Femtosecond-laser Microstructuring of Silicon for Novel Optoelectronic Devices

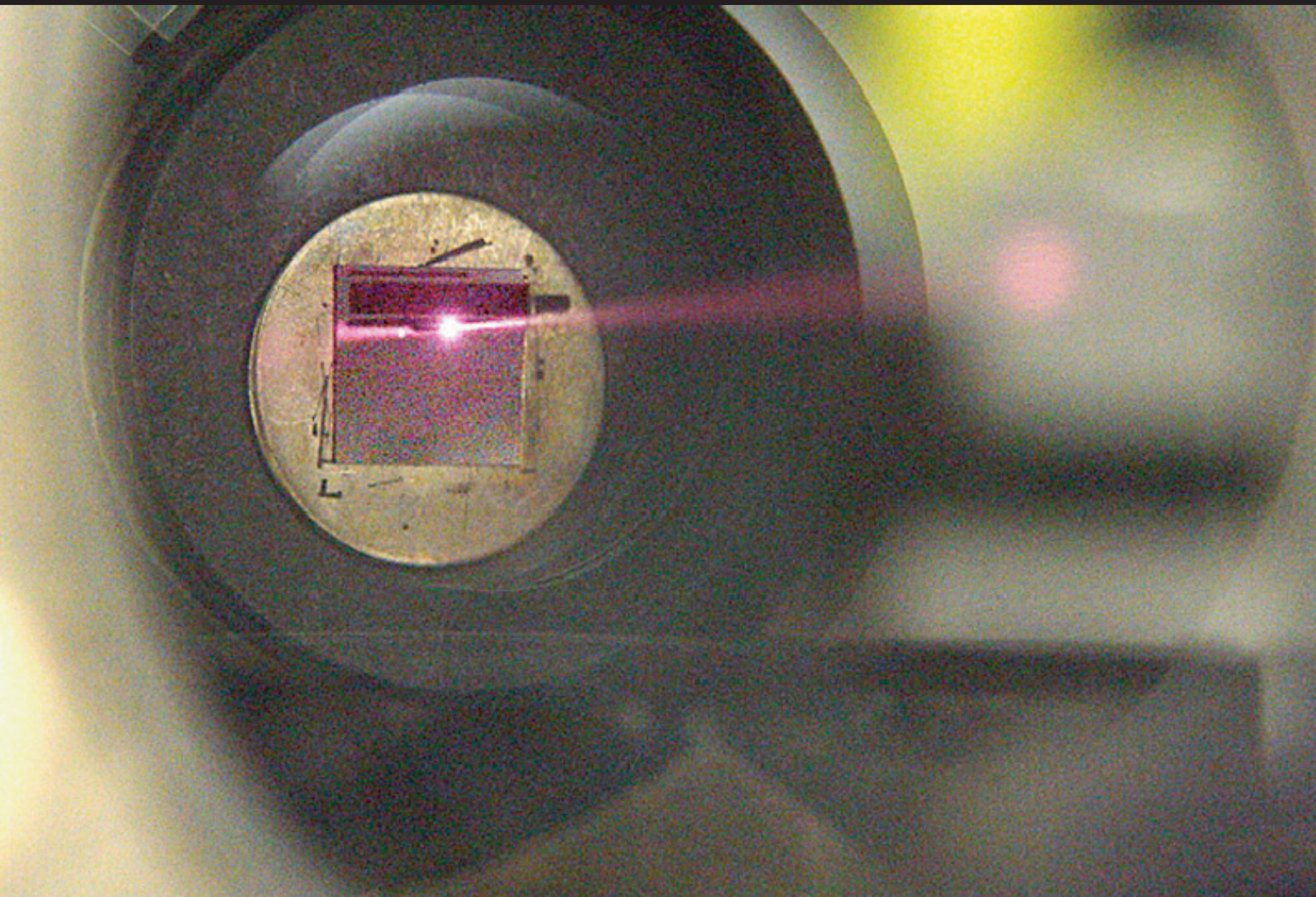
James Carey
Photonics West
San Jose, CA, 25 January 2005

Motivation

Silicon:

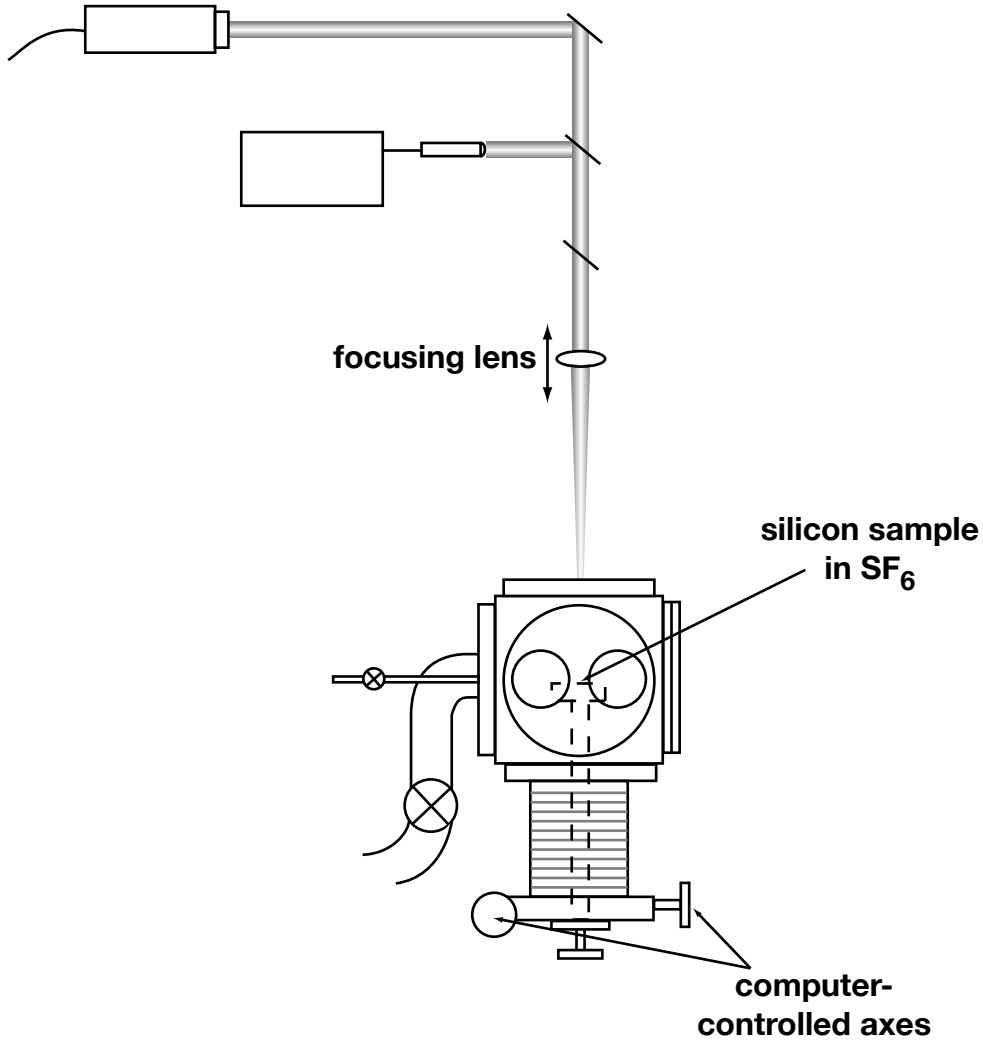
- **most widely used semiconductor**
- **enormous infrastructure, inexpensive**
- **can't do everything**
- **alter silicon to improve functionality**

Introduction



Introduction

apparatus



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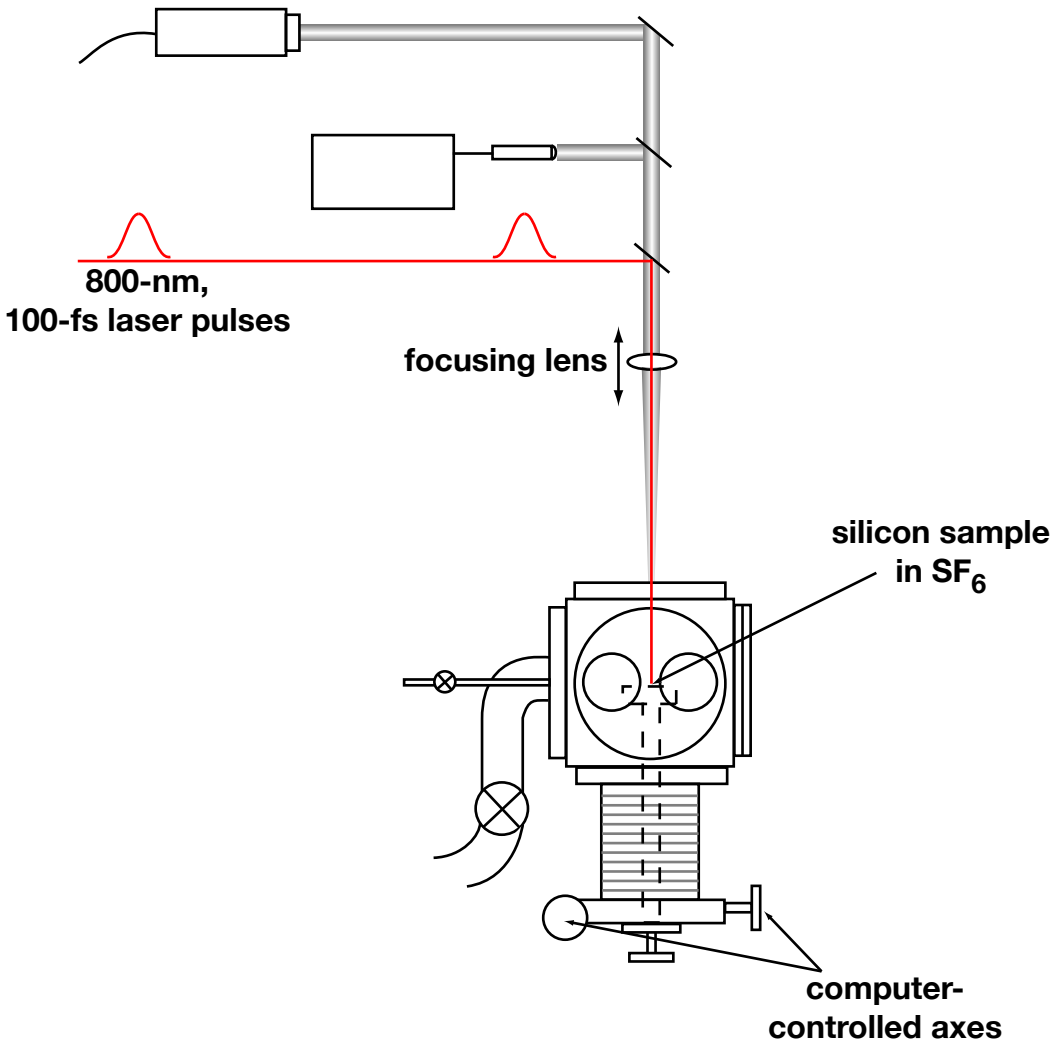

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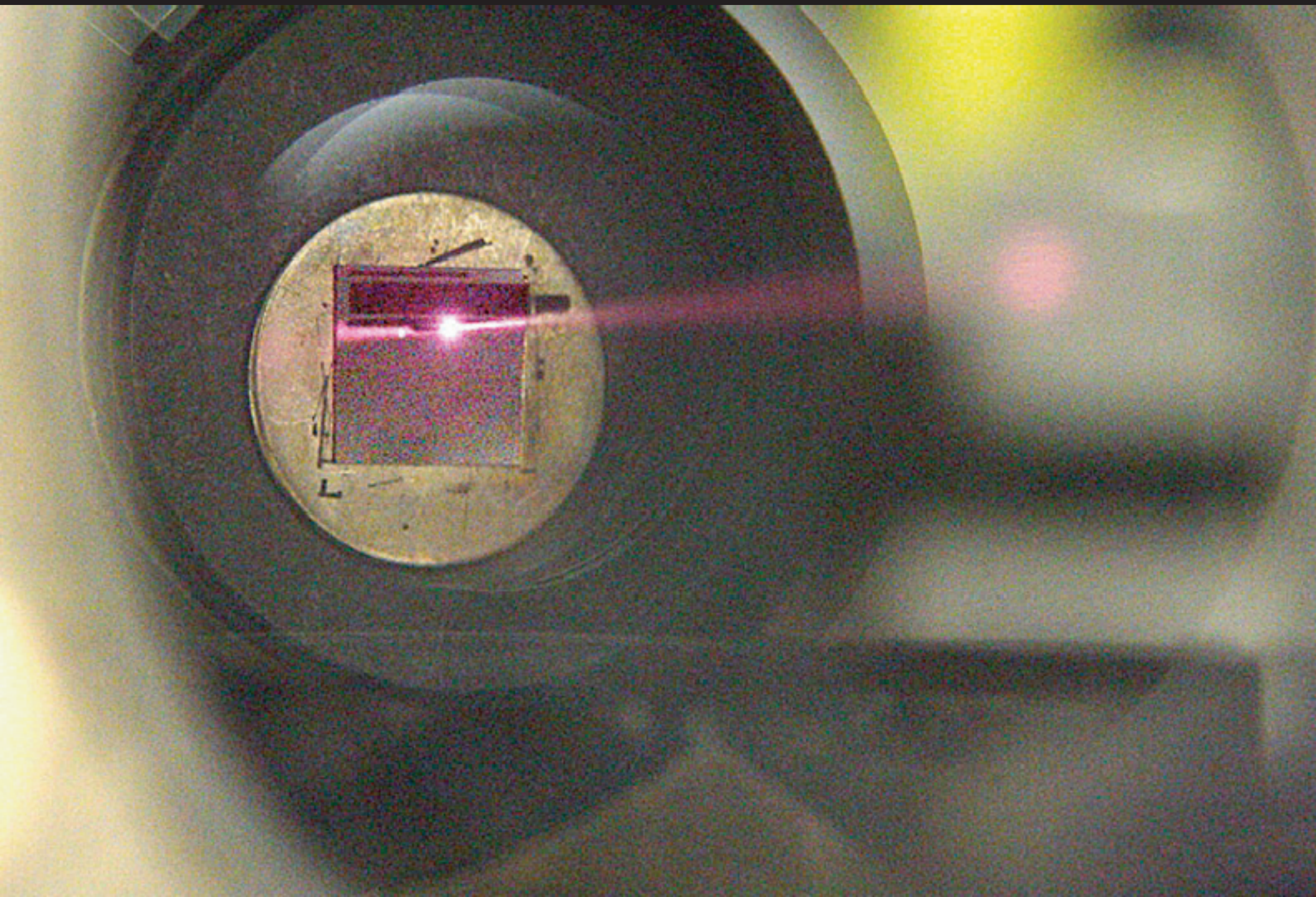

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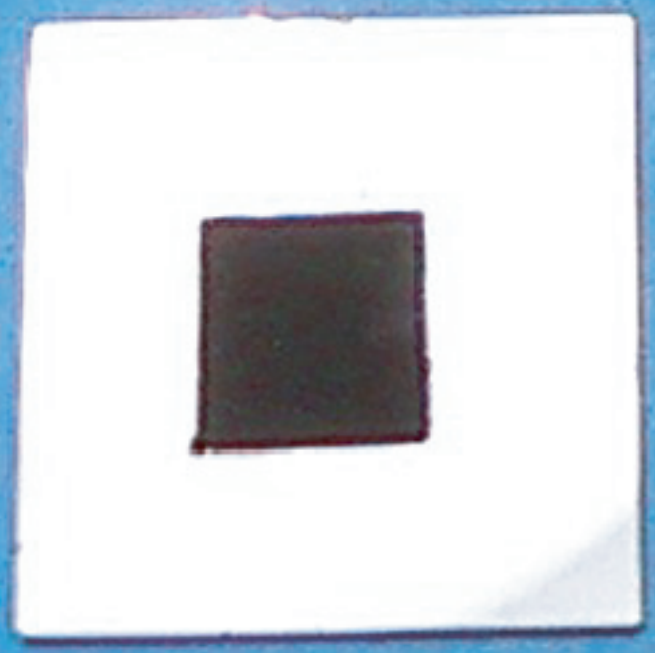
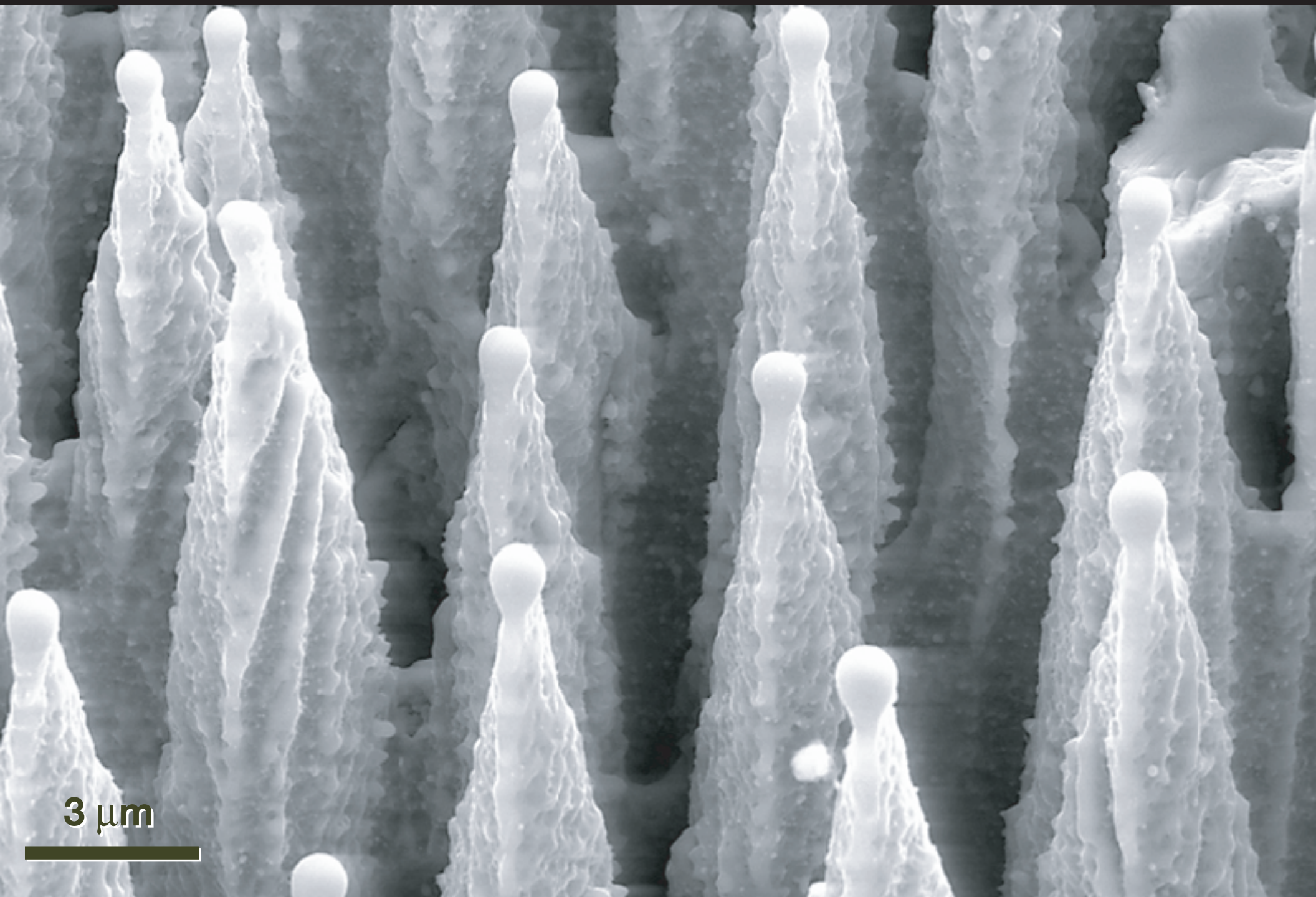


"black silicon"

Introduction



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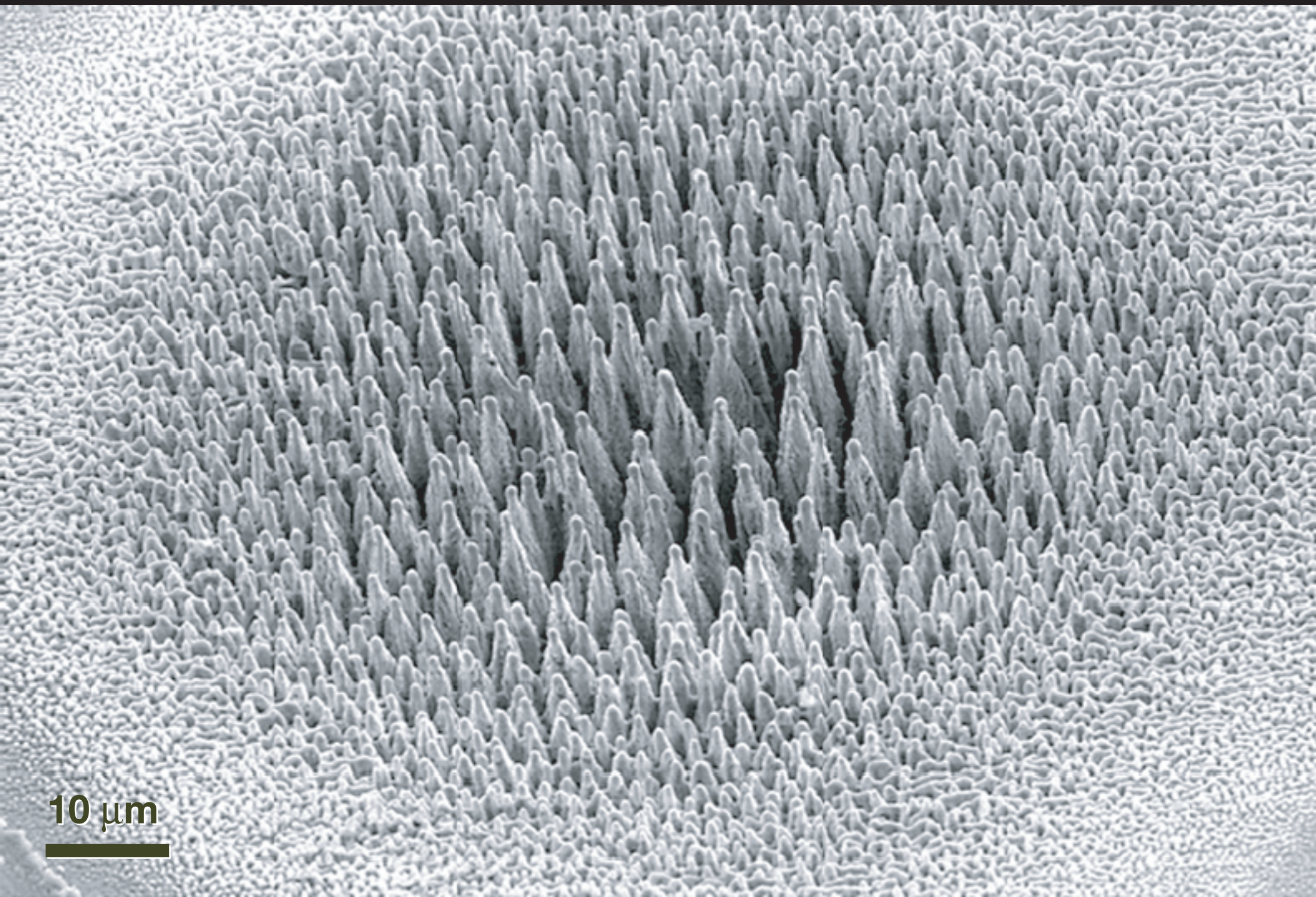

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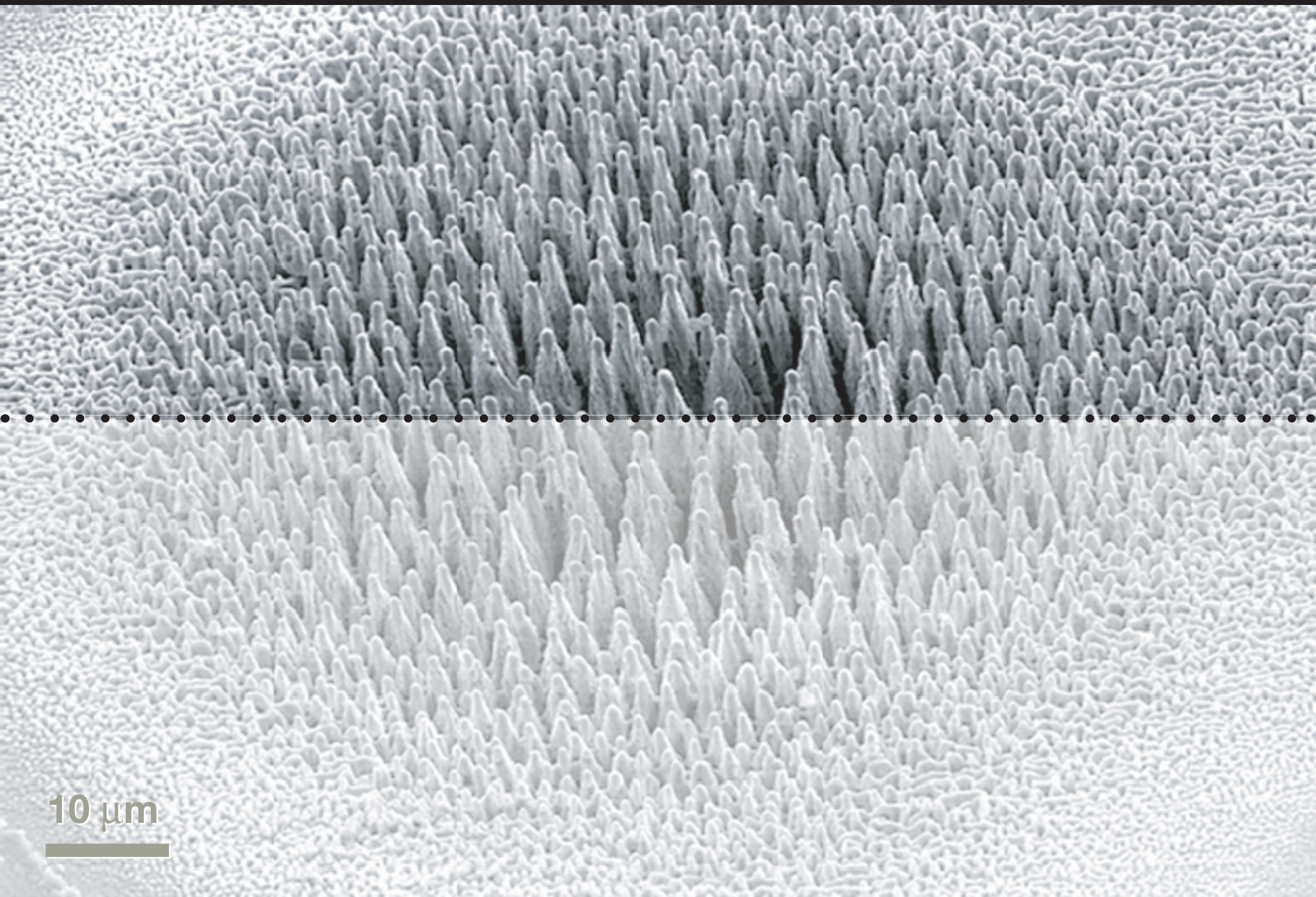

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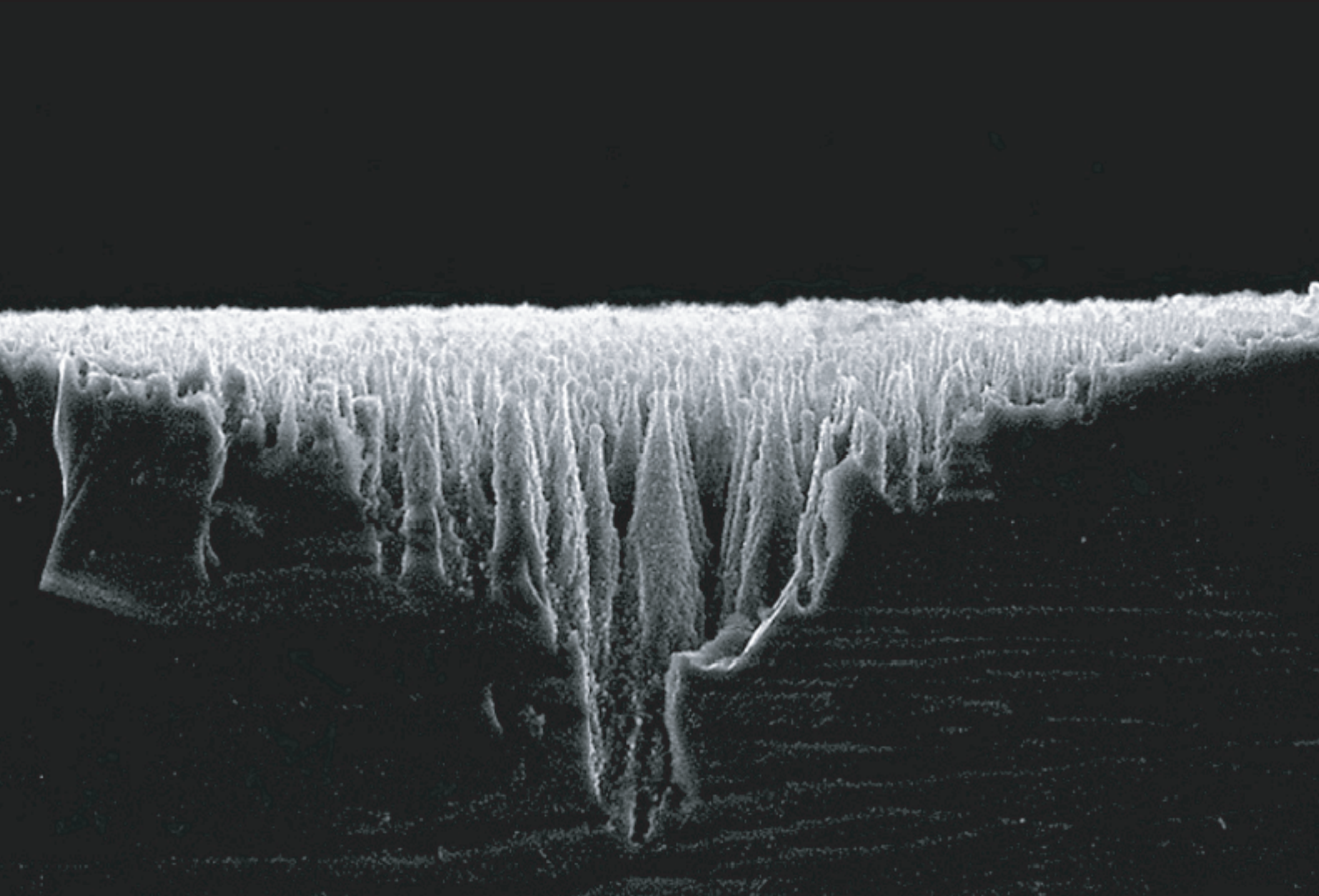

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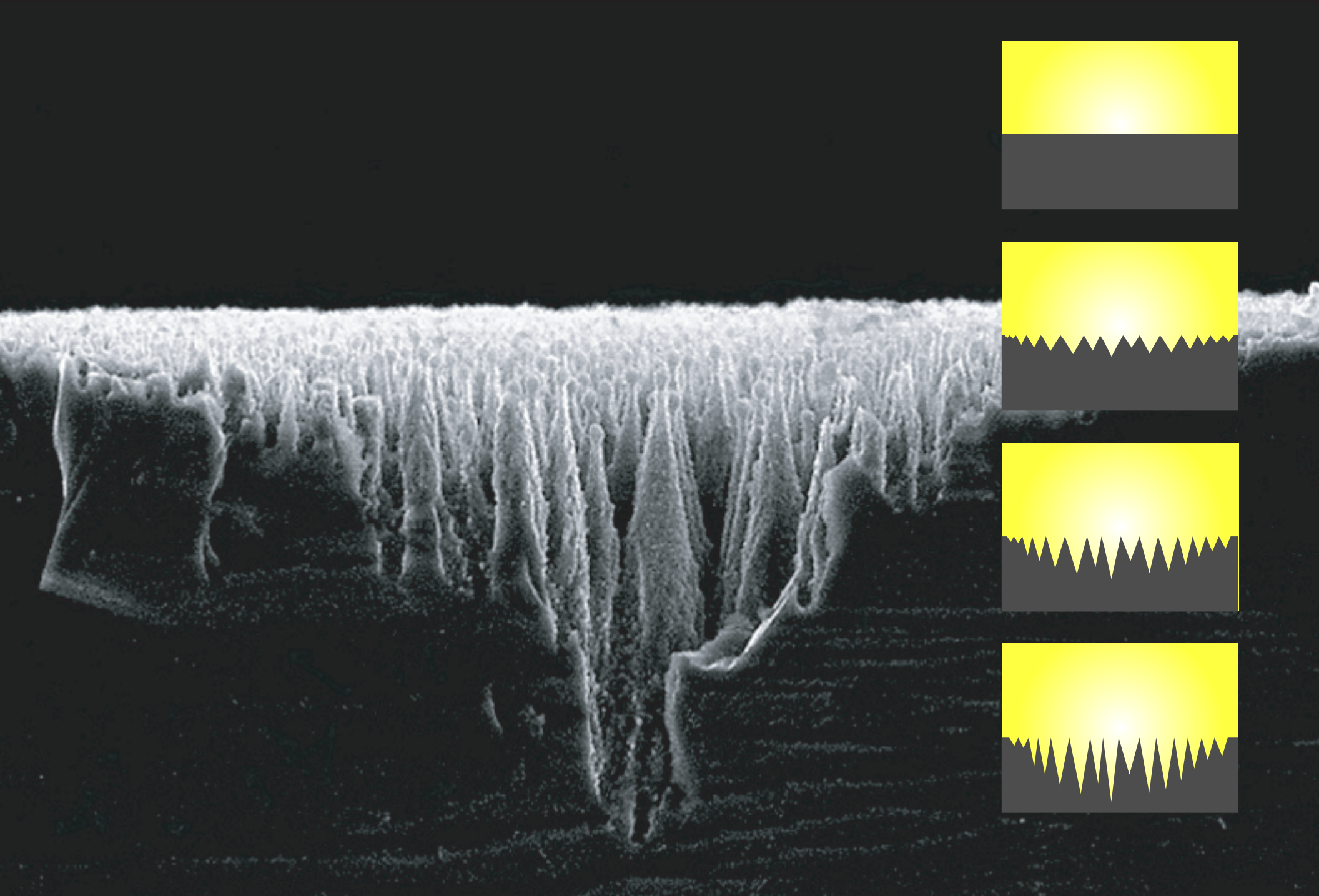


Introduction

- maskless etching process
- self-organized, conical microstructures
- highly light absorbing

Outline

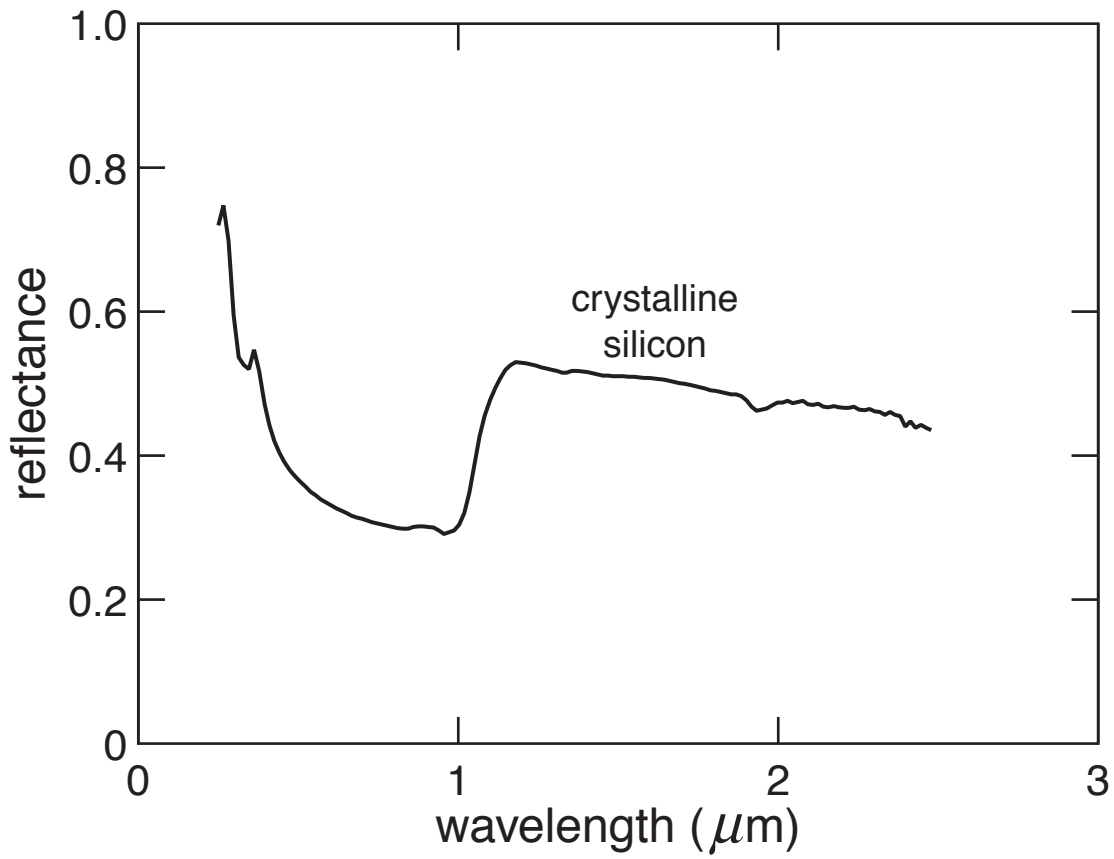
- optical properties
- structural and chemical analysis
- photodetectors
  - the *p-n* junction
  - femtosecond-laser microstructured silicon photodiodes
- outlook

Outline

- **optical properties**
- structural and chemical analysis
- photodetectors
  - the *p-n* junction
  - femtosecond-laser microstructured silicon photodiodes
- outlook

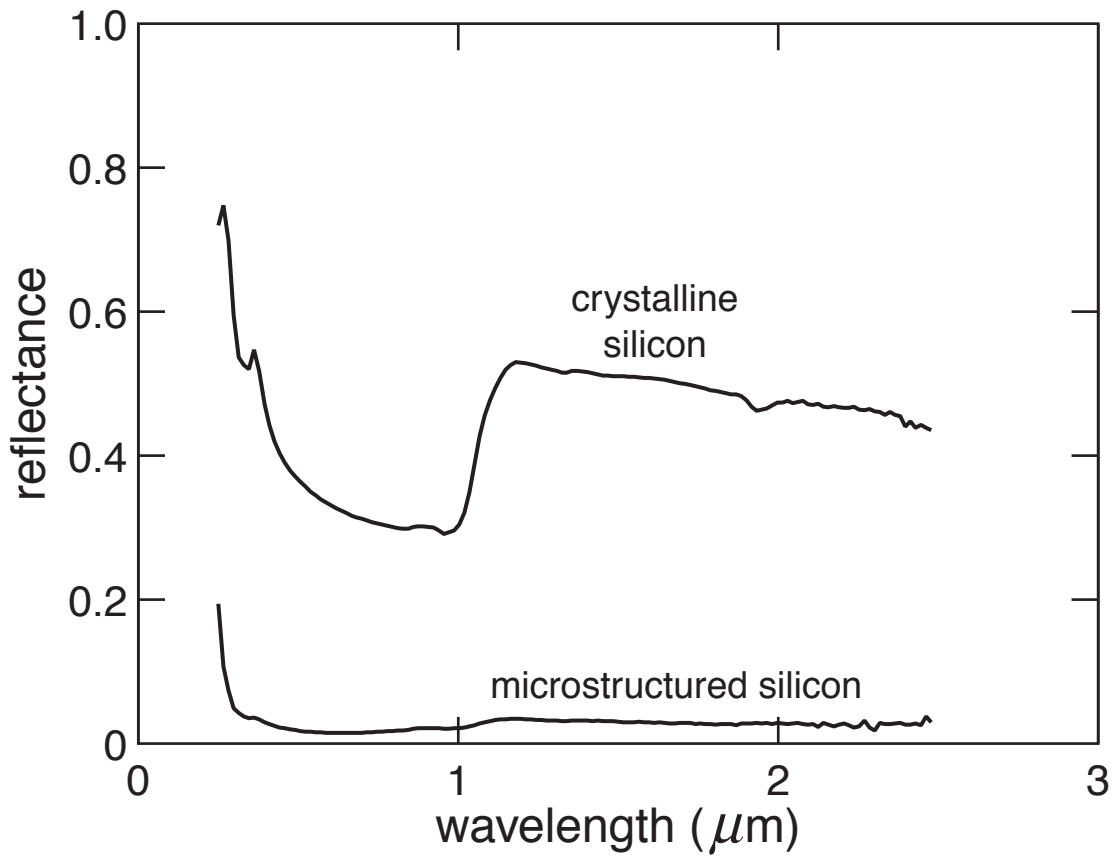
Optical properties

reflectance (integrating sphere)



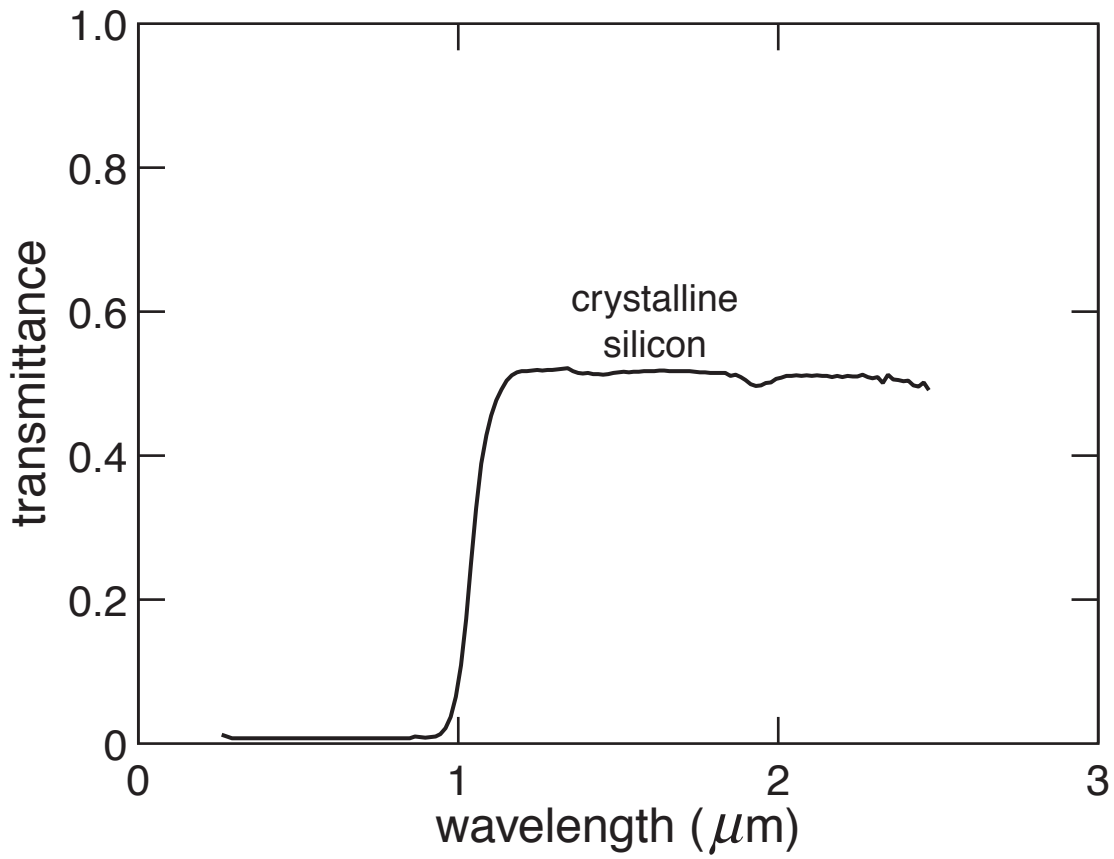
Optical properties

reflectance (integrating sphere)



Optical properties

transmittance (integrating sphere)



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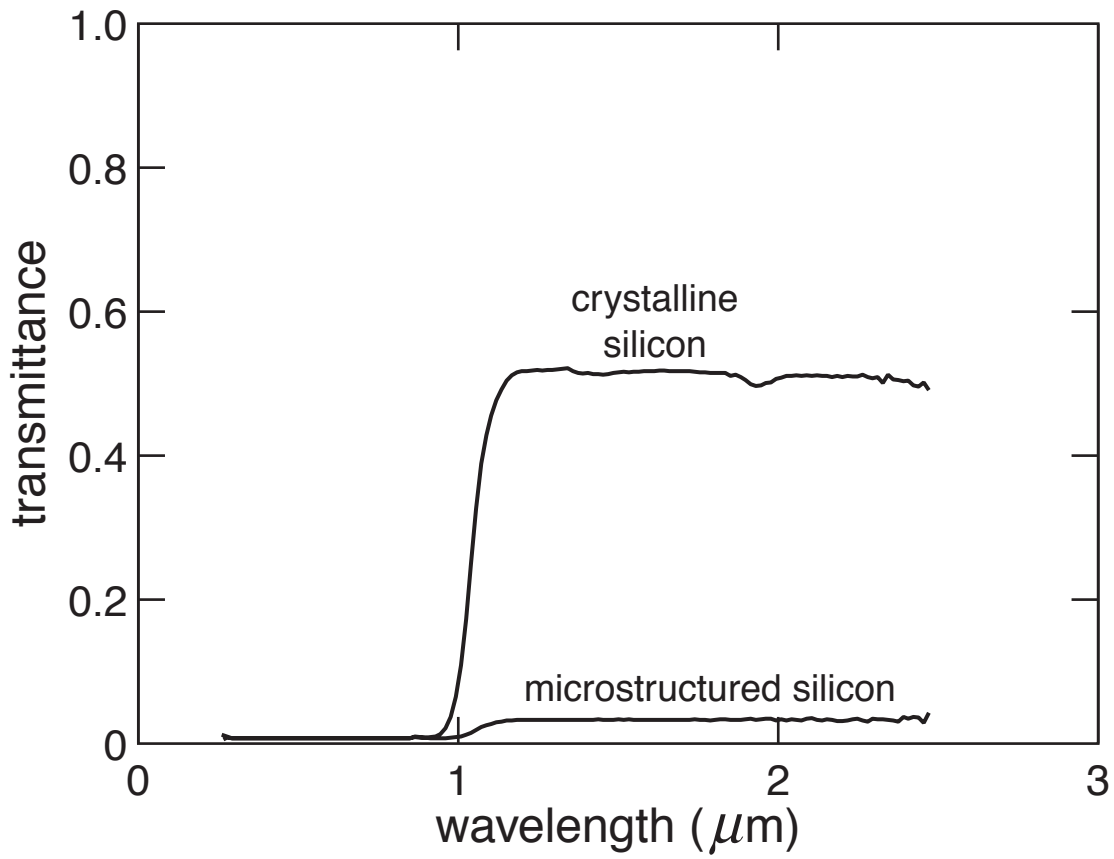
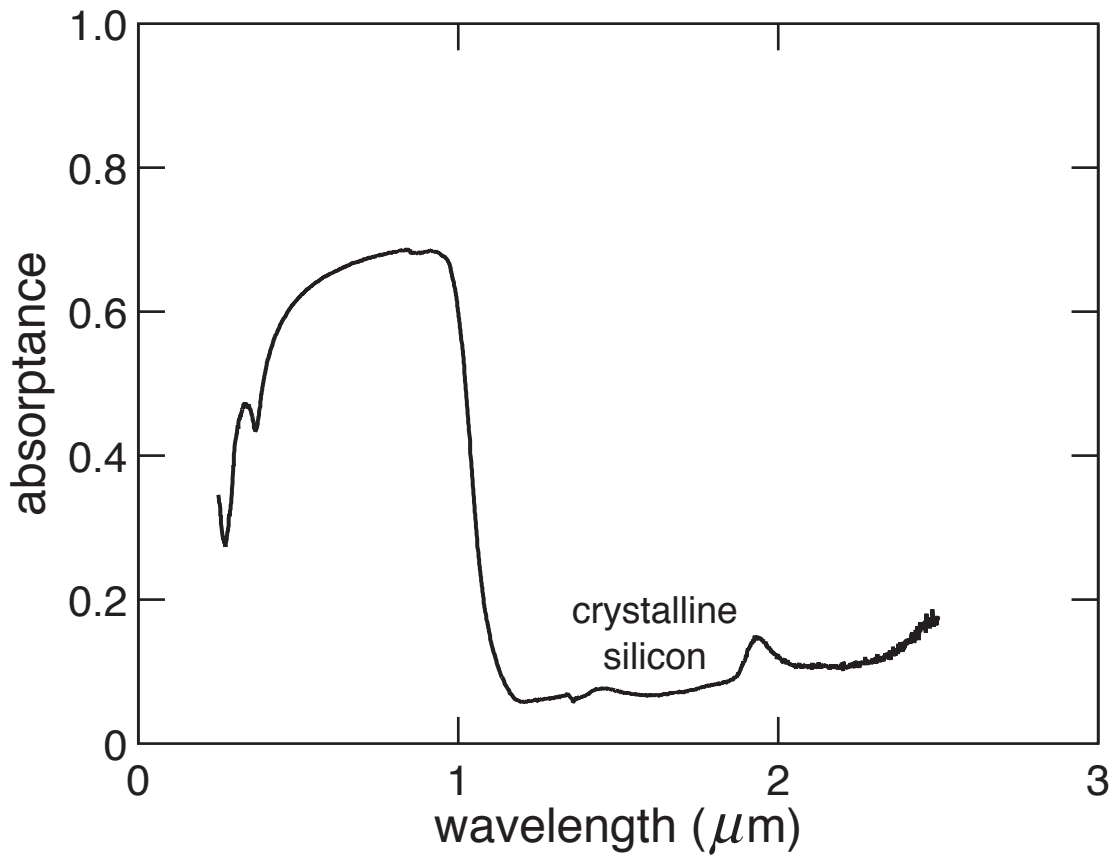


Optical properties

absorptance (1 – *R* – *T*)



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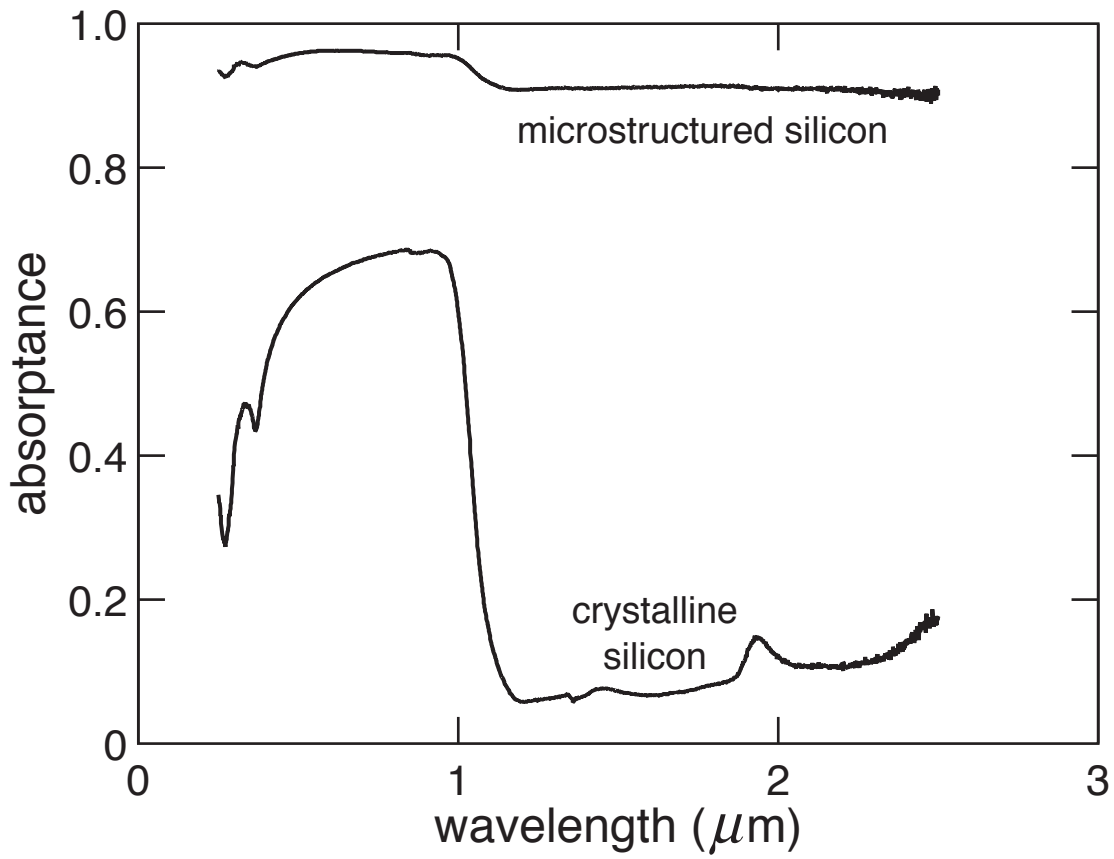
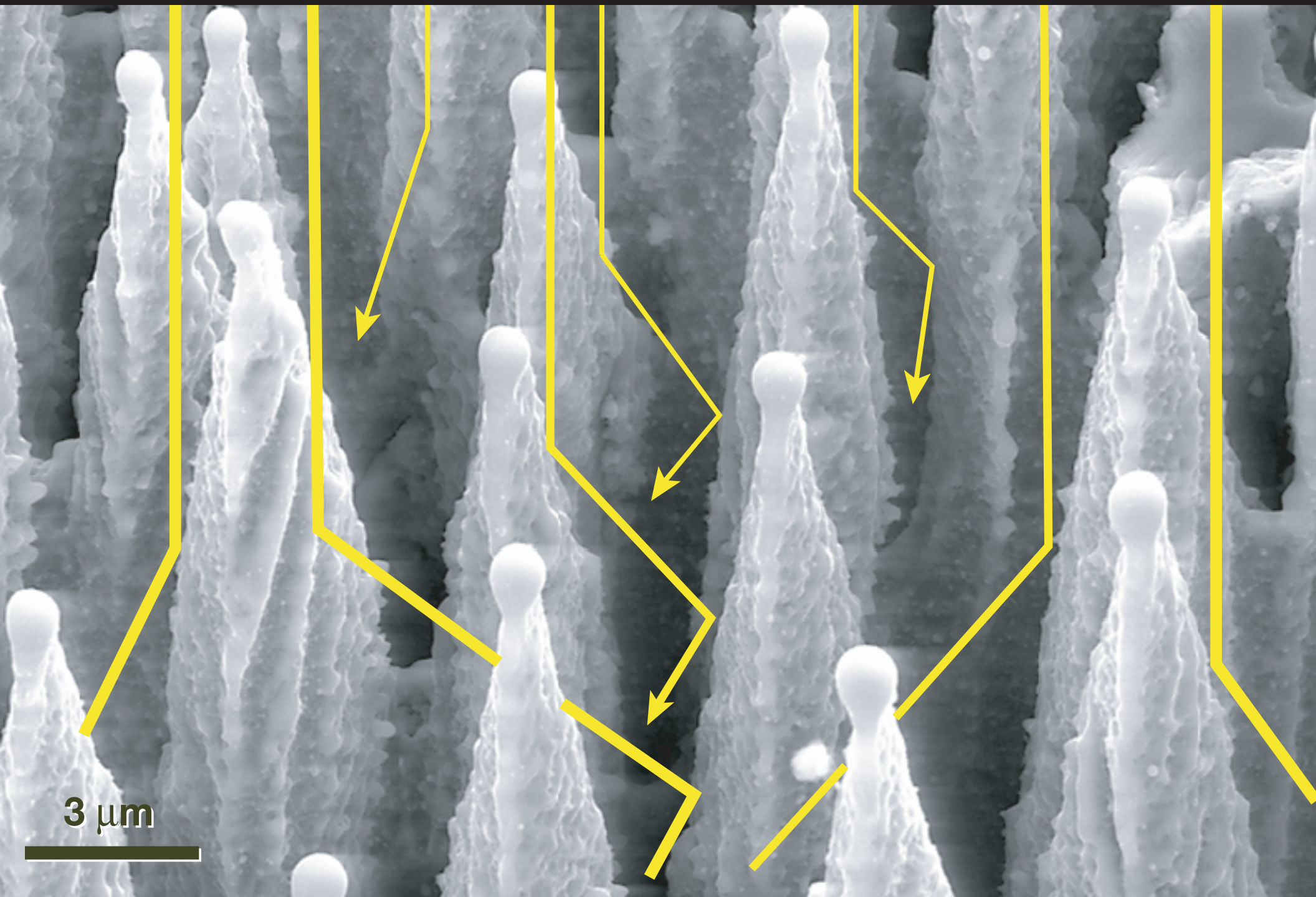


Optical properties

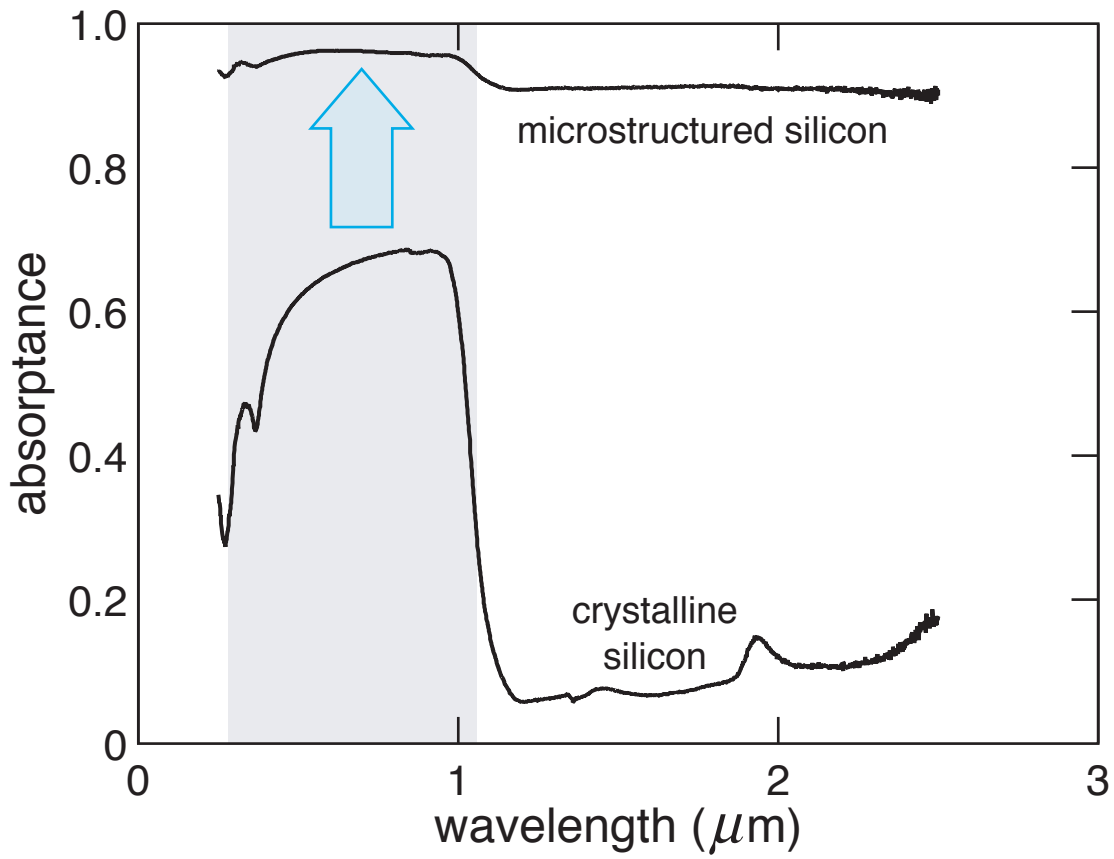
What causes the near-unity absorptance?

Optical properties



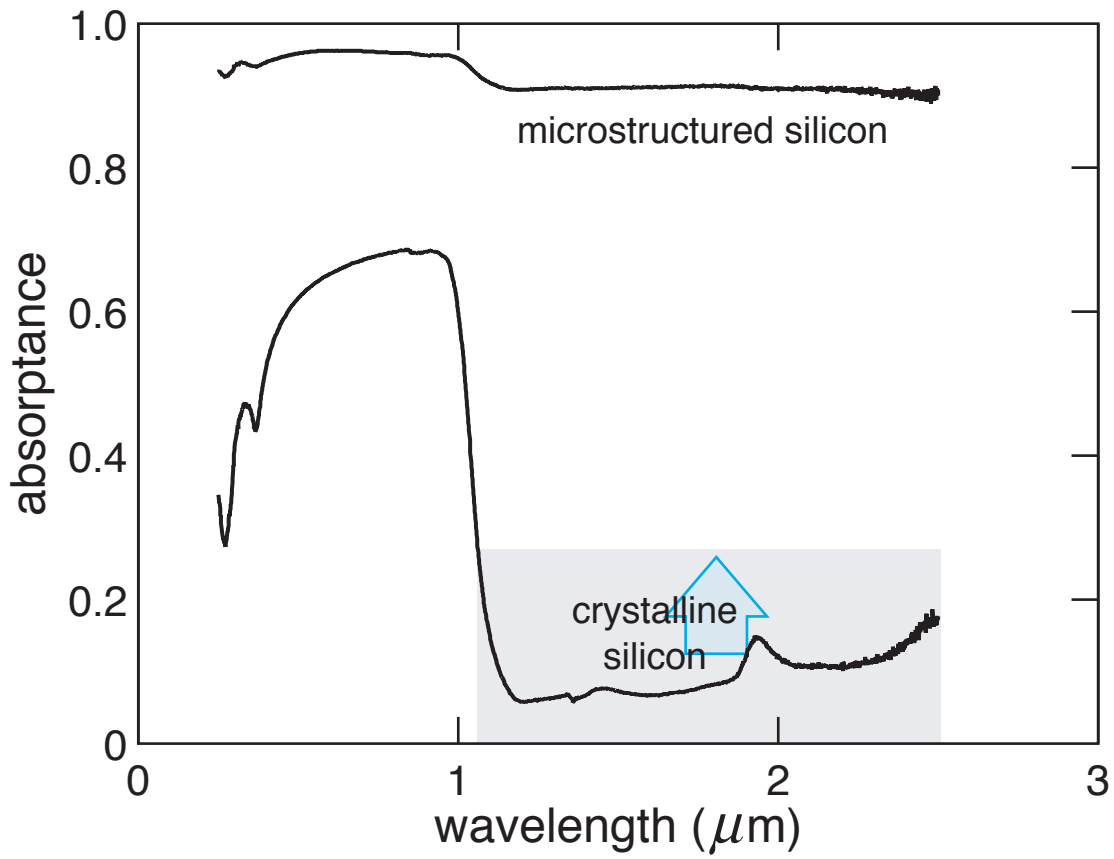
Optical properties

multiple reflections enhance absorption



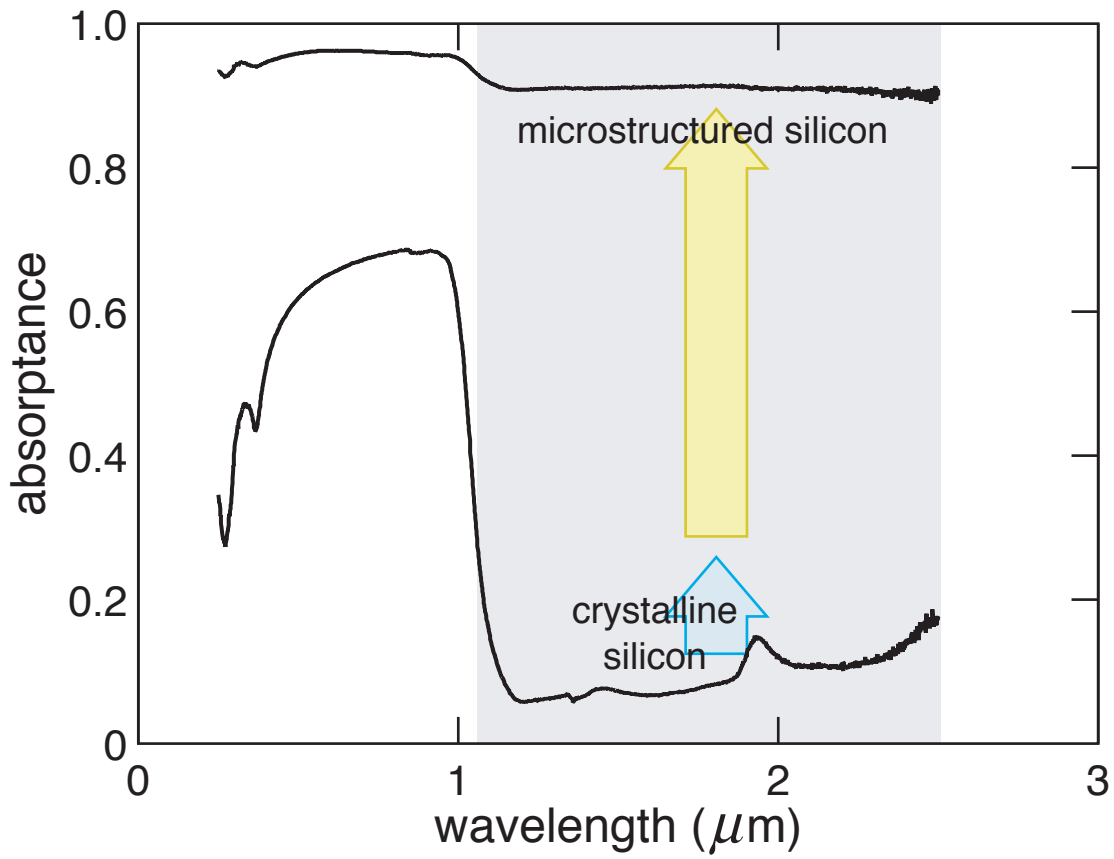
Optical properties

multiple reflections enhance absorption



Optical properties

electronic band structure changes



Optical properties

- enhanced absorption in visible
- near-unity absorption in infrared
- modified electronic band structure

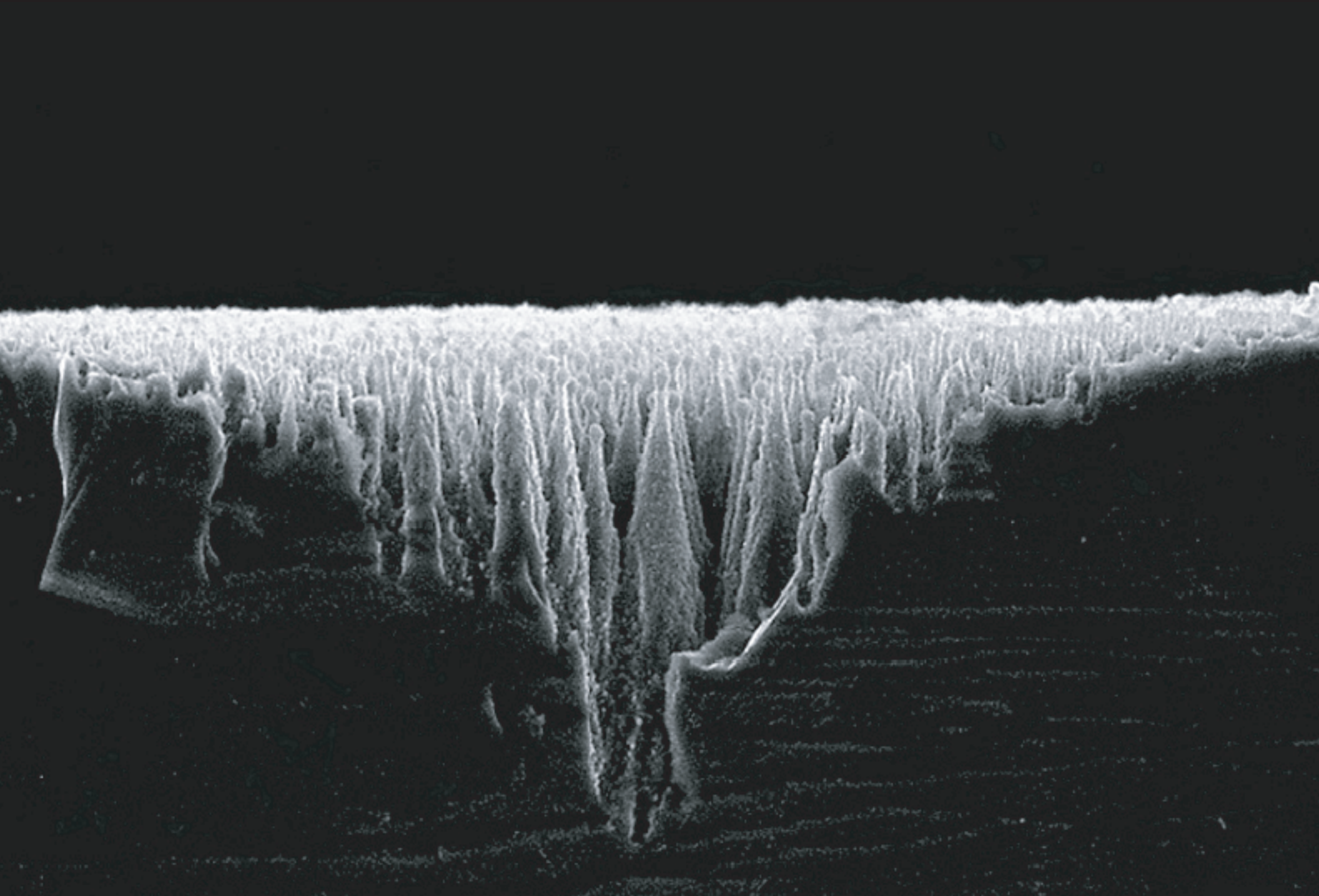
Outline

- optical properties
- **structural and chemical analysis**
- photodetectors
  - the *p-n* junction
  - femtosecond-laser microstructured silicon photodiodes
- outlook

Structural and chemical analysis

Band structure changes: defects and/or impurities.

Structural and chemical analysis



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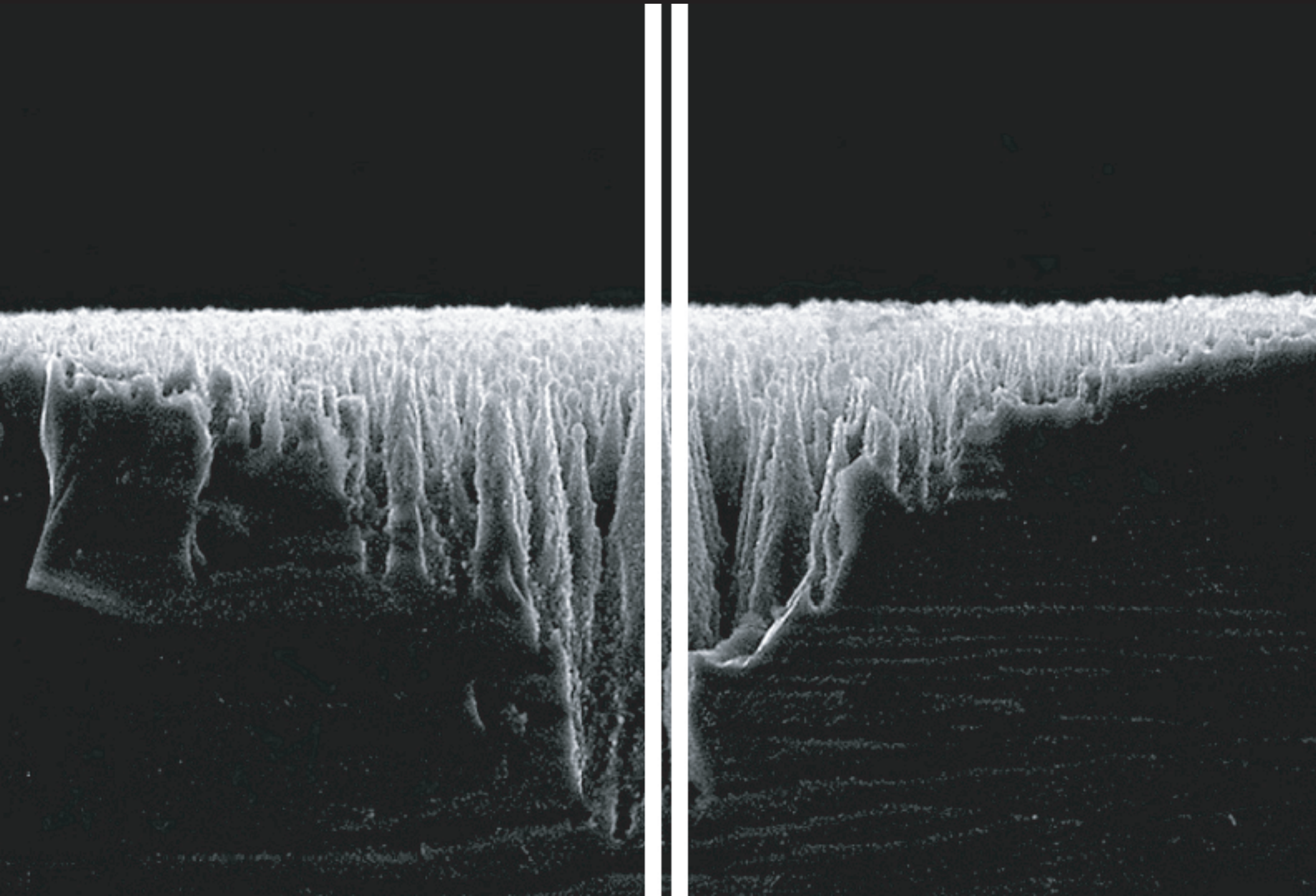
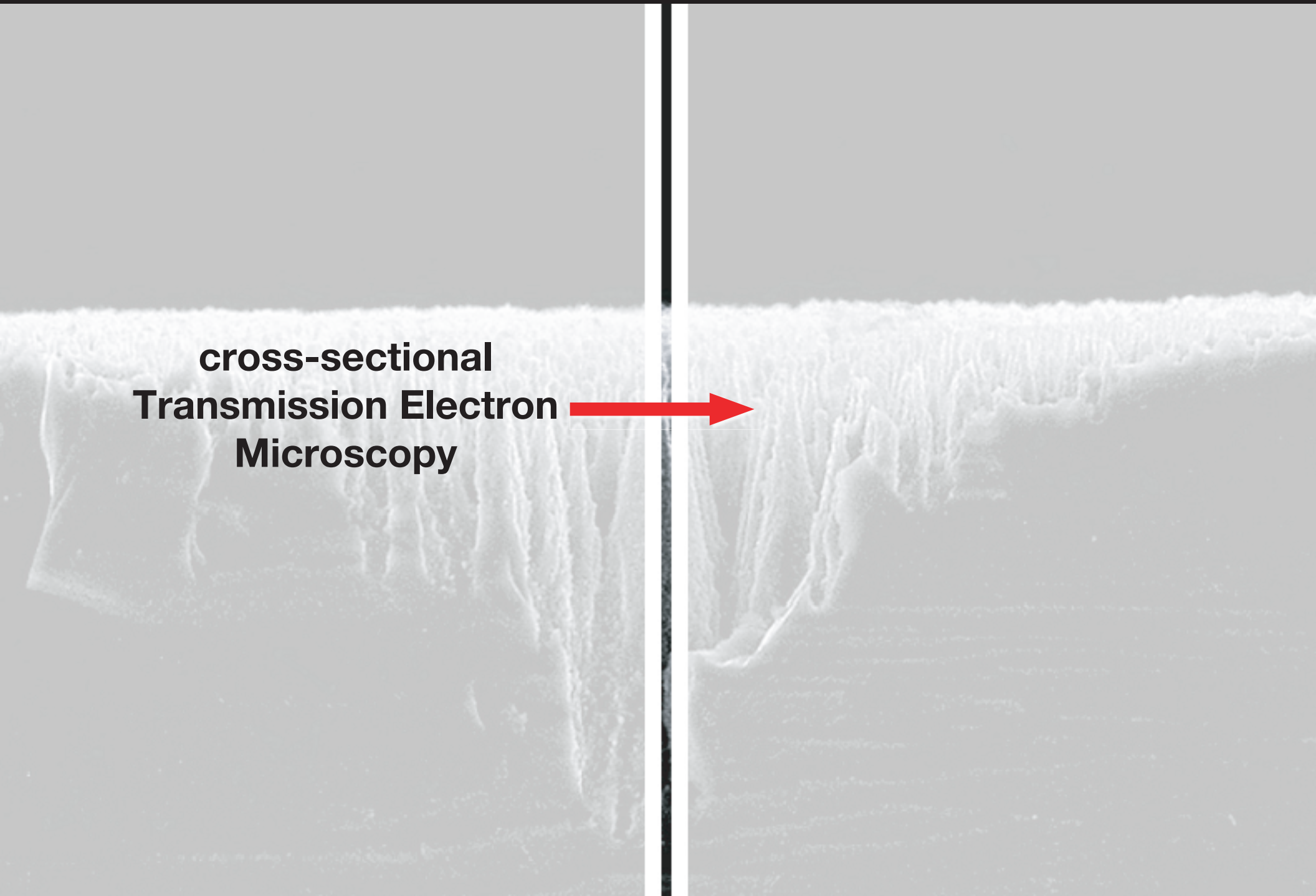
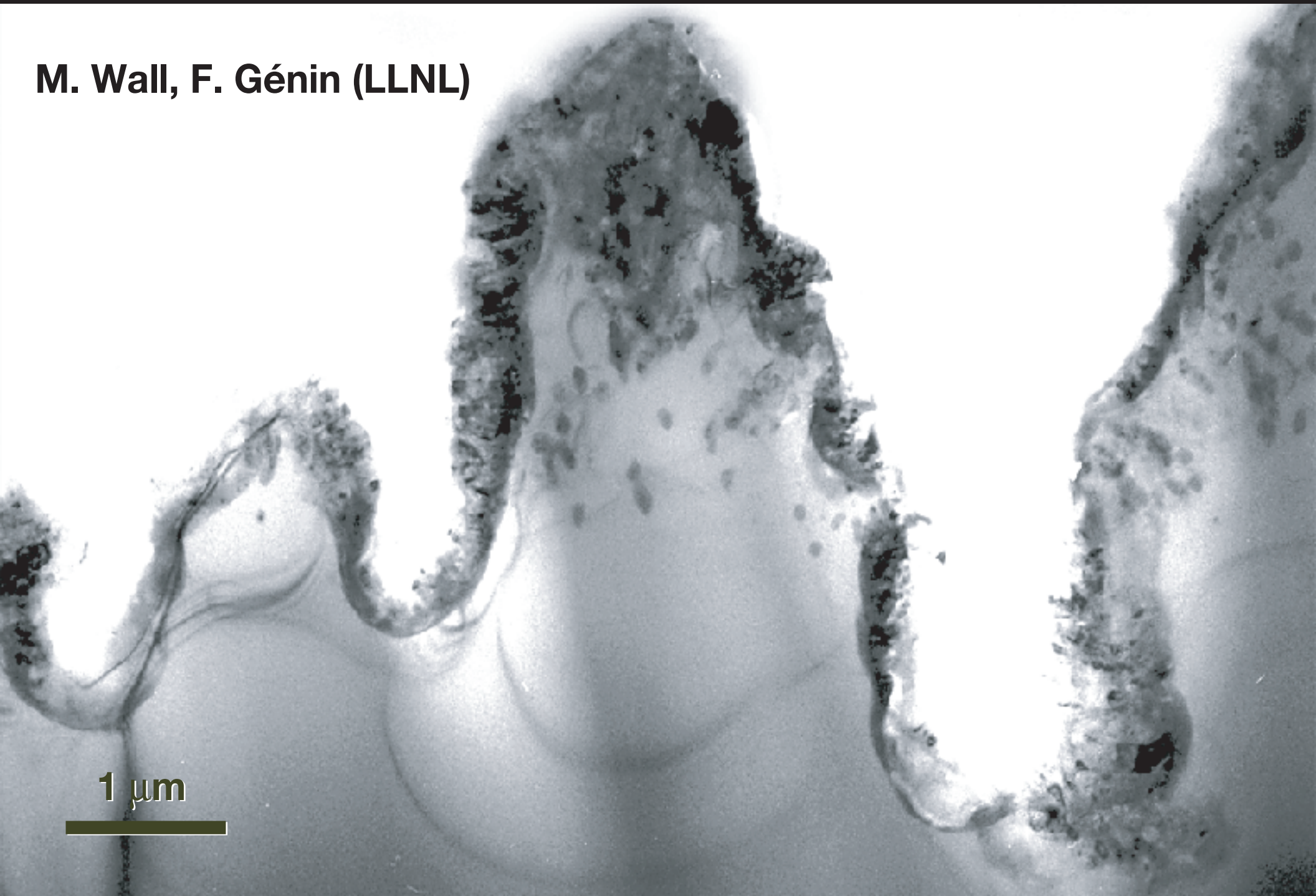


Structural and chemical analysis



Structural and chemical analysis

M. Wall, F. Génin (LLNL)



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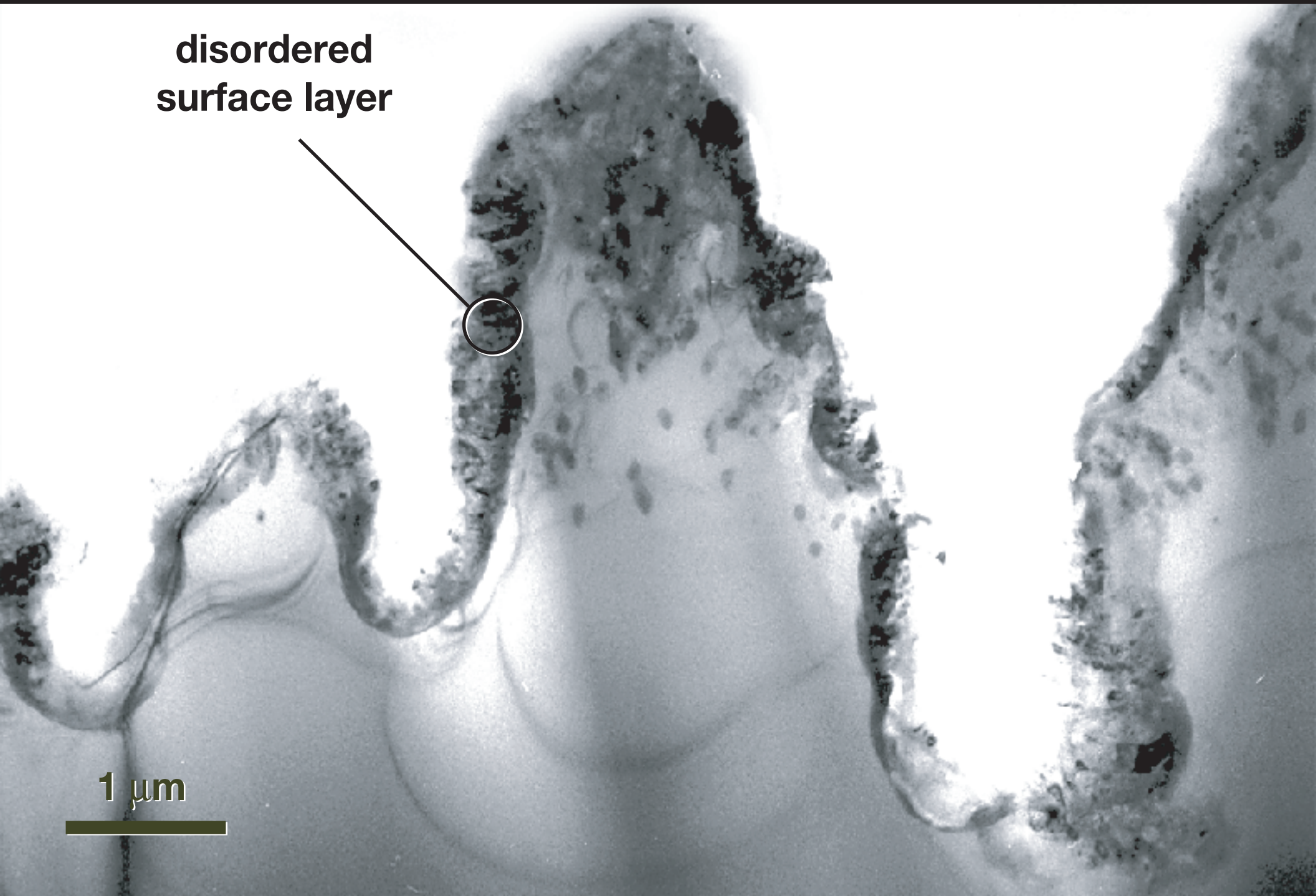

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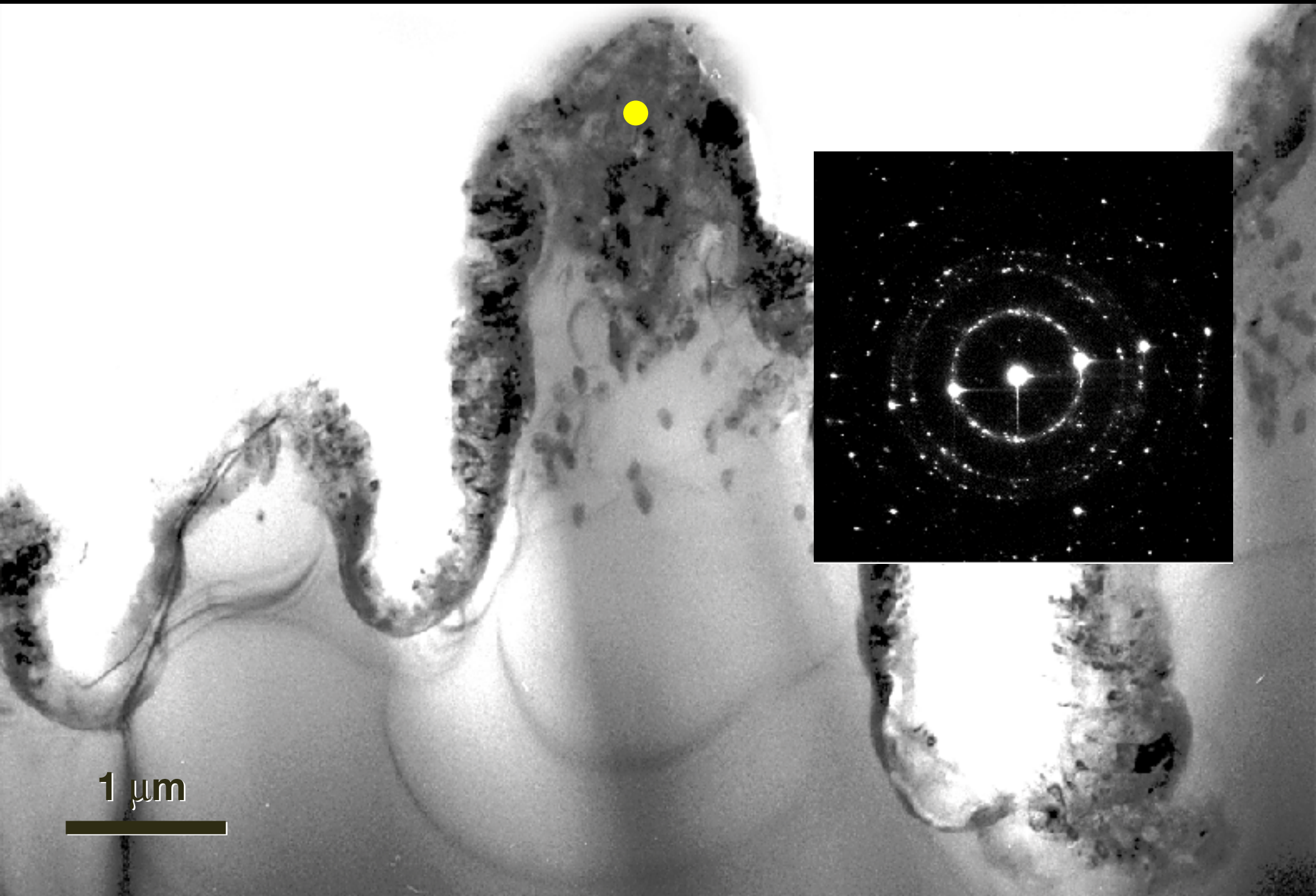

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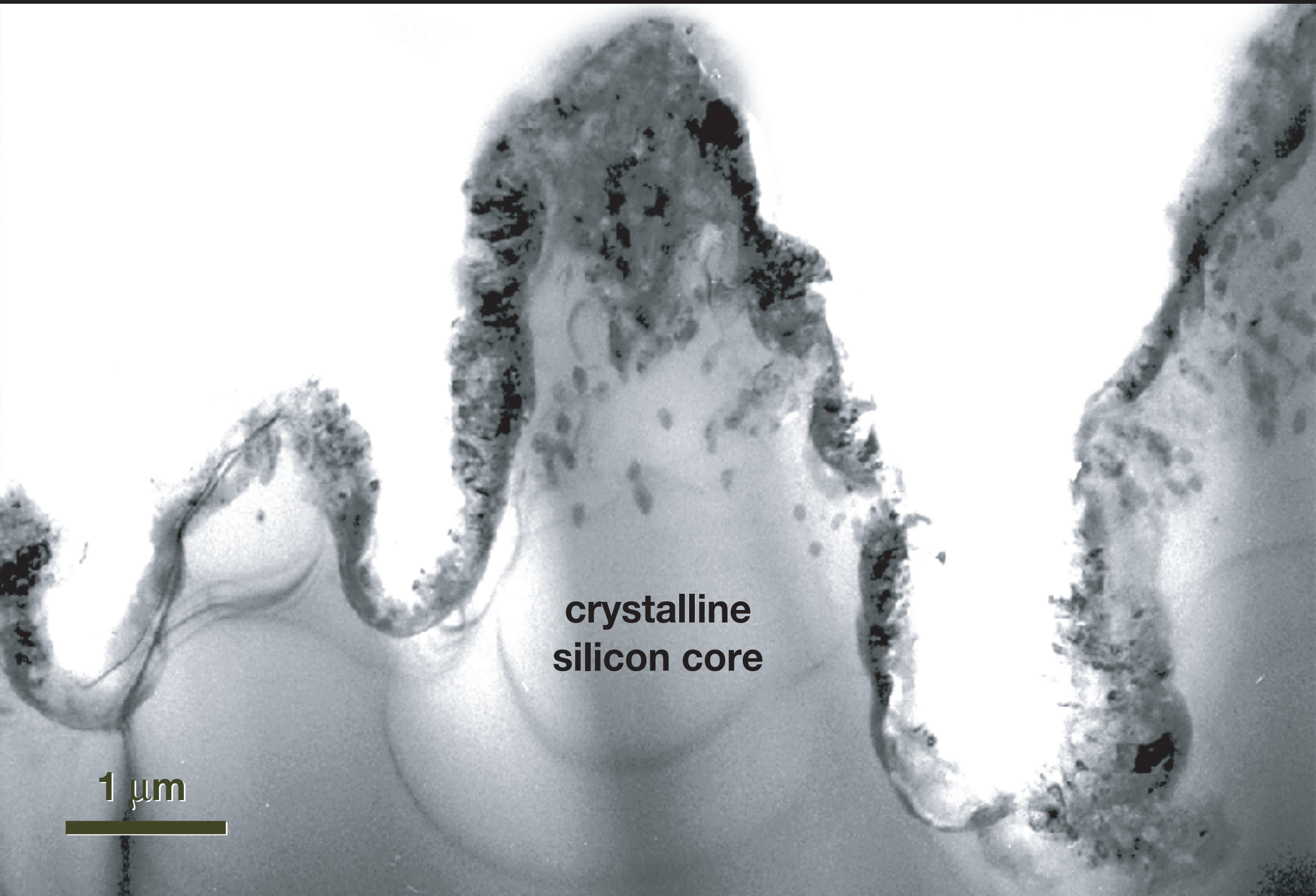

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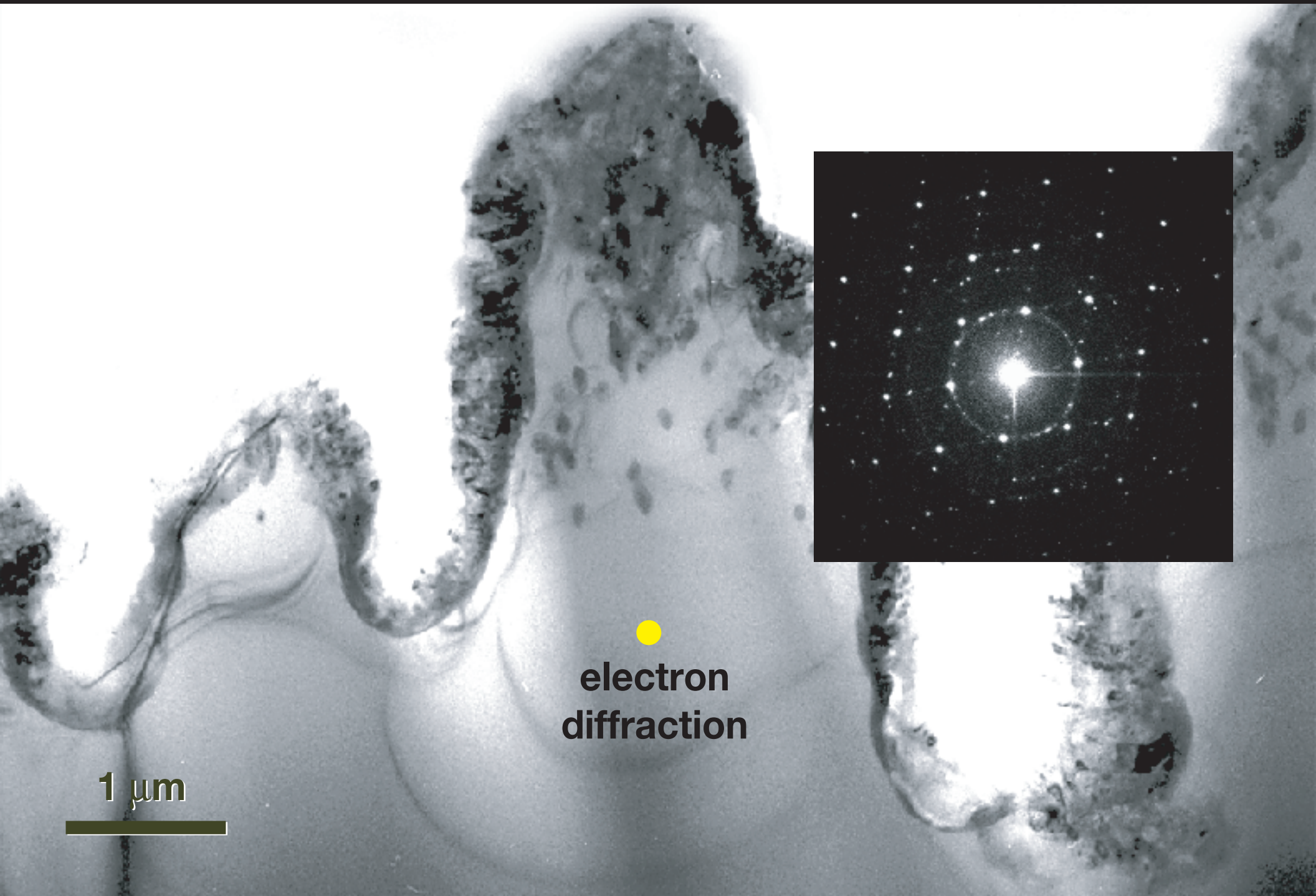
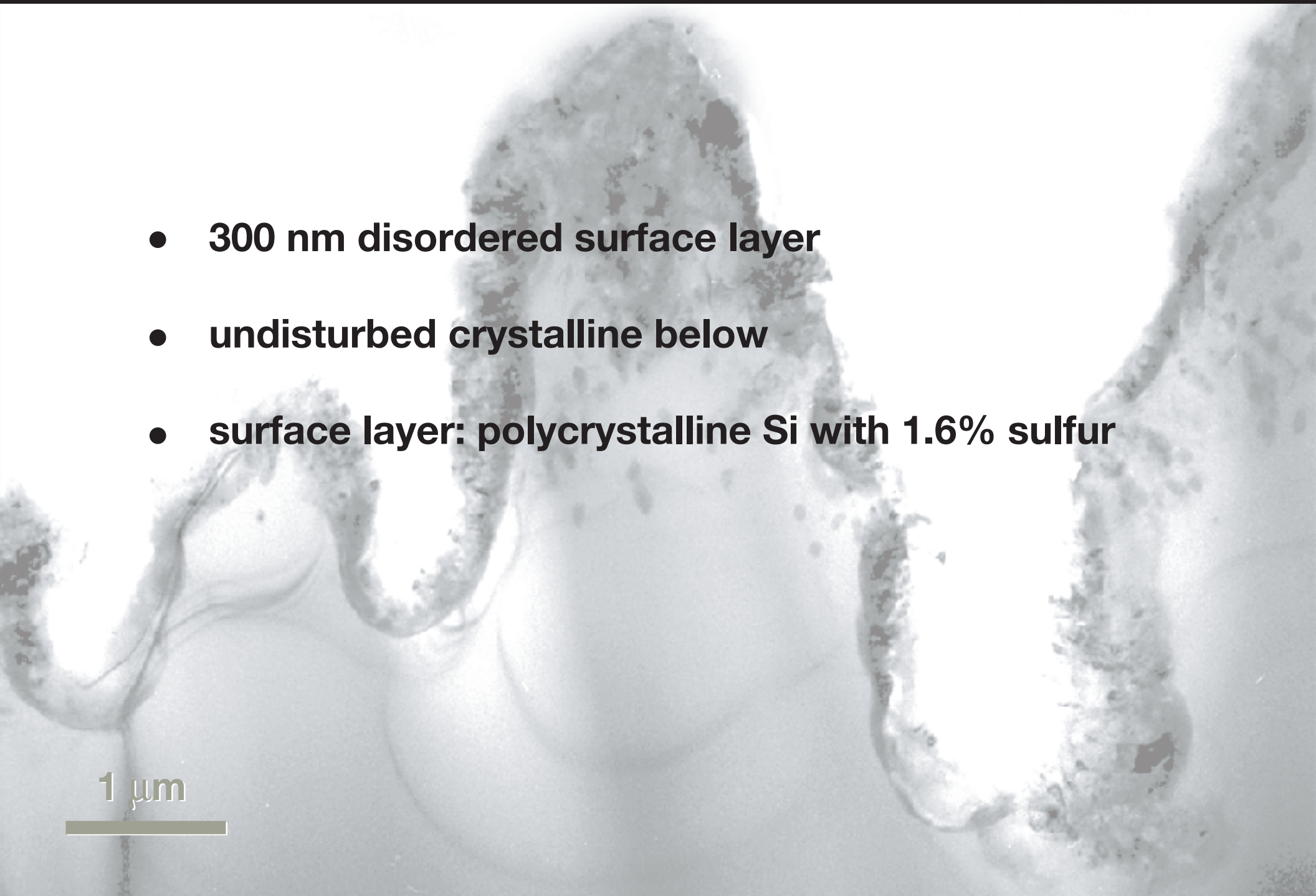


Structural and chemical analysis

- 300 nm disordered surface layer
- undisturbed crystalline below
- surface layer: polycrystalline Si with 1.6% sulfur



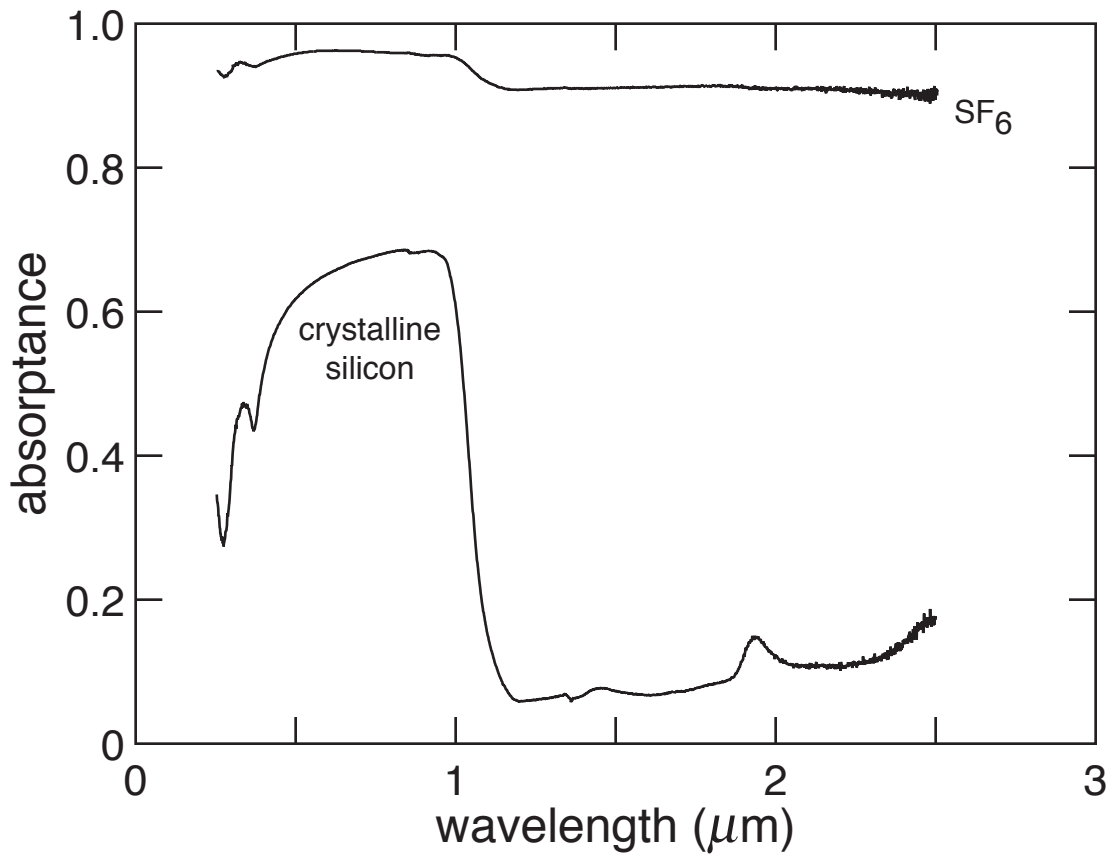
Structural and chemical analysis

Microstructure with different ambient gases:

- **gas species incorporated into surface**
- **sulfur critical for below-band gap absorption**

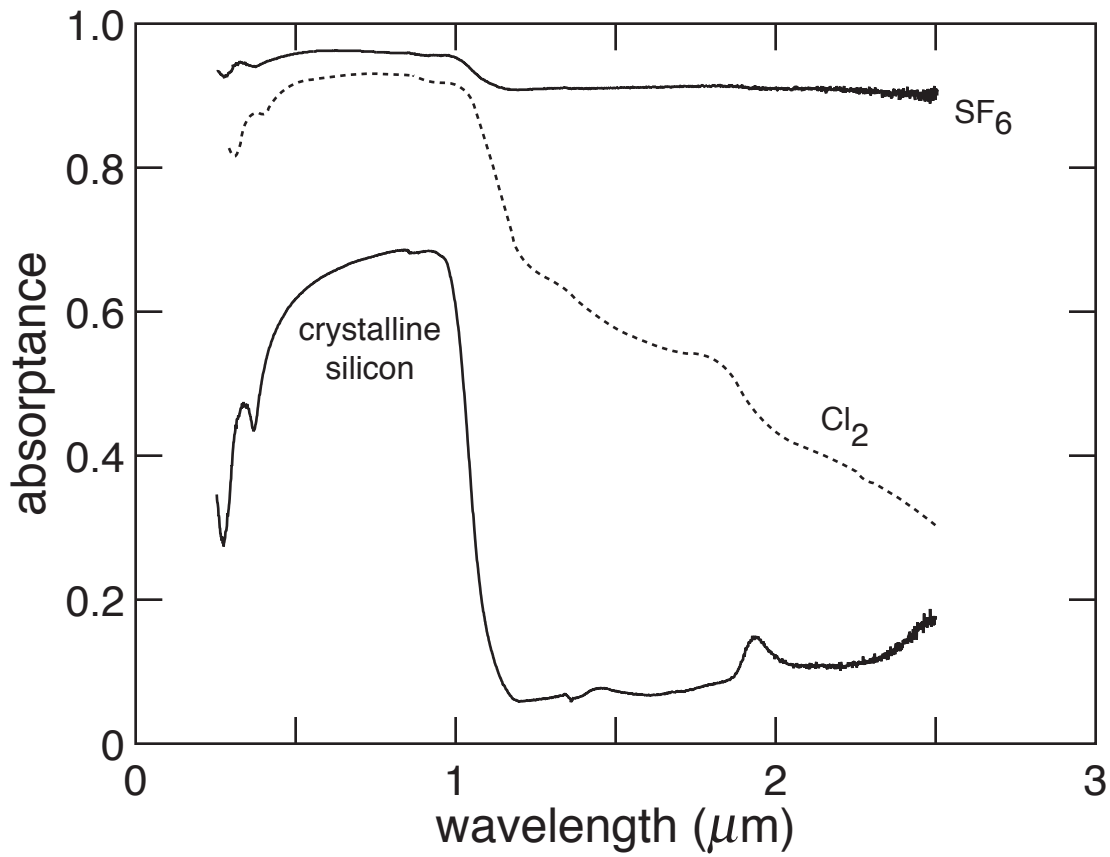
Structural and chemical analysis

microstructure with different gases



Structural and chemical analysis

microstructure with different gases



Structural and chemical analysis

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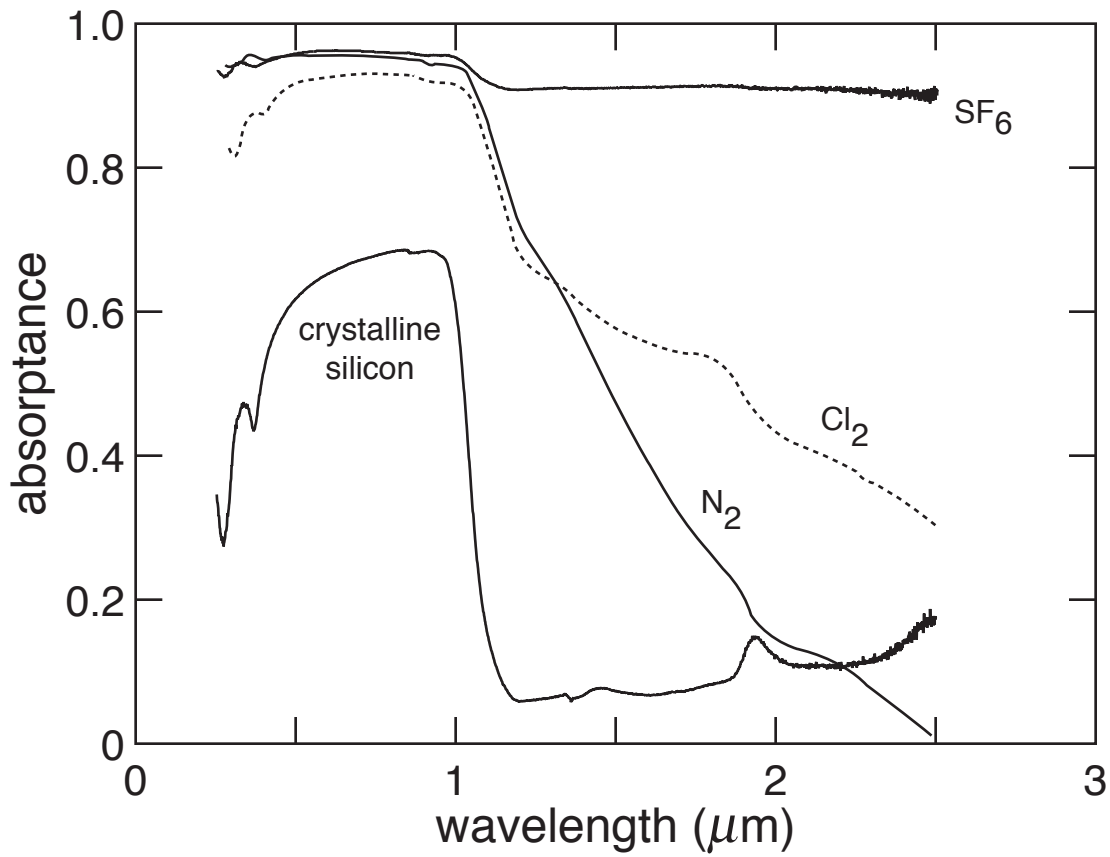
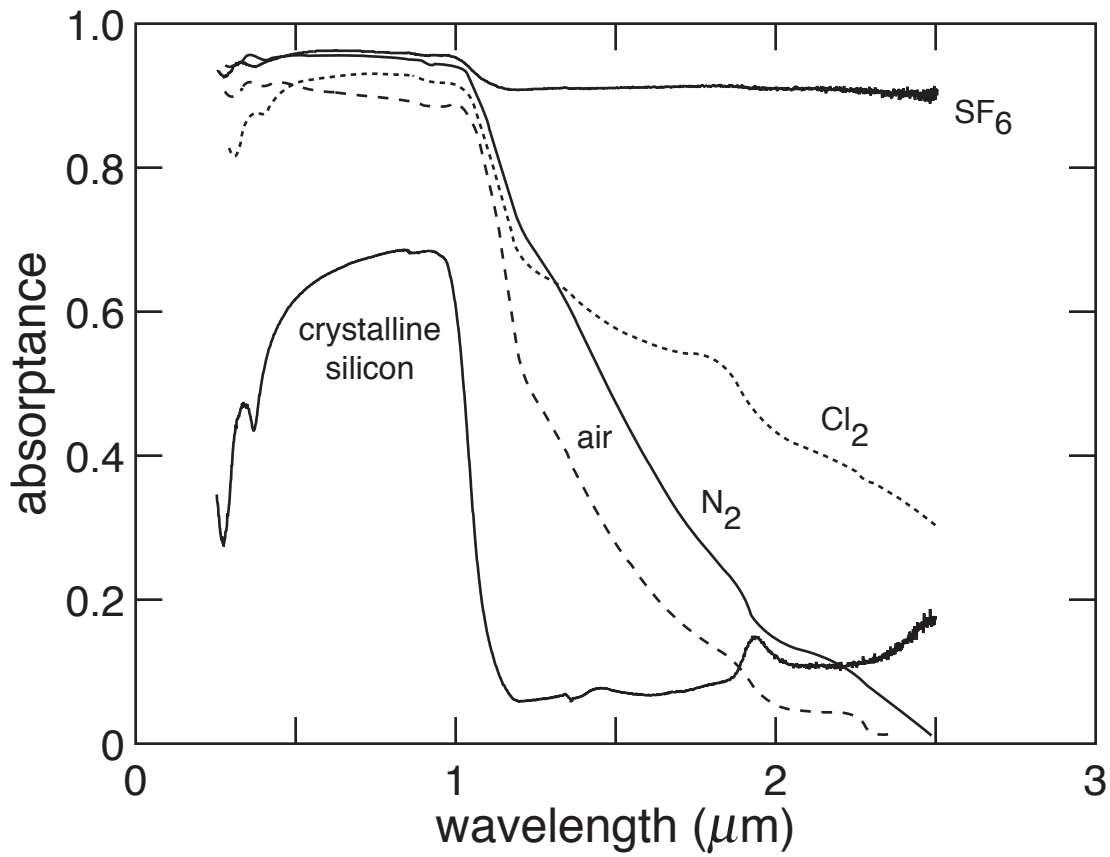


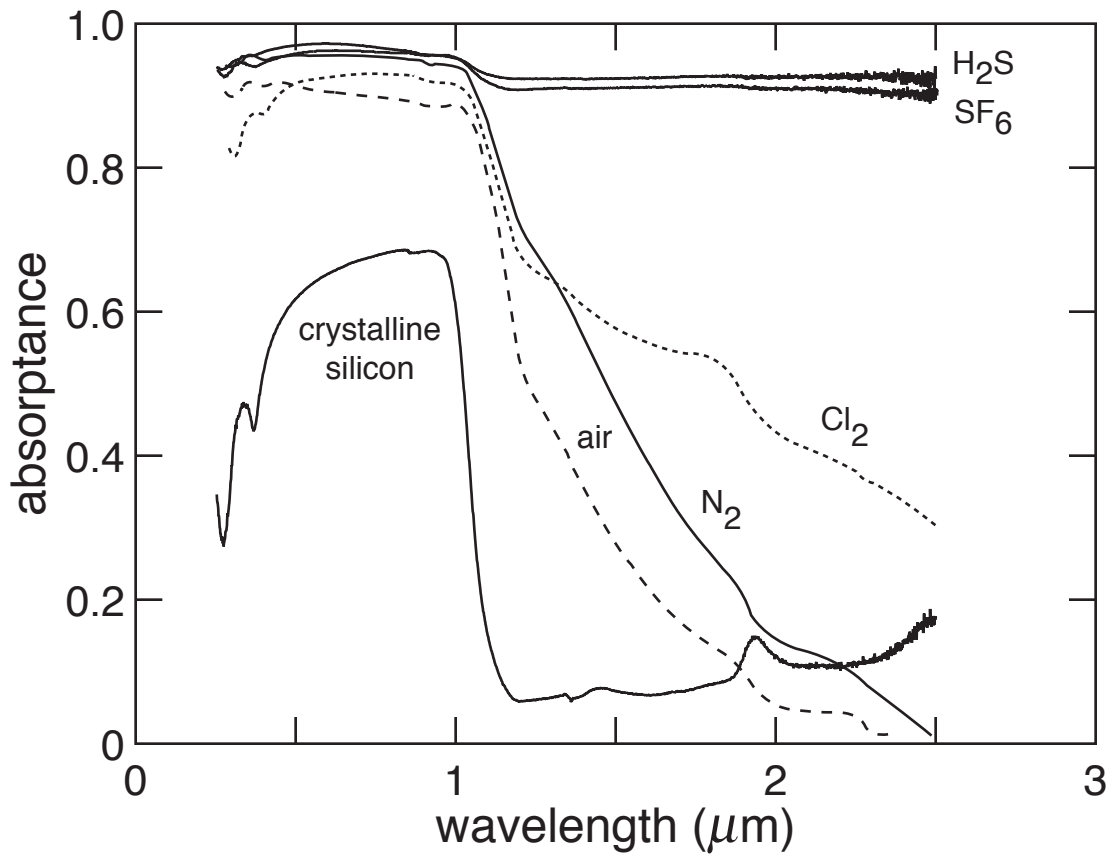
Structural and chemical analysis

microstructure with different gases



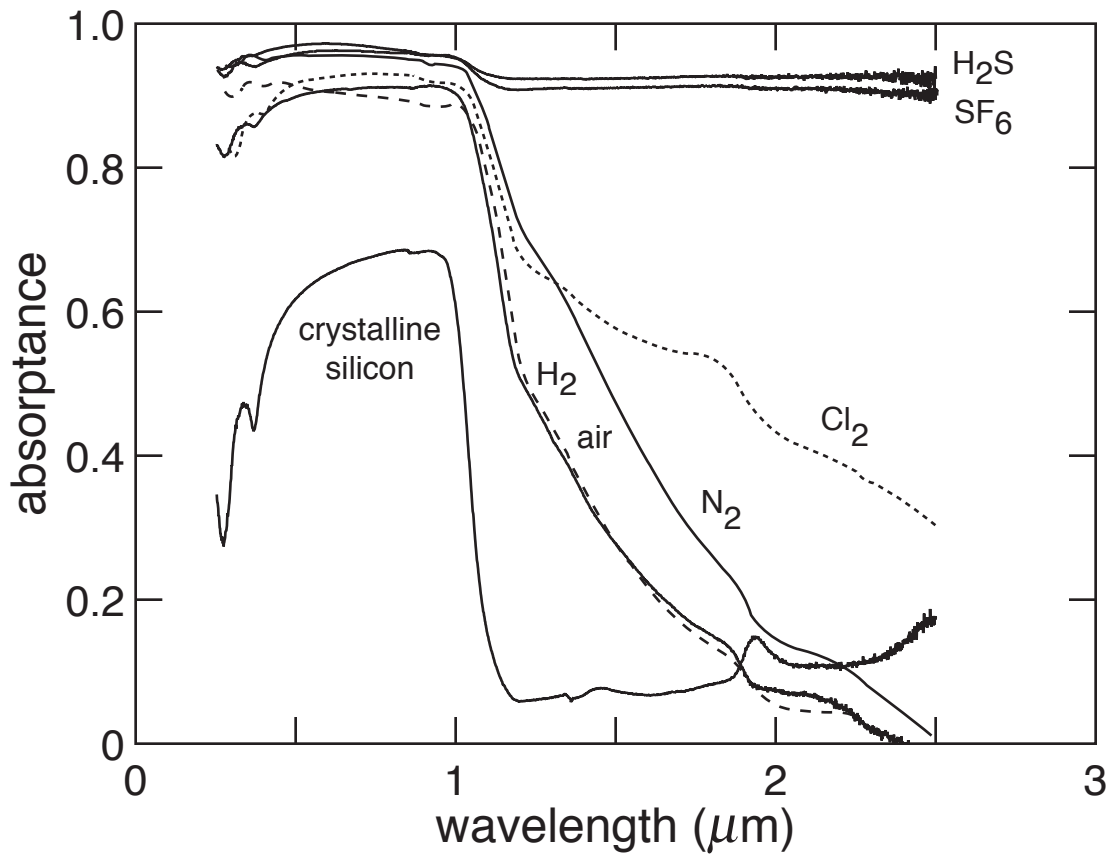
Structural and chemical analysis

microstructure with different gases



Structural and chemical analysis

microstructure with different gases

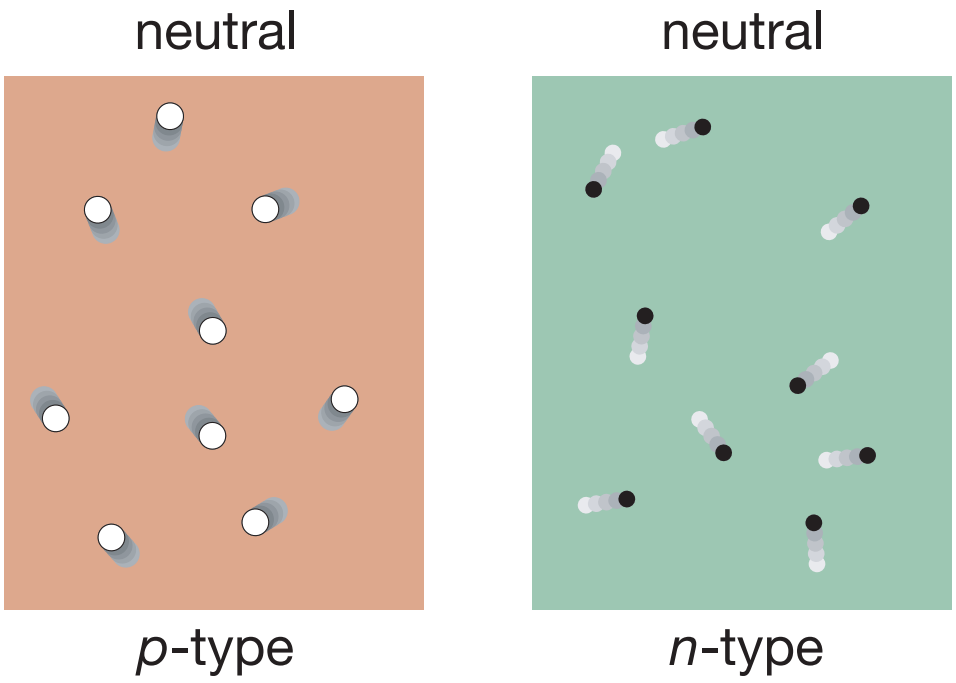


Outline

- optical properties
- structural and chemical analysis
- **photodetectors**
  - **the *p-n* junction**
  - femtosecond-laser microstructured silicon photodiodes
- outlook

Photodetectors

join acceptor and donor type Si...



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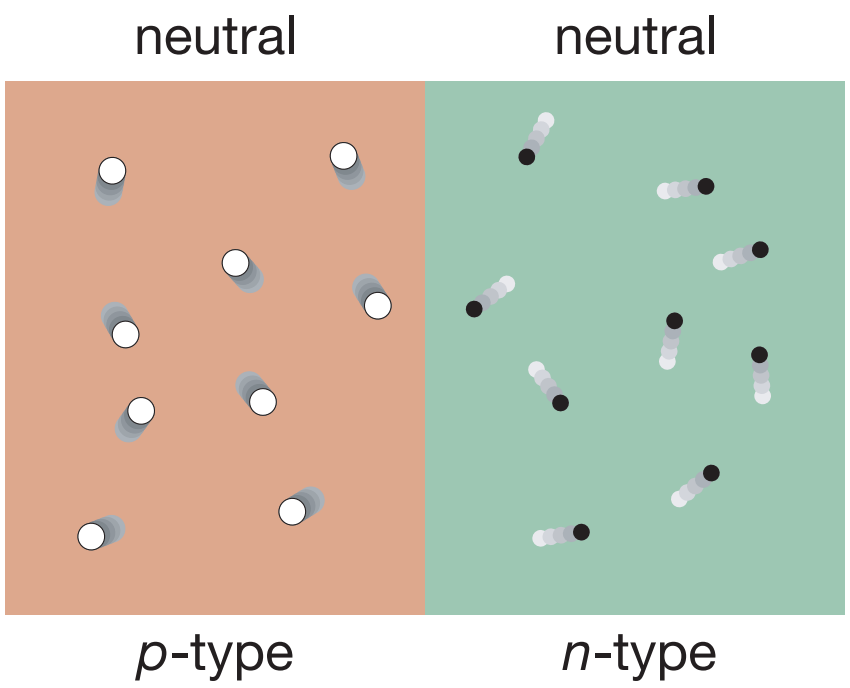
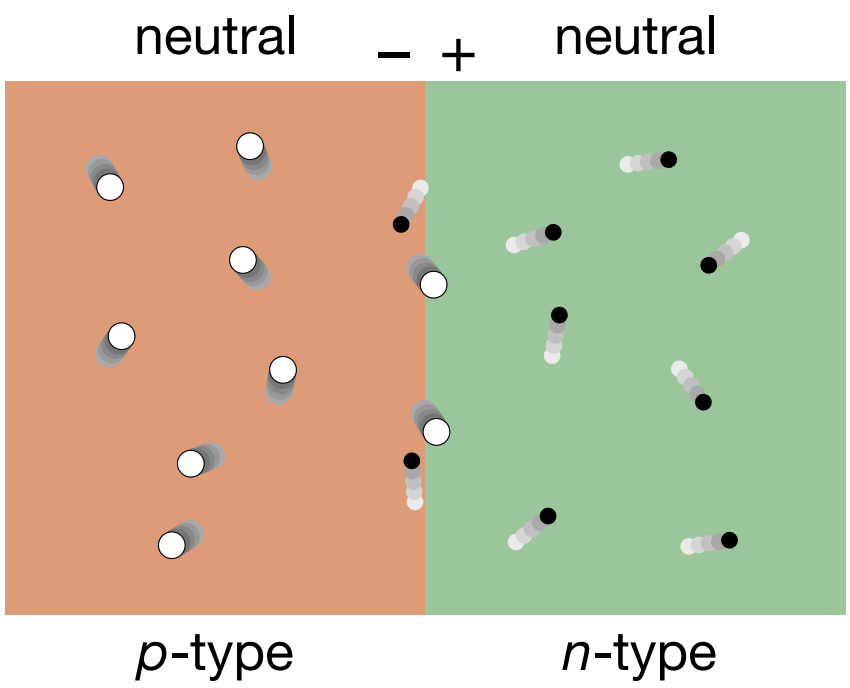


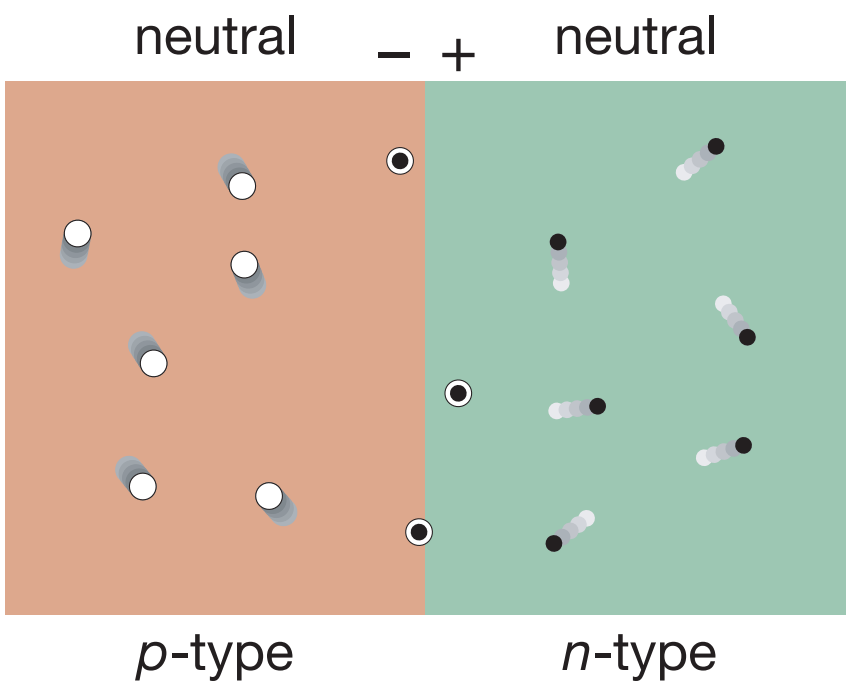
Photodetectors

electrons and holes diffuse across junction...



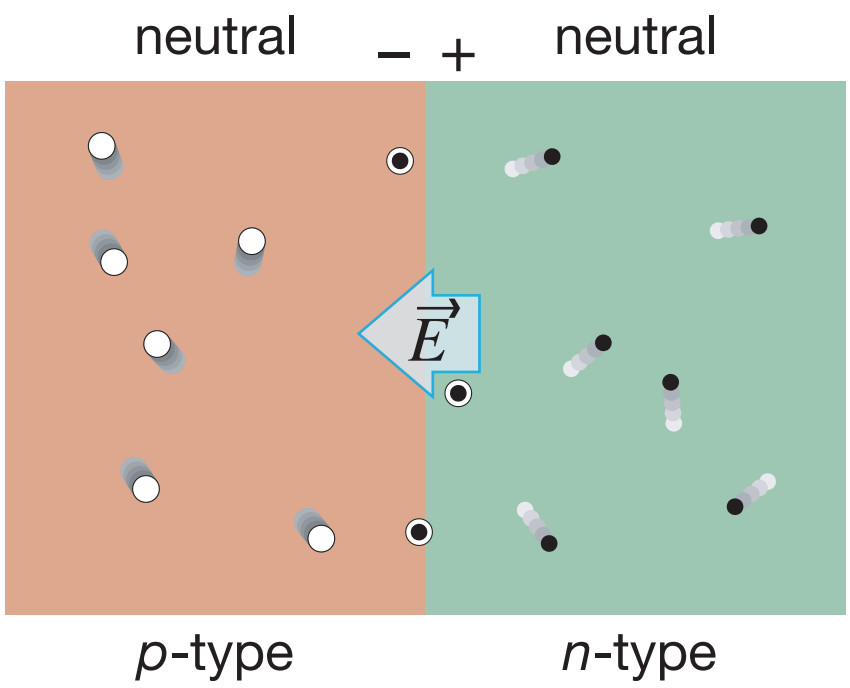
Photodetectors

...and get 'trapped' after they combine



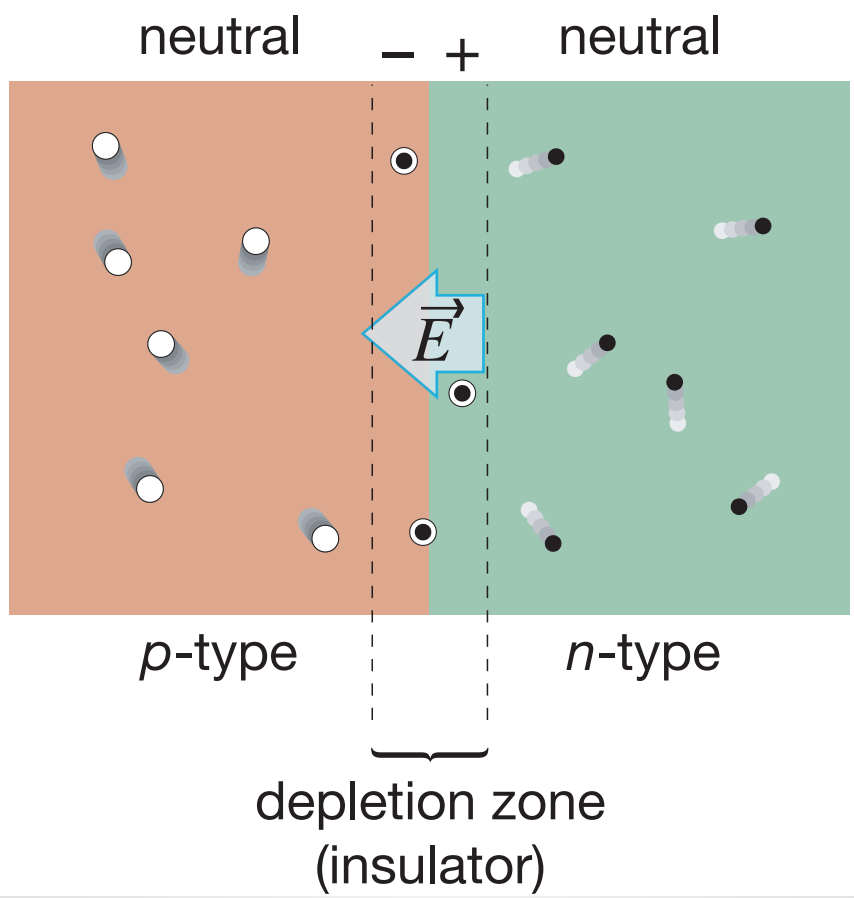
Photodetectors

build-up of charge leads to electric field that stops diffusion



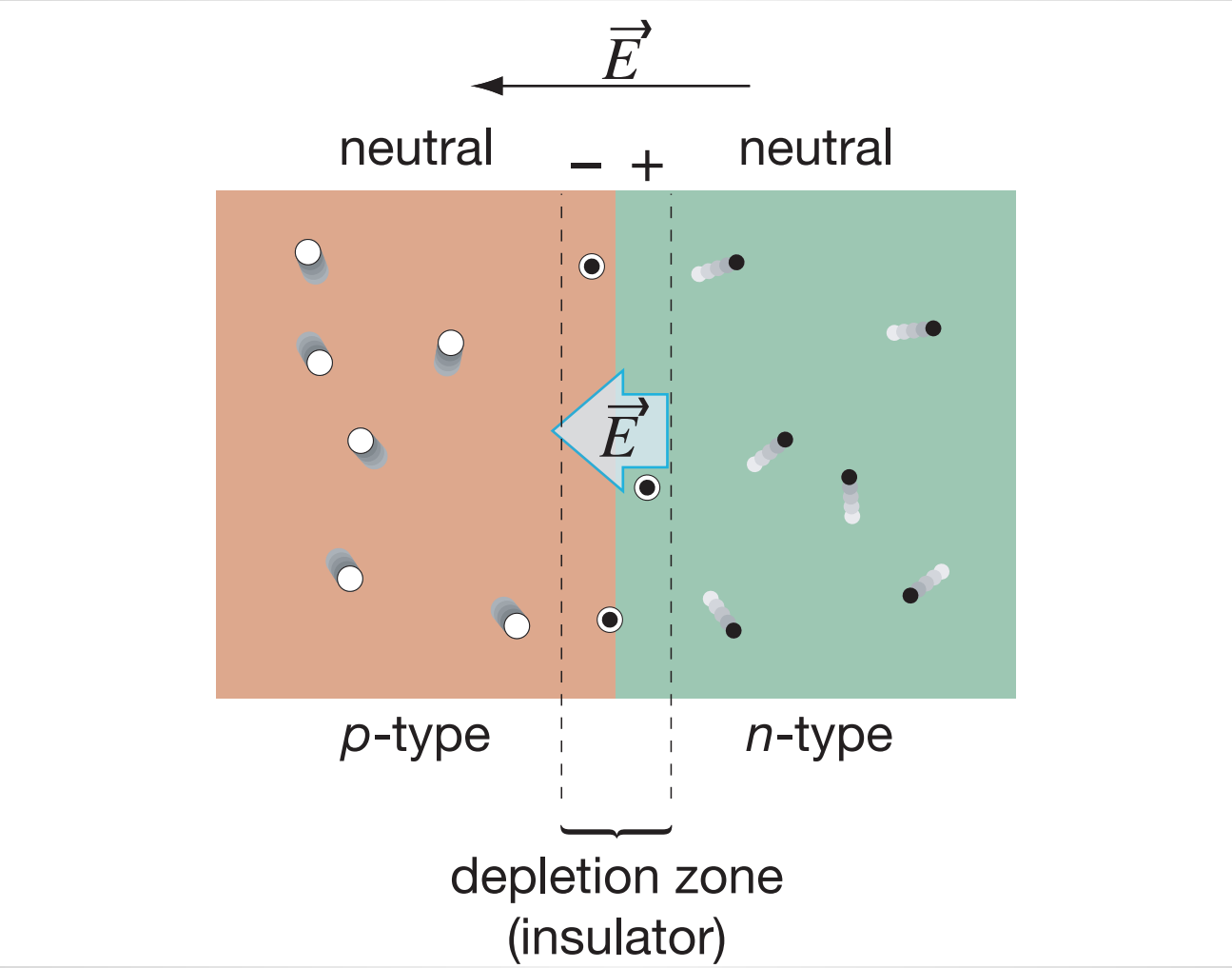
Photodetectors

non-conducting layer at junction



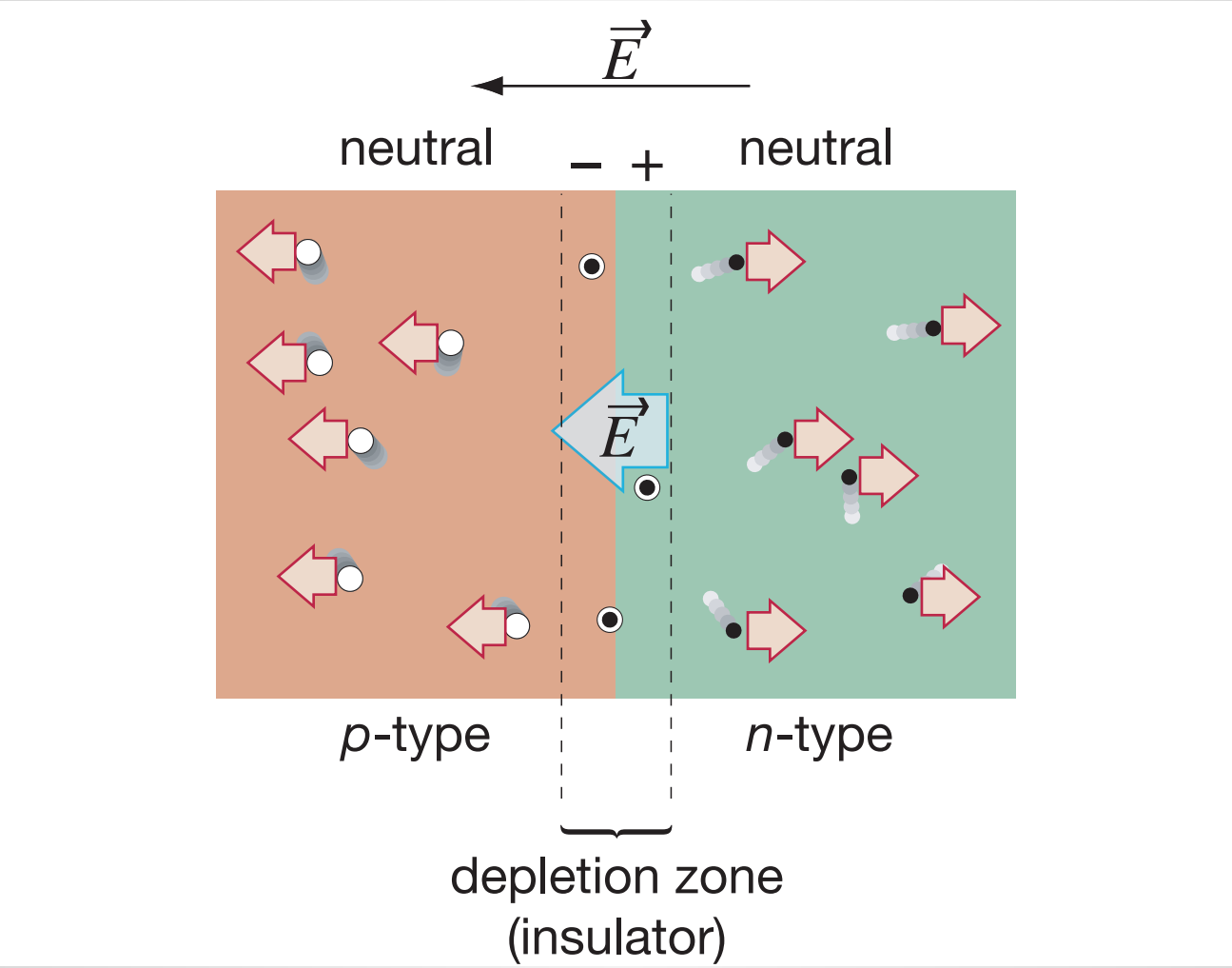
Photodetectors

apply electric field...



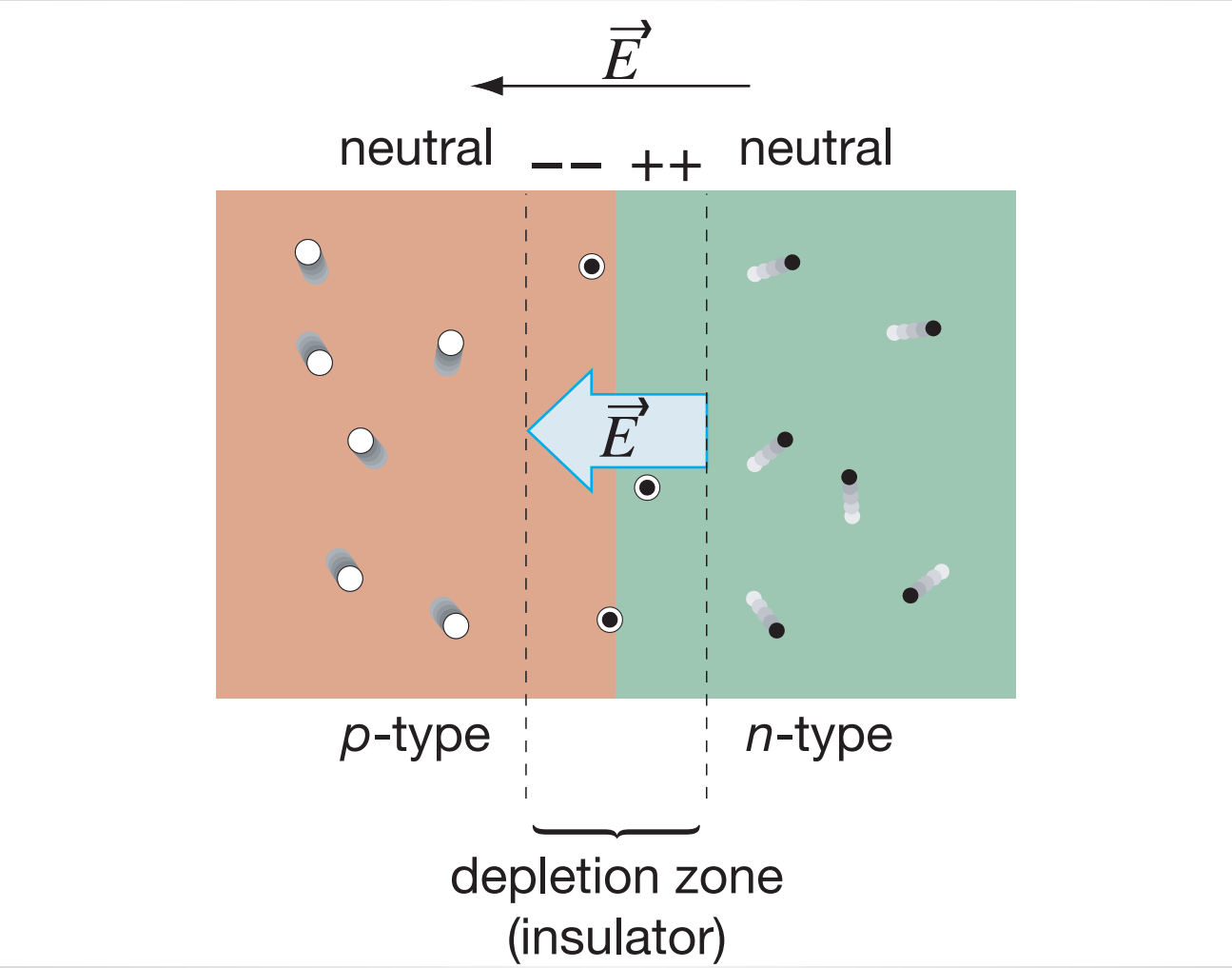
Photodetectors

...holes pushed left, electrons to right...



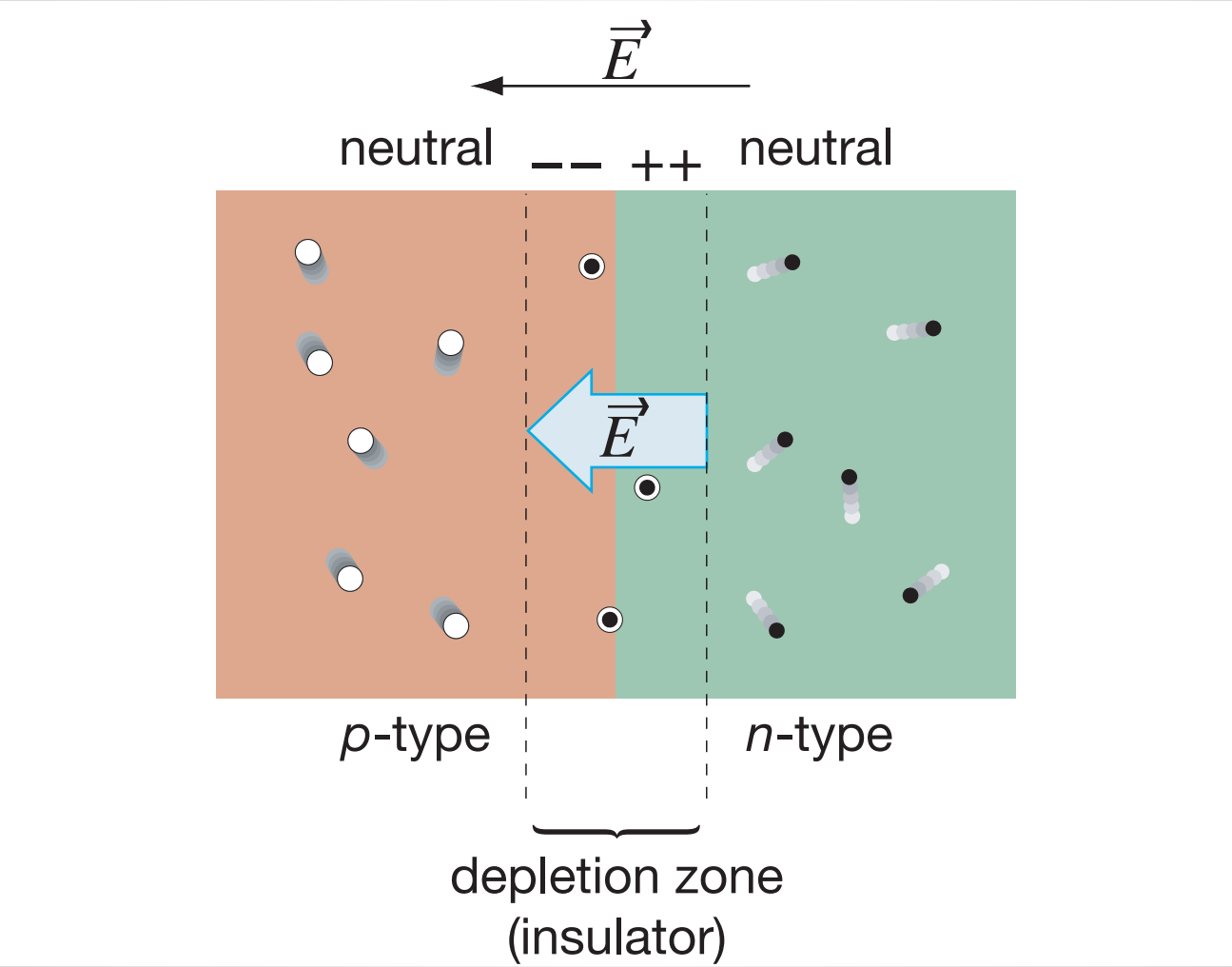
Photodetectors

and so depletion zone expands



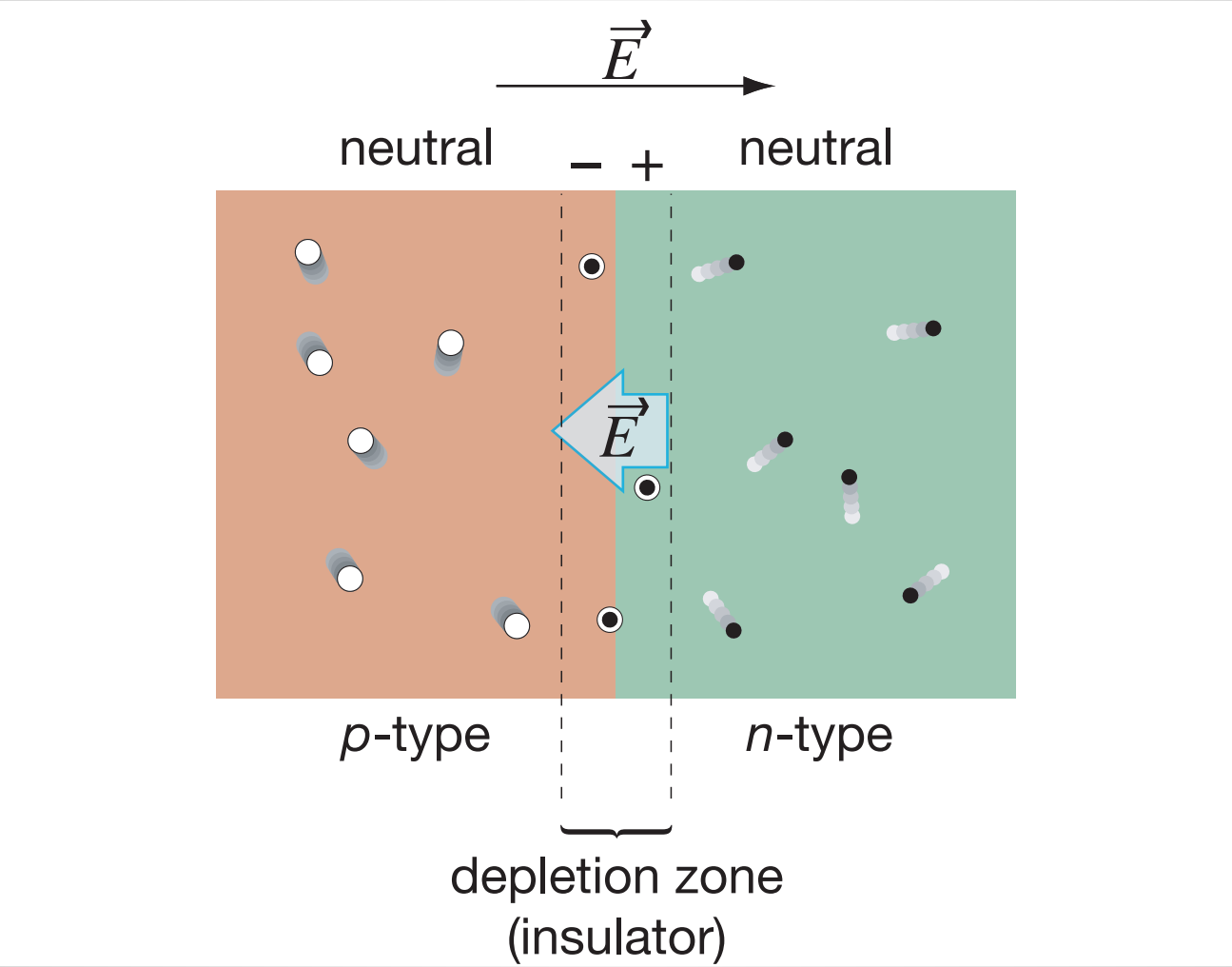
Photodetectors

NO conduction



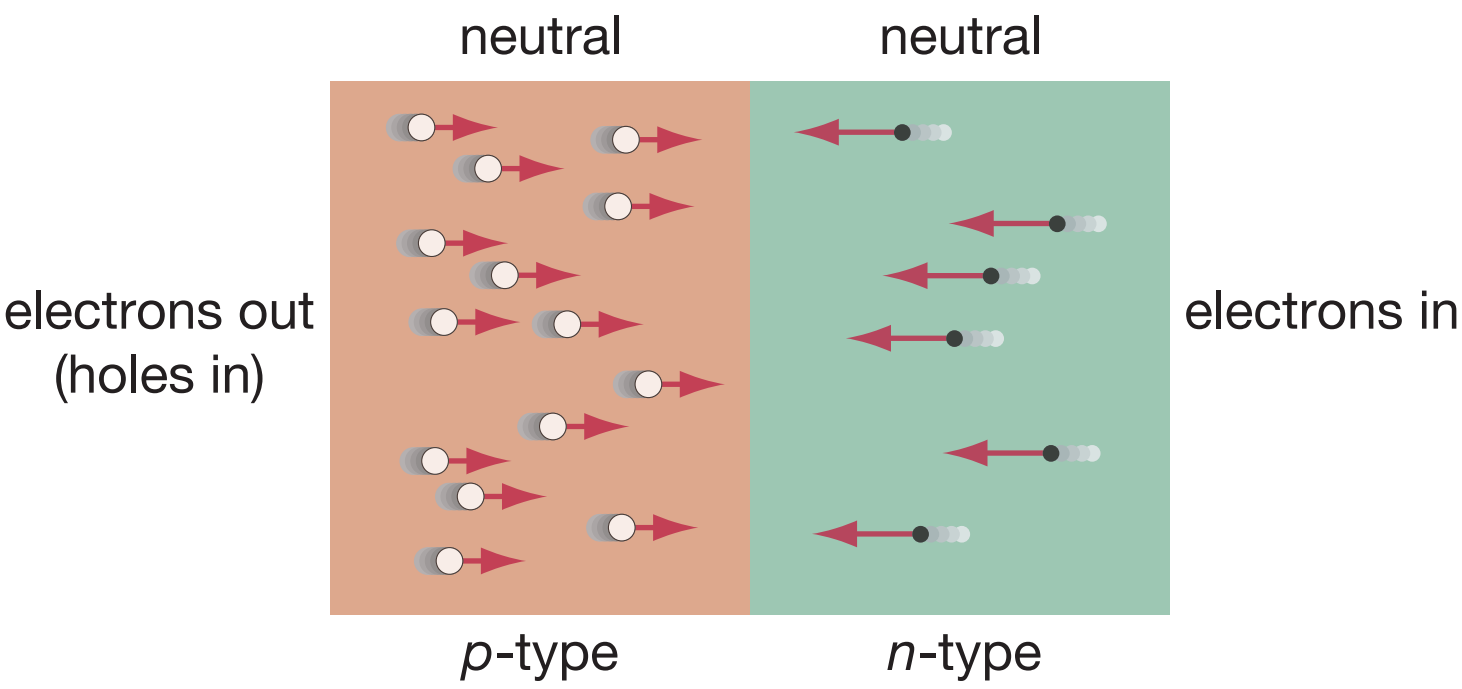
Photodetectors

reverse electric field...



Photodetectors

...depletion zone shrinks and current flows

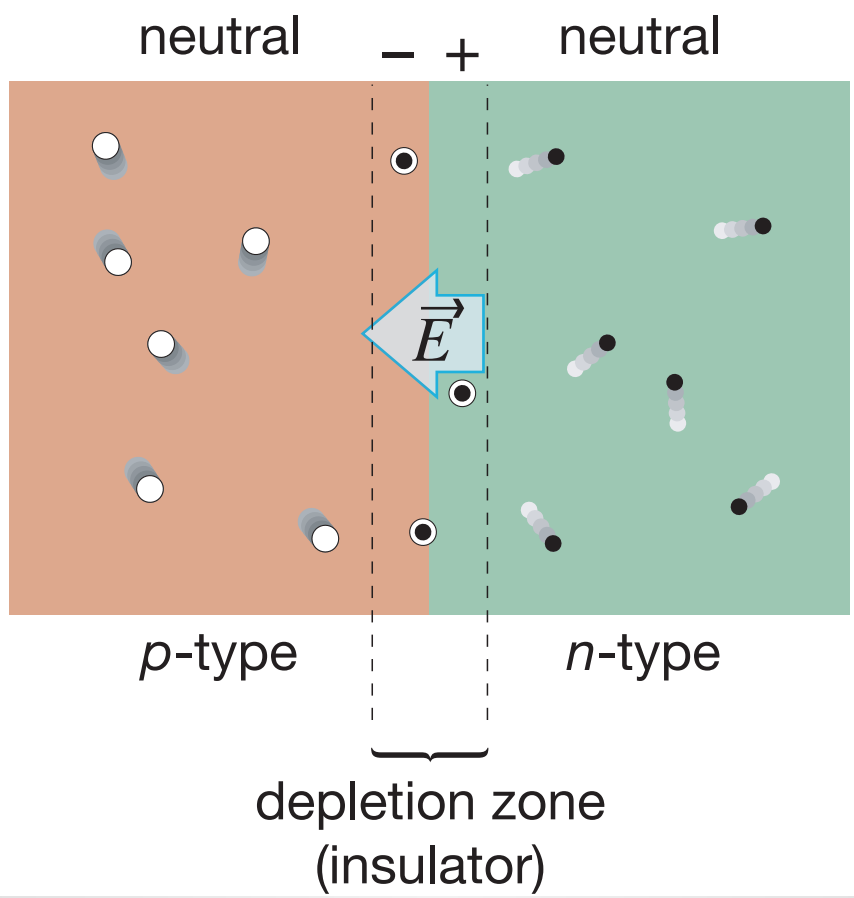


Photodetectors

so pn-junction like one-way valve for charge flow: a diode

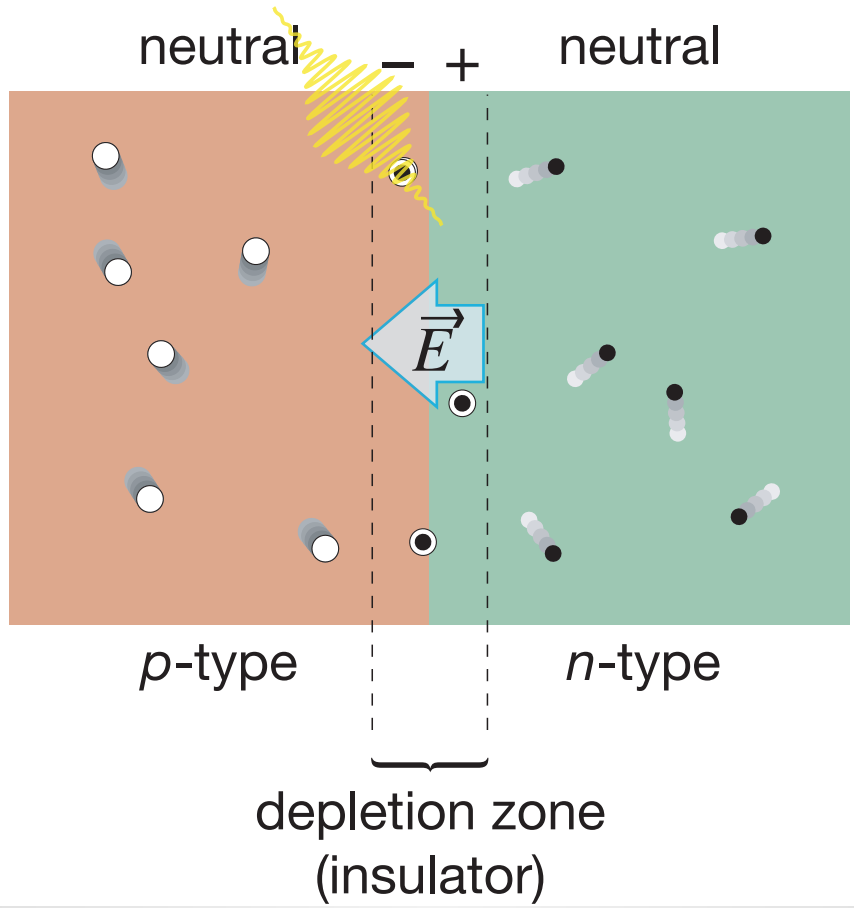
Photodetectors

depletion layer can convert light into electric energy



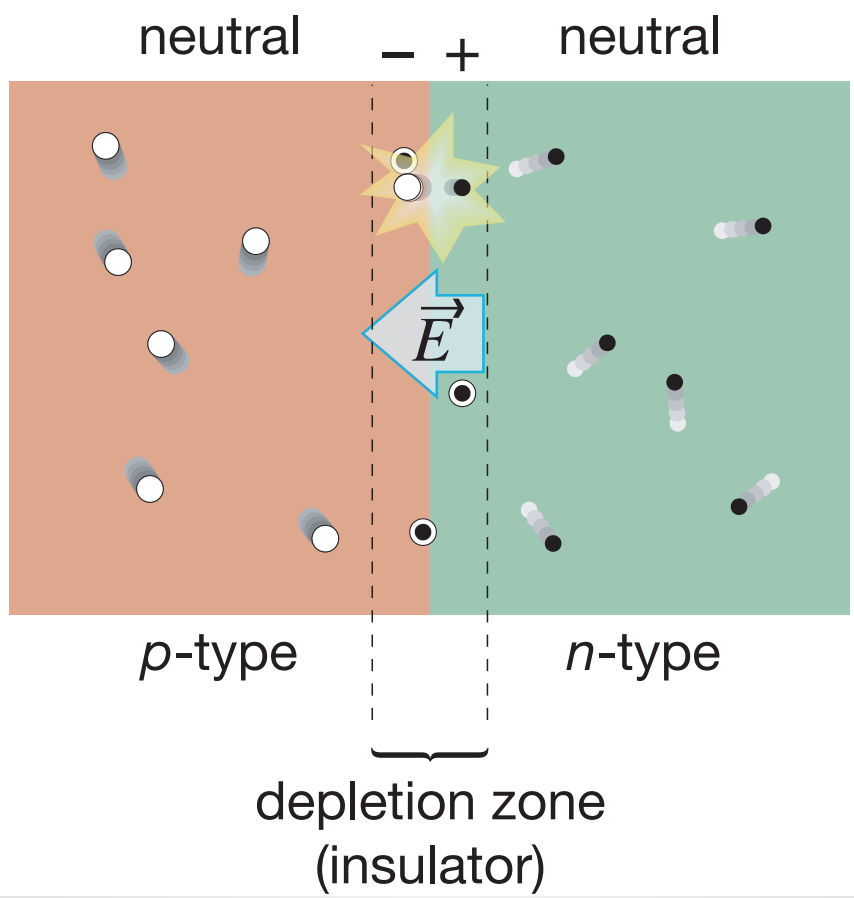
Photodetectors

incident photon knocks out electron...



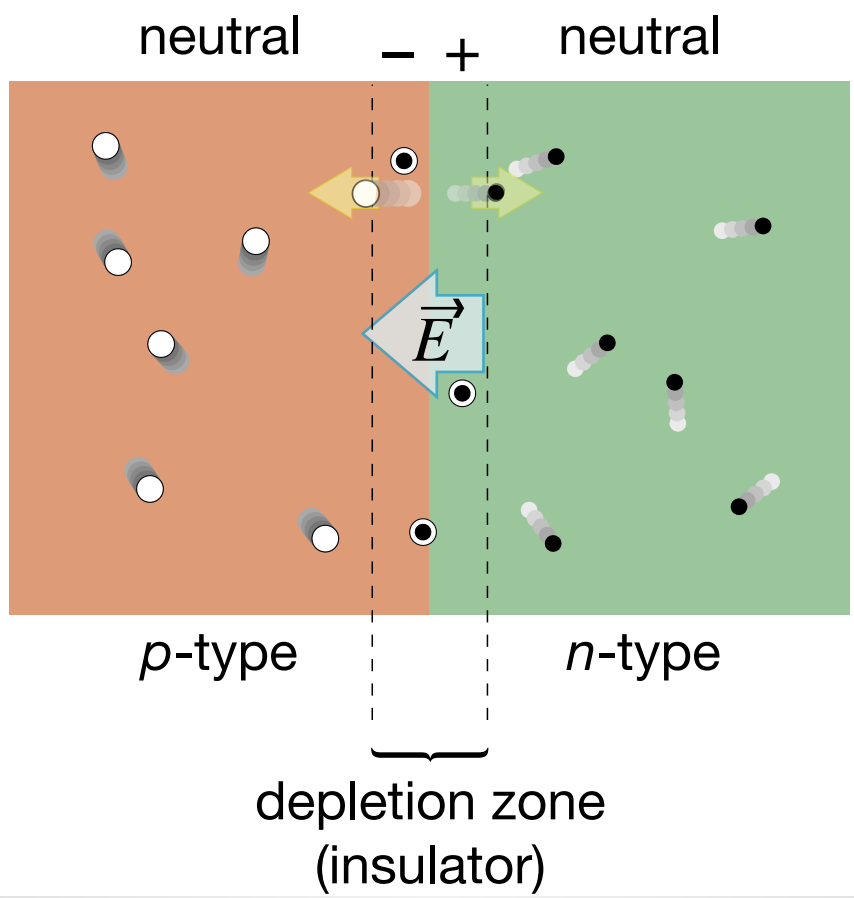
Photodetectors

...creating an electron-hole pair



Photodetectors

E-field separates eh-pair, causing current



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  - the *p-n* junction
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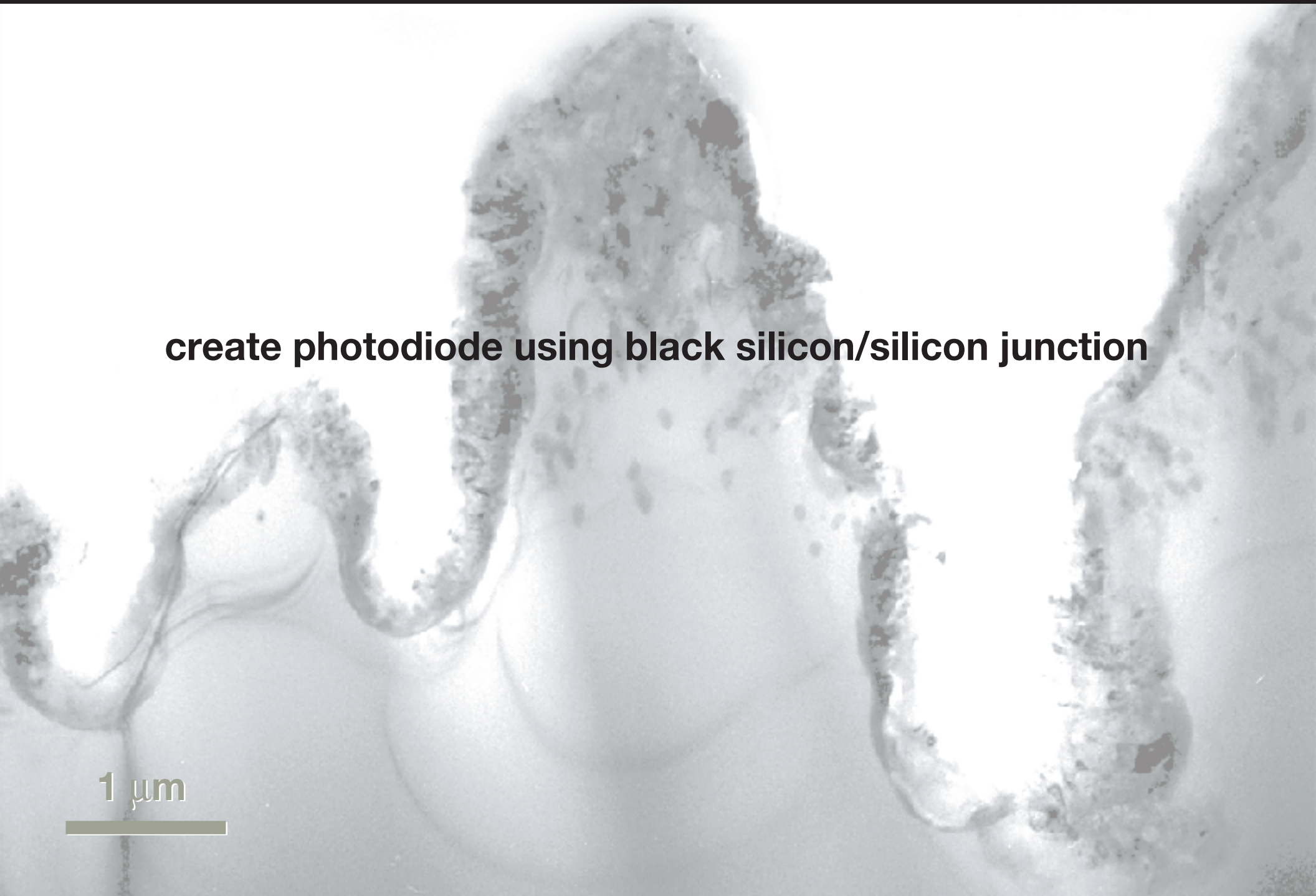
- outlook

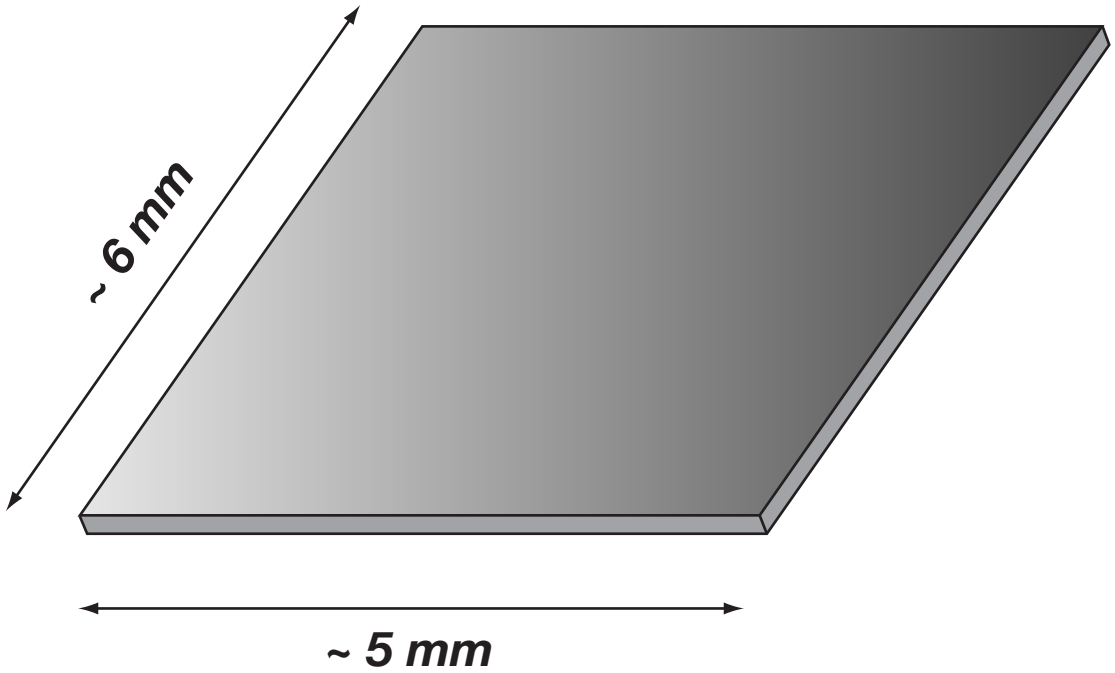
Photodetectors



create photodiode using black silicon/silicon junction

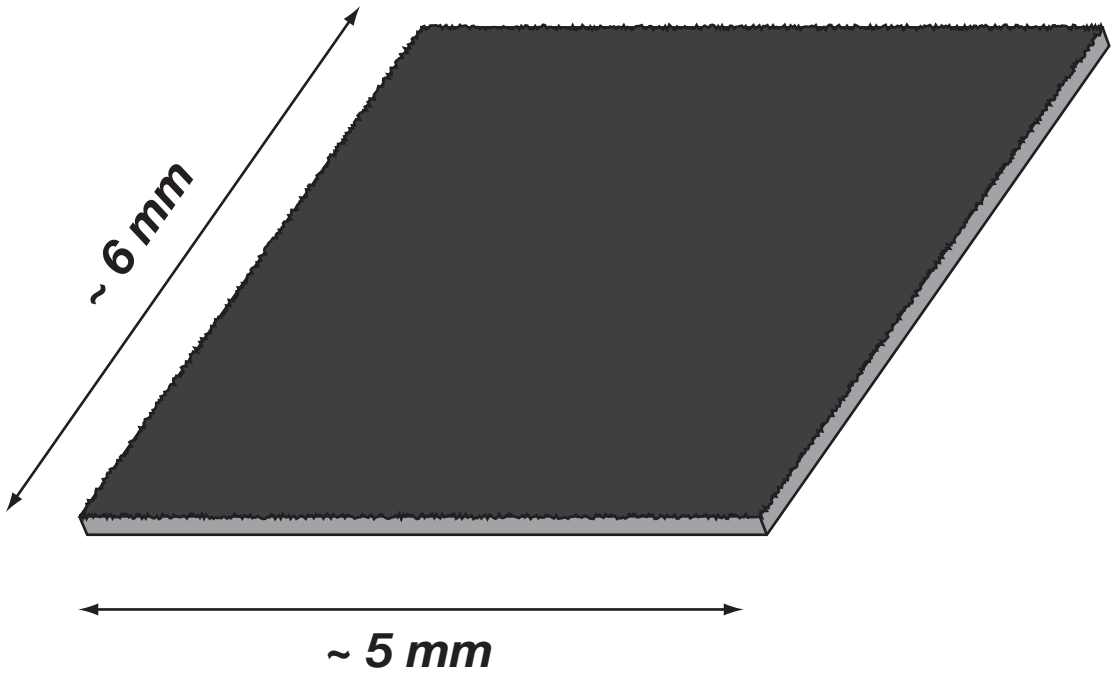
Photodetectors

crystalline Si



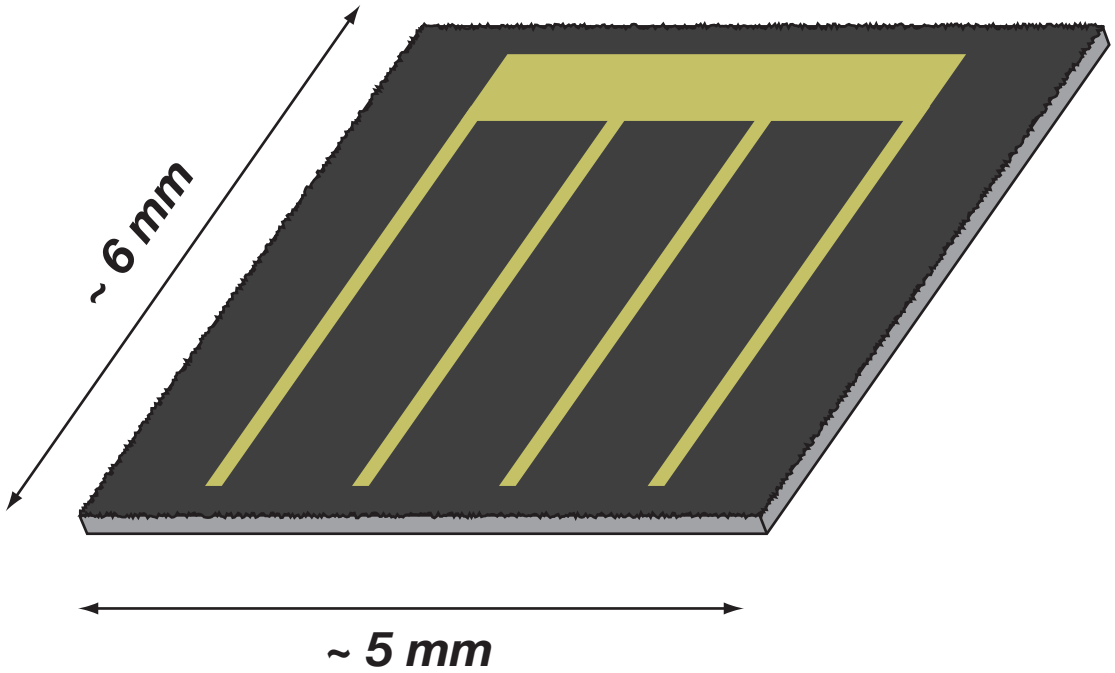
Photodetectors

irradiate with 100-fs laser pulses in SF_6



Photodetectors

Cr/Au contact



Photodetectors

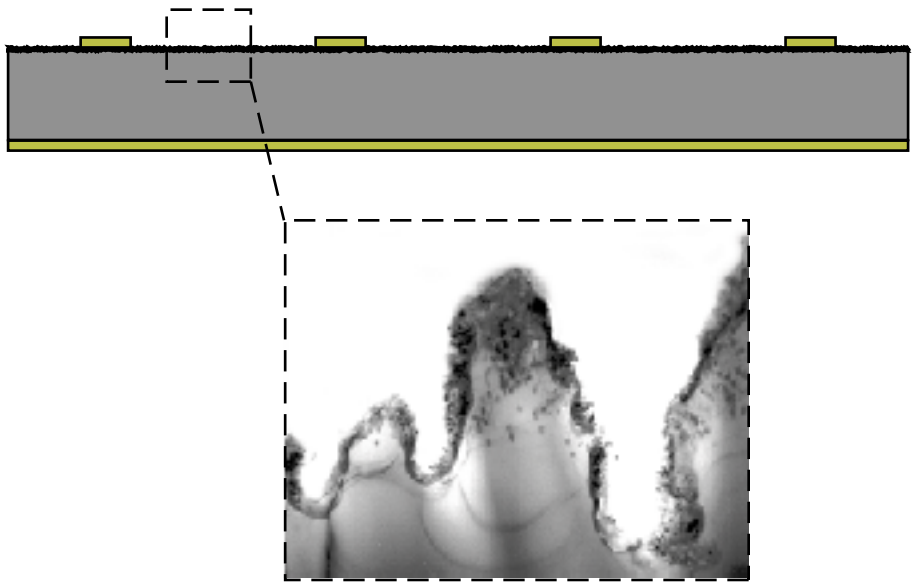
cross section

Photodetectors

Cr/Au contact

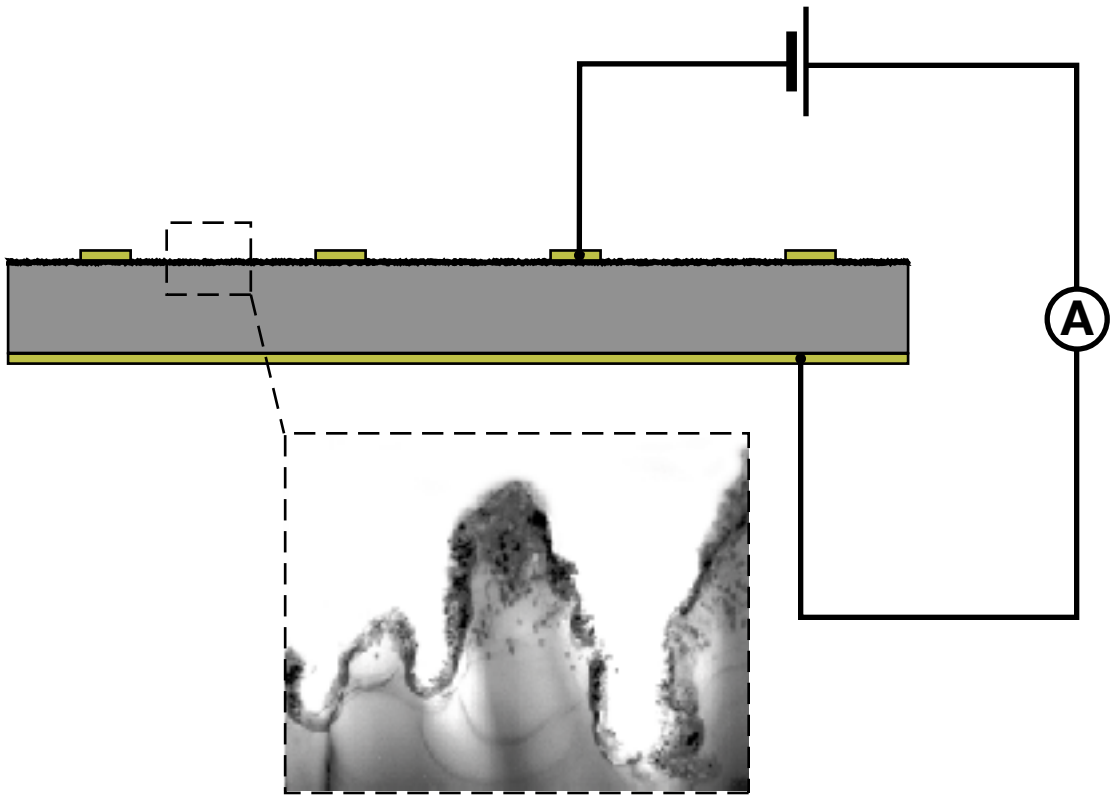
Photodetectors

black silicon/silicon junction



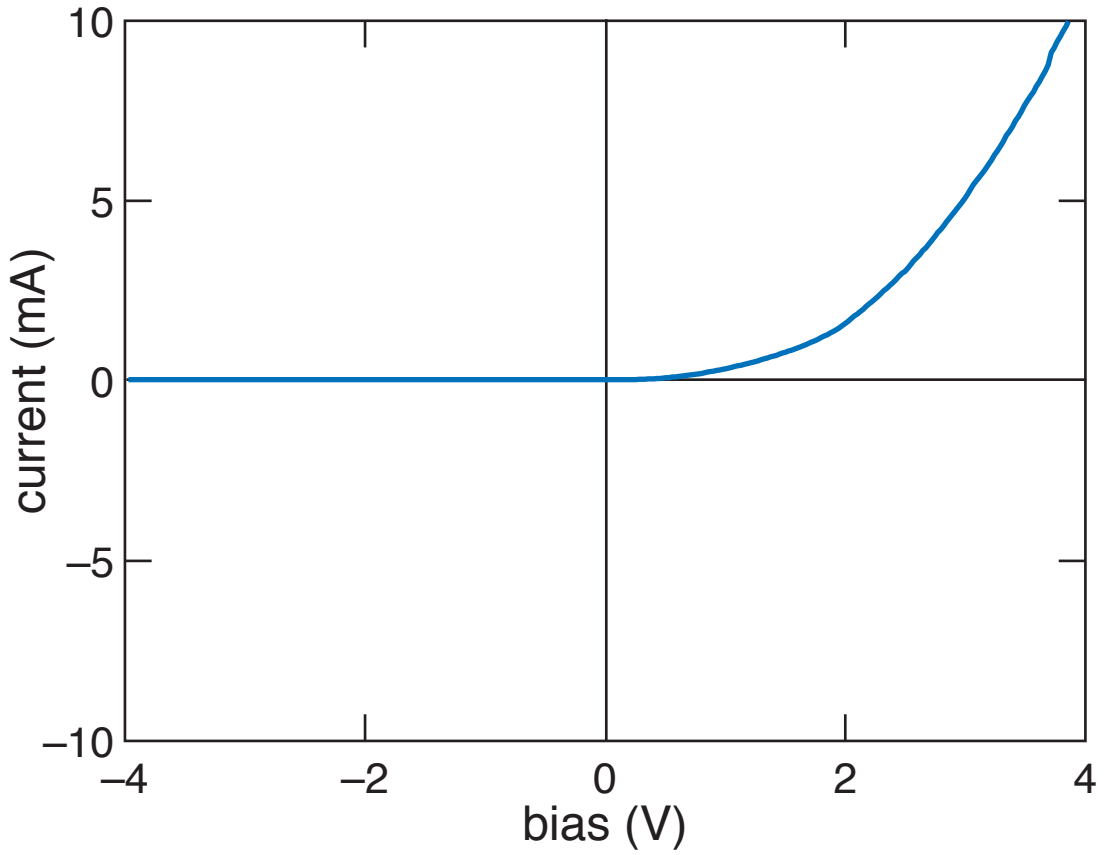
Photodetectors

IV characteristics



Photodetectors

IV characteristics

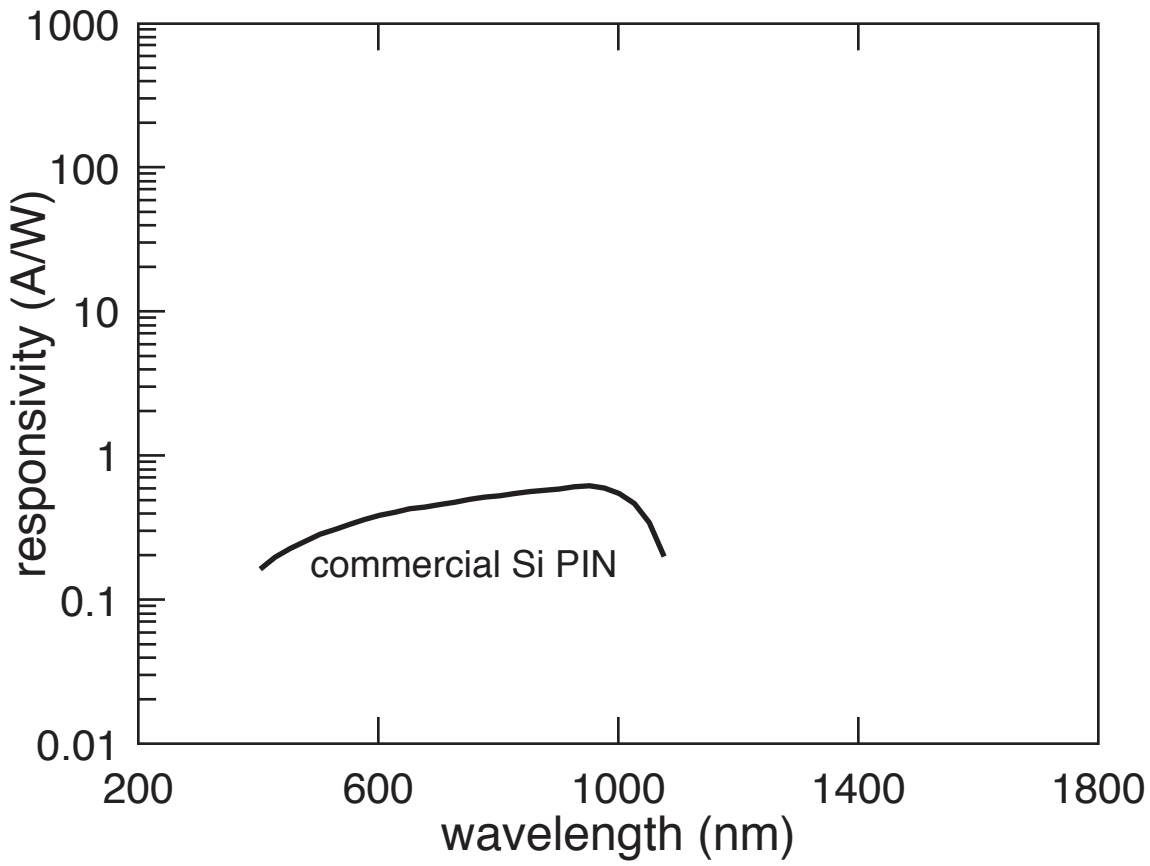


Photodetectors

We have a diode. What about a photodiode?

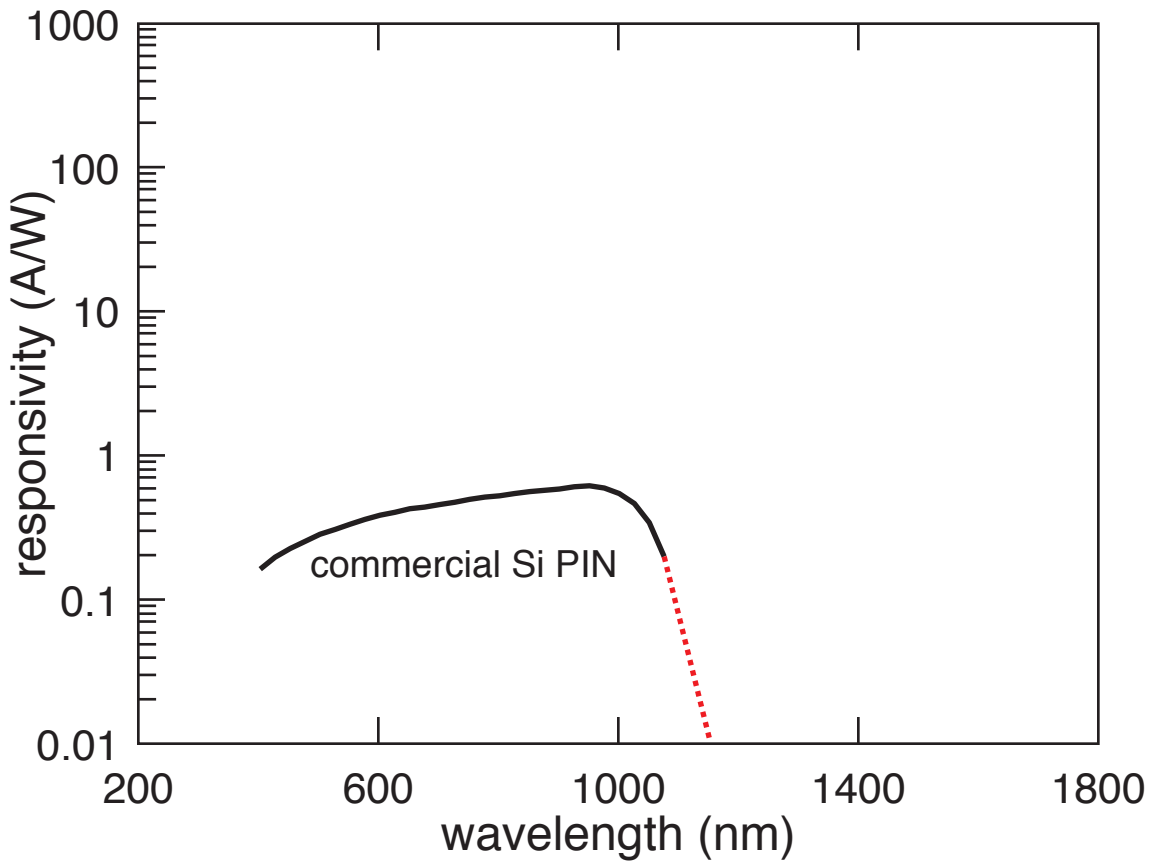
Photodetectors

responsivity



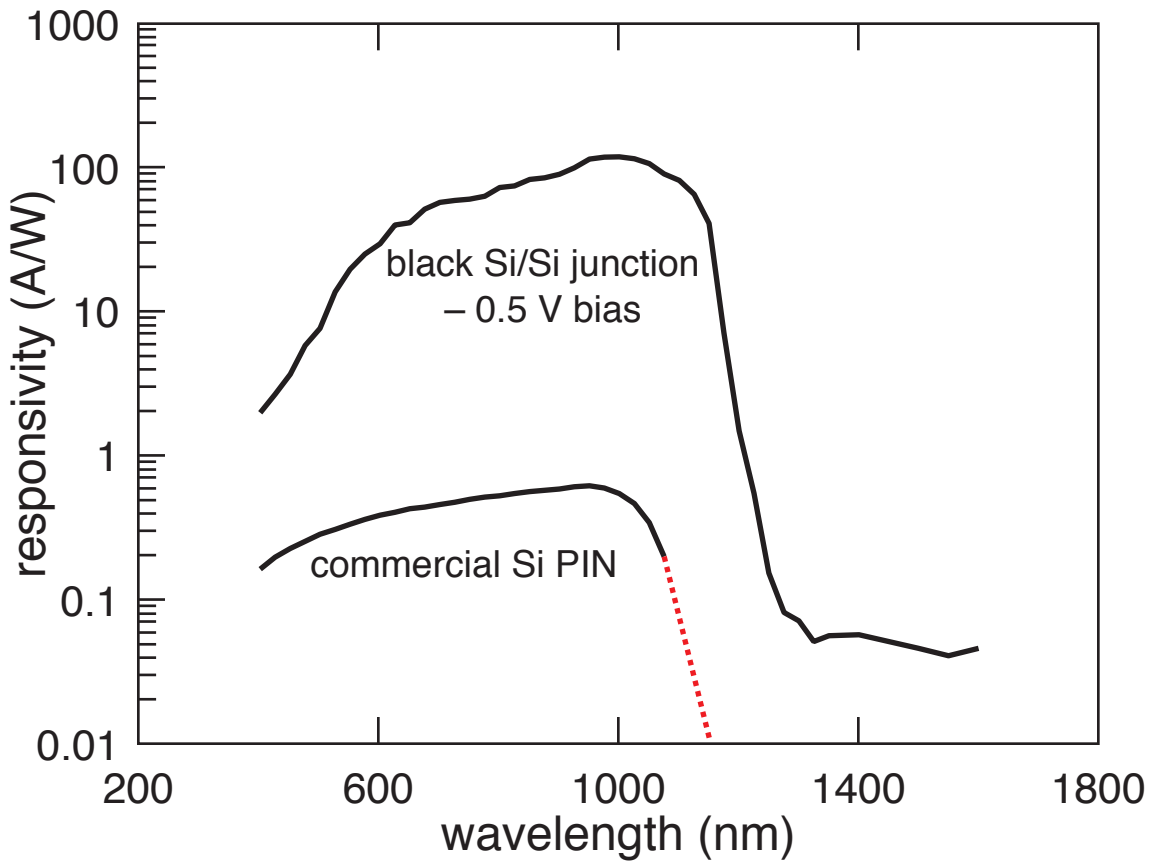
Photodetectors

responsivity



Photodetectors

responsivity



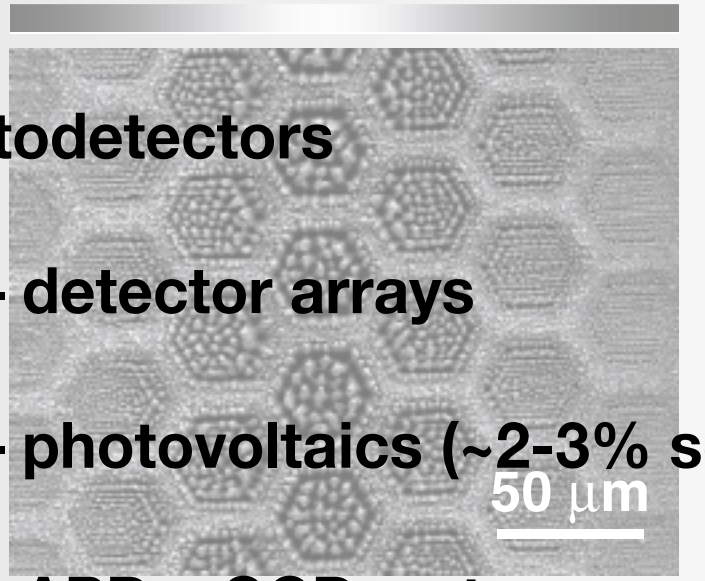
Photodetectors

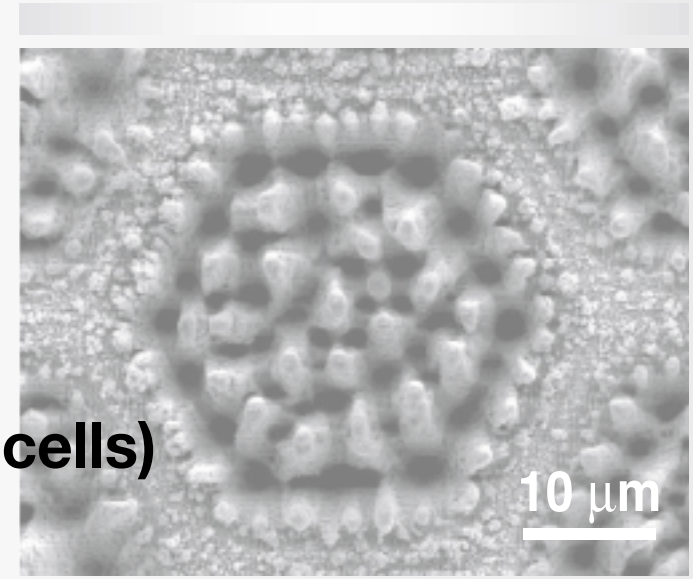
black silicon/silicon photodiode

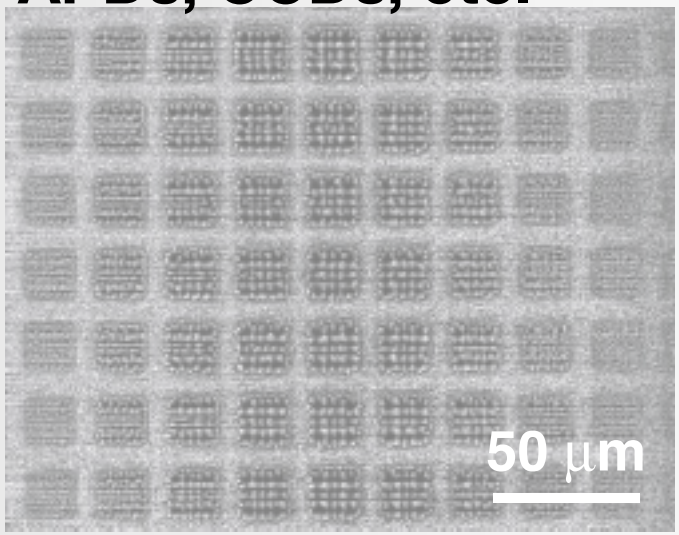
- **nearly 100x larger signal in visible**
- **10^4 larger signal in near-IR**
- **quantum efficiency >> 1, gain!**

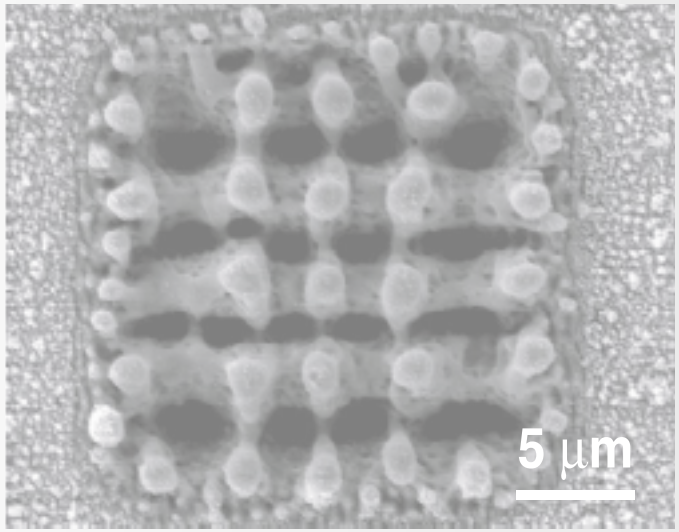
Outlook

- photodetectors
  - detector arrays
  - photovoltaics (~2-3% solar cells)
  - APDs, CCDs, etc.





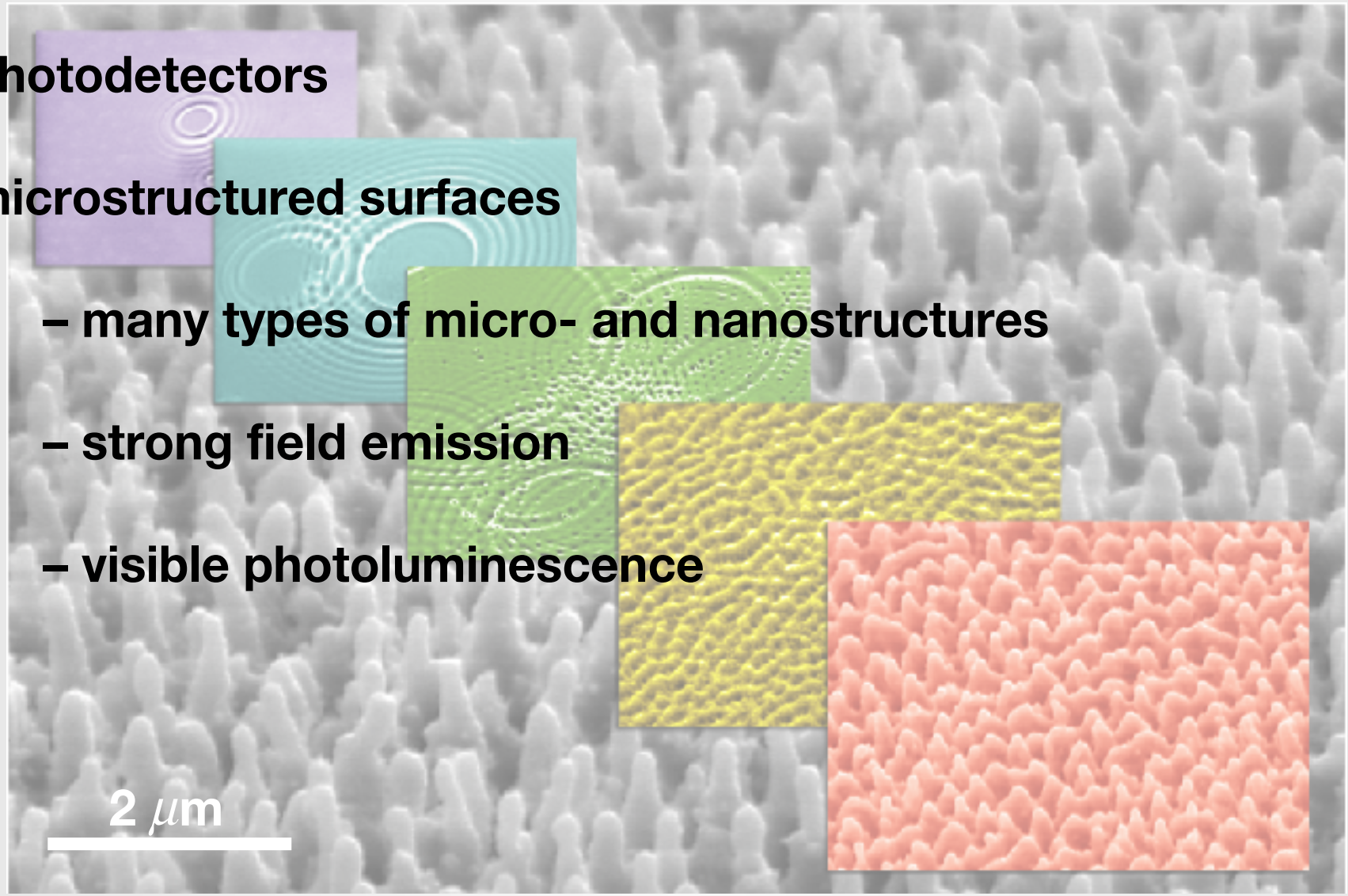




Appl. Phys. Lett., 82, 1715 (2003)

Outlook

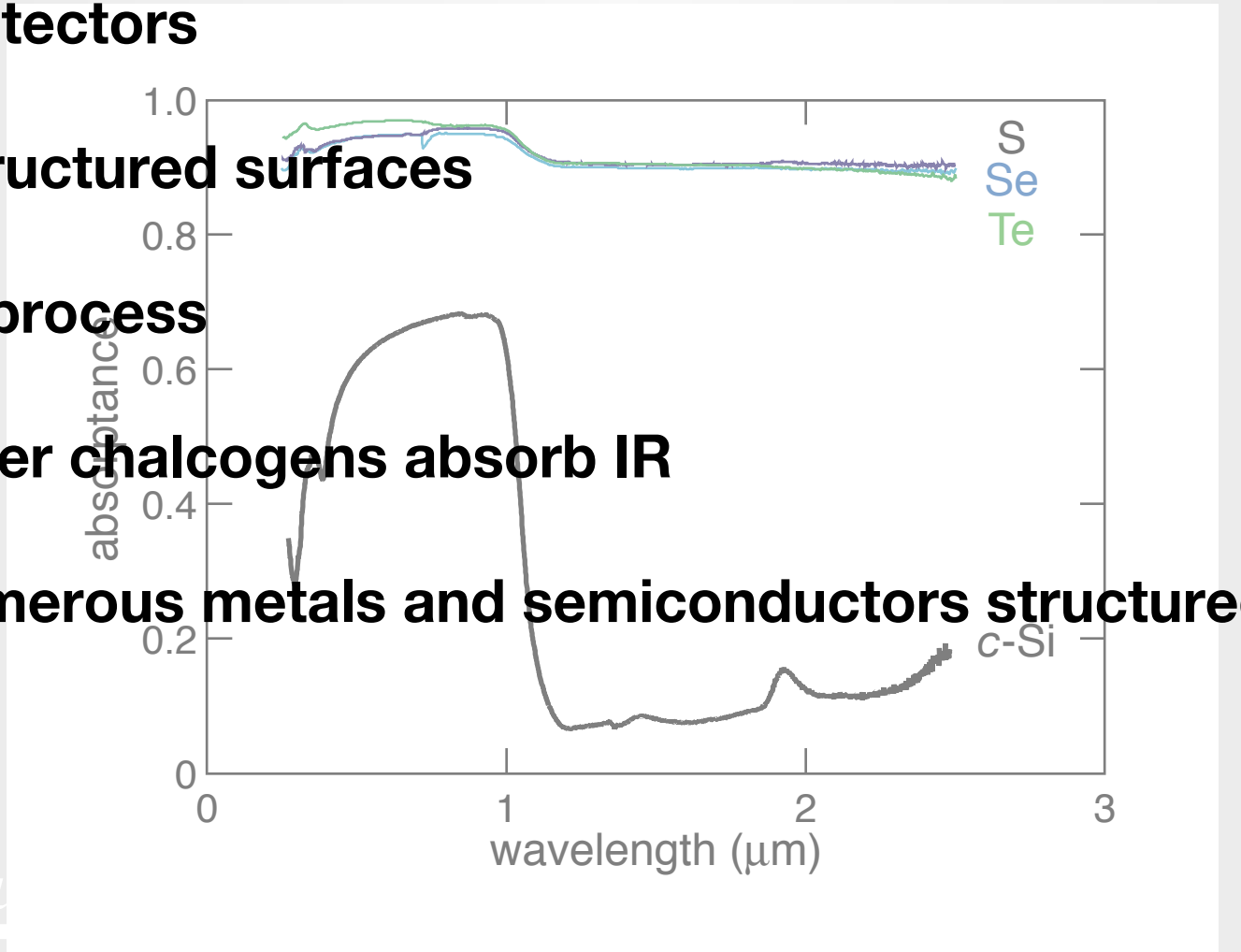
- photodetectors
- microstructured surfaces
  - many types of micro- and nanostructures
  - strong field emission
  - visible photoluminescence



Appl. Phys. Lett., 85, 5694 (2004)

Outlook

- photodetectors
- microstructured surfaces
- flexible process
  - other chalcogens absorb IR
  - numerous metals and semiconductors structured



Summary

Summary

- self-organized, conical microstructures
- near-unity absorption from near-UV to near-IR
- high sensitivity VIS/NIR silicon-based photodiodes
- maskless process, easily integrated with microelectronics
- just the beginning: many promising applications

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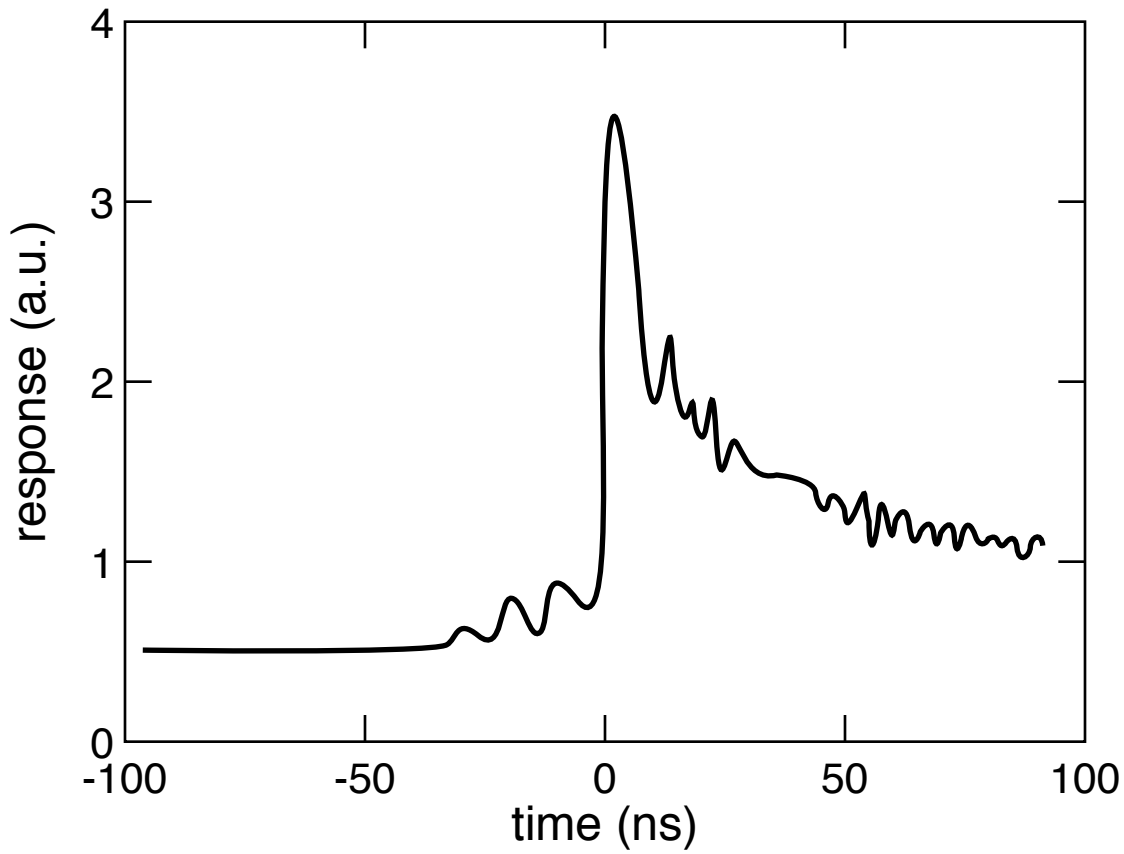
http://mazur-www.harvard.edu/

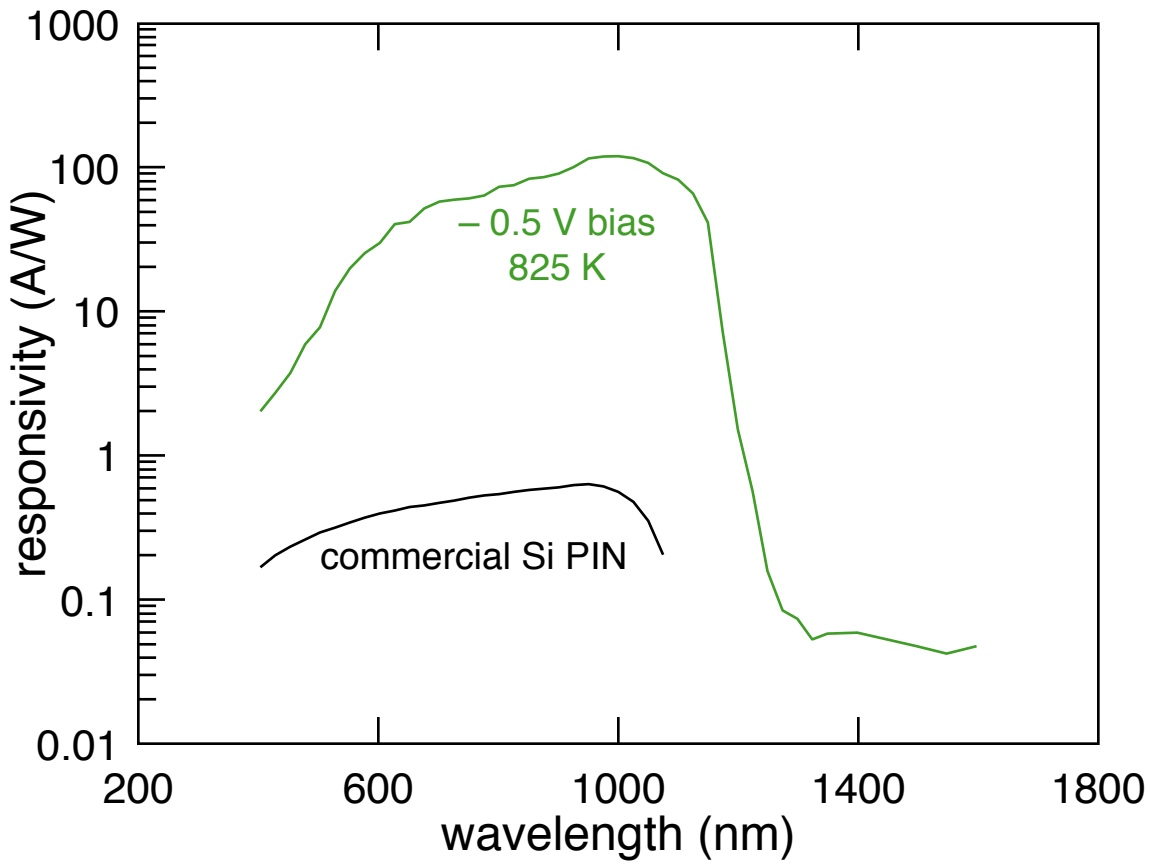
Results

response time: 10 ns rise, 30 ns fall



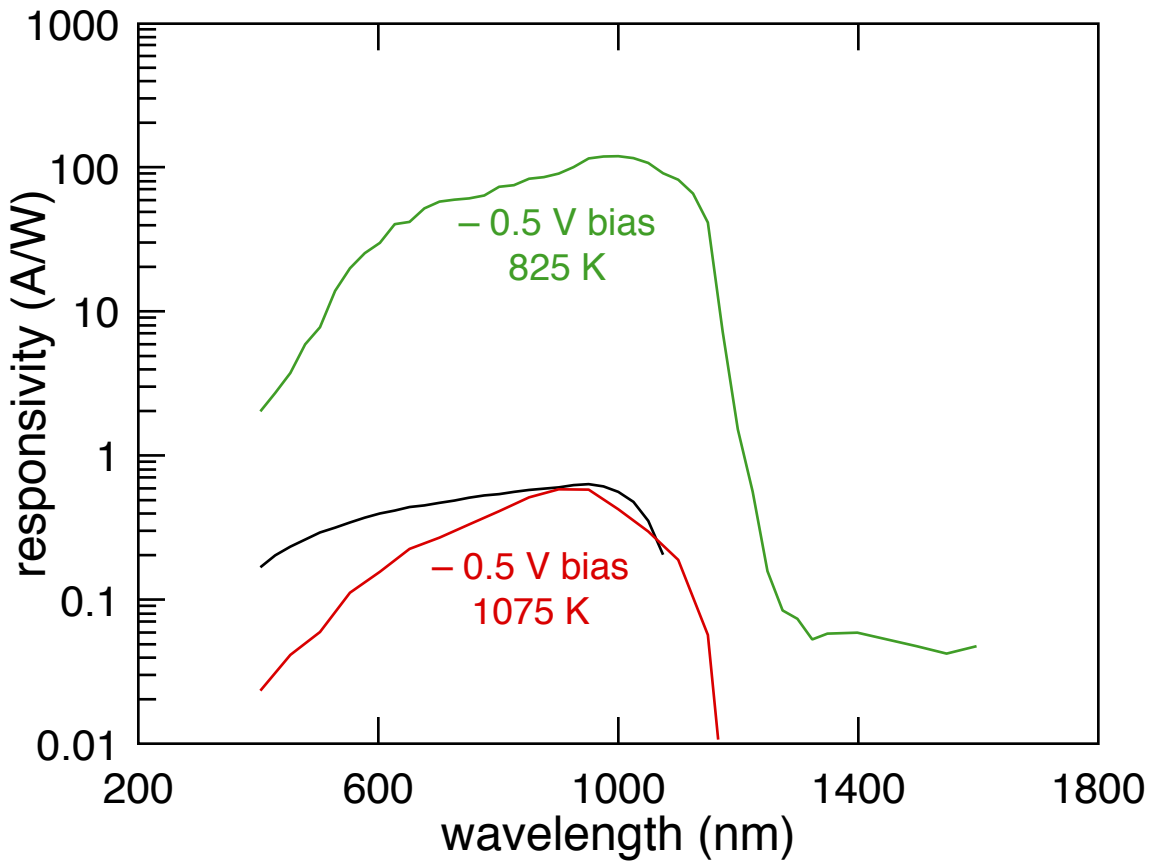
Results

effect of annealing



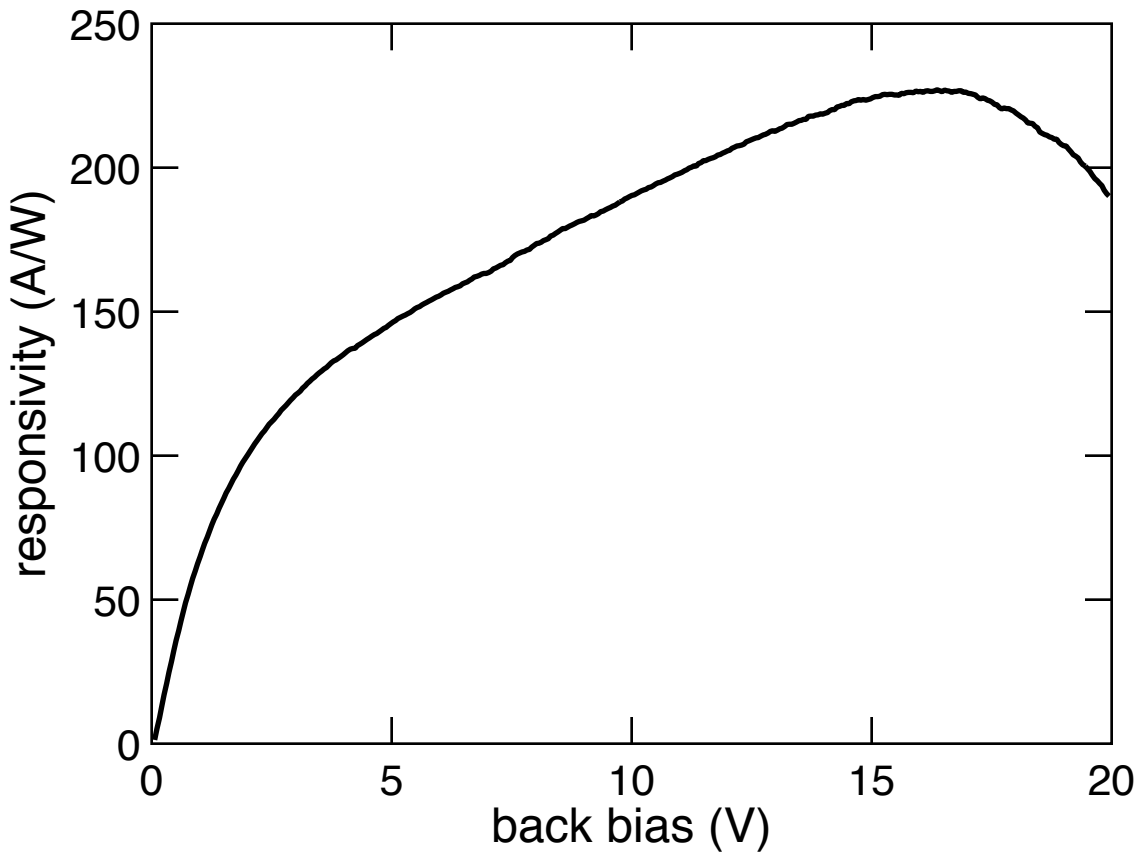
Results

effect of annealing



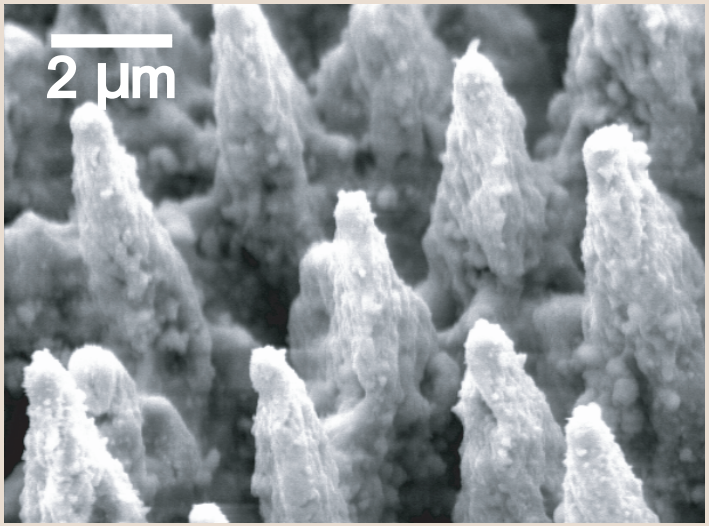
Results

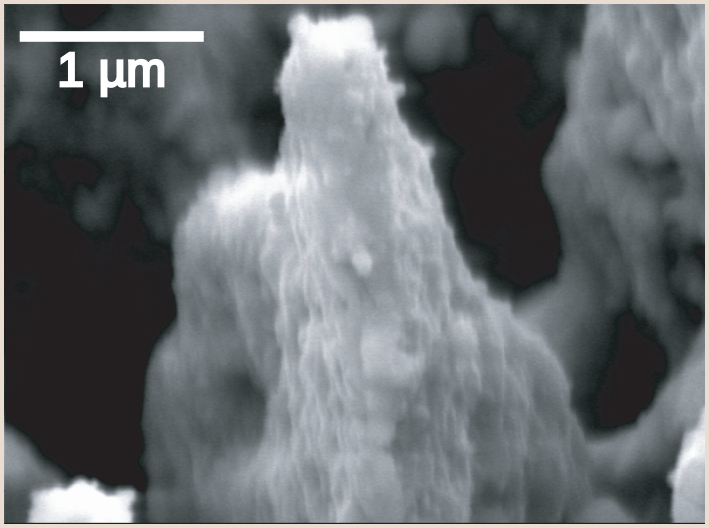
responsivity (white light)



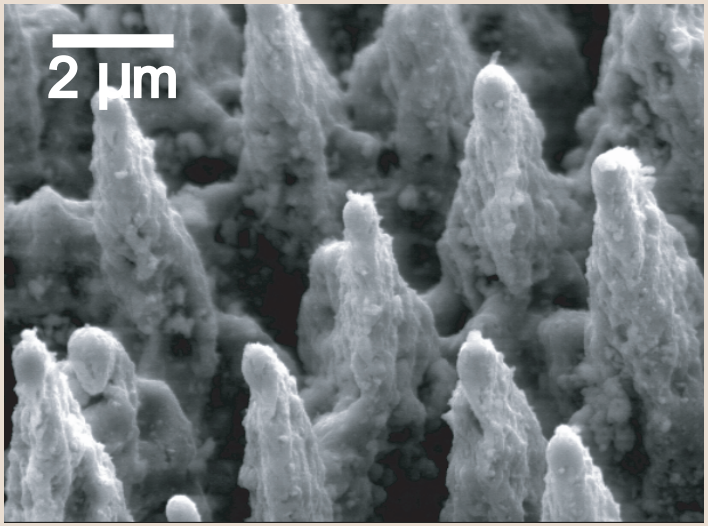
Structural analysis

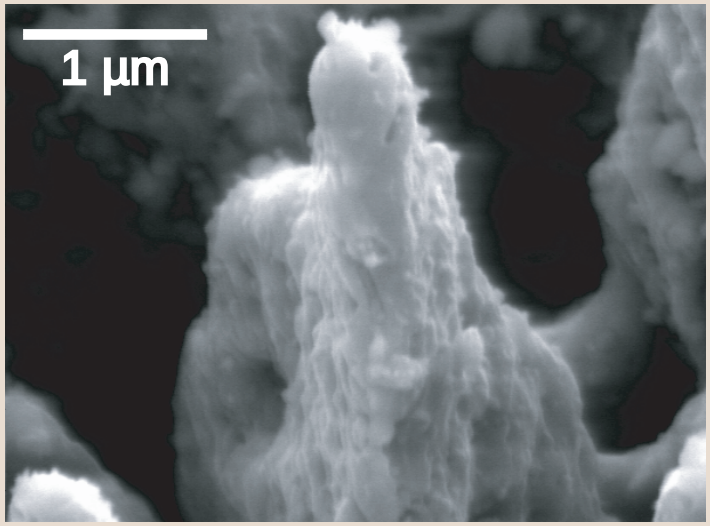
before annealing





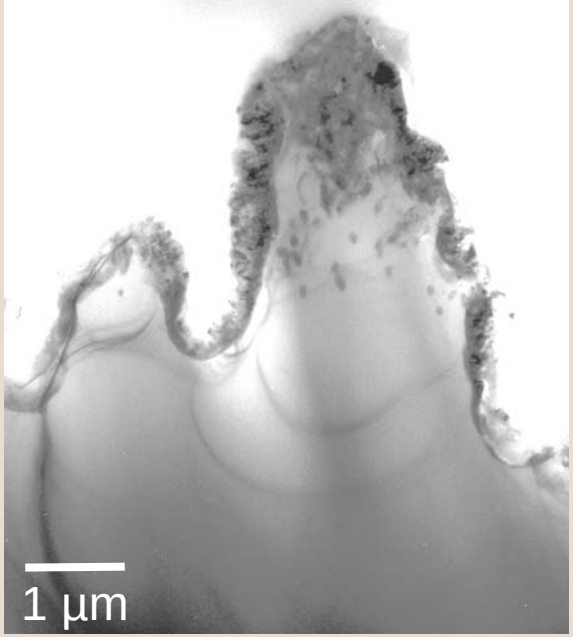
after annealing



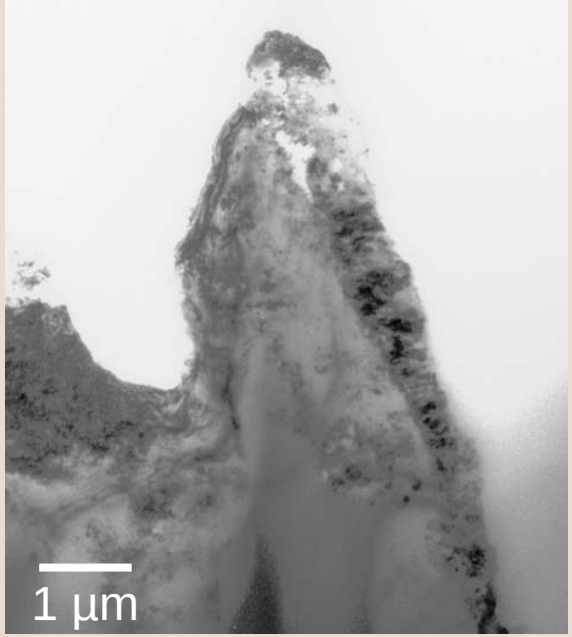


Structural analysis

not annealed



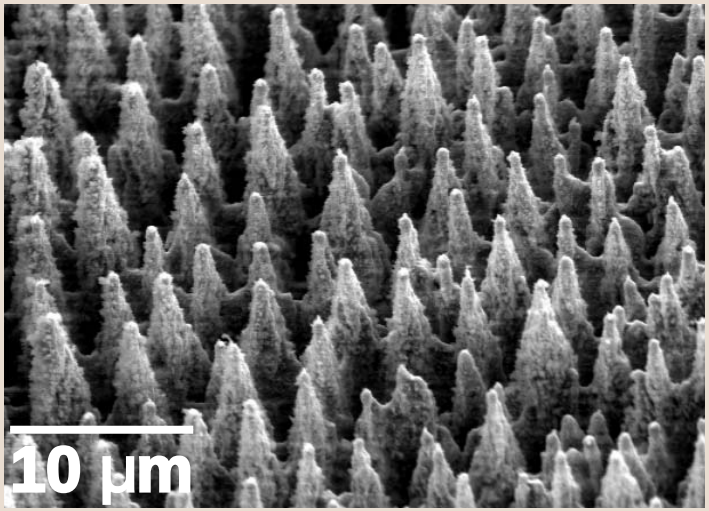
annealed

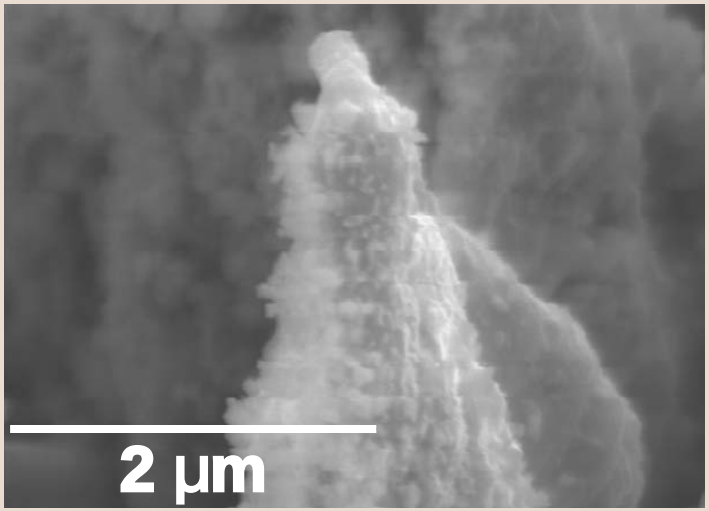


annealing does not affect visible structure

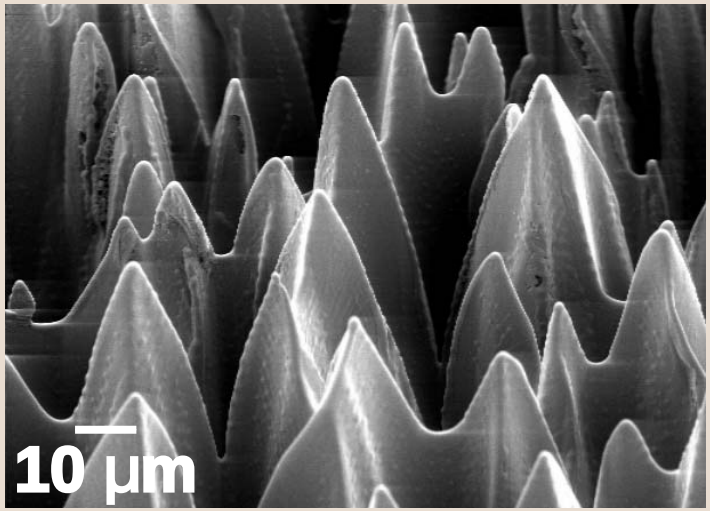
Nanosecond vs femtosecond

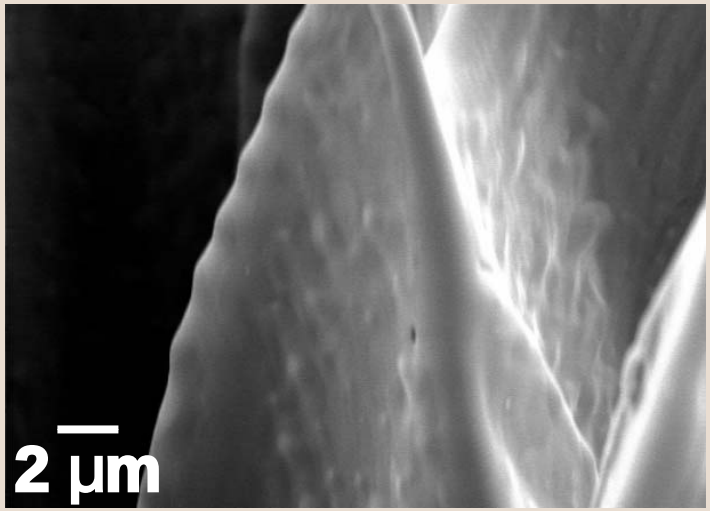
800 nm, 100 fs, 10 kJ/m^2





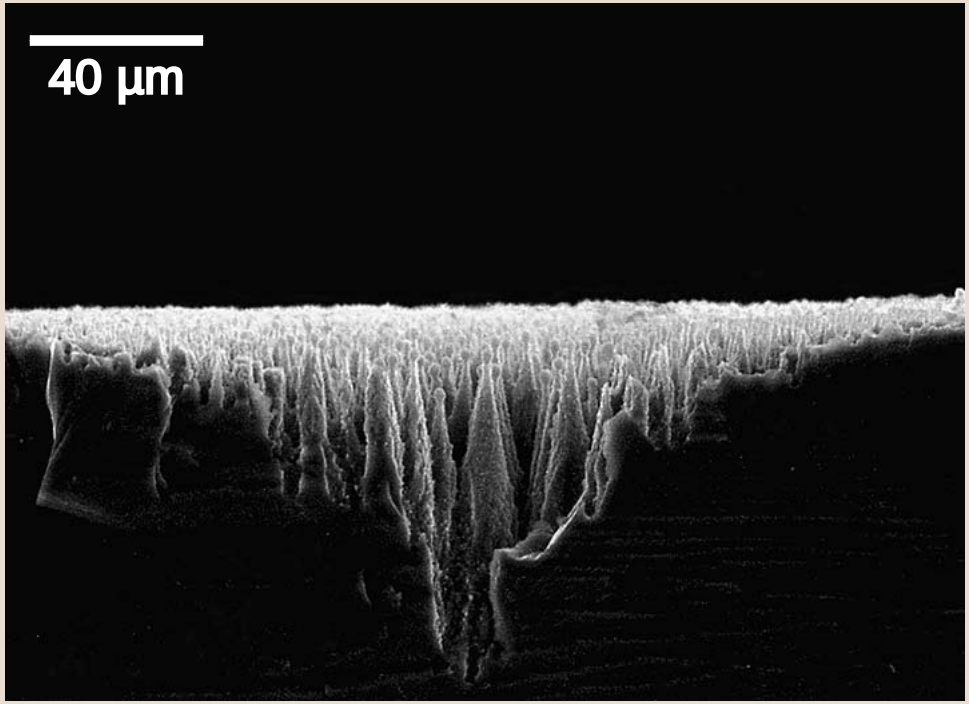
248 nm, 30 ns, 30 kJ/m^2





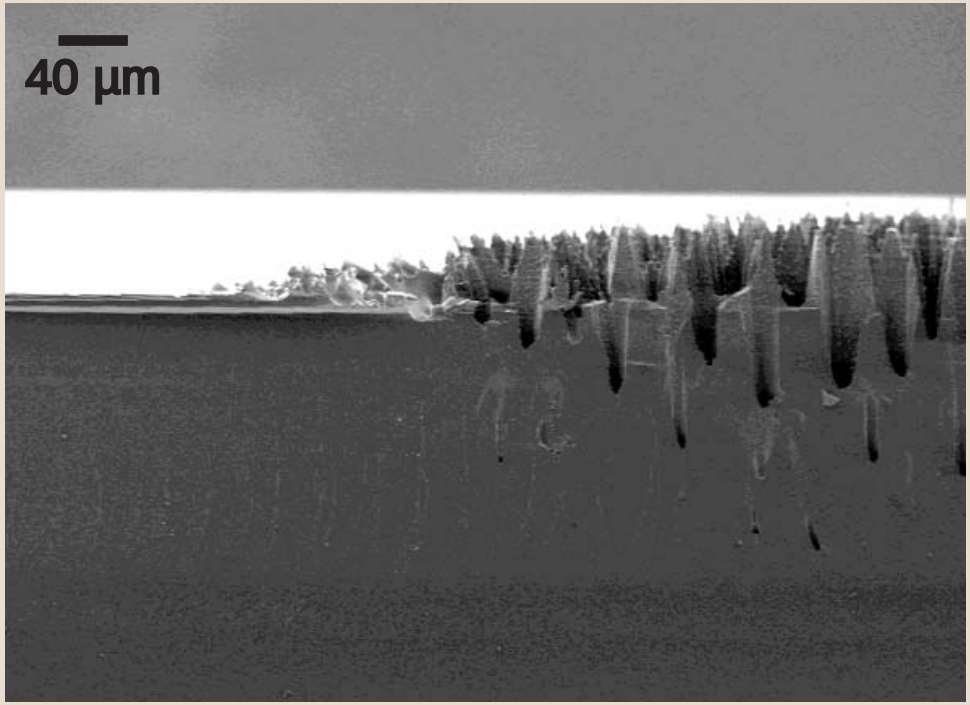
Nanosecond vs femtosecond

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



fs cones etched below surface

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

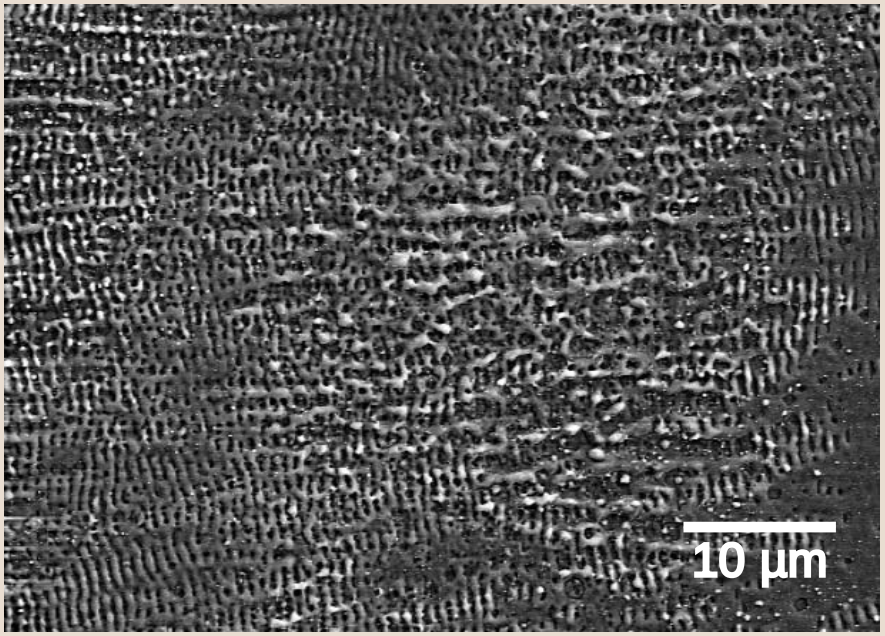


ns cones grow above surface

Formation process

ripples

SF_6 **2 pulses**

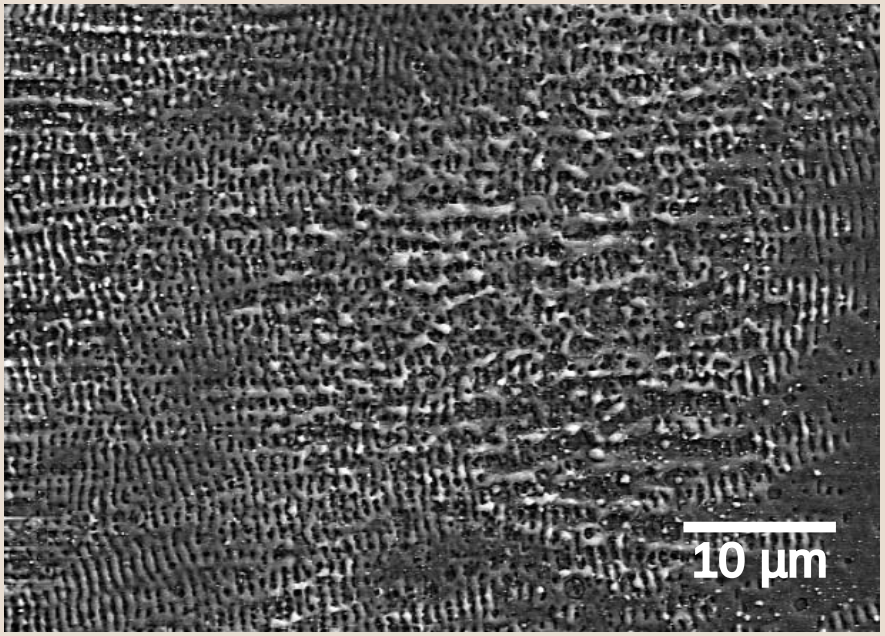


laser polarization

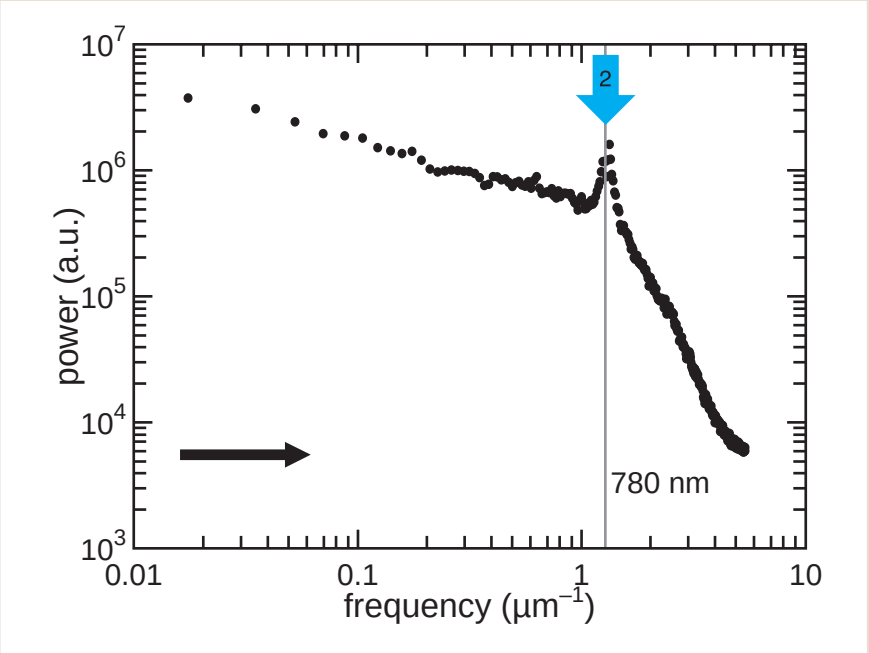
Formation process

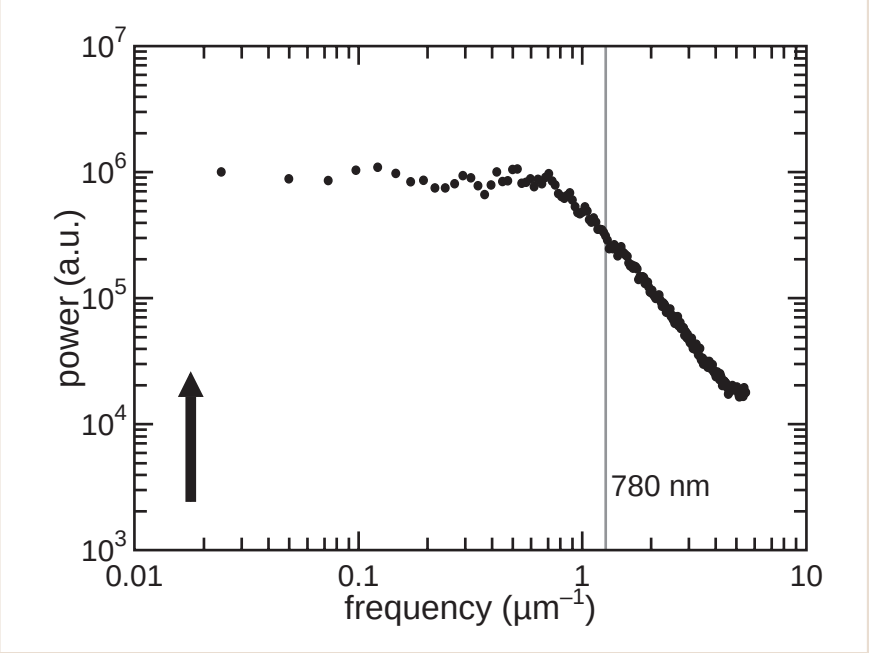
ripples

SF_6 2 pulses



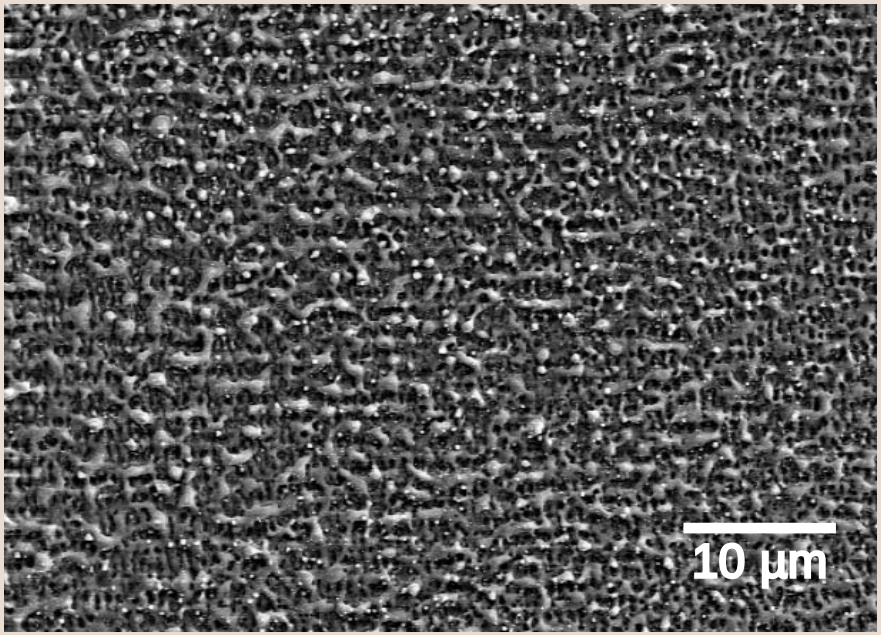
laser polarization



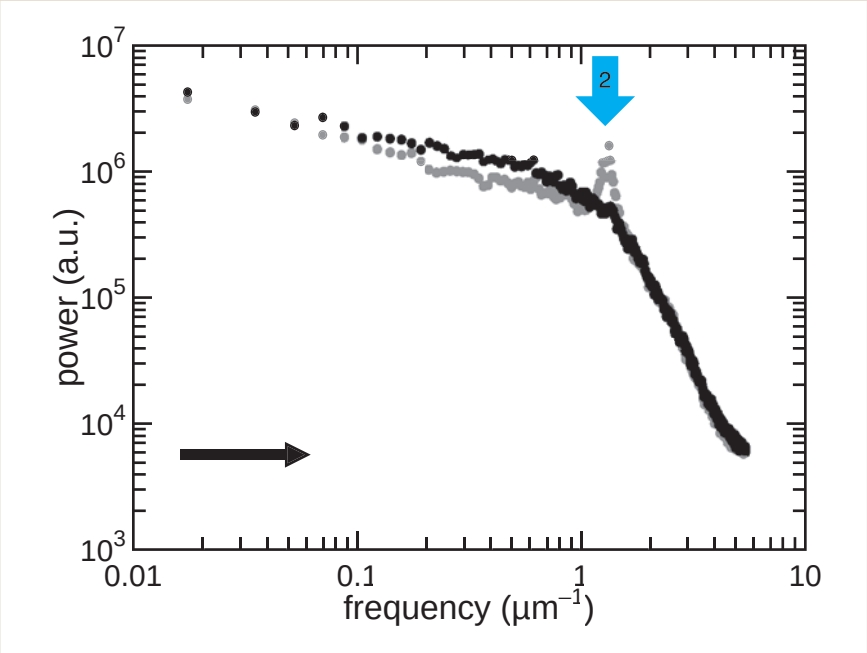


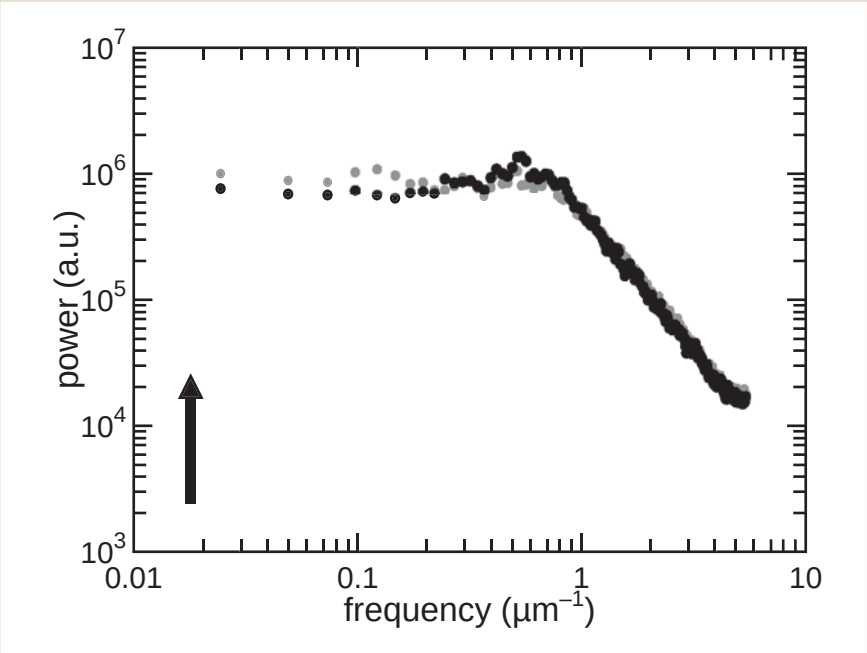
Formation process

SF_6 **3 pulses**



laser polarization

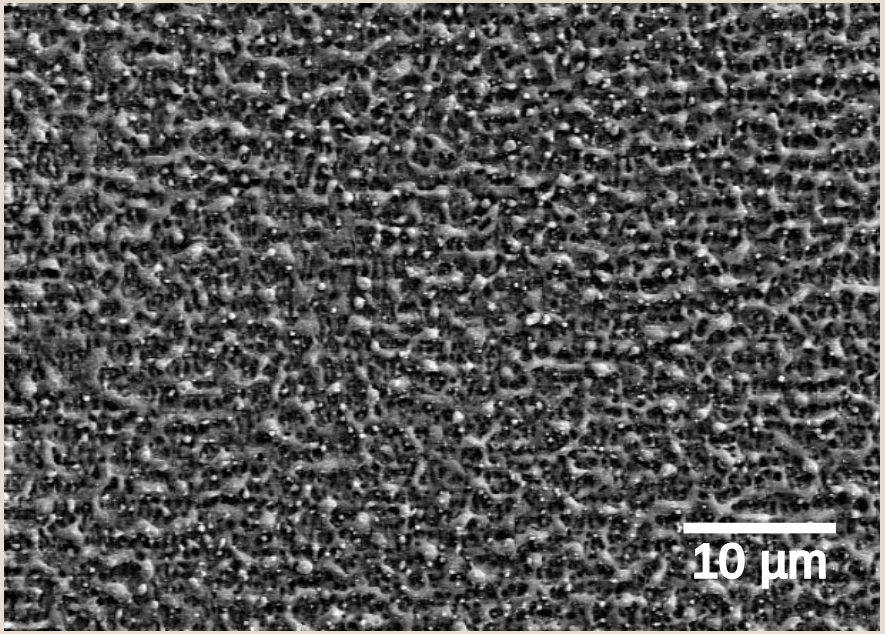




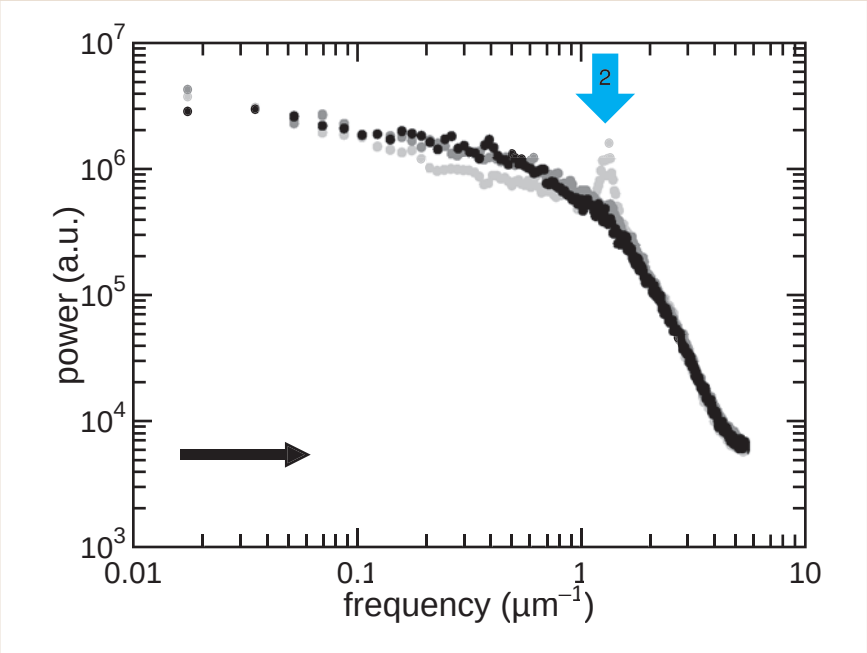
Formation process

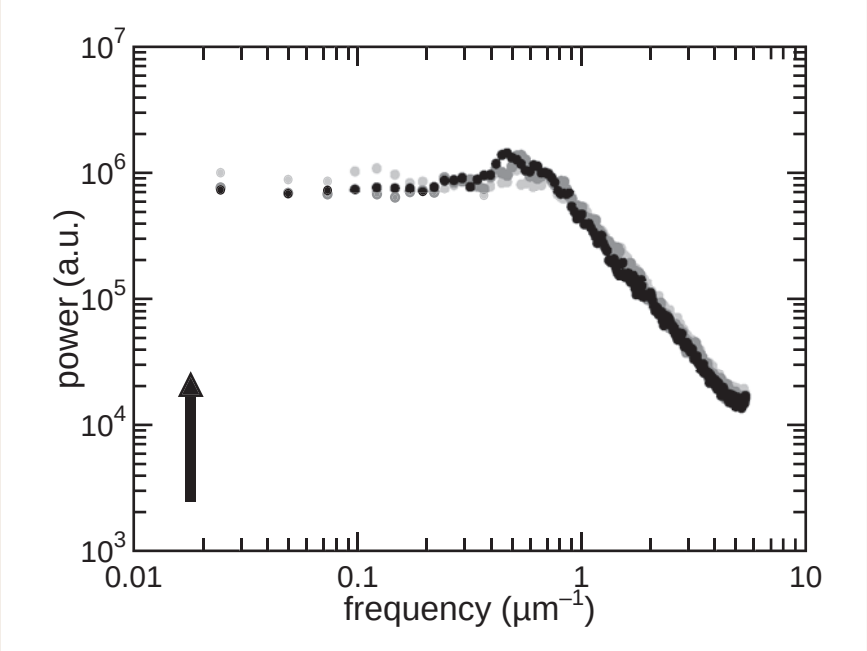
ridges

SF_6 4 pulses



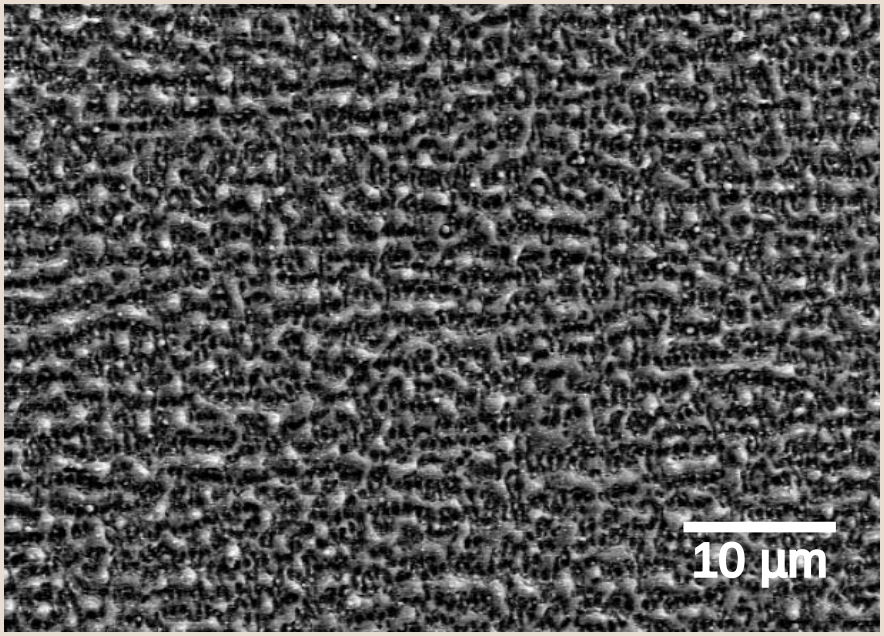
laser polarization



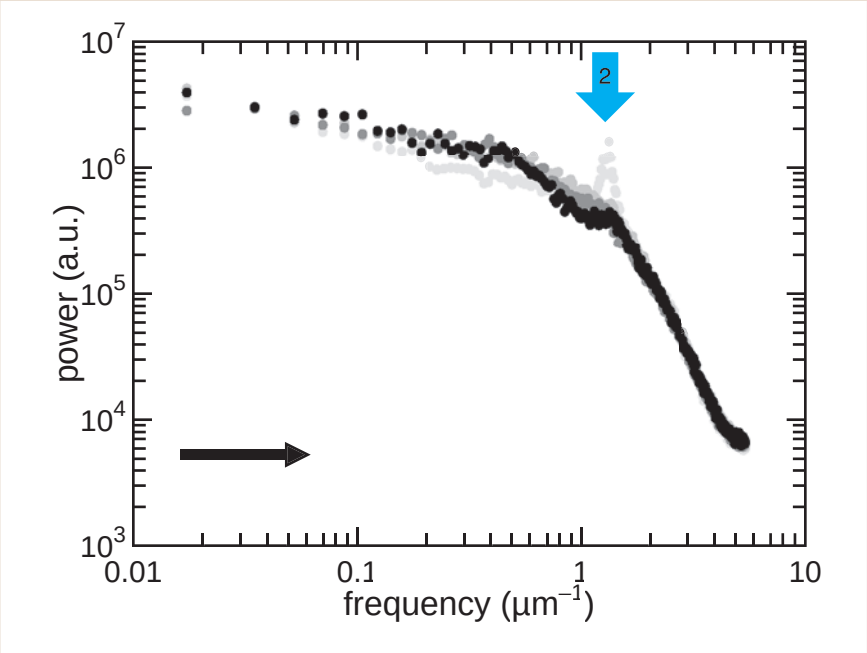


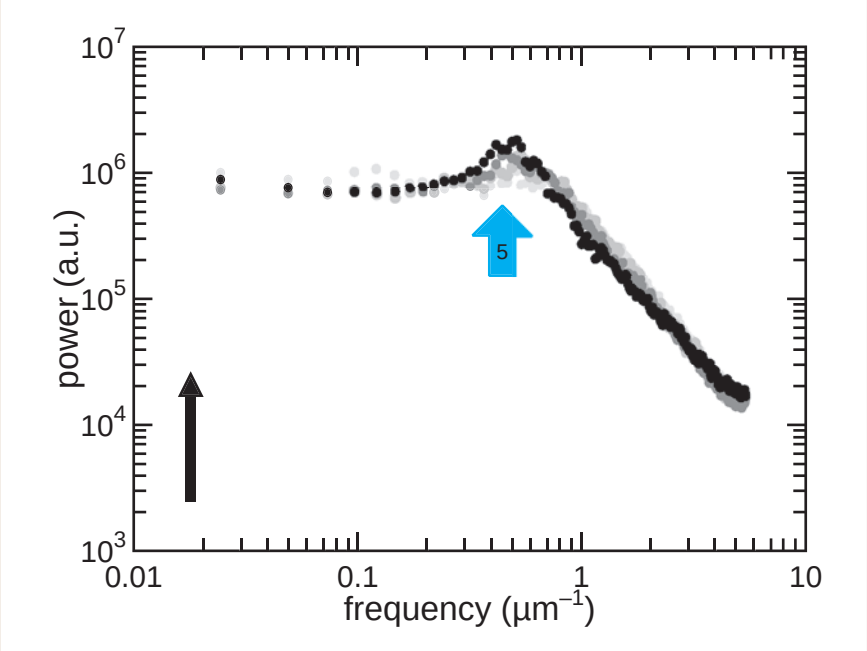
Formation process

SF_6 **5 pulses**



laser polarization

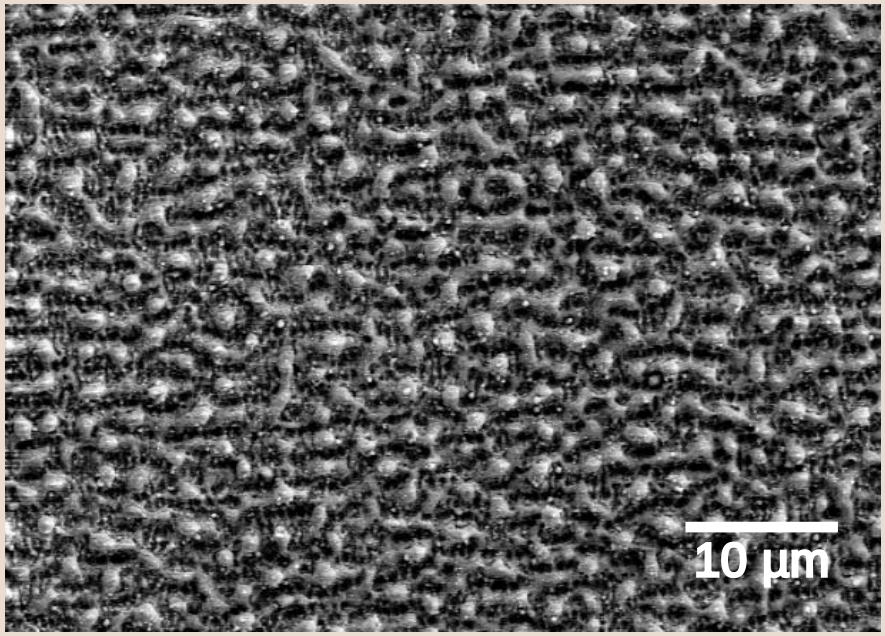




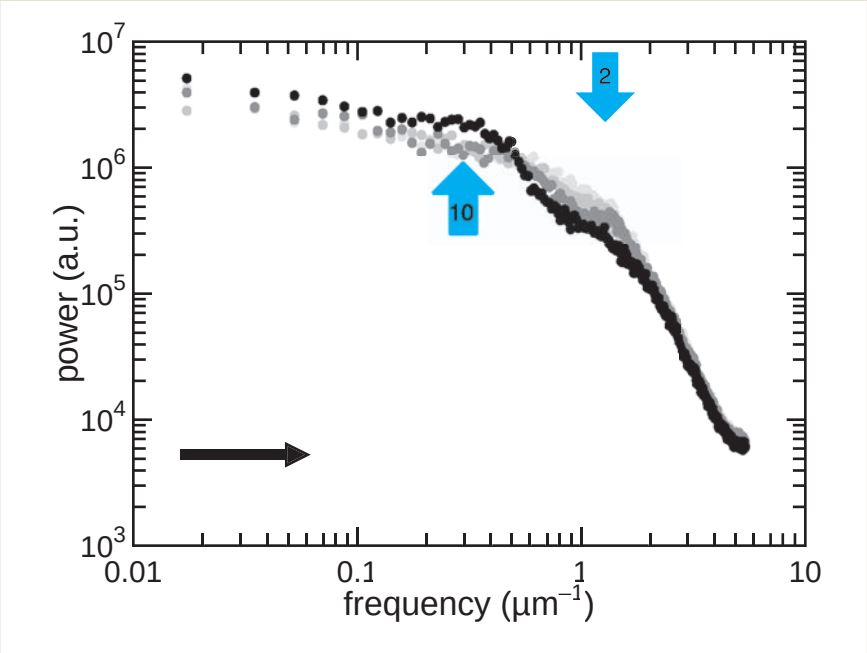
Formation process

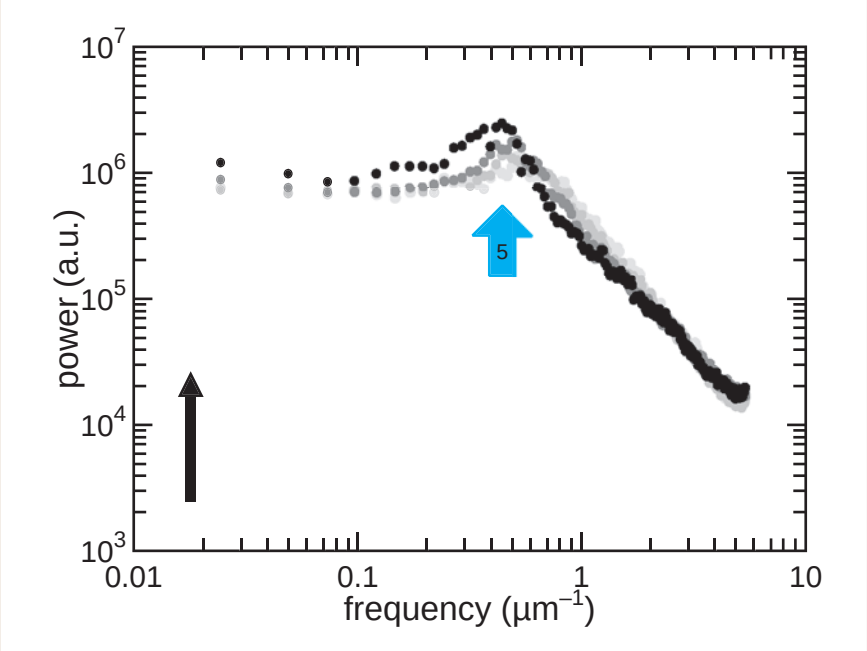
spikes

SF_6 10 pulses



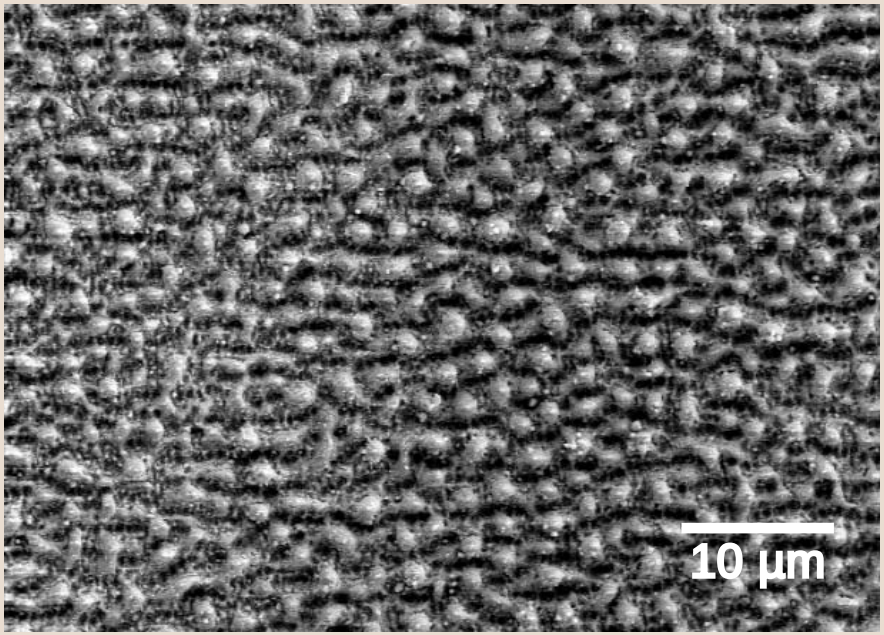
laser polarization



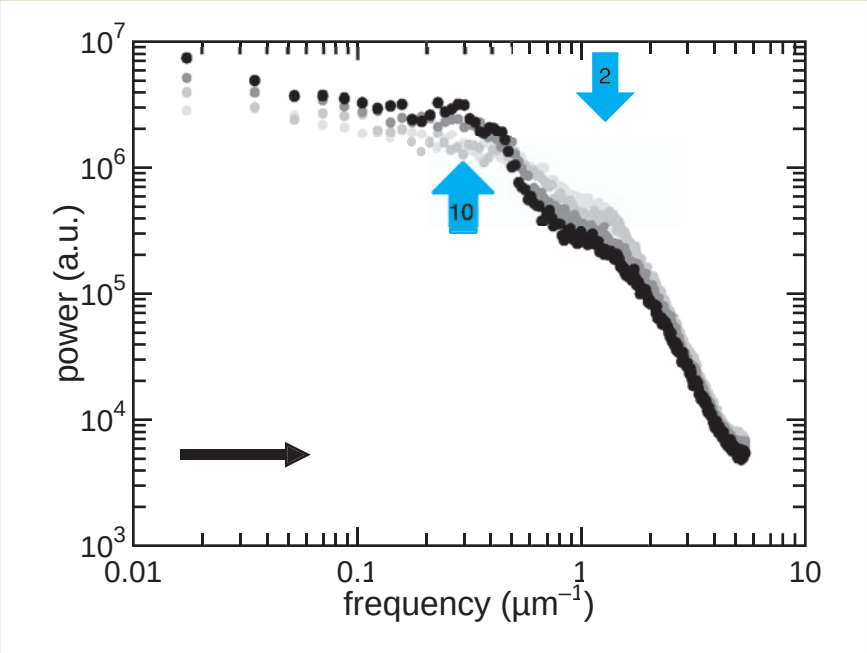


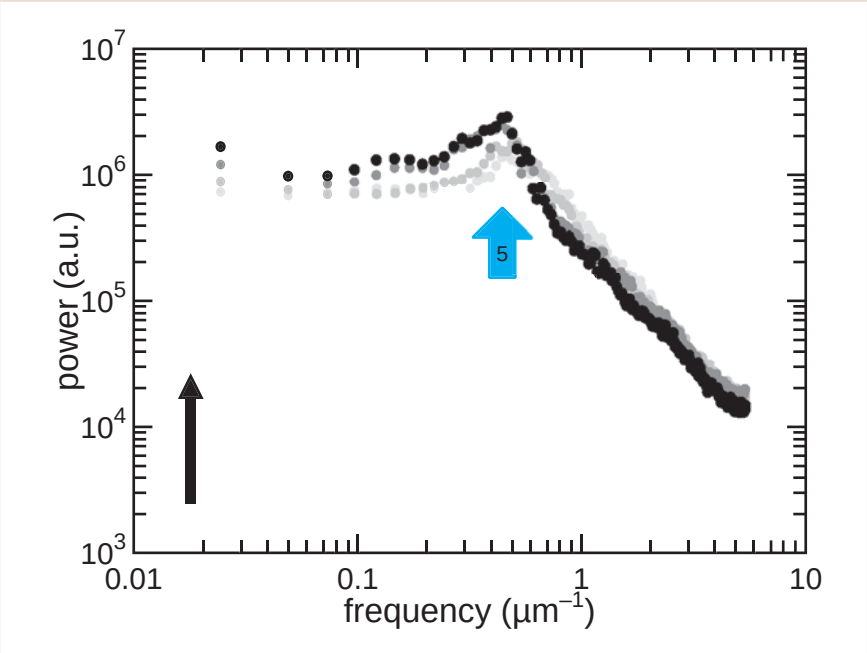
Formation process

SF_6 15 pulses



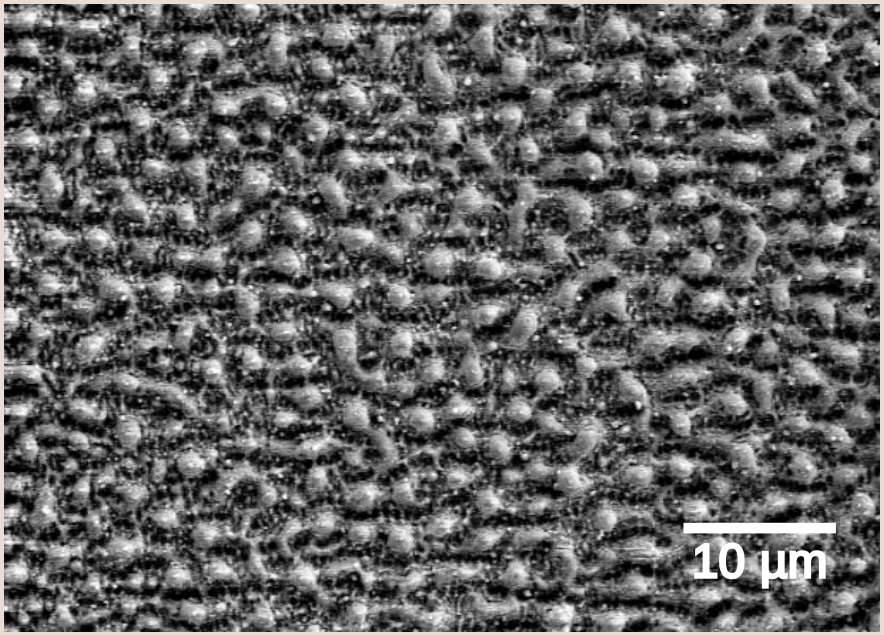
laser polarization



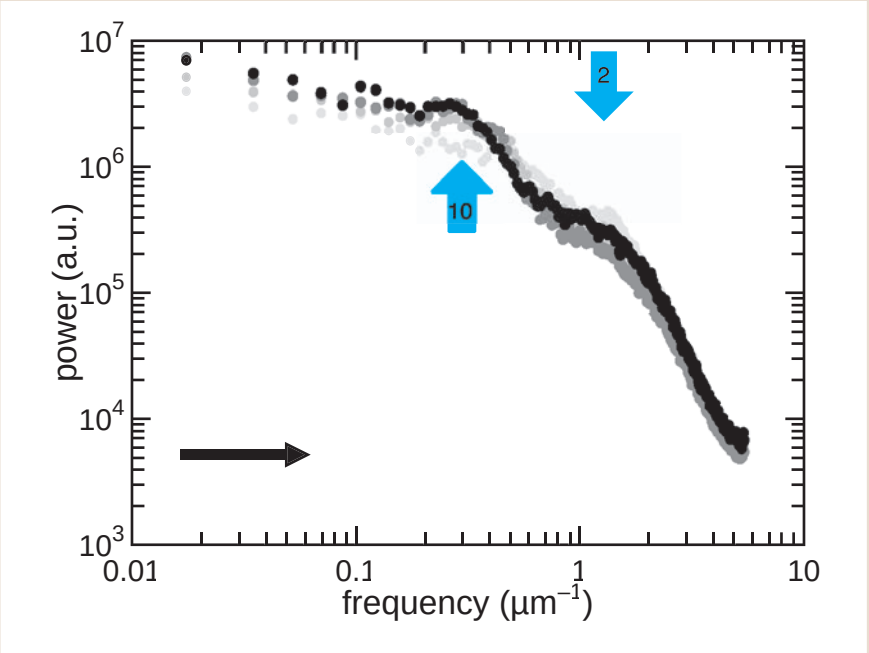


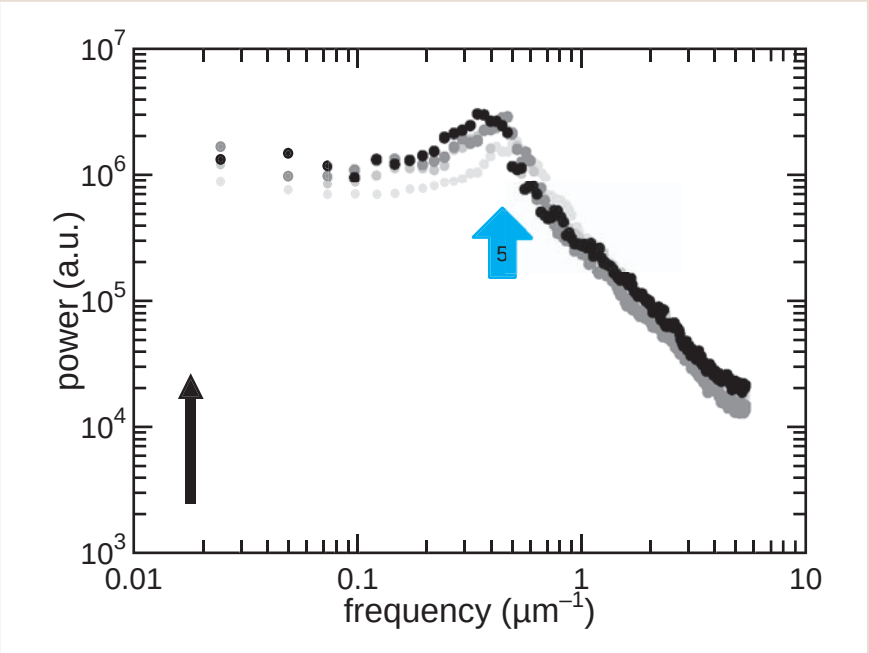
Formation process

SF_6 20 pulses



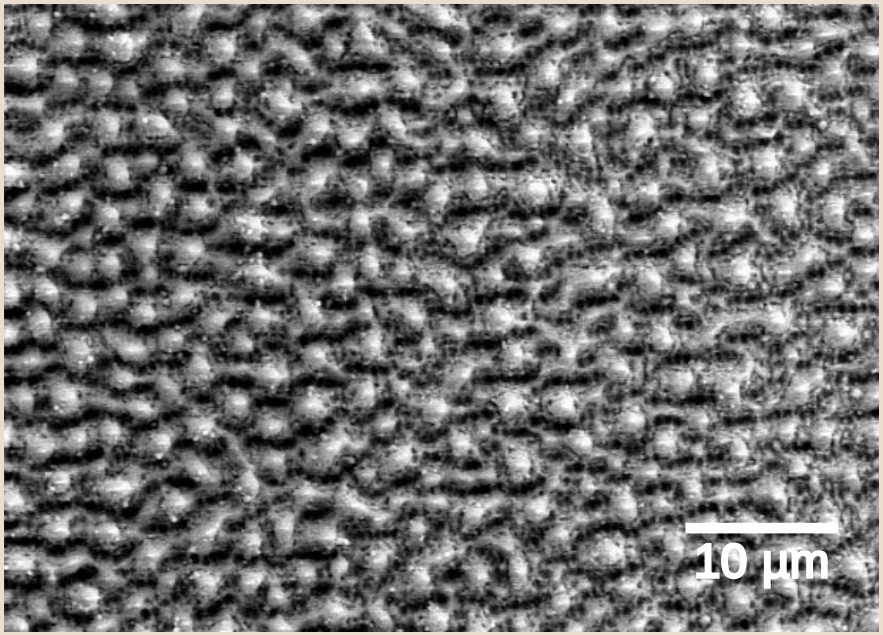
laser polarization



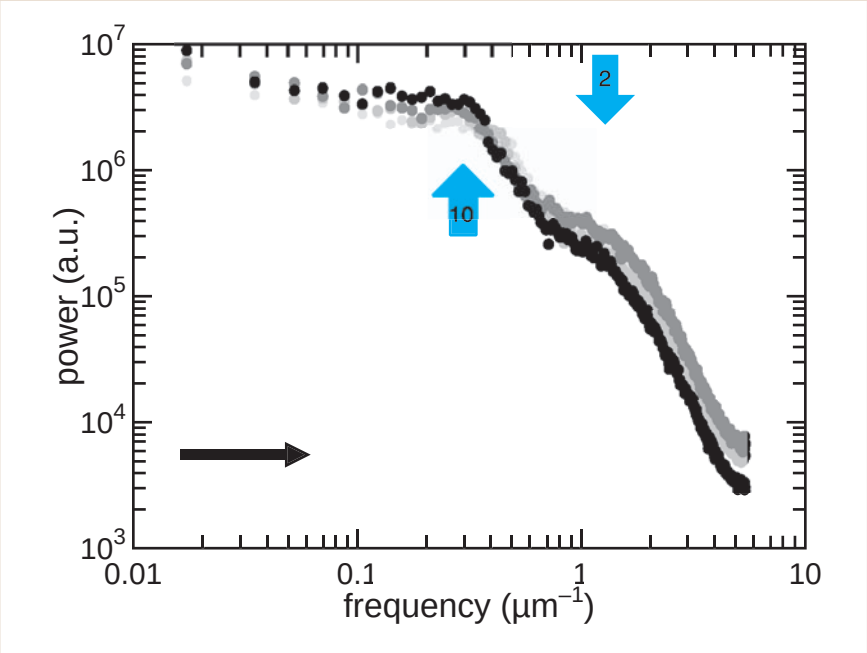


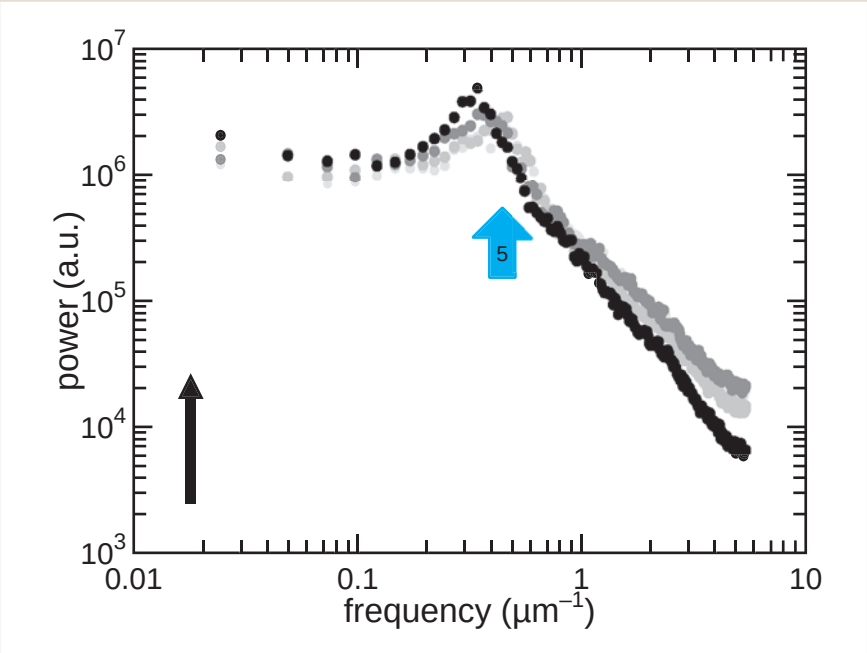
Formation process

SF_6 50 pulses



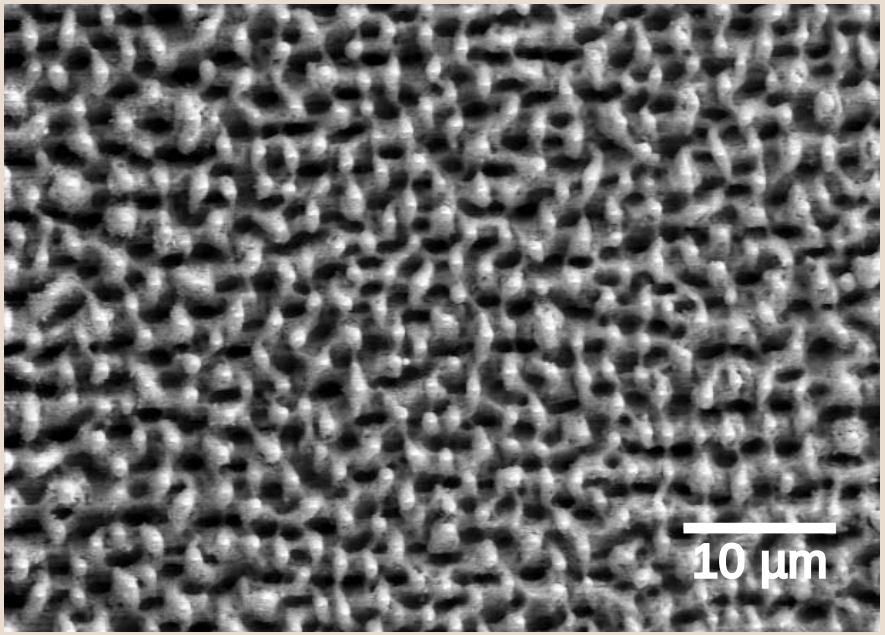
laser polarization



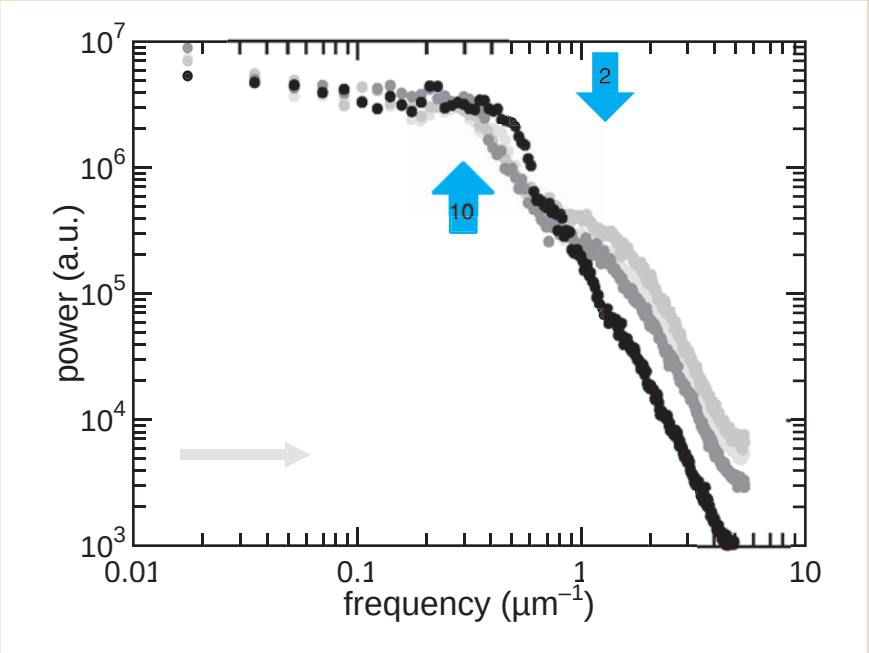


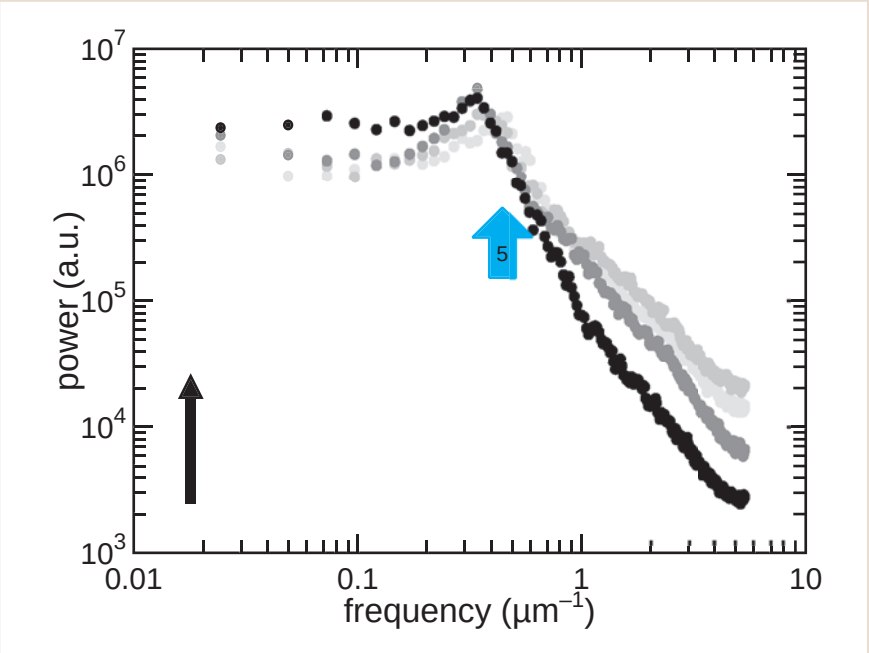
Formation process

SF_6 200 pulses



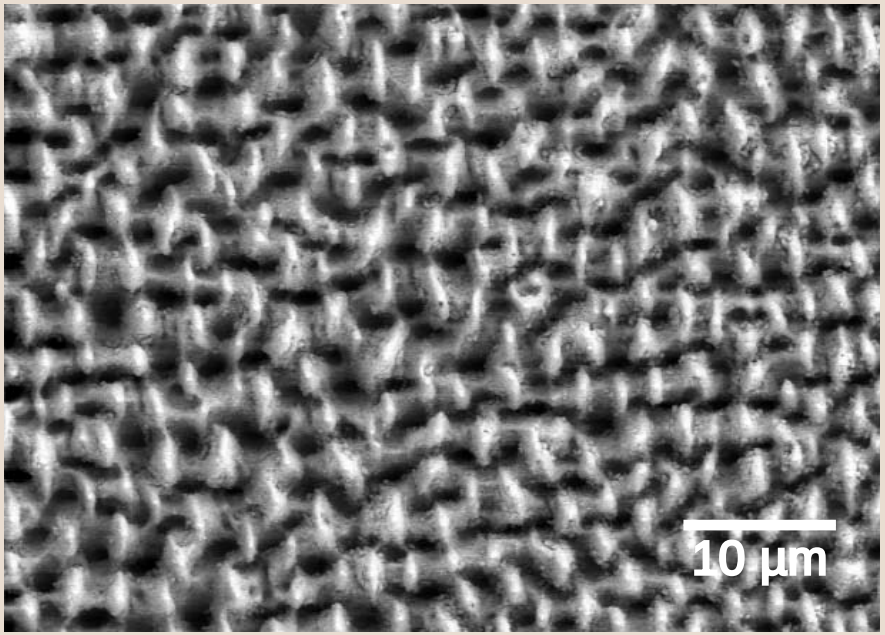
laser polarization



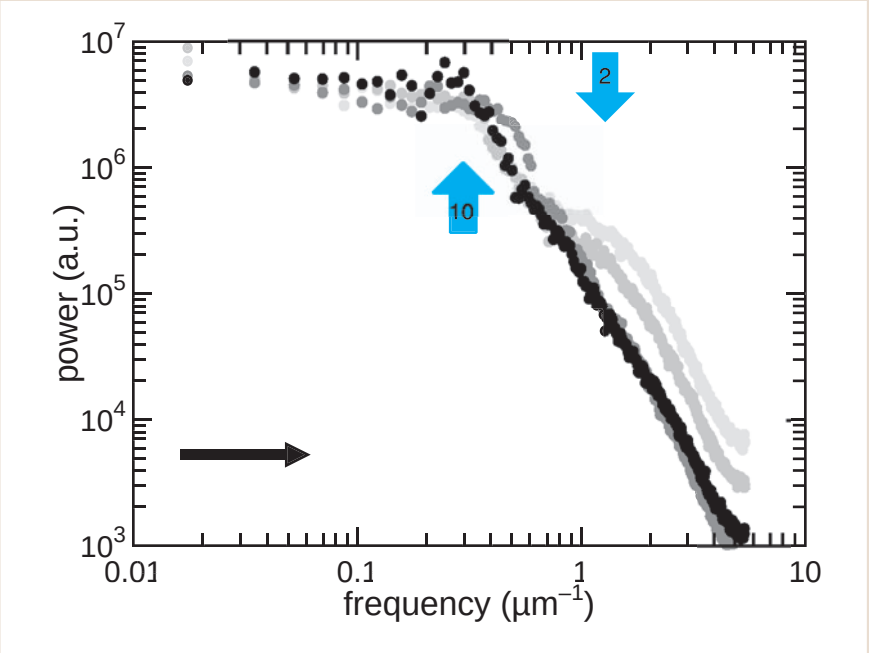


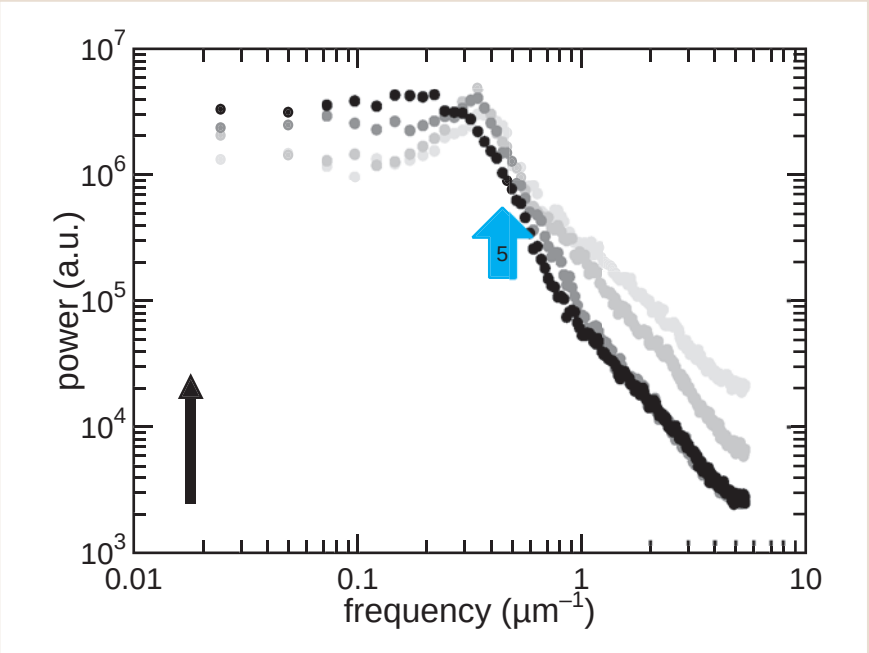
Formation process

SF_6 500 pulses



laser polarization



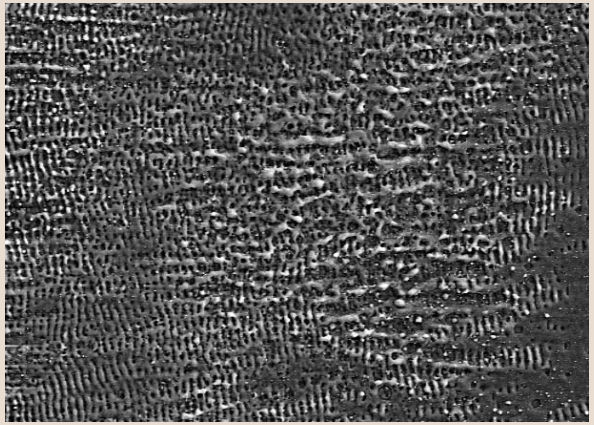


Formation process

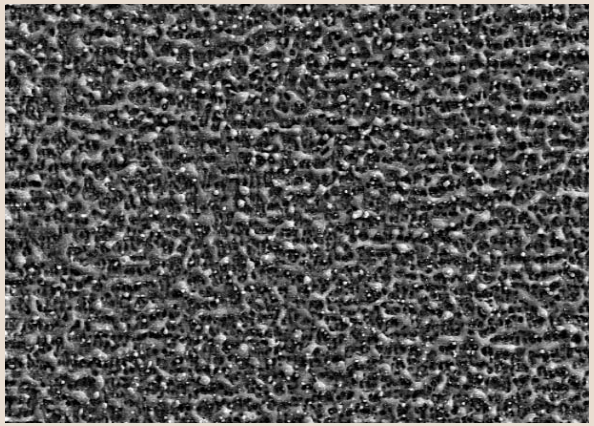
1. **Interference ripples (⊥ to polarization)**

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

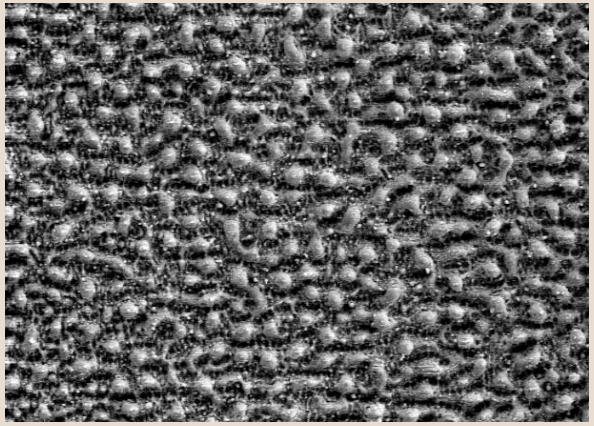
3. **Beads sharpening into spikes**



N = 2



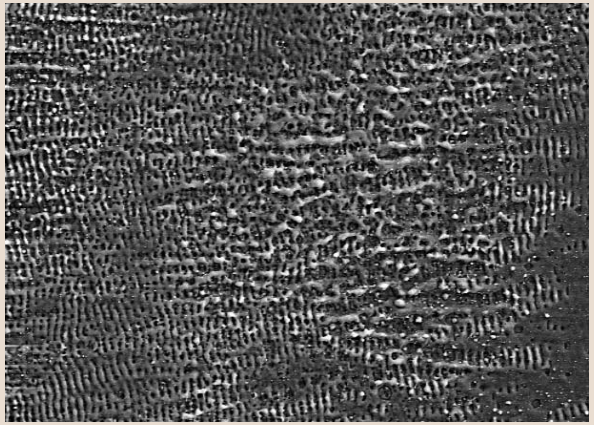
N = 4



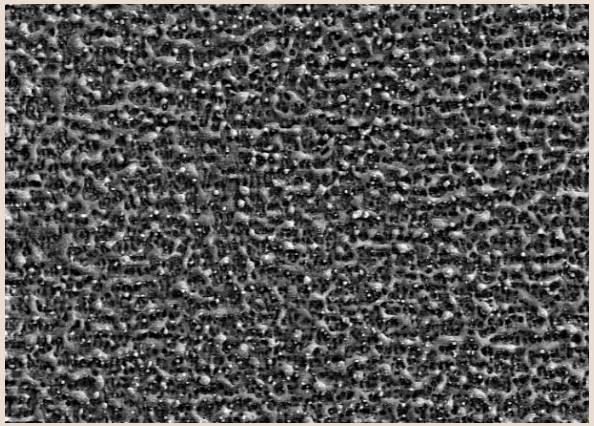
N = 10

Formation process

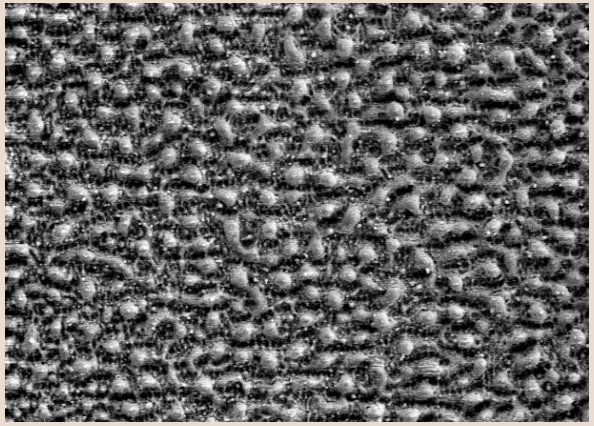
Two distinct wavelengths: ripples and spikes



N = 2



N = 4

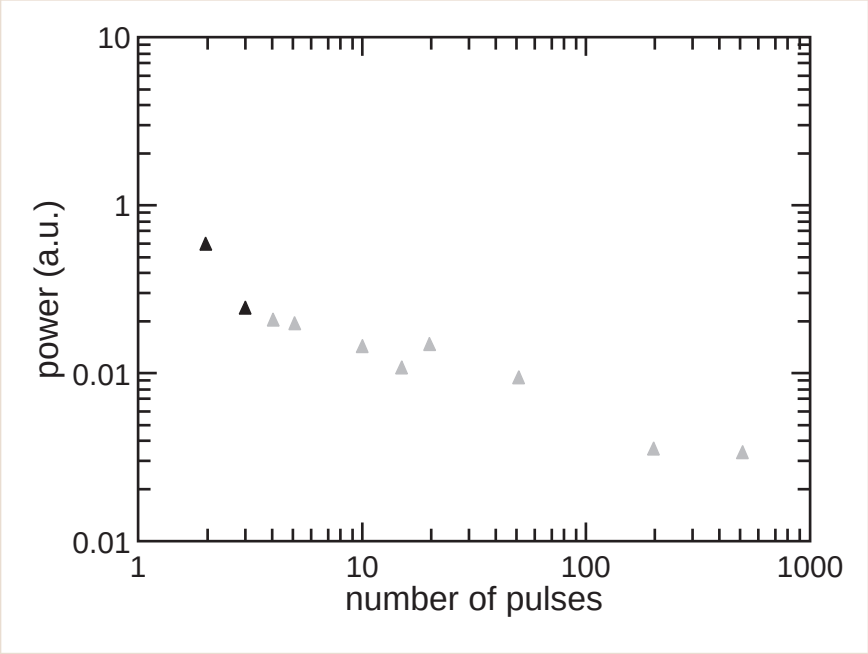


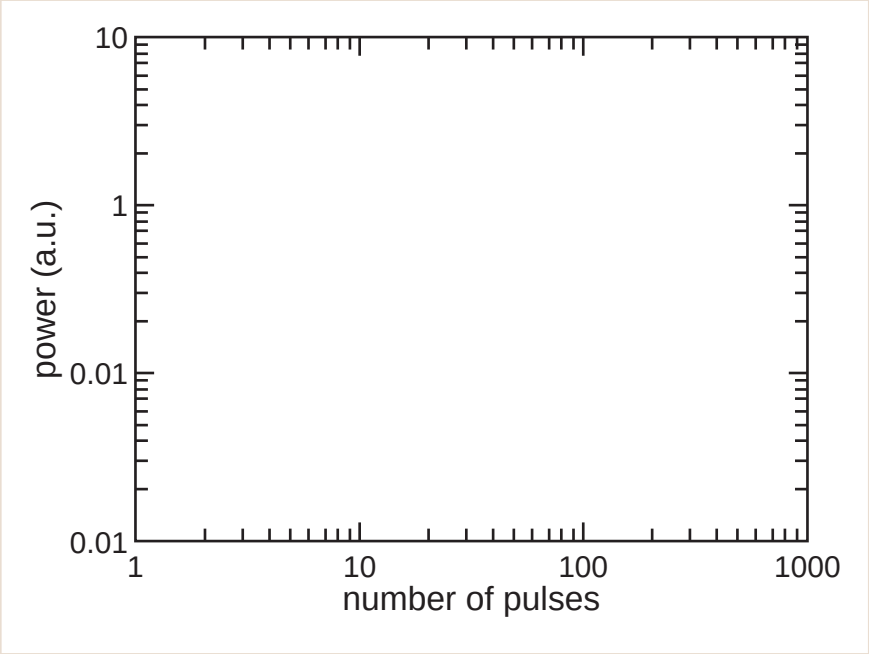
N = 10

Formation process

feature intensities

SF_6 ripples



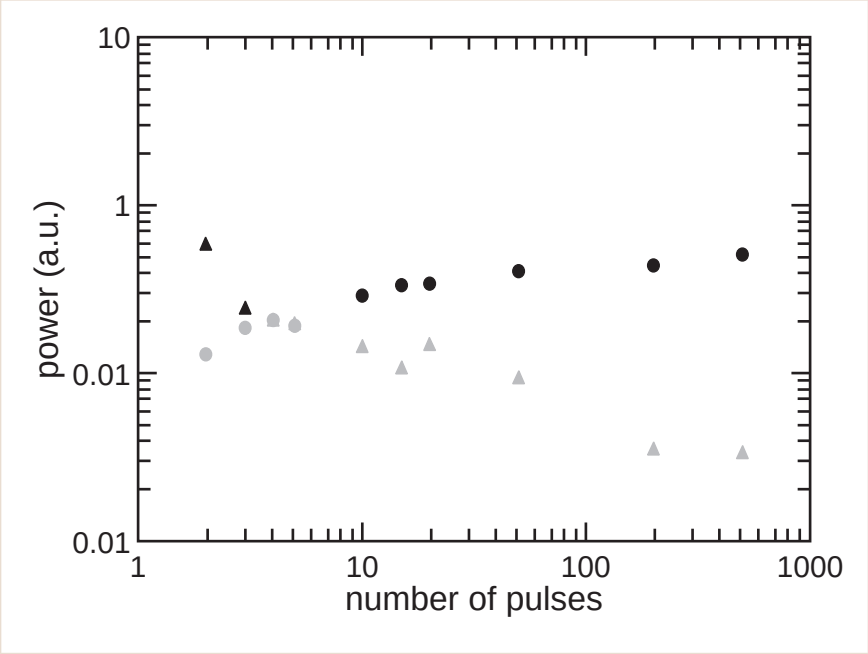


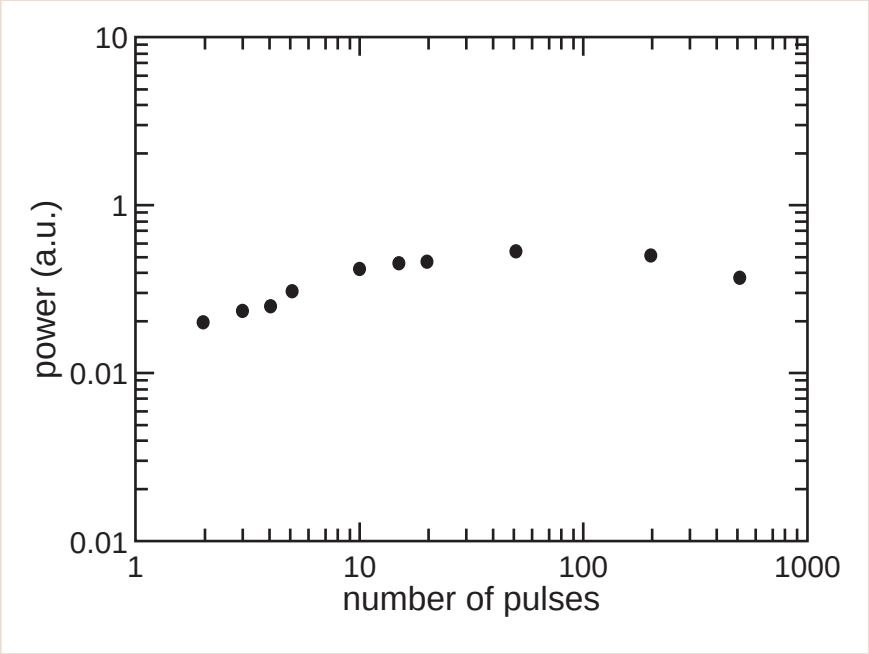
parallel **perpendicular**

Formation process

feature intensities

SF_6 spikes

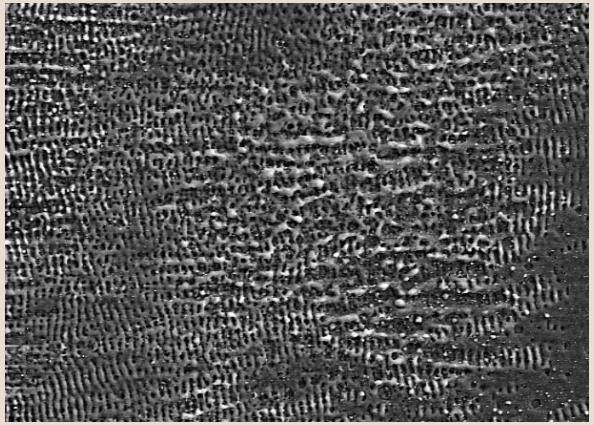




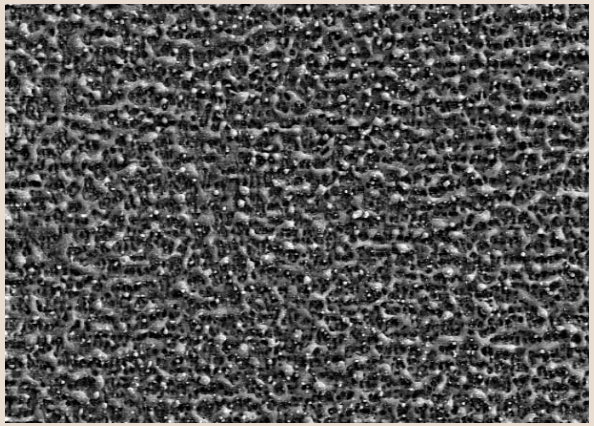
parallel **perpendicular**

Formation process

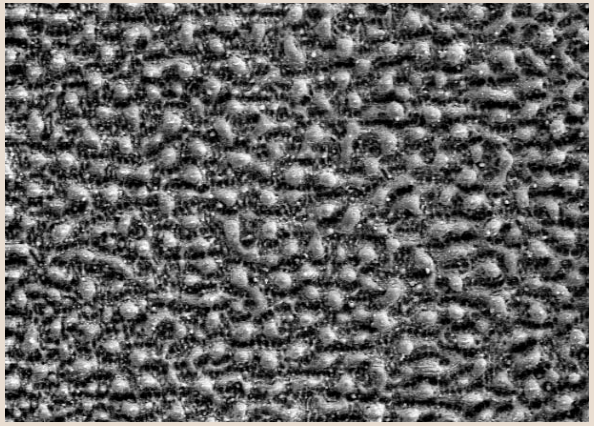
- **spike wavelength appears as ripple wavelength disappears**
- **spike wavelength appears first perpendicular to polarization**



N = 2



N = 4



N = 10

What sets the length scales?

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

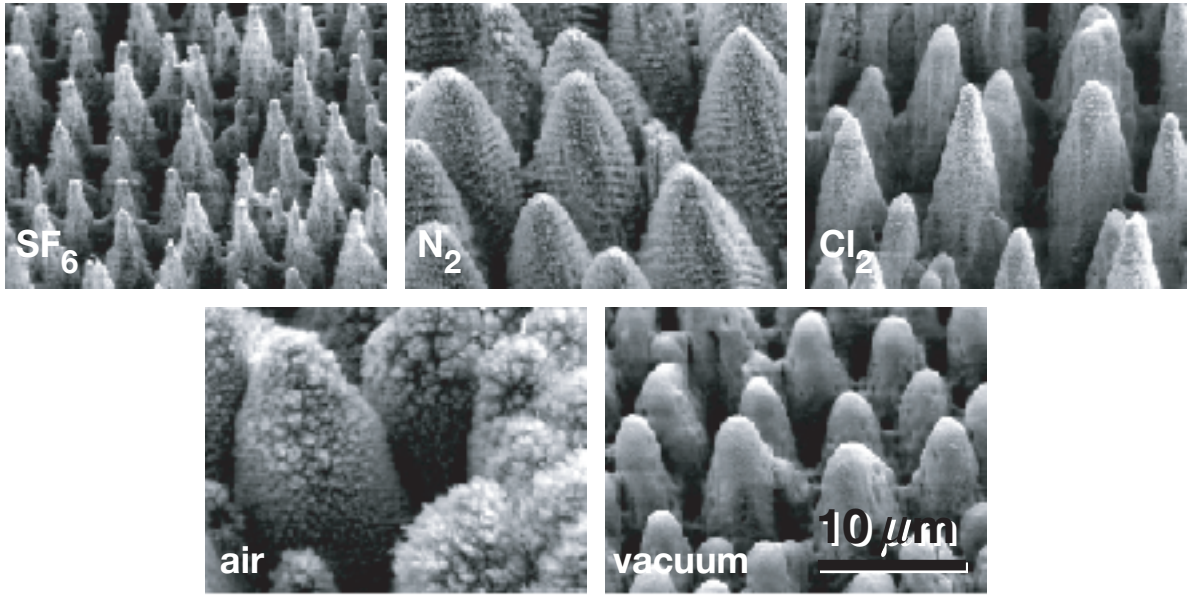
Capillary wavelength set by melt depth, duration

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

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

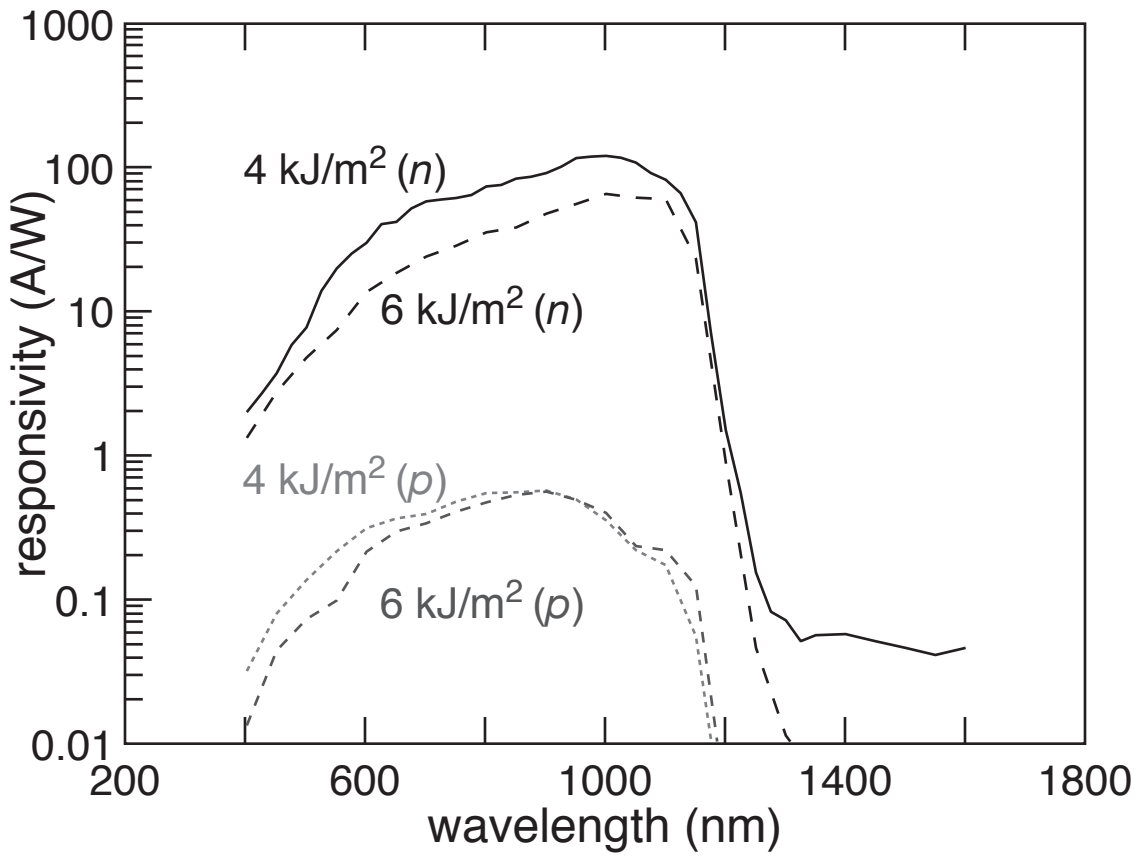
Structural and chemical analysis

microstructured in different gases



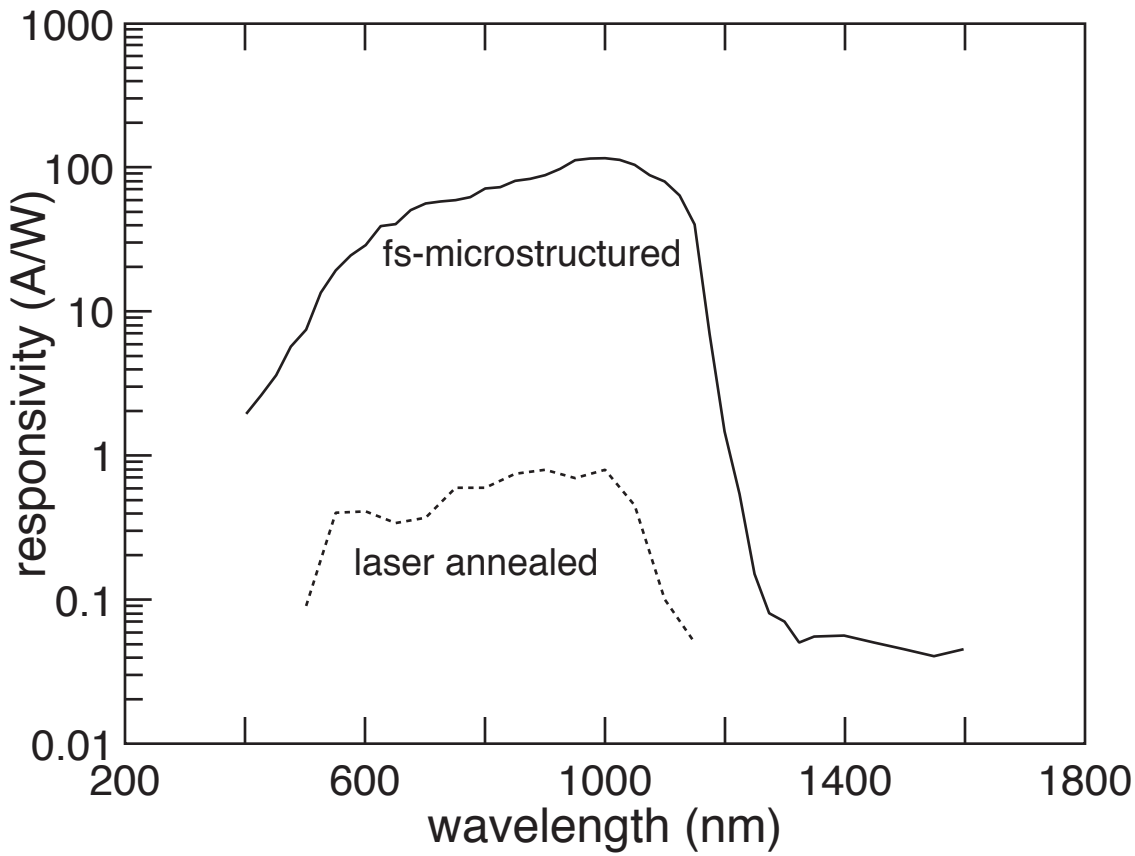
Responsivity

doping



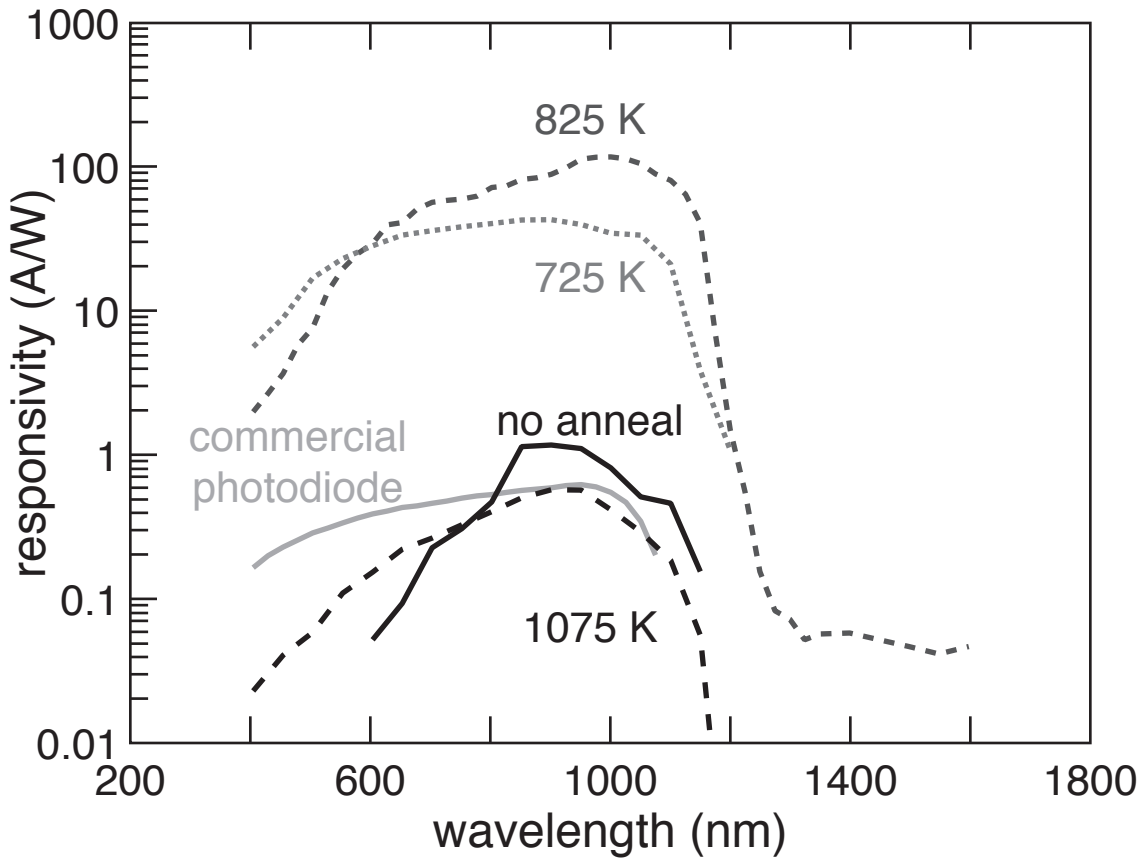
Responsivity

ion implanted/laser annealed



Responsivity

annealing



Responsivity

fluence