## Laser Annealing: Processing Semiconductors Without a Furnace

Because of the deleterious effects of high temperatures during fabrication of electronic devices made from semiconductors, academic and industrial researchers have been looking long and hard for ways to process semiconductors at, or slightly above, room temperature. A part of any such scheme may be laser annealing-the use of a high-intensity laser to rapidly heat selected areas of a semiconductor surface in such a way that the negative consequences associated with heating the entire semiconductor for extended times do not occur. From virtual obscurity a year ago, laser annealing has become one of the hottest areas of applied semiconductor research. The excitement may be well founded, for, if laser annealing pans out, electronic devices ranging from microelectronic circuits (such as computer memories) to solar cells may be among the beneficiaries. The new technique promises more densely packed circuits and cheaper solar cells than are now possible.

Credit is generally given to researchers in the U.S.S.R. for the early work on laser annealing. Publications by I. B. Khaibullin and his colleagues at the Physicotechnical Institute in Kazan, by G. A. Kachurin and his co-workers at the Institute of Semiconductor Physics in Novosibirsk, and by others began appearing in 1975. For one reason or another, this work attracted little attention outside the Soviet Union. Instead it was the striking results produced by Emanuele Rimini, Gaetano Foti, and their colleagues at the Institute of the Structure of Materials, Catania, Italy, that seems to have started the laser annealing ball rolling. One story making the rounds has it that a seminar on laser annealing held at Bell Laboratories by the Italian researchers could not be finished; toward the end of the presentation, the initially filled lecture hall was empty and all that could be heard was the whap of lasers. If this anecdote is not literally true, it is clear that a dramatic increase in interest among U.S. investigators took place following the First U.S.S.R.-U.S.A. Seminar on Ion Implantation, held last summer in Albany, New York, at which both Soviet researchers and the Catania group made presentations.

The role of laser annealing is that of a co-star to another process—ion implantation—that has become widely used in the microelectronics industry although not yet among most solar cell makers. Ion implantation is a means of introducing, in well-controlled concentrations and spatial configurations, certain impurity elements (dopants) into ultrapure semiconductor material (usually silicon). The dopants give the device its particular characteristics. The technique is conceptually quite simple; one accelerates ions of the desired dopant element to an energy from a few to about 250 keV and slams them into the surface of the semiconductor. The ions do not penetrate very far (a few thousand angstroms is typical), but nowadays almost all the action in semiconductor devices takes place in the top micrometer or less.

Unfortunately, the high-energy ions tend to knock the atoms of the semiconductor out of their crystal lattice sites, and the result is a disordered, sometimes completely amorphous layer. To restore order, device makers have to anneal the implanted semiconductor at a high temperature (800° to 900°C). Such heating allows unwanted contaminants from outside the semiconductor to enter: it also causes dimensional changes. Both effects degrade the performance of the device. Laser annealing turns ion implantation into, for all practical purposes, a room-temperature process. No furnaces are required.

For laser annealing to work, the light must be absorbed within a few micrometers of the surface. Most of the energy of the absorbed photons becomes converted to heat, and the surface temperature rises rapidly. The temperature can become so high that the atomic mobility of both dopant and host atoms is high enough to permit the atoms to return to their normal positions in the crystal lattice. In this way damage caused by ion implantation is "annealed out." Moreover, the whole process is so quick and so well confined to the damaged region that the deleterious effects that go with heating the entire semiconductor in a furnace for a much longer time do not have a chance to get started.

One of the first U.S. groups to get started on laser annealing was that headed by Richard Wood of the Oak Ridge National Laboratory, which is interested in finding ways to make large areas of solar cells quickly and inexpensively. Work at Oak Ridge actually predated the Albany ion implantation conference. Much earlier, one of the members of the group, Rosa Young, had noticed the Soviet publications and initiated experiments.

Young and Woody White at Oak Ridge used a pulsed ruby laser in their experiments with ion implanted silicon crystals. The ruby laser can impart more than 1 joule per square centimeter in each pulse of about  $50 \times 10^{-9}$  second. The numbers are important because it is the combination of a high energy density and short pulse length that makes the technique work.

Using a variety of techniques, Young, White, Jagdish Narayan, and their colleagues at Oak Ridge have shown that the damage caused by implantation of boron, phosphorus, arsenic, and antimony in silicon is completely removed by laser annealing; any defects remaining are less than 10 angstroms in size. By contrast, thermal annealing in a furnace of ion implanted silicon can restore an amorphous surface to a crystalline state but leaves a considerable degree of residual damage in the form of structural imperfections (dislocations).

In another study, White and his associates found that the ion implanted dopants move a considerable distance during the laser annealing. Immediately after implantation, the impurity ions are distributed according to a bell-shaped curve which has the maximum impurity concentration about 1000 angstroms below the silicon surface. Thermal annealing causes the curve to broaden slightly; pulsed laser annealing changes the curve altogether. The bell shape is lost, and the dopants assume a nearly constant concentration from the surface to a depth of some 2000 angstroms, at which point the concentration drops off rapidly with further distance into the crystal.

A group at Bell Laboratories and the Western Electric Engineering Research Center is also investigating high-power pulsed lasers for annealing ion implantation damage, according to Walter Brown of Bell. These investigators are, however, going about things somewhat differently. A perhaps minor difference is their use of an infrared laser (yttrium aluminum garnet containing neodymium ions or, as it is popularly known, Nd-YAG). A bigger difference is that in much of the Bell-Western Electric work the researchers focus the laser beam to a small spot (40 micrometers diameter),

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Fig. 1. Transmission electron micrograph of polycrystalline silicon implanted with boron. The diameter of the crystallites in the unannealed material at the left is about 500 angstroms, whereas the grain size of the laser annealed silicon at the right increased to about 250,000 angstroms. [Source: J. F. Gibbons, Stanford University]

whereas at Oak Ridge investigators irradiated 1 square centimeter diameter areas in a single pulse. The difference reflects Bell Labs' interest in microelectronics devices, which are small, rather than in solar cells, which are hundreds of times larger.

Among the Bell-Western Electric findings was evidence that the surface layer of the laser annealed silicon actually melts. Since the laser is on only a short time, there is little opportunity for the ion implanted impurities to diffuse the long distances observed at Oak Ridge unless the surface is heated to above the melting temperature. Diffusion in a liquid is sufficiently rapid to account for the changed impurity distribution. The first evidence was indirect, being based in part on electron microscopy studies of the morphology of the annealed surface layer. More direct confirmation of the melting hypothesis was recently provided by Dave Auston of Bell Labs and his colleagues, who measured the reflectivity of silicon during the laser annealing process. They found that the reflectivity increased from that characteristic of amorphous silicon to that expected for a metal (liquid silicon is metallic) when the laser pulse was applied. Later, the reflectivity decreased to a value associated with crystalline silicon.

Calculations based on a model that includes both heat transfer and mass transfer components by Wood and his coworkers at Oak Ridge provide further evidence for surface melting. Their calculated impurity distributions match those observed.

At about the same time as the Catania group began experimenting, work began on another type of laser annealing in James Gibbons' laboratory at Stanford University. Gibbons and Arnon Gat of Stanford devised a scanning laser system in which a continuous wave (CW) rather than a pulsed laser was used. Because CW lasers generally have a lower instantaneous power output than pulsed lasers, the Stanford investigators had to do two things in order to achieve laser annealing. First was focusing the laser beam to a small (about 30 micrometers) diameter, and second was maintaining the beam for a millisecond or less at each location. Both procedures were necessary to ensure that enough energy was going to the irradiated spot to raise the temperature and allow annealing to occur. The Bell Laboratories group has since developed scanning systems for both CW and pulsed lasers.

The scanning feature carries with it the possibility of selective annealing-that is, only that part of the surface that has been ion implanted need be annealed, or annealing treatments may be tailored for different parts of the surface that may have been implanted in different ways. Scanning, whether with pulsed or CW lasers, is, however, definitely slower than the large-area annealing possible with pulsed lasers having large diameter beams, just as sequential processes are invariably slower than parallel ones.

A major difference between the use of CW and pulsed lasers, according to both Brown and Gibbons, is that the annealing mechanism operative is not the same in the two cases. When CW lasers are used, the surface temperature of the semiconductor can be kept below that required to melt the material, yet high enough to anneal out damage caused by ion implantation. In semiconductor jargon, when melting occurs, one speaks of recrystallization of the disordered layer by the process of liquid phase epitaxy. When melting does not happen, regrowth is by solid phase epitaxy. In either case, epitaxial growth means that the disordered region uses the undamaged bulk of the semiconductor as a "template," and the regrown material has the same structure and orientation as the bulk.

Using lasers that emitted light in the

visible wavelength range (argon ion and krypton gas lasers), Gibbons, Gat, and their co-workers at the Advanced Research and Applications Corporation, Sunnyvale, California, and at the University of Illinois have tried the scanning technique on silicon implanted with arsenic and with boron. General results were consistent with those found by researchers using pulsed lasers, with the important exception that the spatial distribution of the implanted impurities did not change after annealing.

Jim Williams, Harry Leamy, Brown, and their associates at Bell Labs provided evidence for the hypothesis that the impurity distribution did not change because melting did not occur. Transmission electron microscopy and other techniques demonstrated that solid phase regrowth was occurring, starting at the interface between the disordered layer and the bulk silicon. In another study, Gibbons, Gat, and Arton Lietoila of Stanford used a theory of solid state epitaxial regrowth-developed earlier by Laszlo Csepregi, James Mayer, and Thomas Sigmon of the California Institute of Technology-in conjunction with a calculated temperature distribution to determine the growth rate during laser annealing. The theoretical rate was within 10 percent of the measured rate.

The impact of laser annealing may turn out to be considerable. For starters, the absence of impurity redistribution in the scanning technique means that it is possible to ion implant very closely spaced areas on an integrated circuit chip because the borders of the implanted regions would not smear together during annealing. In this way, the precision control of the spatial distribution of dopants possible with ion implantation, but not obtained in current industrial practice, could be fully utilized. Maintaining the integrity of the doped areas means that device makers may be able to pack more devices, such as transistors, on a chip than is now possible, although improvement of other fabrication technologies, such as photolithography, are also needed for this to occur. More densely packed chips, in turn, mean that more computing power or faster signal processing can be obtained for roughly no increase in price.

Laser annealing has a further advantage because changes in the dimensions of a semiconductor wafer (several hundred chips, each containing a microelectronic device, are cut from one wafer) which take place upon annealing at a high temperature are avoided, according to Richard Reynolds of the Advanced Research Projects Agency. Maintaining dimensional stability is a necessity if the minimum dimensions of microelectronic devices are to shrink below 1 micrometer (the minimum feature size of presentday devices is about 3 micrometers). Microelectronic circuits are built up in layers, each of which must be precisely aligned with respect to the preceding one. If it were possible to fabricate devices with characteristic dimensions of 0.5 micrometer and if the wafer on which the device is being built expands or contracts by this amount (a typical value), maintaining the registration of the succeeding layers would be difficult. Since laser annealing heats only the wafer surface, deleterious dimensional changes do not occur.

Application of laser annealing to actual microelectronic circuit fabrication awaits the future. Other ways in which laser annealing may benefit these devices have, however, been demonstrated. Mayer at Caltech, for example, heads a group that is learning how to epitaxially grow crystalline layers of silicon on silicon substrates. Epitaxial growth of doped layers is used by device makers as an alternative to diffusion of impurities directly into undoped silicon or to ion implantation in certain circumstances; but the process used (chemical vapor deposition from a gaseous mixture of silane and doping gases such as arsine, phosphine, or diborane) is complex. It would be simpler to evaporate silicon directly onto the substrate, but layers produced in this way are amorphous and cannot be recrystallized by thermal annealing.

Mayer, Silvanus Lau, and their colleagues at Caltech, together with researchers at the Naval Research Laboratory, have used a Nd-YAG laser to recrystallize an evaporated amorphous layer of silicon on a silicon substrate with a single light pulse. Epitaxy experiments in which amorphous silicon was recrystallized by laser annealing have also been carried out by John Bean, John Poate, Leamy, and their associates at Bell Labs, and by Lavern Hess, C. Lawrence Anderson, and their co-workers at Hughes Research Laboratories.

There is also considerable interest in recrystallizing the polycrystalline silicon that is used in place of metal conductors in some kinds of microelectronic devices. One of several limitations preventing the fabrication of circuits with even smaller dimensions is the low conductivity of polycrystalline silicon; to carry the same current in a smaller conductor requires a higher conductivity. Gibbons, Gat, Levy Gerzberg of Stanford, and their co-workers have shown 28 JULY 1978 that laser annealing with their scanning system increases the size of the crystallites in the silicon some 500 times (Fig. 1). The larger grain size material has a three times higher conductivity, good enough says Gibbons to accommodate nearly a threefold reduction in the size of polycrystalline silicon conductors.

An area of increasing research is the development of gallium arsenide integrated circuits. This semiconductor is now used in certain high-frequency devices for processing radar signals and for similar applications not possible with circuits made of silicon. Development of an integrated circuit technology for gallium arsenide would bring benefits of miniaturization comparable to those of silicon, where all components of a circuit are a part of the same chip.

Laser annealing, in conjunction with ion implantation, may give the progress of gallium arsenide a boost. The problem has been that the material tends to decompose because arsenic vapor is evolved when the gallium arsenide is heated during annealing to repair the damage due to ion implantation. Investigators have physically prevented decomposition by encasing the semiconductor in a capsule, often made of an insulator such as silicon dioxide. Encapsulation, however, causes strains in the gallium arsenide.

Jene Golovchenko and T. C. N. Venkatesan of Bell Laboratories have shown that ruby laser pulses can be used without encapsulation to remove damage due to implantation of tellurium into gallium arsenide. The investigators also demonstrated that the tellurium, after annealing, was in the correct crystal lattice sites to be electrically active (dopants must occupy such sites to perform their function). Experiments by Fred Eisen of the Rockwell International Science Center, working with Mark Nicolet of Caltech and with the Italian researchers at Catania, have shown that the quality of the laser annealed gallium arsenide (implanted with tellurium) was superior to that resulting from thermal annealing.

## Making Solar Cells Cheaper

Just as big an impact on solar cells as on microelectronics is seen by some observers for laser annealing. The overriding problem in solar cells, which at present are made from expensive crystalline silicon, is that of producing acres upon acres of the material at low cost. Although laser annealing cannot yet contribute to making low-cost silicon, it is said to provide a faster and less expensive way of producing solar cells from the existing material.

Once again, it is in conjunction with ion implantation that laser annealing can help. At present, solar cells resemble microelectronic circuits in that doping and thermal annealing steps are necessary. Silicon wafers 7 to 10 centimeters in diameter, having been doped by diffusion or ion implantation, are loaded into a furnace for annealing. Although annealing furnaces can accommodate hundreds of wafers at once, the annealing can take up to 2 hours and is essentially a batch process. An automated assembly line in which silicon wafers pass under an ion implanter and then a laser could be many times faster while producing cells of about the same quality, according to Wood of Oak Ridge.

One company, Spire Corporation, Bedford, Massachusetts, is already at work designing an automated solar cell production facility, which will be able to manufacture 1 acre of cells per day (180 square meters per hour). A team of researchers headed by Allen Kirkpatrick of Spire has demonstrated the ion implantation and annealing stages of such a process. An ion implanter now in operation there can handle the equivalent of 300 wafers per hour. John Mannuci and Anton Greenwald of Spire, using ion implantation and pulsed electron beam annealing, have made cells that are equal in performance to cells made elsewhere by diffusion.

A special aspect of the Spire concept is the use of a pulsed electron beam rather than a laser to carry out the annealing step. According to Kirkpatrick, the physical processes operative in electron and pulsed laser annealing are nearly the same, as evidenced by the similarity in the structure and electrical properties of ion implanted silicon annealed by the two methods. An advantage of electron beams, says Kirkpatrick, is that the technology now exists to make large diameter beams that have a uniform brightness (lasers are brighter in the center of the beam). Electron beams are also more energy efficient than lasers (up to 50 percent as compared to 1 percent or less in converting input to beam energy).

Despite all the enthusiasm, few observers are willing to say when or if laser (or electron beam) annealing will have an impact on the microelectronics and solar cell industries. On the other hand, every semiconductor device company large enough to have a research laboratory is said to be getting involved, and laser sales are brisk. As one researcher noted, activity is still in the "gee whiz" stage, but, during the next year, issues crucial to practical processes will begin to be addressed.—ARTHUR L. ROBINSON