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# Visible and near-infrared responsivity of femtosecond-laser microstructured silicon photodiodes

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We investigated the current-voltage characteristics and responsivity of photodiodes fabricated with silicon that was microstructured using femtosecond-laser pulses in a sulfur-containing atmosphere. The photodiodes we fabricated have a broad spectral response ranging from the visible to the near-infrared (400–1600 nm). The responsivity depends on substrate doping, microstructuring fluence, and annealing temperature. We obtained room-temperature responsivities as high as 100 A/W at 1064 nm, two orders of magnitude higher than standard silicon photodiodes. For wavelengths below the band gap, we obtained responsivities as high as 50 mA/W at 1330 nm and 35 mA/W at 1550 nm.

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## BODY

Silicon is the most commonly used semiconductor in microelectronics and optoelectronic devices. Because the band gap of ordinary bulk silicon is 1.07 eV, the absorption and the photoresponse decrease precipitously for wavelengths longer than 1100 nm. Consequently, silicon photodetectors are insensitive to the two primary telecommunications wavelengths, 1330 nm and 1550 nm. To detect these wavelengths, other semiconductor materials, such as germanium or indium gallium arsenide, are typically used, but these materials are more expensive and difficult to integrate into silicon-based microelectronics. Extending the sensitivity of silicon-based and silicon-compatible photodetectors is therefore an active area of research [1-7].

We previously reported that silicon surfaces irradiated with high-intensity femtosecond [8, 9] or nanosecond [10] laser pulses in the presence of sulfur containing gases have near-unity absorption from the near-ultraviolet (250 nm) to the near-infrared (2500 nm), at photon energies well below the band gap of ordinary silicon. Here we report on the fabrication of a photodiode junction incorporating microstructured silicon. The resulting photodiodes are sensitive to infrared wavelengths up to 1600 nm and have greatly enhanced photoresponse to visible wavelengths over ordinary silicon photodiodes.

To fabricate a microstructured photodiode, we begin by irradiating *n*-doped, Si (111) wafers ( $\rho = 8\text{--}12 \ \Omega \text{ m}$ ) with a 1-kHz train of 100-fs laser pulses at normal incidence in a 0.67-bar atmosphere of SF<sub>6</sub>. In order to structure an area larger than the laser spot size, the silicon substrate is translated relative to the laser beam at a speed such that any given spot on the surface

is exposed to an average of 200 pulses. Figures 1a and 1b show electron micrographs of the silicon surface following irradiation at a fluence of  $4 \text{ kJ/m}^2$ . The resulting surface is covered with microstructures that are  $2\text{--}3 \text{ }\mu\text{m}$  tall and spaced by  $2\text{--}3 \text{ }\mu\text{m}$  (Figure 1a). The microstructure size, aspect ratio, and spacing increase with increasing laser fluence [11]. The microstructures are crystalline silicon covered with a few-hundred nanometer thick laser-altered surface layer (Figure 1b) [9]. Hall measurements of this surface layer show  $n$ -doping with a higher electron concentration than the substrate and an electron mobility on the order of  $100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ . The microstructuring thus creates an  $n/n^+$  heterojunction between the undisturbed substrate and the disordered surface layer. Following microstructuring, we thermally anneal the samples in vacuum for thirty minutes. Next we thermally evaporate Cr/Au ( $3 \text{ nm}/75 \text{ nm}$ ) contacts on either side of the heterojunction. Figure 1c shows a schematic diagram of a finished device; our devices have an active area of approximately  $5 \text{ mm}^2$ .

Figure 2 shows the current-voltage characteristics of samples annealed to various temperatures for 30 minutes. The rectification increases significantly with increasing annealing temperature. Hall measurements show that the free carrier concentration in the disordered layer increases with annealing temperature [12].

We measured the spectral responsivity of the devices at a  $-0.5 \text{ V}$  bias using light from a 300-W xenon arc lamp that is filtered through a monochromator with a spectral resolution of  $0.1 \text{ nm}$ . The monochromator is scanned in  $25\text{-nm}$  increments from  $400 \text{ nm}$  to  $1600 \text{ nm}$ , keeping the output power at each wavelength to  $1 \text{ }\mu\text{W}$ . A neutral-density filter wheel and commercial photodiodes are used to set the output power at each wavelength. A commercial silicon

photodiode is used for measurements between 400 and 1000 nm, and a commercial InGaAs photodiode is used for measurements between 1000 and 1600 nm. Contributions from second-order wavelengths for measurements beyond 1100 nm are eliminated by passing the light through an ordinary silicon wafer and a high-pass filter. All measurements are done at room temperature. Figure 3 shows the dependence of the spectral response on annealing temperature. The unannealed sample is very noisy; for this device the responsivity is only measurable between 600 nm and 1100 nm. The responsivity increases with annealing temperature up to 825 K and then decreases. At the optimum annealing temperature of 825 K, the responsivity increases with bias voltage; however, the leakage current also increases with bias voltage.

Figure 4 shows the dependence of the responsivity on the microstructuring fluence at a fixed annealing temperature of 825 K. The responsivity decreases, narrows, and shifts towards longer wavelengths with increasing laser fluence. At fluences below  $4 \text{ kJ/m}^2$  we do not observe uniform microstructuring of the surface. The optimum response is thus obtained at a microstructuring fluence of  $4 \text{ kJ/m}^2$  and an annealing temperature of 825 K. Under these conditions the peak responsivity reaches 120 A/W at 1000 nm, which is two orders of magnitude higher than the responsivity of commercial silicon PIN photodiodes and similar to that of avalanche photodiodes. In the near infrared, the responsivity is 50 mA/W at 1330 nm and 35 mA/W at 1550 nm; five orders of magnitude higher than the responsivity of non-microstructured silicon photodiodes [13].

At the processing conditions that produce optimum responsivity (namely, a microstructuring fluence of  $4 \text{ kJ/m}^2$  and an annealing temperature of 825 K) the leakage current

is  $1.2 \times 10^{-4}$  A/cm<sup>2</sup> at a bias of  $-0.5$  V. The capacitance of the optimized photodiodes is 64 nF/cm<sup>2</sup>. The signal rise time of the photodiode is 10 ns; the fall time is 30 ns. For the optimized devices, the number of electrons generated per photon is much greater than one, indicating gain in the device. We only observe this gain for devices made on *n*-doped substrates; for *p*-doped substrates we see no gain, regardless of annealing temperature. This observation, combined with the low electron mobility observed in the disordered surface layer, suggests that the gain is due to collisional ionization. Because the impact ionization rate for holes is nearly 1000 times less than that of electrons at these low electric field strengths [14], devices on *p*-doped substrates exhibit no gain.

We reported previously that irradiation with femtosecond laser pulses in an SF<sub>6</sub> environment results in a high concentration of sulfur (~1%) in the disordered surface layer [9,15]. Sulfur, with its two extra valence electrons, should increase the mobile electron concentration in the laser-altered surface layer, producing a difference in carrier concentration across the junction between the laser-altered surface and the undisturbed substrate. This difference in carrier concentration across the junction should in turn result in rectification. Without annealing, however, the *I-V* characteristics following laser irradiation are more representative of a resistor than a diode (see Figure 2), suggesting that the electrons from the laser-implanted sulfur are trapped in defects. Indeed, the resolidification front of a molten silicon layer travels sufficiently fast that it can trap impurity atoms in a nonequilibrium configuration [16].

Thermal annealing allows the lattice to relax toward a more stable configuration, reducing the number of defects at the junction and releasing the additional electrons from the sulfur atoms to contribute to the free carrier concentration. The increased carrier concentration difference across the junction and the reduced number of defects at the interface yield the improved rectification with increasing annealing temperature seen in Figure 2. However, as we reported previously, the below-band-gap absorptance decreases with annealing temperature [9, 10]. The responsivity of the laser-microstructured photodiodes, which depends on both the rectification and absorptance characteristics, is optimum for an annealing temperature of 825 K (see Figure 3). This annealing temperature improves rectification without eliminating the material characteristics that are responsible for below-band-gap absorption and gain. Apparently, annealing to 825 K for 30 minutes leaves the large concentration of sulfur atoms in a unique nonequilibrium configuration that leads to high gain and photoresponse in both the visible and near-infrared.

In summary, we fabricated high responsivity silicon-based photodiodes for the visible and near-infrared using femtosecond laser irradiation in a sulfur-containing environment. The diode characteristics and responsivity depend highly on processing conditions including laser fluence, substrate doping, and thermal annealing temperature. Optimized samples exhibit responsivities that are two orders of magnitude higher than commercial silicon photodiodes in the visible and five orders of magnitude higher in the near-infrared.

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## Figure Captions:

**Figure 1:** (a) Scanning electron micrograph of a silicon surface microstructured with 100-fs laser pulses at a fluence of  $4 \text{ kJ/m}^2$ . The micrograph is at a  $45^\circ$  angle to the surface. (b) Transmission electron micrograph of thin cross section of the sample in *a*. The uppermost few hundred nanometers of each microstructure is a highly disordered, nano-crystalline silicon layer. (c) Schematic diagram of a microstructured silicon photodiode. The disordered surface layer is approximately 300 nm thick and the substrate wafer is  $250 \text{ }\mu\text{m}$  thick.

**Figure 2:** Annealing temperature dependence of the current-voltage characteristics of silicon samples microstructured with 100-fs laser pulses at a fluence of  $4 \text{ kJ/m}^2$ . Rectification improves with increasing anneal temperature. Each sample was annealed for 30 minutes.

**Figure 3:** Annealing temperature dependence of the responsivity of microstructured silicon photodiodes. Each sample was microstructured with 100-fs laser pulses at a fluence of  $4 \text{ kJ/m}^2$  and annealed 30 minutes. The responsivity of a commercial silicon PIN photodiode is shown for reference.

**Figure 4:** Laser fluence dependence of the responsivity of microstructured silicon photodiodes. Each sample was annealed at 825 K for 30 minutes.

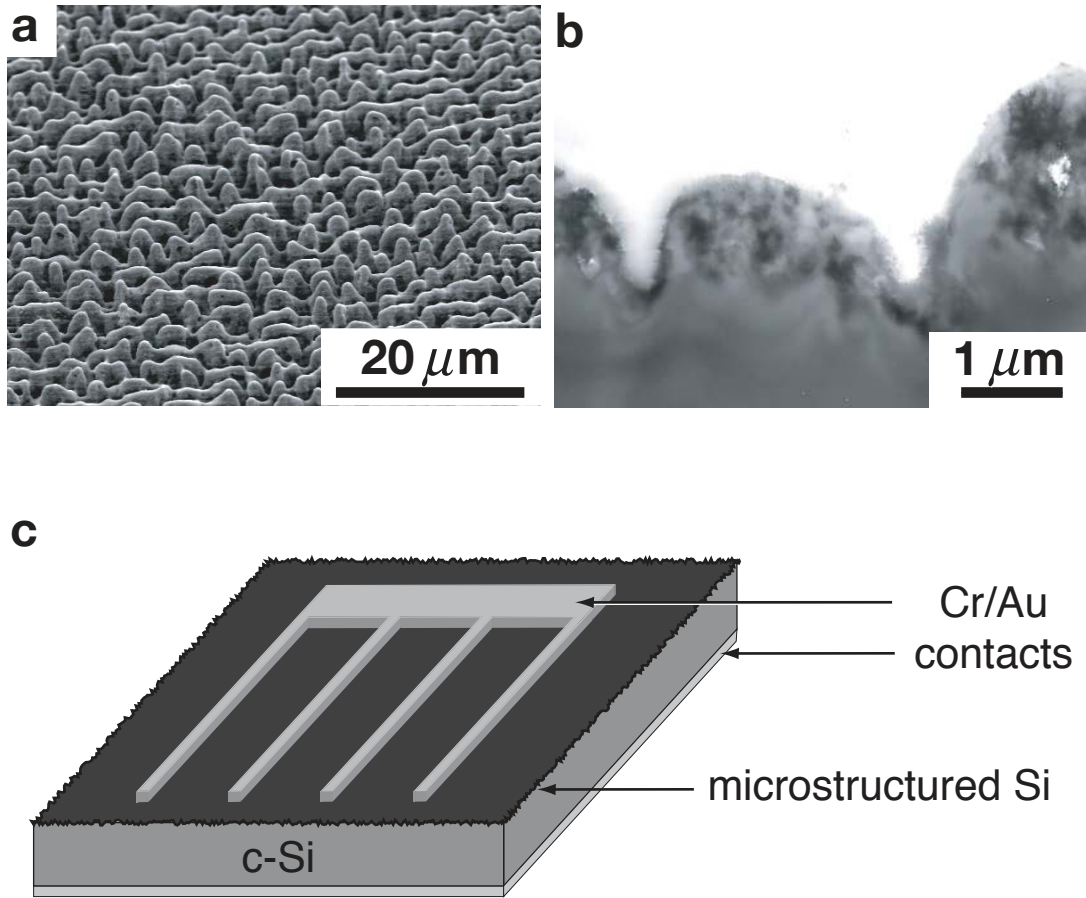


Figure 1 Carey, Crouch, Shen, and Mazur

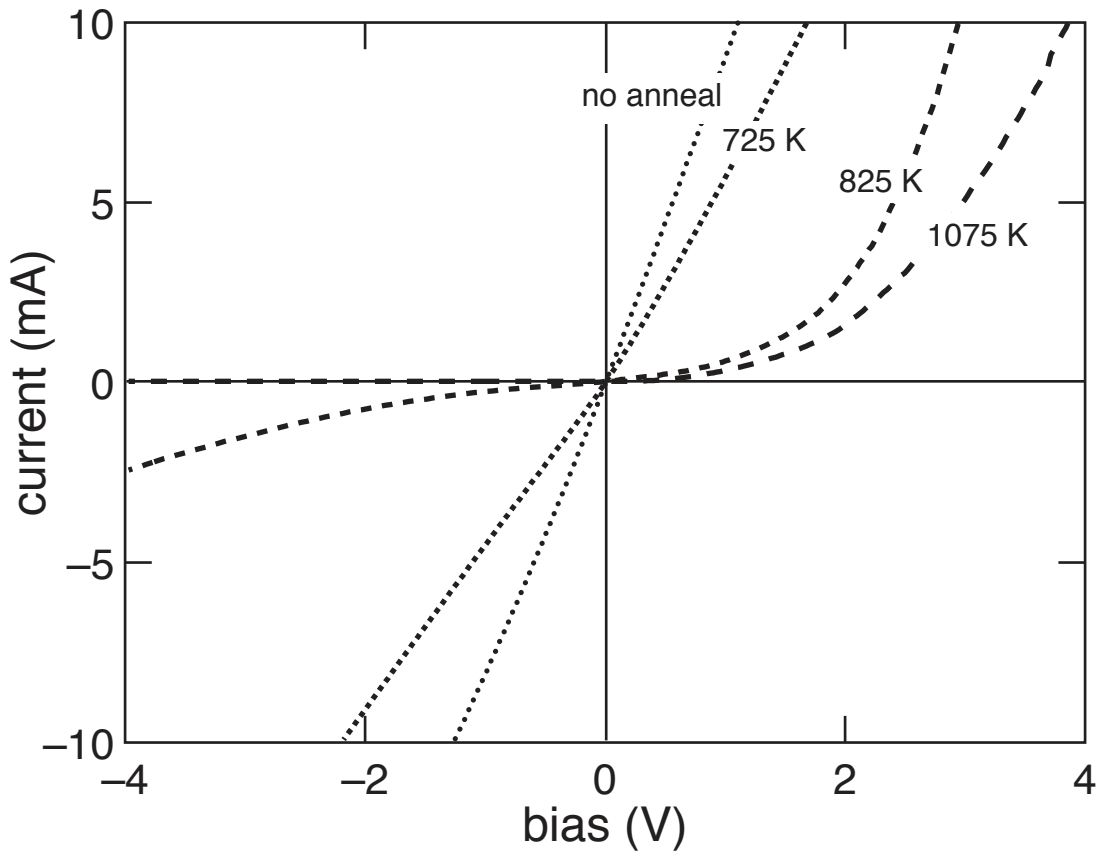


Figure 2 Carey, Crouch, Shen, and Mazur

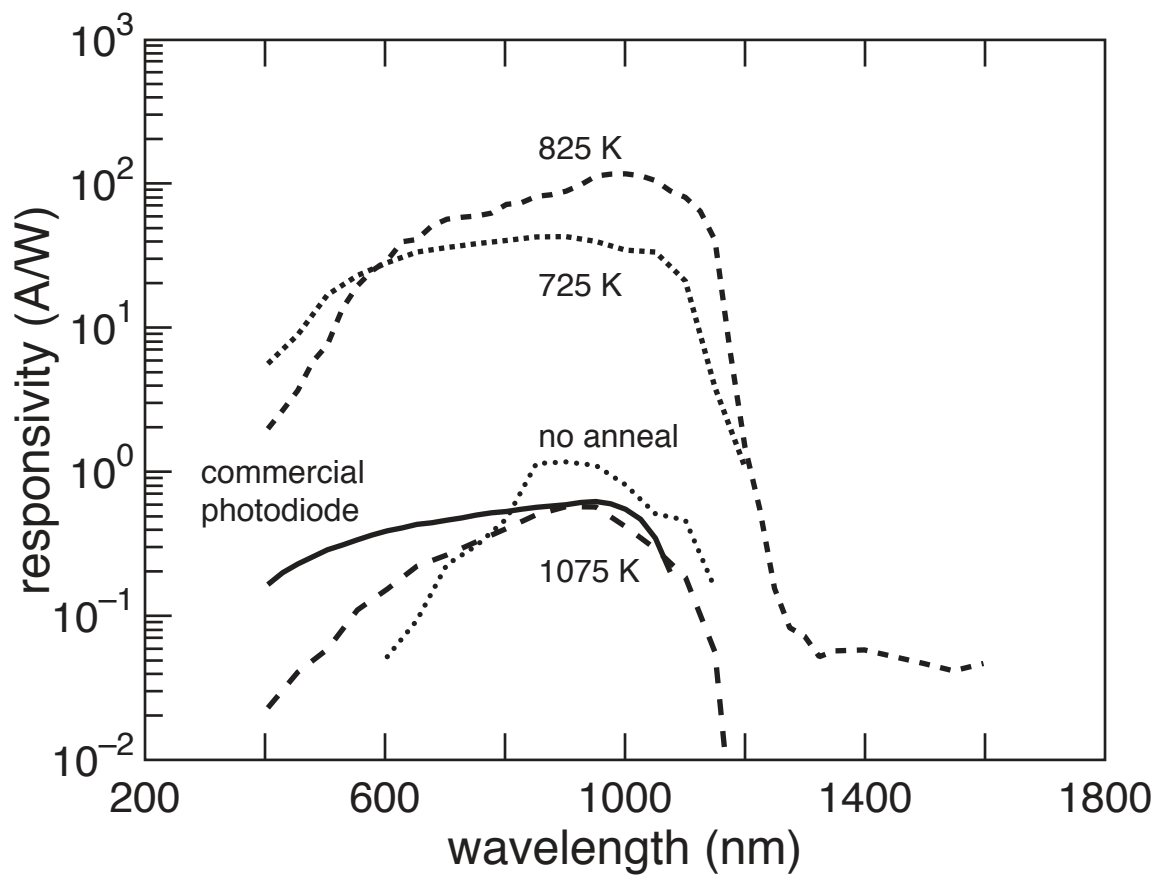


Figure 3 Carey, Crouch, Shen, and Mazur

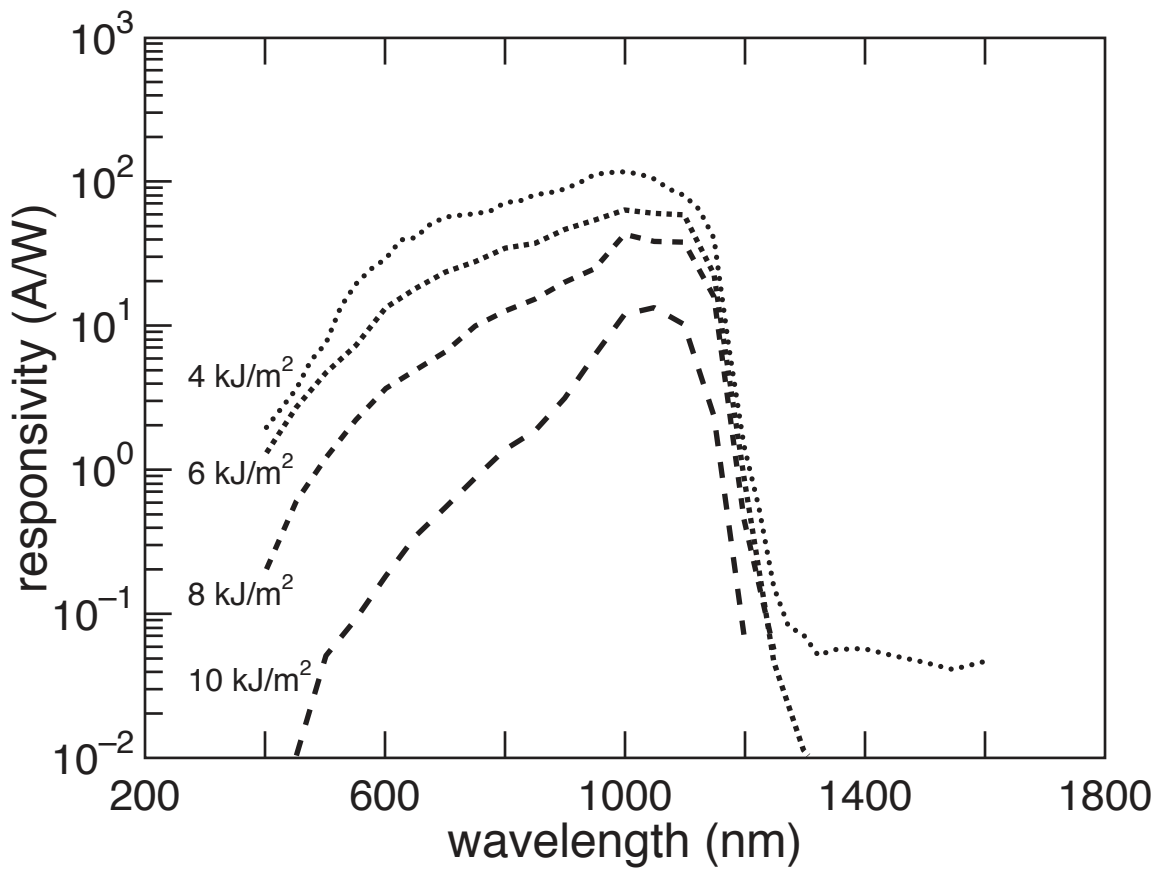


Figure 4 Carey, Crouch, Shen, and Mazur