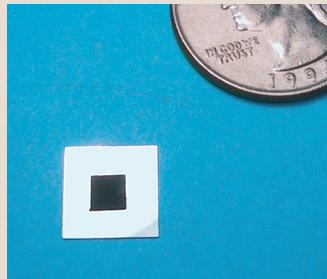


Black silicon: Changing structure and properties with light



Catherine H. Crouch

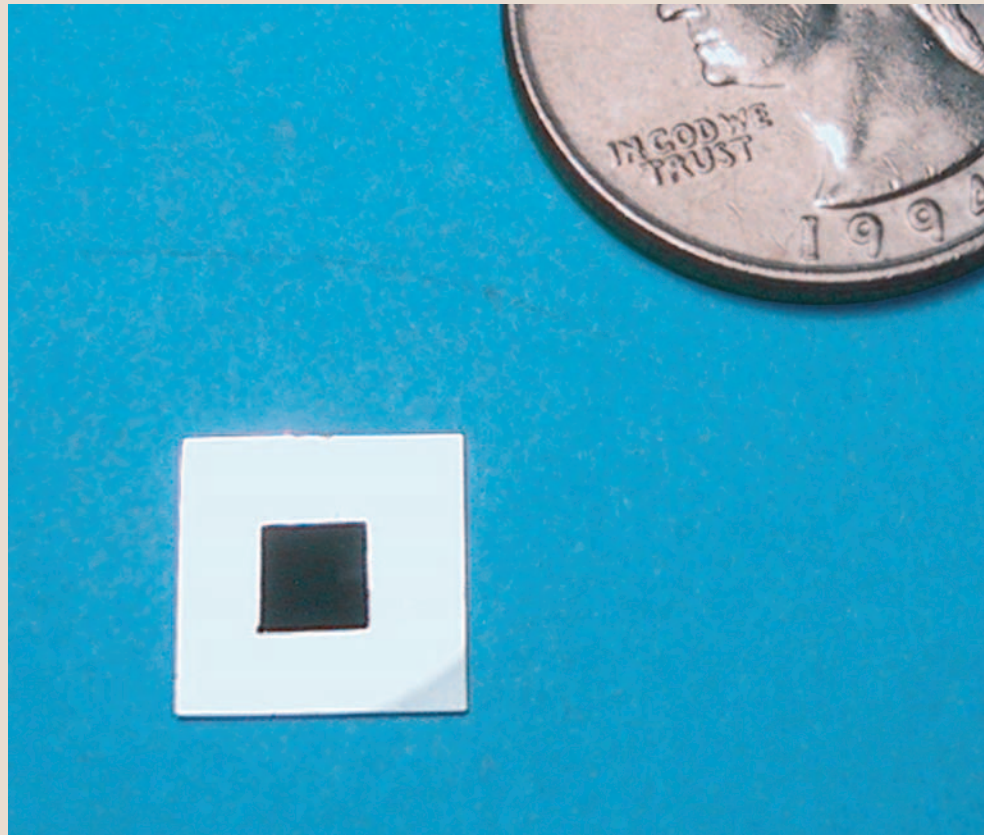
**Clark University
12 December 2002**

**Department of Physics
Harvard University**

Study effect of extremely intense laser pulses

Develop silicon with novel (useful) properties

enhance and extend absorption of light





Introduction to femtosecond laser pulses

Femtosecond laser pulses

800 nm, 100 fs laser pulses

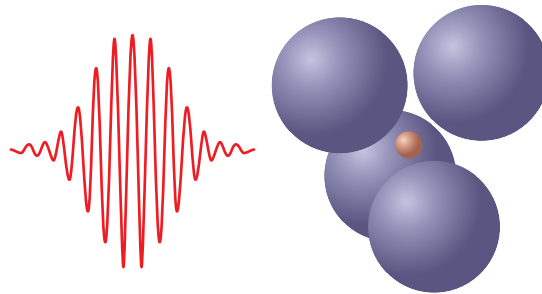
- ▶ last only 10^{-13} seconds
- ▶ 30 cycles of electromagnetic wave
- ▶ extend only $30\text{ }\mu\text{m}$



Extremely high peak power and intensity

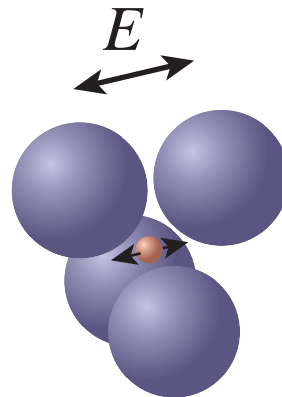
- ▶ peak power $> 10^9\text{ W}$
- ▶ focused beam: $\sim 10^{17}\text{ W/cm}^2$

light-matter interactions



Modification of materials

temporary effect on material

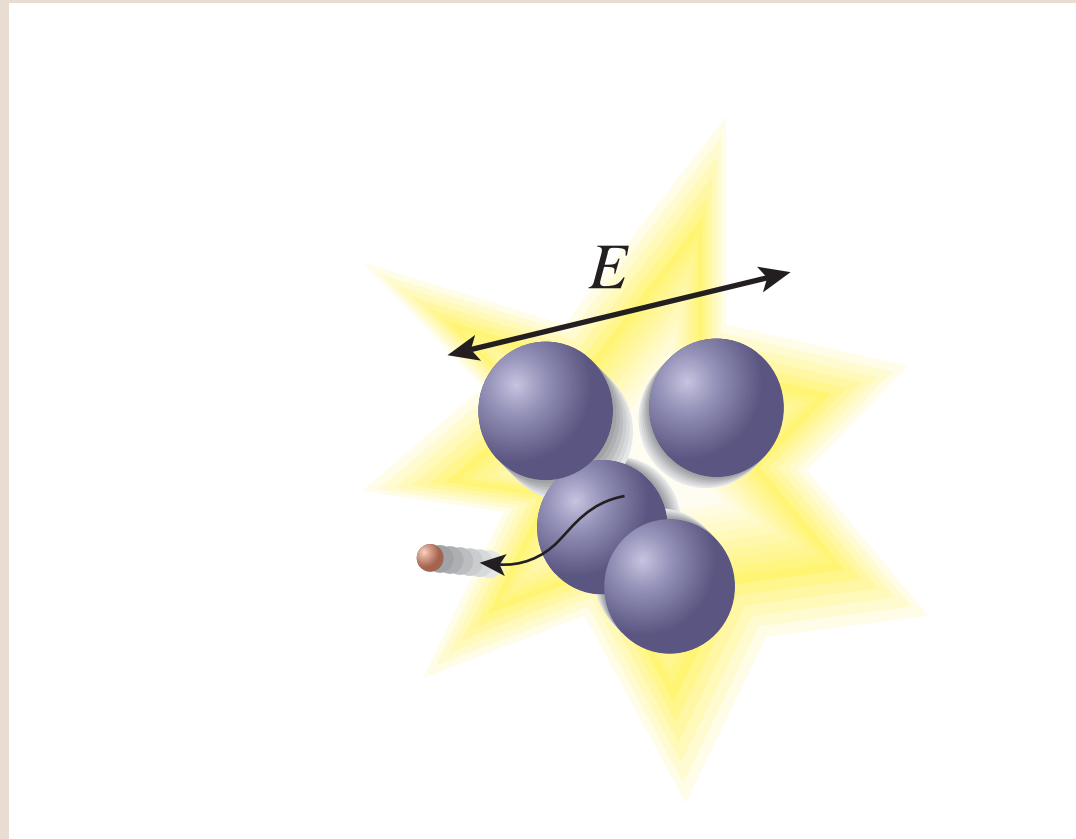


$$\vec{P} = \chi \vec{E}$$

χ is constant

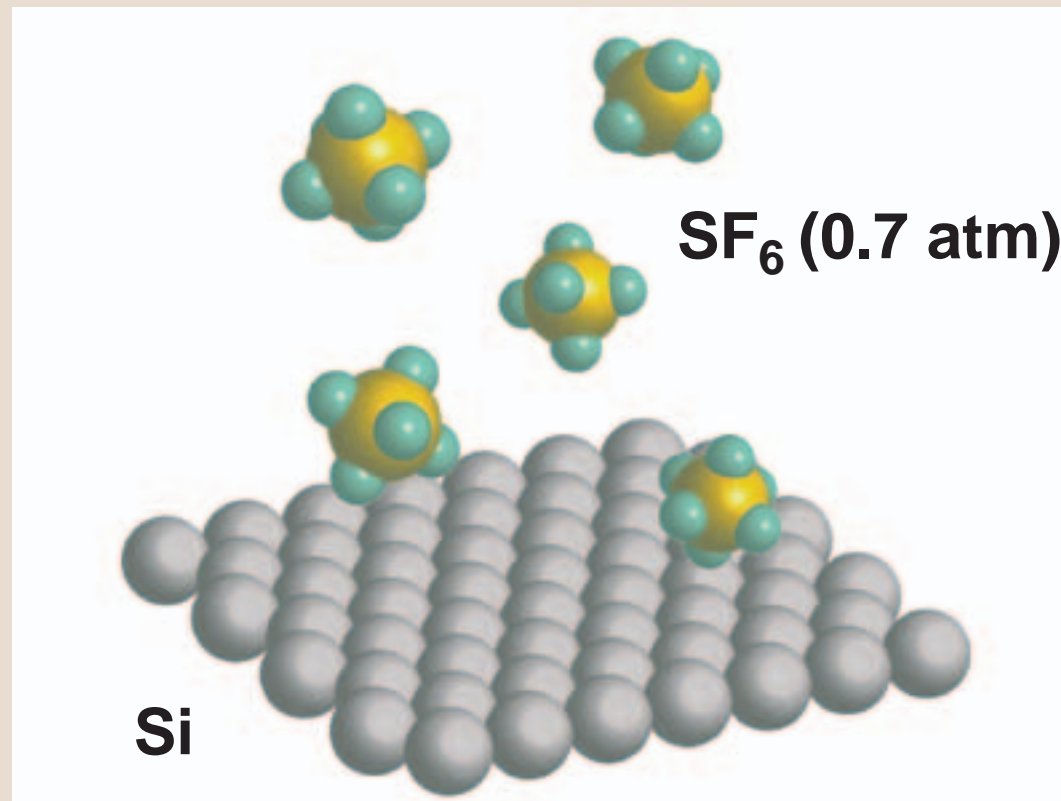
Modification of materials

permanent change to material



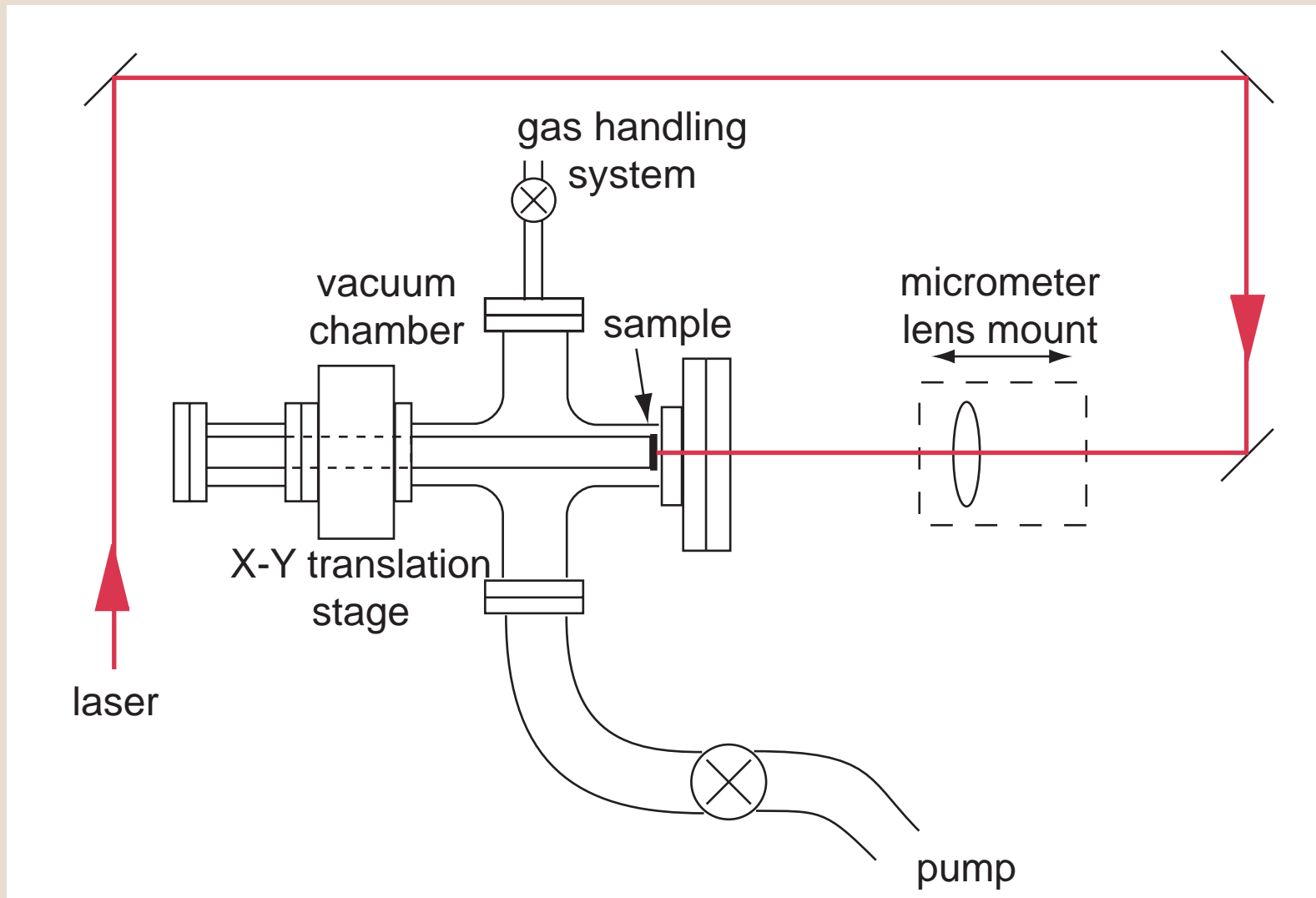
plasma formation

- 1. What is black silicon?**
- 2. Why is it black?**
- 3. How does it get that way?**

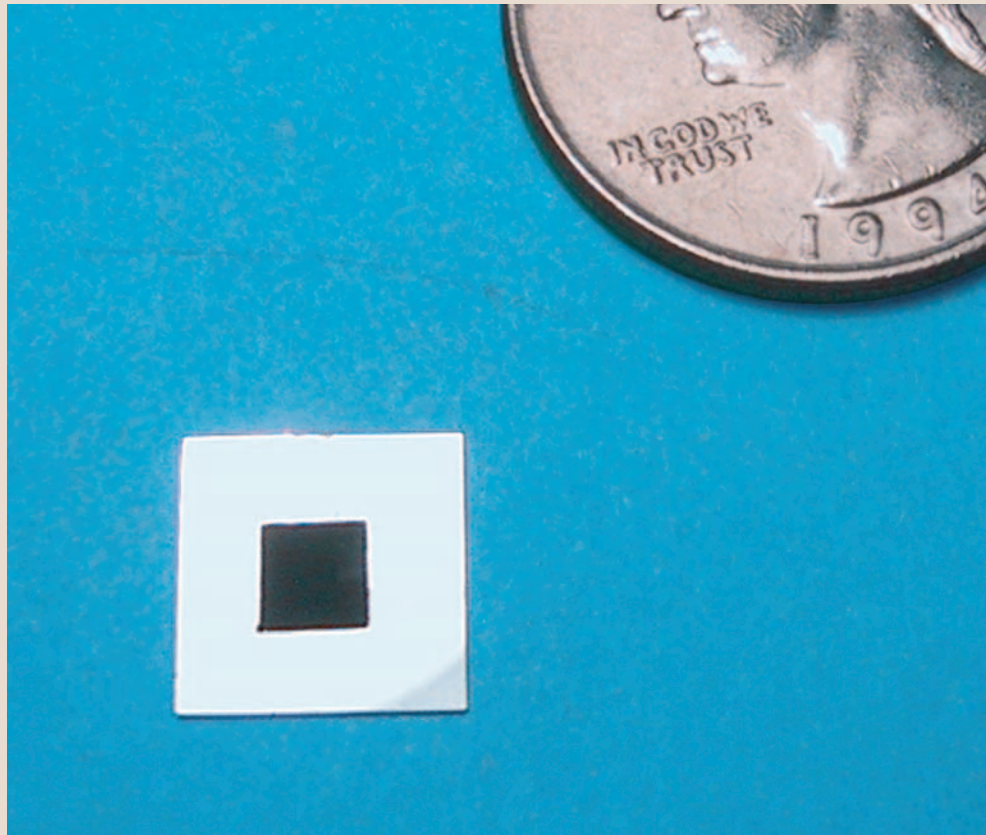


**irradiate surface with femtosecond laser pulses
(800 nm, 100 fs, 500 pulses, 10 kJ/m²)**

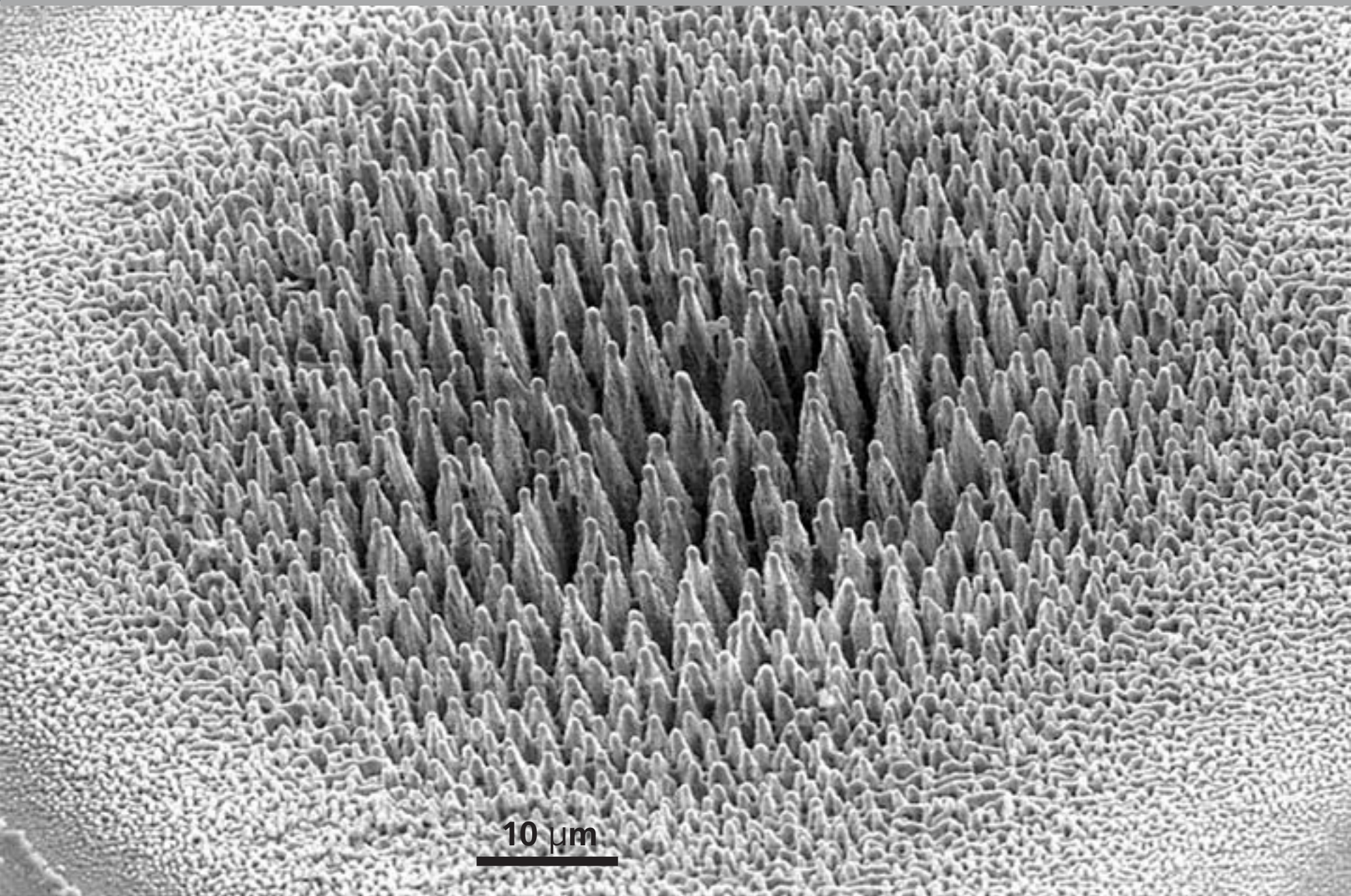
Black silicon



Black silicon

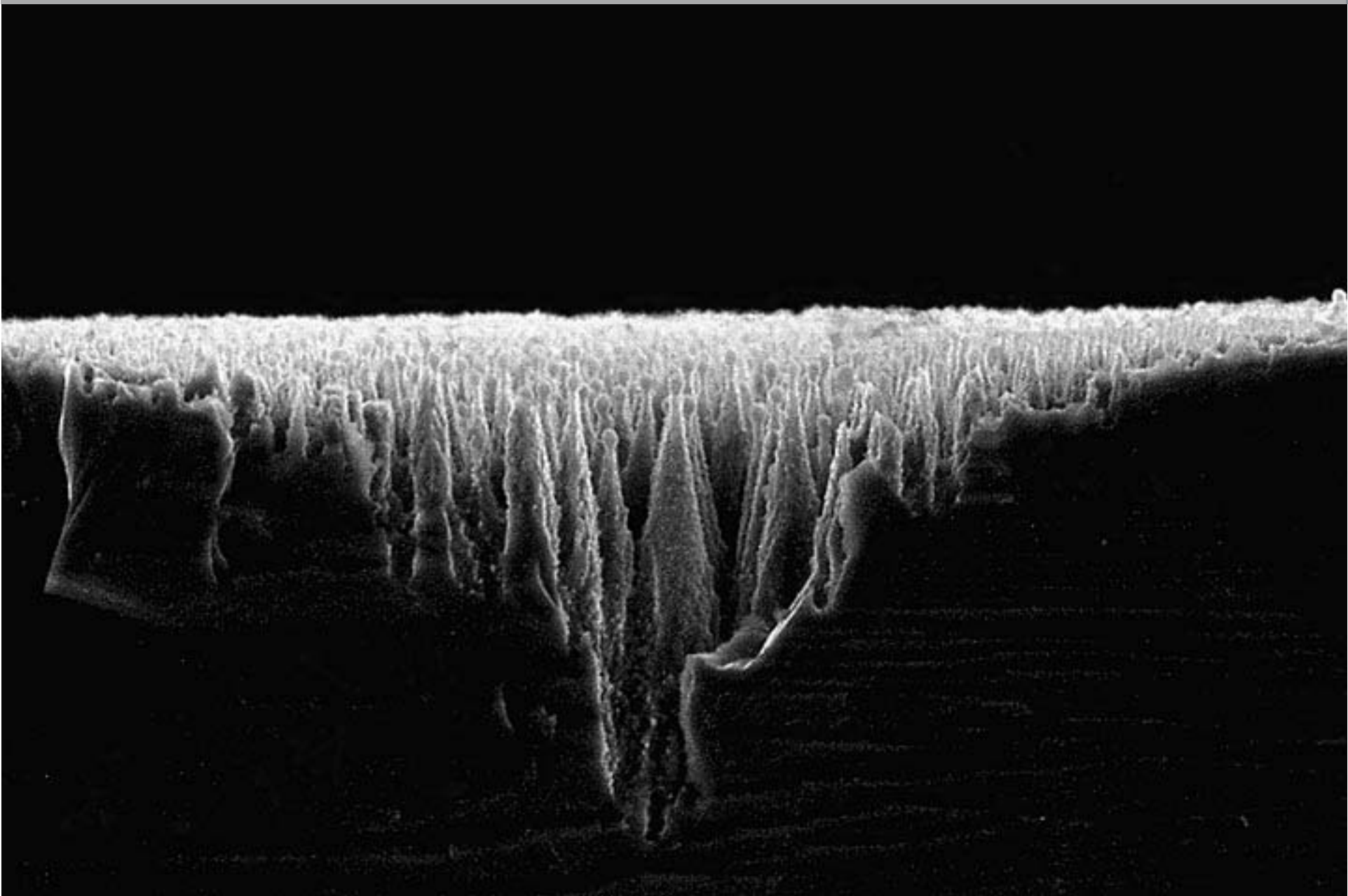


Black silicon



10 μm

Black silicon



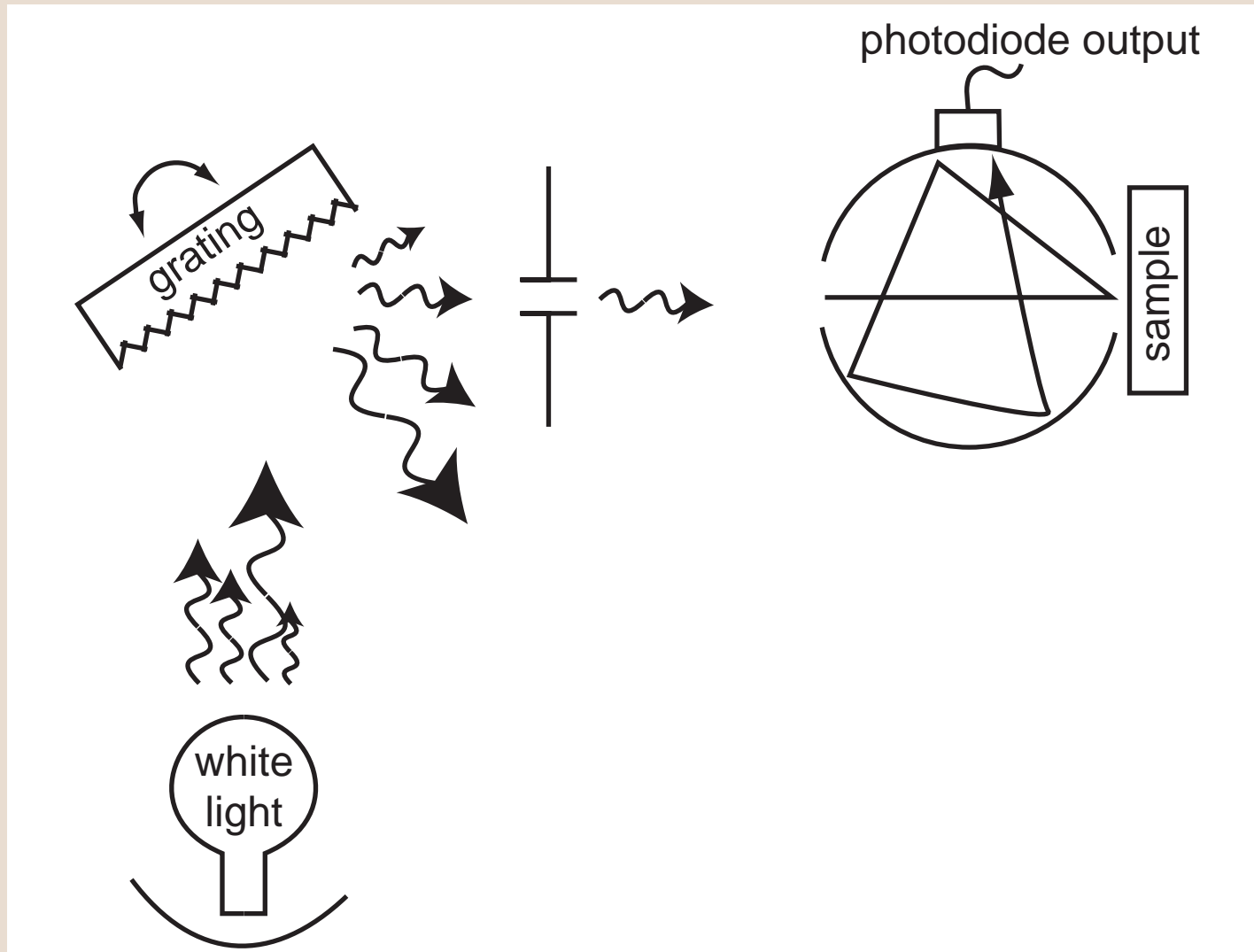
Black silicon

Optical properties

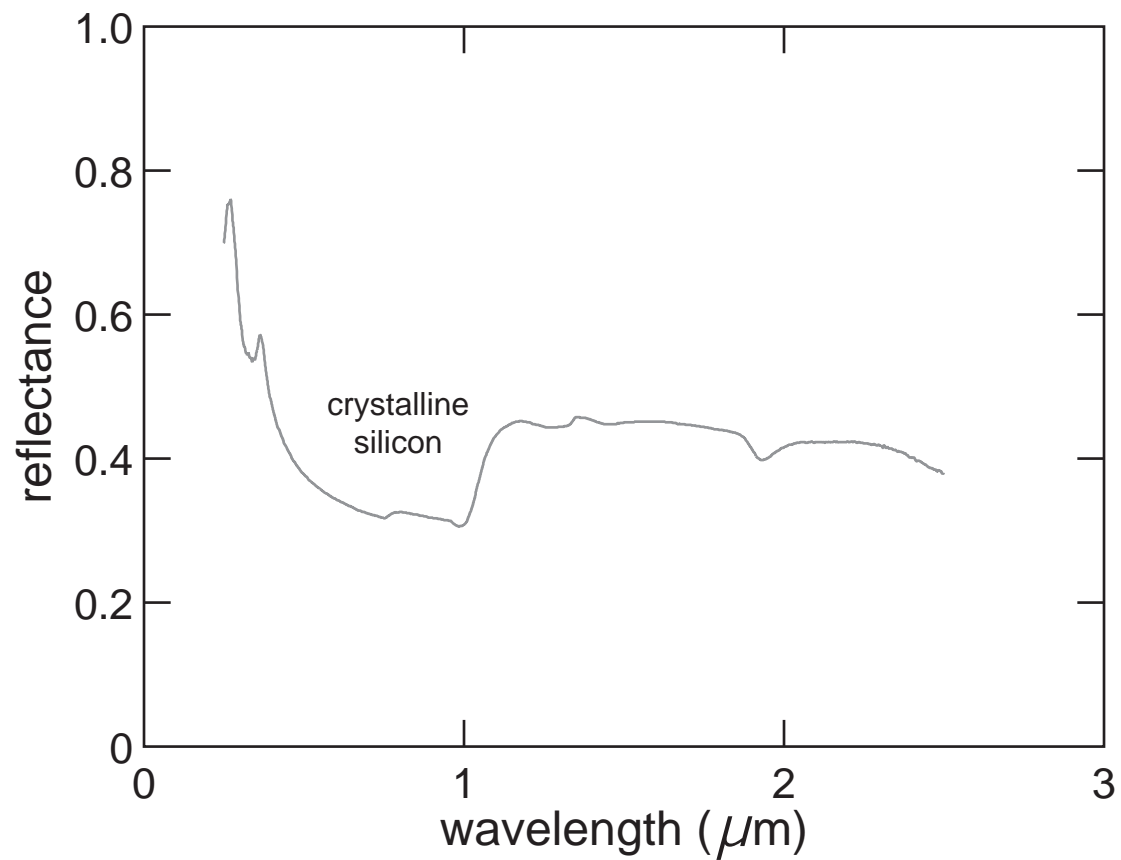
3 μm

A scanning electron micrograph (SEM) showing the surface morphology of black silicon. The surface is covered with a dense array of vertical, tapered silicon nanowires or pillars. Each pillar has a rounded, hemispherical tip. The pillars are closely spaced, creating a forest-like structure. The background between the pillars is dark and textured. A scale bar at the bottom center indicates a length of 3 micrometers.

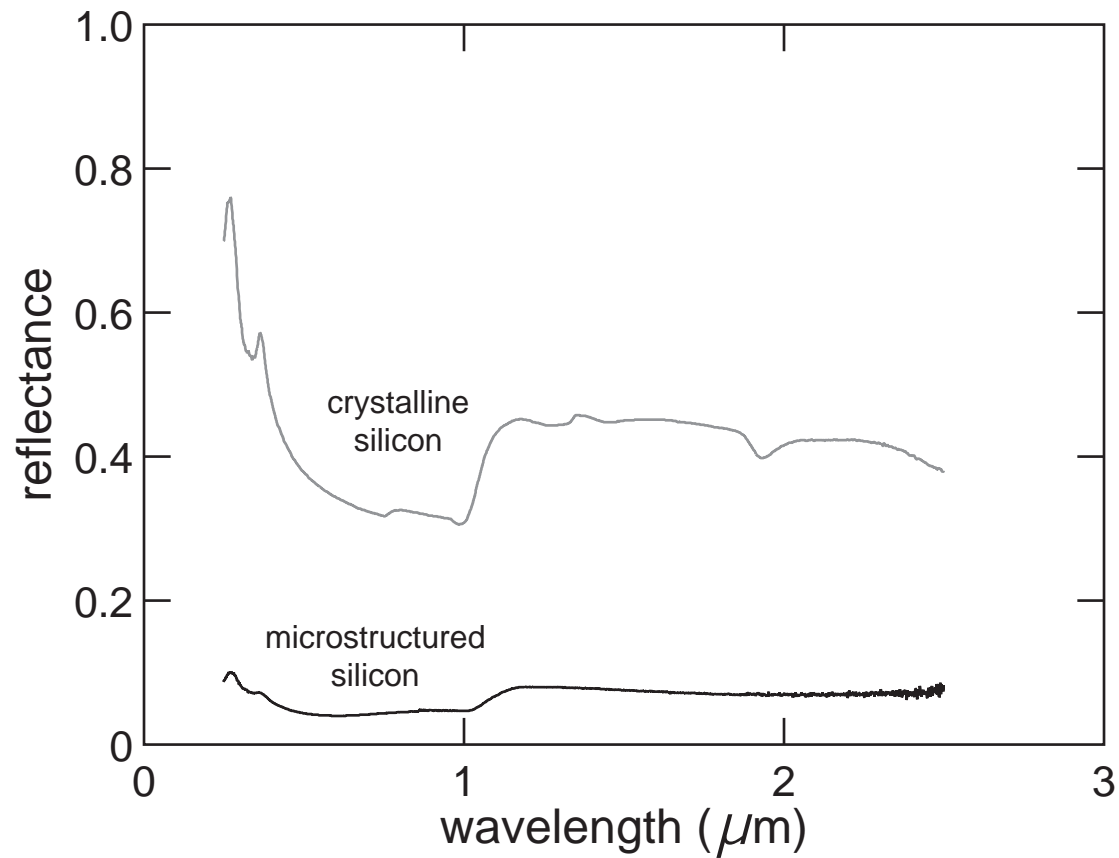
measure reflectance, transmittance with integrating sphere



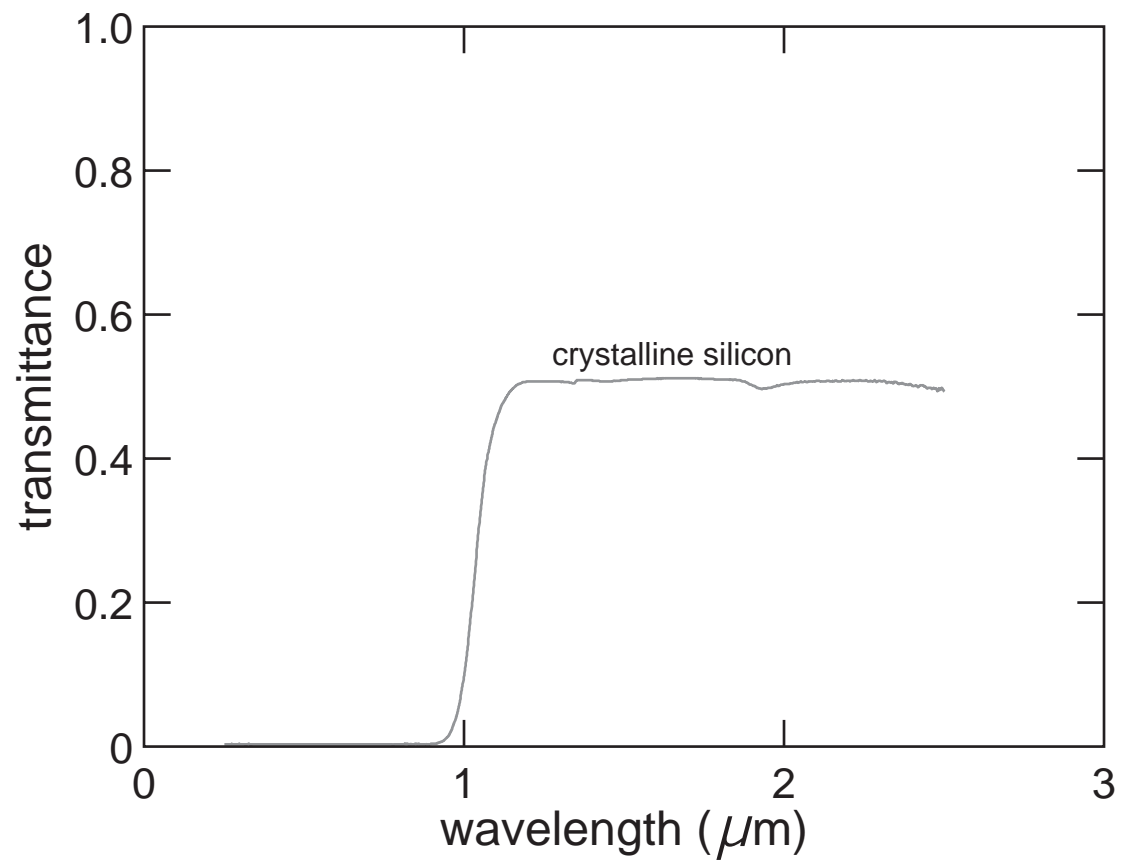
reflectance



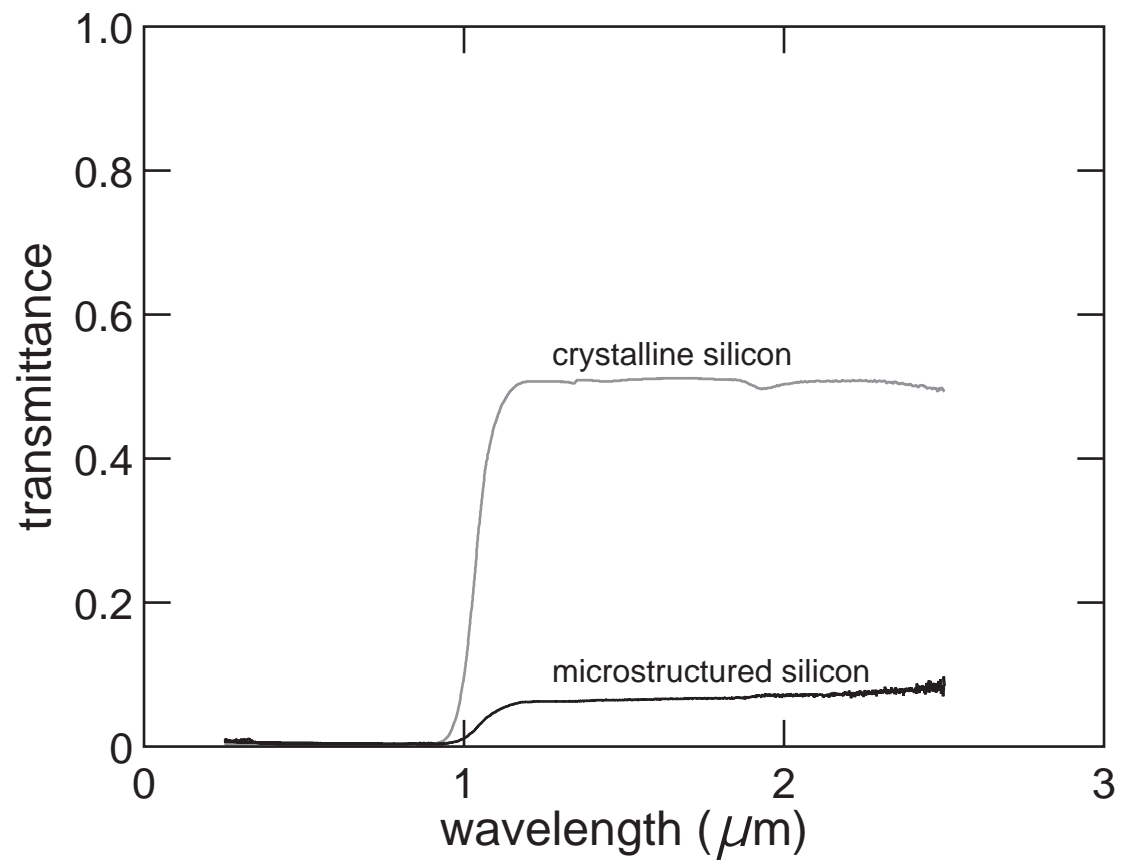
reflectance



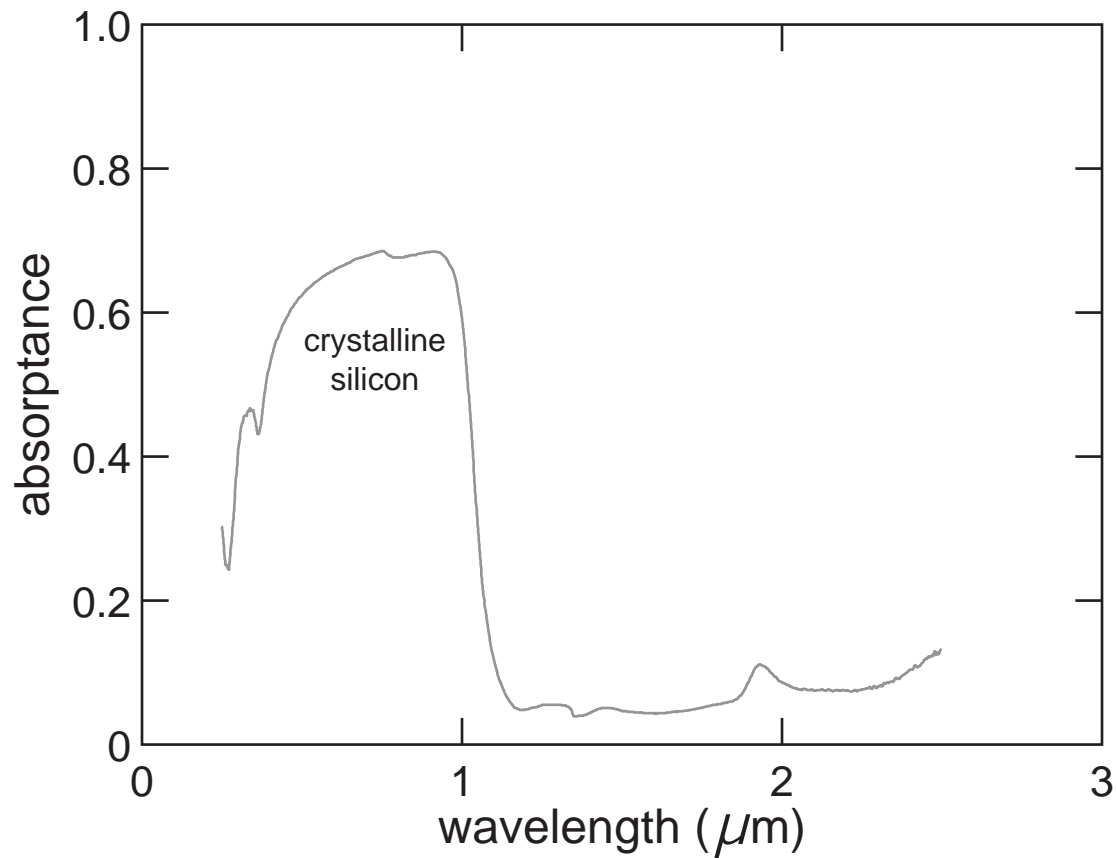
transmittance



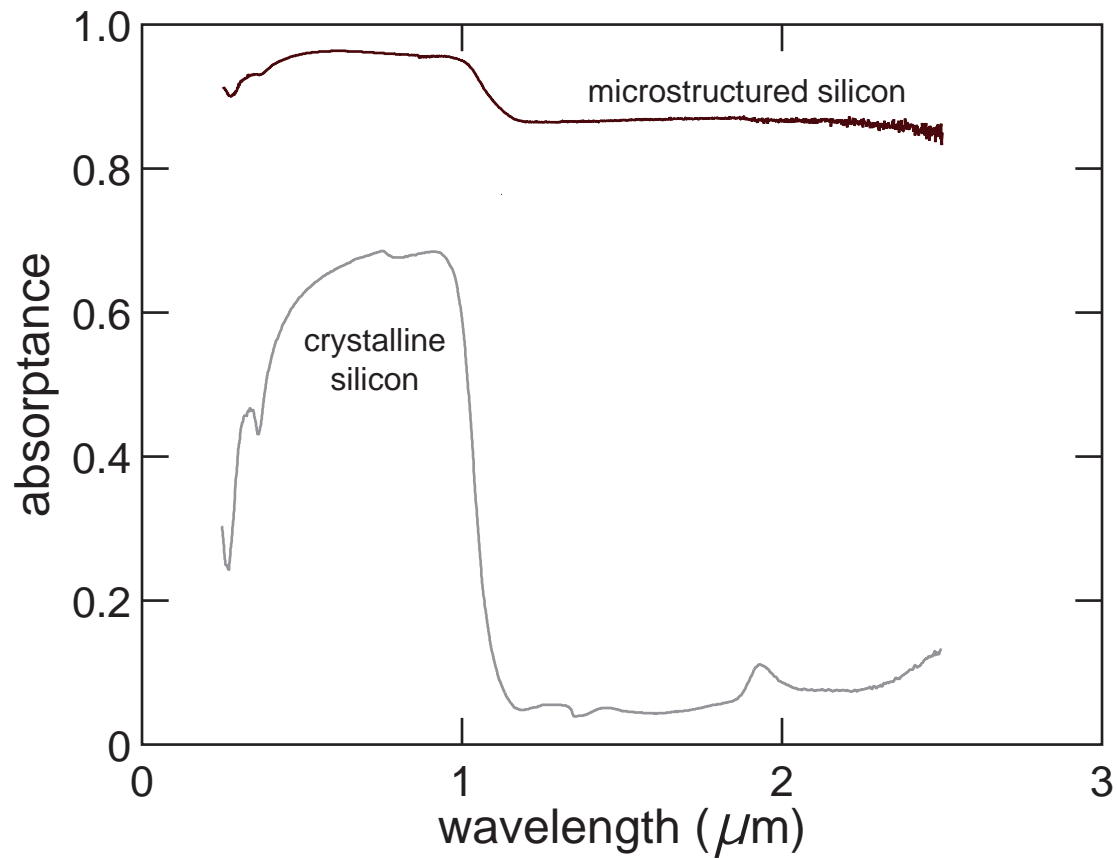
transmittance



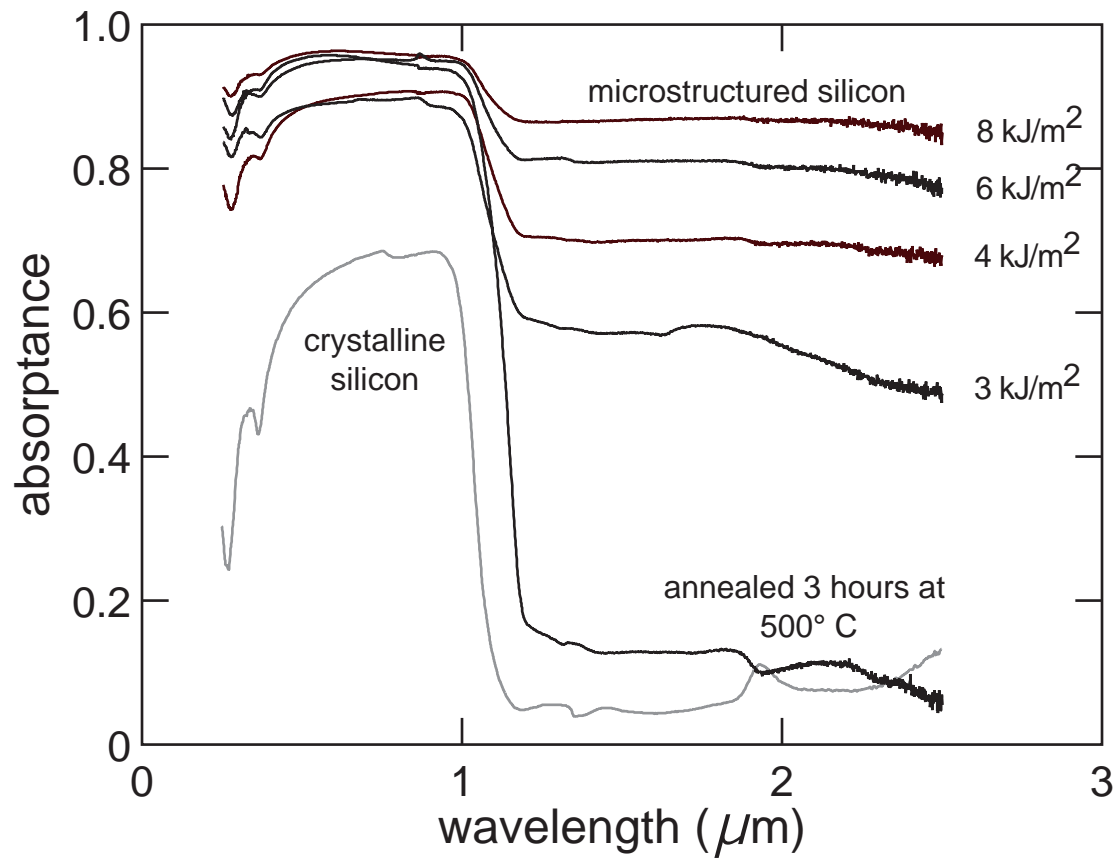
absorptance ($A = 1 - R - T$)



absorptance

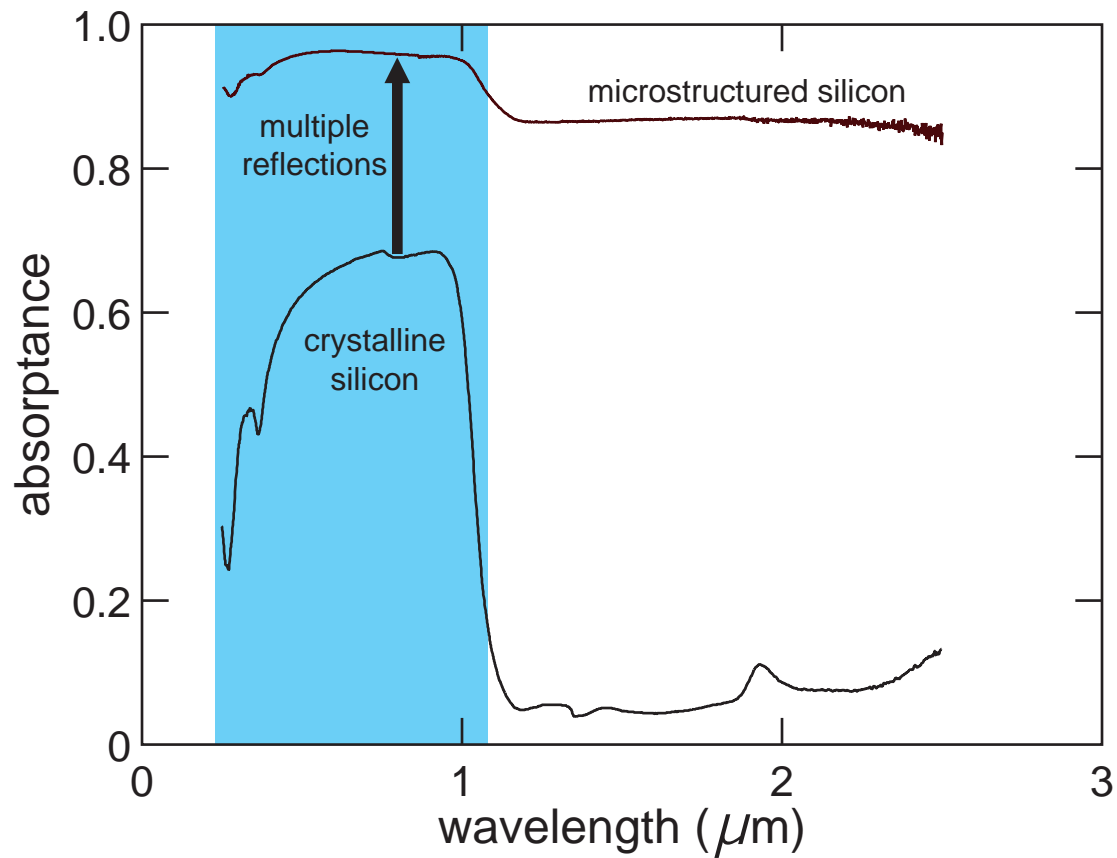


absorptance

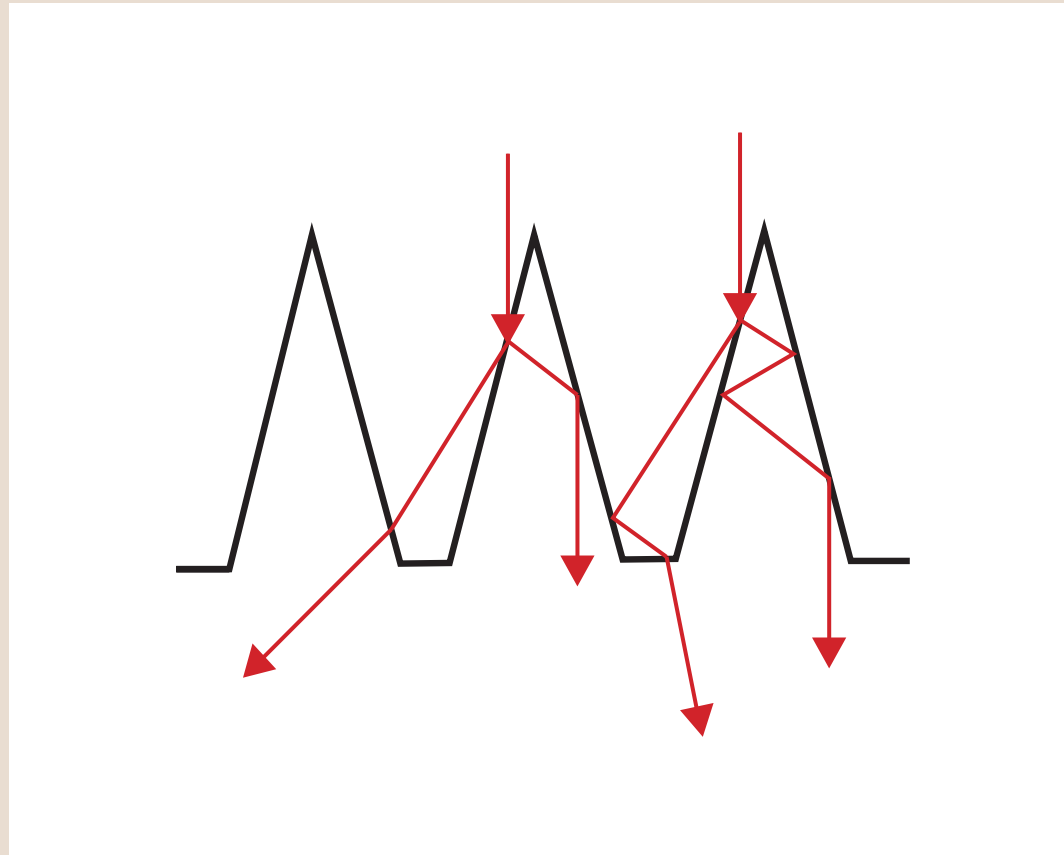


Why is it black?

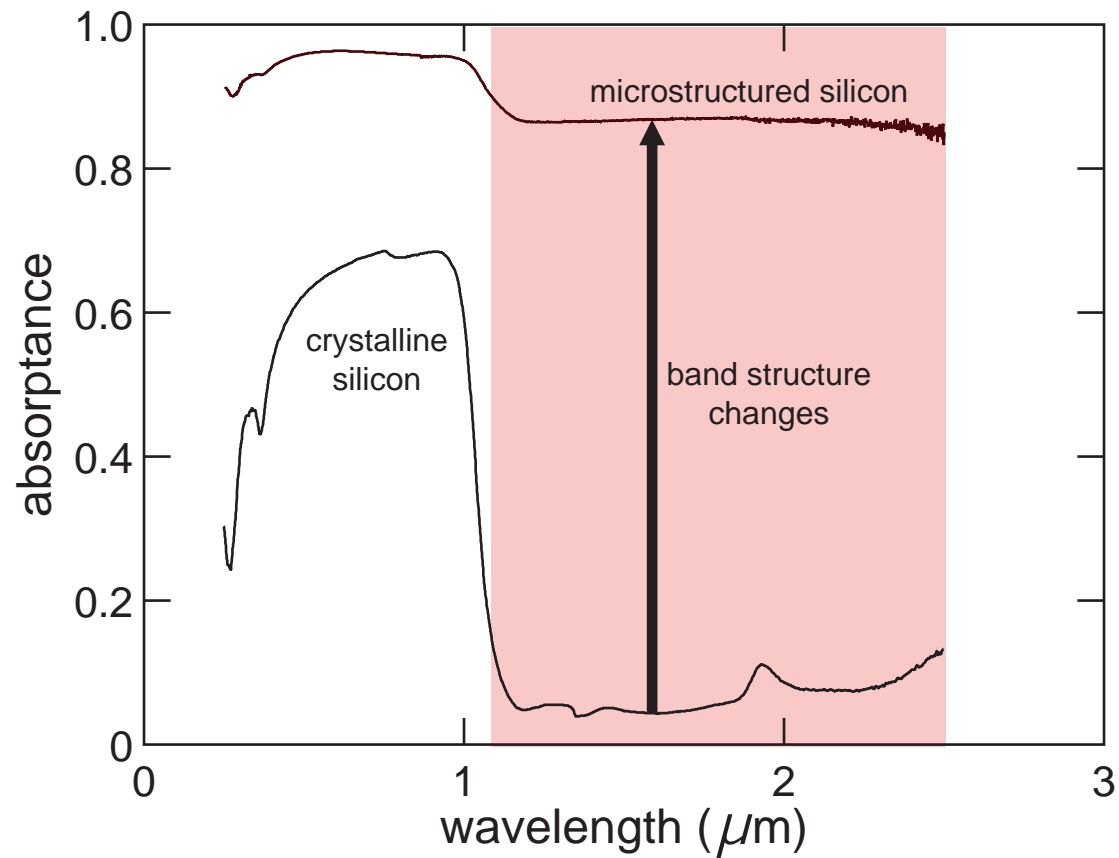
absorptance



Multiple reflections can enhance absorption

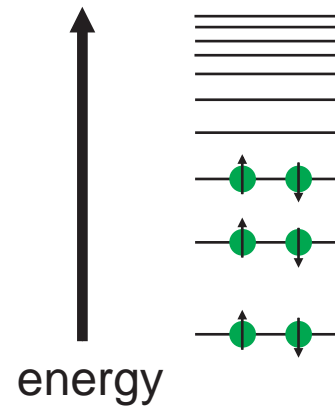


absorptance



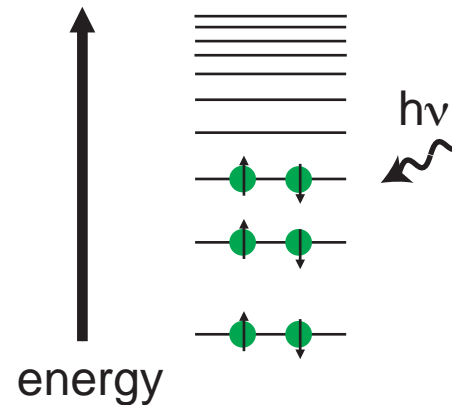
atoms absorb light by electronic transitions

atomic electrons
must occupy
well-defined
energy levels



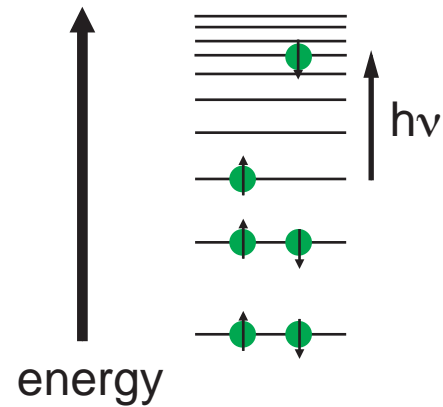
atoms absorb light by electronic transitions

absorbed photon
must promote an
electron to an
empty level



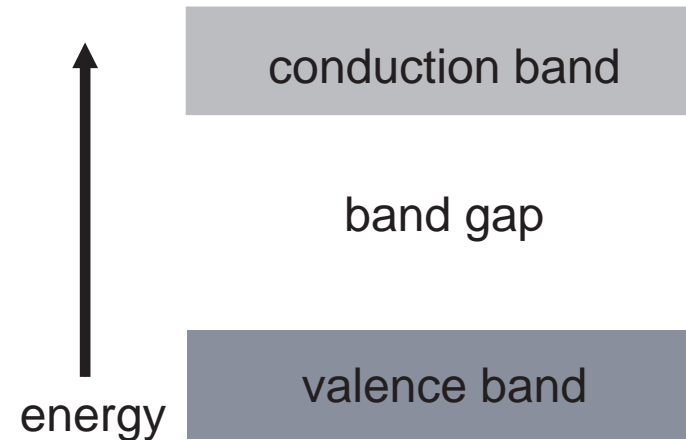
Atoms absorb light by electronic transitions

absorbed photon
must promote an
electron to an
empty level



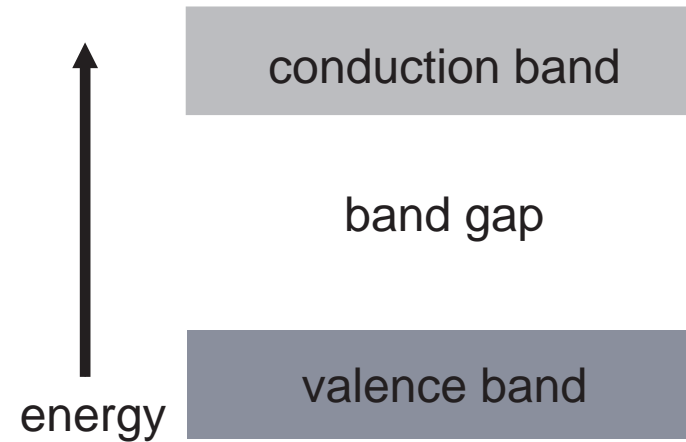
crystalline solids have bands of energy states

crystal has
electronic
energy states in
certain energy
ranges



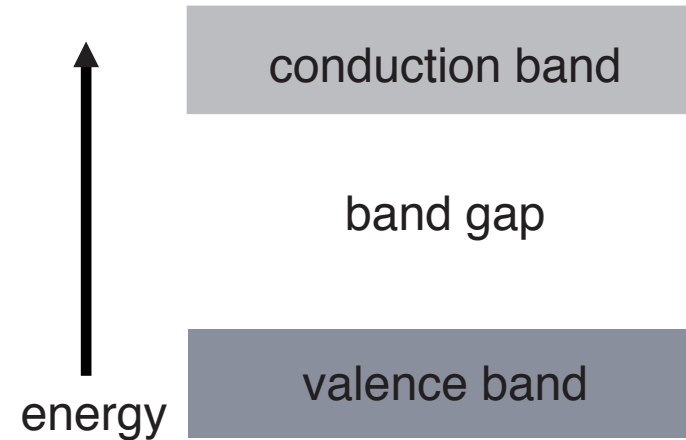
crystalline solids have bands of energy states

semiconductors
have full valence
band and empty
conduction band



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

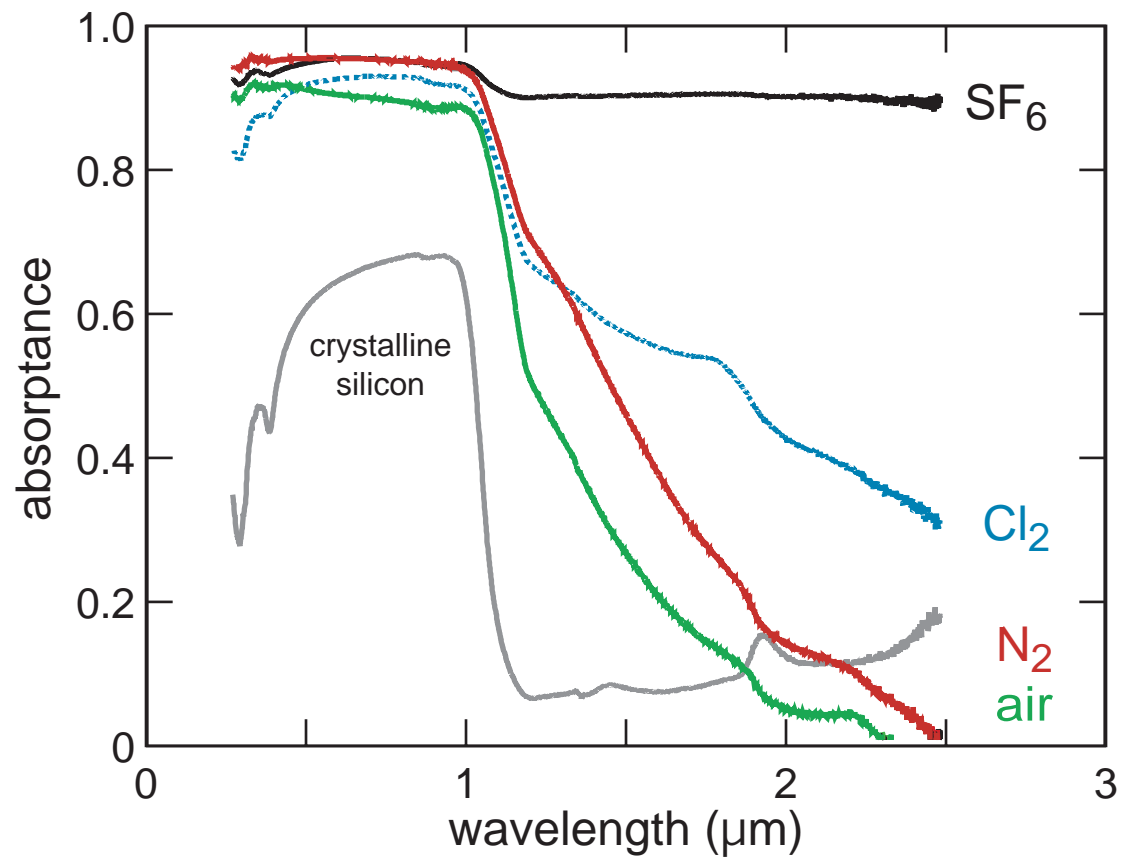
Previous work with other gases:

gas species incorporated into surface layer

sulfur required for below-band gap absorption

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

absorptance



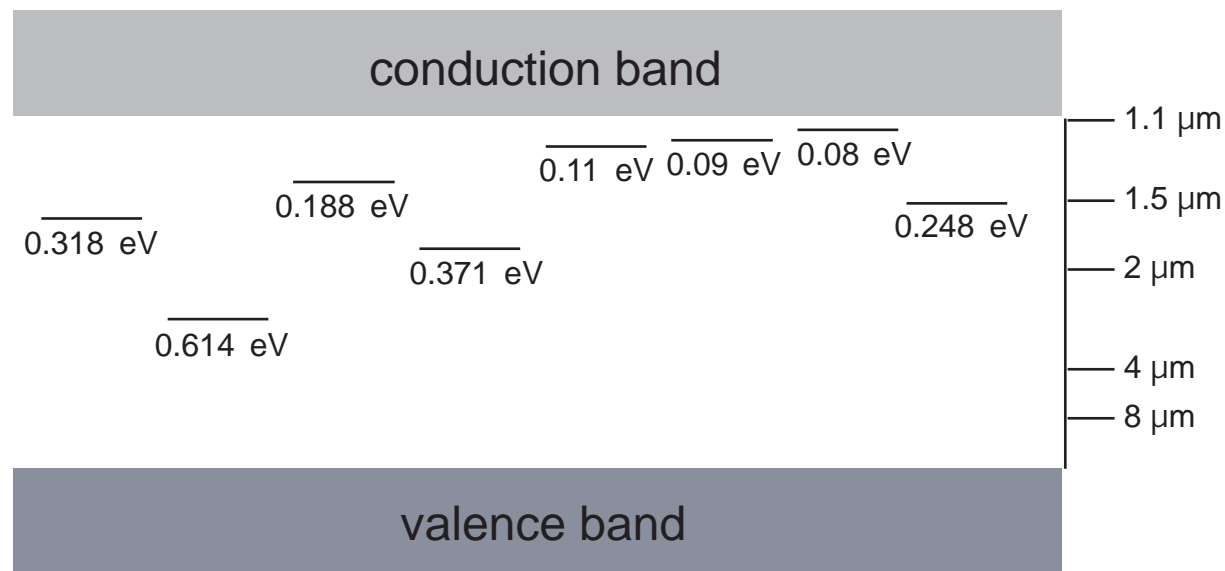
Surfaces structured in SF₆:

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

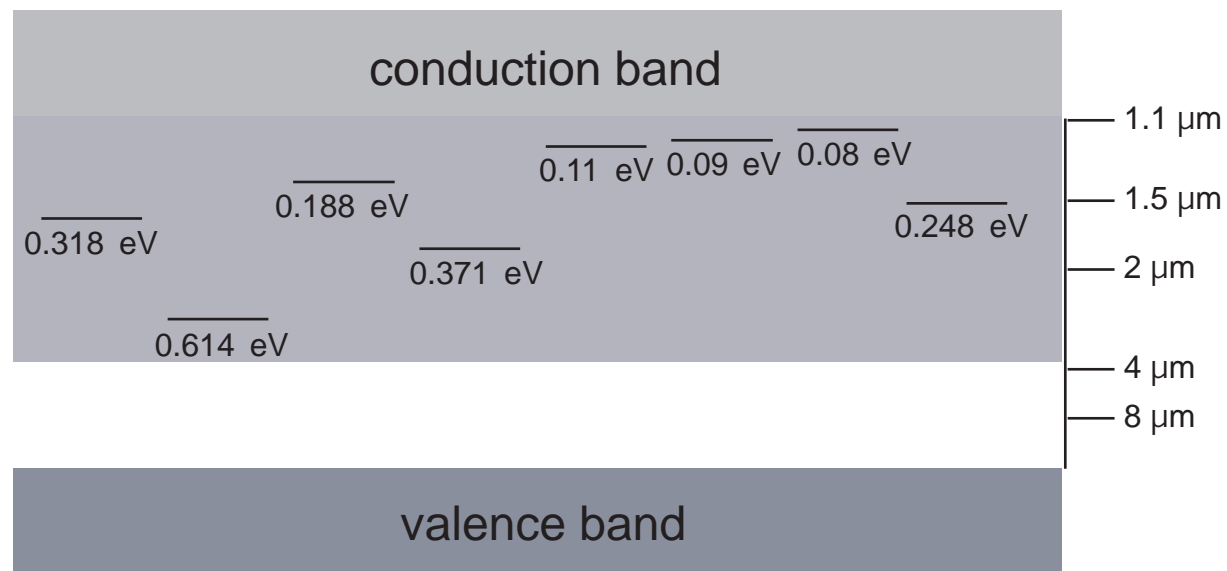
1 part in 10^6 S



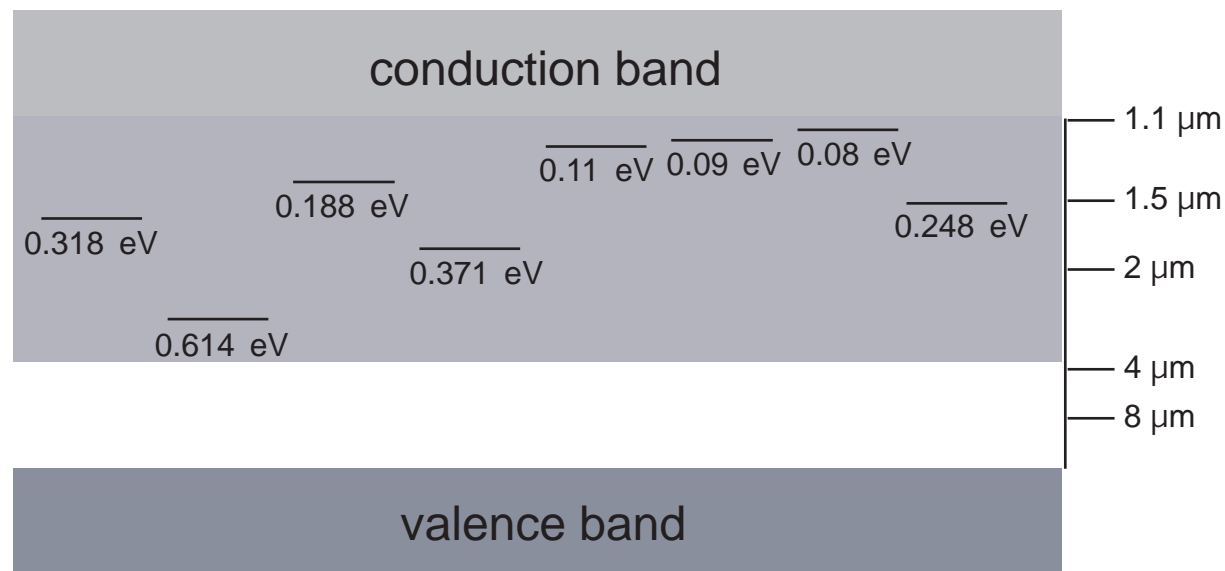
Janzén *et al.*, Phys. Rev. B **29**, 1907 (1984)

at high concentrations, states may broaden into a band

1% S

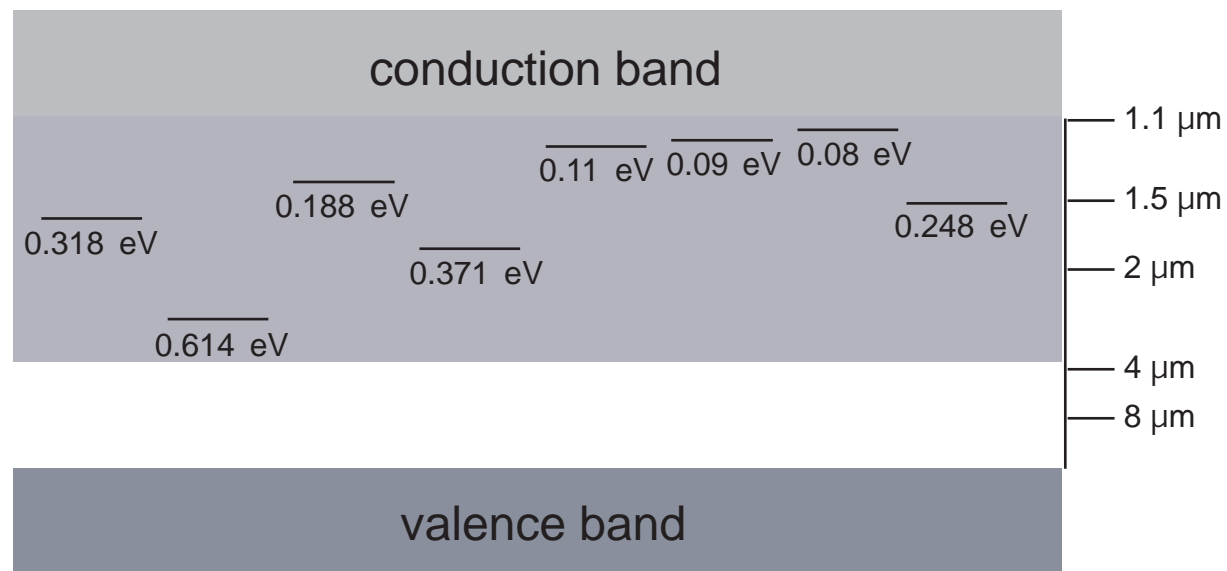


at high concentrations, states may broaden into a band



expect absorption to roughly 3 μm

near-IR transmittance rises around 3 μm



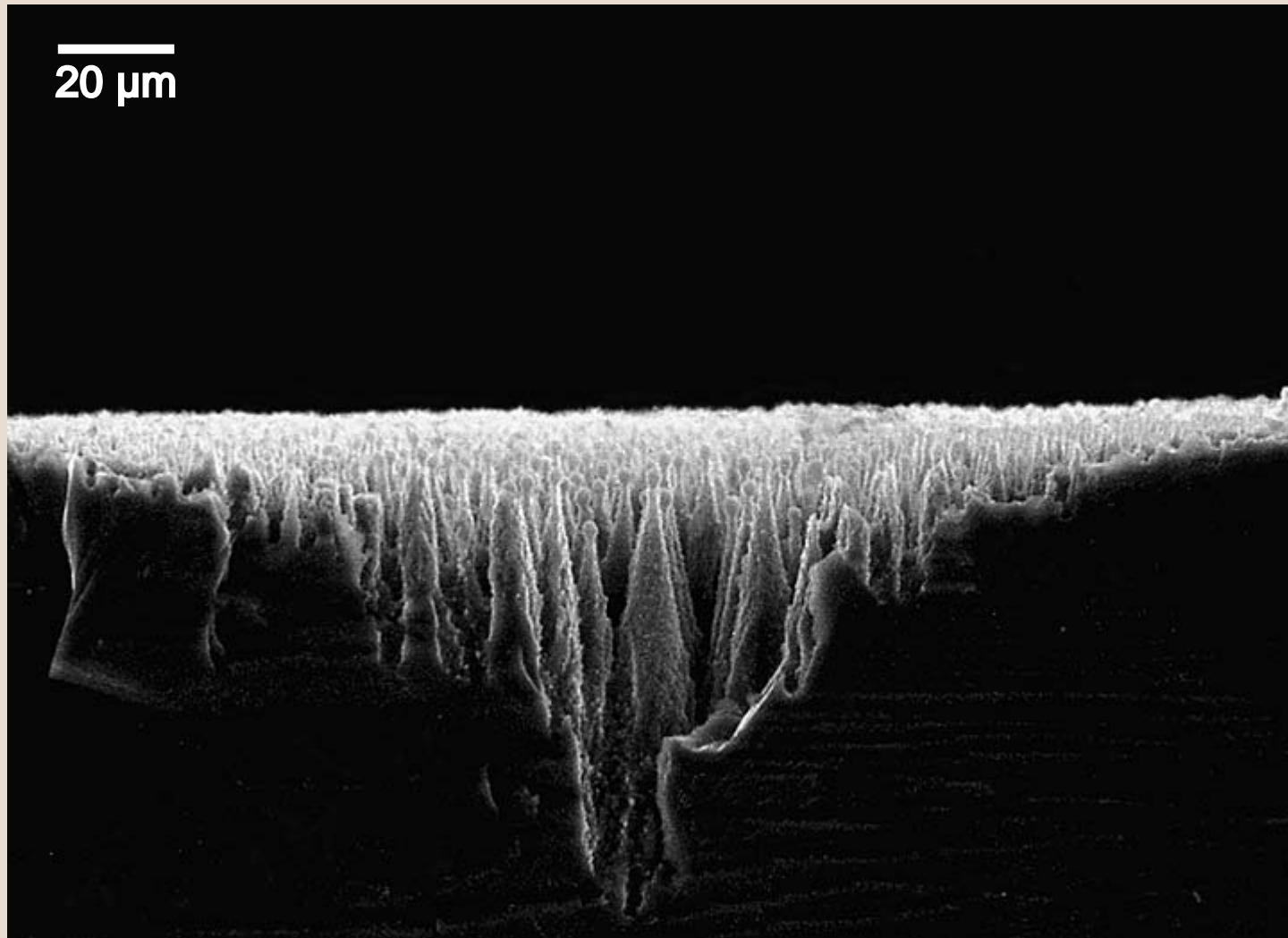
Sulfur a likely explanation:

sulfur required for below-band gap absorption

annealing reduces sulfur and absorption

appropriate wavelength range

What is the underlying structure?



Structural and chemical analysis

1 μm

A cross-sectional transmission electron micrograph (TEM) showing a material with a complex, irregular surface. The surface is characterized by a dark, granular layer, possibly a coating or a reaction product, which is unevenly distributed. The underlying material appears lighter and more uniform. A scale bar in the top left corner indicates a length of 1 μm.

cross-sectional TEM (F. Génin, LLNL)

Structural and chemical analysis

1 μm



This transmission electron micrograph (TEM) shows a cross-section of a material. A scale bar in the top left indicates 1 μm . A central, irregularly shaped region is covered by a dark, textured layer. A circle highlights a portion of this layer, with a line pointing to the label 'porous "fuzz"'. The underlying material appears lighter and more uniform in texture.

porous "fuzz"

cross-sectional TEM (F. Génin, LLNL)

Structural and chemical analysis

1 μm



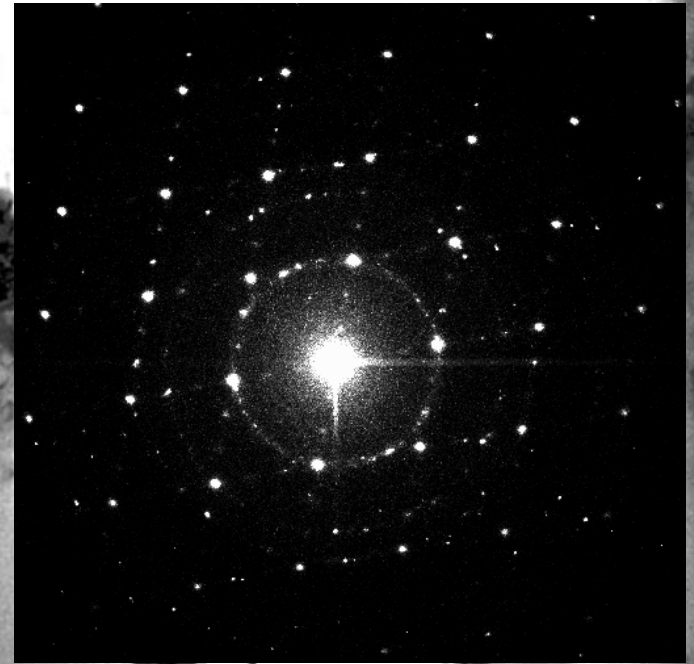
This transmission electron micrograph (TEM) shows a cross-section of a material. The central region is a lighter, more uniform area, while the surrounding regions are darker and more textured. A scale bar in the top left corner indicates a length of 1 μm . A black circle is drawn in the lower part of the central region, and the text 'crystalline Si' is placed above it.

crystalline Si

cross-sectional TEM (F. Génin, LLNL)

Structural and chemical analysis

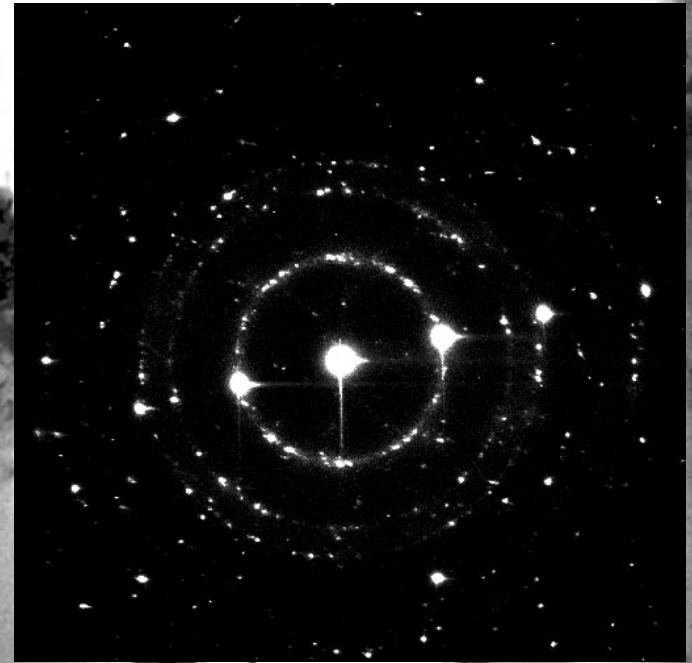
1 μm



electron diffraction (F. Génin, LLNL)

Structural and chemical analysis

1 μm



electron diffraction (F. Génin, LLNL)

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:

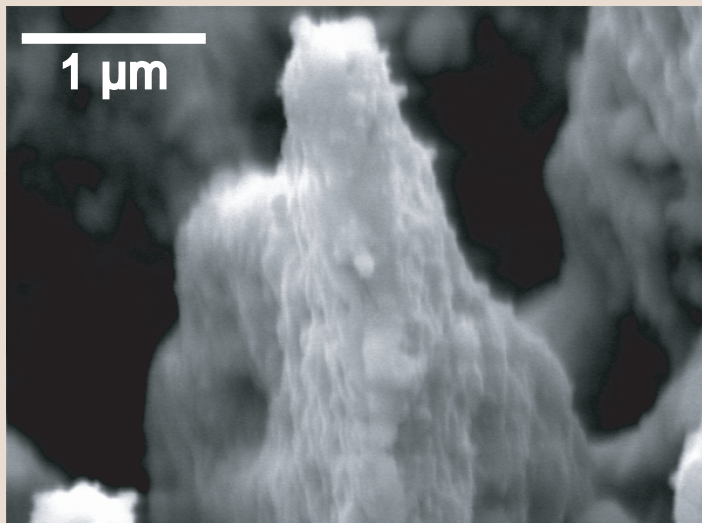
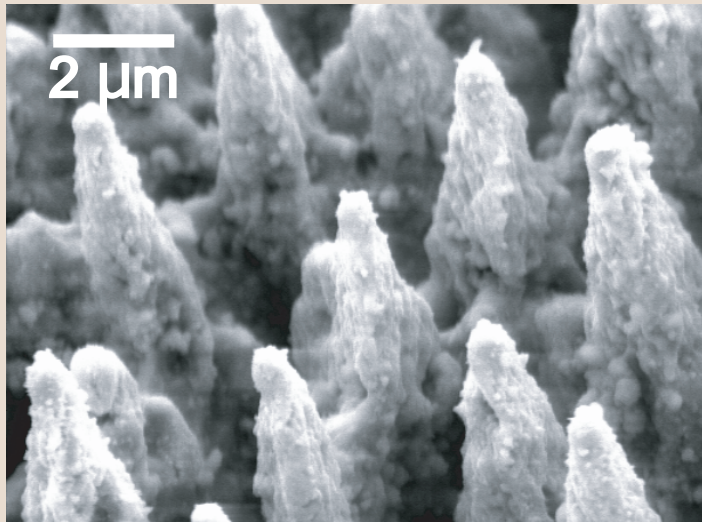
annealing

ns pulses

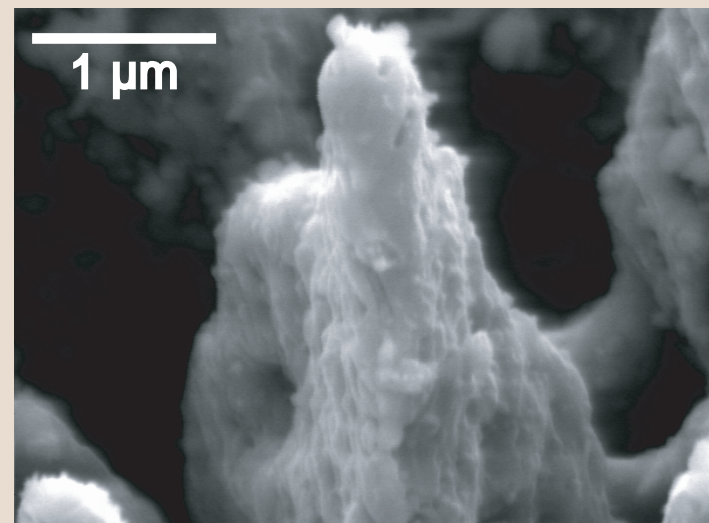
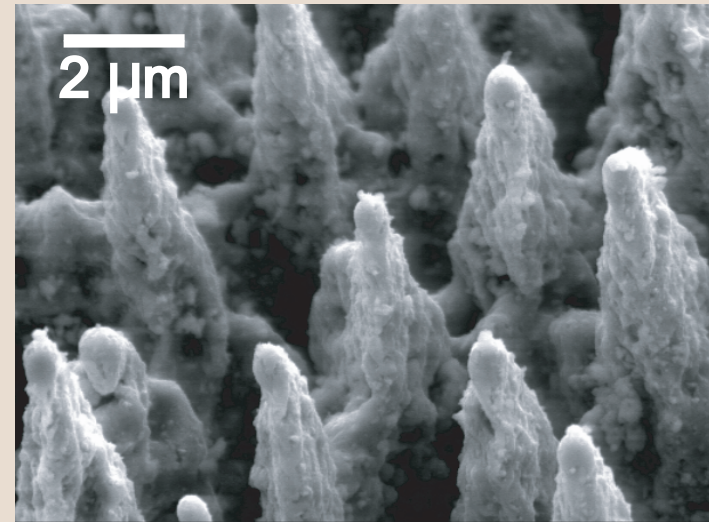
different gases

Structural analysis

before annealing

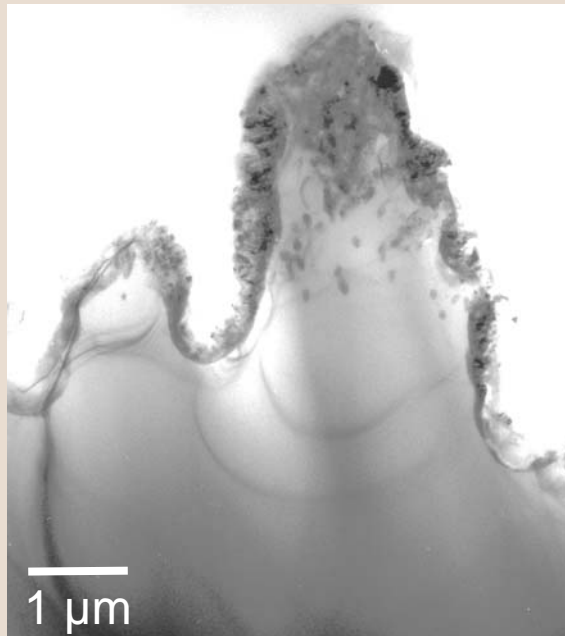


after annealing

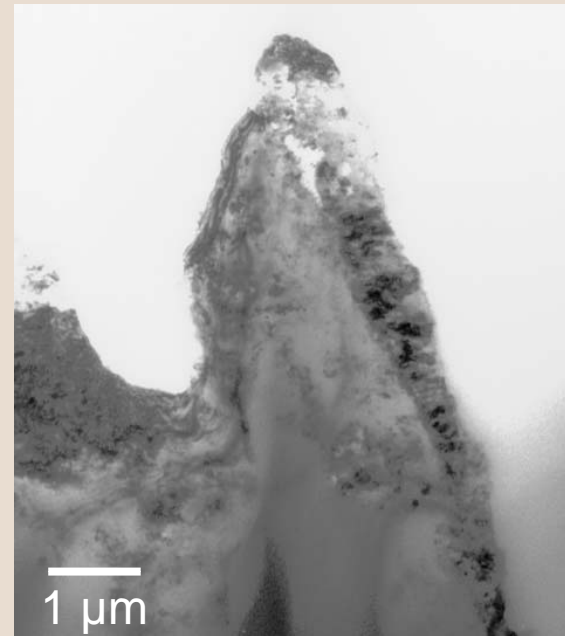


Structural analysis

not annealed



annealed



annealing does not affect visible structure

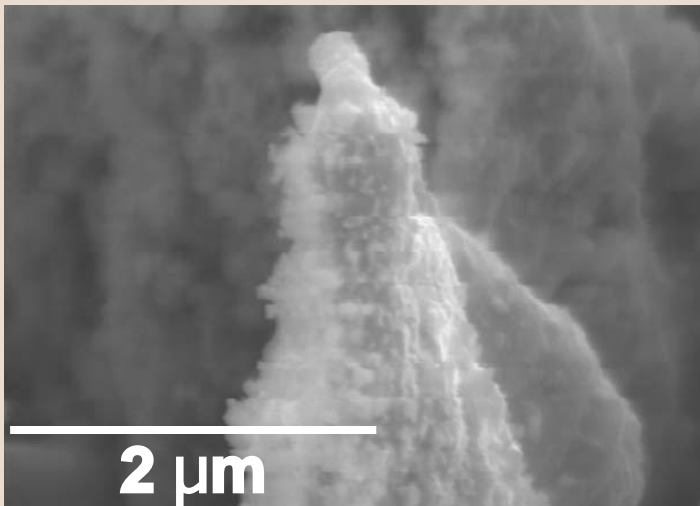
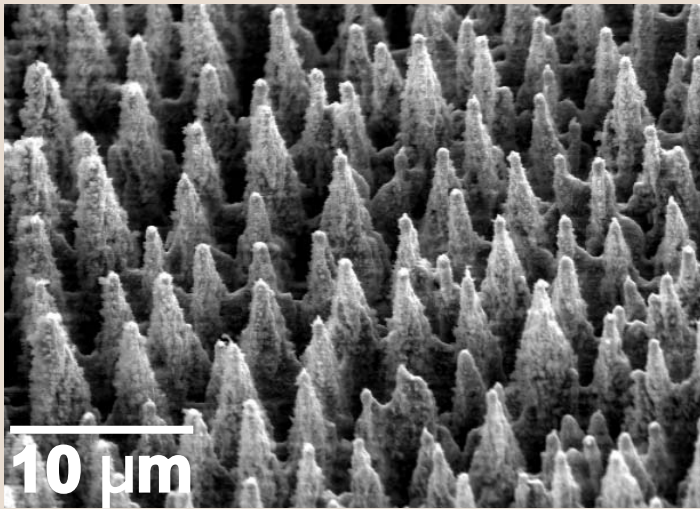
Structure less likely than sulfur:

no evident structural change with annealing
(consistent with multiple reflections in visible)

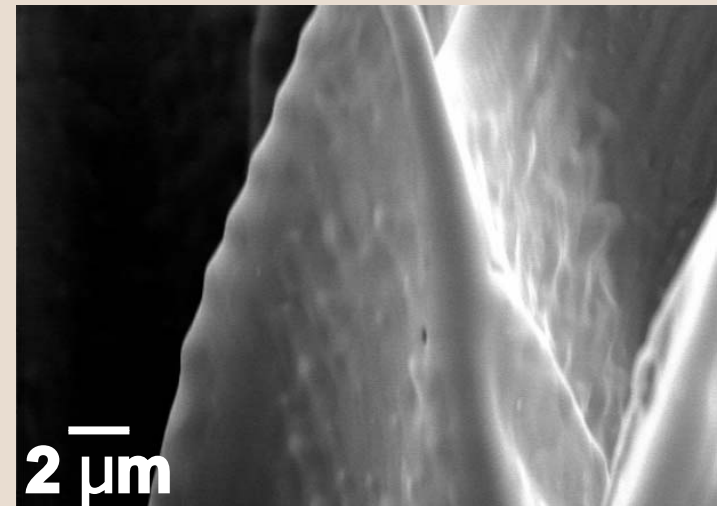
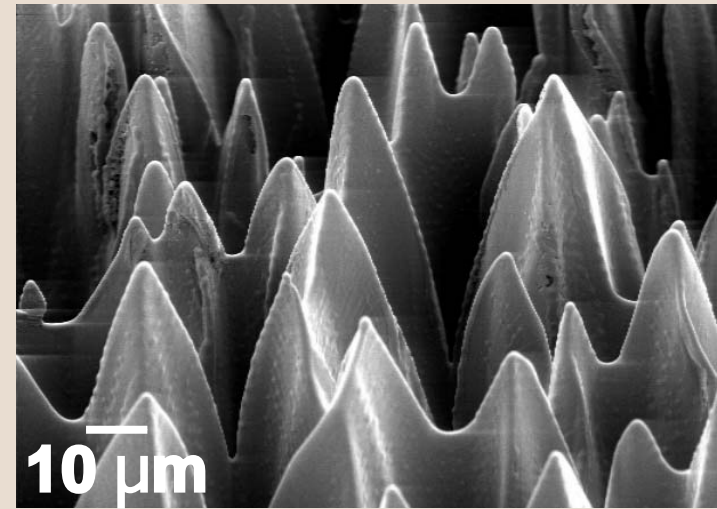
What happens with nanosecond pulses?

Nanosecond vs femtosecond

800 nm, 100 fs, 10 kJ/m²

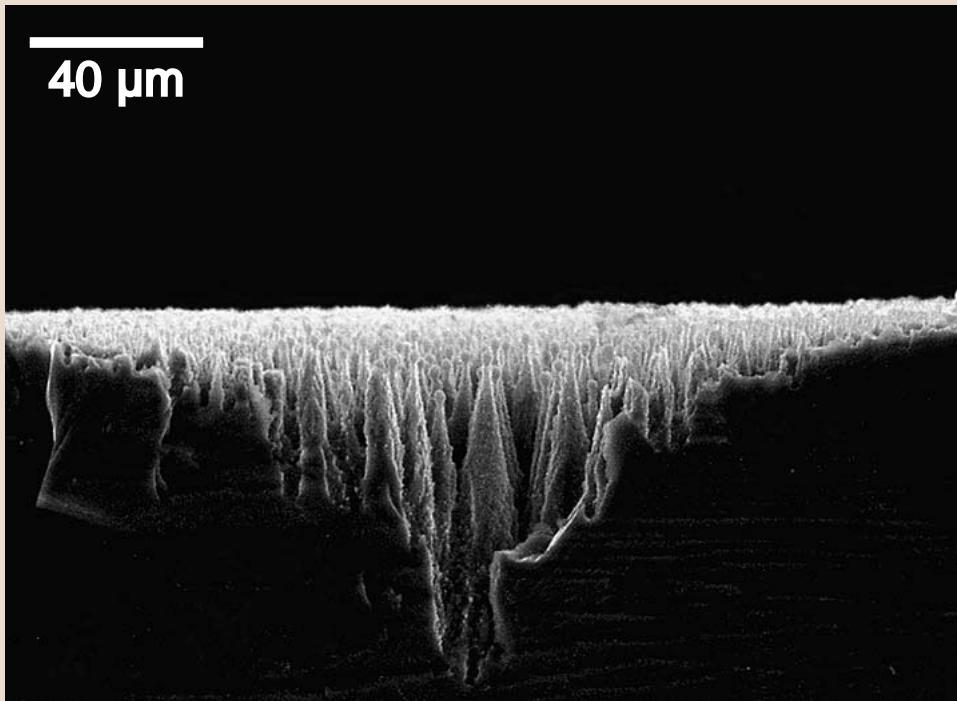


248 nm, 30 ns, 30 kJ/m²



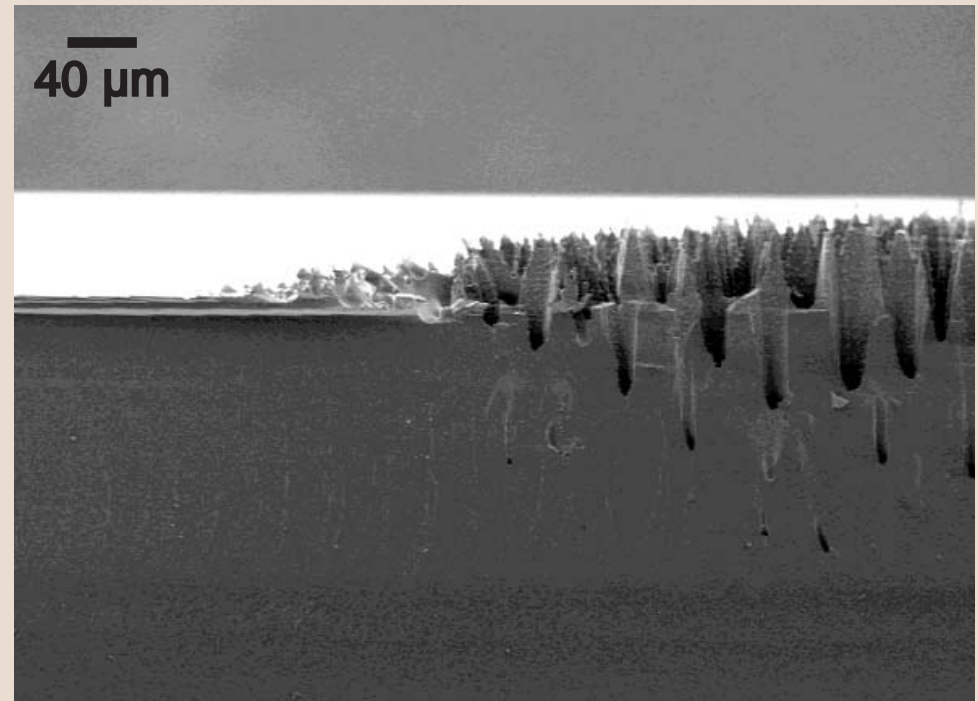
Nanosecond vs femtosecond

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

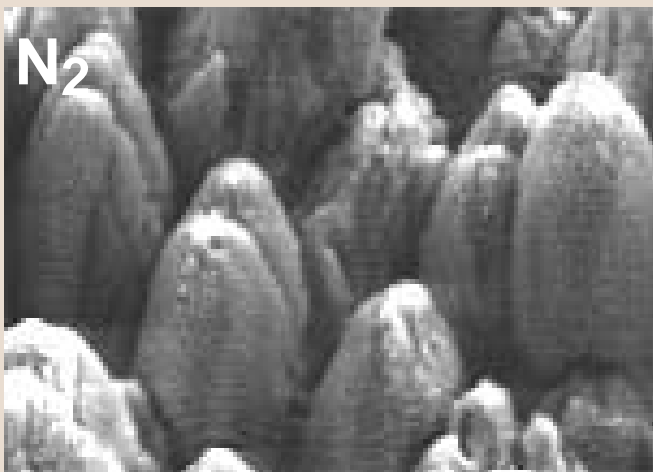
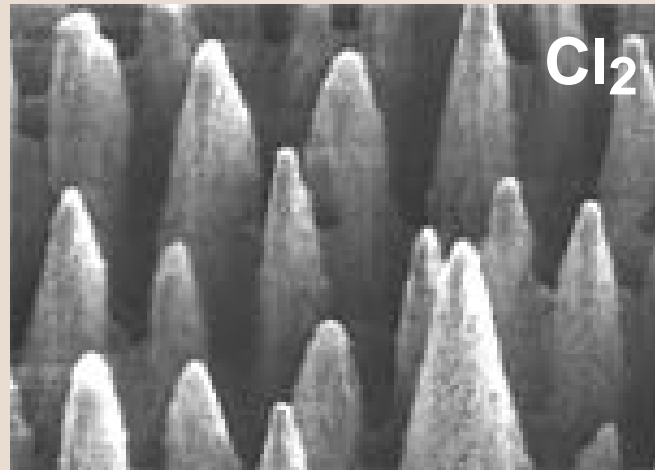
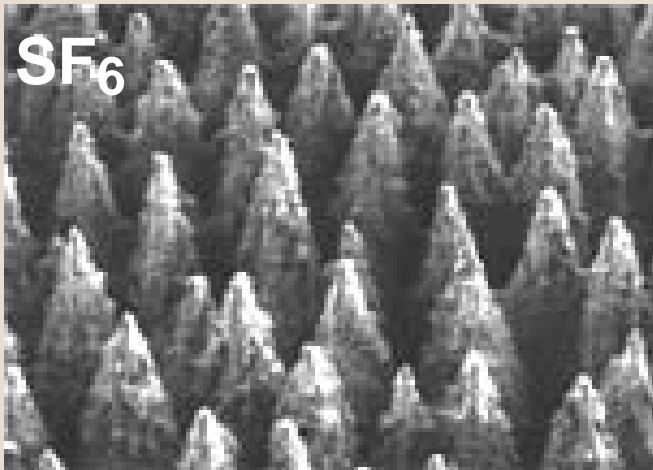
Sulfur content very similar

Structure less likely than sulfur:

no evident structural change with annealing

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

Structural analysis

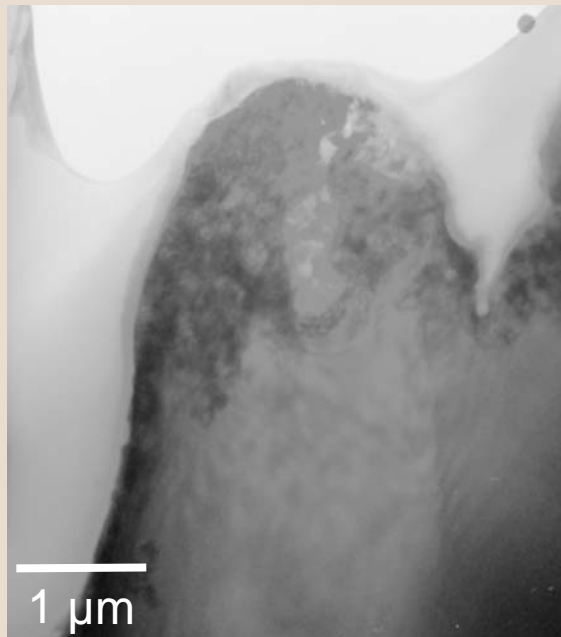


10 μm

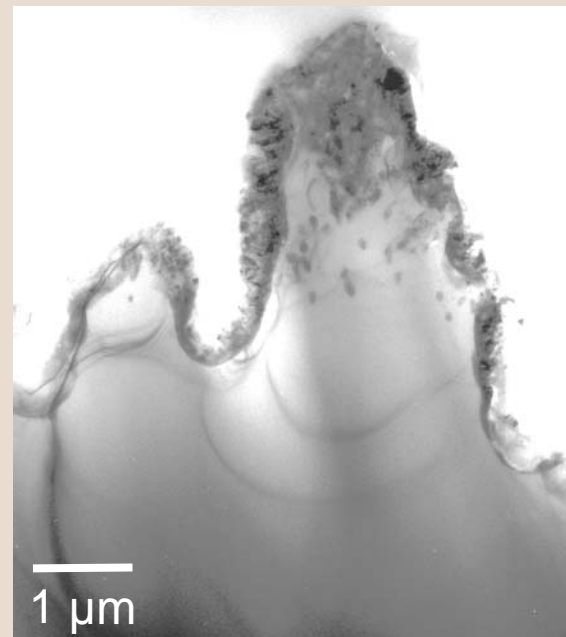
all except Cl₂ show surface nanostructure

Structural analysis

air



SF₆



surface disorder present in air sample

Structure less likely than sulfur:

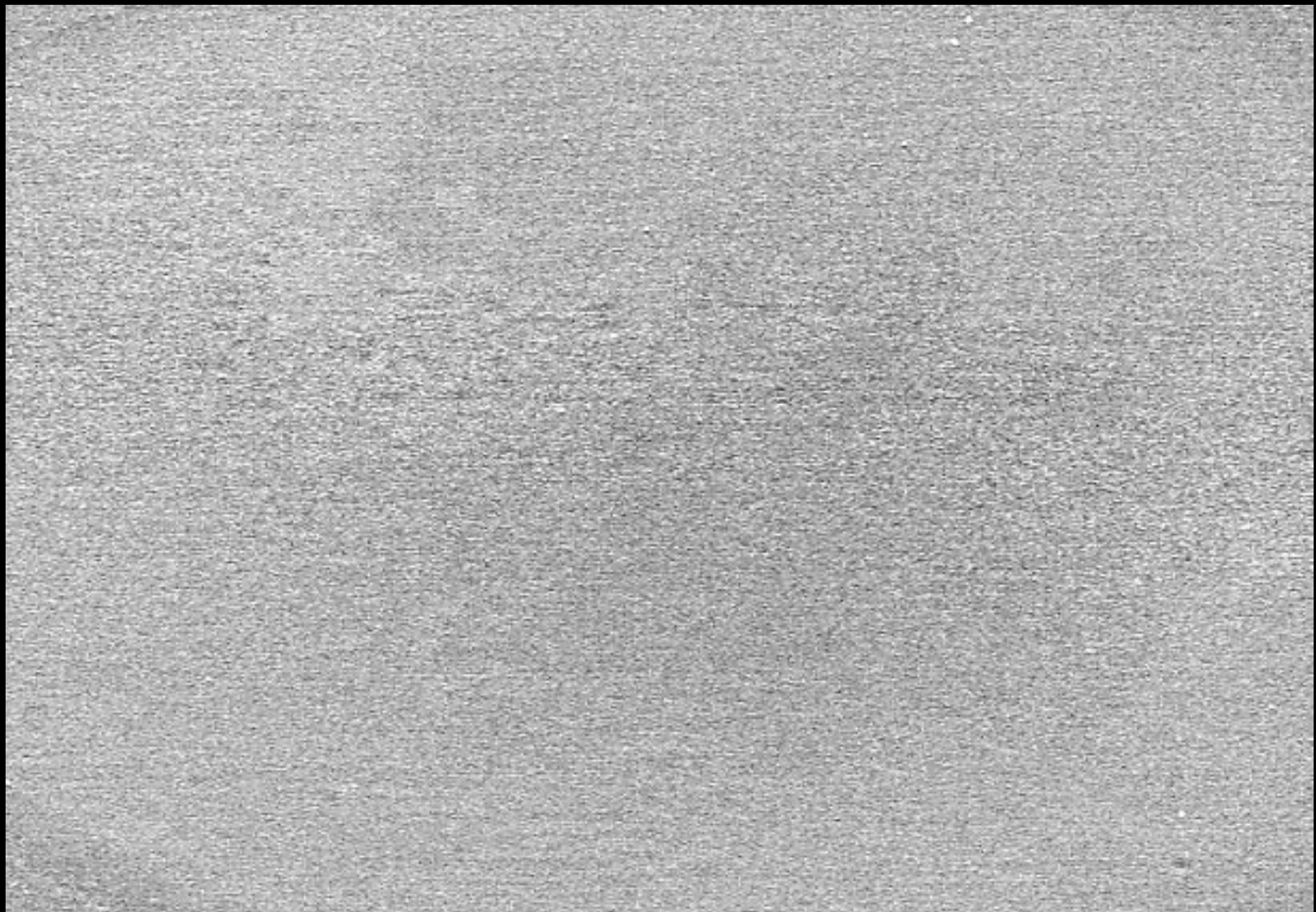
no evident structural change with annealing
ns pulses produce very different structure,
same composition and optical properties
different gases all produce nanostructures

Summary of optical properties

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

A scanning electron micrograph (SEM) showing a surface with a series of vertical, parallel ridges. Each ridge is topped with a smooth, spherical protrusion. The ridges themselves have a rough, textured appearance. The background is dark and recessed between the ridges.

How do the microstructures form?



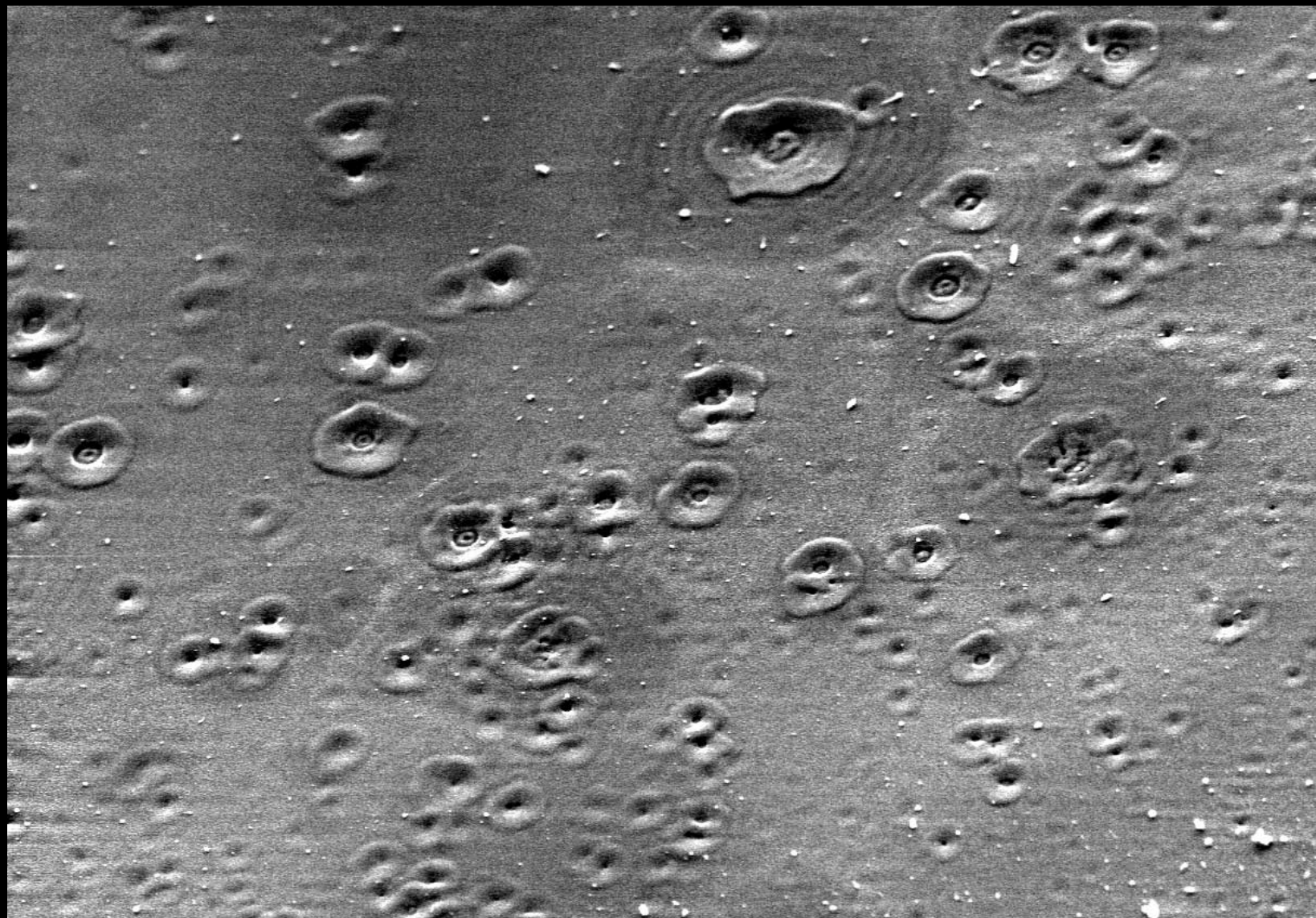
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0000



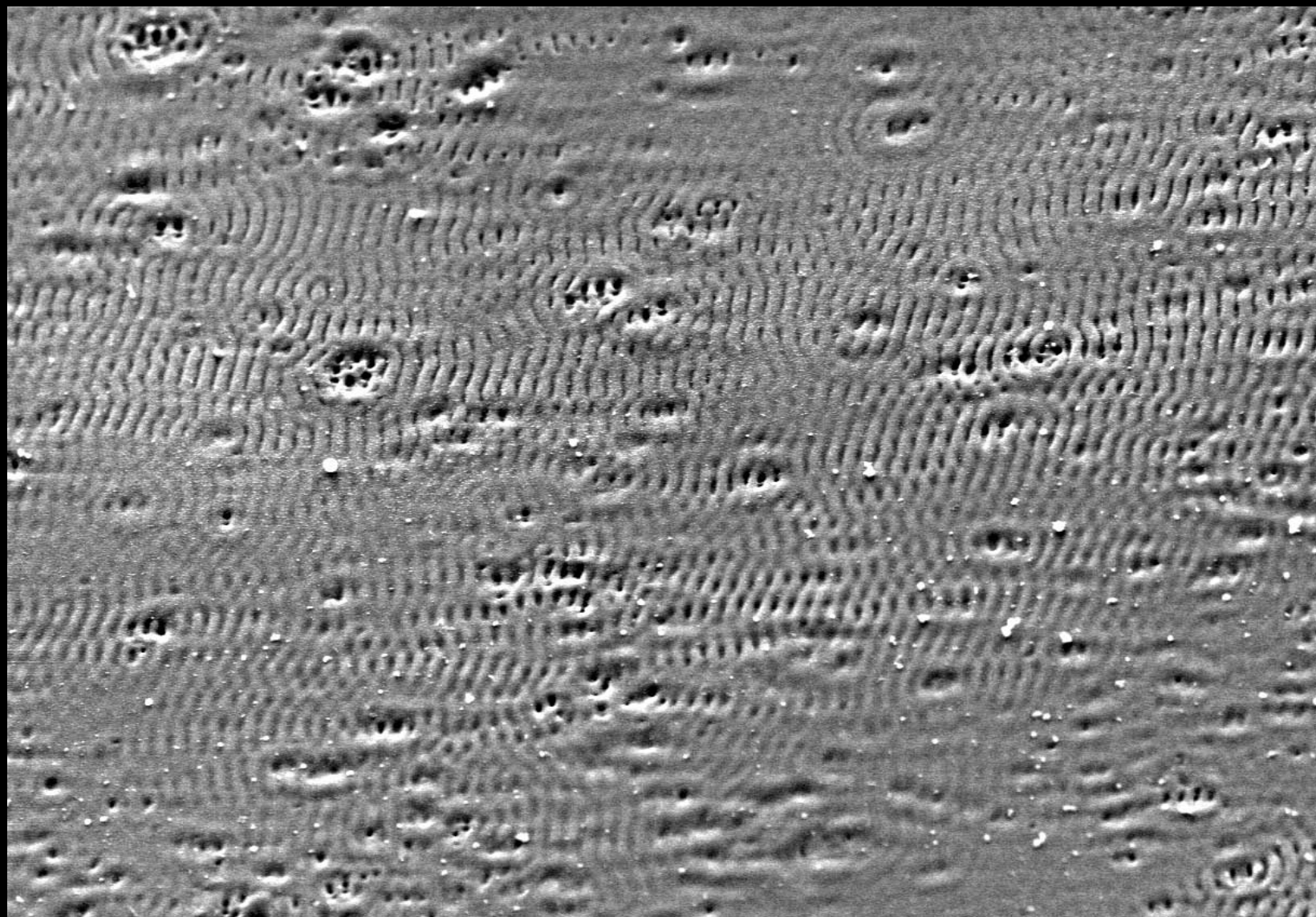
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0001



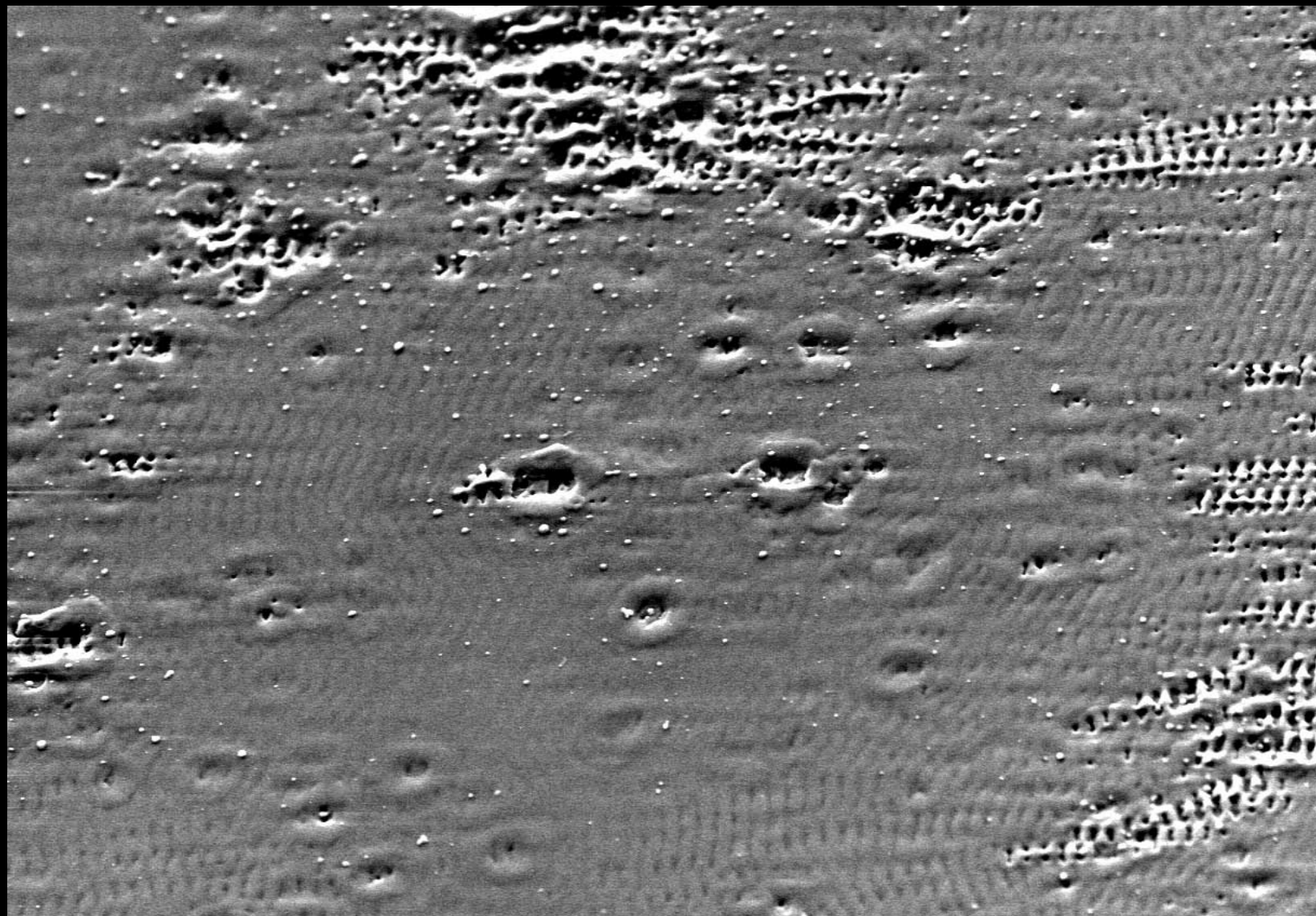
x2000
#3548
512 x 480

20 μm

10kV

15mm

0002



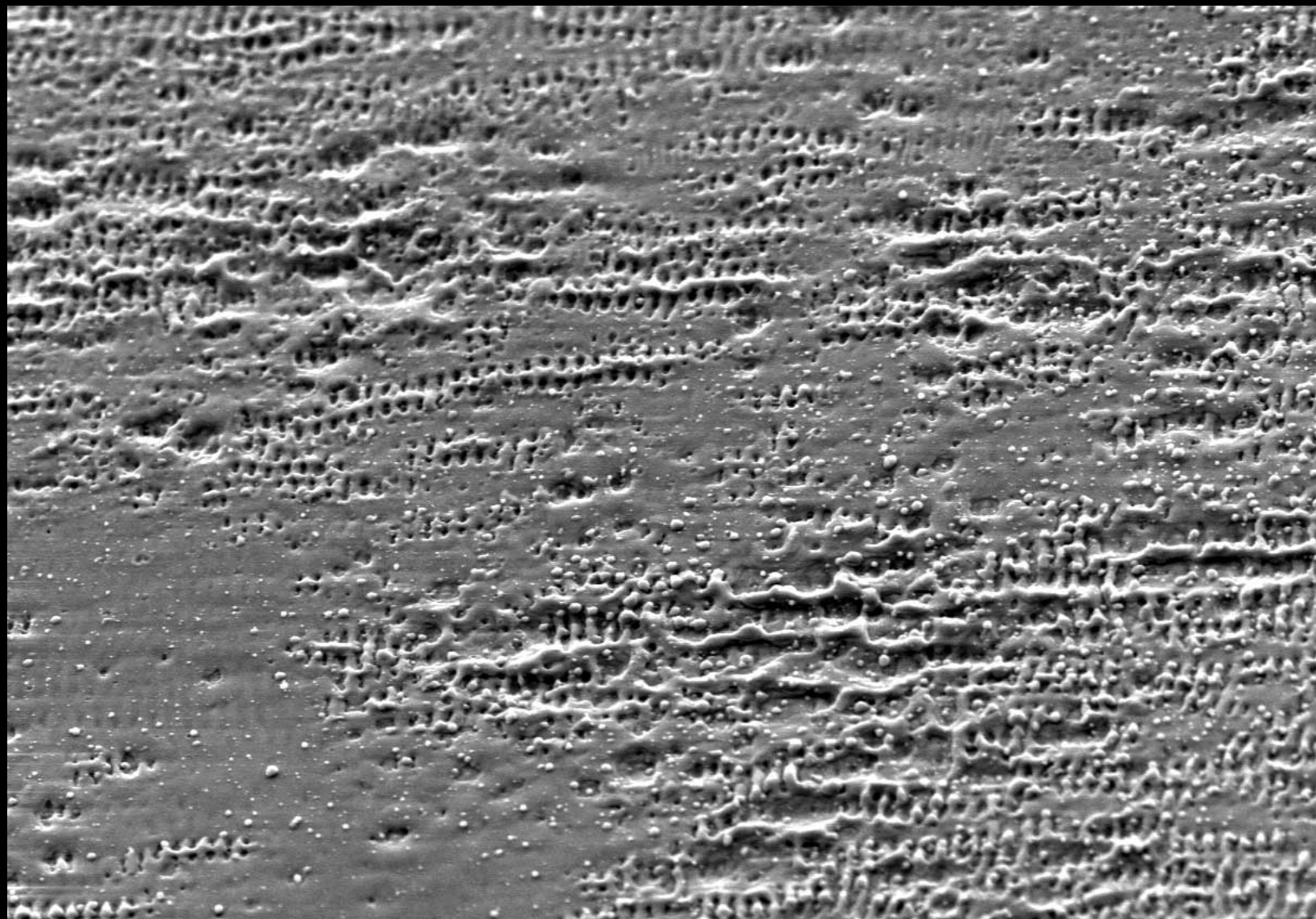
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0003



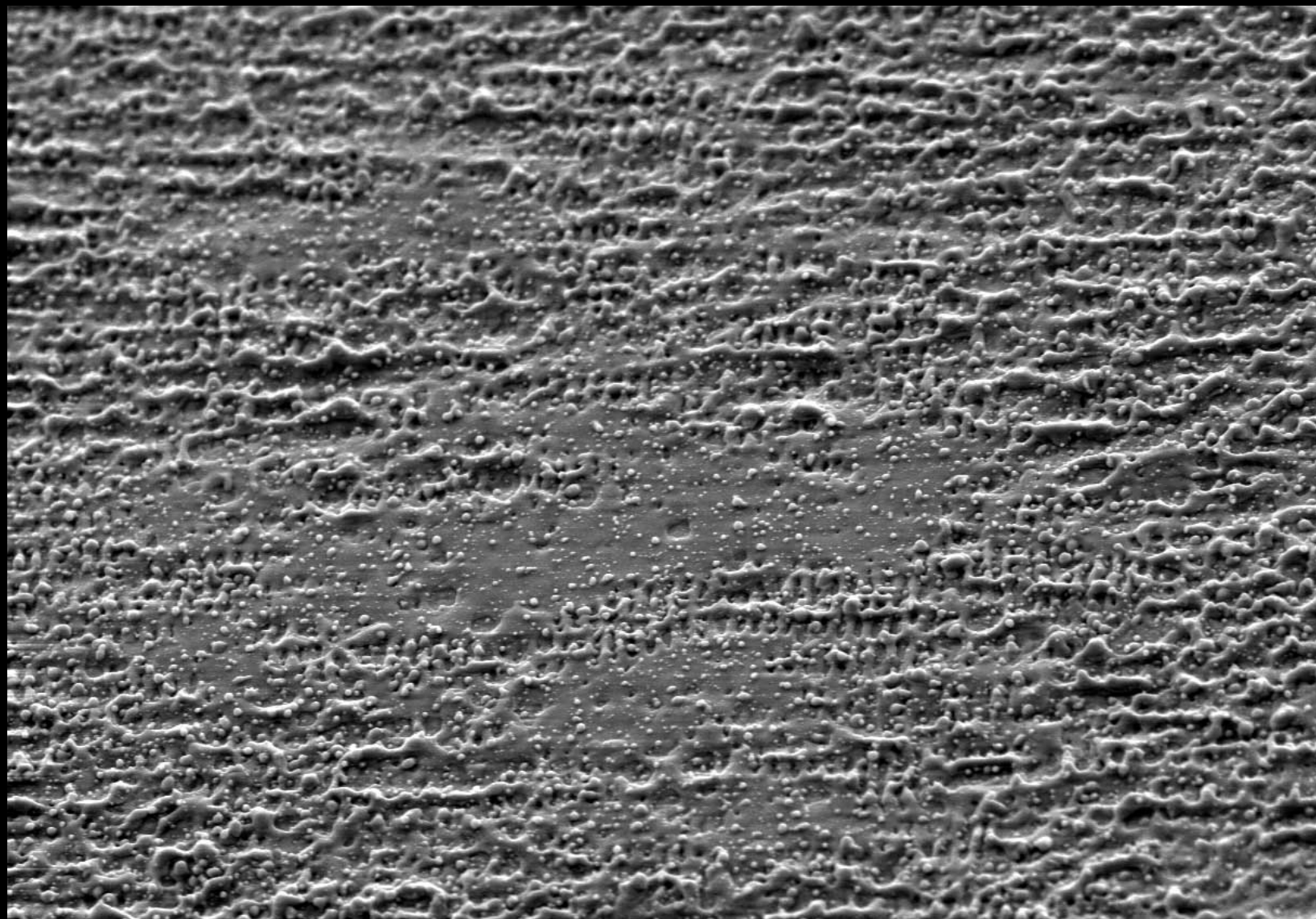
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0004



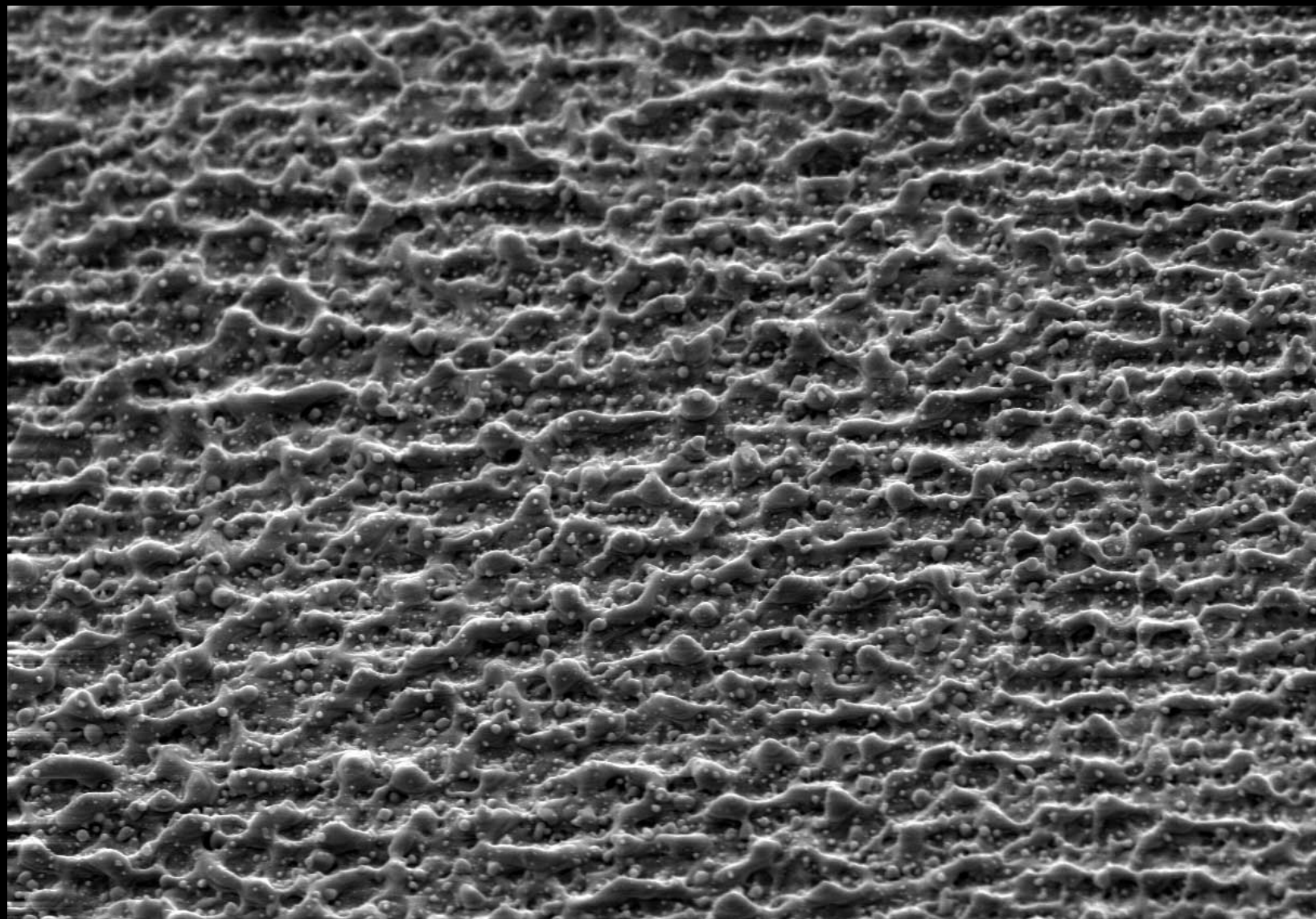
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0005



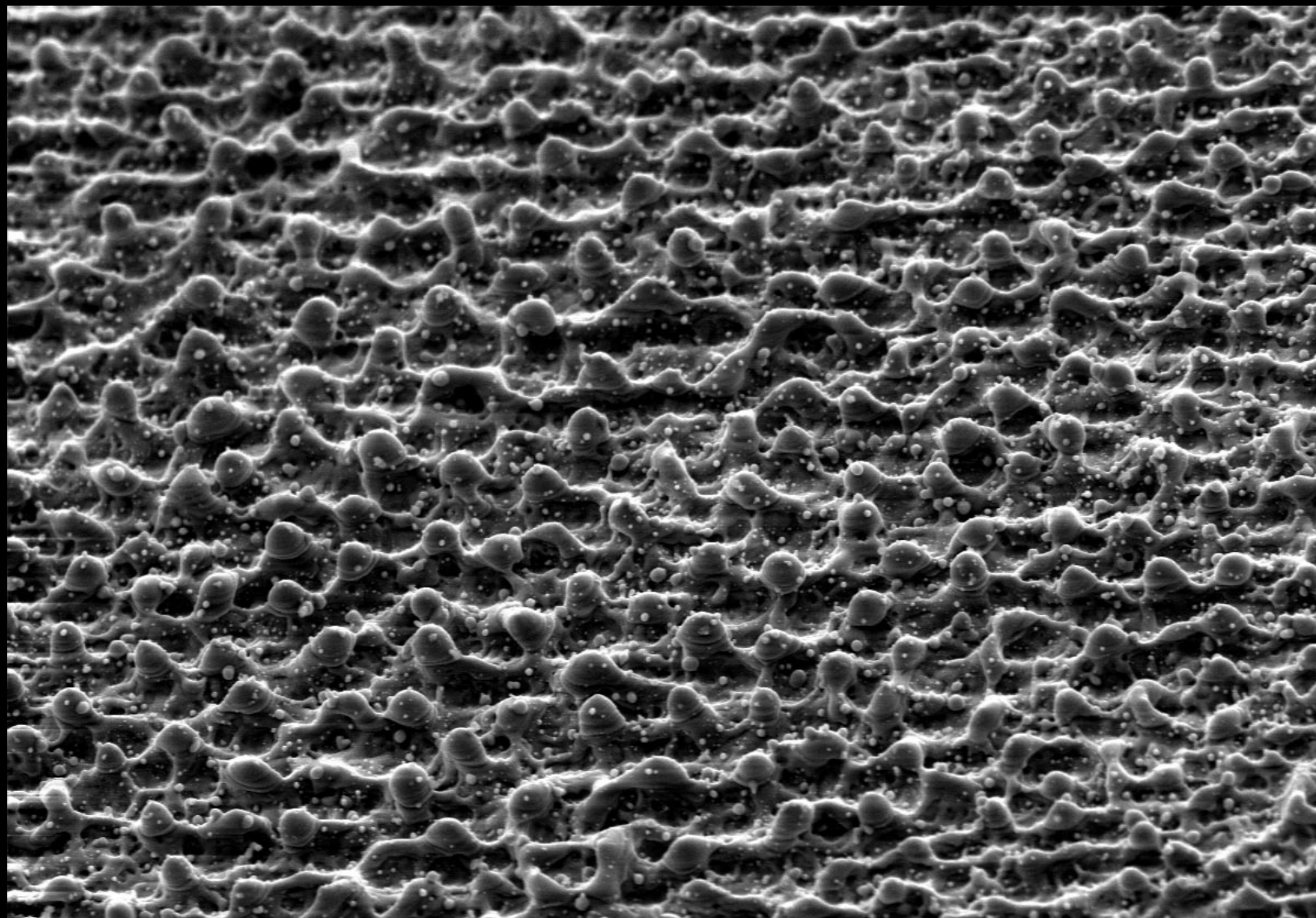
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0008



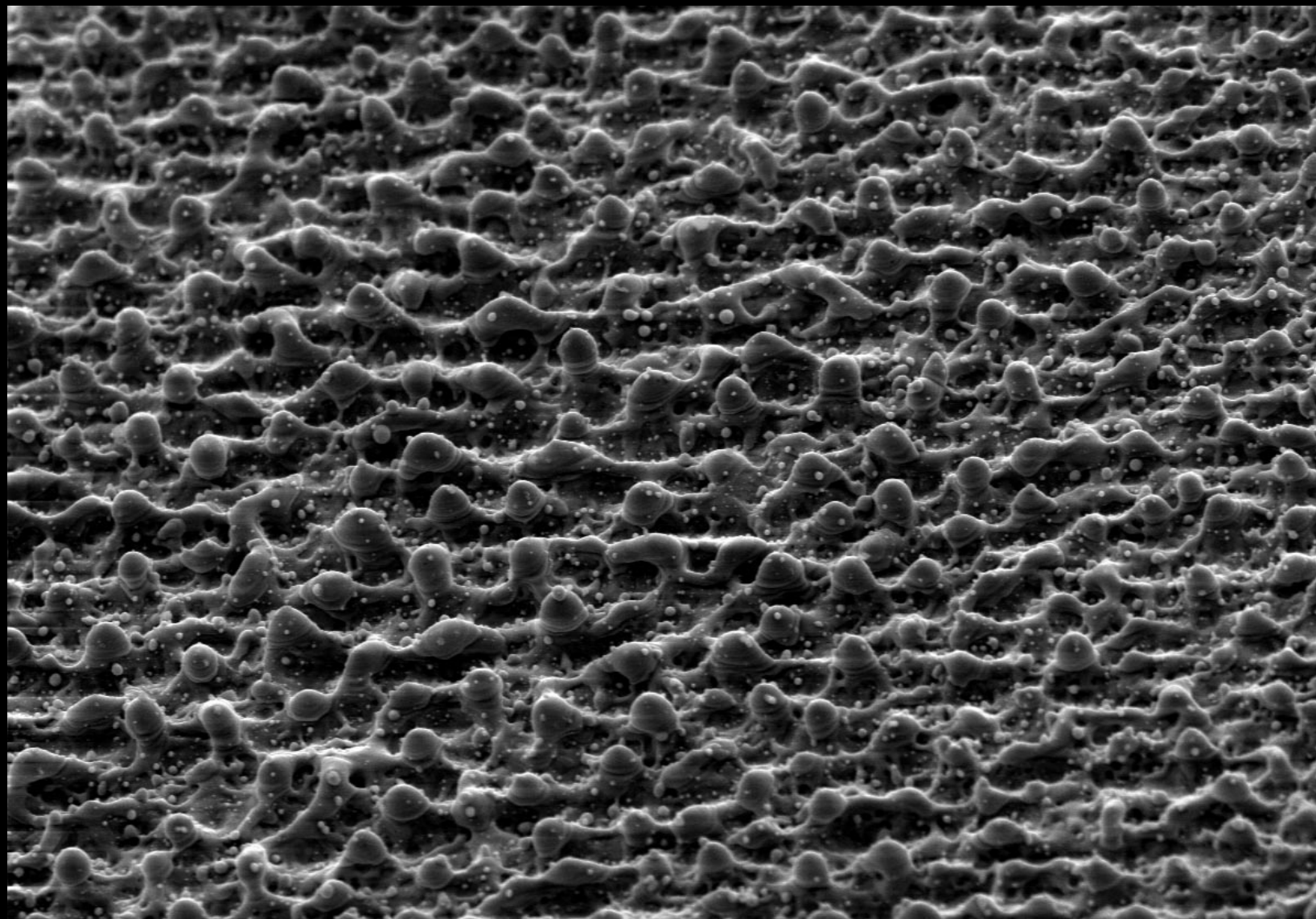
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0010



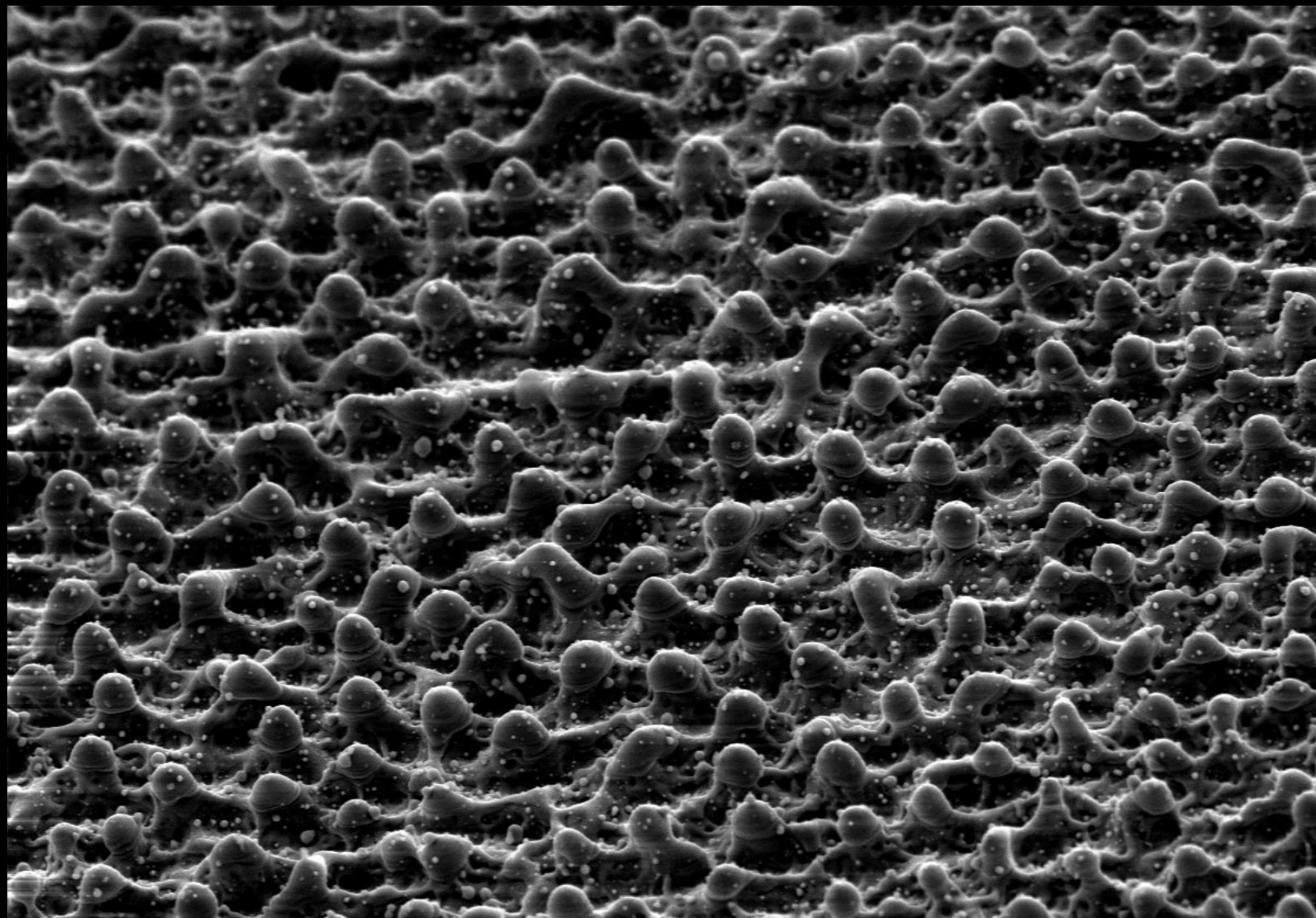
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0012



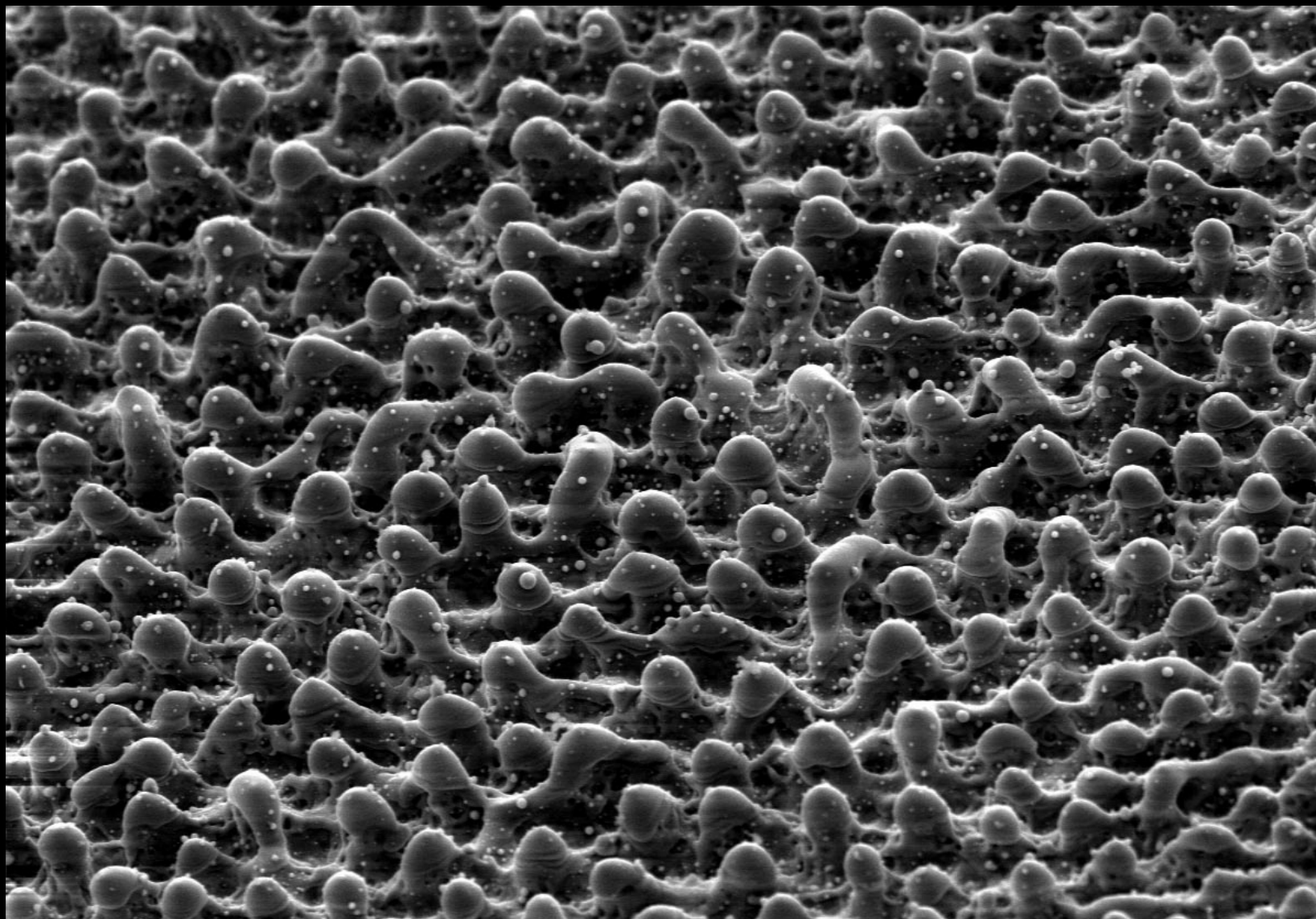
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0015



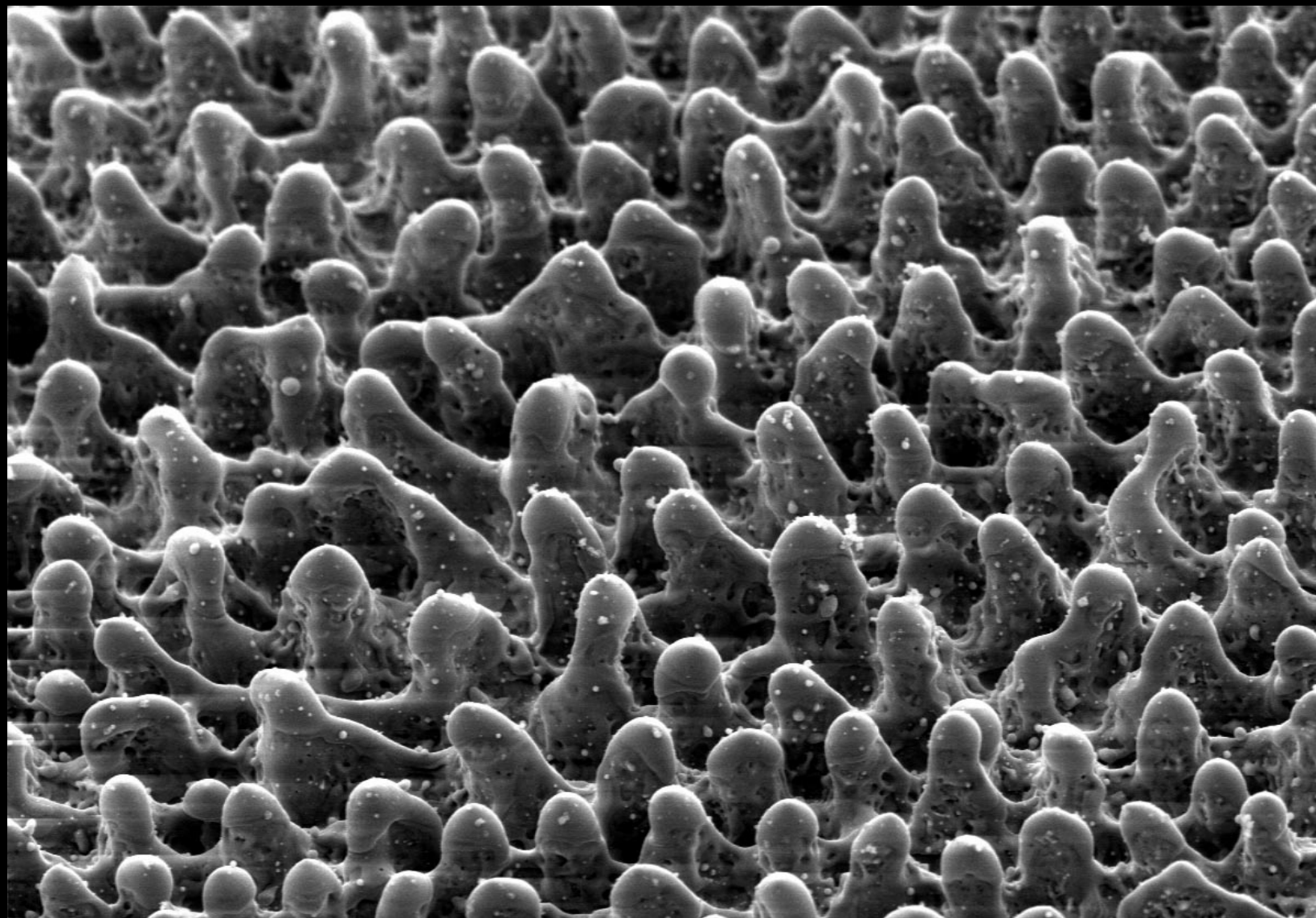
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0020



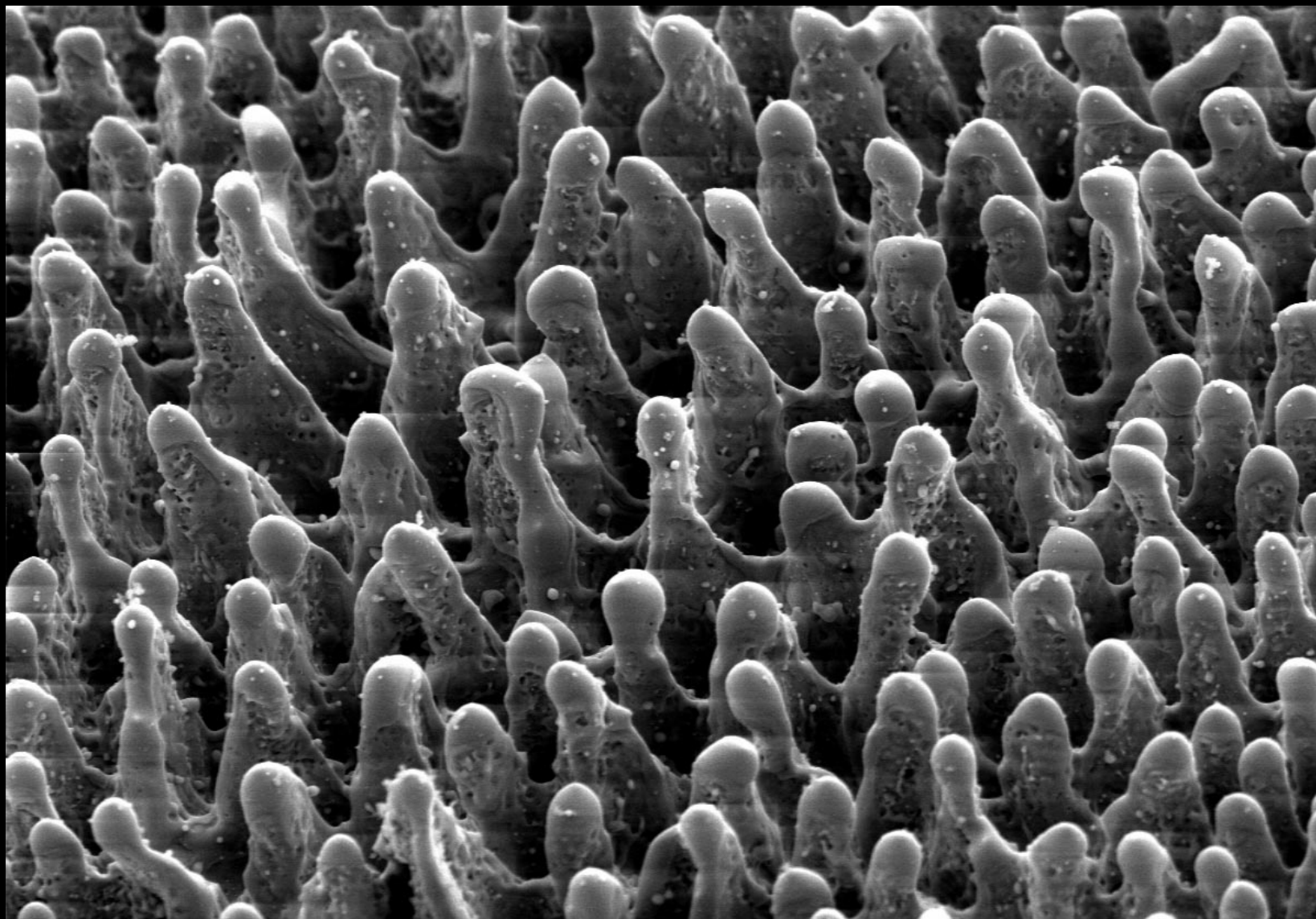
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0030



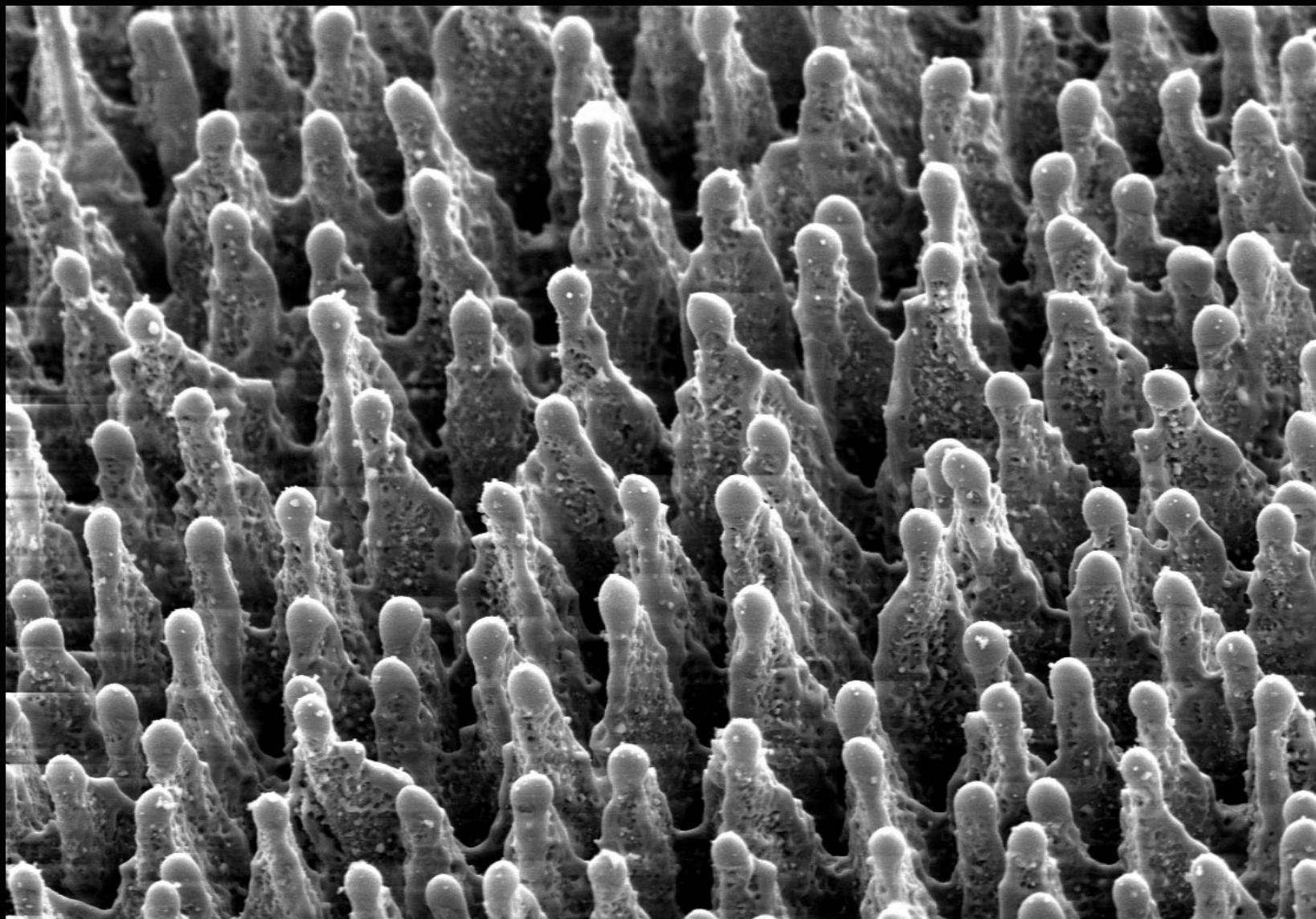
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0050



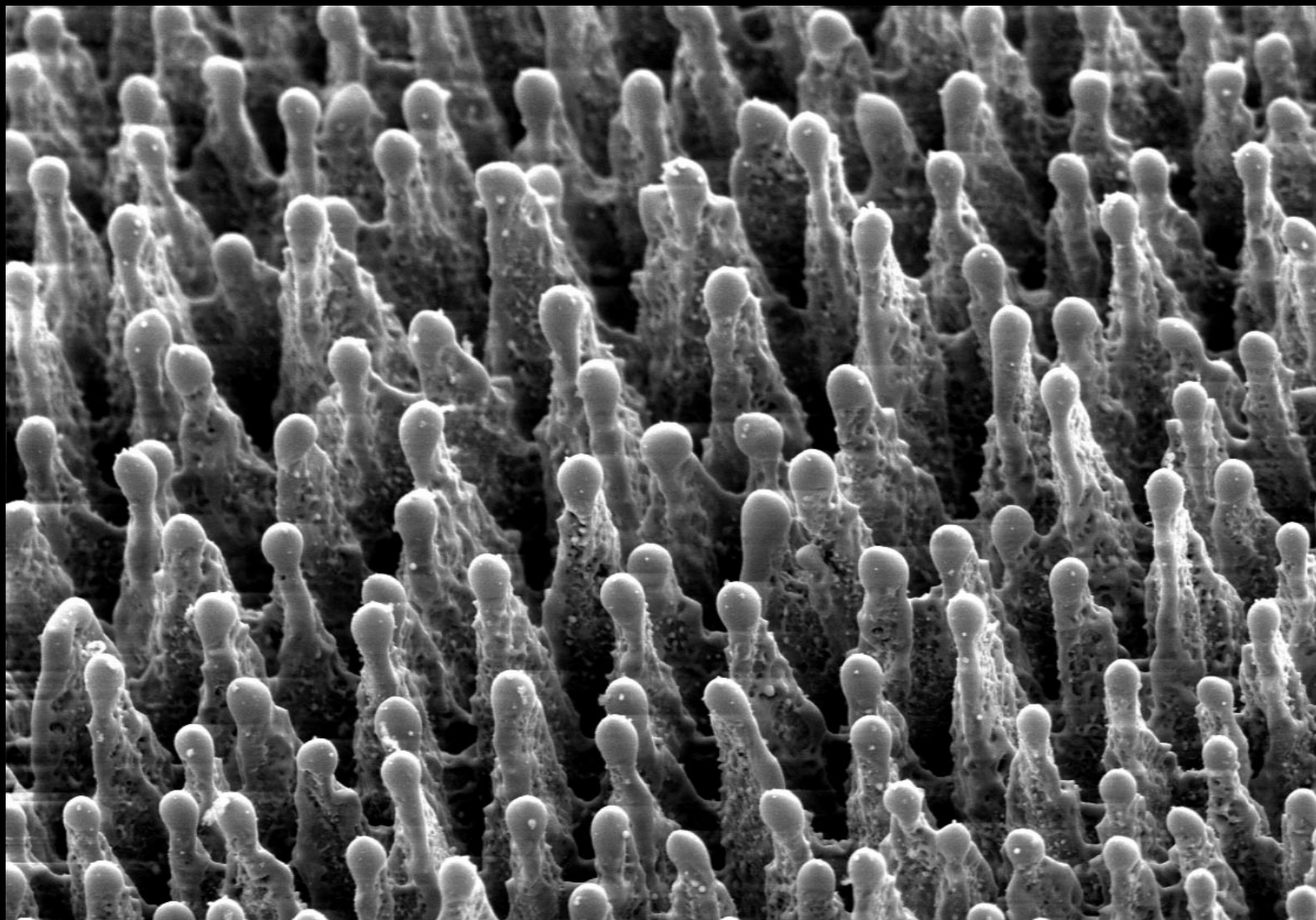
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0070



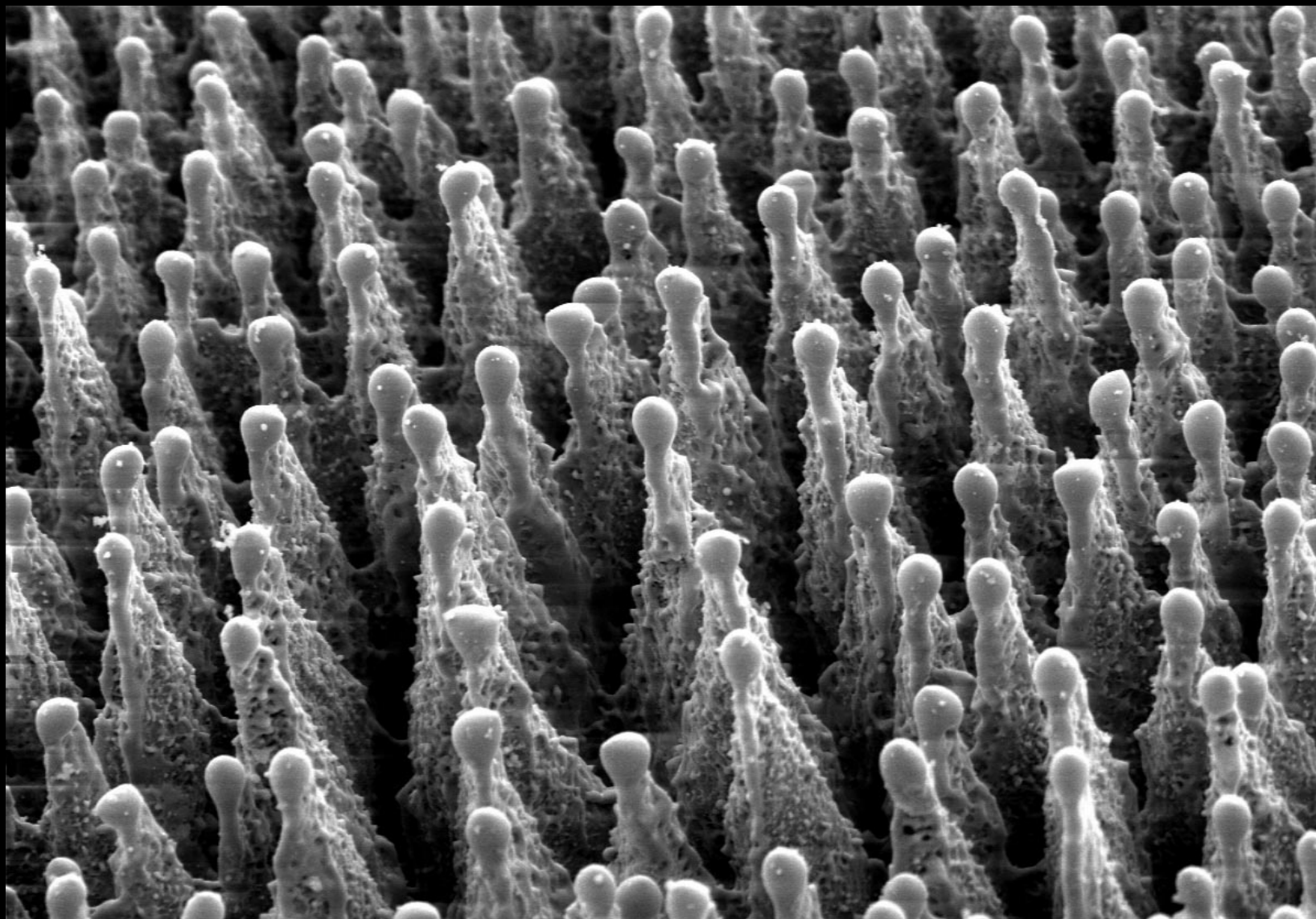
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0100



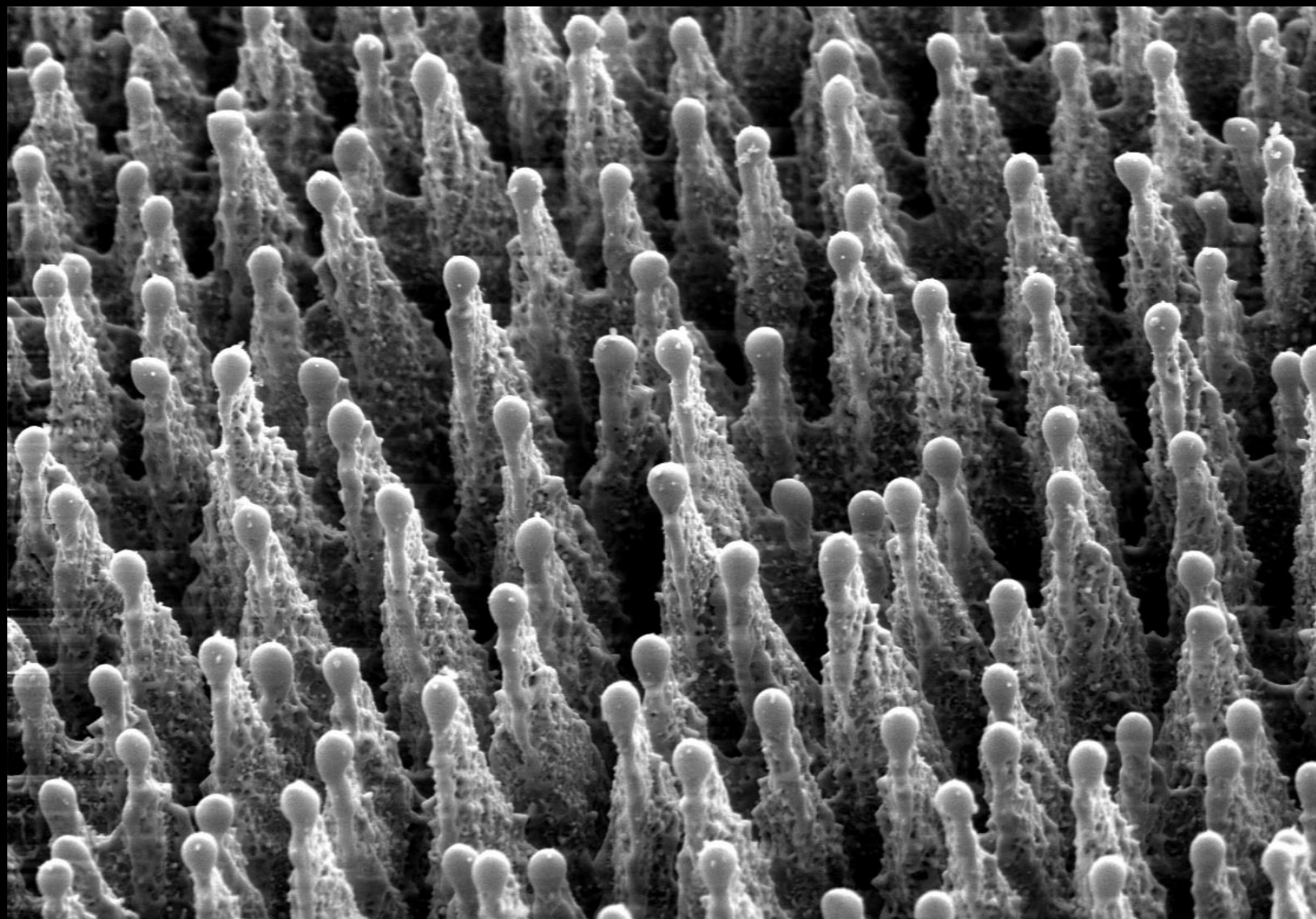
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0200



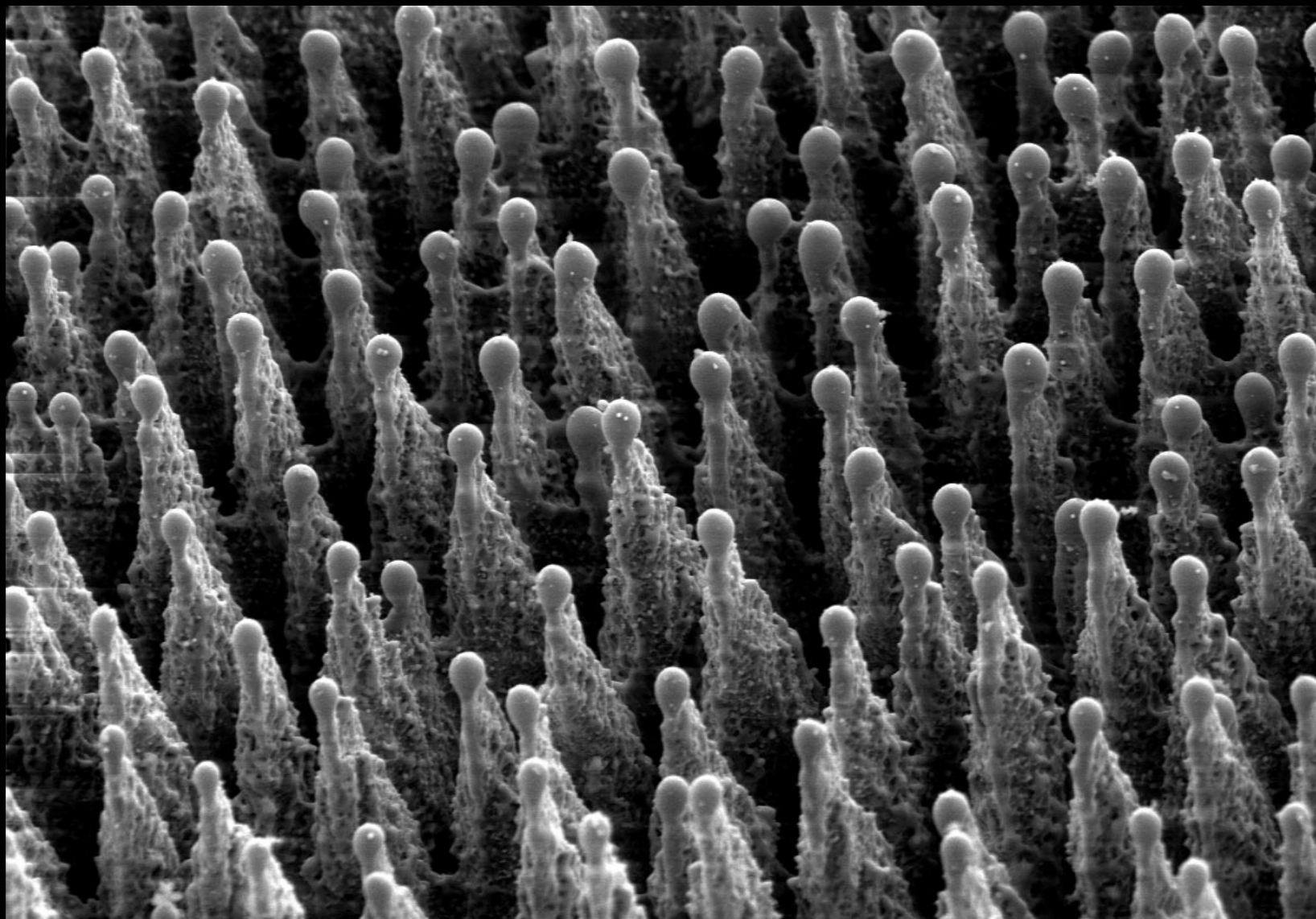
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0400



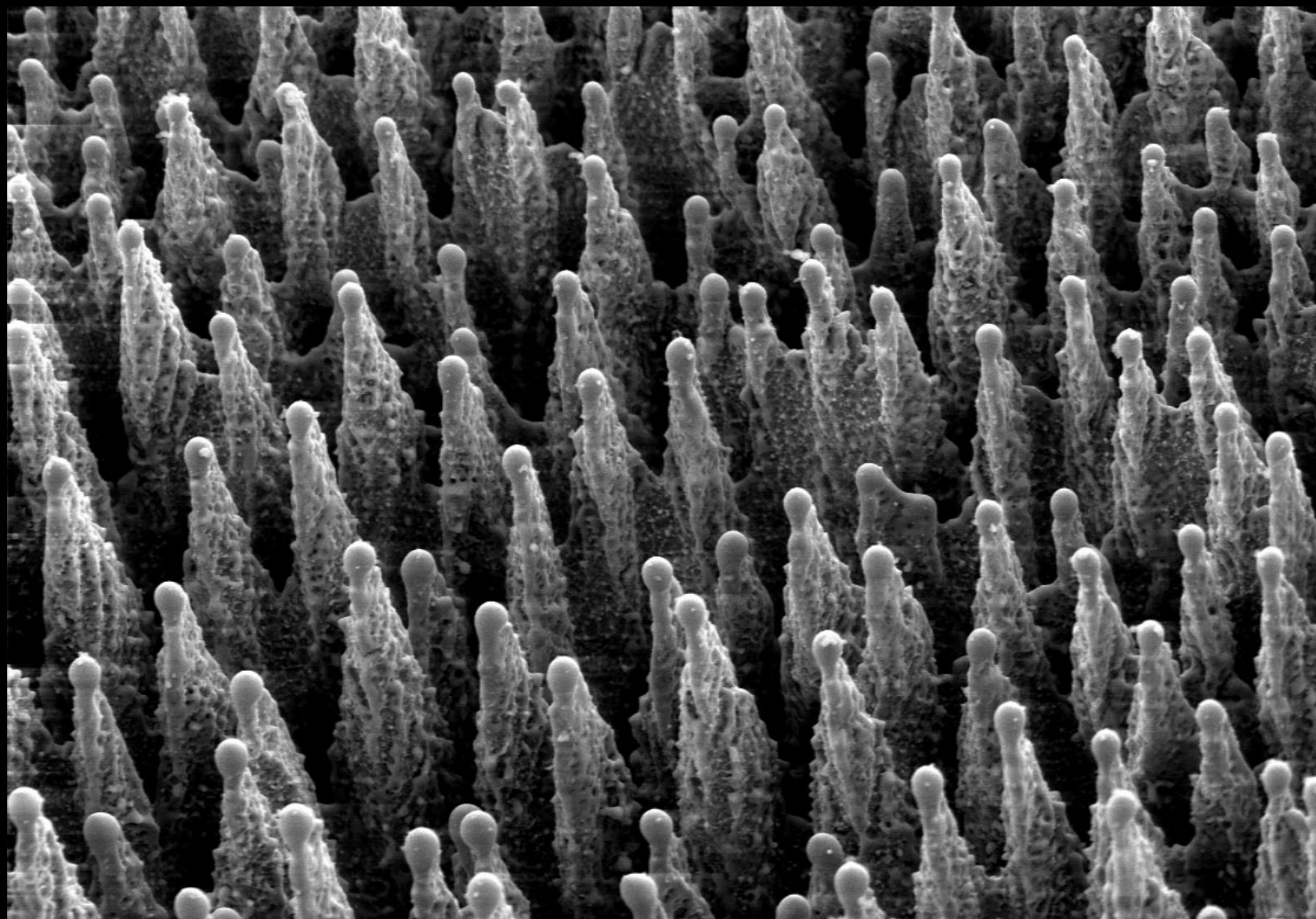
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0600



x2000
#3548
512 x 480

20 μ m

10kV

15mm

1000

How do ripples give way to spikes?

Follow evolution of spatial frequencies

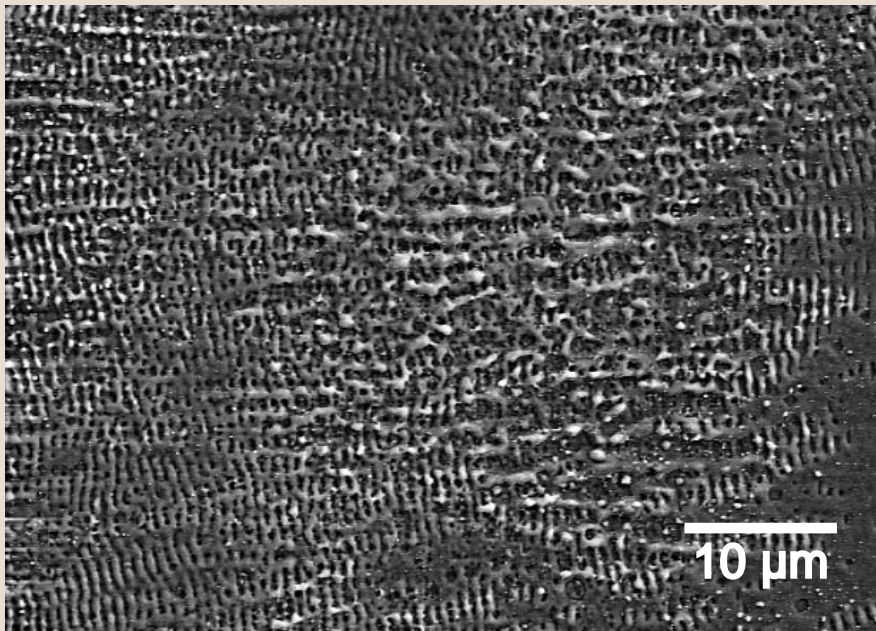
- ▶ vary number of laser pulses
- ▶ calculate Fourier transform of images

Formation process

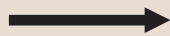
ripples

SF_6

2 pulses



laser polarization

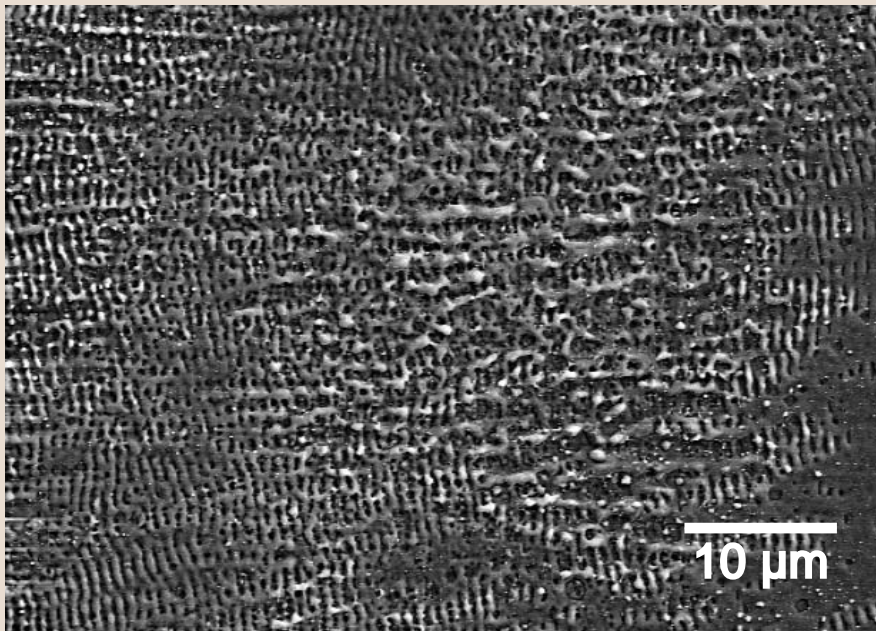


Formation process

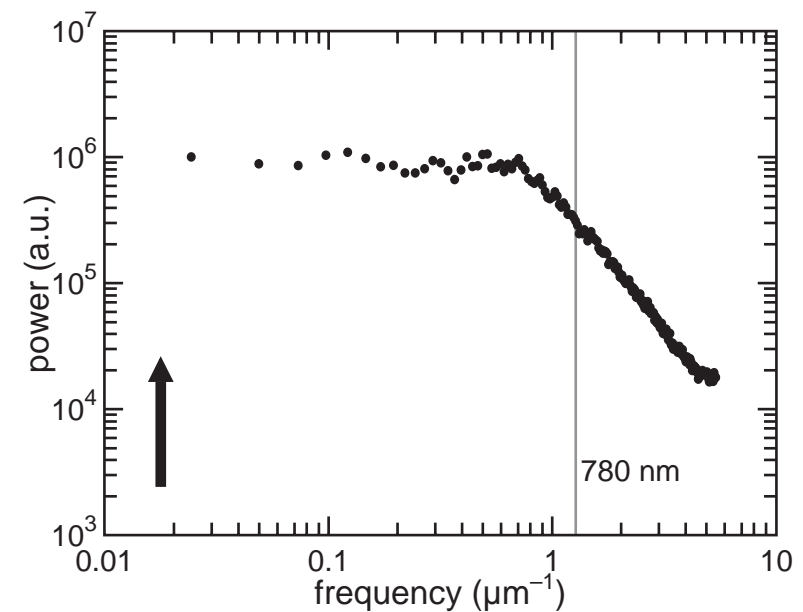
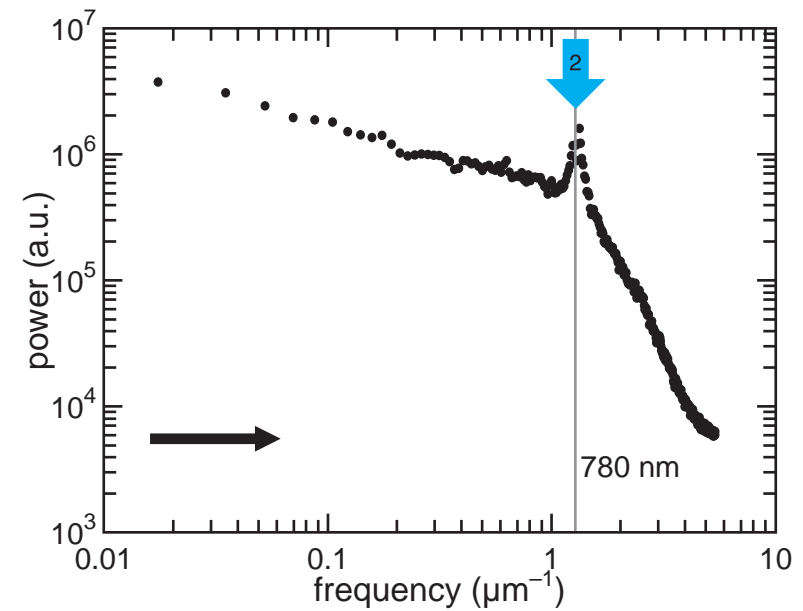
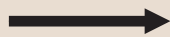
ripples

SF_6

2 pulses



laser polarization

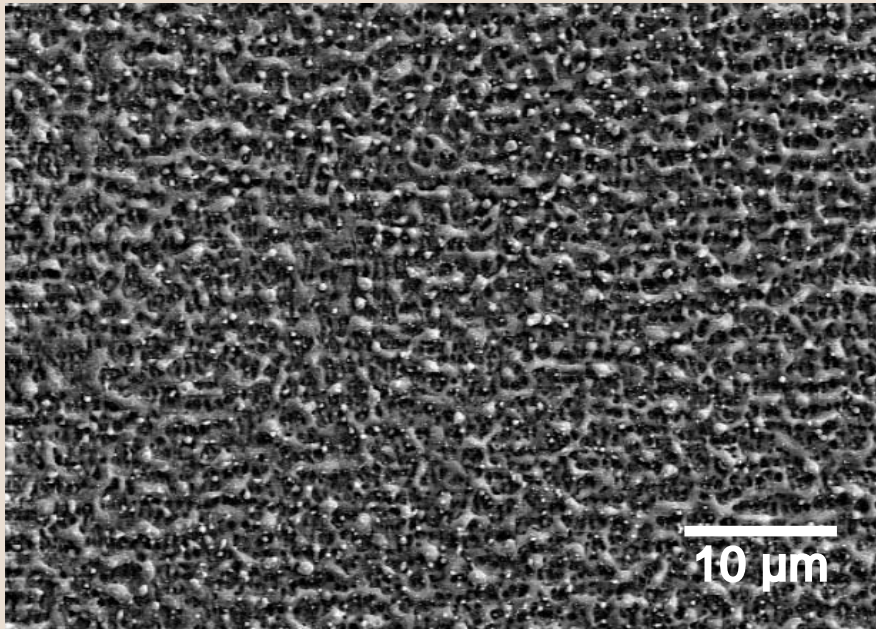


Formation process

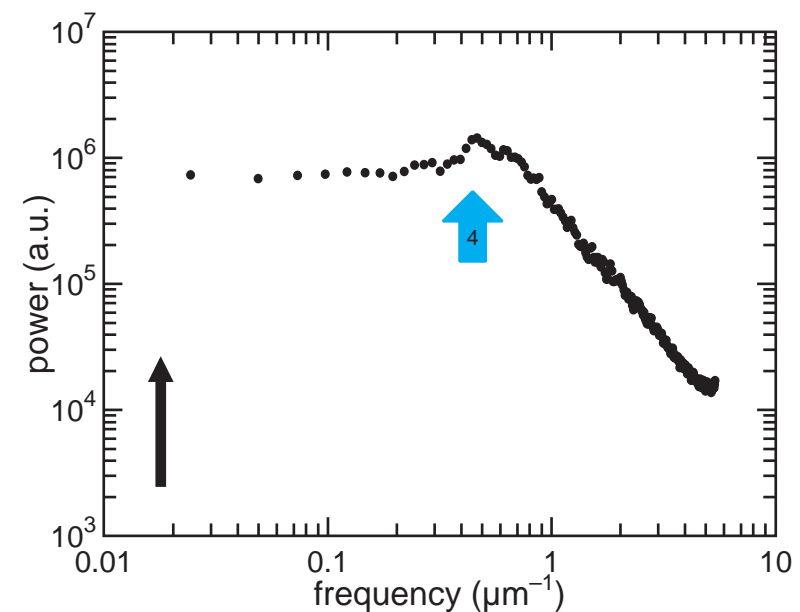
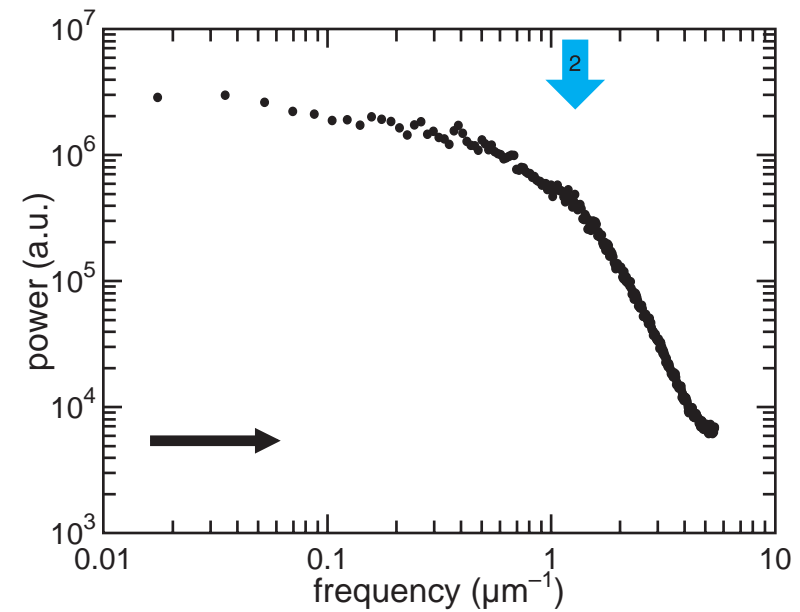
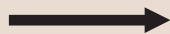
ridges

SF_6

4 pulses



laser polarization

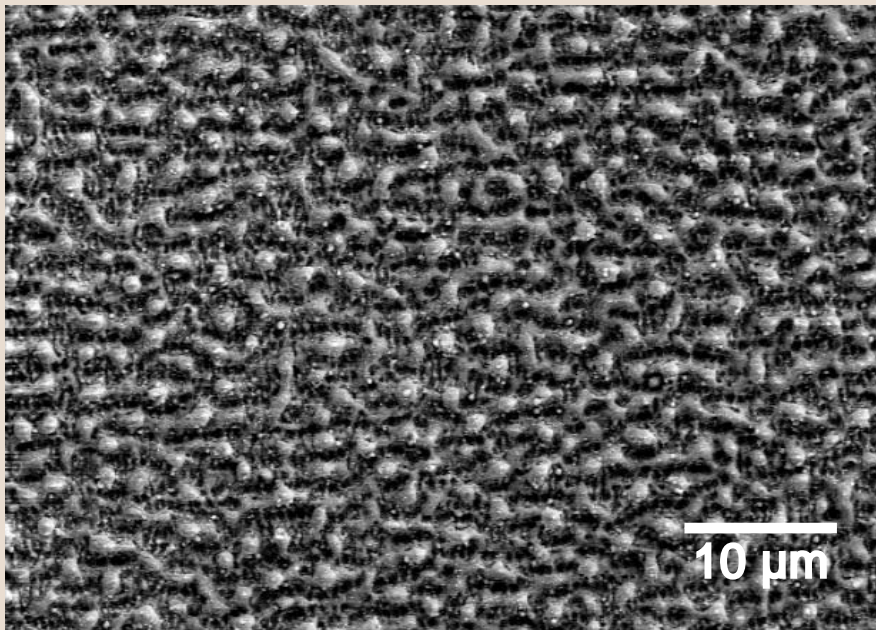


Formation process

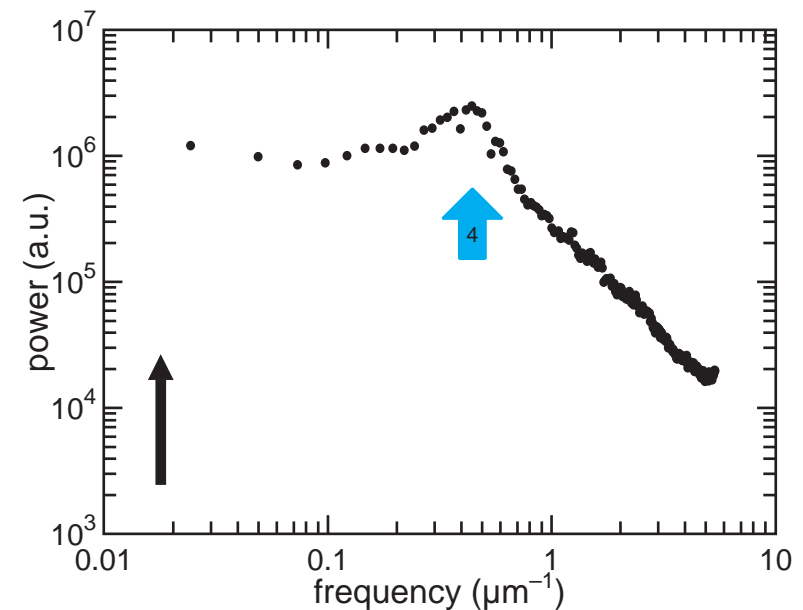
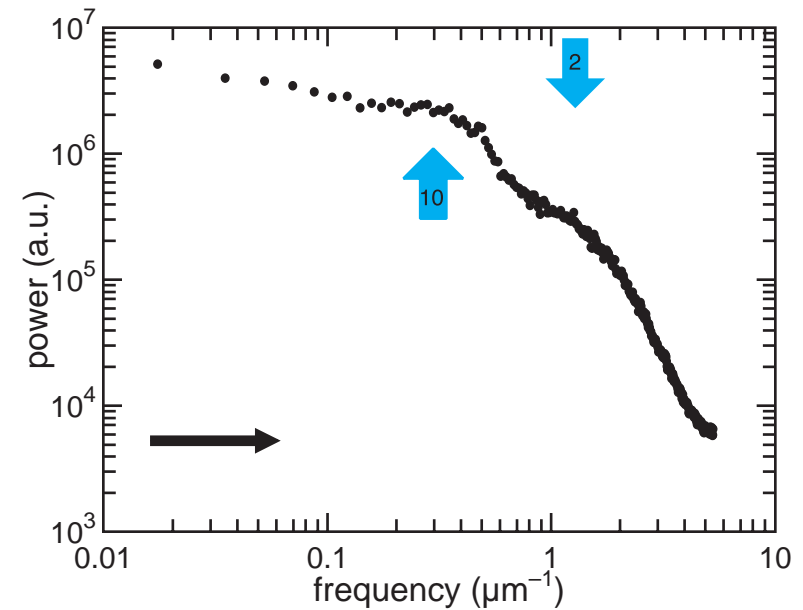
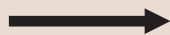
spikes

SF_6

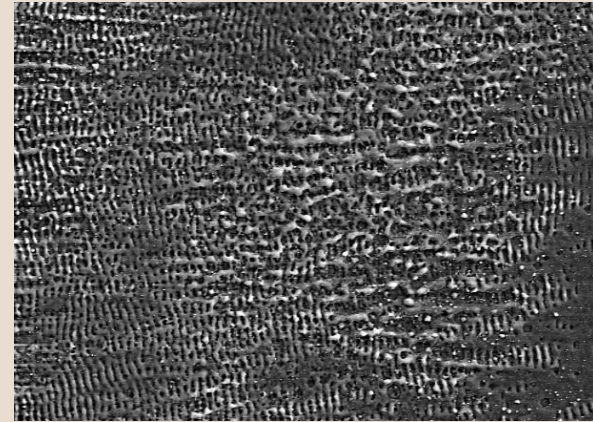
10 pulses



laser polarization

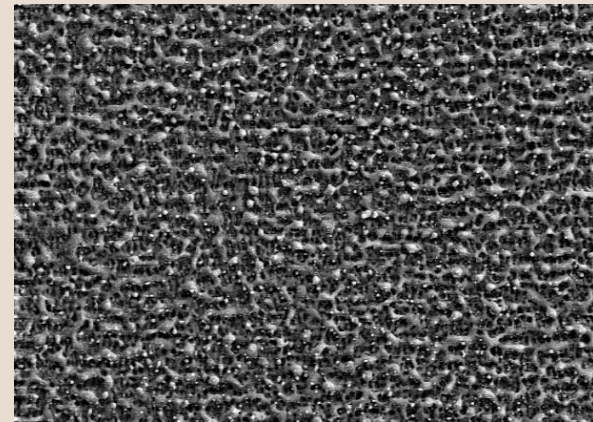


**1. Interference ripples
(\perp to polarization)**



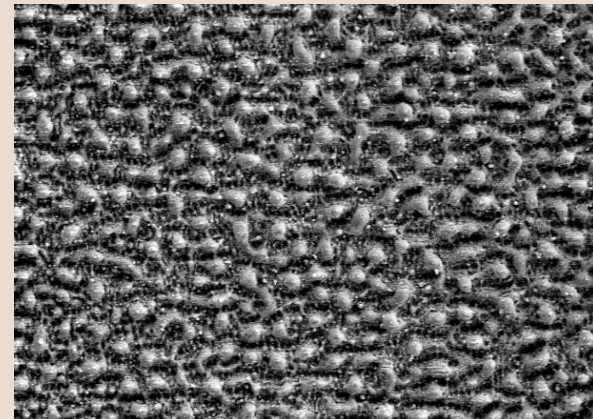
$N = 2$

**2. Coarsened ridges
(\perp to ripples)**



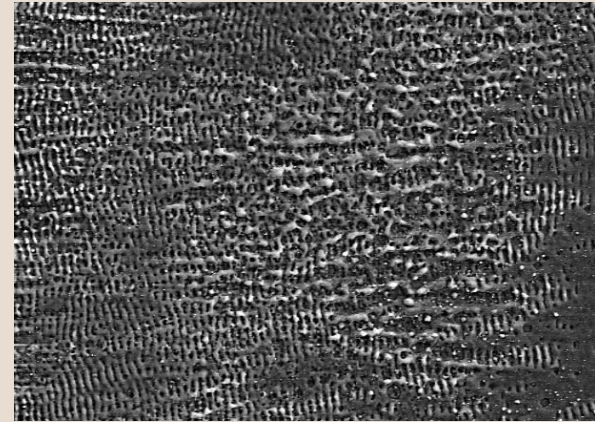
$N = 4$

**3. Beads sharpening
into spikes**

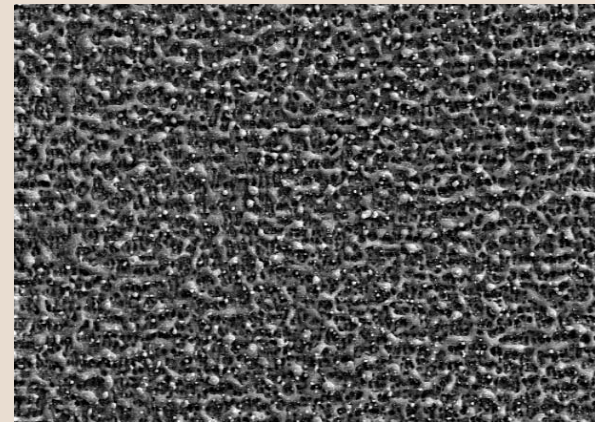


$N = 10$

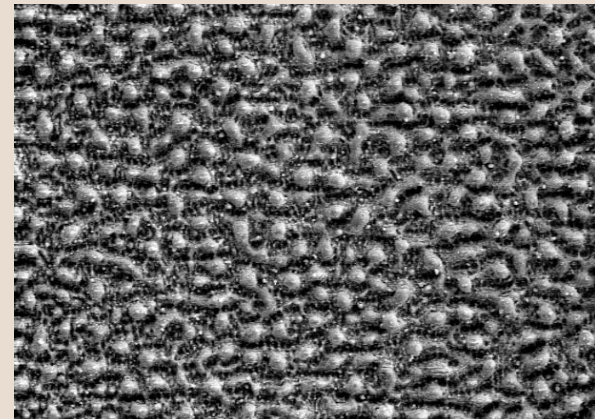
**Two distinct wavelengths:
ripples and spikes**



$N = 2$



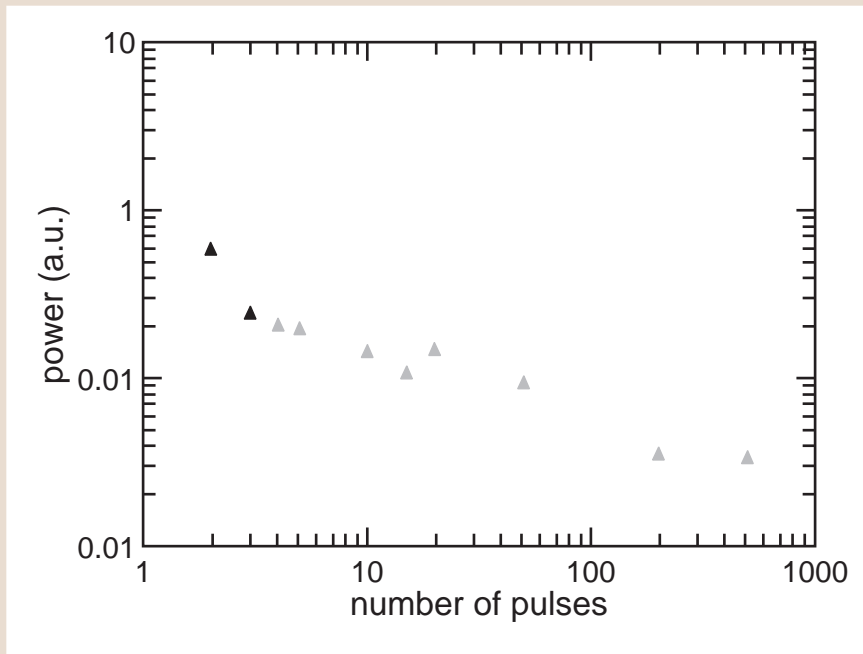
$N = 4$



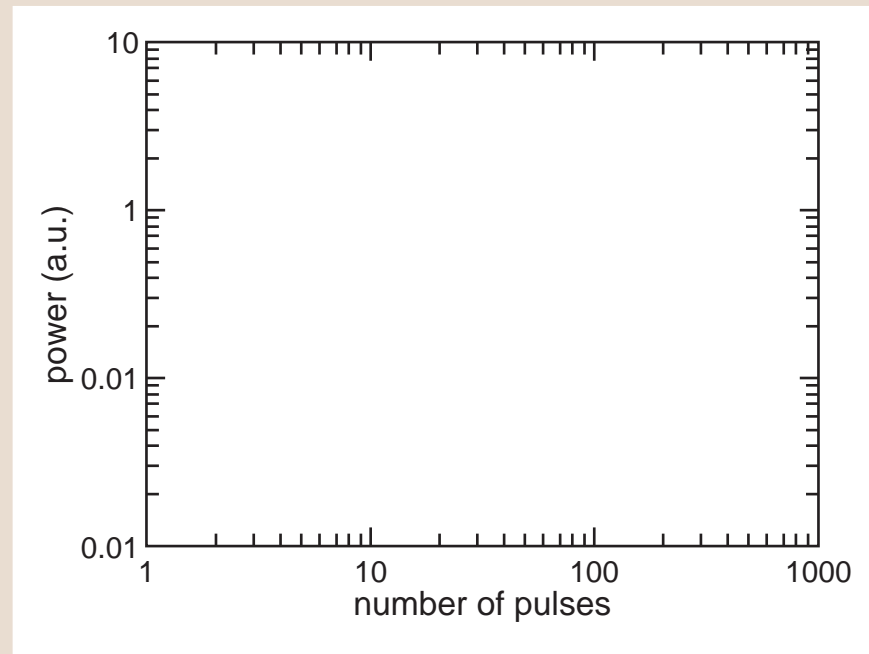
$N = 10$

feature intensities

SF_6 ripples



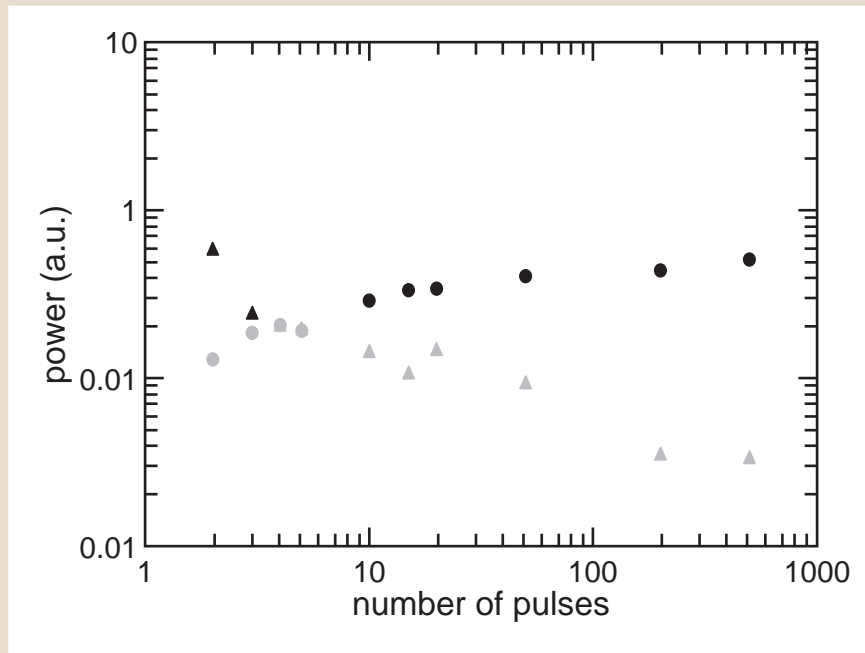
parallel



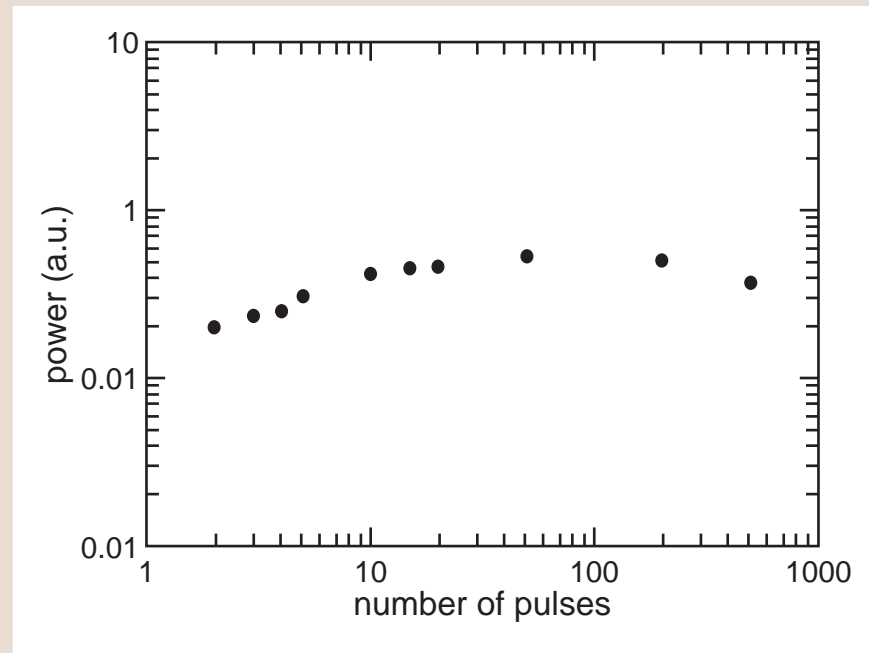
perpendicular

feature intensities

SF₆ spikes



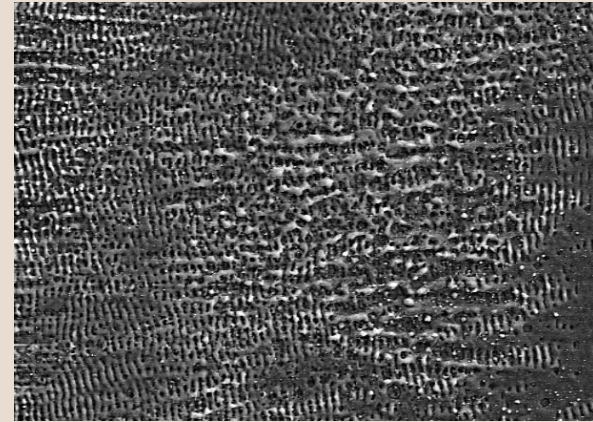
parallel



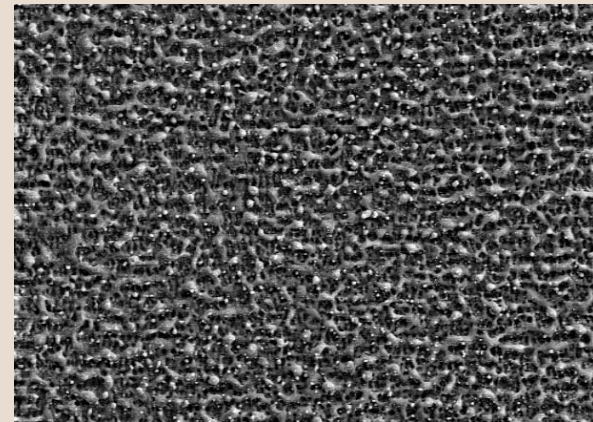
perpendicular

Formation process

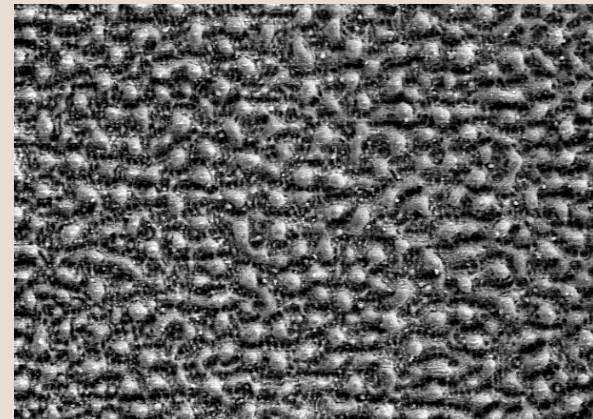
- ▶ spike wavelength appears as ripple wavelength disappears
- ▶ spike wavelength appears first perpendicular to polarization



$N = 2$



$N = 4$



$N = 10$

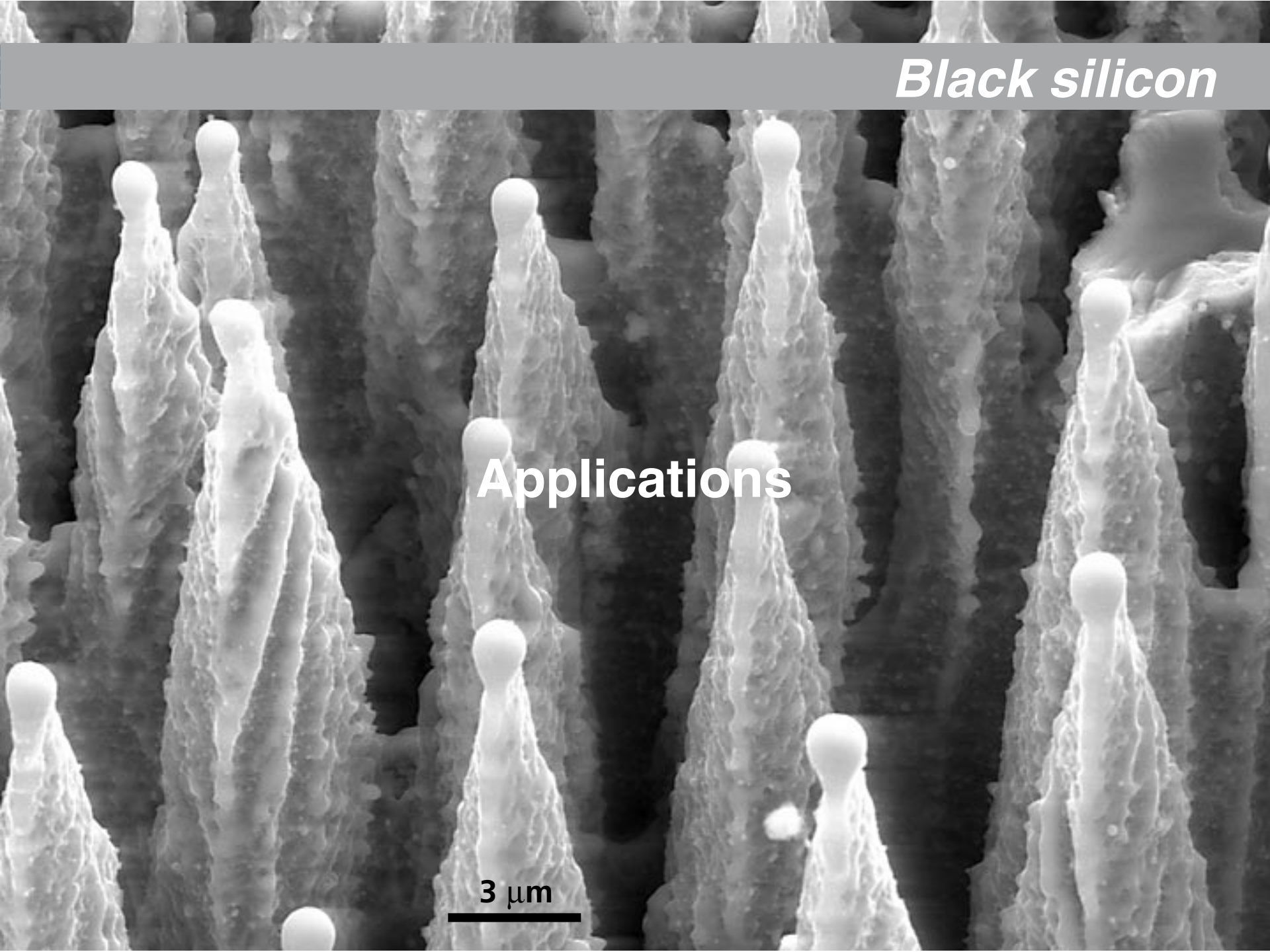
What sets the length scales?

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

Black silicon

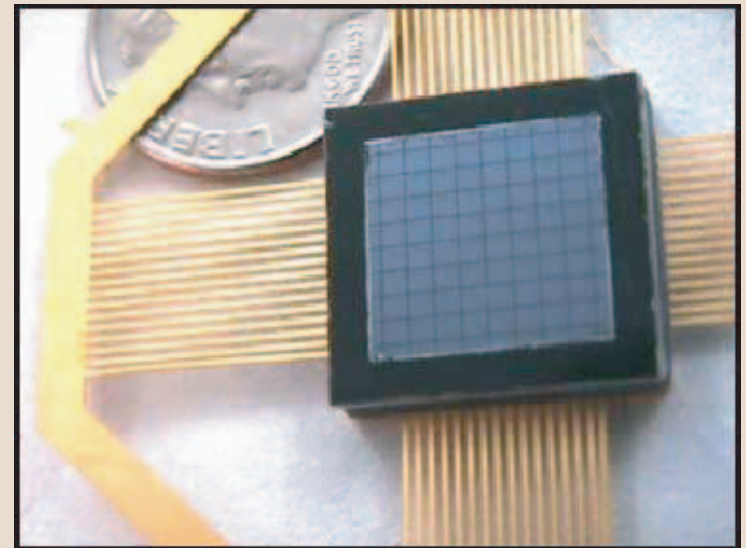
Applications

3 μm

A scanning electron micrograph (SEM) showing the surface morphology of black silicon. The surface is covered with a dense array of vertical, tapered silicon nanowires or pillars. Each pillar has a rounded, hemispherical tip. The background between the pillars is a rough, textured surface. The image is in grayscale, highlighting the three-dimensional structure of the nanowires.

Avalanche photodiode with black silicon

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

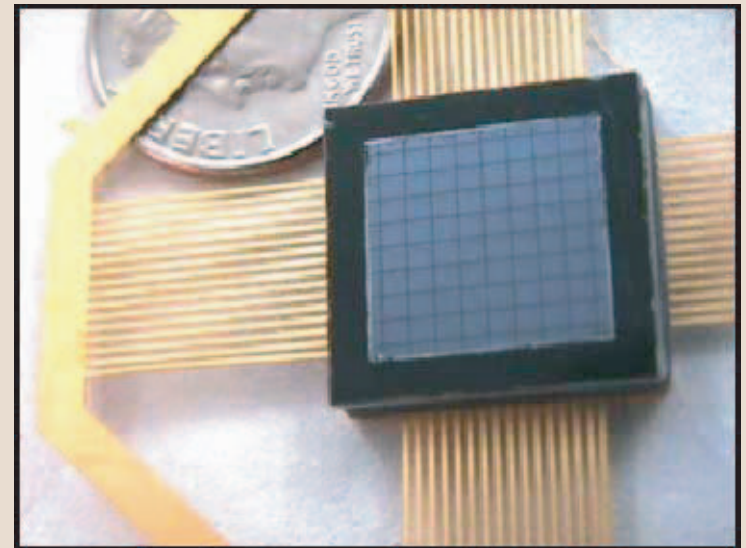


Avalanche photodiode with black silicon

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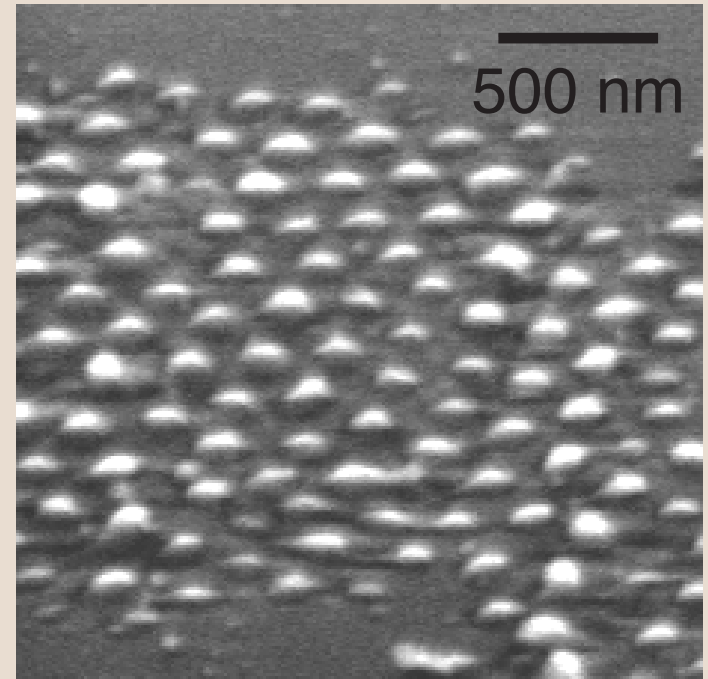
Other applications:

- ▶ field emission arrays
- ▶ light emitters



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!

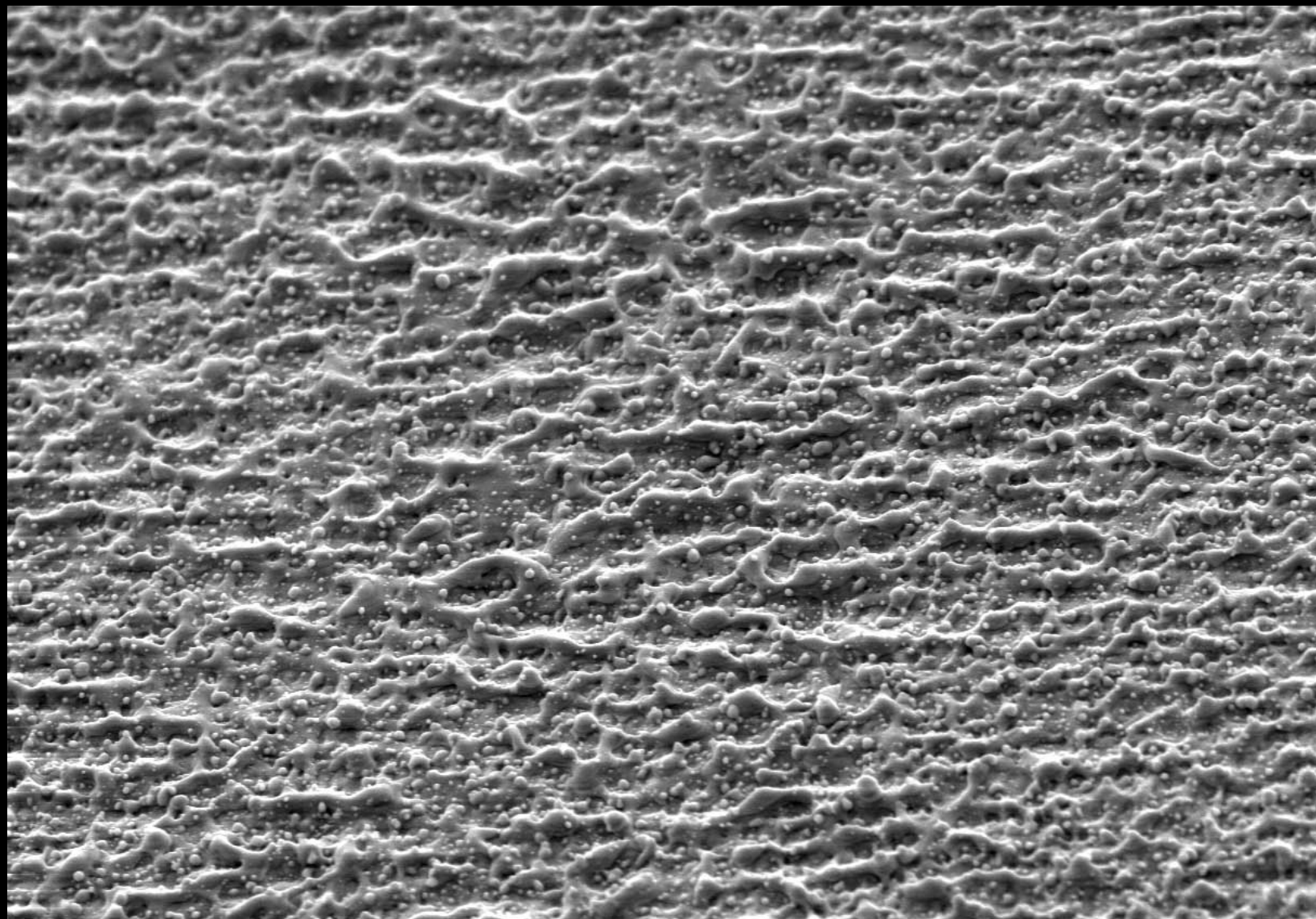
Acknowledgements

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



x2000
#3548
512 x 480

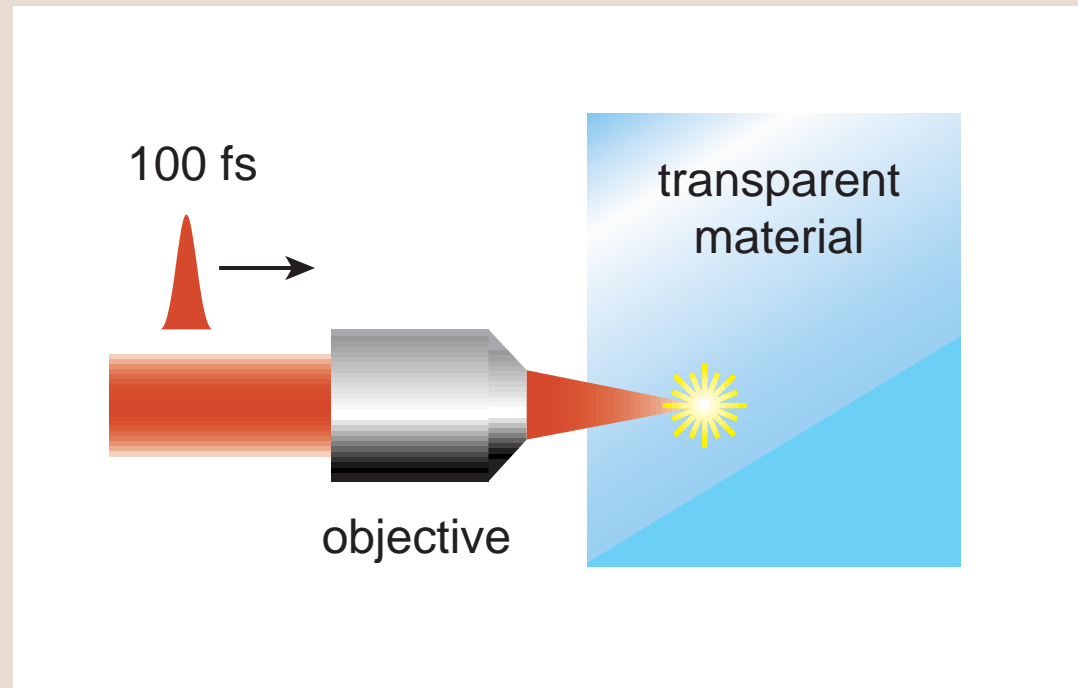
20 μ m

10kV

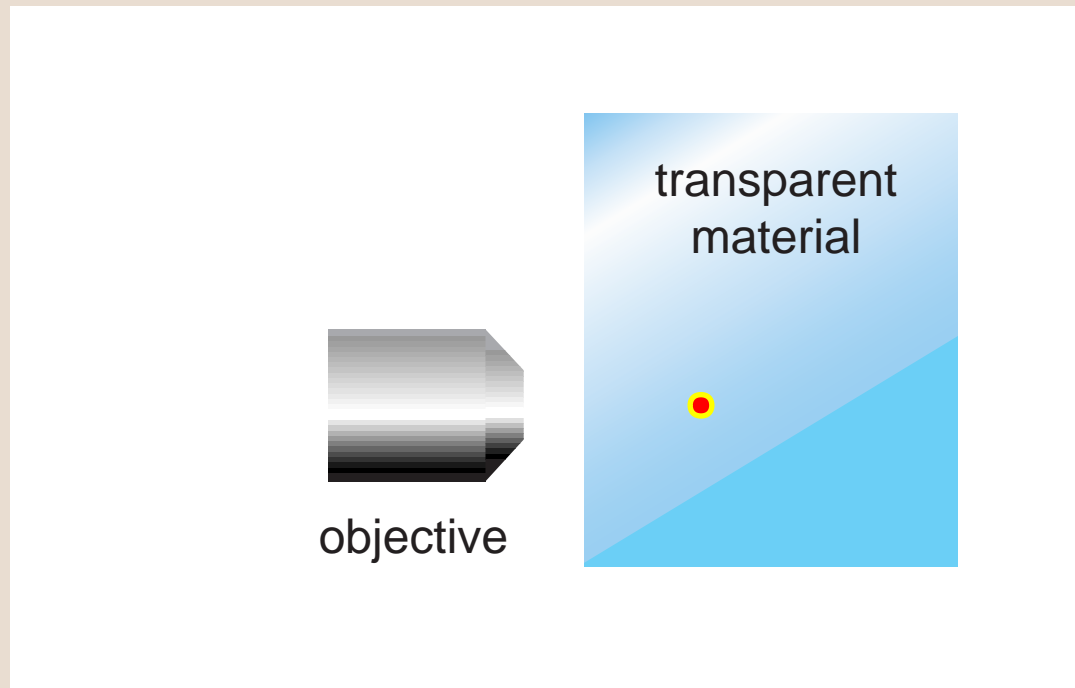
15mm

0006

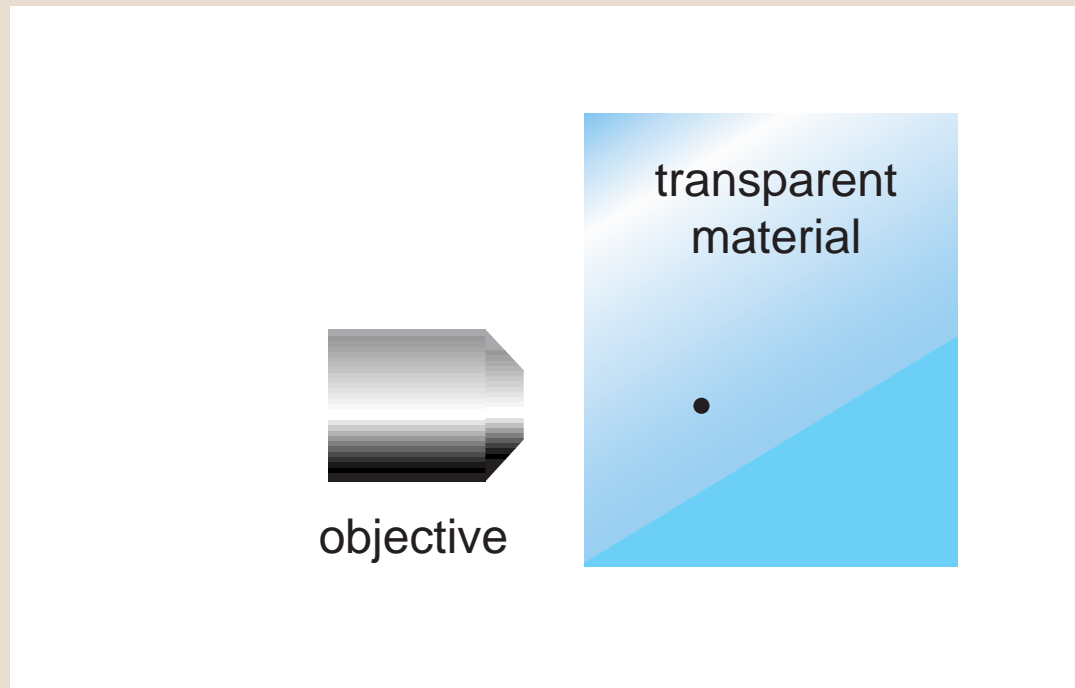
tightly focus beam inside bulk glass



energy is deposited in the focal volume

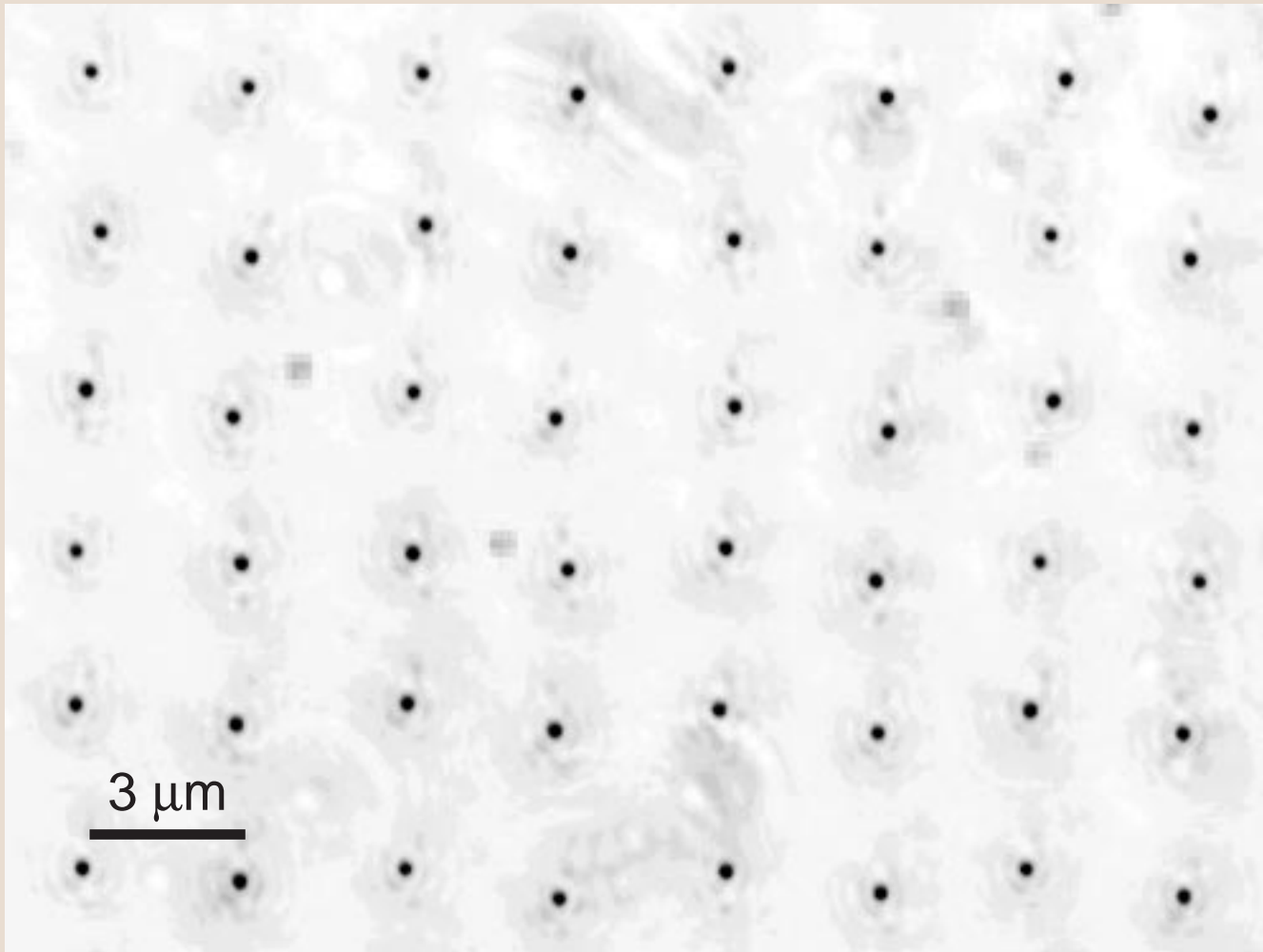


producing microscopic bulk damage



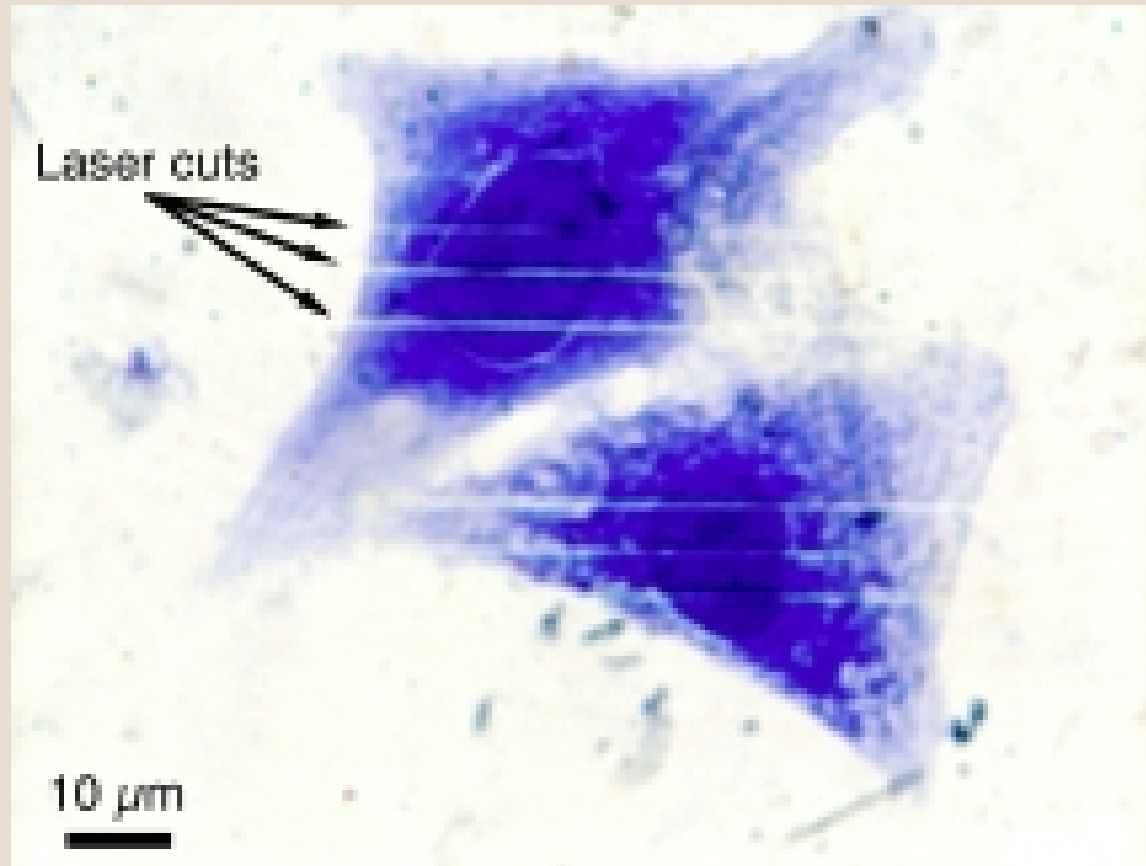
Modification of materials

40 nJ
100 fs
800 nm
0.65 NA
Corning 0211



top view

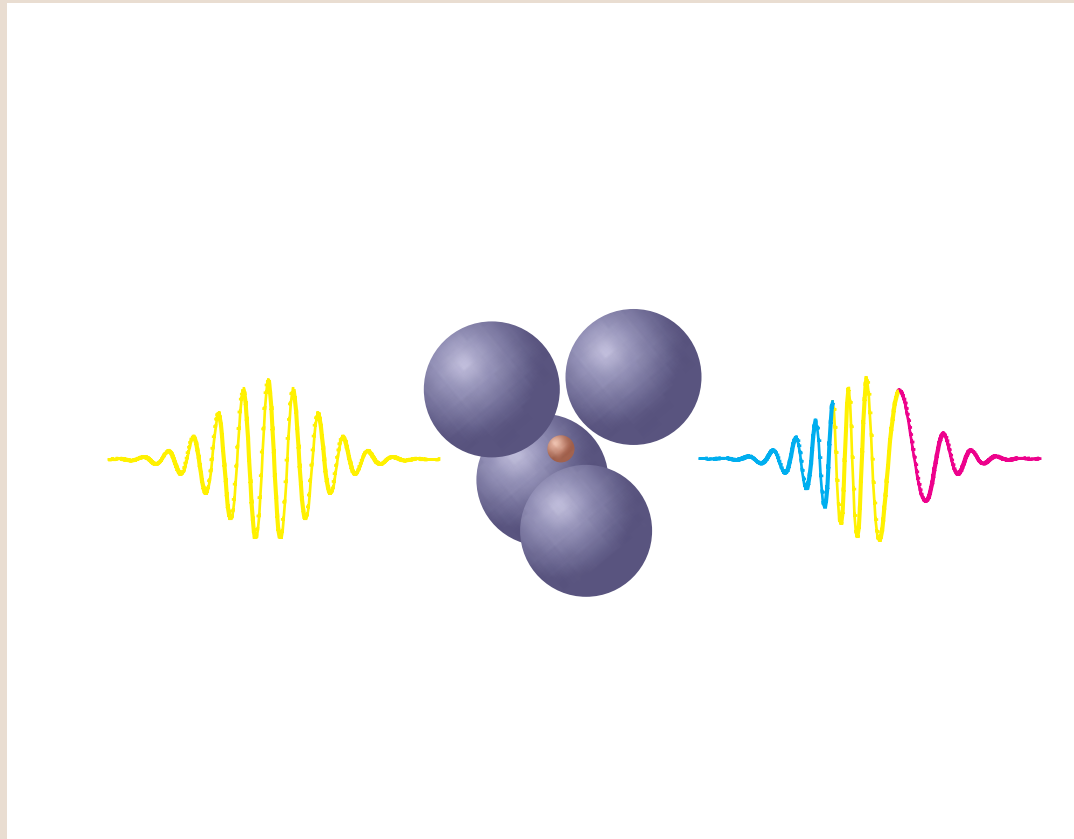
laser cuts through single cell



sub-cellular microsurgery

Nonlinear optical effects

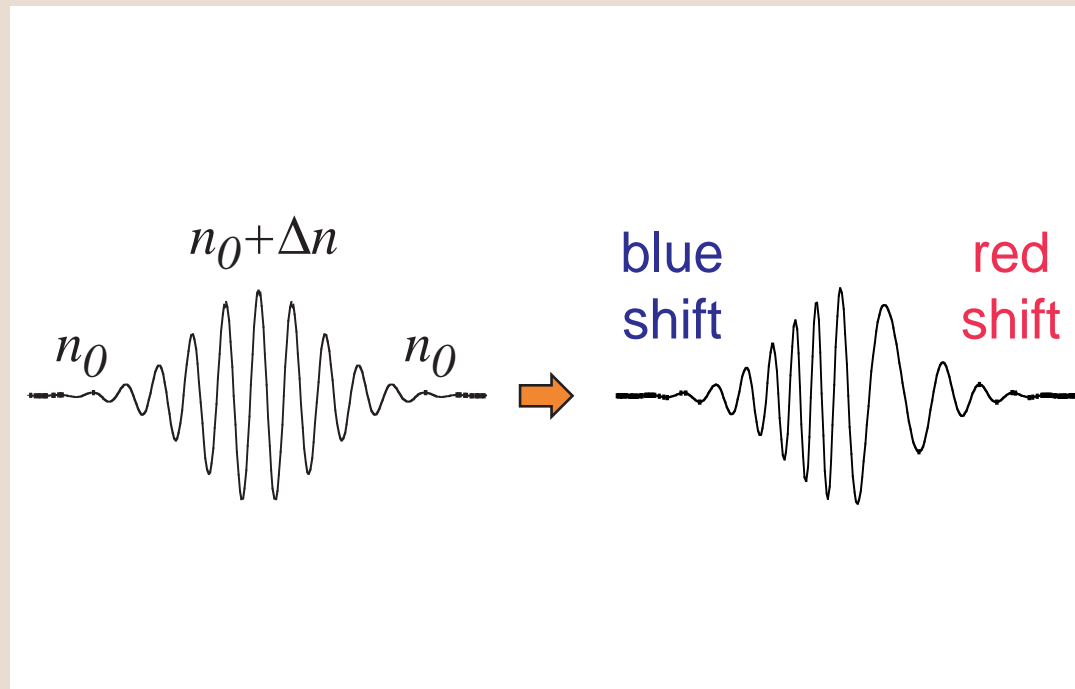
"extremely" nonlinear response



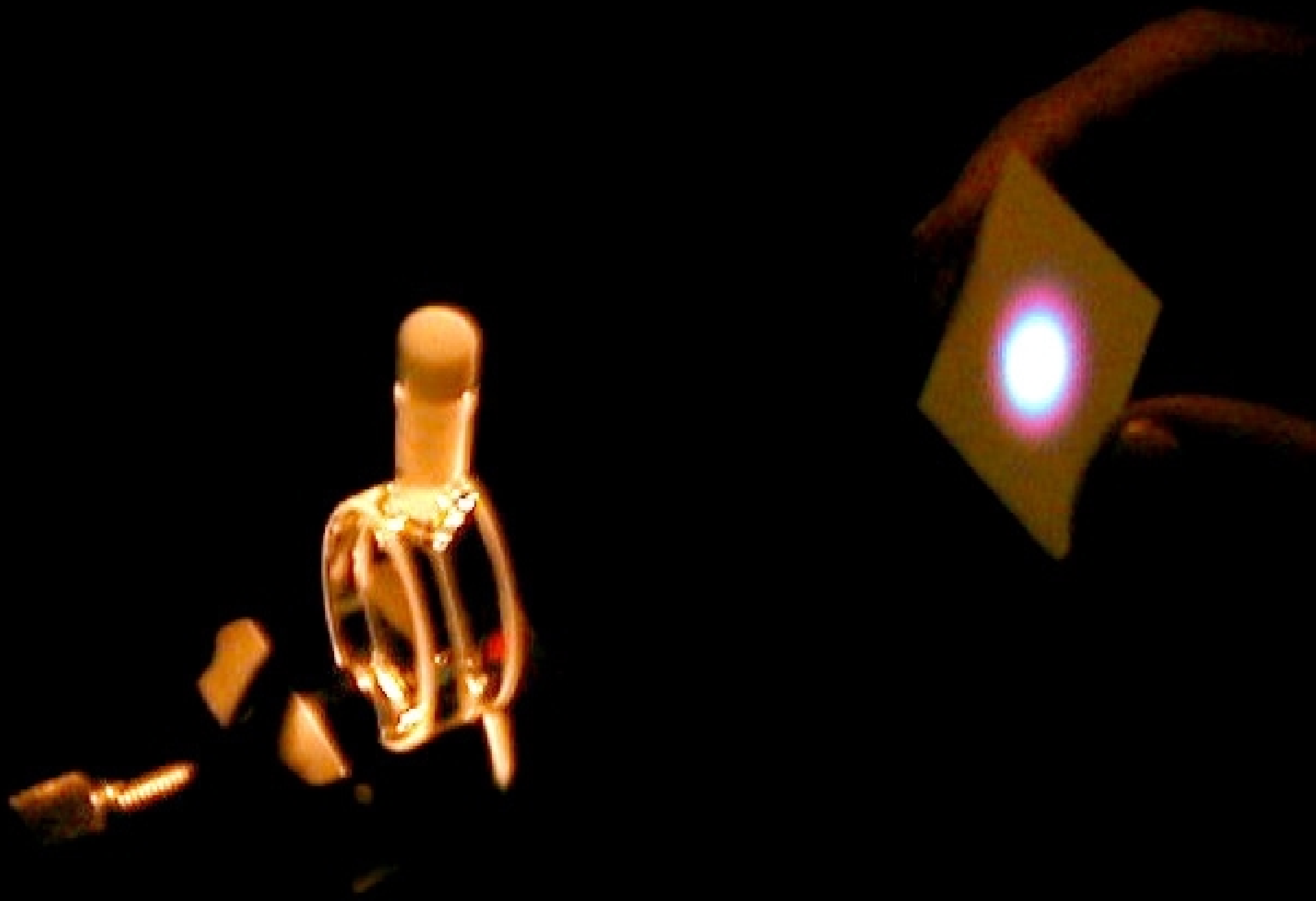
material changes the light

Nonlinear optical effects

light induces time-dependent index of refraction



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

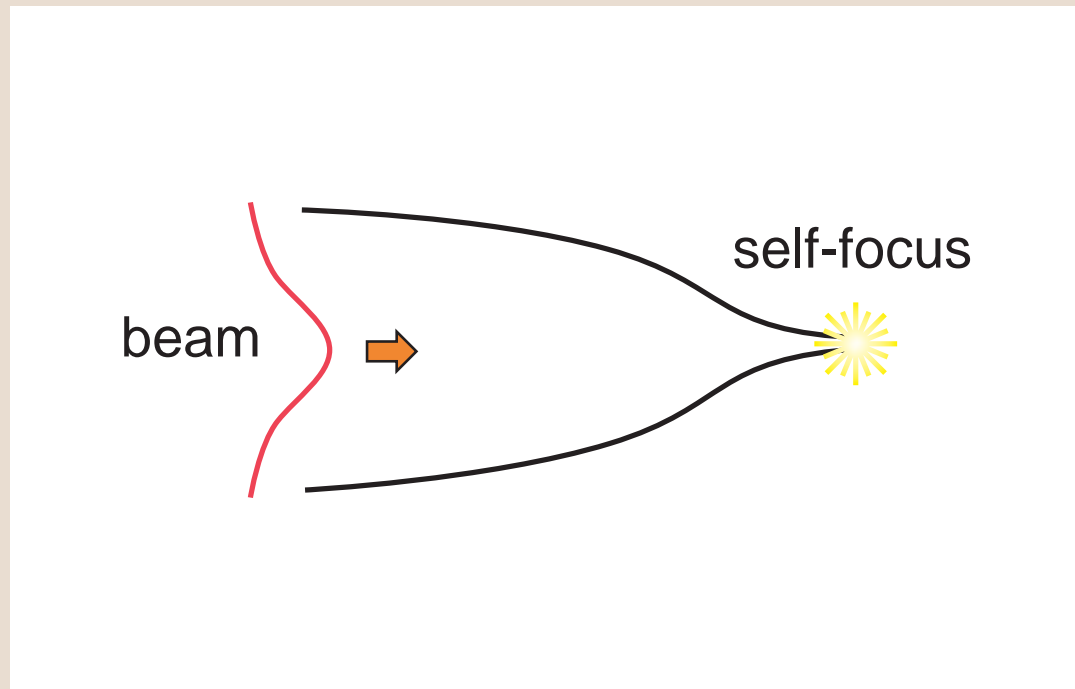


A photograph of a custom-built mechanical assembly mounted on a white breadboard. The assembly includes a black DC motor with a yellow label, a yellow gear, a black gear, and a black pulley. A red laser pointer is attached to the side of the assembly. The breadboard has a grid of holes. The text "Modification of materials" is overlaid in the center.

Modification of materials

Nonlinear optical effects

light induces position-dependent index of refraction



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