Laser-assisted internal and surface microstructuring of materials

Eric Mazur
Harvard University

Keio University, Yokohama
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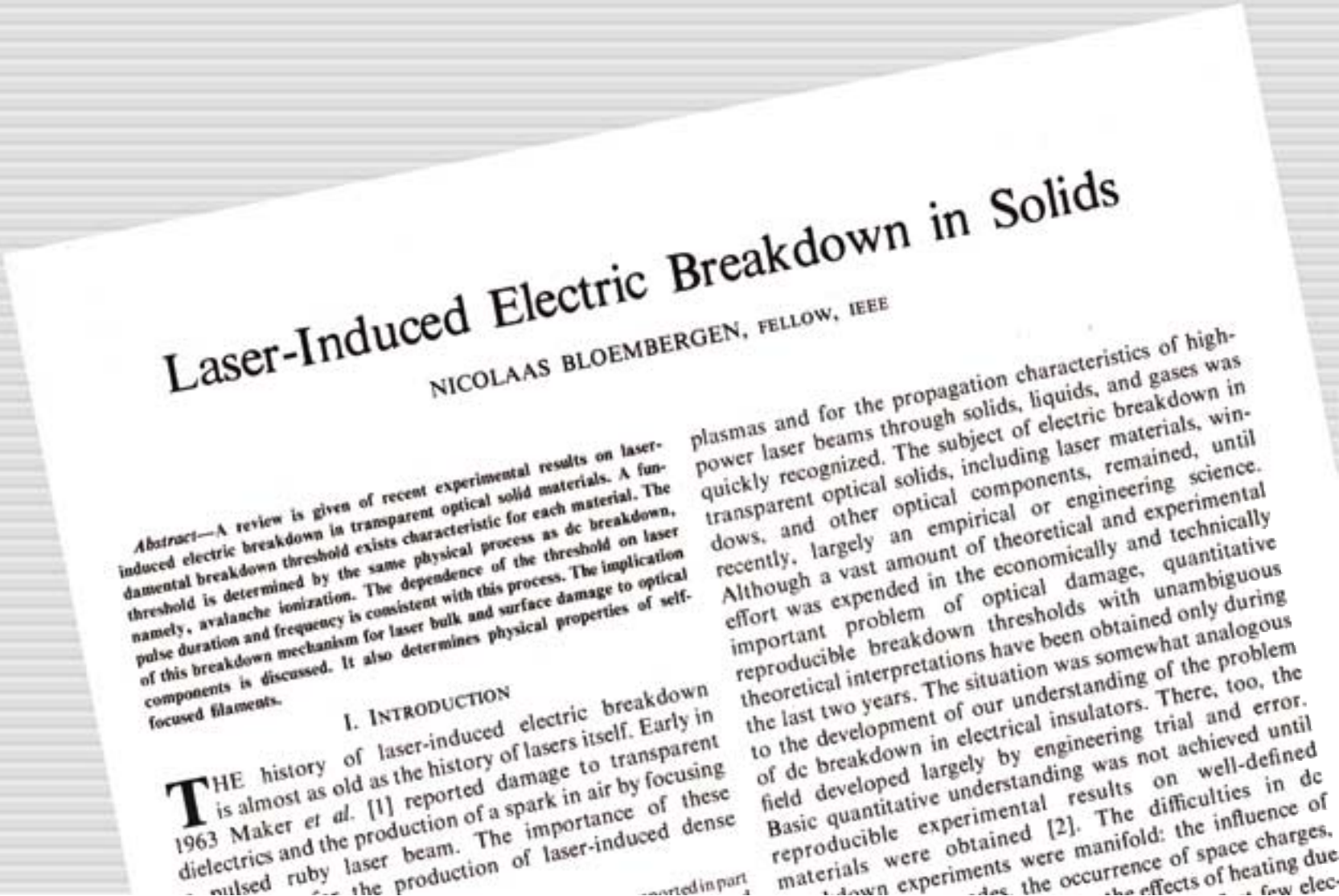
Introduction



Laser-Induced Electric Breakdown in Solids

NICOLAAS BLOEMBERGEN, FELLOW, IEEE

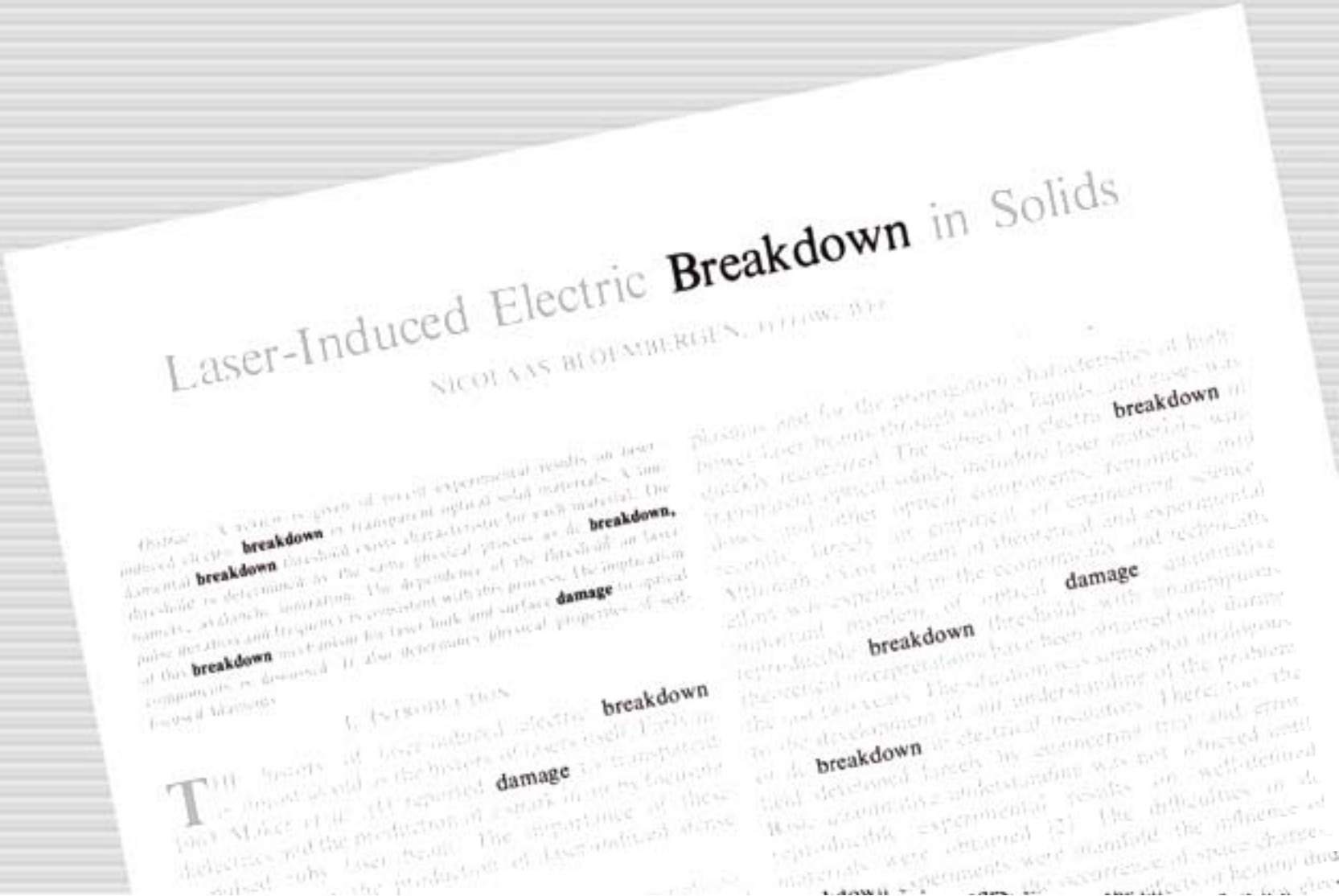
Abstract—A review is given of recent experimental results on laser-induced electric breakdown in transparent optical solid materials. A fundamental breakdown threshold exists characteristic for each material. The threshold is determined by the same physical process as dc breakdown, namely, avalanche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

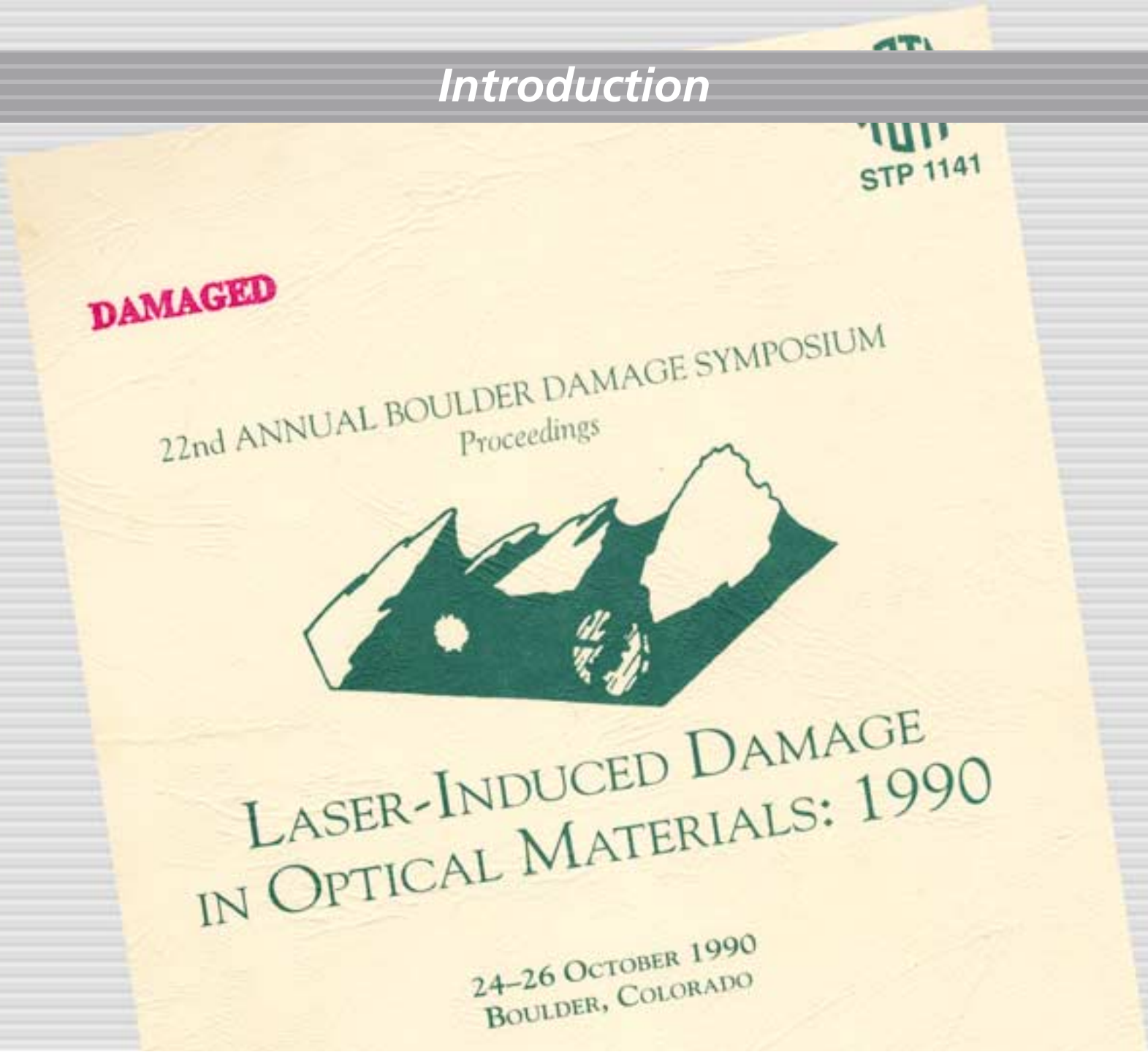
THE history of laser-induced electric breakdown is almost as old as the history of lasers itself. Early in 1963 Maker *et al.* [1] reported damage to transparent dielectrics and the production of a spark in air by focusing pulsed ruby laser beam. The importance of these for the production of laser-induced 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

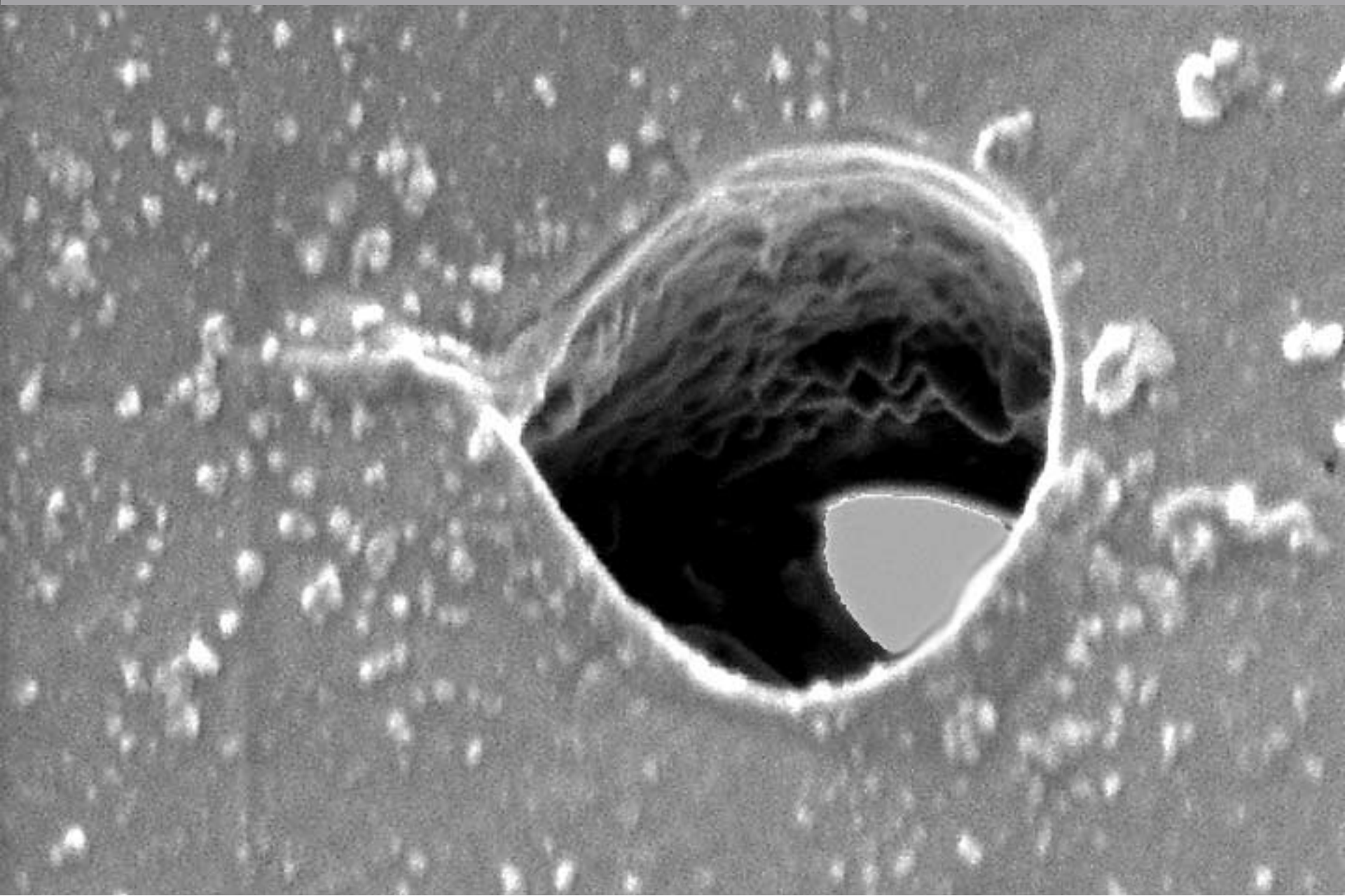
Introduction



Introduction

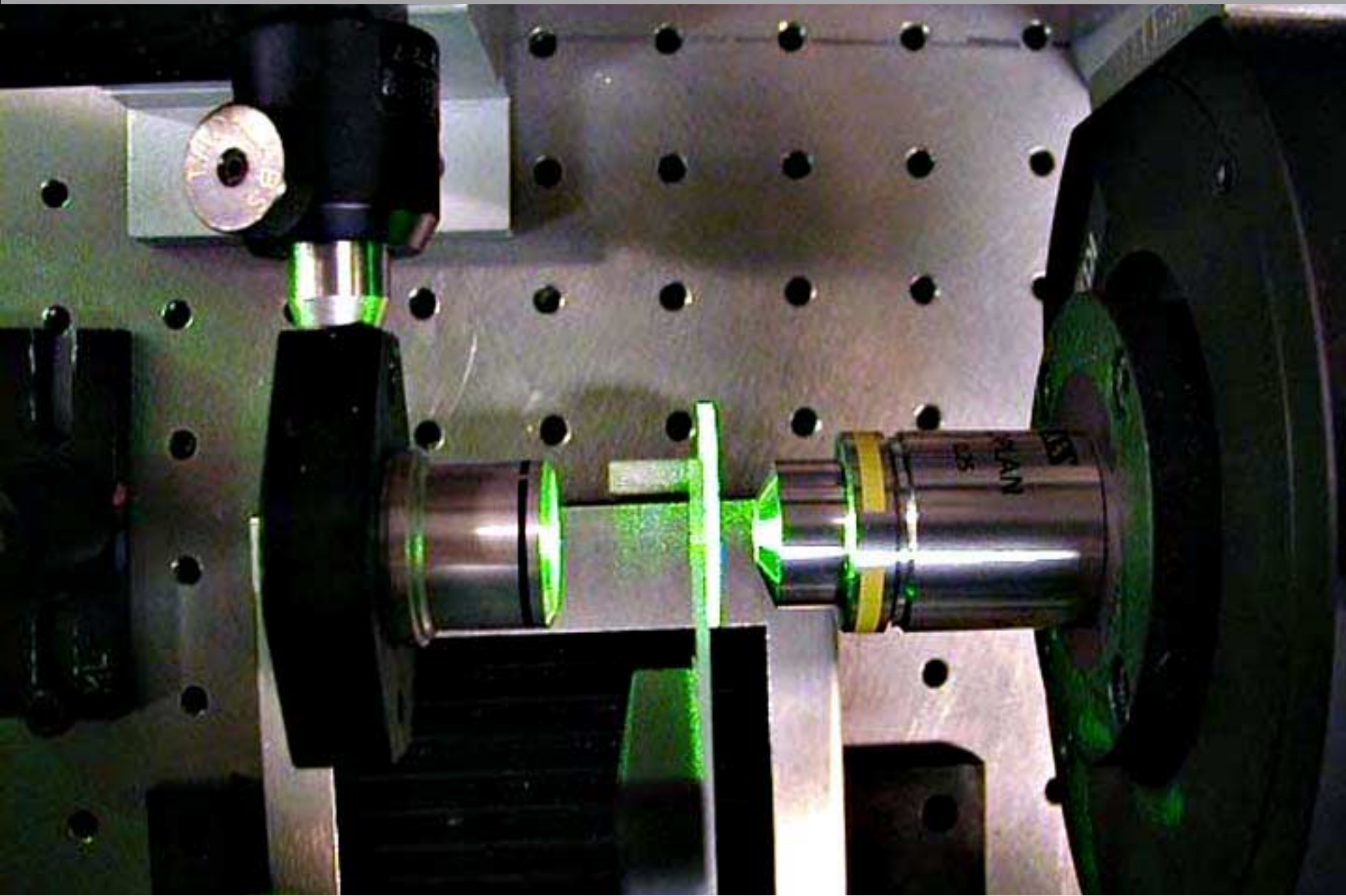


Introduction



use damage for processing!

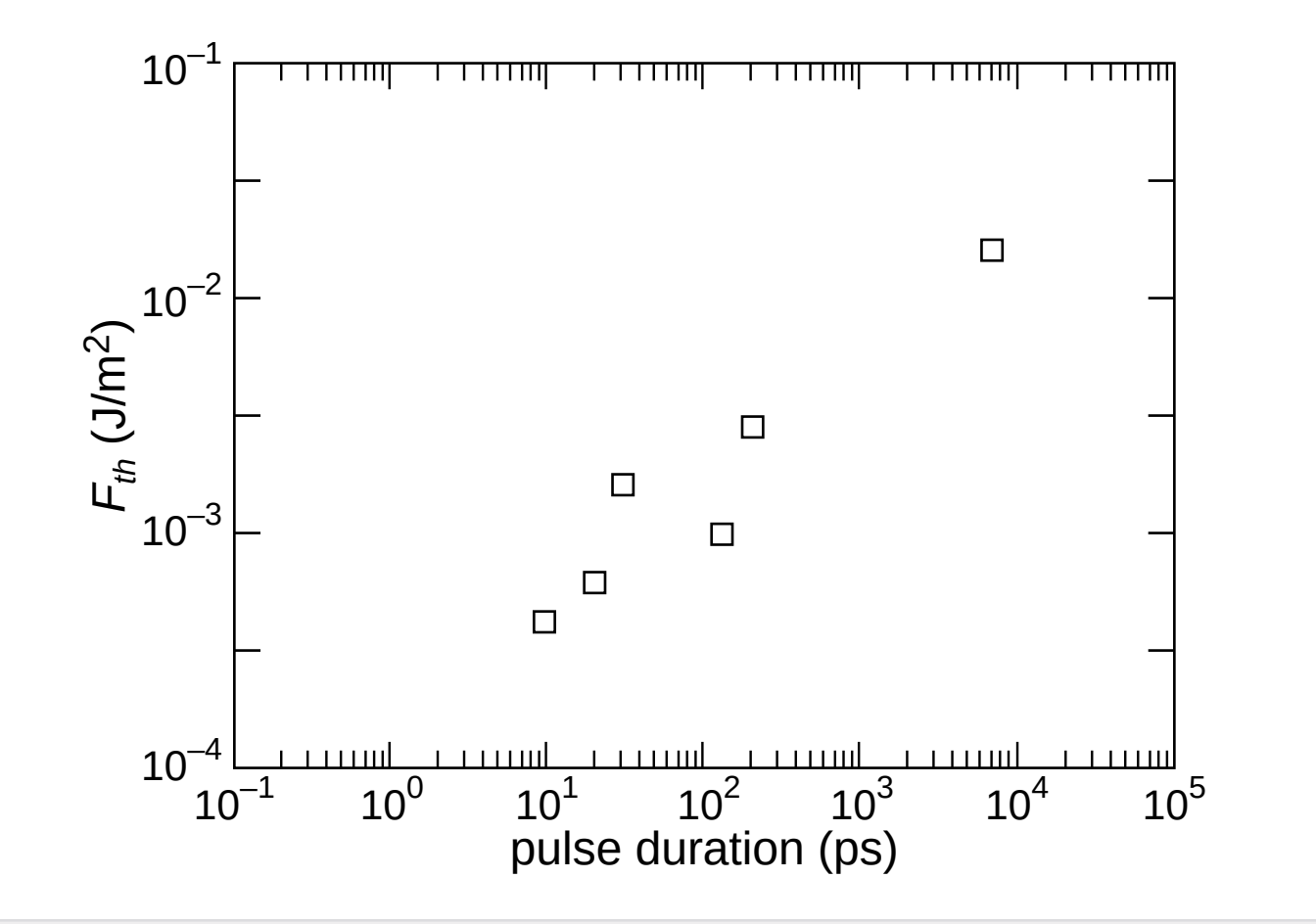
Outline



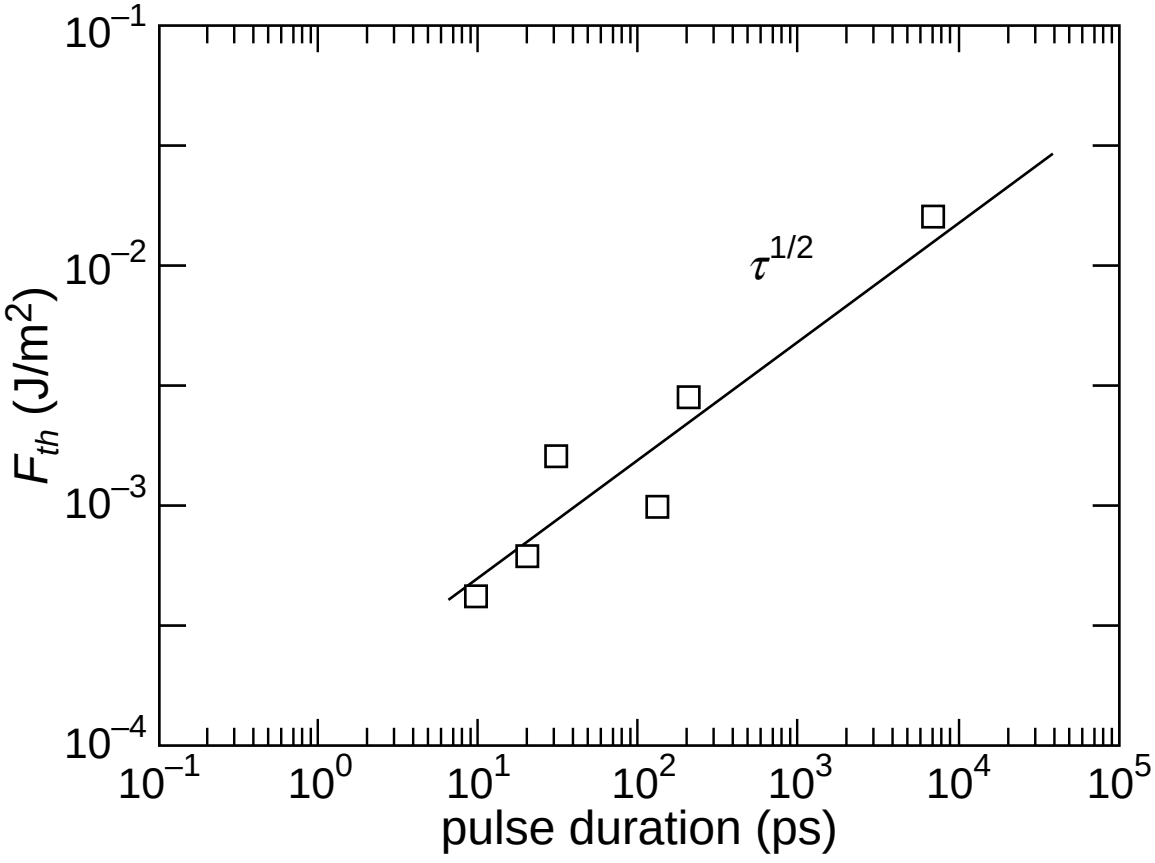
Outline

- Processing with fs pulses
- Role of focusing
- Low-energy processing

Processing with fs pulses



Processing with fs pulses



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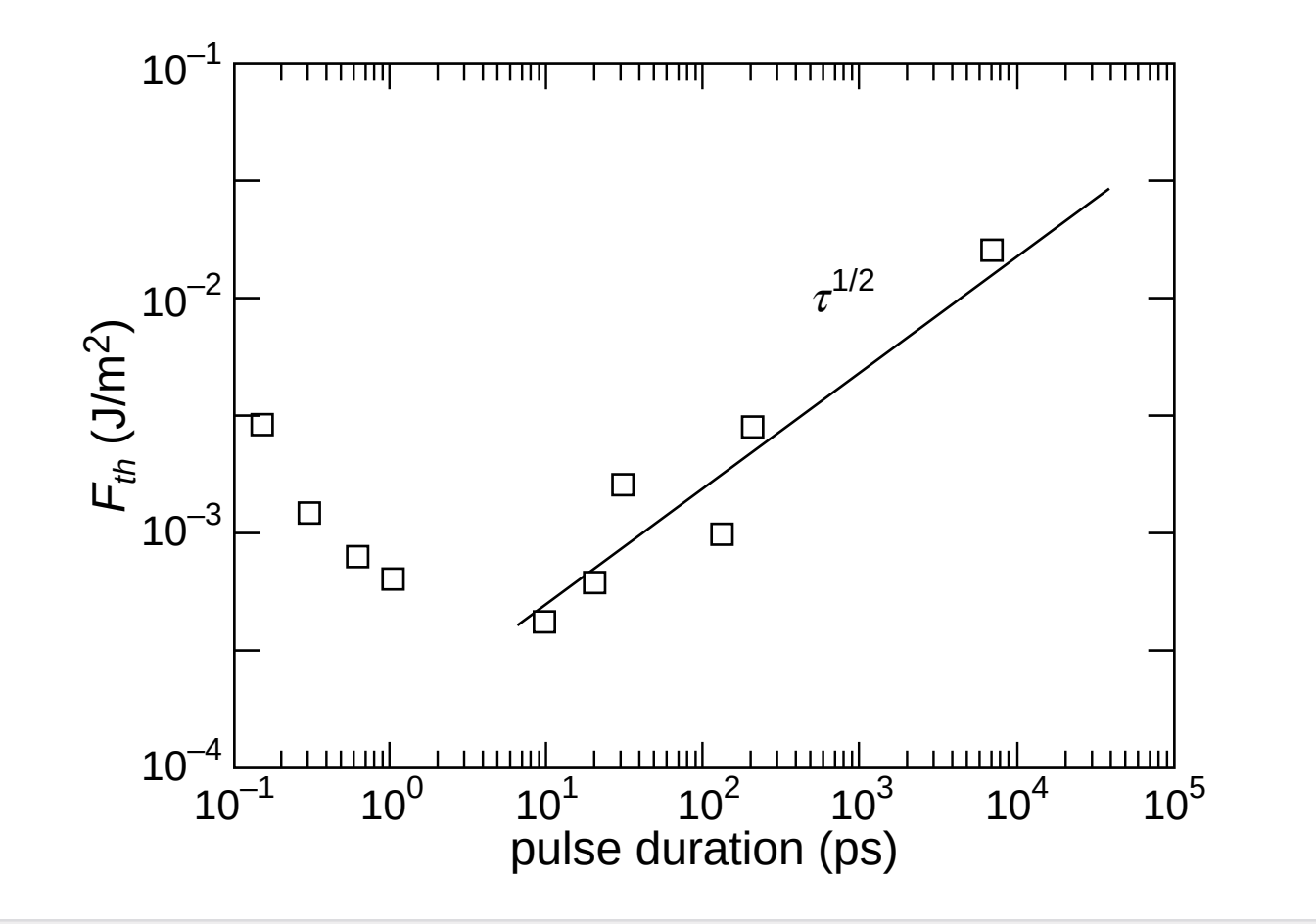
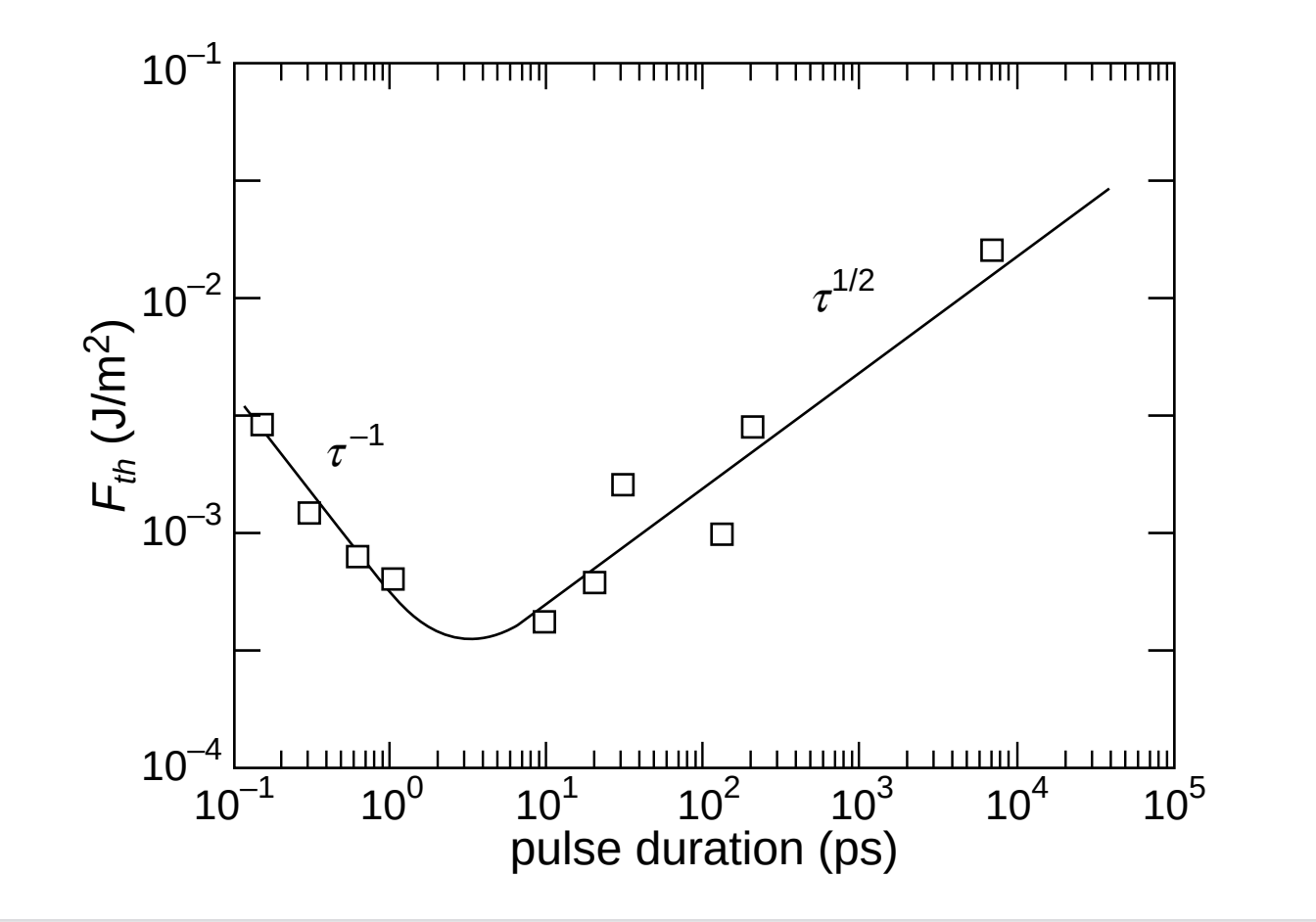


Du *et al.*, *Appl. Phys. Lett.* 64, 3071 (1994)

Processing with fs pulses



Du *et al.*, *Appl. Phys. Lett.* 64, 3071 (1994)

Processing with fs pulses

216 J. Opt. Soc. Am. B/Vol. 13, No. 1/January 1996

Breakdown threshold and plasma formation in femtosecond laser–solid interaction

D. von der Linde and H. Schüler

Institut für Laser- und Plasmaphysik, Universität Essen, D-45117 Essen, Germany

Received March 6, 1995; revised manuscript received June 15, 1995

Combining femtosecond pump–probe techniques with optical microscopy, we have studied laser-induced optical breakdown in optically transparent solids with high temporal and spatial resolution. The threshold of plasma formation has been determined from measurements of the changes of the optical reflectivity associated with the developing plasma. It is shown that plasma generation occurs at the surface. We have observed a remarkable resistance to optical breakdown and material damage in the interaction of femtosecond laser pulses with bulk optical materials.

1. INTRODUCTION

The interaction of intense femtosecond laser pulses with solids offers the possibility of producing a new class of plasmas having approximately solid-state density and spatial density scale lengths much smaller than the wavelength of light. These high-density plasmas with extremely sharp density gradients are currently of great interest, particularly from the point of view of generating short x-ray pulses. To produce such a [illegible] rise from the intensity level [illegible] formation to the [illegible] scale

One of the key points in the research of Bloembergen and his co-workers was the use of very tightly focused laser beams, which allowed them to reach the breakdown threshold of the materials while staying well below the critical power of self-focusing. Self-focusing is one of the major problems in the measurement of bulk breakdown thresholds. In a more recent review Soileau *et al.*[5] carefully examined the role of self-focusing in experiments measuring laser-induced breakdown of bulk dielectric materials. They concluded that the breakdown and damage thresholds are also strongly influenced by extrinsic effects.

Thus far, the issue of breakdown thresholds in femtosecond laser–solid interaction has barely been touched. [illegible]cently, Du *et al.*[6] carried out laser-induced break[illegible] on fused silica with pulses ranging in [illegible] as 150 fs. They reported [illegible]ence threshold on [illegible] of the

Processing with fs pulses

"… clear evidence that no bulk plasmas …

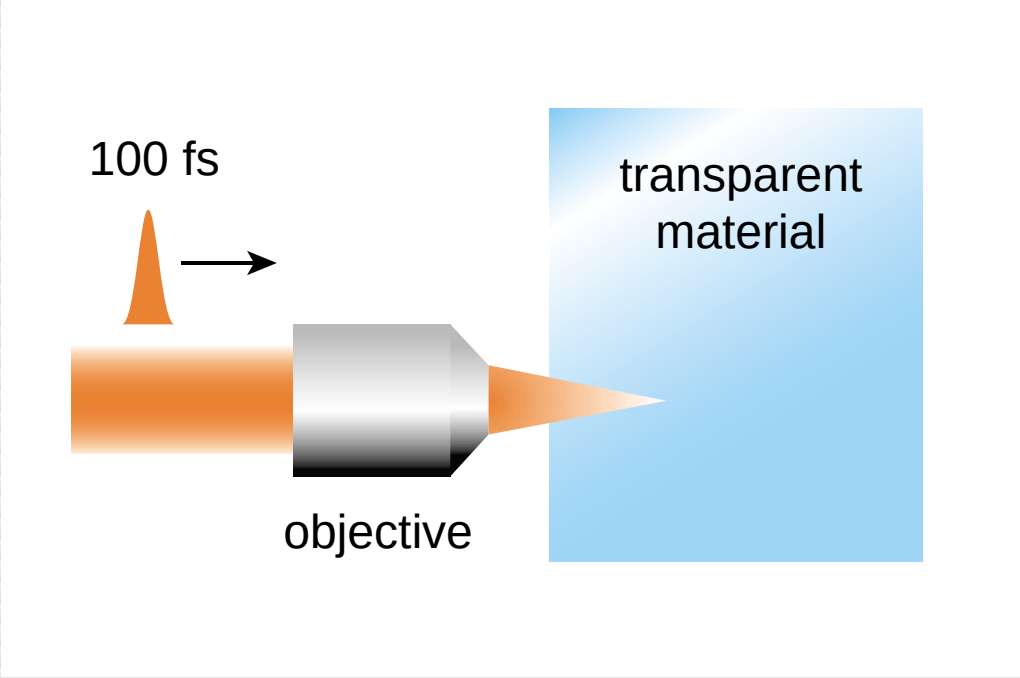
[and] … no bulk damage could be produced

with femtosecond laser pulses."

von der Linde, *et al.*, *J. Opt. Soc. Am.* 13, 216 (1996)

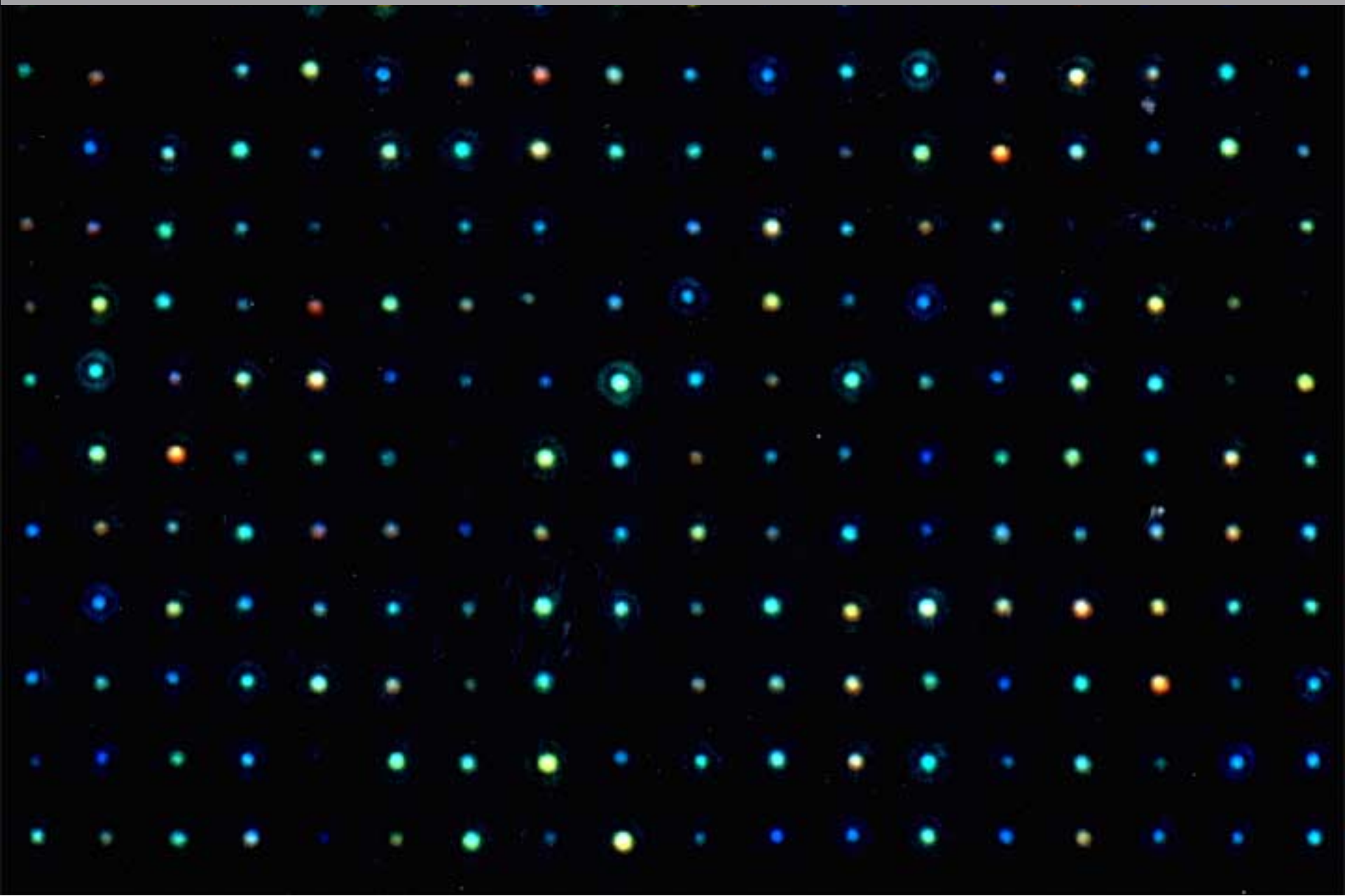
Processing with fs pulses

focus laser beam inside material



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

Processing with fs pulses

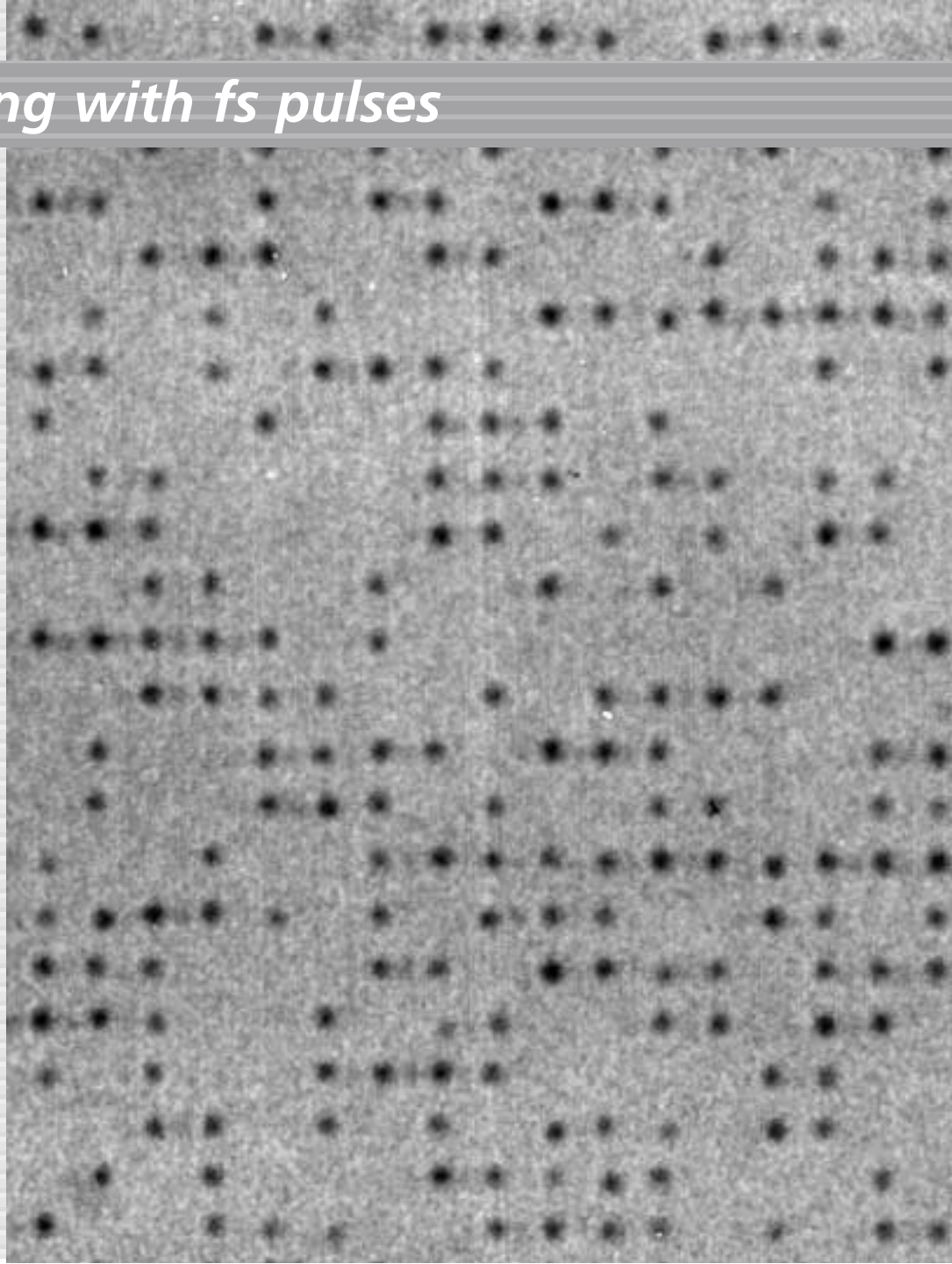


Processing with fs pulses

2 x 2 μm array

fused silica, 0.65 NA

0.5 μJ, 100 fs, 800 nm



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

Processing with fs pulses

2 x 2 µm array

fused silica, 0.65 NA

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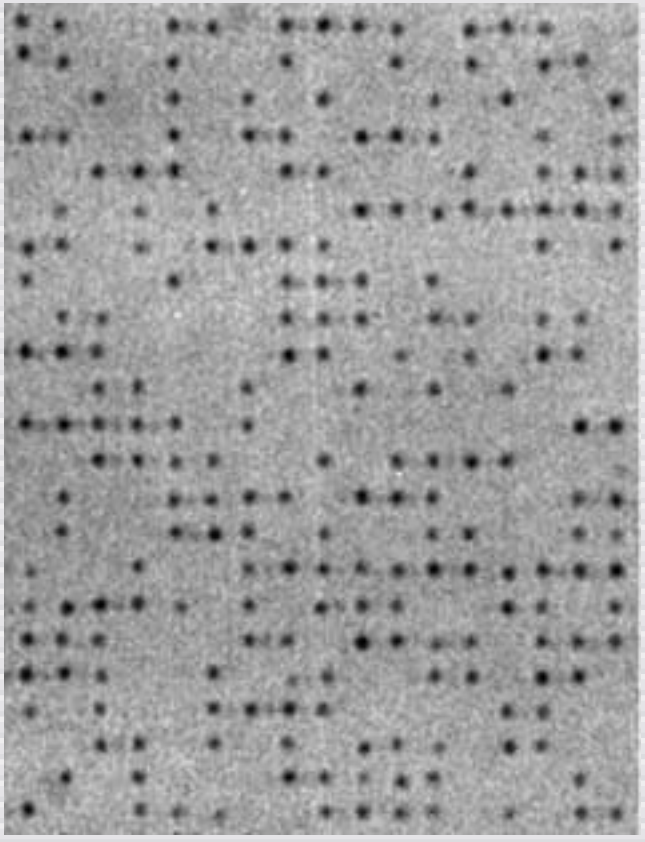


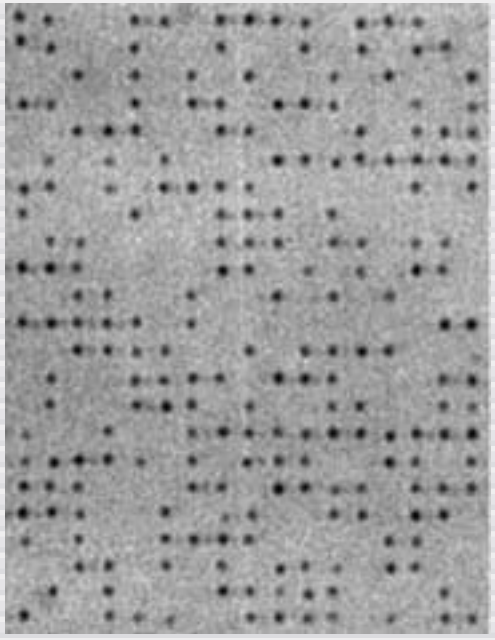
Opt. Lett. **21, 2023 (1996)**

Processing with fs pulses

2 x 2 μm array

fused silica, 0.65 NA

0.5 μJ, 100 fs, 800 nm



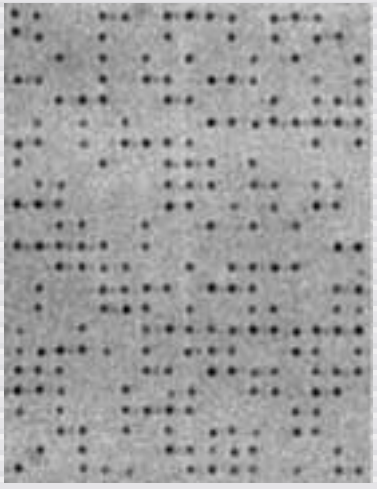
Opt. Lett. **21, 2023 (1996)**

Processing with fs pulses

2 x 2 μm array

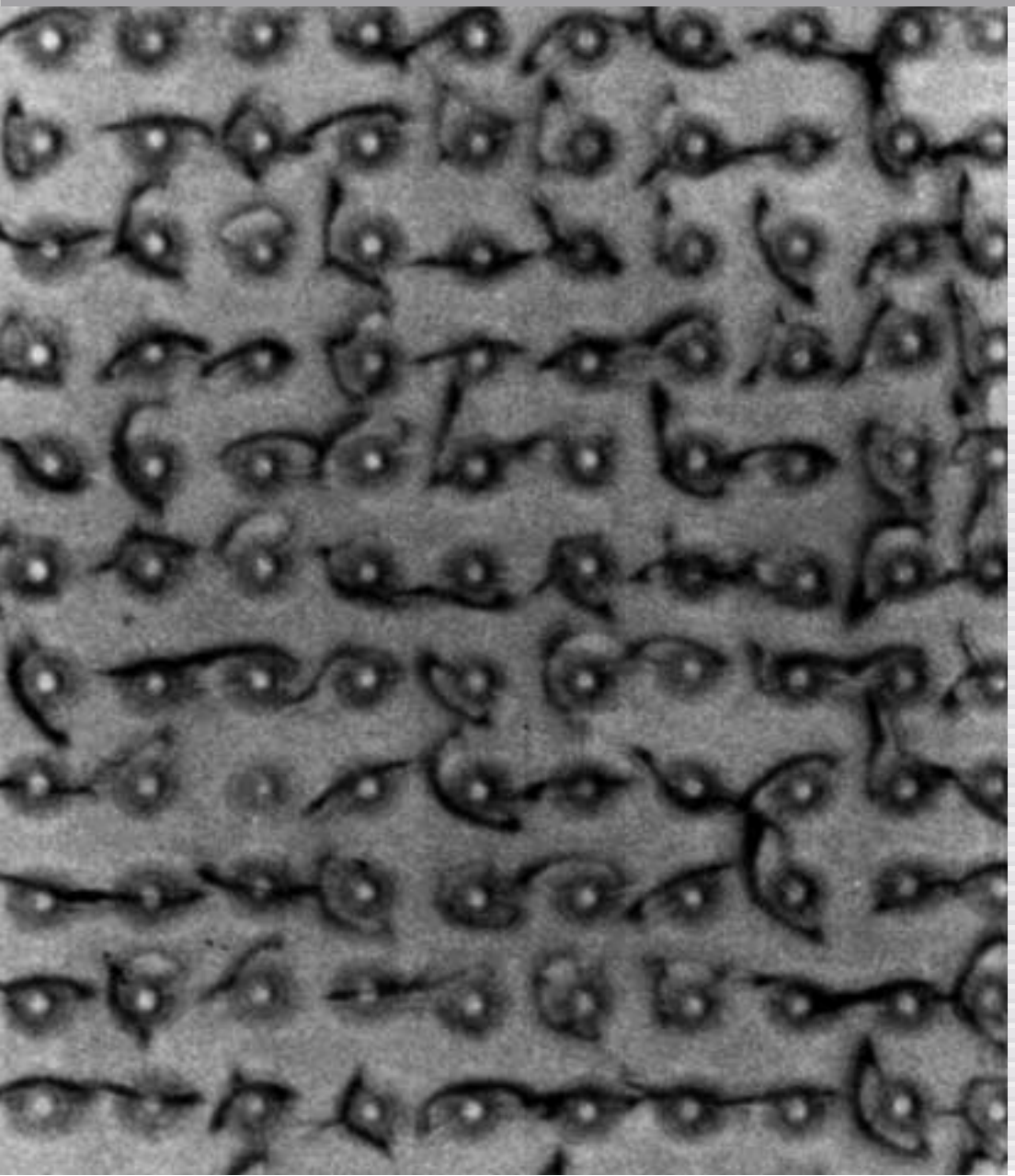
fused silica, 0.65 NA

0.5 μJ, 100 fs, 800 nm

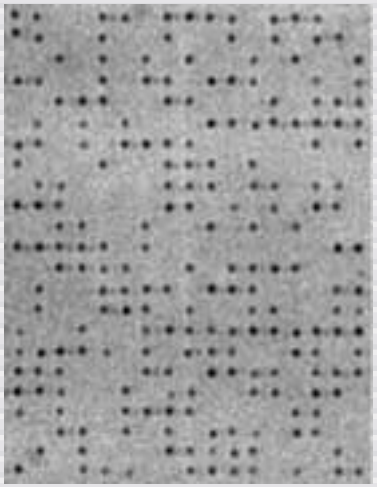


Opt. Lett. **21, 2023 (1996)**

Processing with fs pulses

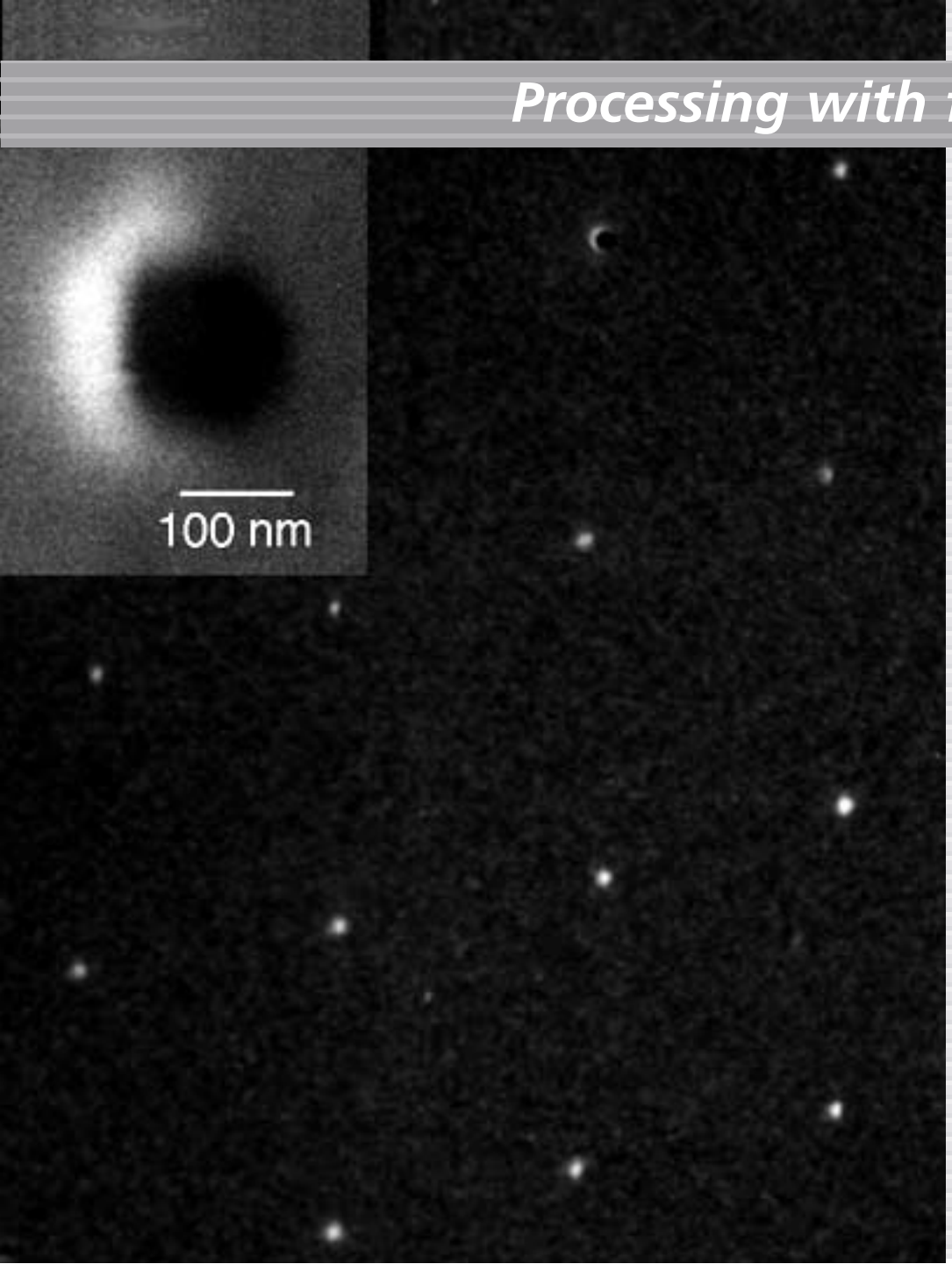


200 ps
9 µJ



100 fs
0.5 µJ

Processing with fs pulses



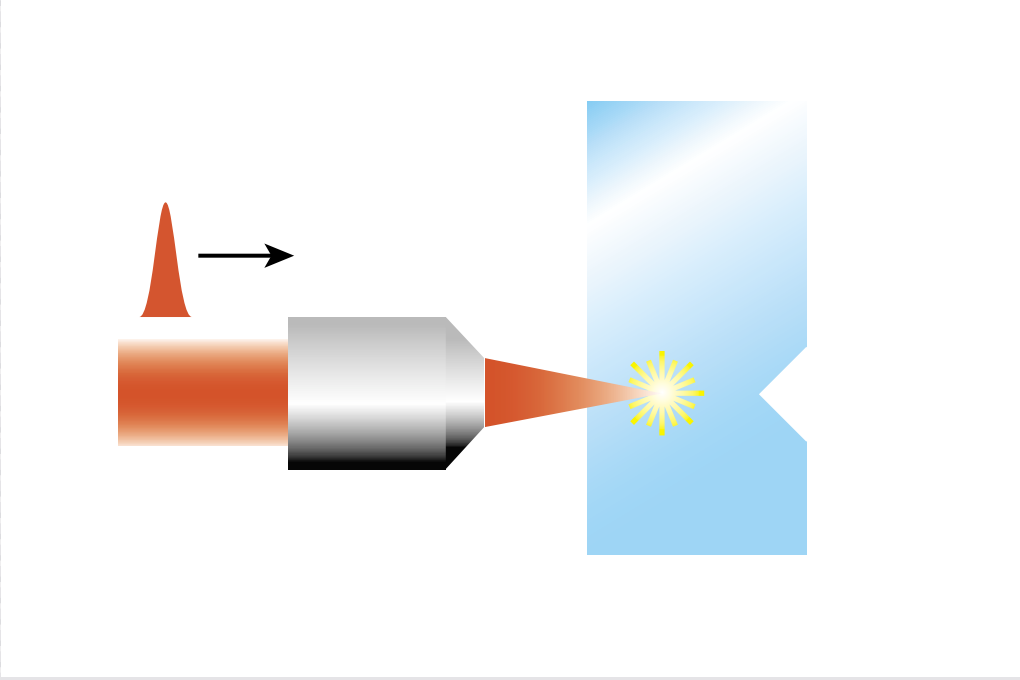
5 x 5 μm array

fused silica, 0.65 NA

0.5 μJ, 100 fs, 800 nm

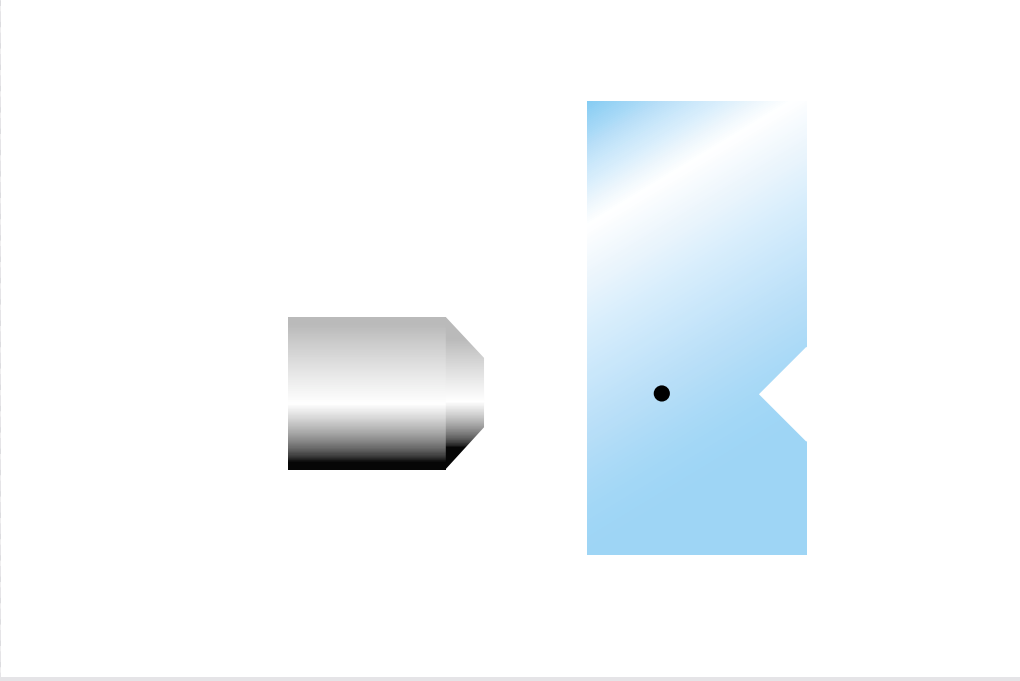
***Opt. Lett.* 21, 2023 (1996)**

Processing with fs pulses



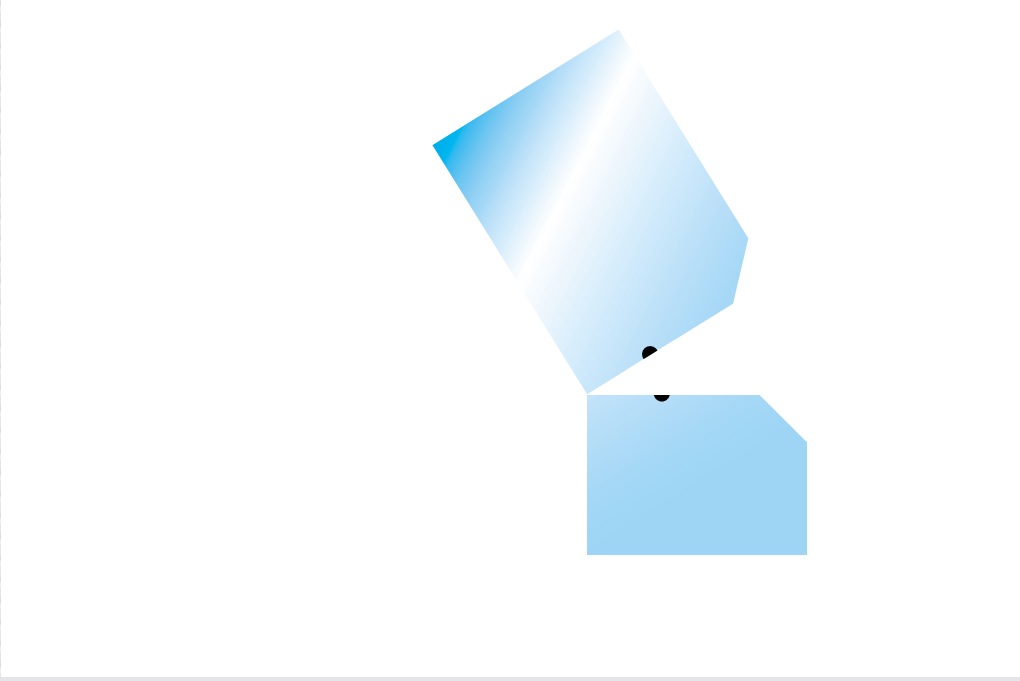
microstructure scribed sample

Processing with fs pulses



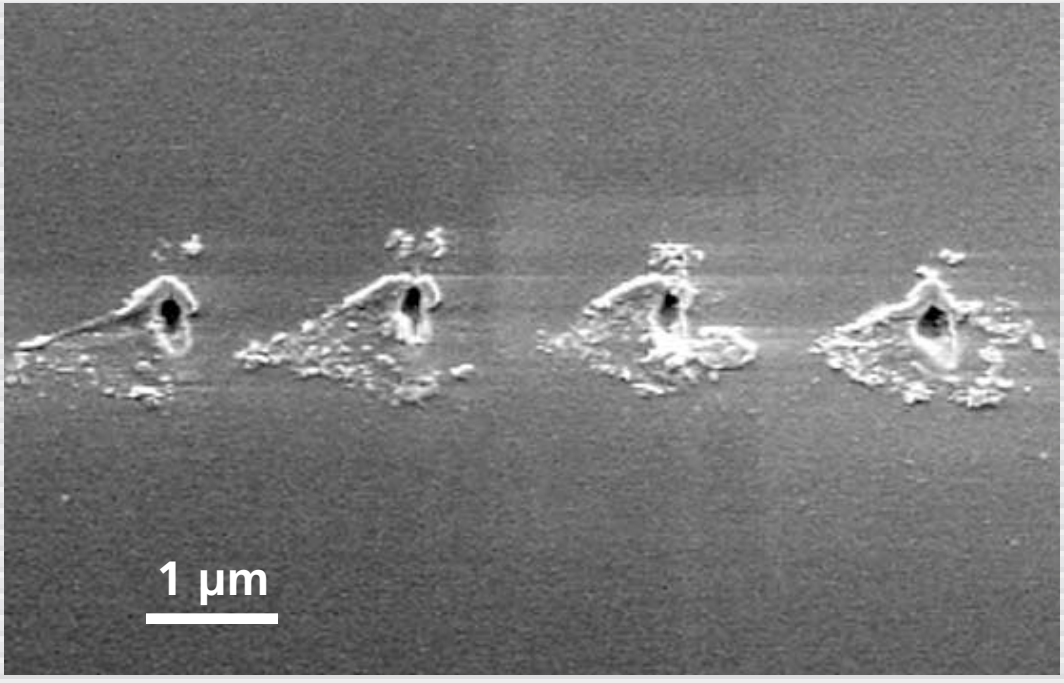
microstructure scribed sample

Processing with fs pulses



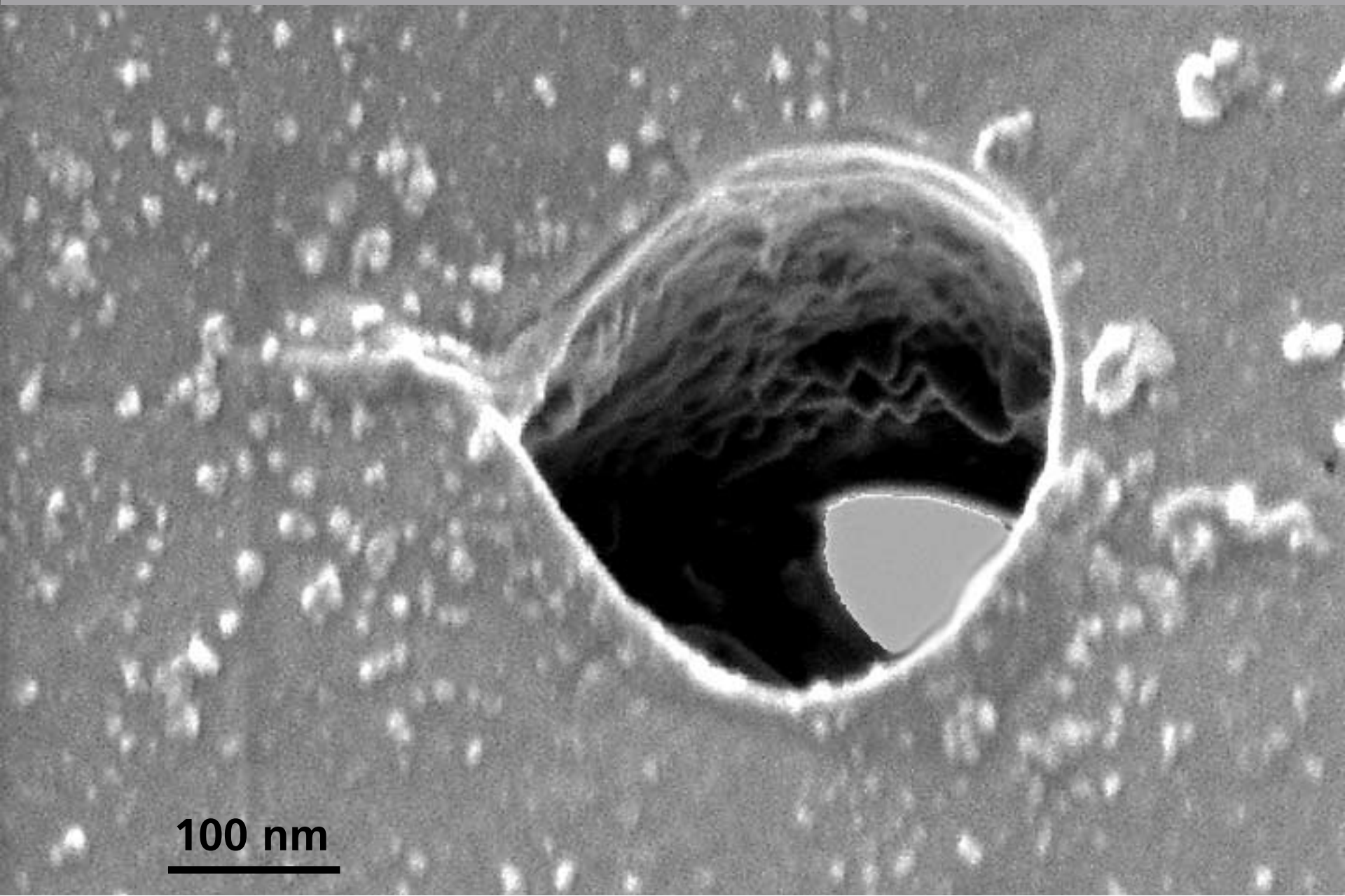
fracture along scribe line

Processing with fs pulses

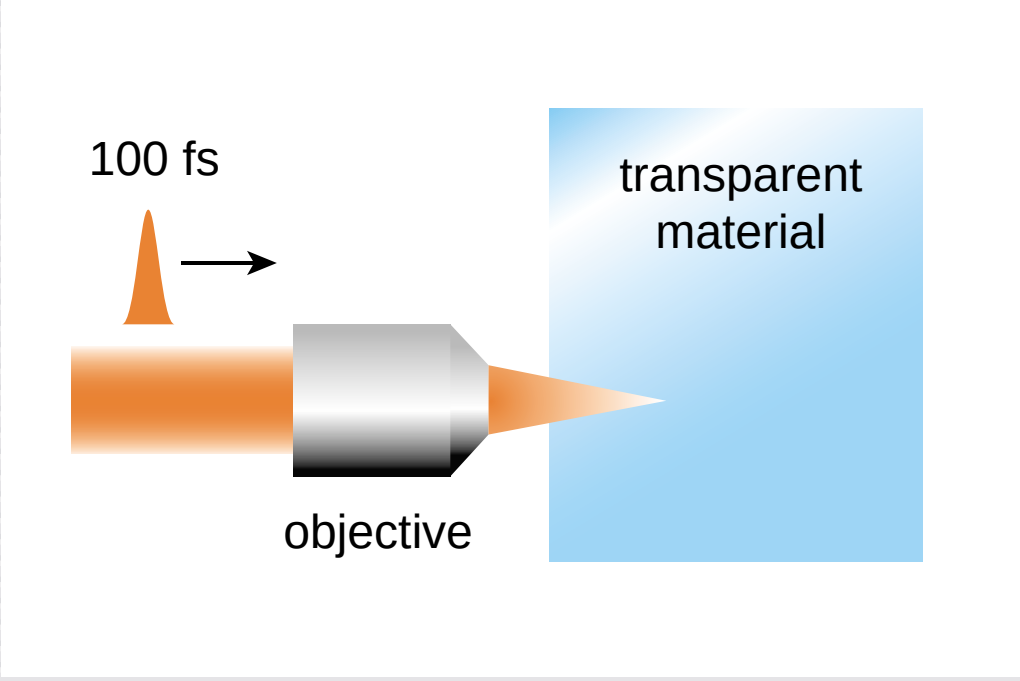


Corning 0211
1.4 NA, 140 nJ

Processing with fs pulses

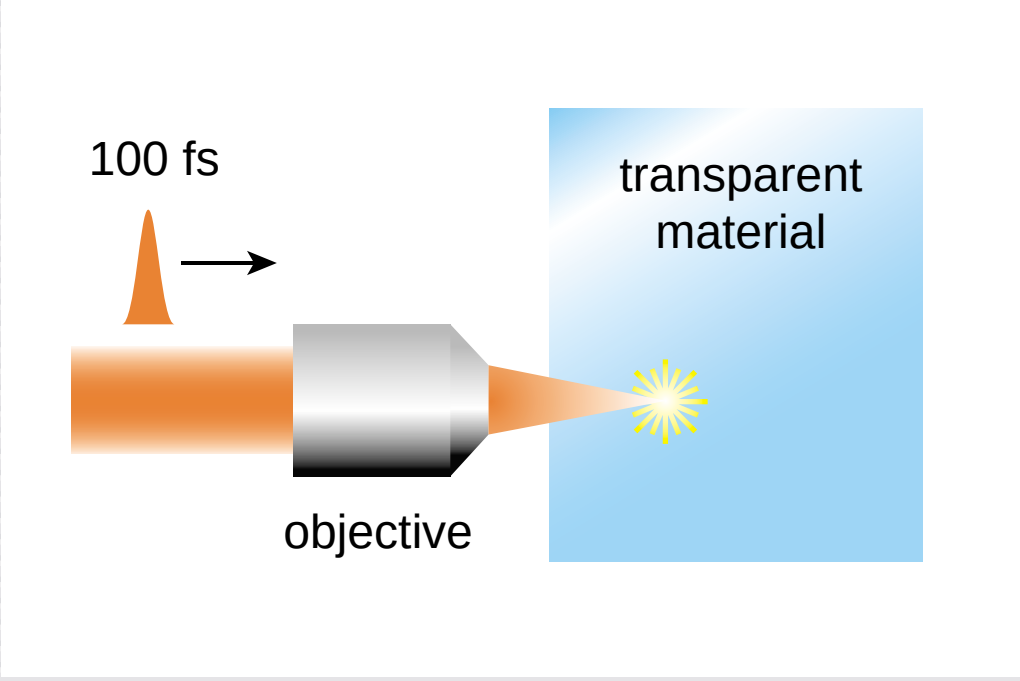


Processing with fs pulses



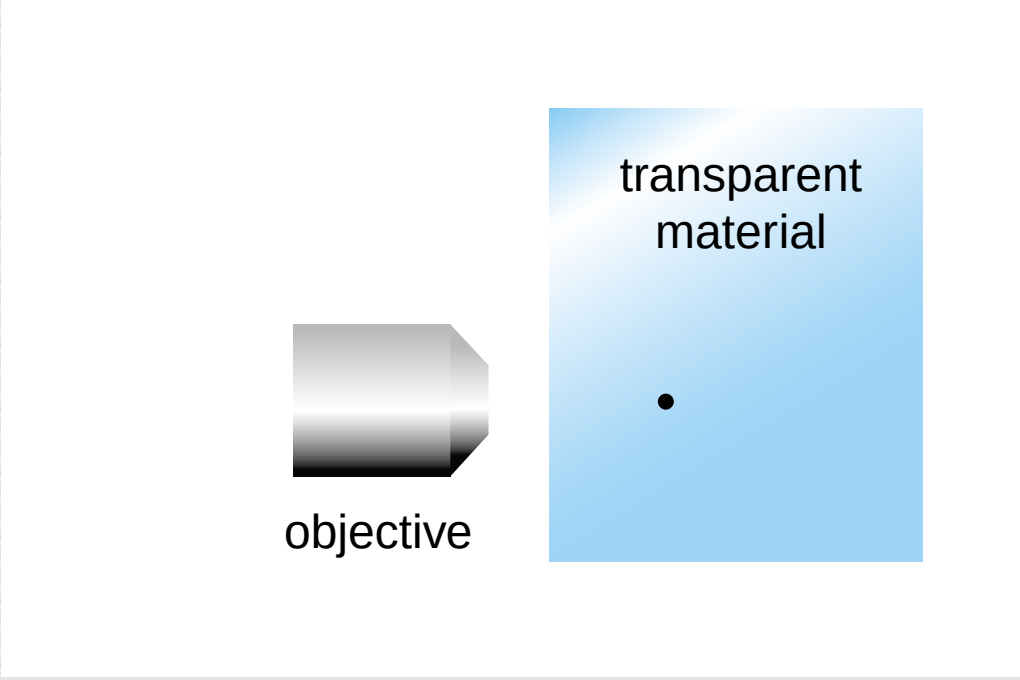
high intensity at focus…

Processing with fs pulses



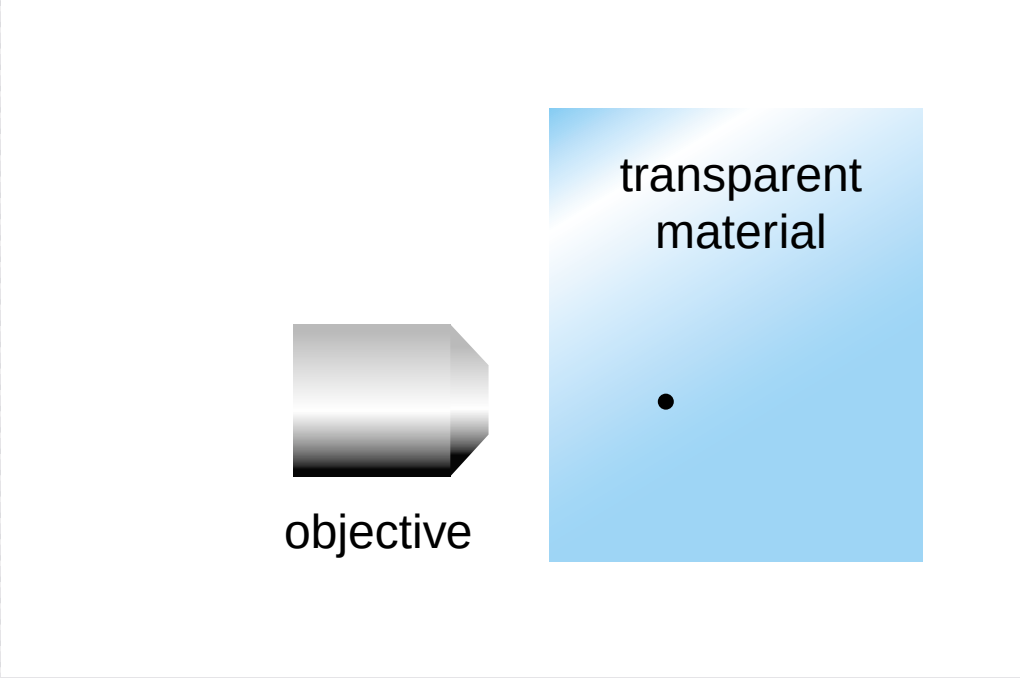
… causes nonlinear ionization…

Processing with fs pulses



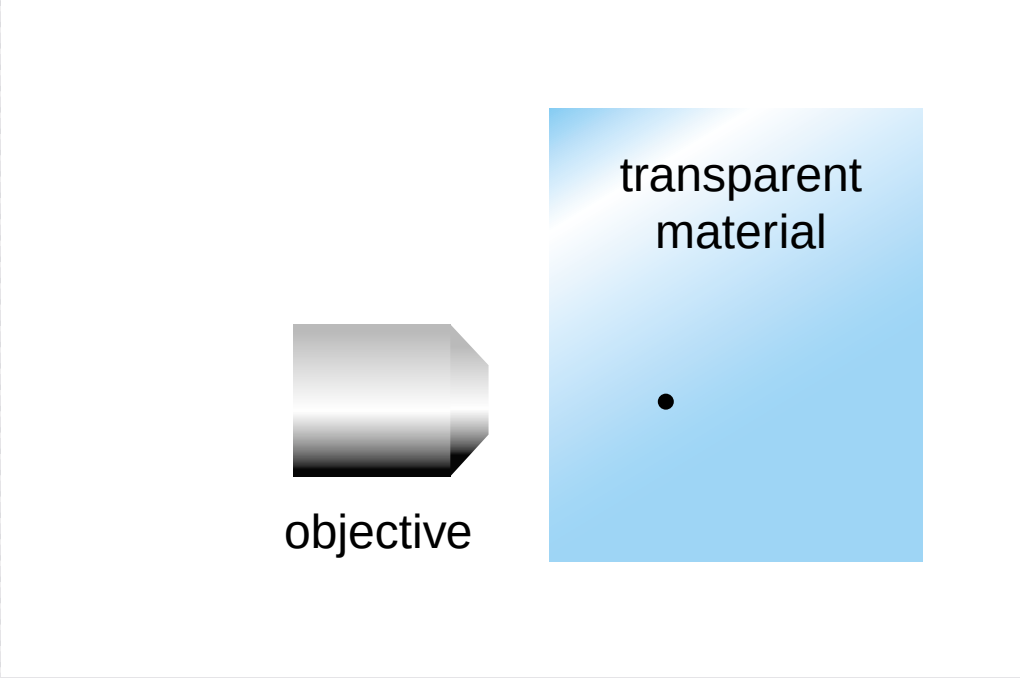
and ‘microexplosion’ causes microscopic damage

What are the conditions at focus?



Processing with fs pulses

What are the conditions at focus?



laser deposits energy in ~1 μm^3

Processing with fs pulses

What temperature?

Processing with fs pulses

What temperature?

$$\Delta E = C_V \rho V \Delta T$$

Processing with fs pulses

What temperature?

$$\Delta E = C_V \rho V \Delta T$$

$$C_V = 0.75 \times 10^3 \text{ J kg}^{-1} \text{K}^{-1}$$

$$\rho = 2.2 \times 10^3 \text{ kg/m}^3$$

Processing with fs pulses

What temperature?

$$\Delta E = C_V \rho V \Delta T$$

$$C_V = 0.75 \times 10^3 \ \mathrm{J\ kg^{-1}\ K^{-1}}$$

$$\rho = 2.2 \times 10^3 \ \mathrm{kg/m^3}$$

So, 1 μJ in 1 μm^3 gives

~1,000,000 K!

Processing with fs pulses

What pressure?

Processing with fs pulses

What pressure?

Treat ionized material as an ideal gas:

$$pV = nRT$$

Processing with fs pulses

What pressure?

Treat ionized material as an ideal gas:

$$pV = nRT$$

Gives

$$p = 10\,\mathrm{MBar}!$$

Processing with fs pulses

So:

	microexplosion
T	≈ 1 MK
p	≈ 10 MBar
ρ	2.2×10^3 kg/m^3

Processing with fs pulses

So:

	microexplosion	**sun**
T	≈ 1 MK	$2-5$ MK
p	≈ 10 MBar	
ρ	2.2×10^3 kg/m^3	$0.15-150 \times 10^3$ kg/m^3

Processing with fs pulses

So:

	microexplosion	**sun**
T	≈ 1 MK	$2-5$ MK
p	≈ 10 MBar	
ρ	2.2×10^3 kg/m^3	$0.15-150 \times 10^3$ kg/m^3

creating stellar conditions in lab!

Processing with fs pulses

Points to keep in mind:

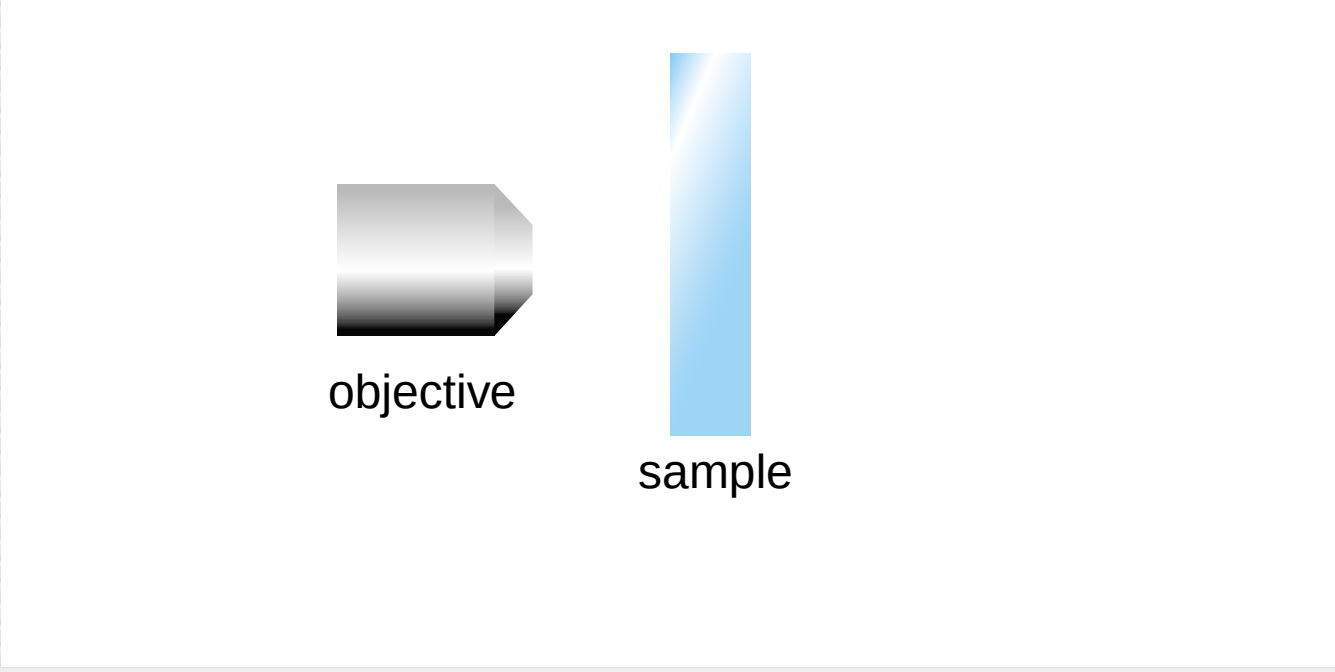
- **fs laser processing works**
- **focusing very important**
- **no collateral damage**

Outline

- Processing with fs pulses
- **Role of focusing**
- Low-energy processing

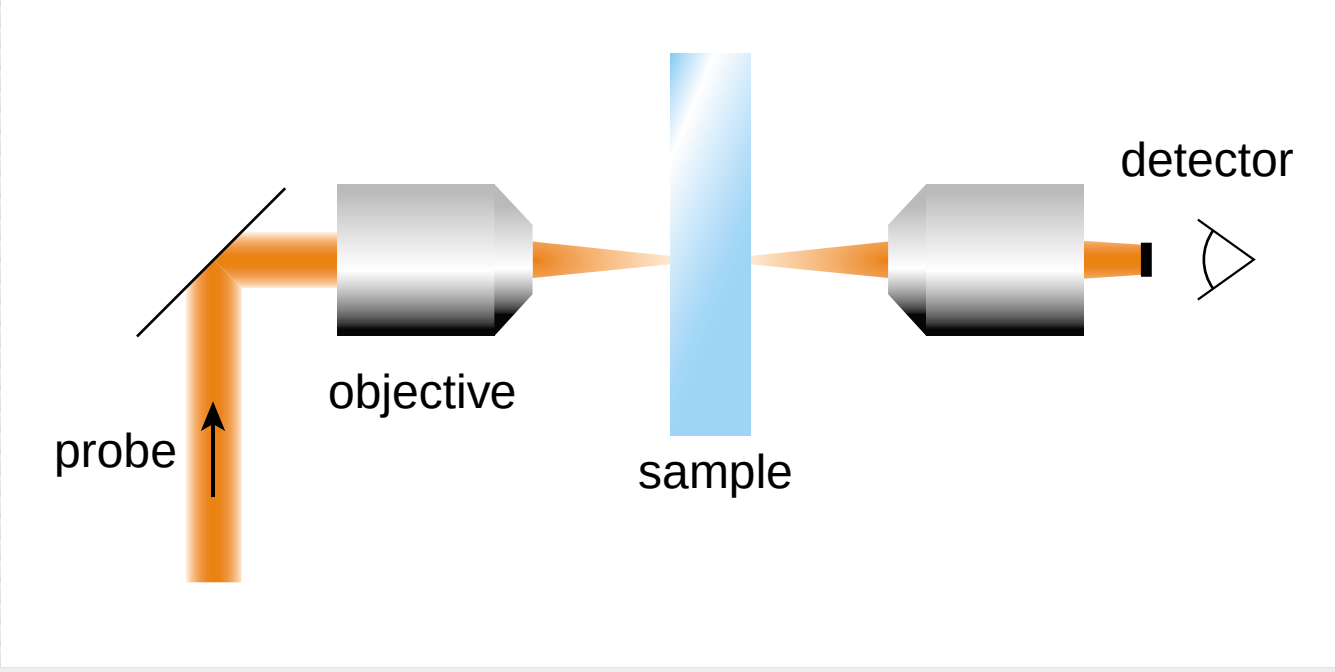
Role of focusing

Dark-field scattering



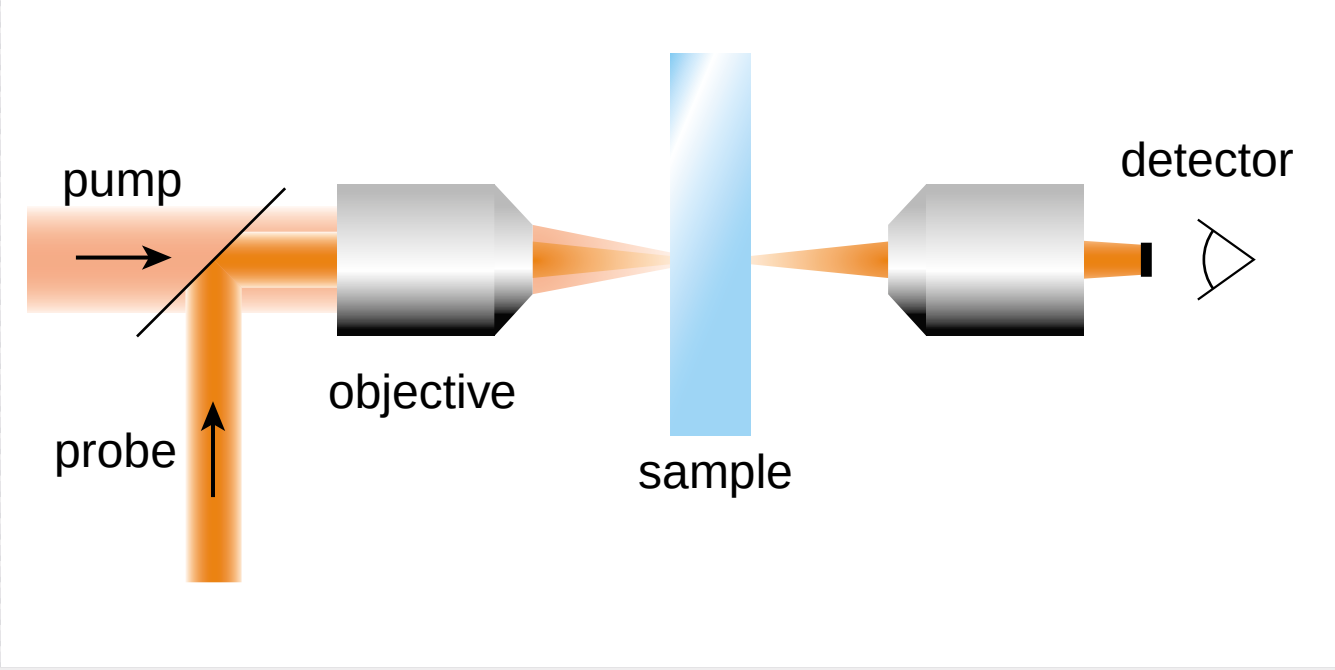
Role of focusing

block probe beam…



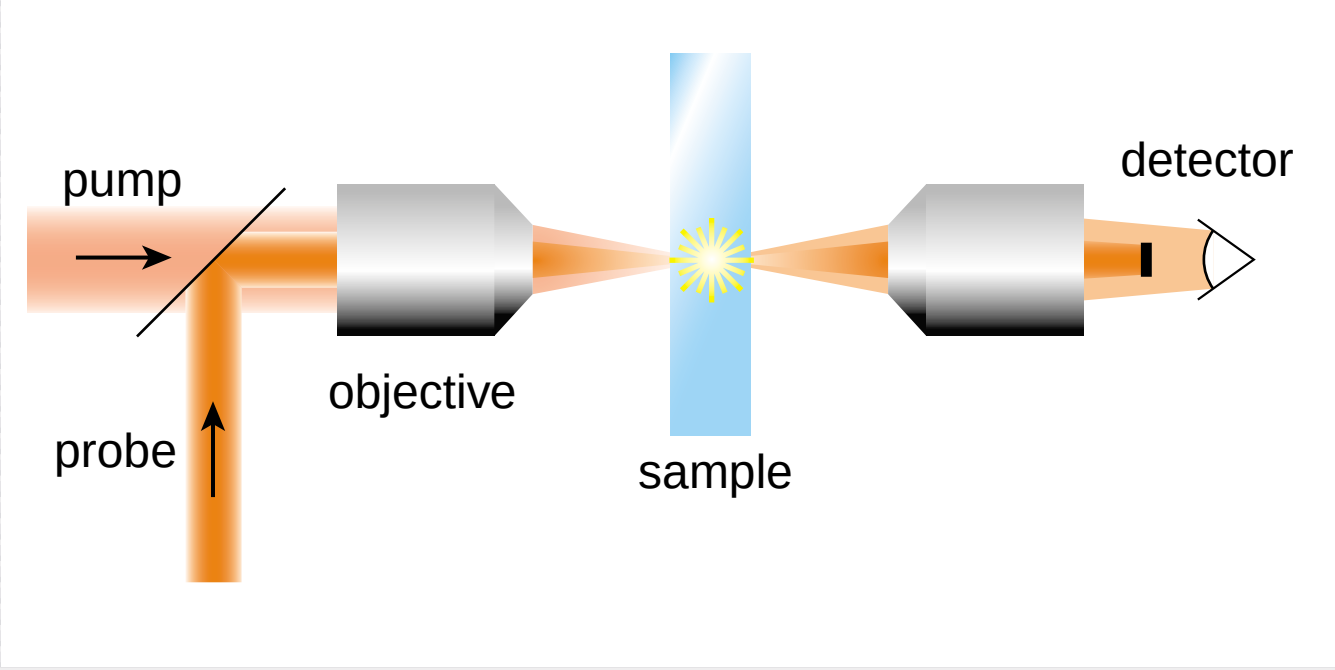
Role of focusing

… bring in pump beam…

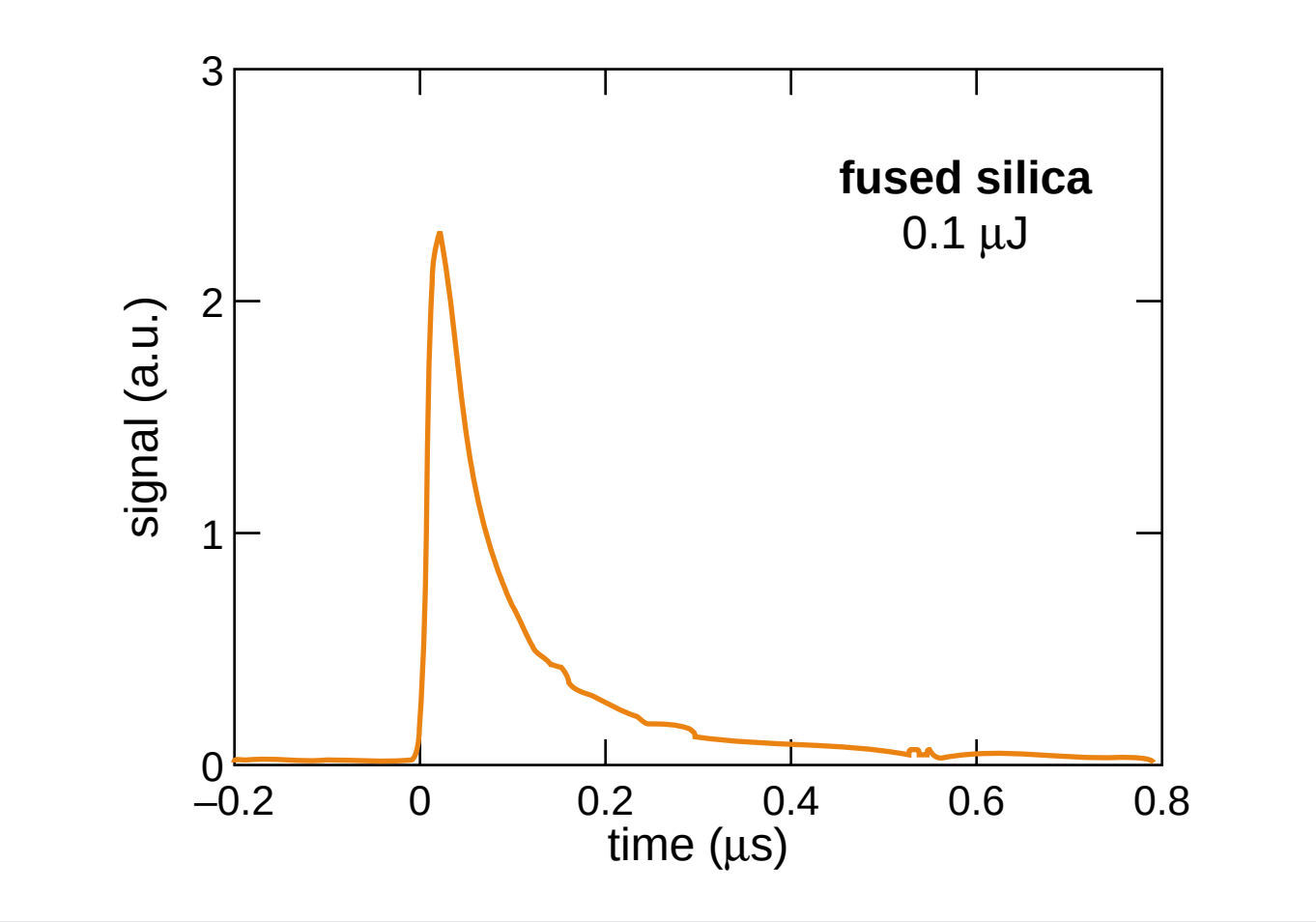


Role of focusing

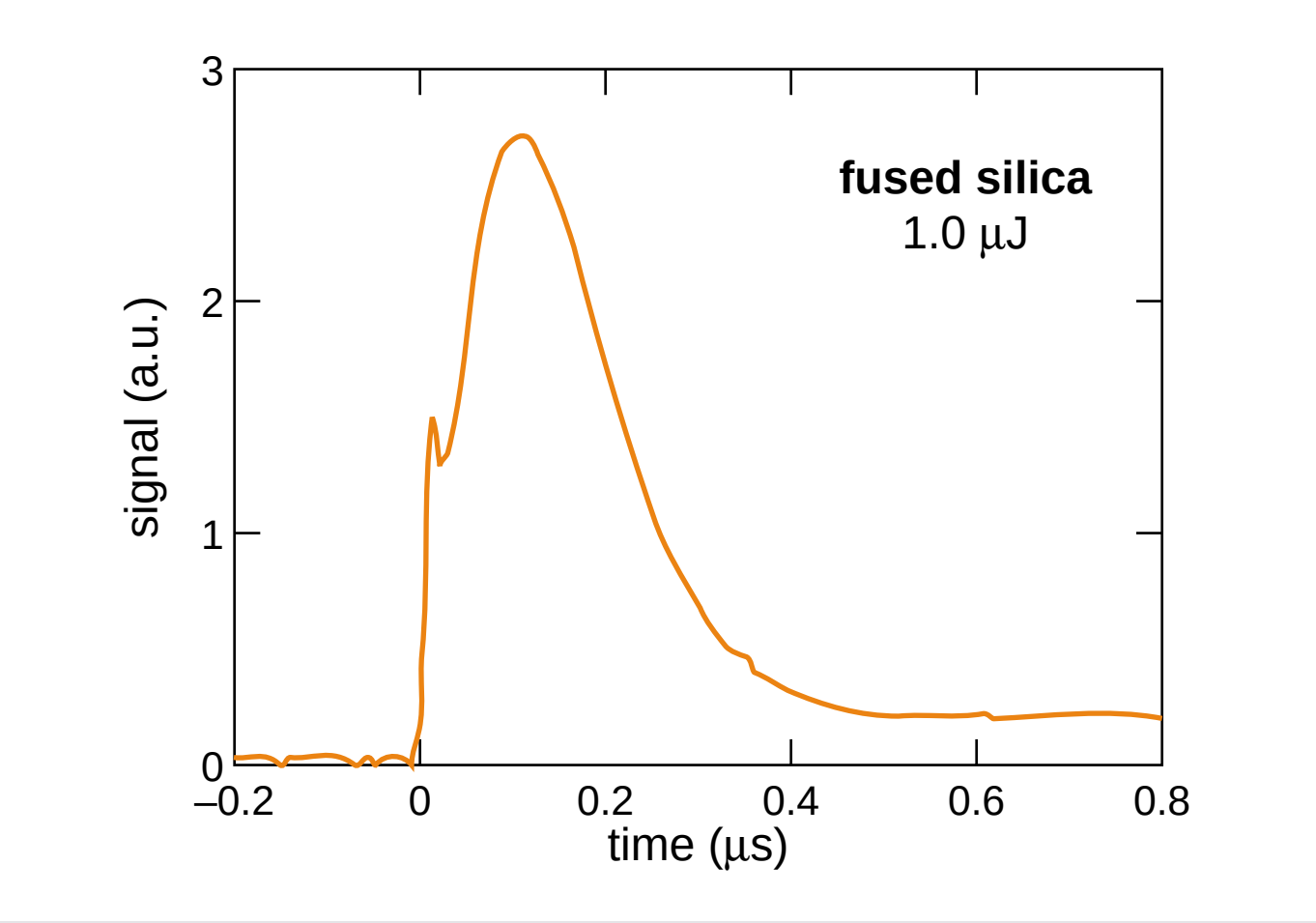
… damage scatters probe beam



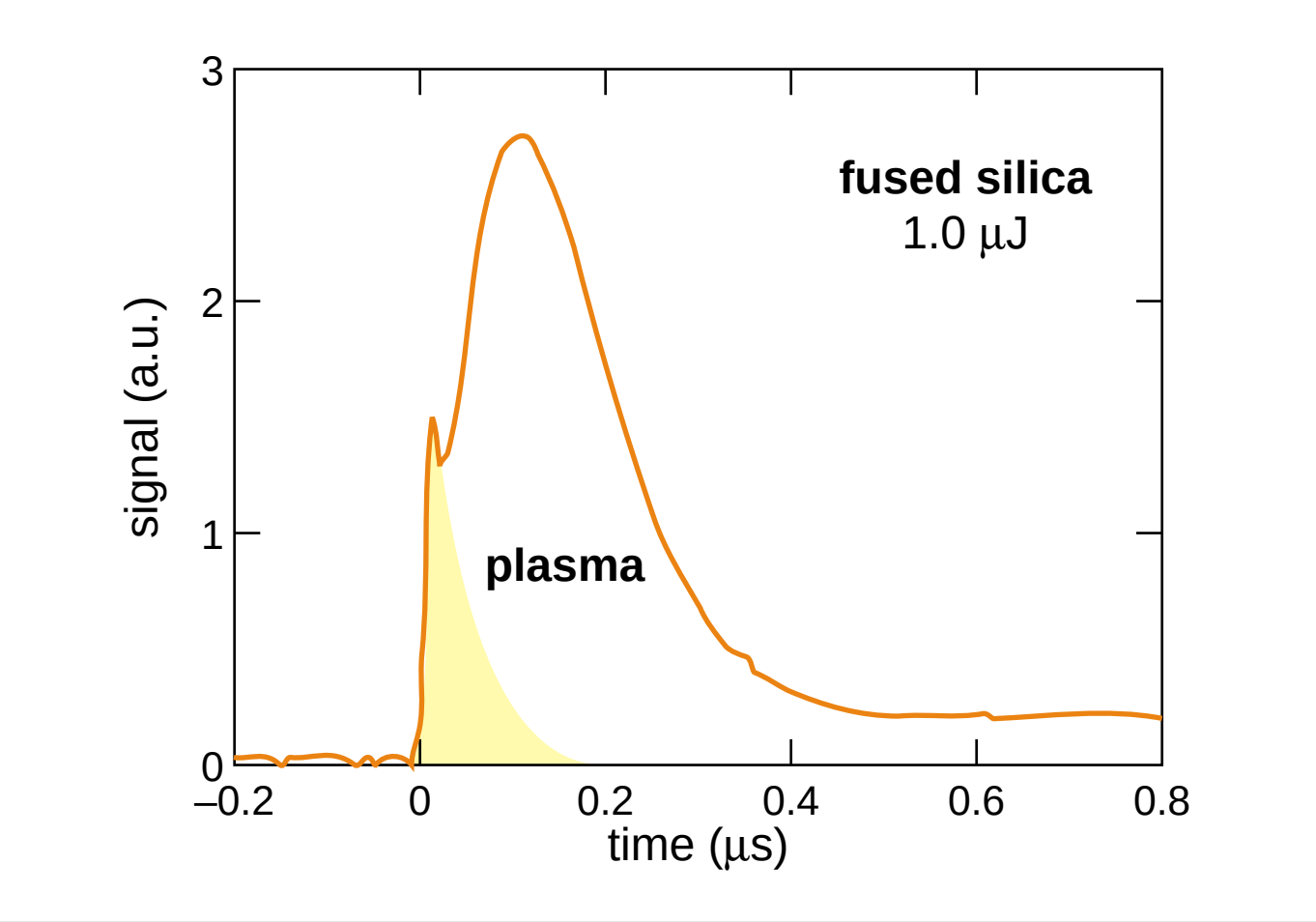
Role of focusing



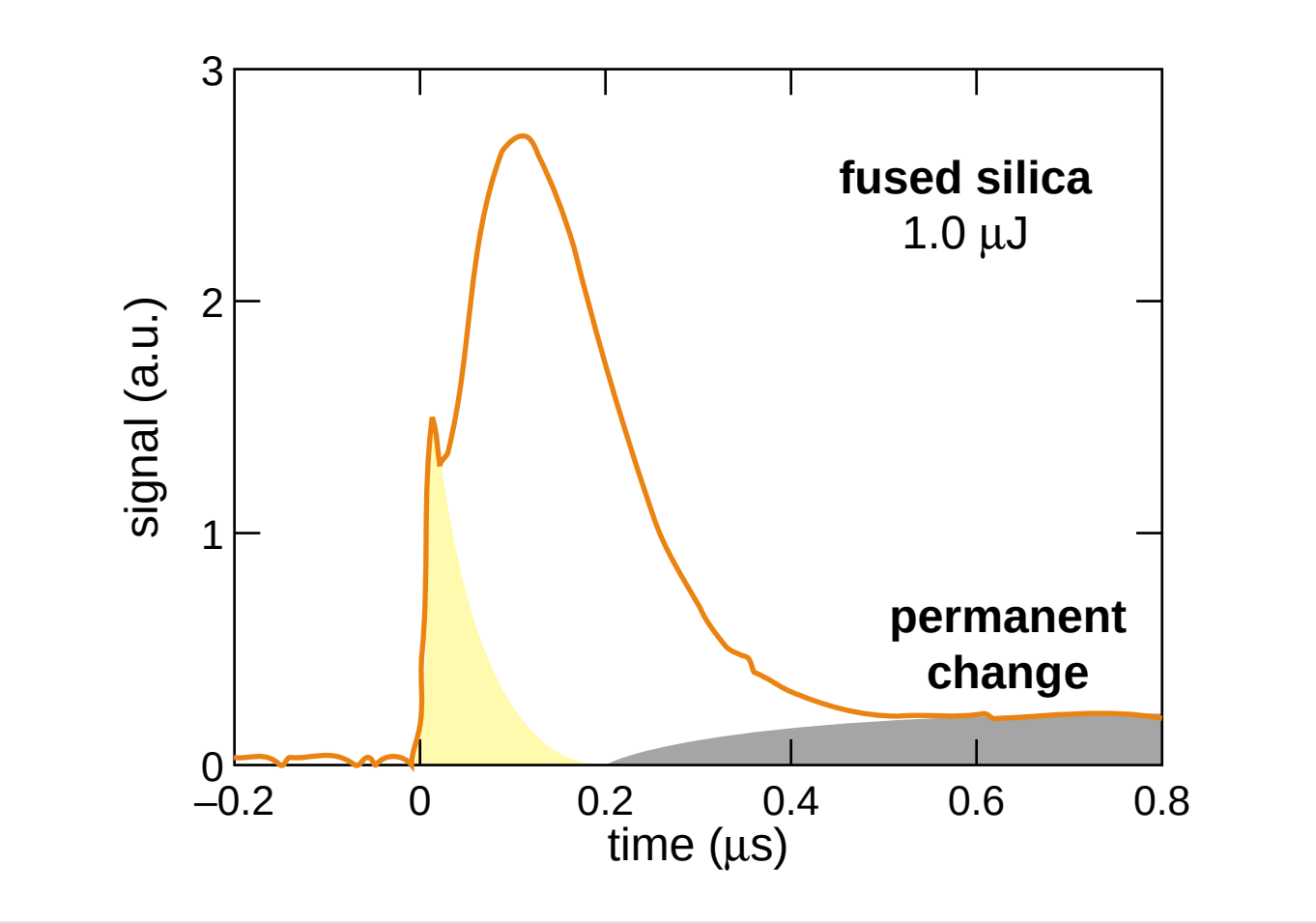
Role of focusing



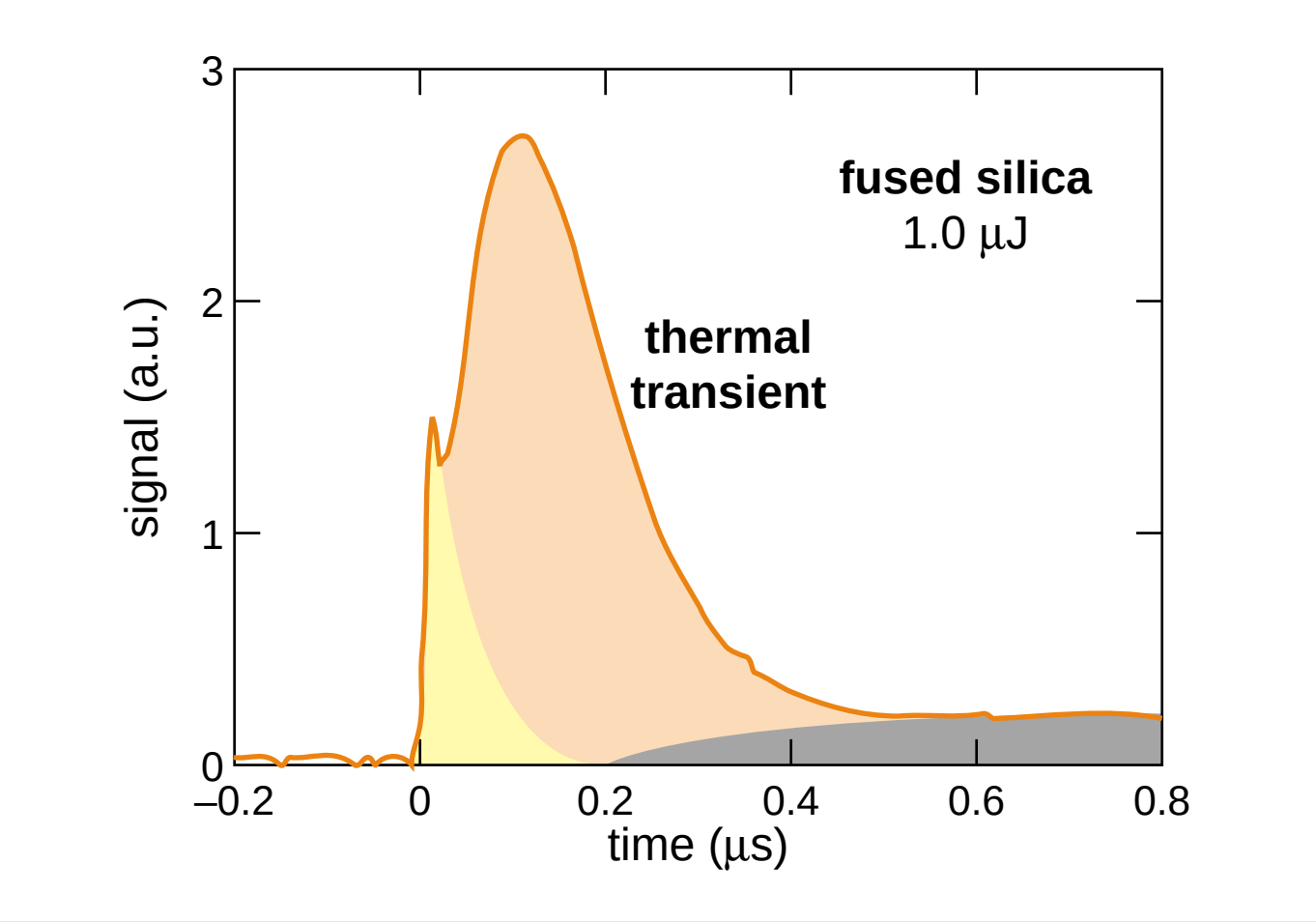
Role of focusing



Role of focusing

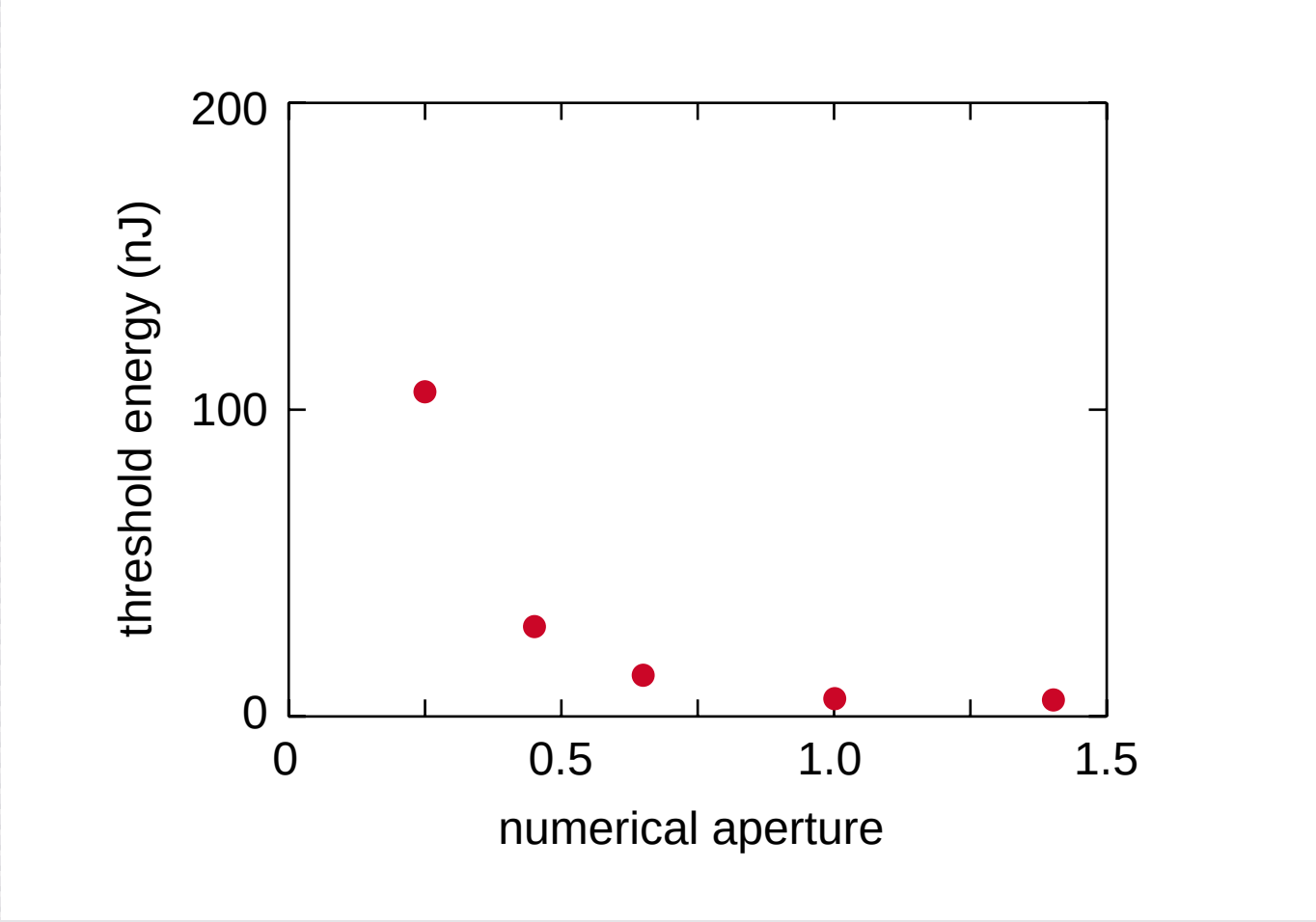


Role of focusing

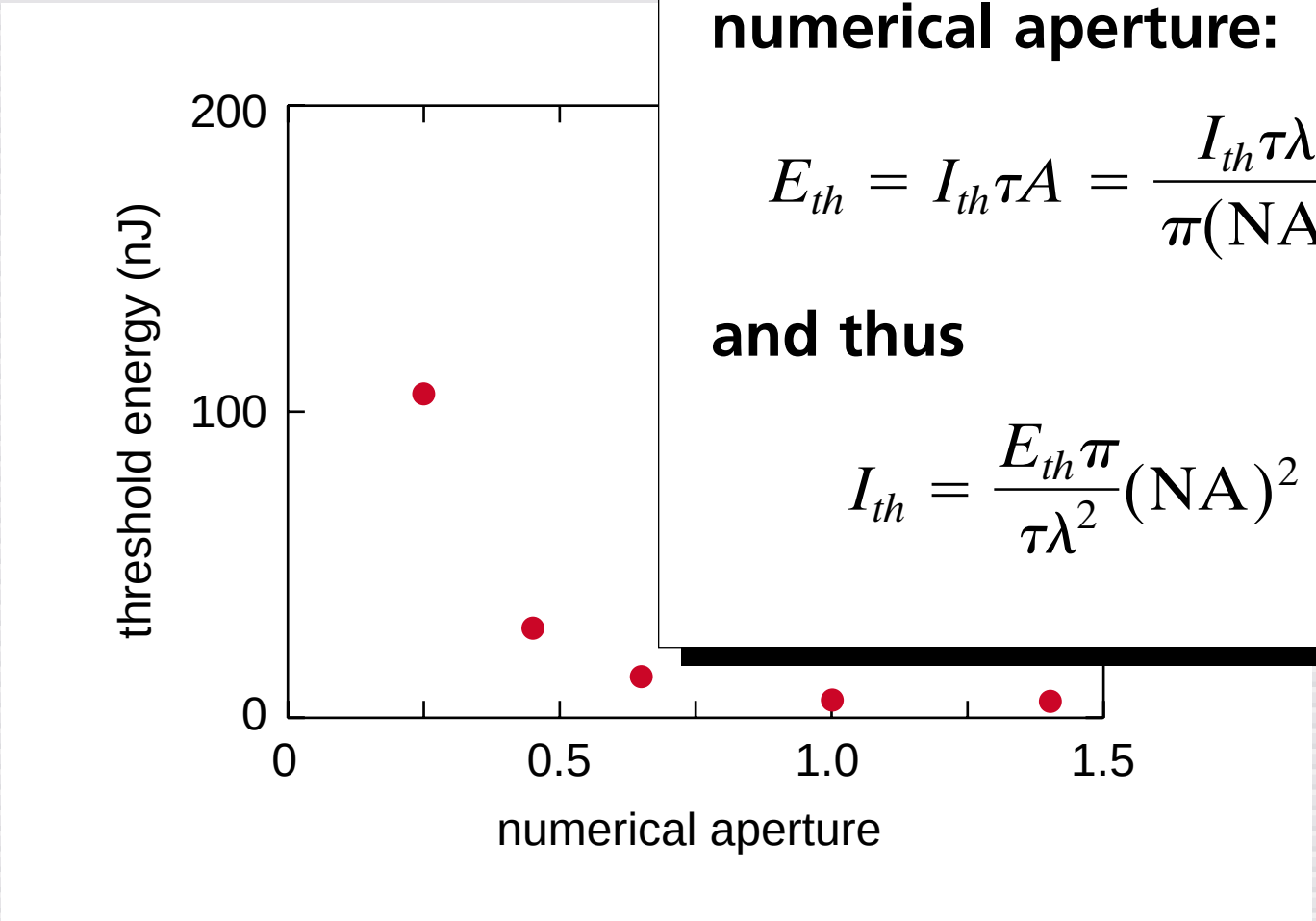


Role of focusing

vary numerical aperture in Corning 0211



Role of focusing



spot size determined by numerical aperture:

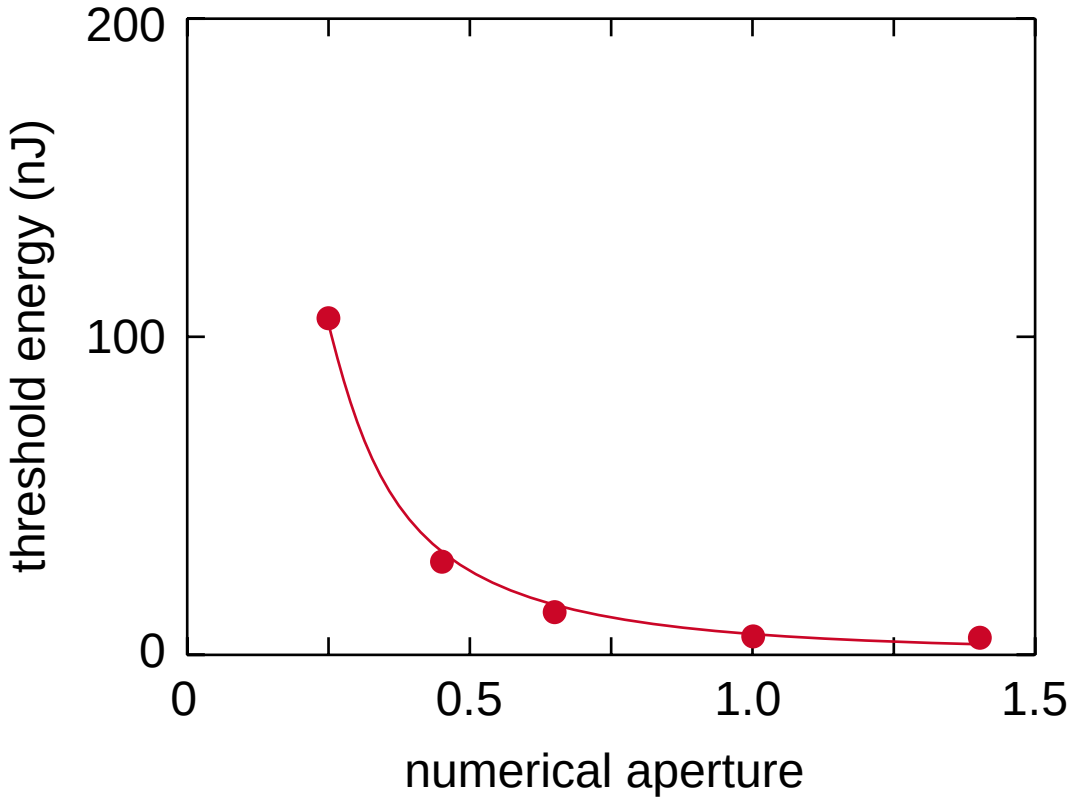
$$E_{th} = I_{th}\tau A = \frac{I_{th}\tau\lambda^2}{\pi(\mathrm{NA})^2}$$

and thus

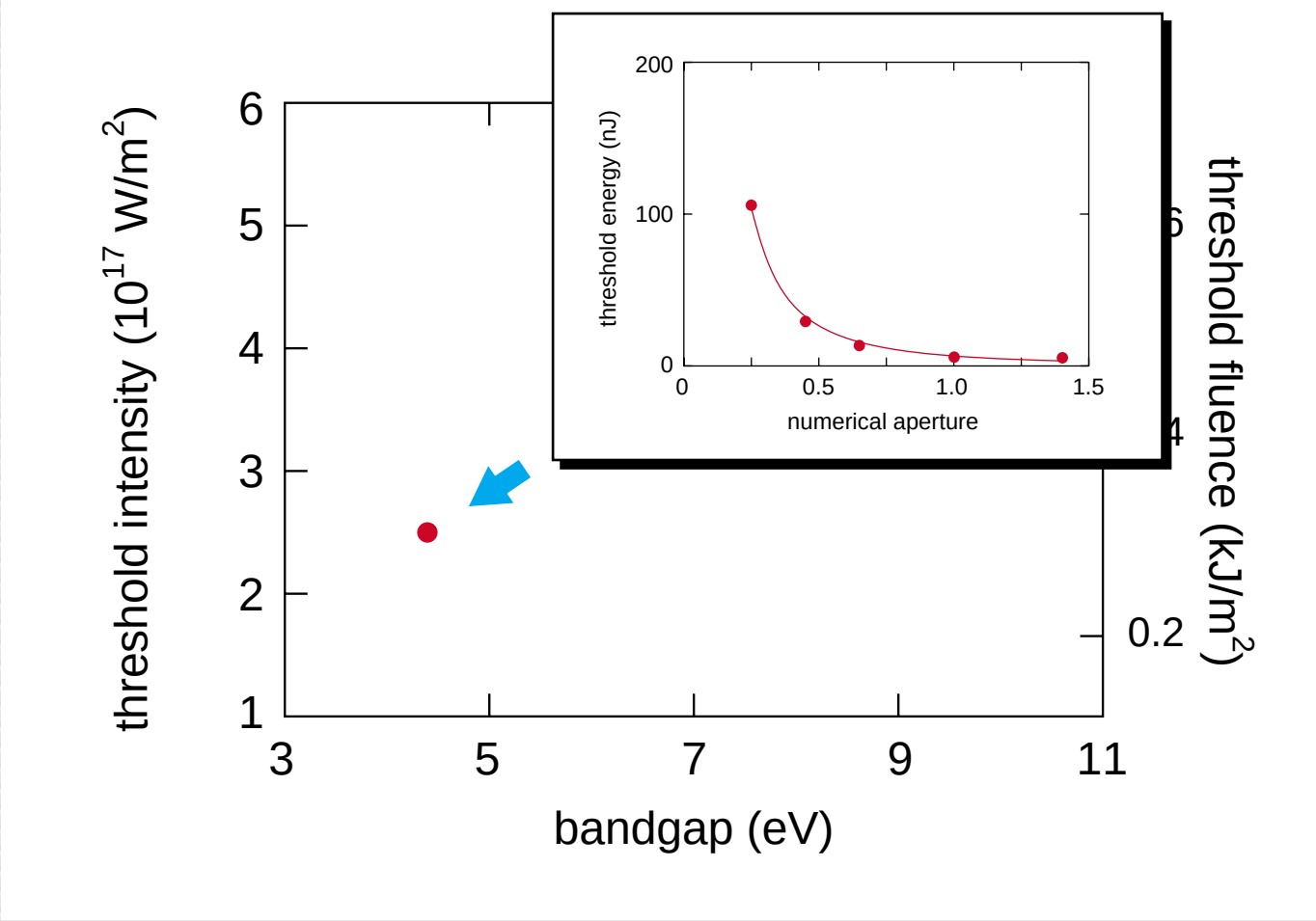
$$I_{th} = \frac{E_{th}\pi}{\tau\lambda^2}(\mathrm{NA})^2$$

Role of focusing

fit gives threshold intensity: I_{th} = 2.5 x 10^{17} W/m^2

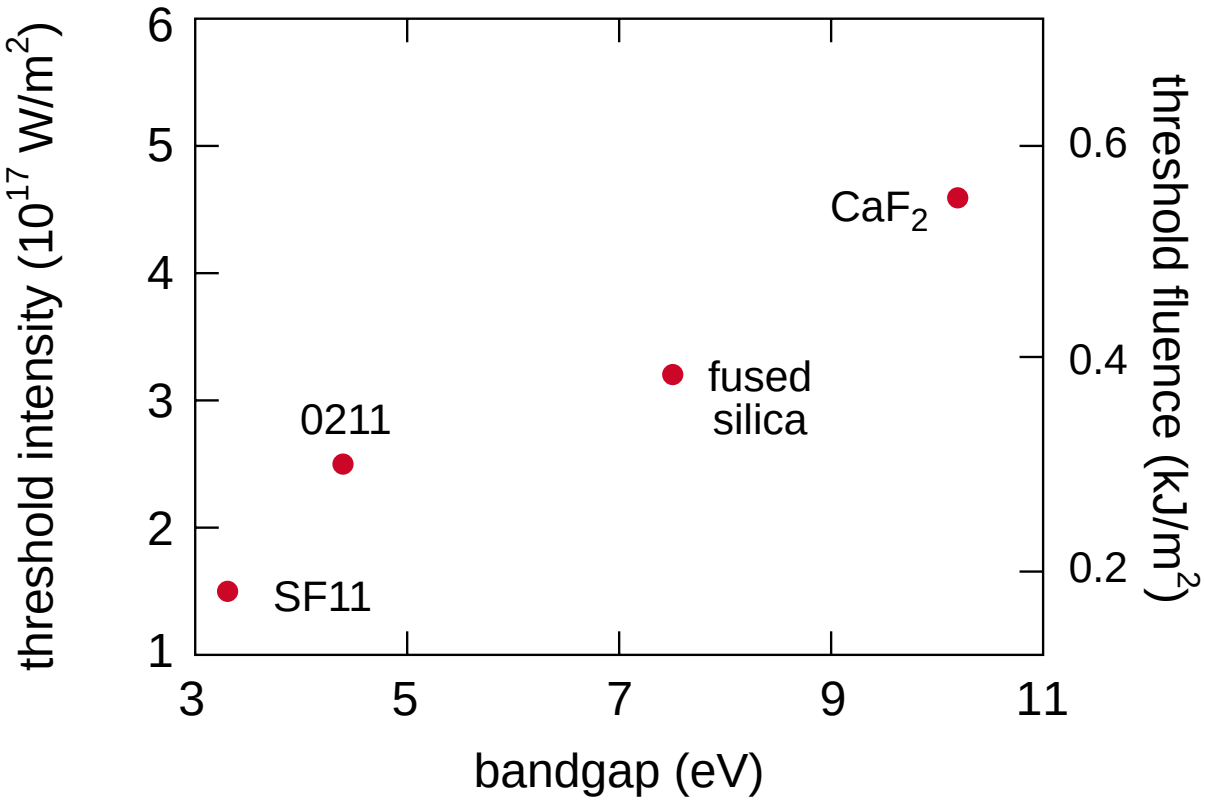


Role of focusing



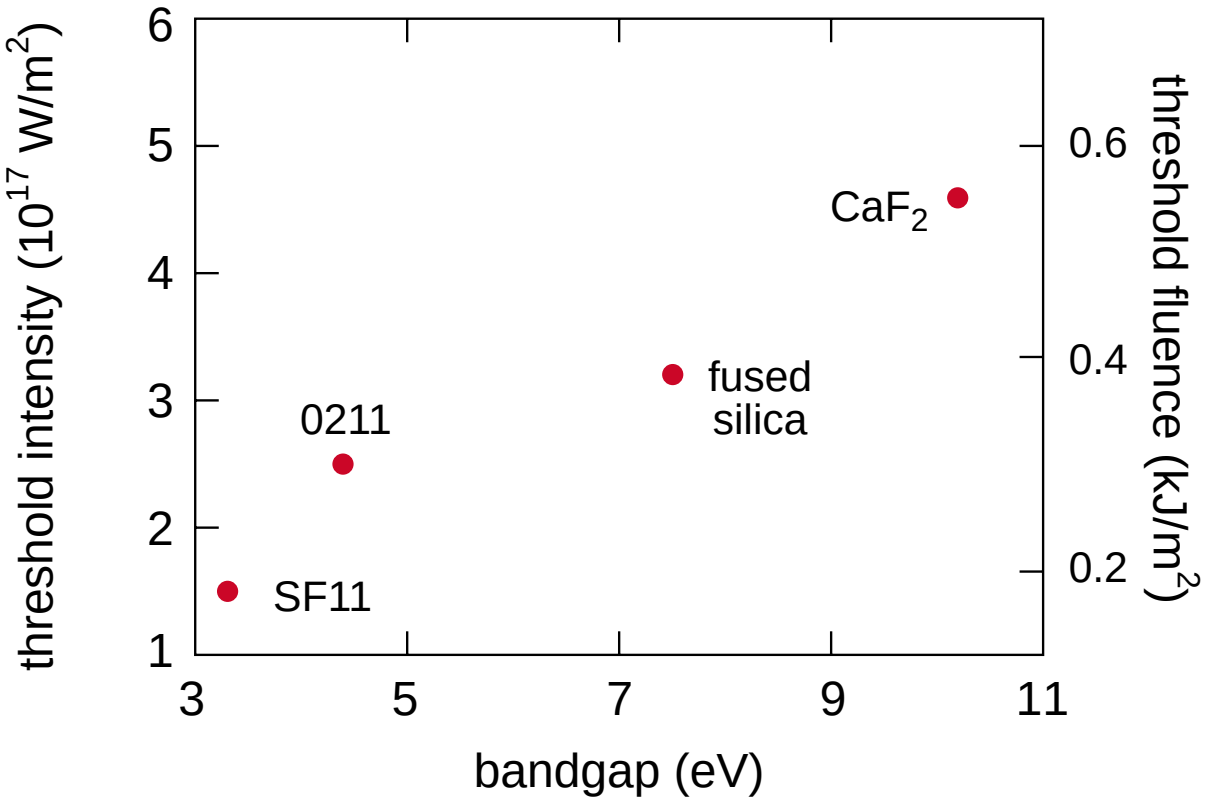
Role of focusing

vary material…



Role of focusing

threshold varies with bandgap



Role of focusing

Points to keep in mind:

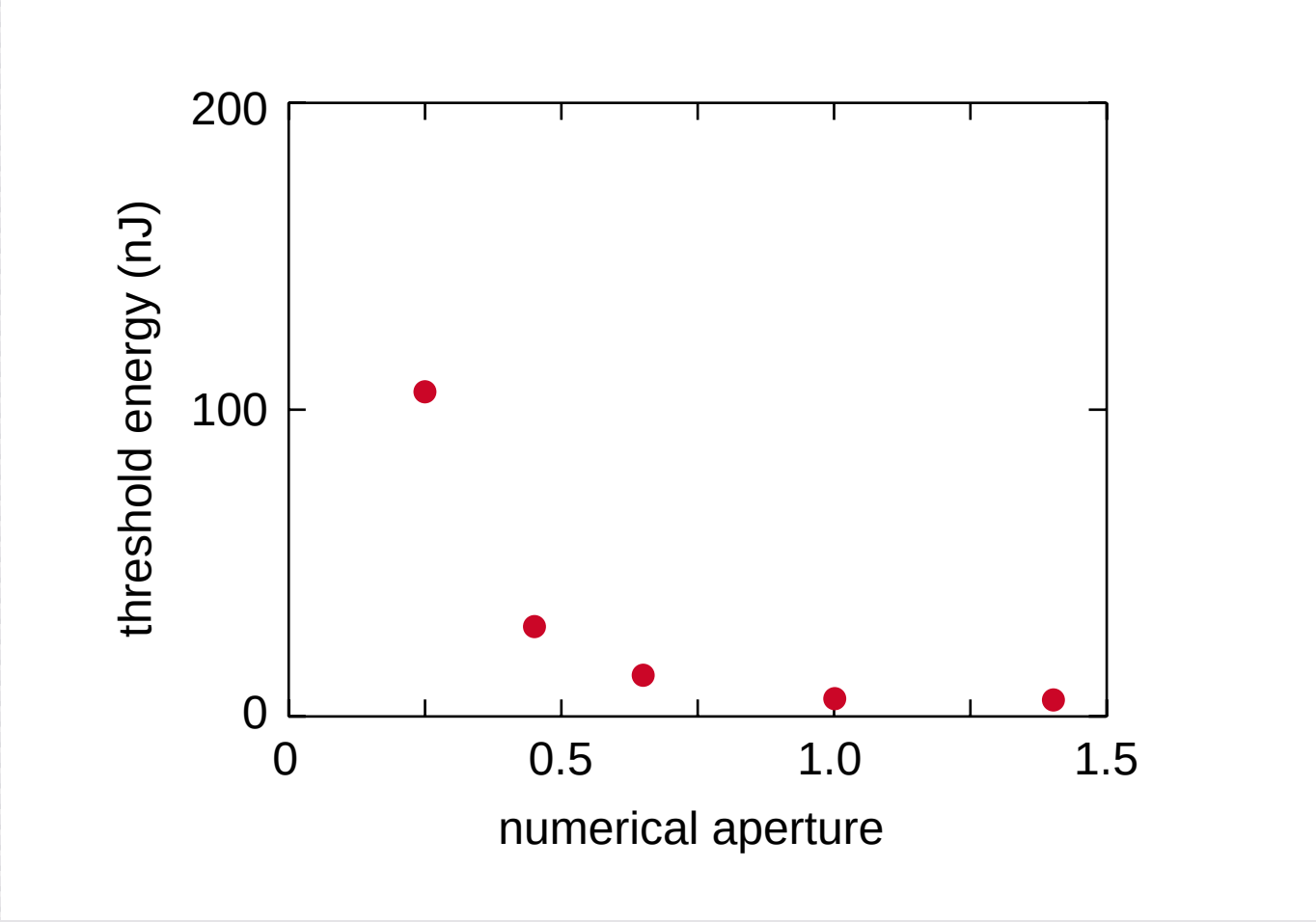
- **threshold critically dependent of NA**
- **surprisingly little material dependence**
- **avalanche ionization important**

Outline

- Processing with fs pulses
- Role of focusing
- **Low-energy processing**

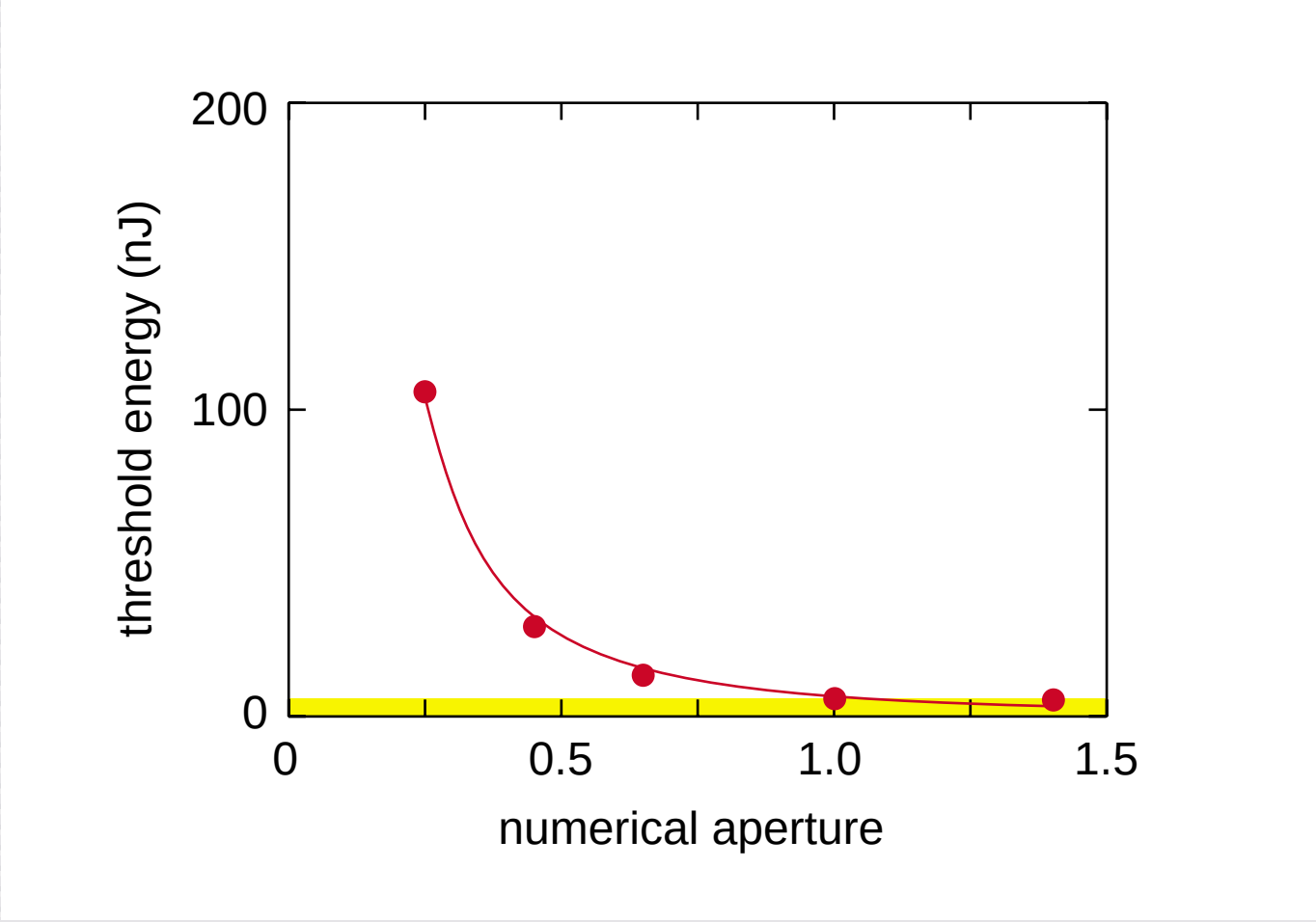
Low-energy processing

threshold decreases with increasing numerical aperture



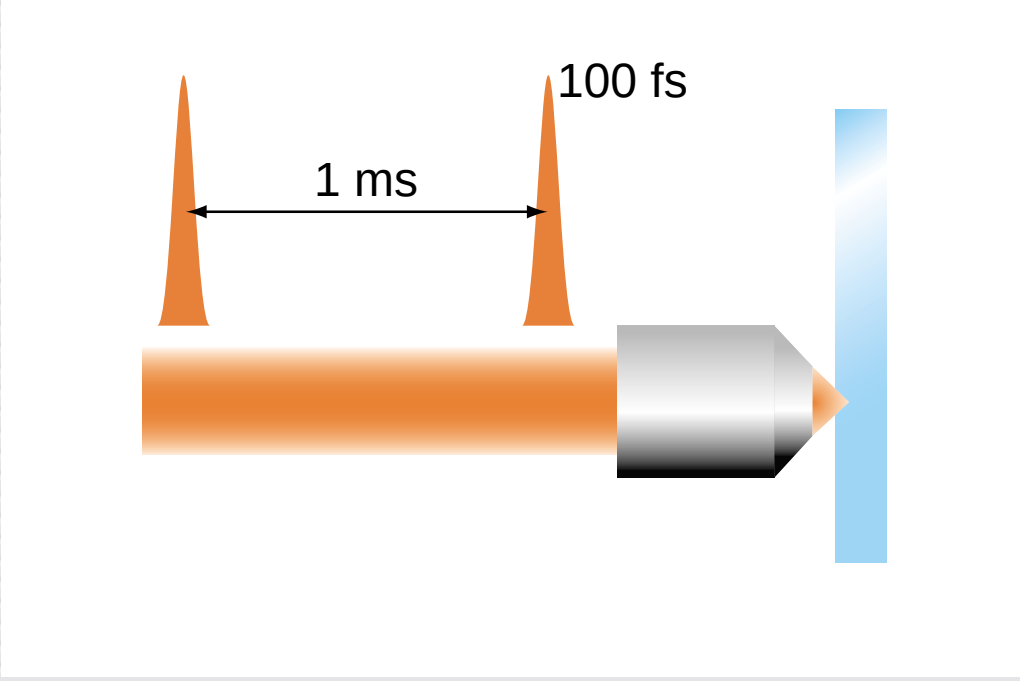
Low-energy processing

less than 10 nJ at high numerical aperture!



Low-energy processing

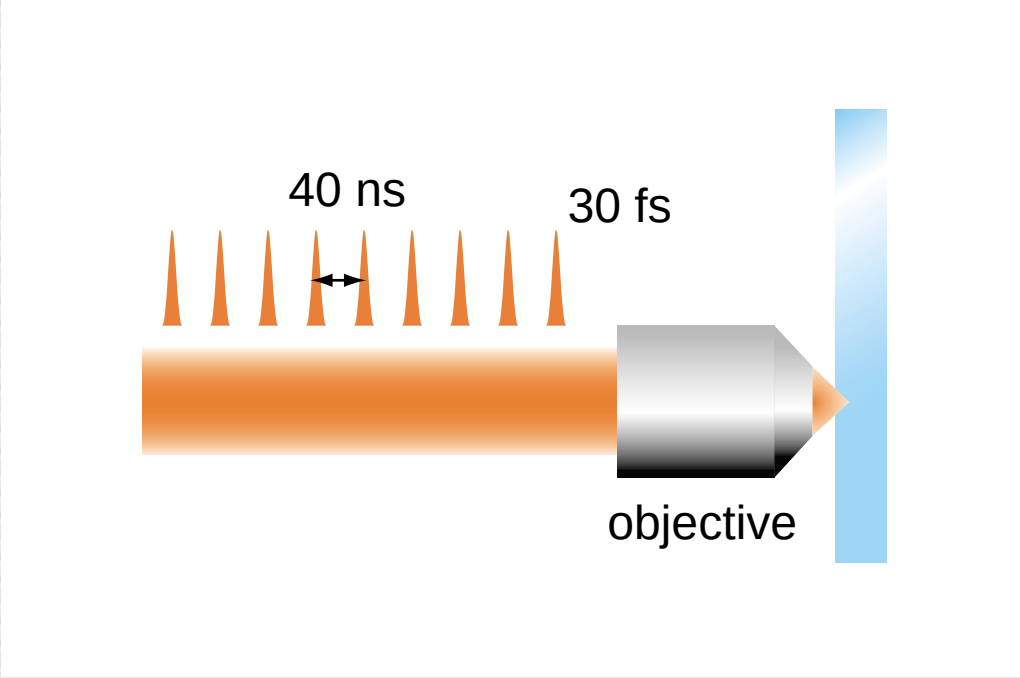
amplified laser



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

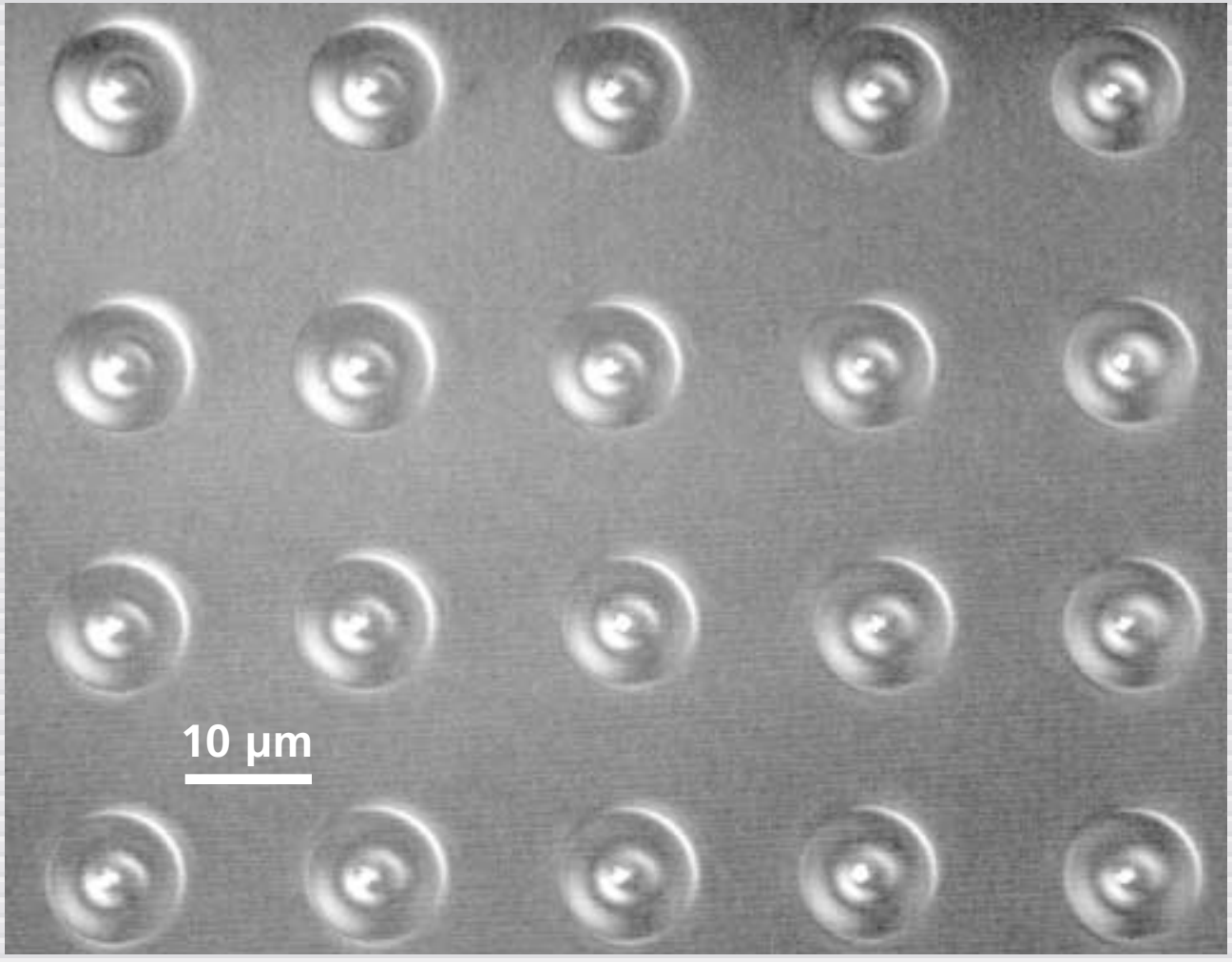
Low-energy processing

long-cavity Ti:sapphire oscillator

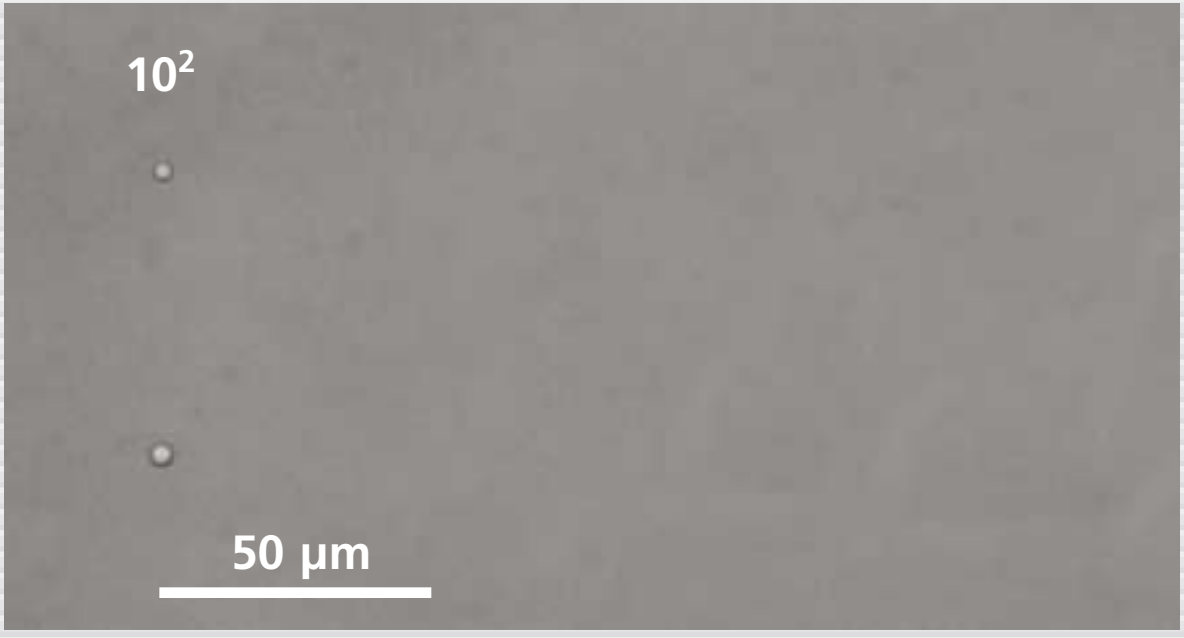


heat-diffusion time: $\tau_{diff} \approx 1\ \mu s$

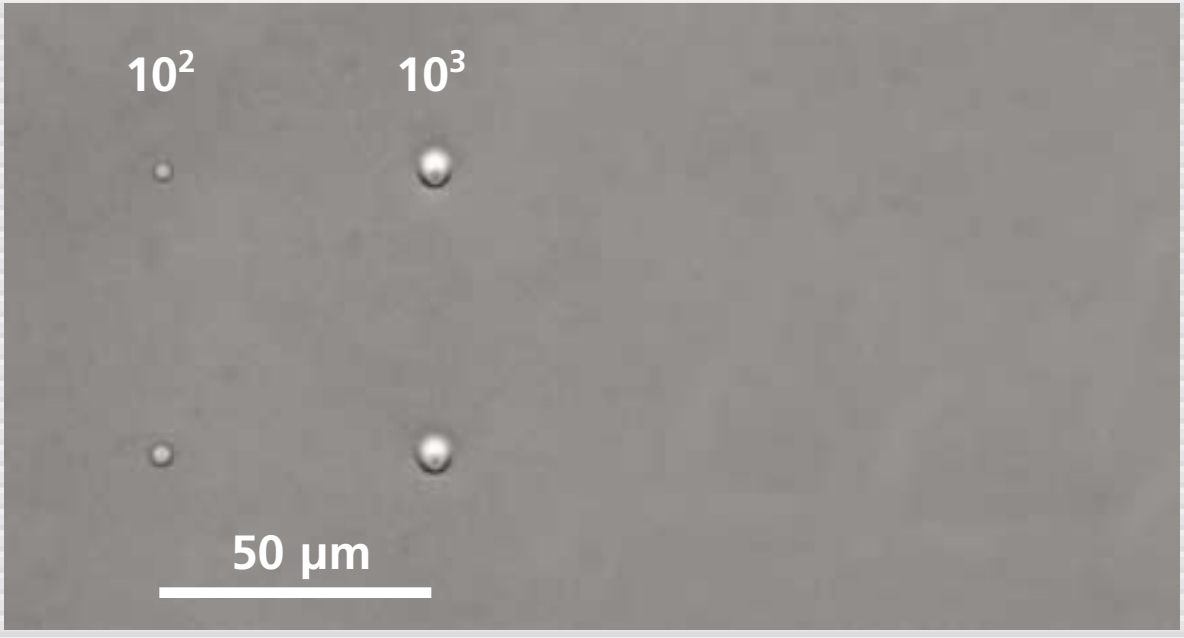
Low-energy processing



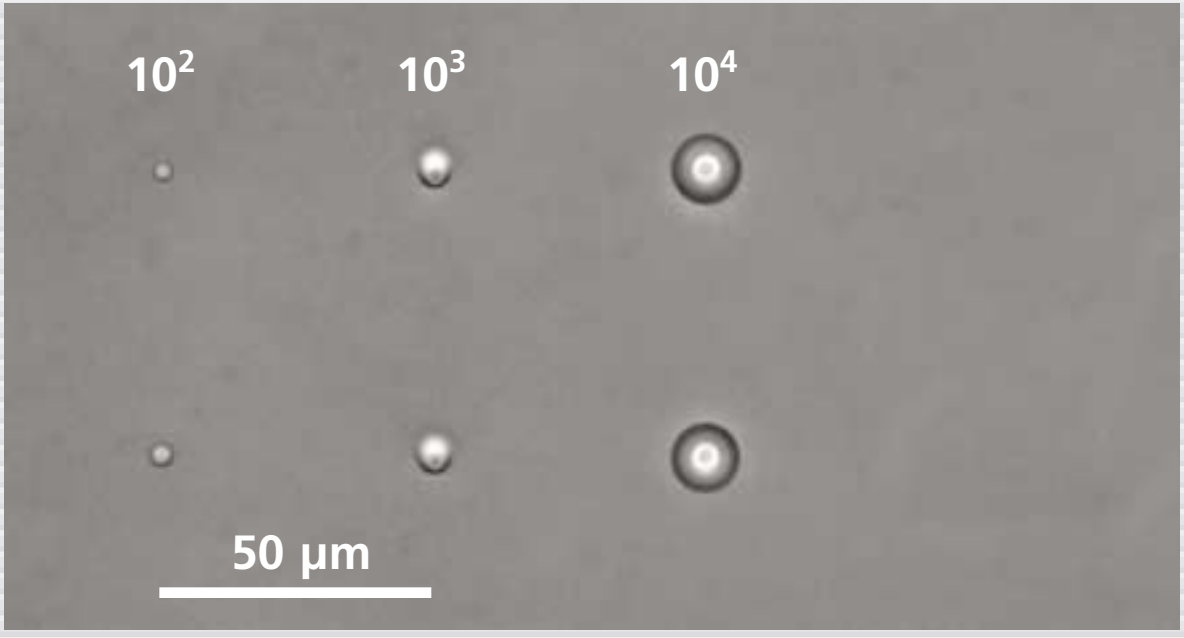
Low-energy processing



Low-energy processing



Low-energy processing



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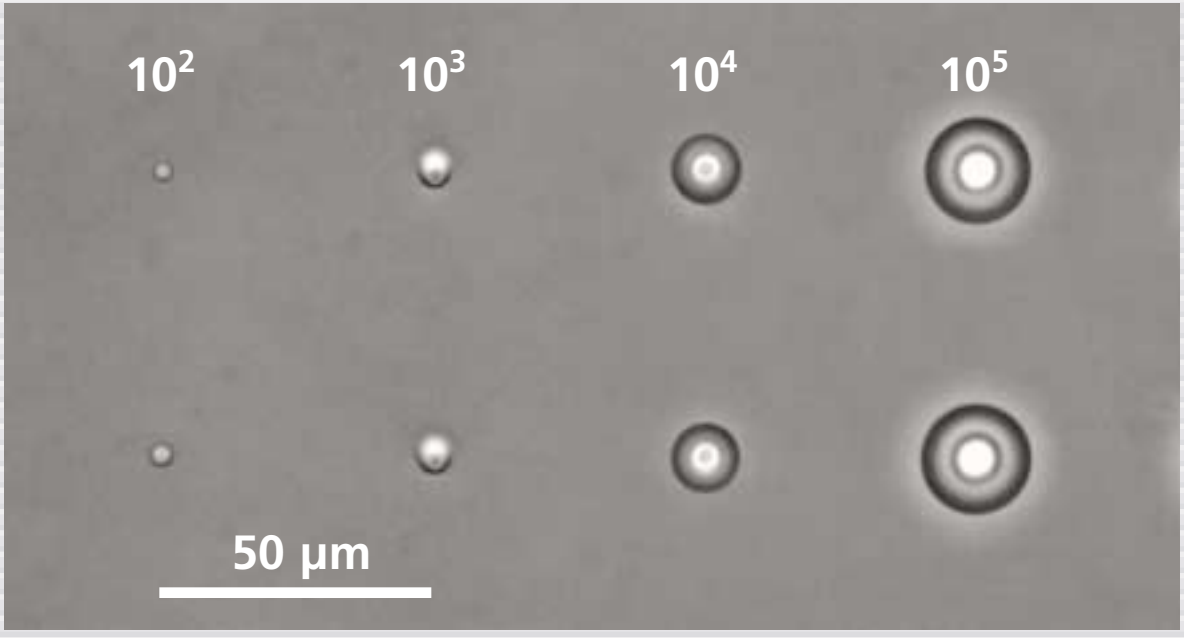
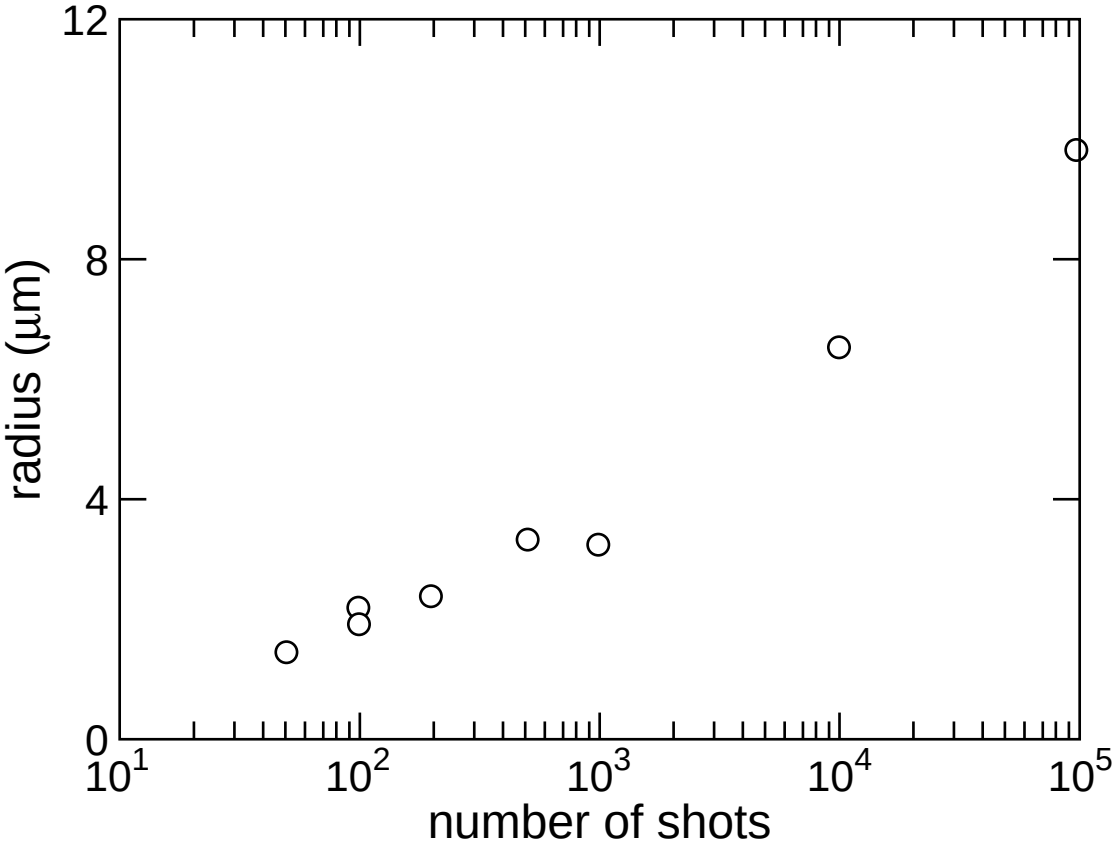
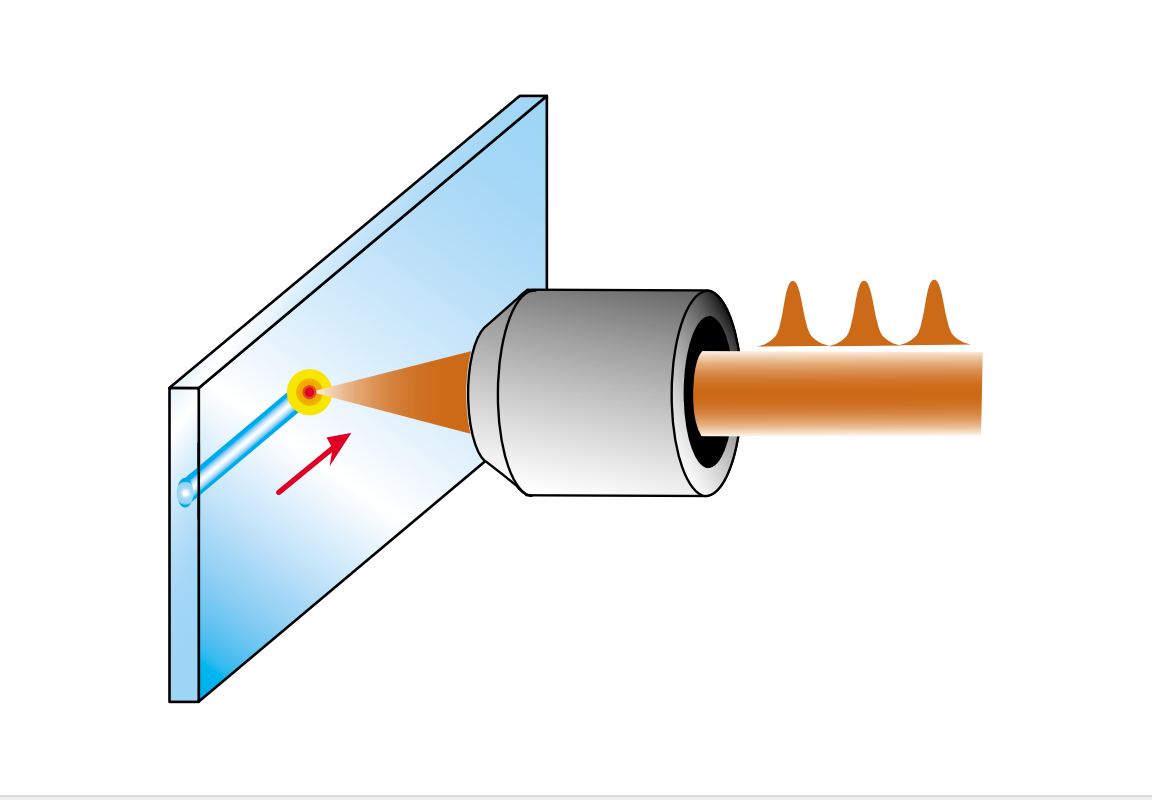


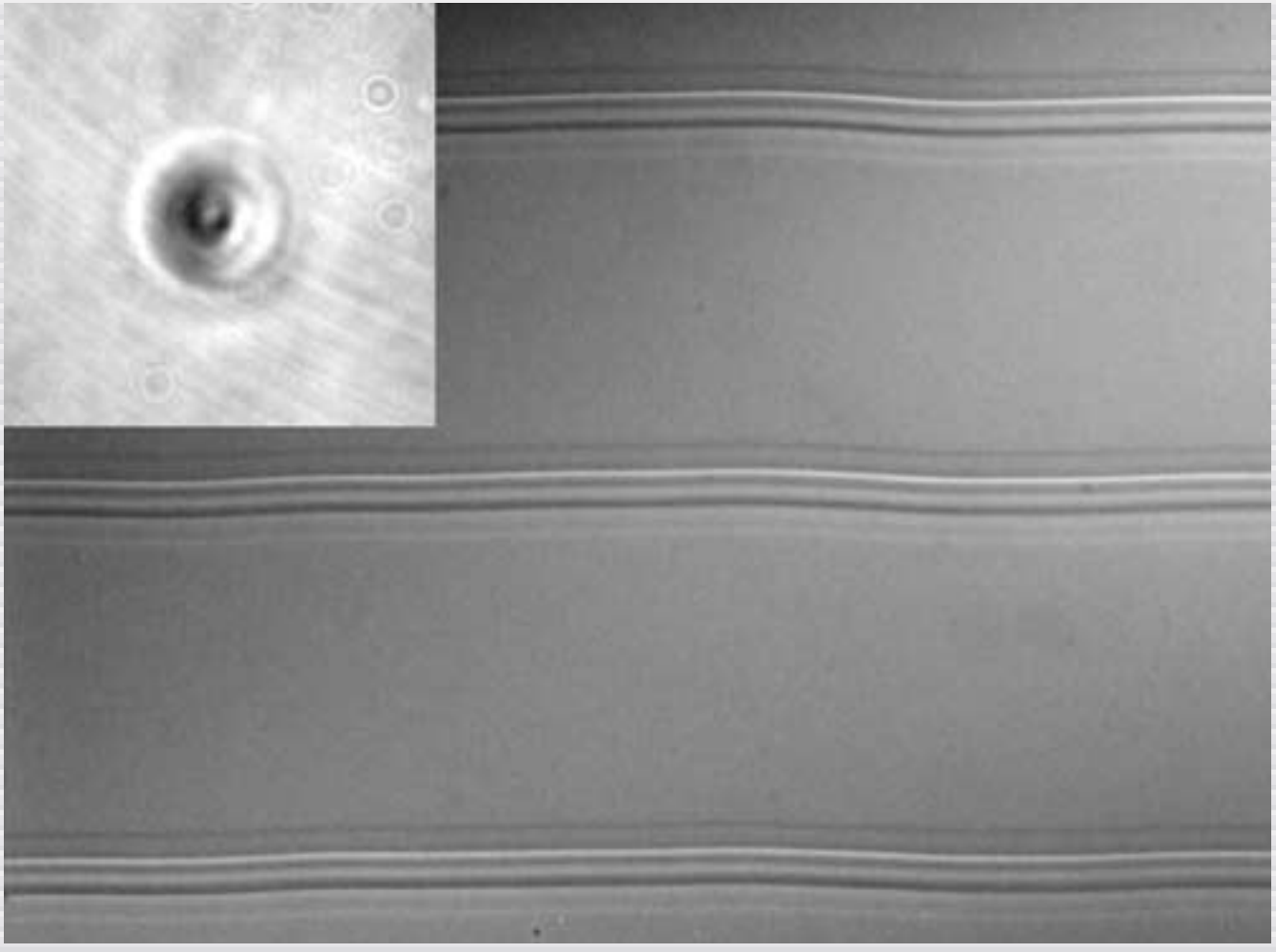
Low-energy processing



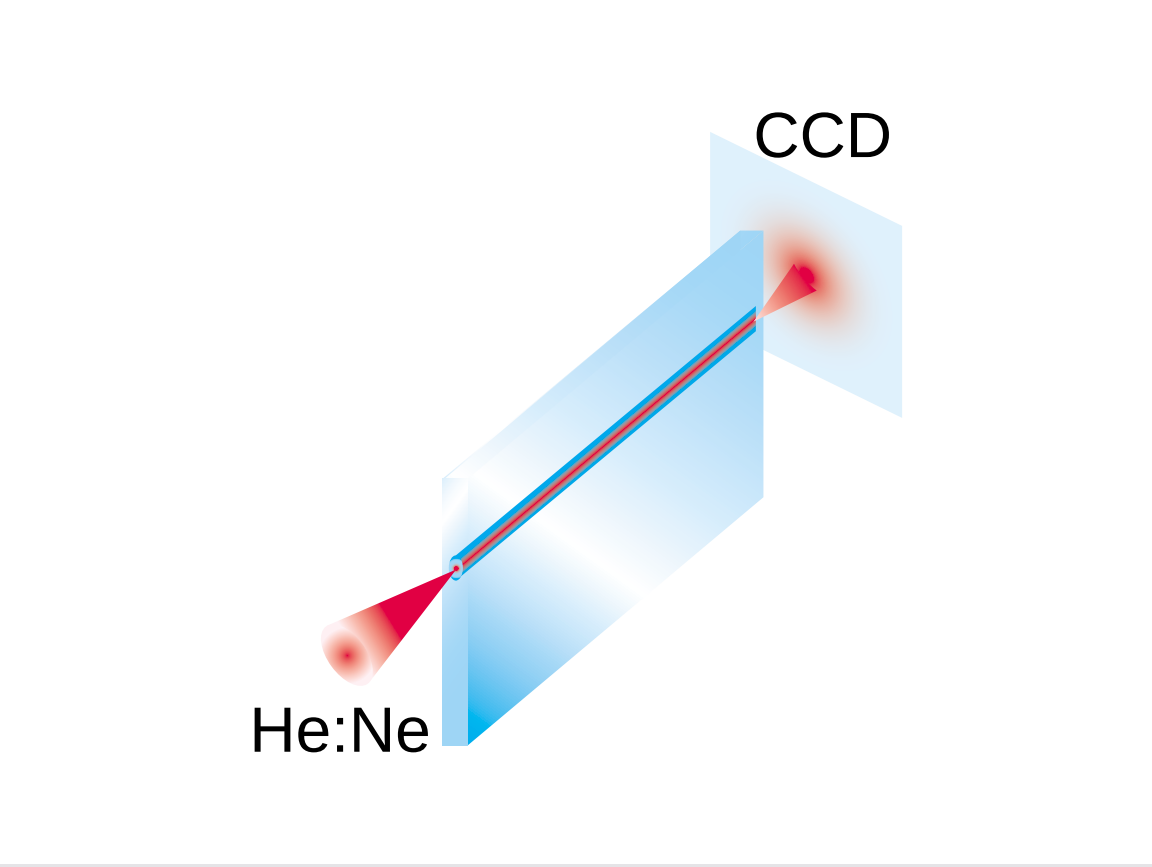
waveguide machining



waveguide machining

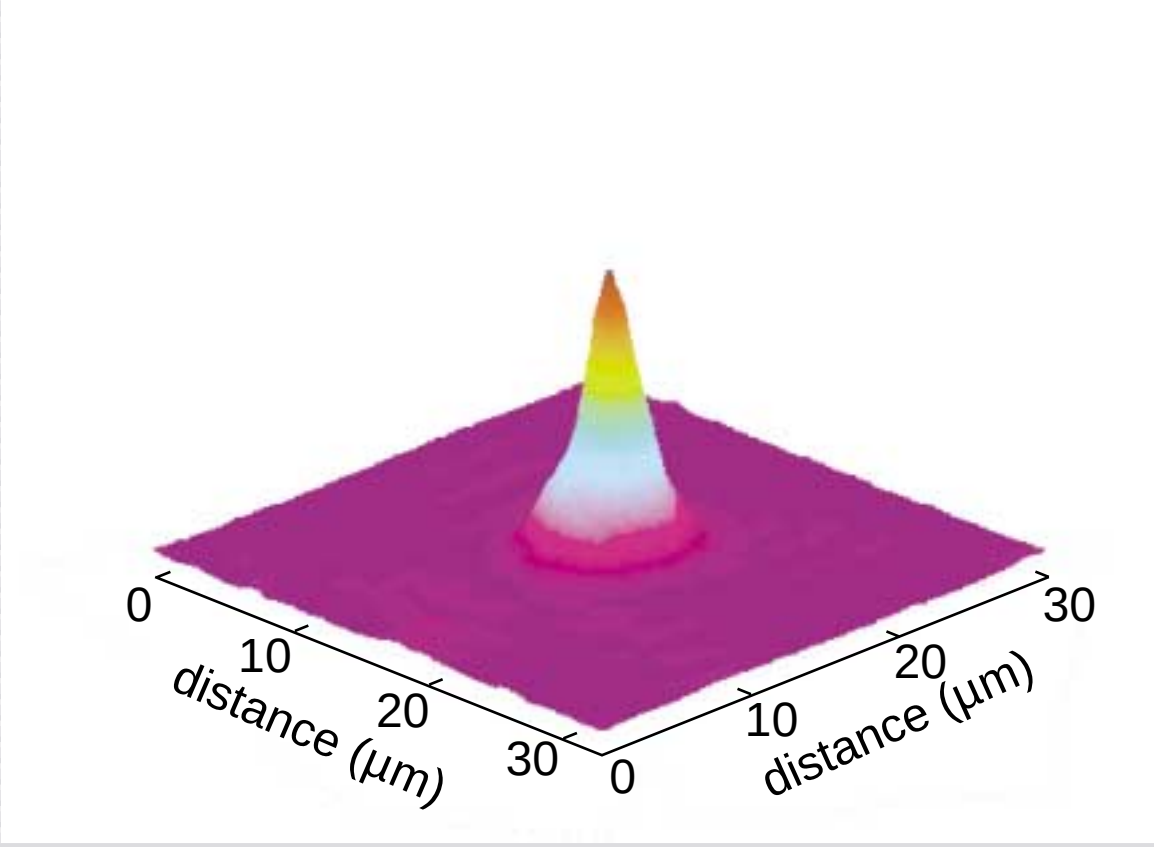


waveguide mode analysis



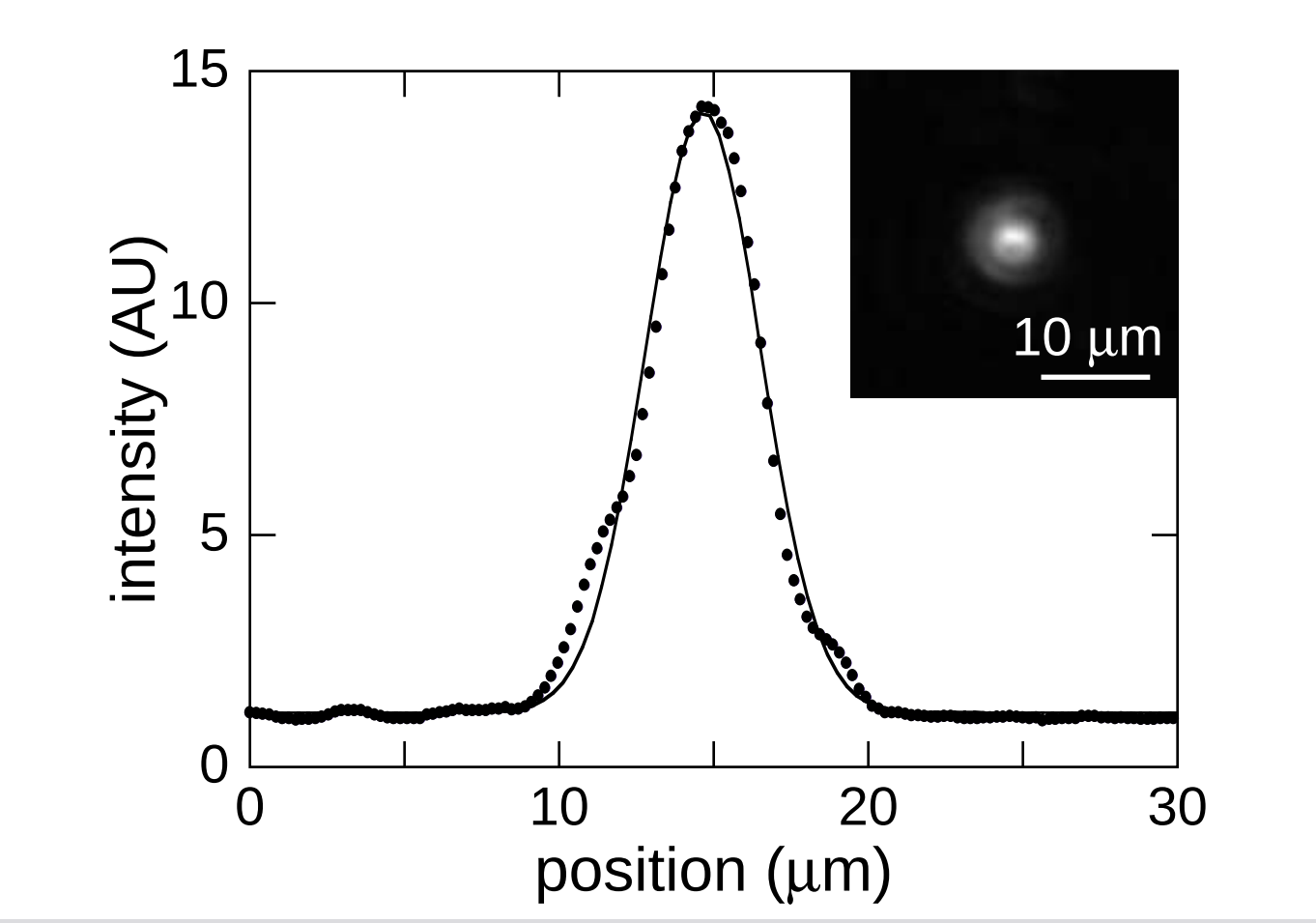
Low-energy processing

near field mode

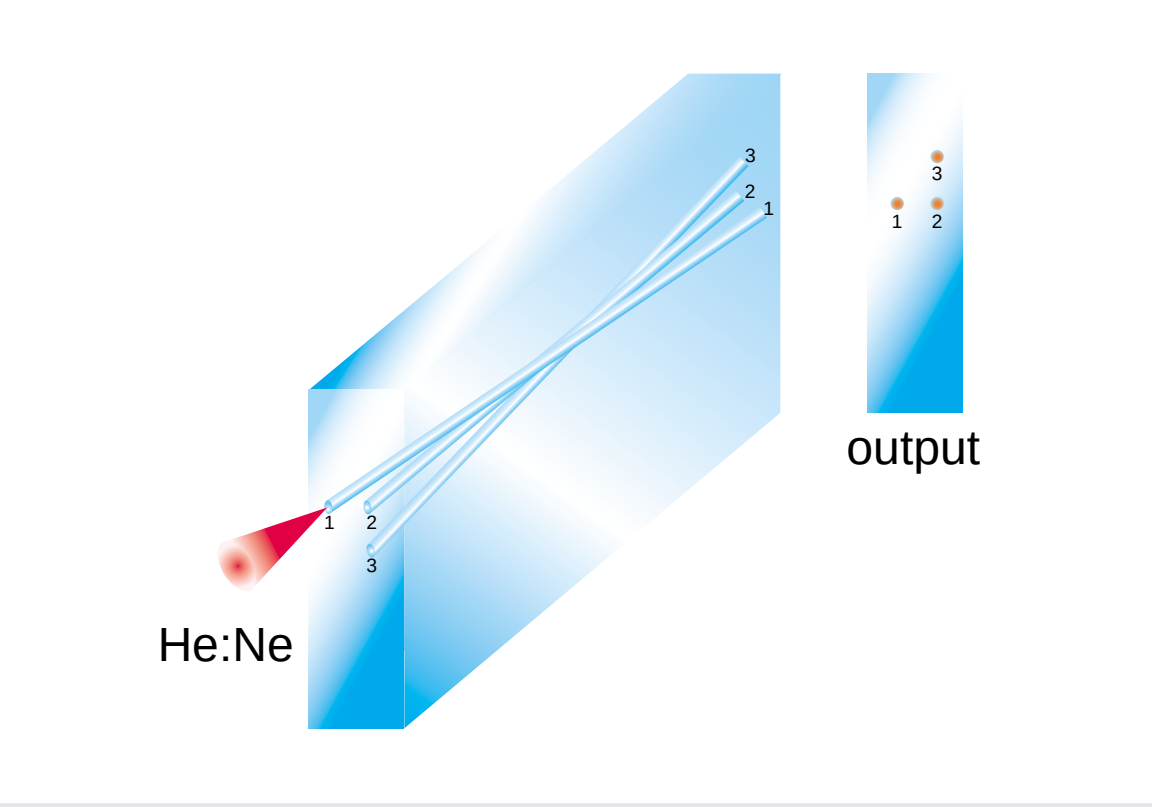


Low-energy processing

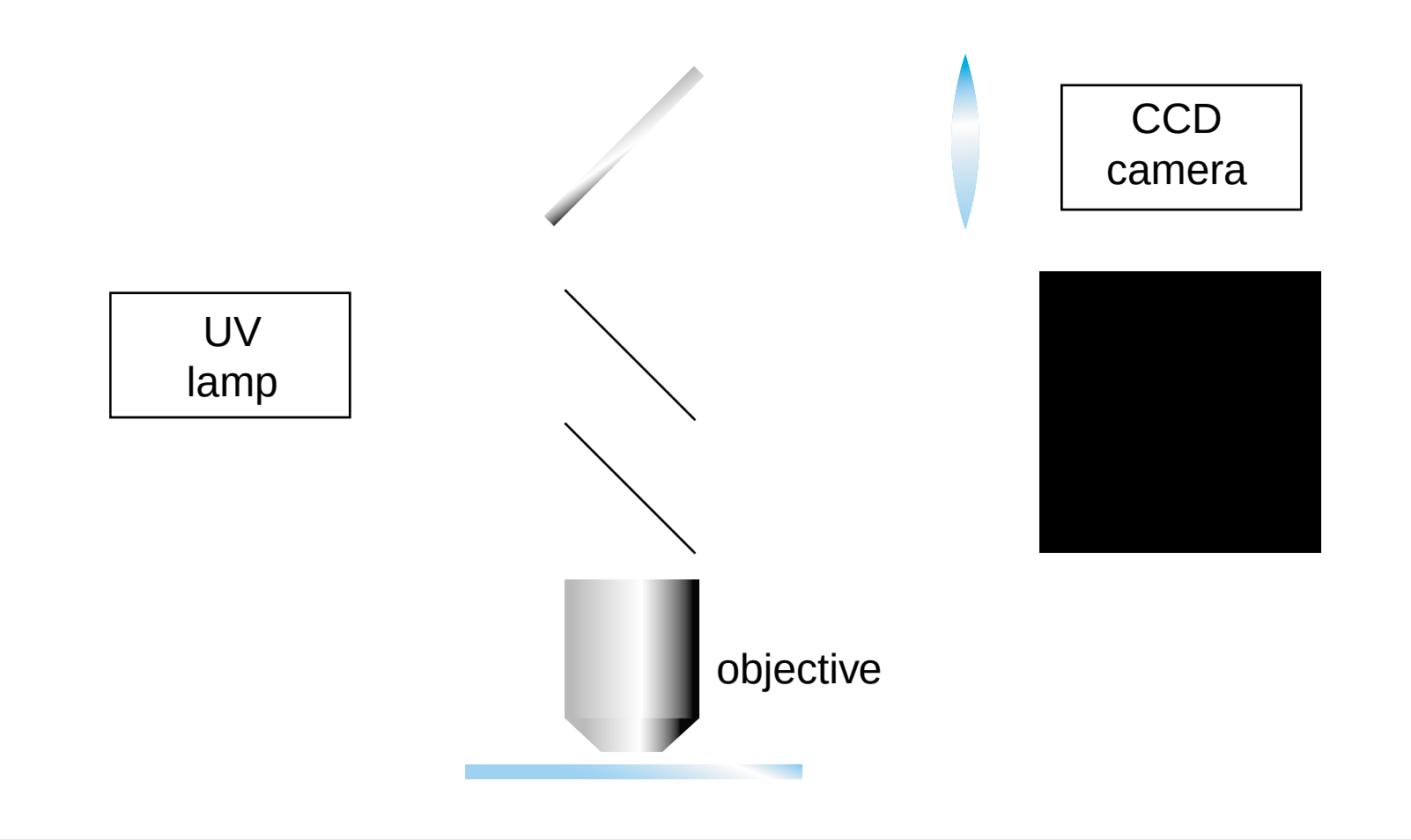
near field mode



3D wave splitter

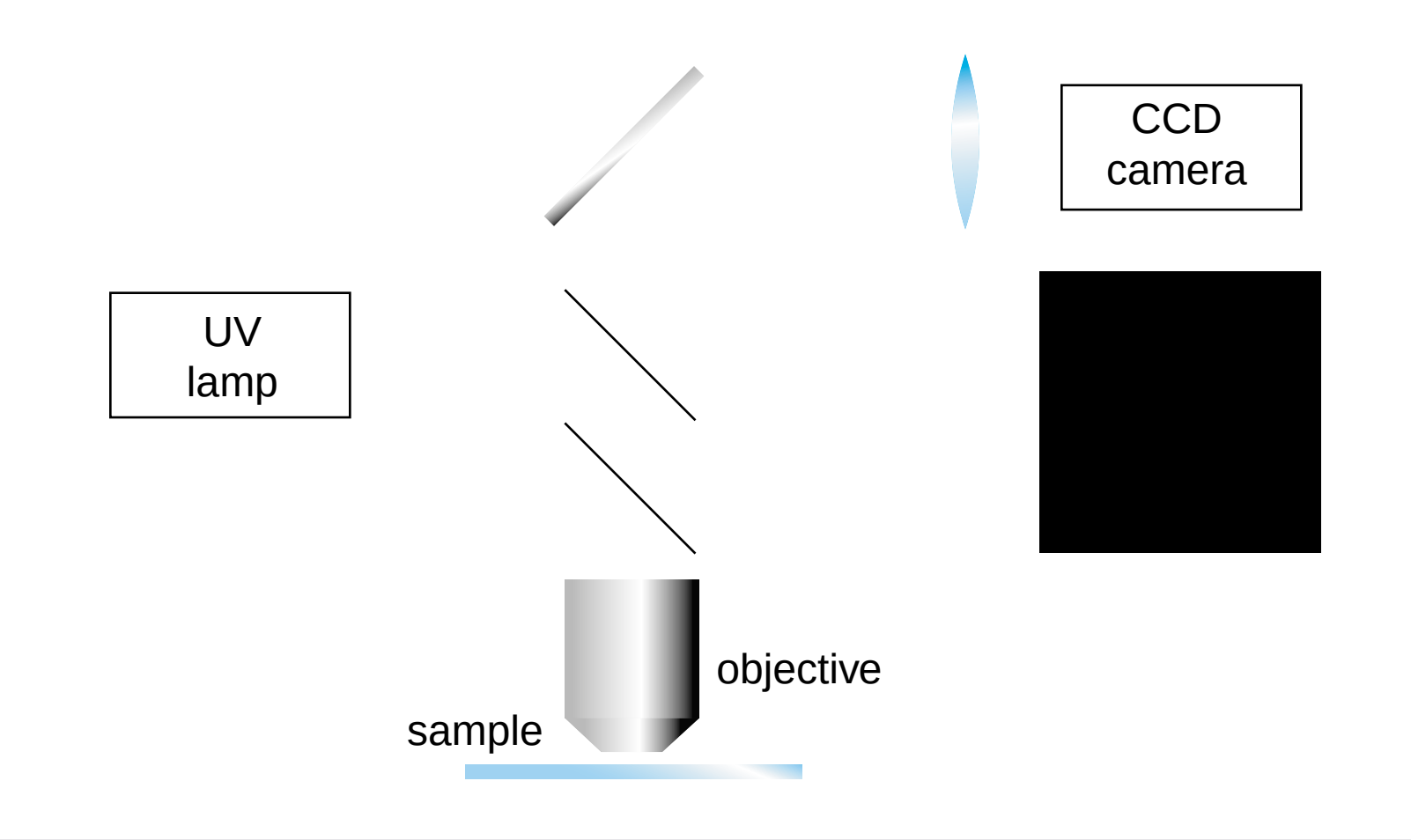


epi-fluorescence microscope

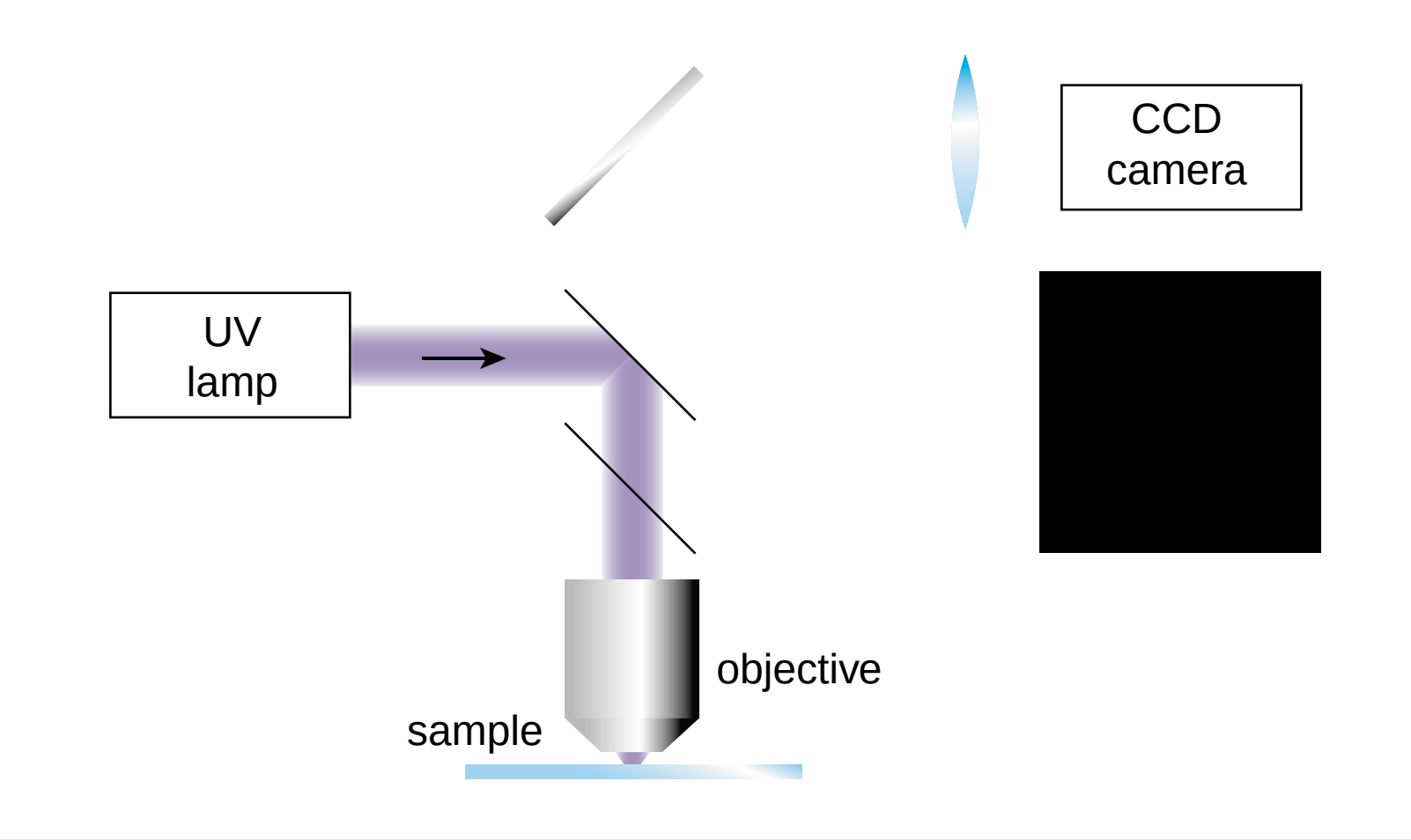


Low-energy processing

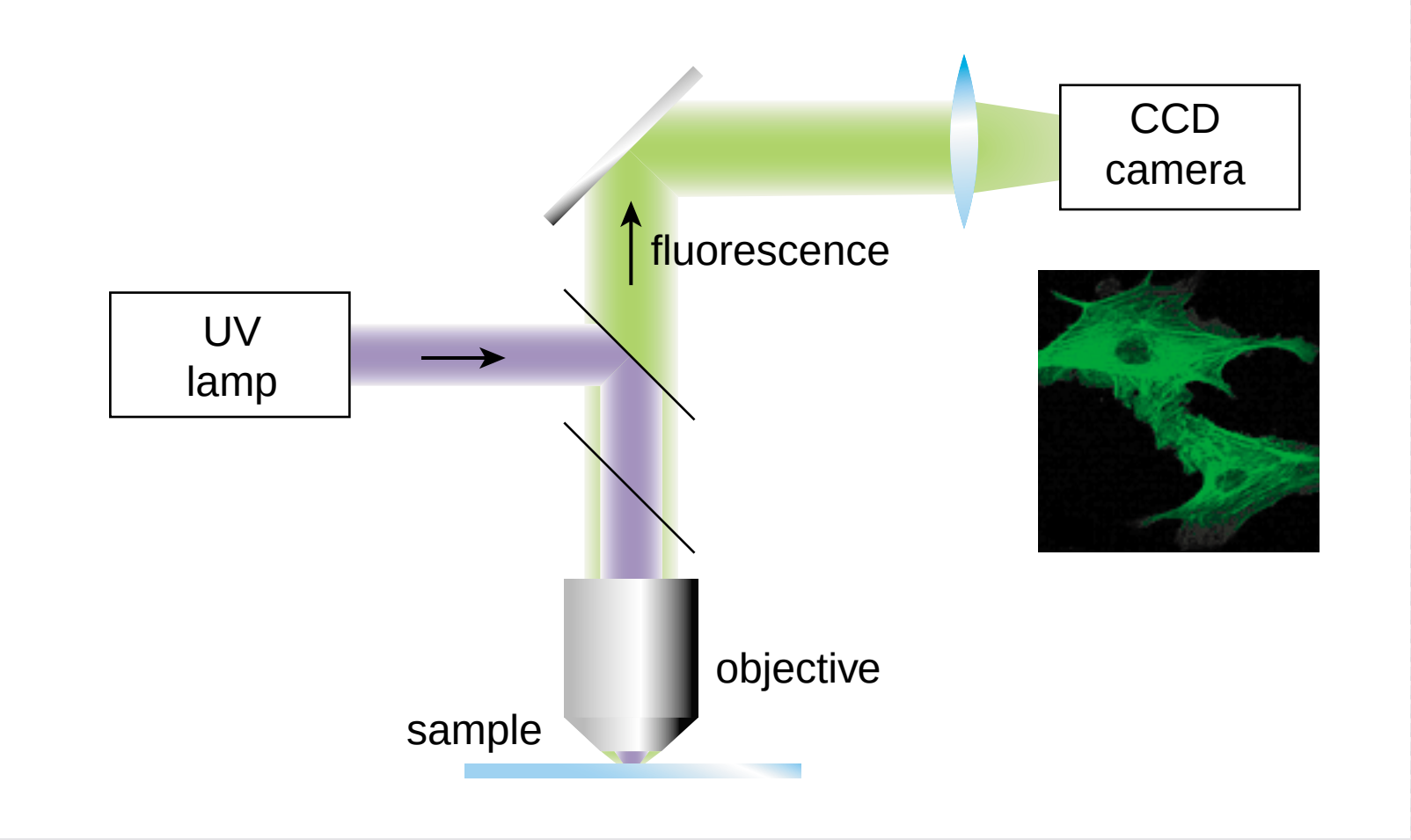
mount fluorescently tagged sample



UV illumination…

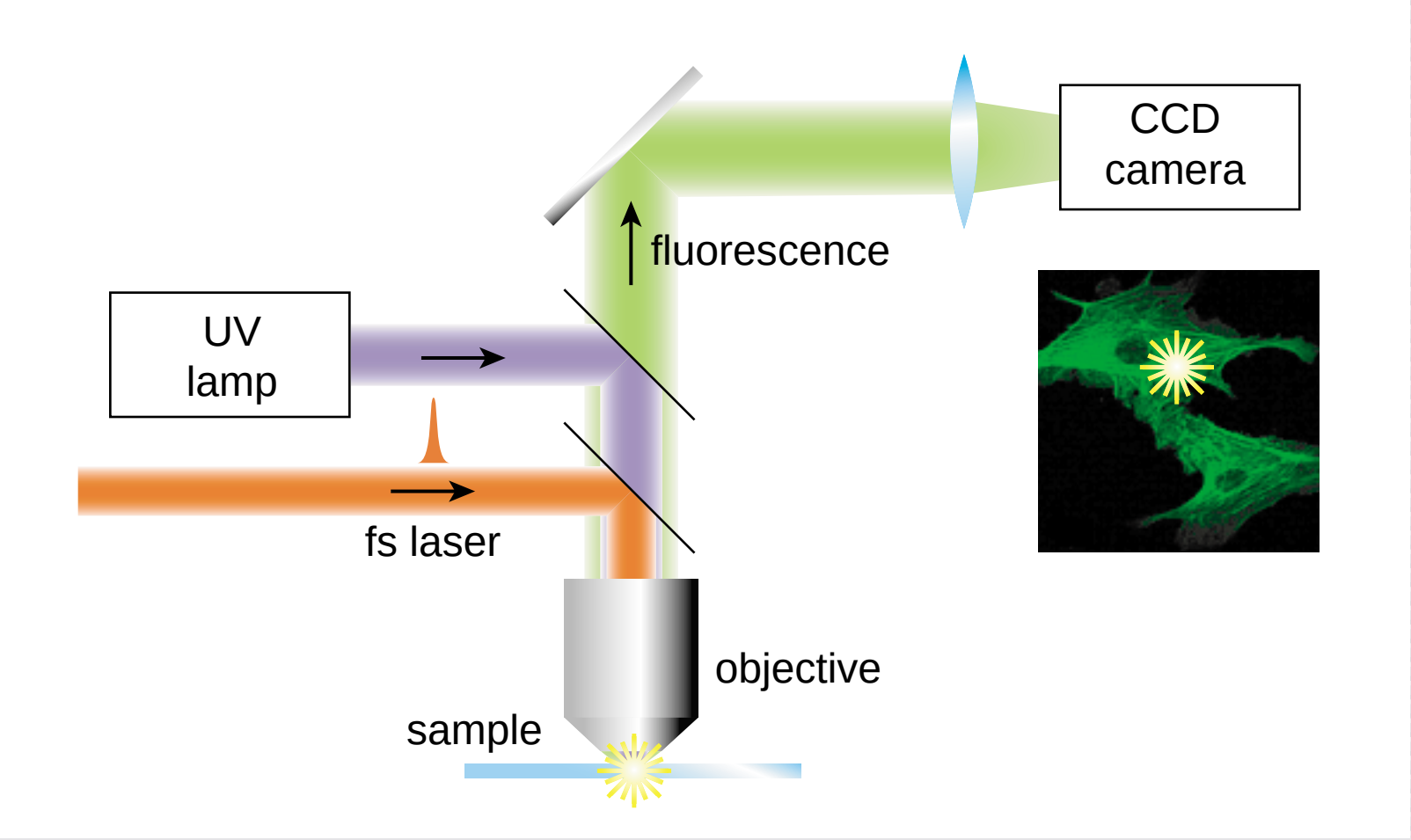


… causes fluorescence

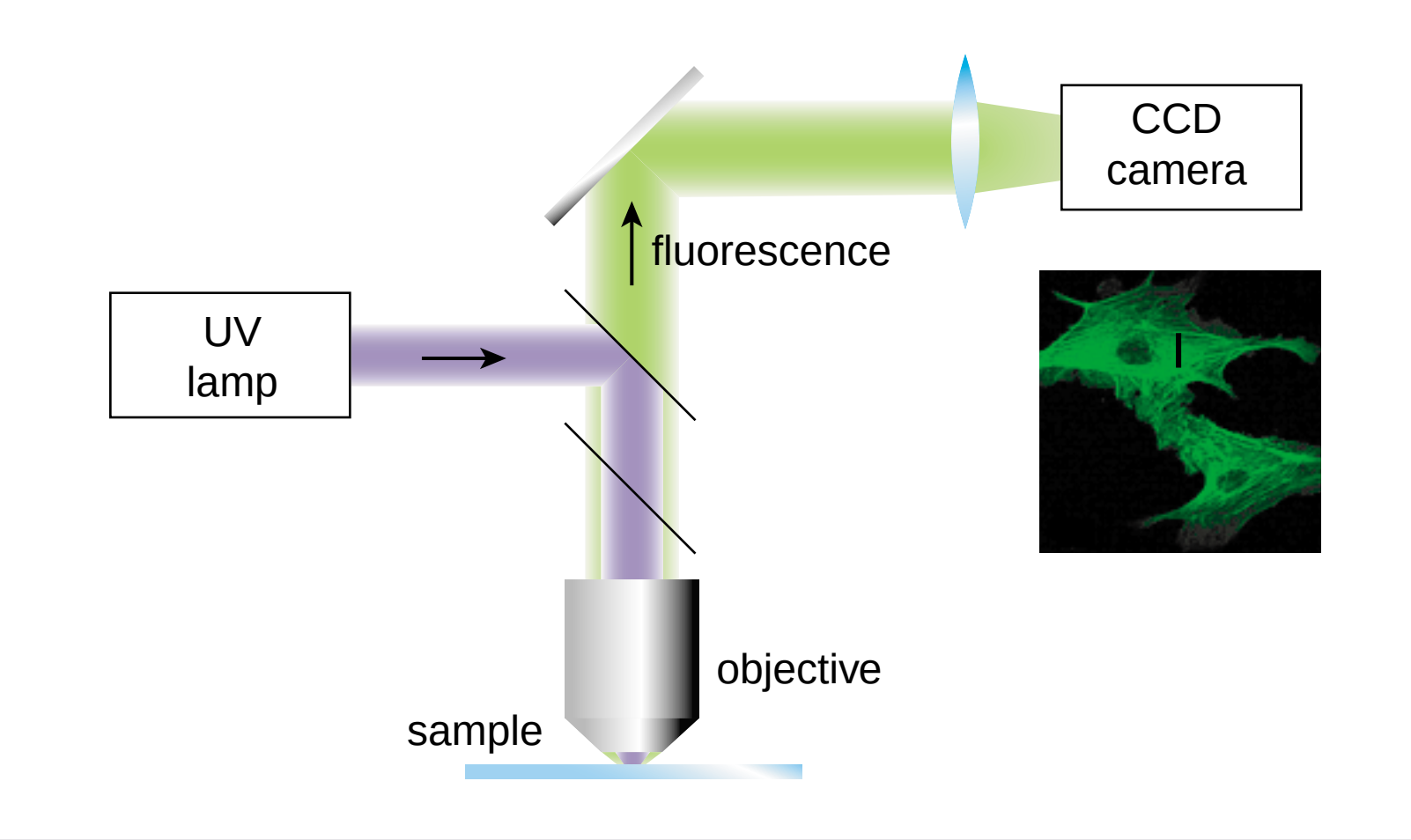


Low-energy processing

process with fs laser beam



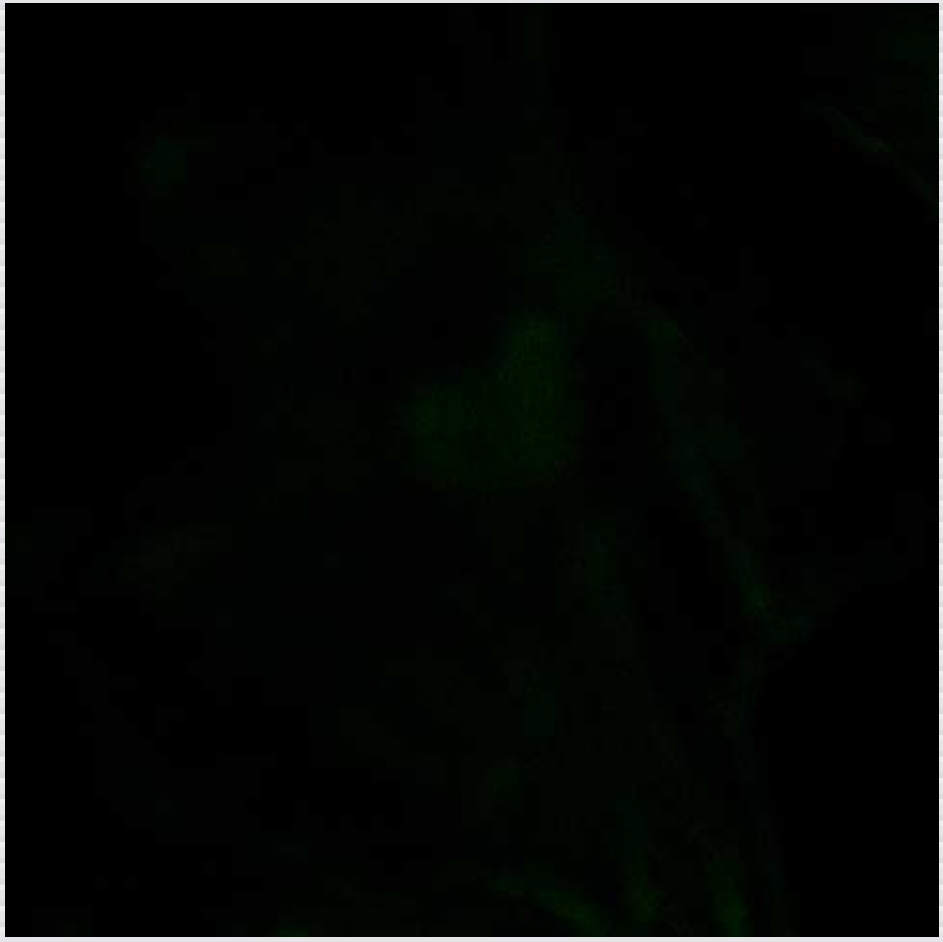
Low-energy processing



Low-energy processing

before

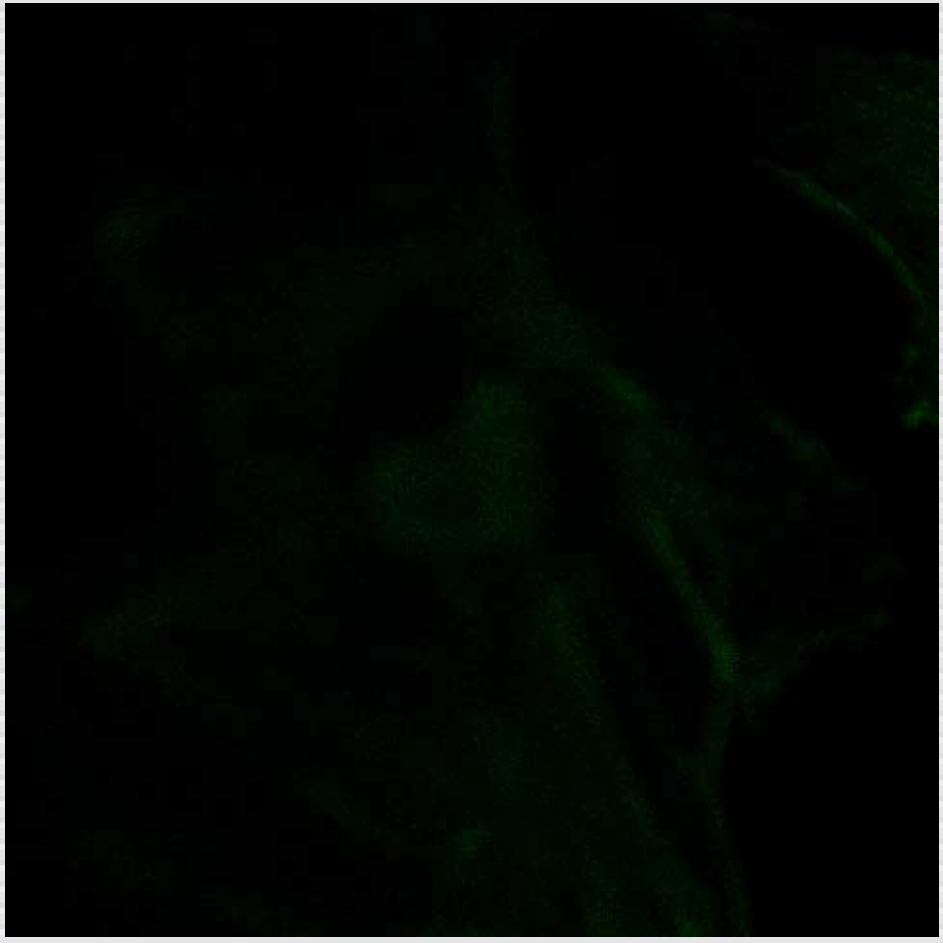
after



examine in confocal microscope

Low-energy processing

before



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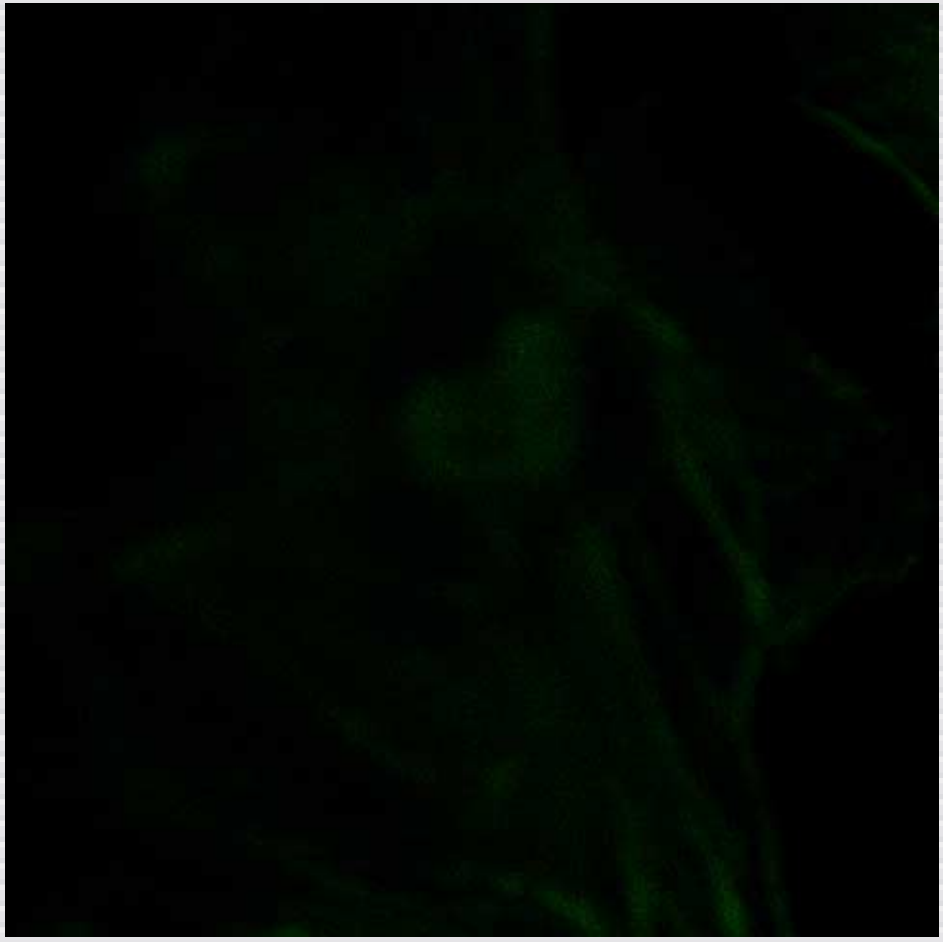
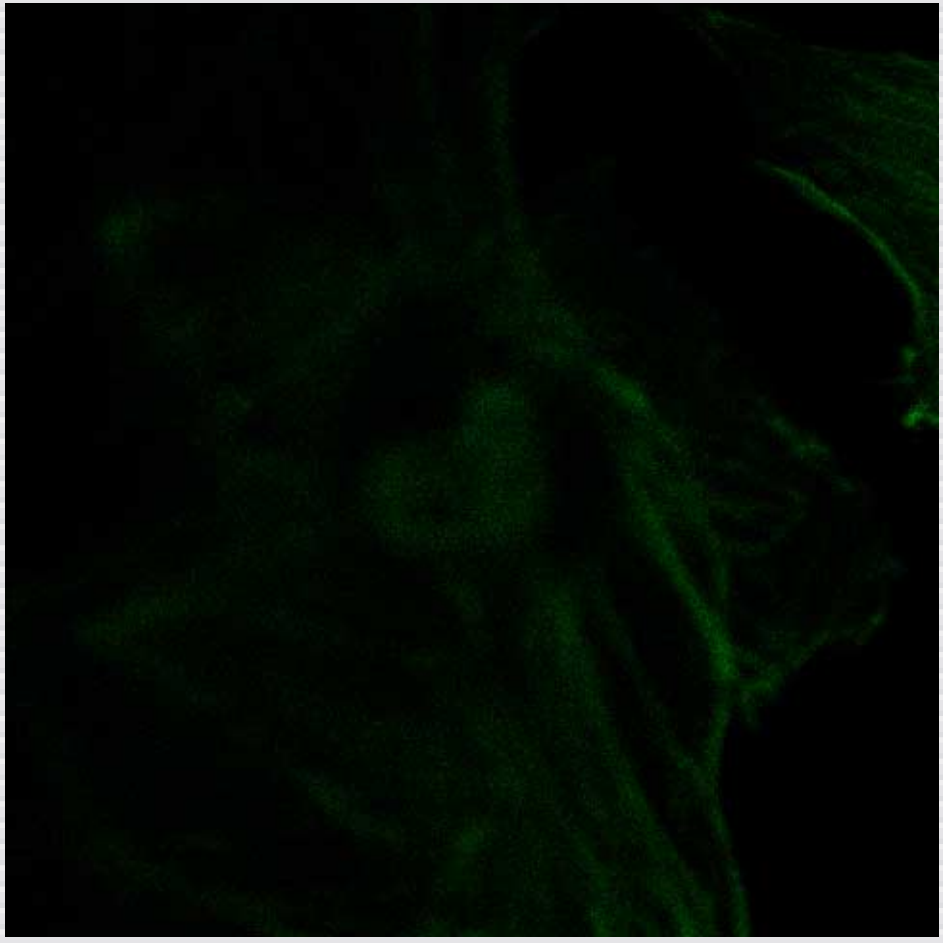


Low-energy processing

before



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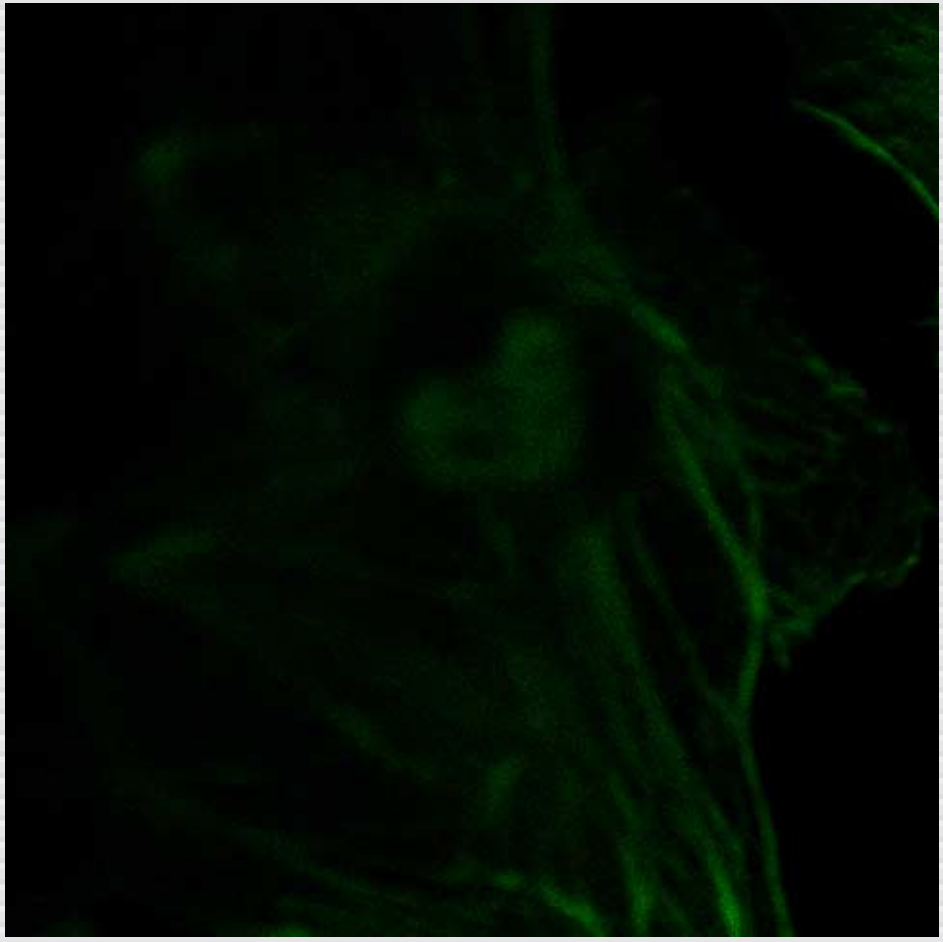
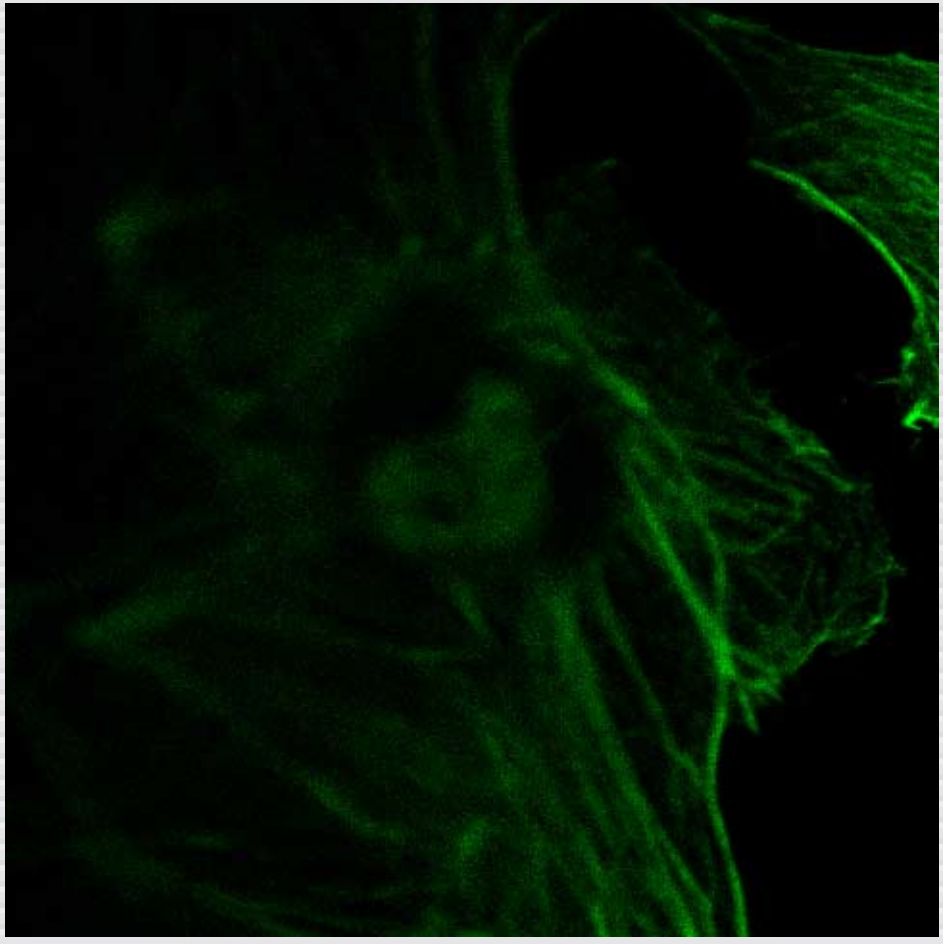


Low-energy processing

before



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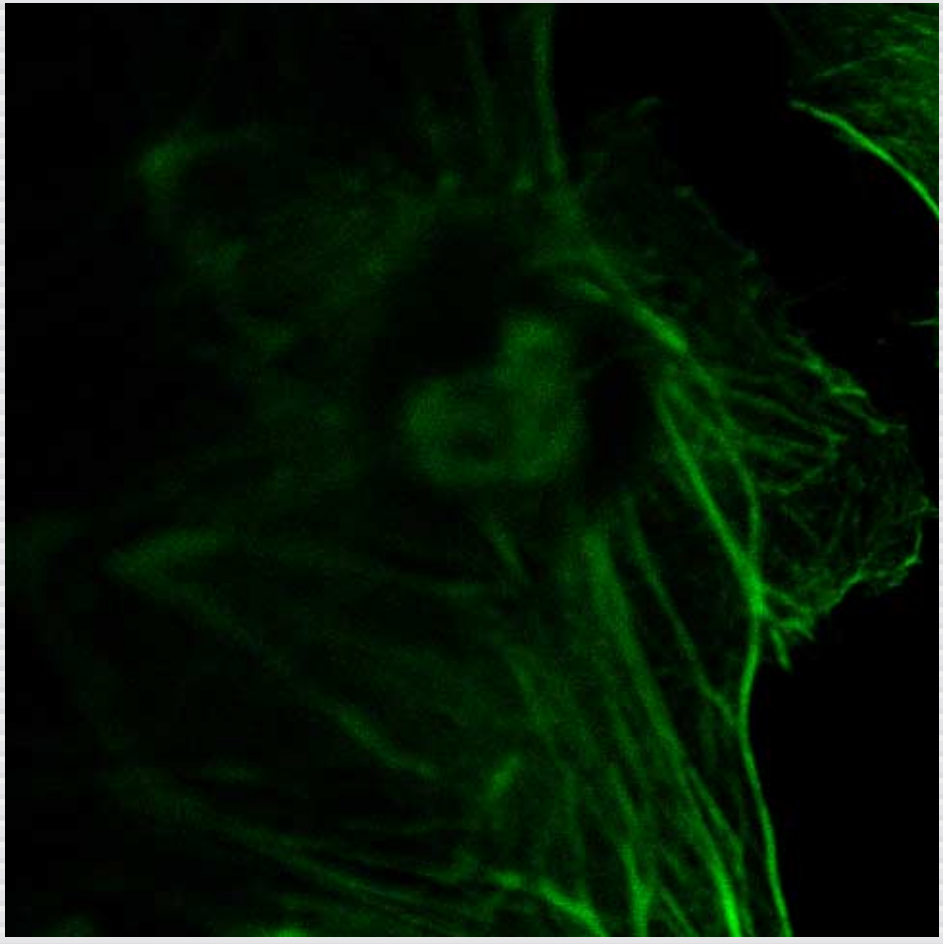
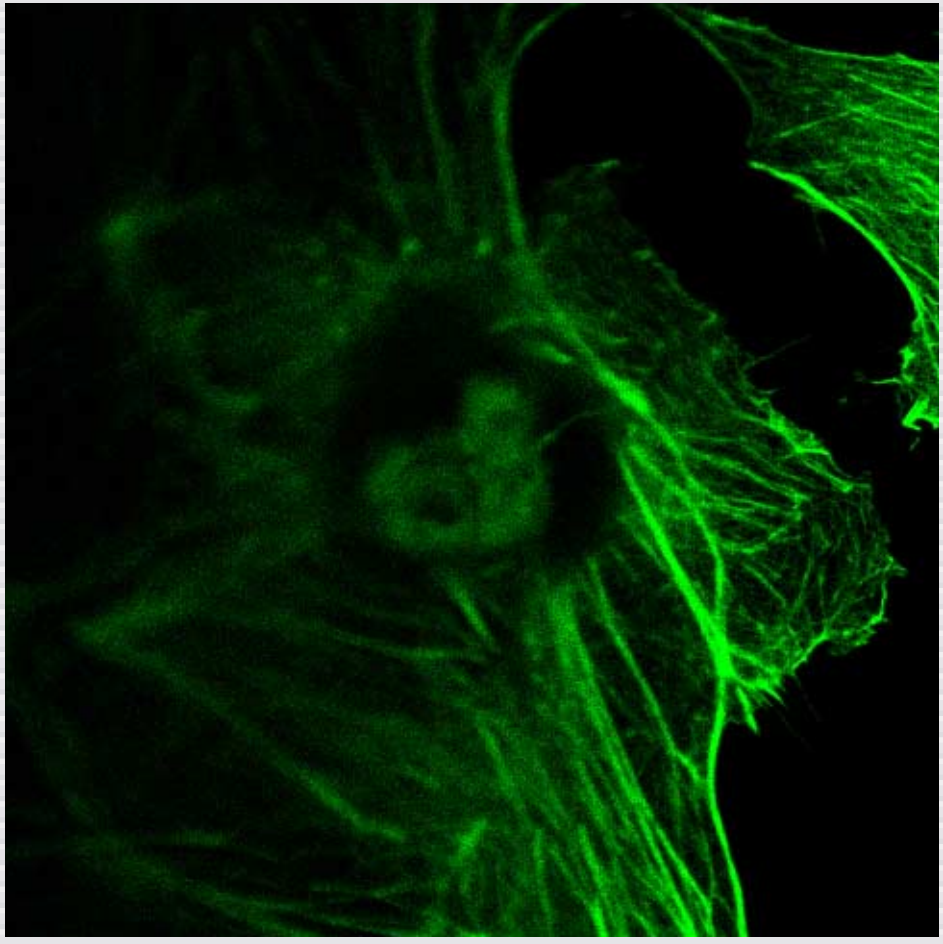


Low-energy processing

before



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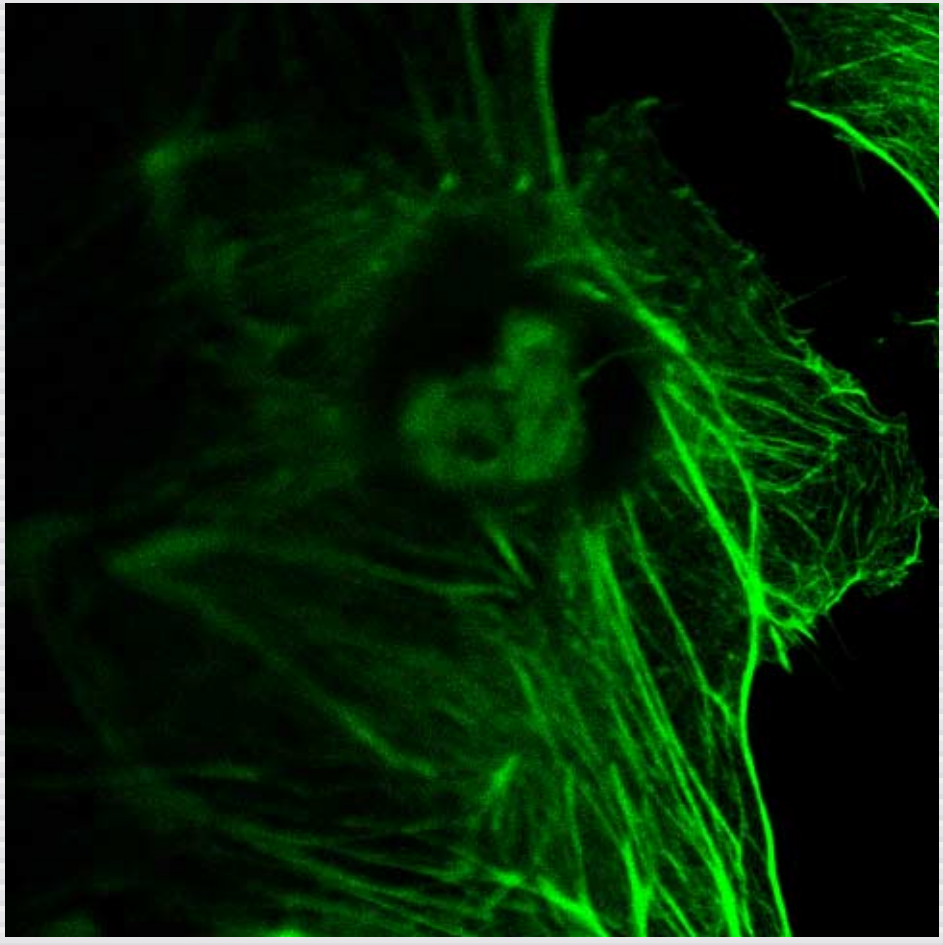

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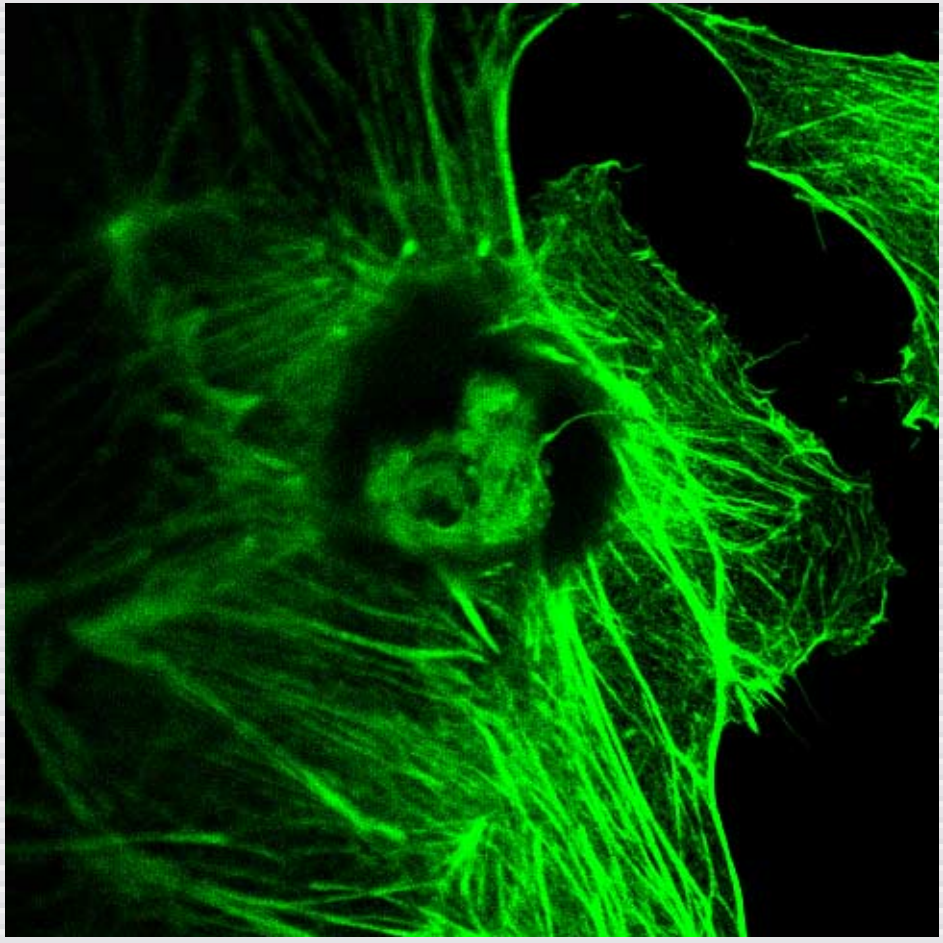

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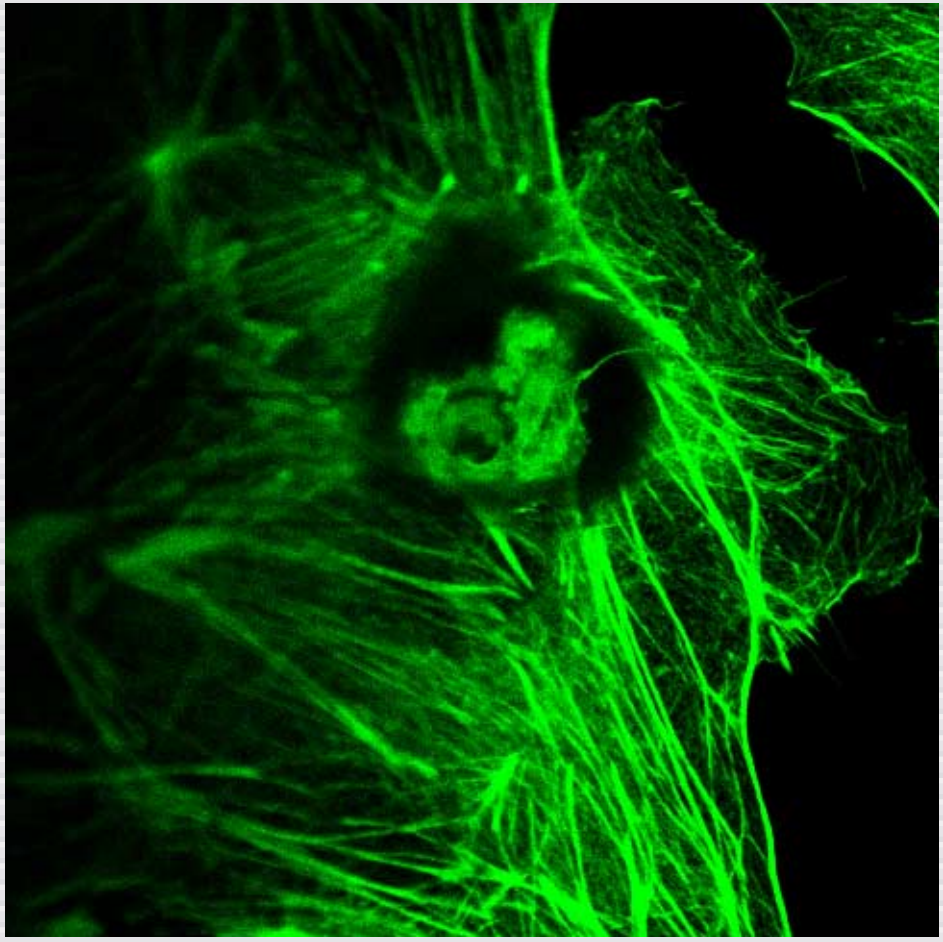
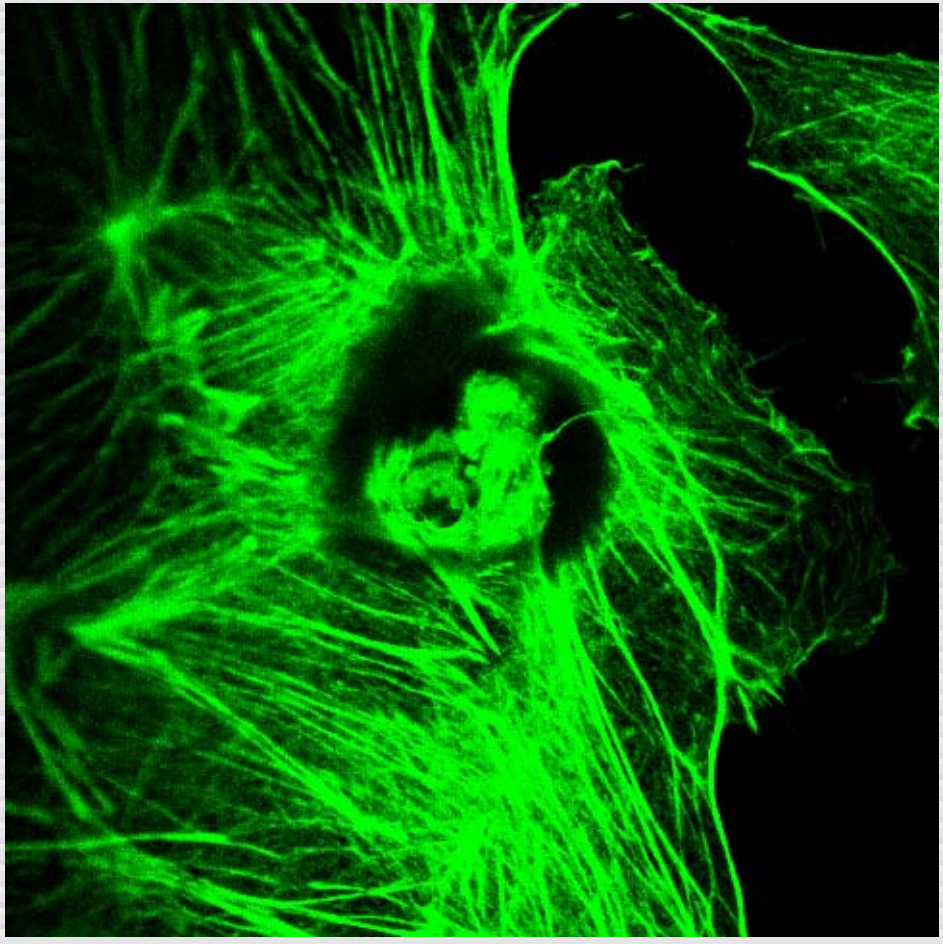


Low-energy processing

before



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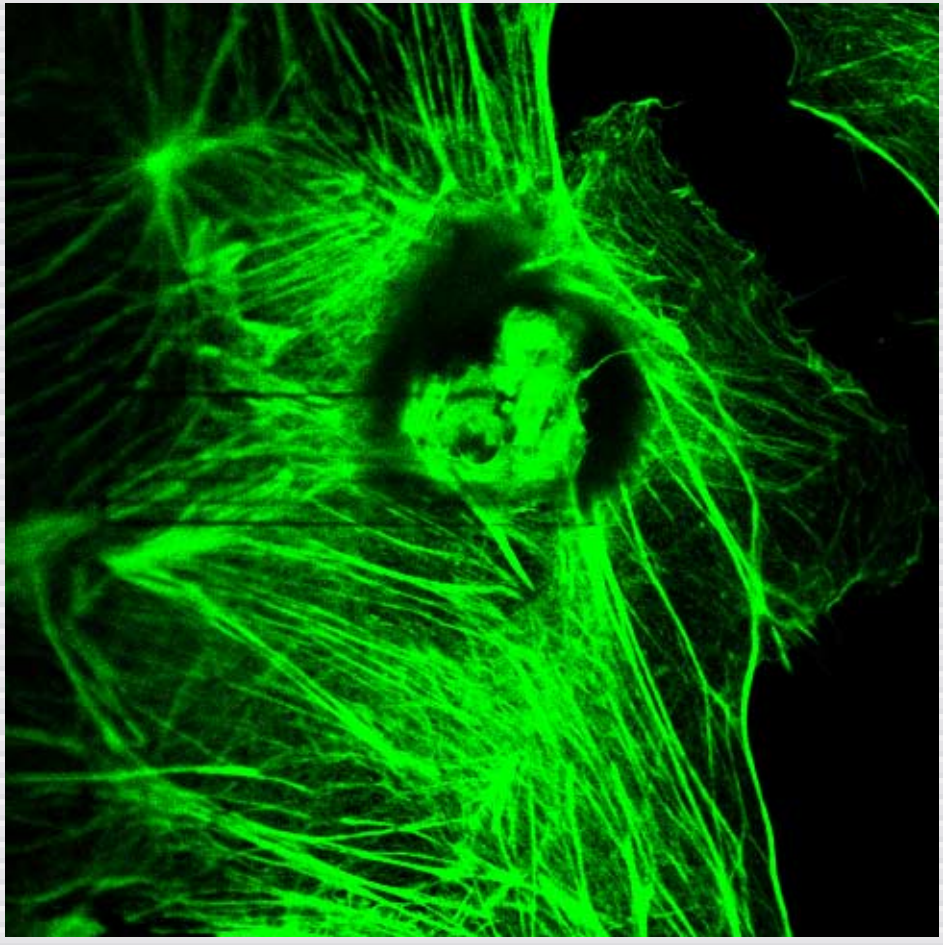
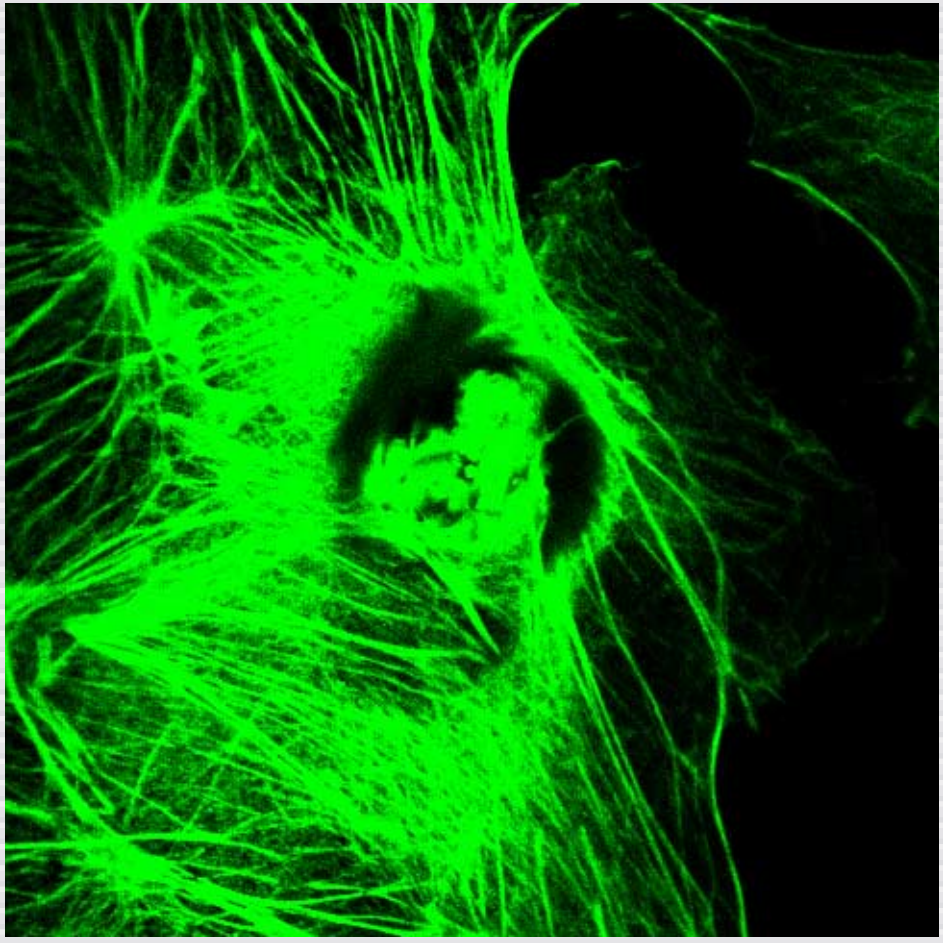


Low-energy processing

before



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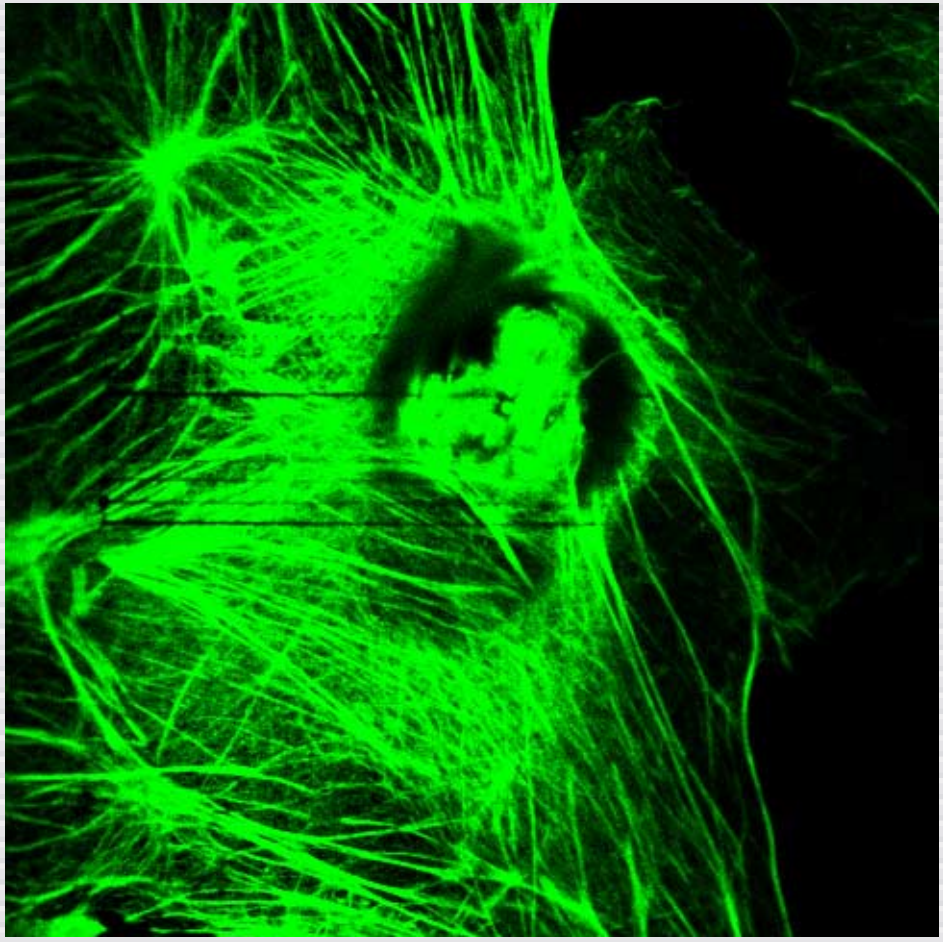
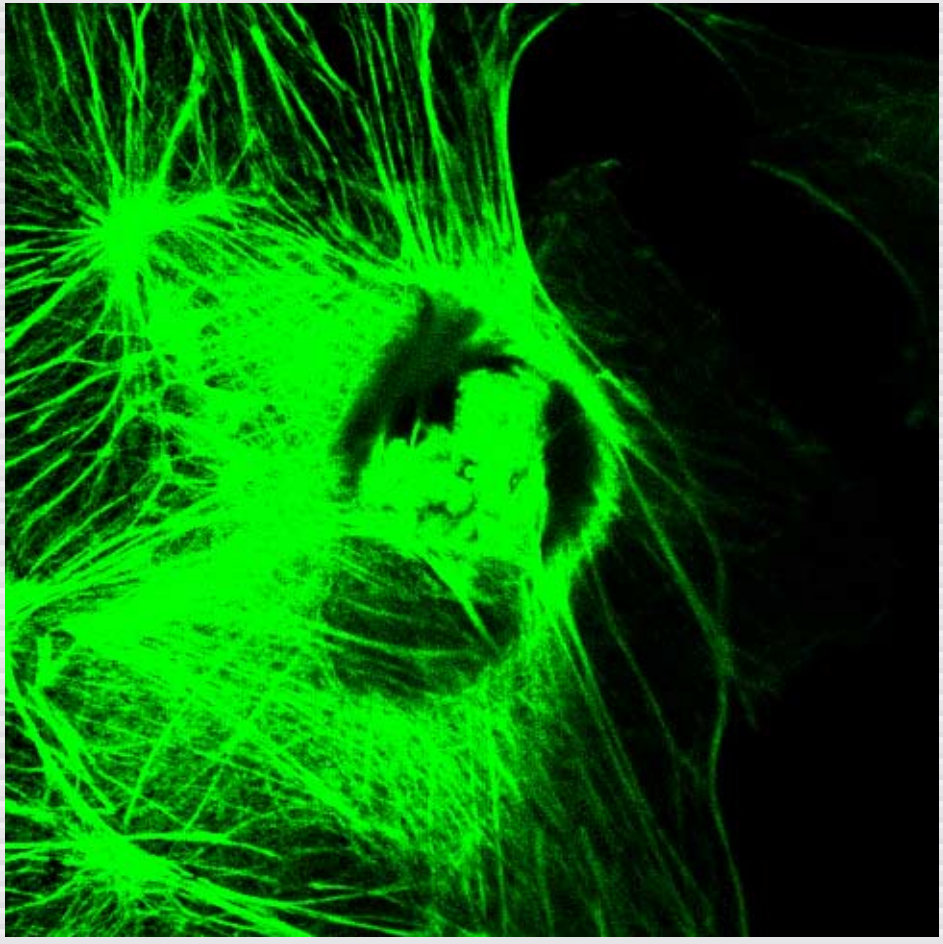


Low-energy processing

before



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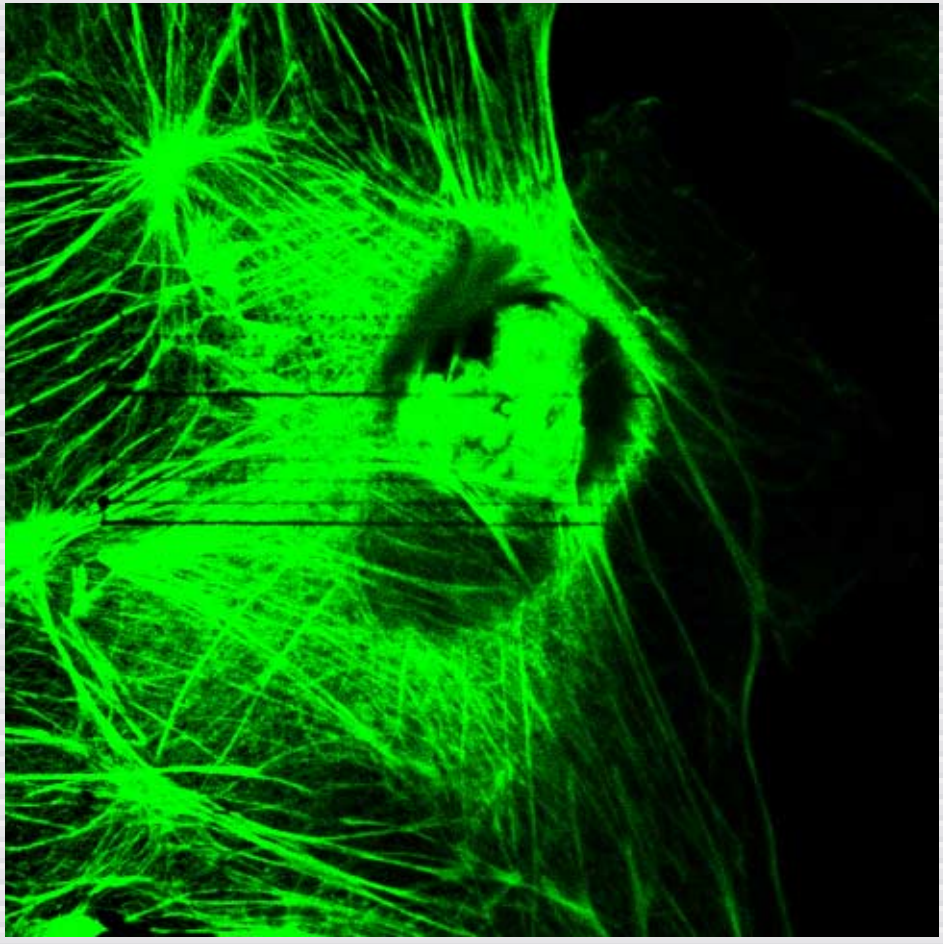
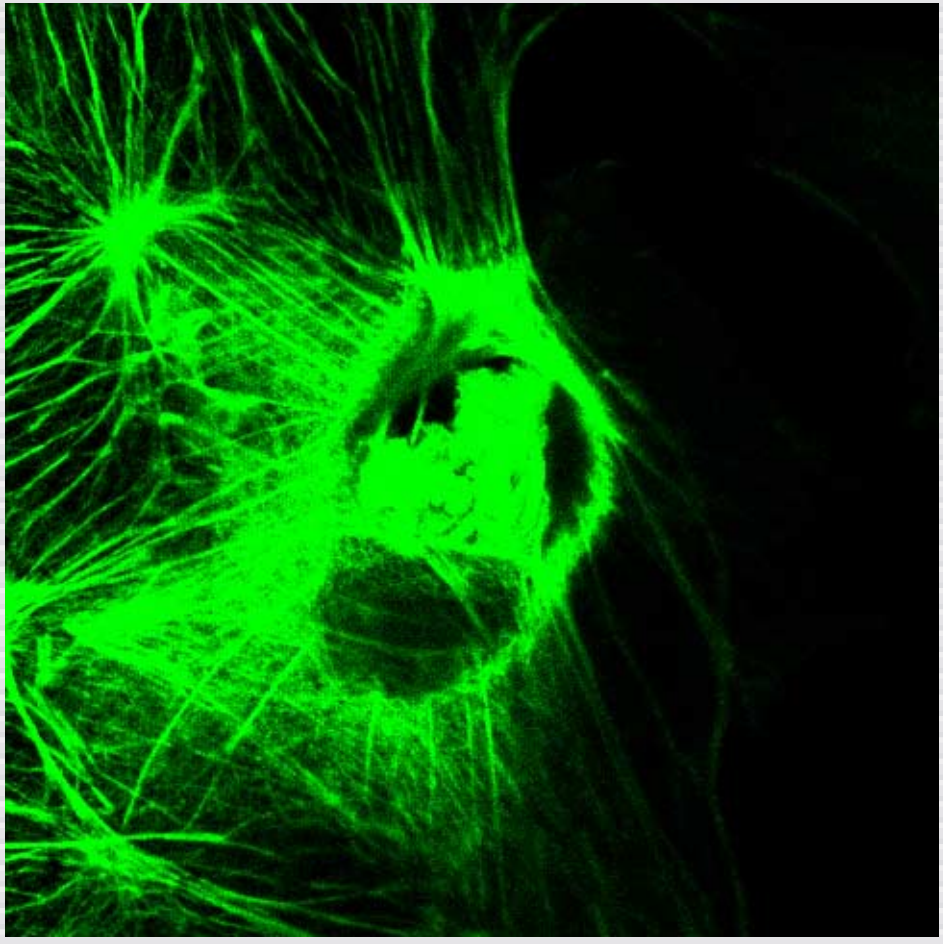


Low-energy processing

before



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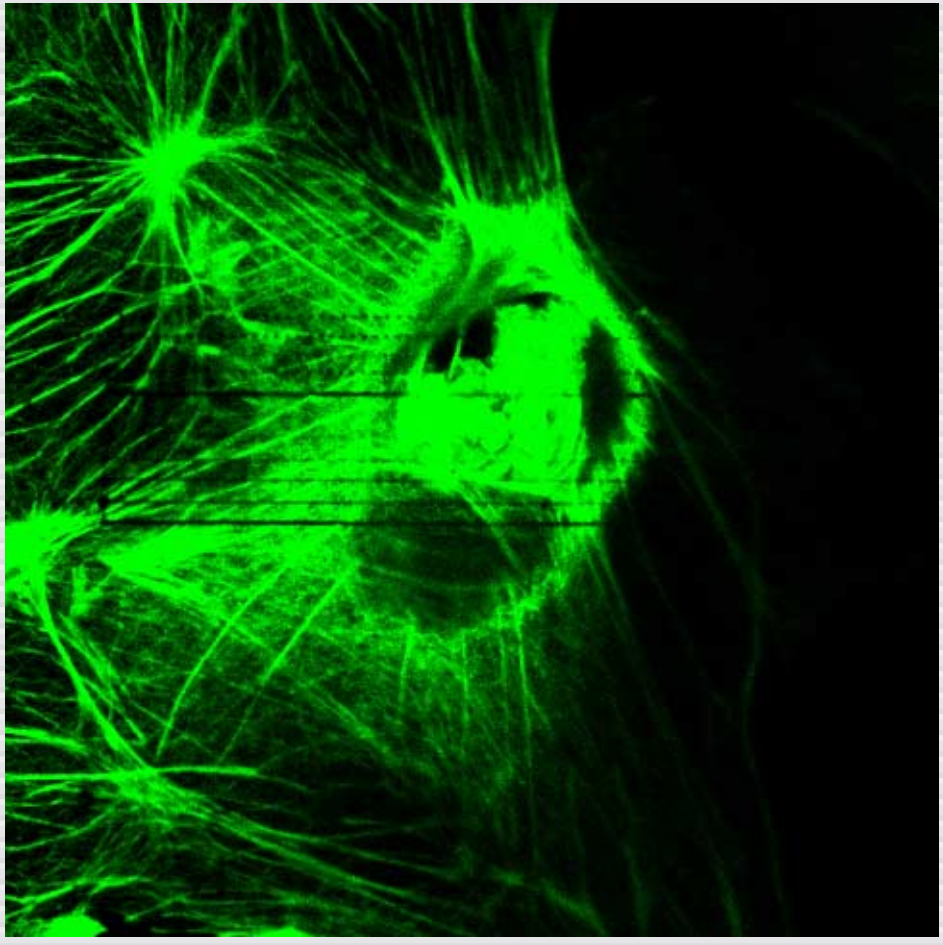

Low-energy processing

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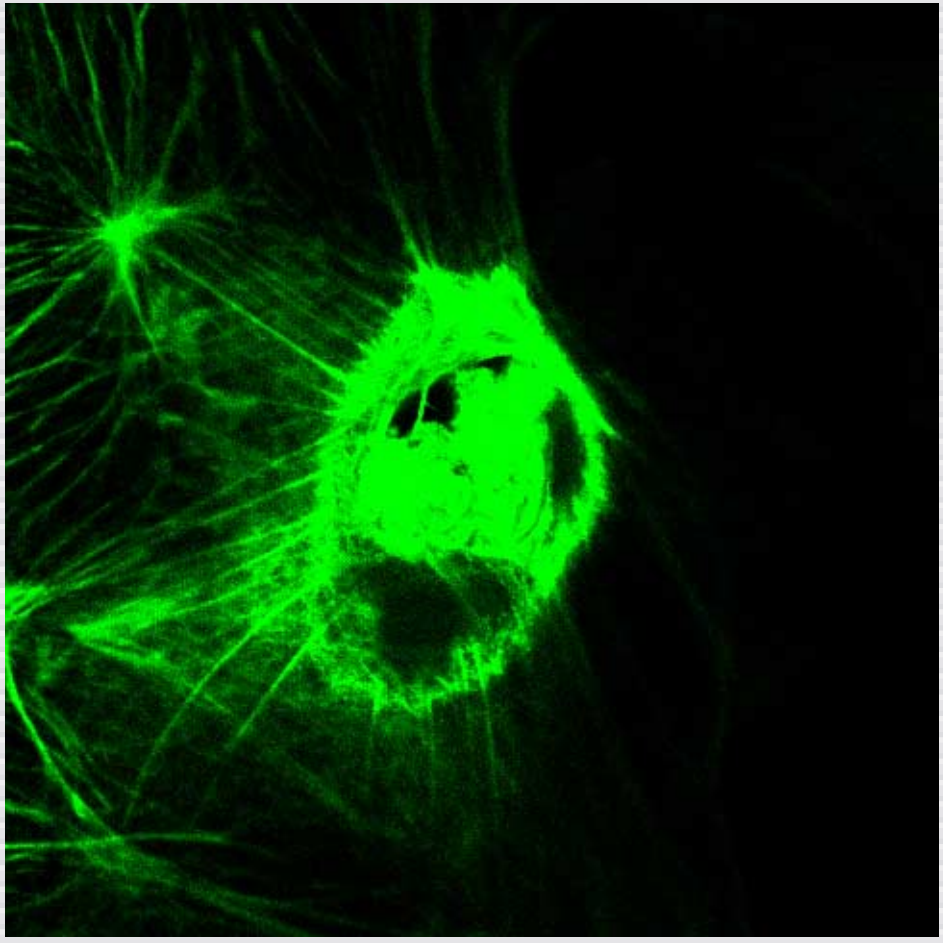

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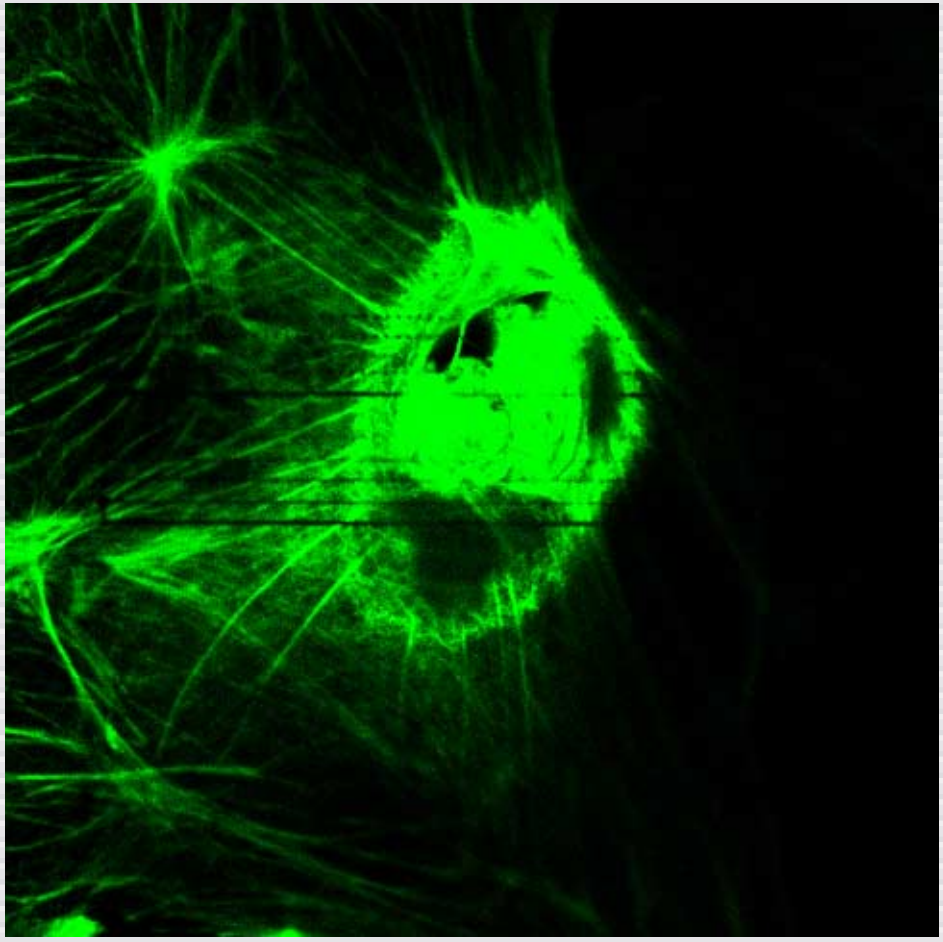
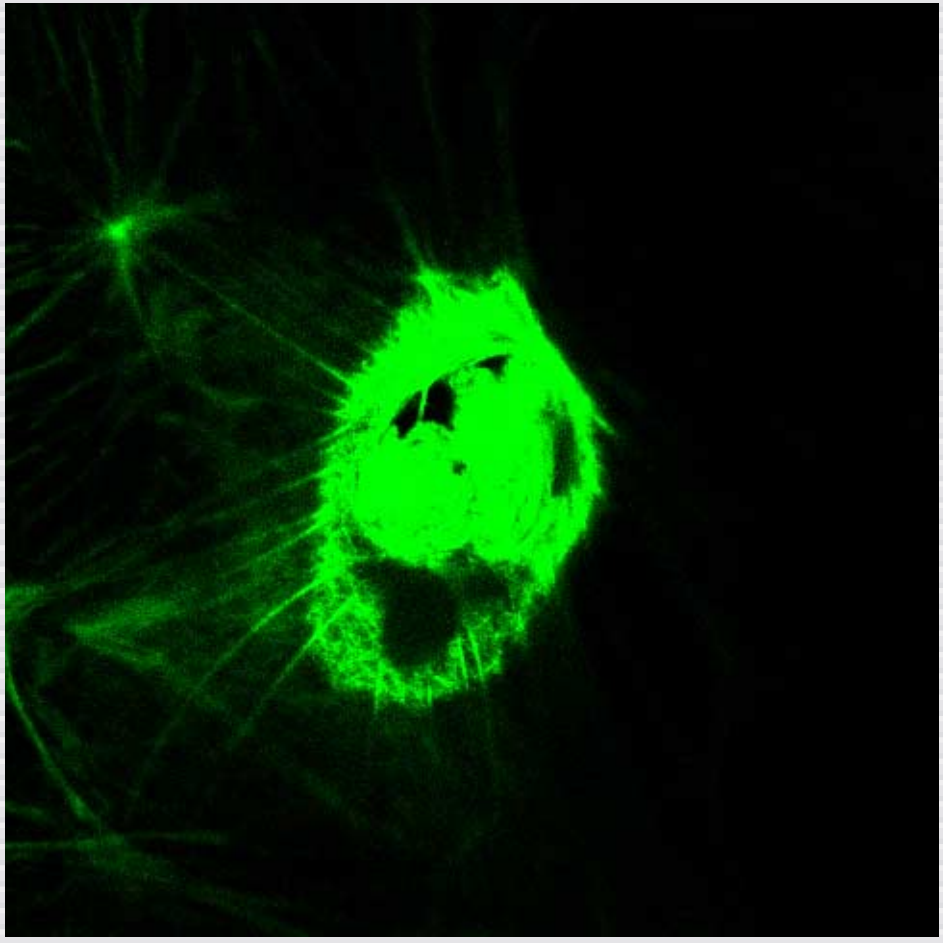


Low-energy processing

before



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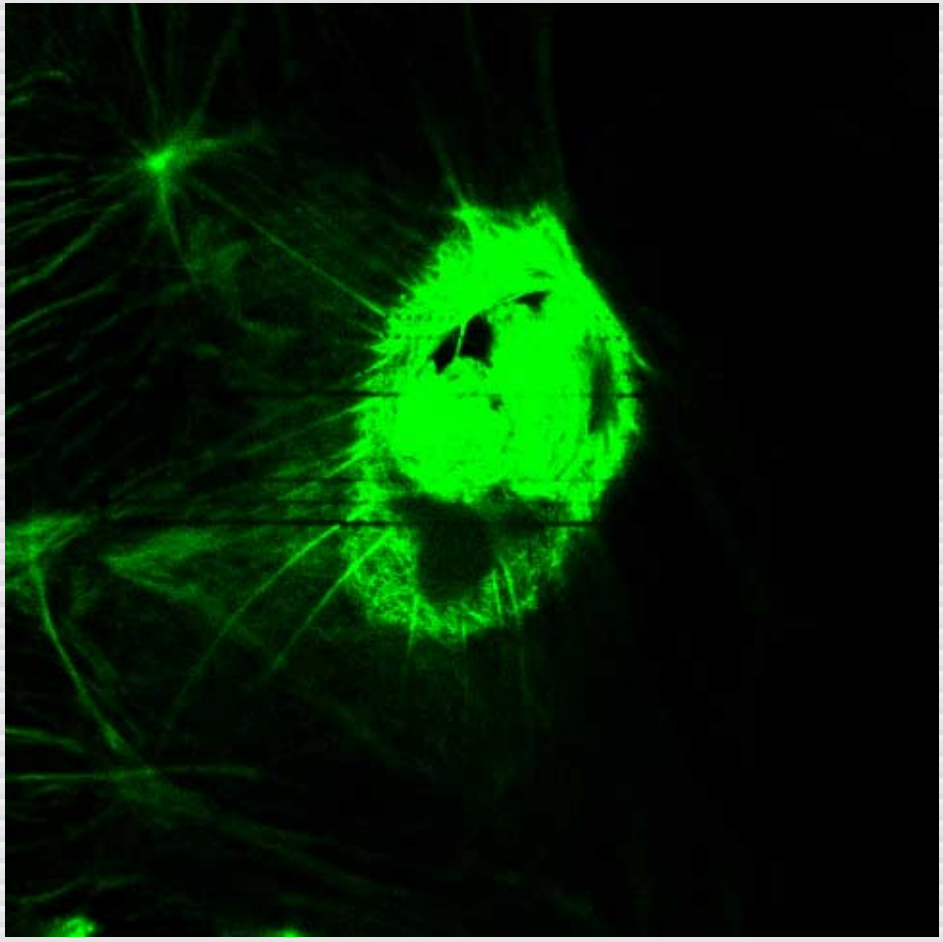

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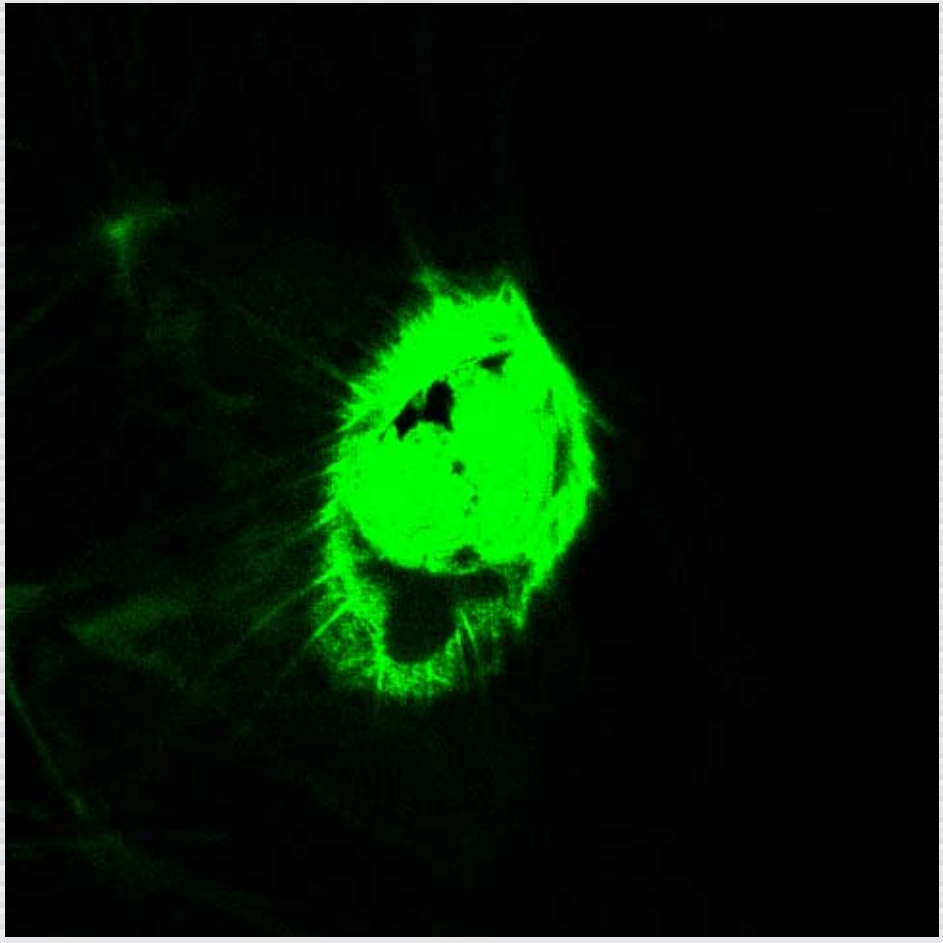
before



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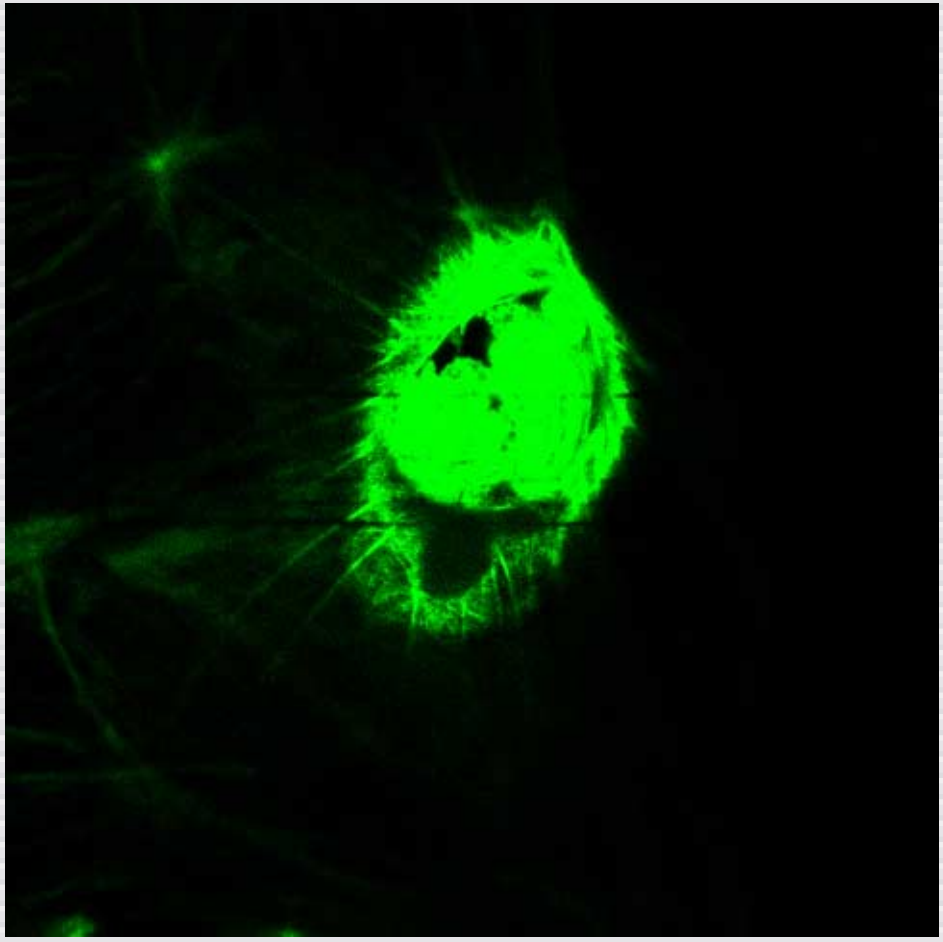

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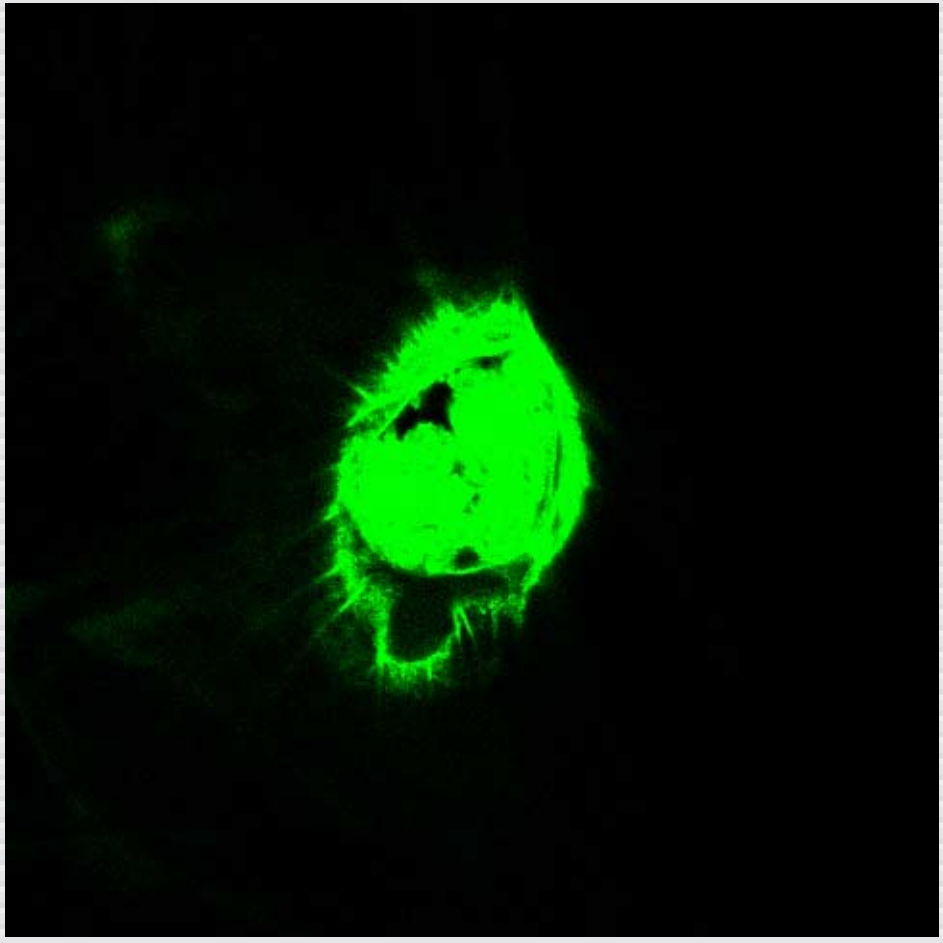

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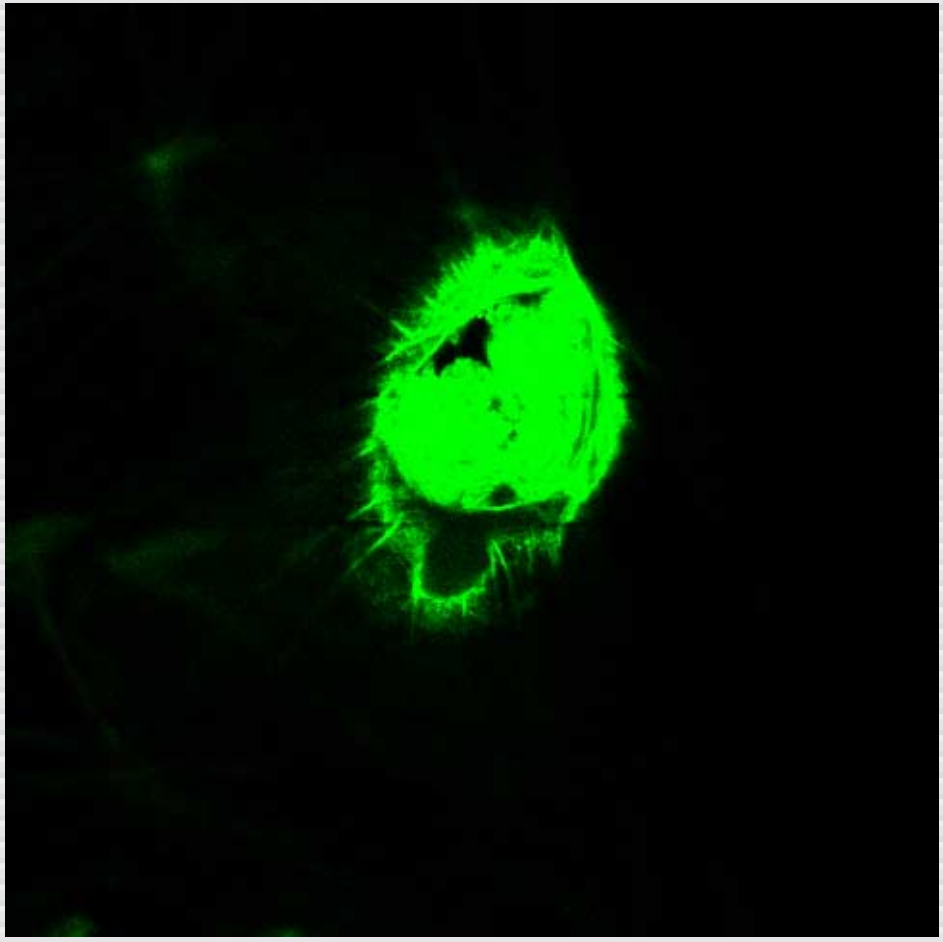

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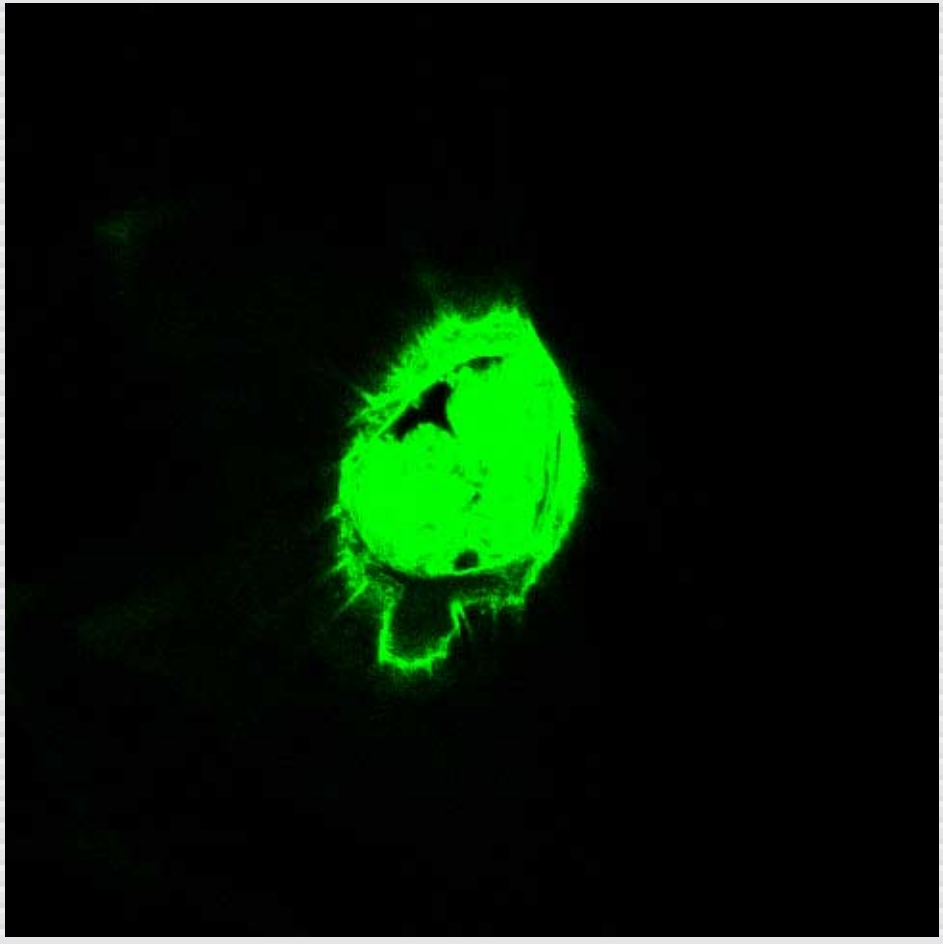

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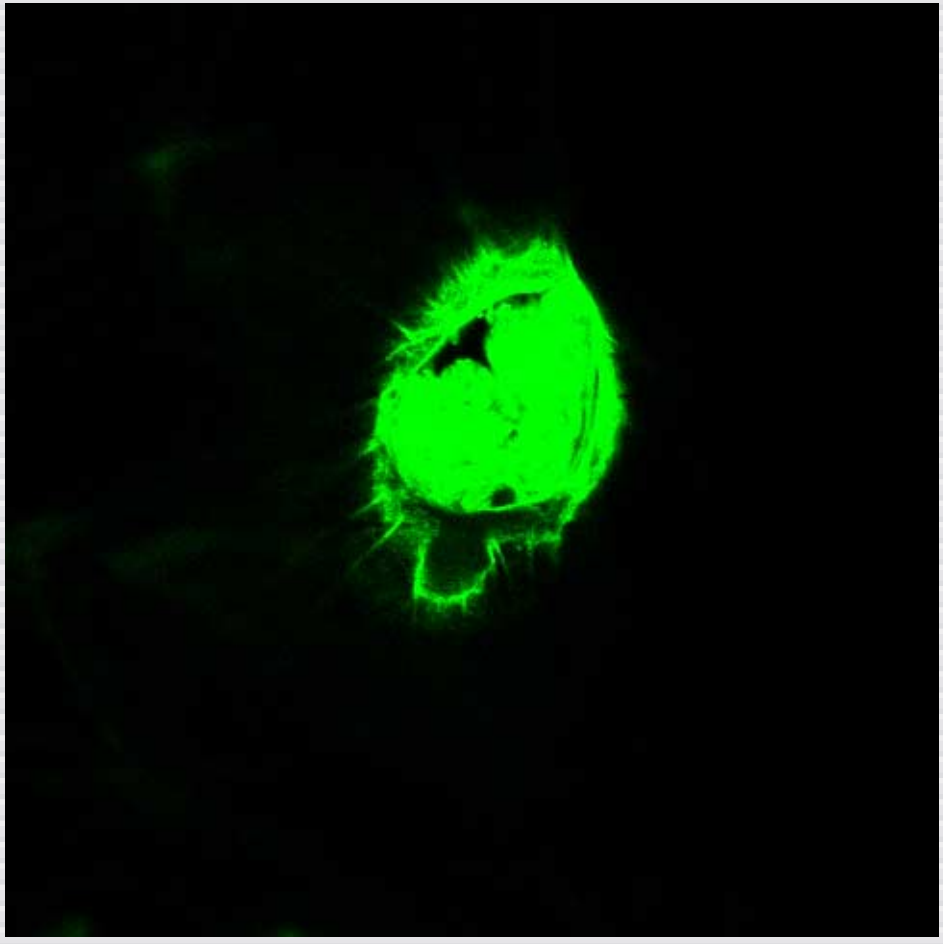

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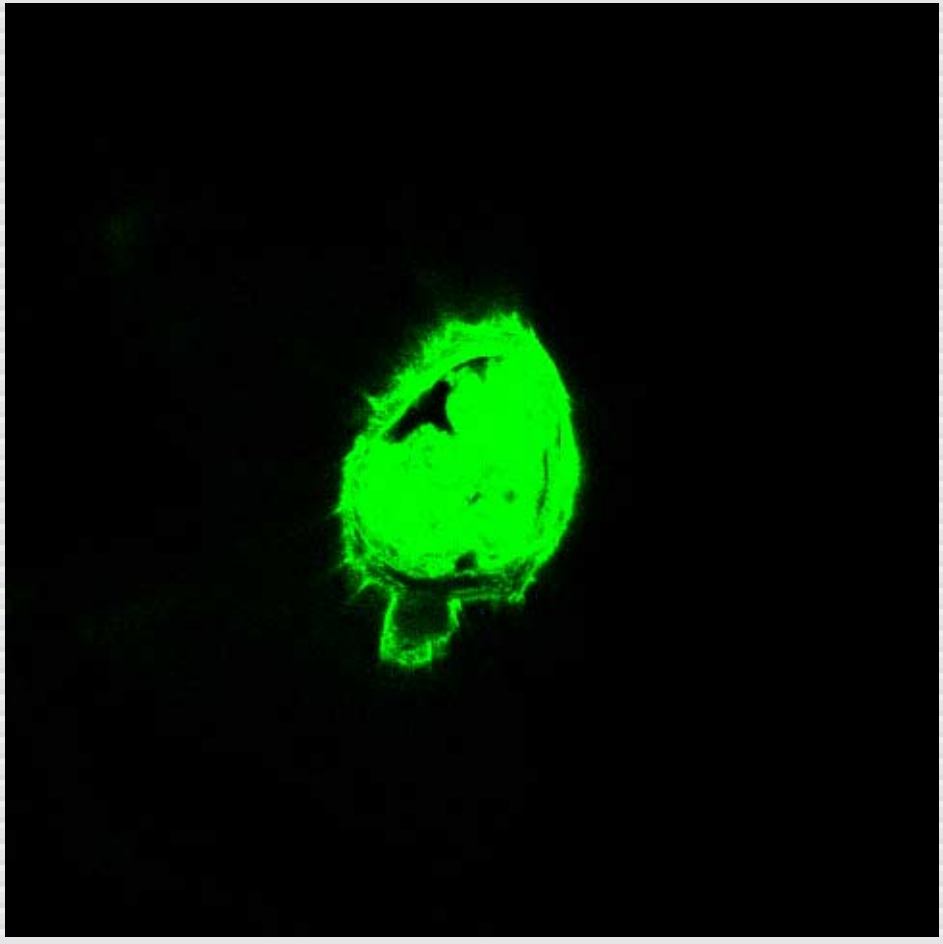

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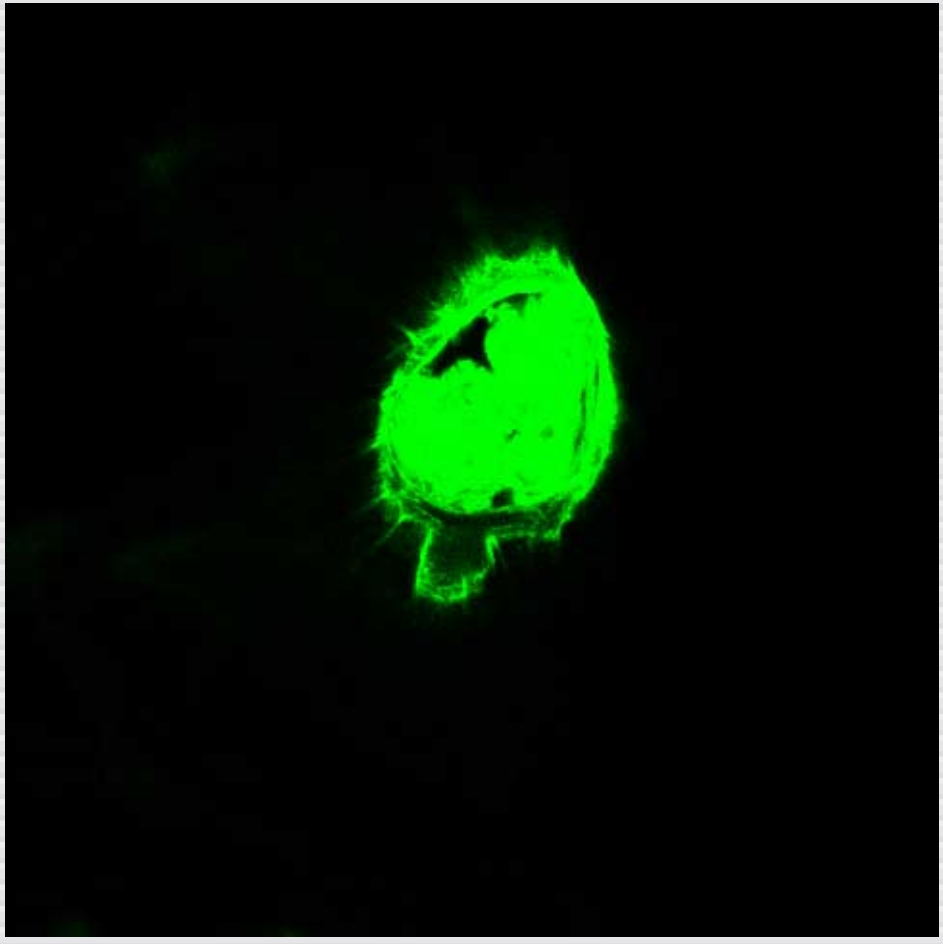

Low-energy processing

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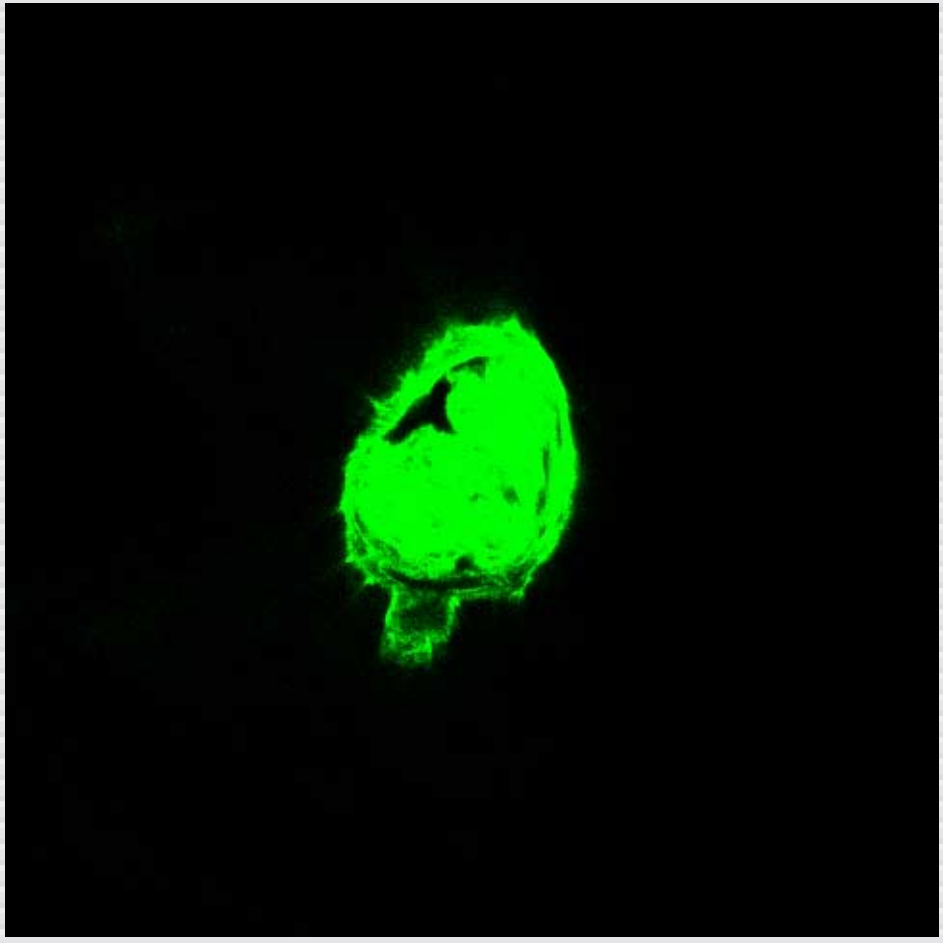

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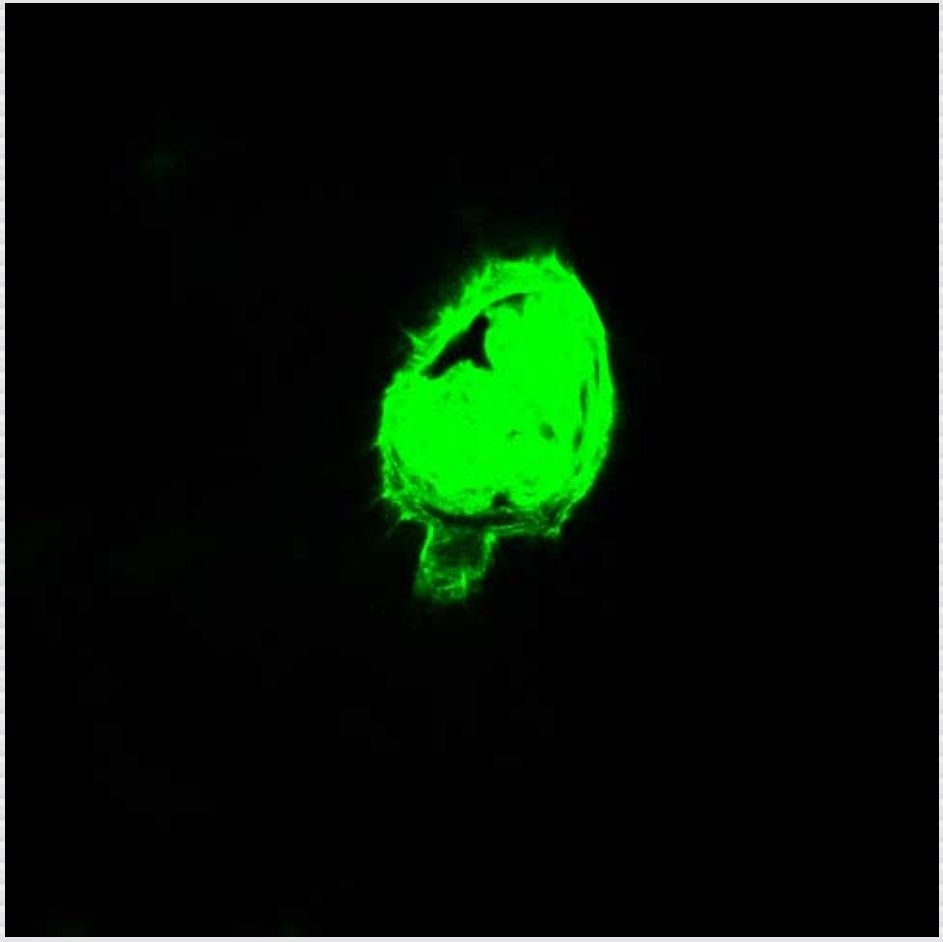
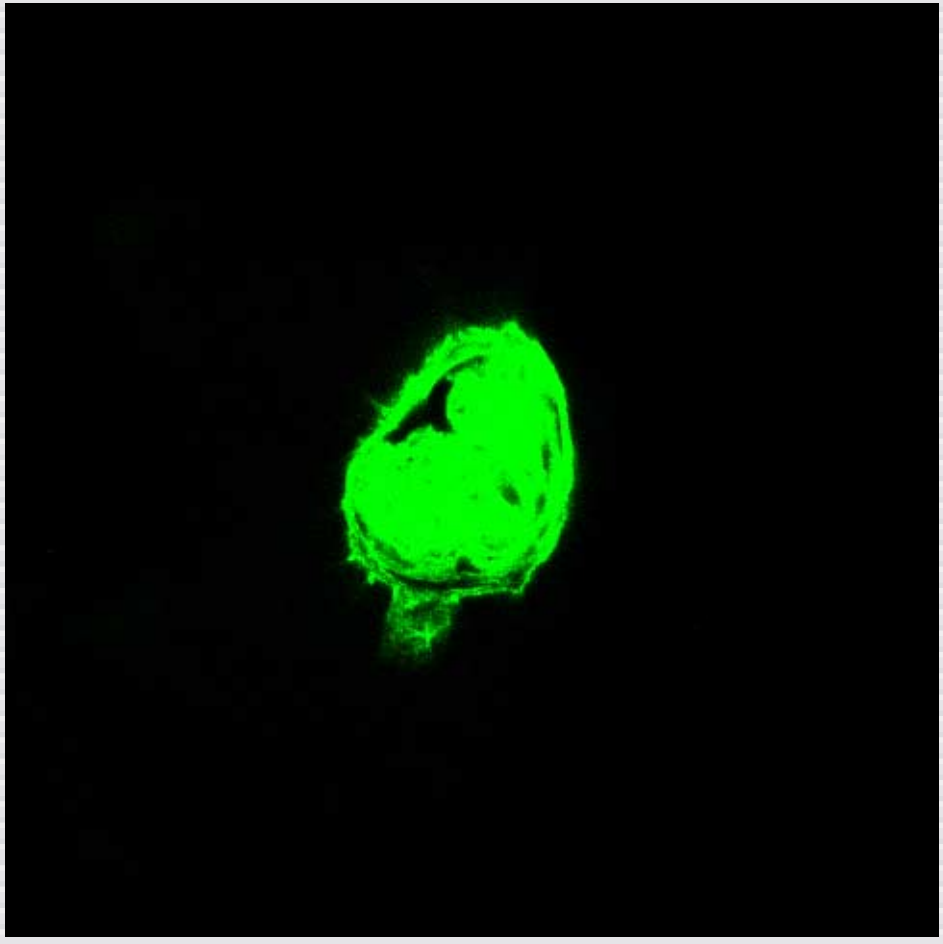


Low-energy processing

before



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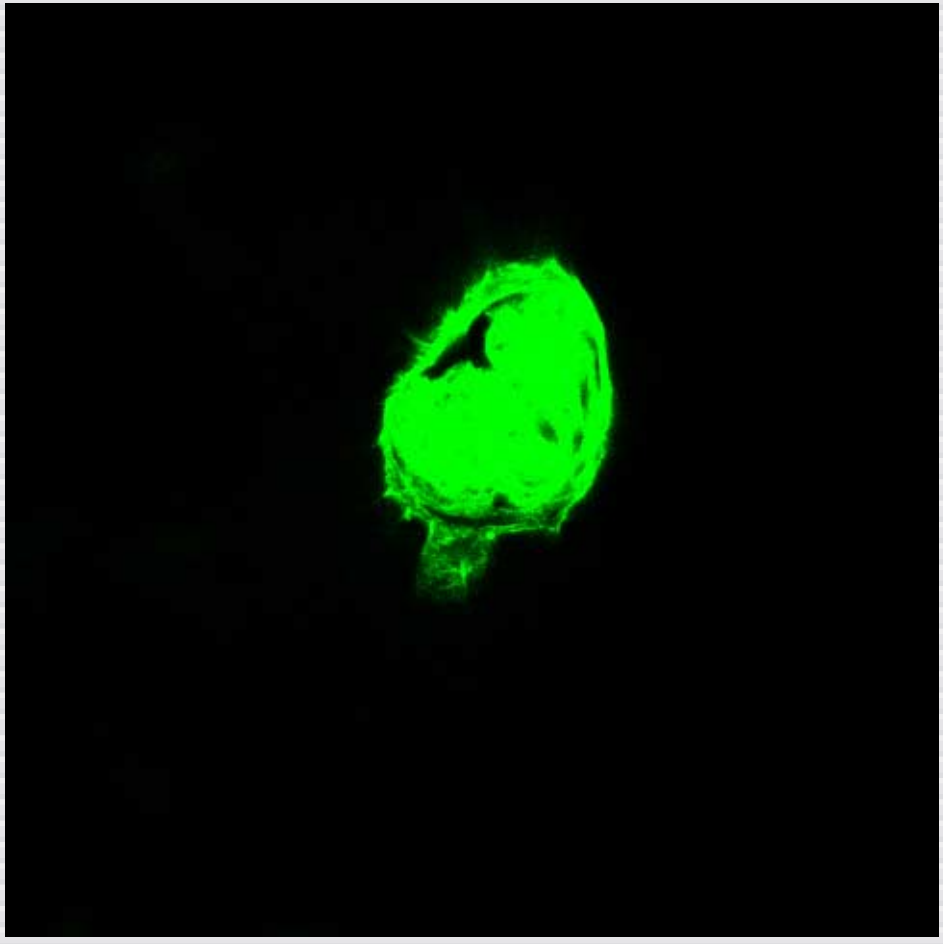

Low-energy processing

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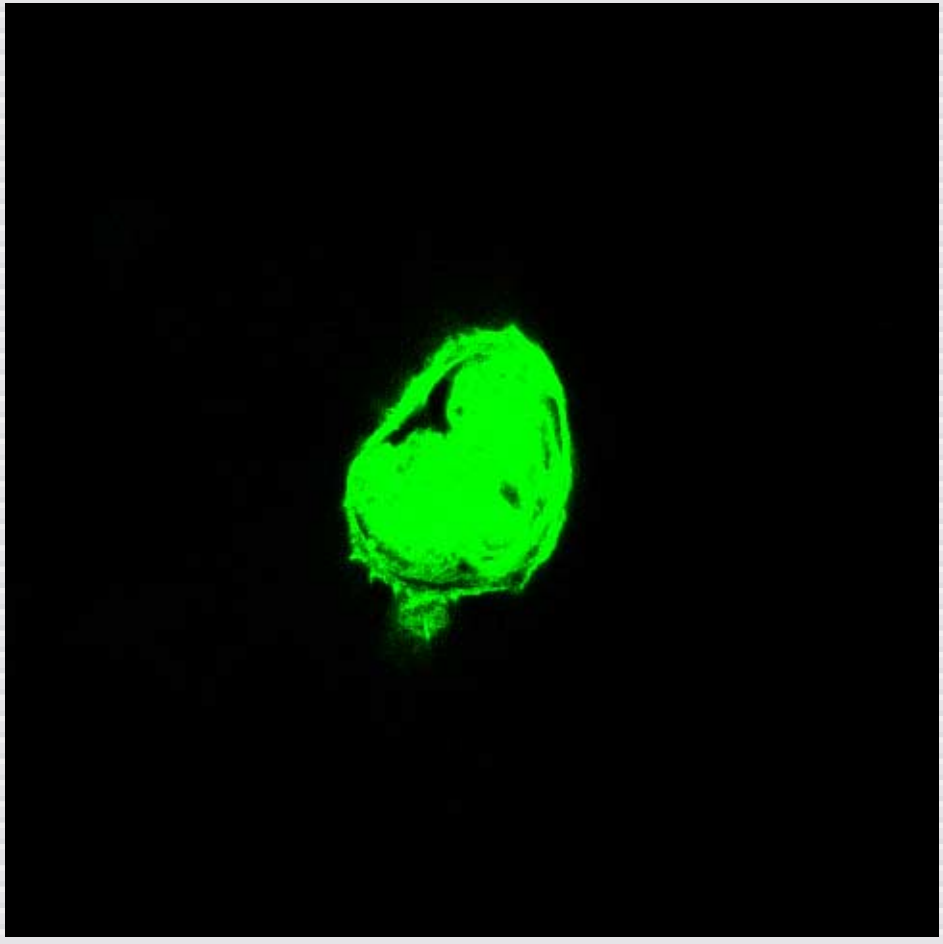

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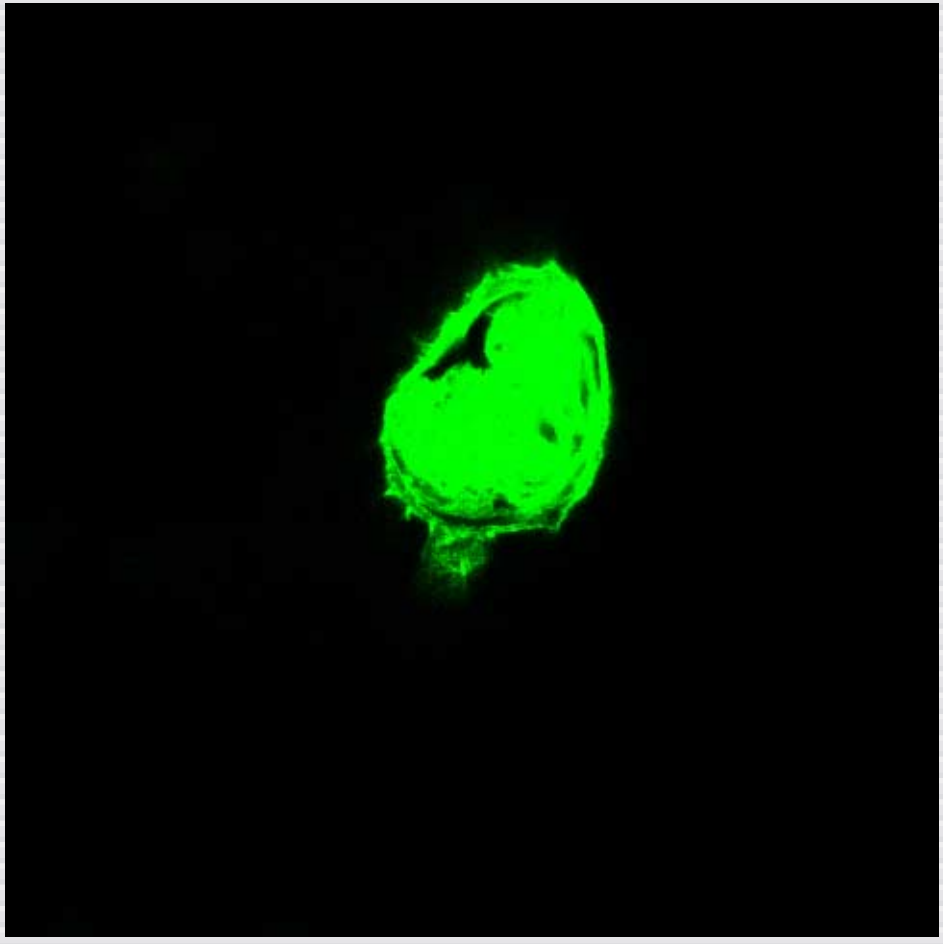
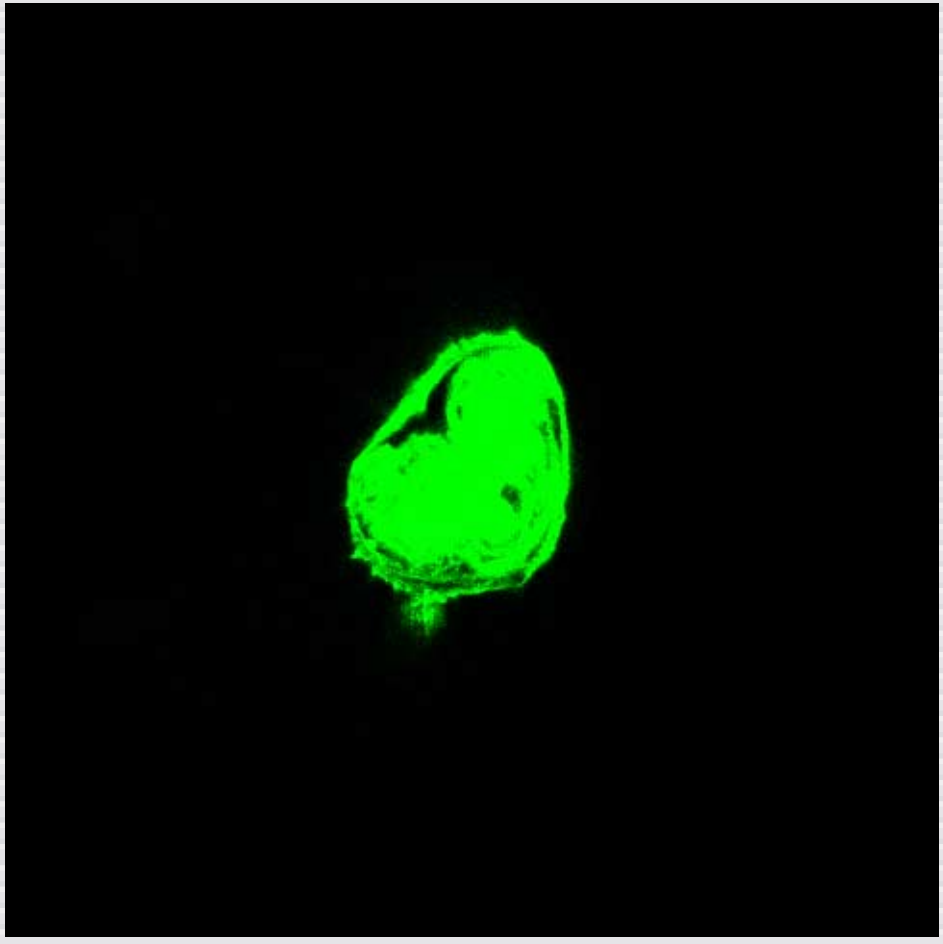


Low-energy processing

before



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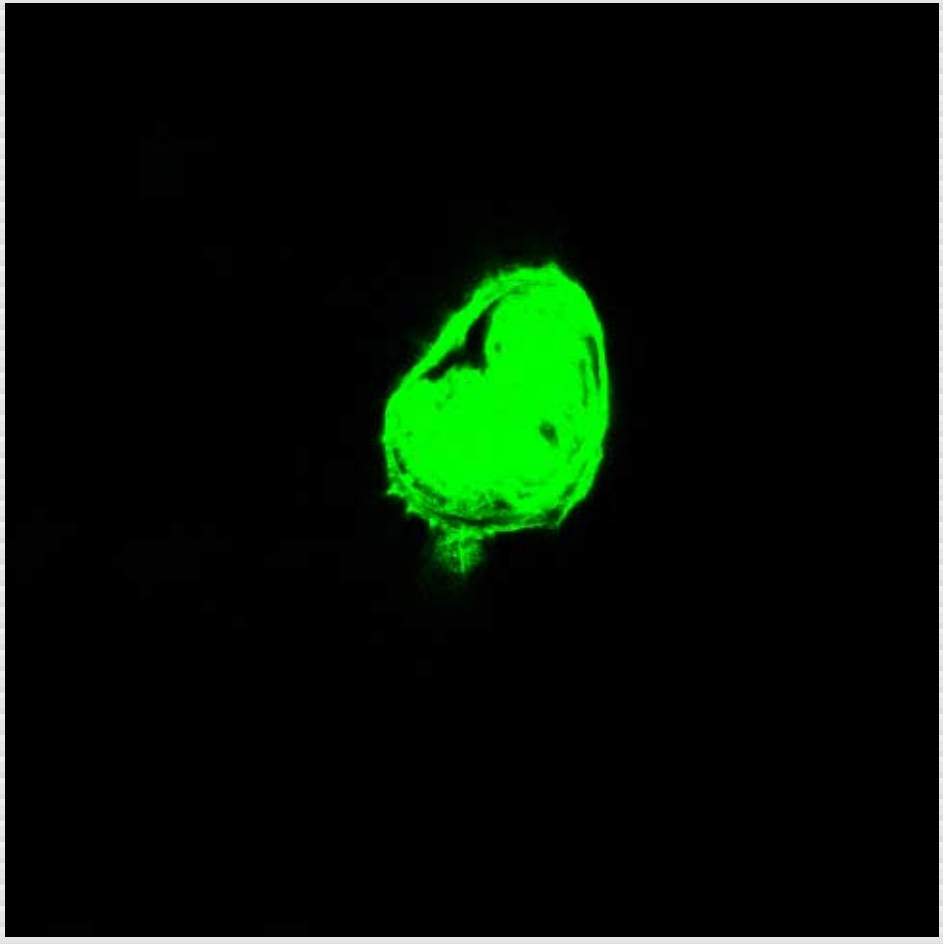
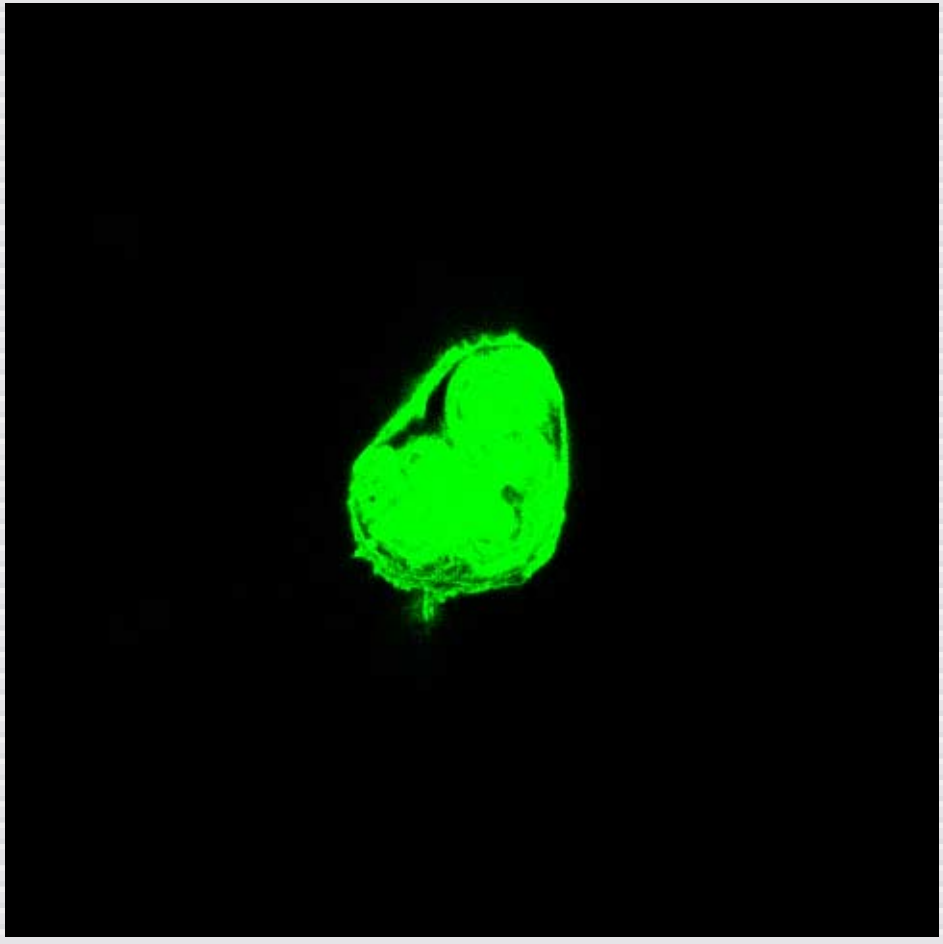


Low-energy processing

before



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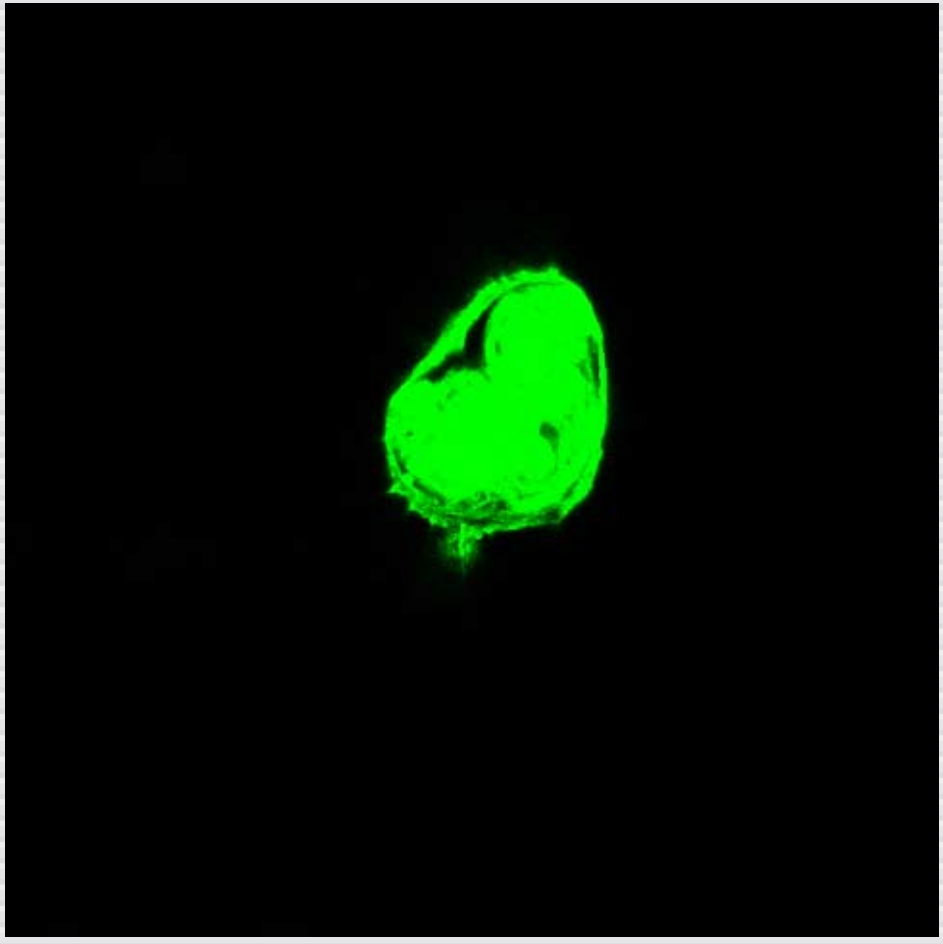
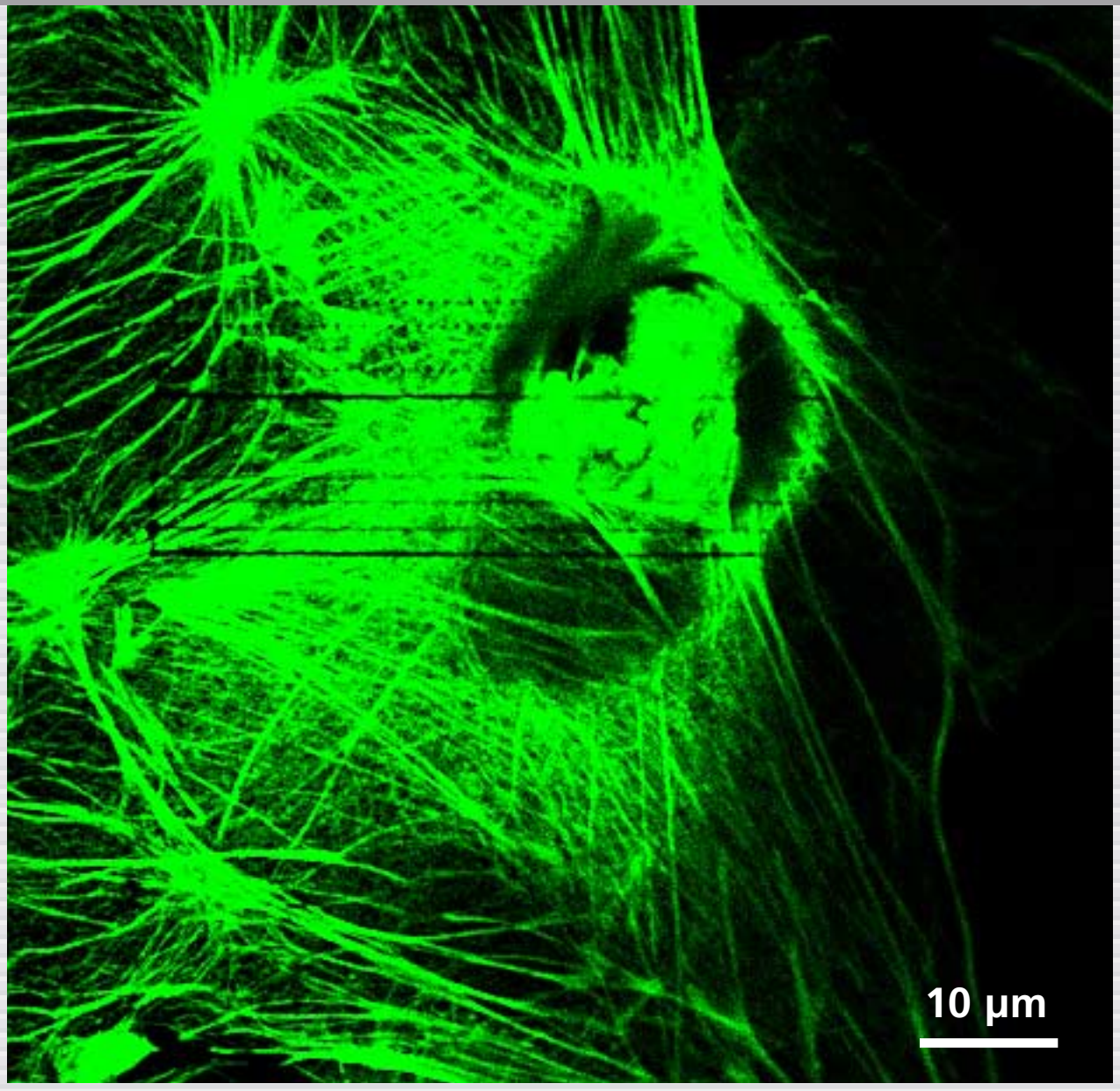


Low-energy processing



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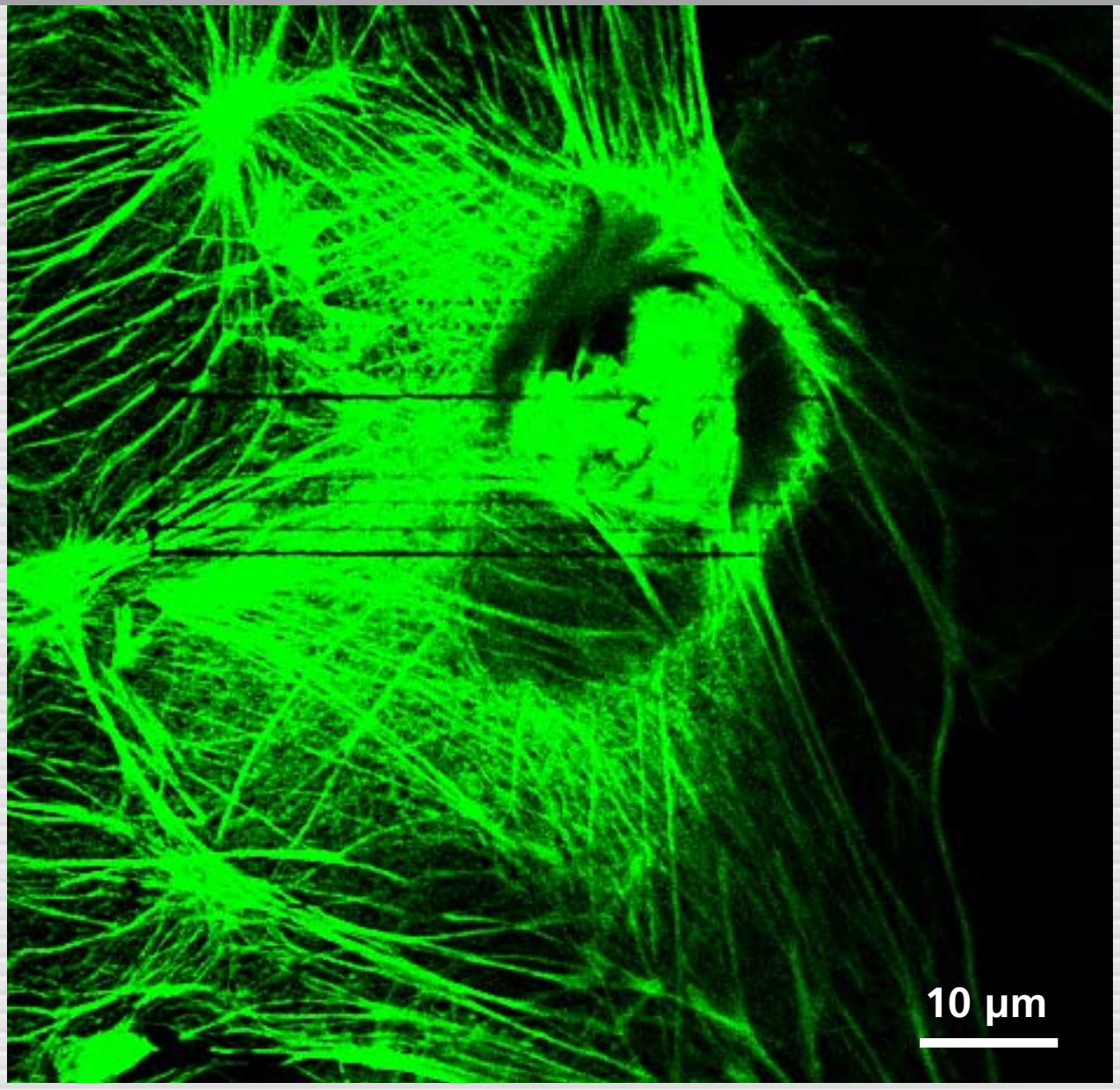

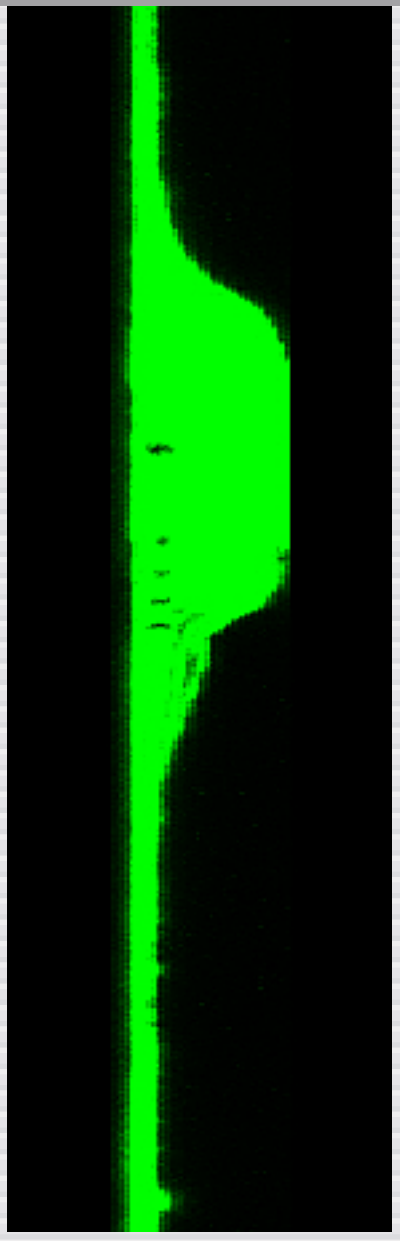

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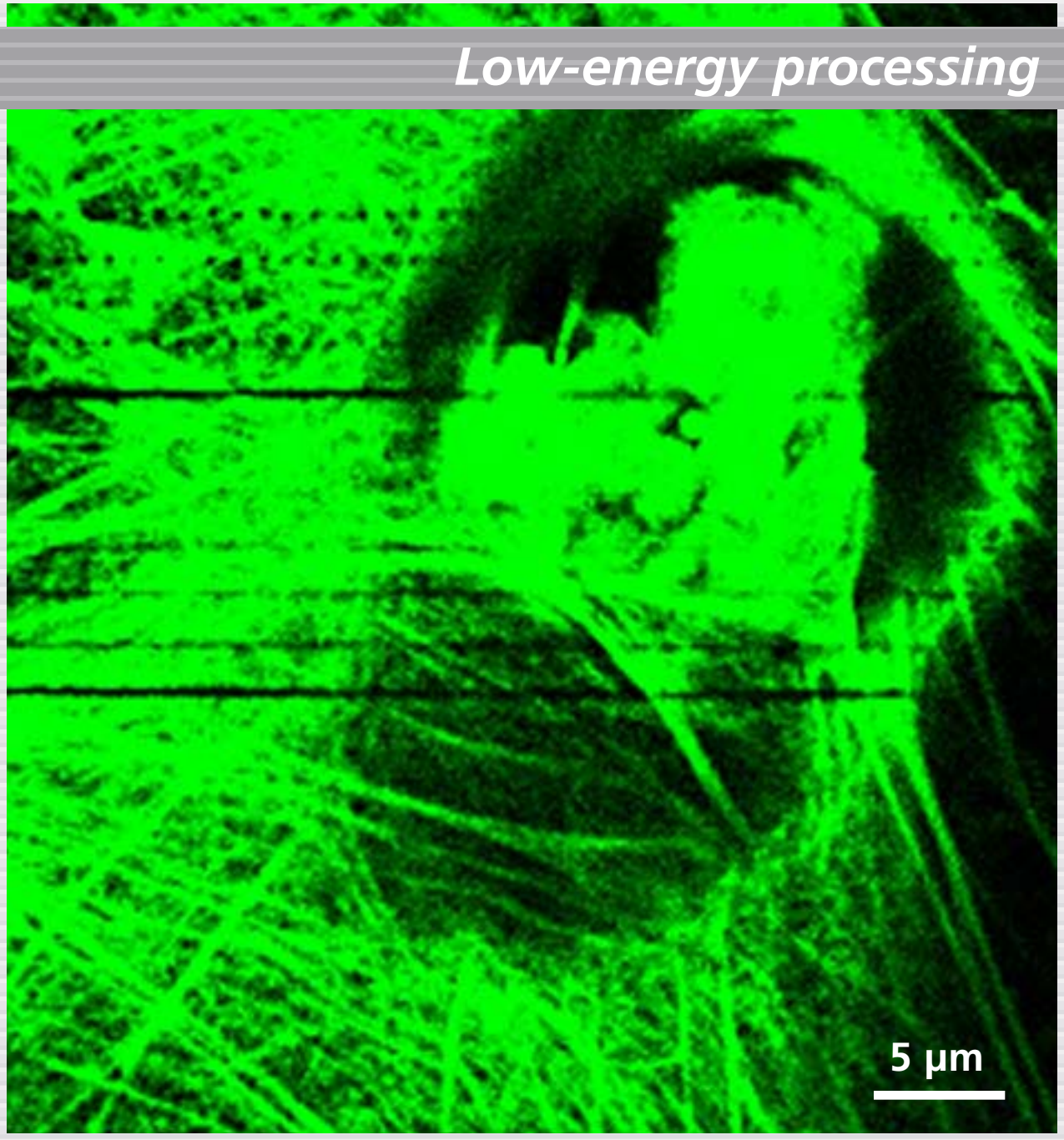

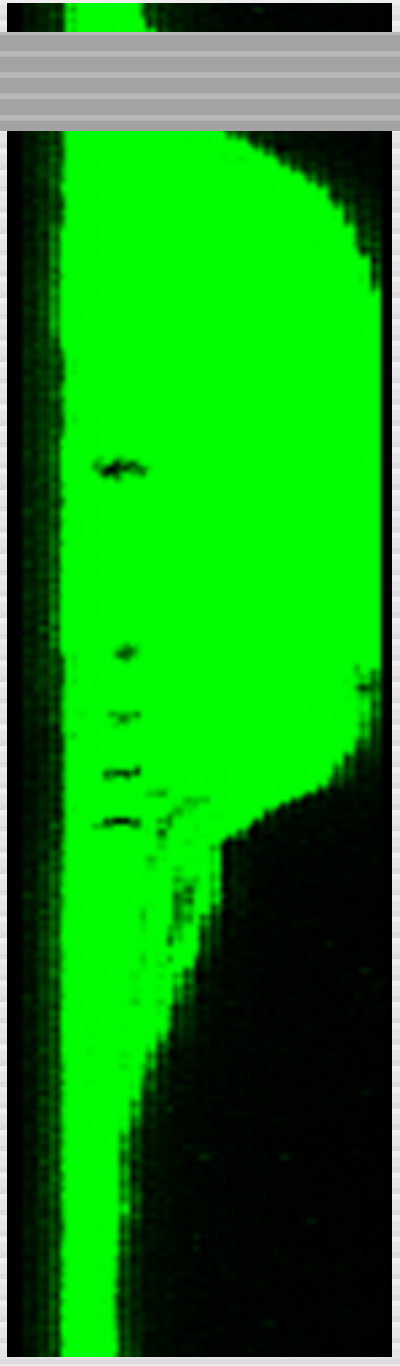

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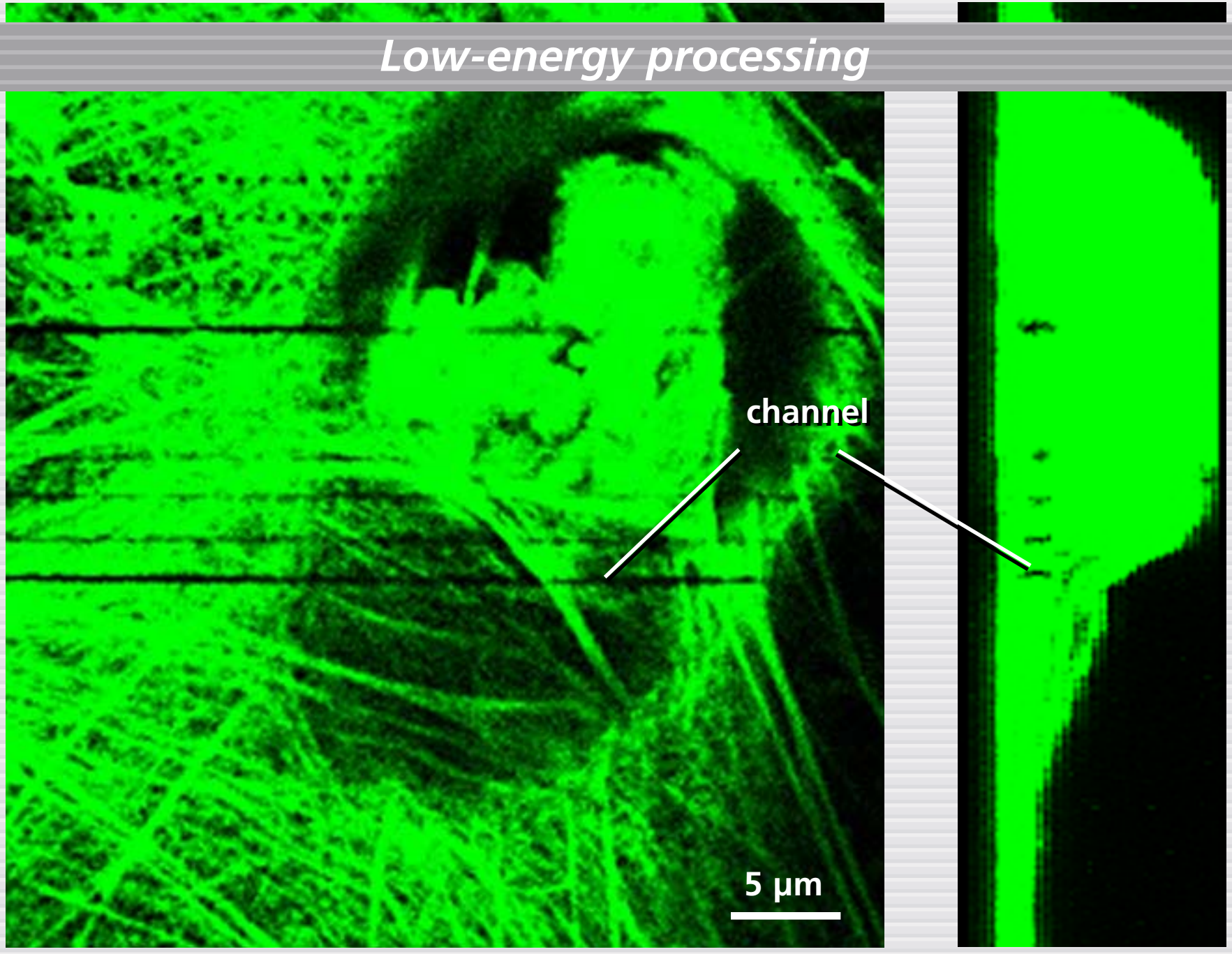

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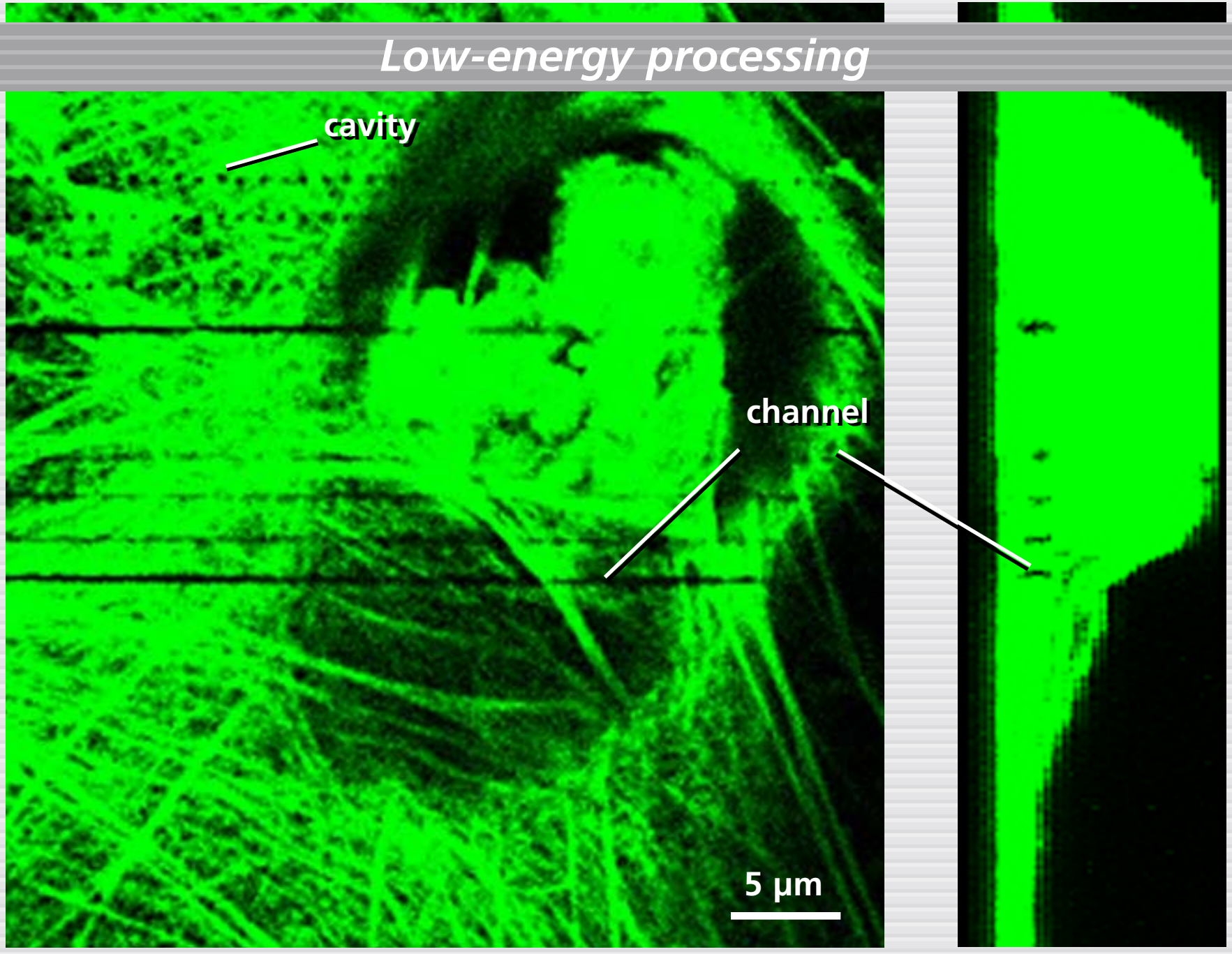

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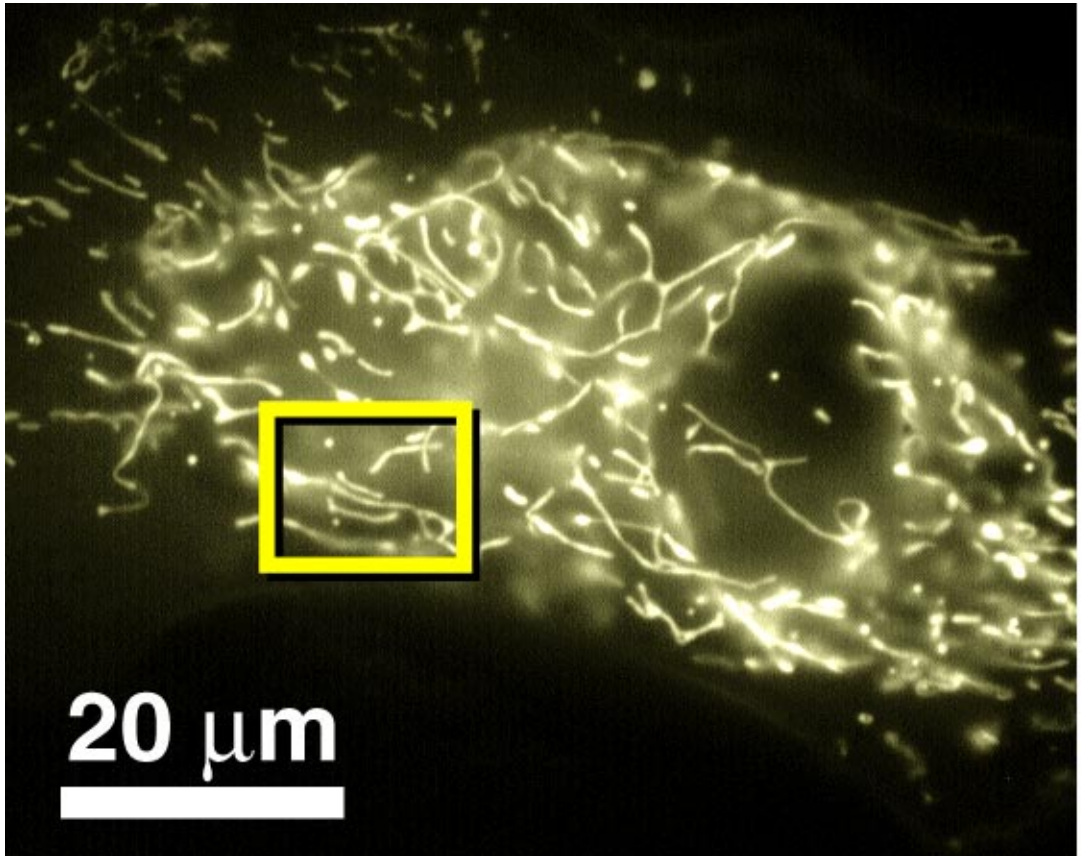
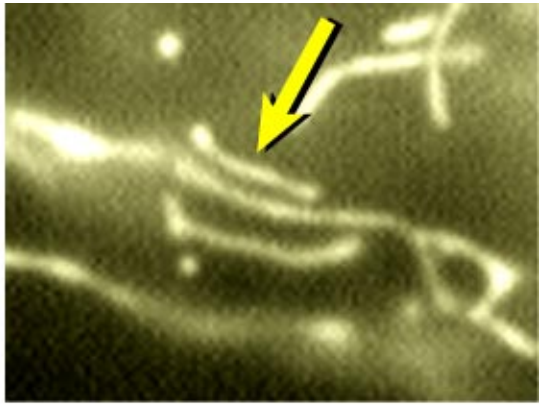
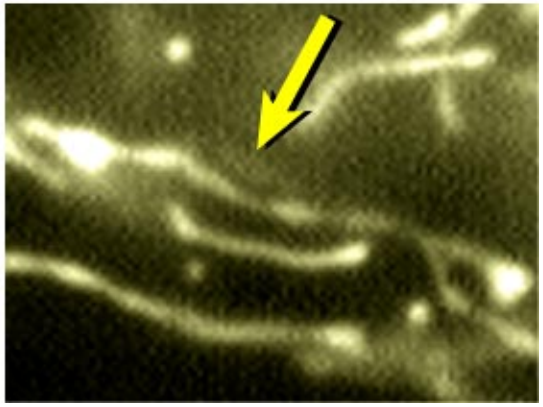
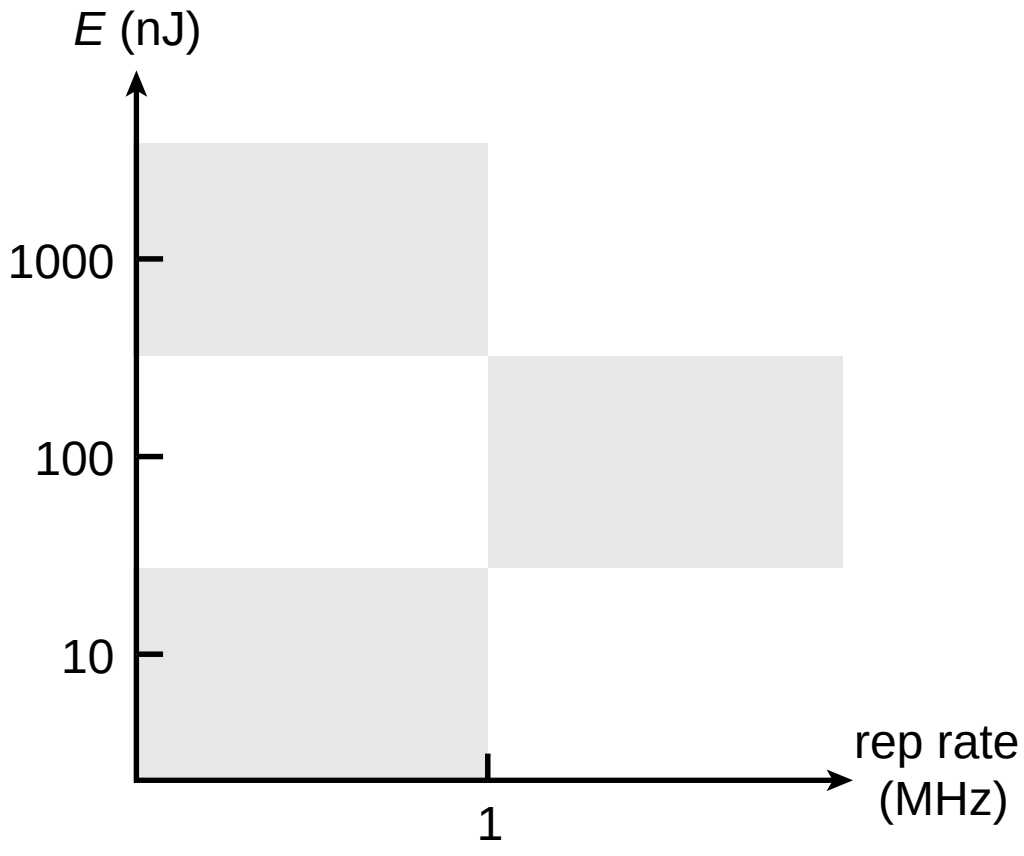


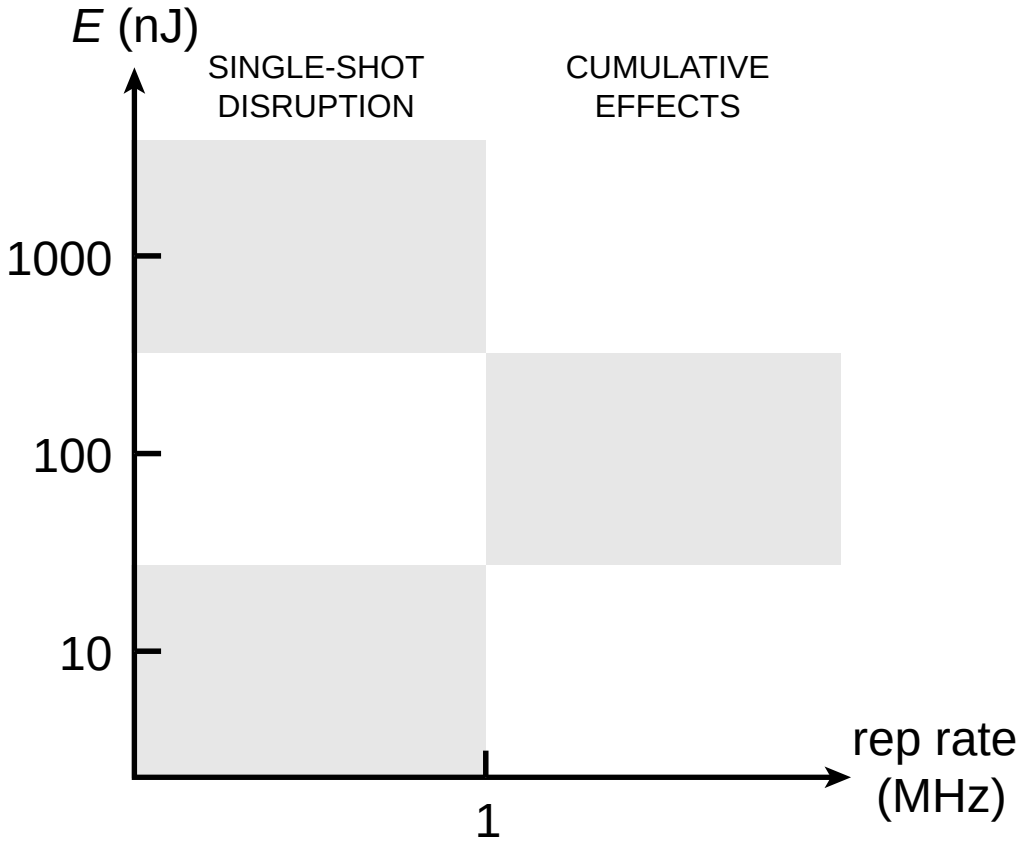




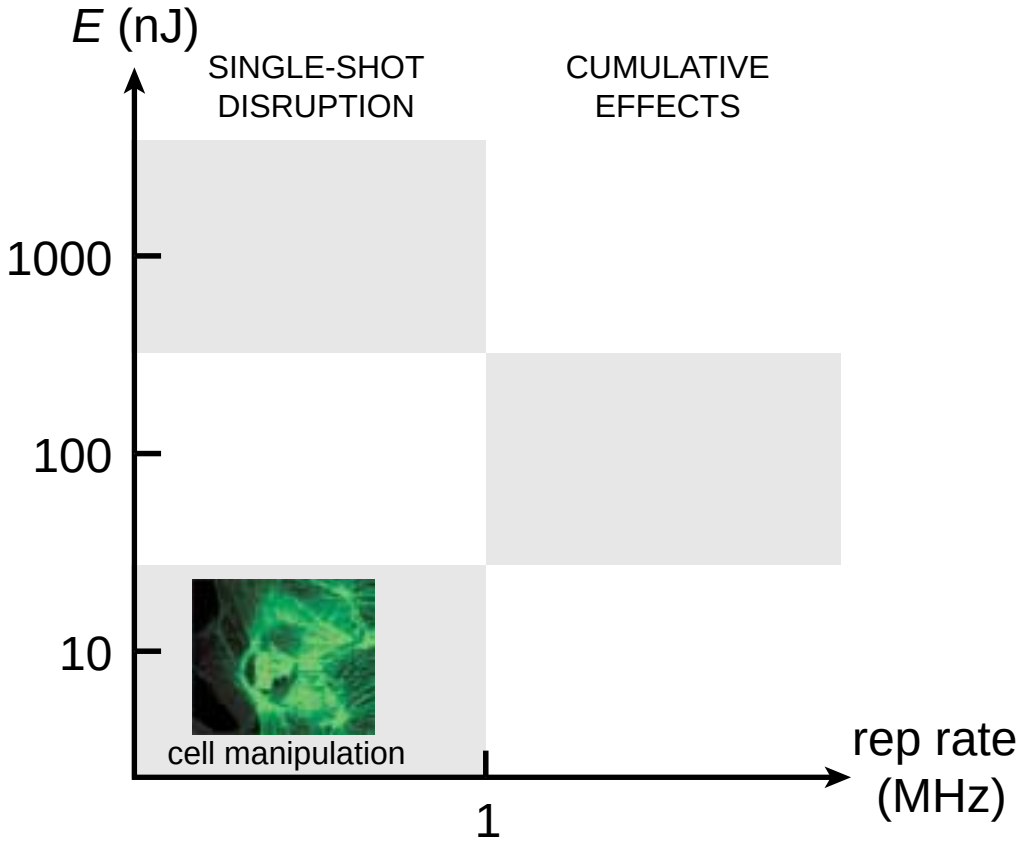
Summary



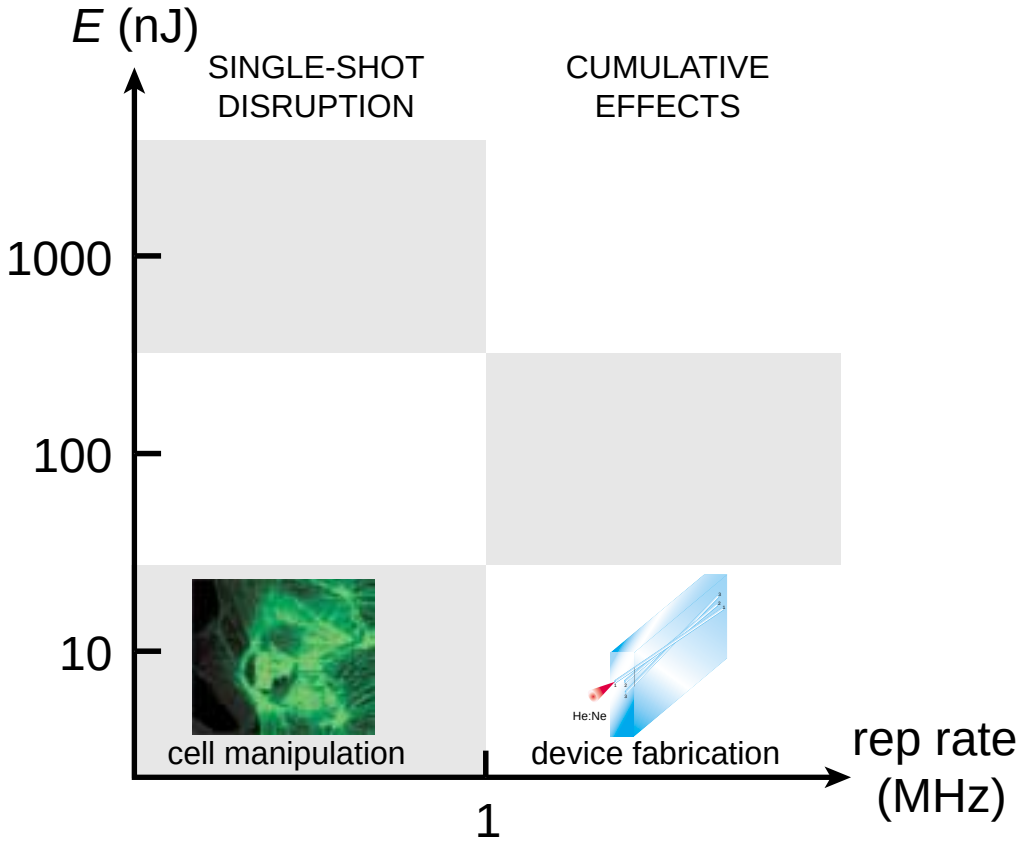
Summary


E (nJ)
SINGLE-SHOT DISRUPTION
CUMULATIVE EFFECTS
1000
100
10
1
rep rate (MHz)

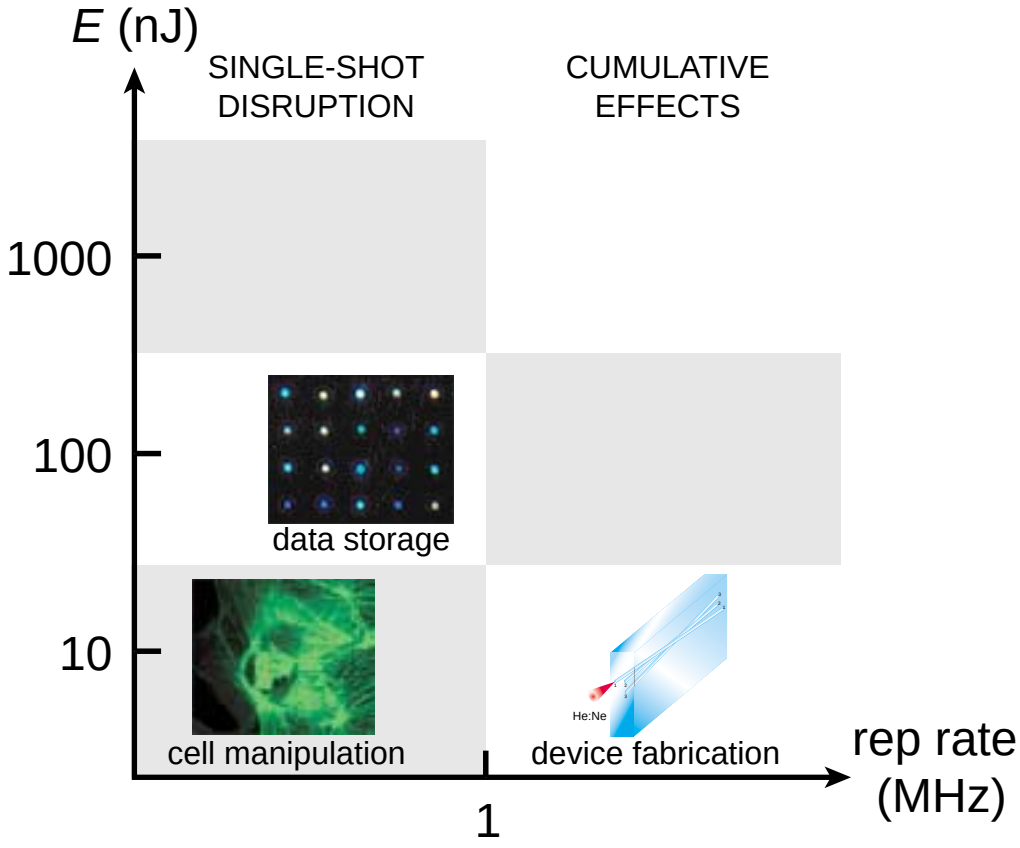
Summary


E (nJ)
SINGLE-SHOT DISRUPTION
CUMULATIVE EFFECTS
1000
100
10
cell manipulation
1
rep rate (MHz)

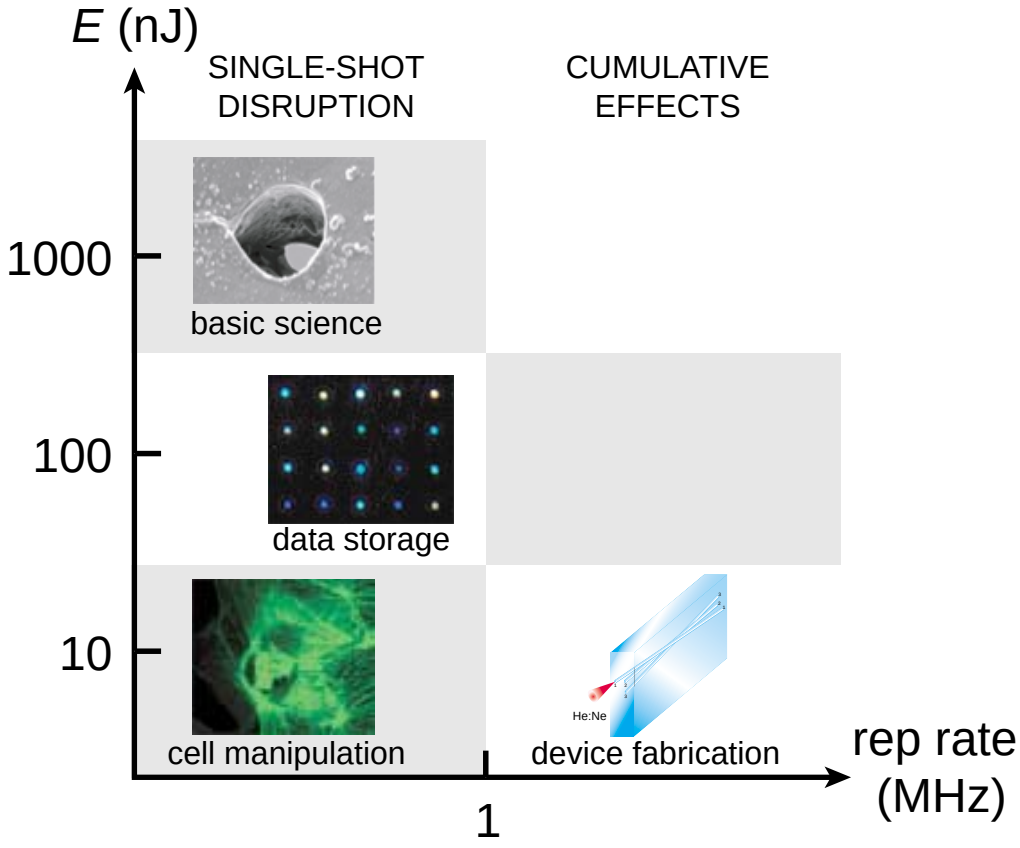
Summary


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

Summary


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

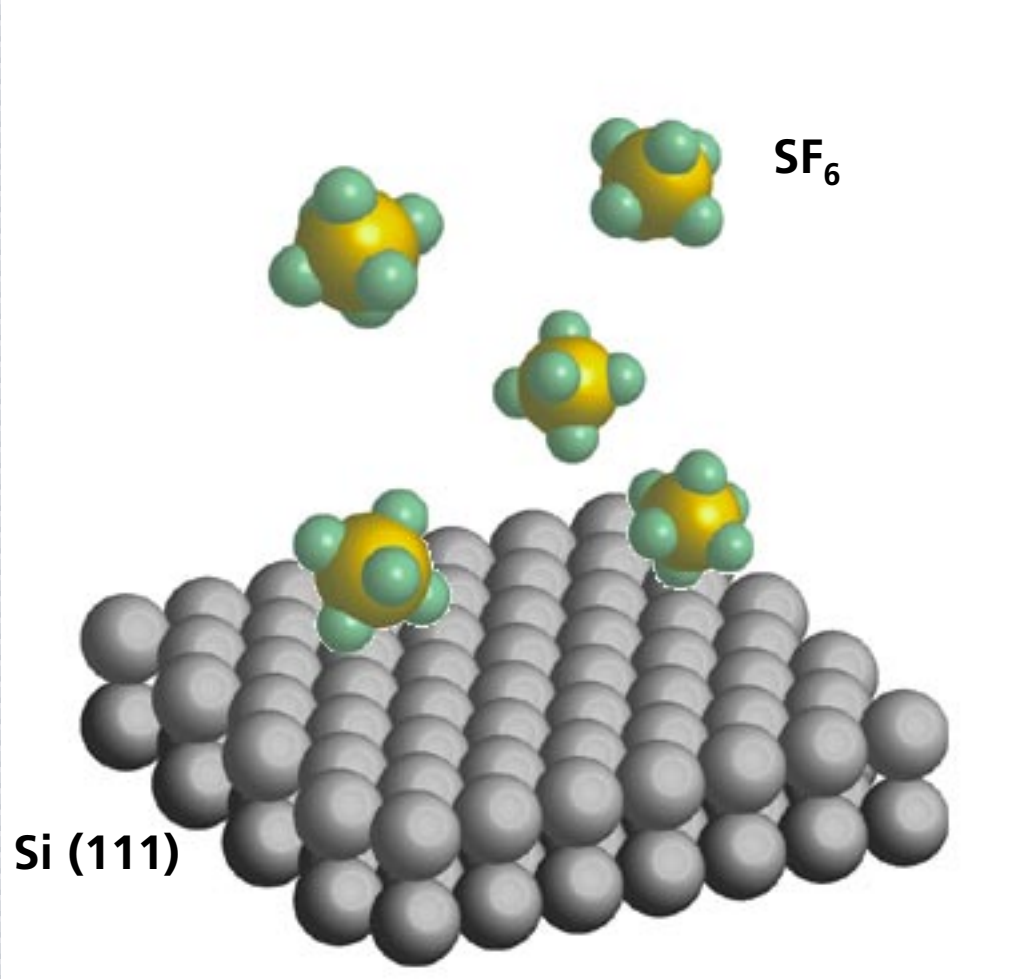
Summary


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

Conclusions

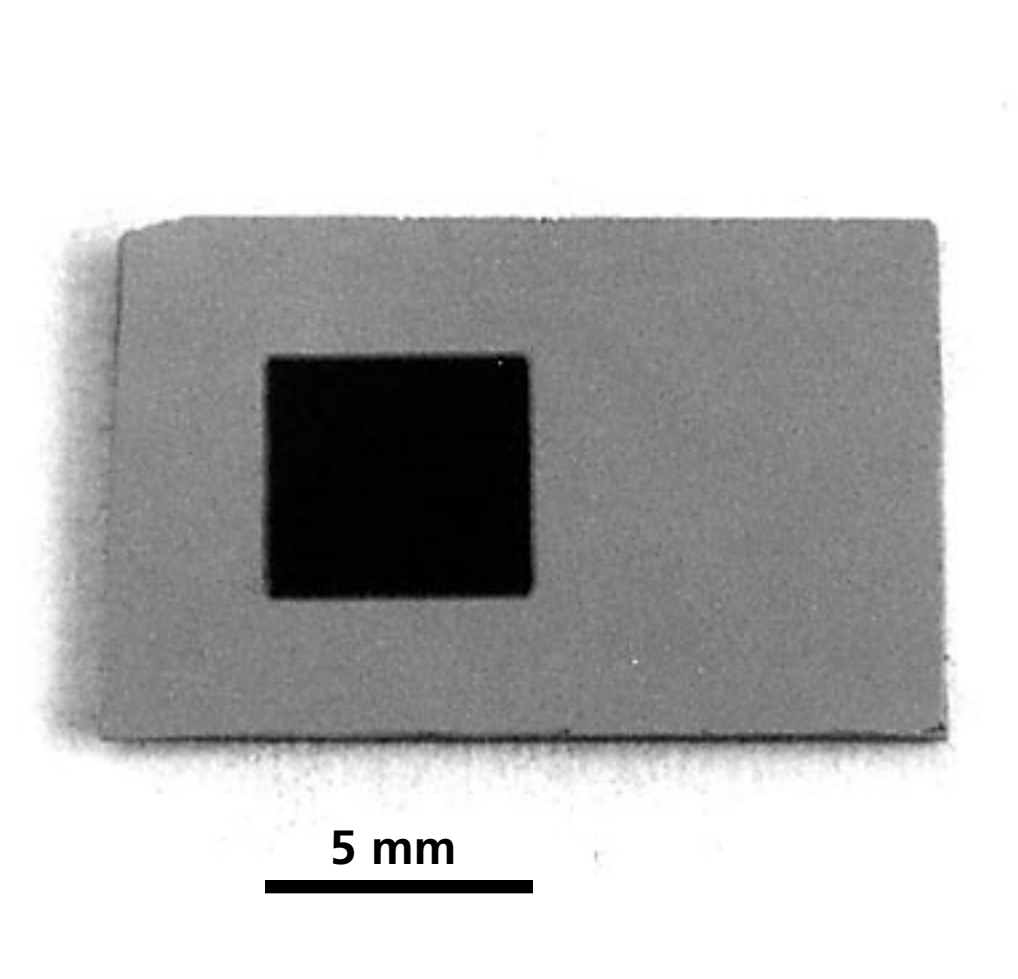
- **stellar conditions**
- **precision micromachining**
- **exciting new applications**

Introduction



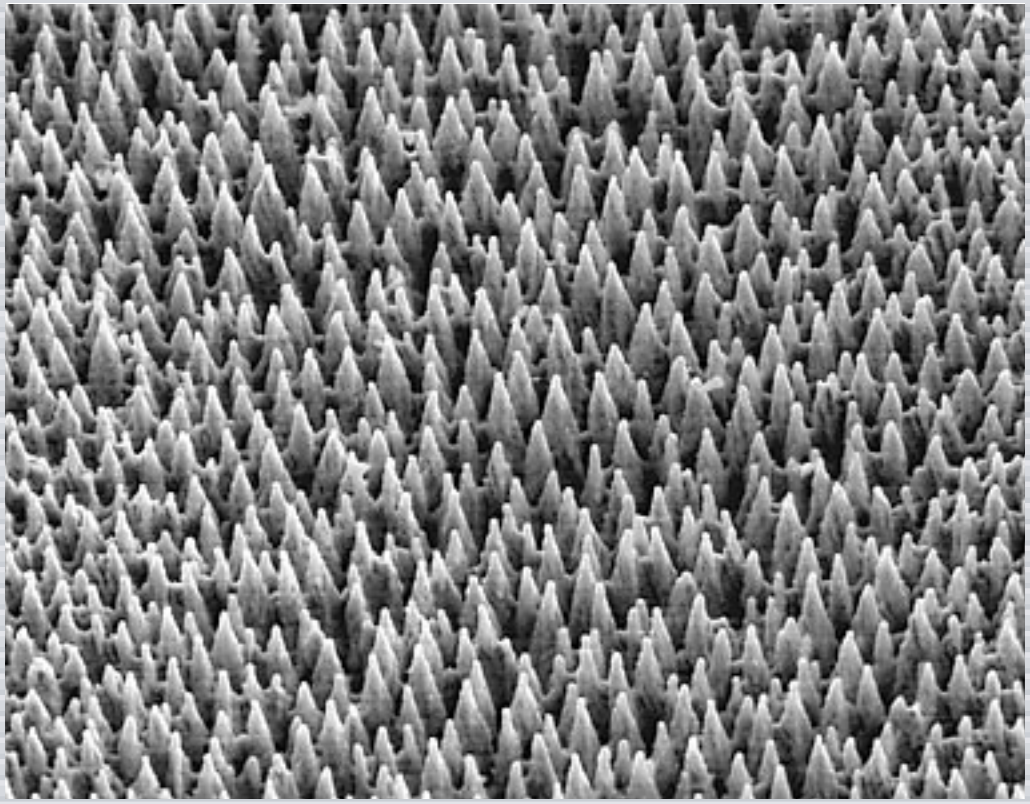
irradiate with 100-fs 10 kJ/m^2 pulses

Introduction



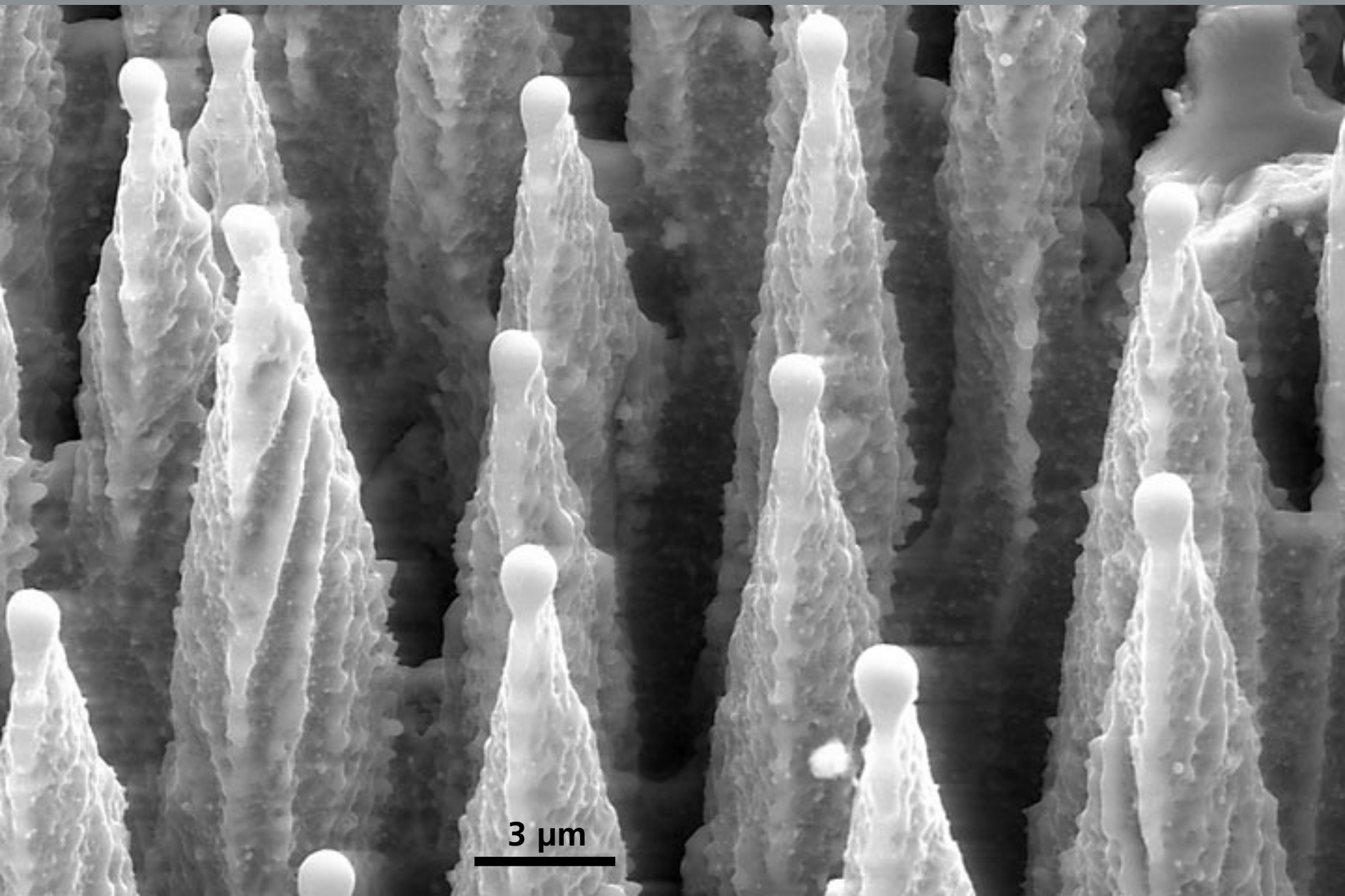
“black silicon”

Introduction

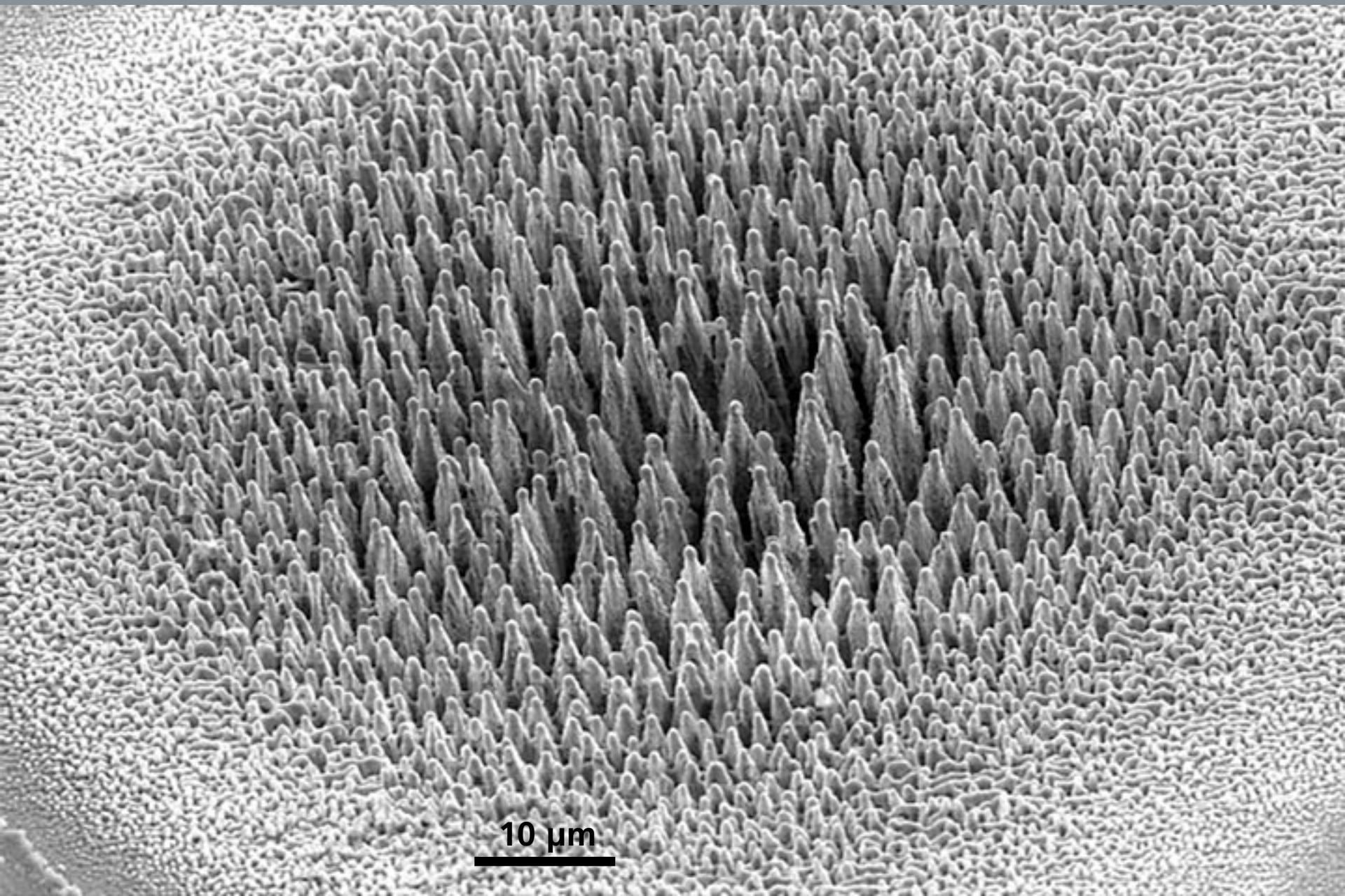


20 μm

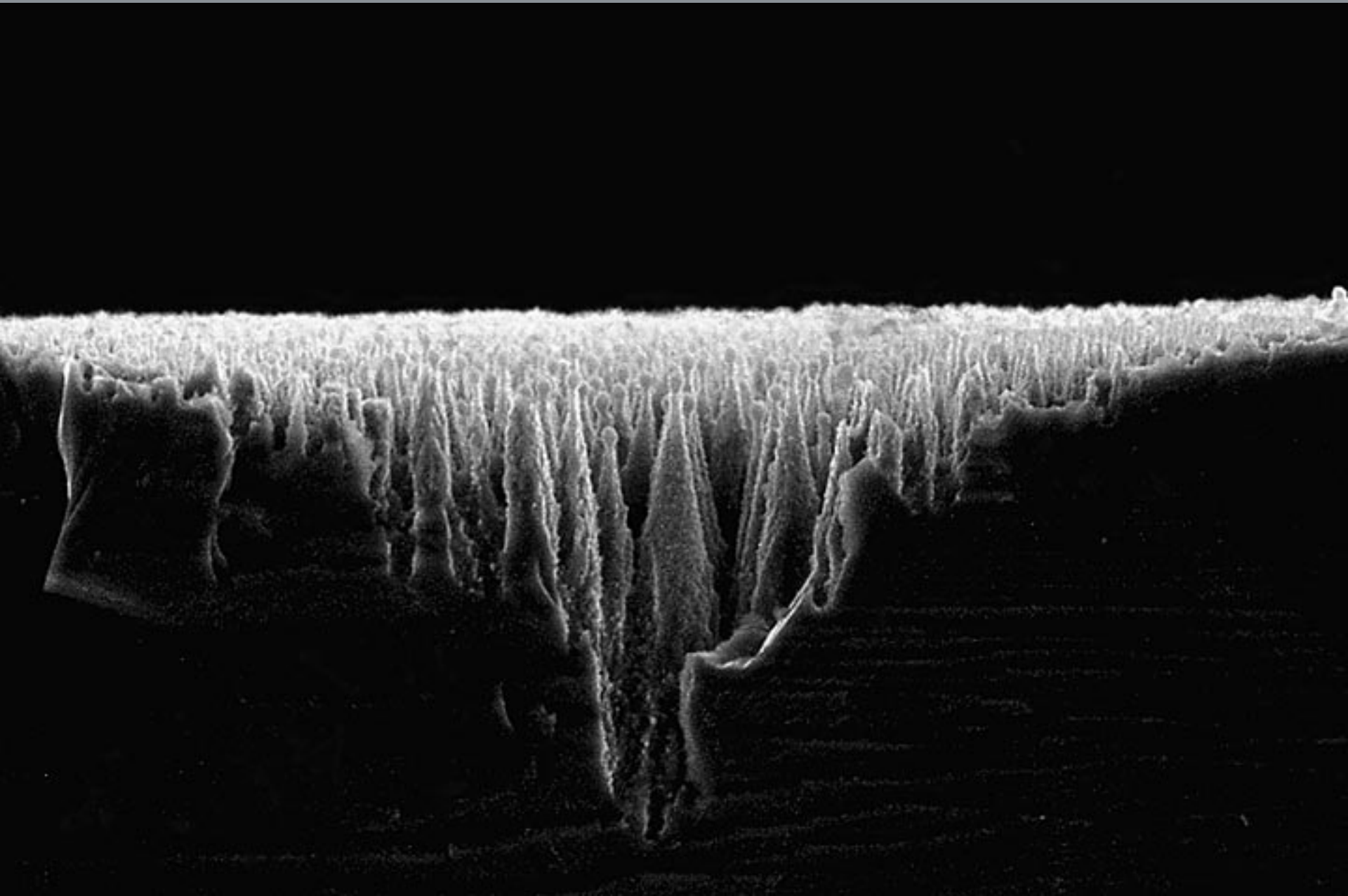
Introduction



Introduction



Introduction



Introduction

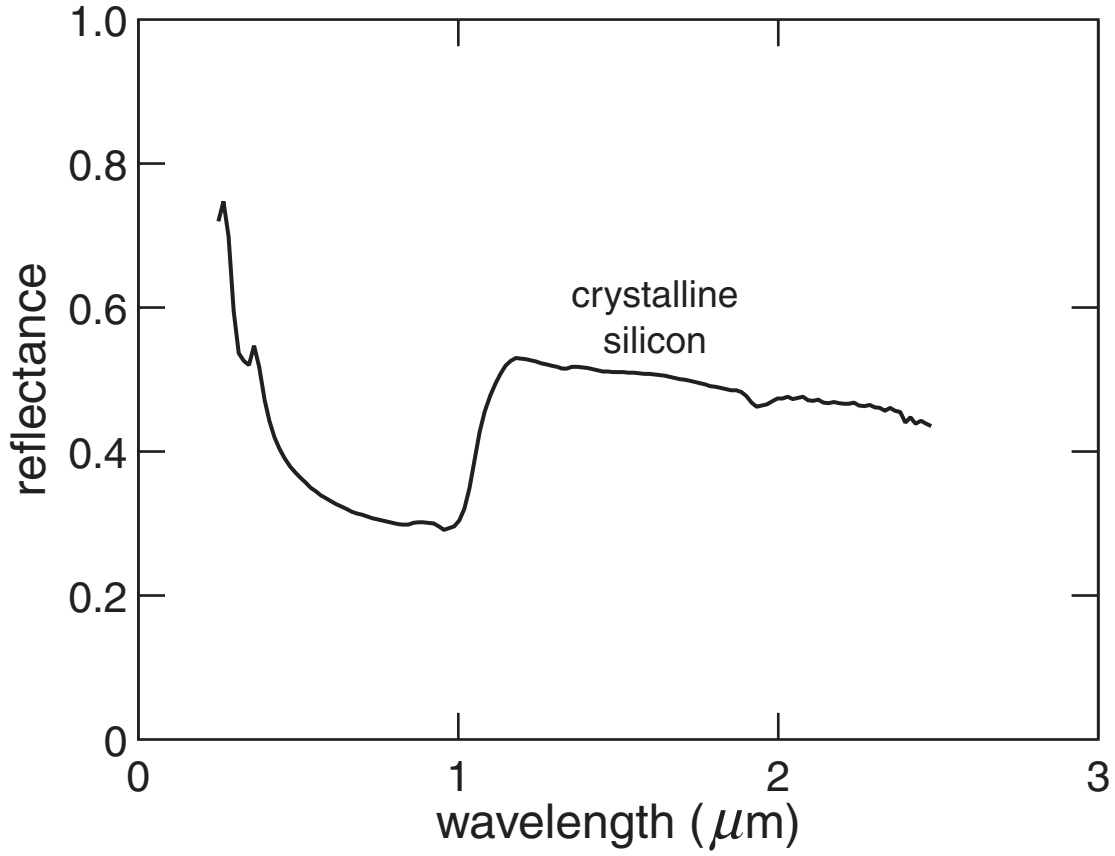
Introduction

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

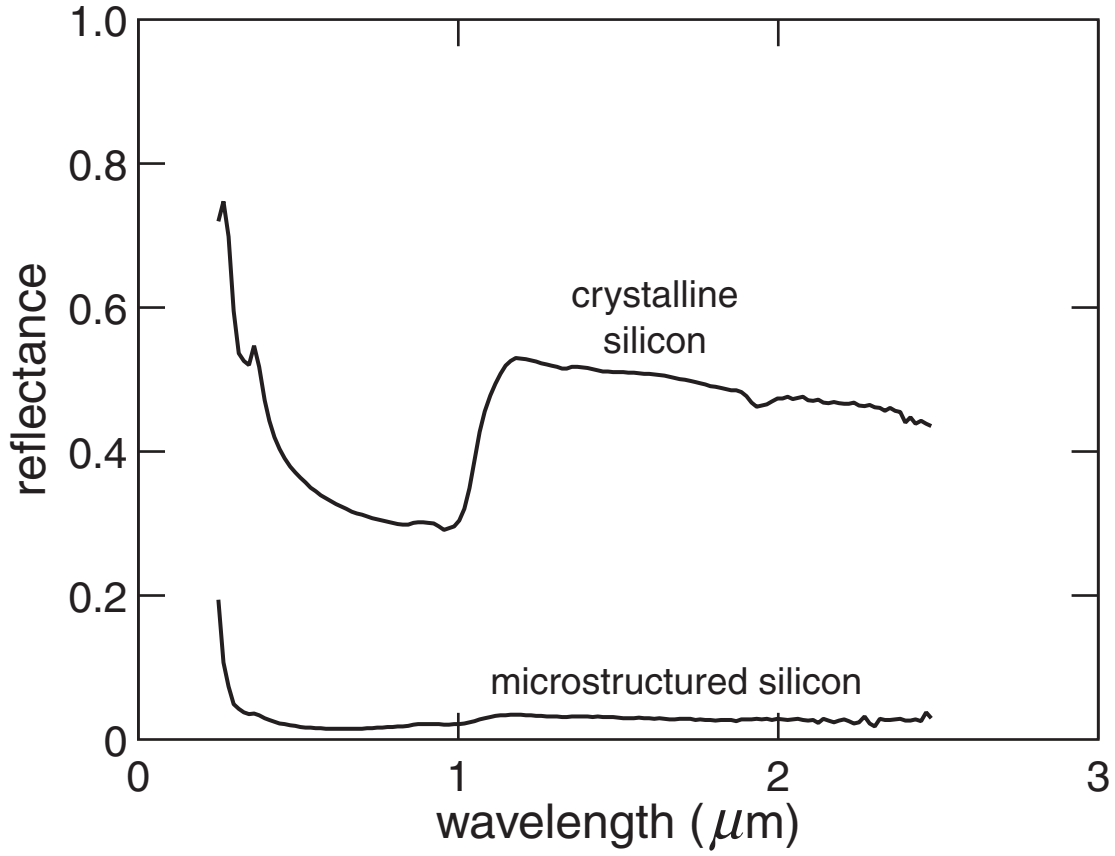
Outline

- Properties
- Structural and chemical analysis
- Outlook

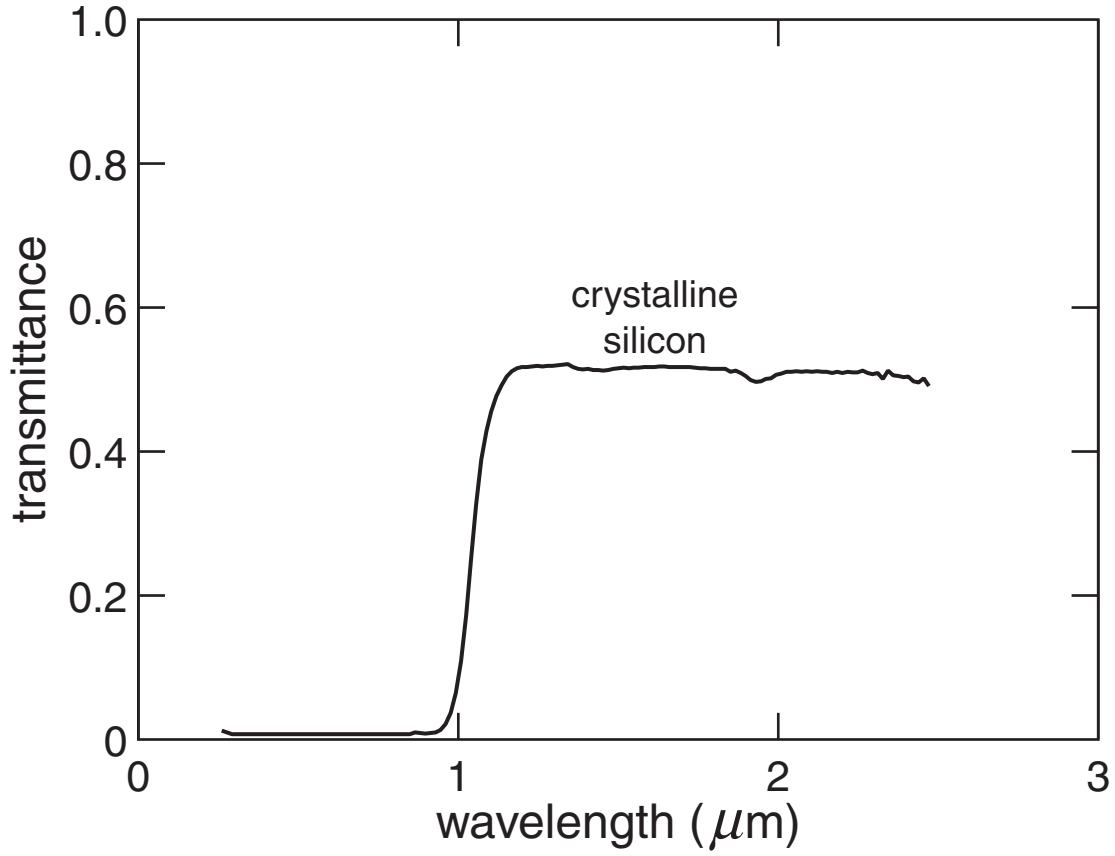
reflectance (integrating sphere)



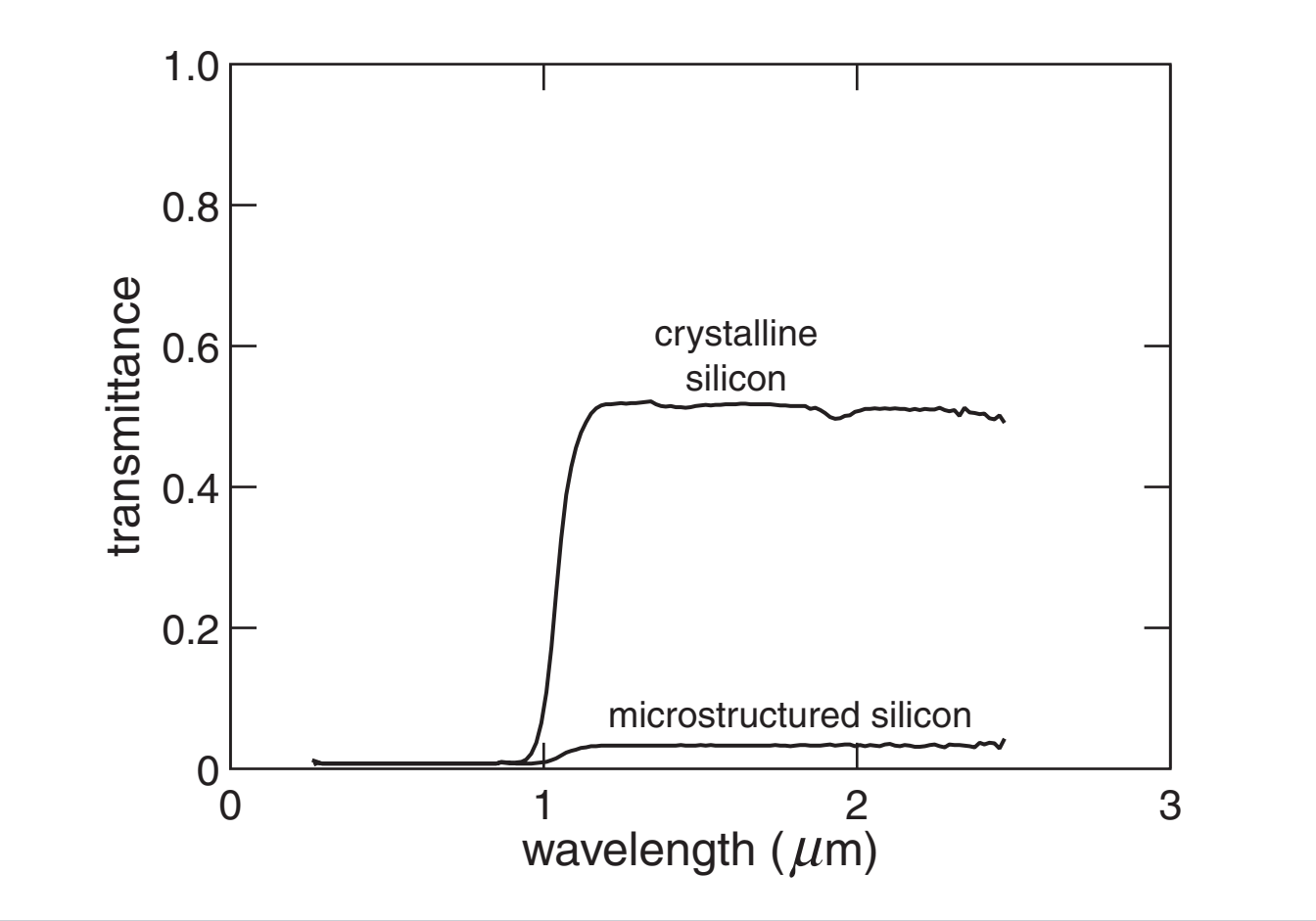
reflectance (integrating sphere)



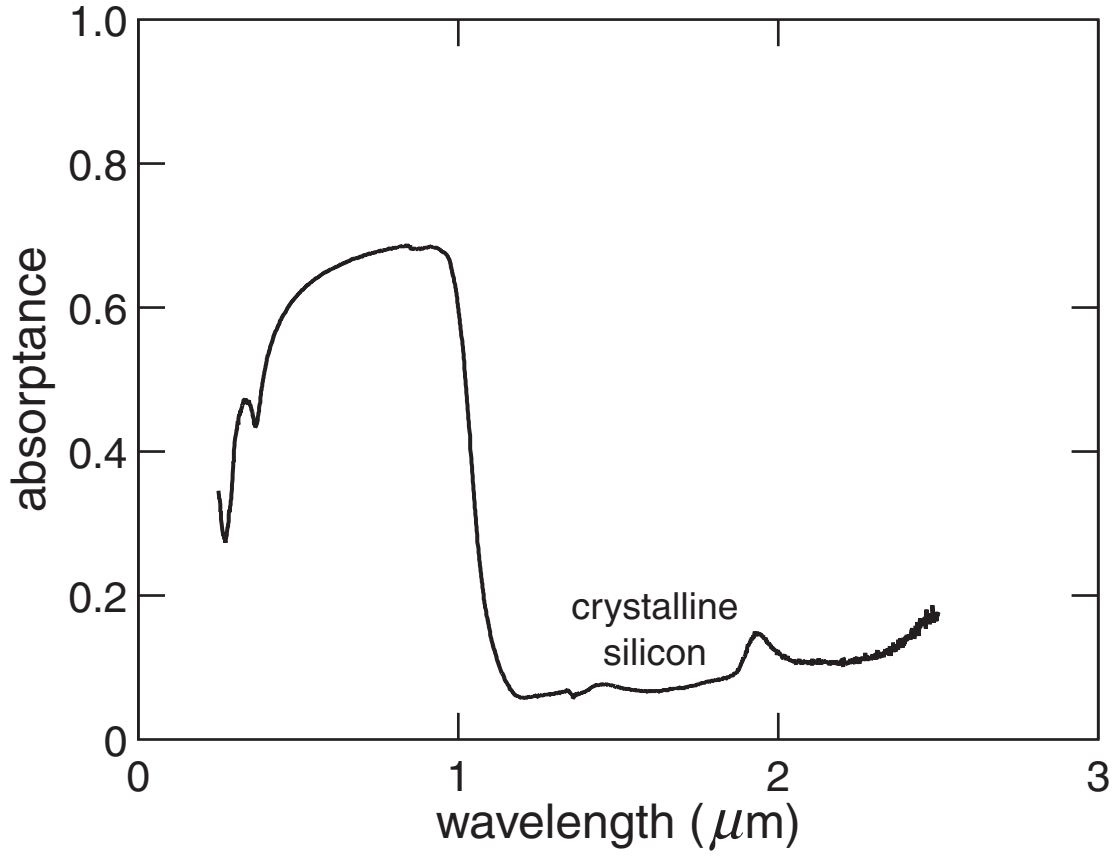
transmittance (integrating sphere)



transmittance (integrating sphere)

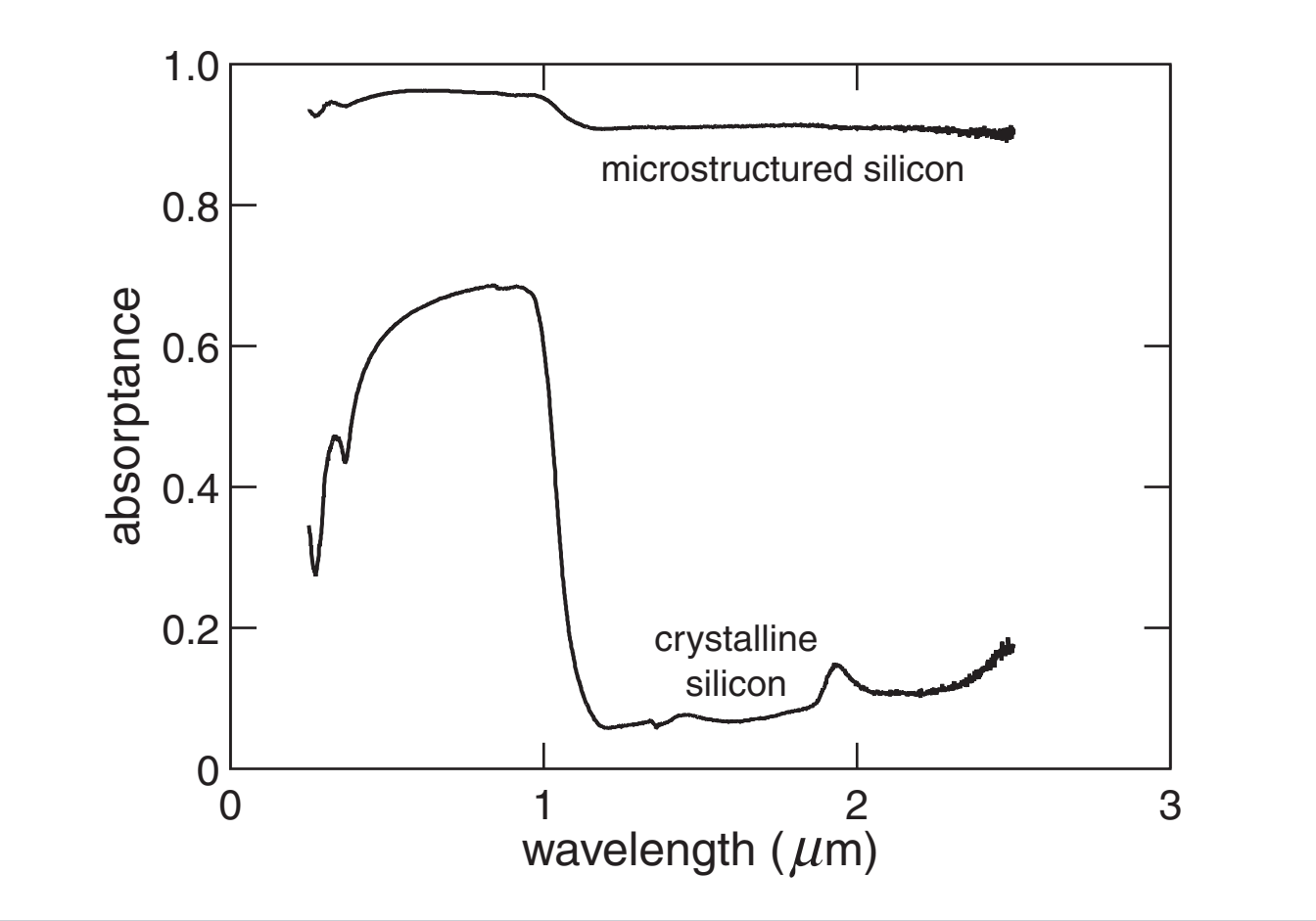


absorptance (1 – *R* – *T*)



Properties

absorptance (1 – *R* – *T*)



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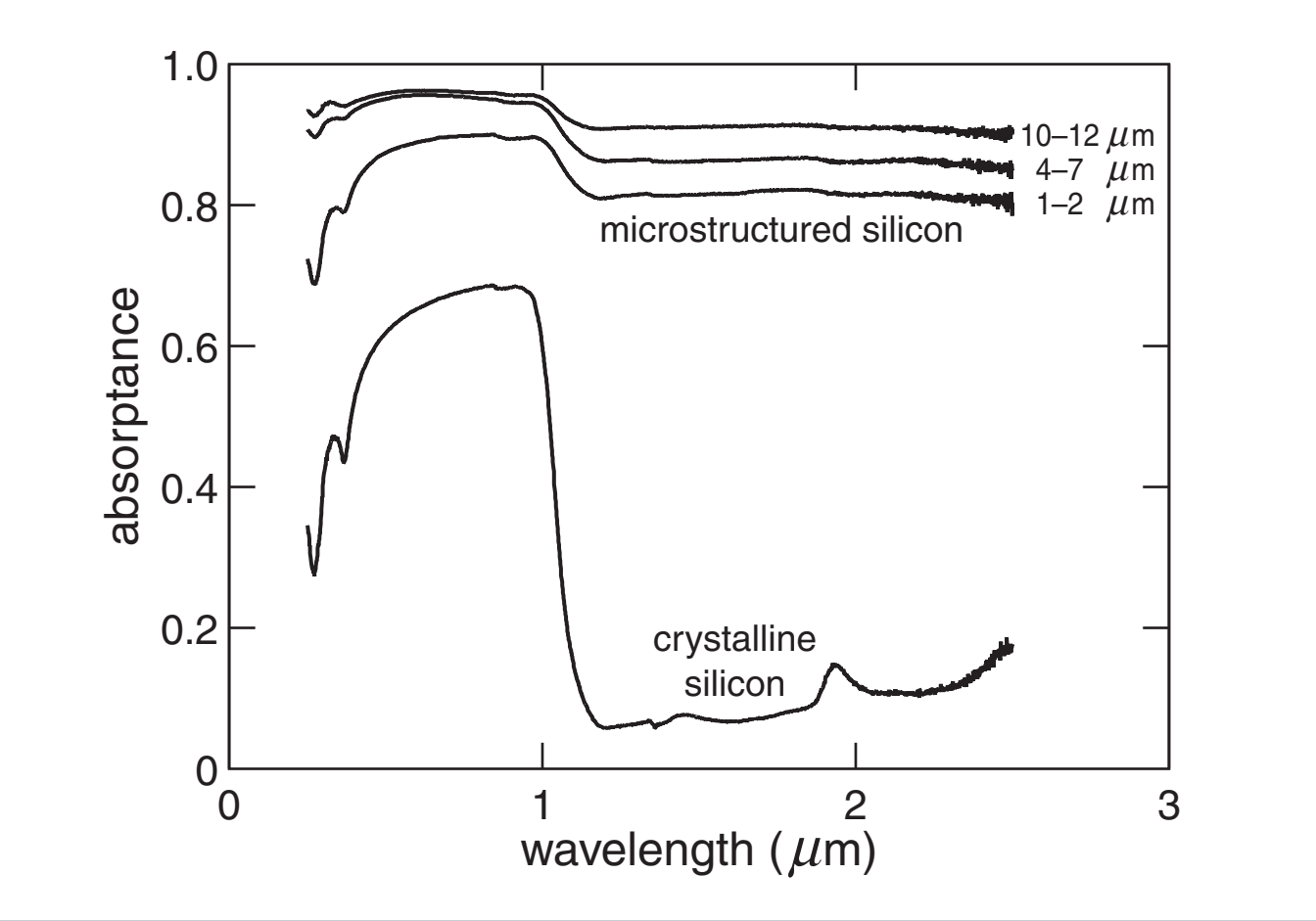
Properties

absorptance (1 – *R* – *T*)



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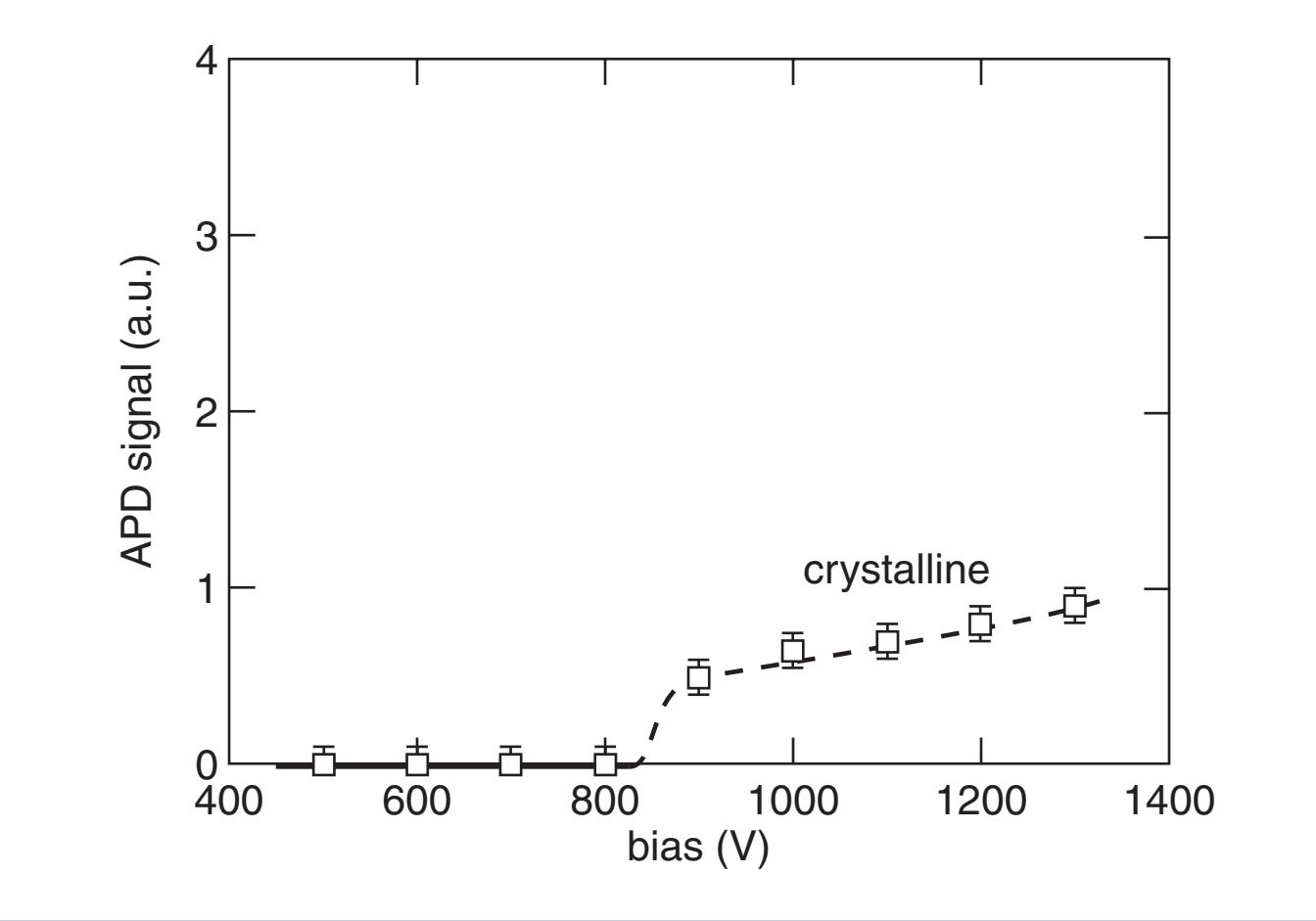
avalanche photodiode response at 1.3 μm



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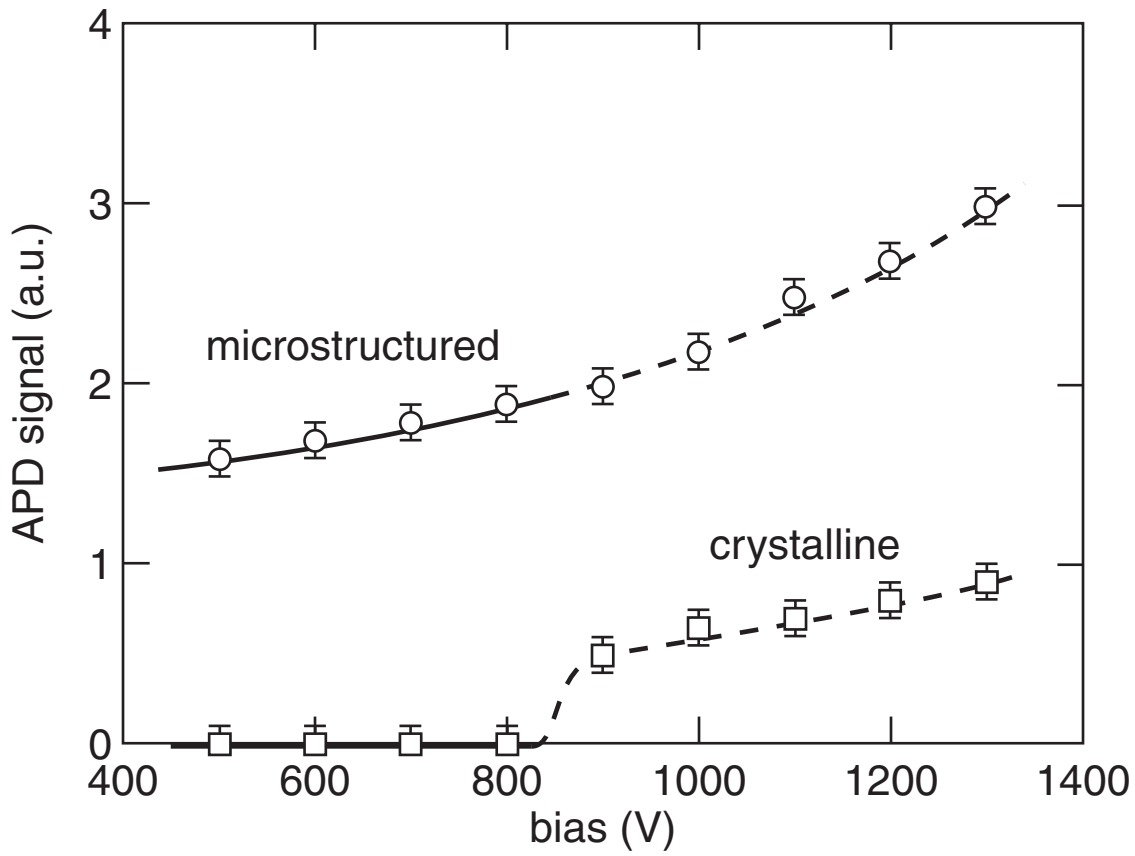
avalanche photodiode response at 1.3 μm



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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**

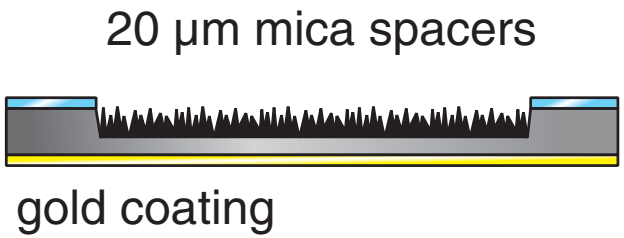
can spikes be used as field emitters?

field emission setup

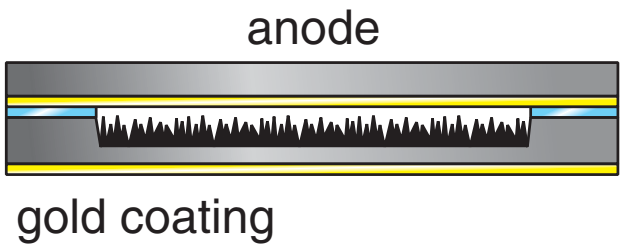
field emission setup

gold coating

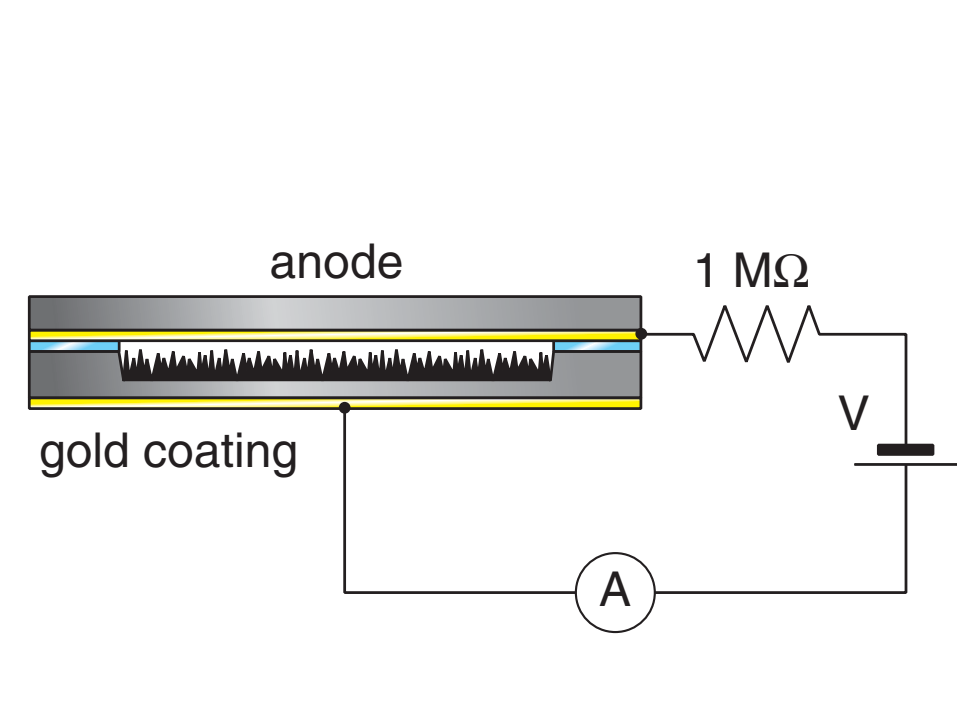
field emission setup



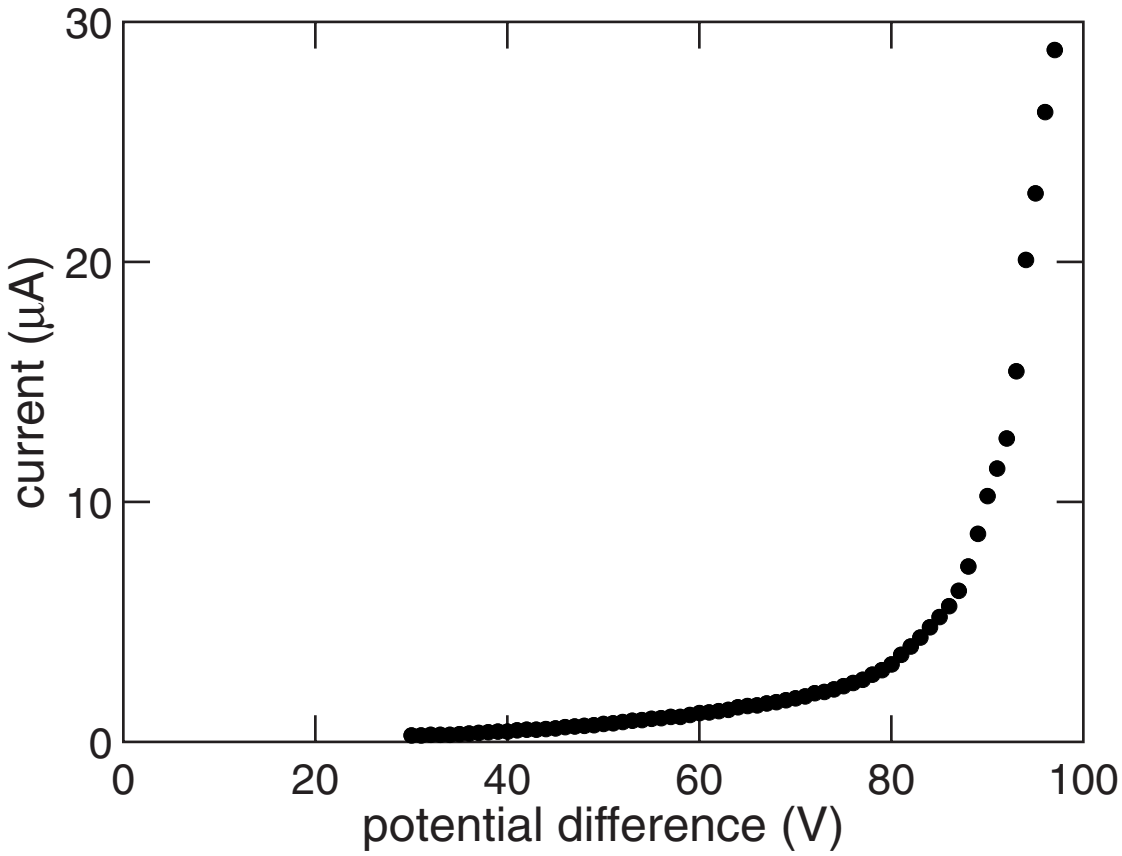
field emission setup



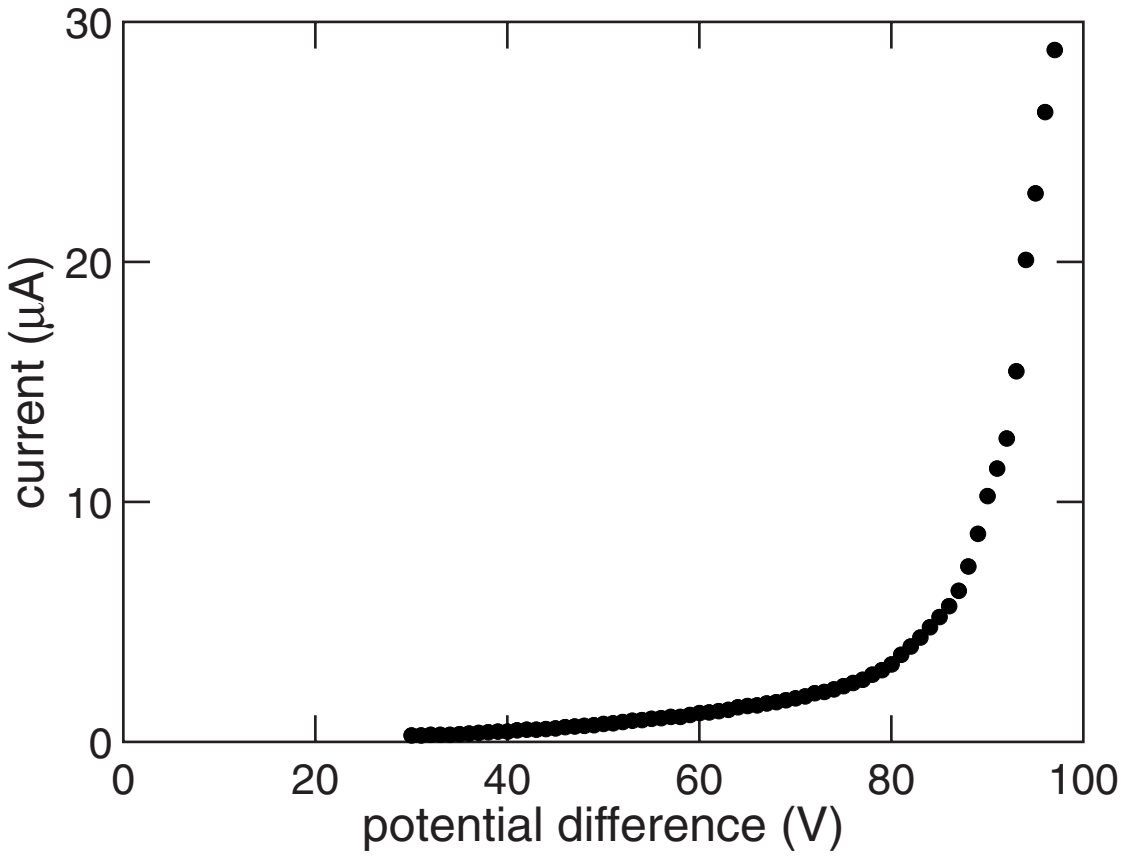
field emission setup



Properties

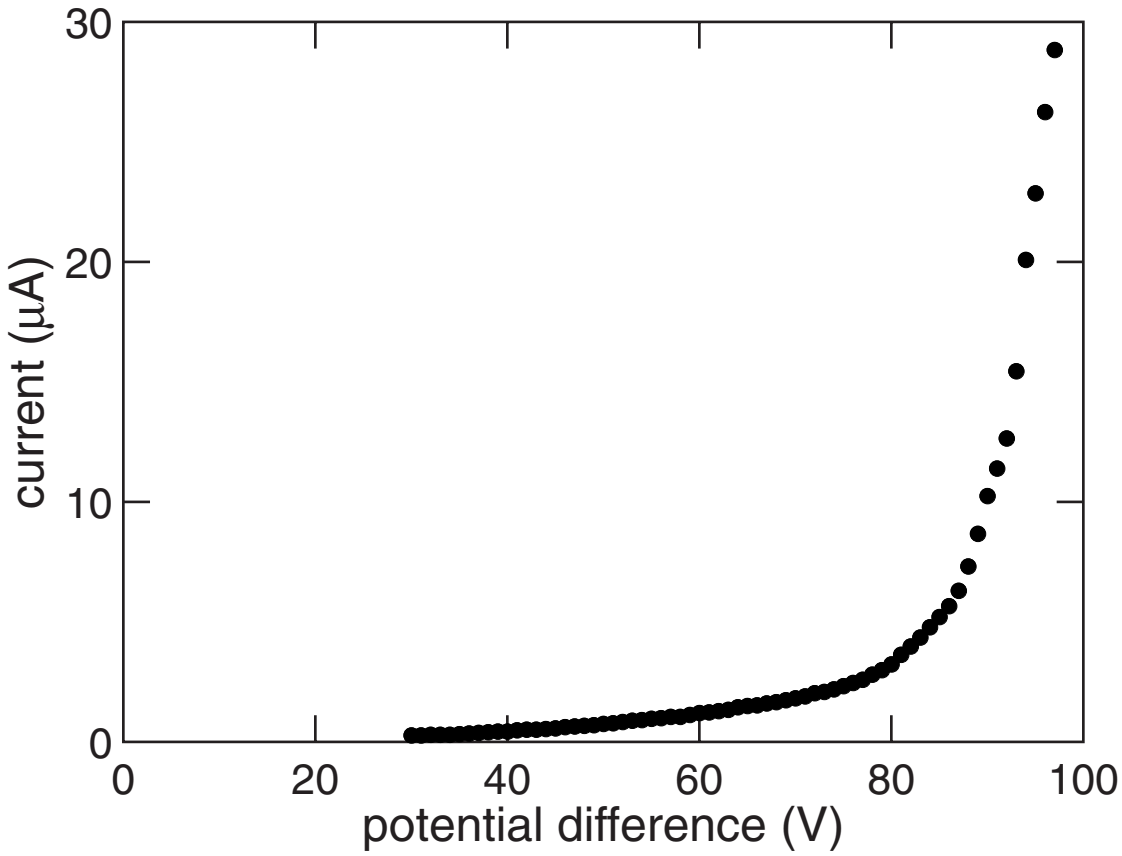


Properties



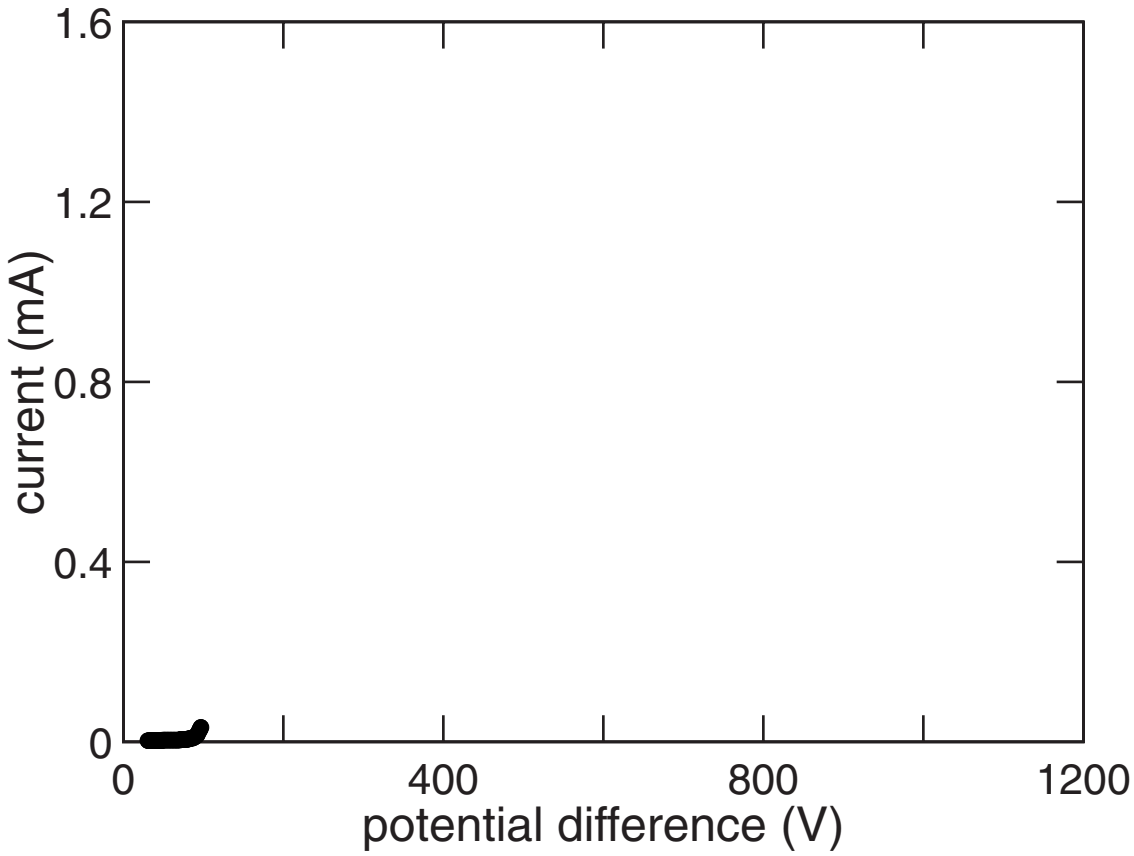
turn-on field (1 μA/cm^2): 1.2 V/μm

Properties

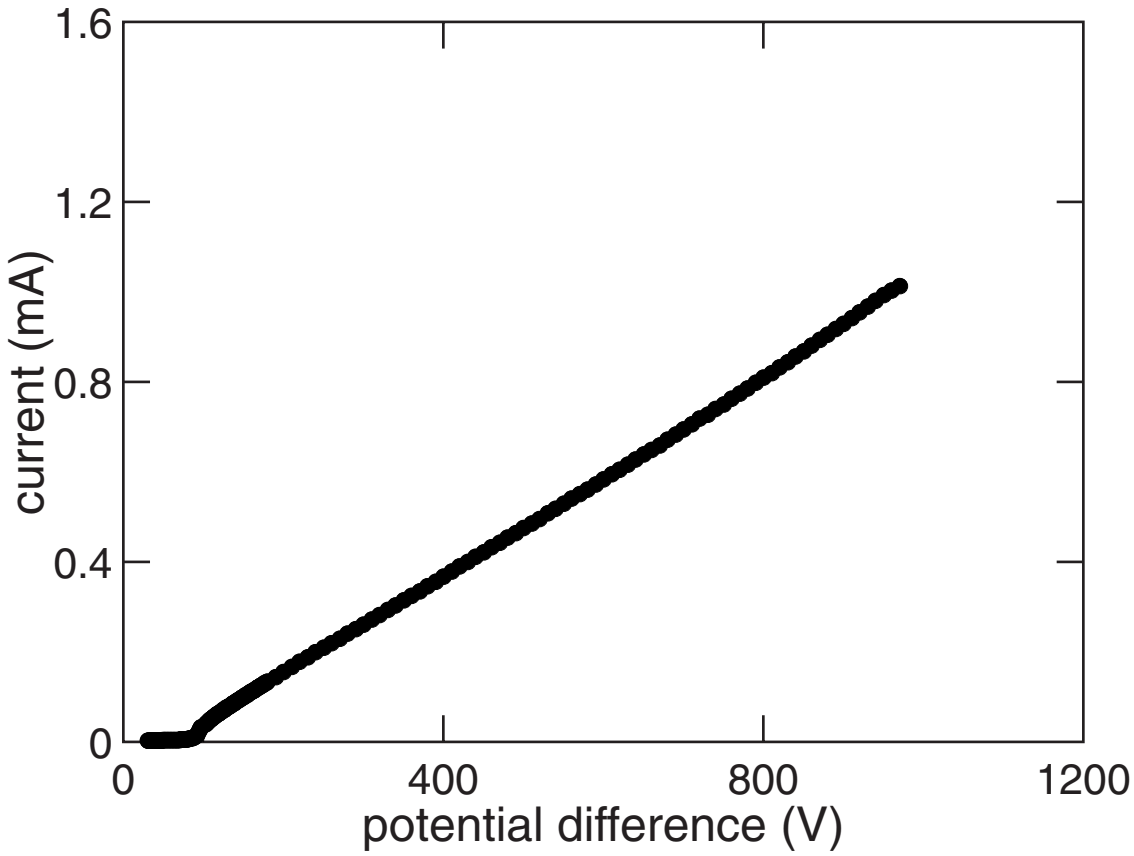


threshold field (10 μA/cm^2): 2.1 V/μm

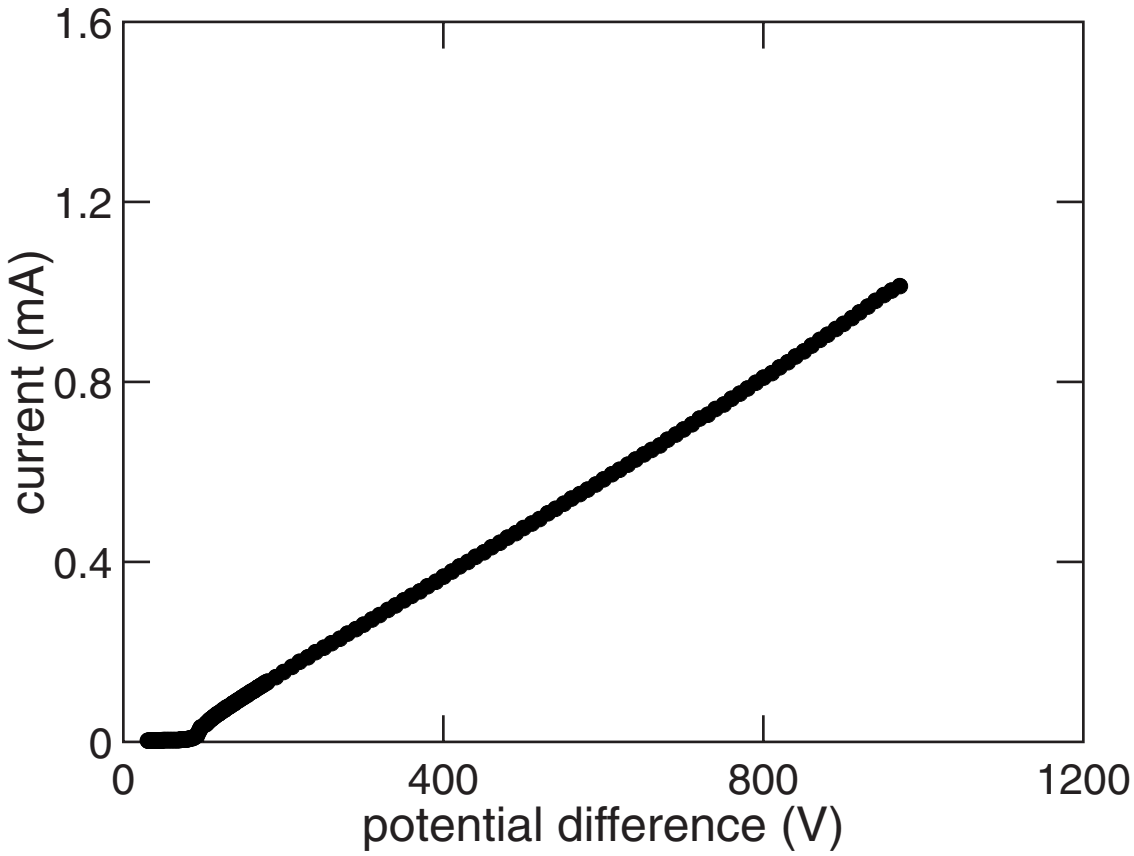
Properties



Properties



Properties



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

Properties

Points to keep in mind:

- near unity absorption
- sub-band gap absorption
- IR photoelectron generation
- high field emission at low fields

Outline

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

Structural and chemical analysis

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

Structural and chemical analysis

Ion channeling and electron backscattering:

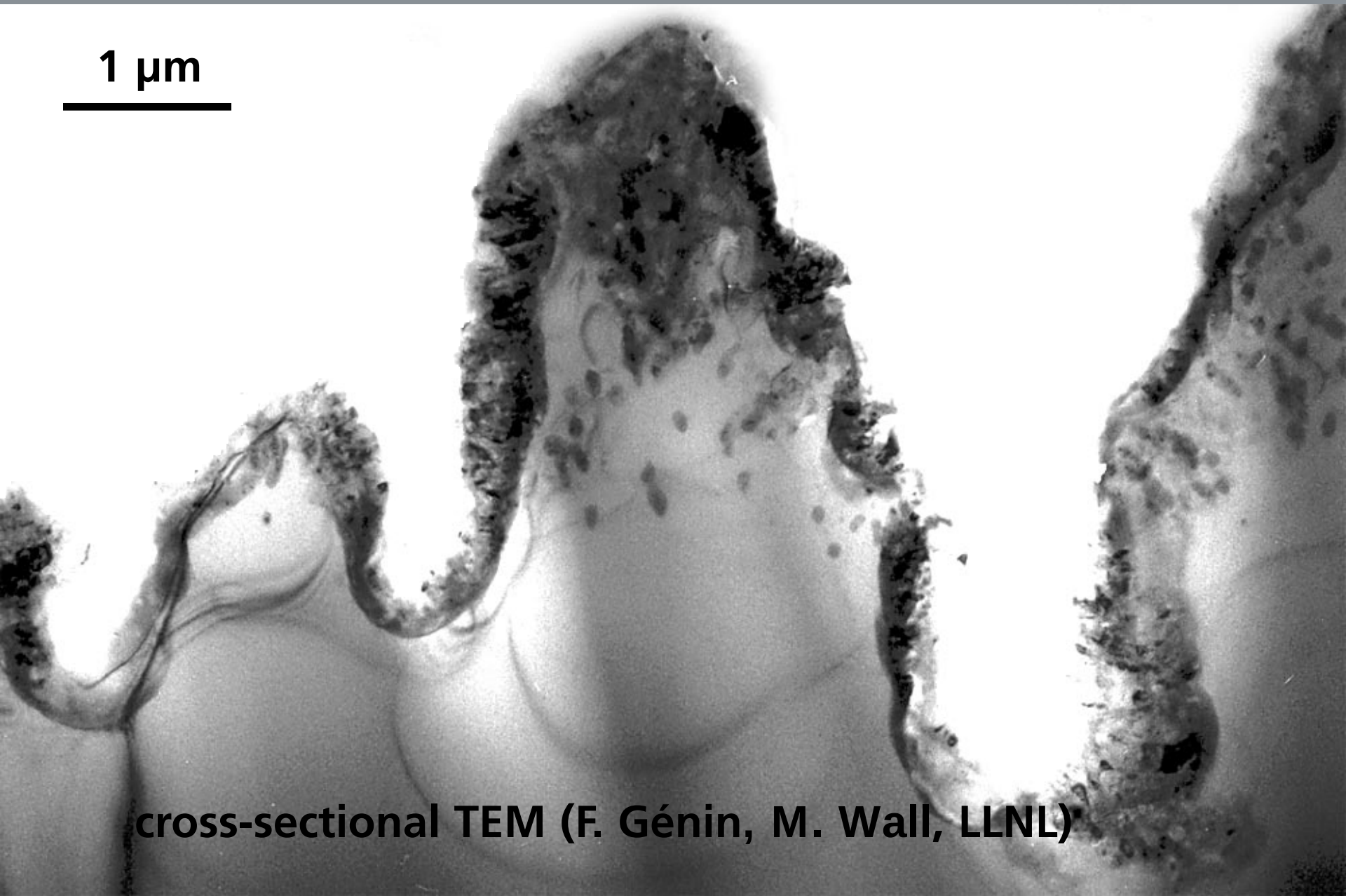
- **spikes retain crystalline order**
- **high density of defects**

Structural and chemical analysis

Secondary ion mass spectrometry:

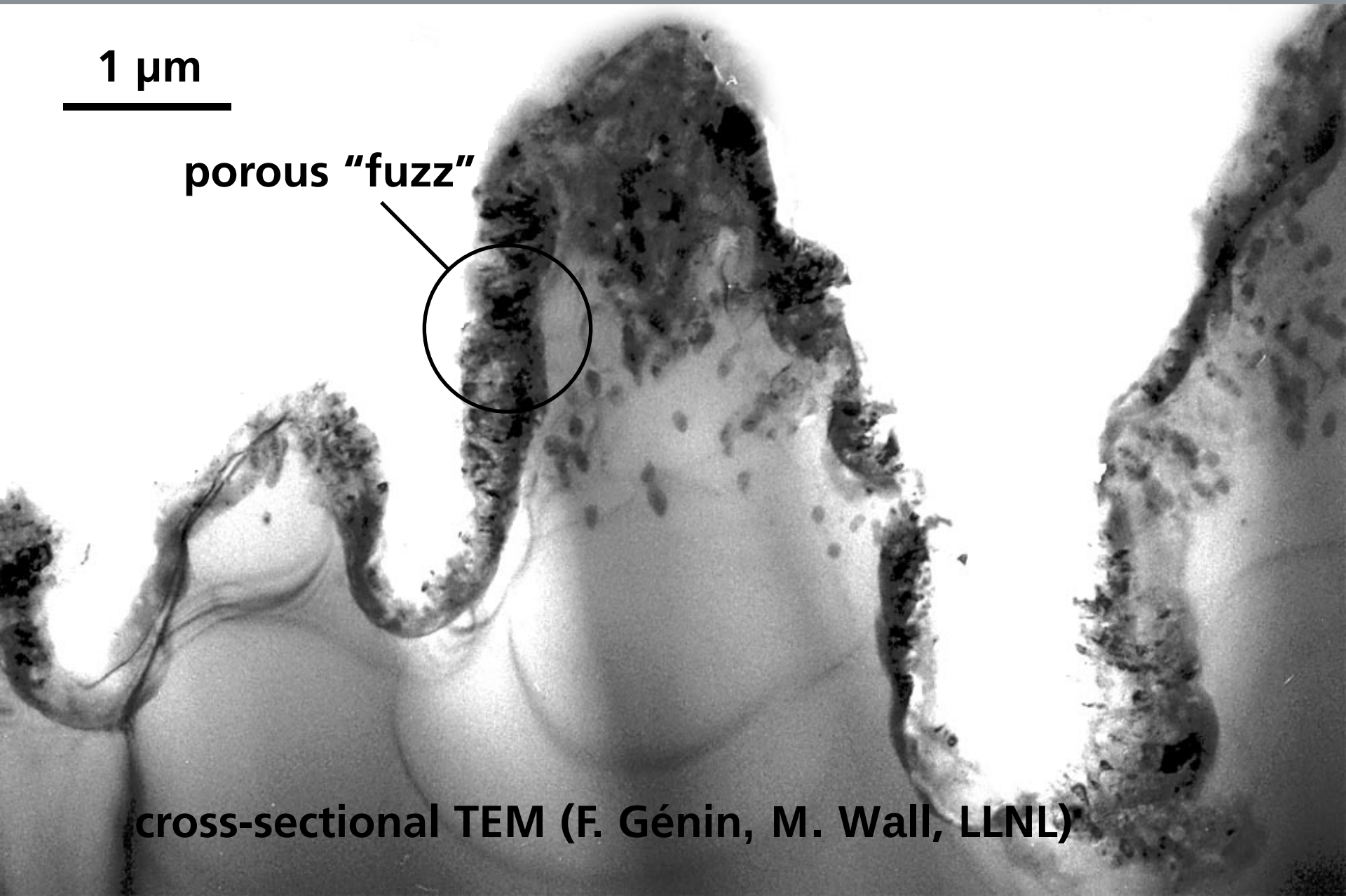
- 10^{20} cm^{-3} sulfur
- 10^{17} cm^{-3} fluorine

Structural and chemical analysis



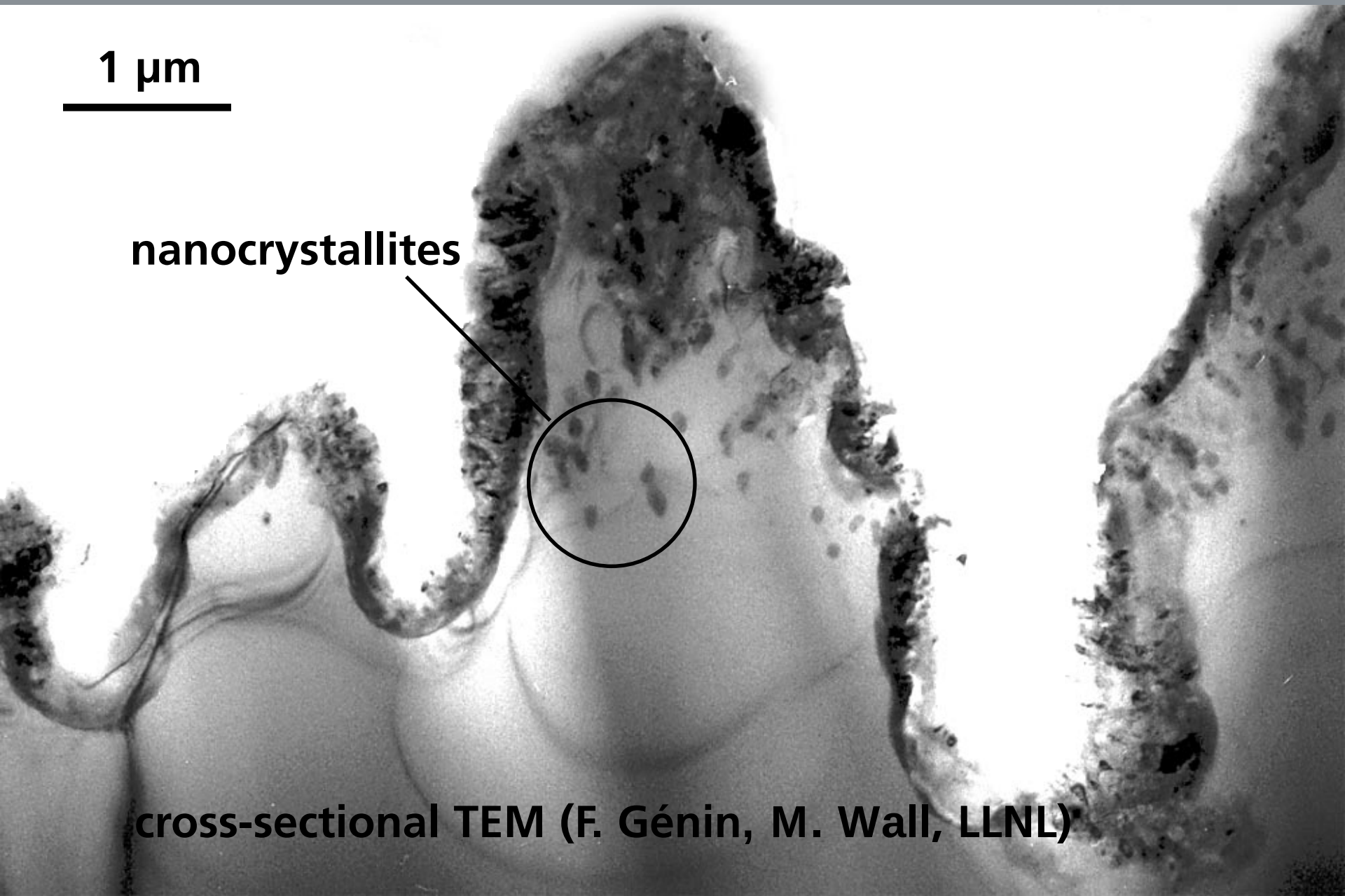
cross-sectional TEM (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



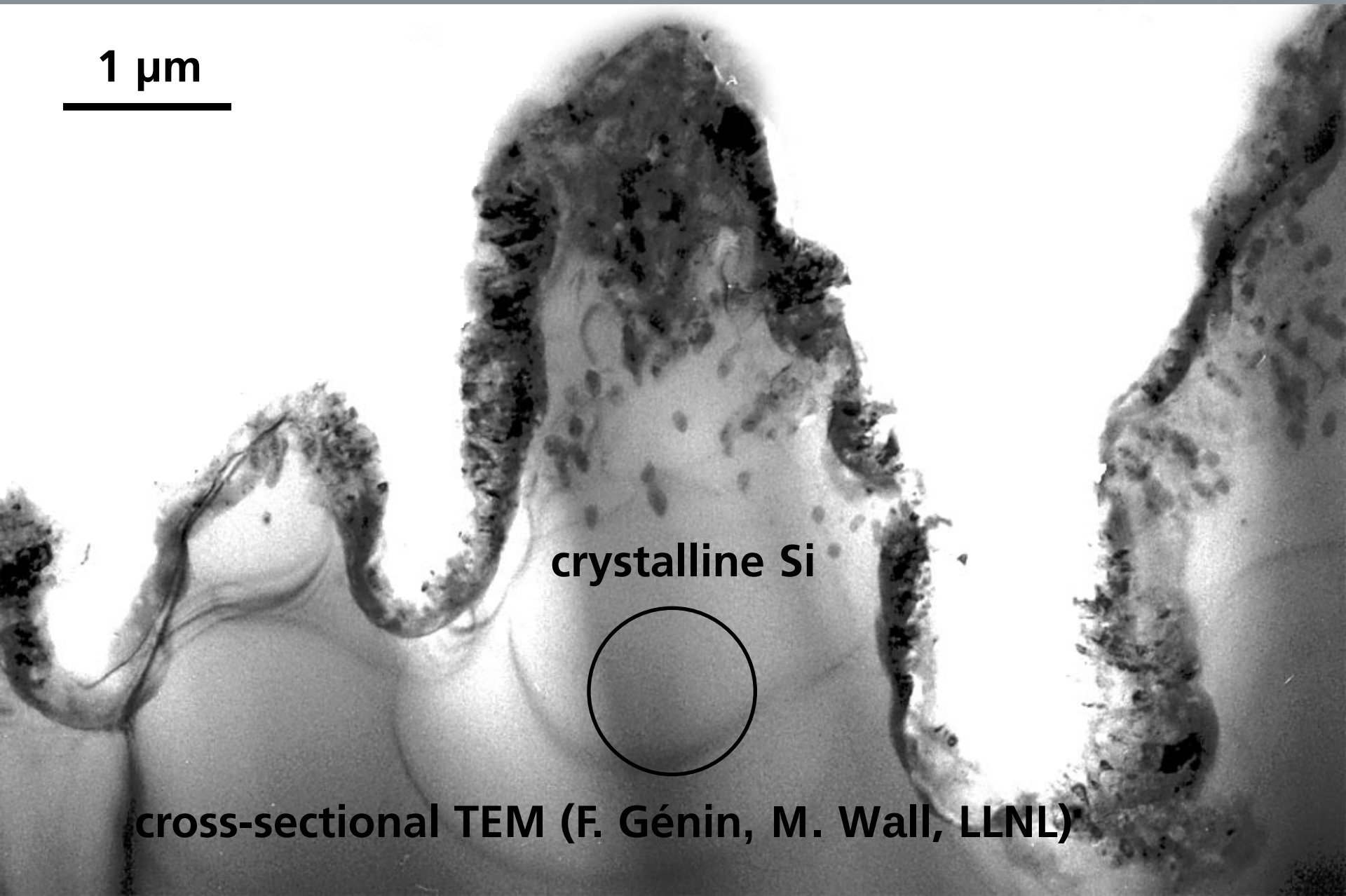
cross-sectional TEM (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



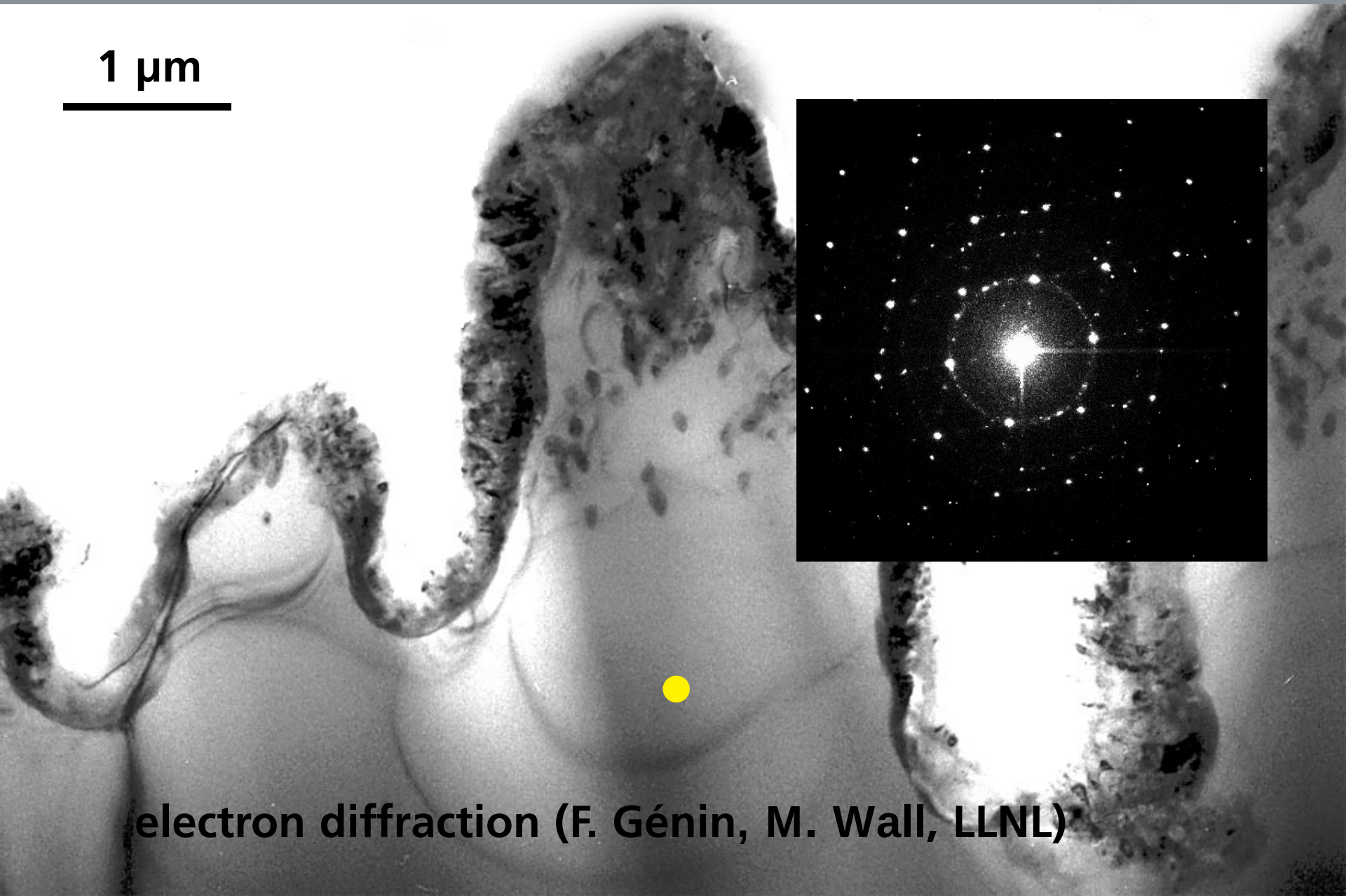
cross-sectional TEM (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



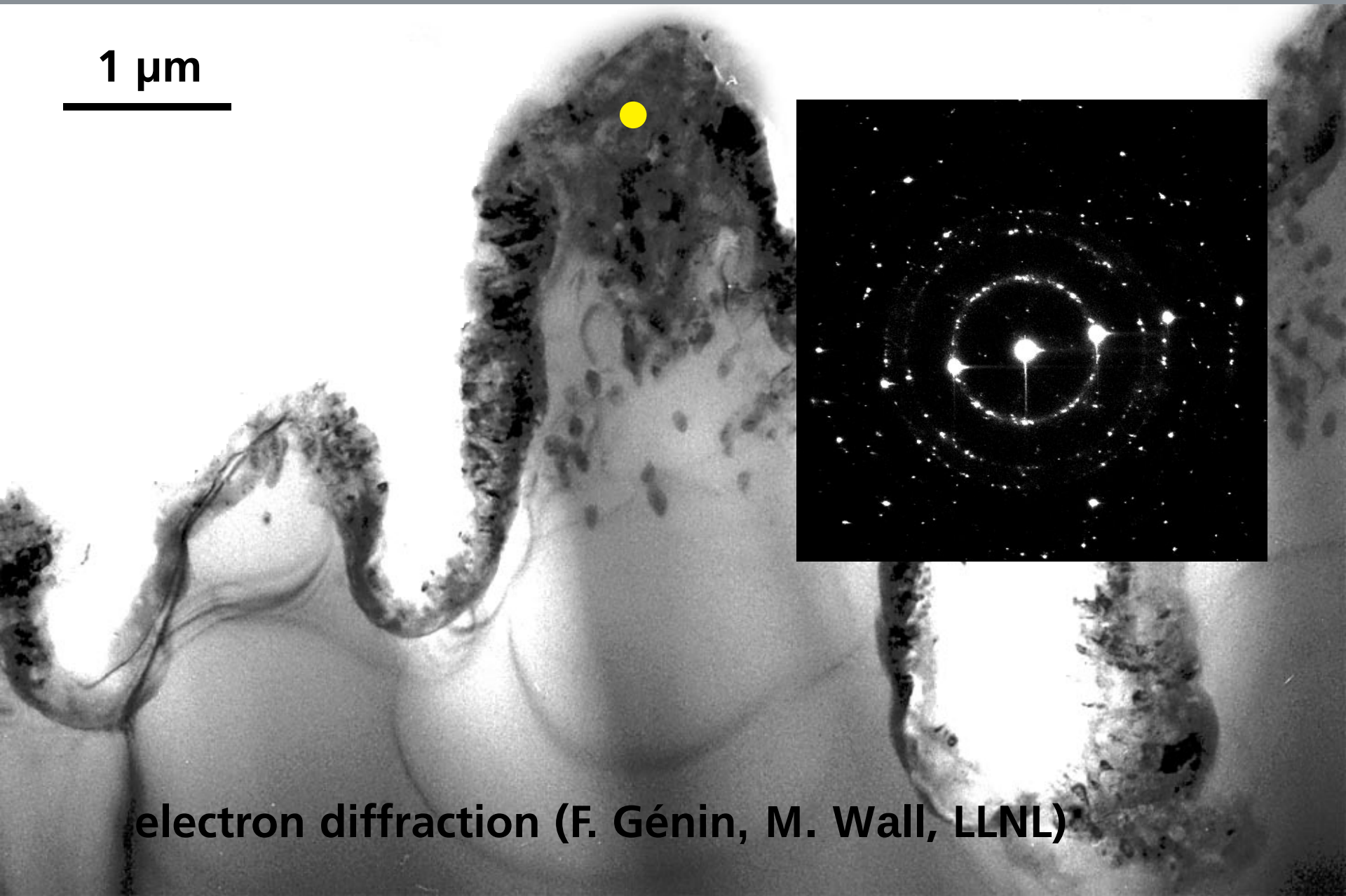
cross-sectional TEM (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



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

Structural and chemical analysis



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

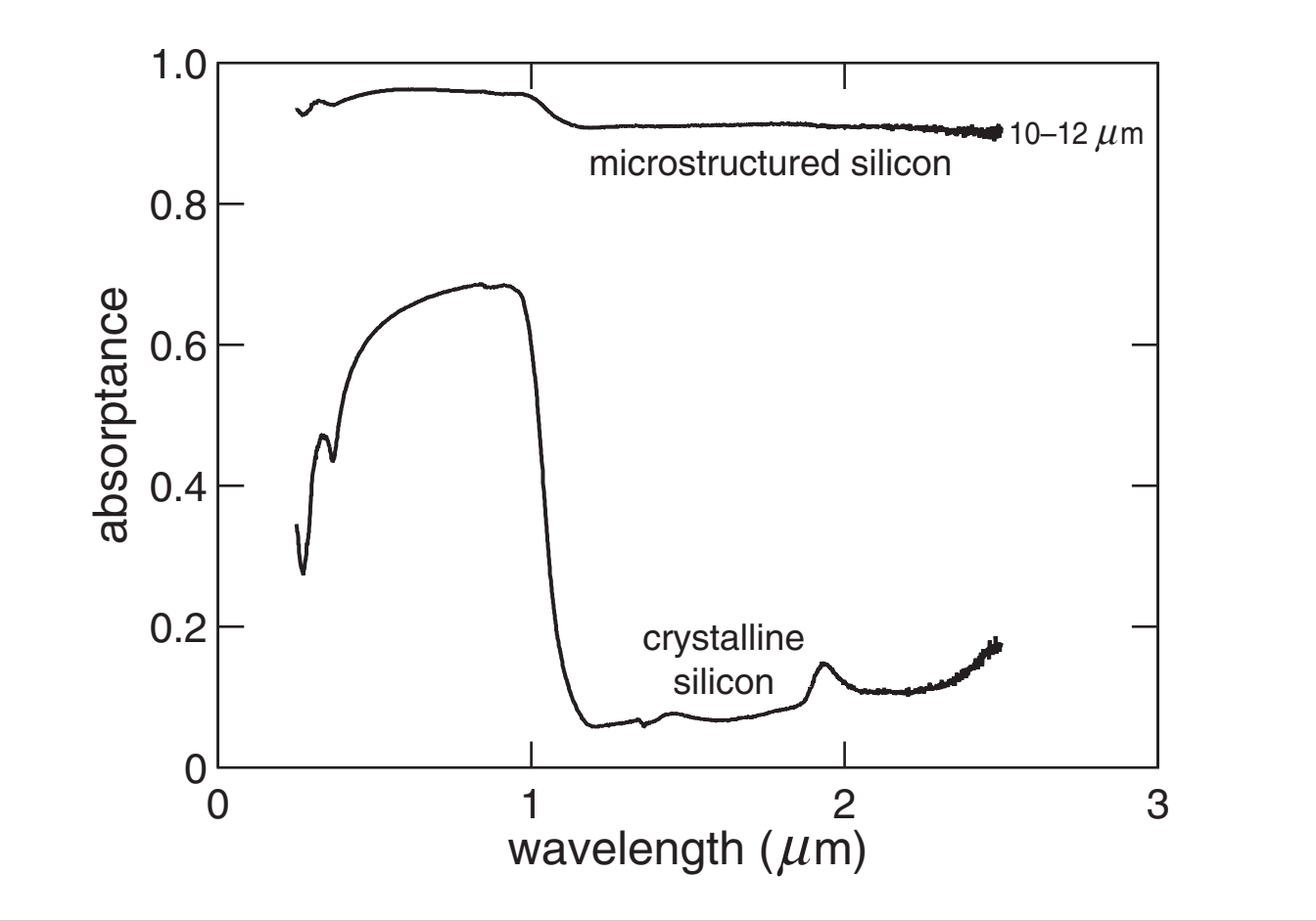
Structural and chemical analysis

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



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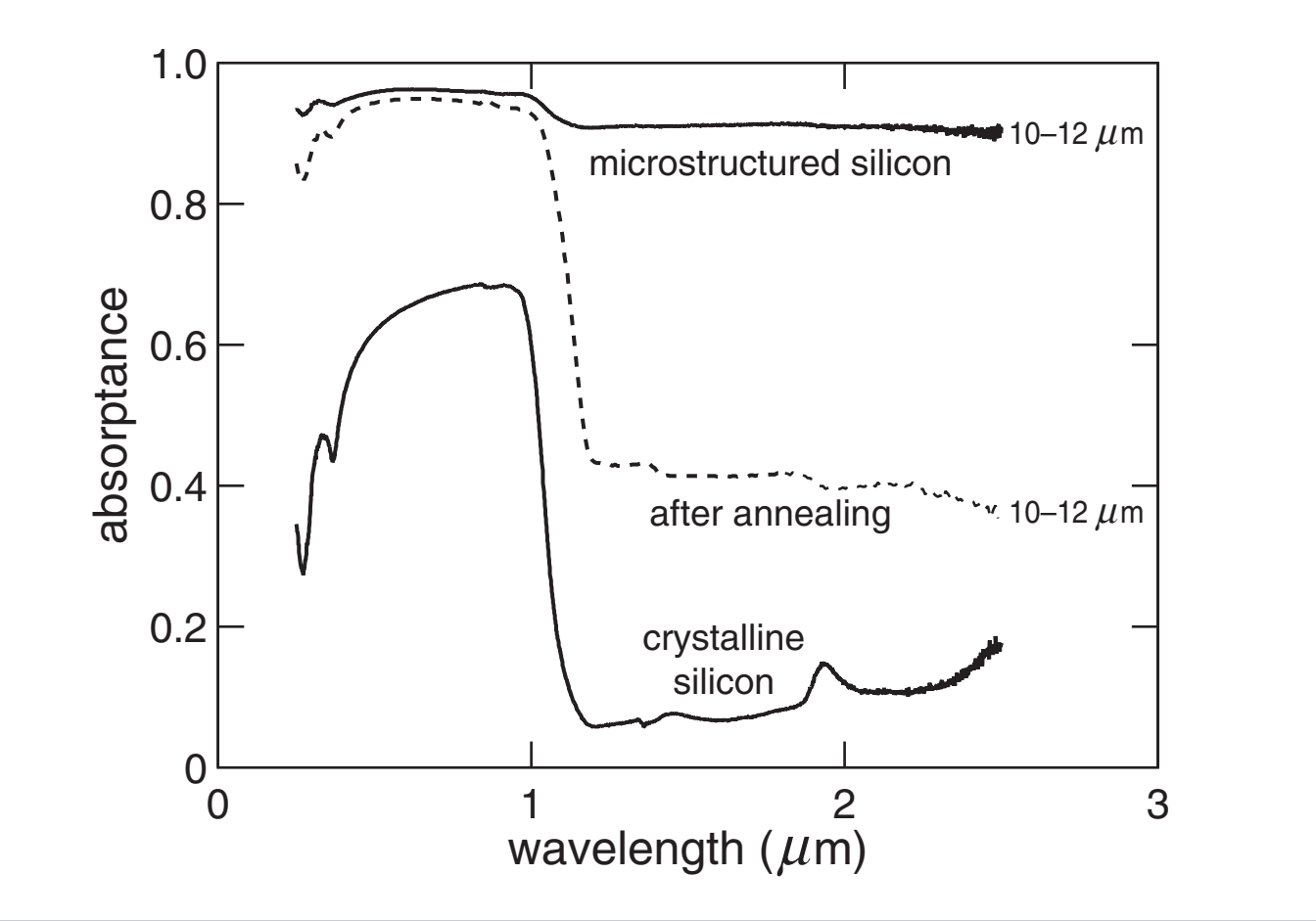
Structural and chemical analysis

anneal 4 hours at 1200 K



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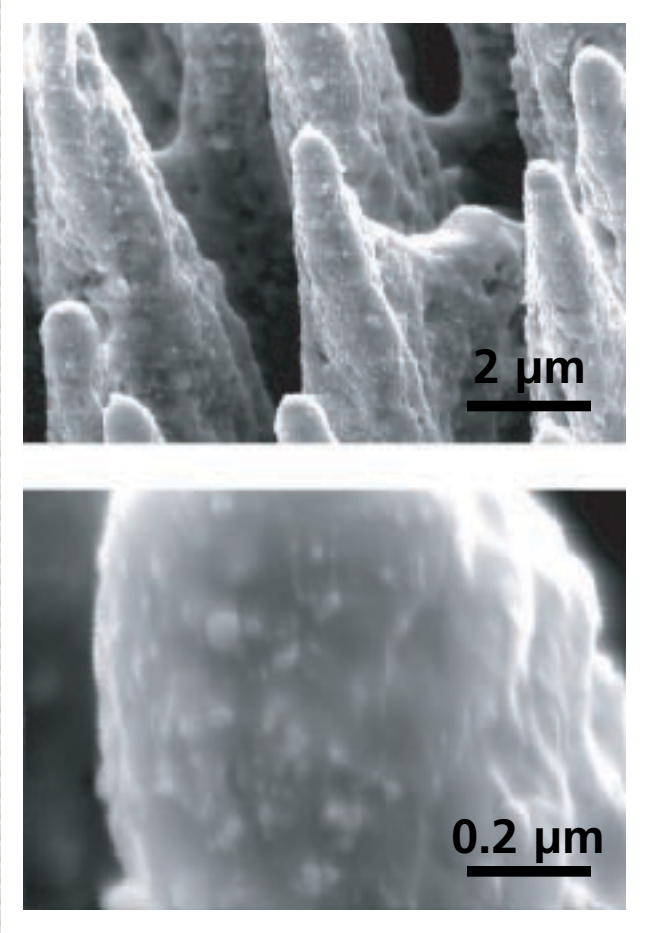
Structural and chemical analysis

anneal 4 hours at 1200 K



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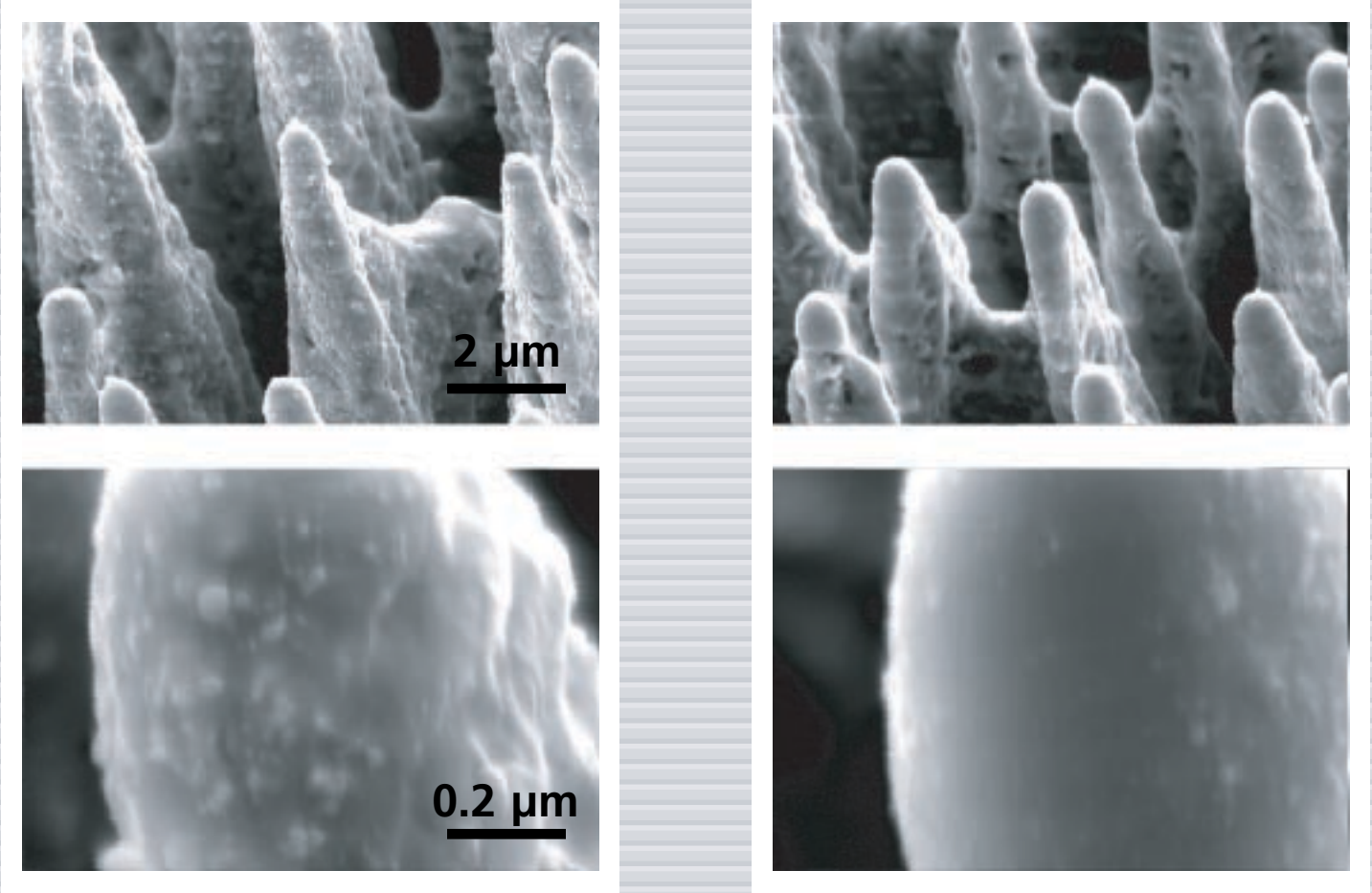
Structural and chemical analysis

anneal 4 hours at 1200 K



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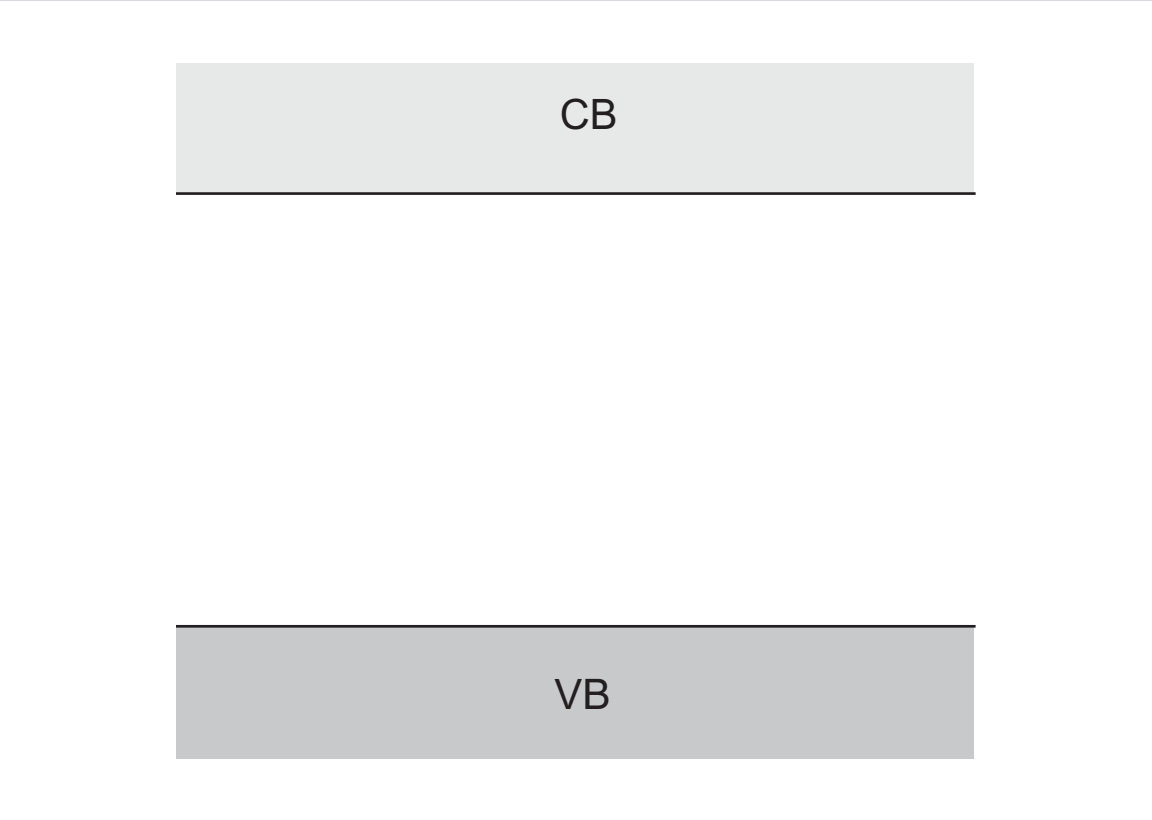
Structural and chemical analysis

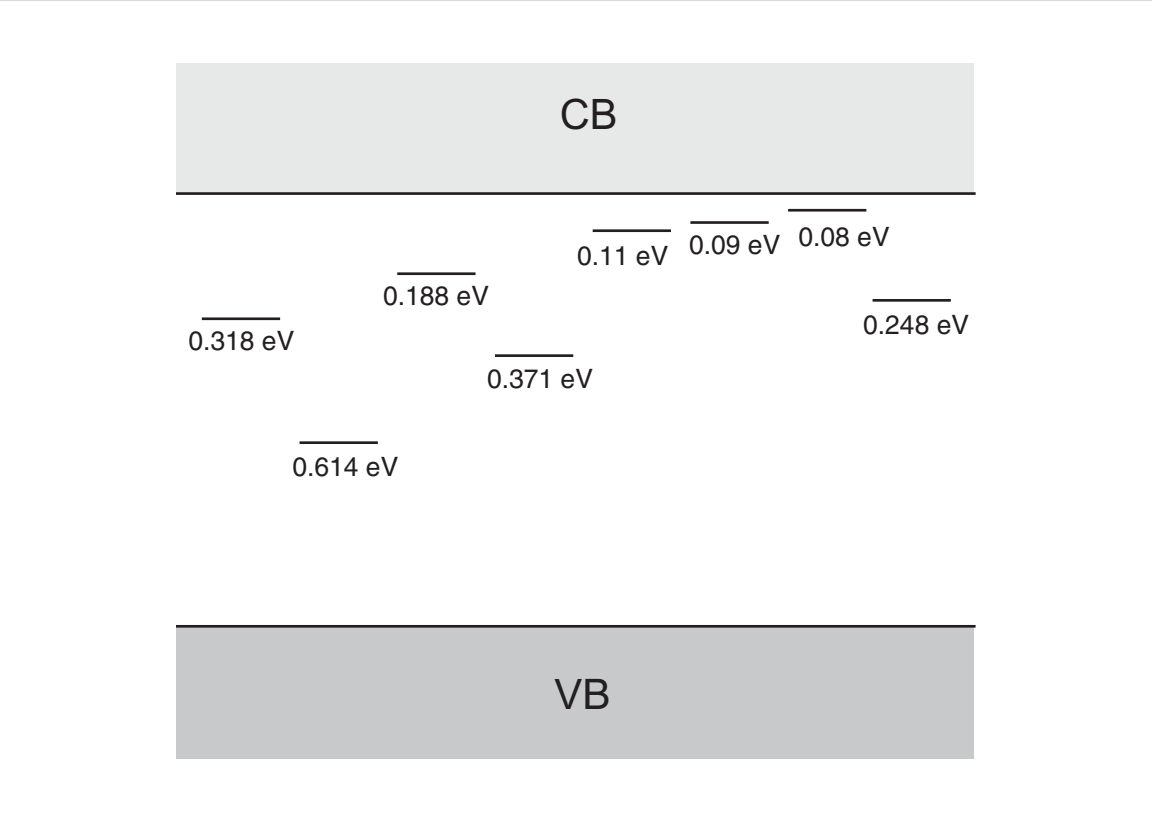
Effects of annealing:

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

sulfur introduces states in the gap

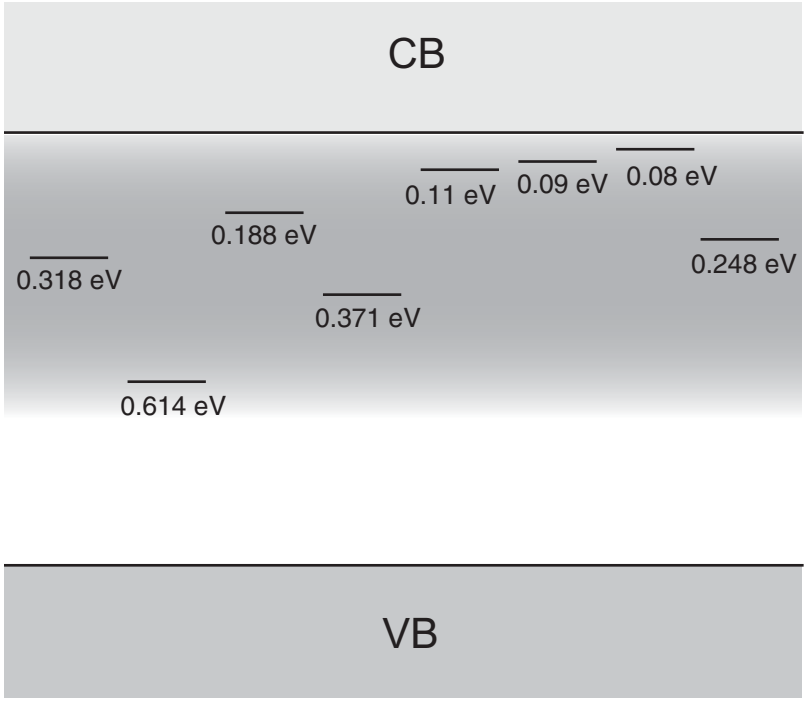


sulfur introduces states in the gap

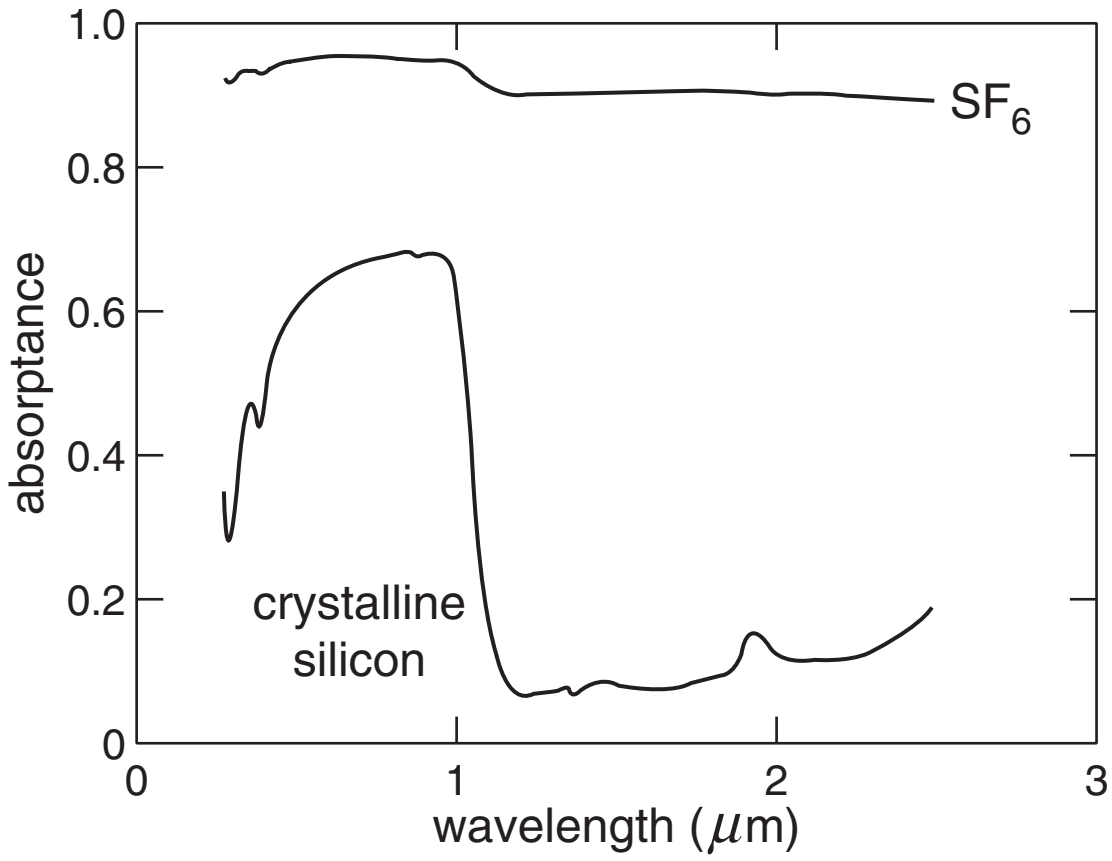


Janzén, *et al.*, *Phys. Rev. B* **29**,1907 (1984)

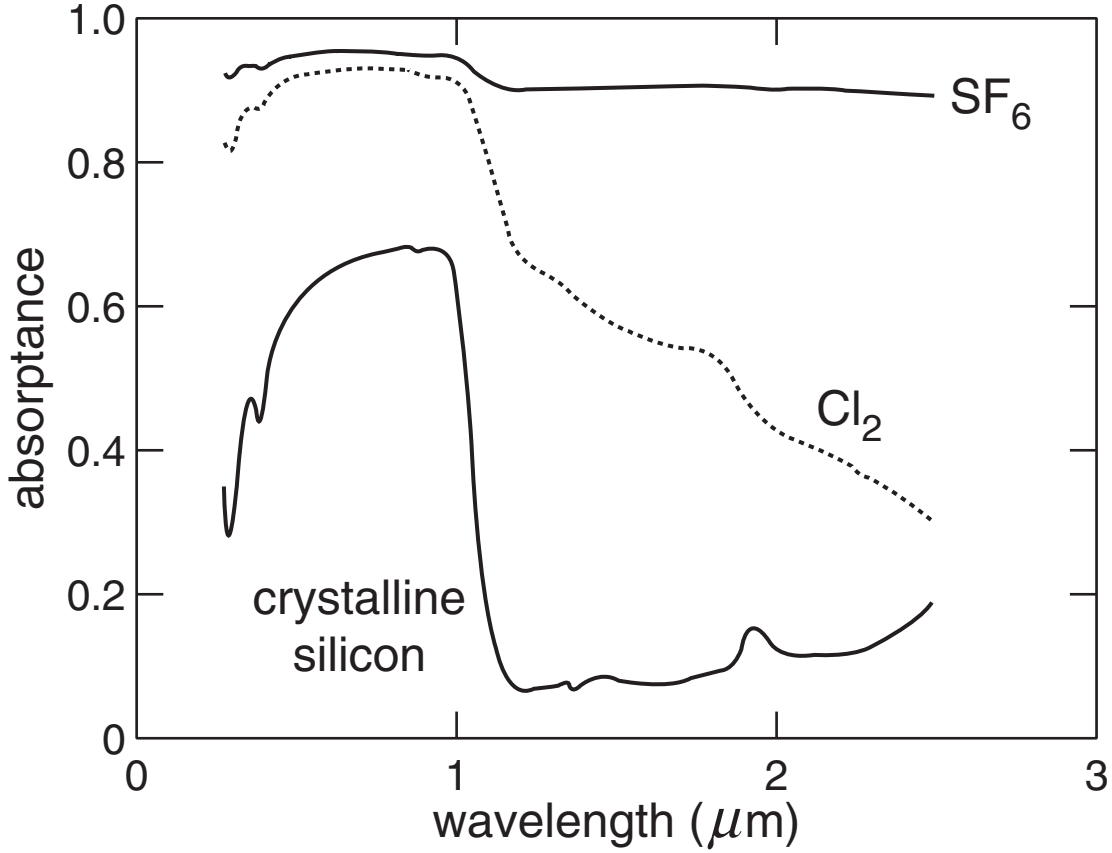
states broaden into a band



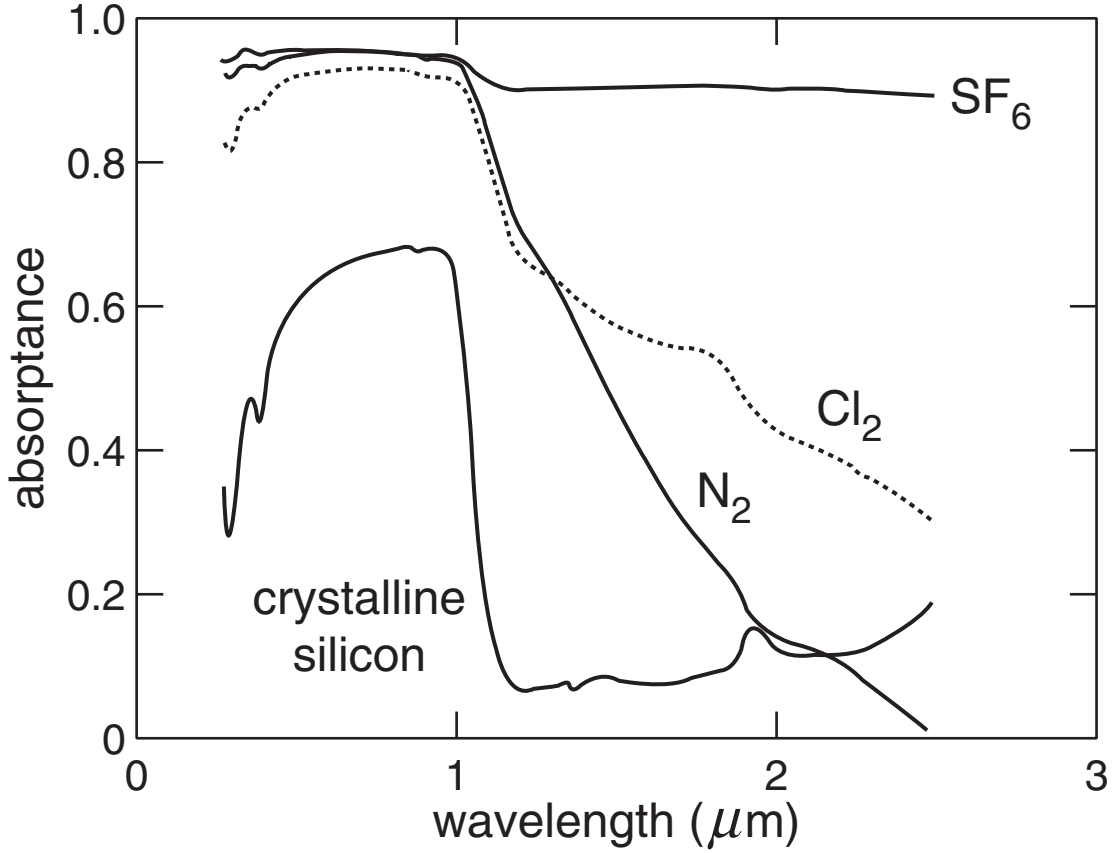
effect of ambient gas on absorptance



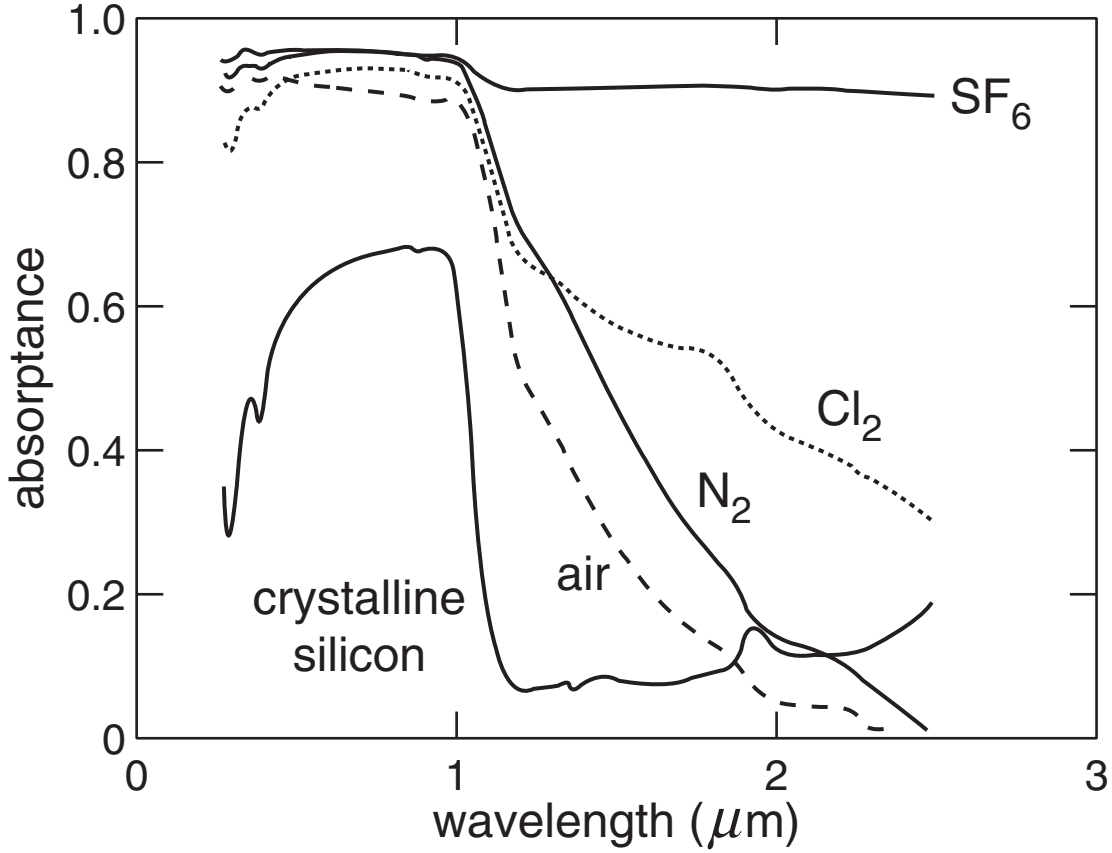
effect of ambient gas on absorptance



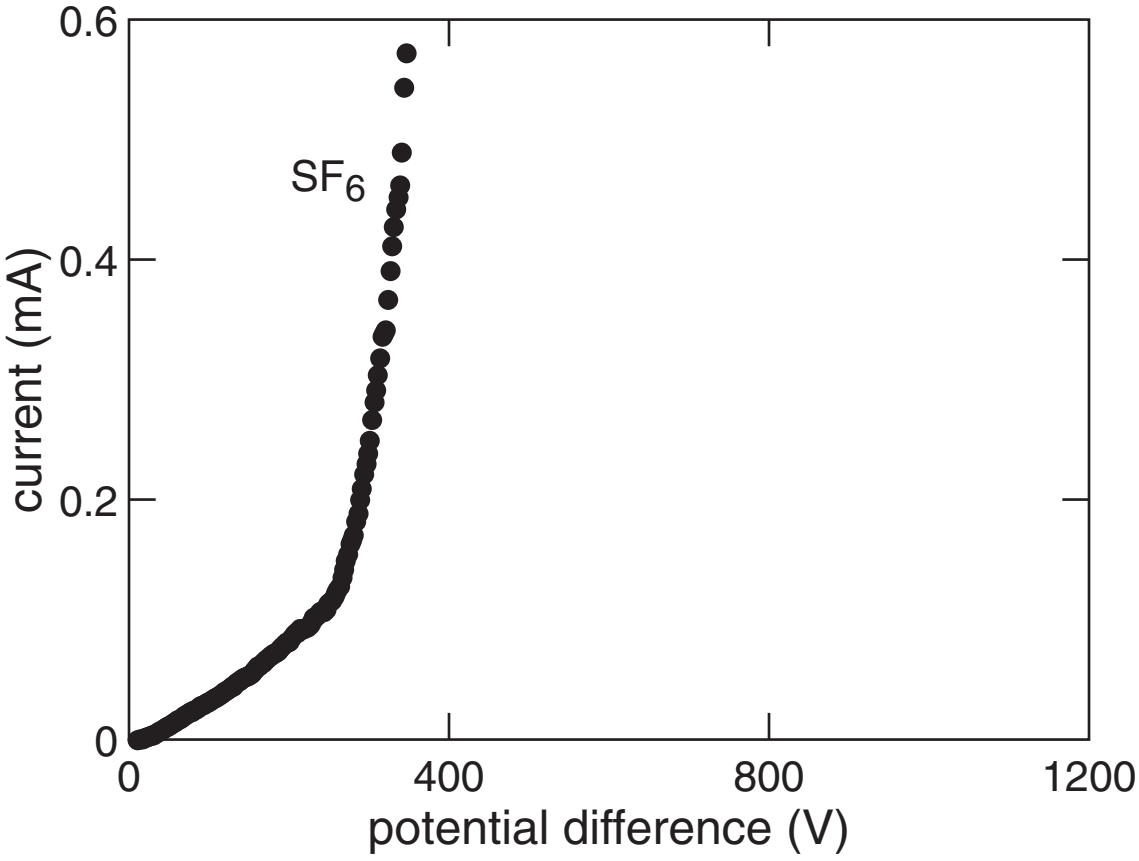
effect of ambient gas on absorptance



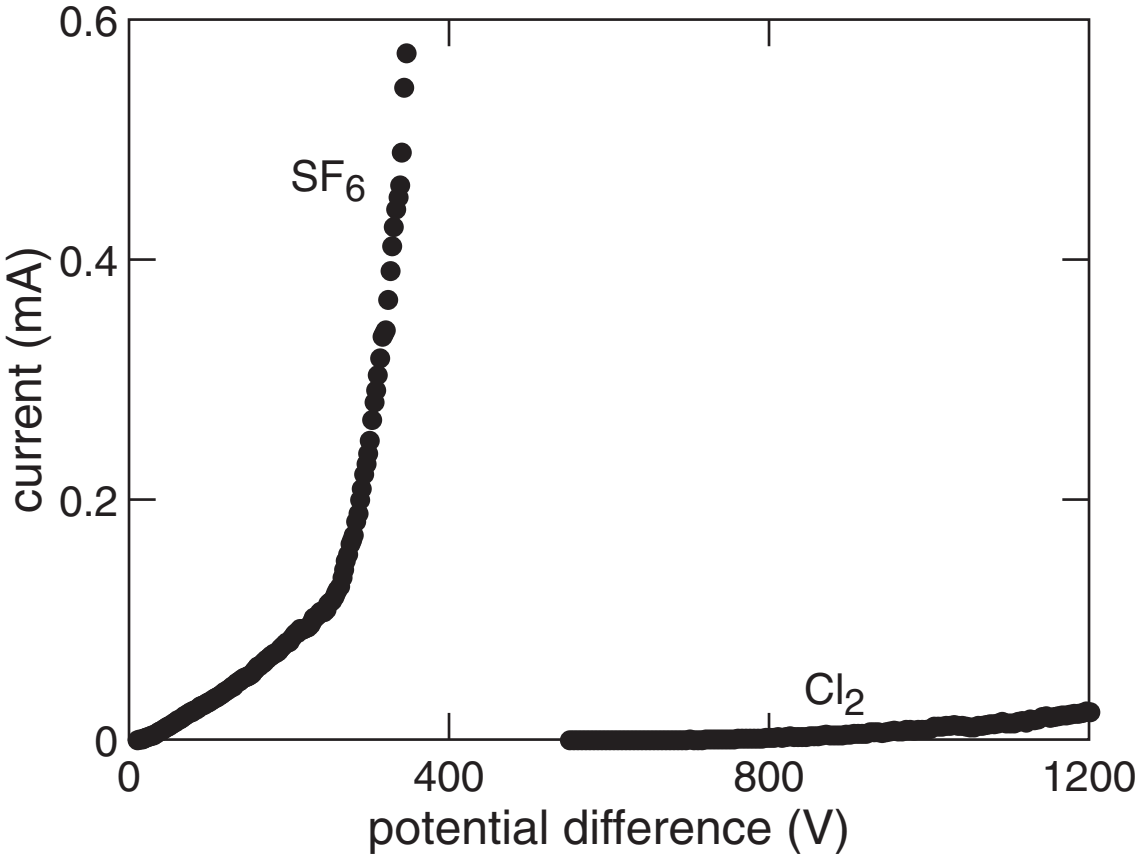
effect of ambient gas on absorptance



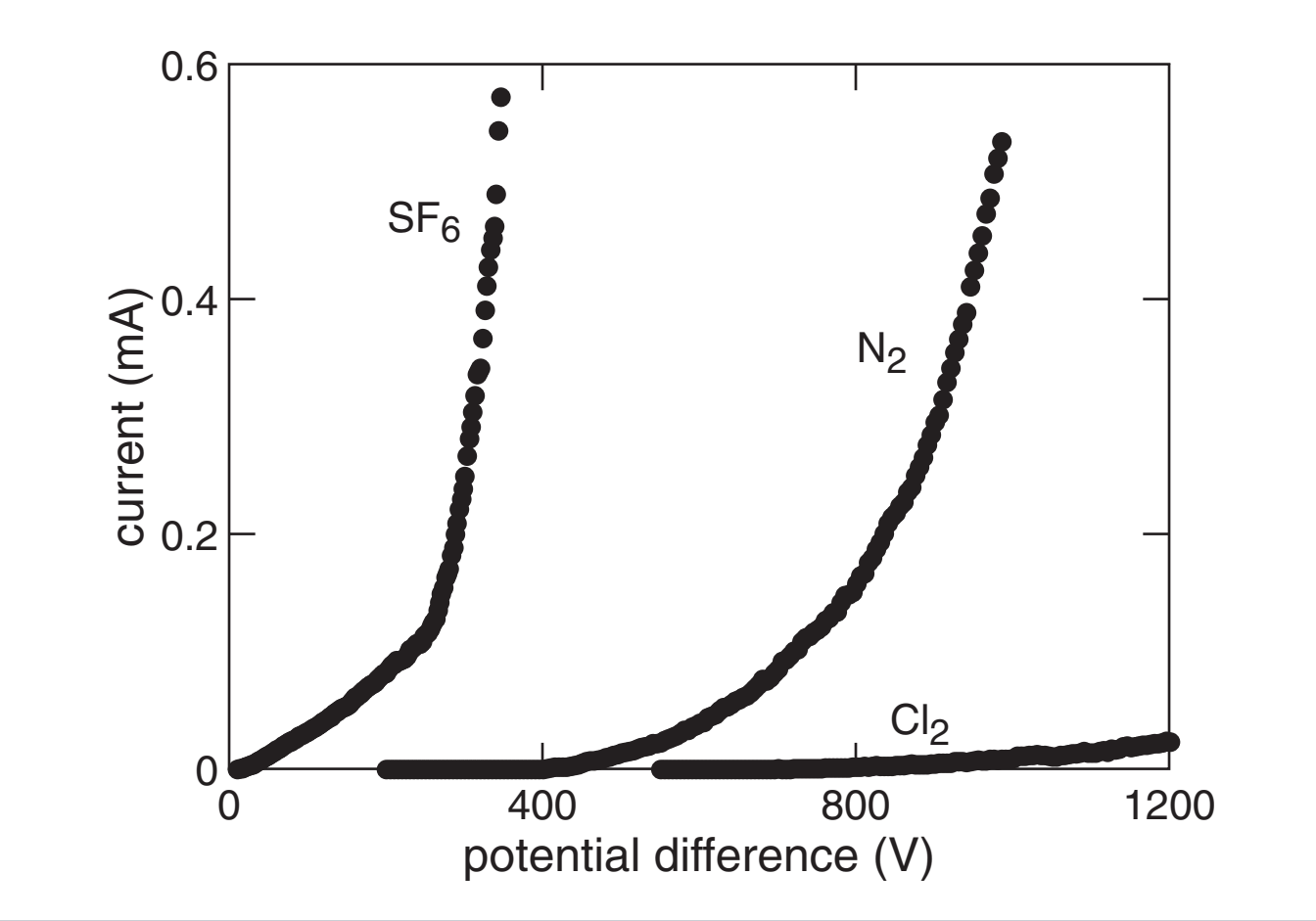
effect of ambient gas on field emission



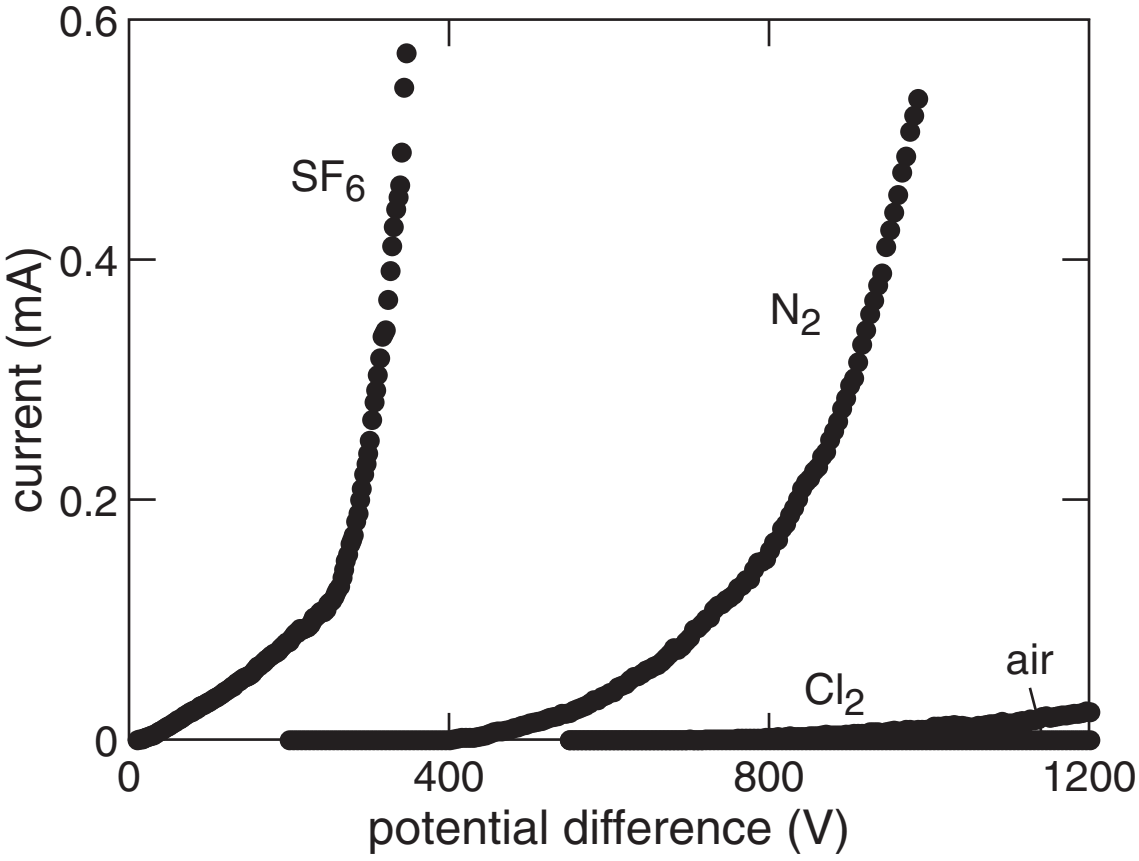
effect of ambient gas on field emission

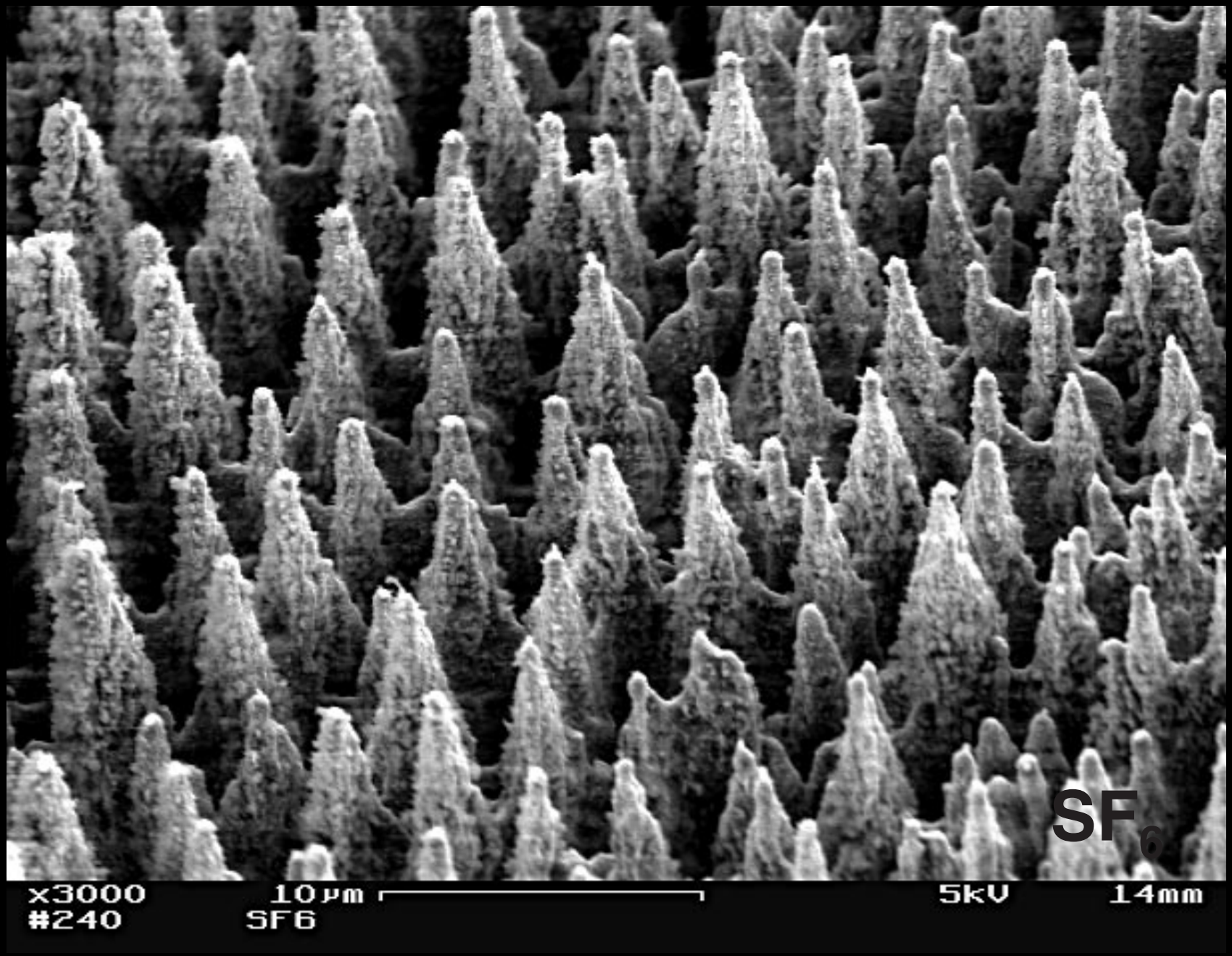


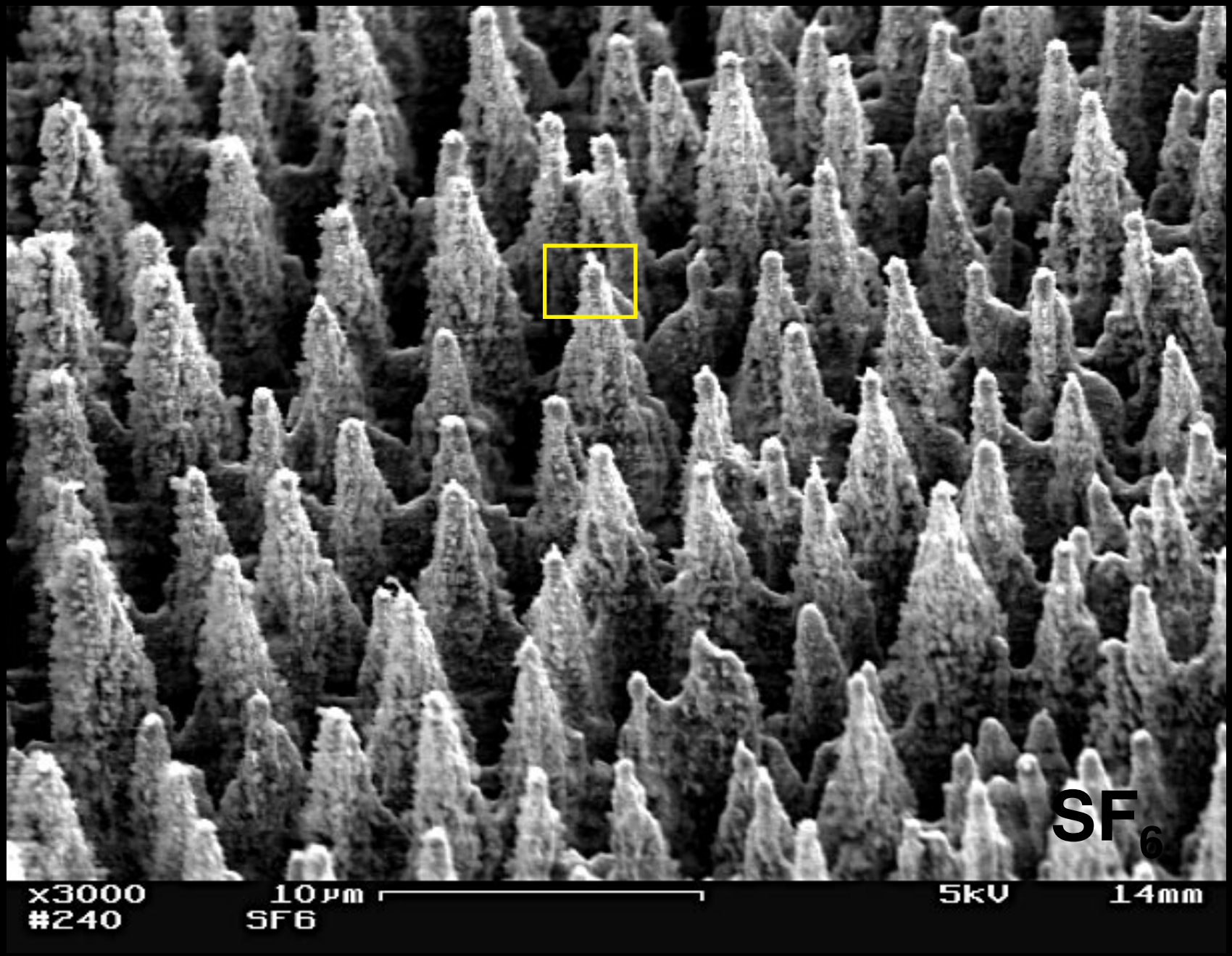
effect of ambient gas on field emission



effect of ambient gas on field emission




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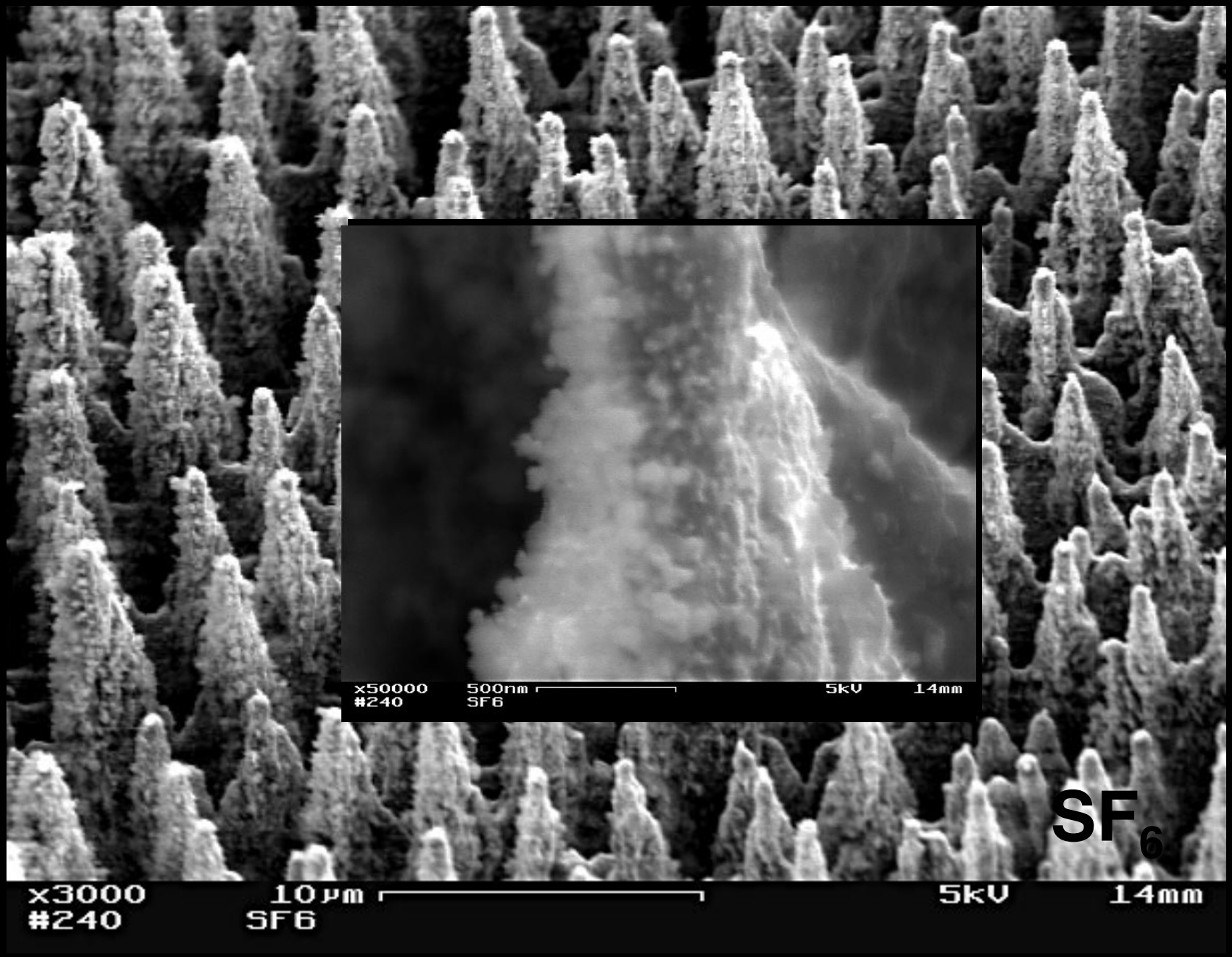
x3000
#240
10 µm
SF6
5kV
14mm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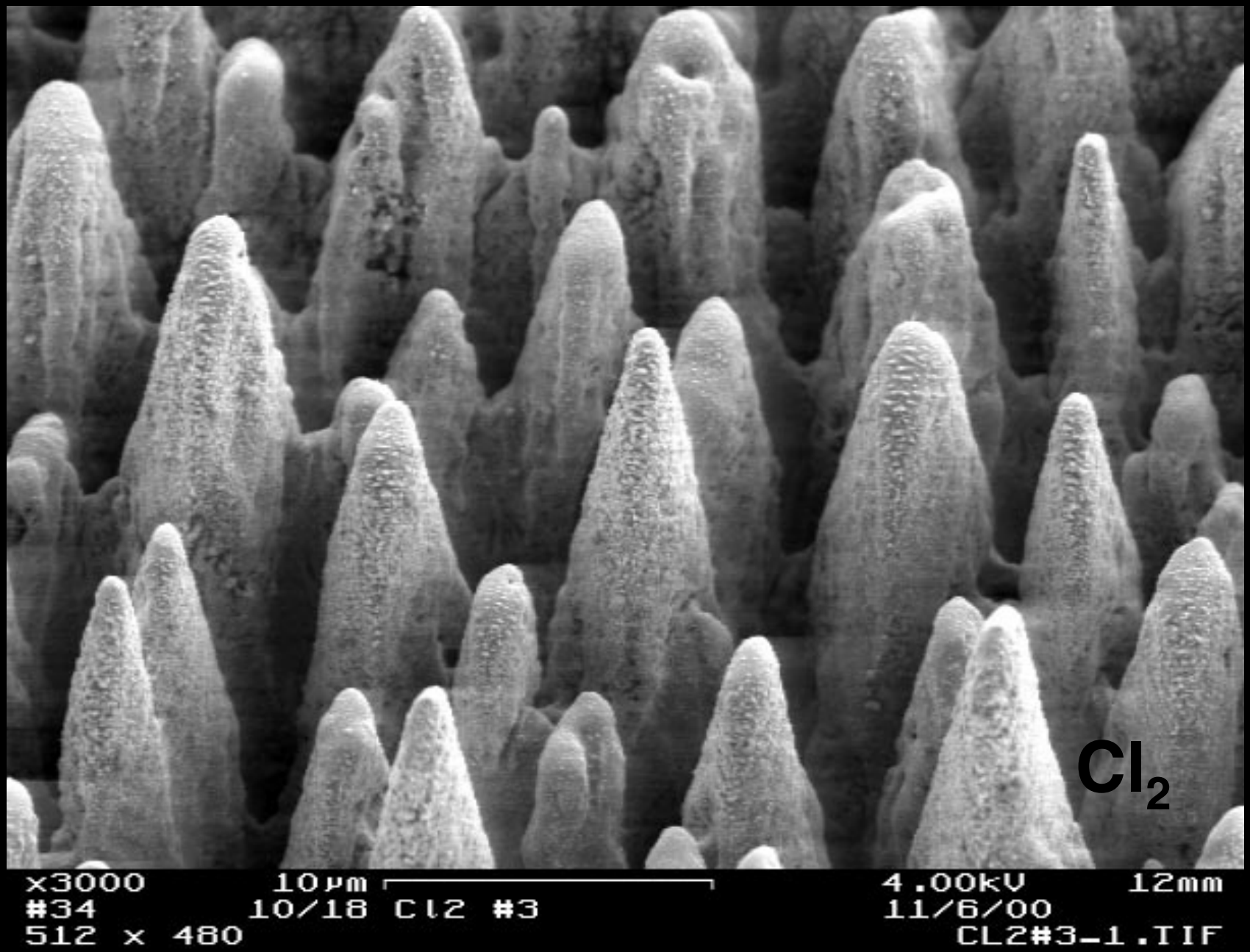
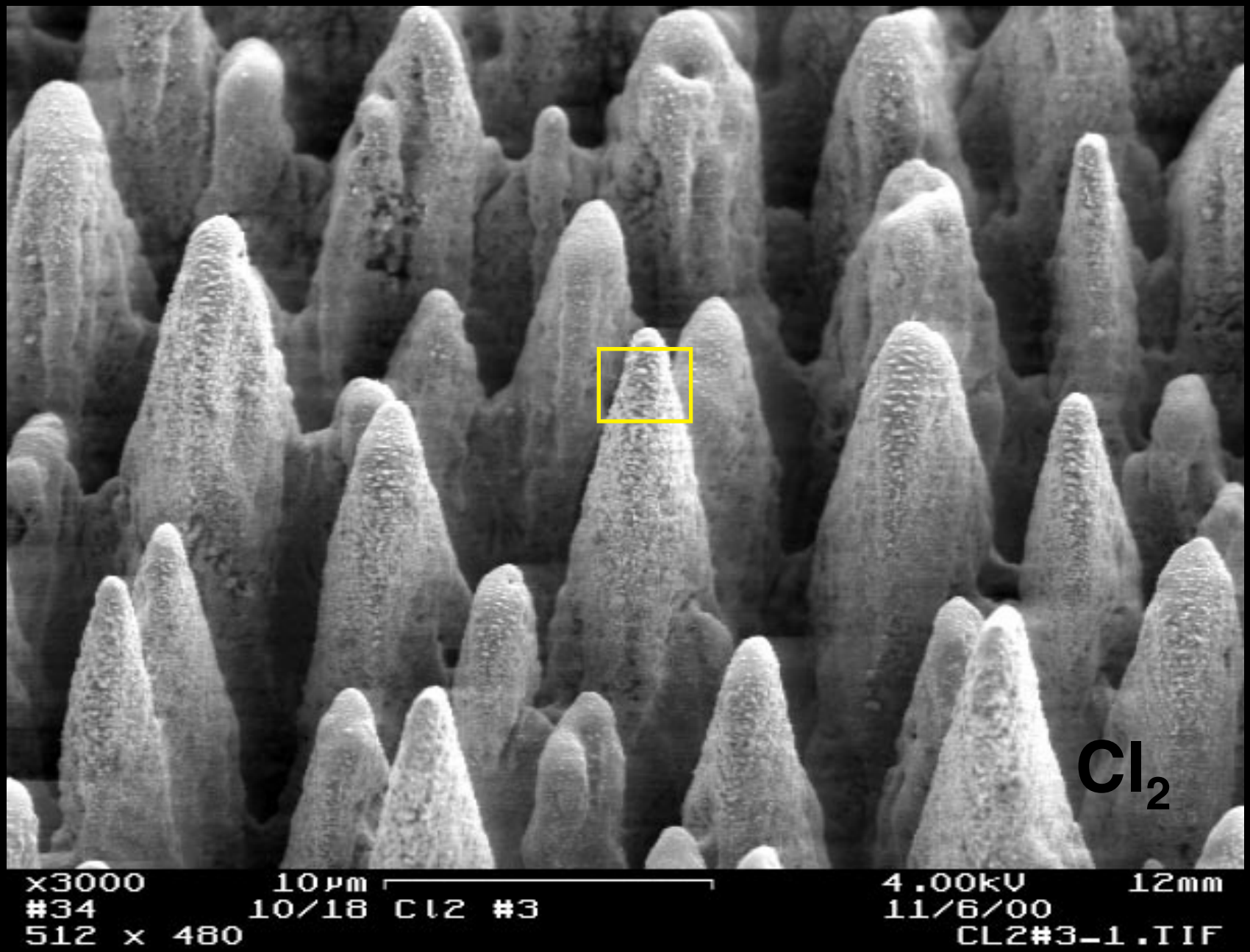
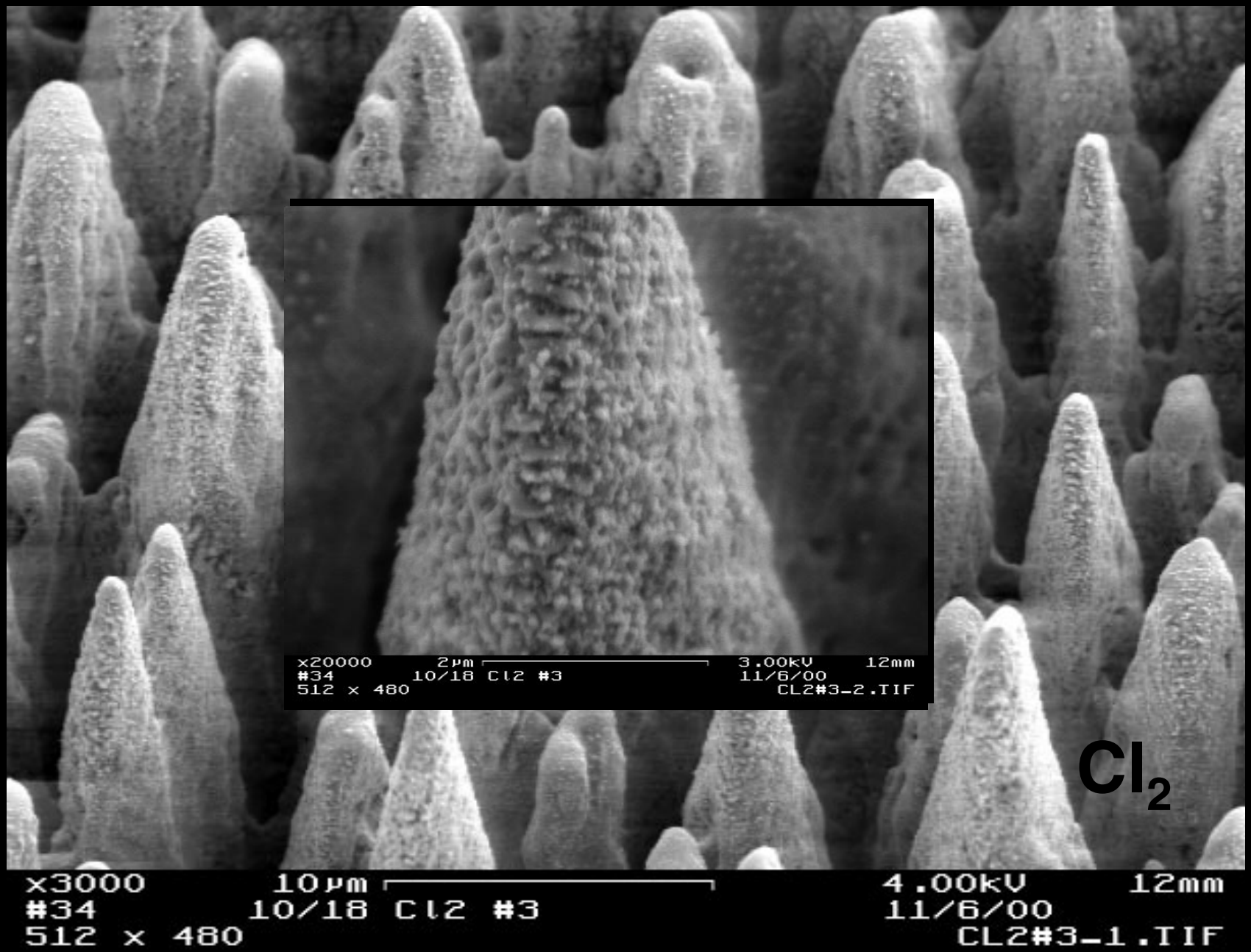
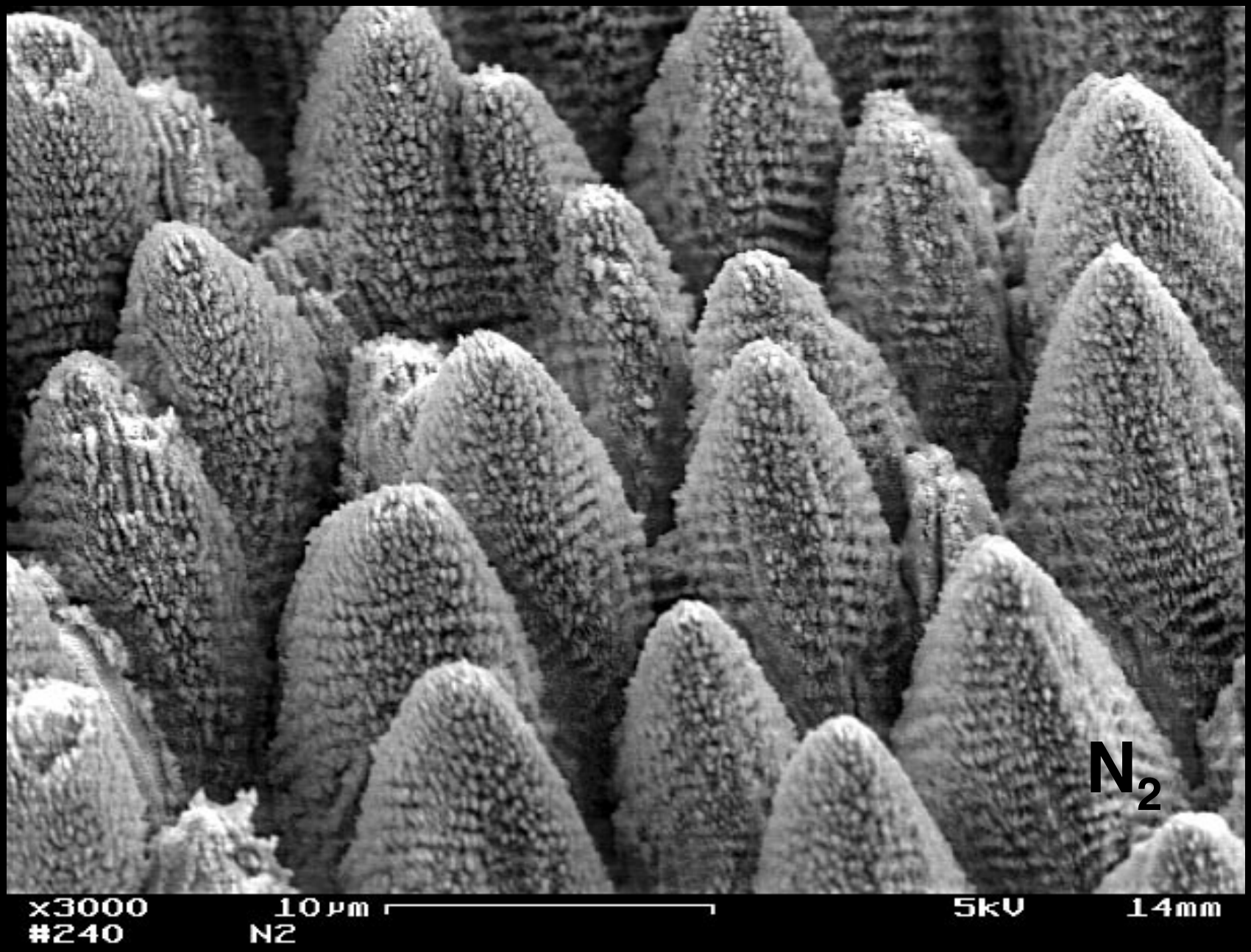
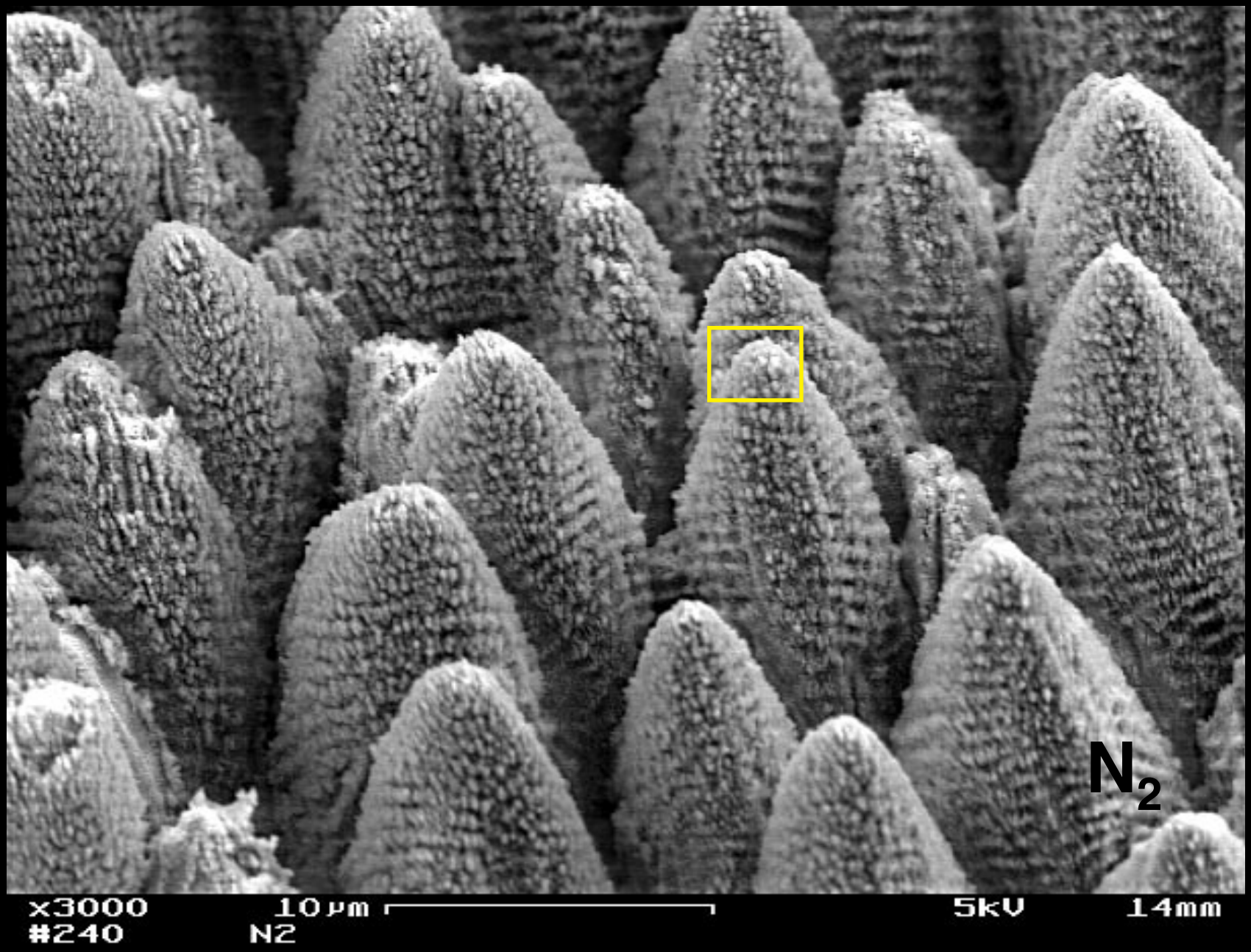
#240
500nm
SF6
5kV
14mm
SF6
x3000
#240
10μm
SF6
5kV
14mm

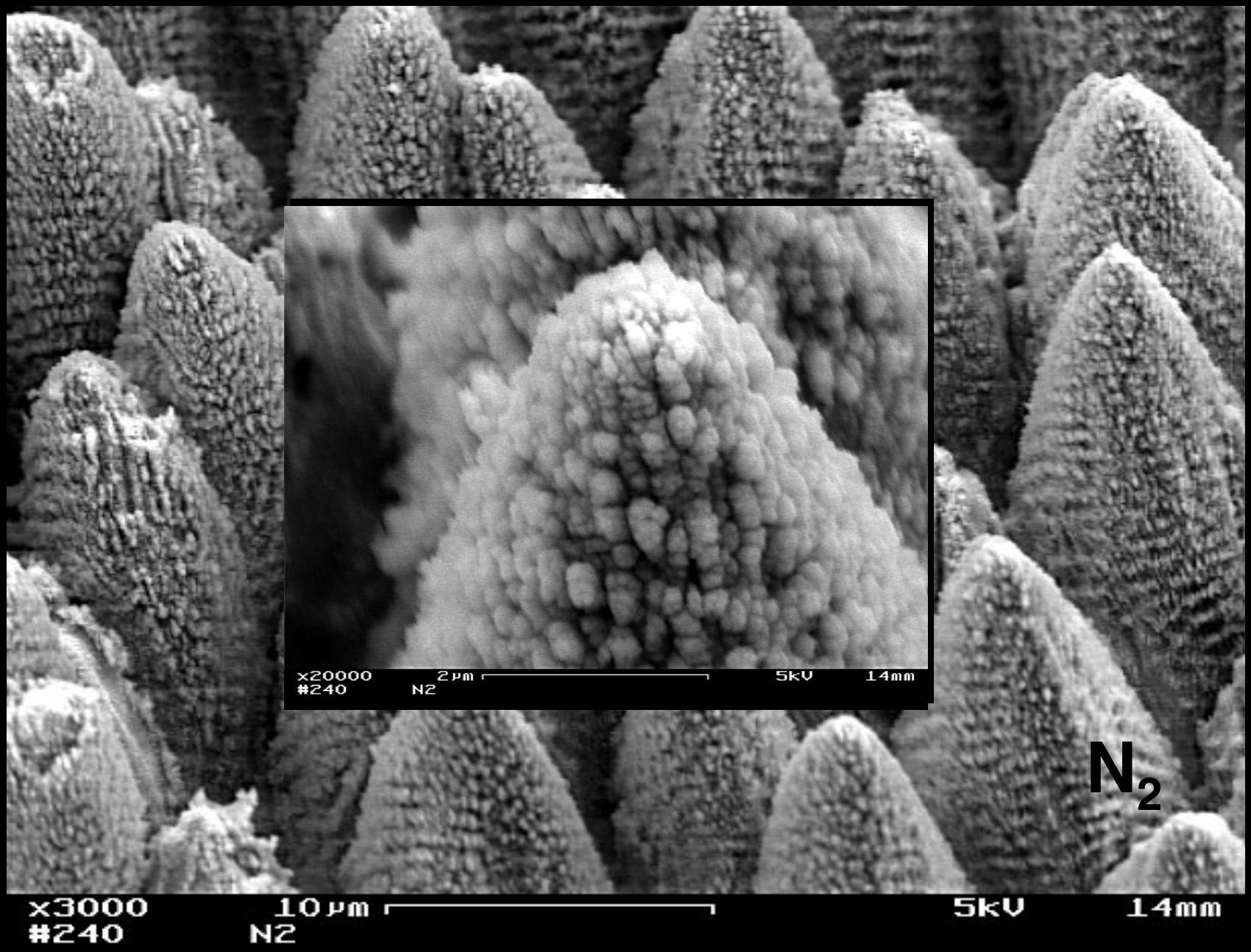

Cl_2
x3000
10μm
4.00kV
12mm
#34
10/18 Cl2 #3
11/6/00
512 x 480
CL2#3-1.TIF

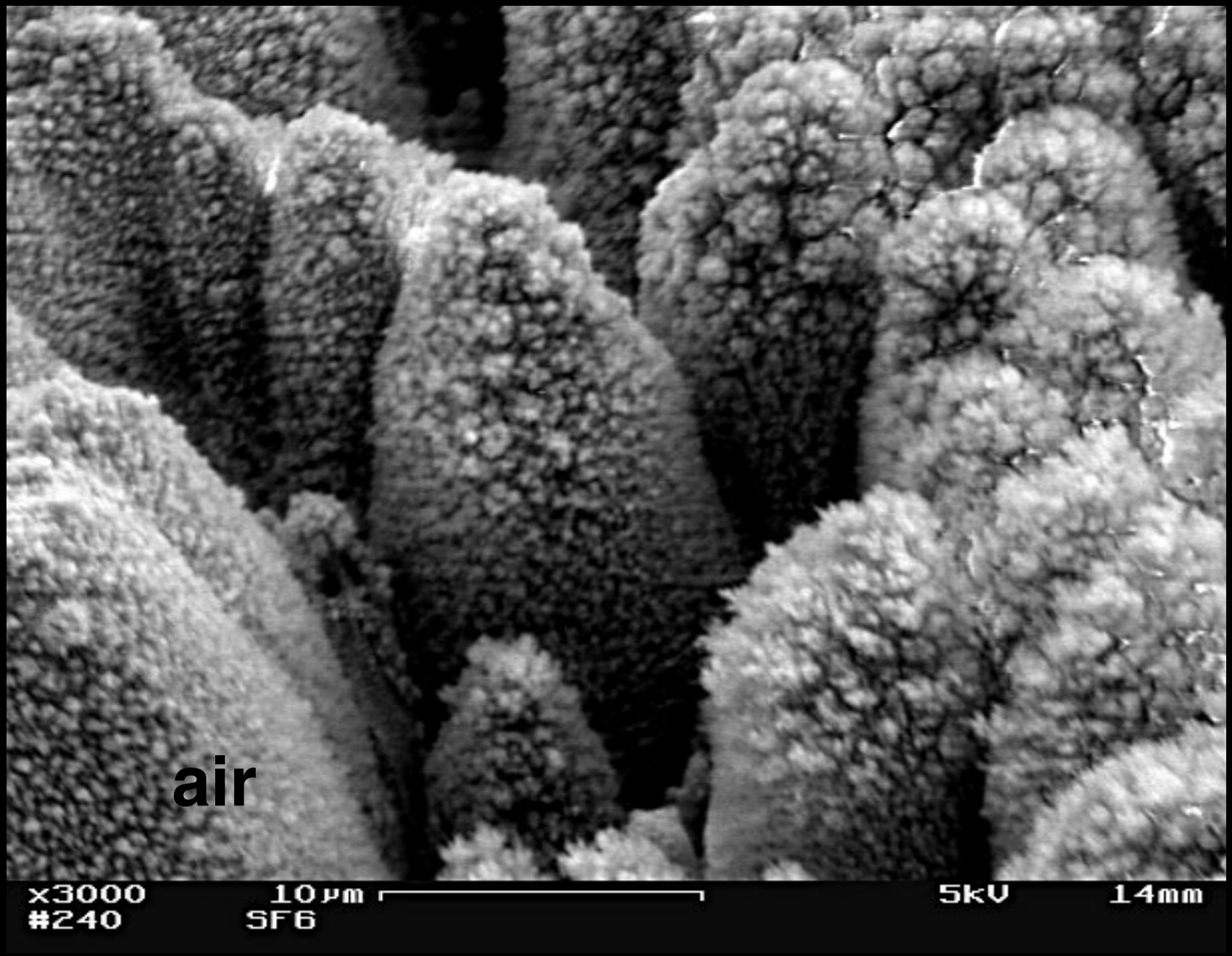

Cl_2
x3000
10μm
4.00kV
12mm
#34
10/18 Cl2 #3
11/6/00
512 x 480
CL2#3-1.TIF

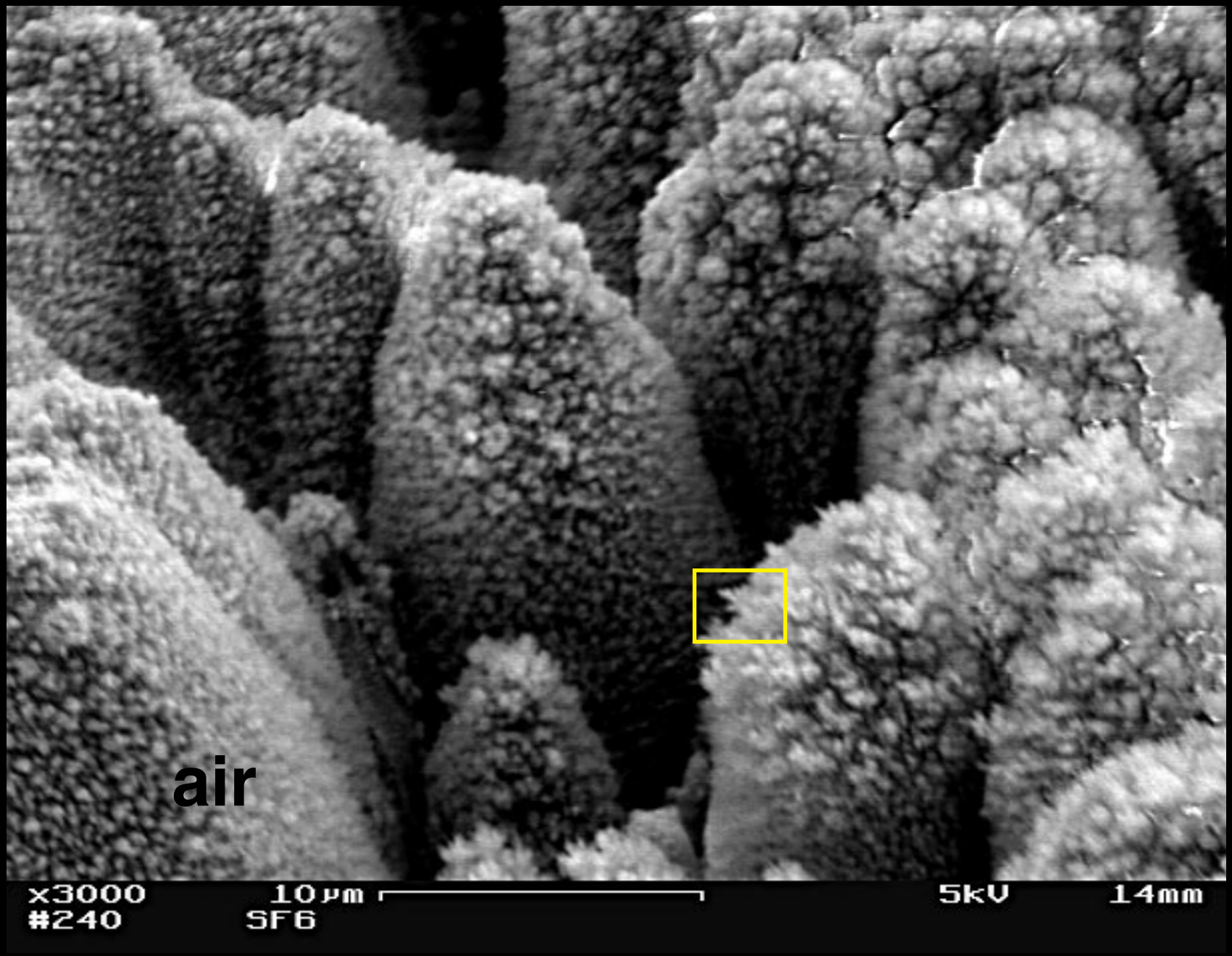

x20000 2µm 3.00kV 12mm
#34 10/18 Cl2 #3 11/6/00
512 x 480 CL2#3-2.TIF
Cl_2
x3000 10µm 4.00kV 12mm
#34 10/18 Cl2 #3 11/6/00
512 x 480 CL2#3-1.TIF

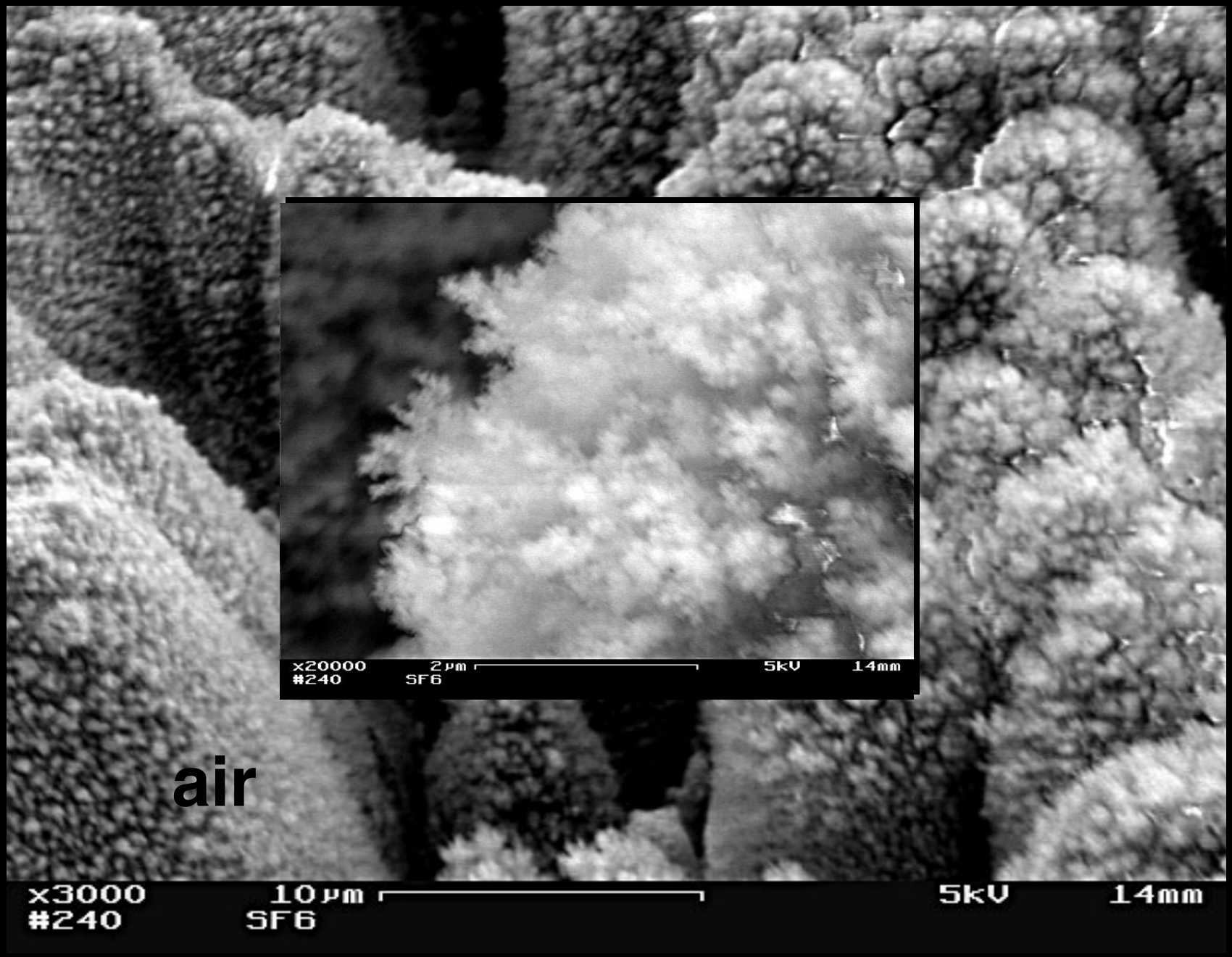

N_2
x3000
#240
10 µm
N2
5kV
14mm


N2
x3000
#240
10 µm
N2
5kV
14mm

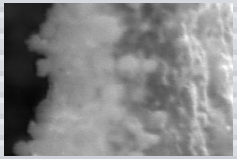
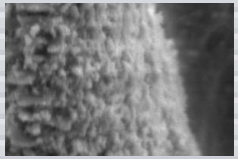
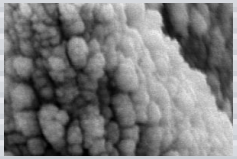

x20000 2μm 5kV 14mm
#240 N2
N_2
x3000 10μm 5kV 14mm
#240 N2


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

***New Scientist* 13, 34 (2001)**

A forest of silicon spikes could revolutionise solar cells and give you painless injections. **Bruce Schechter** peers into the mysterious world of black silicon

TALL, DARK AND STRANGER

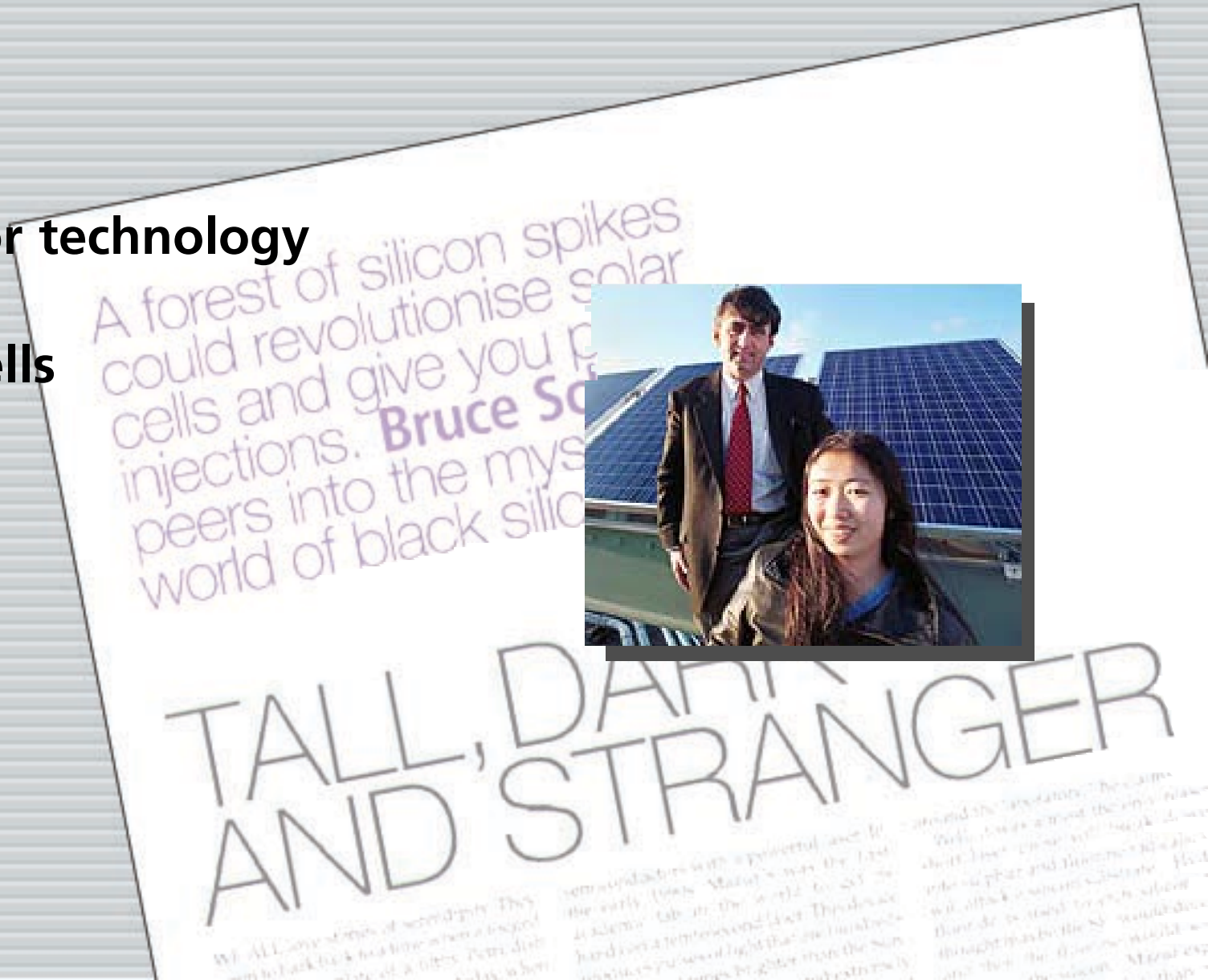
WE ALL love stories of serendipity. They
semiconductors with a powerful laser. In
the early 1990s, Mazur's was the first
academic lab in the world to get its
hands on a femtosecond laser. This device
produces pulses of light that are hundreds
around the laboratory," he claims.
Well, it was almost the only reaso
short laser pulse will break down
into sulphur and fluorine radicals,
will attack a silicon substrate. "Hyd
fluoride is used to etch silicon.
thought maybe the SF_6 would deco
and then the fluorine would so

Outlook

- **detector technology**

Outlook

- detector technology
- solar cells

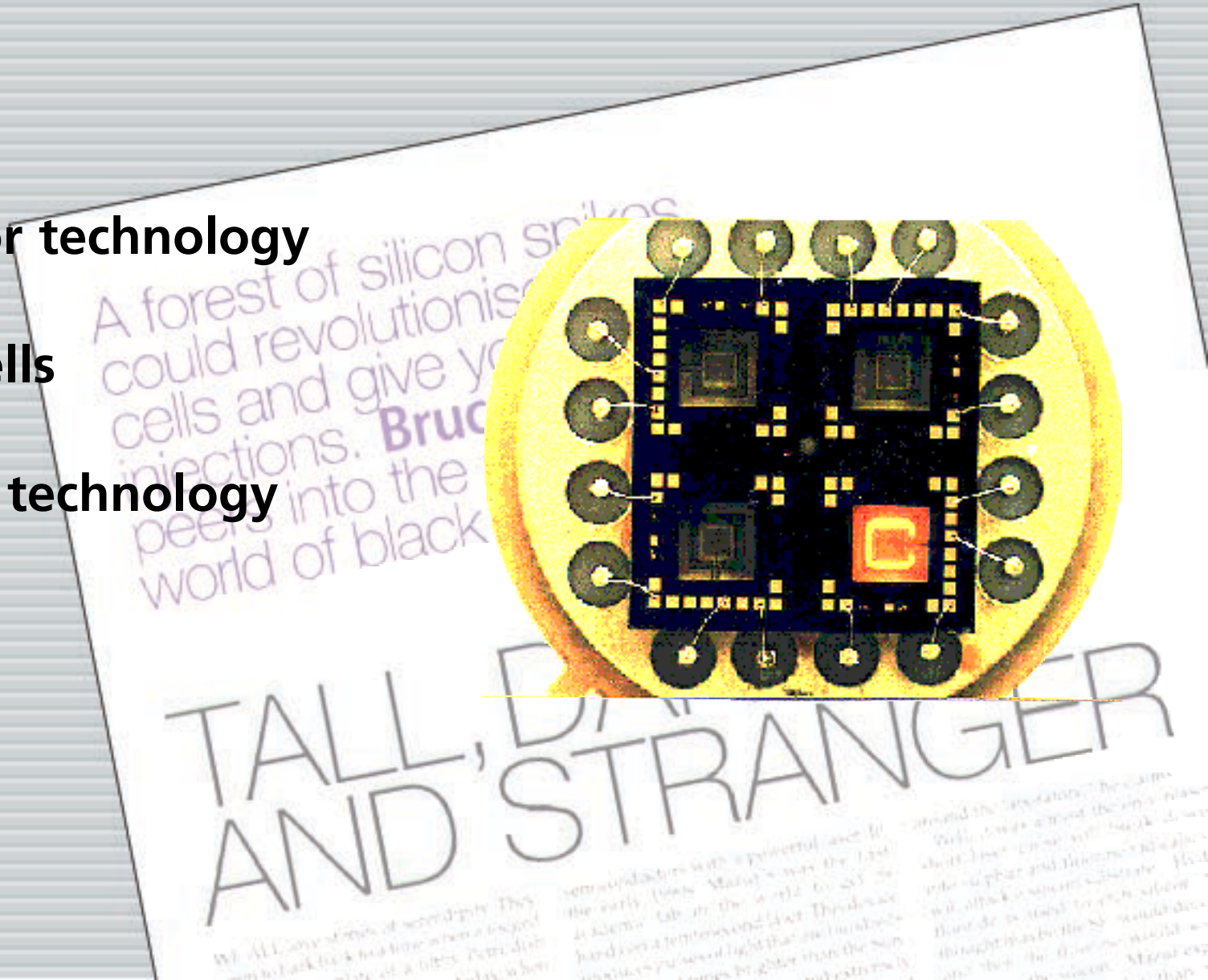


Outlook

- detector technology
- solar cells
- display technology

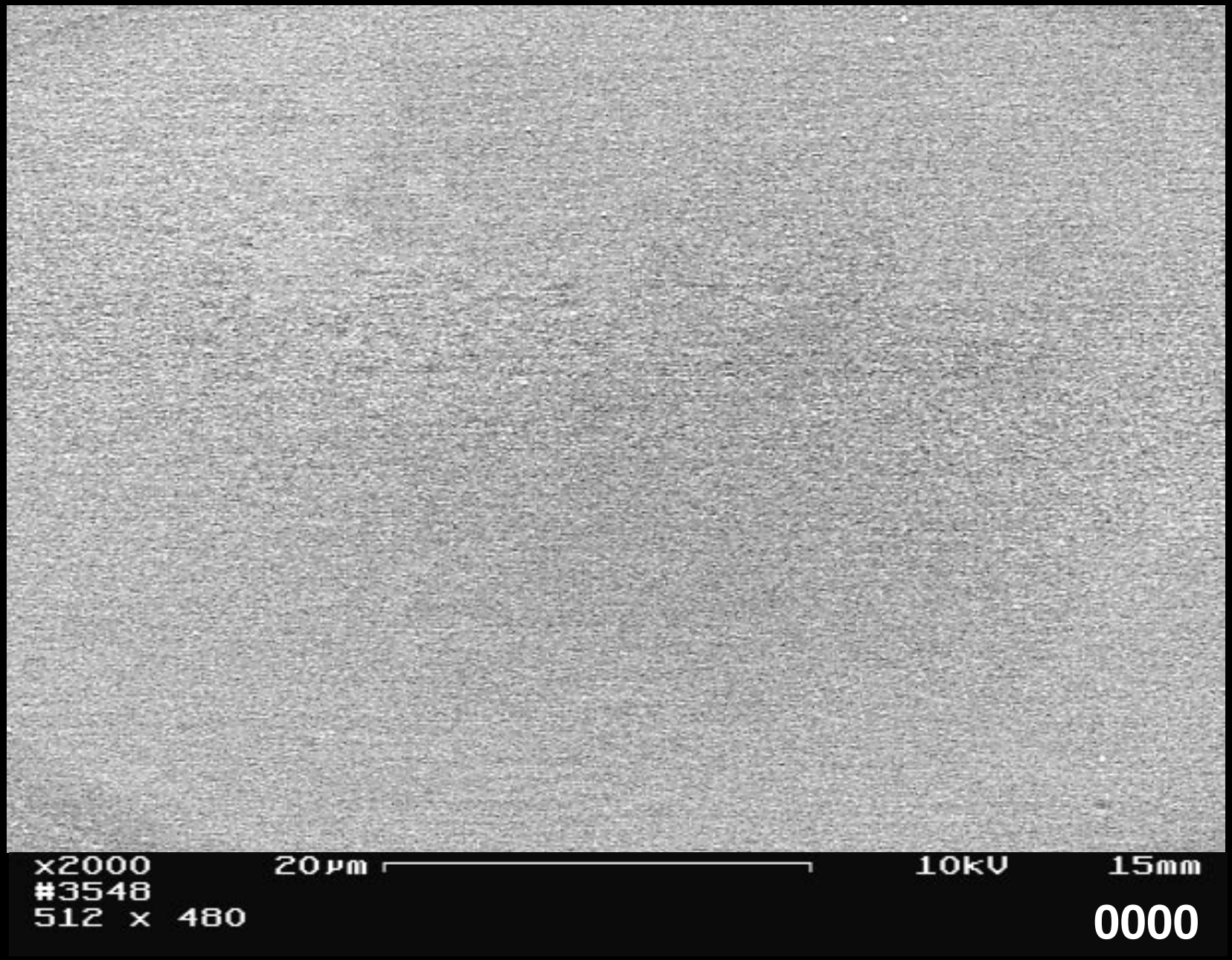
Outlook

- detector technology
- solar cells
- display technology
- sensors



Outlook

- development of spikes
- spike formation through grids
- cell adhesion
- functionalization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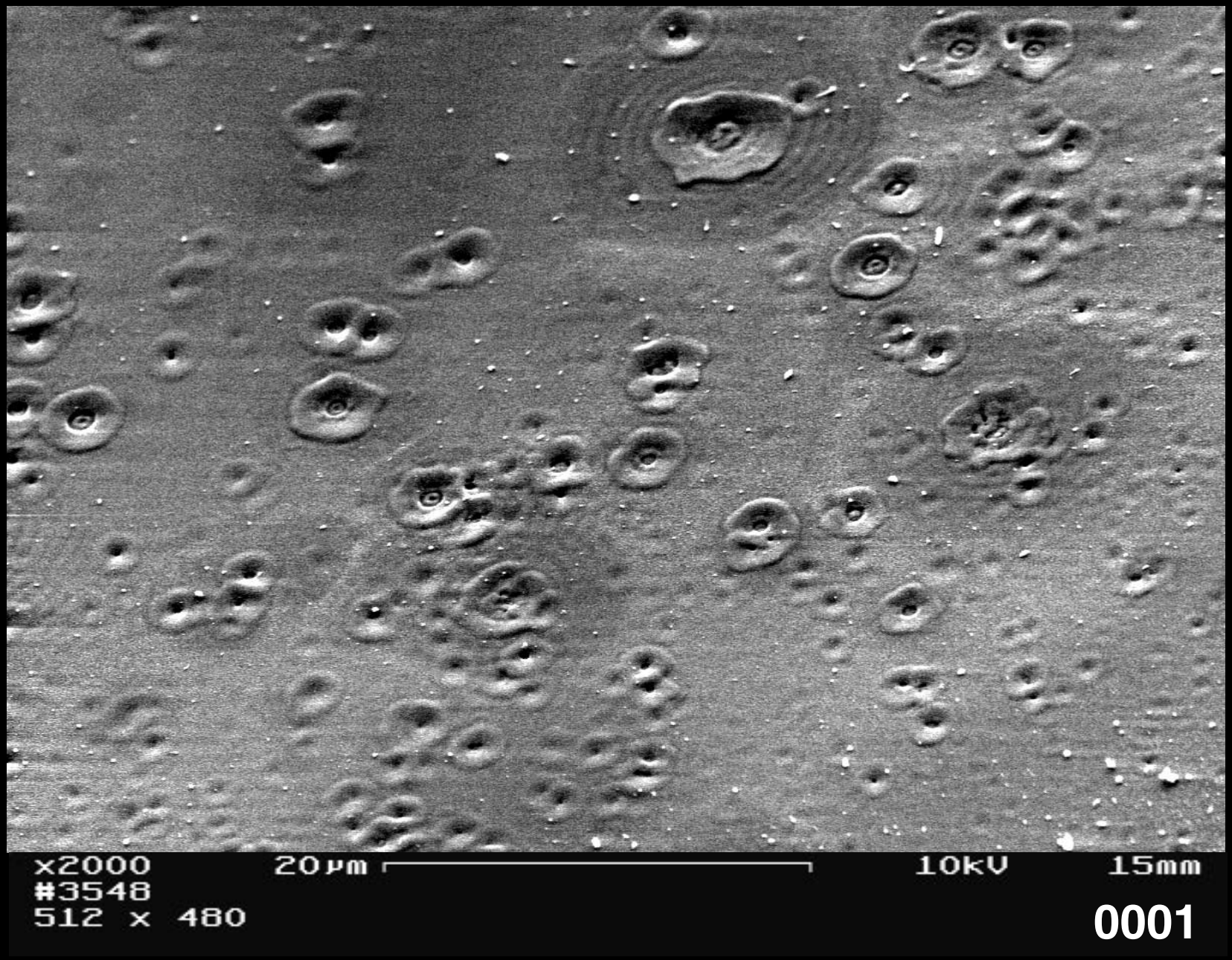
20µm
10kV
15mm
#3548
512 x 480
0000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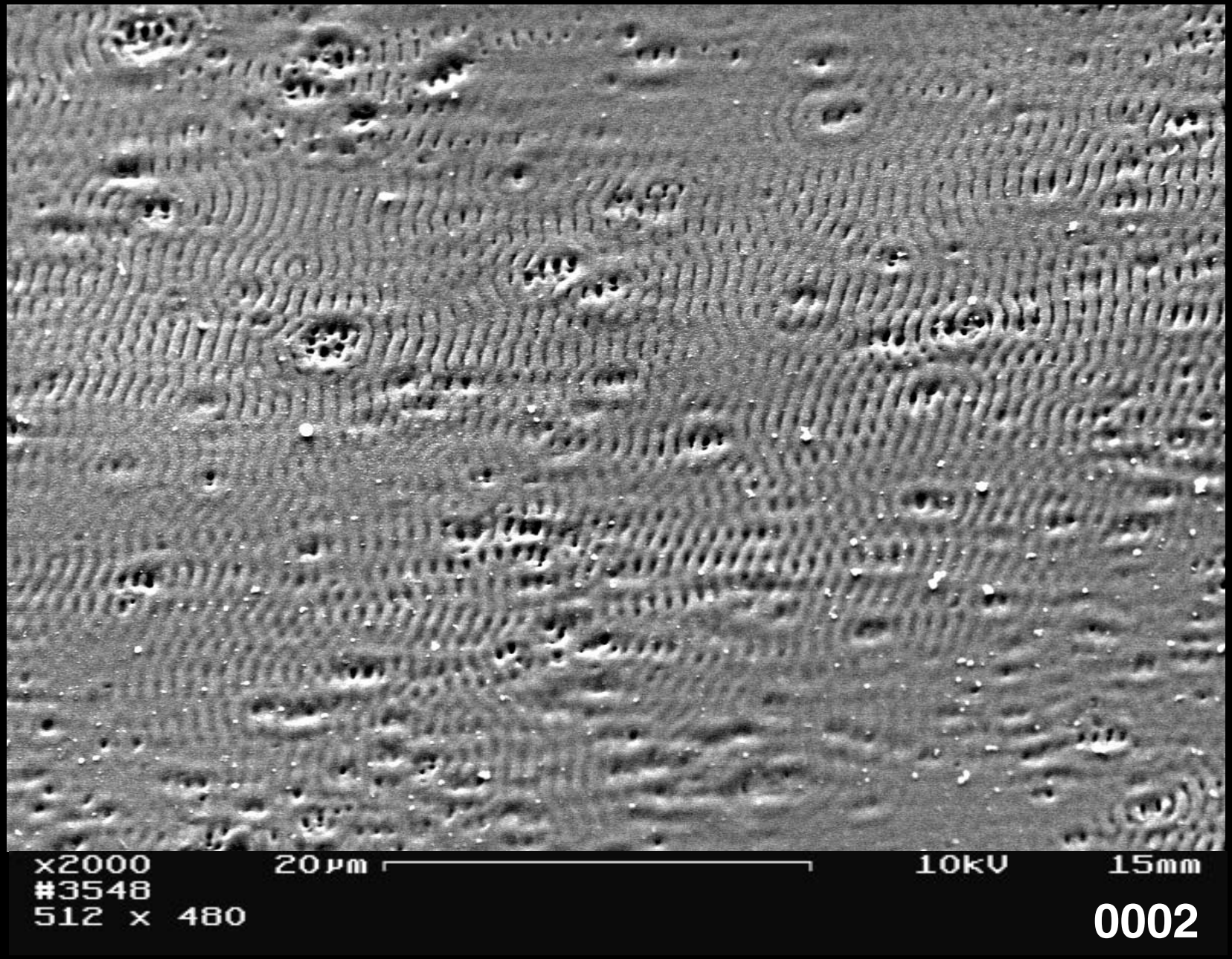
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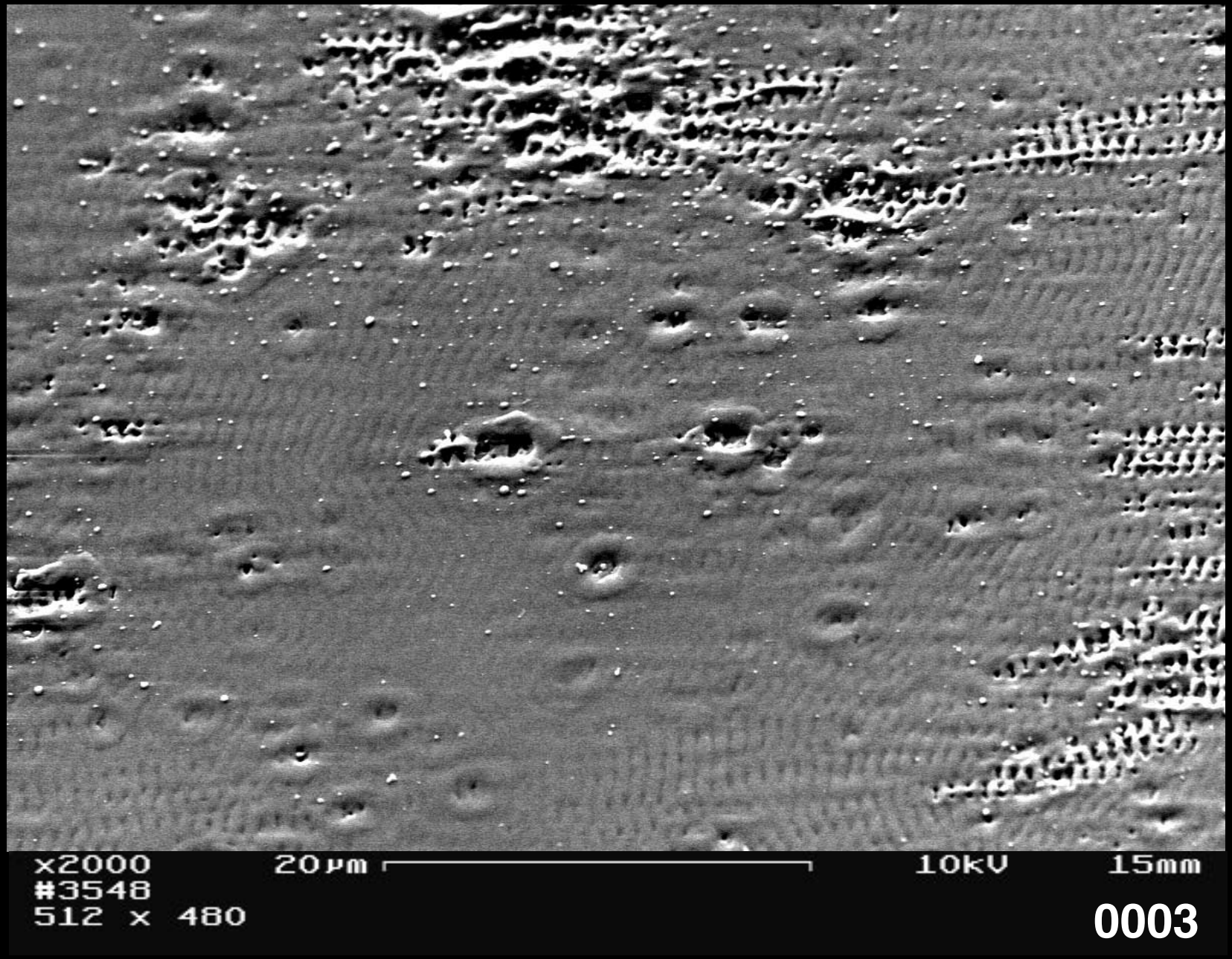
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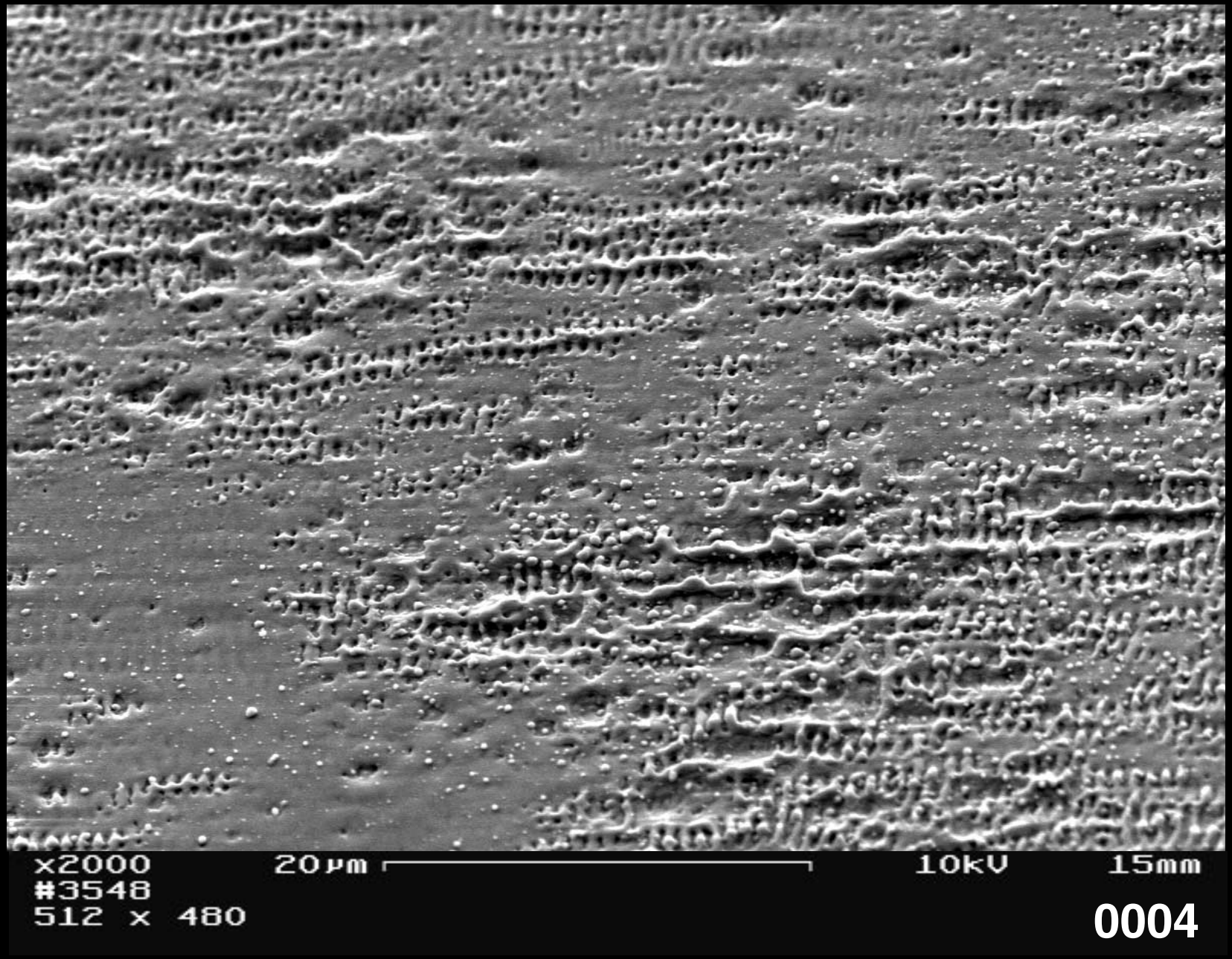
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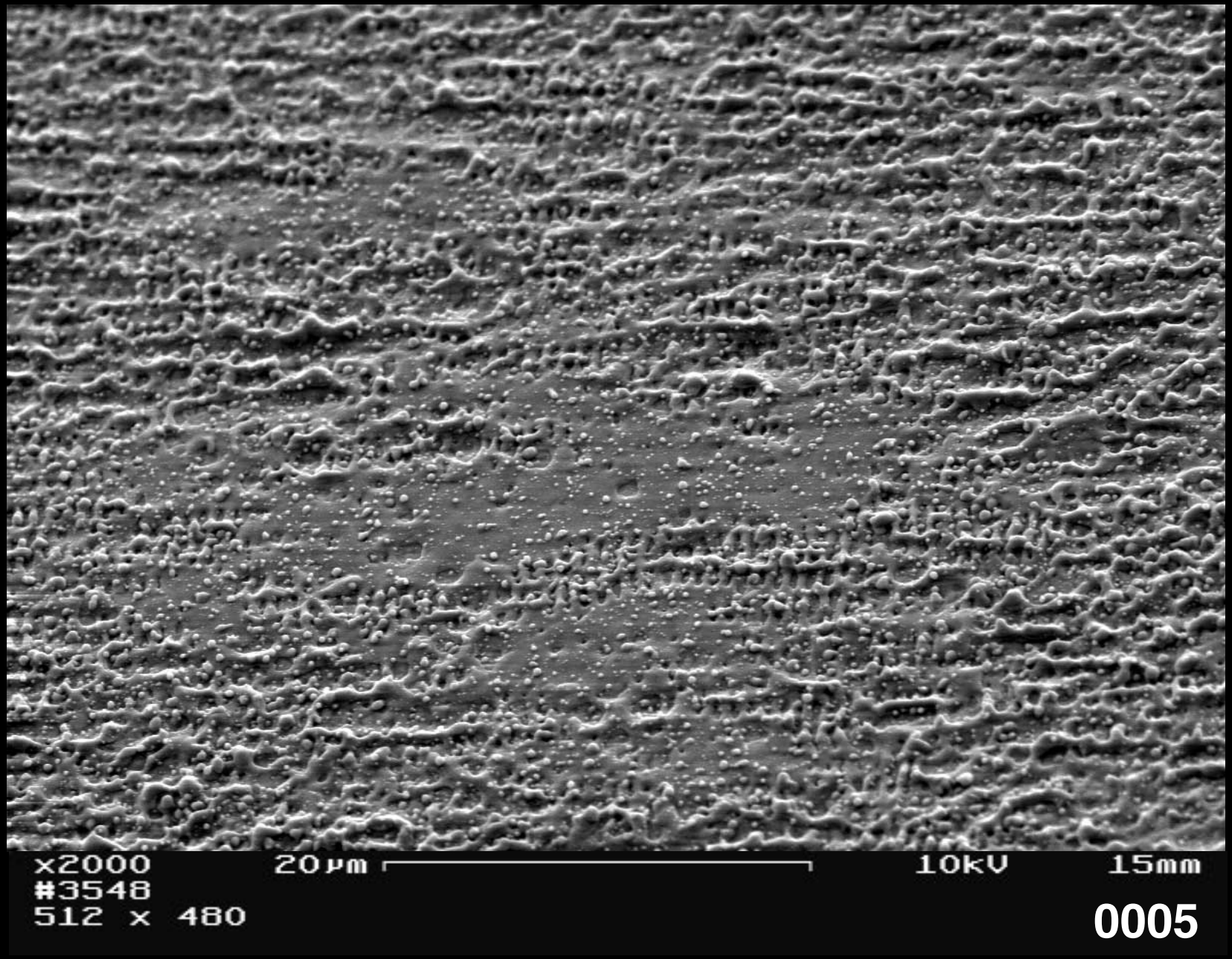
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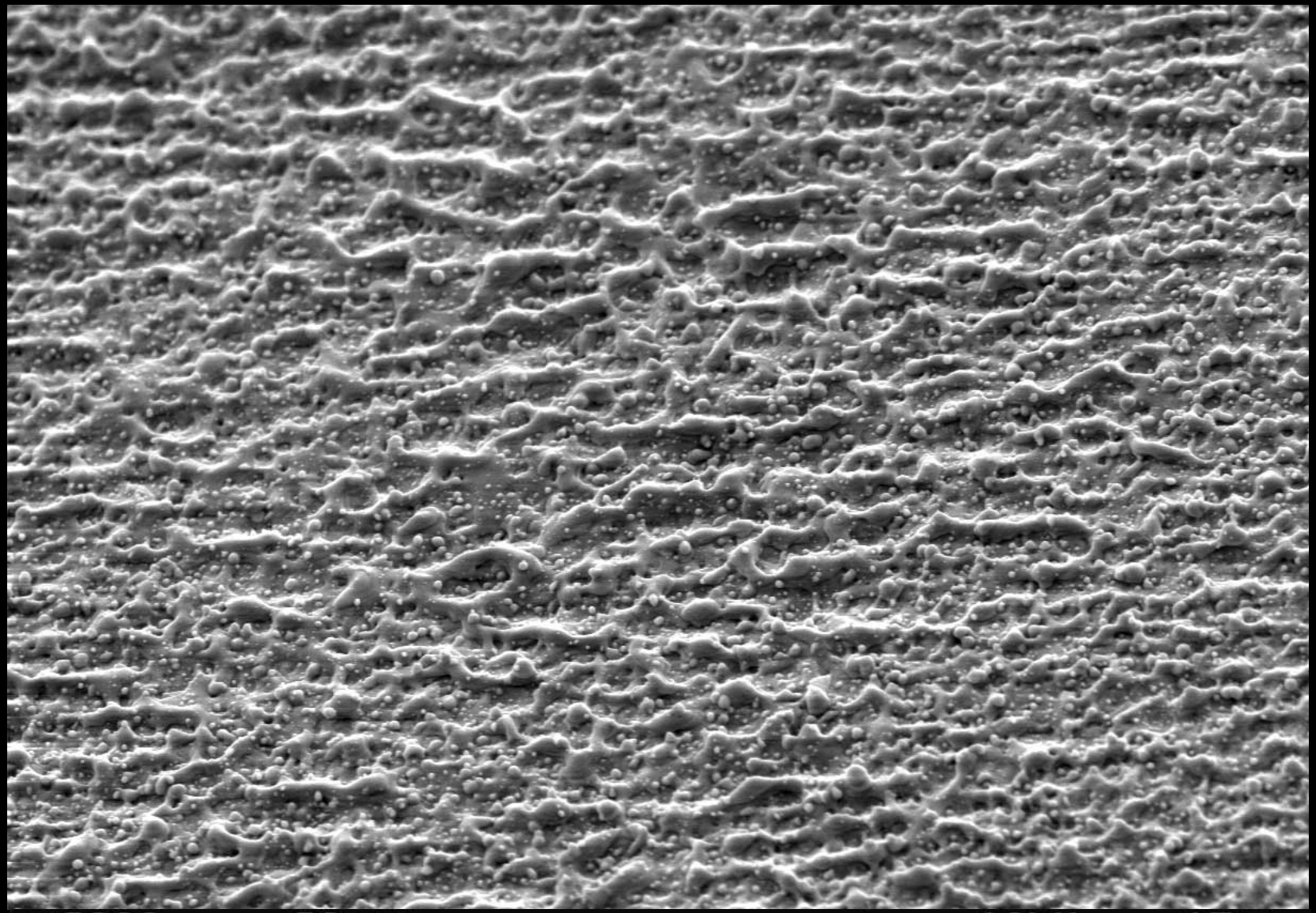

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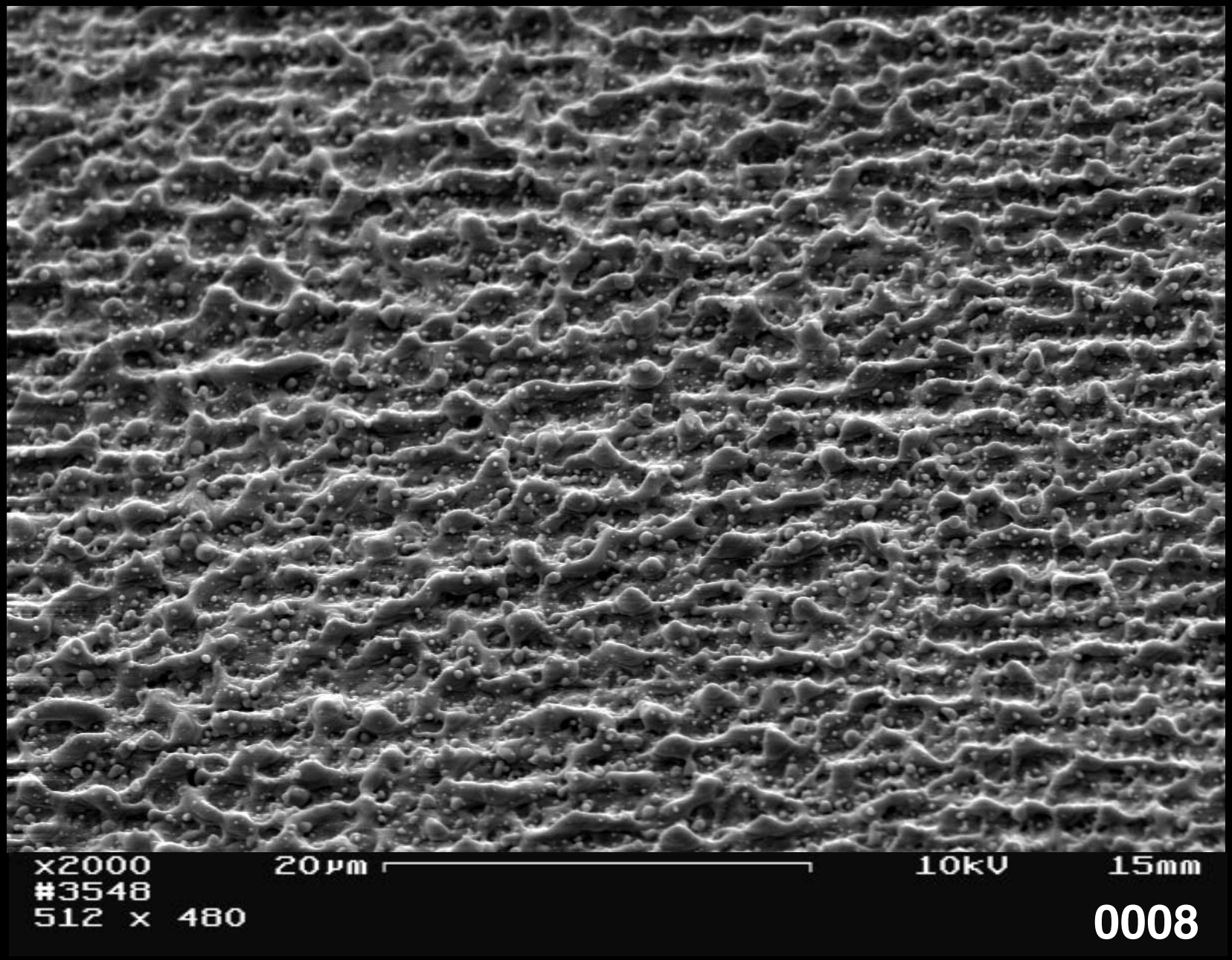
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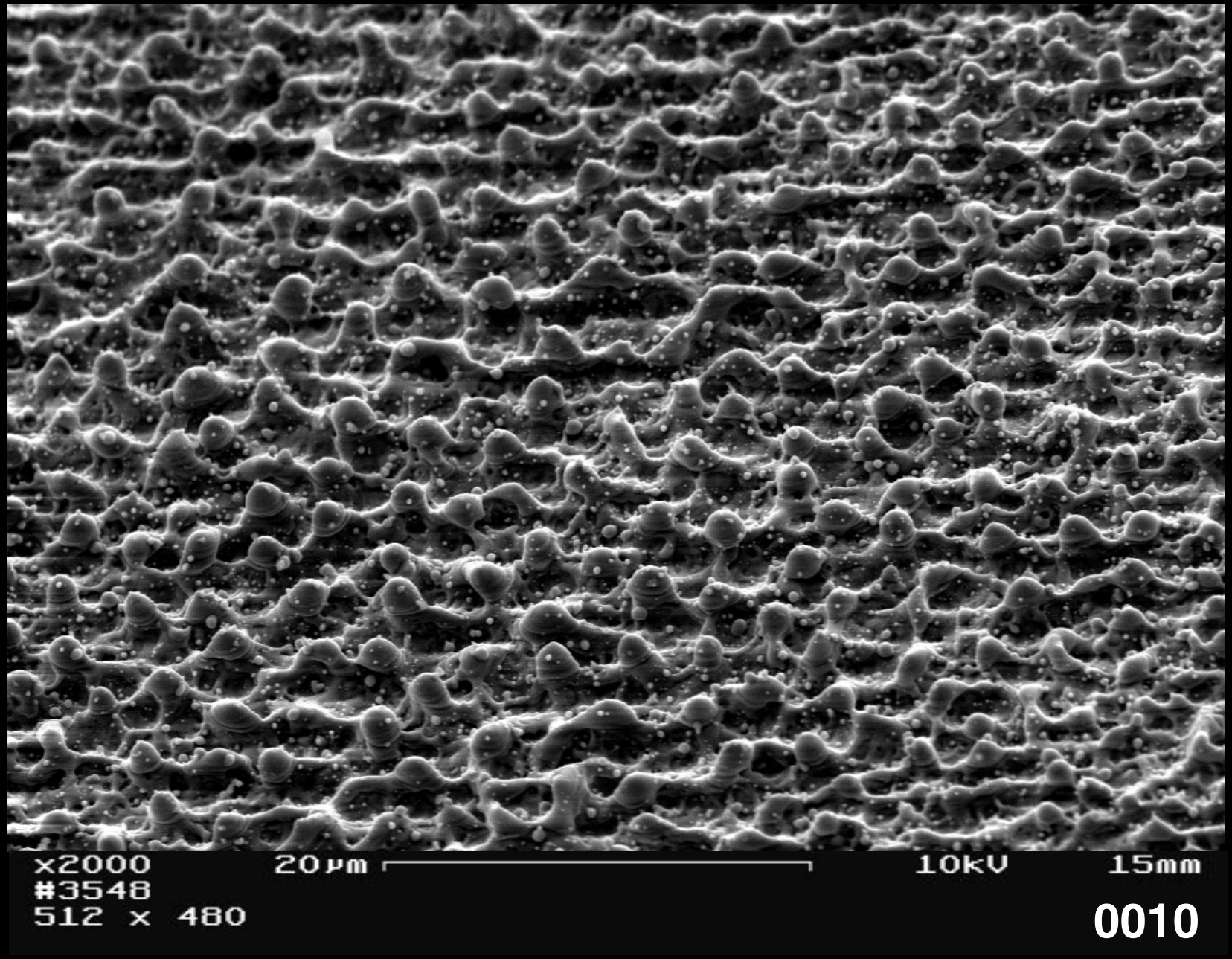
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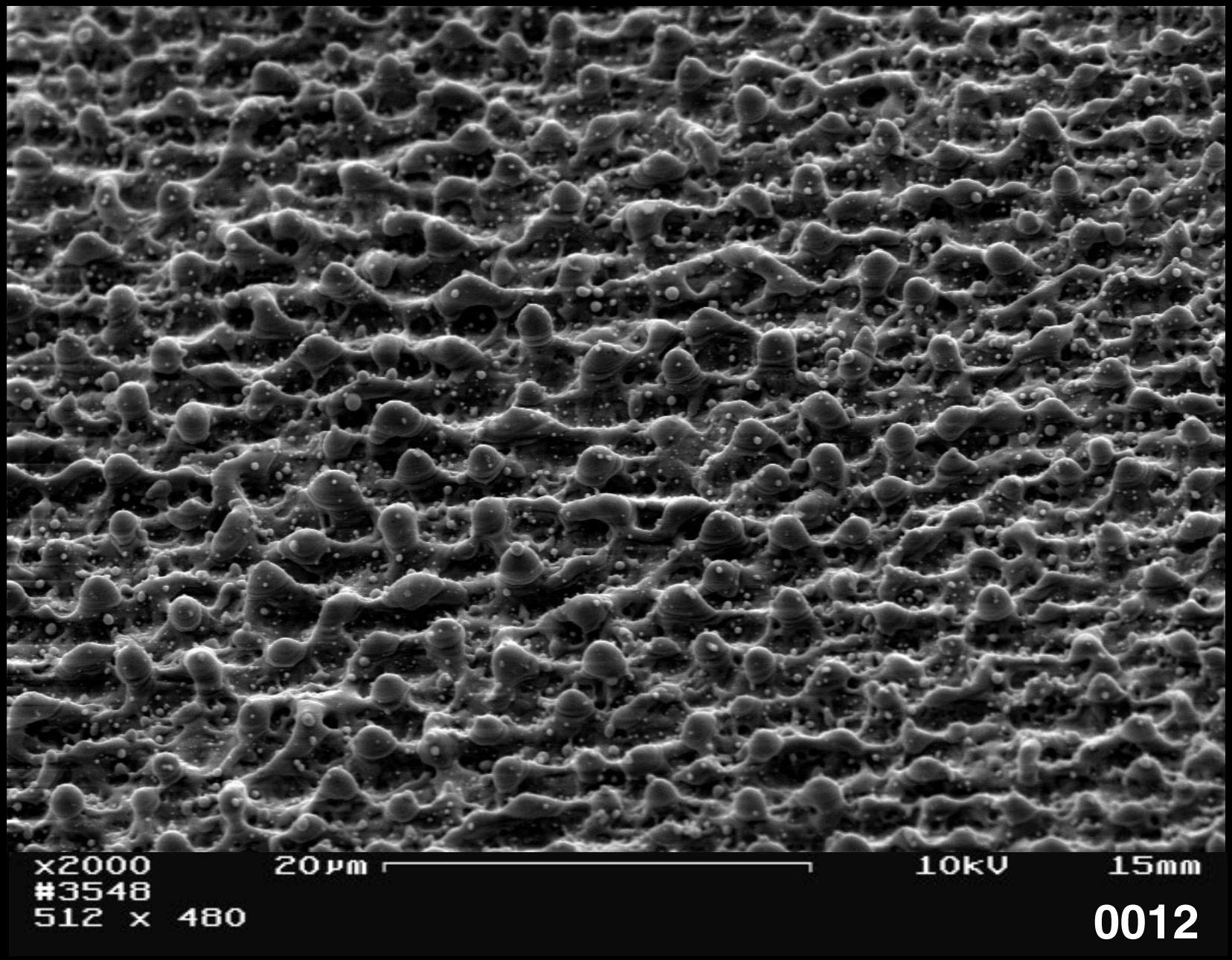
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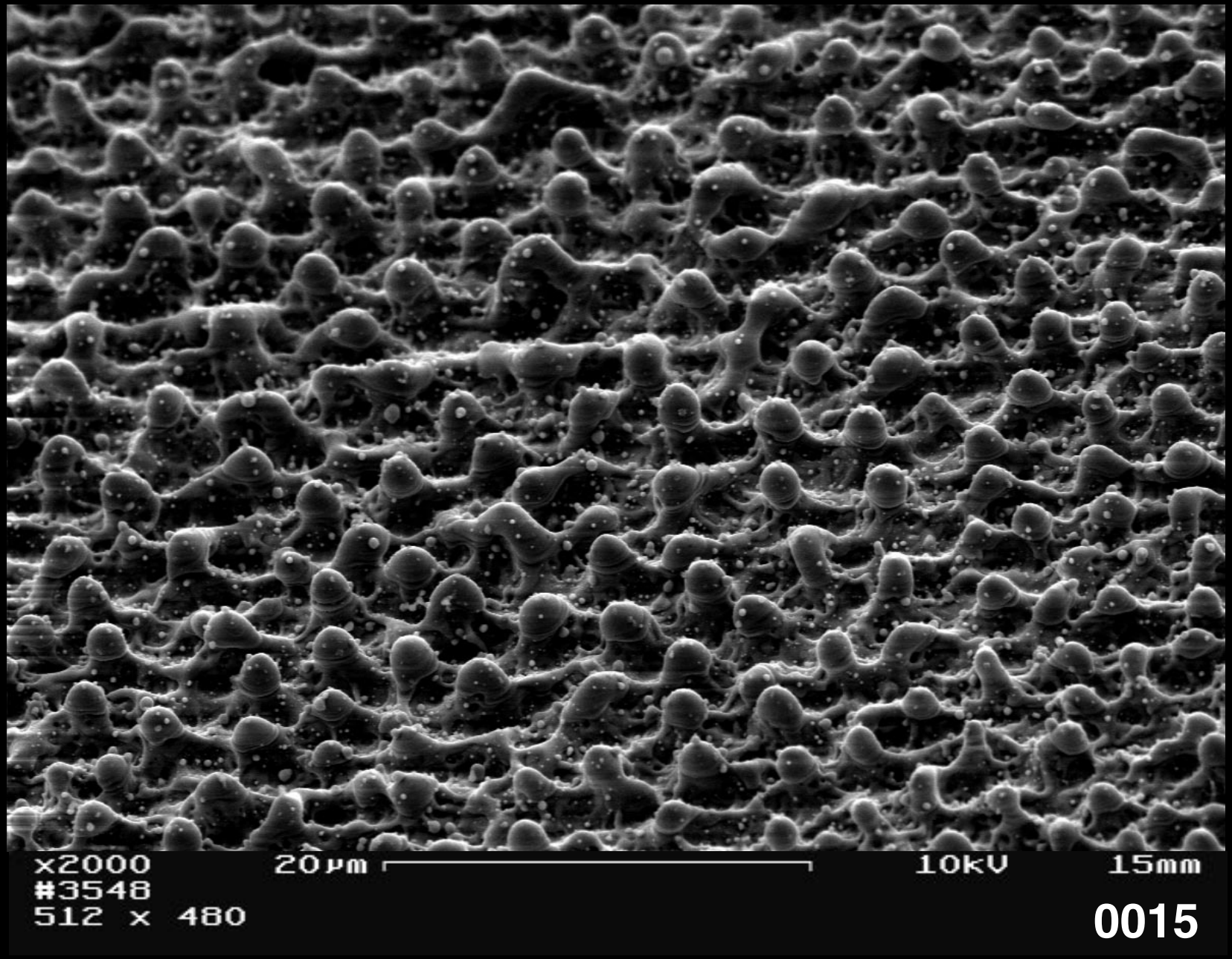
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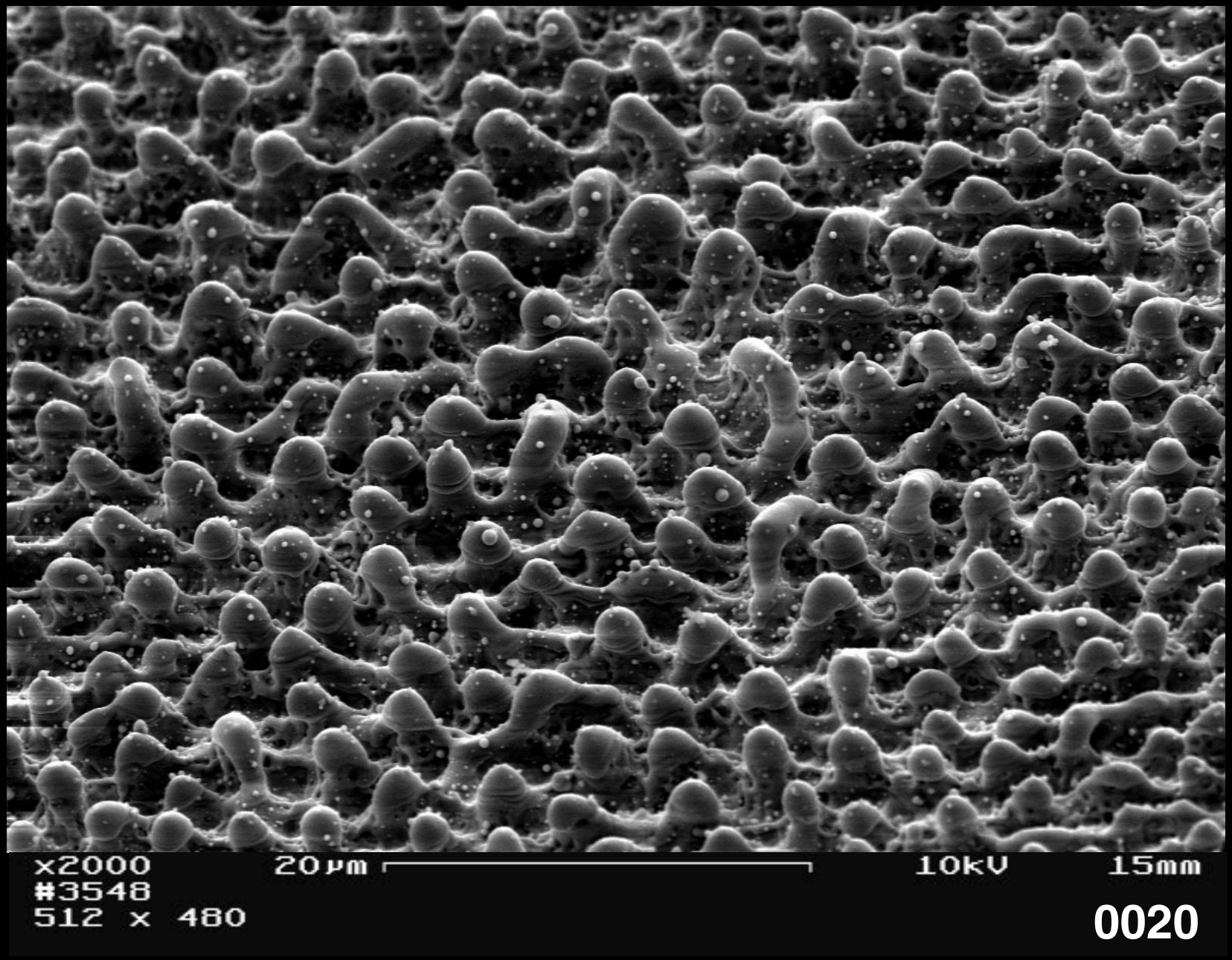
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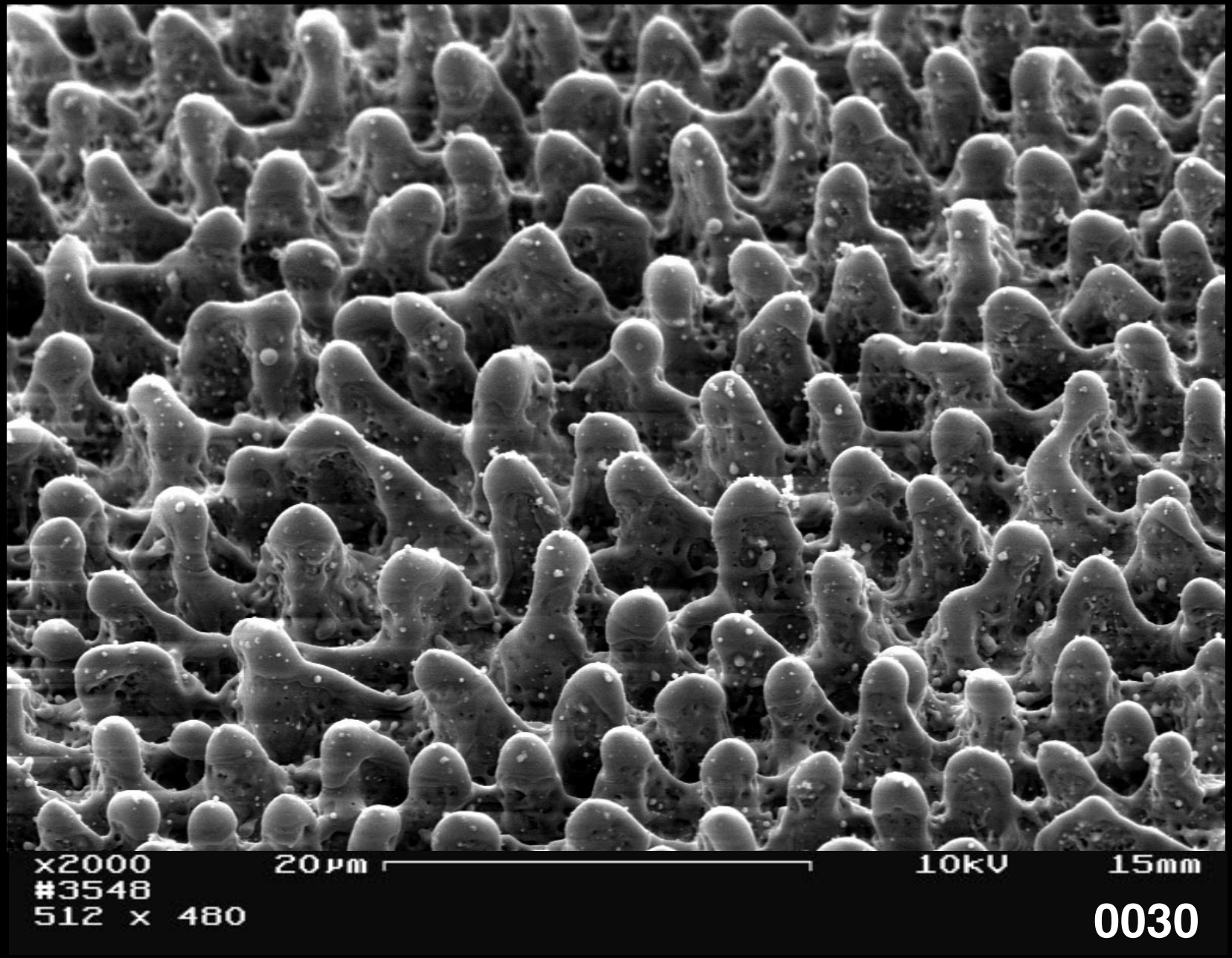
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15mm
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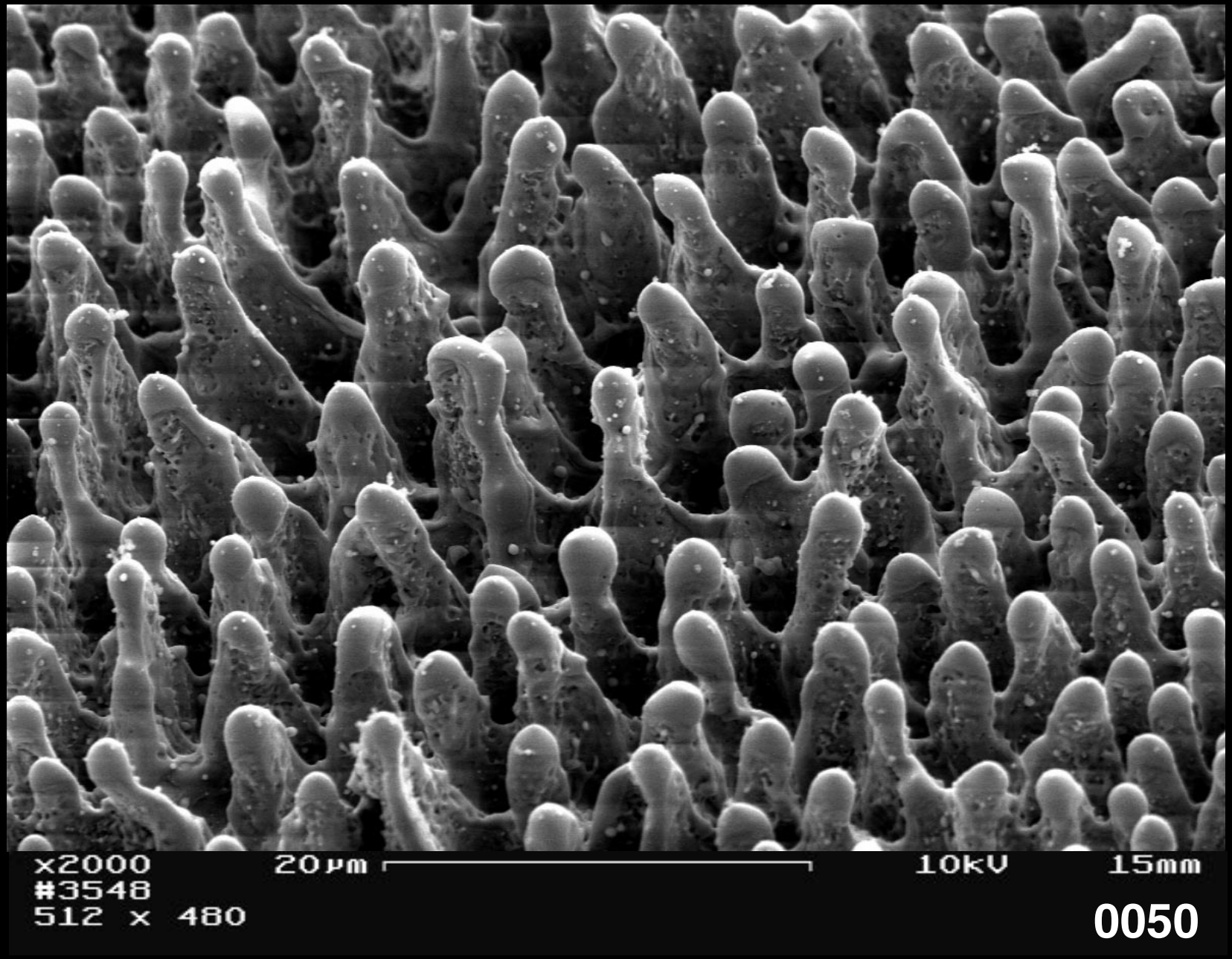
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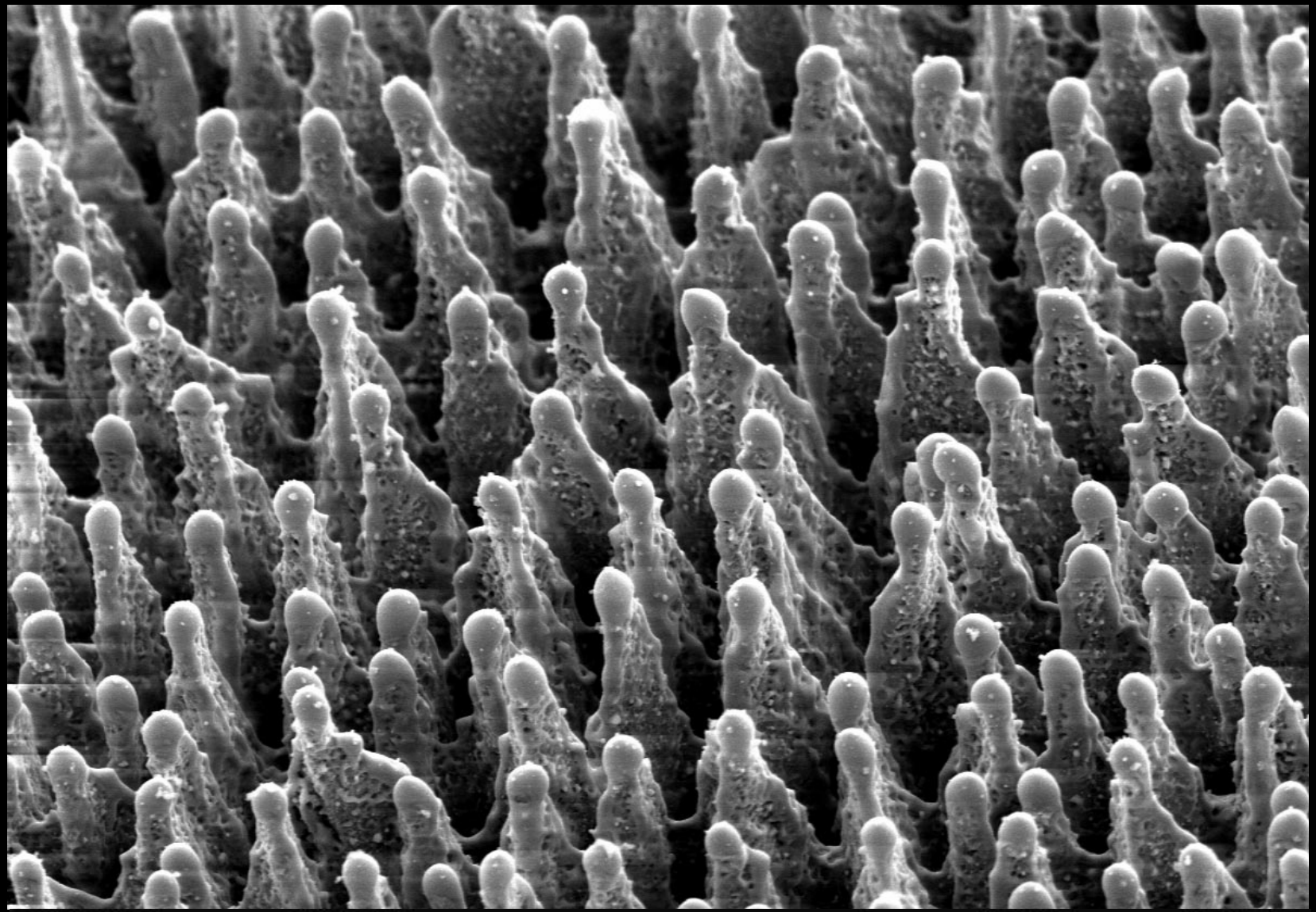

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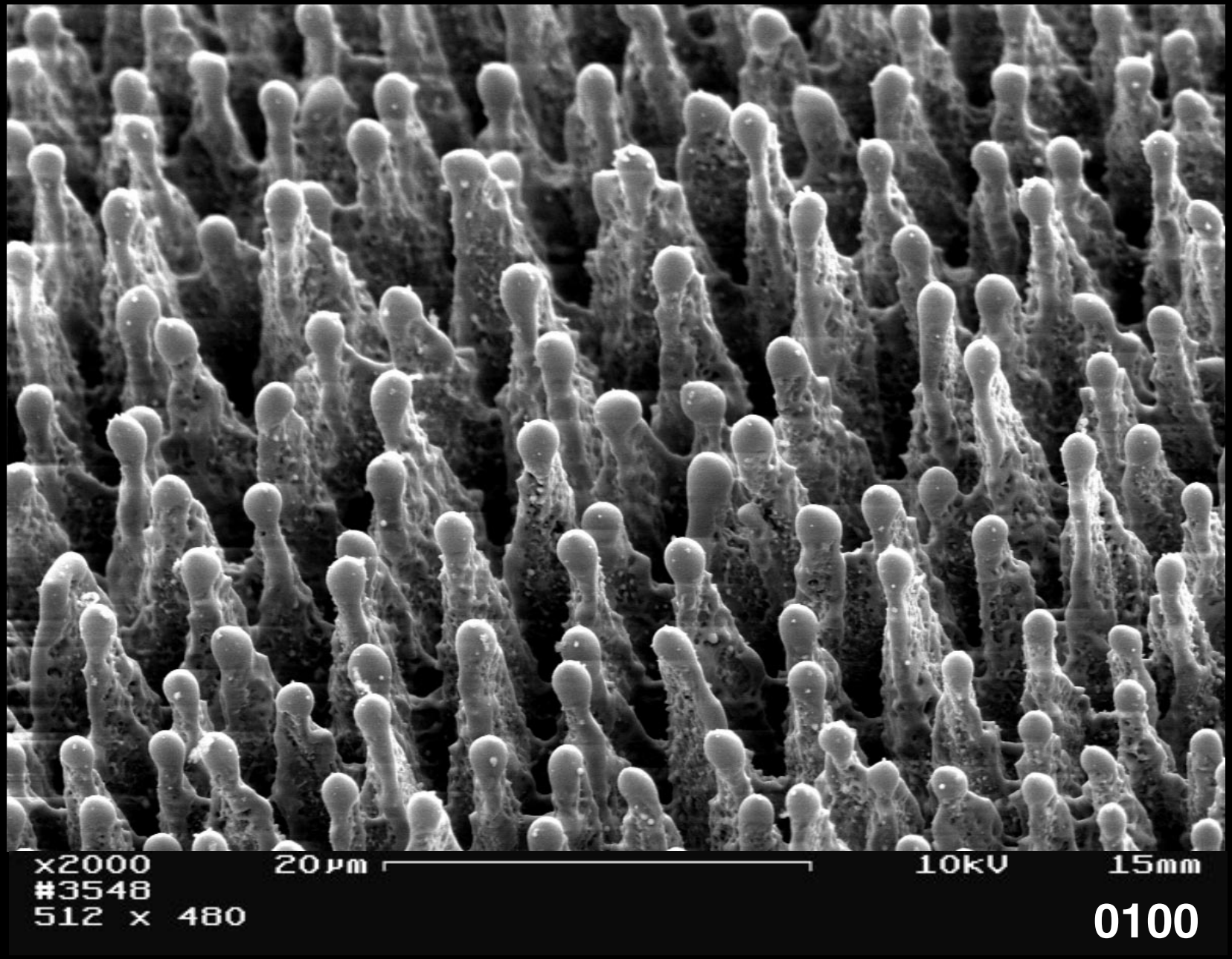
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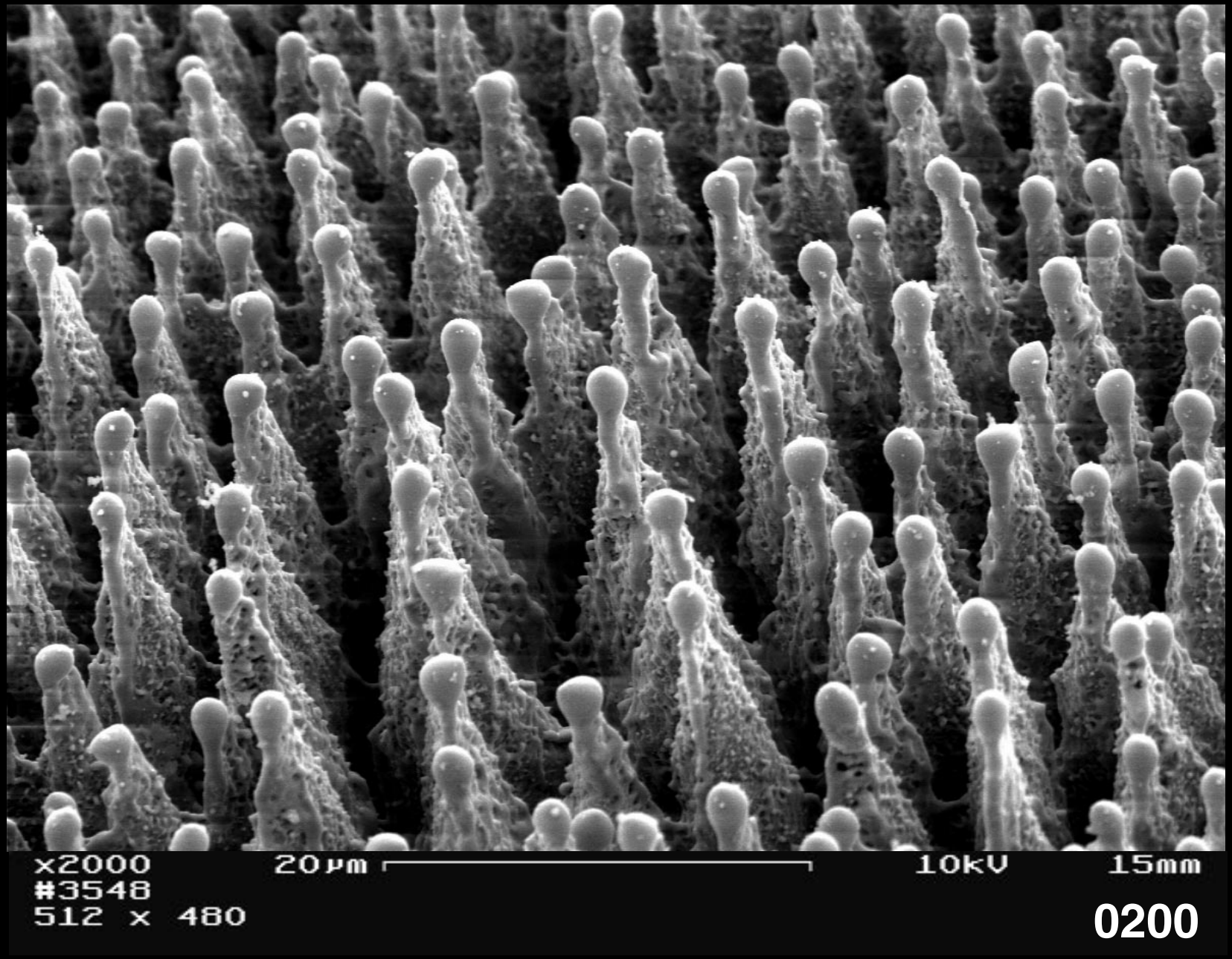
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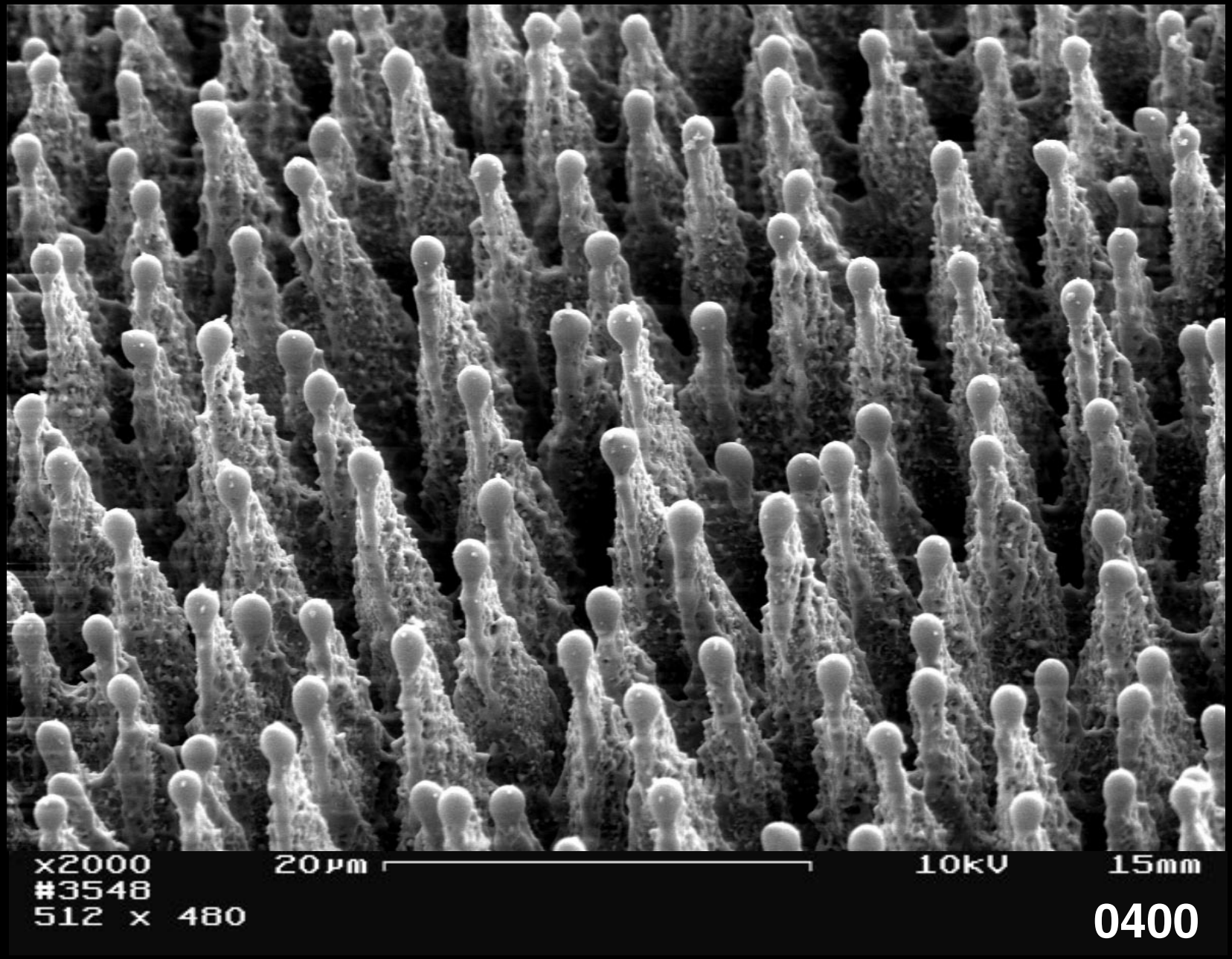
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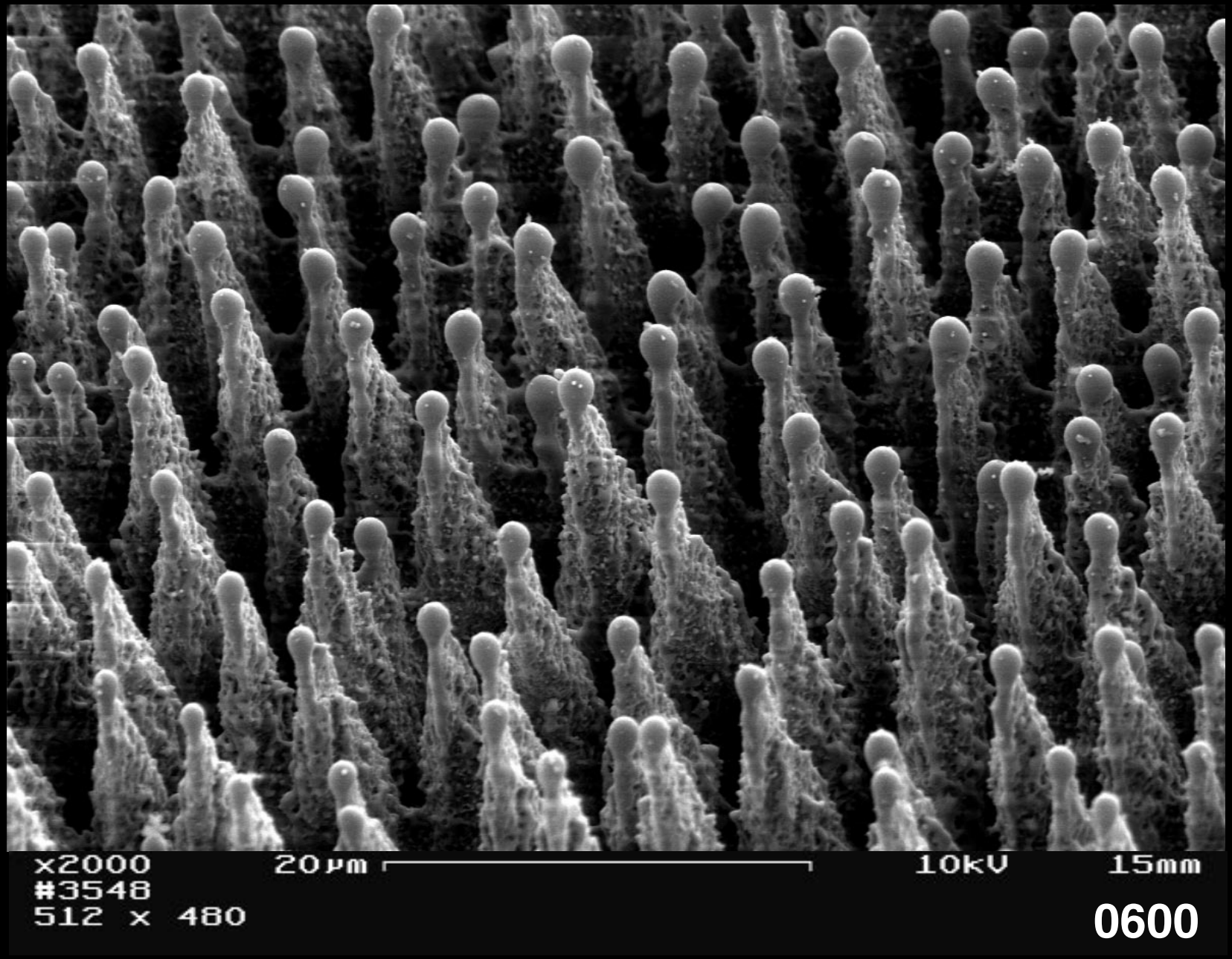
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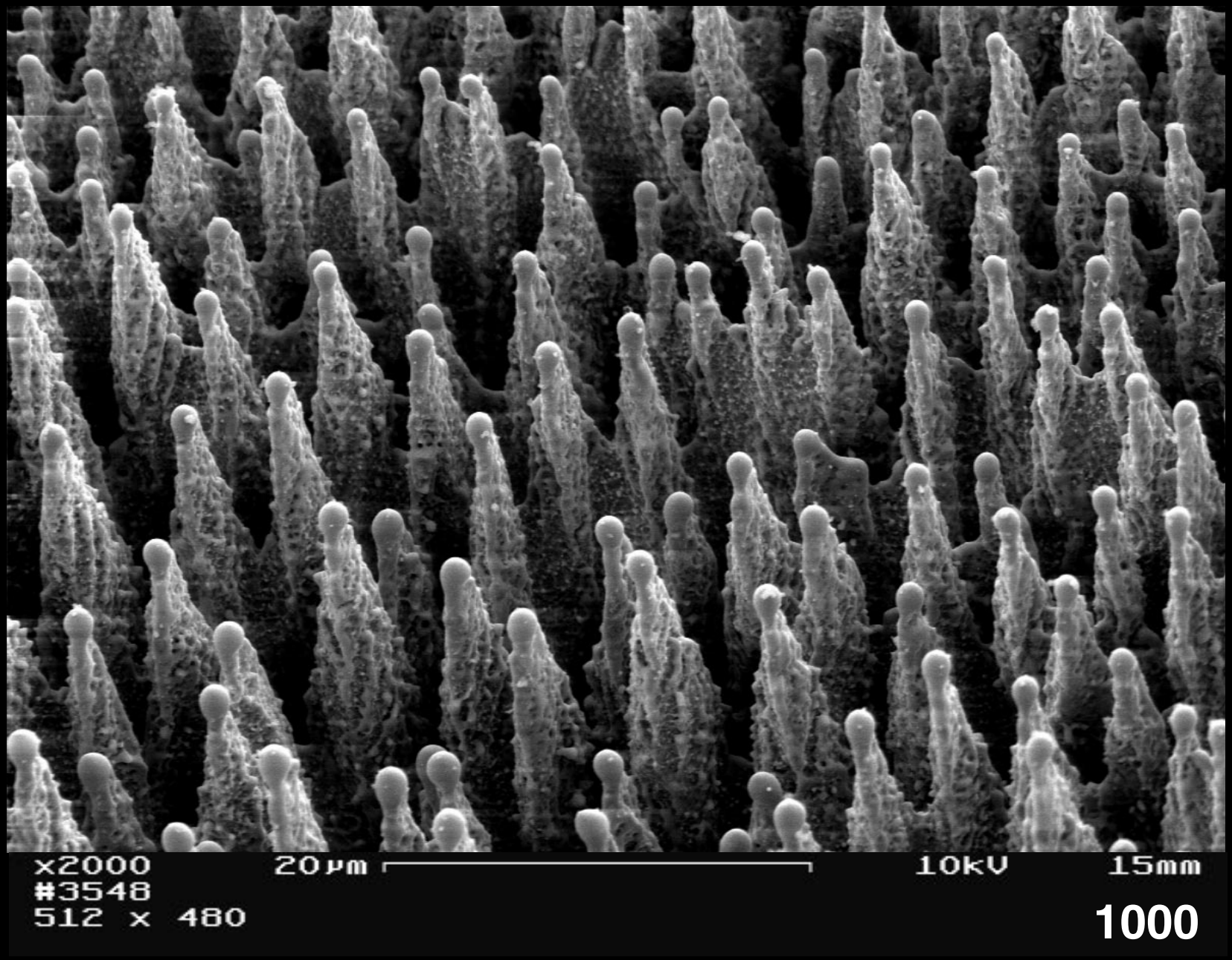
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20µm
10kV
15mm
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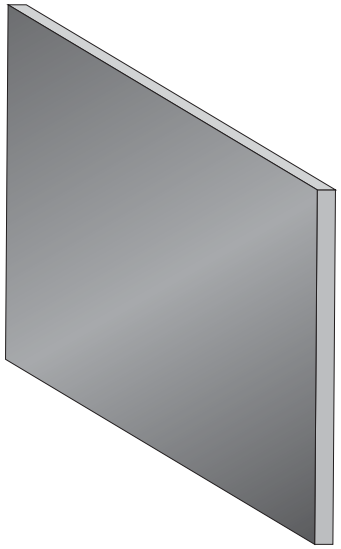
Outlook

can ordering of spikes be improved by using a grid?

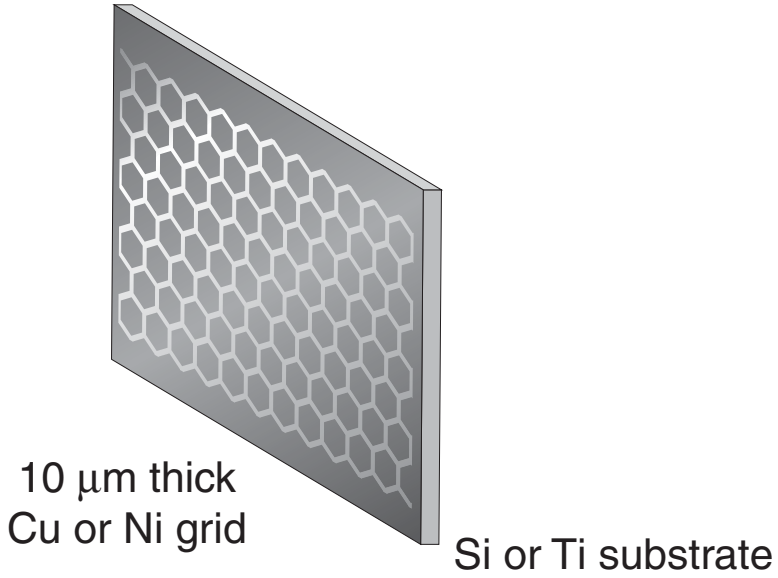
Outlook



Si or Ti substrate

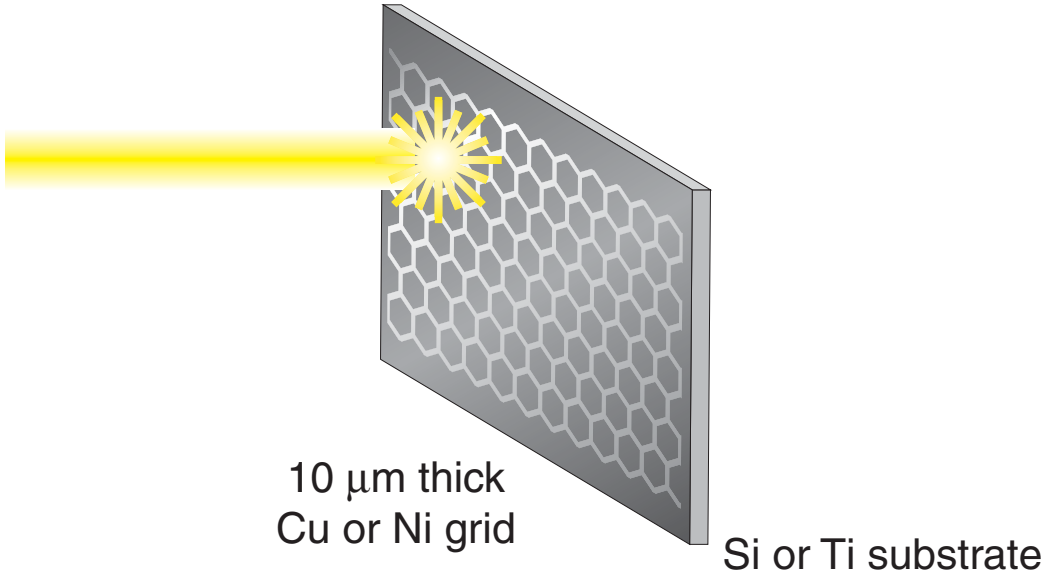
Outlook

place grid in front of substrate



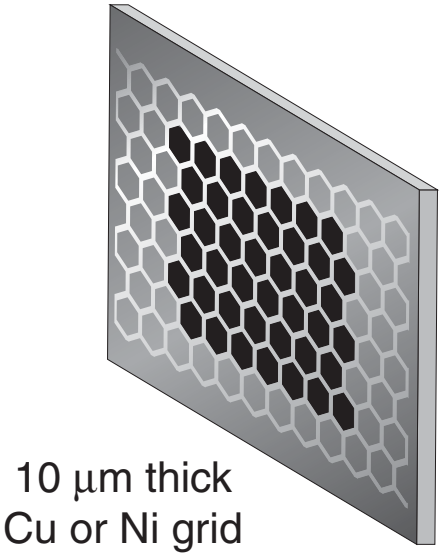
Outlook

scan laser beam



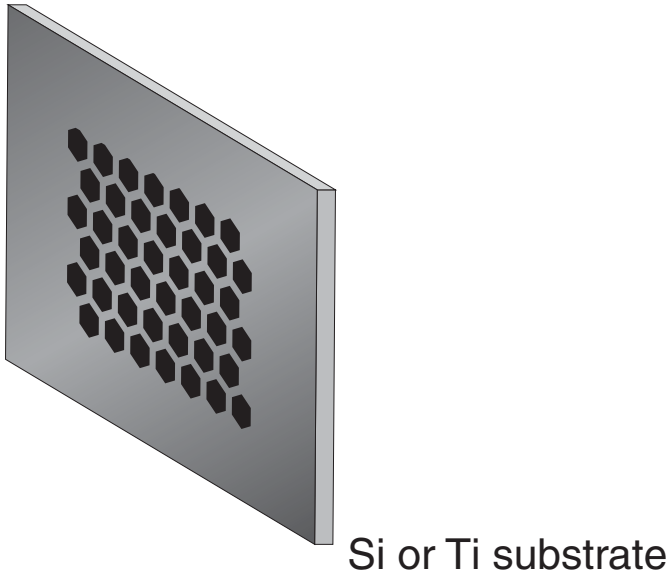
Outlook

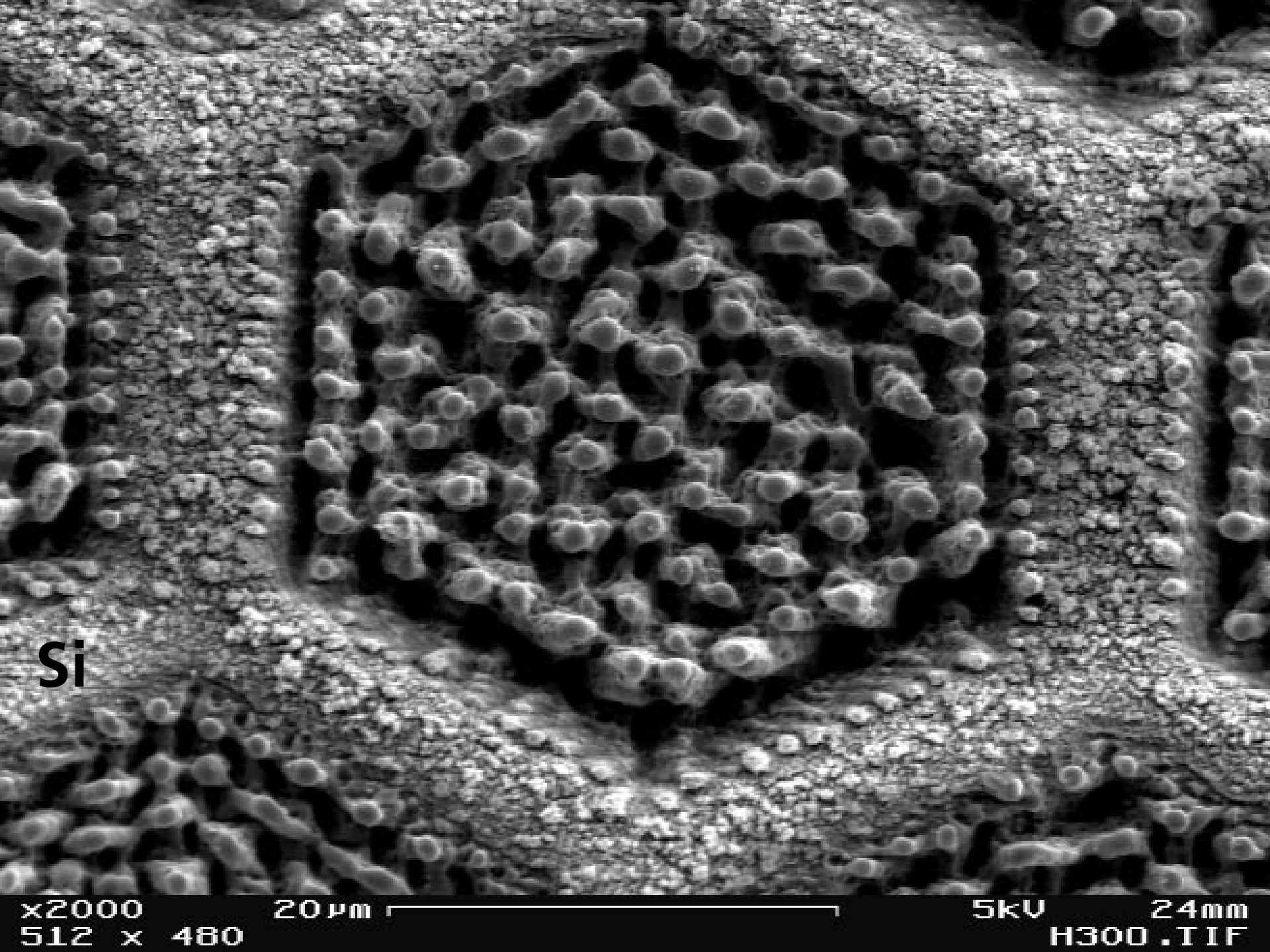
scan laser beam

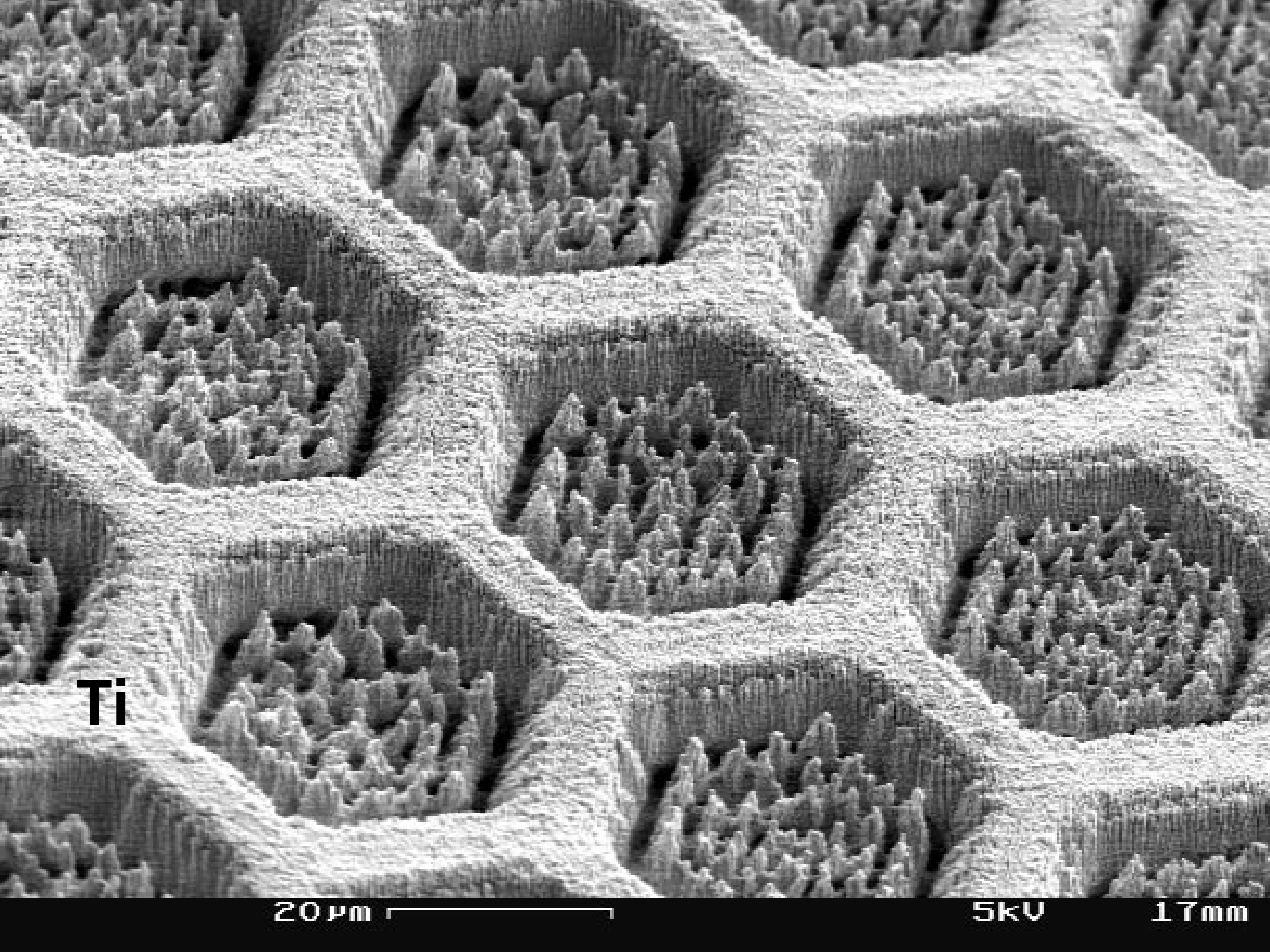


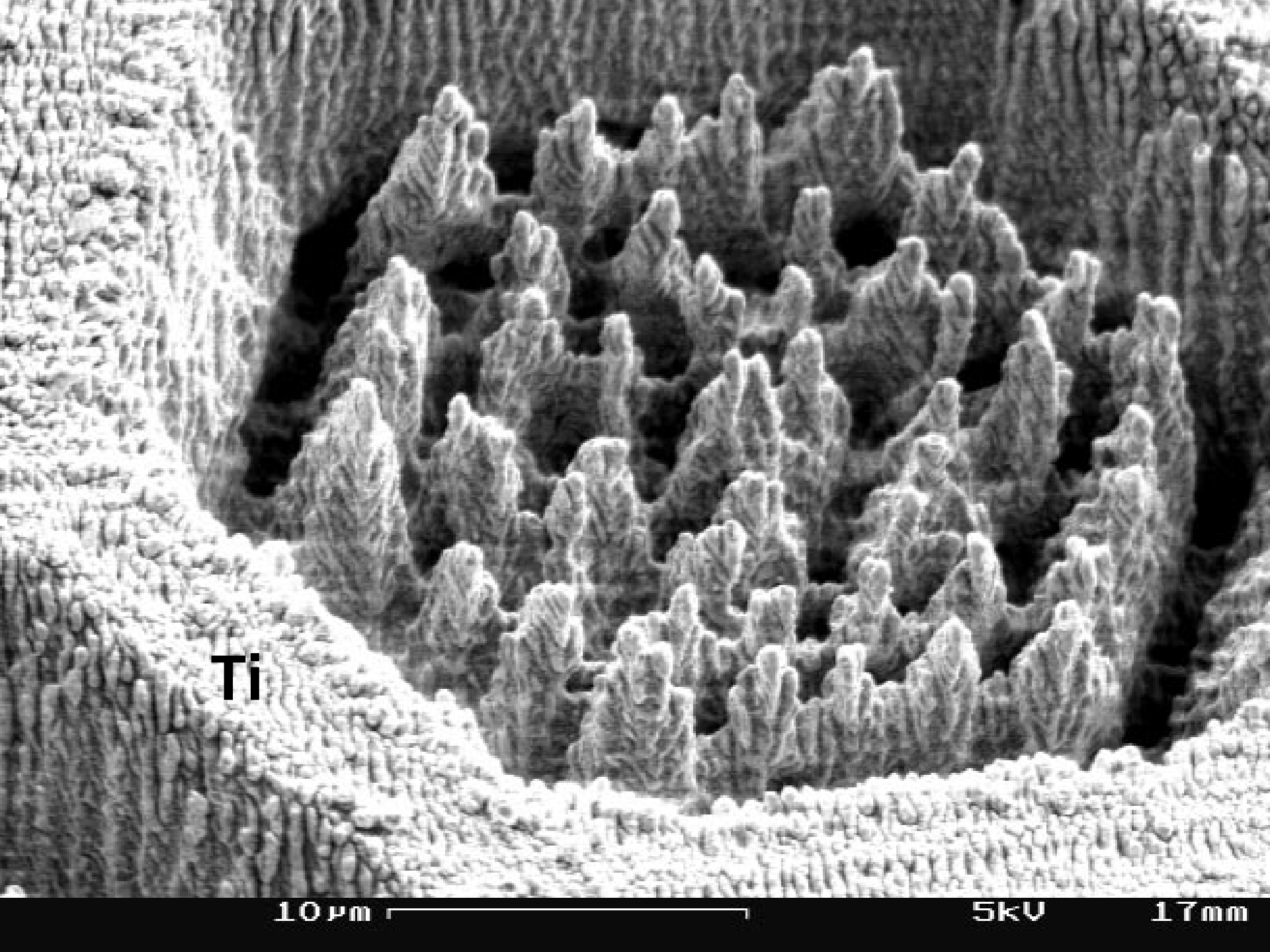
Outlook

remove grid




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


Ti
20μm
5kV
17mm


Ti
10μm
5kV
17mm

Outlook

Summary

Microstructured silicon

- **fabricated by simple, maskless process**

Summary

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- **can be integrated with microelectronics**

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Microstructured silicon

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- **can be integrated with microelectronics**
- **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. François Génin (LLNL)
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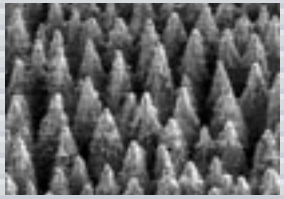
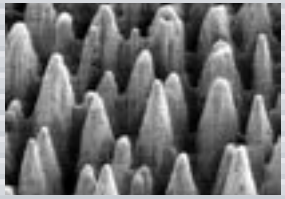
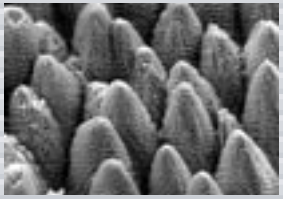
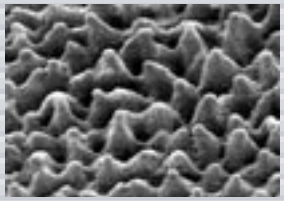
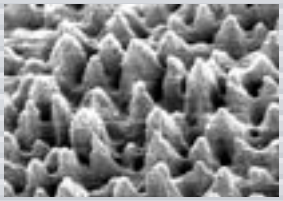
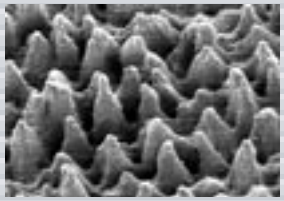
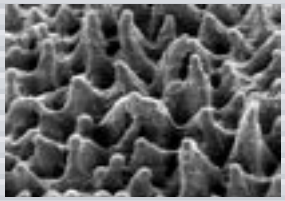
Prof. Nico Bloembergen (Harvard University)
Prof. Cynthia Friend (Harvard University)
Prof. Mike Aziz (Harvard University)

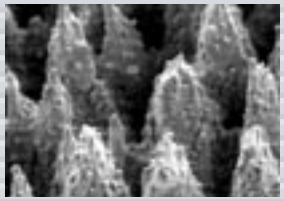
For a copy of this talk and additional information, see:

http://mazur-www.harvard.edu

Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti		reacts			

Only in SF_6:



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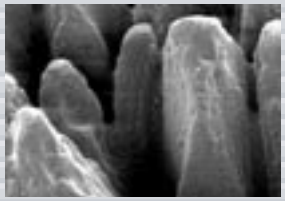

InP

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

Materials

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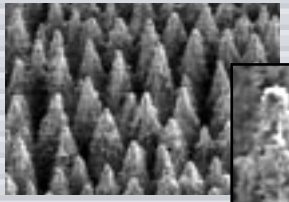
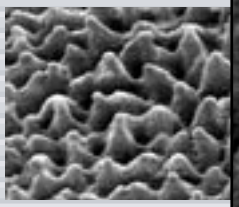
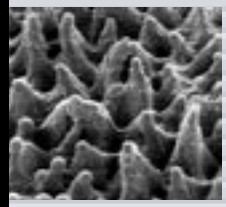
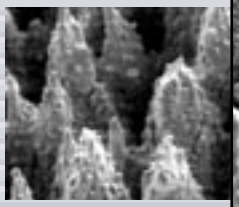
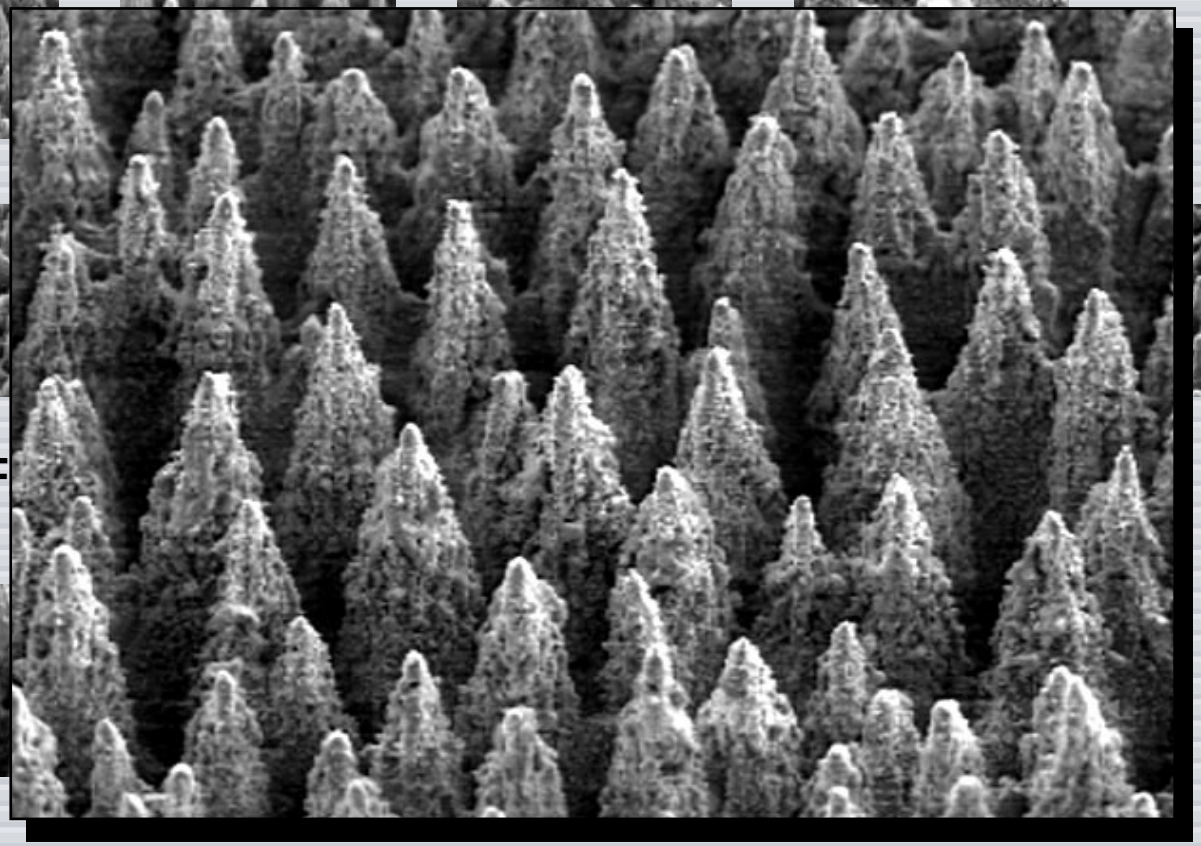
Si					
Ti					
Ge					

Only in SF



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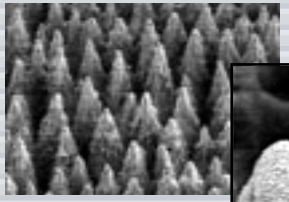
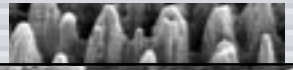
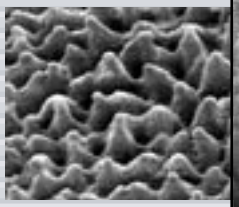
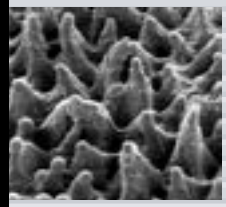
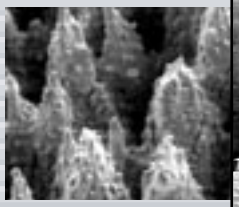
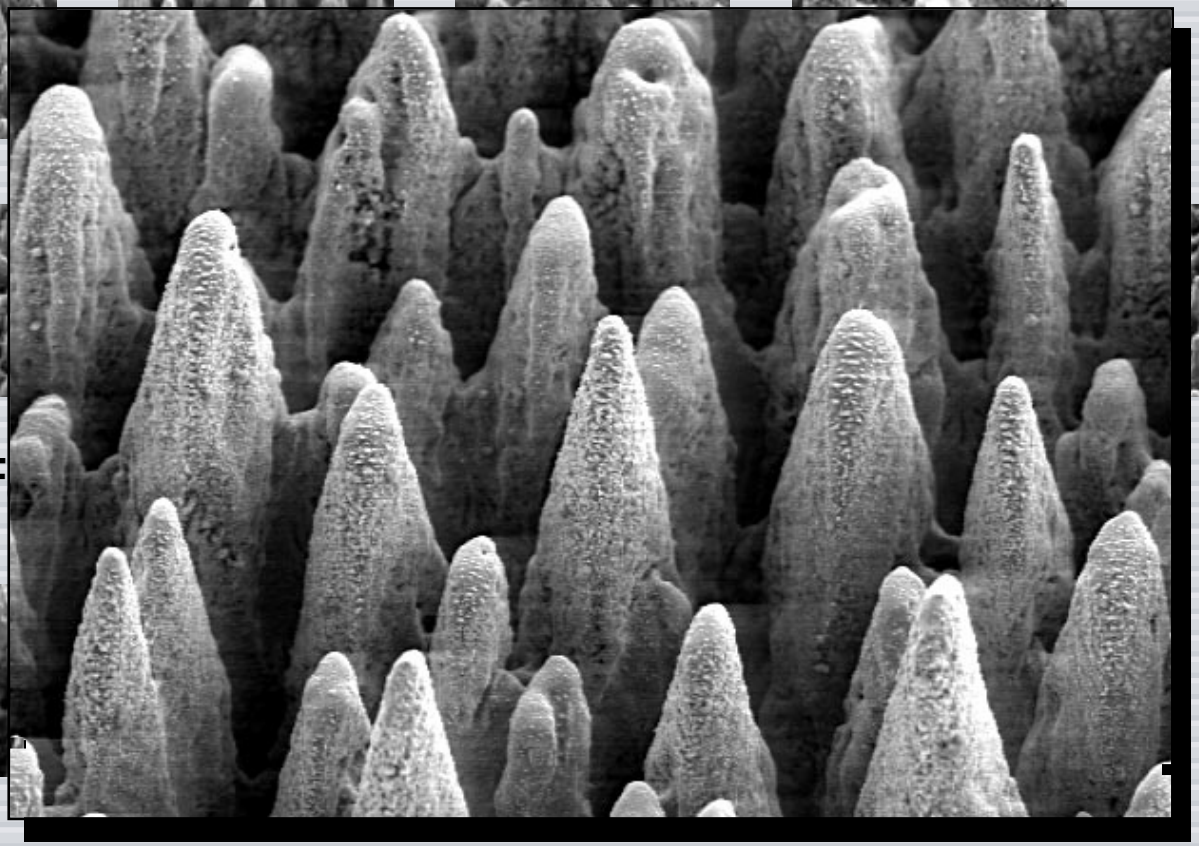
Si					
Ti					
Ge					



Only in SF

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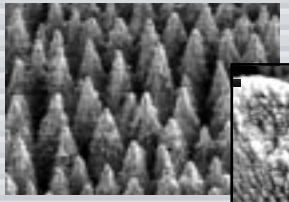
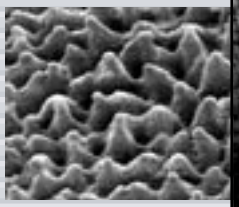
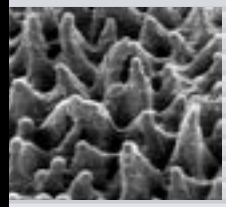
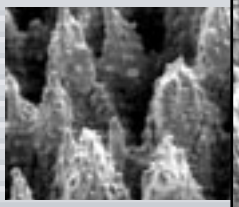
Si					
Ti					
Ge					

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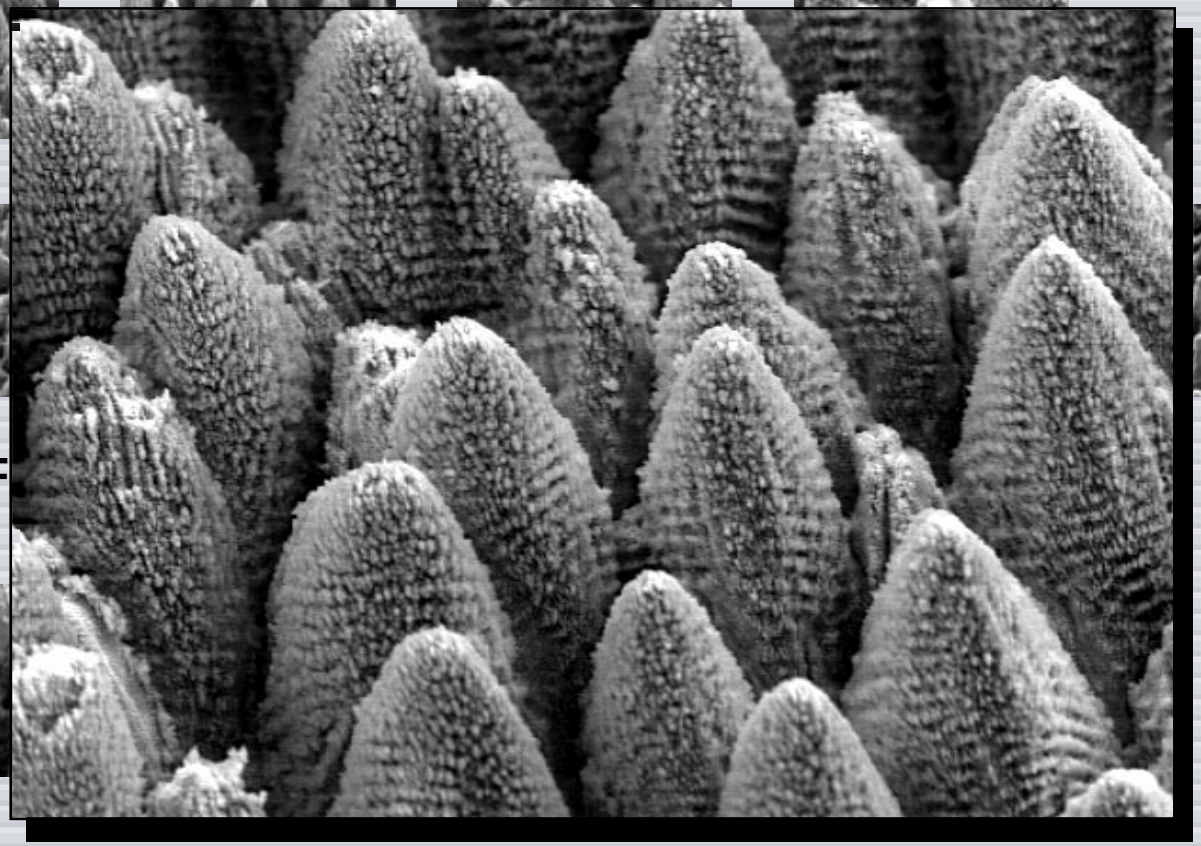

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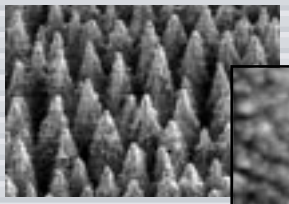
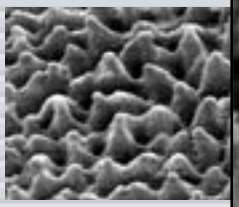
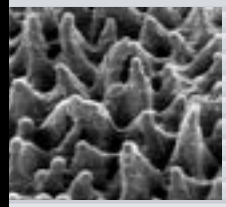
Si					
Ti					
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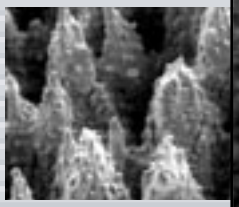
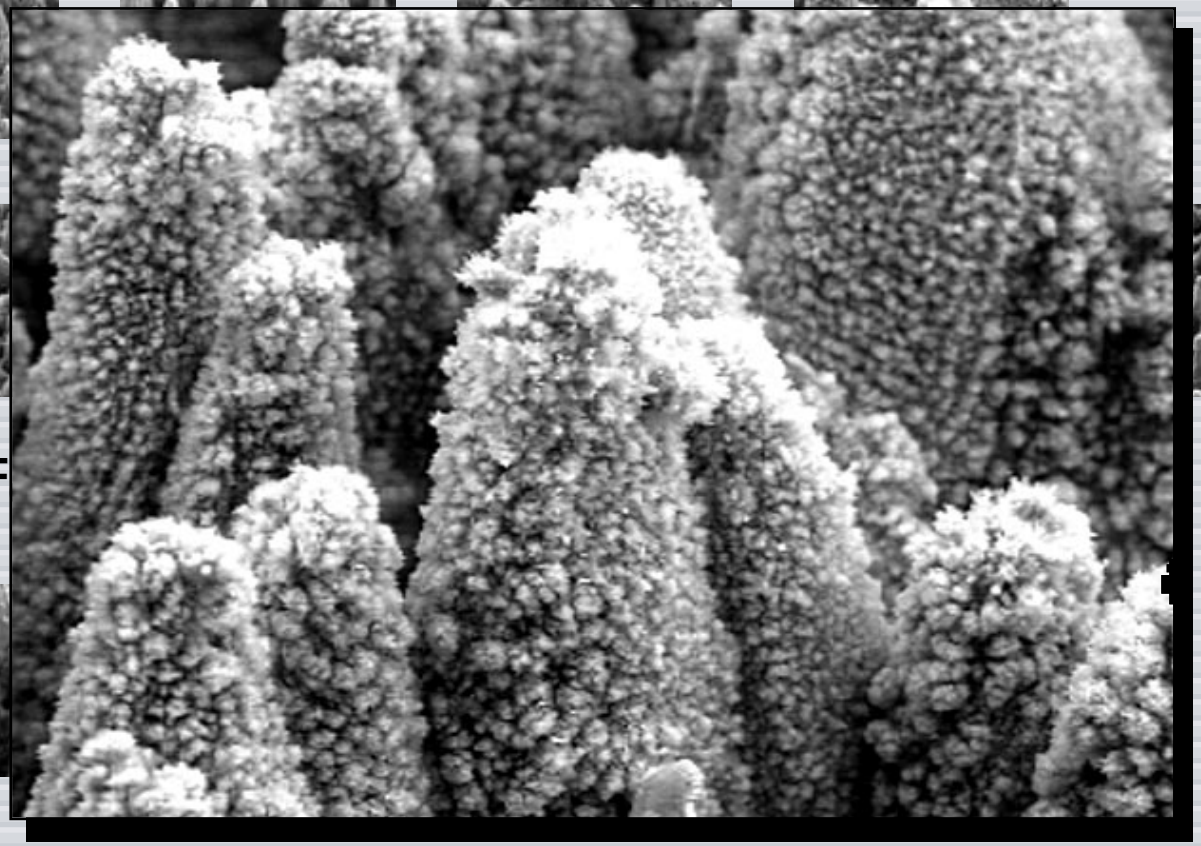
Ge					



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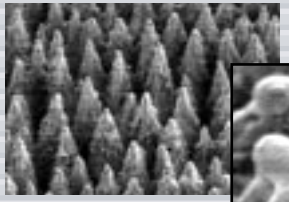
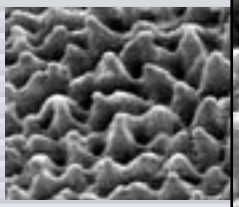
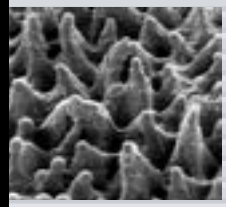
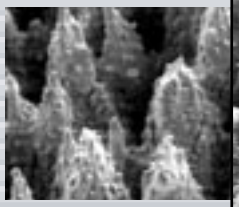
Si					
Ti					
Ge					

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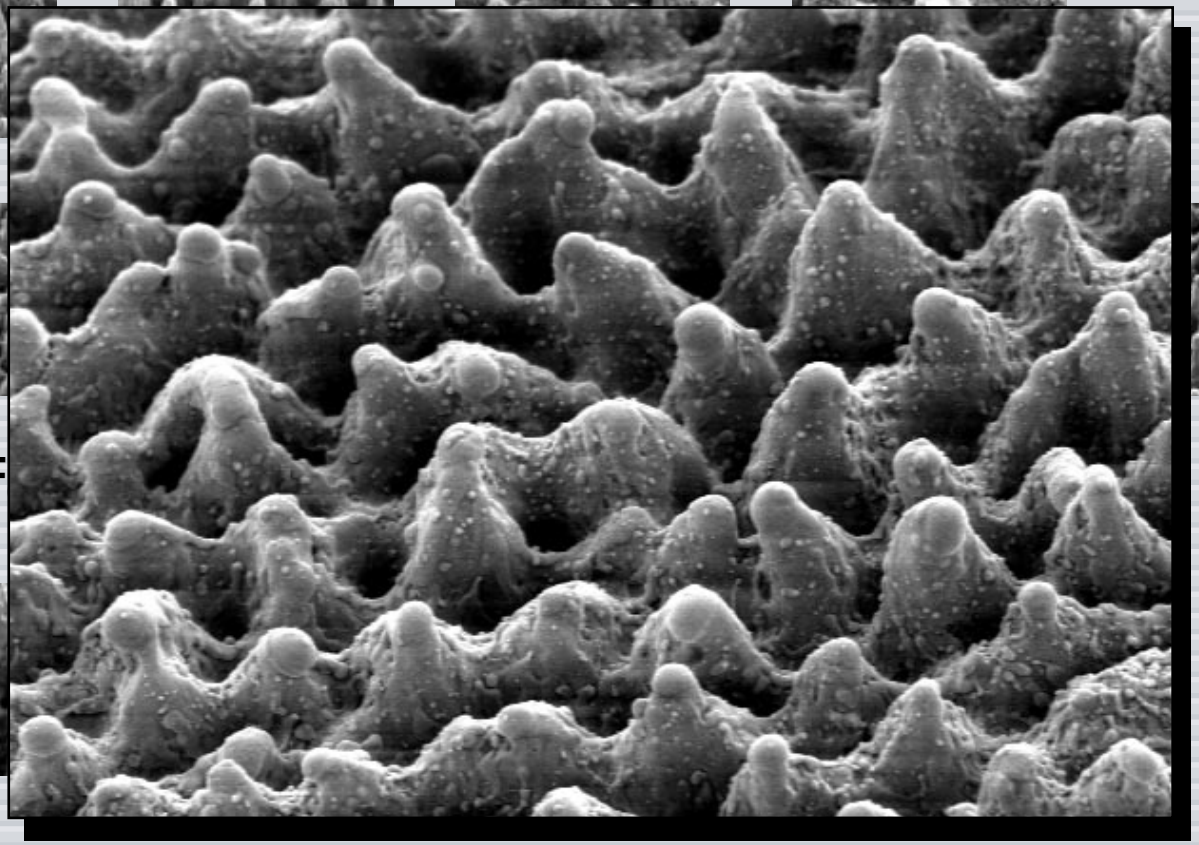

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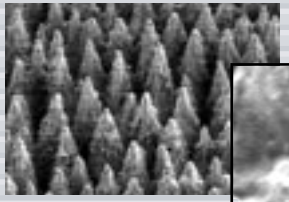
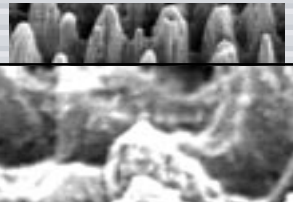
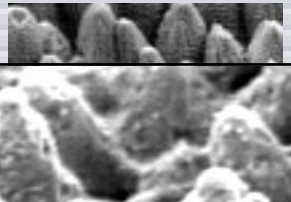
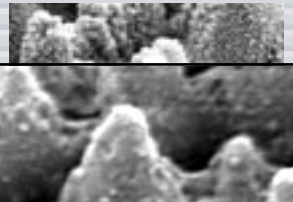
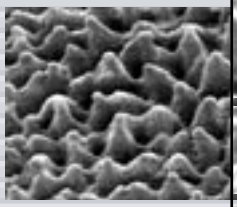
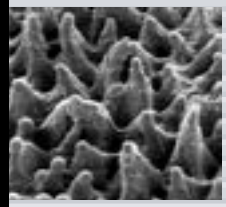
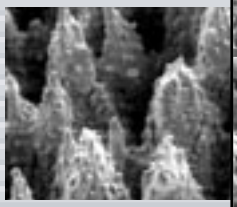
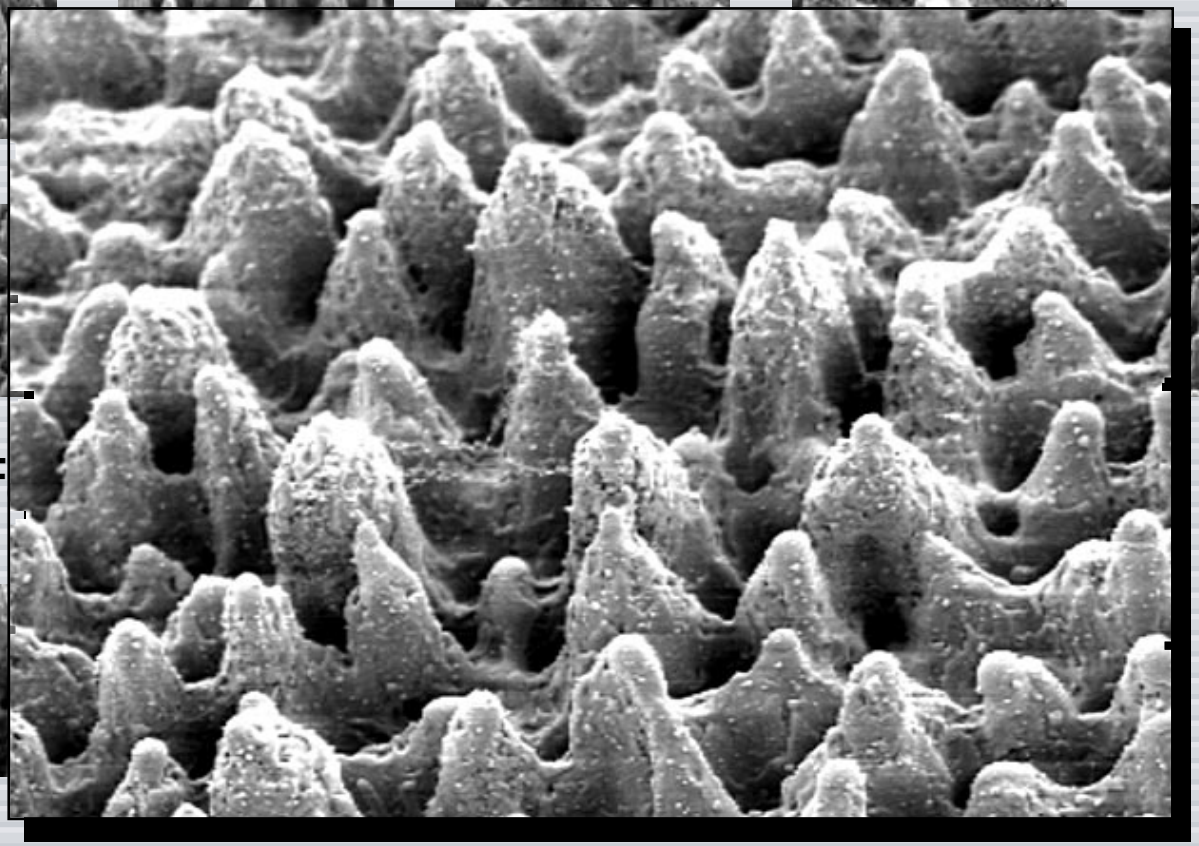
Si					
Ti					
Ge					



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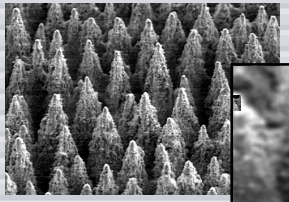
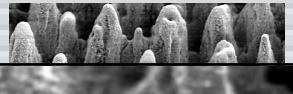
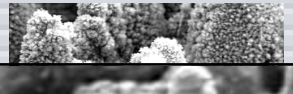
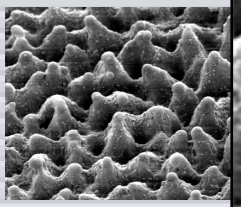
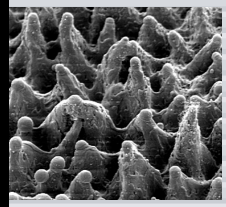
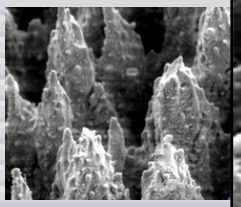
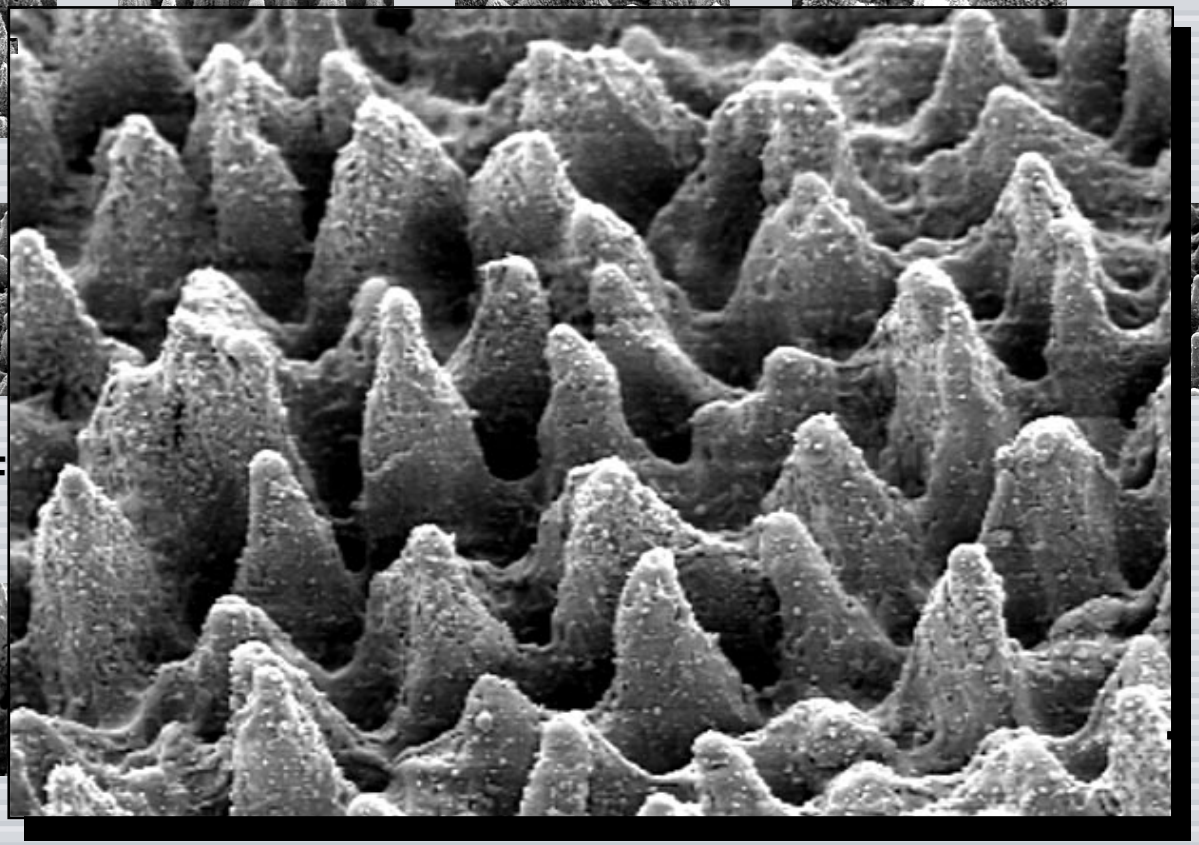
Si					
Ti					
Only in SF					
Ge					



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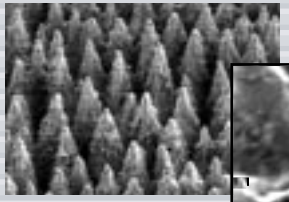
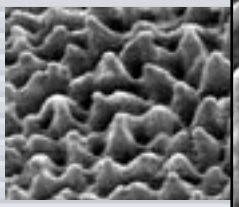
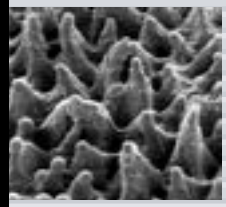
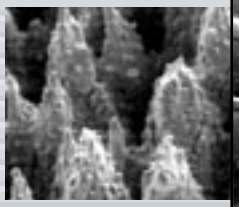
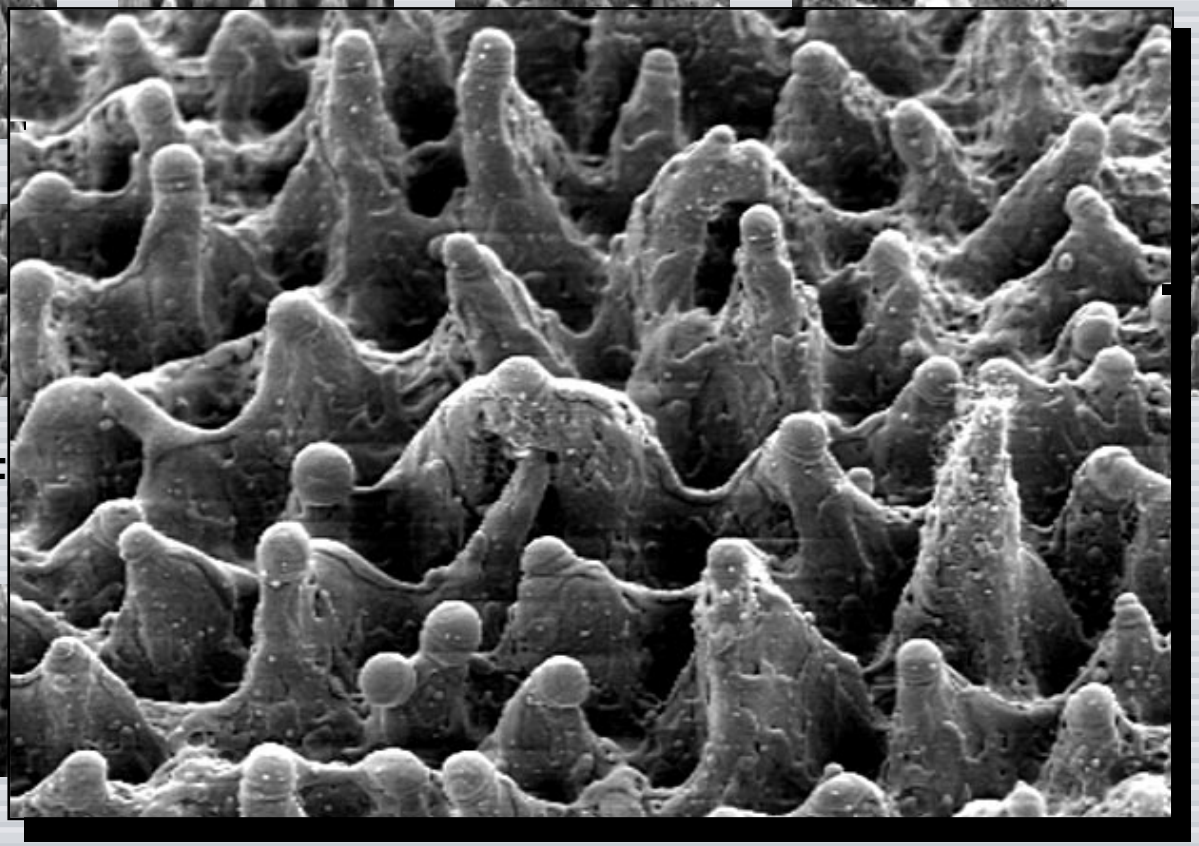
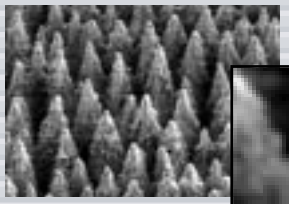
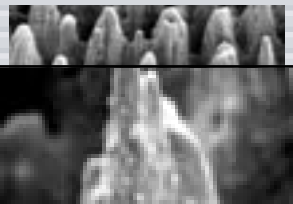
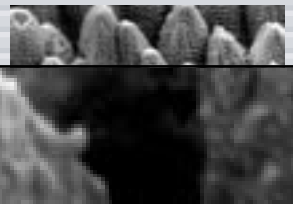
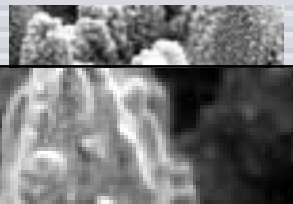
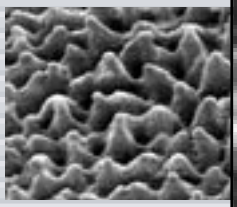
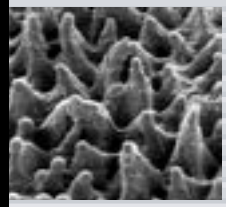
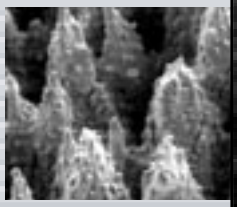
	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					

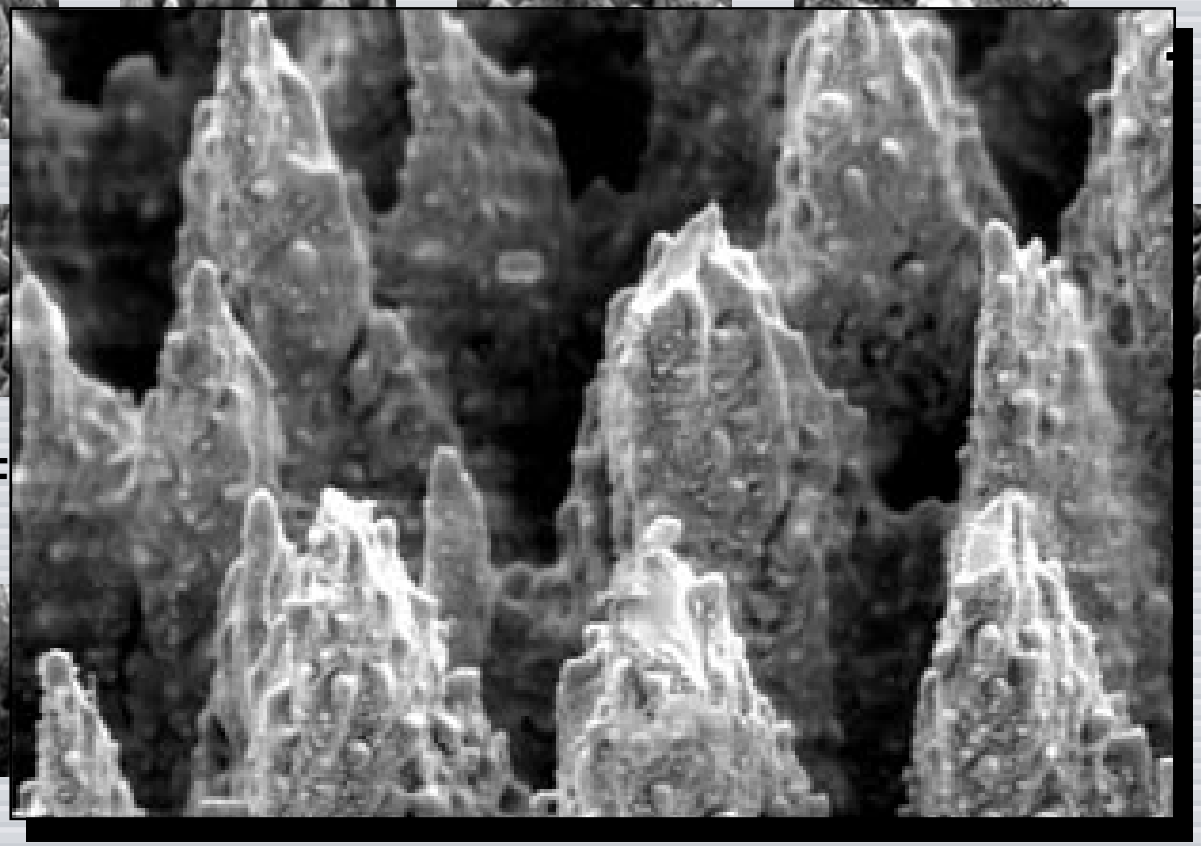


Only in SF

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

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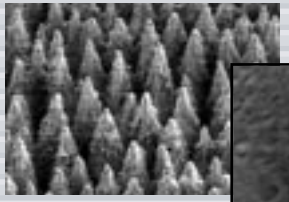
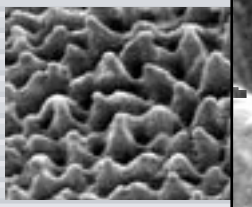
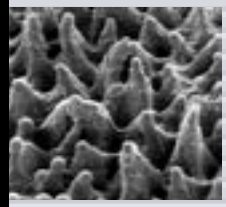
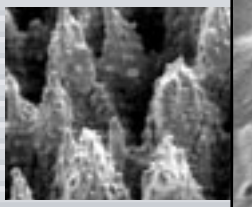
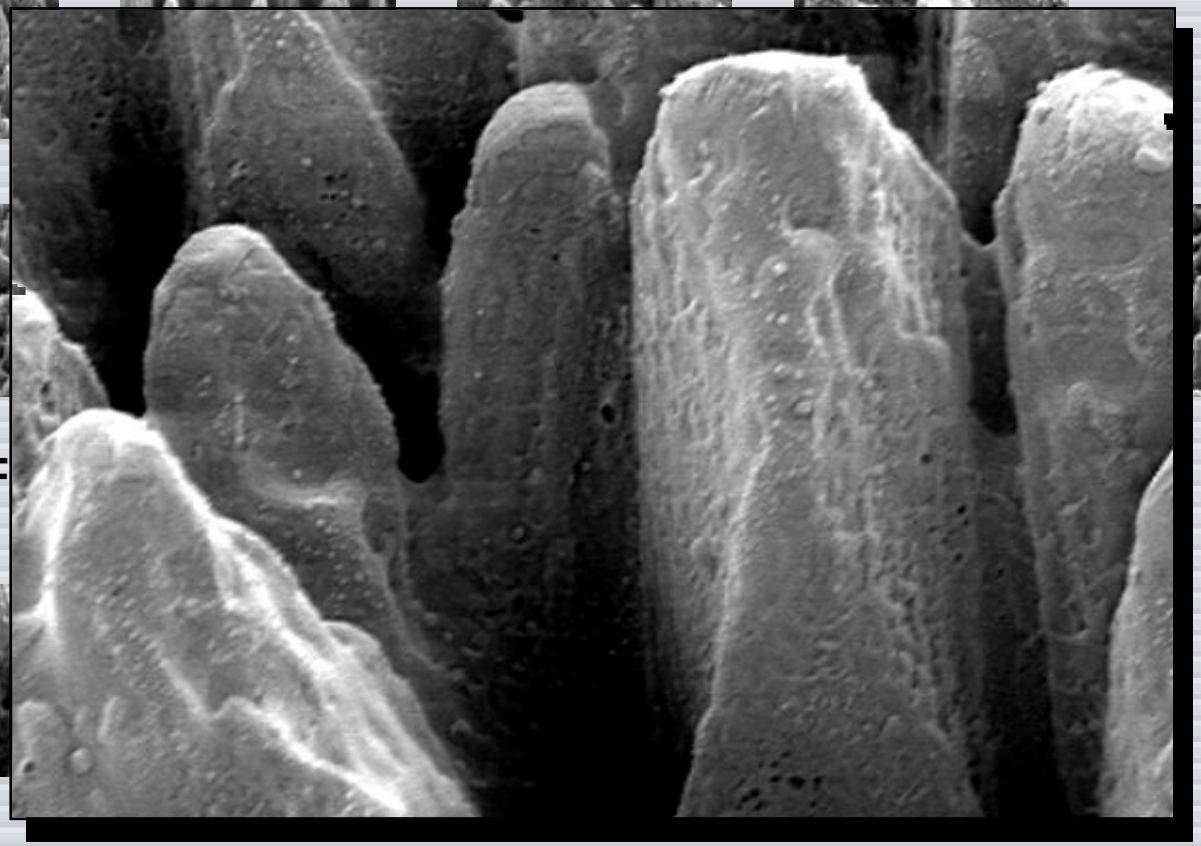
Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					



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