

Infrared absorption by conical silicon microstructures made in a variety of background gases using femtosecond-laser pulses

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We show that the near-unity infrared absorptance of conical microstructures fabricated by irradiating a Si(111) surface with 100 fs laser pulses depends on the ambient gas in which the structures are formed. SF₆ produces an absorptance of 0.9 for radiation in the 1.2–2.5 μm wavelength range, higher than any of the other gases. Use of Cl₂, N₂, or air produces surfaces with absorptances intermediate between that for microstructures formed in SF₆ and that for flat crystalline silicon, for which the absorptance is roughly 0.05–0.2 for a 260 μm thick sample. Secondary ion mass spectrometry shows that elements from the ambient gas are incorporated into the silicon surface in high concentration. © 2003 American Institute of Physics. [DOI: 10.1063/1.1545159]

I. INTRODUCTION

We recently reported the formation of regular, sharply peaked, conical microstructures on the surface of silicon when it is irradiated with 100 fs laser pulses in the presence of halogen-containing gases.^{1–3} Similar structures are also created using longer-duration pulses and a variety of background gases.^{4–7} We observed the formation of microstructures upon irradiation with 100 fs laser pulses using nonhalogen-containing gases, such as N₂ or air, but these structures tend to be more blunt and irregular in shape. Such differences in the nature of the microstructures can be expected to alter the physical, chemical, and electronic properties of the surface.

These conical microstructures are interesting for a variety of reasons: They demonstrate a process for self-organized surface modification, and they suggest an interaction between ultrashort laser pulses and a semiconductor surface. They also absorb infrared light far more effectively than unpatterned silicon.³ Crystalline silicon has a band gap corresponding to light with a wavelength of approximately 1.1 μm, making it unsuitable for detectors or other optoelectronic devices requiring the absorption of infrared light with a wavelength longer than 1.1 μm and the generation of infrared photocurrent. The enhancement of infrared absorption in silicon represents a critical first step toward the design of infrared detectors, solar cells, or other infrared devices fabricated with silicon.

II. EXPERIMENT

In this article, we describe the optical properties of conical microstructures formed on the surface of *n*-type Si(111) (260 μm thick, resistivity $\rho = 8 - 12 \Omega \text{ m}$) in SF₆, Cl₂, N₂, and air upon irradiation with trains of 100 fs laser pulses

with a wavelength of 800 nm. The microstructures are 1–10 μm wide at the top, with a height in the range of 1–20 μm, depending on the pressure of the ambient gas and the laser fluence. In each experiment described here, the background pressure of the ambient gas is 500 Torr. The peak laser fluence is 11 mJ/mm² for a laser beam with a diameter of approximately 150 μm. In order to pattern areas larger than the beam size, the beam is rastered across the surface of the sample. The translation speed of the laser is 200–300 μm/s, and is adjusted to give structures of roughly the same height (10–15 μm) regardless of the ambient gas species used.

We measured the transmittance and reflectance of a patterned 10×10 mm² area using a spectrophotometer equipped with a spherical detector that integrates all transmitted or scattered light, depending on the placement of the sample. The reflectance (*R*) and transmittance (*T*) were then used to obtain the absorptance of the material: $A = 1 - R - T$.

In addition to the optical properties, we used secondary ion mass spectrometry to characterize the chemical species present at the surface of the structures formed in each of the four gases. Briefly, an energetic beam of ions is used to sputter secondary ions from a surface; the chemical composition of the sputtered material is then analyzed with mass spectrometry. To determine the chemical composition of each microstructured surface, the ratio of the mass spectrometry signal from a given chemical species to that of silicon is normalized using literature values for the relative sensitivity factor of each chemical species in a silicon matrix. The relative sensitivity factors are calculated with data taken from flat silicon surfaces, so the compositions reported are approximate due to the rough surface topology of the microstructured silicon.

III. RESULTS AND DISCUSSION

The morphology of the silicon microstructures depends on the gas in which they were formed (Fig. 1). Use of SF₆ or

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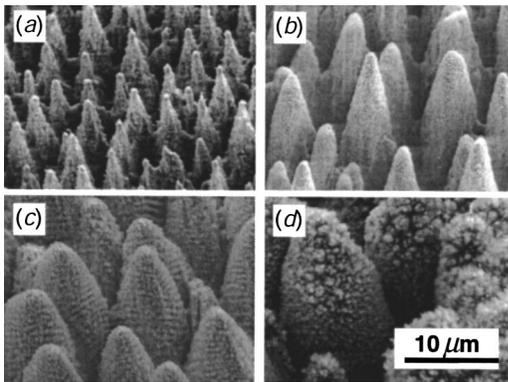


FIG. 1. Scanning electron micrograph of conical silicon microstructures formed in a background gas of (a) SF₆, (b) Cl₂, (c) N₂, and (d) air, upon irradiation with femtosecond laser pulses.

Cl₂ leads to conical structures with sharp tips with a radius of curvature of approximately 500 nm. In comparison to the Cl₂-prepared structures, the structures made in SF₆ have a greater degree of surface roughness, with a characteristic length scale of 100–200 nm for the dendritic formations on the cone surface. Structures made in air or N₂ are much more rounded than those made in the halogen-containing gases; their radius of curvature is approximately 2–3 μm. Additionally, the structures made in air show substantial surface roughness compared to the N₂-prepared structures; this roughness appears less dendritic than the formations on the SF₆-prepared cones. The number density of conical structures on the surface also depends on the ambient gas, with higher densities achieved using halogen-containing gases. Surfaces prepared with SF₆ yield the greatest number density, followed by Cl₂. The number densities obtained with N₂ and air are approximately half the density of the SF₆-prepared surfaces.

We observe a marked increase in the absorption of infrared light by patterned silicon surfaces compared to that of flat silicon. This is due to both a change in the reflectance of the surface and to a decrease in the transmittance through the patterned silicon sample. Figure 2 shows how the optical properties of the patterned silicon depend on the gas present during etching. The reflectance and transmittance change most dramatically for the structures formed in halogen-containing gases. For both SF₆- and Cl₂-prepared samples, the reflectance and transmittance are less than those for unpatterned silicon across the entire 1.2–2.5 μm wavelength range, with the reflectance and transmittance lowest for the surfaces prepared in SF₆. Samples made in air and N₂ show decreased transmittance relative to flat silicon as well as decreased reflectance in the short-wavelength region (λ < 1.5 μm for air and λ < 1.77 μm for N₂). Figure 3 shows the absorbance of the silicon samples, obtained from the reflection and transmission data, for structures made in the four gases. For all gases used, the drop in reflectance accounts for the increase in absorbance in the visible wavelength region. Although all samples show an increase in infrared absorption over ordinary crystalline silicon, the effect is strongest for structures formed in the presence of SF₆: The absorbance is approximately 0.9 in the wavelength region

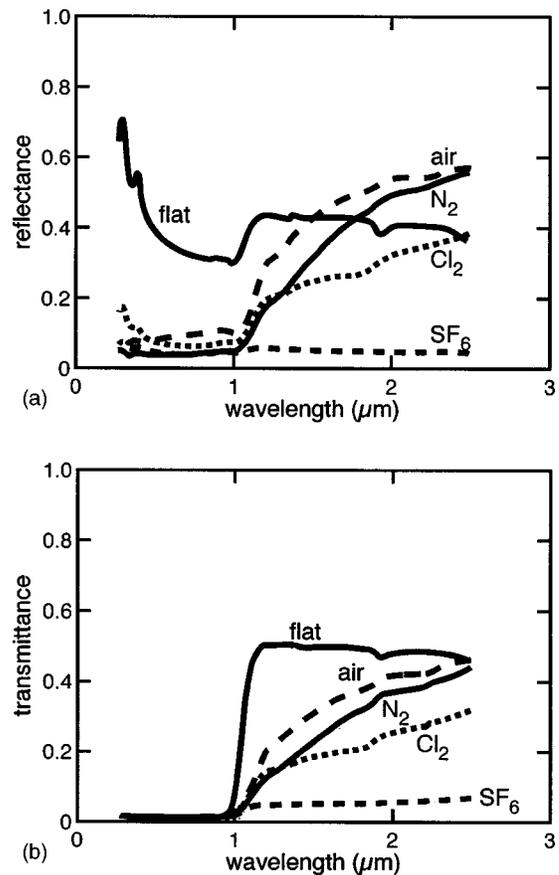


FIG. 2. Reflectance (a) and transmittance (b) of silicon samples patterned in various ambient gases (SF₆, Cl₂, N₂, and air) as a function of wavelength. Traces for flat Si(111) are included for reference. Surfaces structured in SF₆ differ most from the flat silicon.

1.2–2.5 μm. Structures made in Cl₂ show an absorbance of 0.3–0.9 in this wavelength region, while for unmodified silicon, the absorbance at these infrared wavelengths is less than 0.2. Surfaces structured in air or N₂ are less effective absorbers than those made in halogen-containing gases in the wavelength range λ > 0.5 μm for air and λ > 1.3 μm for N₂.

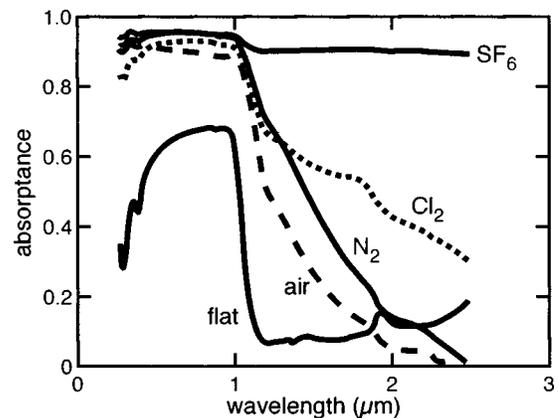


FIG. 3. Wavelength dependence of the optical absorbance of silicon surfaces for four different ambient gases present during the microstructure formation. The absorbance spectrum of an unmodified Si(111) surface is included for reference. Microstructured surfaces exhibit a marked increase in absorbance above the band edge of silicon (~1.1 μm).

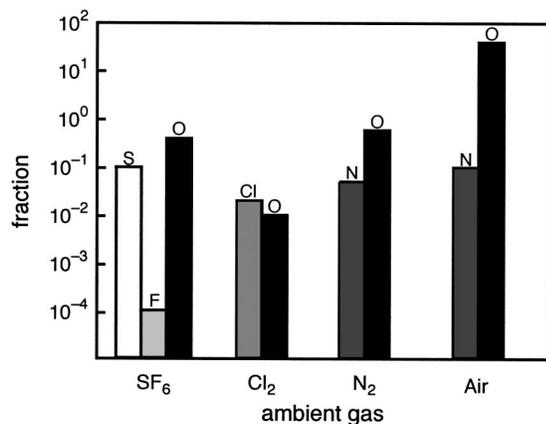


FIG. 4. Fractional concentrations of chemical species present in the surface of the microstructured silicon for each ambient gas (SF₆, Cl₂, N₂, and air). Oxygen is present in each sample due to a native oxide layer that grows after the structuring process. Each column is labeled at the top by the species it represents.

Furthermore, they show lower infrared absorptance than unmodified silicon for long wavelengths ($\lambda > 1.9 \mu\text{m}$ for air and $\lambda > 2.2 \mu\text{m}$ for N₂).

The differences in morphology of the structures made in various gases most likely stem from the relative reactivity of chemically reactive species created in those gases: It is well known that halogens create volatile compounds with silicon, whereas N₂ does not.⁸ Therefore, the microstructures formed in SF₆ and Cl₂ share the same conical shape and those made in air or N₂ are more blunt and rounded.

Because the microstructures made in SF₆ and Cl₂ are very similar in shape and size, we attribute the different infrared absorptance of these surfaces to the introduction of impurities during irradiation. Secondary ion mass spectrometry shows that the elements of the ambient gas are incorporated into the surface of the silicon; different elements are incorporated to varying degrees. Figure 4 shows the fractional concentration of chemical species in the microstructured silicon surfaces. All of the samples contain oxygen from the native oxide layer that grows on the surface after texturing, but the air sample contains two orders of magnitude more oxygen than the other samples. The high oxygen content and further analysis using Rutherford backscattering and transmission electron microscopy suggests that we have formed a silicon rich layer of silica, SiO_x ($x < 2$).⁹ The amount of oxygen in the SF₆, Cl₂, and N₂ samples is correlated with surface roughness.

The secondary ion mass spectrometry measurements show that irradiation under these intense laser conditions incorporates high concentrations of elements from the ambient gas and surface oxide layer. Many groups use longer-pulse and continuous wave lasers to incorporate elements into silicon but the concentrations previously reported are orders of magnitude smaller than the concentrations we obtain with this method.^{10–12}

After the sample is annealed in a vacuum, the sulfur signal in the secondary ion mass spectrometry measurement decreases by approximately a factor of 2 and fewer grains on the walls of the cones are present. At the same time, the

absorptance in the 1.2–2.5 μm range decreases by approximately a factor of 2.³ This result suggests that the sulfur impurities, whether in the cones themselves or in the rough features on the walls of the cones, play a role in the particularly high absorptance of the microstructures formed in SF₆.

The shape of the structures may also affect their absorptance. The conical microstructures made in the halogen-containing gases are sufficiently different from the round shapes of the structures formed in air or N₂ that their geometry can contribute to a higher absorptance. The surface topography may influence the absorptance through both the surface area of the patterned silicon, and the number of multiple reflections of light from the surfaces of the structures.

We recently demonstrated that the high absorptance of structures formed in SF₆ contributes to an increase of at least a factor of 3 in the production of photocurrent in the presence of infrared light ($\lambda = 1.064 \mu\text{m}$ and $\lambda = 1.310 \mu\text{m}$) as compared to the photocurrent produced by flat silicon.³ We are investigating the degree to which patterning in the presence of other gases leads to enhanced photocurrent of modified versus unmodified silicon surfaces.

In conclusion, we have demonstrated that the optical properties of silicon surfaces patterned with ultrashort laser pulses depend significantly on the background gas in which the surfaces are irradiated. Impurities introduced during irradiation are most likely the major contributor to the enhanced infrared absorptance. The shapes of the surface microstructures varies from cone-shaped for a halogen-containing background gas to rounded for air or N₂ and may contribute to the differences in absorptance. We are currently investigating how underlying defect structures depend on the background gas with cross-sectional transmission electron microscopy.

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