Optics at critical intensity: Applications to nanomorphing

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Laser-induced optical breakdown by femtosecond pulses is extraordinarily precise when the energy is near threshold. Despite numerous applications, the basis for this deterministic nature has not been determined. We present experiments that shed light on the basic mechanisms of light–matter interactions in this regime, which we term “optics at critical intensity.” We find that the remarkably sharp threshold for laser-induced material damage enables the structure or properties of materials to be modified with nanometer precision. Through detailed study of the minimum ablation size and the effects of polarization, we propose a fundamental framework for describing light–matter interactions in this regime. In surprising contrast to accepted damage theory, multiphoton ionization does not play a significant role. Our results also reject the use of the Keldysh parameter in predicting the role of multiphoton effects. We find that the dominant mechanism is Zener ionization followed by a combination of Zener and Zener-seeded avalanche ionization. We predict that the minimum feature size ultimately depends on the valence electron density, which is sufficiently high and uniform, to confer deterministic behavior on the damage threshold even at the nanoscale. This behavior enables nanomachining with high precision, which we demonstrate by machining highly reproducible nanometer-sized holes and grooves in dielectrics.

The invention of the laser has led to the generation of increasingly large optical electric fields, which have revealed a succession of new high-intensity optical regimes. This succession started with bound-electron nonlinear optics (1), with laser fields of strength comparable with the Coulomb field that an electron experiences near the nucleus, and has progressed through regimes of multiphoton ionization (MPI) and high harmonic generation to relativistic optics in which the most powerful lasers drive the electrons to quiver velocities close to the speed of light. Perhaps in the excitement of progress toward higher-energy regimes, one important regime has received relatively less attention: optics at critical intensity (OCI). This regime encompasses the remarkably sharp material transitions that occur when the optical field energy is very near the threshold for material breakdown through ionization of valence electrons.

A decade ago chirped-pulse amplification lasers (2) made it possible to study in detail the damage threshold as a function of pulse duration, which led to the discovery of a fundamental property of OCI: for pulses <5 ps, the damage threshold becomes deterministic and is very sharp and reproducible (within 1%), as opposed to the stochastic behavior (20–50%) for longer pulses (3). This property, combined with the lack of thermal diffusion and minimal shock waves, allows for nanomorphing: material modification with subwavelength feature size in virtually any material. This is possible only in the OCI regime: laser damage is only sufficiently precise when using subpicosecond pulses with energy just above the optical-damage threshold. OCI transports the field of laser matter interaction from the macro- and microscale to the submicrometer scale, or as demonstrated here even the nanoscale domain (<100 nm), with important applications including cell surgery, electronics, microelectromechanical systems, and micro- and nanofluidics.

Despite the important current applications and enormous potential for new ones, the fundamental physics of OCI, particularly the deterministic character of dielectric breakdown, remains largely unresolved. To address this issue, we present a detailed study of laser damage in the subpicosecond domain. We find that, contrary to the common belief (1, 4–6), MPI does not play an important role in optical damage; the dominant optical-damage mechanism is a combination of Zener ionization (tunneling) and Zener-seeded saturation avalanche ionization. Furthermore, we find that the remarkable precision and reproducibility of the optical damage can be explained by a mechanism in which the threshold depends on uniformity of the valence electron density in the damaged material. These findings make it clear that the ultimate limits for machining with light are far beyond what was recognized previously; even ultrahigh-precision nanomachining of materials with ill-defined or variable band gaps is possible, and we demonstrate this by machining nanoscale holes and lines in a variety of materials. Furthermore, we demonstrate that ablated regions have truly precise boundaries; surrounding changes, when present, are caused by deposition of extruded material that can be entrained. These findings represent major advances for practical application of nanomorphing and the fundamental understanding that comes from rigorously establishing the physical limits of optical damage, and provide a cohesive understanding of both the incredible precision of OCI and why this precision is possible.

**Laser–Matter Interaction at Critical Intensity**

Focused pulses from a high-power laser can damage virtually any material when the induced electric field is high enough to produce optical breakdown. It is believed that optical breakdown in dielectric materials proceeds by avalanche ionization, in which initial (seed) unbound electrons in the target material are accelerated by the laser electric field to create a cascade of free electrons through collisions. This process occurs even in transparent materials, which become opaque light absorbers when the free-electron density is nearly equal to or greater than the critical density for the light considered. Optical breakdown shows a highly nonlinear dependence on intensity, and this allows damage to be restricted to subdiffraction limit areas by “thresholding” (Fig. 1a). This effect allows fabrication of submicrometer features (7–11), and we demonstrate that even nanoscale features can be produced with ultrahigh precision (Fig. 1 b-d and ref. 12).

For pulses longer than ~10 ps, the threshold fluence for optically induced dielectric breakdown depends strongly on the pulse duration and scales with $T^{1/2}$, where $T$ is the pulse duration.
Example of a nanometer-scale hole. The red circle indicates the optical breakdown, thus allowing formation of subdiffraction features. (Fig. 1.) 

Illustration of how an ultrashort laser pulse can create an ablation. PNAS vol. 101 no. 16 5857 (E. Van Stryland, T. F. Boggess, and M. J. Soileau) detected the beginning of this transition at ~10 ps. They found that the damage threshold was spot-size-dependent and concluded that it had an extrinsic character in which the initial electrons were provided by defects or impurities. Work at the University of Michigan confirmed the transition but also found the damage threshold to be deterministic for short pulses. This work demonstrated that the character of optical damage dramatically changes when the pulse duration is reduced below 10 ps: the pulse-duration dependence of the damage threshold becomes weak and no longer scales as $T^{1/2}$ (refs. 3 and 7). The shot-to-shot threshold variability also decreases with pulse duration, becoming increasingly deterministic. These investigators proposed that the nearly deterministic behavior was the result of a combination of two nonlinear processes: MPI seeding and saturation of the impact-ionization coefficient $\eta(E)$ at high field, as predicted for dc or low-frequency electric fields by Thornber (14). Slightly later, a similar study conducted at the Lawrence Livermore National Laboratory confirmed departure from $T^{1/2}$ scaling even for damage caused by multiple pulses. The investigators hypothesized that the plasma generation was strongly dependent on MPI and predicted a strong decrease in damage threshold for pulses well below 100 fs (5).

Although a role for MPI has been advocated consistently throughout the history of optical-breakdown research, some doubts have been expressed. Studies have failed to confirm the predicted decrease in threshold at very short pulses (5), finding instead that the damage threshold decreases only slightly or remains nearly constant to within a few J/cm$^2$ from 5 to 100 fs (4, 15). It has also been pointed out that frequent electron collisions in solids could strongly attenuate MPI by dephasing the electrons and the driving field (16, 17). Through a careful study of damage threshold and morphology, we conclude that MPI is not important, and in any case would not predict the phenomenally deterministic character that has allowed us to demonstrate laser machining in the nanoscale regime. We propose a theoretical framework in which OCI is dominated by an runaway process of Zener and Zener-seeded avalanche. We propose a theoretical framework in which OCI is dominated by an runaway process of Zener and Zener-seeded avalanche. We base this theory on five independent observations discussed below.

A Significant Role for Avalanche Ionization Is Indicated by the Relation Between Band-Gap and Quiver Energy at Threshold. For avalanche ionization to occur, the kinetic energy of a free electron must be sufficient to ionize a bound electron, i.e., of the order of the band energy gap (band gap). In the case of optically induced ionization, we expect to cross the threshold for avalanche when the band gap is of the order of the electron quiver energy, which is the time average over one light cycle of the square of the electric field average (this is expanded on in the theory section below). Because the quiver energy is proportional to intensity, a scaling of the damage threshold with the energy gap provides a strong confirmation that avalanche ionization plays an important role in breakdown in the OCI regime. We find that, for a wide range of band gaps, composition, and structures, the threshold energy, which is proportional to intensity and thus the electron quiver energy, scales with the band gap (Fig. 2), supporting the role of

Fig. 1. (a) Illustration of how an ultrashort laser pulse can create an ablation localized to a region smaller than the light resolution limit. As the pulse energy is decreased, a smaller portion of focus spot exceeds the energy threshold for optical breakdown, thus allowing formation of subdiffraction features. (b) Example of a nanometer-scale hole. The red circle indicates the $1/e^2$ focus-spot size. Studying OCI in detail required a very stable laser. We selected a directly diode-pumped Nd:glass, chirped-pulse amplification laser system (Intralase Corp., Irvine, CA) operating at 1,053 nm, with a repetition rate of 1.5 kHz and a pulse width of 800 fs, which was focused through a high-numerical-aperture objective of an inverted microscope as described in ref. 12. (c and d) Scanning electron micrographs of ~30-nm-wide channels machined in glass. (Scale bar in c, 2 µm.) A channel was produced by scanning the sample through the laser focus with the help of a piezoelectric nanostage (Mad City Labs, Madison, WI) such that the successive pulses hit the sample 50 nm apart.
avalanche ionization in breakdown. This observation extends,
but remains consistent with, other studies (5, 18). Surprisingly,
we find that the relation holds even for silicon, in which a single
photon is sufficient to ionize an electron, supporting an impor-
tant role for avalanche even in a material that is easily ionized
by the incident light. Note that the threshold in quartz is similar
to the threshold in fused silica. Because quartz has a smaller
number of extended states than fused silica, this suggests that in
large band gap materials, the seed electrons are not produced by
single-photon ionization due to the extended states covering the
whole band gap.

The Initial Free-Electron Density Required for Avalanche Can Be
Deduced from Feature Size and Morphology. The scale of the
sharpness of the holes produced by optical breakdown allows us
to estimate the ionized electron density preceding the onset of
avalanche ionization. Initiation of avalanche requires ionized
seed electrons, the density of which is multiplied on the order of
10 by the series of ionizing collisions. Because the distance
between collisions is equal to the ion average distance (~ 0.5
nm), there must be an upper bound for the avalanche volume
initiated from a single-seed electron. This volume will determine
the smallest feature size.

By reducing the pulse energy to a value slightly above the
threshold for material damage, we consistently machined circu-
lar holes much smaller than 100 nm (e.g., Fig. 1b). Even at these
minute scales the holes have sharply delineated boundaries; the
edges are smooth to the resolution of the scanning electron
microscope (~4 nm), which suggests that even smaller scales
could be achieved by using shorter wavelengths and/or ap-
proaching closer to threshold. By spacing subsequent laser shots
to produce a line of slightly overlapping holes, we found that we
also could machine channels (Fig. 1c and d). This finding, in
addition to further demonstrating the utility of OCI for
nanoscale machining, reinforces the deterministic character of
OCI: if any damage is produced in the region beyond the sharp
borders of an ablation, it is so minimal that it does not affect the
ablation induced by a subsequent shot. Holes often were accom-
panied by surrounding features, usually a raised region imme-
diately around the holes (e.g., Fig. 3a). These raised regions
sometimes broke off to reveal a flat surface below, suggesting

Fig. 2. Linear scaling of the damage threshold with the band gap for 527-nm
(a) and 1,053-nm (b) light. The materials examined and their band gaps were:
silicon, 1.1 eV; fused silica, 7.1 eV; quartz, 8.4 eV; and sapphire, 9.9 eV. In a, the
peak quiver energy (in eV) is ~0.03 times the pulse energy (in nJ) plotted on
the ordinate. The intensity (in W/cm²) is ~1.1 x 10^12 times the pulse energy
plotted. It should be noted that these values are approximate due to the
unknown energy losses in the objective.

Fig. 3. Surrounding features are redeposited material extruded from the
ablated region. (a) Scanning electron micrograph (SEM) of a row of holes in
glass. Before viewing, the sample was blasted with pressurized gas, causing
pieces of the surrounding feature to break off, revealing a flat surface below
(arrowheads). (b) SEM of an array of holes in glass produced at a glass–water
interface. Note that features surrounding the holes are suppressed or absent.
(c) SEM of a groove machined at a glass–water interface by scanning the
sample through the laser focus so that the successive pulses hit the sample 50
nm apart. Note fluting on the edges of the walls, indicating extraordinary
discrimination of the damage produced by each pulse. The circle indicates the
1/ε² focus-spot size of the beam. The effective machining diameter of the
beam thus can be made much smaller than the diffraction-limited diameter of
the beam.
that they are formed by deposition of material extruded from the central hole. In support of this theory, the surrounding features were strongly attenuated when machining was performed at a surface–water interface (Fig. 3f).

From the small size and sharp edges of the holes, we can conclude that the free-electron density before avalanche starts must be at least 10^{18}/cm^3 to ensure one electron in a volume 4 nm across (the upper limit of the roughness of the edges of the holes). This is a very high electron density, especially for large band-gap materials [e.g., 10 eV in sapphire (1 eV = 1.602 × 10^{-19} J)]. It is far too high to be preexisting (1) and definitively demonstrates the widely held view that free electrons are produced before the onset of avalanche by MPI or band-gap (Zener) tunneling of electrons through the atomic field potential barrier, which is suppressed by the strong electric field of the intense light (19).

To Differentiate Between MPI and Zener Tunneling of Electrons, We Studied the Damage Threshold as a Function of Polarization. In contrast to MPI, the efficiency of Zener tunneling is expected to be similar for linearly polarized (LP) and circularly polarized (CP) light (20–24). We note that in gasses, theories variably predict modest reduction of the efficiency of Zener tunneling for CP versus LP light (22–24). Experimentally, the threshold for CP light was found to be ~2-fold higher (22). However, as discussed below, we do not observe this in solids. Therefore, if MPI plays a significant role, the threshold for breakdown should be significantly different for LP and CP light, which has been demonstrated in gasses in which LP and CP light have quite different ionization rates; LP light is much more efficient, especially for fourth- or higher-order photon absorption (17). This is not surprising; CP light is expected to be inefficient for inducing MPI because of dephasing caused by rotation of the driving field. In large band-gap materials such as quartz or sapphire, the predicted rate of MPI is ~3 orders of magnitude less for CP compared with LP light (21, 25, 26). But theories incorporating MPI (5, 18, 27, 28) may be inappropriate in solids, for which there is the possibility of collisions between electrons on neighboring atoms. When the electron excursions become larger than the atomic distance, frequent collisions will dephase an electron and the driving field, suppressing multiphoton effects (21). Indeed an initial study by Du et al. (16) examined the breakdown threshold as indicated by increased light absorption by the target material and could not detect to within 10% a threshold difference between CP and LP light. Using the method of Joglekar et al. (12), we examined the damage threshold polarization dependence with high precision and found no dependence within 1% accuracy (Fig. 2). No polarization effects were detected for materials over a wide range of band gaps, composition, and accuracy (Fig. 2). No polarization effects were detected for materials over a wide range of band gaps, composition, and accuracy (Fig. 2). No polarization effects were detected for materials over a wide range of band gaps, composition, and accuracy (Fig. 2). No polarization effects were detected for materials over a wide range of band gaps, composition, and accuracy (Fig. 2). No polarization effects were detected for materials over a wide range of band gaps, composition, and accuracy (Fig. 2).

Sharp Features in Materials with Variable Band Gap Show That the Onset of Avalanche Is Not in Itself Sufficient for Breakdown. The band-gap energy may vary quite significantly from atom to atom in a given material. This is particularly true in glass, in which the band gap is highly variable, especially at the surface. This variability is not reflected in the threshold energy (Fig. 3), because on the scale of the illuminated spot the average band-gap structure varies little from one location to another. This is true even for a heterogeneous material with an ill-defined band gap such as Corning 211 glass. However, as finer details of damage are examined, we might expect heterogeneities reflecting disparity in the threshold intensity required for the quiver energy to exceed a variable band gap. In particular, the edges of holes should be rough, and their size should be variable. On the contrary, we find that the variability of the band-gap structure is not reflected in the features, which are both sharp and repeatable even across large distances and even in Corning 211 glass (Figs. 1 and 3). From this finding we conclude that, although there is a critical intensity required for breakdown, it does not solely define the onset of damage. We propose that the sharp breakdown threshold is also defined by a critical pulse energy or fluence, which depends only on the valence electron density. Sharp, repeatable machining is then possible, because the valence electron density is expected to be homogeneous across large distances, even down to the nanometer scale for good-optical-quality materials. Once the avalanche starts, it self-terminates when all valence electrons are ionized. This provides a discrete endpoint, which is necessary for deterministic behavior, as discussed below.

The Depth of Features Indicates That Damage Occurs When All Valence Electrons Are Ionized. Because thermal diffusion is extremely limited during subpicosecond pulses, optical breakdown is induced on a surface facing the laser only where sufficient light is absorbed to exceed threshold. Thus, the depth of the damage provides a measure of laser penetration during dielectric breakdown, provided that the damage is limited to depths less than the length of the beam waist. Near threshold, this depth will be of the order of the depth required for an e-fold reduction in light intensity, which for an otherwise optically transparent material corresponds to the skin depth that an electric field penetrates in the conducting ionized region. To measure the depth of ablation features, larger holes were produced in glass by focusing near-threshold energy pulses at 1,053 nm with a weakly focusing objective (0.65 numerical aperture). The depth of such holes (0.5 μm in diameter) was measured to be 50 nm with atomic force microscopy. Similar results have been observed by others (9, 12, 29). This depth is on the order of 30 nm, the skin depth corresponding to ionization of all ~10^{23}/cm^3 valence electrons, and we conclude that all valence electrons are ionized at breakdown.

A Mechanistic Explanation for the Deterministic Character of OCI

The events that lead to optical breakdown begin with the formation of a large number of charge carriers by Zener tunneling in a volume confocal with the laser at or near the surface. Although the probability of avalanche (19) is small before the threshold for avalanche is crossed, the valence electron density is large (10^{23}/cm^3), which leads to a significant number of free electrons tunneling to the conduction band. When the carrier quiver energy given by

\[ E_{osc} = \left( \frac{e^2 E^2}{2m_0 \omega^2} \right) \text{ or } E_{osc} = 9.3 \times 10^{-14} \mu \lambda^2 \]  \[ \text{[1]} \]

becomes greater than the band gap, bonds can be broken and carriers are multiplied further by avalanche ionization. Here \( E_{osc} \) is in eV, the intensity \( I \) is in W/cm², wavelength \( \lambda \) is in μm, \( E \) is the laser electric field in V/cm, \( \omega \) is the angular frequency of the laser, \( m \) is the rest mass of an electron, and \( e \) is the charge of the electron. At the onset of avalanche, the carrier density is ~10^{19}/cm^3, as indicated by the nanoscale-feature size and sharpness. The time between collisions \( \tau \) decreases as the electron energy increases to become of the order of 100 asec for eV quiver energy. The increase in free-electron density sharply augments the plasma frequency \( \omega_p \) and will decrease the dielec-
tric constant to near zero when the plasma frequency reaches the laser frequency. 

\[ e = 1 - \left( \frac{\omega_p}{\omega} \right)^2 \text{ with } \omega_p^2 = \frac{4\pi ne^2}{m} \]  

The electric field in the plasma is equal to \( E \propto \omega^{1/4} \). Thus, when the plasma frequency becomes close to the laser frequency \( \omega \), the electric field experiences a strong enhancement, further increasing impact ionization and producing a run-away process that will stop when all the valence electrons are ionized. When the plasma frequency becomes greater than the laser frequency (\( \omega_p > \omega \)), the electric field in the plasma drops, and the plasma becomes strongly absorbing. The light won’t propagate and will be absorbed over the skin depth \( \delta \) given by (30):

\[ \frac{c}{\omega_p} < \delta < \frac{c}{\omega_p(2\omega)^{1/2}}. \]  

For free-electron density of \( 10^{23}/\text{cm}^3 \), this skin depth is of the order of 30 nm, which is comparable with the impact depth of 50 nm measured by atomic force microscopy. Fig. 4 schematically illustrates distribution of these events across the laser focus (a) and over time (b).

In the absorbing volume, the material exhibits a metallic character and the interaction is overcritical, with a low plasma temperature of several eV set by the bond breaking energy. Because the overcritical spot area is completely metallic, the situation becomes analogous to the interaction with metals in which subwavelength damage has been demonstrated (9). After a few picoseconds, the electrons will transfer their kinetics energy to the ions. Once the ions’ kinetic energy is such that their displacement corresponds to a fraction of the lattice constant, the dielectric undertakes a phase transition to melt and then vaporize.

**Discussion**

We present a thorough characterization of OCI across materials, scales, light polarities, and wavelengths, which precipitates a physical theory for optical breakdown in solids. These fundamental findings illuminate a regime of ultrahigh-precision laser machining that enables a revolutionary approach for manufacturing nanotechnology. In contrast to previous work (13, 14), we find that damage is intrinsic in nature, without a strong local dependence on impurities or defect states within the material. We find that the deterministic character of OCI originates from Zener-seeded self-terminated avalanche ionization and does not appreciably depend on MPI.

These findings explain why laser machining using OCI is ultrahigh-precision, capable of creating features ranging from micrometers to the low end of the nanometer scale. The sharp boundaries of breakdown at OCI make it a simple matter to form more complicated structures by repeatedly machining holes at different locations such that successive features overlap (e.g., Fig. 1 c and d). Because OCI is governed by the valence electron density, it can work with any material with a uniform valence electron density (e.g., optical-quality materials), and for many applications it is simpler and more reliable compared with other methods capable of producing nanometer features (e.g., electron-beam lithography and nanoimprinting). Because all valence electrons are ionized in the region of material damage, the smallest achievable scale will ultimately be limited by the skin depth and/or the diffusion of ionized electrons out of the region of breakdown. The latter limit can be estimated at \( \sim 10 \text{ nm} \), and because it depends on the pulse length, even smaller features might be attained by using shorter pulses. The physics of OCI are extremely well suited for a broad range of applications requiring discrete high-precision material modification, such as microelectromechanical systems construction and design, ultrahigh-density microelectronics, nanofluidics, materials science, optical memory, creation of structures to interface with cells and biological molecules, and targeted disruption of intracellular structures (e.g., refs. 12 and 31).
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