MRS BULLETIN

Serving the International Materials Research Community

A Publication of the Materials Research Society

August 2006, Volume 31, No. 8

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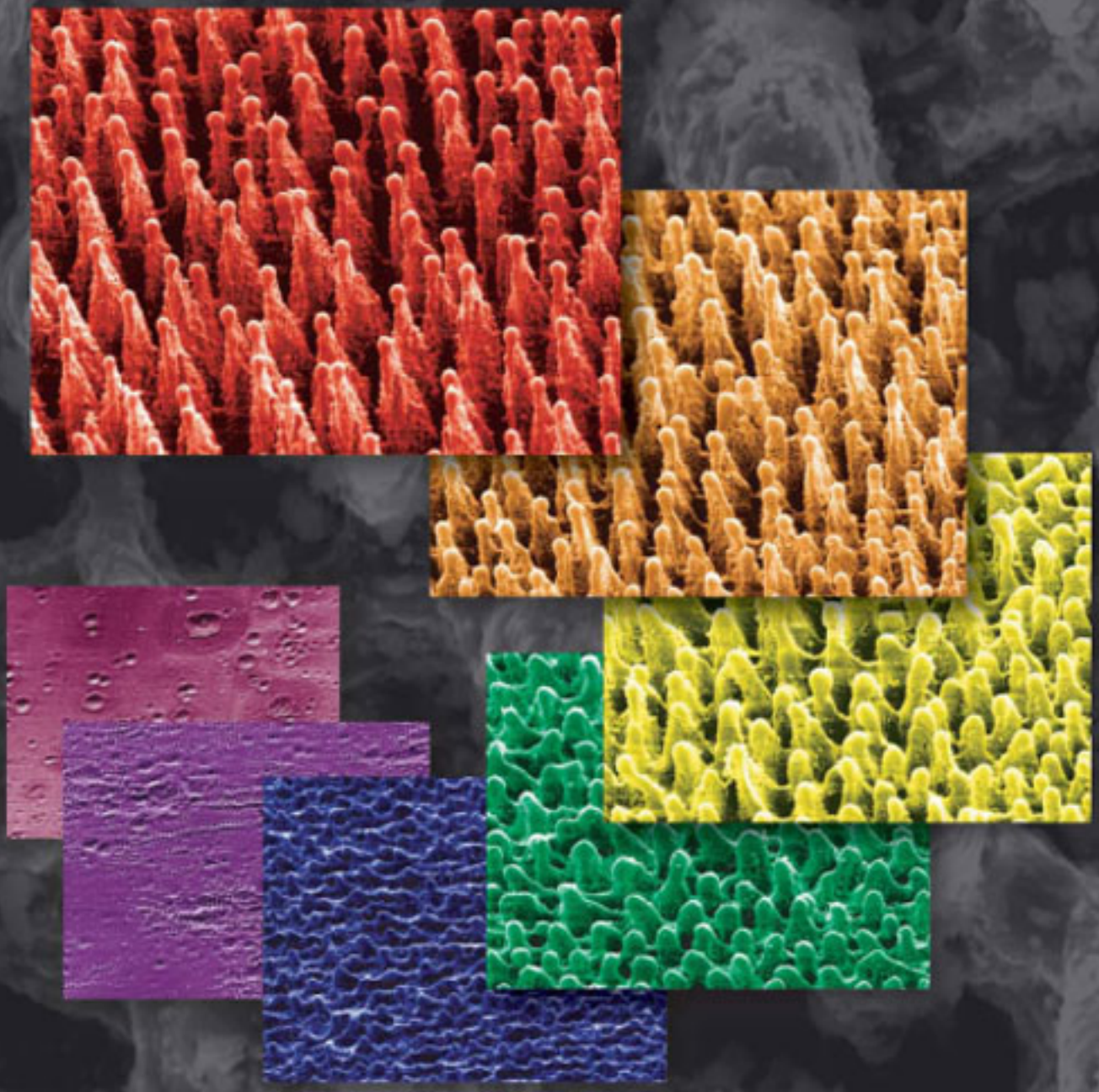

Ultrafast Lasers in Materials Research

David G. Cahill and Steve M. Yalisove,
Guest Editors

Abstract

With the availability of off-the-shelf commercial ultrafast lasers, a small revolution in materials research is underway, as it is now possible to use these tools without being an expert in the development of the tools themselves. Lasers with short-duration optical pulses—in the sub-picosecond (less than one-trillionth of a second) range—are finding a variety of applications, from basic research on fast processes in materials to new methods for microfabrication by direct writing. A huge range of pulse energies are being used in these applications, from less than 1 nJ (a billionth of a joule) to many joules.

Keywords: *laser, ablation.*

Introduction

Ultrafast lasers—that is, lasers that produce optical pulses with a duration of less than a picosecond—are playing an increasingly important role in many science and technology disciplines. Ultrafast, time-resolved measurements are well established in physical chemistry, where fundamental time scales of chemical reactions become accessible,[1] and in solid-state physics and electrical engineering, where carrier dynamics and transport are probed on picosecond time scales directly relevant to the operation of modern high-speed devices.

Applications in materials research have been slower to emerge, because only within the past decade have commercial instruments reached a level of reliability and sophistication that make them practical tools for scientists and engineers who may not be experts in laser technology and the manipulation of short-duration, high-intensity optical pulses. The rapid development of ultrafast laser technology is a principal motivation for this issue of *MRS Bulletin*: the time is ripe for ultrafast lasers to take on a rapidly expanding role in studies of the science of materials and in materials characterization, materials modification, and microfabrication. Ten years ago, very little materials research was conducted using high-intensity, ultrafast lasers. With the commercial availability of off-the-shelf ultrafast tools, a small revolution in materials research is underway.

Ultrafast optical pulses of <1 ps duration are generated by mode-locked laser oscillators. The phases of the longitudinal optical modes of the laser cavity are locked together by either an active element (e.g., an acousto-optic modulator) or by passive effects such as Kerr-lensing in the gain medium or the use of a saturable absorber. Mode-locking produces short-duration optical pulses with a high repetition rate determined by the length of the optical cavity. The wide bandwidth of optical gain in sapphire doped by Ti enables extremely short-duration pulses.

Ti:sapphire lasers dominate the market, but Ti:sapphire laser oscillators are, of course, actually a set of three lasers. Continuous-wave (cw) diode lasers pump a cw solid-state laser, which is frequency-doubled and used to pump the Ti:sapphire oscillator. Ultrafast laser oscillators and amplifiers that can be directly pumped by diode lasers, such as Er:glass-fiber lasers and Yb:tungstate lasers, are becoming more common and may lead to more compact and less expensive instruments, but they have a more limited range of output wavelengths and a longer pulse duration than Ti:sapphire.

The typical repetition rate of a laser oscillator is 80 MHz. Therefore, a laser oscillator with an average power of 1 W produces optical pulses with an energy of approximately 10 nJ. This pulse energy is sufficient for metrology using picosecond acoustics, for experiments that probe heat transfer or carrier dynamics, and for many forms of optical spectroscopy; it is not generally sufficient for materials modification, except with pulses that are tightly focused by high-numerical-aperture microscope objectives. Higher-energy pulses are available from so-called "extended-cavity oscillators" that operate with a lower repetition rate, on the order of 10 MHz, but this technology is currently limited to <100 nJ in commercial Ti:sapphire lasers and <1 μJ in Yb:tungstate lasers.

Optical pulses from laser oscillators must therefore be amplified to reach energies of >1 μJ. The ability to amplify ultrafast lasers was an elusive goal for 20 years following the development of the ultrafast oscillator in the mid-1960s. In 1985, high-intensity ultrafast lasers emerged with the development of the chirped-pulse amplifier.[2] In a chirped-pulse amplifier, pairs of diffraction gratings are used to temporally stretch the optical pulse prior to amplification and then temporally compress the pulse after it leaves the amplifier. Twenty years later, Ti:sapphire chirped-pulse amplifiers that produce 1–2 mJ optical pulses at 1 kHz repetition rates are available from a number of commercial suppliers. Higher-repetition-rate (>100 kHz) lasers with microjoule energy pulses are desirable for many applications in materials removal and modification. These types of lasers are becoming more common. The relative simplicity of amplifiers that are directly pumped by diode lasers is driving the development of systems based on Er:glass and Yb:tungstate. A remarkable feature of the articles in this issue of *MRS Bulletin* is the huge range of pulse energies that are used in the research: from <1 nJ optical pulses applied in metrology to the 1 J energies used for a relativistic optics phenomenon called *plasma wakefield acceleration of electrons* that may one day replace synchrotrons as bright sources of x-rays[5,6] and γ-rays.[7]

How Fast Is Ultrafast?

A simple illustration of the time scale represented by a femtosecond (one-quadrillionth of a second) is the fact that light travels around the Earth about seven times in a second, but only about 300 nm in a femtosecond (see Figure 1).

The answer to the question "How fast is ultrafast?" in materials research more accurately depends on the characteristic time scale of the application or the science being studied. For example, for the generation of high-frequency longitudinal acoustic waves in metal films, an important time scale is the optical absorption

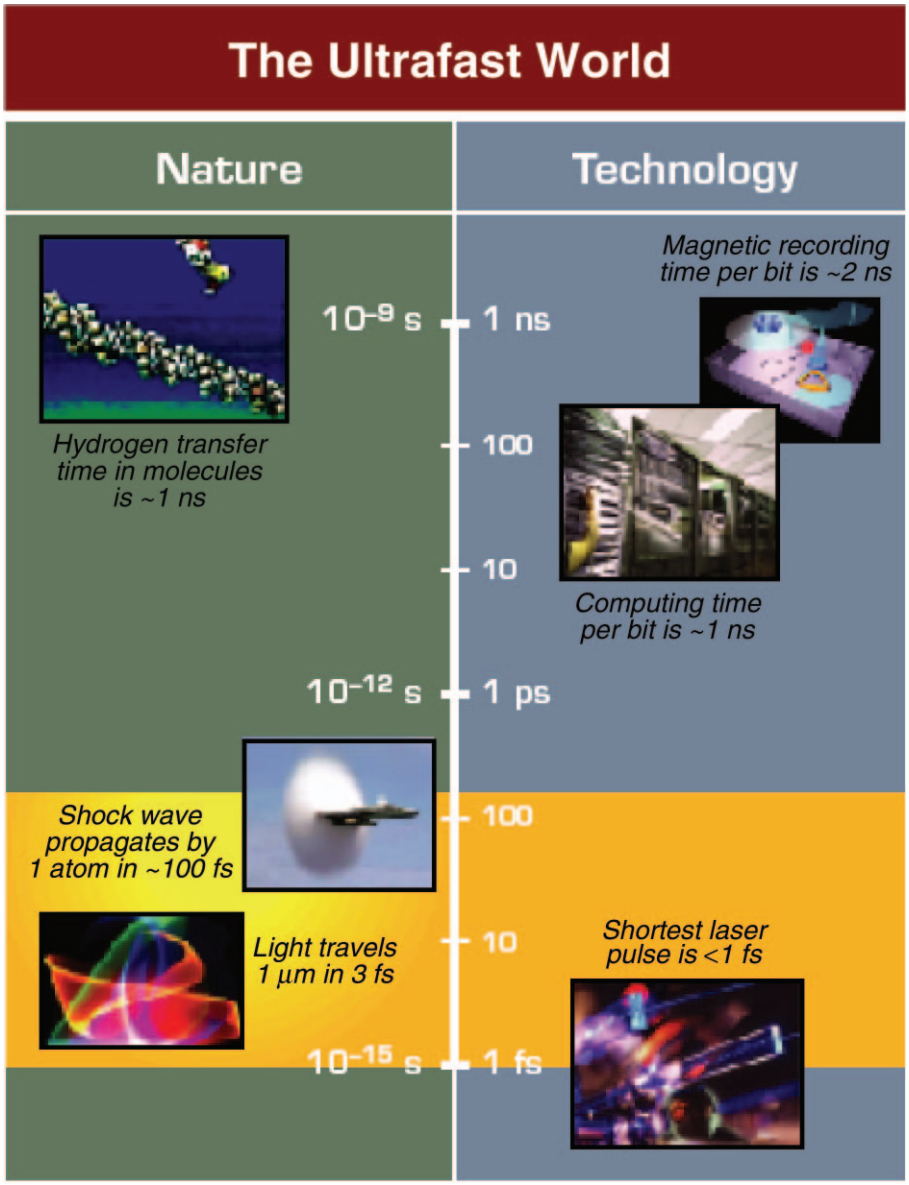

Figure 1. Illustration of ultrafast processes in nature and technology. A femtosecond, the duration of the shortest ultrafast laser pulse, is an extremely short period of time; light can travel around the Earth about seven times in a second, but only about 300 nm in a femtosecond. Adapted from Reference 8.

depth divided by the speed of sound, typically 1–5 ps. Thus, optical pulses with duration of <1 ps are usually sufficient for observing the sharpest possible acoustic signals.

Each of the articles in this issue of *MRS Bulletin* will answer the question differently, and in many cases the answer is complicated by the existence of multiple processes, some of which are not well characterized.

It is often stated that the ultrafast regime is reached when the pulse duration is less than the time scale of electron–phonon coupling. This statement has truth to it but sometimes oversimplifies reality. The laser pulse directly excites the electronic degrees of freedom in a material, and it takes time for the energy absorbed by the electrons to be transferred to the lattice. The complete description of this process is complex, even for the relatively simple case of a laser pulse incident on the surface of a metal. Energetic electrons transfer energy to other electronic excitations and to the motions of the atoms (i.e., the phonons), and despite the popularity of so-called "two-temperature" models that assume the electrons and phonons are independently in thermal equilibrium at two different temperatures, the time scales for these processes are not always well separated.[3] Furthermore, ballistic transport and rapid diffusion of hot electrons can distribute energy in a metal over much longer length scales than the optical absorption depth. Because many scattering events are needed to transfer energy from the highly excited electron system to the motions of the atoms, the time scale for the heating of the lattice can be much greater than 1 ps, depending on the material under study and the density of the energy deposited in the material.

The first article in this issue describes in detail the mechanisms and characteristic time scales of near-threshold laser ablation in metals and semiconductors. Reis and co-authors summarize the x-ray diffraction results obtained last year at the Stanford Linear Accelerator Center. This experiment *tour de force*—the publication in *Science*[4] has 51 authors associated with 18 institutions—represents a diffraction study of ultrafast melting with the fastest time resolution to date. During the initial 200–400-fs period following the laser pulse, a significant fraction (10–15%) of the valence electrons are excited to higher electronic states; this strong excitation greatly reduces the attractive part of the interatomic potential and allows the atoms to freely drift with their room-temperature thermal velocities until the electrons relax, 400–600 fs later. Atoms can drift as much as half of the unit-cell dimension, even though the center of mass, collectively, is still in the original position, without thermal expansion. Yet, once the electrons relax (600 fs to 1 ps), the system evolves in the same way as it would if the lattice of atoms was heated instantaneously by the laser pulse. Large-scale molecular dynamics (MD) and associated hydrodynamics simulations that are described later in the first article bear this out as well.

The articles that follow Reis et al. expand on these ideas and discuss specific applications of ultrafast lasers in the characterization and fabrication of materials.

Antonelli et al. describe how the rapid heating of the near surface of metal films by nanojoule ultrafast optical pulses can be used to generate strain and temperature fields for measurements of the mechanical and thermal properties of thin films and interfaces. Conversely, if the mechanical properties are known, the geometry of thin-film structures can be derived from the spectra of acoustic echoes and oscillations. This approach, termed *picosecond acoustics*, is widely used in the

microelectronics industry for measuring the thicknesses of metal interconnects and interlayer dielectrics.

King et al. describe their efforts to develop an ultrafast imaging tool to observe the time-dependence of phase transformations and shock-driven mechanical processes related to the interaction of ultrafast light and materials. This article discusses progress on two distinct types of instruments, an ultrafast transmission electron microscope and a laser-produced, relativistic electron beam with MeV energies that is subsequently used as a source of high brightness x-rays and γ-rays.

Itoh et al. illustrate how bulk dielectrics can be modified with ultrafast lasers to produce waveguides, Bragg reflectors, optical devices, and microfluidic channels by direct-writing in three dimensions. Again, a thermal mechanism is identified as the root cause of these materials modification processes. In all cases, the extremely sharp thermal gradients produced by ultrafast laser pulses permit such structures to be created—something that would not be possible for laser pulses of longer than 10 ps.

Tull et al. describe the morphological changes that an ultrafast laser can produce at surfaces and interfaces. They describe the use of high-intensity ultrafast light to produce "black silicon" by taking advantage of laser-induced periodic structures and accelerating the process by machining in a halogen gas environment. This morphological variant of Si strongly adsorbs light in the IR, something flat Si does not do. The authors also describe another morphological modification of a Si–SiO_2 interface. Here, the ultrafast light is absorbed at the Si surface and the softened glass is blown into a bubble by the spallation of a thin layer of ejected molten Si, again a thermal mechanism. These bubbles have highly reproducible heights and can be accurately joined to form tubes capable of transporting fluid.

Finally, Haight et al. describe the use of ultrafast lasers to repair lithographic masks at the 20–200-nm scale. This is, to the best of our knowledge, the first application of ultrafast lasers for nanoscale fabrication in a manufacturing facility. Here, the deterministic threshold is exploited to either photo-dissociate precursor molecules to deposit a thin line or ablate unwanted material below the diffraction limit.

These articles describe but a few of the exciting materials research topics that are actively being studied today with ultrafast lasers. Unfortunately, the number of topics in materials research that we could not include because of space constraints is very large: the much more mature field of ultrafast spectroscopy,[8] new areas of spectral and temporal pulse shaping,[9] ultrafast interactions with organic and biological materials,[10] high-harmonic generation as a source of UV and soft x-rays, ultrafast generation of particle beams,[11] terahertz spectroscopy and imaging,[12,13] and ablation mechanisms in dielectric materials[14] (which are quite different from those in metals and semiconductors). Our hope is that the selection of topics will illustrate the breadth of this new area of ultrafast lasers in materials research and the applications that have already been generated.

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Silicon Surface Morphologies after Femtosecond Laser Irradiation

Brian R. Tull, James E. Carey, Eric Mazur, Joel P. McDonald, and Steven M. Yalisove

Abstract

In this article, we present summaries of the evolution of surface morphology resulting from the irradiation of single-crystal silicon with femtosecond laser pulses. In the first section, we discuss the development of micrometer-sized cones on a silicon surface irradiated with hundreds of femtosecond laser pulses in the presence of sulfur hexafluoride and other gases. We propose a general formation mechanism for the surface spikes. In the second section, we discuss the formation of blisters or bubbles at the interface between a thermal silicon oxide and a silicon surface after irradiation with one or more femtosecond laser pulses. We discuss the physical mechanism for blister formation and its potential use as channels in microfluidic devices.

Keywords: *laser ablation, morphology, oxide, Si.*

Introduction

Over the past several decades, ultrashort-pulse laser irradiation of silicon surfaces has been an active area of materials science research that has led to a number of unexpected observations and the formation of new materials. The basic physics of this interaction is fully described in the article by Reis et al. in this issue of *MRS Bulletin*. Starting in the late 1970s, picosecond studies[1–8] and later femtosecond pump-probe studies[9–21] have been used to elucidate the specific mechanism of many processes, including electron–hole plasma formation,[9,10,13,14] melting,[5,9,10,12] ablation,[19–21] and ultrafast melting.[16–18] Ultrafast melting—the disordering of a "cold" lattice within 100 fs of excitation due to covalent bond weakening upon excitation of more than 15% of the valence electrons[22–25]—is a phenomenon unique to irradiation with high-intensity femtosecond laser pulses, because these pulses are shorter than the electron–phonon relaxation time. Technologically, ultrashort laser irradiation offers an alternative method for annealing ion-implanted semiconductors.[6,7]

Early research on the surface morphology resulting from picosecond laser irradiation near the melting threshold revealed the formation of ripples on the surface with a wavelength related to the wavelength of the laser.[4,26] These so-called laser-induced periodic surface structures (LIPSS)[27–30] are similar to ripple structures observed on a variety of materials after irradiation with one or more pulses from a wide range of laser systems (including femtosecond, picosecond, and nanosecond pulses) and are well understood. In short, when the laser pulse is energetic enough to fully melt the surface, the incident pulse interferes with light scattered from defects at the surface, setting up an inhomogeneous melt depth and the formation of capillary waves, which freeze in place.[30] Recently, a number of groups have reported the formation of micro- and nano-sized structures resulting from irradiation with femtosecond laser pulses.[31–41]

The majority of this research deals with the interaction of a single laser pulse with a flat surface. Consequently, the interaction of single laser pulses with various materials is generally well understood. The interaction of multiple laser pulses with a surface that is altered by each pulse, in contrast, is currently not well understood. In this article, we will present two studies on surface morphology resulting from irradiation with multiple femtosecond laser pulses. In the next section, we discuss the evolution of micrometer-sized cones on a silicon surface irradiated with hundreds of femtosecond laser pulses in an atmosphere of sulfur hexafluoride (SF_6) and other gases. After that, we discuss the formation of blisters or bubbles at the interface between a thermal silicon oxide and the silicon surface after irradiation with one or more femtosecond laser pulses.

Formation of Micrometer-Sized Cones on Silicon via Femtosecond Laser Irradiation

For the past ten years, the Mazur group has extensively studied the surface morphology and subsequent properties of silicon surfaces irradiated with femtosecond laser pulses in a variety of environments. In 1998, we published the initial discovery that a flat silicon surface is transformed into a forest of quasi-ordered micrometer-sized conical structures (Figure 1) upon irradiation with several hundred femtosecond laser pulses in an atmosphere of sulfur hexafluoride (SF_6).[42] Shortly afterward, we reported the dependence of cone height on laser fluence and pulse duration.[43] In the subsequent years, we studied the ability of the microstructured surfaces to absorb nearly all incident light in the ultraviolet, visible, and near-infrared (250–2500 nm) as a result of sulfur being trapped in the material during irradiation[44–47] and successfully employed the process to create silicon-based infrared photodetectors.[48] We also studied the morphology and properties that result from microstructuring silicon in a variety of other environments, including gaseous N_2, Cl_2, H_2, H_2S, Ar, and SiH_4, as well as vacuum, liquid water, and air.[45,49–52] When microstructured in air, the resulting surface photoluminesces.[49]

The surface morphology after microstructuring depends strongly on the variables involved in femtosecond laser irradiation, including the number of incident laser pulses, laser fluence (energy per unit area), wavelength, pulse duration, and the ambient gas (or liquid) species and pressure. Despite the large variation in surface morphologies obtained by varying experimental parameters, each resulting surface follows a similar pattern of evolution with increasing number of

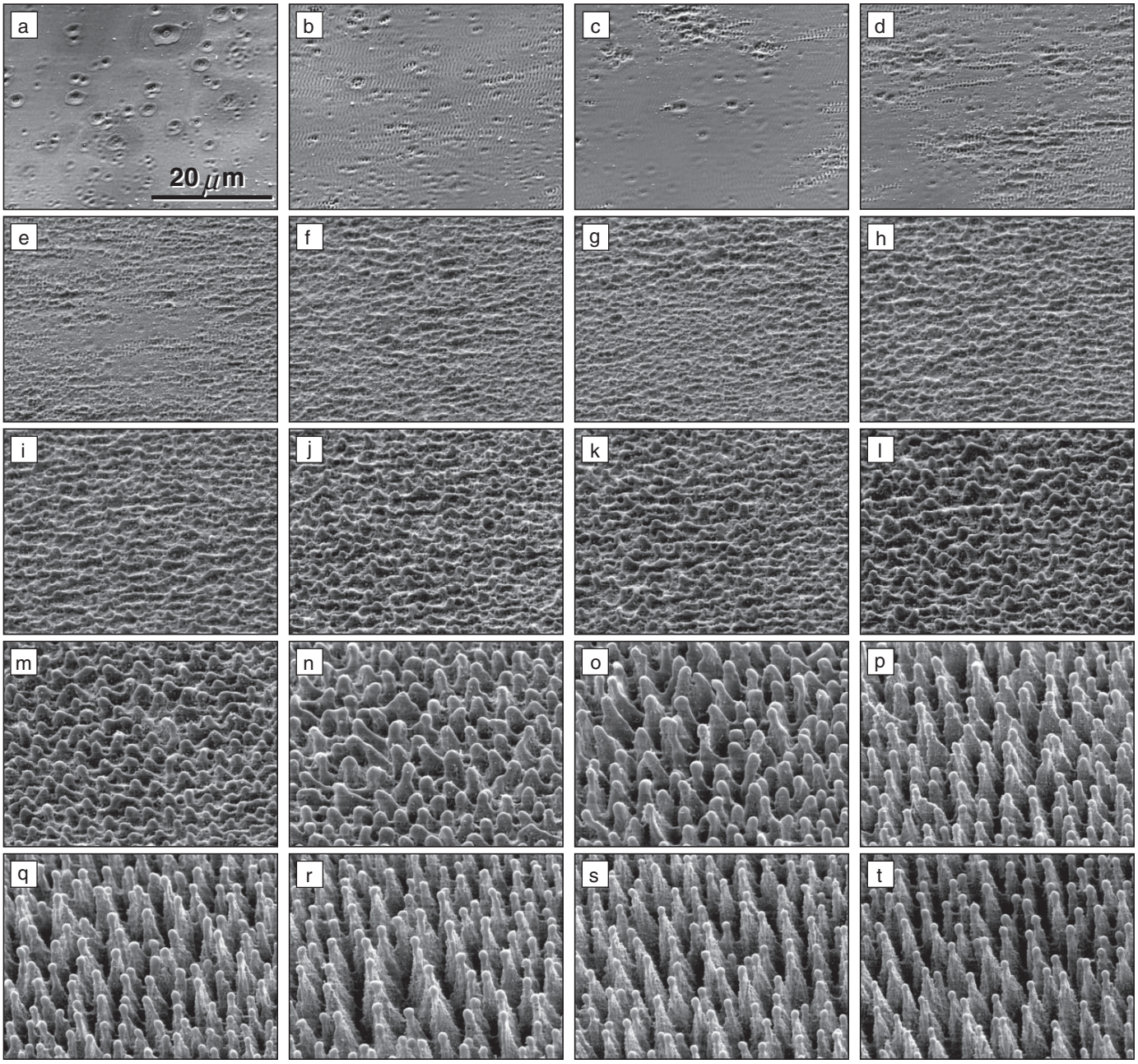

Figure 1. Scanning electron micrographs of a silicon surface after the following number of femtosecond laser pulses: (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, (f) 6, (g) 7, (h) 8, (i) 9, (j) 10, (k) 12, (l) 15, (m) 20, (n) 30, (o) 50, (p) 70, (q) 100, (r) 200, (s) 400, and (t) 600. Each SEM image is taken at a 45° angle to the surface with the same magnification. Adapted from Reference 54.

pulses. After approximately 500 pulses, a quasi-ordered array of conical structures is formed. The resulting cones are approximately 1–15 μm high and spaced by 1–5 μm (with the exception of surfaces irradiated in water, where the cones are an order of magnitude smaller and denser[53]). For linearly polarized light, the cones have an elliptical base, with the long axis of the ellipse perpendicular to the polarization axis of the incident light. In the remainder of this section, we describe the general stages of cone formation that take place for silicon irradiated in SF_6 using specific conditions and then generalize this formation mechanism for other experimental conditions. These specific ("standard") conditions are an *n*-doped Si(111) wafer, 260 μm thick, with resistivity $\rho = 8–12$ Ω m, irradiated by a 1-kHz train of 500–600 laser pulses (duration, 100 fs; central wavelength, 800 nm; spot size, 150 μm FWHM yielding a fluence of 8 kJ/m^2; linearly polarized perpendicular to the optics table), in 67 kPa of SF_6. More detailed experimental procedures can be found in our other papers.[43,46]

Figure 1 shows a series of scanning electron microscope (SEM) images that illustrate how the final morphology evolves

with an increasing number of incident laser pulses. Cross sections of the irradiated samples show that the tips of the cones are at or below the original surface, indicating that the cones are formed by net ablation rather than by deposition and growth.[43] This finding is consistent with our laser fluence (8 kJ/m^2) exceeding both the melting and ablation thresholds for silicon (1.5 kJ/m^2 and 3 kJ/m^2, respectively[21]). As each pulse is absorbed by the sample, the energy density is greatest at the surface and then decreases deeper into the sample. This density profile causes the topmost layer to be ablated away and the material beneath it to melt and then resolidify to form the resulting surface. A simple, uniform ablation process, however, cannot explain the surface morphology, as the valleys between the cones are an order of magnitude smaller than the laser spot size.

The formation of the surface morphology can be separated into two parts, an early stage (1–10 pulses) and a late stage (>10 pulses).[54] The first pulse causes small defects that are randomly distributed over the surface (Figure 1a). Their circular shape suggests that they result from a burst bubble that is frozen in place upon resolidification of the melt. These bubbles can be attributed to a local increase in vaporization of the silicon melt due to defects or impurities at the surface. Apart from these random circular features, the ablation and melting after the first laser pulse appear to be uniform.

After the second pulse, a distinct ripple pattern appears (Figure 1b). The wavelength of the ripple is close to the central wavelength of the incident laser, and the long axis of the ripple is perpendicular to the laser polarization, in agreement with the ripple formation observed in LIPPS. At high fluence, the interference between the incident beam and light scattered by minor surface defects results in inhomogeneous energy deposition. Ablation and melt formation occur at non-uniform depths, creating capillary waves with the wavelength of the laser. Rapid resolidification subsequently freezes the ripple structure in place.

Figure 2 quantifies the evolution of the periodic patterns at the surface. The graphs to the right of the SEM images are Fourier transforms of the intensity of the SEM image in the horizontal and vertical directions. A peak in the Fourier transform (indicated by an arrow) represents a periodicity in the surface at that frequency (corresponding to a periodic distance in the image). In the Fourier spectrums of Figures 2b–2d, the spectrum for the previous figure is shown in gray for comparison. After two pulses (Figure 2a), the Fourier transforms reveal a distinct periodicity of the ripple pattern in the horizontal direction, but not in the vertical direction. After five pulses (Figure 2b), the ripple pattern disappears, along with the peak in the horizontal Fourier spectrum, but a larger periodicity of 2 μm develops in the vertical direction. Visually, the ripple pattern is replaced by small beads spaced approximately 2 μm apart. After 10 pulses (Figure 2c), the periodicity in the vertical direction shifts to larger distances (smaller frequencies), to a wavelength of 3.5 μm. At this point, the periodicity of the final surface morphology is established and the early stage of formation is over. As these pictures show, the periodicity established in the early stage begins with a LIPSS-like ripple formation with a wavelength of the laser (Figure 1b), and then changes to a quasi-periodic array of beads with a larger wavelength (Figures 1c–1j). The nature of the formation of beads and their persistence throughout the ablation process will be discussed after the late-stage formation.

During late-stage formation, from pulse 10 to several hundred pulses (Figures 1j–1t), material is preferentially ablated on the sides of the beads, creating the resulting conical microstructures with the beads at their tips. The beads act to concentrate the light into the valleys between them. Light that hits the sides of the beads has a high angle of incidence, and because reflectivity increases for high angles of incidence, this light is reflected into the valleys, raising the incident fluence and increasing the ablation rate.[55] As the conical structures become steeper, the effect is intensified. A final Fourier analysis of the conical microstructures after 500 pulses is shown in Figure 2d. The periodicity moves to slightly longer wavelengths, and the average spacing of the conical microstructures is 3.5–4 μm.

Toward the end of the evolution (Figures 1q–1t), the tips of the cones start to become wider than regions immediately below the tip, giving the appearance of a sphere perched on top of a cone. This observation may be consistent with some redeposition of vapor material at the tip while the surface is molten via vapor–liquid–solid growth.[56] Similar observations have been made on conical structures grown on silicon with nanosecond laser pulses, which also exhibit spheres at the tip.[57–59] For nanosecond pulses, the tips of the conical structures protrude well above the original surface, suggesting that growth is a more dominant formation mechanism than ablation for nanosecond pulses. A systematic comparison between cones formed with femtosecond and nanosecond laser pulses appears in Reference 47.

The transition from the ripple structure to beads is not fully understood, but several factors may contribute to the development of beads. First, the ripple structure is essentially a half cylinder on the surface, and subsequent melting may cause this structure to bead up. A liquid cylinder that is longer than its radius is unstable and collapses into equal-sized equally spaced drops, a phenomenon known as cylindrical collapse.[60] Second, during ultrashort laser irradiation of silicon, the velocity of the resolidification front is extremely high.[12] As a result, a high concentration of defects can be trapped in the solidified material, including vacancies, interstitials, and elements from the background gas (Rutherford backscattering reveals that the resolidified surface contains approximately 0.5–1% of the ambient species present during the irradiation[46,54]). If the melt depth is non-uniform across the surface, the concentration of defects may also be non-uniform. A recent study[61] predicts that the trapping of defects can be inhomogeneous during femtosecond laser ablation; interstitials collect in extended regions, where the surface height is a maximum and vacancies collect at minima. Regardless of the details of the defect distribution, the inhomogeneous nature of the surface creates a non-uniform melting temperature profile preferentially protecting those regions with a higher melting temperature. It is possible that these regions lead to the formation of beads. The shift in bead periodicity from 2 μm to 3.5 μm at the end of the early stage can be attributed to larger beads being protected by this mechanism while smaller beads are ablated away.

The specific surface features that develop depend to some degree on the conditions, but the formation mechanism follows the overall trend described in the previous few paragraphs for a wide range of experimental parameters. In nearly every case, the surface morphology develops a ripple structure on the order of the wavelength of the incident light after only a few pulses. Different conditions, however, lead to differences in the periodicity and size of the beads that develop, the number of pulses required to create bead-like structures, and the final shape of the cones. These factors depend on the surface tension of the liquid silicon that forms a protective bead, which in turn depends on melt depth, cooling rate, gas species, and pressure as well as the inclusion of elements from the background gas.

For example, when the incident laser pulses are frequency-doubled so they

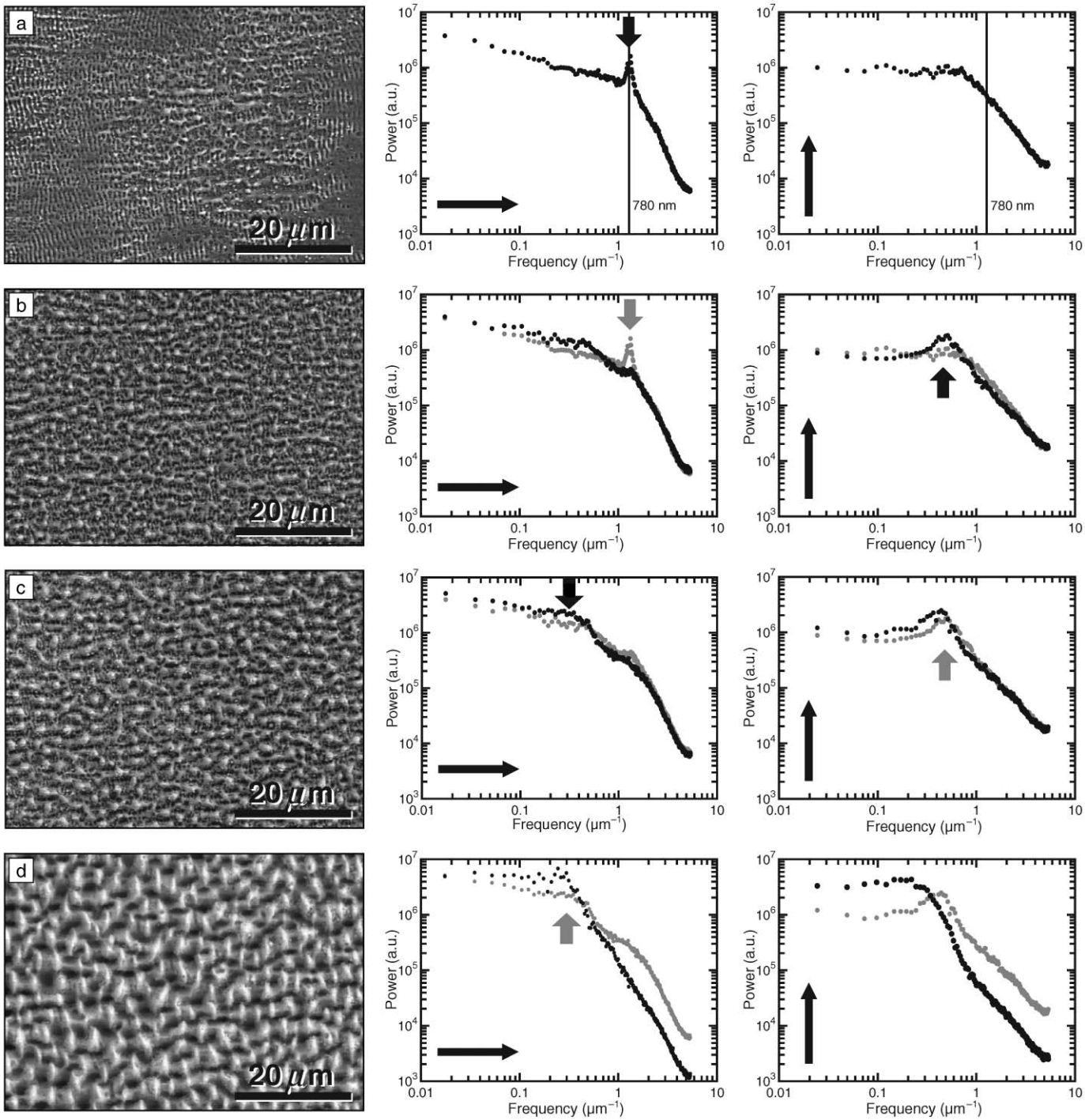

Figure 2. Scanning electron micrographs of a silicon surface after (a) 2, (b) 5, (c) 10, and (d) 500 femtosecond laser pulses. The micrographs were taken normal to the surface. The graphs are Fourier transforms of the intensity of each SEM image in the horizontal (center) and vertical (far right) directions. A peak in the Fourier transform (indicated by an arrow) represents a periodicity in the surface at that frequency (corresponding to a periodic distance in the image). In the Fourier spectra of Figures 2b–2d, the spectrum for the previous figure is shown in gray for comparison. Adapted from Reference 54.

have a wavelength of 400 nm, the resulting LIPSS ripples have a wavelength of 400 nm, and sharp conical structures develop in a manner similar to the formation of structures with 800-nm light, except that they are smaller and their density is doubled.[54] In vacuum, ripples develop after a few pulses, but it takes up to 50 pulses for the ripples to coarsen into beads. The resulting conical structures are broader and more blunt, with a slightly wider spacing than cones formed in SF_6.[54] These

two examples illustrate how the formation mechanism remains similar for different conditions. The first case shows that the wavelength of the laser determines the final density of the structures. The second example shows that the background gas has an effect on the number of pulses required to form structures and their overall final shape. The ambient gas changes the surface tension of the molten silicon and determines the elements that become trapped in the molten silicon. For SF_6, H_2S, and Cl_2, the final cones are sharp, as in Figure 1, but for N_2, H_2, and air, they are blunt, like the cones formed in vacuum.[45,52,54] The difference may indicate that certain elements (such as S and Cl) provide more protection against ablation than other elements (N and H).

Interface Effects from Femtosecond Laser Irradiation of SiO_2-Coated Silicon

Femtosecond-laser-induced damage on single-crystalline silicon has been extensively studied with a large variety of characterization tools, including atomic force microscopy, micro-Raman spectroscopy, and laser scanning microscopy.[31,33,39,40,62–68] These studies typically measure damage thresholds and identify morphological damage features that depend on variables such as fluence (energy per unit area), temporal pulse width, polarization, wavelength, and angle of incidence. Few of these papers, however, address the role of the 2-nm-thick native oxide layer. We recently published[69] results which demonstrate the significant role that the 2-nm native oxide plays on the morphology and damage threshold as compared with atomically clean Si. These results and the model that was developed to explain them motivated us to perform experiments on Si with thicker, thermally grown oxide films.

We studied thicker SiO_2 samples by growing thermal oxides of different thicknesses.[70] Indeed, the morphology that is seen in the native oxide disappears for the thinnest thermally grown oxide (20 nm). Instead, an entirely new morphology—either blisters or craters—appears.

Figure 3 presents atomic force microscopy (AFM) images illustrating a range of morphologies that are produced by varying the thermal oxide thickness, the laser fluence, and the number of laser pulses. For a given oxide thickness, blisters form at low fluence, 1–2 times the damage threshold of Si(100), while craters are formed as the fluence is increased beyond a critical value. Unique to ultrafast-laser material interaction is the inherent reproducibility and control over blister and crater dimensions. Using multiple pulses, blister height can be sequentially increased (or pumped up) from 100 nm to 900 nm (Figures 3d–3g). Alternatively, blister dimensions can be controlled by changing the laser fluence of a single laser pulse (Figures 3i–3l).

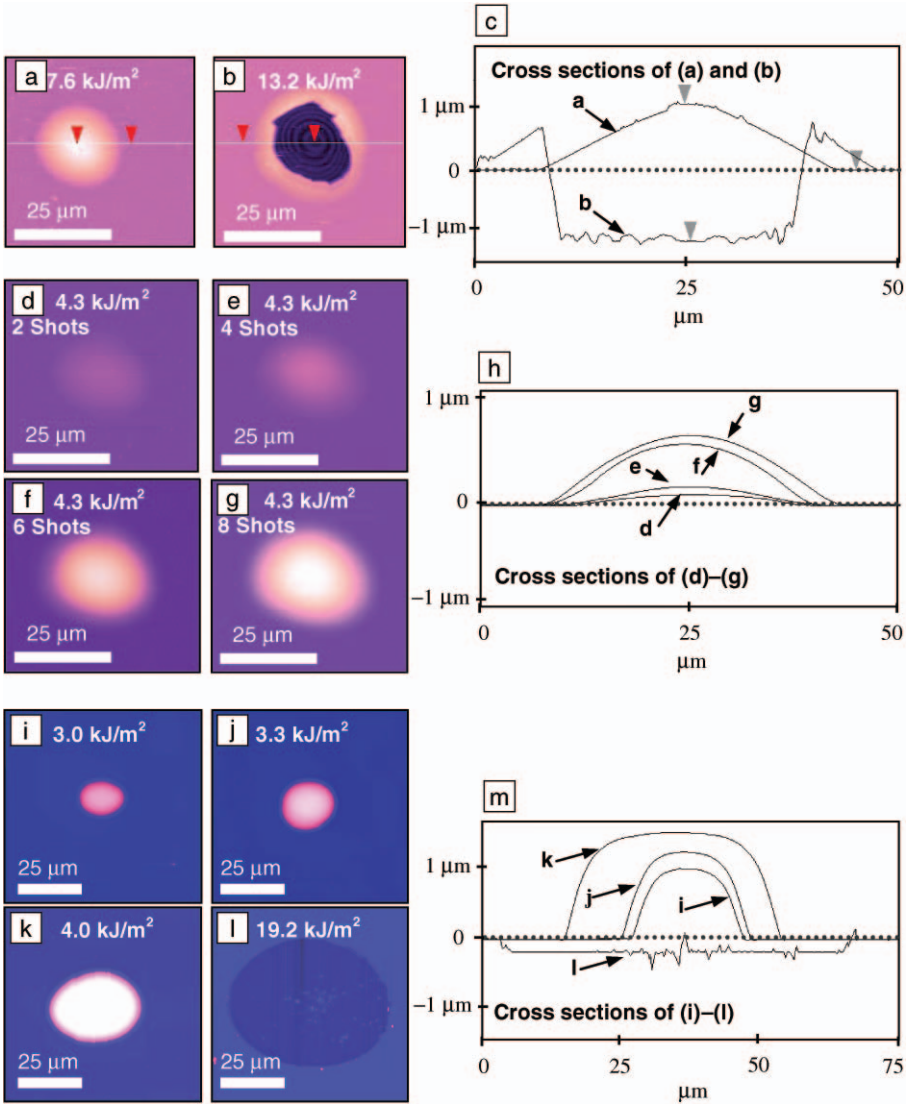

Figure 3. Atomic force microscopy images of femtosecond-laser-induced damage features produced on thermally oxidized Si(100). (a)–(h) Oxide thickness = 1200 nm. (i)–(m) Oxide thickness = 147 nm. (a) Blister; laser fluence = 7.6 kJ/m². (b) Crater; laser fluence = 13.2 kJ/m². (c) AFM section analysis of features in (a) and (b). (d)–(g) Blister features produced in 1200-nm-thick thermal oxide on Si(100) with laser fluence = 4.3 kJ/m² produced using the number of laser pulses as follows: (d) 2, (e) 4, (f) 6, and (g) 8. (h) AFM section analysis of features in (d)–(g). (i)–(l) Damage features produced on thermally oxidized Si(100) with a 147-nm-thick oxide. (i) Blister; laser fluence = 3.0 kJ/m². (j) Blister; laser fluence = 3.3 kJ/m². (k) Blister; laser fluence = 4.0 kJ/m². (l) Crater feature produced in 147-nm-thick thermal oxide on Si(100) with peak fluence = 19.2 kJ/m². (m) AFM section analysis of features in (i)–(l), demonstrating the heights of the blister features and depth of the damage crater.

Blister formation in thin films resulting from laser irradiation is not a new phenomenon, but the conditions and mechanisms at play are quite different for irradiation with femtosecond laser pulses than for longer pulse durations.[71,72] Relaxation of residual stress plays a role but is far from sufficient to explain the observed blister dimensions.[73–75]

The mechanism responsible for blister production by femtosecond laser pulses is

a combination of compressive stress relaxation, softening of the thermal oxide via electron heating and conduction, and momentum transfer from the underlying substrate to the oxide layer.[75] The interaction of an above-damage-threshold femtosecond laser pulse with the Si(100) substrate produces a dense electron–hole plasma in silicon and energetic electrons that expand in all directions from the excitation region.[76] These energetic electrons reach thermal equilibrium with the lattice as they transfer their kinetic energy to the lattice in a few picoseconds, heating the substrate to about 5000 K.[20] Due to its proximity to the highly heated substrate as well as heating by electrons scattered from the substrate, the thermal oxide film is left in a softened state. This softening allows the ablated substrate material to push the oxide film upward, forming a blister. This model is consistent with the picture of near-threshold ablation presented in the article by Reis et al. in this issue. It is also consistent with time-resolved pump-probe imaging experiments of near-threshold ablation of metals and semiconductors, where interference phenomena suggest that a moving liquid layer is expelled.[19,21,77]

By overlapping blisters produced by femtosecond laser pulses in a 1200-nm-thick thermal oxide layer on Si(100), one can produce channels that can be used in microfluidics applications. The top surface of the channel is the delaminated thermal oxide film and the freshly oxidized 40-nm film of Si; the bottom surface is the underlying Si(100) substrate, which has a thermal oxide that forms as the molten Si solidifies in the presence of air.[75,78] A single pass of the sample through the focused laser beam at a speed of 10 mm/s and a laser fluence of 3.5 kJ/m^2 with a focused laser beam diameter of 55 ± 5 μm on the sample produces channels 24 ± 1 μm wide and 355 ± 45 nm in height. To make larger channels, we laterally overlapped single-pass channels, producing channels with widths exceeding 300 μm. The height of the channels is a function of channel width (see Figure 4). We also produced linear channels with lengths exceeding 10 mm, as well as other channel geometries, including intersections, corners, and curves. SEM images of the end of a channel are presented in Figures 4i–4j, showing the morphology of the substrate or bottom surface of the channels. Similar channels have been produced by selectively delaminating diamond-like carbon films via lithographic techniques.[74]

Compared with other femtosecond-laser-based micromachining techniques for producing microfluidic channels, the technique discussed here has the advantage of producing little debris at relatively fast writing speeds.[79,80] In general, direct-writing techniques are simpler than lithographic techniques, because the channels

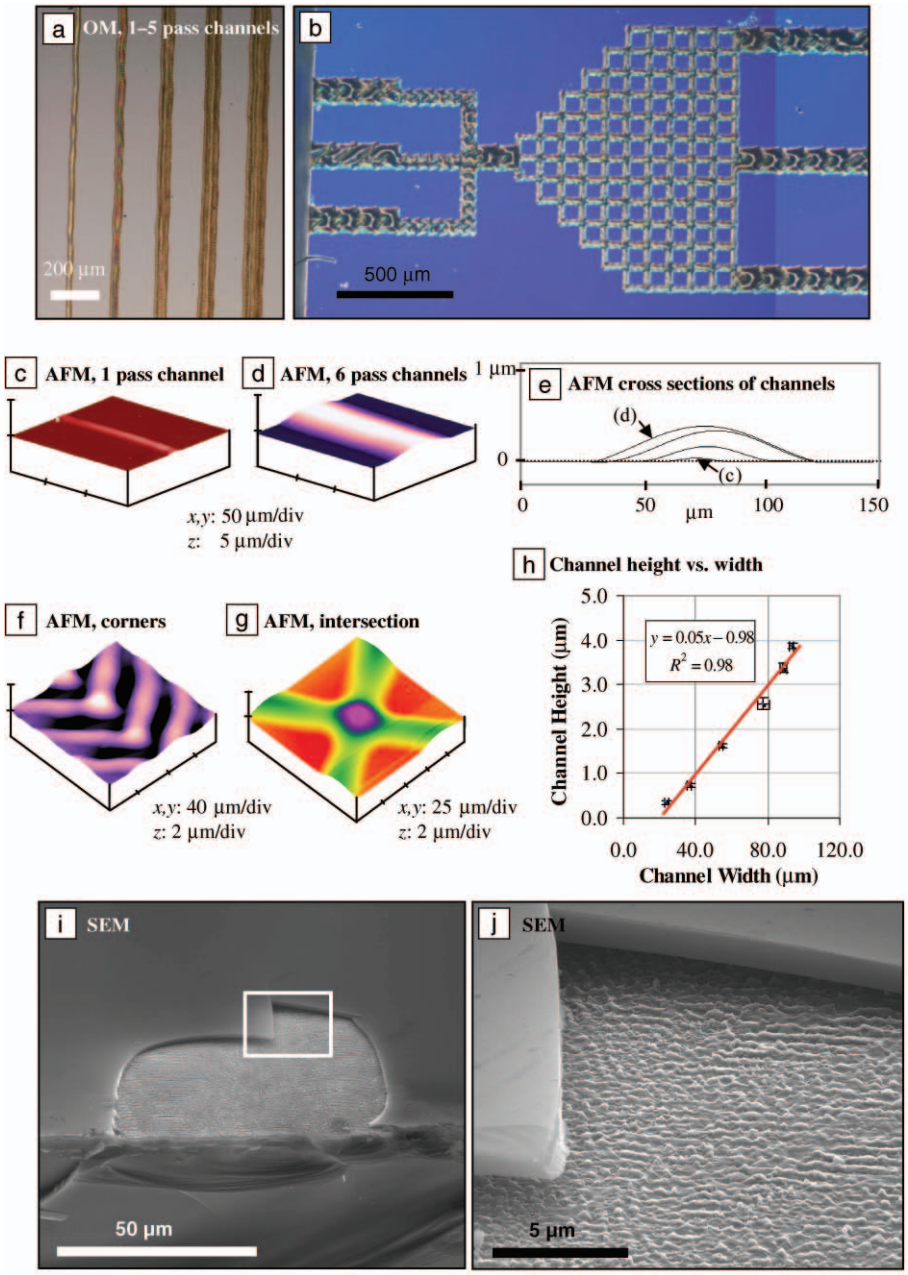

Figure 4. Nano- and microfluidic channels produced with the femtosecond laser direct-write technique with laser fluence of 3.5 kJ/m^2 at a single-pass scan rate of 1 cm/s. (a) Optical microscope image of channels produced with (from left to right) a single pass to 5 overlapped (overlap = 15 mm) passes. (b) Simple grid device produced with the femtosecond laser direct-write technique. (c)–(g) AFM images of channels produced with single and multiple passes. (c) Single pass. (d) Six passes. (e) AFM cross section analysis of channels; (c) and (d) are indicated. (f) AFM of corner channels. (g) AFM of channel intersection. (h) Plot of channel height as a function of channel width, with results of linear fit shown. (i) SEM image (tilt = 59°) of end of channel written to the edge of sample. The interior of the channel was exposed by intentionally fracturing the delaminated glass at the edge of the sample. (j) SEM image from inset in (h), showing the roughness on the substrate surface and bottom surface of the delaminated thermal oxide film.

can be created with a single processing step, allowing adjustments to the fluidic network design to be implemented quickly without the need to produce a new mask. The channels produced via femtosecond-laser-induced delamination of thermal oxide films from Si(100) substrates exhibit a noncircular cross section, which is quite different from those produced by other techniques.[79,81] However, the delaminated glass is very thin and may require a layer of poly(dimethylsiloxane) or other material to make these fragile systems more robust.

Summary

The interaction of intense, ultrafast laser pulses with materials produces a variety of damage morphologies that depend on both the laser irradiation and the material of interest. Many other interesting morphological phenomena have been observed and characterized, including laser-induced periodic surface structures or ripples,[34,82,83] gratings produced by interfering two laser beams on a surface,[84,85] and so-called nanobumps and nanojets in thin gold films on quartz substrates.[86] A number of recent papers report on the effect of liquid[35,87] and gaseous[88,89] environments on the resulting morphology during machining. Controlling damage morphology is essential for improving micromachining capabilities. The resulting damage morphologies can also prove useful in their own right, as in the case of the two studies presented in this article. The intersection of materials research and ultrafast optical science is producing many valuable fundamental scientific results, and the trend is expected to evolve as new and exciting discoveries are made.

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