Laser-assisted internal and surface microstructuring of materials

Eric Mazur
James Carey
Introduction

Laser-Induced Electric Breakdown in Solids

NICOLAAS BLOEMBERGEN, FELLOW, IEEE

Abstract—A review is given of recent experimental results on laser-induced electric breakdown in transparent optical solid materials. A fundamental breakdown threshold exists characteristic for each material. The threshold is determined by the same physical process as dc breakdown, namely, avalanche ionization. The dependence of the threshold on laser pulse duration and frequency is consistent with this process. The implication of this breakdown mechanism for laser bulk and surface damage to optical components is discussed. It also determines physical properties of self-focused filaments.

I. INTRODUCTION

The history of laser-induced electric breakdown is almost as old as the history of lasers itself. Early in 1963 Maker et al. [1] reported damage to transparent dielectrics and the production of a spark in air by focusing a pulsed ruby laser beam. The importance of these results for the production of laser-induced dense plasmas and for the propagation characteristics of high-power laser beams through solids, liquids, and gases was quickly recognized. The subject of electric breakdown in transparent optical solids, including laser materials, windows, and other optical components, remained, until recently, largely an empirical or engineering science. Although a vast amount of theoretical and experimental effort was expended in the economically and technically important problem of optical damage, quantitative reproducible breakdown thresholds with unambiguous theoretical interpretations have been obtained only during the last two years. The situation was somewhat analogous to the development of our understanding of the problem of dc breakdown in electrical insulators. There, too, the field developed largely by engineering trial and error. Basic quantitative understanding was not achieved until reproducible experimental results on well-defined materials were obtained [2]. The difficulties in dc breakdown experiments were manifold: the influence of space charges, the occurrence of space charges, the effects of heating due to high-energy laser pulses, and the effects of heating due to the interaction of a few electrons with a few hot electrons. The situation with laser-induced electric breakdown is quite different.
Introduction

Laser-Induced Electric Breakdown in Solids

NICOLAAS BLOMBERGES

Abstract: A review is given of recent experimental results on laser-induced electric breakdown in transparent optical solid materials. A fundamental threshold exists characteristic for each material. The threshold is determined by the same physical process as the breakdown, depending on the laser pulse duration and intensity. The dependence of the threshold on laser pulse duration and intensity is consistent with this process. The implication of this mechanism for laser-induced damage to optical components is discussed. It also determines physical properties of self-focused laser beams.

The history of laser-induced electric breakdown is traced back to the use of lasers in the early 1960s. More recently, the production of a spark by focusing a high-intensity laser into a material has been an area of intense interest. The importance of these processes has led to the development of an understanding of the physics of laser-induced damage.
use damage for processing!
Outline

- Processing with fs pulses
- High-density carrier dynamics
- Laser-assisted ion etching
Processing with fs pulses

focus laser beam inside material

Processing with fs pulses

100 fs

objective

transparent material

high intensity at focus...
Processing with fs pulses

100 fs

objective

transparent material

... causes nonlinear ionization...
and ‘microexplosion’ causes microscopic damage
Processing with fs pulses

laser deposits energy in ~1 μm³
Processing with fs pulses

100 nm
Processing with fs pulses

2 x 2 µm array

fused silica, 0.65 NA

0.5 µJ, 100 fs, 800 nm

Processing with fs pulses

2 x 2 µm array
fused silica, 0.65 NA
0.5 µJ, 100 fs, 800 nm

2 x 2 µm array

fused silica, 0.65 NA

0.5 µJ, 100 fs, 800 nm

Processing with fs pulses

2 x 2 µm array

fused silica, 0.65 NA

0.5 µJ, 100 fs, 800 nm

Processing with fs pulses

- 100 fs, 0.5 µJ
- 200 ps, 9 µJ
Processing with fs pulses

Dark-field scattering

objective

sample
Processing with fs pulses

block probe beam...
Processing with fs pulses

... bring in pump beam...
Processing with fs pulses

... damage scatters probe beam
Processing with fs pulses
Processing with fs pulses

![Graph showing signal over time for fused silica with 1.0 µJ energy.](image)
Processing with fs pulses

- fused silica
  - 1.0 µJ

- Signal (a.u.):
  - Plasma

- Time (µs):
  - 0.2 0 0.2 0.4 0.6 0.8
Processing with fs pulses

- Signal (a.u.)
- Time (µs)

Fused silica
1.0 µJ

Permanent change
Processing with fs pulses

- Signal (a.u.) vs. time (µs)
- Thermal transient
- Fused silica 1.0 µJ
Low-energy processing

threshold decreases with increasing numerical aperture
Low-energy processing

less than 10 nJ at high numerical aperture!
Low-energy processing

amplified laser

heat-diffusion time: \( \tau_{\text{diff}} \approx 1 \ \mu s \)
Low-energy processing

long-cavity Ti:sapphire oscillator

heat-diffusion time: $\tau_{\text{diff}} \approx 1 \ \mu$s
Low-energy processing

10 µm
Low-energy processing

$10^2$

50 µm
Low-energy processing
Low-energy processing

$10^2$  $10^3$  $10^4$

50 µm
Low-energy processing

$10^2$  $10^3$  $10^4$  $10^5$

50 µm
Low-energy processing

![Graph showing the relationship between number of shots and radius (µm). The x-axis represents the number of shots in a logarithmic scale from $10^1$ to $10^5$, and the y-axis represents the radius in µm from 0 to 12. The graph plots data points that show an increasing trend as the number of shots increases.]
Low-energy processing

waveguide machining
Low-energy processing

waveguide machining
Low-energy processing

waveguide mode analysis
Low-energy processing

near field mode
Low-energy processing

machining speed dependence

refractive index

near field profile

5 mm/s

10 mm/s

20 mm/s

 Courtesy Yossi Chay, Sagitta, Inc.
Low-energy processing

3D wave splitter

He:Ne

output
Processing with fs pulses

- High-density carrier dynamics
- Laser-assisted ion etching
short laser pulses can drive structural transitions
Carrier dynamics

structure determines electronic state

Carrier dynamics

how do femtosecond laser pulses alter a solid?
Carrier dynamics

photons excite valence electrons...
Carrier dynamics

... and create free electrons...
Carrier dynamics

... causing electronic and structural changes...
Carrier dynamics

... which we detect with a second laser pulse
Carrier dynamics

structure

Ga

As
Carrier dynamics

GaAs structure

GaAs –4 –2 energy (eV) 4 2 0

band structure

GaAs

energy (eV)

momentum

L Γ X
Carrier dynamics

structure

GaAs

band structure

momentum

X
Γ
L

GaAs

–4
–2
0
2
4
energy (eV)

dielectric function

Re \( \varepsilon \)

Im \( \varepsilon \)

photon energy (eV)

0
2
4
6

30
20
10
0
–10
–20
–30
–40
dielectric function

GaAs

Carrier dynamics

structure

band structure

dielectric function

GaAs

Ga

As

$E_1$

momentum

GaAs

photon energy (eV)

Re $\varepsilon$

Im $\varepsilon$

$E_1$

energy (eV)

0

2

4

-2

-4

L

$\Gamma$

X
Carrier dynamics

structure

GaAs

band structure

momentum

GaAs

E₁

E₂

energy (eV)

4

2

0

-2

-4

L

Γ

X

dielectric function

GaAs

Re ε

Im ε

dielectric function

photon energy (eV)

30

20

10

0

-10

-20

0

2

4

6

GaAs

E₁

E₂

-20
Carrier dynamics

structure

band structure

GaAs

E₁

E₂

momentum

L
Γ
X

energy (eV)

dielectric function

GaAs

Re ε

Im ε

photon energy (eV)

dielectric function

GaAs

E₁

E₂
Carrier dynamics

structure

GaAs

–4

–2 energy (eV)

4

2

0

GaAs

Γ

L

X

momentum

band structure

dielectric function

–10

–20

–40

–20

–10

0

10

20

30

40

GaAs

Reε

Imε

photon energy (eV)

0.0

10

20

30

40

50

60

0.0

2.0

4.0

6.0

dielectric function
Carrier dynamics

structure

GaAs

band structure

energy (eV)

GaAs

momentum

dielectric function

GaAs

Re $\varepsilon$

Im $\varepsilon$

photon energy (eV)
Carrier dynamics

structure

GaAs

band structure

GaAs

momentum

Γ

X

energy (eV)

0

2

4

–4

Growth

Re \( \varepsilon \)

Im \( \varepsilon \)

dielectric function

photon energy (eV)

0.0

2.0

4.0

6.0

30

20

10

0

–10

–20

–30

–40

GaAs
Carrier dynamics

- dielectric function: ‘fingerprint’ of state
- light can induce structural transitions
broadband time-resolved ellipsometry

Technique

Ti:sapphire

800 nm, 50 fs

0.5 mJ
Technique

broadband time-resolved ellipsometry

Ti:sapphire
800 nm, 50 fs

CaF₂
0.5 mJ
Technique

broadband time-resolved ellipsometry

- Ti:sapphire: 800 nm, 50 fs
- CaF$_2$: 1.7–3.5 eV, 1 µJ
- 0.5 mJ
- Delay
Technique

broadband time-resolved ellipsometry

- Ti:sapphire: 800 nm, 50 fs
- CaF$_2$: 1.7–3.5 eV, 1 µJ
- Delay
- Spectral filter
- 0.5 mJ
Technique

broadband time-resolved ellipsometry

Ti:sapphire
800 nm, 50 fs

CaF$_2$
1.7–3.5 eV
1 µJ

0.5 mJ

spectral filter

spectrograph

delay
Technique

broadband time-resolved ellipsometry
Technique

broadband time-resolved ellipsometry

pump
50 fs, 800 nm, 0.5 mJ

sample

50°
Technique

broadband time-resolved ellipsometry

probes
350–750 nm, 1 µJ

sample
Technique

broadband time-resolved ellipsometry

probes
350–750 nm, 1 µJ

sample

$R_1, R_2$
Technique

broadband time-resolved ellipsometry

probes
350–750 nm, 1 µJ

$R_1$  $R_2$

Fresnel equations
Technique

broadband time-resolved ellipsometry

probes
350–750 nm, 1 μJ

Fresnel equations

Re $\varepsilon(\omega)$
Im $\varepsilon(\omega)$
Results

| energy (eV) | Im $\epsilon$ | Re $\epsilon$ |
| 1.5  | 60            | 0             |
| 2.0  | 40            | 0             |
| 2.5  | 20            | 0             |
| 3.0  | 0             | 0             |
| 3.5  | 0             | 0             |
Results

energy (eV)

Re $\varepsilon$

Im $\varepsilon$

$-500$ fs

dielectric function

energy (eV)
Results
Technique

- direct observation of semiconductor-to-metal transition
- order-disorder transition
Processing with fs pulses

High-density carrier dynamics

Laser-assisted ion etching
Irradiate with 100-fs 10 kJ/m² pulses
Introduction

“black silicon”
Introduction

20 µm
Introduction

- maskless etching process
- self-organized, tall, sharp structures
- nanoscale structure on spikes
Properties

reflectance (integrating sphere)

![Graph](image)

- **wavelength (µm)**
- **reflectance**
- **crystalline silicon**
Properties

reflectance (integrating sphere)

![Graph showing reflectance versus wavelength (μm) for crystalline silicon and microstructured silicon.](image)

- **reflectance**: Reflectance values range from 0 to 1.
- **wavelength (μm)**: The x-axis represents the wavelength in micrometers, ranging from 0 to 3 μm.

The graph illustrates the reflectance properties of crystalline silicon and microstructured silicon over the specified wavelength range.
Properties

transmittance (integrating sphere)

- Transmittance as a function of wavelength in micrometers.
- Crystalline silicon transmittance plot.
Properties

transmittance (integrating sphere)
Properties

absorptance (1 - R - T)

crystalline silicon
Properties

absorptance (1 - R - T)

Properties

Points to keep in mind:

- near unity absorption
- sub-band gap absorption
- IR photoelectron generation
Properties

Points to keep in mind:

- near unity absorption
- sub-band gap absorption
- IR photoelectron generation

Can spikes be used as field emitters?
Properties

field emission setup
Properties

field emission setup

gold coating
Properties

field emission setup

20 µm mica spacers
gold coating
Properties

Field emission setup

Anode

Gold coating
Properties

field emission setup

![Diagram of field emission setup with gold coating and anode.

1 MΩ resistor connected to a voltage source and an ammeter.]}
Properties

- Potential difference (V)
- Current (µA)

Graph showing the relationship between potential difference (V) and current (µA).
turn-on field (1 µA/cm$^2$): 1.2 V/µm
threshold field (10 $\mu$A/cm$^2$): 2.1 V/µm
What causes these properties?

Other gases?
Structural and chemical analysis

Ion channeling and electron backscattering:

- spikes retain crystalline order
- high density of defects
Structural and chemical analysis

Secondary ion mass spectrometry:

- $10^{20}$ cm$^{-3}$ sulfur
- $10^{17}$ cm$^{-3}$ fluorine
Structural and chemical analysis

cross-sectional TEM (F. Génin, M. Wall, LLNL)
Structural and chemical analysis

1 µm

porous “fuzz”

cross-sectional TEM (F. Génin, M. Wall, LLNL)
Structural and chemical analysis

Cross-sectional TEM (F. Génin, M. Wall, LLNL)

1 µm

nanocrystallites
Structural and chemical analysis

Crystalline Si

cross-sectional TEM (F. Génin, M. Wall, LLNL)
Structural and chemical analysis

electron diffraction (F. Génin, M. Wall, LLNL)
Structural and chemical analysis

1 µm

electron diffraction (F. Génin, M. Wall, LLNL)
cross-sectional TEM:

- core of spikes: undisturbed Si
- surface layer: disordered Si, impurities, nanocrystallites and pores
Structural and chemical analysis

anneal 4 hours at 1200 K

![Graph showing absorptance vs. wavelength for microstructured silicon and crystalline silicon.](image)
Structural and chemical analysis

anneal 4 hours at 1200 K

Structural and chemical analysis

anneal 4 hours at 1200 K

Structural and chemical analysis

anneal 4 hours at 1200 K

Structural and chemical analysis

Effects of annealing:

- IR absorption: reduced twofold
- SEM: fewer surface nanostructures
- SIMS: sulfur content reduced twofold
Structural and chemical analysis

sulfur introduces states in the gap

CB

VB
Structural and chemical analysis

sulfur introduces states in the gap

Structural and chemical analysis

states broaden into a band
Structural and chemical analysis

effect of ambient gas on absorptance

![Graph showing the effect of ambient gas on absorptance. The graph plots wavelength (μm) on the x-axis and absorptance on the y-axis. Different gases are compared, including SF6, H2S, H2, and Vacuum. Crystalline Silicon is also shown.]
Structural and chemical analysis

effect of ambient gas on absorptance
Structural and chemical analysis

effect of ambient gas on absorptance

![Graph showing absorptance vs. wavelength for SF$_6$ and Cl$_2$ gases, and crystalline silicon.

- SF$_6$ has a higher absorptance overall compared to Cl$_2$.
- Cl$_2$ shows distinct peaks at certain wavelengths.
- Crystalline silicon has a lower absorptance than both gases across the spectrum.]
Structural and chemical analysis

effect of ambient gas on absorptance

- $\text{SF}_6$
- $\text{Cl}_2$
- $\text{N}_2$

absorptance vs. wavelength (µm)

crystalline silicon
Structural and chemical analysis

effect of ambient gas on absorptance
Cl}_2
## Structural and chemical analysis

<table>
<thead>
<tr>
<th></th>
<th>$\text{SF}_6$</th>
<th>$\text{Cl}_2$</th>
<th>$\text{N}_2$</th>
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<tr>
<td><strong>IR absorption</strong></td>
<td>high</td>
<td>medium</td>
<td>low</td>
<td>low</td>
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<tr>
<td><strong>field emission</strong></td>
<td>high</td>
<td>low</td>
<td>medium</td>
<td>low</td>
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<tr>
<td><strong>SIMS</strong></td>
<td>high $S$</td>
<td>?</td>
<td>?</td>
<td>high $O$</td>
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<tr>
<td><strong>nanostructure</strong></td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
</tr>
</tbody>
</table>
Structural and chemical analysis

- significant incorporation of ambient species
- nanostructured surface layer
- sulfur content correlates with IR absorption
Outlook

- detector technology
- solar cells
- display technology
- sensors
Outlook

- development of spikes
- spike formation through grids
- cell adhesion
- functionalization
can ordering of spikes be improved by using a grid?
Outlook

Si or Ti substrate
Outlook

place grid in front of substrate

10 µm thick Cu or Ni grid

Si or Ti substrate
Outlook

scan laser beam

10 µm thick
Cu or Ni grid

Si or Ti substrate
Outlook

scan laser beam

10 µm thick Cu or Ni grid

Si or Ti substrate
 Outlook

remove grid

Si or Ti substrate
Microstructured silicon

- fabricated by simple, maskless process
Microstructured silicon

- fabricated by simple, maskless process
- can be integrated with microelectronics
Microstructured silicon

- fabricated by simple, maskless process
- can be integrated with microelectronics
- generates IR photocurrent
Summary

Microstructured silicon

- fabricated by simple, maskless process
- can be integrated with microelectronics
- generates IR photocurrent
- provides stable, high field emission current
Microstructured silicon

- fabricated by simple, maskless process
- can be integrated with microelectronics
- generates IR photocurrent
- provides stable, high field emission current
- is durable
Funding: ARO, DoE, NDSEG, NSF

Acknowledgments:

Dr. François Génin (LLNL)
Dr. Arieh Karger (Radiation Monitoring Devices)
Dr. Alf Bjørseth (Scanwafer)
Dr. Tom Mates (UCSB)
Prof. Nico Bloembergen (Harvard University)
Prof. Cynthia Friend (Harvard University)
Prof. Mike Aziz (Harvard University)

For a copy of this talk and additional information, see:

http://mazur-www.harvard.edu
<table>
<thead>
<tr>
<th>Materials</th>
<th>SF$_6$</th>
<th>Cl$_2$</th>
<th>N$_2$</th>
<th>air</th>
<th>vacuum</th>
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<td>![Si SF$_6$]</td>
<td>![Si Cl$_2$]</td>
<td>![Si N$_2$]</td>
<td>![Si air]</td>
<td>![Si vacuum]</td>
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<tr>
<td>Ti</td>
<td>![Ti SF$_6$]</td>
<td>![Ti Cl$_2$]</td>
<td>![Ti N$_2$]</td>
<td>![Ti air]</td>
<td>![Ti vacuum]</td>
</tr>
</tbody>
</table>

**Only in SF$_6$:**

- Ge
- InP

**No spikes in SF$_6$:** Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
Materials

Only in SF$_6$: Si, Ti, Ge

No spikes in SF$_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
No spikes in $\text{SF}_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
Materials

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Si

Ti

Ge

Only in SF$_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
<table>
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Only in SF₆:

- Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
Materials

\begin{tabular}{c c c c c c}
\( \text{Si} \) & \( \text{Cl}_2 \) & \( \text{N}_2 \) & \text{air} & \text{vacuum} \\
\text{Si} & & & & \\
\text{Ti} & & & & \\
\text{Ge} & & & & \\
\end{tabular}

Only in \( \text{SF}_6 \): \( \text{Ag, Al, Cu, Pd, Pt, Rh, Ta} \) and \( \text{GaAs} \)
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Only in SF$_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
Only in SF$_6$: Si, Ge

No spikes in SF$_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
Only in SF$_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

No spikes in SF$_6$: Si, Ti, InP.
### Materials

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Only in SF$_6$: Ge, InP

No spikes in SF$_6$: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
Materials

- Si
- Ti
- Ge

Only in SF<sub>6</sub>: Cl₂, N₂, air, vacuum

No spikes in SF<sub>6</sub>: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs
Results

![Graph showing dielectric function vs. energy](image)

-500 fs

Energy (eV)

Dielectric function

Im $\varepsilon_{\text{ext}}$

Re $\varepsilon_{\text{ext}}$

Im $\varepsilon_{\text{ord}}$

Re $\varepsilon_{\text{ord}}$

1.5 2.0 2.5 3.0 3.5

-20 0 20 40 60
Results

![Graph showing dielectric function vs. energy (eV). The graph includes plots for Im $\varepsilon_{ext}$, Im $\varepsilon_{ord}$, Re $\varepsilon_{ext}$, and Re $\varepsilon_{ord}$, with energy values ranging from 1.5 to 3.5 eV and dielectric function values ranging from -20 to 60. The graph is labeled with the time point -500 fs.]
Properties
Properties

maximum current: 20 mA (4 mm$^2$ sample)
Properties

absorptance \((1 - R - T)\)

![Graph showing absorptance versus wavelength for different silicon materials.](image)

Properties

avalanche photodiode response at 1.3 $\mu$m

[Graph showing the relationship between bias (V) and APD signal (a.u.) for crystalline and microstructured samples.]
Structural and chemical analysis

effect of ambient gas on field emission

![Graph showing the effect of potential difference on current for SF6]
Structural and chemical analysis

effect of ambient gas on field emission

![Graph showing the effect of SF₆ and Cl₂ on field emission](image)
Structural and chemical analysis

effect of ambient gas on field emission

![Graph showing the effect of potential difference (V) on current (mA) for SF$_6$, N$_2$, and Cl$_2$ gases.](image)
Structural and chemical analysis

effect of ambient gas on field emission

![Graph showing the effect of ambient gas on field emission](image.png)
Summary