress in computer simulation of some of these issues. For example, there is now a concerted effort to model the motion of dislocations, during deformation, in simulations of simple metallic systems. We anticipate that within the next decade, as computational power continues to increase, many of these problems will become tractable. The ultimate goal is to design a structural component for a set of specified environmental conditions and for a predictable lifetime.

III. POLYMERS

Polymers, also known as macromolecules, are long-chain molecules in which a molecular unit repeats itself along the length of the chain. The word polymer was coined approximately 165 years ago (from the Greek *polys*, meaning many, and *meros*, parts). However, the verification of the structure of polymers, by diffraction and other methods, had to wait, approximately, another 100 years. We now know that the DNA molecule, proteins, cellulose, silk, wool, and rubber are some of the naturally occurring polymers. Synthetic polymers, derived mainly from petroleum and natural gas, became a commodity starting approximately 50 years ago. Polymers became widely known to the public when nylon was introduced as a substitute for silk and, later, when Teflon-coated pans became commercially available. Polymers are now widely used in numerous household applications. Their industrial use is even more widespread.

Most of the applications associated with polymers have been as structural materials. Since the 1970s it was realized that with suitable doping of the polymers, a wide variety of physical properties could be achieved, resulting in products ranging from photosensitive materials to superconductors. The field of materials physics of polymers has grown rapidly from this period onwards.

Polymers are a remarkably flexible class of materials, whose chemical and physical properties can be modified by molecular design. By substitution of atoms, by adding side groups, or by combining (blending) different poly-

mers, chemists have created a myriad of materials with remarkable, wide ranging, and useful properties. This research is largely driven by the potential applications of these materials in many diverse areas, ranging from cosmetics to electronics. Compared to most other materials, polymers offer vast degrees of freedom through blending and are generally inexpensive to fabricate in large volumes. They are light weight and can have very good strength-to-weight ratios.

Polymers have traditionally been divided into five classes:

(1) Plastics are materials that are molded and shaped by heat and pressure to produce low-density, transparent, and often tough products, for uses ranging from beverage bottles to shatterproof windows.

(2) Elastomers are chemically cross-linked or entangled polymers in which the chains form irregular coils that straighten out during strain (above their glass transition temperatures), thus providing large elongations, as in natural and synthetic rubbers.

(3) Fibers, which are spun and woven, are used primarily in fabrics. About fifty million tons of fibers are produced annually for uses ranging from clothing to drapes. Apart from naturally occurring fibers such as silk and wool, there are regenerated fibers made from cellulose polymers that make up wood (rayon) and synthetic fibers, comprising molecules not found in nature (nylon).

(4) Organic adhesives have been known since antiquity. However, with demanding environments and performance requirements, synthetic adhesives and glues have largely replaced natural ones. The microscopic mechanisms of adhesion and the toughness of joints are still debated. There is an increasing trend to use UV radiation to promote polymerization in adhesives and, more generally, as a method of polymerization and cross linking in polymers.

(5) Finally, polymers, frequently with additives, are used as protective films, such as those found in paints or varnishes.

Physicists have played a significant role in explaining the physical properties of polymeric materials. However, the interest of physicists in polymers accelerated when it was discovered that polyacetylene could be made conductive by doping. This development was noteworthy for it opened the possibility of deliberately controlling conductivity in materials that are generally regarded as good insulators. The structure of all conjugated polymers, as these materials are known, is characterized by a relatively easily delocalized π bond, which, with suitable doping, results in effective charge motion by solitons, polarons, or bipolarons. Since the discovery that polymers could be electrical conductors, active research areas have developed on the physics of polymer superconductors, ferro- and ferri-magnets, piezoelectrics, ferroelectrics, and pyroelectrics. Within the field of doped polymers, devices have been built to demonstrate light-emitting diodes, photovoltaic cells, and transistors.

Conjugated polymers have also been investigated extensively for their large nonlinear, third-order polarizability, which is of interest to the field of nonlinear op-

tics. Large nonlinearities are associated with the strong polarizability of the individual molecules that make up the building blocks of the polymer. Furthermore, the flexibility of polymer chemistry has allowed the optical response of polymers to be tailored by controlling their molecular structure, through the selective addition of photoactive molecules. Hence these materials have been widely investigated by physicists and engineers for optical applications, such as in holographic displays (dichromated gelatin), diffraction gratings, optocouplers, and wave guides.

Polymers have long interested physicists for their conformational and topological properties. This interest has shifted from the conformational behavior of individual molecules to that of a macromolecular assembly, phase behavior, and a search for universal classes. Block copolymers, consisting of two or more polymers, can give rise to nanoscale phases, which may, for example, be present as spheres, rods, or parallel lamellae. The distribution of these phases and their topologies are of current theoretical and practical interest. Block copolymer morphologies are also being used as nanoscale templates for production of ceramics of unique properties having the same morphology.

Block copolymers are also of interest as biomaterials. Proteins are an example of block copolymers, in which the two phases form helical coils and sheets. Attempts to mimic the hierarchical structure present in natural polymers have only been partly successful. The principal difficulty has been to control the length of the polymer chains to the precision that Nature demands. Significant progress has been made in controlling polymer morphologies with the use of new catalysts. For example, metallocenes have been used as catalysts to control branched polymers and organonickel initiators to suppress chain transfer and termination, so that polypeptides with well-defined sequences and with potential for applications in tissue engineering could be made. The growth of well-controlled polymer chains is an example of "living" polymerization.

The static and dynamic arrangement of atoms on the surfaces and interfaces of polymers is another area of active investigation. For example, thin films of polymers, in which the chain lengths are long compared to the thickness of a film, show unusual physical properties: the glass transition temperature for a thin-film polymer decreases significantly, but between solid surfaces polymer liquids solidify.

Even though we have some way to go in making tailored proteinlike structures, polymer research has played a significant role in the class of materials called biomaterials. Polymers have been used, for example, to produce artificial skin, for dental fillings that are polymerized *in situ* by a portable UV lamp, and for high-density polyethylene used in knee prostheses. Physicists play a significant role in these developments, not only for their interest in the materials, but also because of their familiarity with physical processes that can be used to tailor the properties of polymers. A particularly good example of this interplay is the recent and rapidly grow-

ing use of excimer laser radiation to correct corneal abnormalities; using a technology developed from studies of the ablation of polymeric materials for applications in the electronics industry, physicists realized that the small, yet precisely controlled, ablation of a polymeric surface might be useful in shaping the surface of an eye.

IV. ELECTRONIC MATERIALS

The roots of the electronic materials field can be traced back to Europe in the 1920s, with the advent of quantum mechanics and its application to periodic structures like those occurring in crystals. The early experimental focus was on alkali halides, because these materials could be prepared in a controlled way from both a structural and a compositional standpoint. The creation of a strong academic program in solid-state physics at the University of Illinois in the 1930s had an important impact on the early history of the electronic materials field in the United States. This knowledgeable human resource played a significant role in mobilizing the national materials program during World War II, especially in the development of semiconducting materials with enhanced purity, suitable for use in diode detectors at microwave frequencies for communications applications. The availability of these new semiconducting materials in purified, crystalline form soon led to the discovery of the transistor, which ushered in the modern era of electronics, computers, and communications, which is now simply called the "information age."

Semiconductors have been a central focus for electronic materials. Quantum-mechanical treatments of a periodic lattice were successful in laying the groundwork for describing the electronic band structure, which could account for electrical conduction by electrons and holes, carrier transport under the action of forces and fields, and the behavior of early electronic devices. Because of the interest of industrial laboratories and the Defense Department in the newly emerging field of semiconductor electronics, semiconductor physics developed rapidly, and this focus soon led to the development of the integrated circuit and the semiconductor laser.

The strong interplay between technological advances and basic scientific discovery has greatly energized semiconductor physics, by raising challenging fundamental questions and by providing new, better materials and devices, which in turn opened up new research areas. For example, the development of molecular-beam epitaxy in the 1960s and 1970s led to the ability to control layer-by-layer growth of semiconductor quantum wells and superlattices. The use of modulation doping of the quantum wells, whereby the dopants are introduced only in the barrier regions, led to the possibility of preparing semiconductors with low-temperature carrier mobilities, orders of magnitude greater than in the best bulk semiconductors. These technological advances soon led to the discovery of the quantum Hall effect, the fractional quantum Hall effect, and a host of new phenomena, such as Wigner crystallization, which continue to challenge experimentalists and theorists. Lithographic

and patterning technologies developed for the semiconductor industry have led to the discovery of the quantized conductance for one-dimensional semiconductors and to the fabrication of specially designed semiconductor devices, in which the transport of a single electron can be controlled and studied. The ever decreasing size of electronic devices (now less than 0.2 microns in the semiconductor industry) is greatly stimulating the study of mesoscopic physics, in which carriers can be transported ballistically without scattering and the effect of the electrical leads must be considered as part of the electronic system. New materials, such as carbon nanotubes with diameters of 1 nm, have recently been discovered, and junctions between such nanotubes are being considered for possible future electronics applications on the nm scale, utilizing their unique one-dimensional characteristics.

The electronic materials field today is highly focused on the development of new materials with special properties to meet specific needs. Advances in condensed-matter physics offer the possibility of new materials properties. In photonics, new materials are providing increased spectral range for light-emitting diodes, smaller and more functional semiconducting lasers, new and improved display materials. The new field of photonic band-gap crystals, based on structures with periodic variations in the dielectric constant, is just now emerging. Research on optoelectronic materials has been greatly stimulated by the optical communications industry, which was launched by the development of low-loss optical fibers, amplifiers, and lasers.

Ferroelectrics have become important for use as capacitors and actuators, which are needed in modern robotics applications, as are also piezoelectric materials, which are critical to the operation of scanning tunneling probes that provide information at the atomic level on structure, stoichiometry, and electronic structure. The technological development of microelectromechanical systems (MEMS), based on silicon and other materials, is making possible the use of miniature motors and actuators at the micrometer level of integrated circuits. Some of these have already found applications, such as the triggering mechanism for the release of airbags in automobiles. Such developments are not only important to the electronics industry, but are also having great impact on fields such as astronomy and space science, which are dependent on small, light-weight instruments with enhanced capabilities to gather signals at ever increasing data rates and from ever increasing distances from Earth. The developments in new materials and low-dimensional fabrication techniques have recently rejuvenated the field of thermoelectricity, where there is now renewed hope for enhanced thermoelectric performance over a wider temperature range.

Research on magnetic materials has been strongly influenced by applications ranging from the development of soft magnetic materials (by the utilization of rapid solidification techniques) to hard magnetic materials such as neodymium-iron-boron for use in permanent magnets. In the 1980s efforts focused on the development of small magnetic particles for magnetic memory storage applications. New magnetic materials, especially magnetic nanostructures, are now an extremely active research field, where the discovery of new phenomena such as giant magnetoresistance and colossal magnetoresistance are now being developed for computer memory applications.

The strong interplay between fundamental materials physics and applications is also evident in the area of superconducting materials. Early use of superconducting materials was in the fabrication of superconducting magnets, which in turn promoted understanding of type-II superconductors, flux dynamics, and flux pinning phenomena. The discovery of the Josephson tunneling effect led to the development of the SQUID (superconducting quantum interference device), which has become a standard laboratory tool for materials characterization and for the sensitive measurement of extremely small magnetic fields, such as the fields associated with brain stimuli. The discovery of high- T_c superconductivity in 1986 has revolutionized this field, with much effort being devoted to studies of the mechanism for high- T_c superconductivity, along with efforts to discover materials with yet higher T_c and critical current values, to improve synthesis methods for the cuprate superconductors, and to develop applications for these materials to electronics, energy storage, and high-magnetic-field generation.

When viewed from the perspective of time, the developments in electronic materials have been truly remarkable. They have generated businesses that approach a trillion dollars, have provided employment to millions of workers, either directly and indirectly associated with these industries, and have enabled us, as humans, to extend our abilities, for example, in information gathering, communication, and computational capabilities. Science has been the key to these marvellous developments, and in turn these developments have enabled us, as scientists, to explore and understand the subtleties of nature.

V. SUMMARY

In this very brief note, we have only touched on some of the advances made in structural, polymeric, and electronic materials over the last century, showing how materials physics has played a central role in connecting science to technology and, in the process, revolutionized our lives.