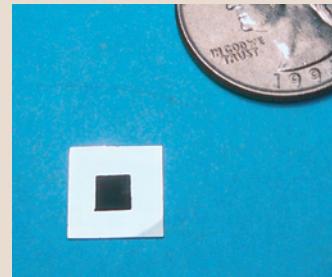


# **Black silicon: Changing structure and properties with light**



**Catherine H. Crouch  
Swarthmore College**

**Haverford & Bryn Mawr Colleges  
1 March 2004**

**work done at  
Harvard University**



**Eric Mazur**



**Jim Carey**



**Mike Sheehy**

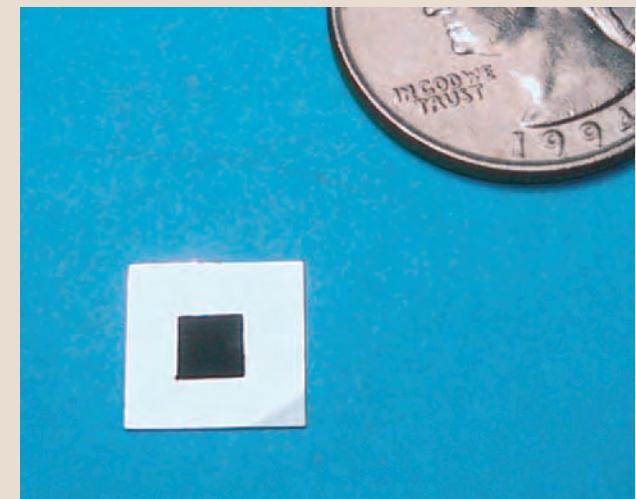
**1. What is black silicon?**

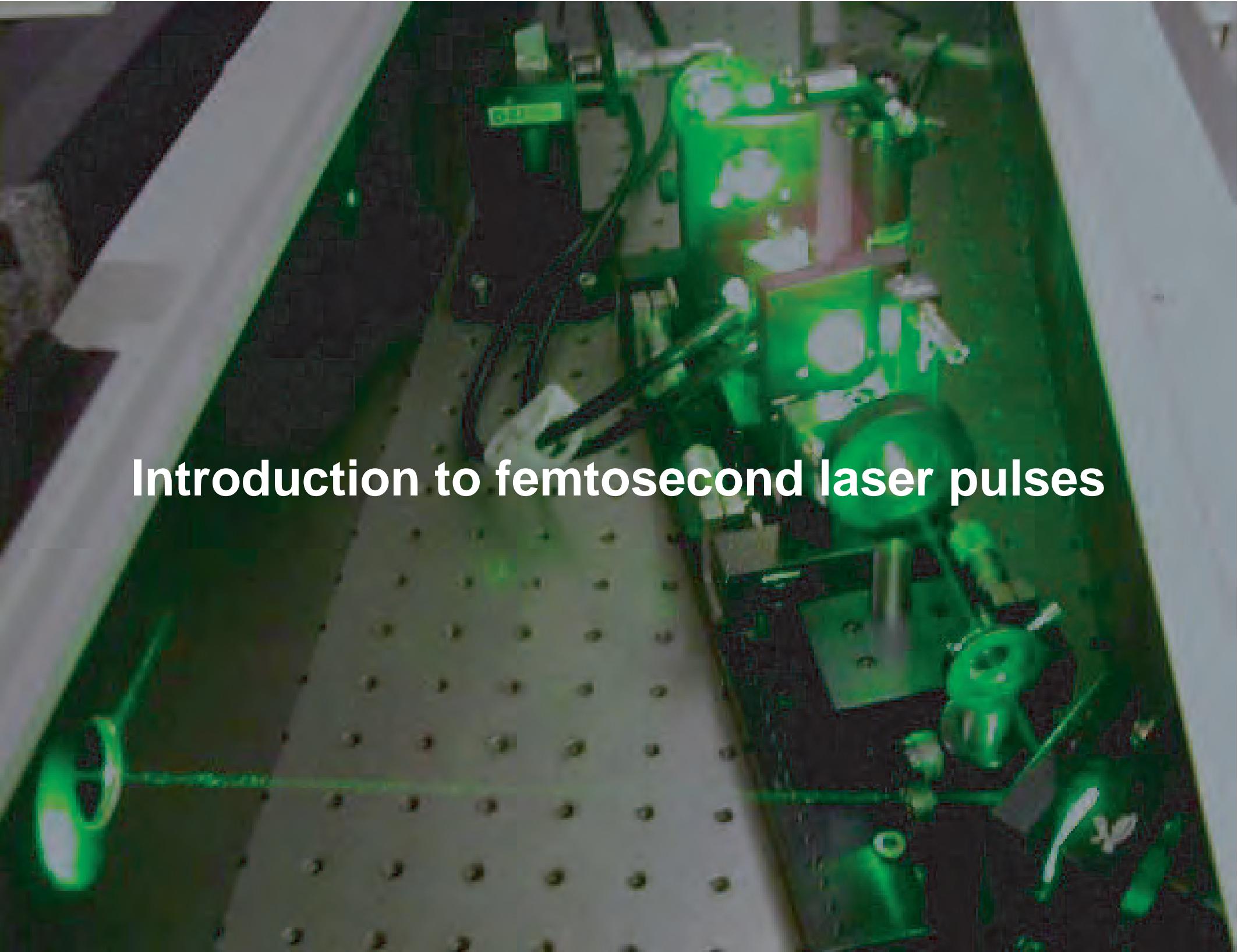
**2. Why is it black?**

**3. How does it get that way?**

**Study effect of extremely intense laser pulses**

**Develop novel materials**



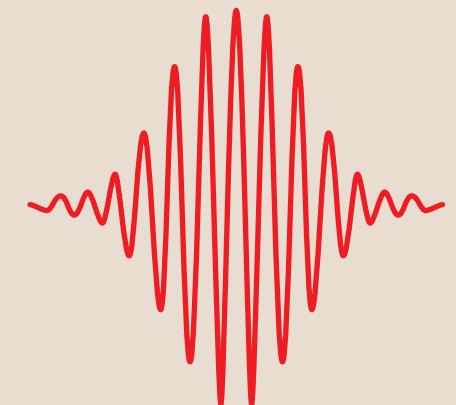


# Introduction to femtosecond laser pulses

# *Femtosecond laser pulses*

## **800 nm, 100 fs laser pulses**

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

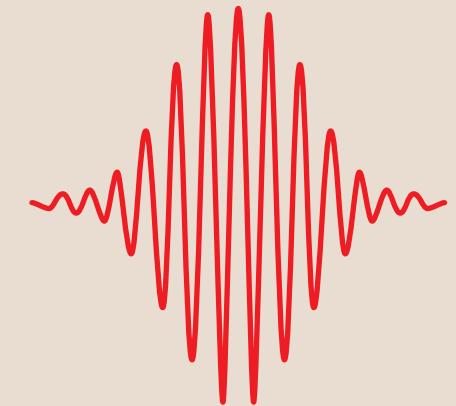


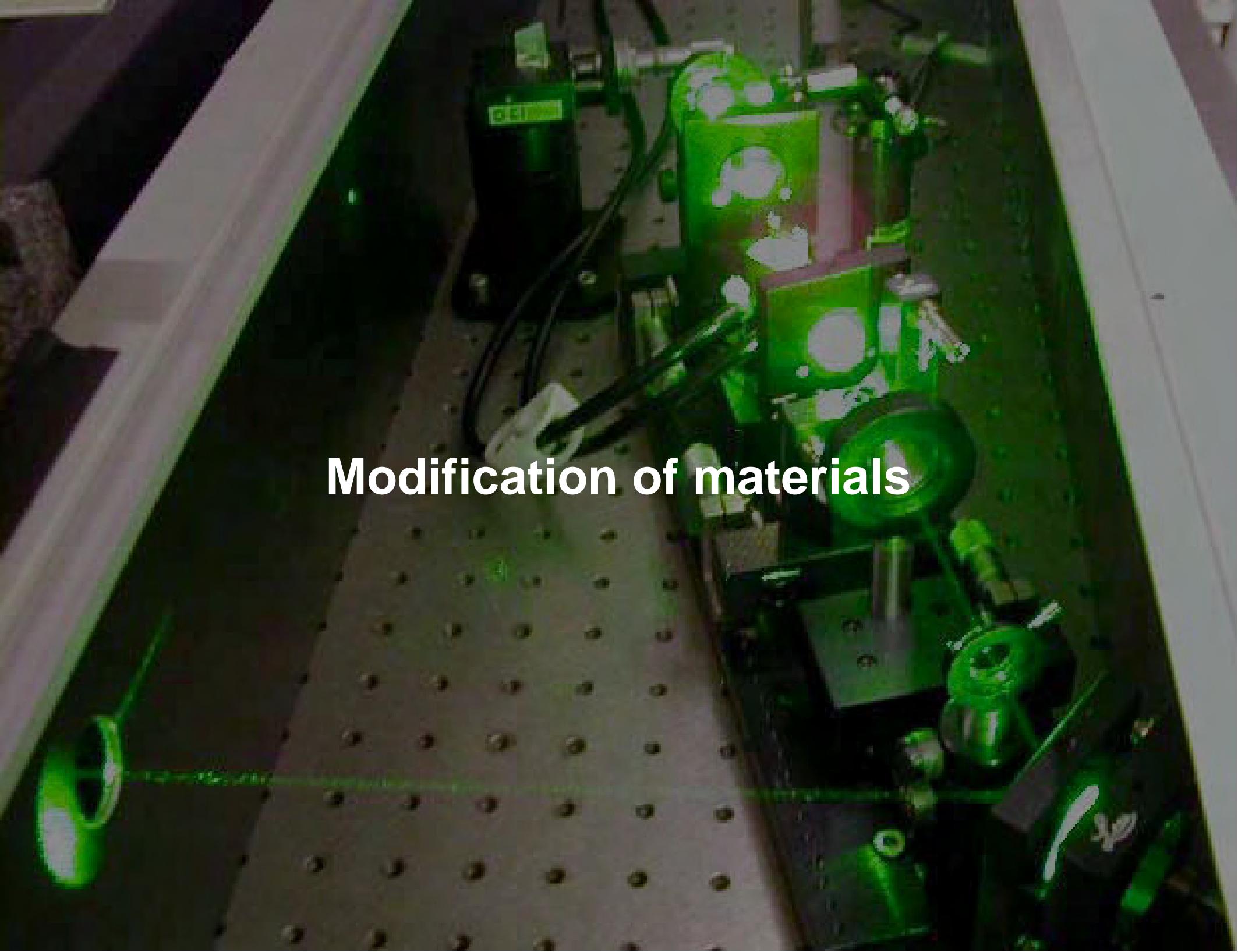
## **Extremely high peak power and intensity**

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

## Uses of fs laser pulses

- ▶ study time-dependent processes
- ▶ control of atoms and molecules
- ▶ material modification

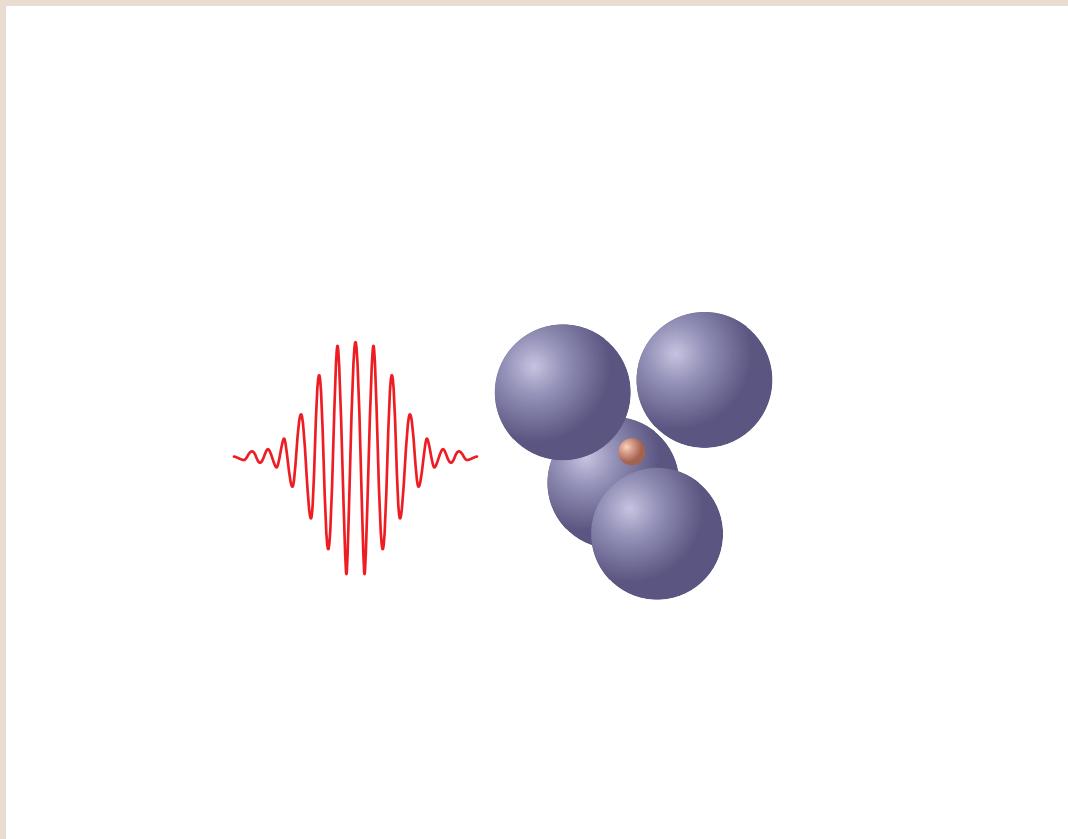




# Modification of materials

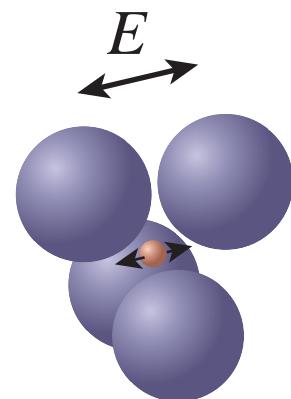
# *Modification of materials*

## light-matter interactions



# *Modification of materials*

**temporary effect on material**

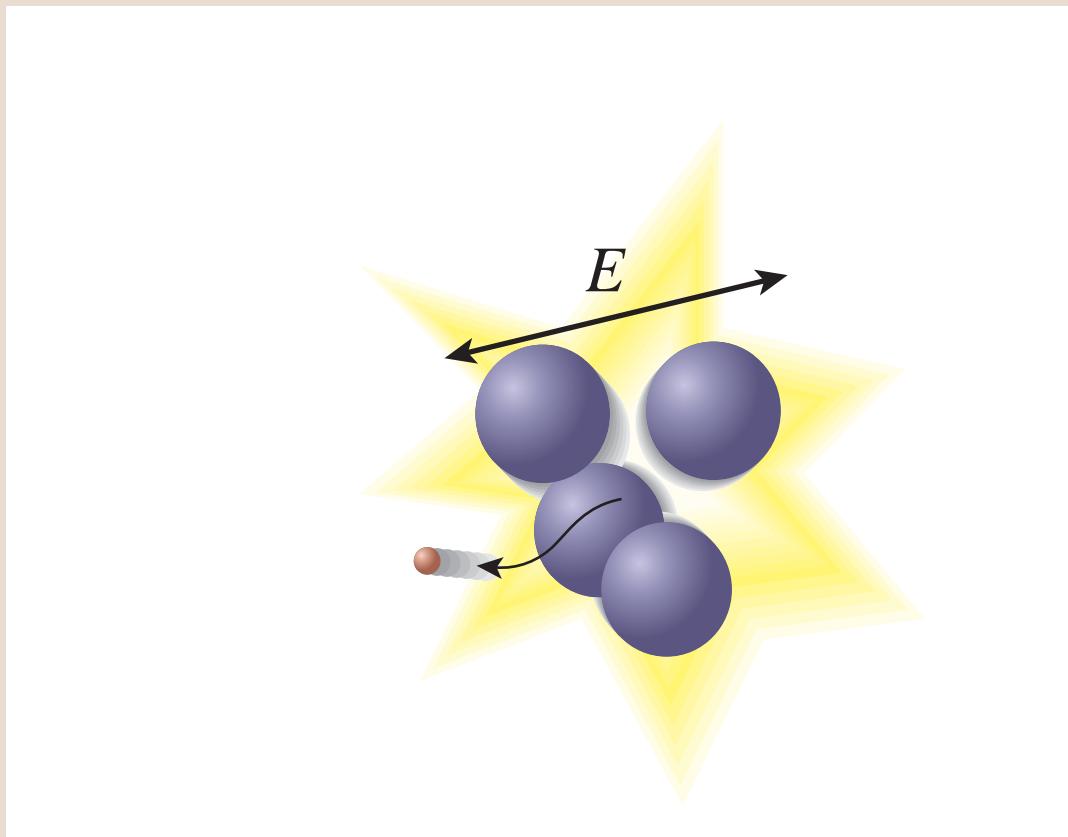


$$\vec{P} = \chi \vec{E}$$

$\chi$  is constant

# *Modification of materials*

**permanent change to material**

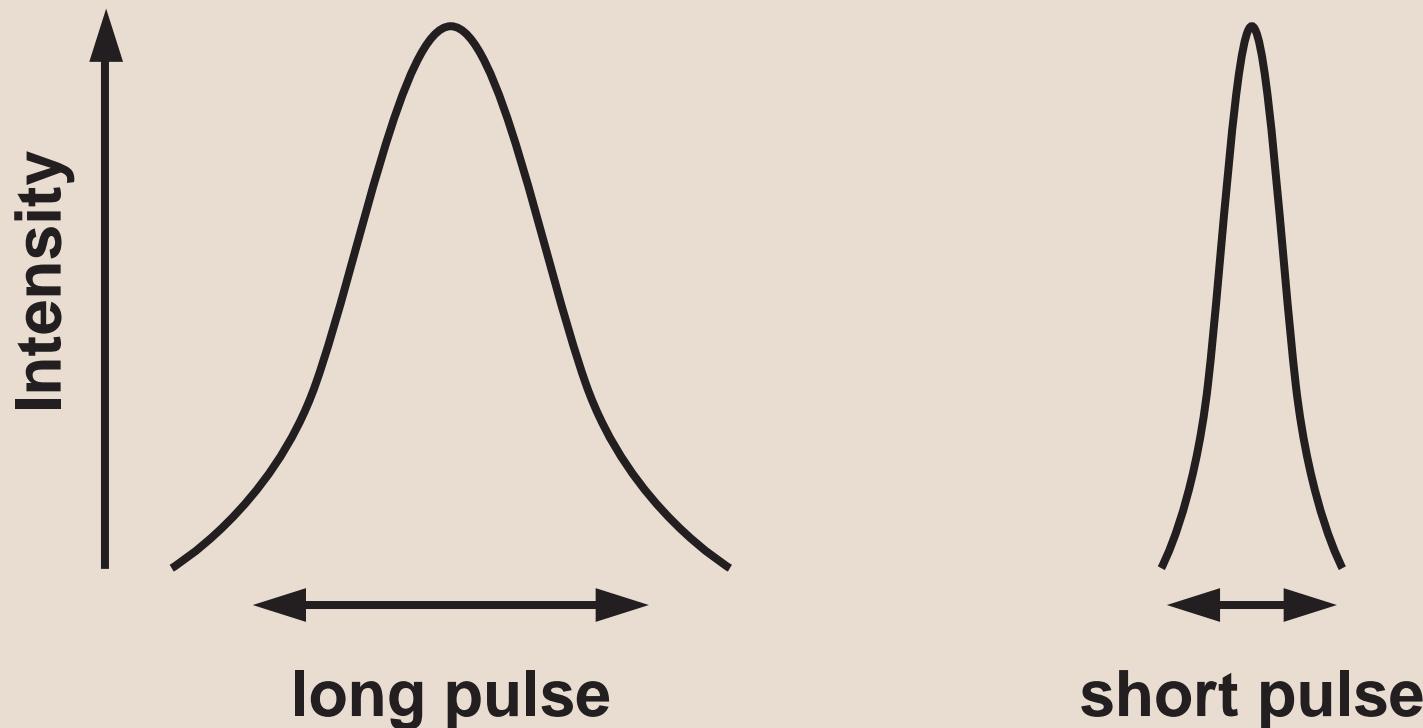


**plasma formation**

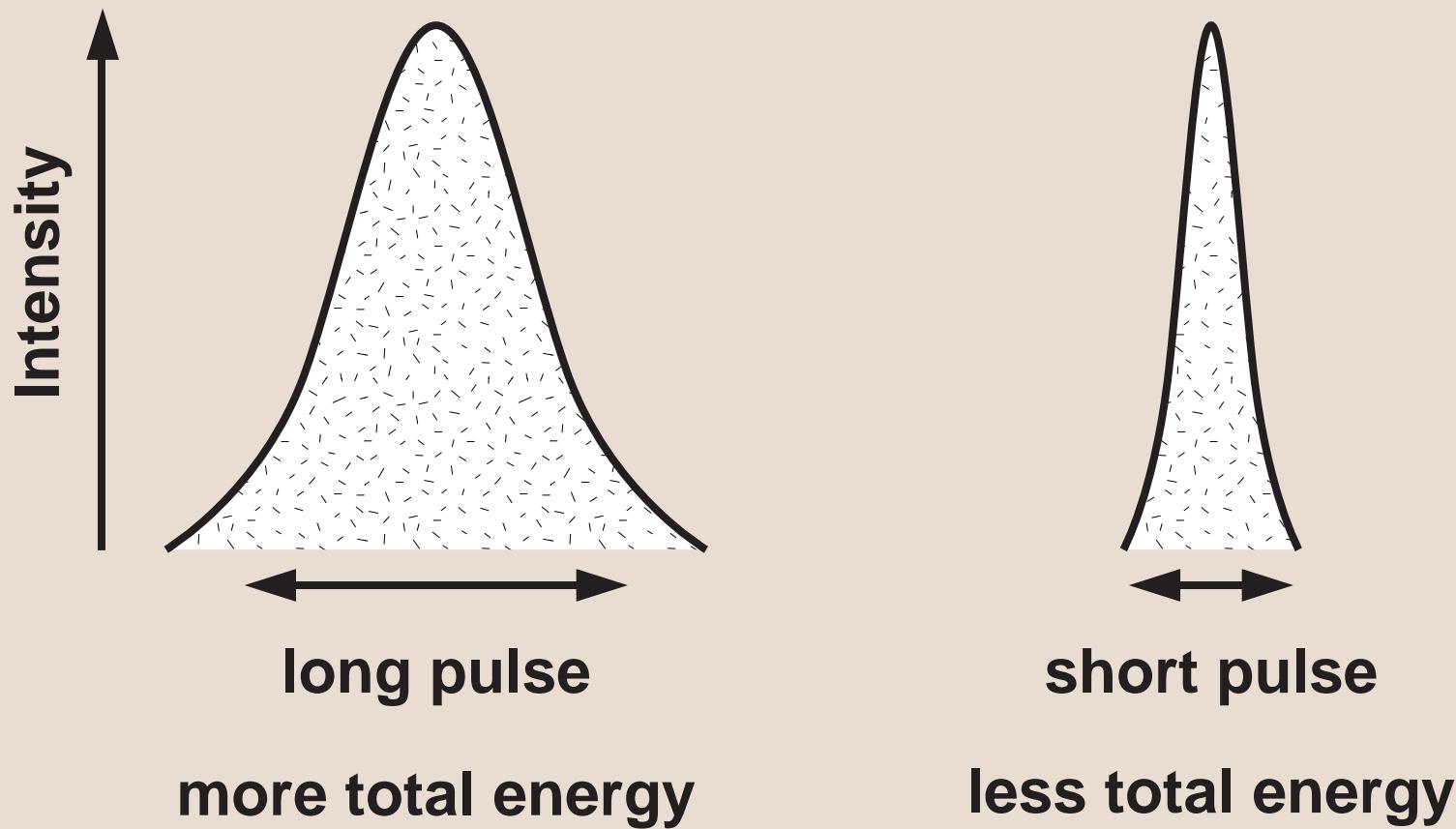
# *Modification of materials*

**focused fs pulses: precise material modification**

For the same peak intensity

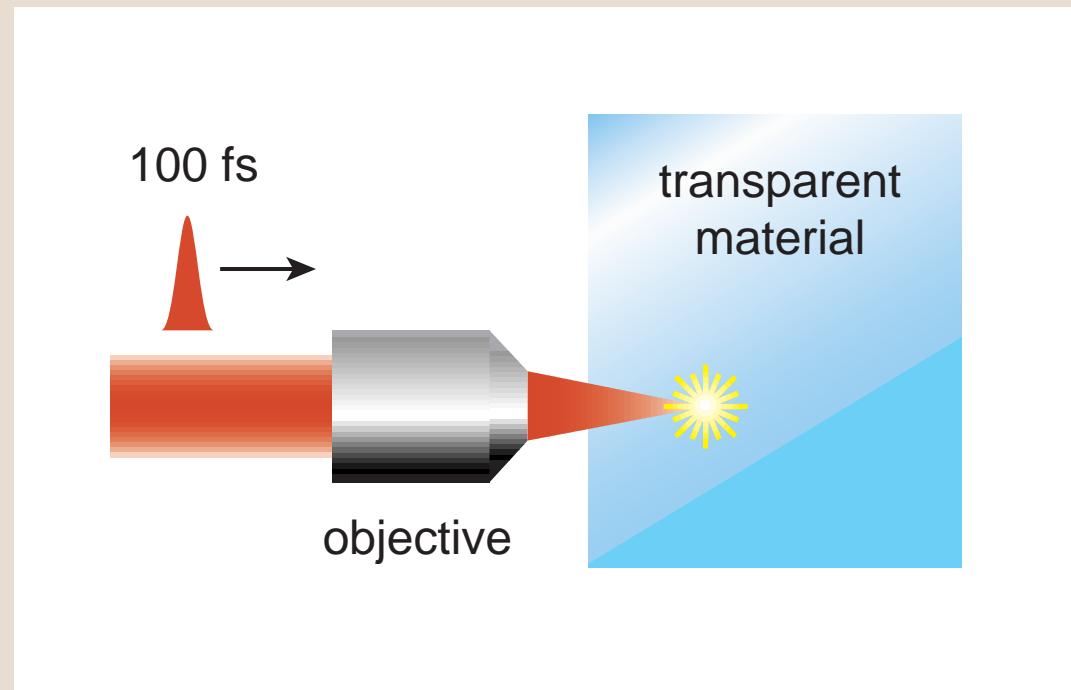


**For the same peak intensity**



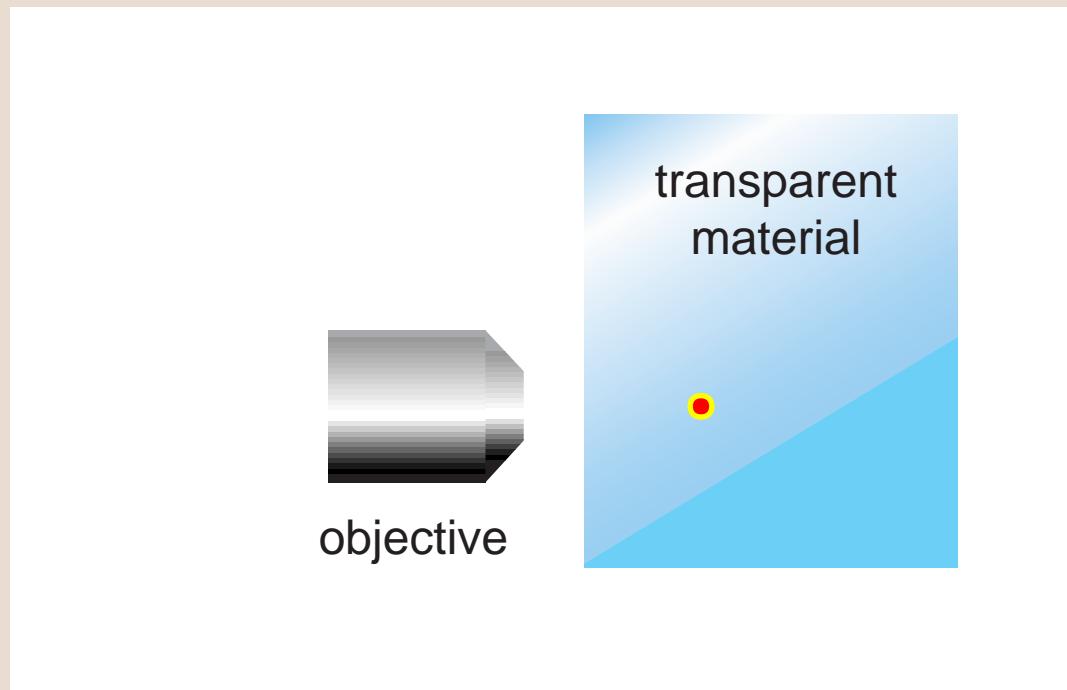
# *Modification of materials*

**tightly focus beam inside bulk glass**



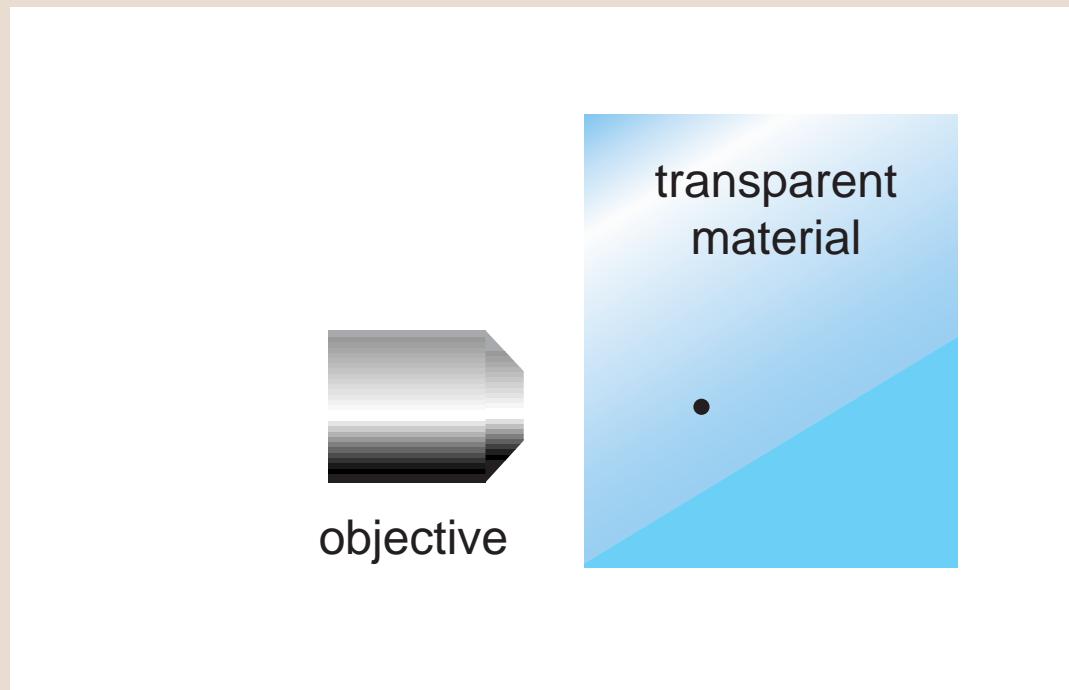
# *Modification of materials*

**energy is deposited in the focal volume**

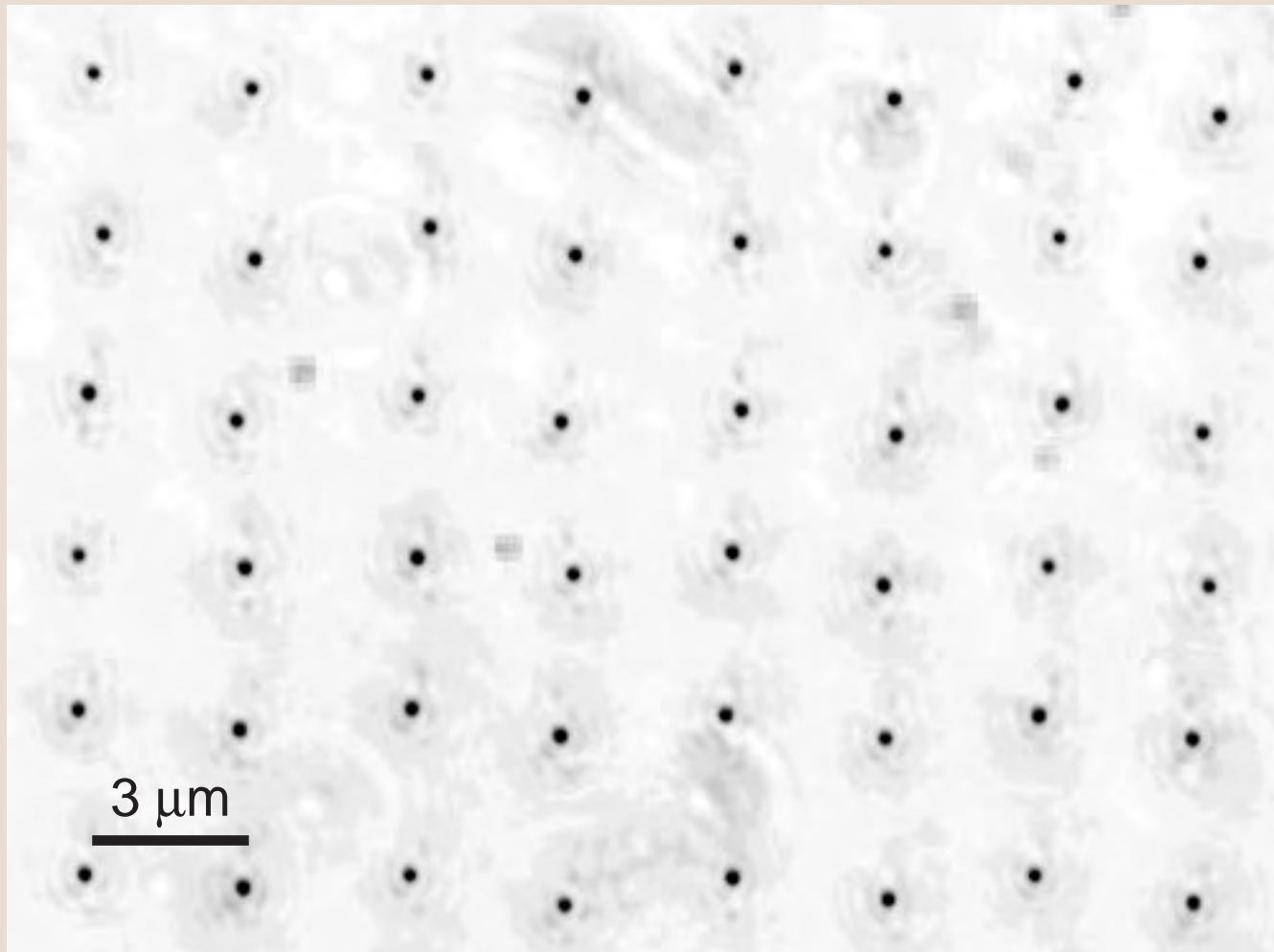


# *Modification of materials*

**producing microscopic bulk damage**



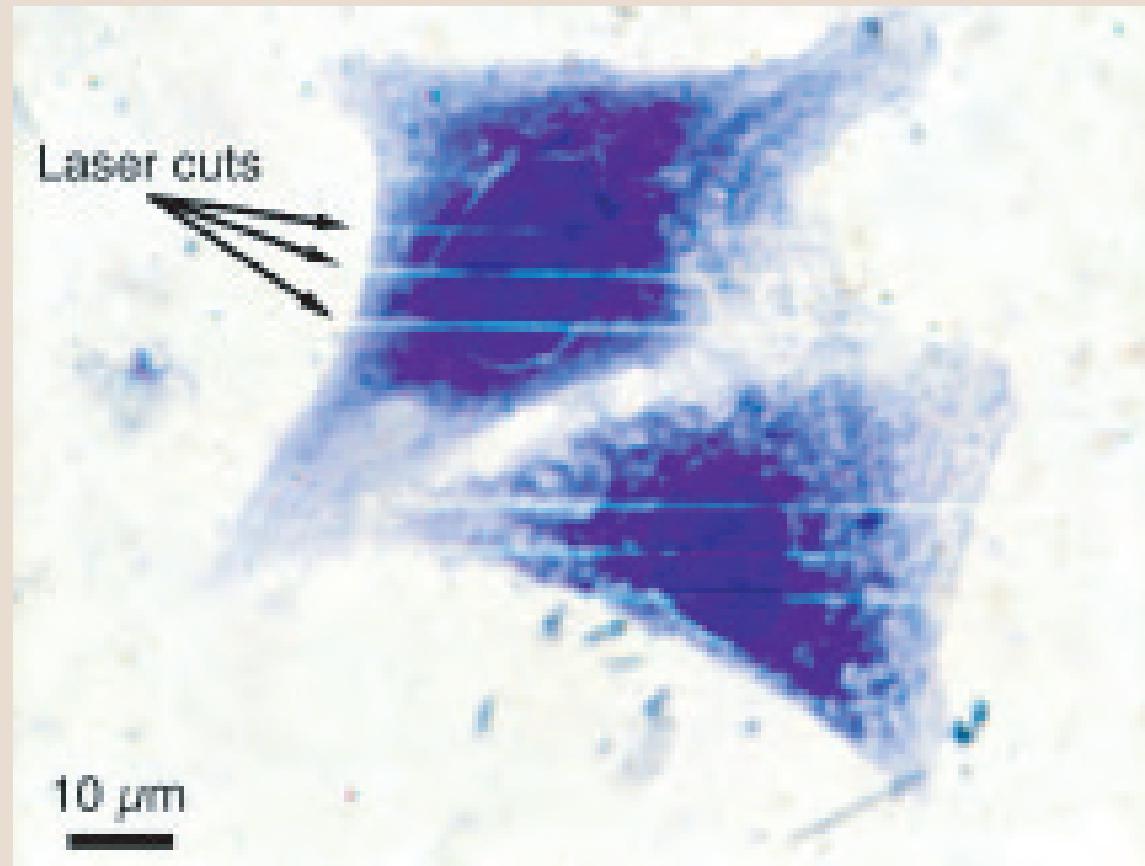
# *Modification of materials*



40 nJ  
100 fs  
800 nm  
0.65 NA  
Corning 0211

**top view**

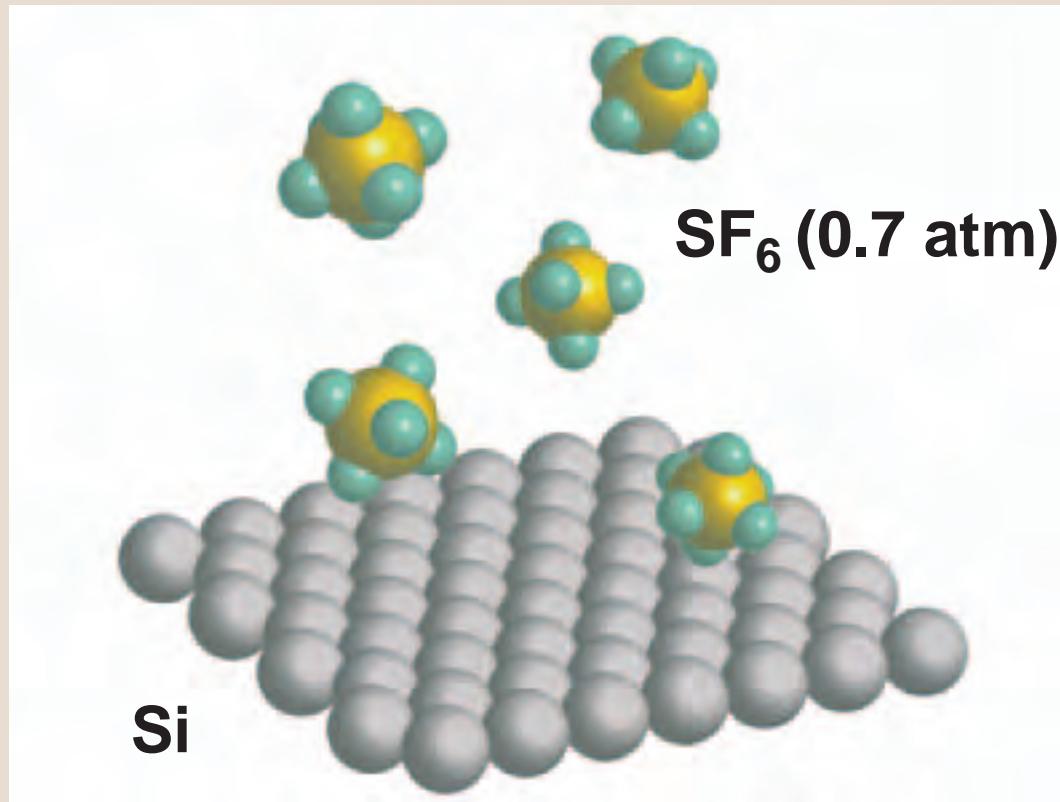
## **laser cuts through single cell**



Shen *et al.*, in press.

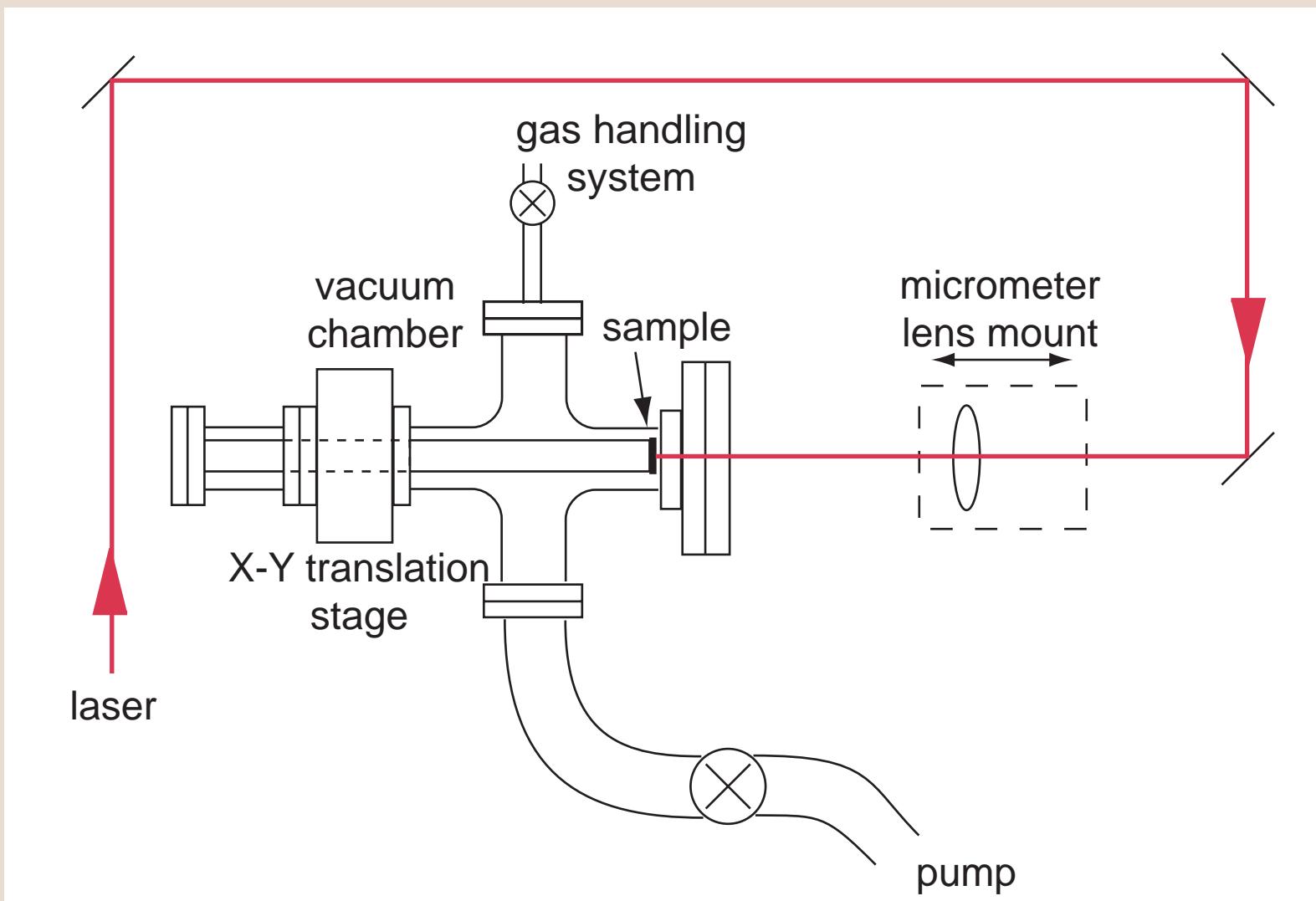
## **Opaque material, broader focus:**

- ▶ laser energy deposited at surface
- ▶ ablation: material removed
- ▶ as material equilibrates, melted layer forms then solidifies

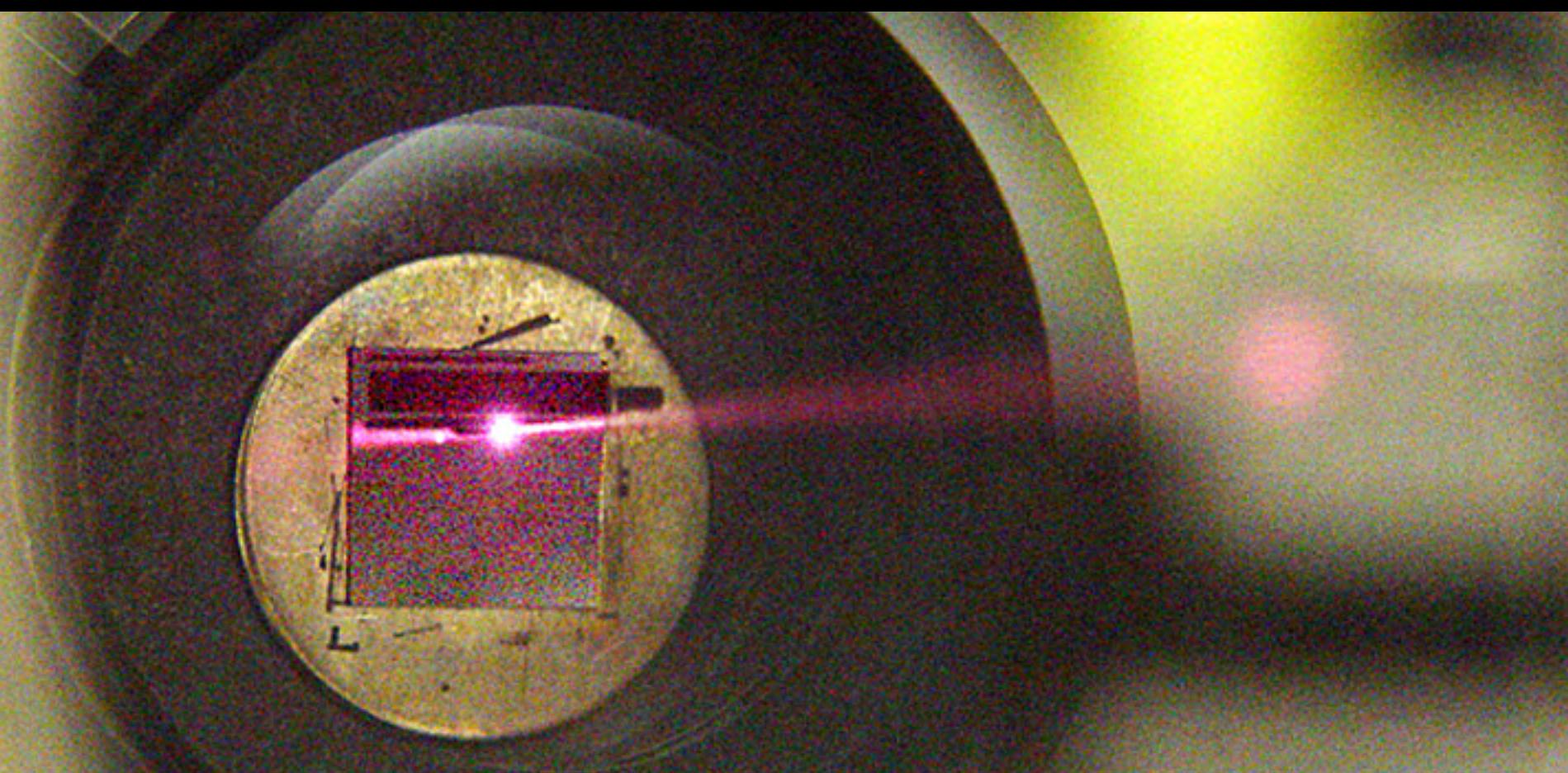


**irradiate surface with femtosecond laser pulses  
(800 nm, 100 fs, 500 pulses, 10 kJ/m<sup>2</sup>)**

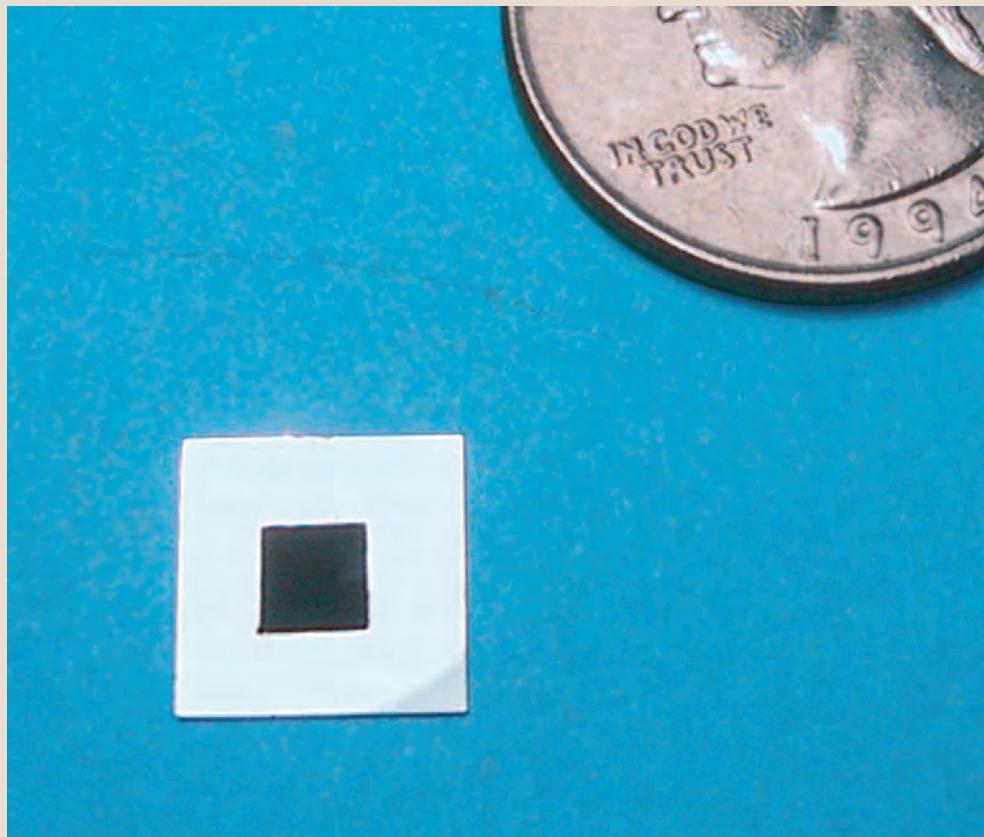
# *Black silicon*



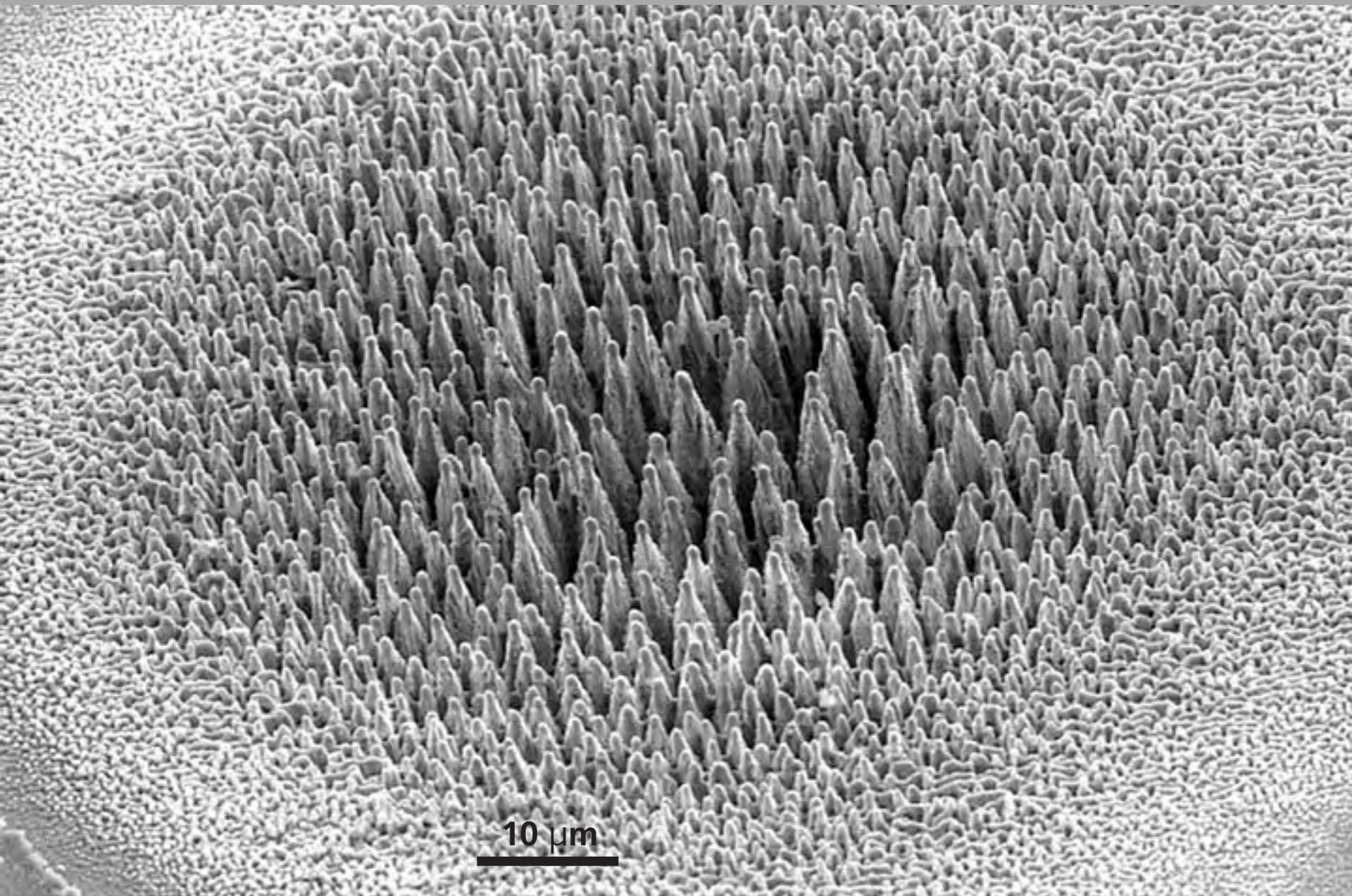
# Black silicon



# *Black silicon*

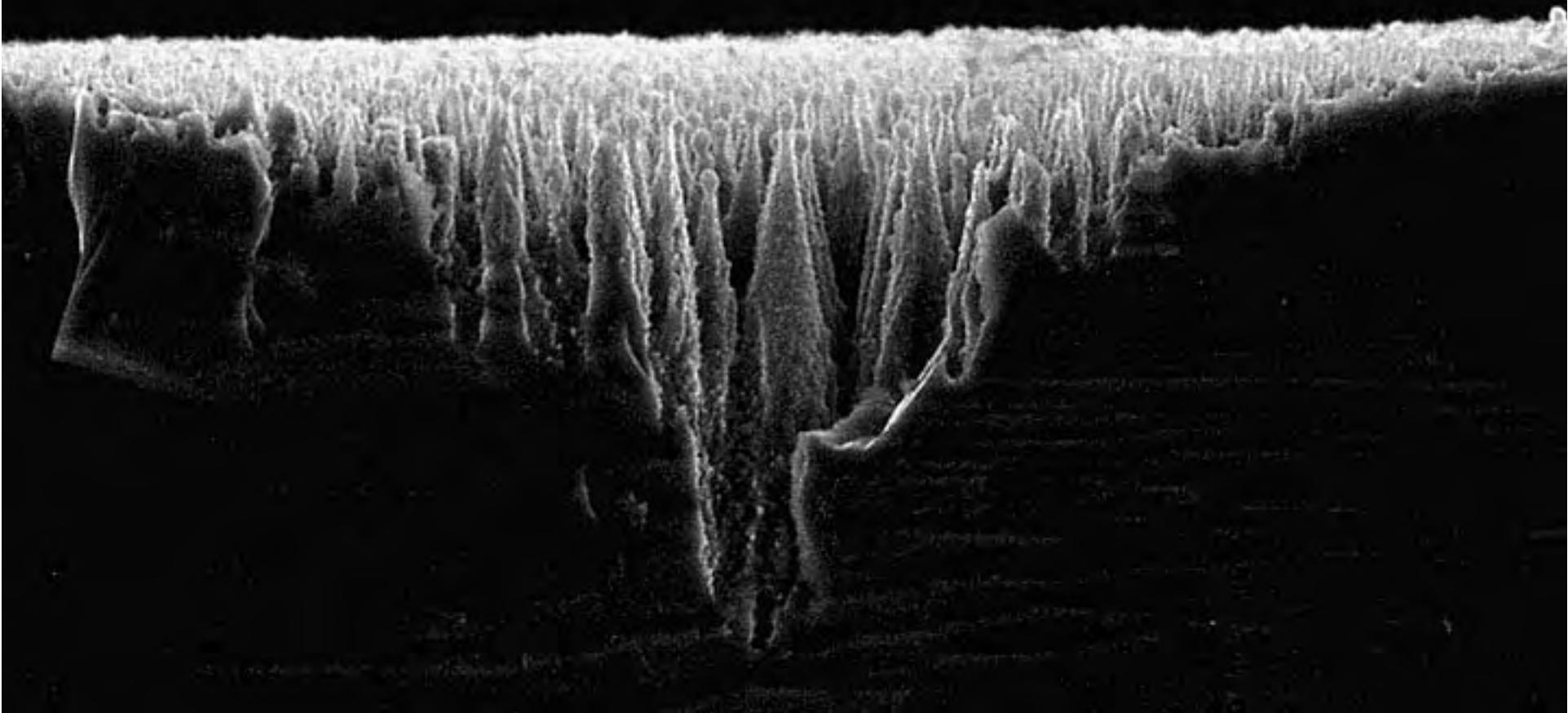


*Black silicon*



10  $\mu\text{m}$

*Black silicon*



**Why does this happen?**

**Is this new material useful?**

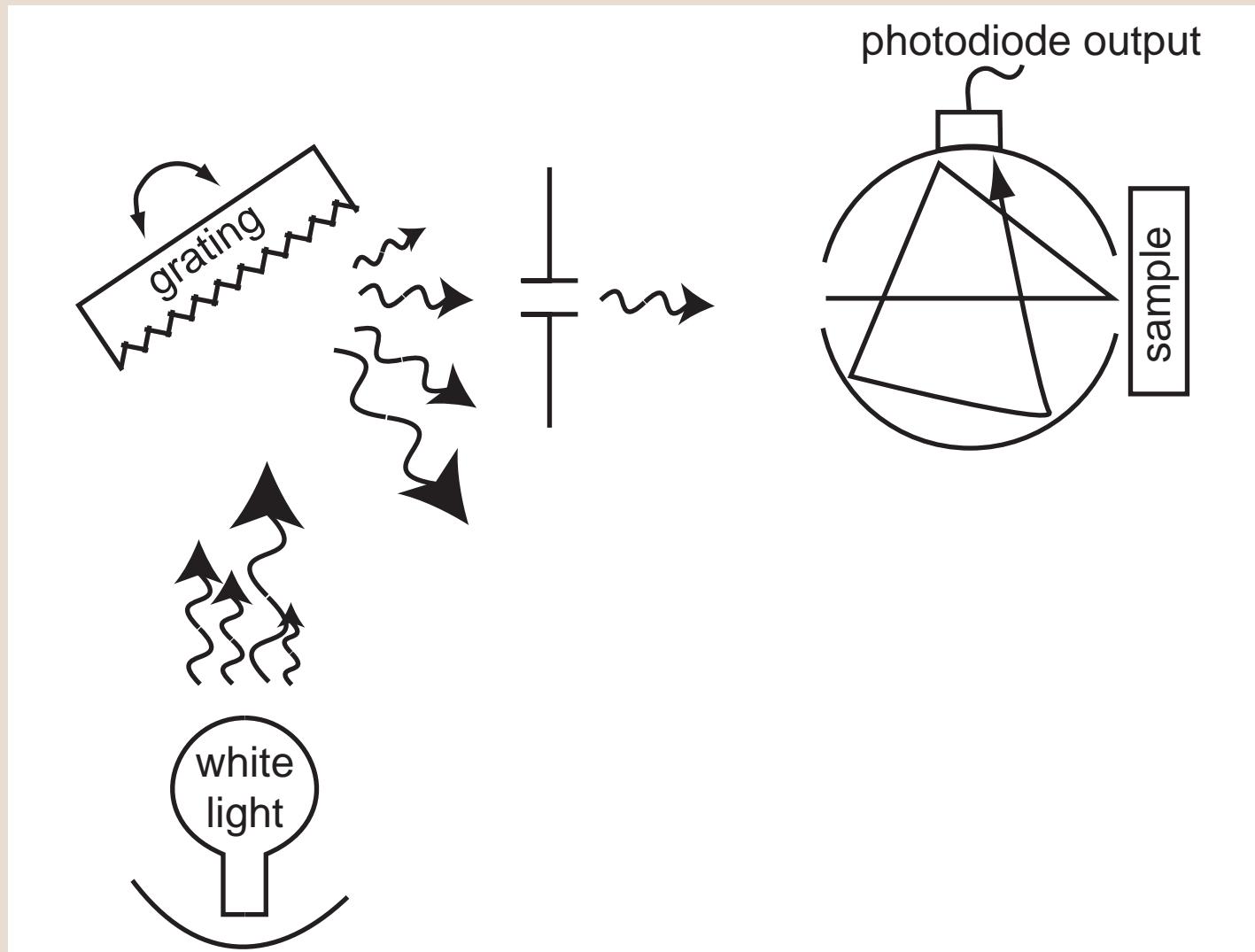
*Black silicon*

Optical properties

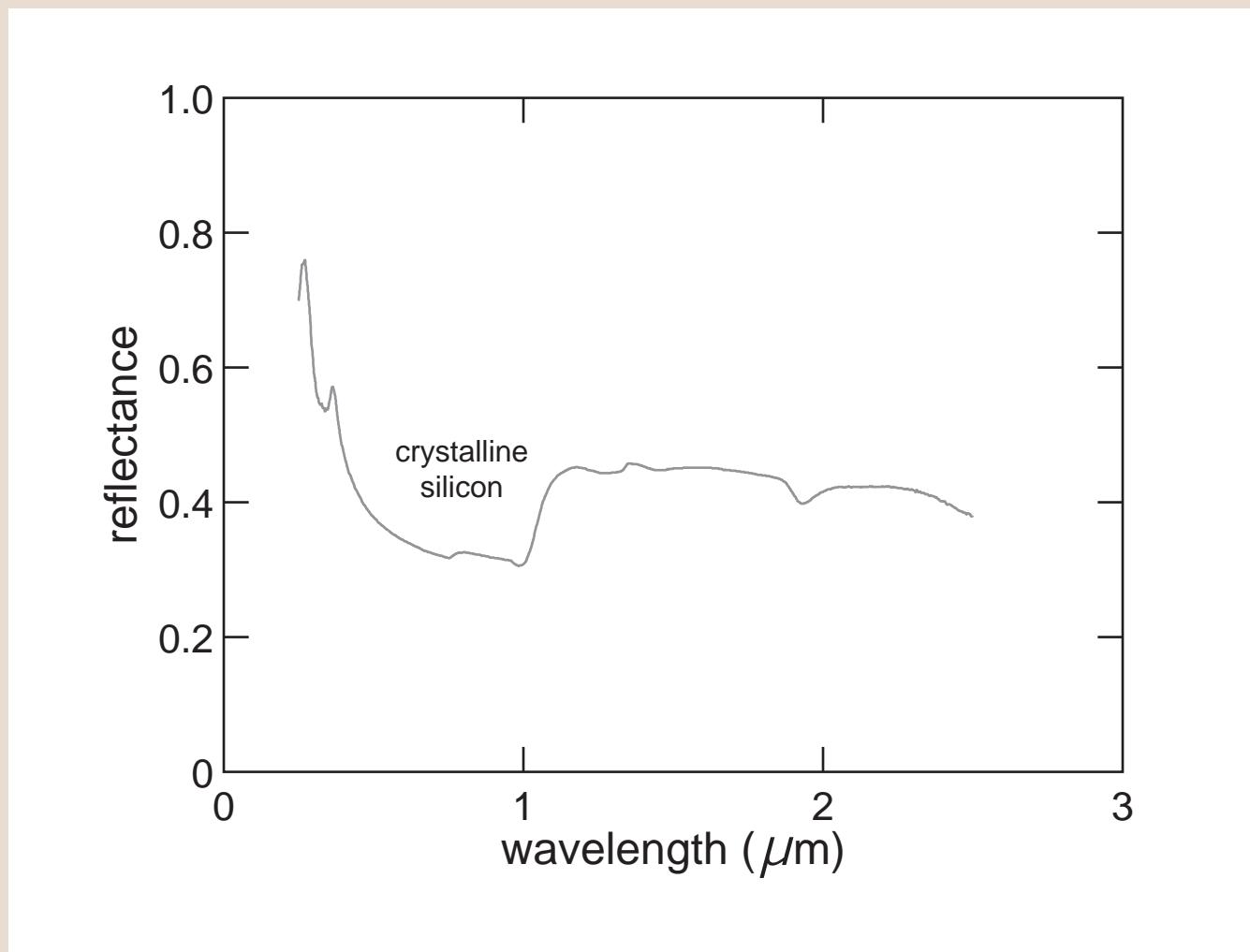
3  $\mu\text{m}$

# *Optical properties*

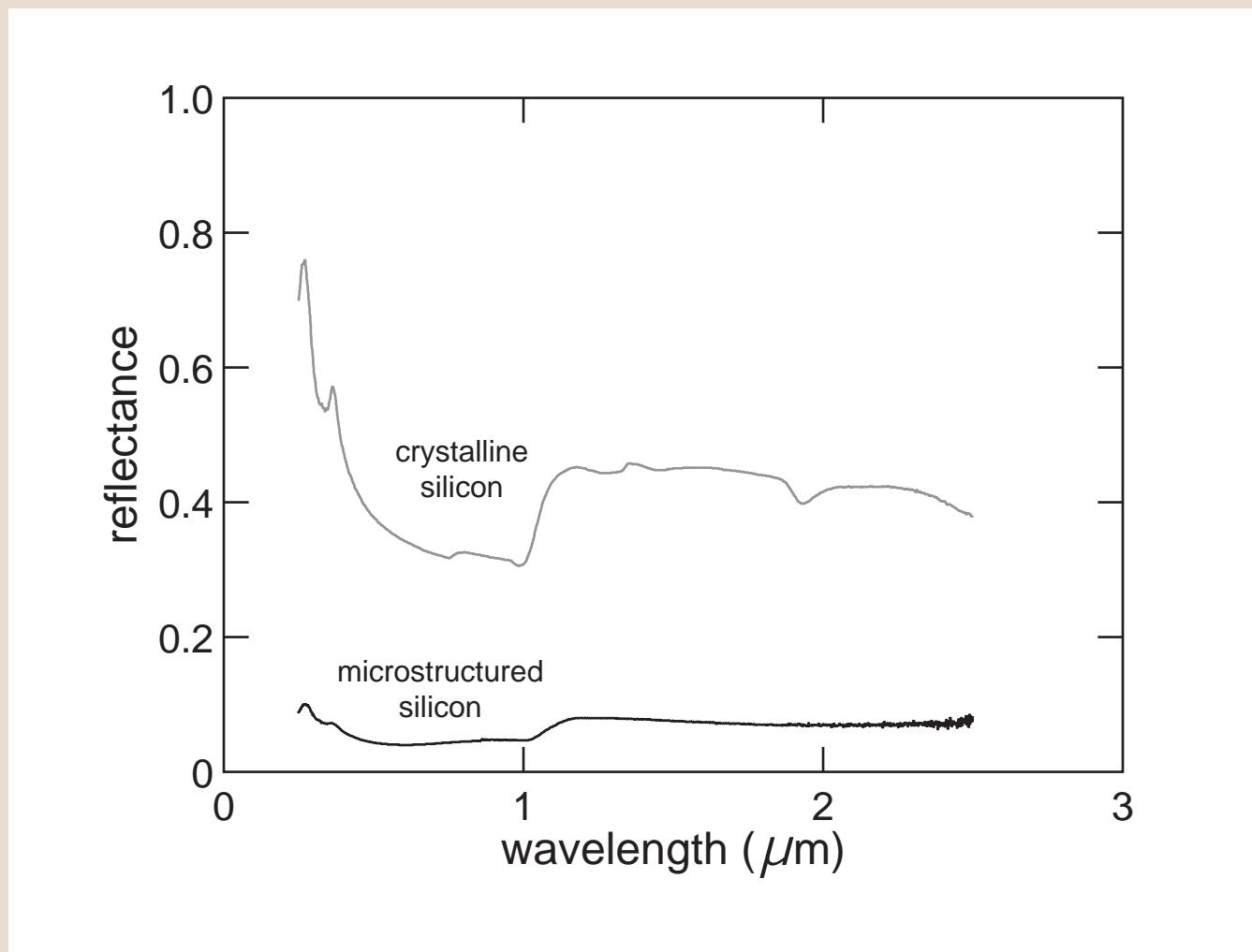
measure reflectance, transmittance with integrating sphere



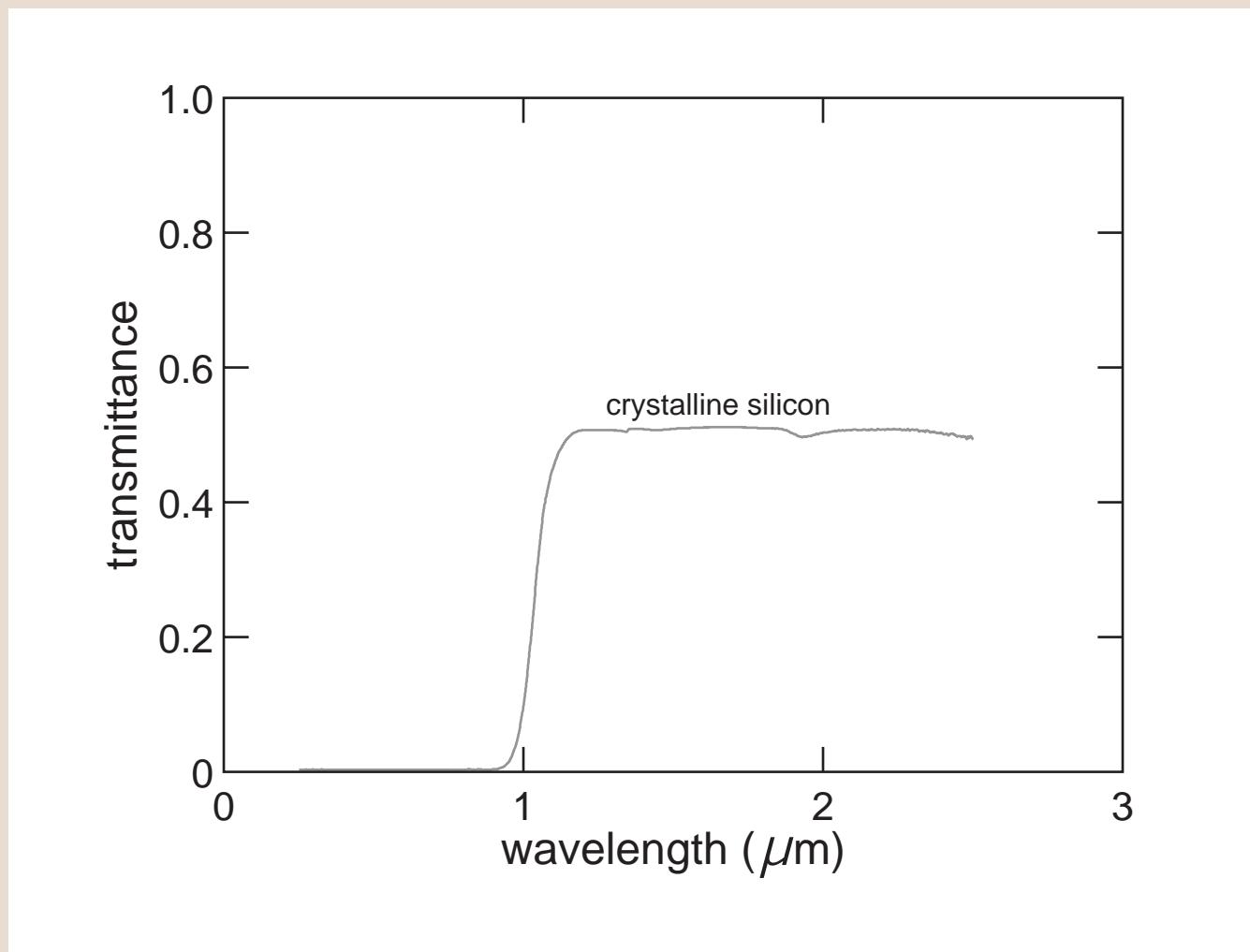
## reflectance



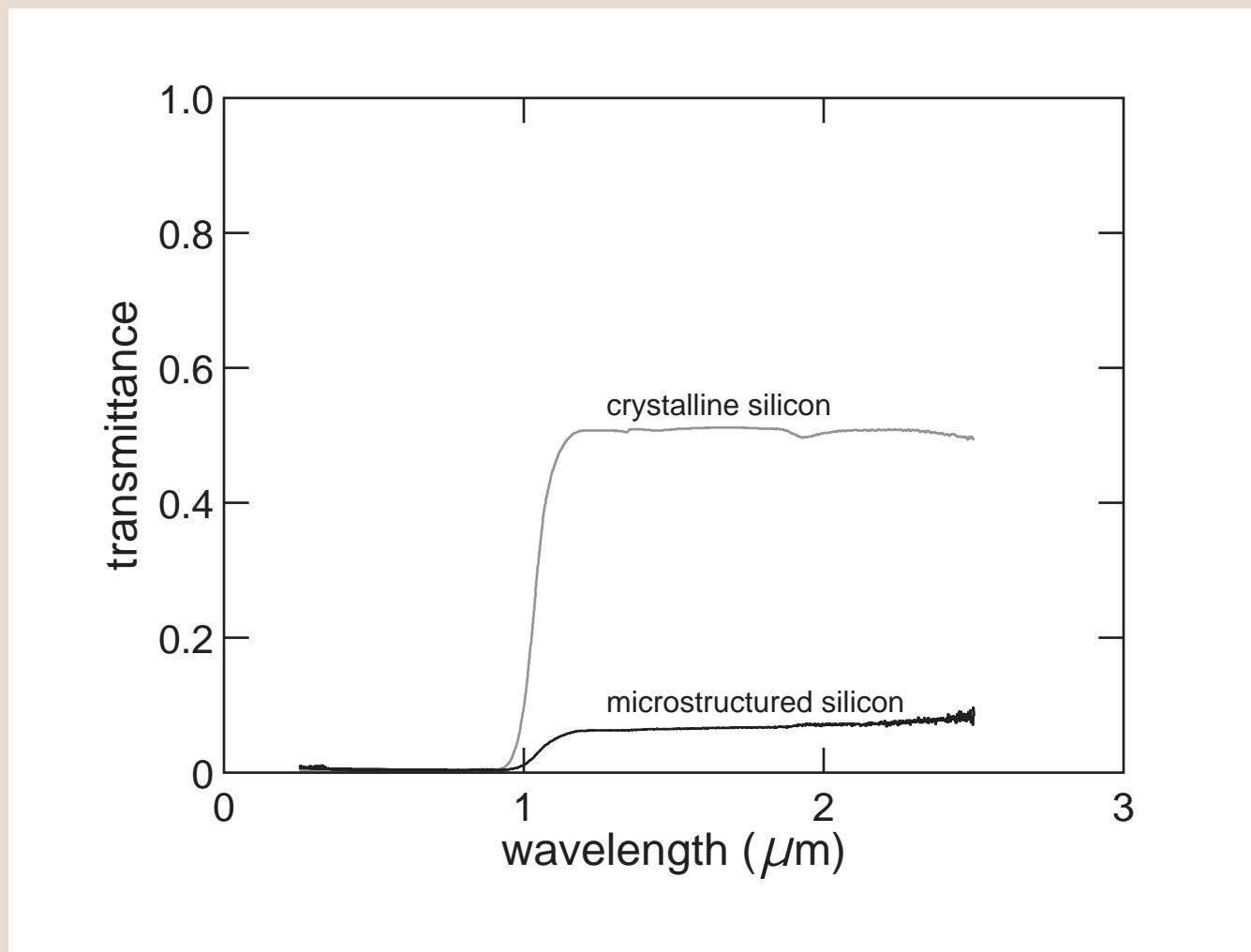
## reflectance



## transmittance

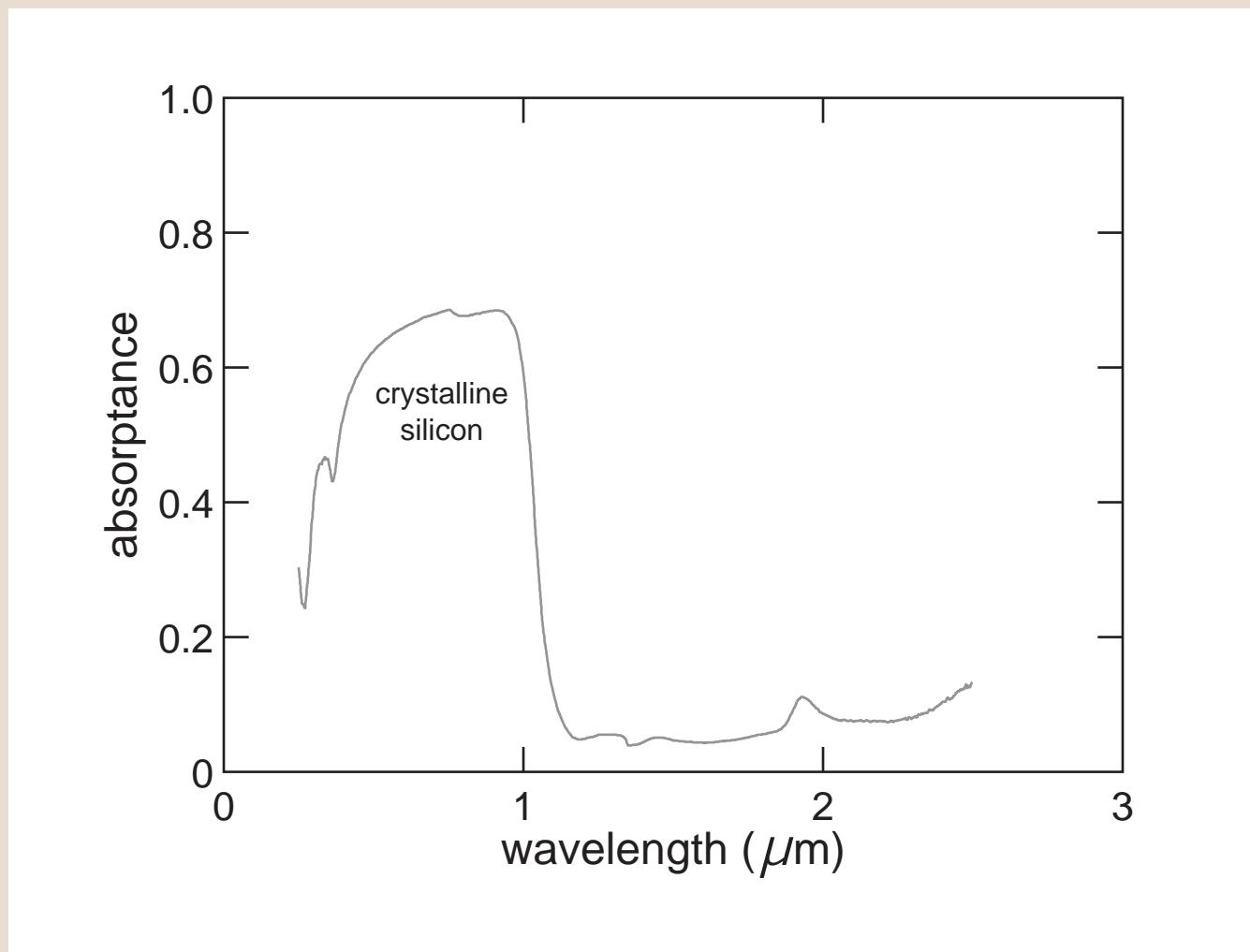


## transmittance

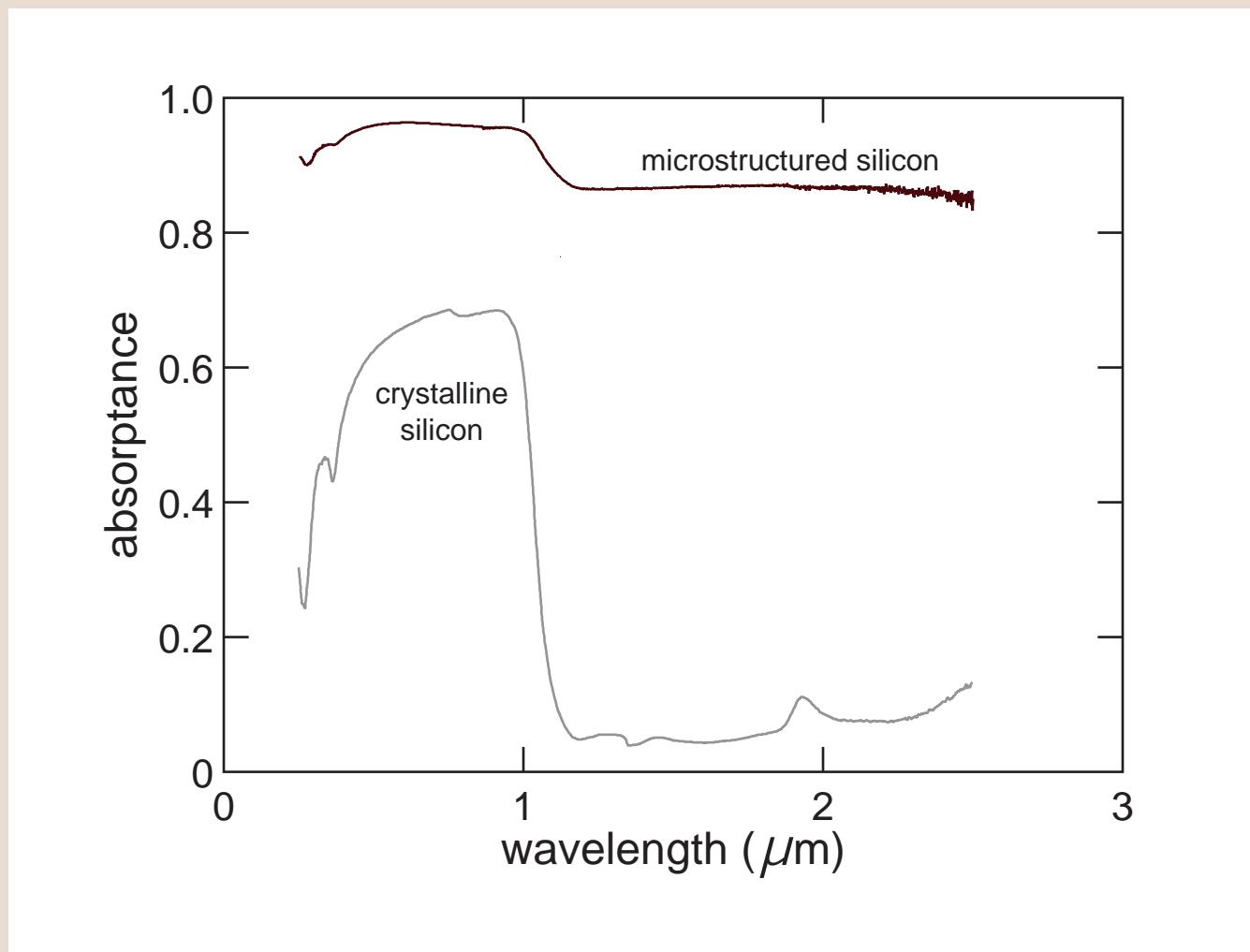


# *Optical properties*

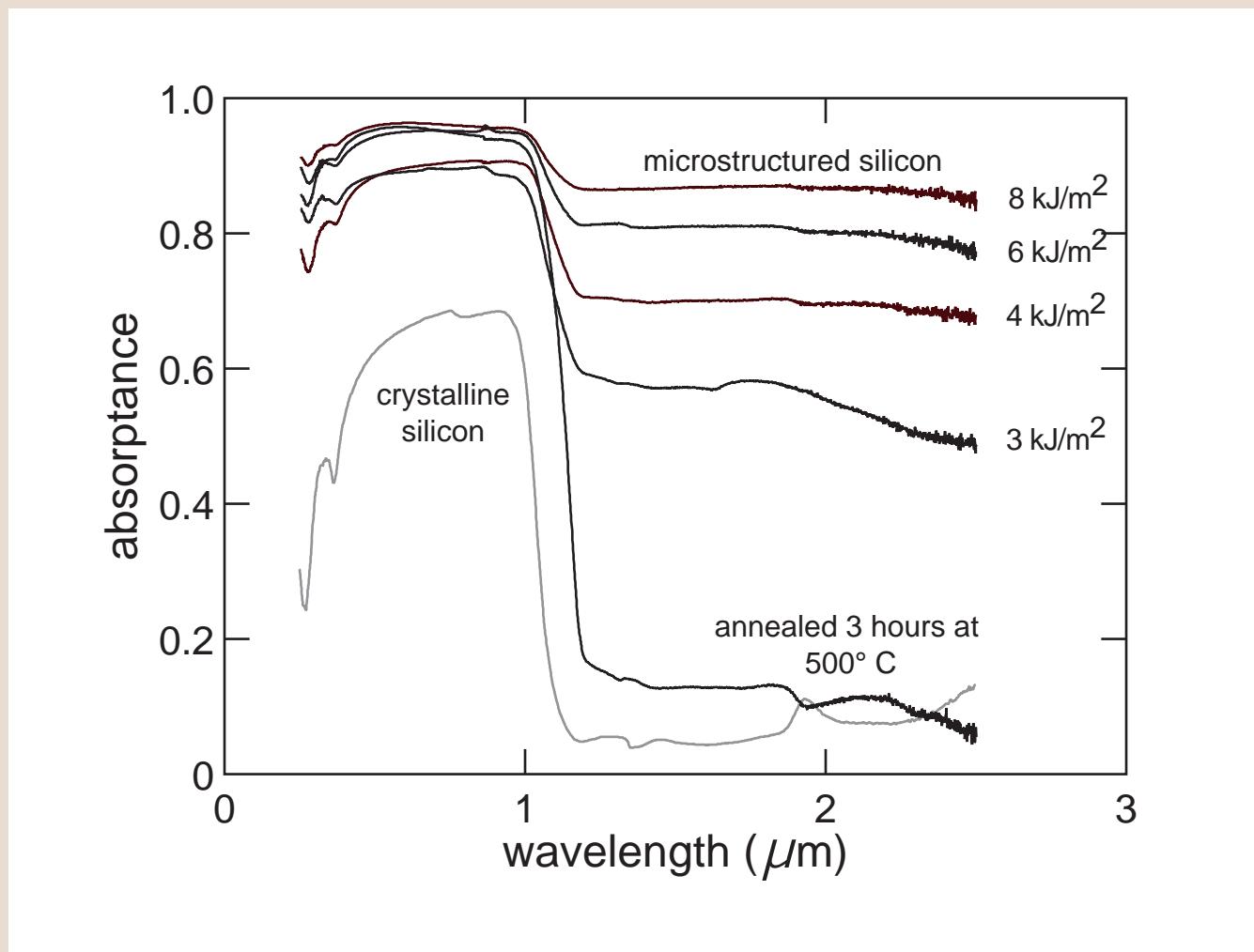
**absorptance ( $A = 1 - R - T$ )**



## absorptance

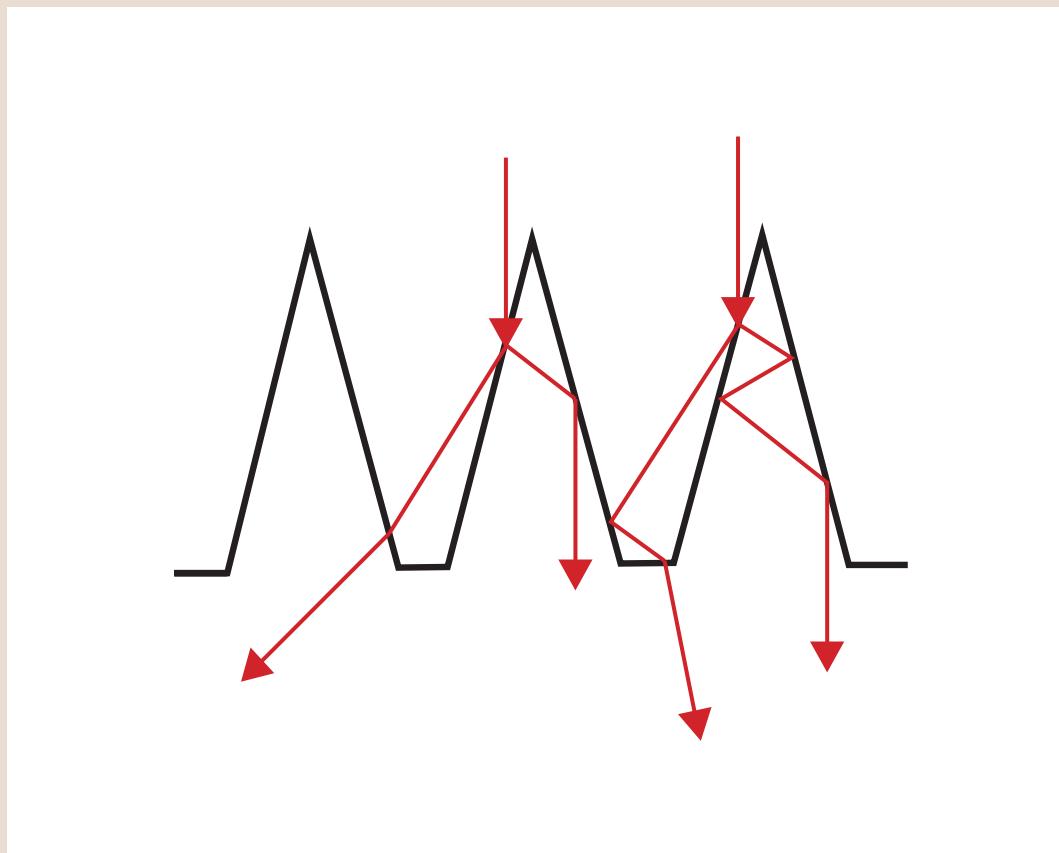


## absorptance

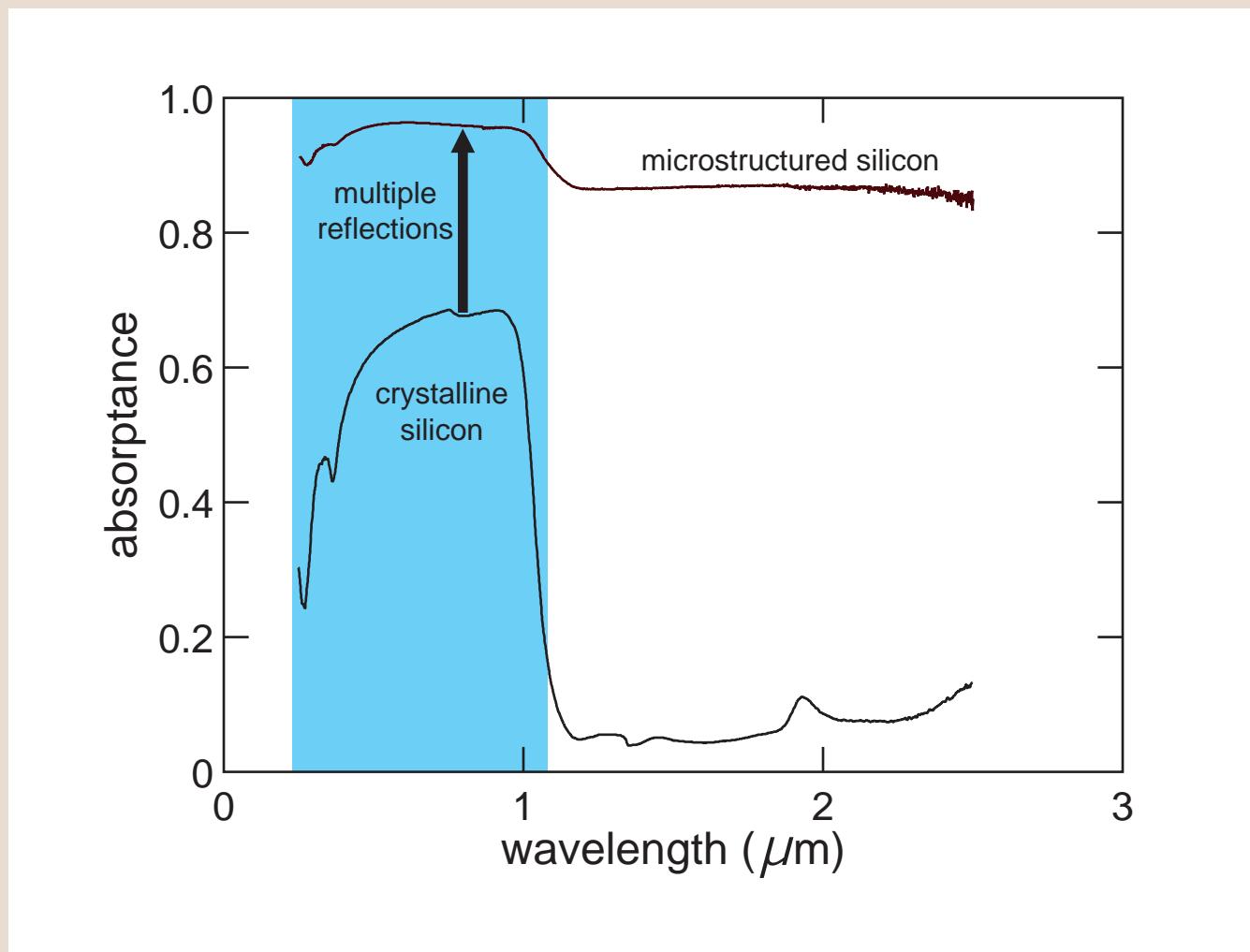


**Why is it black?**

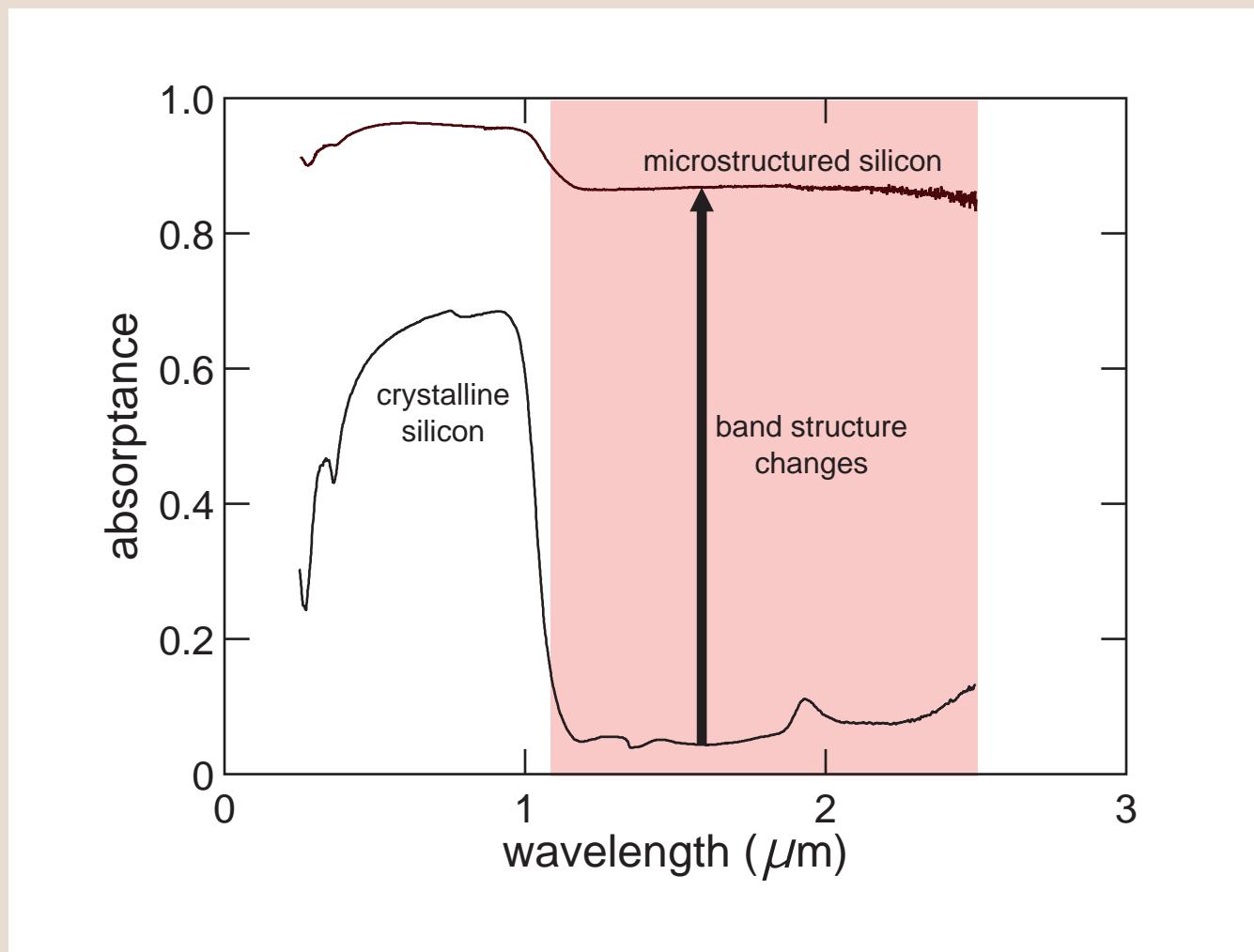
## Multiple reflections can enhance absorption



## absorptance

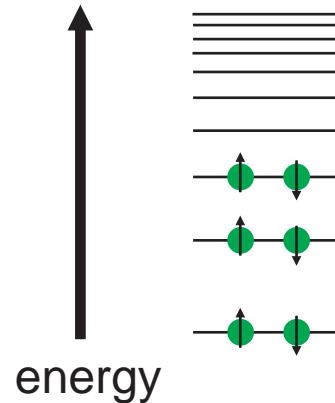


## absorptance



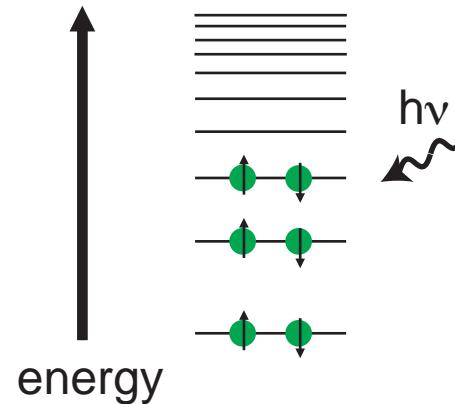
**atoms absorb light by electronic transitions**

atomic electrons  
must occupy  
well-defined  
energy levels



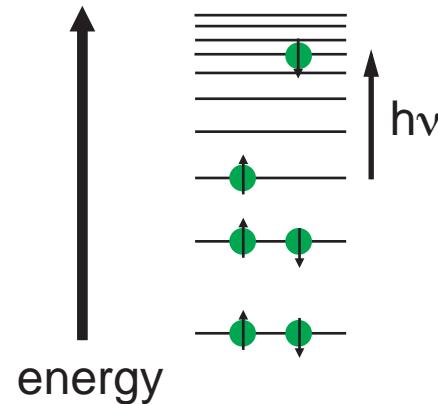
**atoms absorb light by electronic transitions**

absorbed photon  
must promote an  
electron to an  
empty level

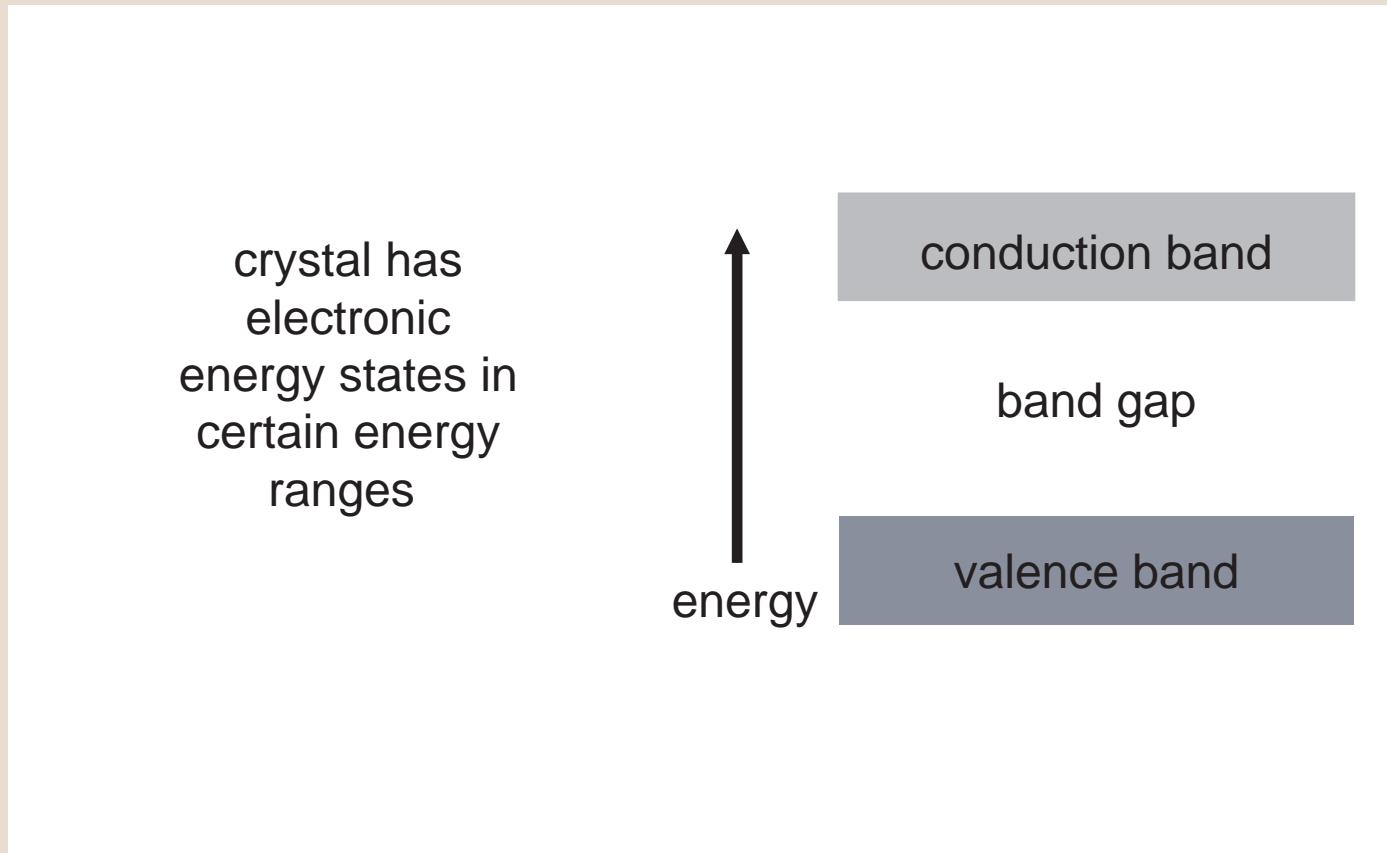


## Atoms absorb light by electronic transitions

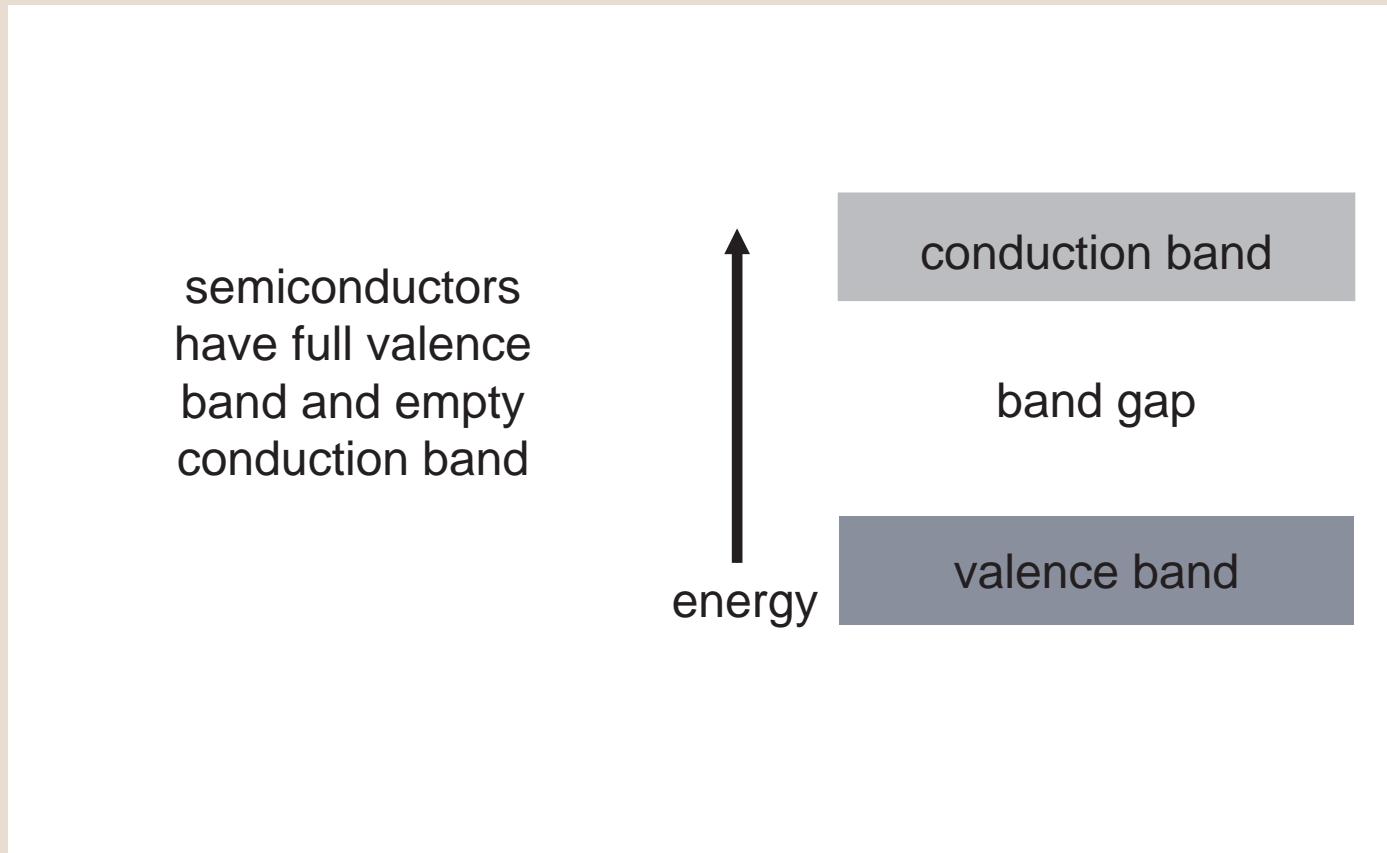
absorbed photon  
must promote an  
electron to an  
empty level



**crystalline solids have bands of energy states**



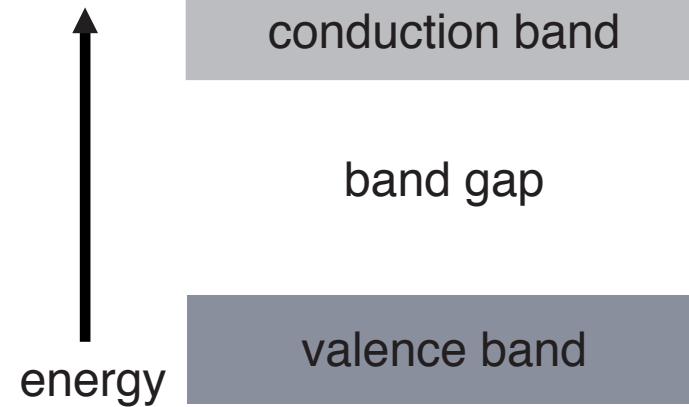
**crystalline solids have bands of energy states**



# *Band structure*

**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

## Gas immersion laser doping:

- ▶ melt chip surface in presence of desired gas
- ▶ gas atoms incorporated just into melt
- ▶ dopes very thin (20-250 nm) surface layer

Carey & Sigmon, Appl. Surf. Sci (1989).

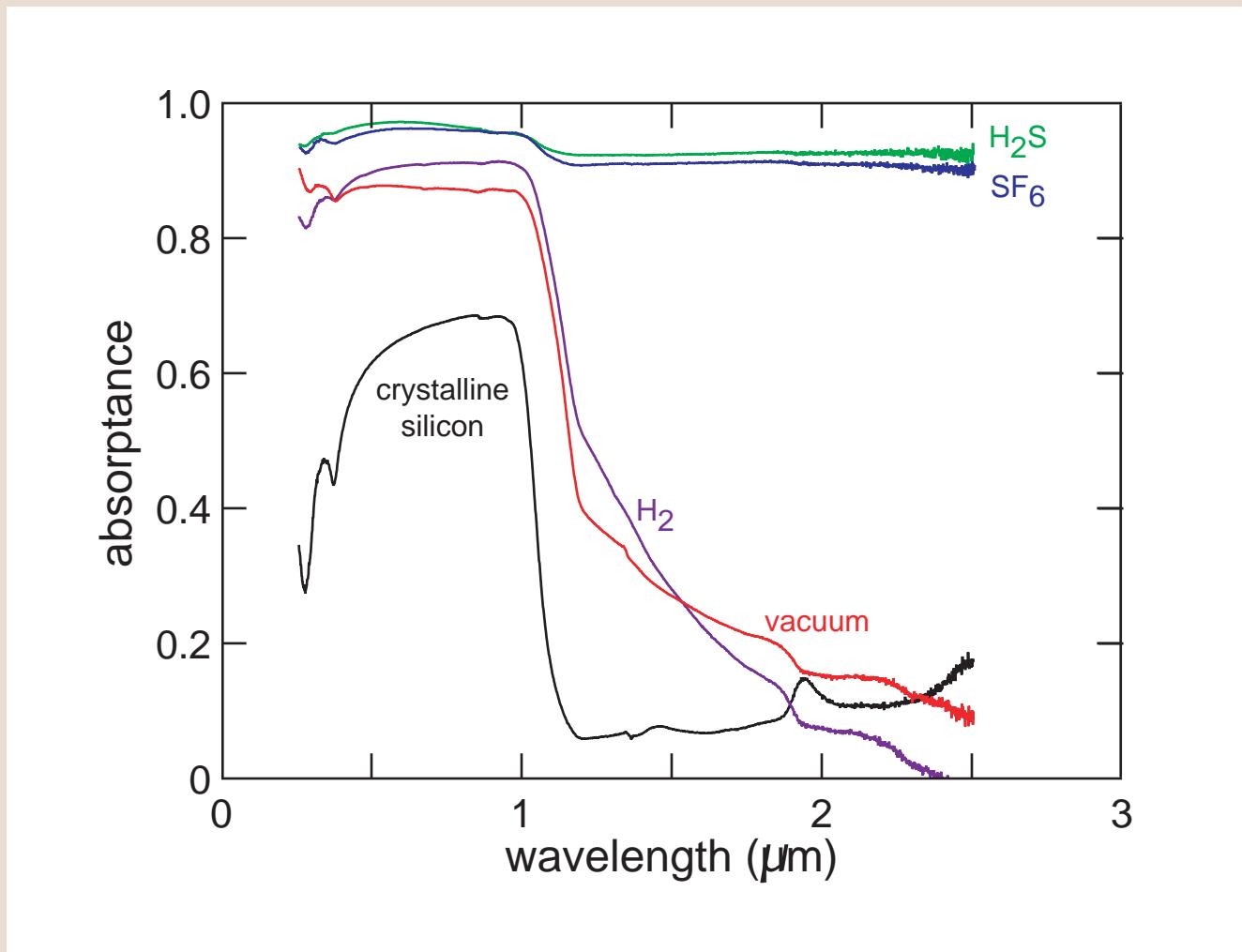
## **Work with other gases:**

gas species incorporated into surface layer

sulfur required for below-band gap absorption  
( $\text{H}_2\text{S}$ ,  $\text{SF}_6$ )

# *Chemical analysis*

## absorptance



## **Surfaces structured in SF<sub>6</sub>:**

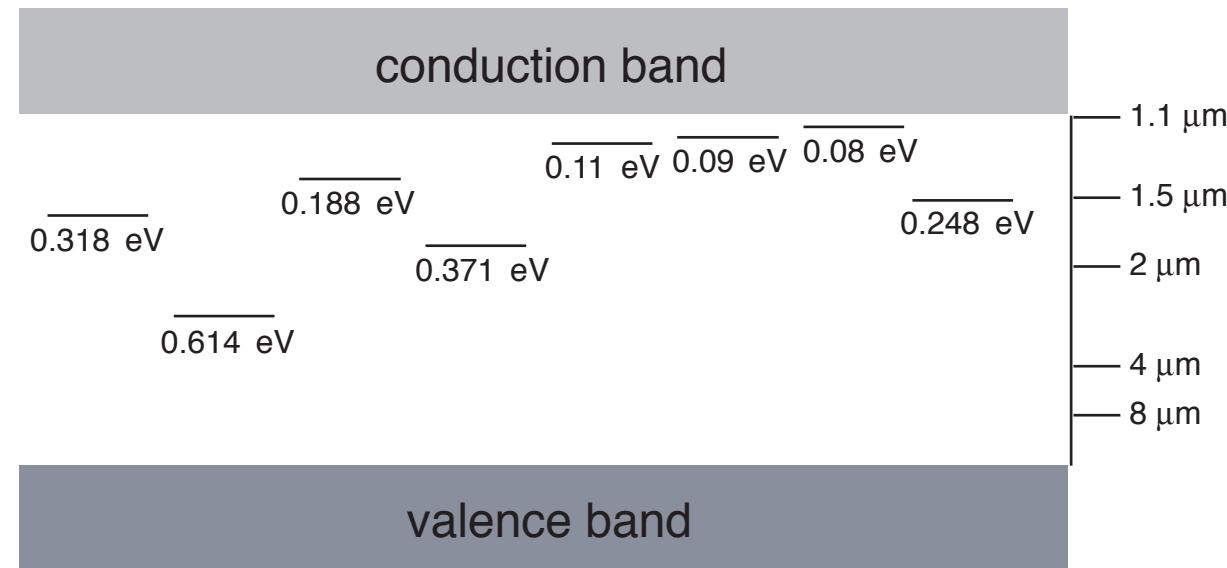
1.6% sulfur in surface layer (RBS)

also fluorine, oxygen

sulfur content decreases significantly on annealing

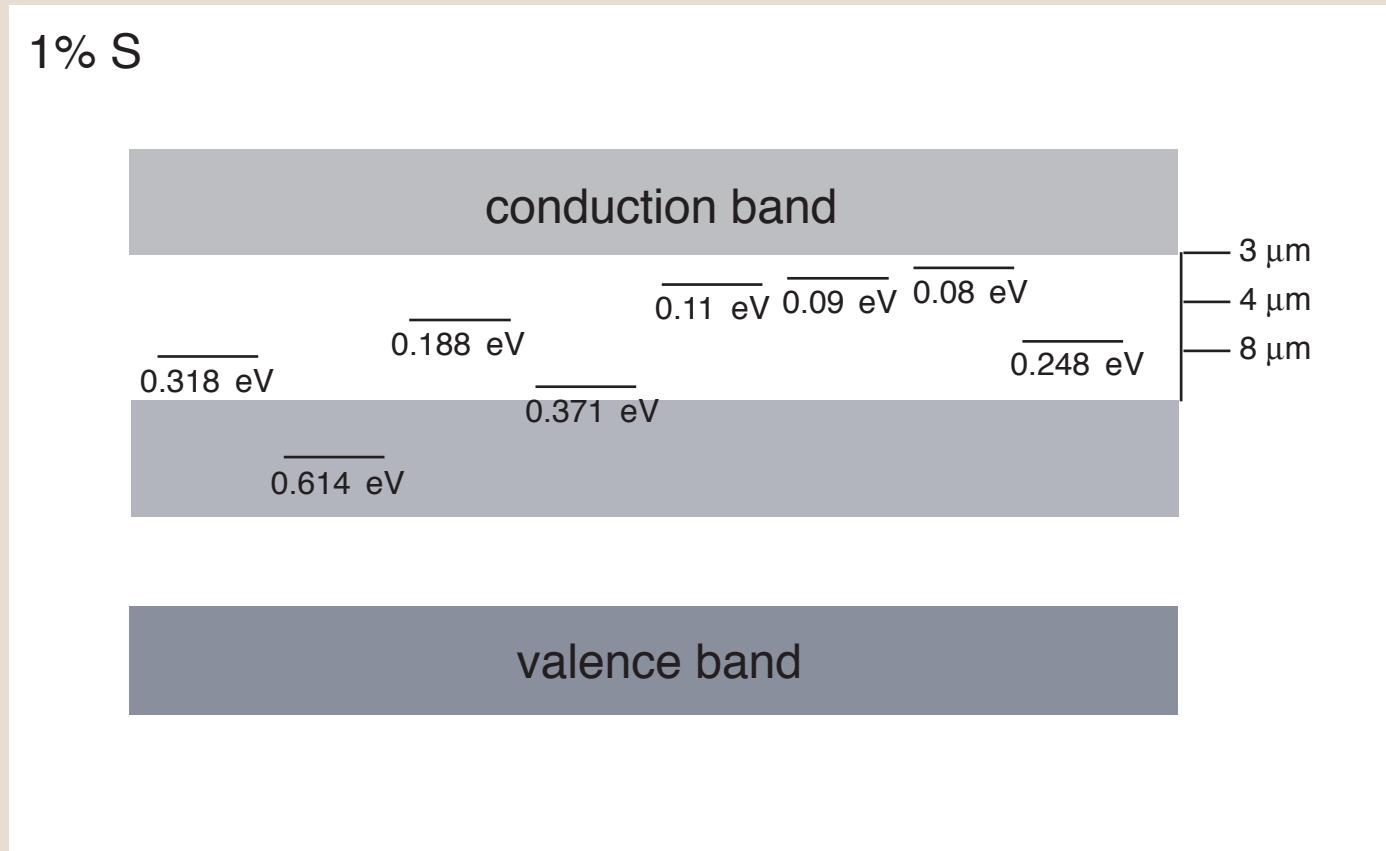
# sulfur introduces states in silicon band gap

1 part in  $10^6$  S

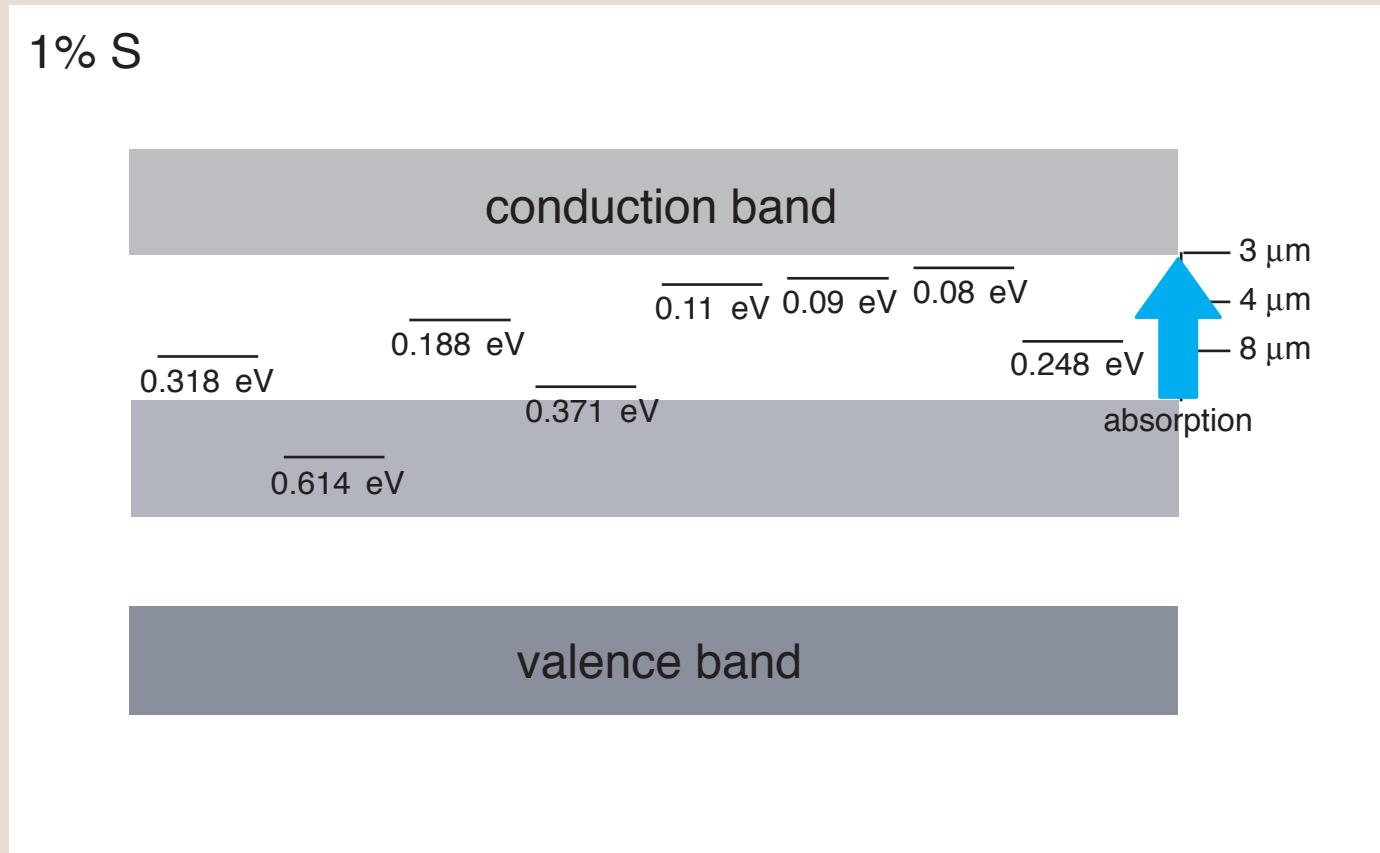


Janzén et al., Phys. Rev. B **29**, 1907 (1984)

**at high concentrations, states may broaden into a band**



## midgap impurity band forms



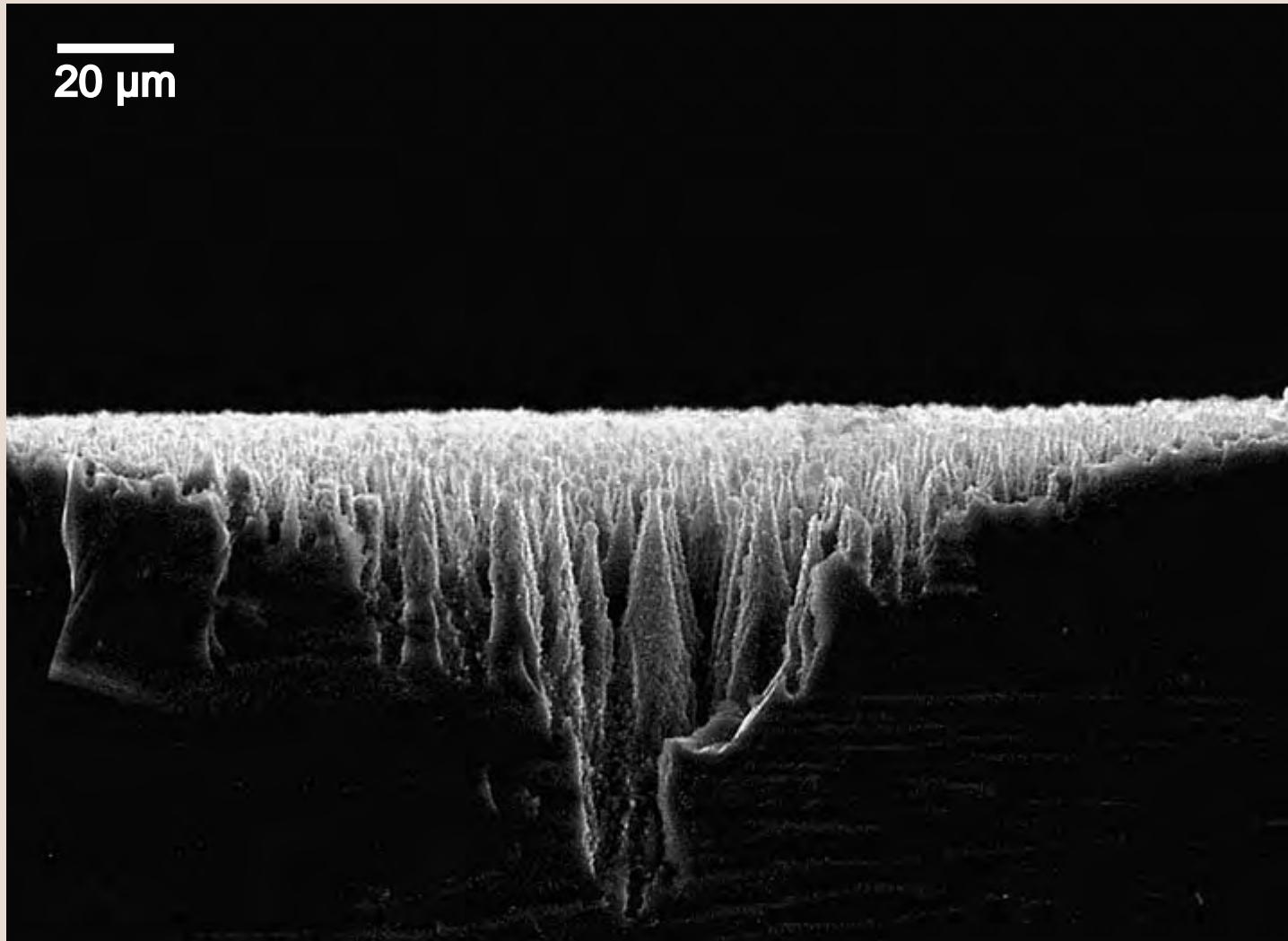
**Hall measurement: n-type impurities**  
**FTIR: absorption drops off around 3 μm**

## **Sulfur a likely explanation:**

sulfur required for below-band gap absorption  
annealing reduces sulfur and absorption  
appropriate wavelength range

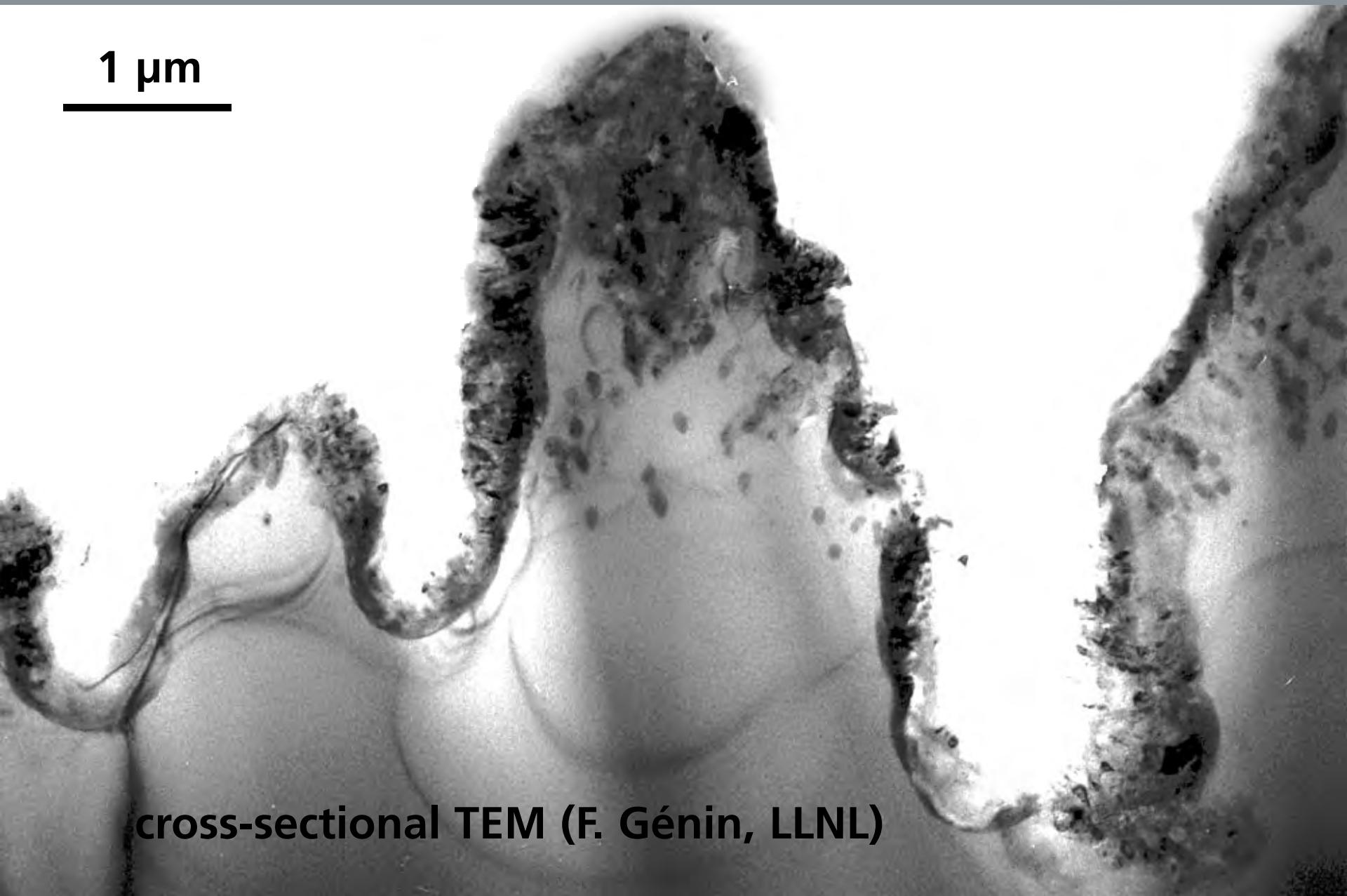
**What is the underlying structure?**

# *Structural analysis*



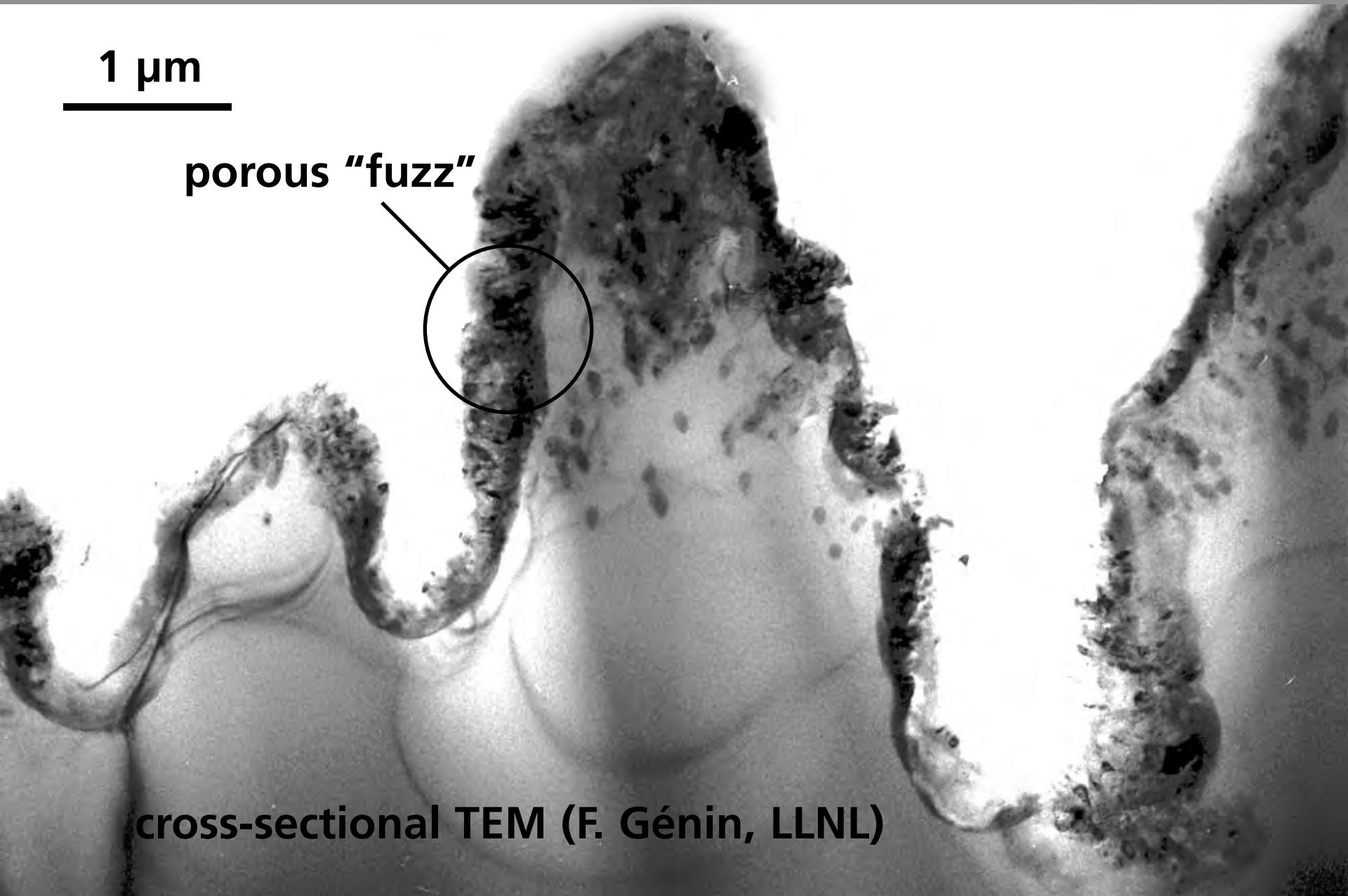
## *Structural and chemical analysis*

1  $\mu\text{m}$



cross-sectional TEM (F. Génin, LLNL)

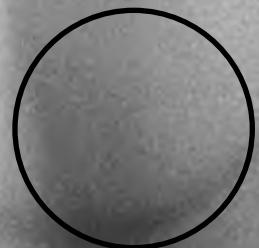
## *Structural and chemical analysis*



## *Structural and chemical analysis*

1  $\mu\text{m}$

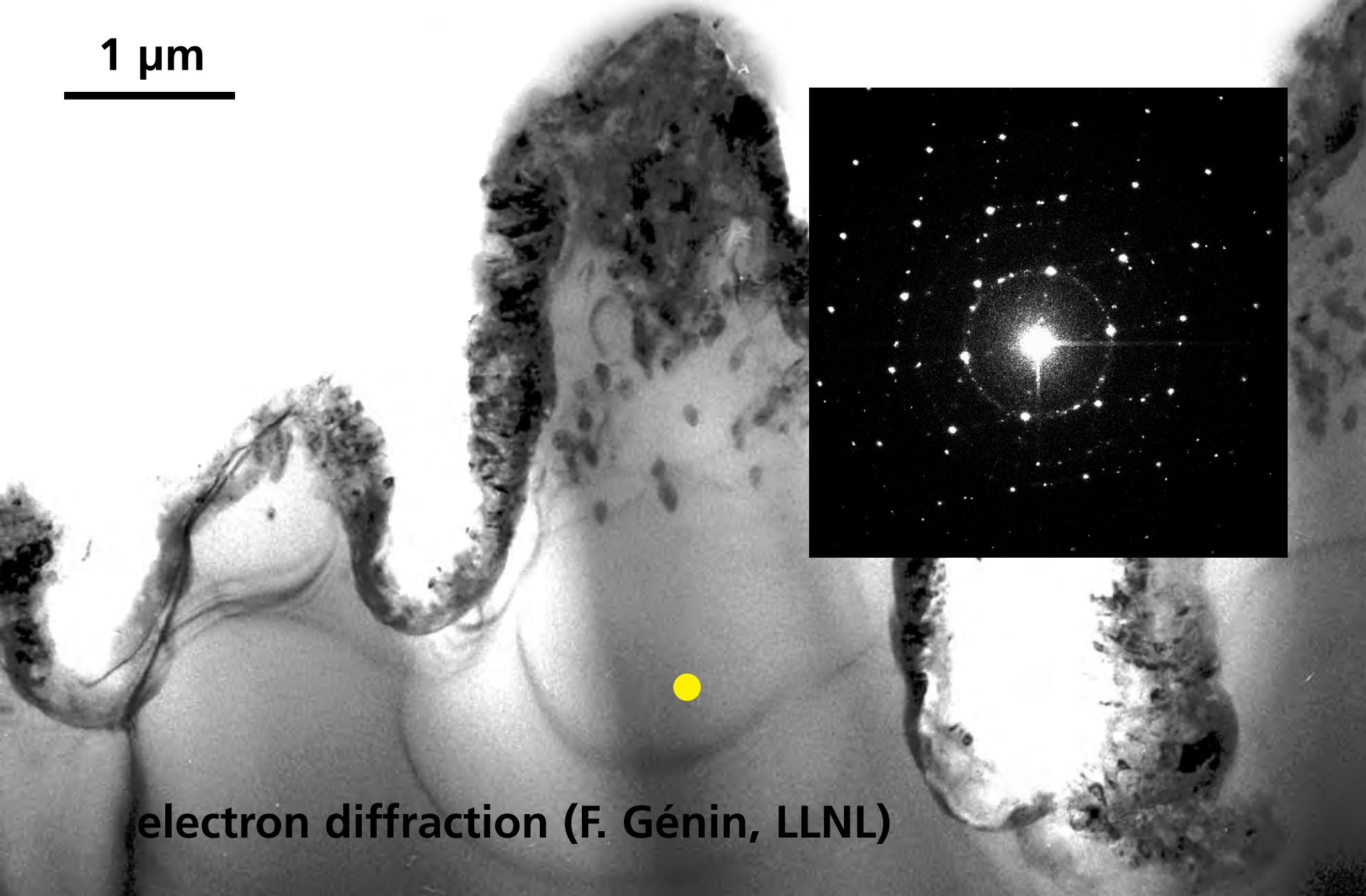
crystalline Si



cross-sectional TEM (F. Génin, LLNL)

## *Structural and chemical analysis*

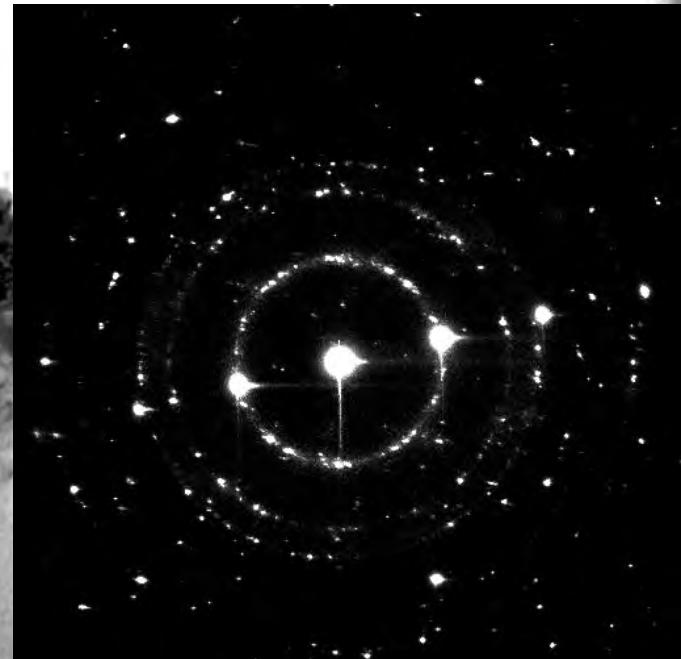
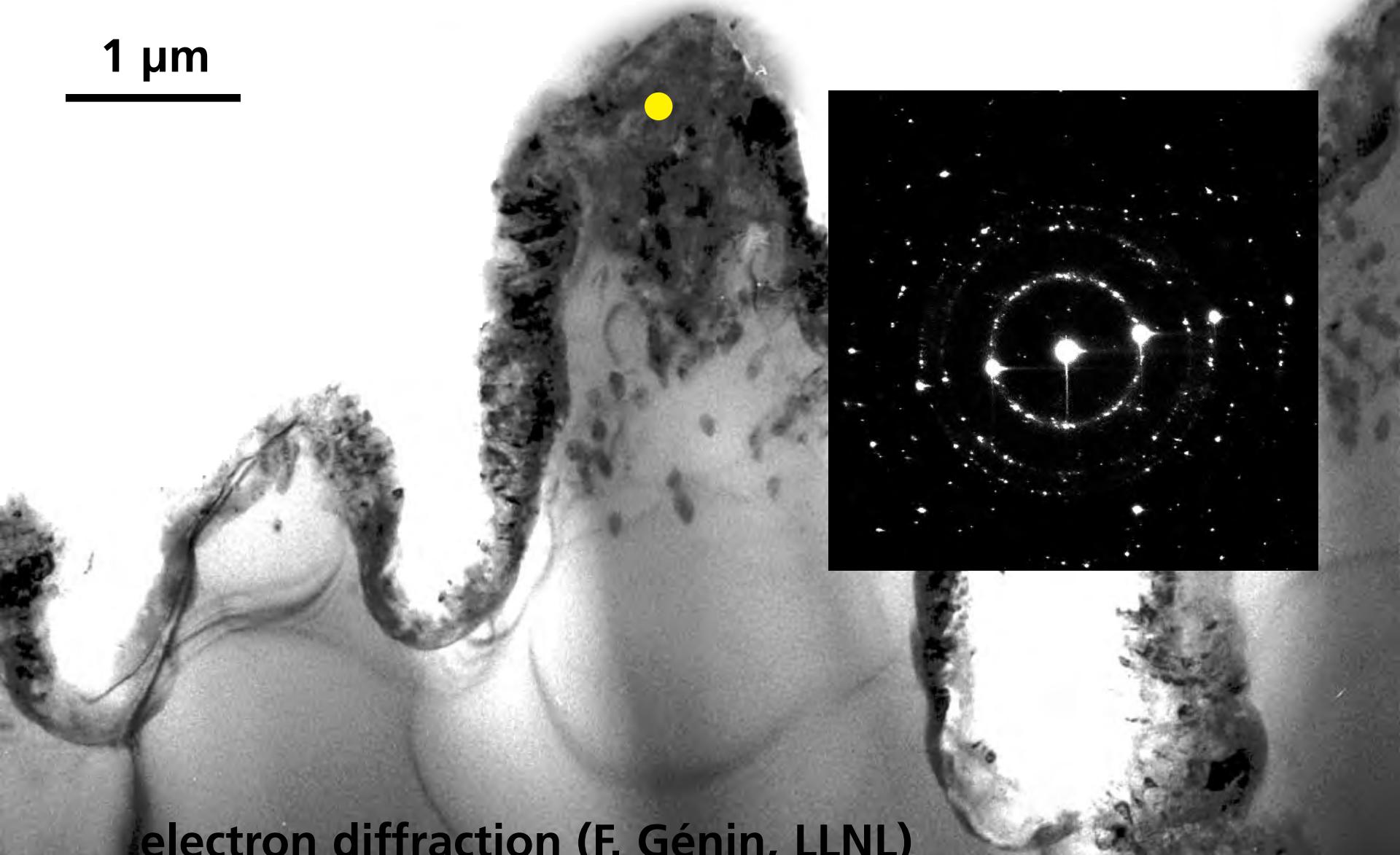
1  $\mu\text{m}$



electron diffraction (F. Génin, LLNL)

## *Structural and chemical analysis*

1  $\mu\text{m}$



electron diffraction (F. Génin, LLNL)

## *Structural and chemical analysis*

### **cross-sectional TEM:**

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

**Could nanostructures explain infrared absorption?**

**Structure less likely than sulfur:**

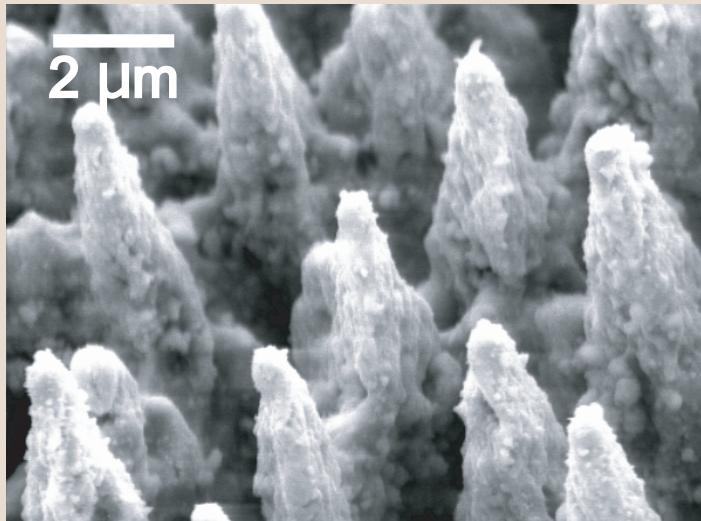
annealing

ns pulses

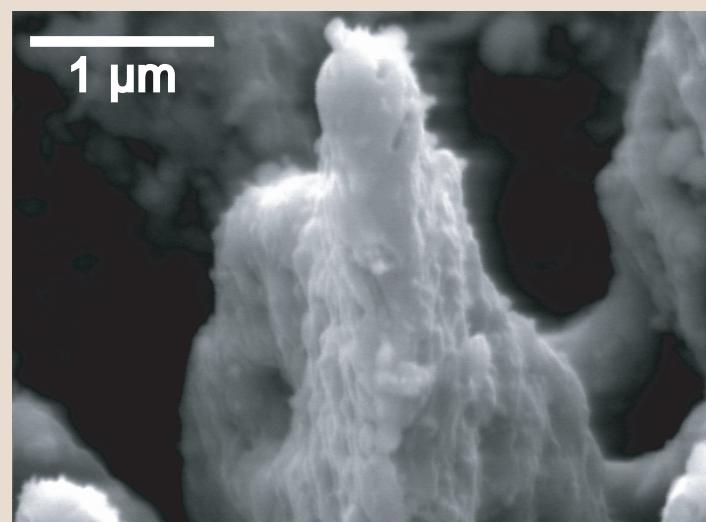
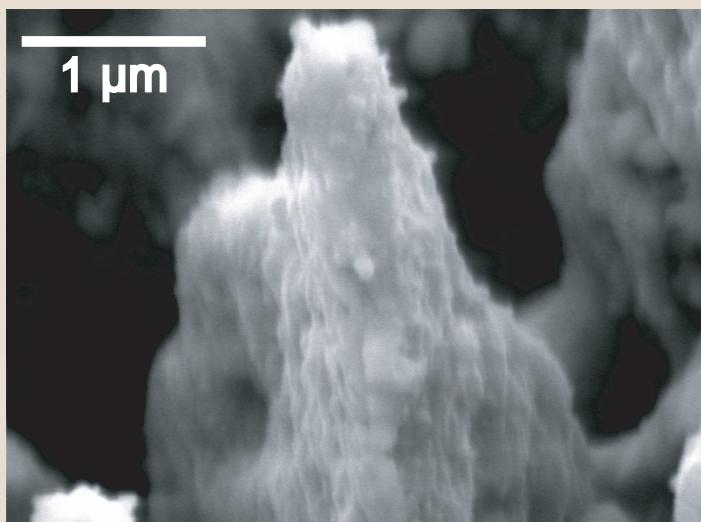
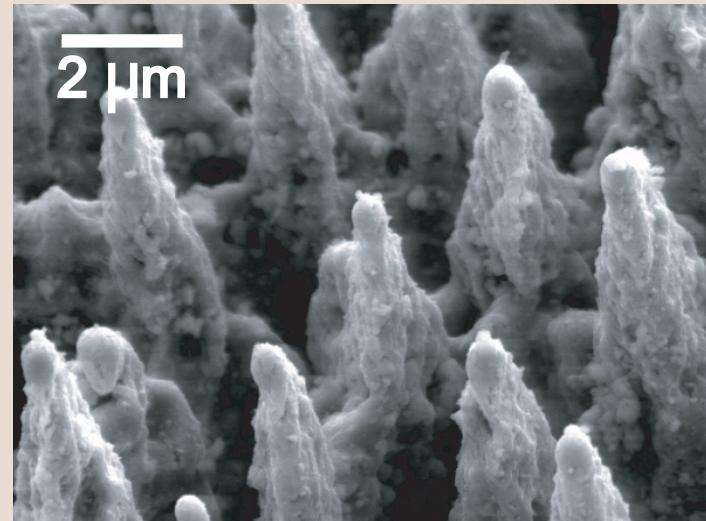
different gases

# *Structural analysis*

before annealing

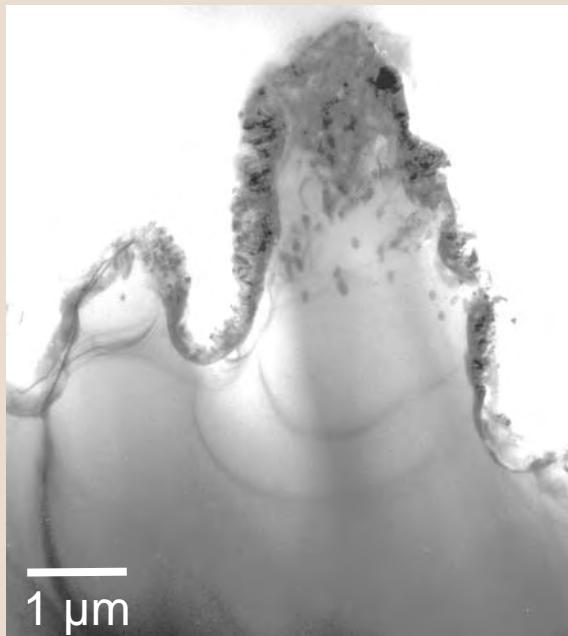


after annealing

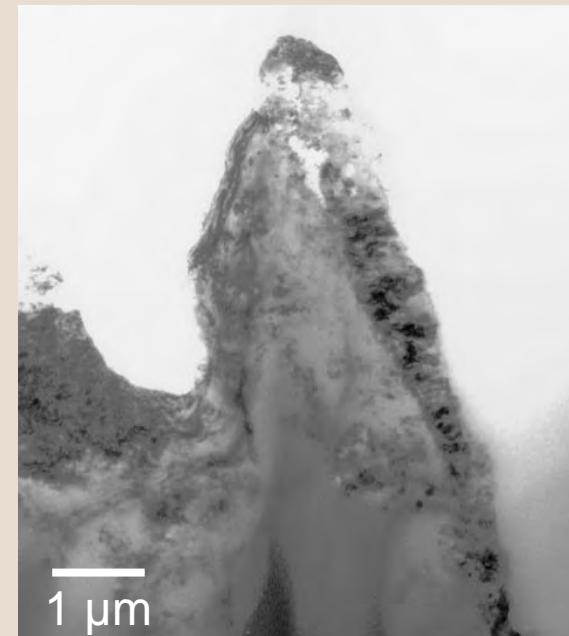


# *Structural analysis*

**not annealed**



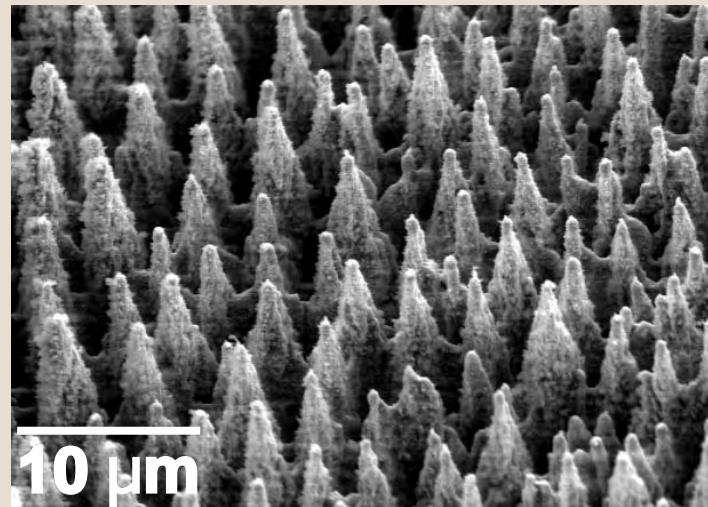
**annealed**



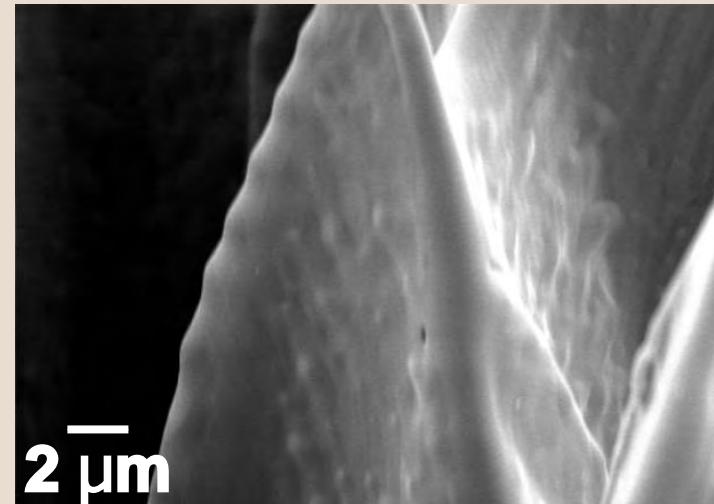
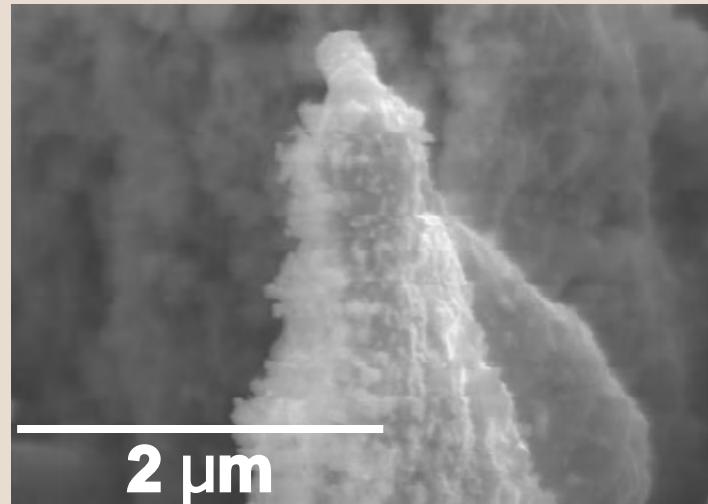
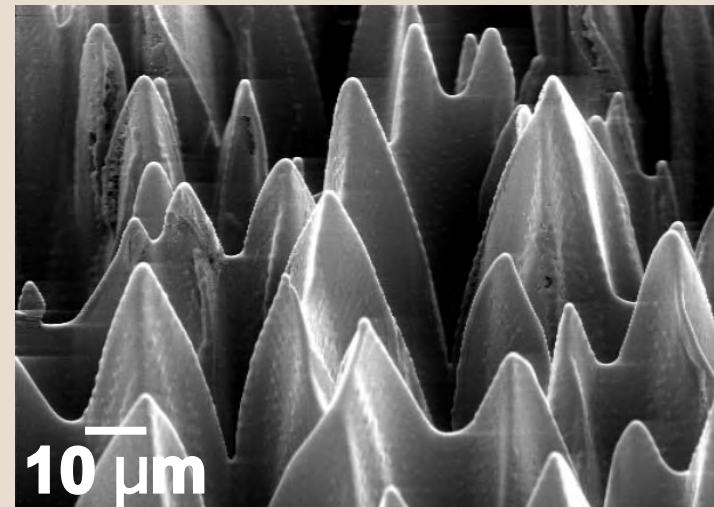
**annealing does not affect visible structure**

# *Nanosecond vs femtosecond*

**800 nm, 100 fs, 10 kJ/m<sup>2</sup>**

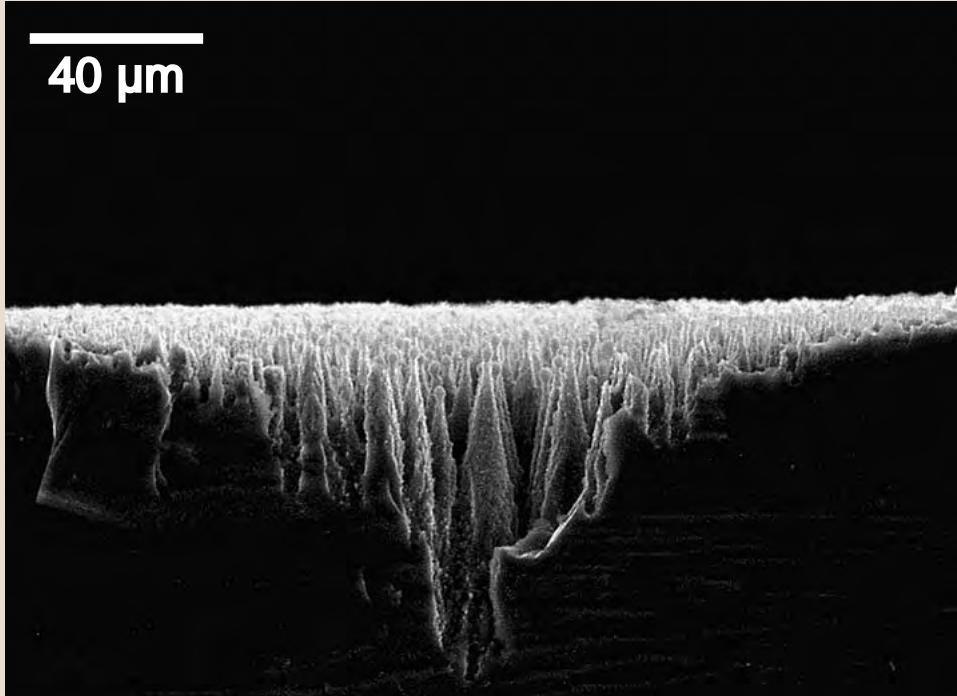


**248 nm, 30 ns, 30 kJ/m<sup>2</sup>**



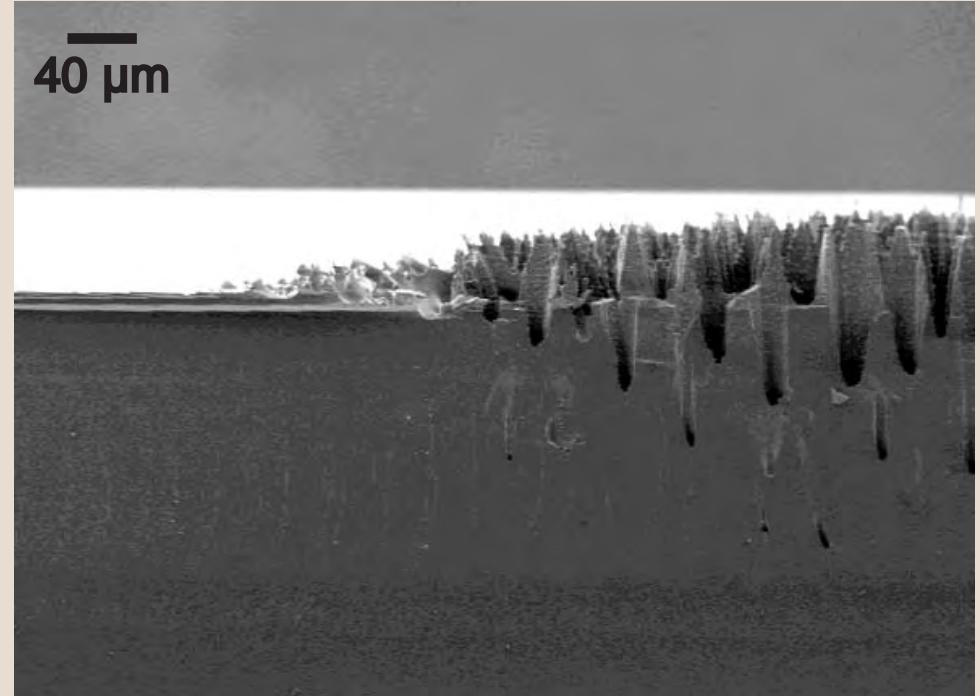
# *Nanosecond vs femtosecond*

**800 nm, 100 fs, 10 kJ/m<sup>2</sup>**



**fs cones etched below surface**

**248 nm, 30 ns, 30 kJ/m<sup>2</sup>**



**ns cones grow above surface**

## Summary of optical properties

- ▶ visible absorptance: multiple reflections
- ▶ infrared absorptance: new electronic states
- ▶ band forms due to 1% sulfur impurities

*Black silicon*

Applications

3  $\mu\text{m}$

## **Ordinary silicon is transparent in IR**

- ▶ Si photodiodes are not sensitive to IR
- ▶ Si solar cells insensitive to IR

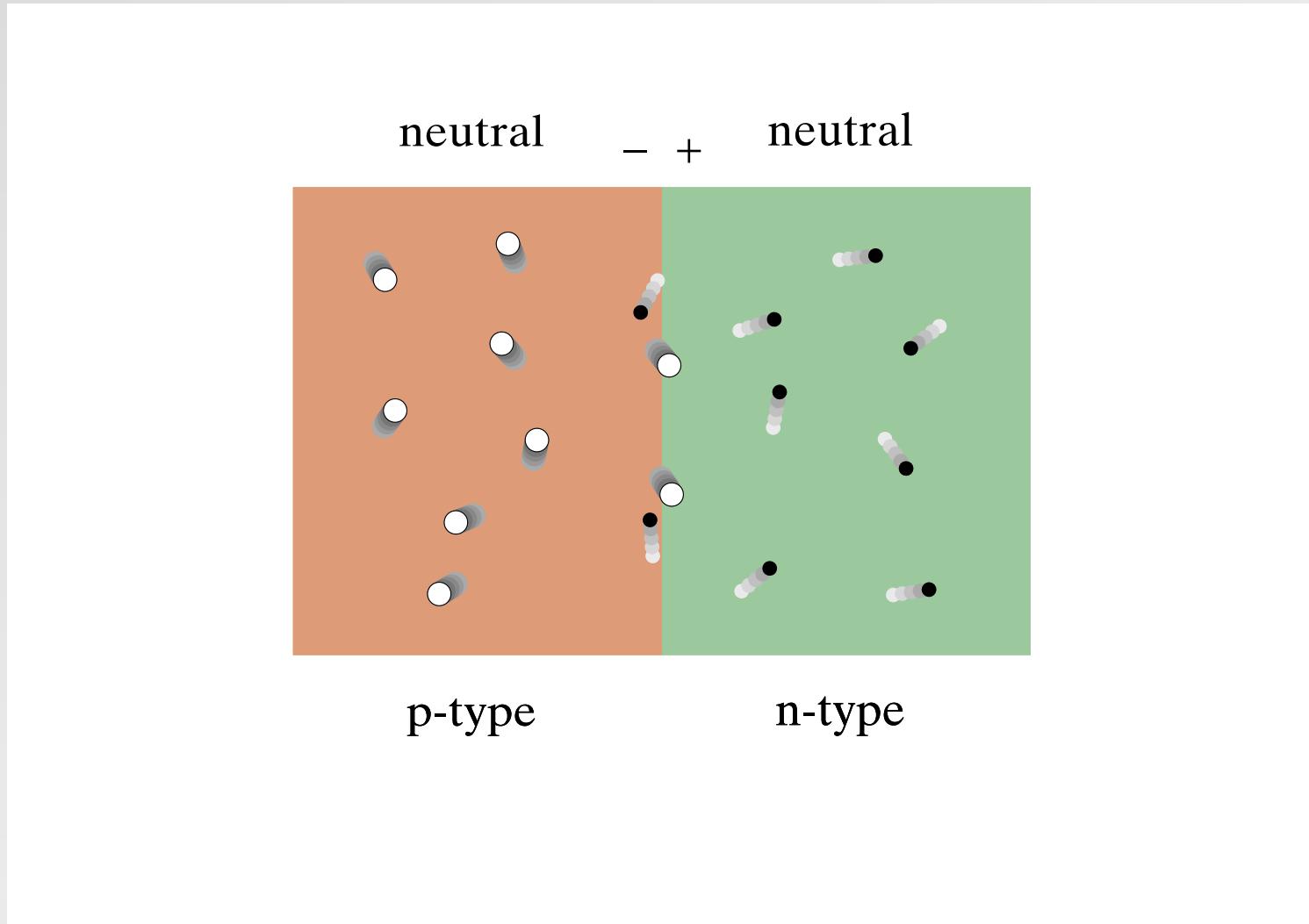
## **Ordinary silicon is highly reflective**

- ▶ Reduce reflectivity for solar cells

## **Spiked surface produces IR photocurrent**

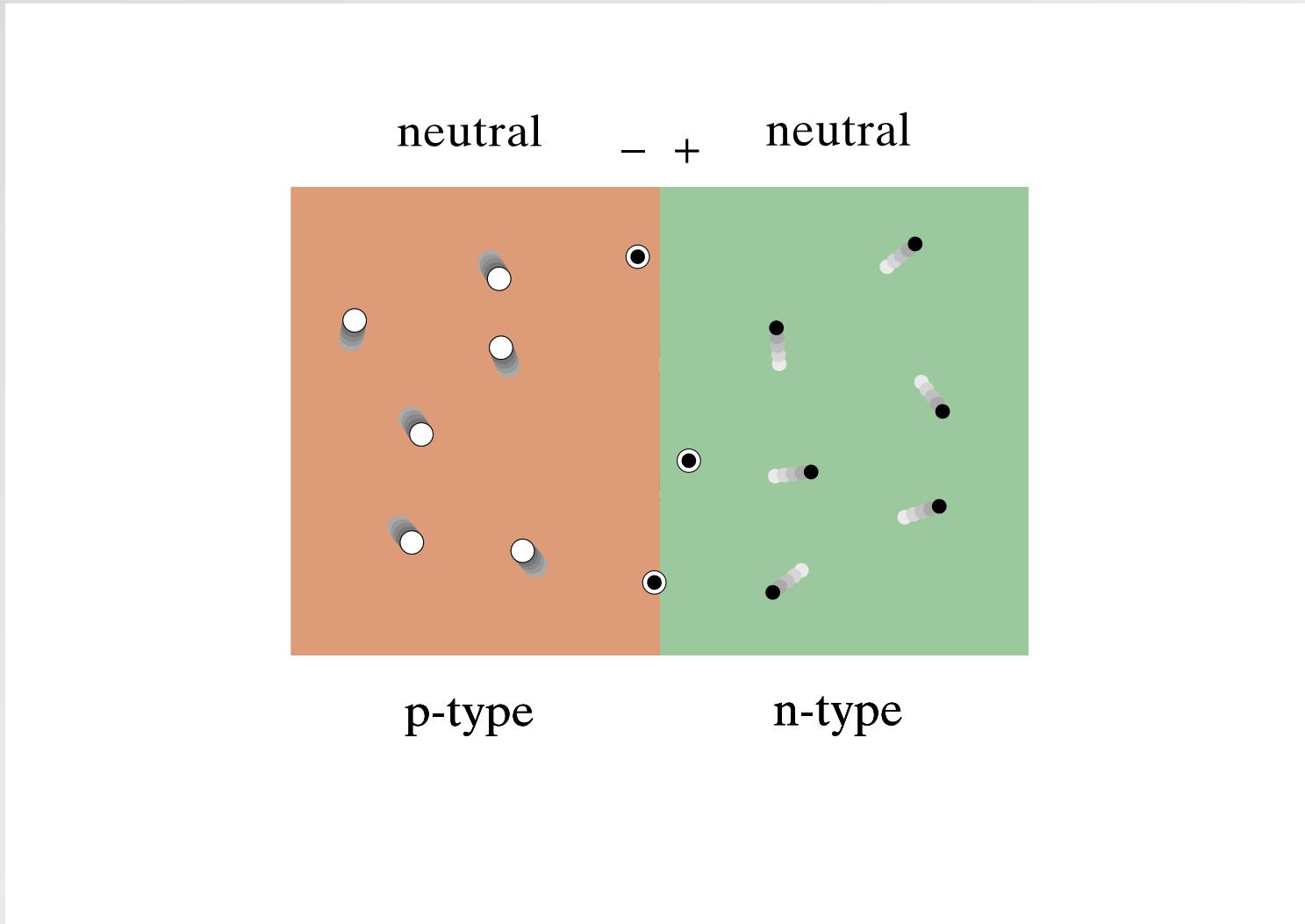
- ▶ >10  $\mu\text{A}$  from 10 mW illumination (1.33, 1.55  $\mu\text{m}$ )
- ▶ 1000x more sensitive than ordinary Si PIN diode
- ▶ annealing improves response

# *pn-junctions*



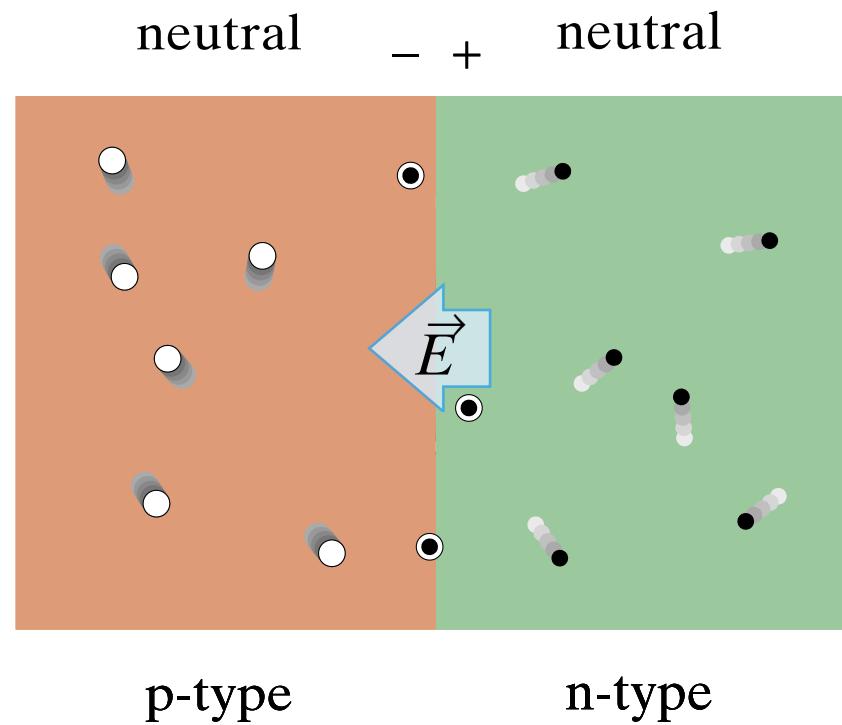
**electrons and holes diffuse across junction...**

# *pn-junctions*



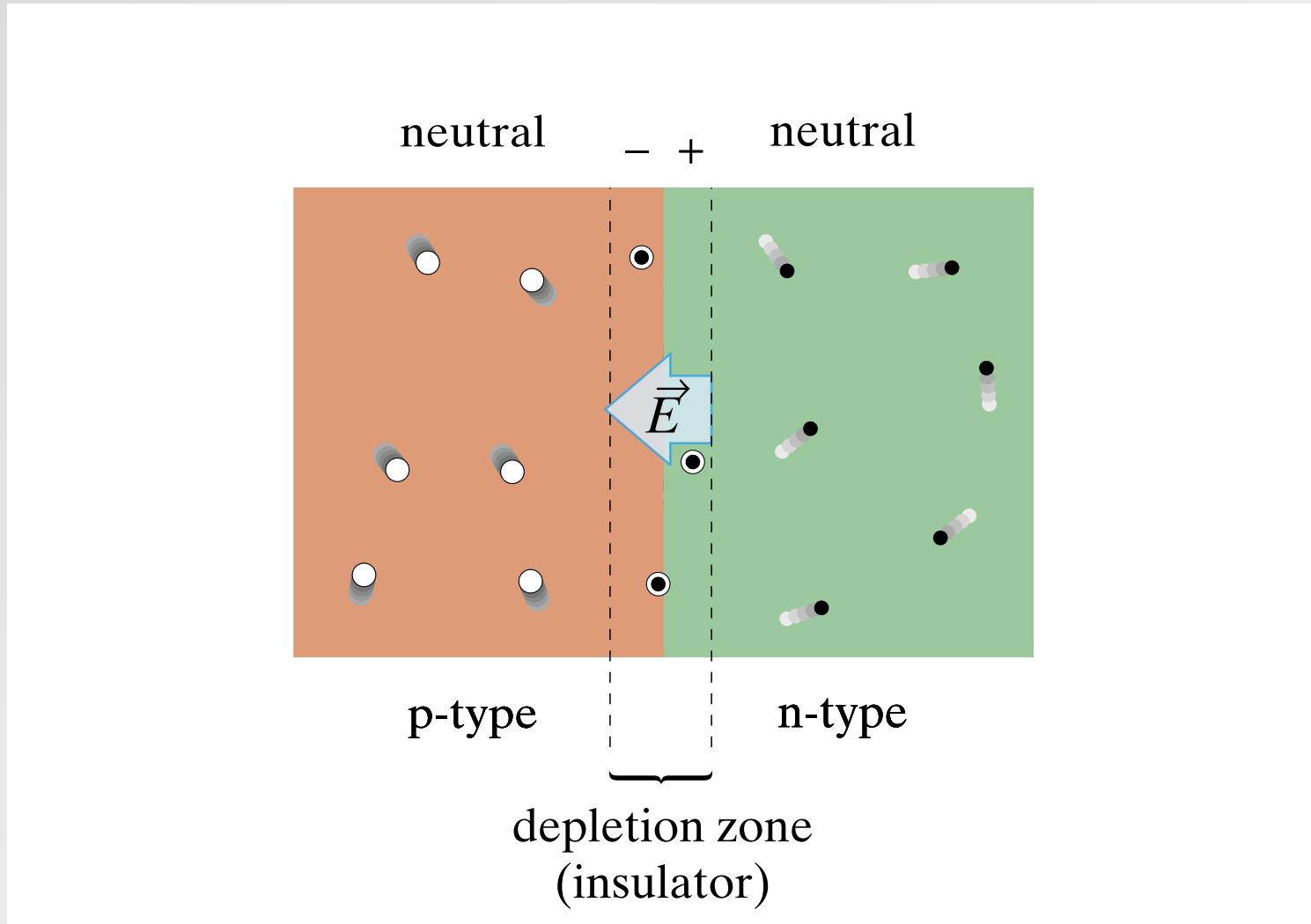
...and get 'trapped' after they combine

# *pn-junctions*



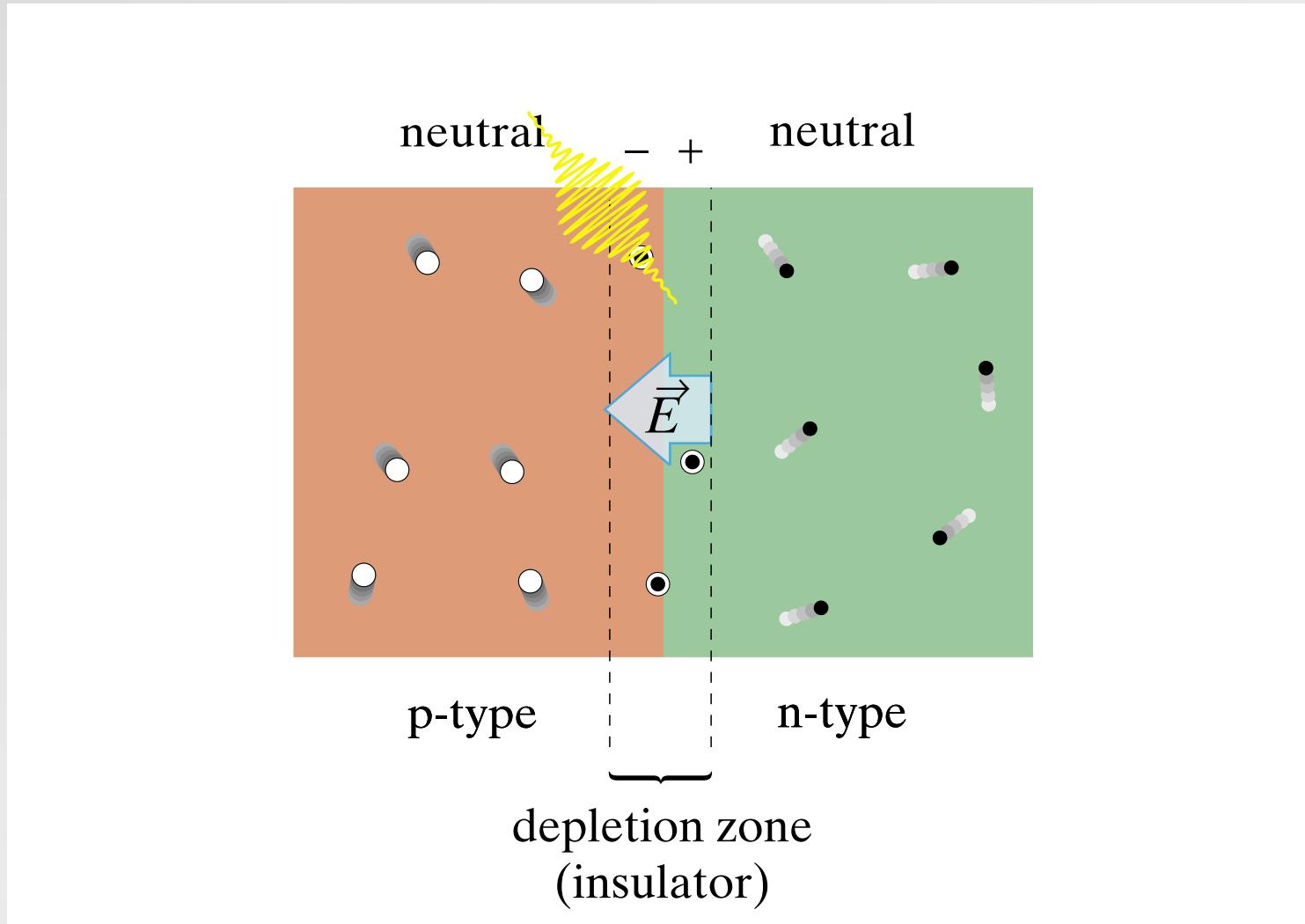
**build-up of charge leads to electric field that stops diffusion**

# *pn-junctions*



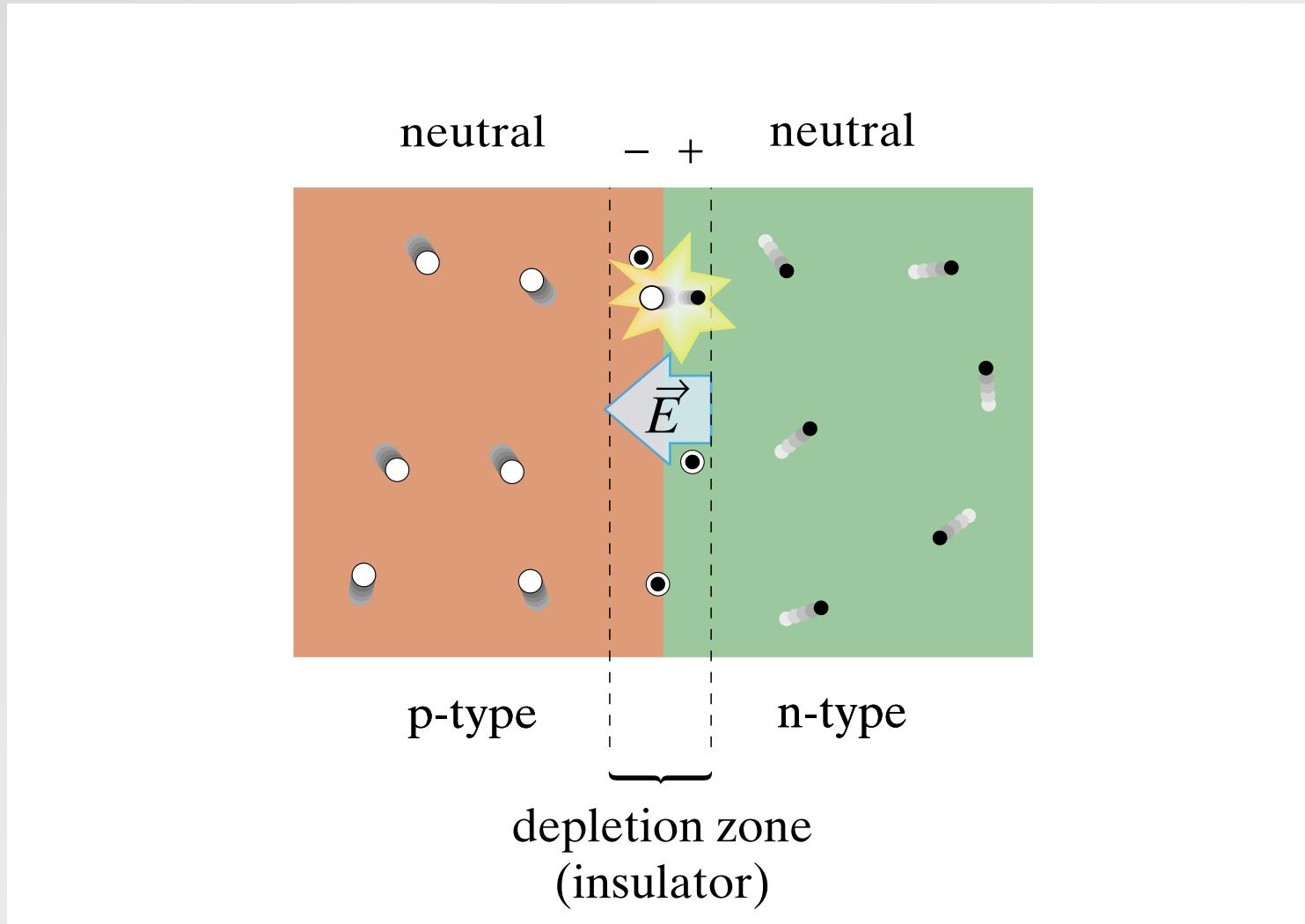
**depletion layer can convert light into electric energy**

# *pn-junctions*



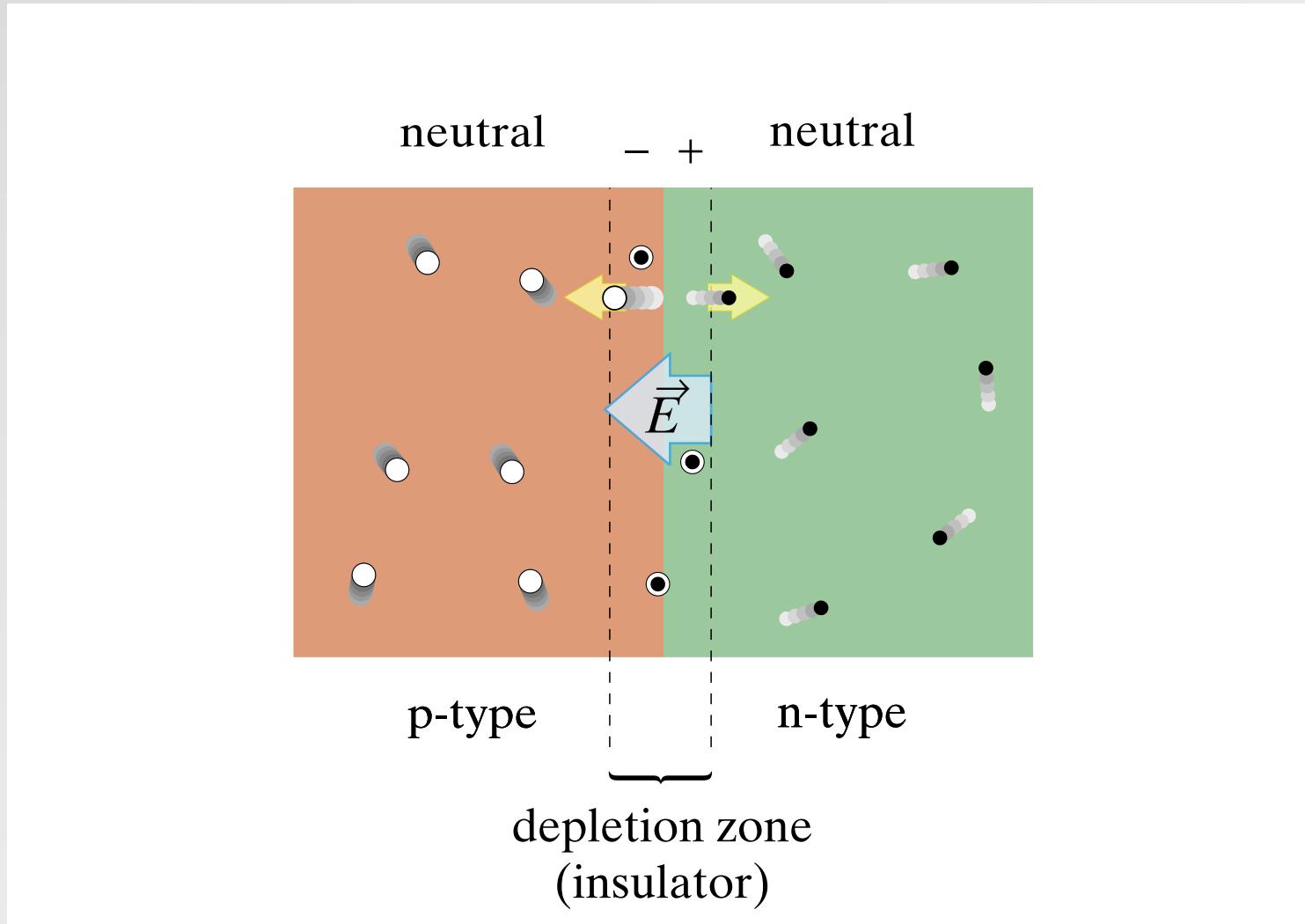
**incident photon knocks out electron...**

# *pn-junctions*



**...creating an electron-hole pair**

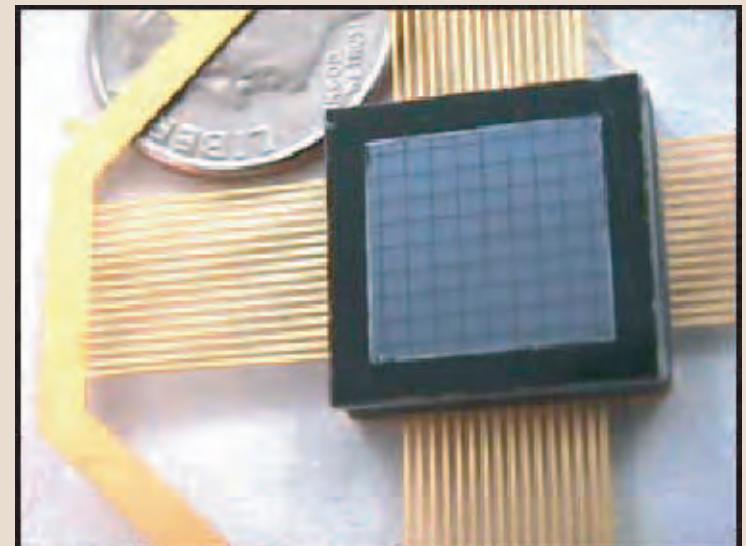
# *pn-junctions*



**E-field separates eh-pair, causing current**

## **Avalanche photodiode with black silicon**

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

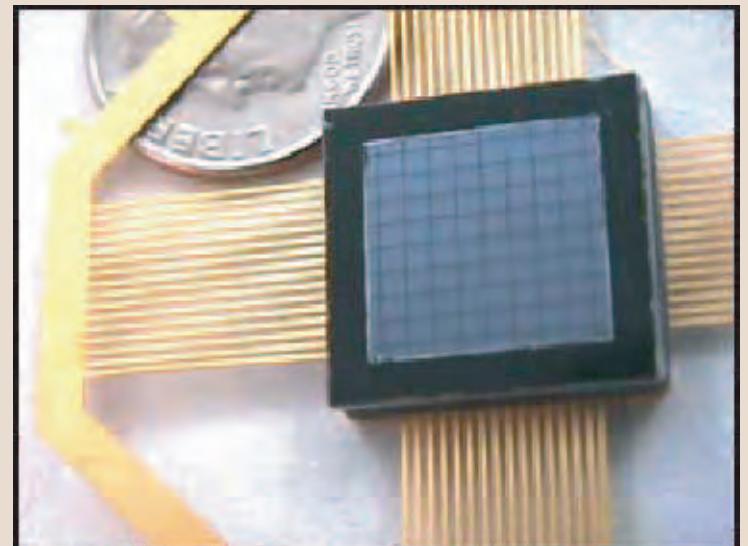


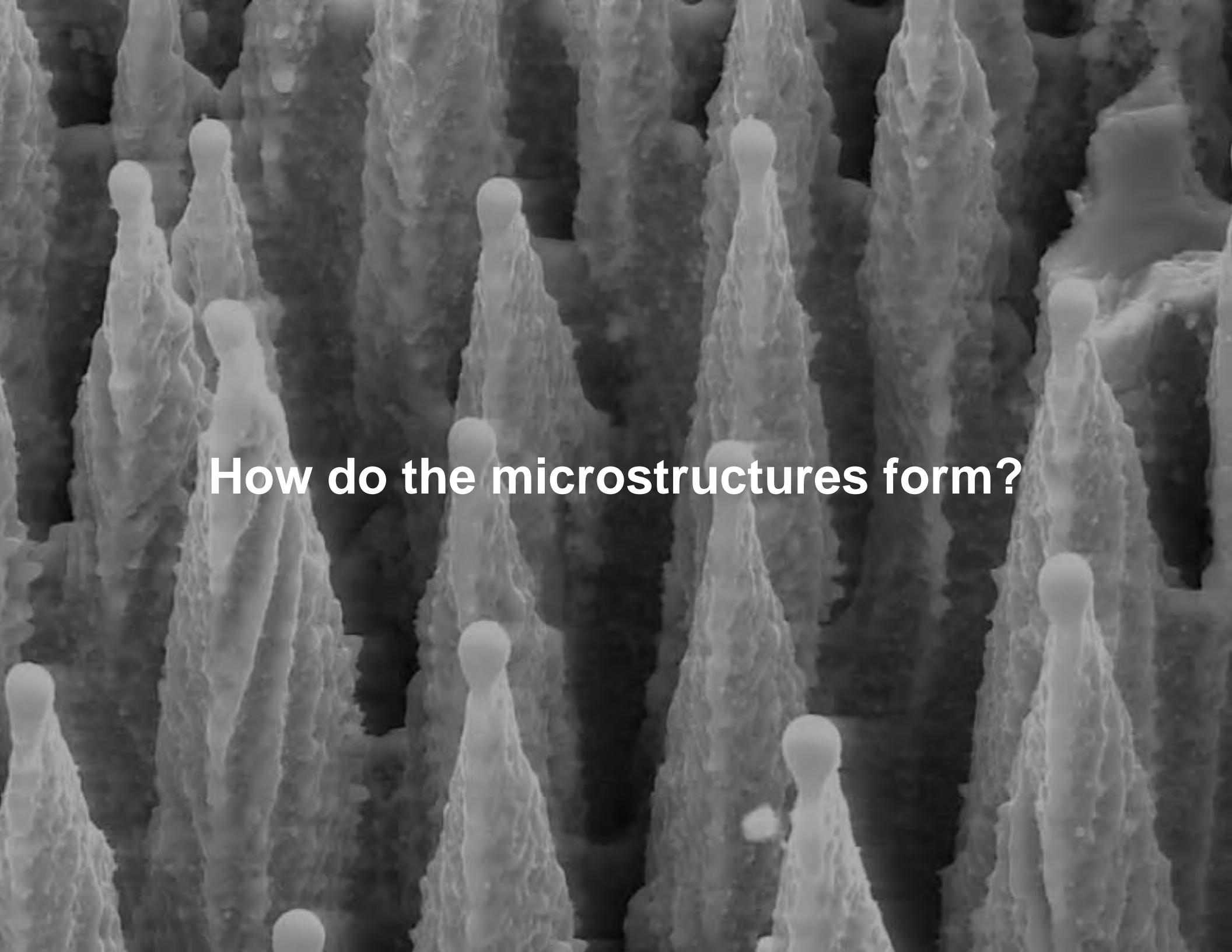
## **Avalanche photodiode with black silicon**

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

## **Other applications:**

- ▶ field emission arrays
- ▶ light emitters





**How do the microstructures form?**

x2000

#3548

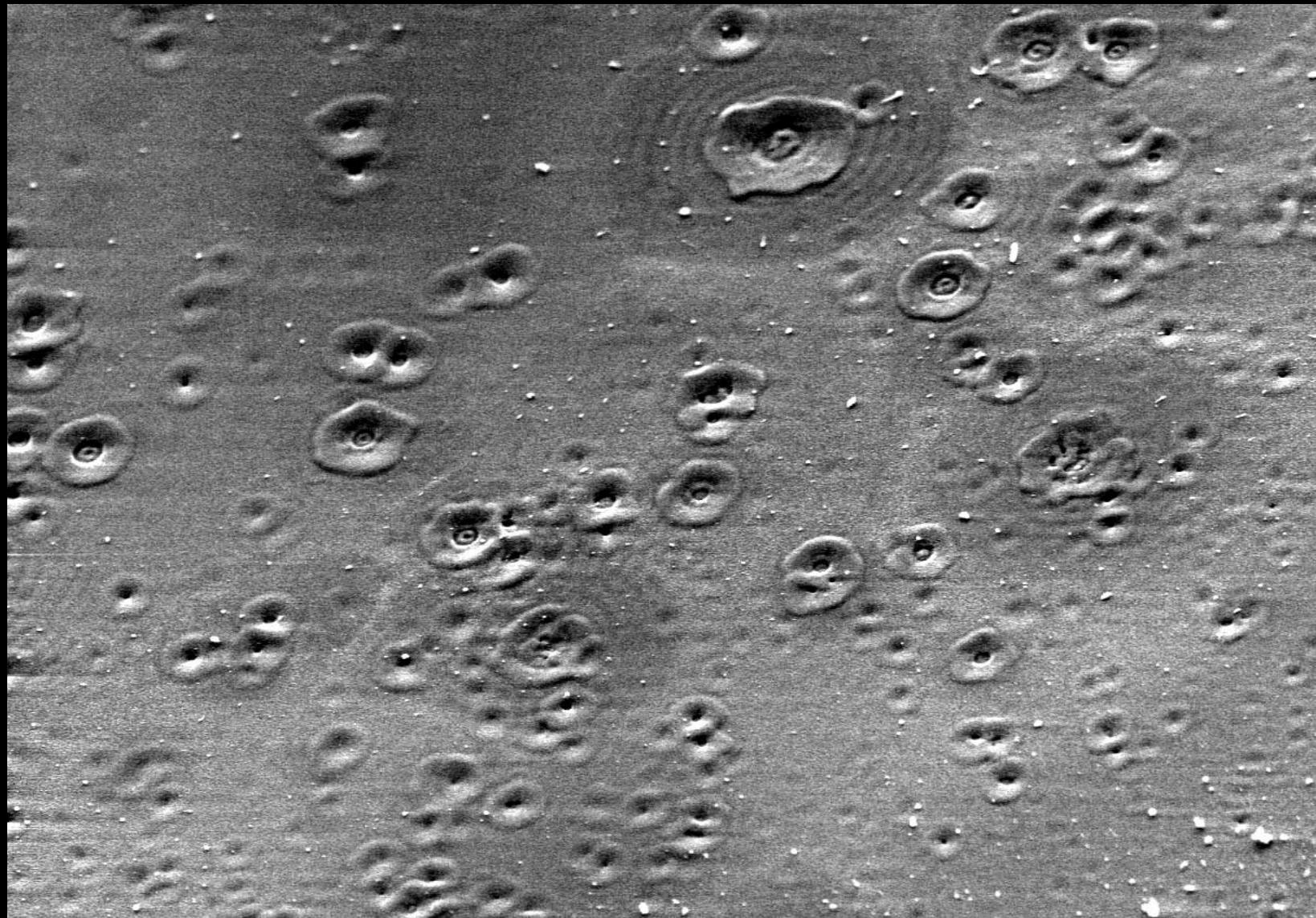
512 x 480

20  $\mu$ m

10kV

15mm

0000



x2000

20  $\mu\text{m}$

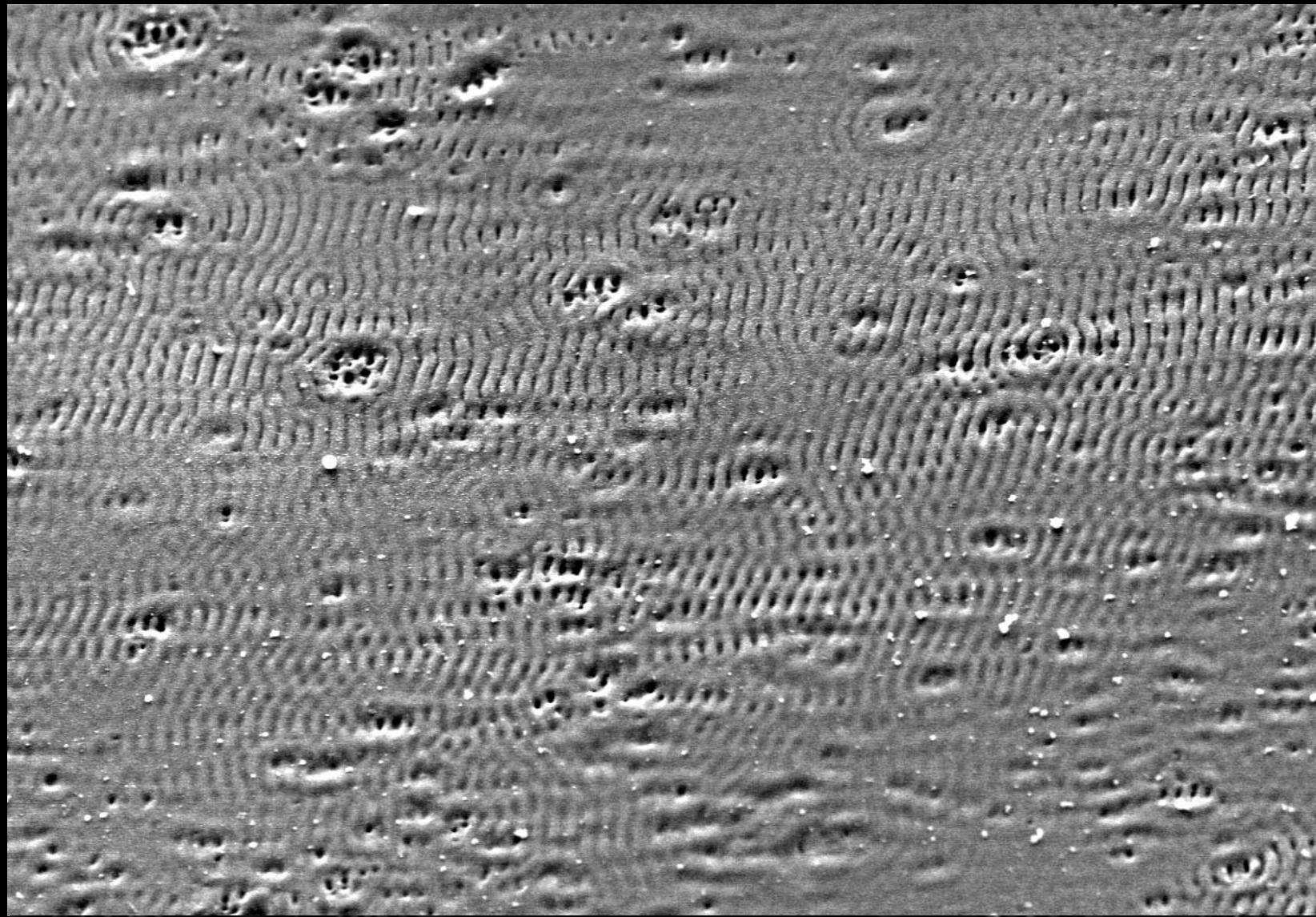
#3548

512 x 480

10kV

15mm

0001



x2000

20  $\mu\text{m}$

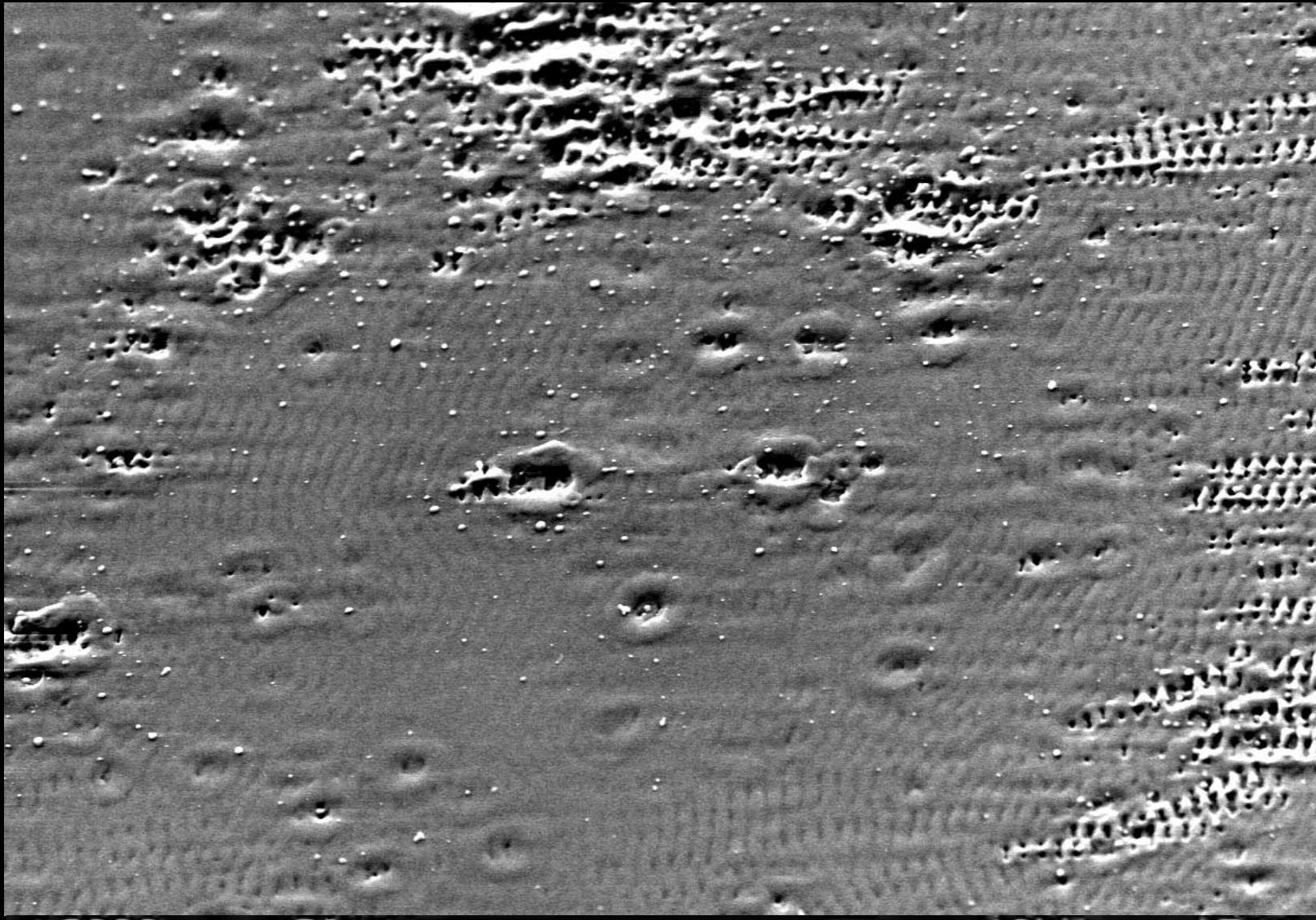
#3548

512 x 480

10kV

15mm

0002



x2000

20  $\mu\text{m}$

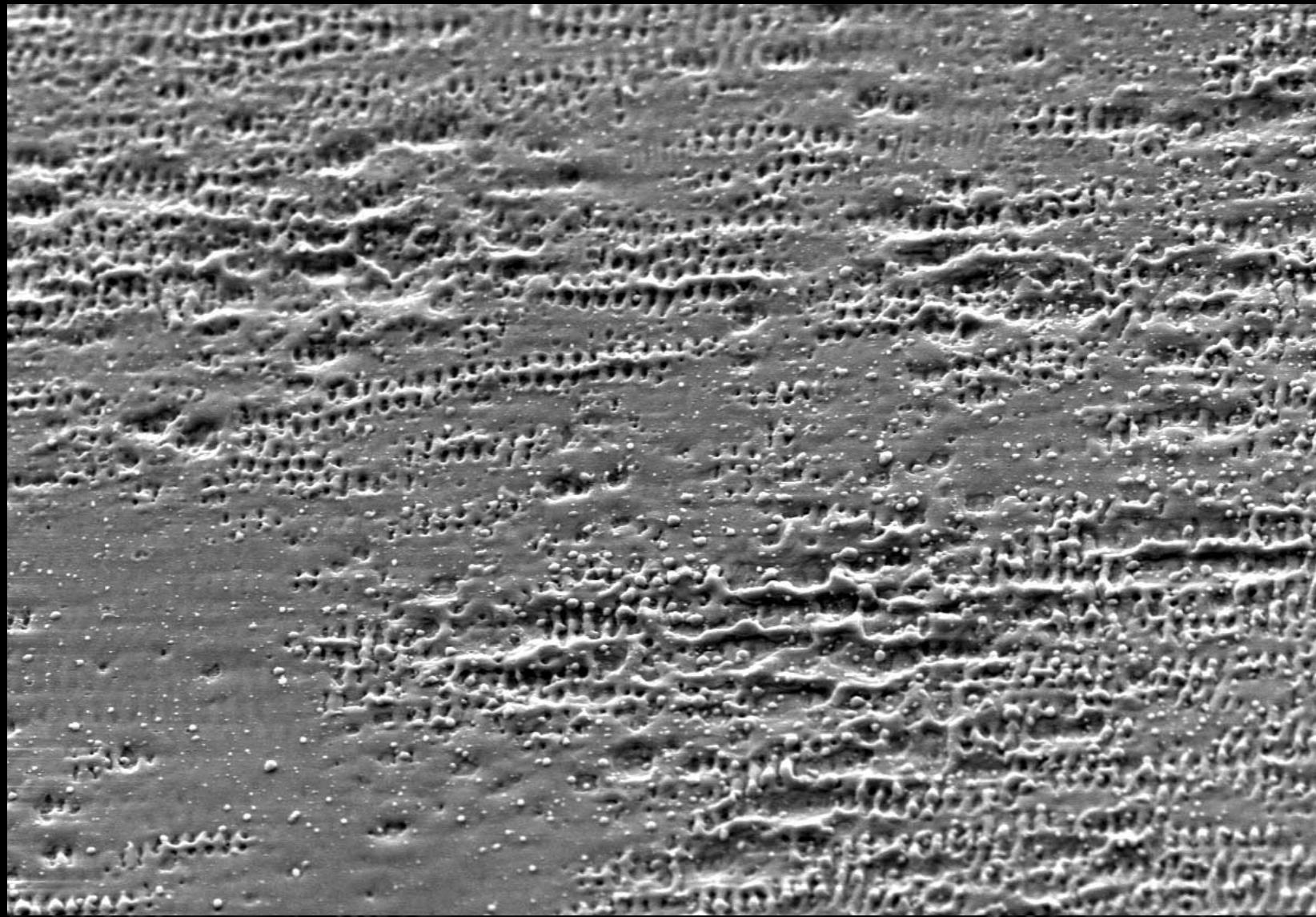
#3548

512 x 480

10kV

15mm

0003



x2000

20  $\mu\text{m}$

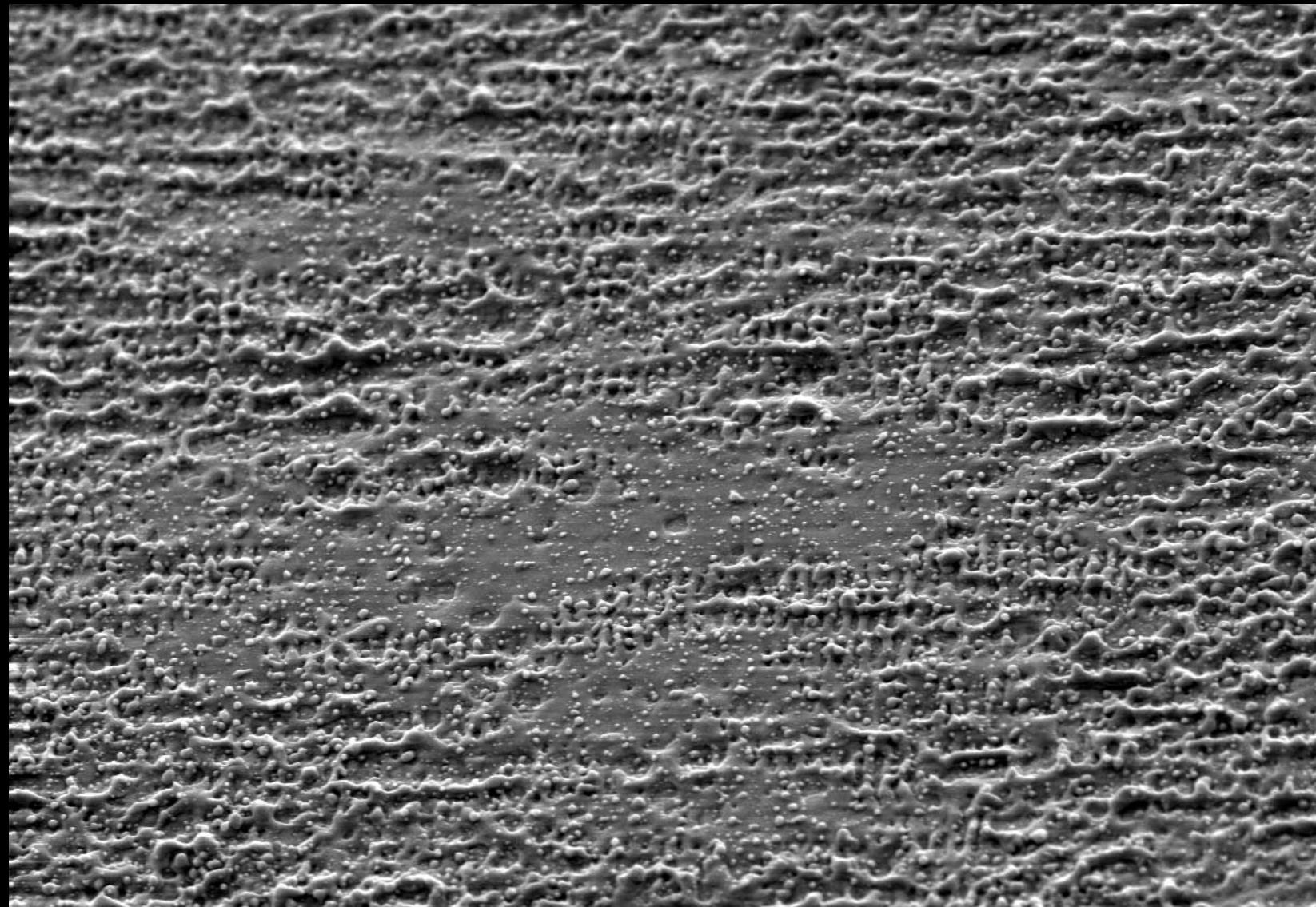
#3548

512 x 480

10kV

15mm

0004



x2000

20  $\mu\text{m}$

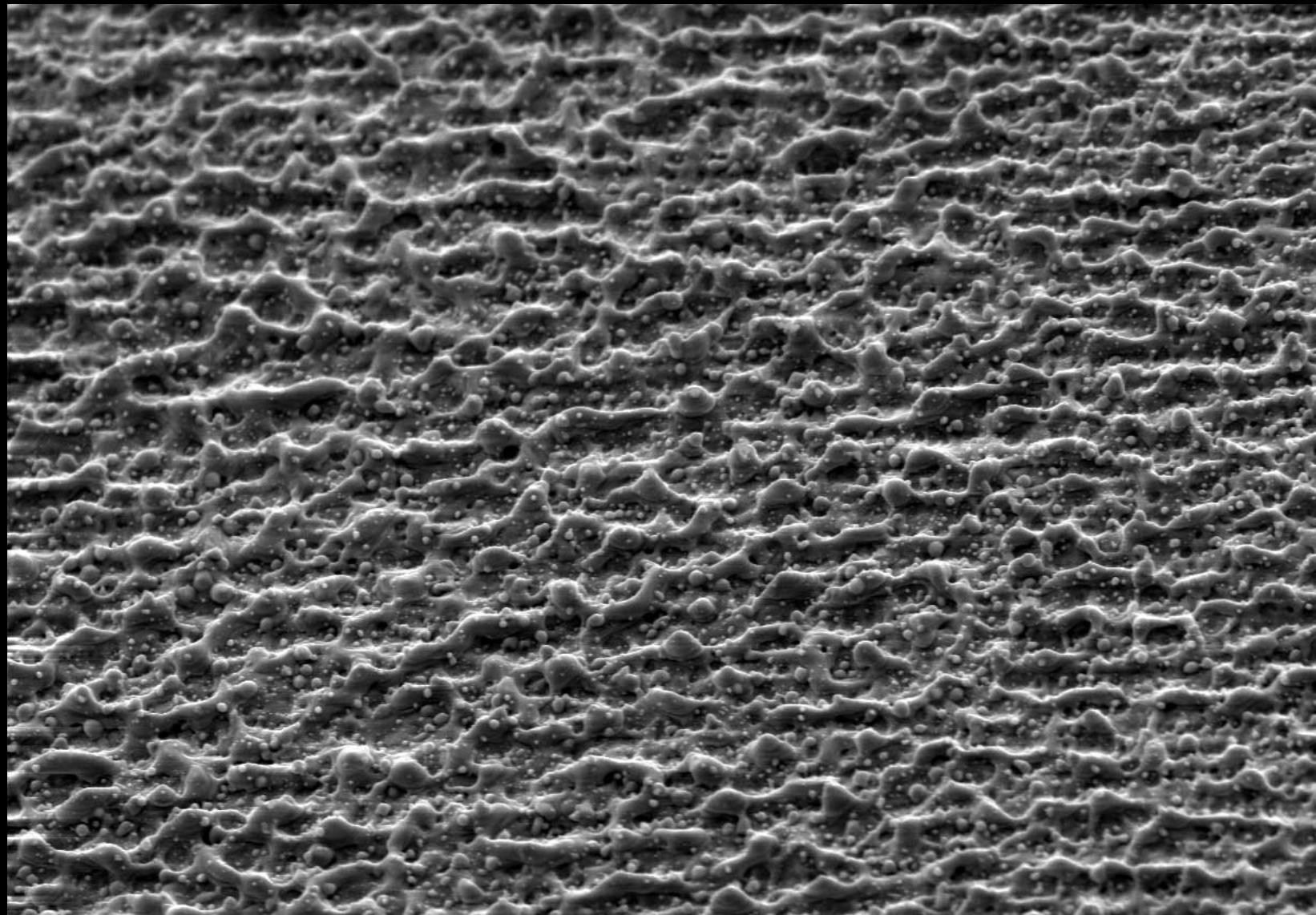
#3548

512 x 480

10kV

15mm

0005



x2000

#3548

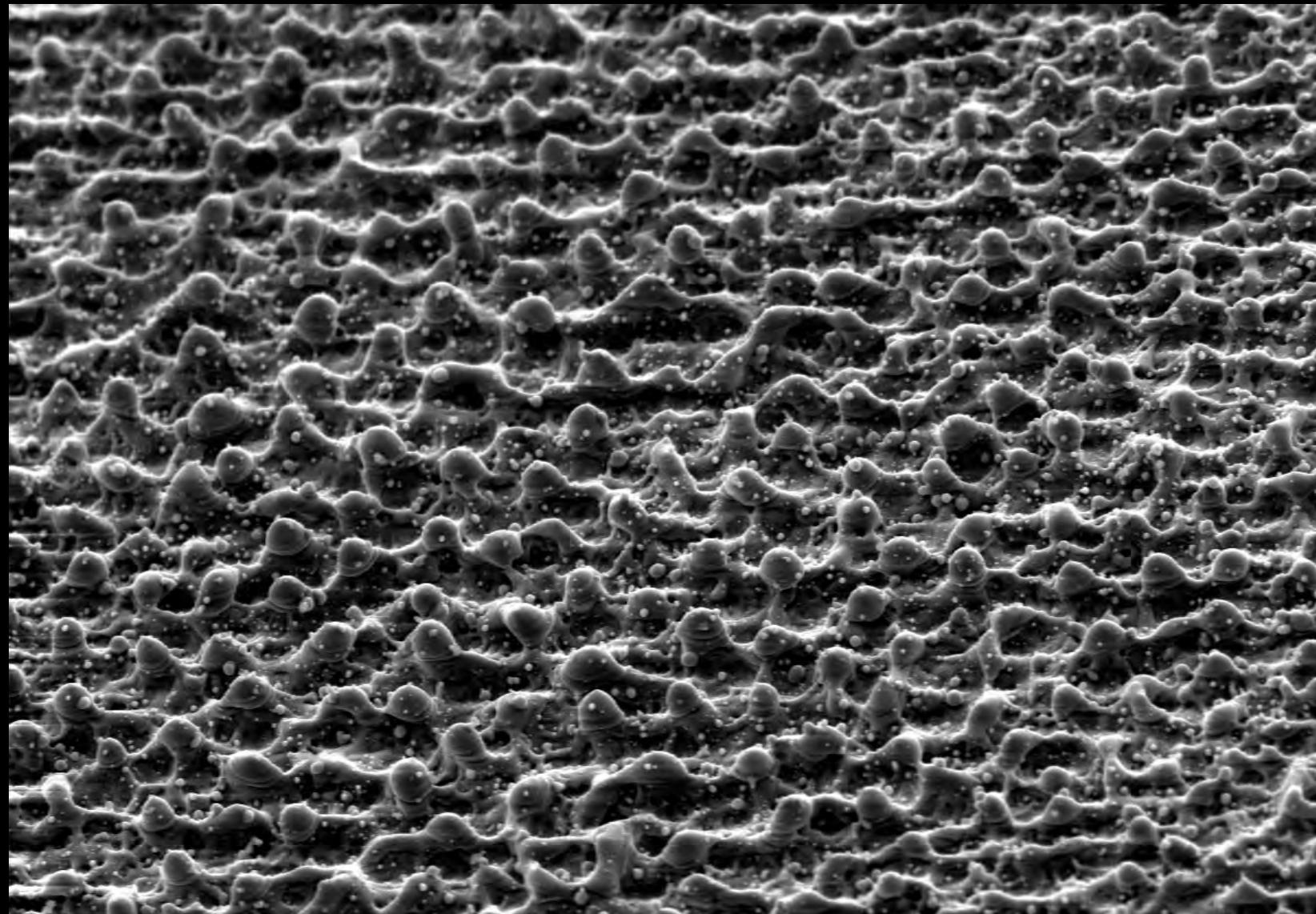
512 x 480

20  $\mu\text{m}$

10kV

15mm

0008



x2000

20  $\mu\text{m}$

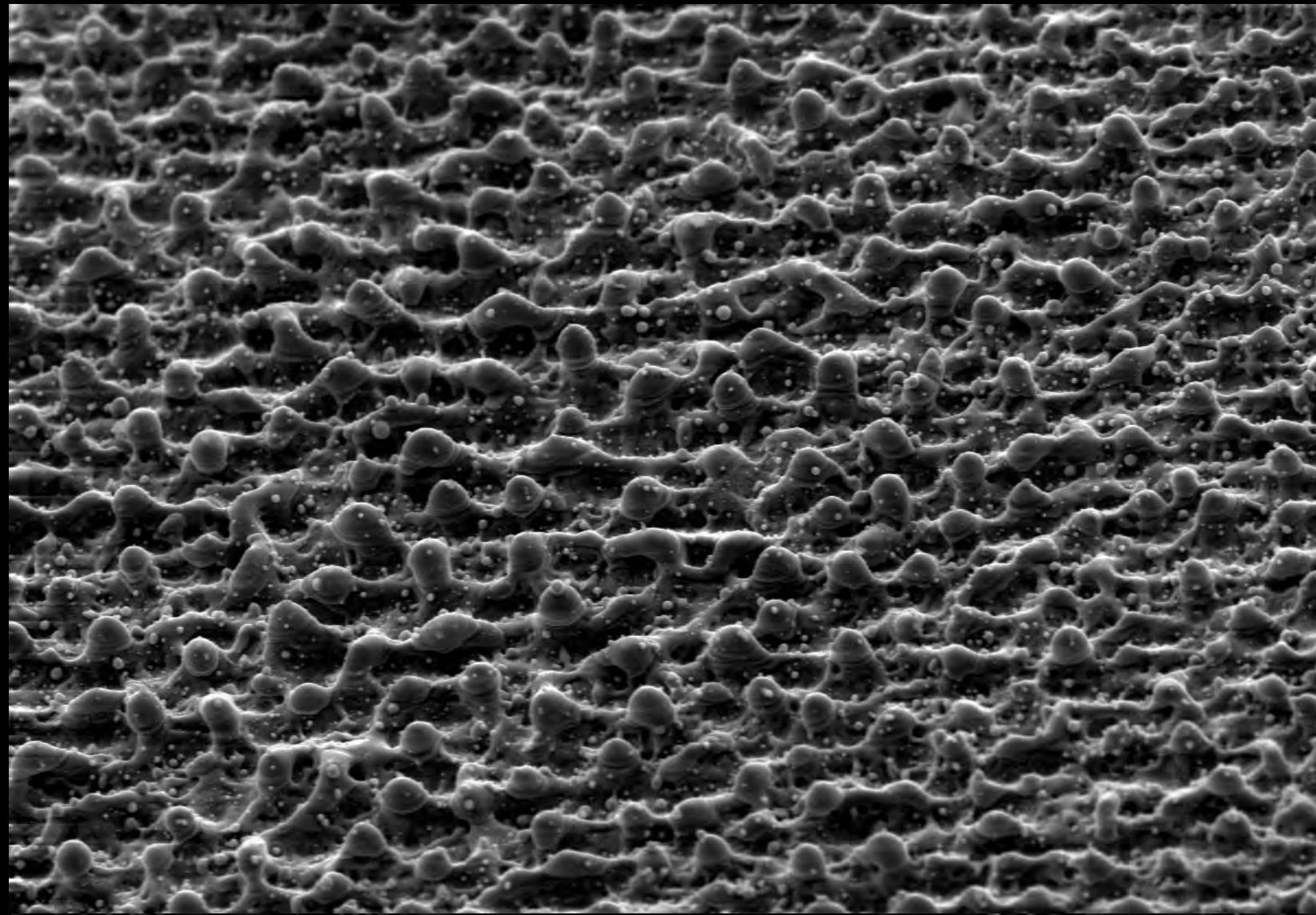
#3548

512 x 480

10kV

15mm

0010



x2000

#3548

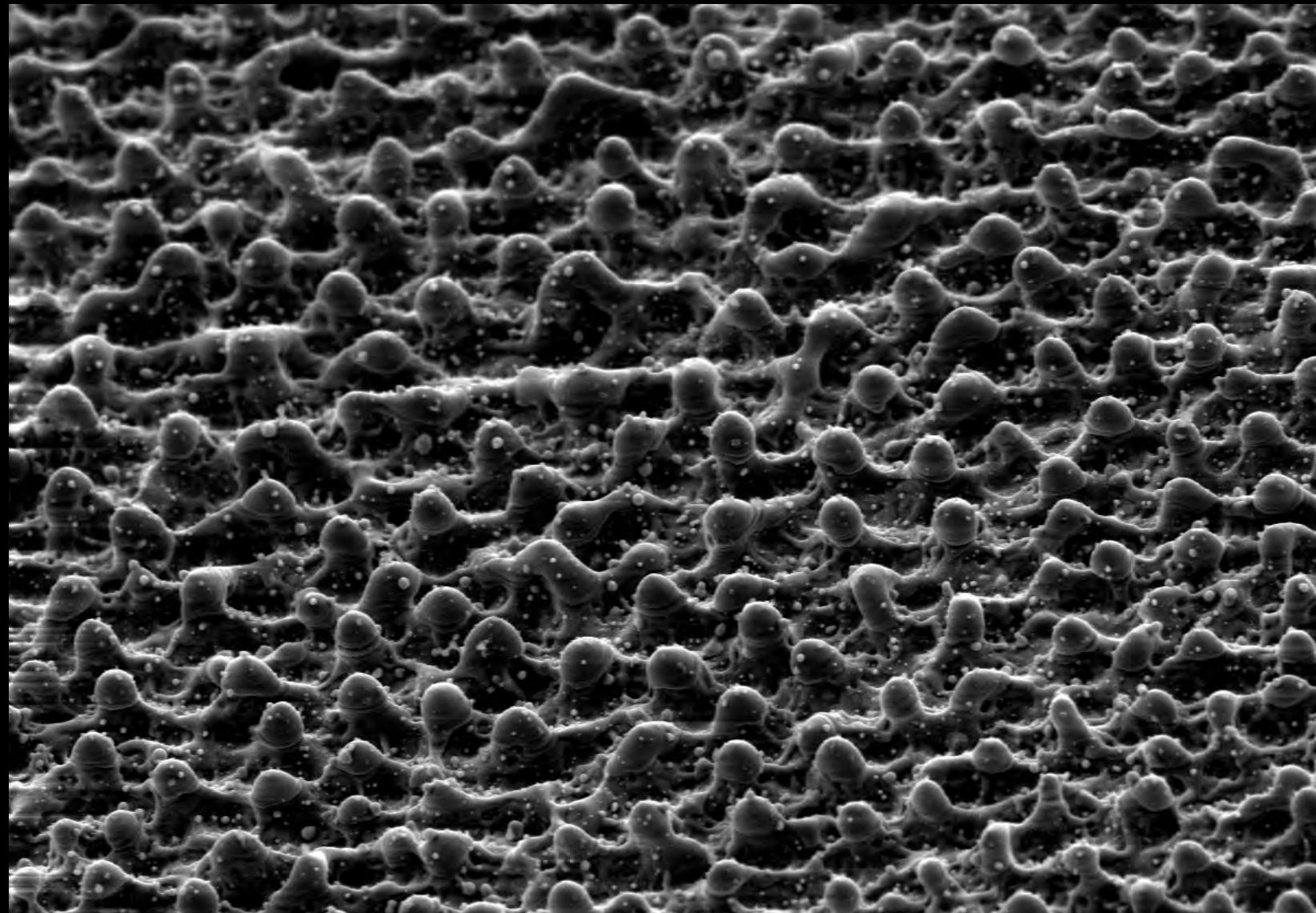
512 x 480

20  $\mu\text{m}$

10kV

15mm

0012



x2000

20  $\mu\text{m}$

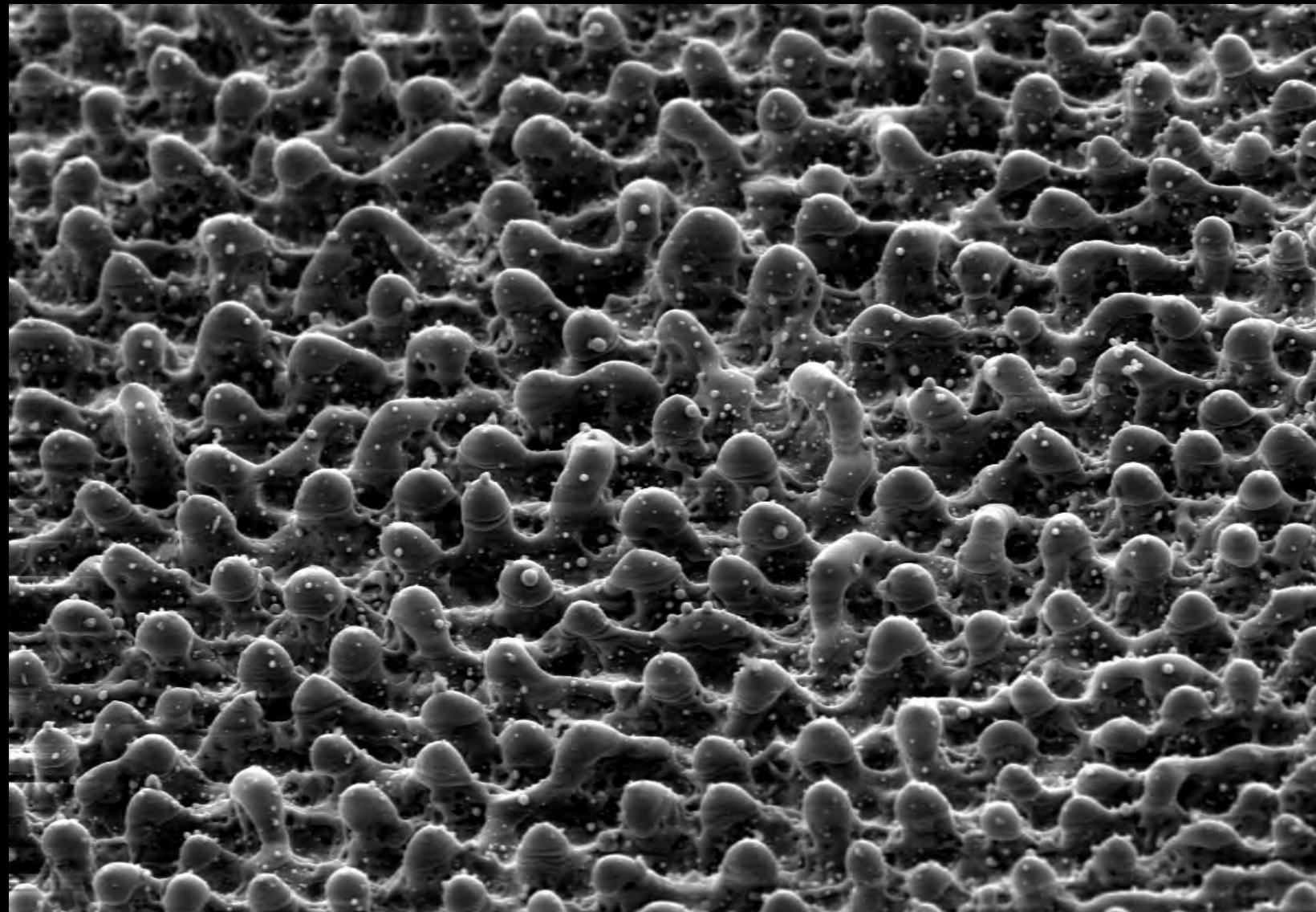
#3548

512 x 480

10kV

15mm

0015



x2000

20  $\mu\text{m}$

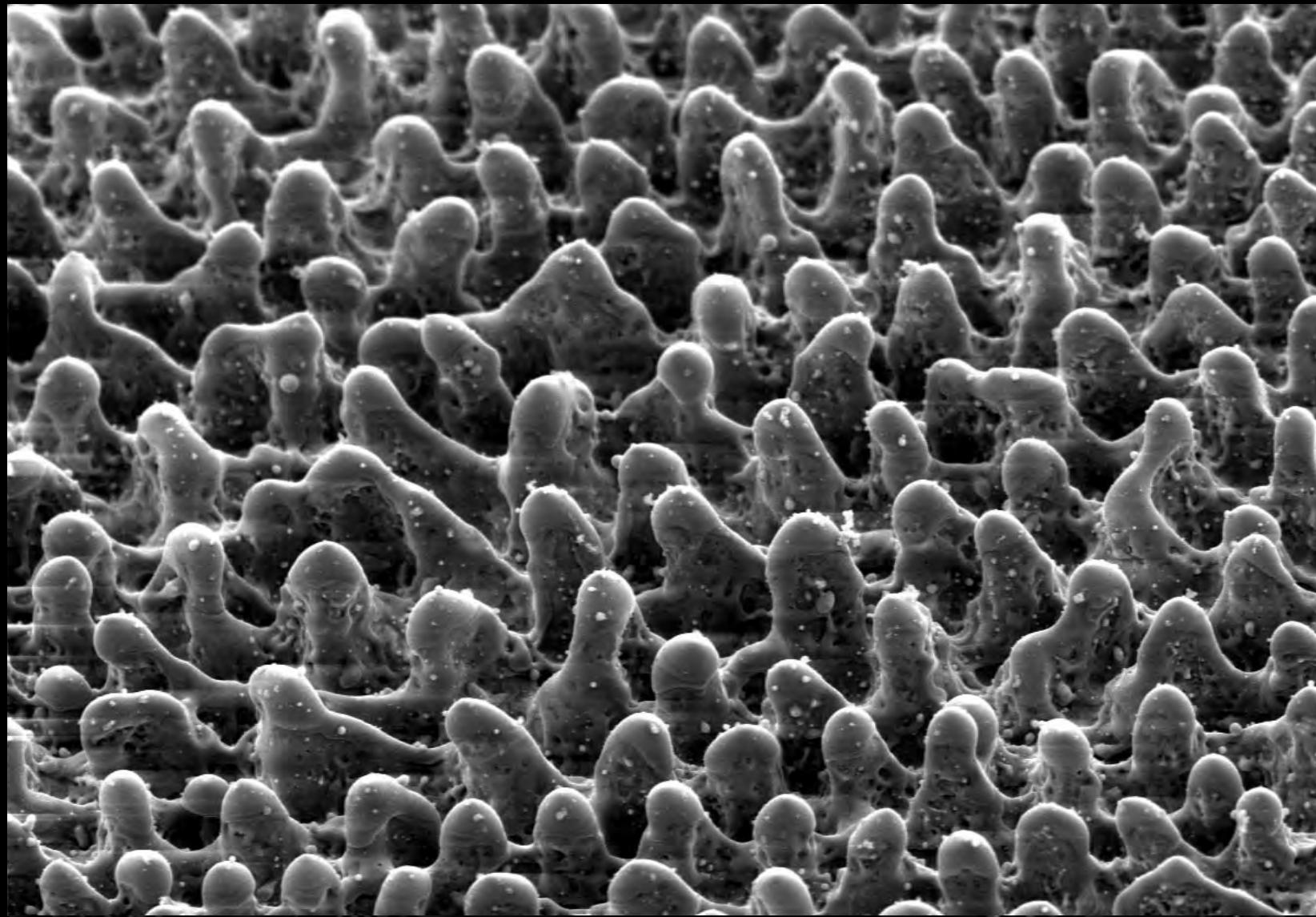
#3548

512 x 480

10kV

15mm

0020



x2000

20 $\mu$ m

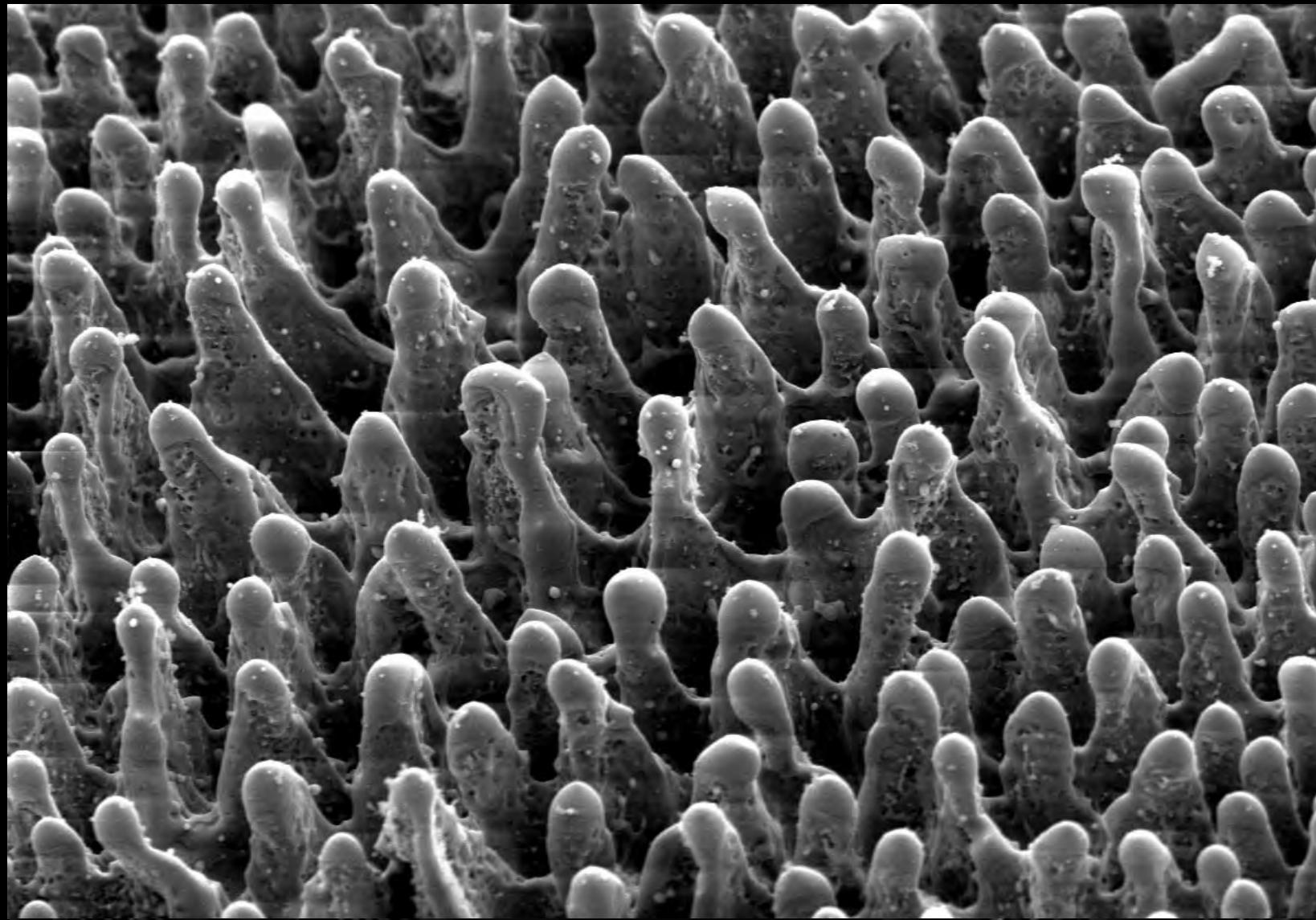
#3548

512 x 480

10kV

15mm

0030



x2000

20  $\mu\text{m}$

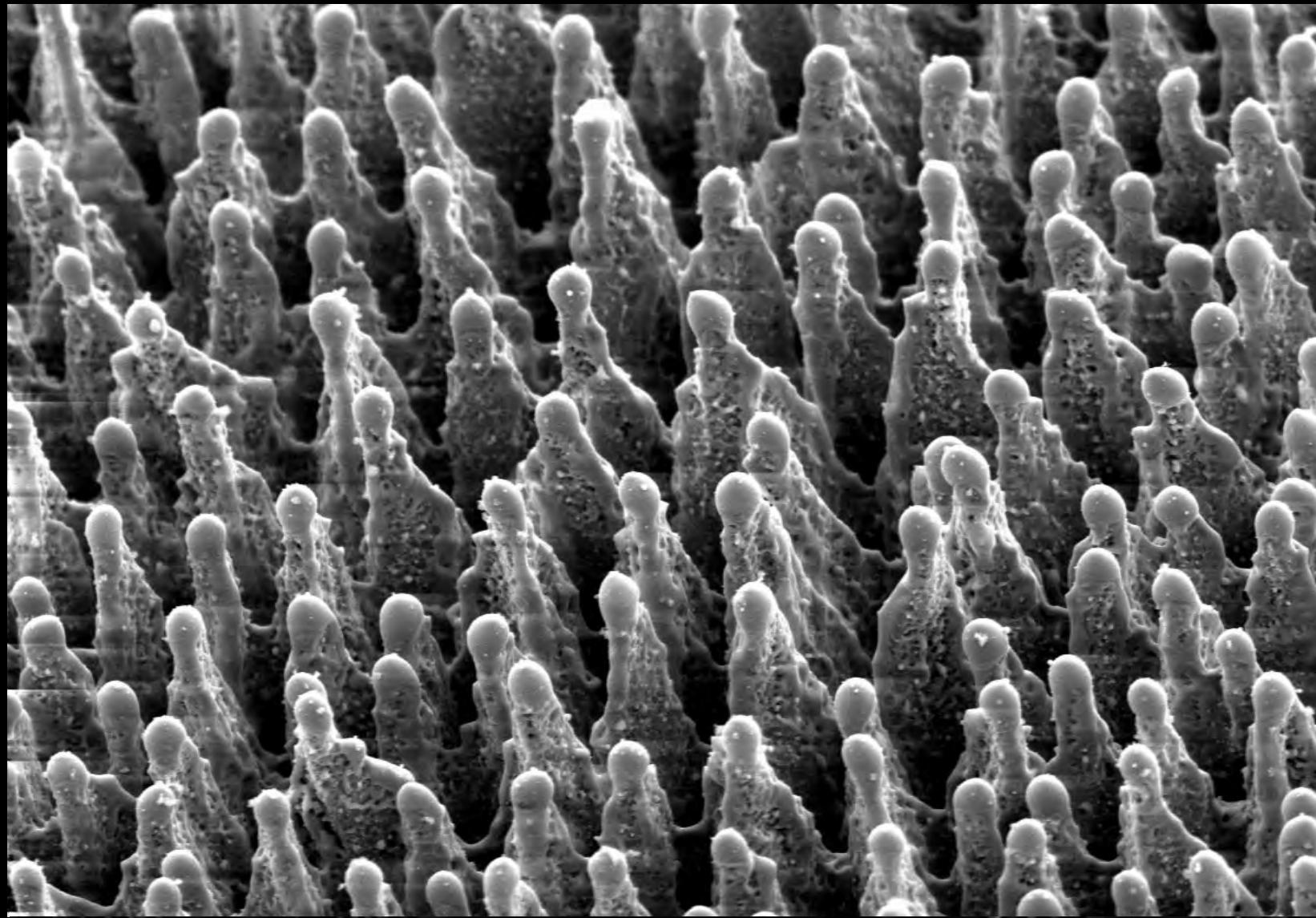
#3548

512 x 480

10kV

15mm

0050



x2000

20  $\mu\text{m}$

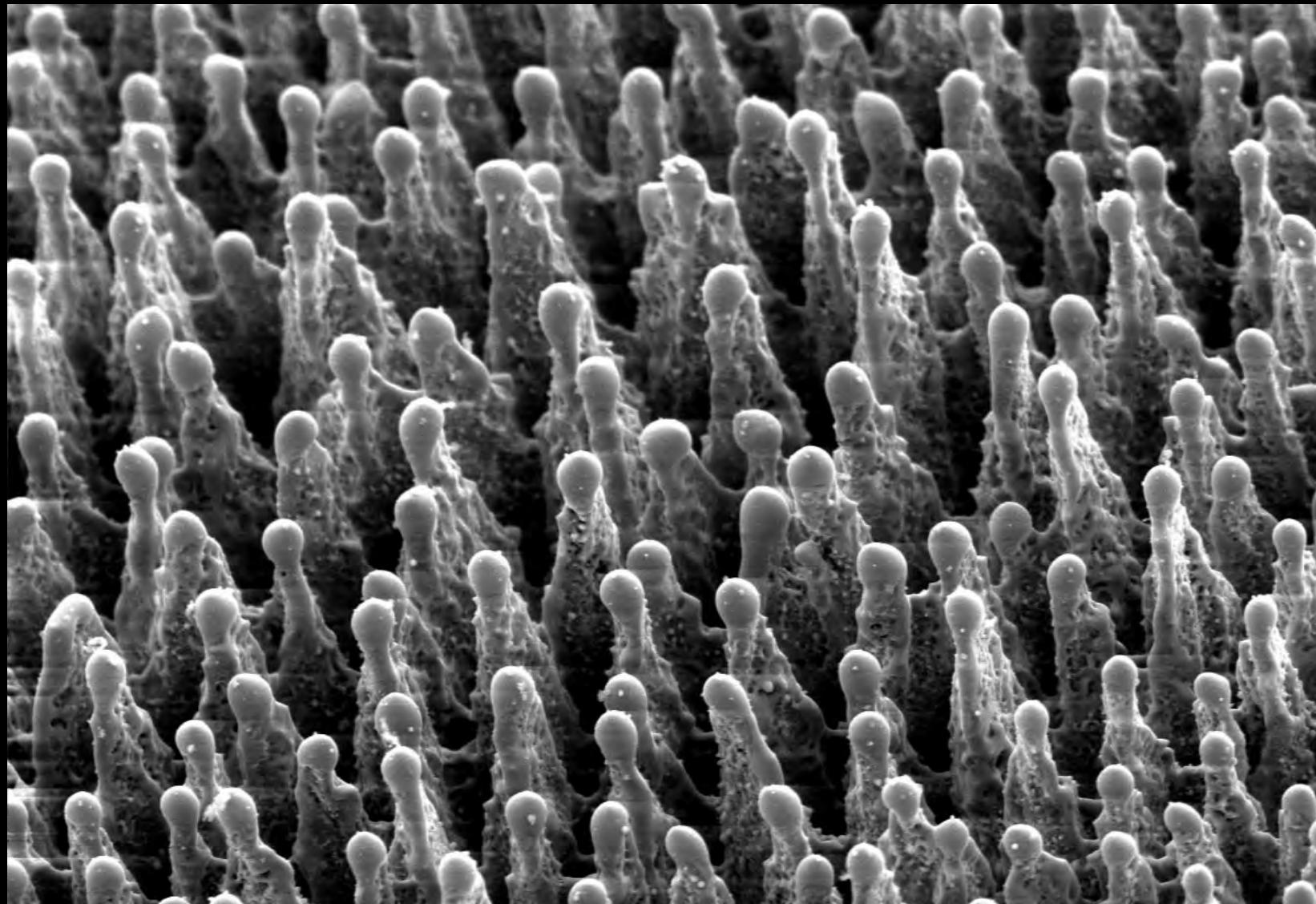
10kV

15mm

#3548

512 x 480

0070



x2000

20  $\mu\text{m}$

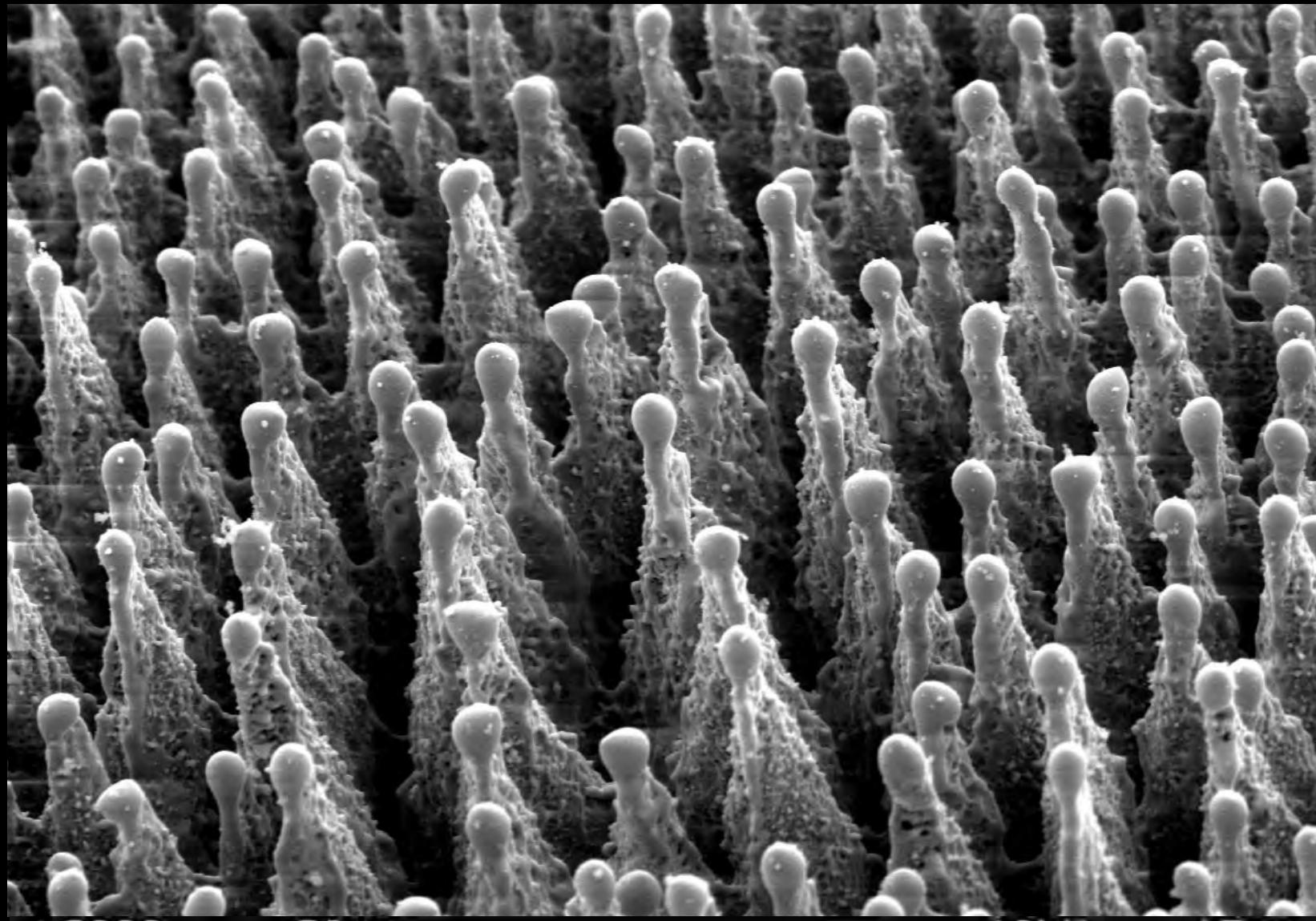
#3548

512 x 480

10kV

15mm

0100



x2000

20  $\mu\text{m}$

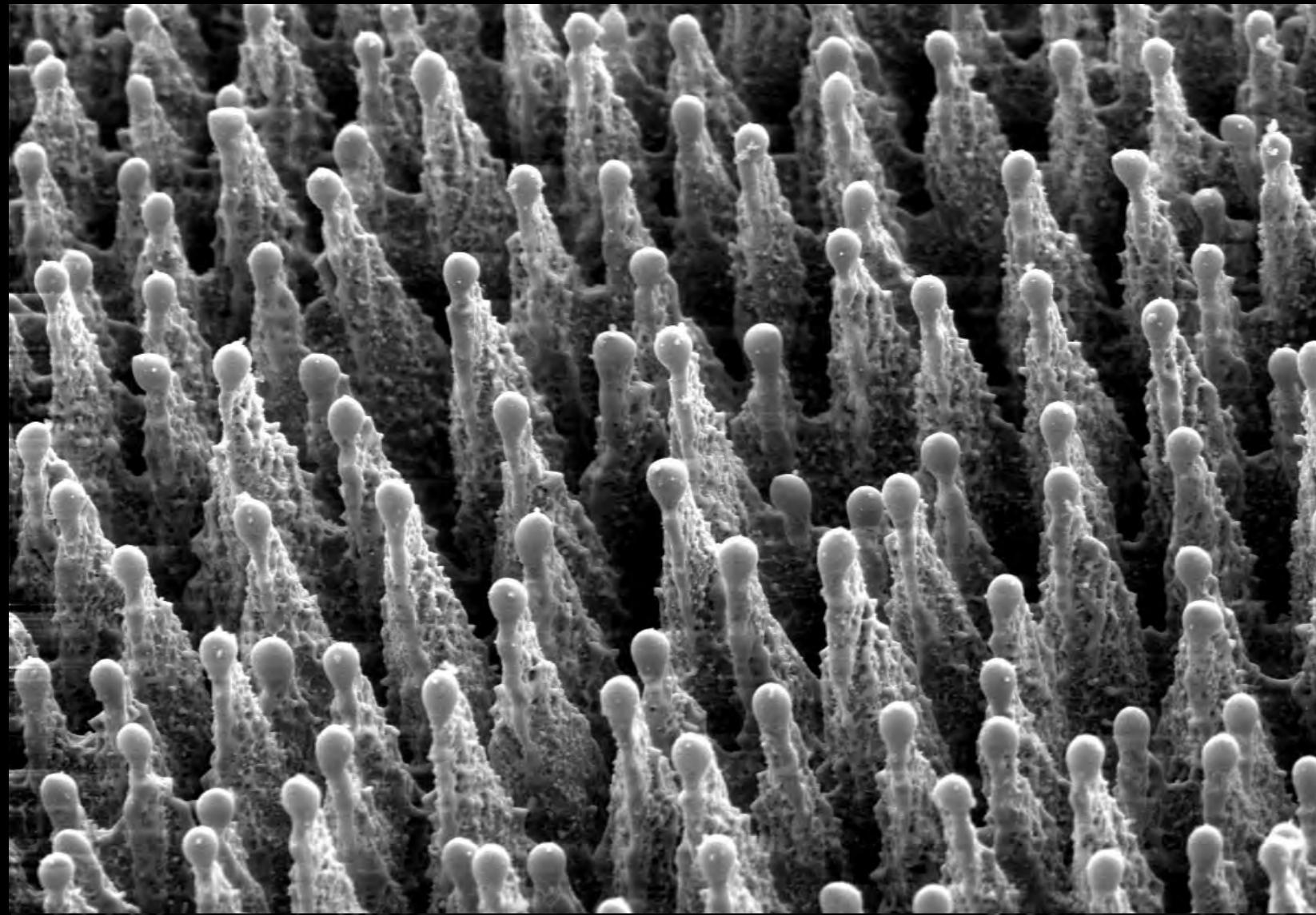
#3548

512 x 480

10kV

15mm

0200



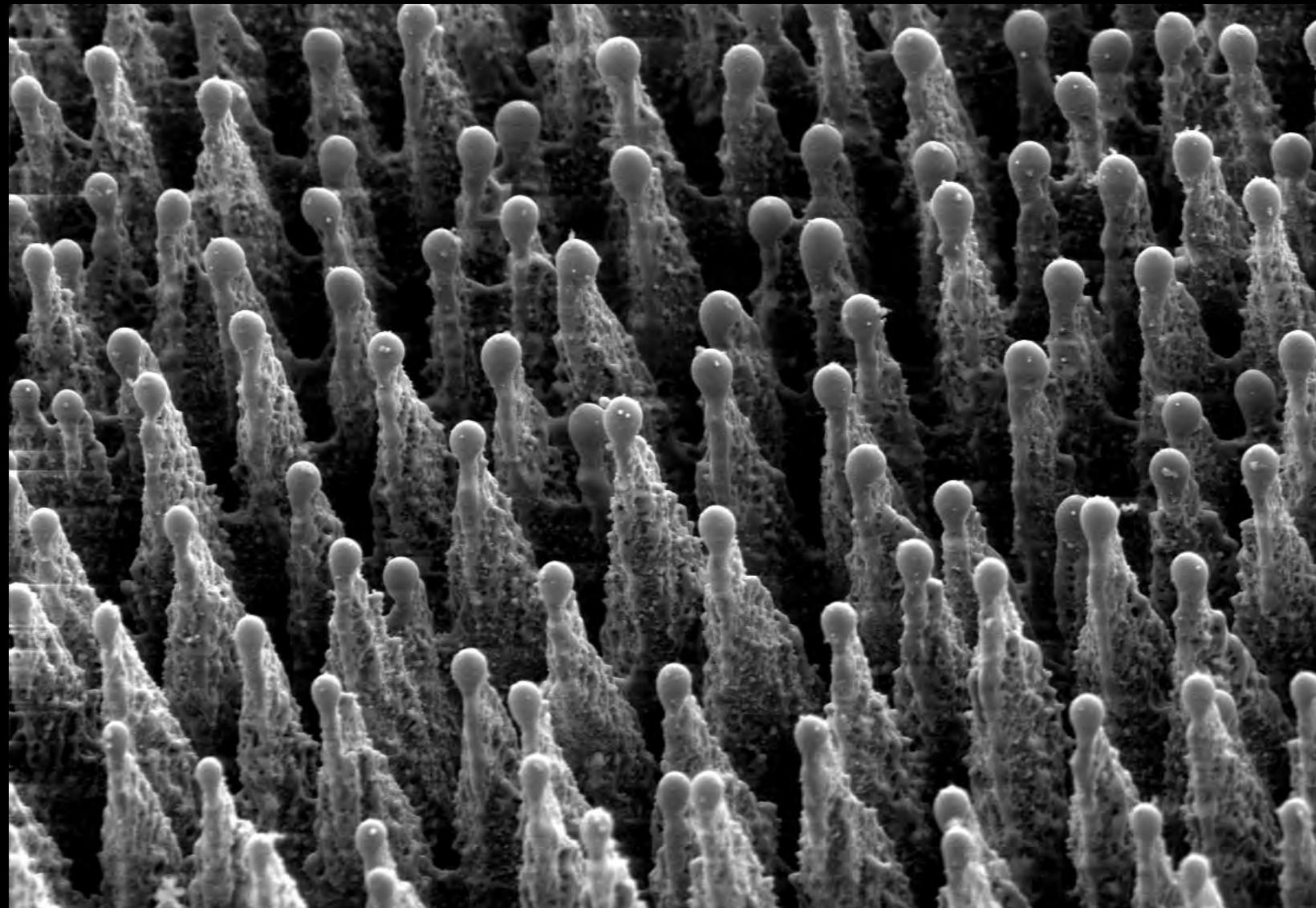
x2000  
#3548  
512 x 480

20  $\mu\text{m}$

10kV

15mm

0400



x2000

20  $\mu\text{m}$

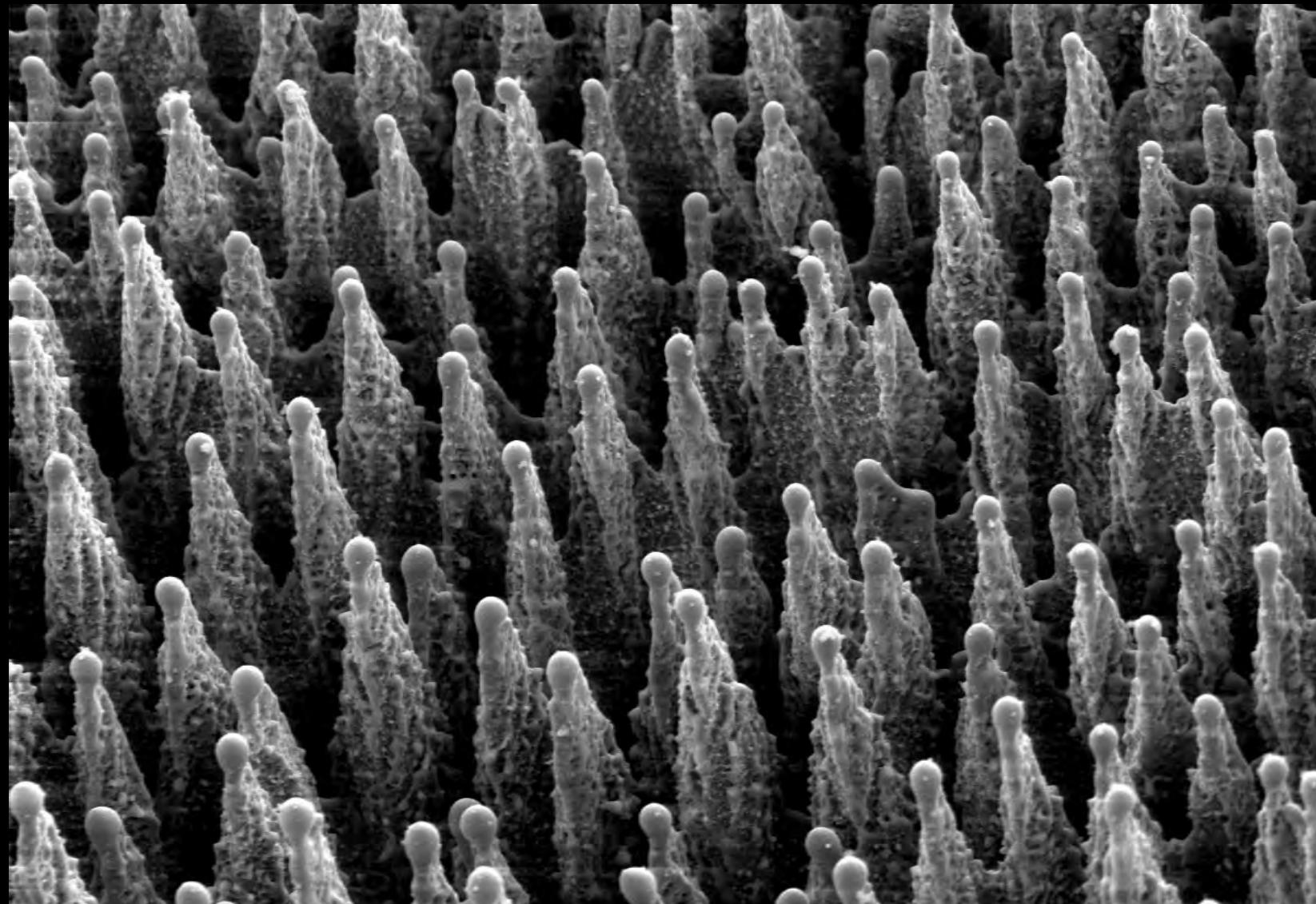
#3548

512 x 480

10kV

15mm

0600



x2000

20  $\mu\text{m}$

#3548

512 x 480

10kV

15mm

1000

# *Formation process*

**How do ripples give way to spikes?**

## **Follow evolution of spatial frequencies**

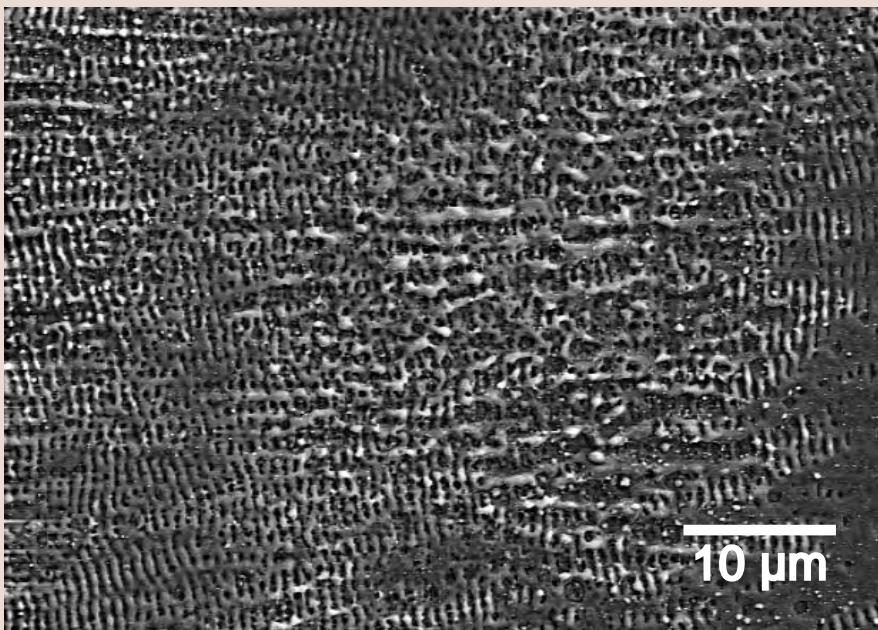
- ▶ vary number of laser pulses
- ▶ calculate Fourier transform of images

# *Formation process*

ripples

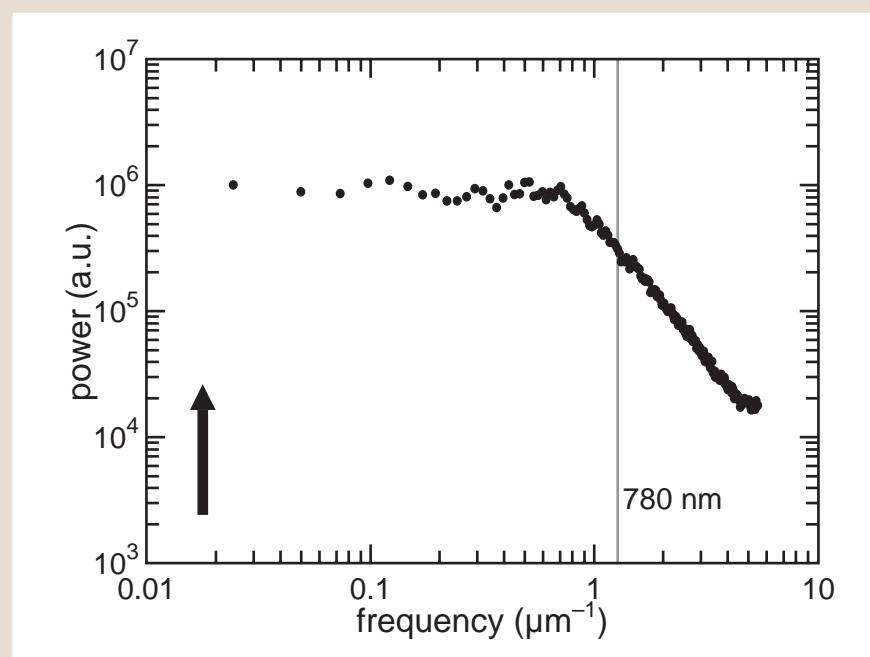
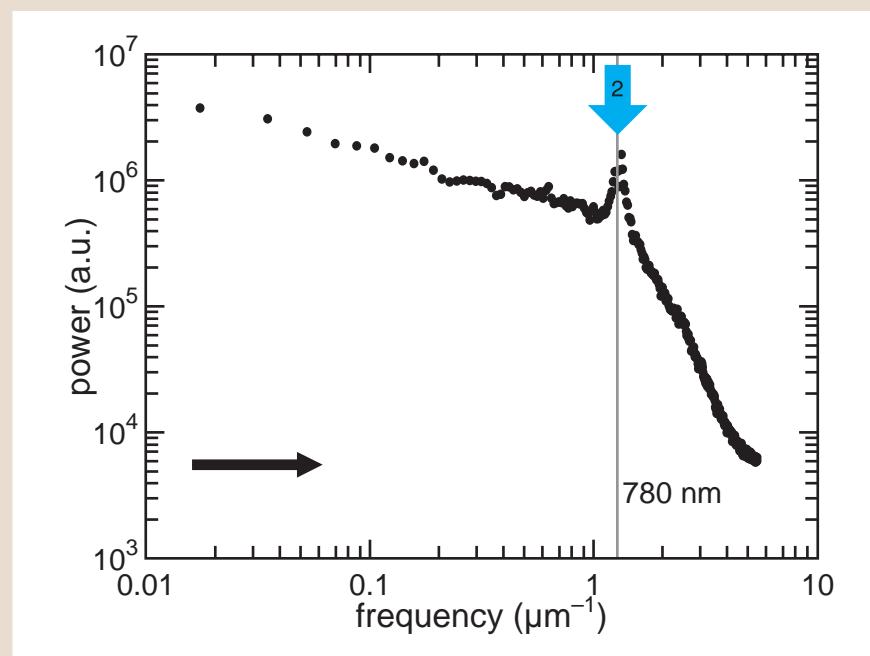
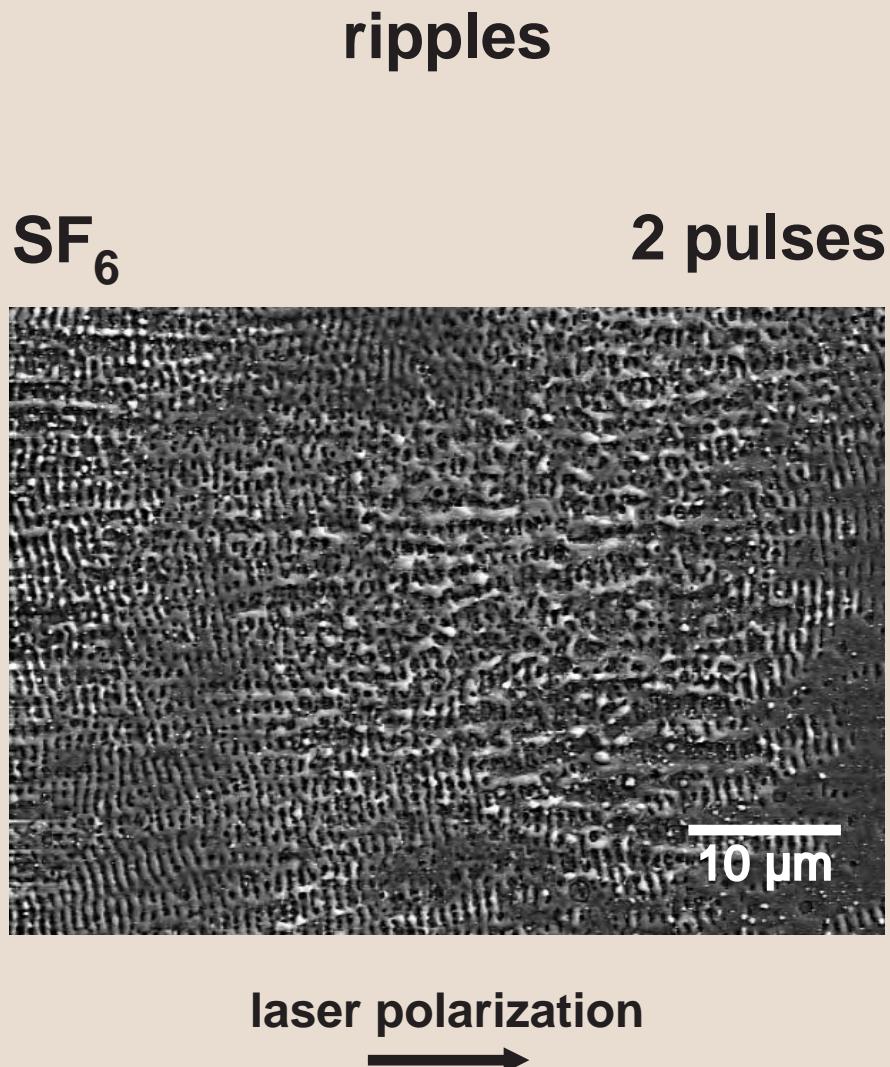
$SF_6$

2 pulses

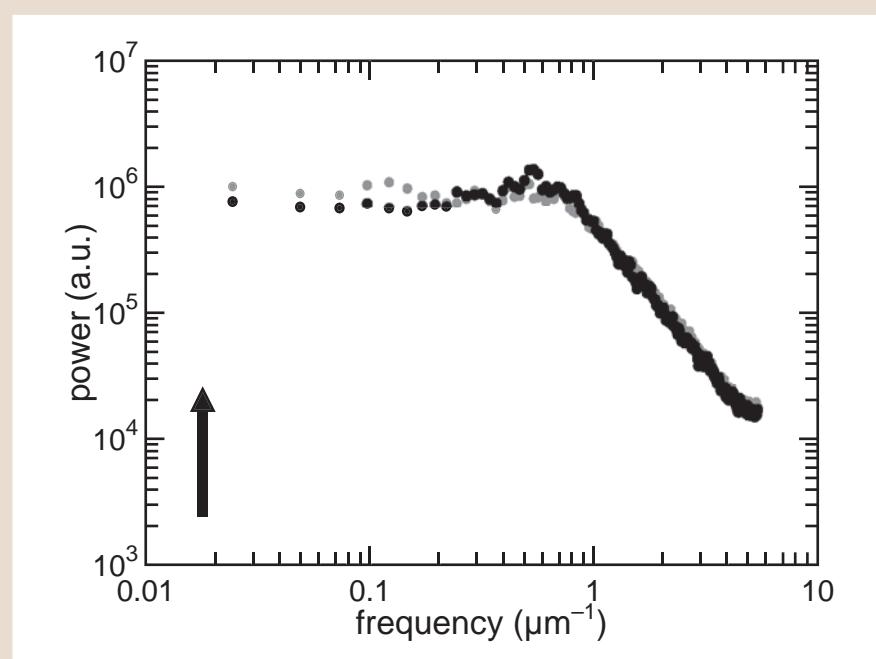
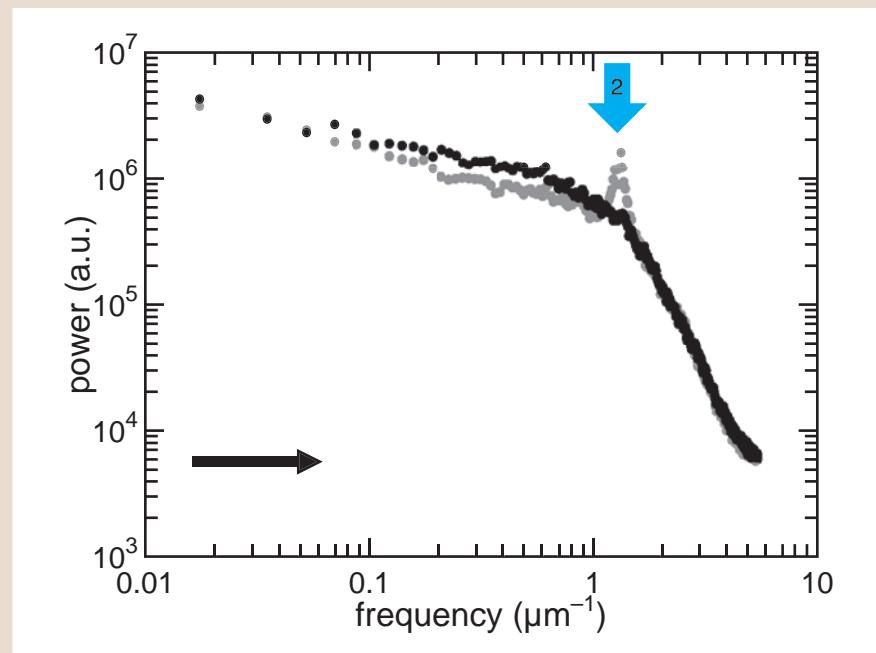
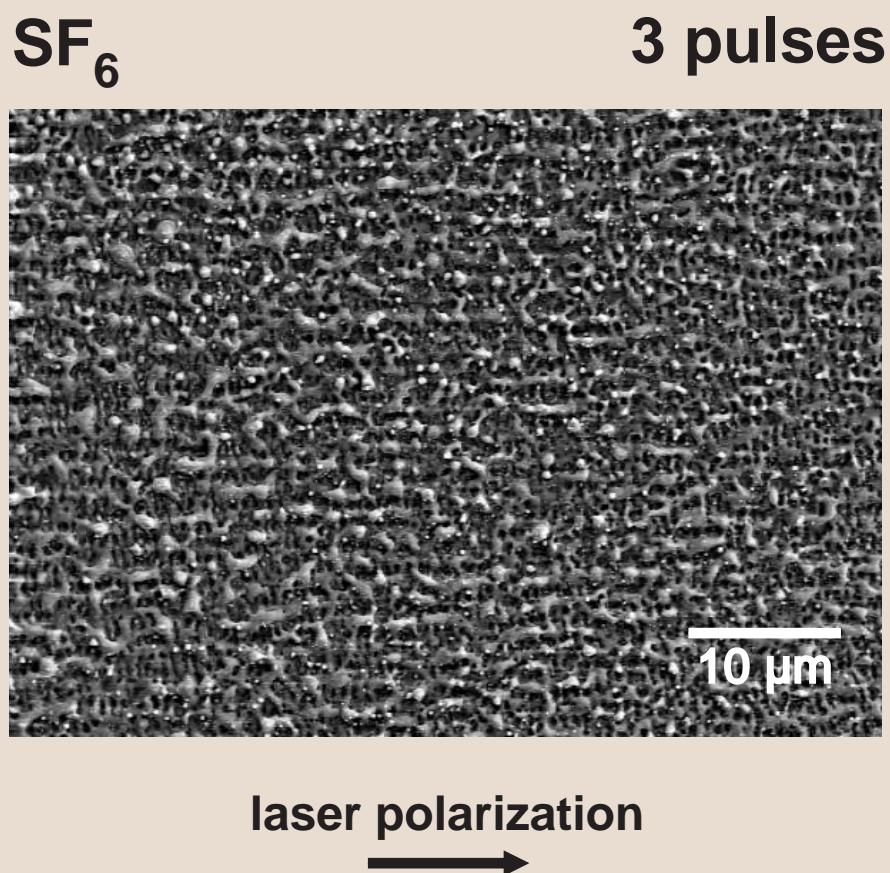


laser polarization  
→

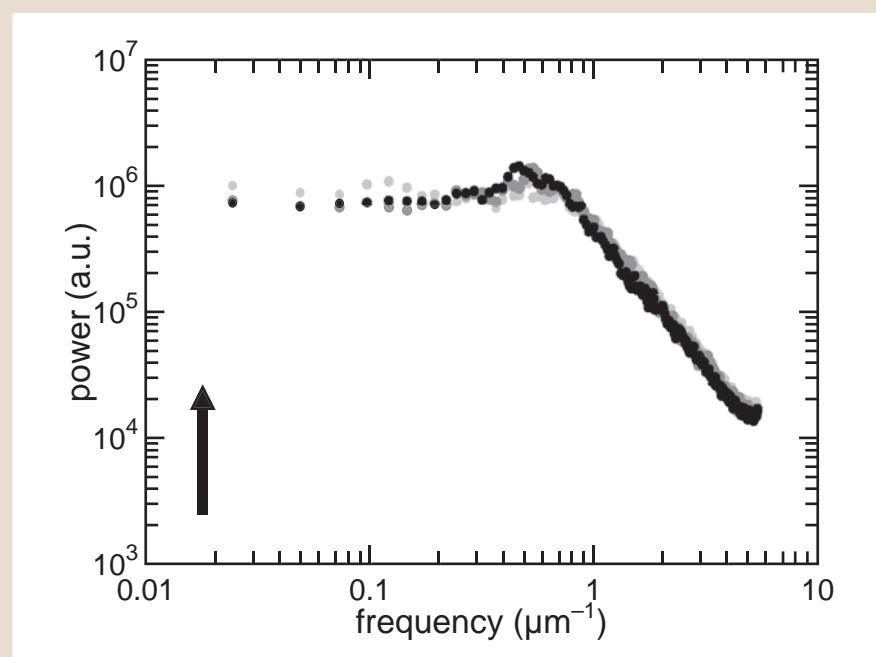
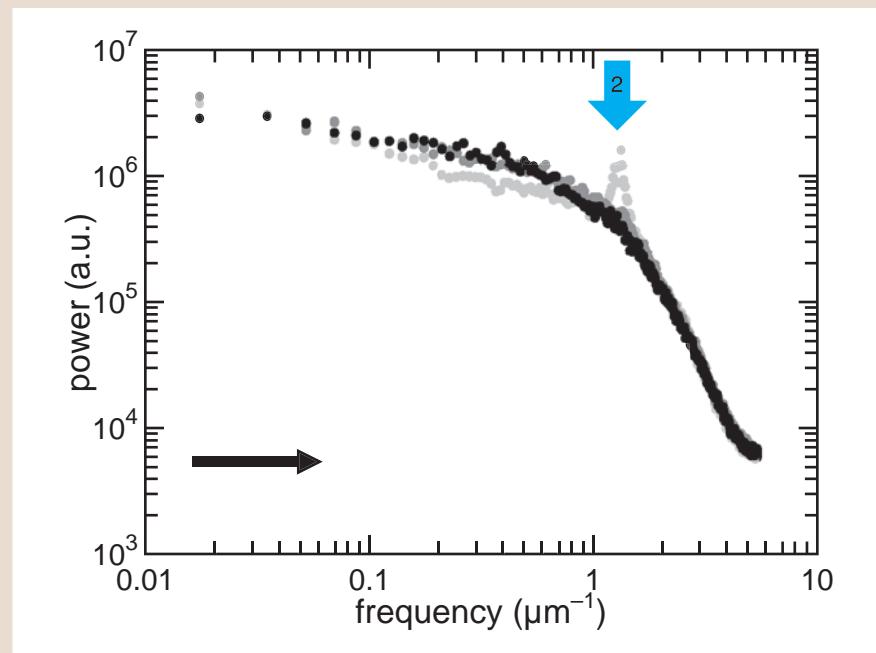
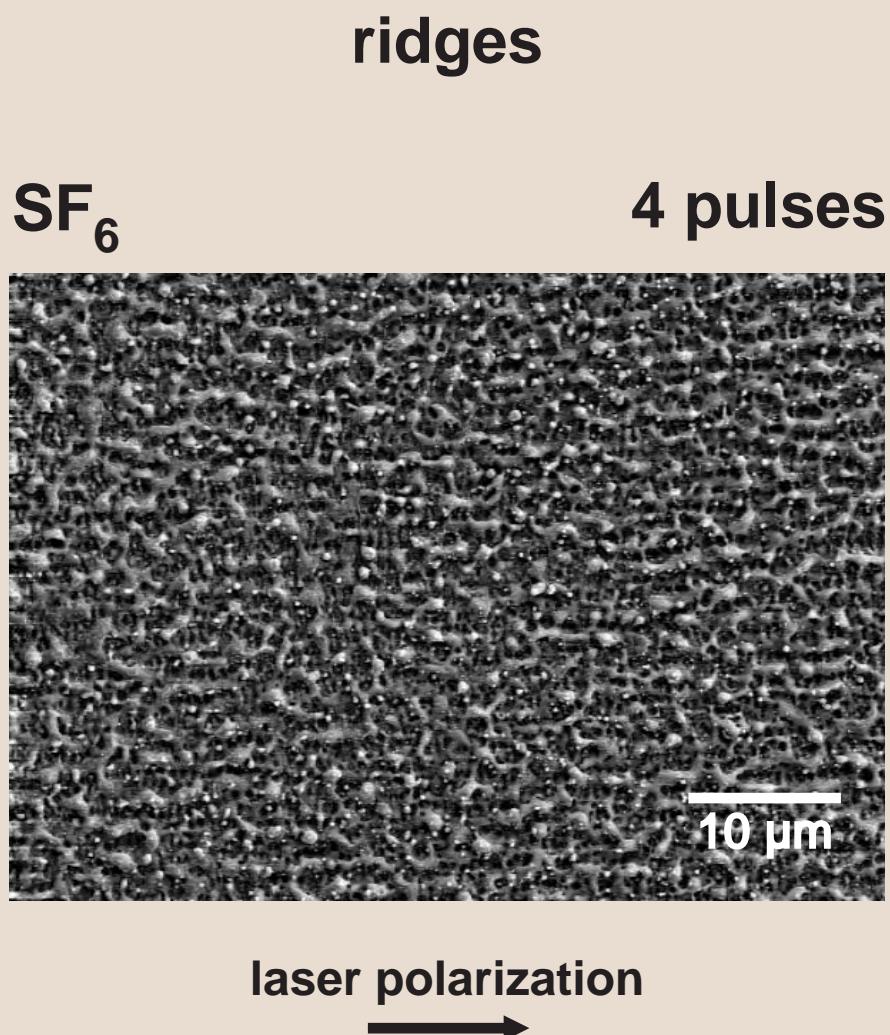
# *Formation process*



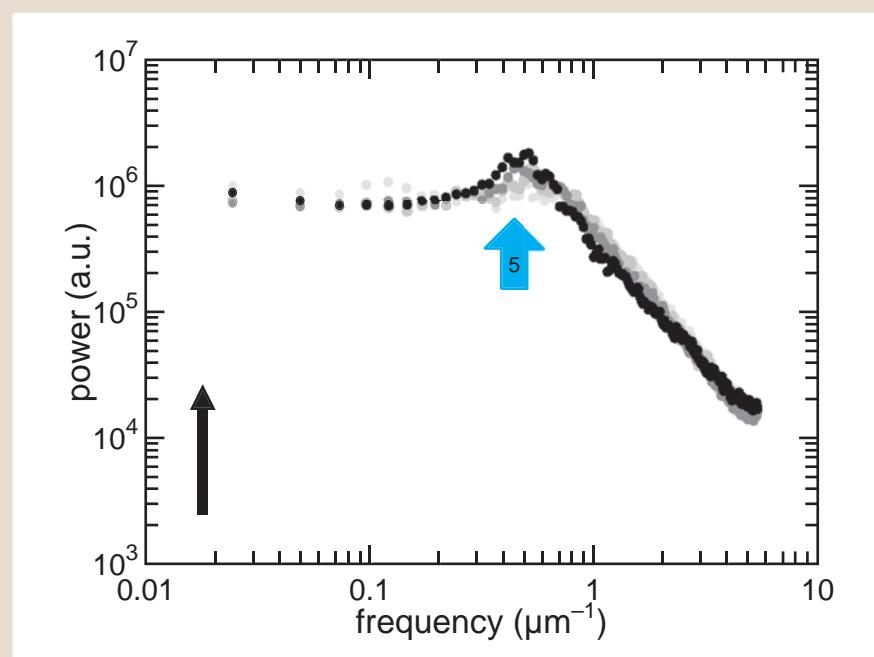
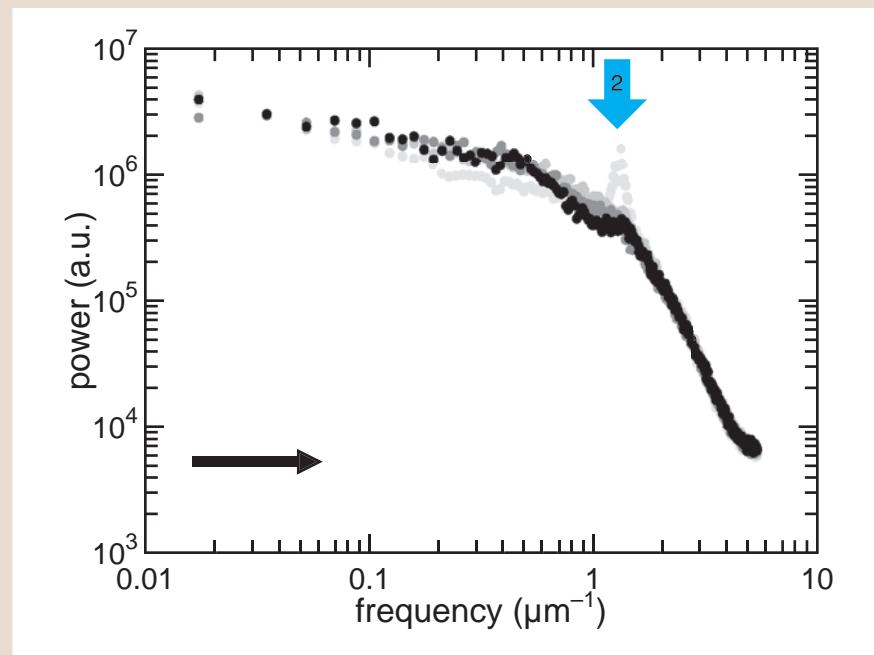
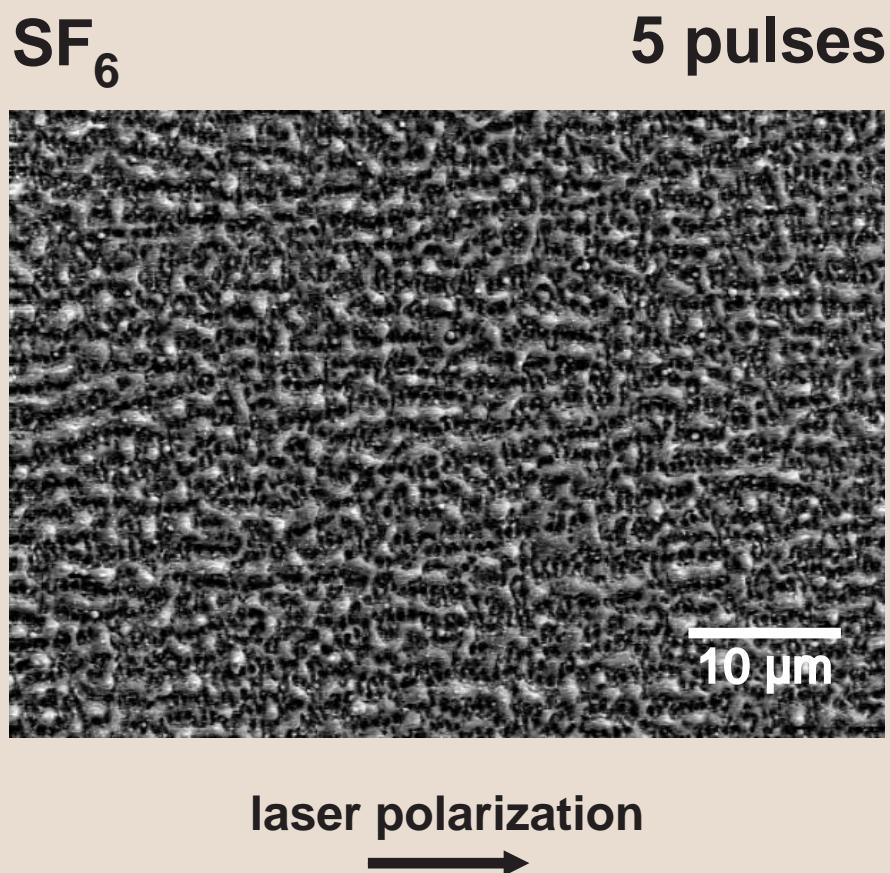
# *Formation process*



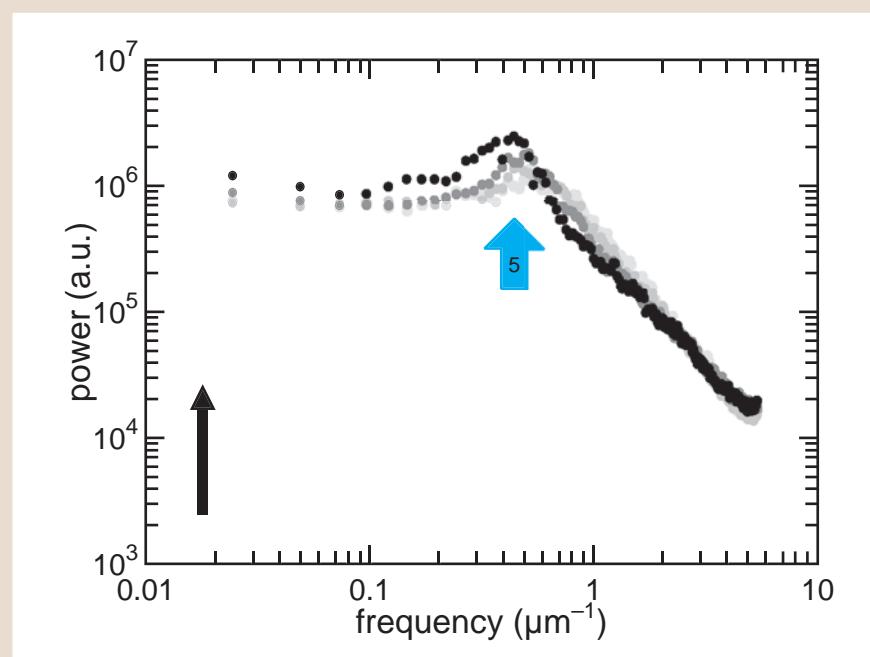
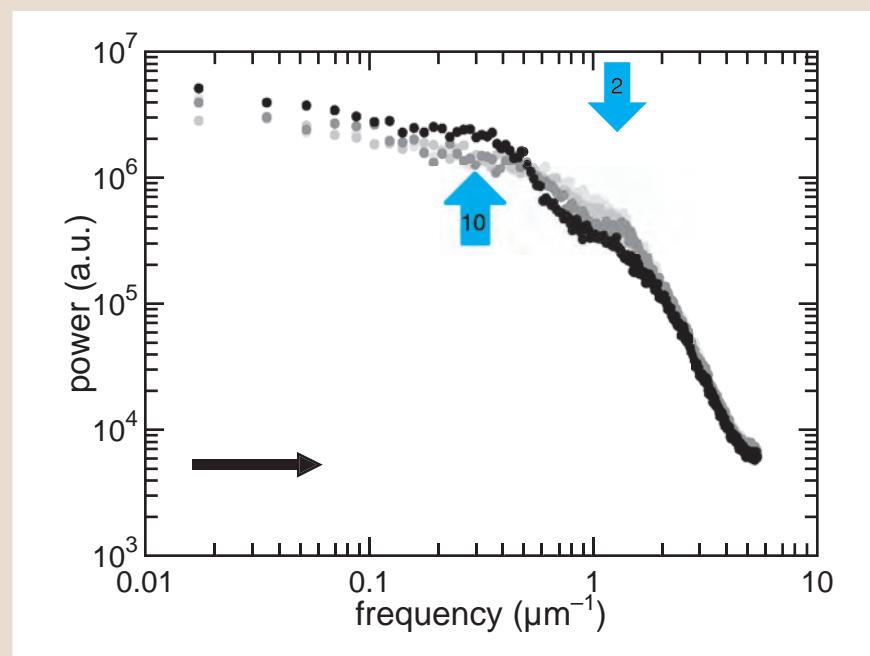
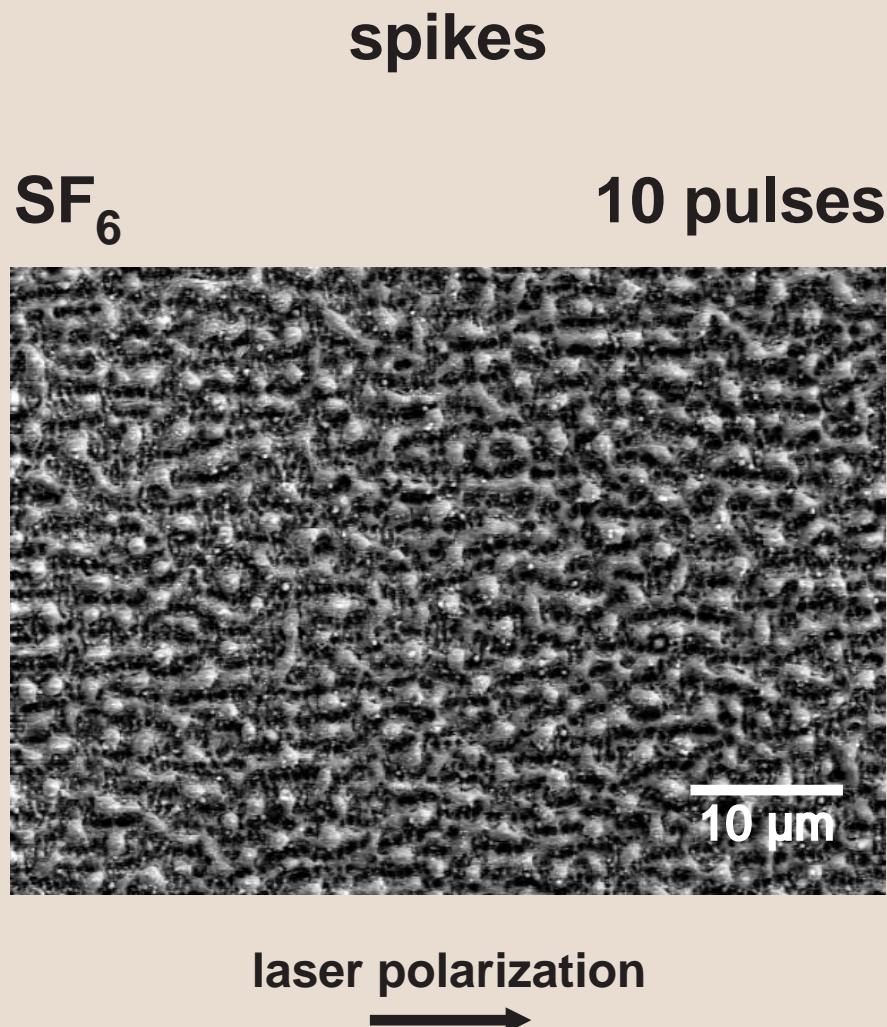
# *Formation process*



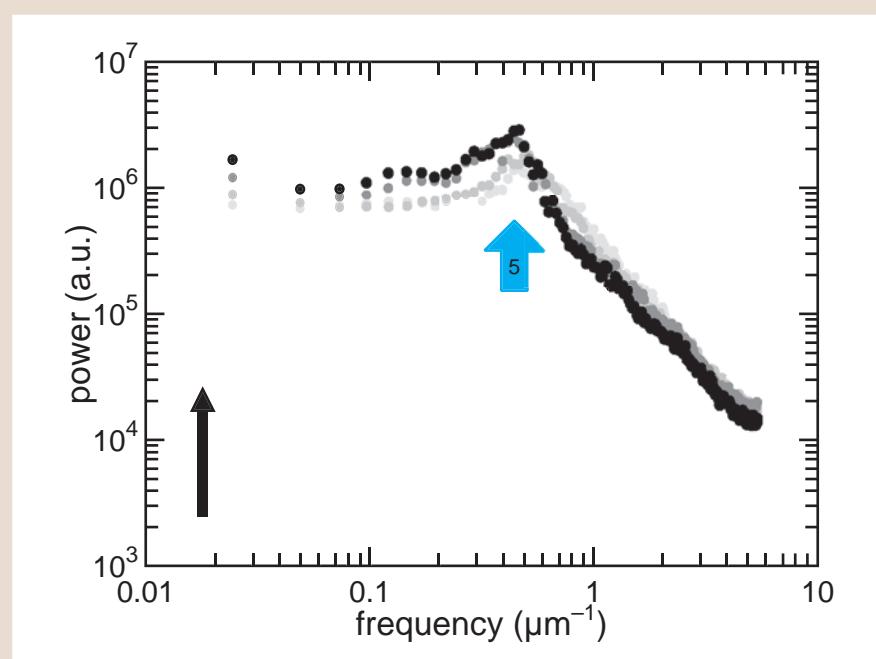
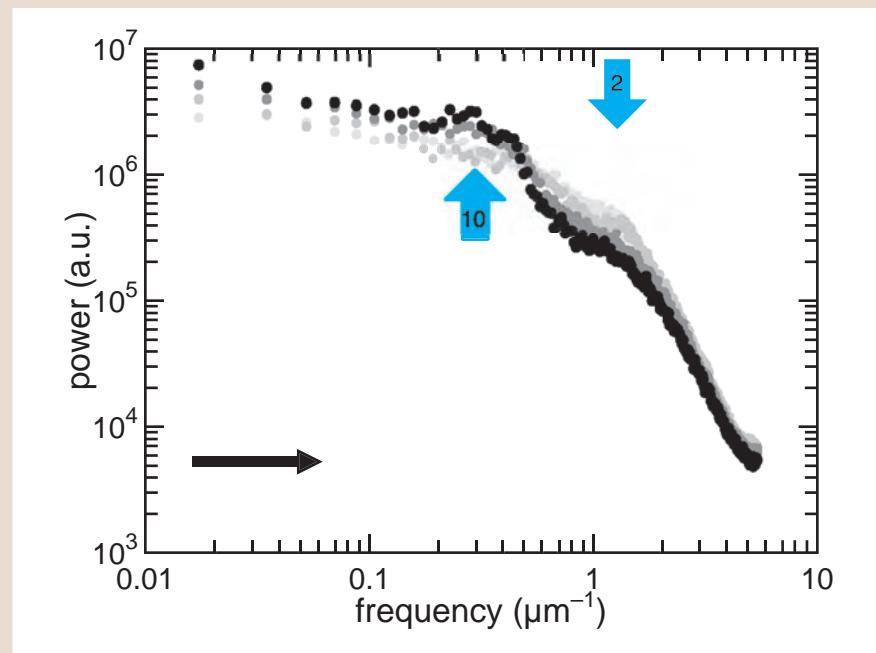
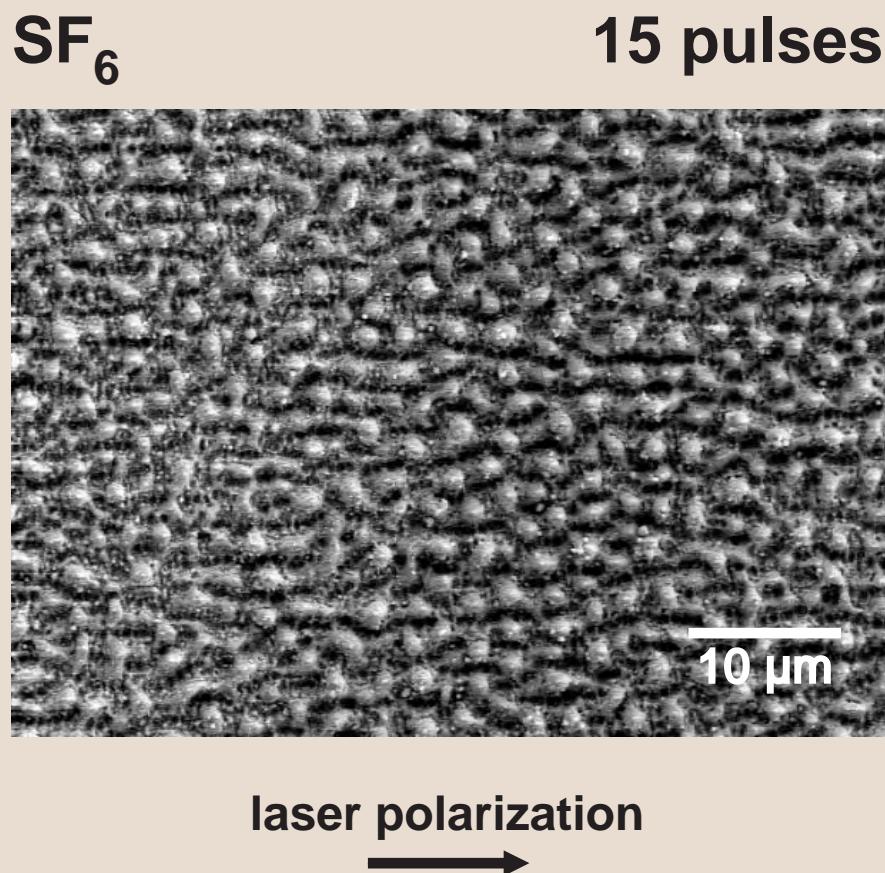
# *Formation process*



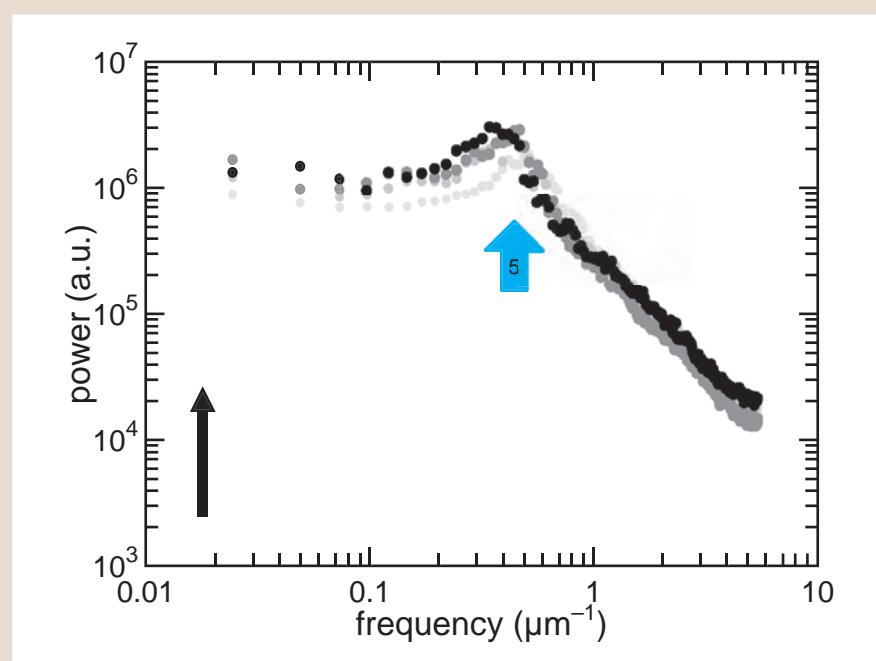
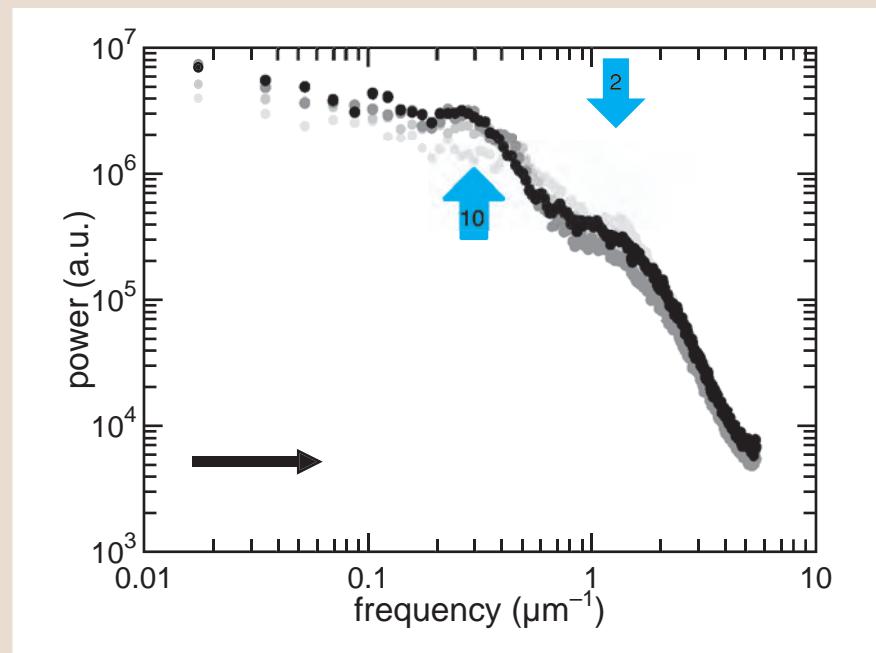
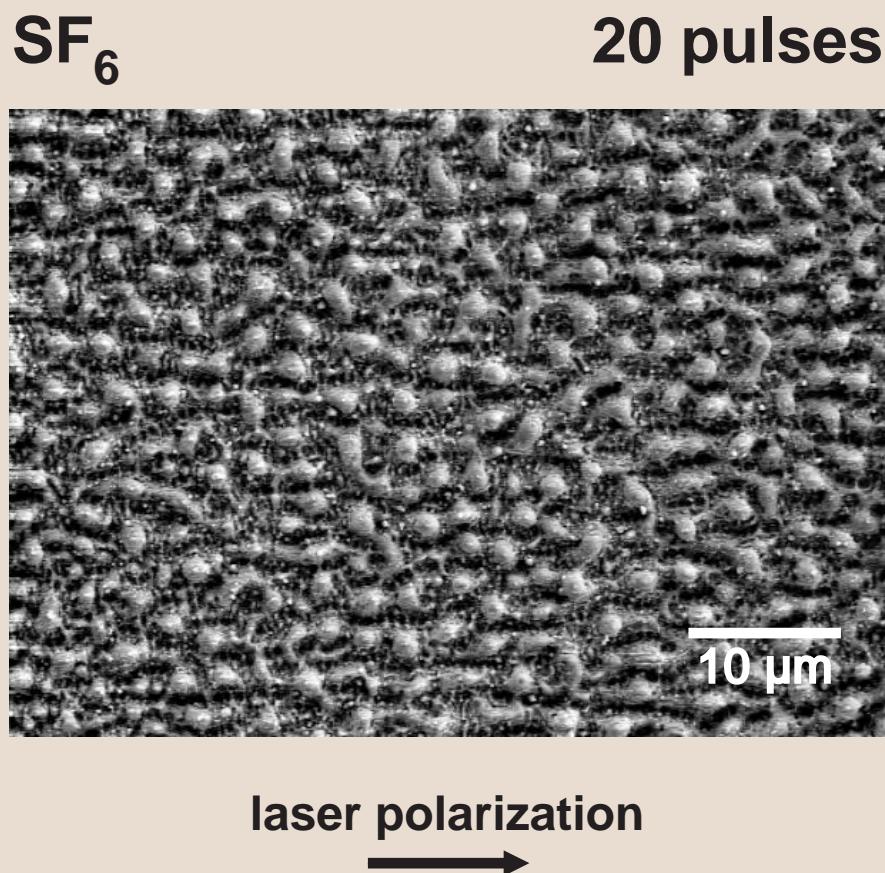
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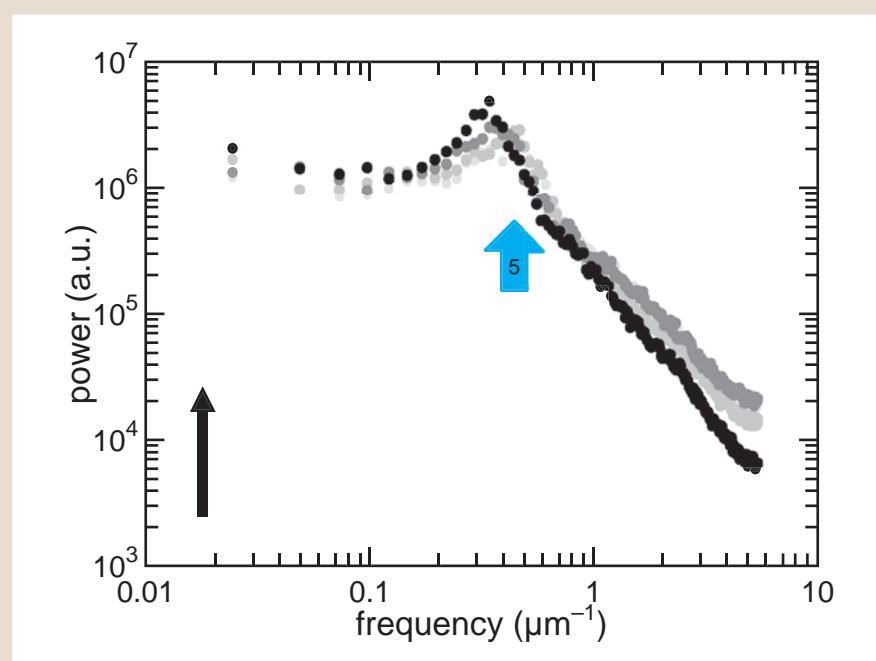
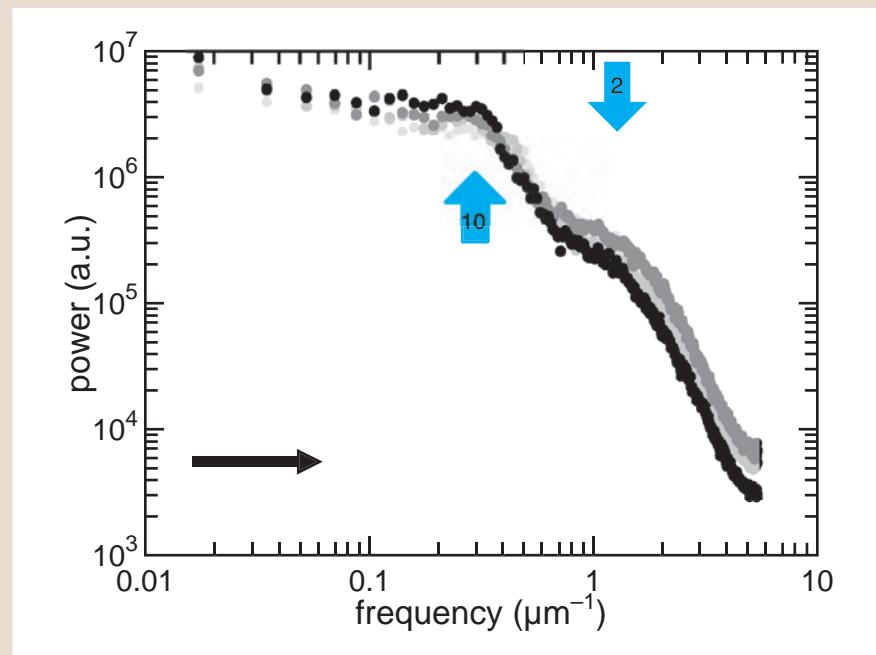
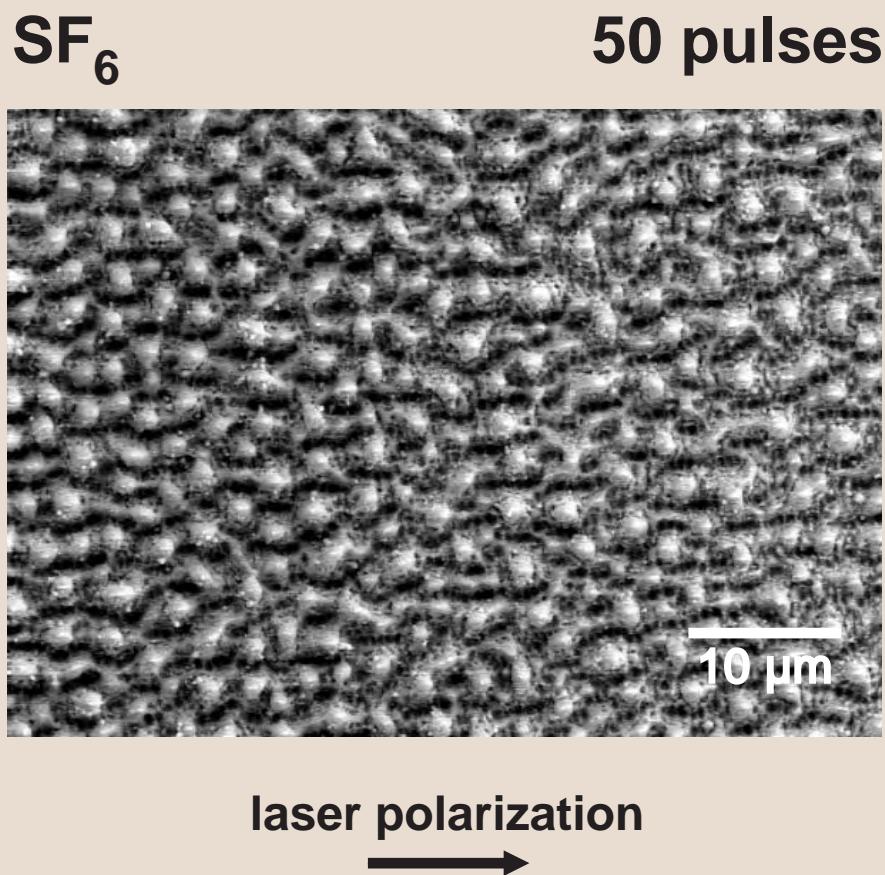
# *Formation process*



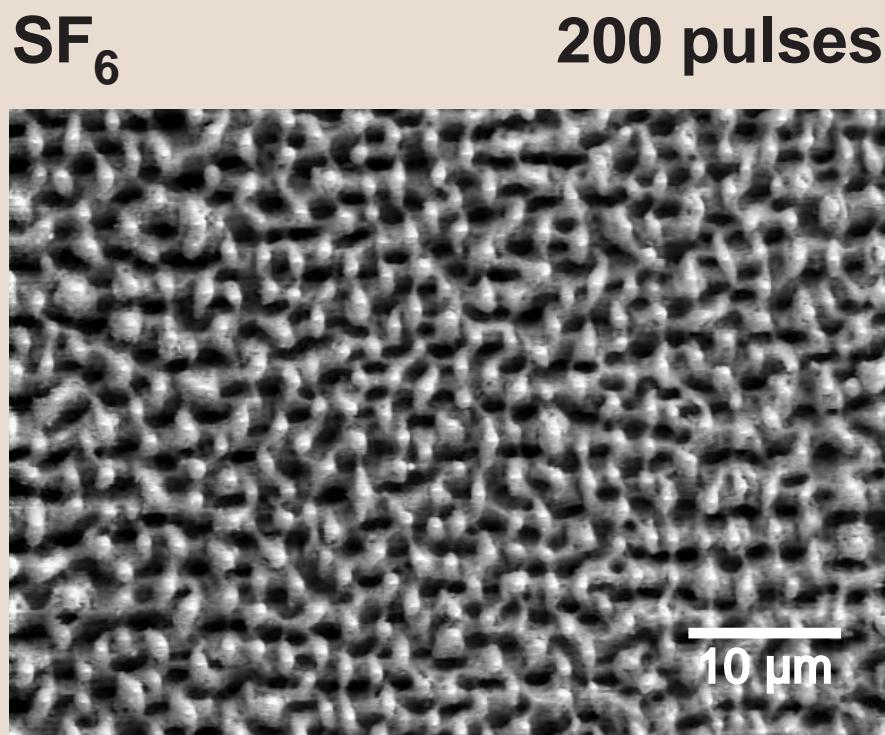
# *Formation process*



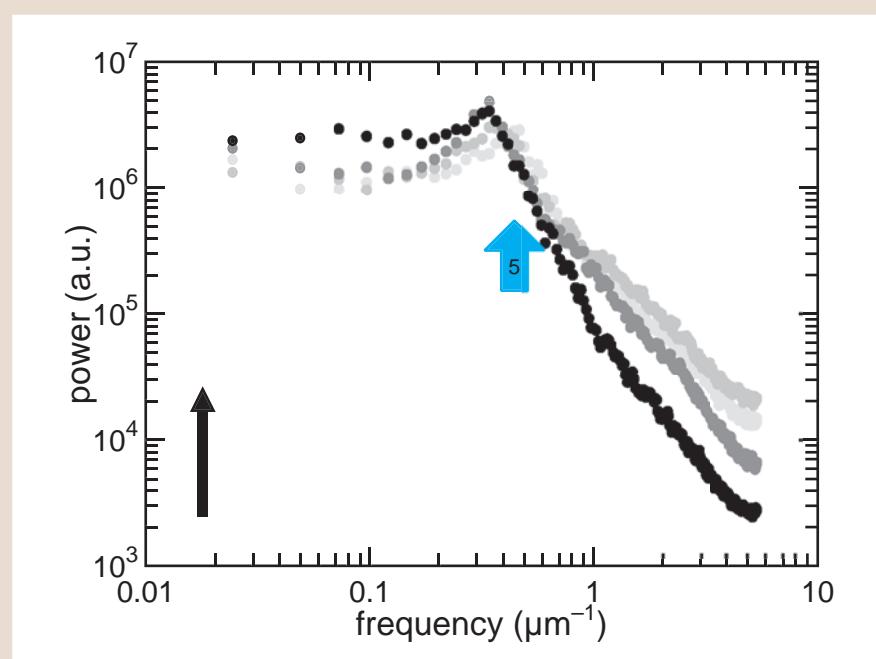
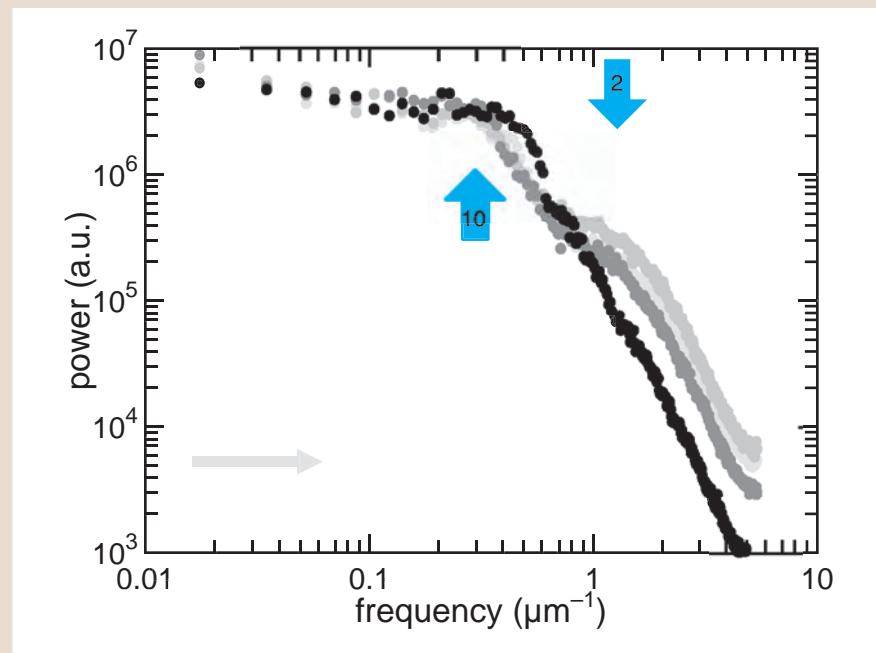
# *Formation process*



# *Formation process*

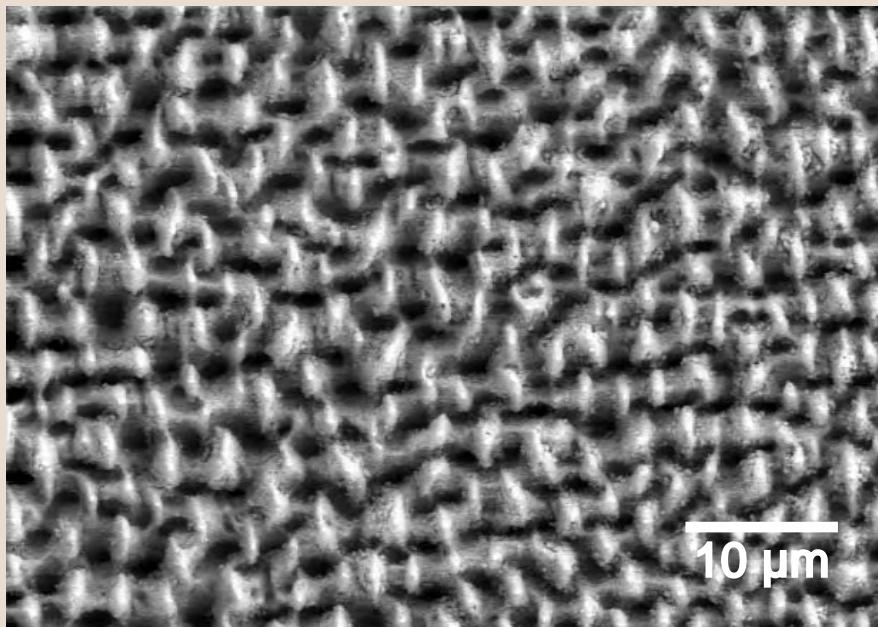


**laser polarization**  
→

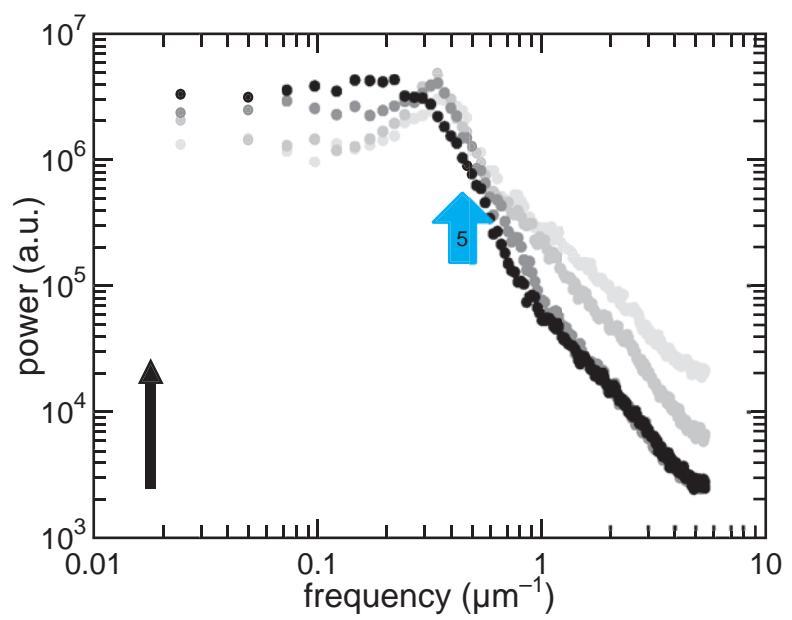
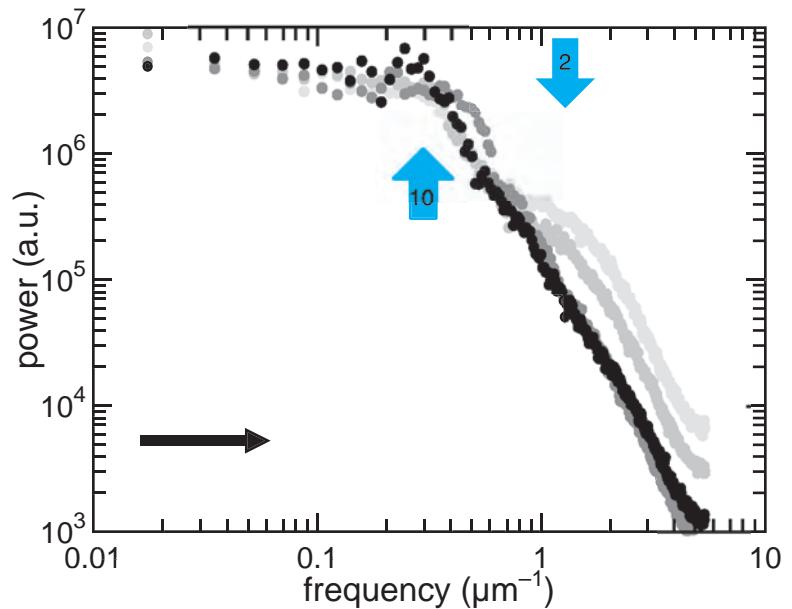


# *Formation process*

**SF<sub>6</sub>**                   **500 pulses**

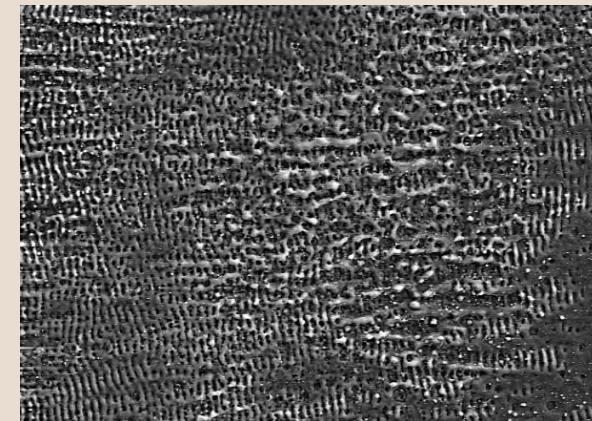


**laser polarization**  
→



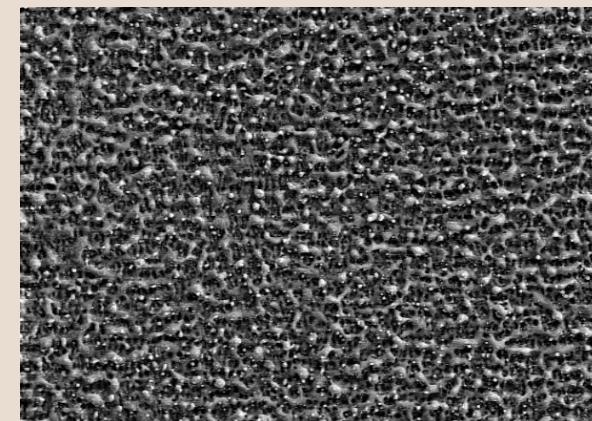
# *Formation process*

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



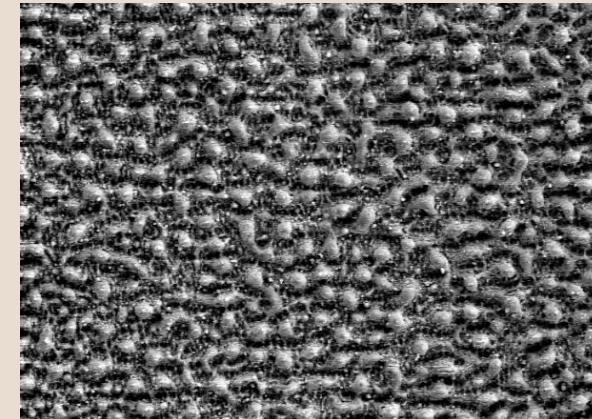
N = 2

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



N = 4

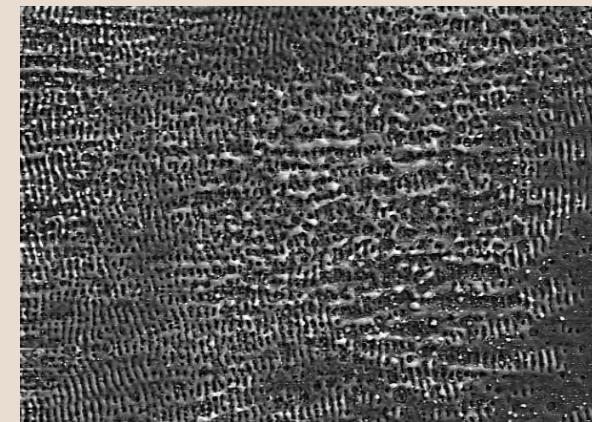
**3. Beads sharpening  
into spikes**



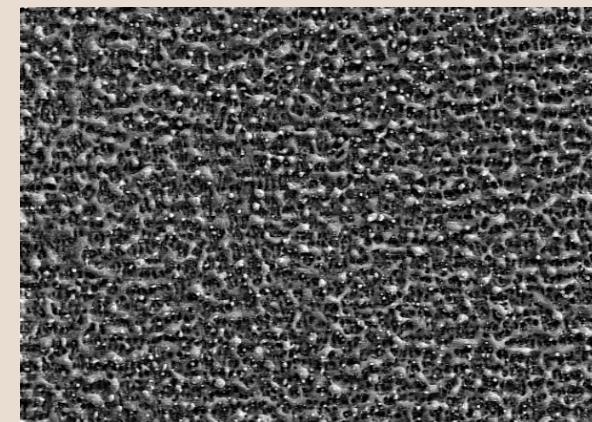
N = 10

# *Formation process*

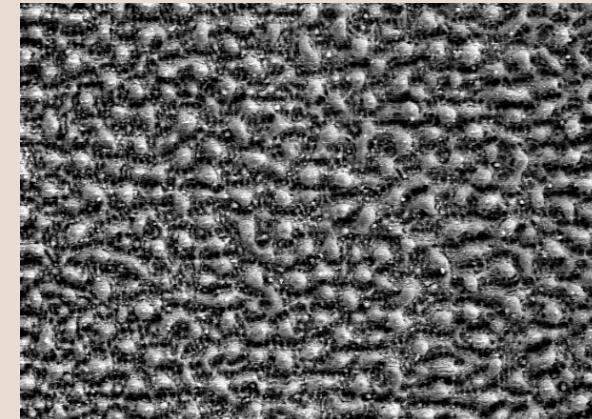
**Two distinct wavelengths:  
ripples and spikes**



N = 2



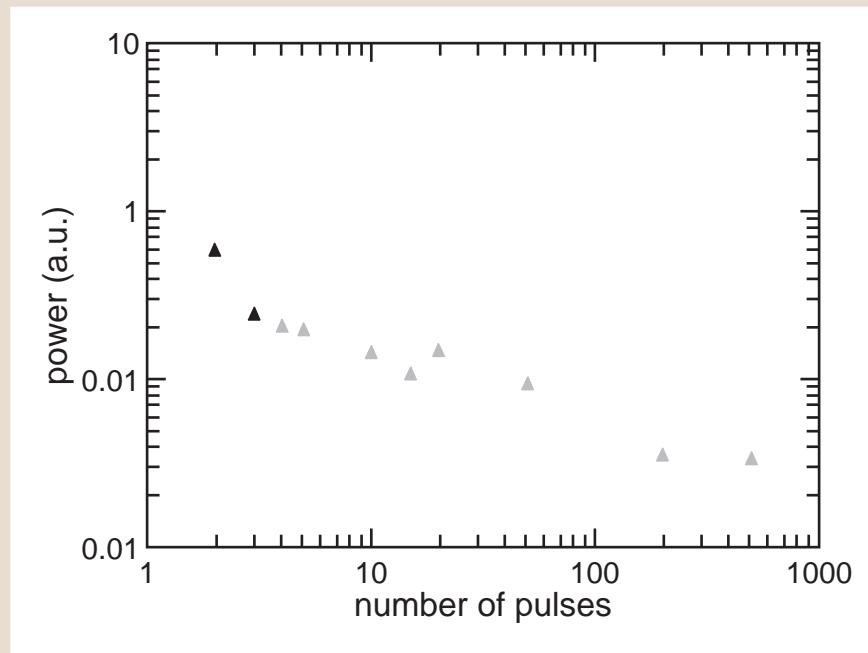
N = 4



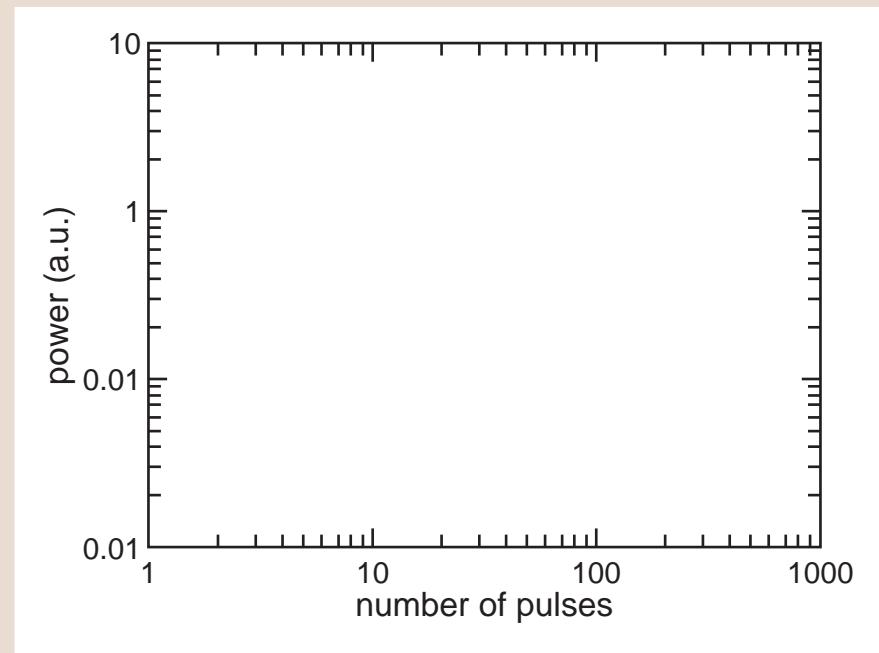
N = 10

## feature intensities

### **SF<sub>6</sub> ripples**



**parallel**

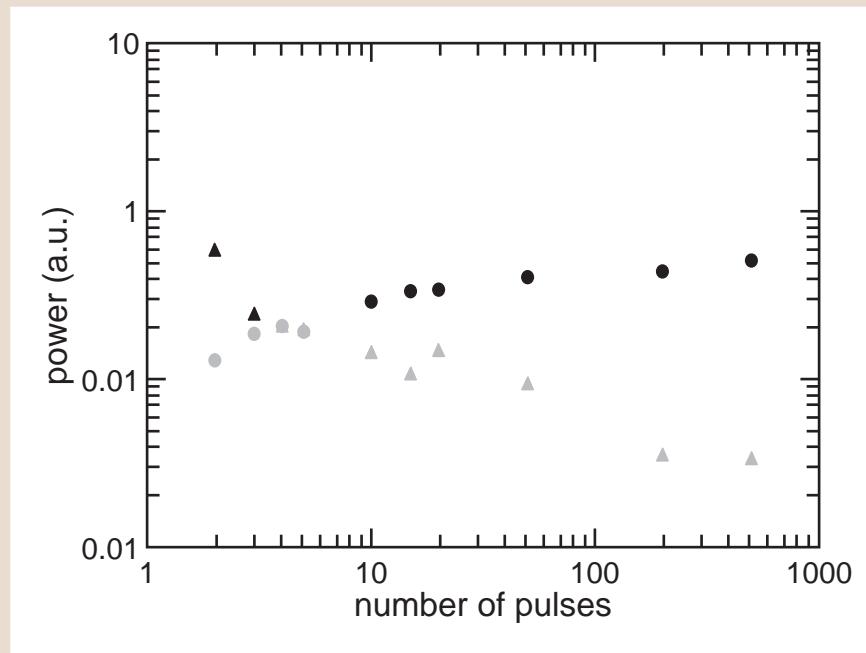


**perpendicular**

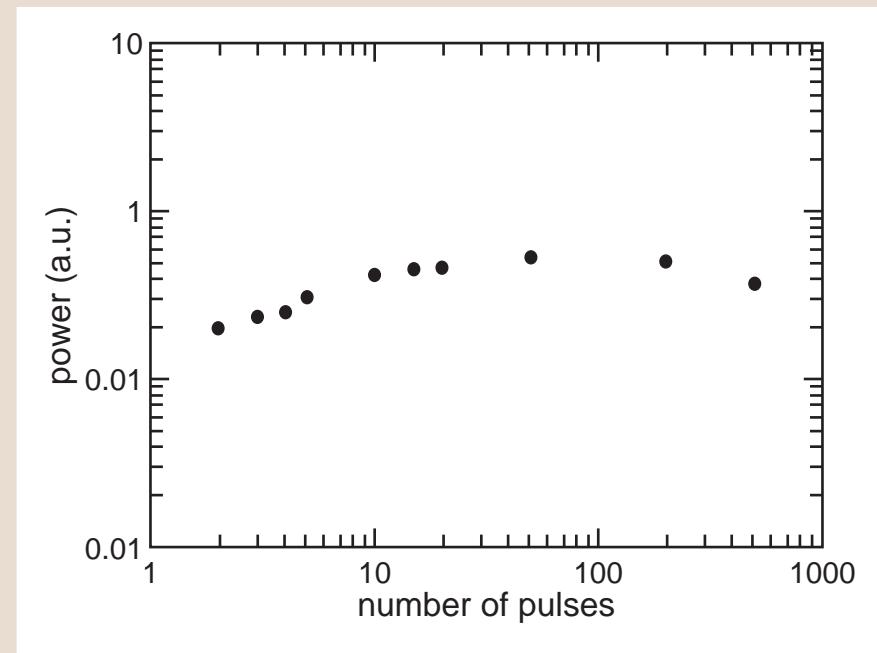
# *Formation process*

## feature intensities

### **SF<sub>6</sub> spikes**



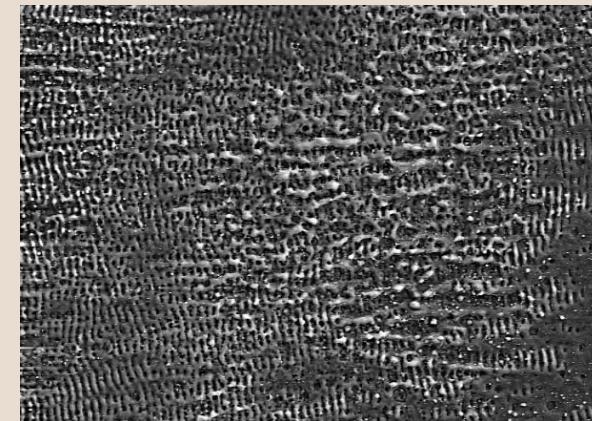
**parallel**



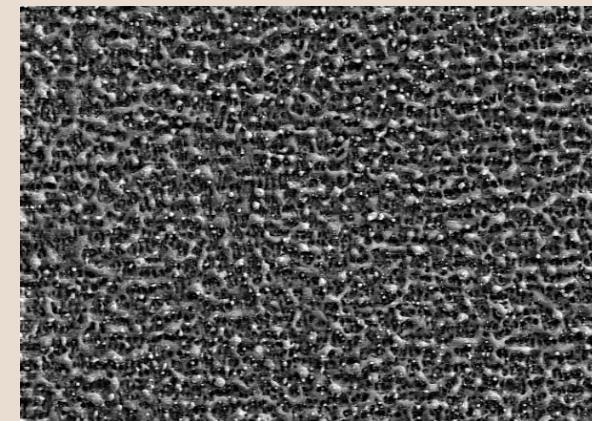
**perpendicular**

# *Formation process*

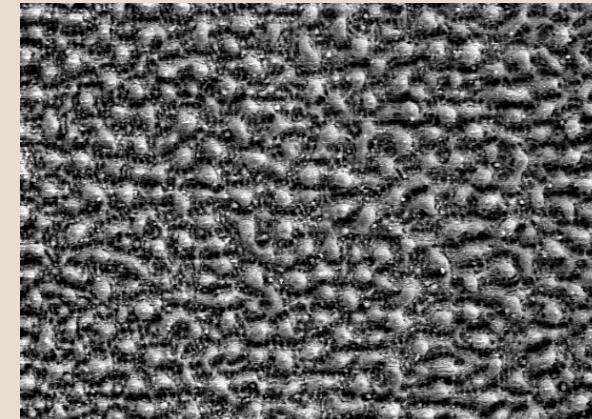
- ▶ **spike wavelength appears as ripple wavelength disappears**
- ▶ **spike wavelength appears first perpendicular to polarization**



N = 2



N = 4



N = 10

## **What sets the length scales?**

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

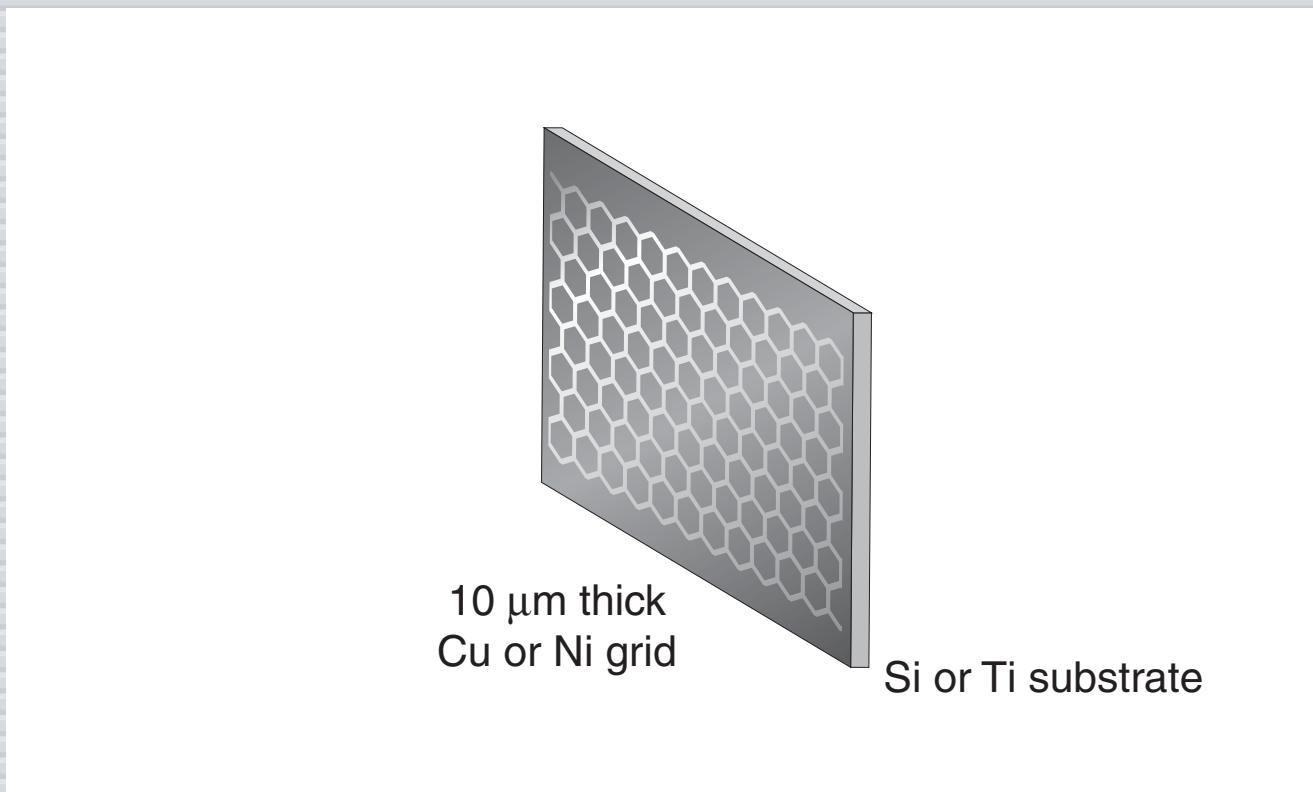
## **Capillary wavelength set by melt depth, duration**

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

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

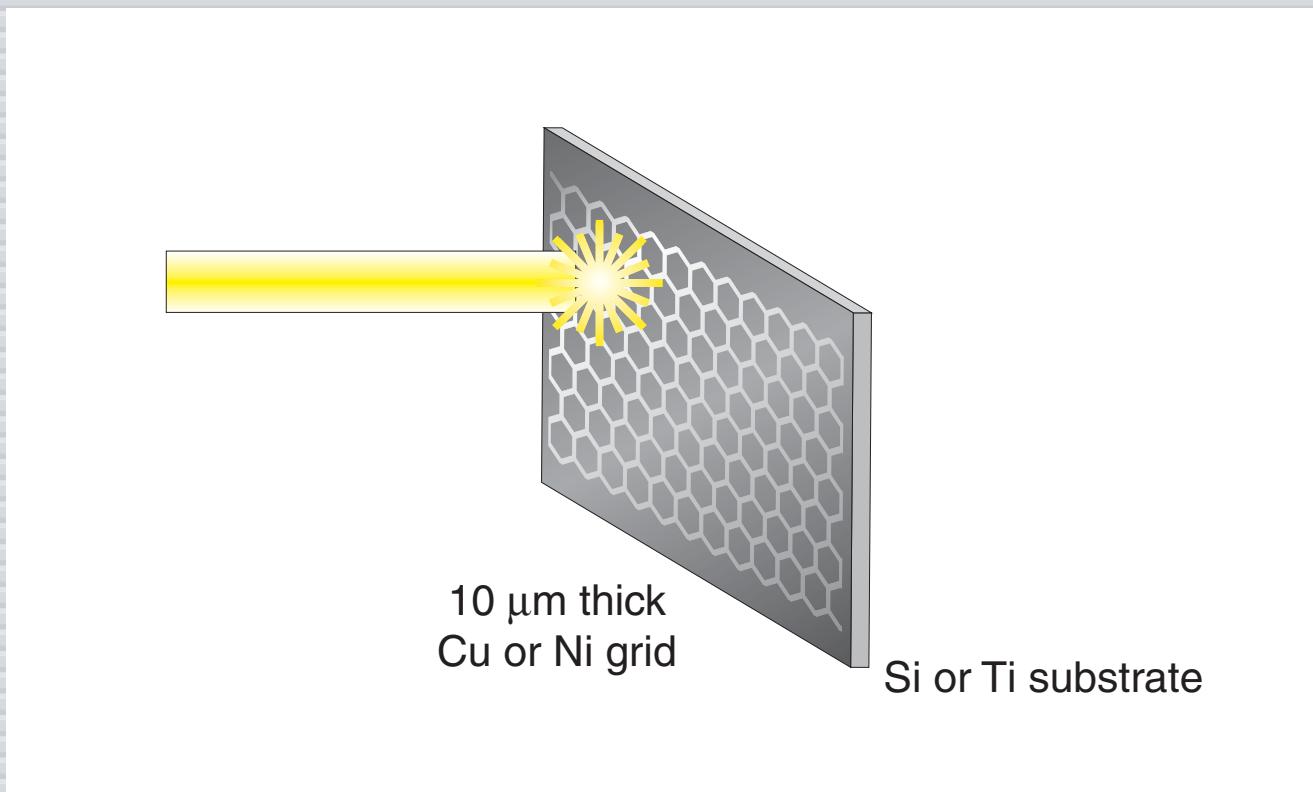
# *Ordering*

**place grid in front of substrate**



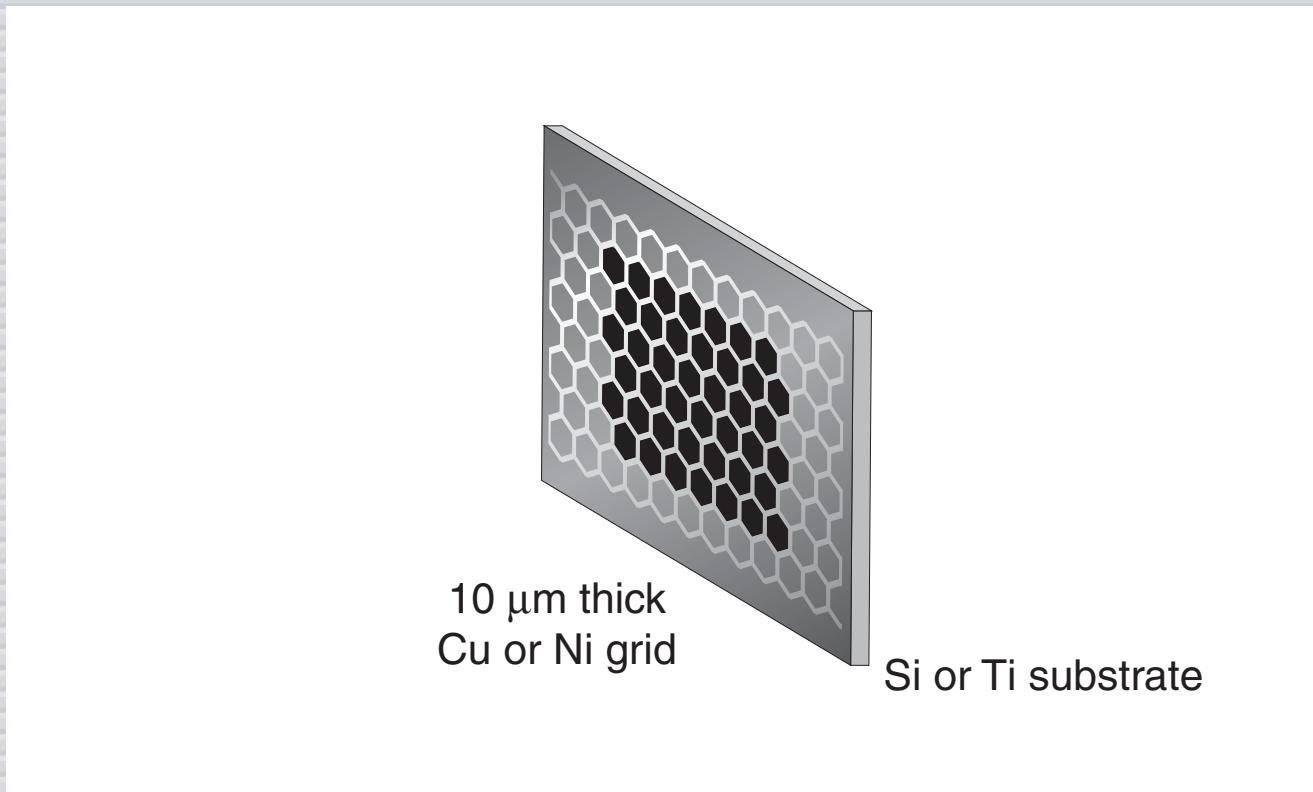
# *Ordering*

## scan laser beam



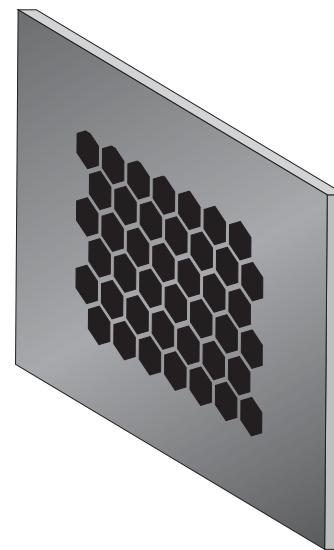
# *Ordering*

**scan laser beam**

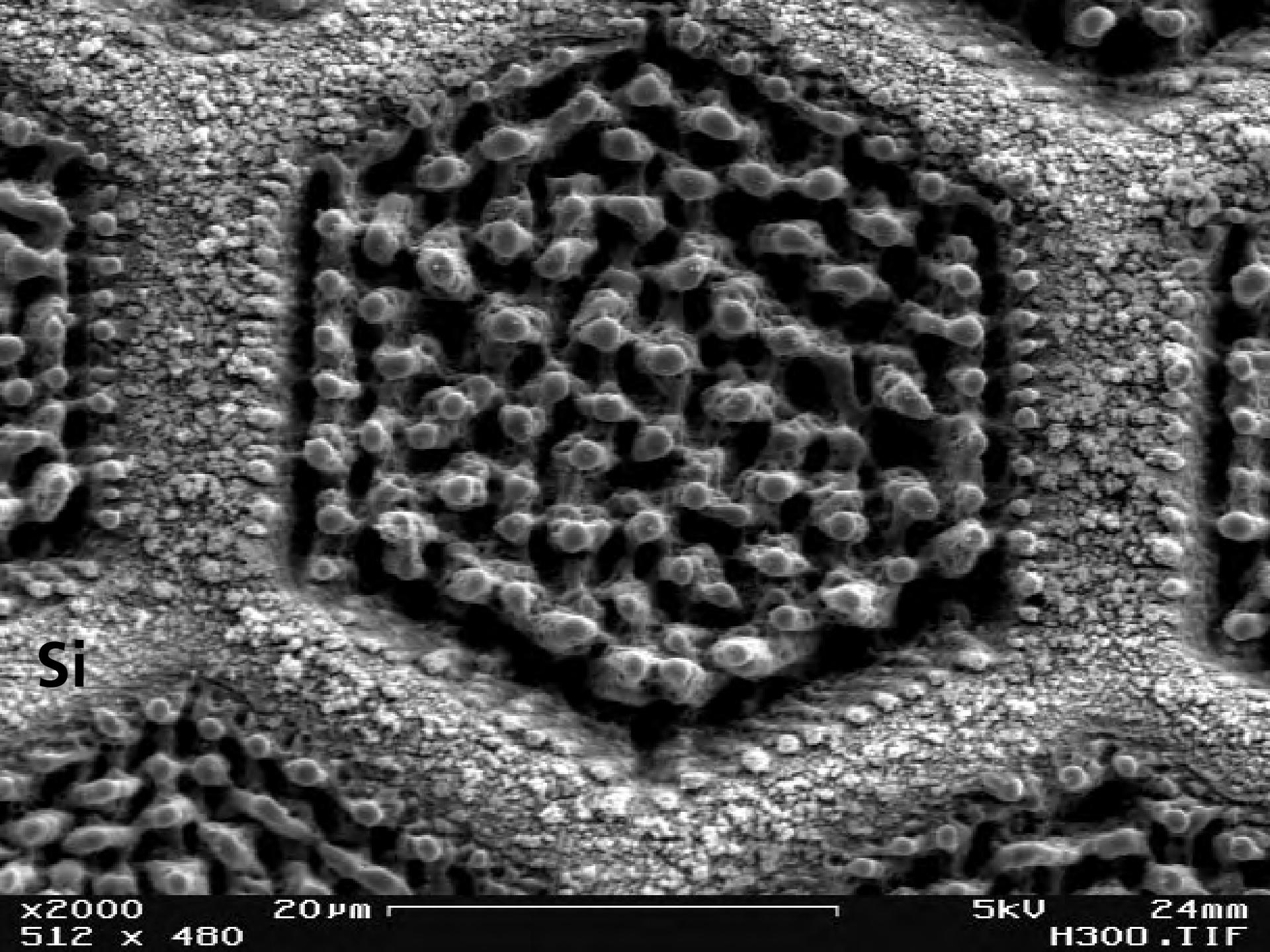


# *Ordering*

**remove grid**



Si or Ti substrate



x2000

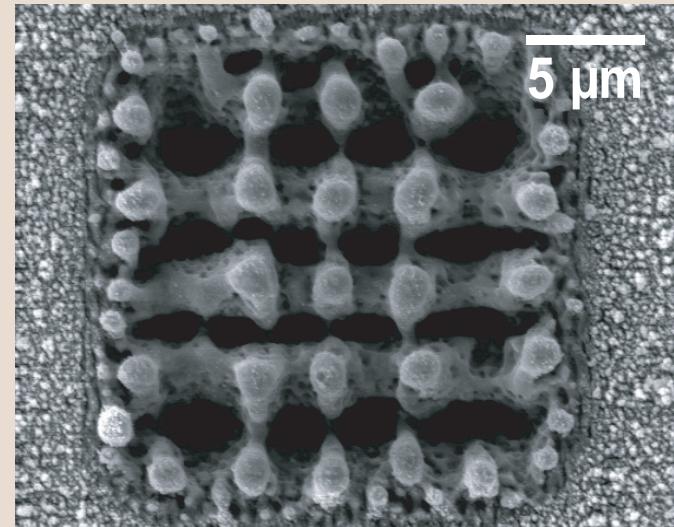
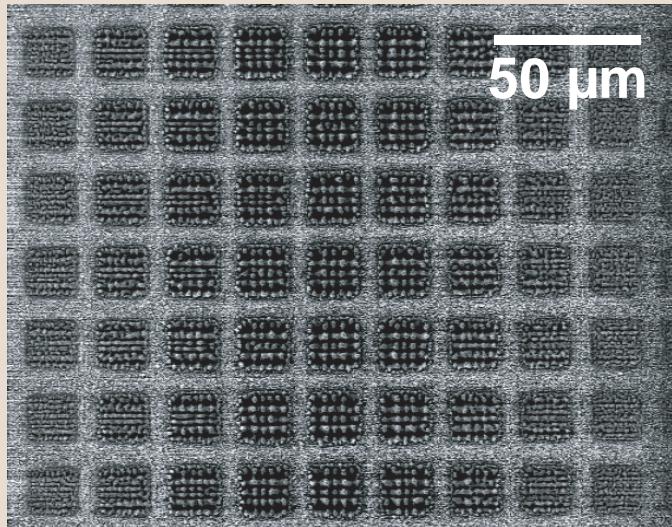
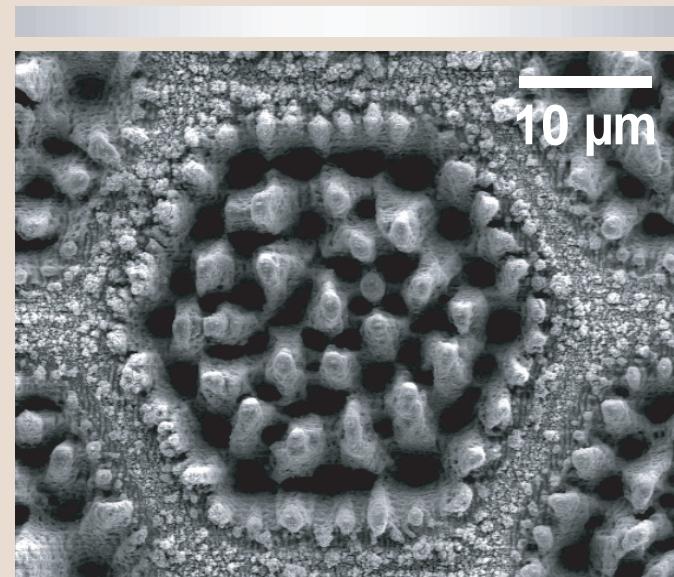
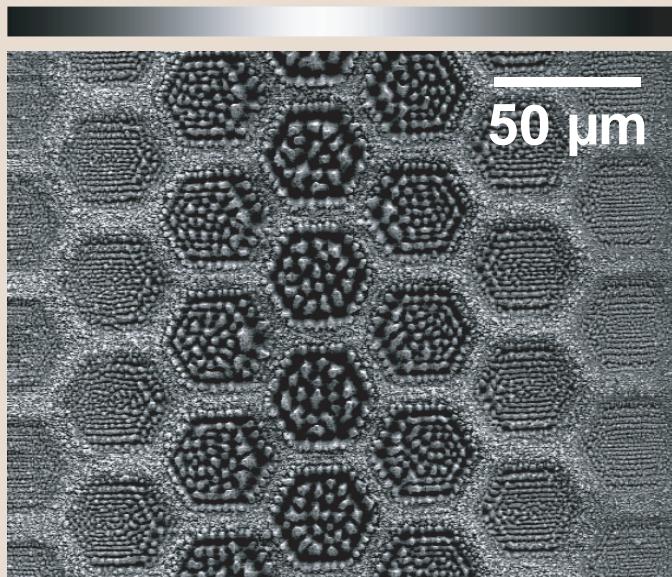
512 x 480

20 μm

5kV

24mm  
H300.TIF

# *Ordering*



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

## **Black silicon:**

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

## *Acknowledgements*

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

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

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

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



## *Nanosecond vs femtosecond*

**ns-structured surface shows less disorder**

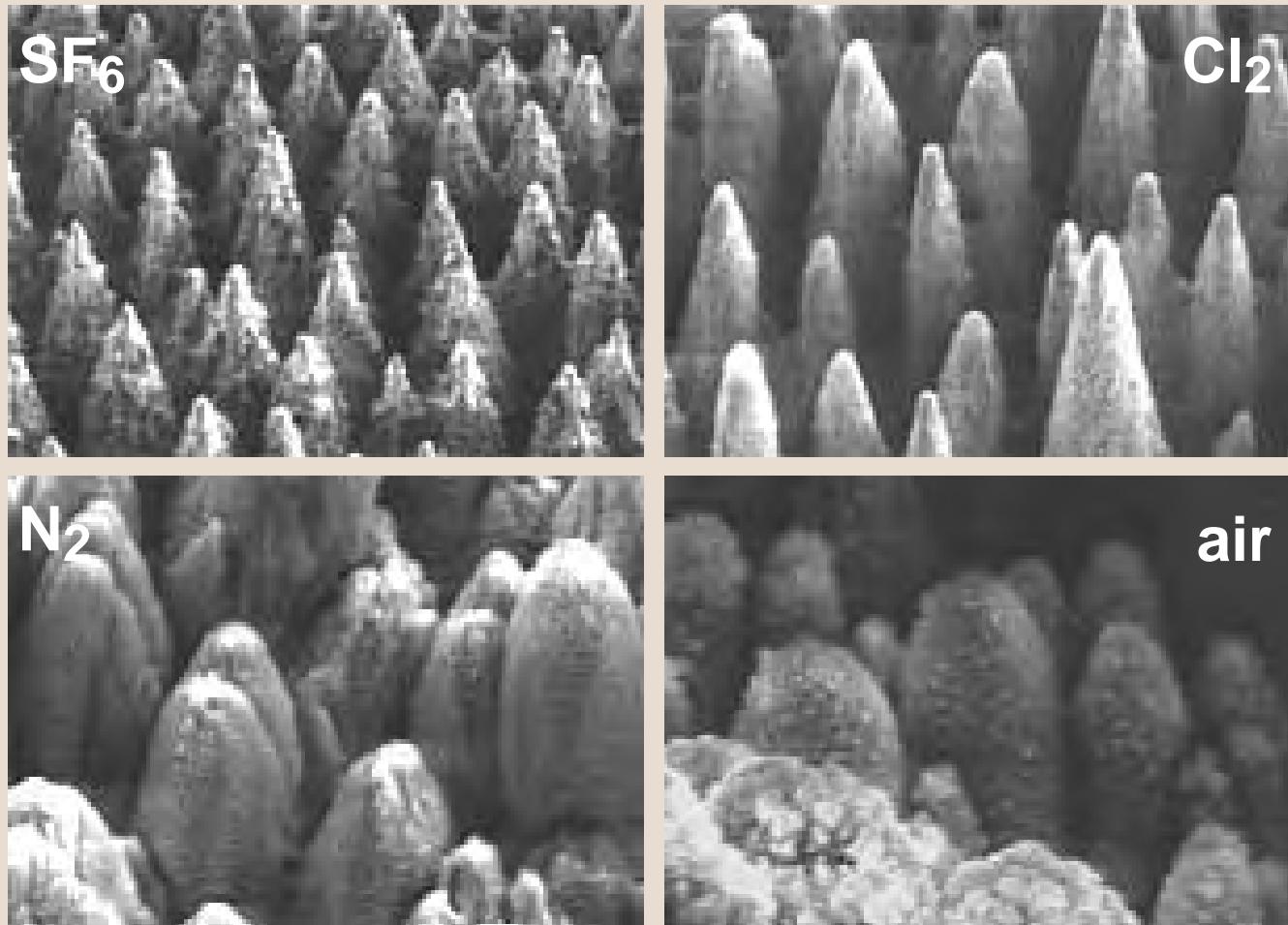
**Optical properties virtually identical**

**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*

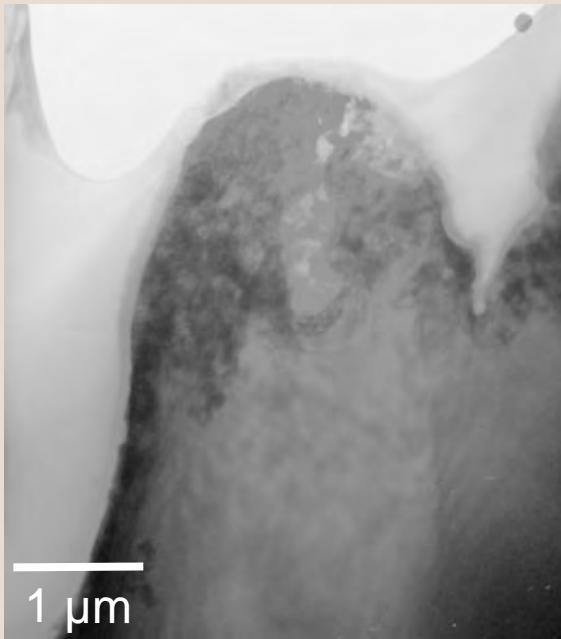


10 μm

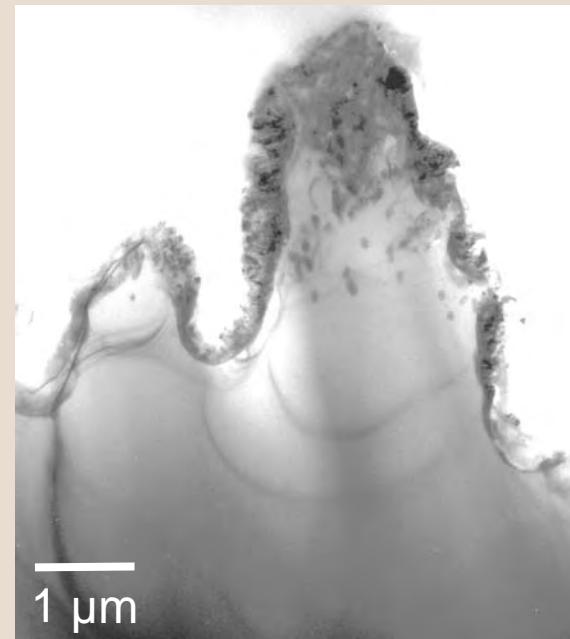
**all except Cl<sub>2</sub> show surface nanostructure**

# *Structural analysis*

**air**



**SF<sub>6</sub>**



**surface disorder present in air sample**

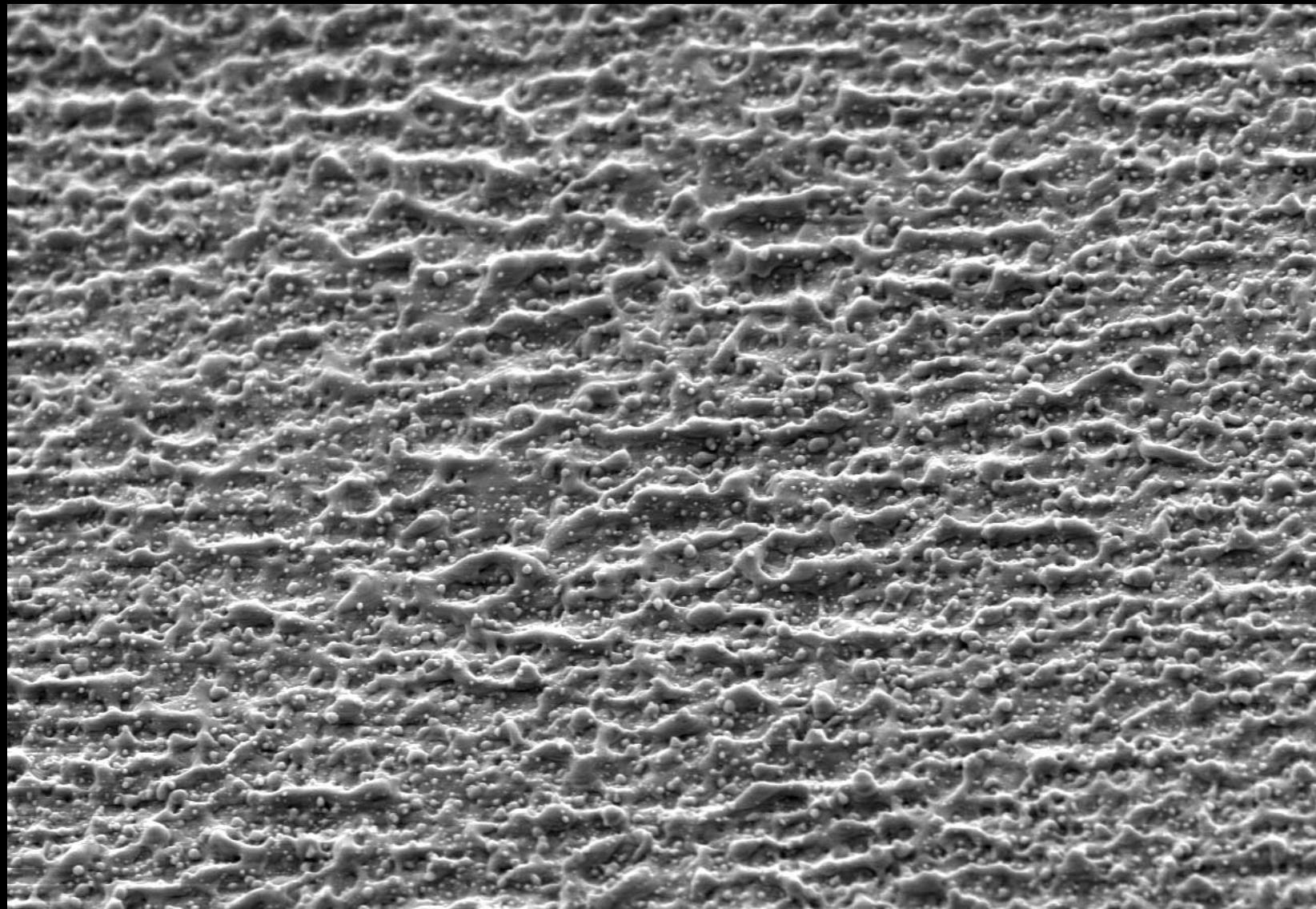
## **Structure less likely than sulfur:**

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

**What happens with nanosecond pulses?**

## **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



x2000

#3548

512 x 480

20  $\mu\text{m}$

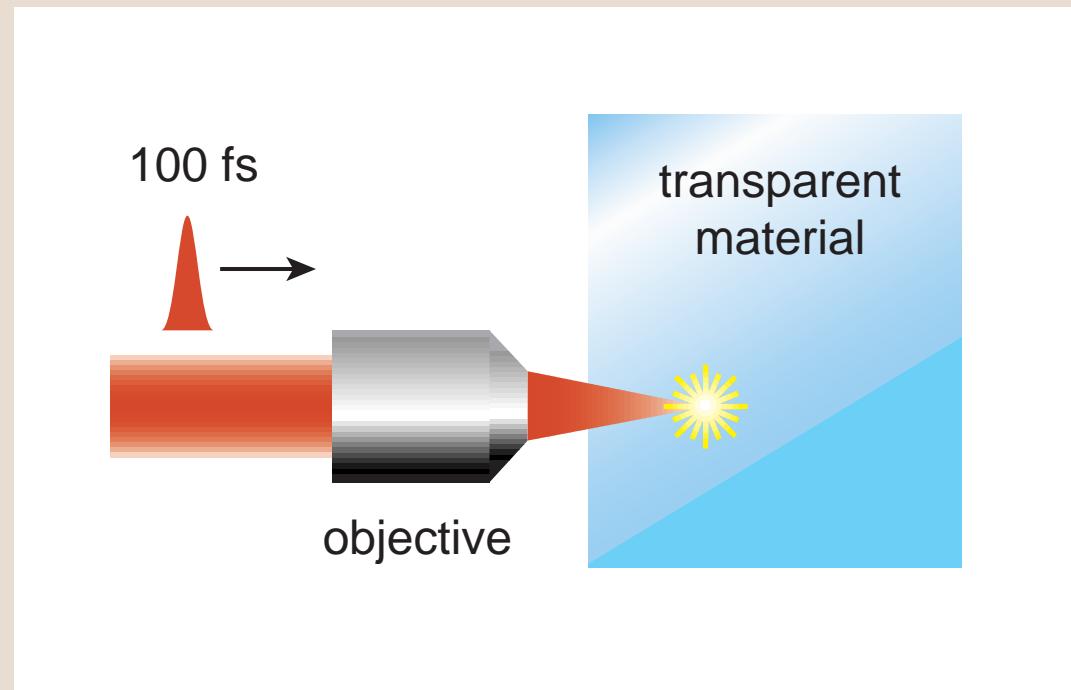
10kV

15mm

0006

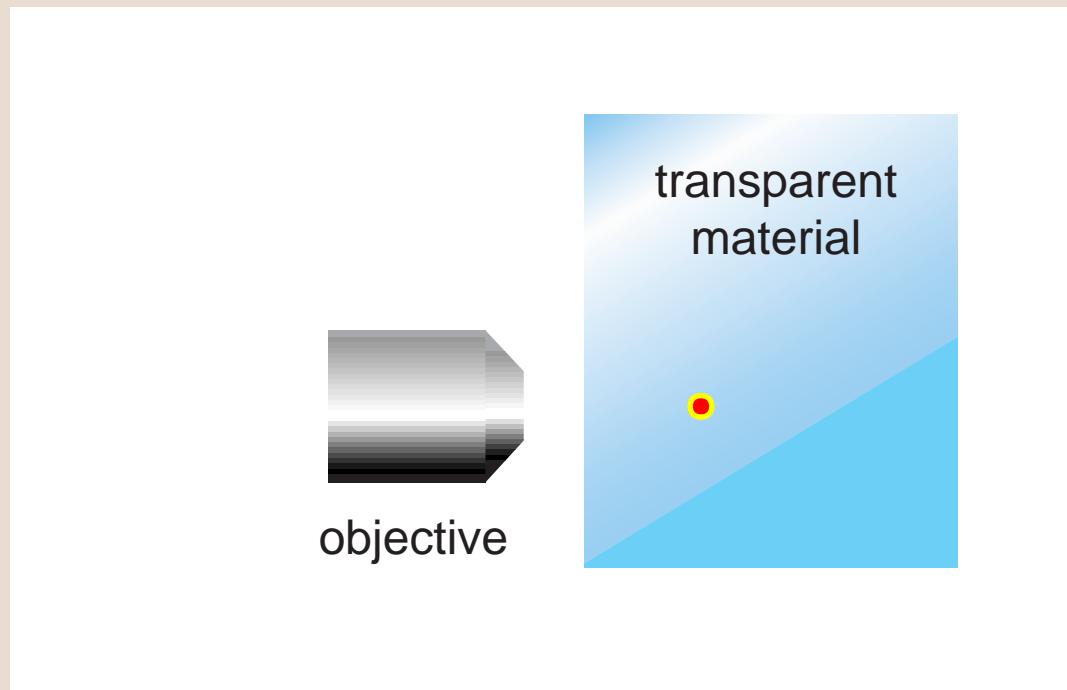
# *Modification of materials*

**tightly focus beam inside bulk glass**



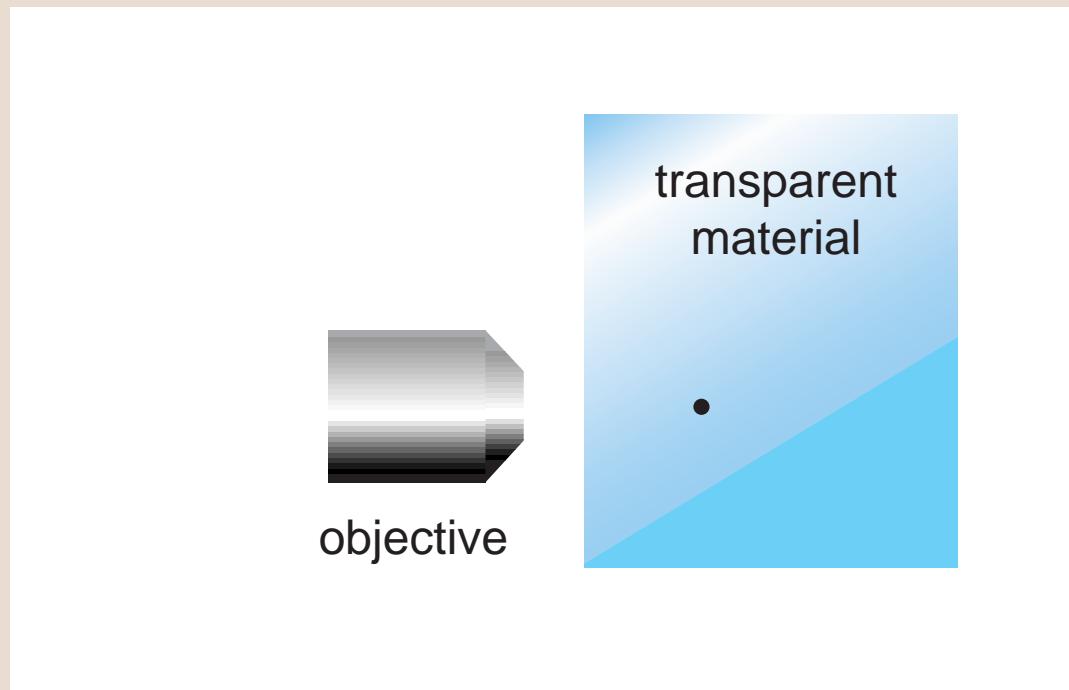
# *Modification of materials*

**energy is deposited in the focal volume**

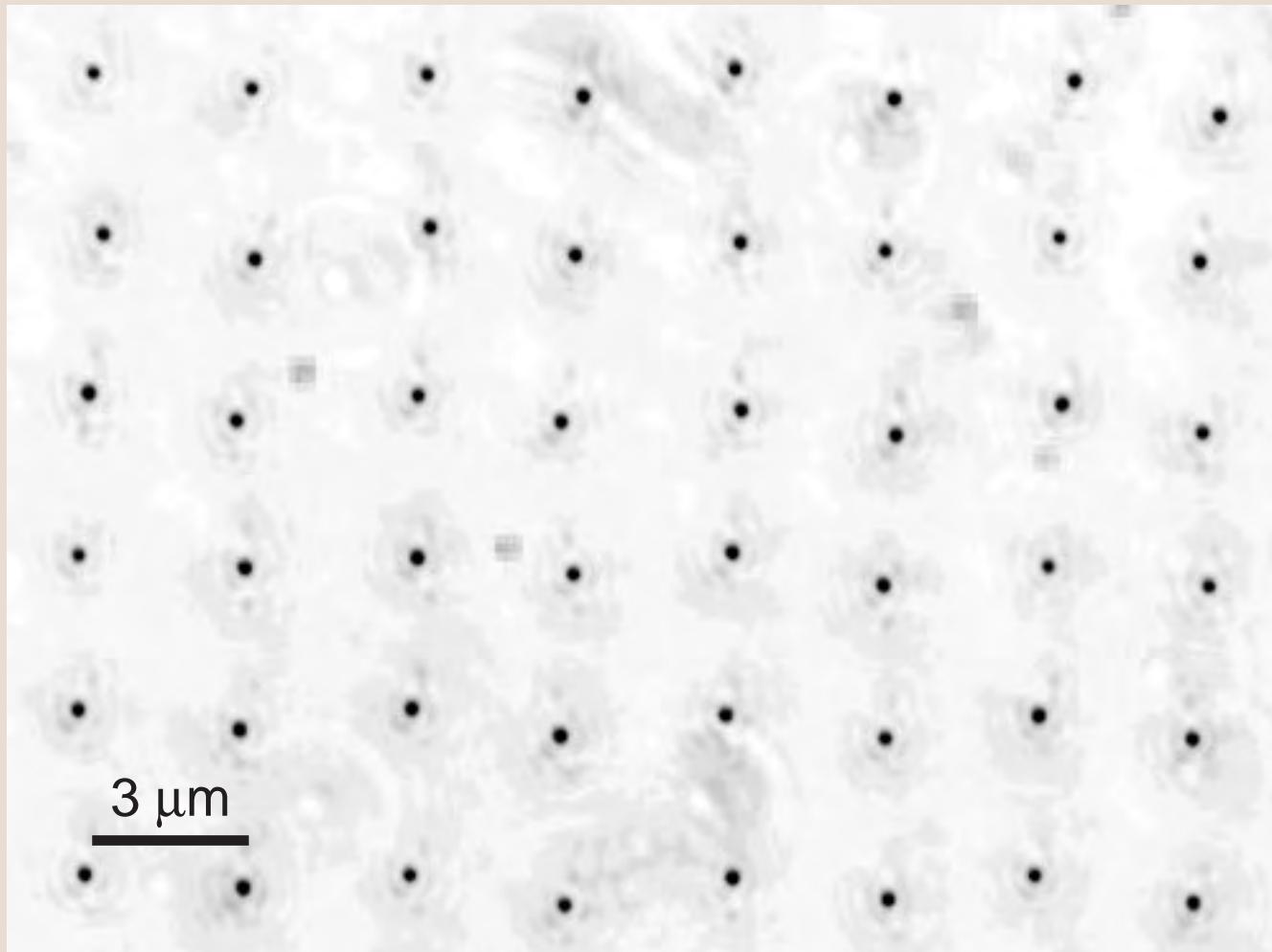


# *Modification of materials*

**producing microscopic bulk damage**



# *Modification of materials*

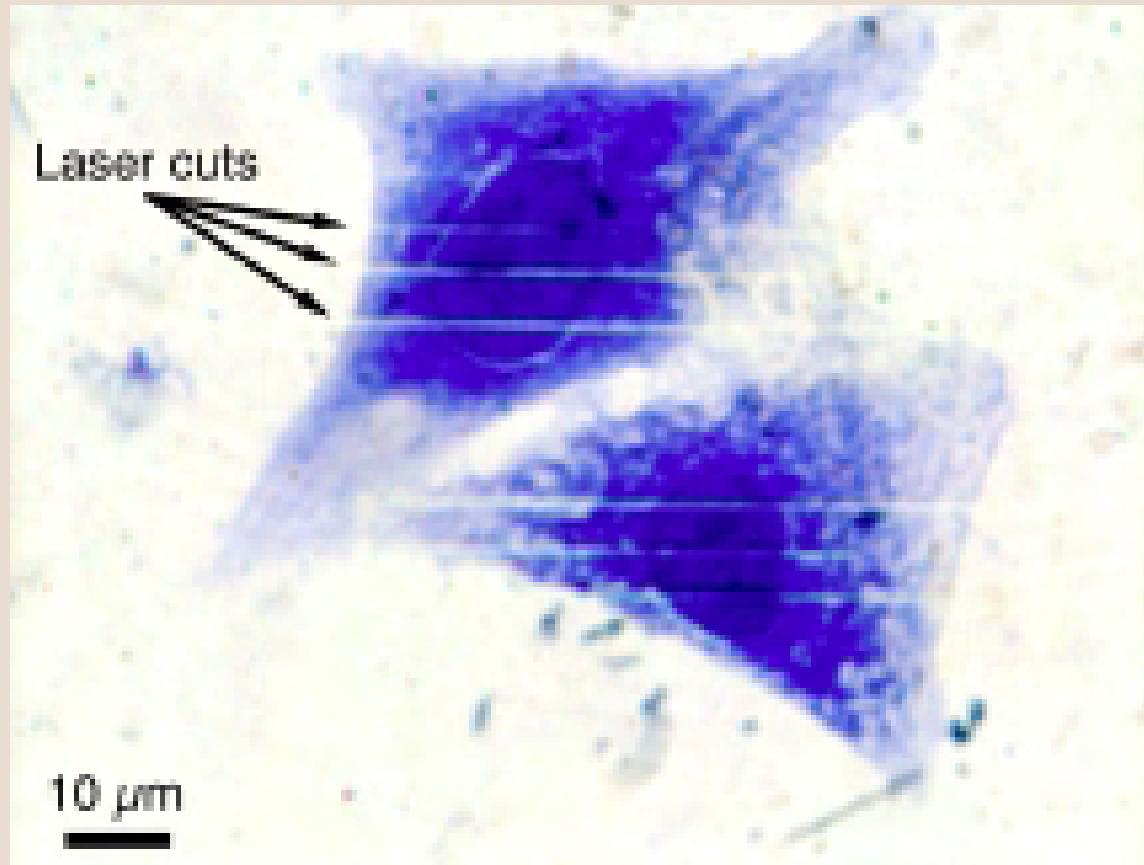


40 nJ  
100 fs  
800 nm  
0.65 NA  
Corning 0211

**top view**

# *Modification of materials*

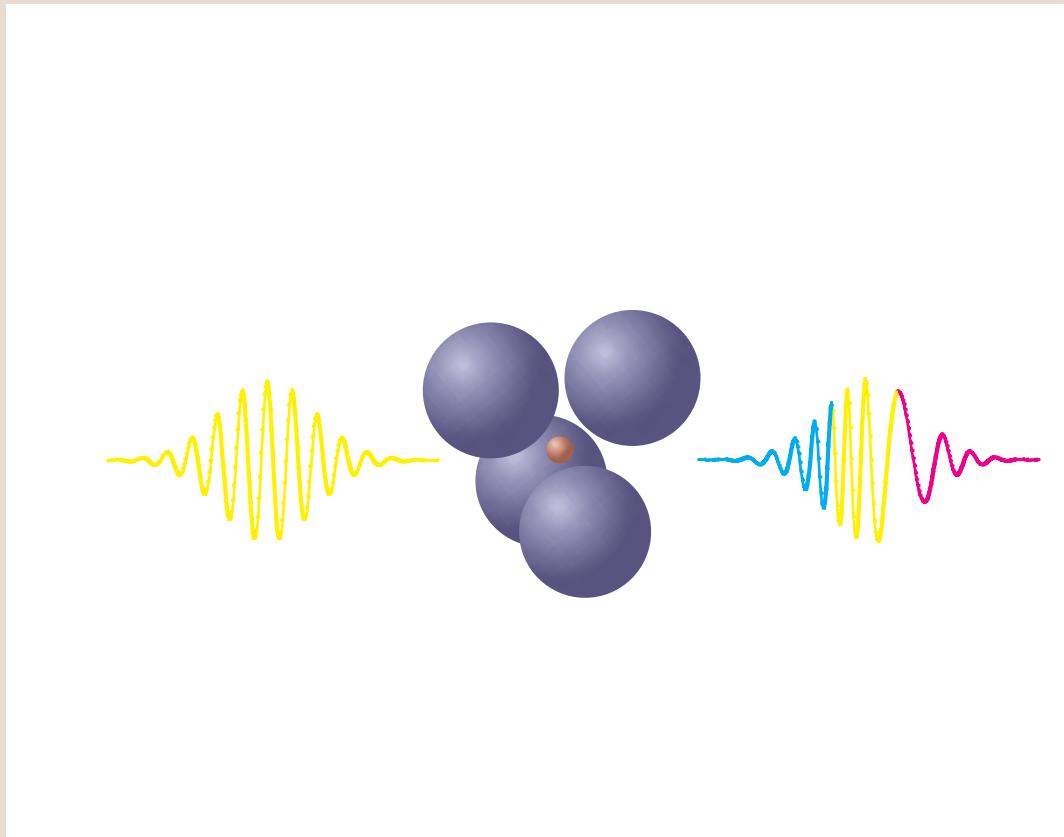
**laser cuts through single cell**



**sub-cellular microsurgery**

# *Nonlinear optical effects*

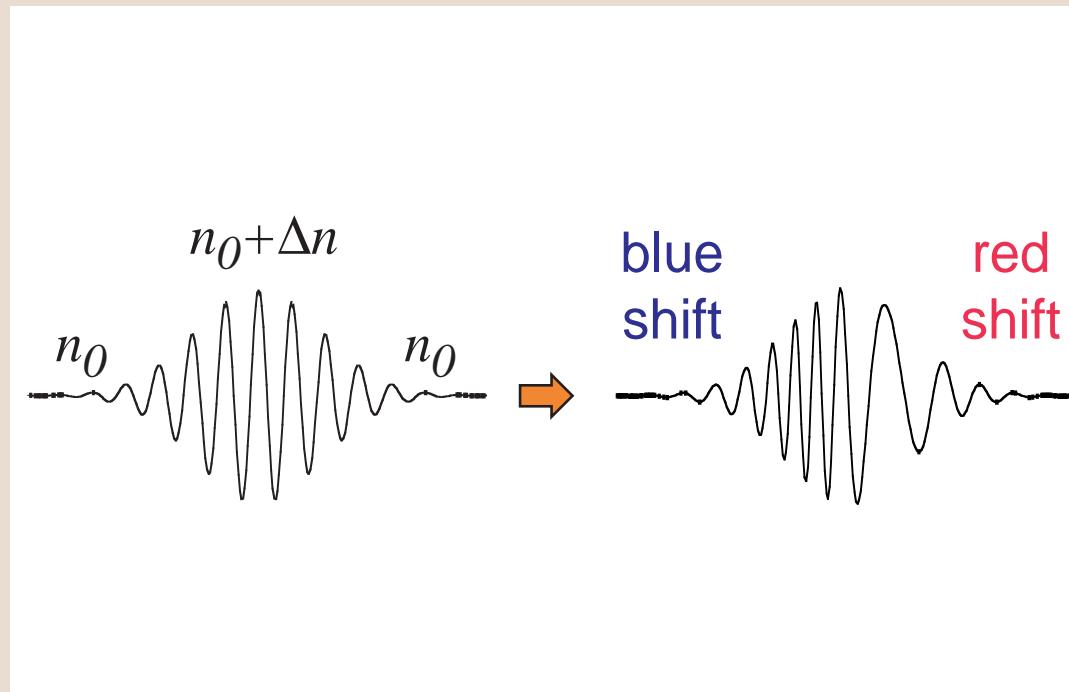
"extremely" nonlinear response



material changes the light

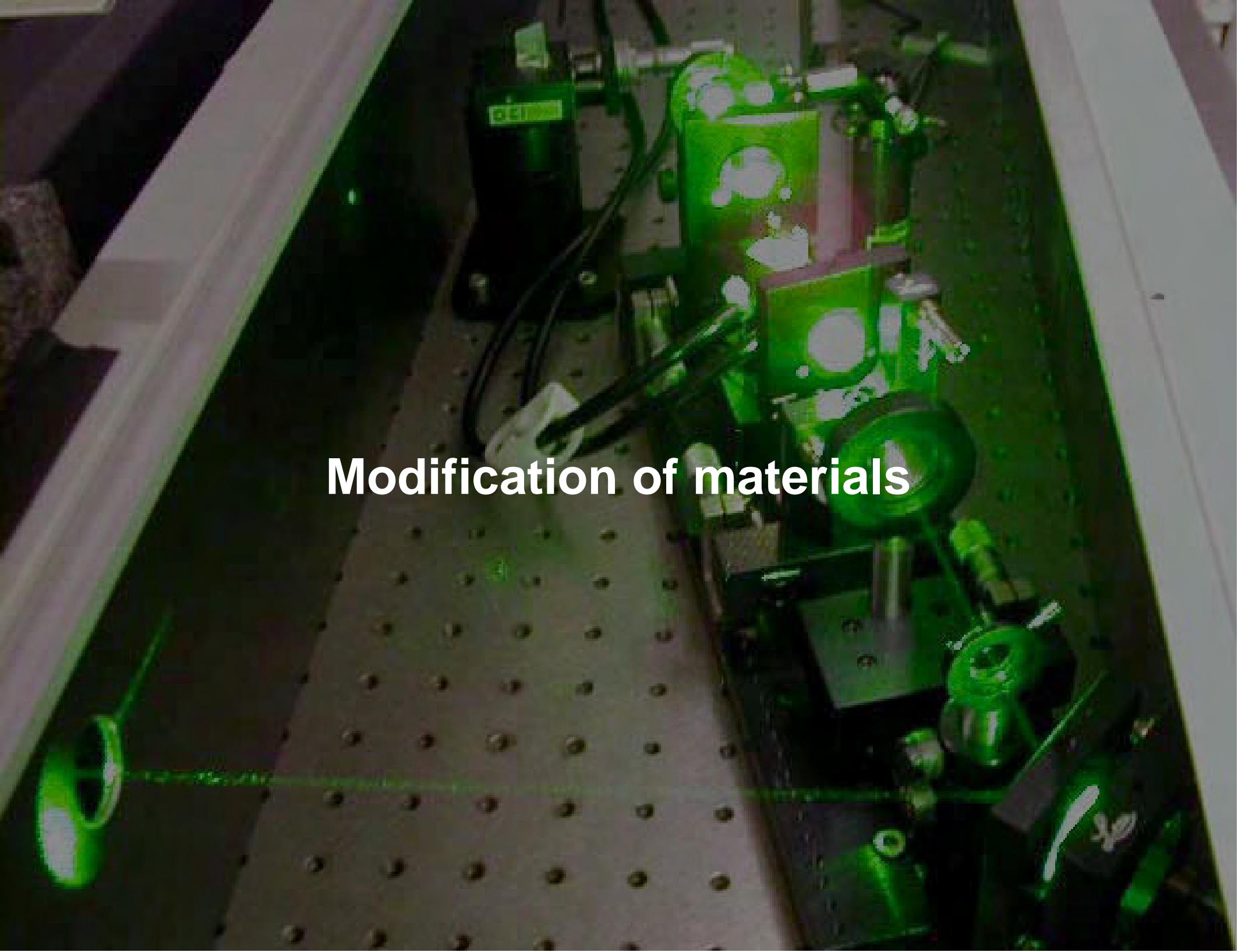
# *Nonlinear optical effects*

**light induces time-dependent index of refraction**



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

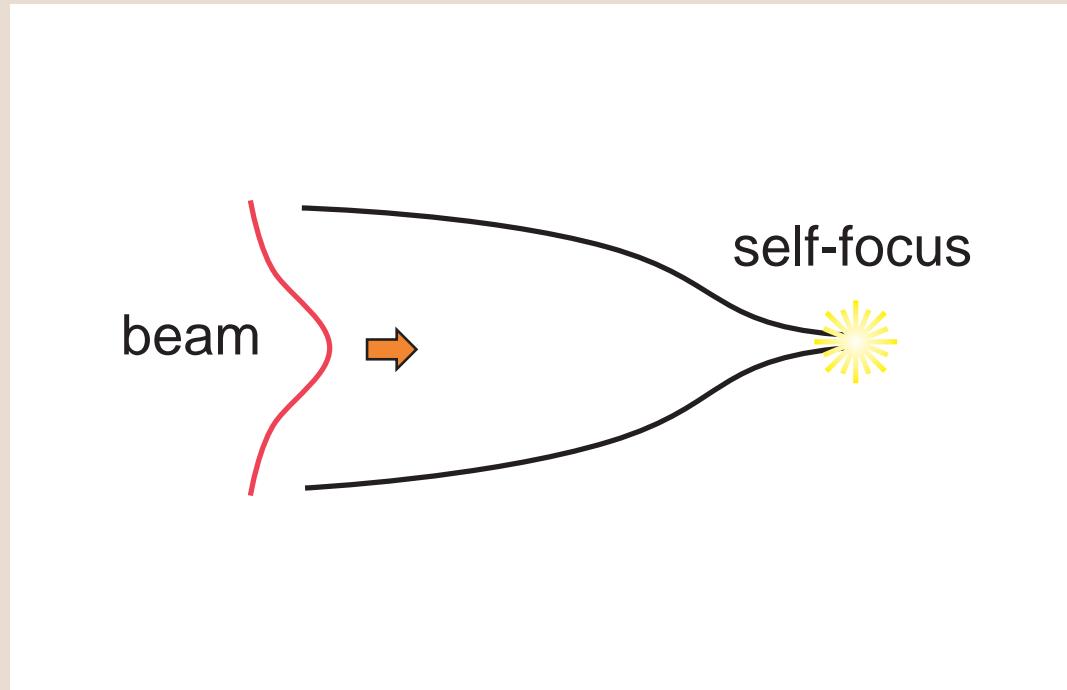




# Modification of materials

# *Nonlinear optical effects*

light induces position-dependent index of refraction



$$\text{self-focusing: } n(r) = n_0 + n_2 I(r)$$