



Viewpoints: Chemists on Chemistry

The Computer as a Materials Science Benchmark

Dean J. Campbell, Julie K. Lorenz, Arthur B. Ellis,
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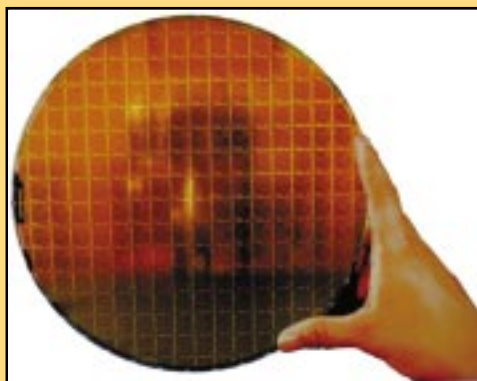
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When initially asked to prepare this Viewpoints piece on materials science, we selected the computer for the story line because of the breadth of materials it encompasses and its profound effect upon our lives. In no way, however, were we prepared for just how rapidly the materials and technologies associated with this remarkable tool are changing. During the four months over which this article was written—from our initial outline in August 1997 until the time it was completed in December 1997—it seemed that each time we de-



veloped a draft, a new technology was announced: IBM, for example, trumpeted a shift from aluminum to copper conductors in integrated circuits and introduced new magnetic read heads based on the giant magnetoresistance phenomenon during this period.

Both of these advances will lead to faster, more powerful computers. Thus, writing this article has given us a distinctly unsettling but nonetheless exhilarating sense of how rapidly materials science is moving. We will not be surprised if, by the time you read this article, some of the materials and processes described will already have been outperformed and displaced, as suggested by the logarithmic plots that dot the landscape of this article. But what we hope will be conveyed is the breakneck pace at which this field is moving, and the vast potential and excitement it holds for all of us.



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The Computer as a Materials Science Benchmark

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The discovery of the transistor 50 years ago at Bell Laboratories ushered in a new age in solid-state chemistry and materials science. In many ways, the computer, whose development is linked to this discovery and whose existence helps define both the Materials Age and the Information Age, provides a benchmark for our history of the past half century and for our aspirations of the next quarter century (1). The materials that comprise the computer provide the context for this article by illustrating the interdependent issues associated with modern materials science: the performance of the computer depends on the physicochemical properties of its components, which in turn depend on their structure and composition and how they were synthesized and processed (Fig. 1) (2). In the past these materials and device issues would have been associated with traditional fields such as chemistry, physics, and engineering; increasingly, they are addressed with the multidisciplinary approaches associated with materials science.

To put the past and future development of the computer in perspective, Moore's law provides a compelling frame of reference. Gordon Moore, cofounder of Intel, estimated in 1965 that the transistor density on microprocessors would double about every two years (1a, 3). A semilog plot illustrating how closely this prediction has been followed is shown in Figure 2; its extrapolation suggests that the ability to squeeze a billion transistors onto microprocessors will be realized in roughly the next decade, although, as will be discussed below, there are significant challenges associated with sustaining this trend (4, 5).

Another eye-opening view of the computer is that the wafers currently used in manufacturing computers have more electronic components than there are people on earth (Fig. 3). But instead of being distributed over our planet, they are organized into an area of only several hundred square centimeters. In fact, if we have not already done so, we will probably soon have constructed more transistors than any other single "thing", including bricks!

This article focuses on selected materials that are critical to the computer's construction, and it explores some of the materials issues associated with the computer's past and future development. In sections below, materials are linked to

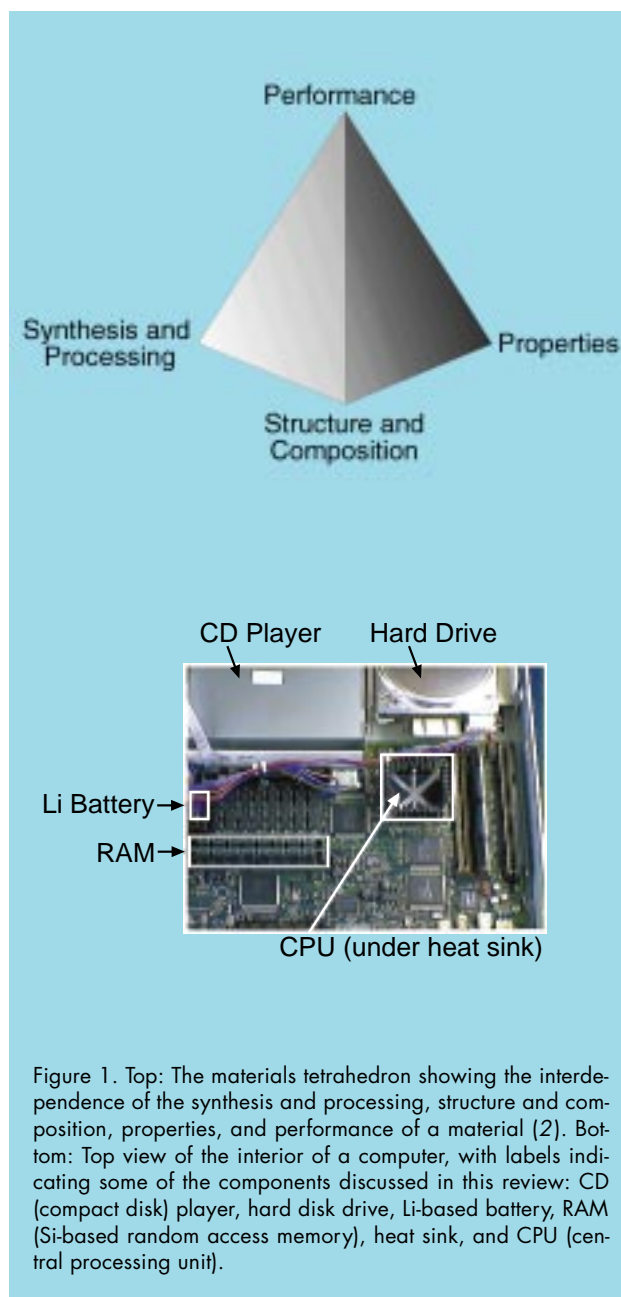


Figure 1. Top: The materials tetrahedron showing the interdependence of the synthesis and processing, structure and composition, properties, and performance of a material (2). Bottom: Top view of the interior of a computer, with labels indicating some of the components discussed in this review: CD (compact disk) player, hard disk drive, Li-based battery, RAM (Si-based random access memory), heat sink, and CPU (central processing unit).

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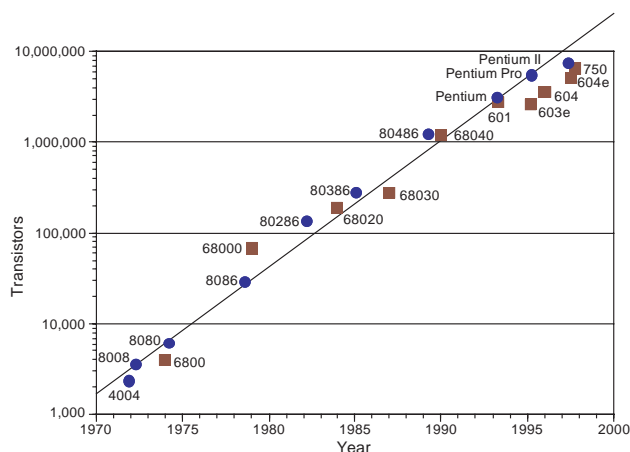


Figure 2. Plots of Moore's law showing the number of transistors on a microprocessor chip vs the year in which such chips were introduced, for Intel microprocessors (circles) and Motorola microprocessors (squares).

the roles they play in information technology:

- silicon-derived solids to the manipulation of information
- magnetic materials to the storage and retrieval of data
- laser diodes to data portability through compact disk (CD) technology
- phosphors, light-emitting diodes (LEDs), and liquid crystals to displays
- intercalation compounds to batteries
- diamond films, dielectrics, and high-temperature superconductors to a futuristic accelerated flow of information

The overarching theme connecting the vignettes below is that the past half century has witnessed a revolution in our ability to purposefully design materials and interfaces (2). For centuries preceding this period, solid-state chemistry provided

a means for combining bulk solids at high temperatures. These "heat and beat" methods generally produce thermodynamically favored products by enhancing diffusion processes required for mixing atoms on the atomic scale. This "top down" preparation of bulk solids has led to many useful materials, such as the oxides and sulfides in phosphors and batteries, and to empirically developed control of some kinds of microstructural and nanostructural features.

In the past half century, development of a variety of new synthetic tools, many of which involve lower temperatures, has led to the creation of a broad range of solids and interfaces that can be grown virtually one atomic layer at a time. Such "bottom up" approaches can yield kinetically controlled products such as multilayer structures used in LEDs and integrated circuits, affording additional control over material properties. Given our current trajectory, we can confidently predict that the next quarter century will see the assembly of increasingly sophisticated solid-state architectures using both nanoscale and bulk synthetic methods. As is illustrated by the breathtaking contributions of materials to computer hardware, chemists of the next century may well describe themselves as "molecular engineers".

Manipulating Information: Silicon and Integrated Circuits

The term "Silicon Valley", which identifies the geographic cradle of the computer industry, pays homage to the key chemical element supporting this technology. The "brain" of the computer is the integrated circuit, IC, comprising a silicon chip bearing billions of electronic components. Silicon is a solid that possesses the diamond structure shown in Figure 4 (2, 6).

The silicon used in creating these wafers illustrates the use of "top down" methods to bring atoms together on the atomic scale to form thermodynamically stable extended solids. Reasonably pure silicon (96–99%) can be prepared from sand, SiO_2 , and high-purity coke (a poorly graphitized form of

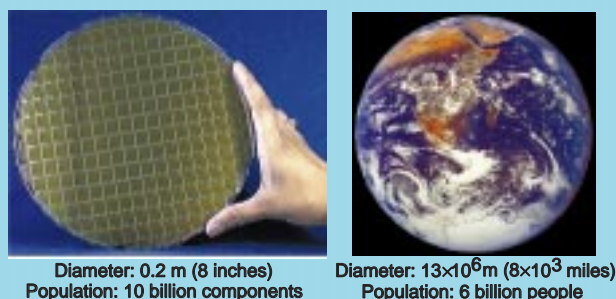


Figure 3. A comparison of the population density of the electronic components on a silicon wafer (left) with that of people on earth (right). We thank Paul Peercy of Sematech for permission to adapt this figure. The right-hand picture may be found at http://nssdc.gsfc.nasa.gov/image/planetary/earth/apollo17_earth.jpg in the National Space Science Data Center Photo Gallery, Edwin V. Bell, II, curator (accessed January 1998).

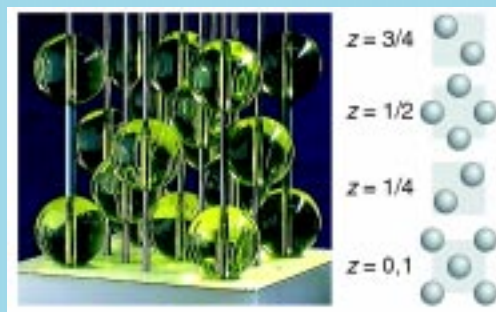
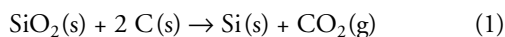


Figure 4. Left: The structure of diamond, built with the ICE Solid State Model Kit (6). Right: The corresponding layer sequence represents planes parallel to the base of the unit cell that pass through the centers of the atoms contributing to the unit cell (2). The coordinate z is the fraction of the unit cell's length; i.e., the base of the unit cell is represented by the plane at $z = 0$, and the top of the unit cell is represented by the plane at $z = 1$. Many of the structures mentioned in this article are described in Wells (6).

carbon) at high temperature using an electric arc (eq 1) (7).



But this level of purity pales beside the ultrapure materials required by the semiconductor industry, which reach 99.9999996% (8). In this case, impurity levels approaching a part per billion are needed in order to control reliably the electrical properties of the solid. Finding an impurity atom in such a sample is analogous to trying to locate a particular individual in one of the most populous countries on Earth! To attain this control over impurities, several additional processing steps are needed (9).

First, the silicon is reacted with HCl at high temperature to form volatile chlorosilanes, of which trichlorosilane, HSiCl_3 (TCS), is the desired product. After the vapor mixture is condensed, TCS is purified by distillation and passage down an absorption column. The next stage, the so-called Siemens process, is a chemical vapor deposition (CVD) process. Methods such as CVD, a "bottom up" synthetic route, grow solids essentially an atomic layer at a time by decomposing precursor gases on a heated substrate (Fig. 5) (2). In this particular process, TCS and hydrogen gas react at $\sim 1200^\circ\text{C}$ to deposit polycrystalline, electronic-grade silicon onto a silicon rod; the other reaction product in the Siemens process is gaseous HCl, which can be reused for the conversion of low-purity silicon material to TCS. To complete the process, the polycrystalline silicon must be converted to single-crystal silicon, a feat accomplished using the Czochralski method. In this method, the silicon is melted ($\sim 1420^\circ\text{C}$) and a seed crystal that has been immersed in the melt and that serves as a template is slowly withdrawn to form a large single-crystal boule, as illustrated in Figure 6 (9–12).

There have been dramatic increases in the size of ultrapure, almost defect-free crystals that can be grown this way,

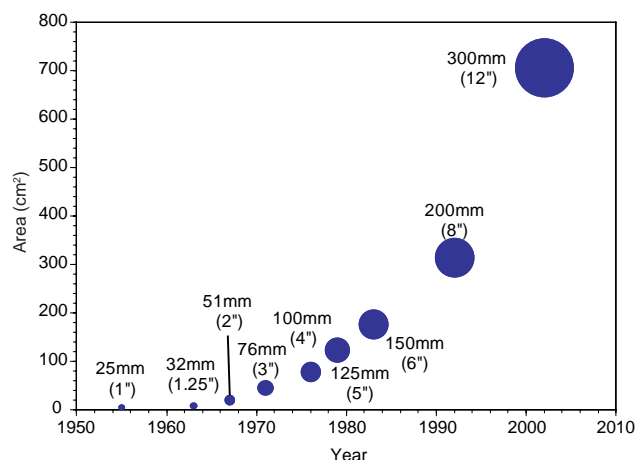


Figure 7. Plot of the size of silicon wafers vs the year of their commercial introduction. A 200-mm (8-in.) diameter wafer is shown in Figure 3. Data were obtained through the courtesy of Don Shaw.

as illustrated by the plot in Figure 7. The growth of ultrapure Si ingots having a 20-cm diameter and 1-m length, with impurities at the parts-per-billion level, represents a benchmark of perfection in crystal growth. These ingots are sliced to make wafers on which ICs are prepared through a series of manufacturing steps, as described below, and the wafers are then cut into individual chips. (Each of the squares on the wafer in Figure 3 becomes a chip.) There are projections that a limiting wafer size will eventually be reached (13).¹

Fabricating the Si wafer into an IC illustrates more of the modern materials science toolbox (Fig. 8). The IC arises from juxtaposing metals, insulators, and semiconductors that are all grown on the Si wafer in complex interconnected struc-

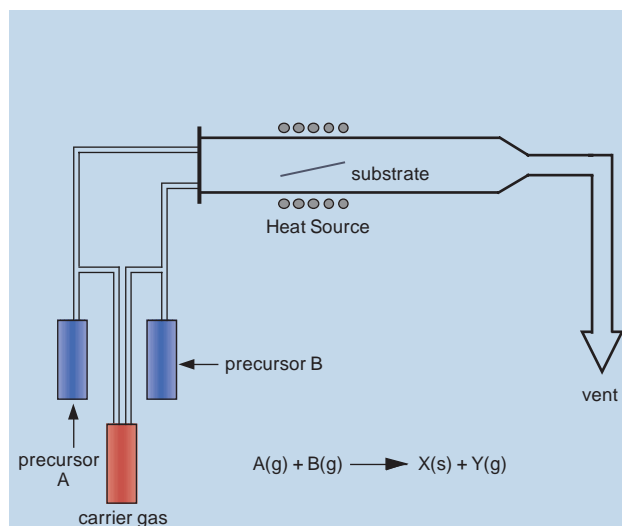


Figure 5. General schematic of the chemical vapor deposition (CVD) apparatus. Reaction of precursor gases A and B results in the deposition of X and formation of byproduct Y. As described in the text, when precursor gas A is trichlorosilane (TCS) and precursor gas B is H_2 , they react to produce Si on the heated substrate and gaseous HCl is vented.

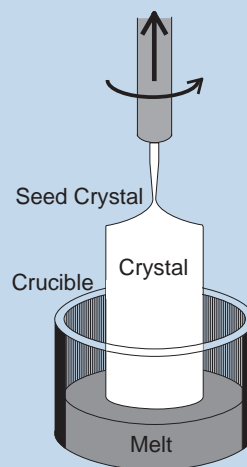


Figure 6. Schematic of the Czochralski method used for preparing single-crystal silicon boules from a melt of polycrystalline, electronic-grade silicon. A seed crystal is slowly withdrawn from the melt in this method. The sample is rotated during crystal growth as shown to gently stir the melt and promote homogeneous solidification.

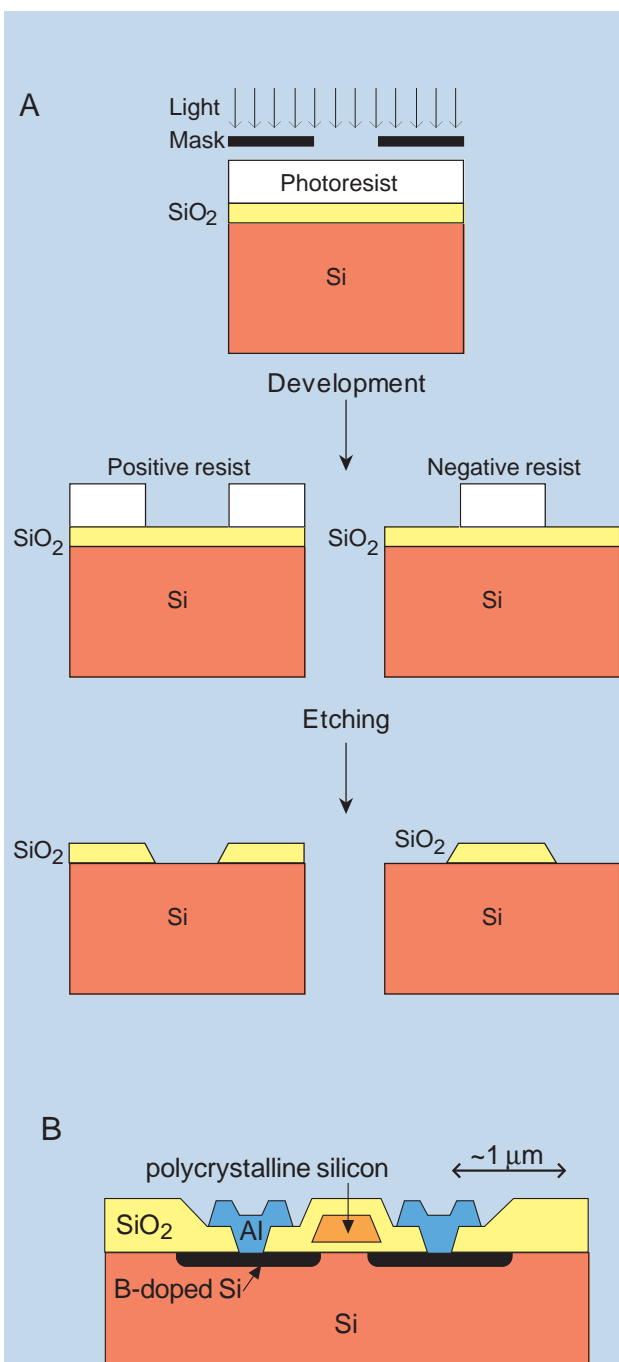
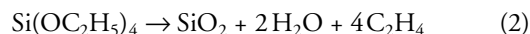


Figure 8. Simplified description of the fabrication of an IC. A: A wafer that is coated with SiO₂ and photoresist is illuminated through a mask. In a subsequent washing, the polymer is selectively removed from the region that was illuminated if it is a positive resist and selectively retained if it is a negative resist. The SiO₂ layer in the unprotected region is then removed by etching (e.g., HF solution) to create the structures shown in the figure. B: Cross-sectional view of the construction of part of a transistor that is grown on a silicon wafer. Each of the layers shown typically requires multiple processing steps such as the masking and etching steps shown in part A.

tures, produced in layers. The range of materials commonly employed in ICs currently includes the undoped Si substrate, p- and n-doped Si (doping introduces impurity atoms to control electrical conductivity [see below]), SiO₂, Si₃N₄, and Al. Critical steps in creating the IC involve photolithography, a process of using light to form patterns on a surface. As shown in Figure 8, Si or SiO₂, for example, can be coated with a light-sensitive polymer called a photoresist. When the polymer is illuminated through a mask, the polymer from the irradiated region is selectively removed or retained in a subsequent washing, depending on its chemical nature. This leaves the underlying substrate exposed in a pattern; this substrate may subsequently be chemically modified by, for example, doping or etching.

Thin p- and n-type regions can be prepared by the controlled introduction of impurity or dopant atoms into the crystal. Atoms such as B and P have, respectively, one fewer and one more valence electron than Si, and their introduction into the Si can result in the generation of electronic carriers, mobile electrons and holes (missing valence electrons that act as positively charged particles [2]). Doped regions are produced through such processes as thermal diffusion and ion implantation. In thermal diffusion, a high concentration of the dopant on the Si surface diffuses into the bulk Si under conditions of high temperature, creating an electrically active region. Shallower doped regions are produced by ion implantation, a process in which the dopant atoms are accelerated to a high velocity in a vacuum chamber and subsequently bombard the Si wafer surface. The atoms come to rest in the Si very near the surface. Once thermally treated, these atoms can form a thin doped region. The p- and n-type regions in contact with each other form a p-n junction that is a basic building block of many diodes and transistors (2, 9–12).

Silicon dioxide, which electrically insulates various regions of the IC from one another, is grown on the Si surface by thermal oxidation at nearly 1000 °C in the presence of oxygen gas. Alternatively, the aforementioned CVD technique can be employed: a silicon- and oxygen-containing precursor gas such as tetraethoxysilane (TEOS) can react to deposit amorphous layers of SiO₂ on the Si surface, as shown in eq 2.



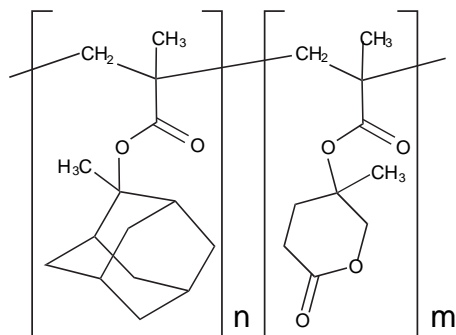
Another insulating material that can be grown by CVD is Si₃N₄, where silane and ammonia are the precursor gases (eq 3).



To confine these materials to different regions of the chip, a combination of selective chemical reactivity and photolithographic techniques has been employed. A Si₃N₄ layer can, for example, prevent oxygen from oxidizing the Si directly beneath it during a thermal oxidation treatment. And an SiO₂ layer can mask the Si directly beneath it from dopants introduced during an ion implantation step.

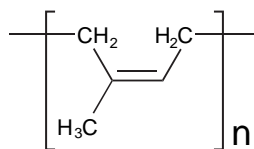
Polymers such as methacrylates also play a critical role as photoresists: photoinduced bond cleavage enhances solubility in organic solvents, permitting removal of the polymer chains from the illuminated region in subsequent processing steps. This is the property of a “positive photoresist” (9). The solubility of the methacrylate polymer below is increased

when photogenerated acid (from triphenylsulfonium trifluoromethanesulfonate) removes the adamantane (left) and lactone (right) pendant groups (14).



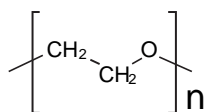
A methacrylate polymer

Other polymers such as *cis*-polyisoprene undergo cross-linking of polymer chains upon illumination, leading to reduced solubility and permitting their retention during later processing steps in the regions that had been irradiated (the characteristic of a “negative photoresist”).



cis-Polyisoprene

In addition, the circuit boards on which all of the electronic components are mounted are made from polyethylene oxide (PEO), which is thermally stable, machinable, and electrically insulating.



PEO

Aluminum is used for electrical connections between materials on the chip and for connecting the chip to other electrical components in the computer. Recently, copper, which has better electrical conductivity than aluminum, was introduced (2, 14, 15).

Once created on the chip, p-n junctions and metal-oxide-semiconductor (MOS; Al-SiO₂-Si, e.g.) structures permit logic operations to be conducted and the information to be stored. The “bit” of computer jargon represents one unit of information in the binary system of zeroes and ones. In an IC, capacitors and transistors work in combination: capacitors can store a bit as an electrical charge and the transistors can transfer it (10, 11). In this manner, the computer can manipulate the information using the binary formalism.

The smallest circuit features (electronic components) are currently about 0.25 μm; for comparison, the diameter of a human hair is about 100 μm. It is anticipated that over the next decades feature scales of less than 0.1 μm will be achieved and physical limits to further size reductions will rapidly be

approached (16). There are strong incentives to continue to shrink computer circuitry: as feature spacings are reduced, electricity travels over shorter distances, enabling the circuits to operate faster and with less power consumption. However, electrical circuitry poses several problems as size is reduced.

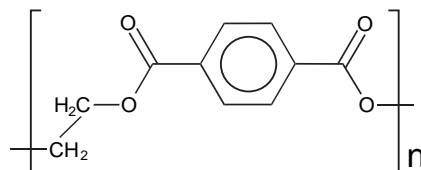
One problem is the enormous number of interconnections that are needed and the heat generated both from electrical resistance and from the switching operations that transfer electrical charge in the circuits. Overall, there is a net increase in the amount of heat generated per unit area with miniaturization, because the area density of heat-generating circuit elements rises more rapidly than the reduction in heat generated by the individual circuit elements. For this reason, the central processing unit (CPU) in Figure 1 is situated under a large heat sink to dissipate the heat generated by its operation. Another problem associated with miniaturization is that it leads to stronger electric fields; electrons can acquire so much energy in such fields that the circuit will cease to operate properly. Finally, if dimensions of ~100 Å are reached, the tunneling of electrons out of circuit components will become a problem (4, 5).

There are also optical problems associated with miniaturization, such as the diffraction limit imposed by the wavelength of the light source used in photolithography (16; also see the section on compact disks below). Although mask features in lithography can be made significantly smaller than current IC features—using, for example, electron beams or X-rays from synchrotron sources, diffraction occurs through the mask slits, compromising spatial resolution. As the wavelength used in photolithography is reduced, another difficulty that arises is maintaining a focused image using the system's lenses. A variety of alternative strategies are being pursued to address the issues associated with continued size reductions, which, although beyond the scope of this article, will most assuredly make demands on the materials and interfaces needed for IC construction (16).

Storing and Retrieving Information: Magnetic Media and Readers

Another aspect of materials science that is represented in computers is magnetism (17). Magnets are used in data storage media, data read and write heads, motors and actuators, and speakers; they also control the electron beams that sweep across monitor screens. Perhaps the portion of the computer most prominently impacted by magnets and magnetism is its data storage system.

Although semiconductor-based memory has greater speed, magnetism permits more permanent data storage and has led to floppy disks and hard drives, which use magnetic material on thin, flexible polyesters like poly(ethylene terephthalate) (PET) and on stiffer sheets (glass or aluminum), respectively.



PET

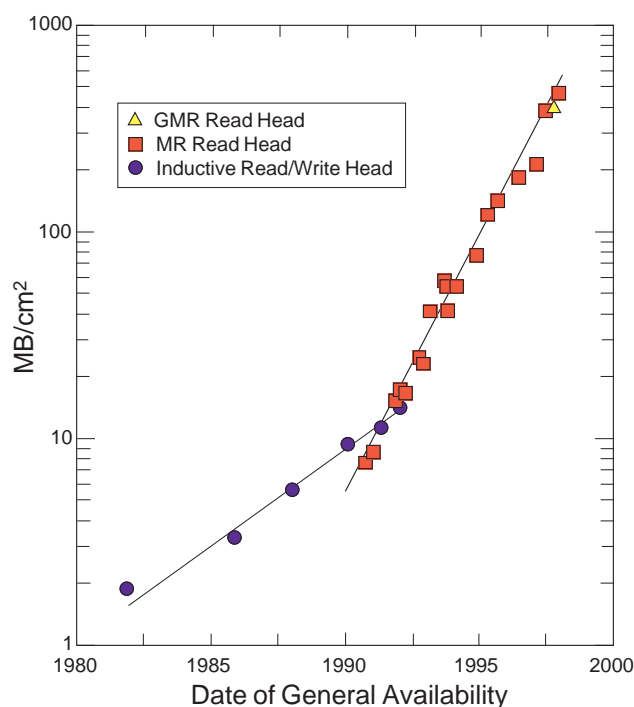


Figure 9. Areal data storage density in units of megabytes (MB) per square centimeter vs the year in which the storage density became commercially available.

Today, thin films (less than 10 nm) are used as the magnetic storage medium on hard drives, with magnetic cobalt–platinum alloy grains (~10–20 nm in width) segregated by a nonmagnetic chromium coating. This magnetic isolation of the grains prevents them from magnetically coupling and interfering with each other. Bits of binary information are stored on the disks as one of two opposing (antiparallel) magnetic spin orientations within the film. Each of these areas of magnetic

spin orientation encompasses many magnetic grains and is oriented parallel to the plane of the disk (18–20).

Devices used to read and write to magnetic storage areas must be magnetic themselves. Write heads generate magnetic fields when a current flows through their copper coils (21). These fields align the magnetic spin orientations of regions within the disk, storing magnetic data bits. Most read heads currently use materials that experience a change in electrical resistance upon exposure to a magnetic field, a property called magnetoresistance (MR).

Many read heads contain permalloy, a magnetic $\text{Ni}_{0.8}\text{Fe}_{0.2}$ alloy, and utilize a phenomenon called anisotropic magnetoresistance (AMR) (18). The electrical resistance to the net motion of electrons depends on their direction of movement relative to the magnetization of the alloy. Magnetic fields from disk surfaces rotate the magnetization in such a way as to alter the resistance to current flow in the AMR read head; in the case of permalloy, the resistance increases by a few percent relative to the resistance in the absence of the magnetic field. The use of MR read head technology rather than older technologies utilizing induction has allowed a dramatic increase in available disk storage density, because smaller areas of magnetic disk surface may be used to stimulate the read head. The impact of MR technology can be seen by the increase of the slope in Figure 9, in 1992 (19, 22).

Recently, much larger magnetoresistance effects have been observed. A phenomenon called giant magnetoresistance (GMR) corresponds to a several-hundred-percent reduction in resistance associated with metal multilayer structures in passing from the absence to the presence of a magnetic field. Many GMR materials contain a sandwich of magnetic, nonmagnetic, and magnetic layers (e.g., Co, Cu, and NiFe layers, respectively), each layer having a thickness on the order of a few nanometers (23). The Cu layer is less than 15 atomic layers thick (24). The multilayers operate as a kind of “spin valve”, as sketched in Figure 10. Without the influence of an external magnetic field (Fig. 10a), the magnetic layers adopt

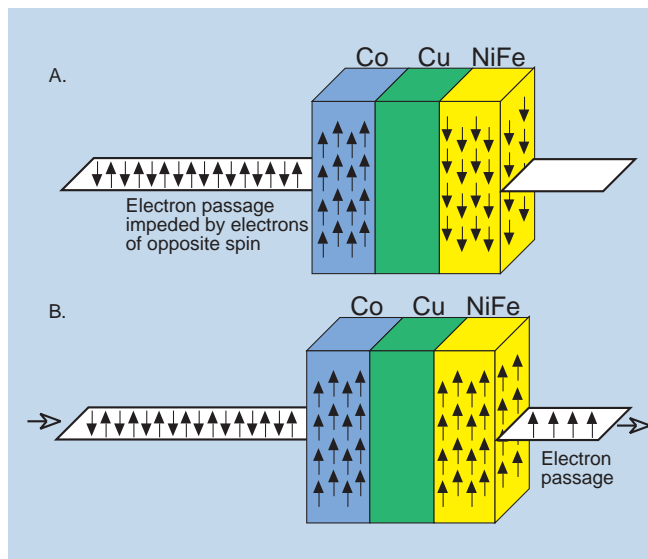


Figure 10. An idealized schematic of how the relative electron spin orientations of a metal trilayer structure influence electrical resistance. Small arrows represent electron spins, and we assume a higher electrical potential at the left of the figure so that electrons have a tendency to flow from left to right. (A) In the absence of an applied magnetic field, the dominant electron spin orientations in the two magnetic layers spontaneously oppose one another (electrons of opposite spin within each magnetic layer are omitted for clarity) and lead to high resistance, as described in the text and represented by the absence of arrows at the right-most part of the figure. This is analogous to blocking light transmission by use of crossed optical polarizers. (B) With the influence of an applied magnetic field, the dominant electron spin orientations in the magnetic layers align in the same direction as the magnetic field and lead to lower resistance, as described in the text and represented by the arrows at the right-most part of the figure. This is analogous to transmitting light by the use of parallel polarizers.

an antiparallel magnetic orientation (one layer is magnetically oriented exactly opposite the orientation of the other layer). When an external magnetic field is applied (Fig. 10b) both magnetic layers adopt a parallel magnetic orientation. The majority of electron spins point in the same direction as the magnetic orientation of a material and are referred to as majority spins. A minority of electron spins point in the opposite direction, and are referred to as minority spins (the minority spins are omitted from the magnetic layers of Figure 10 for clarity).

In Figure 10a, there is no applied magnetic field. A flow of electrons enters the spin valve from the left side; the spins of these electrons are represented by small arrows pointing up and down. These electrons collide with electrons in the metal layers. Based on the nature of these magnetic layers, collisions between minority spins are more likely to result in energy loss and slowing of electrons in the current flow (resistance) than collisions involving majority spins. The left-most magnetic layer (Co) has an excess of majority spins represented by the up-pointing arrows. Since it is harder to transfer energy to a majority spin than to a minority spin, the current entering the middle nonmagnetic layer contains, from the perspective of the Co layer, an excess of majority spins. From the perspective of the magnetic layer at the right-most side (NiFe), whose magnetic orientation is opposite to that of the Co layer, the current contains an excess of minority spins. The minority spins (not shown) of this NiFe layer absorb energy from what is now a predominantly minority spin current and therefore the net resistance is high. The high resistance is represented in Figure 10a by the absence of arrows leaving the right side of the spin valve.

In Figure 10b, there is an external magnetic field that forces both magnetic layers to adopt a parallel magnetic orientation. Again, the left-most magnetic layer, with its excess of majority spins, causes the current entering the nonmagnetic Cu layer to have an excess of majority spins. This time, the magnetic layer on the right has the same magnetic orientation as the magnetic layer on the left. The current therefore passes through the NiFe magnetic layer with much less resistance. This lowered net resistance is represented by the up-pointing arrows leaving the right side of the spin valve in Figure 10b. The applied magnetic field needed for this effect is generated by areas of magnetic spin in the hard disk. IBM has recently announced the production of read heads based on the GMR phenomenon (24).

Even more substantial are up to thousandfold reductions in electrical resistance induced by magnetic fields that have recently been discovered in perovskite-based solids such as $\text{La}_x\text{Sr}_{(1-x)}\text{MnO}_3$ (Fig. 11). Dubbed "colossal magnetoresistance (CMR)", the effect is derived from mixed-valence Mn atoms, whose unpaired electron spins seem to play an analogous role in mediating the flow of electrons to that described for metal multilayers. The development of CMR materials could lead to yet more storage density in the near future (23).

Transporting Information: Laser Diodes and CDs

The compact disk (CD) has emerged as a convenient technology for portable storage of enormous amounts of digital

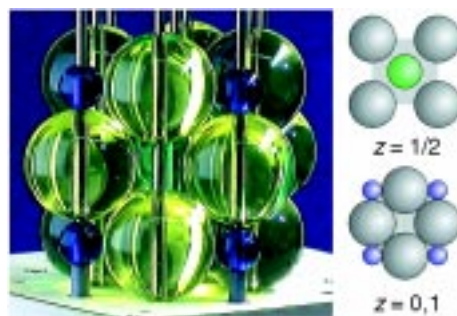
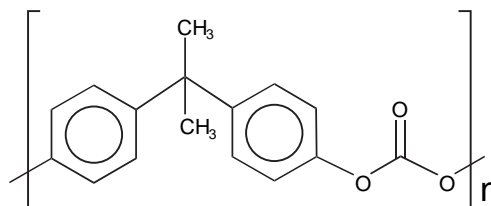


Figure 11. A perovskite unit cell structure built with the ICE Solid State Model Kit (6) and corresponding layer sequence, defined in Figure 4. For LaMnO_3 the color key is gray, oxygen; purple, manganese; and green, lanthanum. For BaTiO_3 : gray, oxygen; purple, titanium; and green, barium.

information. Nonrecordable CDs are made of rigid, transparent polycarbonate with a reflective metal coating atop the plastic; information is encoded digitally as physical features or "pits and lands" of differing reflectivity at the plastic/metal interface.



A polycarbonate polymer

A recordable CD contains an organic cyanine dye between the polycarbonate and the metal film. A laser creates areas of decreased transparency in the dye layer through photochemical reactions, allowing reflection from the metal film in the transparent regions.

A beam from a semiconductor diode laser interrogates the underside of both types of disks. Reflected and unreflected light correspond to ones and zeroes, respectively—that is, the "bits" of digital information (25–27). It is desirable to use laser wavelengths that are as short as possible in order to compress more information onto the CD: as the laser wavelength decreases, the smallest possible diffraction-limited focused laser spot on the disk surface proportionally decreases, and smaller "pits and lands" can be interrogated (28, 29). Using a blue laser light source rather than the current near-infrared laser light sources will shrink the spot diameter by a factor of nearly two, based on relative wavelength, permitting a roughly fourfold increase in storage density (and thus a fourfold increase in playing time) with current disk dimensions (30). A current goal, therefore, is to produce inexpensive, durable, blue-emitting diode lasers.

The wavelength of a diode laser depends on the band gap energy, which depends on the sizes of atoms in the solid and the electronegativity differences between them, as illustrated in Figure 12 (2, 31, 32). In a simple localized bond

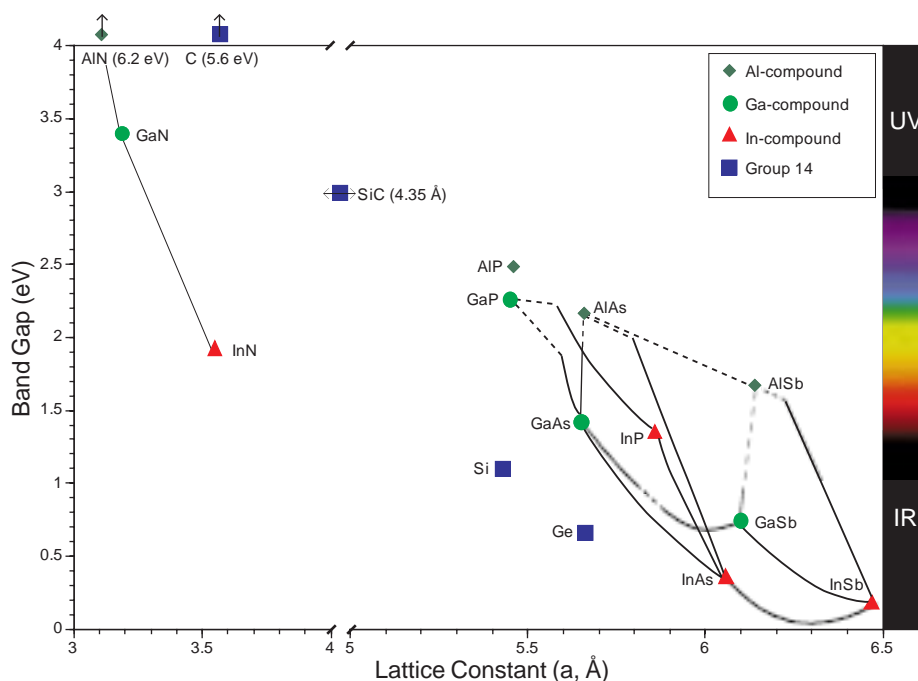


Figure 12. Band gap energies and lattice constants of semiconductors from elements in group 14 and from compounds derived from elements in groups 13 and 15. AlN and C (diamond) are off scale as indicated, and SiC falls in the break along the x axis. The data on the right side of the break in the diagram represent compound semiconductors having the zinc blende structure; these data were obtained through the courtesy of V. Keramidis and R. E. Nahory of Bellcore. On the left side of the break in the diagram

are compound semiconductors having the wurtzite structure (2, 32). Throughout the diagram, lines represent solid solutions formed from the compounds at the end points of the lines. For example, the line connecting InP and InAs corresponds to solid solutions of composition $\text{InP}_x\text{As}_{1-x}$ ($0 \leq x \leq 1$). Solid lines represent direct bandgaps and dashed lines represent indirect bandgaps (2). The color bar at the right edge of the figure correlates the band gap energy with its corresponding color in the visible spectrum.

picture, band gap energy can be defined as the energy it takes to excite electrons from bonds, allowing the electrons to be mobile and carry electricity in the solid. When electrons return to restore the bonds, they release roughly the band gap energy, which can be in the form of heat or light (i.e., photons having the band gap energy).

The ability to form solid solutions, represented by the lines connecting compositions in Figure 12, and p-n junctions from these groups of elements provides enormous flexibility in designing diodes that emit efficiently at desired wavelengths. Present generation CD players use an $\text{Al}_x\text{Ga}_{1-x}\text{As}$ diode laser that emits in the near infrared (780 nm). Band gap control of these diodes has recently received a huge boost with the discovery that robust nitride solid solutions, such as $\text{Ga}_x\text{In}_{1-x}\text{N}$, can now be manufactured using chemical vapor deposition (CVD) processes. These GaN-based semiconductors have made possible the fabrication of durable LEDs that emit blue light. Now that these blue LEDs have been commercialized, there is reason to be optimistic that blue diode lasers will be available soon and that further reductions in the wavelength of diode laser output will occur over the next decades.

One other feature of diode laser construction worth emphasizing is that the mobile electrons and holes whose recombination leads to light emission can be spatially confined by layering materials of differing chemical composition. Indeed,

scientists have learned over the past few decades how to confine these particles in three dimensions (quantum boxes), two dimensions (quantum sheets), one dimension (quantum wires), and as a quantum dot by abruptly changing chemical composition at the level of atomic layers. The "particle in a box" of quantum mechanics is now readily grown in real boxes that, within material-determined limits, can be arbitrarily wide, with potential walls that can be arbitrarily high (1a, 16, 33–35).

Displaying Information: Phosphors, LEDs, and Liquid Crystals

Materials chemistry has figured prominently in our ability to visualize information through the computer. The entire visible spectrum can be accessed by using additive color mixing, combining small red, green, and blue light sources in an array of pixels to form a display screen.² At normal viewing distances, variable contributions from each of the three basic colors creates the effect of a full palette of colors for each pixel (36).

Monitors typically use phosphors to provide visible light output from pixels that are excited by cathode ray tube (CRT) electron beams. In liquid crystal display panels (see below), phosphors serve as a backlighting source excited by ultraviolet light. In electroluminescent (EL) display technology, pixels or a backlighting panel can be excited by electrical current (37–41).

The conditions under which phosphors are required to operate present challenges. Low pressures can lead to outgassing, and high energy electrons and photons used for excitation can lead to defects in the solids, such as F-centers (2), compromising device performance. From decades of experimentation, phosphor production has converged on the use of sulfide salts for cathode ray tubes (CRTs) in monitors and televisions, and on oxide salts for narrow fluorescent lamps in flat-panel displays. Phosphor performance has been optimized in the red, green, and blue parts of the visible spectrum.³

The synthesis and processing of phosphors has required substantial empirical work. A typical preparative route involves co-precipitating the components of the precursor solid (host and dopants) from solution, followed by firing them at high temperatures using a flux. The flux is a high-temperature molten salt that serves as the solvent and is subsequently removed through its volatility or water solubility. The resulting powder is used to make the thin-layer phosphor screen. Sol-gel methods, wherein precursors achieve atomic-scale mixing at low temperatures, can also be utilized but are not currently economically competitive (2).

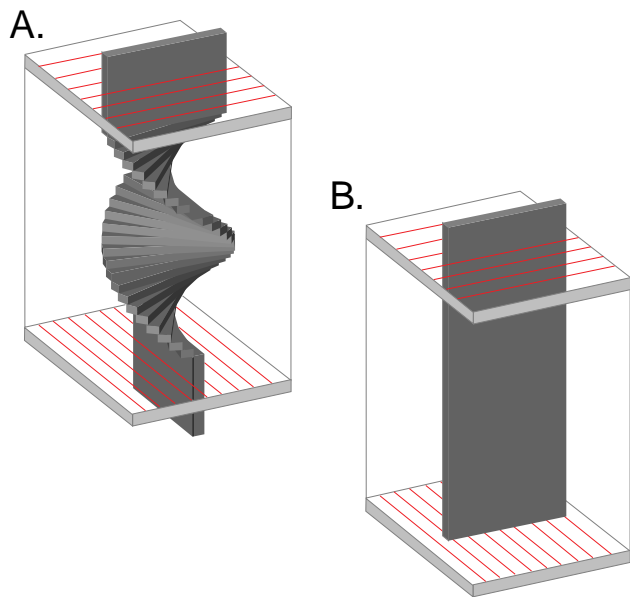


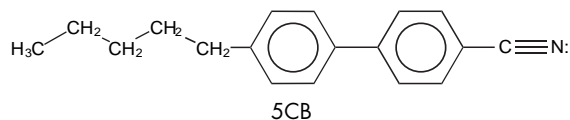
Figure 13. Diagram of a twisted nematic display element used in laptop computer screens. There are liquid crystal molecules between crossed polarizers; polarizer orientations are represented by the lines on the top and bottom of each element. A: At zero applied voltage, the orientation of the long axes of the liquid crystal molecules parallel and next to the top polarizer is rotated by 270° with respect to the long axes of the molecules parallel and next to the bottom polarizer; the light passing through the top polarizer follows this rotation and is properly aligned to emerge through the bottom polarizer. B: With an applied voltage, the liquid crystal molecules align so that their long axes are perpendicular to both polarizers; the light passing through the top polarizer is not rotated and is thus blocked by the bottom polarizer (48).



Figure 14. Top: A device used to demonstrate the colors that may be generated from a "white" LED by adjusting the variable resistors and thus the voltage applied to each of its three color components.⁴ Bottom: Some of the many colors produced from this LED. The extreme right-hand color mimics white light by additively combining the red, green, and blue individual LED outputs.

Recently, combinatorial methods have been employed that may permit rapid selection of compositions and synthetic conditions leading to improved phosphor efficiency (42). A UV light can be used to interrogate a matrix of phosphor compositions to assess their suitability for use in backlighting. Several goals of phosphor research for the next decades may be furthered by combinatorial synthetic methods. These include identifying higher-efficiency systems in which, through the intermediacy of excited states, multiple emitted photons are obtained per incident photon; a better chromaticity match with the receptors in our eyes; and yet more robustness in the display environment.

In the flat-panel displays of laptops, liquid crystals, through their electrically controlled ability to transmit light by virtue of their interaction with polarized light, serve as optical shutters for the backlight emission (Fig. 13) (43–47). Each display pixel typically consists of at least three shutters and red, green, and blue color filters. An array of these shutters placed over the backlight light source controls light transmission by changing the orientation of liquid crystals in the nematic phase. The nematic liquid crystal phase refers to a structure in which molecules have orientational order (they are oriented in the same direction), but not positional order, as would be found in the repeating array of a crystal (46); a typical rod-shaped compound that forms this kind of ordered structure is *p*-*n*-pentyl-*p*'-cyanobiphenyl (5CB) (48).



More recently, supertwisted nematic displays have been developed, which rotate the polarization of light by 270°. These displays have lower power consumption, better viewing parameters such as greater contrast, and fuller integration of color using filters (49). Advances in such computer displays will result in higher resolution, better viewing characteristics, and faster speed. For pure viewing ease, they probably will not compete with the CRT of monitors for some time, so

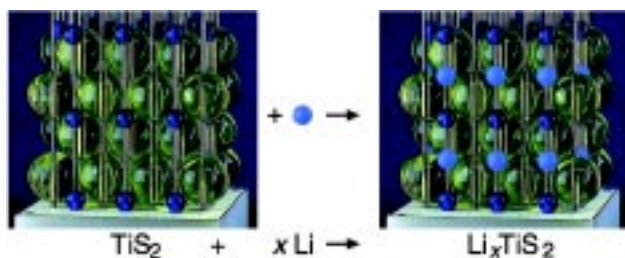


Figure 15. Reaction showing the intercalation of Li into some of the octahedral holes in TiS_2 . Colorless spheres represent S atoms, translucent blue spheres represent Ti atoms, and opaque blue spheres represent Li atoms.

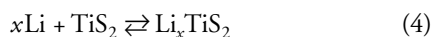
their use is likely to remain in laptops where low weight and low power consumption are important.

A potential challenge to phosphors as color light sources is the LED. LEDs are also used as backlighting sources in liquid crystal displays (50). Now that blue LEDs are available, combining them with red and green ones permits access to the entire visible spectrum. Shown in Figure 14 is such a "white" LED that is derived from this trio of colored LEDs.⁴ As the panels in Figure 14 illustrate, by varying the relative outputs of the three constituent LEDs, any desired color can be created.

Protecting Information: Intercalation-Based Batteries

Batteries, which allow laptops to be used remotely and all computers to protect vital data when their normal source of power is disconnected, are a critical part of computer technology. Issues of lifetime, weight, voltage, and reversibility are important. The highest possible energy densities are required to give maximum life between charges, and thus electrochemical couples with the highest voltages compatible with system safety are used. Lead-acid car batteries meet the requirements of reversibly storing electrical energy through many cycles, but fail weight and safety requirements for use in a computer. At present, computer batteries contain lithium as the active anode material and an oxide or sulfide salt as the cathode. Larger voltages come from more active metals, but these active metals lead to safety difficulties. Achieving maximum rechargeability and discharge rates requires fast, reversible chemical reactions; this, in turn, restricts solid-state electrode reactions to those that do not demand a significant change in crystalline structure. One class of such reversible reactions involves intercalation, wherein guest species enter a host solid.

The first example of a battery based on this type of process used a pure lithium anode and a titanium disulfide cathode (51–53) (eq 4).



where $0 \leq x \leq 1$. Titanium disulfide has a sandwich-type structure, with hexagonal close-packed sulfur sheets and titanium



Figure 16. A demonstration of the large thermal conductivity of synthetic diamond: Heat transferred from a human hand enables the diamond sample to cut rapidly through a cube of ice, even with minimal application of pressure (2). The diamond almost immediately feels cold to the touch.

occupying all the octahedral sites between alternate sulfur layers. This leaves only weak van der Waals bonding between pairs of sulfur sheets, as indicated in Figure 15, facilitating the intercalation of lithium guest atoms into the host TiS_2 structure. Such cells generate up to 2.5 V, but present central processing units (CPUs) require around 3 V. A breakthrough occurred in 1980 with the discovery that lithium could be removed electrochemically from LiCoO_2 , which has the same sandwich structure as LiTiS_2 , except that the oxide ions are cubic close-packed (54). This cell has a mean discharge voltage of around 4 volts for the reaction of eq 5



where $0.4 \leq x \leq 1$. As the battery discharges, Li ions move from a graphitic carbon anode through an organic solvent or polymeric electrolyte to the Li_xCoO_2 cathode; during recharging the Li ions are moved back into the anode (55–57).

The use of pure lithium metal in these cells is not safe, as the cells employ electrolytes based on organic solvents that can explode in the presence of finely divided lithium. A second breakthrough occurred with the development of an anode based upon intercalation, wherein the lithium was stored in graphite-based coke. The cell shuttles lithium between two host compounds, carbon and lithium cobalt oxide, generating around 3.7 V (58). These lithium-ion cells are now used in almost all portable computers and for the battery in desktop systems, as well as in a host of other consumer items such as CD players and cellular phones. Because cobalt is expensive, current and future research efforts will focus on identifying intercalation hosts that are cheaper and that store more energy by, for example, cycling over greater compositional ranges.

Accelerating the Flow of Information: Diamond, Dielectrics, and High-Temperature Superconductors

We conclude this paper with examples of emerging technologies that illustrate the vitality of materials science and its potential for profoundly influencing a multitude of technologies. Diamond films, dielectrics, and high-temperature superconductors highlight the kinds of unexpected developments that can open new technological opportunities. With the

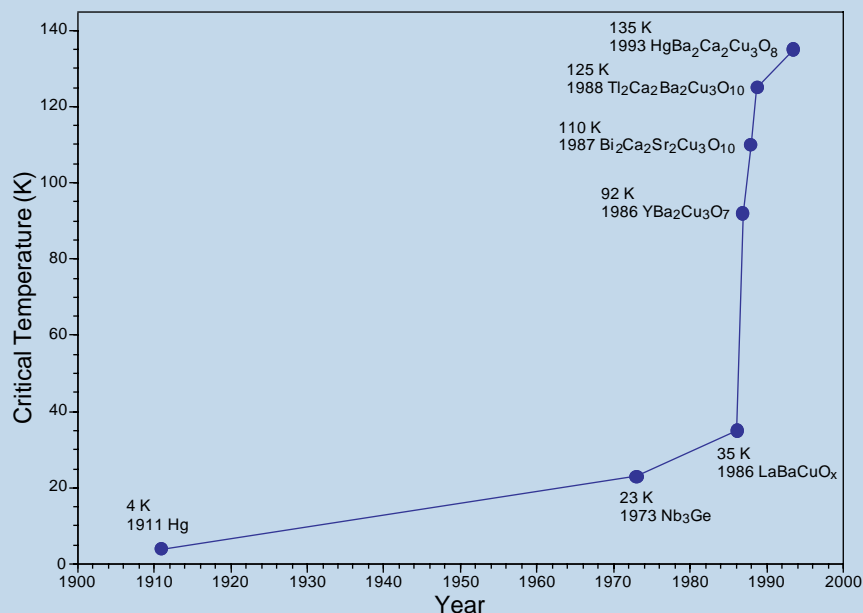


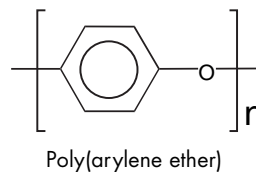
Figure 17. Plot of superconductor critical temperature, T_c , vs the year in which the indicated material having this value of T_c was prepared. Oxide stoichiometric ratios should be regarded as approximate, as there can be significant deviations from ideal stoichiometry. We thank Art Sleight and David Larbalestier for providing some of the information for this figure.

exceptional ability of diamond to conduct heat, the potential superiority of xerogels and perovskite-based solids over silicon dioxide as low and high dielectric materials, respectively, and the capability of superconductors to conduct electricity without resistance, new materials could permit computers to become far smaller and faster, accelerating the rate at which information flows within them.

The growth of synthetic diamonds, a process developed at General Electric in the 1950s, represents one of the most significant materials breakthroughs of the past half century (59–62). Diamond, whose structure is shown in Figure 4, is an extraordinary material, setting the standard for such properties as hardness and thermal conductivity (Fig. 16).⁵ Although less thermodynamically stable than graphite, diamond is the denser of the two phases, and its formation at high pressure and temperature has resulted in a multibillion dollar industry of synthetic diamonds in applications ranging from superabrasives to high-quality optical windows; it may also be possible to coat hard disks with diamond (63). The discovery, in the early 1980s, that diamond films can be grown by chemical vapor deposition (CVD) from precursors like acetylene and hydrogen could lead to enhanced durability of many products by increasing wear resistance and reducing damage from heat. The ability to dissipate heat in computers with diamond-based heat sinks could facilitate future size reductions.

Besides heat dissipation, another roadblock to reduction in the size of computers is the silicon dioxide dielectric material, with a dielectric constant of only about 4 (10, 11). While this material has many advantages (including ease of preparation from silicon), as the size of the layer is reduced, eventually electron tunneling will begin to occur though it, compromising the integrity of the electrical circuitry in the

IC. Perovskite materials such as BaTiO₃ (Fig. 11) have significantly higher dielectric constants (κ on the order of $\sim 10^3$) and may permit far more charge to be stored in IC memory capacitors for a given voltage (64, 65). The origin of the enhanced dielectric constant is the mobility of the Ti⁴⁺ cation within its coordination environment. As oxygen vacancies are introduced into the solid, the cations have yet more freedom to move in response to an electric field, enhancing the solid's dielectric constant. Methods to adequately control these properties during synthesis, however, will need to be developed, as will strategies for integrating the materials into the computer's architecture. Lower dielectric constant materials such as silica xerogel ($\kappa < 2$), an interconnected, rigid polymeric network with pores of submicrometer dimensions, and poly(arylene ether) ($\kappa < 3$) are being explored for use in the IC at locations where reducing capacitance and improving electrical insulation can increase speed and reduce power consumption (2, 14).



Entirely new technologies for computer construction could come from superconductors. When they were first identified in the mid-1980s, high-temperature perovskite-based superconductors like YBa₂Cu₃O_{7-x} astonished the scientific world (2, 66). The unexpected ability of these materials to pass current without electrical resistance and to exhibit the Meissner effect (expulsion of a magnetic field from the interior of the



solid) at record high temperatures of ~ 90 K meant that liquid nitrogen could be used to access superconducting properties. Combinations of different elements with oxygen, as shown in Figure 17, have continued to raise the so-called critical temperature, T_c , below which superconducting behavior is observed. A goal of superconductivity at or near room temperature will continue to be vigorously pursued in the decades ahead.

In parallel with attempts to raise T_c by varying chemical composition are efforts to process these materials into current-carrying structures such as wires and films. Great progress has been made, considering the brittleness of these ceramic solids, and flexible wires and films capable of carrying 10^5 A/cm² (considered the minimum needed for many applications) are now available (67). Key research efforts involving polycrystalline samples of these superconductors involve the transport of current across grains, which act as so-called weak links. Growth of superconducting grains with well-defined boundaries shows promise of contributing to the control of these structures and permitting their incorporation into computer circuitry. Ultimately, because silicon and superconducting materials are sufficiently different, a superconductor-based computer will likely require a completely different design (68).

Conclusion

Materials science has emerged as an engine for enormous technological advances in the past half century, as represented by the components of the computer highlighted in this article. The Information Age and Materials Age have resulted from revolutionary developments that are causing fundamental personal and societal changes (69). If the technological developments of our recent past are a true indication of what lies ahead, the design and customization of materials and devices, using powerful computational and synthetic tools, will soon be routine. We hope to have shown in this article that while it is steeped in history, materials science is in many respects a young science that offers extraordinary opportunities and promise in the decades ahead.

Acknowledgments

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Notes

1. Wafer size may ultimately be limited by dislocations that occur in the crystal; dislocations are a type of defect characterized by having groups of atoms out of their normal alignment (2). In the Czochralski crystal growth process, "necking" is used to prevent the propagation of dislocations from the seed crystal into the larger boule that is being grown. By use of a small-diameter region (neck) between the seed and the boule, inclined dislocations propagating from

the seed will terminate at the edge of the neck region and thus not extend into the boule. However, calculations suggest that, if stress fracture is to be avoided, crystal diameters may ultimately be limited by the mass of the boule that the neck must support. A seed crystal 3 mm in diameter is estimated to be able to support a 144-kg silicon crystal (13).

2. Computer pixels, which are addressable points on a computer display, have red, green, and blue contributions. These color components can be viewed with a low-magnification hand lens or Radio Shack microscope. Try it!

3. Currently, red light in the CRTs of monitors is obtained with europium-doped yttrium oxide sulfide, $Y_2O_3:S:Eu^{3+}$; blue light with ZnS co-doped with Ag and Cl—that is, $ZnS:Ag, Cl$; and green light with $ZnS:Cu, Au, Al$. The variation in the color of the emitted light in the ZnS phosphors arises from donor-acceptor complexes in the solid. Emissive efficiencies range from 12 to 22%. For backlighting in laptops, red light is emitted by $Y_2O_3:Eu^{3+}$; green light by $CeMgAl_{11}O_{19}:Tb^{3+}$; and blue light by $BaMgAl_{10}O_{17}:Eu^{2+}$. Quantum efficiencies of these materials are 85–90%; energy efficiencies are about 40%. We thank Niel Yocom for providing this information.

4. We thank Tom Baraniak of Baraniak Robotics and Tricia Ferrett of Carleton College for bringing this demonstration to our attention. The "white" LED can be obtained from CREE Research, Inc., 2810-T Meridian Pkwy, Suite 176 Durham, NC 27713 (tel. 919-361-2674); part no. CRGB-5D18. Contact Tom Baraniak at Baraniak@src.wisc.edu for further design details on the "white" LED device. A nontunable white light source incorporating a phosphor material that emits red and green light, along with a blue LED, which excites the phosphor material, is available from the Nichia America Corporation, 3775 Hempland Rd., Mountville, PA 17554. Its catalog number is 960910k.

5. "Isotopically pure" diamond films containing 99.9% carbon-12 (rather than 99% carbon-12, as is found in natural diamonds) have been grown and have been found to conduct heat 50% better than natural diamonds, reflecting the reduction in isotope "defects" in the solid (61).

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Viewpoints: Chemists on Chemistry

The Computer as a Materials Science Benchmark

The authors of this review have collaborated on research and education projects related to materials chemistry. Through the Institute for Chemical Education and the National Science Foundation's Materials Research Science and Engineering Center on Nanostructured Materials and Interfaces, and as participants in the Ad Hoc Committee for Solid-State Instructional Materials, the group has developed a variety of new educational tools. For additional information about these projects and others, please refer to these web sites:

<http://www.mrsec.wisc.edu/edetc/edetc.html>

<http://jchemed.chem.wisc.edu/icel>

<http://imr.chem.binghamton.edu/teaching.html>



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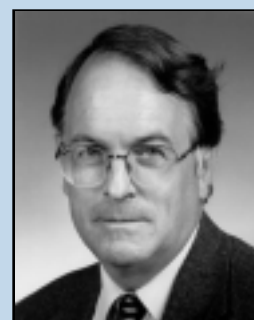
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