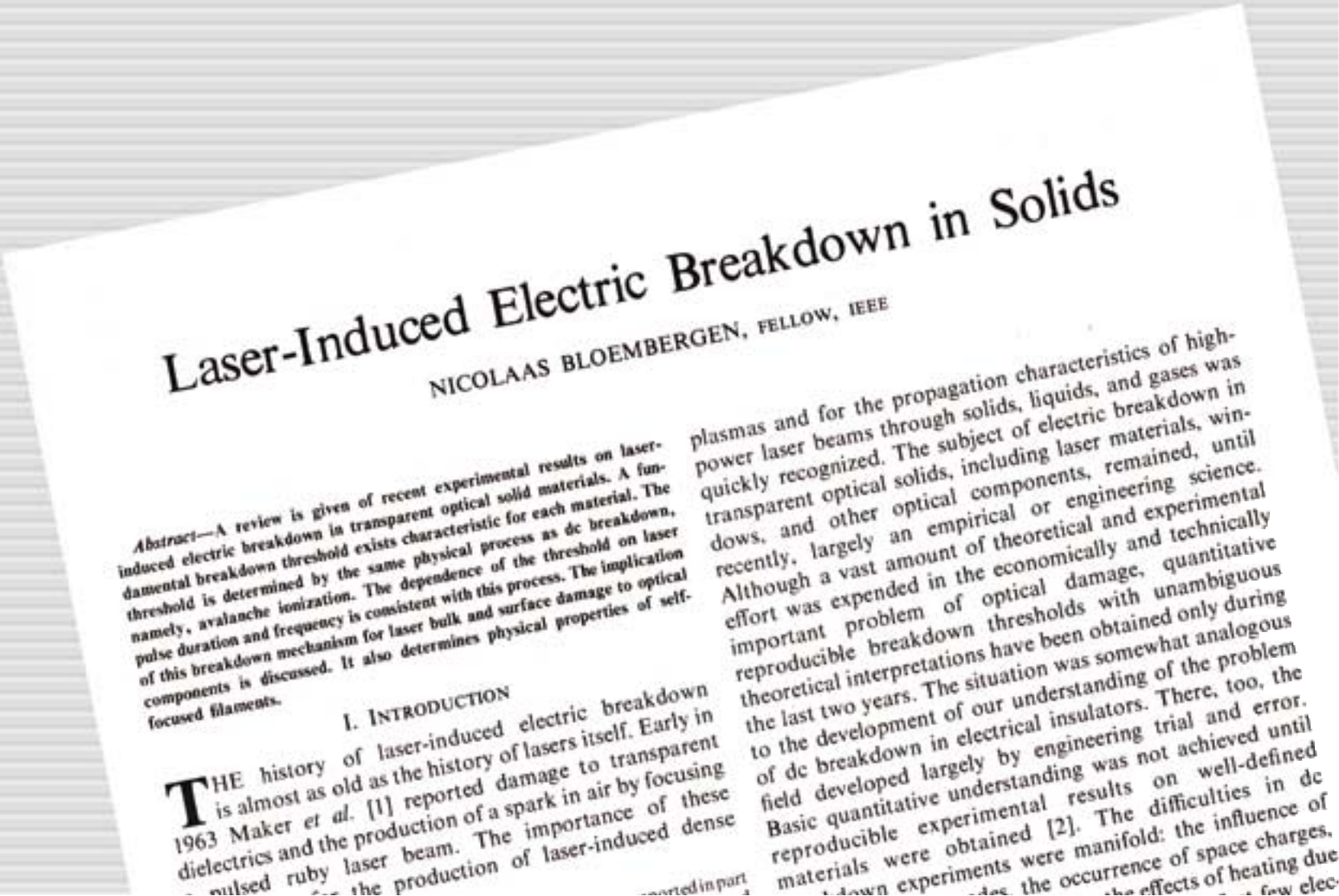
Laser-assisted internal and surface microstructuring of materials

Eric Mazur
James Carey

University of Michigan
29 August 2002

Introduction



Laser-Induced Electric Breakdown in Solids

NICOLAAS BLOEMBERGEN, FELLOW, IEEE

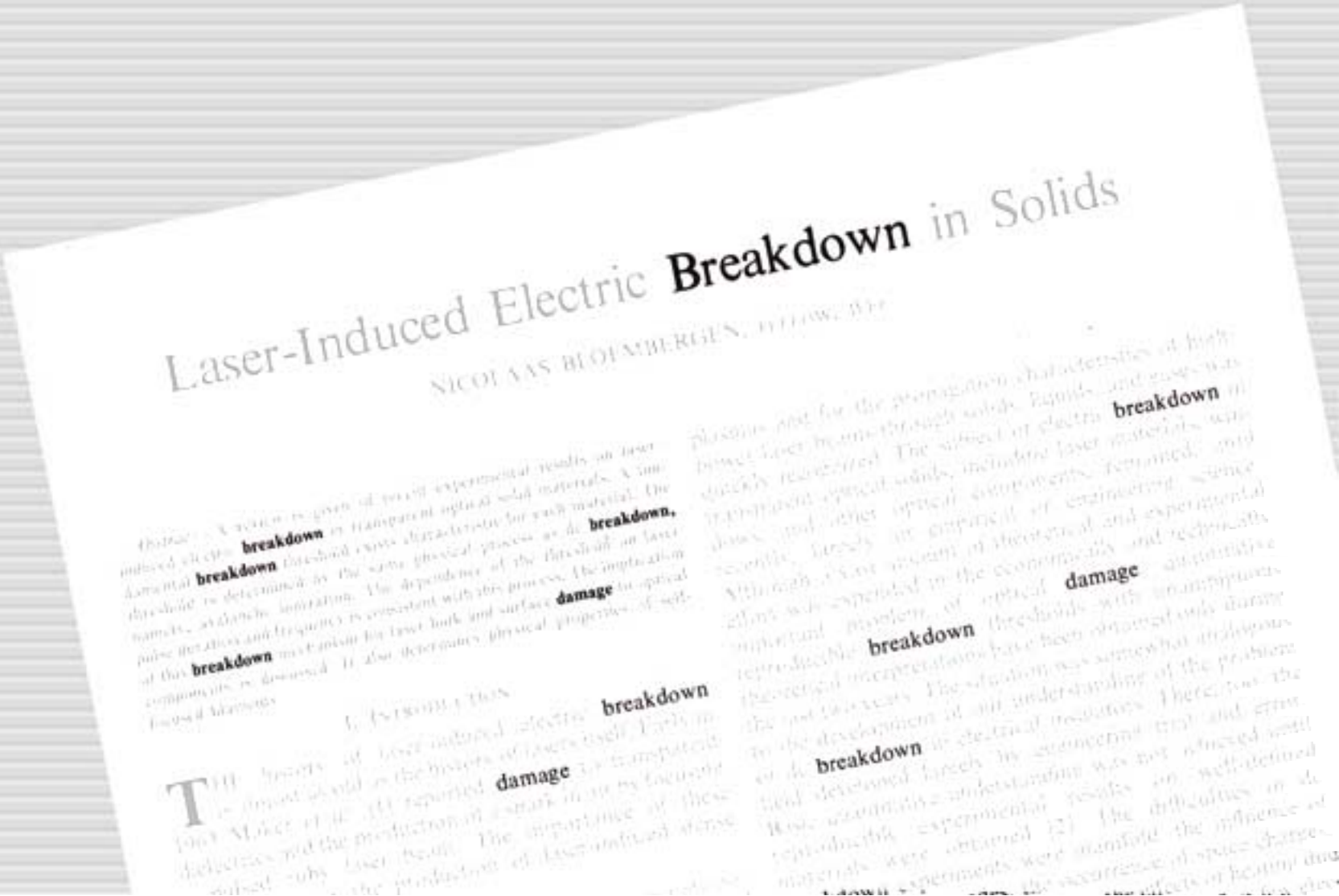
Abstract—A review is given of recent experimental results on laser-induced electric breakdown in transparent optical solid materials. A fundamental breakdown threshold exists characteristic for each material. The threshold is determined by the same physical process as dc breakdown, namely, avalanche 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 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 electrodes, the occurrence of space charges, the effects of heating due

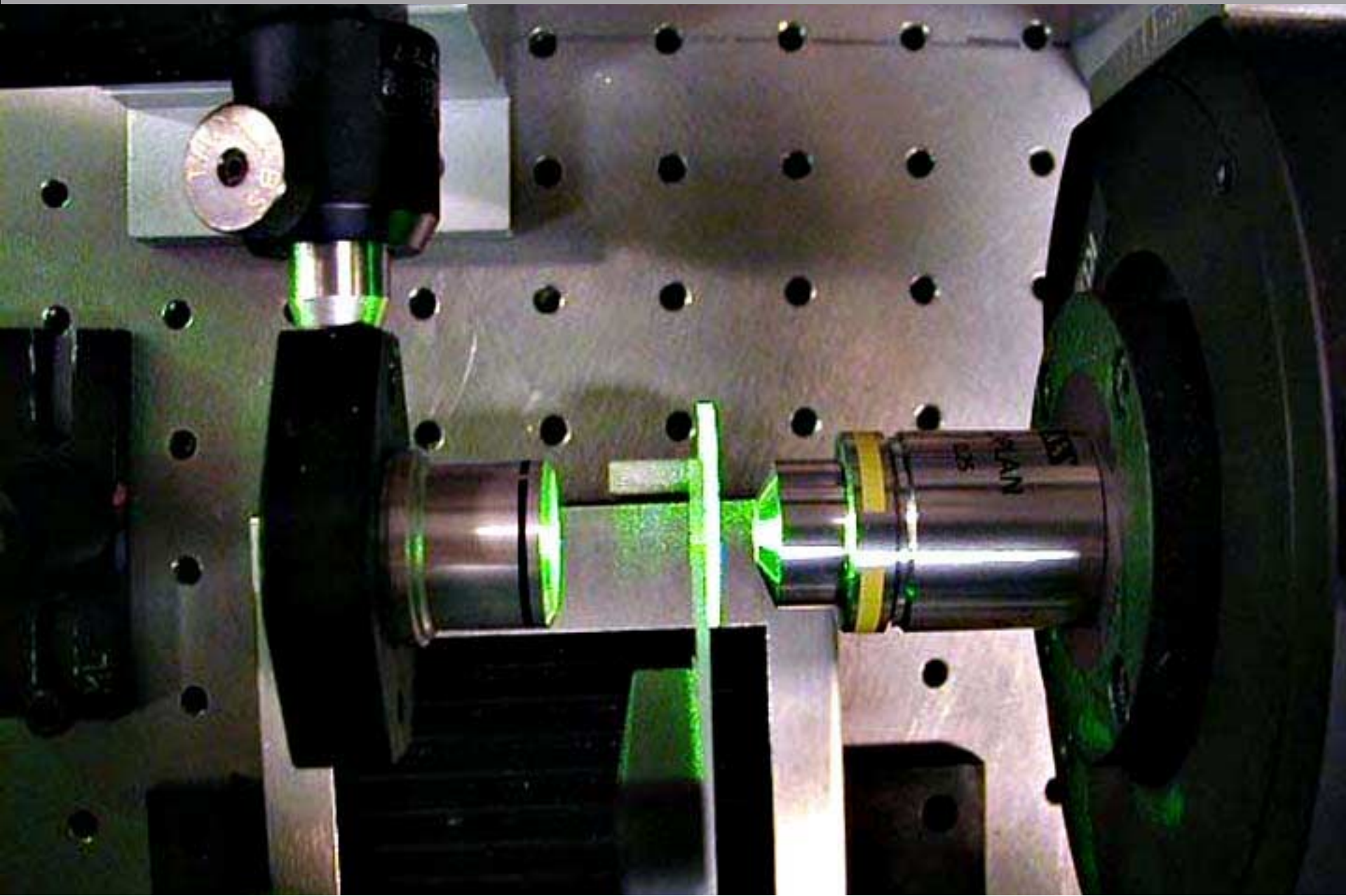
Introduction



Introduction

use damage for processing!

Outline

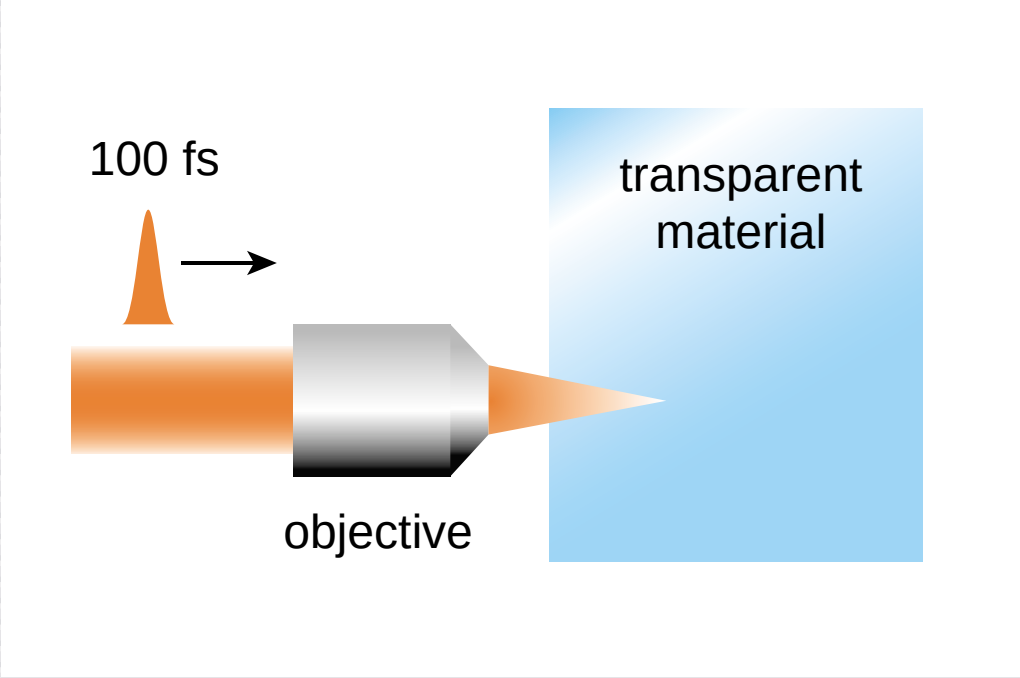


Outline

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

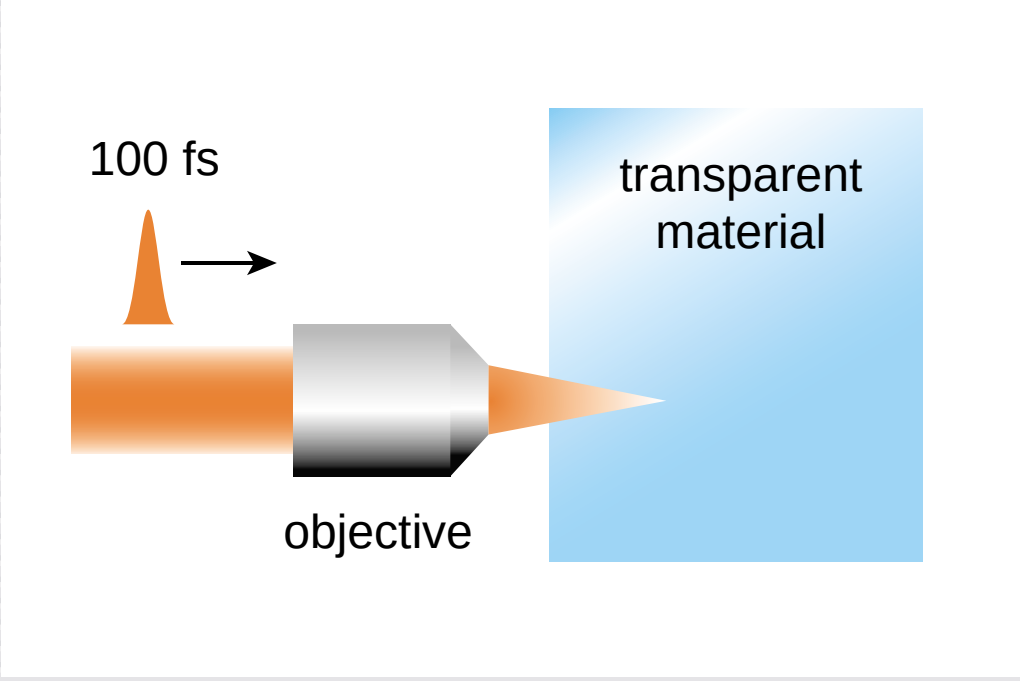
Processing with fs pulses

focus laser beam inside material



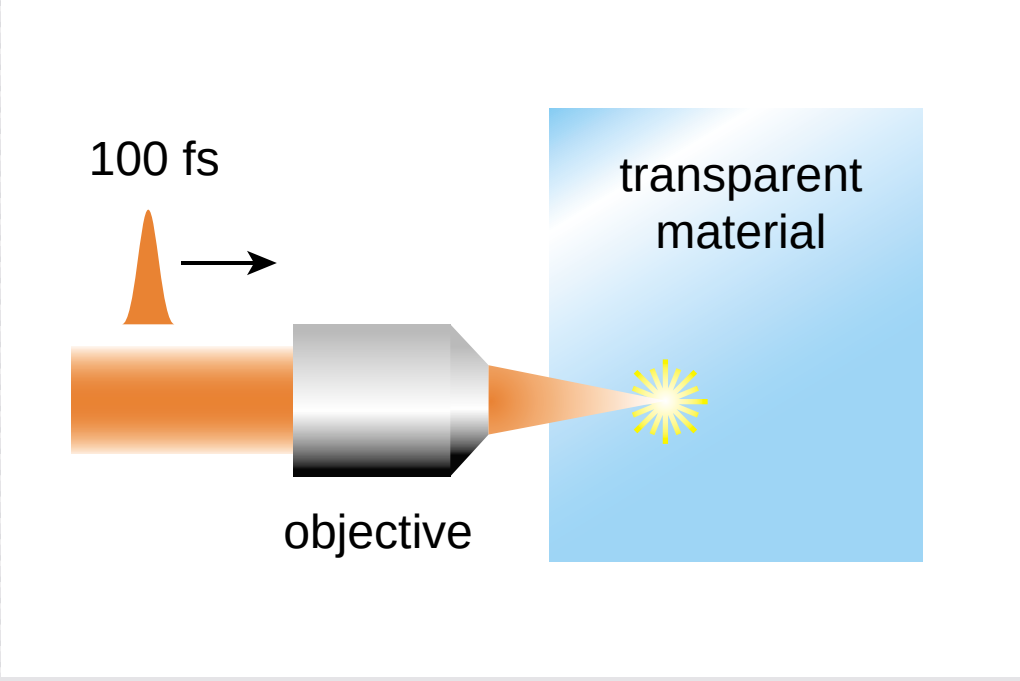
Glezer, *et al.*, *Opt. Lett.* 21, 2023 (1996)

Processing with fs pulses



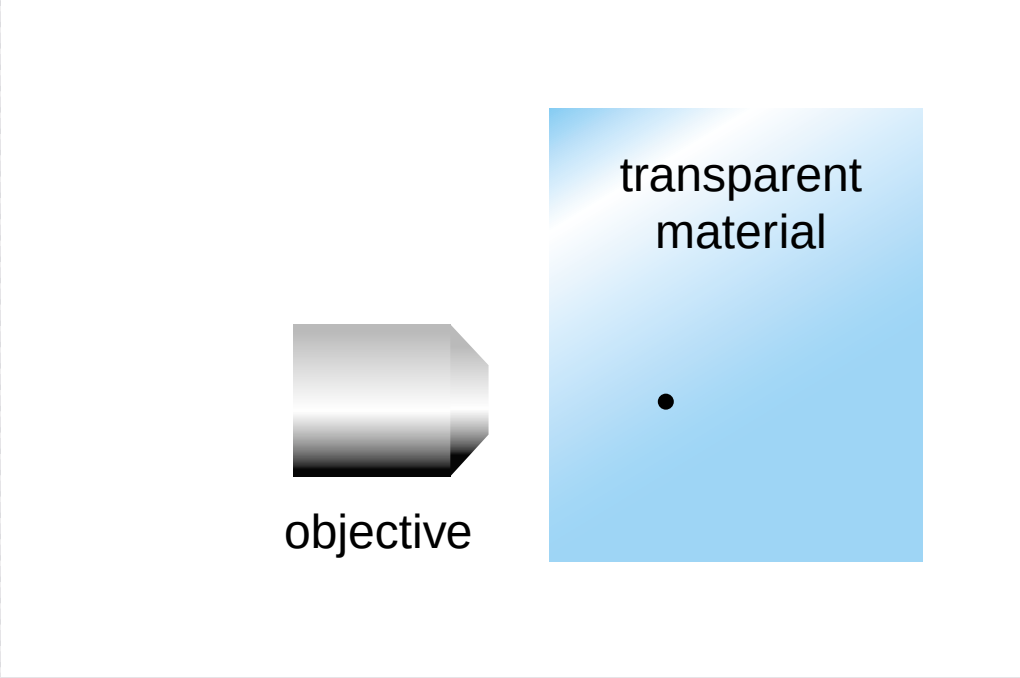
high intensity at focus…

Processing with fs pulses



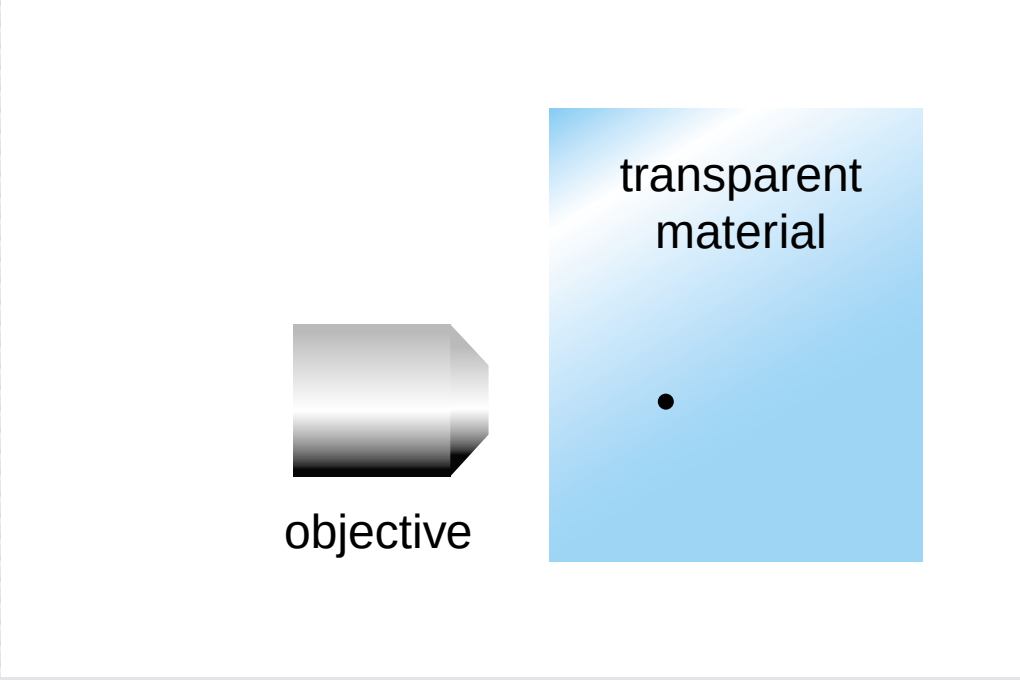
… causes nonlinear ionization…

Processing with fs pulses



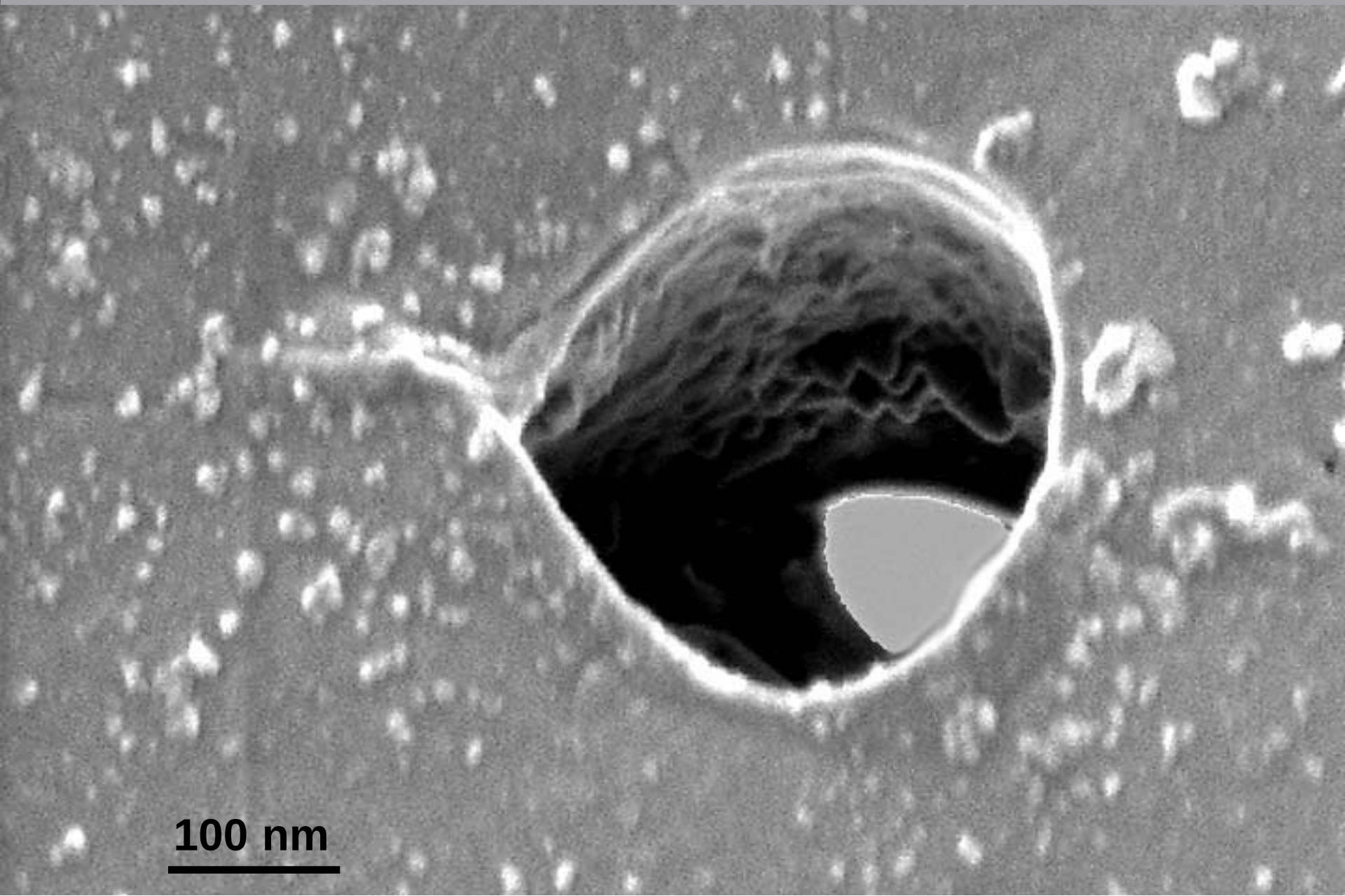
and ‘microexplosion’ causes microscopic damage

Processing with fs pulses



laser deposits energy in ~1 μm^3

Processing with fs pulses

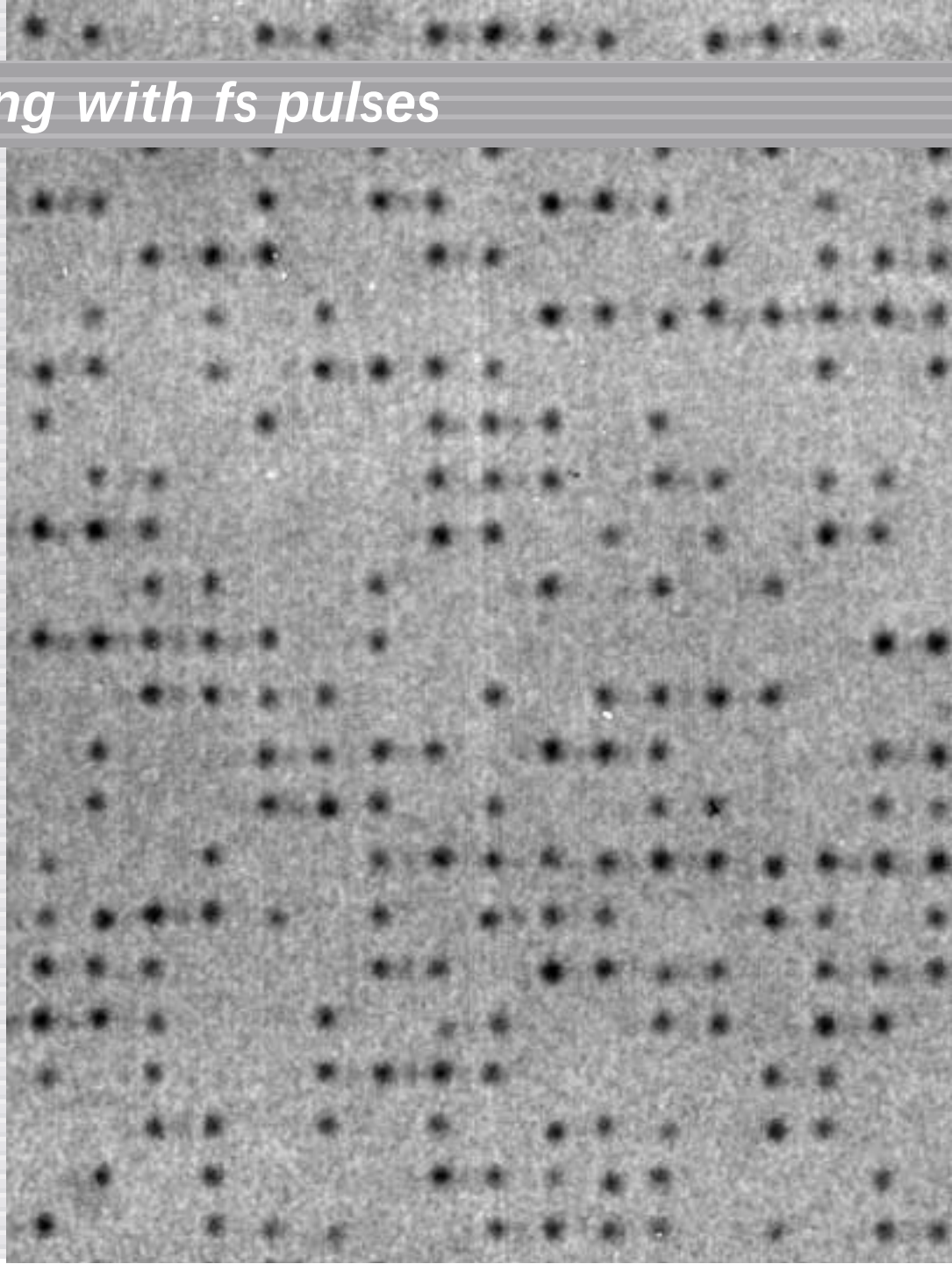


Processing with fs pulses

2 x 2 μm array

fused silica, 0.65 NA

0.5 μJ, 100 fs, 800 nm



***Opt. Lett.* 21, 2023 (1996)**

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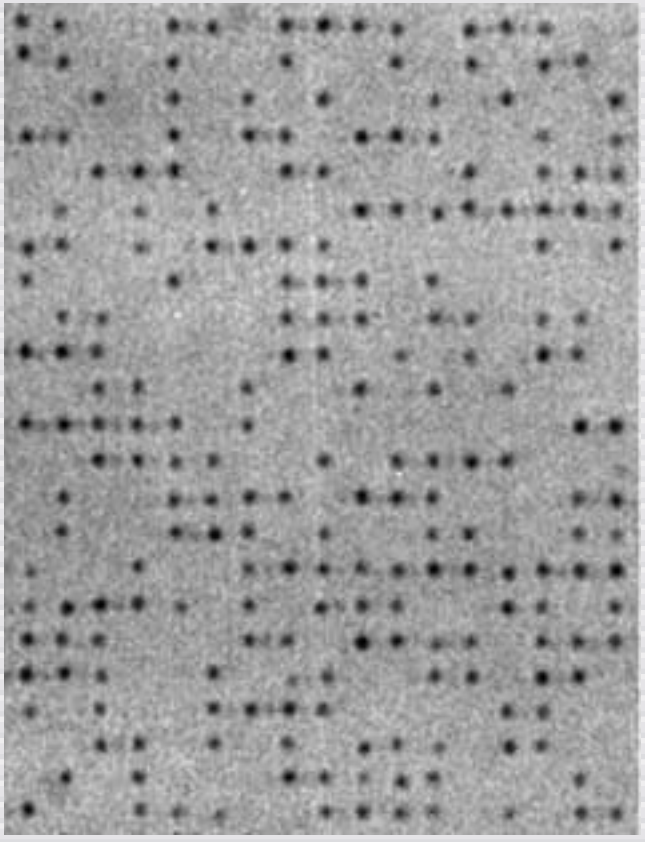

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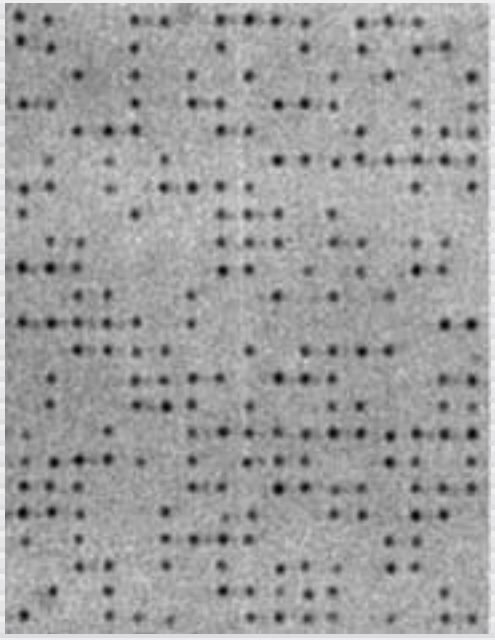

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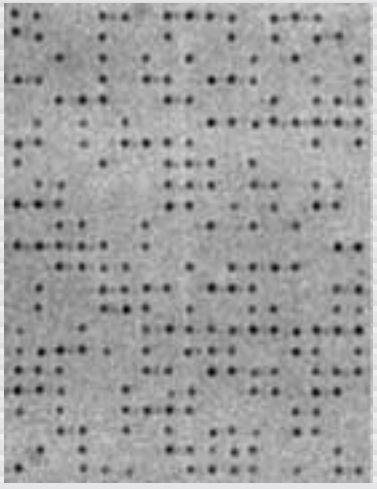
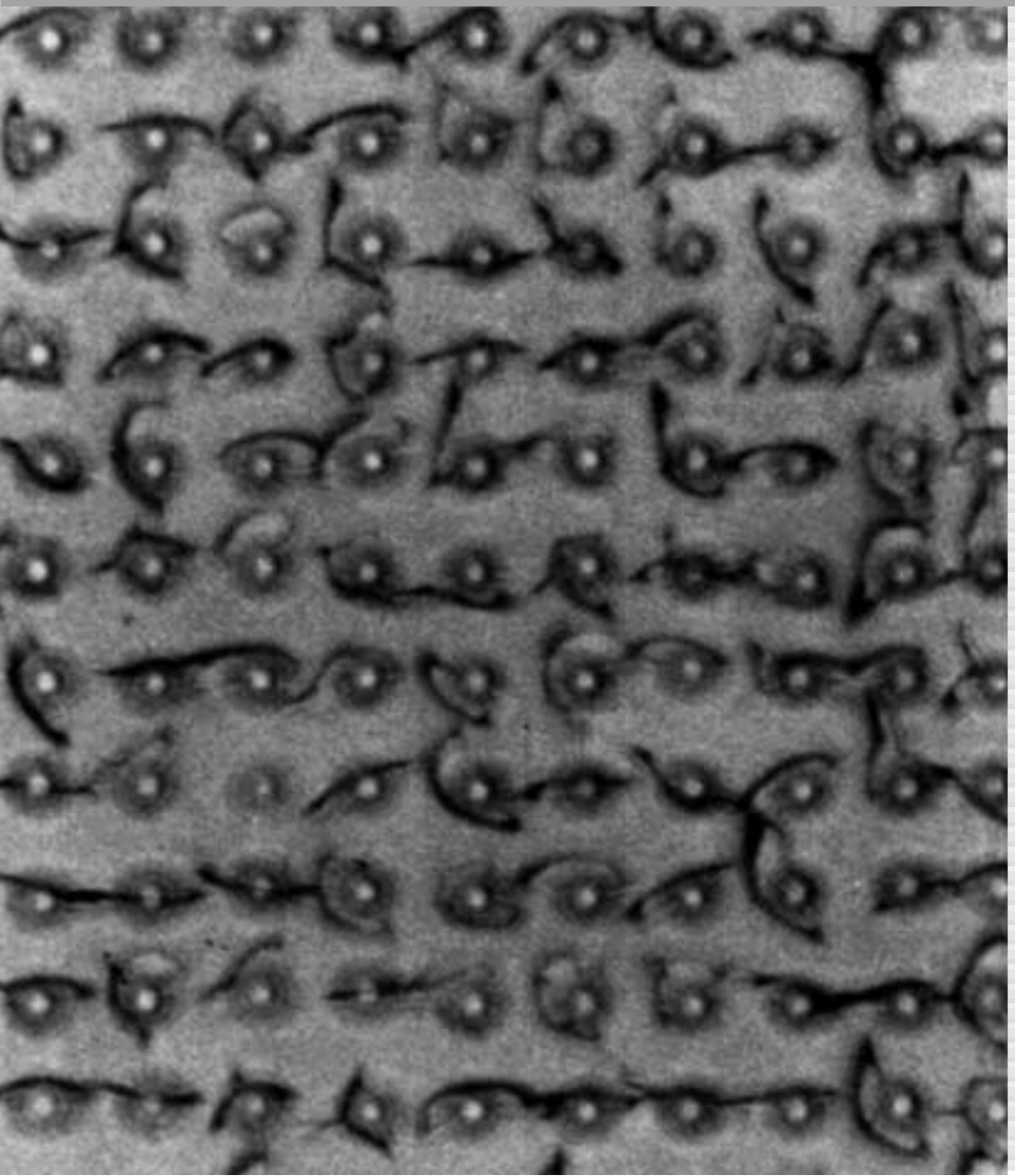
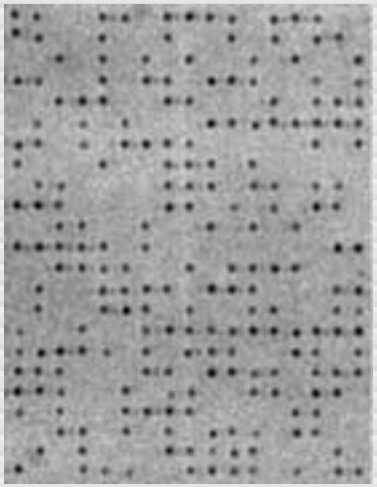


***Opt. Lett.* 21, 2023 (1996)**

Processing with fs pulses

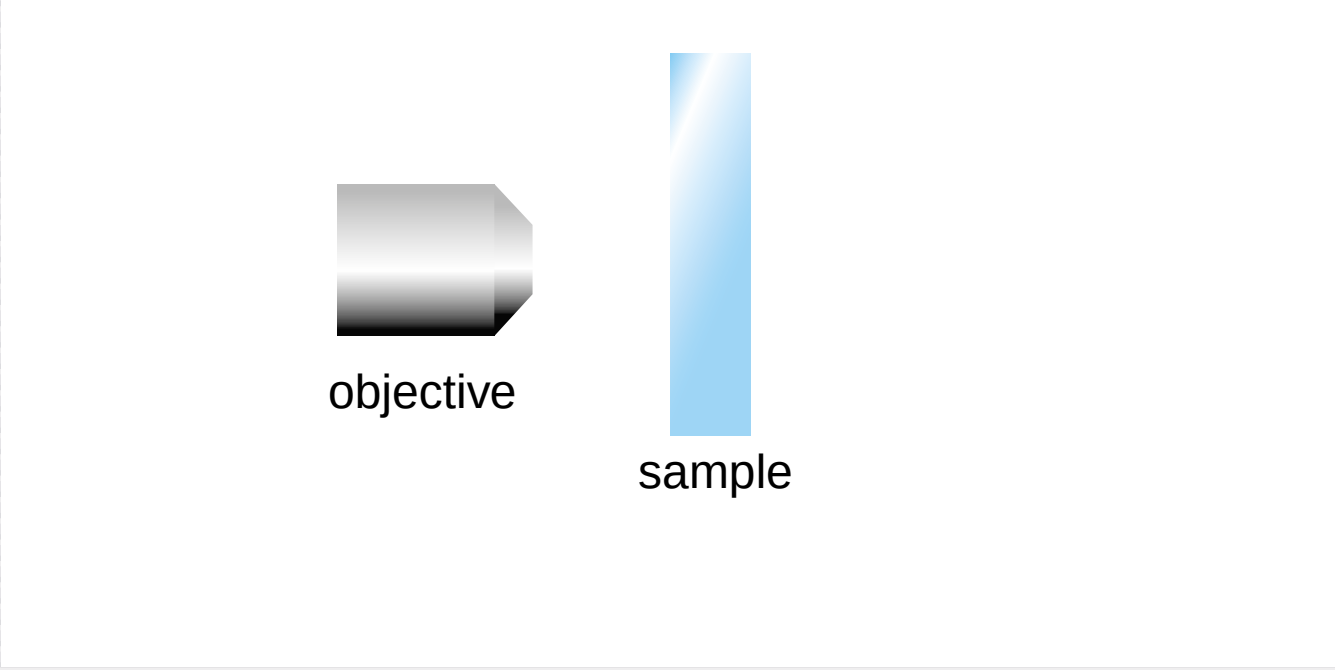




100 fs
0.5 µJ

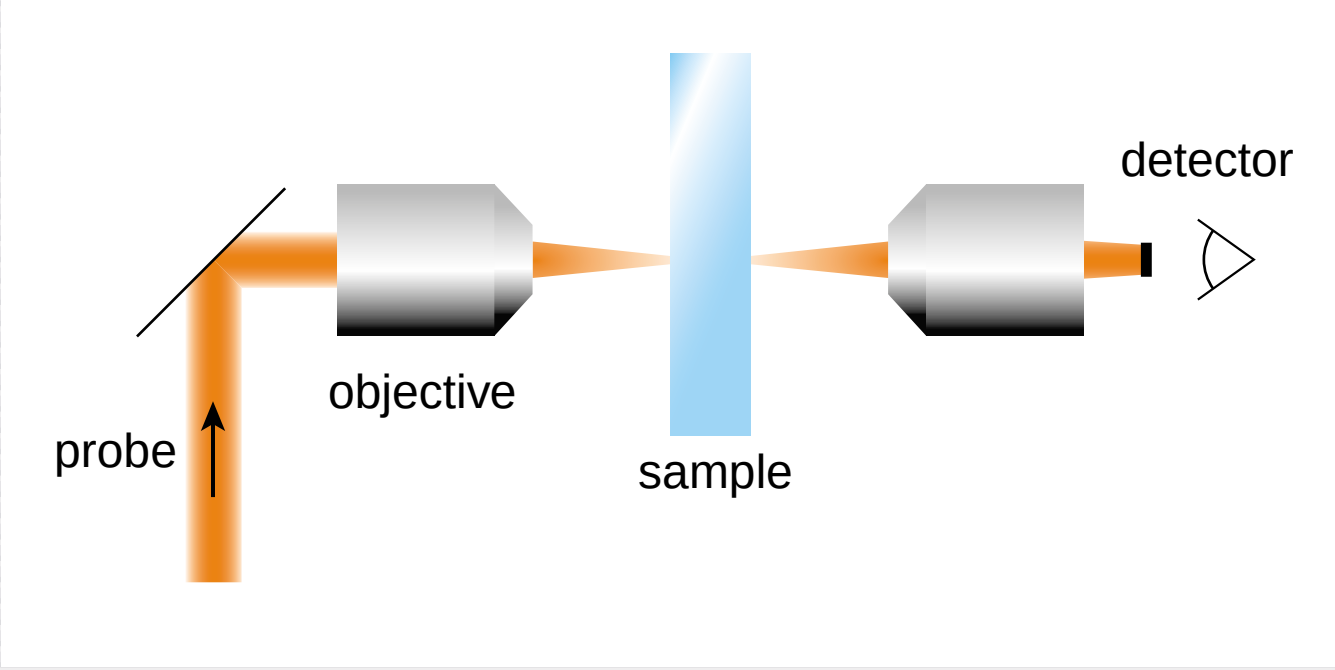
200 ps
9 µJ

Dark-field scattering



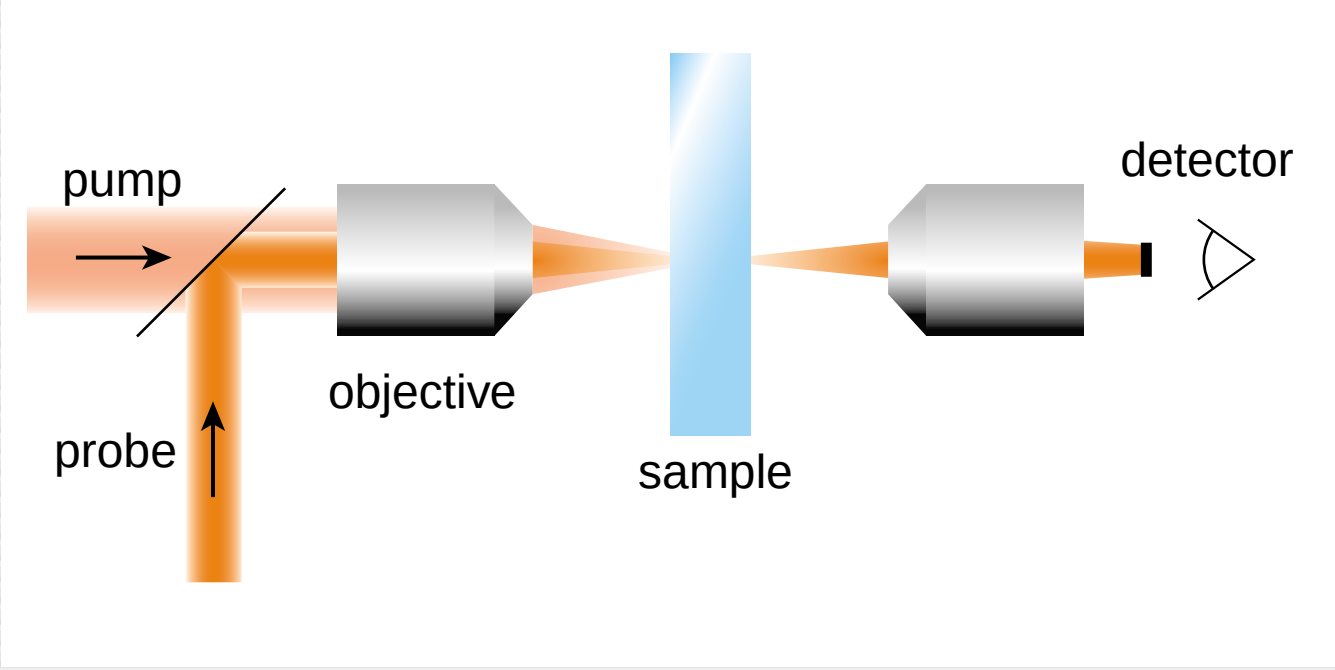
Processing with fs pulses

block probe beam…



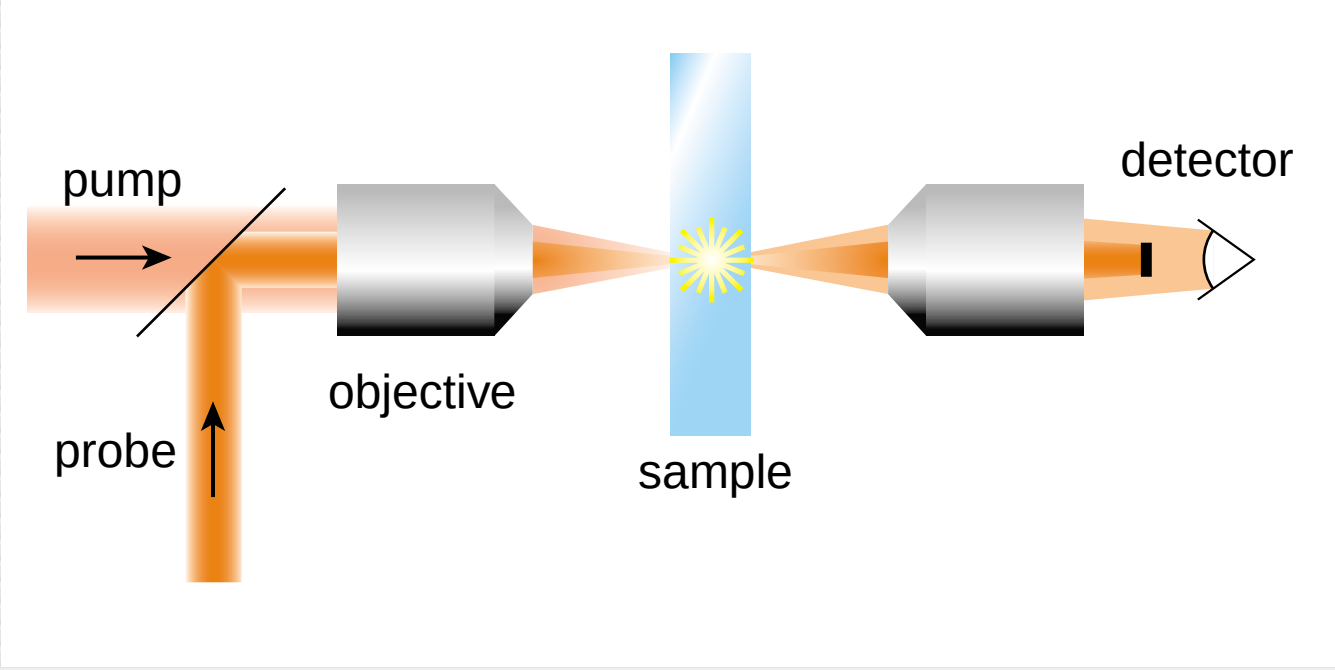
Processing with fs pulses

… bring in pump beam…

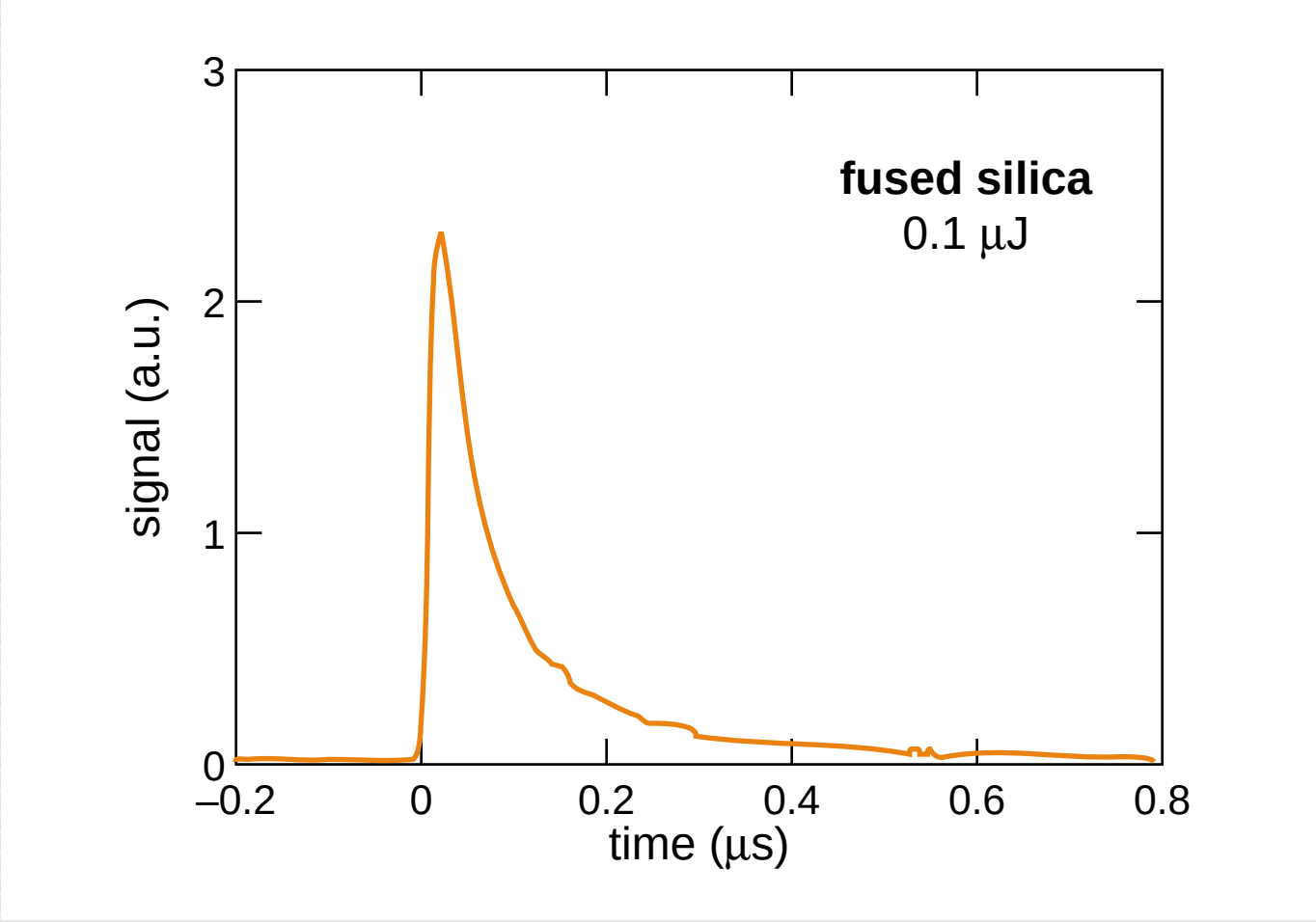


Processing with fs pulses

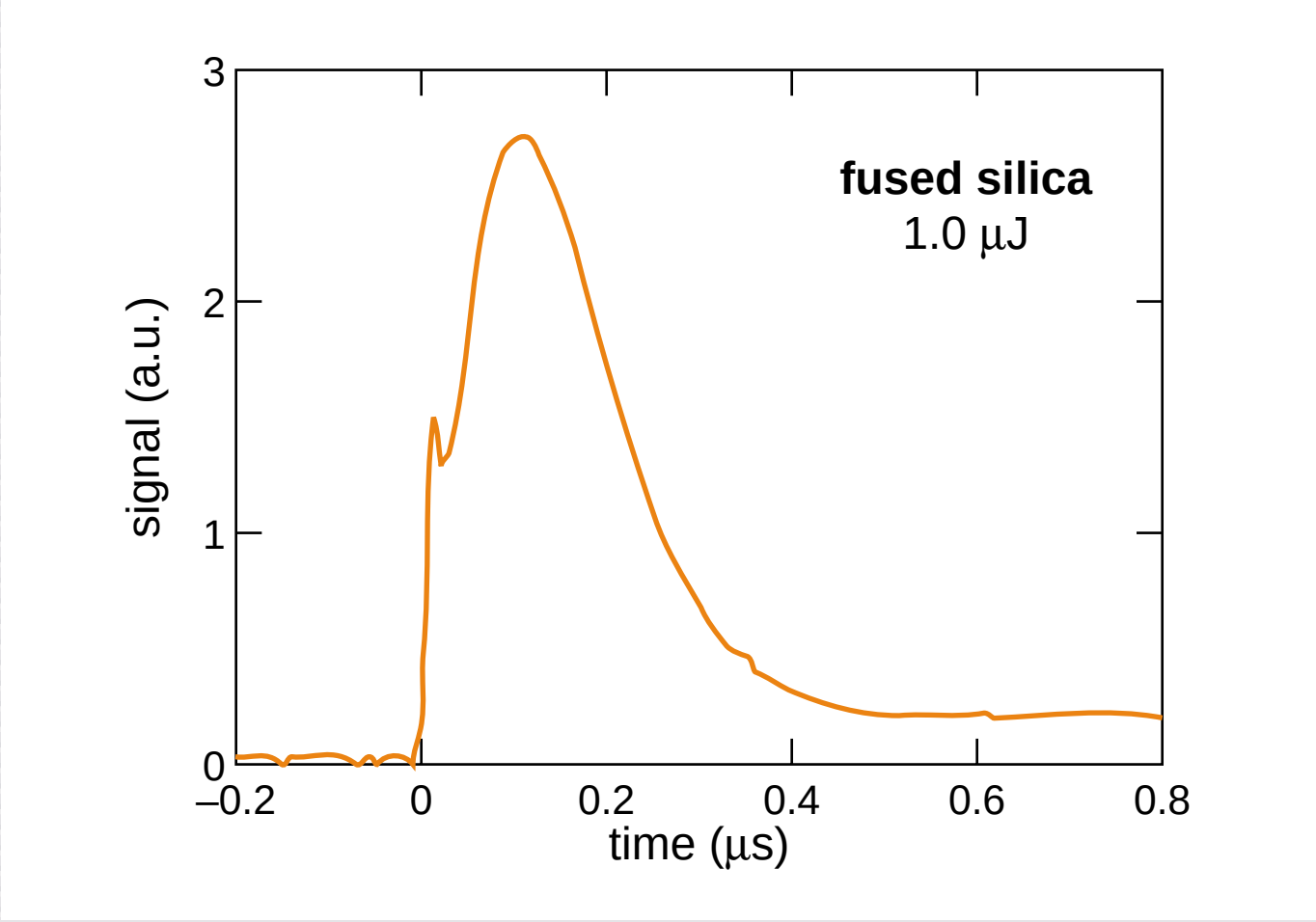
… damage scatters probe beam



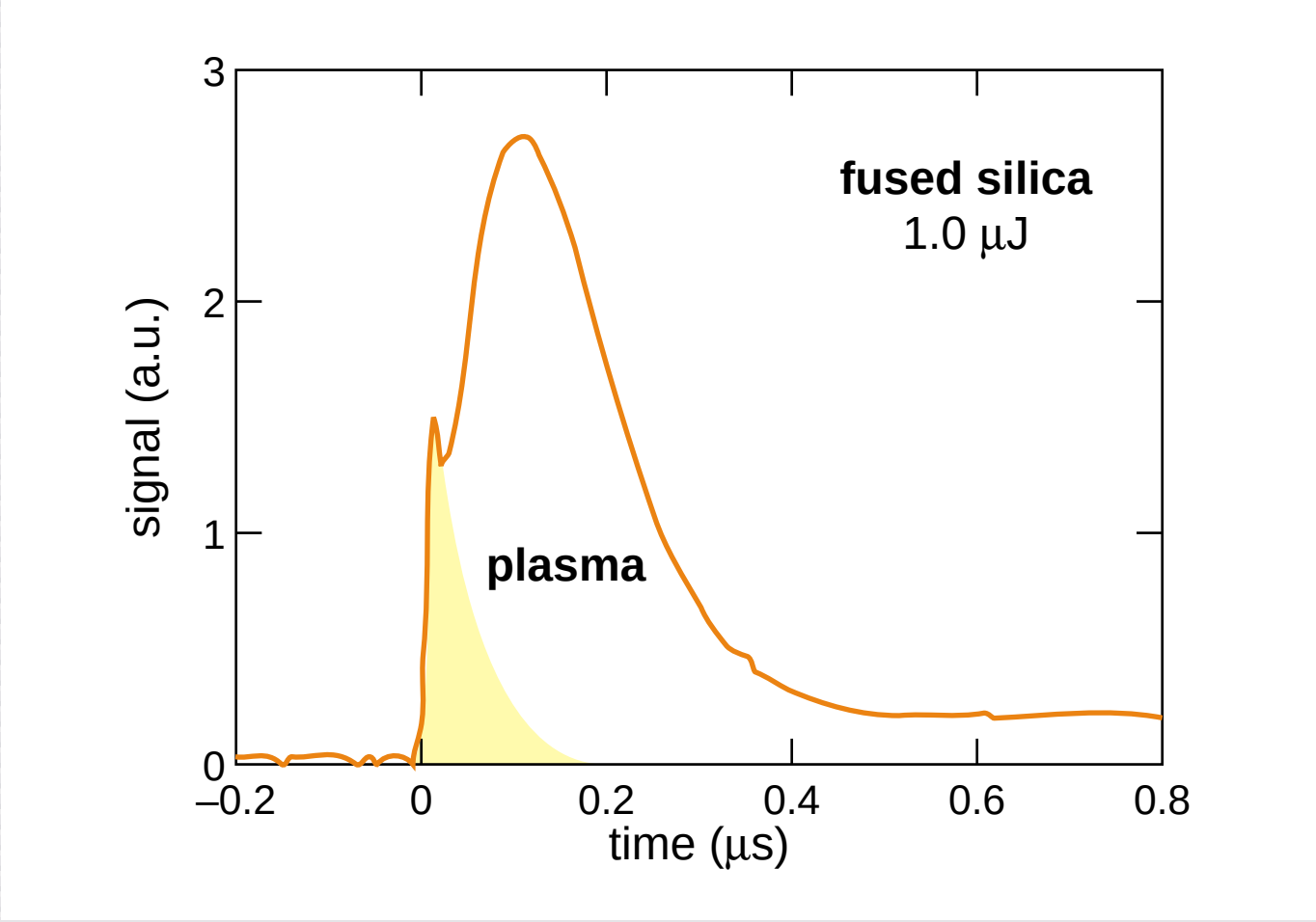
Processing with fs pulses



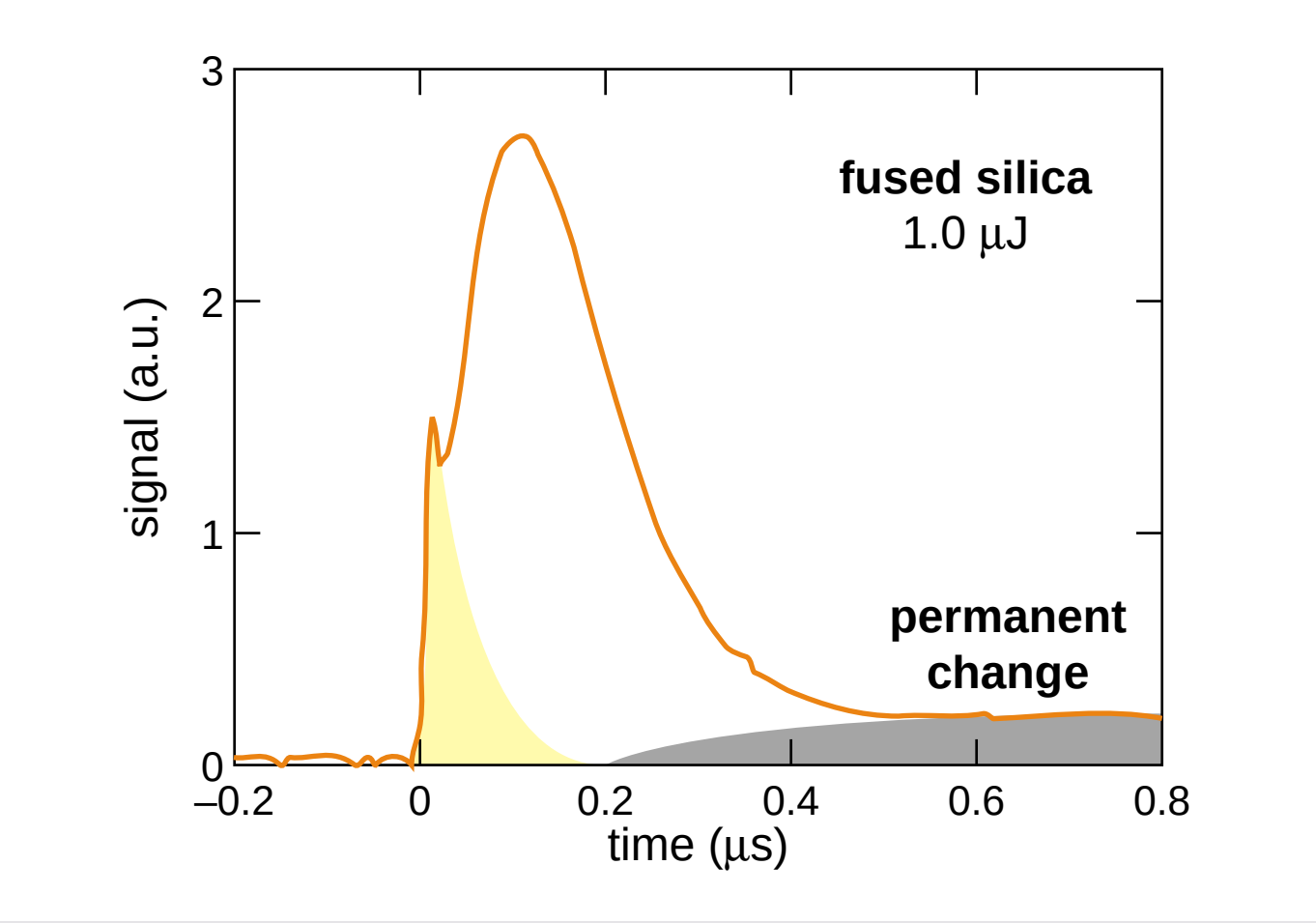
Processing with fs pulses



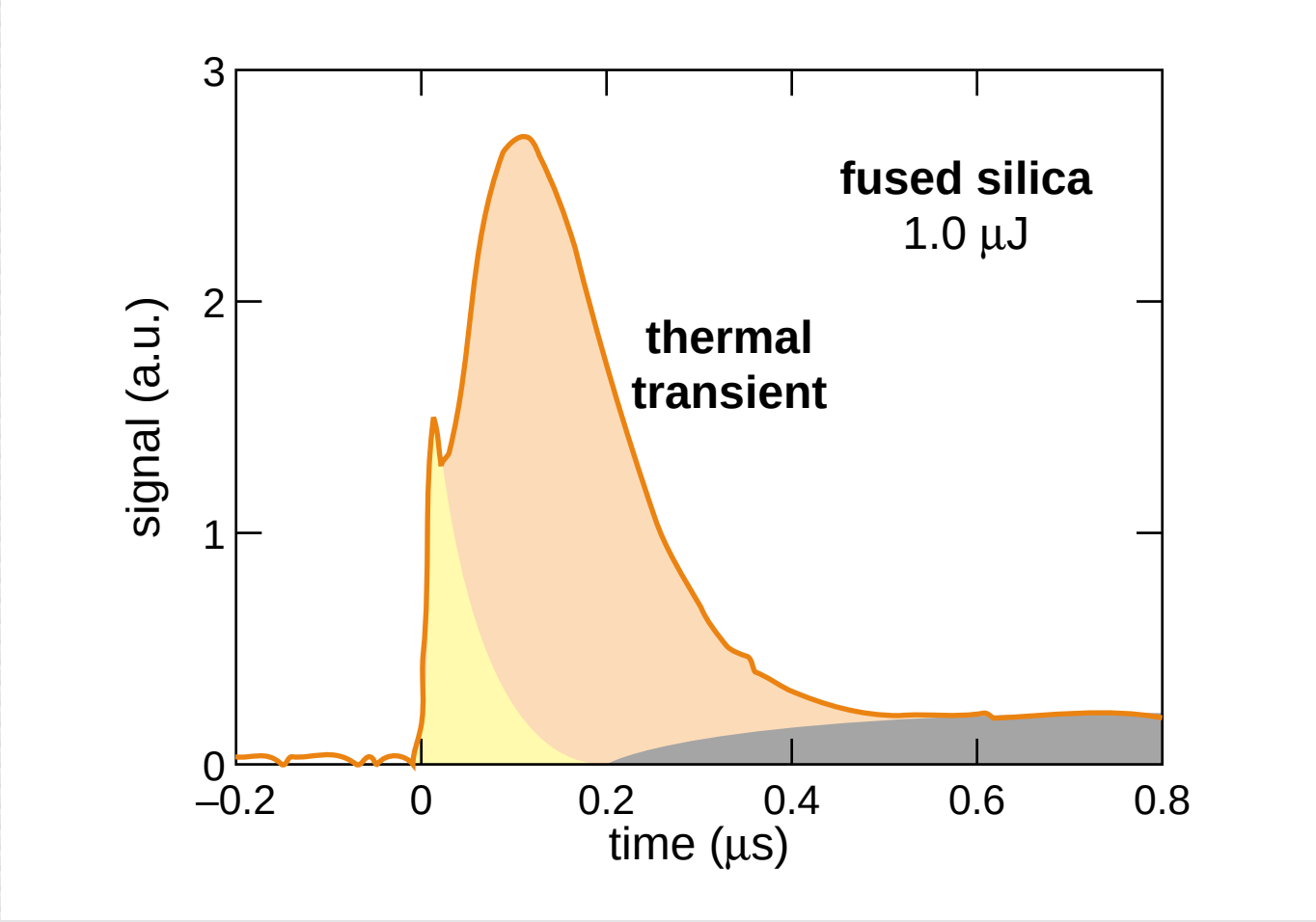
Processing with fs pulses



Processing with fs pulses

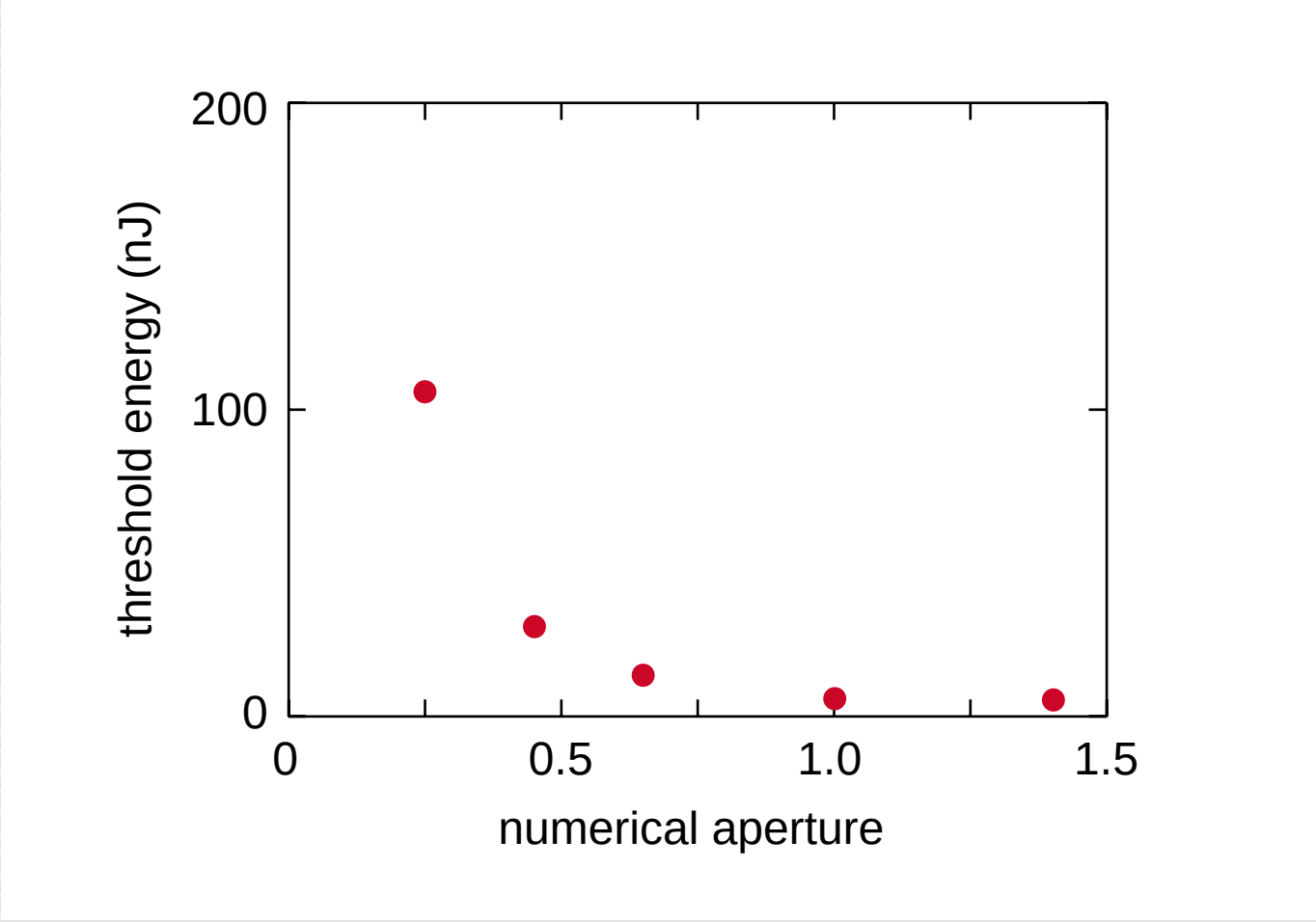


Processing with fs pulses



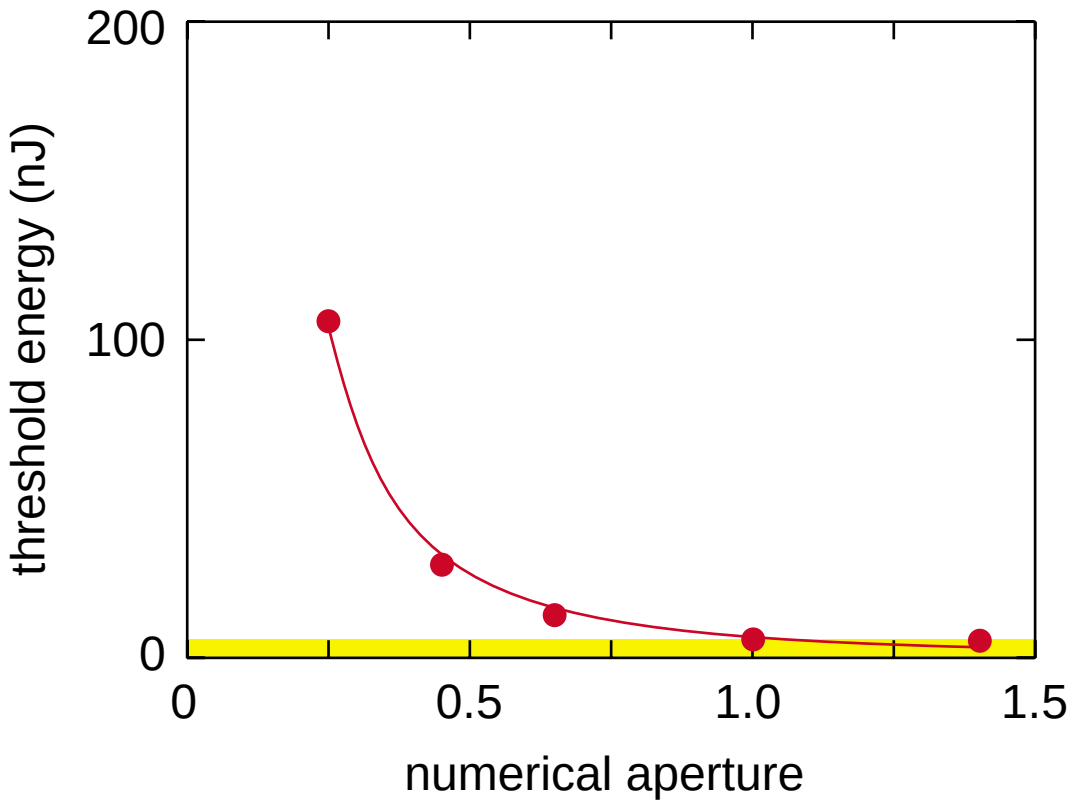
Low-energy processing

threshold decreases with increasing numerical aperture



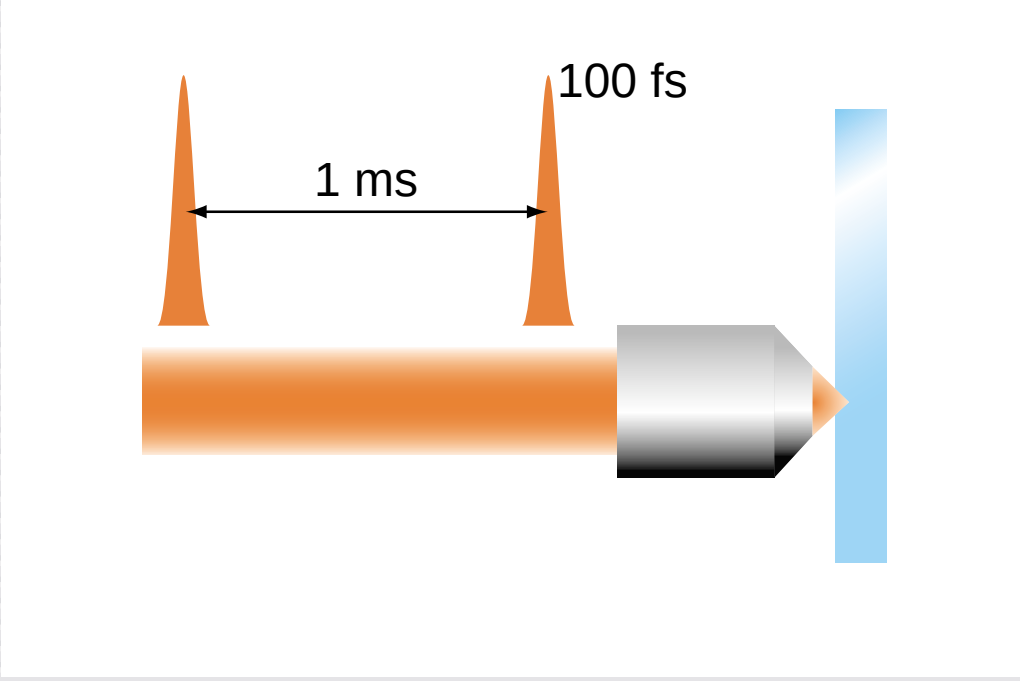
Low-energy processing

less than 10 nJ at high numerical aperture!



Low-energy processing

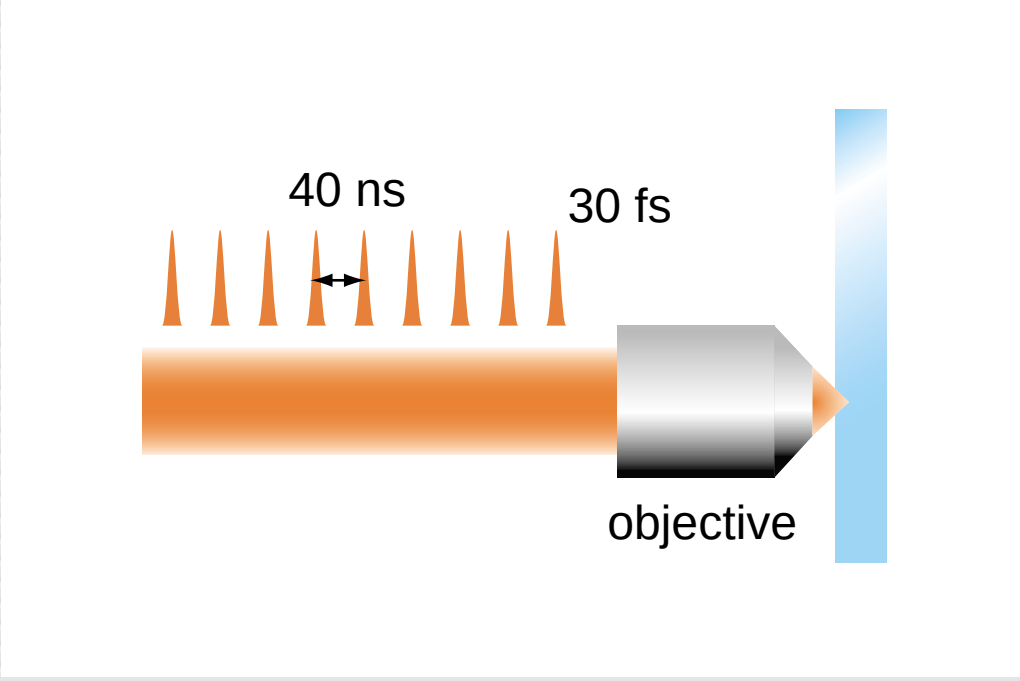
amplified laser



heat-diffusion time: $\tau_{diff} \approx 1\ \mu s$

Low-energy processing

long-cavity Ti:sapphire oscillator



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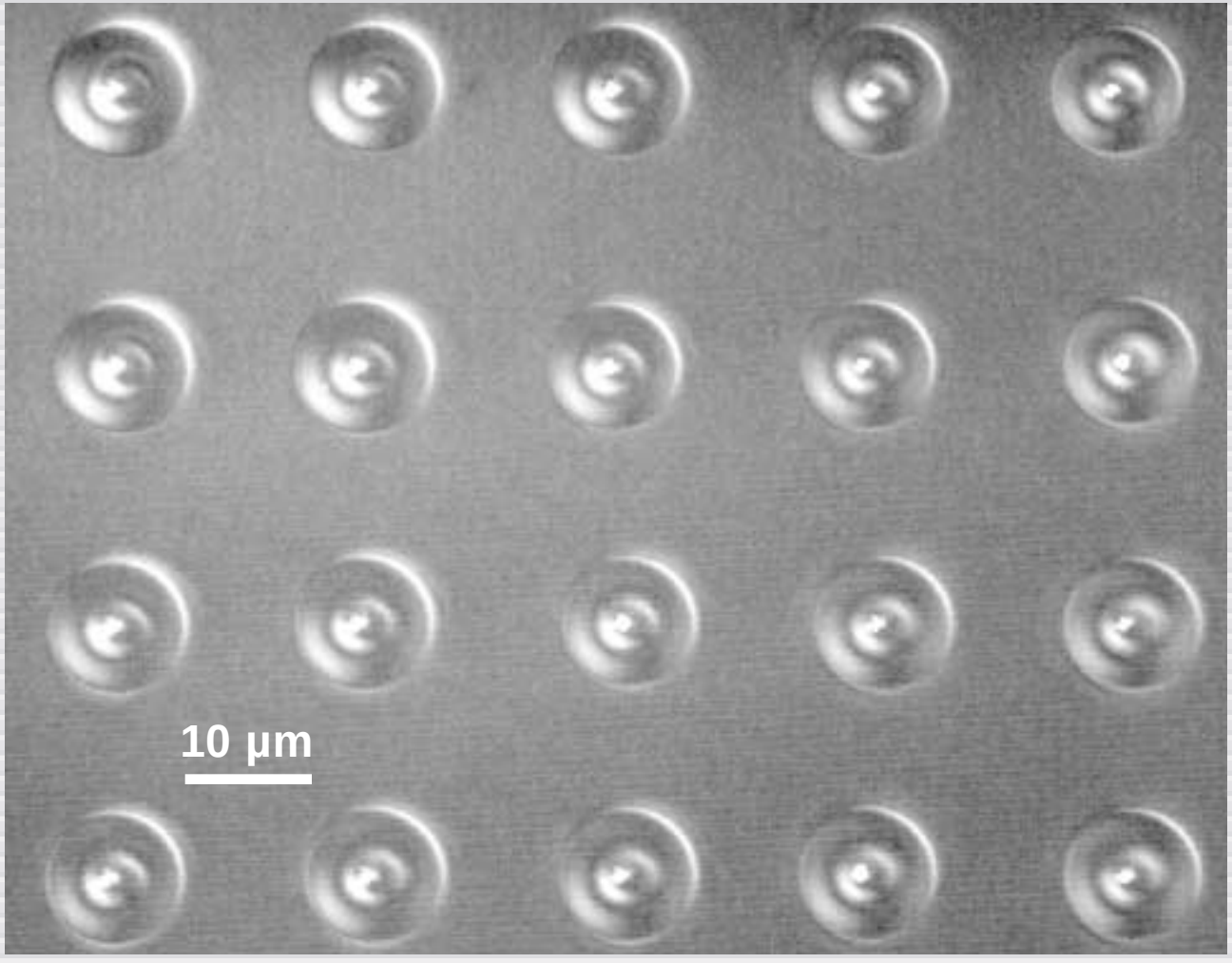
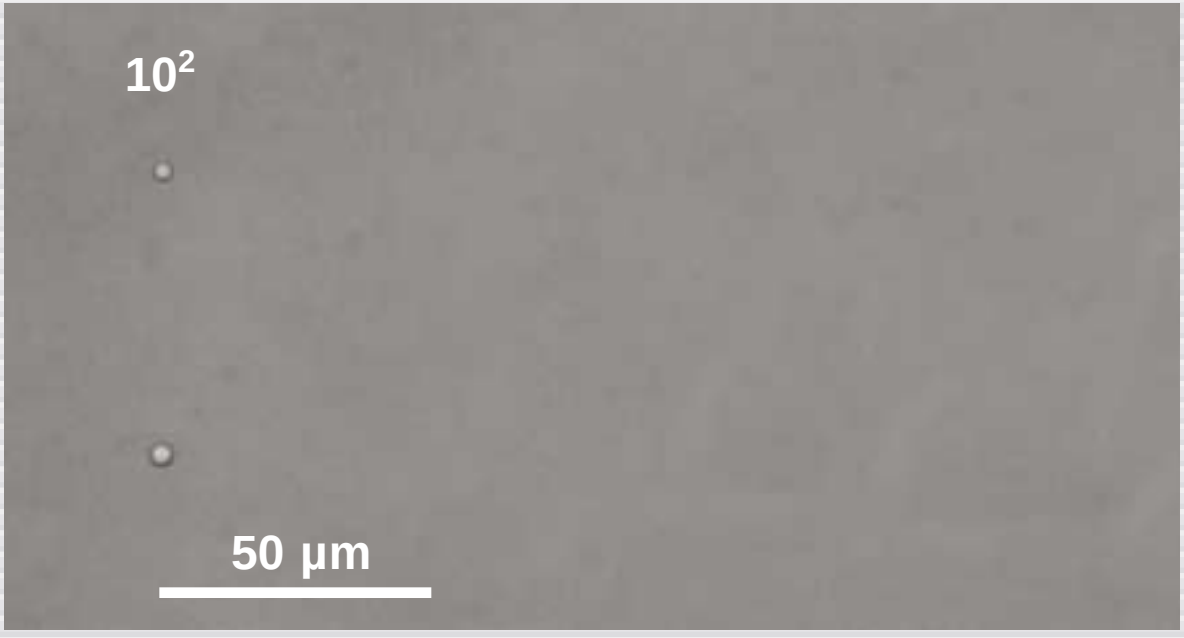
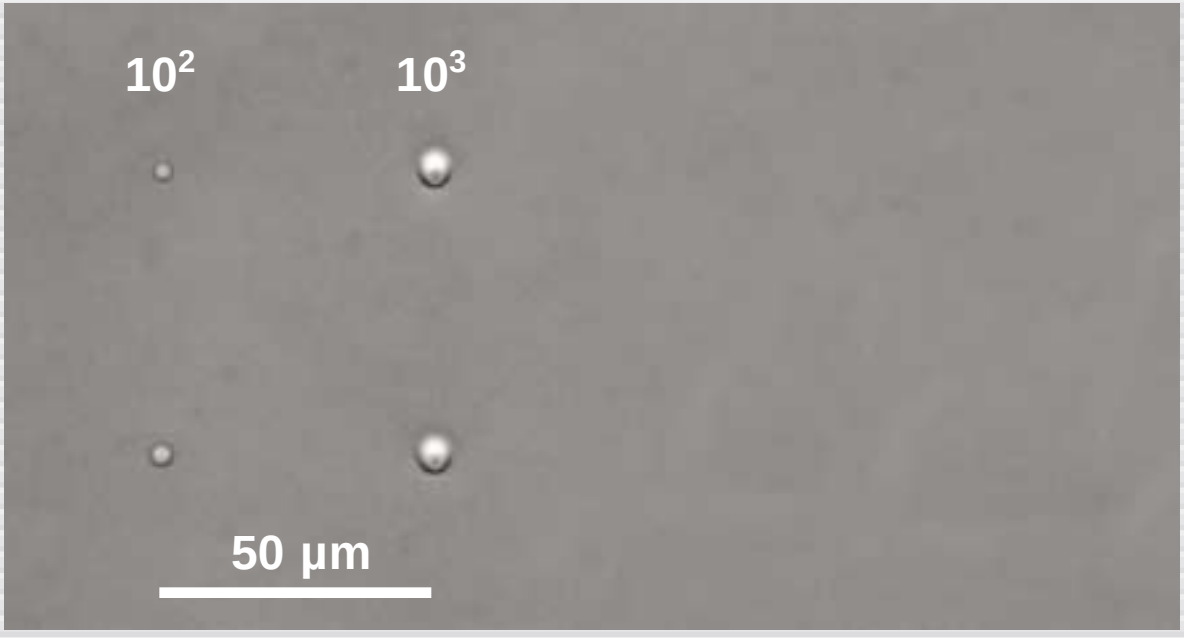
Low-energy processing



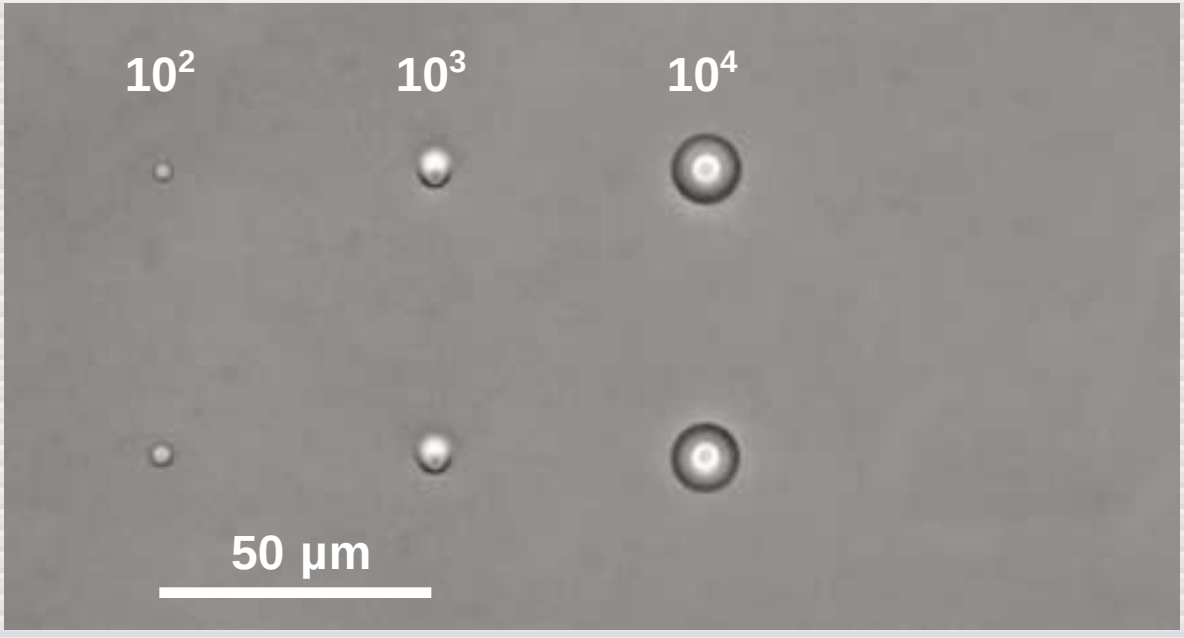
Low-energy processing



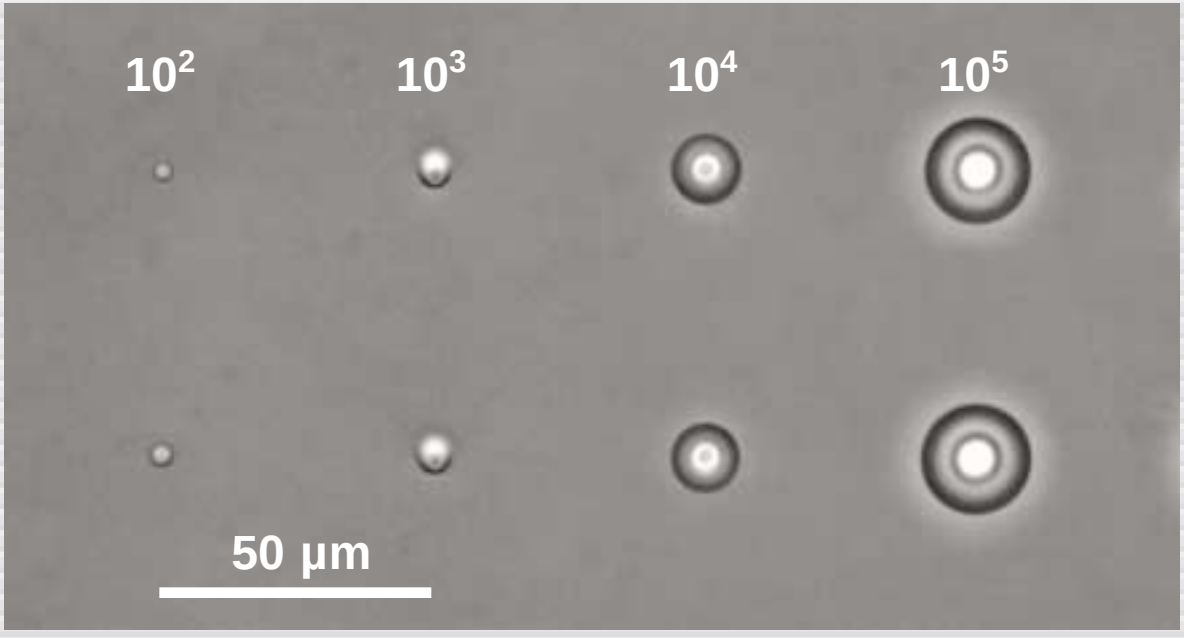
Low-energy processing



Low-energy processing



Low-energy processing



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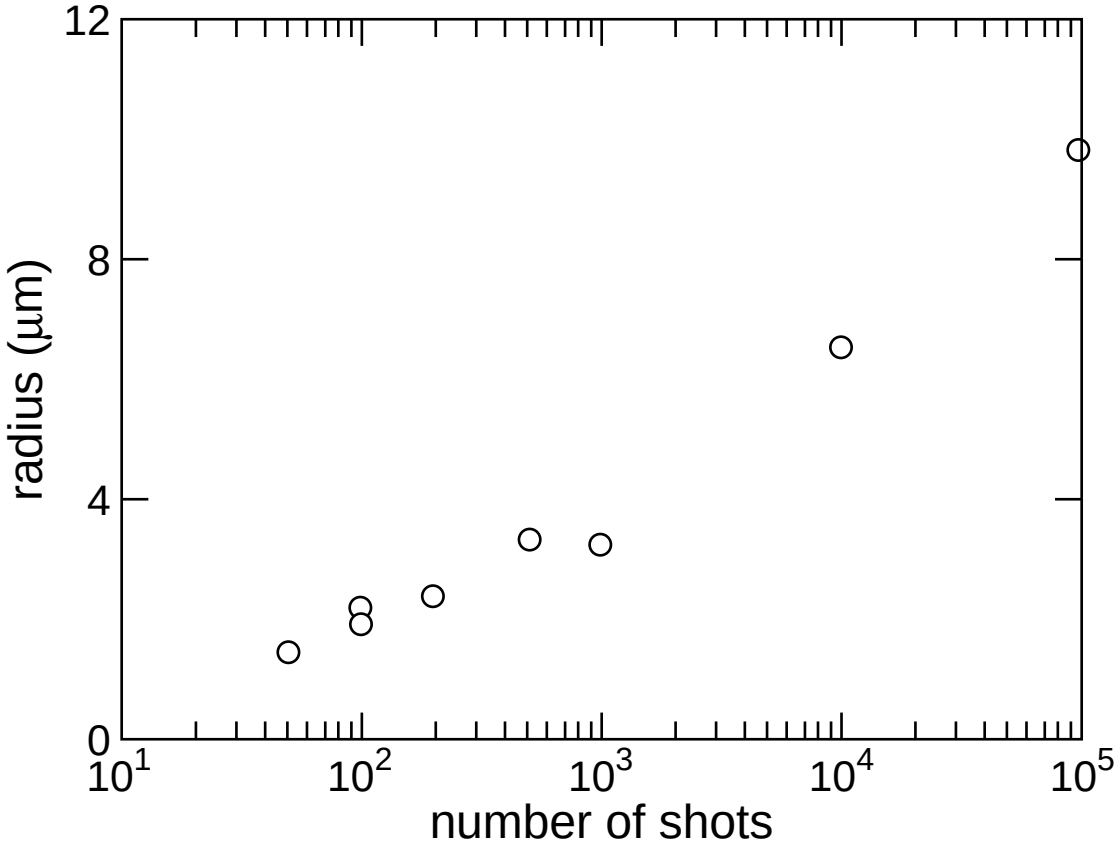
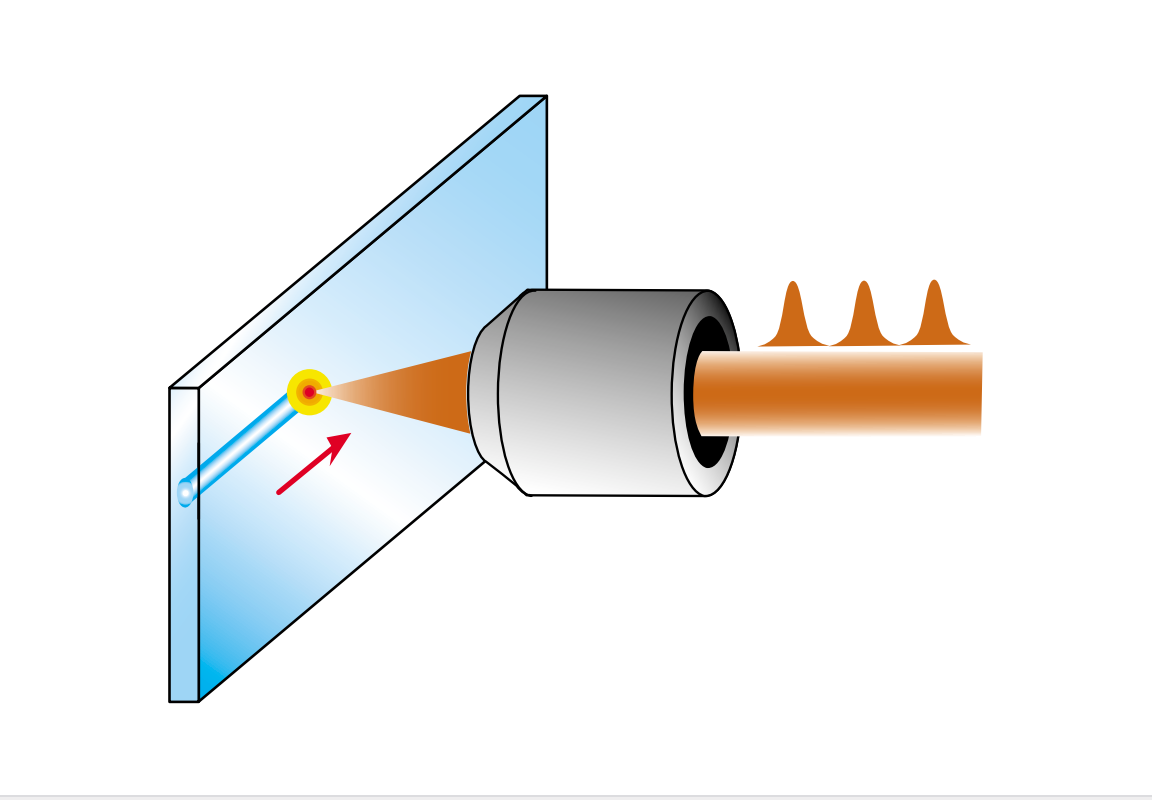
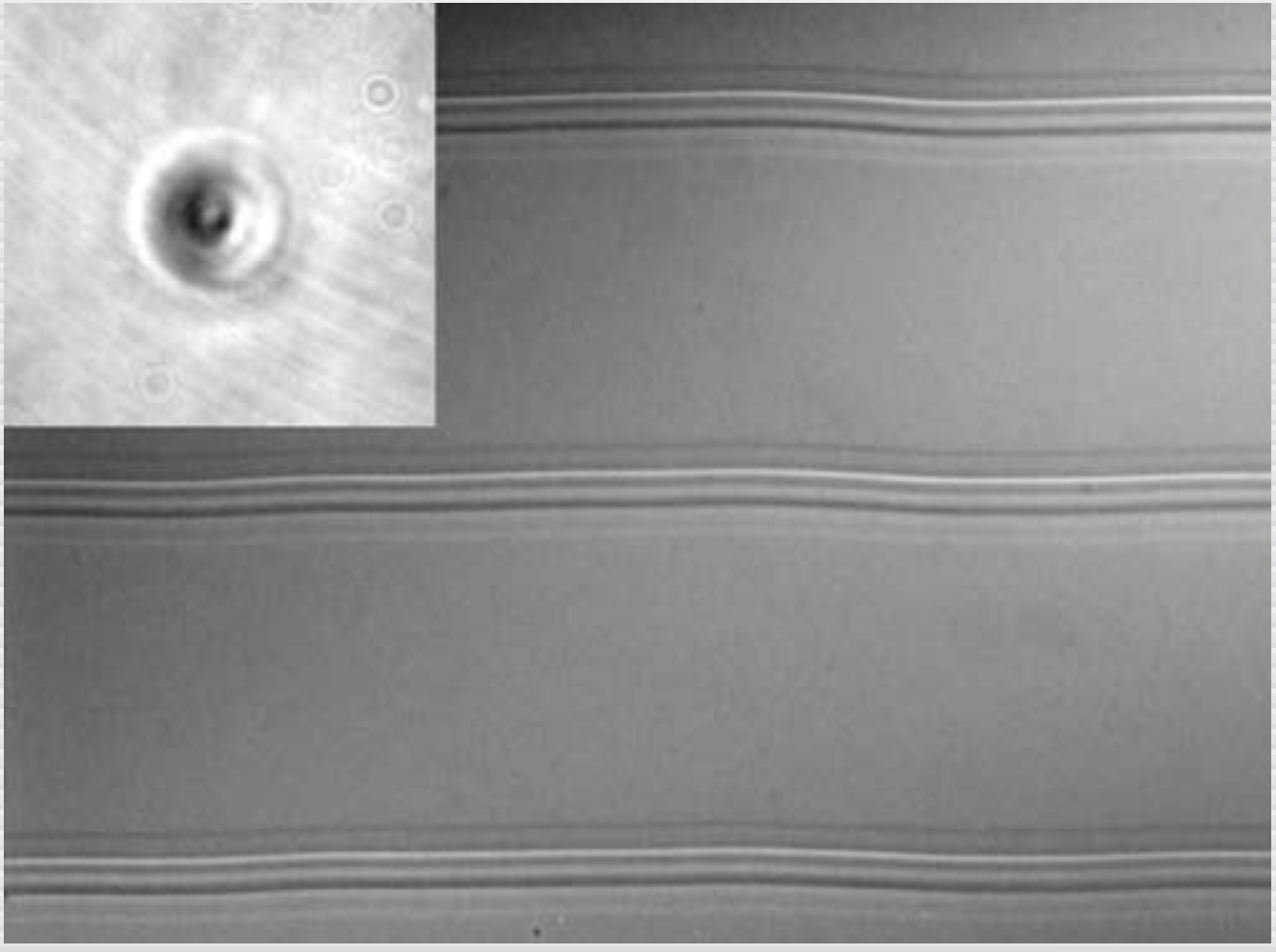


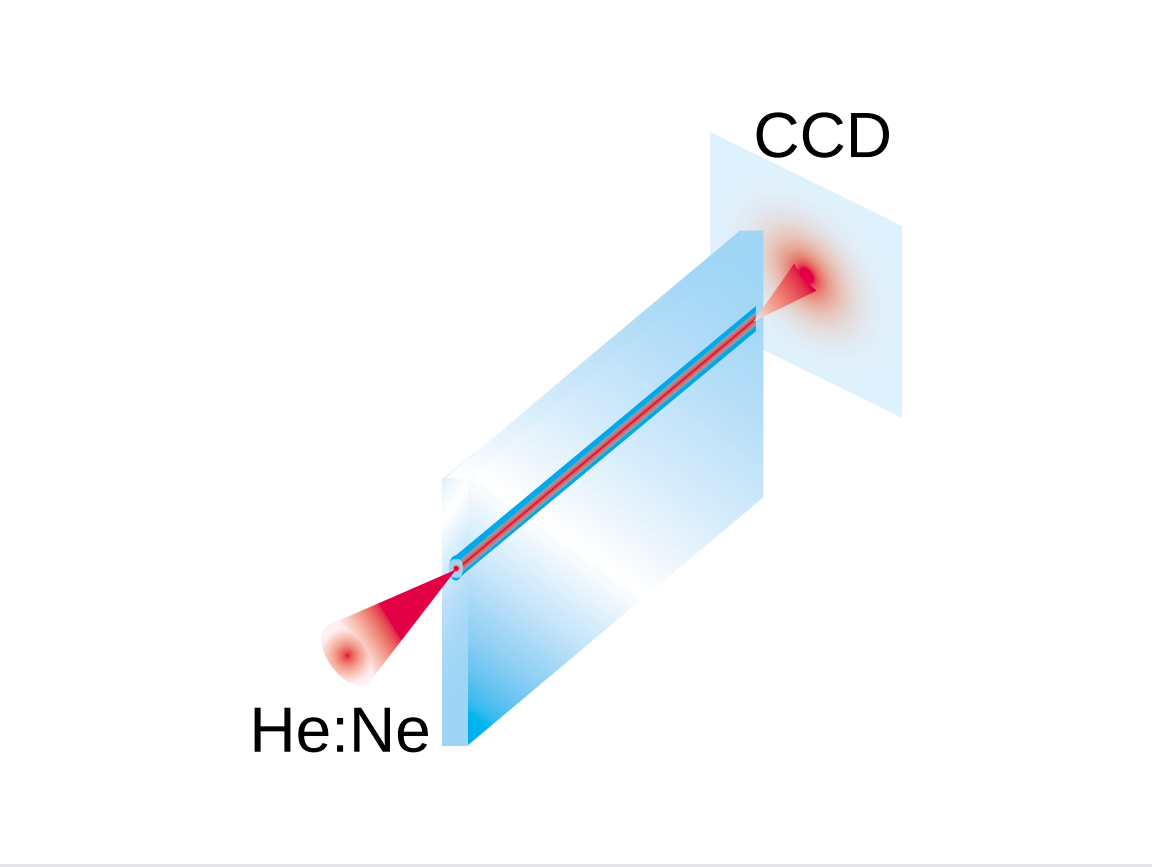
waveguide machining



waveguide machining

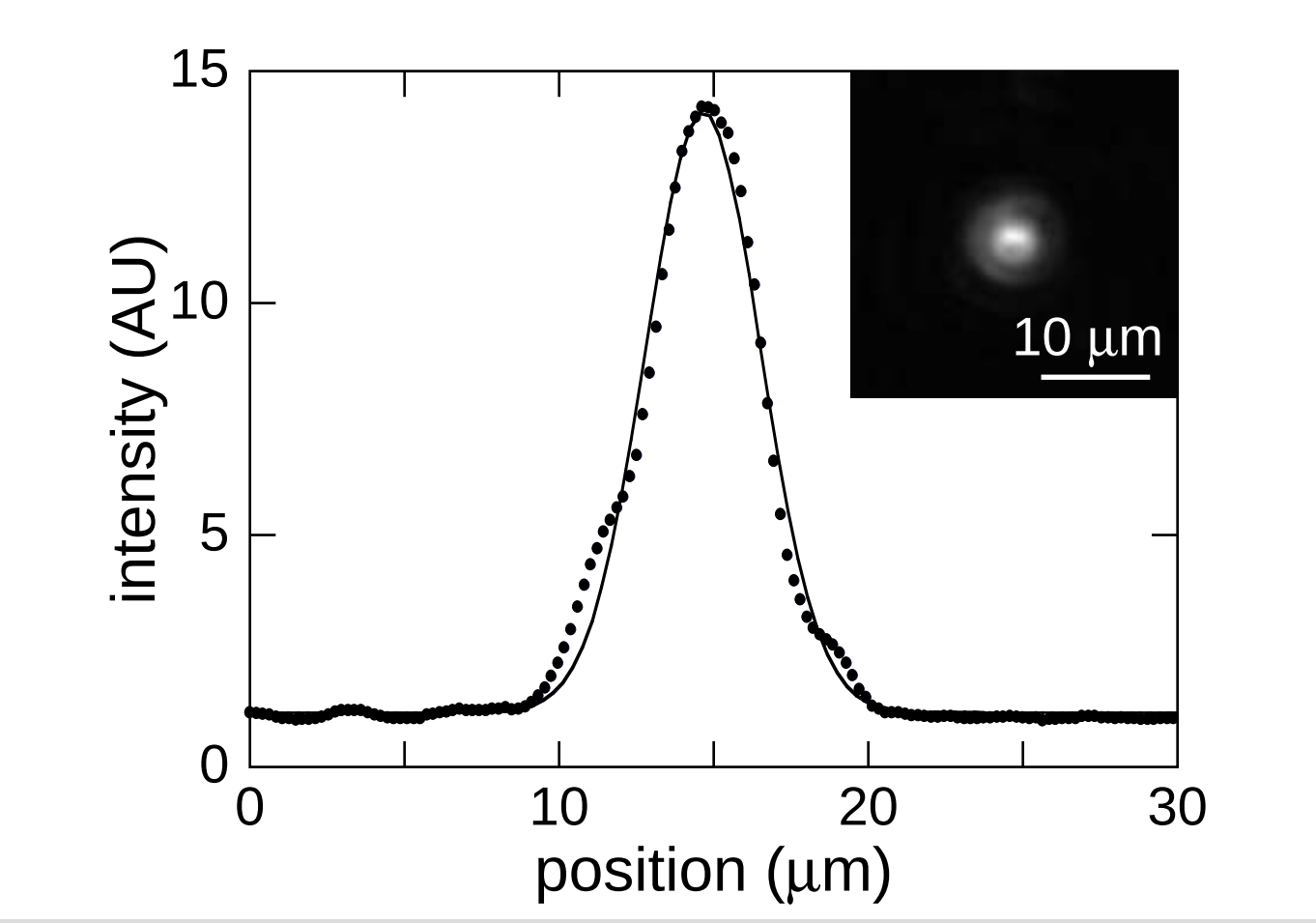


waveguide mode analysis

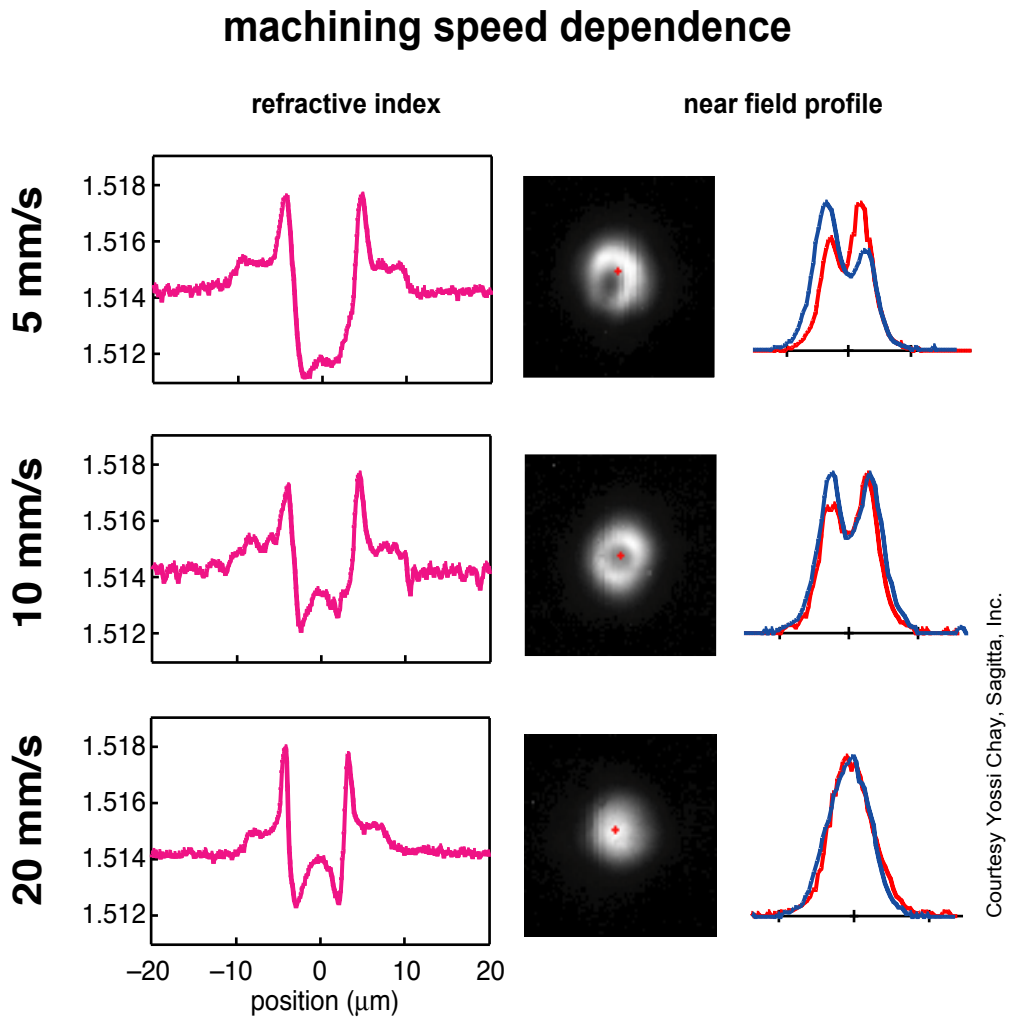


Low-energy processing

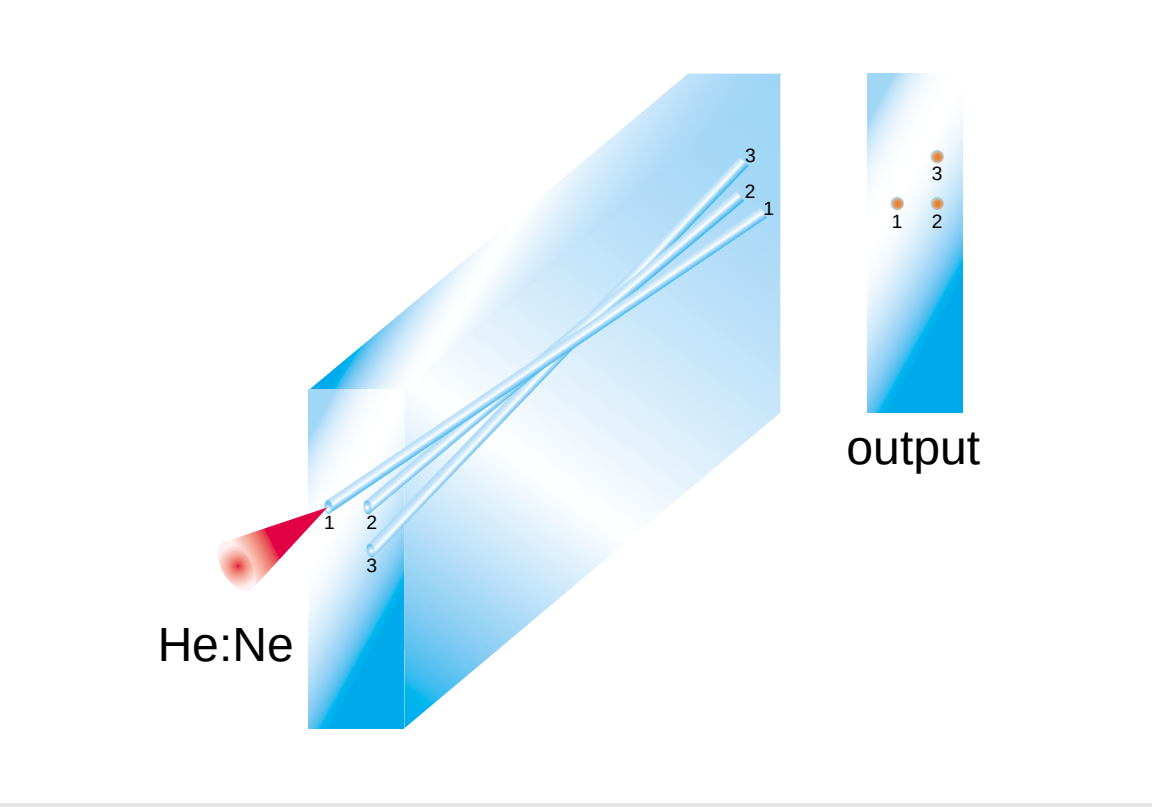
near field mode



Low-energy processing



3D wave splitter



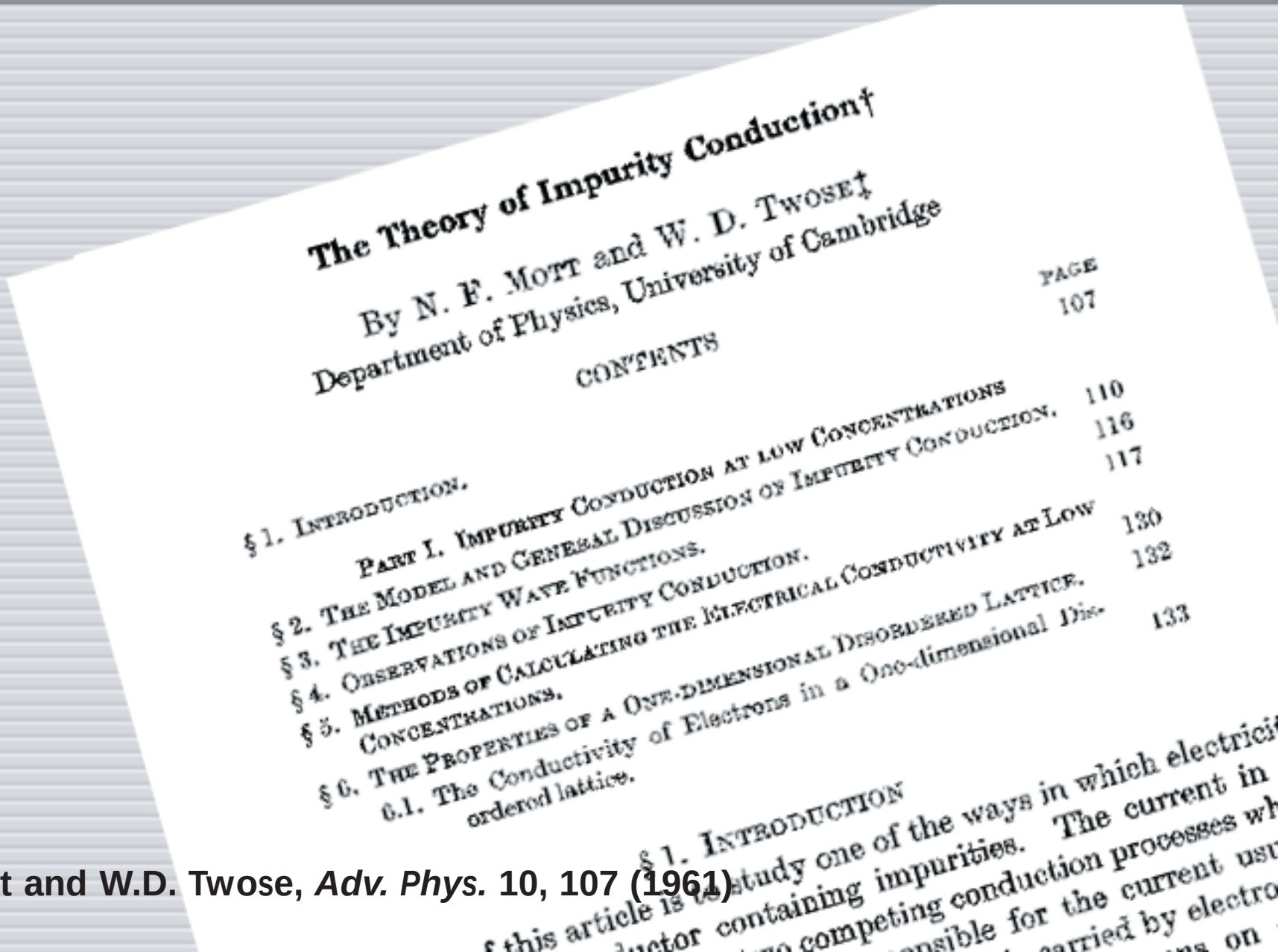
Outline

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

Carrier dynamics

short laser pulses can drive structural transitions

Carrier dynamics



The Theory of Impurity Conduction†

By N. F. Mott and W. D. Twose‡
Department of Physics, University of Cambridge

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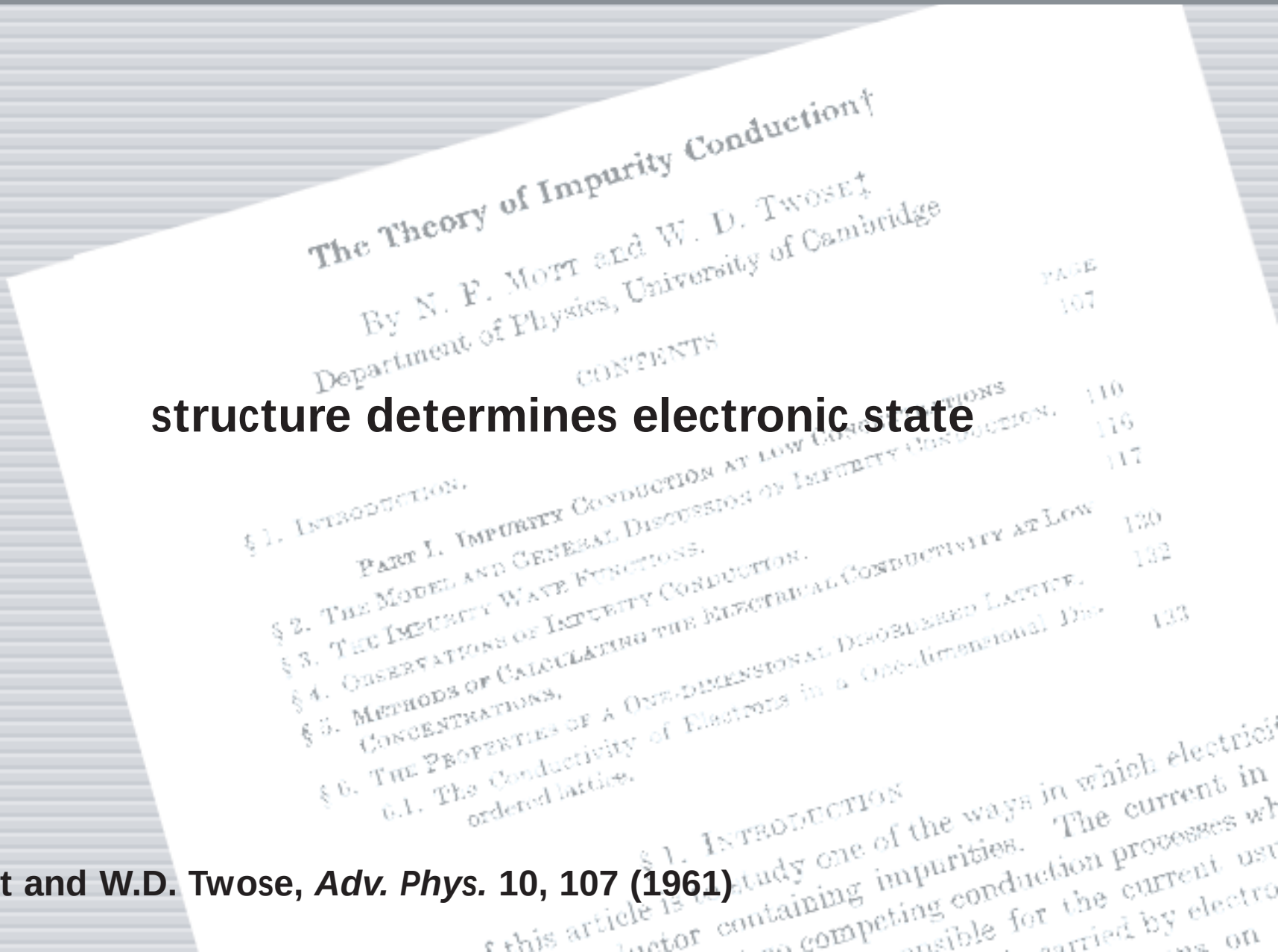
§ 1. Introduction

N. Mott and W.D. Twose, *Adv. Phys.* 10, 107 (1961)

Carrier dynamics


The Theory of Impurity Conduction†

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Department of Physics, University of Cambridge

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§ 1. Introduction.

Part I. Impurity Conduction at low Concentrations

§ 2. The Model and General Discussion of Impurity Conduction.

§ 3. The Impurity Wave Functions.

§ 4. Observations of Impurity Conduction.

§ 5. Methods of Calculating the Electrical Conductivity at Low Concentrations.

§ 6. The Properties of a One-dimensional Disordered Lattice.

6.1. The Conductivity of Electrons in a One-dimensional Disordered lattice.

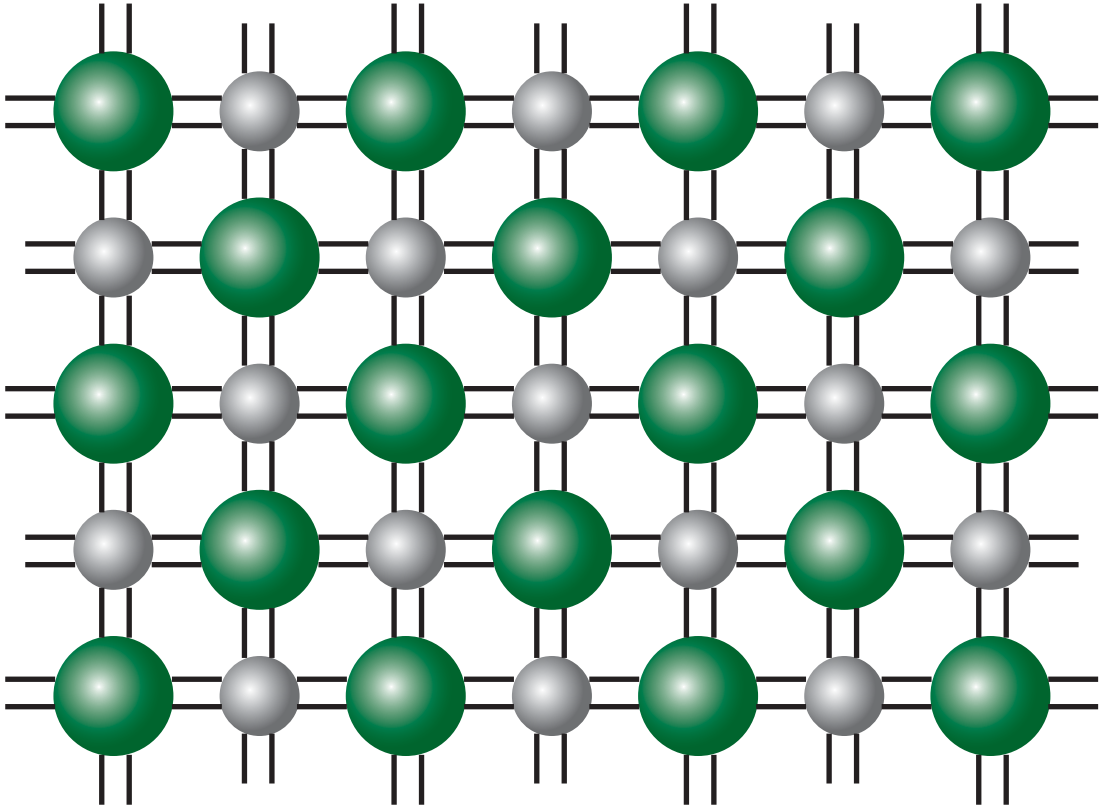
§ 1. Introduction

structure determines electronic state

N. Mott and W.D. Twose, *Adv. Phys.* 10, 107 (1961)

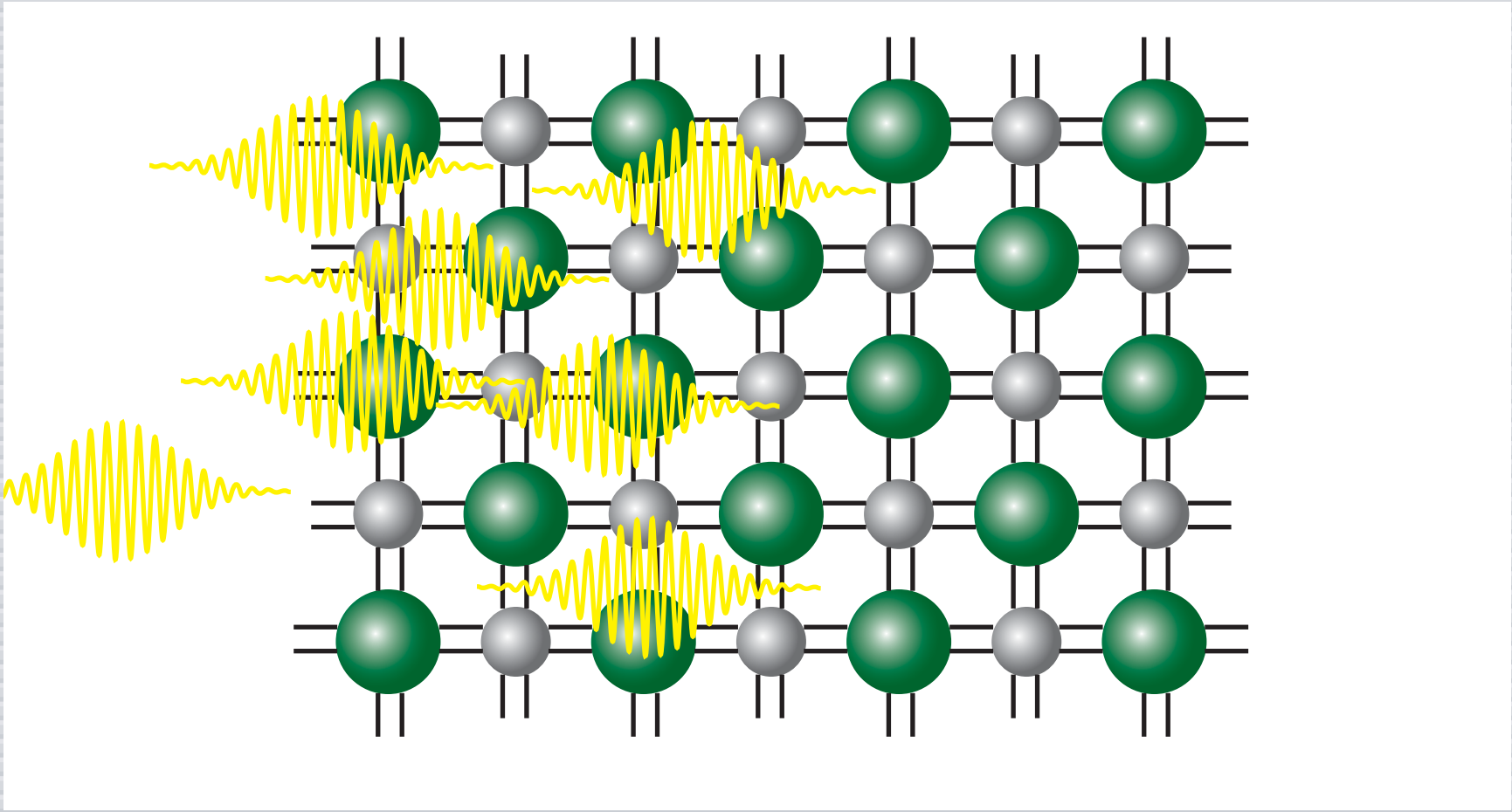
Carrier dynamics

how do femtosecond laser pulses alter a solid?



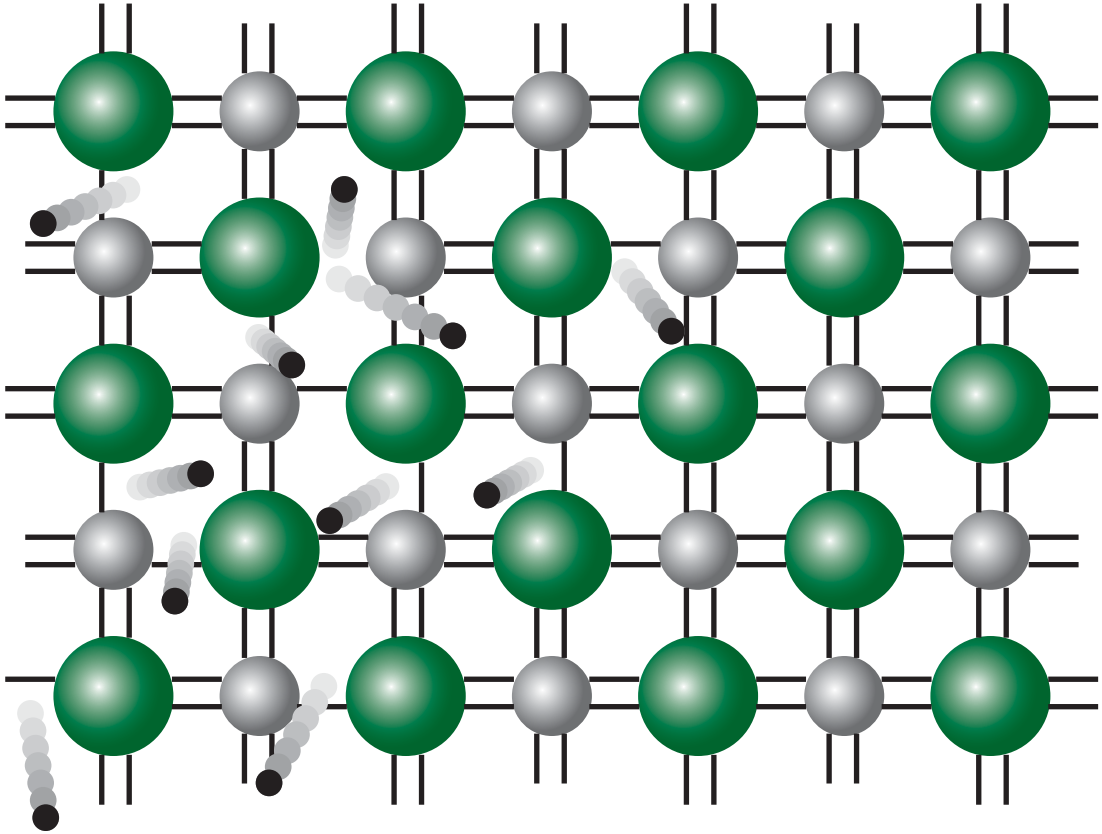
Carrier dynamics

photons excite valence electrons…



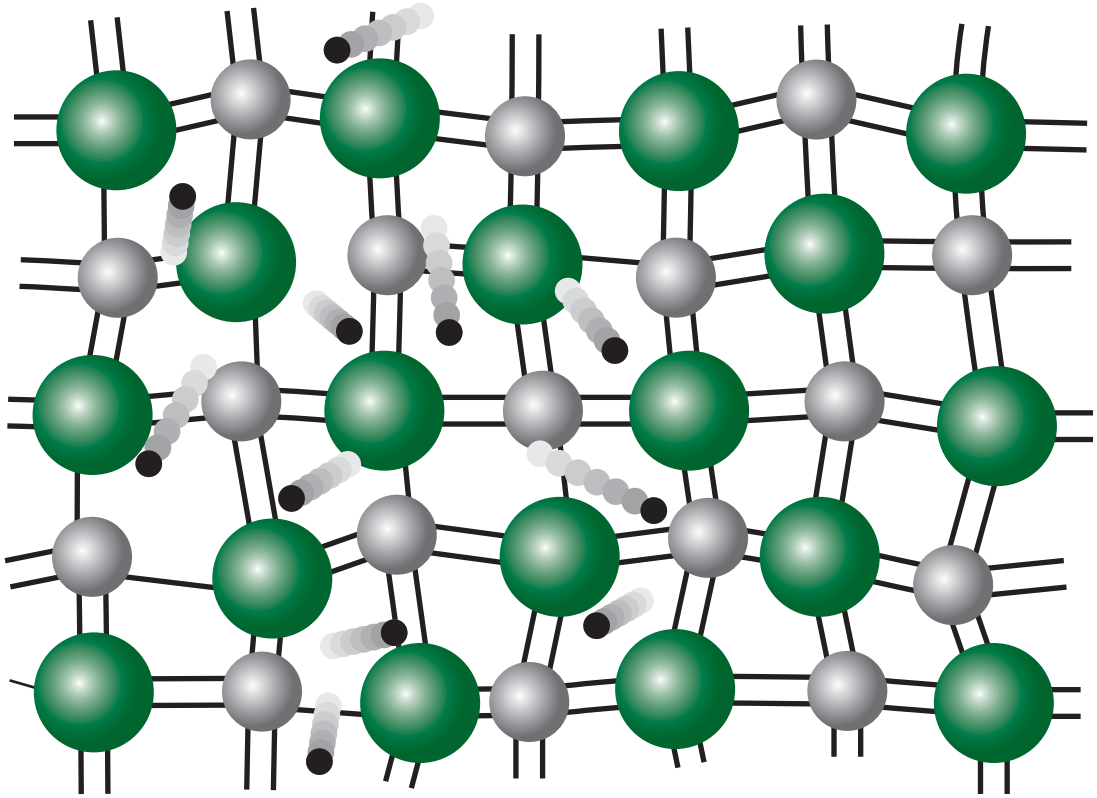
Carrier dynamics

… and create free electrons…



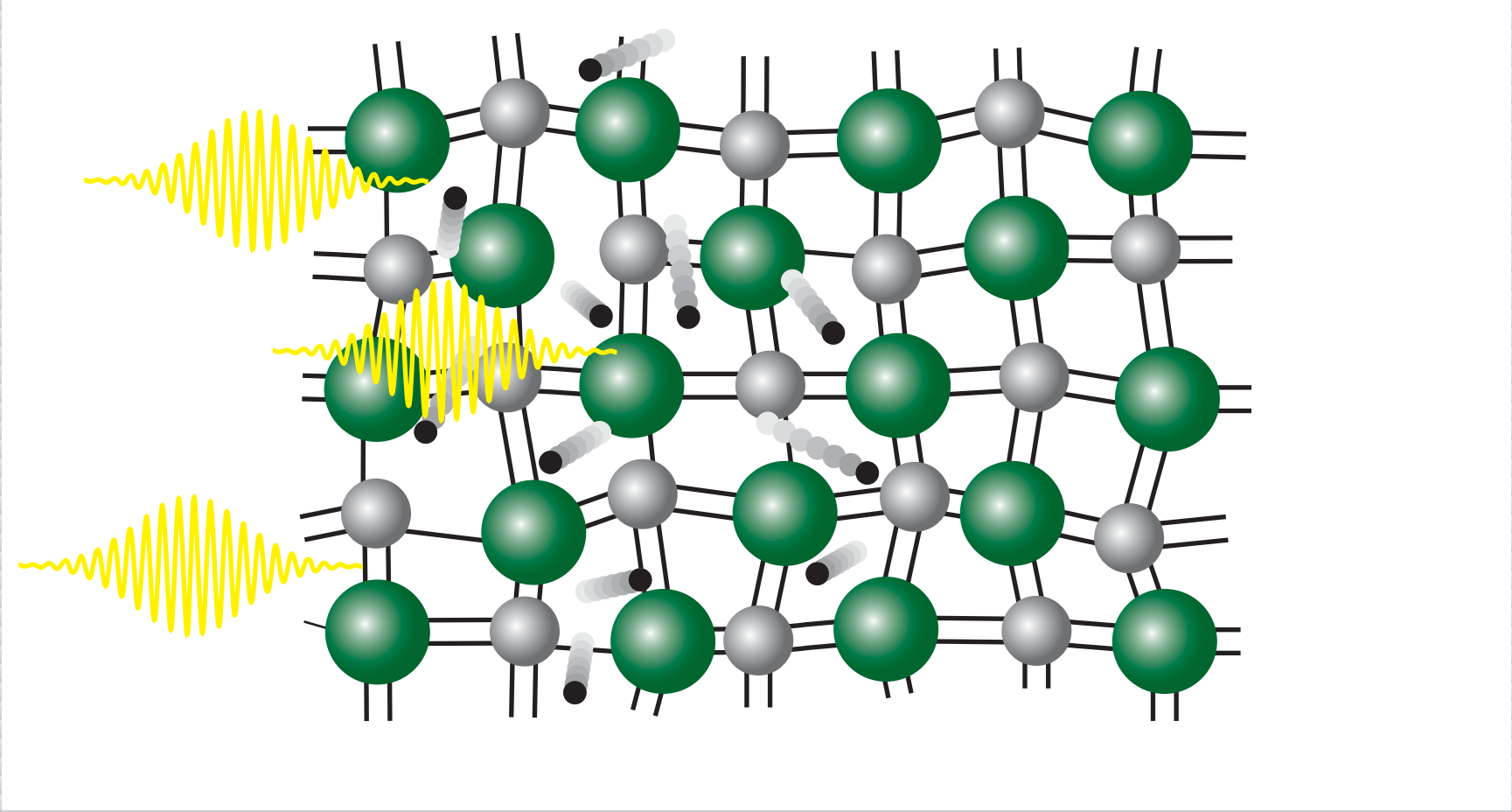
Carrier dynamics

… causing electronic and structural changes…



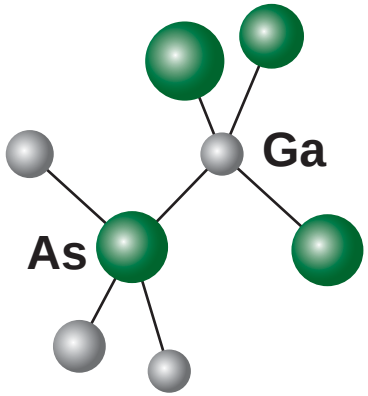
Carrier dynamics

… which we detect with a second laser pulse



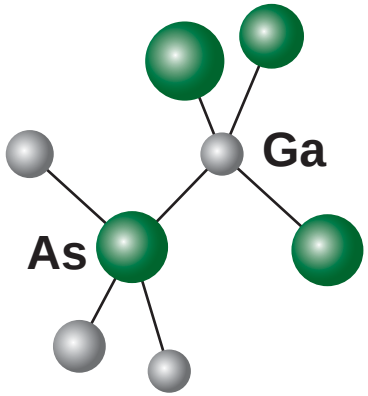
Carrier dynamics

structure

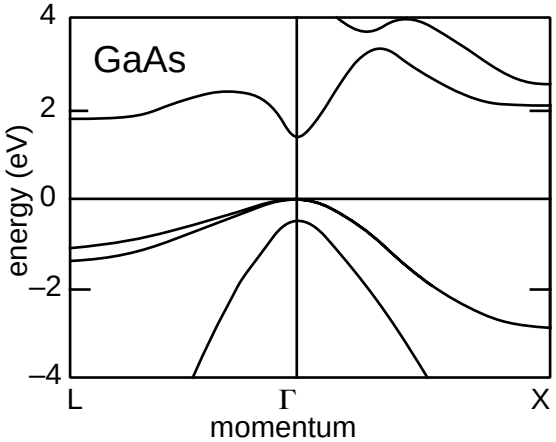


Carrier dynamics

structure

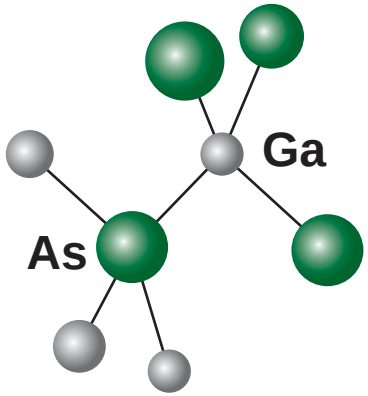


band structure

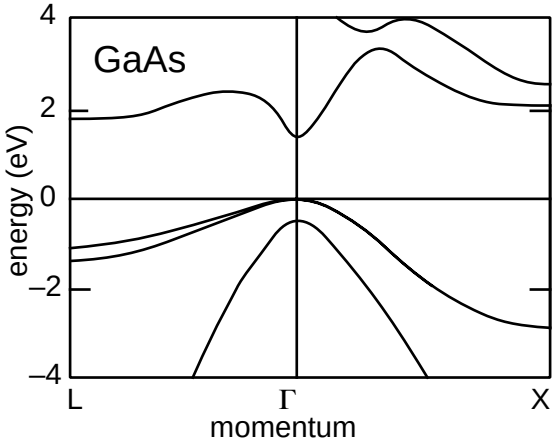


Carrier dynamics

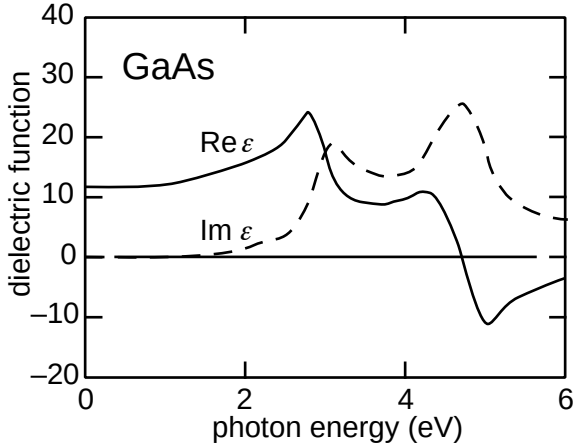
structure



band structure

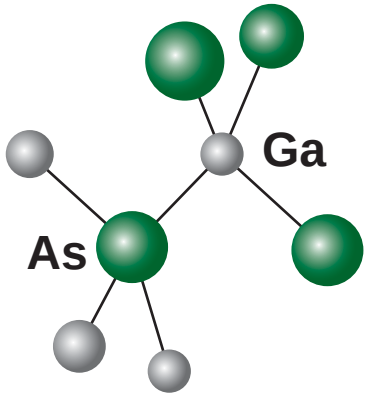


dielectric function

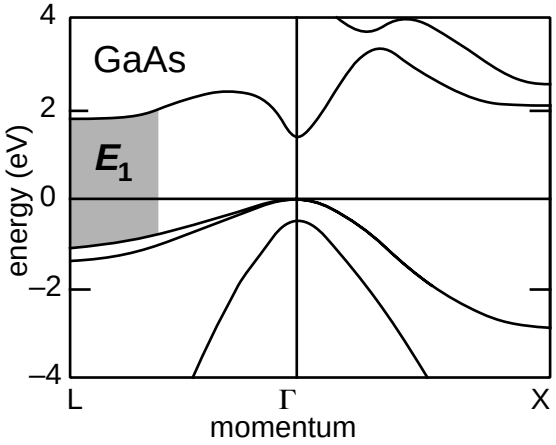


Carrier dynamics

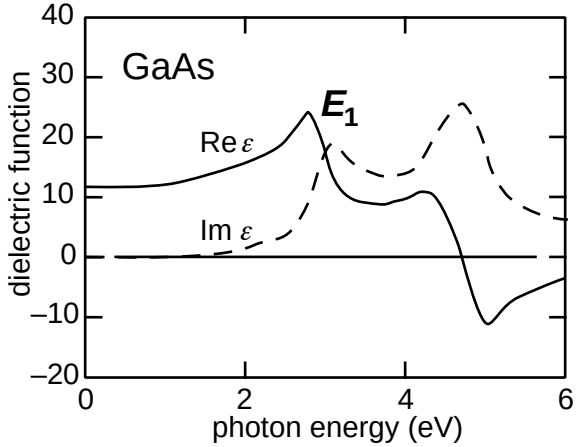
structure



band structure

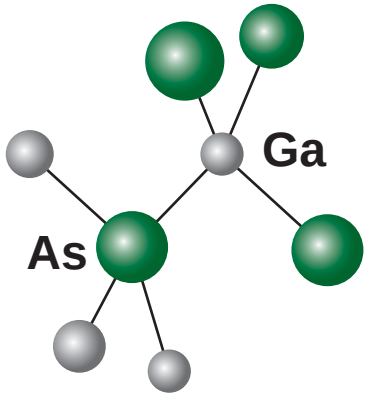


dielectric function

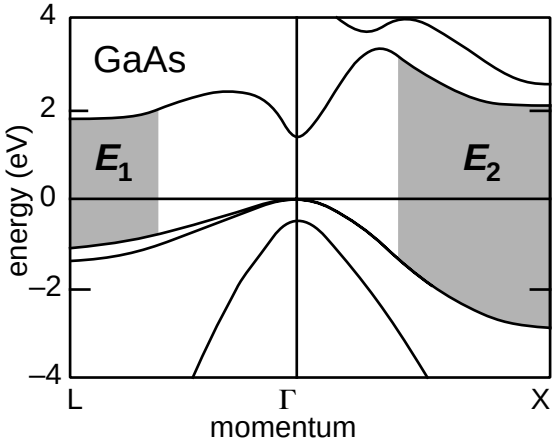


Carrier dynamics

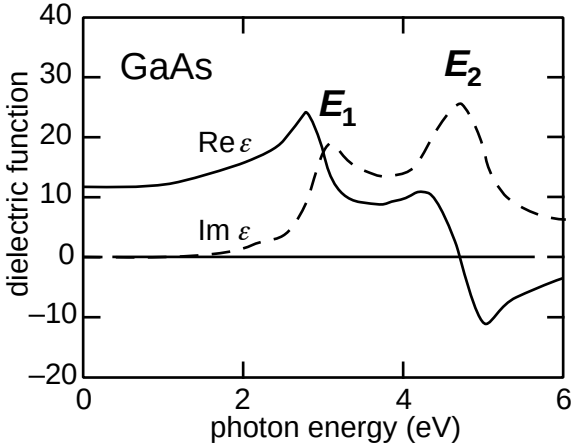
structure



band structure

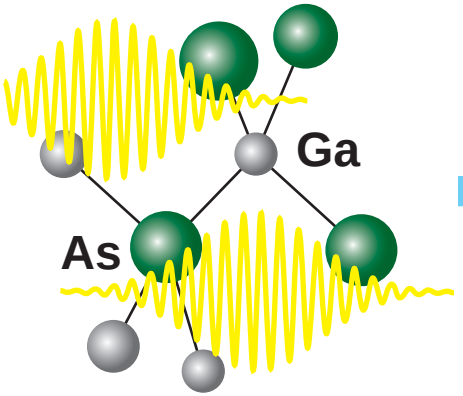


dielectric function

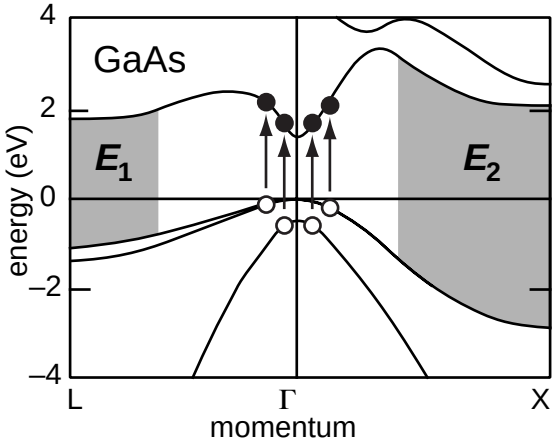


Carrier dynamics

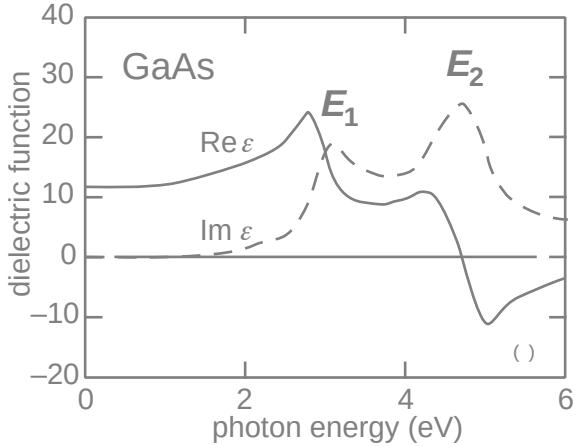
structure



band structure

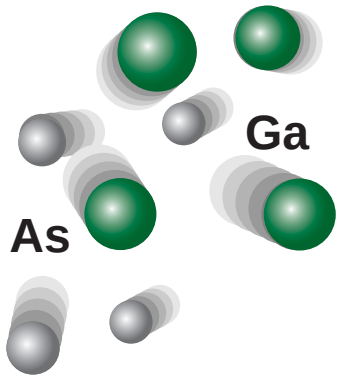


dielectric function

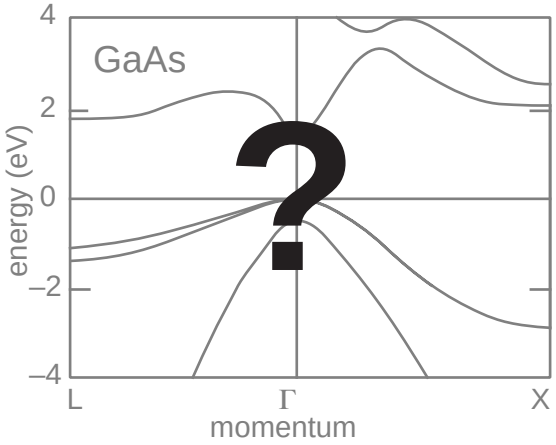


Carrier dynamics

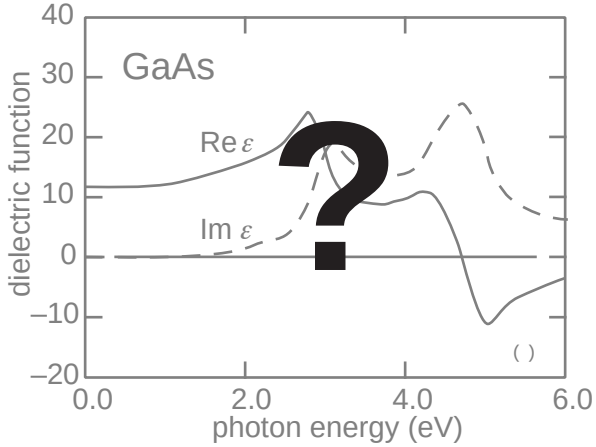
structure



band structure

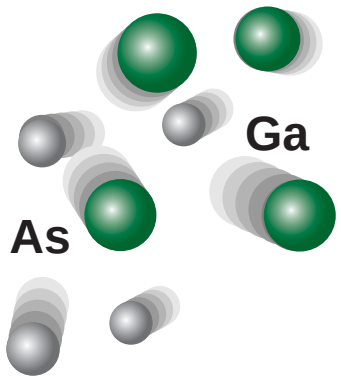


dielectric function

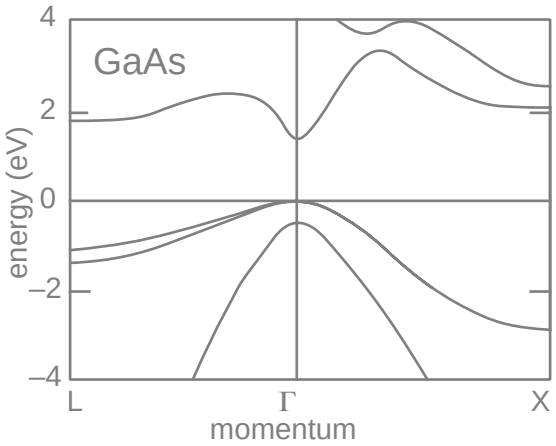


Carrier dynamics

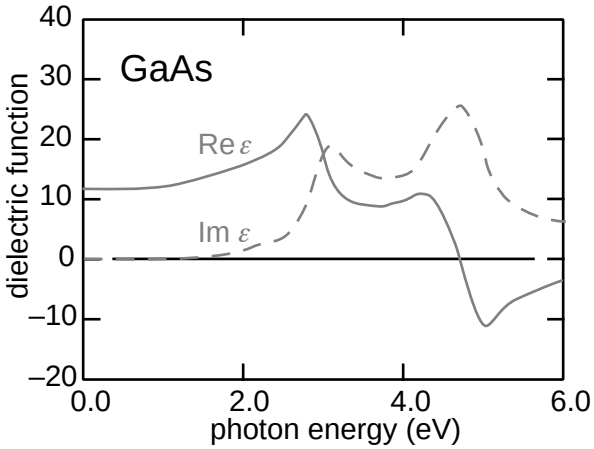
structure



band structure

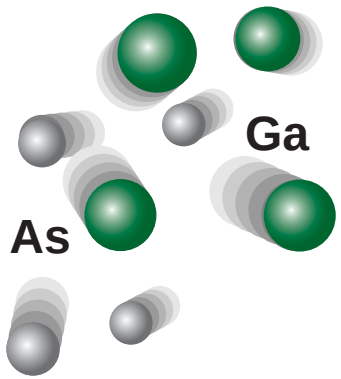


dielectric function

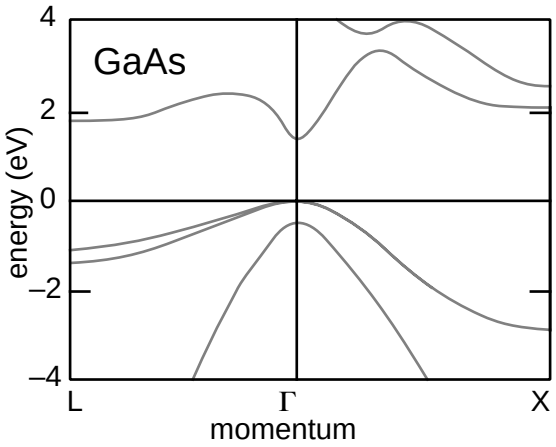


Carrier dynamics

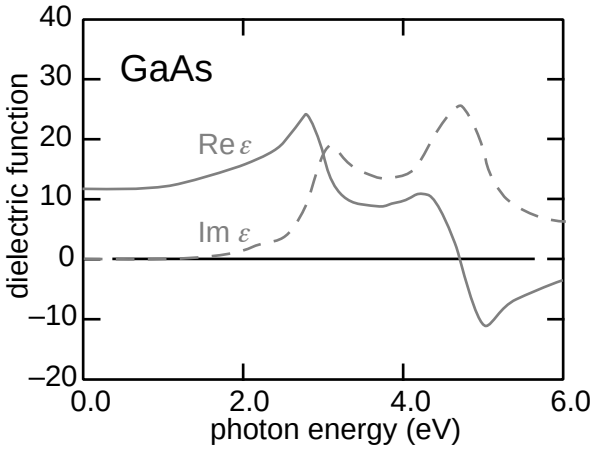
structure



band structure



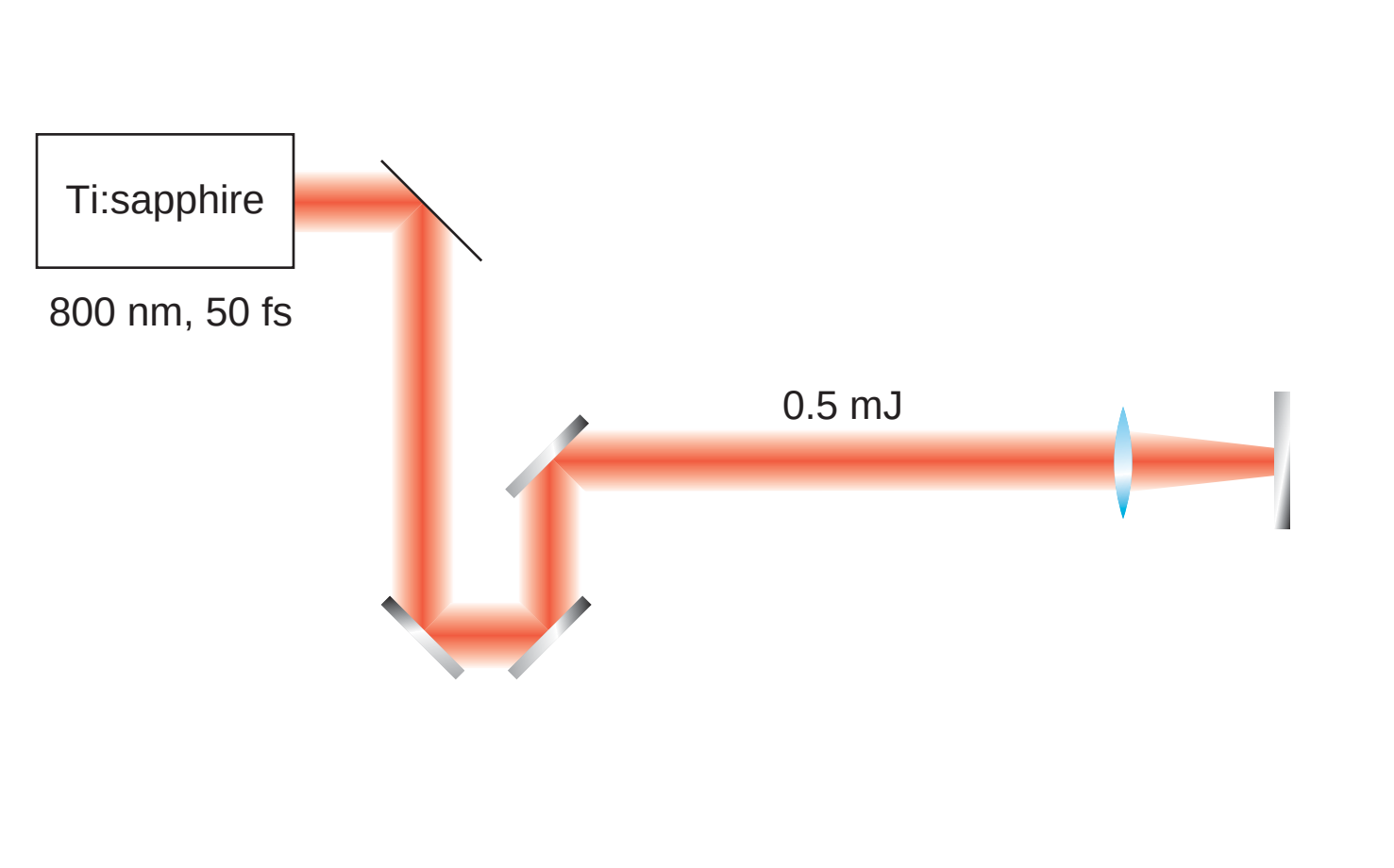
dielectric function



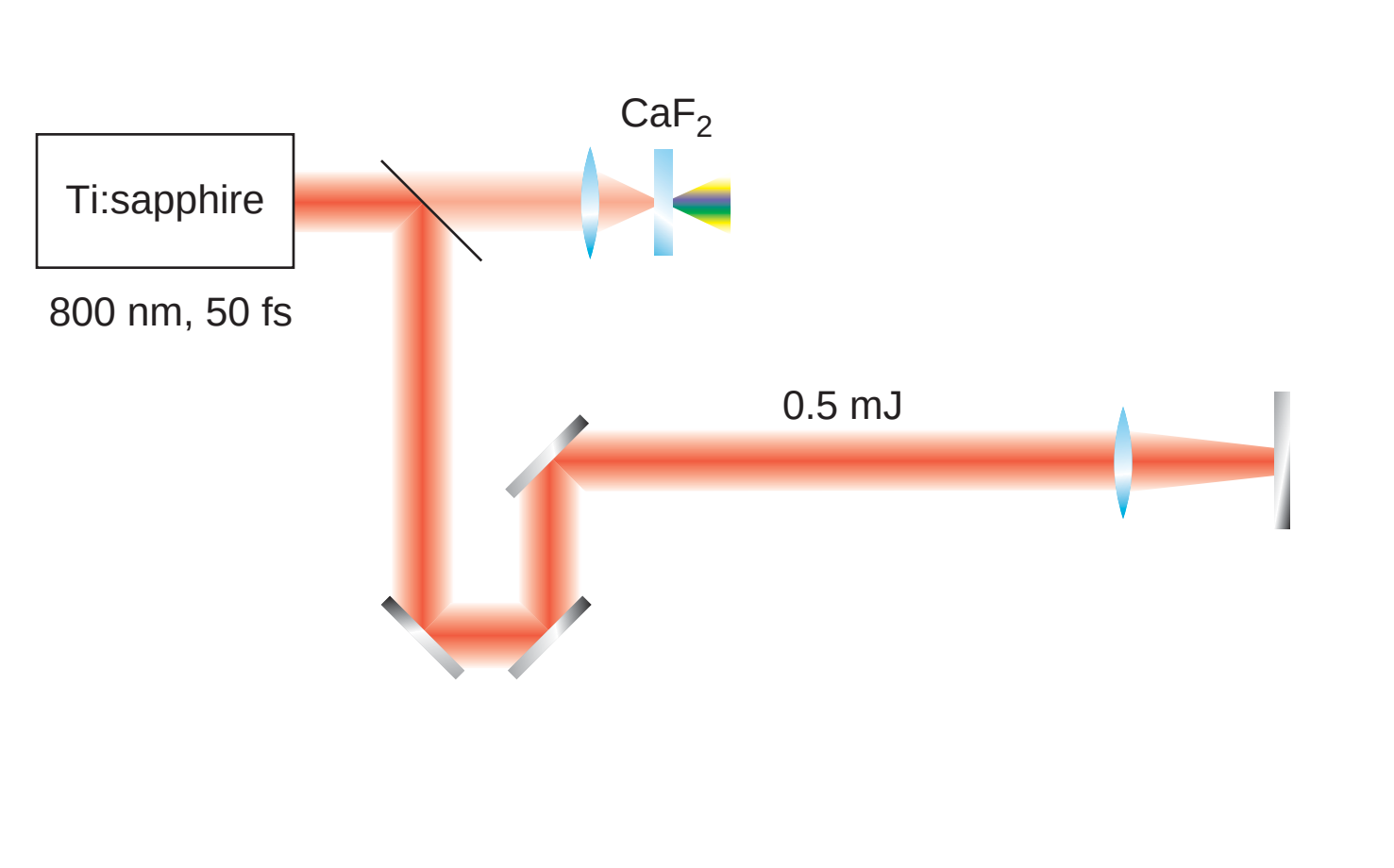
Carrier dynamics

- **dielectric function: ‘fingerprint’ of state**
- **light can induce structural transitions**

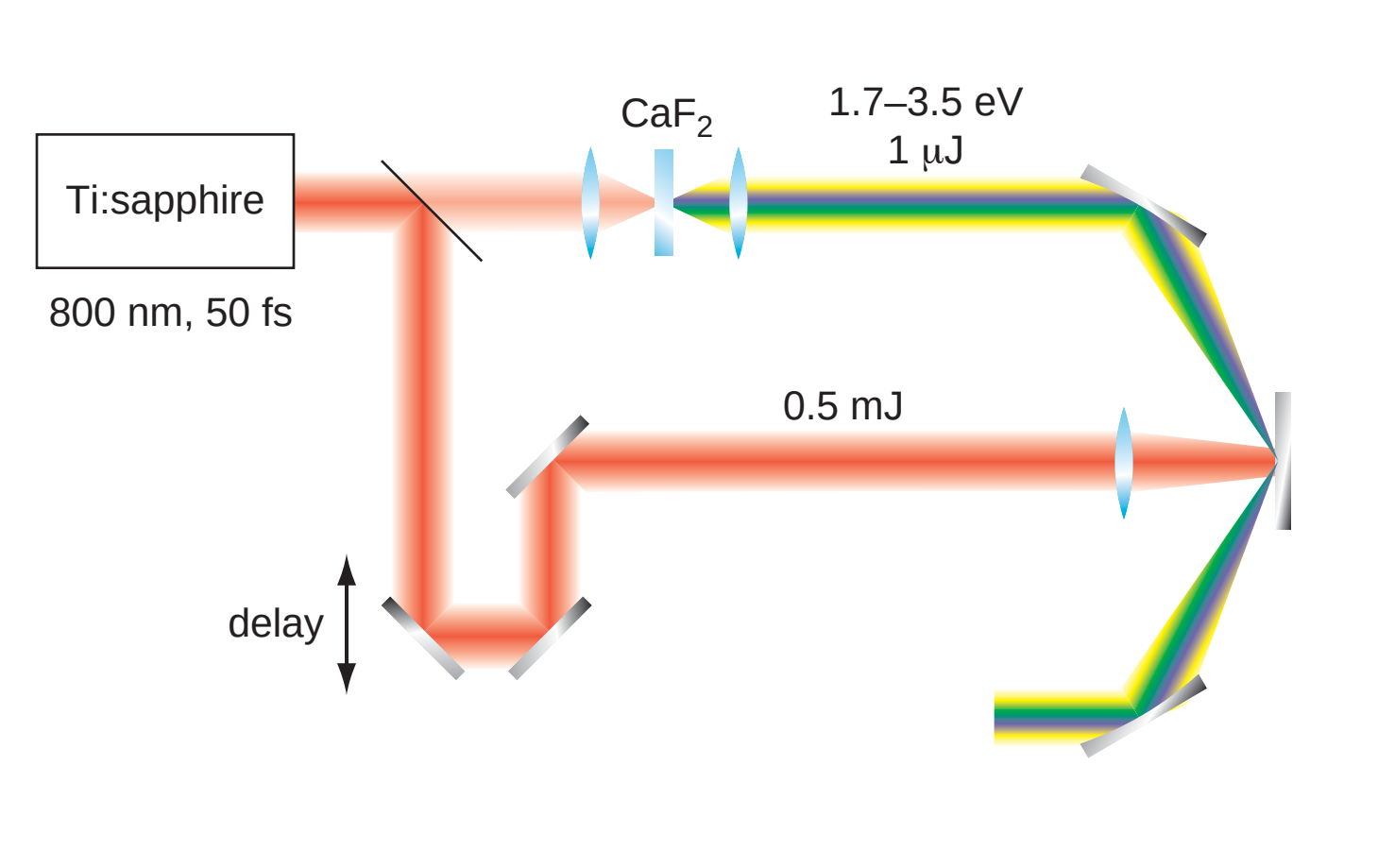
broadband time-resolved ellipsometry



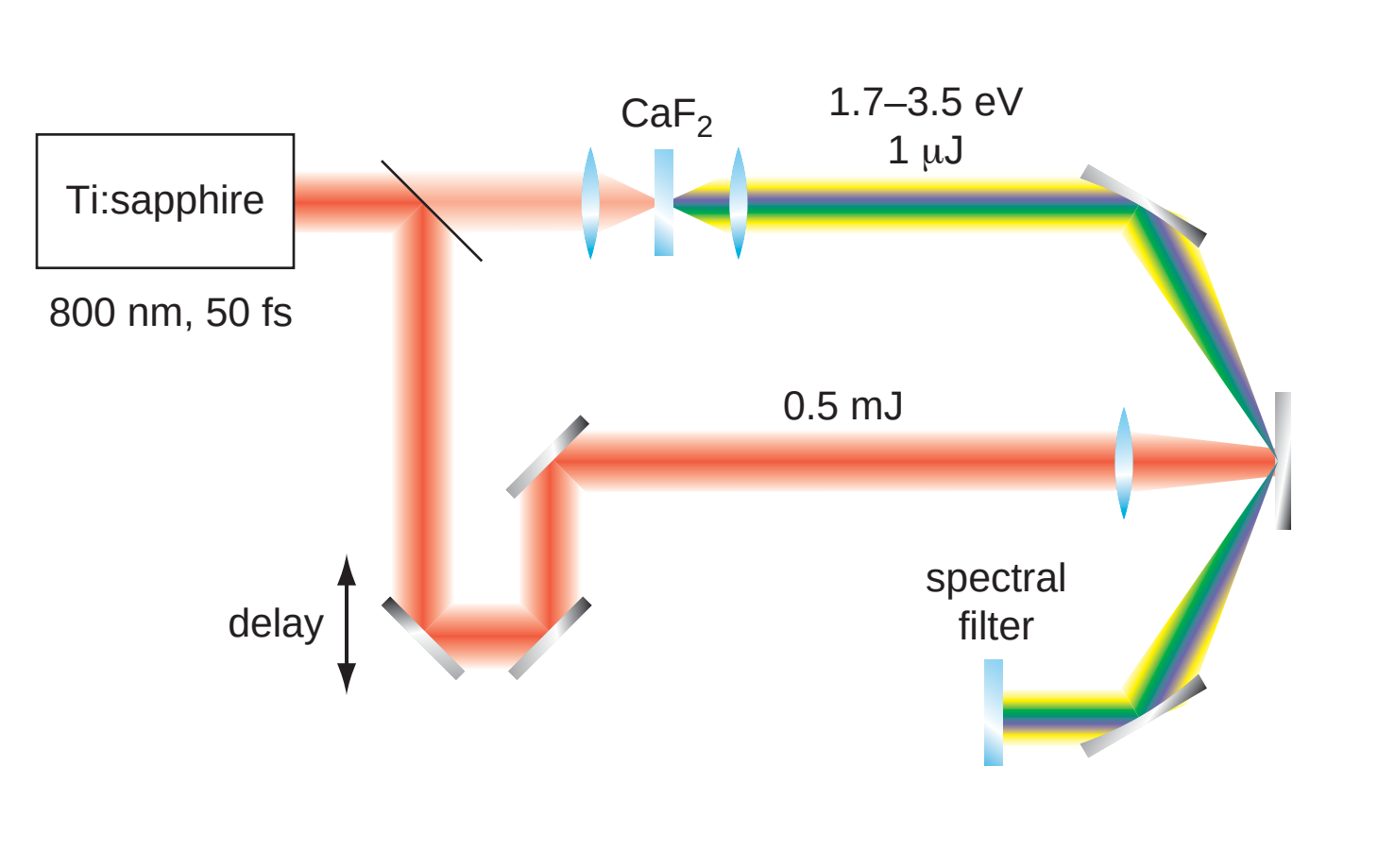
broadband time-resolved ellipsometry



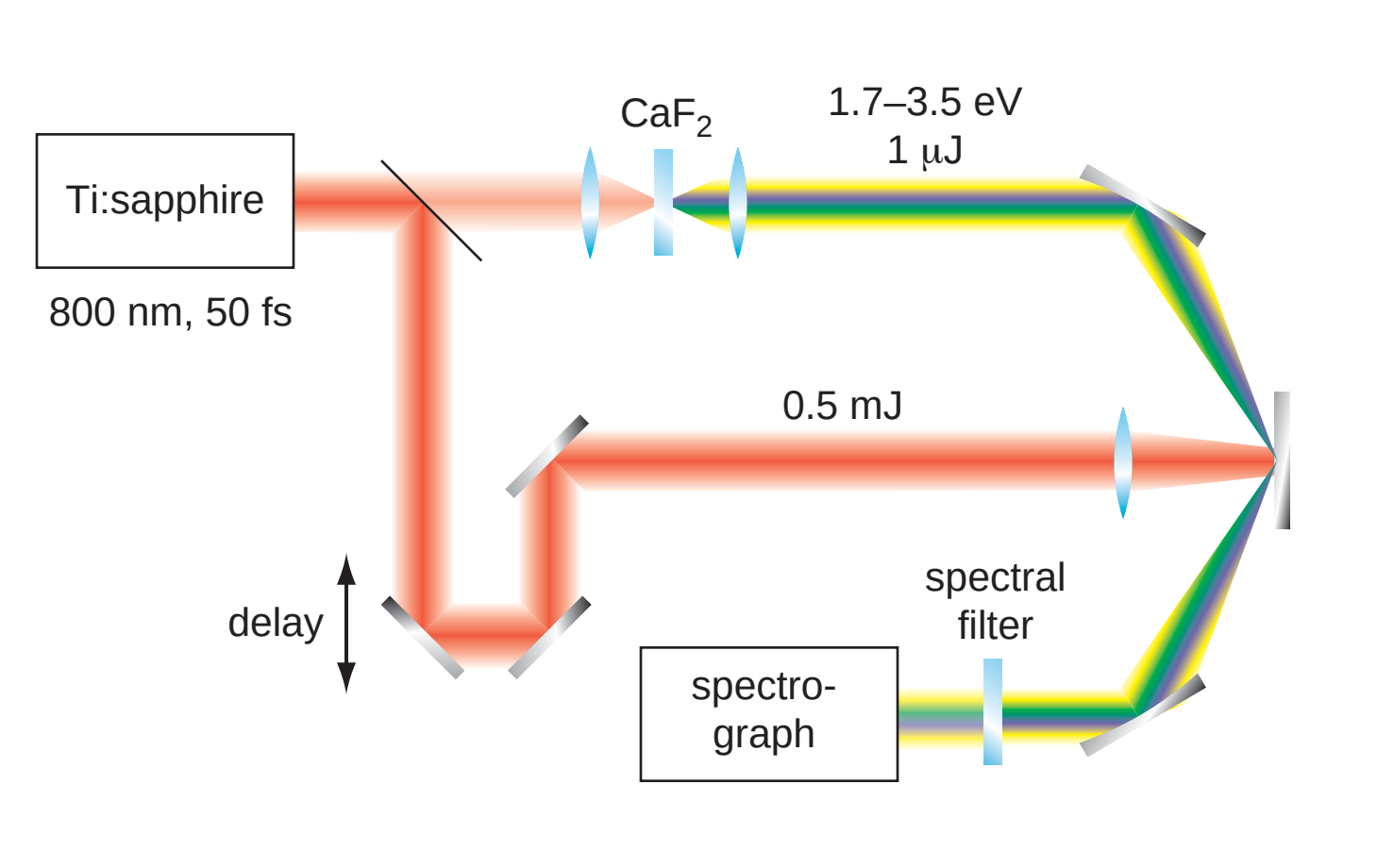
broadband time-resolved ellipsometry



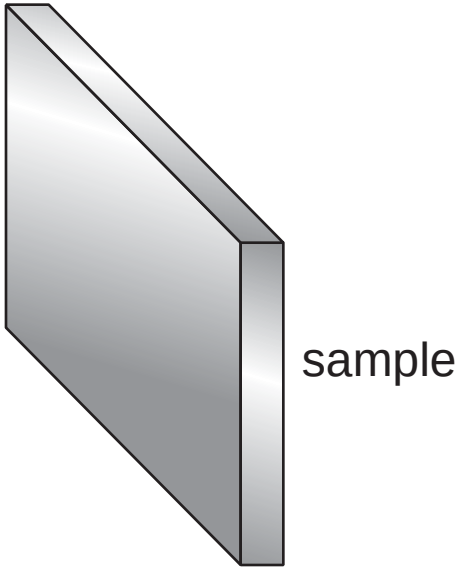
broadband time-resolved ellipsometry



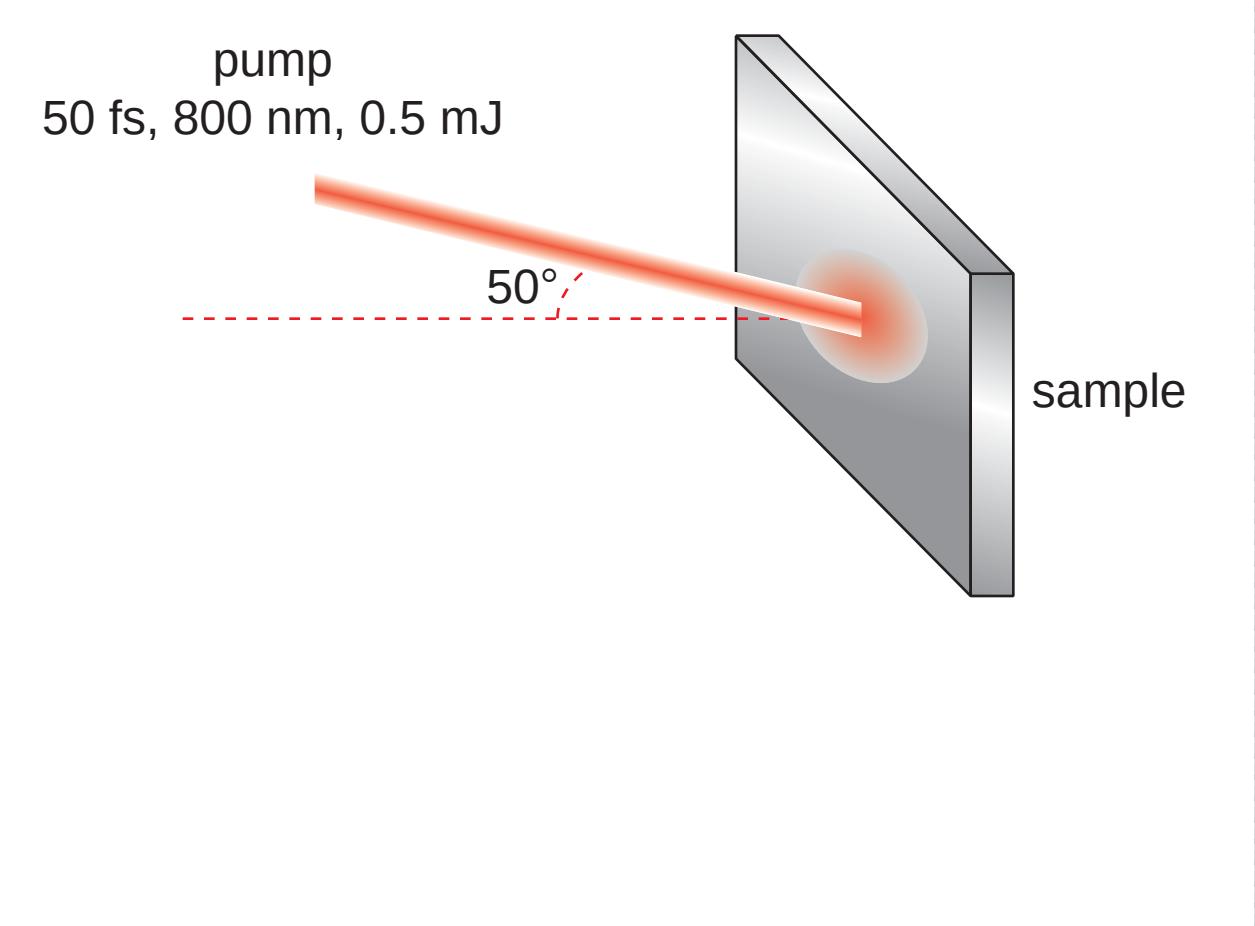
broadband time-resolved ellipsometry



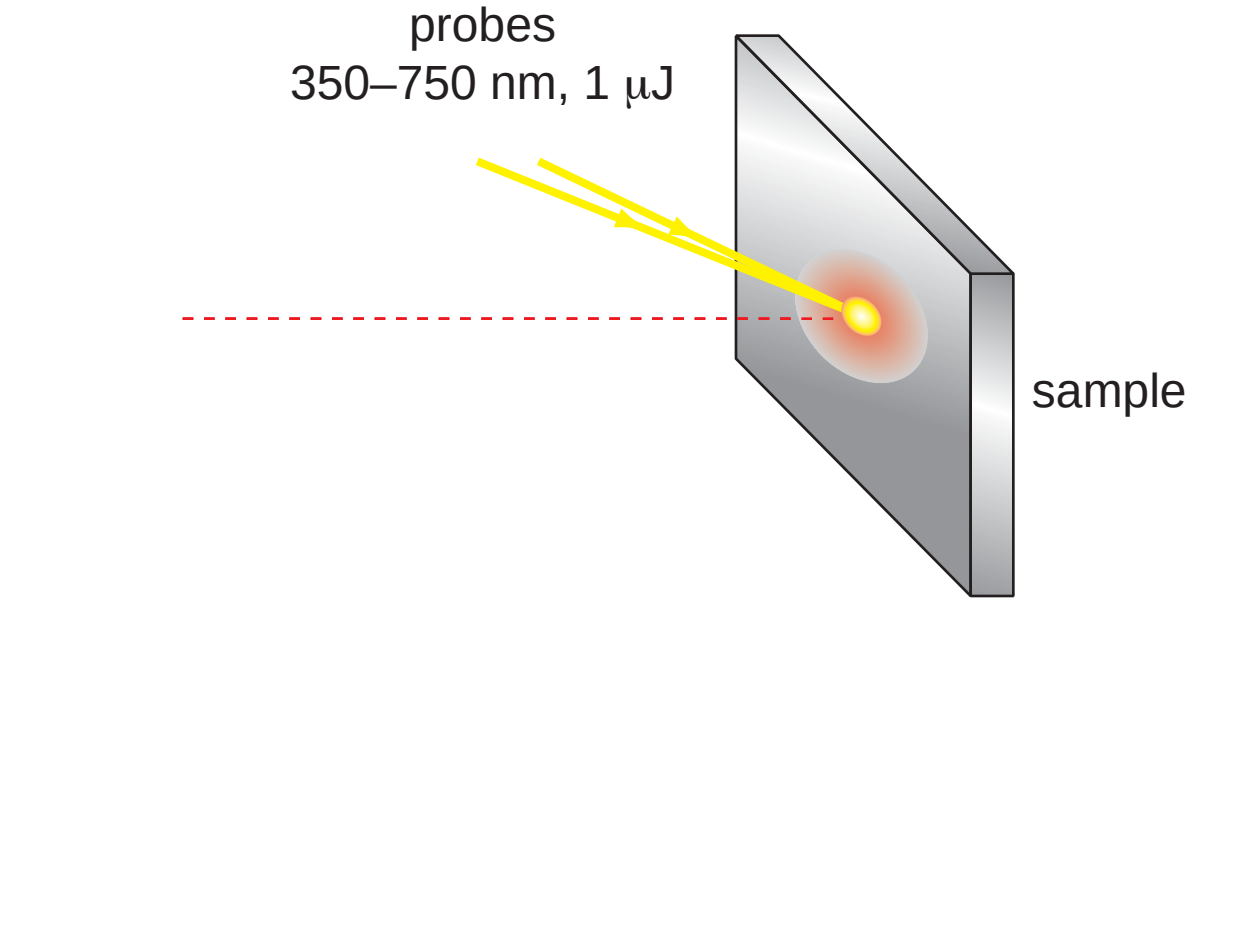
broadband time-resolved ellipsometry



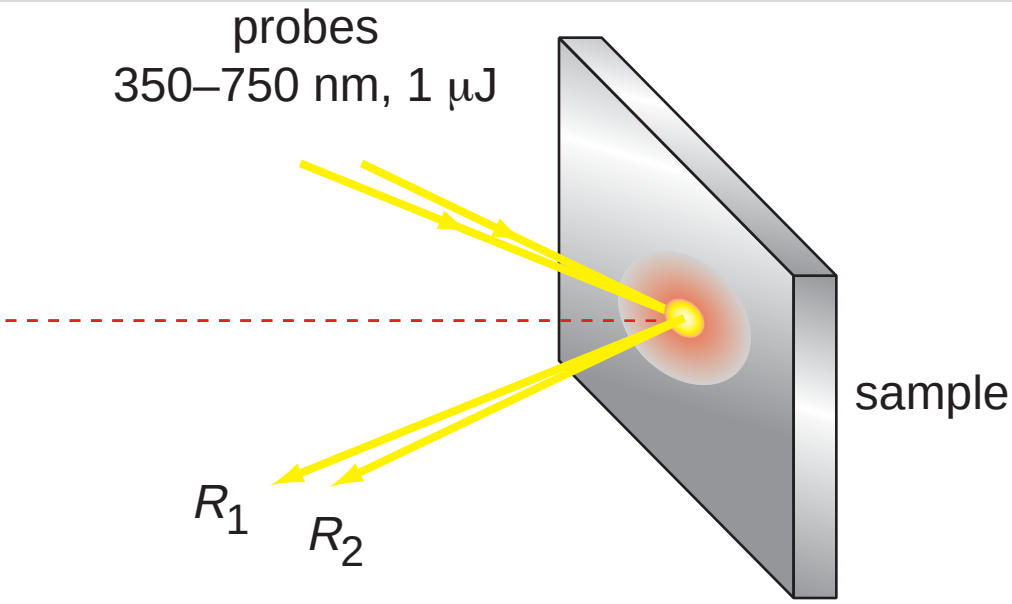
broadband time-resolved ellipsometry



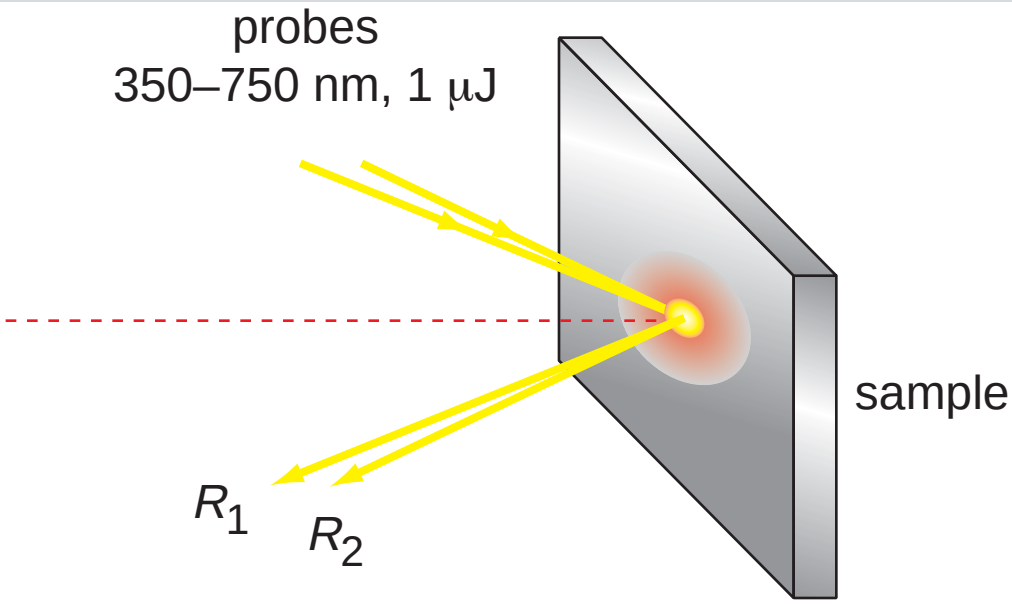
broadband time-resolved ellipsometry



broadband time-resolved ellipsometry

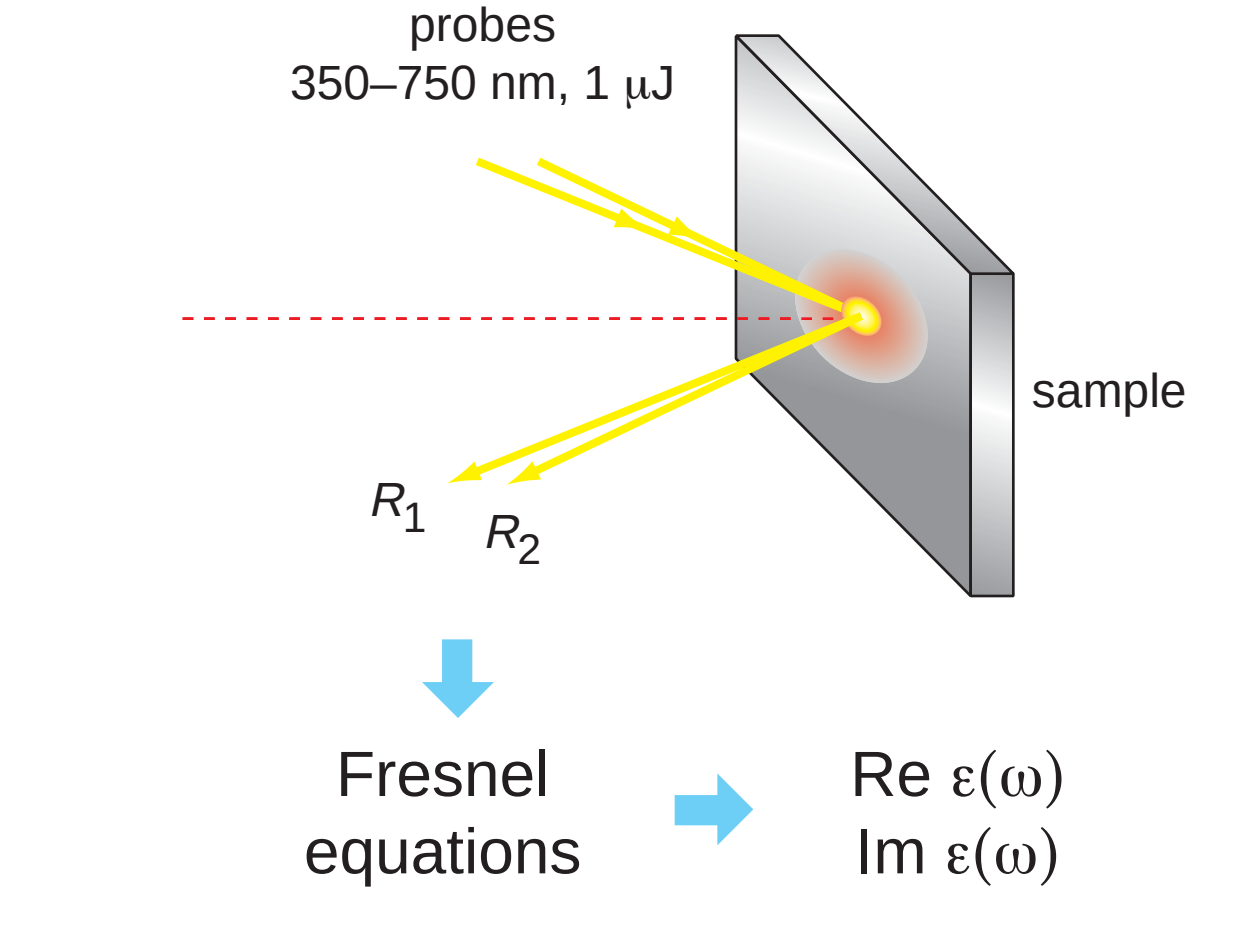


broadband time-resolved ellipsometry

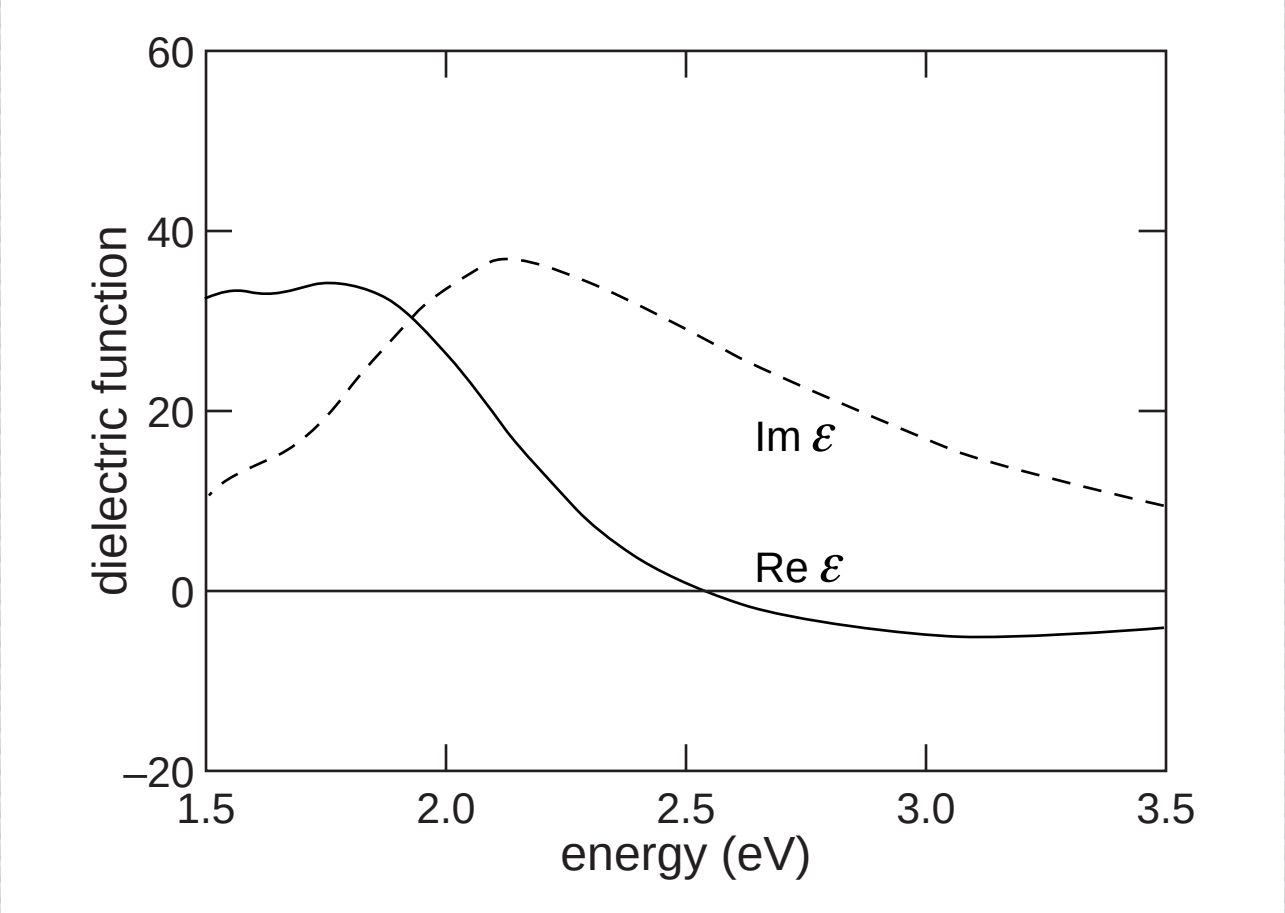


Fresnel equations

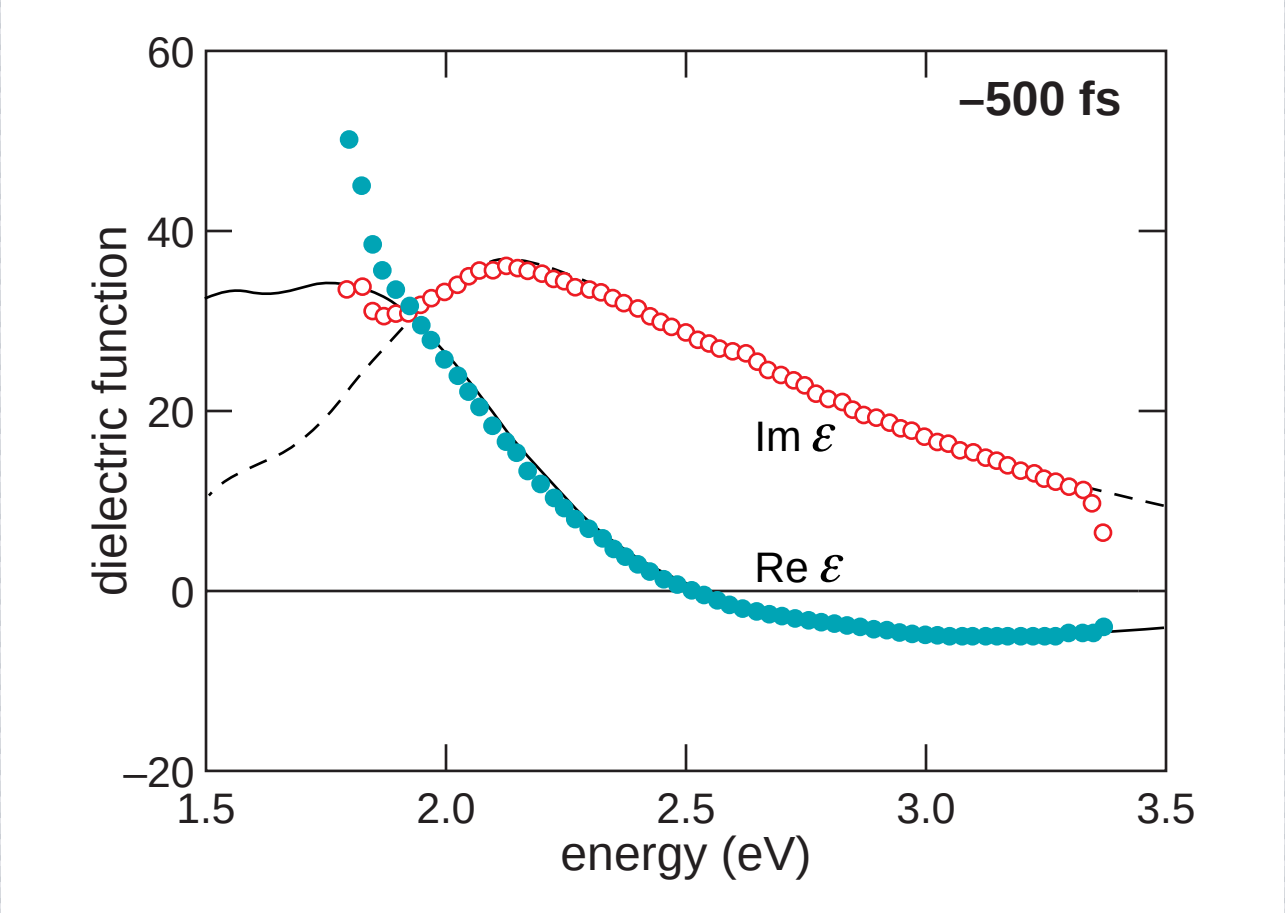
broadband time-resolved ellipsometry



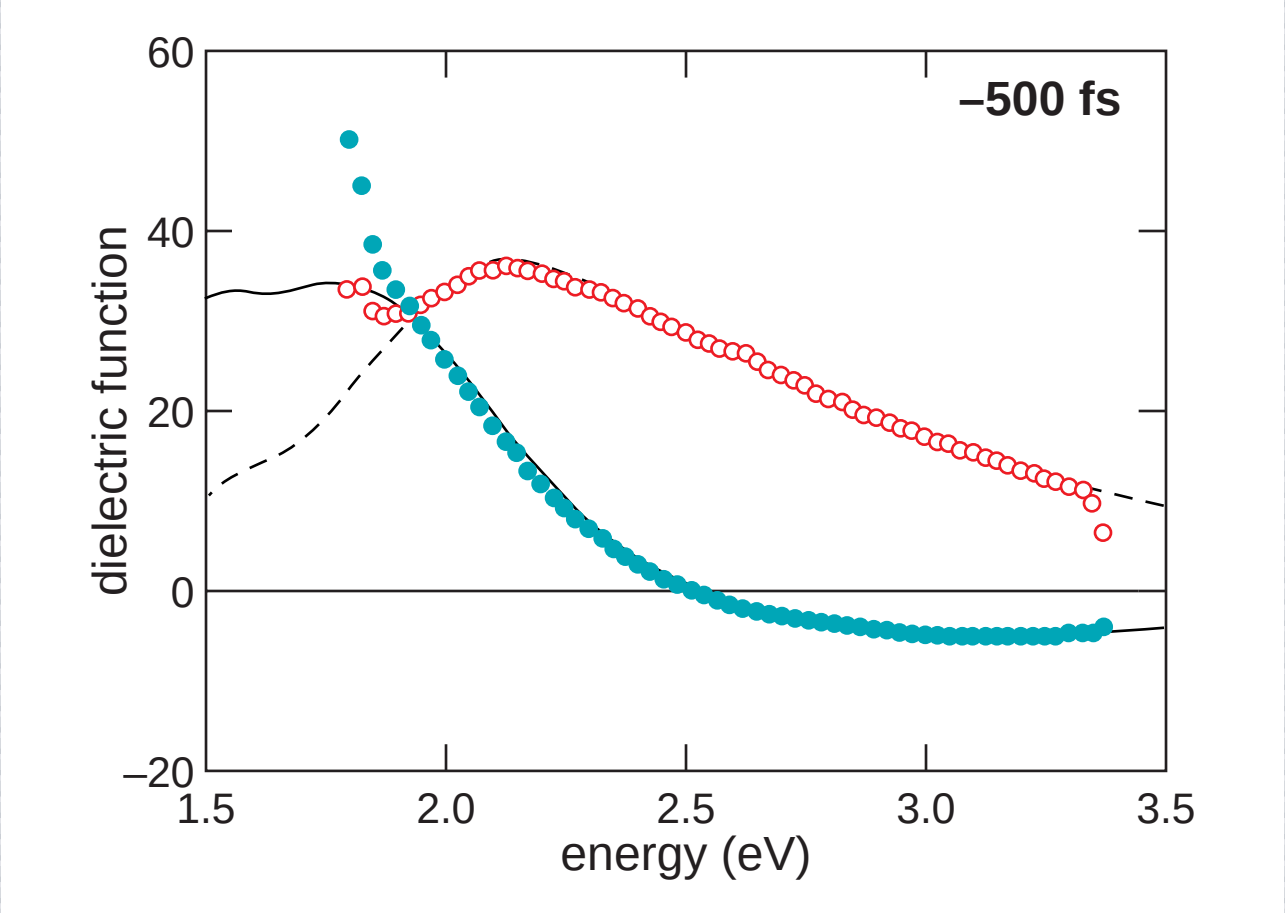
Results


60
40
20
0
–20
dielectric function
1.5
2.0
2.5
3.0
3.5
energy (eV)
Im ε
Re ε

Results


–500 fs
Im ε
Re ε
dielectric function
energy (eV)
60
40
20
0
–20
1.5
2.0
2.5
3.0
3.5

Results


–500 fs
60
40
20
0
–20
1.5
2.0
2.5
3.0
3.5
dielectric function
energy (eV)

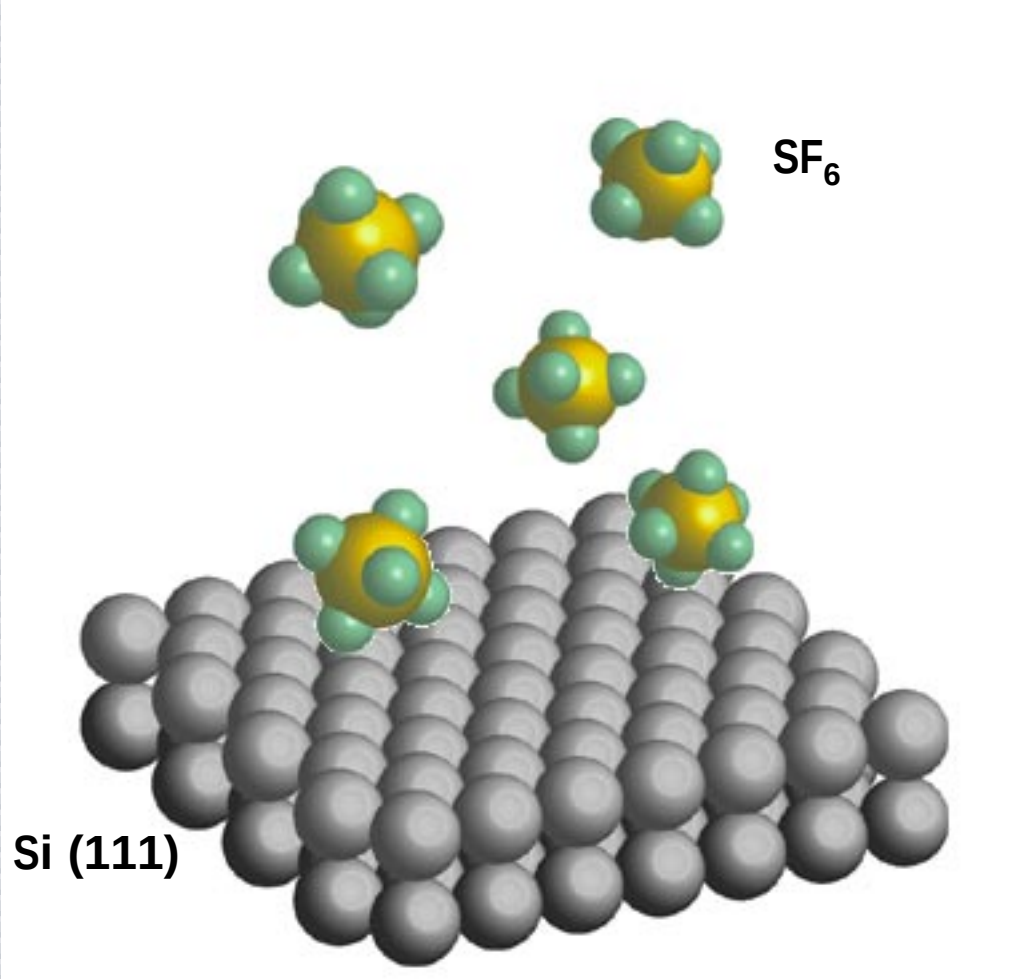
Technique

- direct observation of semiconductor-to-metal transition
- order-disorder transition

Outline

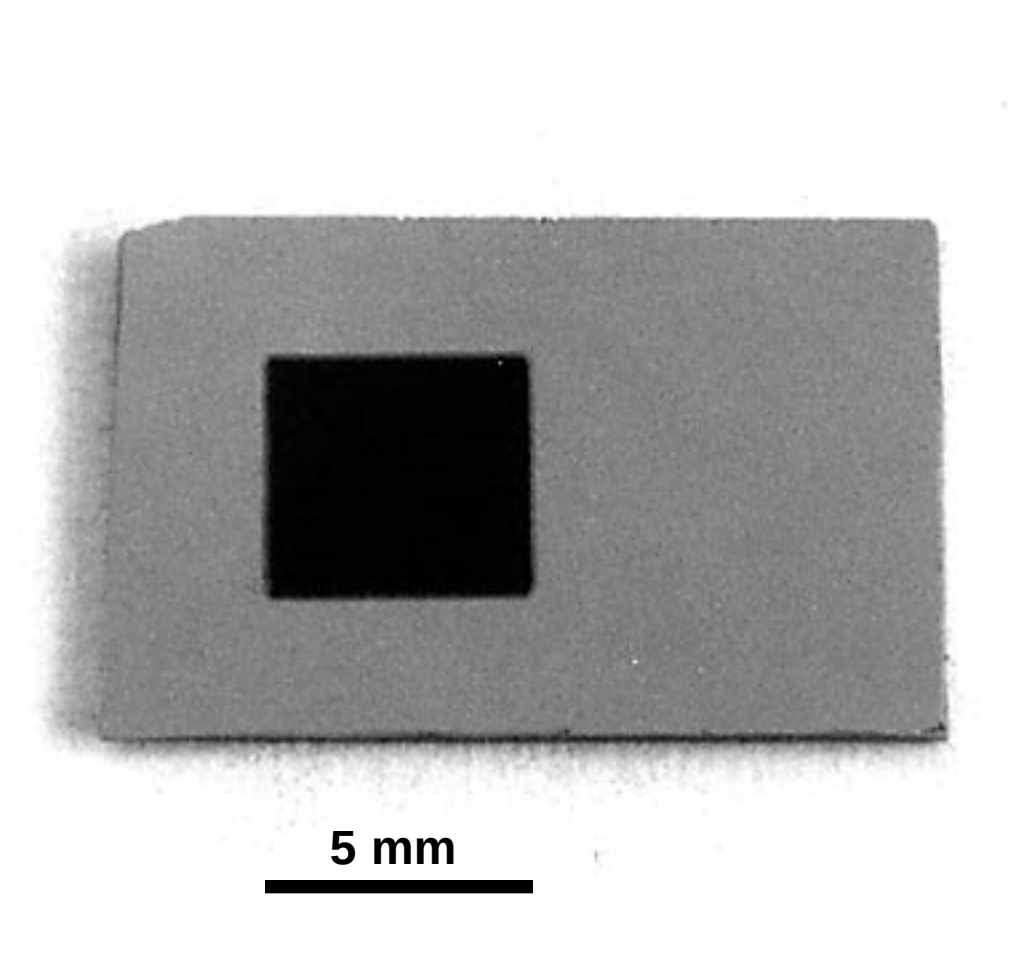
- Processing with fs pulses
- High-density carrier dynamics
- **Laser-assisted ion etching**

Introduction



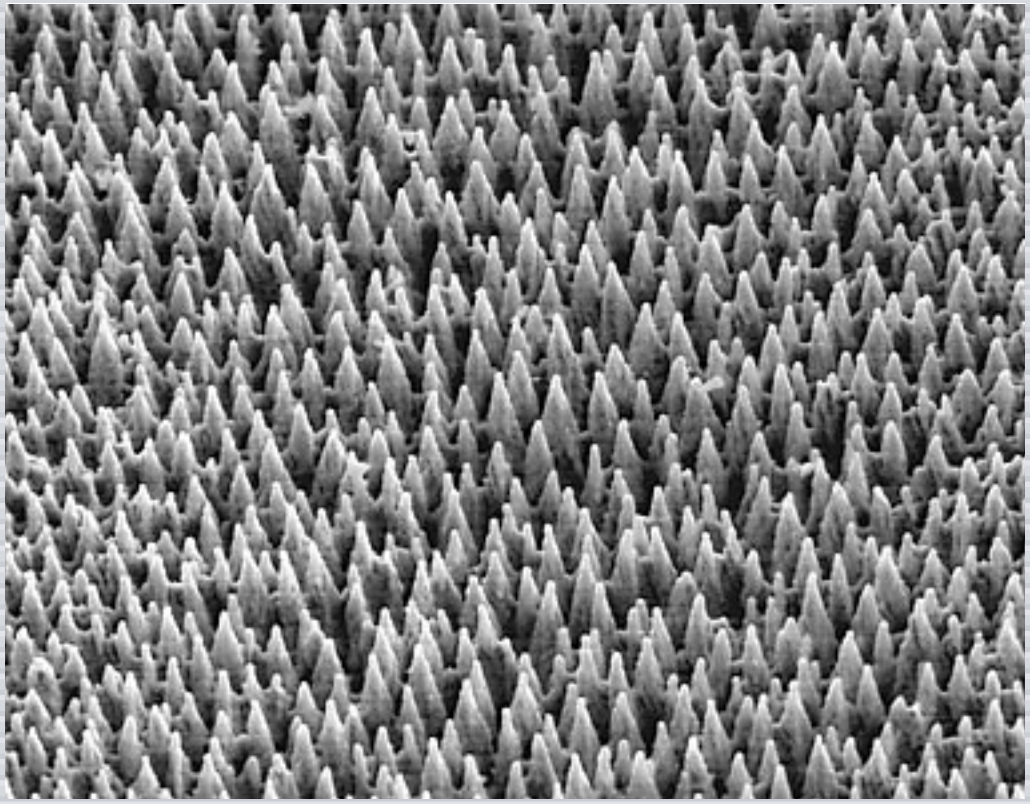
irradiate with 100-fs 10 kJ/m^2 pulses

Introduction



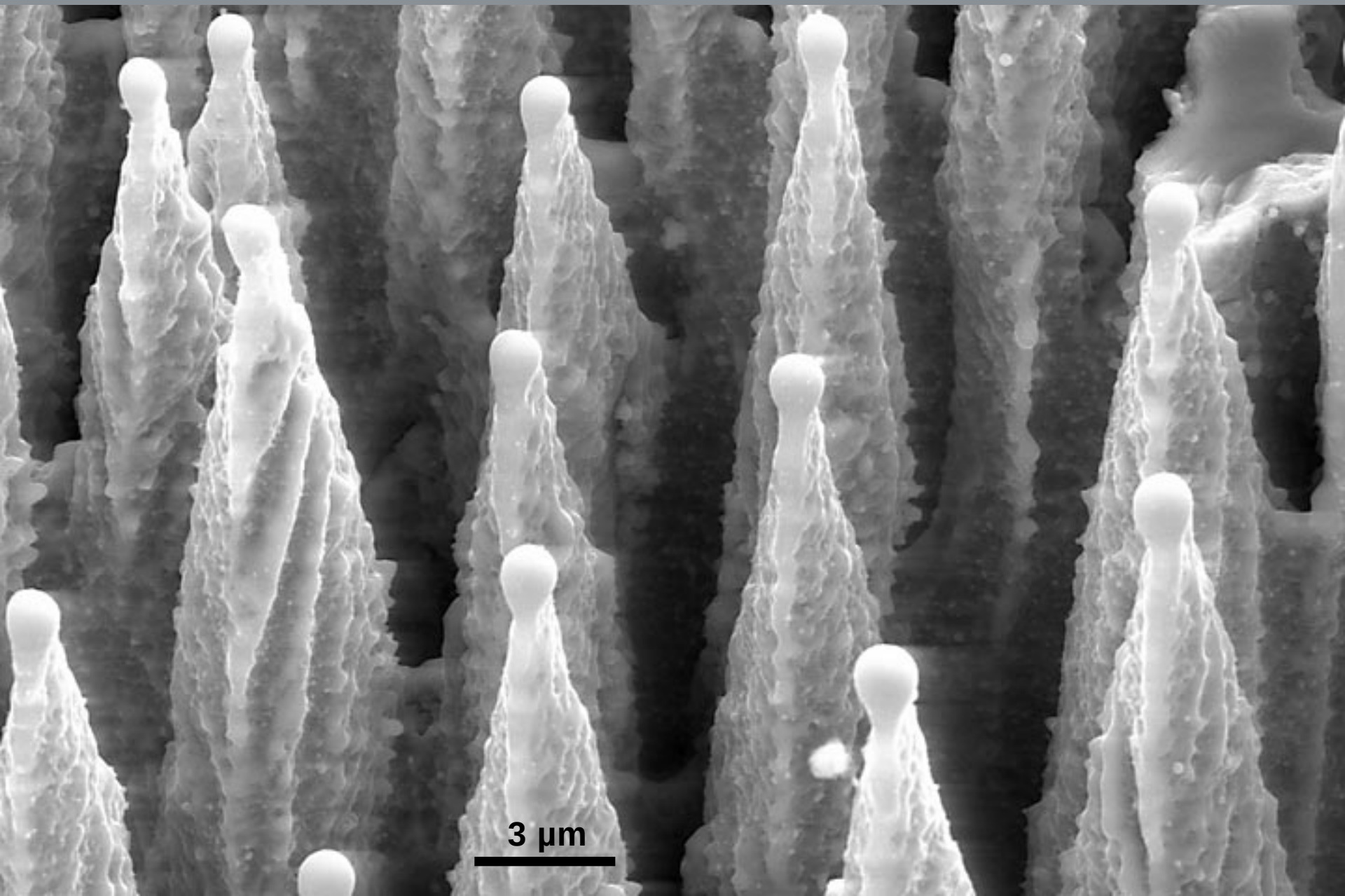
“black silicon”

Introduction

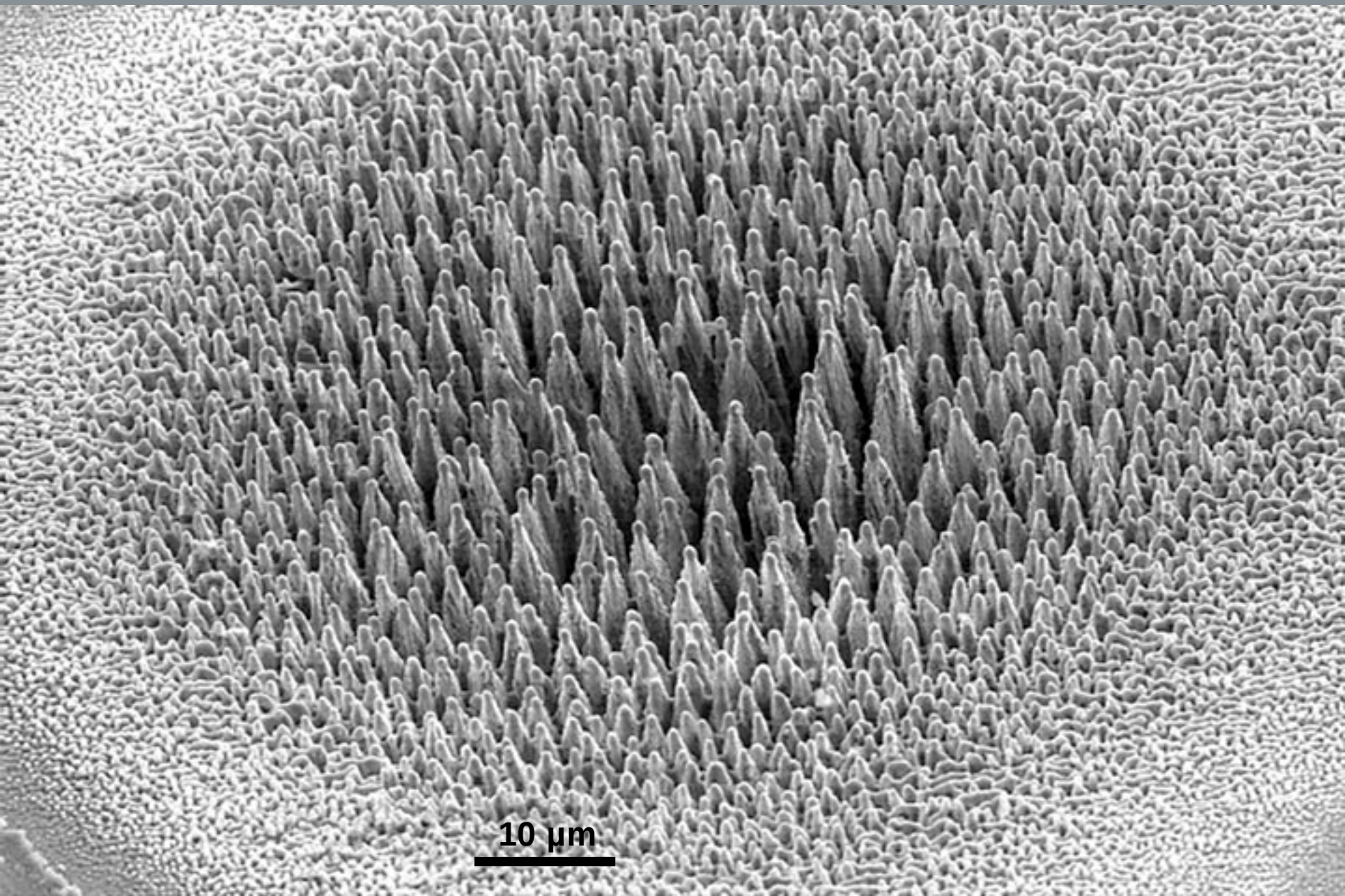


20 µm

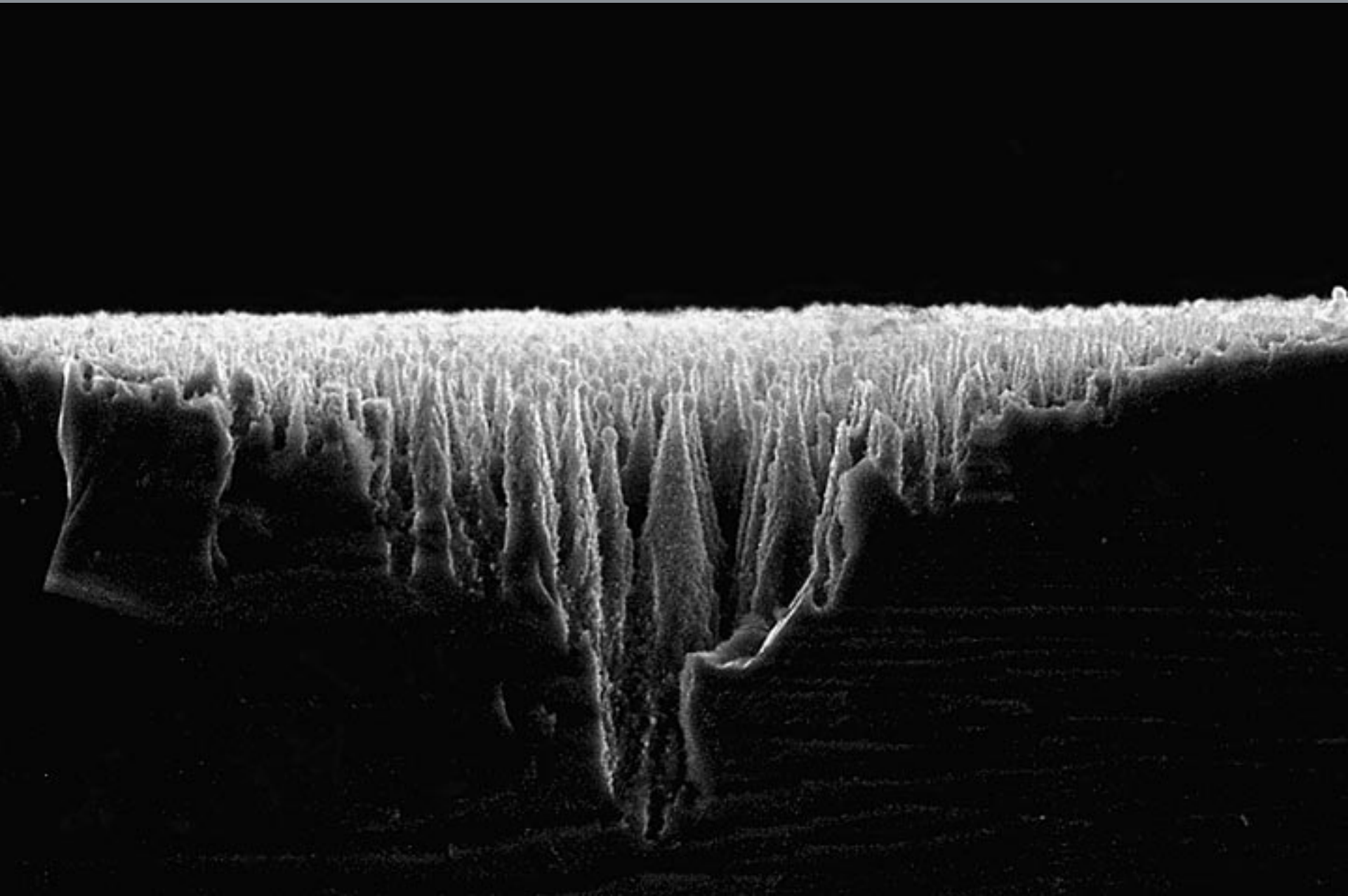
Introduction



Introduction



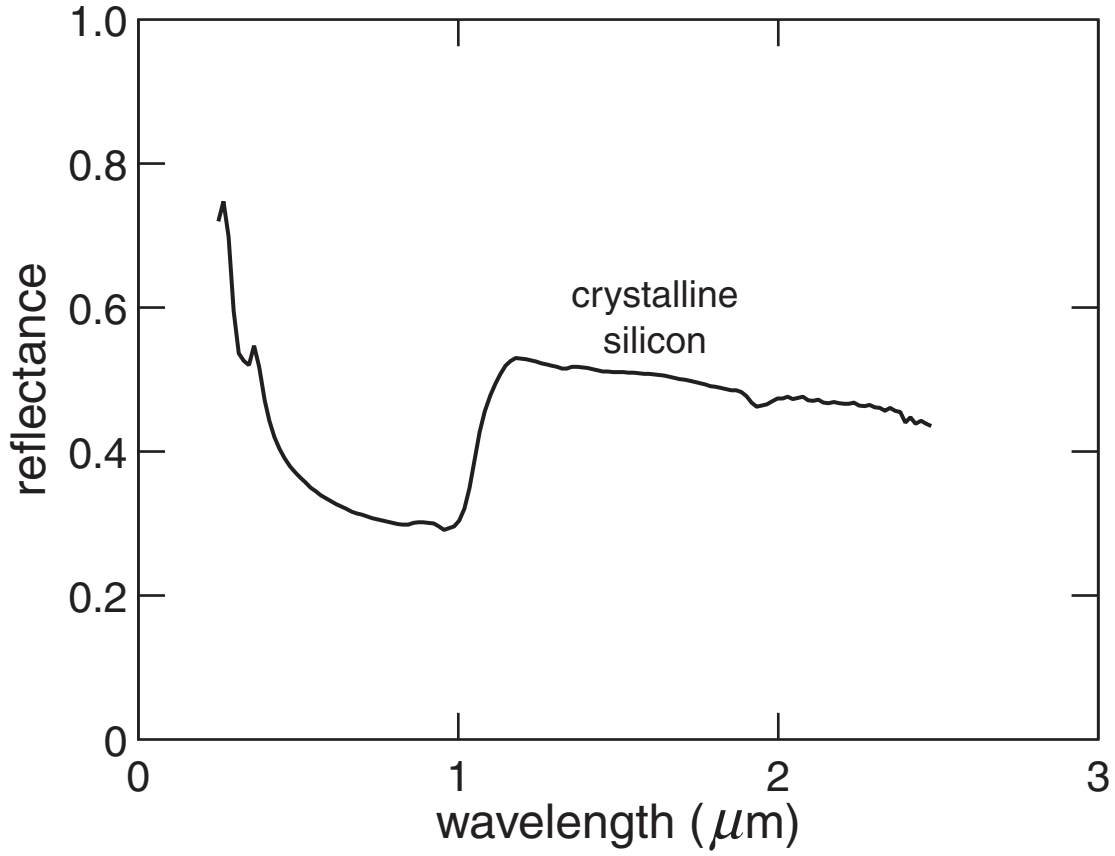
Introduction



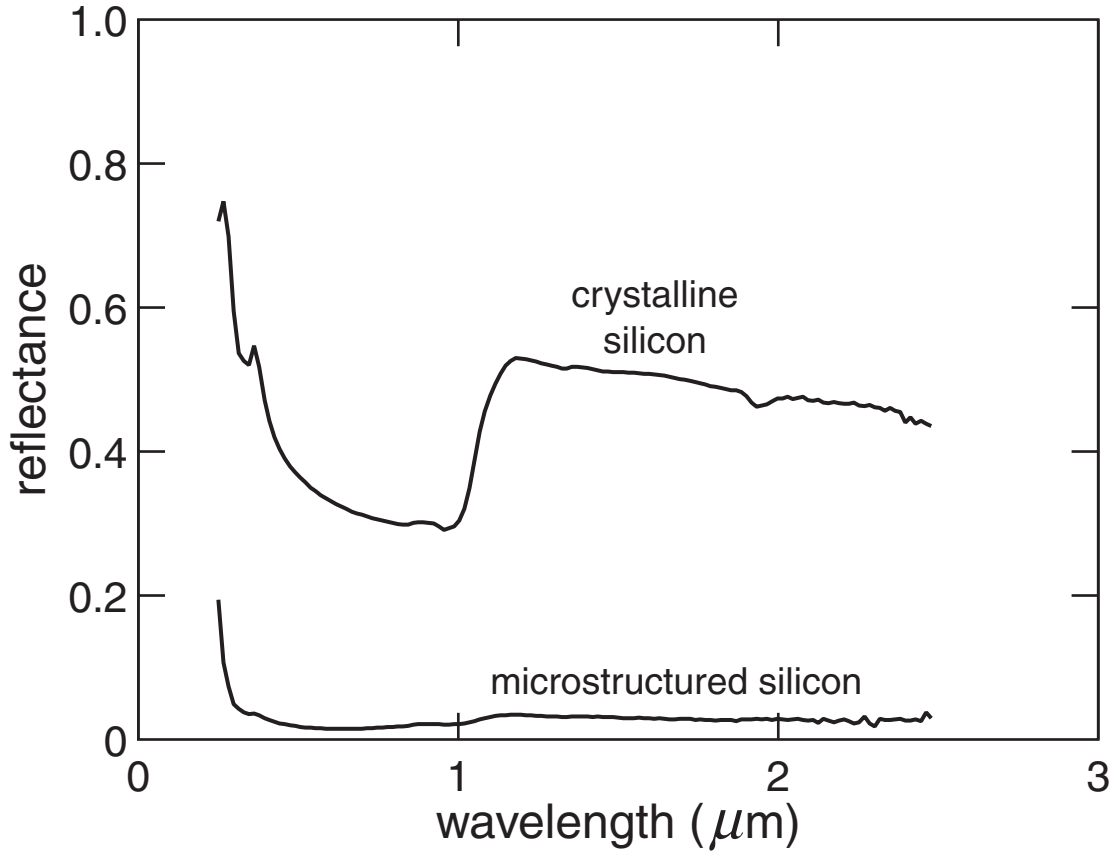
Introduction

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

reflectance (integrating sphere)

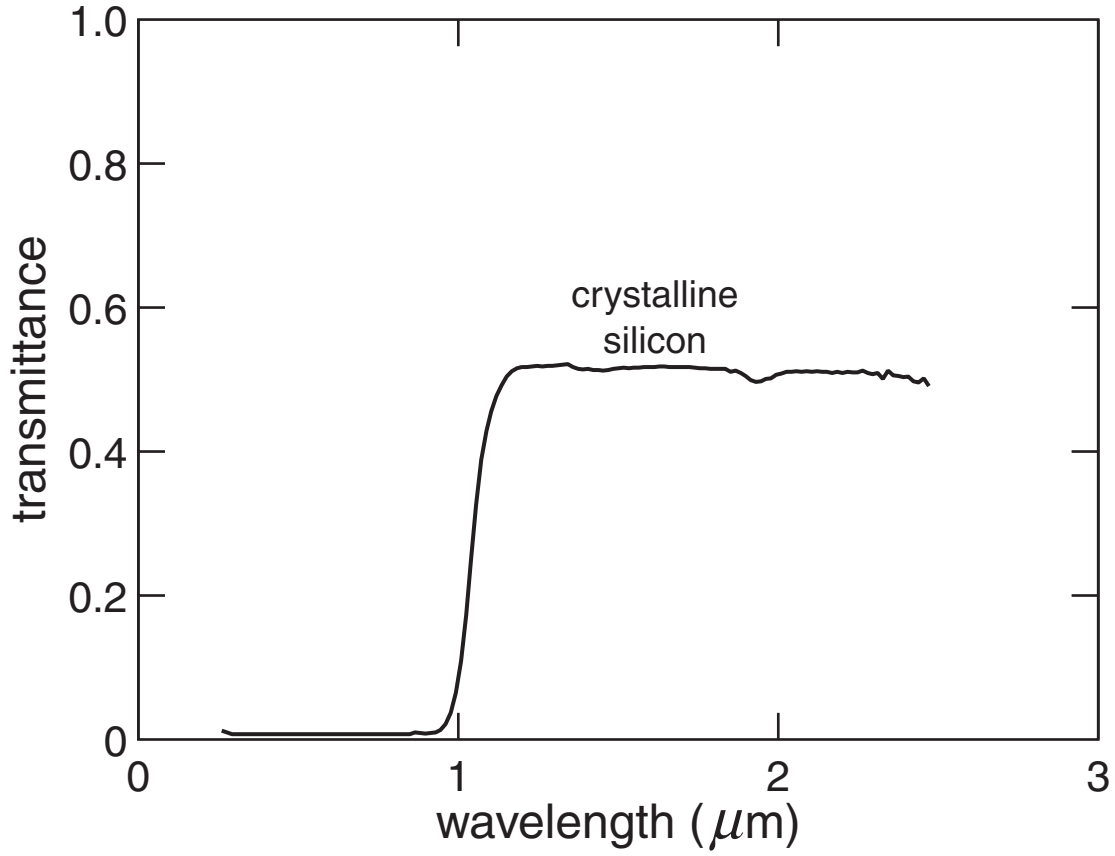


reflectance (integrating sphere)

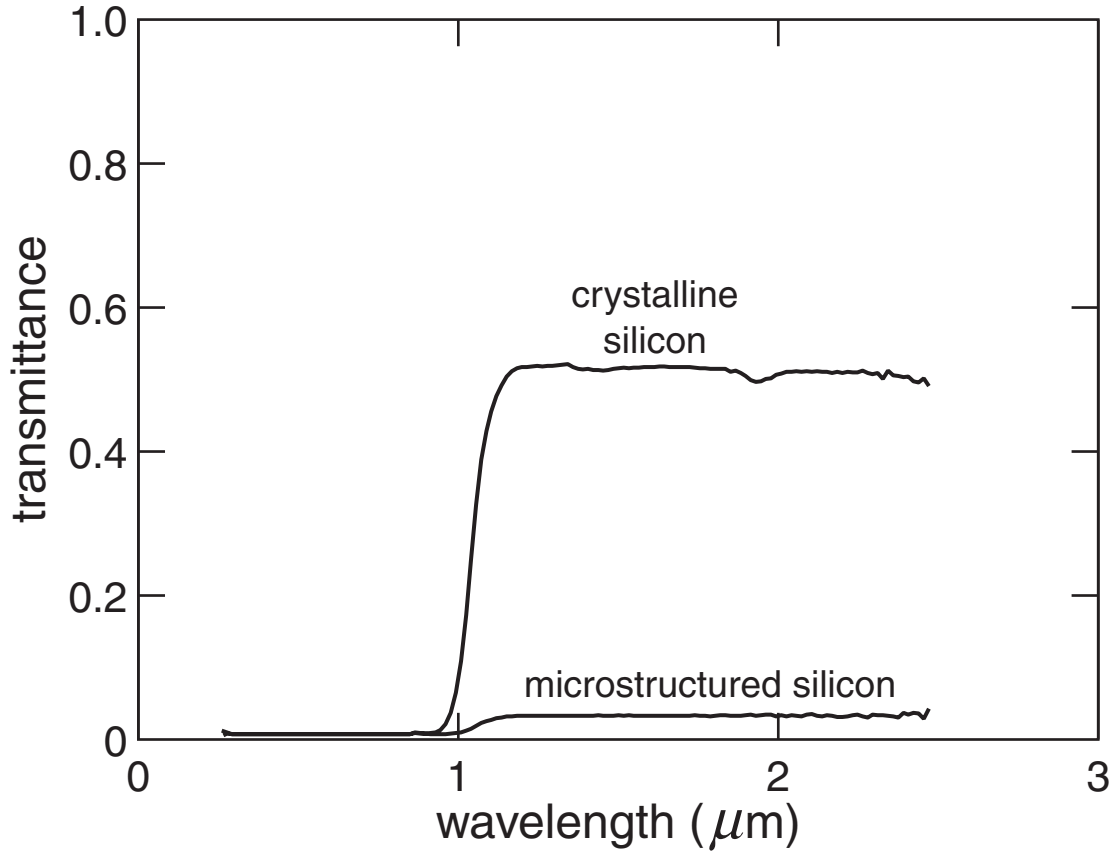


Properties

transmittance (integrating sphere)

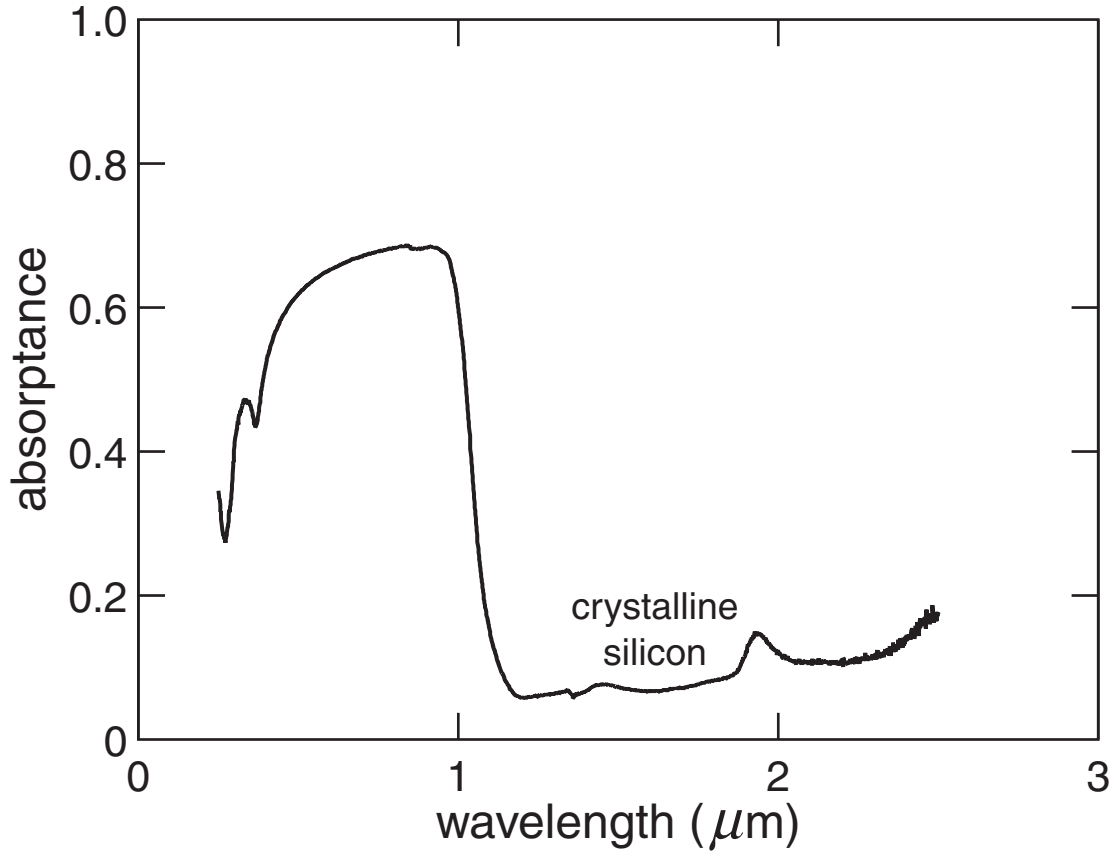


transmittance (integrating sphere)



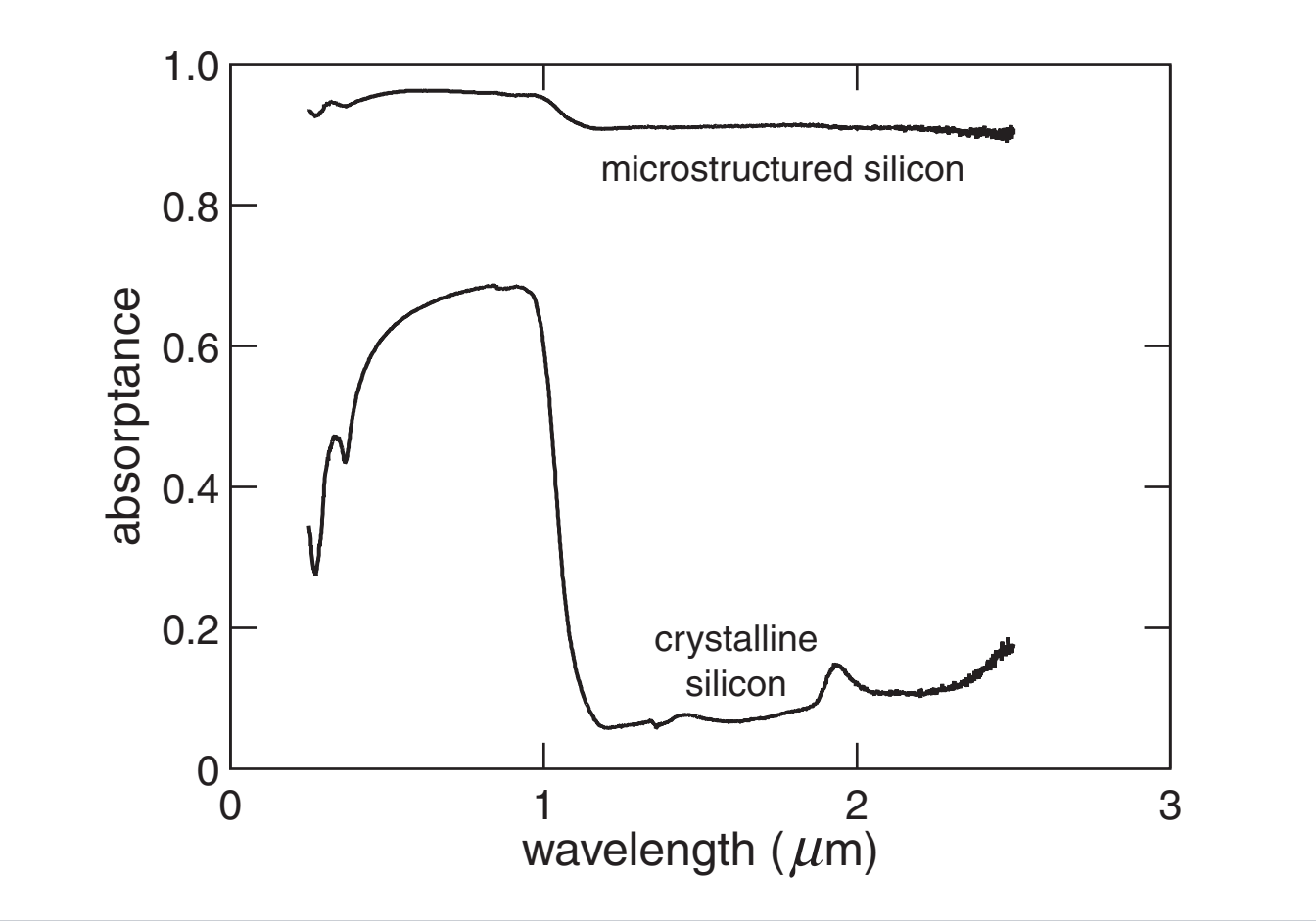
Properties

absorptance (1 – *R* – *T*)



Properties

absorptance (1 – *R* – *T*)



***Appl. Phys. Lett*. 78, 1850 (2001)**

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**

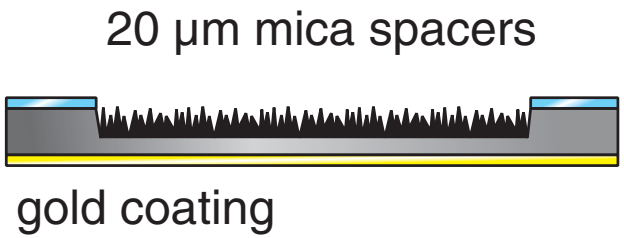
can spikes be used as field emitters?

field emission setup

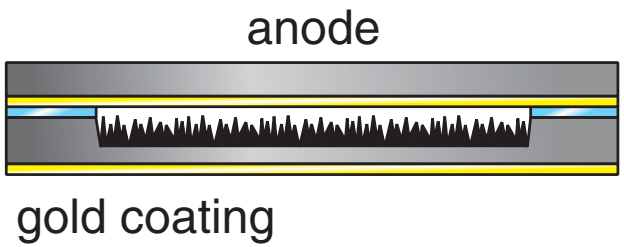
field emission setup

gold coating

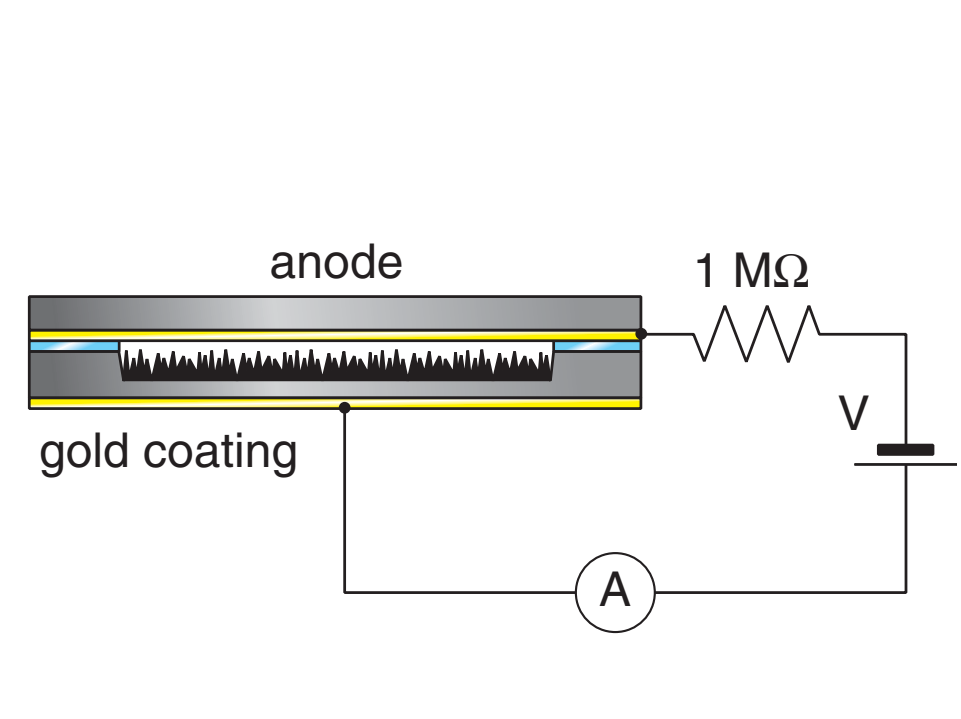
field emission setup



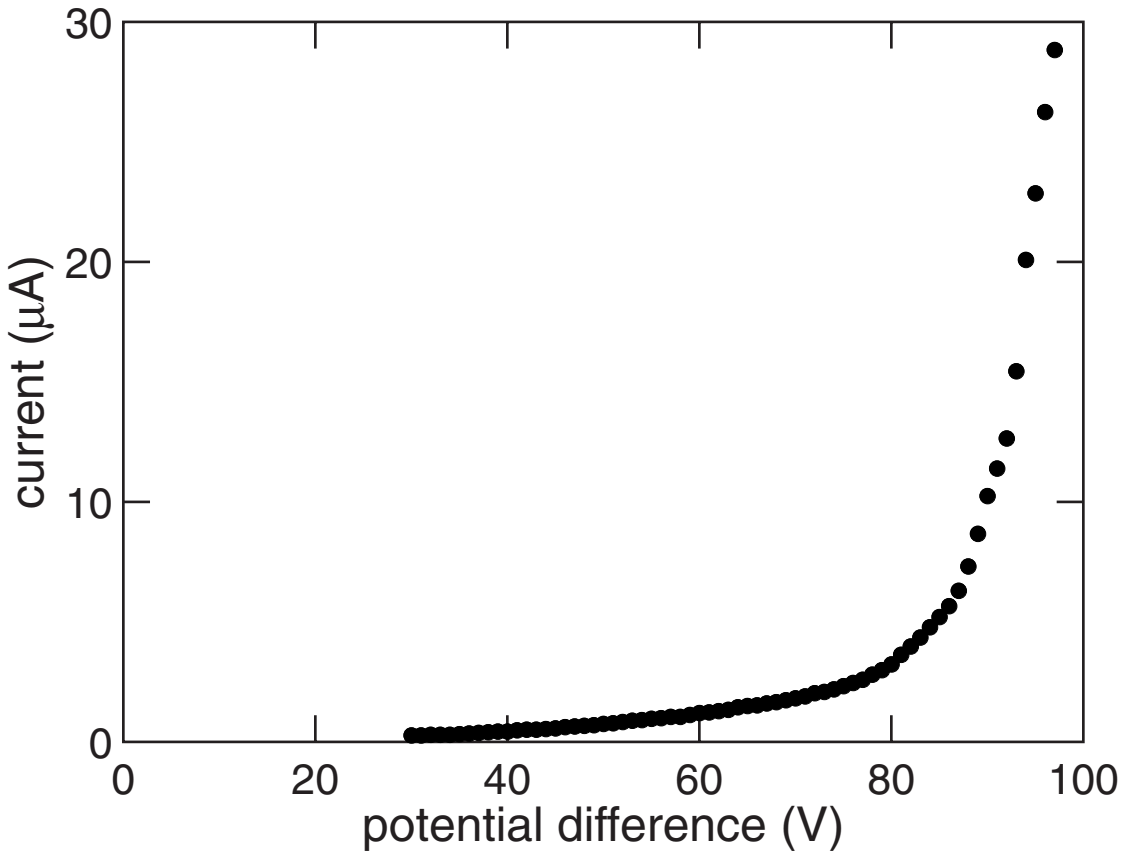
field emission setup



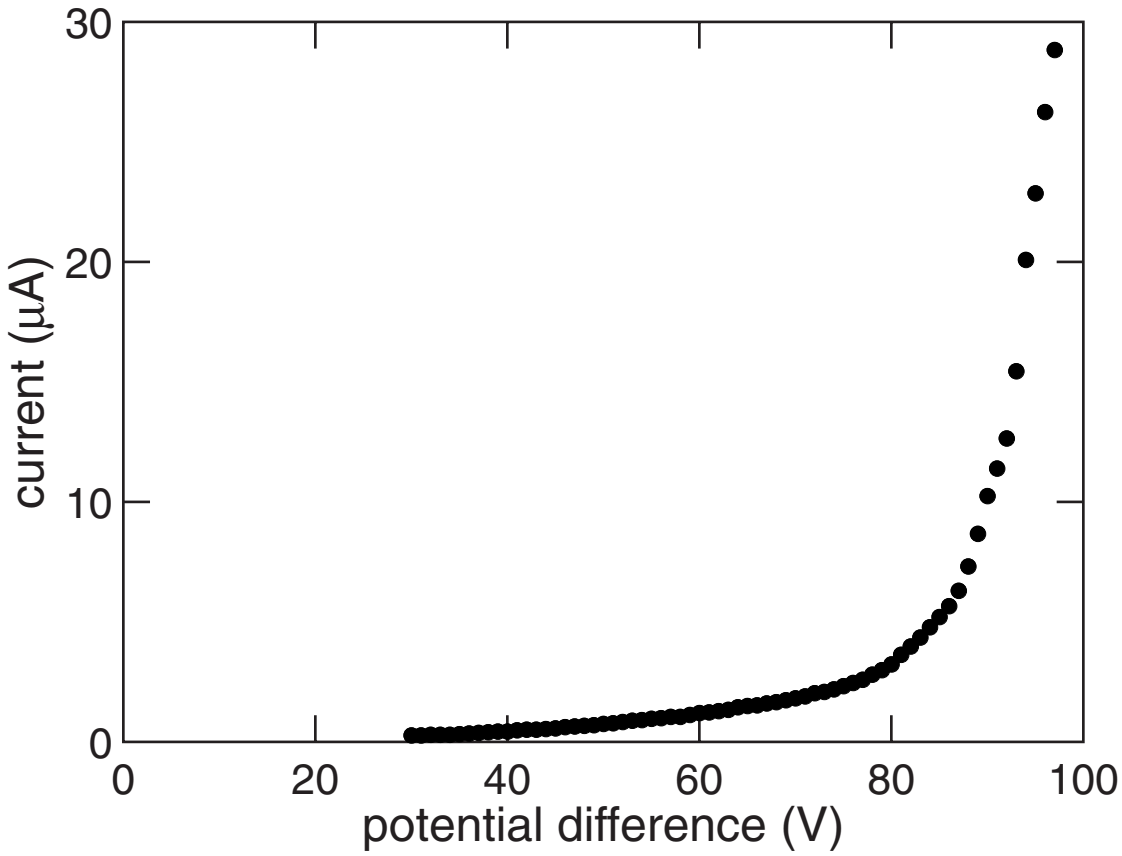
field emission setup



Properties

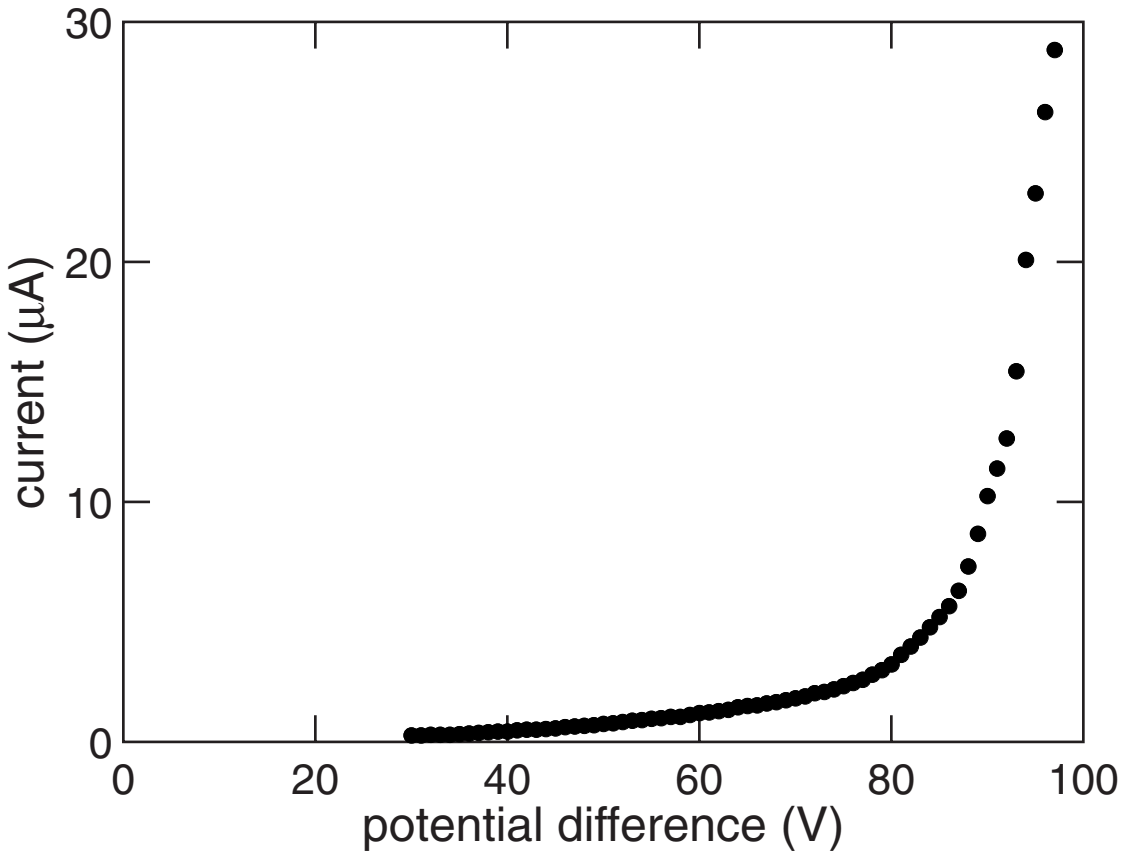


Properties



turn-on field (1 μA/cm^2): 1.2 V/μm

Properties



threshold field (10 μA/cm^2): 2.1 V/μm

Structural and chemical analysis

- **What causes these properties?**
- **Other gases?**

Structural and chemical analysis

Ion channeling and electron backscattering:

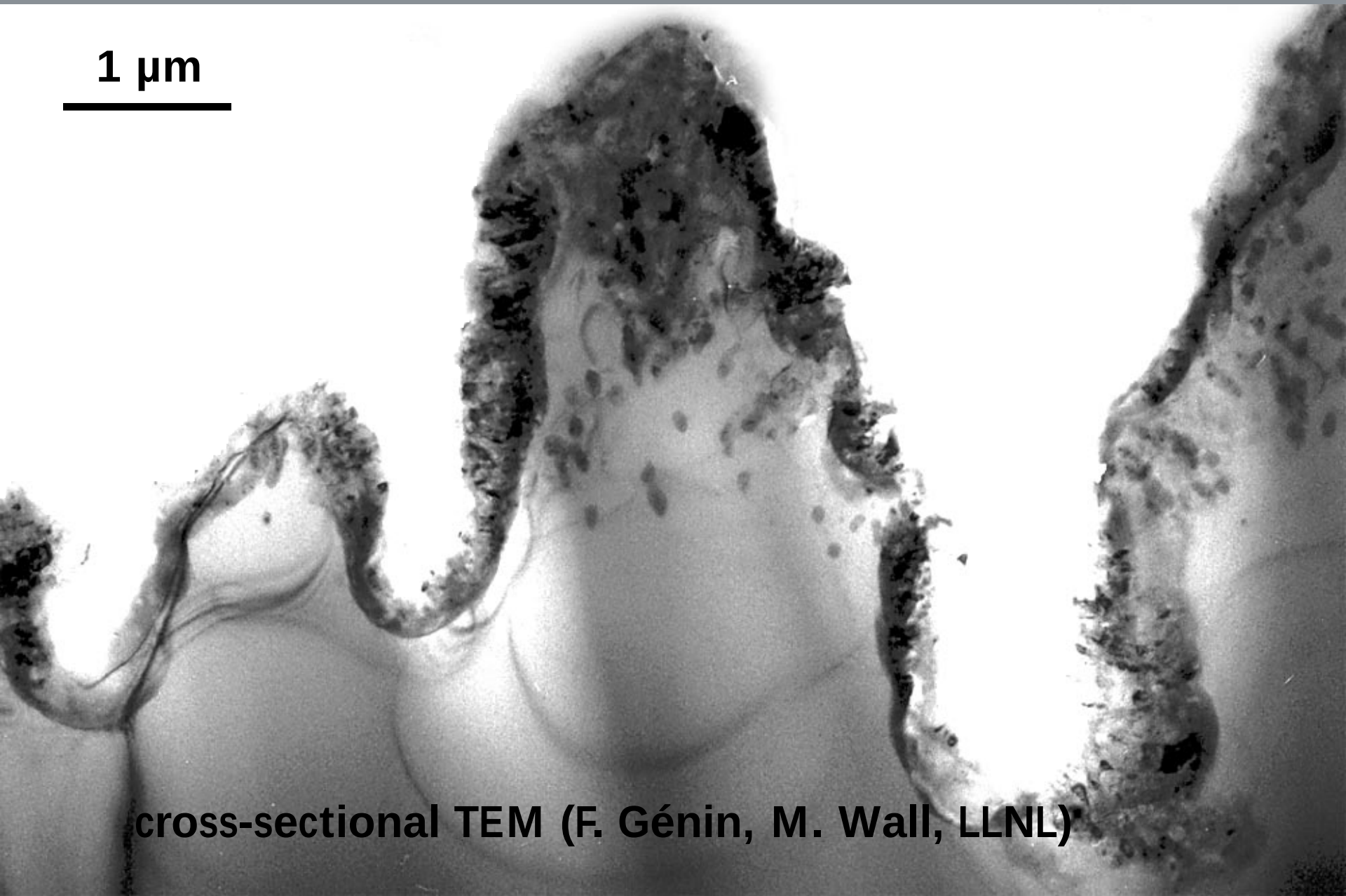
- **spikes retain crystalline order**
- **high density of defects**

Structural and chemical analysis

Secondary ion mass spectrometry:

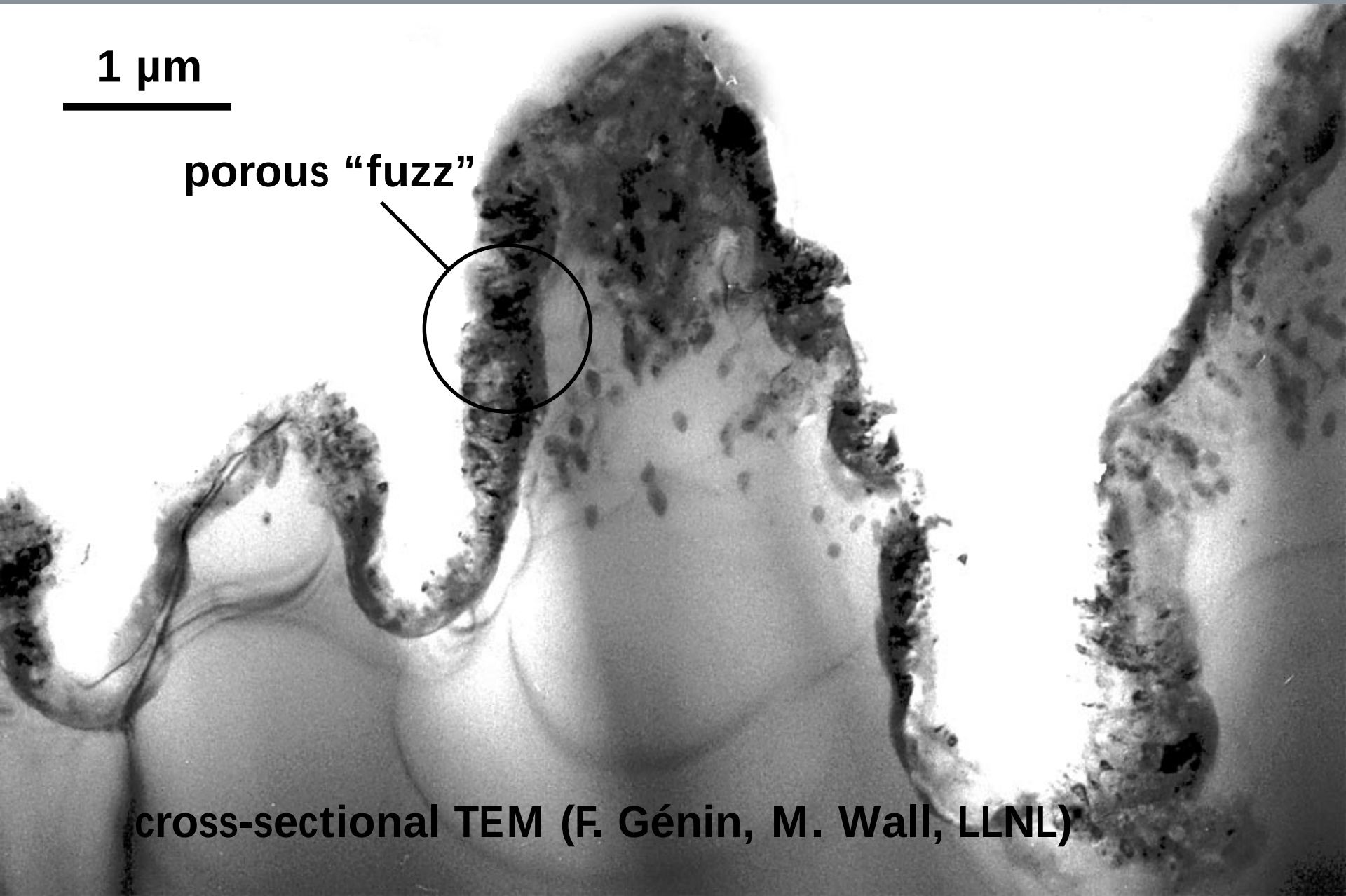
- **10^{20} cm^{-3} sulfur**
- **10^{17} cm^{-3} fluorine**

Structural and chemical analysis



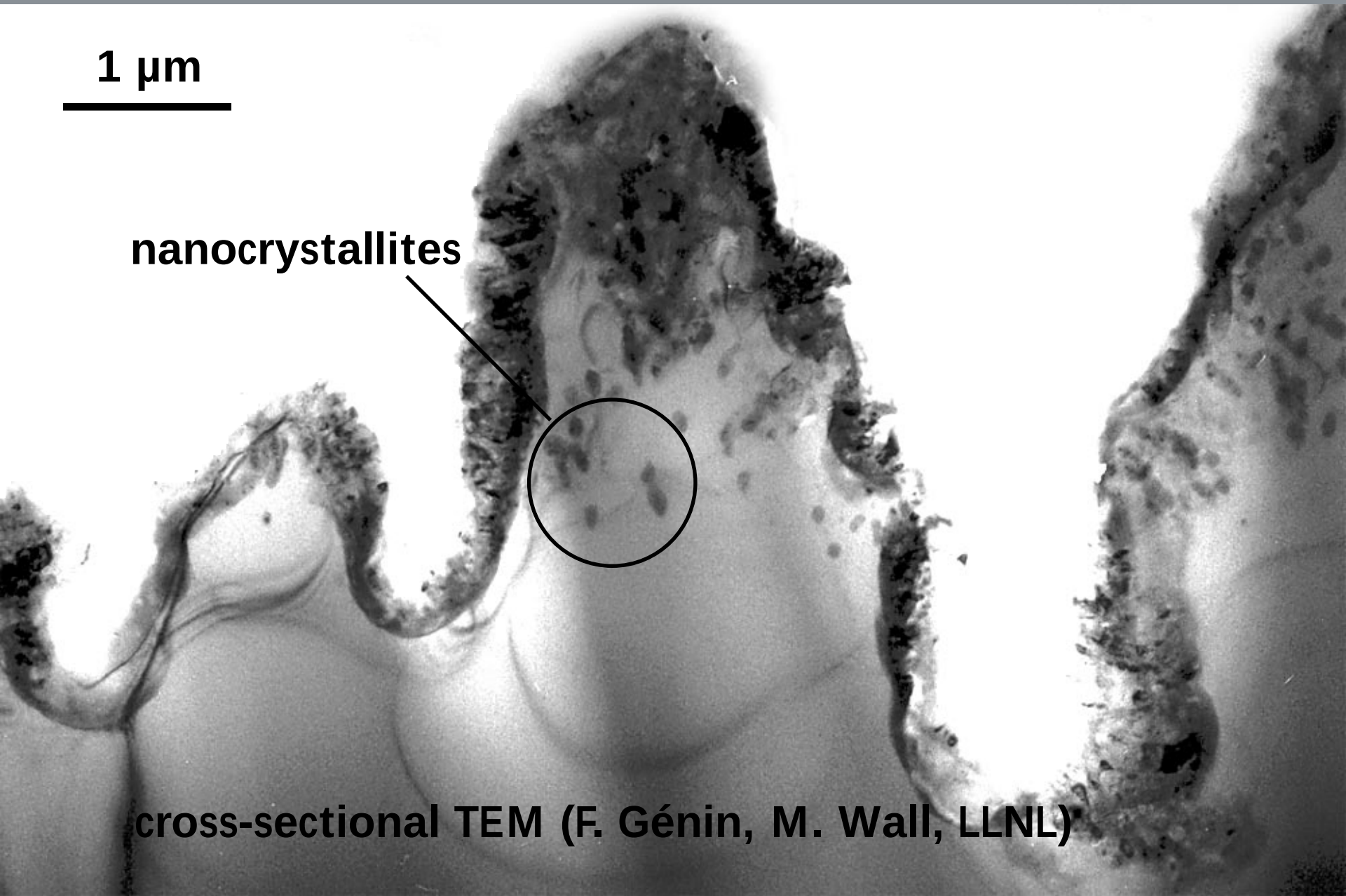
cross-sectional TEM (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



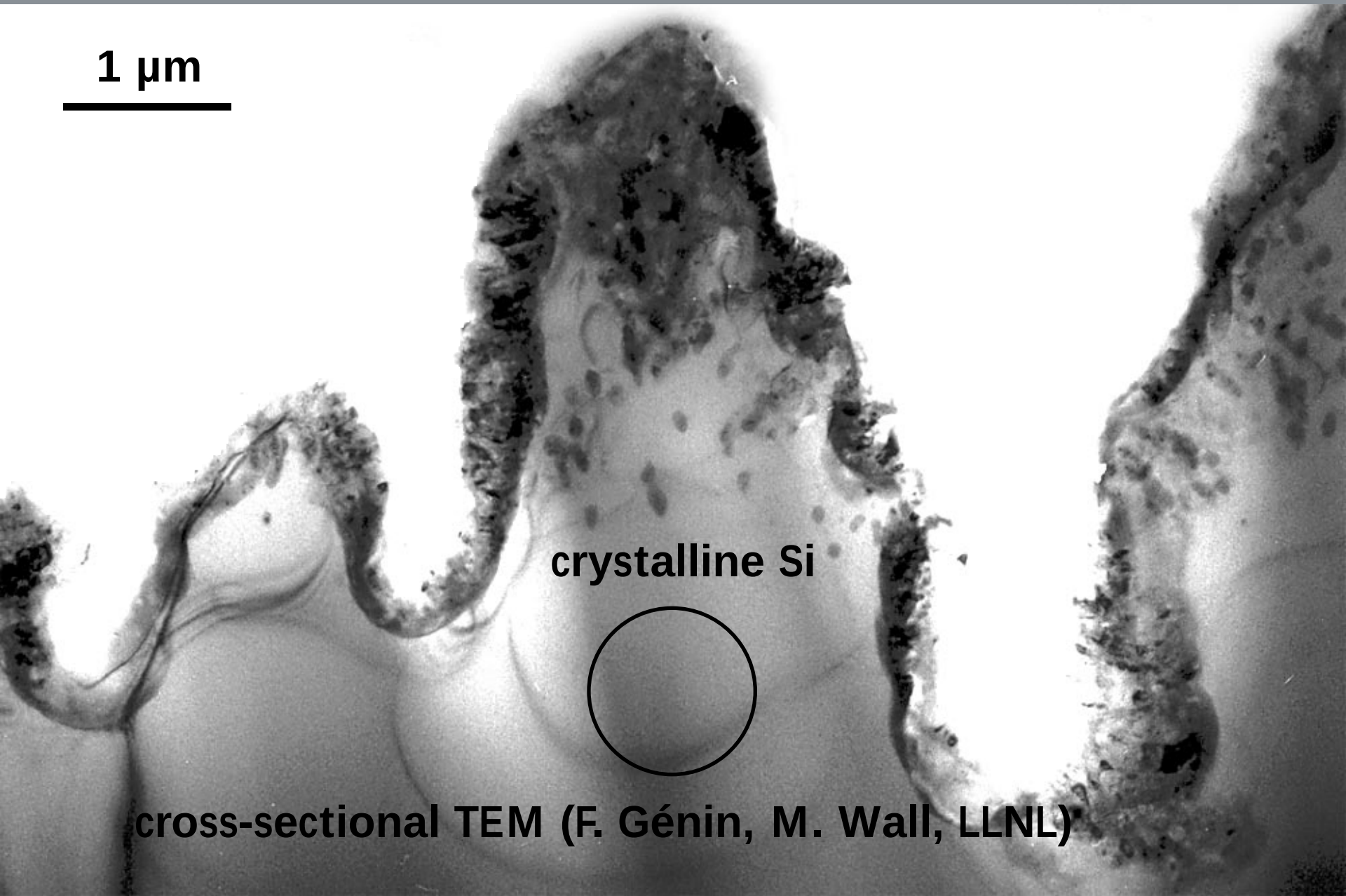
cross-sectional TEM (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



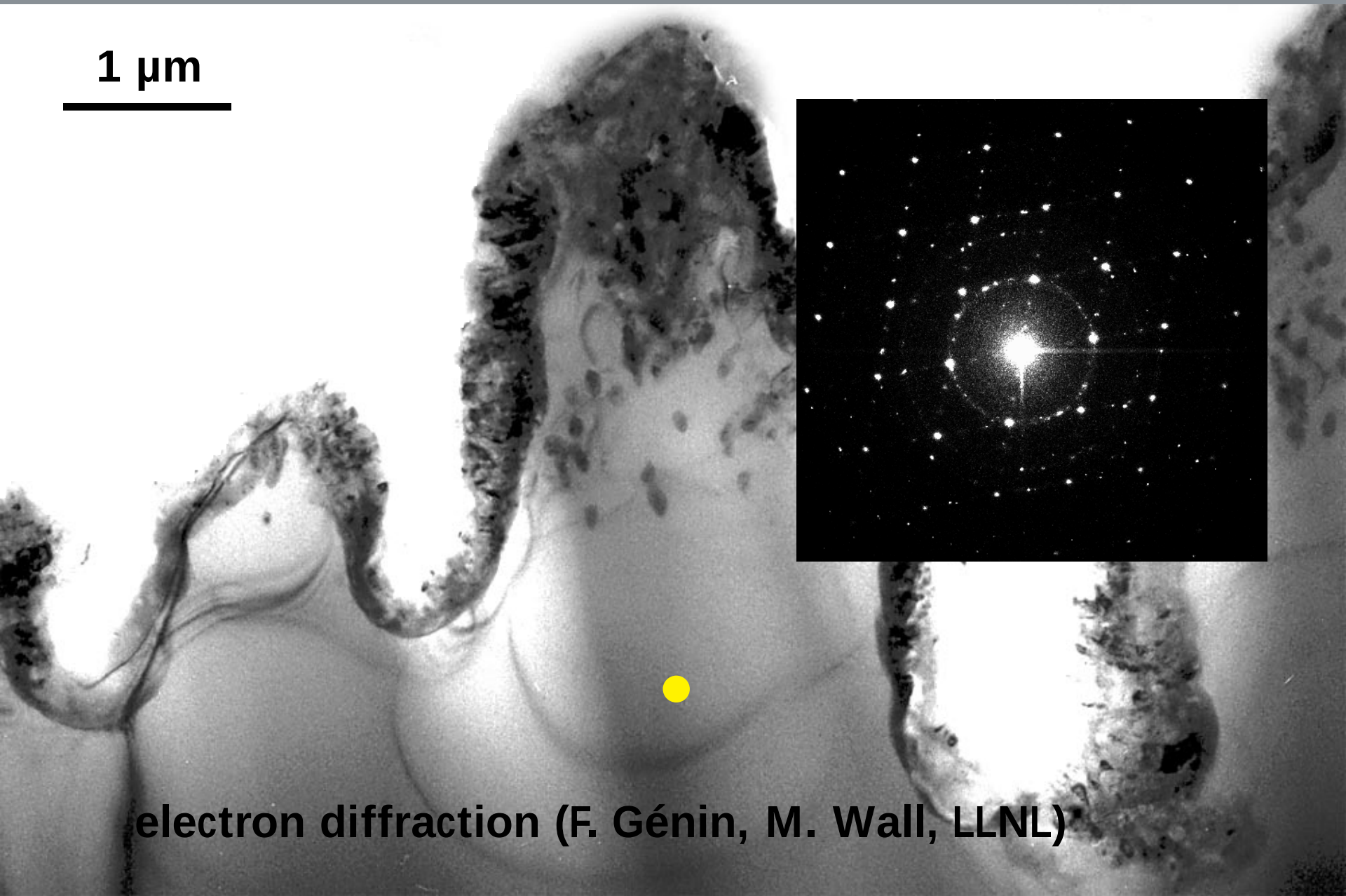
cross-sectional TEM (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



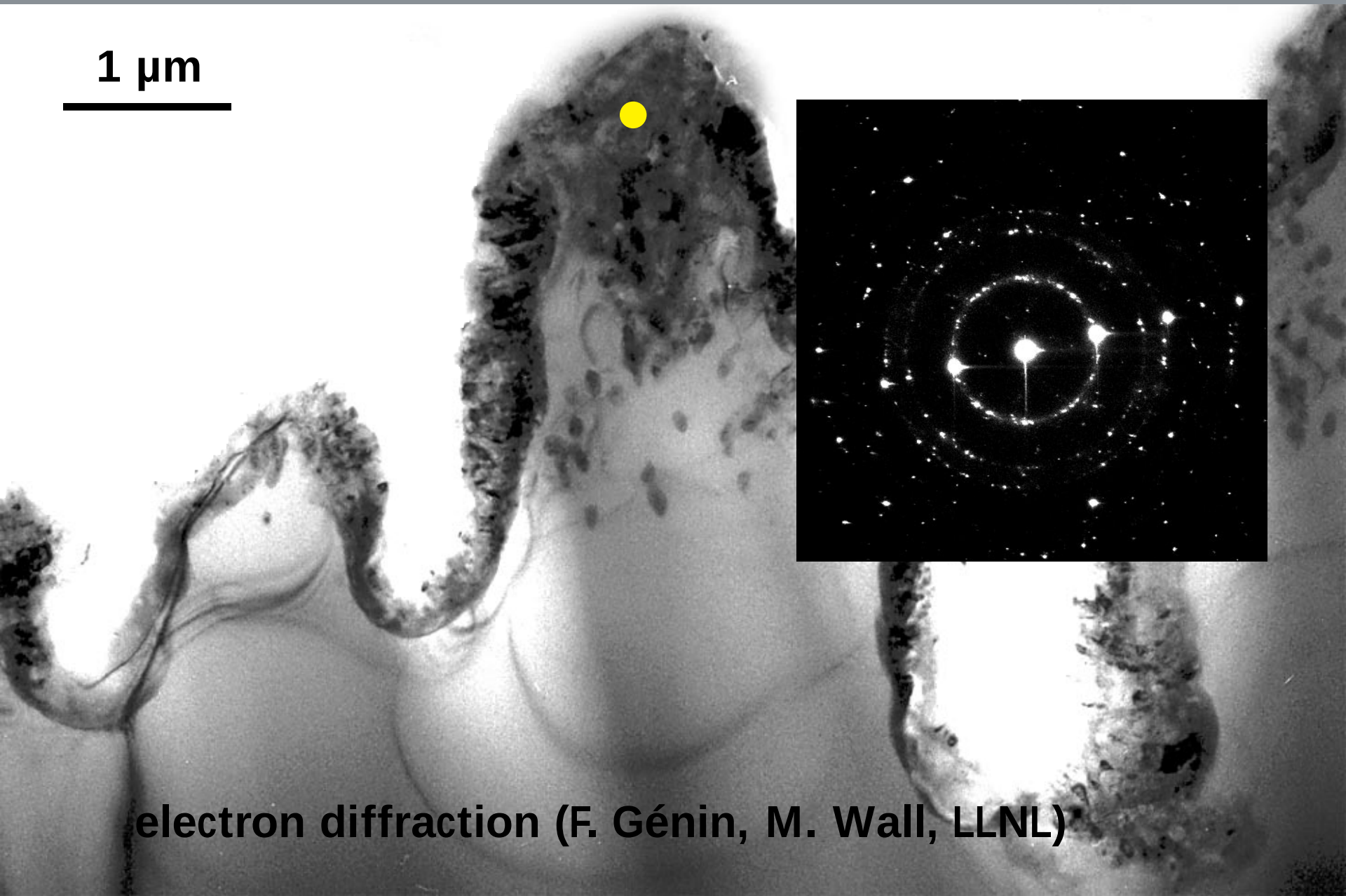
cross-sectional TEM (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



electron diffraction (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



electron diffraction (F. Génin, M. Wall, LLNL)

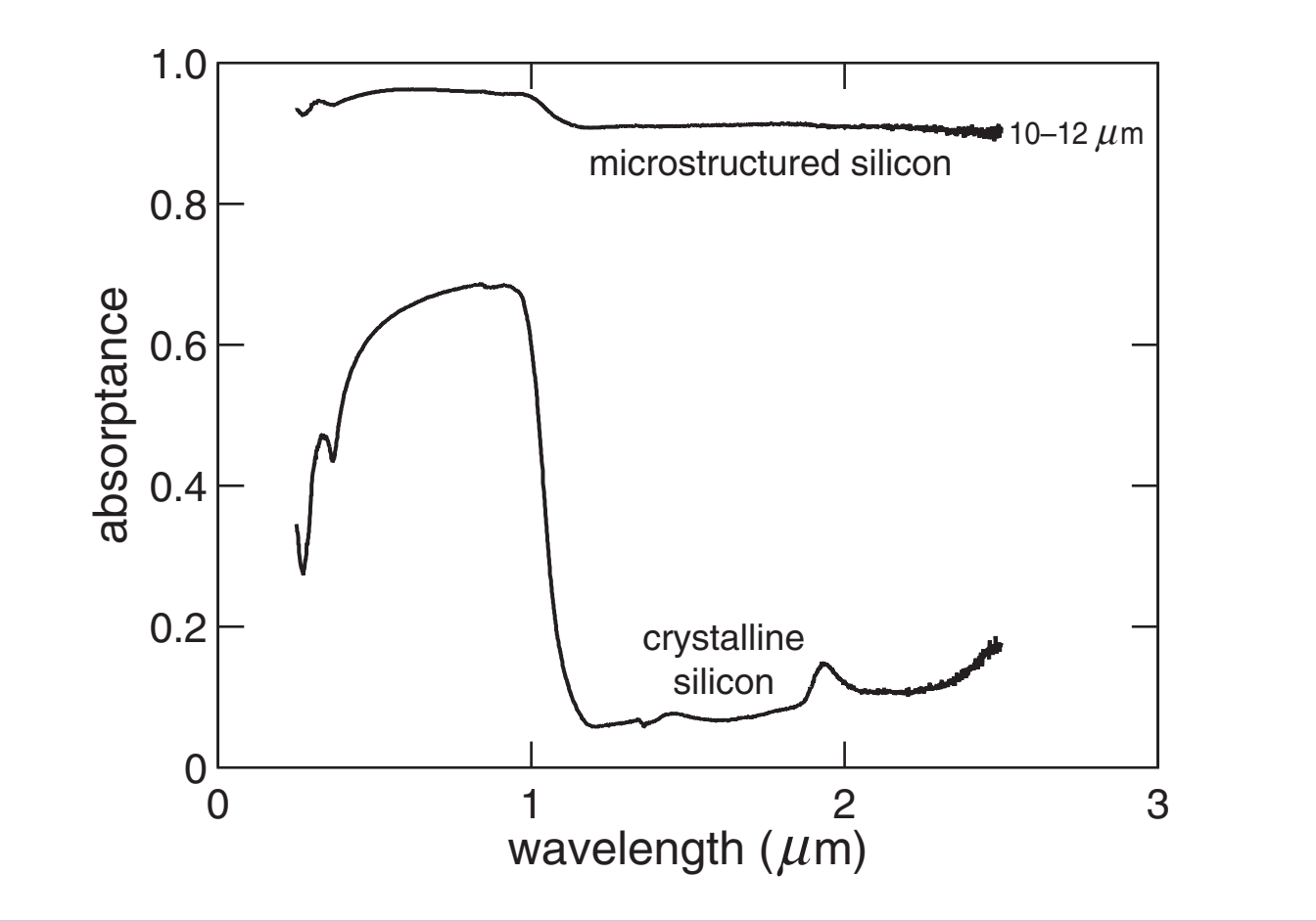
Structural and chemical analysis

cross-sectional TEM:

- **core of spikes: undisturbed Si**
- **surface layer: disordered Si, impurities, nanocrystallites and pores**

Structural and chemical analysis

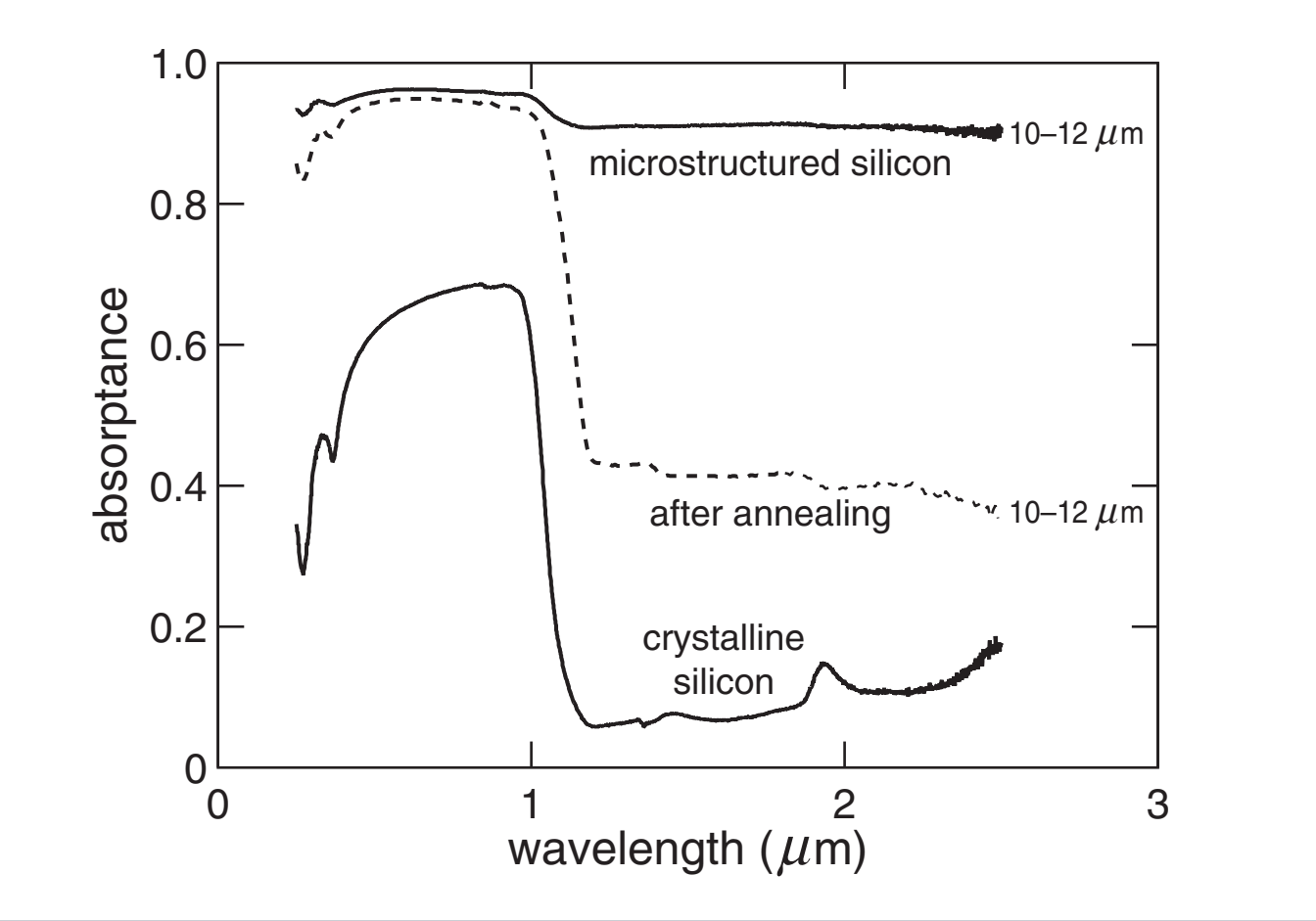
anneal 4 hours at 1200 K



Appl. Phys. Lett. **78**, 1850 (2001)

Structural and chemical analysis

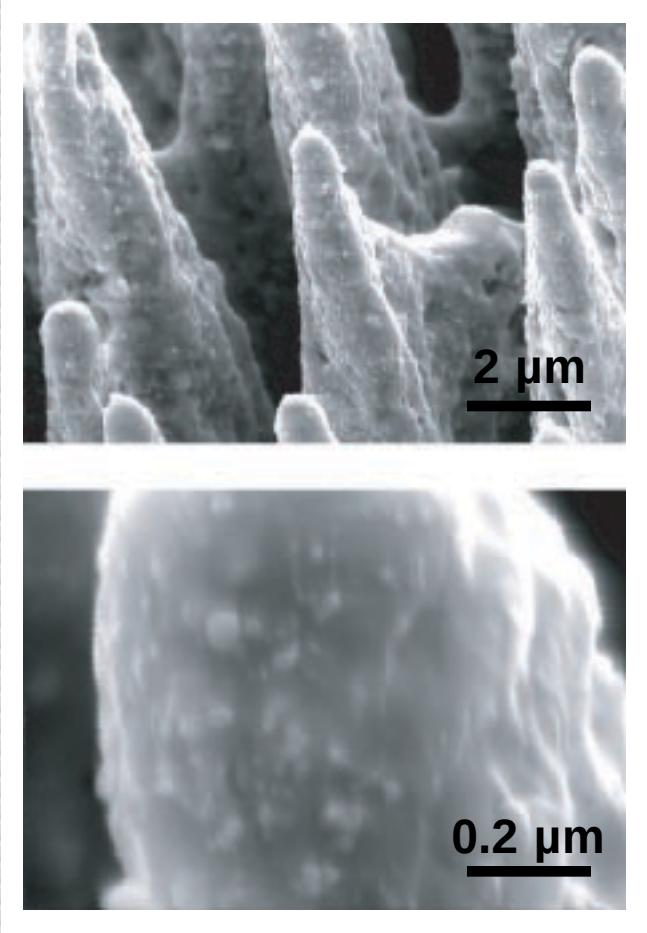
anneal 4 hours at 1200 K



Appl. Phys. Lett. **78**, 1850 (2001)

Structural and chemical analysis

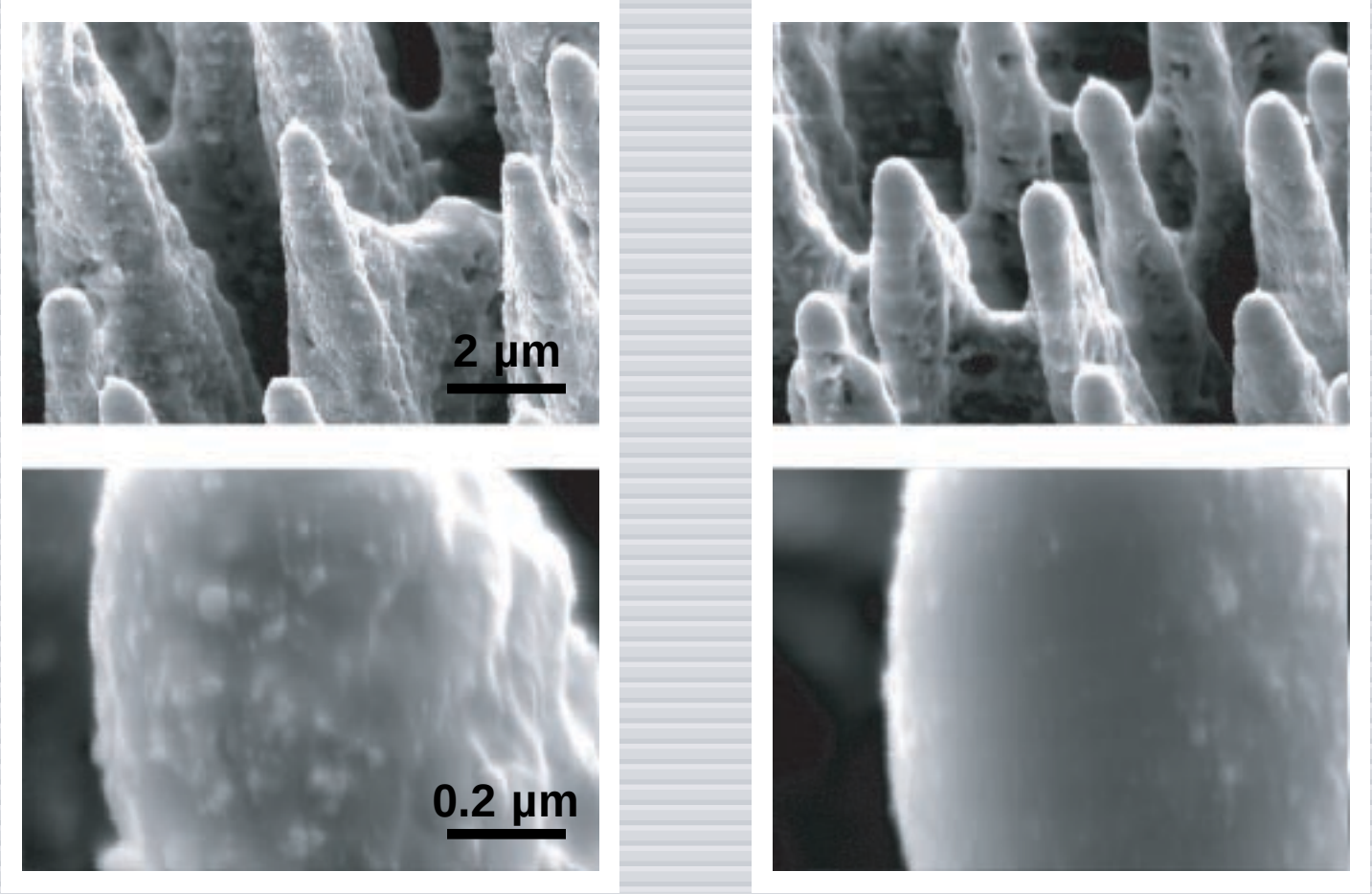
anneal 4 hours at 1200 K



Appl. Phys. Lett. **78**, 1850 (2001)

Structural and chemical analysis

anneal 4 hours at 1200 K



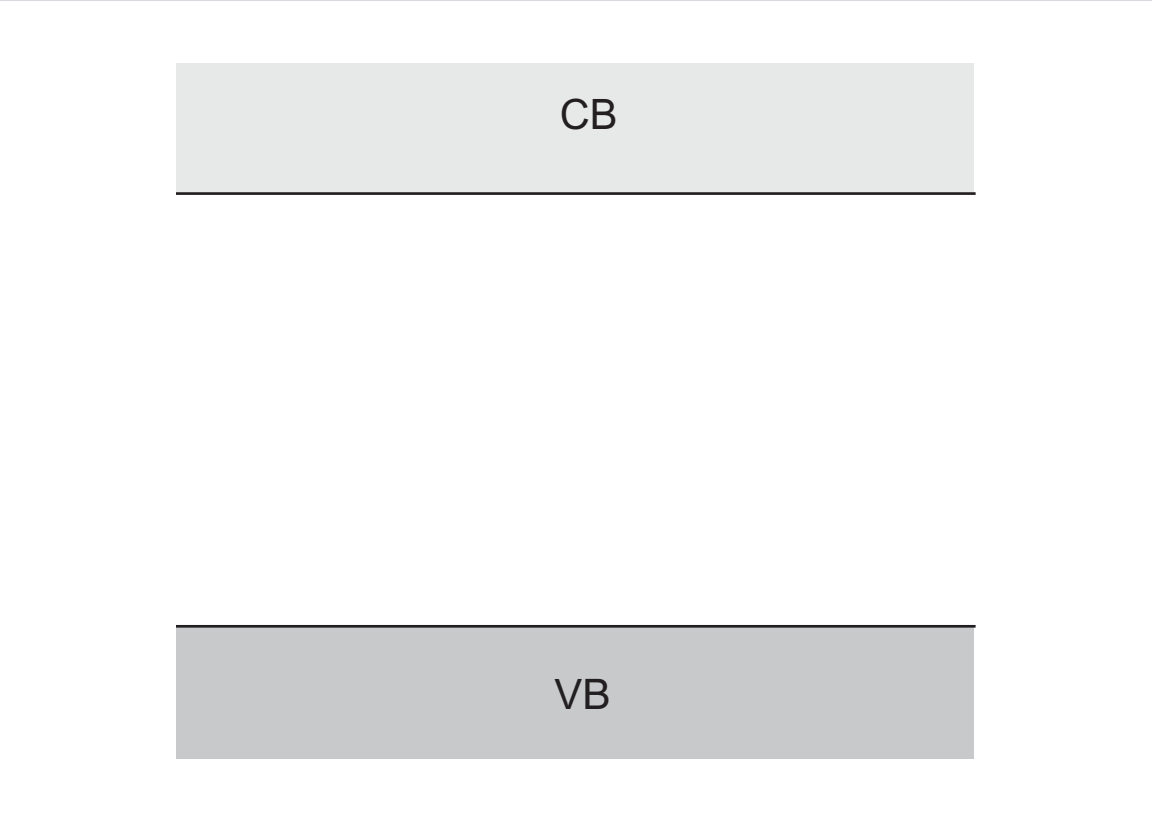
Appl. Phys. Lett. **78**, 1850 (2001)

Structural and chemical analysis

Effects of annealing:

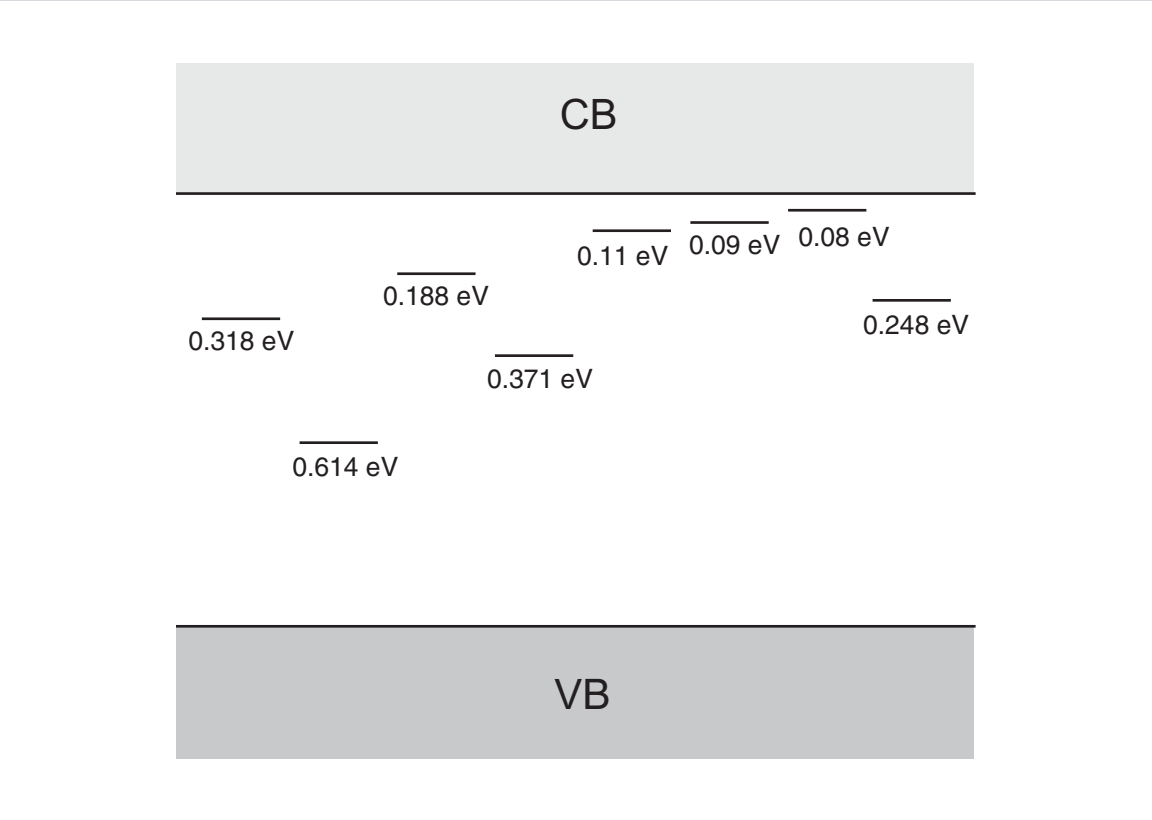
- **IR absorption: reduced twofold**
- **SEM: fewer surface nanostructures**
- **SIMS: sulfur content reduced twofold**

sulfur introduces states in the gap



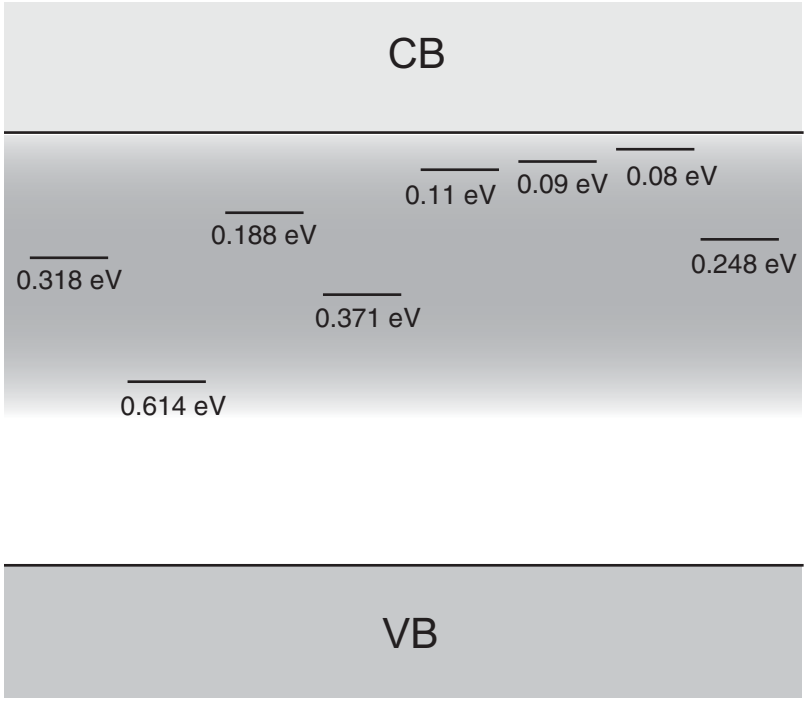
Structural and chemical analysis

sulfur introduces states in the gap

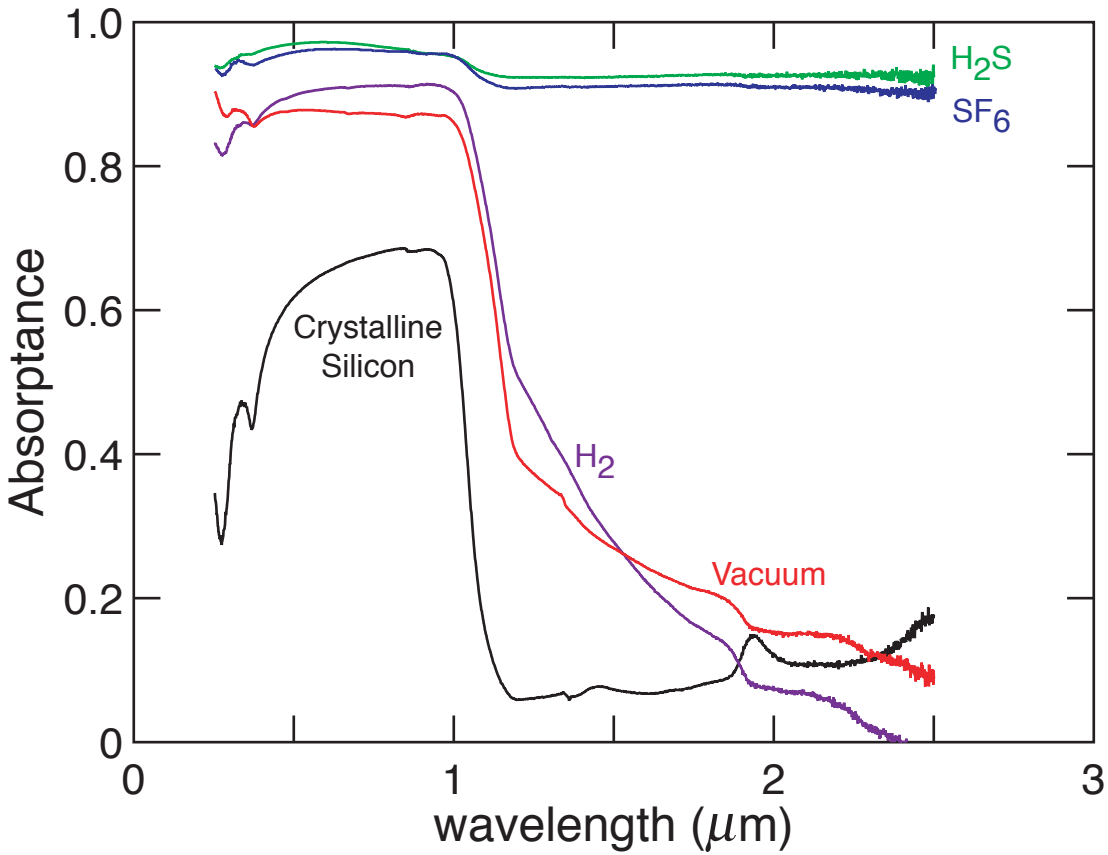


Janzén, *et al.*, *Phys. Rev. B* **29**,1907 (1984)

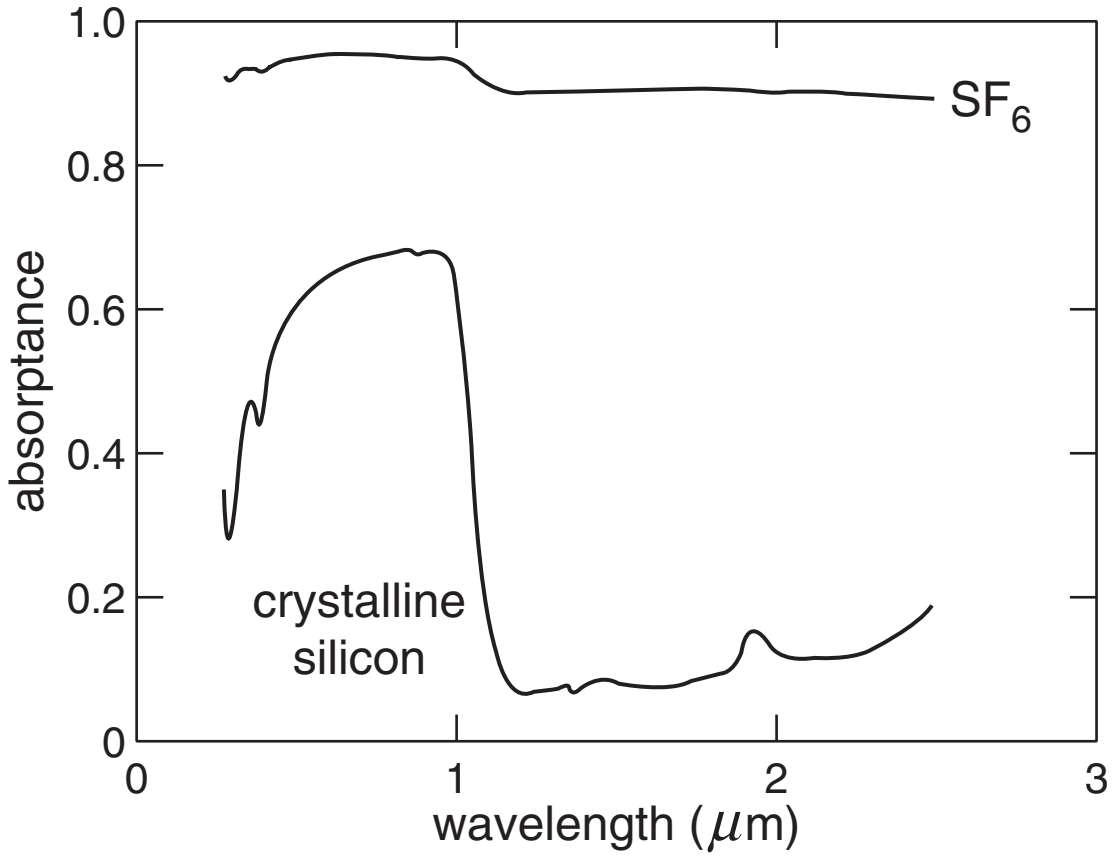
states broaden into a band



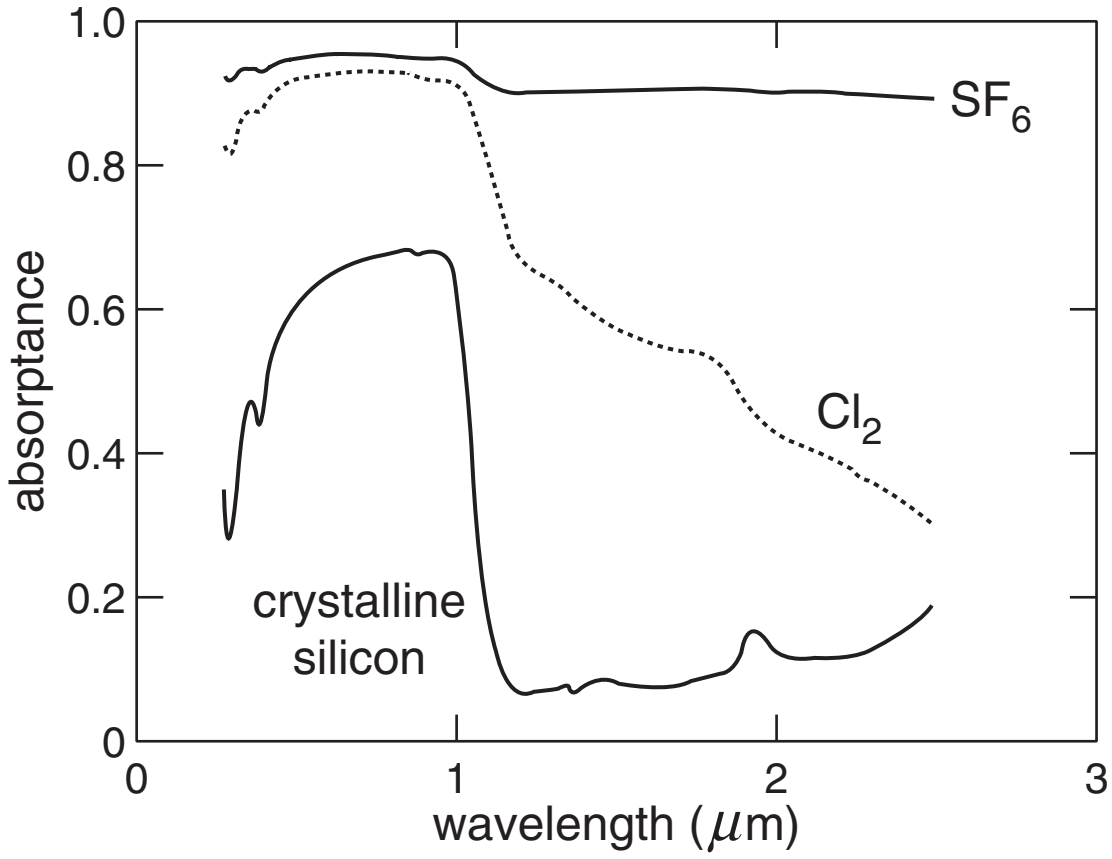
effect of ambient gas on absorptance



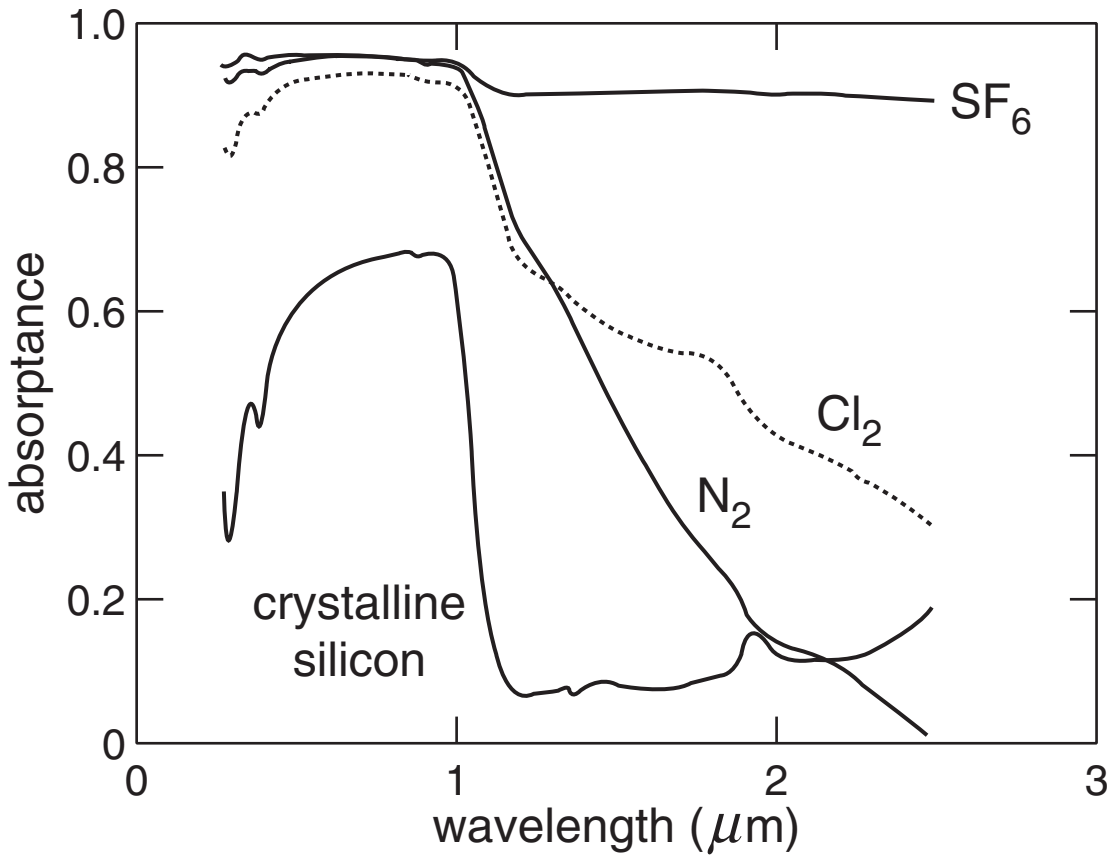
effect of ambient gas on absorptance



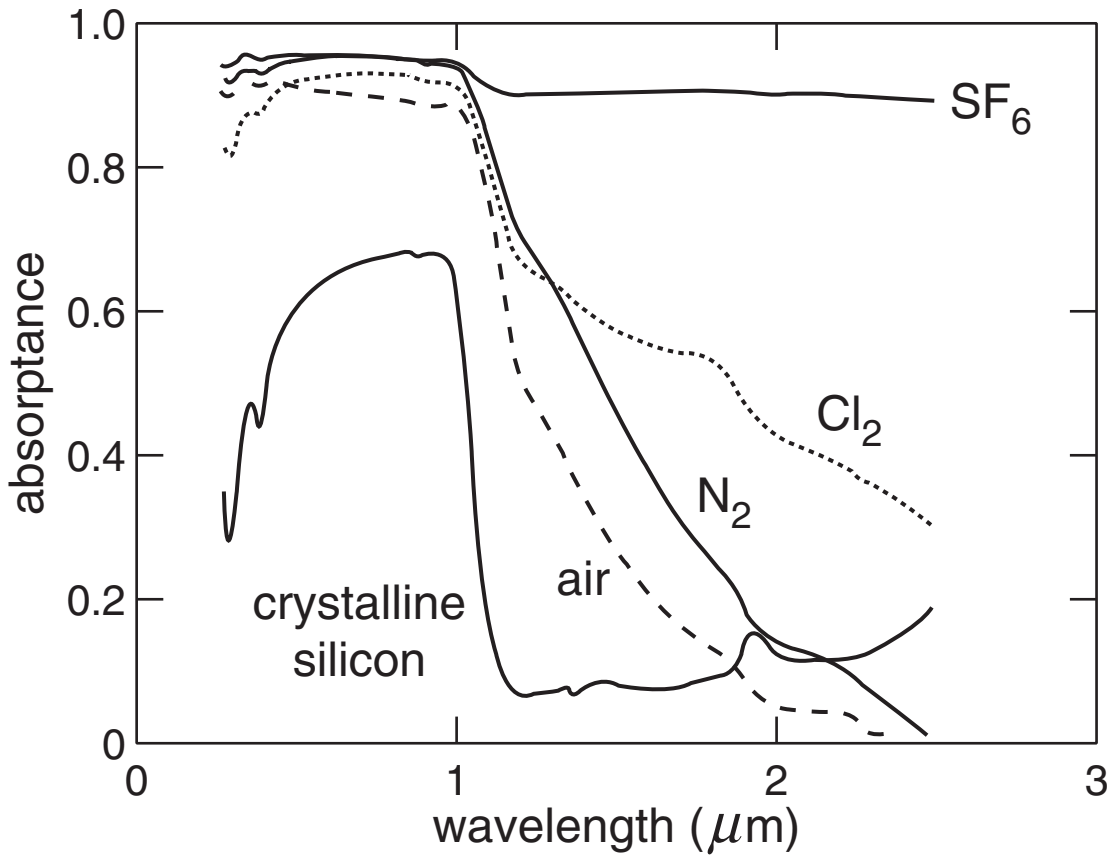
effect of ambient gas on absorptance

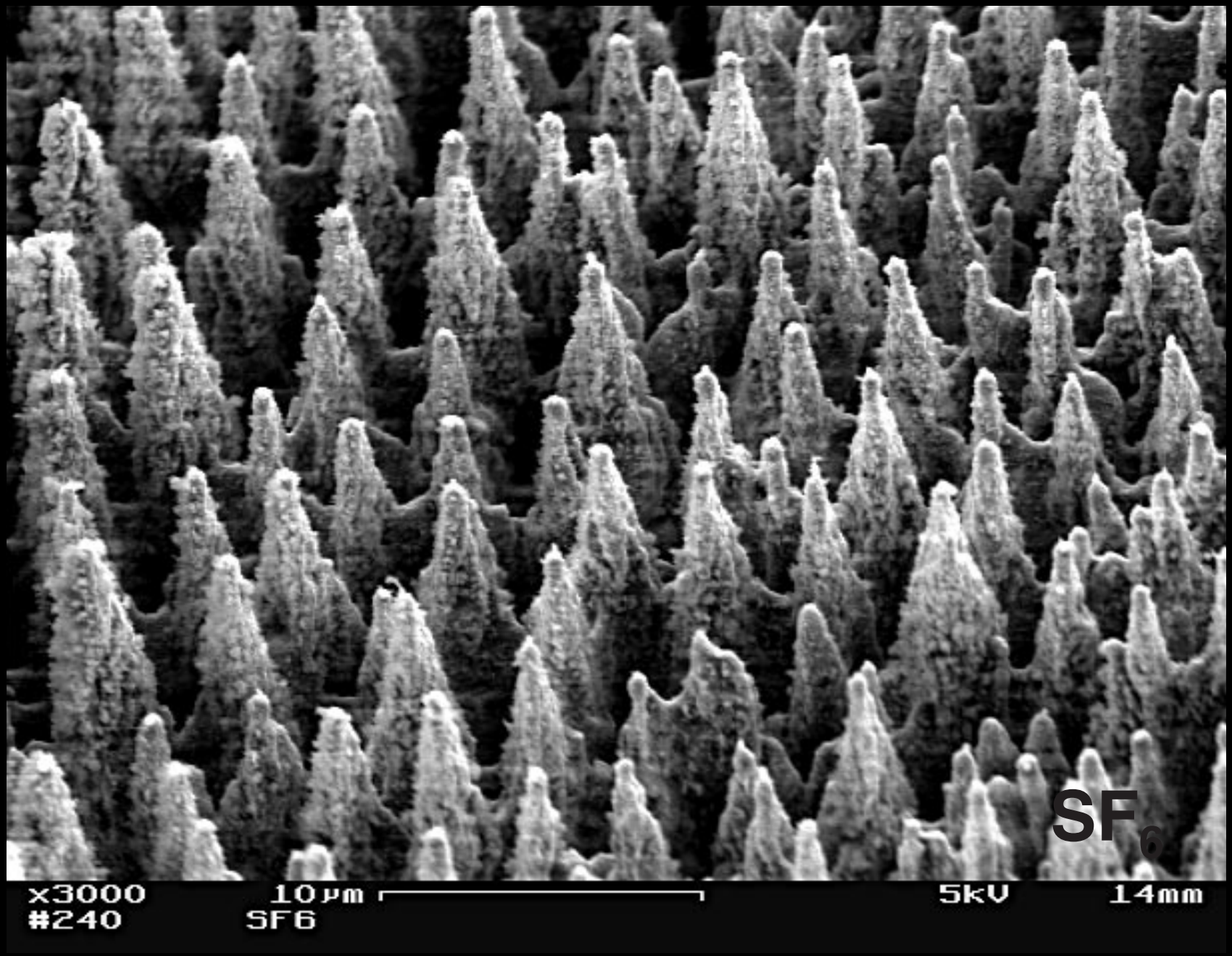


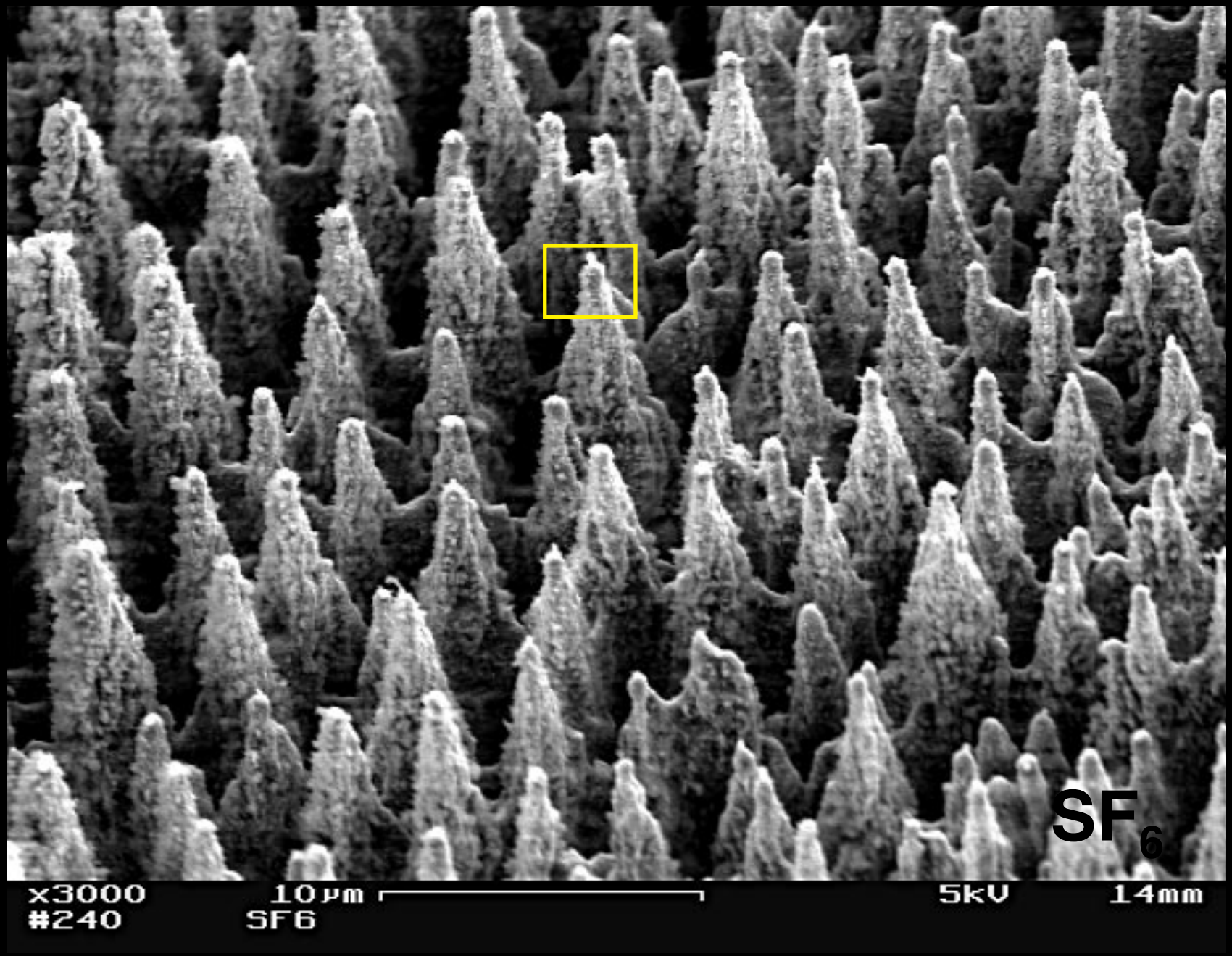
effect of ambient gas on absorptance

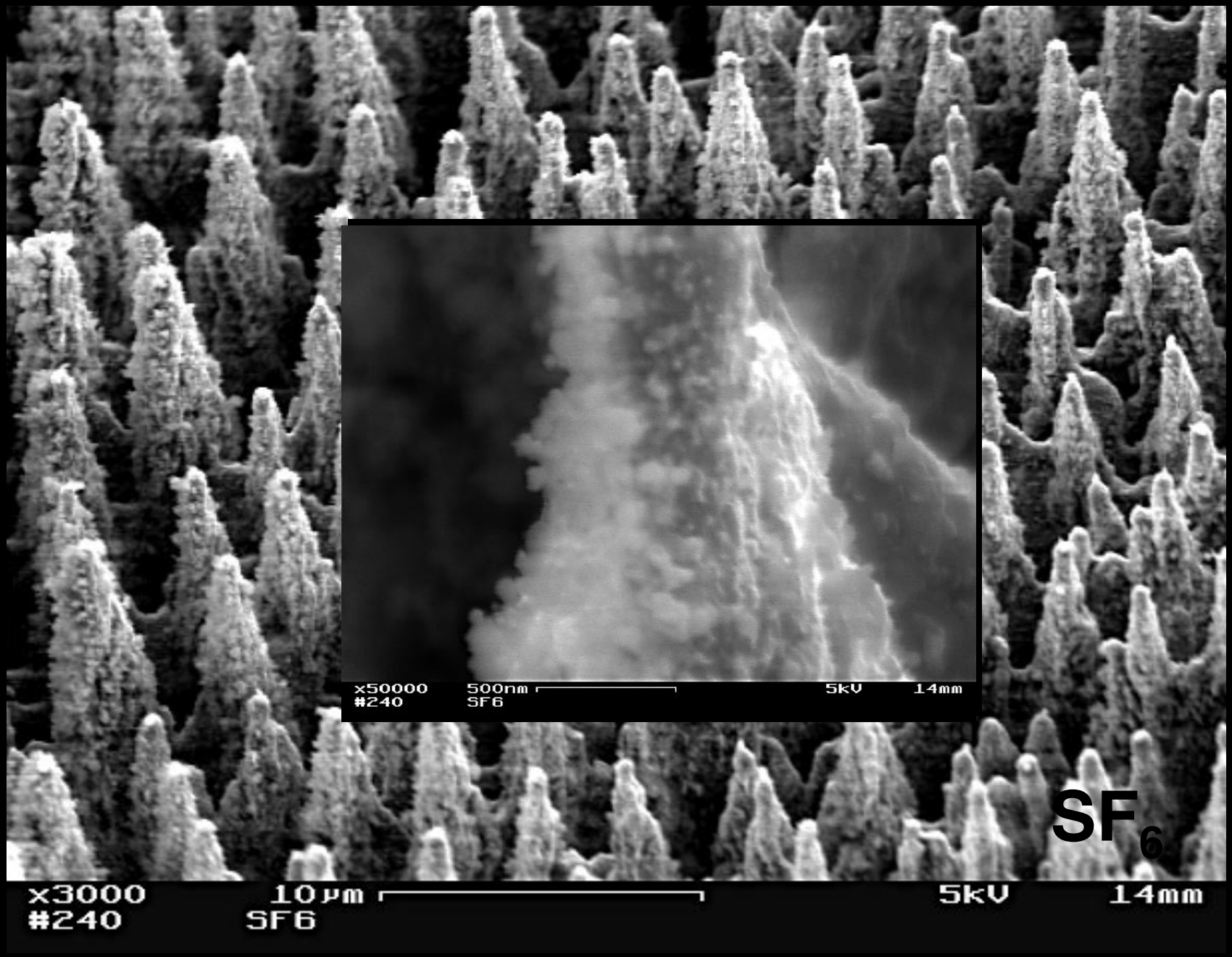


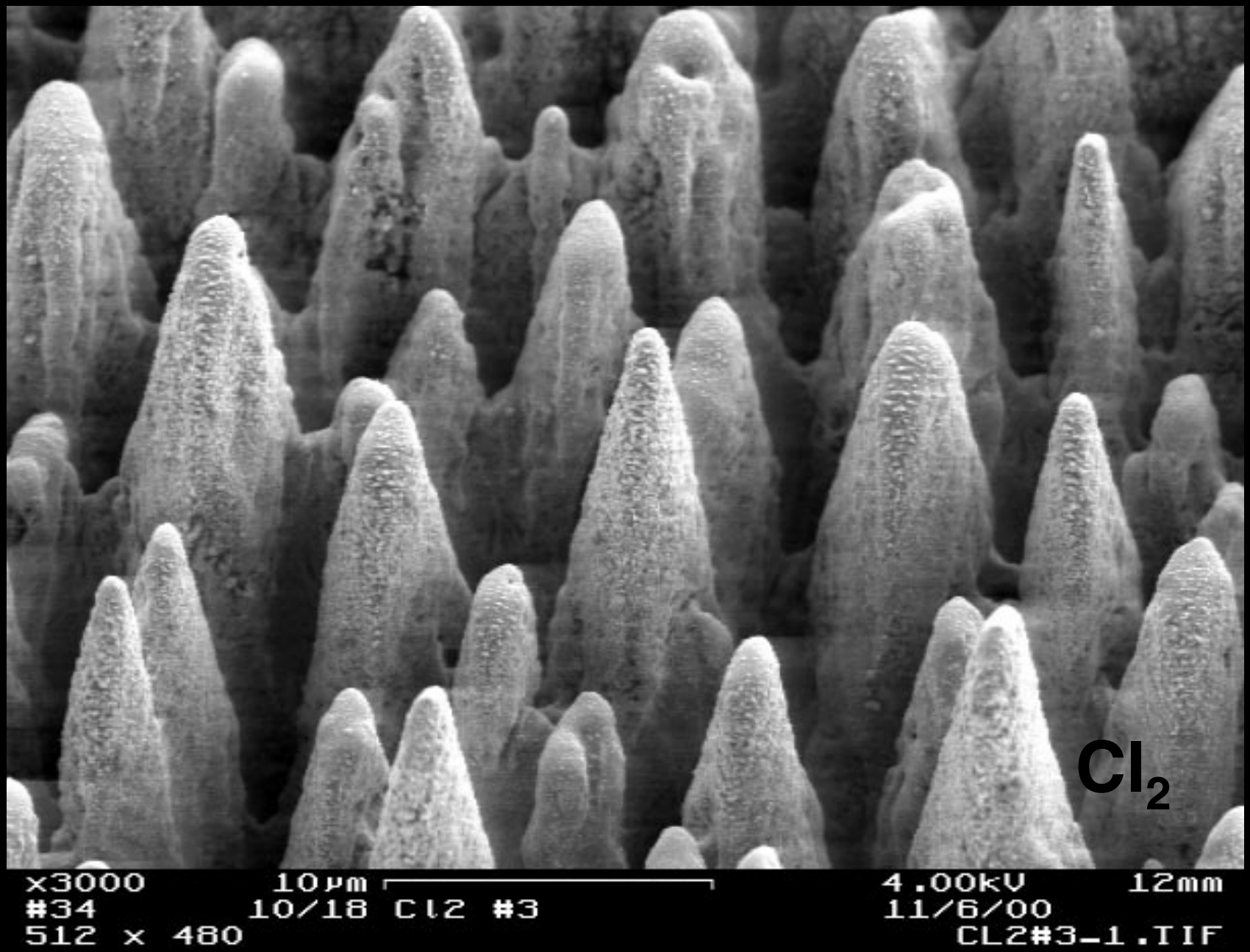
effect of ambient gas on absorptance

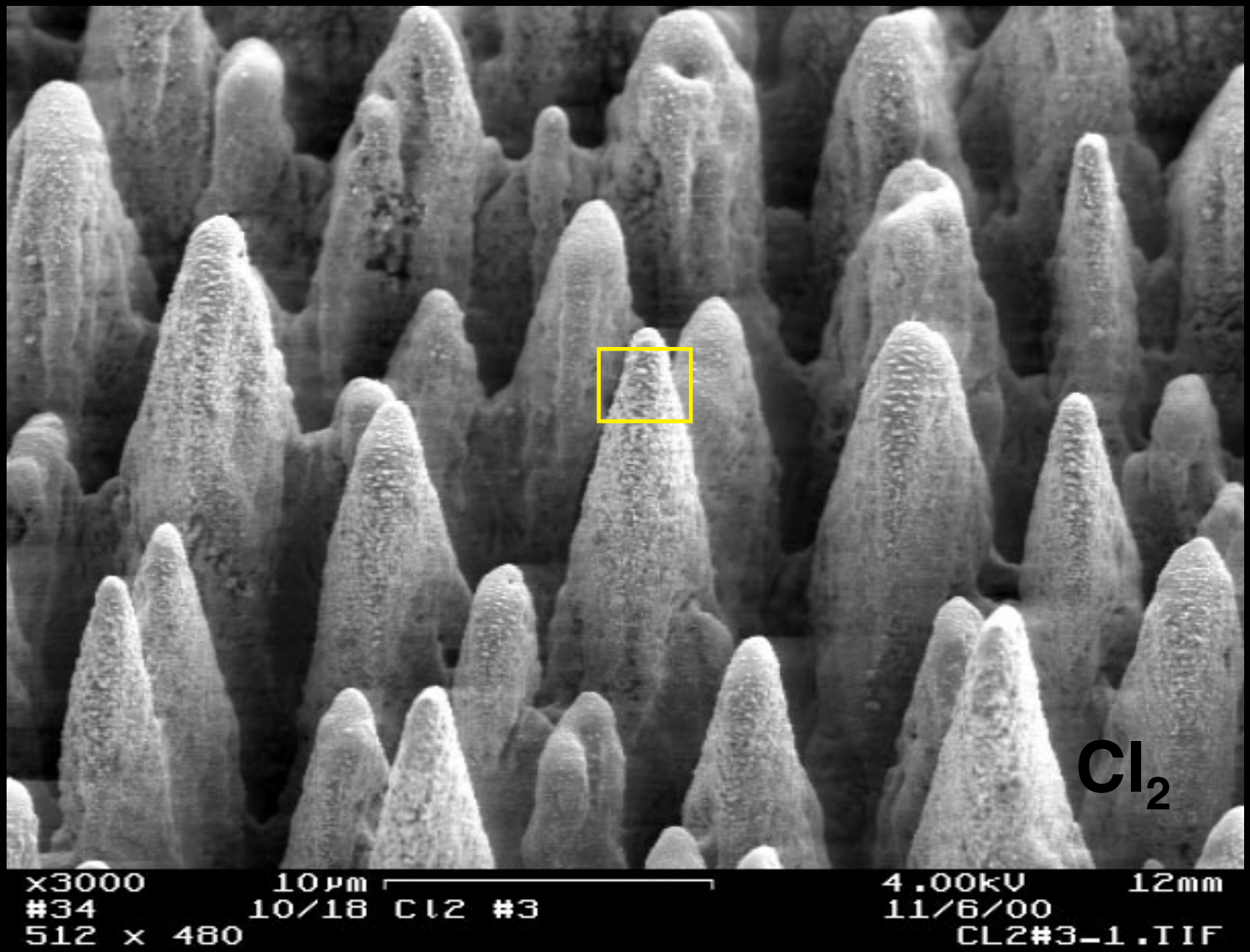


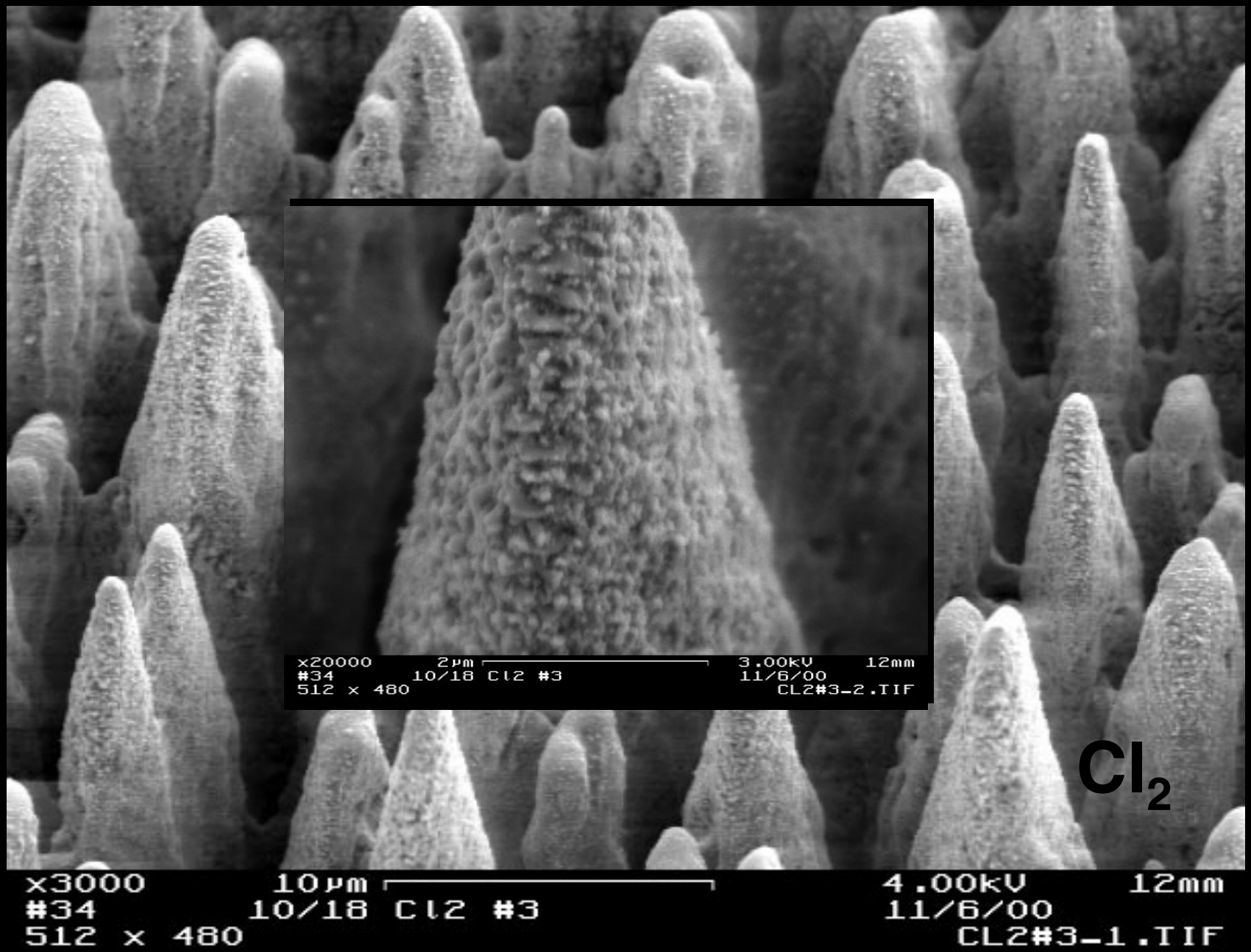

SF6
x3000
#240
10 µm
SF6
5kV
14mm

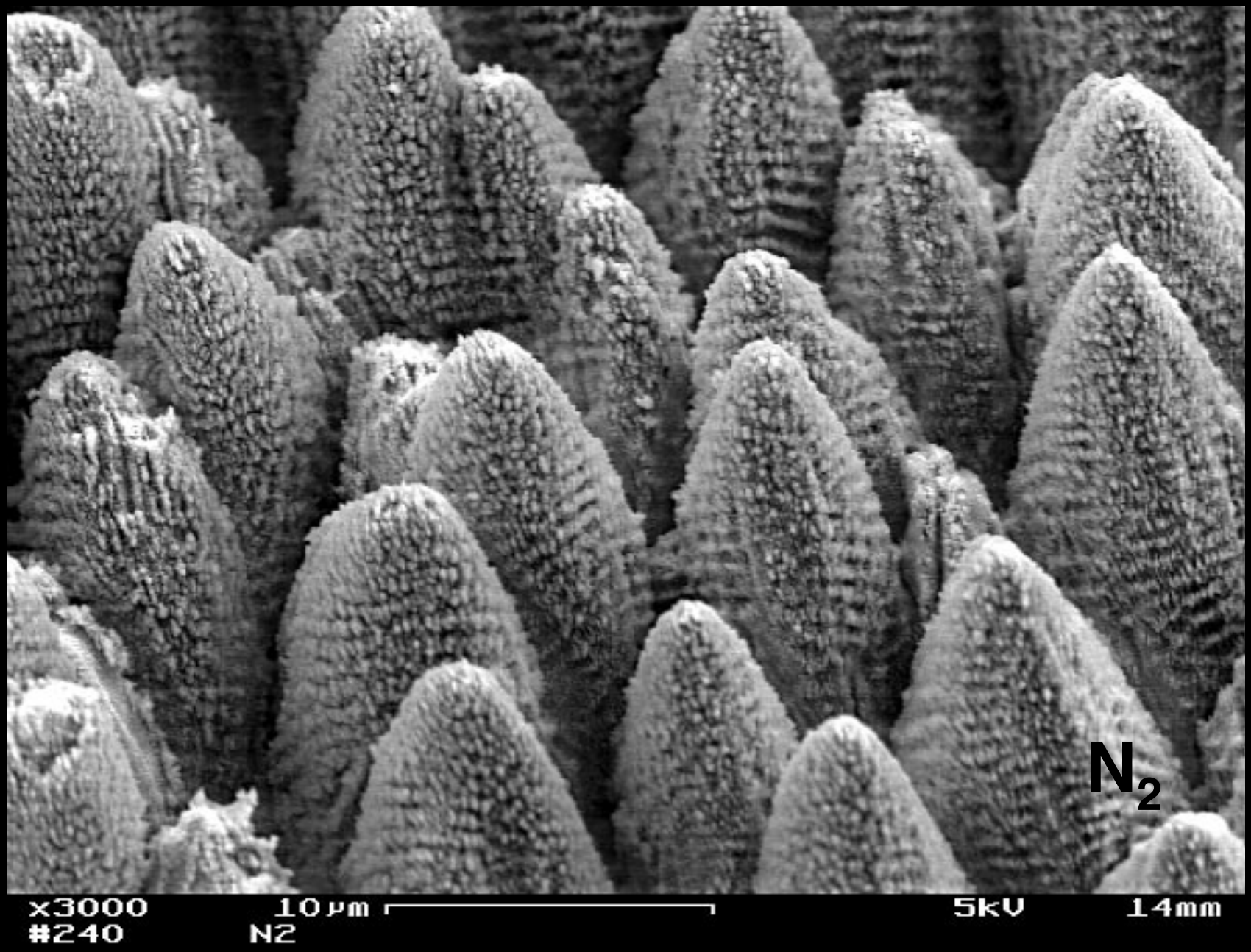

SF6
x3000
#240
10 µm
SF6
5kV
14mm

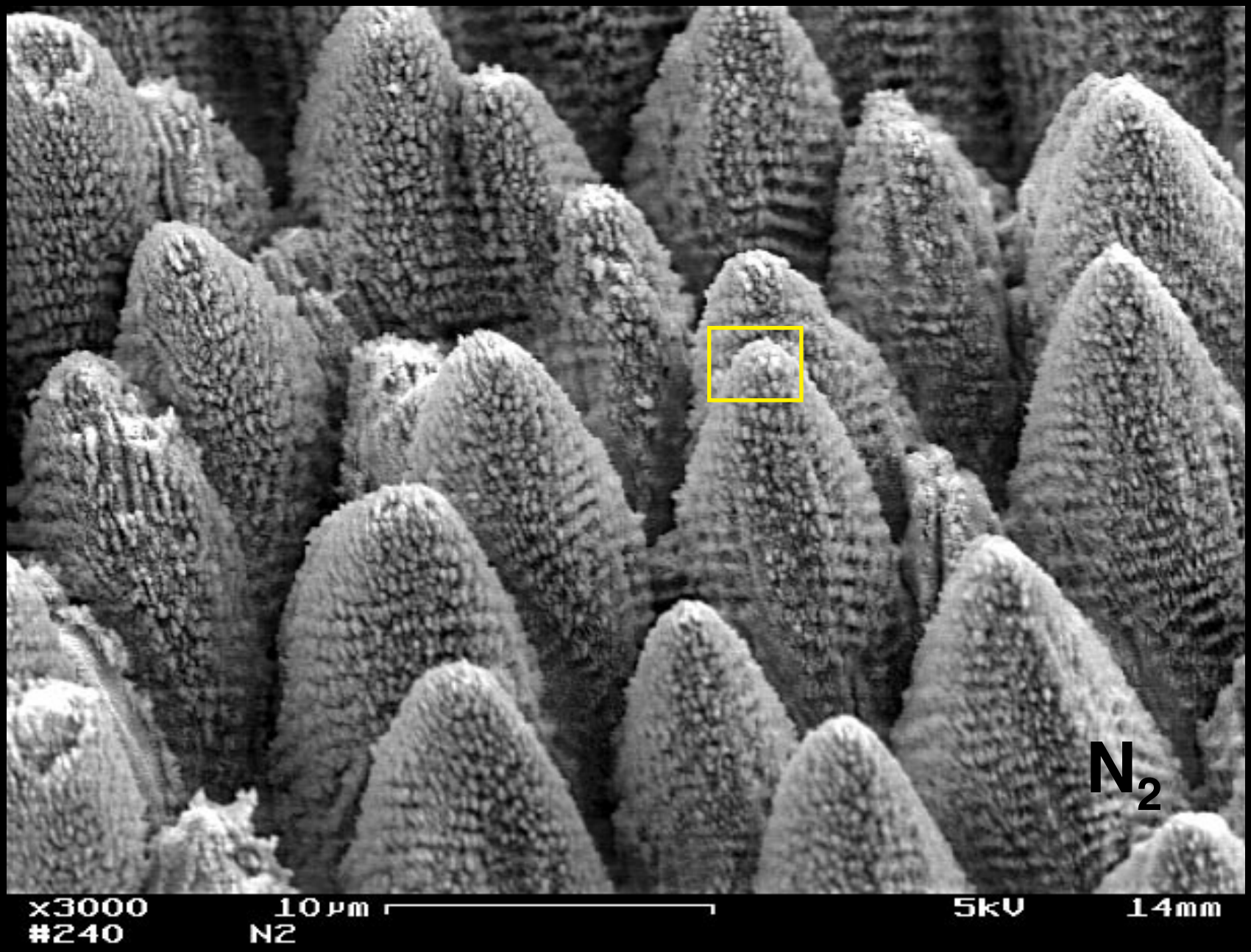

x50000
#240
500nm
SF6
5kV
14mm
SF6
x3000
#240
10μm
SF6
5kV
14mm

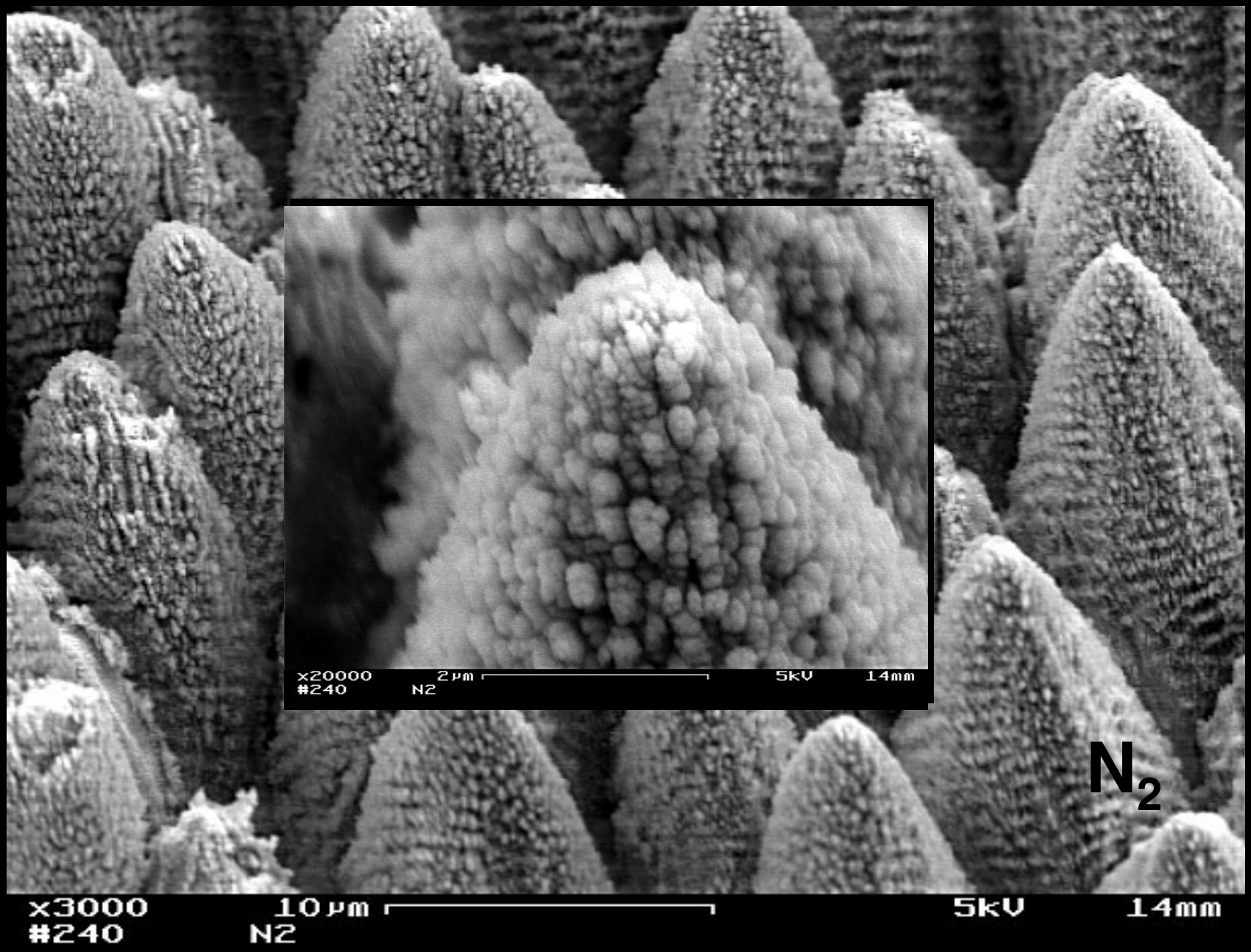

Cl_2
x3000
10μm
4.00kV
12mm
#34
10/18 Cl2 #3
11/6/00
512 x 480
CL2#3-1.TIF

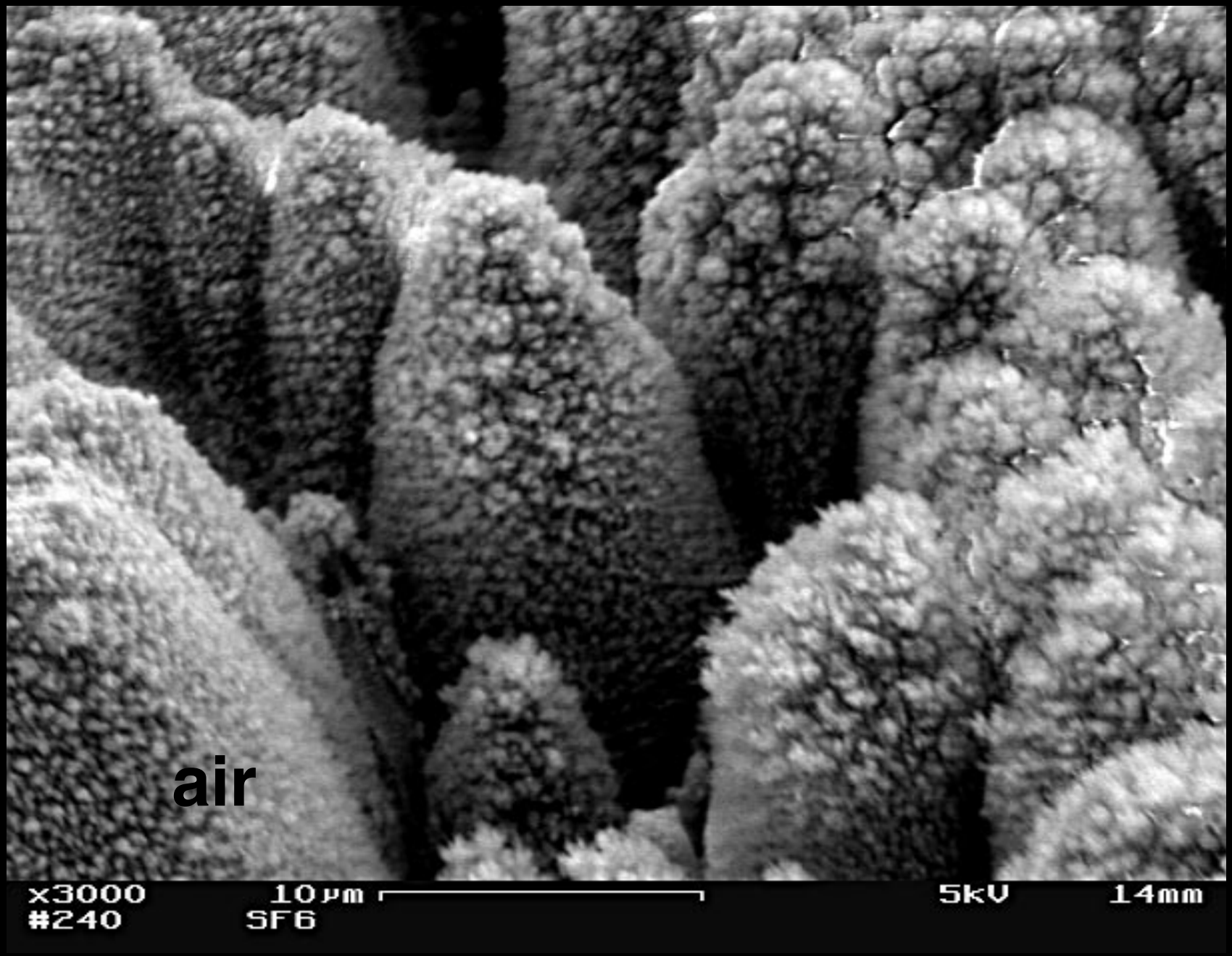

Cl_2
x3000
10μm
4.00kV
12mm
#34
10/18 Cl2 #3
11/6/00
512 x 480
CL2#3-1.TIF

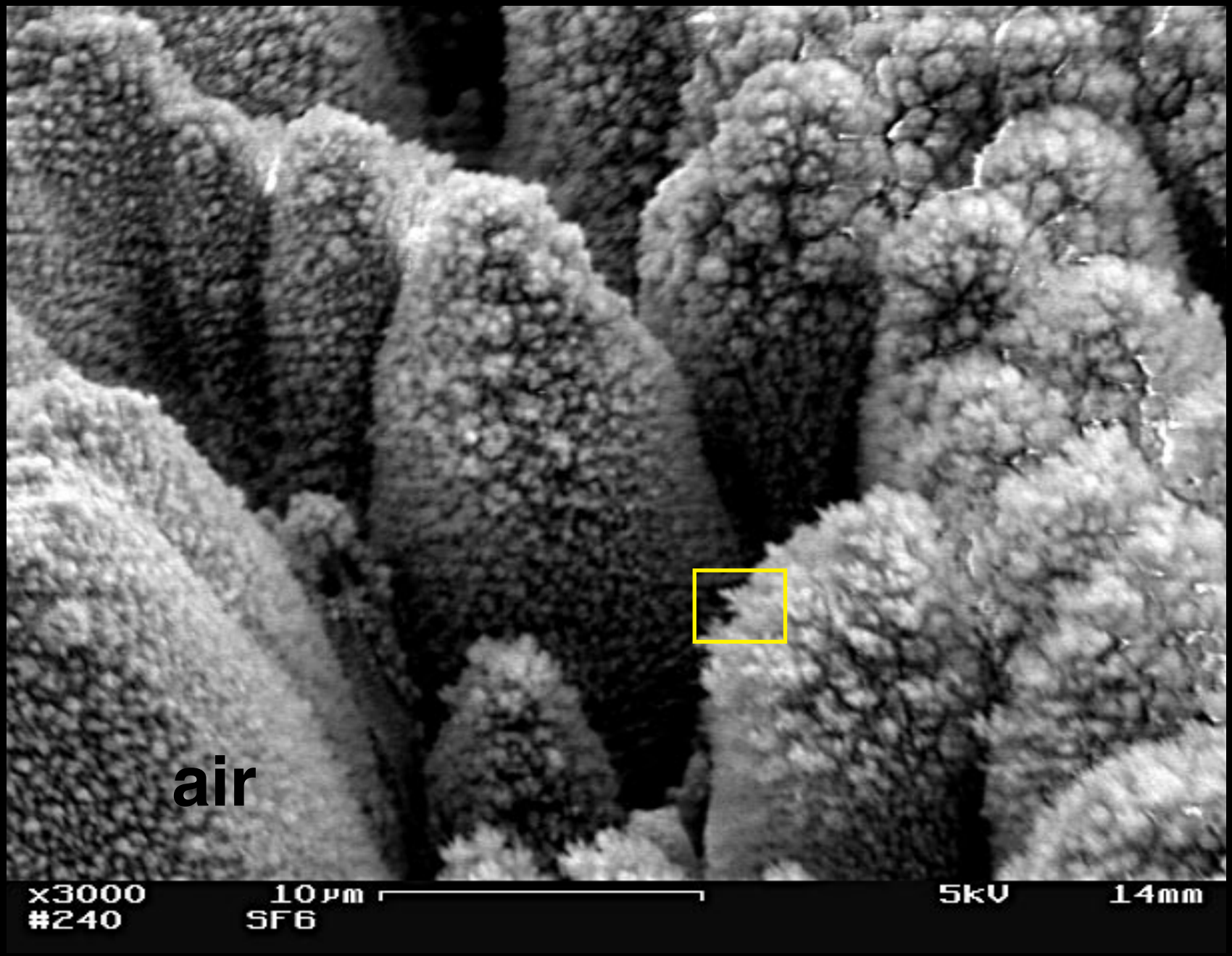

x20000 2µm 3.00kV 12mm
#34 10/18 Cl2 #3 11/6/00
512 x 480 CL2#3-2.TIF
Cl_2
x3000 10µm 4.00kV 12mm
#34 10/18 Cl2 #3 11/6/00
512 x 480 CL2#3-1.TIF

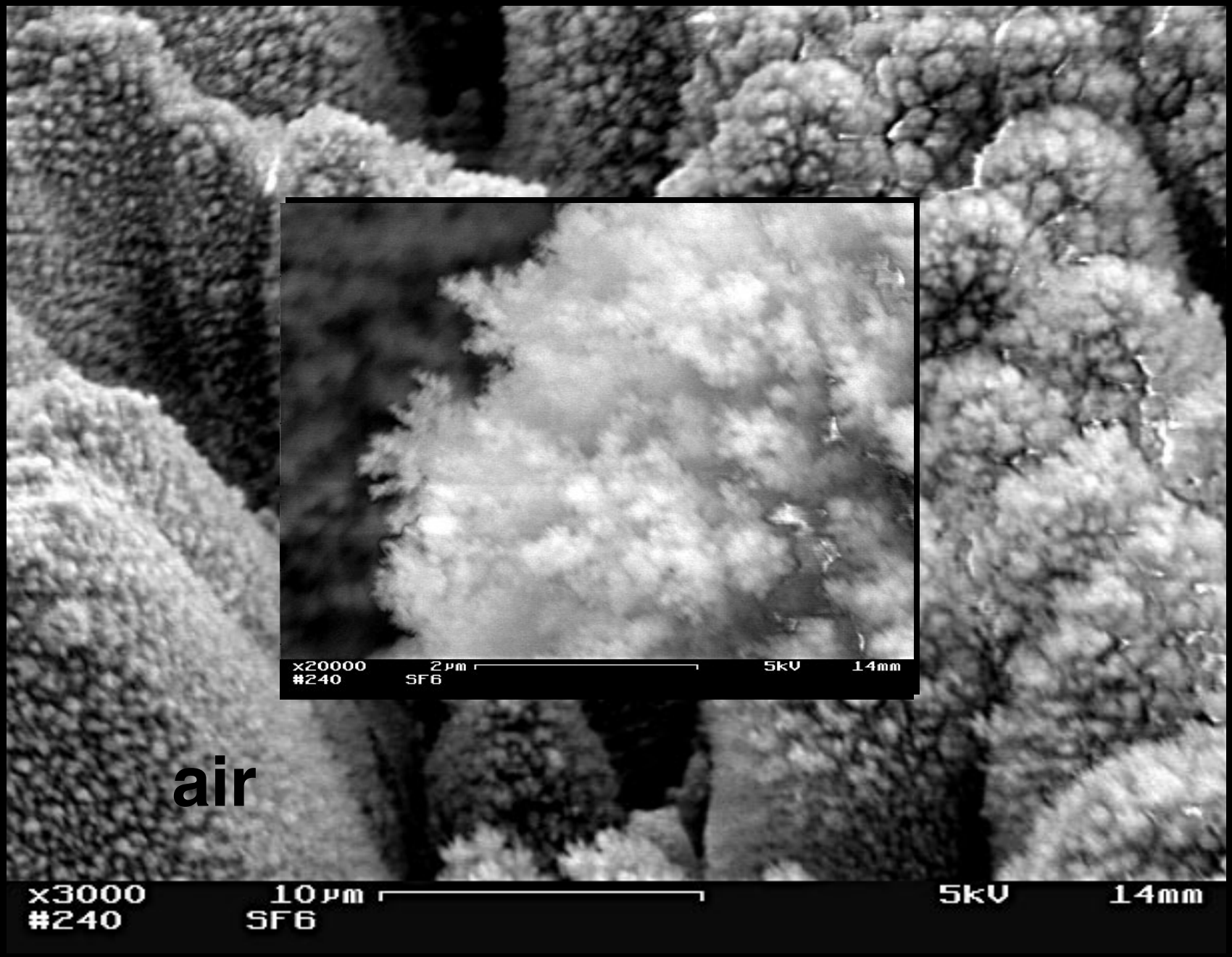

N_2
x3000
#240
10 µm
N2
5kV
14mm


N2
x3000
#240
10 µm
N2
5kV
14mm

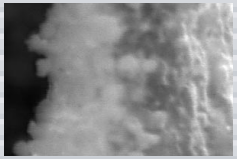
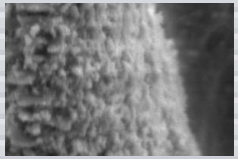
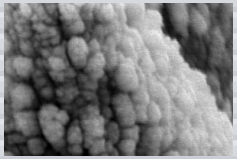

x20000 2μm 5kV 14mm
#240 N2
N_2
x3000 10μm 5kV 14mm
#240 N2


air
x3000
#240
10 µm
SF6
5kV
14mm


air
x3000
#240
10 µm
SF6
5kV
14mm


x20000 2μm 5kV 14mm
#240 SF6
air
x3000 10μm 5kV 14mm
#240 SF6

Structural and chemical analysis

	SF_6	Cl_2	N_2	air
IR absorption	high	medium	low	low
field emission	high	low	medium	low
SIMS	high S	?	?	high O
nanostructure				

Structural and chemical analysis

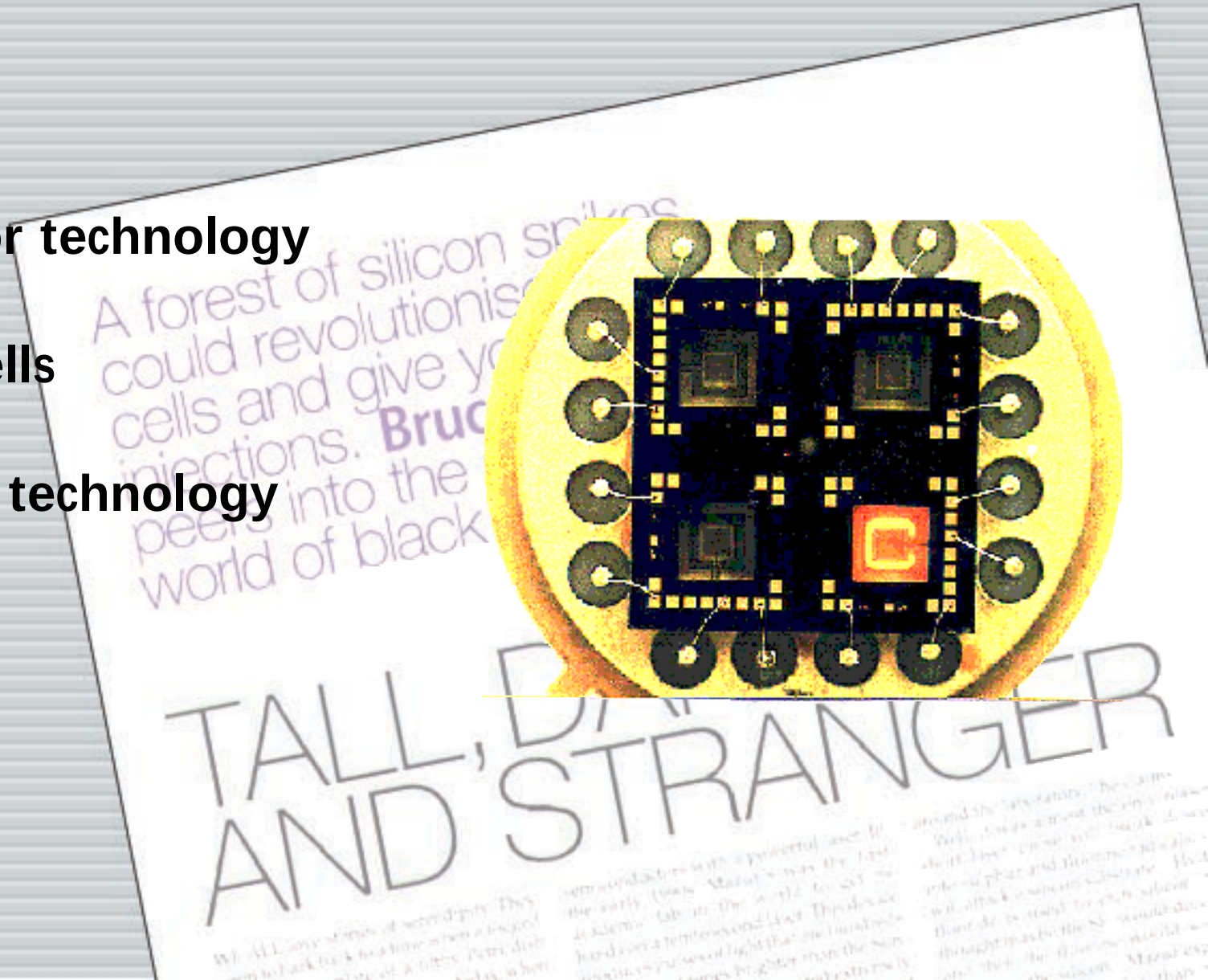
- **significant incorporation of ambient species**
- **nanostructured surface layer**
- **sulfur content correlates with IR absorption**

Outline

- Properties
- Structural and chemical analysis
- **Outlook**

Outlook

- detector technology
- solar cells
- display technology
- sensors



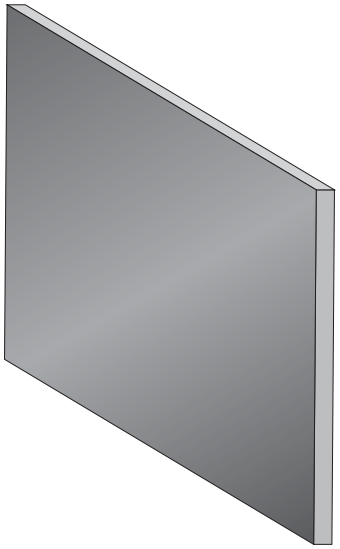
Outlook

- development of spikes
- spike formation through grids
- cell adhesion
- functionalization

Outlook

can ordering of spikes be improved by using a grid?

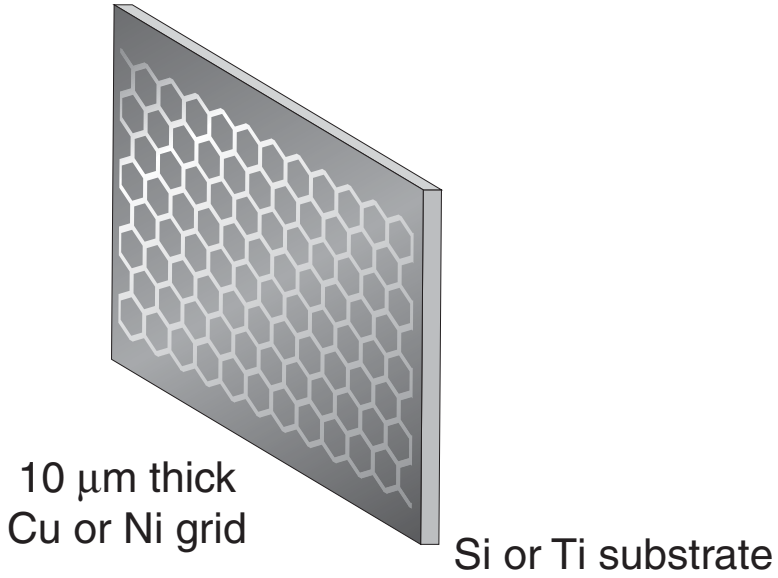
Outlook



Si or Ti substrate

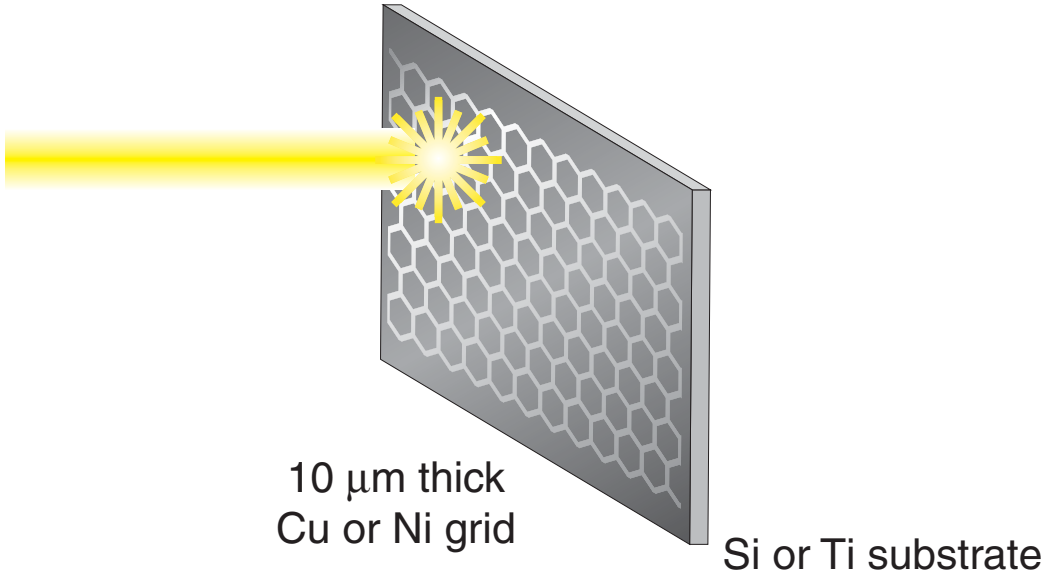
Outlook

place grid in front of substrate



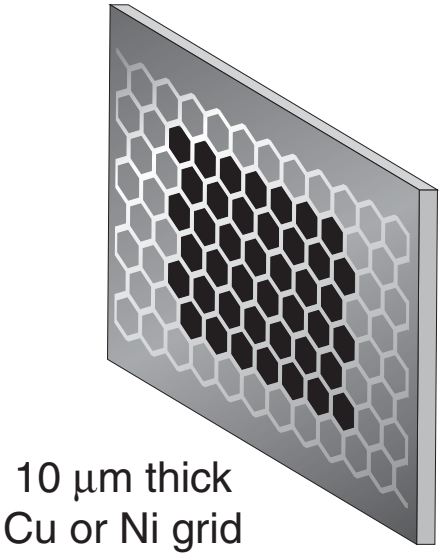
Outlook

scan laser beam



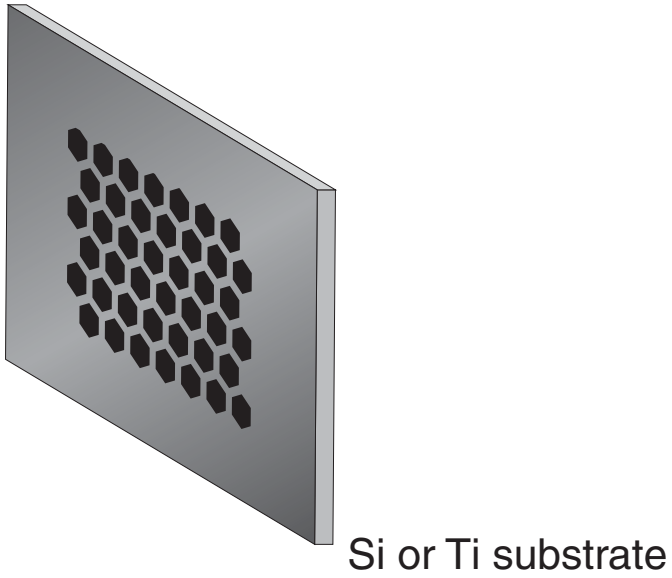
Outlook

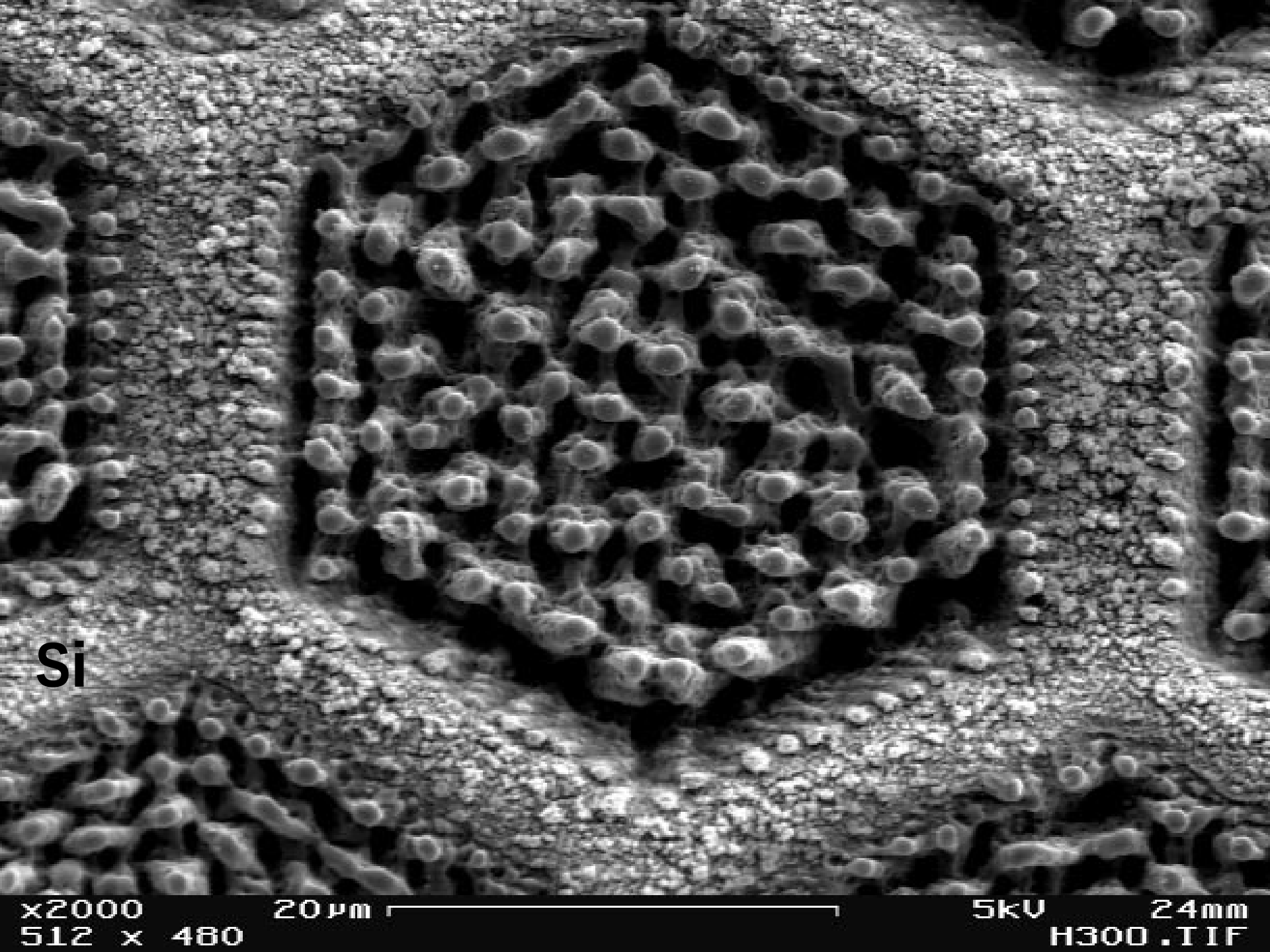
scan laser beam

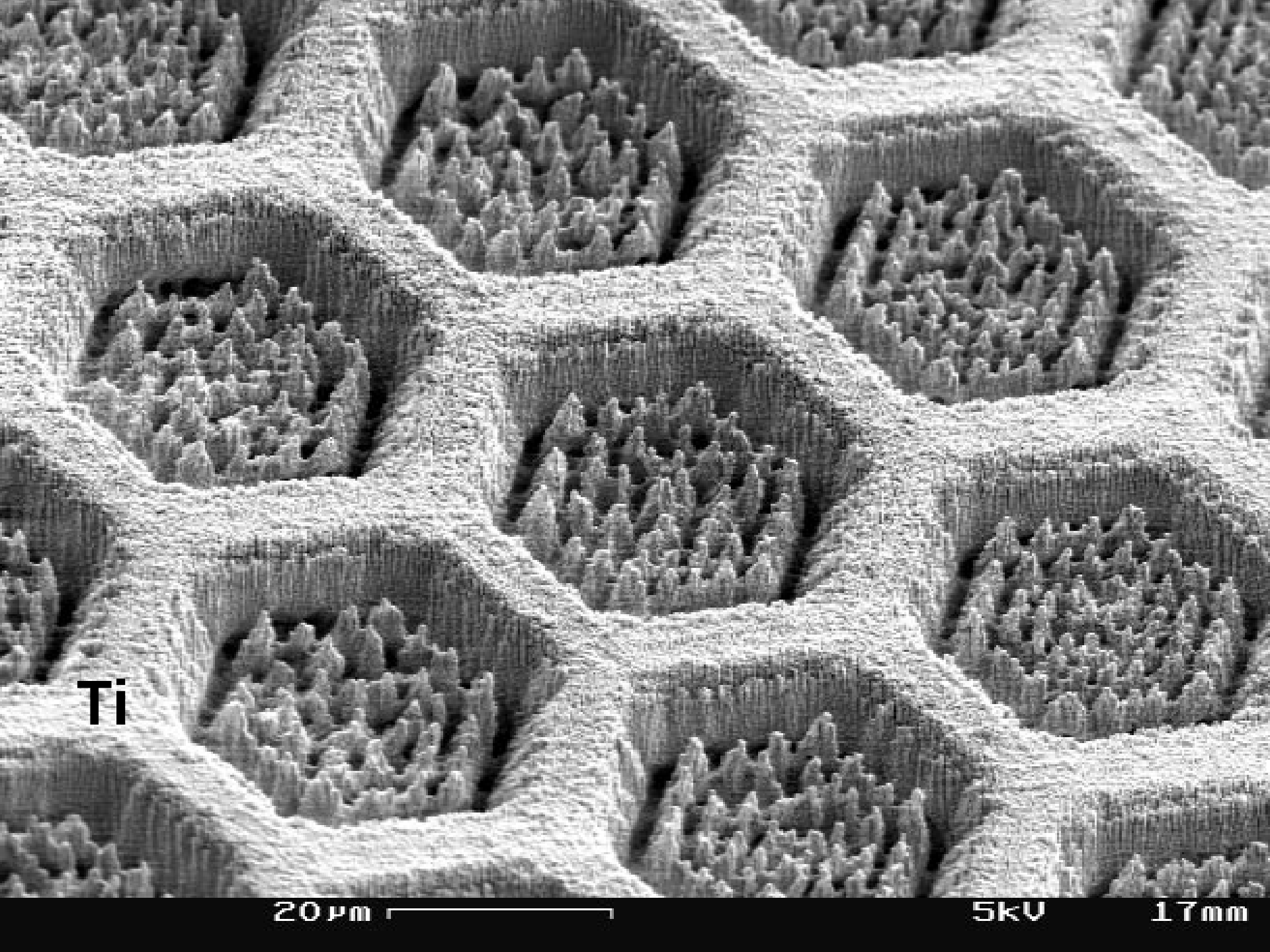


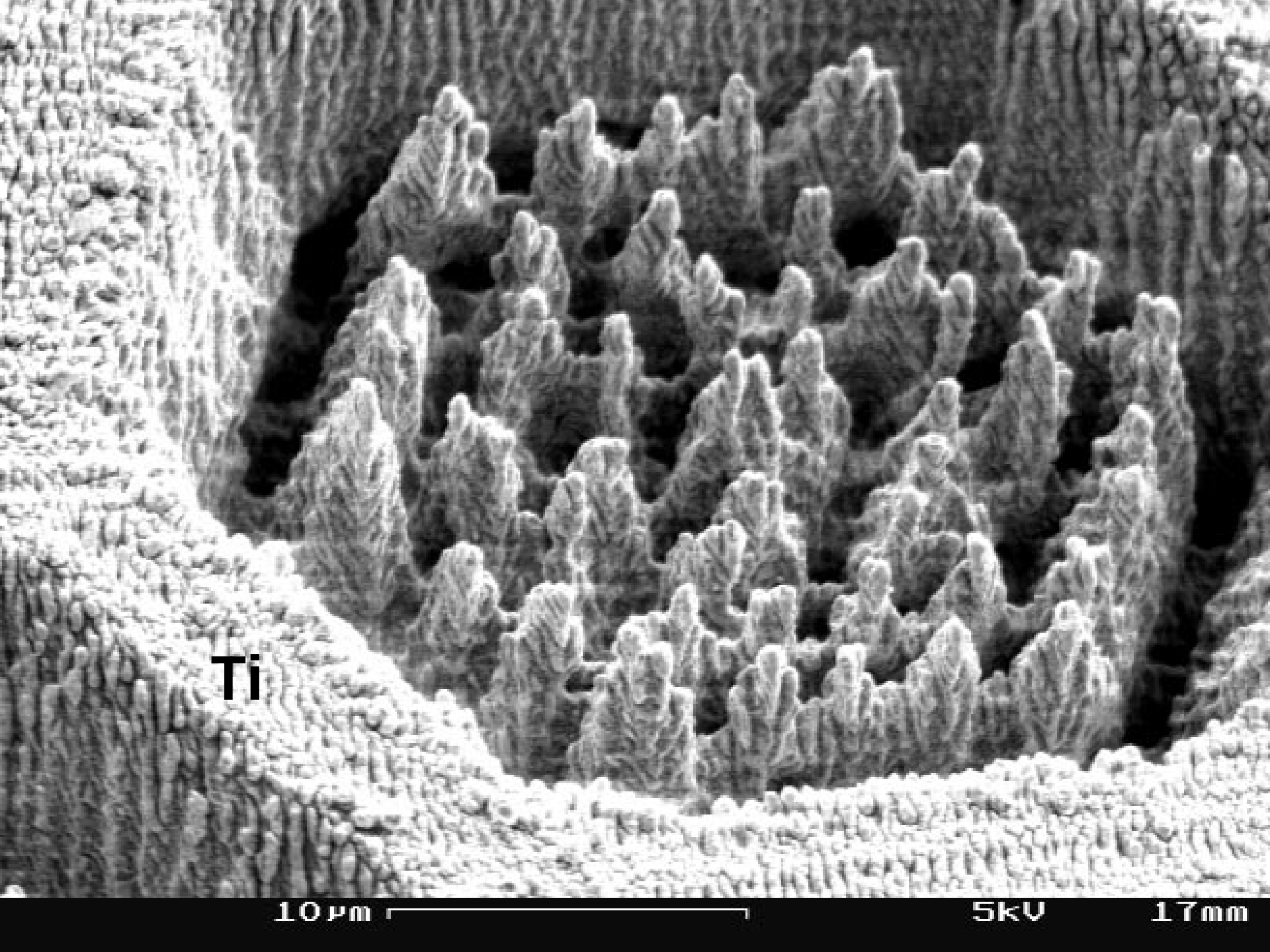
Outlook

remove grid




Si
x2000
20μm
5kV
24mm
512 x 480
H300.TIF


Ti
20μm
5kV
17mm


Ti
10μm
5kV
17mm

Summary

Microstructured silicon

- **fabricated by simple, maskless process**

Summary

Microstructured silicon

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

Summary

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- **fabricated by simple, maskless process**
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- **generates IR photocurrent**

Summary

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- **fabricated by simple, maskless process**
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- **generates IR photocurrent**
- **provides stable, high field emission current**

Summary

Microstructured silicon

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


GORDON McKAY
LABORATORY OF
APPLIED SCIENCE

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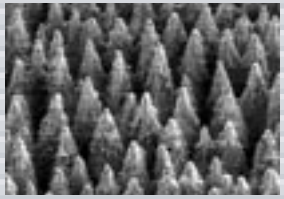
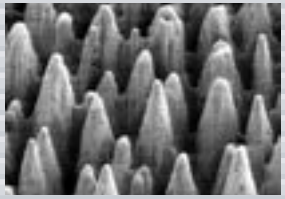
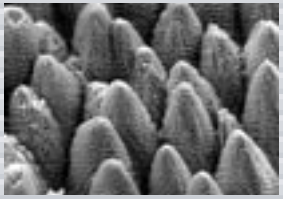
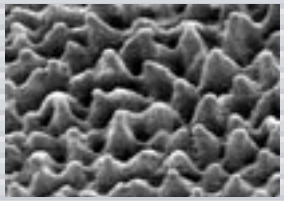
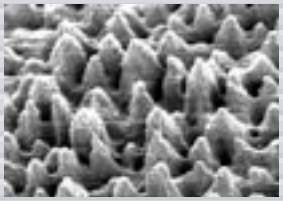
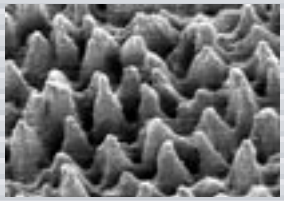
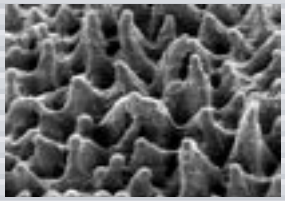
Dr. Alf Bjørseth (Scanwafer)
Dr. Tom Mates (UCSB)
Prof. Nico Bloembergen (Harvard University)
Prof. Cynthia Friend (Harvard University)
Prof. Mike Aziz (Harvard University)

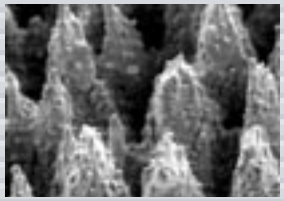
For a copy of this talk and additional information, see:

http://mazur-www.harvard.edu

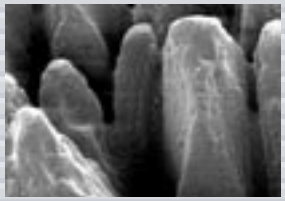
Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti		reacts			

Only in SF_6:



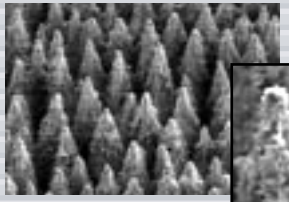
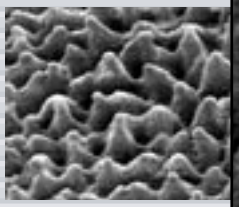
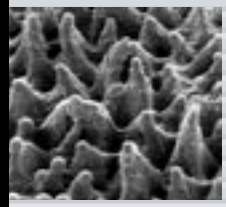
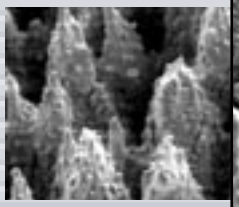
Ge



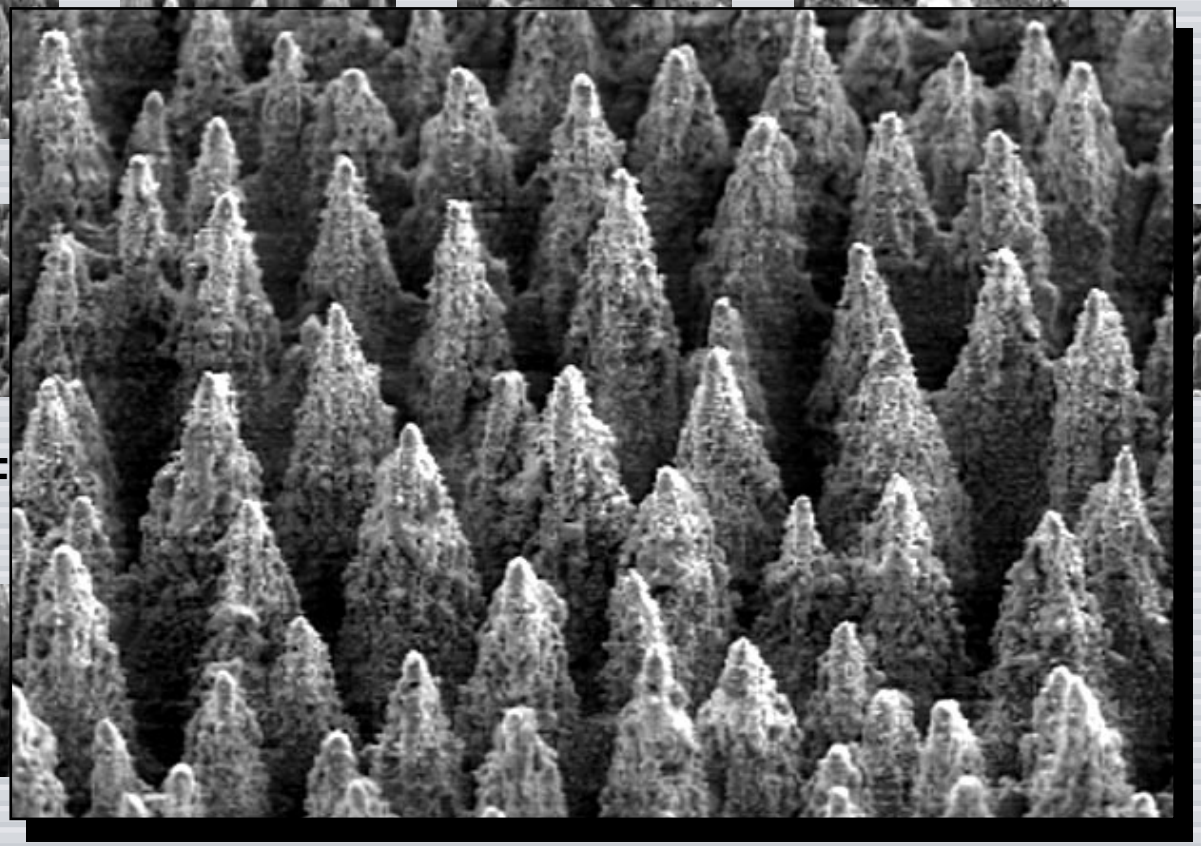
InP

No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

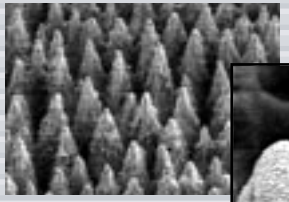
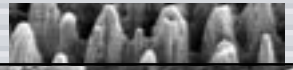
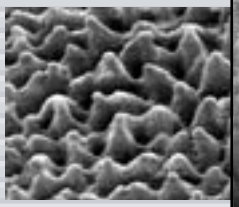
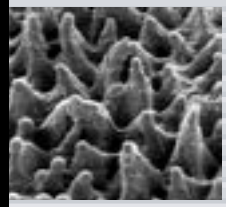
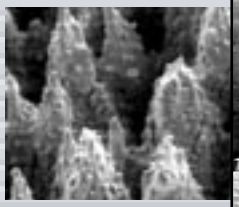
	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					

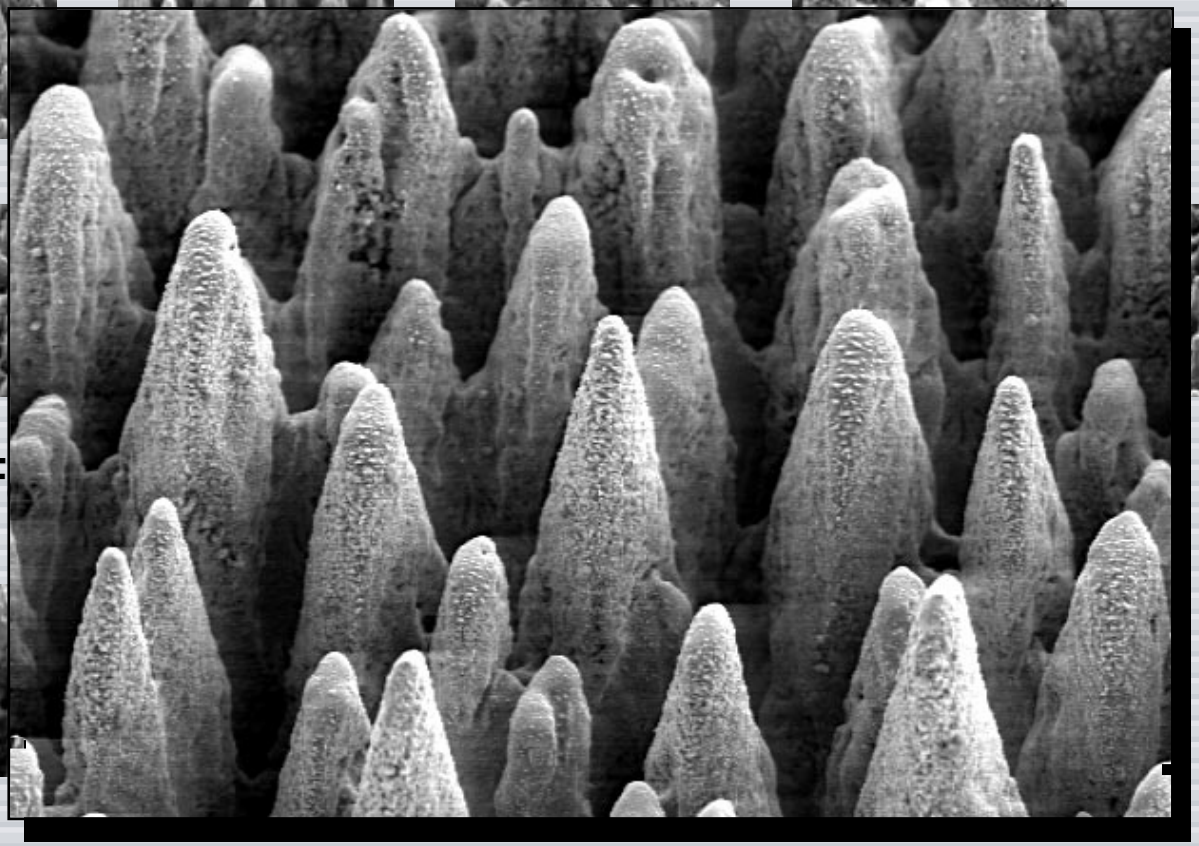
Only in SF



No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

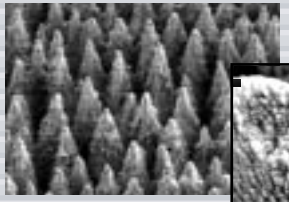
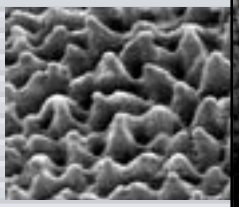
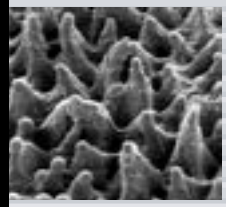
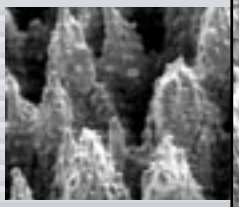
	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					



Only in SF

No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					

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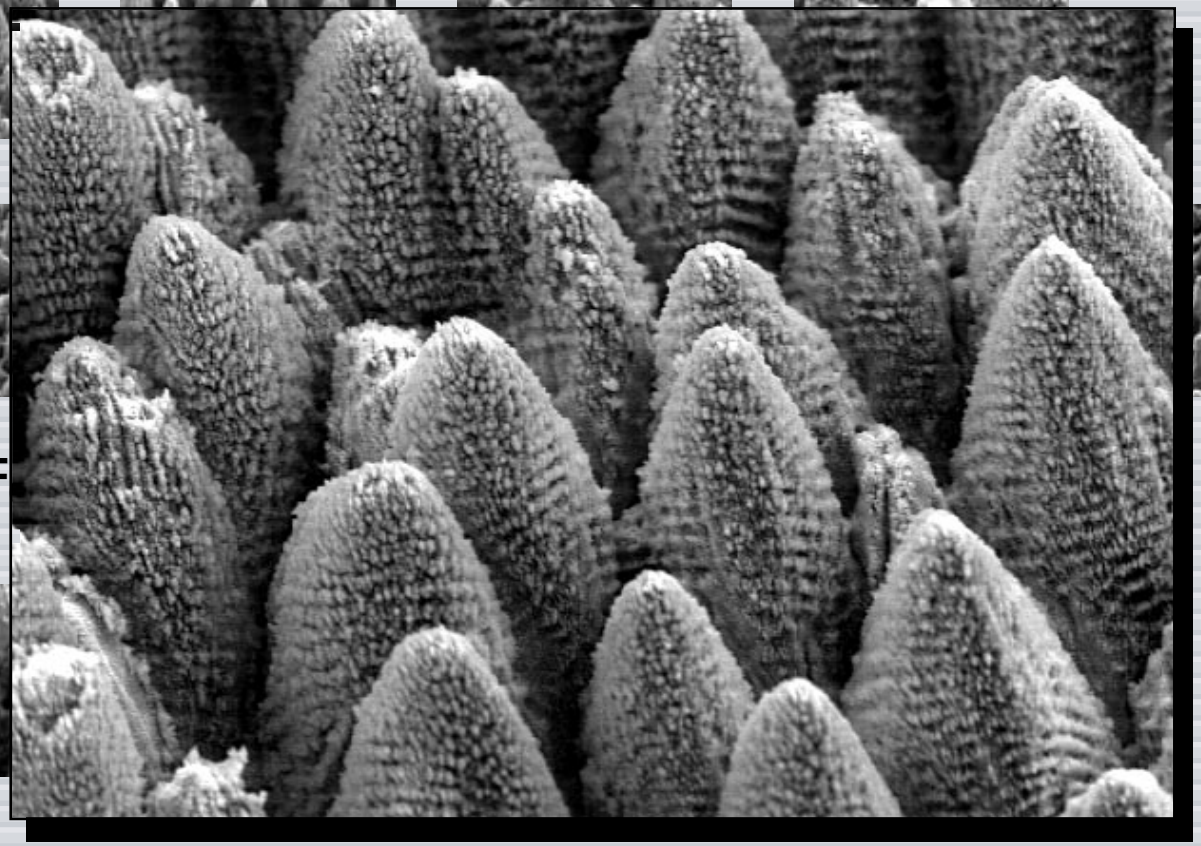
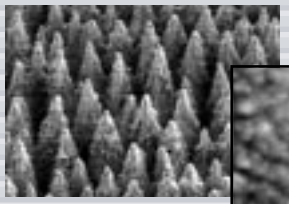
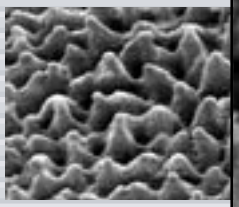
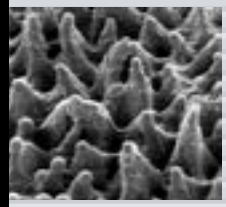


No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
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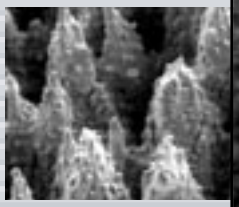
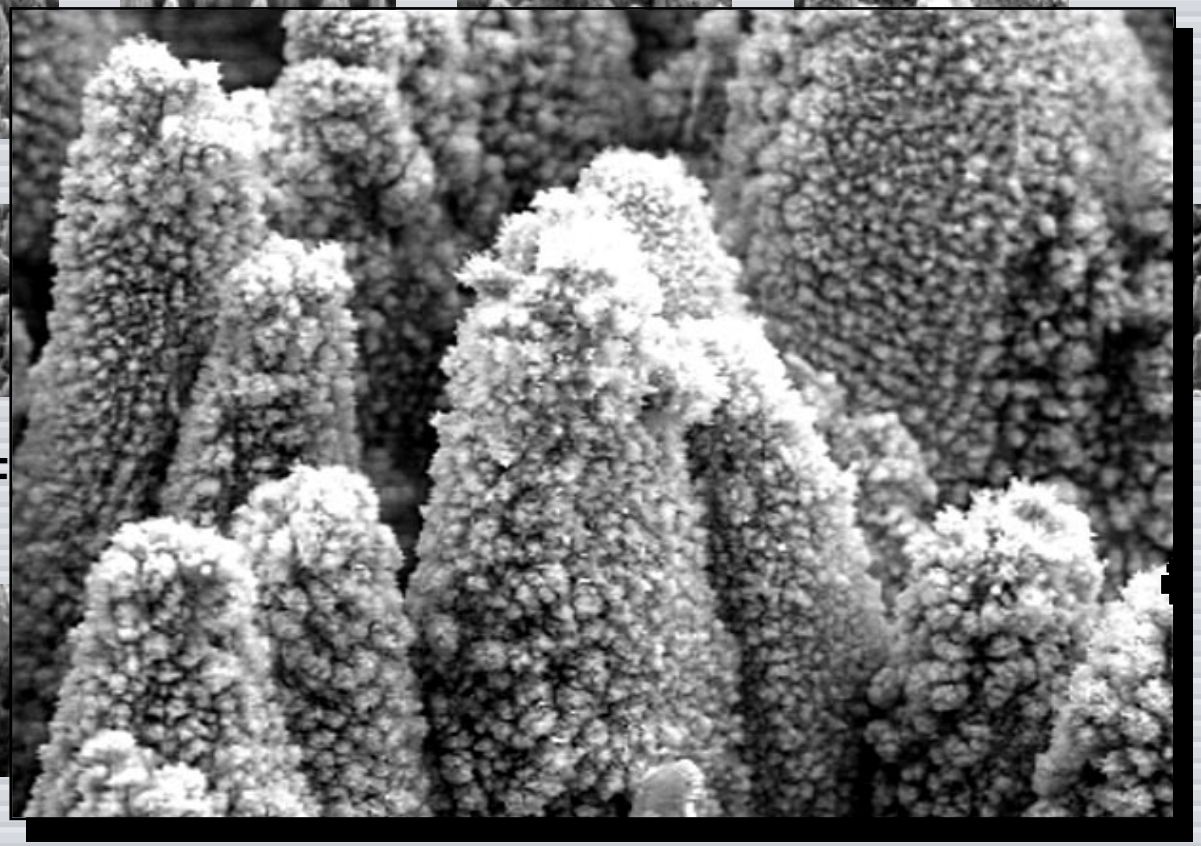
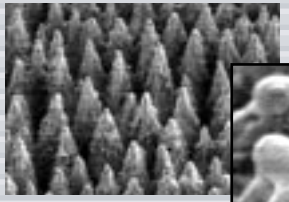
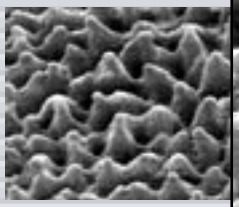
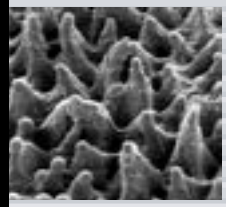
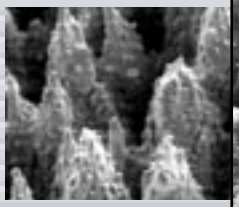
Ge					

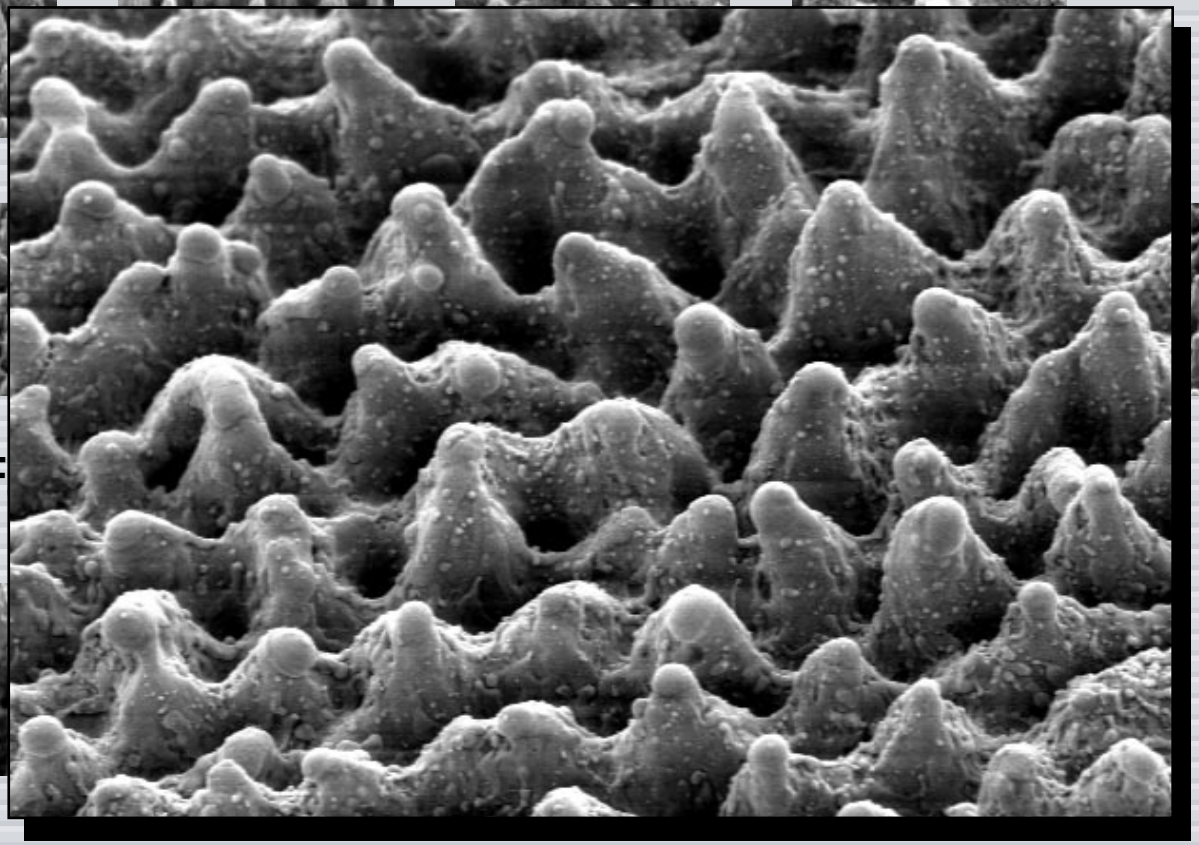


No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

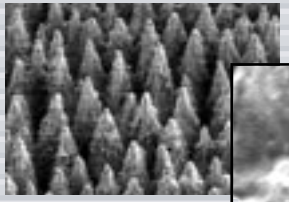
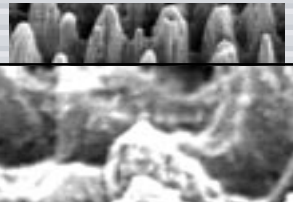
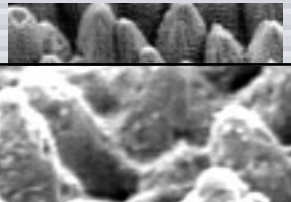
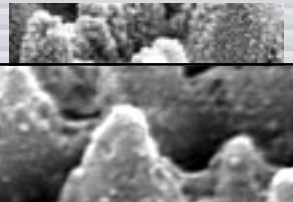
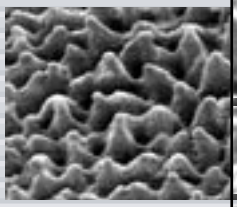
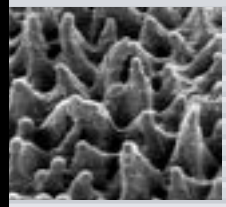
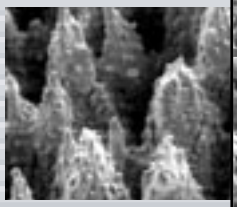
	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					

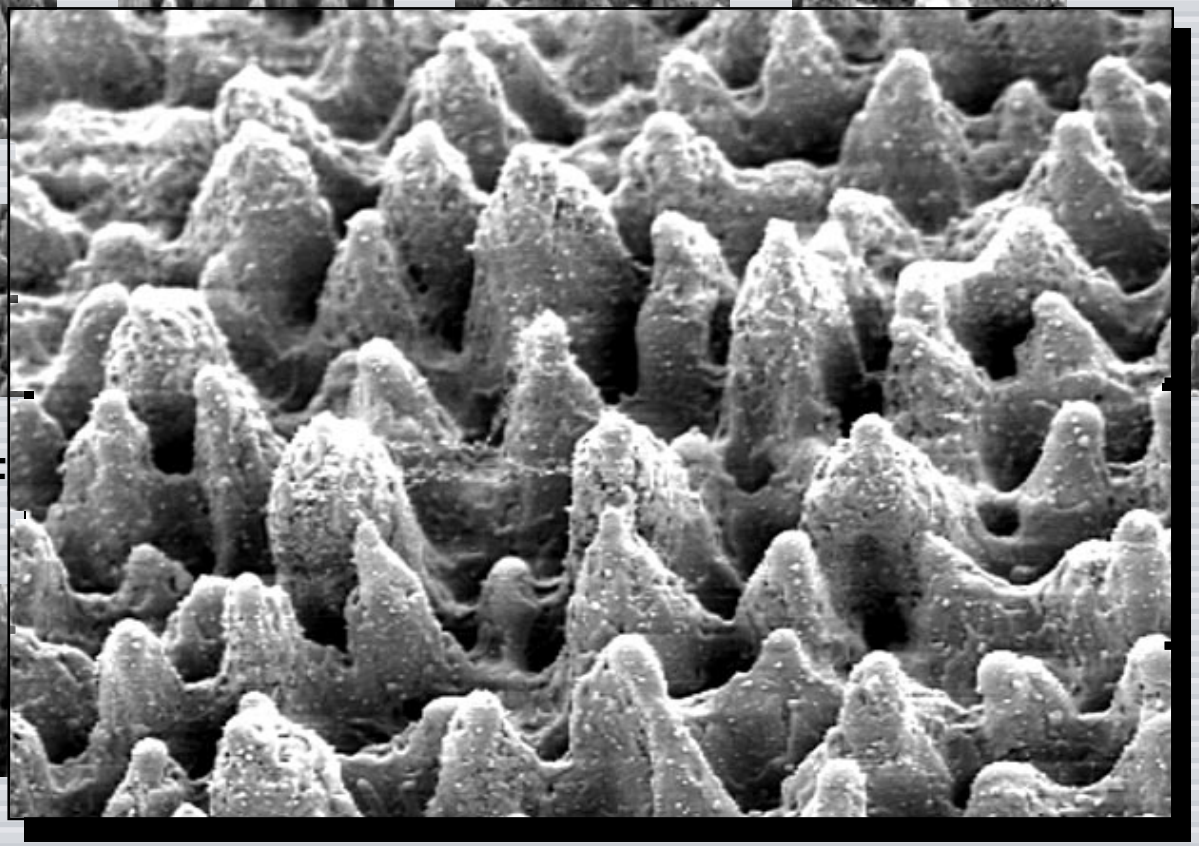
Only in SF



No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

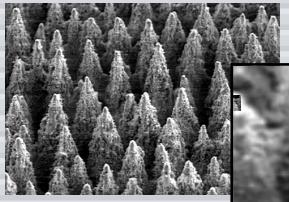
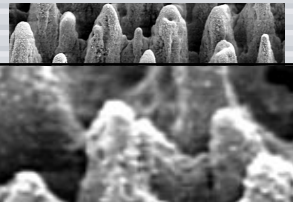
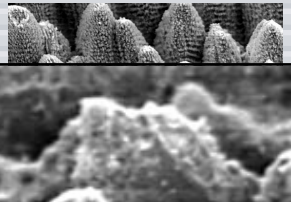
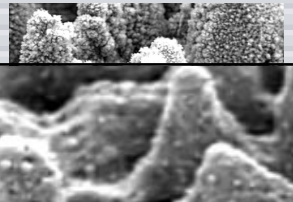
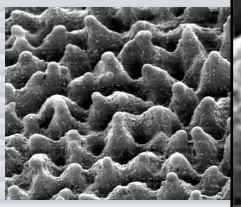
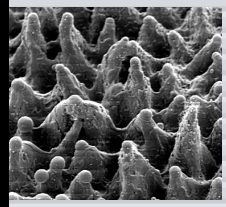
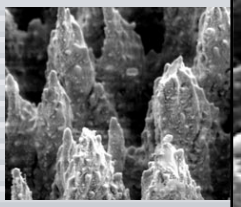
	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					

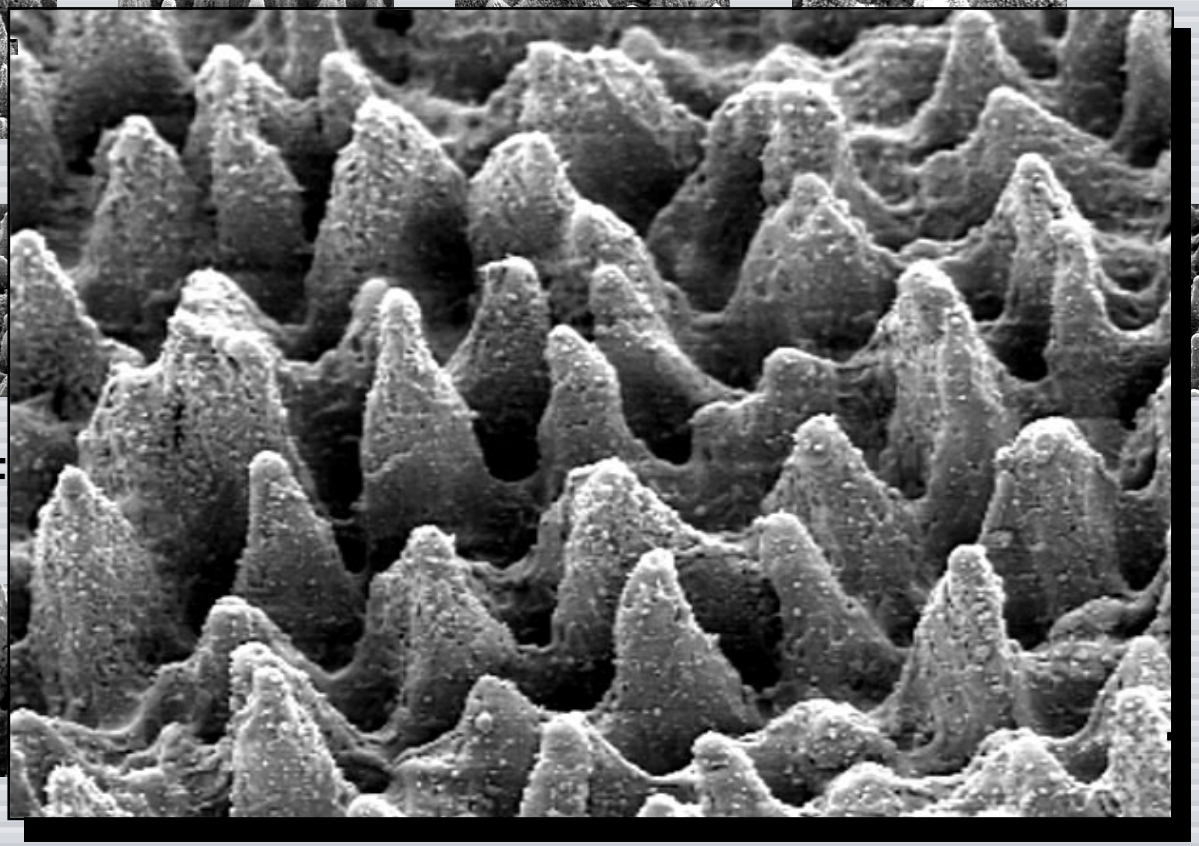


Only in SF

No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

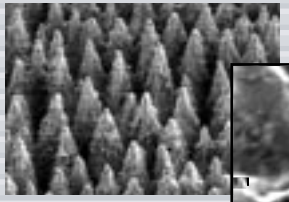
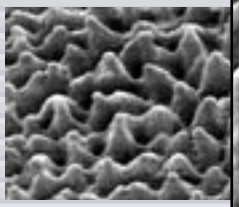
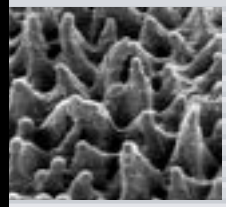
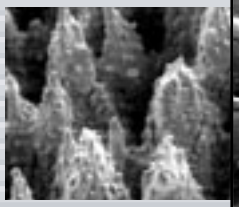
Materials

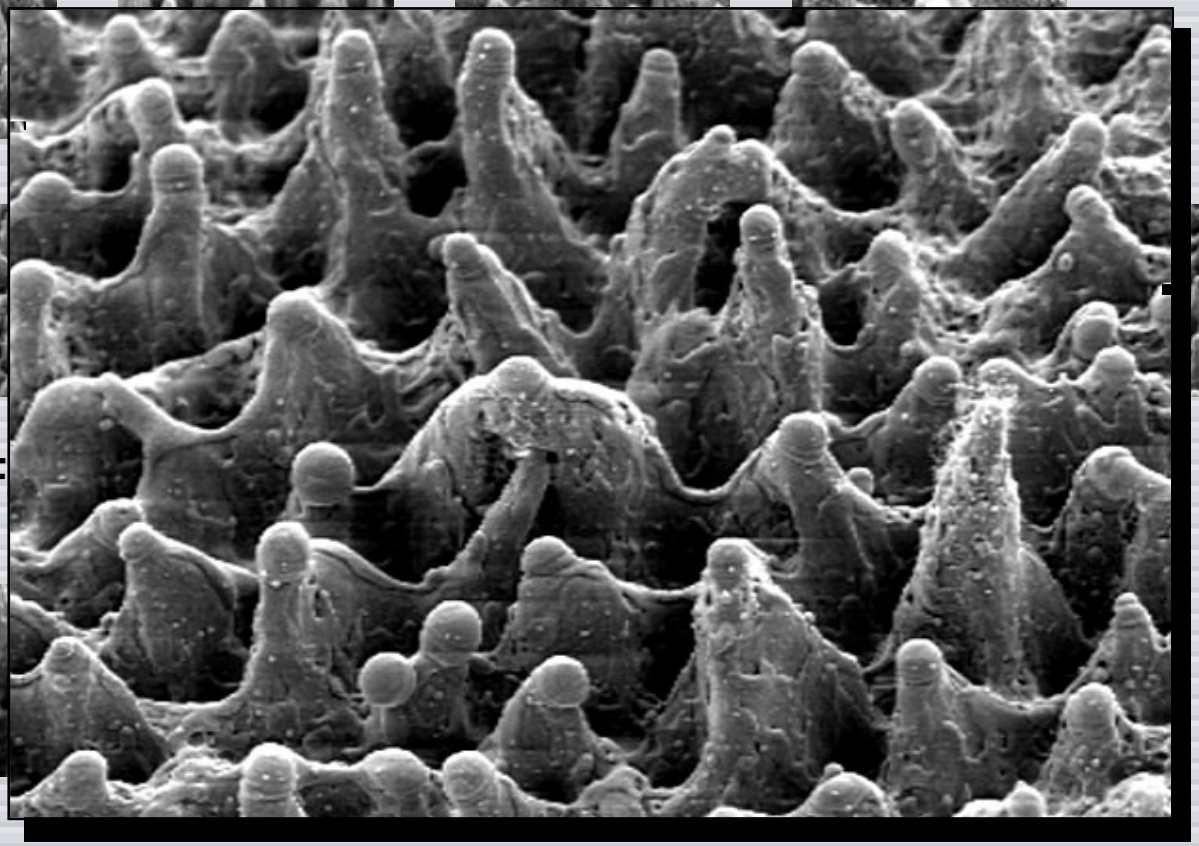
	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
	Only in SF				
Ge					



No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

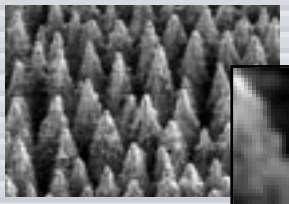
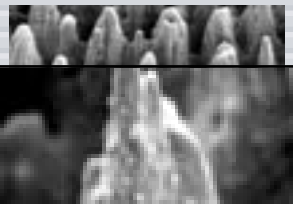
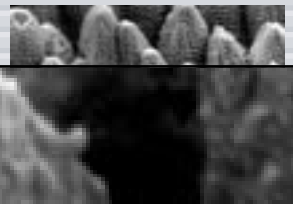
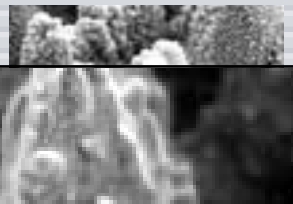
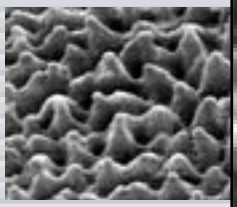
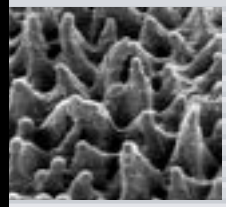
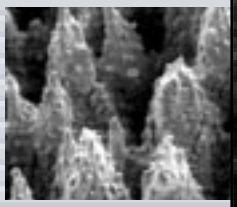
	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					

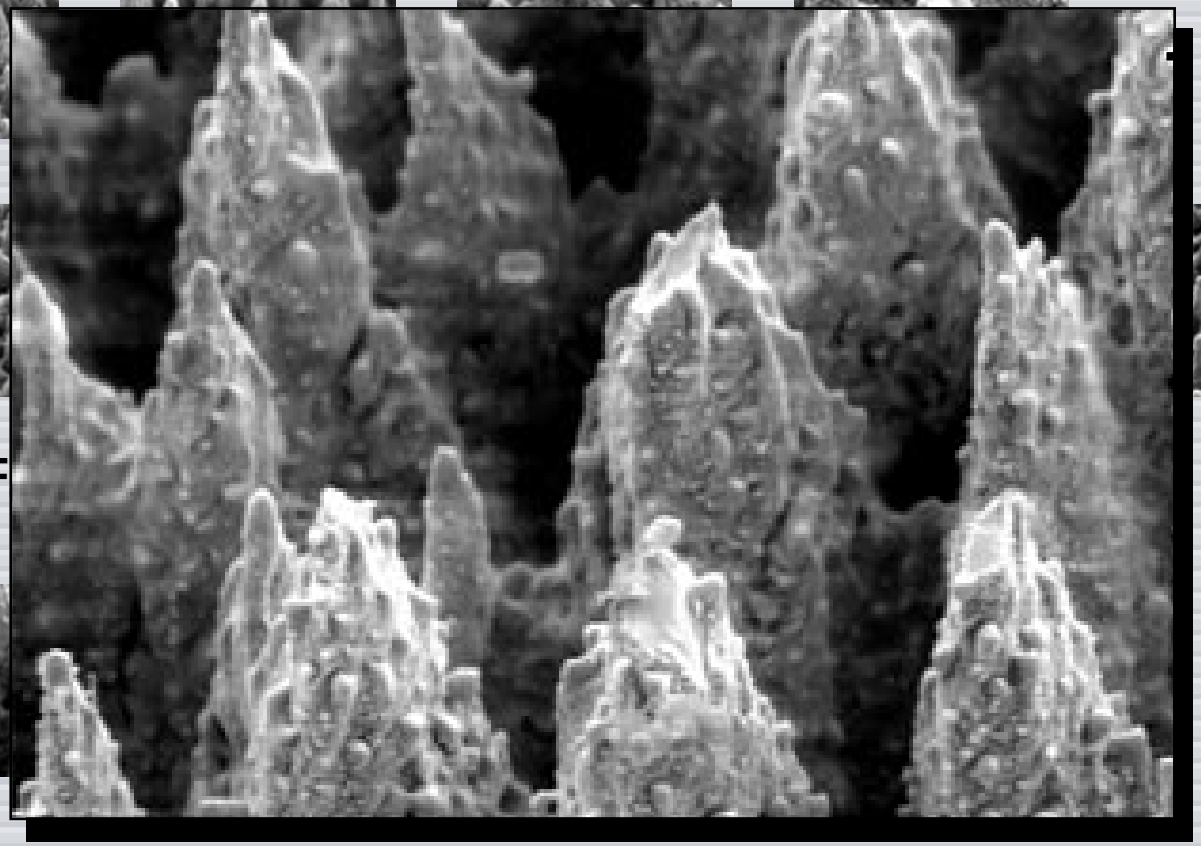


Only in SF

No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

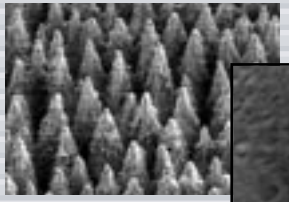
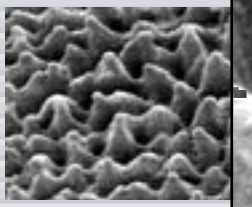
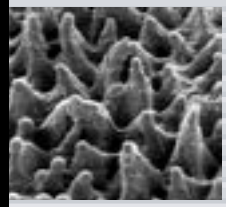
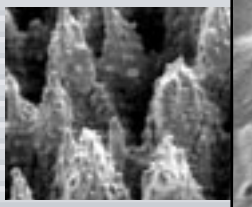
	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					

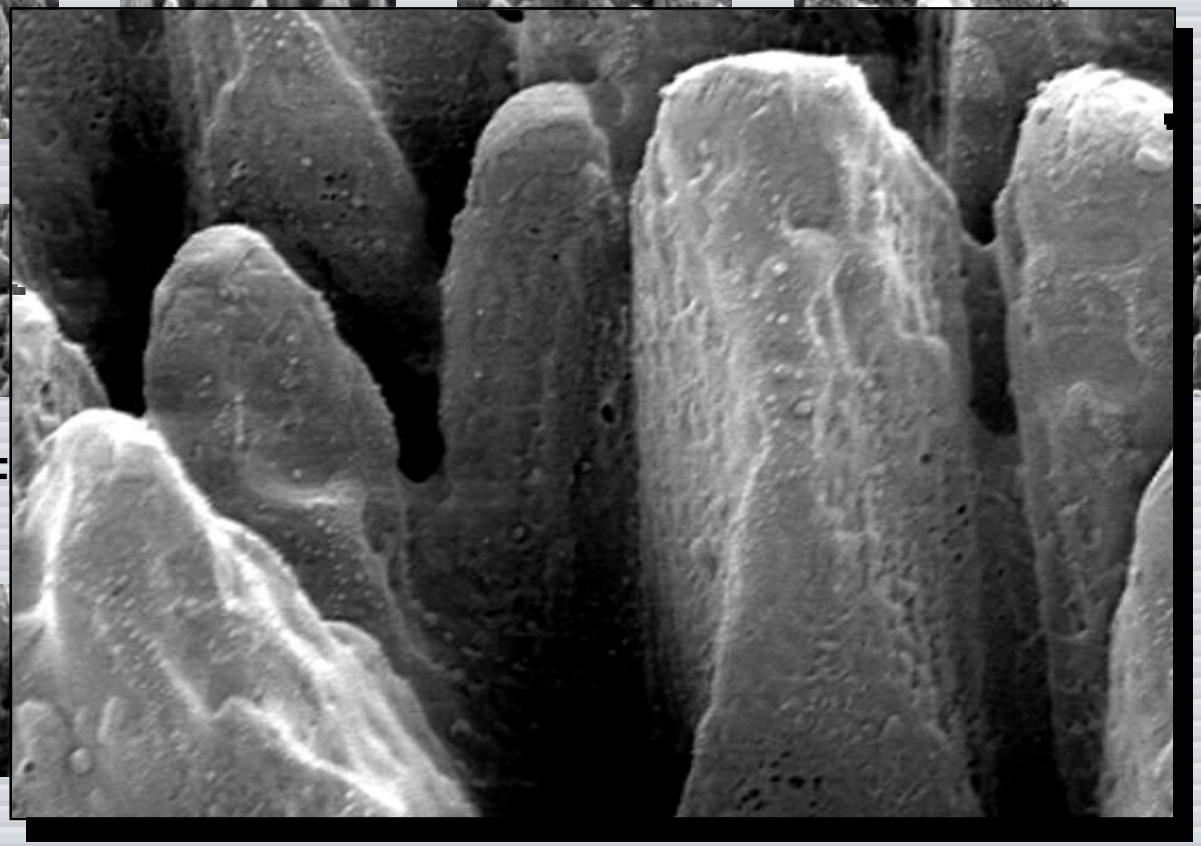


Only in SF

No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

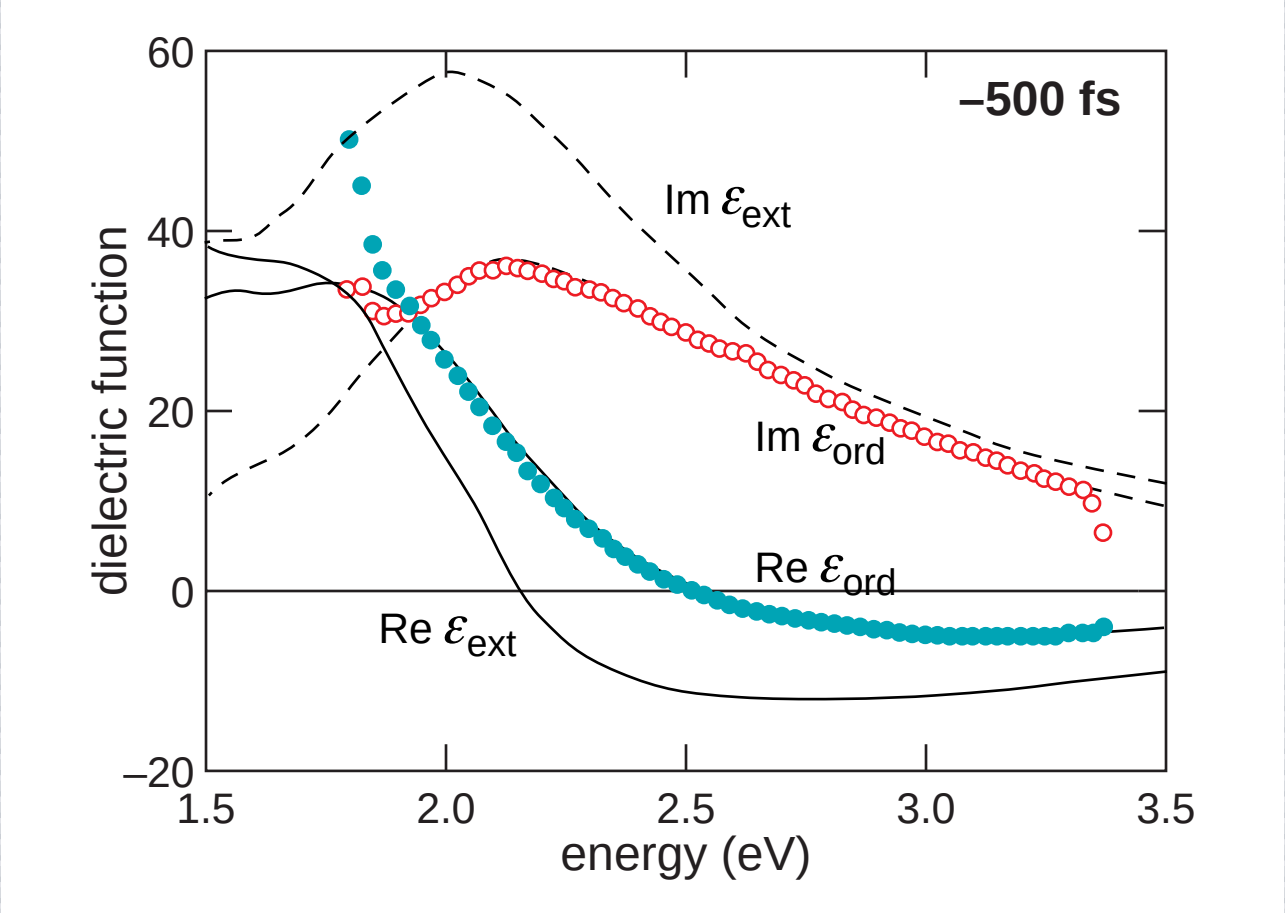
	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					



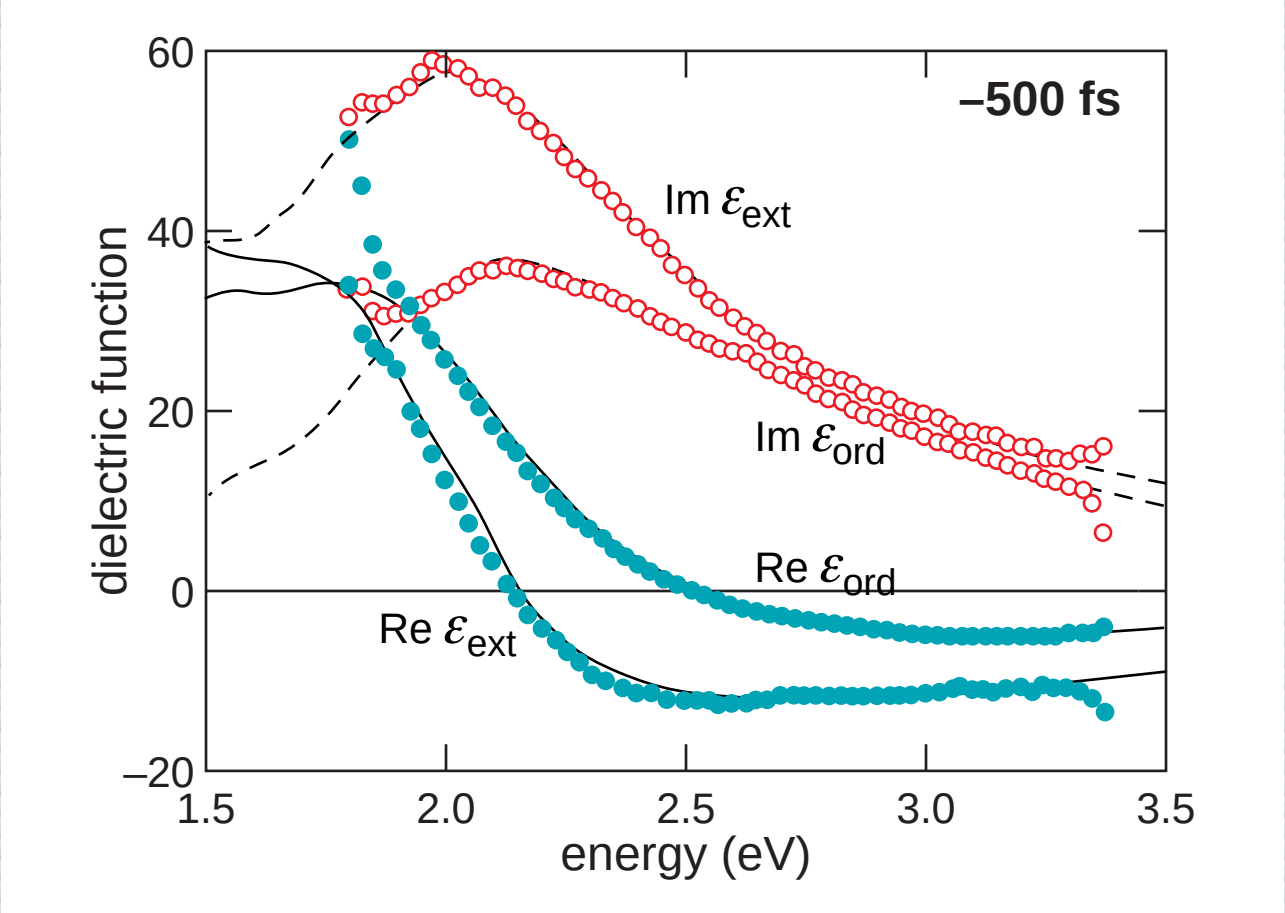
Only in SF

No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

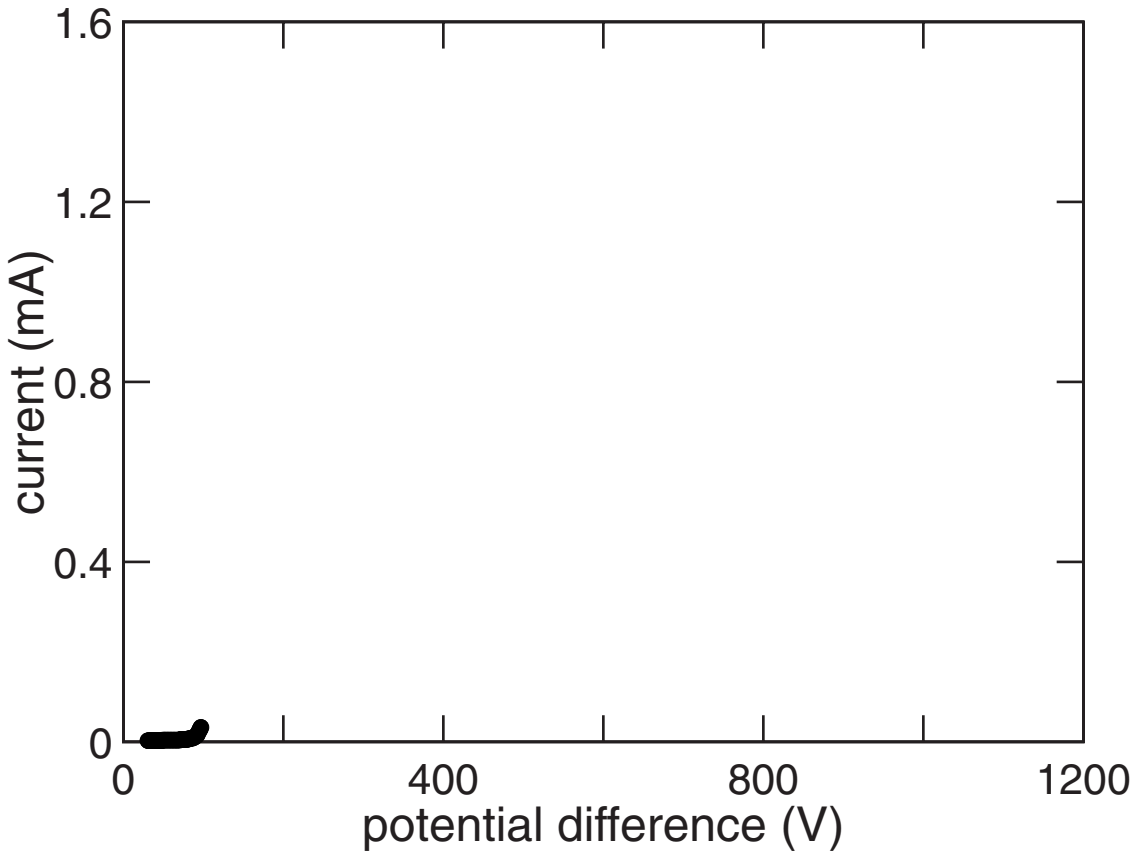
Results


–500 fs
Im ε_{ext}
Im ε_{ord}
Re ε_{ord}
Re ε_{ext}
dielectric function
energy (eV)
60
40
20
0
–20
1.5
2.0
2.5
3.0
3.5

Results


–500 fs
Im ε_{ext}
Im ε_{ord}
Re ε_{ord}
Re ε_{ext}
dielectric function
energy (eV)
60
40
20
0
–20
1.5
2.0
2.5
3.0
3.5

Properties



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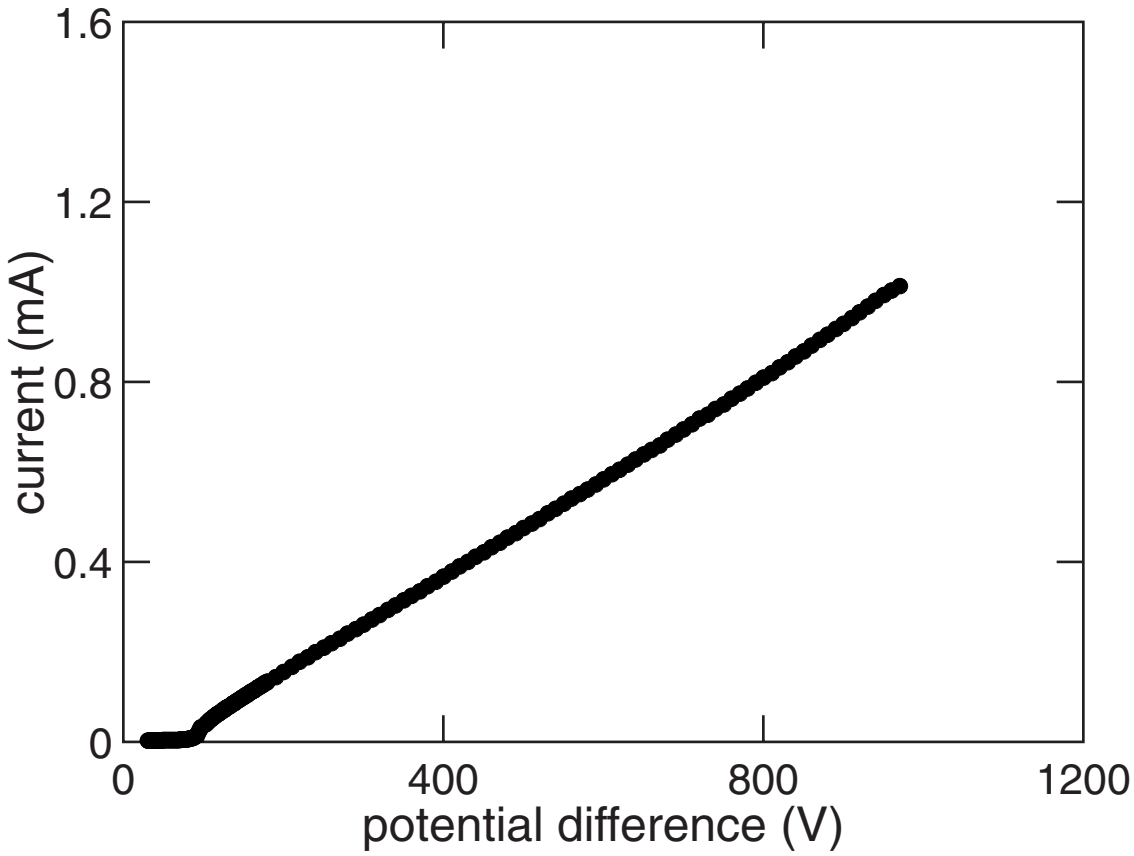

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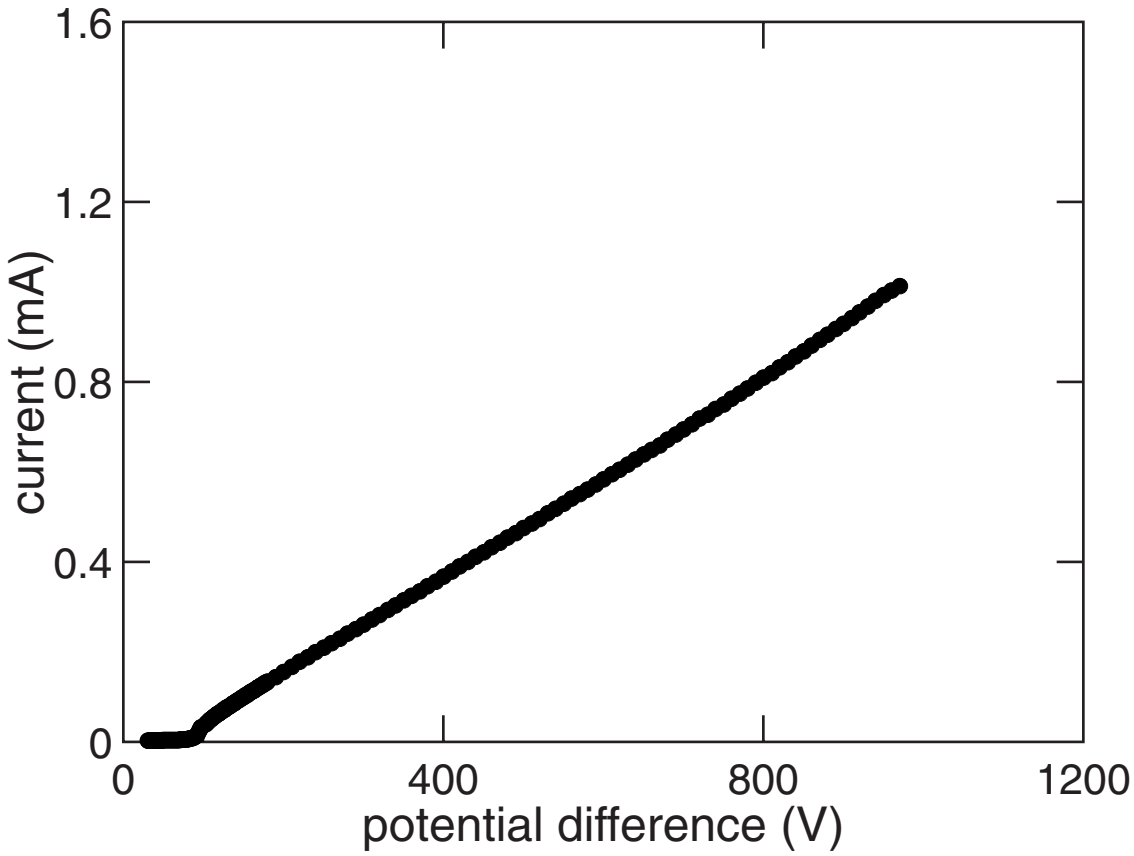
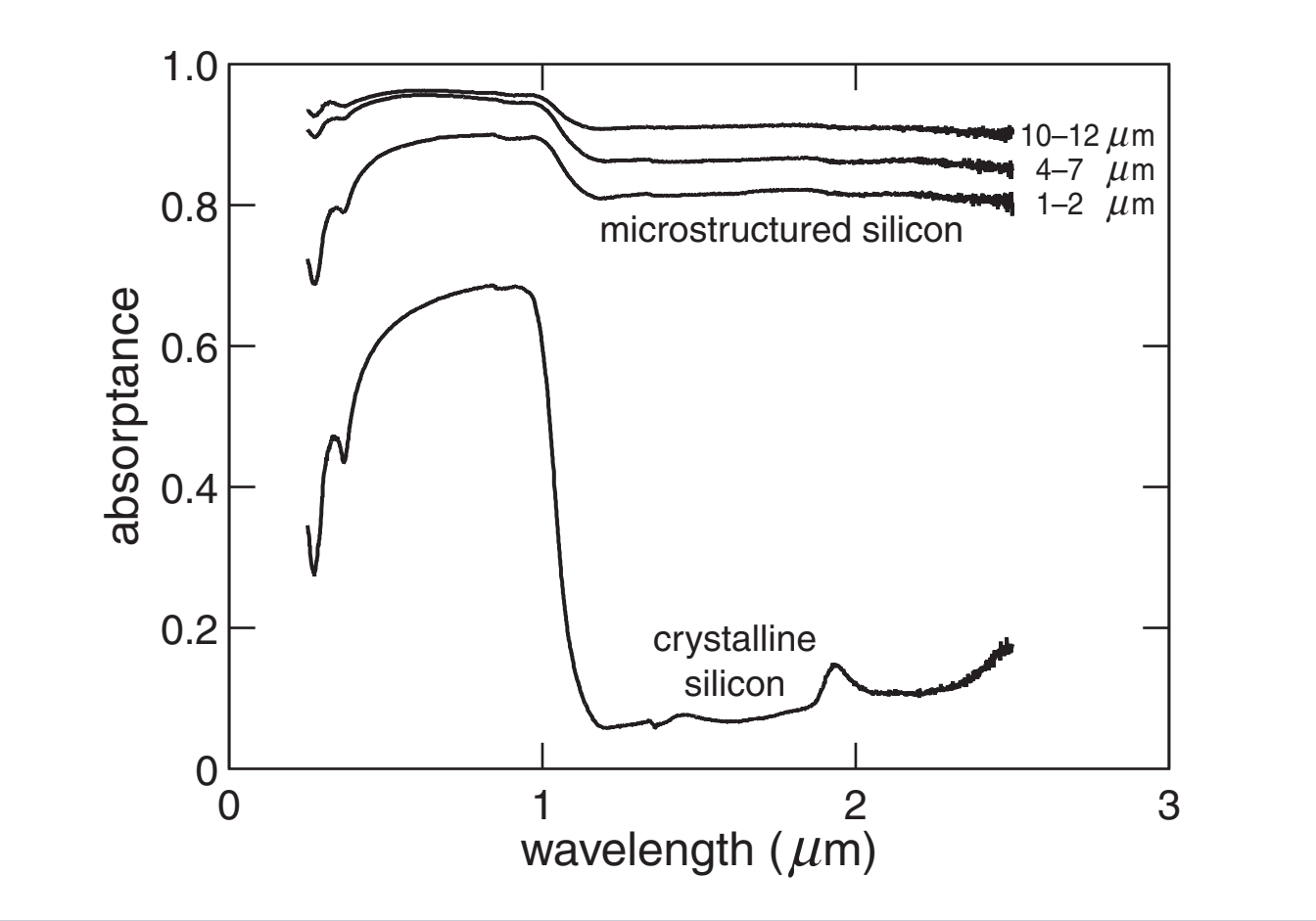


maximum current: 20 mA (4 mm^2 sample)

Properties

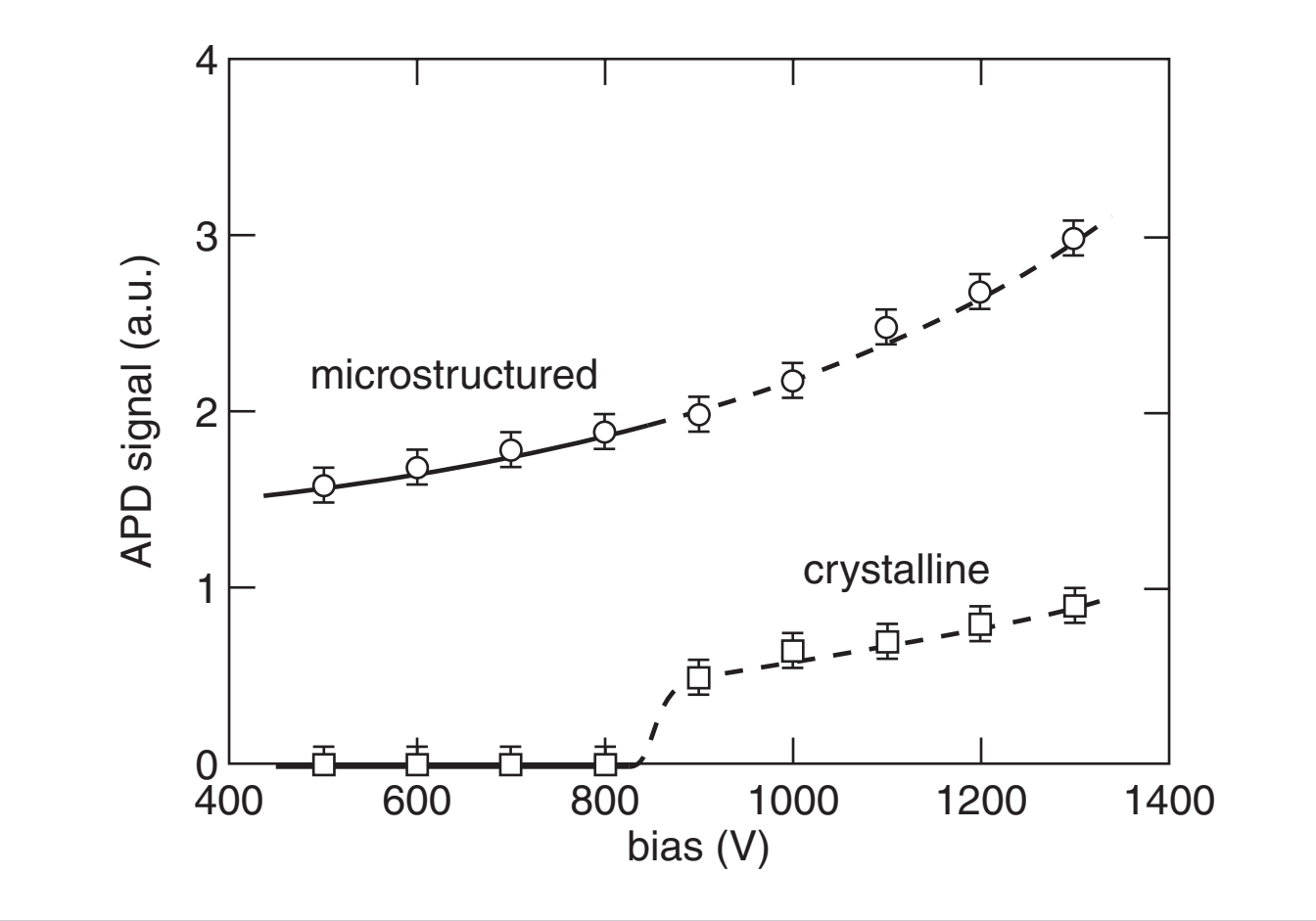
absorptance (1 – *R* – *T*)



Appl. Phys. Lett. **78**, 1850 (2001)

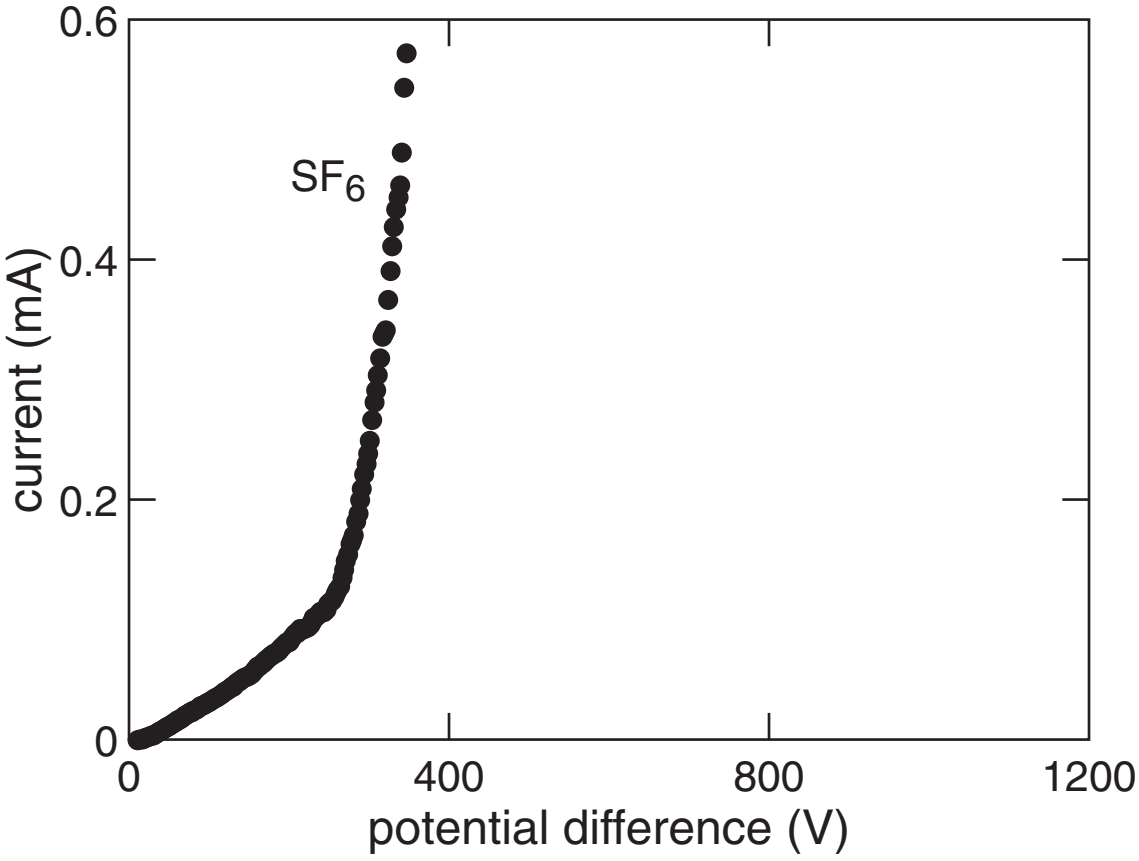
Properties

avalanche photodiode response at 1.3 μm

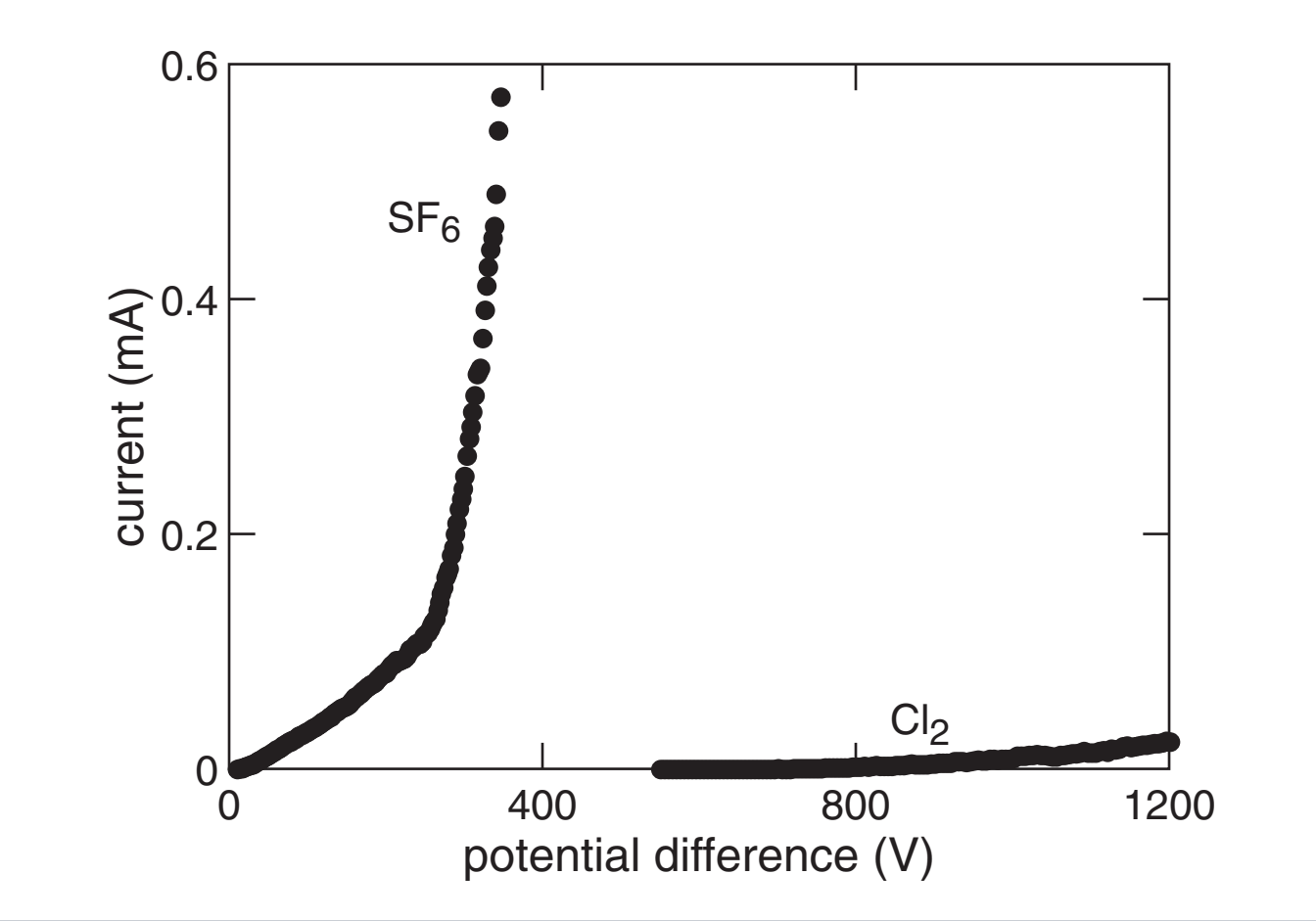


Appl. Phys. Lett. **78**, 1850 (2001)

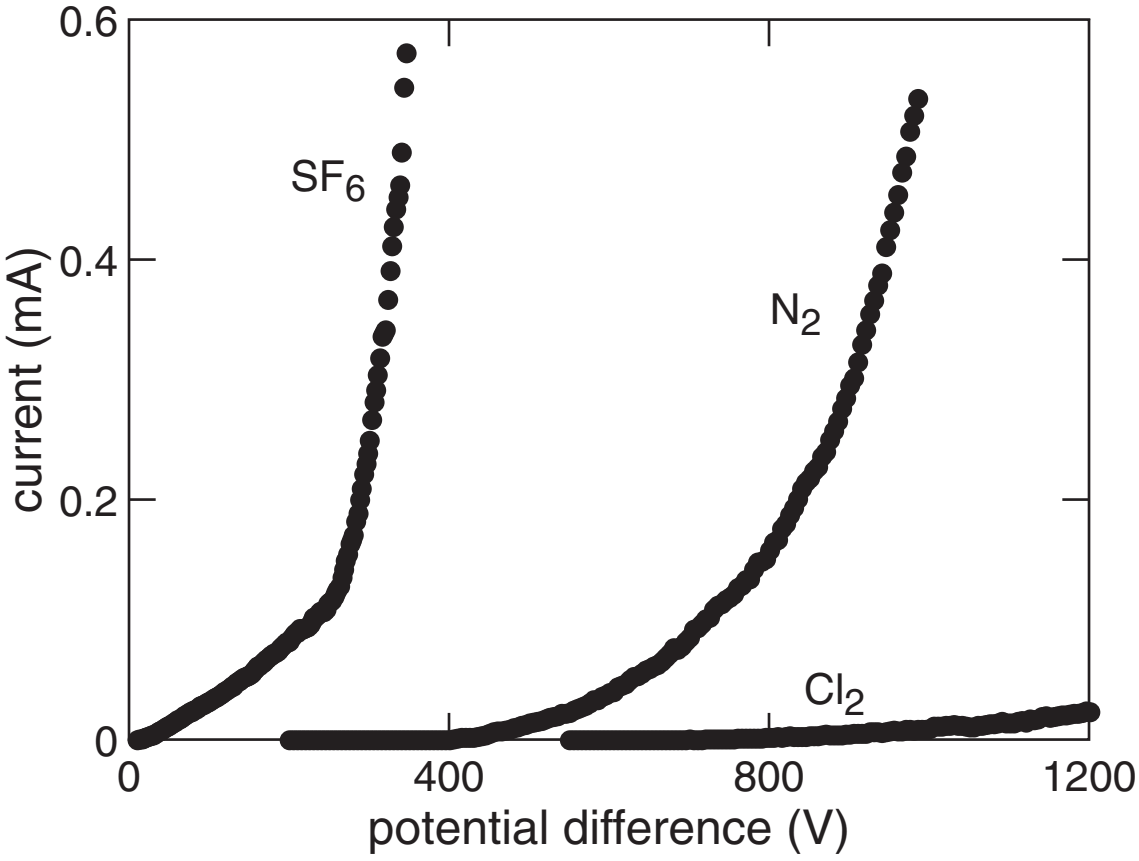
effect of ambient gas on field emission



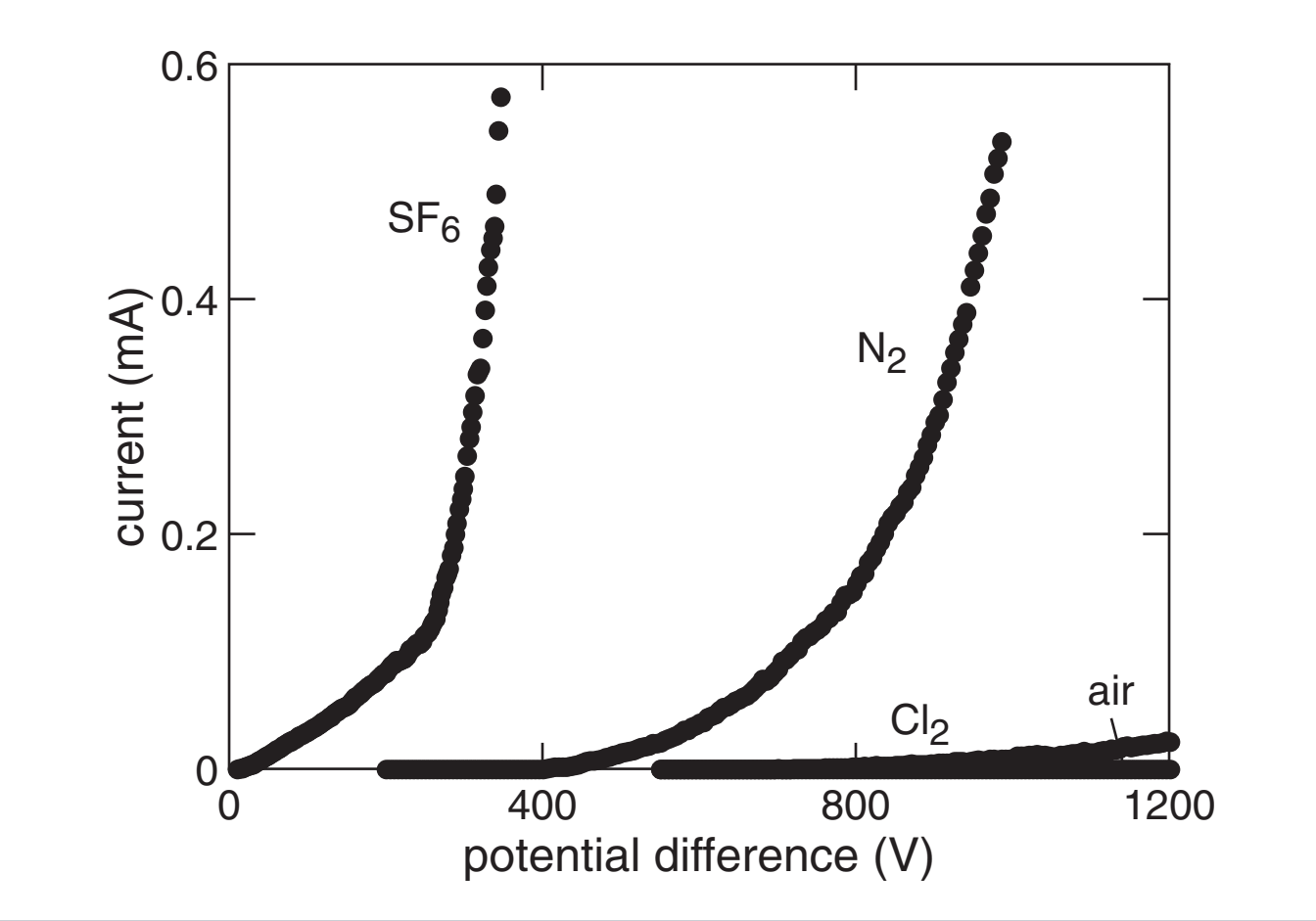
effect of ambient gas on field emission



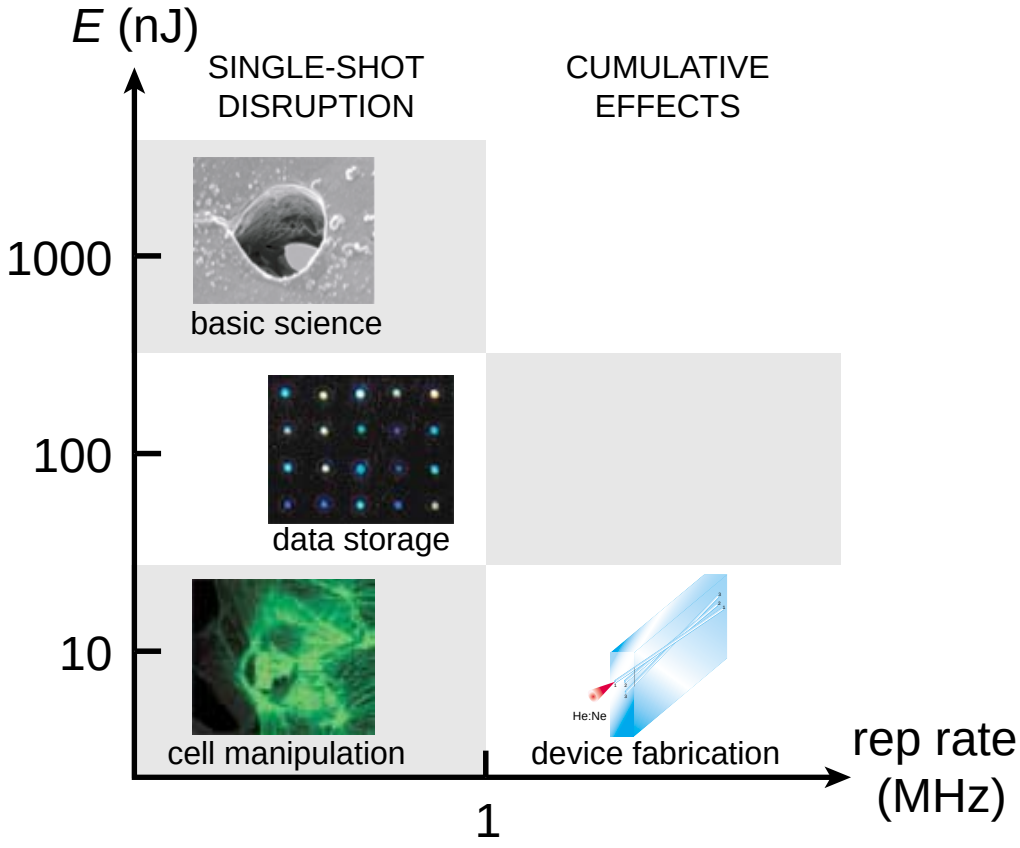
effect of ambient gas on field emission



effect of ambient gas on field emission



Summary


E (nJ)
SINGLE-SHOT DISRUPTION
CUMULATIVE EFFECTS
1000
100
10
basic science
data storage
cell manipulation
He:Ne
device fabrication
1
rep rate (MHz)