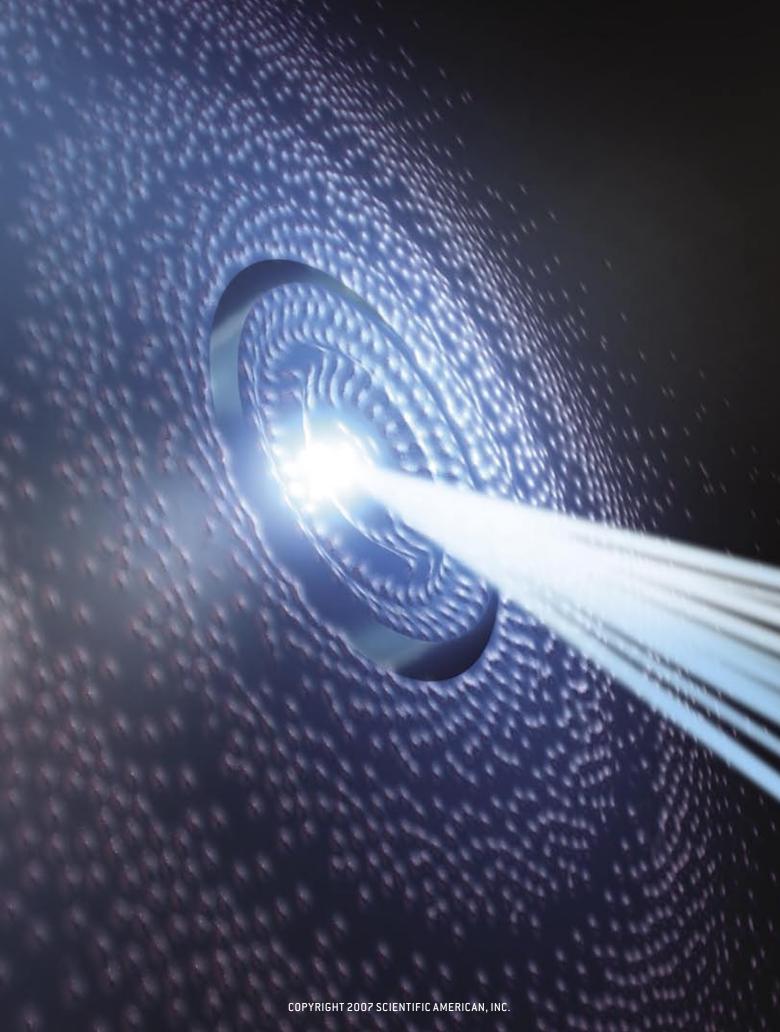
A technology that squeezes electromagnetic waves into minuscule structures may yield a new generation of superfast computer chips and ultrasensitive molecular detectors

The Promise of PLASMONICS

By Harry A. Atwater

LIGHT BEAM striking a metal surface can generate plasmons, electron density waves that can carry huge amounts of data. If focused on a surface etched with a circular groove, as in this artist's rendering, the beam produces concentric waves, organizing the electrons into high- and low-density rings.



Light is a wonderful medium for carrying information.

Optical fibers now span the globe, guiding light signals that convey voluminous streams of voice communications and vast amounts of data. This gargantuan capacity has led some researchers to prophesy that photonic devices—which channel and manipulate visible light and other electromagnetic waves—could someday replace electronic circuits in microprocessors and other computer chips. Unfortunately, the size and performance of photonic devices are constrained by the diffraction limit; because of interference between closely spaced light waves, the width of an optical fiber carrying them must be at least half the light's wavelength inside the material. For chip-based optical signals, which will most likely employ near-infrared wavelengths of about 1,500 nanometers (billionths of a meter), the minimum width is much larger than the smallest electronic devices currently in use; some transistors in silicon integrated circuits, for instance, have features smaller than 100 nanometers.

Recently, however, scientists have been working on a new technique for transmitting optical signals through minuscule nanoscale structures. In the 1980s researchers experimentally confirmed that directing light waves at the interface between a metal and a dielectric (a nonconductive material such as air or glass) can, under the right circumstances, induce a resonant interaction between the waves and the mobile electrons at the surface of the metal. (In a conductive metal, the electrons are not strongly attached to individual atoms or molecules.) In other words, the oscillations of electrons at the surface match those of the electromagnetic field outside the metal. The result is the generation of surface plasmons—density waves of electrons that propagate along the interface like the ripples that spread across the surface of a pond after you throw a stone into the water.

Overview/Plasmonics

- Researchers have discovered that they can squeeze optical signals into minuscule wires by using light to produce electron density waves called plasmons.
- Plasmonic circuits could help the designers of computer chips build fast interconnects that could move large amounts of data across a chip. Plasmonic components might also improve the resolution of microscopes, the efficiency of light-emitting diodes, and the sensitivity of chemical and biological detectors.
- Some scientists have even speculated that plasmonic materials could alter the electromagnetic field around an object to such an extent that it would become invisible.

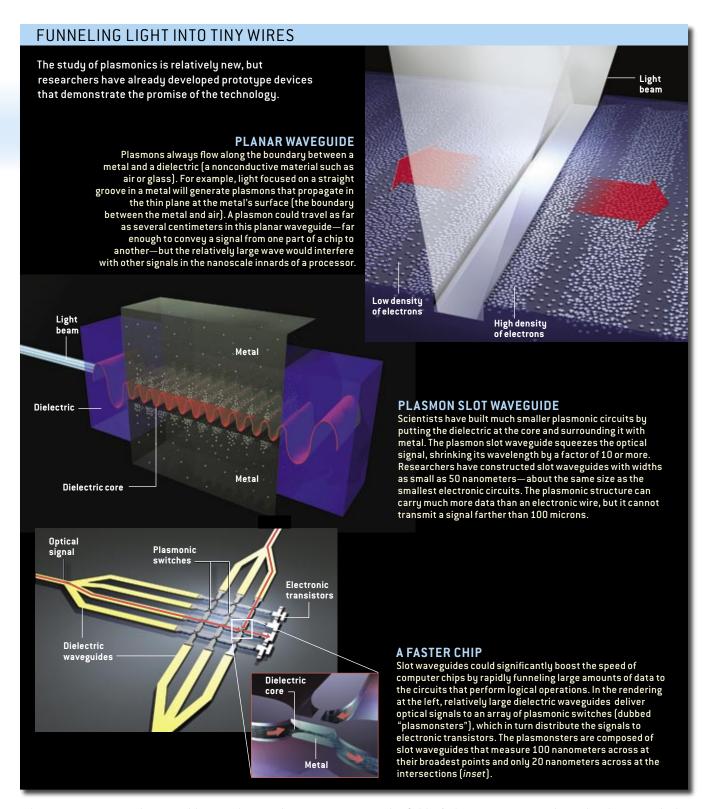
Over the past decade investigators have found that by creatively designing the metal-dielectric interface they can generate surface plasmons with the same frequency as the outside electromagnetic waves but with a much shorter wavelength. This phenomenon could allow the plasmons to travel along nanoscale wires called interconnects, carrying information from one part of a microprocessor to another. Plasmonic interconnects would be a great boon for chip designers, who have been able to develop ever smaller and faster transistors but have had a harder time building minute electronic circuits that can move data quickly across the chip.

In 2000 my group at the California Institute of Technology gave the name "plasmonics" to this emerging discipline, sensing that research in this area could lead to an entirely new class of devices. Ultimately it may be possible to employ plasmonic components in a wide variety of instruments, using them to improve the resolution of microscopes, the efficiency of light-emitting diodes (LEDs) and the sensitivity of chemical and biological detectors. Scientists are also considering medical applications, designing tiny particles that could use plasmon resonance absorption to kill cancerous tissues, for example. And some researchers have even theorized that certain plasmonic materials could alter the electromagnetic field around an object to such an extent that it would become invisible. Although not all these potential applications may prove feasible, investigators are eagerly studying plasmonics because the new field promises to literally shine a light on the mysteries of the nanoworld.

Shrinking Wavelengths

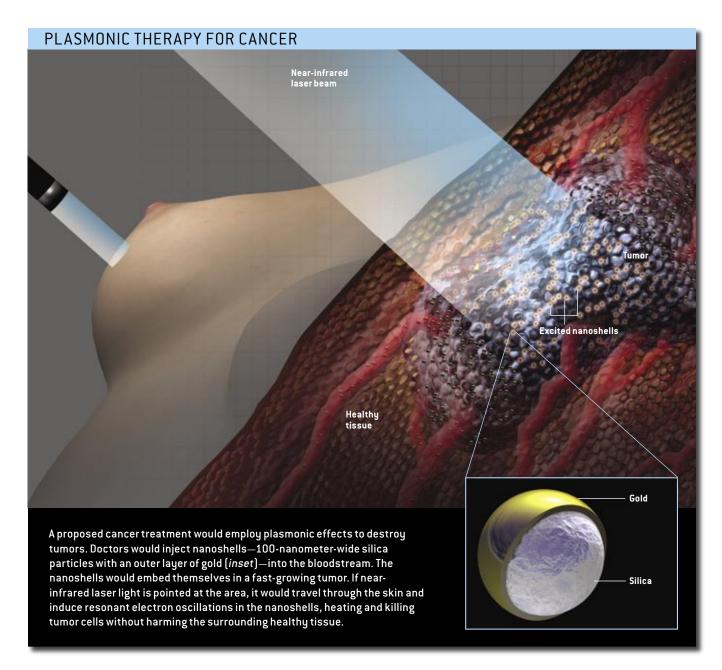
FOR MILLENNIA, alchemists and glassmakers have unwittingly taken advantage of plasmonic effects when they created stained-glass windows and colorful goblets that incorporated small metallic particles in the glass. The most notable example is the Lycurgus cup, a Roman goblet dating from the fourth century A.D. and now held in the British Museum [see illustration on page 62]. Because of plasmonic excitation of electrons in the metallic particles suspended within the glass matrix, the cup absorbs and scatters blue and green light—the relatively short wavelengths of the visible spectrum. When viewed in reflected light, the plasmonic scattering gives the cup a greenish hue, but if a white light source is placed within the goblet, the glass appears red because it transmits only the longer wavelengths and absorbs the shorter ones.

Research into surface plasmons began in earnest in the 1980s, as chemists studied the phenomenon using Raman spectroscopy, which involves observing the scattering of laser light off a sample to determine its structure from molecular



vibrations. In 1989 Thomas Ebbesen, then at the NEC Research Institute in Japan, found that when he illuminated a thin gold film imprinted with millions of microscopic holes, the foil somehow transmitted more light than was expected from the number and size of the holes. Nine years later Ebbesen and his colleagues concluded that surface plasmons on the film were intensifying the transmission of electromagnetic energy.

The field of plasmonics received another boost with the discovery of novel "metamaterials"—materials in which electron oscillations can result in astounding optical properties [see "The Quest for the Superlens," by John B. Pendry and David R. Smith; Scientific American, July 2006]. Two new classes of tools have also accelerated progress in plasmonics: recent increases in computational power have enabled investi-



gators to accurately simulate the complex electromagnetic fields generated by plasmonic effects, and novel methods for constructing nanoscale structures have made it possible to build and test ultrasmall plasmonic devices and circuits.

At first glance, the use of metallic structures to transmit light signals seems impractical, because metals are known for high optical losses. The electrons oscillating in the electromagnetic field collide with the surrounding lattice of atoms, rapidly dissipating the field's energy. But the plasmon losses are lower at the interface between a thin metal film and a dielectric than inside the bulk of a metal because the field spreads into the nonconductive material, where there are no free electrons to oscillate and hence no energy-dissipating collisions. This property naturally confines plasmons to the metallic surface abutting the dielectric; in a sandwich with

dielectric and metal layers, for example, the surface plasmons propagate only in the thin plane at the interface [see top illustration in box on preceding page].

Because these planar plasmonic structures act as waveguides, shepherding the electromagnetic waves along the metal-dielectric boundary, they could be useful in routing signals on a chip. Although an optical signal suffers more loss in a metal than in a dielectric such as glass, a plasmon can travel in a thin-film metal waveguide for several centimeters before dying out. The propagation length can be maximized if the waveguide employs an asymmetric mode, which pushes a greater portion of the electromagnetic energy away from the guiding metal film and into the surrounding dielectric, thereby lowering loss. Because the electromagnetic fields at the top and bottom surfaces of the metal film interact with each other,

the frequencies and wavelengths of the plasmons can be adjusted by changing the thickness of the film. In the 1990s research groups led by Sergey Bozhevolnyi of Aalborg University in Denmark and Pierre Berini of the University of Ottawa developed planar plasmonic components that could perform many of the same functions—such as splitting guided waves-usually done by alldielectric devices. These structures could prove useful in transmitting data from one part of a chip to another, but the electromagnetic fields accompanying the plasmons are too large to convey signals through the nanoscale innards of a processor.

To generate plasmons that can propagate through nanoscale wires, researchers have explored more complex waveguide geometries that can shrink the wavelength of the signal by squeezing it into a narrow space. In the late 1990s my lab group and a team led by Joachim Krenn of the University of Graz in

Austria launched parallel efforts to produce these "subwavelength" surface-plasmon waveguides. Working with me at Caltech, Stefan Maier built a structure consisting of linear chains of gold dots, each less than 100 nanometers across. A visible beam with a wavelength of 570 nanometers triggered resonant oscillations in the dots, generating surface plasmons that moved along the chains, confined to a flattened path only 75 nanometers high. The Graz group achieved similar results and imaged the patterns of the plasmons carried along the chains. The absorption losses of these nanowires were relatively high, however, causing the signal to die out after it traveled a few hundred nanometers to a few microns (millionths of a meter). Thus, these waveguides would be suitable only for very short-range interconnections.

Fortunately, the absorption losses can be minimized by turning the plasmonic waveguides inside out, putting the dielectric at the core and surrounding it with metal [see middle illustration in box on page 59]. In this device, called a plasmon slot waveguide, adjusting the thickness of the dielectric core changes the wavelength of the plasmons. My lab at Caltech and Mark Brongersma's Stanford University group have shown that plasmon slot waveguides are capable of transmitting a signal as far as tens of microns. Hideki Miyazaki of the National Institute for Materials Science in Japan obtained a striking result by squeezing red light (with a wavelength of 651 nanometers in free space) into a plasmon slot waveguide that was only three nanometers thick and 55 nanometers wide. The researchers found that the wavelength of the surface plasmon propagating through the device was 51 nanometers, or about 8 percent of the free-space wavelength.

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Plasmonics can thus generate signals in the soft x-ray range of wavelengths (between 10 and 100 nanometers) by exciting materials with visible light. The wavelength can be reduced by more than a factor of 10 relative to its free-space value, and yet the frequency of the signal remains the same. (The fundamental relation between the two-frequency times wavelength equals the speed of light—is preserved because the electromagnetic waves slow as they travel along the metal-dielectric interface.) This striking ability to shrink the wavelength opens the path to nanoscale plasmonic structures that could replace purely electronic circuits containing wires and transistors.

Just as lithography is now used to imprint circuit patterns on silicon chips, a similar process could massproduce minuscule plasmonic devices with arrays of narrow dielectric stripes and gaps. These arrays would guide the waves of positive and negative

charge on the metal surface; the alternating charge densities would be very much akin to the alternating current traveling along an ordinary wire. But because the frequency of an optical signal is so much higher than that of an electrical one—more than 400,000 gigahertz versus 60 hertz—the plasmonic circuit would be able to carry much more data. Moreover, because electrical charge does not travel from one end of a plasmonic circuit to another—the electrons bunch together and spread apart rather than streaming in a single direction—the device is not subject to resistance and capacitance effects that limit the data-carrying capacity of integrated circuits with electrical interconnects.

Plasmonic circuits would be even faster and more useful if researchers could devise a "plasmonster" switch—a three-terminal plasmonic device with transistorlike properties. My lab at Caltech and other research groups have recently developed low-power versions of such a switch. If scientists can produce plasmonsters with better performance, the devices could serve as the core of an ultrafast signal-processing system, an advance that could revolutionize computing 10 to 20 years from now.

THE AUTHOR

HARRY A. ATWATER is Howard Hughes Professor and Professor of Applied Physics and Materials Science at the California Institute of Technology. His research interests center on subwavelength-scale photonic devices for computing, imaging and renewable energy applications. In addition to devising plasmonic nanostructures, his group is actively exploring the use of new materials for solar power generation (photovoltaics), as well as the solar-driven generation of chemical fuels.

Nanoshells and Invisibility Cloaks

THE POTENTIAL USES of plasmonic devices go far beyond computing, however. Naomi Halas and Peter Nordlander of Rice University have developed structures called nanoshells that consist of a thin layer of gold-typically about 10 nanometers thick—deposited around the entire surface of a silica particle about 100 nanometers across. Exposure to electromagnetic waves generates electron oscillations in the gold shell; because of the coupling interaction between the fields on the shell's inner and outer surfaces, varying the size of the particle and the thickness of the gold layer changes the wavelength at which the particle resonantly absorbs energy. In this way, investigators can design the nanoshells to selectively absorb wavelengths as short as a few hundred nanometers (the blue end of the visible spectrum) or as long as nearly 10 microns (the near infrared).

This phenomenon has turned nanoshells into a promising

tool for cancer treatment. In 2004 Halas, working with her Rice colleague Jennifer West, injected plasmonic nanoshells into the bloodstream of mice with cancerous tumors and found that the particles were nontoxic. What is more, the nanoshells tended to embed themselves in the rodents' cancerous tissues rather than the healthy ones because more blood was circulated to the fast-growing tumors. (The nanoshells can also be attached to antibodies to ensure that they target cancers.)

Fortunately, human and animal tissues are transparent to radiation at certain infrared wavelengths. When the researchers directed near-infrared laser light through the mice's skin and at the tumors, the resonant absorption of energy in the embedded nanoshells raised the temperature of the cancerous tissues from about 37 degrees Celsius to about 45 degrees C.

The photothermal heating killed the cancer cells while leaving the surrounding healthy tissue unharmed. In the mice treated with nanoshells, all signs of cancer disappeared within 10 days; in the control groups, the tumors continued to grow rapidly. Houstonbased Nanospectra Biosciences is currently seeking permission from the Food and Drug Administration to conduct clinical trials of nanoshell therapy in patients with head and neck cancer.

making LEDs bright enough to compete with incandescent bulbs. Beginning in the 1980s, researchers recognized that the plasmonic enhancement of the electric field at the metaldielectric boundary could increase the emission rate of luminescent dyes placed near the metal's surface. More recently, it has become evident that this type of field enhancement can also dramatically raise the emission rates of quantum dots and quantum wells-tiny semiconductor structures that absorb and emit light—thus increasing the efficiency and brightness of solid-state LEDs. In 2004 my Caltech colleague Axel Scherer, together with co-workers at Japan's Nichia Corporation, demonstrated that coating the surface of a gallium nitride LED with dense arrays of plasmonic nanoparticles (made of silver, gold or aluminum) could increase the intensity of the emitted light 14-fold.

Furthermore, plasmonic nanoparticles may enable researchers to develop LEDs made of silicon. Such devices,

which would be much cheaper than conventional LEDs composed of gallium nitride or gallium arsenide, are currently held back by their low rates of light emission. My group at Caltech, working with a team led by Albert Polman of the FOM Institute for Atomic and Molecular Physics in the Netherlands, has shown that coupling silver or gold plasmonic nanostructures to silicon quantum-dot arrays could boost their light emission by about 10 times. Moreover, it is possible to tune the frequency of the enhanced emissions by adjusting the dimensions of the nanoparticles. Our calculations indicate that careful tuning of the plasmonic resonance frequency and precise control of the separation between the metallic particles and the semiconductor materials may enable us to increase radiative rates more than 100-fold, allowing silicon LEDs to shine just as brightly as traditional devices.

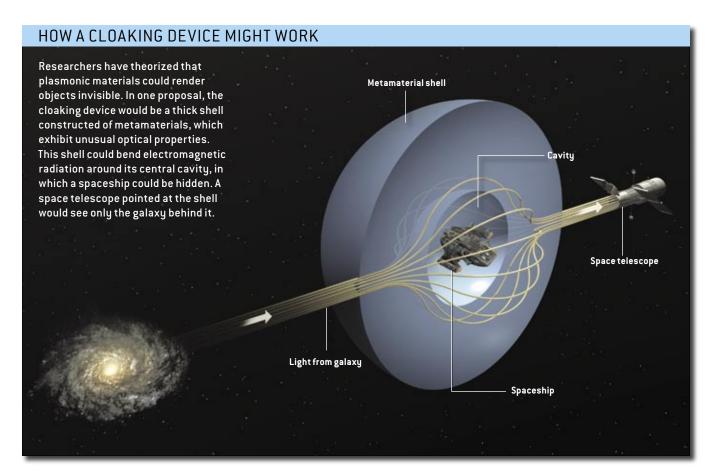
Scientists are even working on a plasmonic analog to a laser. Mark Stockman of Georgia State University and David Bergman of Tel Aviv University have described the physics of such a device, which they called a SPASER (for surface plasmon amplification of stimulated emission of radiation). Although the SPASER exists only in theory so far, the researchers have suggested routes to fabricating it using semiconductor quantum dots and metal particles. Radiative energy

LYCURGUS CUP, a Roman goblet dating from the fourth century A.D., changes color because of the plasmonic excitation of metallic particles within the glass matrix. When a light source is placed inside the normally greenish goblet, it looks red.





Plasmonic materials may also revolutionize the lighting industry by



from the quantum dots would be transformed into plasmons, which would then be amplified in a plasmonic resonator. Because the plasmons generated by a SPASER would be much more tightly localized than a conventional laser beam, the device could operate at very low power and selectively excite very small objects. As a result, SPASERs could make spectroscopy more sensitive and pave the way for hazardous-materials detectors that could identify minute amounts of chemicals or viruses.

Perhaps the most fascinating potential application of plasmonics would be the invention of an invisibility cloak. In 1897 H. G. Wells published *The Invisible Man*, a tale of a young scientist who discovers how to make his own body's refractive index equal to that of air, rendering him invisible. (A material's refractive index is the ratio of the speed of light in a vacuum to the speed of light in the material.) Exciting a plasmonic structure with radiation that is close to the structure's resonant frequency can make its refractive index equal to air's, meaning that it would neither bend nor reflect light. The structure would absorb light, but if it were laminated with a material that produces optical gain—amplifying the transmitted signal just as the resonator in a SPASER would—the increase in intensity would offset the absorption losses. The structure would become invisible, at least to radiation in a selected range of frequencies.

A true invisibility cloak, however, must be able to hide anything within the structure and work for all frequencies of visible light. The creation of such a device would be more difficult, but some physicists say it is possible. In 2006 John B. Pendry of Imperial College London and his colleagues showed that a shell of metamaterials could, in theory, reroute the electromagnetic waves traveling through it, diverting them around a spherical region within [see box above].

Although Wells's invisible man may never become a reality, such ideas illustrate the rich array of optical properties that inspire researchers in the plasmonics field. By studying the elaborate interplay between electromagnetic waves and free electrons, investigators have identified new possibilities for transmitting data in our integrated circuits, illuminating our homes and fighting cancer. Further exploration of these intriguing plasmonic phenomena may yield even more exciting discoveries and inventions.

MORE TO EXPLORE

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Plasmonics: Fundamentals and Applications. Stefan A. Maier. Springer Verlag, 2007.