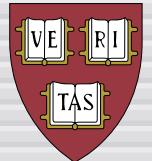
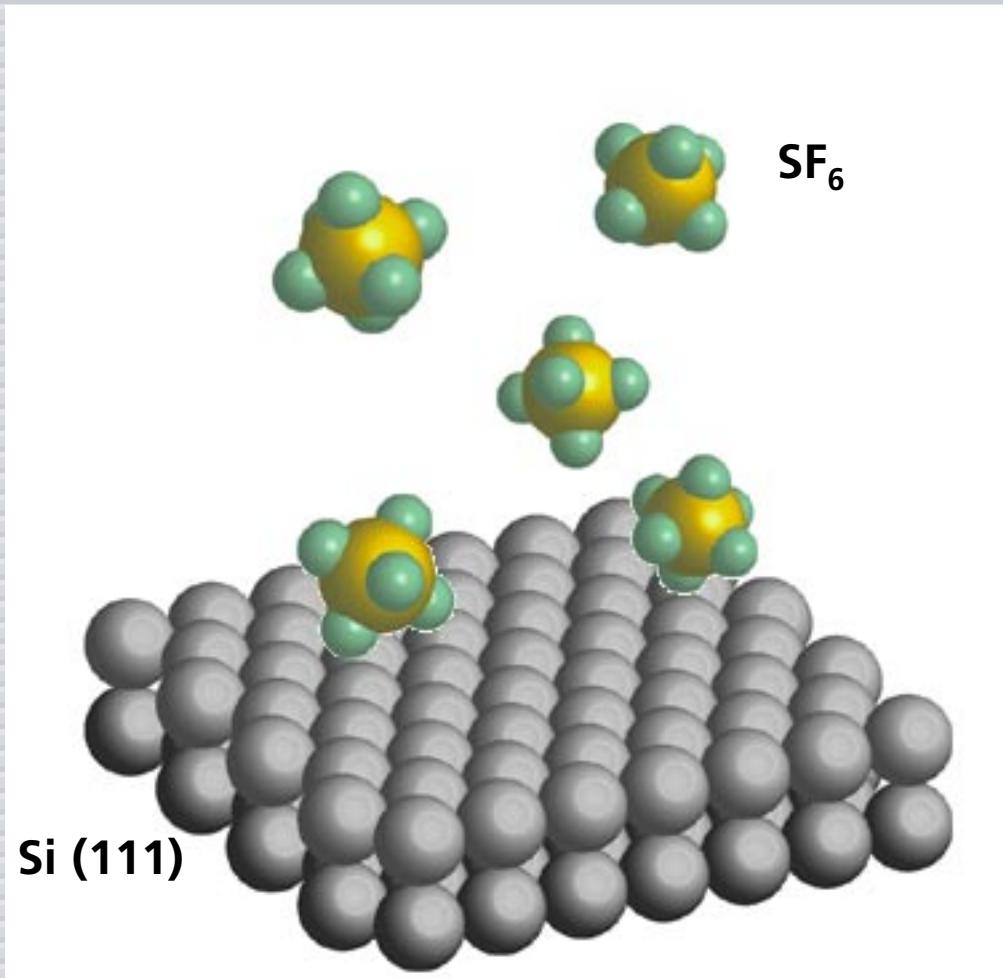


Nano-textured surfaces

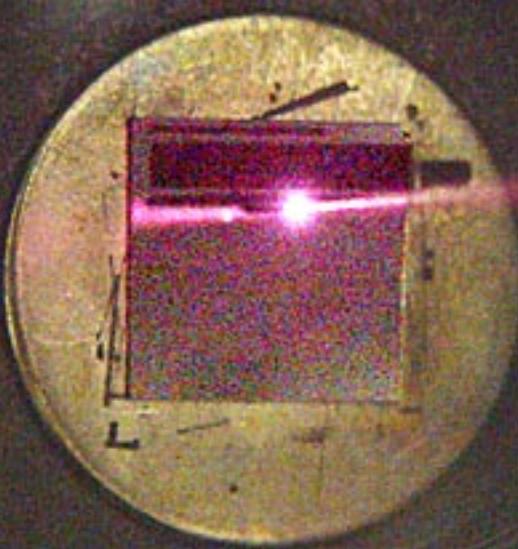
**Eric Mazur
DEAS/Physics**



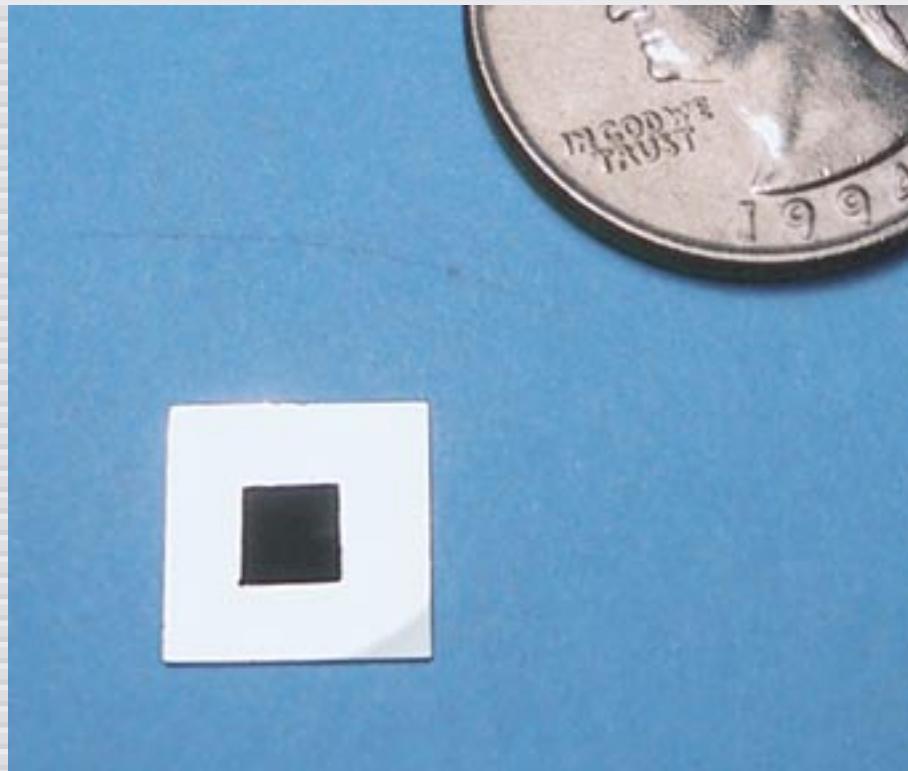
Introduction



irradiate with 100-fs 10 kJ/m^2 pulses

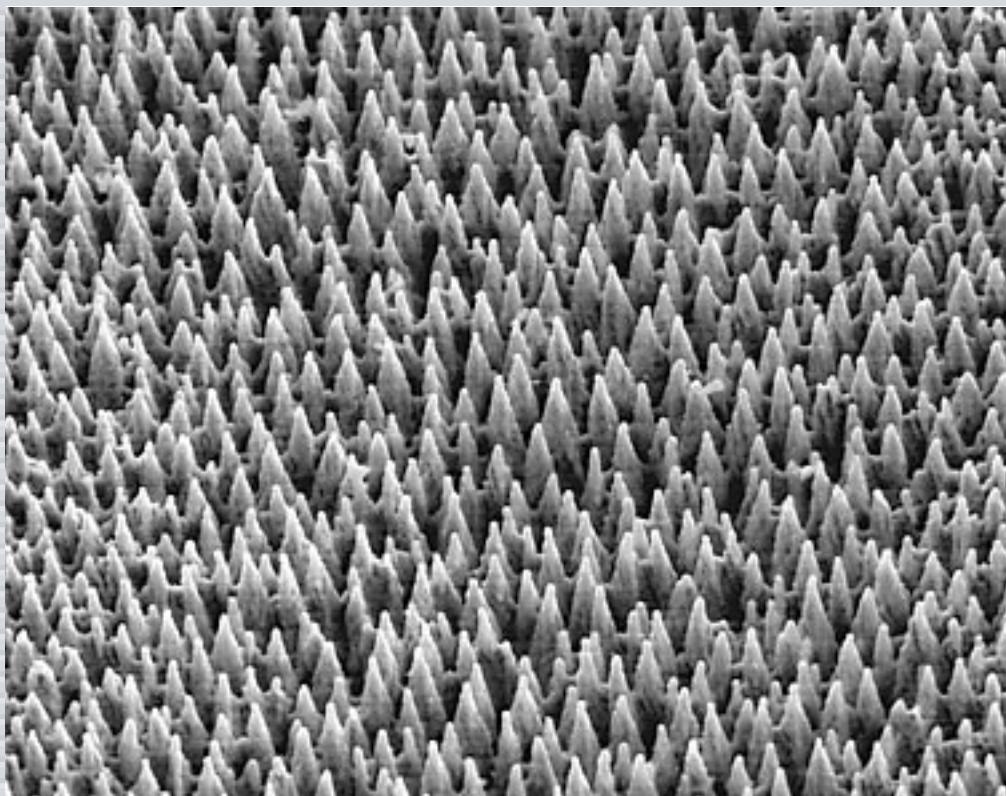


Introduction



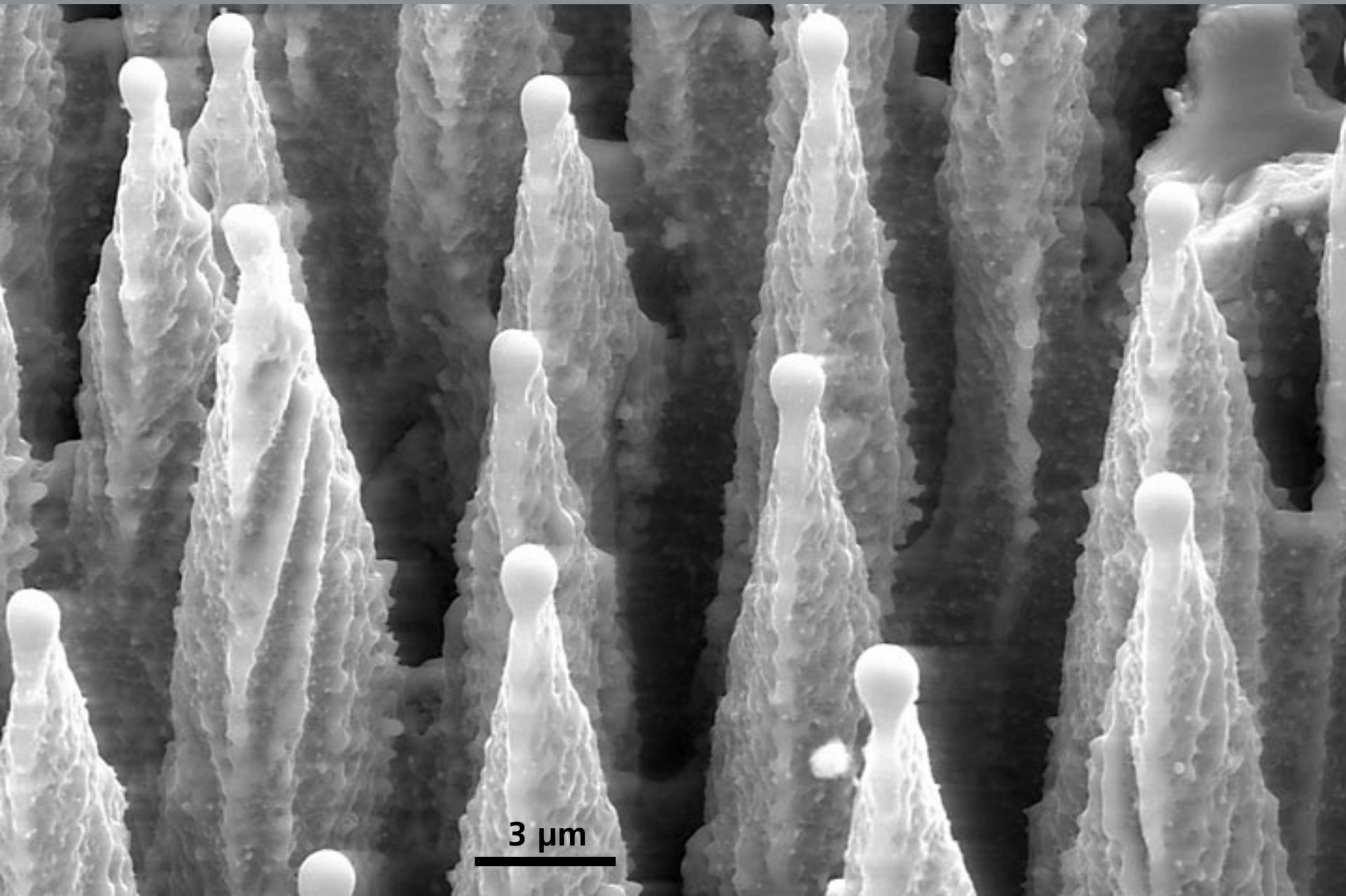
'black silicon'

Introduction

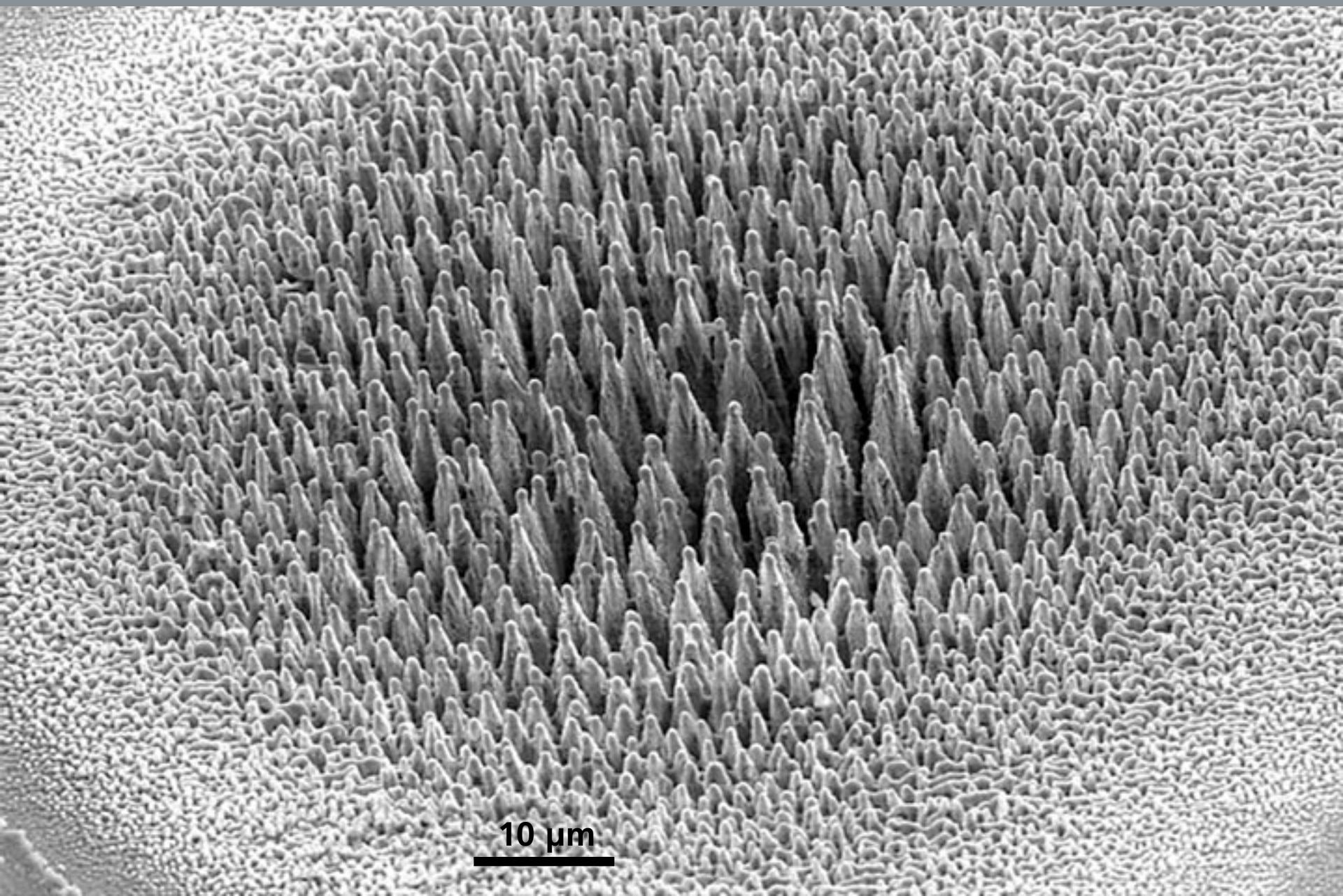


20 μm

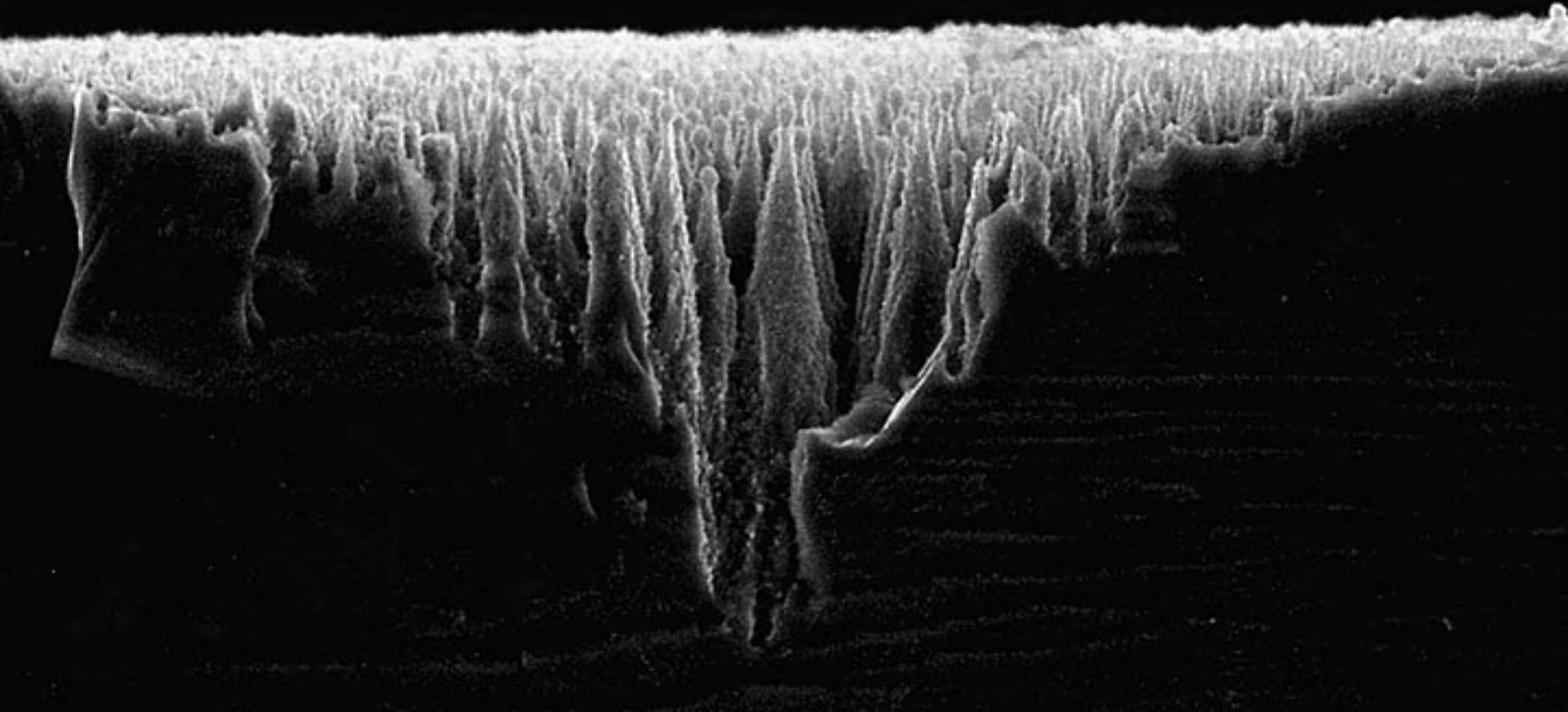
Introduction



Introduction



Introduction



Introduction

Introduction

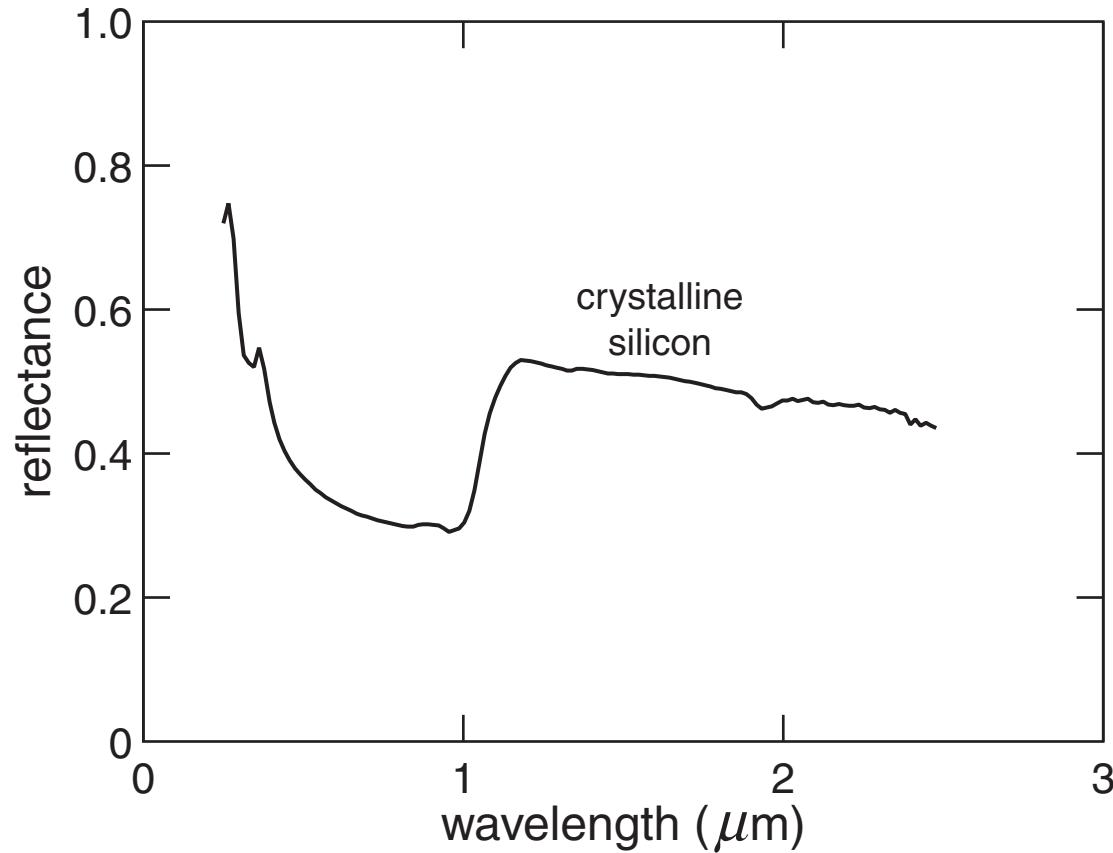
- ▶ **maskless etching process**
- ▶ **self-organized, tall, sharp structures**
- ▶ **nanoscale structure on spikes**

Outline

- ▶ **Properties**
- ▶ **Structural and chemical analysis**
- ▶ **Outlook**

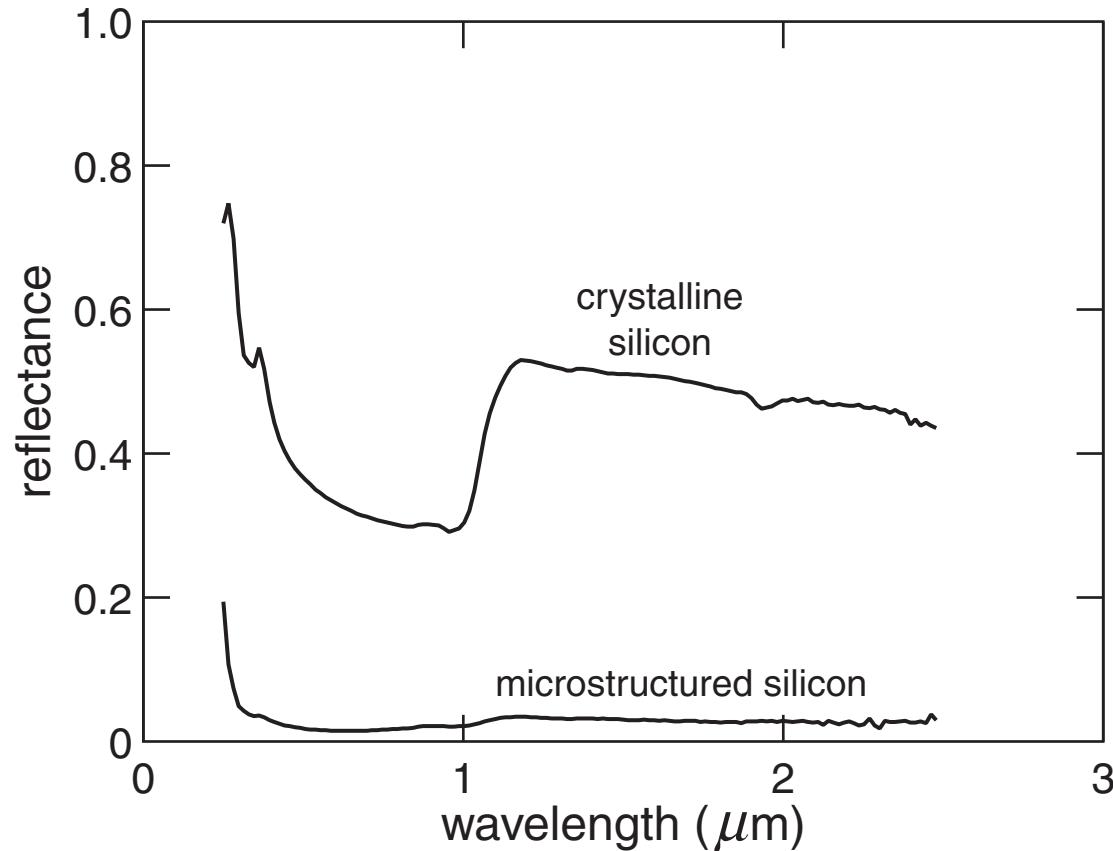
Properties

reflectance (integrating sphere)



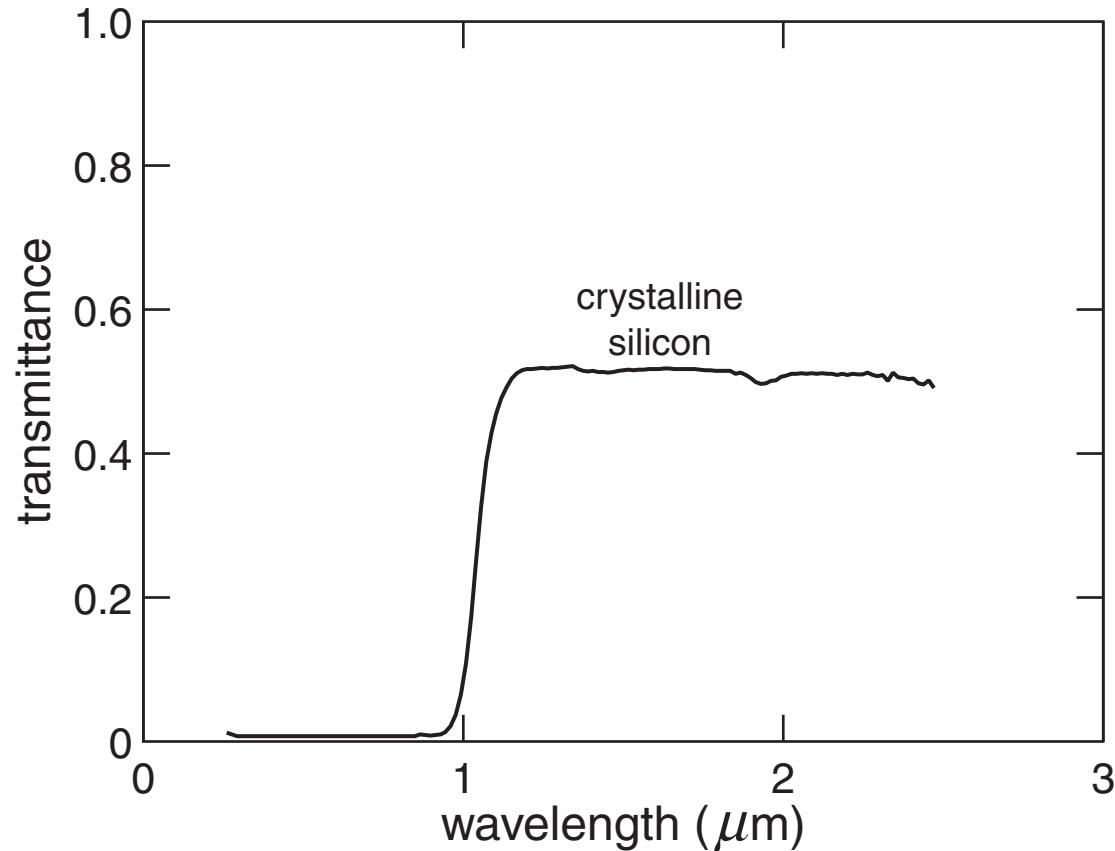
Properties

reflectance (integrating sphere)



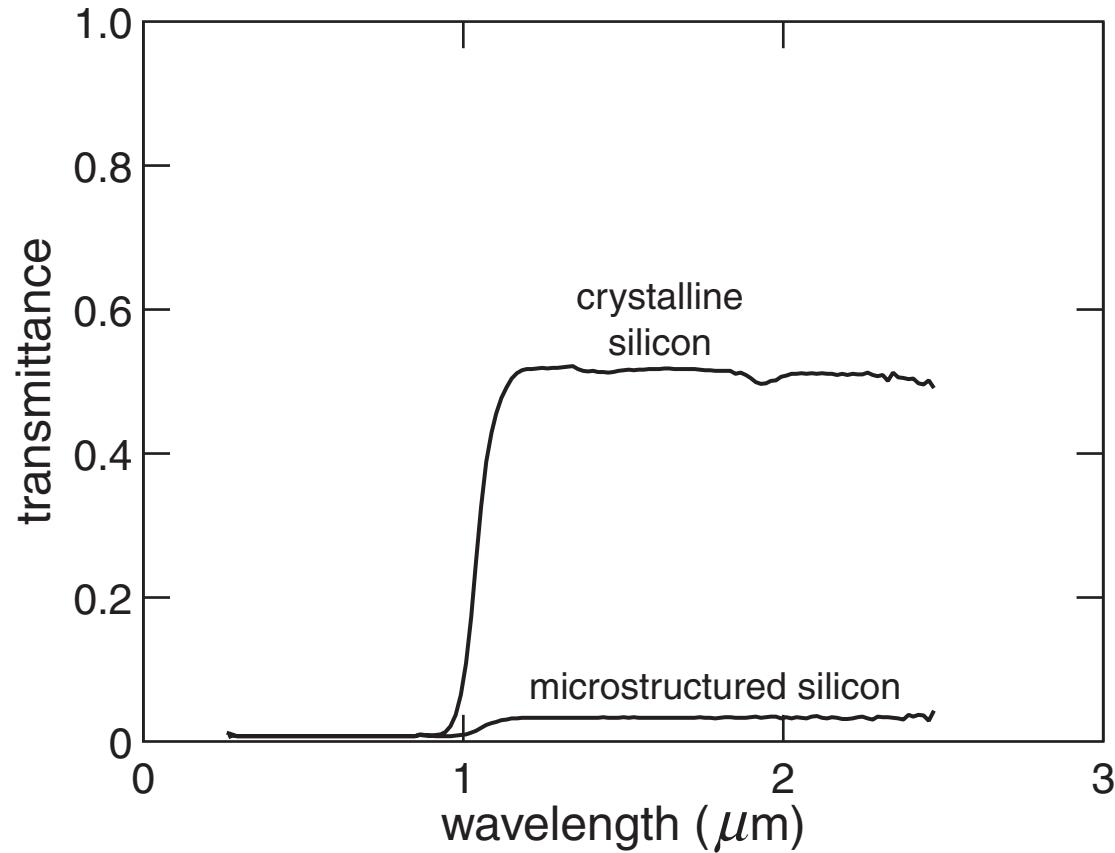
Properties

transmittance (integrating sphere)



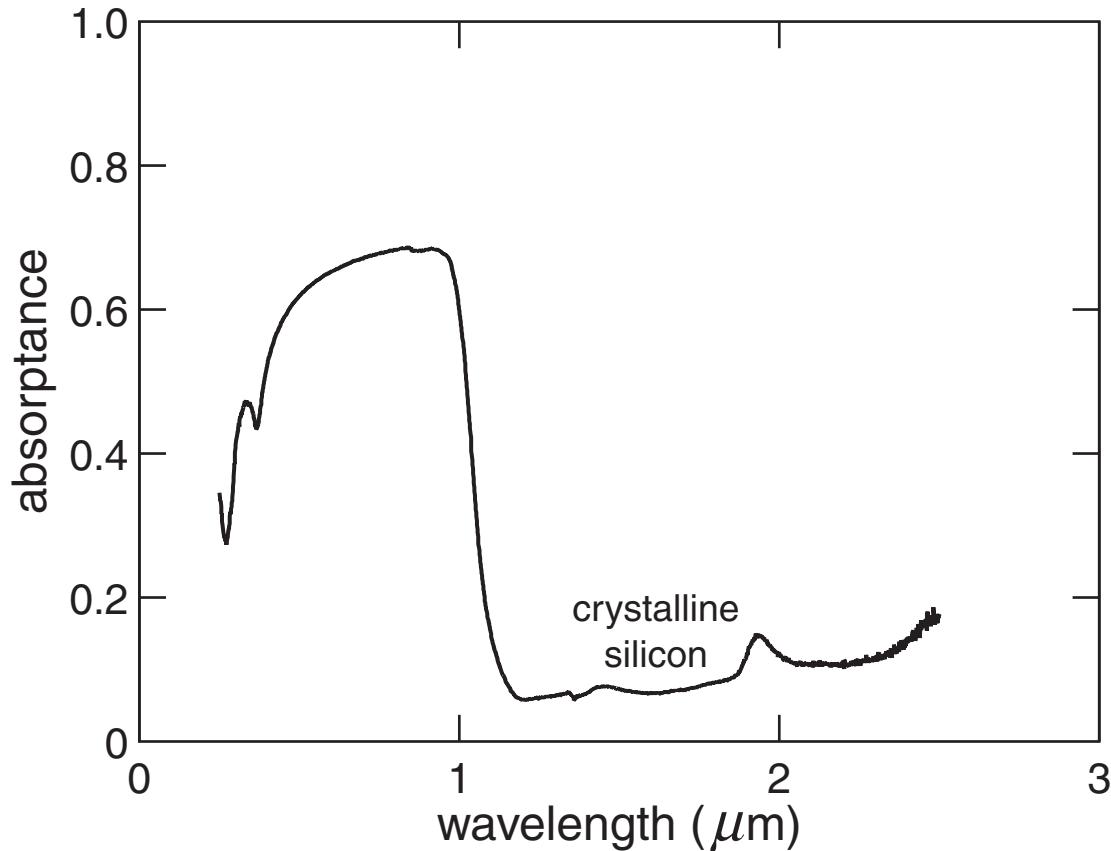
Properties

transmittance (integrating sphere)



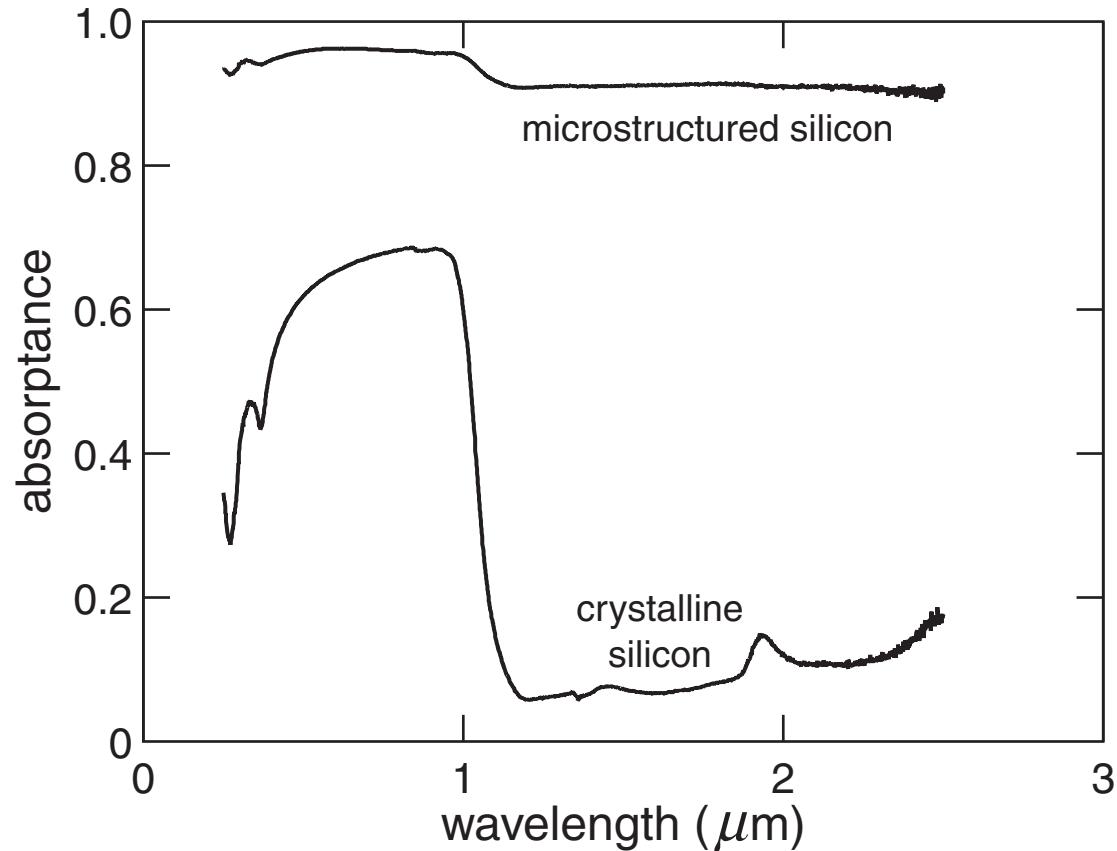
Properties

absorptance ($1 - R - T$)



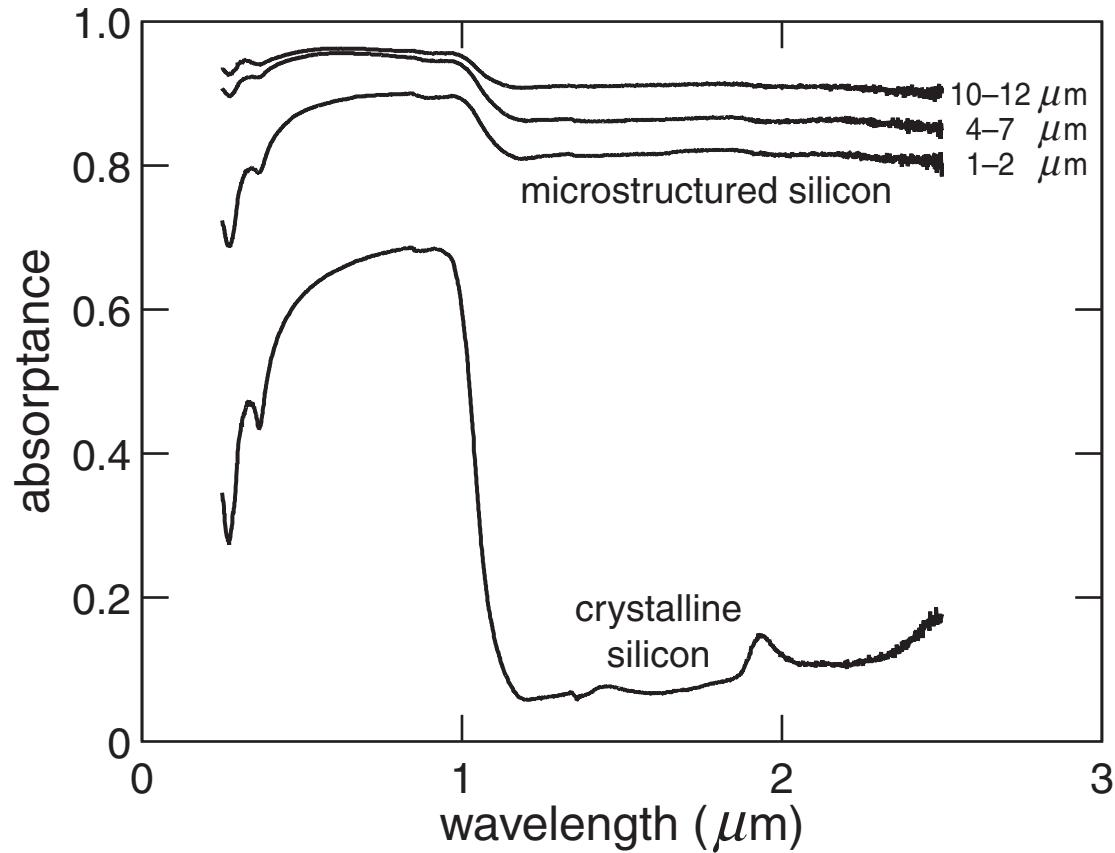
Properties

absorptance ($1 - R - T$)



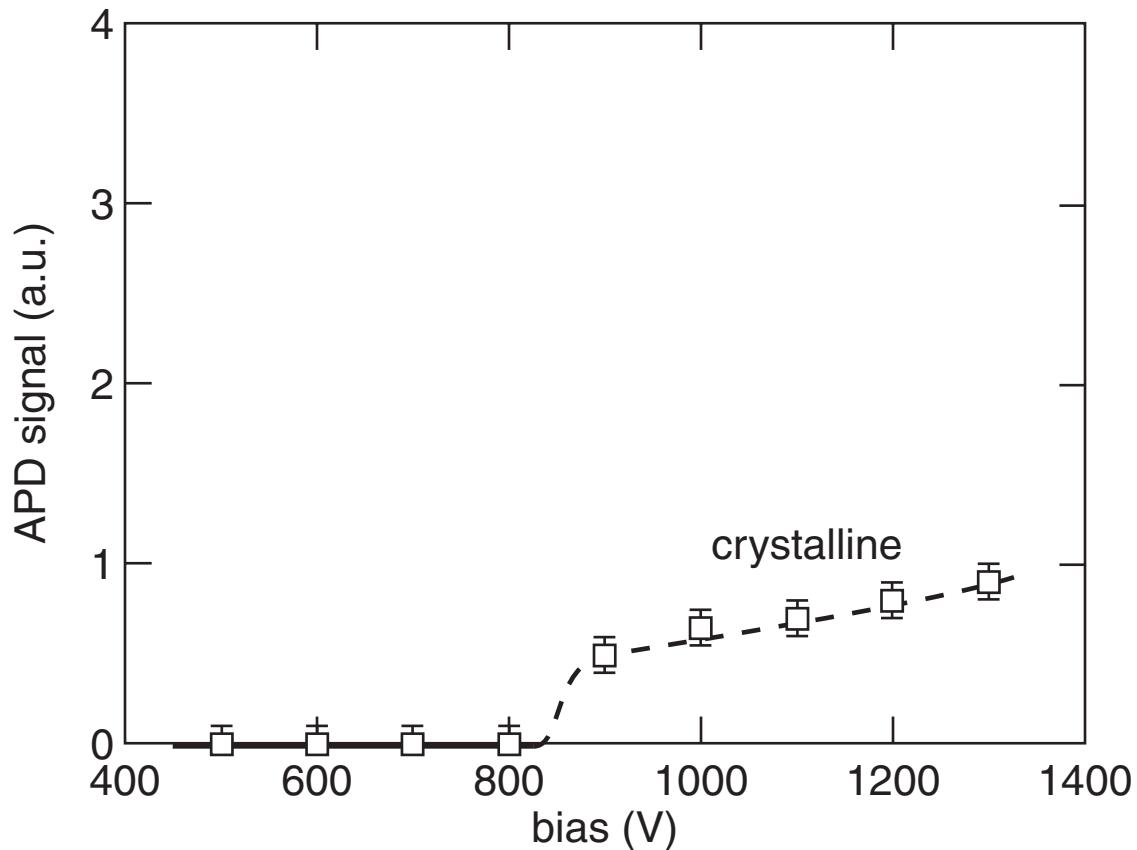
Properties

absorptance ($1 - R - T$)



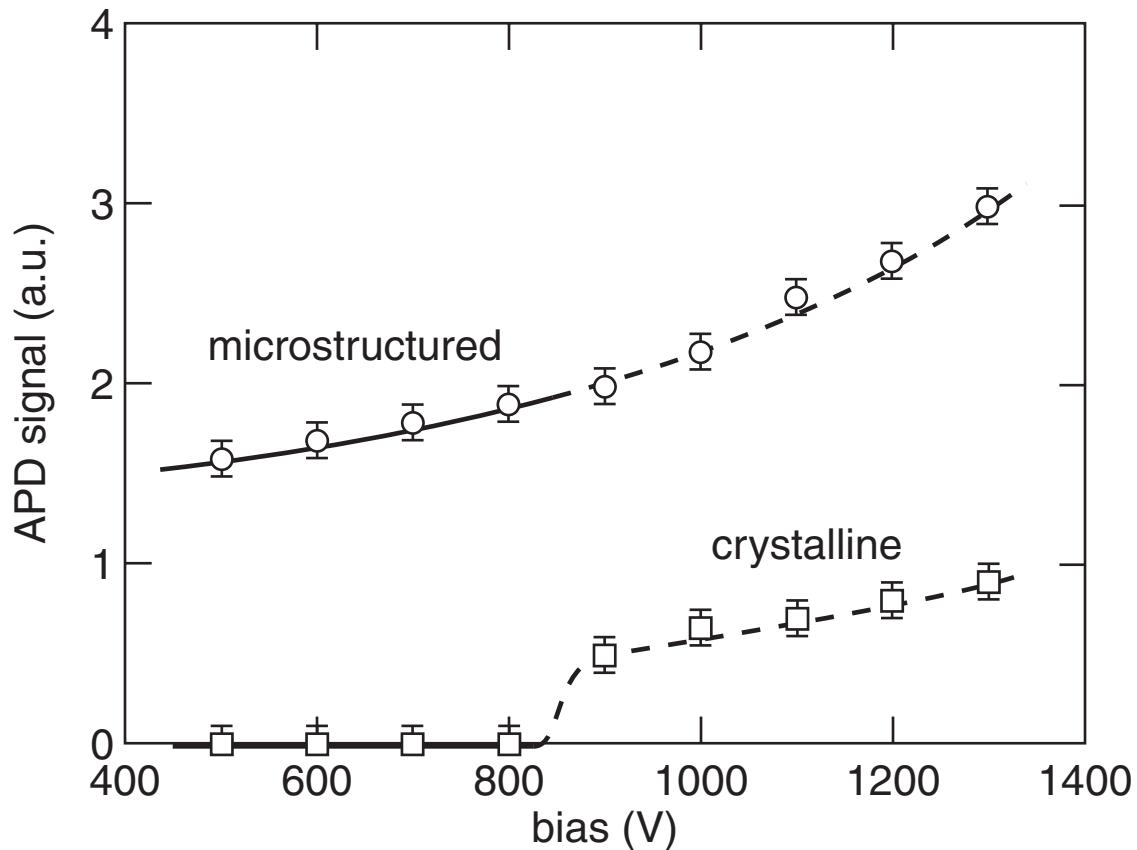
Properties

avalanche photodiode response at 1.3 μ m



Properties

avalanche photodiode response at 1.3 μ m



Properties

Points to keep in mind:

- ▶ **near unity absorption**
- ▶ **sub-band gap absorption**
- ▶ **IR photoelectron generation**

Properties

Points to keep in mind:

- ▶ **near unity absorption**
- ▶ **sub-band gap absorption**
- ▶ **IR photoelectron generation**

can spikes be used as field emitters?

Properties

field emission setup



Properties

field emission setup



gold coating

Properties

field emission setup

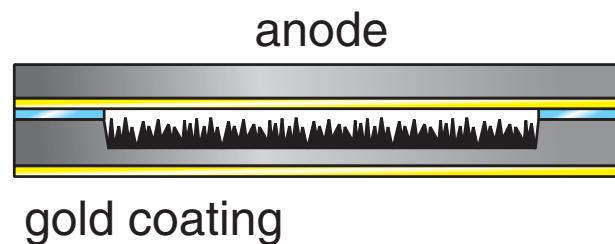
20 μm mica spacers



gold coating

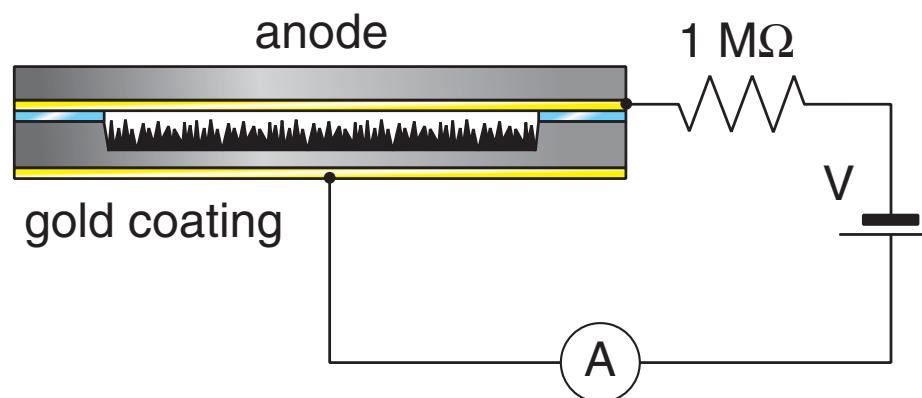
Properties

field emission setup

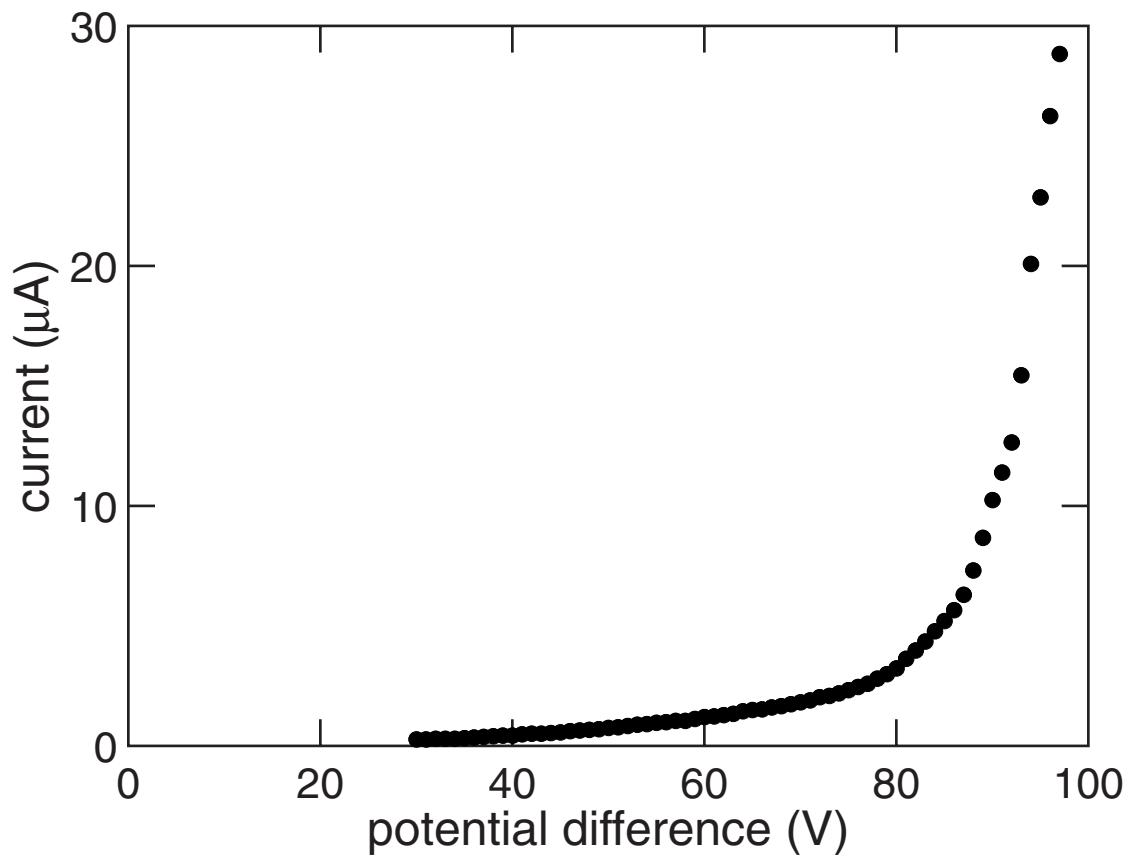


Properties

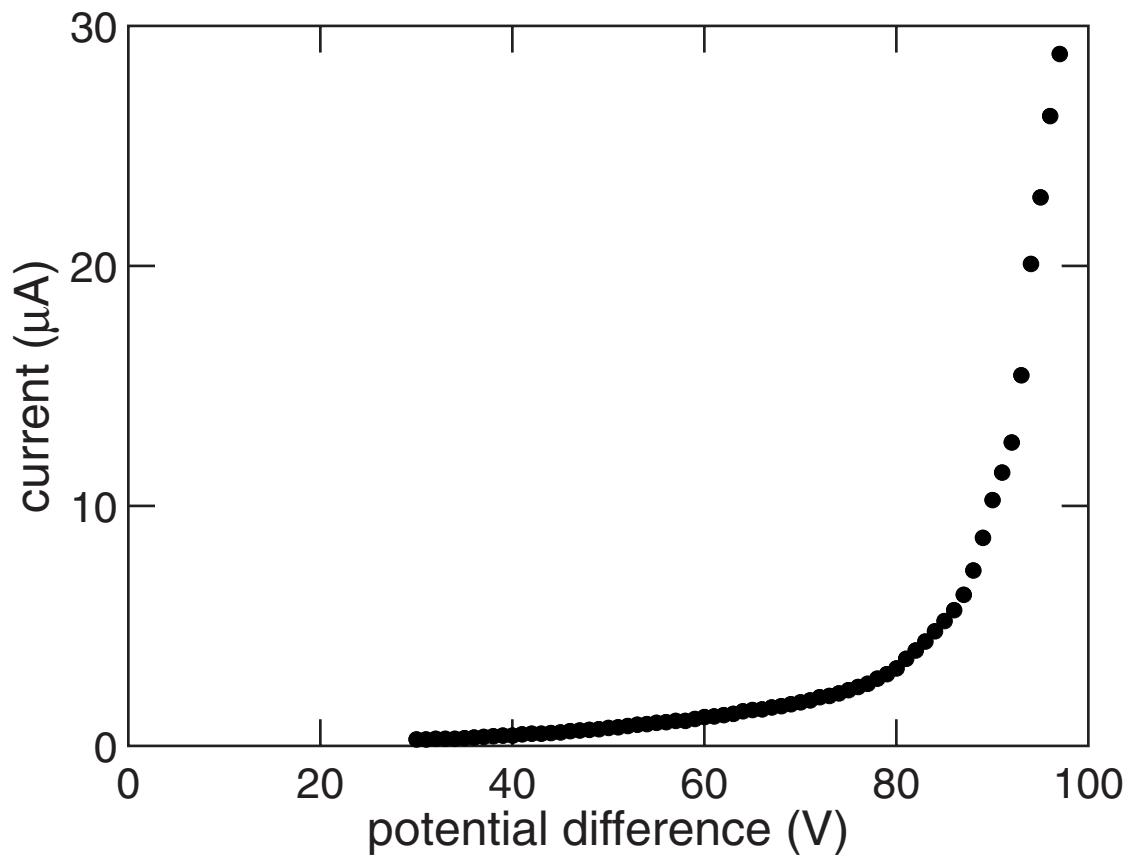
field emission setup



Properties

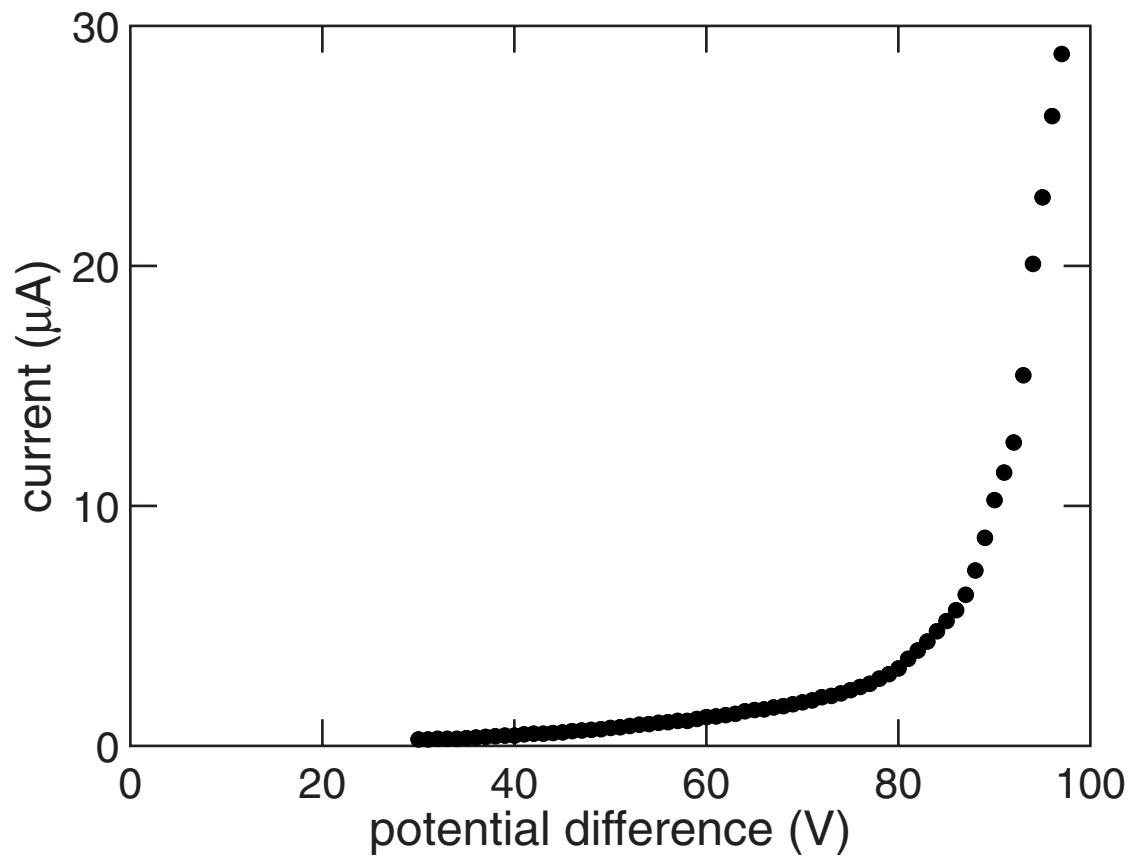


Properties



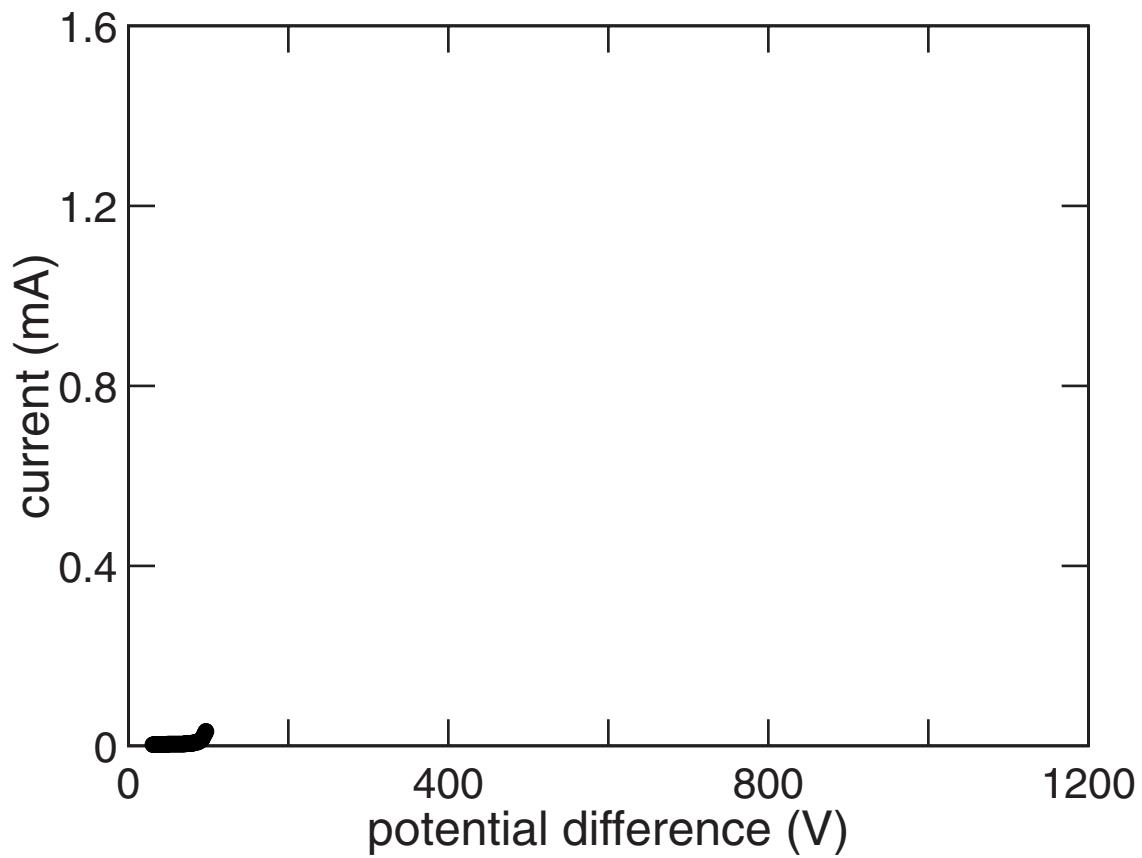
turn-on field (1 μ A/cm 2): 1.2 V/ μ m

Properties

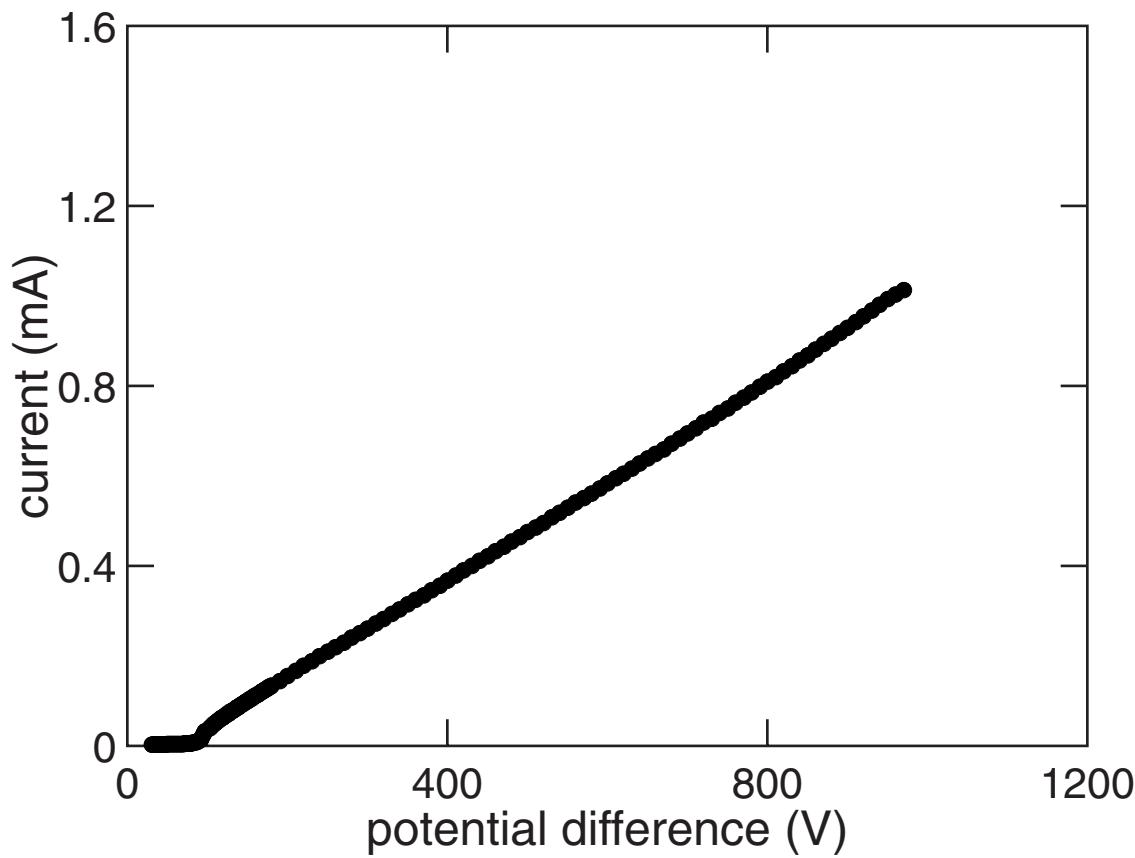


threshold field ($10 \mu\text{A}/\text{cm}^2$): $2.1 \text{ V}/\mu\text{m}$

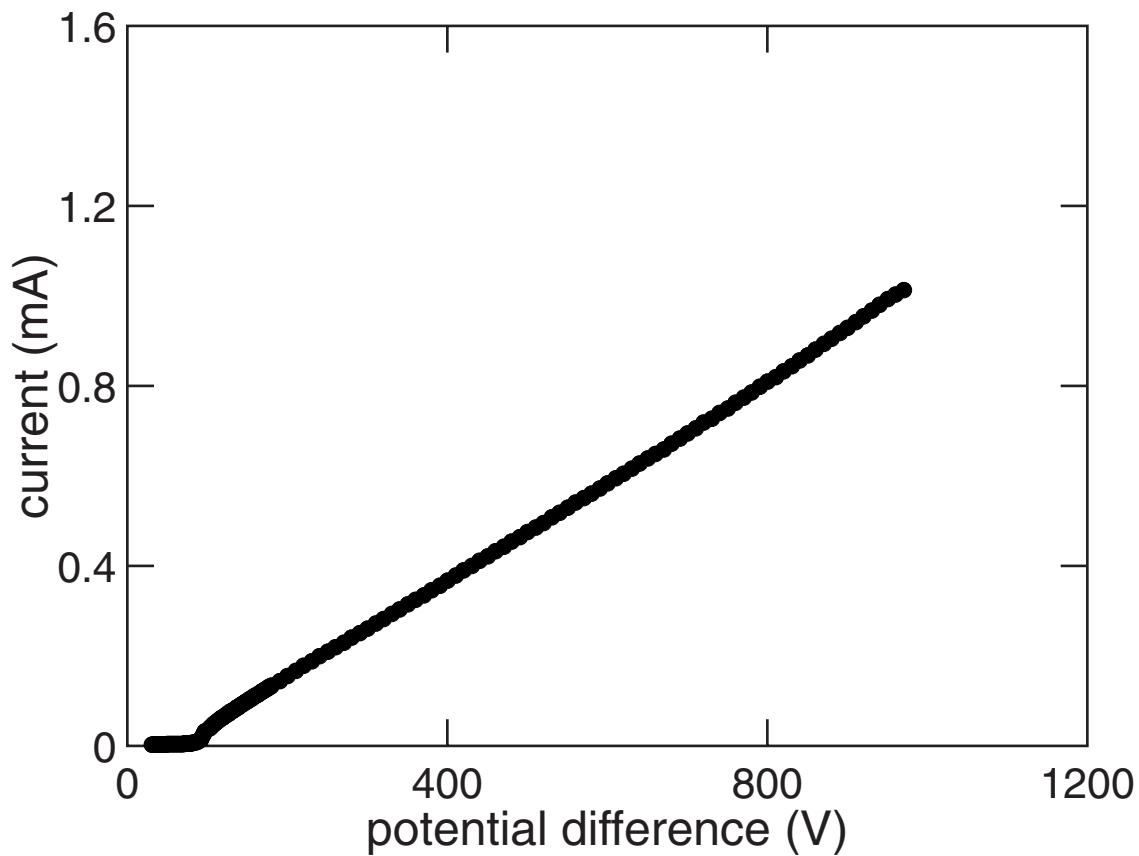
Properties



Properties



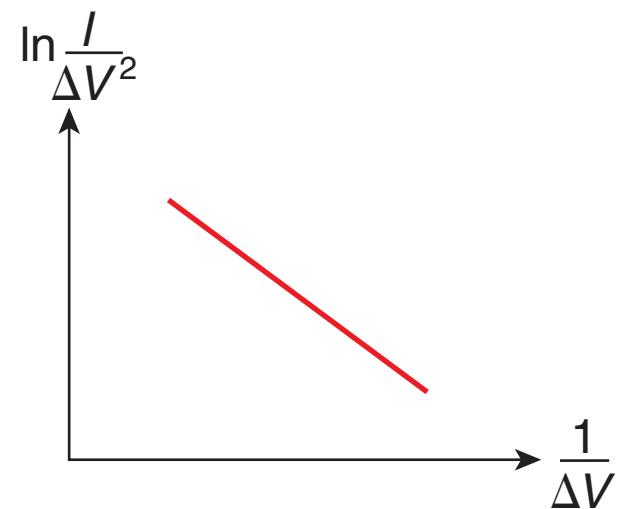
Properties



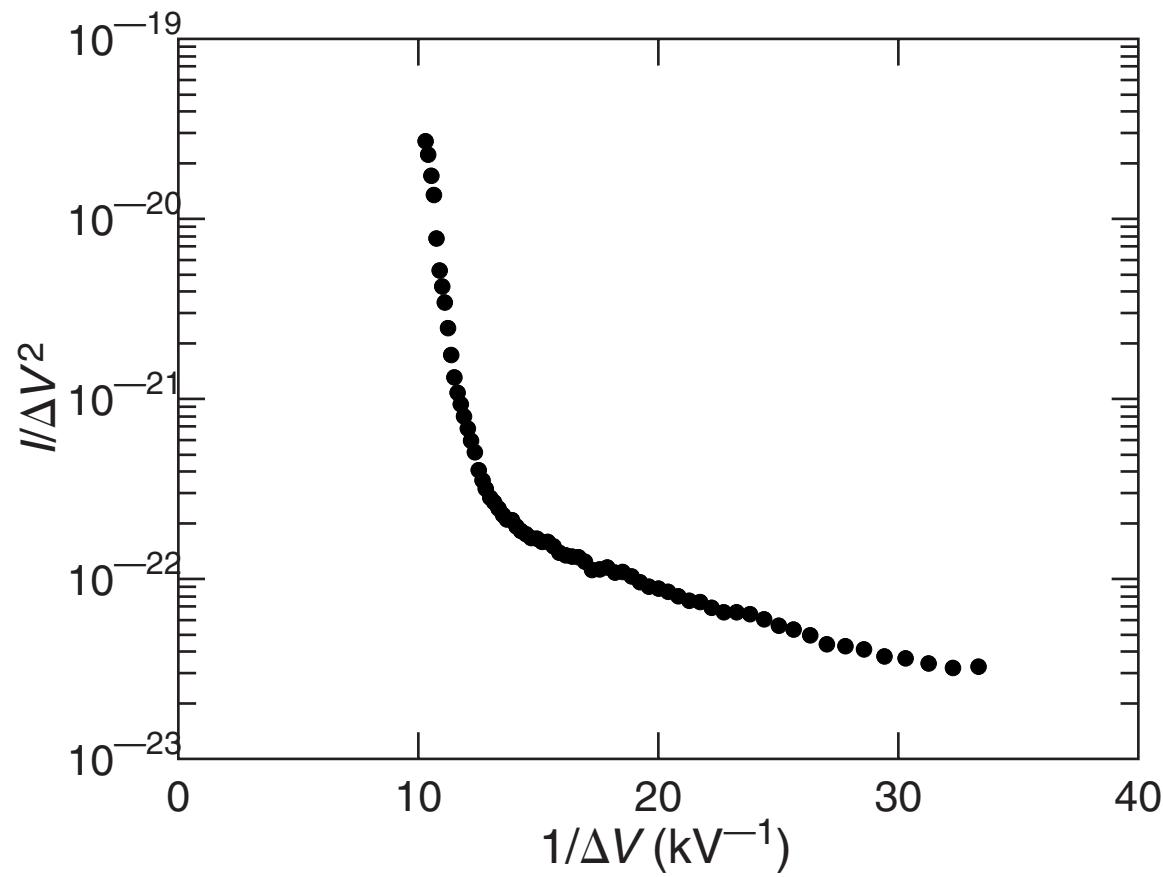
maximum current: 20 mA (4 mm² sample)

Properties

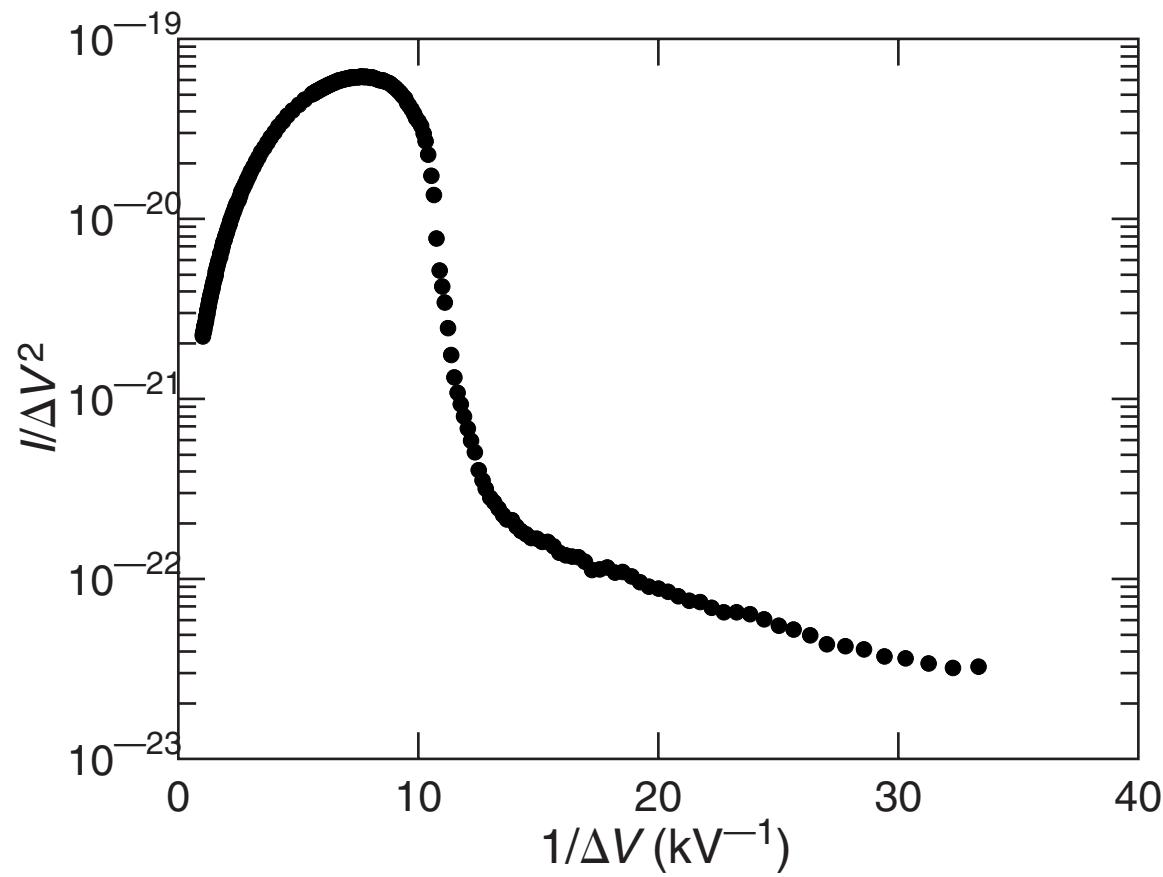
$$\ln \frac{I}{\Delta V^2} = \ln a - b \frac{1}{\Delta V}$$



Properties



Properties



Properties

Points to keep in mind:

- ▶ **near unity absorption**
- ▶ **sub-band gap absorption**
- ▶ **IR photoelectron generation**
- ▶ **high field emission at low fields**

Outline

- ▶ Properties
- ▶ Structural and chemical analysis
- ▶ Outlook

Structural and chemical analysis

- ▶ **What causes these properties?**
- ▶ **Other gases?**

Structural and chemical analysis

Ion channeling and electron backscattering:

- ▶ **spikes retain crystalline order**
- ▶ **high density of defects**

Structural and chemical analysis

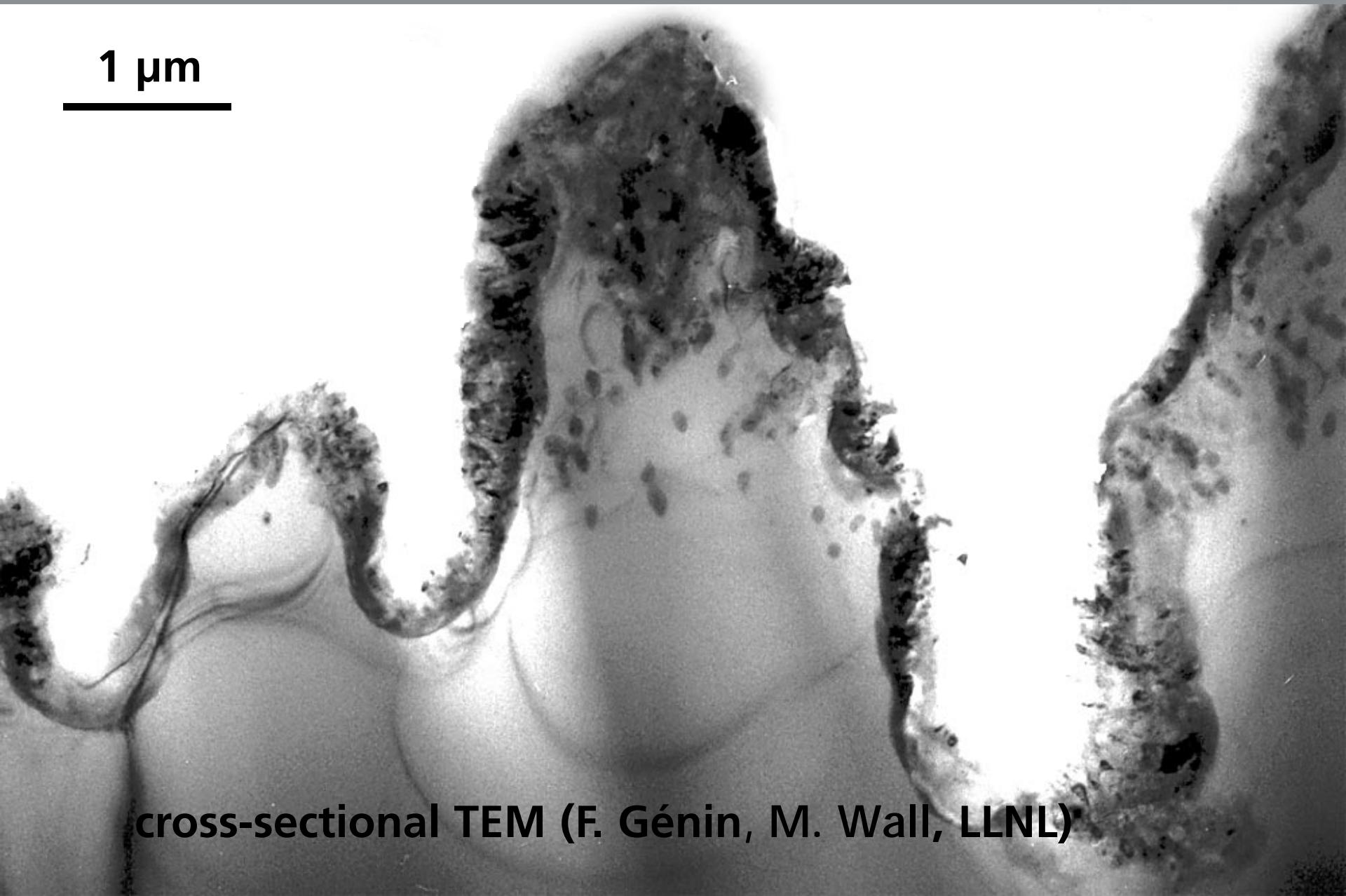
Secondary ion mass spectrometry:

- ▶ 10^{20} cm^{-3} sulfur

- ▶ 10^{17} cm^{-3} fluorine

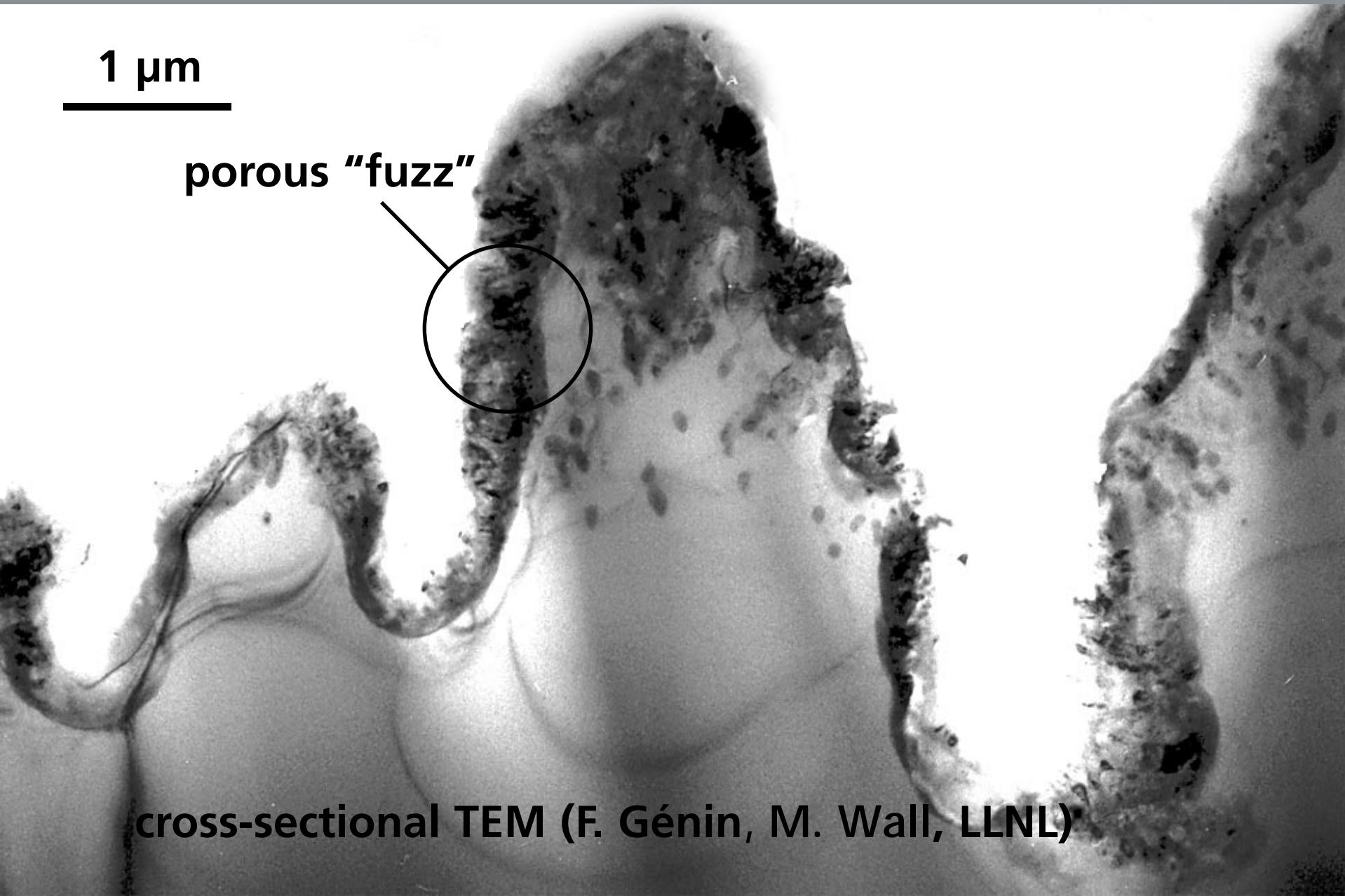
Structural and chemical analysis

1 μm



cross-sectional TEM (F. Génin, M. Wall, LLNL)

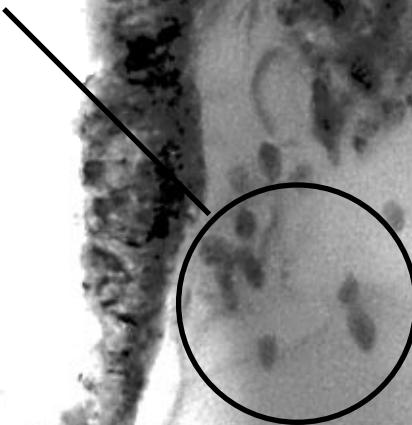
Structural and chemical analysis



Structural and chemical analysis

1 μm

nanocrystallites

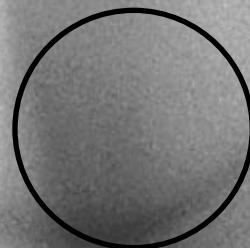


cross-sectional TEM (F. Génin, M. Wall, LLNL)

Structural and chemical analysis

1 μm

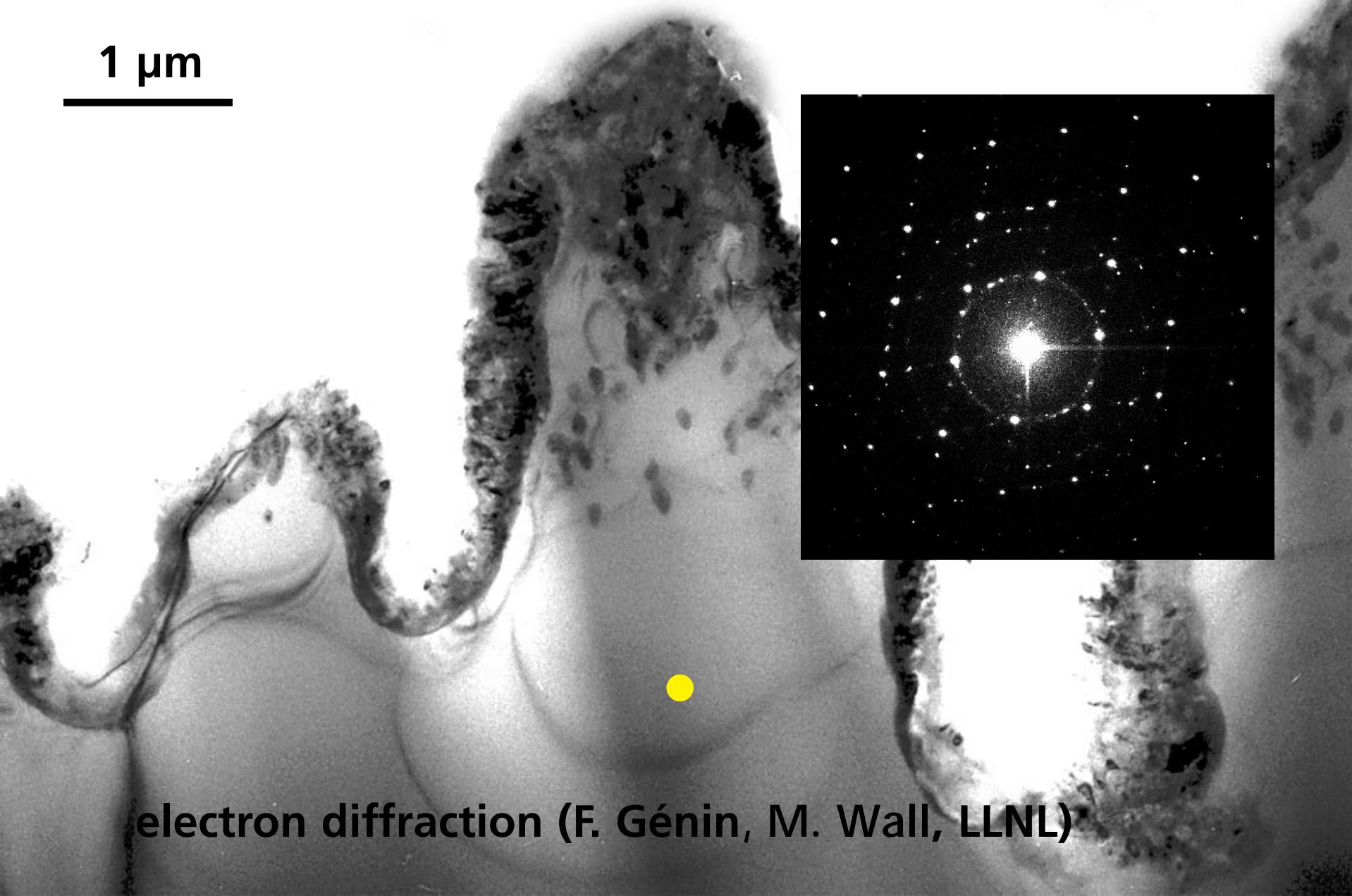
crystalline Si



cross-sectional TEM (F. Génin, M. Wall, LLNL)

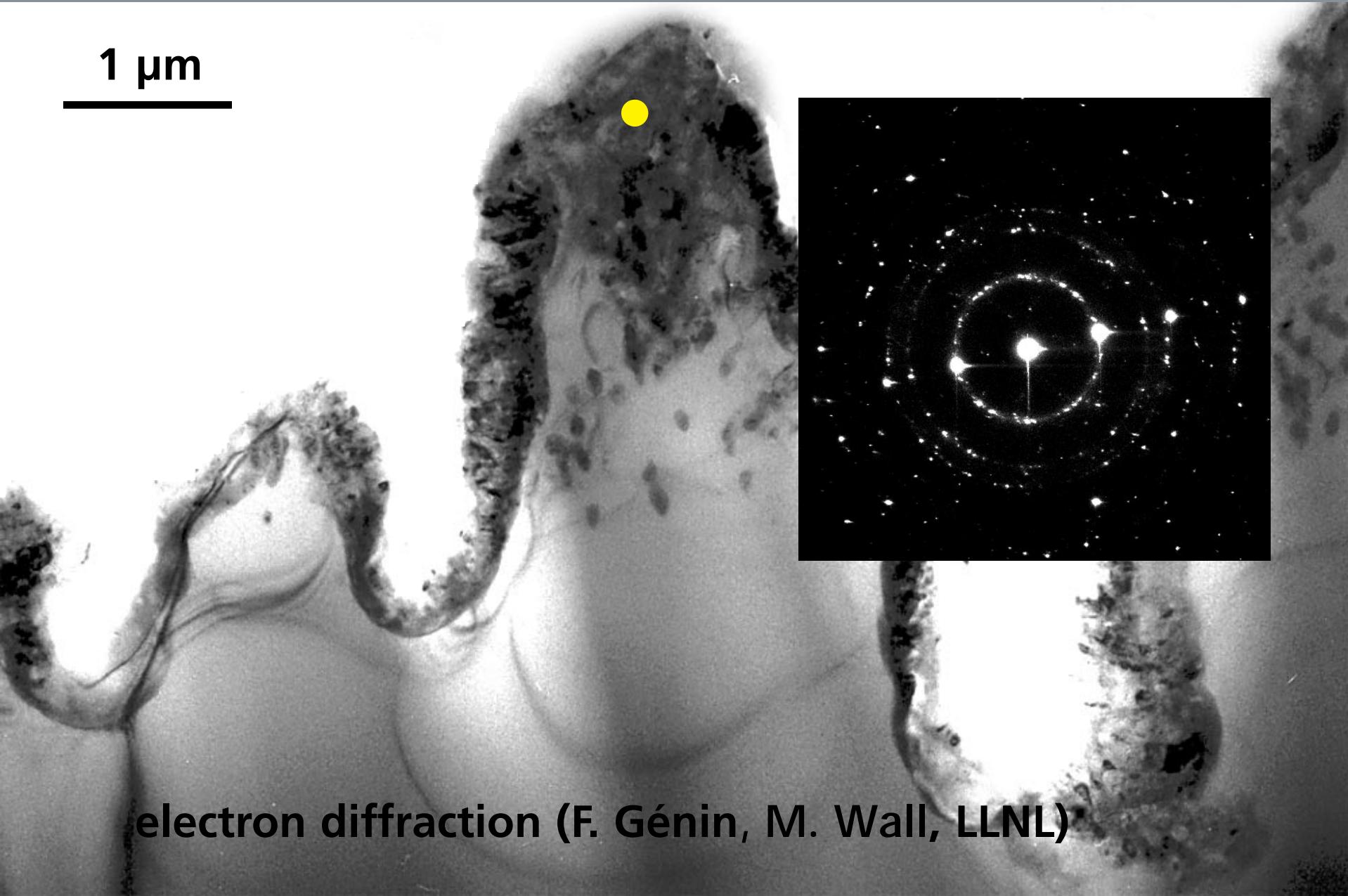
Structural and chemical analysis

1 μm



electron diffraction (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



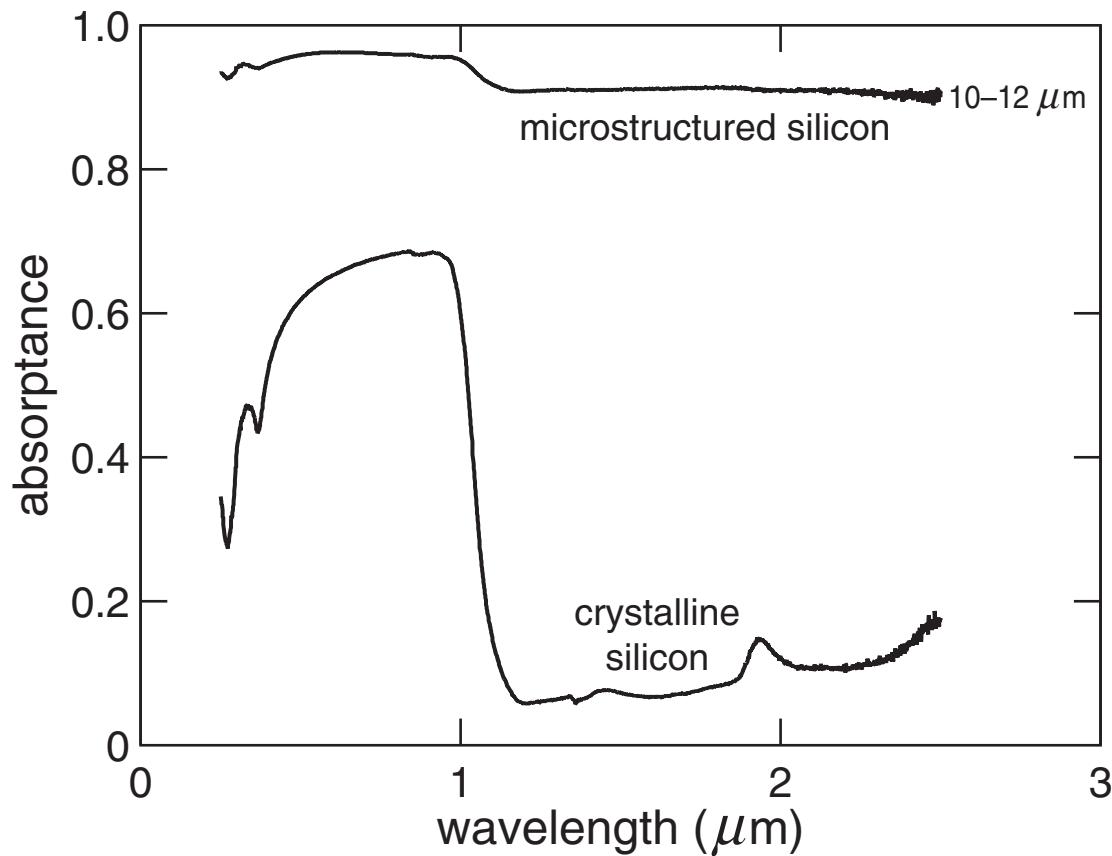
Structural and chemical analysis

cross-sectional TEM:

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

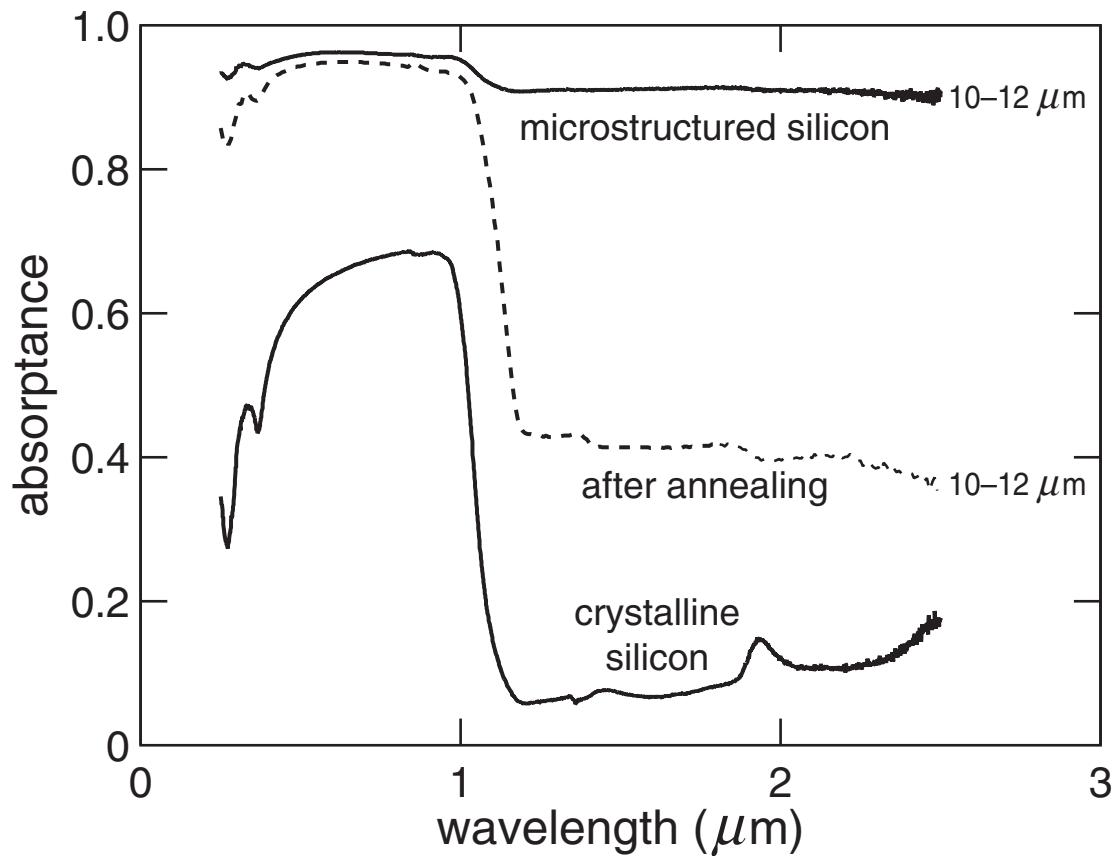
Structural and chemical analysis

anneal 4 hours at 1200 K



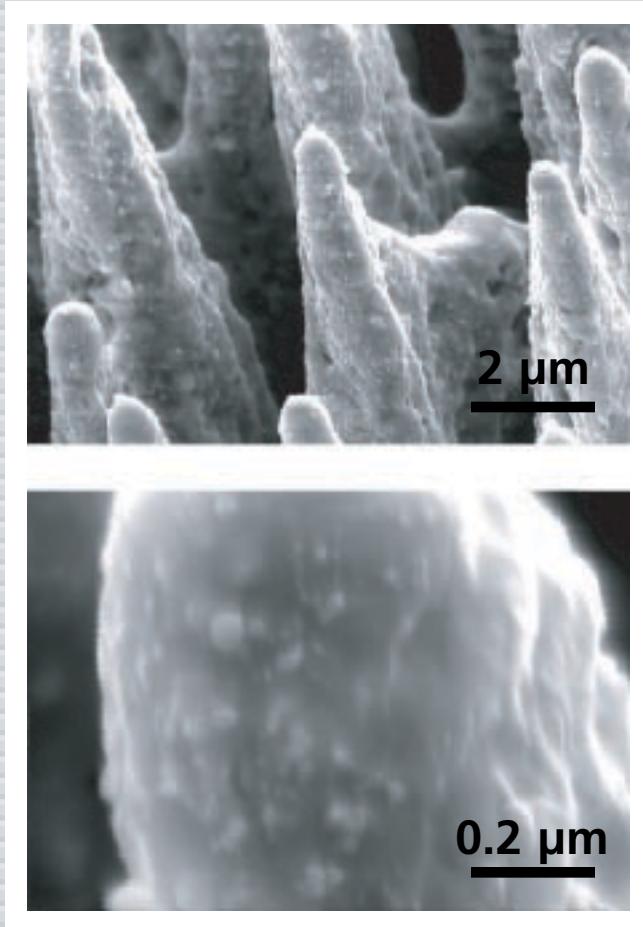
Structural and chemical analysis

anneal 4 hours at 1200 K



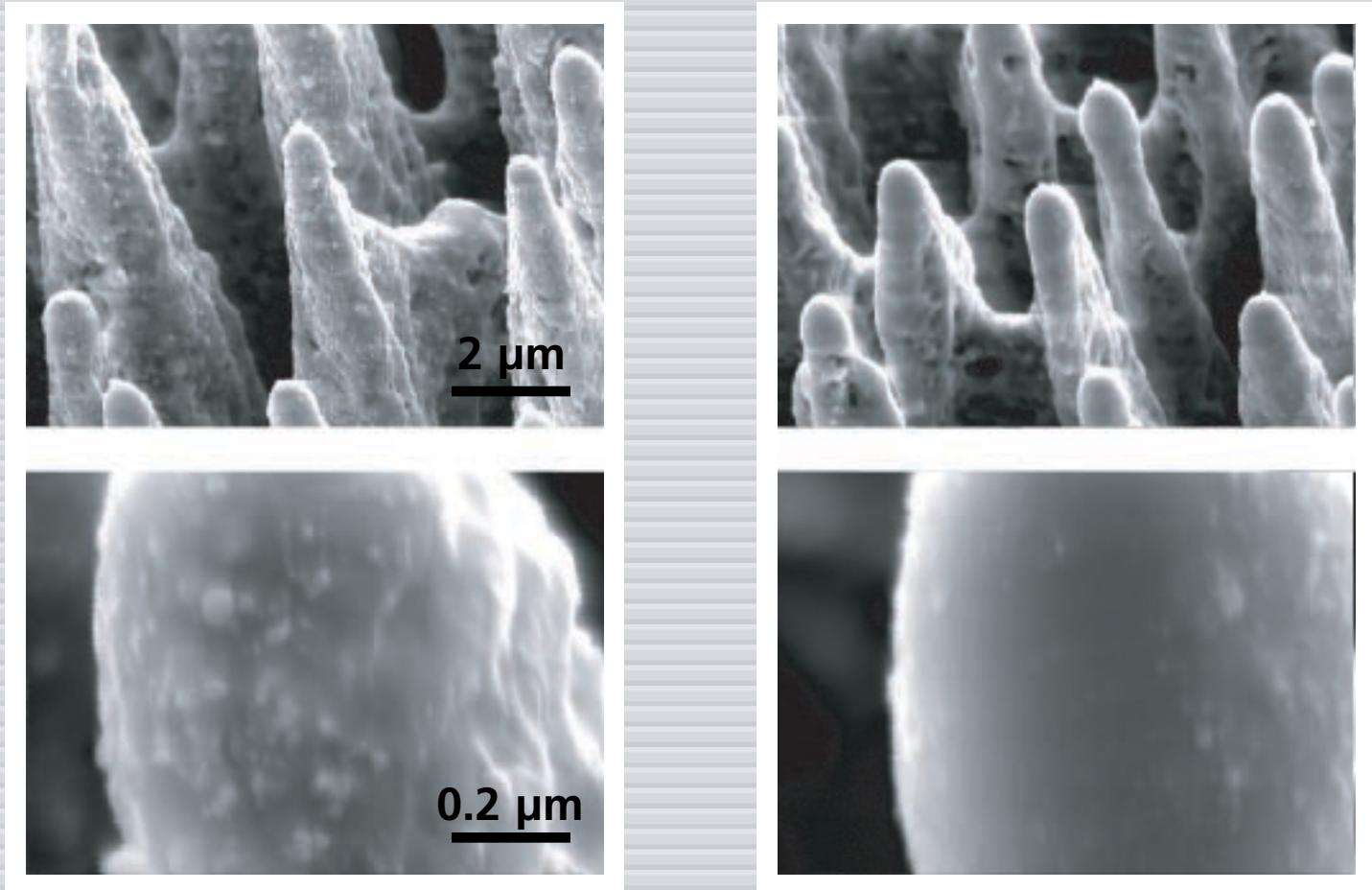
Structural and chemical analysis

anneal 4 hours at 1200 K



Structural and chemical analysis

anneal 4 hours at 1200 K



Structural and chemical analysis

Effects of annealing:

- ▶ **IR absorption: reduced twofold**
- ▶ **SEM: fewer surface nanostructures**
- ▶ **SIMS: sulfur content reduced twofold**

Structural and chemical analysis

sulfur introduces states in the gap

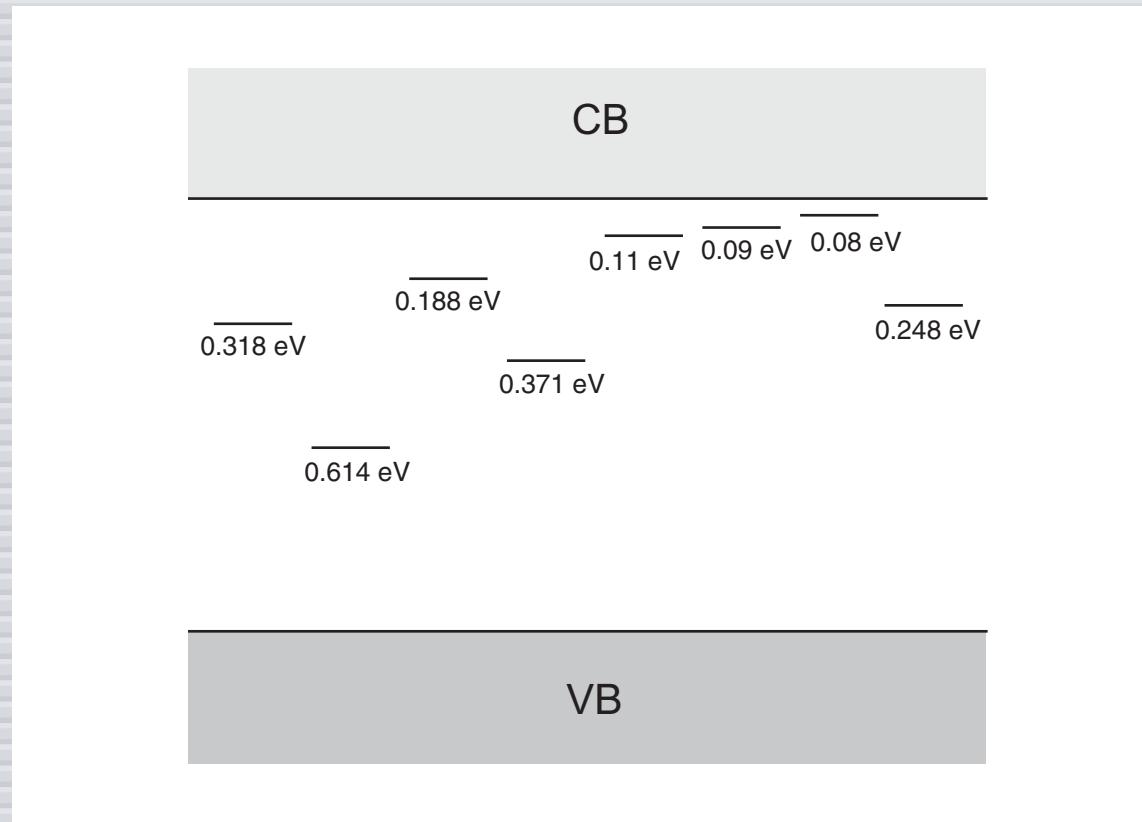
CB

A diagram illustrating the electronic structure of a material. It features two horizontal grey bars representing energy bands. The upper bar is labeled "CB" (Conduction Band) and the lower bar is labeled "VB" (Valence Band). A thin black horizontal line separates the two bars, representing the energy gap between them.

VB

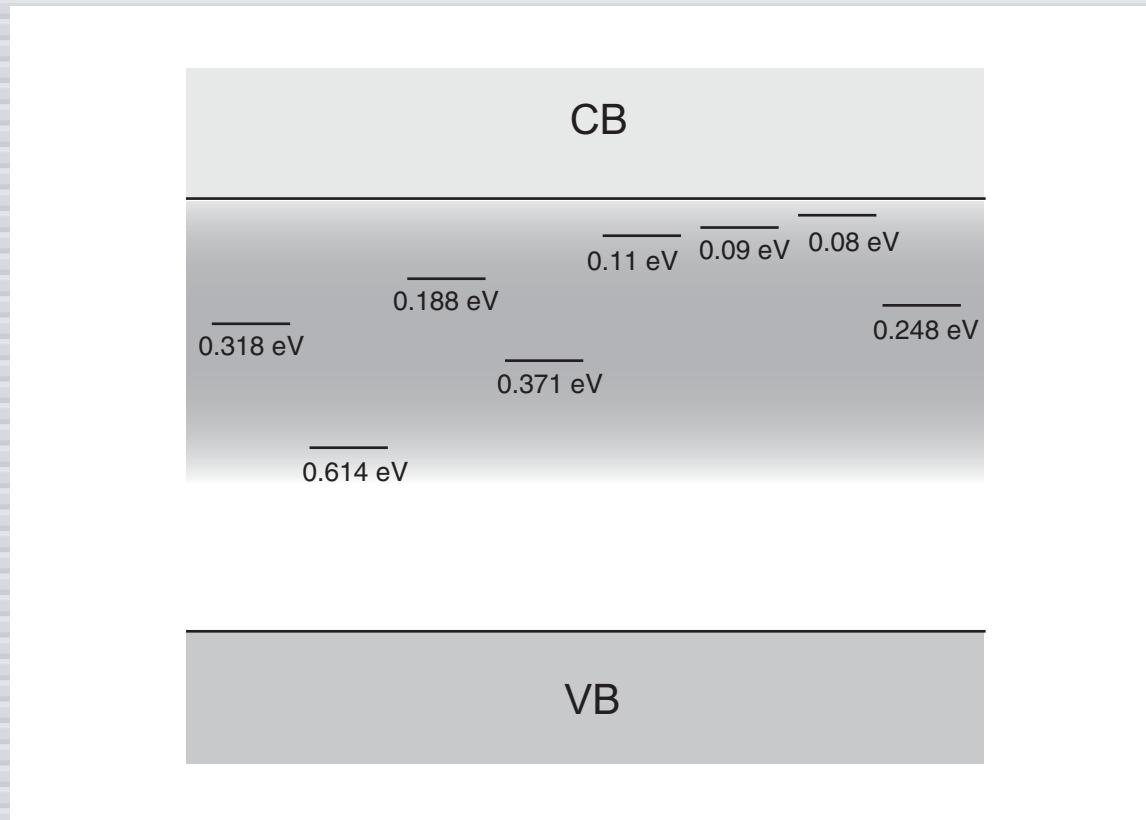
Structural and chemical analysis

sulfur introduces states in the gap

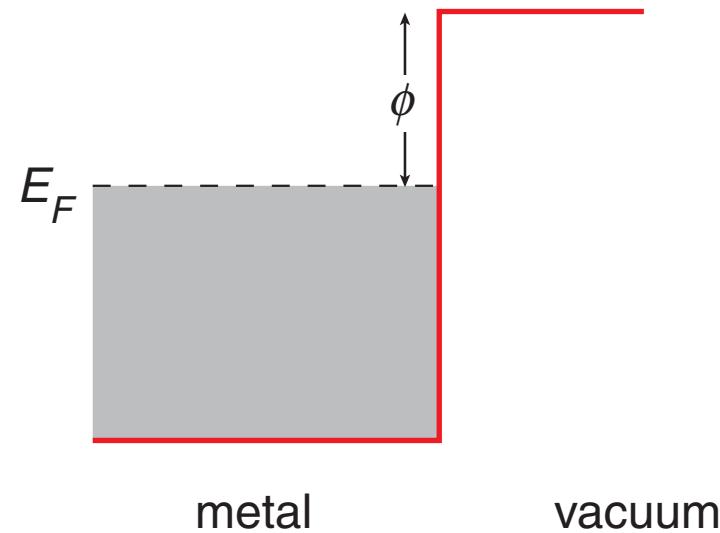


Structural and chemical analysis

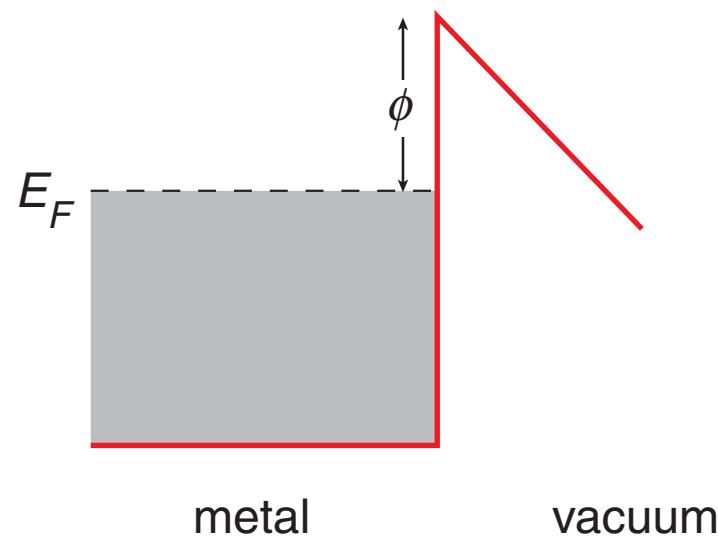
states broaden into a band



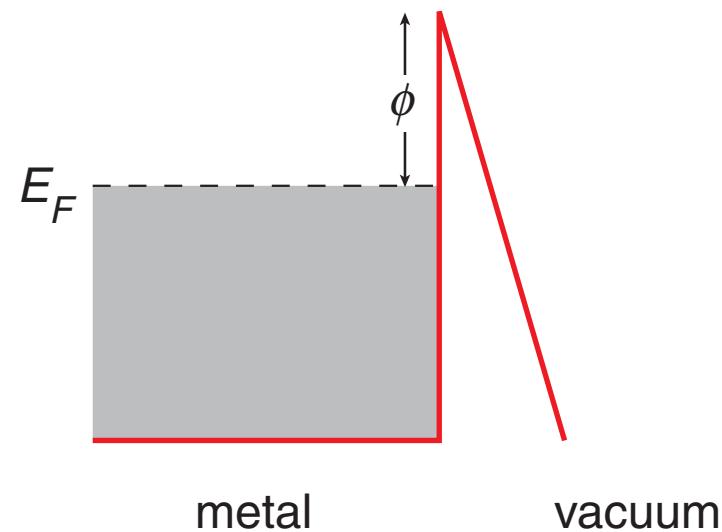
Structural and chemical analysis



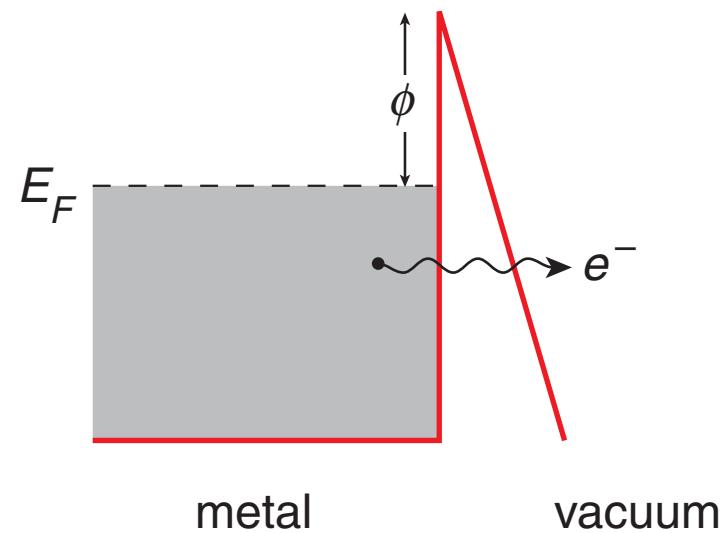
Structural and chemical analysis



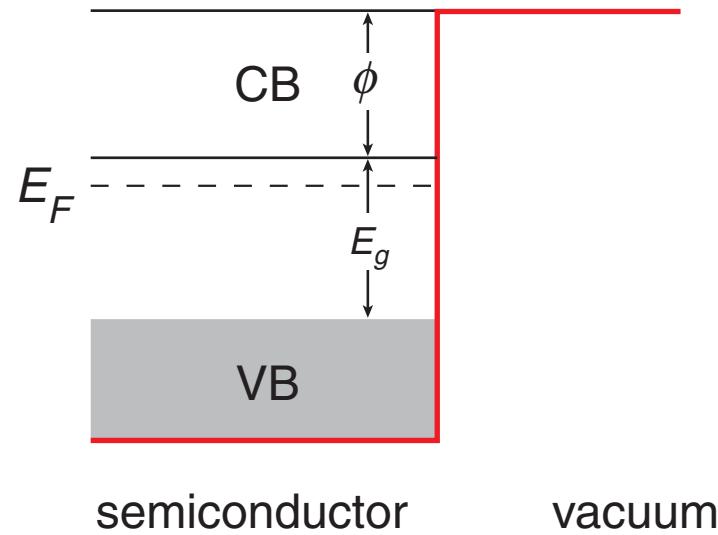
Structural and chemical analysis



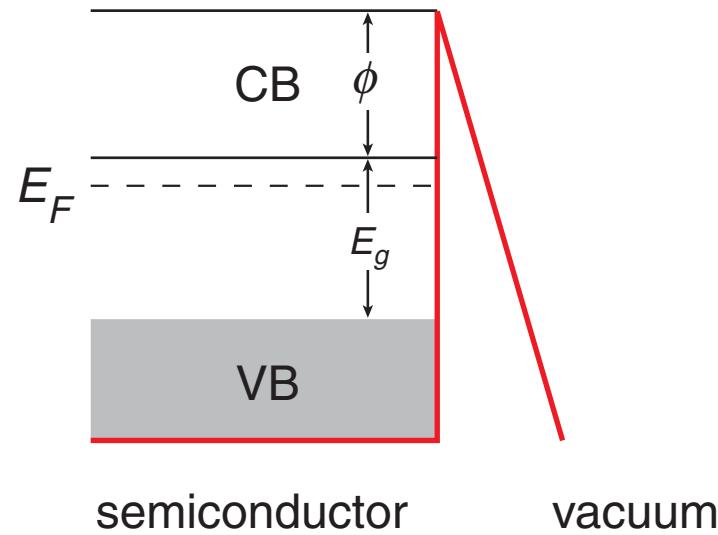
Structural and chemical analysis



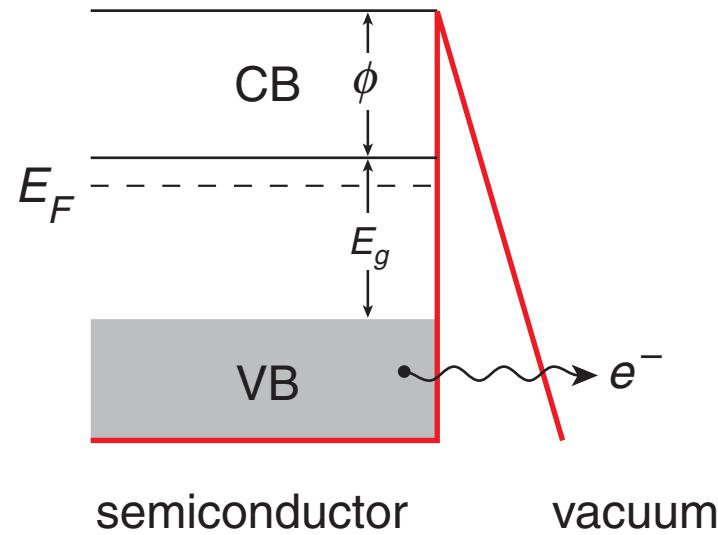
Structural and chemical analysis



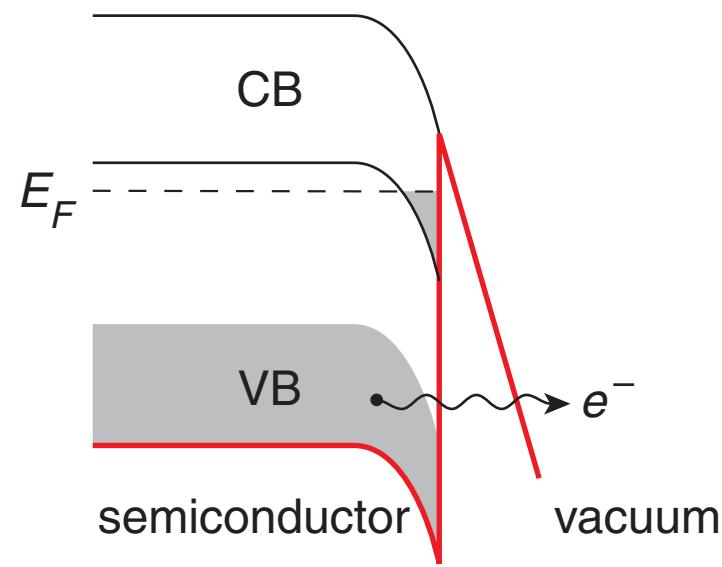
Structural and chemical analysis



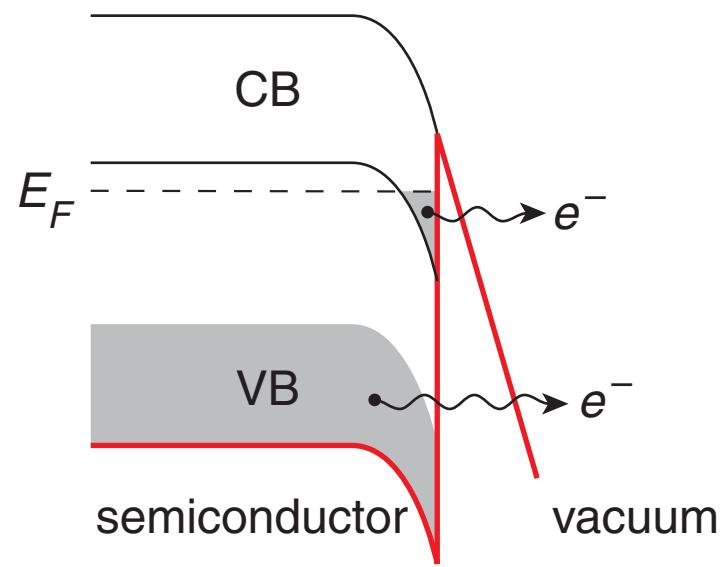
Structural and chemical analysis



Structural and chemical analysis

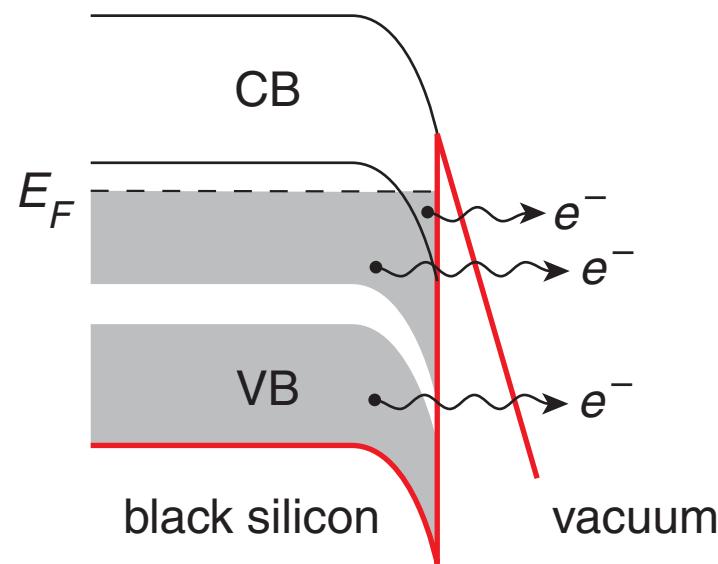


Structural and chemical analysis



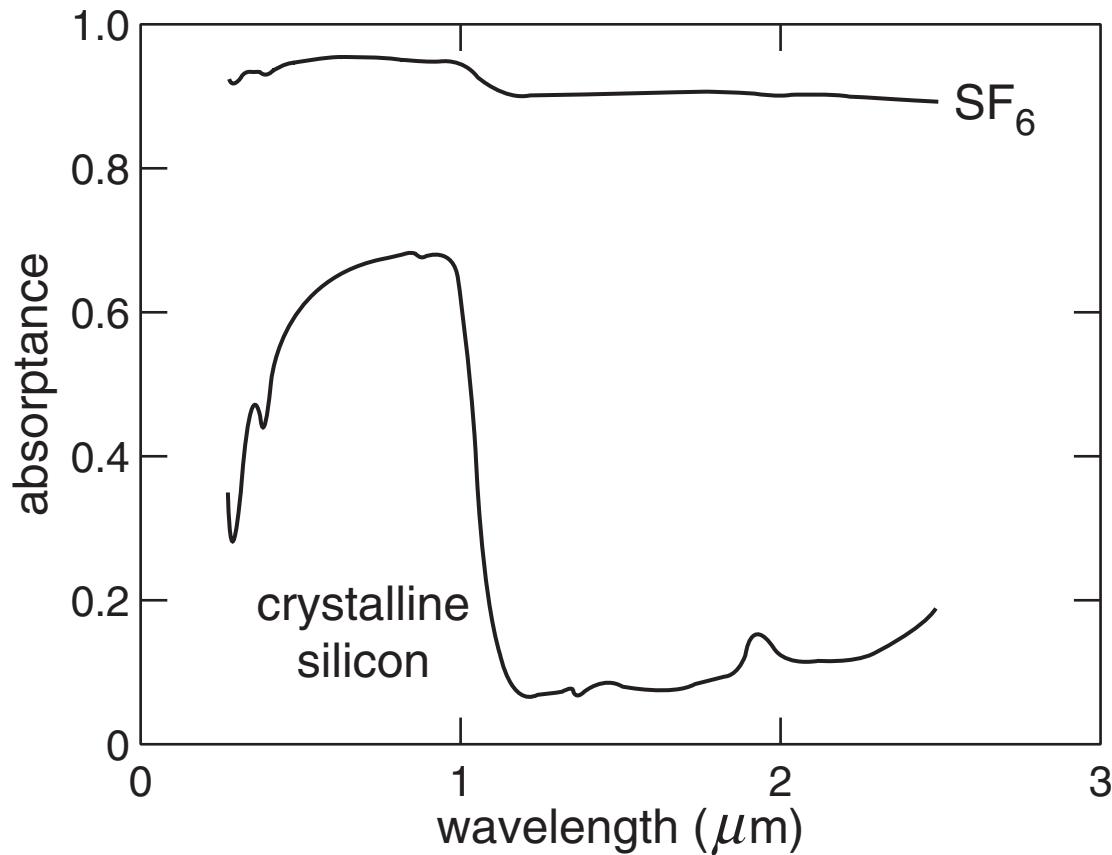
Structural and chemical analysis

sulfur band provides additional electrons



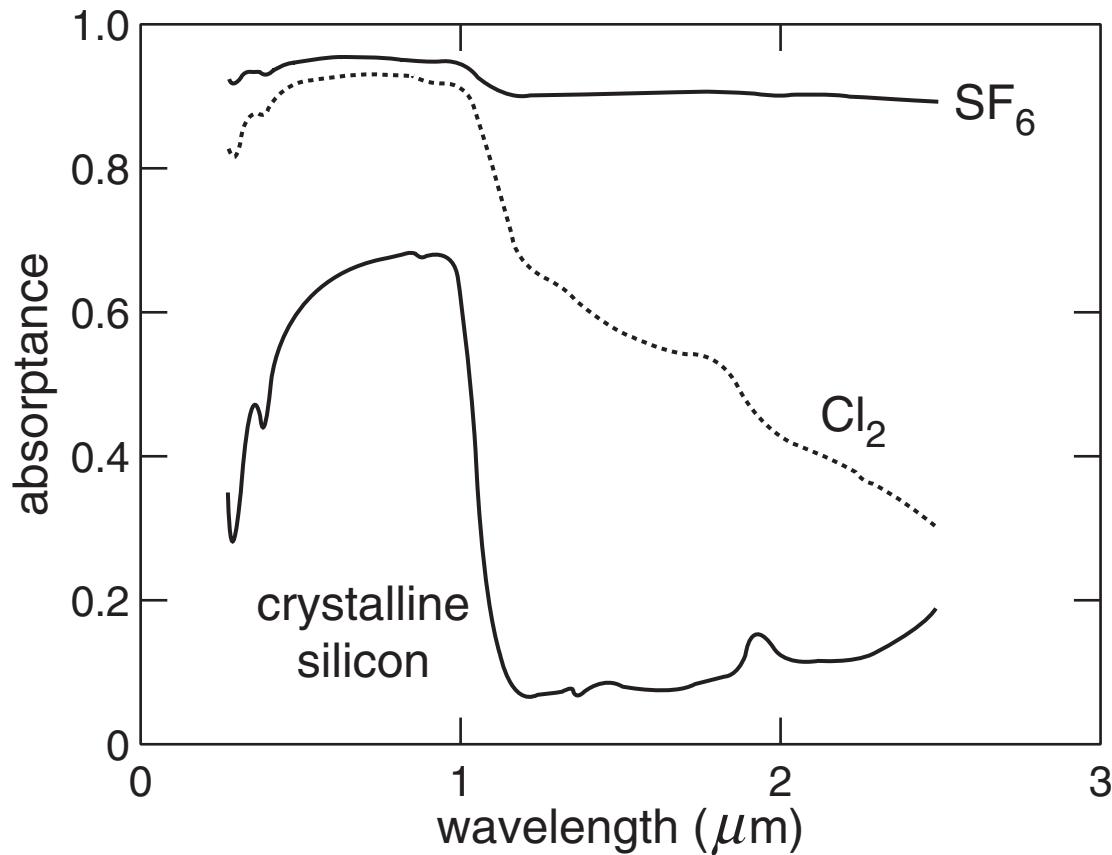
Structural and chemical analysis

effect of ambient gas on absorptance



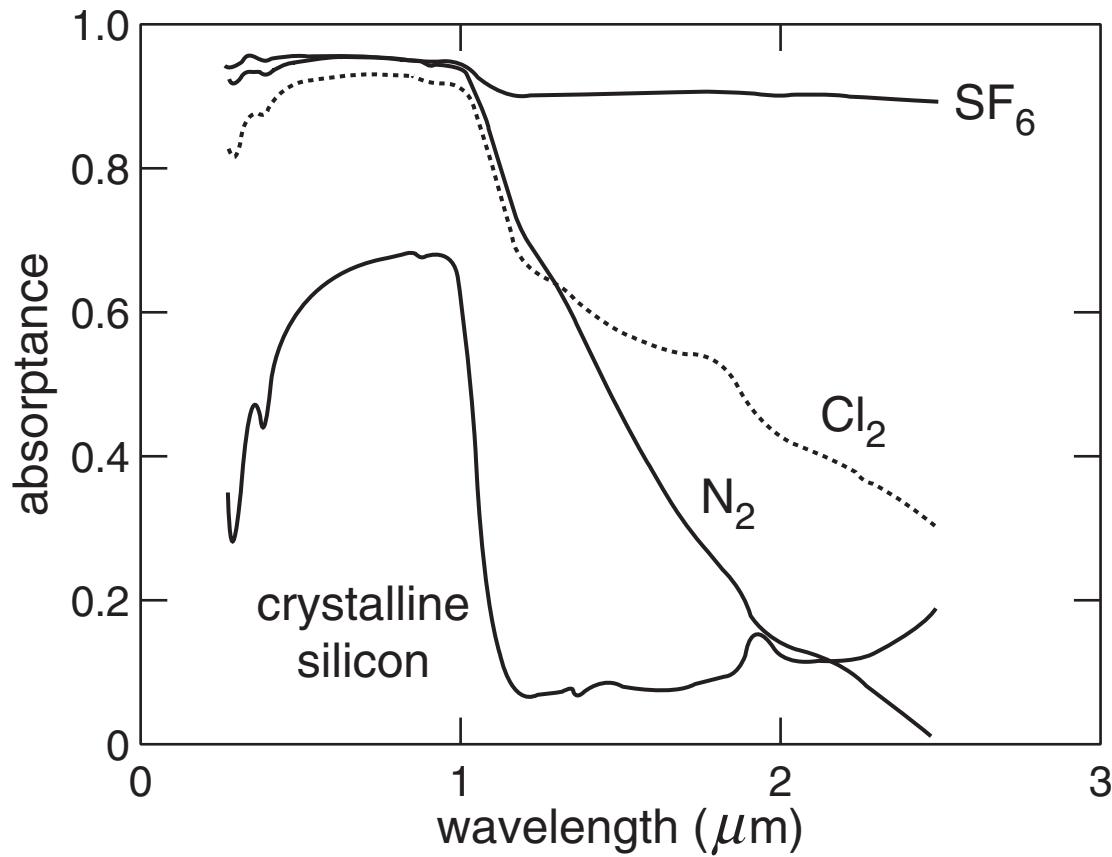
Structural and chemical analysis

effect of ambient gas on absorptance



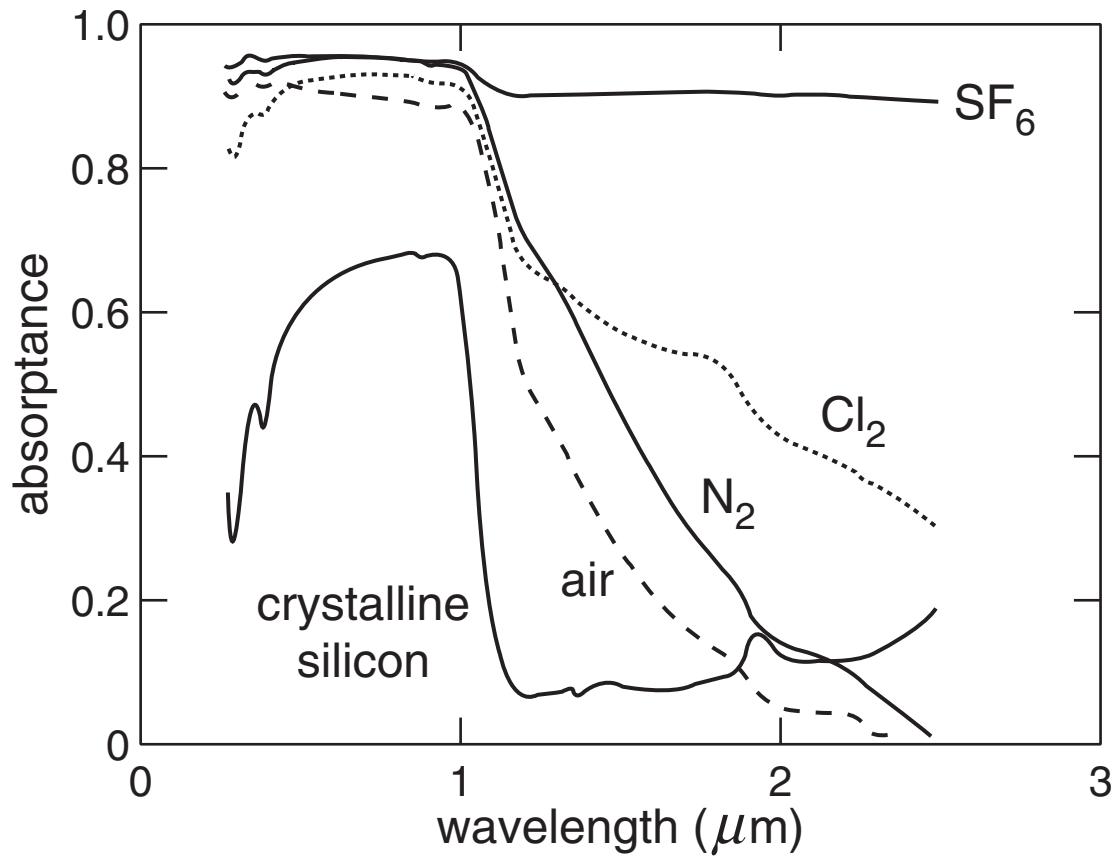
Structural and chemical analysis

effect of ambient gas on absorptance



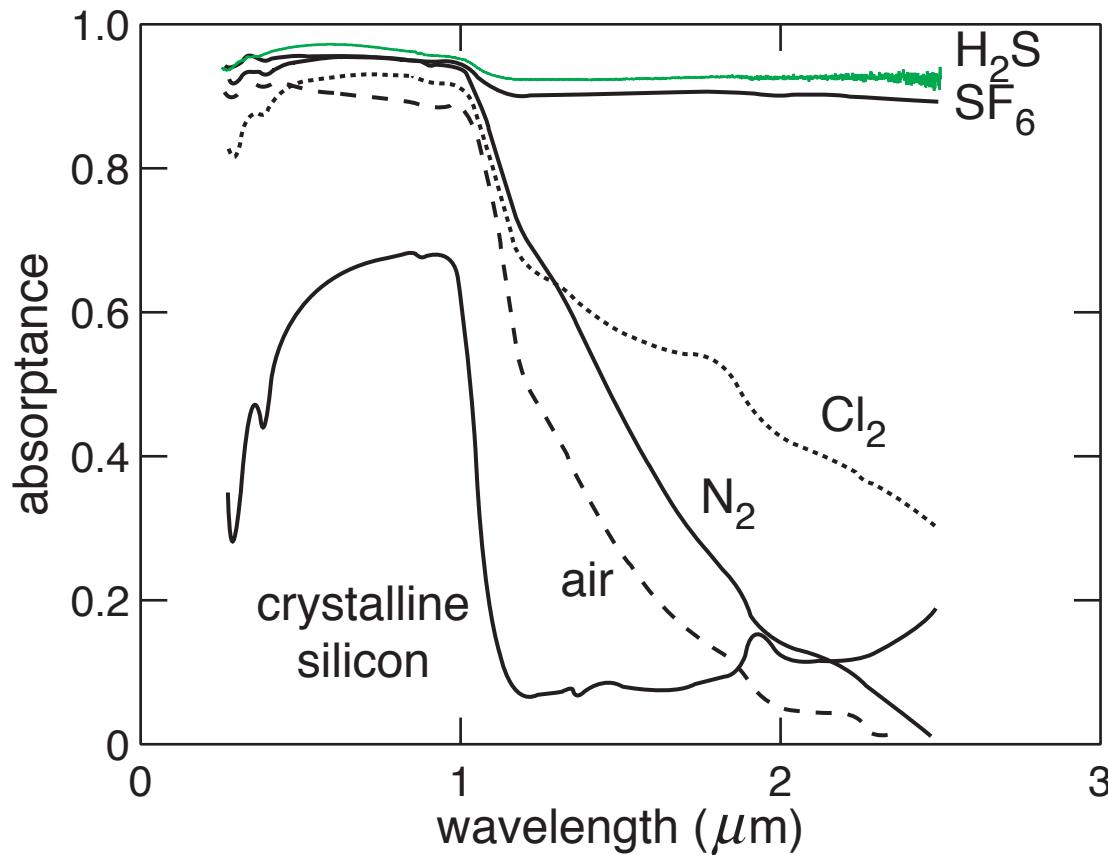
Structural and chemical analysis

effect of ambient gas on absorptance



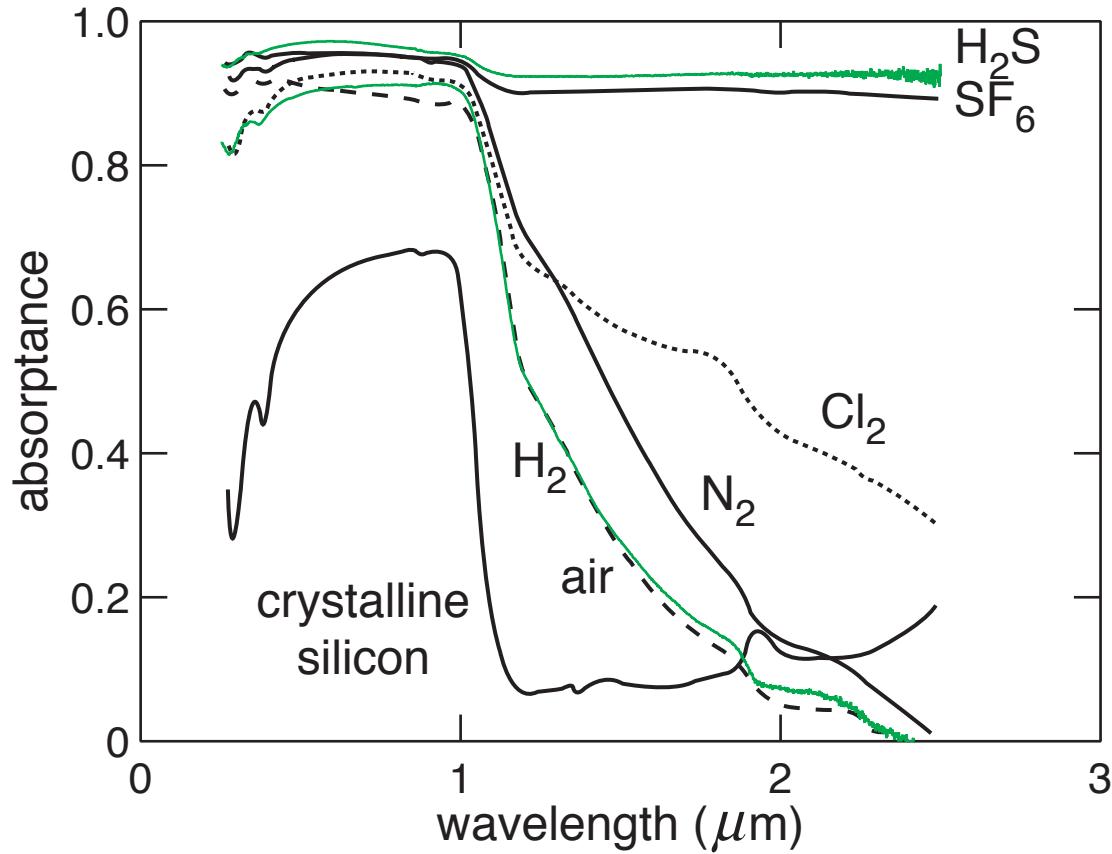
Structural and chemical analysis

effect of ambient gas on absorptance



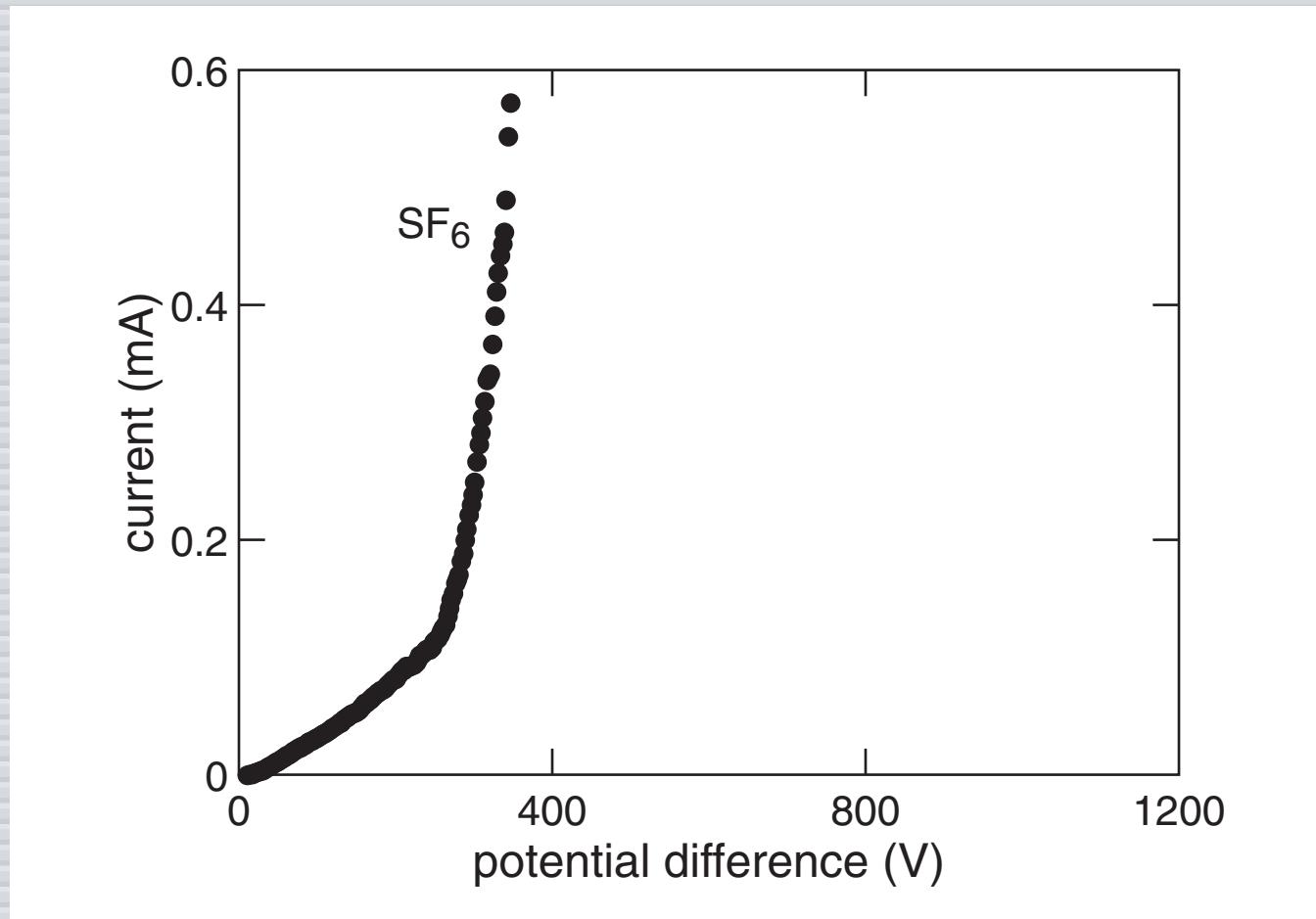
Structural and chemical analysis

effect of ambient gas on absorptance



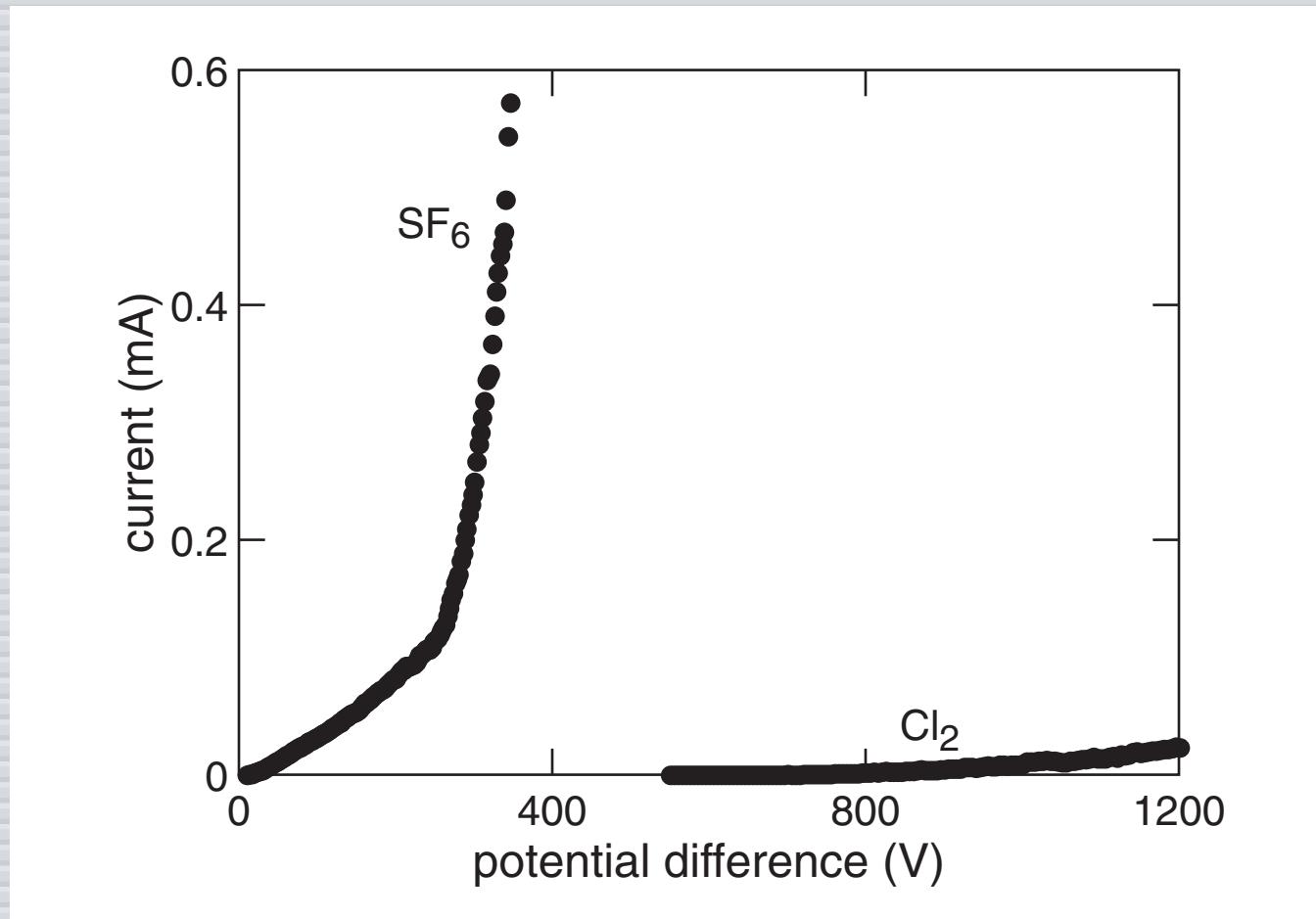
Structural and chemical analysis

effect of ambient gas on field emission



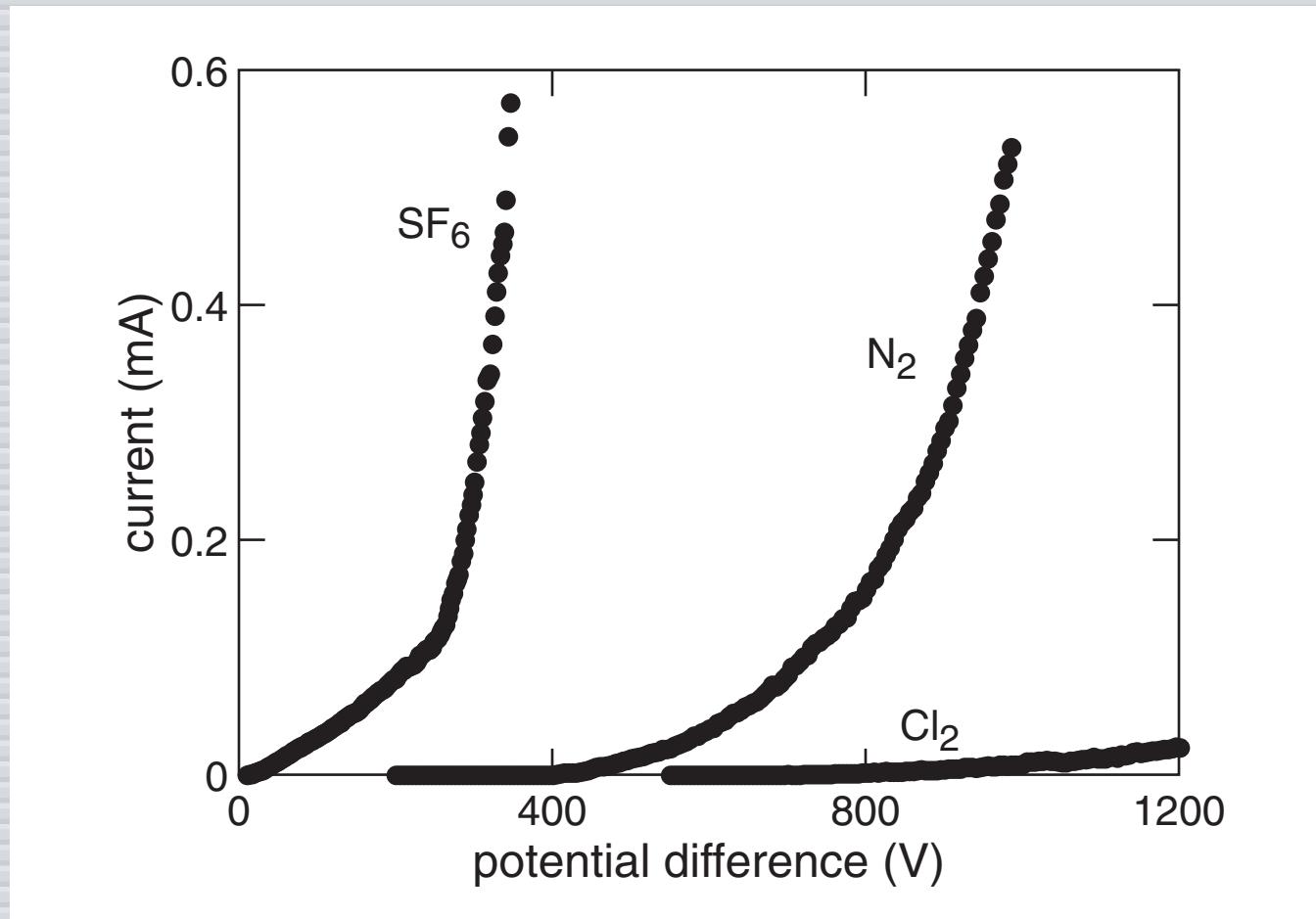
Structural and chemical analysis

effect of ambient gas on field emission



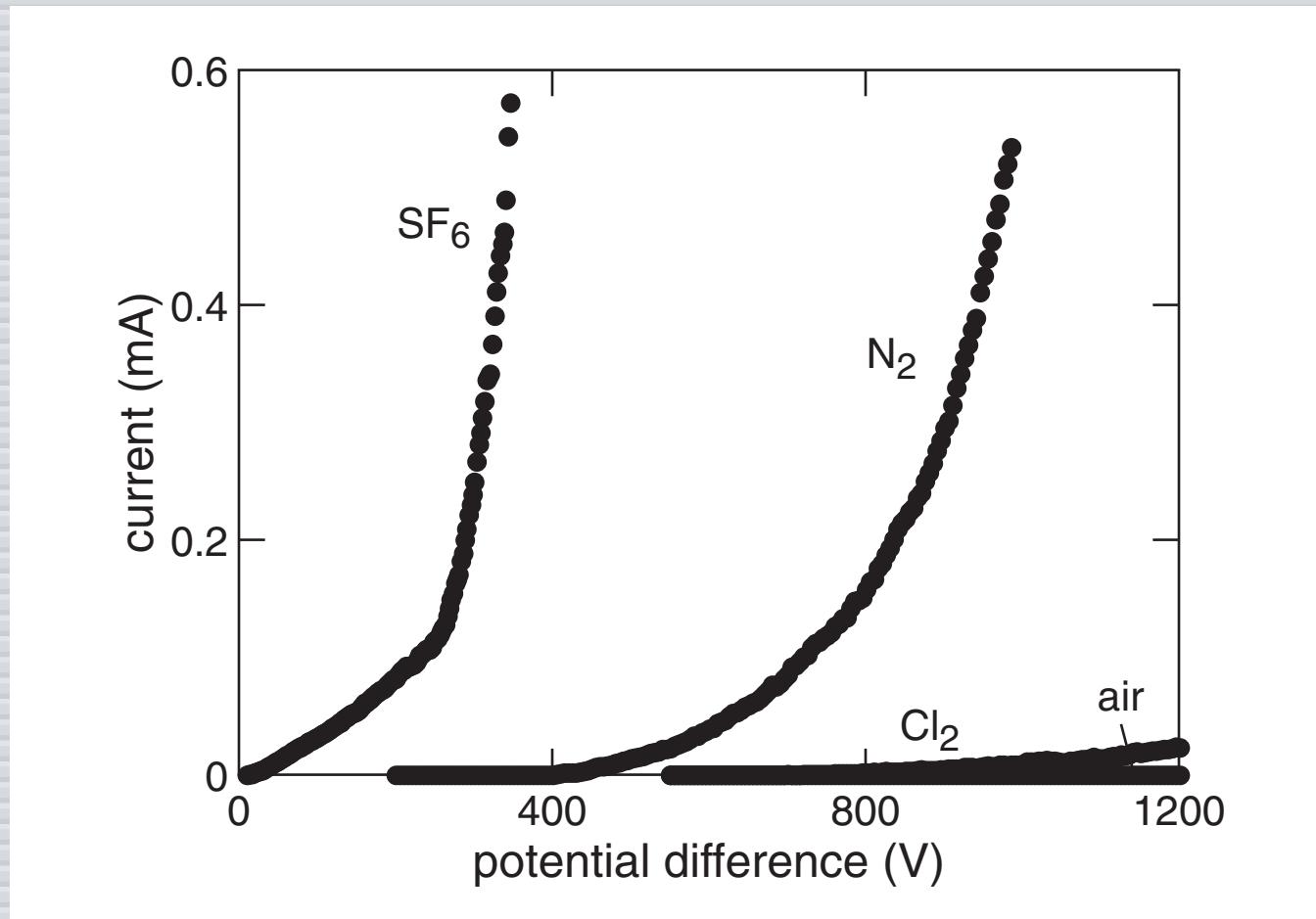
Structural and chemical analysis

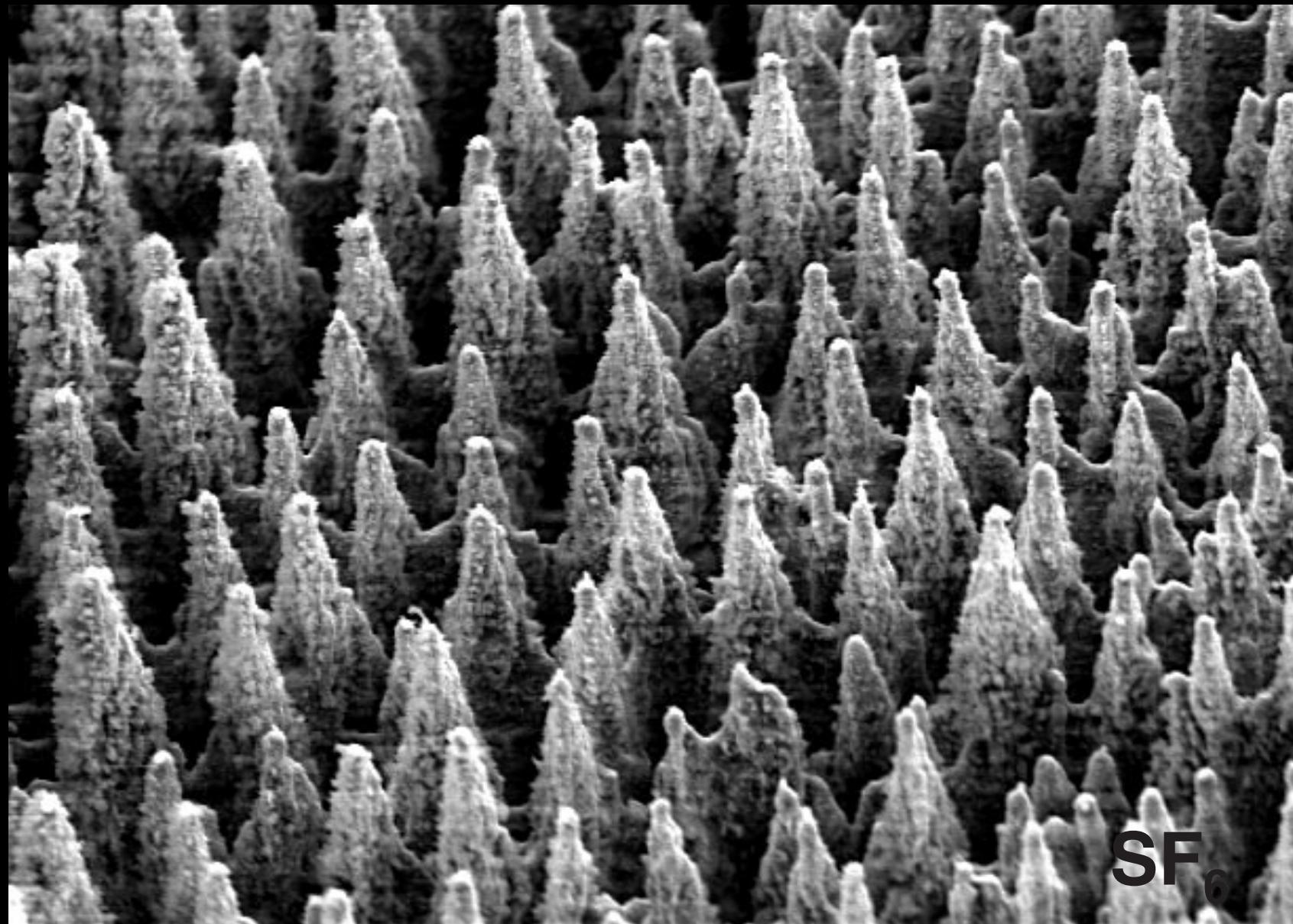
effect of ambient gas on field emission



Structural and chemical analysis

effect of ambient gas on field emission



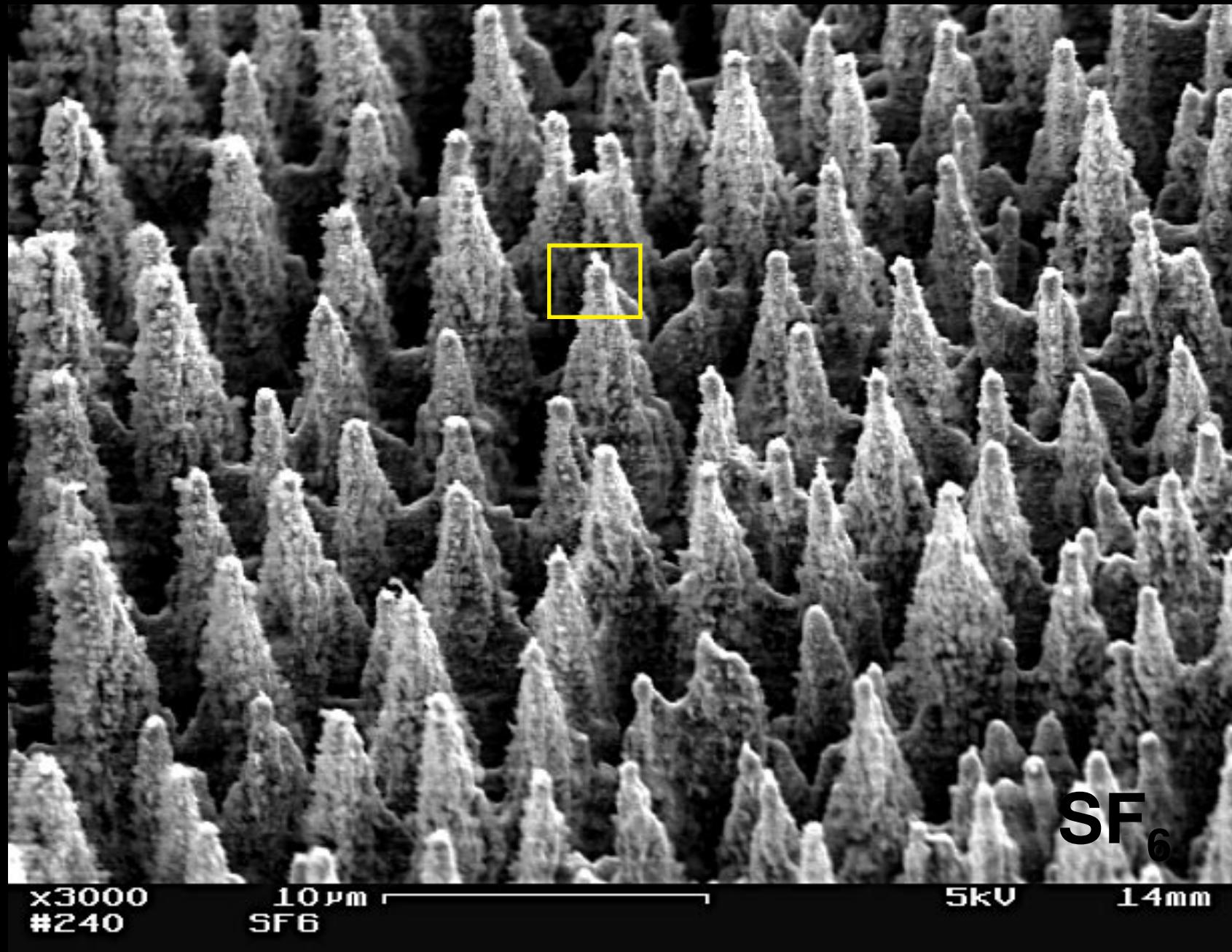


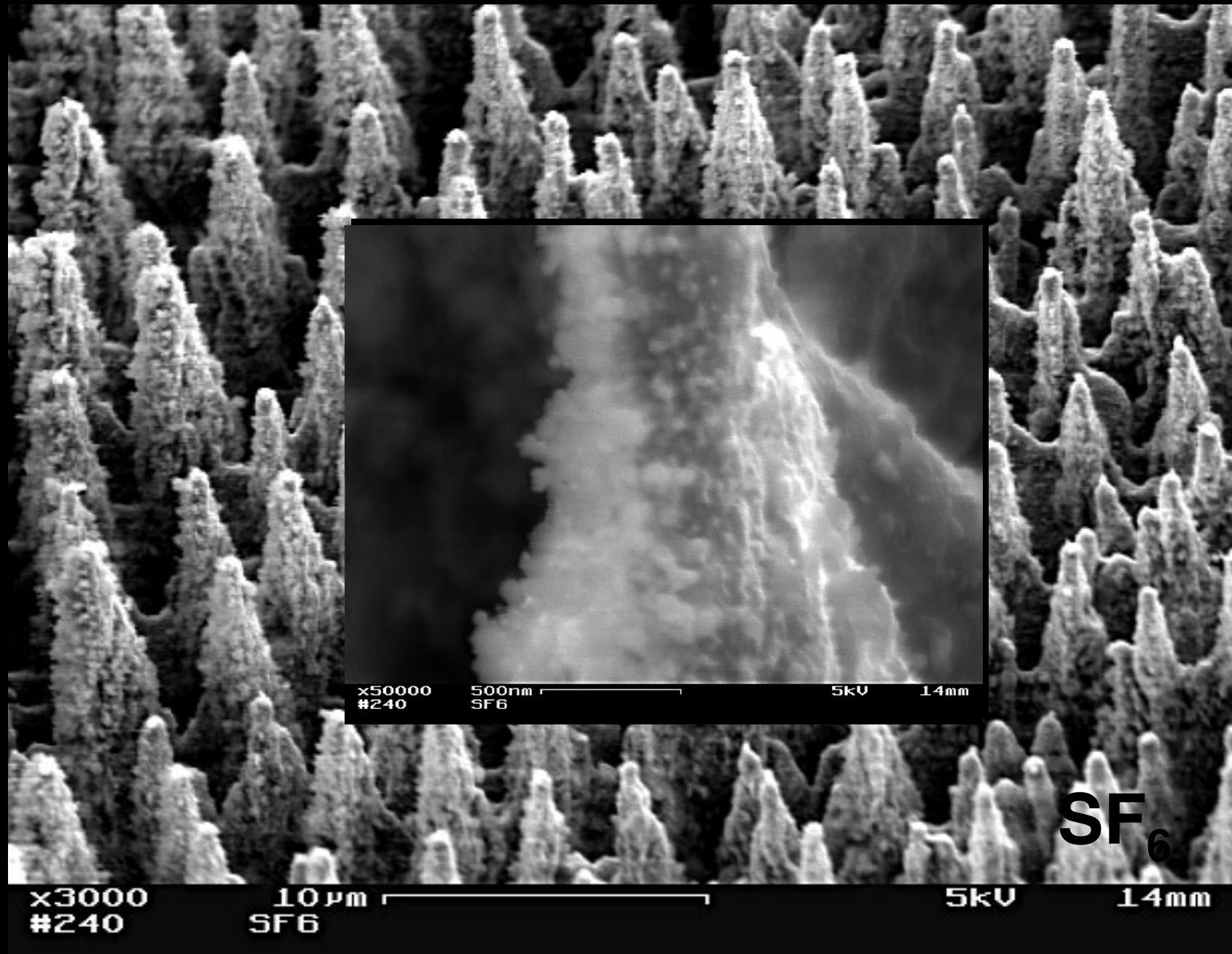
x3000
#240

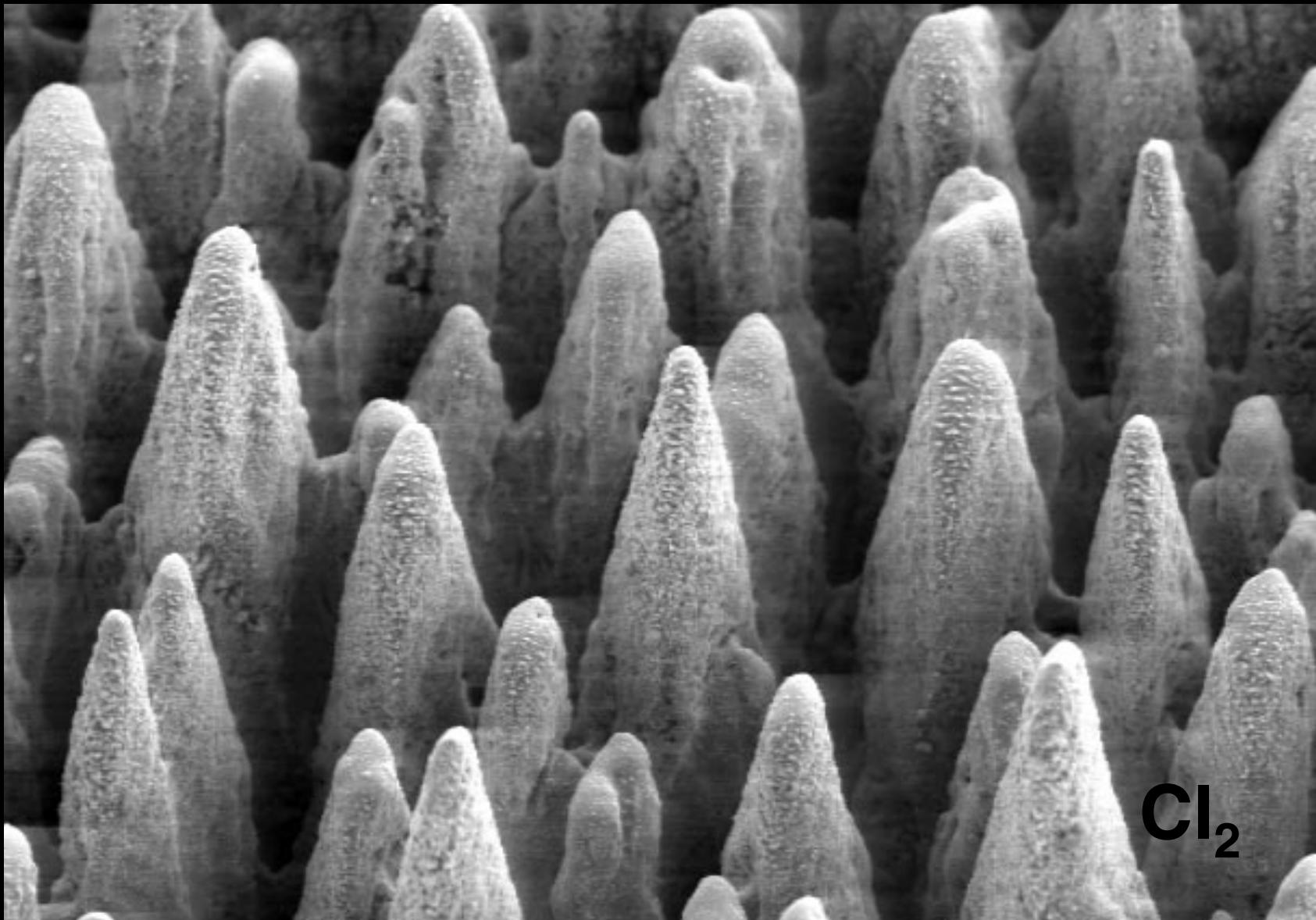
10 μm
SF6

5kV 14mm

SF₆







Cl₂

x3000

#34

512 x 480

10 μm

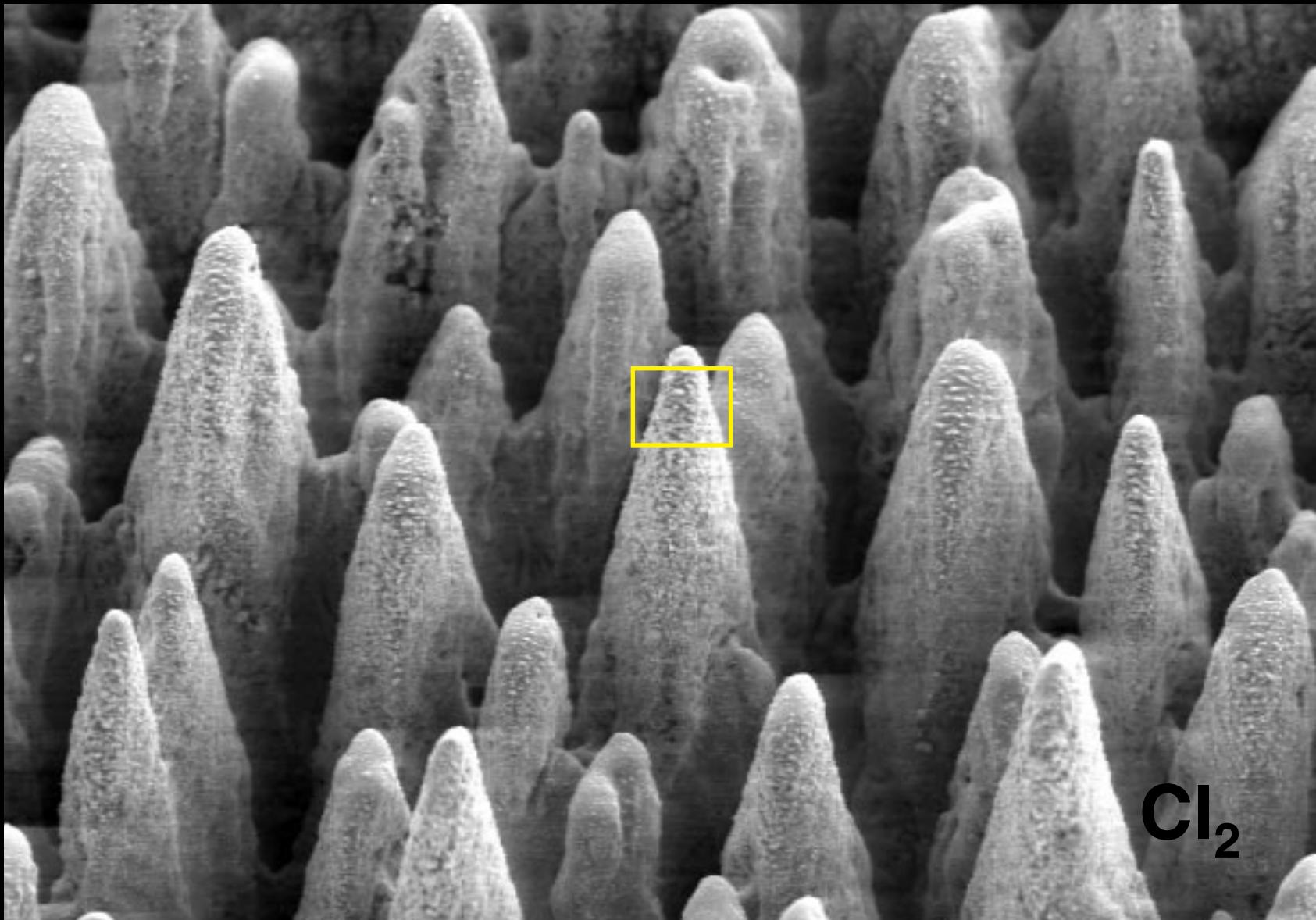
10/18 Cl2 #3

4.00kV

11/6/00

CL2#3-1.TIF

12mm



x3000

#34

512 x 480

10 μm

10/18 Cl2 #3

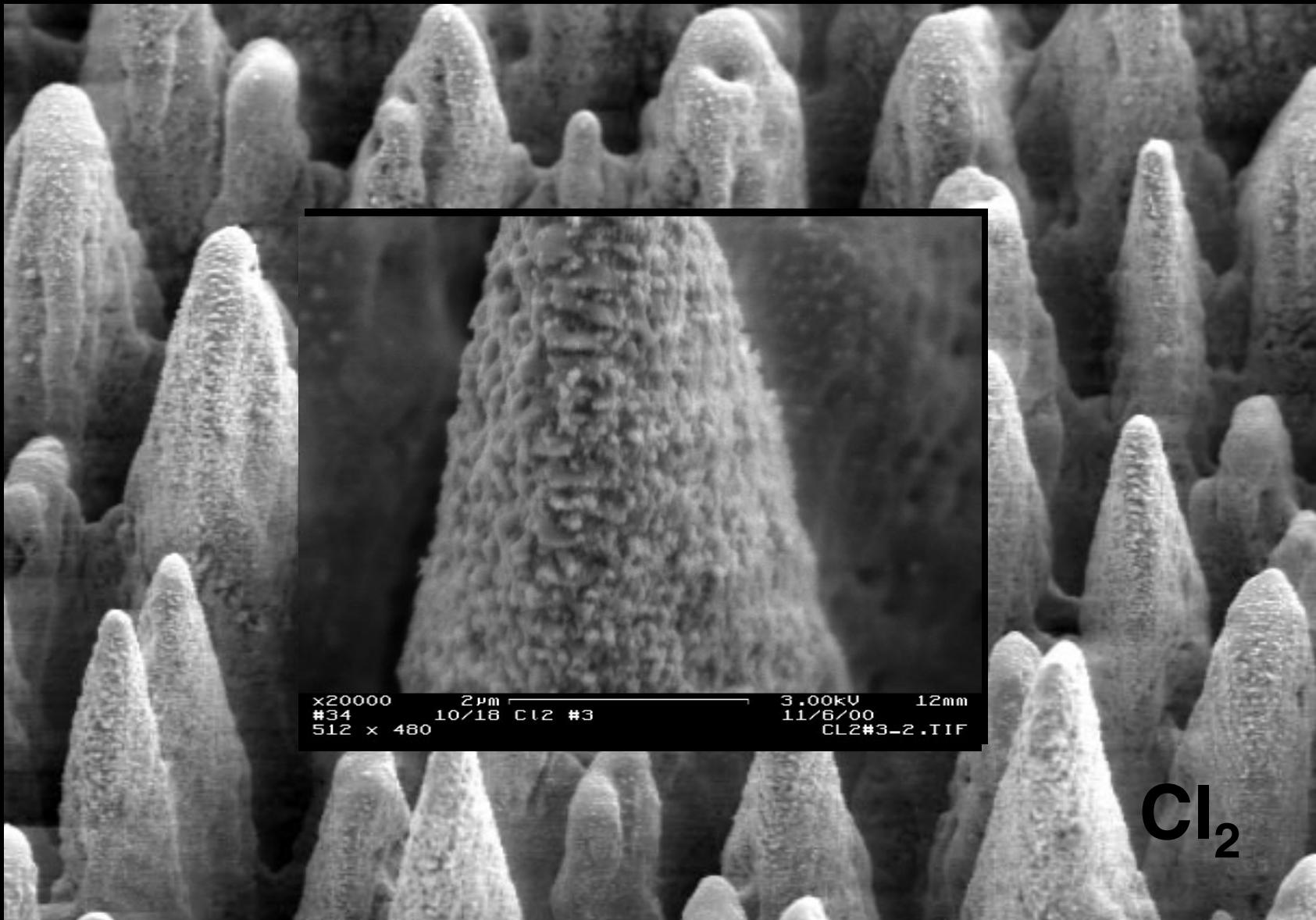
4.00kV

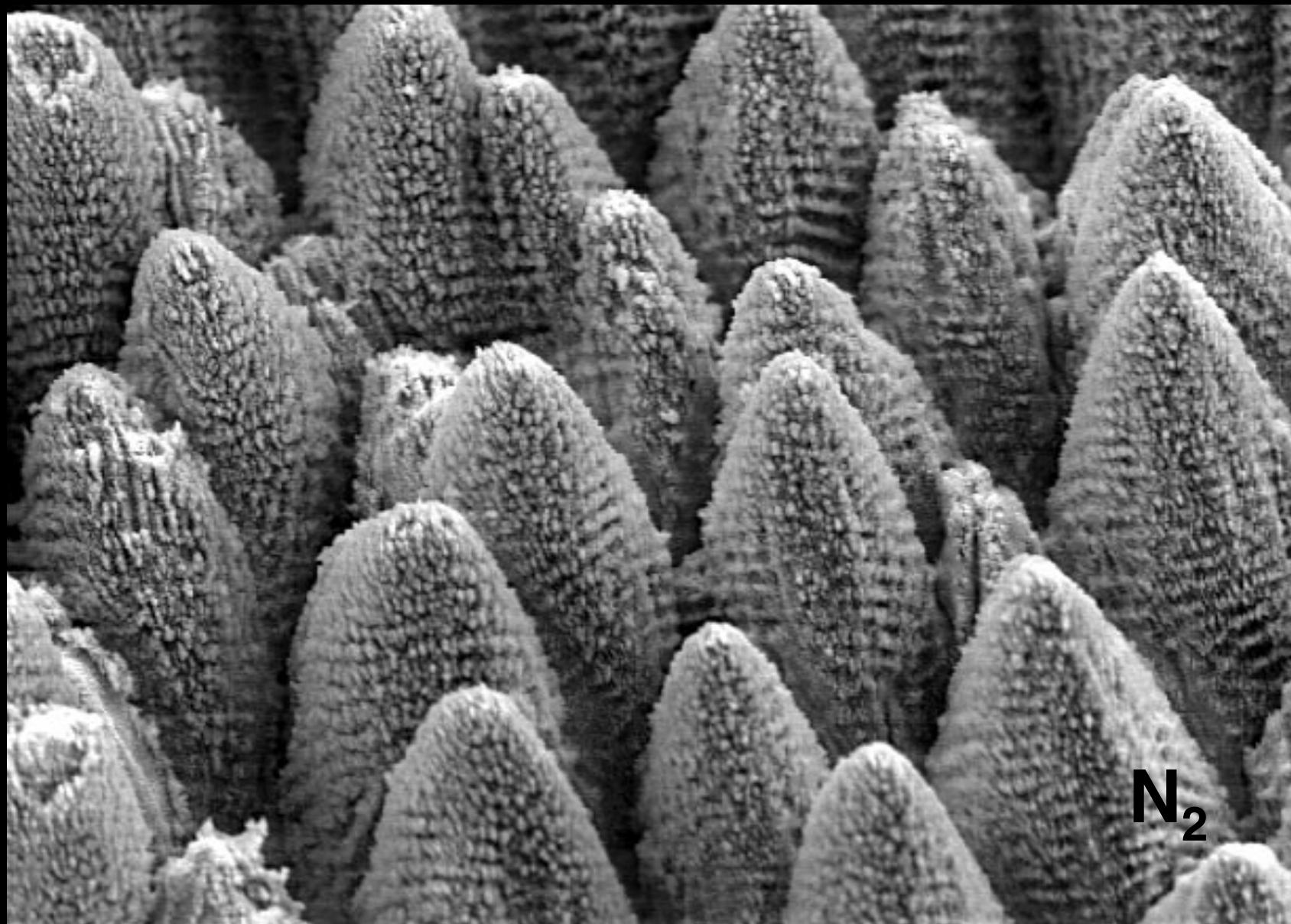
11/6/00

CL2#3-1.TIF

Cl₂

12mm

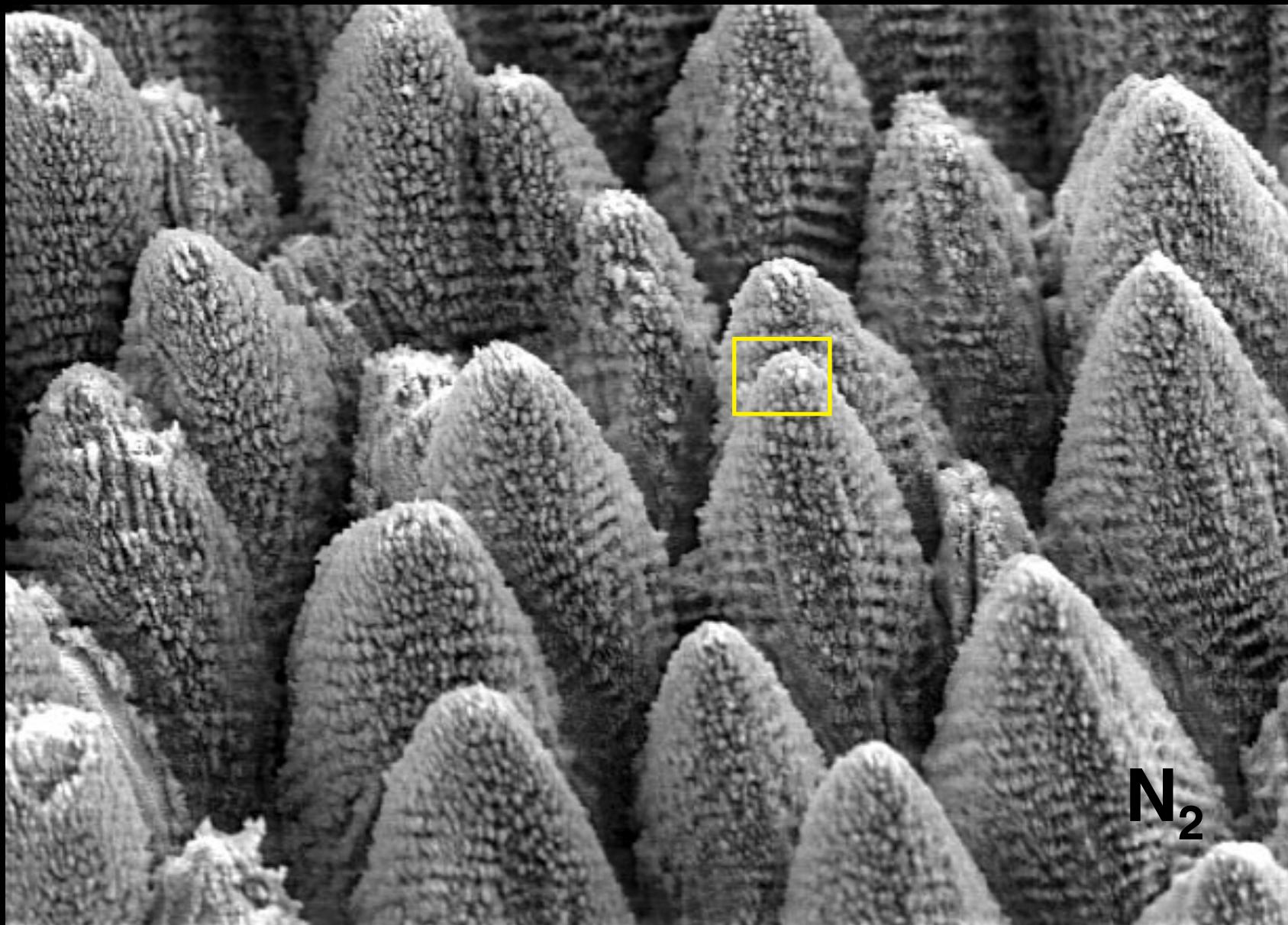




x3000
#240

10 μm
N2

5kV 14mm

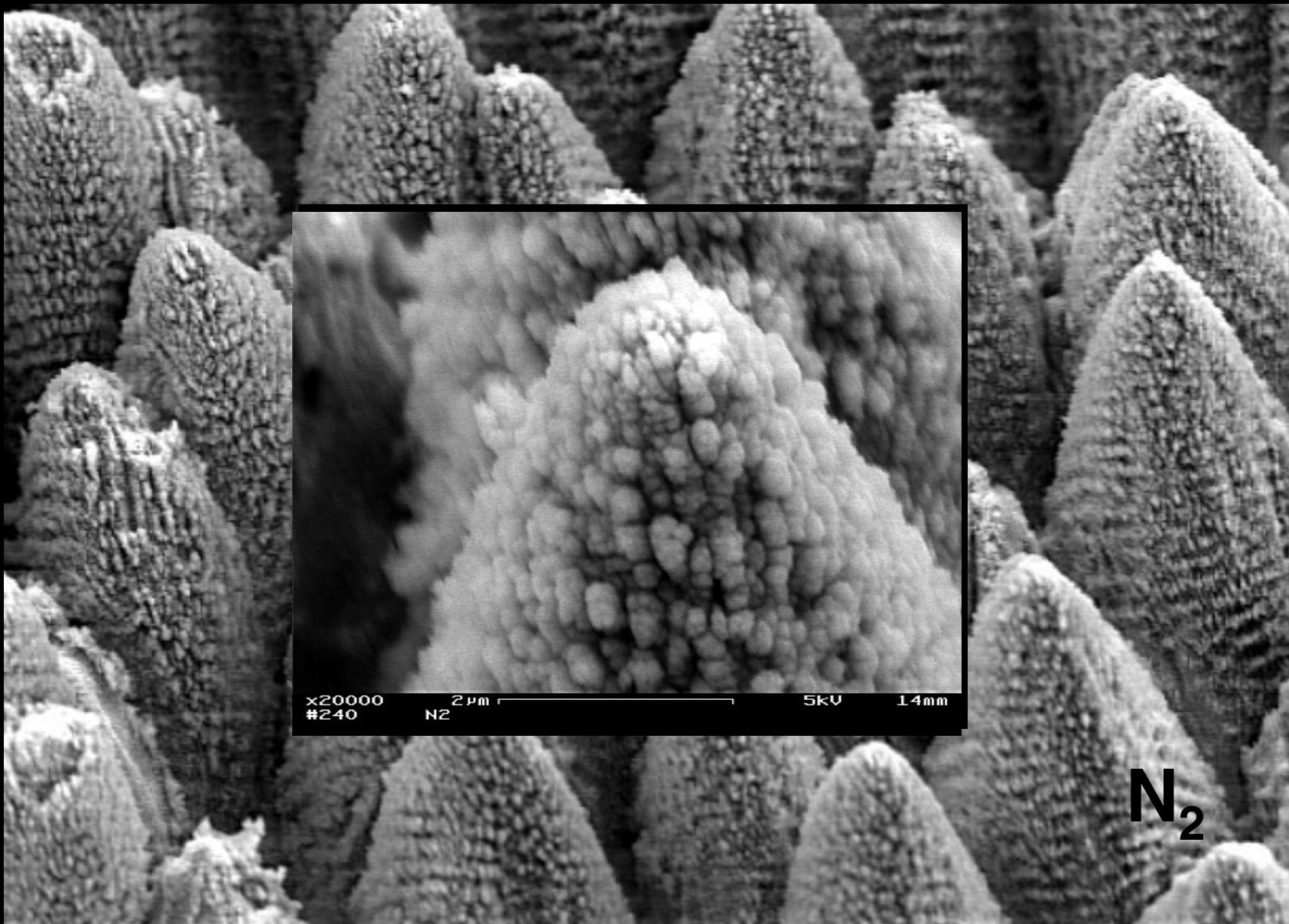


x3000
#240

10 μm N₂

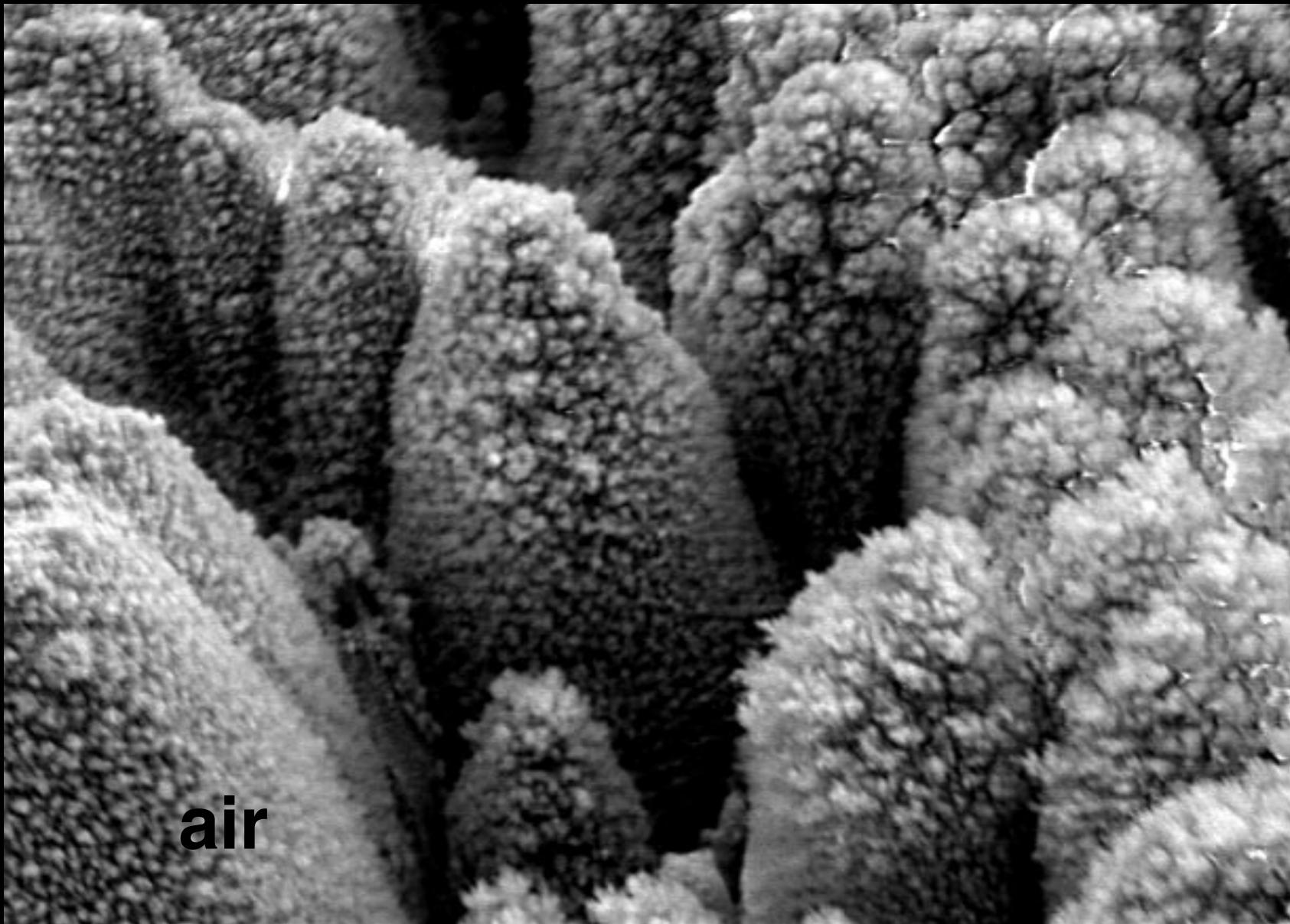
5kV 14mm

N₂



x3000 10 μ m 5kV 14mm
#240 N2

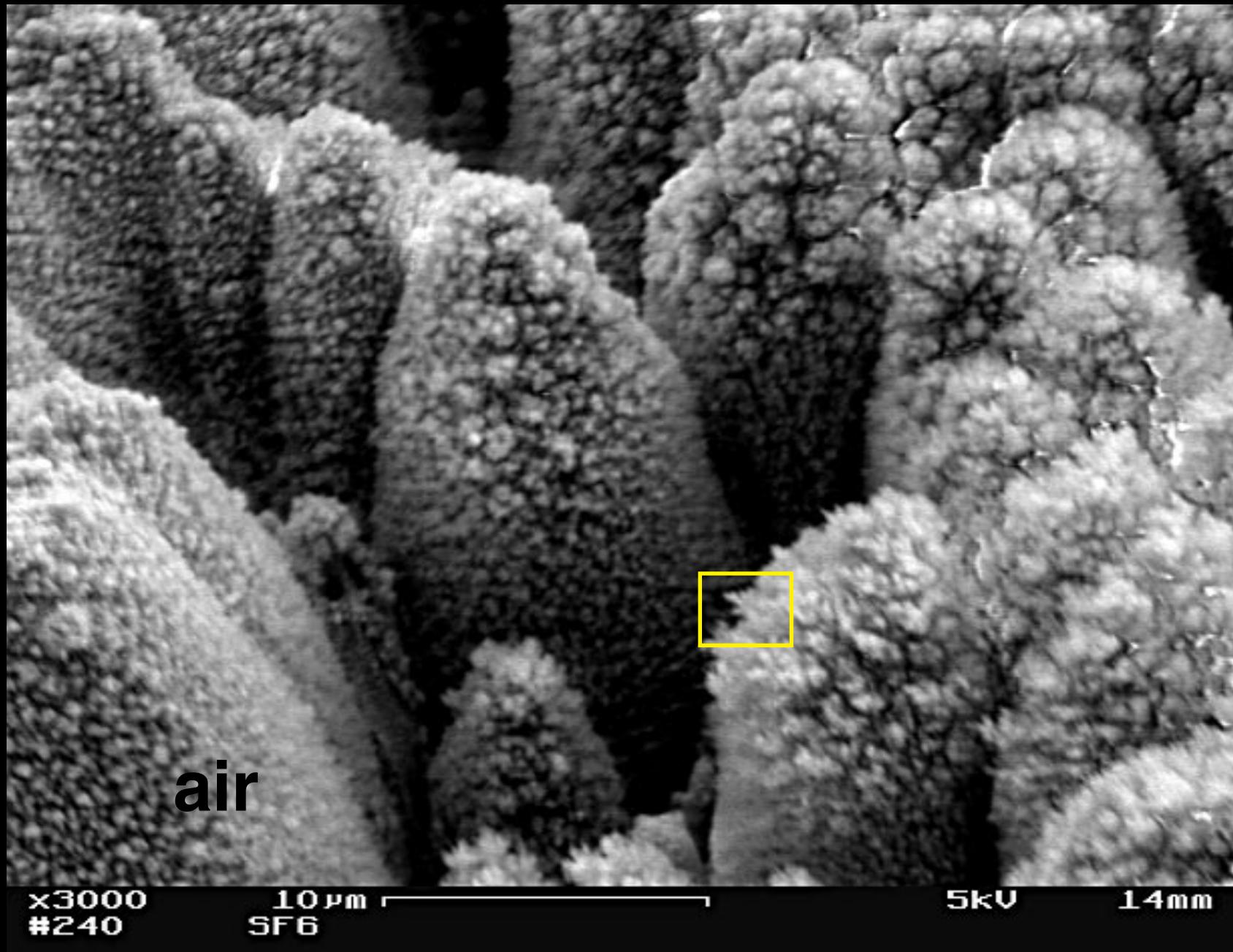
N₂



x3000
#240

10 μm
SF6

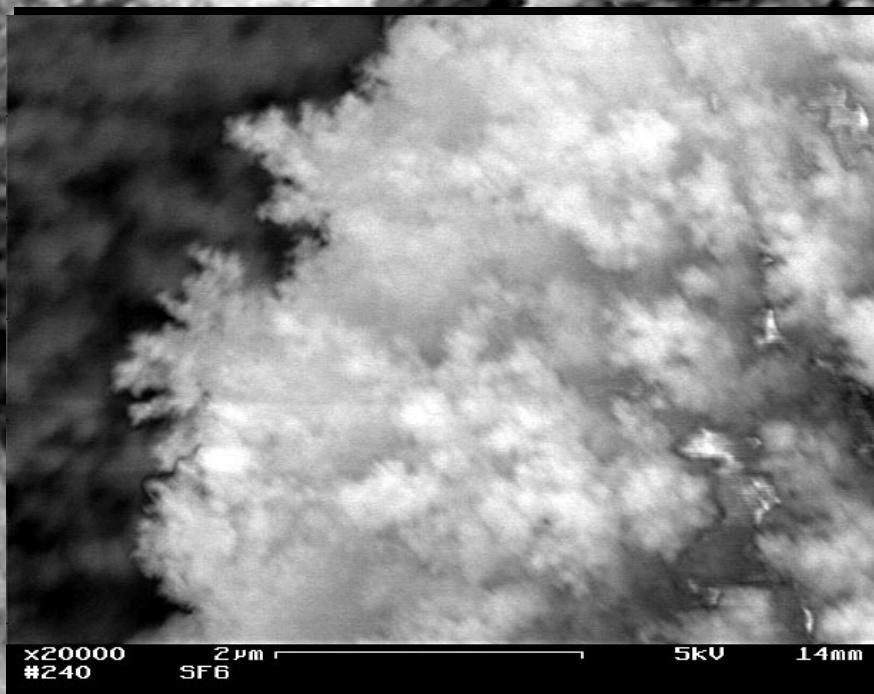
5kV 14mm



x3000
#240

10 μm
SF6

5kV 14mm



air

x3000
#240

10 μm
SF6

5kV 14mm

Structural and chemical analysis

	SF_6	Cl_2	N_2	air
IR absorption	high	medium	low	low
field emission	high	low	medium	low
SIMS	high S	?	?	high O
nanostructure	A scanning electron micrograph showing a dense, granular nanostructure with irregular, rounded features.	A scanning electron micrograph showing a more uniform, finely granular nanostructure compared to SF6.	A scanning electron micrograph showing a highly porous, sponge-like nanostructure with large interconnected cavities.	A scanning electron micrograph showing a sparse, irregular nanostructure with fewer distinct particles than the other gases.

Structural and chemical analysis

- ▶ **significant incorporation of ambient species**
- ▶ **nanostructured surface layer**
- ▶ **sulfur content correlates with IR absorption**

Outline

- ▶ Properties
- ▶ Structural and chemical analysis
- ▶ Outlook

Outlook

New Scientist 13, 34 (2001)

A forest of silicon spikes could revolutionise solar cells and give you painless injections. **Bruce Schechter** peers into the mysterious world of black silicon

TALL, DARK AND STRANGER

WE ALL love stories of serendipity. They seem to hark back to a time when a fogged microscope or a filthy Petri dish

semiconductors with a powerful laser. In the early 1990s, Mazur's was the first academic lab in the world to get its hands on a femtosecond laser. This device produces pulses of light that are hundreds

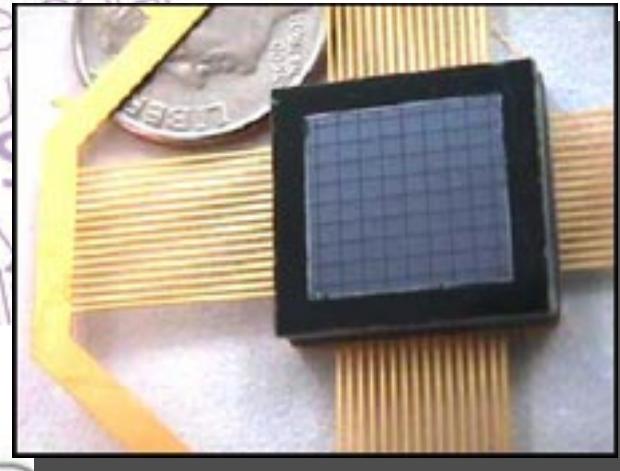
of times brighter than the Sun and extremely short laser pulse will break down around the laboratory," he claims.

Well, it was almost the only reason into sulphur and fluorine radicals, which will attack a silicon substrate. "Hydrogen fluoride is used to etch silicon. I thought maybe the SF₆ would decompose the silicon," Mazur says.

Outlook

► **detector technology**

A forest of silicon spikes could revolutionise cells and give you injections. **Bruce S** peers into the my world of black sil



TALL, DARK AND STRANGER

We ALL know stories of weirdness. They come back to us again when a design fails to live up to expectations. But this time it's different. It's when

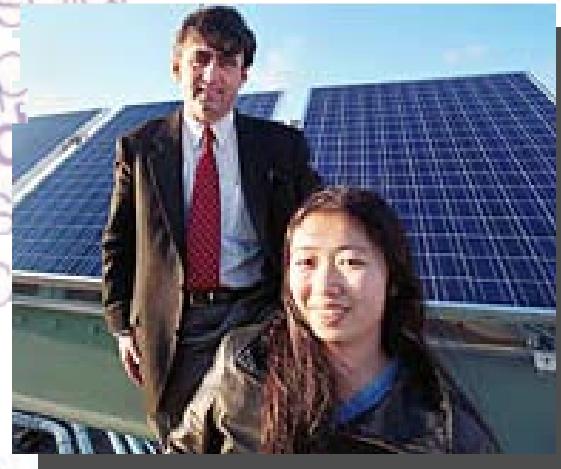
semiconductors with a powerful base to the early 1980s. Moxtek's was the first academic lab in the world to do so, based on a temperature-based threshold voltage that is so low that it can measure 20 times faster than the best

around the "strange" detector. The James Park detector is based on the same basic principle that has been used since the 1950s to detect particles and other radiation. It will attack a specific element. And because it is able to do so, it can detect a single photon by the Si semiconductor and then the detector will detect it and extremely

Outlook

- ▶ **detector technology**
- ▶ **solar cells**

A forest of silicon spikes could revolutionise solar cells and give you pain-free injections. **Bruce Sales** peers into the mysterious world of black silicon



TALL, DARK AND STRANGER

We ALL know stories of weirdness. They come back to us from time to time when a friend tells us about a little pet rock he has or when we see a tall, dark and mysterious figure lurking in the shadows. But what about the world of science? It's full of strange things, too, and one of the most mysterious is the world of black silicon. It's a material that's been around since the late 1950s, but it wasn't until the early 1990s that it started to become more popular. Now, it's used in everything from mobile phones to cars, and it's even being used in some medical applications. So, what exactly is black silicon?

Silicon is a semiconductor with a powerful base. In the early 1950s, Mervin K. Mizell was the first to demonstrate the use of a laser beam to etch a pattern onto a silicon wafer. This device was called a "laser-etched silicon wafer" and it was used to create a series of patterns on the surface of the silicon. Mizell es-

tablished the "laser-etched silicon wafer" company, which became the first manufacturer of laser-etched silicon wafers. The company's first product was a laser-etched silicon wafer that had a pattern of 100 micrometers on its surface. This device was used to create a series of patterns on the surface of the silicon. Mizell es-

Outlook

- ▶ **detector technology**
- ▶ **solar cells**
- ▶ **display technology**

A forest of silicon snakes could revolutionise cells and give you injections. Bruce S... peers into the my... world of black

TALL, DARK AND STRANGE

We ALL know stories of weirdness. They come back to us from time to time when a legend of a lifeless planet disappears into thin air, or when

semiconductors with a powerful base to around the "unconscious" becomes Park. It's not a word the only reason that Bruce S... peers into the my... world of black

the early 1990s. Marzal's was the last academic lab in the world to do so. Hardison, a former student of Marzal's, has now joined a research team that has made some surprising discoveries. The new device, which may be the first to be able to

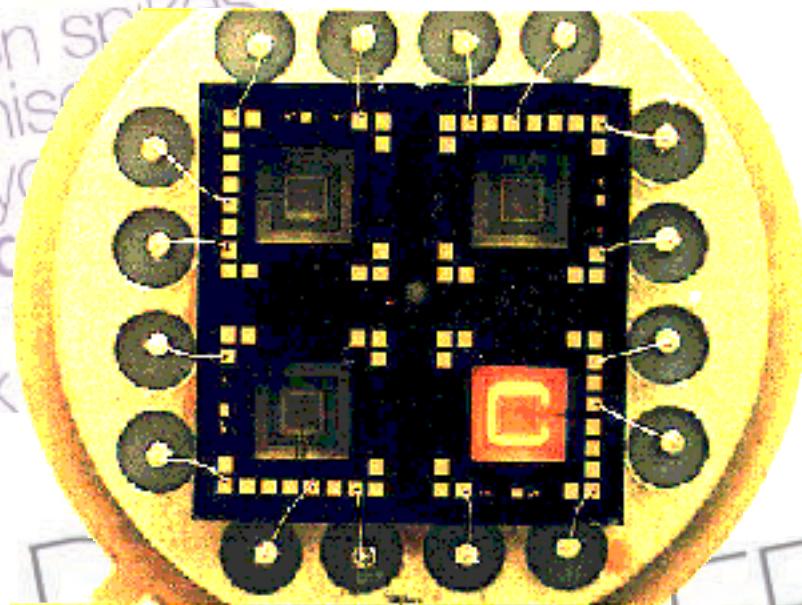
attack a specific cancer, has been named "Bionano" and it's about to go into clinical trials. Marzal says that the



Outlook

- ▶ **detector technology**
- ▶ **solar cells**
- ▶ **display technology**
- ▶ **sensors**

A forest of silicon sprouts could revolutionise cells and give you injections. Bruce peers into the world of black



TALL, DARK AND STRANGER

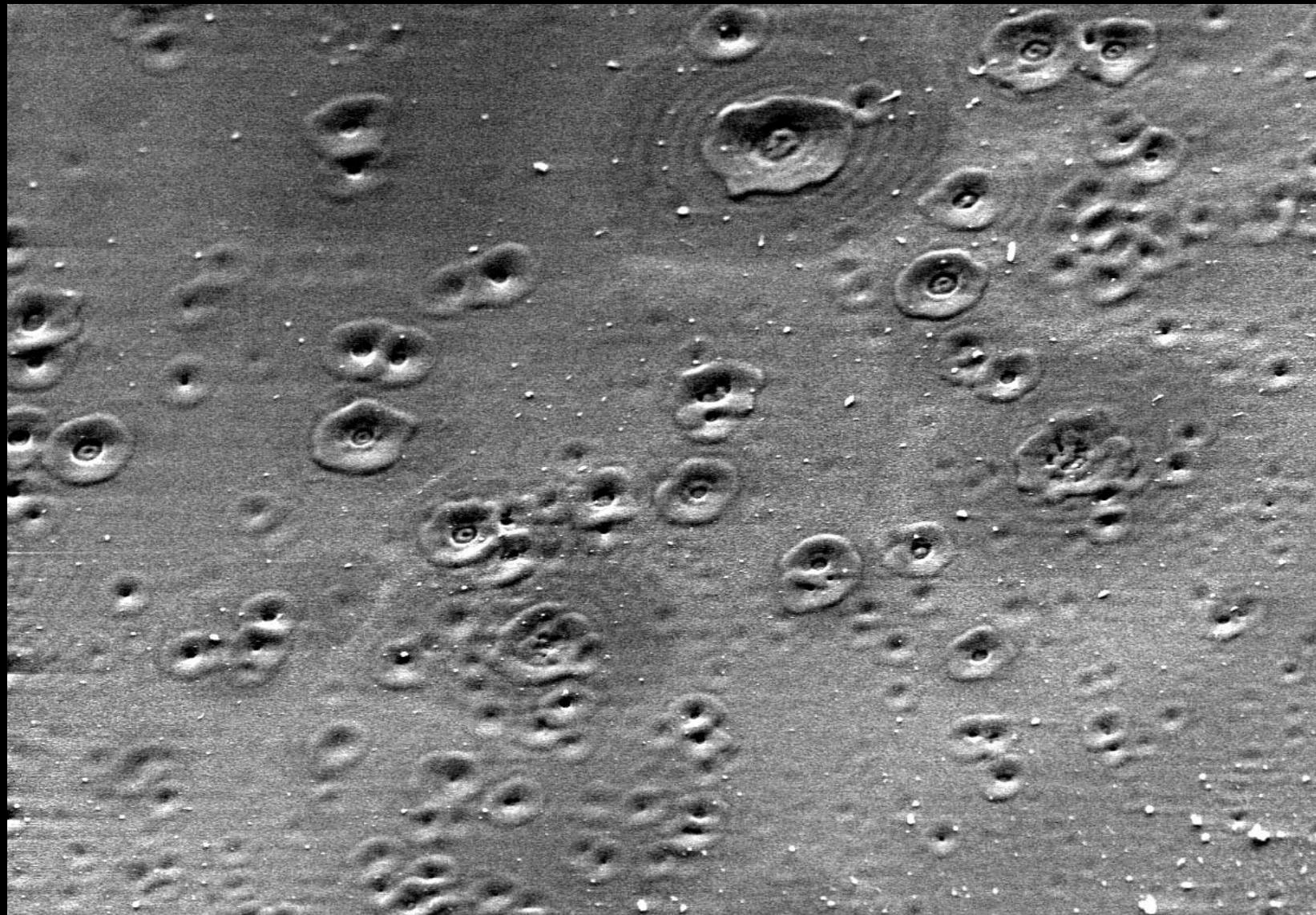
Outlook

- ▶ **development of spikes**
- ▶ **spike formation through grids**
- ▶ **cell adhesion**
- ▶ **functionalization**

x2000
#3548
512 x 480

20 μ m

10kV 15mm
0000



x2000

#3548

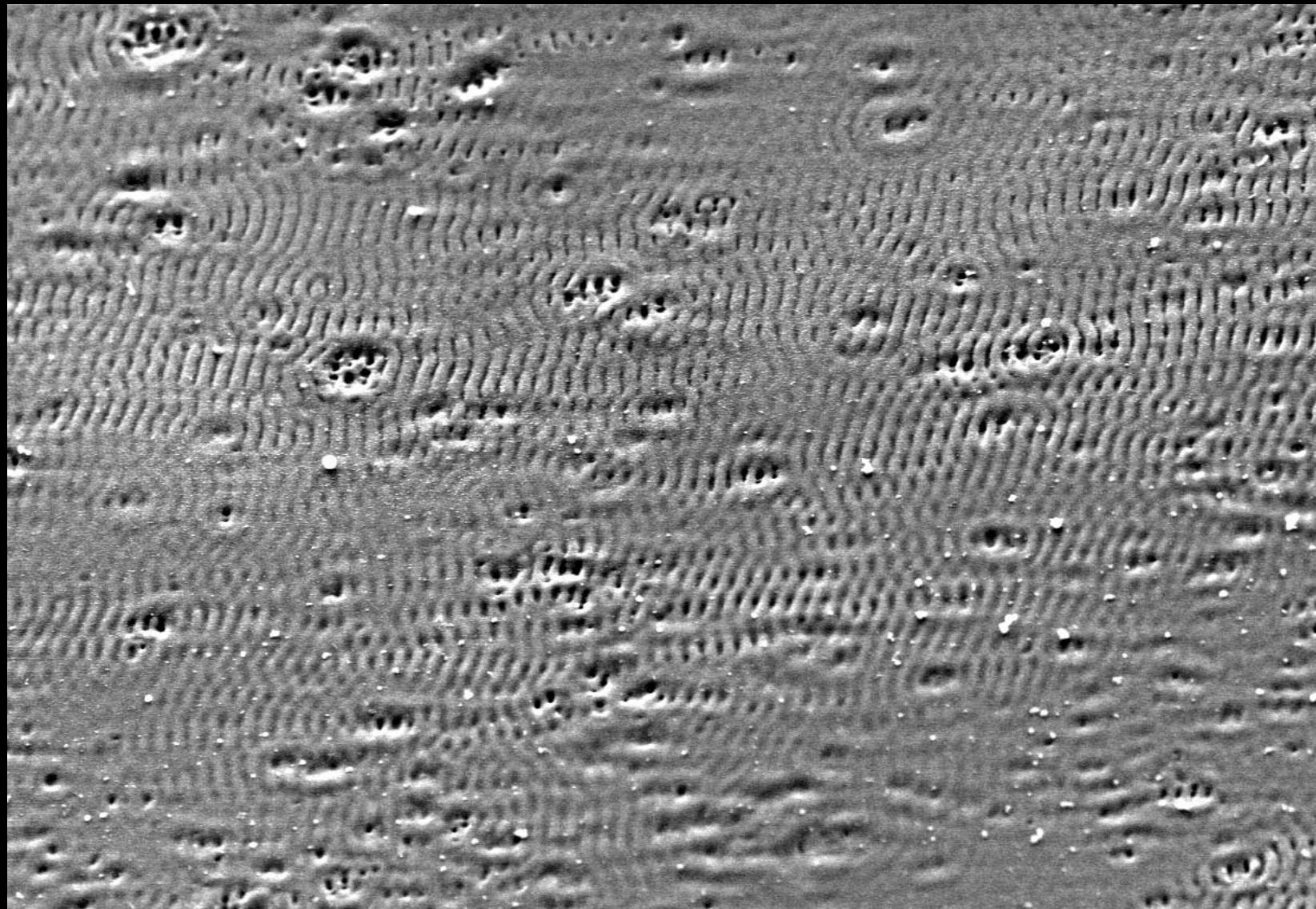
512 x 480

20 μm

10kV

15mm

0001



x2000

#3548

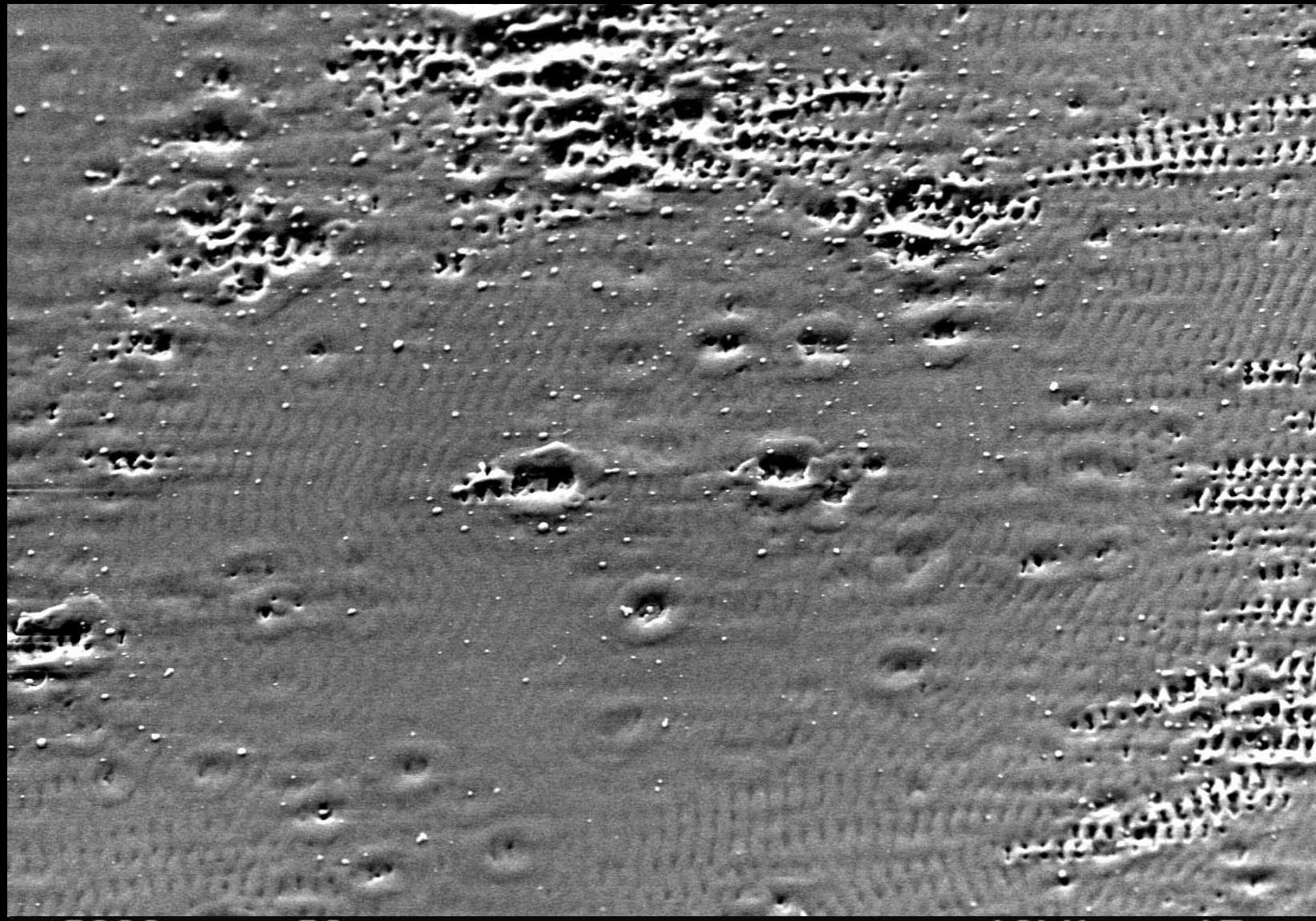
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20 μm

10kV

15mm

0002



x2000

#3548

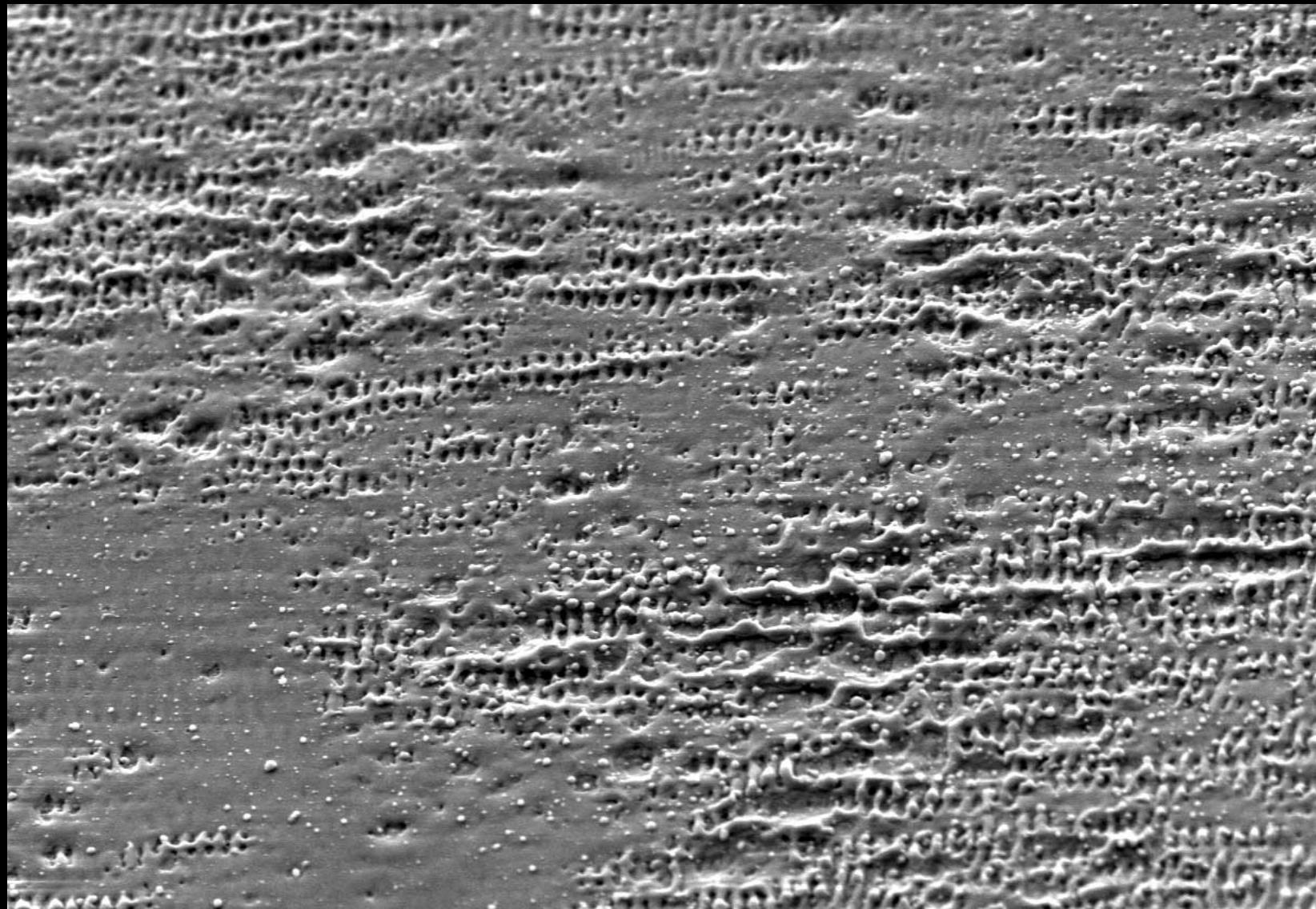
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20 μm

10kV

15mm

0003



x2000

#3548

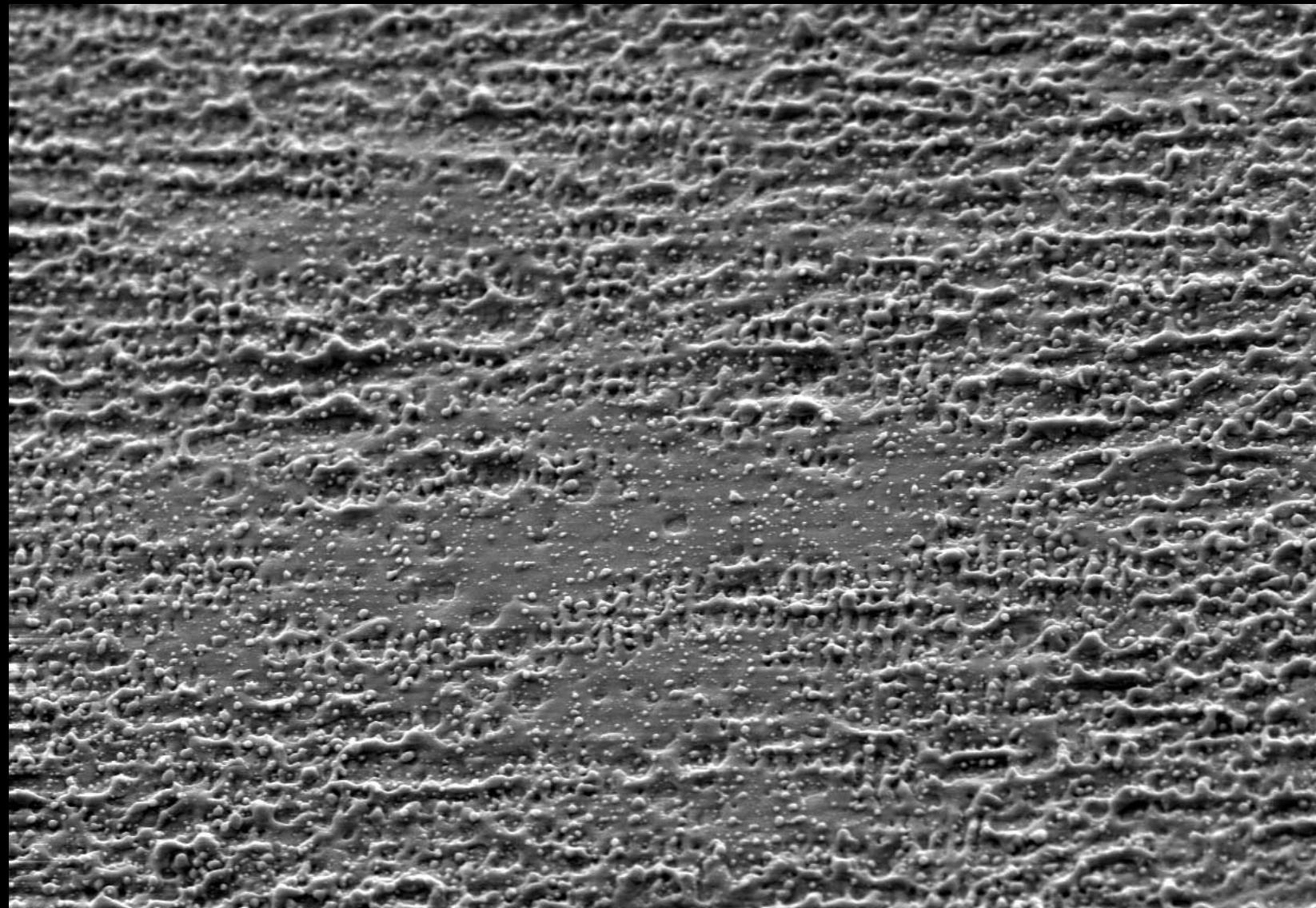
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20 μm

10kV

15mm

0004



x2000

#3548

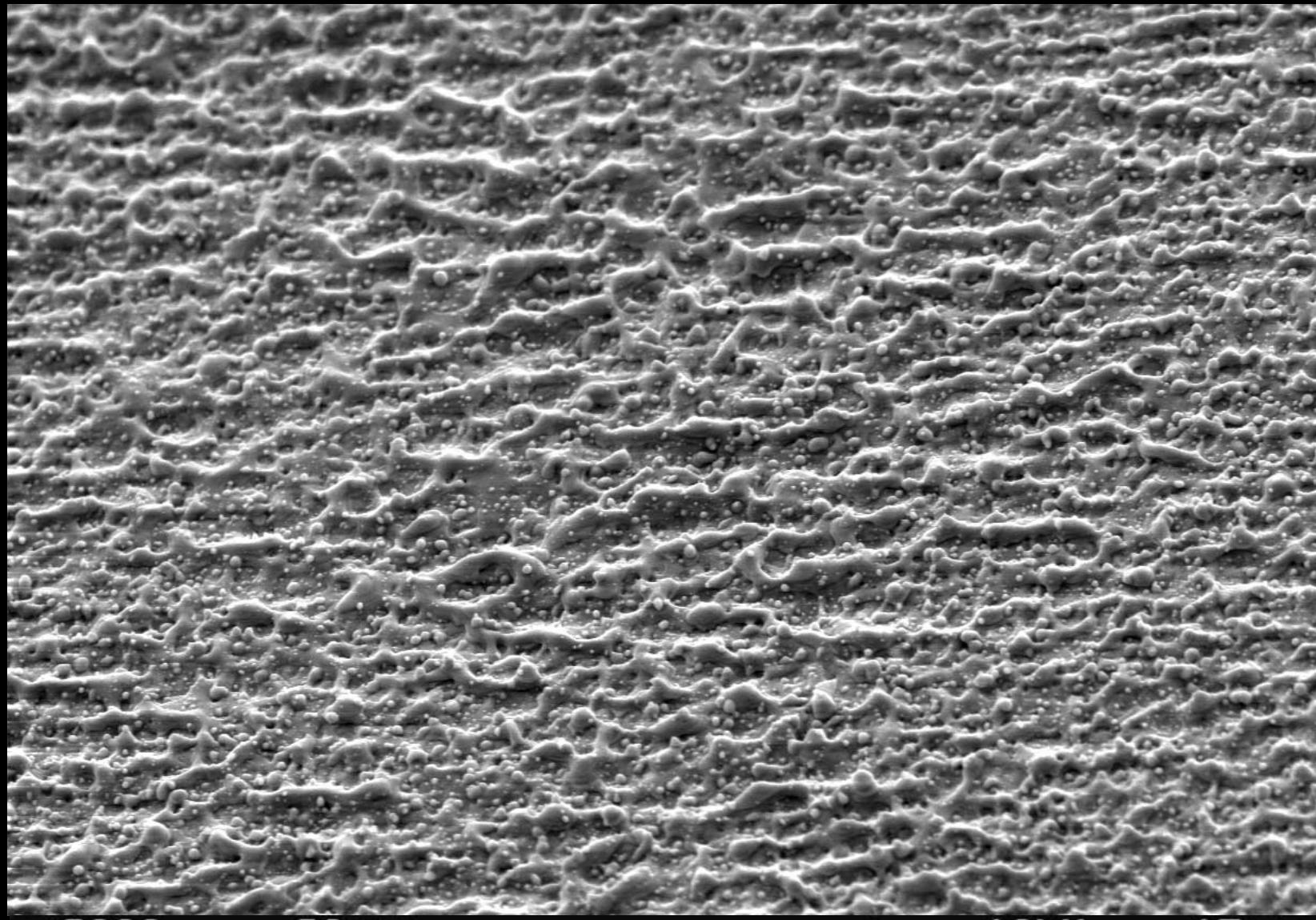
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20 μm

10kV

15mm

0005



x2000

#3548

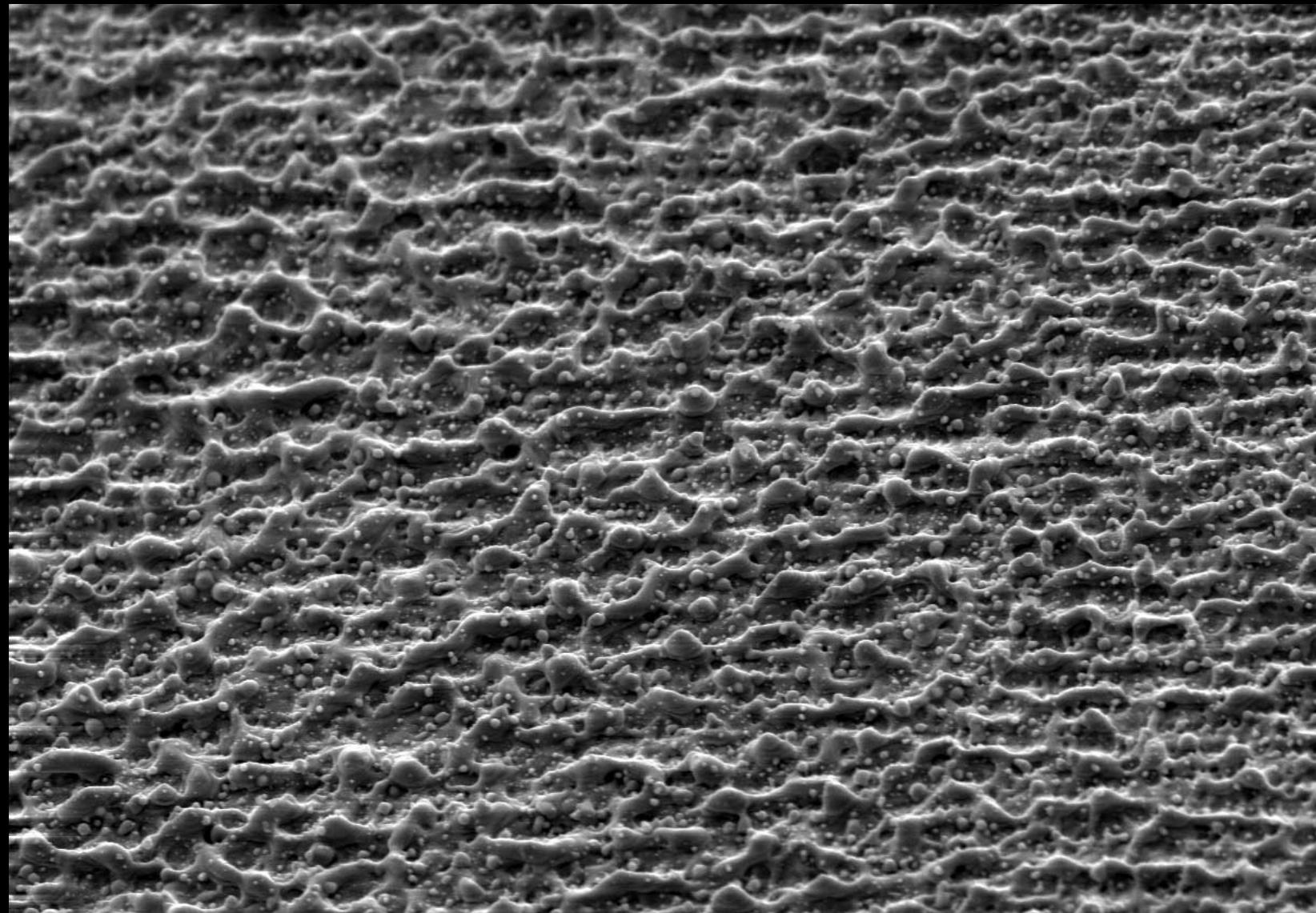
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20 μ m

10kV

15mm

0006



x2000

#3548

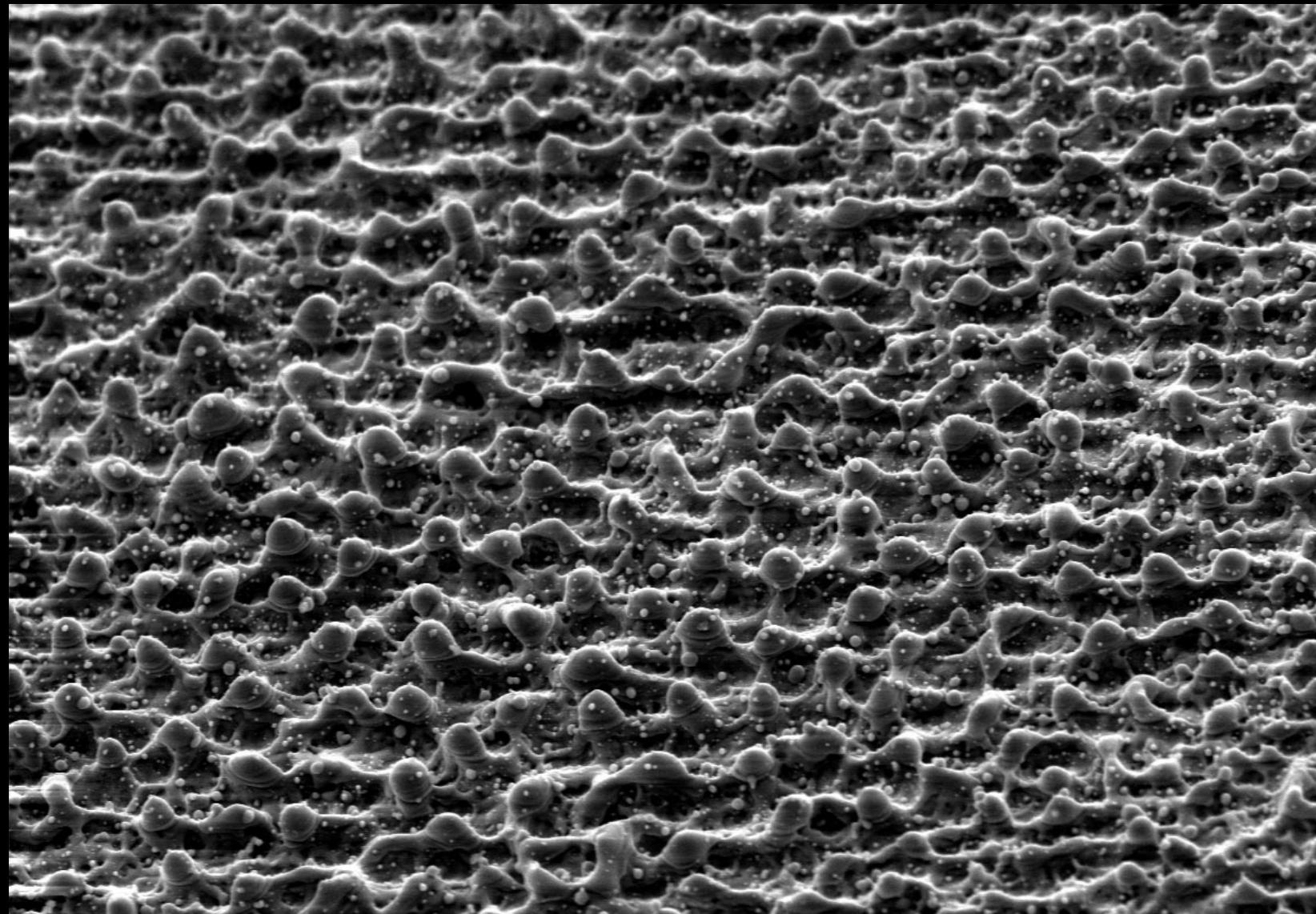
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20 μm

10kV

15mm

0008



x2000

#3548

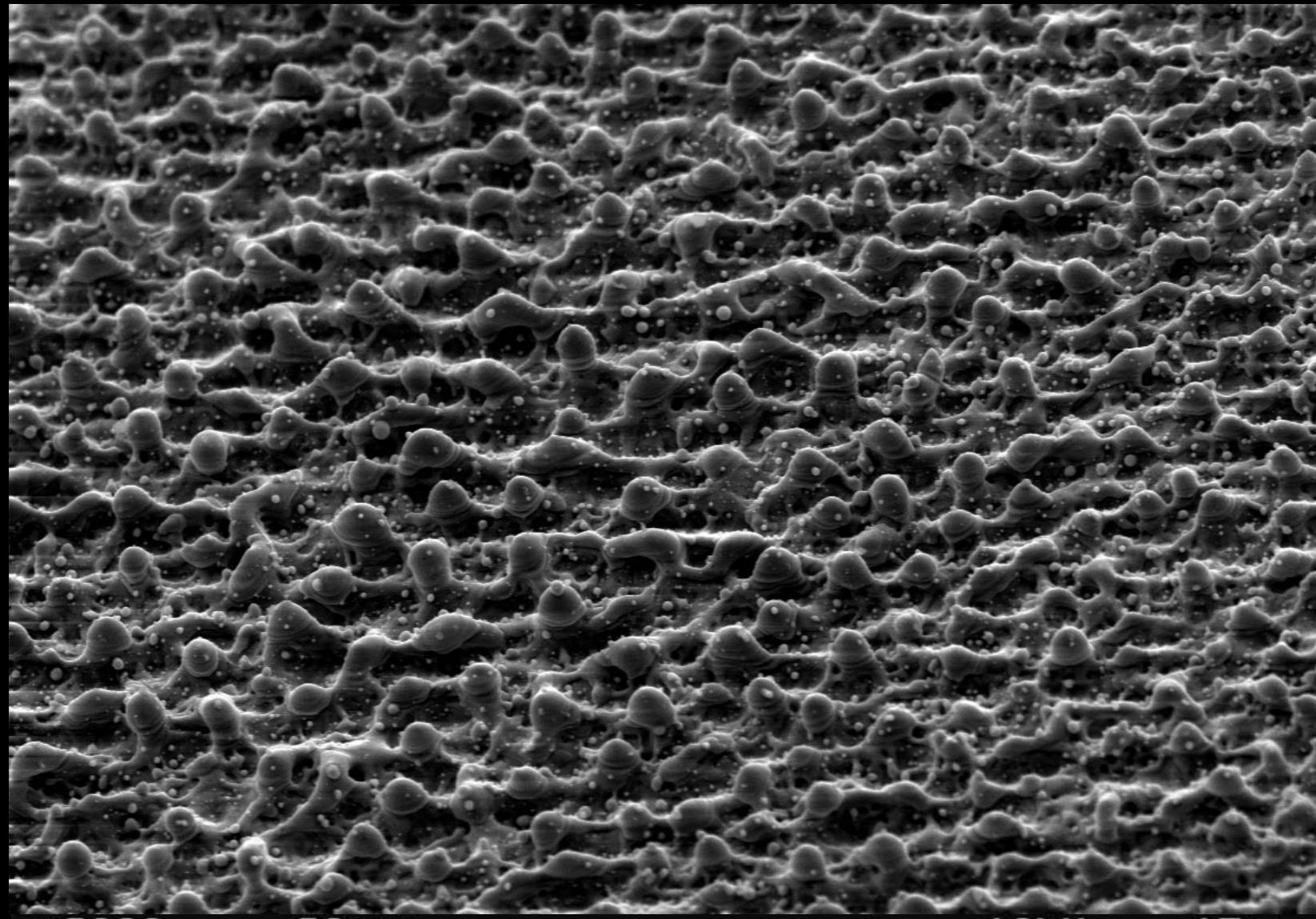
512 x 480

20 μm

10kV

15mm

0010



x2000

#3548

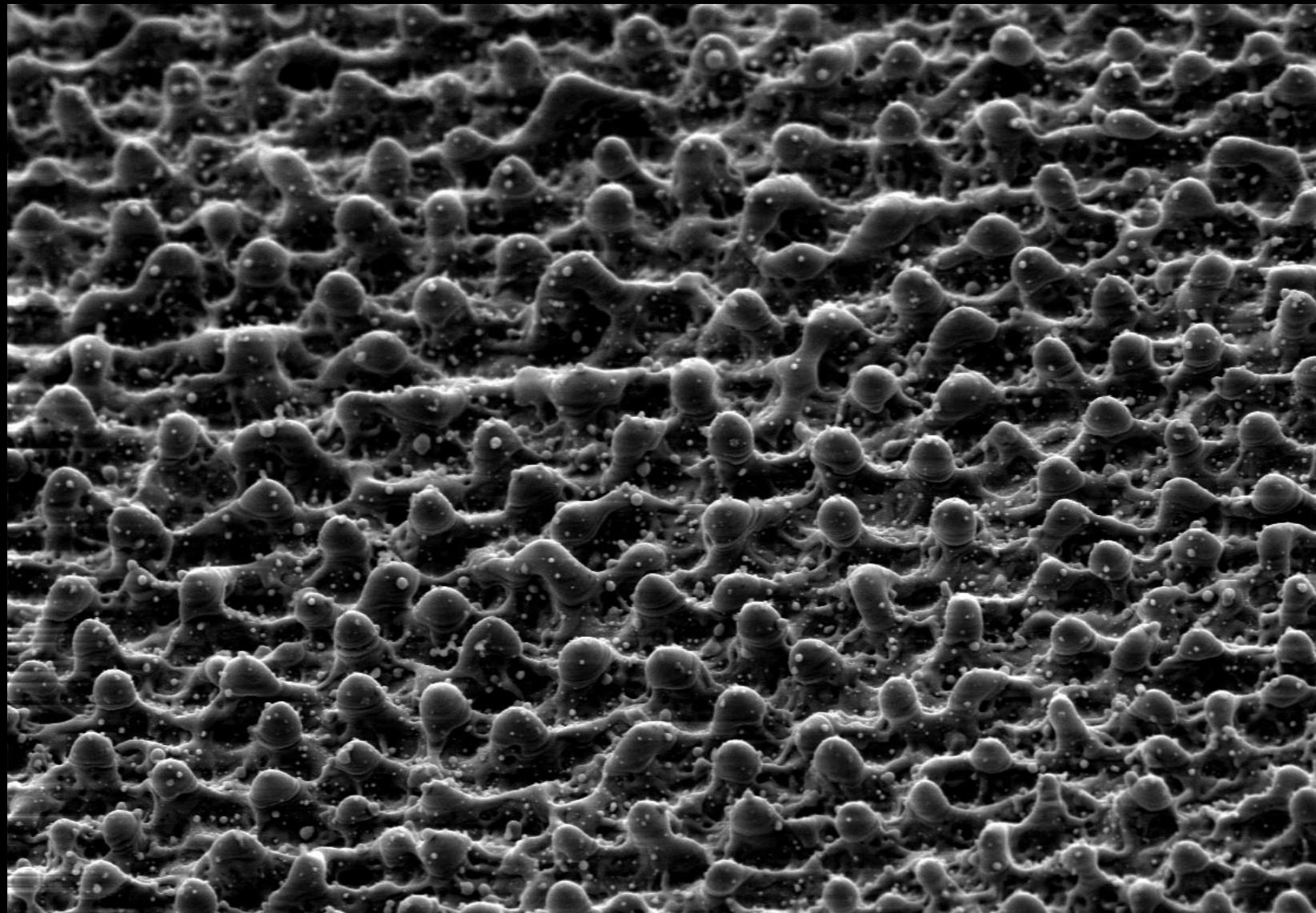
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20 μm

10kV

15mm

0012



x2000

#3548

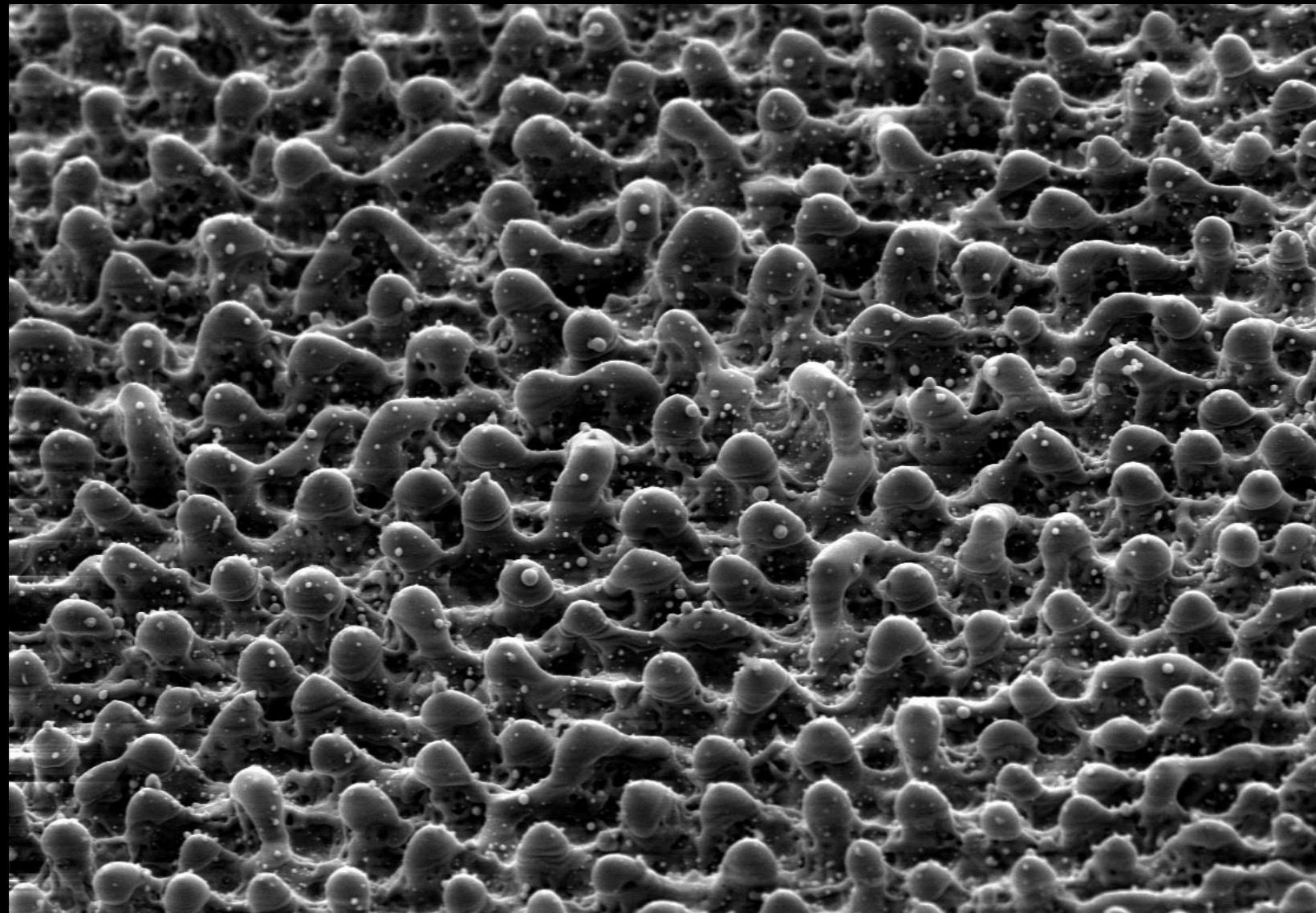
512 x 480

20 μm

10kV

15mm

0015



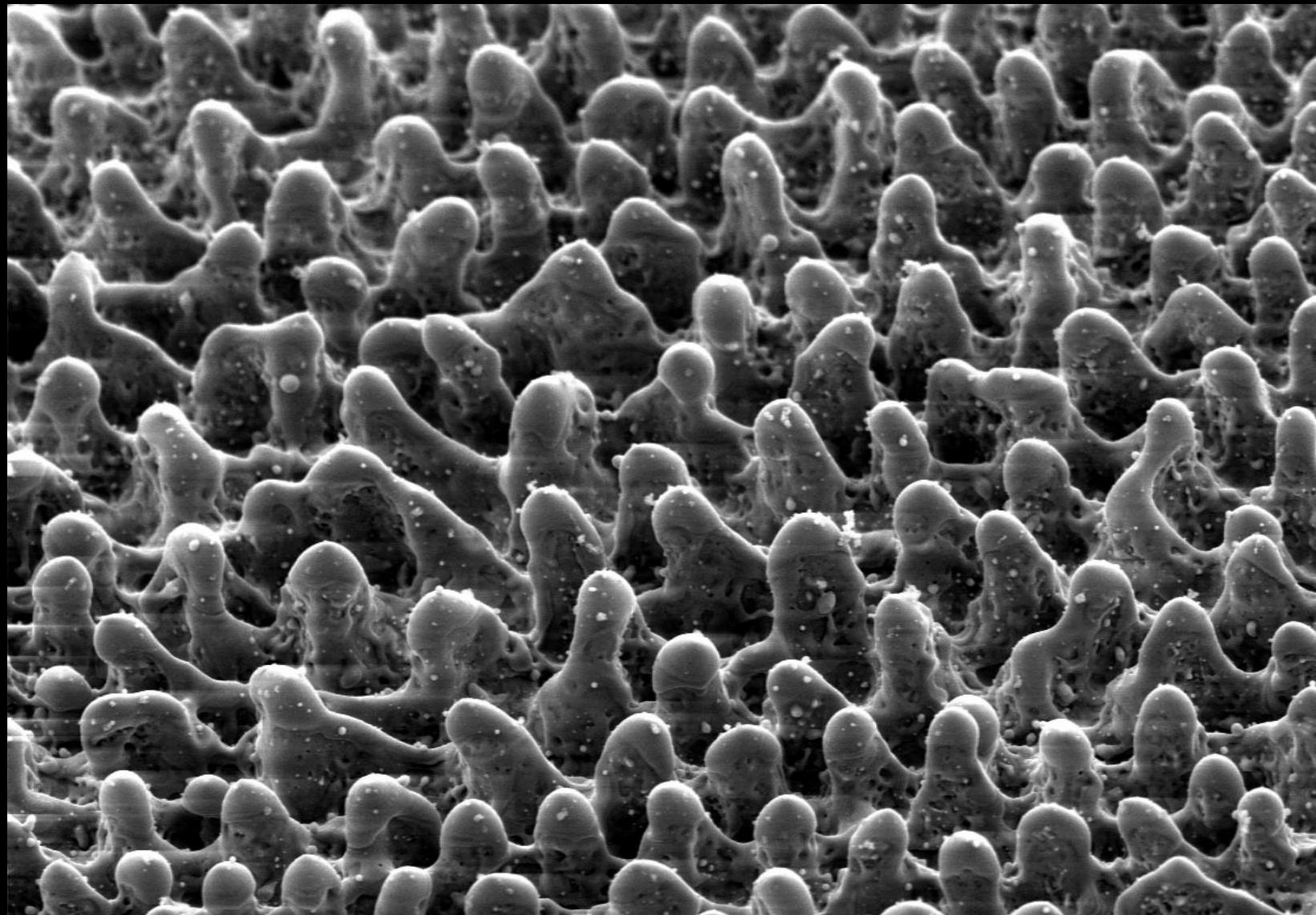
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#3548
512 x 480

20 μ m

10kV

15mm

0020



x2000

#3548

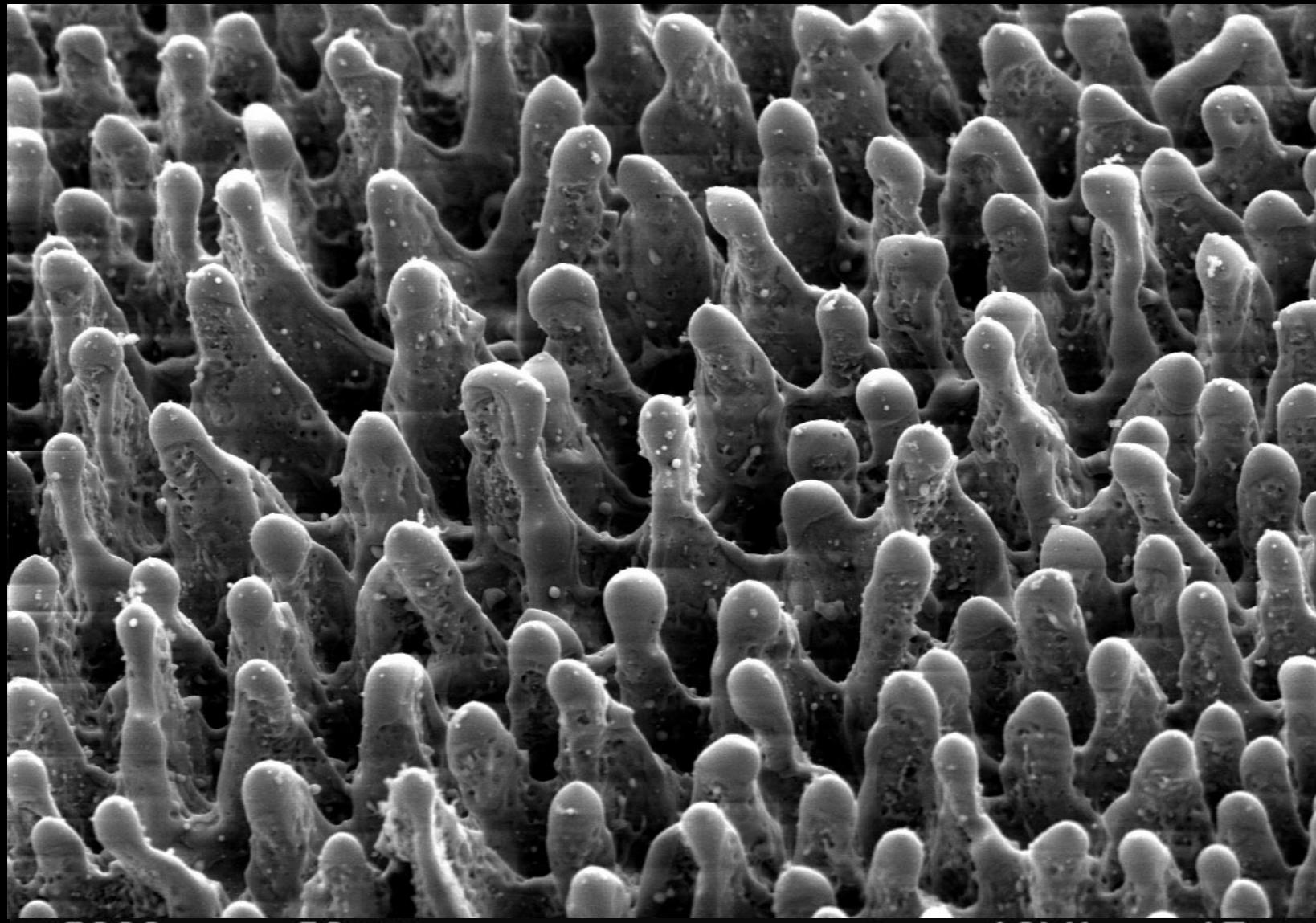
512 x 480

20 μm

10kV

15mm

0030



x2000

#3548

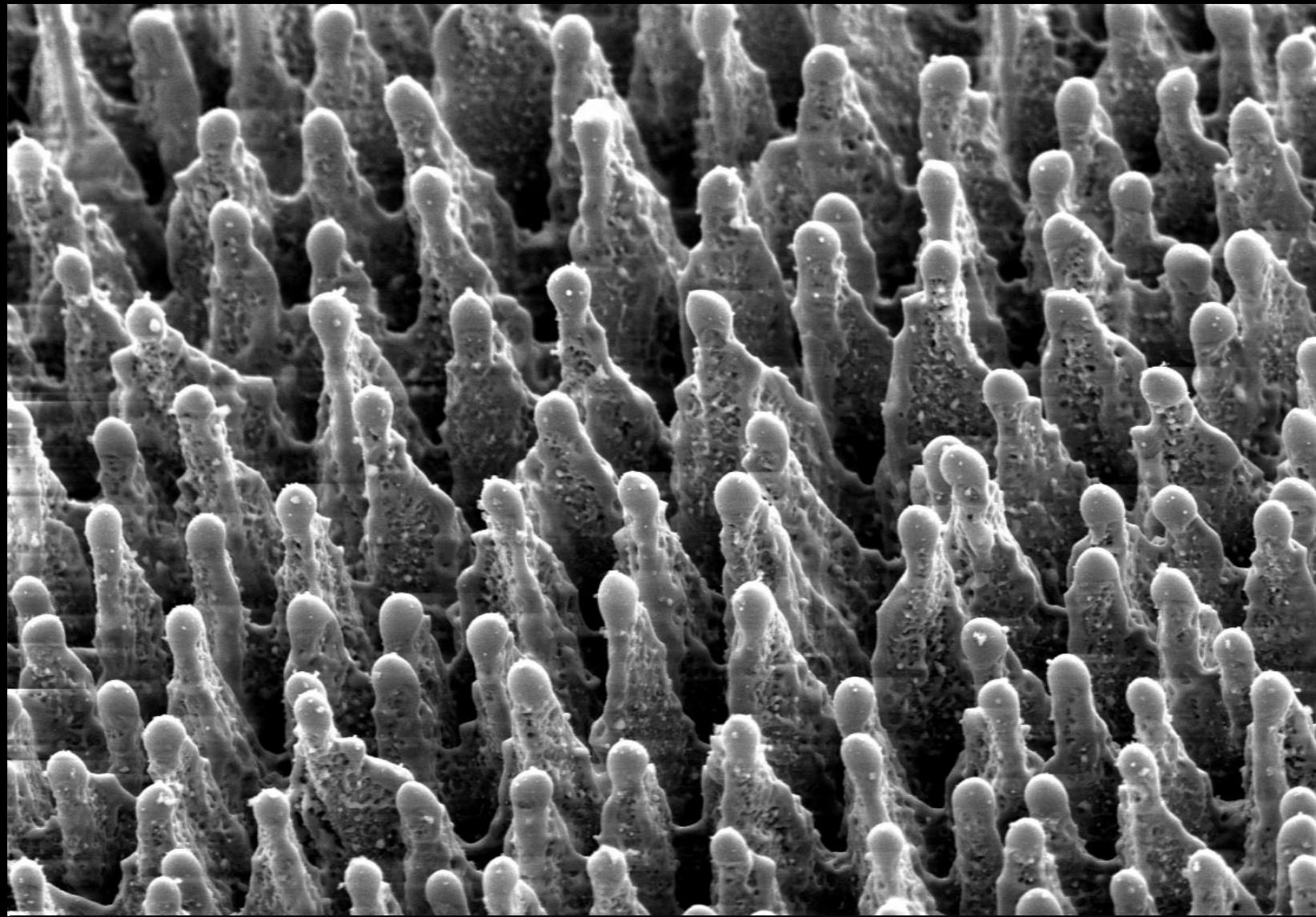
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20 μ m

10kV

15mm

0050



x2000

20 μ m

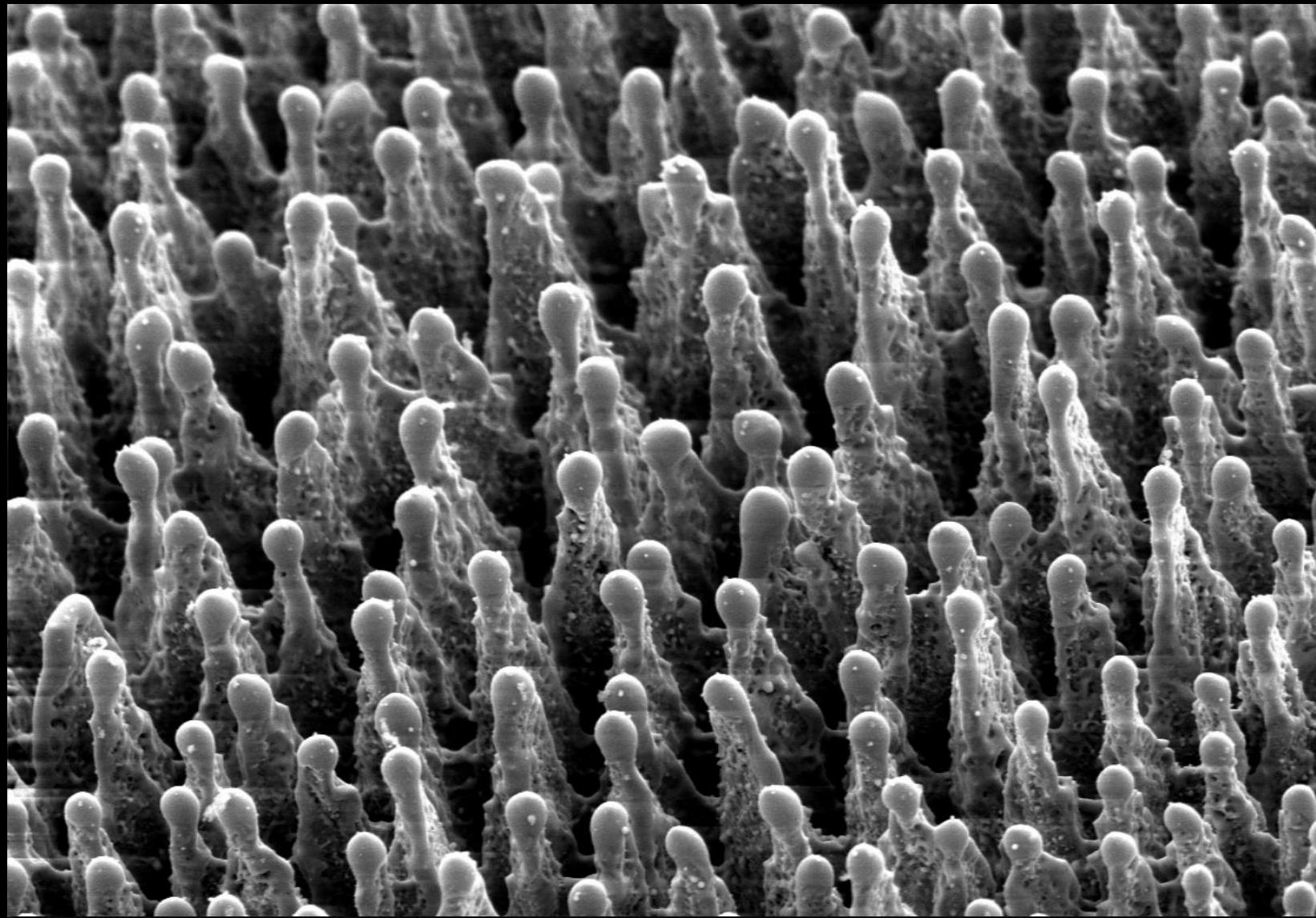
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512 x 480

10kV

15mm

0070



x2000

20 μm

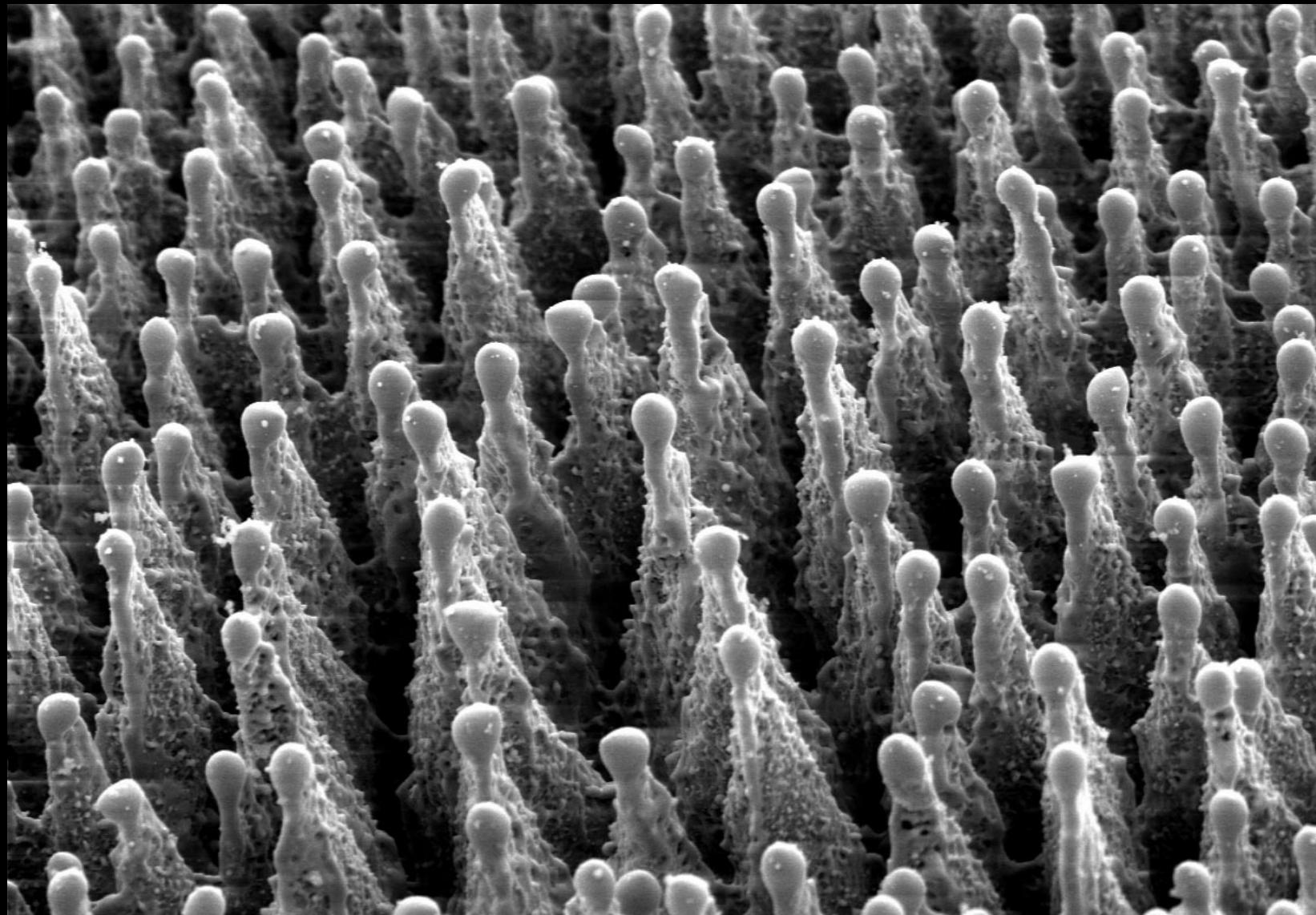
#3548

512 x 480

10kV

15mm

0100



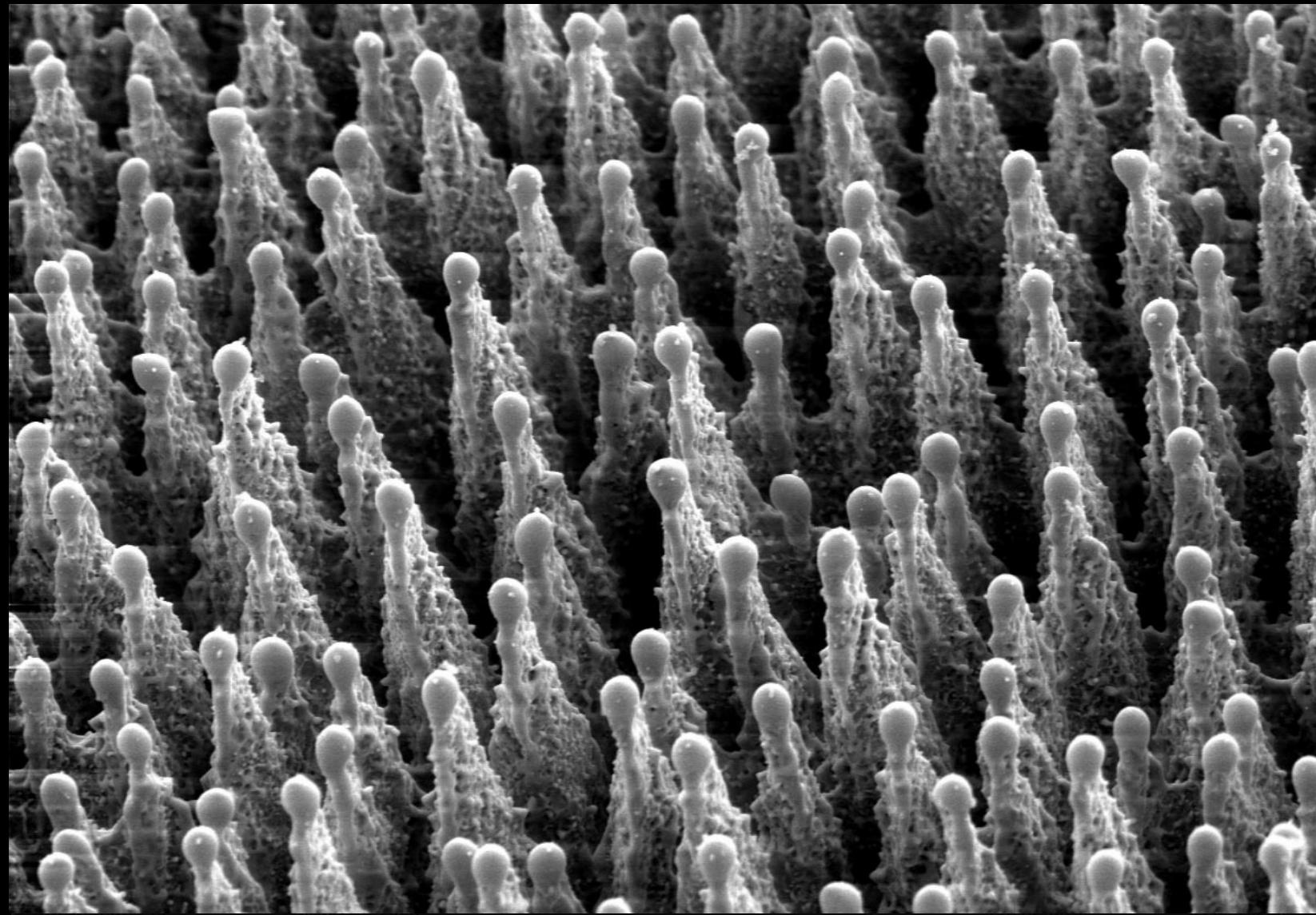
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0200



x2000

#3548

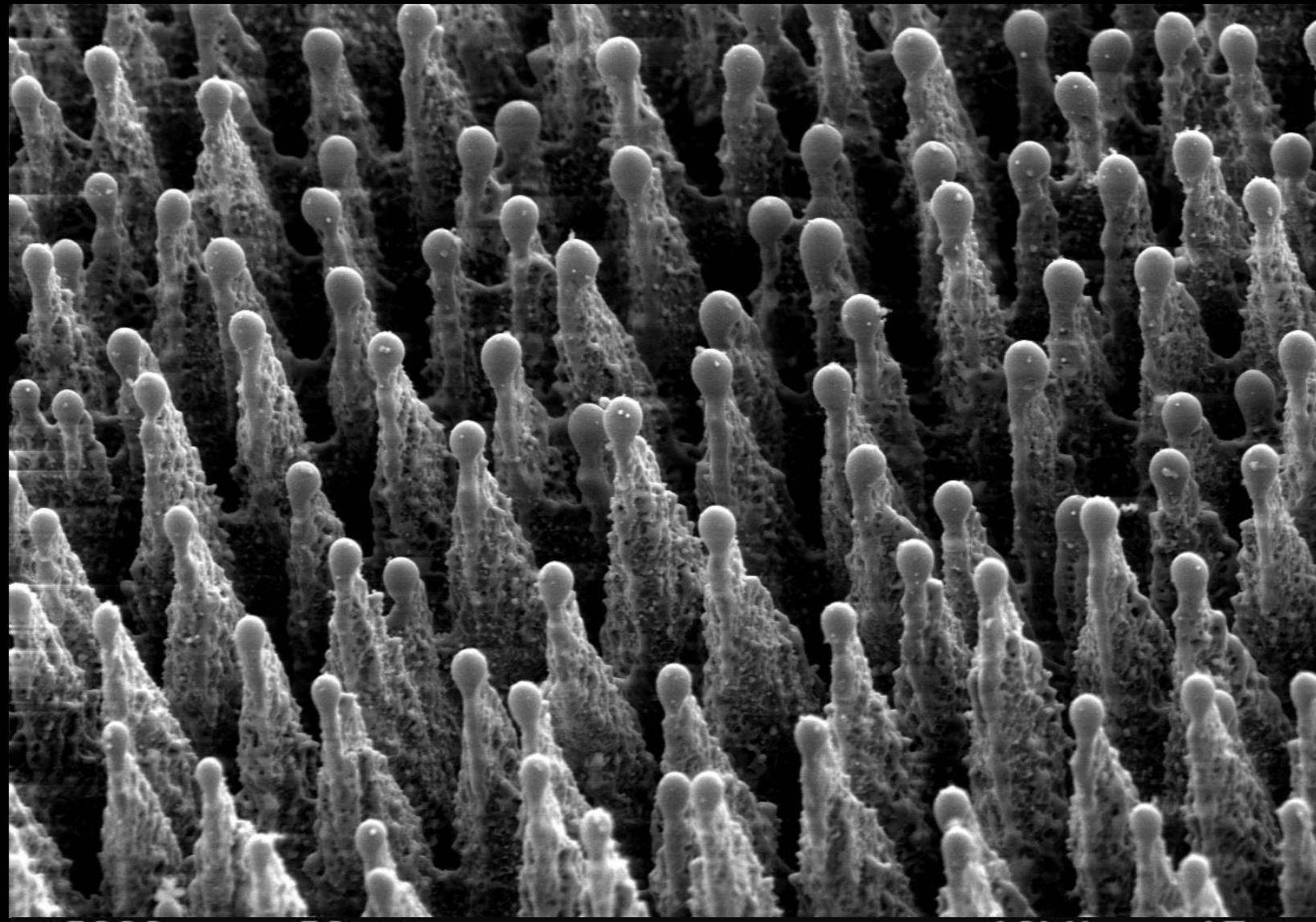
512 x 480

20 μm

10kV

15mm

0400



x2000

#3548

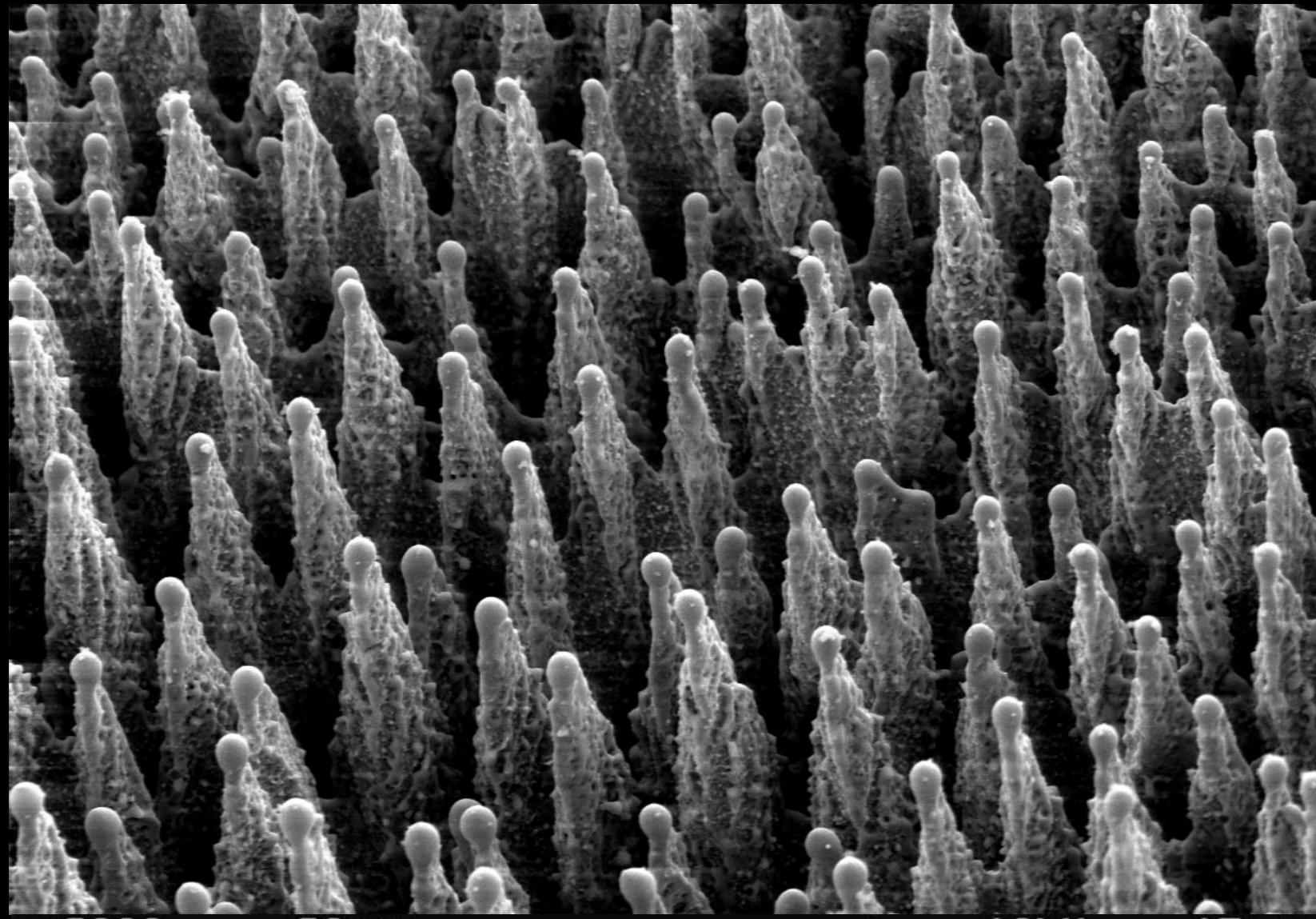
512 x 480

20 μm

10kV

15mm

0600



x2000

#3548

512 x 480

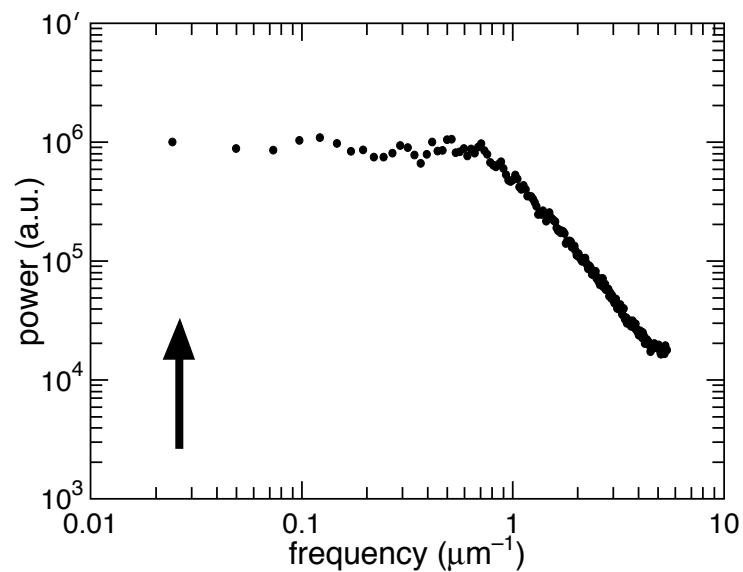
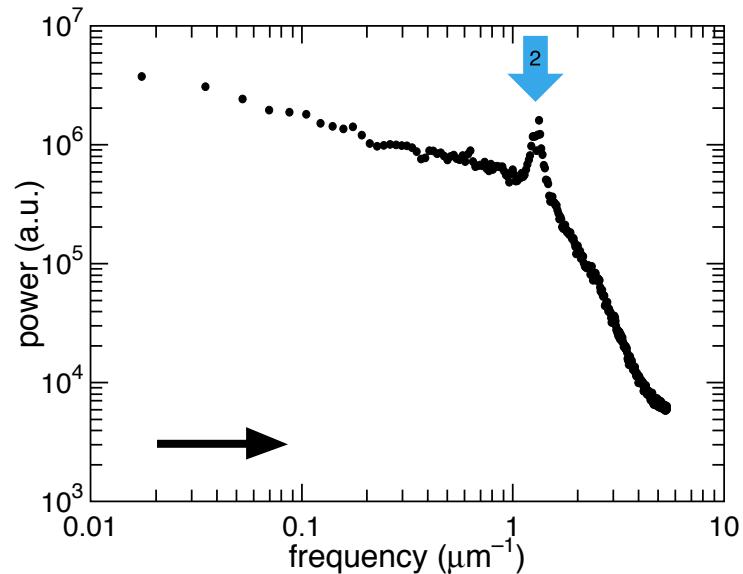
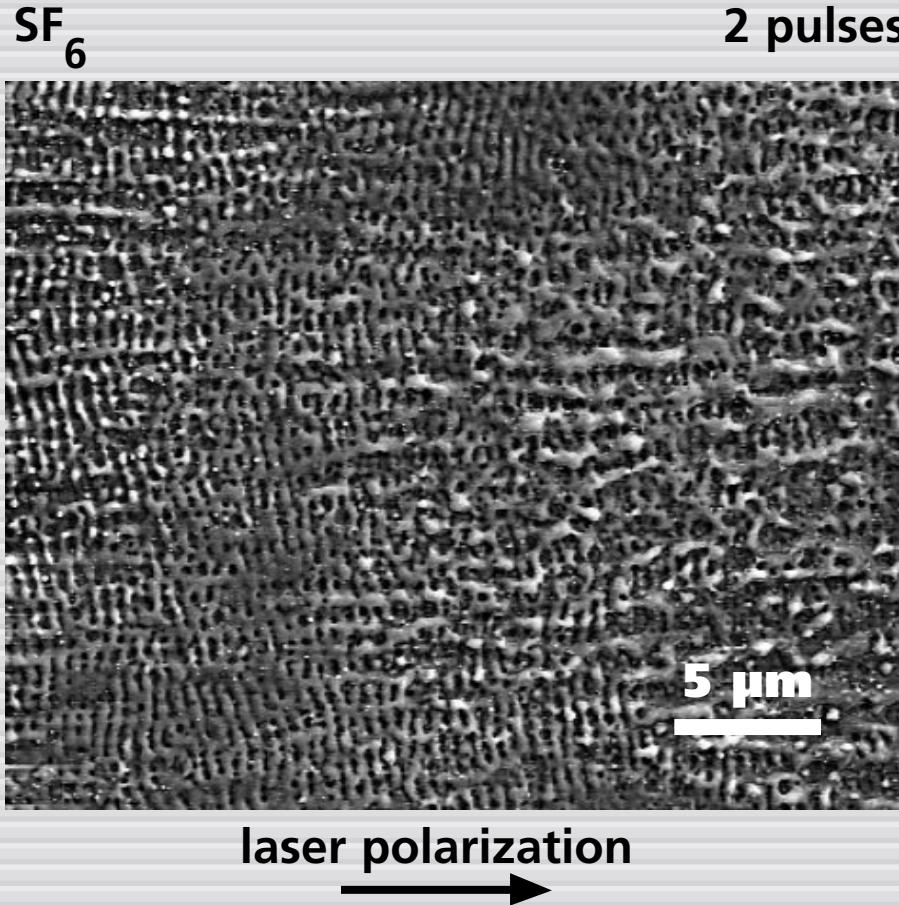
20 μm

10kV

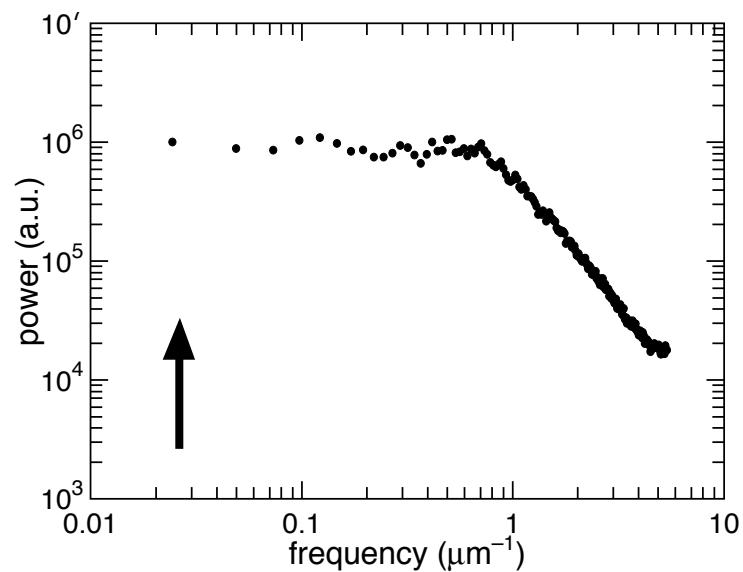
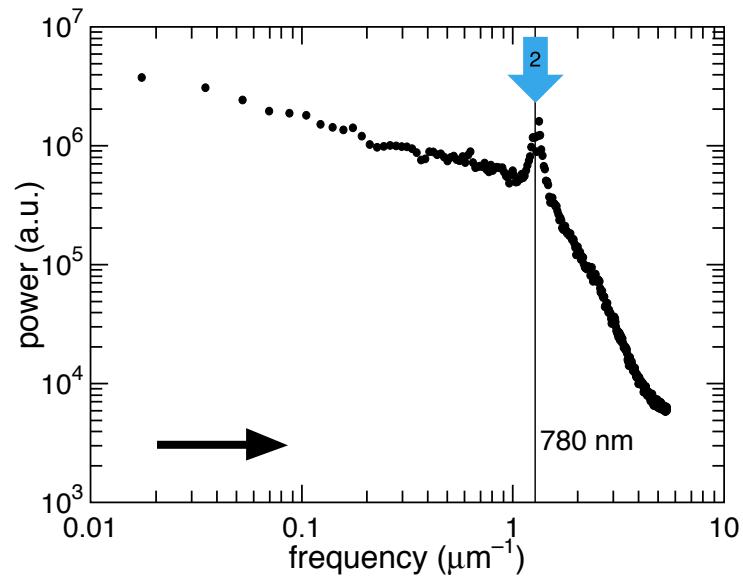
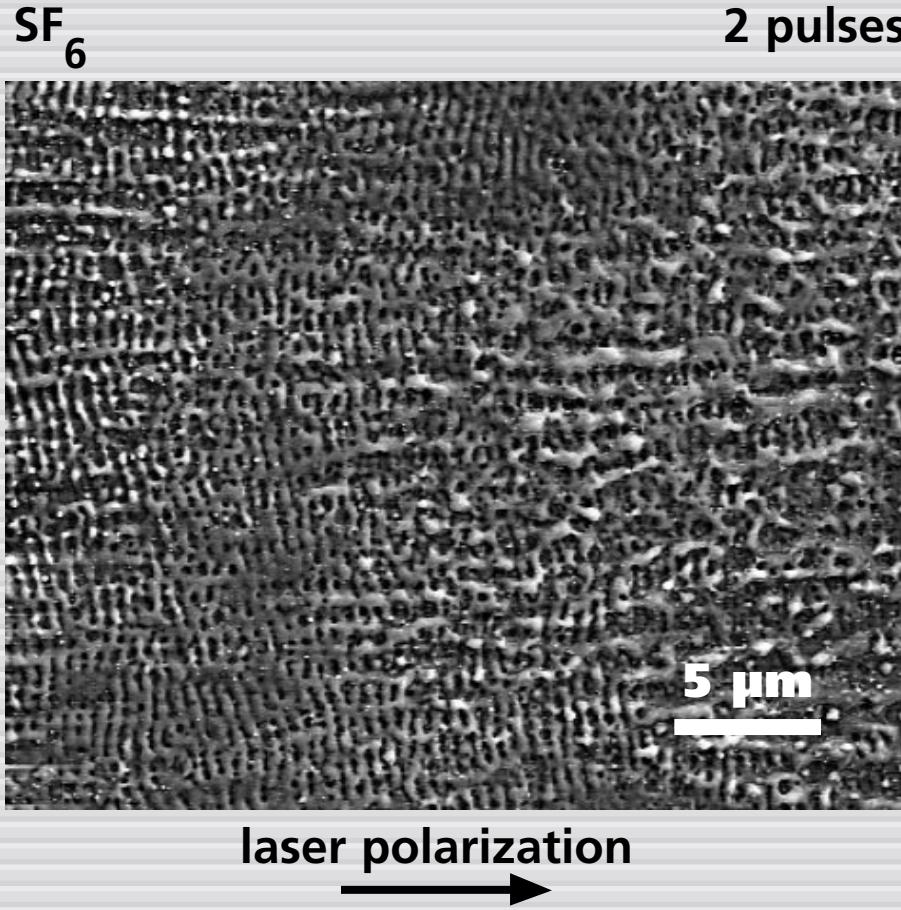
15mm

1000

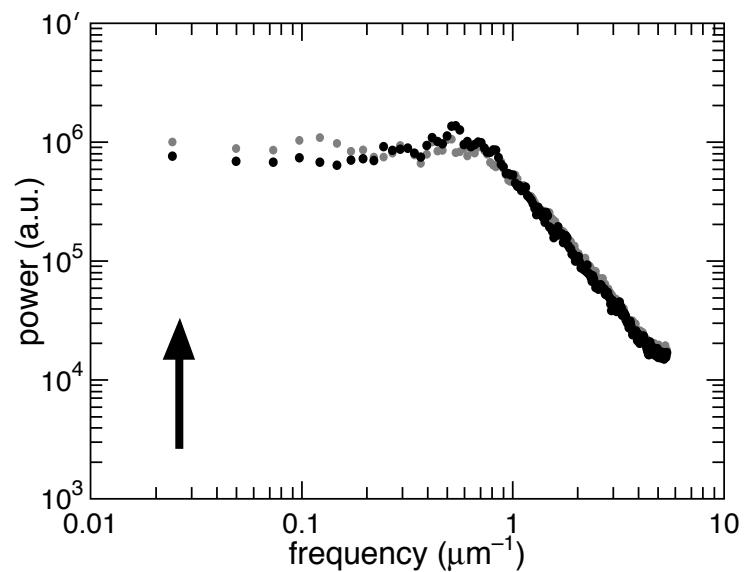
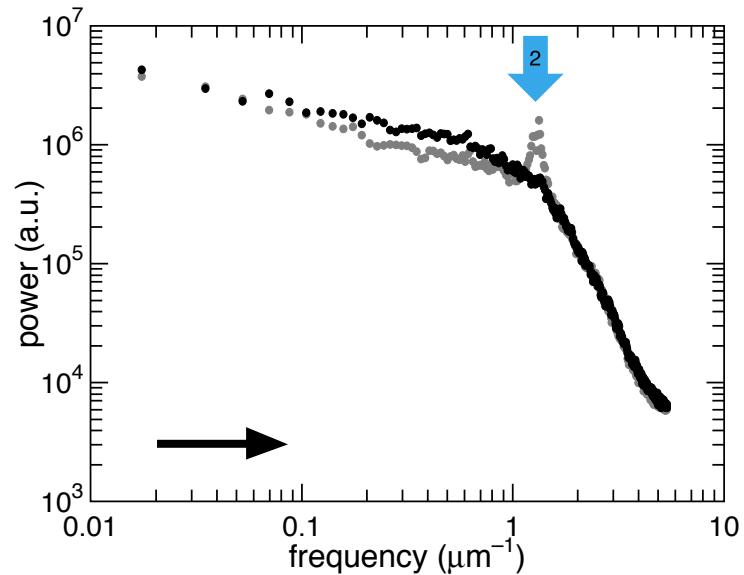
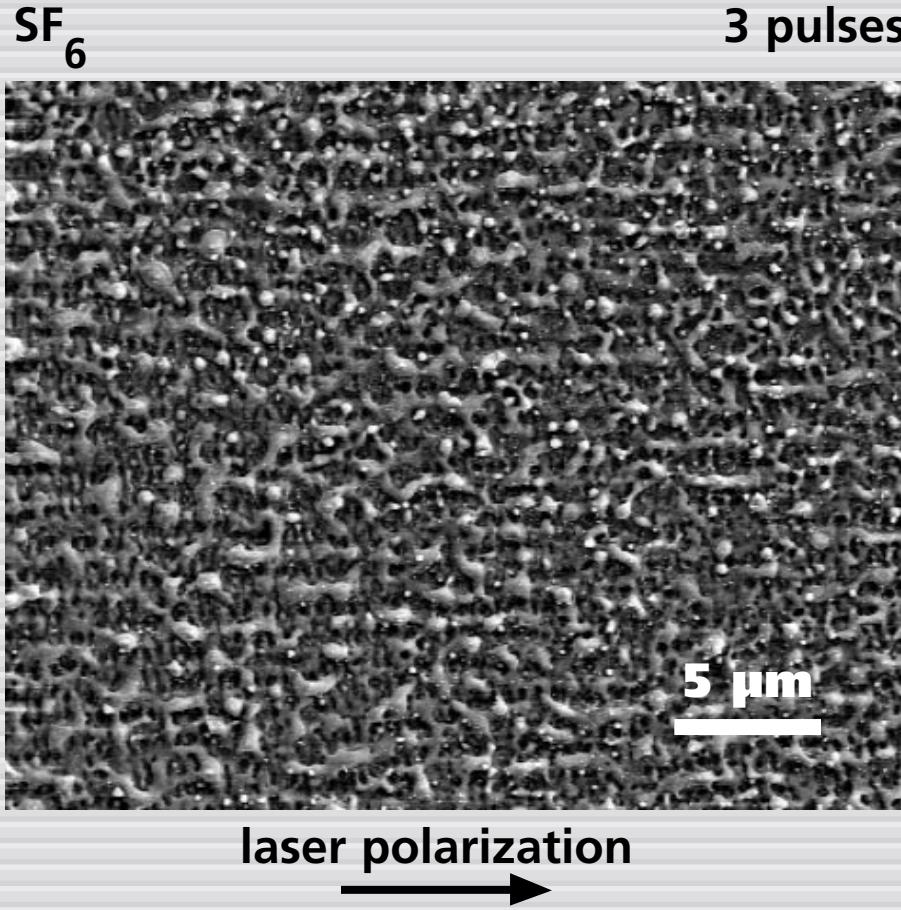
Formation



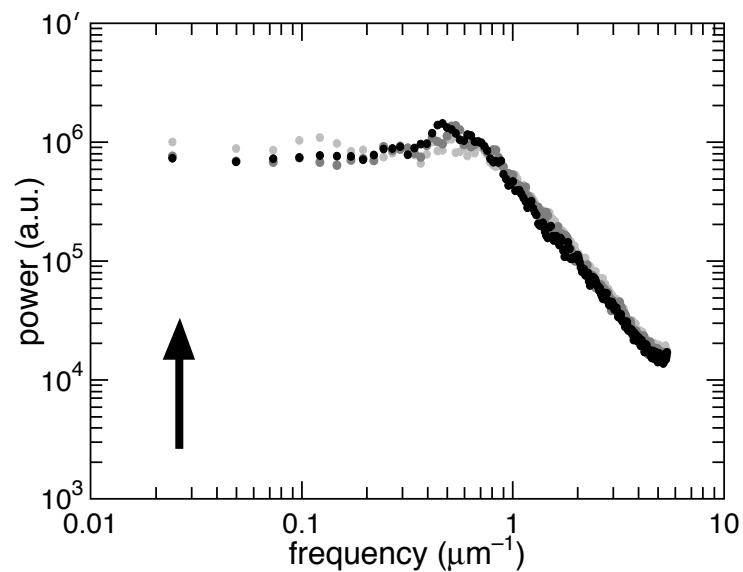
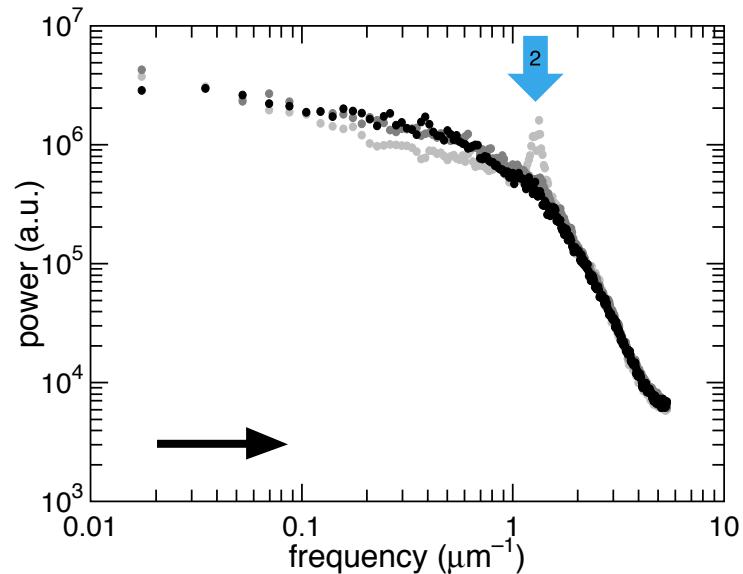
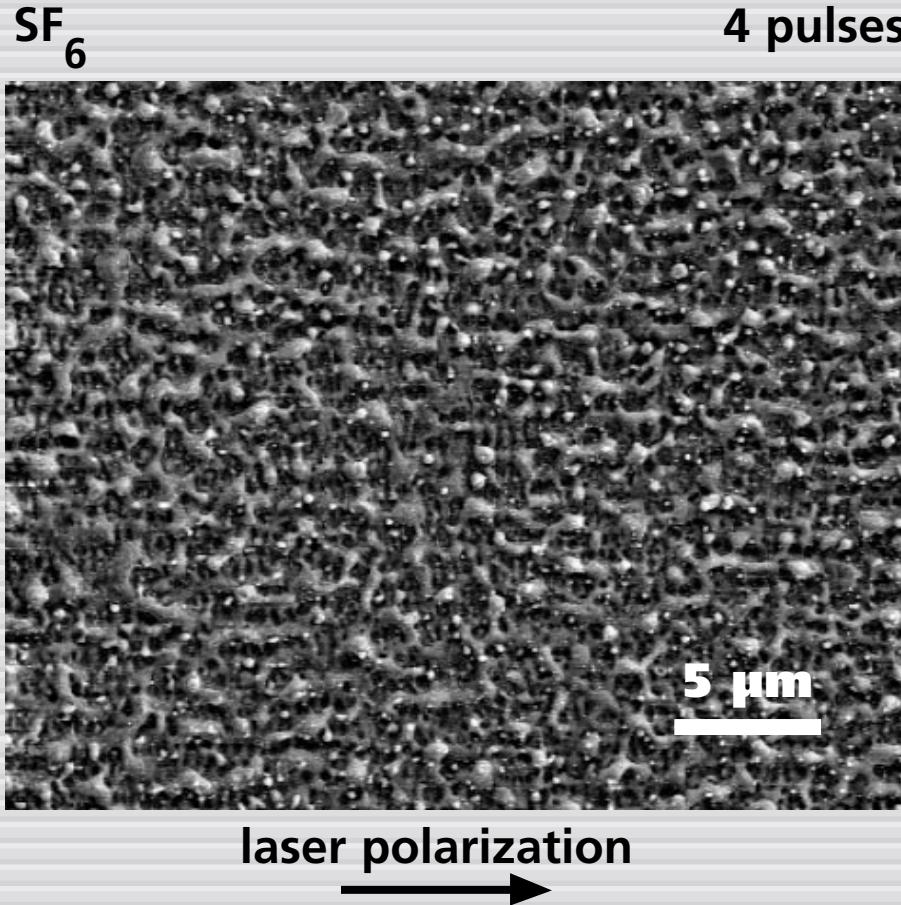
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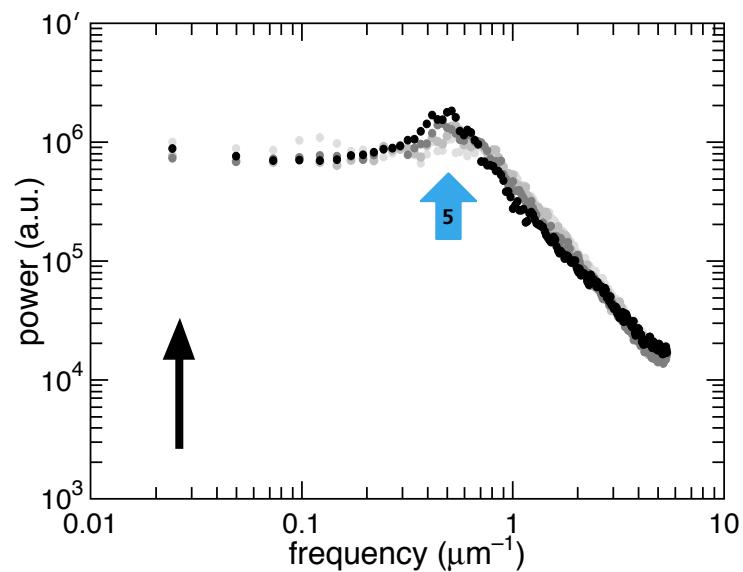
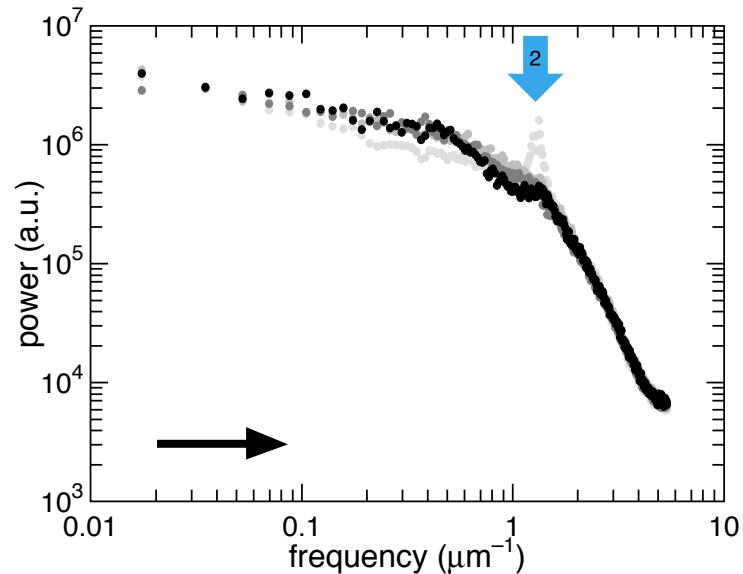
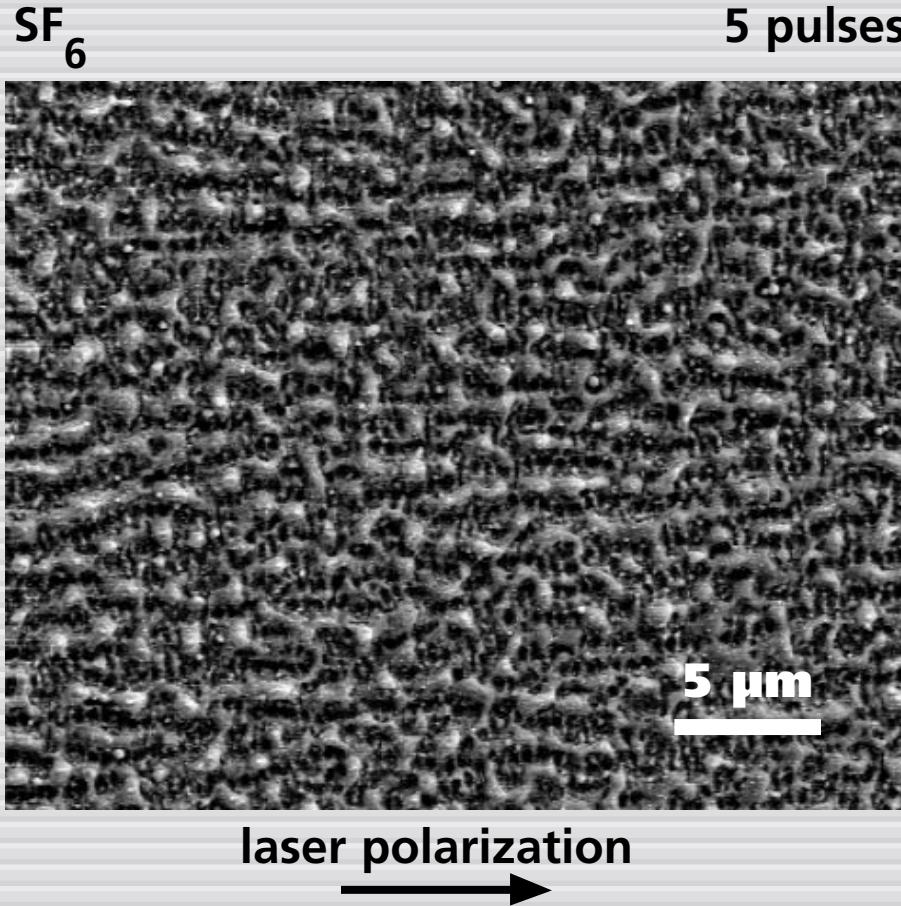
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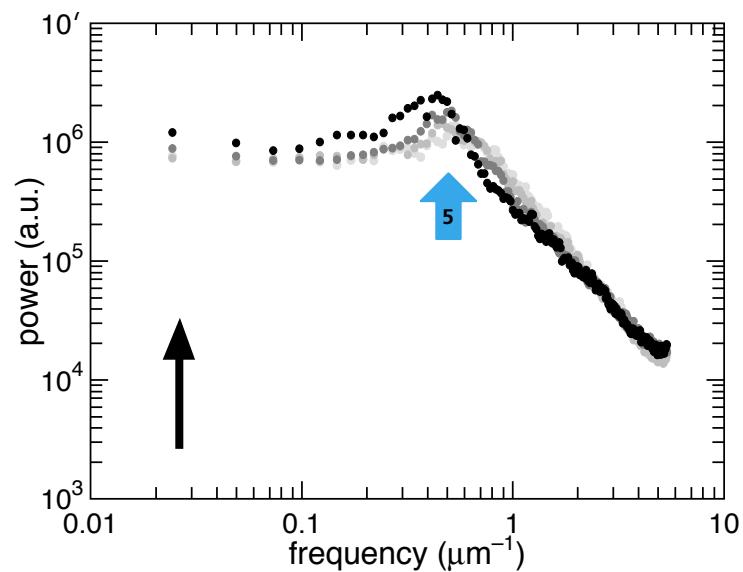
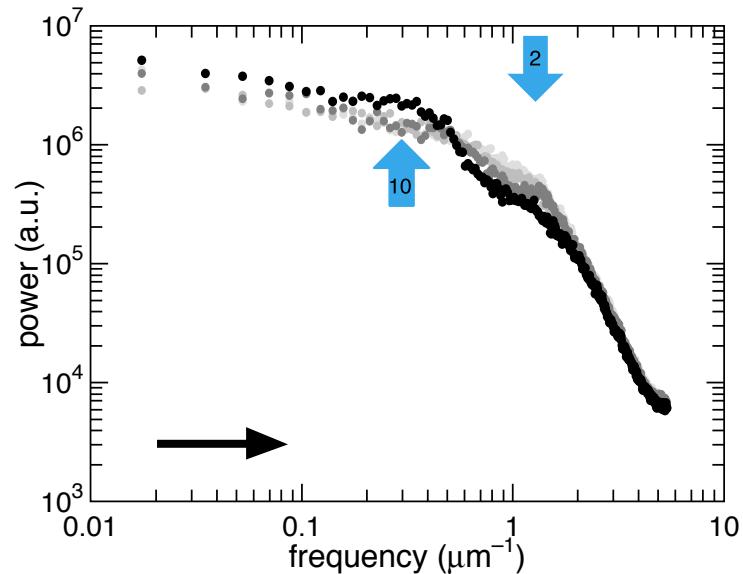
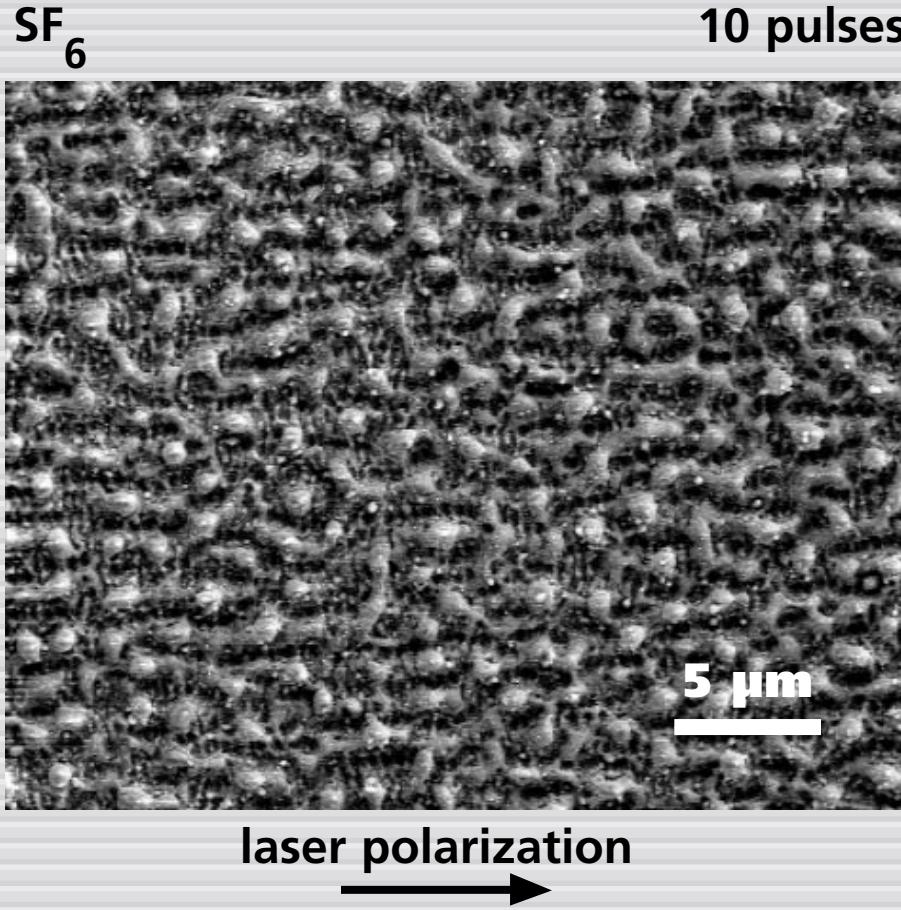
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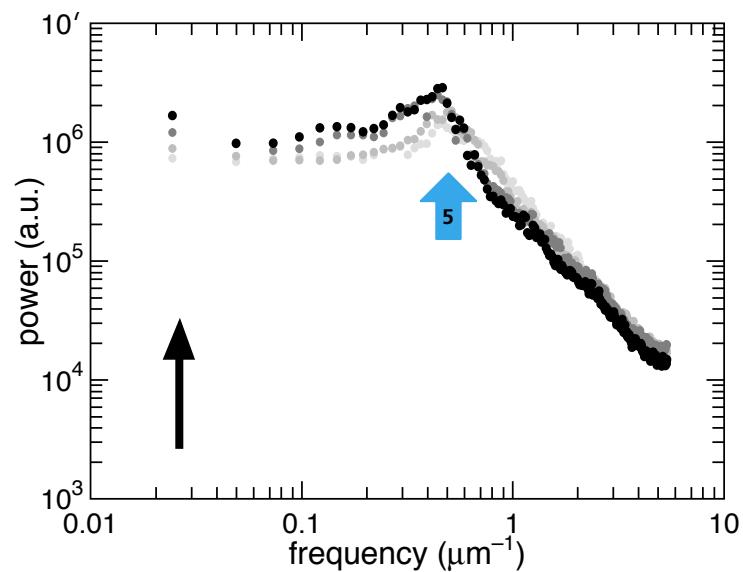
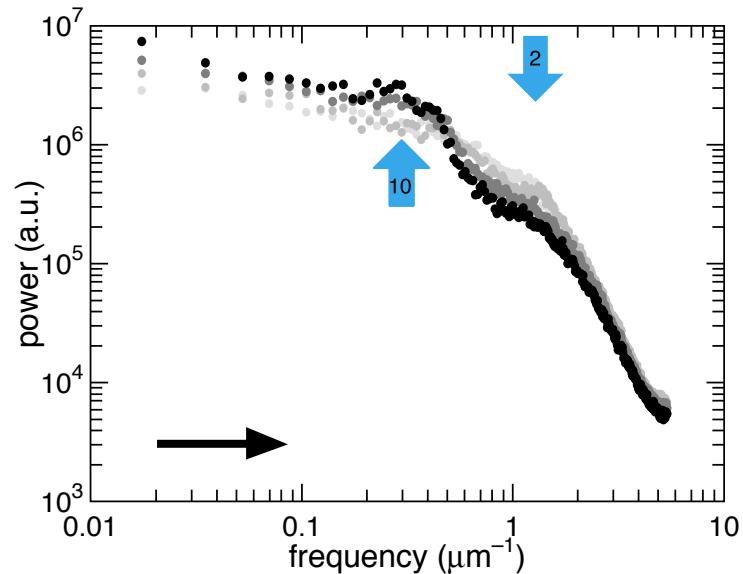
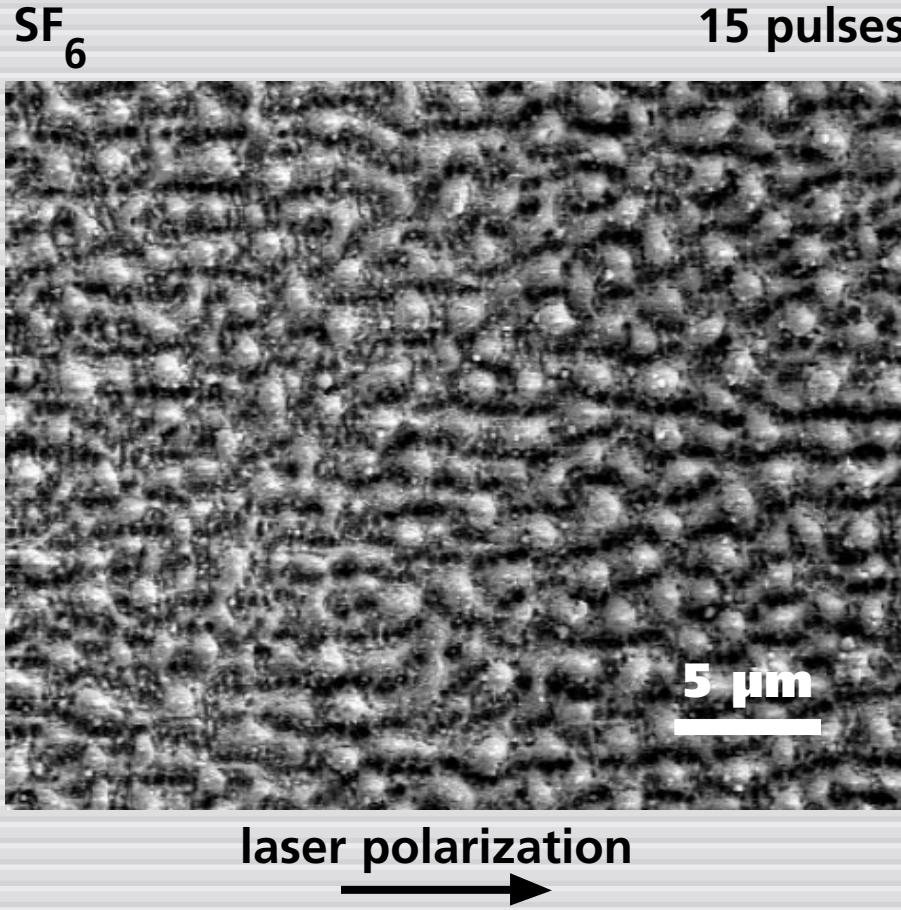
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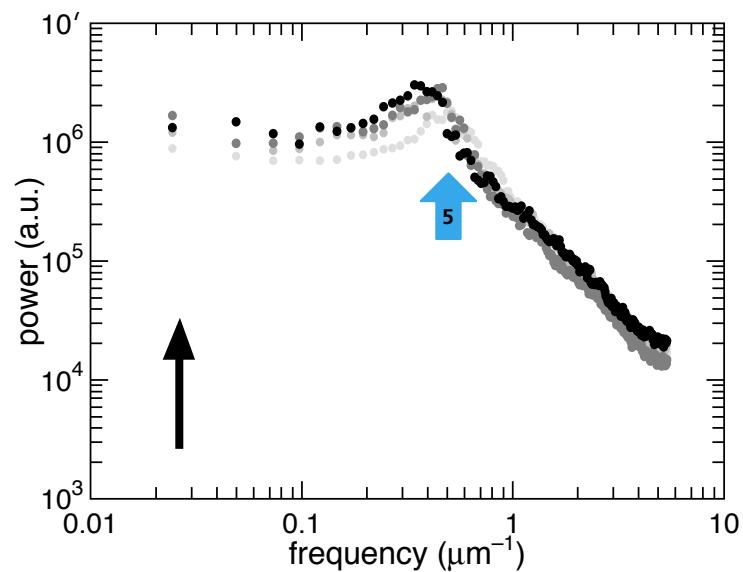
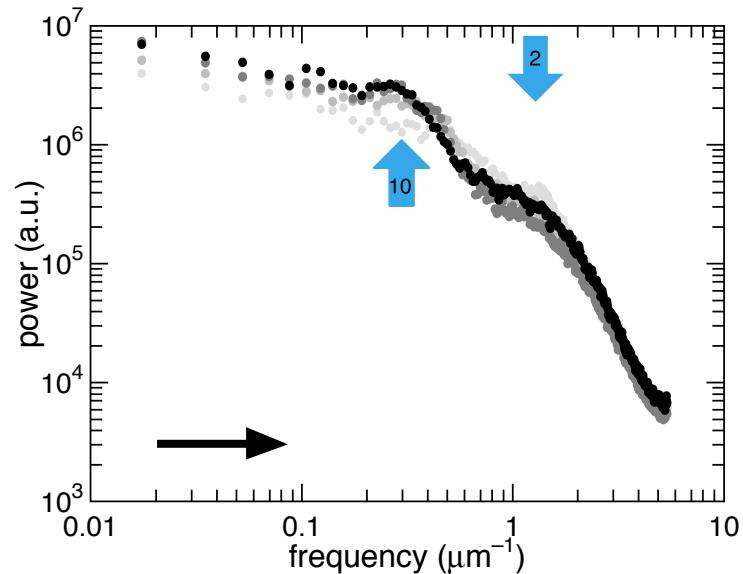
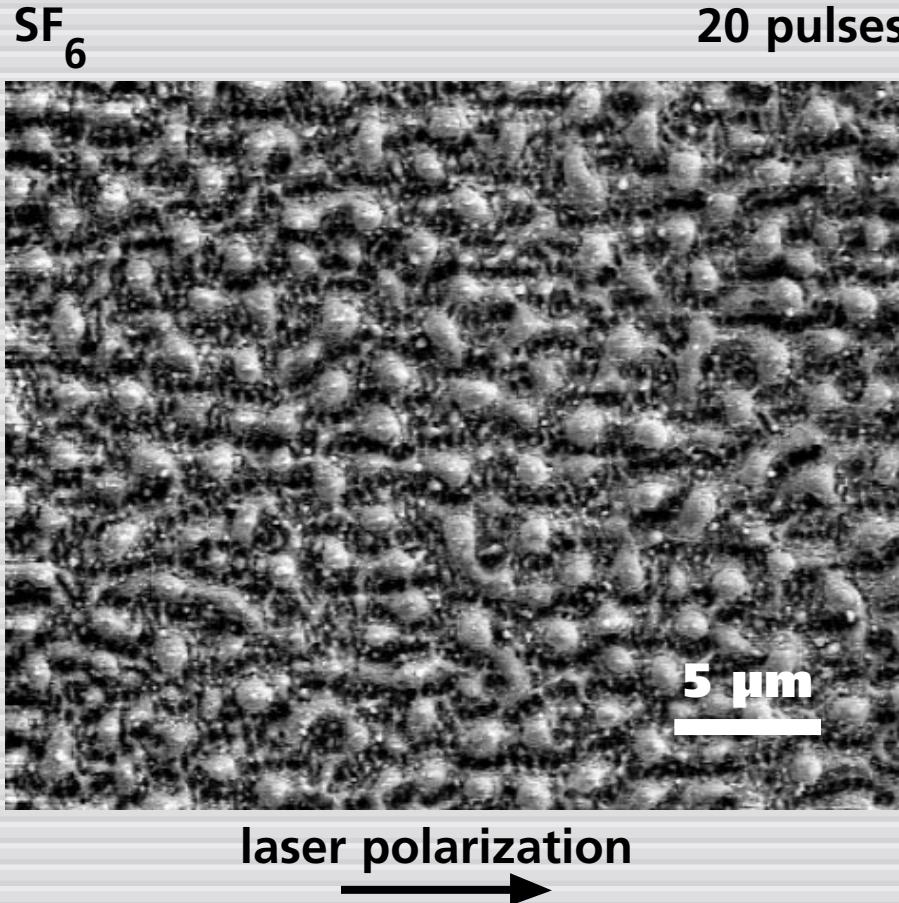
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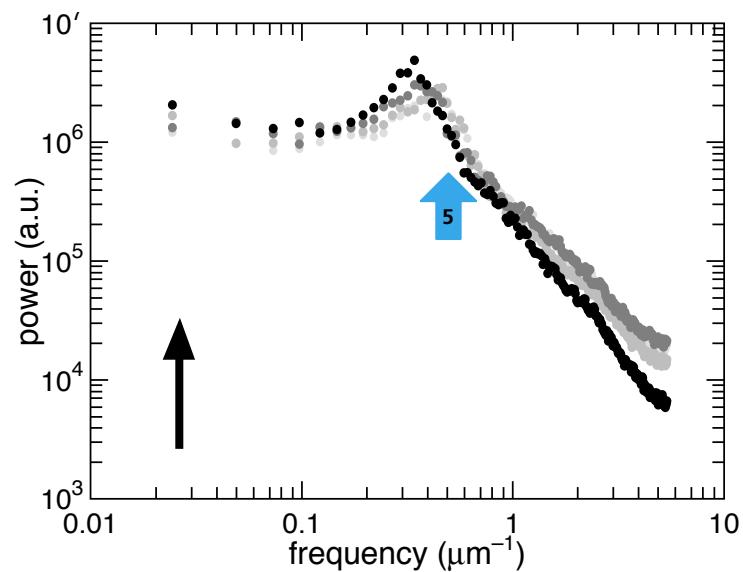
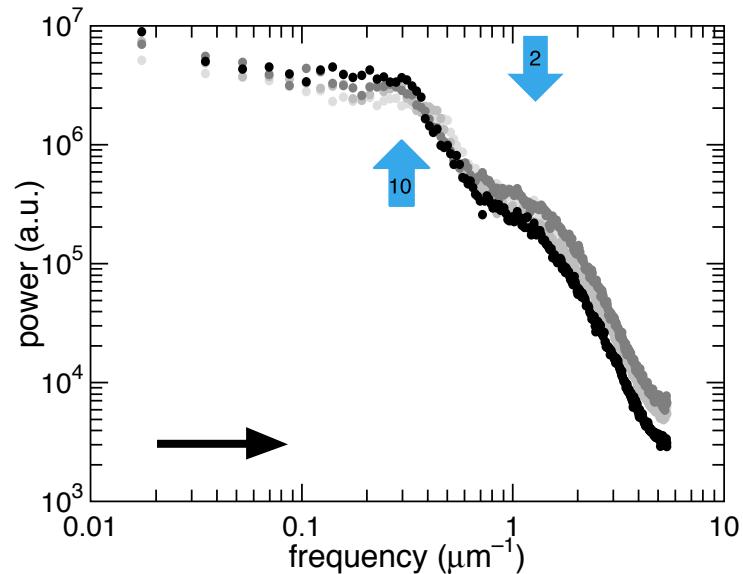
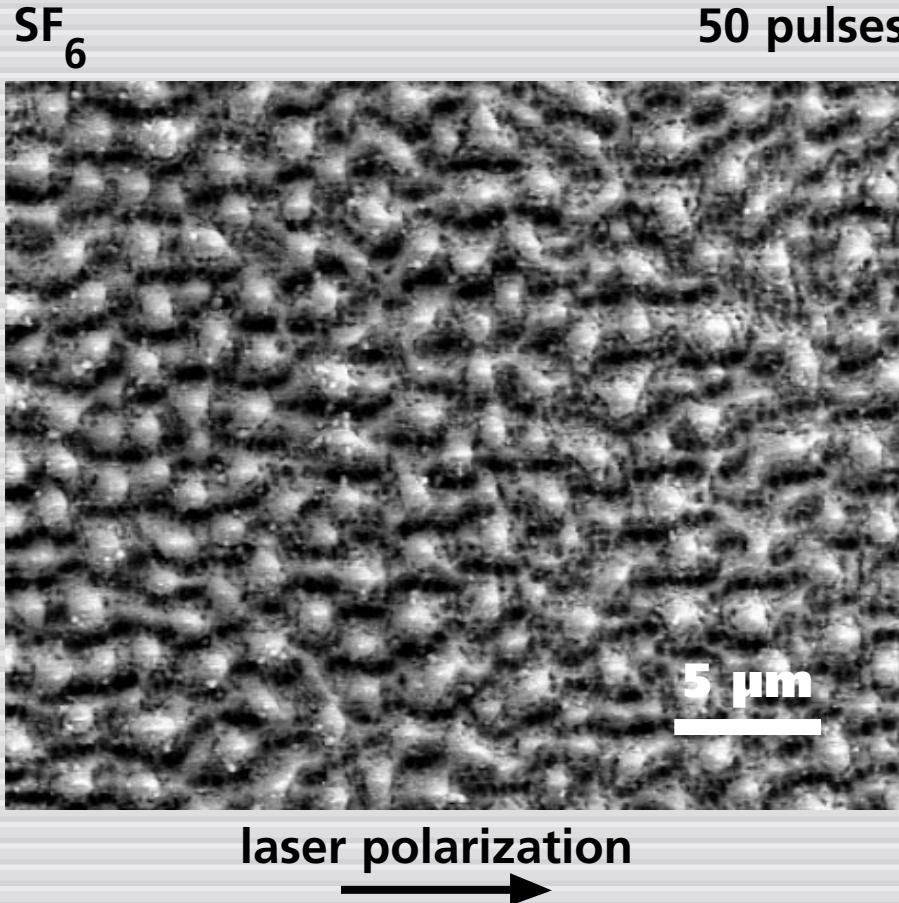
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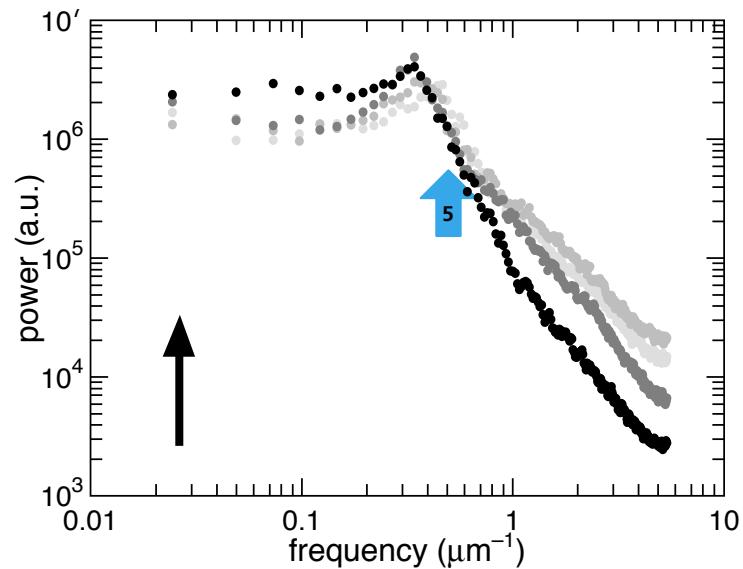
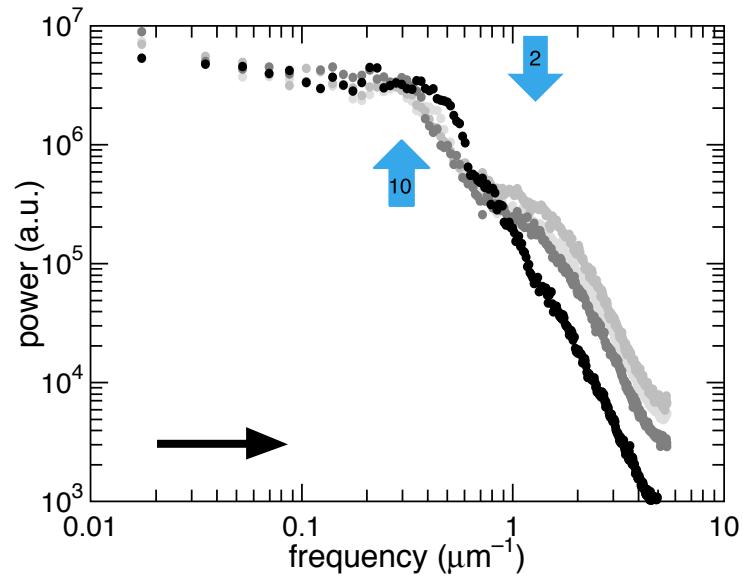
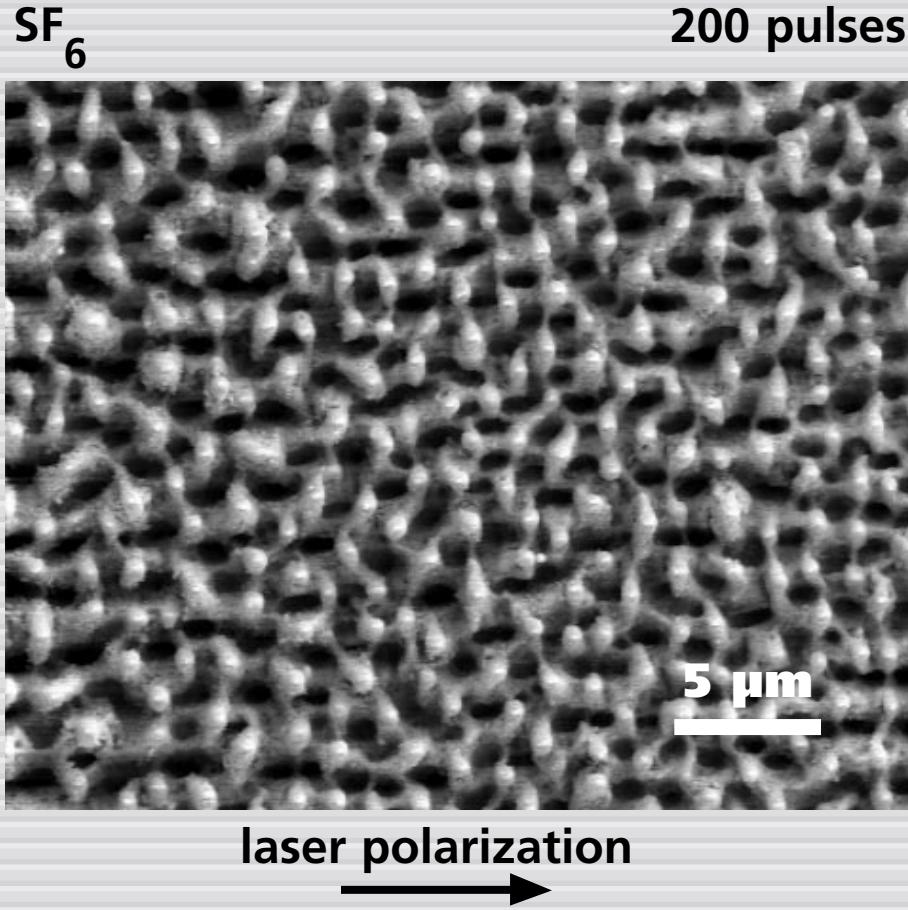
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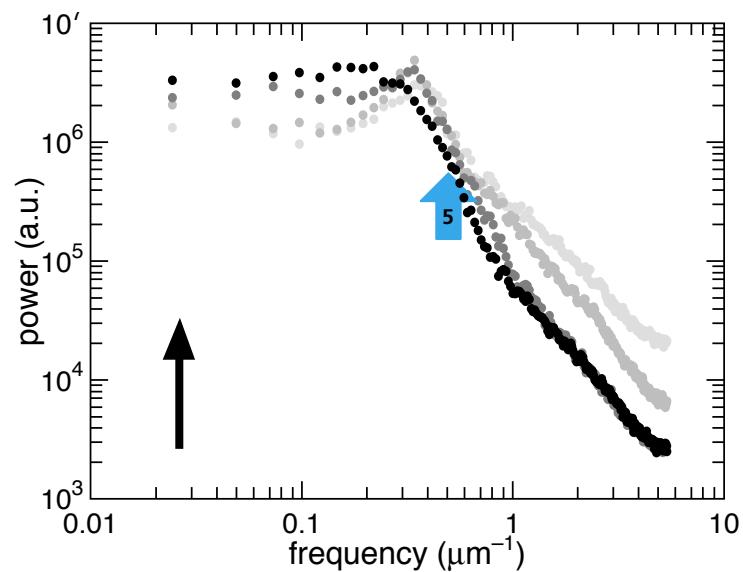
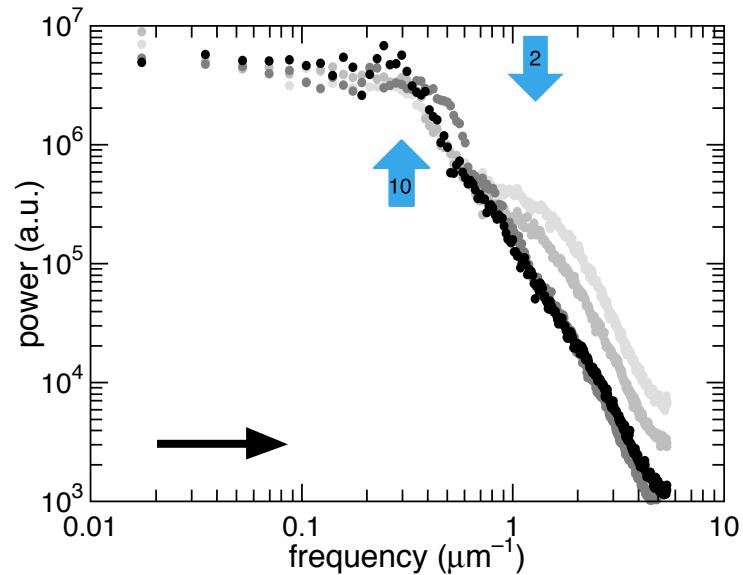
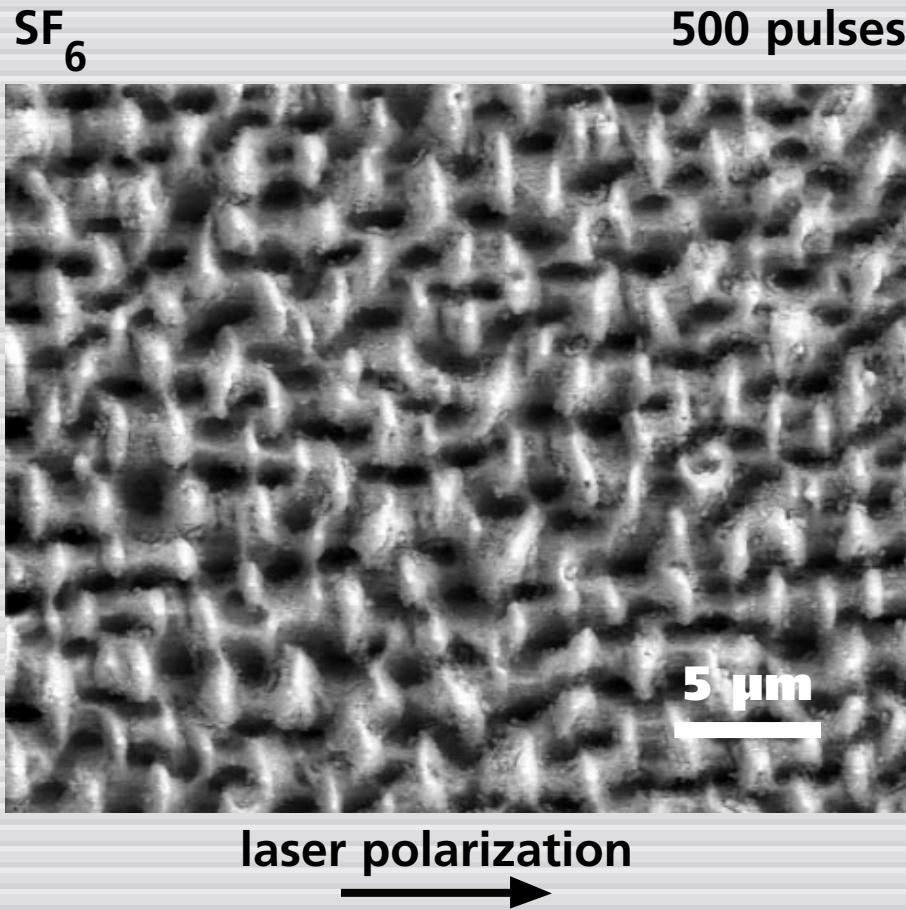
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Formation



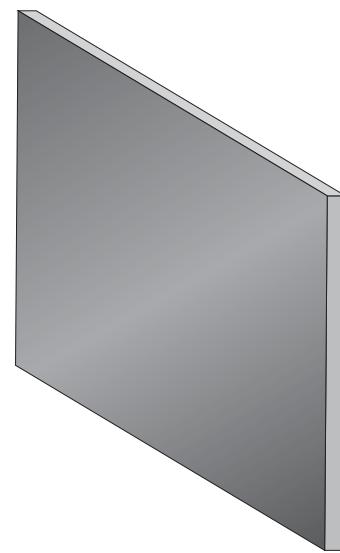
Formation



Outlook

can ordering of spikes be improved by using a grid?

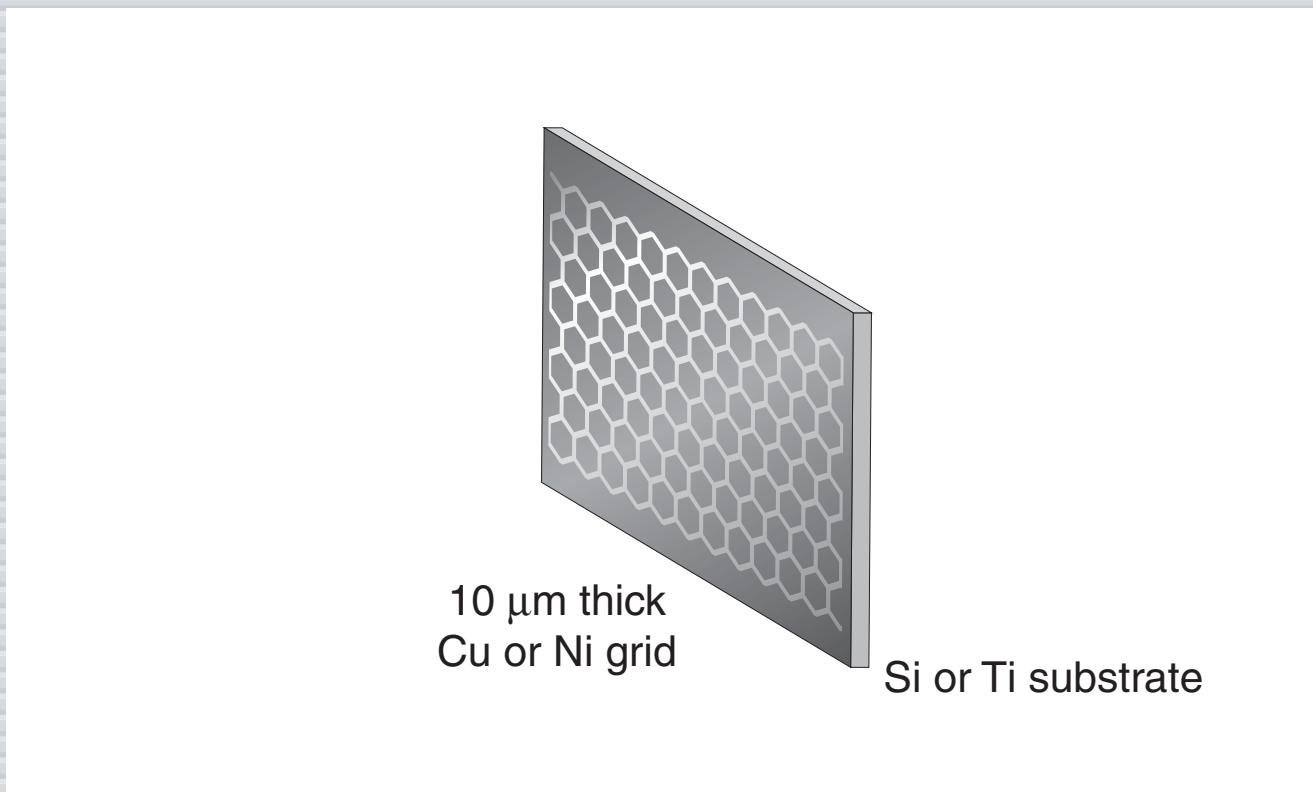
Outlook



Si or Ti substrate

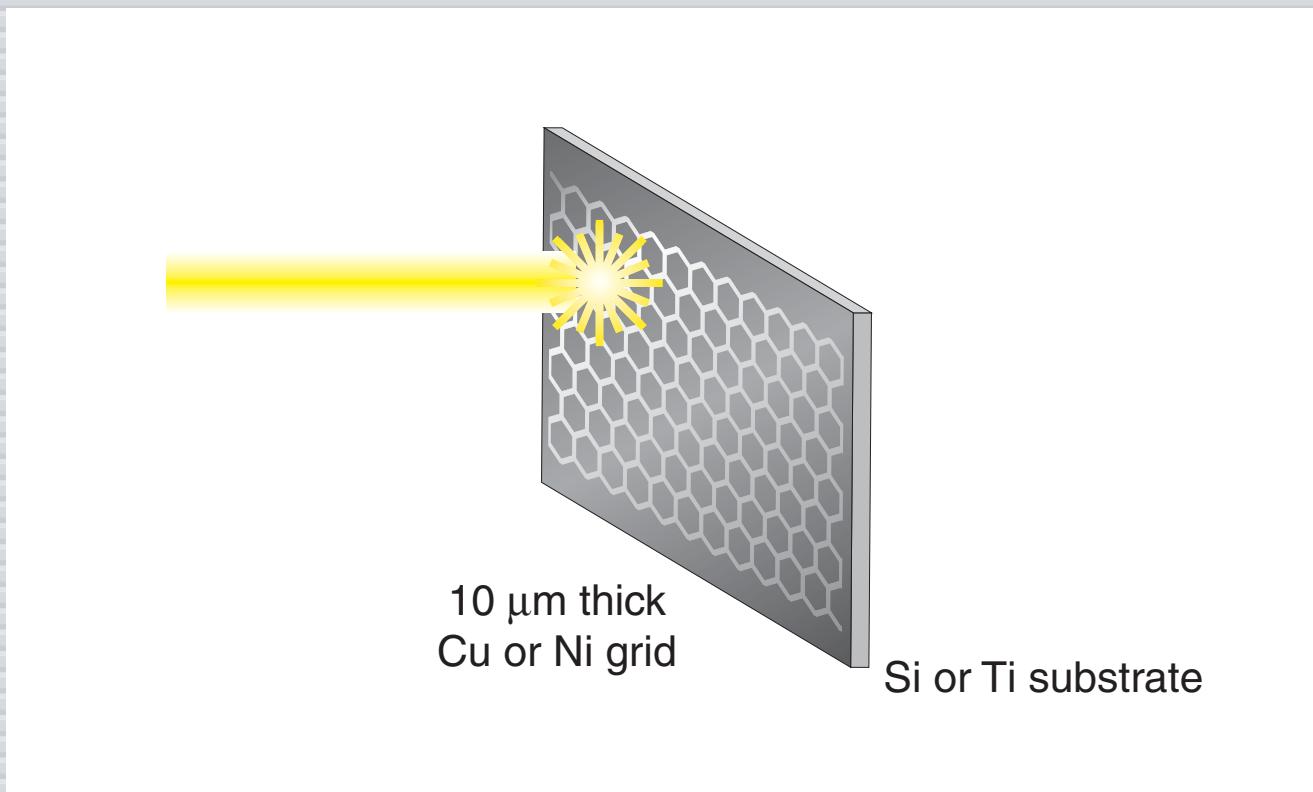
Outlook

place grid in front of substrate



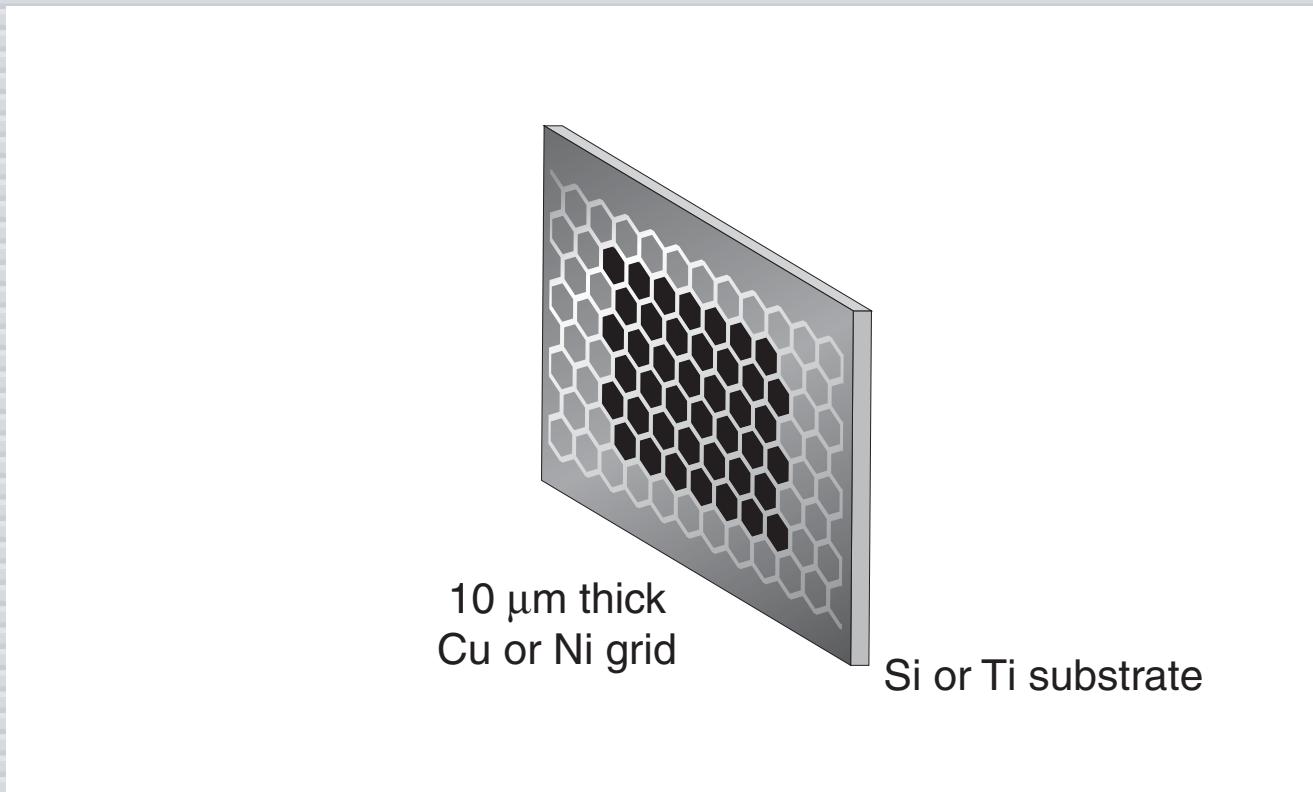
Outlook

scan laser beam



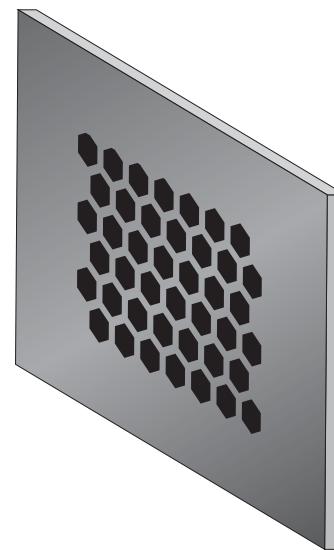
Outlook

scan laser beam

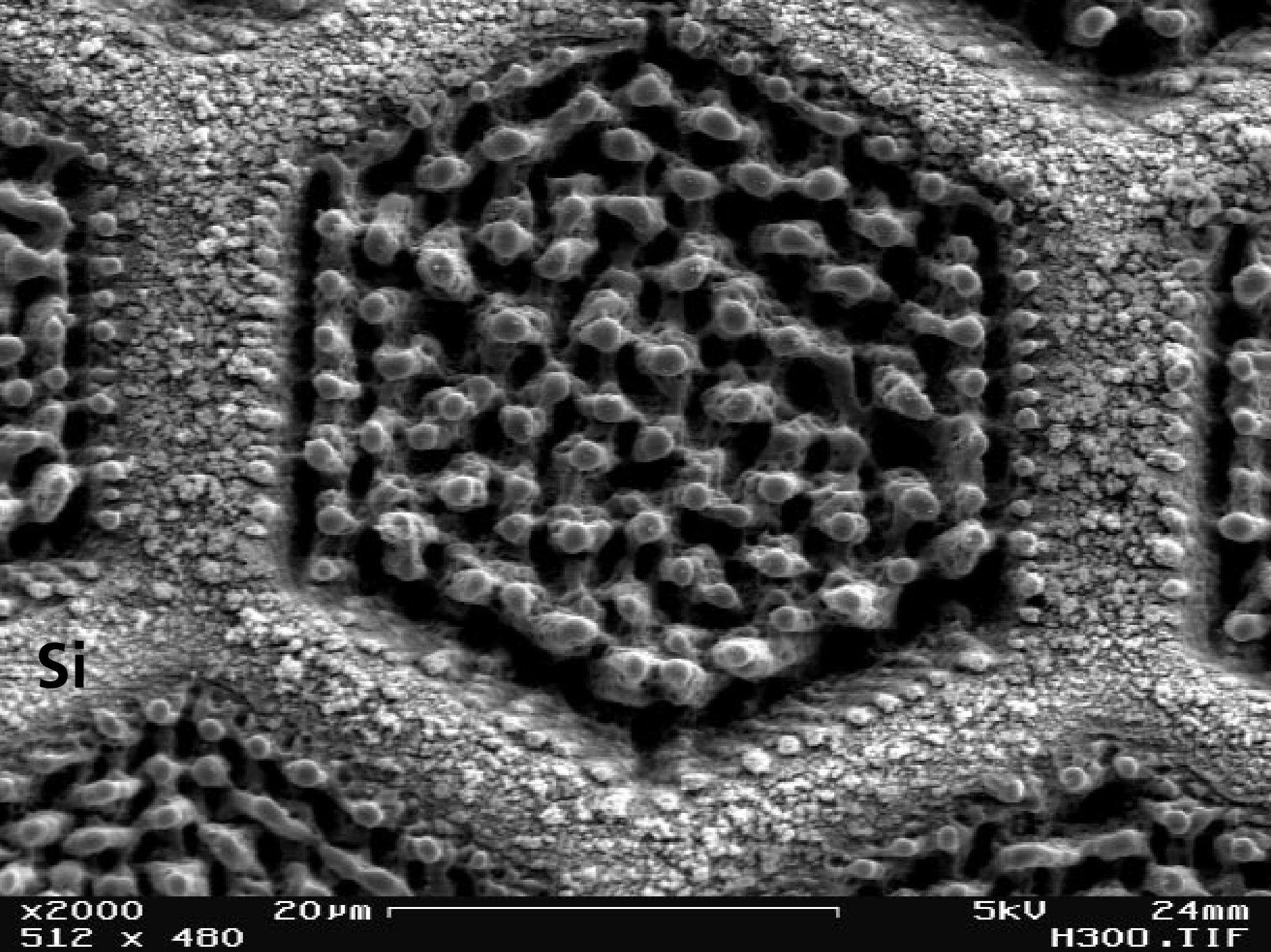


Outlook

remove grid



Si or Ti substrate



x2000

512 x 480

20 μm

5kV

24mm

H300.TIF

Ti

20 μm

5kV 17mm

Ti

10 μm

5kV

17mm

Outlook

Summary

Microstructured silicon

- ▶ **fabricated by simple, maskless process**

Summary

Microstructured silicon

- ▶ **fabricated by simple, maskless process**
- ▶ **can be integrated with microelectronics**

Summary

Microstructured silicon

- ▶ **fabricated by simple, maskless process**
- ▶ **can be integrated with microelectronics**
- ▶ **generates IR photocurrent**

Summary

Microstructured silicon

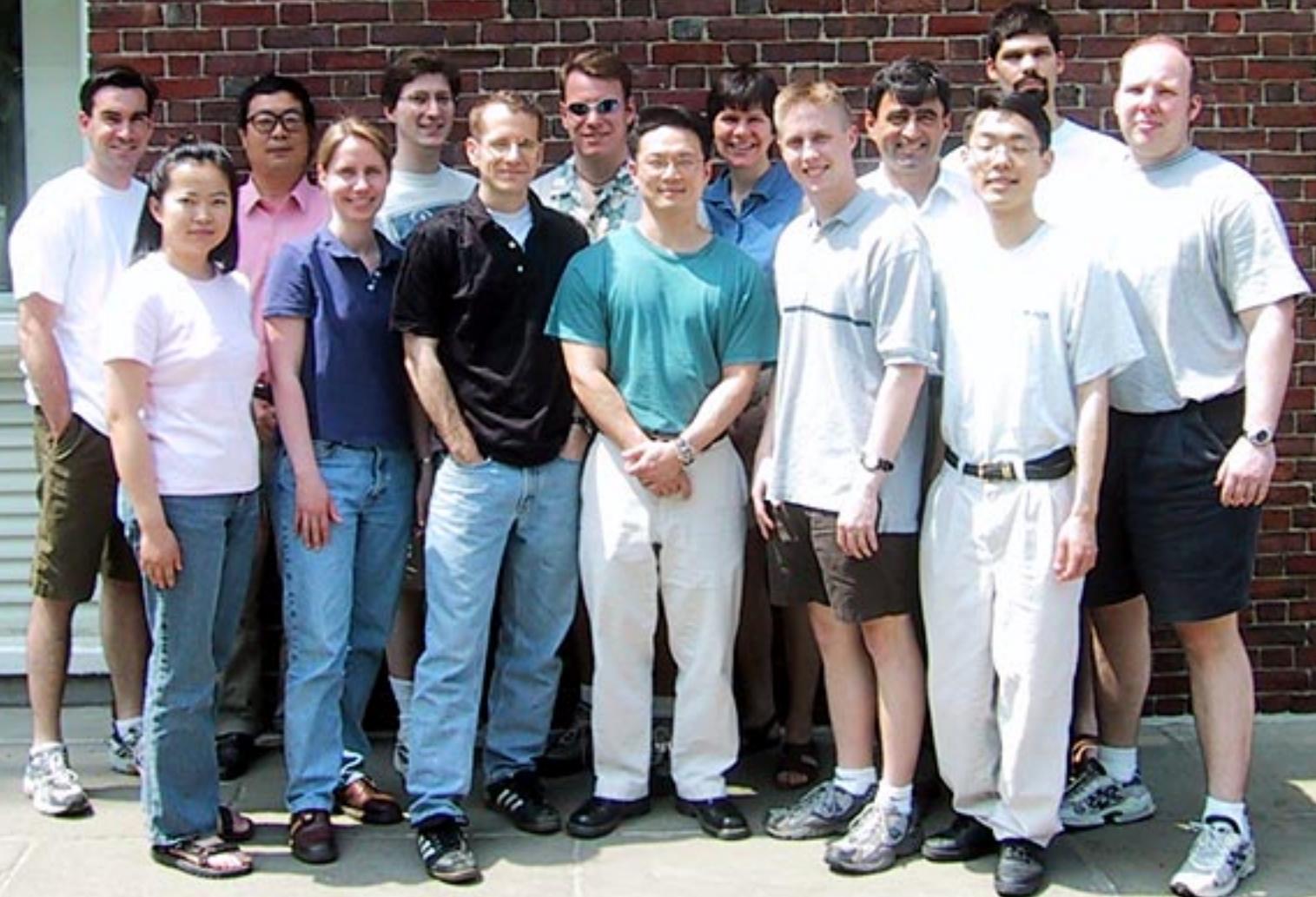
- ▶ **fabricated by simple, maskless process**
- ▶ **can be integrated with microelectronics**
- ▶ **generates IR photocurrent**
- ▶ **provides stable, high field emission current**

Summary

Microstructured silicon

- ▶ **fabricated by simple, maskless process**
- ▶ **can be integrated with microelectronics**
- ▶ **generates IR photocurrent**
- ▶ **provides stable, high field emission current**
- ▶ **is durable**

CORDON MCKAY
LABORATORY OF
APPLIED SCIENCE



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Dr. François Génin (LLNL)

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Dr. Alf Bjørseth (Scanwafer)

Dr. Tom Mates (UCSB)

Dr. John Chervinsky (Harvard University)

Prof. Cynthia Friend (Harvard University)

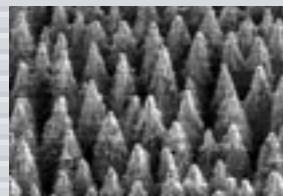
Prof. Mike Aziz (Harvard University)

**For a copy of this talk and
additional information, see:**

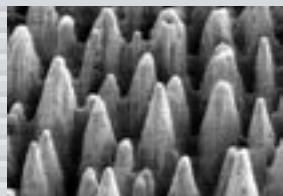
<http://mazur-www.harvard.edu>

Materials

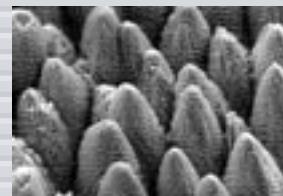
SF₆



Cl₂



N₂

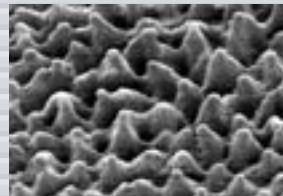


air



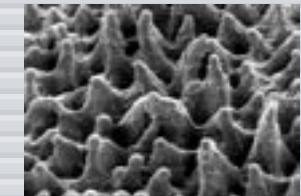
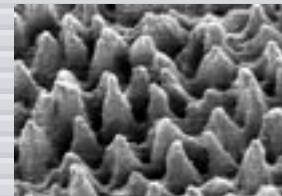
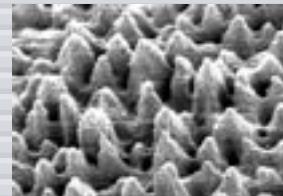
vacuum

Si

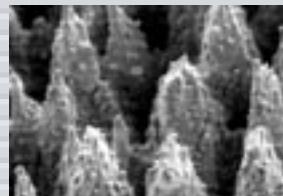


Ti

reacts



Only in SF₆:



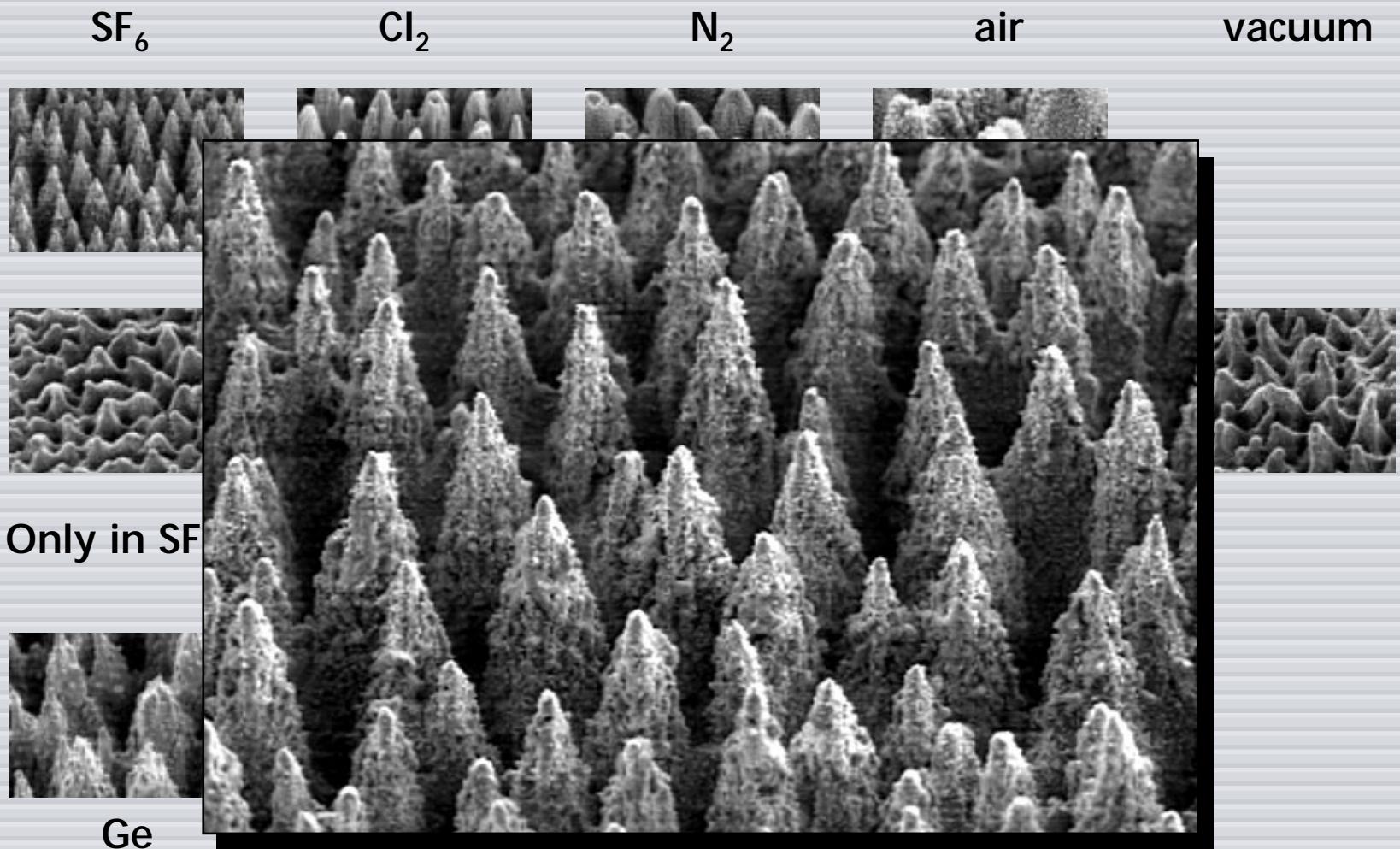
Ge



InP

No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

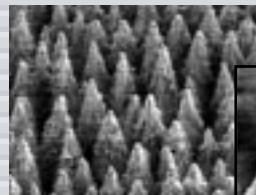
Materials



No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

SF₆



Cl₂



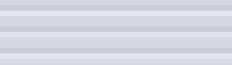
N₂



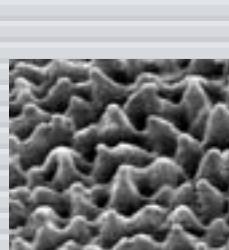
air



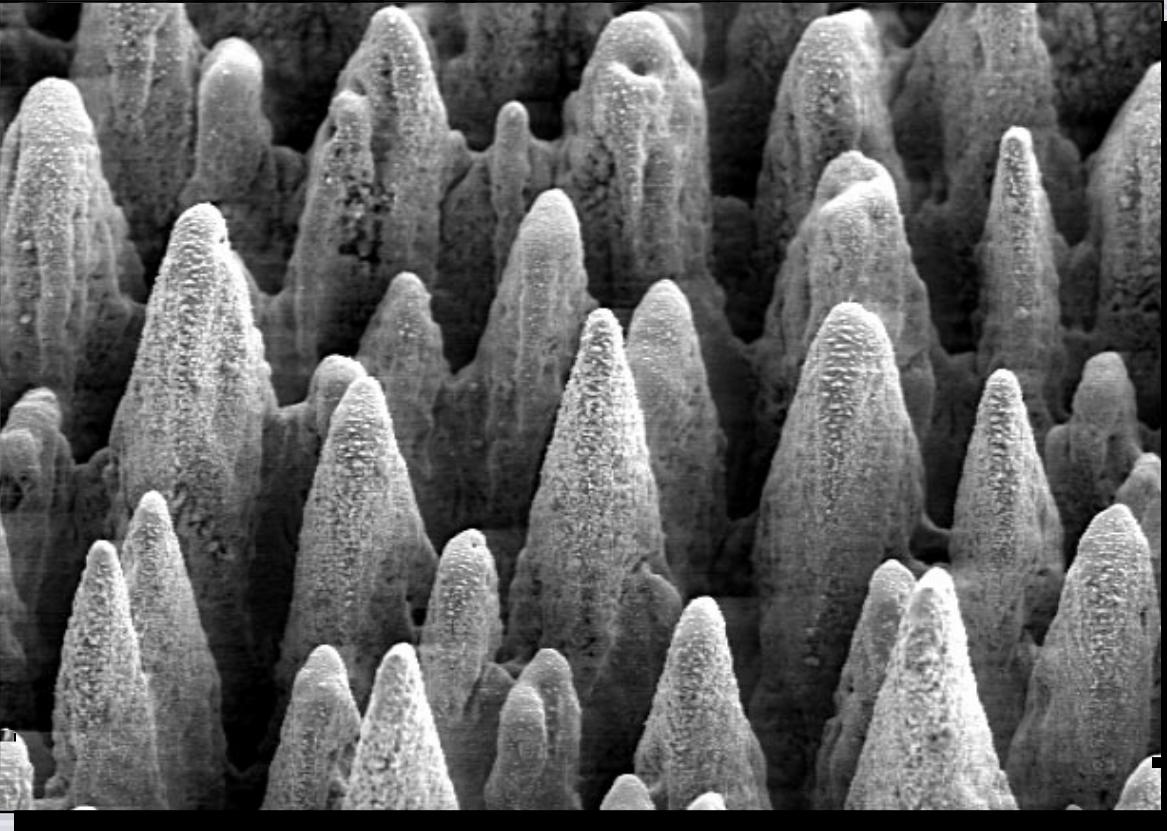
vacuum



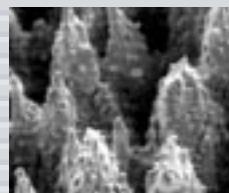
Si



Ti



Only in SF₆

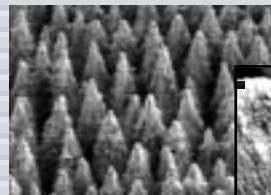


Ge

No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

SF₆



Cl₂



N₂

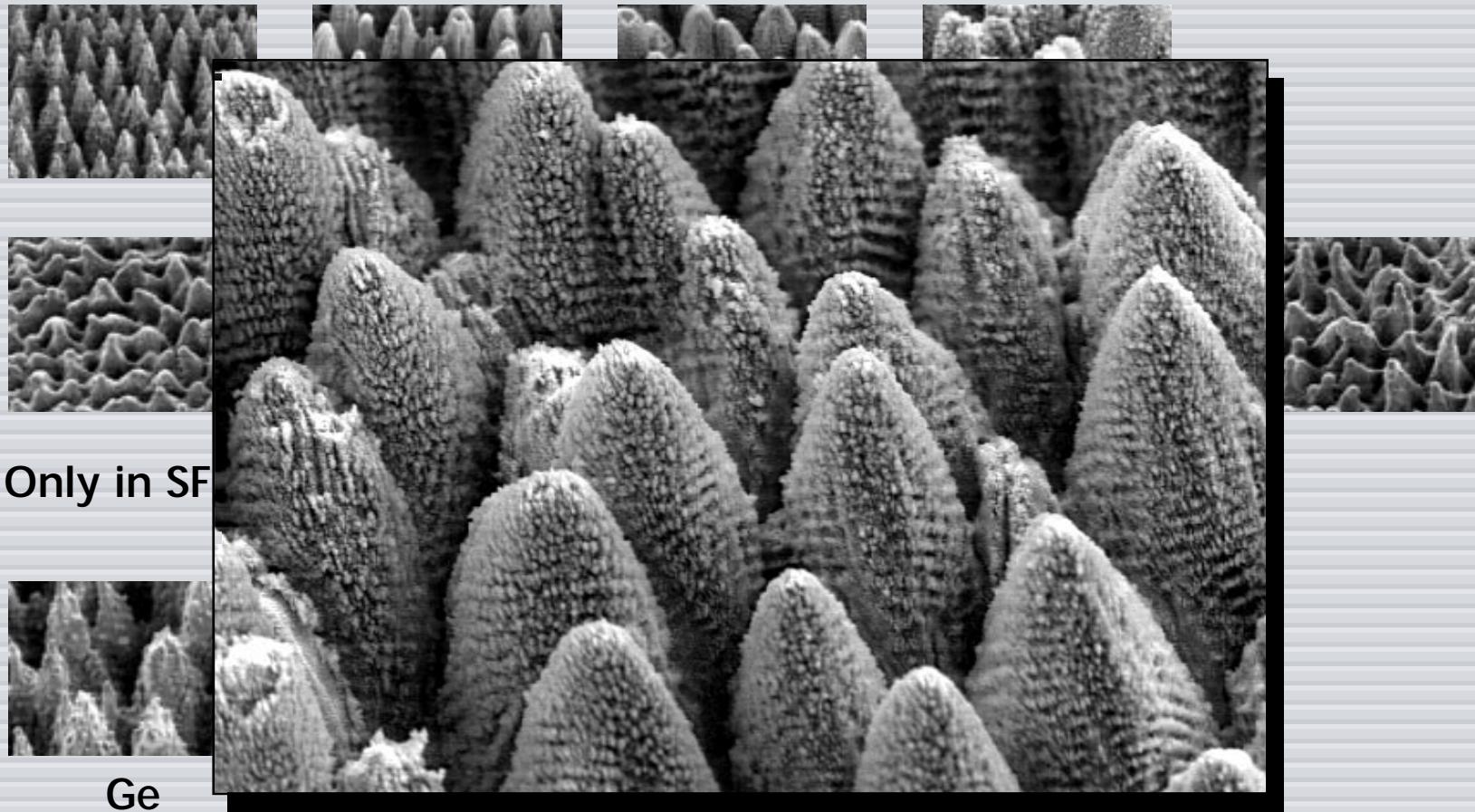


air

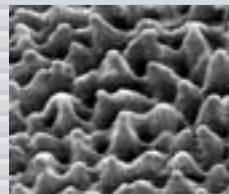


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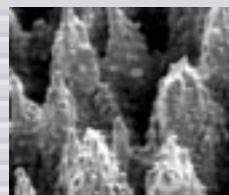
Si



Ti



Only in SF₆

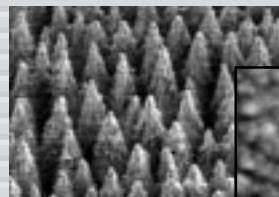


Ge

No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

SF₆



Cl₂



N₂



air

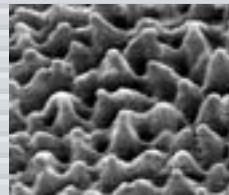


vacuum

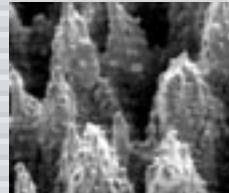
Si



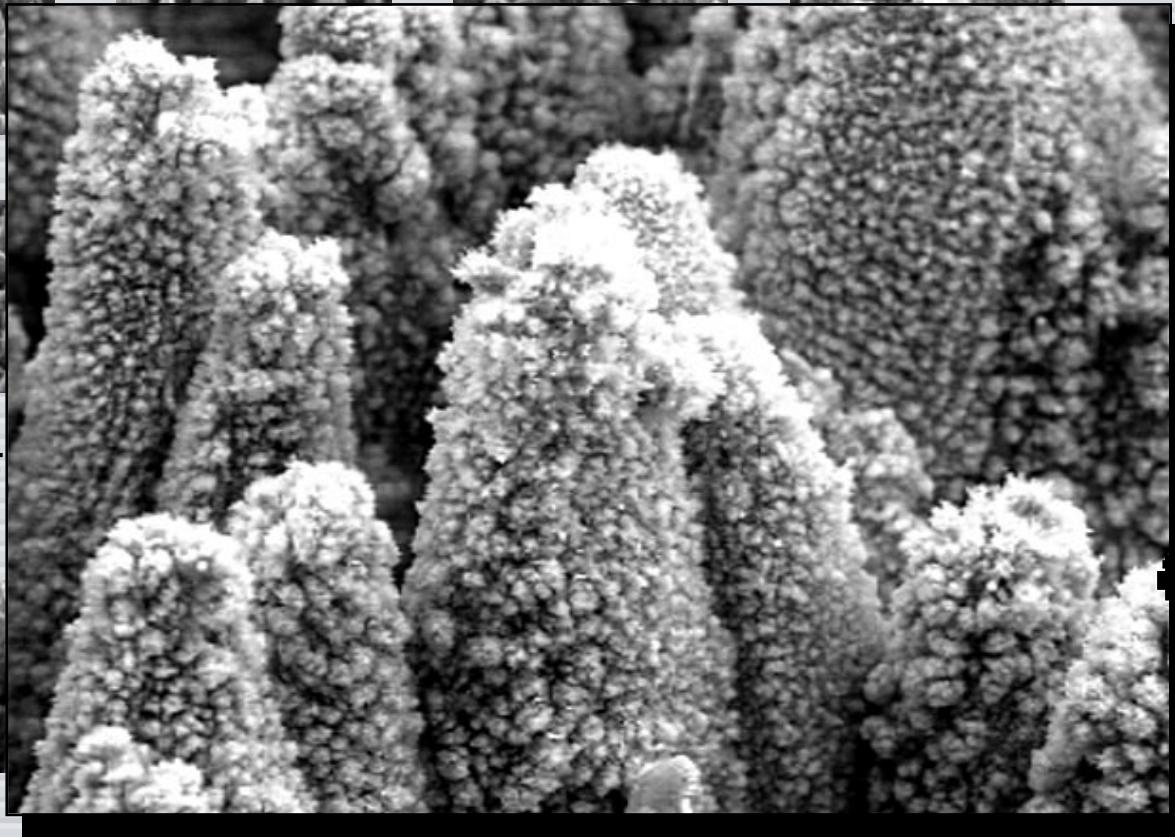
Ti



Only in SF₆



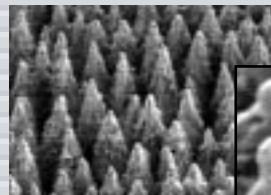
Ge



No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

SF₆



Cl₂



N₂

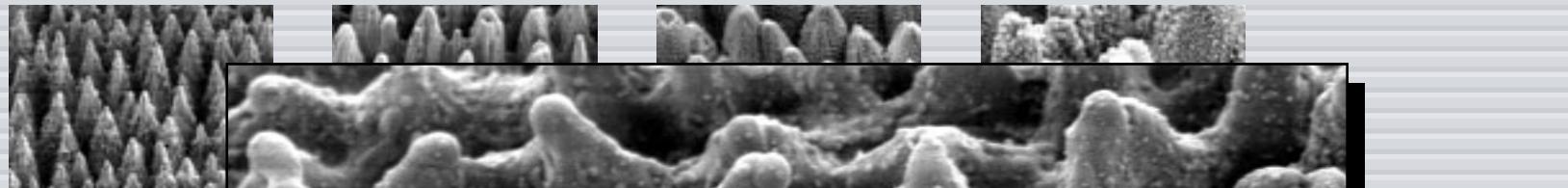


air

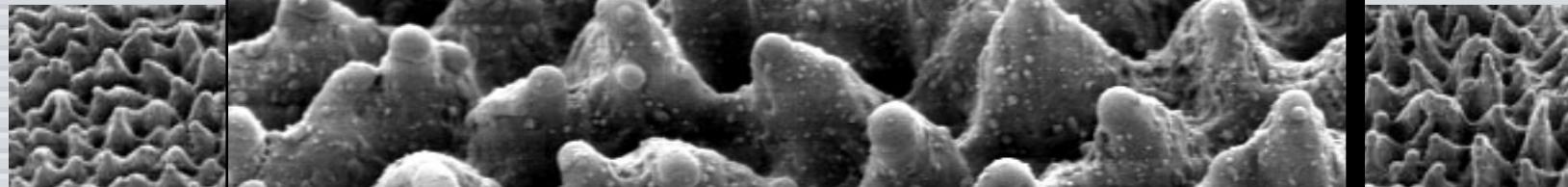


vacuum

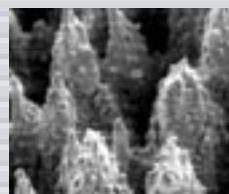
Si



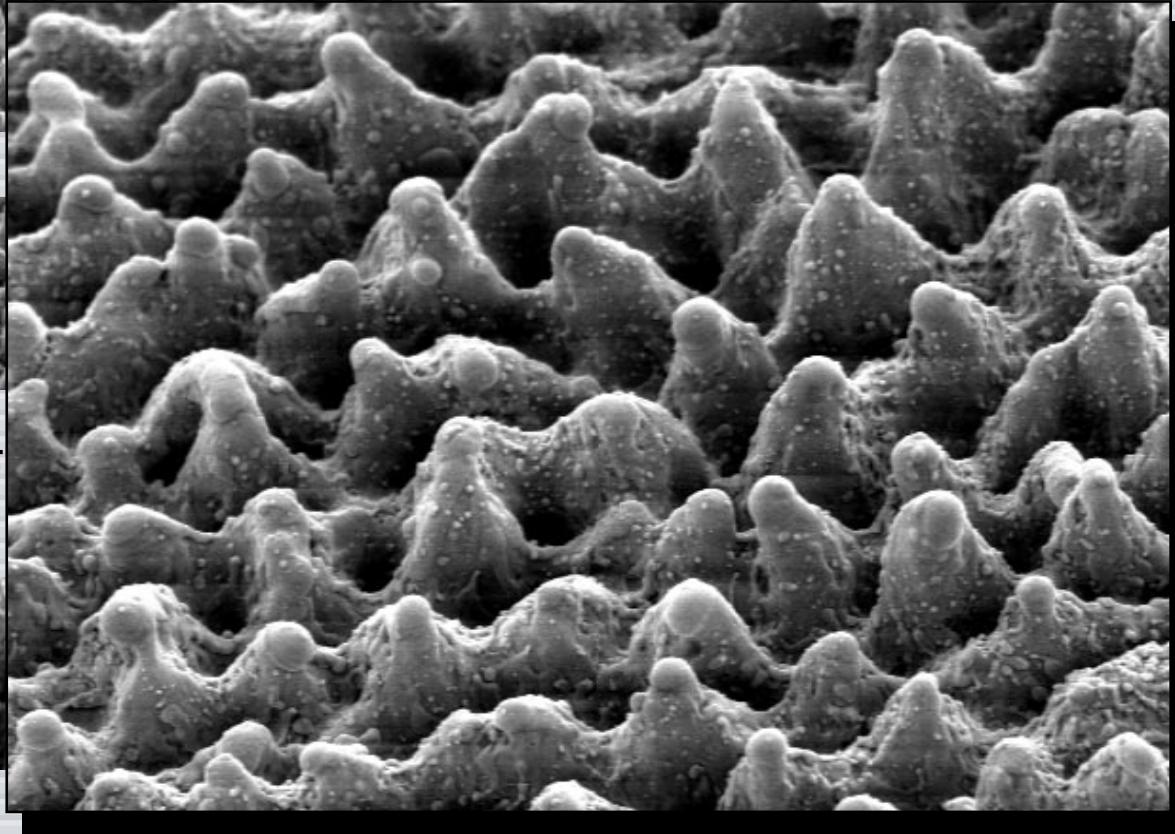
Ti



Only in SF₆

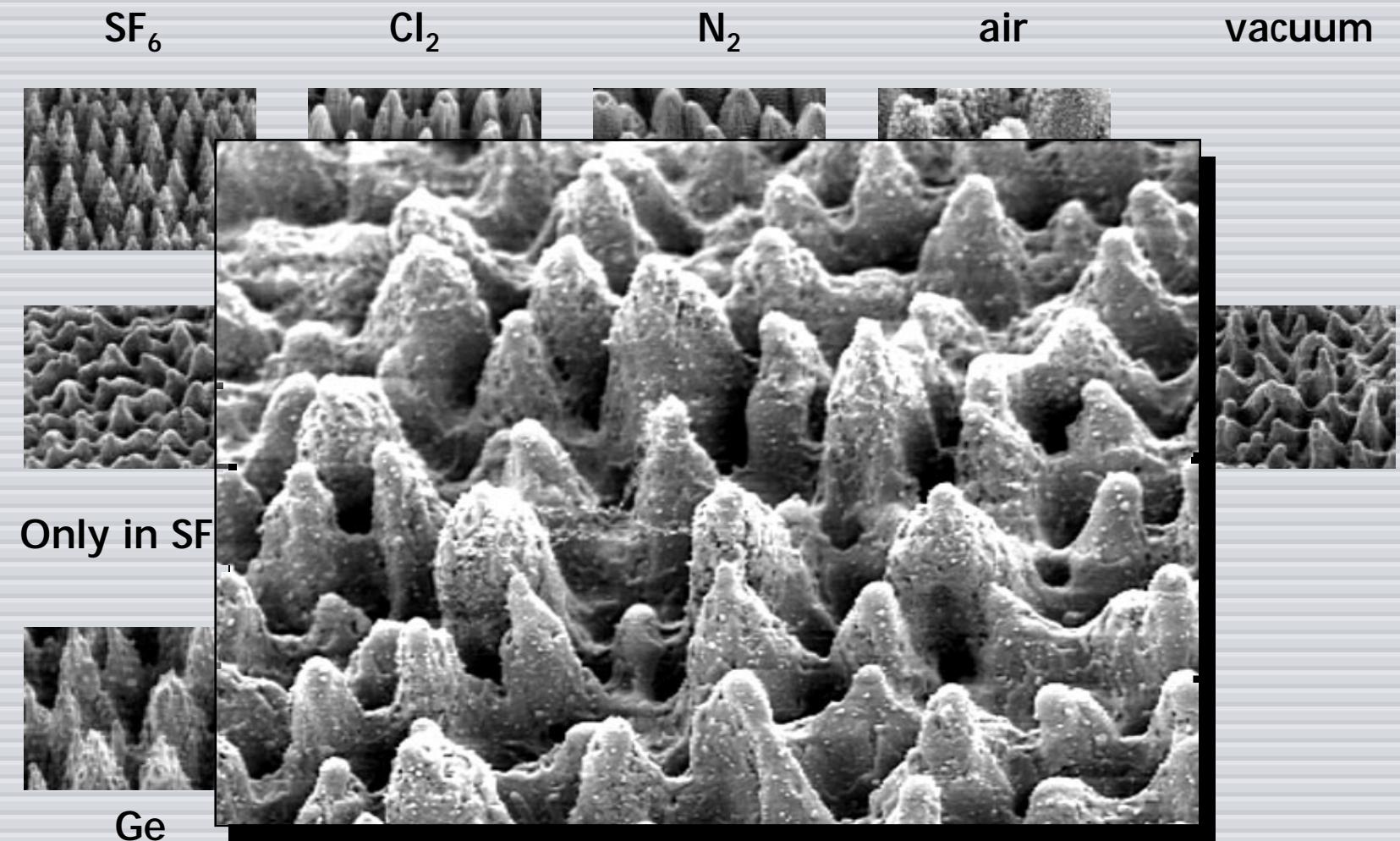


Ge



No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

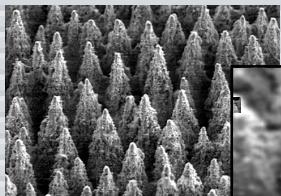
Materials



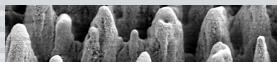
No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

SF₆



Cl₂



N₂

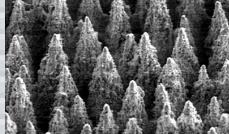


air

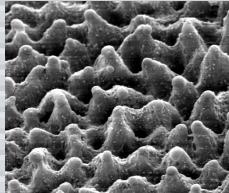


vacuum

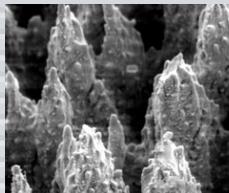
Si



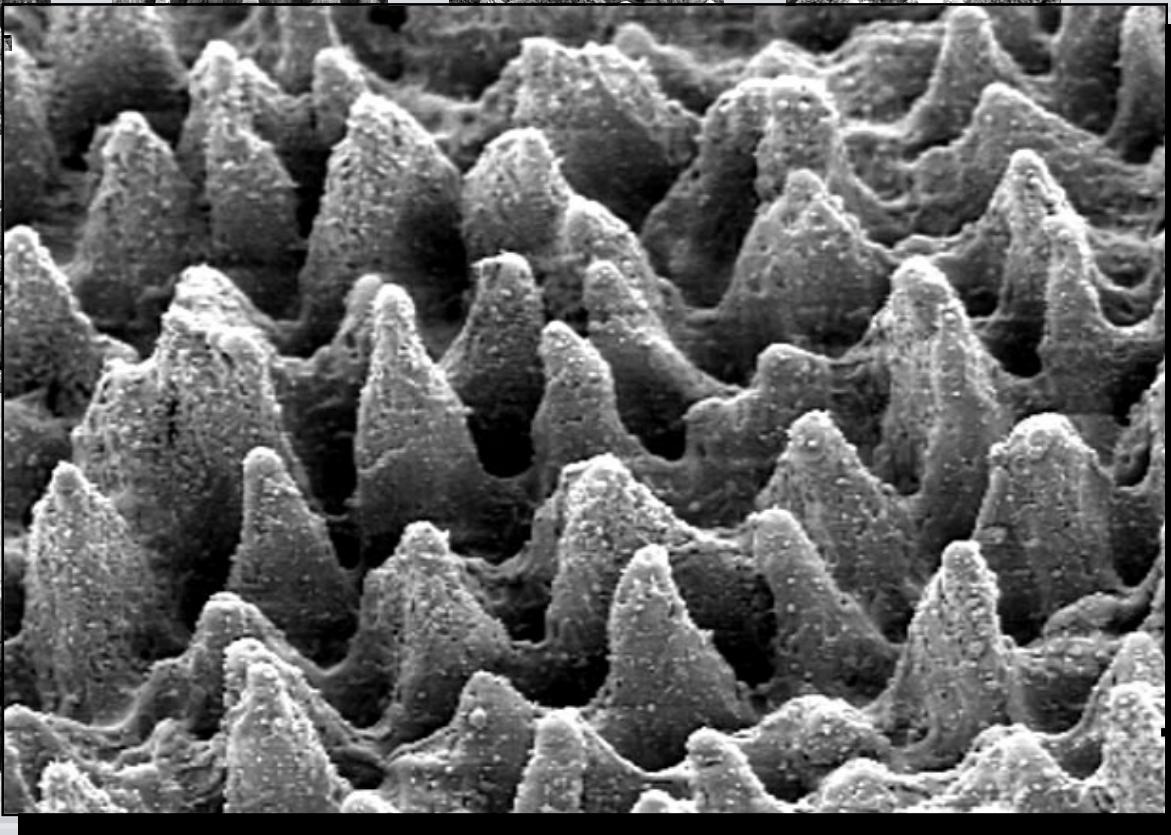
Ti



Only in SF₆



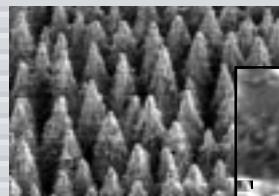
Ge



No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

SF₆



Cl₂



N₂

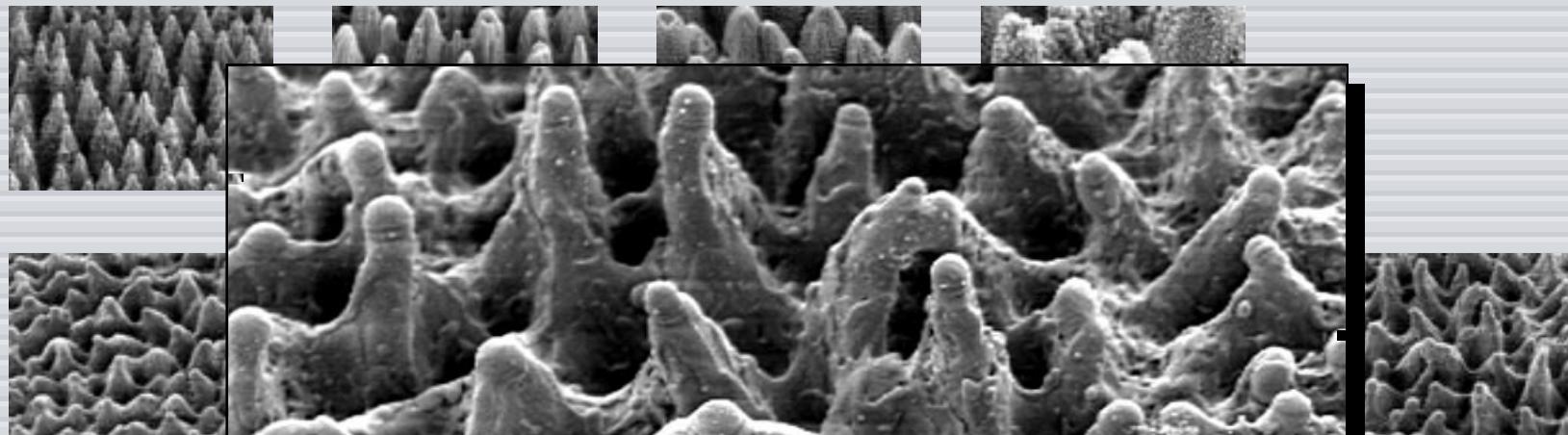


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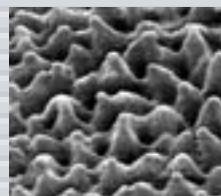


vacuum

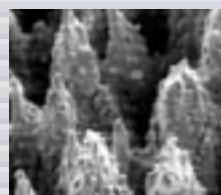
Si



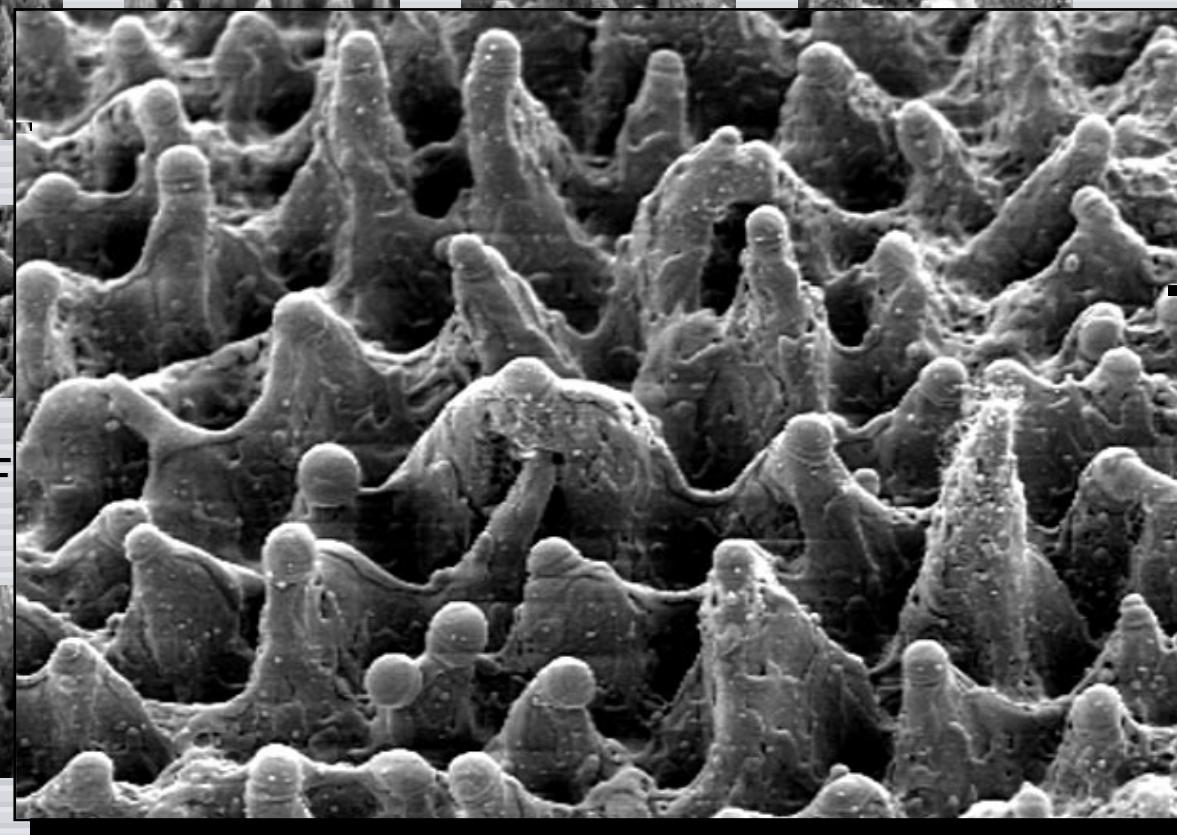
Ti



Only in SF₆



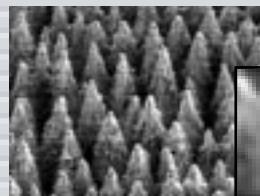
Ge



No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

SF₆



Cl₂



N₂

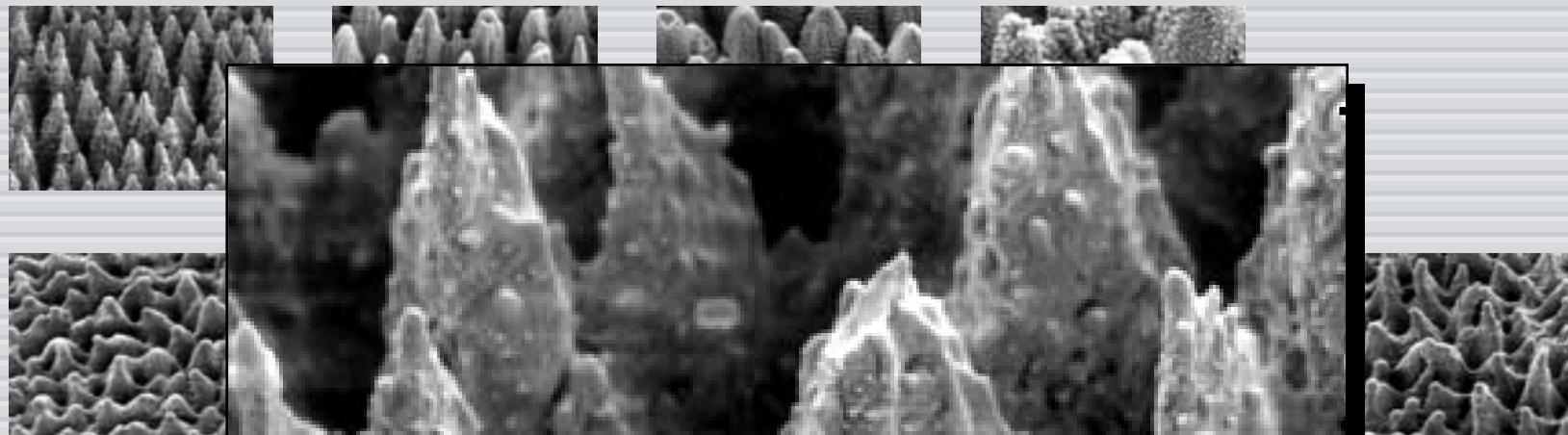


air

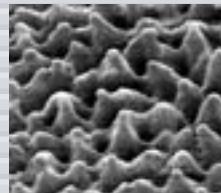


vacuum

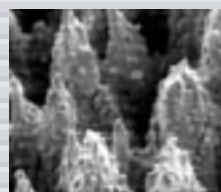
Si



Ti



Only in SF₆

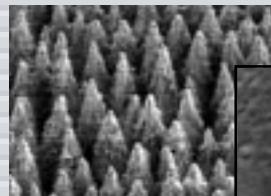


Ge

No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

SF₆



Cl₂



N₂

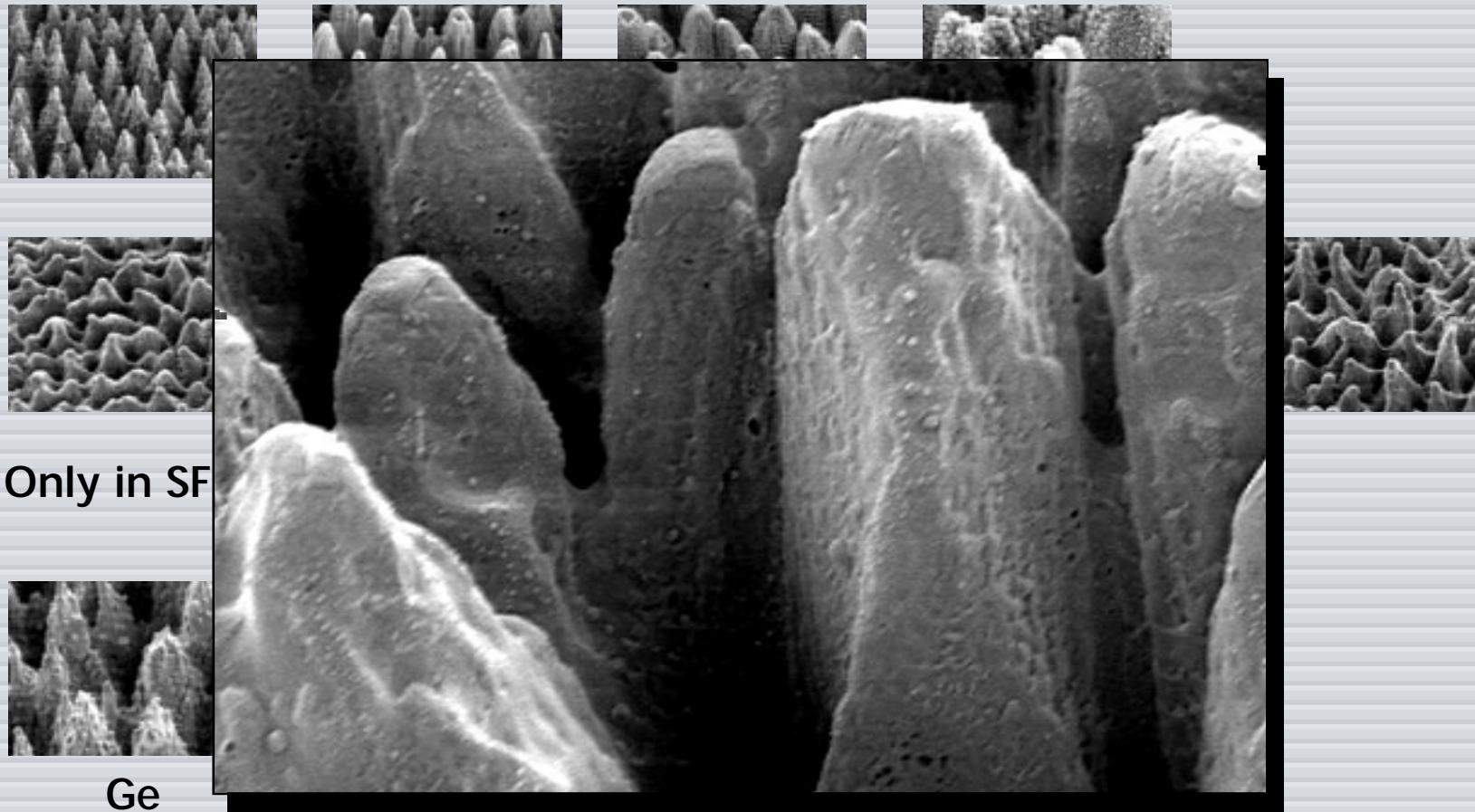


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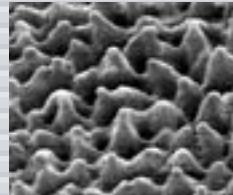


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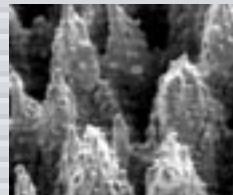
Si



Ti



Only in SF₆



Ge

No spikes in SF₆: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs