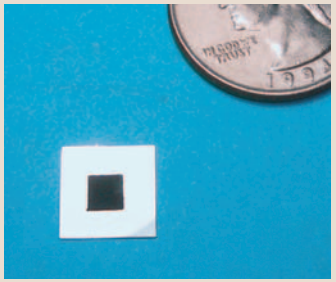
Black silicon:
Using lasers to make novel materials



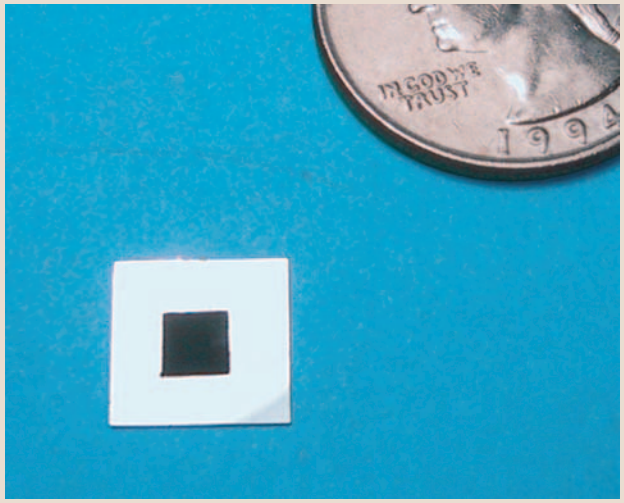
Catherine H. Crouch
Harvard University

Harvard University
14 February 2003

Motivation

Study effect of extremely intense laser pulses

Develop novel materials



Femtosecond laser pulses

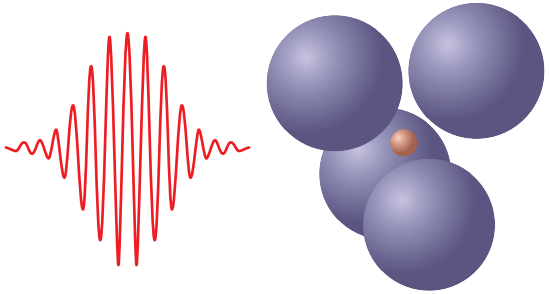
800 nm, 100 fs laser pulses

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

Extremely high peak power and intensity

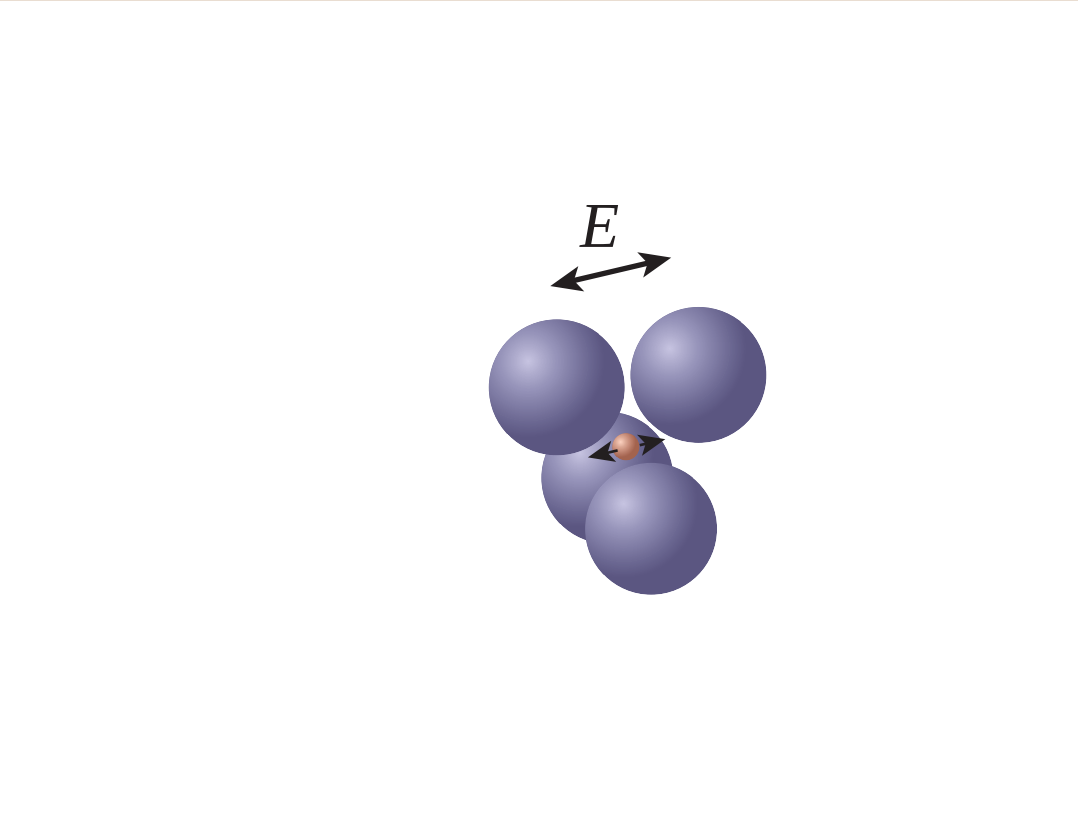
- peak power > 10^9 W
- focused beam: ~ 10^{17} W/cm^2

light-matter interactions



Modification of materials

temporary effect on material

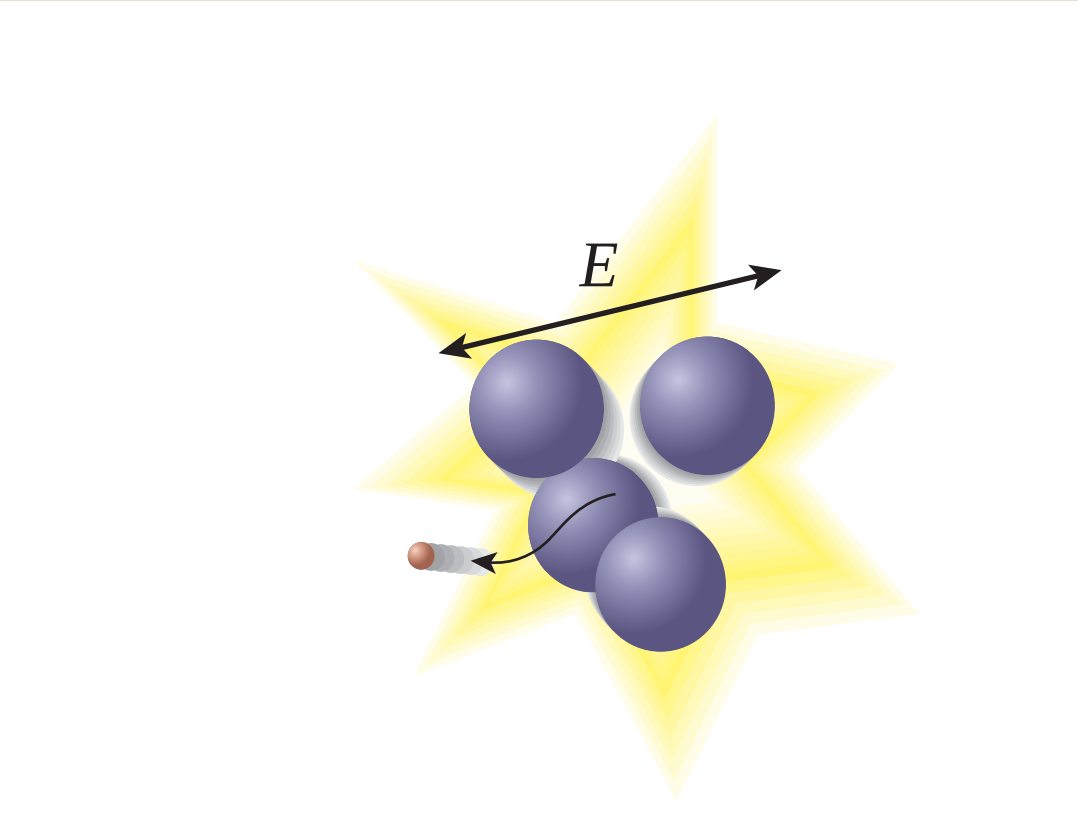


$$\vec{P} = \chi \vec{E}$$

χ is constant

Modification of materials

permanent change to material



plasma formation

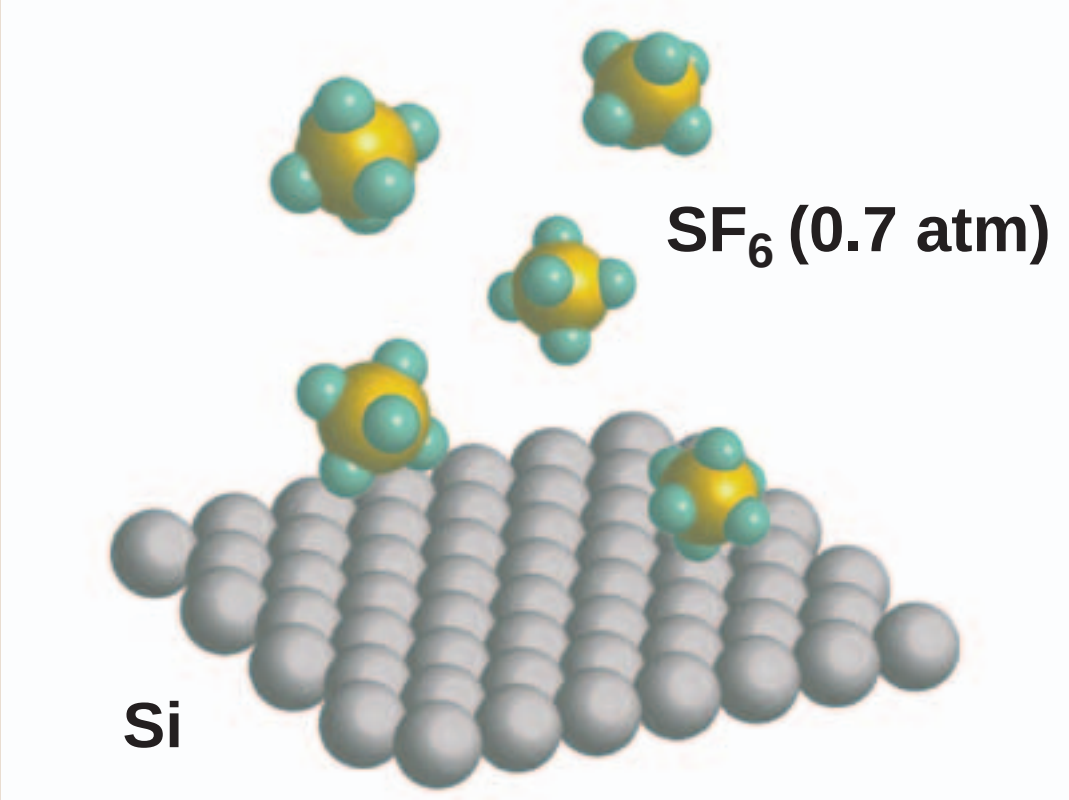
Outline

1. What is black silicon?

2. Why is it black?

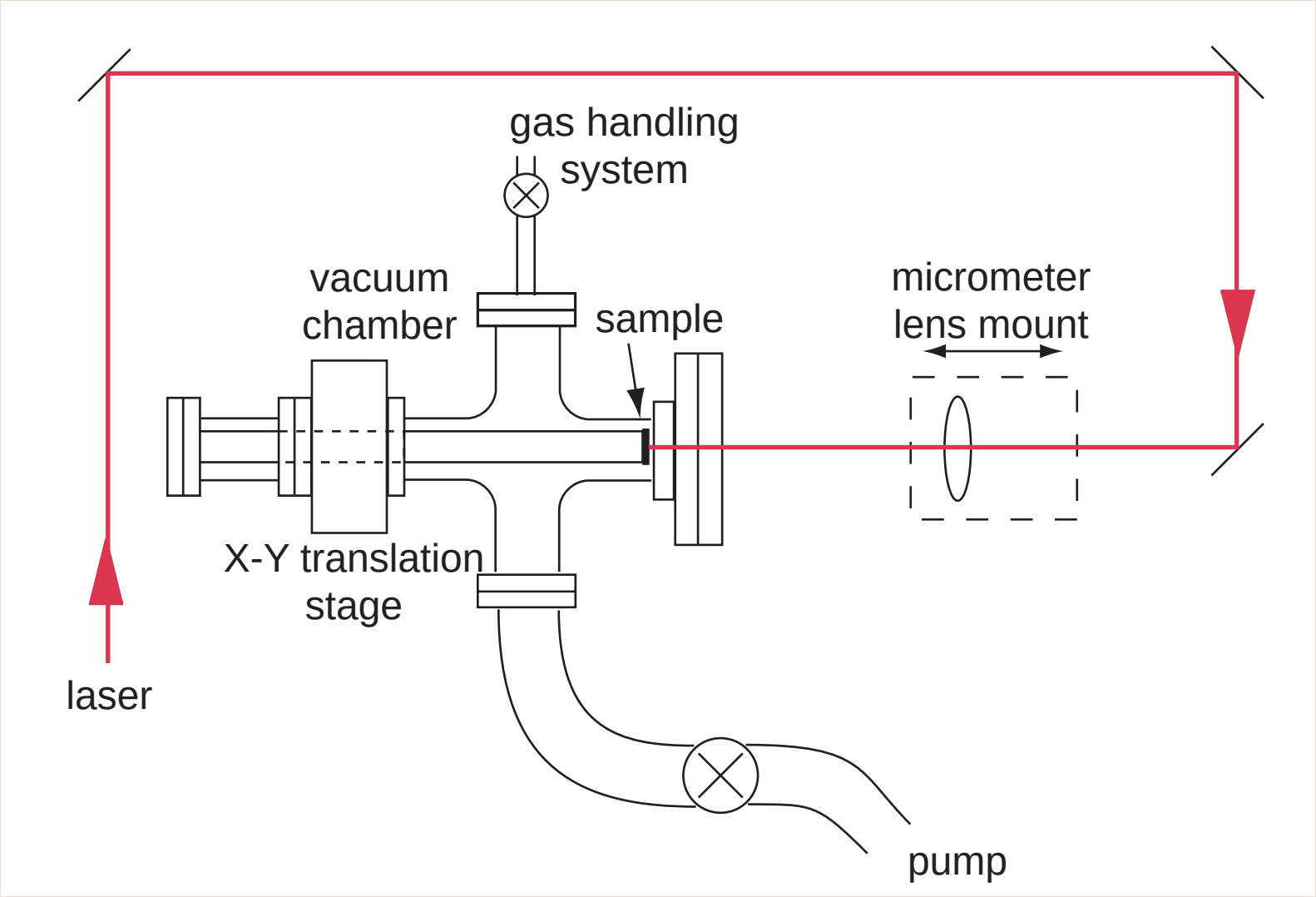
3. How does it get that way?

Black silicon

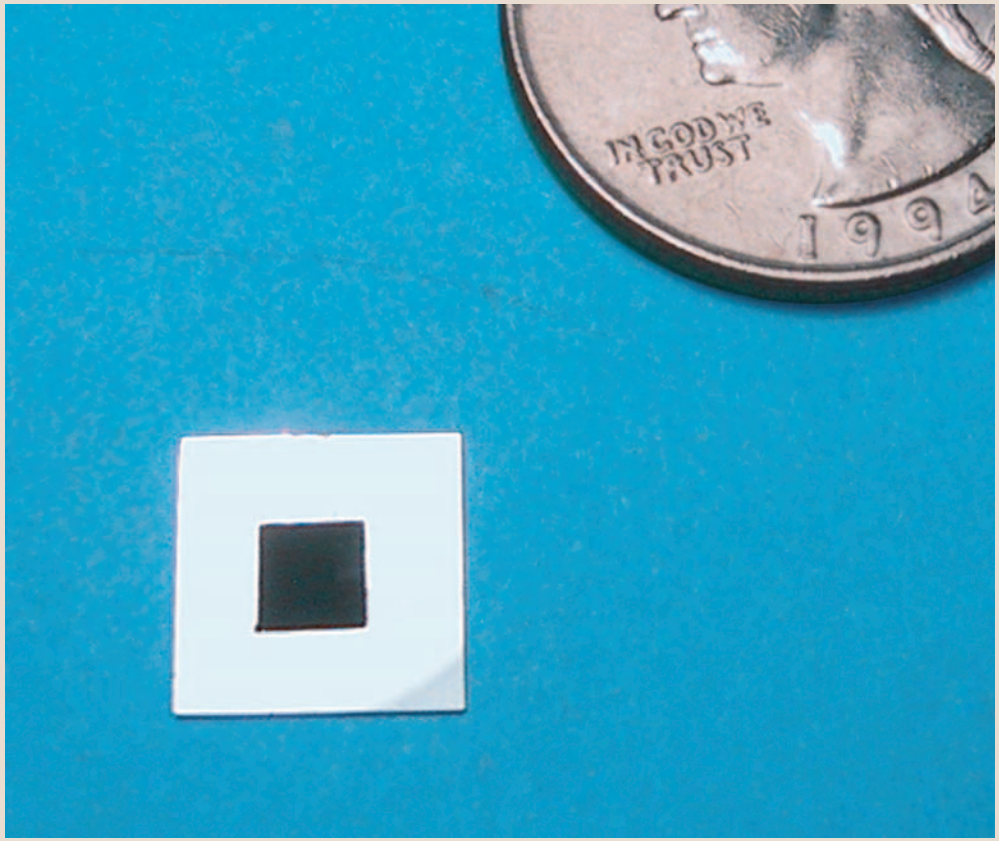


irradiate surface with femtosecond laser pulses
(800 nm, 100 fs, 500 pulses, 10 kJ/m^2)

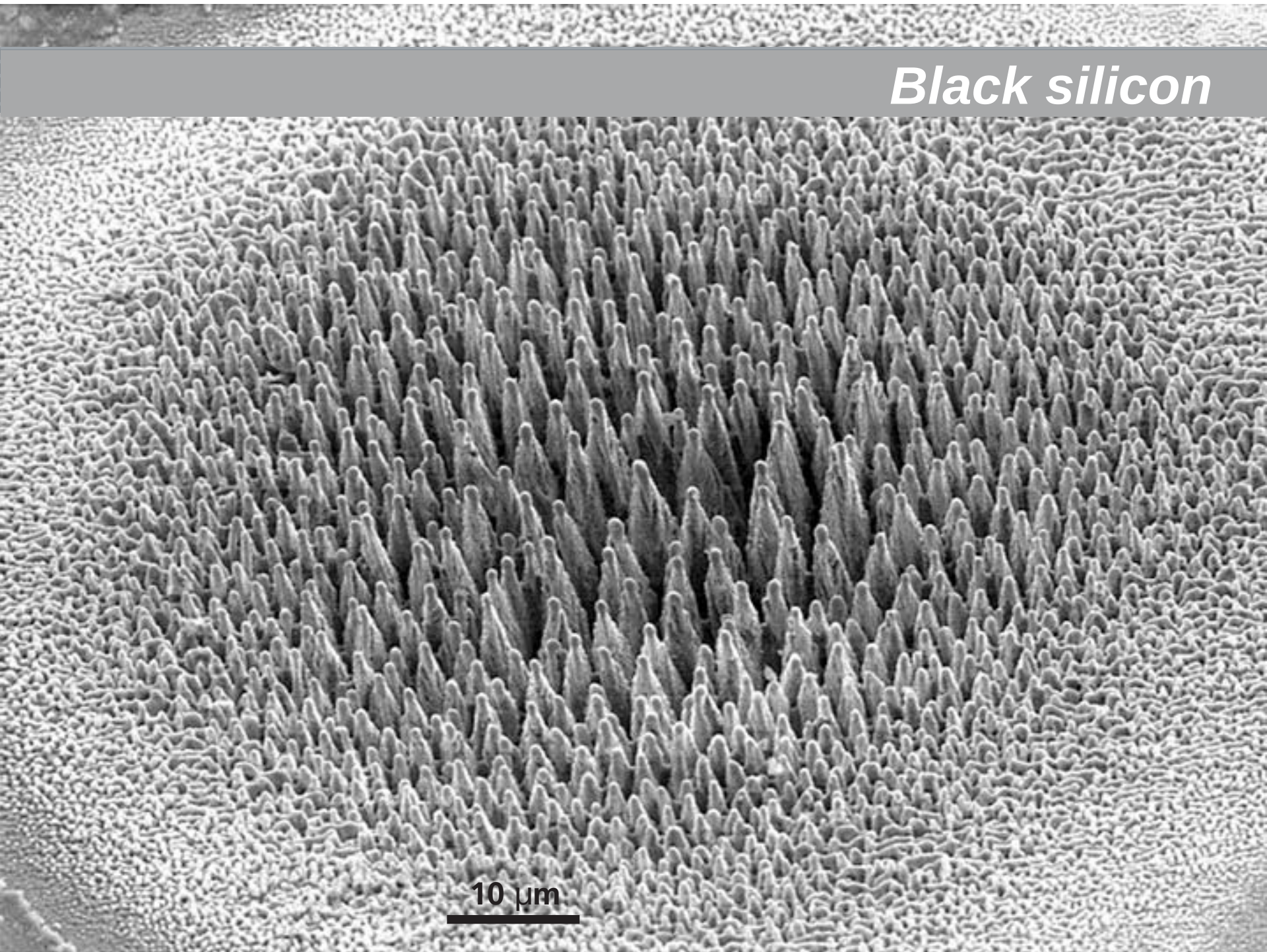
Black silicon



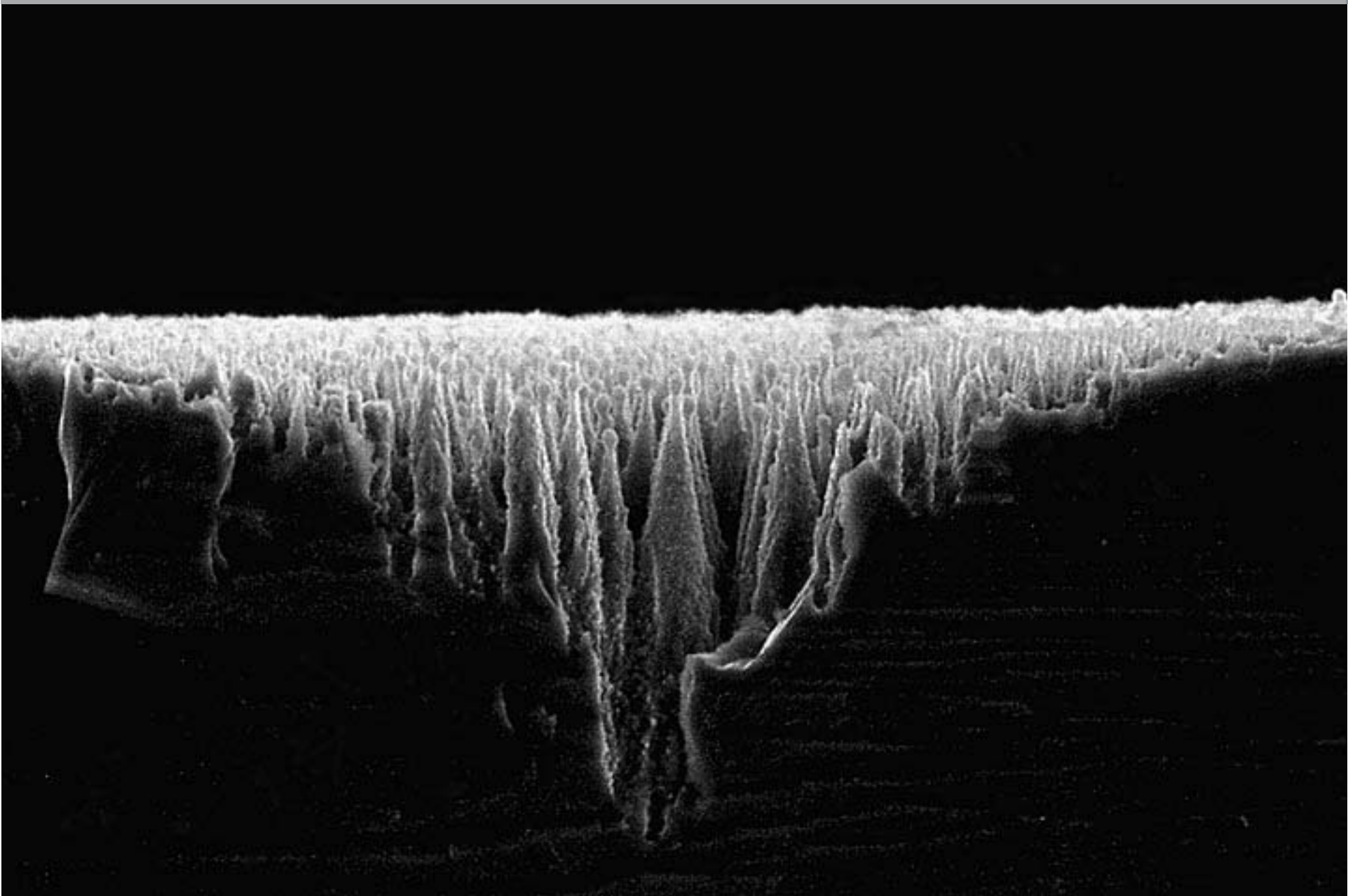
Black silicon

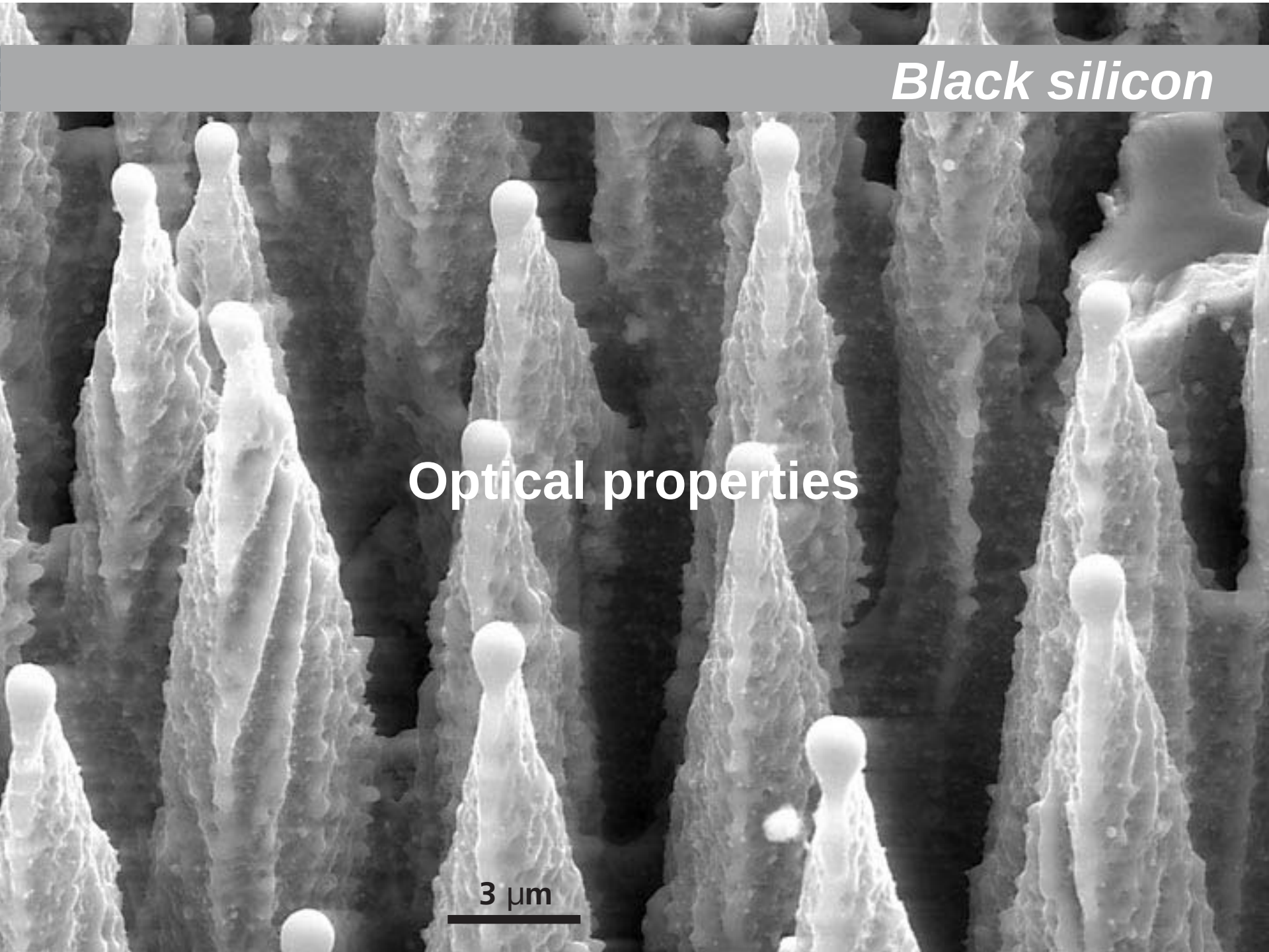


Black silicon



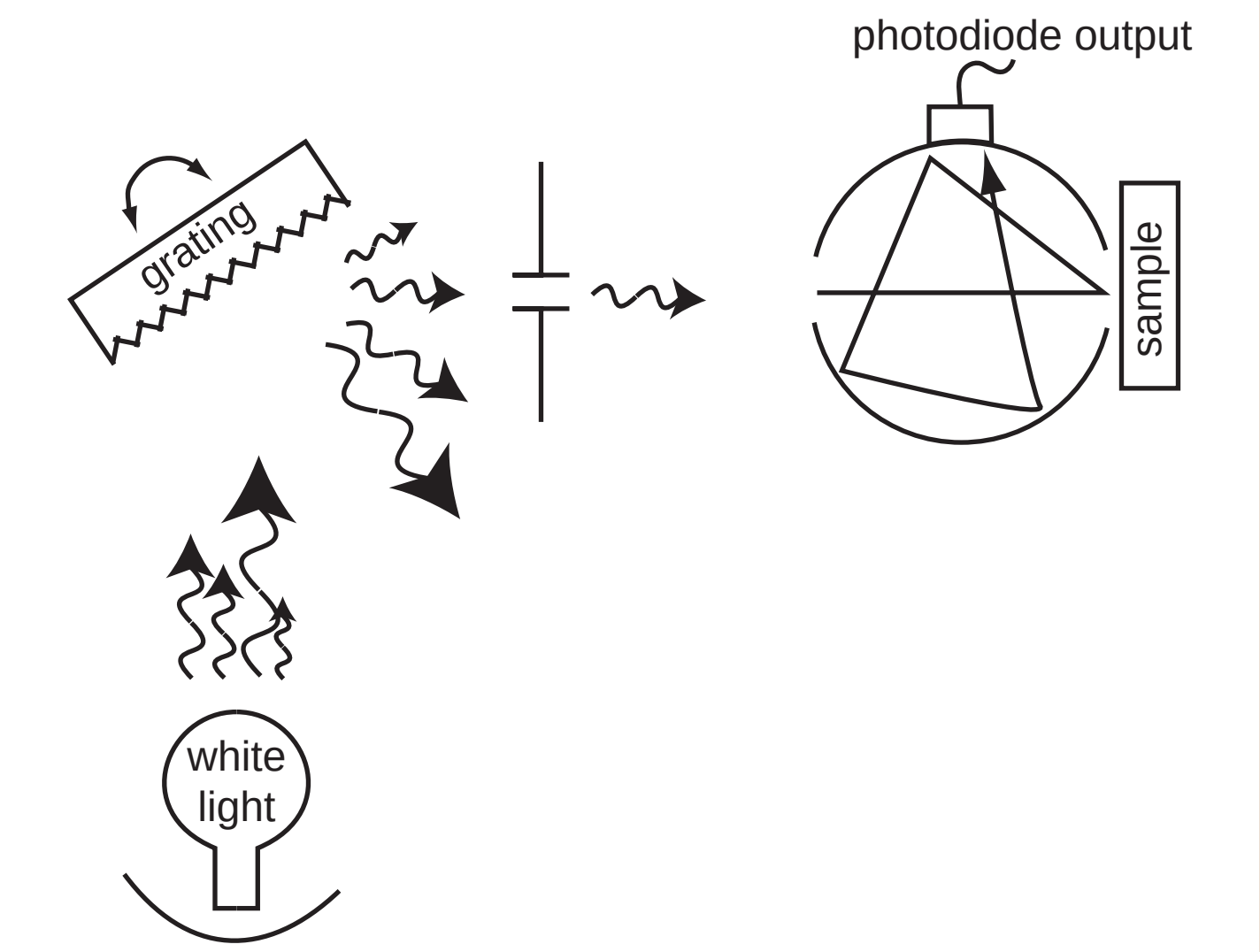
Black silicon





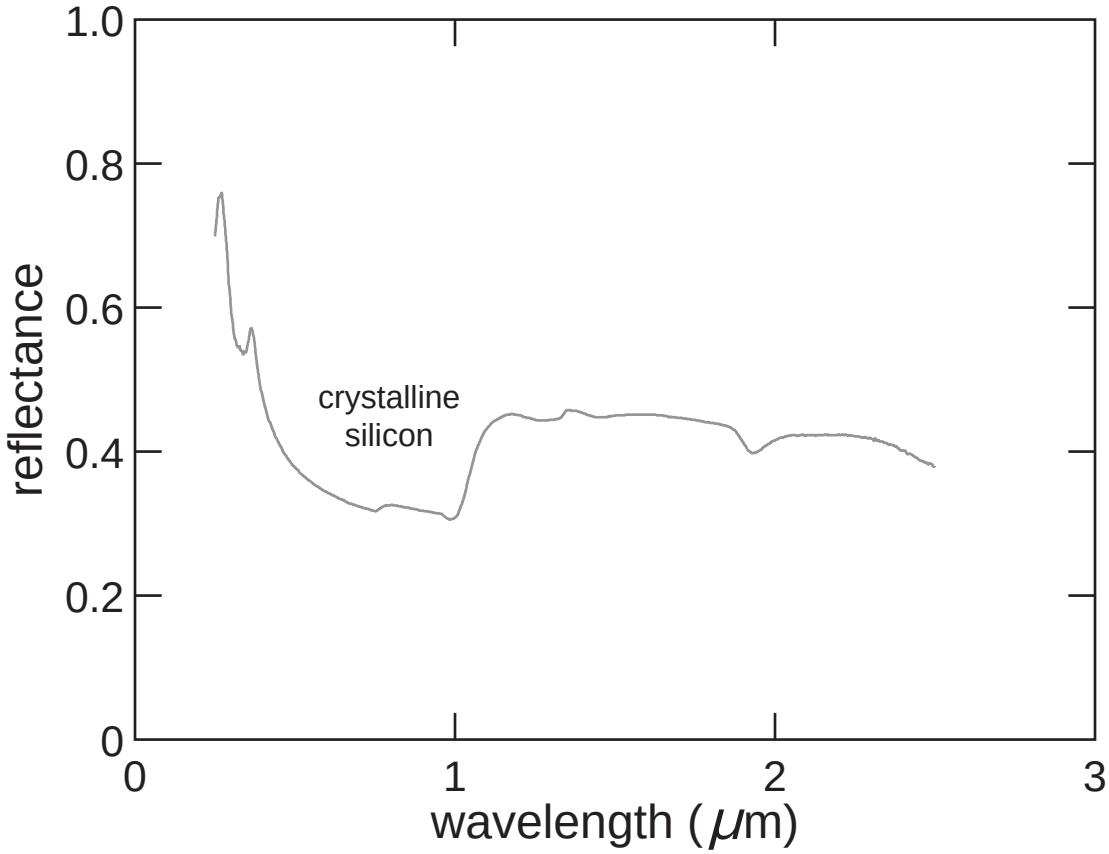
Optical properties

measure reflectance, transmittance with integrating sphere

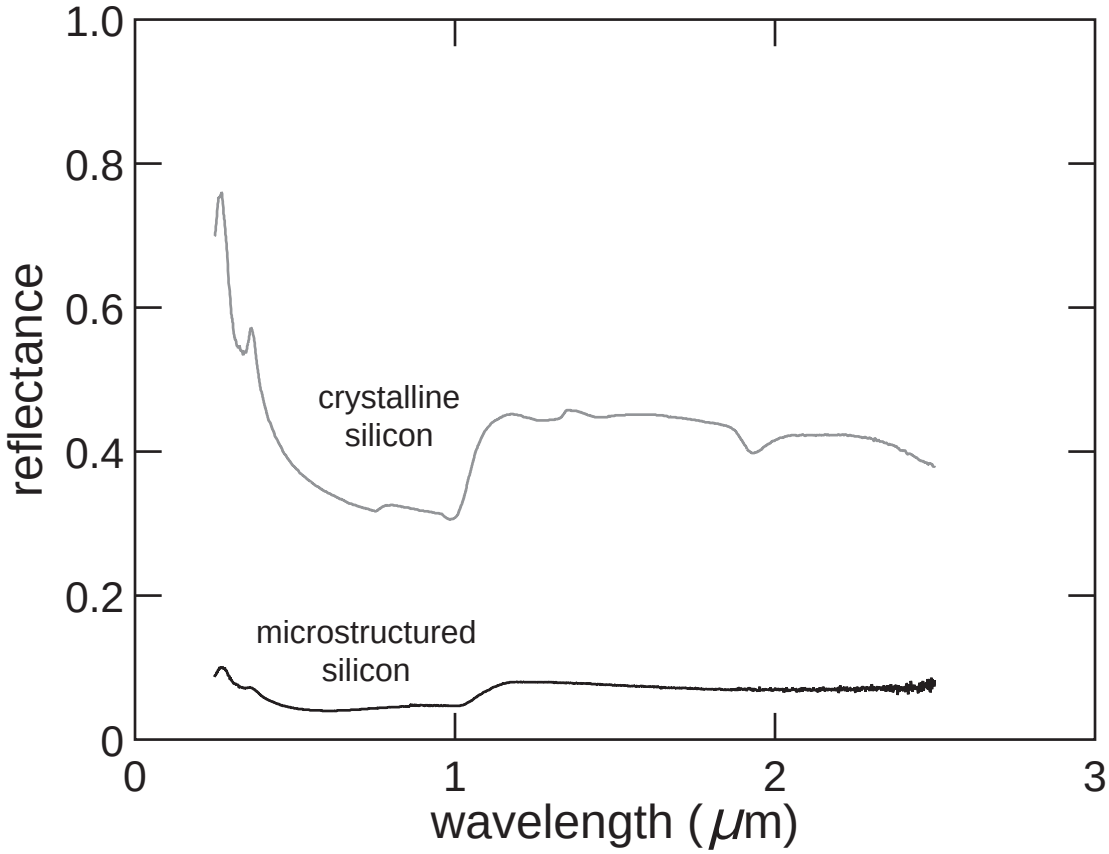


Optical properties

reflectance

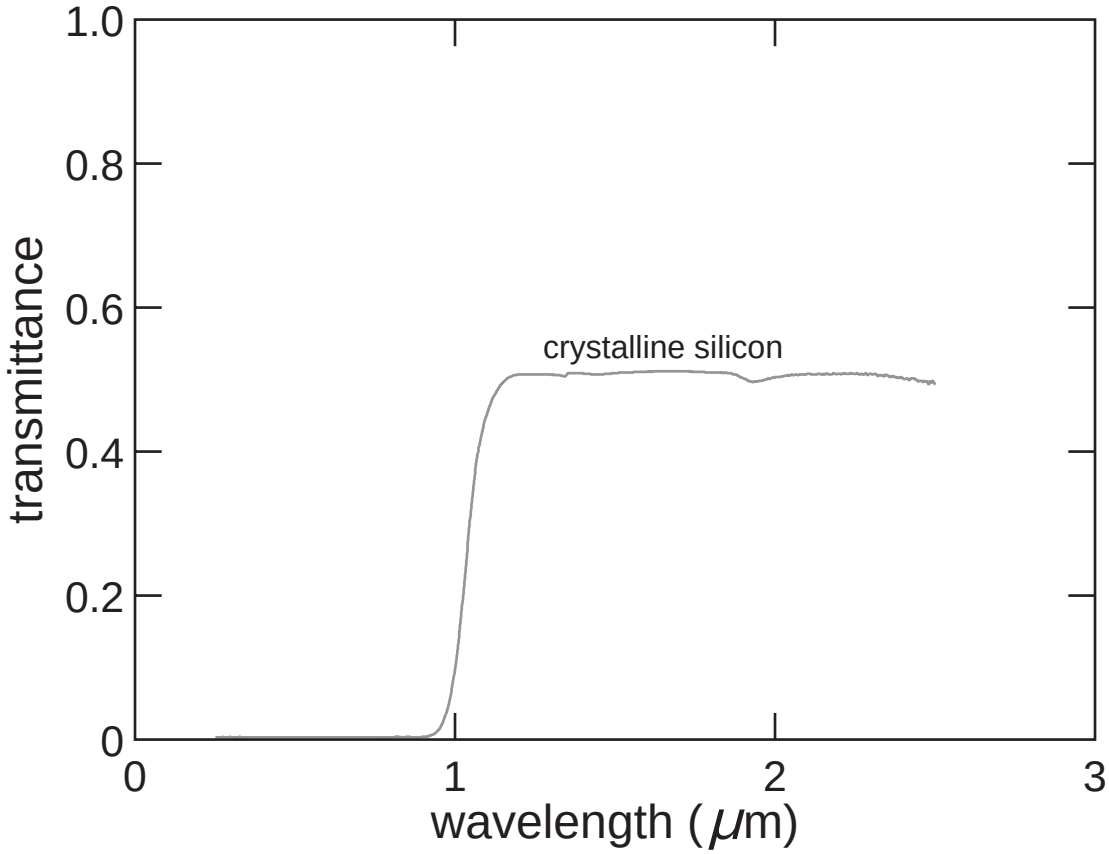


reflectance



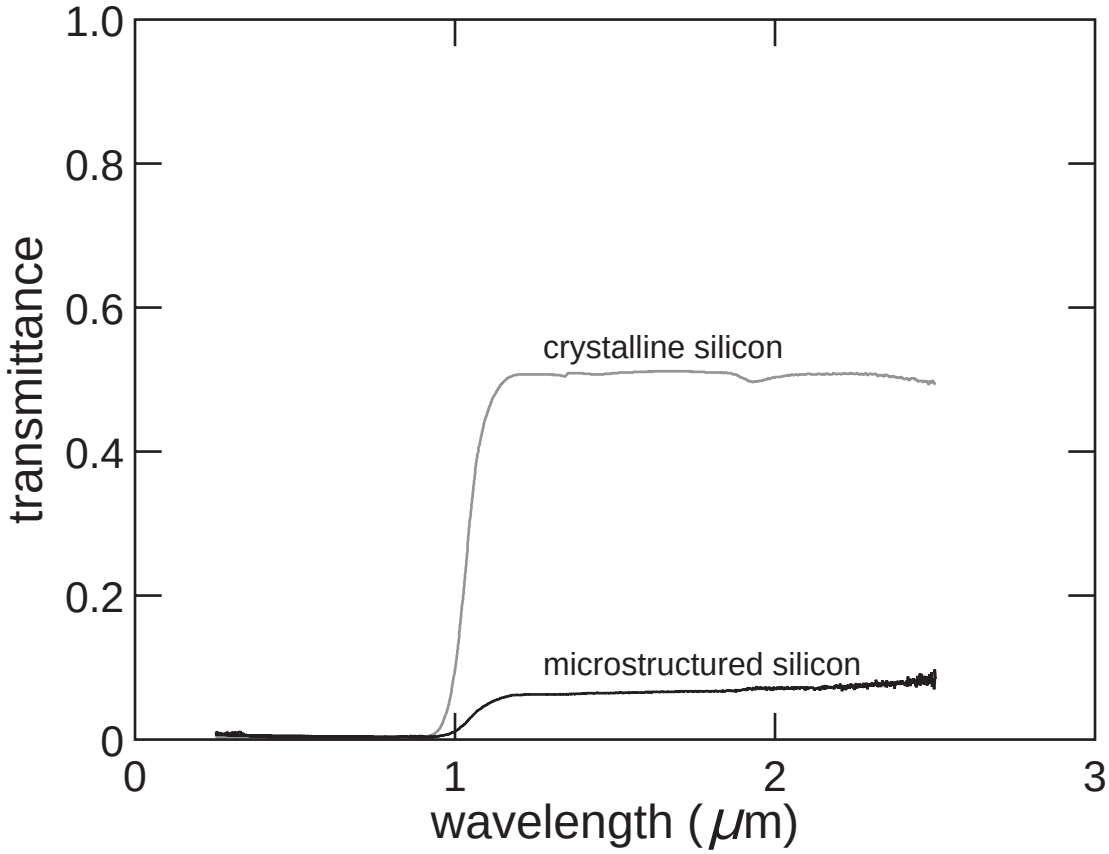
Optical properties

transmittance



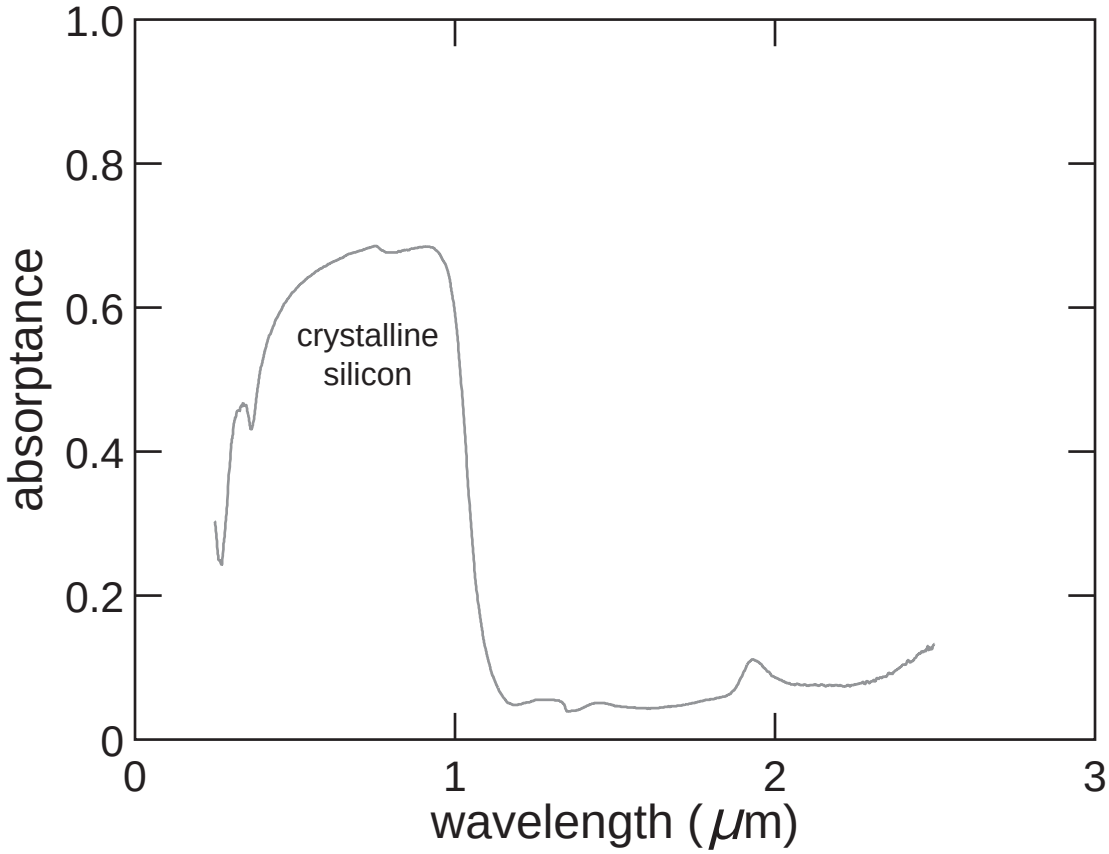
Optical properties

transmittance



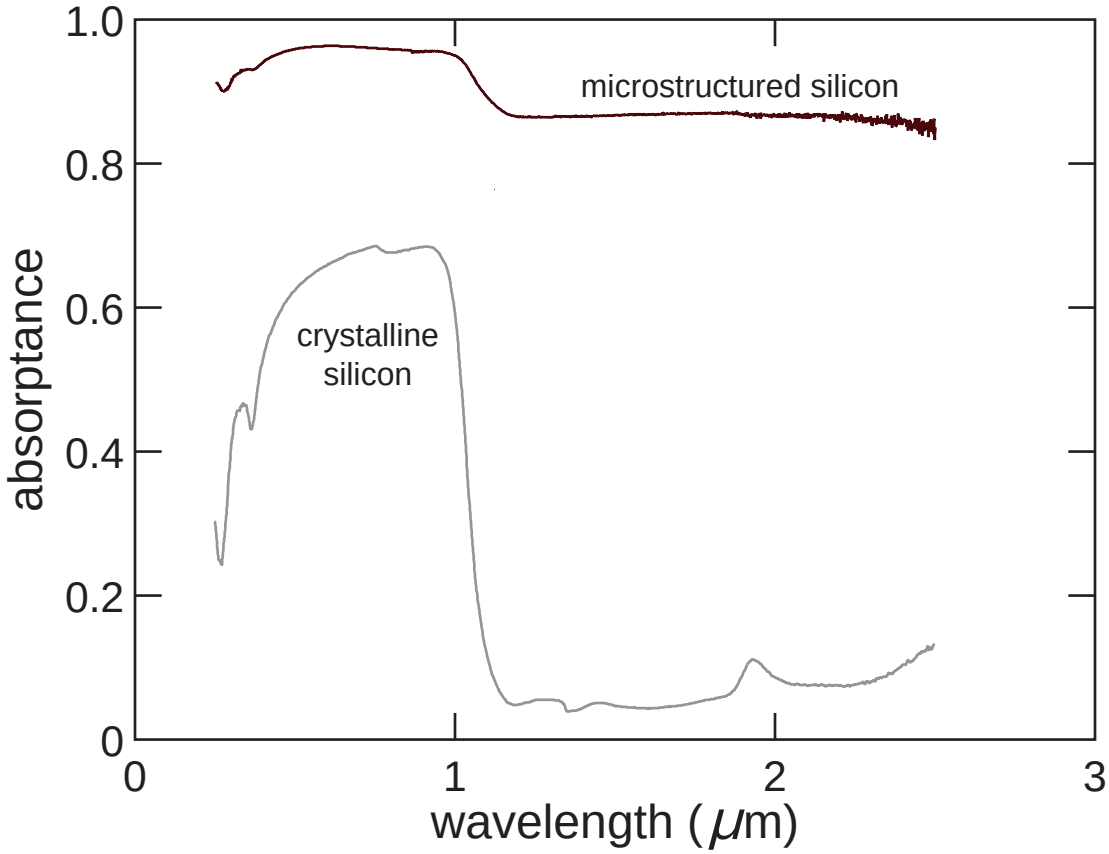
Optical properties

absorptance (A = 1 - R - T)



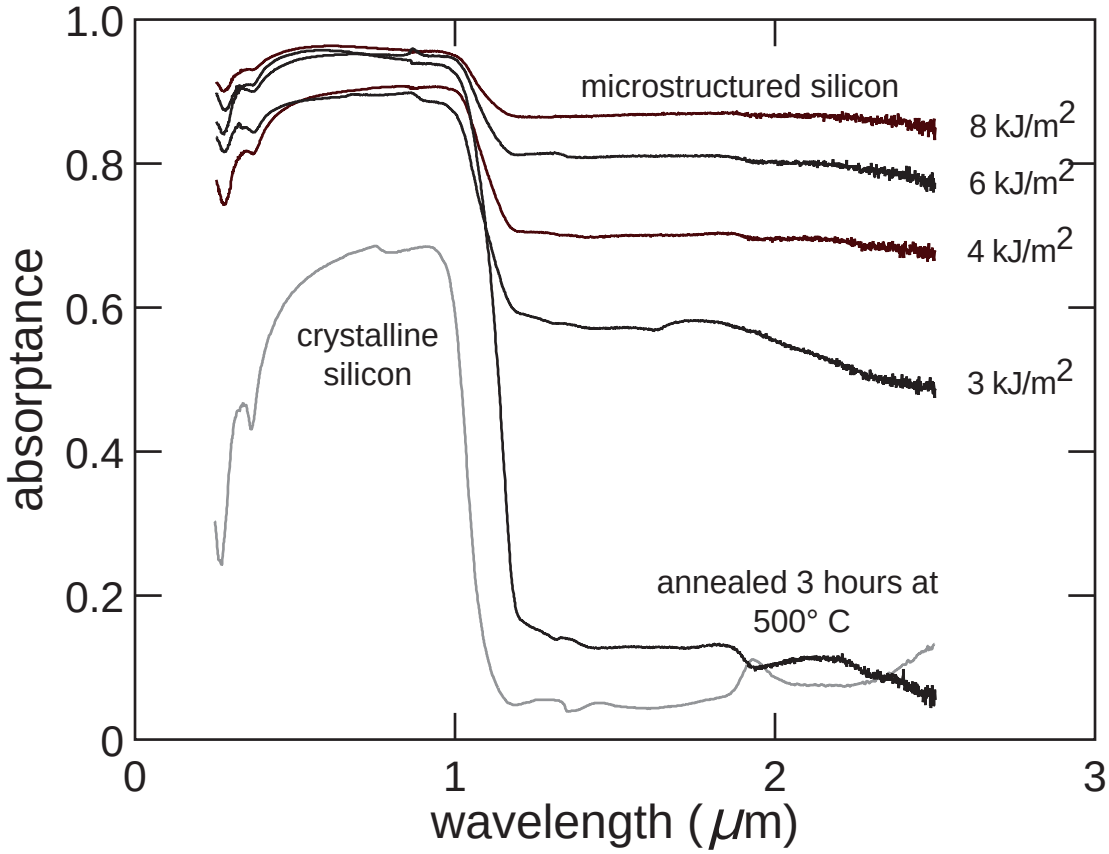
Optical properties

absorptance



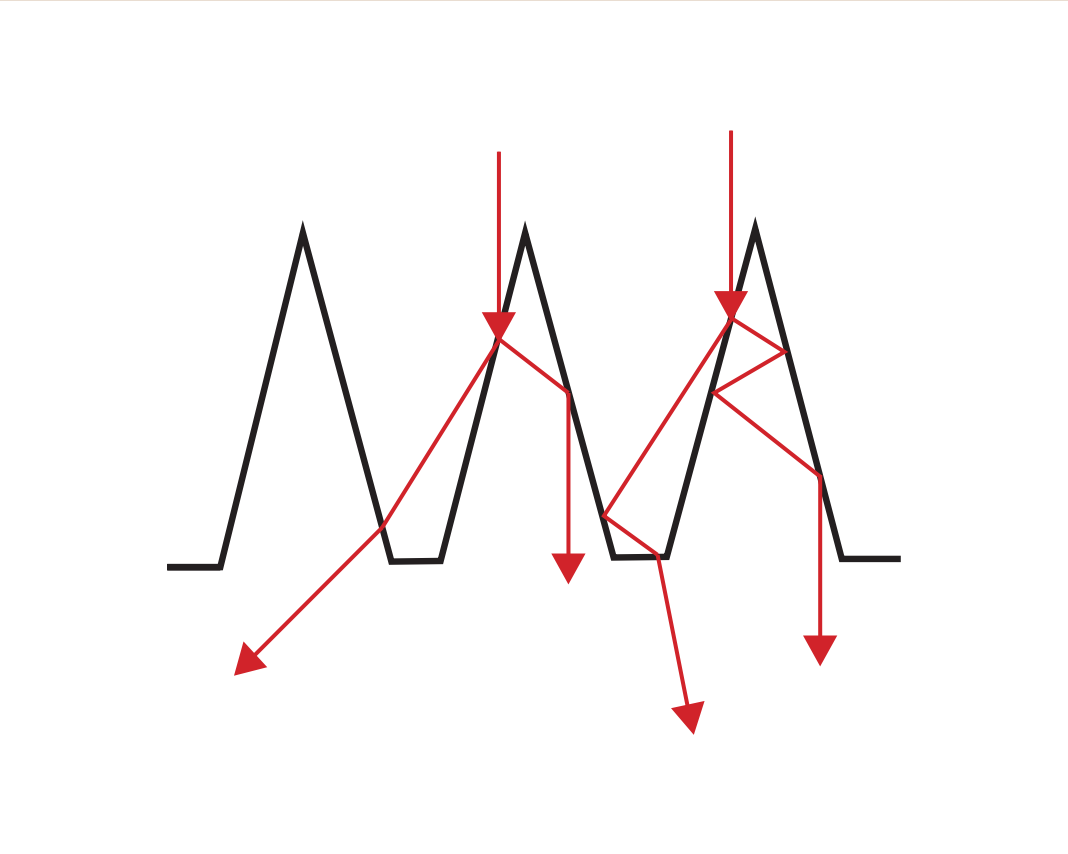
Optical properties

absorptance



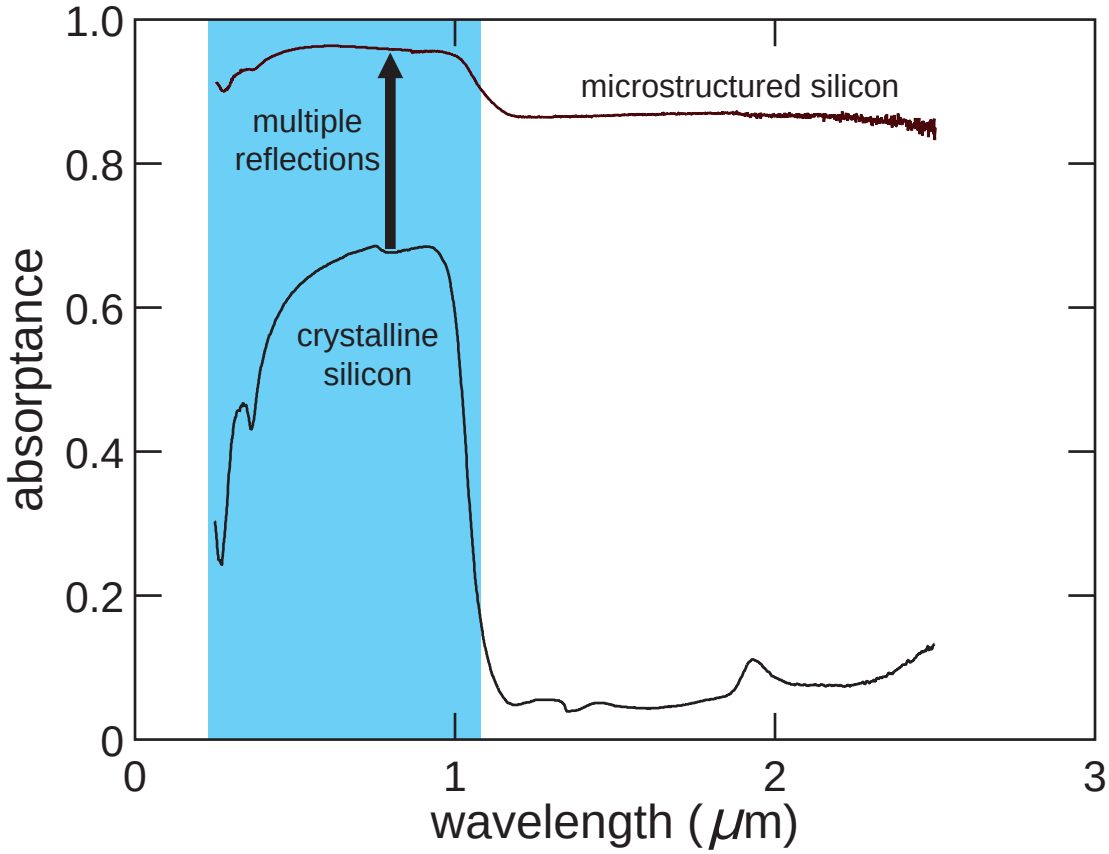
Why is it black?

Multiple reflections can enhance absorption



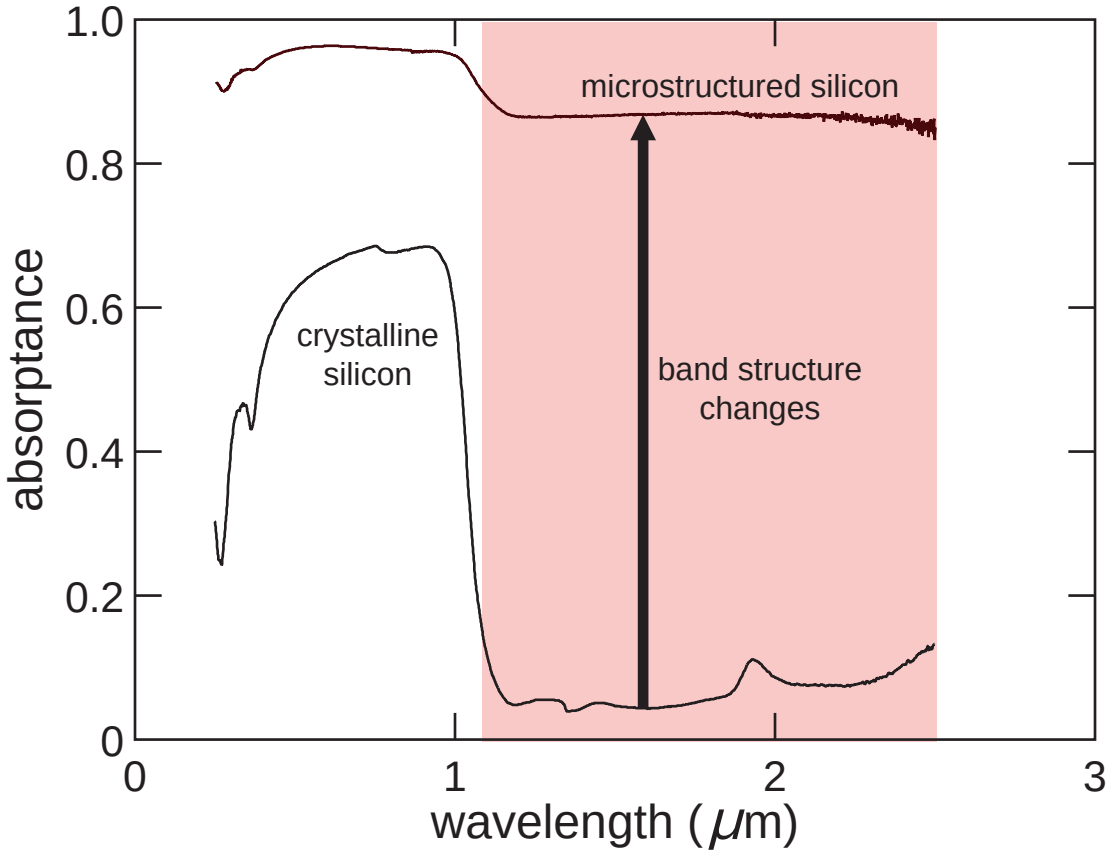
Optical properties

absorptance



Optical properties

absorptance



What produces the below-band gap absorption?

What changes band structure?

- impurities
- defects

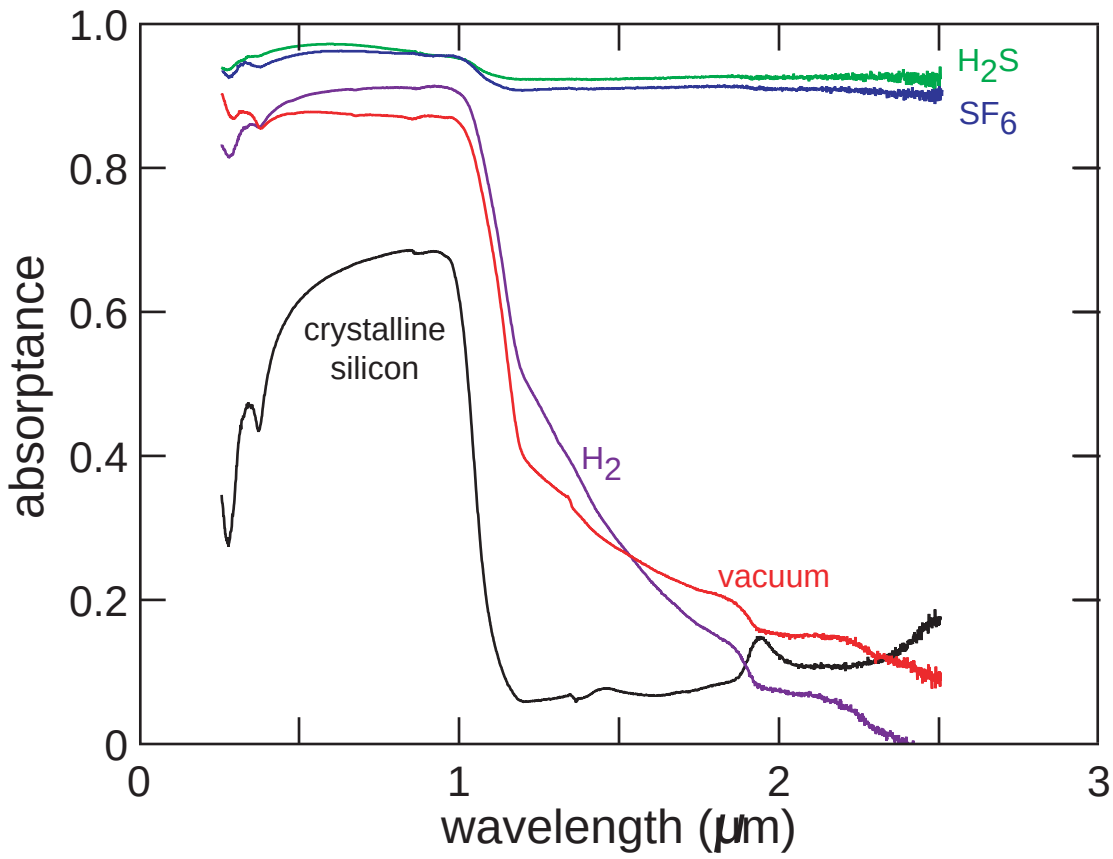
Work with other gases:

gas species incorporated into surface layer

sulfur required for below-band gap absorption (H_2S, SF_6)

Chemical analysis

absorptance



Sheehy *et al.*, in preparation

Surfaces structured in SF_6:

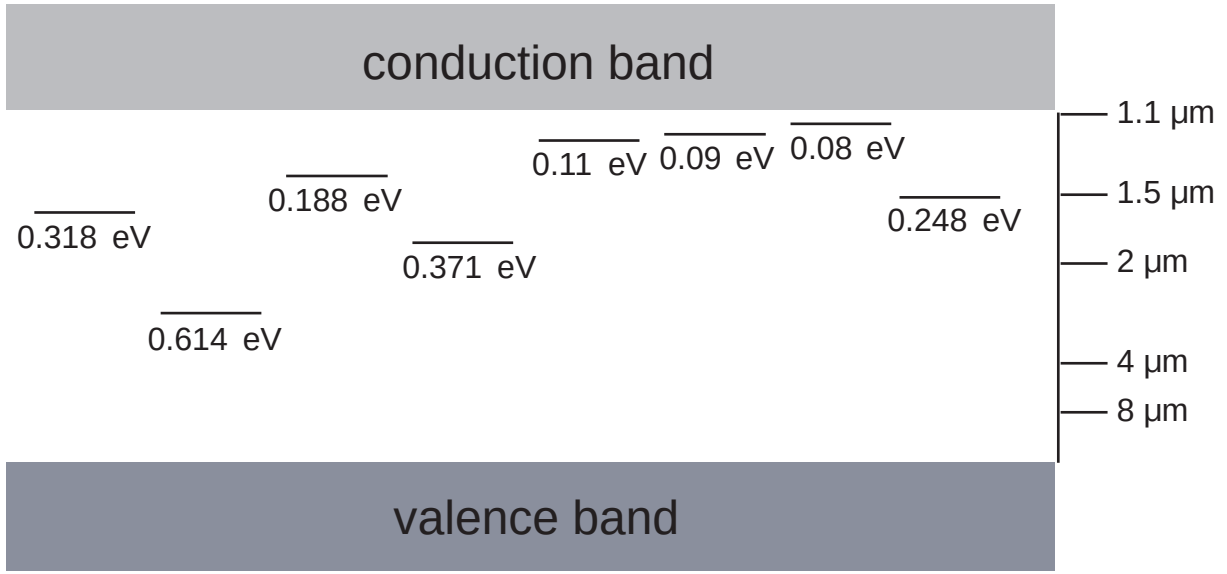
1.6% sulfur in surface layer (RBS)

also fluorine, oxygen

sulfur content decreases significantly on annealing

sulfur introduces states in silicon band gap

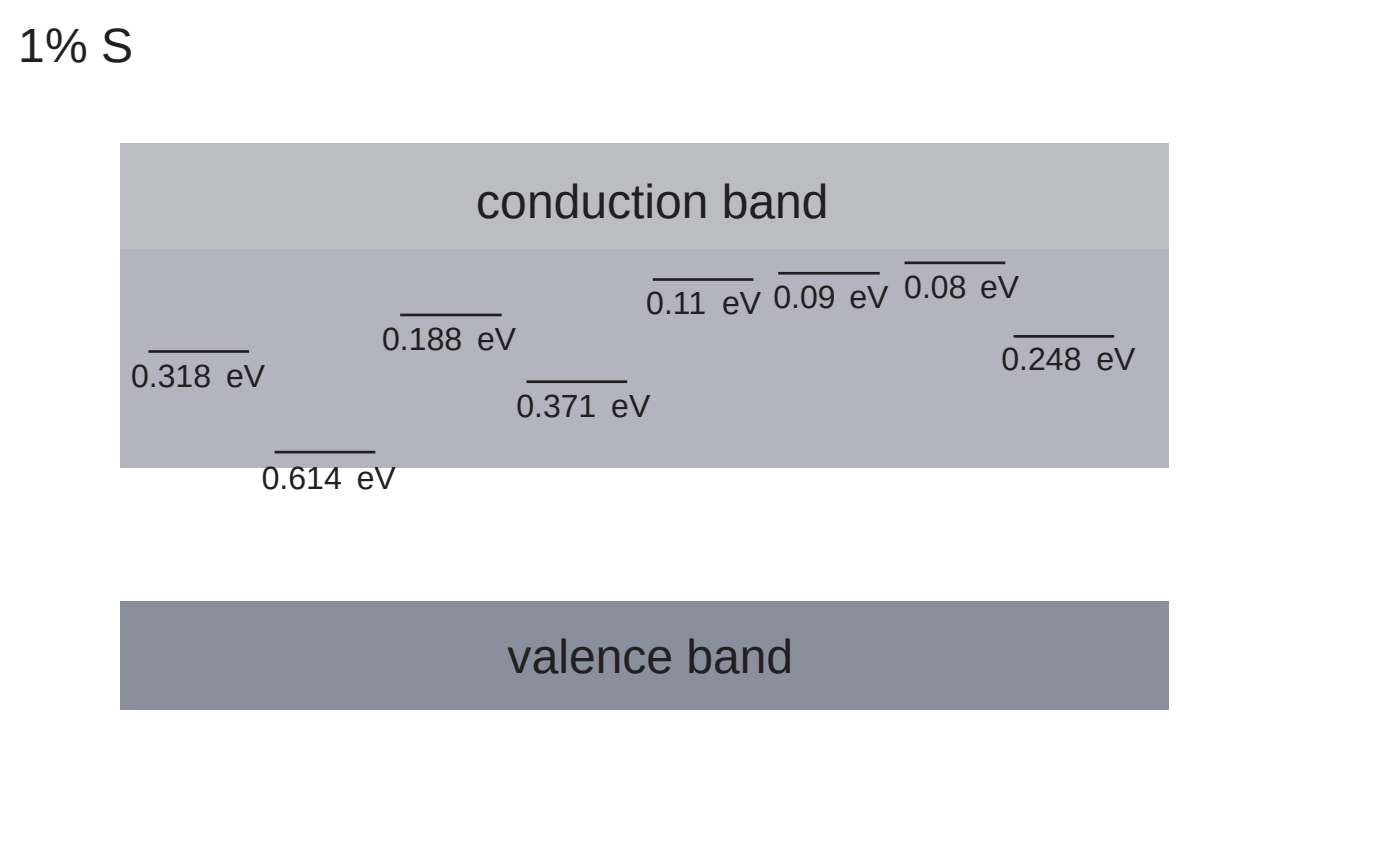
1 part in 10^6 S



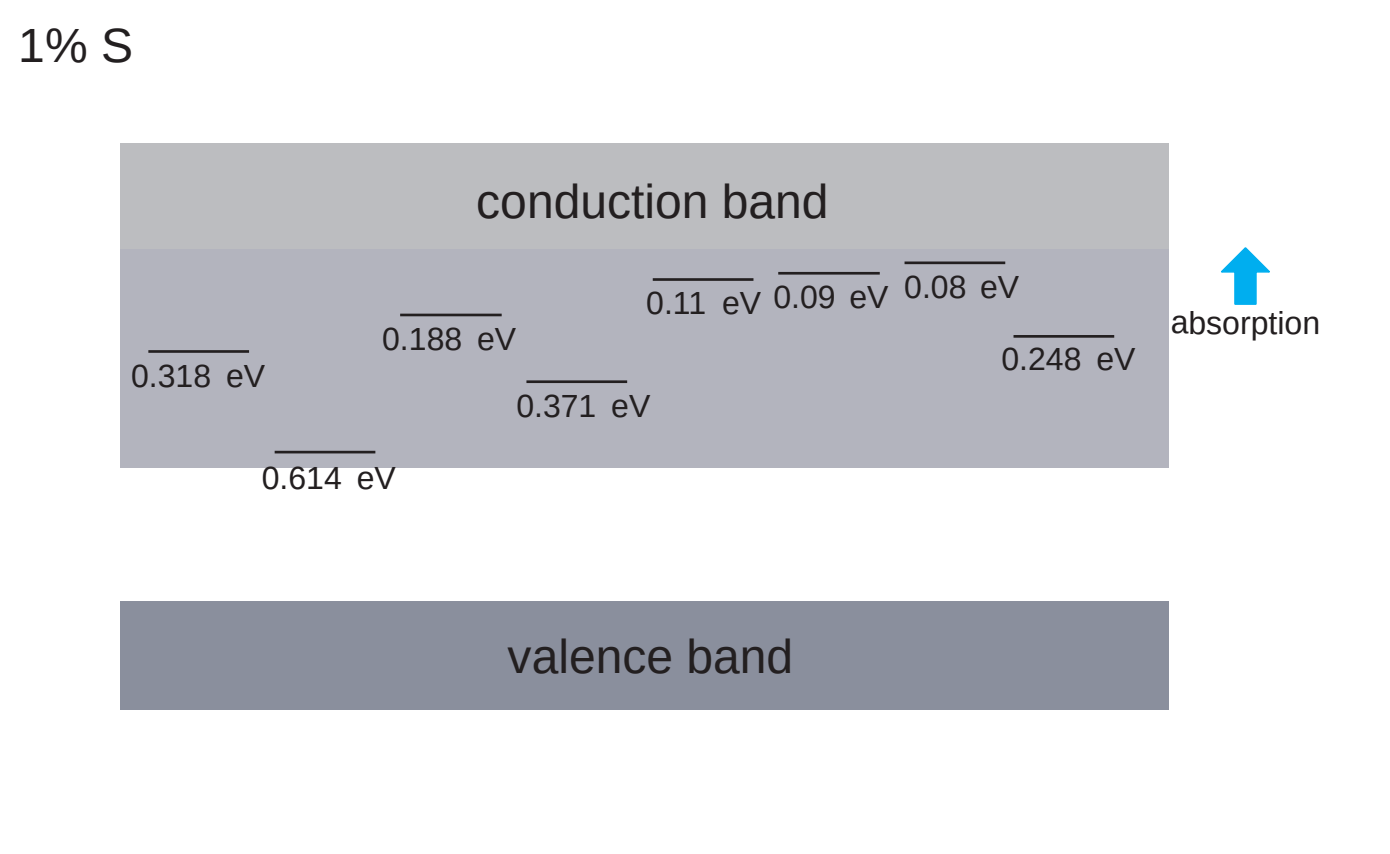
Janzén *et al.*, Phys. Rev. B **29**, 1907 (1984)

Chemical analysis

at high concentrations, states may broaden into a band



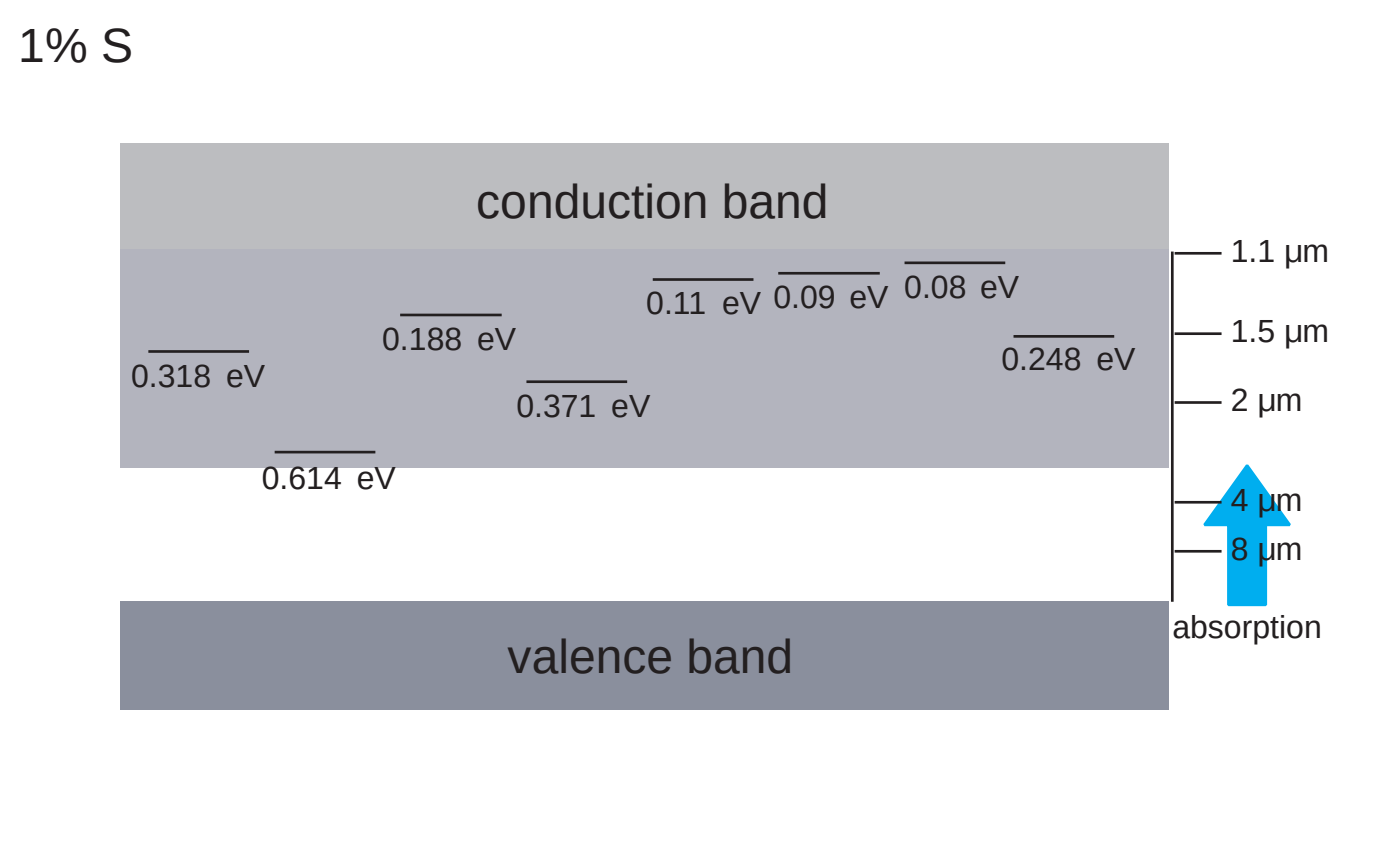
at high concentrations, states may broaden into a band



***n*-type impurity band: metallic**

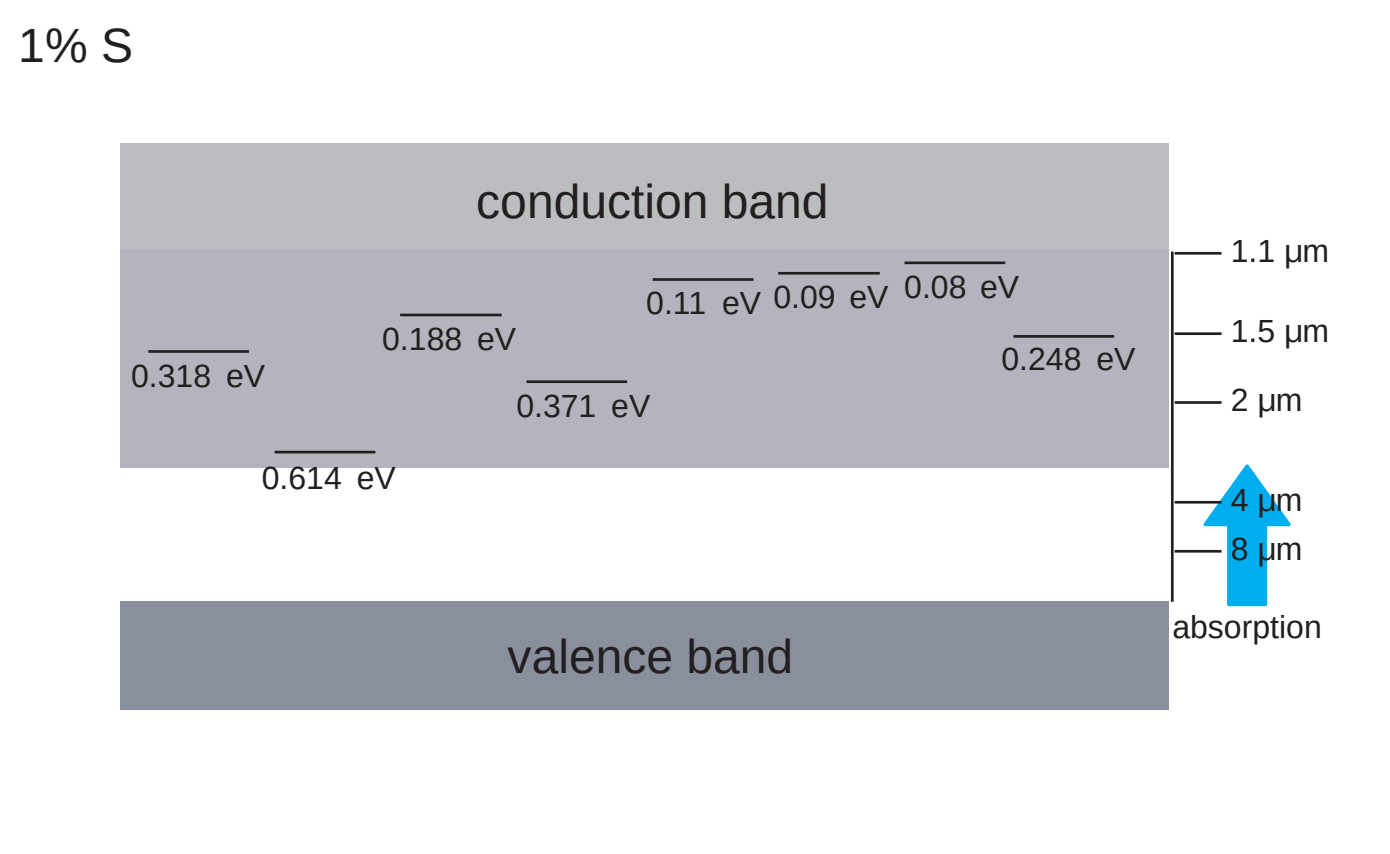
Chemical analysis

at high concentrations, states may broaden into a band



***p*-type impurity band: reduced band gap, absorption should drop off around 3 µm**

near-IR transmittance rises around 3 μm: *p*-type



Further evidence for *p*-type impurity band:

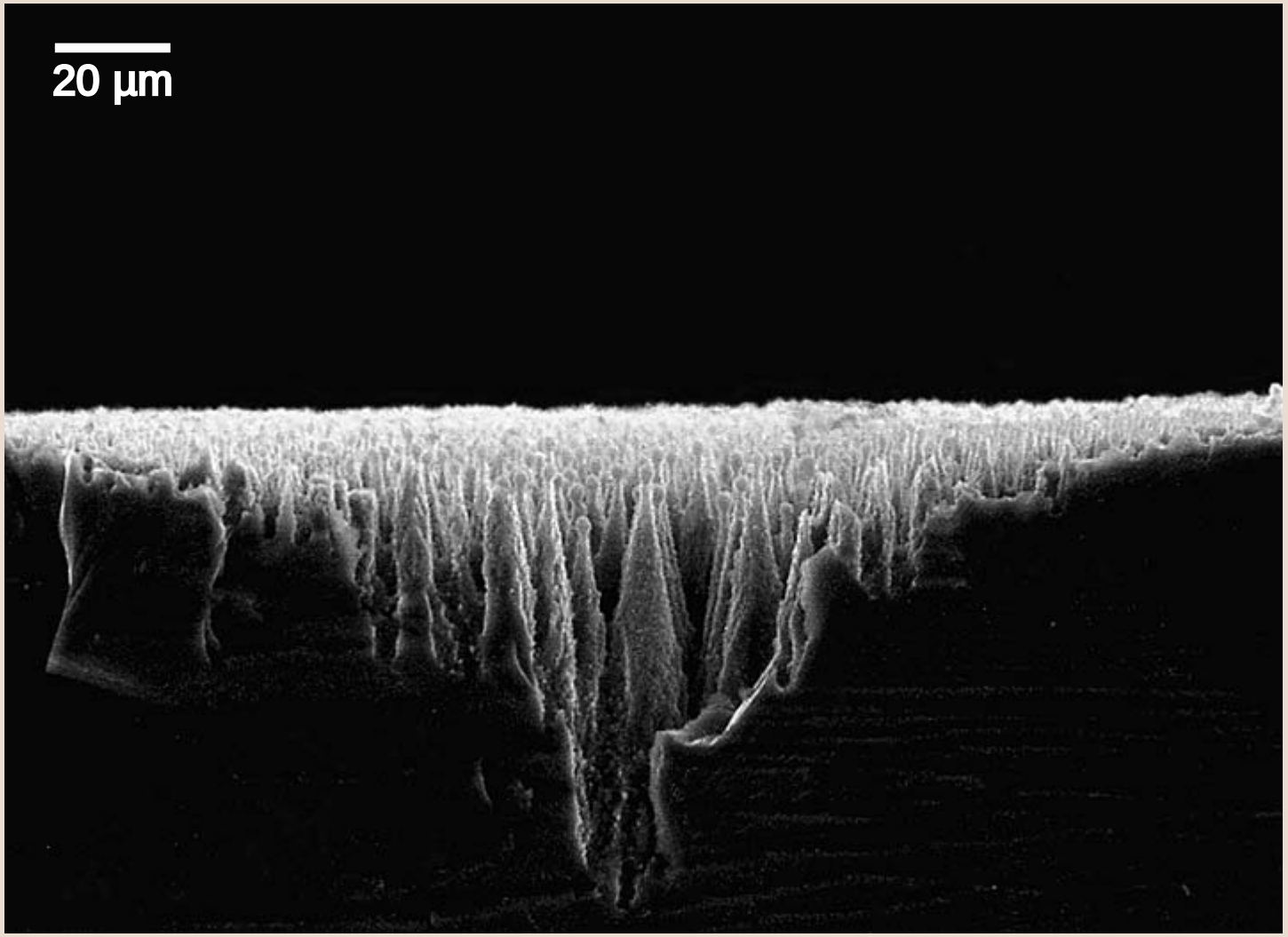
- *n*-type material behaves like *p*-*n* junction after structuring
- *p*-type material does not

Sulfur a likely explanation:

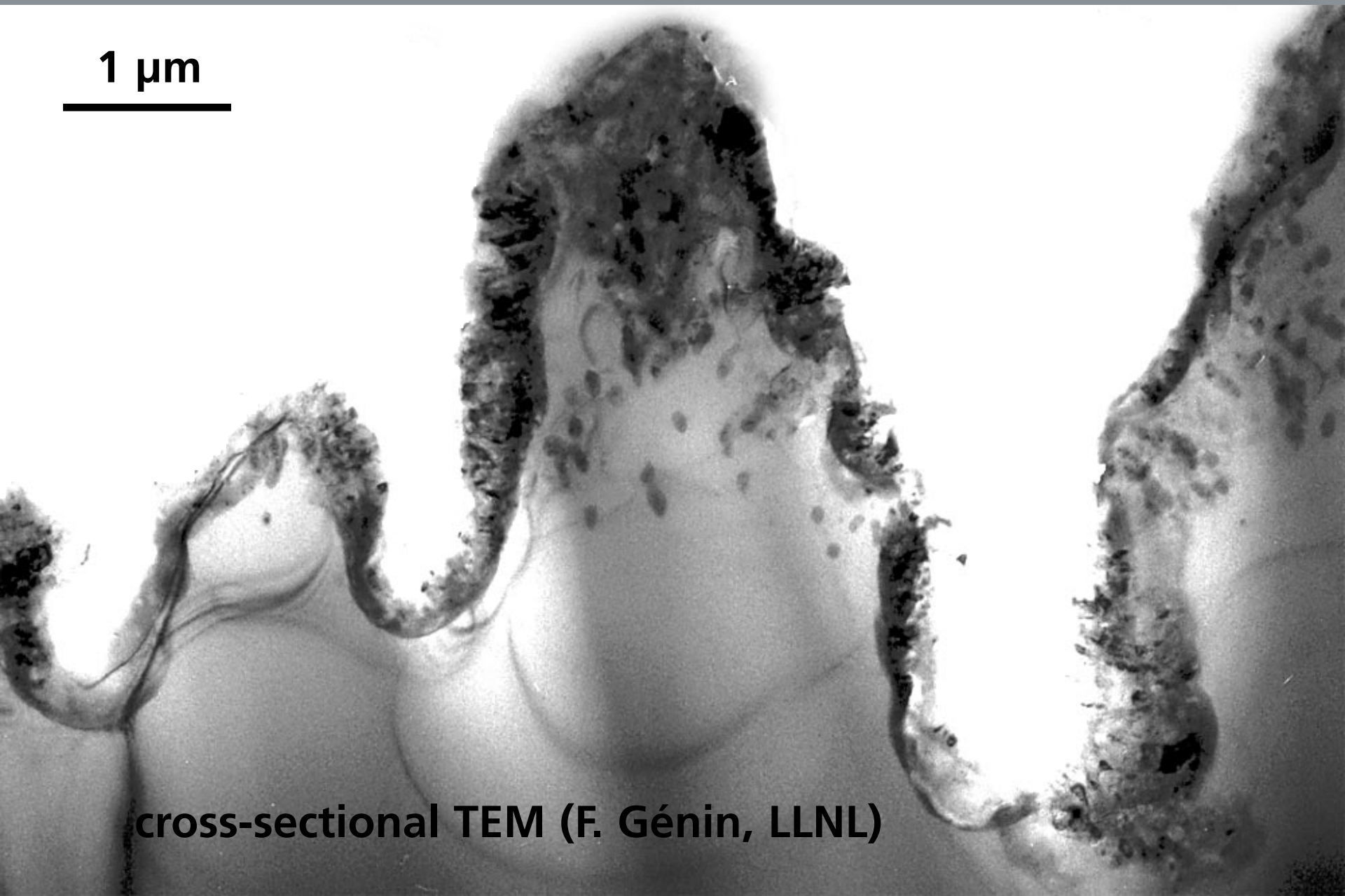
- sulfur required for below-band gap absorption
- annealing reduces sulfur and absorption
- appropriate wavelength range (*p*-type)

What is the underlying structure?

Structural analysis

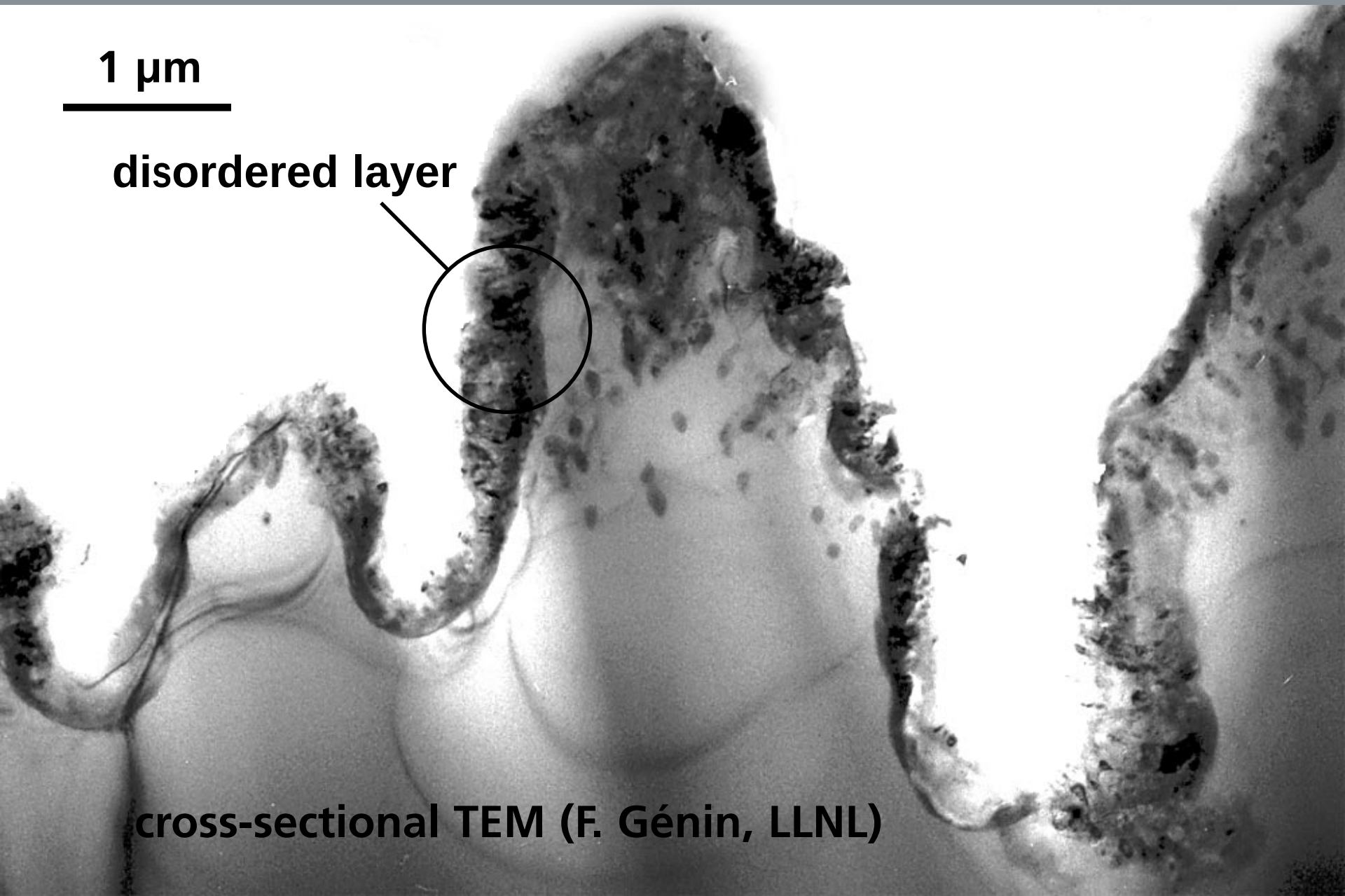


Structural and chemical analysis



cross-sectional TEM (F. Génin, LLNL)

Structural and chemical analysis



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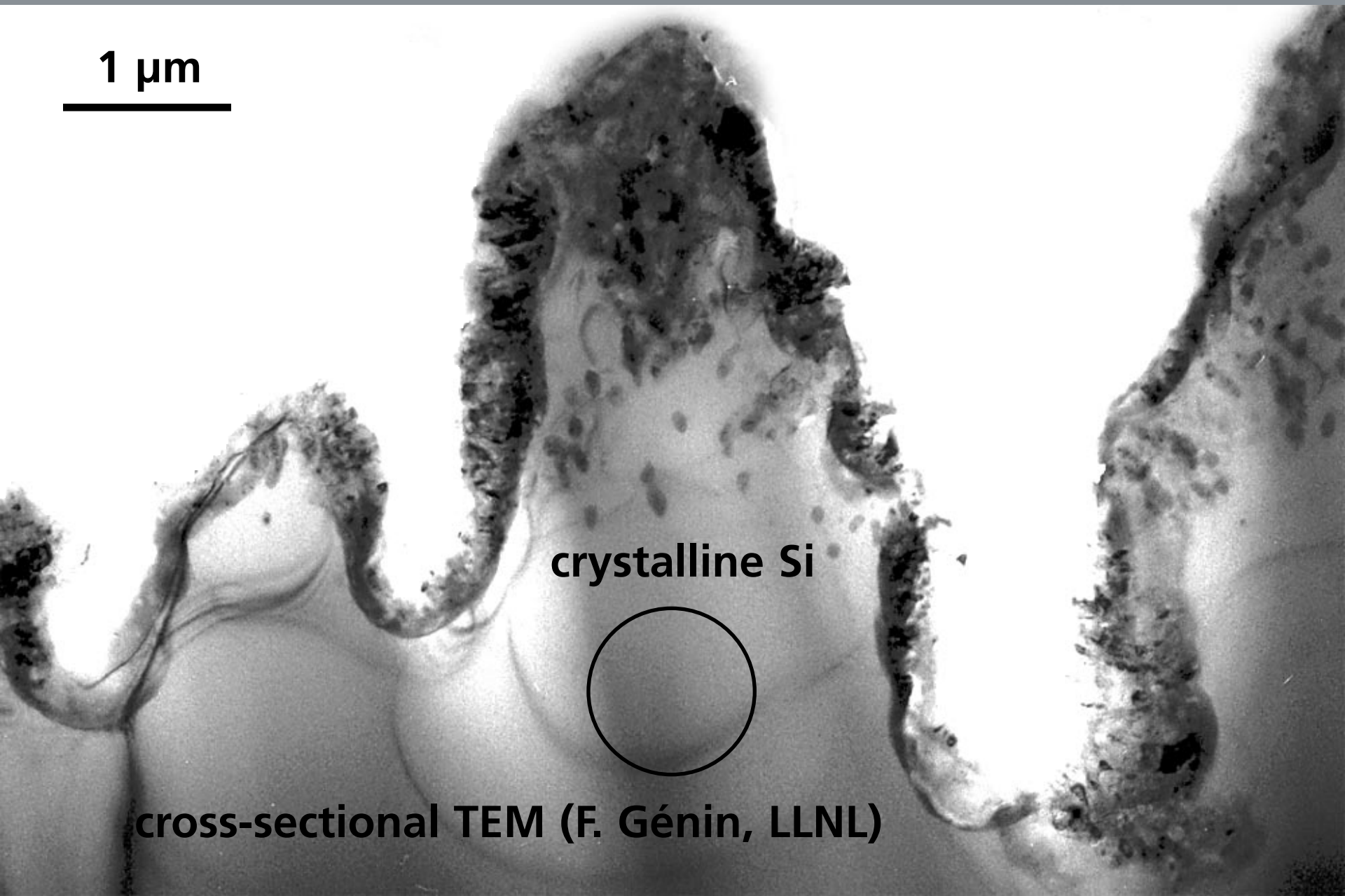
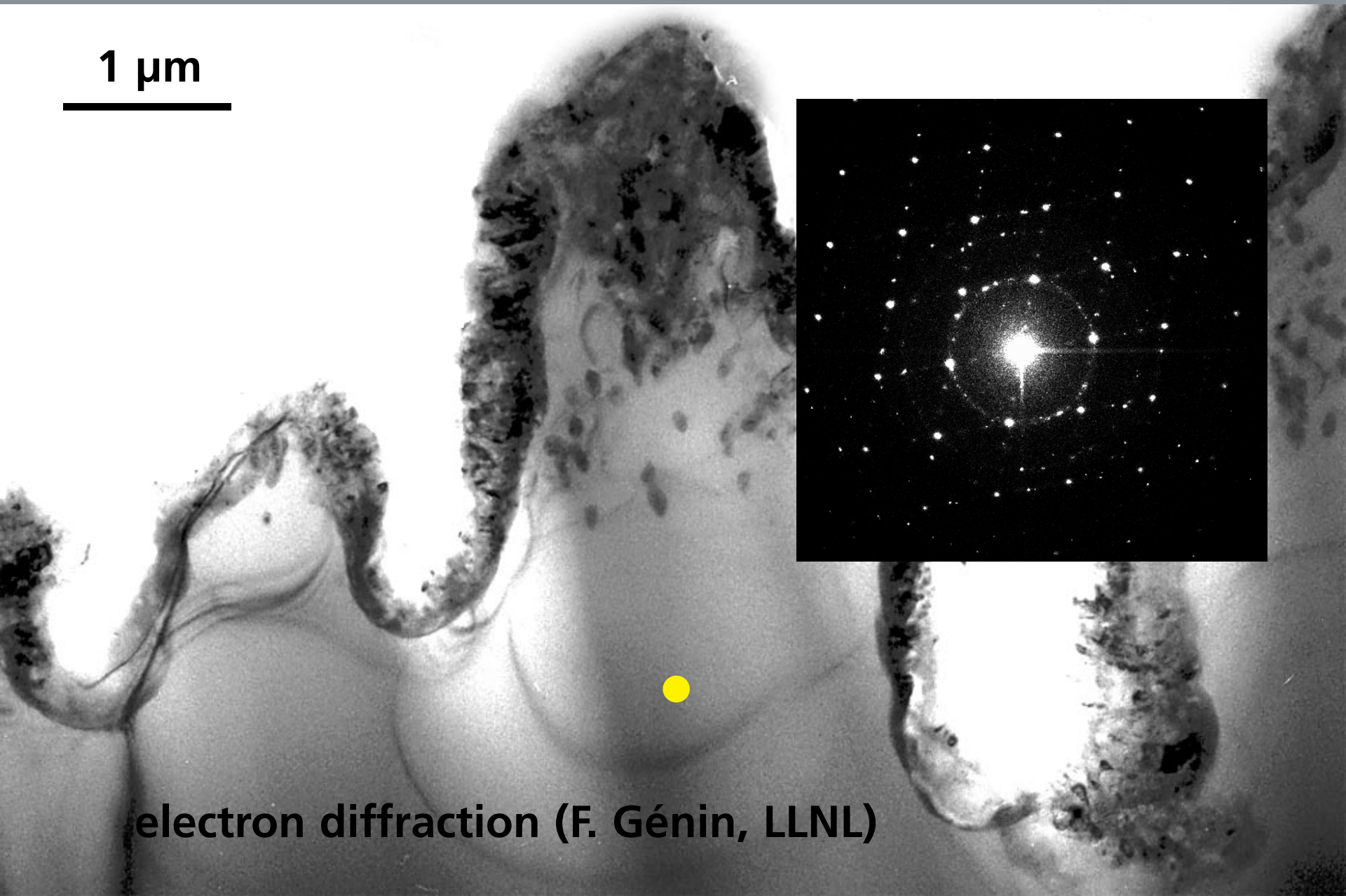
Structural and chemical analysis



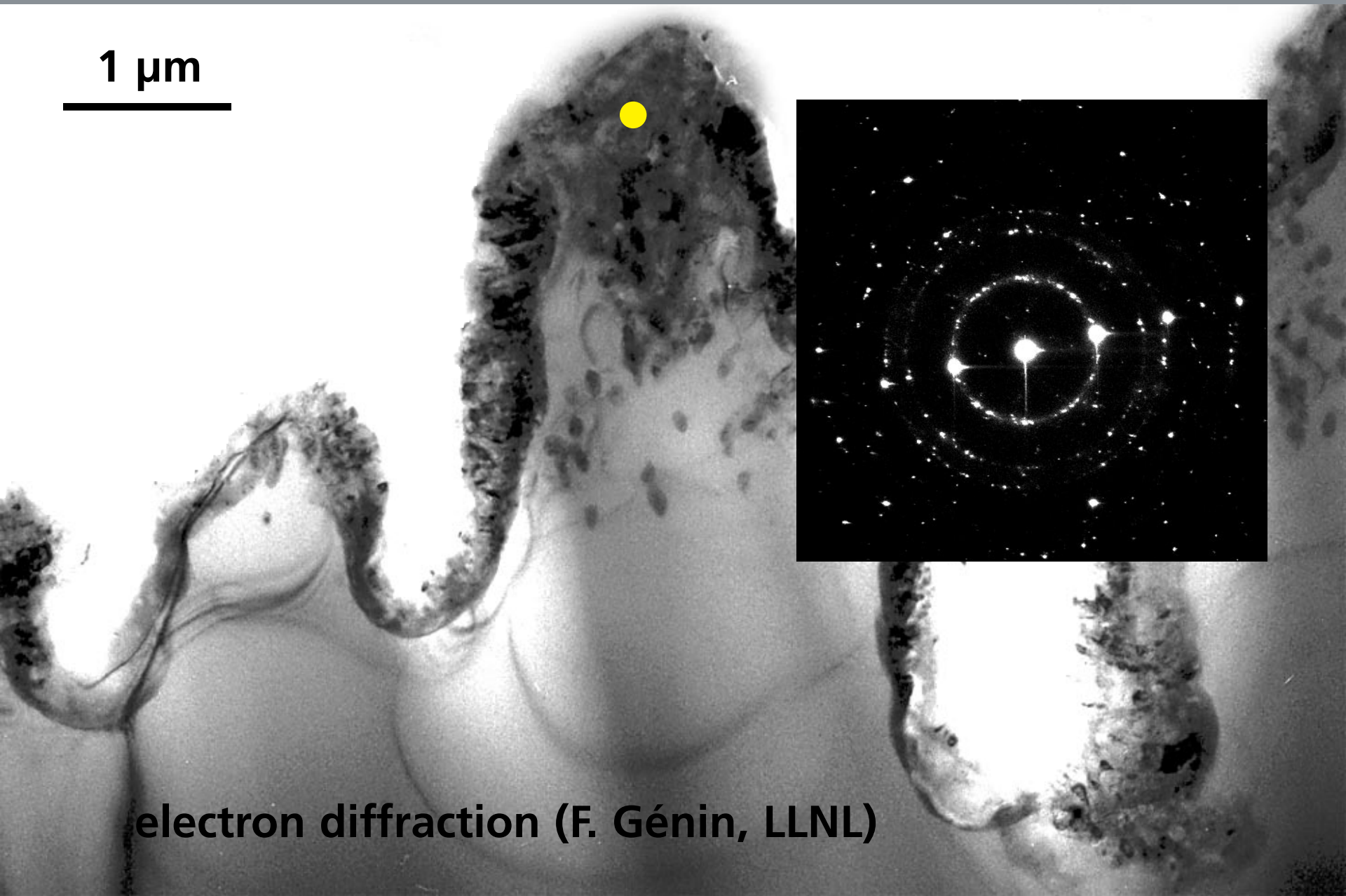
cross-sectional TEM (F. Génin, LLNL)

Structural and chemical analysis



electron diffraction (F. Génin, LLNL)

Structural and chemical analysis



electron diffraction (F. Génin, LLNL)

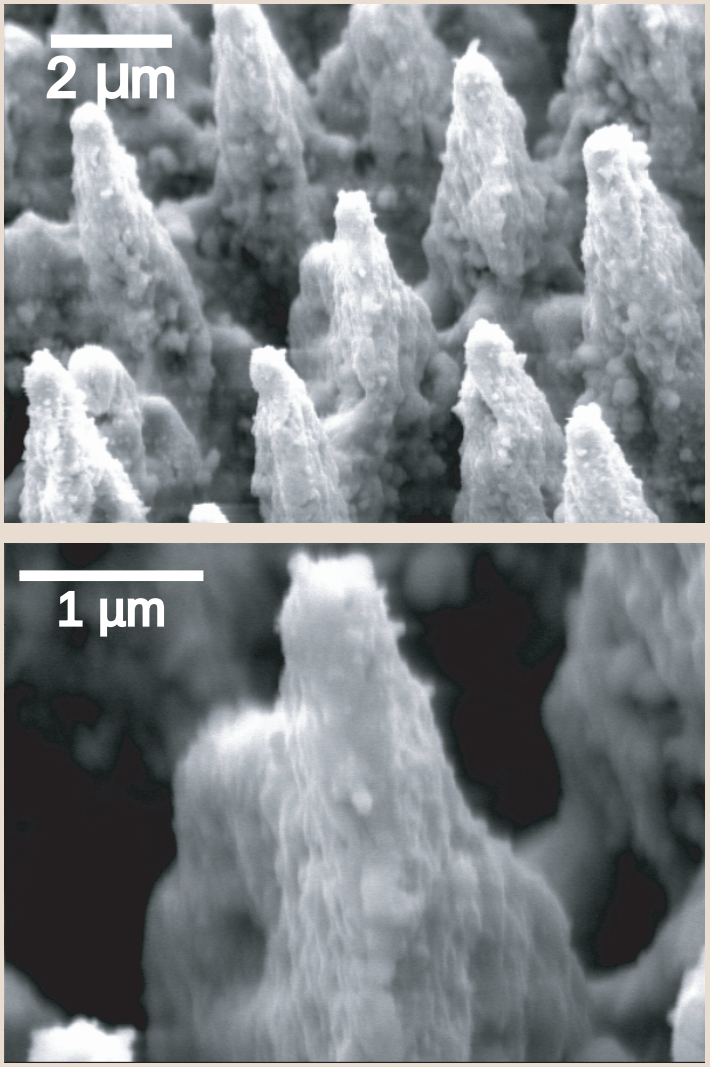
Structural and chemical analysis

cross-sectional TEM, ion channeling:

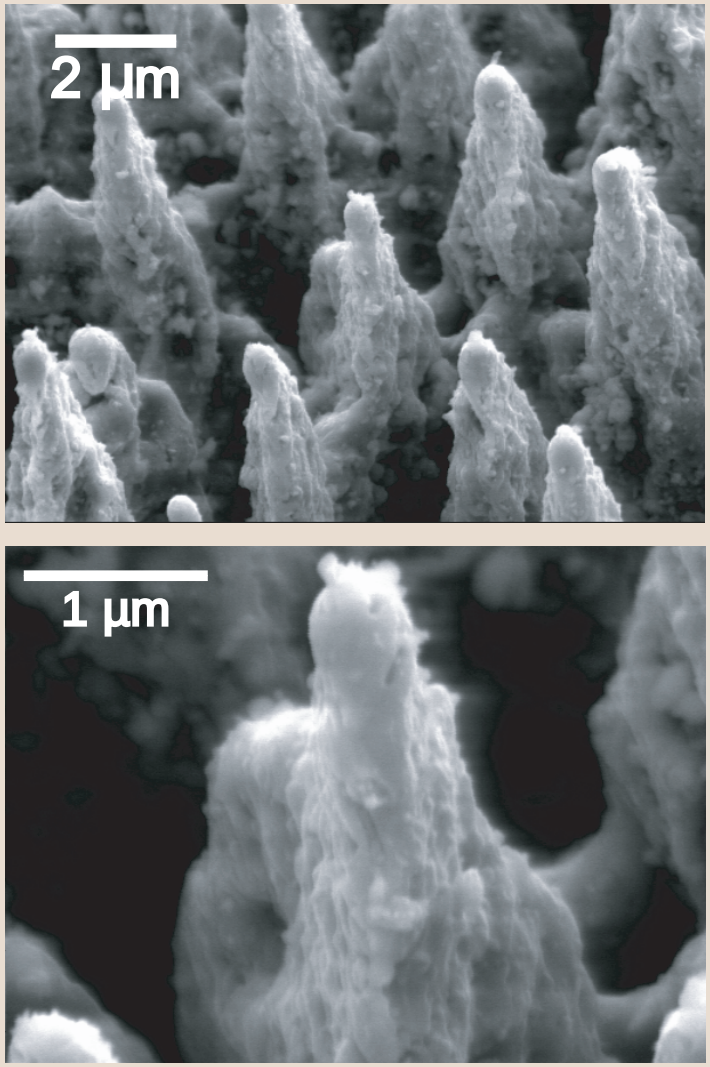
- **core of spikes: undisturbed Si**
- **surface layer: polycrystalline Si, impurities, embedded nanocrystallites and pores**

Annealing at 500 C for three hours:

before

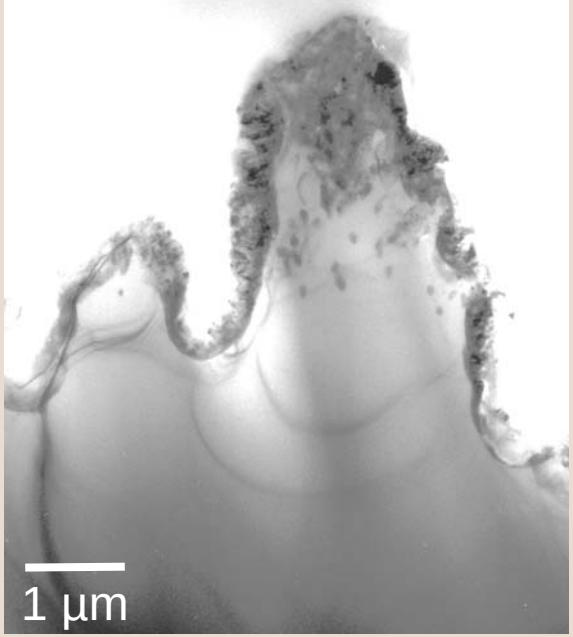


after

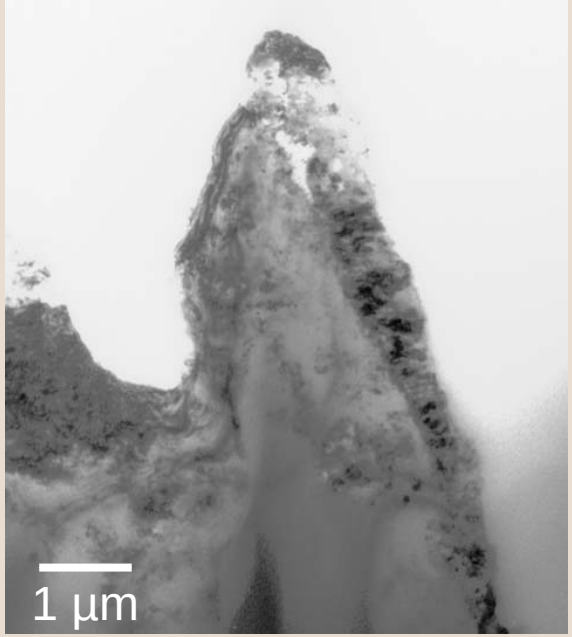


Structural analysis

not annealed



annealed



annealing does not affect visible structure

What happens with nanosecond pulses?

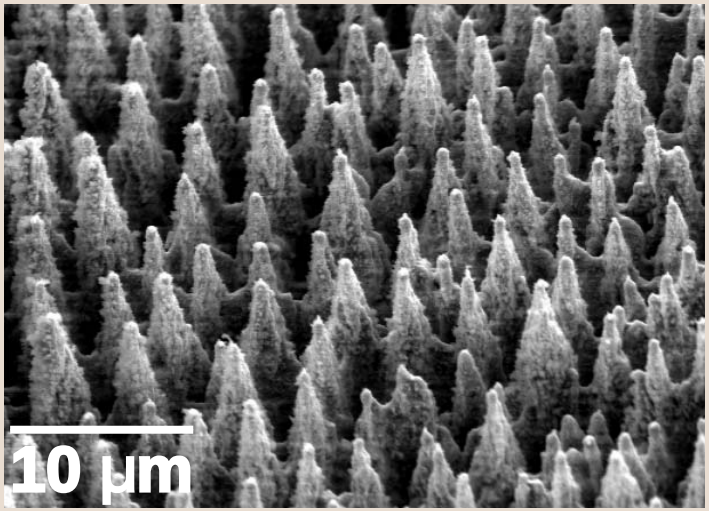
Nanosecond vs. femtosecond

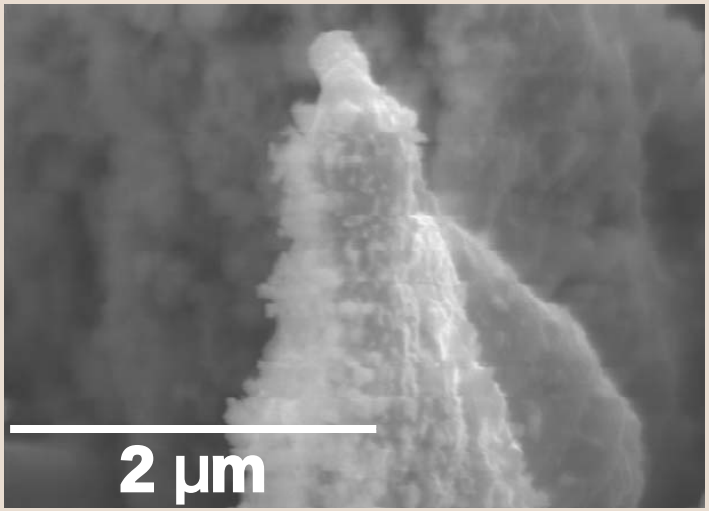
fs pulses: Her *et al.*, APL **73**, 1673 (1998)
ns pulses: Pedraza *et al.*, APL **74**, 2322 (1999).

How do nanosecond and femtosecond compare?

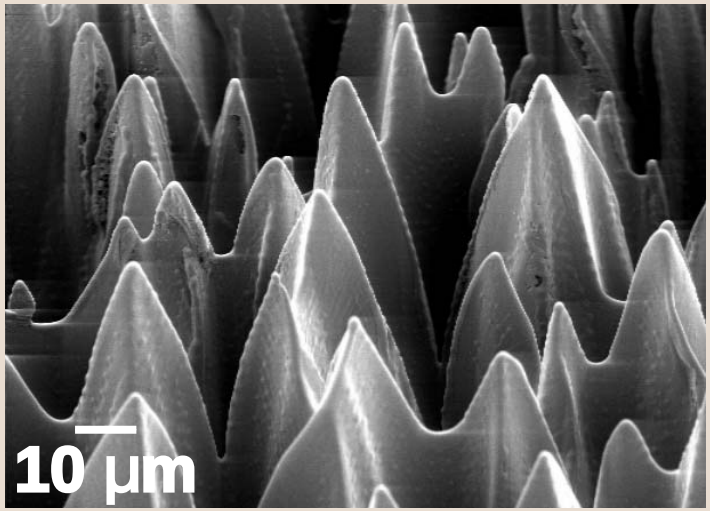
Nanosecond vs. femtosecond

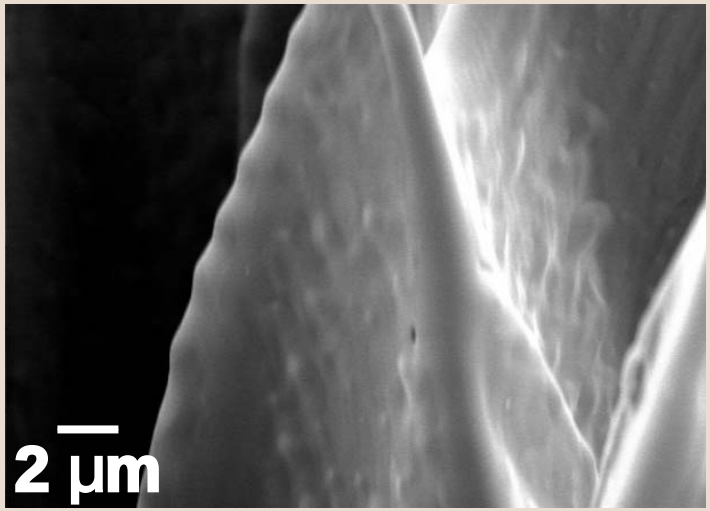
800 nm, 100 fs, 10 kJ/m^2





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



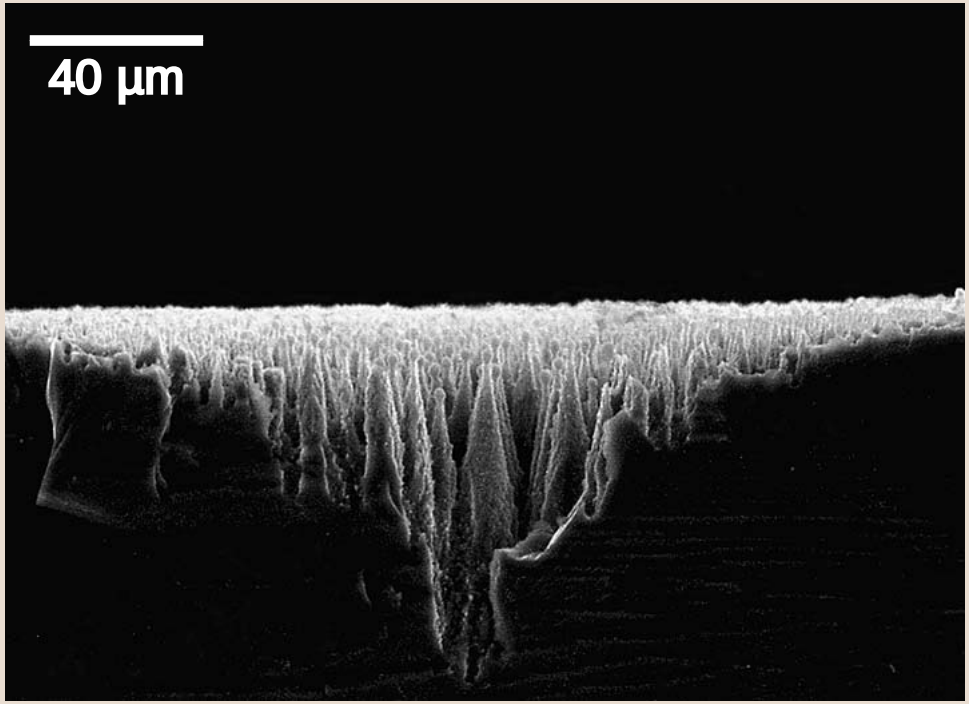


Nanosecond vs. femtosecond

Nanosecond cones bigger, smoother

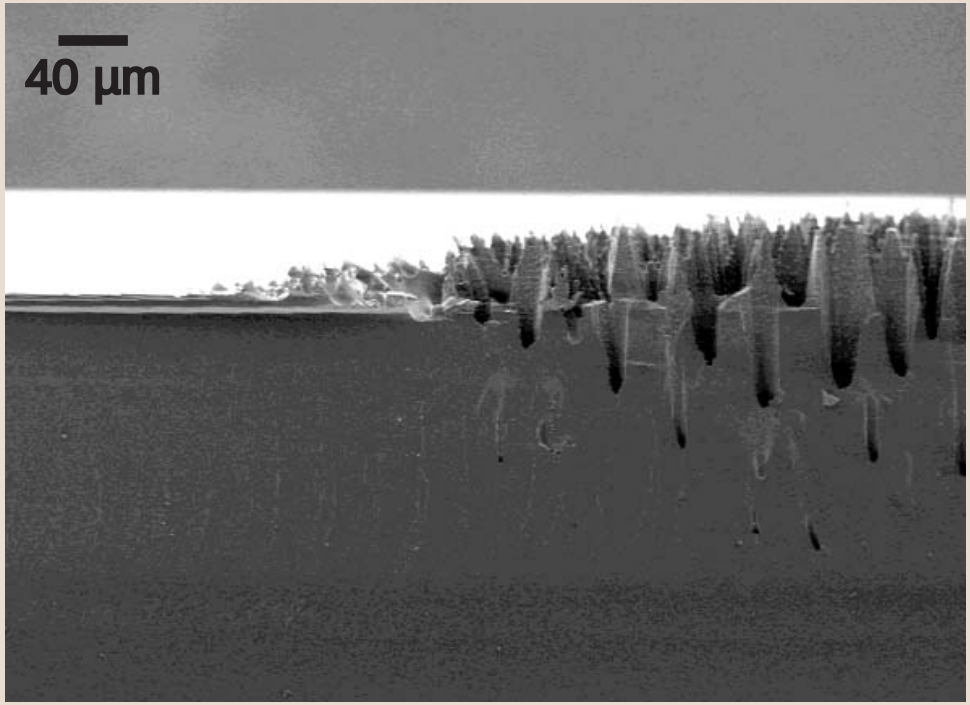
Nanosecond vs. femtosecond

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



fs cones etched below surface

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



ns cones grow above surface

Nanosecond vs. femtosecond

Nanosecond cones bigger, smoother

Nanosecond cones grow, femtosecond cones are etched

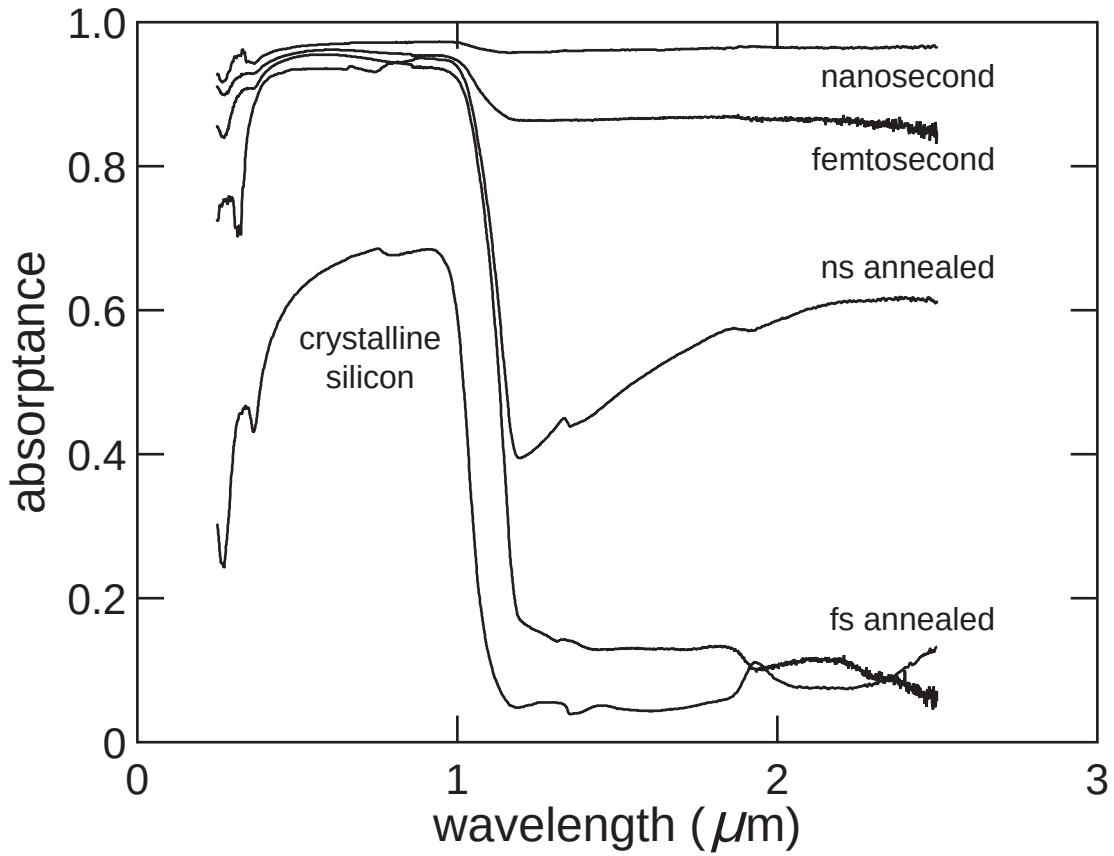
Nanosecond vs. femtosecond

Very different morphology!

How do optical properties compare?

Nanosecond vs. femtosecond

absorptance



Nanosecond vs. femtosecond

Ns and fs cone composition similar

ns: 0.7% sulfur (ion channeling)

fs: 1.6% sulfur (ion channeling)

both: sulfur content decreases significantly on annealing

also high fluorine content (ToF SIMS)

Ns and fs ion channeling: structural differences

both: polycrystalline (not amorphous)

ns: significant crystallinity, sulfur 50% substitutional

fs: no substitutional sulfur

Nanosecond vs. femtosecond:

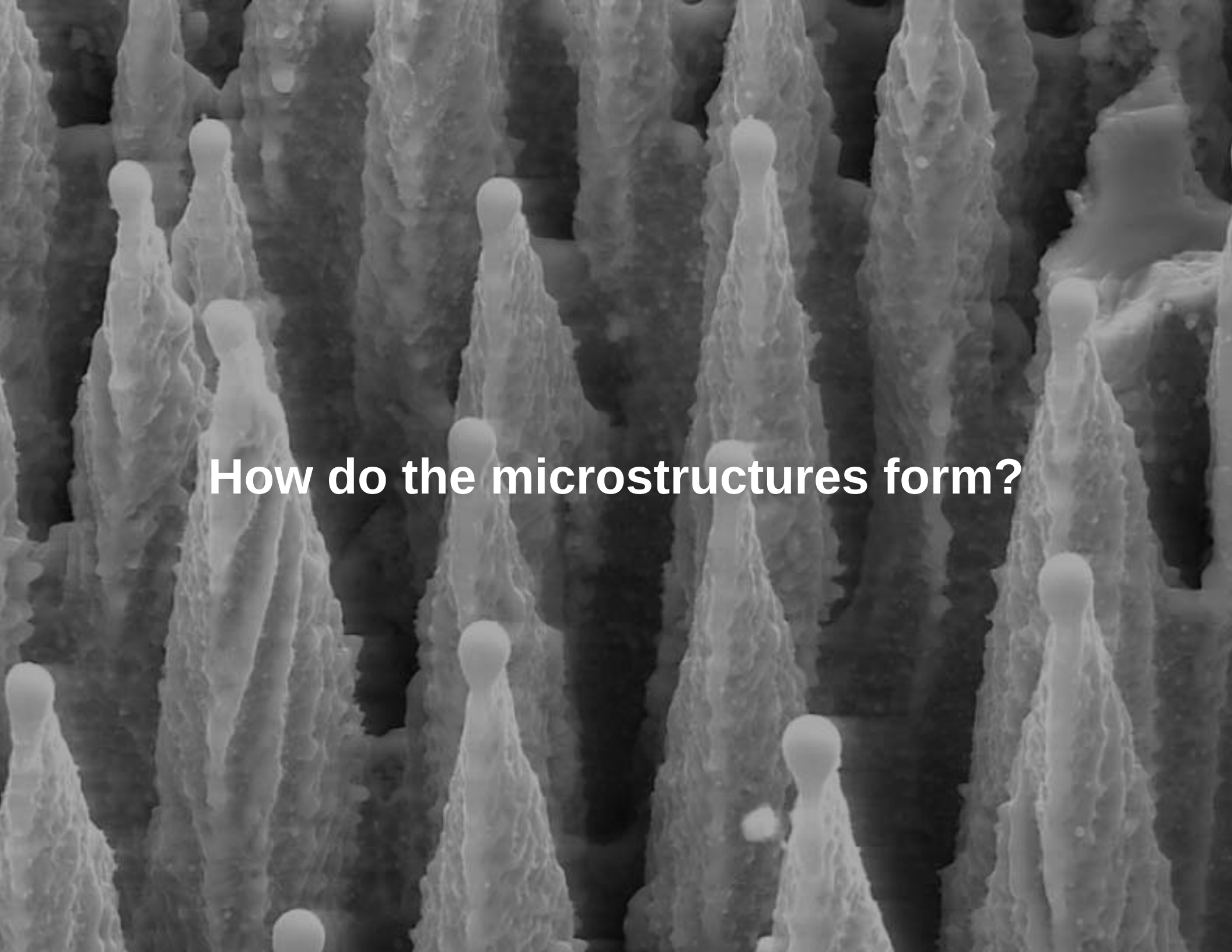
optical properties virtually identical

sulfur content similar

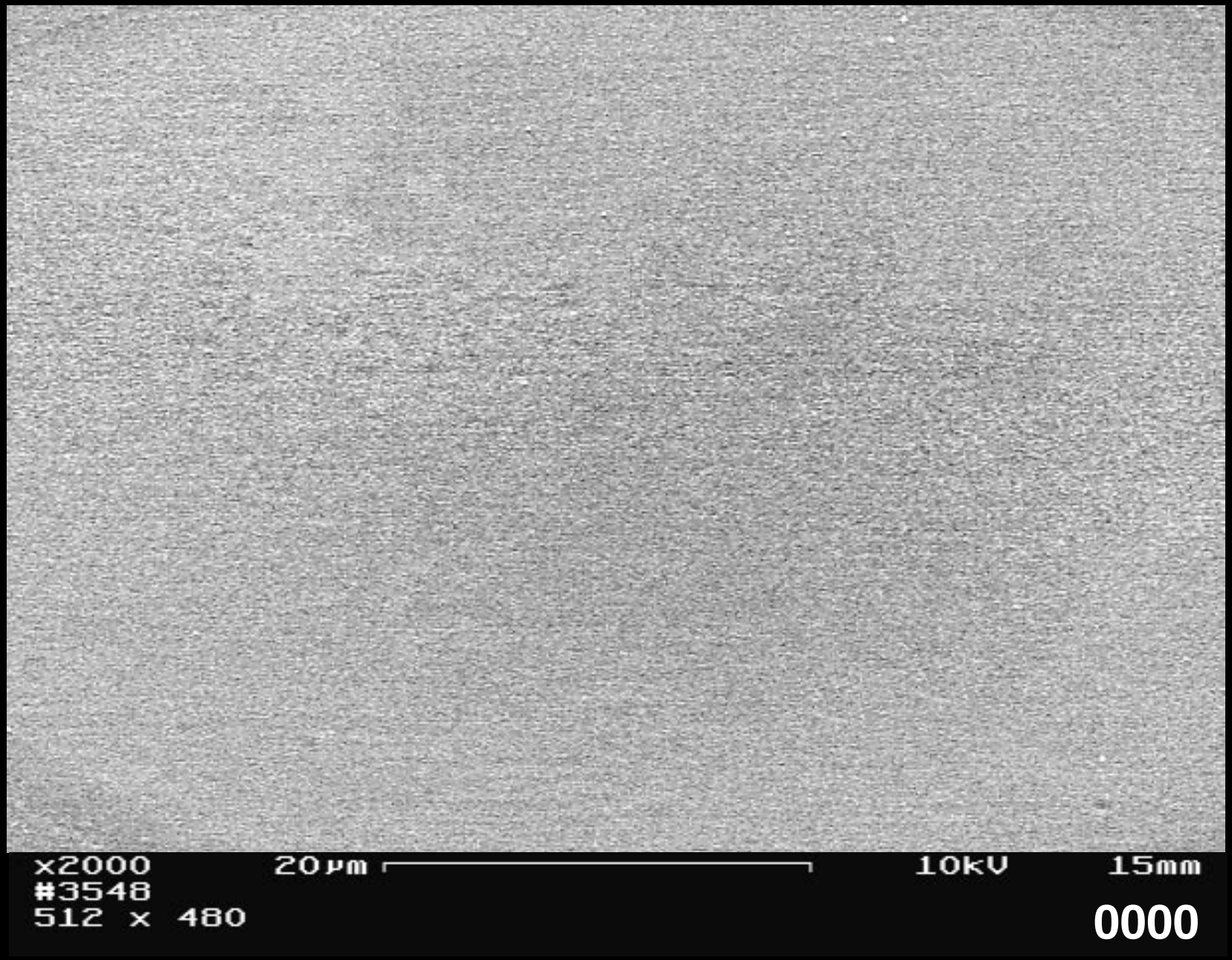
structure and morphology very different!

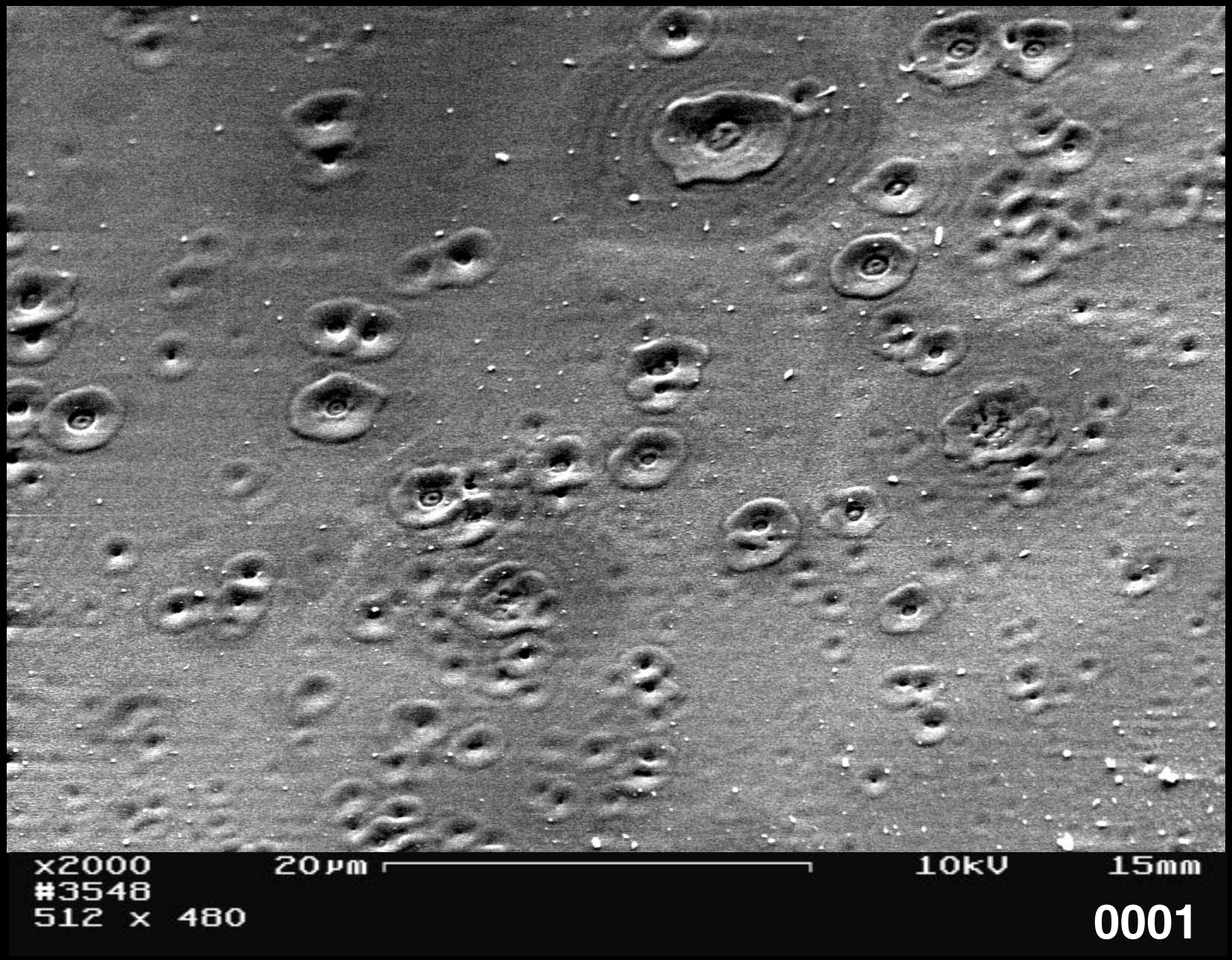
Summary of optical properties

- visible absorptance: multiple reflections
- infrared absorptance: new electronic states
- p-type sulfur impurity band below CB edge



How do the microstructures form?


x2000
20µm
10kV
15mm
#3548
512 x 480
0000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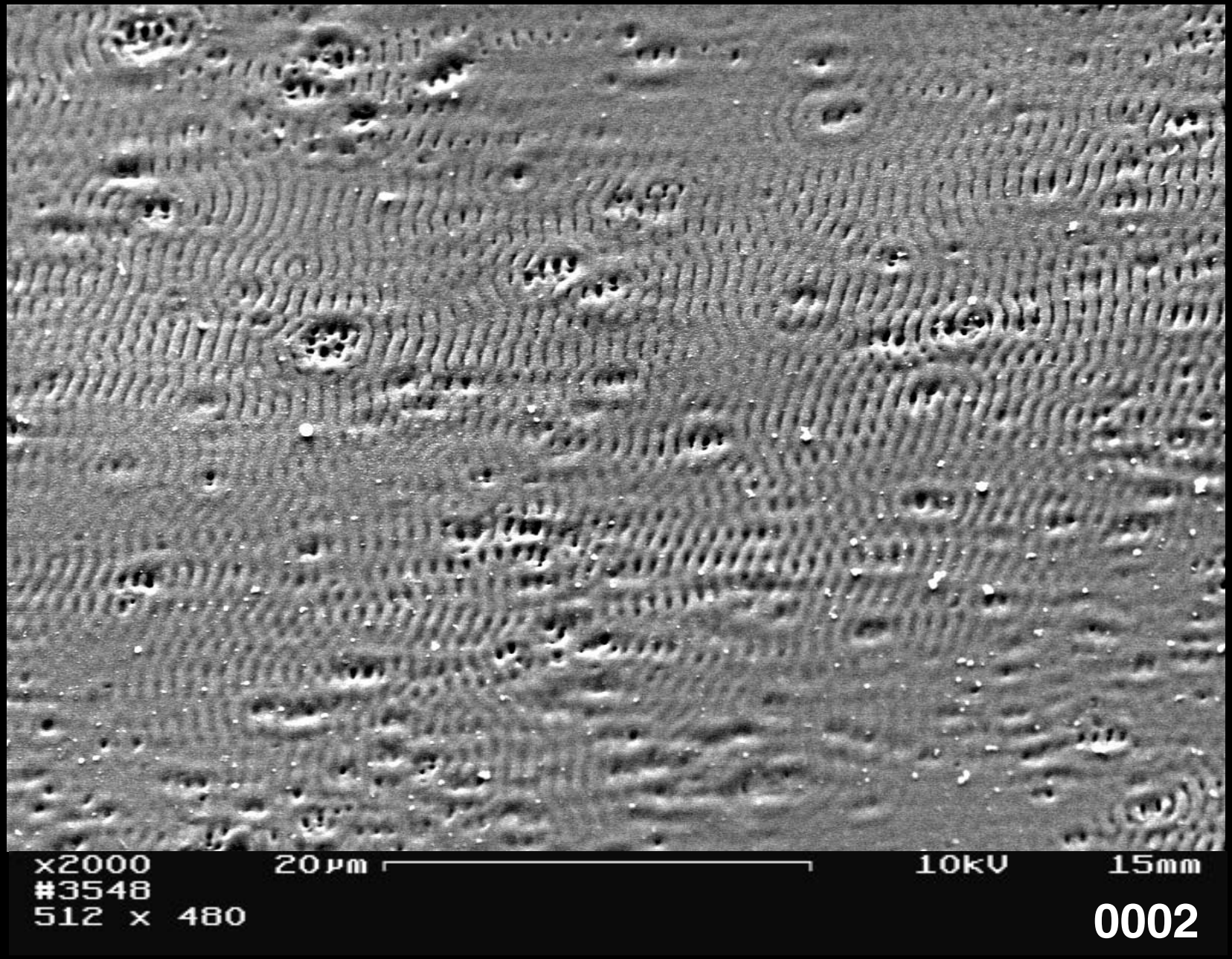
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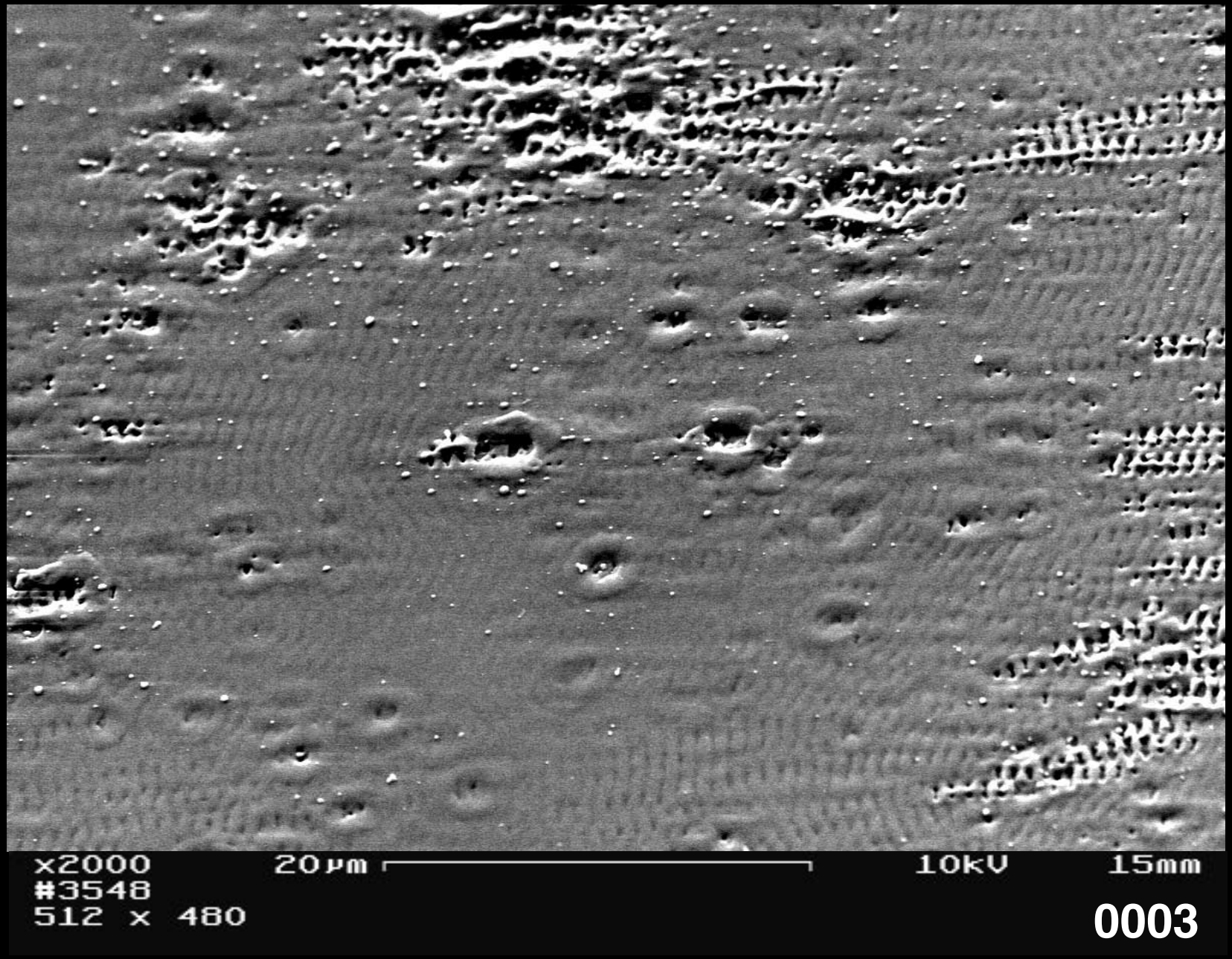
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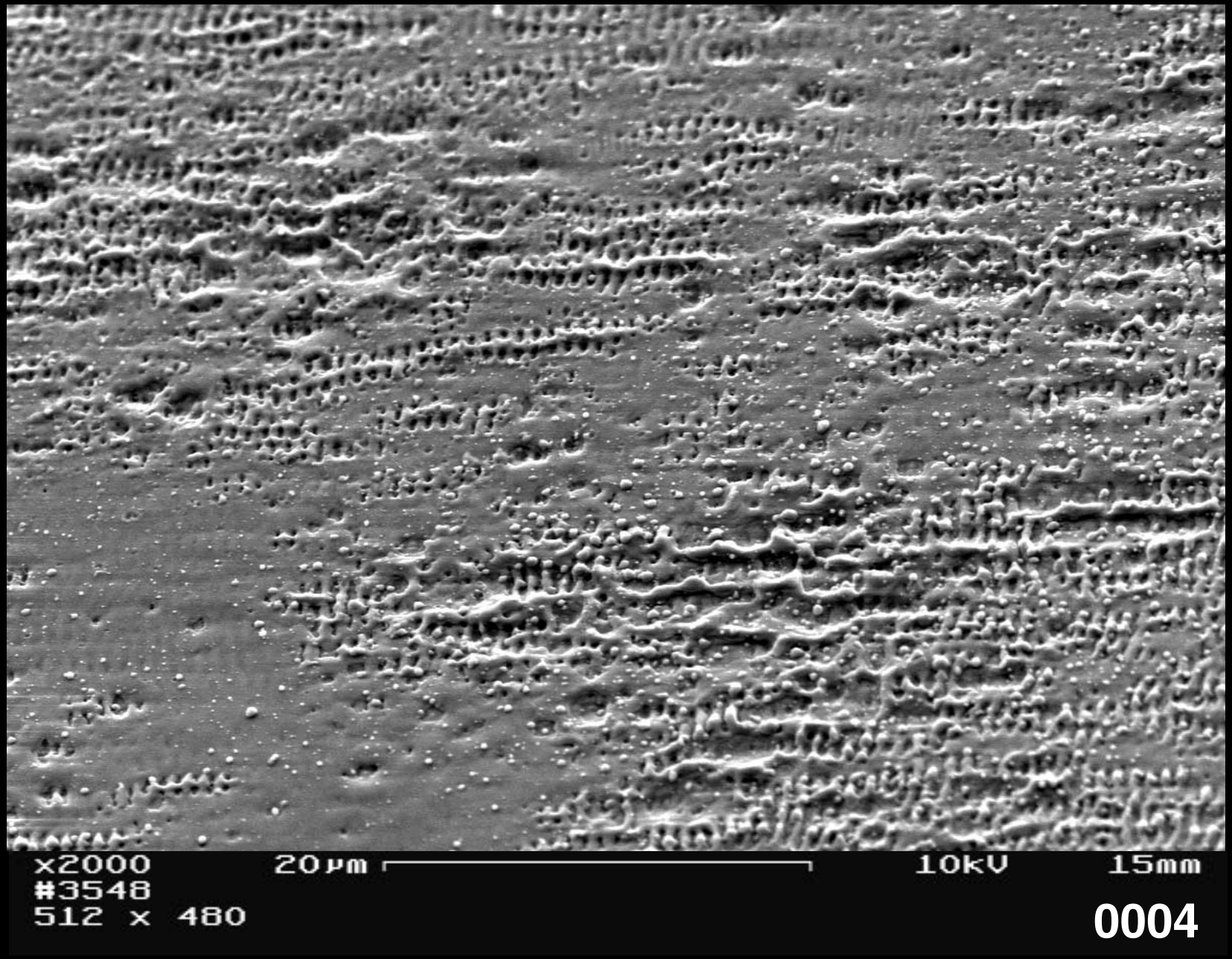
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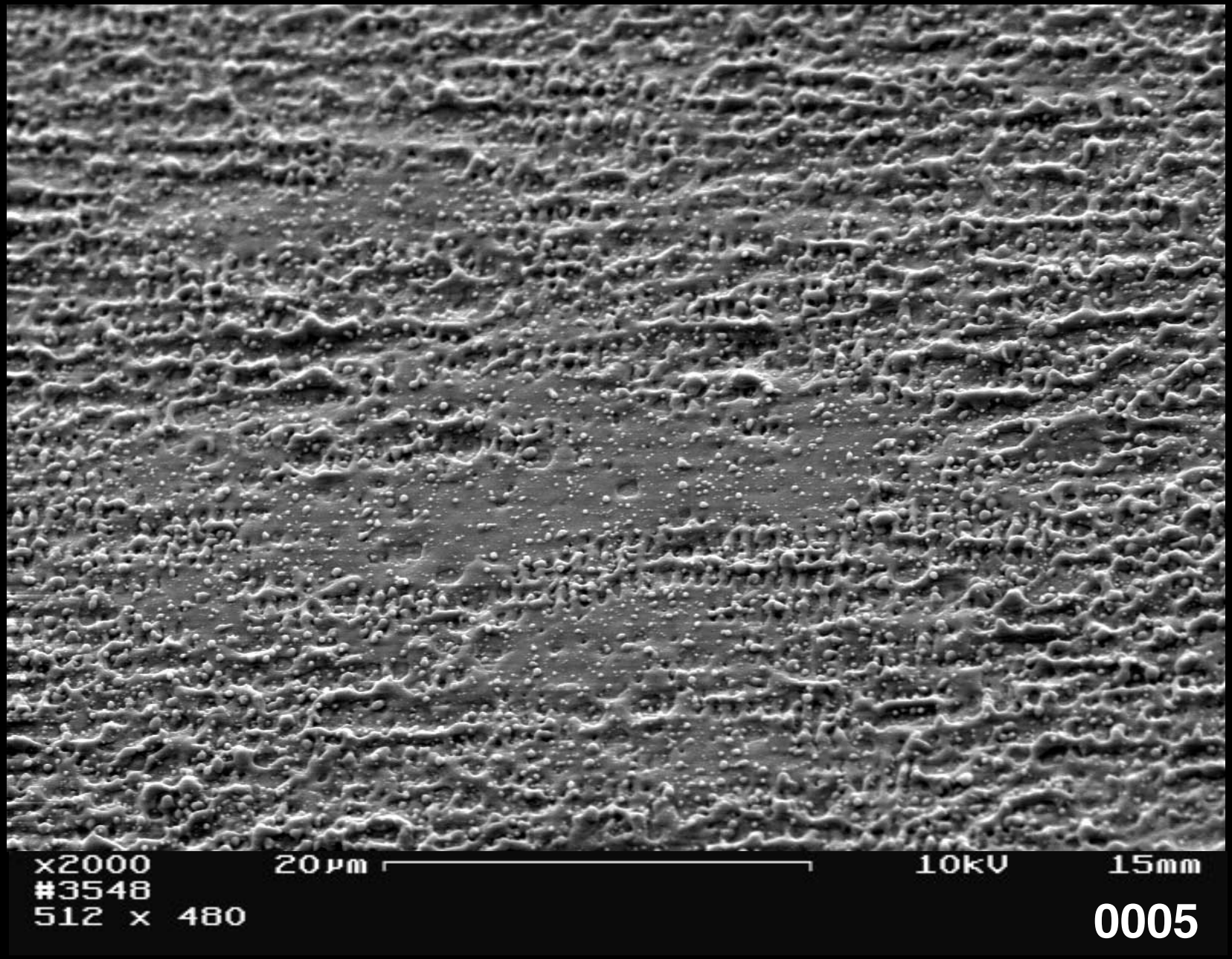
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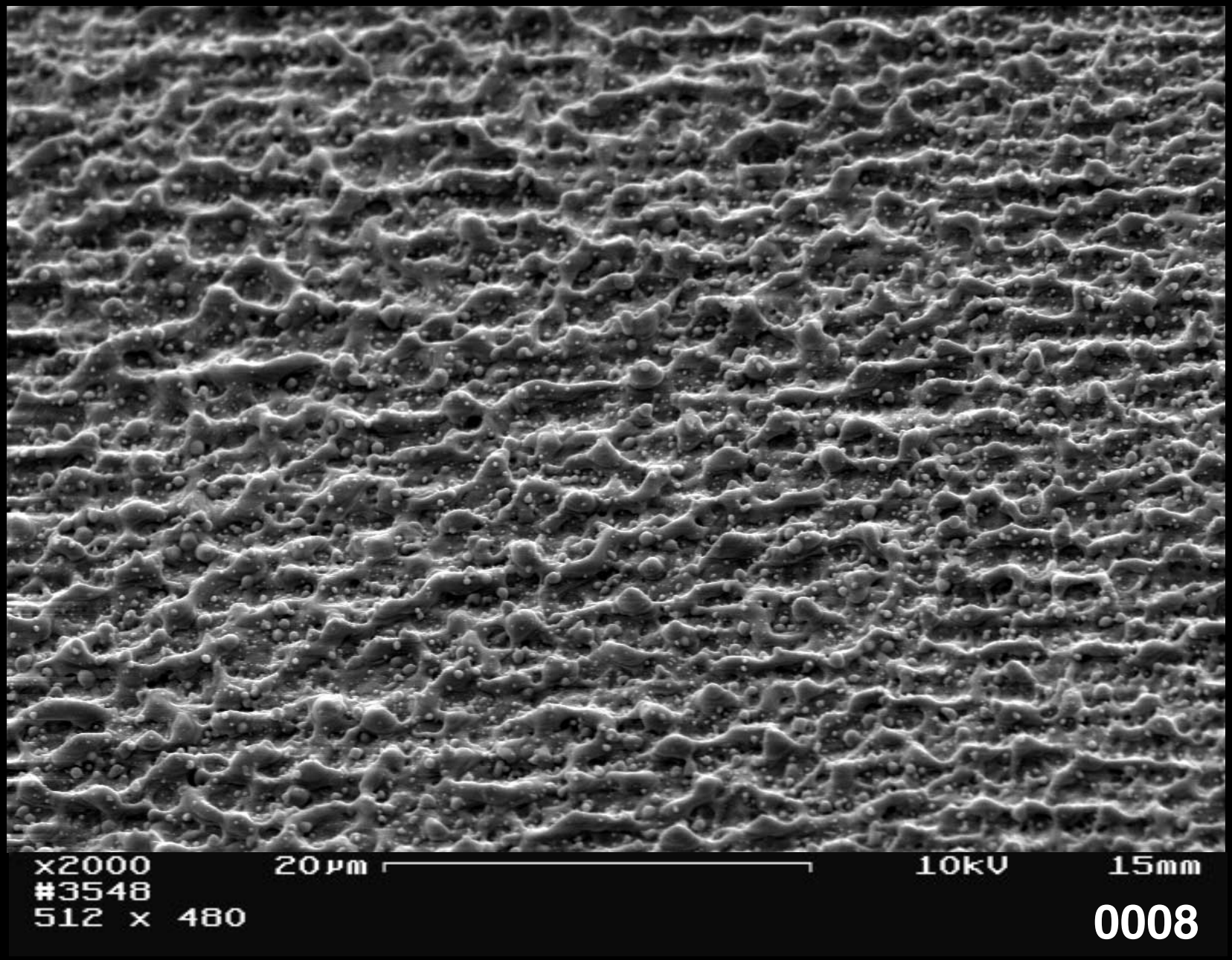
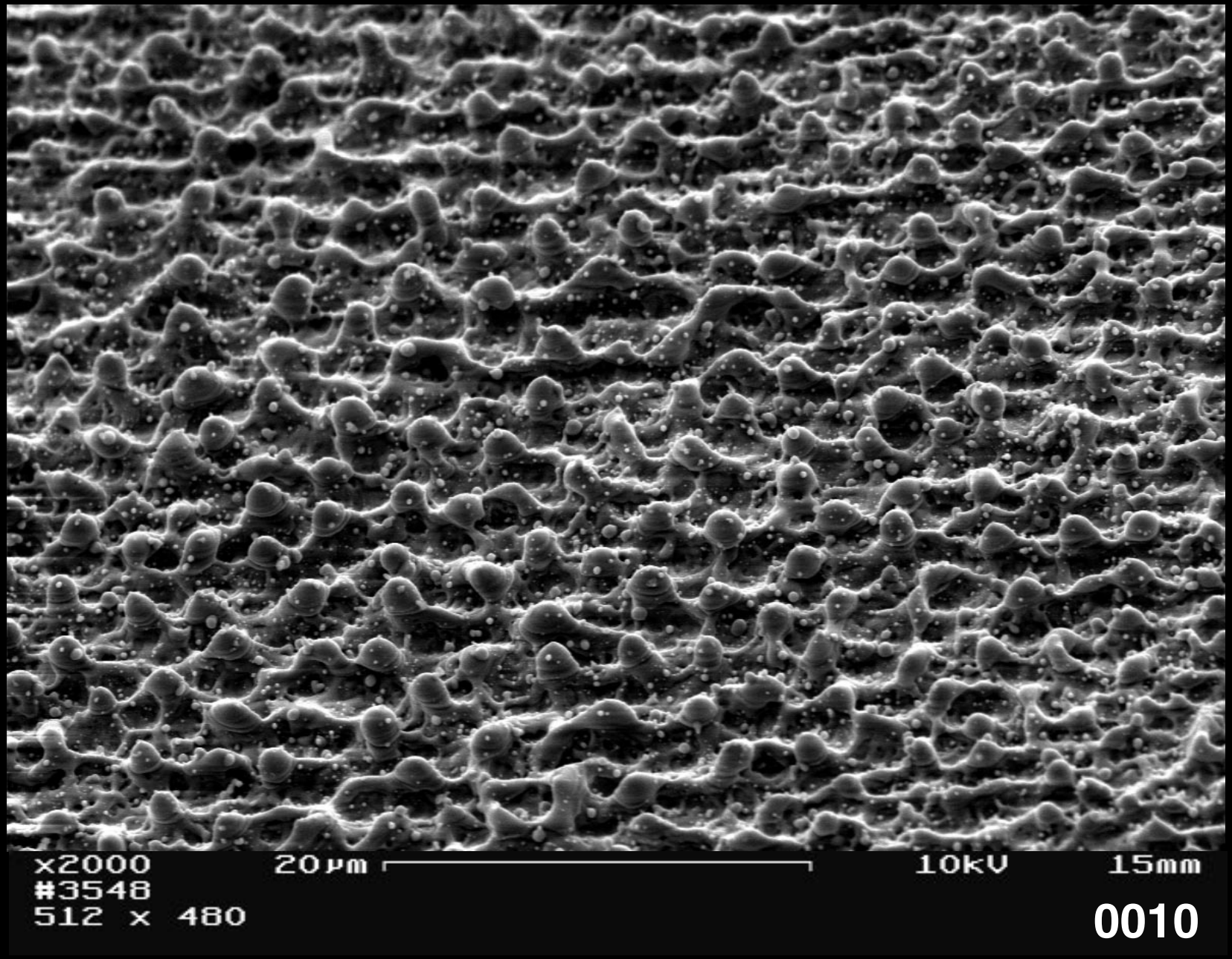
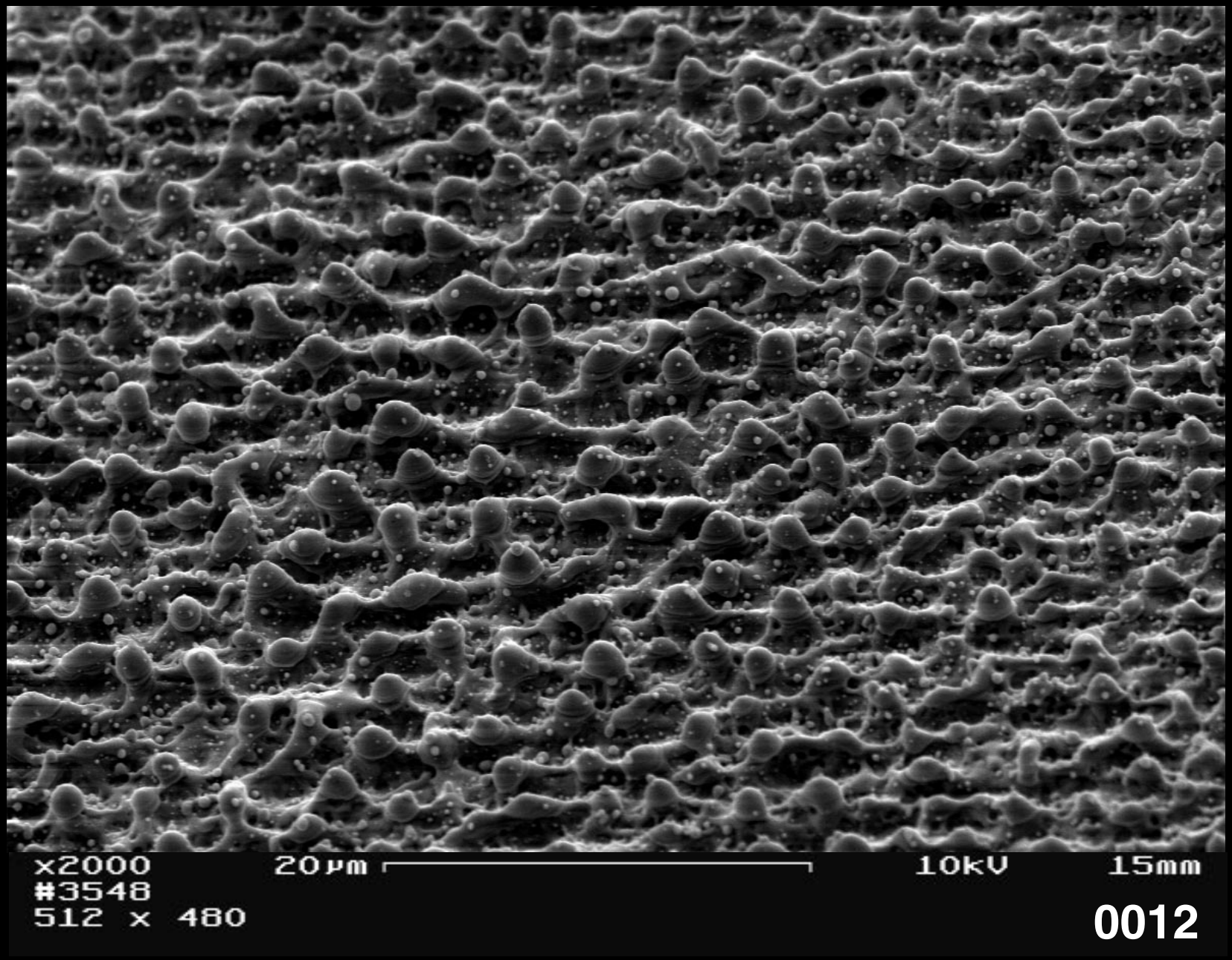
10kV
15mm
#3548
512 x 480
0005


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


x2000
#3548
512 x 480
20µm
10kV
15mm
0010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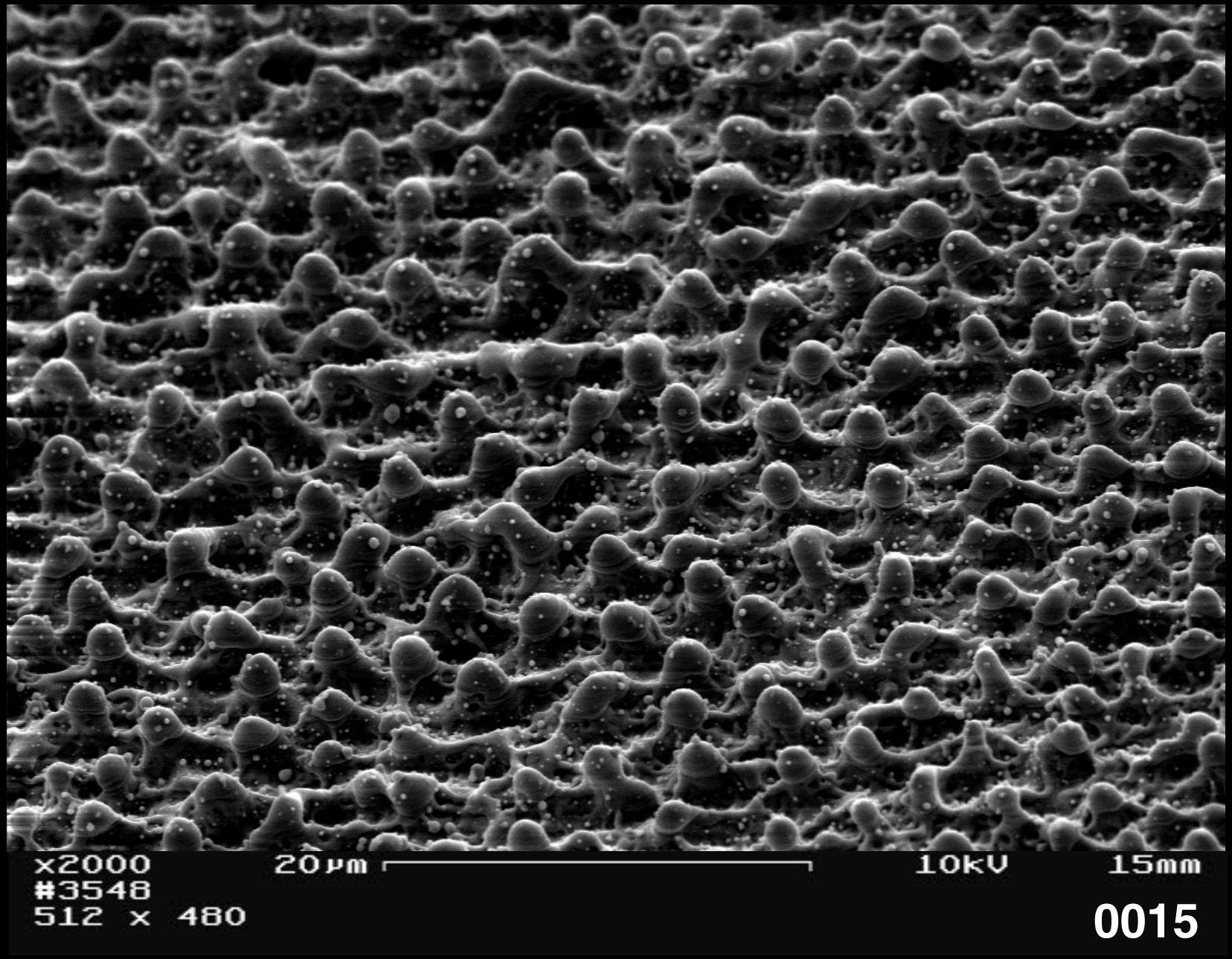
512 x 480
20µm
10kV
15mm
0012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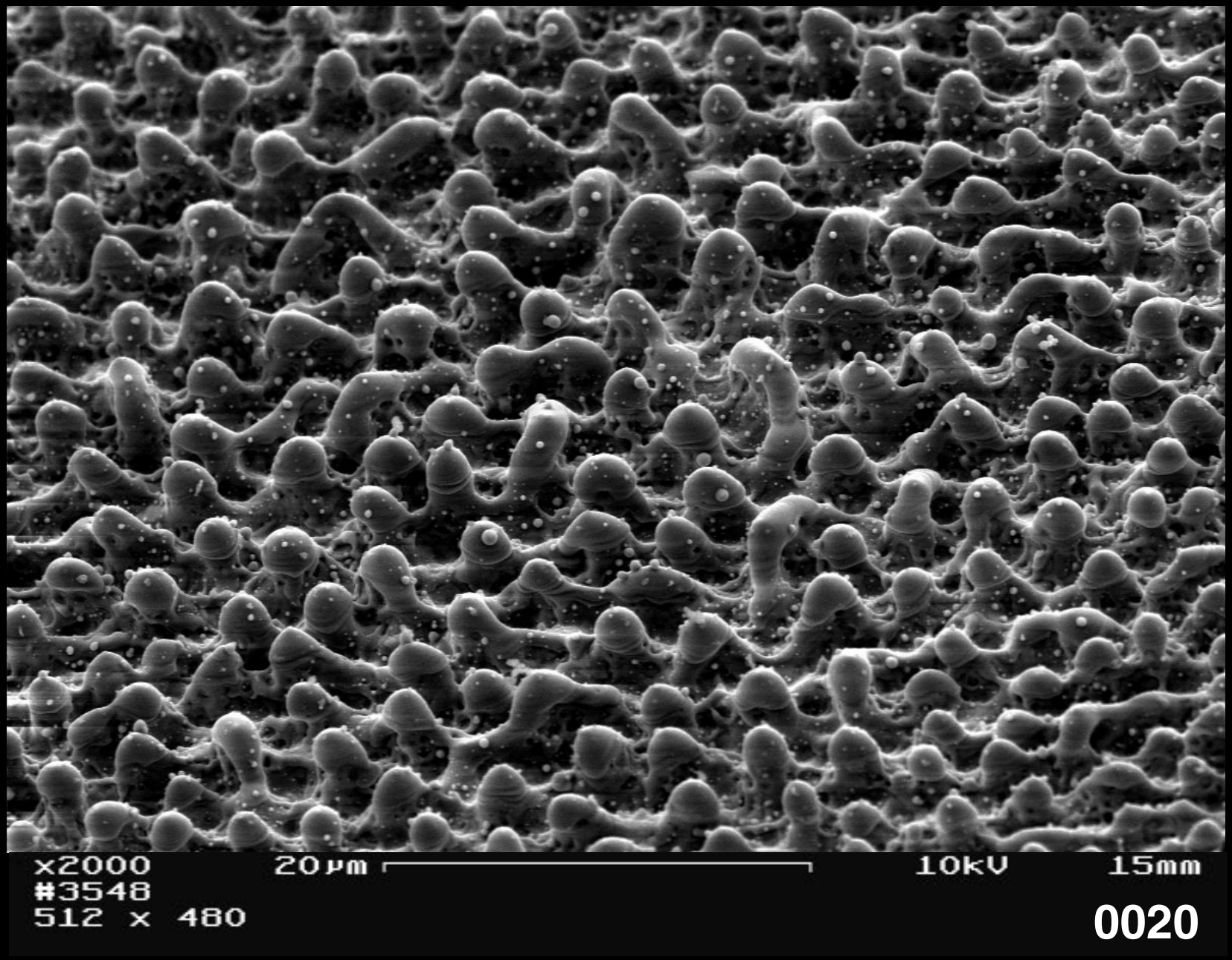
512 x 480
20µm
10kV
15mm
0015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#3548
512 x 480
20µm
10kV
15mm
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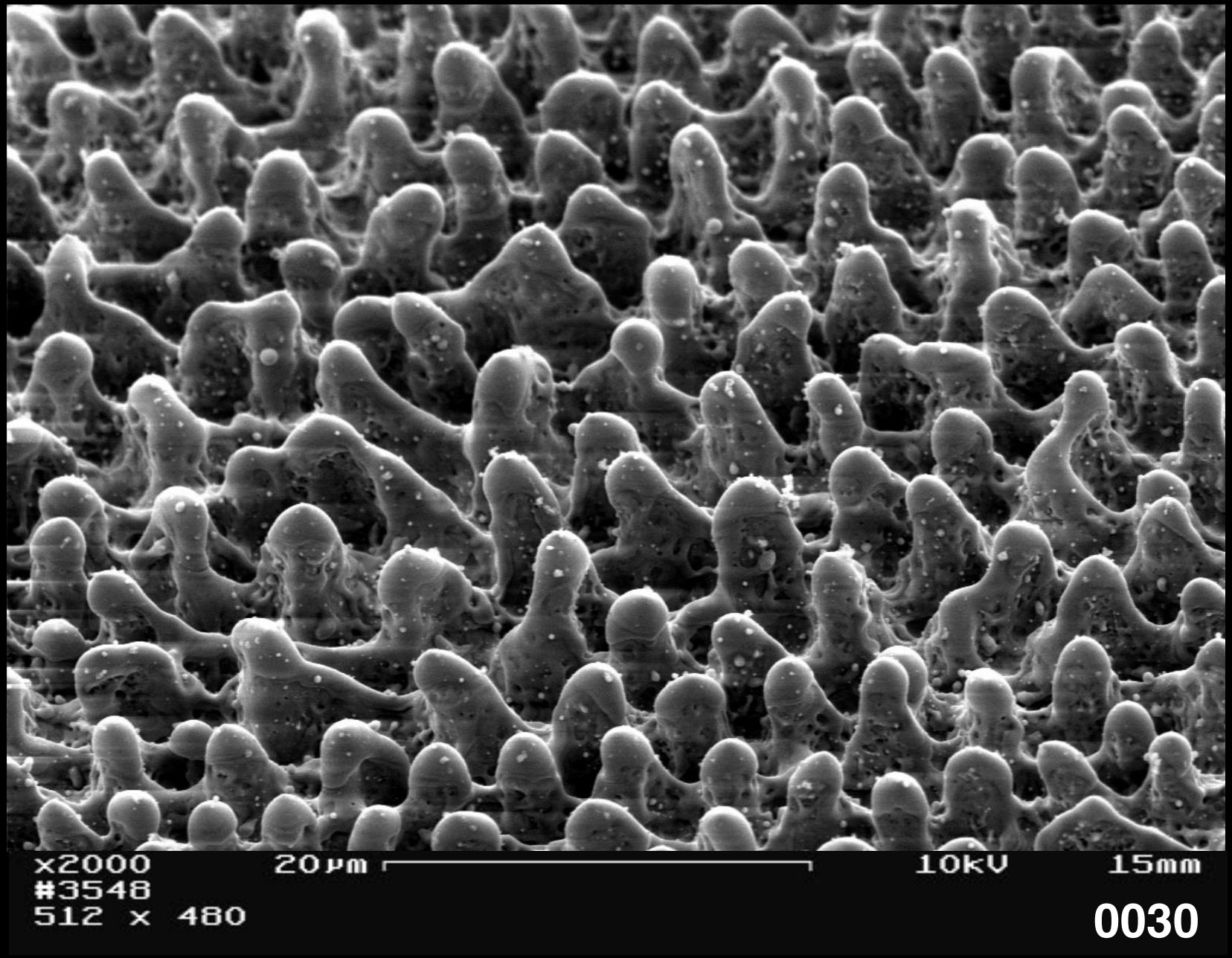
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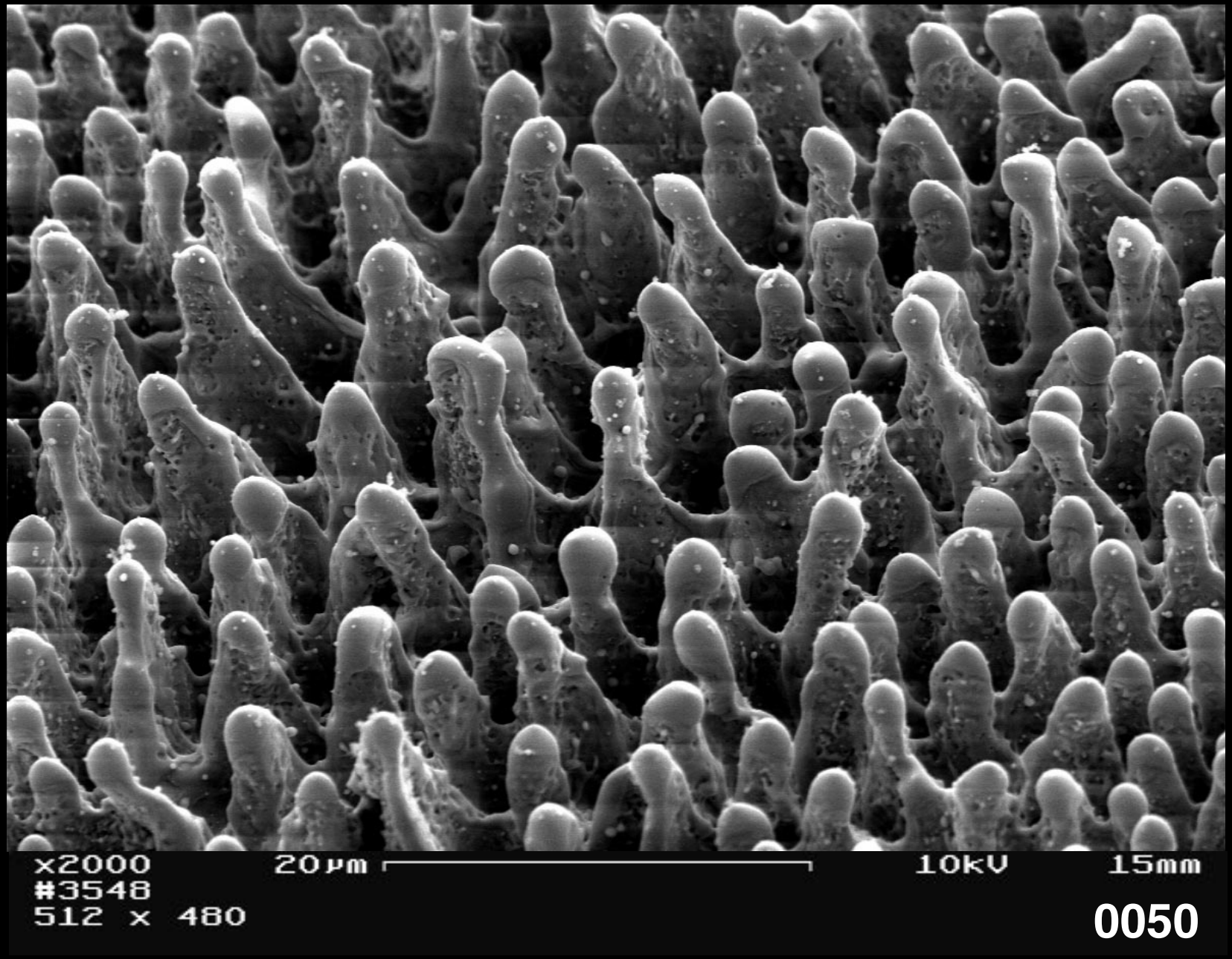
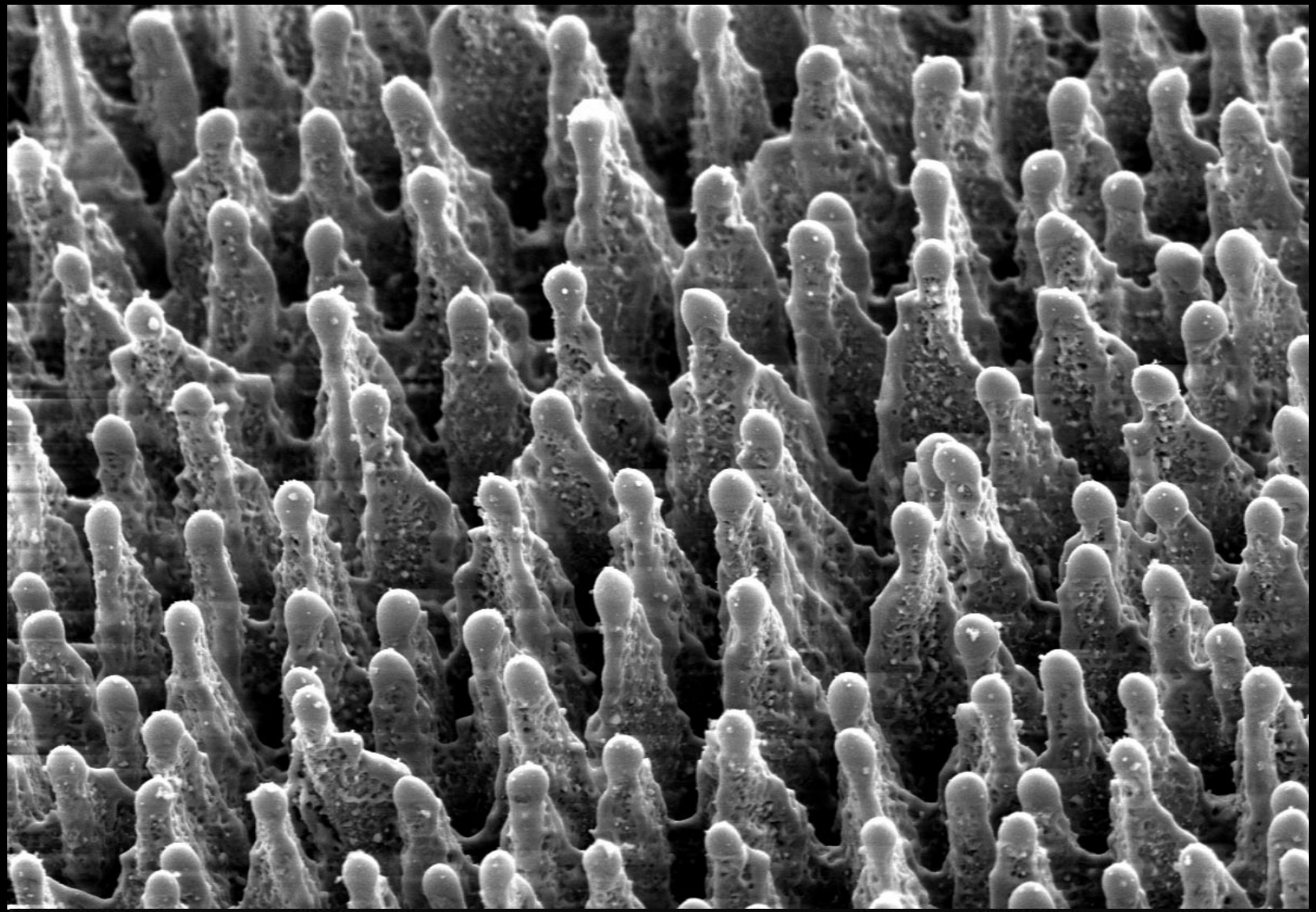
512 x 480
20µm
10kV
15mm
0030


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



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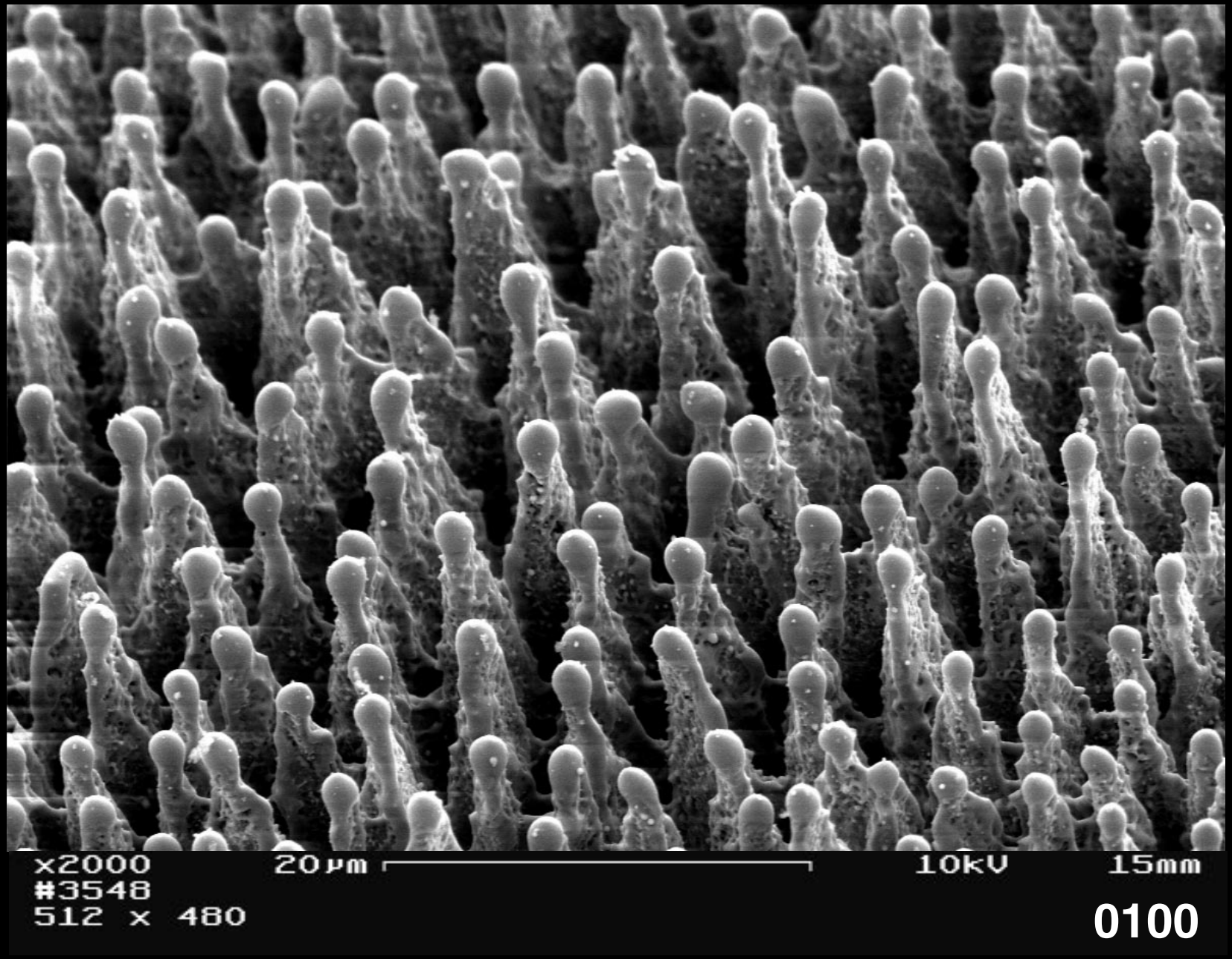
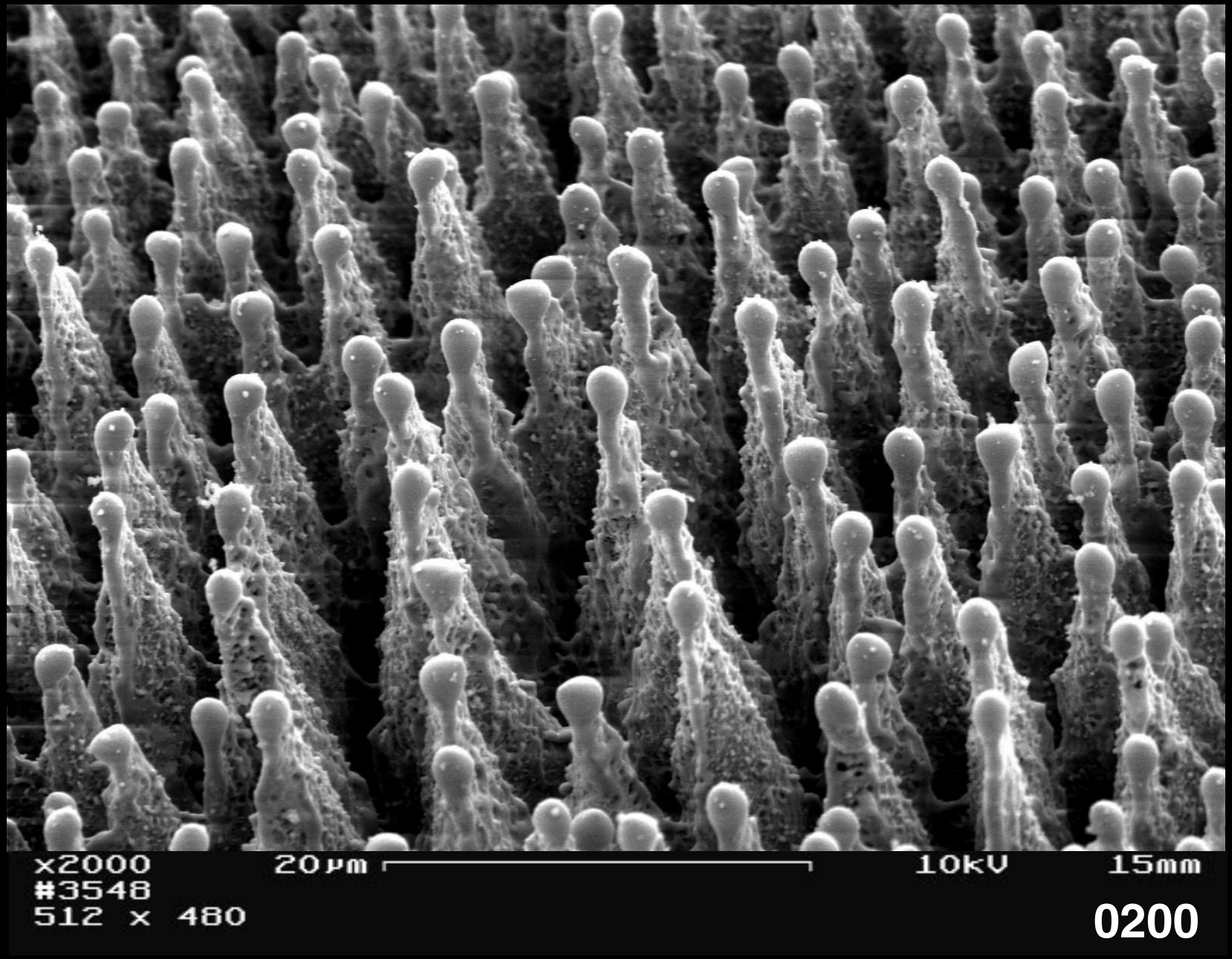
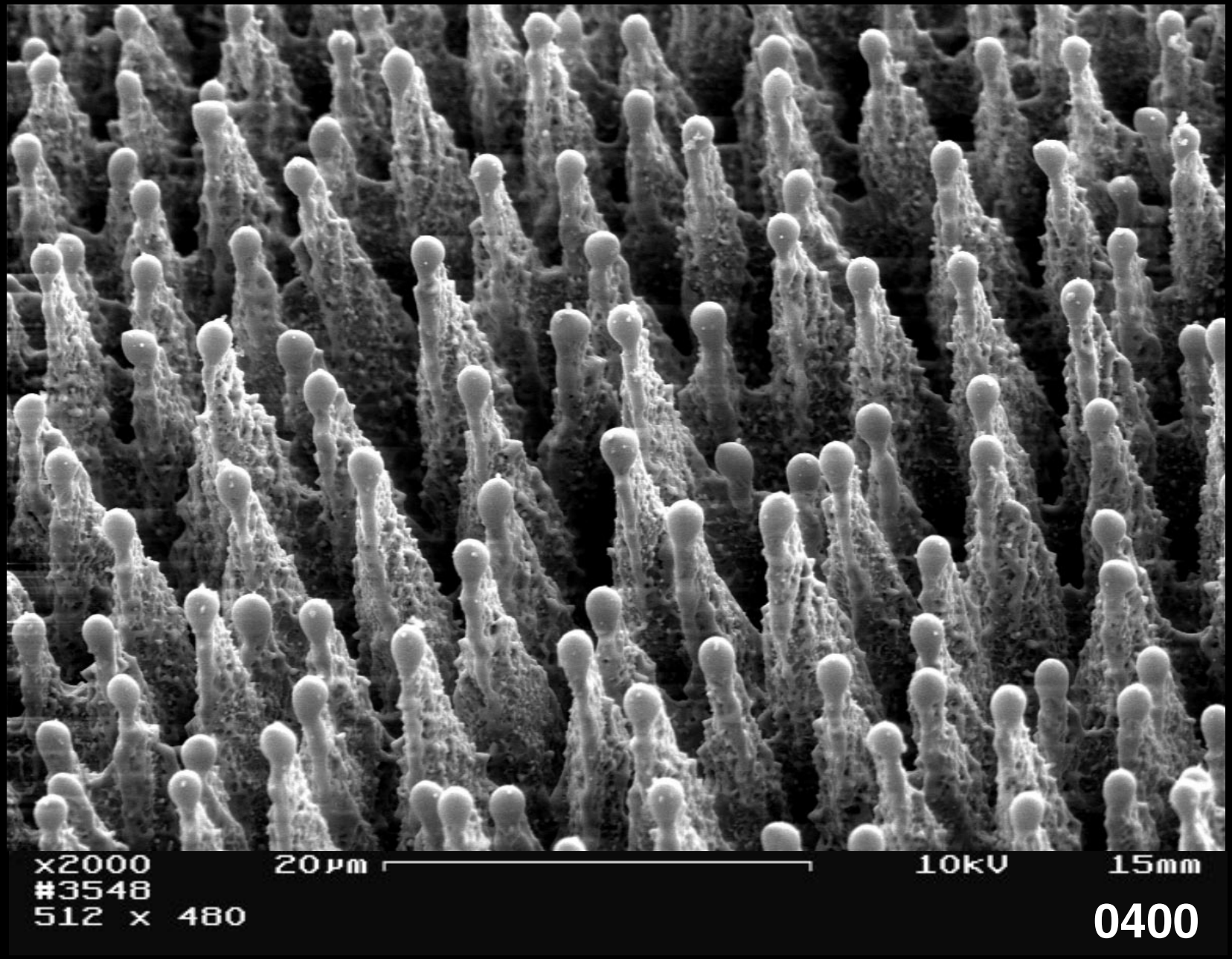
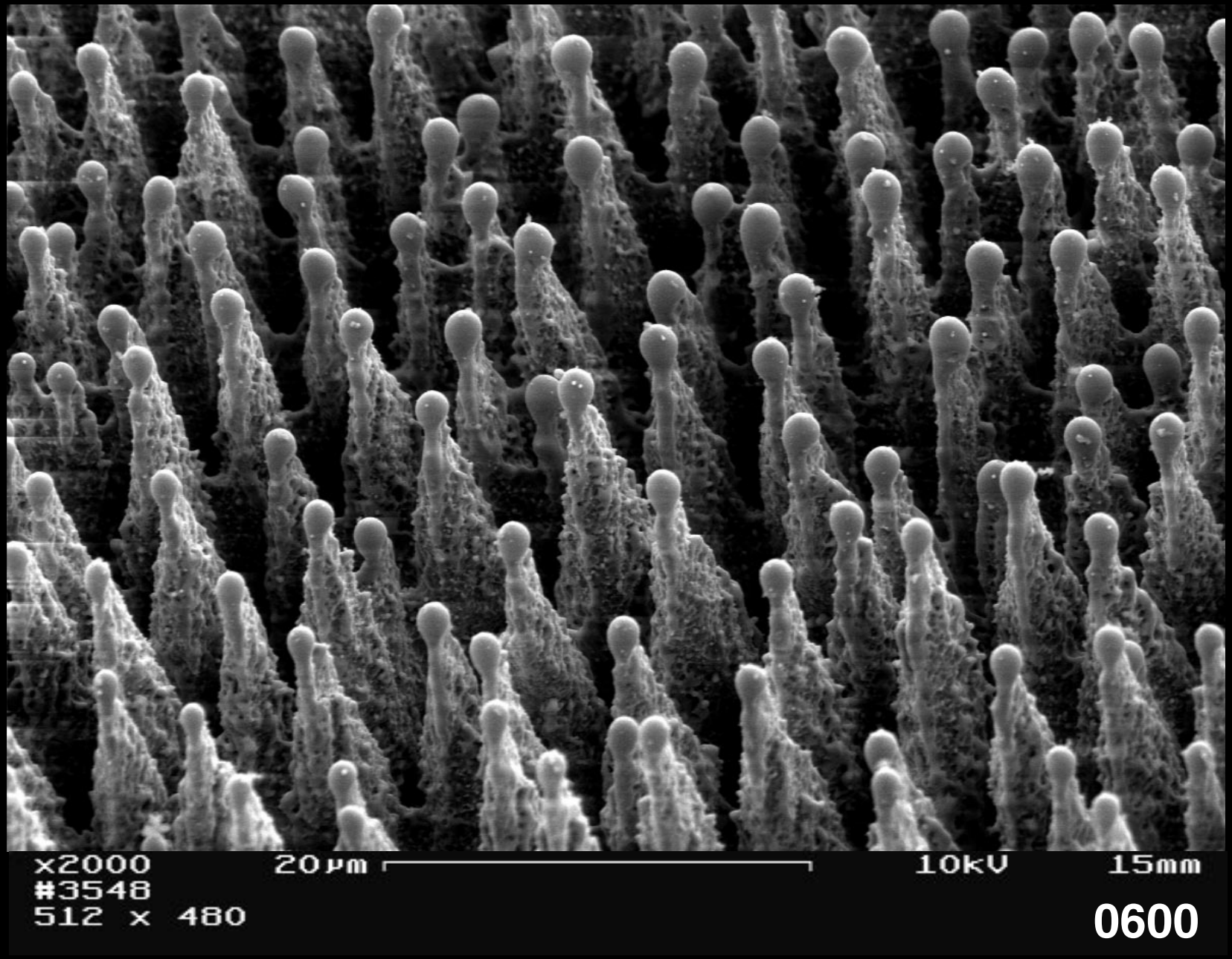
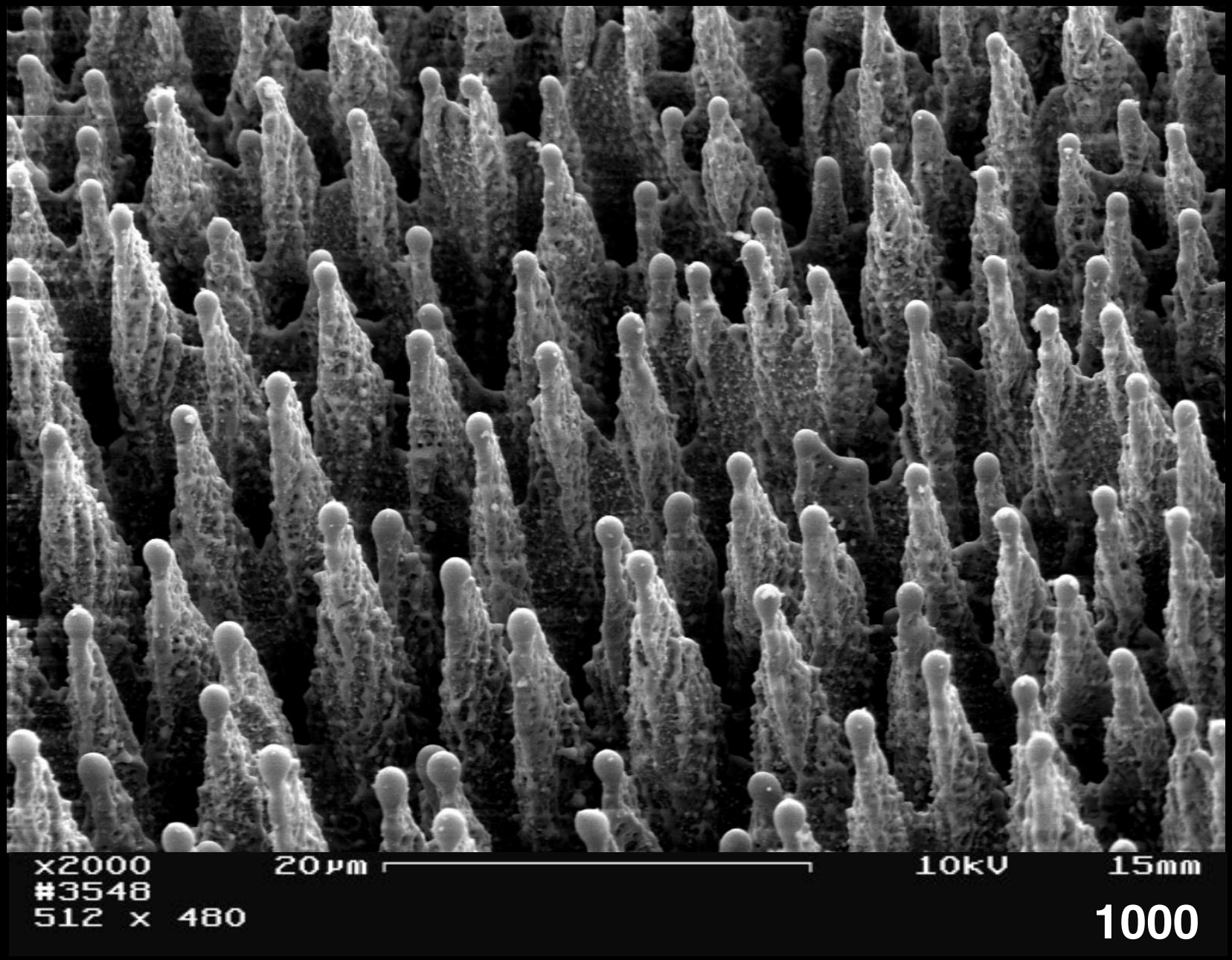

x2000
#3548
512 x 480
20µm
10kV
15mm
0100


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


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


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


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

How do ripples give way to spikes?

Formation process

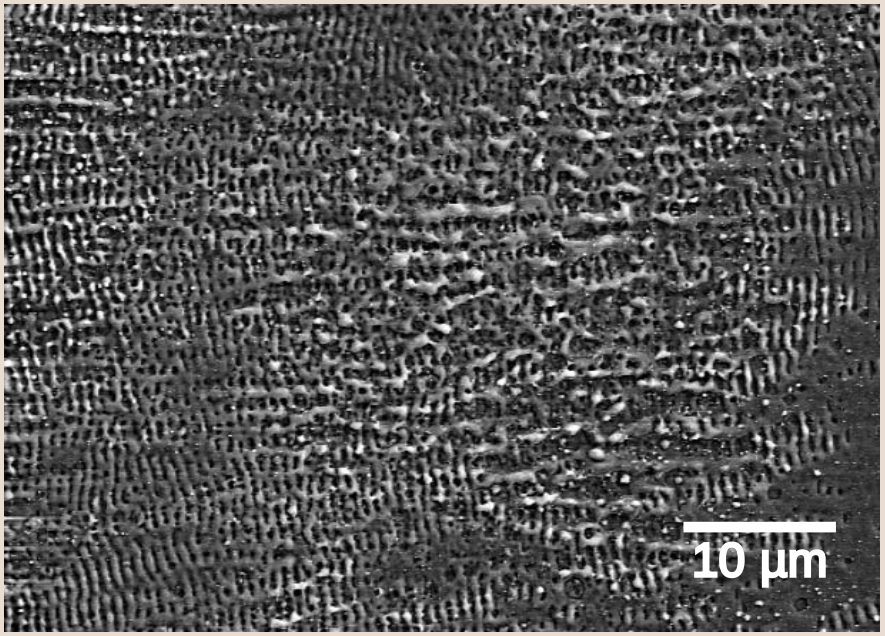
Follow evolution of spatial frequencies

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

Formation process

ripples

SF_6 **2 pulses**

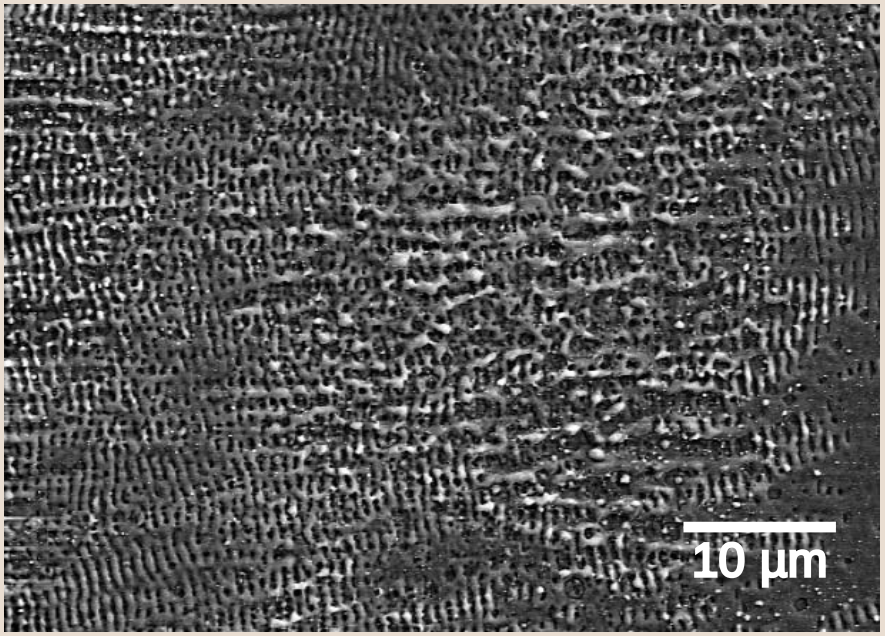


laser polarization

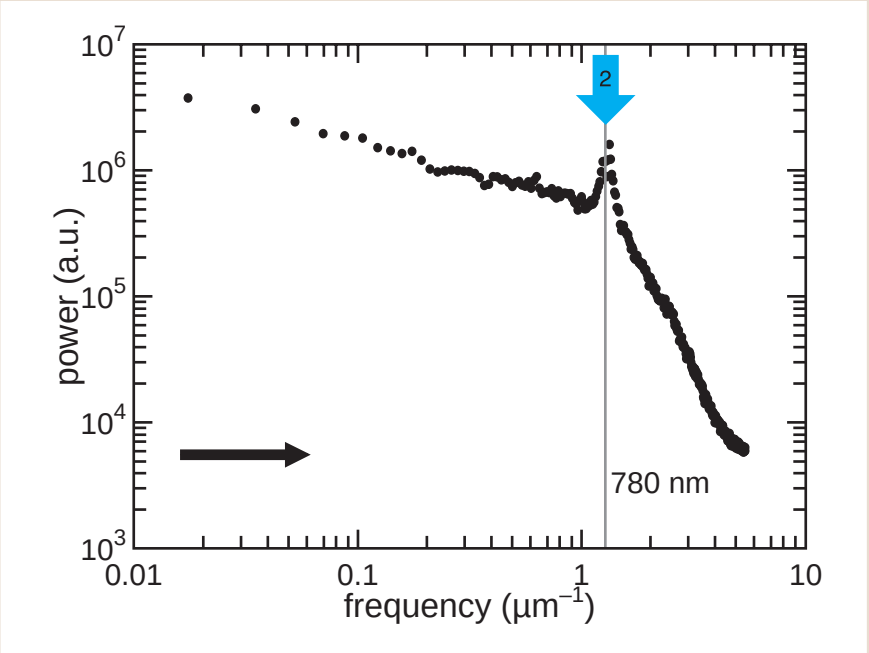
Formation process

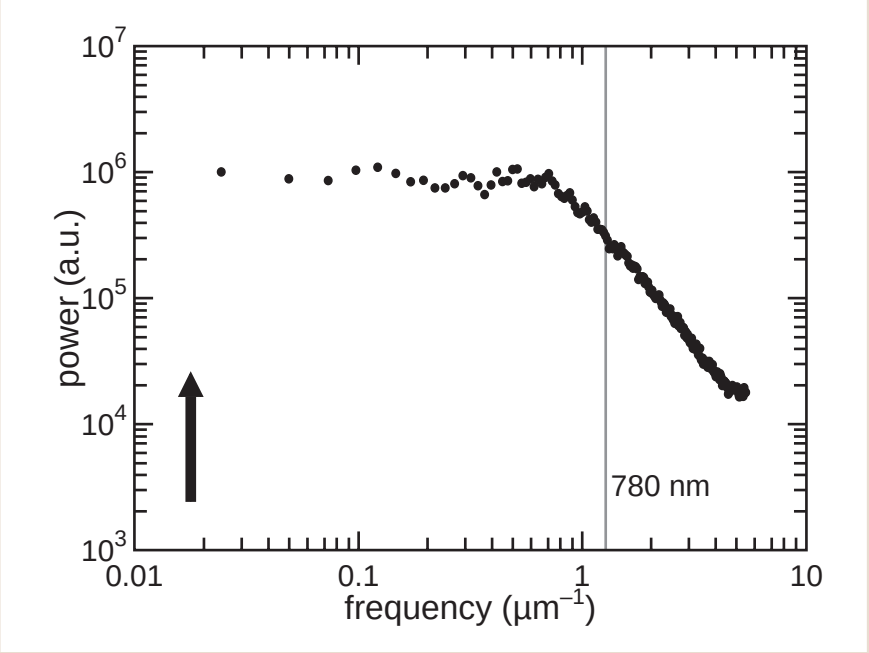
ripples

SF_6 2 pulses



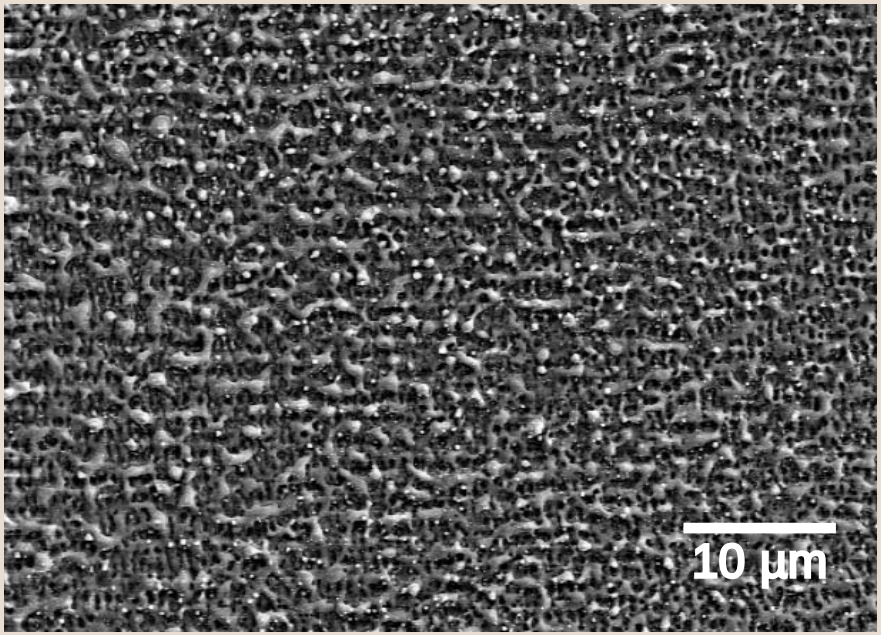
laser polarization



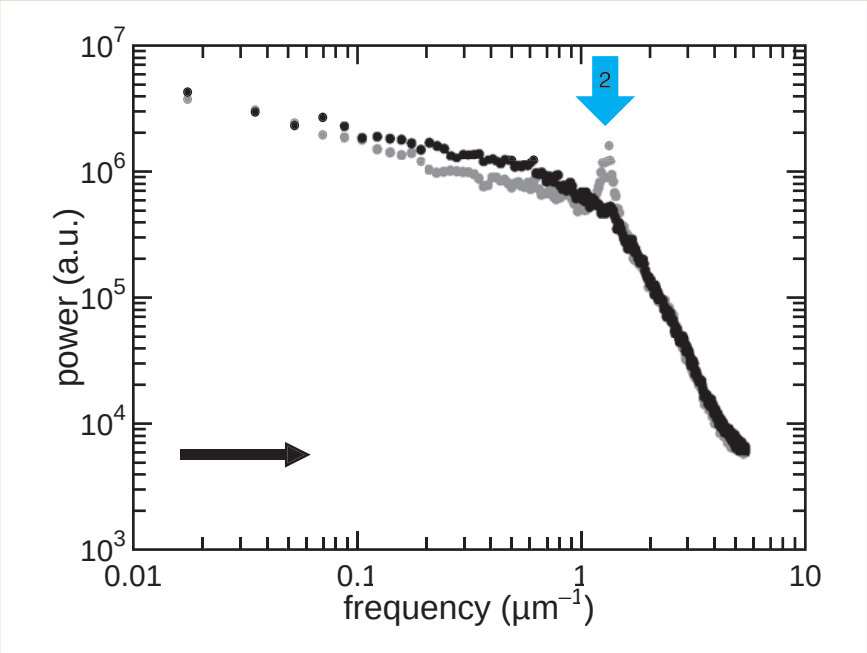


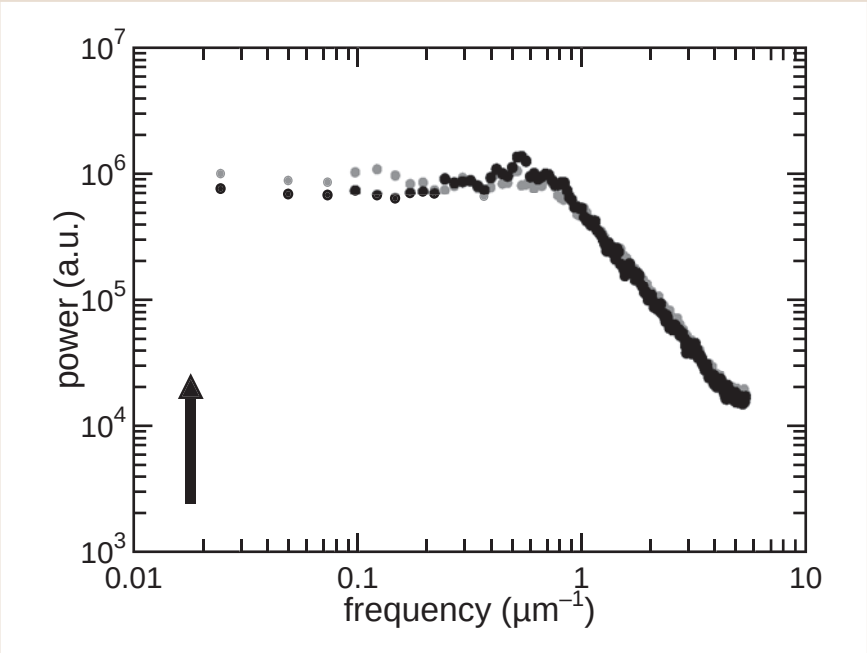
Formation process

SF_6 **3 pulses**



laser polarization

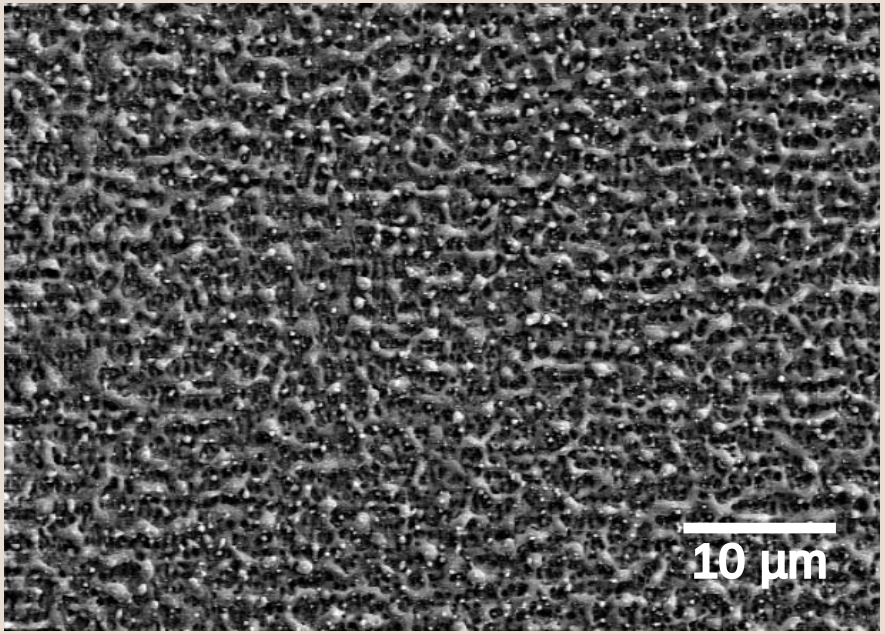




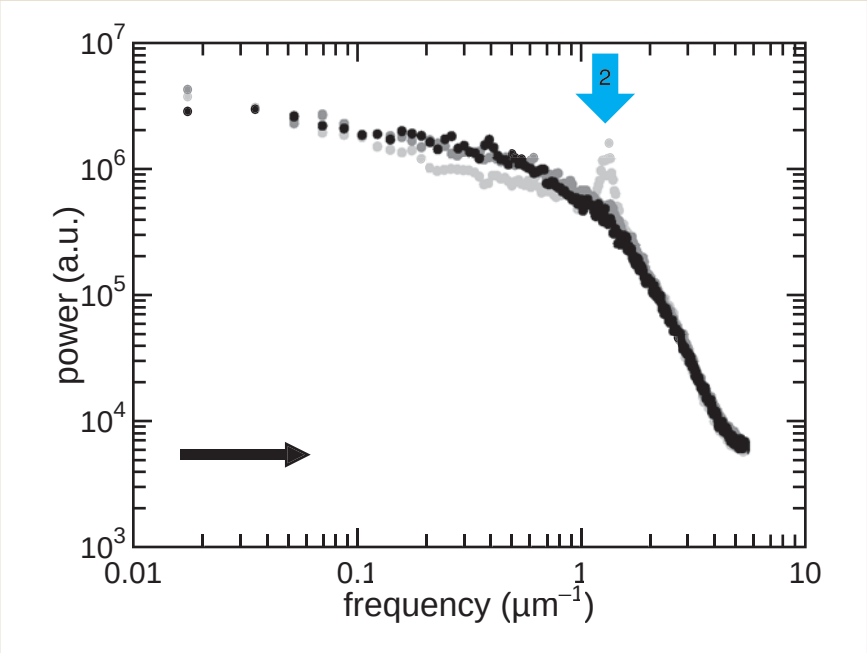
Formation process

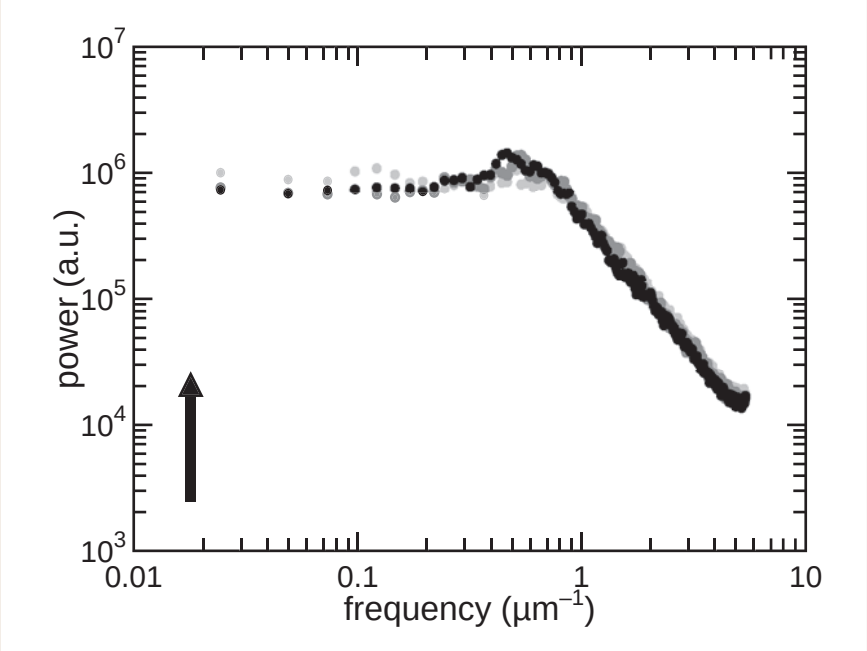
ridges

SF_6 4 pulses



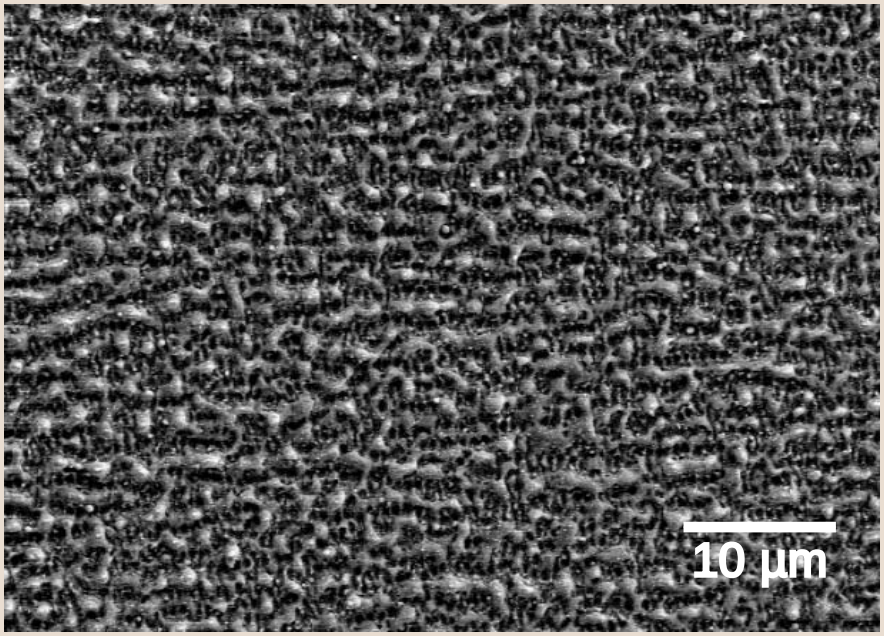
laser polarization



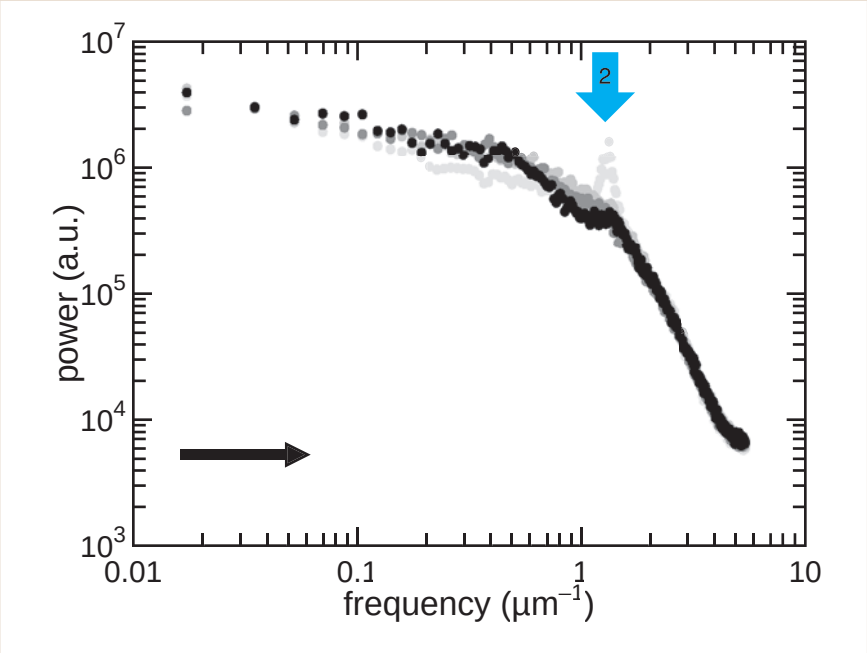


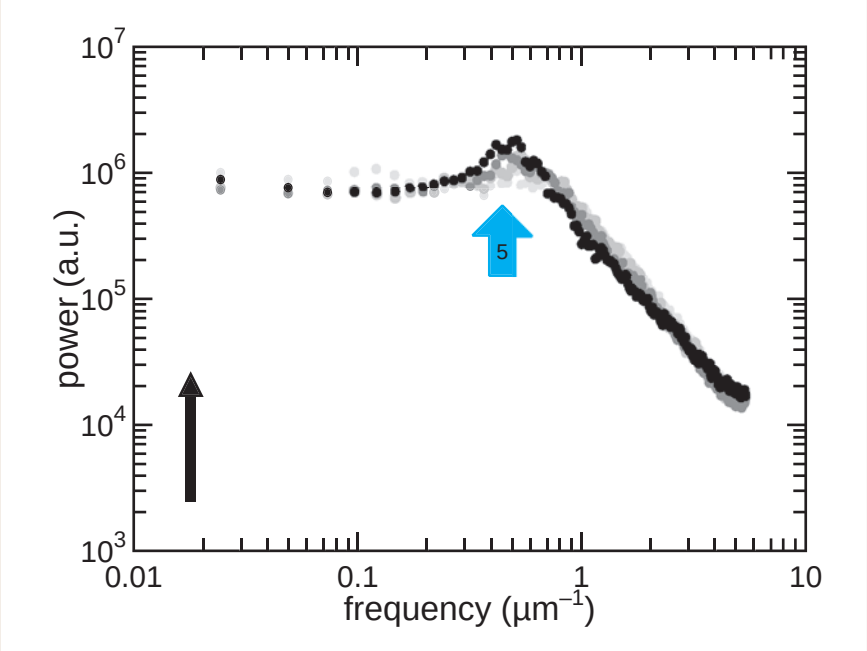
Formation process

SF_6 **5 pulses**



laser polarization

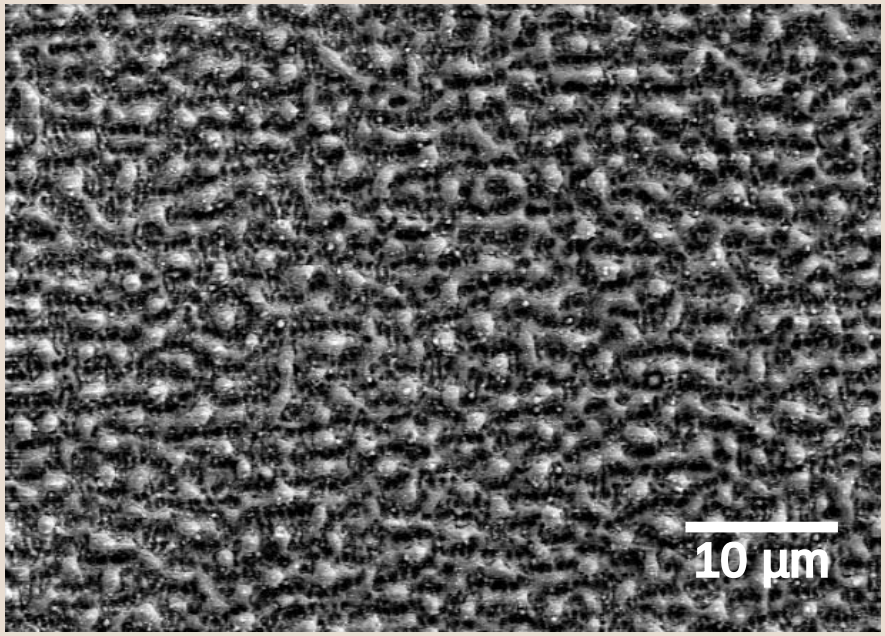




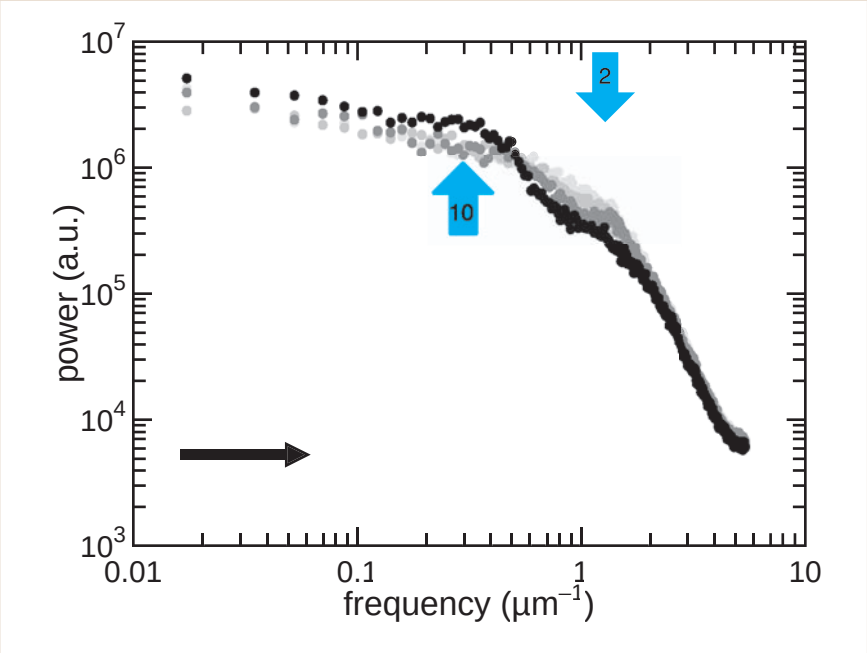
Formation process

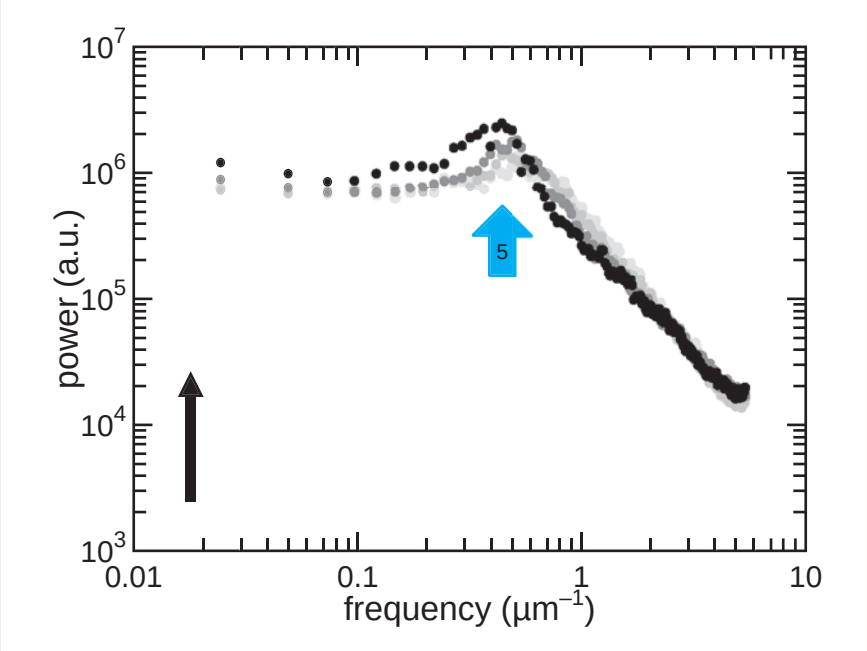
spikes

SF_6 10 pulses



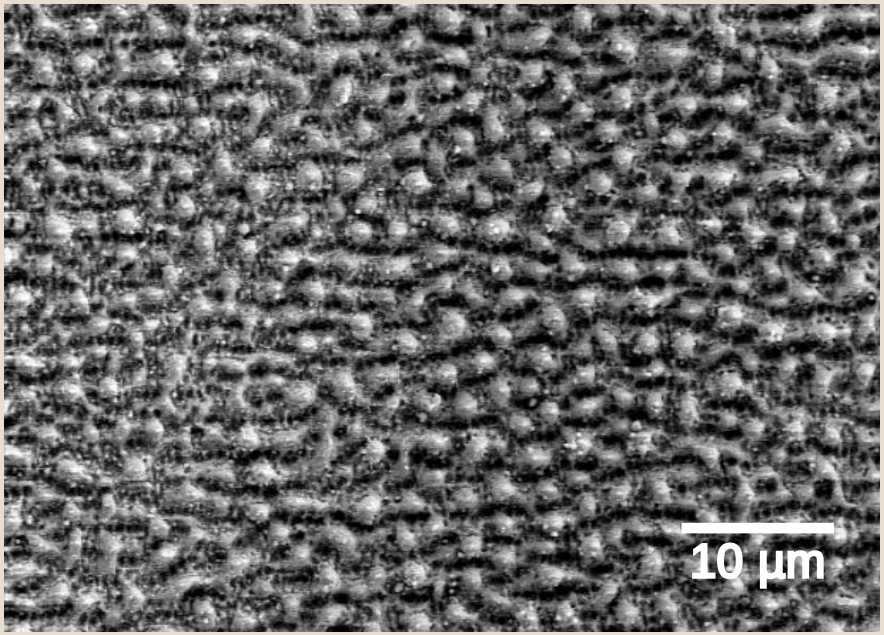
laser polarization



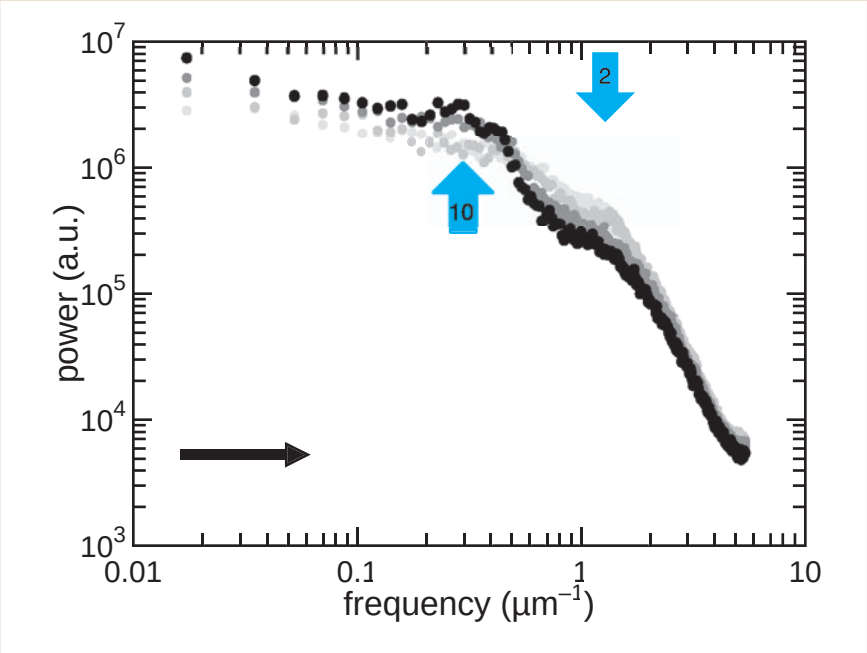


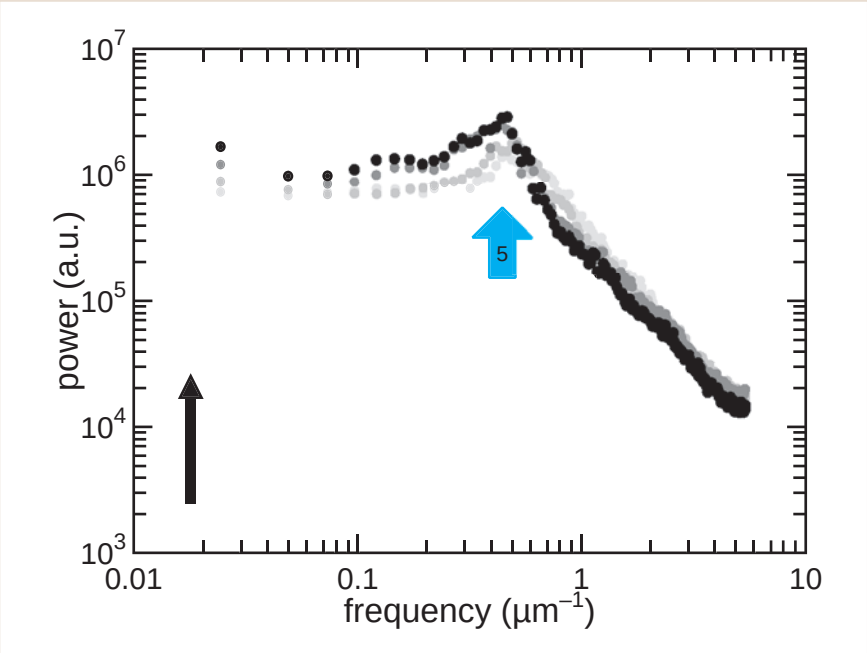
Formation process

SF_6 15 pulses



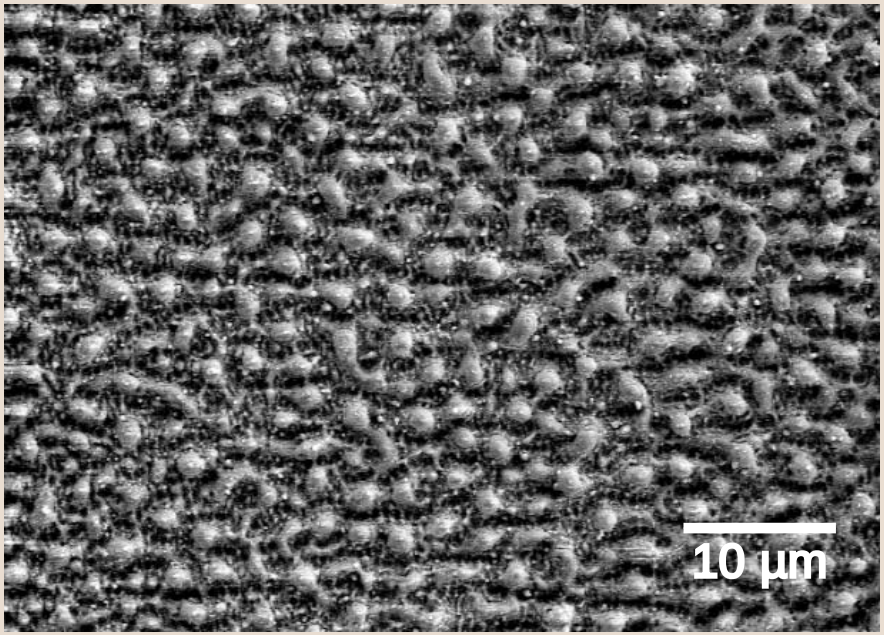
laser polarization



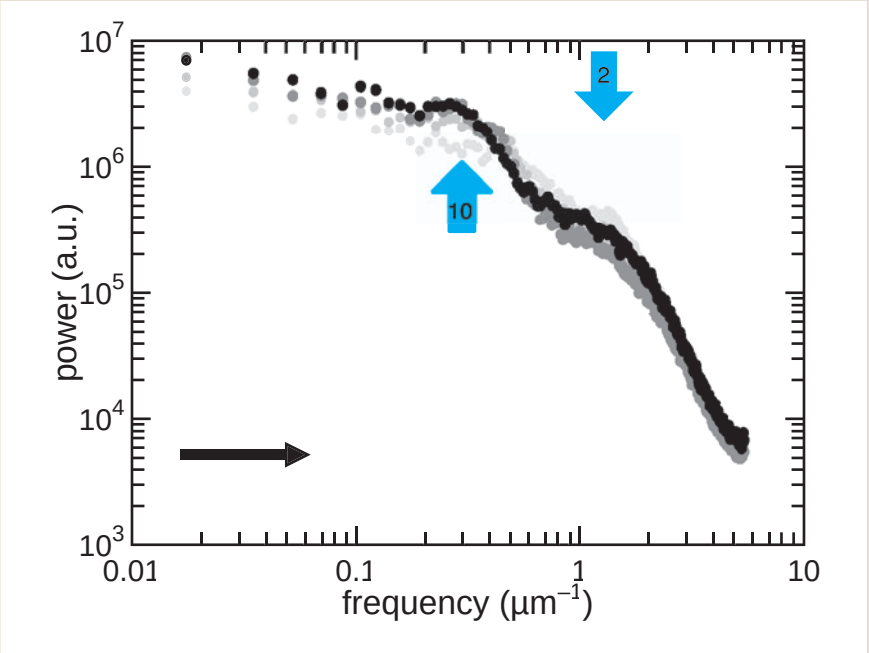


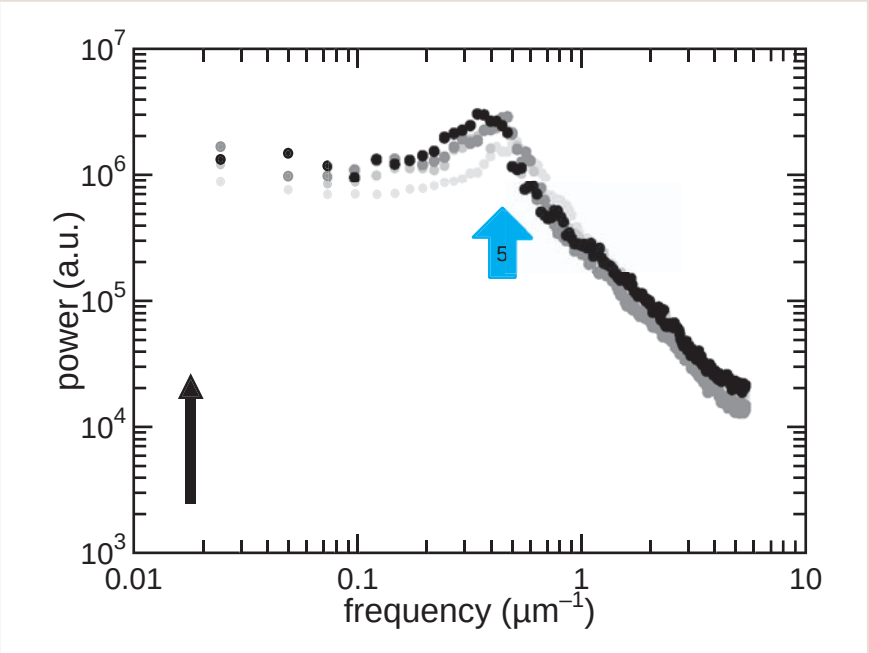
Formation process

SF_6 20 pulses



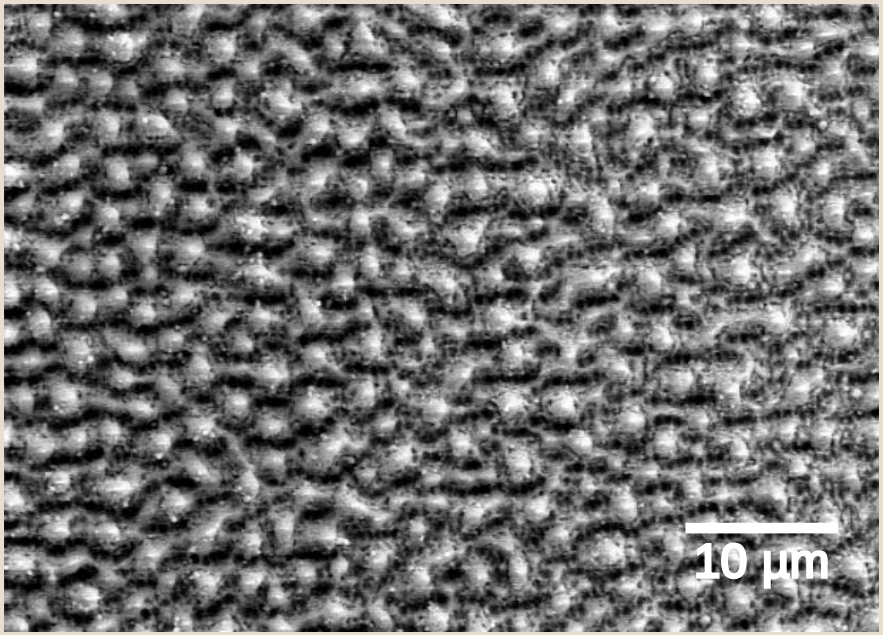
laser polarization



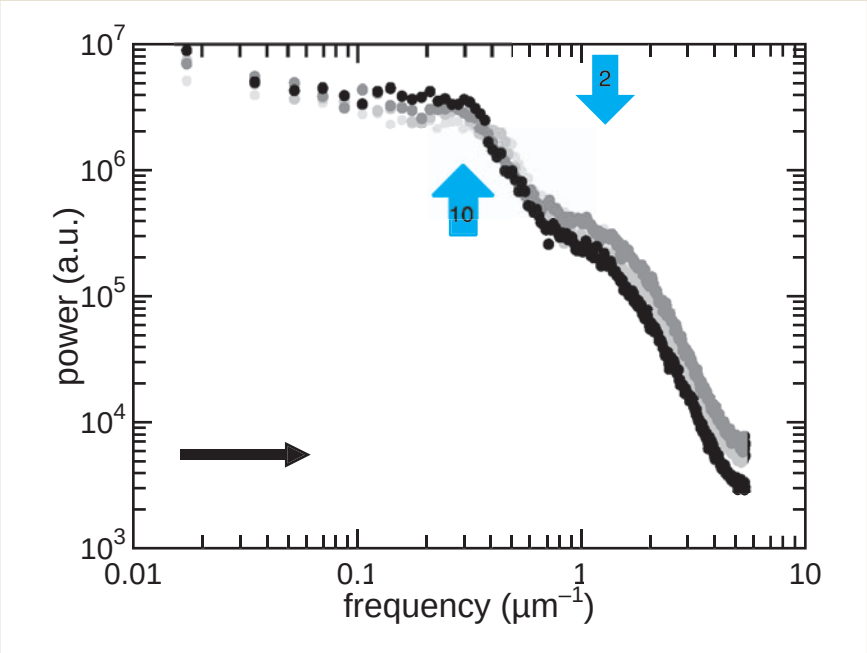


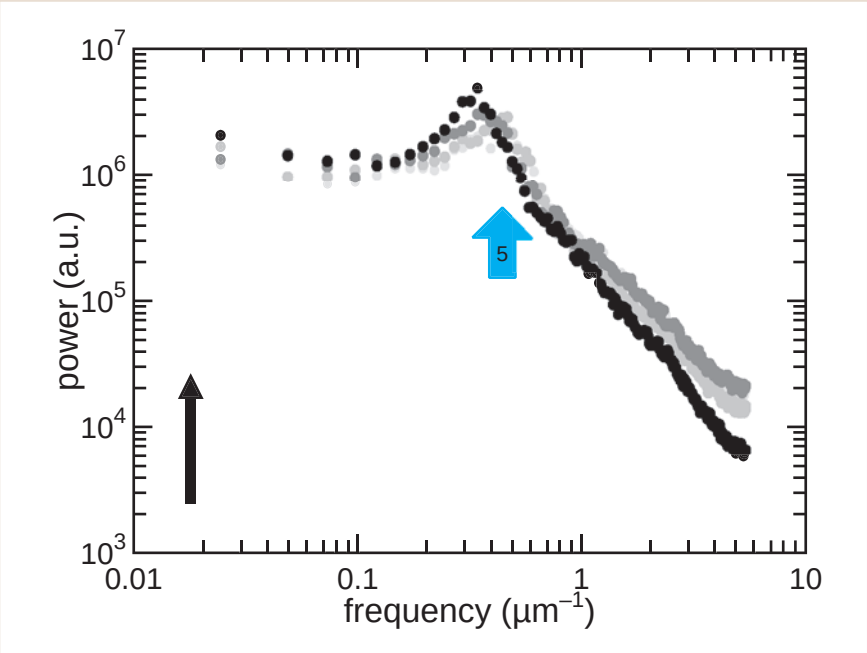
Formation process

SF_6 50 pulses



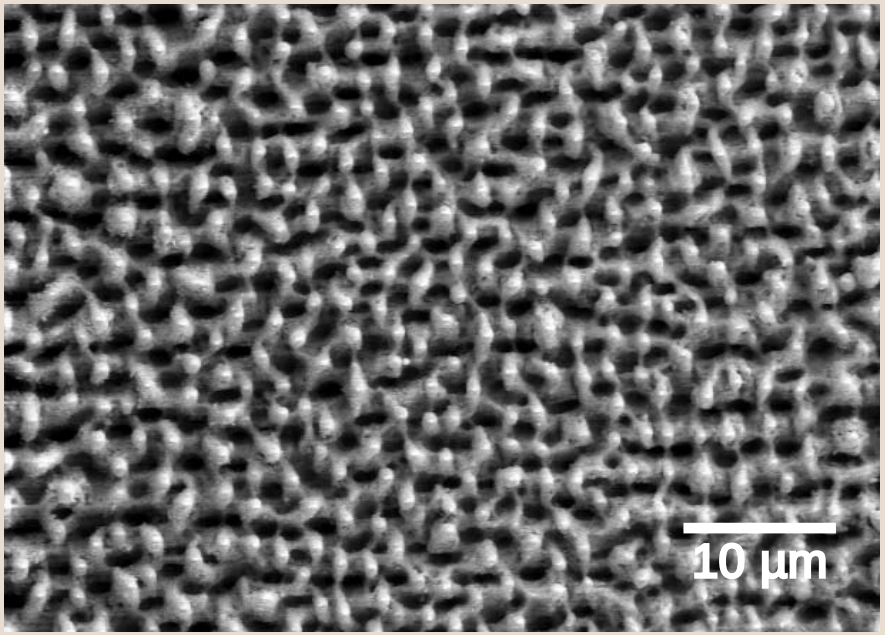
laser polarization



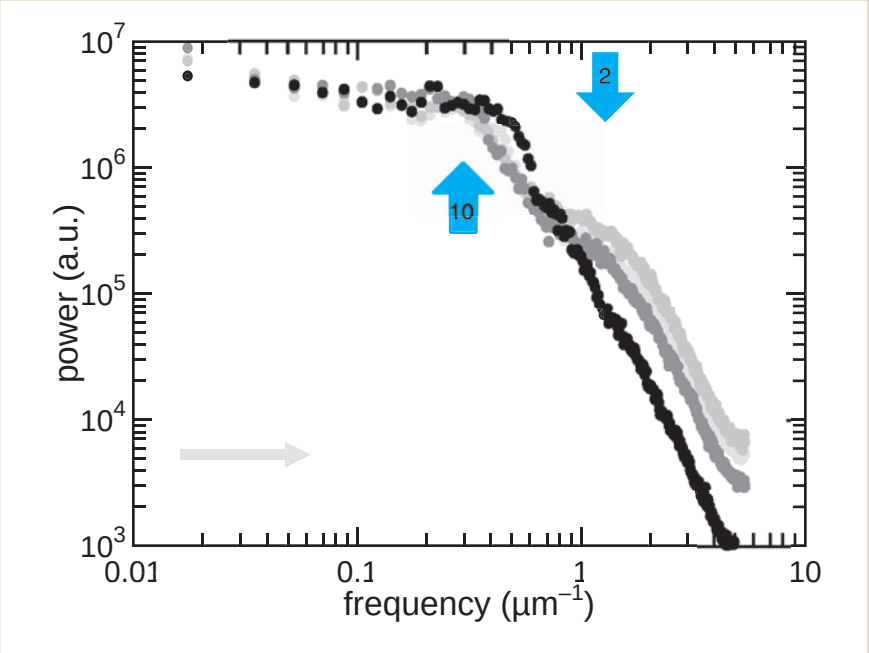


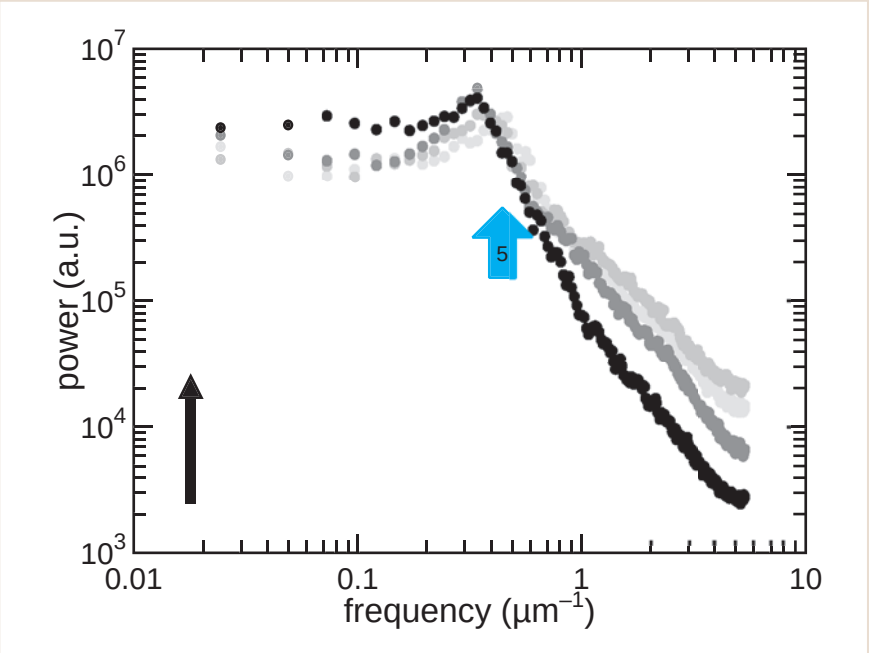
Formation process

SF_6 200 pulses



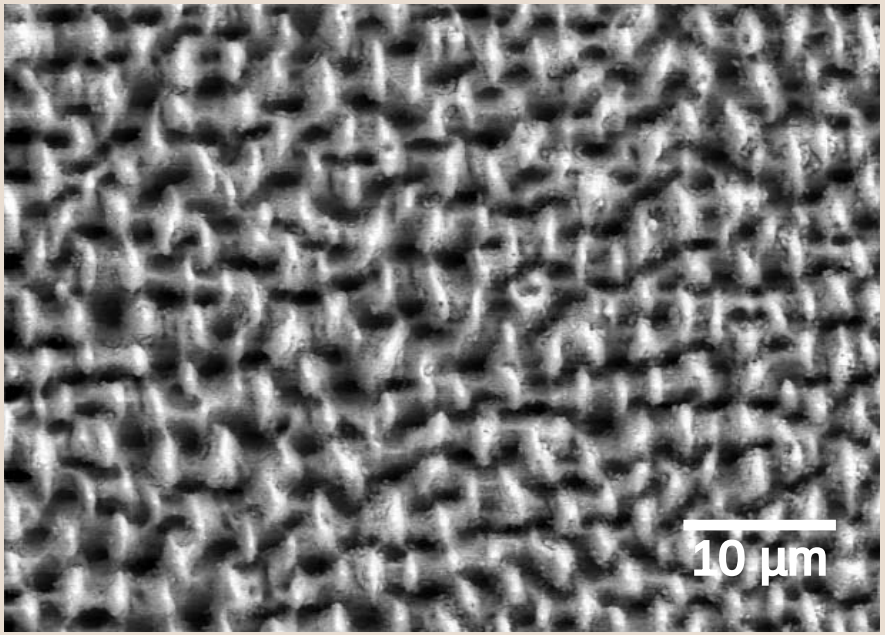
laser polarization



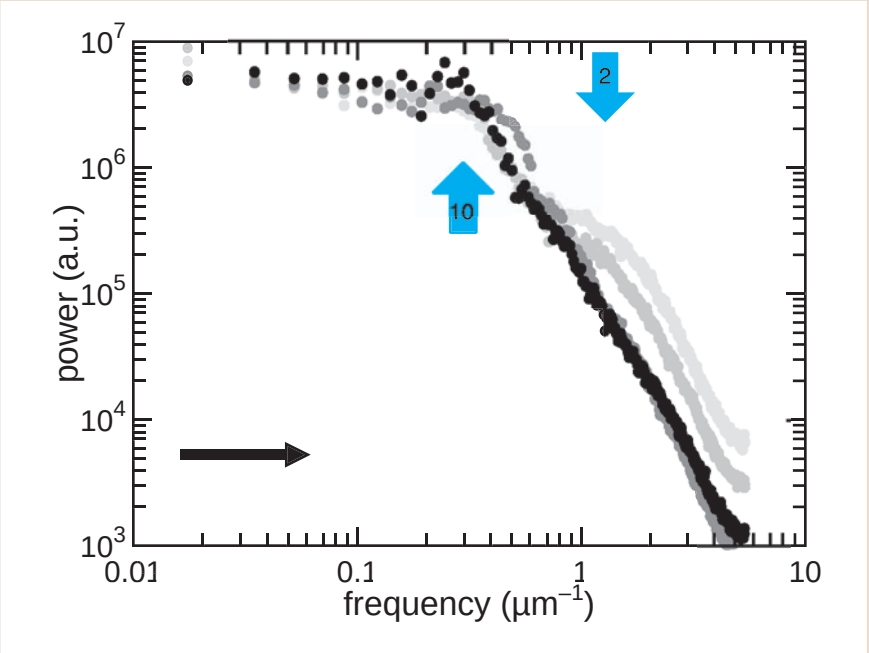


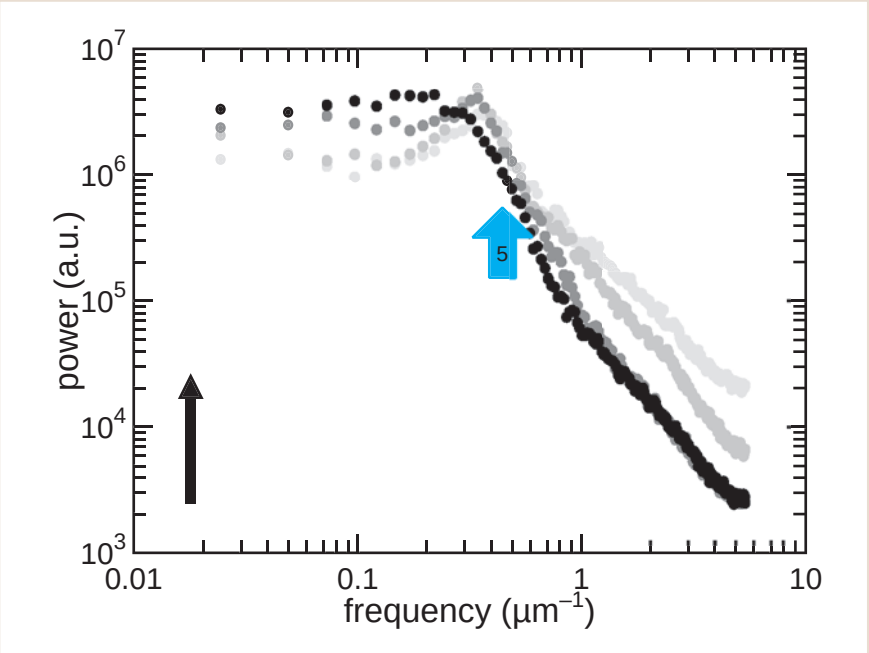
Formation process

SF_6 500 pulses



laser polarization



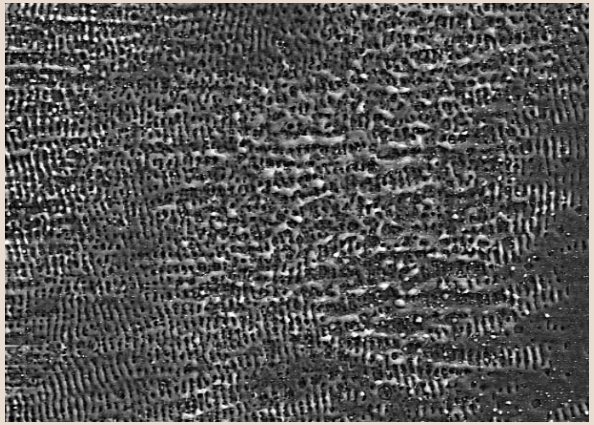


Formation process

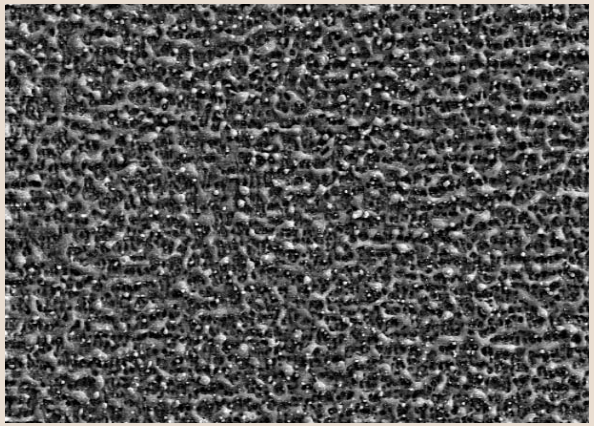
1. **Interference ripples (⊥ to polarization)**

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

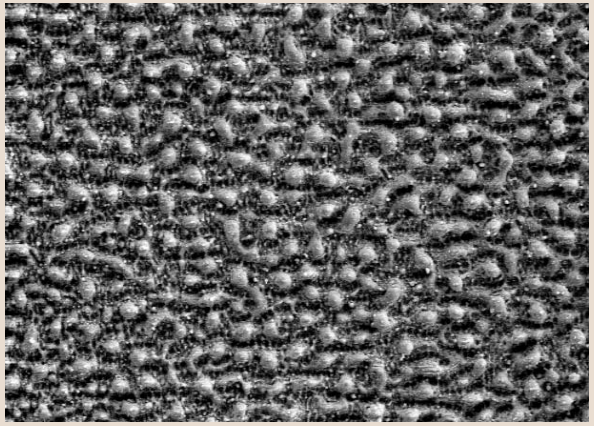
3. **Beads sharpening into spikes**



N = 2



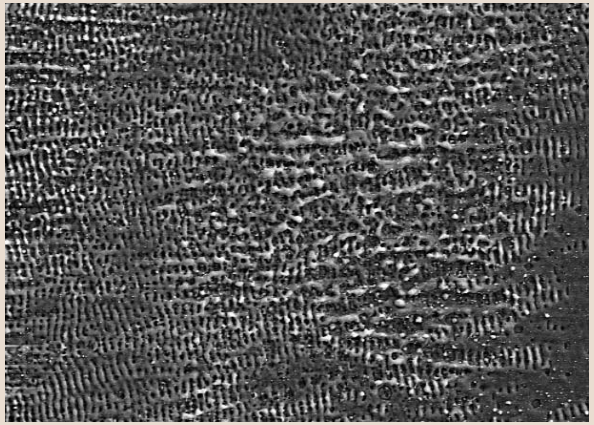
N = 4



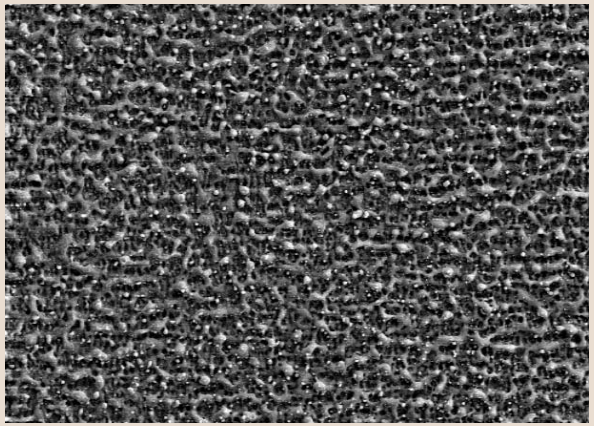
N = 10

Formation process

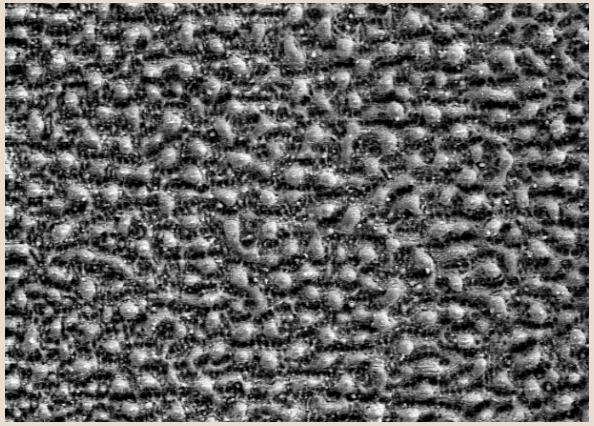
Two distinct wavelengths: ripples and spikes



N = 2



N = 4

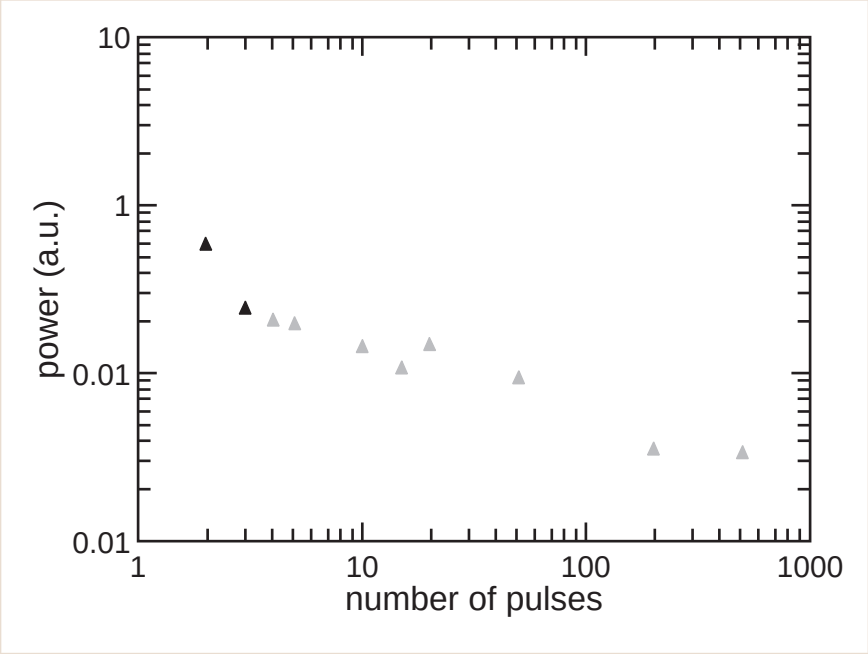


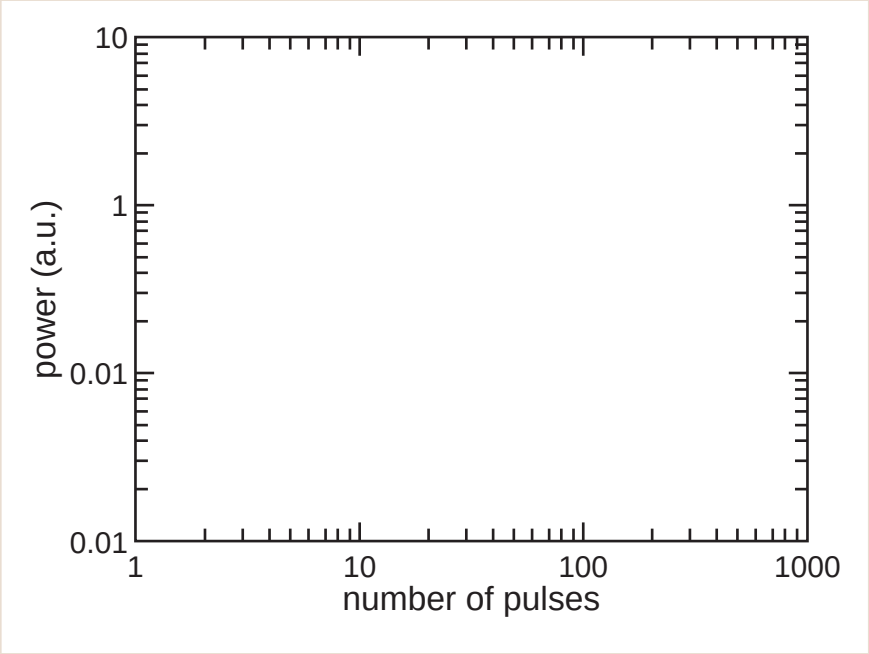
N = 10

Formation process

feature intensities

SF_6 ripples



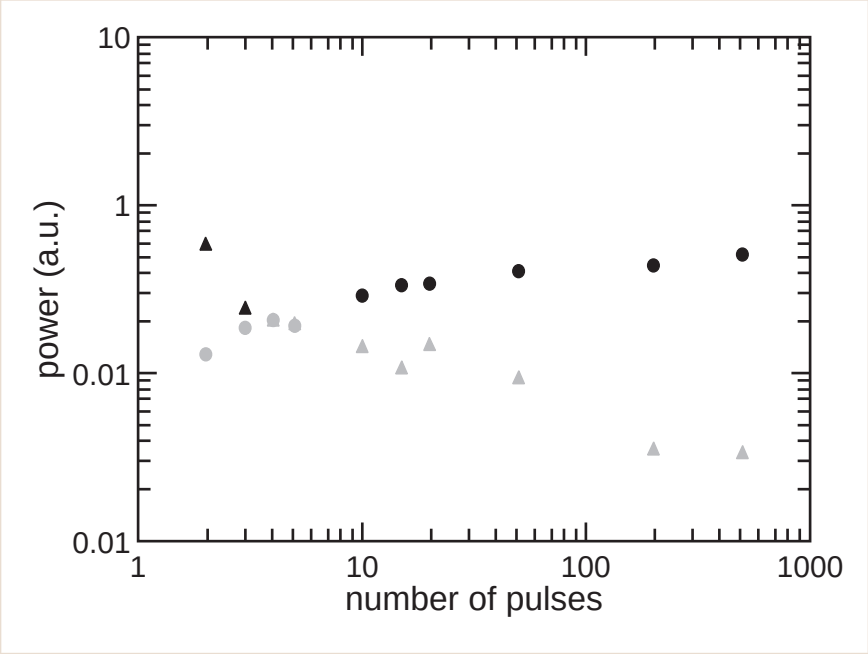


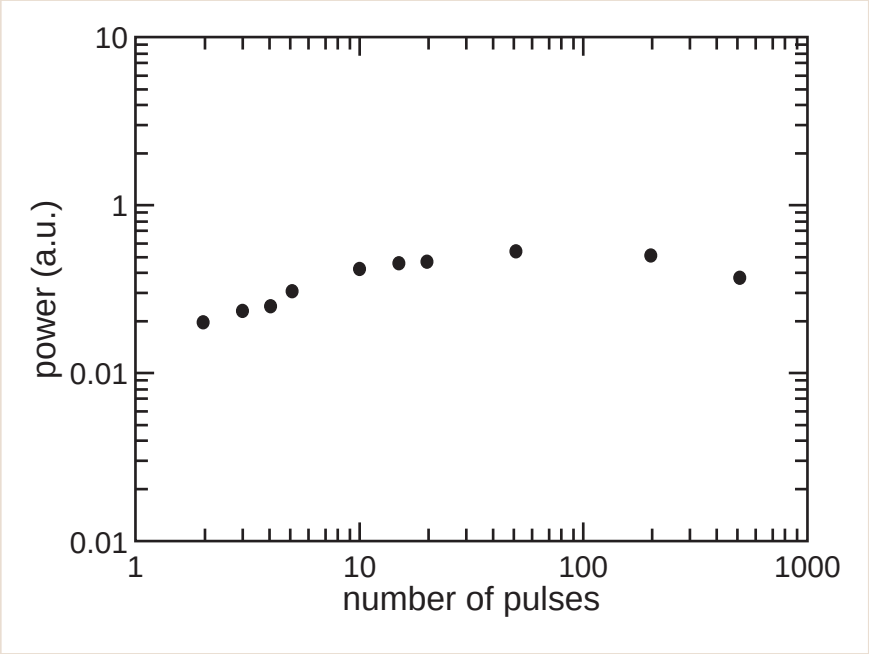
parallel **perpendicular**

Formation process

feature intensities

SF_6 spikes

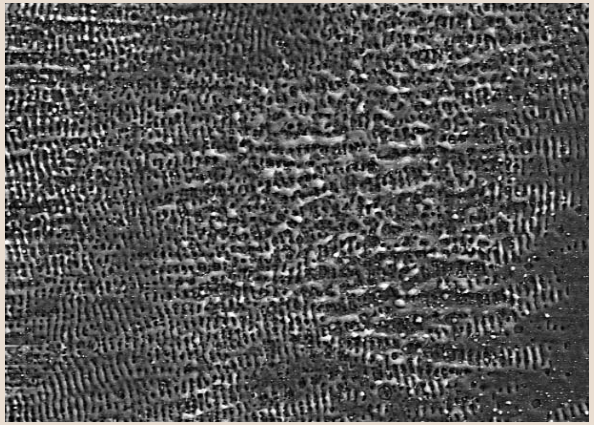




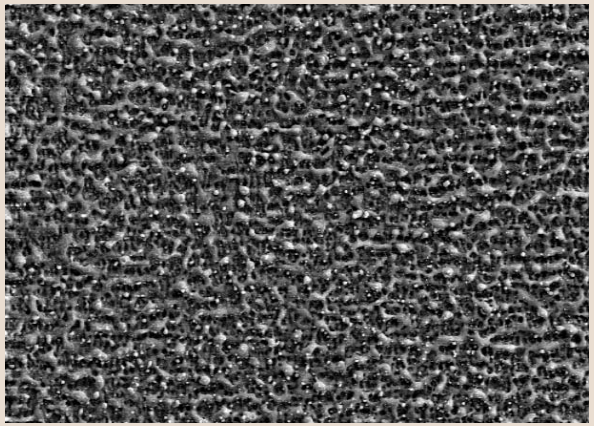
parallel **perpendicular**

Formation process

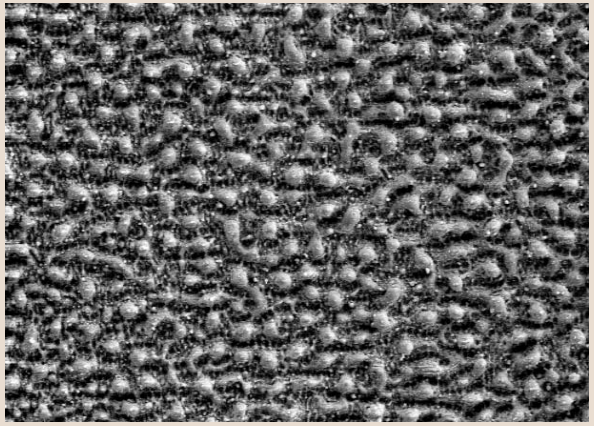
- **spike wavelength appears as ripple wavelength disappears**
- **spike wavelength appears first perpendicular to polarization**



N = 2



N = 4



N = 10

What sets the length scales?

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

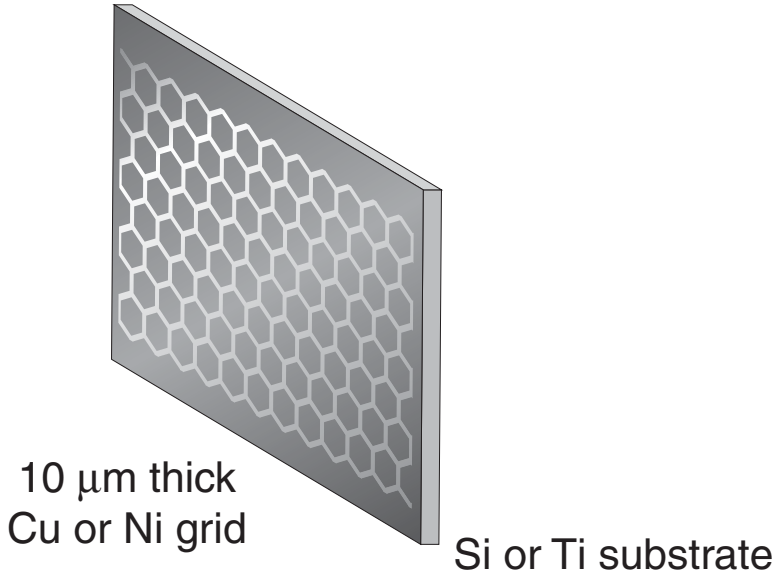
Capillary wavelength set by melt depth, duration

$$\lambda = \left[\frac{\sigma d}{\rho}\right]^{\frac{1}{4}} (2\pi\tau)^{\frac{1}{2}}$$

- longest wavelength similar to spike spacing (10 µm)
- both spike spacing and capillary wavelength increase with laser fluence

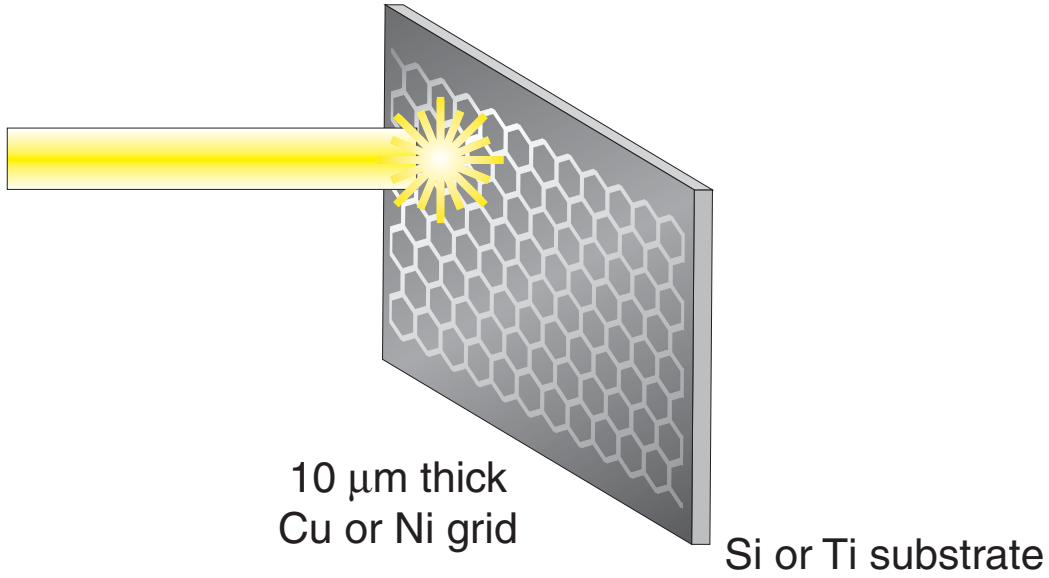
Ordering

place grid in front of substrate



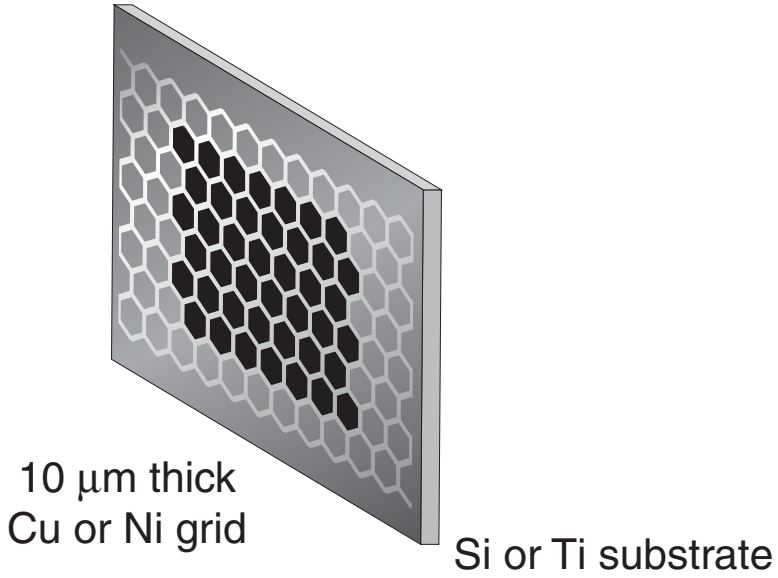
Ordering

scan laser beam



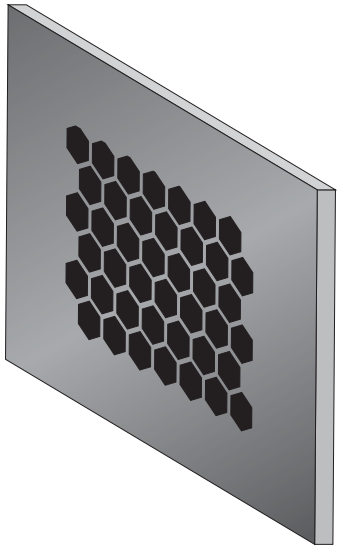
Ordering

scan laser beam

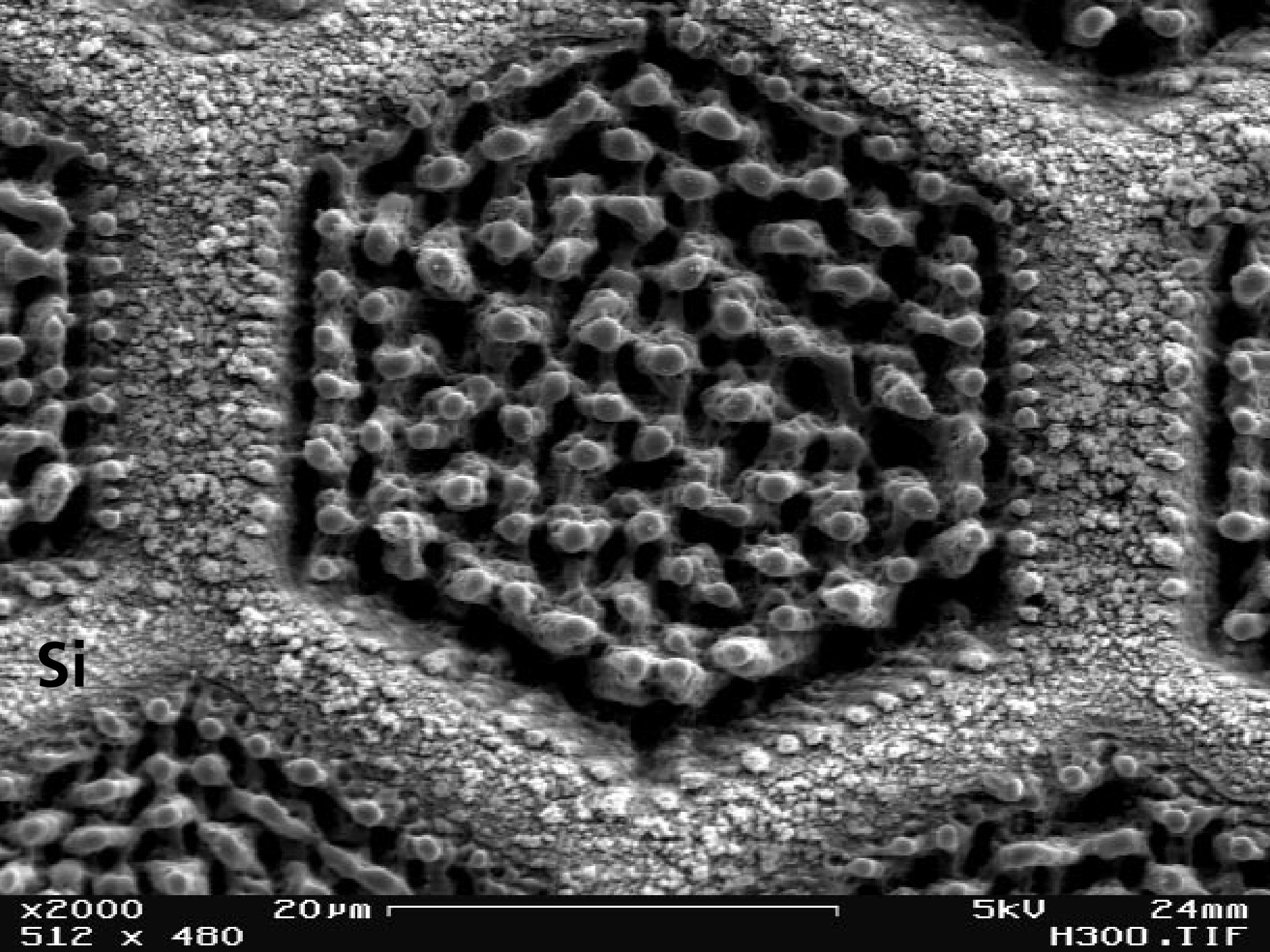


Ordering

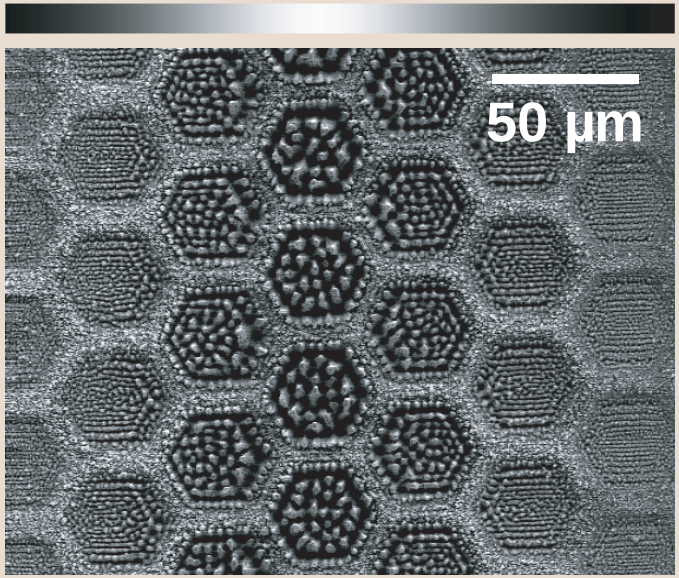
remove grid

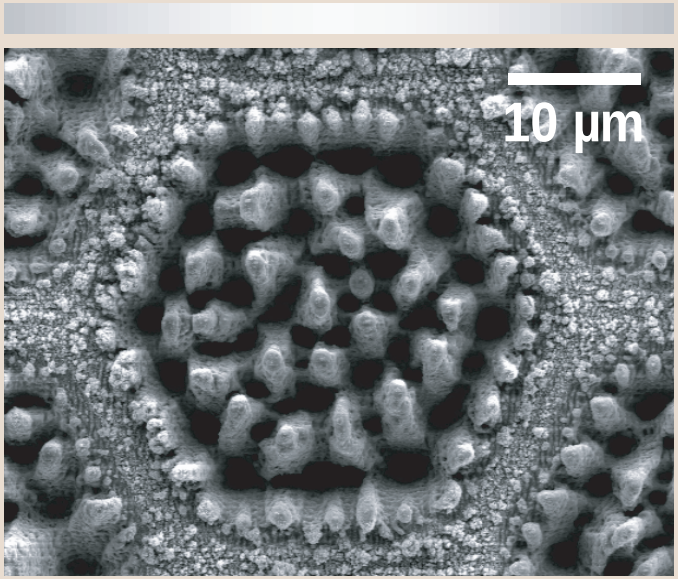


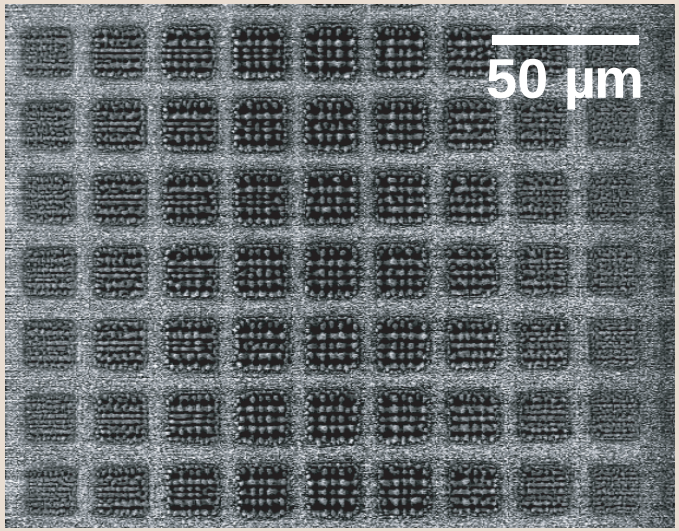
Si or Ti substrate

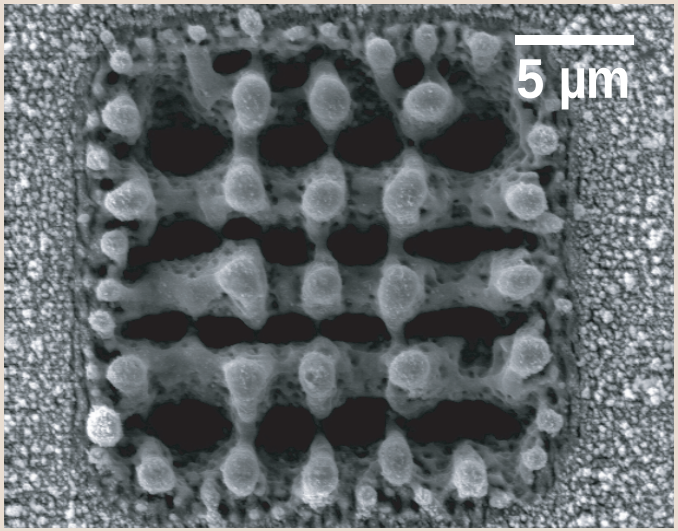

Si
x2000
20µm
5kV
24mm
512 x 480
H300.TIF

Ordering

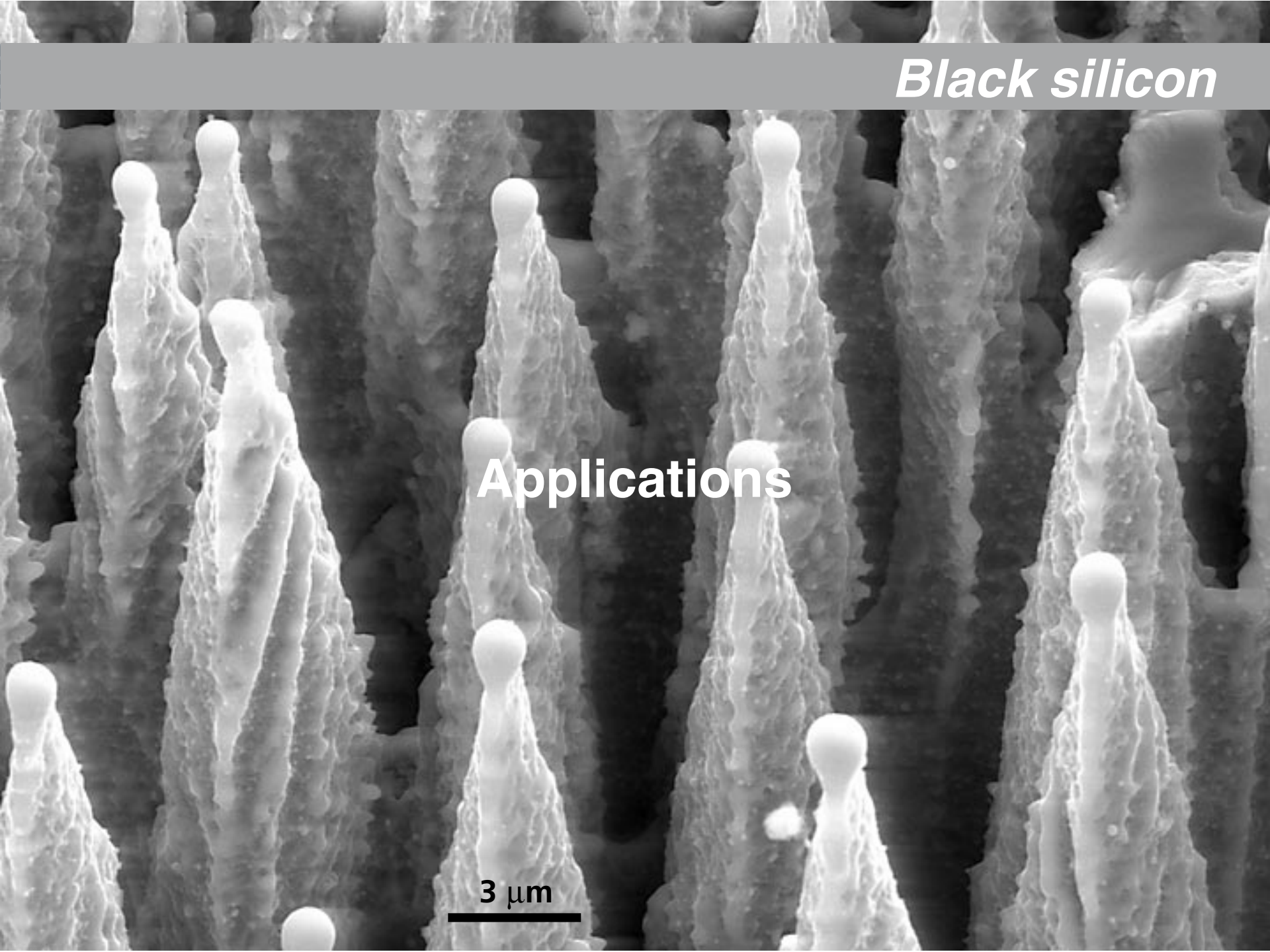








Shen *et al.*, to appear in *Appl. Phys. Lett.*



Applications

Summary

Black silicon:

- near-unity absorption from near-UV to near-IR
- *p*-type sulfur impurity band below CB edge
- self-organized surface microstructures
- many promising applications!

Acknowledgements

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Eric Mazur
Michael Aziz, Cynthia Friend, Howard Stone

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

Could nanostructures explain infrared absorption?

Structure less likely than sulfur:

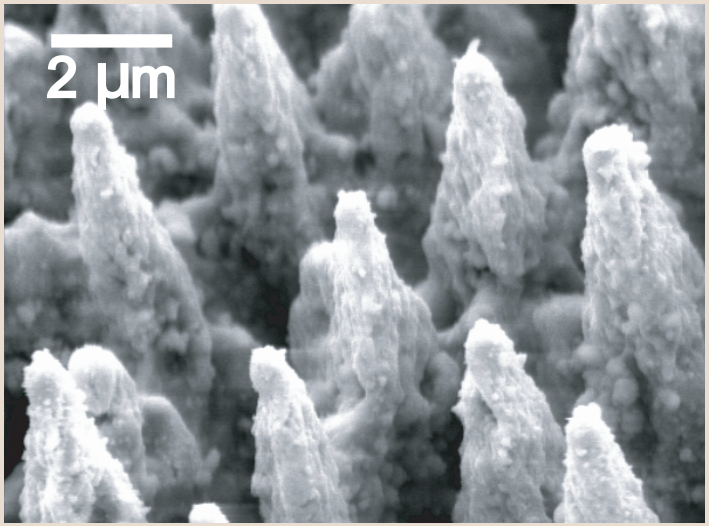
annealing

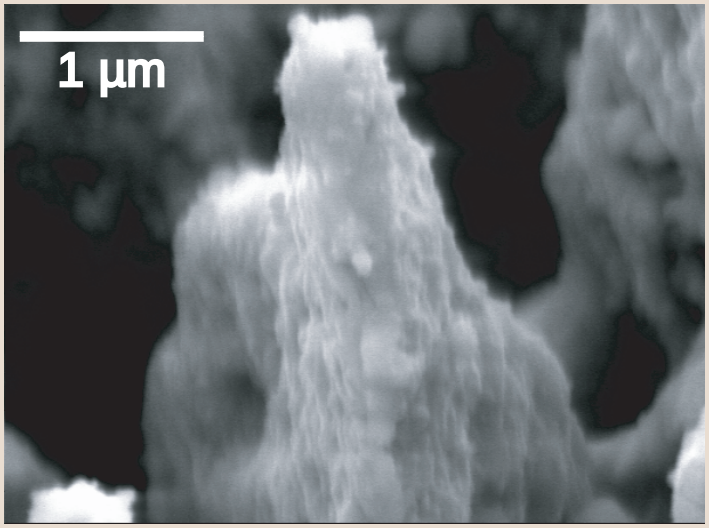
ns pulses

different gases

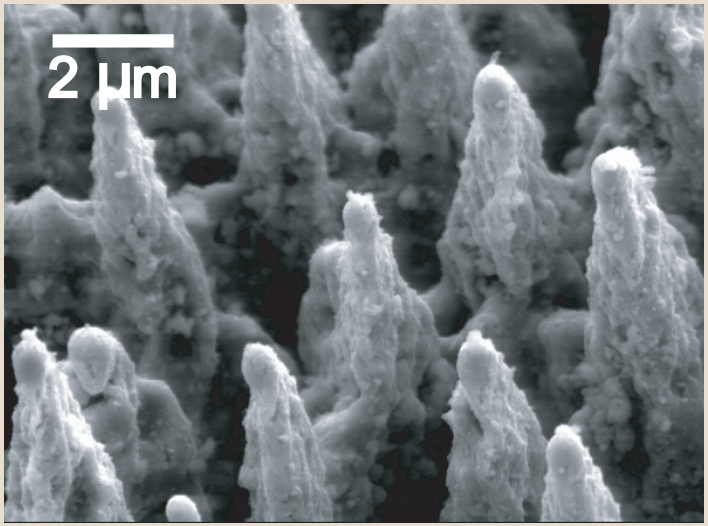
Structural analysis

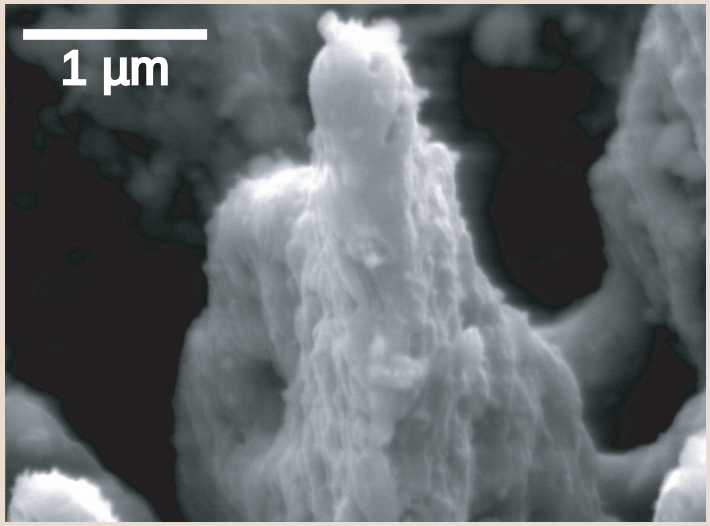
before annealing





after annealing





Structure less likely than sulfur:

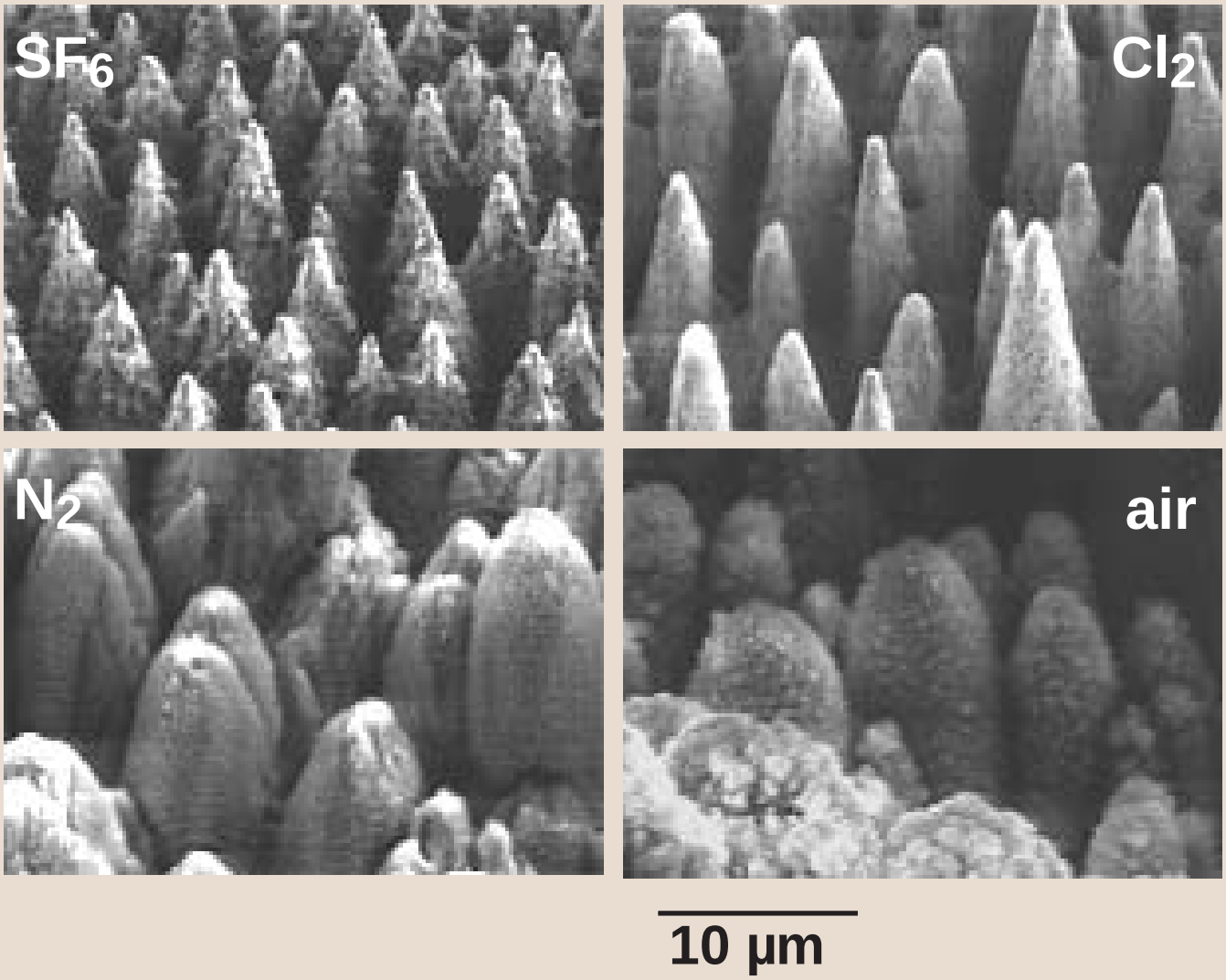
no evident structural change with annealing

(consistent with multiple reflections in visible)

Structure less likely than sulfur:

- no evident structural change with annealing
- ns pulses produce very different structure, but same composition and optical properties

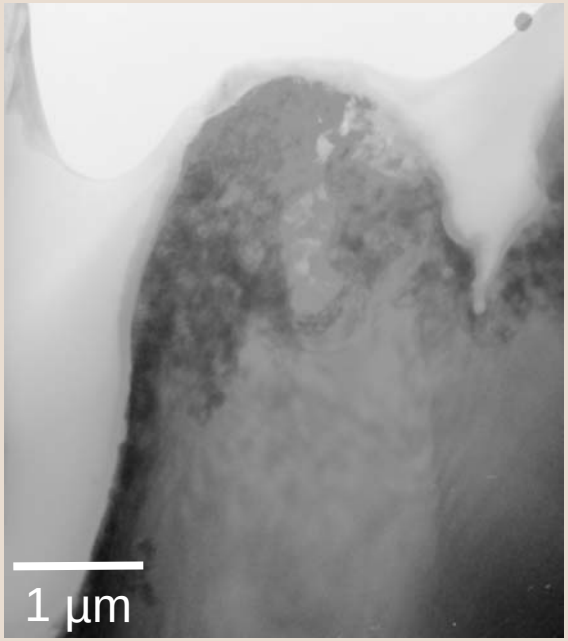
Structural analysis



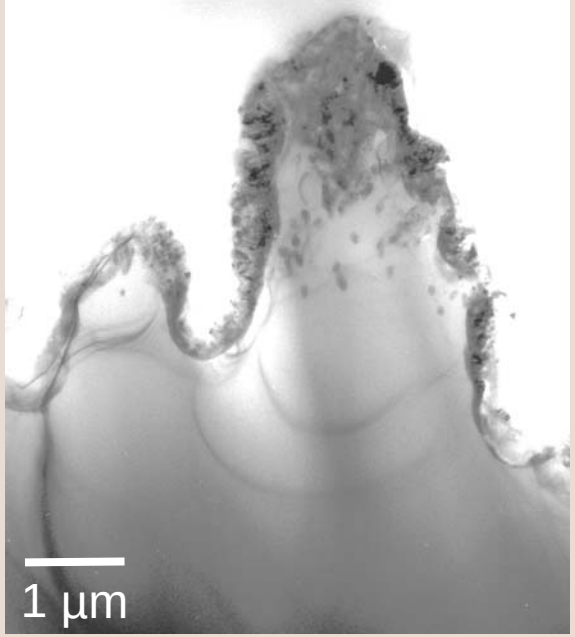
all except Cl_2 show surface nanostructure

Structural analysis

air



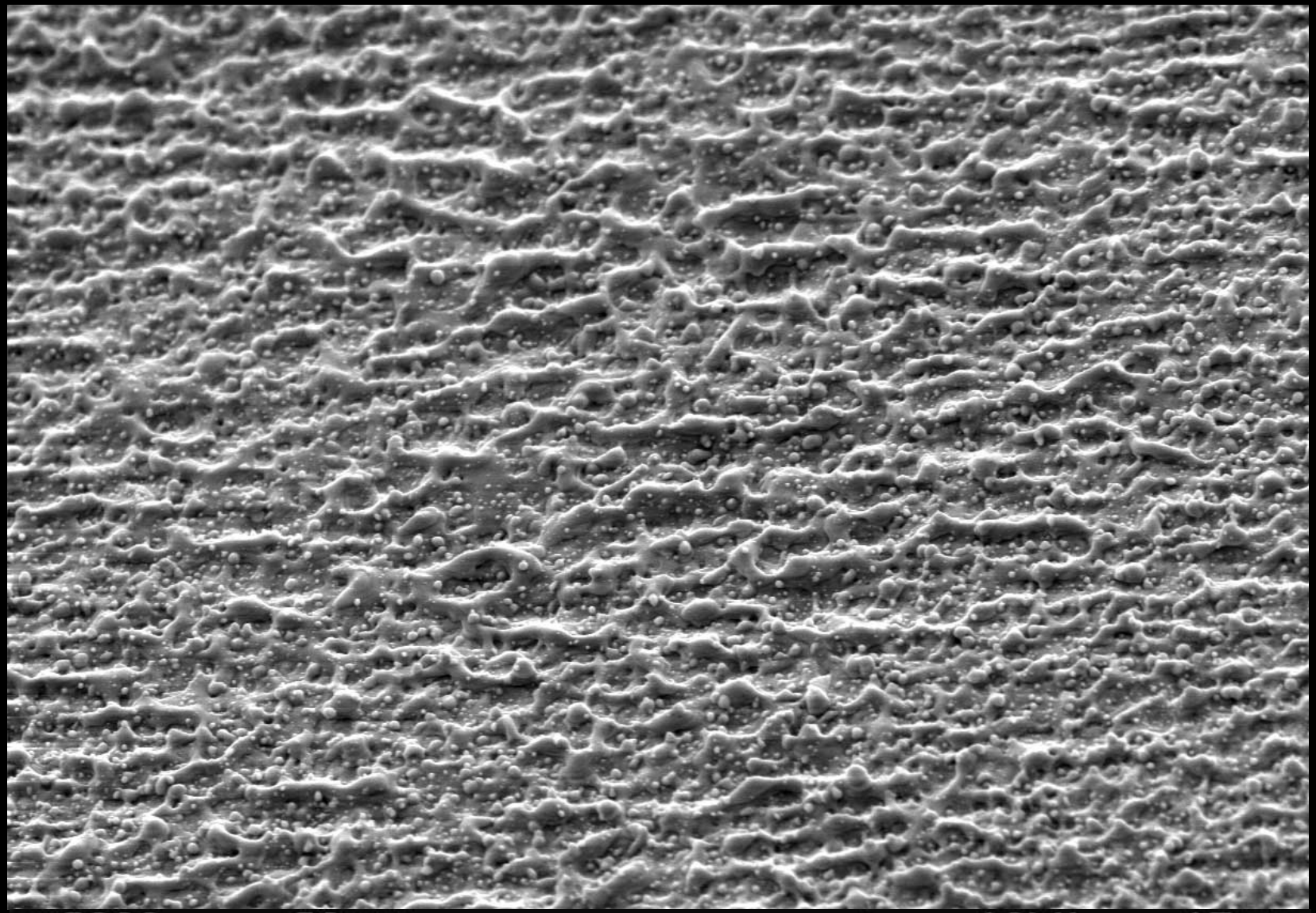
SF_6



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



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