Silicon, thoroughly characterized and inexpensive, is the most widely used substrate for semiconductor microelectronics. From computer chips to photodetectors, silicon has found its way into countless commercial applications. Ordinary silicon has certain limitations as far as optoelectronics is concerned, however. For example, because it is transparent to the near-infrared radiation wavelengths used for telecommunications (1.3 μm and 1.55 μm), it cannot be used to detect these wavelengths. Because of its indirect bandgap, it is also a poor light emitter.

We developed a technique for microstructuring silicon surfaces with femtosecond laser pulses that overcomes some of these shortcomings. The resulting microstructured surfaces have novel optoelectronic properties that provide new functionality for silicon.\(^1,2\)

After we irradiate the surface of a silicon wafer with a 1-kHz train of 100-fs, 800-nm laser pulses of fluence 8 kJ/m\(^2\) in an environment of sulfur hexafluoride (SF\(_6\)), the originally shiny surface of the wafer becomes velvet black. Scanning electron microscopy reveals that the laser-treated surface is covered with a quasi-ordered array of conical microstructures. Figure 1 (page 34) shows a macroscopic view of a microstructured silicon wafer and a scanning electron micrograph of the surface. Areas ranging from tens of micrometers to tens of millimeters in diameter can be microstructured without the use of lithographic masks. The process also yields reproducible average spacing, height and aspect ratio of the conical microstructures.

A series of scanning electron micrographs showing the development of the surface structure is shown in Fig. 2. When the first laser pulse strikes the silicon surface, the energy deposited in the material near the surface creates a plasma, melting the surface and producing a plume of ablated material. The plasma dissociates the normally inert SF\(_6\) molecules, and fluorine radicals react with the molten silicon surface. The volatile species created in these reactions can either travel away from the surface with the expanding plasma or diffuse into the molten surface. After a few microseconds, the surface
The authors present a technique for microstructuring silicon surfaces using femtosecond-laser-assisted chemical etching. The microstructuring process dramatically changes both the surface morphology and the optoelectronic properties. The authors discuss the reasons behind these changes and the possibilities for new uses in photodetector, sensor and display applications.

Optical properties of microstructured silicon

The striking blackness of the microstructured surfaces indicates that the optical properties of the silicon substrate have been altered. To quantify the optical properties, we measured the transmittance and reflectance of a microstructured sample using a spectrophotometer equipped with a spherical detector that collects all transmitted or scattered light. The spherically integrated reflectance, $R$, and transmittance, $T$, were then used to obtain the absorptance, $A$, of the material using the formula: $A = 1 - R - T$. Figure 3 shows the absorptance of silicon measured before and after microstructuring in an SF$_6$ atmosphere as a function of wavelength from 250 nm to 2500 nm. The absorptance for visible wavelengths increases from about 65% to nearly 95%, giving rise to the black appearance of the surface after microstructuring.

Multiple reflections, however, cannot account for the surprisingly high absorption of light with wavelengths from 1.1 to 2.5 $\mu$m. Because the minimum in the bandgap energy of silicon is 1.07 eV, corresponding to a wavelength of about 1.1 $\mu$m, the absorptance of infrared light by intrinsic, unstructured silicon is very small. Simply increasing the number of reflections cannot cause the observed absorptance.
near-unity infrared absorptance. Furthermore, thermal annealing of the microstructured surface causes a significant drop in infrared absorptance without changing the surface morphology. We therefore conclude that the band structure of the material is very different from that of ordinary silicon.

The high infrared absorptance of microstructured silicon opens up the possibility of developing broadband silicon photodetectors sensitive to infrared regions of the spectrum. To function as a photodetector, however, the absorption must create photocarriers that can be collected and turned into an electronic signal. In collaboration with Radiation Monitoring Devices of Watertown, Massachusetts, we performed a proof-of-principle experiment to demonstrate that microstructured silicon can be used for infrared photodetection. By microstructuring the detection area of a commercial avalanche photodiode, we produced a significant increase in the photocurrent generated by 1.3 μm radiation. The unstructured avalanche photodiode showed no response to 1.3 μm radiation at bias voltages below 900 volts. After microstructuring, the photodiode responded to illumination at 1.3 μm with bias voltages as low as 400 V and the photocurrent generated for bias voltages above 900 V increased three-fold. We also demonstrated a thirty percent increase in the quantum efficiency of avalanche photodiodes at 1.064 μm. Inexpensive silicon-based photodetectors at these wavelengths would be extremely useful for both research and communications.

Field emission properties of microstructured silicon

When a potential difference is applied across sharp tips, such as those of microstructured silicon, the electric field lines are concentrated near the tips, greatly enhancing the strength of the electric field in the vicinity of the tip. This geometric enhancement can make the electric field so strong that it reduces the potential barrier for electrons to escape from the material. If the barrier is lowered far enough, quantum mechanical tunneling allows electrons to be emitted from the surface, a process known as field emission. Cathodes based on field emission...
sion are much more efficient than those based on thermionic emission from resistive heating, such as those found in conventional cathode ray tubes.

We have found that silicon microstructured in SF$_6$ has remarkable field emission characteristics. Figure 4 shows the current versus voltage characteristics for a $2 \times 2$ mm$^2$ sample of microstructured silicon. The so-called turn-on field—that is, the magnitude of the applied electric field necessary to achieve an emission current density of 10 nA/mm$^2$—is only 1.2 V/$\mu$m, equal to the lowest turn-on field achieved with carbon nanotube field emitters. Moreover, microstructured silicon achieves a stable current density that is slightly higher than that of carbon nanotubes (12 versus 10 mA/mm$^2$, respectively$^3$) at an applied field of 100 V/$\mu$m and the silicon microstructures are more robust as field emitters than those based on carbon nanotubes. Emission remains constant for several days even at high current and the field emission properties do not degrade after months of exposure to the atmosphere.

Because of the potential for efficient and inexpensive operation, the development of silicon-based field emitters has recently received much attention. Possible applications of field emission arrays include flat panel displays and microwave amplification. Conventional techniques for fabricating micrometer-sized silicon-tip arrays require a multi-step process, including photolithography, etching and oxidation. Femtosecond laser microstructuring, on the other hand, provides a simple one-step method for fabricating powerful and efficient silicon-based field-emission arrays.

What causes the altered optoelectronic properties?

As stated earlier, the high infrared absorptance indicates that the band structure of the structured silicon is different from that of ordinary silicon. We investigated the chemical and structural composition of the structured surface to determine what might be responsible for the altered band structure. Using secondary ion mass spectrometry, we characterized the chemical species present at the surface of the microstructures formed in SF$_6$. Briefly, an energetic beam of ions is used to sputter secondary ions off the surface; the chemical composition of the sputtered material is then analyzed by means of mass spectrometry. The measurements show that sulfur makes up about 1 part in $10^9$ of the surface. Other groups have reported incorporation of elements into silicon after irradiation with longer-pulse and continuous wave lasers, but the concentrations previously reported are orders of magnitude smaller than the concentrations we obtain with femtosecond irradiation.$^{4,5}$ Studies of crystalline silicon doped with sulfur by diffusion implantation show that sulfur concentrations of 1 part in $10^9$ produce localized donor states within the bandgap.$^6$ We believe that at the very high concentrations of sulfur achieved after femtosecond laser microstructuring in SF$_6$, these states broaden to form an impurity band within the bandgap. This allows infrared light to promote electrons from this impurity band into the conduction band.

In addition, the large concentration of electrons at higher energy states contributes to the field emission current, which explains the high emission currents we observe.
By microstructuring silicon in other gases, we obtained additional evidence for the role of sulfur. Figure 5 shows the absorptance for silicon microstructured in these different gases. A silicon wafer irradiated in an ambient atmosphere of Cl₂ is covered in microstructures that are similar in morphology to those made in SF₆, but does not display high infrared absorption or high field emission current. Furthermore, silicon microstructured in H₂S exhibits near-unity infrared absorption, whereas silicon microstructured in H₂ does not. Finally, annealing a SF₆ sample decreases both the sulfur concentration and the infrared absorptance by approximately a factor of two. These observations strongly suggest that sulfur impurities are responsible for the high infrared absorptance and field emission current of the microstructures formed in SF₆.

Future directions
By altering the morphology and optoelectronic properties of silicon, we have created a novel material for near-infrared light detection and field emission devices. By varying the sample material, laser conditions, and the ambient gas, we can also produce other surfaces with unique optoelectronic properties. For example, after irradiating a silicon wafer in air, we obtain the rounded microstructures with a large amount of nanostructure shown in the top of Fig. 6. Chemical analysis of the air-structured sample shows that the irradiation forms a layer of silicon-rich silica, or SiOₓ (x<2), at the surface. This substoichiometric silicon dioxide surface is photoluminescent, highly robust, and does not degrade over time when exposed to air.

Because microstructuring increases the surface area of the material by more than an order of magnitude, it offers a promising strategy for making silicon-based chemical or biological sensors. We are therefore developing approaches for terminating the microstructured surface with molecules that have attachment sites for specific chemical species. Changes in an optoelectronic property of the surface, such as photoluminescence, can then be used to monitor attachment of this chemical species.

Finally, by covering the substrate with a copper grid containing micrometer-scale holes, we have made patterned regions of microstructures as shown in the bottom of Fig. 6. These pixel-sized regular arrangements of microstructures are ideal for field emission displays. In addition to restricting the area of the surface exposed, the masks impose sharp boundary conditions on the irradiated material and produce more regularly arranged microstructures within each pixel.

The novel optoelectronic properties and ease of integration into microelectronics make microstructured silicon an attractive substrate for use in detectors, sensors and display technologies. We continue to find new applications and properties of interest from substrates microstructured using femtosecond laser pulses.

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