15 February 1985, Volume 227, Number 4688 SCIENCE

Laser-Induced Chemistry for Microelectronics

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Summary. Laser-controlled chemical reactions are being explored for use in all phases of the processing of semiconductor devices. Laser-induced chemical processing can produce submicrometer features without the aid of photolithography. Research is also providing new information on light-excited and light-enhanced interface reactions.

In the early stages of the development of the integrated circuit, solid-state physics and materials science were viewed as the fundamental basis of microelectronics. Chemistry, in particular heterogeneous chemistry, which involves two different material phases such as a gas and a solid, now plays a major role in the fabrication of microelectronic circuits. Recently, laser-initiated, heterogeneous chemical reactions have been used in a variety of novel processing operations for the fabrication of microelectronics components. The study of these reactions has, in turn, led to new insights into the nature of light-driven chemical reactions at the surfaces of solids.

The development of laser-induced chemical processing for microelectronics drew on a considerable body of research in laser-induced chemistry. In general, the goal of early research was to use laser light to initiate specific chemical reactions in order to fabricate specific chemicals or to separate isotopes. In microelectronics fabrication, the specificity of laser-induced chemistry is important; however, the ability of laser light to confine reactions to submicrometer-scale regions is an equally important feature.

The ability to localize chemical reactions on solid surfaces has led to a number of techniques for semiconductor processing (*1, 2*). In addition, chemical reactions confined to such small regions of a solid-gas interface are sufficiently different from previously studied reactions that a new form of chemistry, laser-induced microchemistry, is evolving (*3*).

Historical Background

The fabrication of an integrated circuit, containing many transistors on a single silicon chip, can be viewed as the assembly of a patterned, multilayer, thin-film structure (*4*). In most semiconductor processing, photolithography is used extensively to pattern these layers of dielectrics or conductors. A photographic emulsion, or photoresist, is spun onto a wafer, exposed to light through a mask (akin to a photographic negative), and developed to reveal a patterned structure whose features may be as small as one micrometer. This photoresist layer serves to confine subsequent thin-film processing steps to the uncovered regions on the wafer, illustrated in Fig. 1. Insulating or conducting films can be grown by a variety of techniques, including condensation of vaporized metals, deposition using gas-phase chemical reactions (chemical vapor deposition), and oxidation of the silicon substrate. The films can also be etched, either by immersion in appropriate acids (wet chemistry) or by gases excited with an electrical discharge (plasma etching), transferring patterns in the photoresist to the underlying films. Doping involves the controlled introduction of electrically active impurities to portions of the wafer in order to change its electrical conductivity, again using an overlying film to determine the regions the dopant atoms can enter.

Since the current trend in microelectronics is to increase the number of components on a chip, it is desirable to make each component as small as possible. Whereas the features on commercial integrated circuits typically are 3 to 5 μm long, the features on chips that incorporate very large scale integration (VLSI), loosely defined as 65,000 to 2,000,000 components per chip, will be about 1 μm long. Ultradense circuits have put new demands on electronic materials and processing technology. For example, the unique electrical requirements of small devices have required the development of new insulating and conducting materials. The high component densities also put a premium on yield per component or transistor and require, furthermore, that strategies be developed to overcome the effect of defects in individual components.

Semiconductor processing has increasingly moved to dry processing, in part to realize the high resolution needed for VLSI circuits. Dry processing includes such gas-phase operations as plasma etching and chemical vapor deposition. While most of these processes are well developed for silicon technology, they have features that are sometimes undesirable. For example, the high temperatures involved in some chemical vapor depositions, 900° to 1200°C, limit

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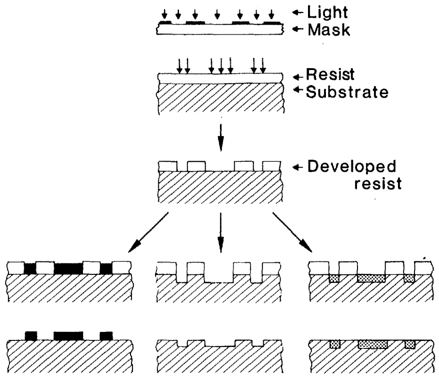


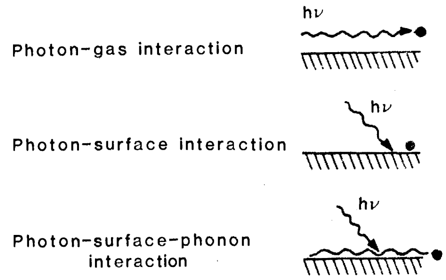


Fig. 1 (left). The main steps in conventional photolithographic processing of semiconductors. Fig. 2 (right). Possible interactions of a laser beam with a gas-solid interface.

the kind and number of thin films that can be used, since those temperatures can cause unwanted reactions between layers or material degradation. Some compound semiconductors, such as gallium arsenide (GaAs) which is being used increasingly in fast circuits, decompose at these temperatures and require low-temperature processing.

With these considerations in mind, researchers have turned to lasers for the development of new methods of chemical processing for microelectronics. In comparison with other light sources, lasers offer several special capabilities. One of the better known ones is that a laser beam can be focused to dimensions comparable to the wavelength of the laser light. Thus, even a low-power laser can produce highly intense spots of light with micrometer dimensions. The localized heating generated by focused pulsed-laser beams has previously been used to produce a number of purely thermal effects useful in some areas of semiconductor processing, such as the trimming of thin-film resistors to achieve specified resistance values (*5*). Such a focused beam can also be used to initiate a chemical reaction that is confined to a region with dimensions comparable to or smaller than the laser spot. By focusing the laser beam onto the substrate and moving the substrate in a plane perpendicular to the beam axis, patterns can be written on a wafer using the laser-initiated doping, deposition, or etching processes described in more detail below. This form of microchemical processing has been termed "direct writing" (*6*) since it allows one to pattern a wafer directly in one or two steps, without need for the masking steps so important in standard photolithography. Because the patterning is direct, this technique is particularly useful for making discretionary changes in microelectronic components.

Lasers also have a high degree of temporal coherence; this makes it possible to use lasers to perform interferometric imaging. For example, by dividing the output of a laser into two beams and then recombining them at a substrate surface, an interference pattern with extremely fine features can be made. As in the case of direct writing, interferometric processing does not require prior photolithographic masking.

The monochromatic or near-monochromatic output of lasers offers another advantage. In many photochemical reactions, a specific excitation wavelength leads to a specific set of molecular fragments and, ultimately, reaction products. For photochemical reactions, there is a threshold photon energy, generally corresponding to a wavelength in the ultraviolet region, below which no reaction occurs. As a result, the comparatively recent development of high-power ultraviolet lasers has greatly enhanced the ability to perform laser-controlled chemistry. One class of ultraviolet lasers, pulsed excimer lasers, is capable of producing high average power (>40 W) and high peak power (>10 MW) from 150 to 350 nm (*7*). These lasers are able to dissociate a variety of molecular gases and produce large amounts of specific free radicals, atoms, or molecules that can then deposit on or etch a semiconductor wafer. In this case, laser-induced chemistry performs some of the same processing operations as conventional fabrication methods. However, the monochromatic light produced by the laser allows a specific or, at least, a limited number of reaction channels to be addressed, while conventional techniques, such as plasma etching, generally initiate complex chemical reactions. Hence, laser-induced chemistry has the potential of being both simpler and more controllable than the conventional techniques.

A final property of laser radiation is that it can often be generated in the form of very short pulses, $<10^{-8}$ second long. Laser heating using these short pulses allows an irradiated surface layer to melt and then resolidify before there is substantial conduction of heat into the bulk of the material. At ultraviolet wavelengths, many materials absorb so strongly that light penetrates only a very thin layer at the solid surface. The rapid heating and cooling of a surface region by these lasers has been used in the annealing of semiconductors (*8*) and in the formation of new kinds of metastable compounds (*9*), as well as in the doping of semiconductors, discussed below.

Laser-Initiated Surface Chemistry

When a laser beam initiates a chemical reaction near a solid surface, the reaction can occur on or above the surface and may be due to either thermal processes, photochemical processes, or a combination of both (Fig. 2).

Reactions in a gaseous medium above a solid surface are typically based on primary or secondary photochemical phenomena such as:

$$AB \xrightarrow{h\nu} A + B\downarrow$$

or

$$AB \xrightarrow{h\nu} A + B$$
$$B + CD \longrightarrow BC\downarrow + D$$

where $\downarrow$ indicates a species that interacts with the surface, such as an etchant or an atom that deposits on the surface, and $h\nu$ indicates irradiation by photons of energy $h\nu$. Gas-phase transport influences the resolution of the process, since atoms produced far away from the surface spread laterally in the gas as they diffuse toward the surface. Surface-controlled nucleation processes, as well as gas-phasing scavenging processes, minimize this problem, confining the deposit to the region illuminated by the laser beam (*10*).

Reactions on the surface can be due to either direct or photochemical dissociation of adsorbed molecules or to surface excitation followed by chemical reactions. Even in the case of direct photochemical phenomena, the surface may play a major role in the dissociation chemistry. For example, the yields from photochemical reactions on metal surfaces are expected to be low because of the transfer of molecular excitation to the surface. However, suitably altering the morphology of the metal surface in order to increase the surface excitation can result in a dramatic enhancement in the rate of a photoreaction on or near a surface (*11*).

Recent experiments using crossed molecular and laser beams have clarified some of the dynamics of energy transfer to the surface in nonreactive gas-surface collisions (*12*), but studies of the dynamics of surface reactions, with or without light, have not yet been made.

Laser excitation of the surface can also initiate chemical reactions indirectly, through surface heating or through the creation of electron-hole pairs. In the case of surface heating, the reaction mechanism is similar to that of conventional chemical vapor deposition (*13*). However, in laser-initiated chemical vapor deposition, the heating of the substrate can be localized to a thin surface layer or to a small spot by using a pulsed or a focused laser beam, respectively. Since heating occurs because of absorption of the laser beam by the solid substrate, the reaction rate is sensitive to the optical as well as the thermal properties of the surface. Initiation of reactions via the production of electron-hole pairs requires that the reaction involve an ionic species or a charge complex; thus, a liquid-solid interface is the ideal environment in which to observe these effects (*14*).

Laser-Assisted Dry Processing

The high average power produced by excimer lasers has led to numerous demonstrations of photon-assisted dry processing wafer-size areas. For example, one application of considerable importance, which can only be touched in here, is the use of excimer lasers as ultraviolet light sources for photolithography. Ultraviolet light can be focused to submicrometer dimensions before the limits imposed by diffraction are reached, so photolithography with ultraviolet rather than visible light offers a decrease in the size of features that can be produced by the lithographic process. The output of ultraviolet light from conventional lamp sources is so weak that exposure times on the order of minutes are required to expose photoresists that are relatively insensitive to ultraviolet light. However, the ultraviolet emission from excimer lasers is 100 to 1000 times higher than from conventional sources, which reduces exposure times to seconds. In fact, the output from excimer lasers can be so intense that new forms of lithography have been demonstrated. Several groups have used excimer lasers to produce a dry photoresist technology based on directly ablating away the resist photochemically. This eliminates the usual wet-chemical development needed in photolithography (*15*).

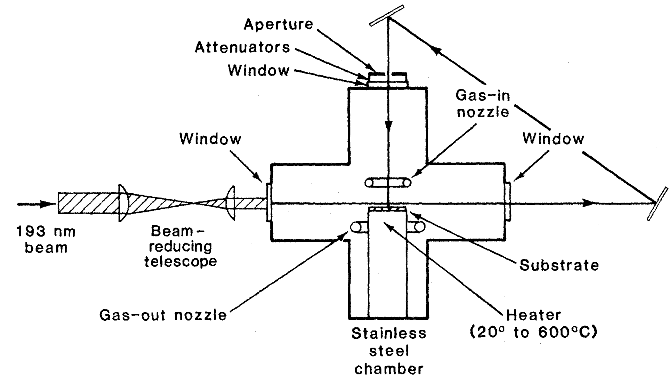


Fig. 3. Schematic diagram of a system for depositing materials using a pulsed excimer laser.

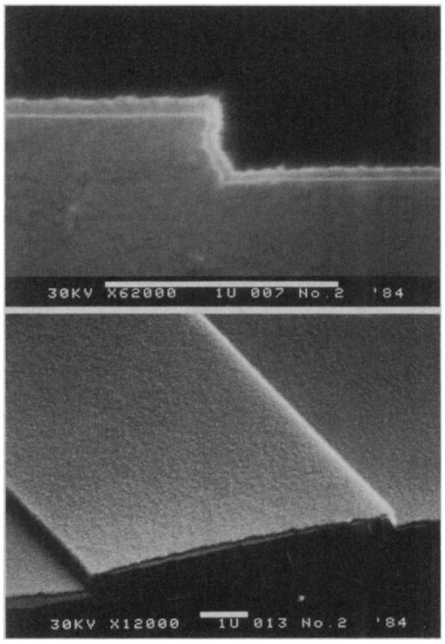
Lasers have also been used to initiate specific chemical reactions over large areas at low substrate temperatures with purely gas-phase reagents. Excimer-laser chemistry has been used to dope, deposit, and etch electronic materials. The high average power available from some excimer lasers can allow the reaction zone to be large enough to process an entire wafer with a 2- to 3-inch diameter without scanning it. Several research groups have reported etching silicon and GaAs by dissociating halogen-bearing gases, such as CH_3Br, with excimer-laser radiation (*16*); and at least one industrial group is actually using laser etching in the fabrication of 64-Kbit memory chips. This approach to etching uses the projection of a patterned laser beam to etch the silicon surface directly, eliminating the need for masking the wafer.

Metals, insulators, and semiconductors have been deposited using an apparatus such as that shown in Fig. 3. The laser beam passes several millimeters above a substrate while decomposing one or more photosensitive gases. The resultant photodecomposition products then either react with each other or move as atoms to the substrate and form a film. The substrate may be heated to about 300°C to increase the density of the deposited film by thermally enhanced adatom mobility or by desorption of impurity gases. Several groups have reported that irradiating the surface with a low dosage of ultraviolet light enhances the film quality, but the mechanism involved is not yet understood.

Metal films have been deposited by dissociating metal carbonyls. For example, when $Mo(CO)_6$ is irradiated with 193-nm radiation, CO ligands are released from the molybdenum atoms, and molybdenum films form (*17*). Tungsten films have been deposited on silicon and SiO_2 using ArF laser radiation to initiate the reaction of WF_6 with H_2 (*18*). Figure 4 shows micrographs of a laser-deposited tungsten film over SiO_2 steps on a silicon substrate. The film has excellent conformal coverage, a property needed in depositing metal conductors over sharp edges on a patterned silicon chip. Deposition of compound films, such as SiO_2 or Si_3N_4, requires the initiation of a gas-phase chemical reaction (*19*). For example, SiO_2 films have been deposited by irradiating a mixture of SiH_4 and N_2O with excimer-laser radiation having a wavelength of 193 or 248 nm. The ultraviolet photons dissociate the N_2O, releasing oxygen atoms that then react with the SiH_4 to form SiO_2. The deposited SiO_2 films cover the sharp vertical walls found on some microstructures without breaks, a feature not always achieved with conventional techniques such as plasma deposition. Finally, laser-enhanced growth of single-crystal films has been demonstrated for deposition of germanium from GeH_4 (*20*).

Lasers have been used to dope semiconductors with impurities that control the electrical properties of the doped region. Figure 5 illustrates the approach used in pulsed-laser doping. The laser serves both to release dopant atoms from an appropriate molecule and to heat the surface to the melting point, allowing the atoms to diffuse into the substrate. The substrate is translated perpendicular to the beam axis in Fig. 5, and the doping is accomplished in a single step. By contrast, the technology often used for doping semiconductors, implantation of high-energy ions, requires a subsequent annealing step to remove damage to the crystal lattice created during the implantation.

Chemical doping with lasers has been performed on both elemental and compound semiconductors, and it has been used to make low-resistance electrical contacts and to form *p-n* junctions (*21*).



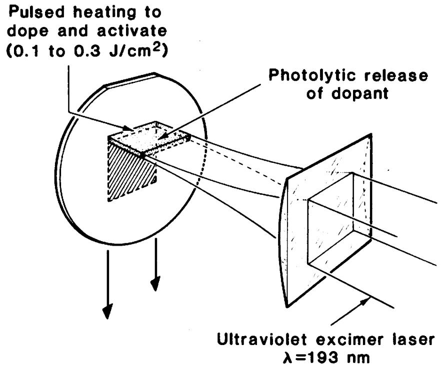


Fig. 4 (left). Micrographs from a scanning electron microscope showing a side and top view of a tungsten film over SiO_2 steps on a silicon substrate. An ArF laser was used to initiate the reaction of WF_6 with H_2. Illustration from (*18*). Fig. 5 (right). Schematic diagram of the doping of a semiconductor with a pulsed excimer laser.

Solar cells have been made from the *p-n* junctions in silicon that result from doping it with boron. In this process, the boron is produced by irradiating BCl_3 with ArF laser radiation. The solar cells have shown efficiencies of 10.6 percent without any antireflection coating to increase the efficiency of their light collecting, and higher efficiencies should be possible with process optimization. The electrical properties of laser-doped silicon are comparable to those of thermally diffused silicon, and several groups are attempting to apply the technique to the fabrication of transistors.

Direct Writing with Lasers

Direct writing is the production of patterned features on a substrate using localized, laser-initiated chemical reactions. This contrasts with the conventional techniques for producing patterned features described earlier, in which a thin patterned film serves to confine deposition or etching to specific regions. The design and fabrication of the masks used to pattern the films is an expensive and time-consuming process, which is justified for mass production of integrated-circuit chips. While conventional techniques are satisfactory for most production operations, there are cases where it would be convenient to produce the patterned layer directly. These cases include the repair, design, and modification of circuits. Direct writing may even make it possible to monitor a device's performance during fabrication.

In the United States, direct writing is being investigated by groups at the MIT Lincoln Laboratory, the Lawrence Livermore National Laboratory, and Columbia University. Although direct writing is simple in principle, its implementation requires high-quality diffraction-limited optics, translators capable of moving a sample smoothly and positioning it with submicrometer accuracy, and both the hardware and software to allow a computer to control the sample position.

In direct writing, an ultraviolet or visible laser beam is focused onto the surface of a semiconductor wafer that is in a cell containing the appropriate reagent gases. Typically, argon-ion laser radiation at 514 nm is used directly; alternatively, the beam is first passed through a nonlinear crystal to obtain 257-nm radiation. If the laser wavelength is in the ultraviolet region, the laser light causes photochemical reactions such as:

$$CF_3Br \xrightarrow{h\nu} CF_3 + Br$$

or

$$Al(CH_3)_3 \xrightarrow{h\nu} Al + 3CH_3$$

to occur. Atoms that may either etch, deposit on, or dope a solid surface are produced. If the laser wavelength is in the visible region and the substrate absorbs light at the laser wavelength, surface heating occurs and the reactions are initiated by thermal chemistry. Figure 6 shows a silicon line drawn over an SiO_2 step on a silicon wafer. In this case a focused argon-ion laser beam was used to initiate the pyrolysis of SiH_4 by heating the silicon substrate (*22*).

Several unexpected phenomena occur when tightly focused laser beams are used to initiate chemical reactions. First, the rates of deposition for direct writing can be much greater than for conventional chemical vapor deposition. In the conventional process, the deposition rate is generally limited by the need to transport fresh, gaseous reagents to the surface. In focused-laser chemistry, the distance over which gas transport must occur is only about one beam diameter, so the reaction rates are consequently very fast (*22, 23*).

Under appropriate conditions in direct-writing processes, the region written on the substrate is considerably smaller than the laser spot. This occurs because the overall rate for the process can have a nonlinear dependence on either laser power or energy. Such nonlinearities allow laser writing to be used to produce the submicrometer features that are important in many microelectronic structures.

One example of such a nonlinearity occurs in the photodeposition of zinc or cadmium from the respective alkyl derivatives (*10*). The metal atoms produced by gas-phase photolysis only stick to or condense on surface areas that already have metal nuclei in place. The nucleated surface is formed by irradiating adsorbed molecules with an ultraviolet beam at a power intensity above a characteristic threshold value. By choosing the beam's power so that only a small portion of the beam has an intensity above the threshold, a deposit can be produced that has dimensions smaller than the Gaussian width of the laser beam.

Another example of a process nonlinearity, which results in improved resolution, occurs in the direct writing of a doping pattern with continuous-wave lasers. As in doping with a pulsed laser, the direct writing of a doping pattern can be based on one of two different methods of releasing the doping atoms, thermally cracking molecules at the surface or dissociating gas-phase molecules with a separate ultraviolet laser beam. With either approach, a focused visible laser beam heats the surface, driving the dopant into a local region of the substrate. Using the thermal-cracking technique, D. J. Ehrlich and J. Y. Tsao at the MIT Lincoln Laboratory have written doped lines 0.2 μm wide in a silicon substrate (*24*). In this case, the relevant process nonlinearity is the exponential dependence of the diffusion constant of dopant atoms in silicon on the temperature of the substrate.

Direct writing with lasers is just beginning to be applied to the fabrication of complete devices and the modification of actual circuits. Laser writing has been used to fabricate a complete metal-oxide-semiconductor transistor by using laser heating to initiate localized doping, etching, and deposition (*25*). While the dimensions of that device do not reflect the limits imposed by the laser resolution, the experiment indicated that a working device can be fabricated almost entirely with laser techniques.

At present, the processing rates attainable with lasers are probably too low to produce custom circuits entirely by laser writing. A more attainable goal is to use laser writing to connect standard circuit elements produced by conventional techniques in customized configurations. In an example of this approach, computer-controlled etching and deposition with laser-writing techniques was used to reconfigure a circuit, called a ring oscillator, in a manner that allowed the high-frequency-transmission characteristics of the individual transistors and the metal interconnects between them to be determined (*26*). Such on-line custom operations, combined with simultaneous testing of the circuit elements, may be useful in shortening the design and test cycle in the development of integrated circuits. Another application amenable to laser writing techniques is the repair or reconfiguration of an integrated circuit. In this case, the defective portion would be disconnected using laser etching and then reconnected by laser writing a conducting link of metal or semiconductor material.

Laser-Assisted Wet Chemistry

Although semiconductor device fabrication relies increasingly on dry processing, liquid-phase chemistry has many powerful features, such as well-established etch rates that are dependent on crystal orientation, low processing temperatures, and, in many cases, the availability of efficient ionic chemical reactions. For example, aqueous solutions can be used to etch crystalline silicon anisotropically and to dissolve relatively inert elements, such as gold. Consequently, wet chemistry is still used in many phases of electronics production, including electroplating, etching of compound semiconductors, and substrate preparation.

Lasers have been used to modify many of these wet chemical techniques. When a solid is placed in an ionic solution, the requirement that the electrochemical potential be the same on both sides of the interface results in charge segregation in a thin layer on both sides

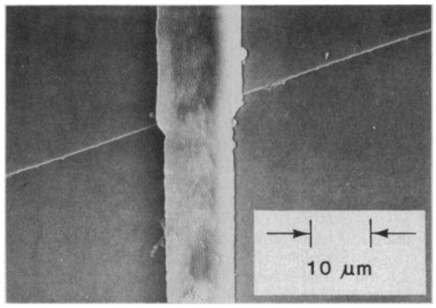


Fig. 6. Micrograph from scanning electron microscope showing a silicon line written by thermochemical dissociation over a SiO_2 step on a silicon substrate. Illustration from (*22*).

of the interface. In those cases where ionic reactions with the surface dominate the chemistry between the solid and the solution, the charged layers near the interface can control the reaction rate. Light, in particular laser light, can alter the dynamics of such interface reactions by several mechanisms (*14*). The mechanisms include altering the chemical constituents in the solution by photochemical reactions, and, in the case of semiconductor substrates, creating charge carriers by optical absorption.

Thermal alteration of the electrochemical potential is the basis of laser-enhanced electroplating, one of the earliest examples of laser-induced chemical processing. The technique was developed by R. J. Von Gutfeld and co-workers at IBM (*27*). They used a tightly focused beam from a visible argon-ion laser to illuminate a small region on the electrode of an electrochemical cell. The illuminated region, which could be as small as a few micrometers, then had an electrochemical potential different from that of the rest of the electrode, and the electrode voltage could be adjusted so that plating occurred only in the illuminated region.

This technique has been used for selectively gold plating a variety of conducting substrates. An important application is the localized plating of gold on metal, leaf-spring contacts. Because of the high cost of gold, which is necessary for good electrical contact, it is desirable to apply gold plating only at the point of contact. The complex, three-dimensional shapes of the springs make conventional photomasking techniques difficult and time-consuming.

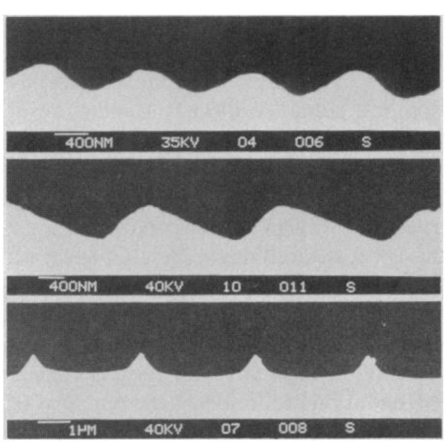


Fig. 7. Profiles of GaAs gratings fabricated using laser-initiated aqueous etching.

Laser-enhanced electrochemical processing can also be applied to the plating and etching of semiconductors. In this case, the laser light itself generates the current that drives the electrochemistry, eliminating the need for an externally applied voltage.

Recently a group at Columbia University has used laser sources to produce high-resolution, optical-diffraction gratings on both conducting and semi-insulating GaAs (*28*). The high electrical resistance of semi-insulating GaAs, important in many of its applications, makes it difficult to etch using standard electrochemical techniques. The laser-based technique uses the interference of two beams from a visible laser to produce a series of alternating light and dark stripes on the semiconductor surface. In the illuminated region, positive charges, created by optical absorption, move to the surface and allow the surface to be oxidized. The oxide then dissolves in the solution, resulting in etching of the illuminated region.

The high-resolution diffraction gratings made this way have groove profiles that are determined by the diffusion of the photogenerated carriers out of the illuminated regions. When ultraviolet light, which is strongly absorbed in GaAs, is used, the charge carriers are primarily created at the surface and their lateral diffusion in the solid is minimized. Gratings with groove spacings as small as 100 nm have been made using ultraviolet laser radiation. Gratings with sinusoidal and cusped profiles have also been made. Figure 7 shows some of the structures.

Conclusion

Research in laser-assisted chemical processing has led to the development of new fabrication techniques for microelectronics. Some of the techniques, such as laser-assisted etching and excimer-laser photolithography, are immediately applicable to manufacturing. This research has also generated an increasing interest in the basic physics and chemistry of light-assisted interface reactions. Among the topics that have been investigated are the role of charged carriers in desorbing molecules from semiconductor surfaces (*29*), the influence of surface microstructure on photochemical reactions (*11*), the role of collective surface electromagnetic waves on the deposition process (*30*), and the effect of surfaces on ultraviolet molecular spectra (*31*), to name only a few. These studies have not only uncovered unexpected physical and chemical phenomena, but some of them have, in turn, led to novel techniques for microelectronics production. Applications to other disciplines, such as catalysis, can be expected in the future.

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32. Preparation of this manuscript was supported in part by contracts from the National Science Foundation (R.O.), the Department of the Air Force, in part under a specific program sponsored by the Air Force Office of Scientific Research (R.O. and T.D.), and by the Army Research Office (R.O. and T.D.).

Melatonin: A Coordinating Signal for Mammalian Reproduction?

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The pineal gland and its anatomical relation (Fig. 1) were known as early as the third century B.C., when Herophilus suggested that it might serve as a sphincter regulating the flow of thought in the ventricular system of the brain. Galen, about 450 years later, pointed out that the pineal was unlike brain tissue in structure, lay outside the cerebral ventricles, and probably had a function similar to that of the lymph nodes. In the 17th century René Descartes revived the ancient concept of the pineal as the "seat of the soul," and this view dominated scientific thought for the next 250 years (*1*).

Systematic investigations of the mammalian pineal began in the 1880's. Ahlborn, de Graaf, and others described its gross anatomy, vascularization, innervation, histology, and embryology and noted its similarity to the "third eye" or photosensory epiphyseal organ of lower vertebrates (*1, 2*). Around 1900 the biological role of the pineal began to be studied by means of glandular extirpation and administration of glandular extracts (*3*). Perhaps the most significant developments at that time were Heubner's report of precocious puberty in a boy with a pinealoma and Marburg's theory that the pineal regulates onset of puberty (*1*). Their papers triggered investigations into interactions between the pineal and reproduction.

In 1943 Bargmann (*4*) proposed that the endocrine function of the pineal was regulated by light via the central nervous system. This concept, dubbed neuroendocrine transduction by Wurtman and Axelrod (*5*), has proven to be accurate. The pineal receives environmental information through the brain and relays it to the body by means of its humoral secretions. While the pineal contains a host of indoleamines and peptides, this article will focus on the indoleamine *N*-acetyl-5-methoxytryptamine or melatonin, the only one of these compounds for which a function has been ascertained.

The Melatonin Signal

Melatonin is synthesized from a second pineal indoleamine, serotonin, through the action of two enzymes: *N*-acetyltransferase (NAT), which is responsible for the *N*-acetylation of serotonin, and hydroxyindole-*O*-methyltransferase (HIOMT), which is responsible for the *O*-methylation of the indole ring (*6*). Quay (*7*) observed that levels of serotonin in the pineal are high during the day and low at night and that alterations in the lighting cycle caused corresponding changes in pineal serotonin

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