Optical Materials

A. M. Glass

Optical technologies are becoming increasingly important in areas that were traditionally the domain of electronics. This trend is likely to continue into the foreseeable future with optics and electronics being integral, mutually compatible components of systems for consumer markets, industry, and defense. The basis of this progress is the development of materials that have the required purity, physical properties, and optical quality; glass fibers for optical transmission, semiconductors for lasers and detectors, and nonlinear materials for optical switching are examples. In this article, some of the materials of choice for a variety of applications are described and the frontiers of materials research for new areas of opportunity are discussed. Particular emphasis is placed on optical materials for the transmission and processing of information.

NOT LONG AGO OPTICAL TECHNOLOGIES INFLUENCED OUR lives only through the display interface between us and machines—namely, television cathode-ray tubes, alphanumeric light-emitting diodes (LEDs) and liquid-crystal displays. In recent years, however, optics has been spreading more and more into areas that were traditionally the domain of electronics. This is most noticeable in communications, where an entire network of optical fibers, LEDs, lasers, and detectors has already been installed for transmission of voice and data. Optical disk recordings with semiconductor-laser playback are replacing the conventional piezoelectric pickup. Solar cells are now common components in toys, calculators, and other consumer electronics. Infrared detectors and lasers are the basis of many intrusion detection systems. There are numerous other examples.

The trend toward optical technologies will likely continue in consumer markets, industry, and defense systems. The development of materials with the necessary optical properties is the basis of each technology whether it be ultralow optical-loss fibers, semiconductor lasers emitting milliwatts of power, or gigawatt lasers for destroying missiles. The optics research community is now very diverse and the materials requirements are generally different for each application.

In Table 1, I list a number of optical technologies together with some examples of the materials of current interest. It is immediately evident that optical materials are diverse, including inorganics, organics, polymers, semiconductors, glasses, single crystals, and composites. Because of the breadth of the topic, it is possible to address here only a few of the materials issues involved. Emphasis will be placed on materials of importance for optical communication and information processing. These are areas where the full capabilities of optics can be effectively utilized. With the optical carrier frequency exceeding 10^{14} Hz, communication bandwidths and information switching in the multi-terabit per second range is potentially achievable. At the present, the bandwidths are limited by current materials technologies, and the challenge is for optical materials research to develop improved components that will allow us to approach the theoretical optical limits.

Optical Fibers

In the 20 years since the first proposal to use glass fibers for optical transmission (*1*), there has been dramatic progress in the materials technology. Optical losses have been reduced from about 100 dB km^{-1} to almost 0.1 dB km^{-1} by elimination of absorbing impurities, careful choice of material composition, improvements in fiber design, and the development of fiber-drawing techniques which give uniform low-scatter light guides. Optical communication systems have been developed in which light can be transmitted over distances beyond 100 km without signal regeneration (*2*). Communication bandwidths in excess of 1 Gbit sec^{-1} have been demonstrated over these distances—a feat not possible with electrical transmission lines.

To avoid leakage out of a glass fiber, the light is guided along a core of refractive index higher than that of the surrounding cladding material. The light intensity is then confined to the central region of the fiber and is not affected by the outer fiber walls. The radial variation in refractive index of the fiber is achieved by appropriately doping the core of the silica preform with higher index germania and the cladding with fluorosilicates during the preform fabrication. The fiber drawn from the preform maintains this profile but with greatly reduced lateral dimensions.

The material parameters of importance for long-distance light propagation are scattering loss, absorption loss, and dispersion. Absorption loss has been effectively eliminated in silica fiber materials at communication wavelengths (λ) of 1.3 and 1.55 μm by reducing absorbing impurity levels to below 1 part per billion. Propagation losses are now essentially limited by Rayleigh scattering from density fluctuations in the glass. This fundamental loss parameter is about 0.1 dB km^{-1} in fused silica at a wavelength of 1.55 μm. At shorter wavelengths, Rayleigh scattering losses increase as λ^{-4}, whereas at longer wavelengths multiphonon absorption is the dominant loss. The total theoretical loss is shown in Fig. 1 as a function of wavelength. To achieve a loss lower than 0.1 dB km^{-1}, other materials systems such as chlorides and fluorides or even modified silicates containing alkali metals and aluminate modifiers must be considered (*3*). In halides the multiphonon absorption edge is shifted to longer wavelengths and the fundamental Rayleigh scattering losses are reduced. The theoretical (*4*) minimum loss for these new fibers is expected to be some 1/10 to 1/100 of that of fused silica fibers at longer wavelengths. This would allow communication over thousands of miles without repeaters. At present, fibers have been drawn from heavy metal (zirconium, barium, lanthanum, and aluminum) fluoride compositions with total losses of below 1 dB km^{-1} (*5*) but this is constantly being reduced as purification techniques improve. ZnCl and BeF_4 (*6*) have low ultimate losses as seen in Fig. 1 but, because of the reactivity of chlorides with atmospheric moisture and the toxicity of beryllium compounds, there has been less effort in these directions. Even the fluorides, for which there is much research in progress, are attacked

---

The author is head of the Device Materials Research Department, AT&T Bell Laboratories, Murray Hill, NJ 07974.

by moisture, have a tendency to crystallize, and currently have a mechanical strength about 1/10 of that of fused silica. They represent a considerable challenge for the development of purification techniques and procedures for fabricating practical fiber. The optical losses actually achieved in these fibers are compared with those predicted theoretically in Table 2.

As losses in new fiber materials decrease, new limitations for light transmission will likely emerge. Nonlinear optical effects such as Raman and Brillouin scattering and self-phase modulation will set an upper limit to the power that can be launched into a fiber, and this limit will ultimately affect the repeater spacing. Present estimates place the acceptable power levels in fluoride fibers at about 1 mW. On the other hand, fiber materials having high cross section for these nonlinear effects may well find applications as parametric amplifiers, optical frequency converters, or optical pulse compressors.

Material dispersion is also another critical parameter for optical fiber technology. Because of the finite spectral line width of laser sources, a short optical pulse injected into the fiber is broadened by the dispersion during propagation, eventually leading to pulse overlap and errors in pulse discrimination. In silica, the wavelength of minimum dispersion occurs at $\lambda = 1.3\ \mu m$, somewhat separated from the wavelength of minimum total loss (1.55 μm). The effects of dispersion can be minimized by using narrow line width lasers. Alternatively, by careful design of the index profile of the fiber, fibers can be made in which material dispersion can be canceled at specific wavelengths by waveguide dispersion (*7*). Theoretically, techniques of this kind can be applied to longer wavelengths and lower loss fibers as these become available.

Table 1. Examples of optical materials currently in use for a variety of applications.

Technology	Materials
Communications	Semiconductors
Lasers/detectors	InGaAsP/InP, GaAlAs/GaAs
Fibers	SiO_2, halides, plastic
Modulator, switch	$LiNbO_3$, GaAs, InP
Amplifiers	Raman fibers
Signal processing and interconnection	Electro-optical materials ($LiNbO_3$) Acousto-optic (quartz, $LiNbO_3$) Photorefractive ($BaTiO_3$, $BiSi_{12}O_{20}$, InP, GaAs, CdTe) Organics (polydiacetylenes) Semiconductors (GaAs multilayers) $CdS_{1-x}Se_x$ particles in glass
Strategic defense and laser fusion	High average-power lasers and high damage threshold components. Graded index surfaces
Remote sensing	Tunable lasers (Ti: sapphire), alkali halides, parametric oscillators (chalcopyrites)
Thermal detection	Pyroelectrics (triglycene sulfate, $LiTaO_3$, PLZT), narrow-gap semiconductors (HgCdTe)
Fiber sensors	SiO_2 fibers, infrared fibers
Display	Liquid crystals, phosphors, light-emitting diodes (GaP)
Light valves	Liquid crystals, PLZT ceramics
Storage	Short wavelength lasers, chalcogenides, magneto-optics
Frequency conversion	$K(TiO)PO_4$, BaB_2O_4, organics, KH_2PO_4
Optical isolation	$Y_3Fe_5O_{12}$:Bi

Although the main driving force for fiber technology is in communications, there is increasing interest in the use of fibers for sensing (*8*) and power transmission. A wide variety of sensors have been fabricated including hydrophones, gyroscopes, temperature sensors, gas detectors, and many others. Several approaches to making such sensors have been studied, some of which incorporate active impurities within the fiber core, or special designs of the fiber structure, while others use the temperature and pressure dependence of the refractive index of the fiber. Large changes in the phase of light propagating down lengths of fiber can be measured as a result of very small pressure or temperature changes. Infrared-transmitting fibers such as chalcogenide glasses GeS_2, As_2S_3, and As_2Se_3 and even polycrystalline thallium bromo-iodide (KRS5) and heavy metal (cadmium, cesium, and lead) halides are under active investigation for the delivery of CO_2 laser power in surgical (*9*) and robotic applications, or even for remote sensing of thermal images. Most of these are short fiber-length applications and ultralow loss is not required. Because of the simplicity and low cost of remote monitoring, sensing, and power transmission with fibers, we can anticipate expansion in this area of research.

Semiconductor Lasers and Detectors

Probably the largest effort in optical materials is currently being devoted to semiconductors because of their importance in light-emitting devices (lasers and LEDs), detectors, and microelectronics, as well as the hope of combining optical and electronic functions on the same chip. Although silicon is now the dominant material for electronics technology, it plays a relatively small role in optics. Silicon has an indirect band gap and is not an efficient light emitter. It has a center of symmetry and is not useful for nonlinear optics. For wavelengths shorter than about 1 μm, however, silicon is the material of choice for photodetection because of the high quantum efficiency, high degree of uniformity, well-established technology, and low price. In addition, the avalanche cross section for electrons is very different from that for holes and this leads to exceptionally low-noise detectors for high-bandwidth optical detection.

Group III-V semiconductors. For LEDs, it is necessary to use direct band-gap compound semiconductors. The first semiconductor laser ever fabricated was made from GaAs (*10*), which efficiently emits light near 0.88 μm in the near infrared. This material is still important for lasers and LEDs in consumer electronics. Since a strong parallel effort is under way to develop high-speed GaAs electronic integrated circuits, the dominance of GaAs optoelectronics is likely to continue for some time. However, since the optical loss of fibers at $\lambda = 1.5\ \mu m$ is some 1/10 of that at 0.88 μm, it is necessary to go to InP-GaAs alloys operating at longer wavelengths for long-distance communication. Some of these alloys have electronic properties superior to those of GaAs and may well find extensive application for high-speed electronics once the technology is fully developed.

In conventional technology, semiconductor structures for lasers and detectors are first deposited as thin films on a substrate of equivalent lattice parameter by means of techniques described in another article of this issue (*11*). The material composition is determined first by the wavelength of operation and second by the choice of substrate. Since the perfection of the epitaxial layers (and the resulting device performance) depends on the quality of the substrate material, extensive research has been invested in the growth of substrates having low defect densities. InPGaAs alloys, which form devices that emit light in the 1.3- to 1.55-μm region of interest to fiber-optic communications, can be matched to an InP substrate. This system is somewhat more difficult to work with than

GaAs because of the greater volatility of phosphorus at the growth temperature. Nevertheless, the crystal quality now available is comparable in both InP- and GaAs-based materials (*12*).

The longest wavelength for a device that can be grown on InP is about 1.7 μm. [This is demonstrated in figure 1 of (*9*).] Operation at longer wavelengths to achieve ultralow loss can be accomplished within the III-V semiconductor system by incorporating antimony in the alloy and using either InAs or GaSb substrates. Less has been done with these materials but it appears that there is no basic limitation to achieving materials and devices with quality similar to GaAs- and InP-based systems. There are wide regions within the quaternary field of antimonides where the composition phase separates (miscibility gap), but with the proper choice of composition such difficulties can generally be avoided.

An active area of current research is the fabrication of ultrathin multilayer structures. Alternating layers of two different compositions are deposited on a substrate, in which the thickness of each layer is about 100 Å. The resulting composite material then has properties different from either of the constituents. If the compositions are GaAs and GaAlAs (for which most of this work has been done), then electrons in the conduction bands and holes in the valence band occupy energy levels intermediate between those of either GaAs or GaAlAs. These levels are quantum states of the carriers confined within the GaAs layers. The positions of these energy states depend on the thickness of GaAs layers. Thus the band-gap and electronic properties of structures of this kind can be tailored not only by modifying the compositions of the layers but also by appropriately designing the thickness of the layers to give the required properties (*11*). An interesting recent advance is the realization that transitions between quantized states within the conduction band of doped GaAs multilayer structures can be used for efficient far-infrared detection, in much the same way as intrinsically narrow band-gap semiconductors (*13*).

Group II-VI semiconductors. If III-V semiconductors have received the major share of attention for lasers and near-infrared detectors, II-VI semiconductors have received the major attention for far-infrared detection, particularly in the wavelength range from 5 to 10 μm, which is of importance for night vision and thermal imaging. Warm objects, from human beings to aircraft engines, emit radiation in this wavelength region which can be detected with semiconductors having a sufficiently narrow band gap.

Table 2. Experimentally observed losses of various optical fiber materials compared with ultimate theoretical expectations.

Fiber material	Optical loss* (dB km^{-1})	
	Experimental	Theoretical
SiO_2	0.16 (1.55)	~0.1 (1.55)
GeO_2	4 (2.0)	0.1 (2.5)
Fluorides	0.9 (2.5)	0.001 (3.5)
Chalcogenides	35 (2.5)	0.05 (5)
Plastic	20 (0.7)	

*Values in parentheses are wavelengths in micrometers.

Figure 2 lists the II-VI binary semiconductors (*14*) in the same format as shown in (*11*) for III-V compounds. It is evident from the figure that a wide range of band gaps is available in the II-VI system, and many of these have direct band gaps and emit light. So why do we bother with III-V compounds? The main reason is that when II-VI materials were investigated in the 1960s, it was not possible except in HgCdTe, to make both *p*-type (hole conduction) and *n*-type (electron conduction) material from the same composition for thermodynamic reasons. It requires less energy to create structural defects (that is, anion or cation vacancies) than to create free carriers in the conduction or valence bands. For injection lasers it is essential to have *p-n* junctions in order to excite light emission with electric current. This is readily accomplished in GaAs by doping, and consequently this technology gained momentum.

Group II-VI materials have recently received increased attention

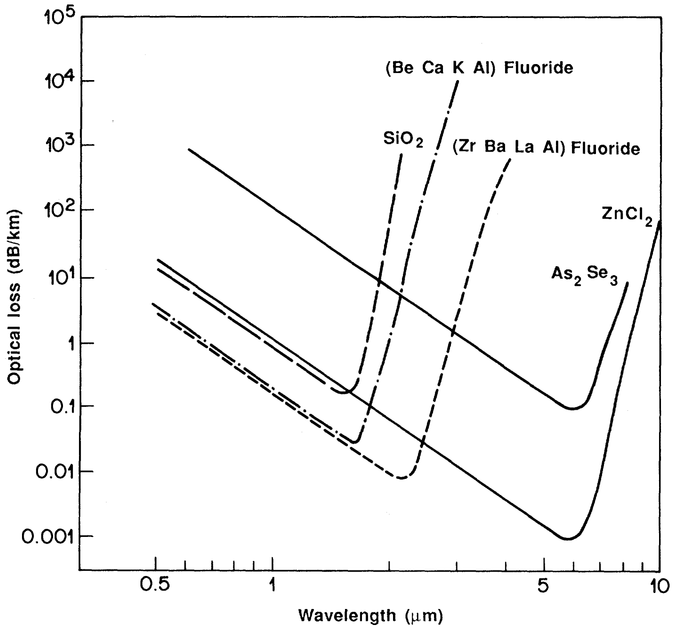

Fig. 1. Wavelength dependence of the theoretical optical loss of various fiber materials.

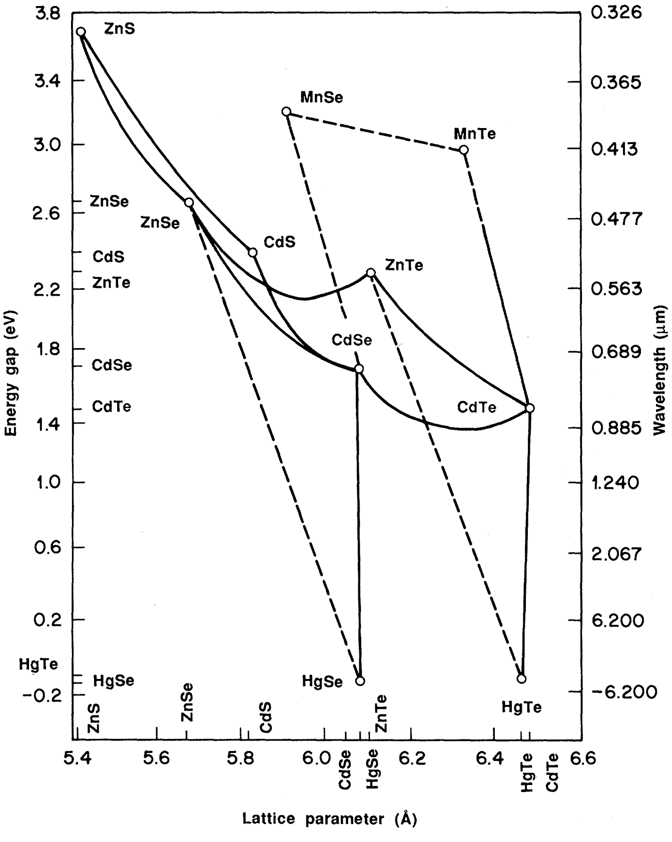

Fig. 2. Optical energy gap as a function of lattice parameter for some II-VI semiconductors.

Table 3. Electro-optic coefficient, refractive index *n*, and dielectric constant ϵ of some important electro-optic materials. The product n^3r and n^3r/ϵ are important figures of merit for switching applications.

Material	r ($\times 10^{12}$ m V^{-1})	n	ϵ	n^3r	n^3r/ϵ
		Oxides			
$BaTiO_3$	1,640	2.46	3,600	24,400	6.8
$BiSi_{12}O_{20}$	5	2.54	47	82	1.7
$LiNbO_3$	32	2.27	43	374	8.7
$Sr_{0.75}Ba_{0.25}Nb_2O_6$	1,340	2.30	3,400	16,303	4.8
		Semiconductors			
InP	1.45	3.29	12.6	52	4.1
GaAs	1.2	3.60	13.2	56	4.2
CdTe	6.8	2.82	9.4	1.52	16

because of the need for semiconductor lasers and LEDs that emit in the blue. Blue lasers would allow higher density data storage on video disks, and blue LEDs are useful for information display. With new low-temperature crystal growth procedures and novel multilayer structures, this area of research is likely to yield important new results.

For wavelengths beyond 0.85 μm mercury is a necessary constituent for II-VI materials (Fig. 2). HgTe is a semimetal, and alloys with other II-VI compounds can be made that cover the entire wavelength range from the far-infrared to the visible. Material can be made both *p*- and *n*-type and high-quality infrared detectors are commercially available that are made from HgCdTe alloys. Mercury is, however, a difficult element to work with in a crystal growth environment because of its high vapor pressure at normal crystal growth temperatures. Furthermore, mercury diffuses rapidly through crystals, even at temperatures as low as 250°C. To fabricate sharp interfaces or multilayer structures, it is necessary to grow mercury compounds below this temperature. The most promising approaches appear to be molecular beam epitaxy or chemical vapor deposition techniques (*15*). One of the major driving forces for HgCdTe is the desire of the military to have a two-dimensional detector array for thermal imaging. These require very good uniformity of composition because the semiconductor band gap varies rapidly with mercury content. The required uniformity is difficult to achieve in practice. Another obstacle is the fact that large CdTe substrates are difficult to grow with low defect density, owing to the difficulty in reducing thermally induced stress in the crystals. New crystal growth techniques or alternative substrate materials are needed to overcome those problems. Some progress has been made with the use of CdMnTe and CdZnTe substrates that reduce the defect density. The presence of the third constituent hardens the material against dislocation and twin formation (*16*).

Although II-VI semiconductors have advantages over III-V compounds in both the very short and very long wavelength regimes, it is also possible to induce unique magnetic characteristics in certain compositions. Ternary compounds such as CdMnTe and CdMnSe are magnetic semiconductors in which the magnetic moment of the manganese ions interacts with the conduction electrons of the semiconductors. This results in huge effective magnetic moments. Giant magneto-optic effects occur near the semiconductor band edge and are currently under investigation for optical switches and isolators (*17*). The Verdet constant of CdMnTe at room temperature, which is a measure of the magnetic field dependence of the Faraday rotation of polarized light, is about 1° cm^{-1} G^{-1} near the band edge at 620 nm. This means that with a magnetic field of 1 kG the 45° optical rotation required for isolators can be achieved in a 0.5-mm path length. Similar values are achieved at shorter wavelengths in ZnMnTe and ZnMnSe. These are some two orders of magnitude greater than the Verdet constants of paramagnetic glasses. The rotation achievable with practical ferromagnets such as bismuth-substituted yttrium-iron-garnet is 200° to 1000° cm^{-1} in the infrared near 1.5 μm (a permanent magnetic field is not required for ferromagnetic isolators). Thus, these magnetic semiconductors produce comparable optical rotation with moderate magnetic fields in the visible spectrum.

II-VI materials also have certain band structure advantages for avalanche detection in the near-infrared region of importance for optical communication. In III-V alloys the avalanche ionization ratio of electrons and holes is close to unity (except in special multilayer structures), and this results in noisy detectors. In some HgCdTe compositions, however, the ratio becomes extremely large (*18*), giving these materials the same advantage as silicon for avalanche detectors but for longer wavelength applications.

These special characteristics of II-VI alloys have encouraged a great deal of research in recent years, and it appears likely that many of the difficulties will be overcome with the new approaches to crystal growth and processing. If the cost of II-VI devices can be reduced, an expansion of interest for consumer products for seeing in the dark and communications can be anticipated in addition to military applications.

Alternative substrates. Conventional wisdom in the field of semiconductor epitaxial growth has been that the lattice parameter of the deposited layer should match that of the substrate to within 0.1 percent. Thus, for each new material of interest, a new substrate technology had to be developed. This is a time-consuming process which inhibits the development of new device materials.

Because of the high perfection, large size, low cost, high mechanical strength, and good thermal conductivity of silicon single crystals, much effort is being dedicated to the growth of GaAs on silicon substrates (*19*), even though the lattice mismatch is 4 percent. To date the GaAs films grown this way have better quality than might be expected and devices fabricated on thin films have shown comparable performance to those fabricated on GaAs substrates. The future of this new approach to the growth of GaAs is not yet clear, but it is off to a promising start. Likewise, CdTe is currently being grown on GaAs (*20*), which has a 14 percent lattice mismatch, with reasonable success, but again the quality is not yet as good as that of CdTe grown on CdTe substrates. In each of these research directions, it is essential to discover exactly what is required for device yield, reproducibility, and long-term stability.

Group IV superlattices. The ability to tailor optical and electrical properties by depositing alternating layers of two different compositions to generate new material properties is, as mentioned above, one of the most active areas of semiconductor research. Silicon-germanium superlattices (*21*) represent an exciting area of research in this direction. It is now possible (*22*) to deposit by molecular beam epitaxy individual atomic layers of silicon and germanium with very high accuracy and to prepare ordered superlattices in which the superlattice period is comparable to or smaller than the elementary unit cell of germanium or silicon. Not only is it possible to combine the advantages of both silicon and germanium in one material, but the material can have completely new properties that are not characteristic of either germanium or silicon. A particular challenge, which has not yet been realized, is to design group IV structures that efficiently emit light.

Other semiconductor systems. Although most research in semiconductor materials is being carried out on those materials already discussed, many other semiconductor materials systems have received less attention or have even been ignored. Group IV-VI semiconductors such as PbTe and PbSnTe have been developed and are commercially available as lasers for the middle infrared. Figure 3 shows the optical band gap versus the lattice parameter (*23*) of the lead-tin chalcogenides. These materials have not shown promise for infrared detection because of the high-background free-carrier concentration associated with natural defects in the material. The energy to create vacancies in PbTe type materials is very low and typical materials have 10^{17} vacancies per cubic centimeter. This problem is even more severe than that for II-VI materials but may also be reduced by low-temperature growth techniques.

Complex materials in the II-III-VI system, such as $ZnIn_2S_4$ and $CdIn_2Se_4$, exhibit fascinating optical switching behavior (*24*). Materials in the I-III-VI system, such as $CuInS_2$, have been studied for solar cells (*25*). II-IV-VI materials, such as $ZnGeP_2$, have interesting nonlinear optical properties (*26*). Because there is little existing materials technology, efforts to develop new materials occur only if they exhibit special characteristics that cannot be achieved with the more advanced materials.

Electro-Optic Switching and Modulation

Communication systems generally need some form of switching system to couple specific input channels to specific output channels. In optical communications, this can be accomplished with electronic switching systems by first detecting the optical signal and then converting back to optics with lasers after the switching functions are completed. This entire process can be simplified by directly switching the optical signals with electro-optic waveguide switches (*27*) fabricated in $LiNbO_3$. Electro-optic switching with $LiNbO_3$ has only been accomplished on a relatively small scale—four fibers in, four fibers out, or one fiber in, sixteen fibers out. The real advantage of electro-optic switching is the extremely wide bandwidth of the switch. At present, $LiNbO_3$ is the material of choice for this application because it has a moderately large electro-optic coefficient (*28*), crystals can be grown with good optical quality, and waveguides can be fabricated by titanium diffusion below the $LiNbO_3$ substrate (*29*). Titanium increases the refractive index of the $LiNbO_3$ so that light is guided within the diffused region in the same way as it is in an optical fiber. Light propagating in one guide can be coupled into a neighboring guide by application of an electric field, thereby switching the light. The electric field and the length of the switch that are required are both inversely proportional to the electro-optic coefficient, so that materials of high electro-optic coefficient are desirable for efficient switching. A list of electro-optic materials is shown in Table 3, together with an important figure of merit for switching, n^3r, where n is the refractive index and r the electro-optic coefficient (only the largest coefficient of each materials is listed). GaAs and InP are electro-optic materials and offer the possibility of combining electro-optic switches or modulators on the same substrate as the lasers or detectors. The electro-optic coefficients of GaAs and InP are small compared with those of $LiNbO_3$, however, and so these materials are of limited use for many switching applications. Electro-absorption, on the other hand, offers an alternative to the electro-optic effect for modulation and limited switching operations in monolithic GaAs/GaAlAs multilayer structures (*30*). This effect is a result of the electric field–induced shift of the optical absorption edge. Sufficient absorption change can be achieved to permit switching in just a few micrometers of optical path length.

Ferroelectric materials, such as $Sr_{1-x}Ba_{1-x}Nb_2O_6$ (SBN) and $BaTiO_3$, have particularly large coefficients, but these materials are extremely difficult to grow with adequate size and optical quality and so a waveguide technology has not yet been developed. Transparent polycrystalline ceramics in the lanthanum-doped lead zirconate–titanate system (PLZT) have large electro-optic coefficients and, though adequate for incoherent light applications, scatter light too strongly for most laser and switching applications. SBN, PLZT, and $BaTiO_3$ have large dielectric constants and large dielectric loss, which can be a disadvantage for high-speed switching. The difficulty in growing high-quality single crystals with large electro-optic coefficients is fundamental: Because small electric fields create large changes in refractive index, so do small changes in material composition and elastic strain. Thus the perfection required of highly nonlinear materials is greater than that required of linear optical materials. To achieve the optical quality necessary for simple switching applications will require a novel approach to crystal growth. Perhaps thin-film techniques used for quaternary semiconductors may be used to advantage in these materials systems.

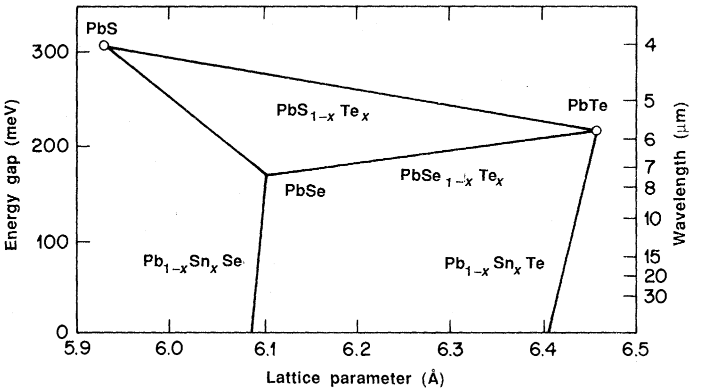

Fig. 3. Optical energy as a function of lattice parameter for some IV-VI semiconductors.

Organic materials offer the potential for a large electro-optic effect where the nonlinear behavior is of electronic origin and the problems mentioned for ionic crystals should disappear. Despite the fact that large second-order nonlinear polarizabilities were measured in organic molecules many years ago (*31*), no practical material has yet emerged with an electro-optic coefficient close to that of $LiNbO_3$. Because the molecular dipoles tend to align in an antiparallel manner in organic crystal structures rather than in a parallel manner required for electro-optics, it has been difficult to utilize the full molecular nonlinear polarizability. This area of research is still being actively pursued. It is not yet clear whether achieving high optical quality together with high optical nonlinearity will be as difficult as for ionic crystals.

To avoid the crystal growth problems, some groups have investigated the alignment of organic molecules in noncrystalline polymers and liquid crystals (*32*). Such approaches would permit simple device fabrication. However, at this time the electro-optic coefficients are too small for organic crystals to compete with $LiNbO_3$.

Although $LiNbO_3$ technology is now quite advanced, this material is not without problems. Careful control of crystal growth is critical to achieve uniform stoichiometry and reproducible characteristics. Photorefractive effects unfortunately prohibit the use of this material at room temperature with visible wavelengths. Because of the importance of this material, considerable effort is being devoted to overcoming these problems.

Although electro-optic switching has dominated optical switching research, acousto-optic derives are finding application in laser mode-lockers and Q-switches (usually quartz crystals are used) and for radio-frequency spectrum analyzers (with $LiNbO_3$ waveguides). In this case, the switching is based on the diffraction of light from a refractive index grating created by an acoustic wave propagating in the material. The speed of this kind of switching is limited by the acoustic velocity and is not adequate for communication requirements.

All-Optical Information Processing

A logical extension of the development of optics for data transmission and switching is to perform all information processing with light beams alone, that is, to use light beams to control other light beams. Because photons do not directly interact with each other the way electrons do, a nonlinear optical medium that mediates the interaction of two light beams is required. To this end, the search for materials having large optical nonlinearities has recently gathered momentum. If there is to be an optical computer of the future, it will have an architecture quite different from that of digital electronic computers. The goal of such a machine would be to take advantage of the ultrahigh speeds available with optics [laser pulses as short as 8 fsec have been measured (*33*)] or the high degree of parallelism and simple interconnection offered by optics. With existing materials, however, an energy of about 0.1 to 1 pJ is still required for each switching event, which limits the data rate to 10^{12} to 10^{13} bits per second for a 1-W laser, regardless of whether serial or parallel processing architectures are used (*34*). The achievement of both a high degree of parallelism and a high pulse throughput will require considerable advances in nonlinear optical materials. In the meantime it seems certain that applications will emerge, such as image processing, that benefit from optics without competing directly with electronic computers.

Nonlinear optical materials under investigation for optical processing are semiconductors, both in bulk form and as multilayer quantum-well structures, glasses containing semiconductor crystallites, photorefractive materials, and organic materials. The common goal with these materials is to rapidly create a large change in the optical properties of the material, either the refractive index, the optical absorption, or the reflectivity when the "control" light beam passes through the material. Nonlinear absorption (photochromism) has long been studied for such applications as optical memory and variable-density sunglasses where high speed is not a critical factor. A nonlinear index n_2 can be defined by $\Delta n = n_2 I$ where Δn is the index change created by light of intensity I (nonlinear absorption and nonlinear reflection can be defined in the same way). This change then affects the propagation of the "signal" beam. On a microscopic scale, this is achieved by creating a large change in the electronic dipole moment with a photon. If the control light beam is absorbed by the material and excites electrons to a higher energy state, the nonlinearities are generally larger than when the material is transparent. If the material is transparent, the nonresonant nonlinearity is due solely to the effects of the optical electric field on the valence electrons of the solid. Such effects can exhibit subpicosecond response with minimum power dissipation, but the nonlinearities are small and require very high optical intensities for switching. Resonant (absorbing) nonlinearities can be orders of magnitude larger, thereby permitting much lower switching intensities. The penalty is higher power dissipation and slower response: The excited state must relax to the ground state before the medium can be used for a second switching event. The power dissipation is serious not only because of the difficulty of cooling the device, but also because resonant nonlinearities are generally very temperature sensitive.

Both resonant and nonresonant nonlinearities in organic materials are being investigated. Polydiacetylenes [*p*-toluene sulfonate (PTS), for example] currently have the highest known nonlinearities of all organic materials. This molecule is a long conjugated diacetylene polymer with appreciable electronic delocalization along the polymer chain. The intense optical transitions in these molecules give rise to the large optically induced dipole and the large nonlinearity.

Extremely large resonant effects were observed at the peak of the molecular exciton resonance in PTS—some three orders of magnitude larger than measurements in the absorption tail (*35*). Large changes in the reflectivity ($\Delta R \sim 0.05$) were observed in transient diffraction at intensities of 100 MW cm^{-2} with an intrinsic material response time of 2 psec. The exciton length in this case (the extent of the exciton wave function) was about 30 Å, and the ratio of nonlinear index n_2 to the absorption coefficient α was approximately constant over the exciton absorption line. The higher nonlinearity is achieved at the expense of decreased optical interaction length and increased local heating.

Knowledge of the effects of electron delocalization in organic molecules has been invaluable for developing other material systems. Many semiconductors including GaAs (*36*) and InSb (*37*) exhibit large resonant optical nonlinearities near the electronic band edges where excitons (electrons in the conduction band bound to holes in the valence band) have sharp absorption bands. These excitons have diameters typically in the 10- to 100-Å range—comparable to that of molecular excitons in PTS. In some semiconductors, the exciton absorption lines can be extremely sharp, giving rise to a large oscillator strength and low energies for saturating the absorption. Because the exciton lifetimes are quite long ($>10^{-9}$ second) and temperature-sensitive, exciton saturation in these materials is not likely to be useful for very high speed, high repetition rate applications. Intersubband transitions in doped superlattices provide much faster response (*38*) but heating remains an issue.

In multilayer semiconductor structures such as GaAs-GaAlAs quantum wells (*11*), it is possible to confine the exciton within the layers of thickness comparable to the exciton diameter. This increases the exiton binding energy and, unlike the situation in bulk materials, the absorption peaks are sharp and well-resolved at room temperature (*36*). The nonlinear index increases as a result of the confinement, but saturation effects occur at such low intensities that it is difficult to achieve sufficient index change for practical application unless the material is placed inside a Fabry-Perot cavity. On the other hand, electric field–induced shifts of the exciton absorption peak can form the basis of an efficient electroabsorption switch on a nanosecond time scale (*30*) with the electric field variation induced optically by the drift of photoexcited carriers.

Further confinement of excitons in three dimensions, either by appropriately structuring the multilayers on a scale of 100 Å to produce "quantum dots" (*39*) or by preparing semiconductor crystallites within a glass matrix, can give rise to further enhancement of the nonlinear index (*40*). Experiments have been performed with optical filter glasses which contain small CdS and CdSe precipitates in a glass matrix. The electronic states in these quantum dots now become well-separated one-electron states similar to the molecular states of large molecules. The available exciton oscillator strength is squeezed into a narrower spectral region. As in the case of PTS, the ratio of the nonlinear index to the optical absorption coefficient remains approximately constant as the exciton becomes confined (*39*), which implies that the switching energy remains constant. Nonlinear optics with small particles might be advantageous because of a local field effect that enhances the optical field within the particles (*40, 41*) so that they act like small lenses. For dilute systems of semiconductors (such as CdS particles in silicate glasses) and metal particles (such as silver and gold colloids), enhancements as a result of the local field effect have been observed. As the particle density increases, these local field effects are expected to decrease as a result of particle interactions.

Semiconductors offer several options for tailoring materials for specific needs, but at this time it is not clear which approach or which material is best suited for general purpose applications. Factors such as wavelength of operation (which determines the limiting pixel size), nonlinear index n_2, and the magnitude of the change of the optical path length that is achievable under saturation, are all important. In any application involving two or more nonlinear switching elements in cascade, then the effects of optical loss in absorbing materials must be considered, or multiple wavelength operation must be used.

The photorefractive effect is another nonlinear mechanism that is especially well-suited to image processing (*42*). Indeed, a wide range of applications including phase conjugation, real-time holographic interferometry, matrix multiplication, image amplification, convolution, and correlation have already been demonstrated (*42*). Typical energy requirements are about 1 pJ per resolution element—about the same as for the other nonlinear mechanisms. The photorefractive effect is based on electronic charge separation in electro-optic crystals: Local space-charge fields created by redistribution of photoexcited carriers can give rise to an index change by the electro-optic effect. In optimized materials, carriers are transported by drift or diffusion over distances of several hundred nanometers, thereby creating a large dipole that polarizes the surrounding lattice. The effect is large only in thick crystals (typically several millimeters) and usually involves volume holography. It is only weakly temperature dependent and is nonresonant. Presumably, resonant photorefractive effects near a sharp absorption edge would be larger, but this has not yet been demonstrated.

The photorefractive effect has been regarded as a slow effect, useful only in applications involving a high degree of parallelism (images with $\sim 10^8$ bits cm^{-2}). This is because the effect was first studied in highly resistive, low-mobility ferroelectric oxides such as $LiNbO_3$, SBN, $BaTiO_3$, and the electro-optic photoconductor $BiSi_{12}O_{20}$. Efficient submicrosecond photorefractive effects have now been demonstrated in high-resistivity InP, GaAs, and CdTe (*43*), and very recently effects have been observed on a 40-psec time scale (*44*). These semiconductors can be tailored for specific applications: The response time can be varied from milliseconds (for applications requiring memory) to picoseconds; the wavelength of operation can be varied throughout the near-infrared; and the photorefractive sensitivity can be varied with an external electric field or light beam. Since the effect depends on absorbed energy, a compromise must be reached between the desired speed of operation and the desired index change. For phase conjugation, large index changes are required and this implies slow materials with large electro-optic coefficients such as SBN and $BaTiO_3$, which have large values of n^3r, as shown in Table 3. For optical information processing, small index changes can be tolerated such as those achievable with InP, GaAs and CdTe, and high-speed operation is possible with pulsed lasers.

With all the activity in recent years, a wide range of new ideas have emerged that will provide the basis for future optical processing. Nonlinear optical elements have been placed within optical cavities to provide feedback and perform digital switching with amplified sensitivity. Several simple optical logic schemes have been demonstrated. At present, however, there is no architecture suitable for using the existing materials for general-purpose computation and the materials requirements are not well defined. It is, therefore, not prudent to focus research on any specific materials system or physical mechanism. Limited image processing has been demonstrated with existing photorefractive materials with effective throughputs of $>10^{10}$ bits per second and 1-W lasers, and these are probably the first applications of optical processors. It is not clear that optics can meet the requirements of a high-speed general-purpose optical computer, even if we use projections based on our current understanding of materials. The hope is that this can be overcome by completely novel approaches to architecture.

Conclusion

Since optics already has a strong foothold in several technologies, we can expect a continuing expansion in the foreseeable future as the frontier between optics and electronics is pushed forward. Current technology is based on materials discovered decades ago. Commercially successful materials are not necessarily those with the largest technical figures of merit. Compromises are always made on the basis of such factors as optical quality, damage threshold, and difficulty of material preparation as well as the basic physical parameters of the materials. Materials synthesis and processing techniques have not been discussed in this article but they are clearly vital factors in the development of a new materials technology. Optical materials research must continue in all of these areas to discover new alternatives for future applications.

REFERENCES AND NOTES

1. K. C. Kao and G. A. Hochham, *Proc. Inst. Electr. Eng.* **13**, 1151 (1966).
2. L. G. Cohen, *IEEE J. Sel. Areas Commun.* **SAC4**, 488 (1986).
3. L. G. Van Uitert, A. J. Bruce, W. H. Grodkiewicz, D. L. Wood, *Mater. Sci. Forum* **5**, 591 (1985).
4. M. E. Lines, *J. Appl. Phys.* **55**, 4052 (1984).
5. D. C. Tran, K. H. Levin, M. J. Burk, C. F. Fisher, D. Brower, *Soc. Photo-Optical Instrum. Eng.* **618**, 48 (1986).
6. D. A. Pinnow and L. G. Van Uitert, U.S. Patent No. 3 722 981 (1973).
7. L. G. Cohen, C. Lin, W. French, *Electron. Lett.* **15**, 334 (1979).
8. T. G. Giallorenzi *et al.*, *IEEE J. Quantum Electron.* **QE-18**, 626 (1982).
9. H. Ishiwatari, M. Ikedo, F. Tateishi, *IEEE J. Lightwave Technol.* **LT-4**, 1273 (1986).
10. I. Hayashi, M. B. Panish, P. W. Foy, S. Sumski, *Appl. Phys. Lett.* **17**, 109 (1970).
11. V. Narayanamurti, *Science* **235**, 1023 (1987).
12. W. A. Gault, E. M. Monberg, J. E. Clemans, *J. Cryst. Growth* **74**, 491 (1986).
13. B. Levine, K. K. Choi, C. G. Bethea, J. Walker, R. J. Malik, personal communication.
14. P. M. Bridenbaugh, personal communication.
15. S. J. C. Irvine *et al.*, *J. Cryst. Growth* **77**, 437 (1986).
16. P. M. Bridenbaugh, *Mater. Lett.* **3**, 287 (1985).
17. J. A. Gaj, R. R. Galazka, M. Nawrocki, *Solid State Commun.* **25**, 193 (1978).
18. B. Orsal, R. Alabedra, M. Valenza, *J. Cryst. Growth* **72**, 496 (1985).
19. A. L. Robinson, *Science* **232**, 826 (1986).
20. H. A. Mar, K. T. Chee, N. Solansky, *Appl. Phys. Lett.* **44**, 237 (1984).
21. J. Bean, in *Proceedings of the 1984 Fall Symposium on Epitaxy and Layered Structures*, J. M. Gibson and L. R. Dawson, Eds. (Materials Research Society, Pittsburgh, 1985), p. 245.
22. J. Bevk, J. P. Mannaerts, A. Ourmazd, L. C. Feldman, B. A. Davidson, *Appl. Phys. Lett.* **49**, 286 (1986).
23. H. M. Preier, *Proceedings of Conference on the Physics of Narrow Gap Semiconductors* (Linz, Austria, 1981) (Springer, New York, 1982), p. 289.
24. V. F. Zhitar, N. A. Moldovyan, S. I. Radautsan, *Sov. Phys. Semicond. (Engl. Transl.)* **14**, 353 (1980).
25. A. N. Georgobiani, S. J. Radautsan, I. M. Tiginyanu, *ibid.* **19**, 121 (1985).
26. R. L. Byer, *Annu. Rev. Mater. Sci.* **4**, 147 (1974).
27. R. C. Alferness, *Science* **234**, 825 (1986).
28. G. E. Peterson, A. A. Ballman, P. V. Lenzo, P. M. Bridenbaugh, *Appl. Phys. Lett.* **3**, 62 (1964).
29. R. V. Schmitt and I. P. Kaminow, *ibid.* **25**, 458 (1974).
30. D. A. B. Miller *et al.*, *ibid.* **45**, 13 (1984).
31. B. F. Levine, *J. Chem. Phys.* **63**, 115 (1975).
32. K. D. Singer, J. E. Sohn, S. J. Lalama, *Appl. Phys. Lett.* **49**, 248 (1986).
33. C. V. Shank, *Science* **233**, 1276 (1986).
34. A. M. Glass, *ibid.* **226**, 657 (1984).
35. B. I. Greene, J. Orenstein, R. R. Millard, L. R. Williams, *Phys. Rev. Lett.*, in press.
36. D. A. B. Miller *et al.*, *Appl. Phys. Lett.* **42**, 925 (1983).
37. D. A. B. Miller, C. T. Seaton, M. E. Prise, S. D. Smith, *Phys. Rev. Lett.* **47**, 197 (1981).
38. L. C. West and S. J. Eglash, *Appl. Phys. Lett.* **46**, 1156 (1985).
39. S. Schmitt-Rink, D. A. B. Miller, D. S. Chemla, in preparation.
40. C. Flytzanis, F. Hache, D. Ricard, Ph. Roussignol, in *Proceedings of the Winter School on Physics and Fabrication of Microstructures and Microdevices*, M. J. Kelly and C. Weisbuch, Eds. (Springer Verlag, New York, 1986).
41. J. P. Heritage and A. M. Glass, in *Surface Enhanced Raman Scattering*, R. K. Chang and J. E. Furtak, Eds. (Plenum, New York, 1982), p. 391.
42. P. G. Gunther, *Phys. Rep.* **93**, 200 (1983).
43. J. S. Strait and A. M. Glass, *J. Opt. Soc. Am. B* **3**, 342 (1986).
44. G. C. Valley, A. L. Smirl, M. B. Klein, K. Bohnert, T. F. Boggess, *Opt. Lett.* **11**, 647 (1986).

45. I gratefully acknowledge the help given to me by a large number of my colleagues who provided me with reprints and other information I found most helpful in preparing this manuscript.