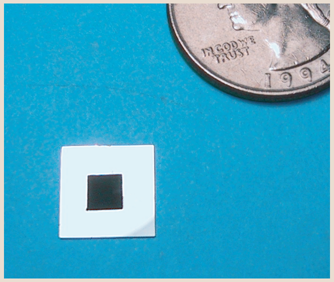
Black silicon:
Changing structure and properties with light



Catherine H. Crouch

Clark University
12 December 2002

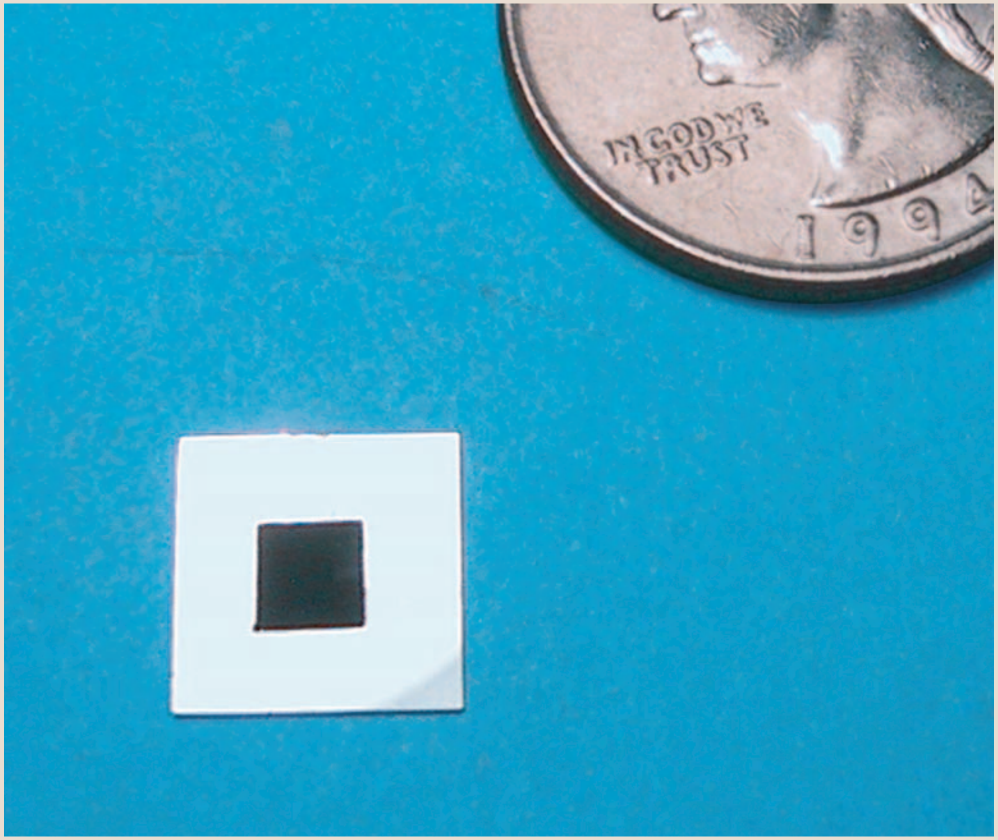
Department of Phyics
Harvard University

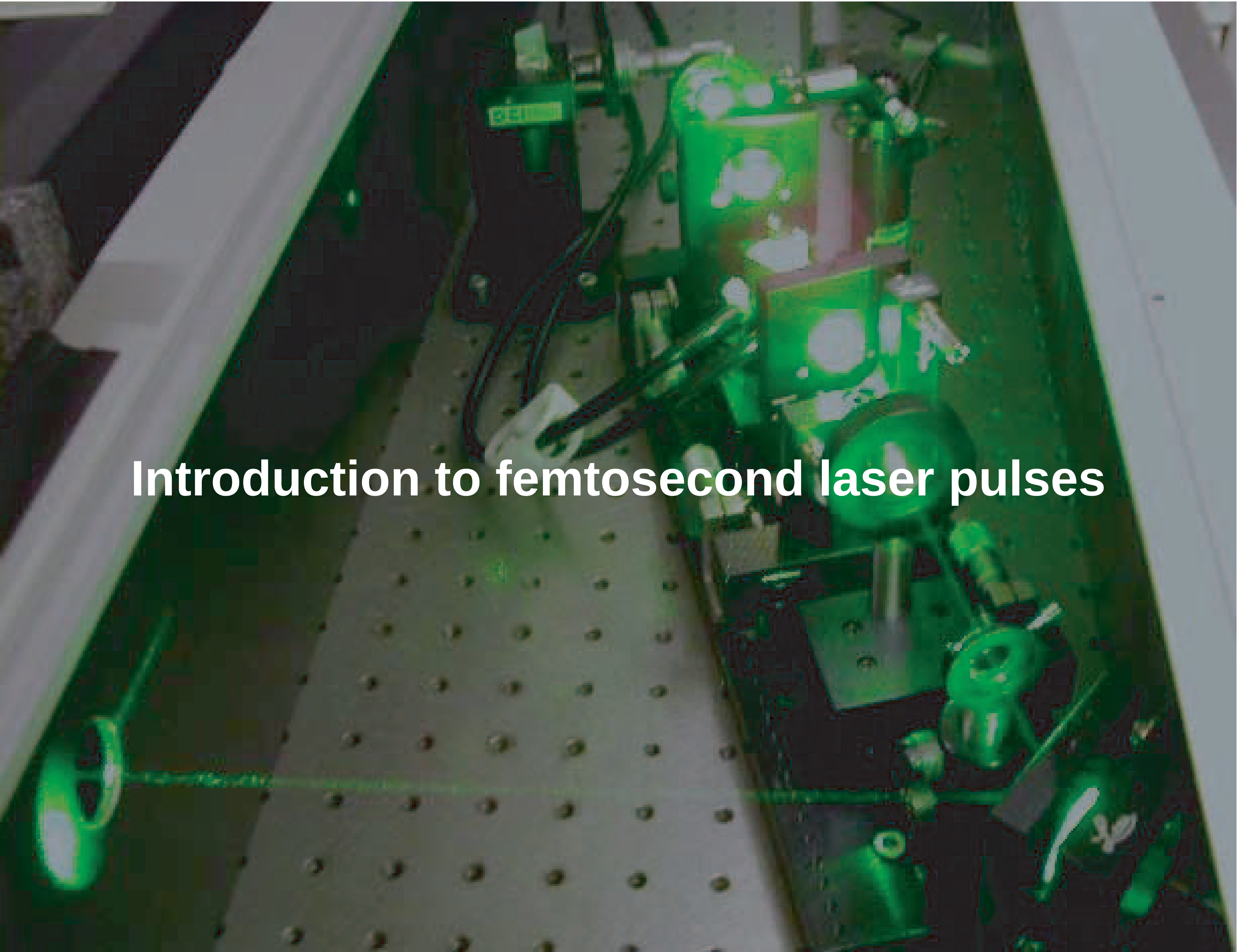
Motivation

Study effect of extremely intense laser pulses

Develop silicon with novel (useful) properties

enhance and extend absorption of light





Introduction to femtosecond laser pulses

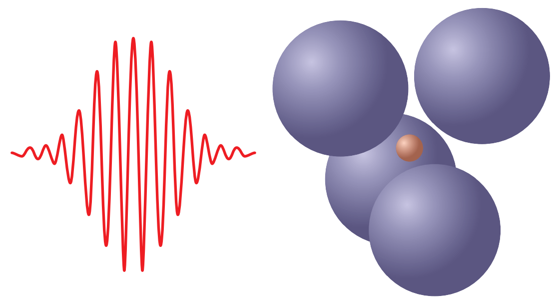
800 nm, 100 fs laser pulses

- last only 10^{-13} seconds
- 30 cycles of electromagnetic wave
- extend only 30 μm

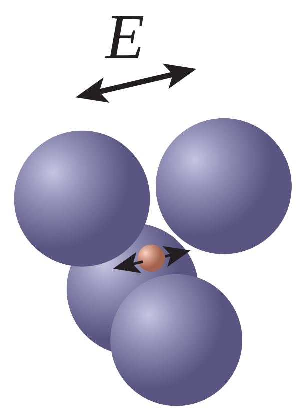
Extremely high peak power and intensity

- peak power > 10^{9} W
- focused beam: ~ 10^{17} W/cm^{2}

light-matter interactions



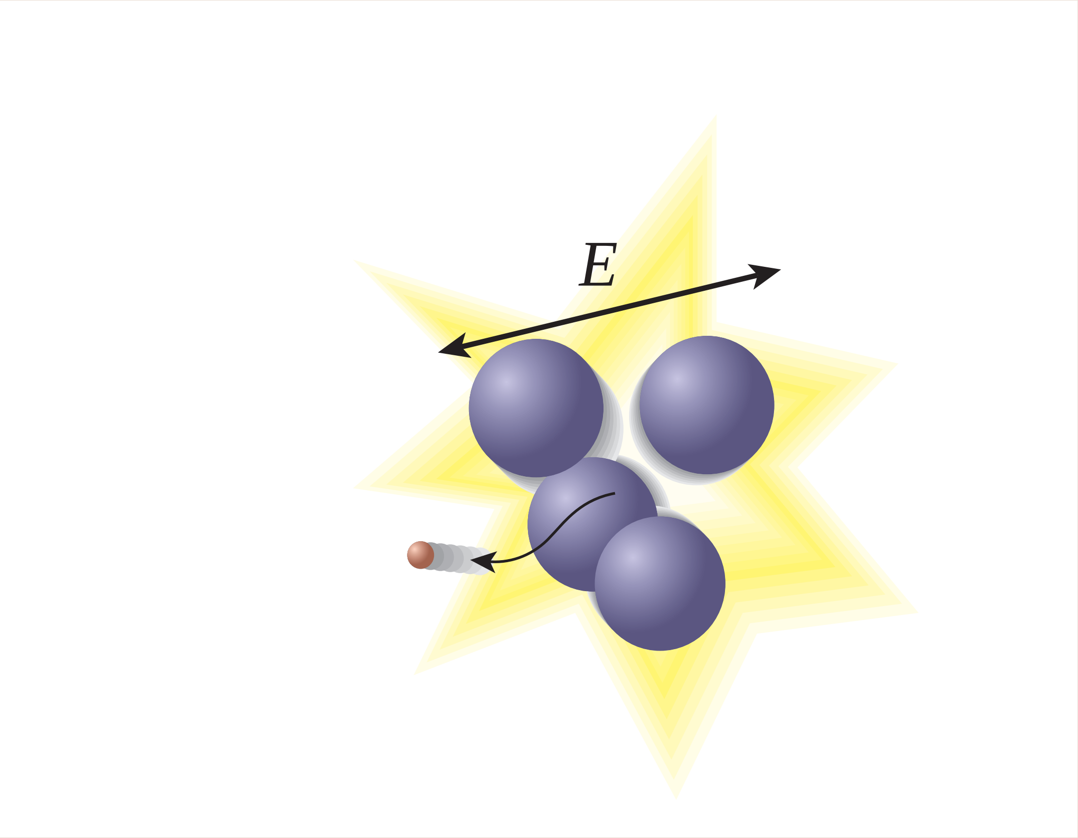
temporary effect on material



$$\vec{P} = \chi \vec{E}$$

χ is constant

permanent change to material

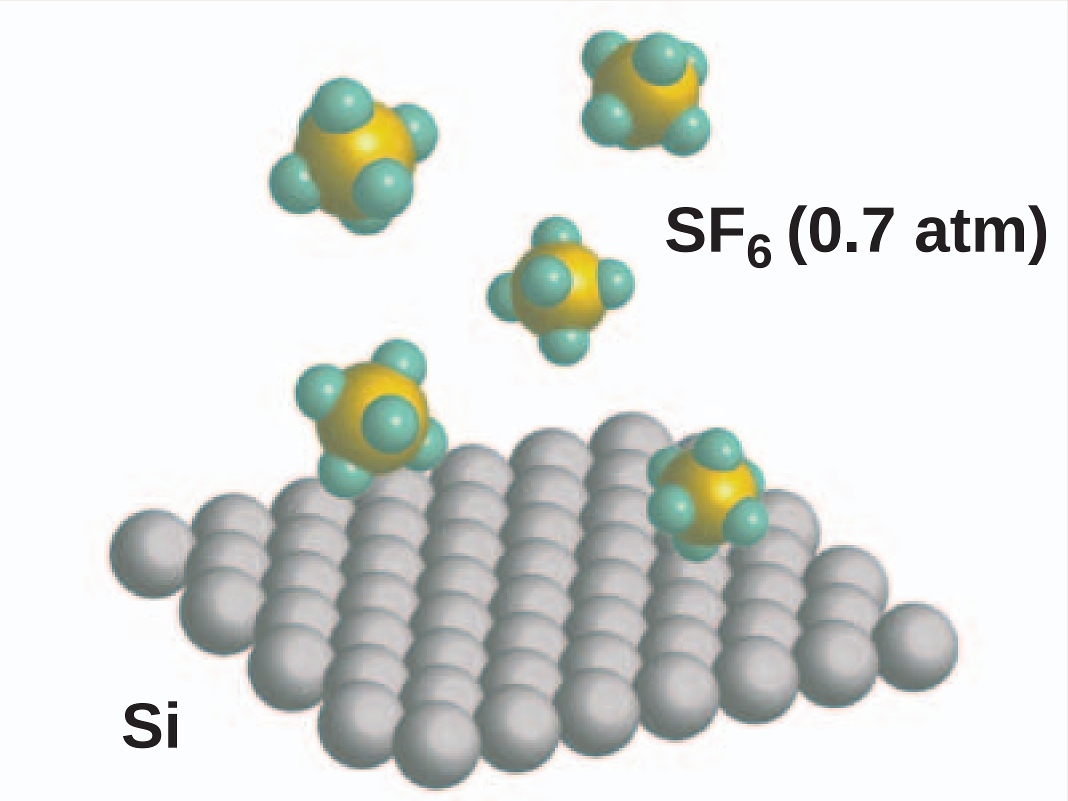


plasma formation

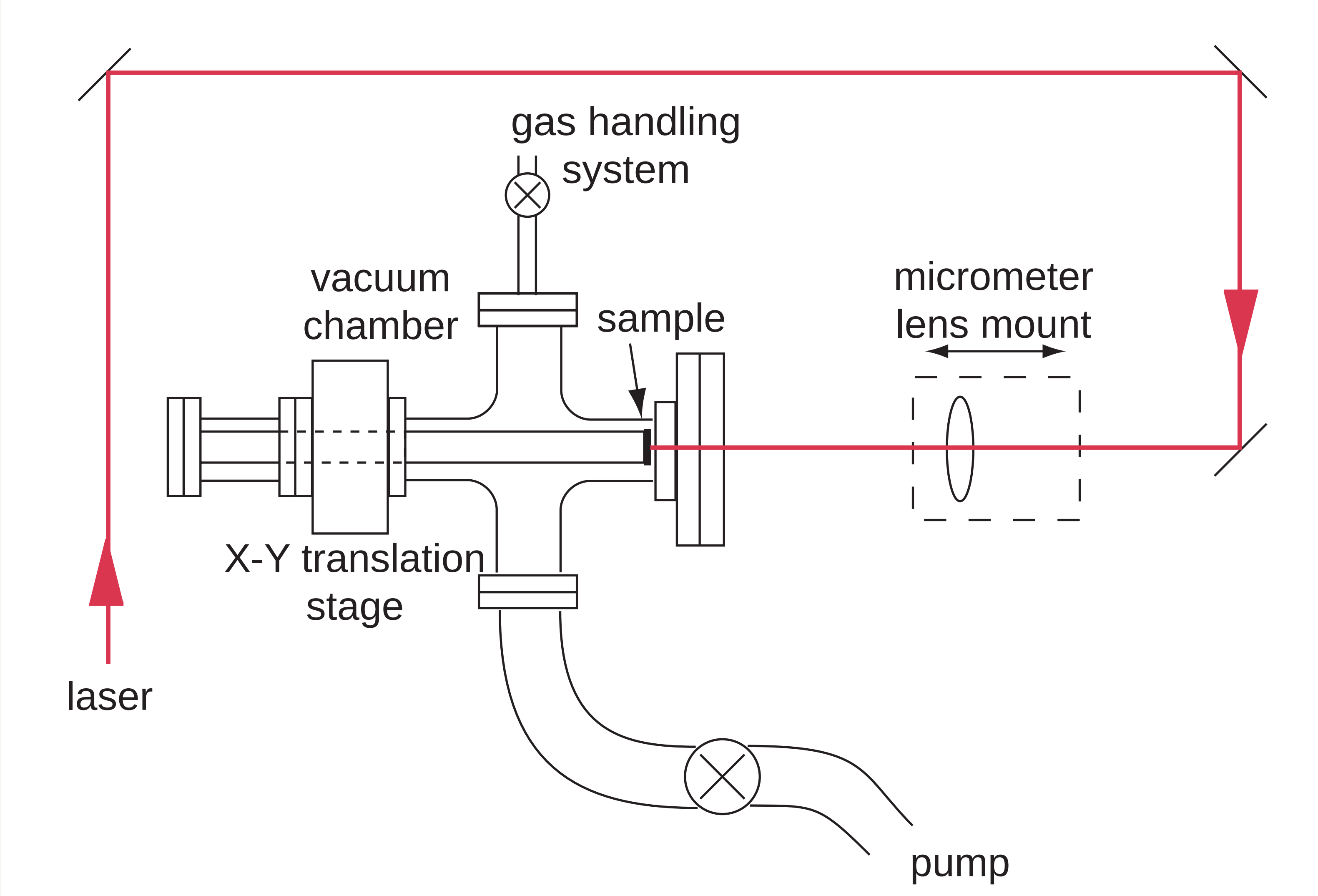
1. What is black silicon?

2. Why is it black?

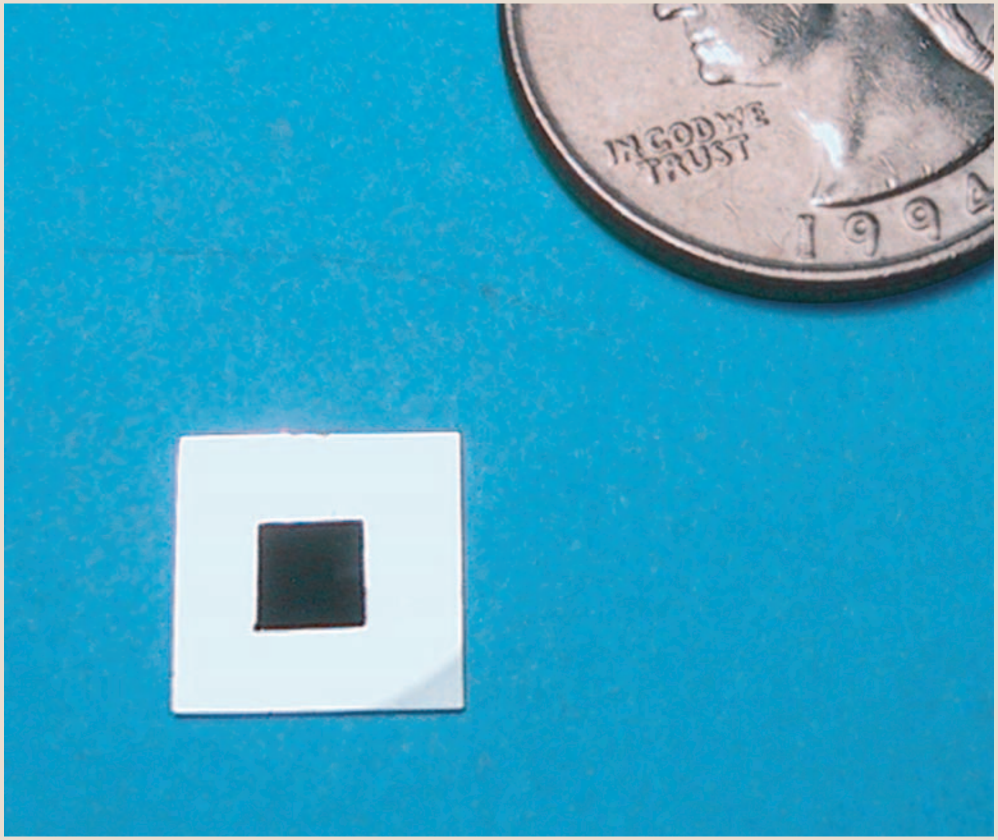
3. How does it get that way?



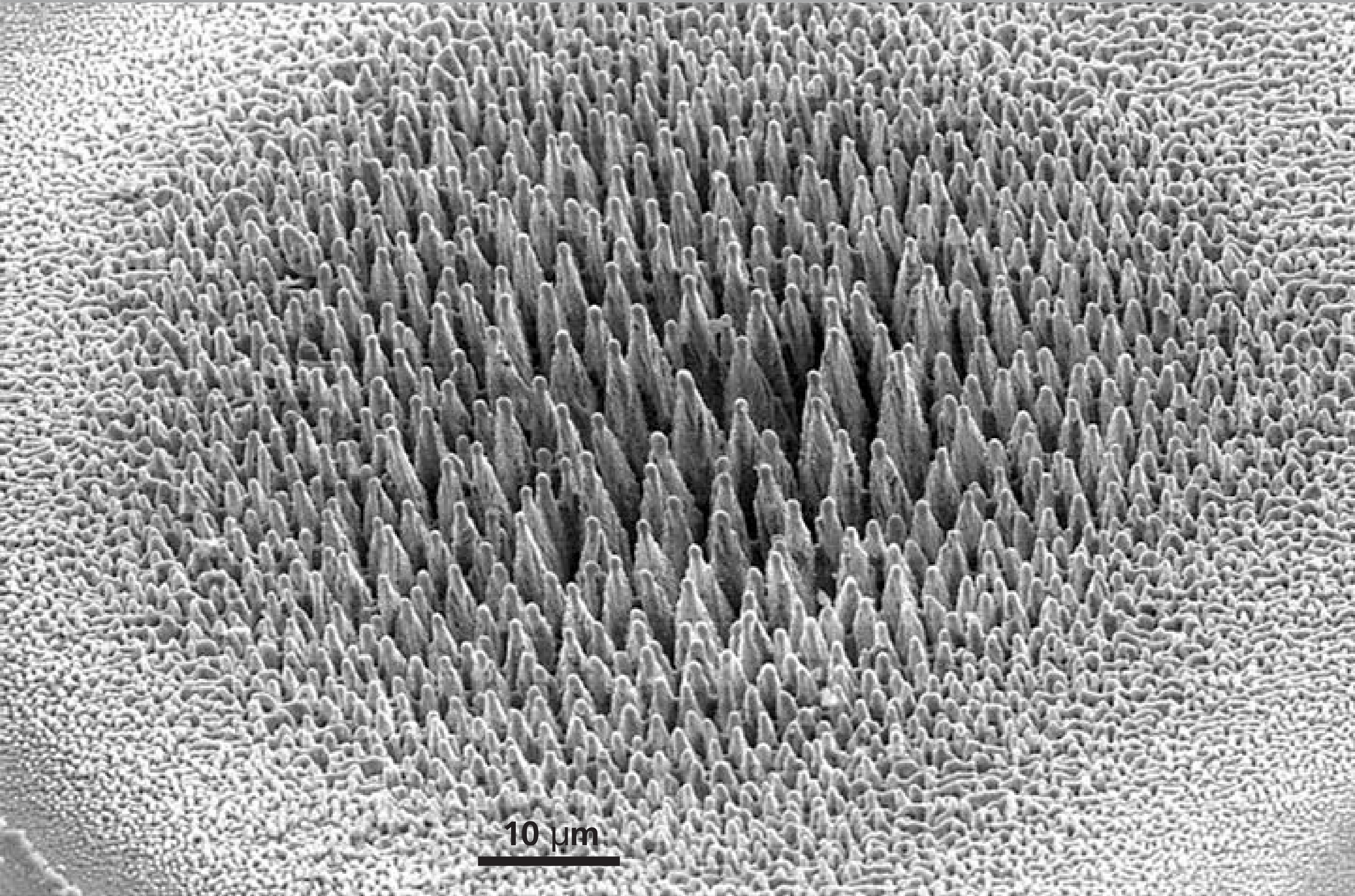
irradiate surface with femtosecond laser pulses
(800 nm, 100 fs, 500 pulses, 10 kJ/m^2)


gas handling system
vacuum chamber
sample
micrometer lens mount
X-Y translation stage
laser
pump

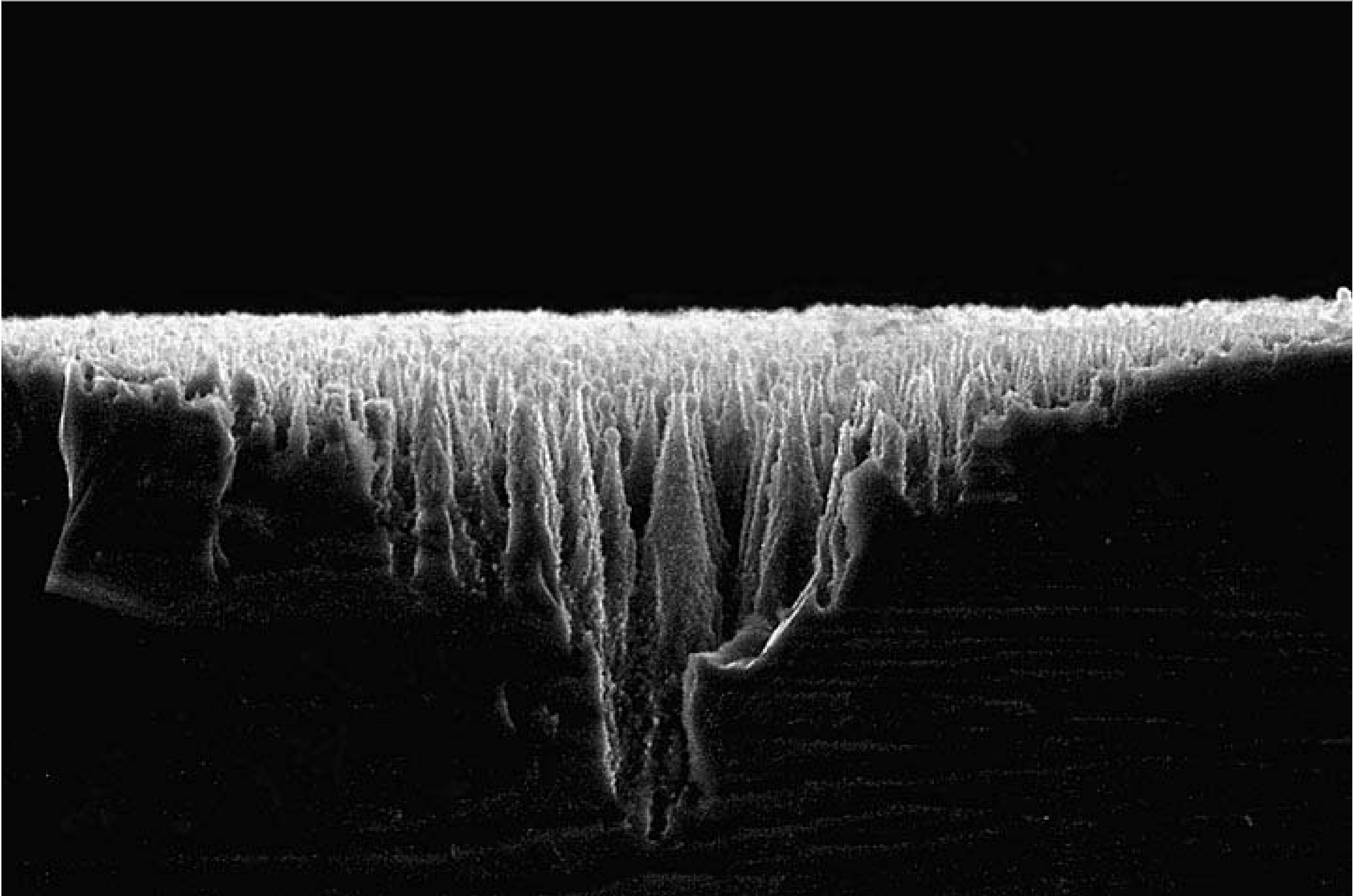
Black silicon



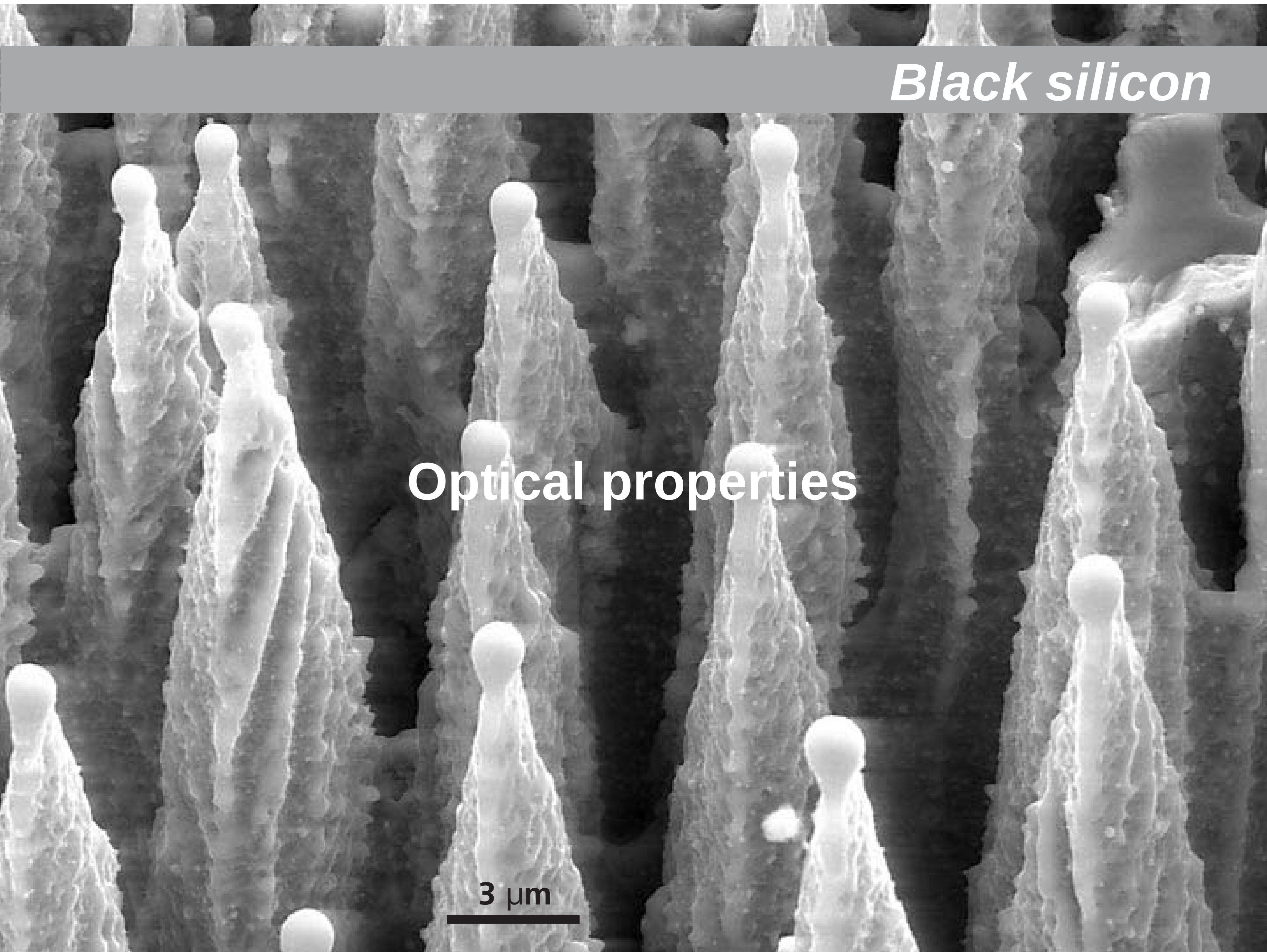
Black silicon



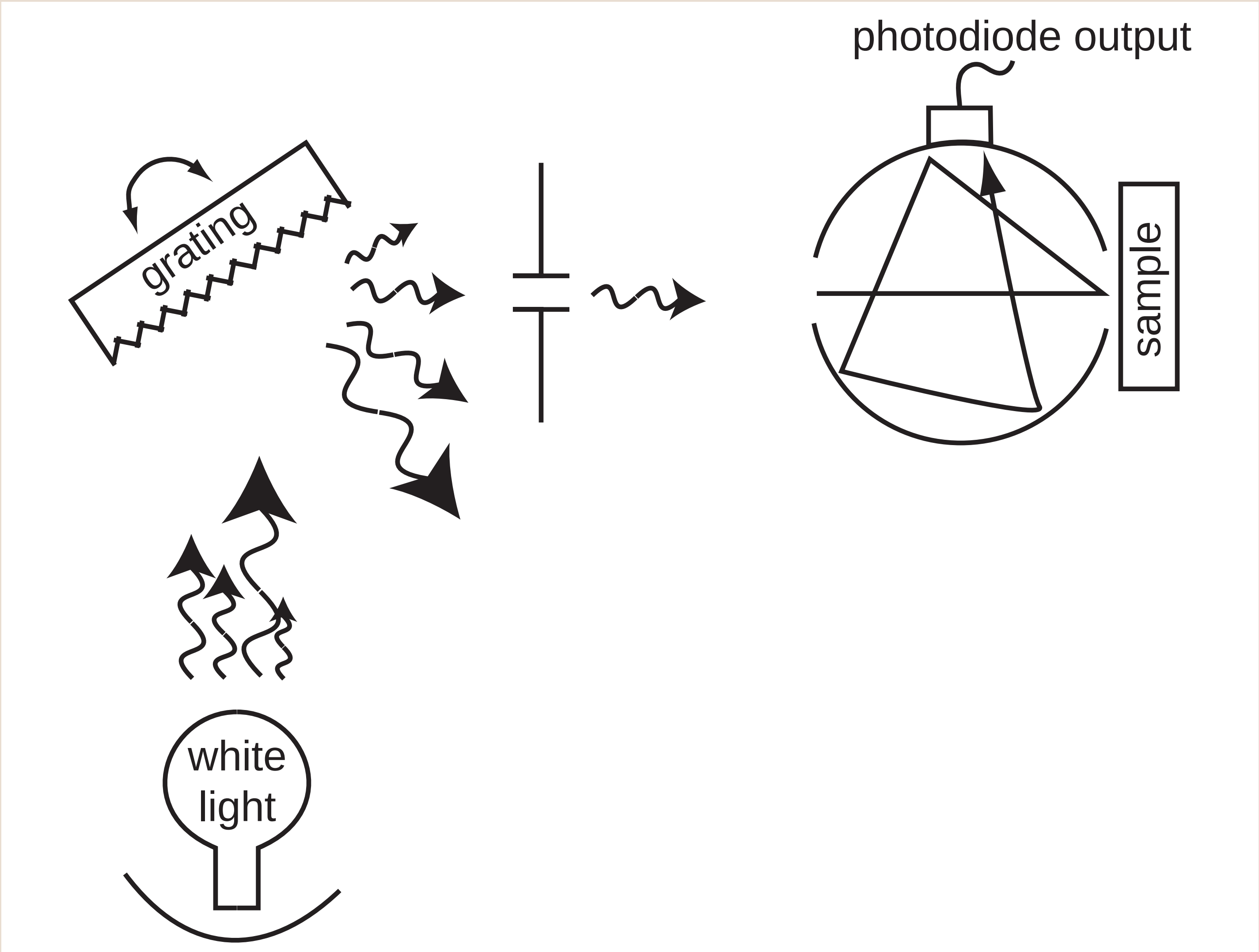
Black silicon



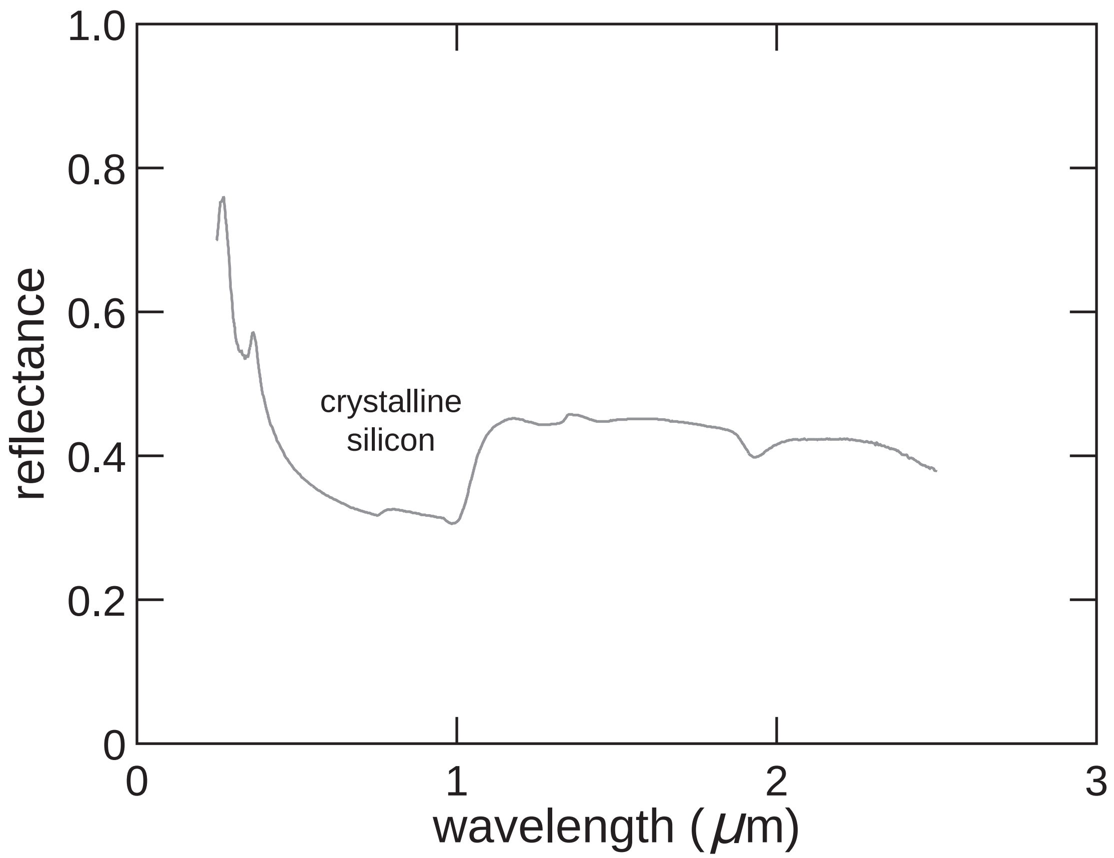
Optical properties



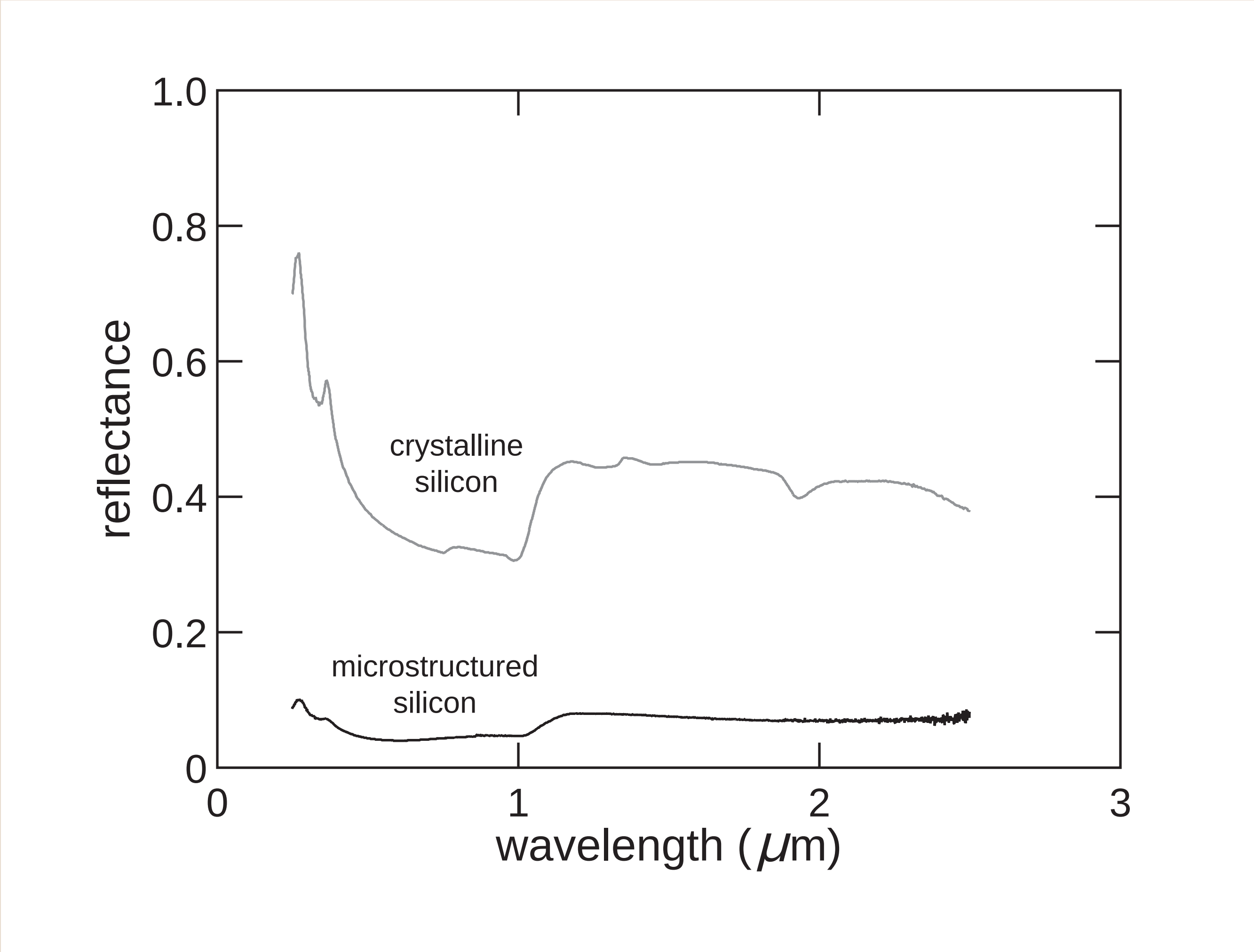
measure reflectance, transmittance with integrating sphere



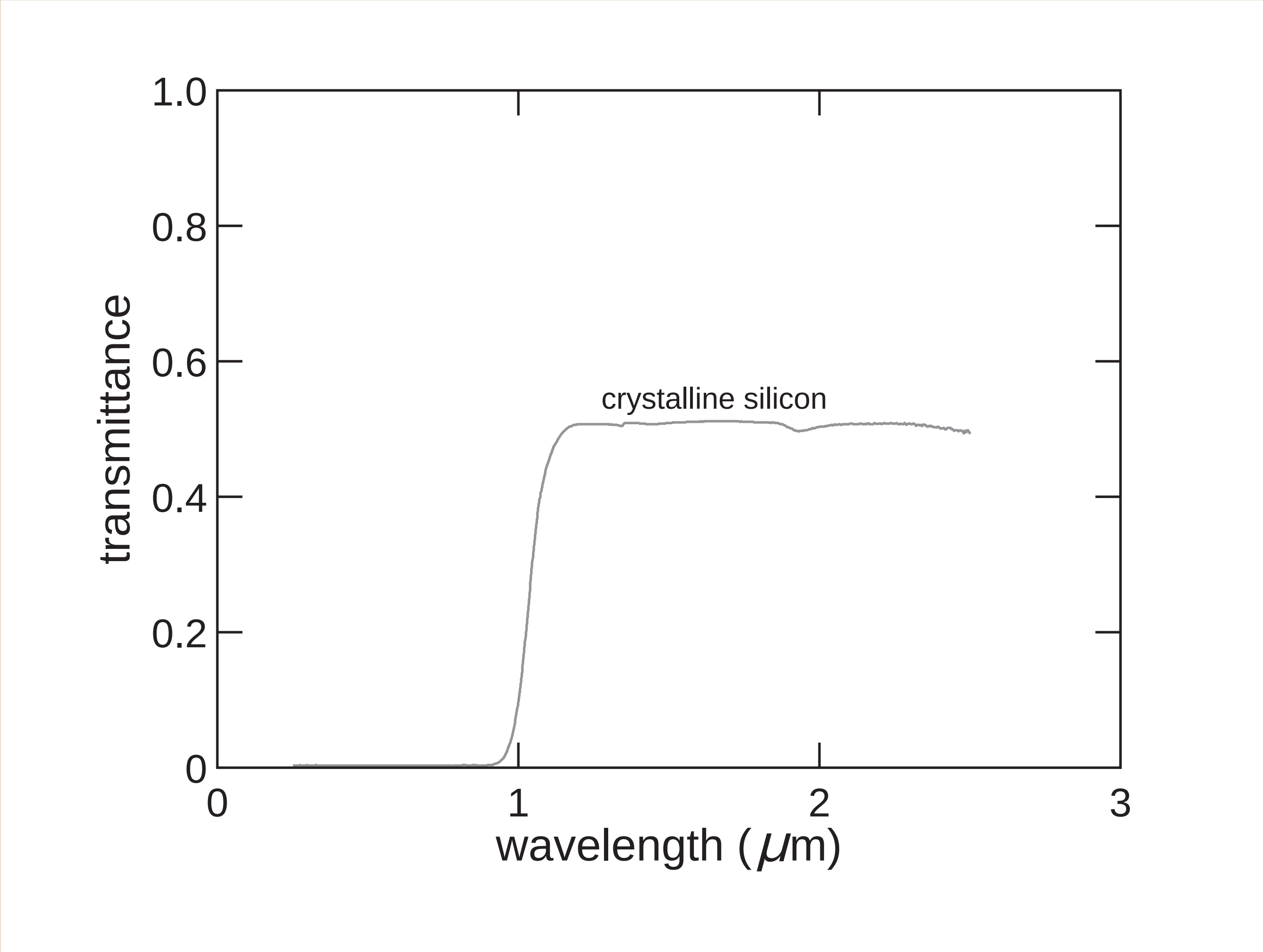
reflectance



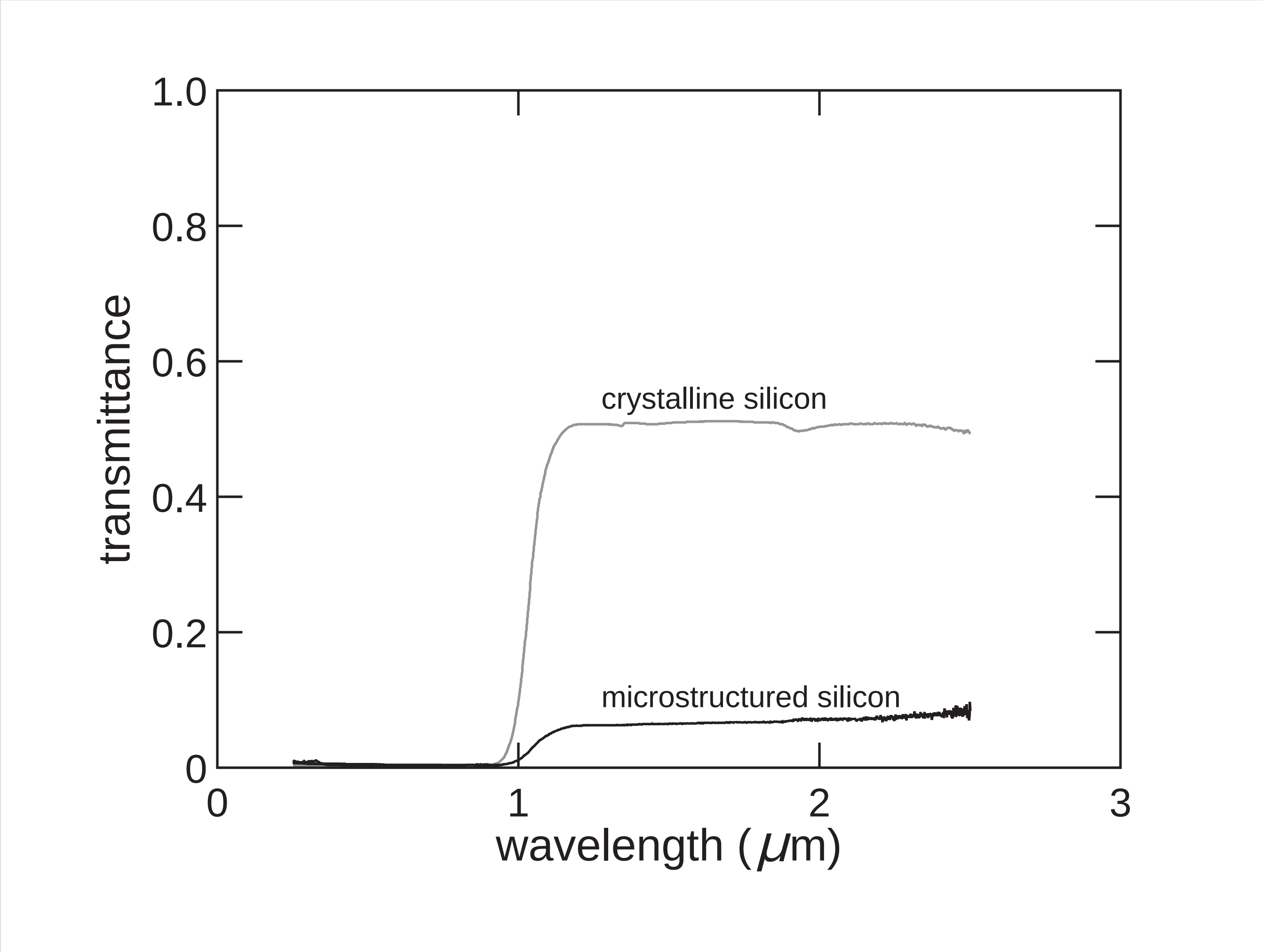
reflectance



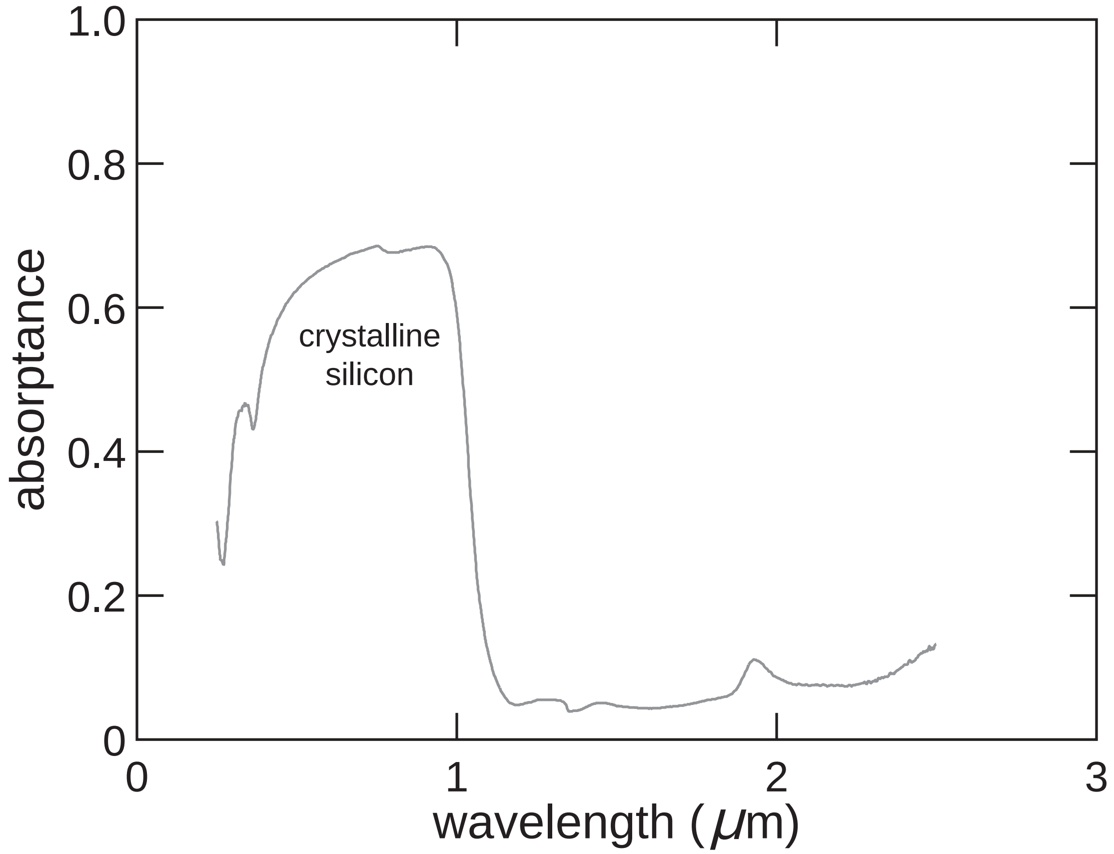
transmittance



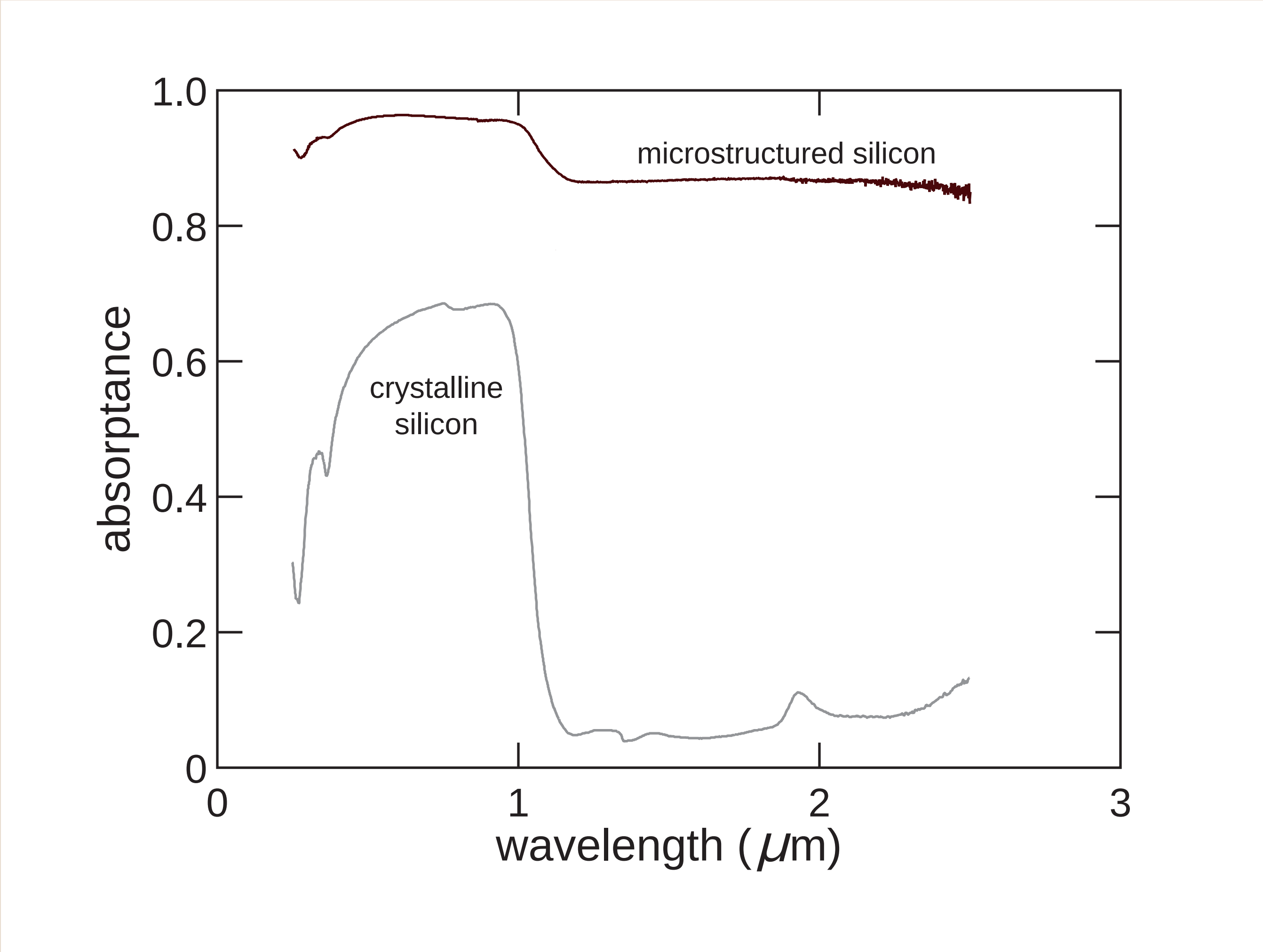
transmittance



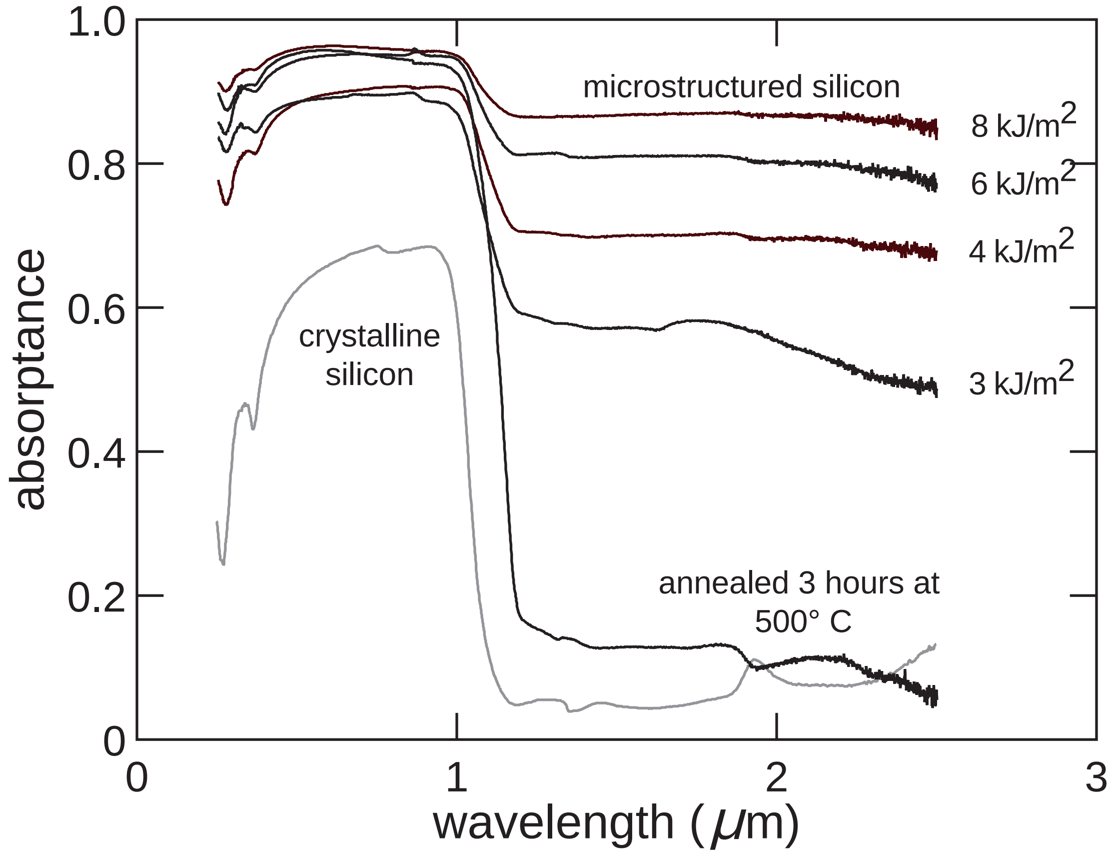
absorptance (A = 1 - R - T)



absorptance

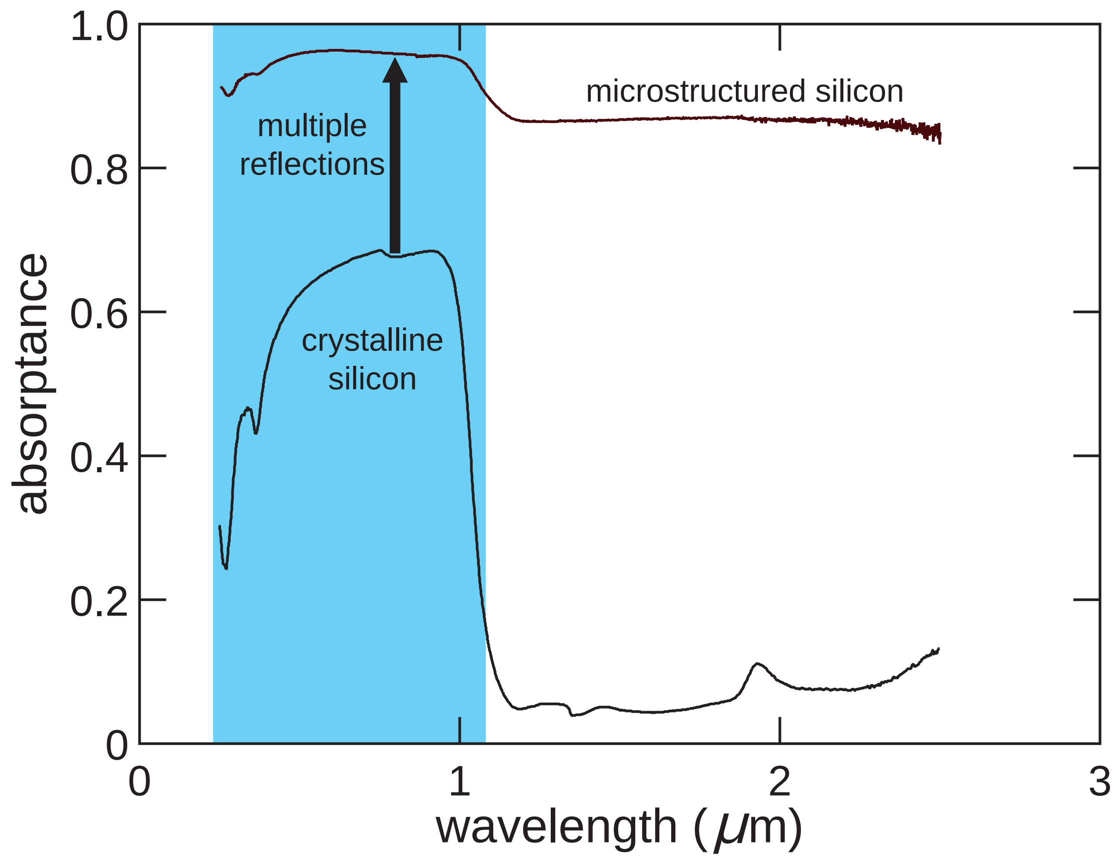


absorptance

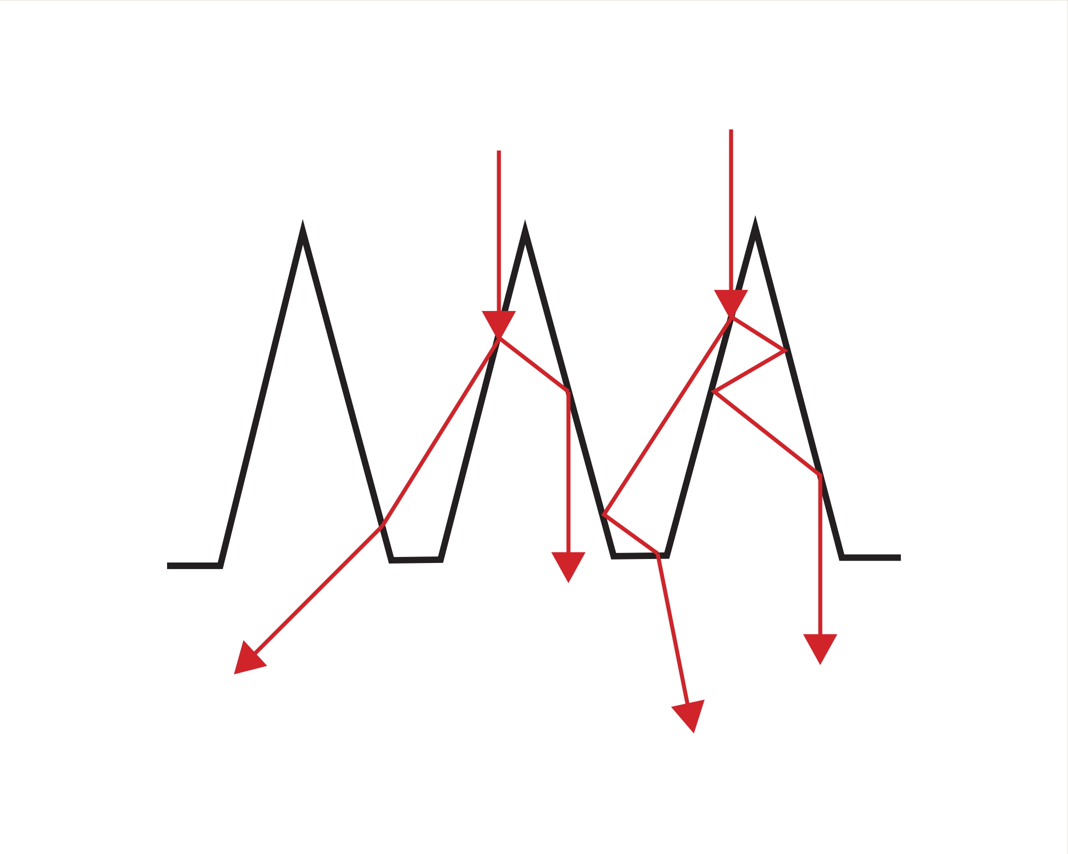


Why is it black?

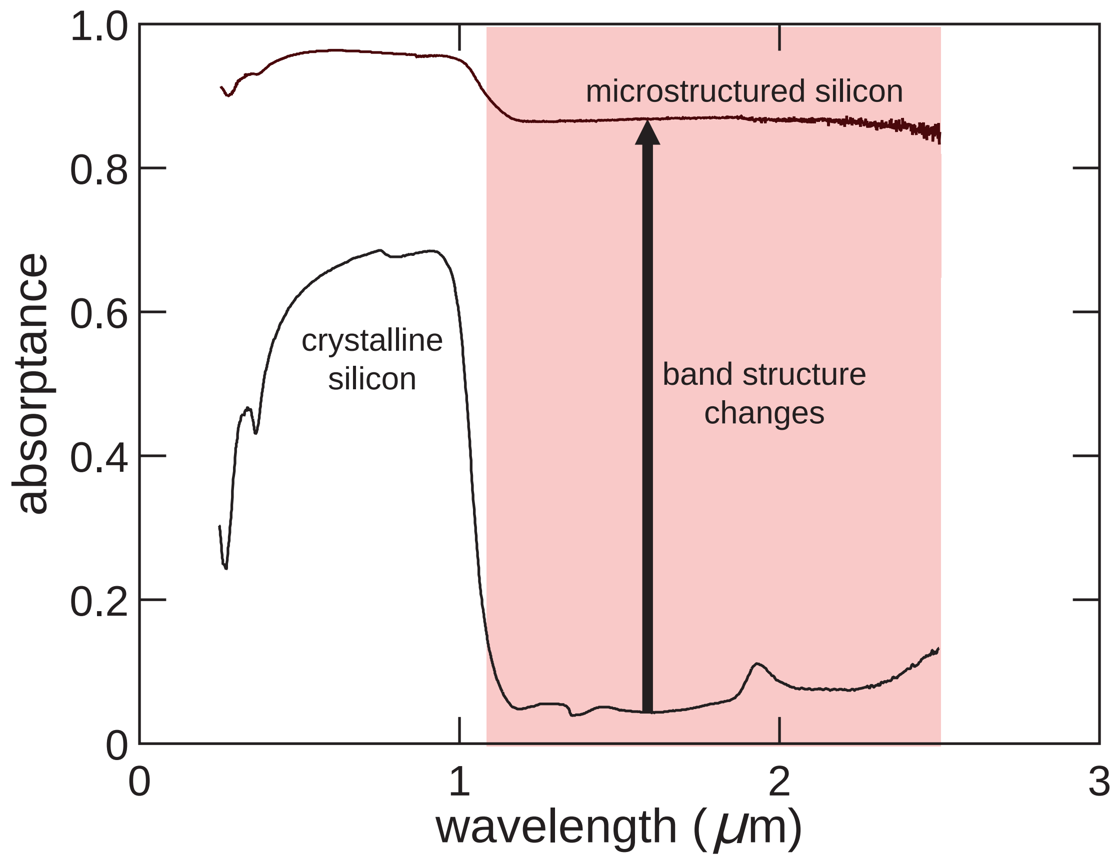
absorptance



Multiple reflections can enhance absorption

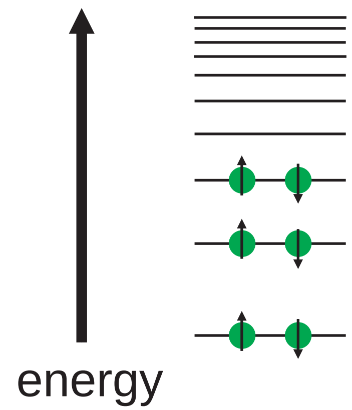


absorptance



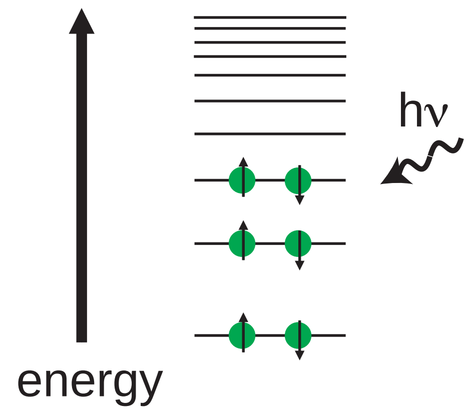
atoms absorb light by electronic transitions

atomic electrons
must occupy
well-defined
energy levels



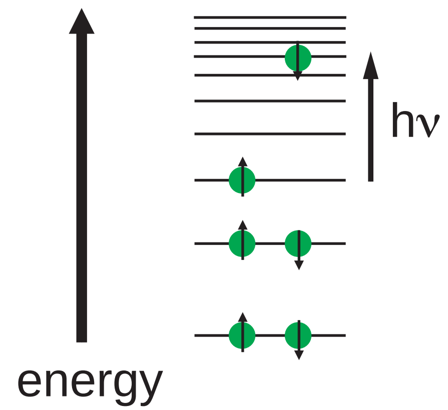
atoms absorb light by electronic transitions

absorbed photon must promote an electron to an empty level

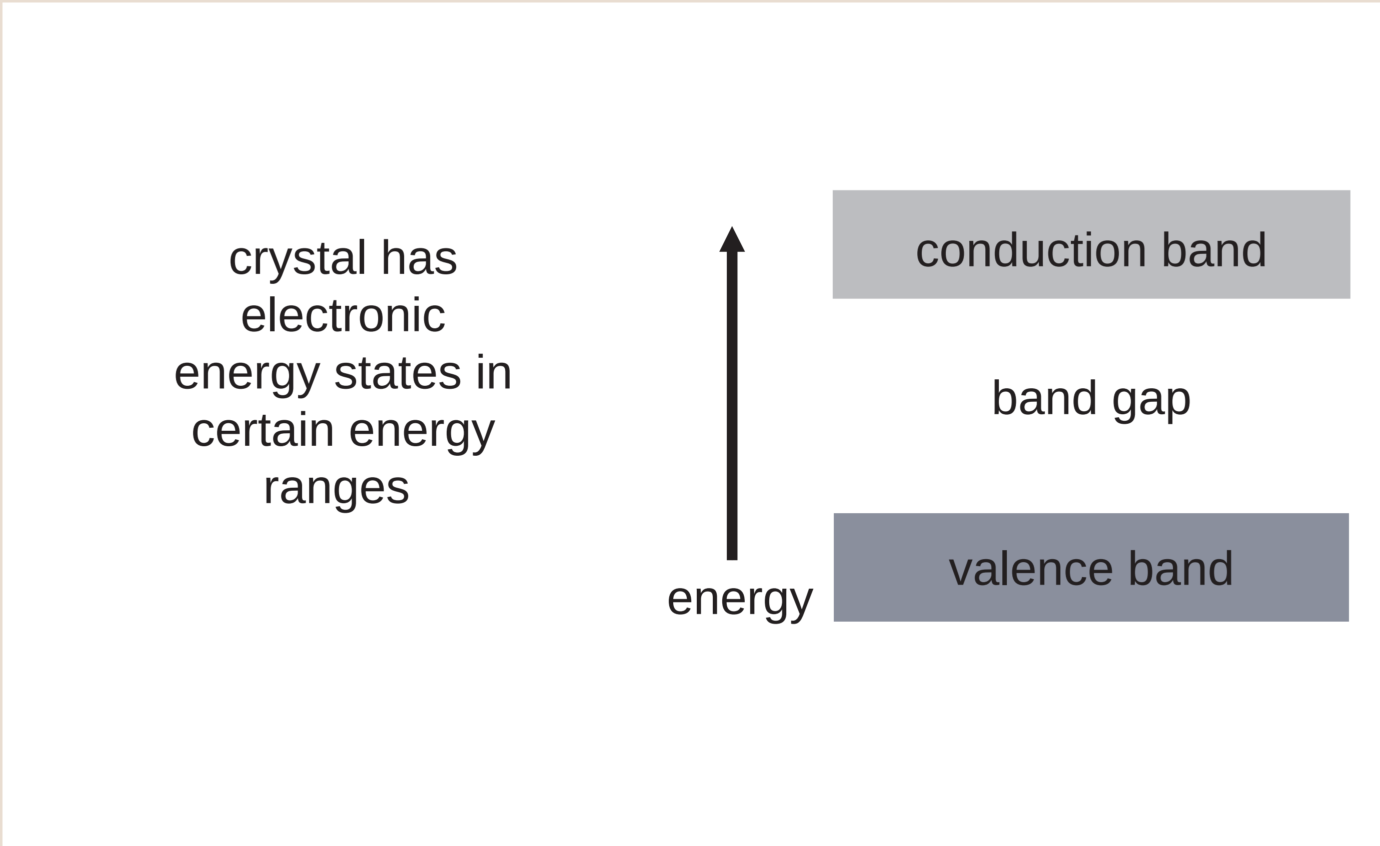


Atoms absorb light by electronic transitions

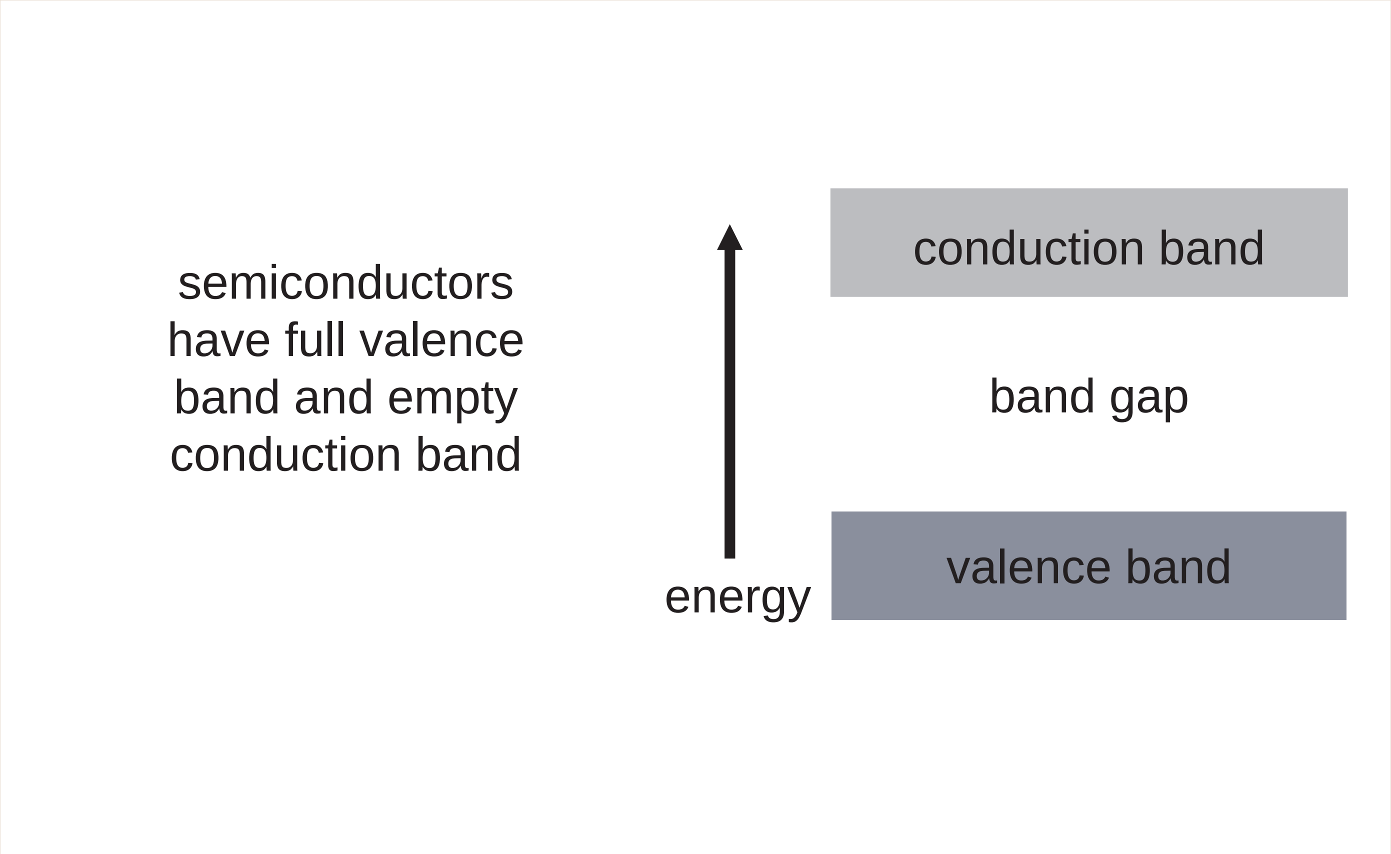
absorbed photon
must promote an
electron to an
empty level



crystalline solids have bands of energy states

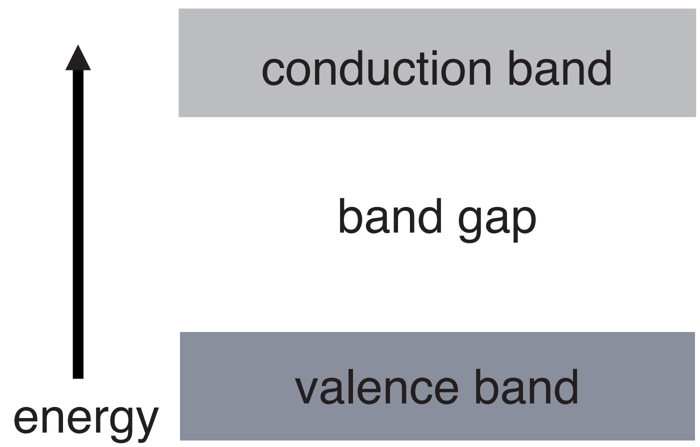


crystalline solids have bands of energy states



crystalline solids have bands of energy states

semiconductors are transparent to light with energy less than the band gap



What produces the below-band gap absorption?

What changes band structure?

- impurities
- defects

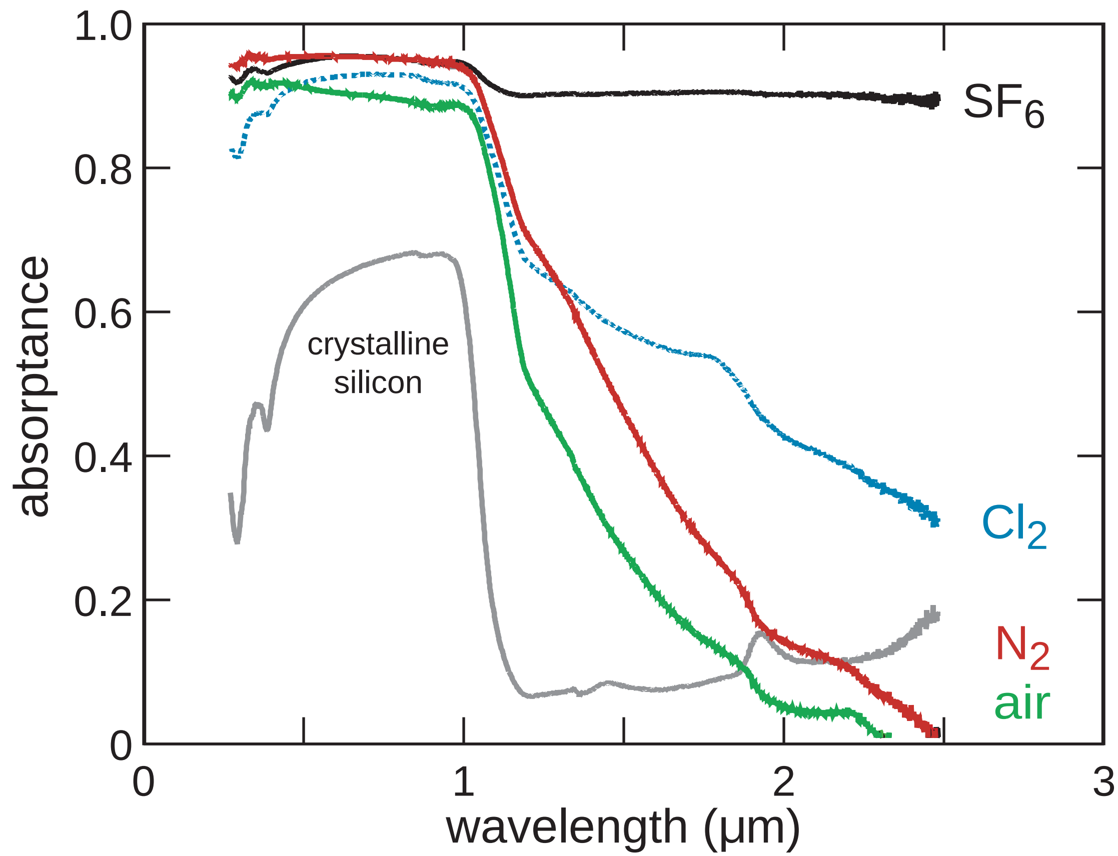
Previous work with other gases:

gas species incorporated into surface layer

sulfur required for below-band gap absorption

Younkin *et al.*, to appear in J. Appl. Phys.

absorptance



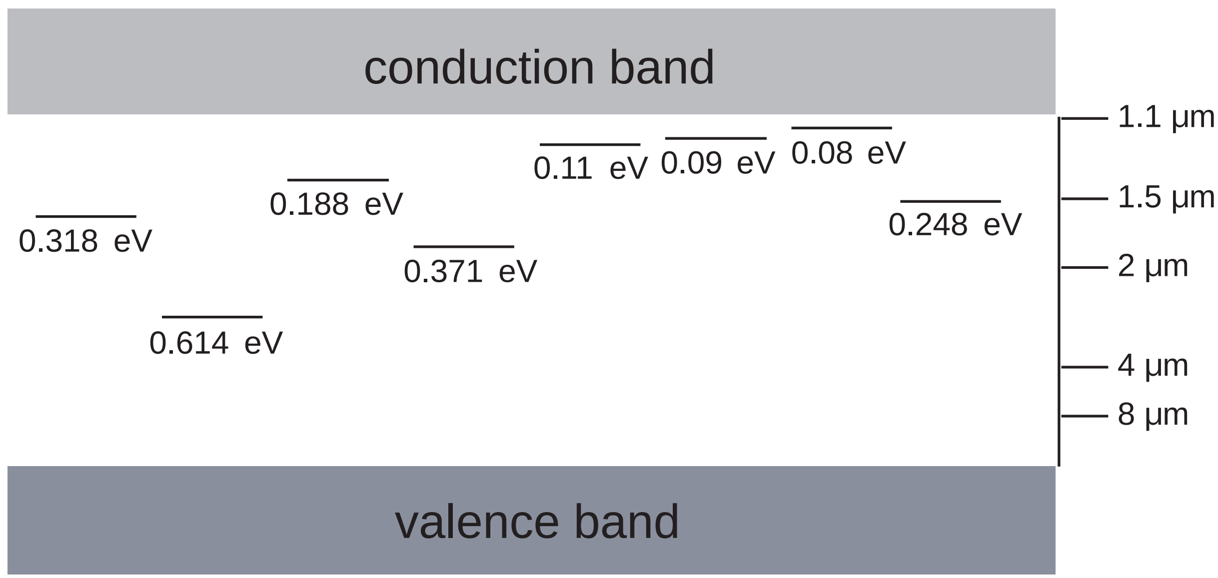
Surfaces structured in SF_6:

roughly 1% sulfur in surface layer (ion channeling, energy dispersive X-ray spectroscopy)

sulfur content decreases significantly on annealing

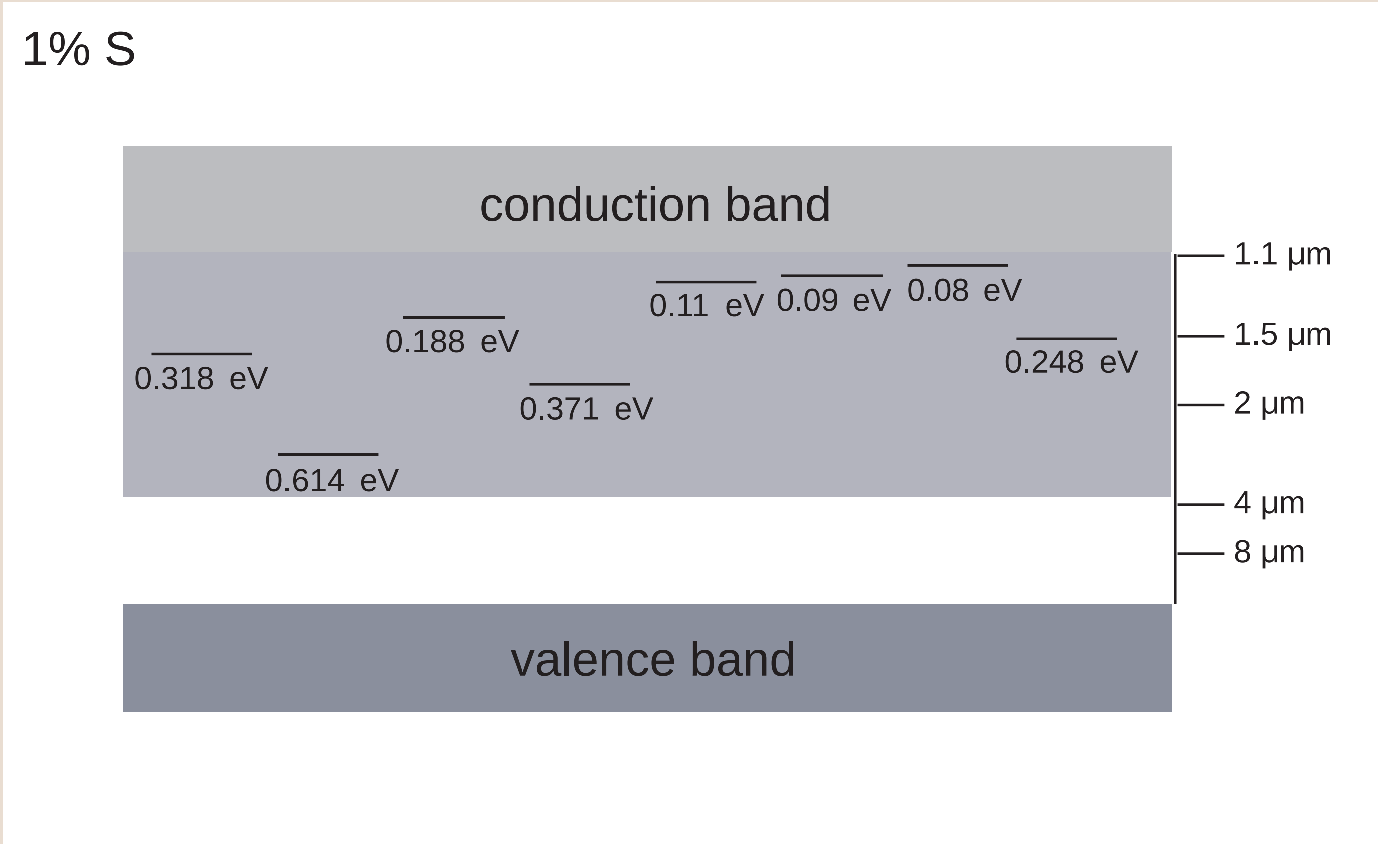
sulfur introduces states in silicon band gap

1 part in 10^6 S

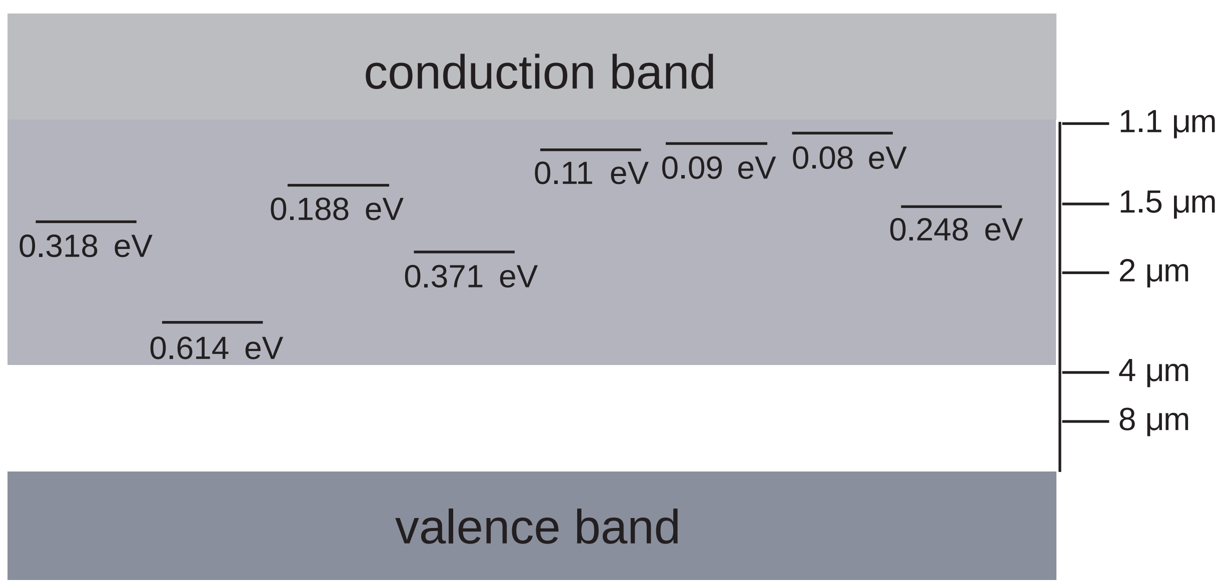


Janzén *et al.*, Phys. Rev. B **29**, 1907 (1984)

at high concentrations, states may broaden into a band

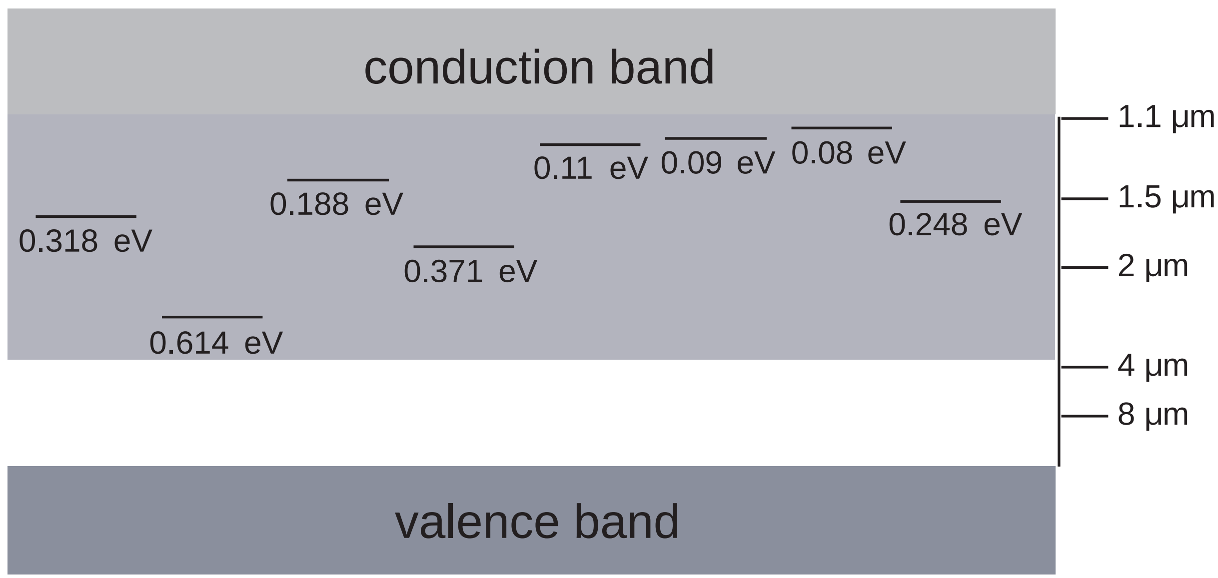


at high concentrations, states may broaden into a band



expect absorption to roughly 3 µm

near-IR transmittance rises around 3 μm



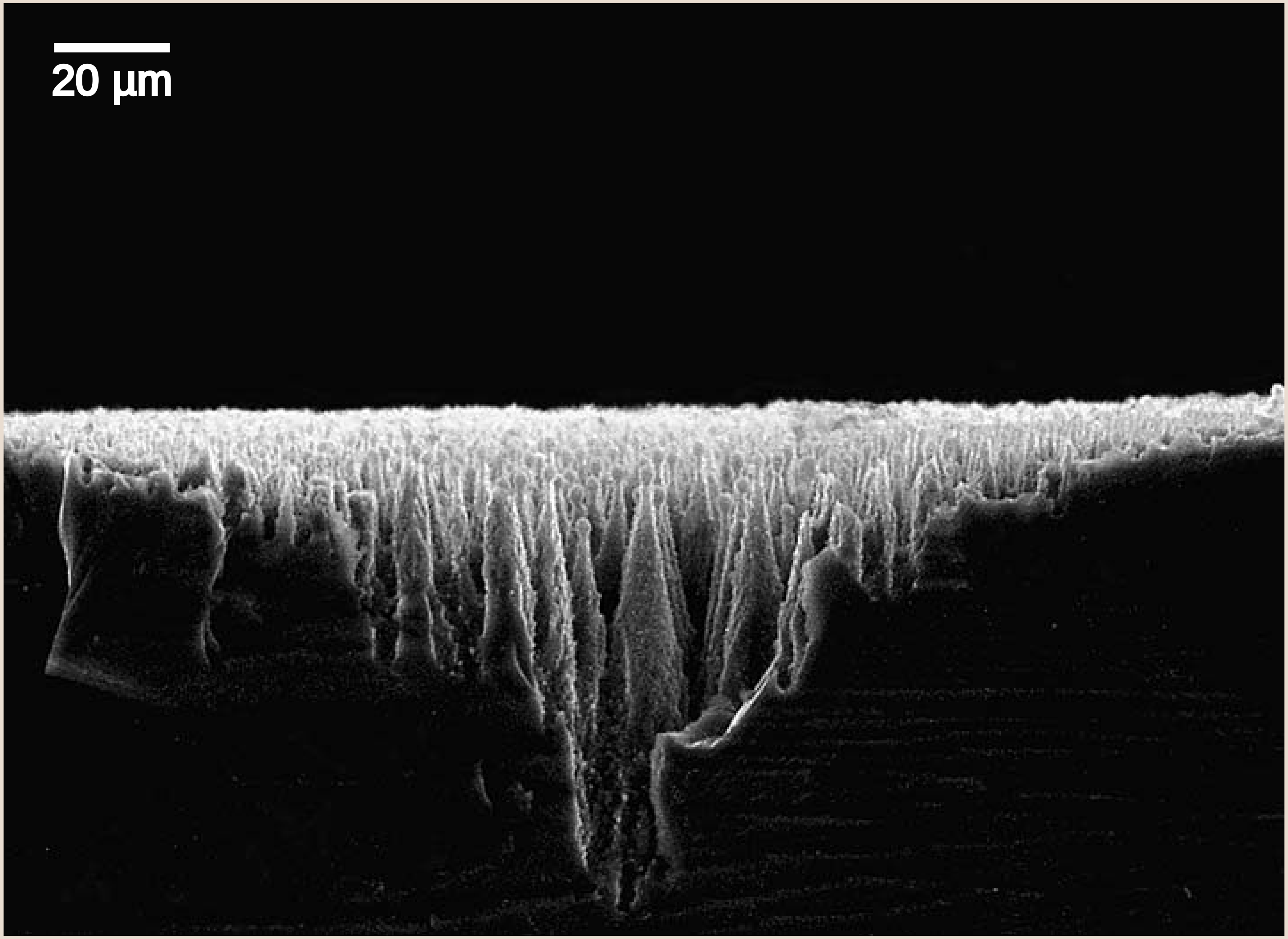
Sulfur a likely explanation:

sulfur required for below-band gap absorption

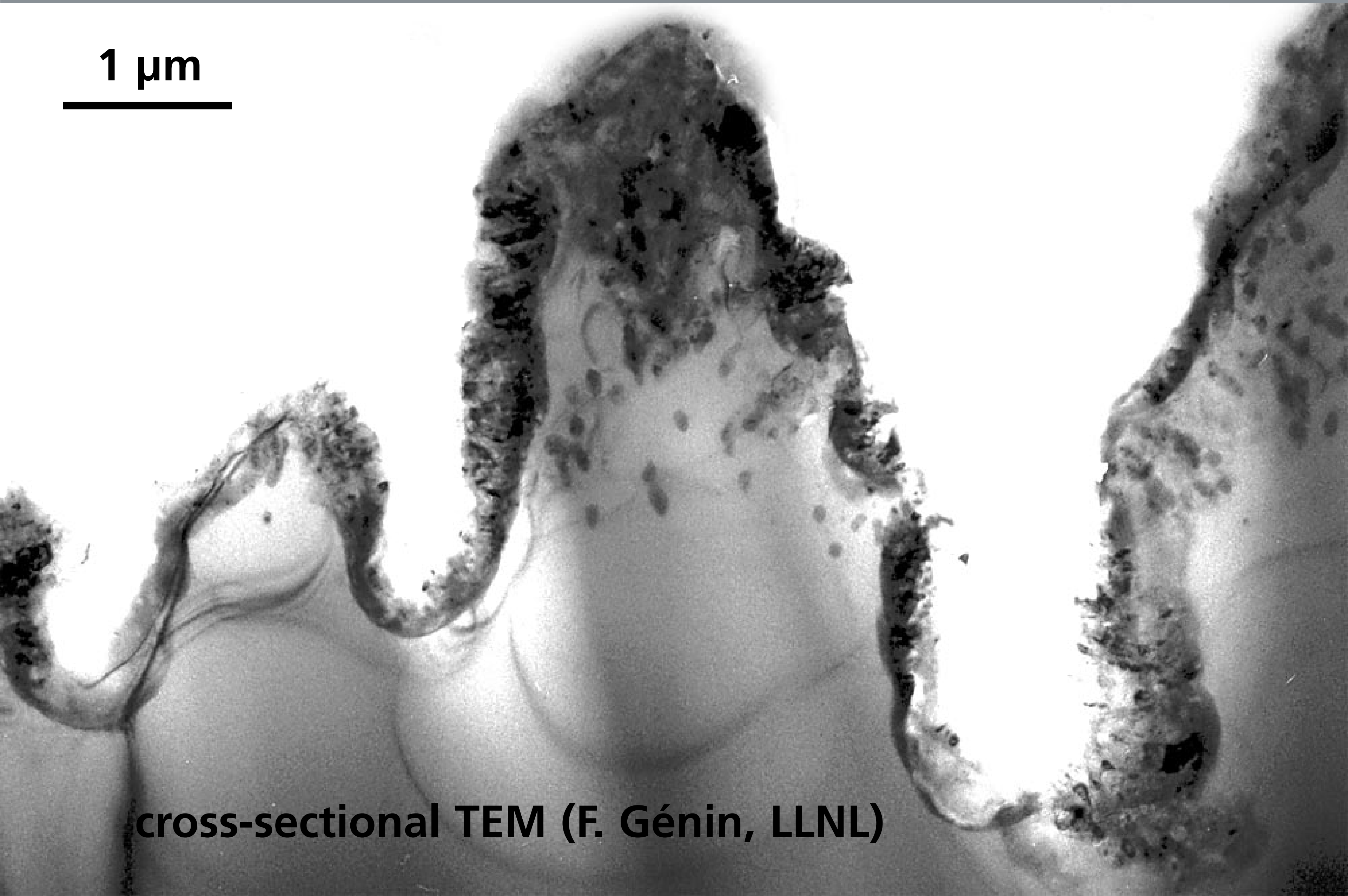
annealing reduces sulfur and absorption

appropriate wavelength range

What is the underlying structure?

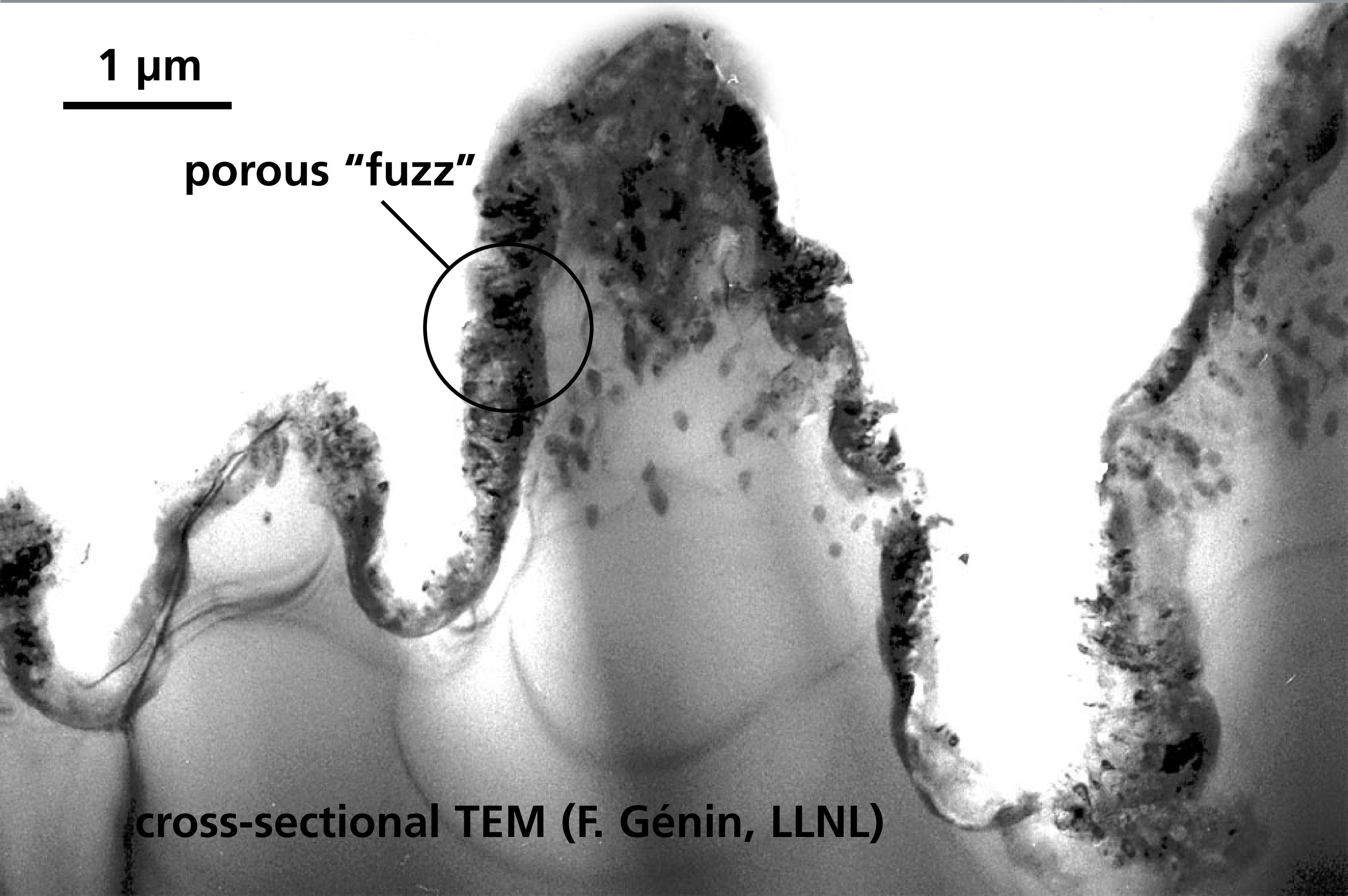

20 µm

Structural and chemical analysis

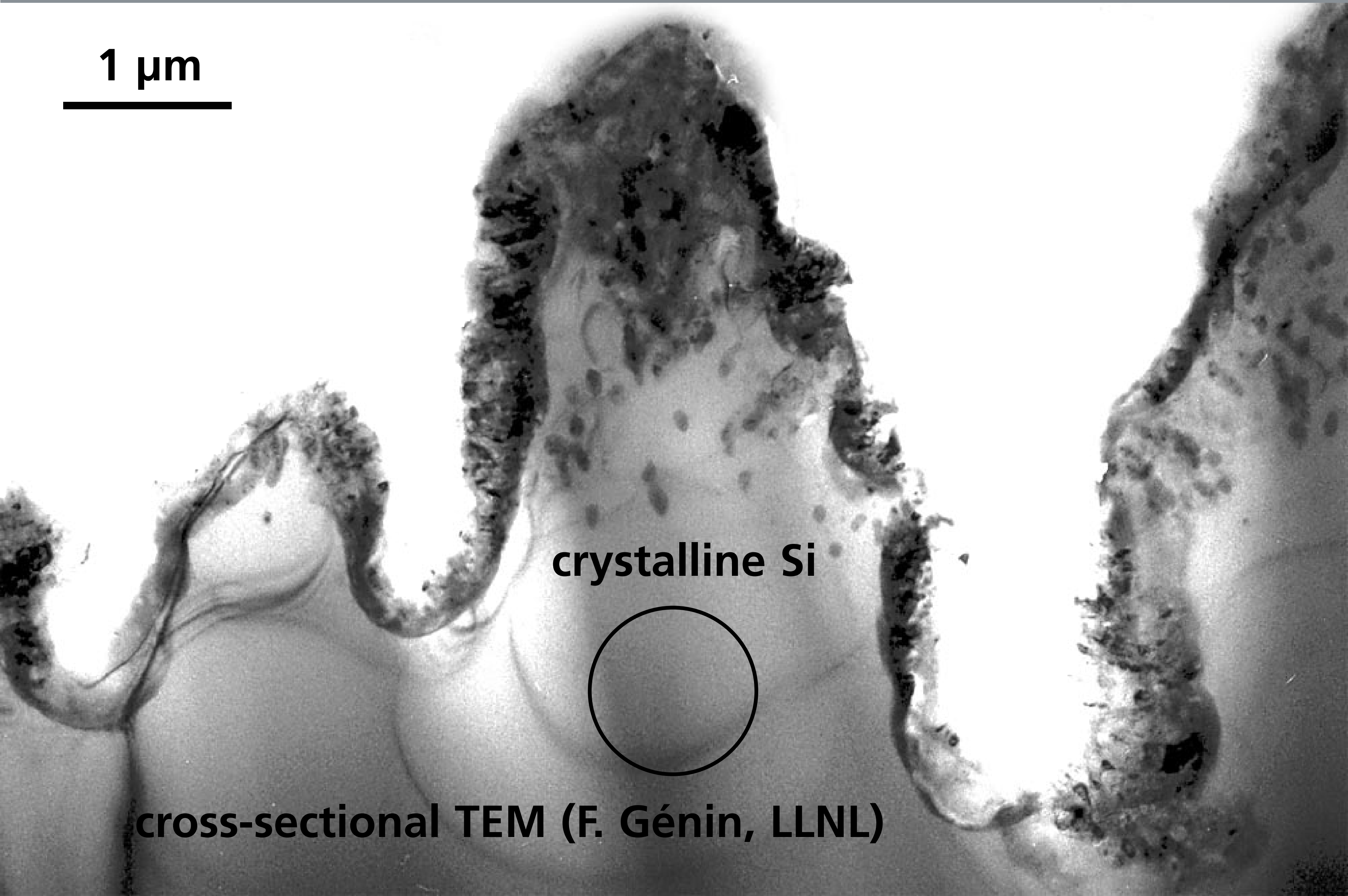


cross-sectional TEM (F. Génin, LLNL)

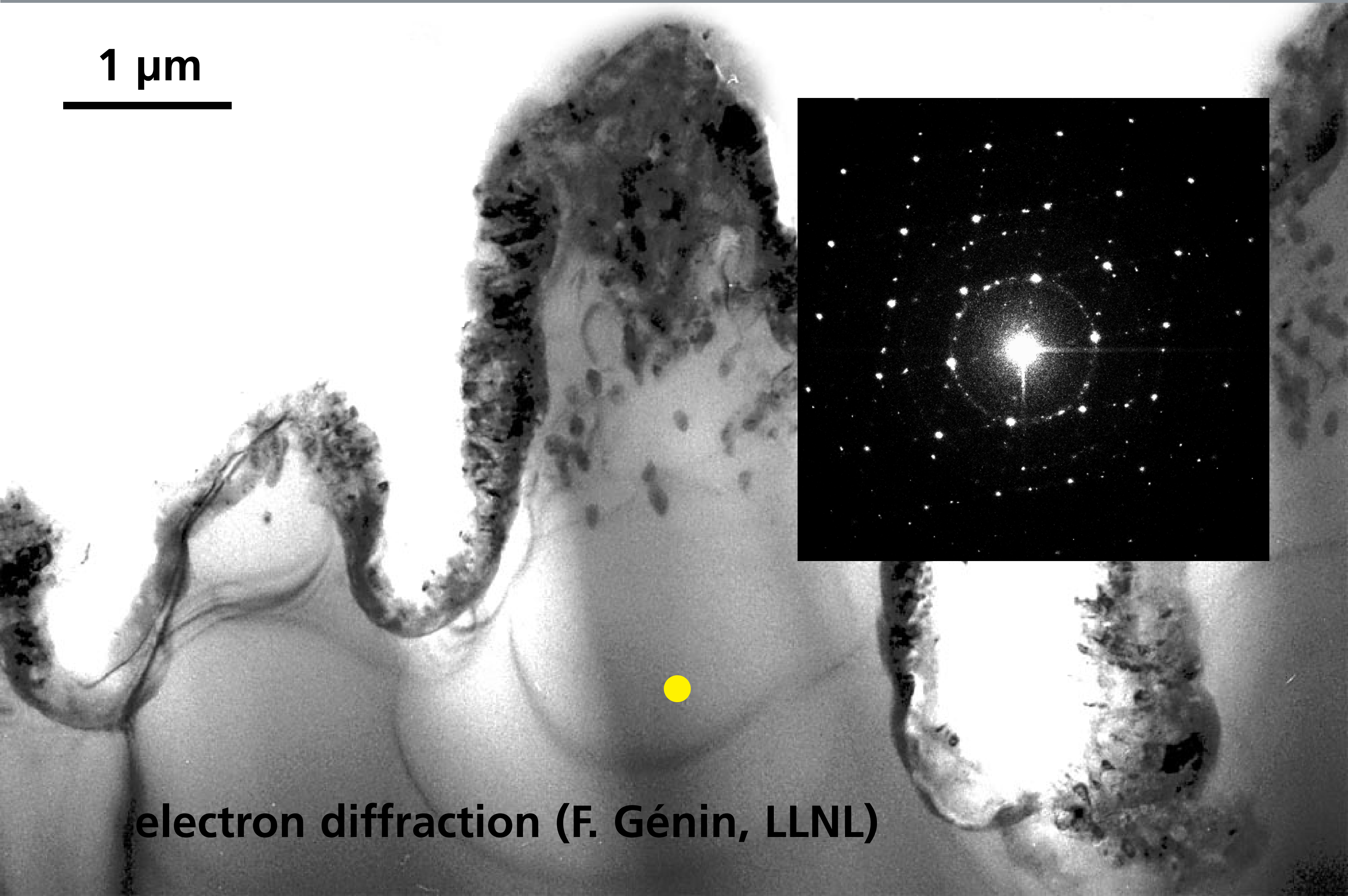
Structural and chemical analysis



Structural and chemical analysis

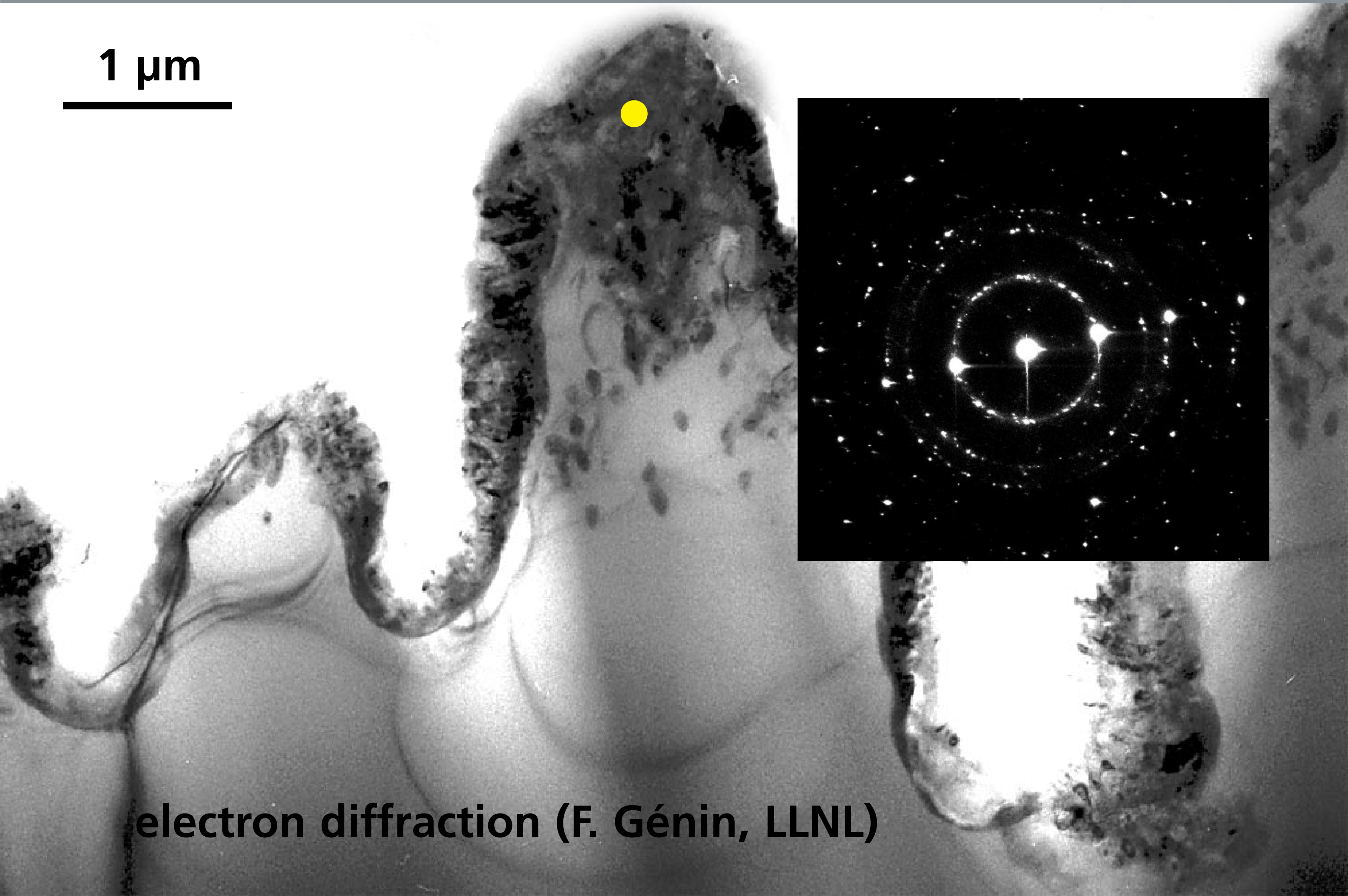


Structural and chemical analysis



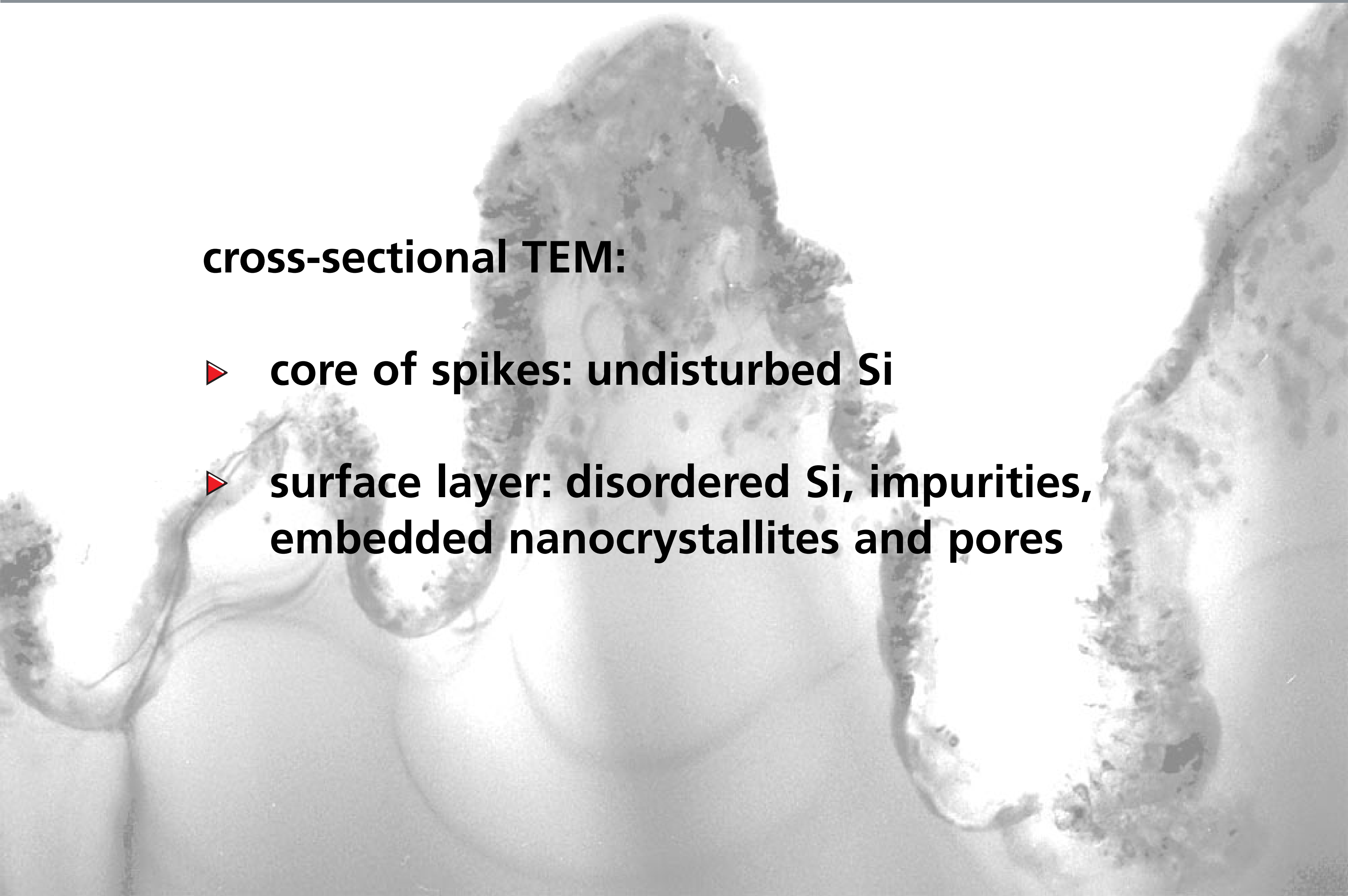
electron diffraction (F. Génin, LLNL)

Structural and chemical analysis



electron diffraction (F. Génin, LLNL)

Structural and chemical analysis



cross-sectional TEM:

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

Could nanostructures explain infrared absorption?

Structure less likely than sulfur:

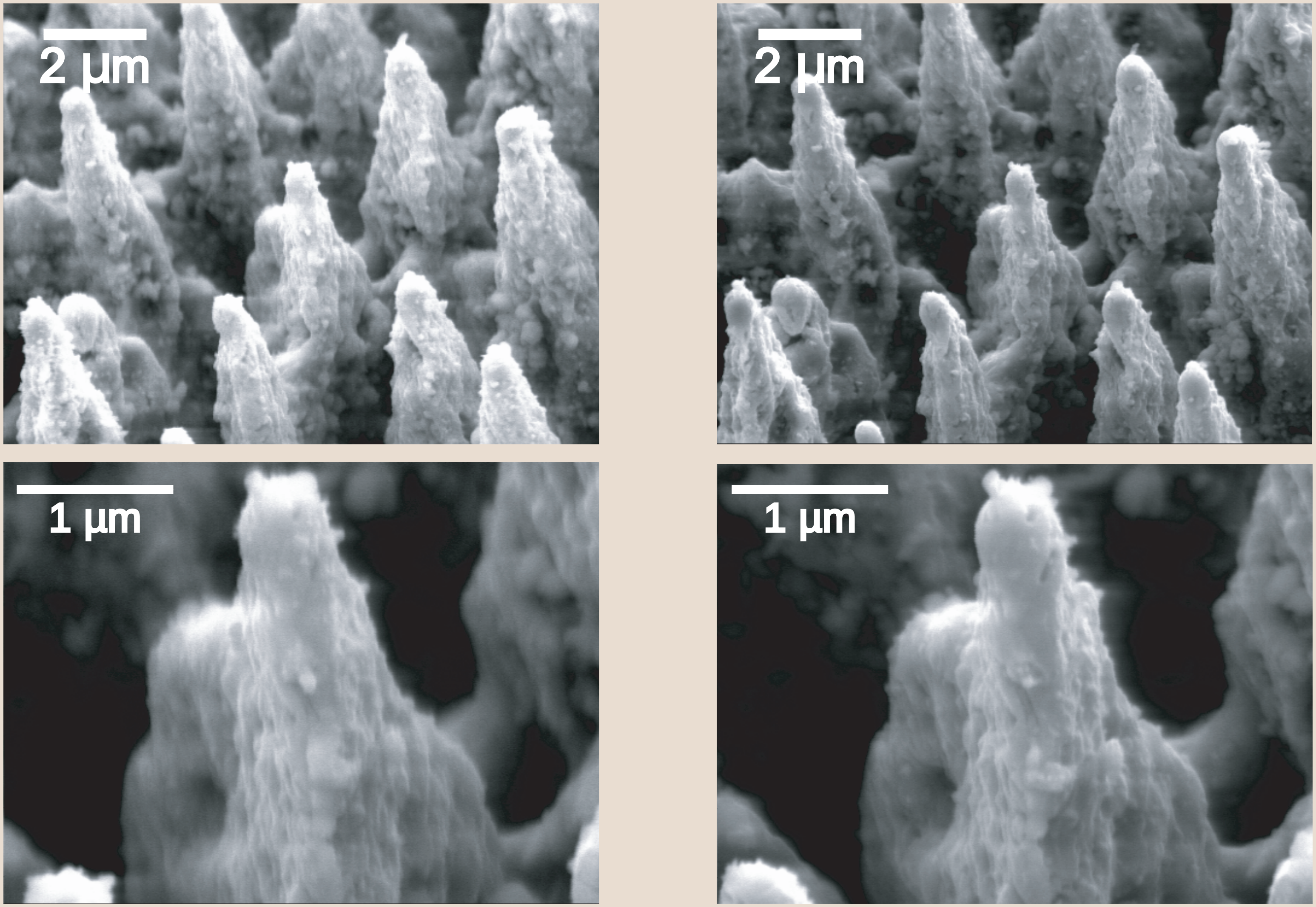
annealing

ns pulses

different gases

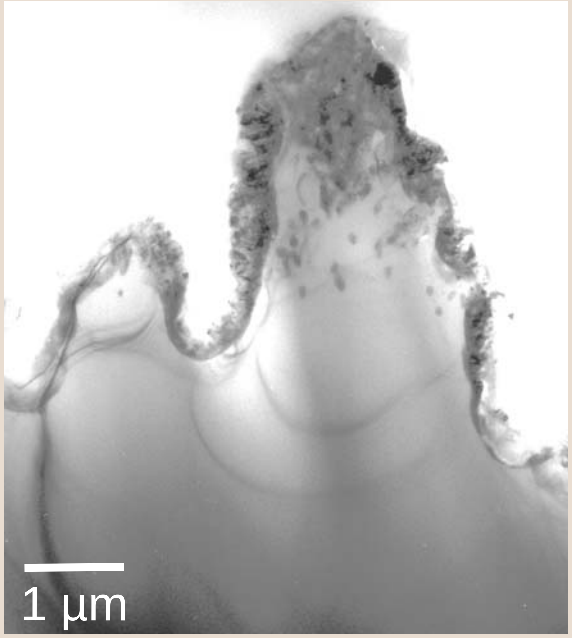
Structural analysis

before annealing after annealing

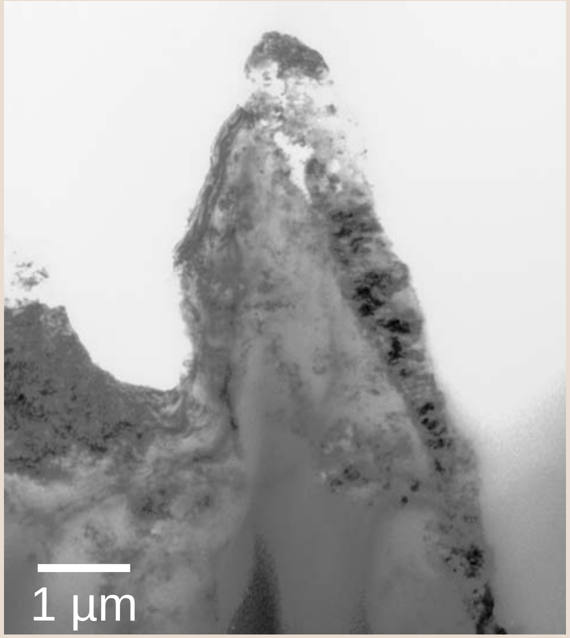


Structural analysis

not annealed



annealed



annealing does not affect visible structure

Structure less likely than sulfur:

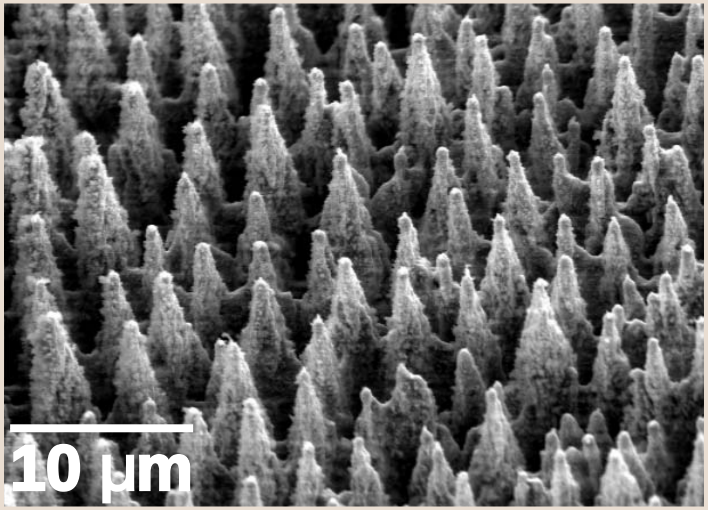
no evident structural change with annealing

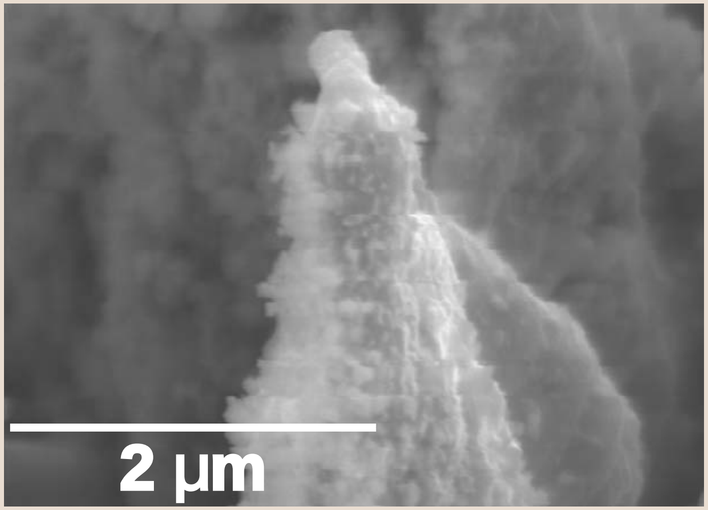
(consistent with multiple reflections in visible)

What happens with nanosecond pulses?

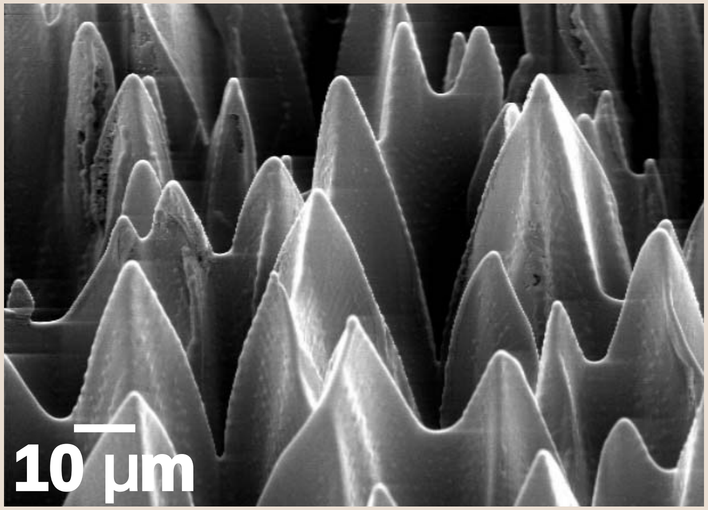
Nanosecond vs femtosecond

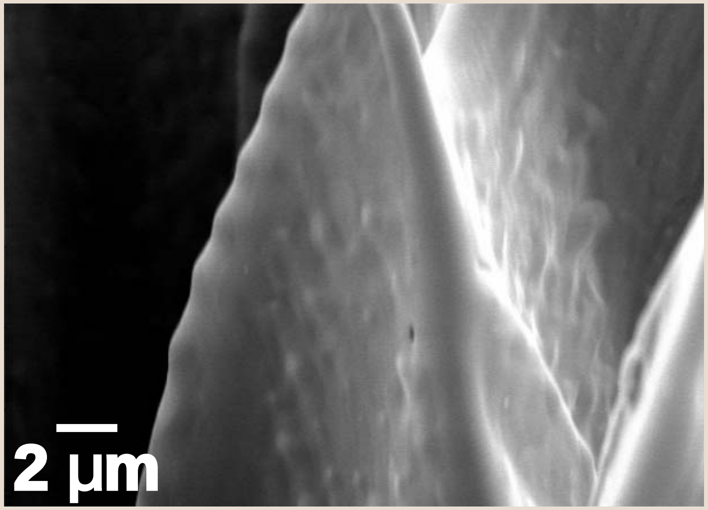
800 nm, 100 fs, 10 kJ/m^2





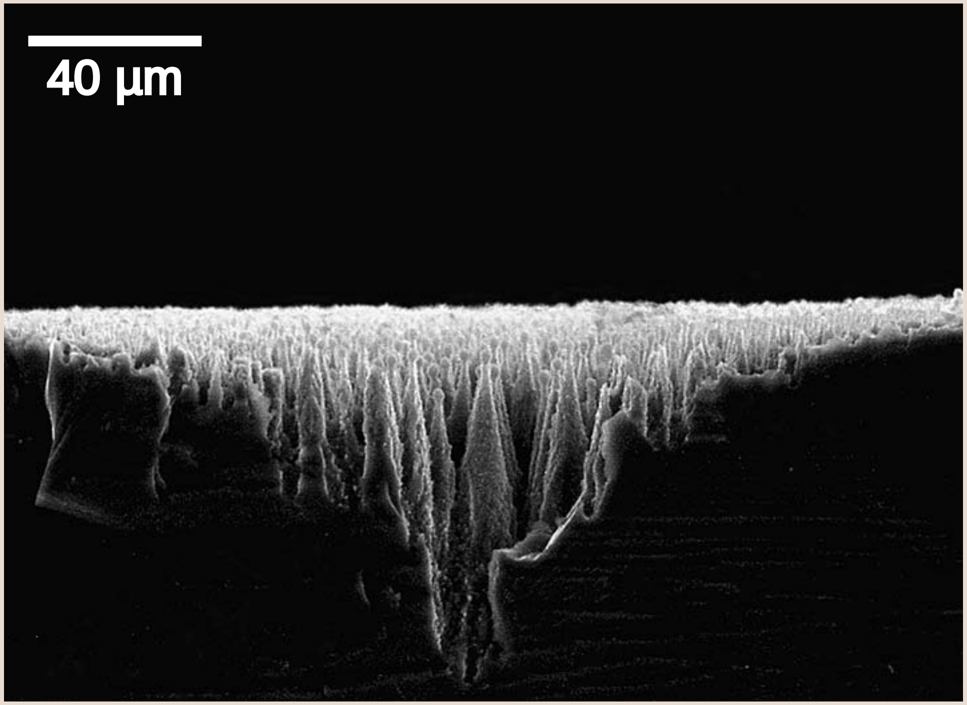
248 nm, 30 ns, 30 kJ/m^2





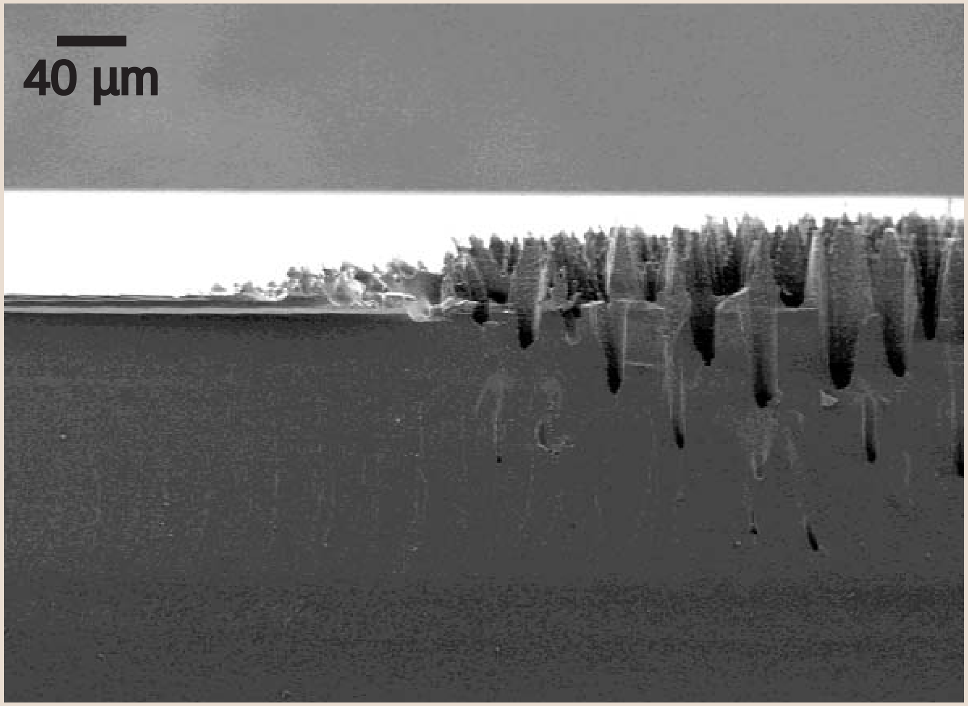
Nanosecond vs femtosecond

800 nm, 100 fs, 10 kJ/m²



fs cones etched below surface

248 nm, 30 ns, 30 kJ/m²



ns cones grow above surface

Nanosecond vs femtosecond

ns-structured surface shows less disorder

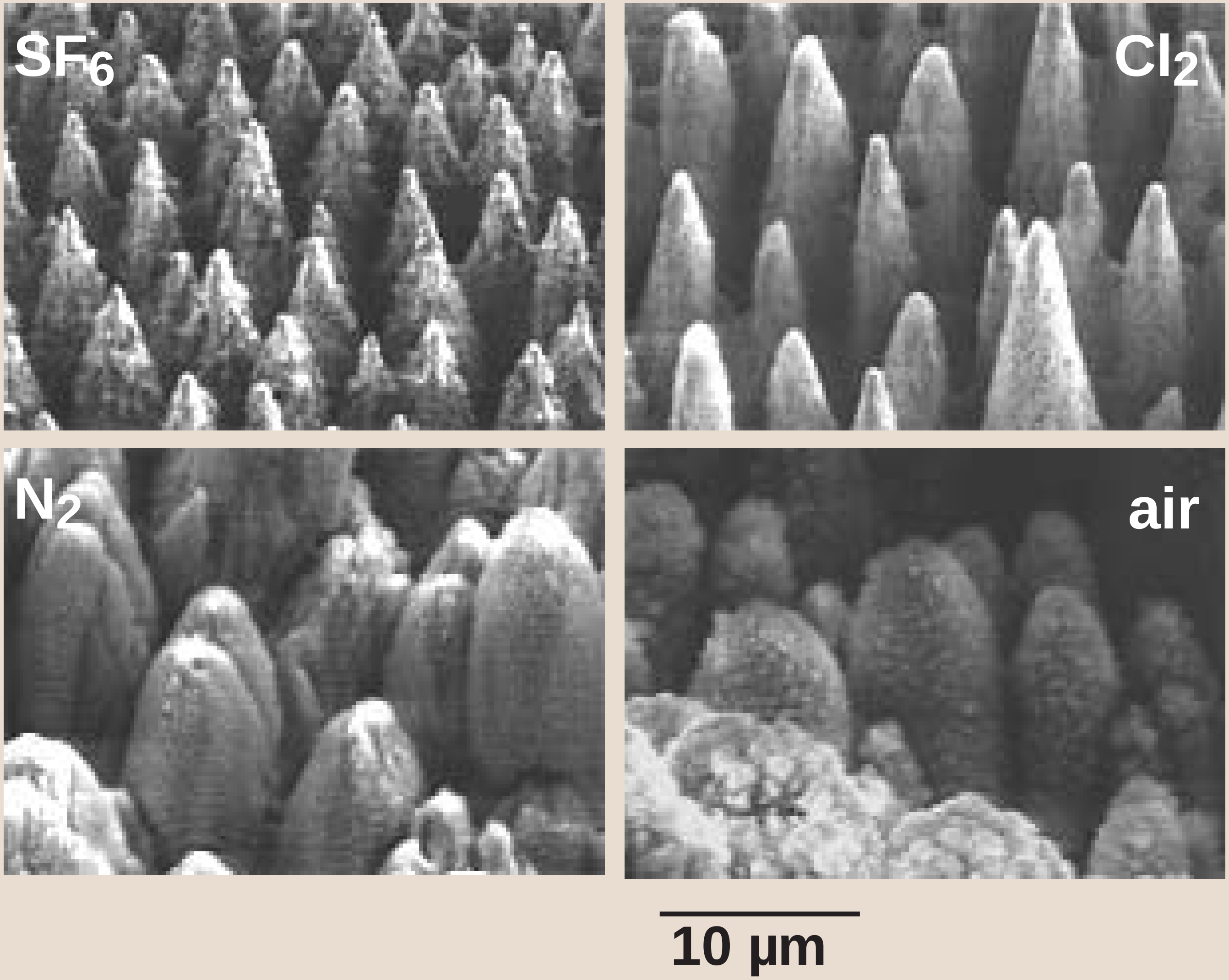
Optical properties virtually identical

Sulfur content very similar

Structure less likely than sulfur:

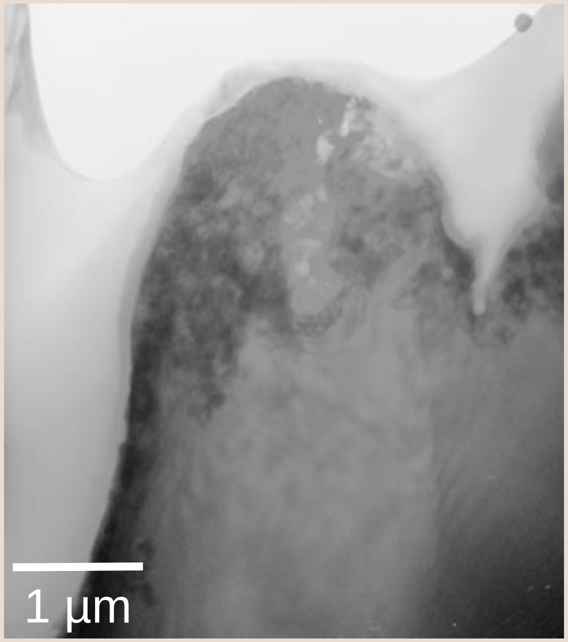
no evident structural change with annealing

ns pulses produce very different structure, but same composition and optical properties

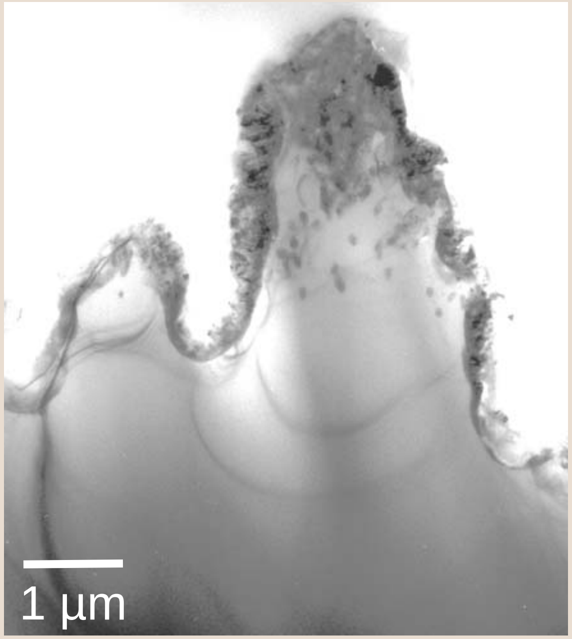


all except Cl_2 show surface nanostructure

air



SF_6



surface disorder present in air sample

Structure less likely than sulfur:

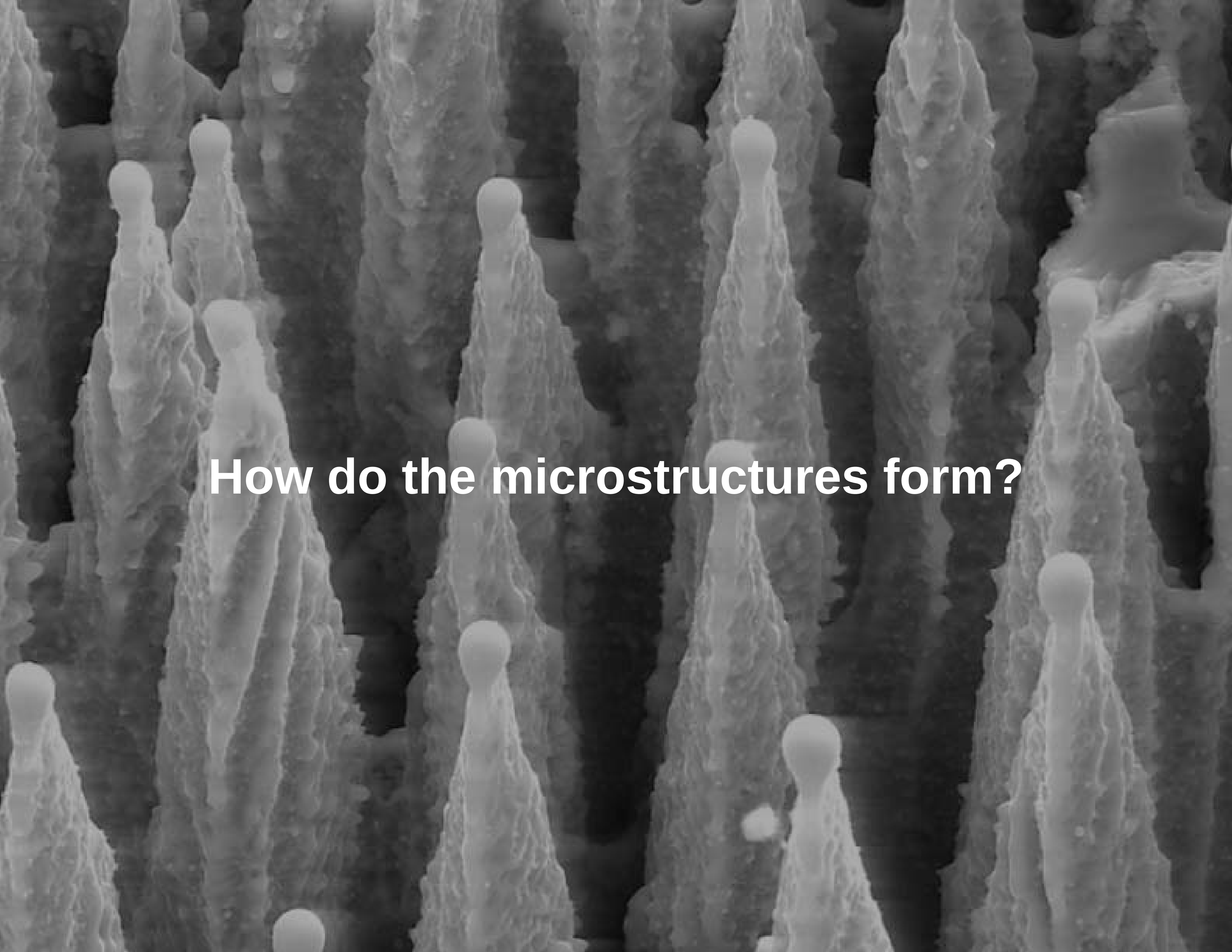
no evident structural change with annealing

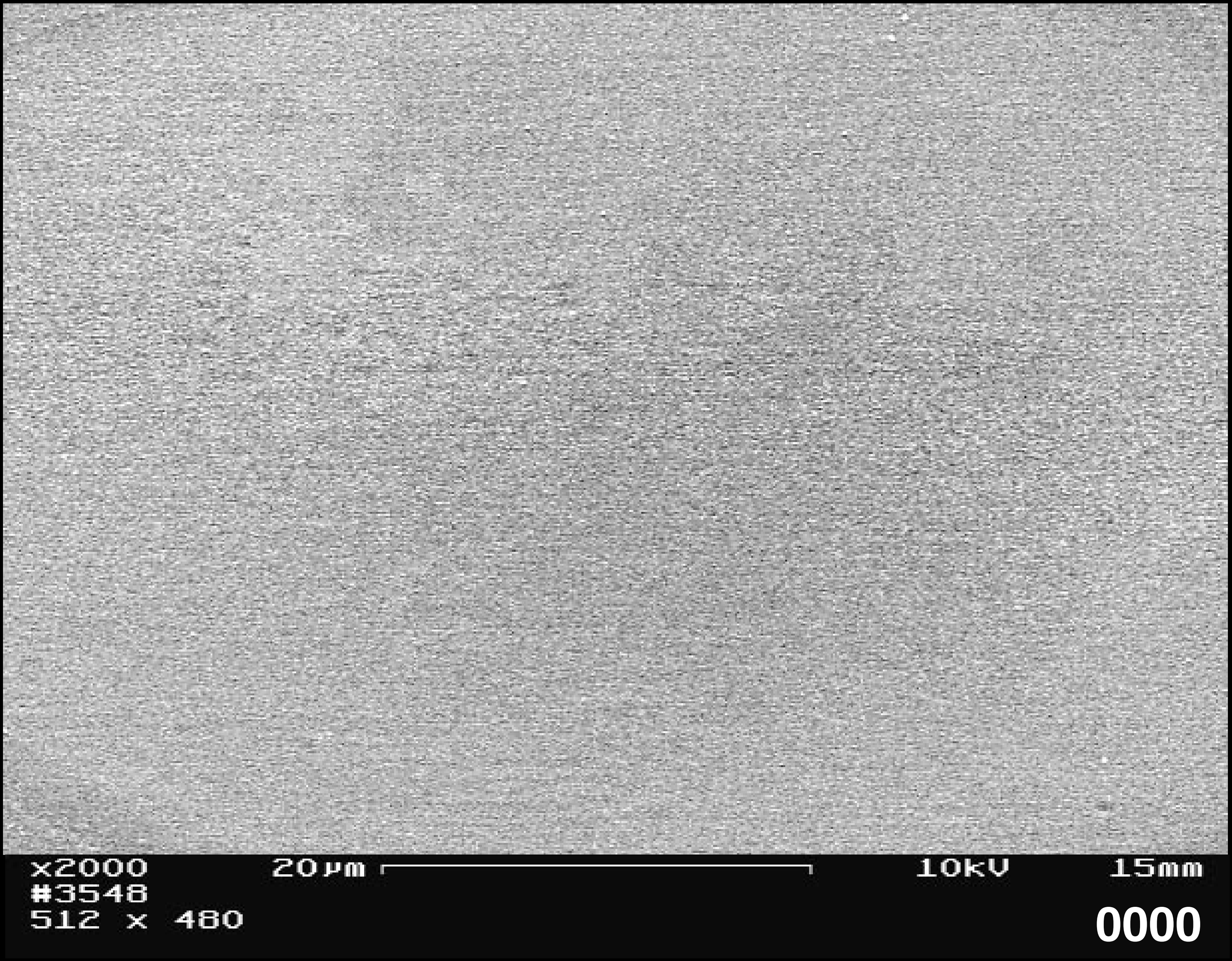
ns pulses produce very different structure, same composition and optical properties

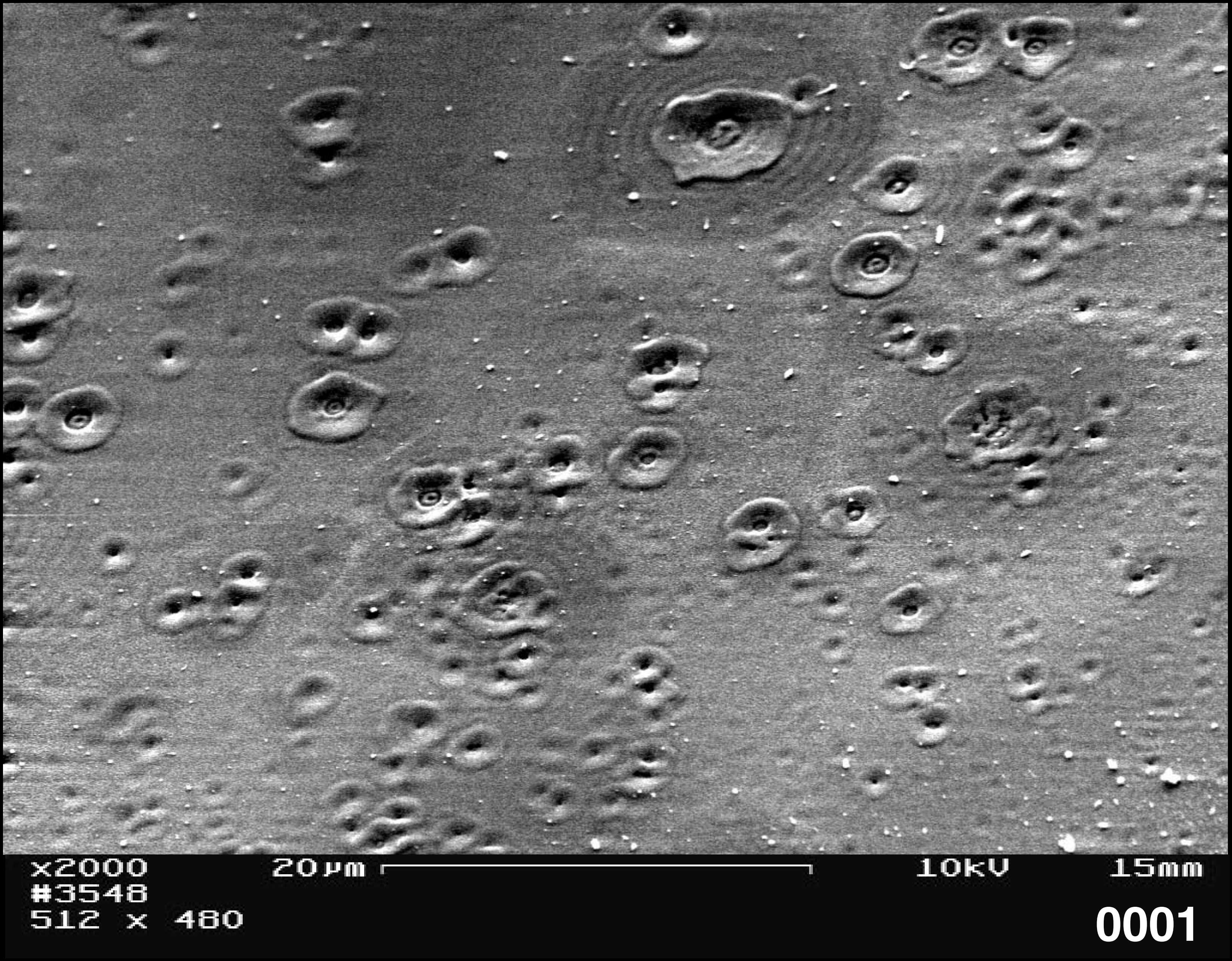
different gases all produce nanostructures

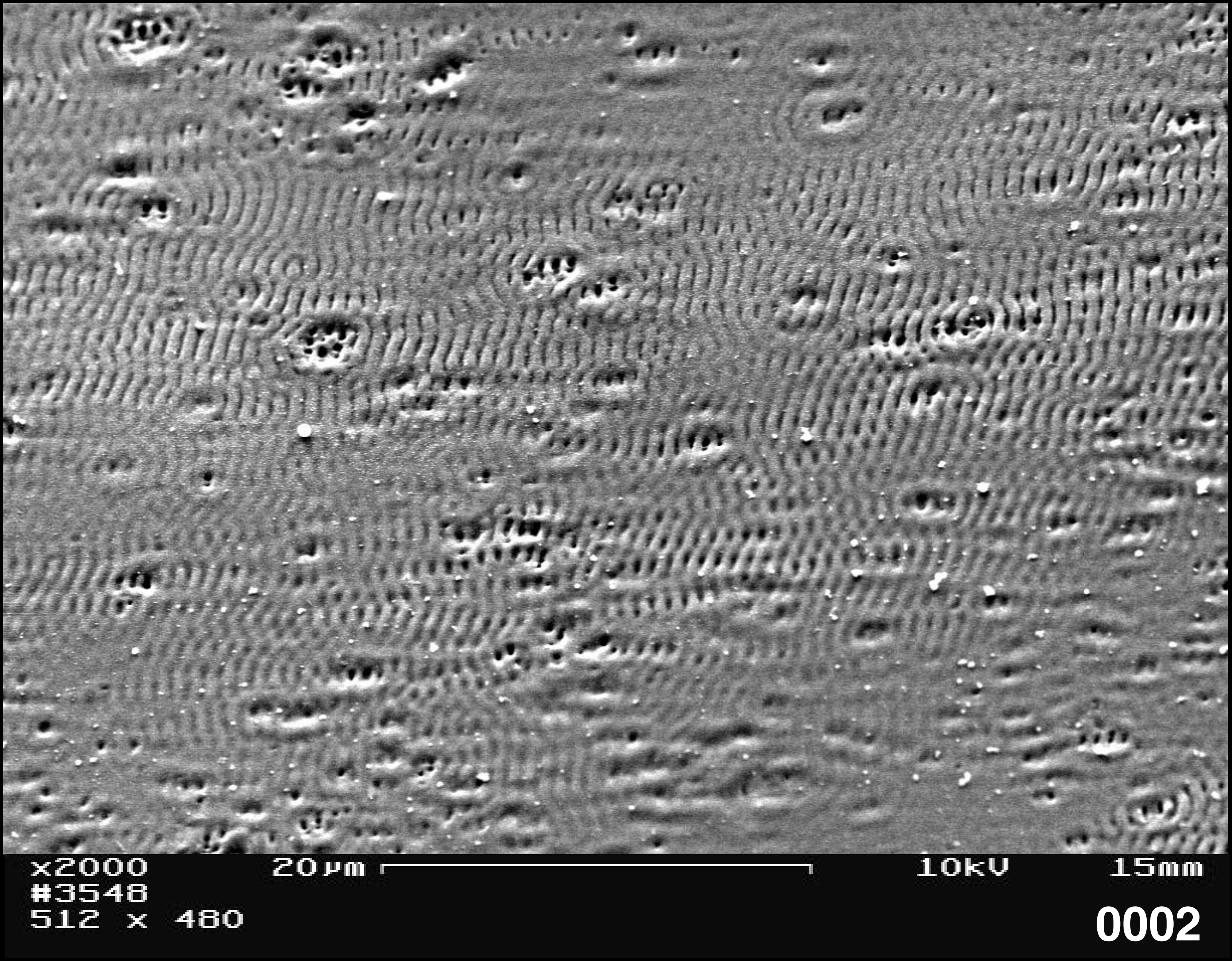
Summary of optical properties

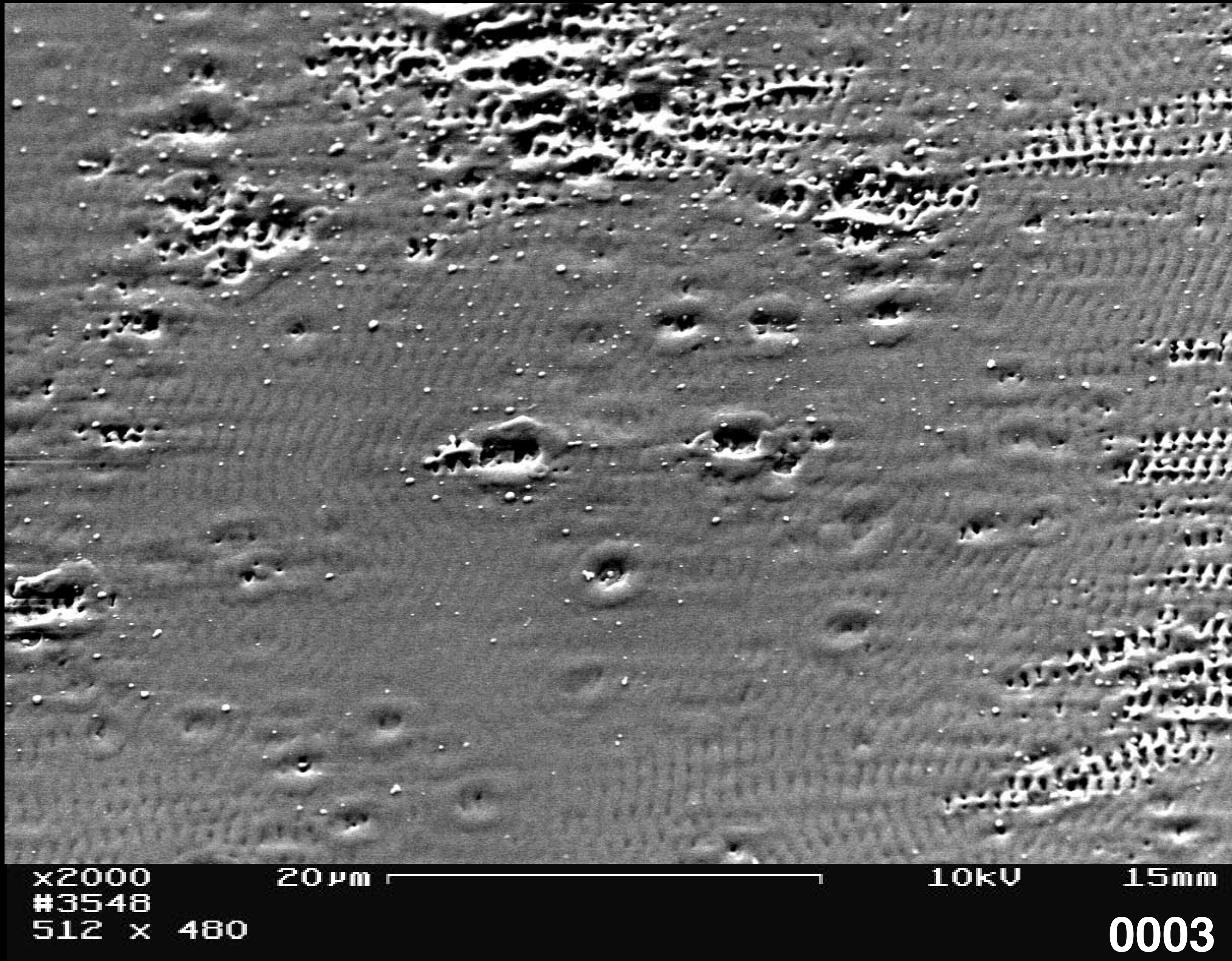
- visible absorptance: multiple reflections
- infrared absorptance: new electronic states
- new states most likely from sulfur impurities

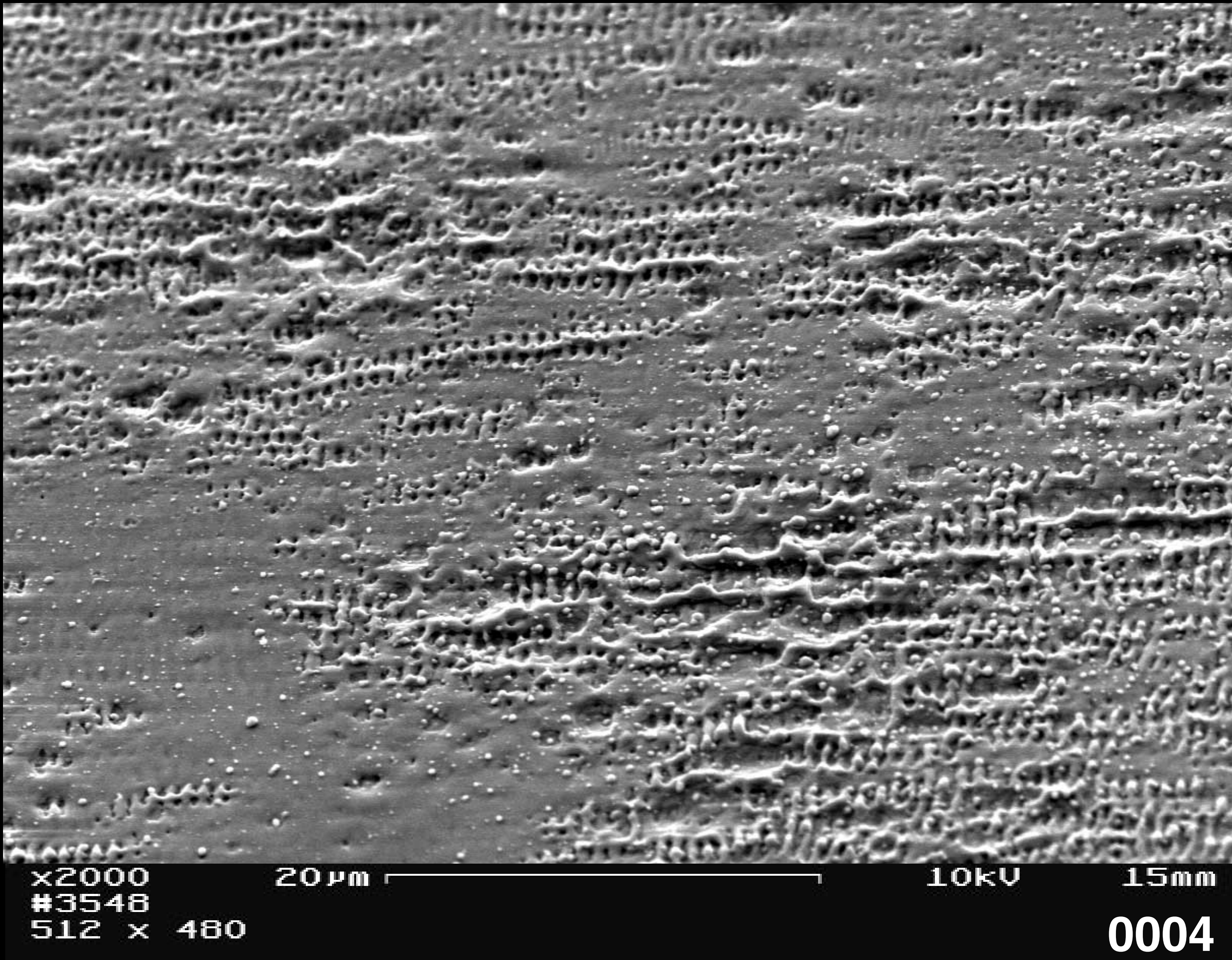

How do the microstructures form?

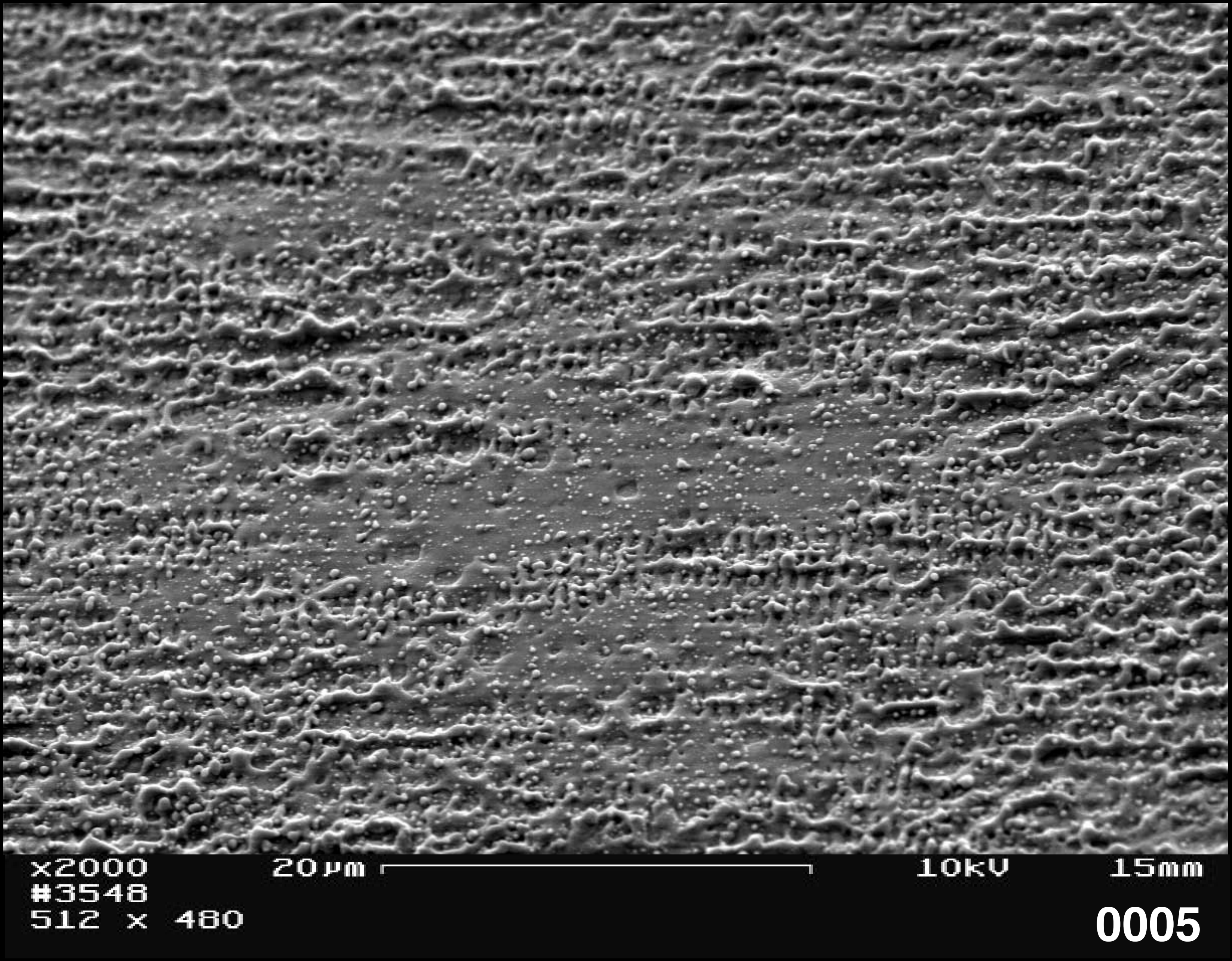

x2000
20μm
10kV
15mm
#3548
512 x 480
0000

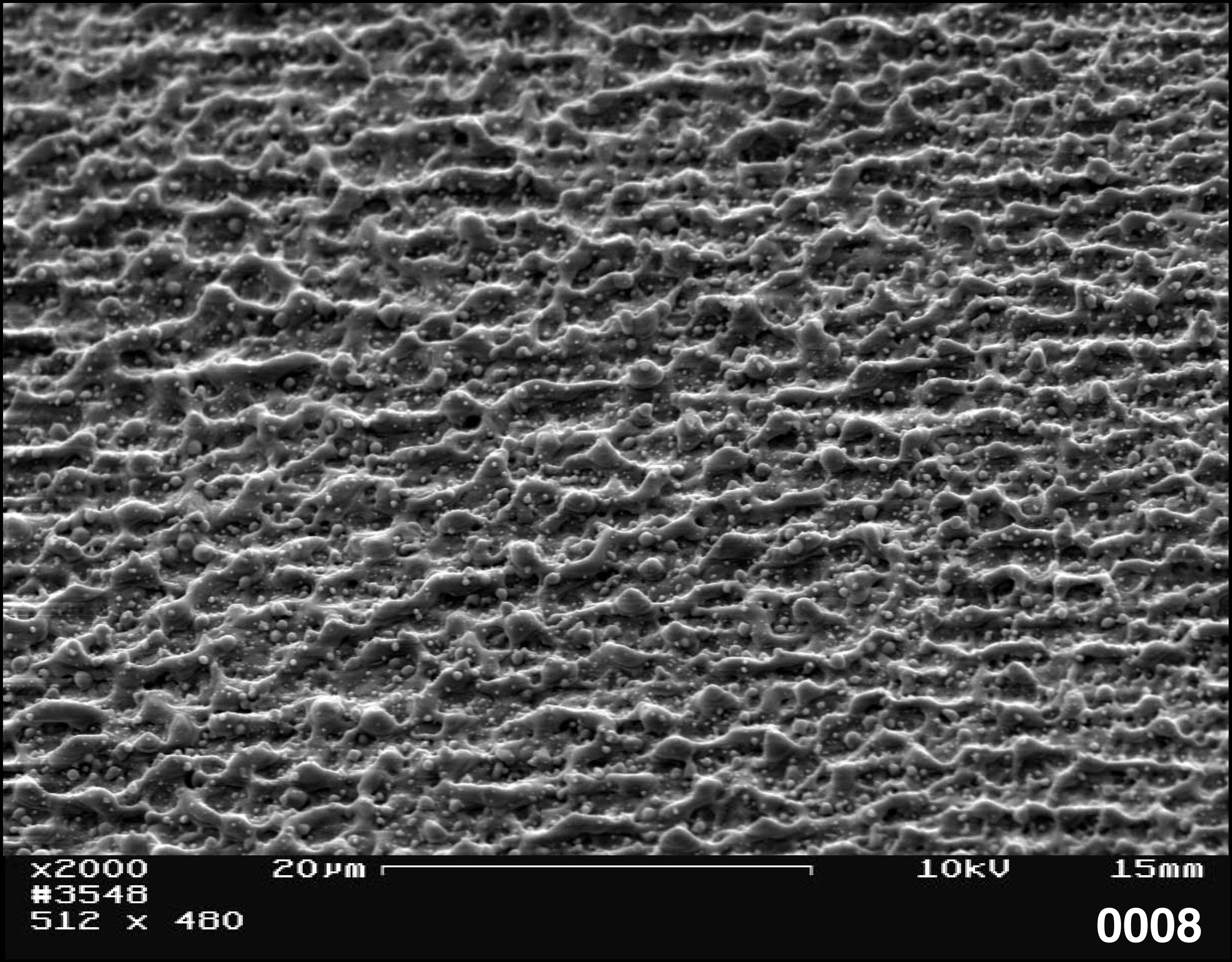

x2000
20μm
10kV
15mm
#3548
512 x 480
0001

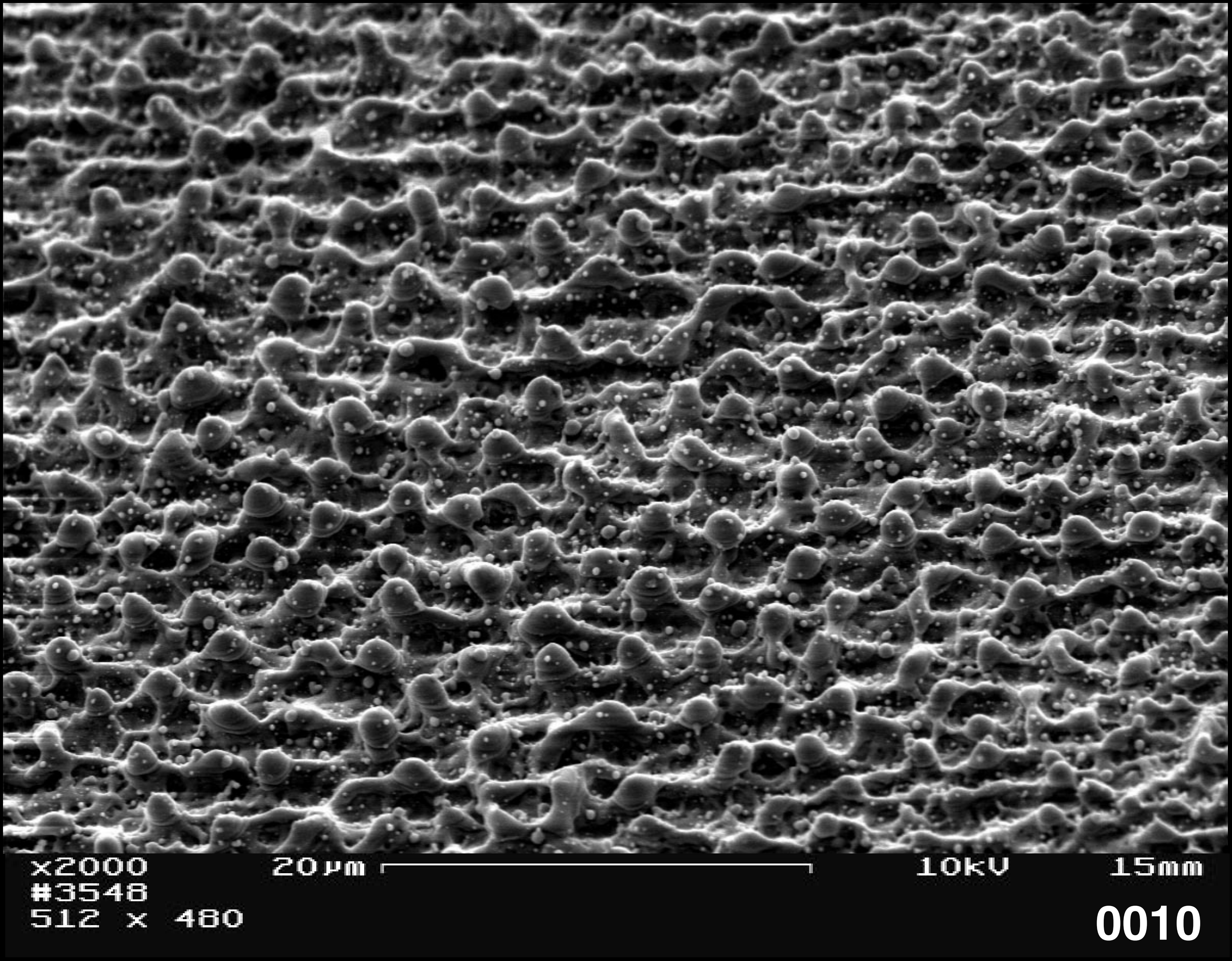

x2000
20µm
10kV
15mm
#3548
512 x 480
0002

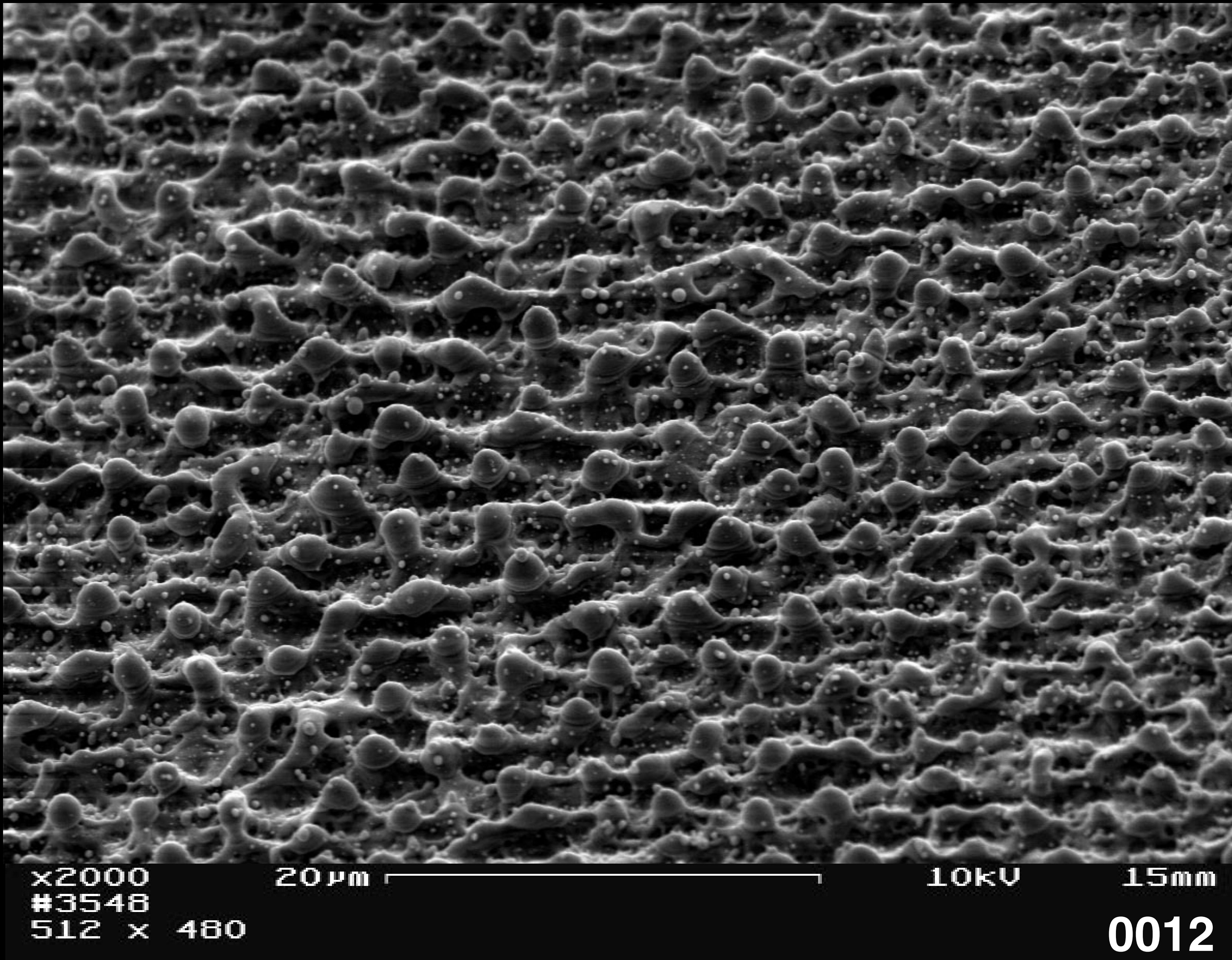

x2000
20μm
10kV
15mm
#3548
512 x 480
0003

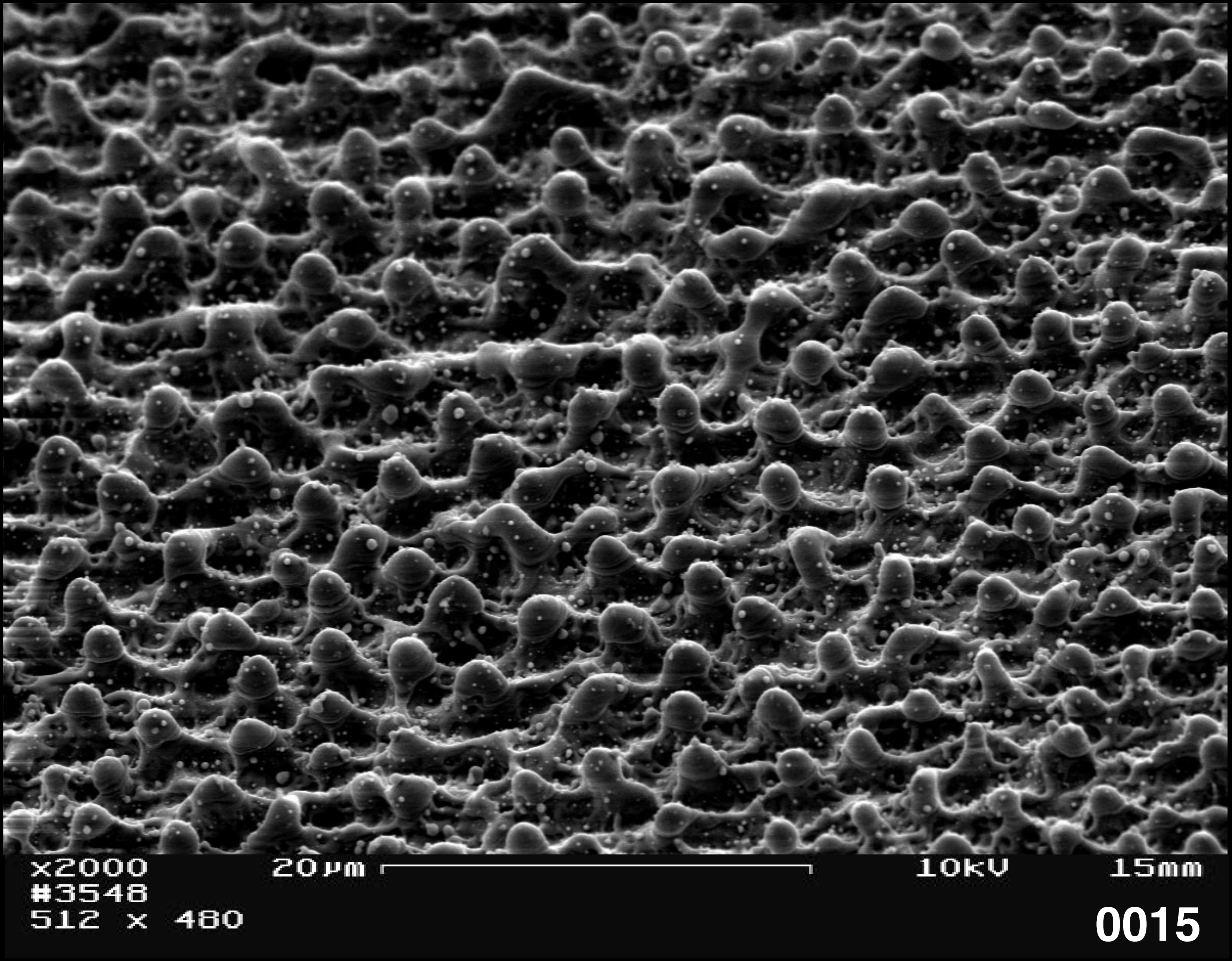

x2000
20μm
10kV
15mm
#3548
512 x 480
0004

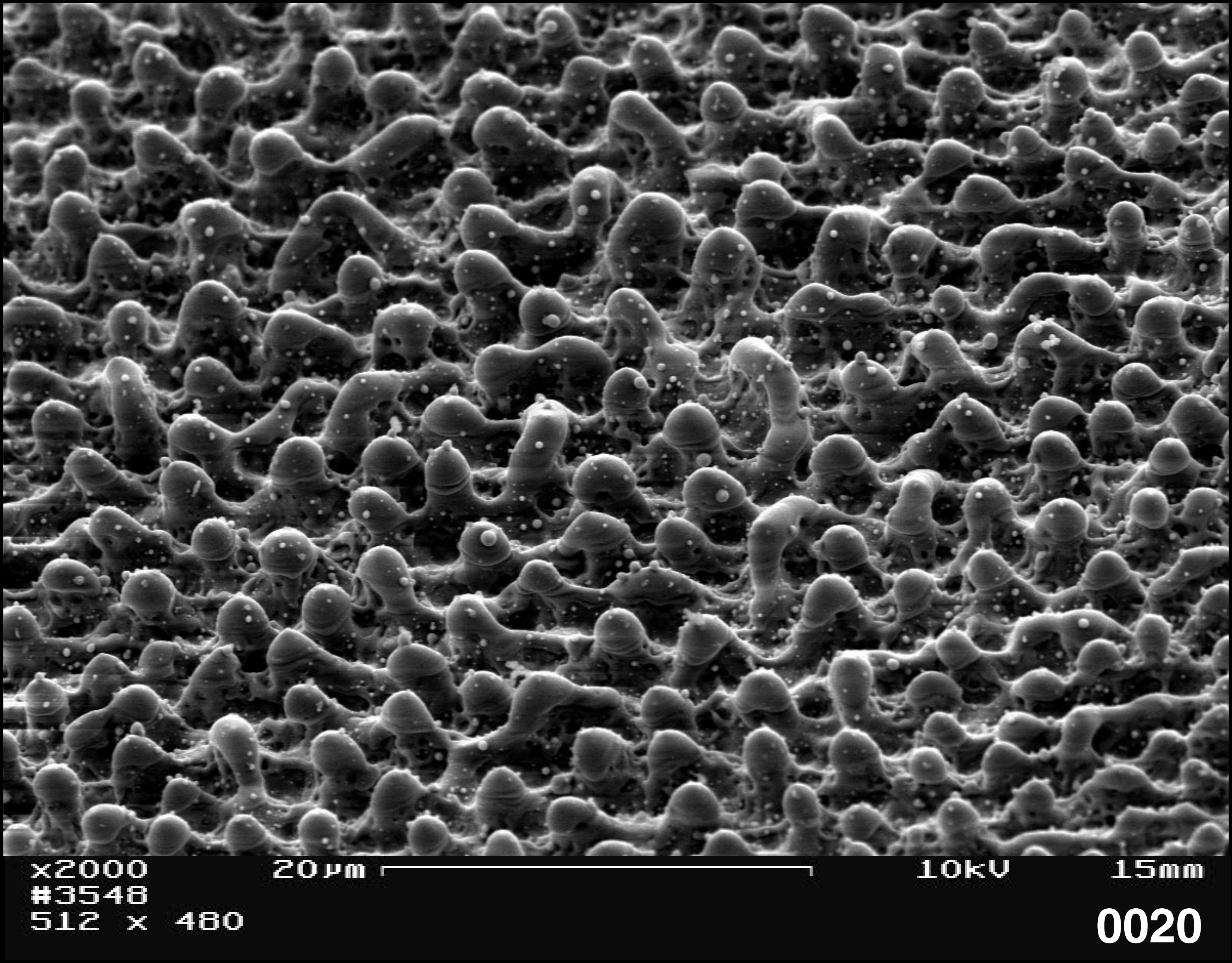

x2000
20μm
10kV
15mm
#3548
512 x 480
0005

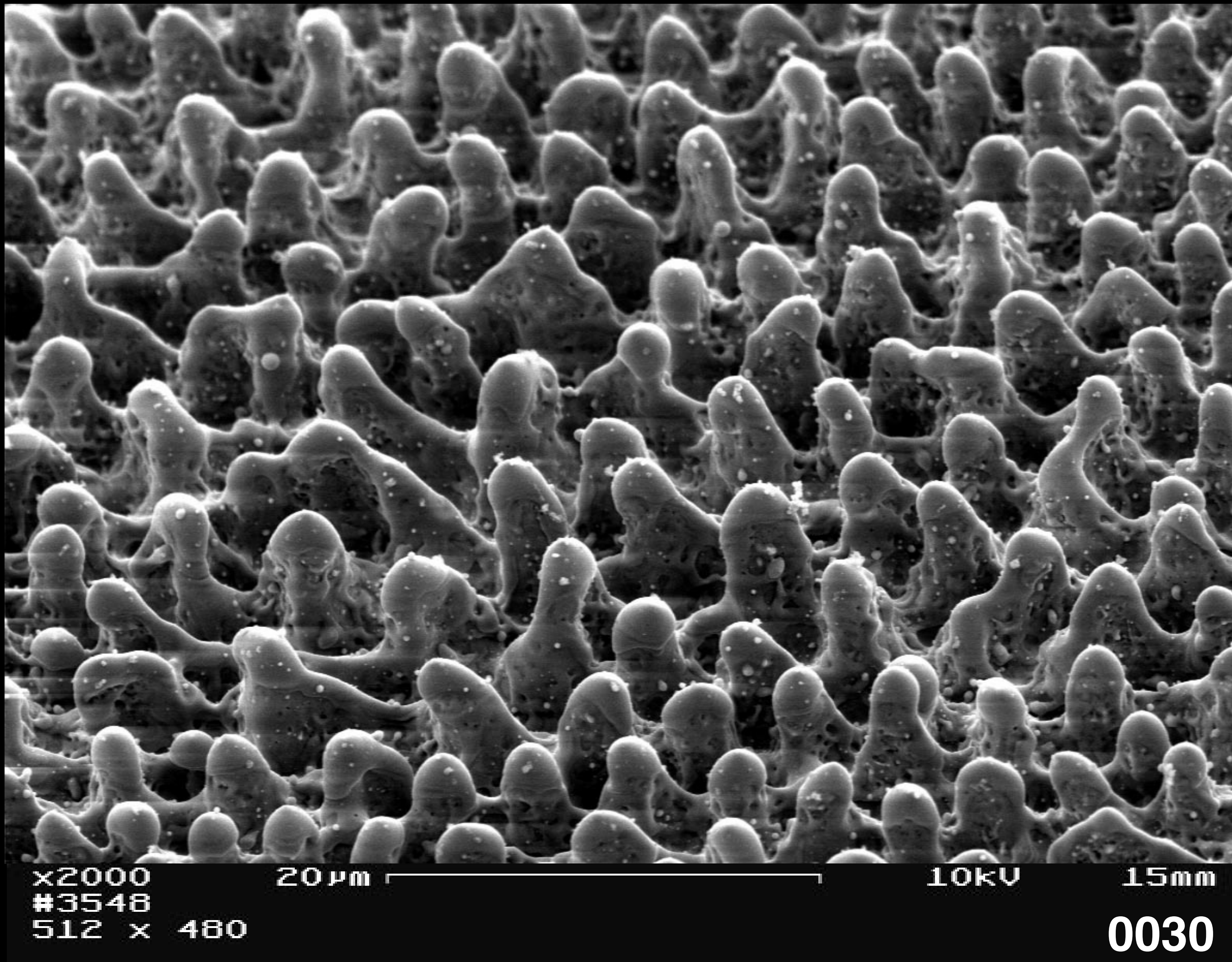

x2000
20μm
10kV
15mm
#3548
512 x 480
0008

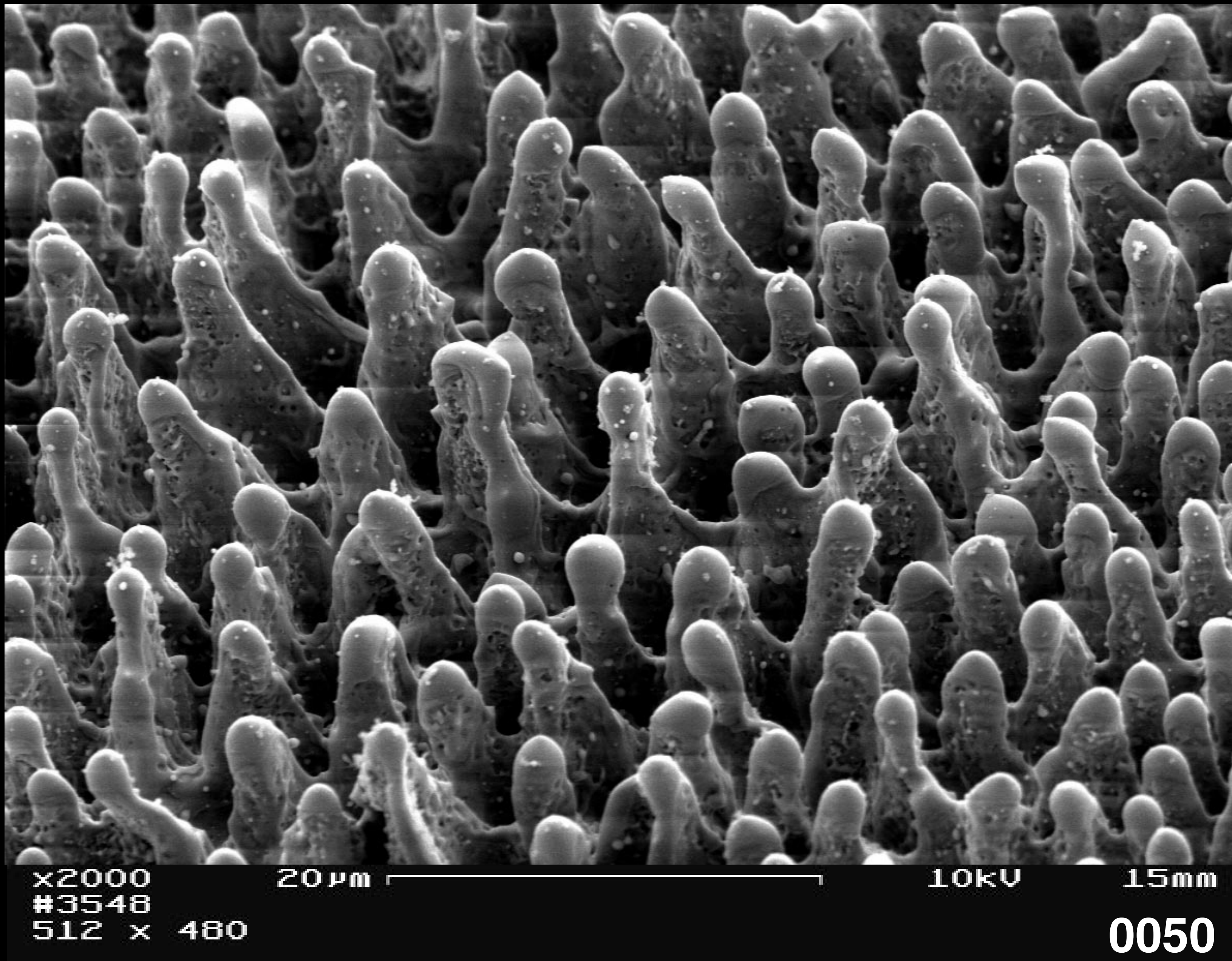

x2000
#3548
512 x 480
20μm
10kV
15mm
0010

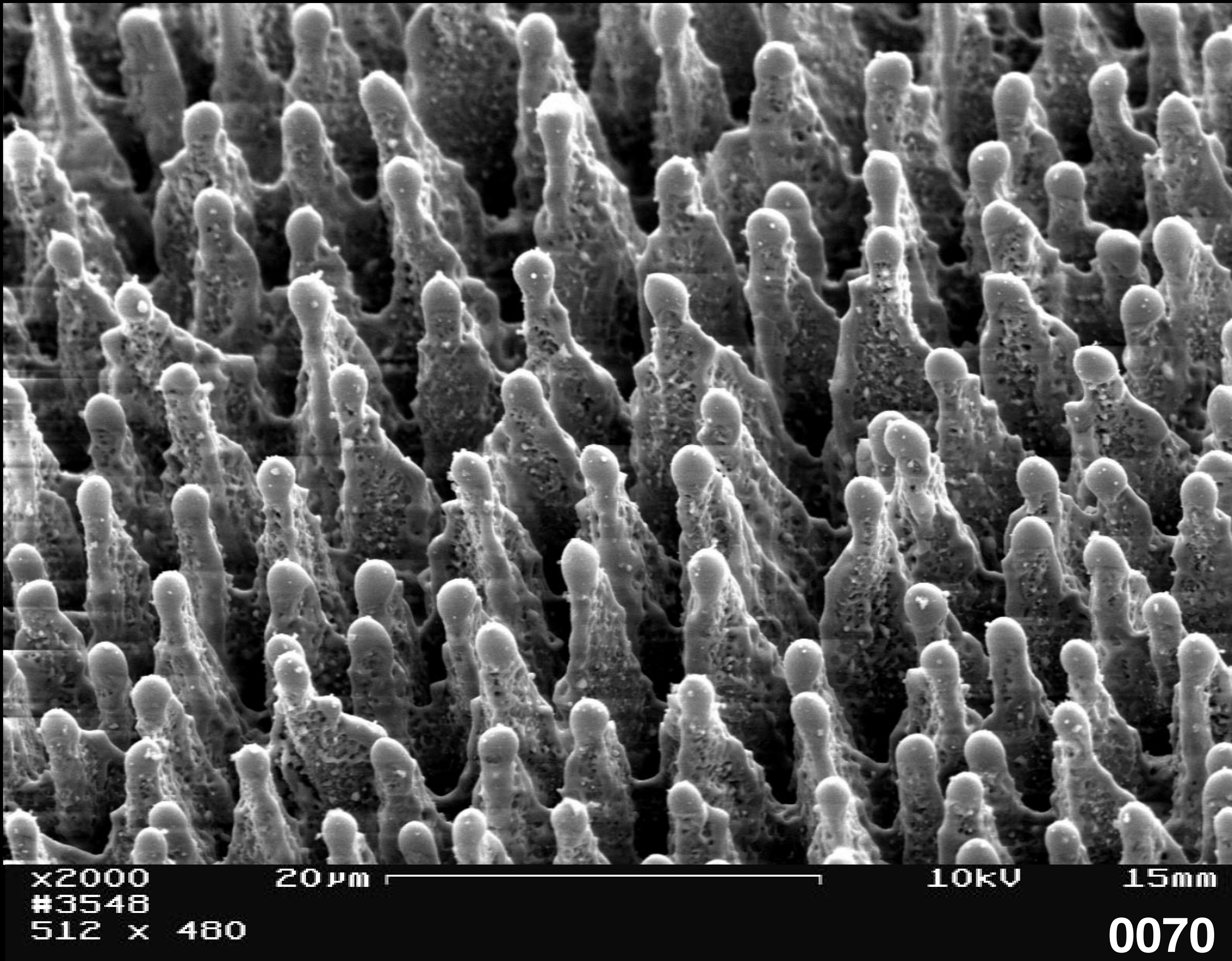

x2000
20µm
10kV
15mm
#3548
512 x 480
0012

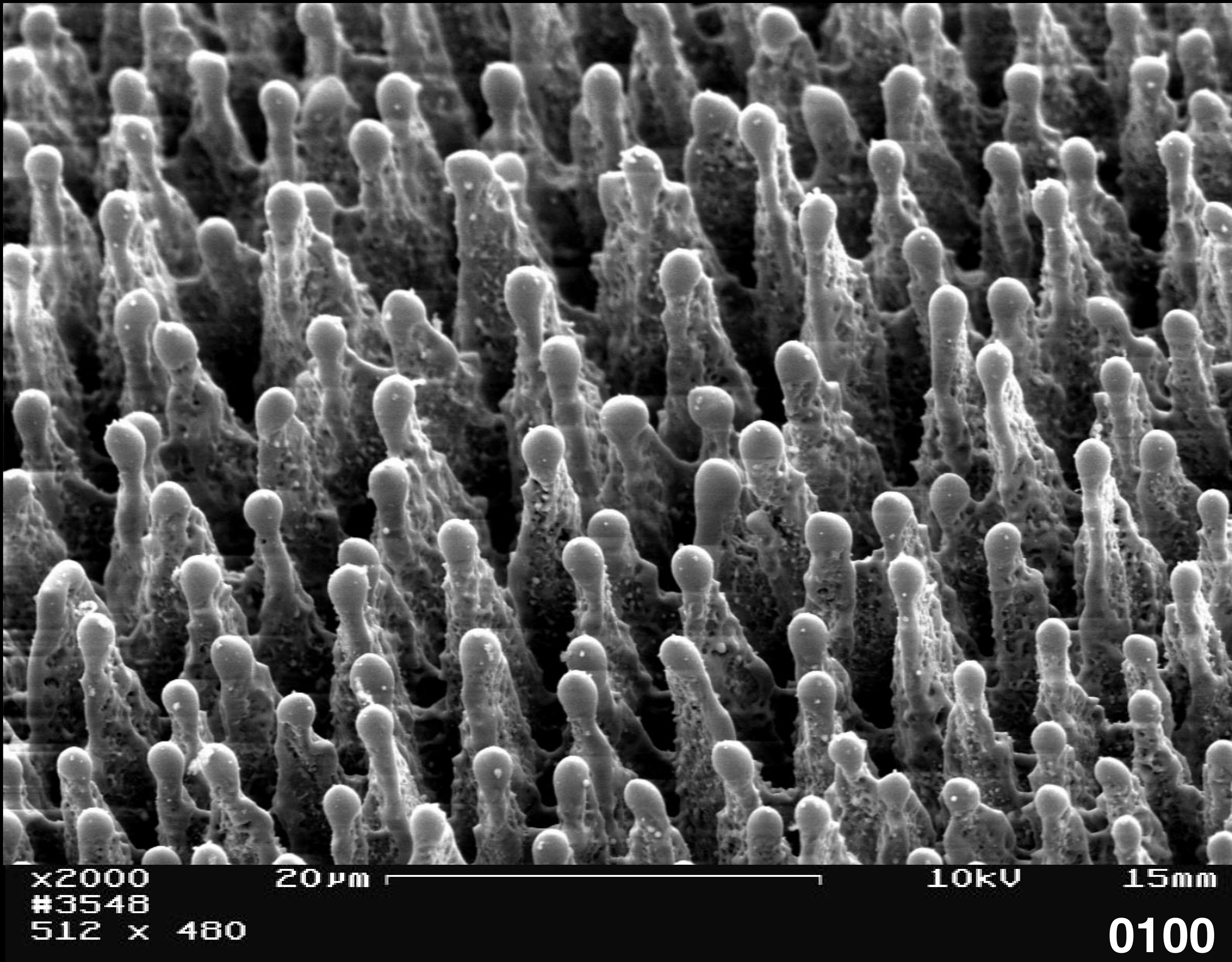

x2000
20μm
10kV
15mm
#3548
512 x 480
0015

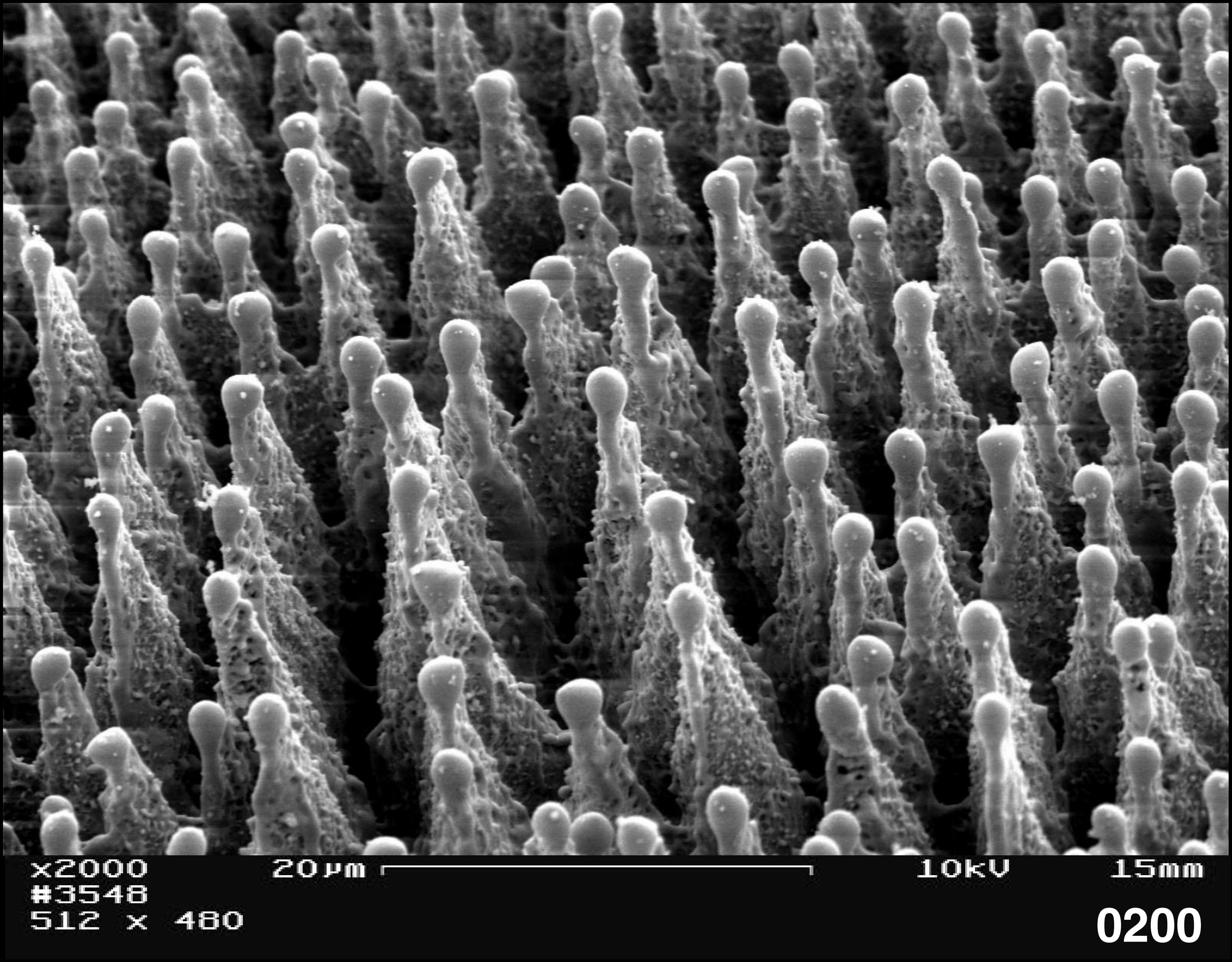

x2000
20μm
10kV
15mm
#3548
512 x 480
0020

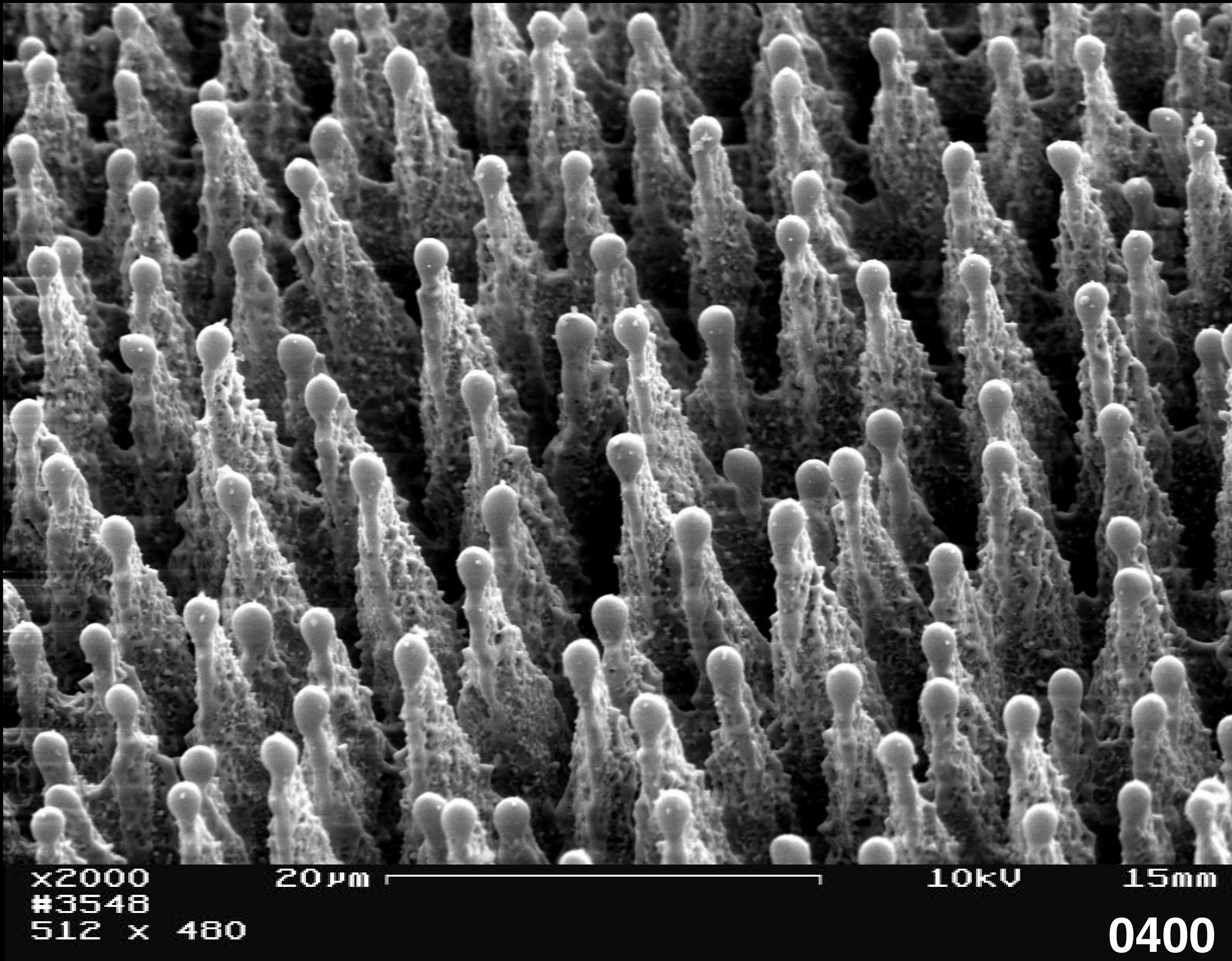

x2000
20µm
10kV
15mm
#3548
512 x 480
0030

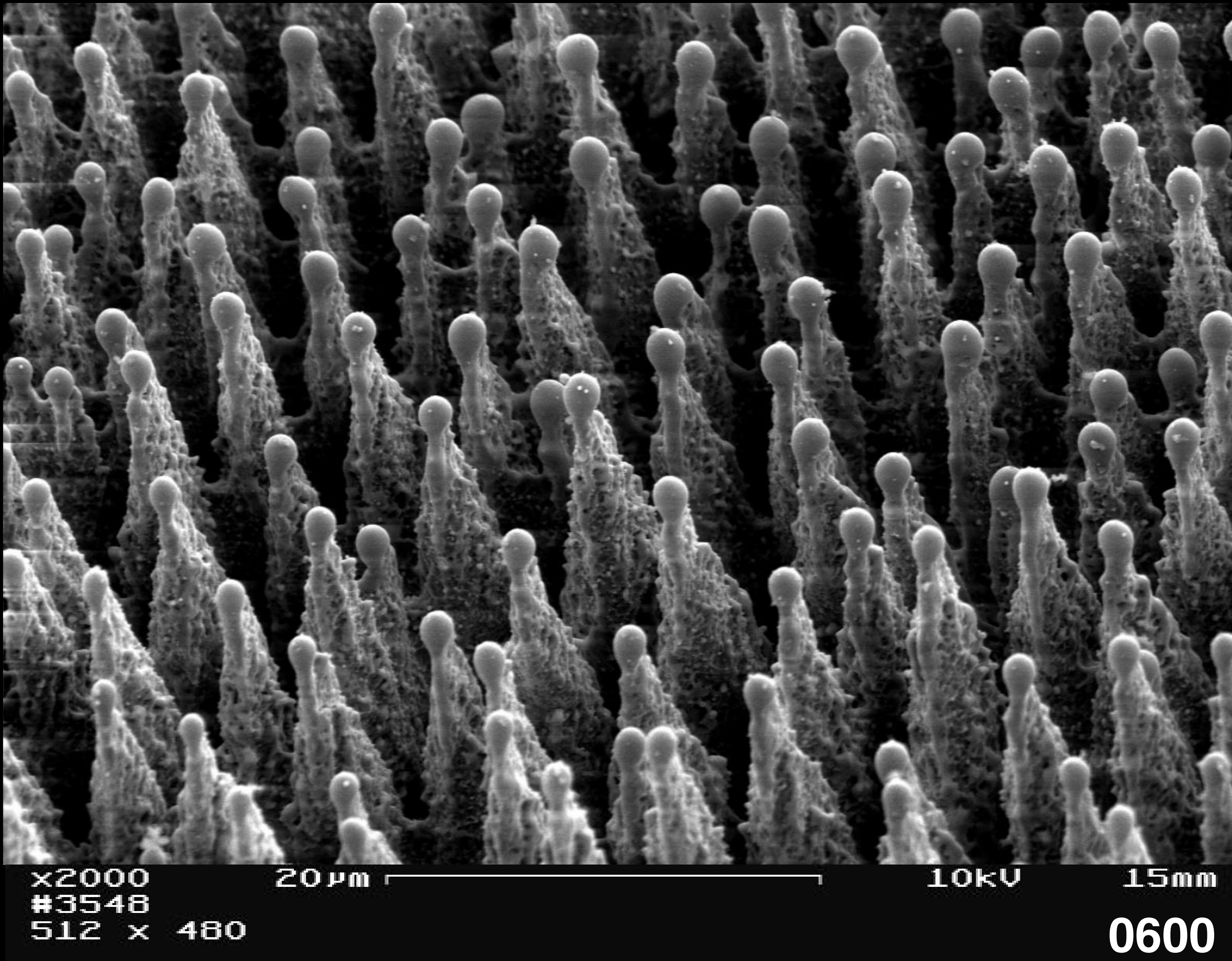

x2000
20μm
10kV
15mm
#3548
512 x 480
0050

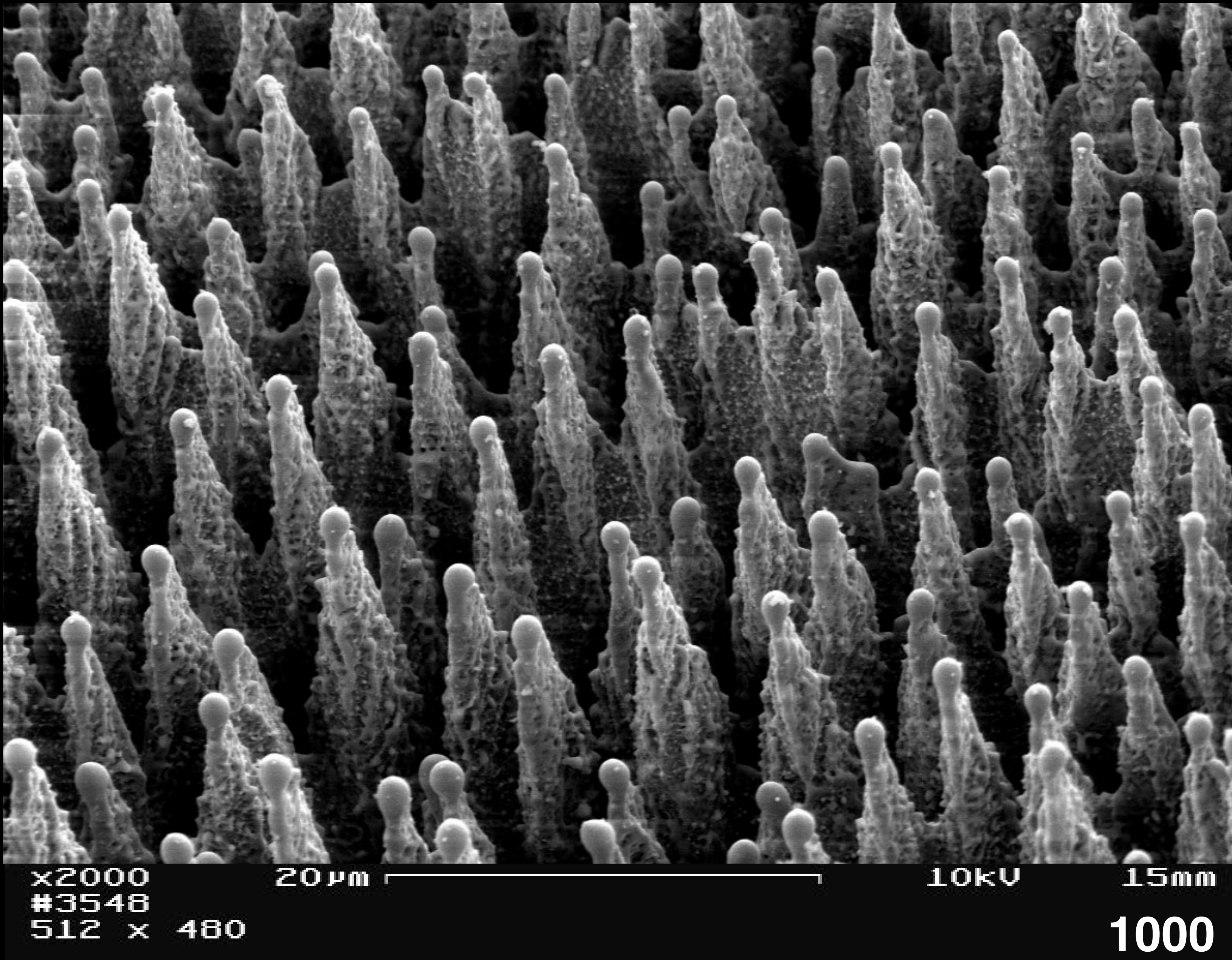

x2000
20μm
10kV
15mm
#3548
512 x 480
0070


x2000
20µm
10kV
15mm
#3548
512 x 480
0100


x2000
#3548
512 x 480
20µm
10kV
15mm
0200


x2000
20μm
10kV
15mm
#3548
512 x 480
0400


x2000
20μm
10kV
15mm
#3548
512 x 480
0600


x2000
20μm
10kV
15mm
#3548
512 x 480
1000

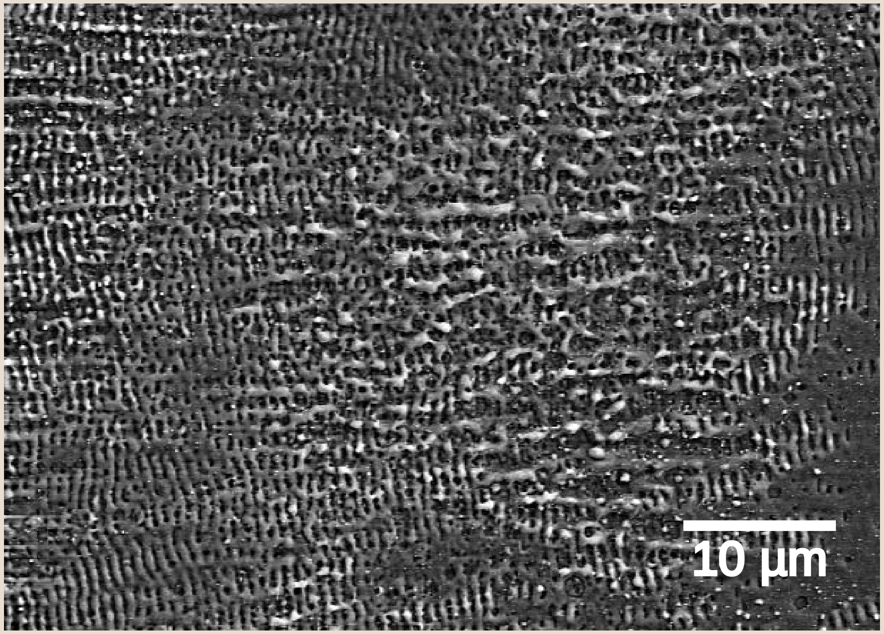
How do ripples give way to spikes?

Follow evolution of spatial frequencies

- vary number of laser pulses
- calculate Fourier transform of images

ripples

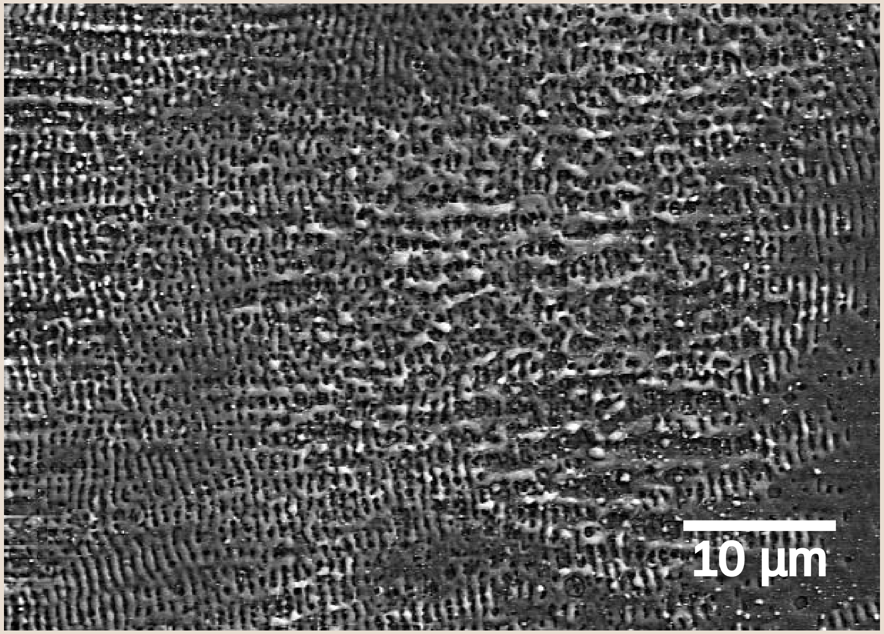
SF_6 2 pulses



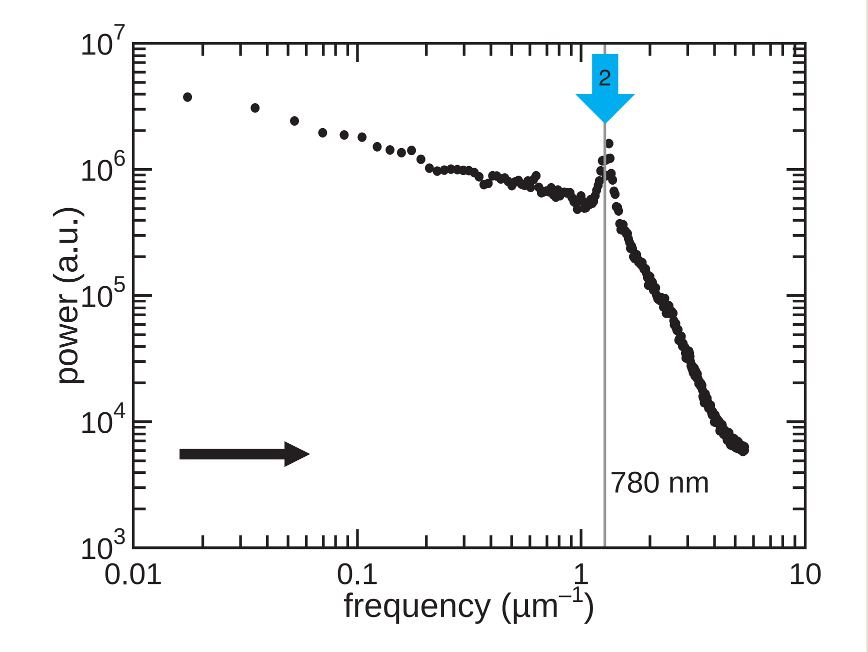
laser polarization

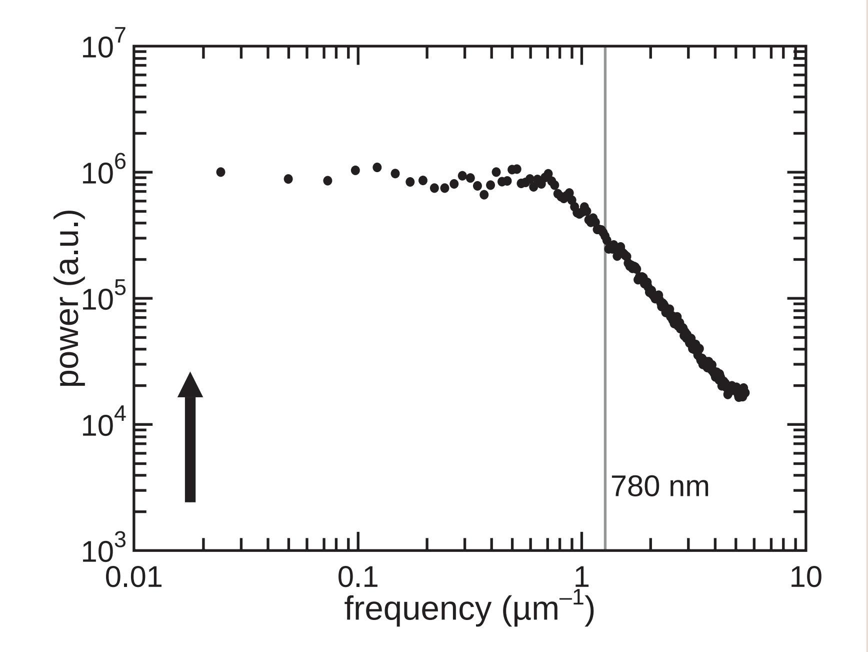
ripples

SF_6 **2 pulses**



laser polarization

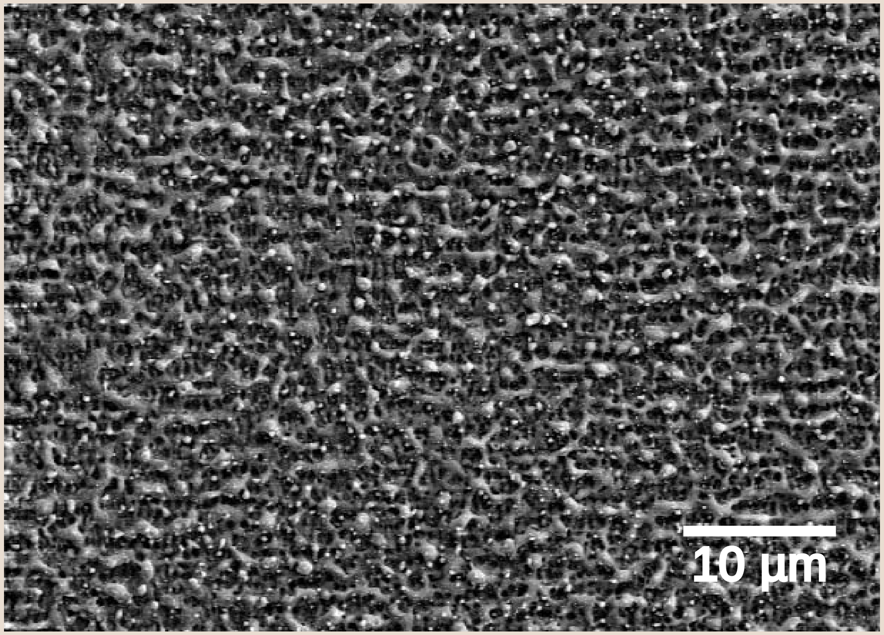




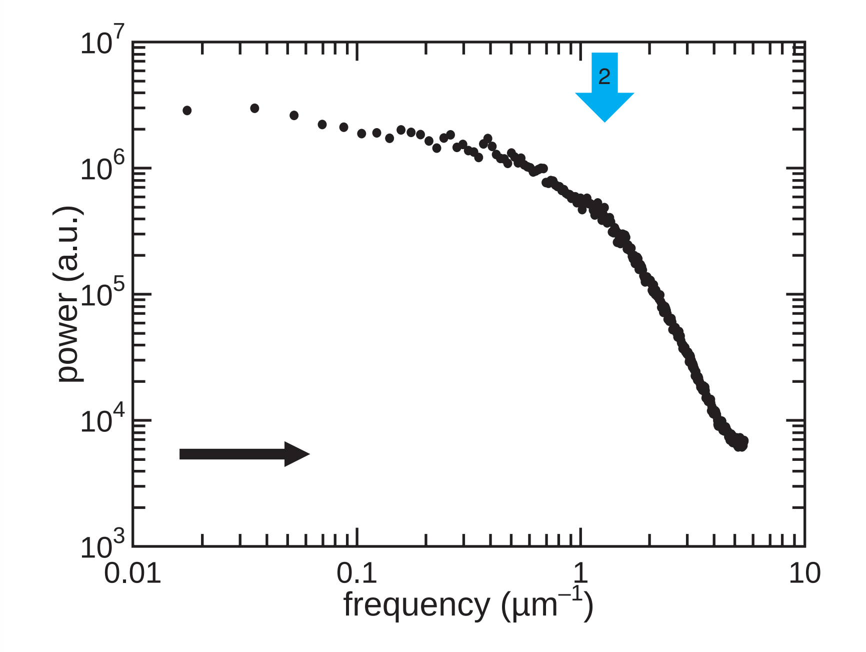
Formation process

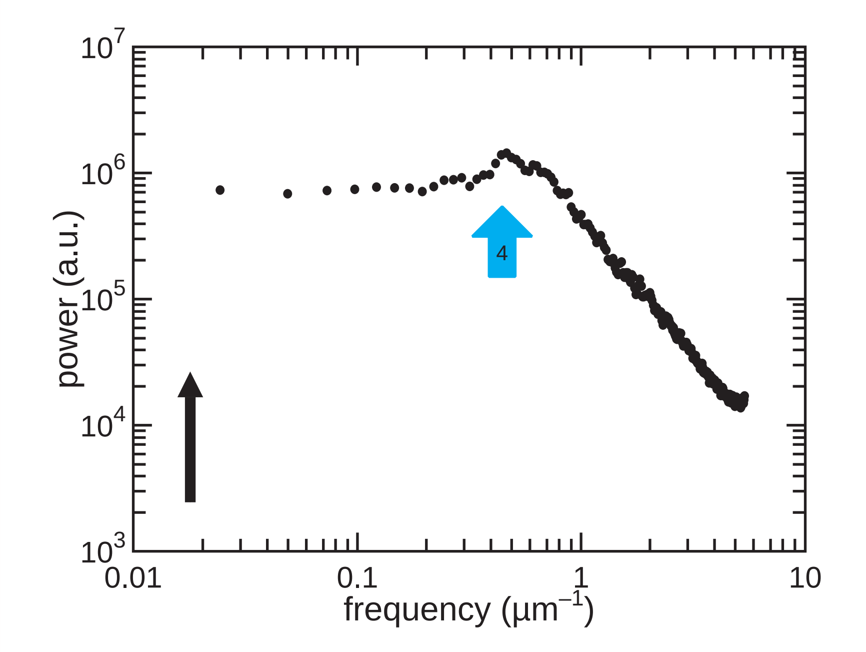
ridges

SF_6 4 pulses



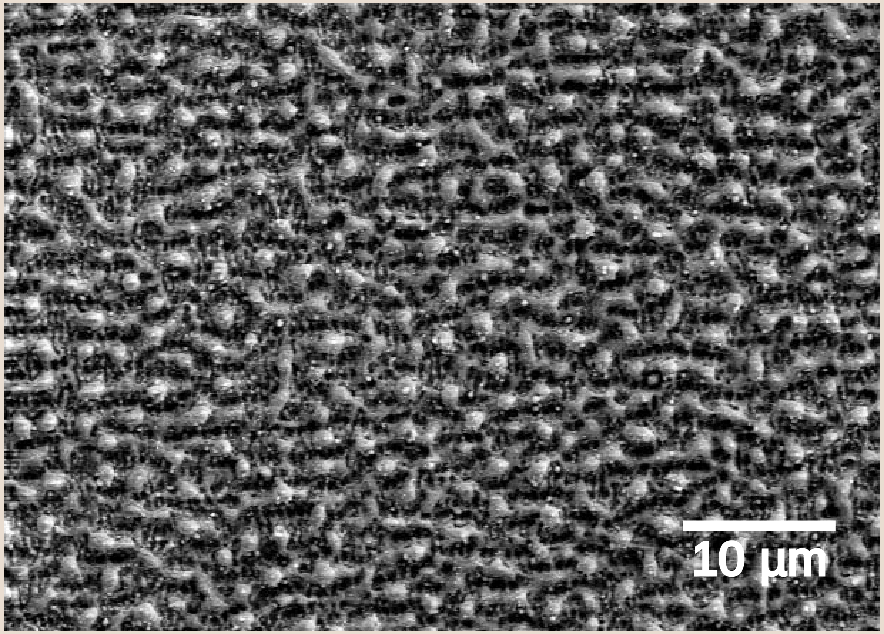
laser polarization →



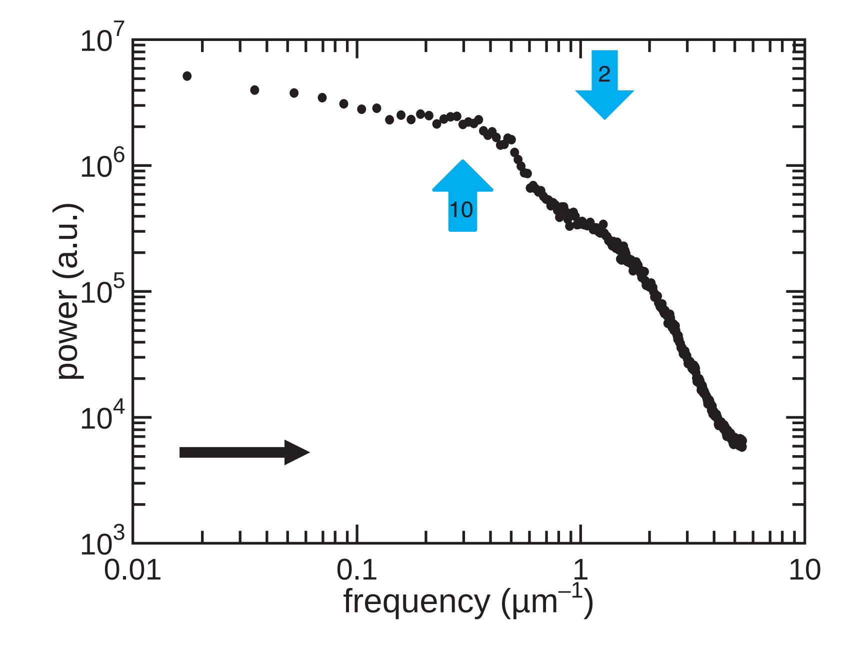


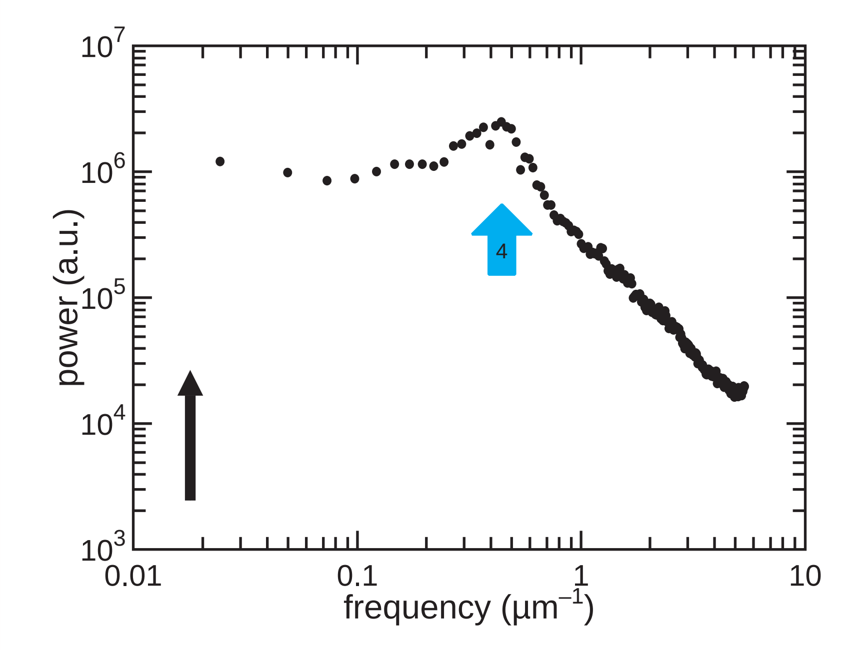
spikes

SF_6 **10 pulses**



laser polarization



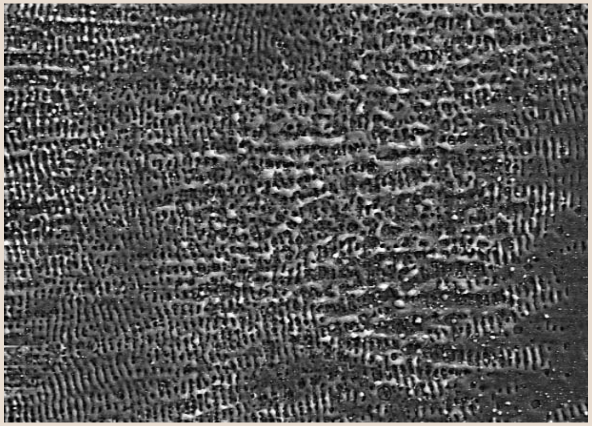


Formation process

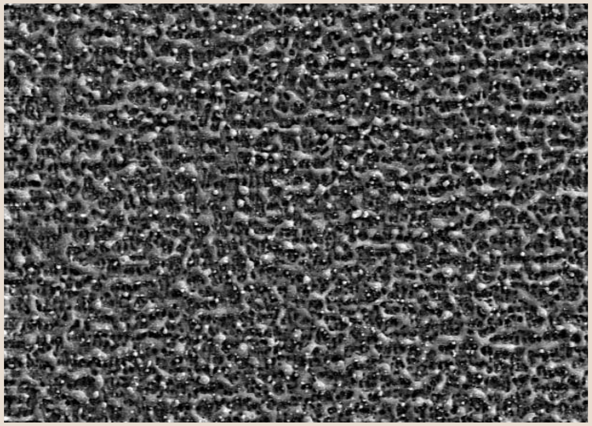
1. **Interference ripples (⊥ to polarization)**

2. **Coarsened ridges (⊥ to ripples)**

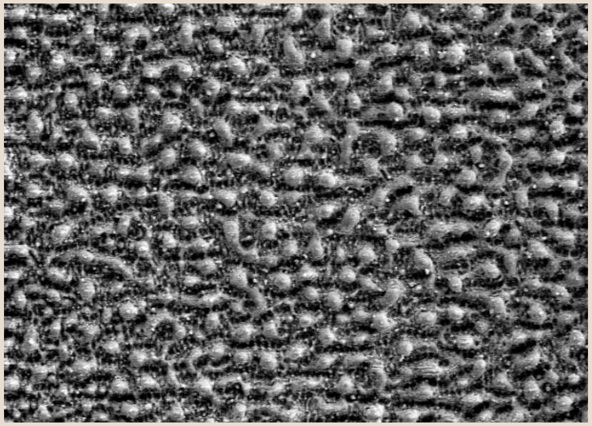
3. **Beads sharpening into spikes**



N = 2

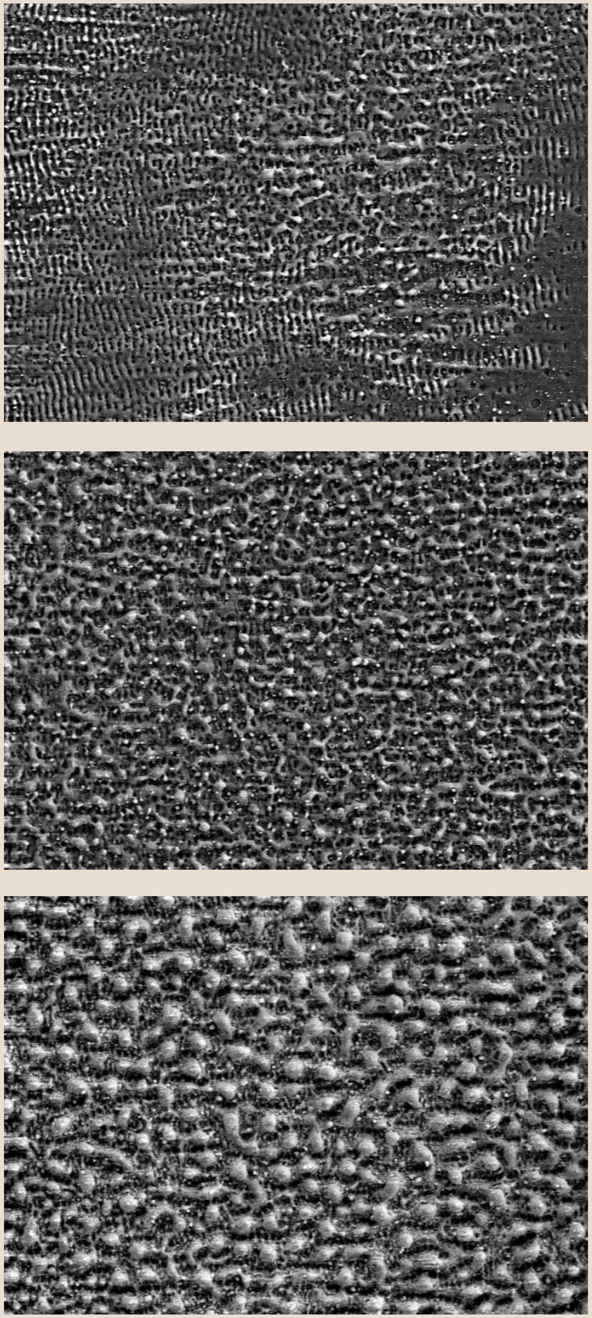


N = 4



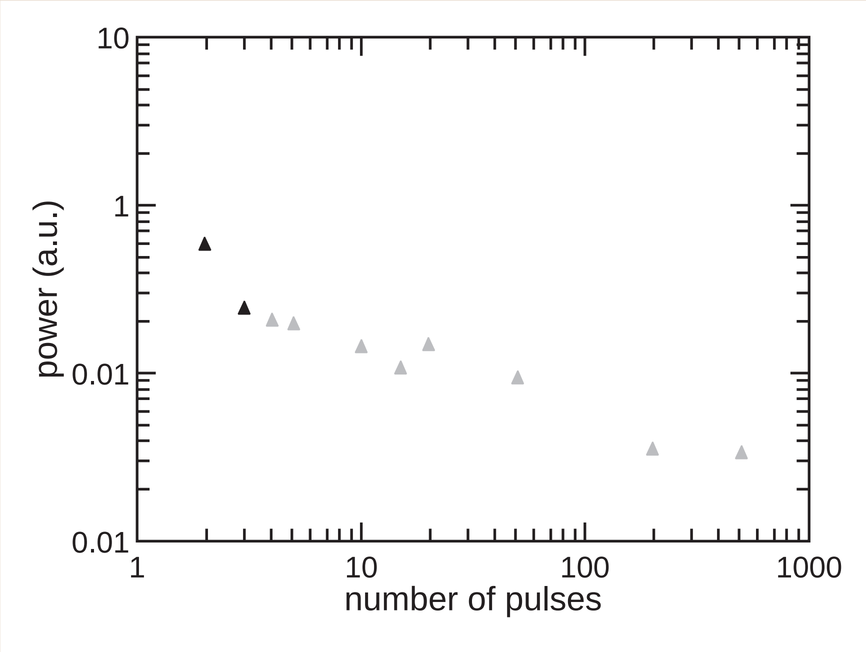
N = 10

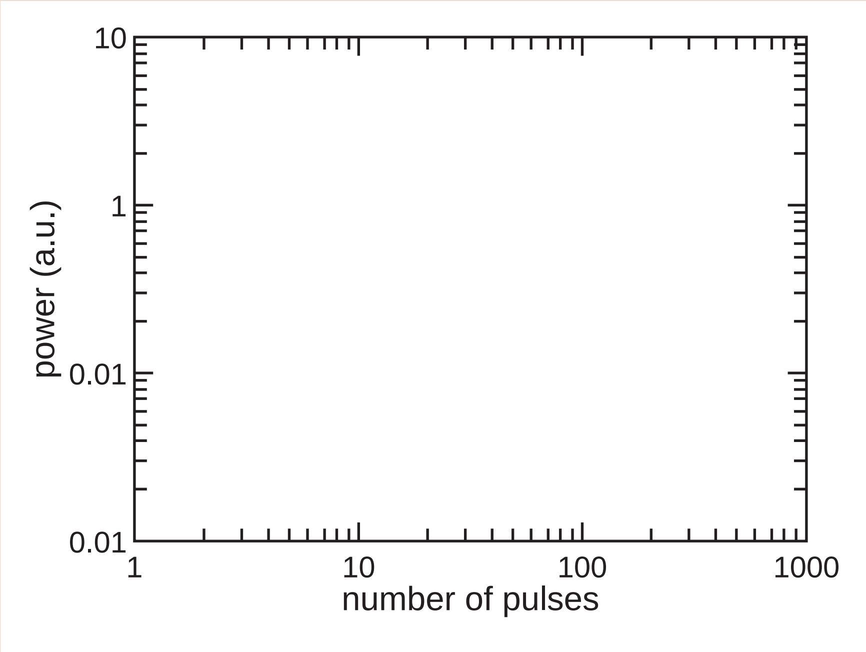
Two distinct wavelengths: ripples and spikes



feature intensities

SF_6 ripples



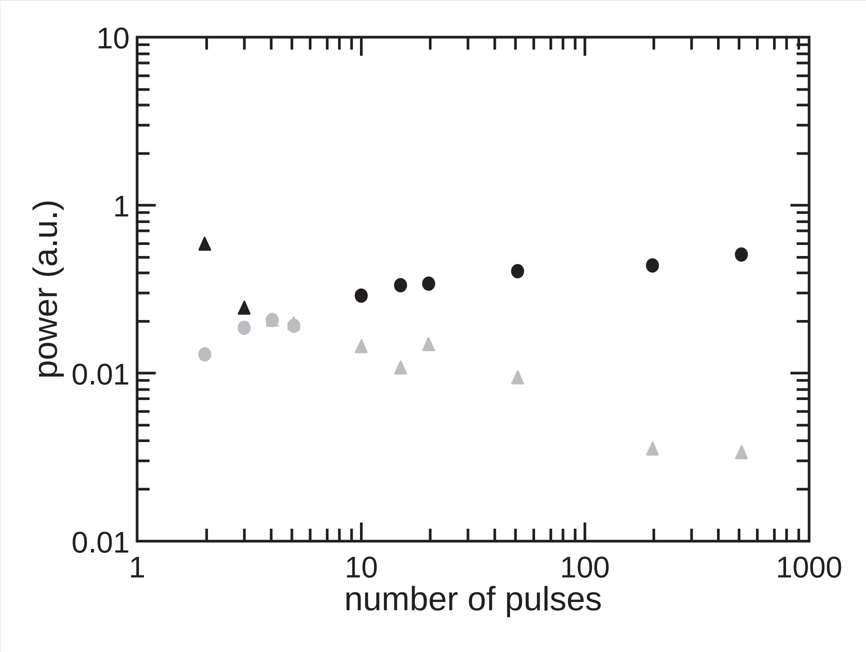


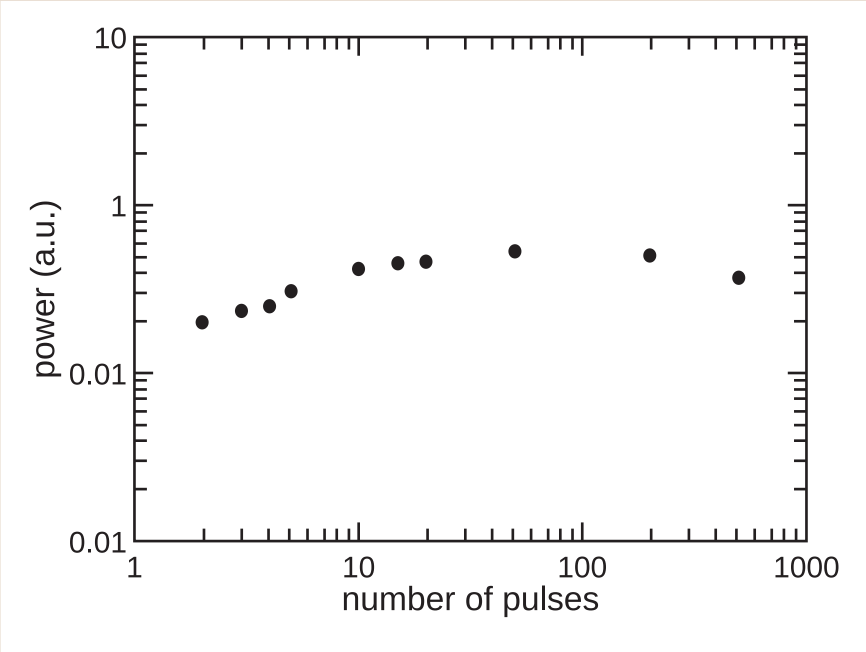
parallel

perpendicular

feature intensities

SF_6 spikes



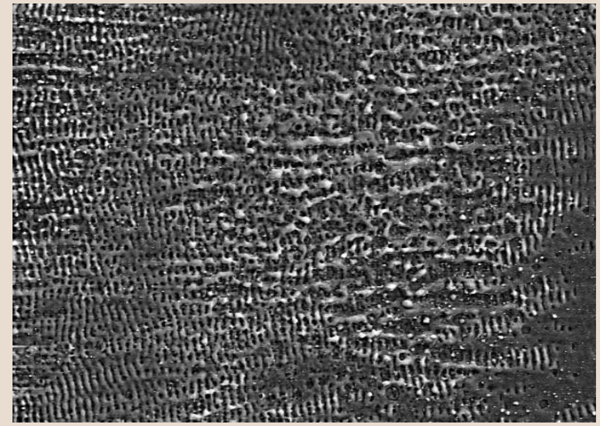


parallel **perpendicular**

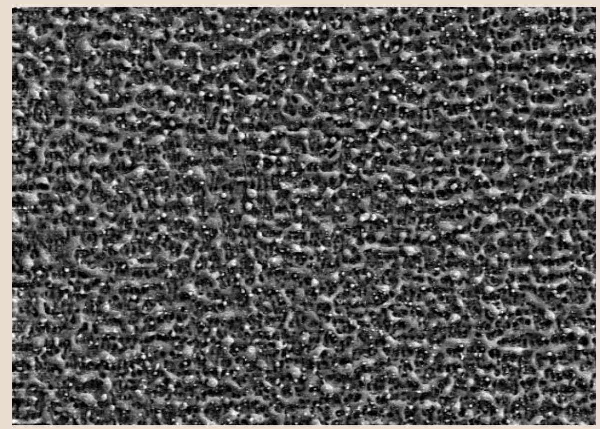
Formation process

- **spike wavelength appears as ripple wavelength disappears**

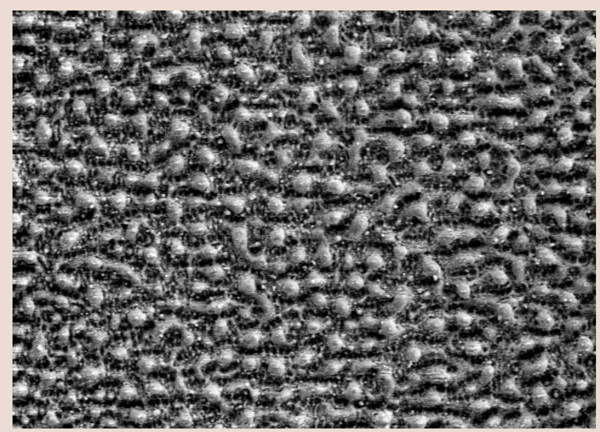
- **spike wavelength appears first perpendicular to polarization**



N = 2



N = 4

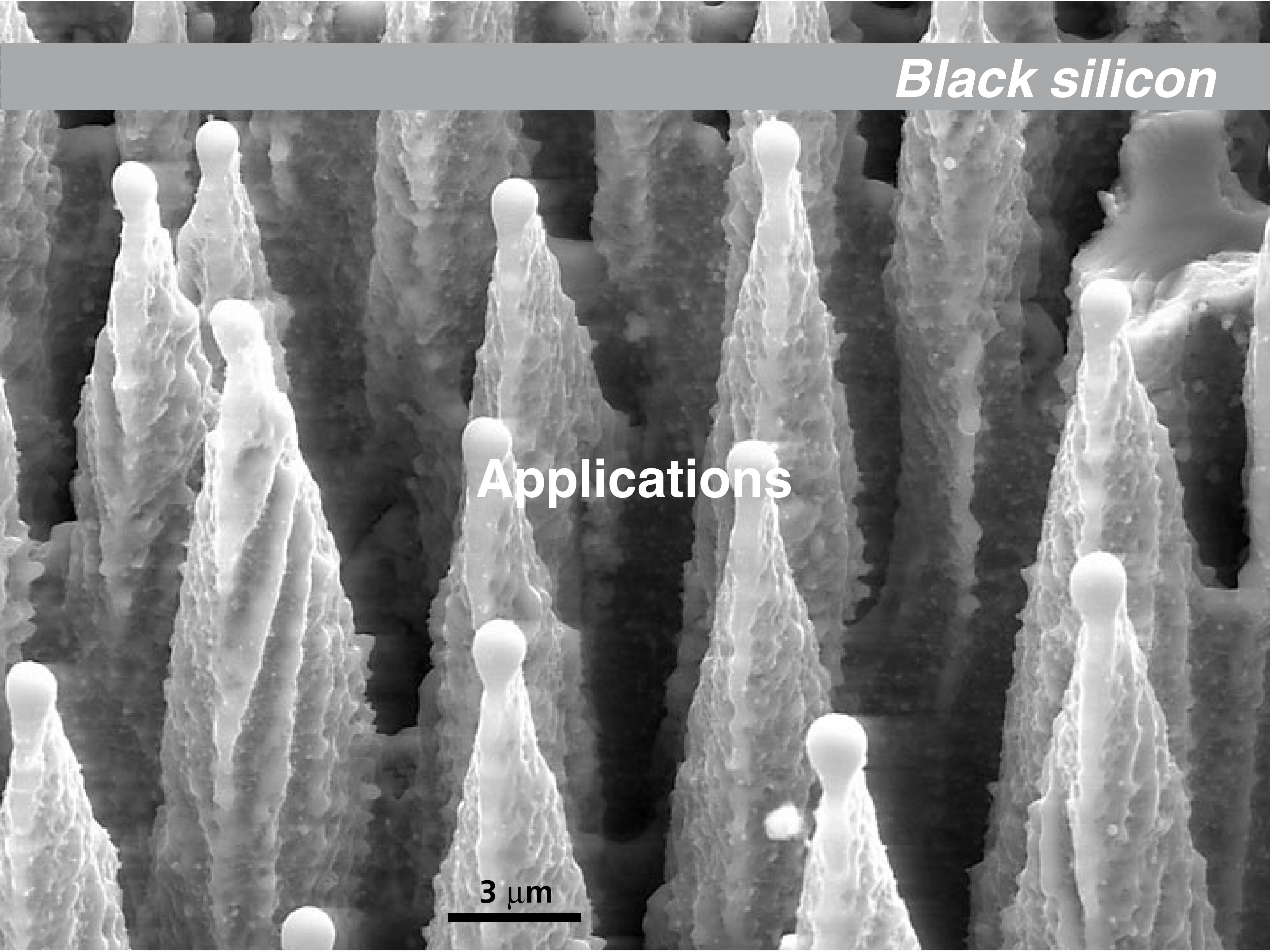


N = 10

What sets the length scales?

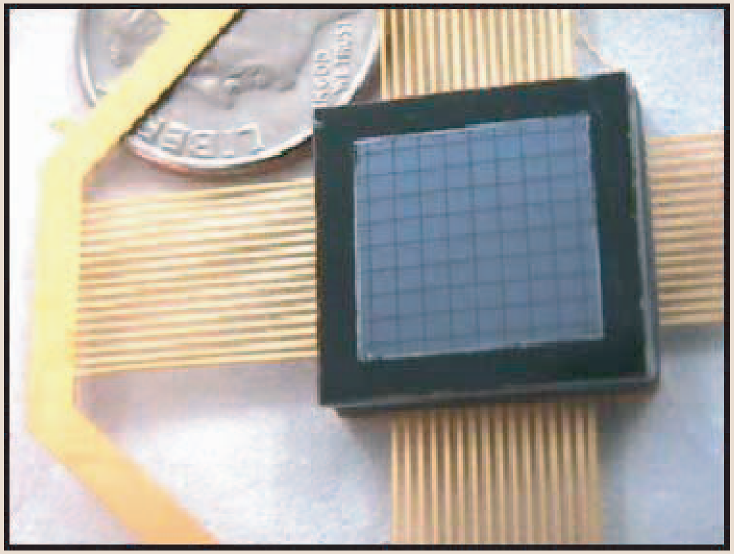
- ripples: laser wavelength
- ridges and spikes: perhaps capillary waves

Applications



Avalanche photodiode with black silicon

- doubles quantum efficiency at 1064 nm
- promising results at 1.33 µm

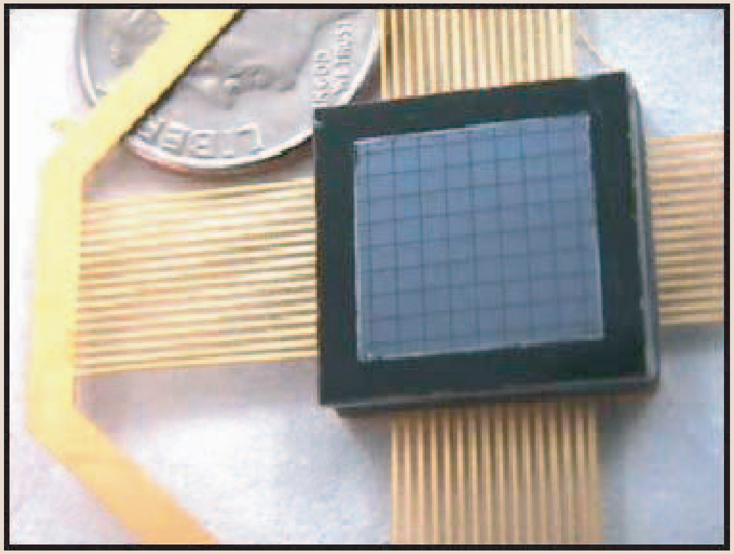


Avalanche photodiode with black silicon

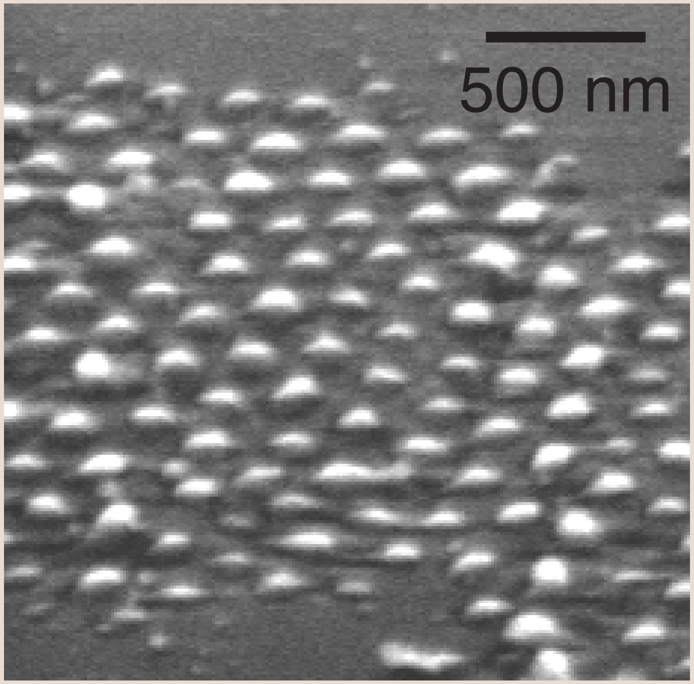
- doubles quantum efficiency at 1064 nm
- promising results at 1.33 µm

Other applications:

- field emission arrays
- light emitters



Outlook



Self-organization

- ridge formation
- ordered nanoparticles

Laser-structured surface properties

- interactions with biomaterials
- visible luminescence

Black silicon:

- near-unity absorption from near-UV to near-IR
- new electronic states from sulfur impurities
- self-organized surface microstructures
- many promising applications!

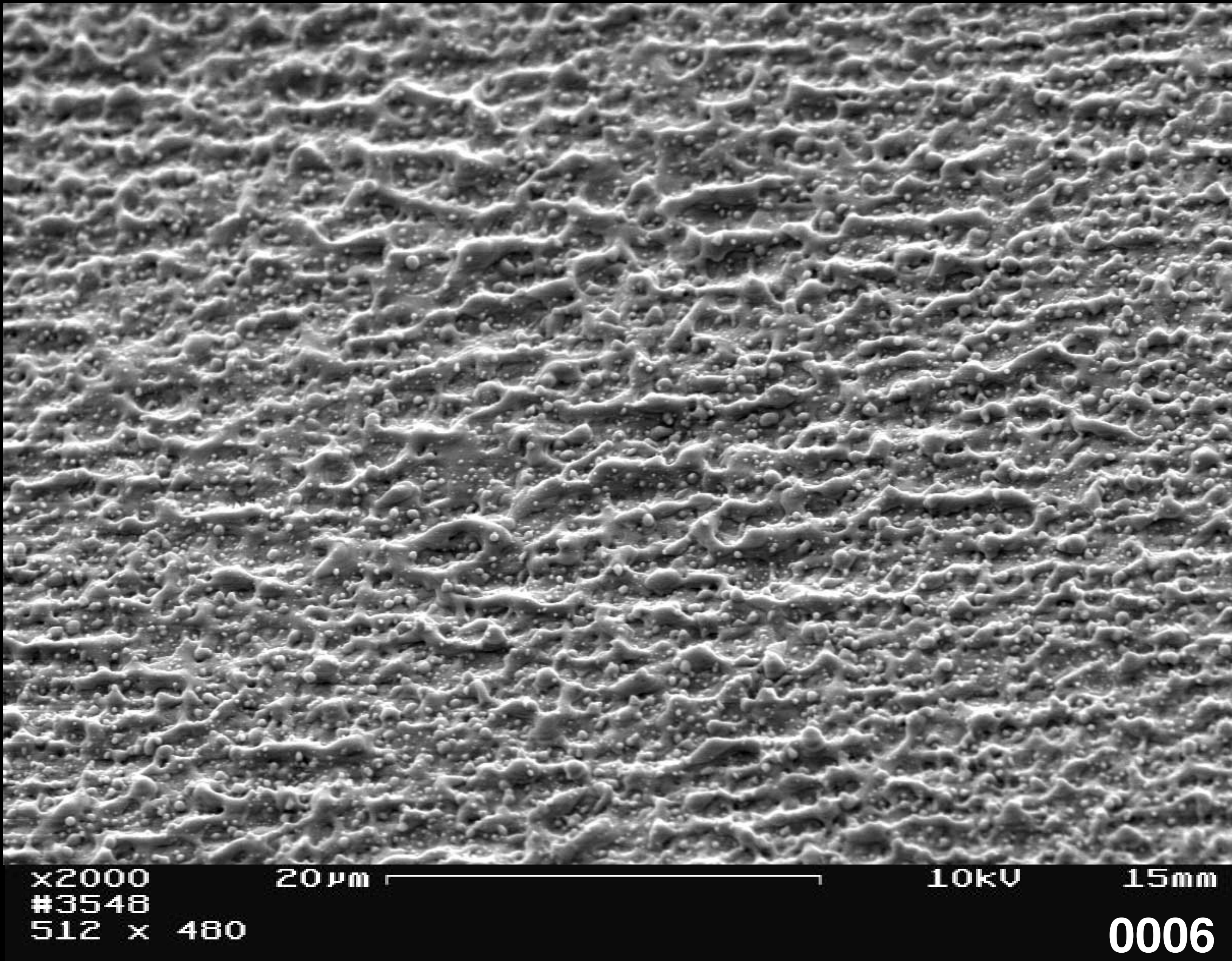
Acknowledgements

Collaborators: Jim Carey, John Chervinsky, François Génin (TEM), Michael Sheehy, Mengyan Shen, Jeffrey Warrender, Rebecca Younkin

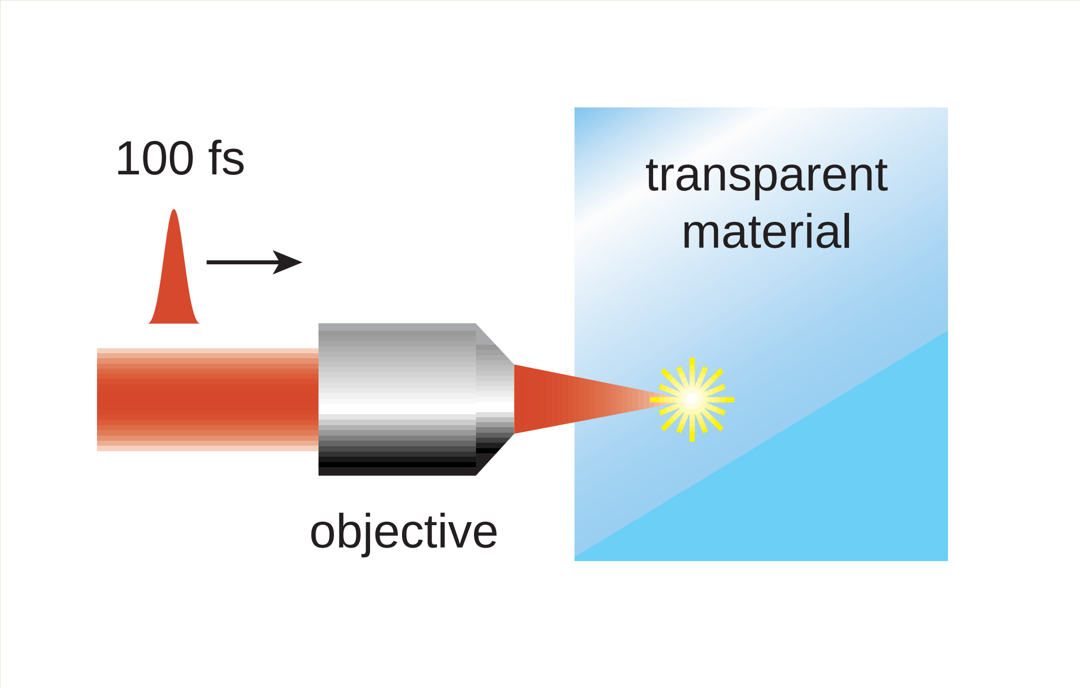
Advisors: Michael Aziz, Cynthia Friend, Eric Mazur, Howard Stone

Funding: Department of Energy, National Science Foundation (Harvard MRSEC)

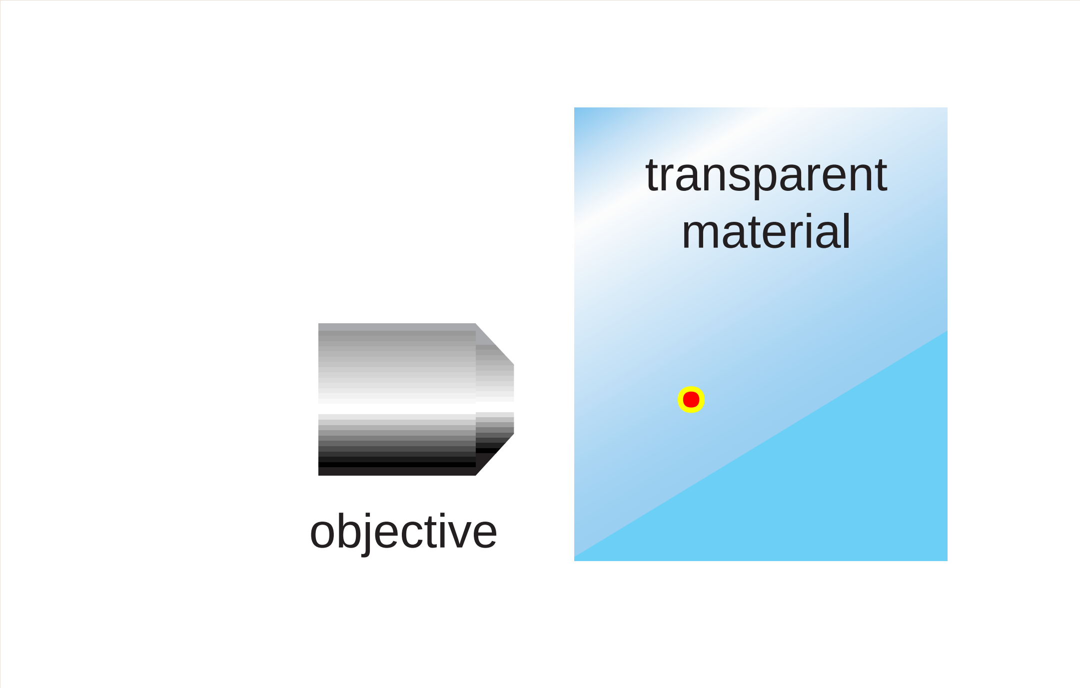
For a copy of this talk and additional information: http://mazur-www.harvard.edu


x2000
20μm
10kV
15mm
#3548
512 x 480
0006

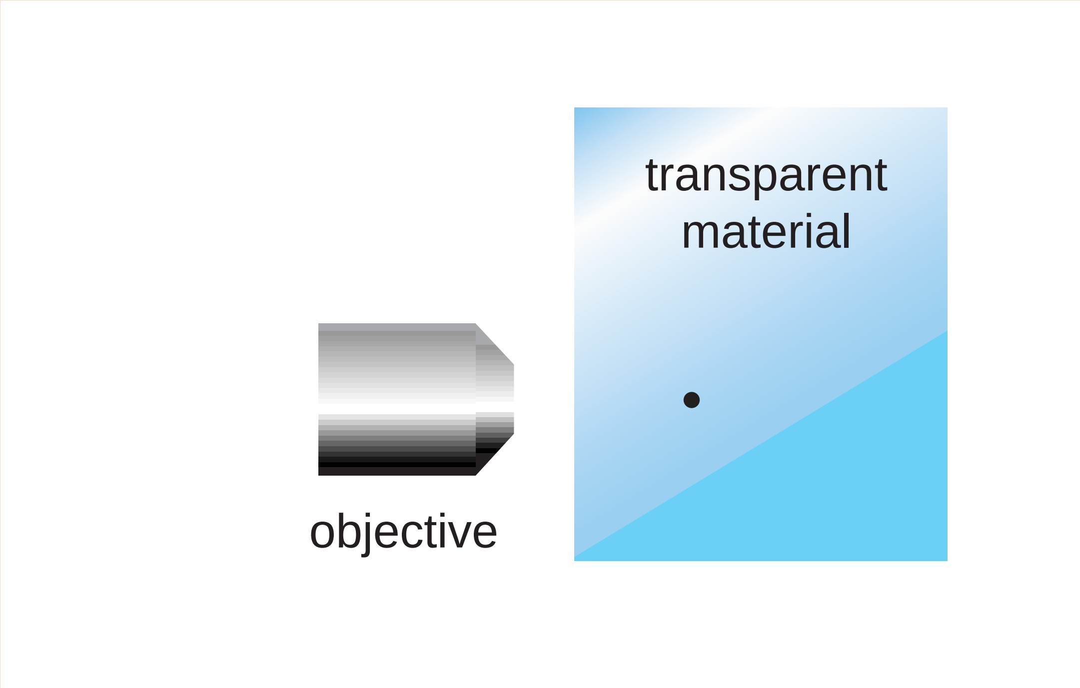
tightly focus beam inside bulk glass

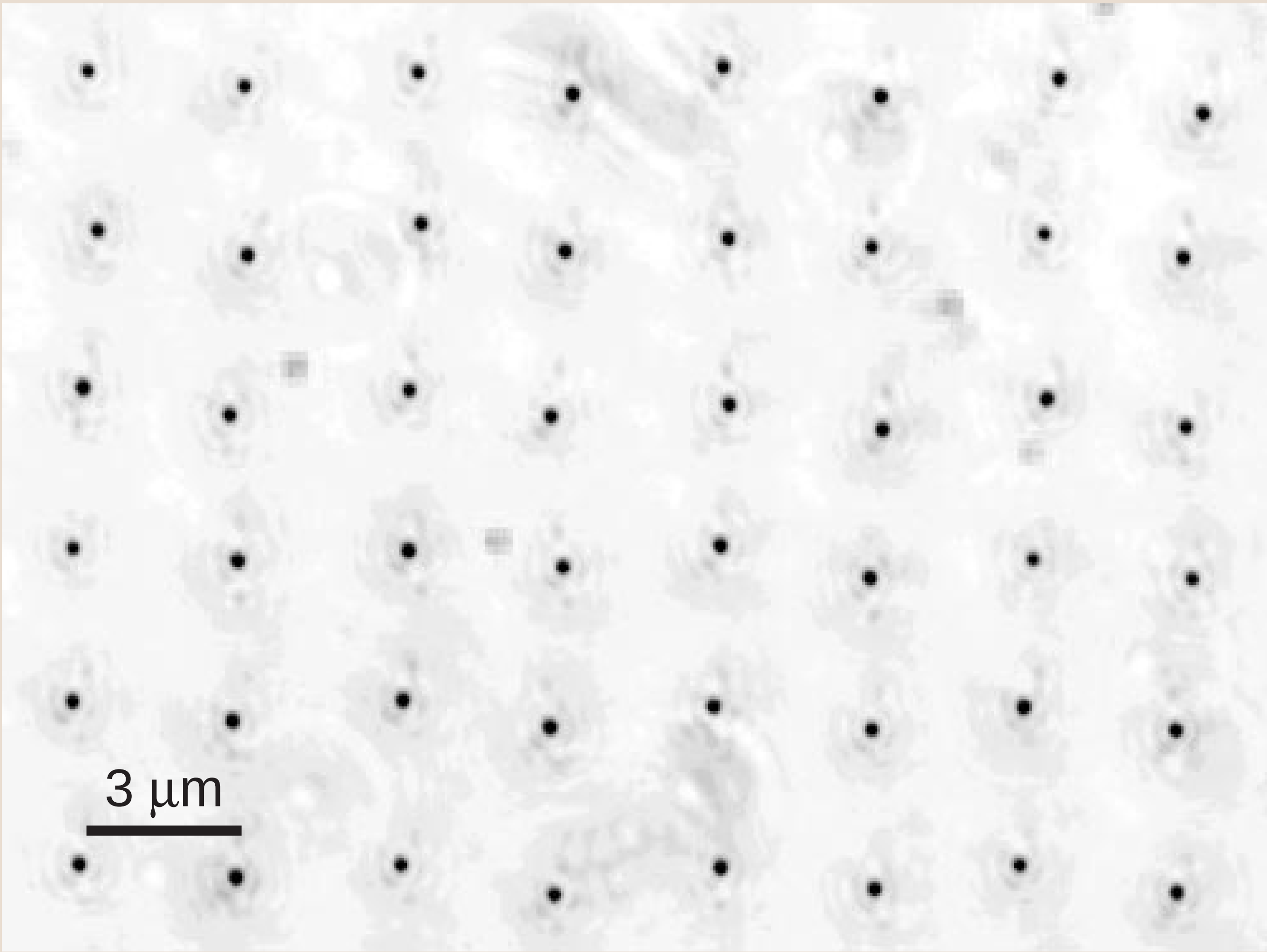


energy is deposited in the focal volume



producing microscopic bulk damage

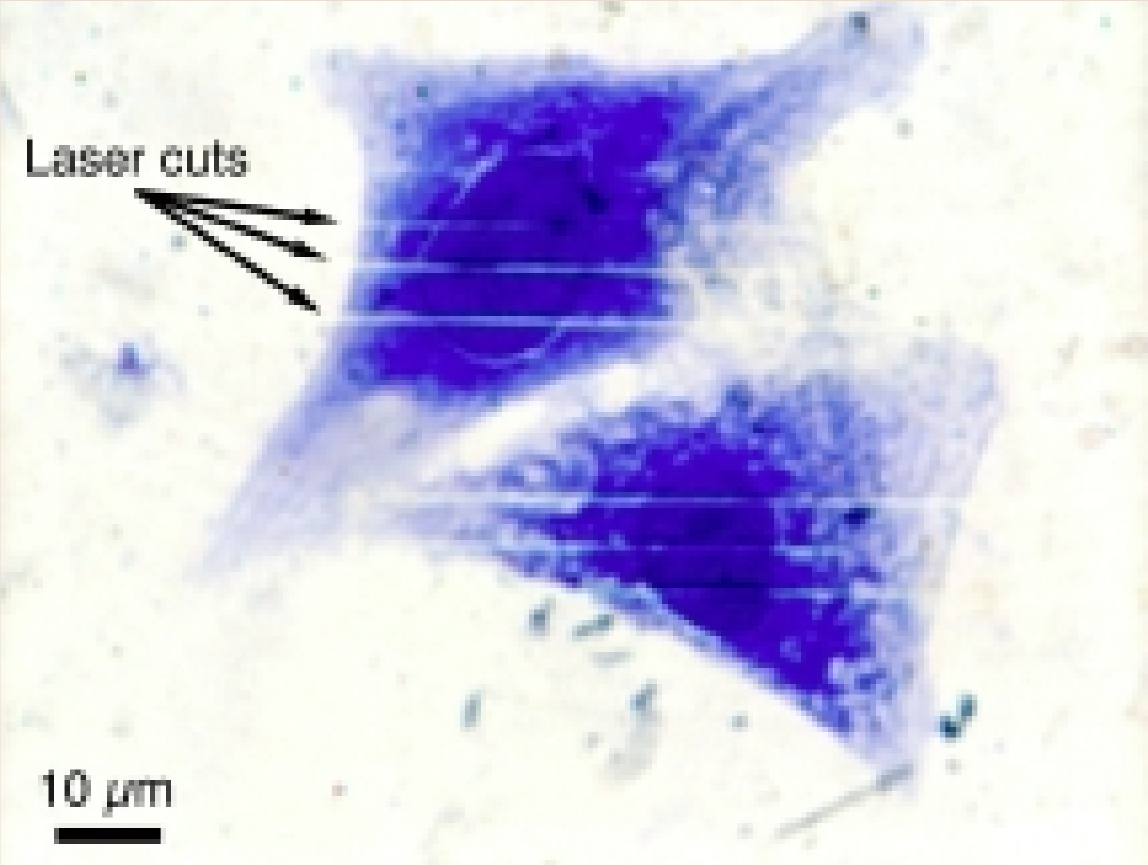




40 nJ
100 fs
800 nm
0.65 NA
Corning 0211

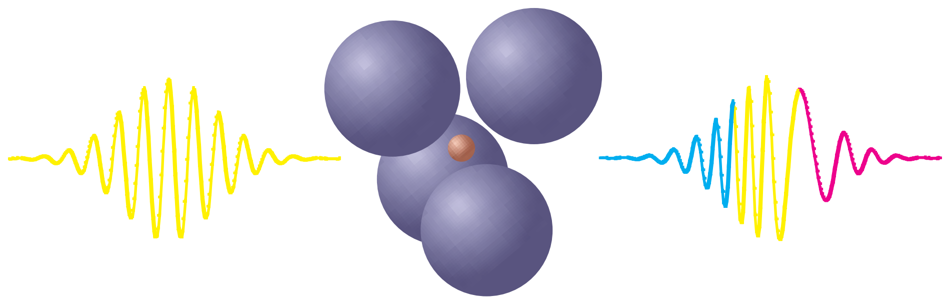
top view

laser cuts through single cell



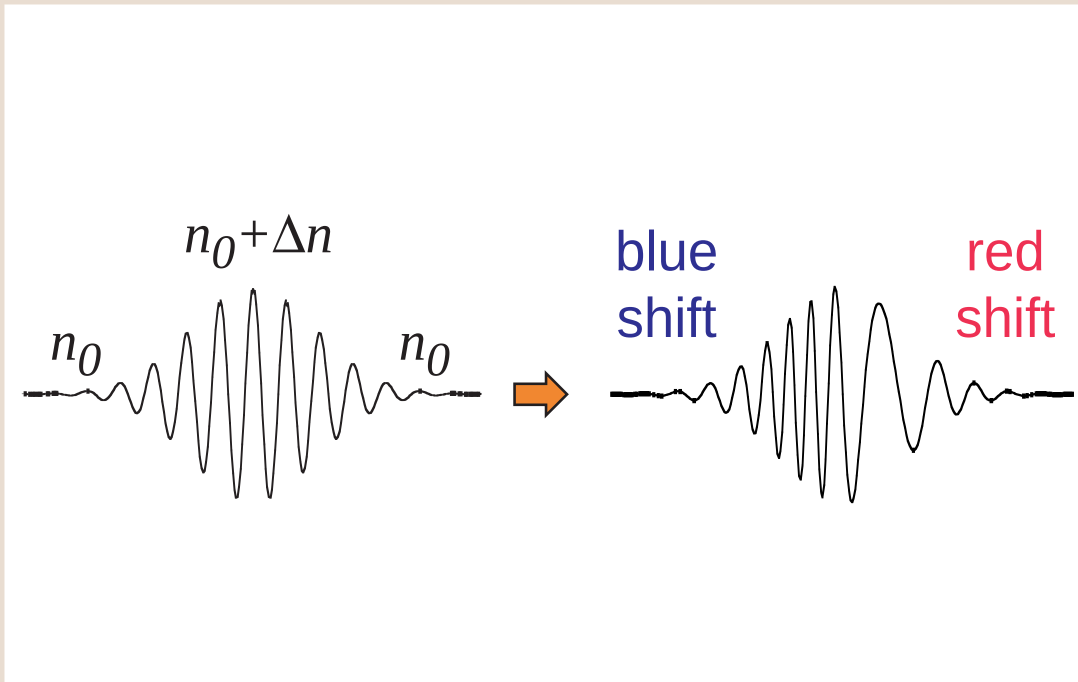
sub-cellular microsurgery

"extremely" nonlinear response

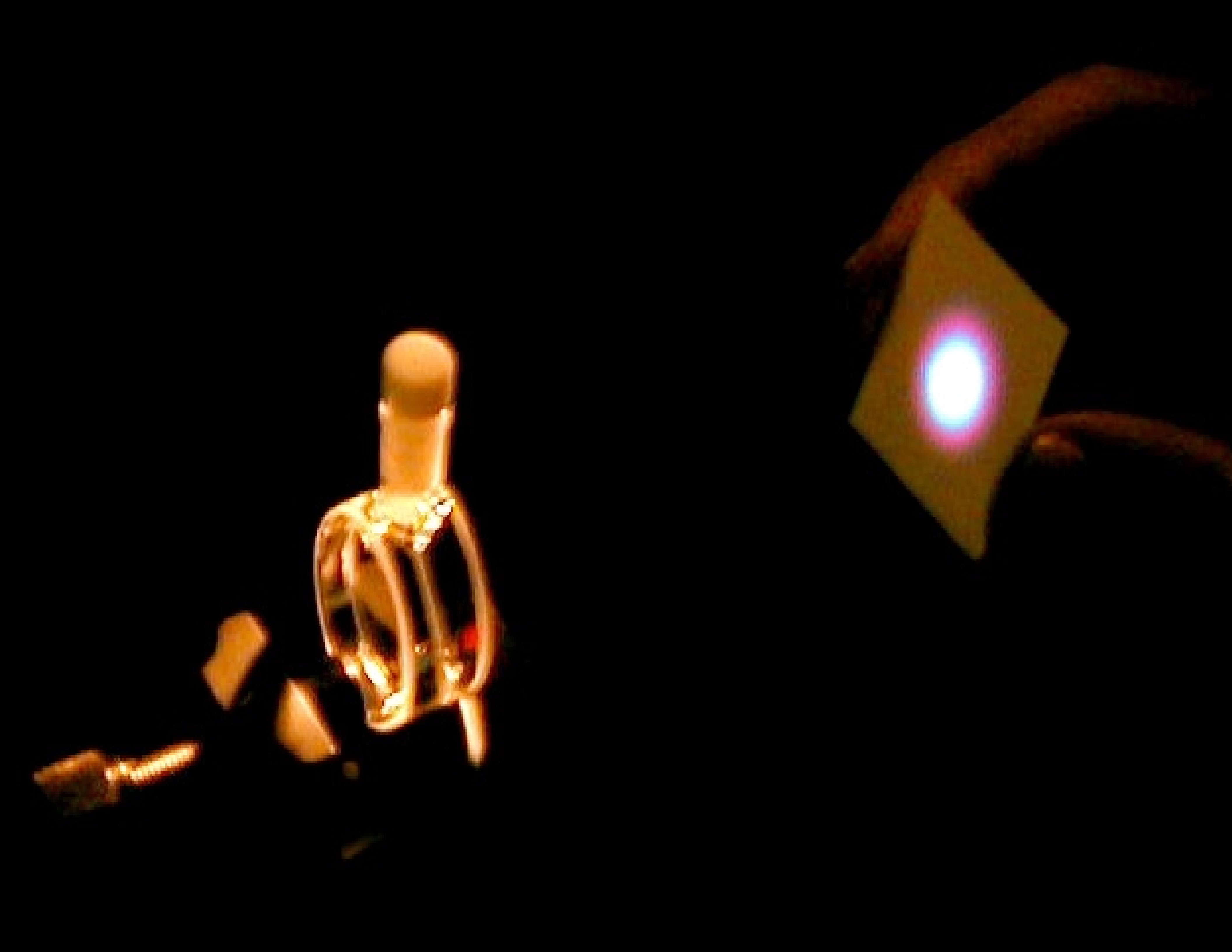


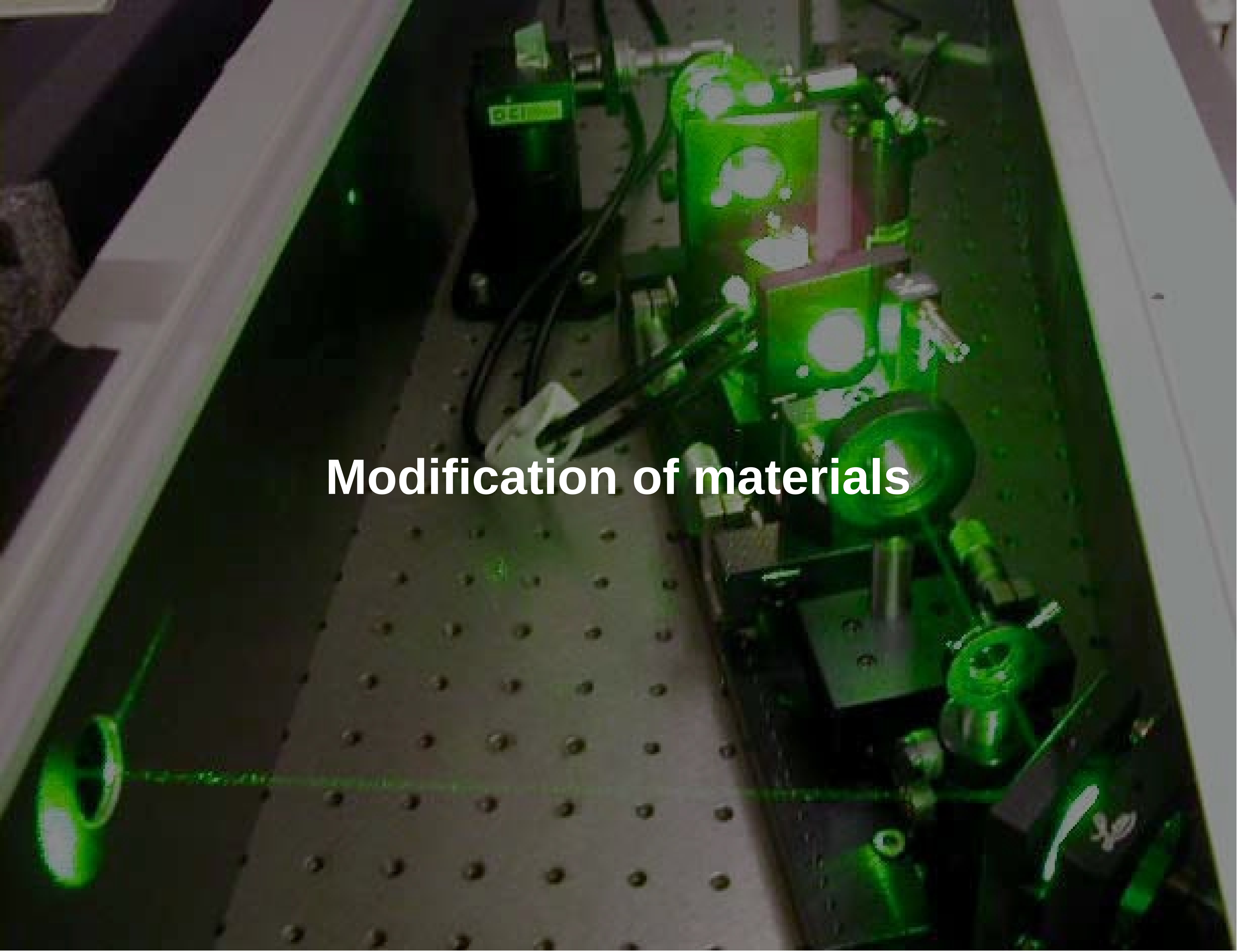
material changes the light

light induces time-dependent index of refraction



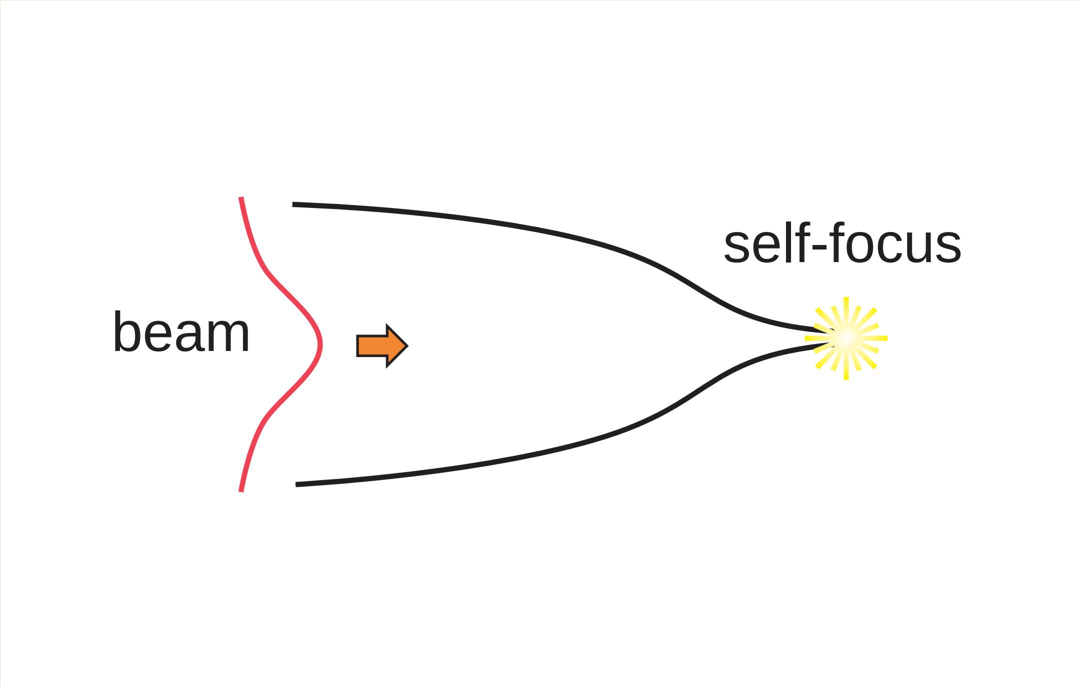
self phase modulation: $n(t) = n_0 + n_2 I(t)$





Modification of materials

light induces position-dependent index of refraction



self-focusing: $n(r) = n_0 + n_2 I(r)$