Femtosecond Laser Annealing of Silicon

The thermal melting and recrystallization processes invoked at slower speeds fail for subpicosecond pulses, a new twist on an old controversy

Michael Downer, Richard Fork, and Charles Shank of AT&T Bell Laboratories are showing what must be the current record for slow-motion movies. Their film, with a time resolution of 100 femtoseconds, shows the melting of the surface of a silicon crystal irradiated with an 80-femtosecond pulse of laser light and the subsequent evaporation of particles from the molten material. The entire film spans less than 1 nanosecond.

Although physicists do not have complete microscopic models of what happens when a crystalline solid melts, the normal process involves lattice vibrations, which get increasingly violent as the temperature rises. When the amplitude exceeds a certain fraction of the equilibrium spacing between atoms, the bonds between them catastrophically fail, and the once rigid solid becomes a fluid.

But with pulsed lasers of 100 femtoseconds and less, scientists can deposit enough energy to melt a solid in a time comparable to or shorter than one lattice vibration period. Under these conditions, does it still make sense to describe melting in the usual way? This is the new question now confronting investigators of laser annealing (*Science*, 28 July 1978, p. 333), who have been using ever faster pulsed lasers in an attempt to resolve an old controversy concerning how laser annealing works.

Laser annealing experiments date back at least as far as 1968, but interest grew dramatically in 1977 following reports by researchers in the Soviet Union ~~and in~~ Italy, which showed that laser irradiation of silicon could restore crystalline perfection to a surface layer severely damaged by ion implantation. Ion implantation is an increasingly important way of introducing the electrically active impurities (dopants) that control silicon's electrical properties.

While the commercial future of laser annealing remains uncertain, the old debate over the mechanism of annealing by pulsed lasers is taking a new twist. Discussion once centered on the question: Does the temperature of the irradiated surface exceed the melting point? Continuous wave lasers deposit their energy uniformly over a long time, so there is ample time for heat dissipation mechanisms to keep the temperature relatively low. Pulsed lasers inject the same energy in a short time, so the temperature rises much higher.

Although the earliest investigators thought the surface did not melt, the majority since the new wave of interest began have concluded it does. In this view, pulsed laser annealing is a melting and recrystallization (liquid phase epitaxy) phenomenon in which the nearly perfect new crystal regrows on the unmelted silicon beneath.

In brief, the supposed chain of events goes as follows: All of the light is absorbed in a thin surface layer, creating a dense soup of highly energetic electrons and vacant bonding states (holes) called an electron-hole plasma. By means of collisions, the excess energy of the electrons and holes is quickly transferred to lattice vibrations, thereby heating the surface. If the laser pulse energy is above a threshold value, the surface melts. After the pulse passes, the heat diffuses into the unmelted material, cooling the surface layer, which recrystallizes.

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A large number of experiments supported this simple model. The first direct evidence was that from the 1978 experiment by David Auston and his Bell Laboratories co-workers, who monitored the reflectivity of silicon before, during, and after irradiation with a 50-nanosecond pulse. The reflectivity rose from that characteristic of amorphous silicon to a value close to that of molten silicon during the pulse and quite a while later dropped to that appropriate for crystalline material.

One ambiguity of the reflectivity is that it directly probes the condition of electrons in a solid but not lattice vibrations. It is possible that the high reflectivity ascribed to a molten silicon surface is due to some other effect. Raman scattering does probe lattice vibrations. The frequency of the scattered light shifts downward when scattering occurs by the creation of phonons (Stokes line) and increases when it occurs by the annihilation of phonons (anti-Stokes line). Phonons are the quanta of the vibrational field in analogy with photons in electromagnetic fields.

A 1980 report of Raman scattering from silicon heated by 5-nanosecond pulses by Ho Wai Lo (now at Poly Solar, Inc., Garland, Texas) and Alvin Compaan of Kansas State University indicated that the lattice temperature during laser annealing rose to only 600 K, far below the silicon melting temperature of 1685 K.

The temperature comes from the ratio of Stokes to anti-Stokes line intensities. At higher temperatures, the population of phonons increases and with it the probability of anti-Stokes Raman scattering as compared to Stokes Raman scattering, which does not require the presence of phonons. These early Raman results have been the main experimental evidence against the melting hypothesis, indicating that the high reflectivity is due to some other effect.

Even before the Kansas State result, however, James Van Vechten of IBM's Yorktown Heights laboratory and several collaborators pointed to numerous instances where details of reflectivity and other experiments seemed at odds with melting during pulsed laser annealing.

Van Vechten made a counter proposal that considered what would happen in the presence of a very high concentration of electrons and holes. With a high enough concentration, enough silicon bonds would be weakened by the missing electrons to cause a phase transition to a fluid phase that is characterized by flexible bonds that allow imperfections to move rapidly.

The rise in reflectivity was at first ascribed to the very high density plasma, a well-known effect in solid-state theory. Later, Van Vechten modified his idea to account for certain inconsistencies. He proposed the electron-hole plasma condensed into a superfluid state (Bose condensation) that was responsible for the high reflectivity.

In 1981, researchers in Nicolaas Bloembergen's group at Harvard University pushed the time resolution of reflectivity measurements into the picosecond range and began to see plasma effects, but these have turned out to elaborate on rather than contradict the melting model. A detailed account of time-resolved reflectivity with 20-picosecond pulses published in 1982 by Jia-Min Liu (now at GTE Laboratories), Heinrich Kurz (now at the Technical University of Aachen, West Germany), and Bloembergen established the behavior pattern now seen at Bell Labs with femtosecond lasers.

The researchers used the well-known experimental technique called pump and probe. An infrared laser pulse is split into two parts, one of which is frequency doubled to the visible. By varying the arrival times of the visible pump that heats the silicon and the infrared probe that is reflected, they obtained a time trace of the reflectivity.

For pulse energies below the threshold for formation of the high-reflectivity phase, the Harvard researchers observed a transient reflectivity decrease as the visible pump pulse passed. When the pulse energy exceeded the threshold for the high-reflectivity phase, the investigators recorded a direct rise in the reflectivity to the molten silicon value. However, very shortly after, Dietrich von der Linde and N. Fabricius of the University of Essen, West Germany, reported similar picosecond reflectivity measurements that showed the plasma effect even above the threshold for melting; that is, a slight decrease in reflectivity prior to the rapid increase to the molten silicon value during the passage of the pump pulse.

The reflectivity dip is due to the large number of electrons and holes excited by the laser. If the frequency of the laser is above that of a resonance called the plasma frequency, which is proportional to the square root of the concentration of electrons, the plasma depresses the reflectivity. It raises the reflectivity, if the laser is below the plasma frequency.

From the magnitude of the reflectivity decrease, it is possible to determine the plasma frequency. This year at Harvard Henry van Driel of the University of Toronto, Louis-André Lompré of the Center for Nuclear Studies at Saclay near Paris, and Bloembergen used lower frequency infrared probe pulses in pump and probe reflectivity experiments to accomplish this and thereby obtain the concentration of electrons.

Taken together, the picosecond reflectivity measurements suggest that the plasma is created prior to the high reflectivity phase and that the electron concentration is considerably lower than that postulated in Van Vechten's plasma annealing model. The interpretation is that the plasma transfers its energy to lattice vibrations and that the surface melts in the usual way, albeit rather more rapidly.

The latest Raman scattering results now support this view, as well. G. Wartmann, M. Kemmler, and von der Linde at Essen have just published time-resolved Raman scattering data that follow the lattice temperature of silicon heated by 10-nanosecond visible laser pulses. For pulse energies just below threshold, the temperature rises to 1500 K or so, and for those above threshold, the temperature reaches the melting temperature during the passage of the pulse.

Von der Linde told *Science* that high-temperature Raman measurements are difficult to interpret. For one thing, the scattered intensity drops drastically, while thermal emission of radiation increases. The new measurements better disentangle these complications than the older ones. Compaan at Kansas State also has come around to the melting point of view. He, Ming Chih Lee, and Gary Trott are completing analysis of new Raman scattering experiments of their own. The preliminary result is that the lattice temperature is much higher than measured before and could be as high as the melting temperature.

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Femtosecond reflectivity measurements clearly put the plasma stage before the melting. Last year at Bell Labs, Shank, Richard Yen, and Charles Hirlimann (now at the University of Paris VI) reported time-resolved reflectivity measurements using the pump and probe method. The pump pulse is in the red region of the visible spectrum, whereas the probe is a broadband "white light." By selecting a particular frequency of reflected light, the investigators could look above and below the plasma frequency, which was higher in these experiments than in the picosecond case.

The reflectivity behavior with 90-femtosecond pulses replicated that seen in the picosecond experiments. Below the plasma frequency, there was a transient dip for pulse energies below threshold and a transient dip followed by a rapid rise to the molten silicon value for pulse energies above threshold. Above the plasma frequency, the reflectivity initially rose, as the plasma built up; then it declined as the plasma dissipated; finally, it rose to the molten silicon value within a few picoseconds.

Subsequently, the same group reported on a variation of reflectivity measurements. With the pump and the probe both in the red, they measured the angular distribution of reflected light with a frequency twice that of the probe. The nonlinear optics effect of second harmonic generation normally does not occur in silicon because of the symmetry of the crystal structure. However, the symmetry is reduced at the surface, and theory predicts three lobes in the second harmonic intensity as the measurement angle rotates about the surface normal.

The researchers found this to be the case for pulse energies below threshold, but above threshold the intensity dropped and the lobes smeared out within a few hundred femtoseconds. The interpretation is that the high reflectivity phase is isotropic, which is what one expects if the surface has melted.

Finally, there are the femtosecond "movies" taken by Downer, Fork, and Shank. By imaging and recording the reflected white light as the delay time between the pump and probe pulses is varied, they made their film frame by frame. Within 100 femtoseconds, the surface begins to brighten as the reflectivity rises. At 1 picosecond it is quite bright.

Nearly everyone agrees that the traditional picture of melting is unlikely to hold during such short times. The typical period of a lattice vibration is about 100 femtoseconds, for example. Can lattice vibrations draw energy from the electron-hole plasma and then break bonds in the space of one period? Shank's position is that "all experiments support surface melting, but the details of how it melts are still open."

One view of how melting occurs is reminiscent of Van Vechten's earlier proposal. Two years ago, Monique Combescot and Julien Bok of the Ecole Normale Supérieure (University of Paris VII) theorized that even the normal thermal melting process was characterized by the generation of a high concentration of electrons and holes that then weakened bonds and caused a sudden phase transition to a fluid. The extra electrons and holes created by laser pulses would hasten the process, so that "melting" would occur at a lower than normal temperature. However, there is already some experimental evidence against the proposal, and several groups are looking more deeply into the melting problem.

—**Arthur L. Robinson**