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High-Density Regular Arrays of Nanometer-Scale Rods Formed on Silicon Surfaces via Femtosecond Laser Irradiation in Water

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ABSTRACT

We report on the formation of high-density regular arrays of nanometer-scale rods using femtosecond laser irradiation of a silicon surface immersed in water. The resulting surface exhibits both micrometer-scale and nanometer-scale structures. The micrometer-scale structure consists of spikes of 5−10 μm width, which are entirely covered by nanometer-scale rods that are roughly 50 nm wide and normal to the surface of the micrometer-scale spikes. The formation of the nanometer-scale rods involves several processes: refraction of laser light in highly excited silicon, interference of scattered and refracted light, rapid cooling in water, roughness-enhanced optical absorptance, and capillary instabilities.

As semiconductor processing reaches smaller and smaller feature sizes, much research is dedicated to the development of new methods for producing regular, nanometer-scale structures on solid surfaces. Lithography and chemical etching are powerful methods that offer control over the shape and size of structures, but they are often complex and costly.[1–3] In contrast, pulsed laser-assisted etching[4,5] is a simple but effective method for fabricating small structures directly onto a substrate. However, most of the cross sections of such structures are typically larger than the laser wavelength.[4–14]

A variety of micrometer-scale structures have been observed on substrates of different materials after pulsed laser irradiation.[6–14] Upon irradiation with laser pulses at a fluence close to the melting threshold, the surfaces of the substrates develop ripples with a spacing equal to or larger than the laser wavelength.[6–10,14] By irradiating silicon surfaces with femtosecond laser pulses above the ablation threshold in the presence of a variety of background gases, we previously reported the formation of quasi-periodic sharp conical micrometer-sized spikes.[11] Others have also reported laser-induced formation of much larger conical microstructures using high-intensity nanosecond pulses.[6,12,13] By irradiating silicon surfaces with 400 nm femtosecond laser pulses in water, we created submicrometer-sized silicon spikes with diameters down to 200 nm and a spacing of about 500 nm.[15] Here, we use 800 nm femtosecond laser irradiation below the ablation threshold to produce high-density arrays of nanometer-scale rods with diameters as small as 50 nm and a spacing of less than 50 nm. These nanometer-scale rods cover the entire surface of the underlying micrometer-scale structure and are always approximately normal to it, regardless of the original surface morphology or the angle of incidence of the laser.

We place a single crystalline silicon substrate in a glass container filled with water, which is mounted on a three-axis translation stage. The sample is irradiated by a 1 kHz train of 100 fs, 800 nm laser pulses from an amplified Ti:sapphire laser, with pulse energies up to 400 μJ. The laser pulses are focused by a 0.25 m focal length lens and travel through approximately 10 mm of water before striking the surface at normal incidence.[15] The focal point is approximately 10 mm behind the substrate surface, and the spatial profile of the laser spot is nearly Gaussian. The spatial profile of the laser is analyzed with a CCD. The laser spot size on the substrate is about 100 μm. The sample is translated in a direction perpendicular to the laser beam at a speed 500 μm/s, which results in an average irradation of 200 laser pulses at a laser repetition rate of 1 kHz. When irradiating just a single spot, we use a mechanical shutter to control the laser pulse number. The structures formed within a single laser spot are uniform and similar to the structures we observe when scanning the laser. In this paper, we only

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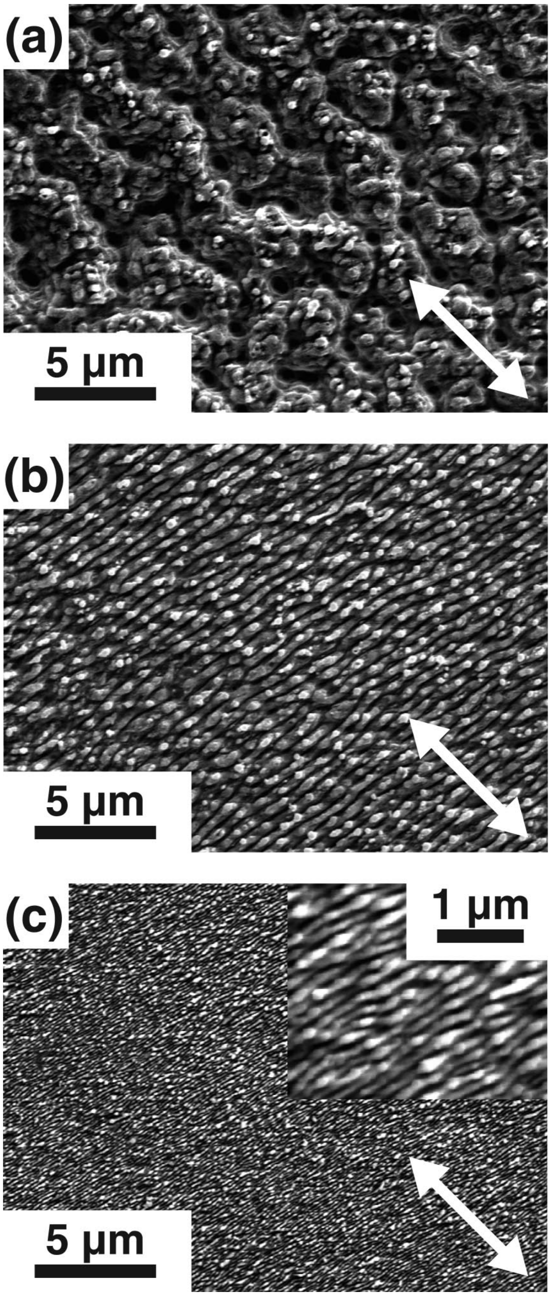

Figure 1. SEM picture of silicon surfaces after irradiation in water with an average of 200 800 nm laser pulses of 100 fs duration at fluences of (a) 25 kJ/m^2, (b) 5 kJ/m^2, and (c) 3 kJ/m^2. The inset in (c) shows the ripple pattern at higher magnification. The arrow indicates the direction of the laser polarization.

show results obtained when scanning the laser because the scanning allows us to make larger samples of arbitrary shapes.

Figure 1 shows scanning electron microscope (SEM) images of structures formed on silicon substrates in water at three different laser fluences using an average irradiation of 200 laser pulses per area. In the high fluence regime (>10 kJ/m^2), micrometer-scale structures and submicrometer holes form (Figure 1a). At medium fluences (4−10 kJ/m^2), straight ripples form with spacing equal to the laser wavelength (Figure 1b).[16] The long axis of the ripples is perpendicular to the laser polarization. At low fluences (2−4 kJ/m^2), straight ripples form with a spacing of about 120 nm (Figure 1c). The long axis of the ripples is perpendicular to the laser polarization.[17] At fluences below about 2 kJ/m^2, no structure is observed on the silicon surface.

If the ripples shown in Figure 1c are irradiated a second time in water at a fluence of 0.5 kJ/m^2 by an average of 200 800 nm laser pulses per area, with the polarization rotated by 90° so that it becomes parallel with the long axis of the ripples, the ripples break up into the nanometer-scale structure shown in Figure 2. This two-step irradiation results in a surface that is uniformly covered with nanometer-scale rods, which are about 50 nm in diameter and up to 400 nm tall.[18]

The inset of Figure 2a shows a Fourier transform of Figure 2a: the two bright dots in the Fourier image reflect the regularity of the nanorods forming along the straight nanoripples. The diffuse ellipse behind the two dots has its long axis parallel to the straight nanoripples, indicating that the separation between two nanorods along the straight ripple direction is random and smaller than that perpendicular to the direction of the ripples. In contrast, Fourier analysis of previously reported microspikes[6–14] and submicrospikes[15] formed by femtosecond laser irradiation shows only a diffuse circular background, indicating that the micro- and submicrospikes are much less regular than the nanorods presented here.

We observe formation of nanorods at second-irradiation fluences as low as 0.2 kJ/m^2, which is about a factor of 10 below the damage threshold of silicion and well below the 4 kJ/m^2 used for the formation of silicon nanostructures reported in the literature.[15,19] A similar two-step irradiation method is used in ref 19, but the size of the resulting structures and the mechanism of their formation are very different from those in the present work. In ref 19, the size of the structures is on the order of the laser wavelength or about 10 times larger than the nanorods reported in this work.

To better understand the mechanism of the nanostructure formation, we examined the effect of substrate surface roughness on nanometer-scale rod formation. In order to induce surface roughness, we started by irradiating a flat silicon substrate to form micrometer-sized spikes.[11] We then exposed the microstructured surface to the two-step procedure for creating the nanometer-scale rods in Figure 2. Figure 3 shows an SEM image of the resulting surface after these three irradiations. Silicon nanometer-scale rods cover the entire microstructured surface, protruding normal to the surface regardless of the original surface morphology.

Figure 1 shows that the basic surface morphology formed after irradiation with 800 nm femtosecond laser pulses in water exhibits three distinct morphologies: micrometer-scale structures and submicrometer holes at high fluence (Figure 1a), straight ripples with a spacing equal to the laser wavelength at medium fluence (Figure 1b), and straight nanometer-scale ripples with a spacing of about 120 nm at low fluence (Figure 1c). These distinct morphologies can be attributed to different types of laser interaction with the silicon/water system: ultrafast melting and resolidification at low fluence,[20] ultrafast melting and ablation at medium

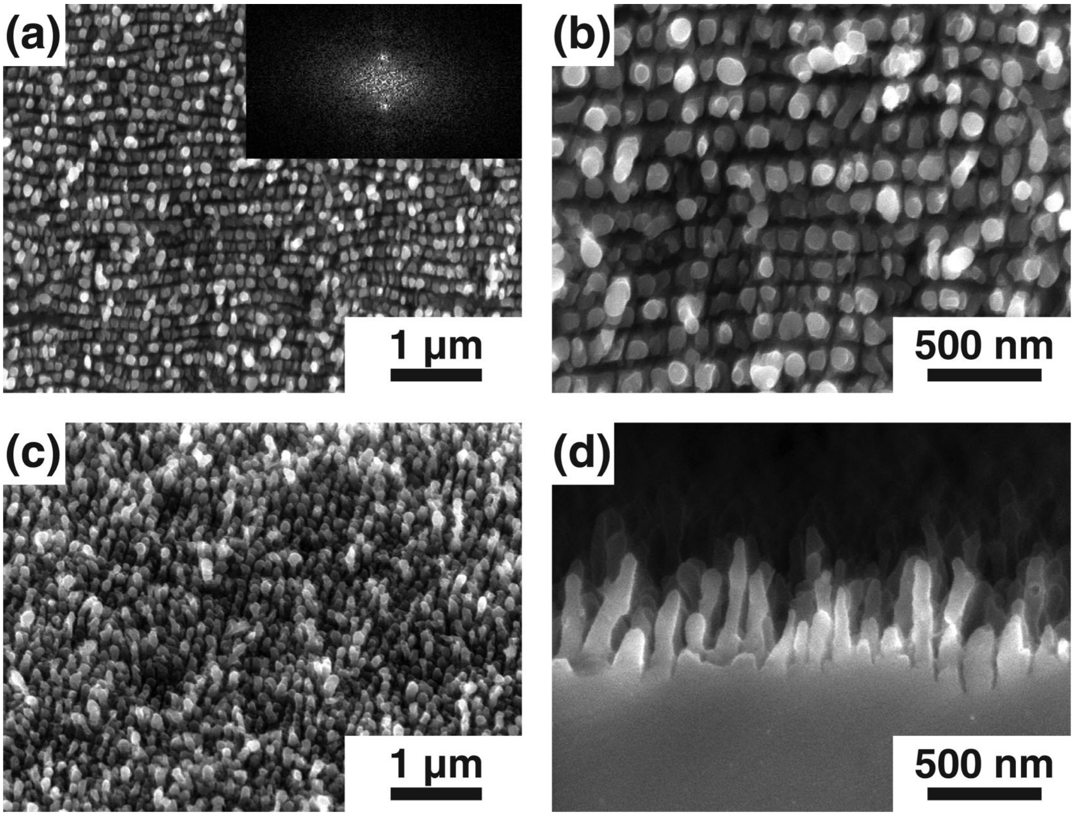

Figure 2. SEM picture of nanometer-scale rods formed using a two-step irradiation process of a silicon surface: the nanoripples of Figure 1c are irradiated a second time in water at a fluence of 0.5 kJ/m^2 by an average of 200 800 nm laser pulses, with the polarization rotated by 90°. (a,b) Top view, (c) 45° view, and (d) cross-sectional side view of the nanometer-scale rods. The inset of (a) shows a Fourier transform of the image in (a).

fluence,[21] and ultrafast melting, ablation, and bubble cavitation at high fluence.[22–24]

In the medium fluence regime, straight ripples form approximately normal to the light polarization, with a spacing equal to the laser wavelength (Figure 1b).[16] Such structures are the most commonly observed periodic structures on pulsed-laser-irradiated surfaces and have been studied thoroughly.[6–10] The structures have been attributed to interference between light that is scattered at a roughened surface and light that is refracted at the surface; the light interferes just below the surface and is absorbed in a nonuniform periodic ripple pattern.[8] For an optically thick molten layer, the periodic absorption pattern excites surface waves in the molten layer and the ripples are "frozen" into the surface upon solidification. The long axis of the periodic ripple pattern is perpendicular to the laser polarization and has a spacing approximately equal to the laser wavelength at normal incidence.[7–10]

Irradiation at low fluence (2−4 kJ/m^2) is below the ablation threshold of silicon in water, but it is still intense enough to cause ultrafast melting.[20] In this regime, we find that the spacing of the ripples is reduced to around 120 nm, significantly smaller than the wavelength. Several groups have recently observed the formation of nanometer-scale ripples, but an explanation of their formation is still lacking.[25,26] During the irradiation of silicon with a femtosecond pulse in the low-fluence regime, the front portion of the laser pulse excites a large number of electrons that increase the index of refraction in a thin surface layer of silicon.[27] Within this high-index layer, the effective wavelength of refracted and scattered light is reduced, and the periodicity of the interference pattern is likewise reduced. Approximately one picosecond after the laser pulse strikes the surface, ultrafast melting produces a liquid layer whose evolution is dictated by surface−wave driven growth dynamics.[10,14] The periodic absorption excites nanometer-scale surface waves in the liquid layer, and upon resolidification, nanometer-scale ripples are "frozen" into the surface. In the medium and high fluence regimes, the irradiation is above the ablation threshold. Consequently, the thin layer of high-index silicon is ablated away and no nanometer-scale ripples are observed.

The surface morphology after laser irradiation is due to an interplay between surface wave dynamics and the lifetime of the molten layer.[10,14] Taking into account that the melt depth is large compared to 120 nm, the lifetime τ of a capillary wave is proportional to the square of its wavelength λ, $\tau = \lambda^2/8\pi^2\nu$, where ν is the kinematic viscosity of the liquid. Taking ν to be 2×10^{-7} m^2/s, we obtain a lifetime of approximately 1 ns for a capillary wave with a wavelength of 120 nm.[10,28] For surfaces irradiated in a gas, the lifetime of the melt is longer than 30 ns,[14] much longer than the lifetime of a surface wave with a wavelength of 120 nm. By the time the surface resolidifies, any nanometer-scale surface waves have died out and been replaced by surface waves with longer wavelengths and longer lifetimes.[10] The thermal conductivity of water, however, is over 1 order of magnitude

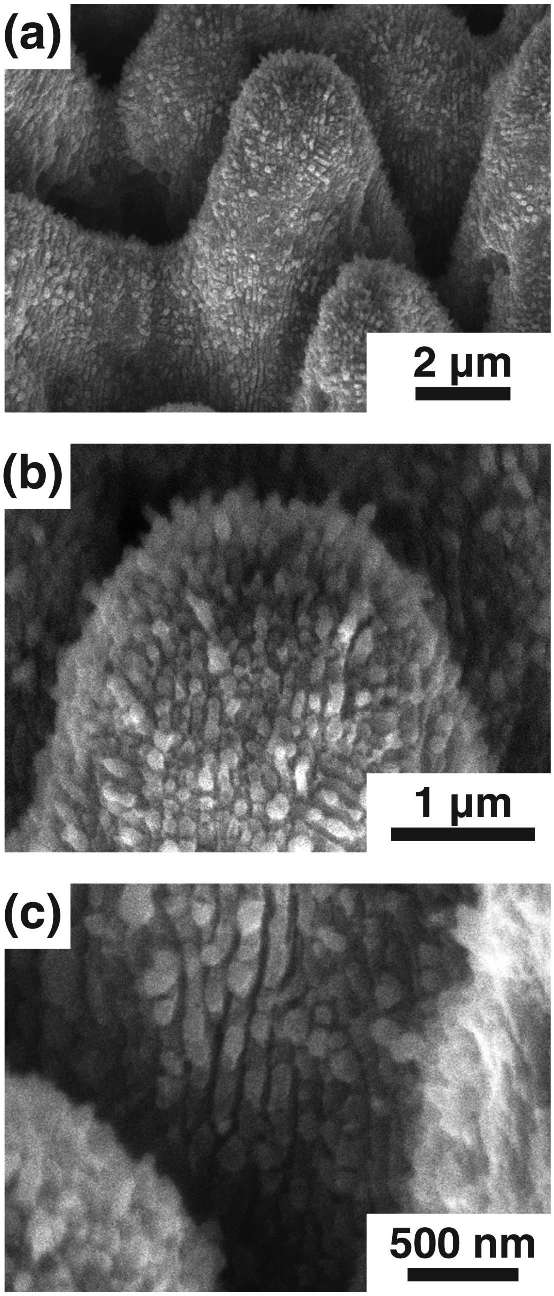

Figure 3. SEM picture of nanometer-scale rods formed on a microstructured silicon surface using a three-step irradiation process. (a) Low-magnification image showing micrometer-scale spikes covered with nanometer-scale rods; high-magnification images showing nanometer-scale rods (b) at the top of and (c) in the space between the micrometer-scale spikes.

higher than that of a typical gas, and water vaporizes and dissociates on the substrate surface.[15] The larger thermal conductivity of the water and the vaporization and dissociation of water result in a large heat transfer out of the molten layer, and so the lifetime of the molten layer in water is less than 1 ns.[29] The presence of water and the associated increase in the cooling rate of the molten layer allow for the nanometer-scale ripple patterns to be frozen into the surface before they die away.

During the second irradiation step nanometer-scale rods form along the straight nanometer-scale ripples, as shown in Figure 2. Although the second irradiation is at much lower fluence than the first one, the laser pulses melt the nanometer-scale ripples, because the absorptance of a rippled surface is higher than that of a smooth surface.[30] Once they are molten, the ripples tend to break up into beads because a molten half-cylinder is unstable.[31,32] As in the formation of the ripples, the scale of beads is set by the interference between incident and scattered laser light below the surface, which produces a periodic absorption pattern along the long axis of the ripples[7–10] and excites a surface wave along the length of the ripples. Once the ripples break up into beads, subsequent laser irradiation sharpens the beads into rods through preferential removal of material around the beads by laser-assisted ablation.[14,15,33,34]

Further evidence of the role of a high-index, molten silicon layer in the formation of nanometer-scale ripples and rods is provided in Figure 3: the nanometer-scale rods cover the entire surface of each micrometer-scale spike and are always normal to the surface of the spikes. The high-index layer at the surface of each micrometer-scale spike strongly refracts the laser light and the refracted laser light becomes nearly perpendicular to every part of the solid silicon surface, which creates a temperature gradient approximately perpendicular to the surface. Consequently, the nanometer-scale rods are always approximately normal to the sample surface.

Femtosecond laser irradiation of silicon surfaces immersed in water gives rise to the formation of high-density regular arrays of nanometer-scale rods that are much smaller than the laser wavelength. The formation of regular arrays of nanometer-scale rods involves an interplay between refraction of laser light in a thin molten layer of silicon, interference of scattered and refracted light in this layer, a high cooling rate in water, roughness enhanced optical absorptance, and surface instabilities. The roughness enhanced optical absorptance[30] and the surface instabilities[31] play the most important role in the formation of the final nanorods. Sequential irradiation of silicon makes it possible to form complex structures with both micrometer-scale and nanometer-scale features. The method presented in this paper can also be applied to other materials such as titanium and stainless steel.

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(16) The wavelength of laser light in water is shortened from 800 to 600 nm because of the index of refraction of water.

(17) The ripples observed in Figure 1b,c are very different from the ripple structures formed by irradiating substrates in a gas.[7] The ripple spacing is largely unaffected by the type of immersion liquid (water, oil, or alcohol).

(18) The same two-step laser structuring process can be used to fabricate similar nanometer-scale rods on stainless steel and titanium immersed in a liquid.

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