12-6-2004

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Recommended Citation

M. Y. Shen et al. (2004). "Femtosecond Laser-Induced Formation Of Submicrometer Spikes On Silicon In Water". *Applied Physics Letters*. Volume 85, Issue 23. 5694-5696. DOI: 10.1063/1.1828575
https://works.swarthmore.edu/fac-physics/205

AIP Applied Physics Letters

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Citation: Applied Physics Letters **85**, 5694 (2004); doi: 10.1063/1.1828575
View online: http://dx.doi.org/10.1063/1.1828575
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/85/23?ver=pdfcov
Published by the AIP Publishing

Femtosecond laser-induced formation of submicrometer spikes on silicon in water

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(Received 3 August 2004; accepted 2 September 2004)

We fabricate submicrometer silicon spikes by irradiating a silicon surface that is submerged in water with 400 nm, 100 fs laser pulses. These spikes are less than a micrometer tall and about 200 nm wide—one to two orders of magnitude smaller than the microspikes formed by laser irradiation of silicon in gases or vacuum. Scanning electron micrographs of the surface show that the formation of the spikes involves a combination of capillary waves on the molten silicon surface and laser-induced etching of silicon. Chemical analysis and scanning electron microscopy of the spikes show that they are composed of silicon with a 20-nm-thick surface oxide layer. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1828575]

A number of different techniques have been reported to form micrometer-sized structures on silicon surfaces using pulsed laser irradiation.[1–4] Previously we reported that quasi-ordered arrays of conical spikes form spontaneously on silicon under irradiation with high-fluence femtosecond laser pulses in the presence of SF_6.[2] The silicon spikes have many potential applications, such as electron emitters[5] and infrared photodetectors.[6] We found that capillary waves at the molten silicon surface play a role in the spike formation and that imposing boundary conditions on the capillary wave produces ordered arrays of spikes.[7,8]

Most previous studies of laser-induced spike formation on silicon were performed by irradiating samples in vacuum or in the presence of a gas. Here we report the results of femtosecond laser irradiation of silicon in water. When silicon is irradiated with femtosecond laser pulses of 400 nm wavelength, we observe the formation of submicrometer spikes at the silicon surface. For 800 nm pulses we do not observe the formation of spikes. Instead we observe a combination of roughening and hole formation. In contrast, in a gas, we observe virtually no difference in the structures that form at 400 and 800 nm.[9] In this letter we concentrate on the spike formation at 400 nm. We will report on the very different hole formation at 800 nm in a forthcoming letter.

We performed our experiments on Si(111) wafers that are cleaned with acetone and then rinsed in methanol. The wafer is placed in a glass container, which is mounted on a three-axis translation stage and filled with distilled water. The silicon surface is irradiated by a 1 kHz train of 100 fs, 60 μJ pulses at 400 nm wavelength from a frequency-doubled, amplified Ti:sapphire laser. A fast shutter is used to control the number of laser pulses incident on the silicon surface. The laser pulses are focused by a 0.25 m focal-length lens and travel through 10 mm of water before striking the surface at normal incidence. The focal point is about 10 mm behind the silicon surface and the spatial profile of the laser spot is nearly Gaussian, with a fixed beam waist of 50 μm at the sample surface. To correct for chirping of the laser pulse in the water and ensure minimum pulse duration at the silicon surface, we prechirp the pulse to obtain the lowest possible damage threshold at the silicon surface. The results presented here, however, do not depend strongly on the chirping of the laser pulse.

During sample irradiation, we monitor the sample surface with an optical imaging system with a spatial resolution of about 5 μm. The irradiation causes the formation of micrometer-sized water bubbles at the silicon–water interface. After a single pulse we observe two or three microbubbles; for irradiation with trains of laser pulses thousands of bubbles are generated. Sometimes the bubbles coalesce to form larger bubbles; some of these large bubbles adhere to the silicon surface and remain there until the cell is shaken vigorously.

Figure 1 shows electron micrographs of the silicon surface after irradiation with 1000 laser pulses. The shape of the spikes is more columnar than the conical spikes formed in the presence of SF_6. The spikes are typically 200 nm in diameter and 500 nm tall, and they protrude up to 100 nm above the original surface of the wafer [Fig. 1(c)].

We measured the x-ray photoelectron spectrum (XPS) to determine the chemical composition of the uppermost 10 nm of the spikes' surface layer. The XPS spectra show that this layer is composed of about 83% SiO_2 and 17% Si. To remove the oxide, we etched the sample in 5% HF for 15 min, which removes the 20-nm SiO_2 layer but leaves the underlying unoxidized Si intact. Electron micrographs of the spikes before [Fig. 2(a)] and after [Fig. 2(b)] etching show that etching reduces the width of the spikes by about 40 nm and renders their surface smoother. After etching, we detect no SiO_2 in the x-ray photoelectron spectra indicating that the interior of the spikes consists of silicon and that the spikes are covered by an oxide layer of at most 20 nm thickness.

To study the development of the spikes we irradiated samples with various numbers of laser pulses. Figure 3 shows a series of scanning electron micrographs of the surface of silicon irradiated with an increasing number of laser pulses. The pictures only show the central portion of the irradiated area. A single laser pulse forms surface structures resembling ripples on a liquid surface with a wavelength of

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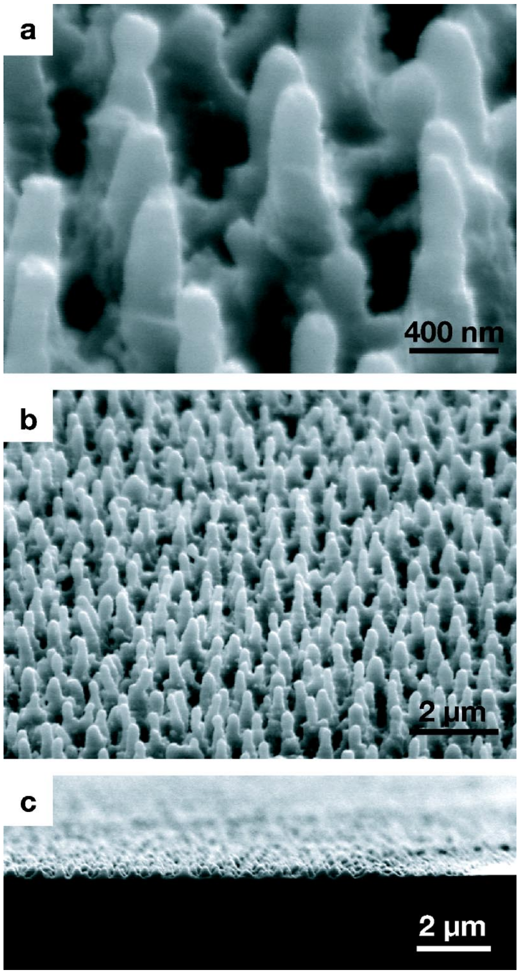

FIG. 1. Scanning electron micrographs of silicon spikes formed by irradiation with 100 fs, 400 nm, 60 µJ laser pulses on a silicon surface in distilled water [(a,b)] viewed at 45° to the surface normal, and (c) viewed from the side.

about 500 nm. Lower magnification micrographs (not shown here) show that the irradiated region typically contains two or three of these ripple-like structures. We believe each ripple structure corresponds to one of the two or three microbubbles we observe after irradiation. After two pulses, the surface shows overlapping ripple structures. As the number of laser pulses is increased from 5 to 20, the silicon surface roughens from the interaction of many ripple structures. After 50 laser pulses, the surface is covered with submicrometer bead-like structures, which then evolve into spikes as the number of pulses is further increased. The average separation of the resulting spikes is roughly 500 nm and equal to the wavelength of the initial ripple structures.

The silicon spikes prepared in water described in this letter are one to two orders of magnitude smaller than spikes induced by lasers in gases.[1–9] This remarkable size difference suggests different formation mechanisms for the two types of spikes. When the 400 nm laser pulse interacts with the silicon surface, most of the light is absorbed by a silicon layer tens of nanometers thick near the silicon–water interface. The absorption of intense light in such a thin silicon layer excites a plasma at the silicon–water interface; the plasma then equilibrates with the surrounding water and silicon, leaving behind a molten silicon layer on the surface, which solidifies before the next laser pulse arrives. Due to the high temperature of the plasma, some of the water vaporizes or

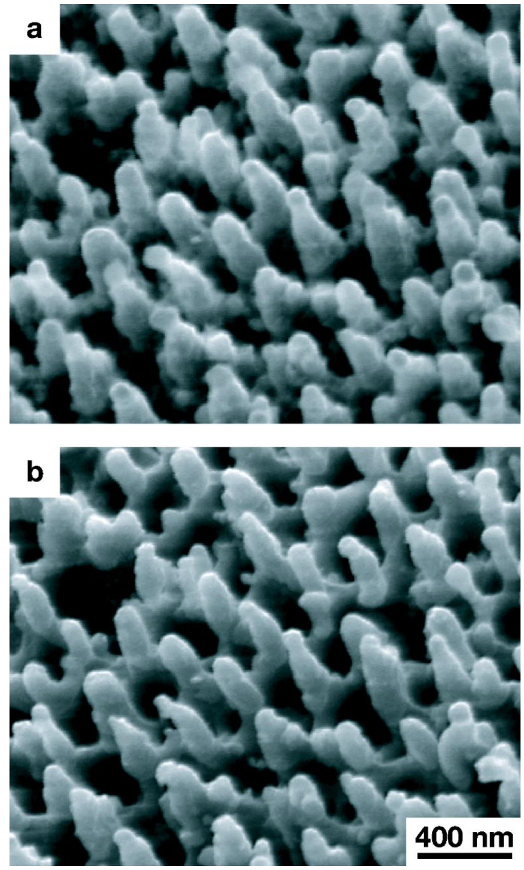

FIG. 2. Scanning electron micrographs of silicon spikes formed in distilled water (a) before and (b) after HF etching.

dissociates,[10] generating bubbles at the silicon–water interface. Because the large bubbles we observe after irradiation can remain in the water for days, they must consist primarily of gaseous hydrogen and oxygen rather than water vapor.

There are several possible mechanisms by which the bubbles may produce the wave-like structures shown in Fig. 3. Diffraction of the laser beam by the bubbles may produce rings of light intensity on the silicon surface, or the heat of

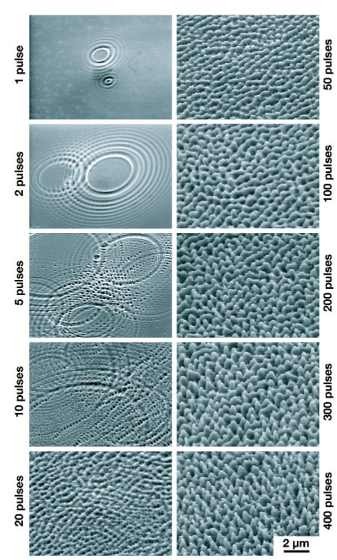

FIG. 3. Scanning electron micrographs of a silicon surface irradiated in distilled water by an increasing number of laser pulses. The width of the irradiated area is approximately 50 µm.

vaporization and dissociation required to form a bubble at the silicon–water interface may cool the silicon surface locally, exciting a capillary wave in the molten silicon through Marangoni flow.[11] The latter is the most likely formation mechanism for the structures observed after a single pulse; those structures cannot be formed by diffraction from a laser-induced bubble, as the pulse duration is only 100 fs, and the observed wave-like structures can be several micrometers in diameter. A micrometer-sized bubble requires much longer than 100 fs to form[12,13] and therefore cannot diffract the first pulse.

Roughness on the silicon surface causes the laser pulse energy to be absorbed unevenly across the surface;[14] the resulting nonuniform temperature of the surface produces a random arrangement of bubbles. Silicon–water has a contact angle of 45°, making a gaseous layer between the silicon and water unstable and leading to the formation of bubbles. The vaporization and dissociation remove thermal energy from the molten silicon surface just below the bubble causing it to cool rapidly. Because the surface tension of liquid silicon decreases with increasing temperature,[15] the surrounding hot liquid silicon flows toward the cooled region, deforming the surface.[11] This deformation can then excite a circular capillary wave at the liquid-silicon surface. Superposition of ripple structures caused by multiple laser pulses produces the randomly distributed submicrometer beads that appear after 20 laser pulses in Fig. 3. These beads subsequently sharpen into spikes through preferential removal of material around the beads by laser-assisted etching.[1,16]

The early stages of submicrometer spike formation in water is different from that in gaseous SF_6, while the later stages are very similar.[7–9] In SF_6, straight submicrometer-sized ripple structures first form on the silicon surface, then coarser, micrometer-scale ridges form on top of (and perpendicular to) the ripples. Next, the coarsened layer breaks up into micrometer-sized beads, and finally the beads evolve into spikes through etching. In both SF_6 and water, the length scale of the final structures is set by the arrangement of bead-like structures that form after roughly 10–20 pulses, and this length scale appears to be determined by capillary waves in the molten silicon.[4,8] The much smaller size of the spikes formed in water must therefore be due to a difference in capillary wavelength in the two cases.

The molten silicon layer should solidify much faster in water than in SF_6, as the thermal conductivity and heat capacity of liquid water are much greater than those of gaseous SF_6. The dispersion relation for capillary waves in a shallow layer of molten silicon[8] indicates that decreasing the lifetime of the liquid layer should also decrease the longest allowed capillary wavelength. Using a simple model[17] that neglects the effects of ablation and cooling by heat transfer to the environment to calculate the lifetime and depth of the liquid layer, we find that the longest allowed capillary wavelength is about 1 μm. Because the lifetime is certainly reduced by the flow of heat to the surrounding water in the experiments presented here, the longest allowed wavelength should be less than 1 μm, in agreement with submicrometer spike separation observed here.

In summary, we find that irradiating a silicon surface with 100 fs, 400 nm laser pulses in water produces submicrometer-sized spikes; the spikes consist of silicon covered with a 20-nm-thick layer of silicon oxide. Scanning electron micrographs of the silicon surface after irradiation with increasing number of laser pulses suggest that capillary waves generated by bubble formation on the molten silicon surface and laser-induced etching of the resulting structures give rise to the observed spike formation.

This work was supported by the Harvard NSEC program (NSF-PHY 0117795) and the Department of Energy (DOE DE FC36 01GO11053). We thank Professor Howard Stone for helpful discussions and Yuan Lu for assistance with the XPS measurements.

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