

Near-unity below-band-gap absorption by microstructured silicon

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We increased the absorptance of light by silicon to approximately 90% from the near ultraviolet (0.25 μm) to the near infrared (2.5 μm) by surface microstructuring using laser-chemical etching. The remarkable absorptance most likely comes from a high density of impurities and structural defects in the silicon lattice, enhanced by surface texturing. Microstructured avalanche photodiodes show significant enhancement of below-band-gap photocurrent generation at 1.06 and 1.31 μm , indicating promise for use in infrared photodetectors. © 2001 American Institute of Physics. [DOI: 10.1063/1.1358846]

Light absorption by unmodified silicon is limited by two factors: silicon is highly reflective across the electromagnetic spectrum, and the band gap of silicon is 1.07 eV, making unmodified silicon essentially transparent to wavelengths longer than 1.1 μm . Both factors limit the useful wavelength range, sensitivity, and efficiency of silicon-based optoelectronic devices. Because of silicon's technological importance, overcoming these limitations would open up new possibilities for applications.

In this letter, we report increasing the optical absorptance of silicon from a few percent to roughly 90% in the near-infrared region (1.1–2.5 μm) as well as from roughly 60% to roughly 90% at shorter wavelengths (0.25–1.1 μm). The increased absorptance leads to photoelectron generation by 1.31 μm illumination of a microstructured avalanche photodiode (APD) with a bias voltage of 500 V. For bias voltages below 900 V, an unstructured APD gives no response to 1.31 μm illumination, and for higher bias voltages, the signal is a factor of 3 lower than that obtained from the structured device. The microstructured APD response to 1.06 μm illumination is similarly improved. These properties are obtained by microstructuring the surface of silicon using laser-assisted chemical etching.^{1–3}

One well-established strategy for reducing reflection is surface texturing. In silicon, various texturing techniques^{4–10} have been used to reduce the total hemispherical reflectance (i.e., specular and diffuse reflectance combined) for normal

incidence to a few percent for visible light and somewhat more for infrared radiation. While reducing reflectance increases absorptance for visible wavelengths, reducing reflectance below the band gap without simultaneously introducing absorbing states into the gap leads primarily to increased transmittance.

We produced microstructured silicon surfaces that have visible to near-infrared reflectance of a few percent and absorptance of about 90%. The surfaces are microstructured by irradiating a Si(111) surface with a train of 800 nm, 100 fs laser pulses in the presence of SF₆.¹ This process creates a quasicrystalline array of sharp conical microstructures up to 50 μm high that are about 0.8 μm wide near the tip and up to 10 μm wide near the base. The pattern forms spontaneously without the use of masks, and forms only in the region illuminated by the laser. Figure 1 shows scanning electron micrographs of the surface after 10, 25, 100, and 450 laser pulses with fluence 10 kJ/m². Areas up to 10 mm × 10 mm were microstructured by scanning the laser beam across the sample; the laser parameters and scan speed determine the height of the spikes.² On the sides of the spikes, nanoscale structures (10–100 nm across) are formed, as shown in Fig. 2(a); many of these surface nanostructures disappear after annealing in vacuum at 1200 K for 3 h, as shown in Fig. 2(b). The spikes themselves, however, are not significantly altered by annealing.

We measured total hemispherical (specular and diffuse) reflectance (R) and transmittance (T) to determine the absorptance ($A = 1 - R - T$) of the microstructured surfaces. Measurements were performed with a Hitachi U-4001 UV-VIS spectrophotometer equipped with an integrating sphere

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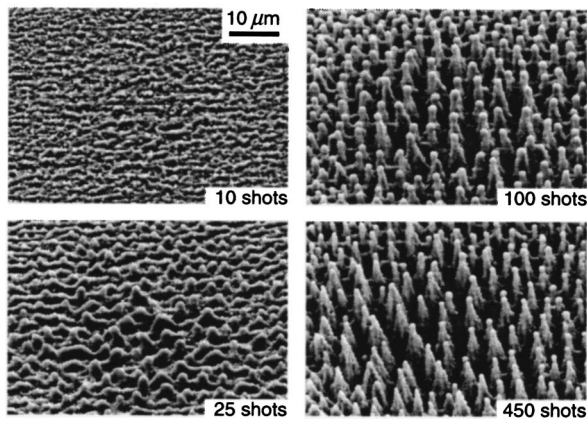


FIG. 1. Scanning electron micrographs of silicon spikes formed in SF₆ after 10, 25, 100, and 450 laser pulses (pulse duration: 100 fs; fluence: 10 kJ/m²). Spike height increases with increasing number of laser pulses.

detector. Figure 3 shows the absorbance for three microstructured surfaces of varying spike heights (1–2, 4–7, and 10–12 μm), for an annealed sample (spike height 10–12 μm), and for the substrate silicon prior to microstructuring [*n*-Si(111), 260 μm thick, with resistivity $\rho = 8\text{--}12 \Omega \text{ m}$].¹¹ Removing the native oxide layer by etching with HF does not affect the absorbance. Annealing was performed in vacuum for 3 h at 1200 K. The absorbance is 90% or more over the range 0.3–2.5 μm for the surface with 10–12 μm spikes, and decreases somewhat for surfaces with shorter spikes. The absorbance of the annealed sample is essentially unchanged above the band gap ($\lambda < 1.1 \mu\text{m}$), but decreases significantly below the band gap ($\lambda > 1.1 \mu\text{m}$).¹²

We observe significantly enhanced photocarrier production in microstructured silicon at infrared wavelengths near and below the band gap. We microstructured half of the light collection area of ordinary silicon APDs, leaving half unaltered. With no further processing of the devices, we measured the response (photocurrent) of both areas to illumination from the 1.064 μm line of a Nd:YAG pulsed laser and from a 1.310 μm diode laser (cw, chopped at 100 Hz). Figure 4 shows the response of the flat and the microstructured areas to 1.310 μm light (response at 1.064 μm is similar).

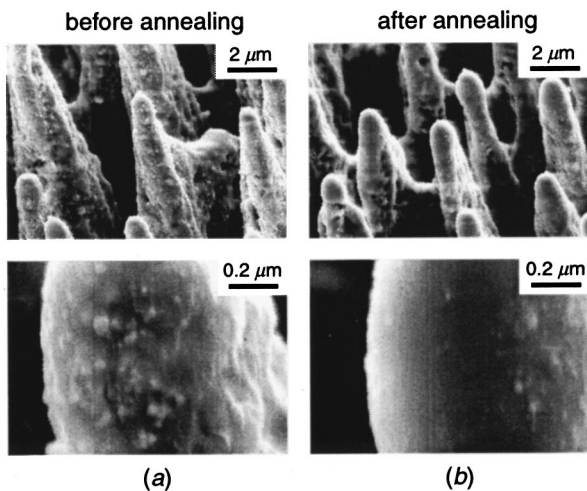


FIG. 2. Scanning electron micrograph of the sides of the spikes (a) before and (b) after annealing in vacuum at 1200 K for 3 h. Note that annealing eliminates many of the surface nanostructures.

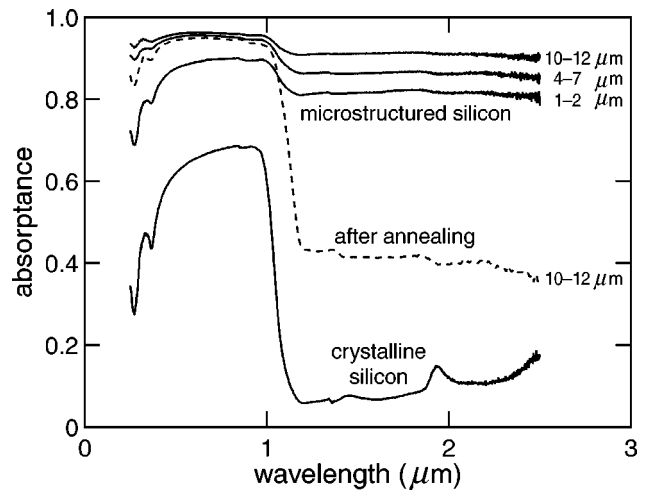


FIG. 3. Absorbance (*A*) of microstructured silicon surfaces and unstructured silicon substrate.

Illuminating the microstructured area generates a response at bias voltage 500 V and higher, whereas the unstructured area shows no measurable response for bias voltage less than 900 V. For a bias of 900 V or greater, at both 1.064 and 1.310 μm, photocarrier production from the microstructured area is at least three times that from the unstructured area. There is no detectable difference in noise from the two areas.

To identify a mechanism for the observed below-band-gap absorption and photocarrier production of microstructured silicon, we analyzed the chemical composition and the structure of the spikes. We performed secondary ion mass spectrometry (SIMS) to determine the chemical composition of our samples to a depth of approximately 1 μm. The results reveal an extremely high concentration of sulfur after microstructuring ($\sim 1 \text{ part in } 10^3$), and a substantially lower, but still significant, concentration of fluorine ($\sim 1 \text{ part in } 10^5$). Both the sulfur and fluorine content are highest just below the surface and decrease deeper into the sample. After annealing for 3 h at 1200 K, both concentrations decrease by roughly a factor of 2.

We examined the crystallinity of microstructured silicon with electron backscattering and ion channeling. The electron backscattering measurements show that the surface lay-

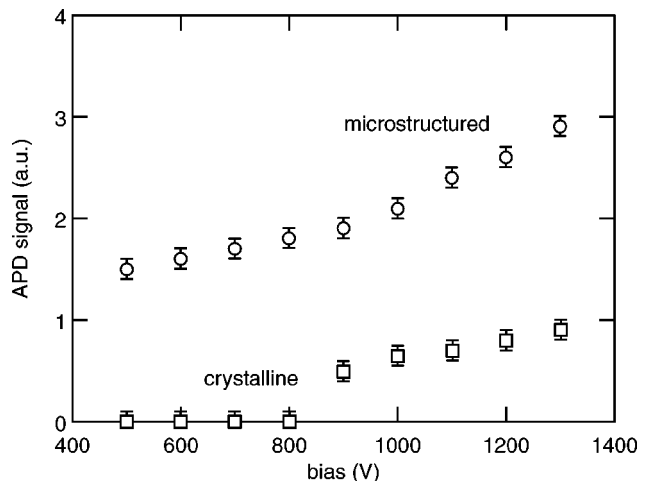


FIG. 4. Photocurrent from 1.310 μm excitation of microstructured and ordinary silicon detection areas of an avalanche photodiode (APD).

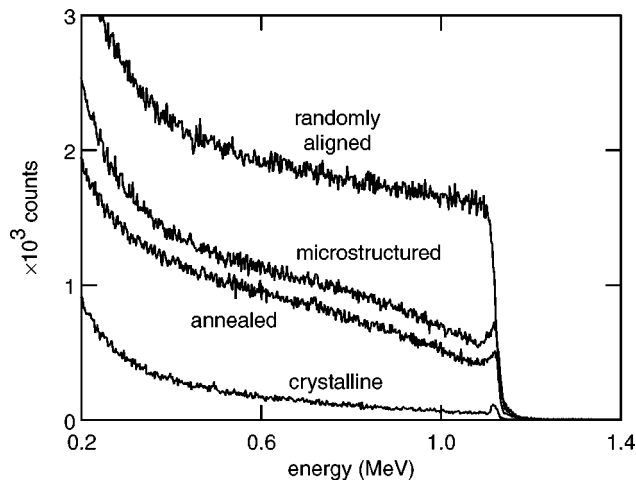


FIG. 5. Ion channeling spectra of the microstructured silicon surface with 10–12 μm spikes before and after annealing for 3 h at 1200 K in vacuum. For comparison, ion channeling spectra of a crystalline sample and of a randomly aligned sample (indicating maximum disorder) are also shown. Ion channeling spectra were measured with 2.0 MeV alpha particles backscattered into an annular solid-state detector.

ers have crystalline order, but do not exclude the possibility of a high density of defects. The ion channeling spectra (Fig. 5) show a background level higher than that of crystalline silicon but lower than that of a randomly aligned sample, which has a spectrum identical to that of amorphous silicon.¹³ These measurements indicate that the material is crystalline and is likely to have a high density of defects. The background remains high in ion channeling spectra from samples annealed for 3 h at 1200 K, indicating that a significant amount of disorder in the microstructured material is unaffected by annealing under these conditions.

The high infrared absorptance of microstructured silicon most likely comes from the incorporation of a high density of impurities and structural defects into the lattice in the microstructuring process. Sulfur impurities are likely to be particularly important; sulfur is known to introduce states into the band gap of silicon, both near the band edge and in the middle of the gap, and structural defects are known to introduce infrared-absorbing states near the band edge.^{14–17} The intrinsic absorptance caused by impurities and defects is enhanced by multiple reflections that reduce the reflectance significantly for the wavelength range shown in Fig. 3. The high, featureless infrared absorptance suggests that the extremely high concentration of sulfur impurities forms a band of infrared-absorbing states, since otherwise one would expect to see features in the infrared absorptance corresponding to sulfur impurity states. Bands of impurity states can form at concentrations as low as $10^{16}/\text{cm}^3$.¹⁸ Such bands would also explain the observed below-band-gap carrier generation; carrier generation via impurity levels, known as the impurity photovoltaic effect (IPV), has been previously demonstrated to improve the efficiency of silicon solar cells.^{19,20}

In conclusion, we have developed a microstructured form of silicon with roughly 90% light absorption at wavelengths from the near ultraviolet to the near infrared. Photocarriers are generated in this material by below-band-gap ra-

diation. We find that in the microstructuring process, a high concentration of impurities and structural defects are incorporated into the silicon lattice, most likely producing bands of impurity states in the band gap that can absorb infrared radiation. The resulting subgap absorption is enhanced by the surface texture. These remarkable properties may make possible silicon-based detectors for infrared radiation. In order to optimize microstructured silicon infrared detectors, we are investigating further the optoelectronic properties of this material and the dependence of these properties on surface morphology such as spike height and density.

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¹¹Our previous results (1, 2) indicate that microstructure formation is independent of the doping and the crystal plane of the substrate silicon.

¹²Another sample made and annealed under the same conditions shows an even greater drop in infrared absorptance than that shown in Fig. 3. Prior to annealing, we see a few percent variation in the infrared absorptance of samples made under the same conditions; we surmise that annealing enhances the underlying structural differences which produce these variations.

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