

Femtosecond laser-assisted microstructuring of silicon for novel detector, sensing, and display technologies

Tsing-Hua Her

Claudia Wu

Jim Carey

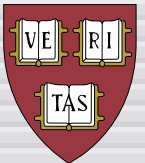
Mike Sheehy

Brian Tull

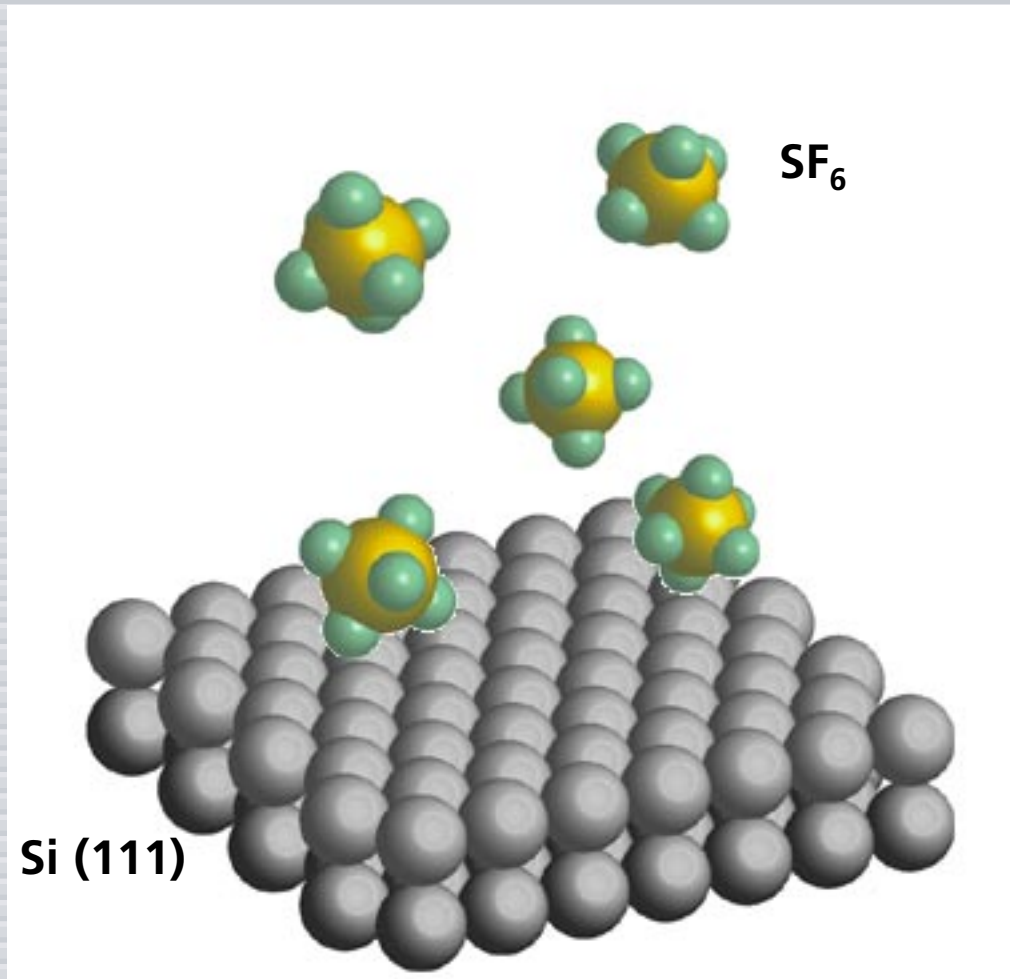
Meng Yan Shen

Catherine Crouch

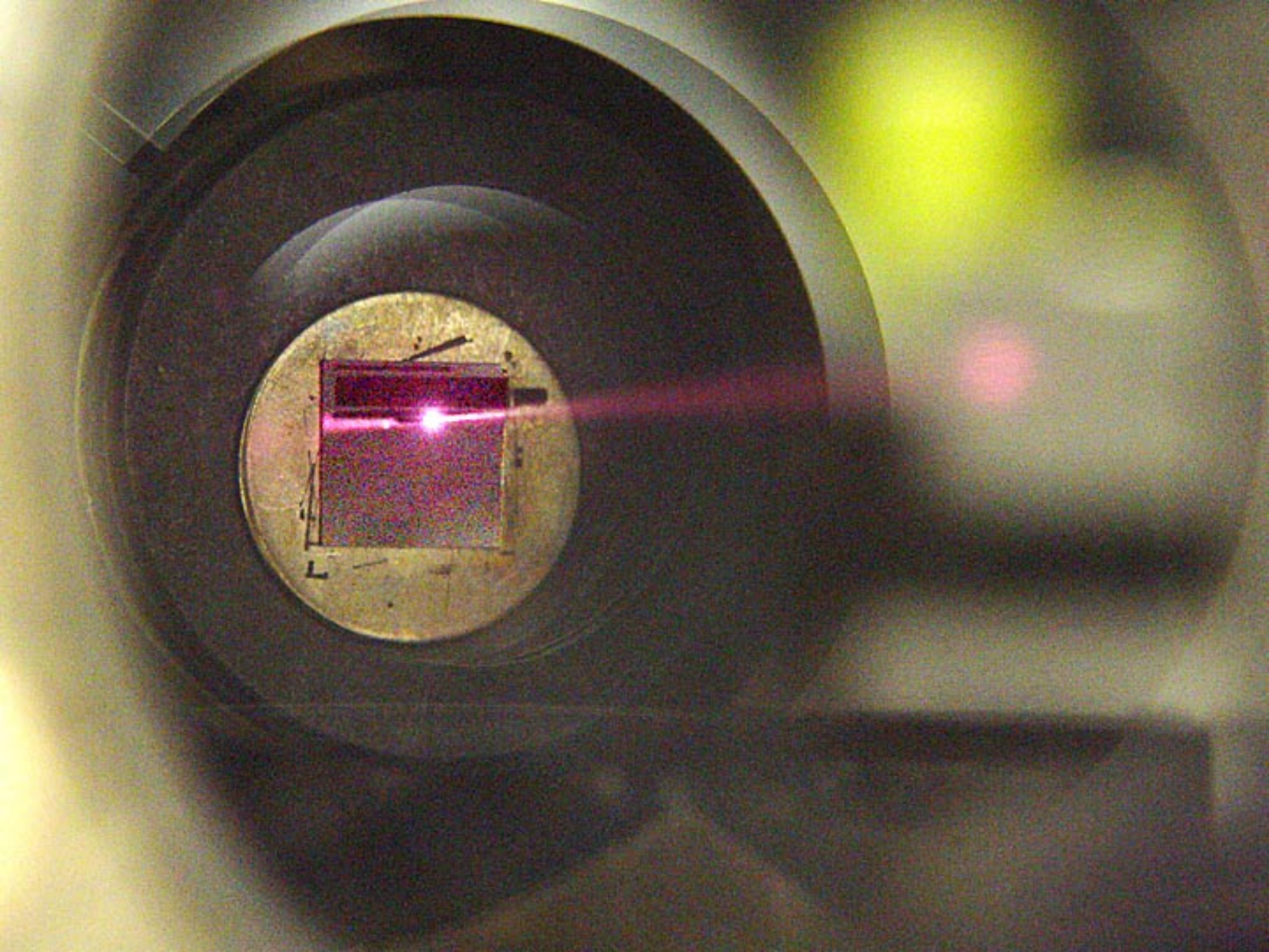
Cynthia Friend



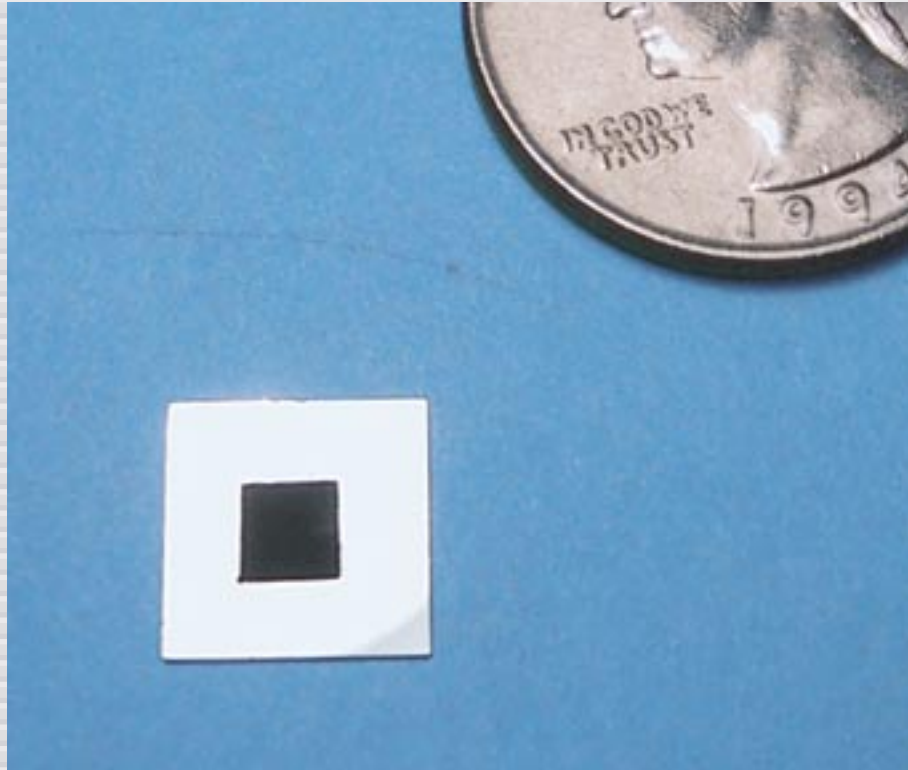
Introduction



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



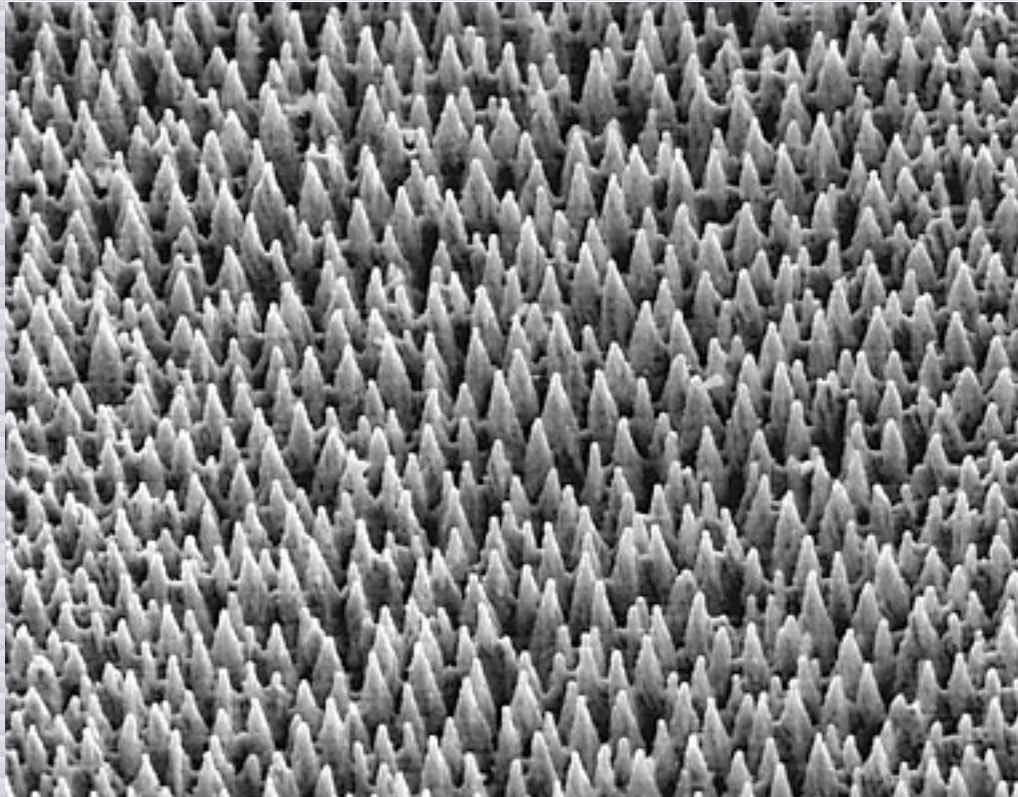
Introduction



'black silicon'

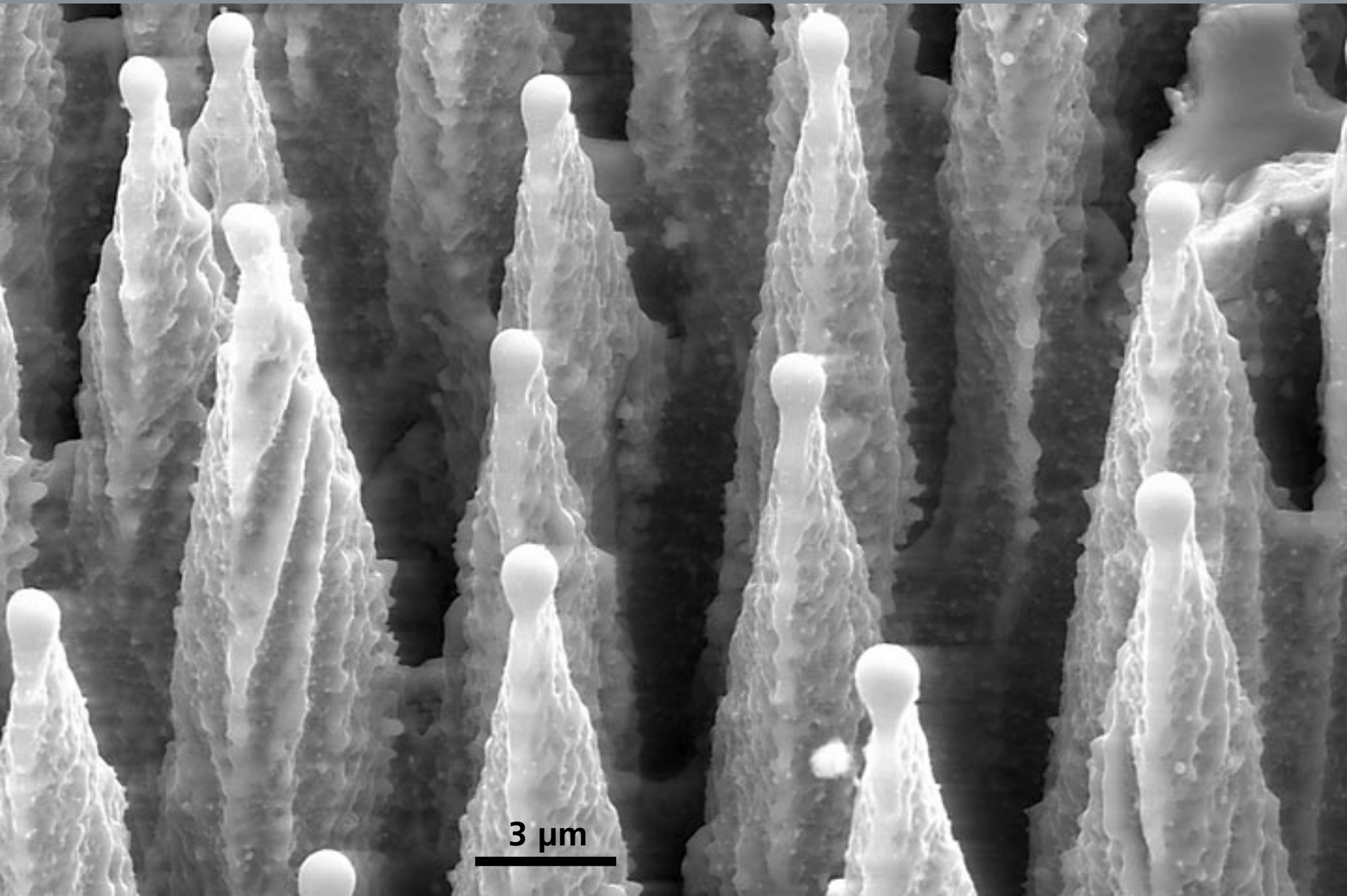
Appl. Phys. Lett. 73, 1673 (1998)

Introduction

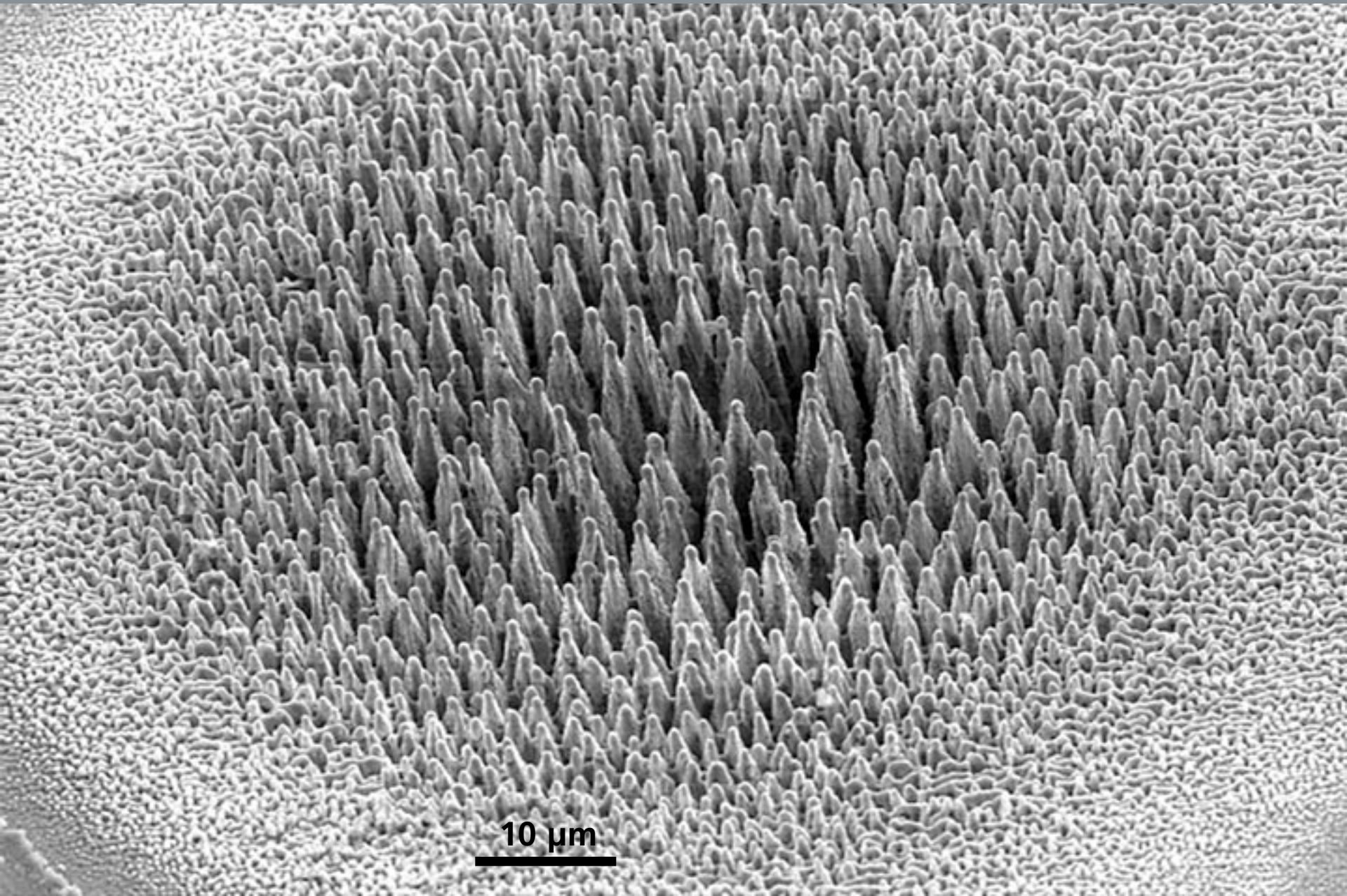


20 μm

Introduction

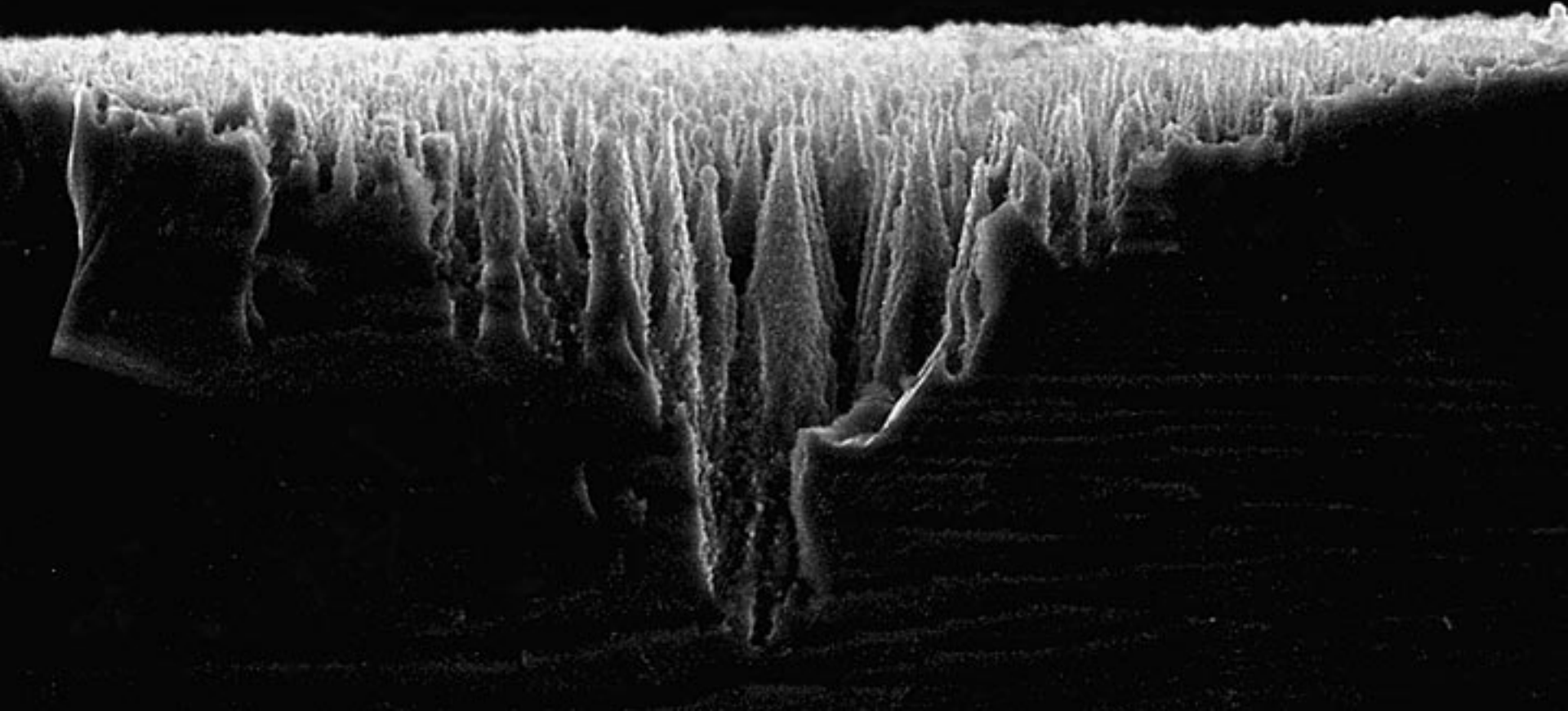


Introduction



10 μm

Introduction



Introduction

Introduction

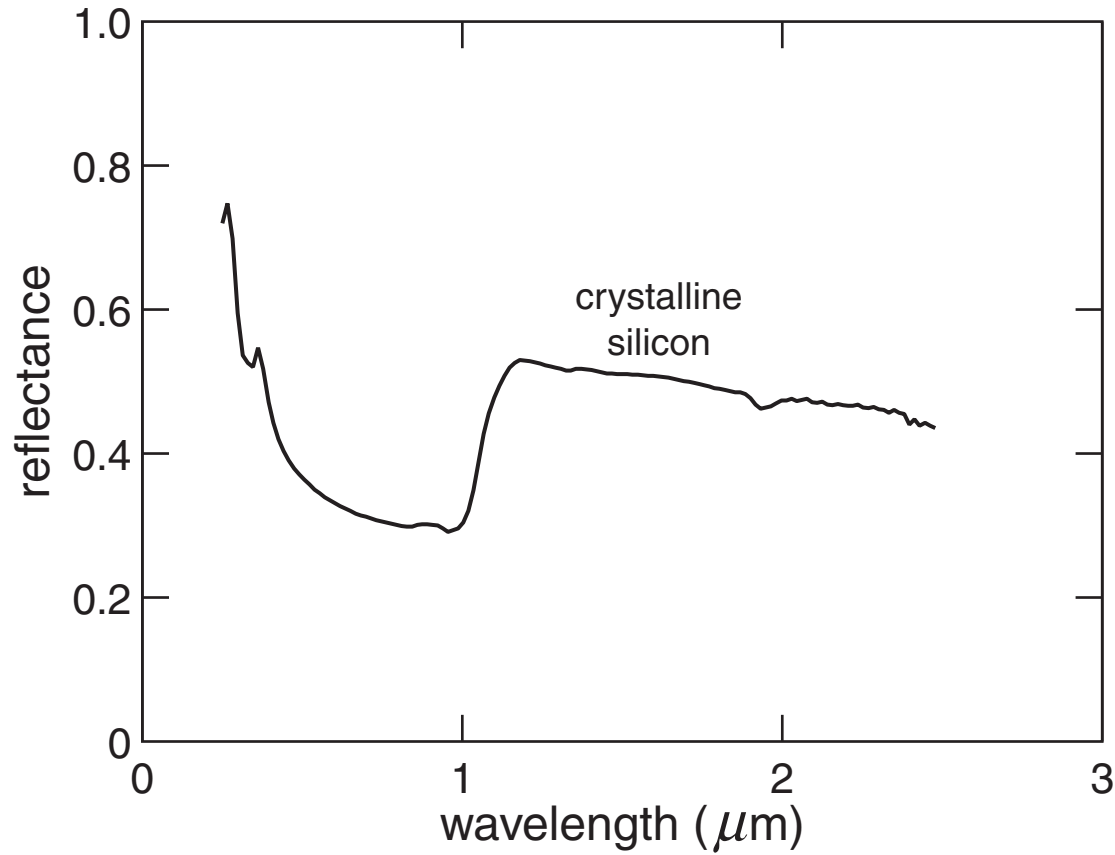
- ▶ **maskless etching process**
- ▶ **self-organized, tall, sharp structures**
- ▶ **nanoscale structure on spikes**

Outline

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

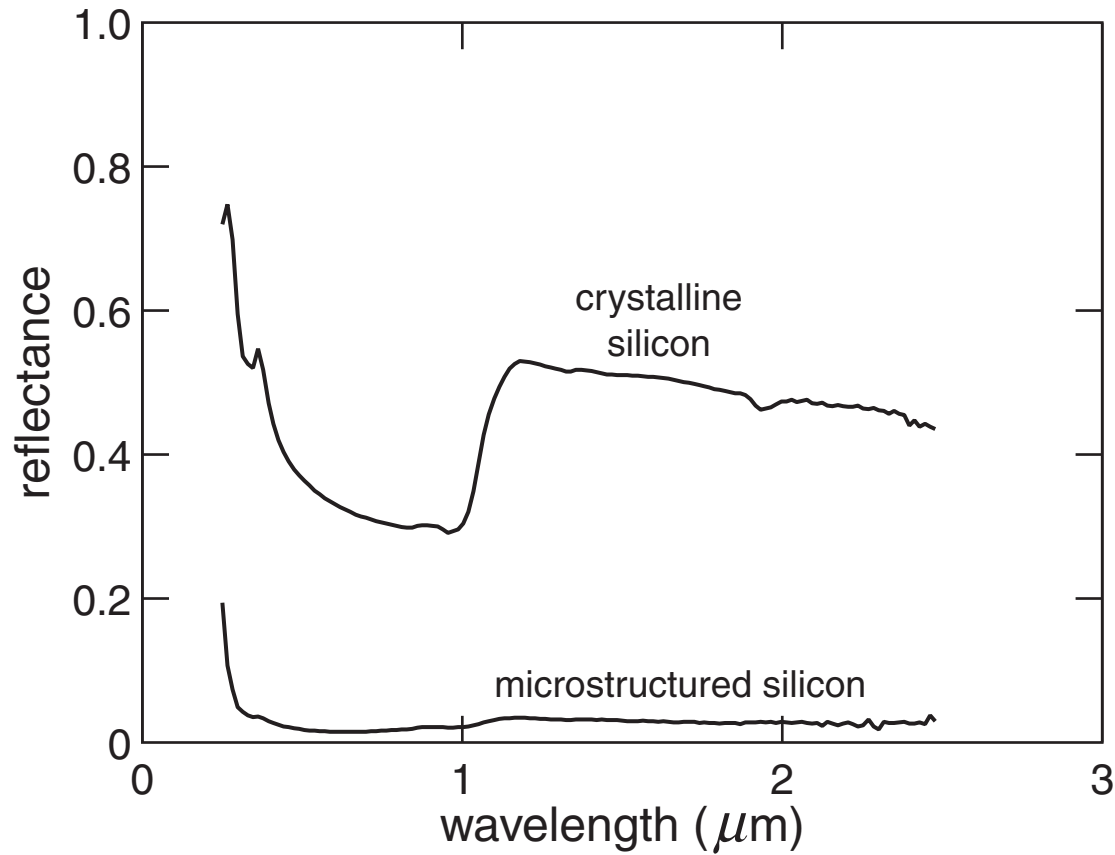
Properties

reflectance (integrating sphere)



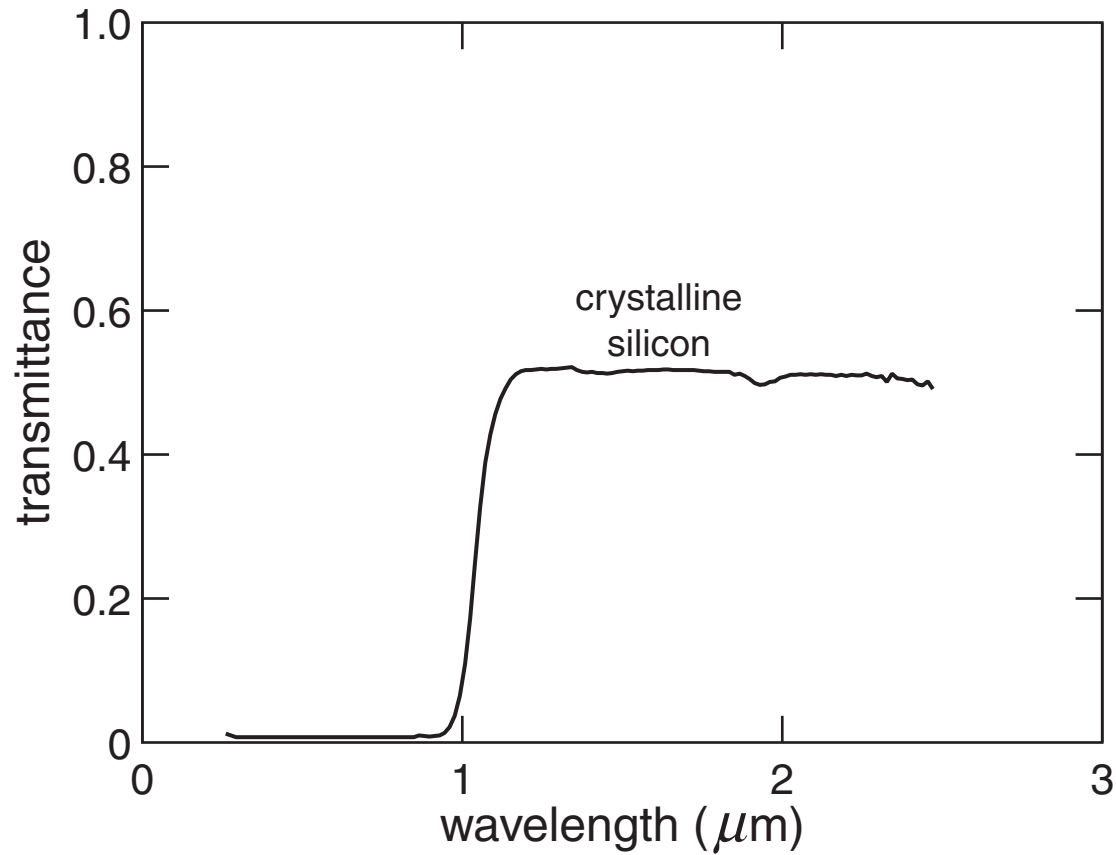
Properties

reflectance (integrating sphere)



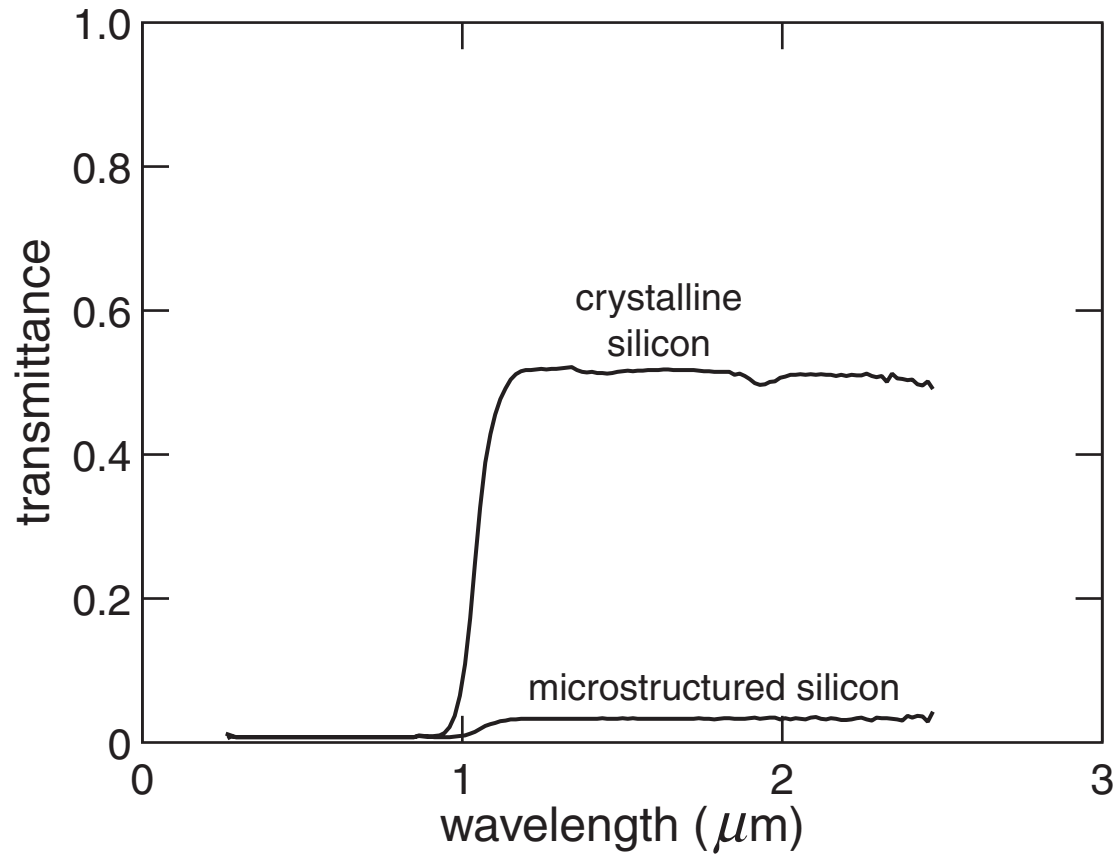
Properties

transmittance (integrating sphere)



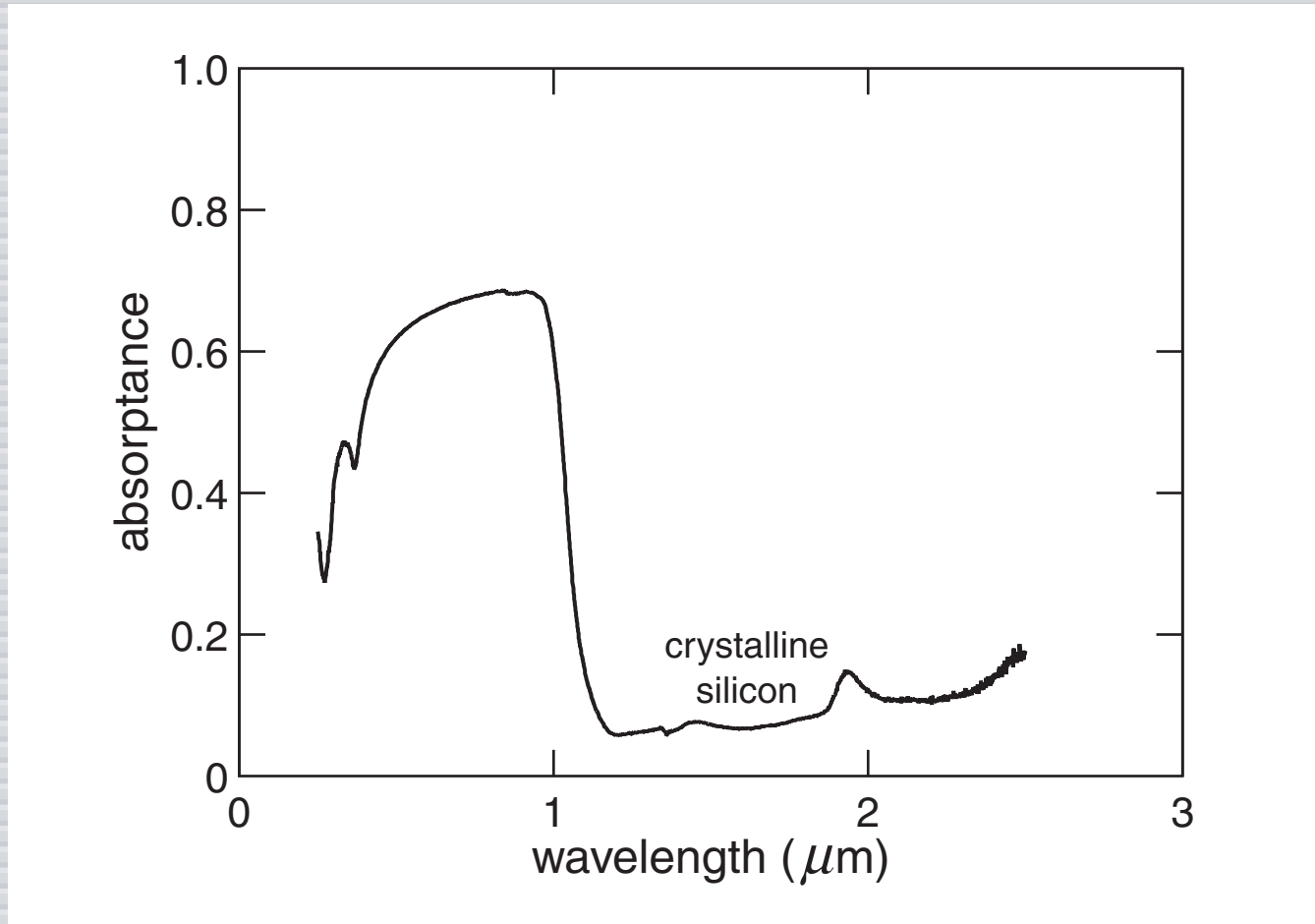
Properties

transmittance (integrating sphere)



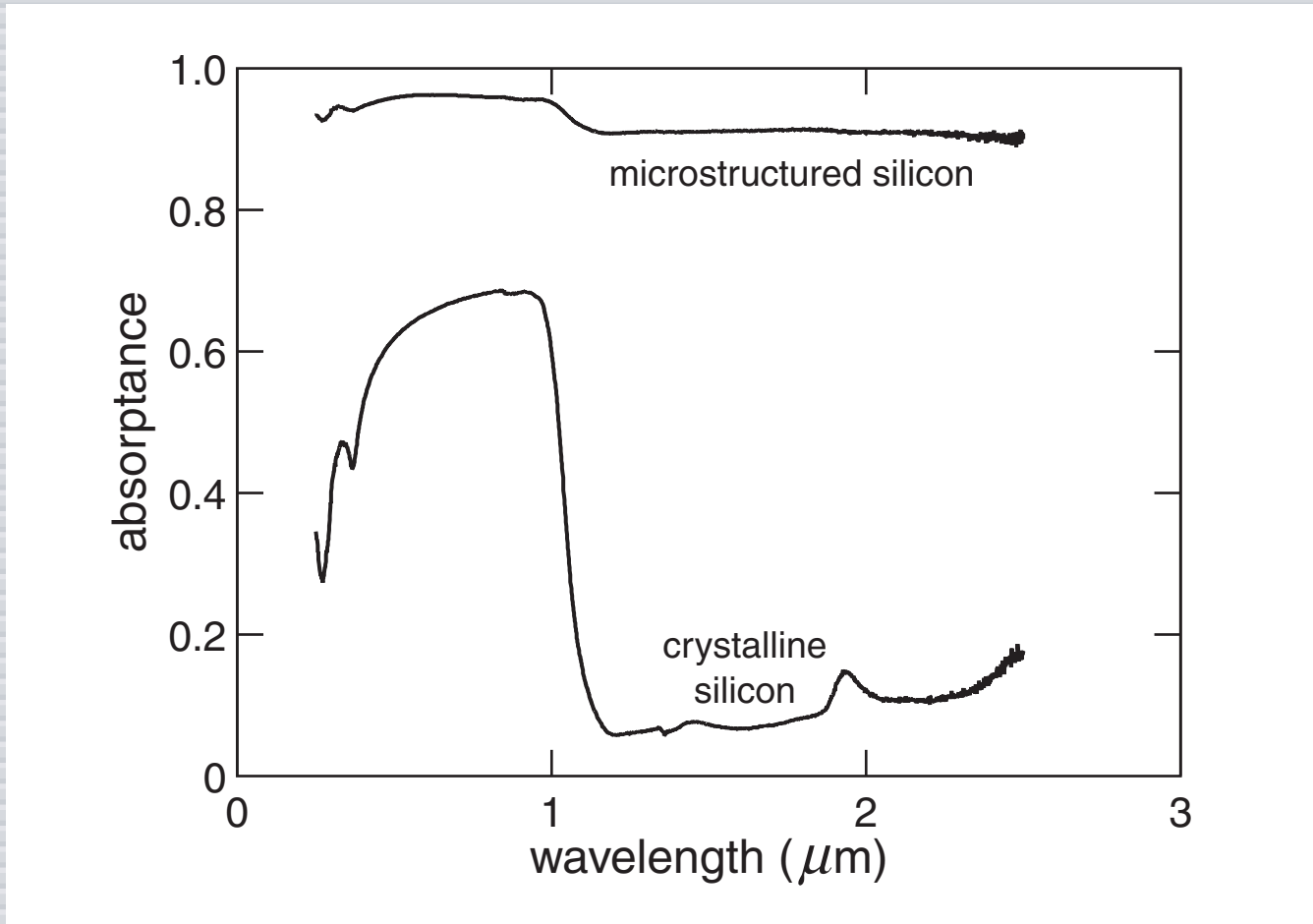
Properties

absorptance ($1 - R - T$)



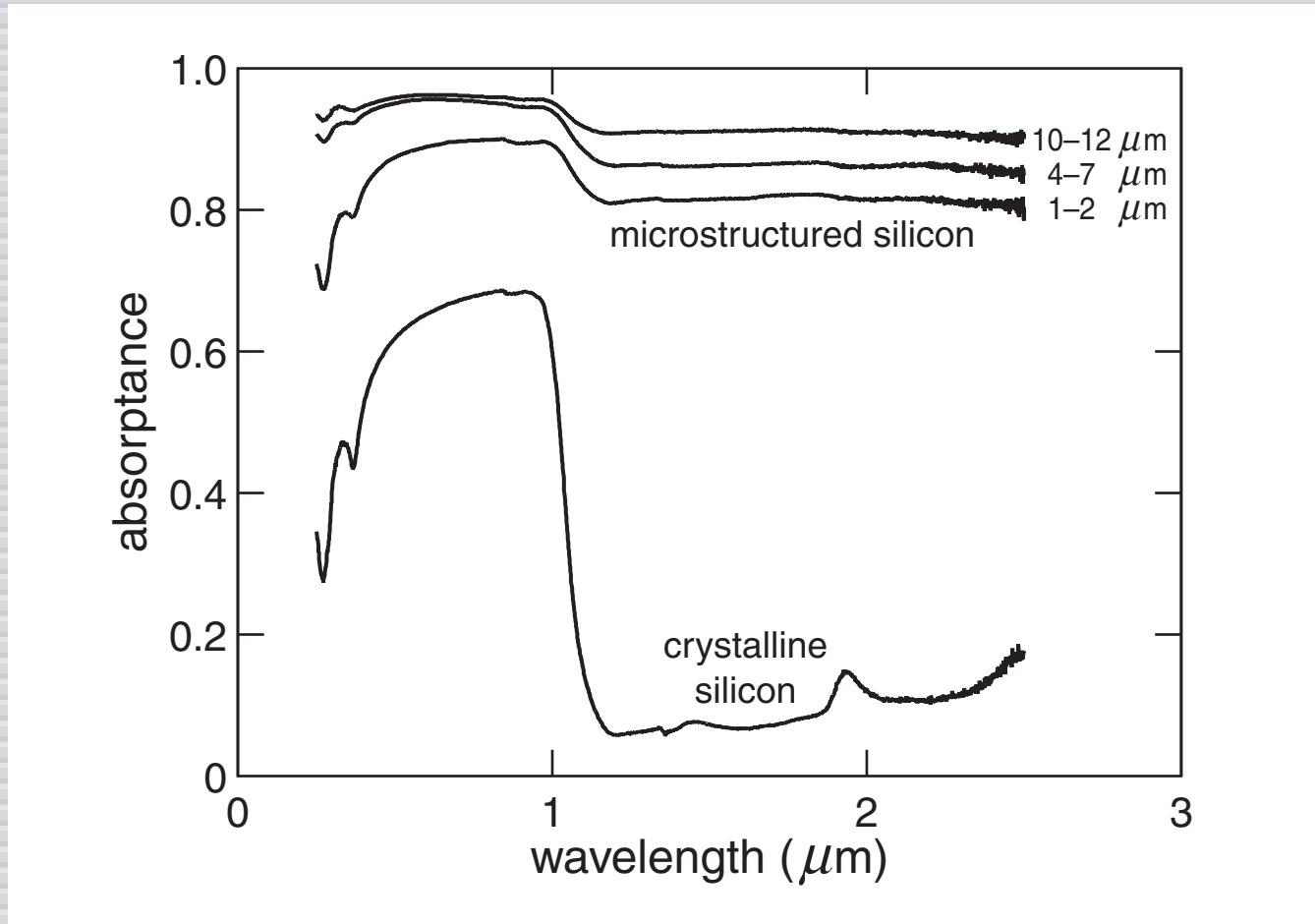
Properties

absorptance ($1 - R - T$)



Properties

absorptance ($1 - R - T$)



Properties

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

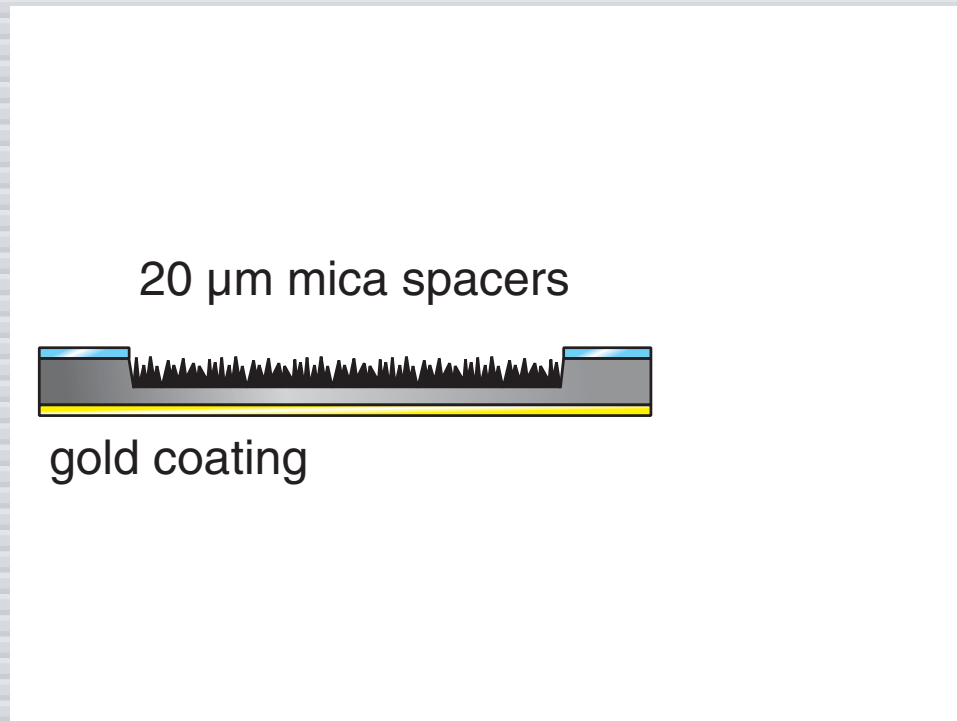
field emission setup



gold coating

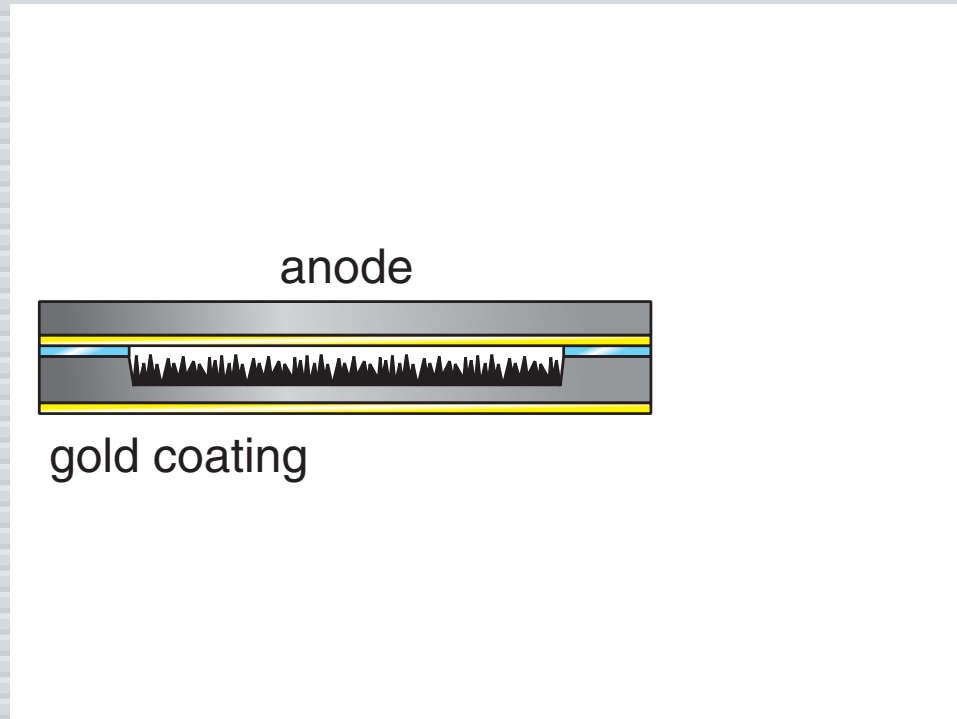
Properties

field emission setup



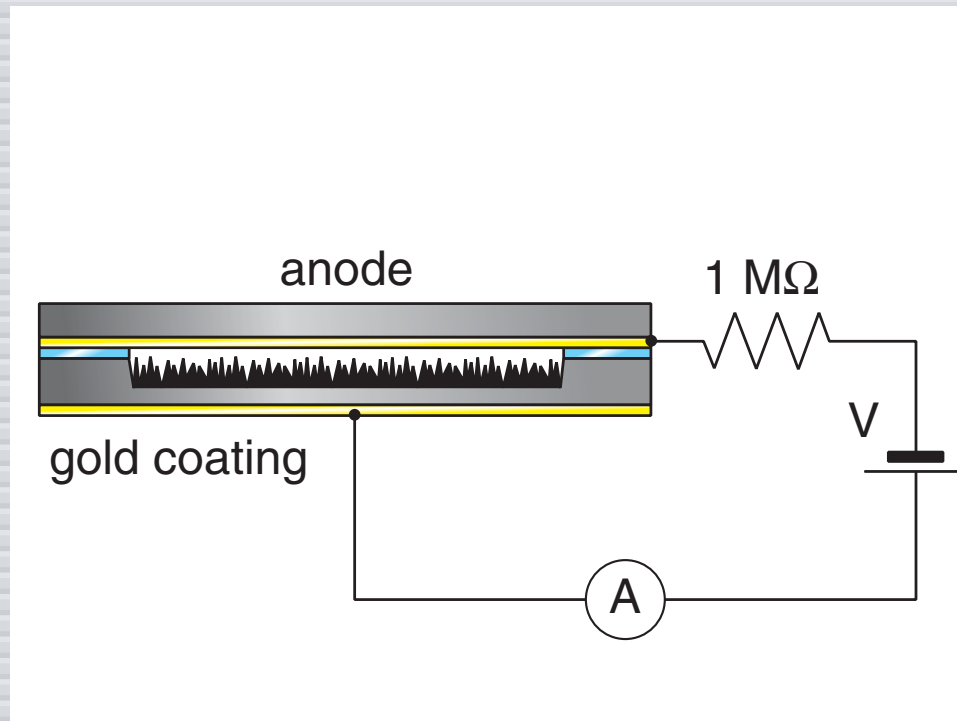
Properties

field emission setup

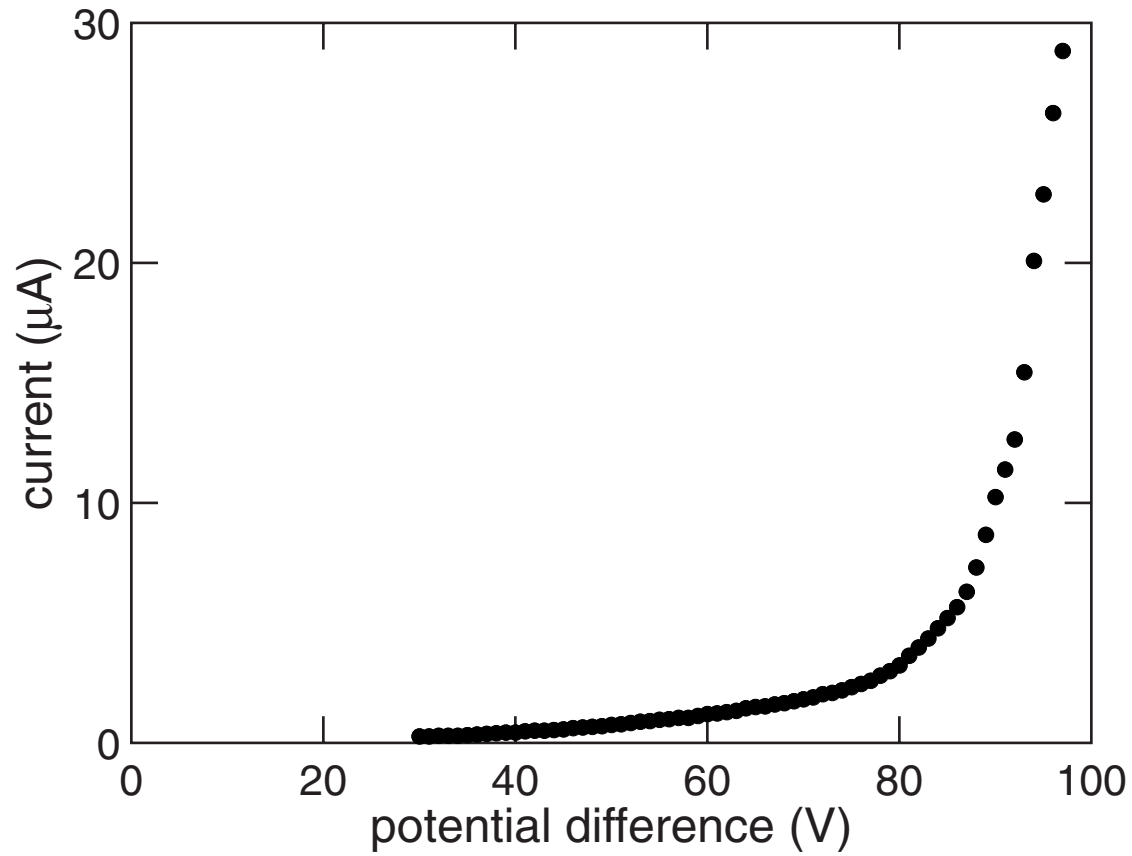


Properties

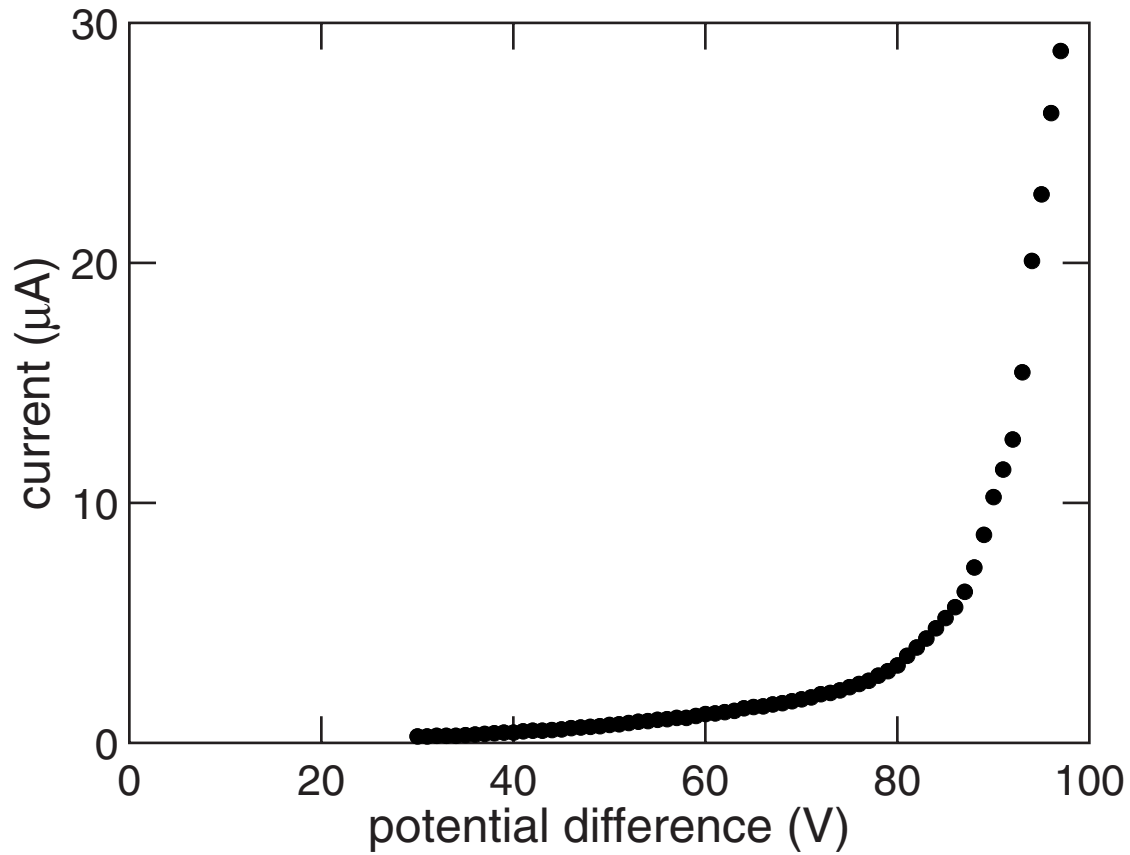
field emission setup



Properties

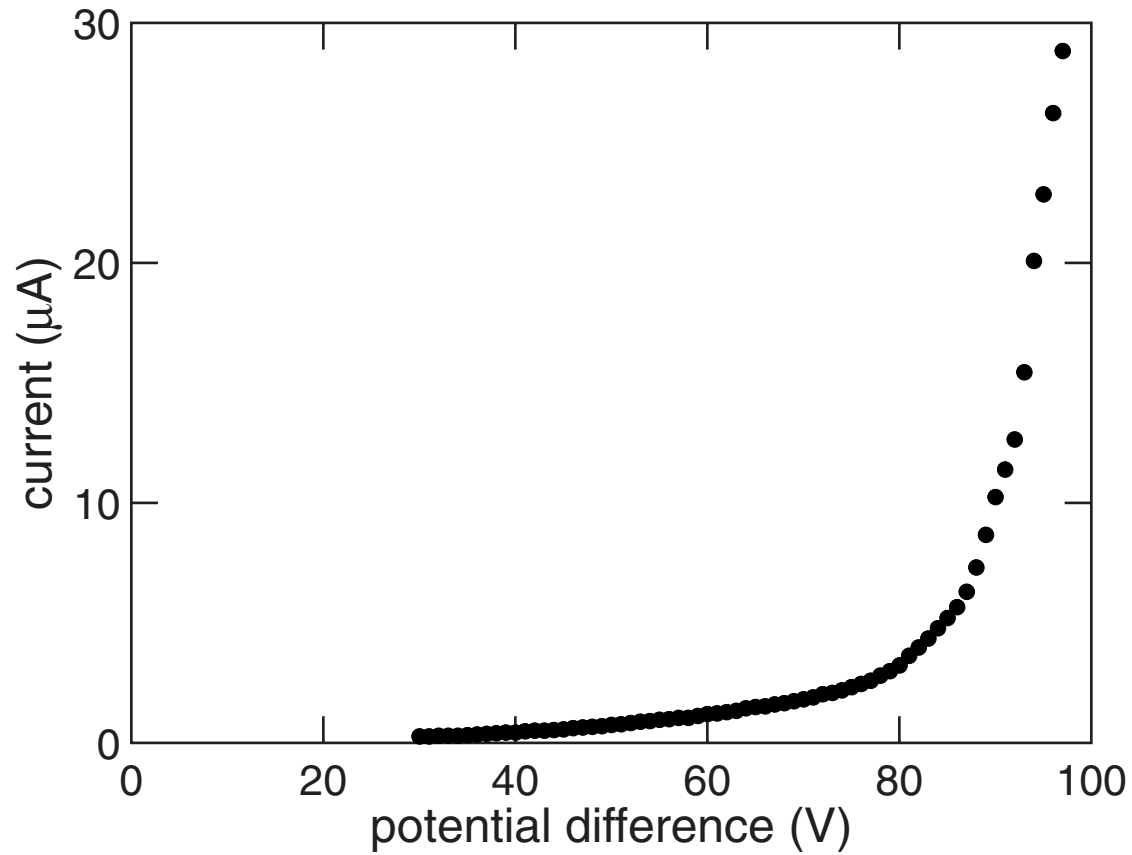


Properties



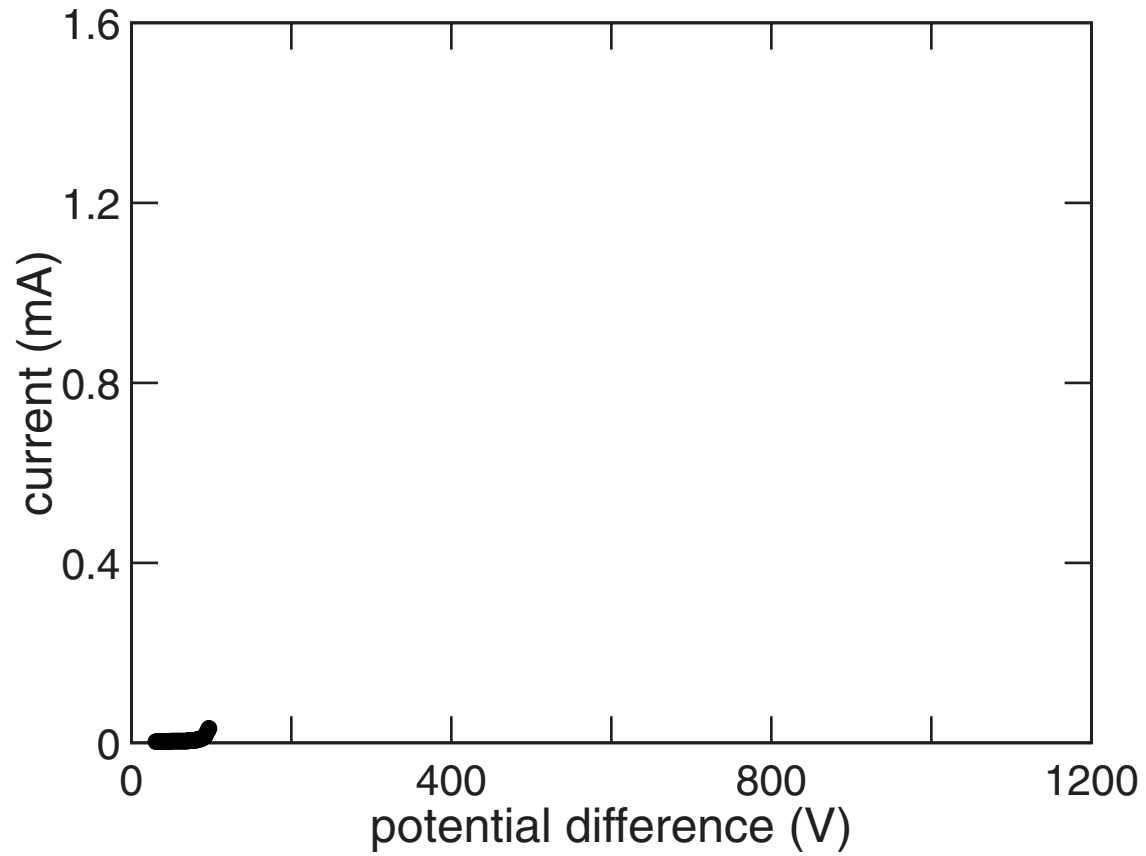
turn-on field ($1 \mu\text{A}/\text{cm}^2$): $1.2 \text{ V}/\mu\text{m}$

Properties

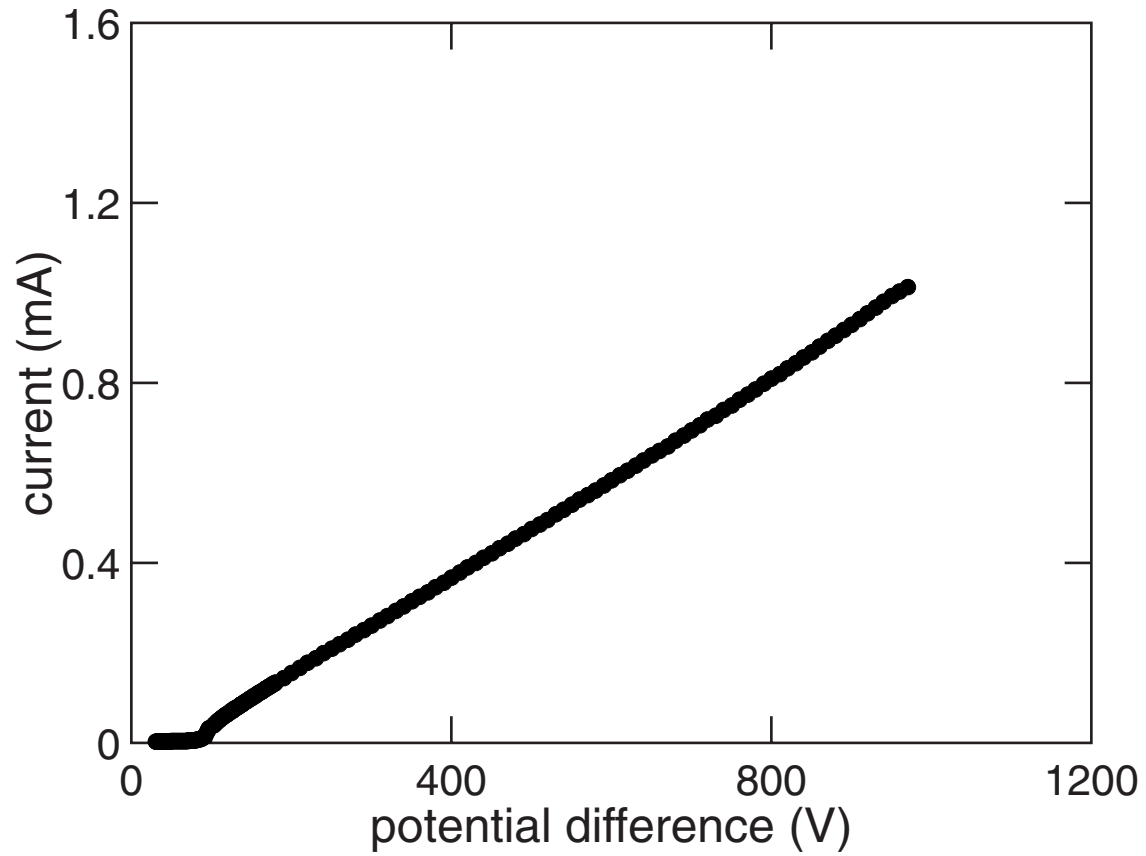


threshold field ($10 \mu\text{A}/\text{cm}^2$): $2.1 \text{ V}/\mu\text{m}$

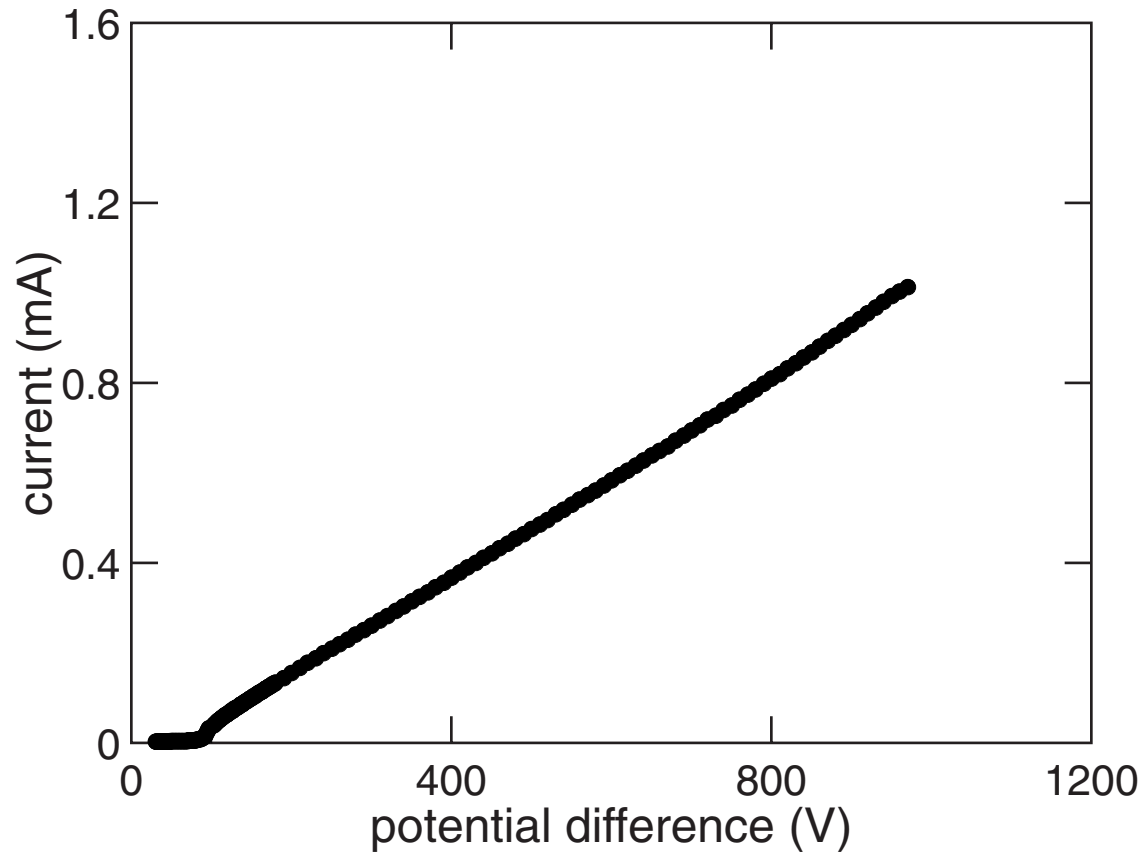
Properties



Properties



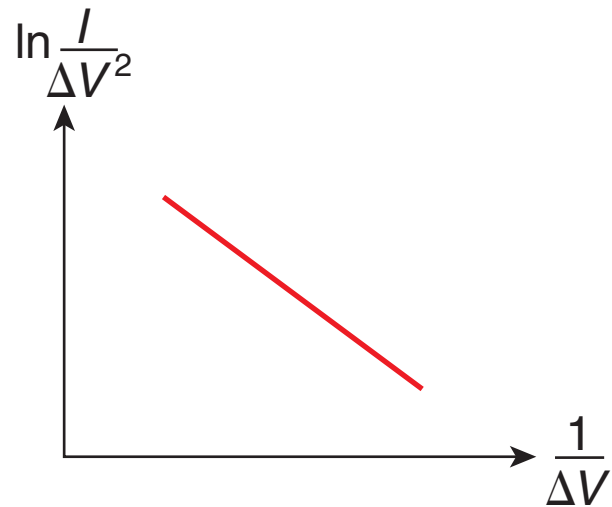
Properties



maximum current: 20 mA (4 mm² sample)

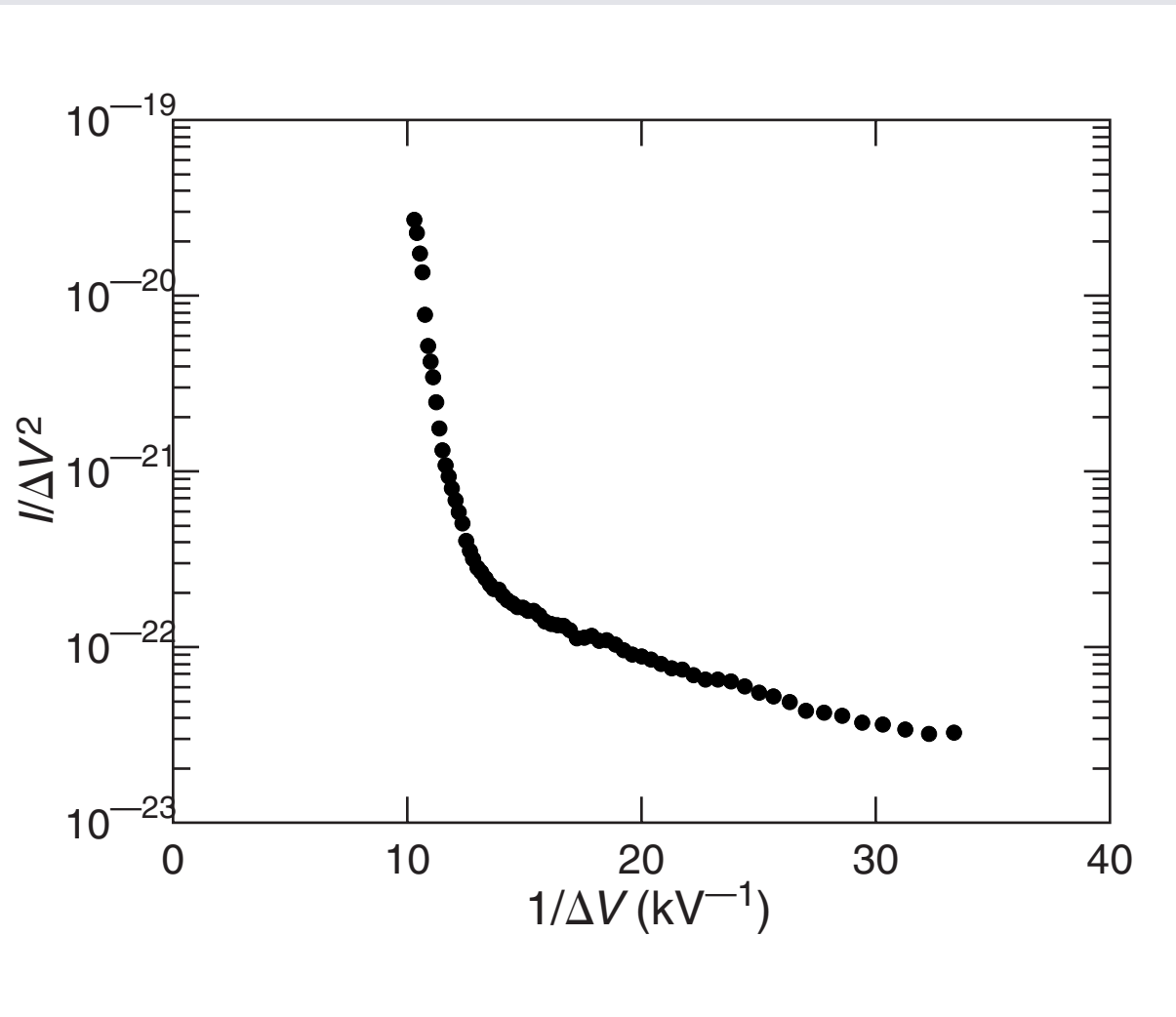
Properties

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

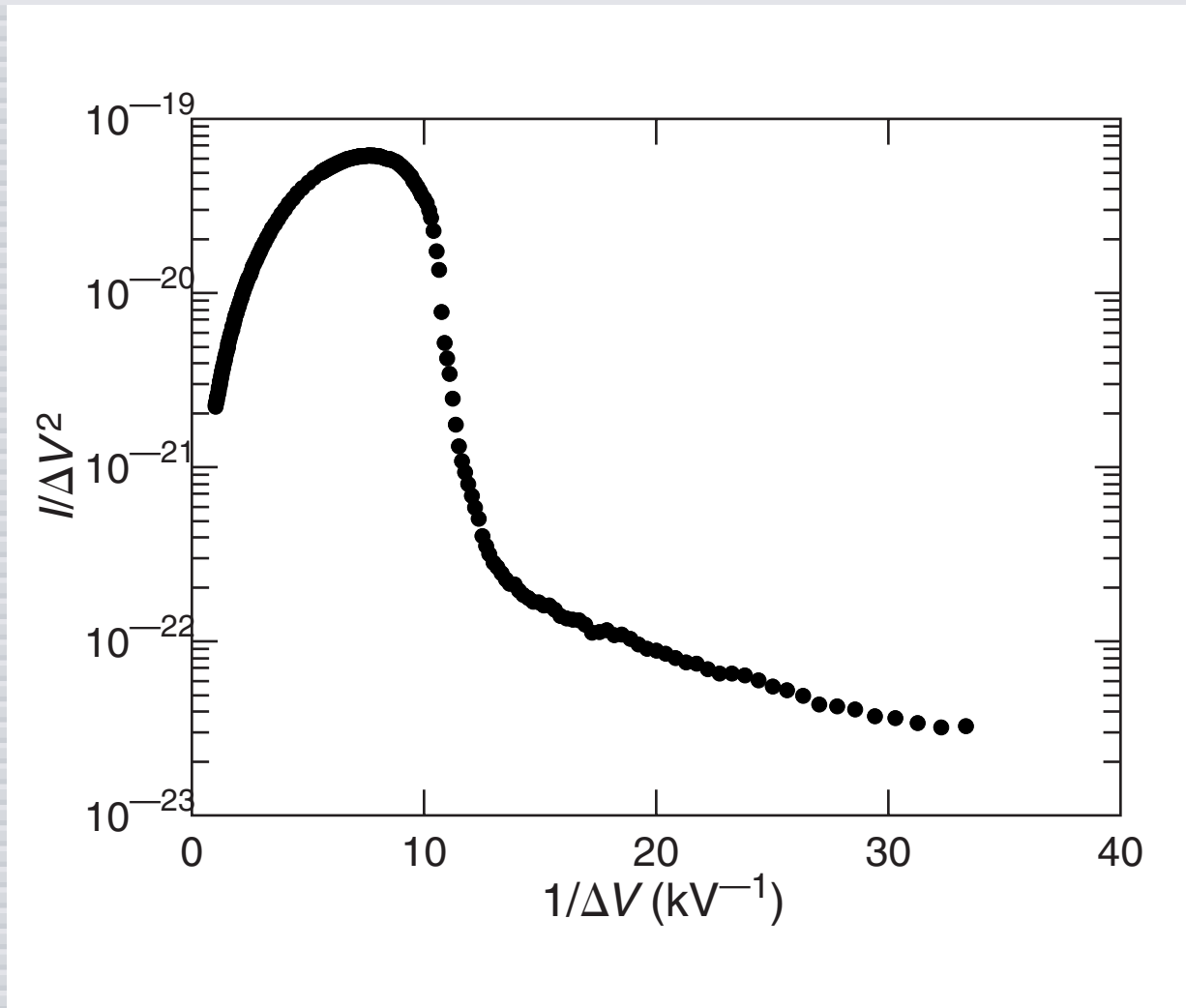


R.H. Fowler and L. Nordheim, *Proc. R. Soc. Lond. A* (1928)

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

- 
- A scanning electron micrograph (SEM) showing a surface covered with a dense, regular array of vertical, conical structures. The structures are uniform in size and shape, and are arranged in a grid-like pattern. The background surface is relatively smooth and flat.
- ▶ **What causes these properties?**
 - ▶ **Other gases?**

Ion channeling and electron backscattering:

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

Secondary ion mass spectrometry:

- ▶ **10^{20} cm^{-3} sulfur**
- ▶ **10^{17} cm^{-3} fluorine**

Structural and chemical analysis

1 μm

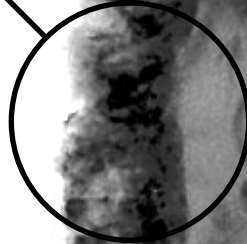


cross-sectional TEM (F. Génin, M. Wall, LLNL)

Structural and chemical analysis

1 μm

porous "fuzz"



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

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

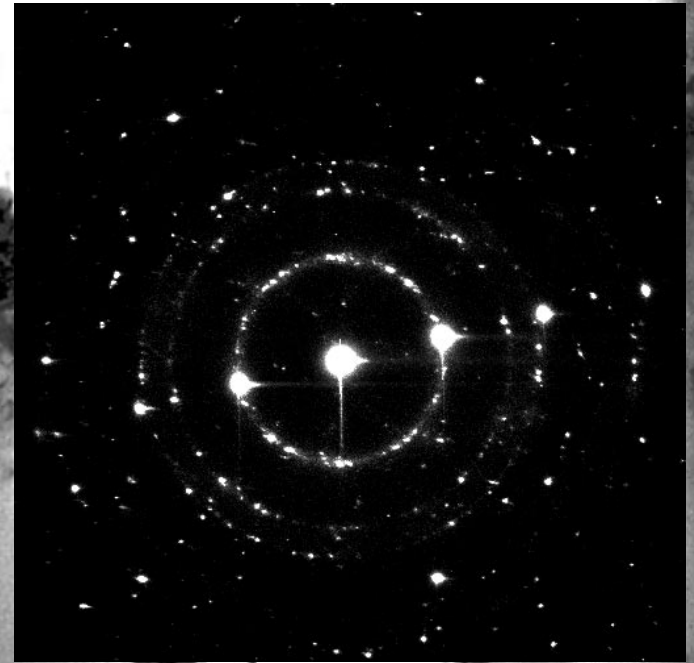
1 μm

The image is a transmission electron micrograph (TEM) showing a biological specimen, possibly a cross-section of a plant stem or root. The specimen has a central, lighter-colored region surrounded by darker, more textured layers. A scale bar in the top left corner indicates a length of 1 micrometer. A yellow dot is placed on the central region of the specimen. An inset in the top right corner shows the electron diffraction pattern corresponding to the area marked by the yellow dot. The diffraction pattern consists of a central bright spot surrounded by a grid of smaller, dimmer spots, indicating a crystalline structure.

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

Structural and chemical analysis

1 μm

A transmission electron micrograph (TEM) showing a biological specimen, possibly a cross-section of a plant stem or root. The specimen exhibits a central, elongated, and somewhat irregular structure with a darker, more textured interior. A yellow dot is placed on the upper part of this central structure. To the left of the specimen, a horizontal scale bar is labeled "1 μm".

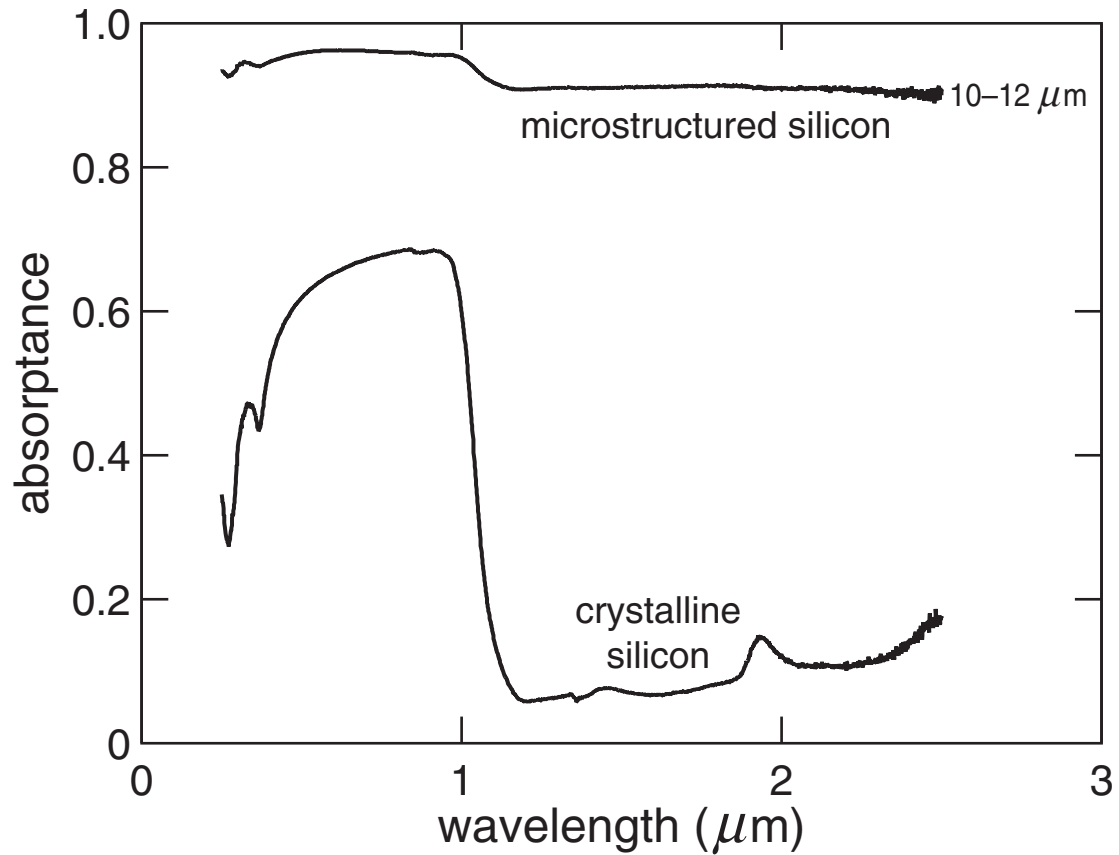
electron diffraction (F. Génin, M. Wall, LLNL)

cross-sectional TEM:

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

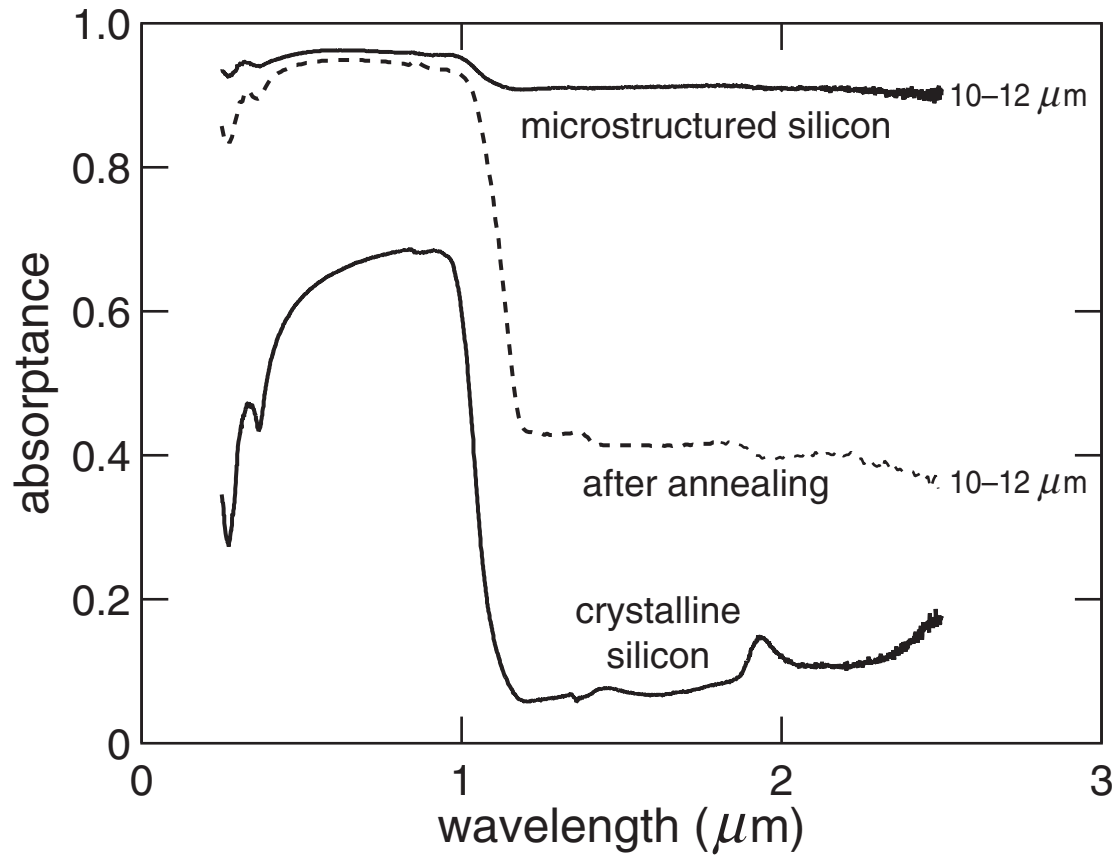
Structural and chemical analysis

anneal 4 hours at 1200 K



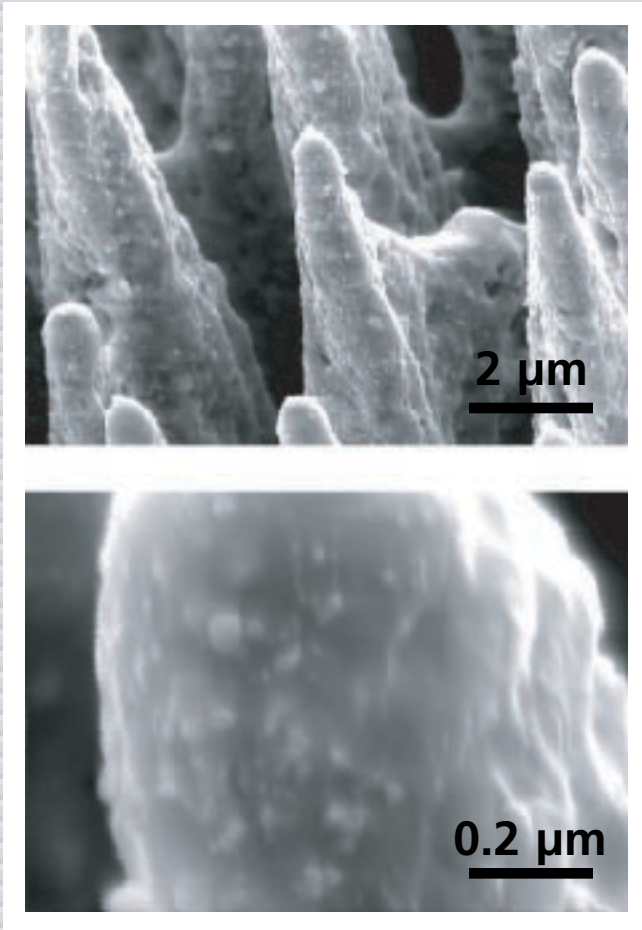
Structural and chemical analysis

anneal 4 hours at 1200 K



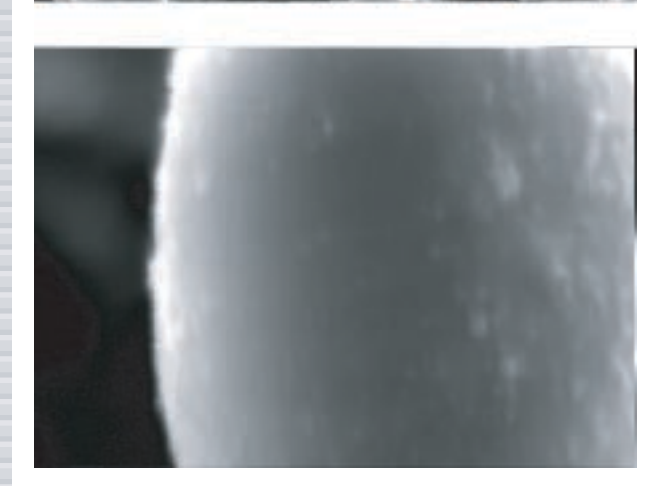
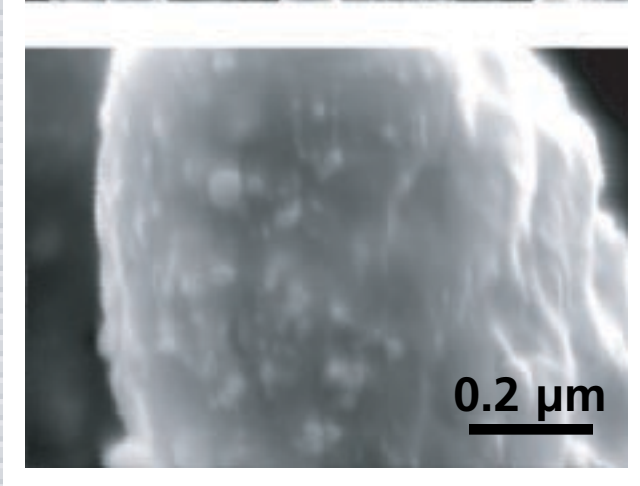
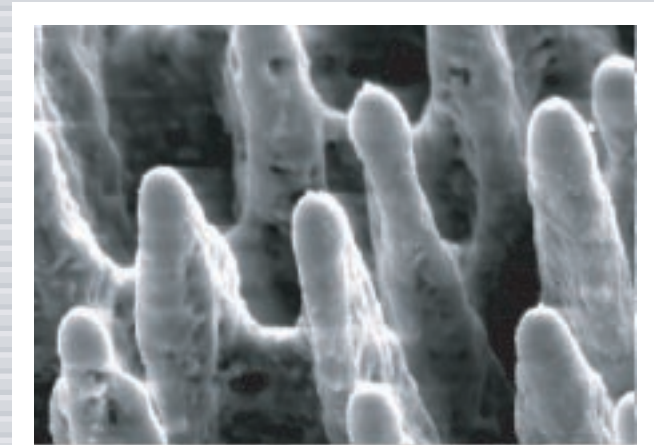
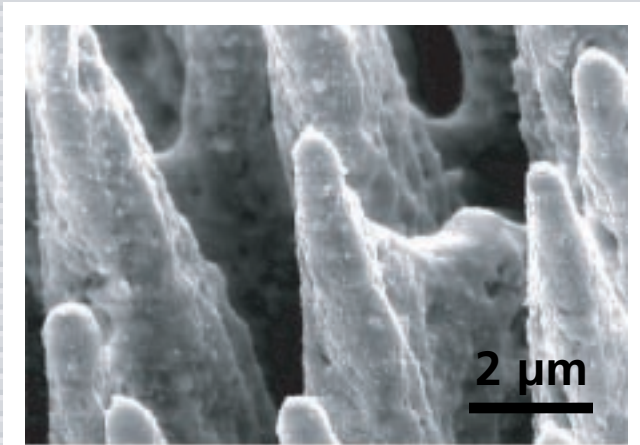
Structural and chemical analysis

anneal 4 hours at 1200 K



Structural and chemical analysis

anneal 4 hours at 1200 K



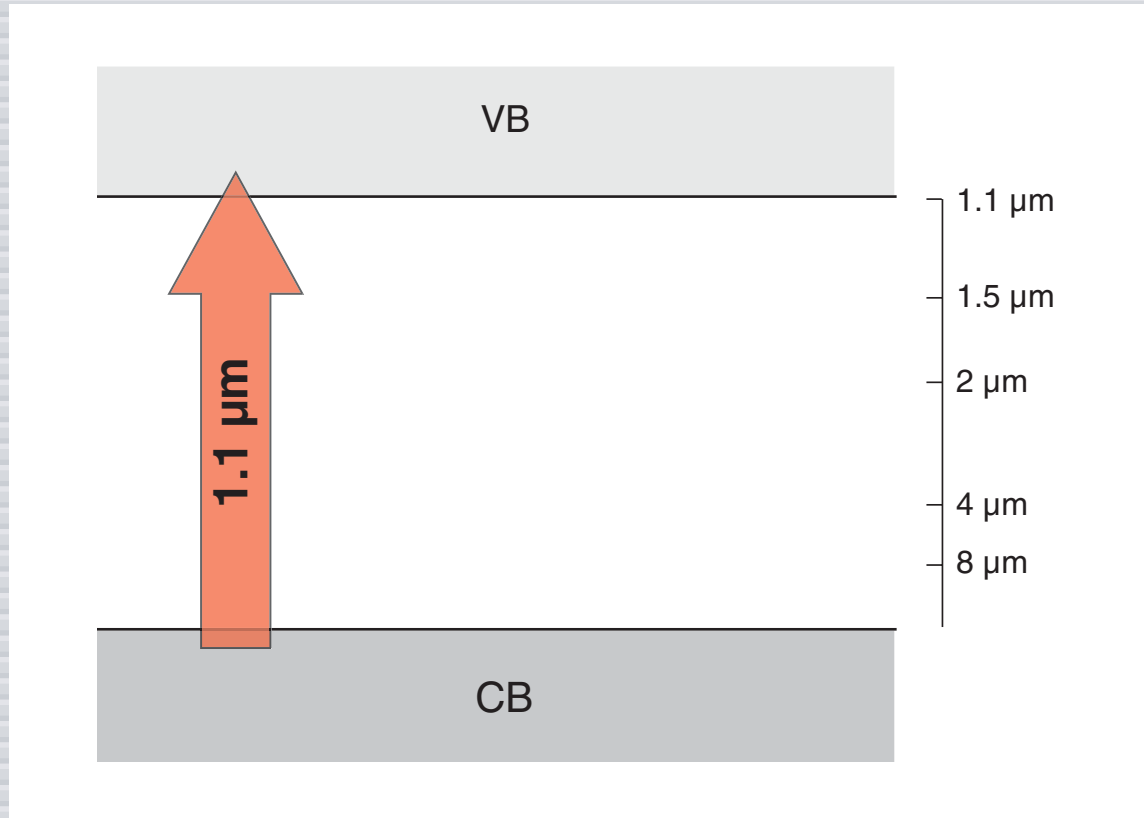
Structural and chemical analysis

Effects of annealing:

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

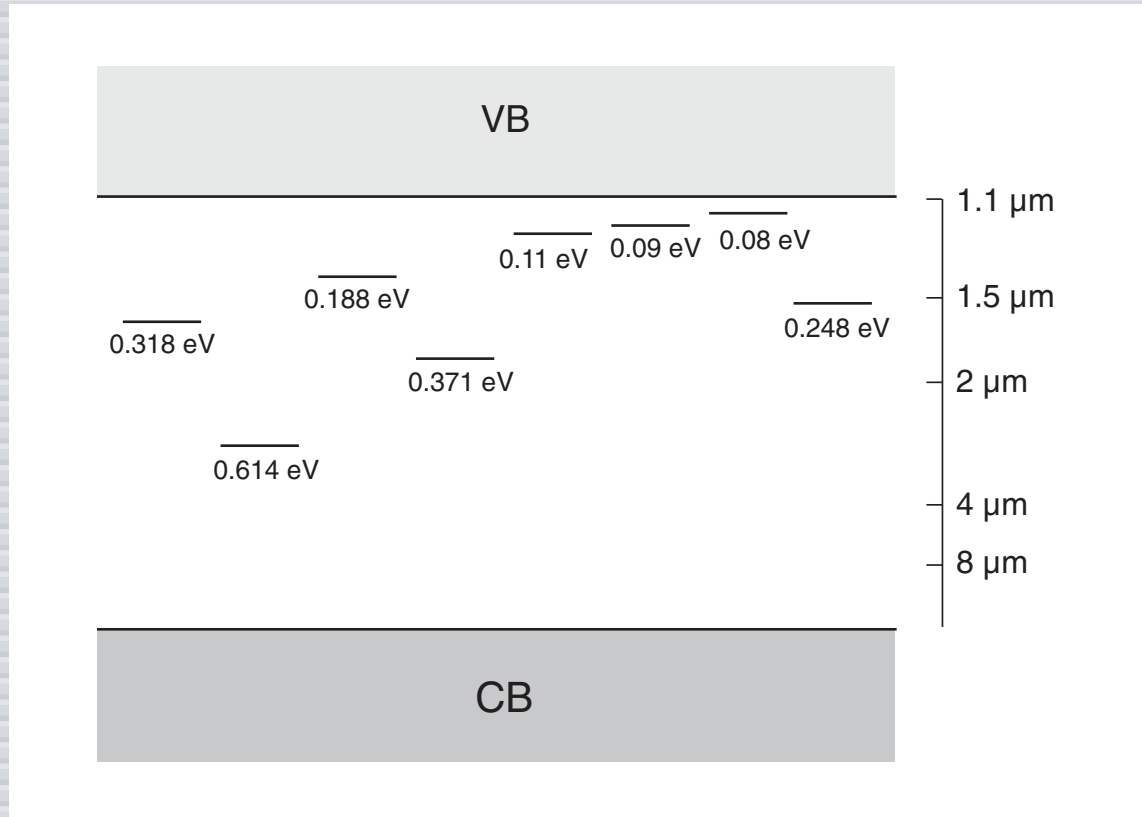
Structural and chemical analysis

sulfur introduces states in the gap



Structural and chemical analysis

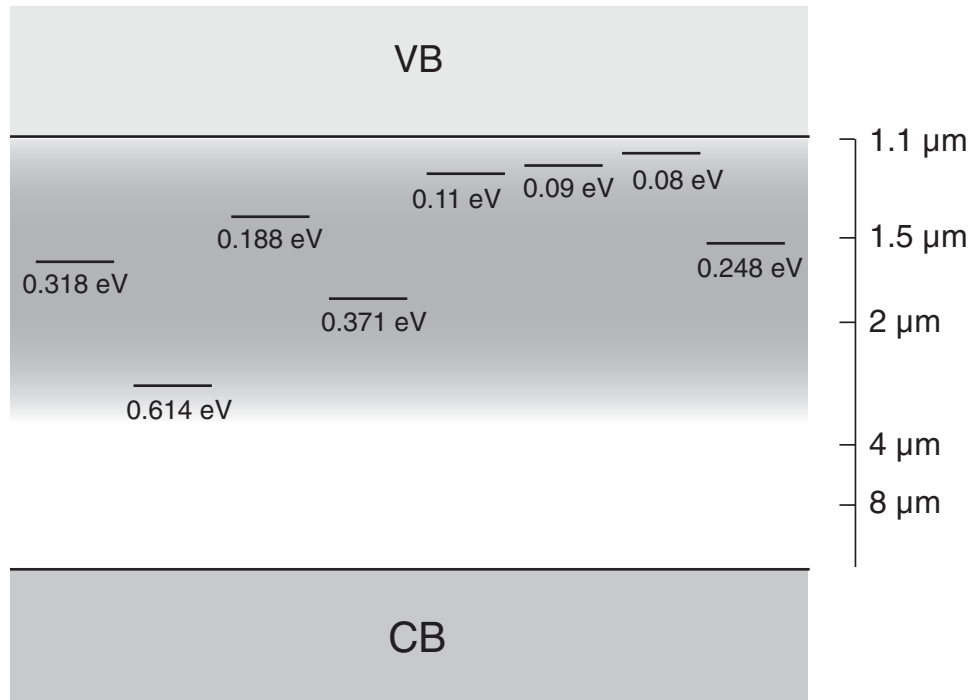
sulfur introduces states in the gap



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

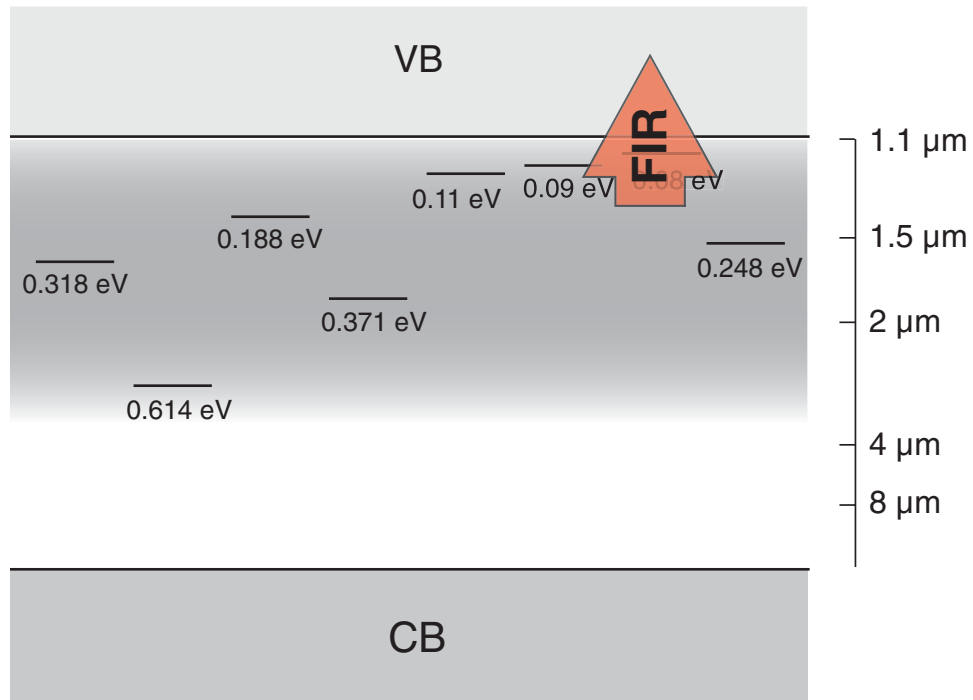
Structural and chemical analysis

states broaden into a band



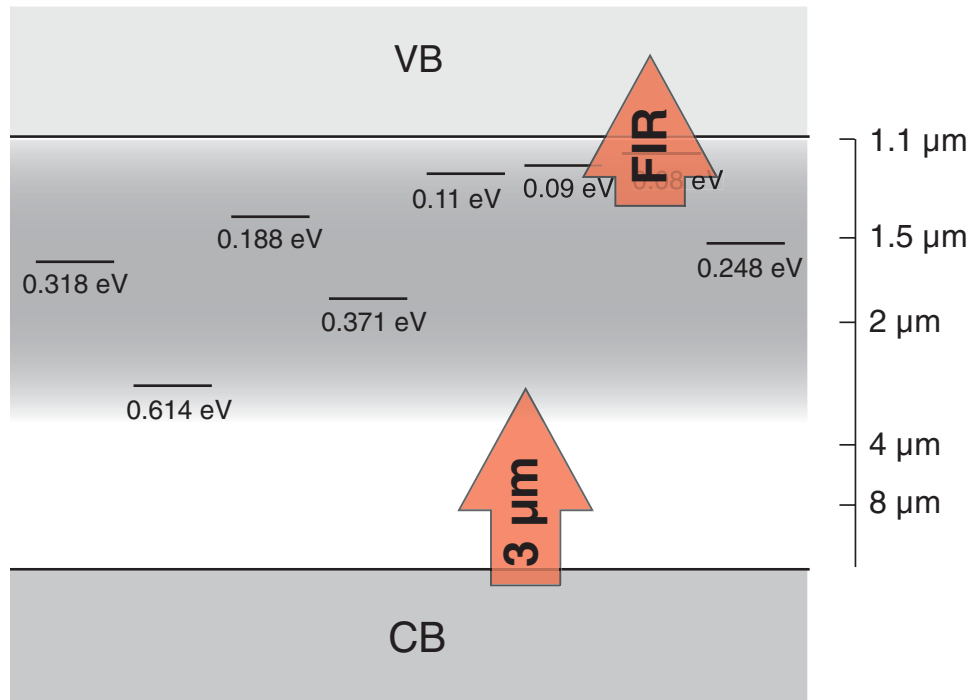
Structural and chemical analysis

donor: metal-like behavior



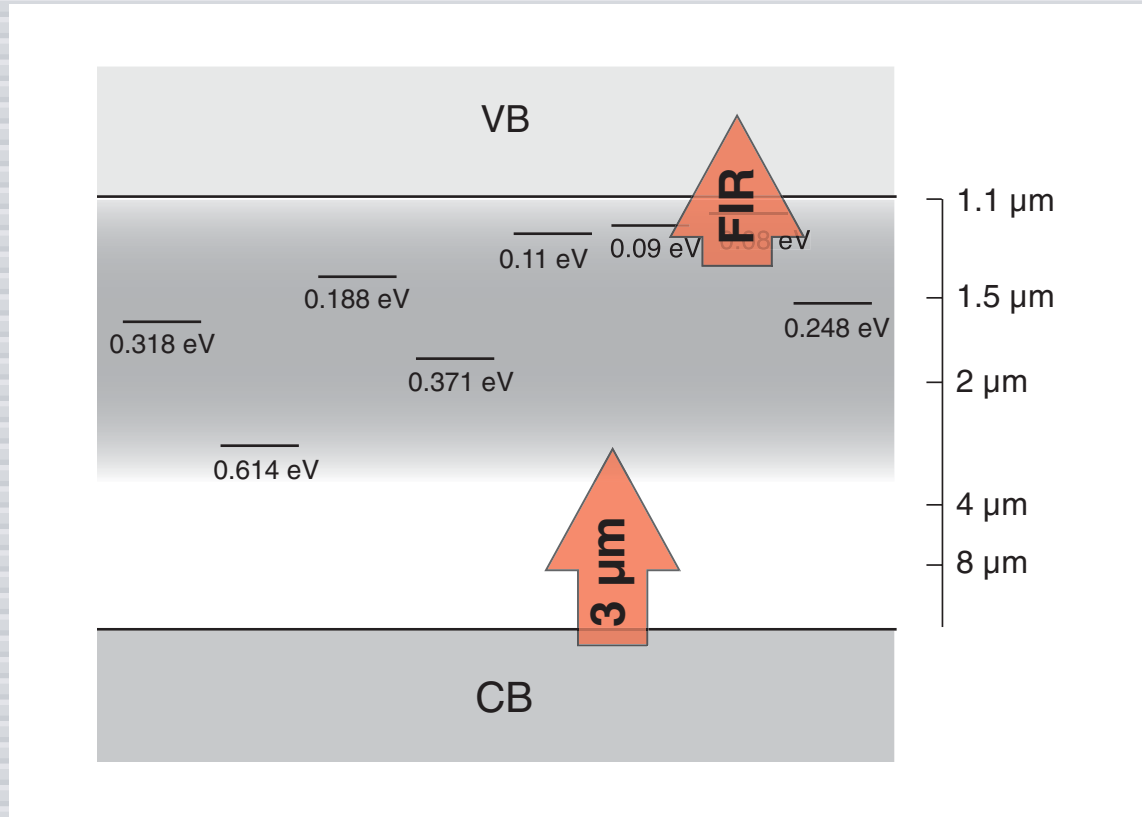
Structural and chemical analysis

acceptor: absorption until 3 μm



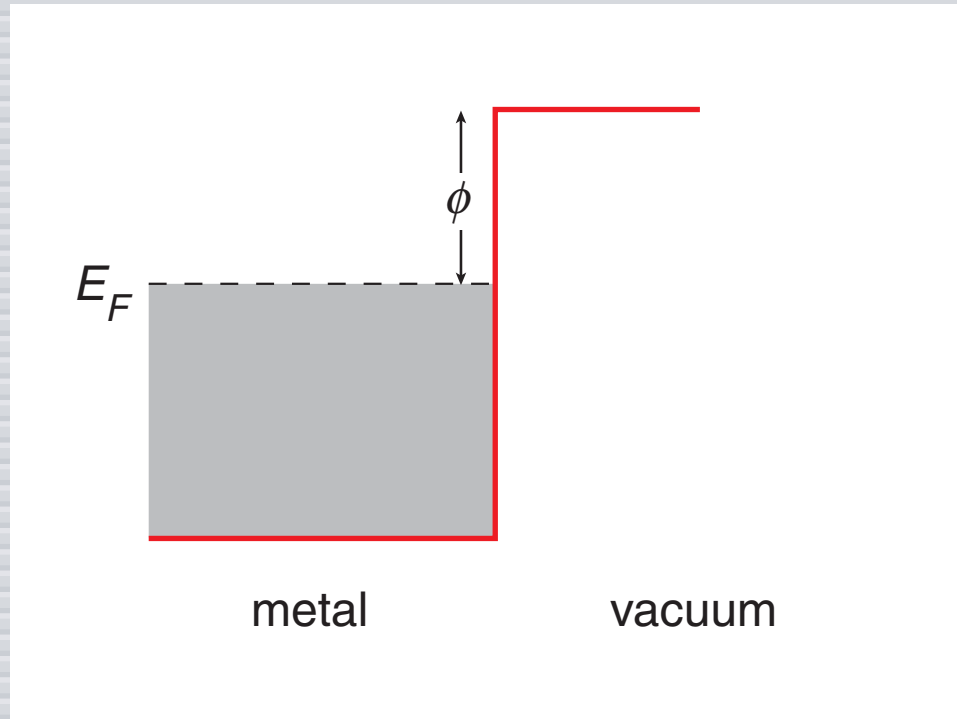
Structural and chemical analysis

acceptor: absorption out to 3 μm

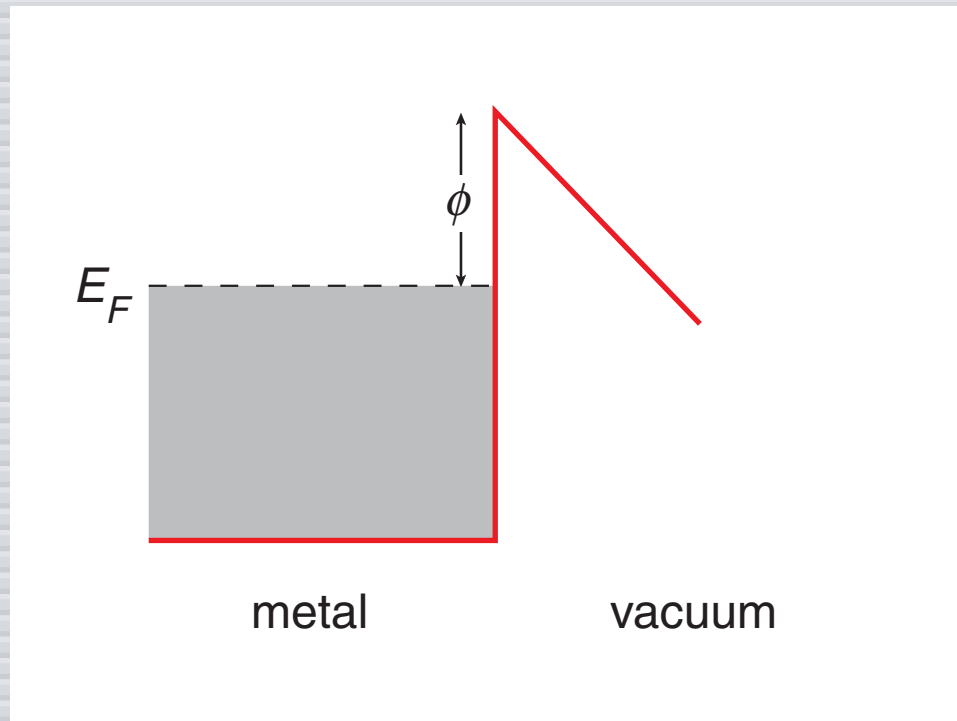


near-IR transmittance rises around 3 μm

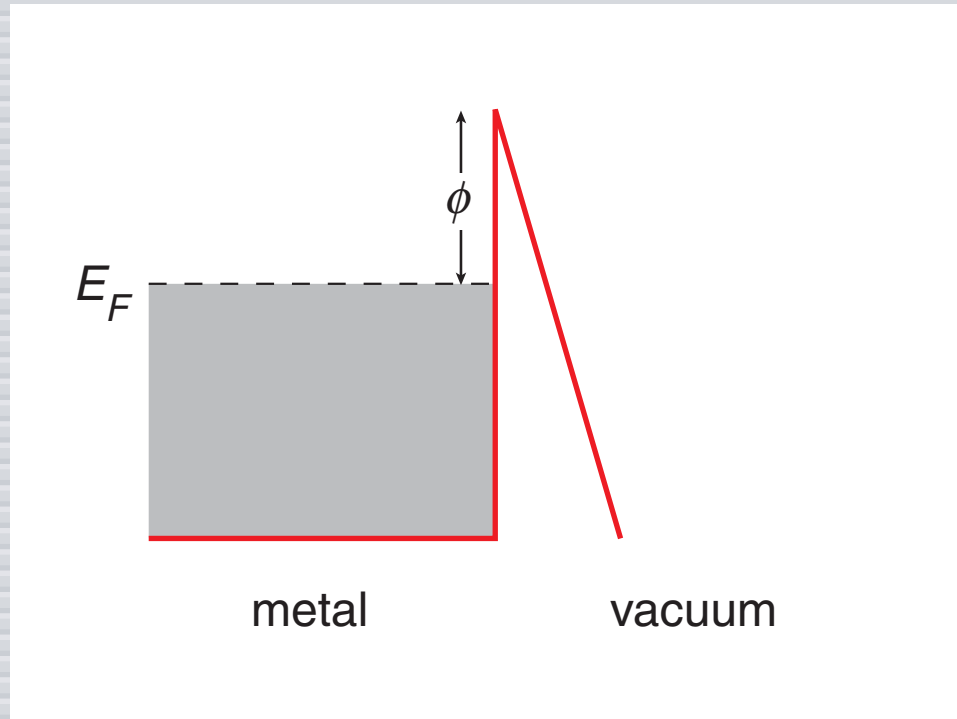
Structural and chemical analysis



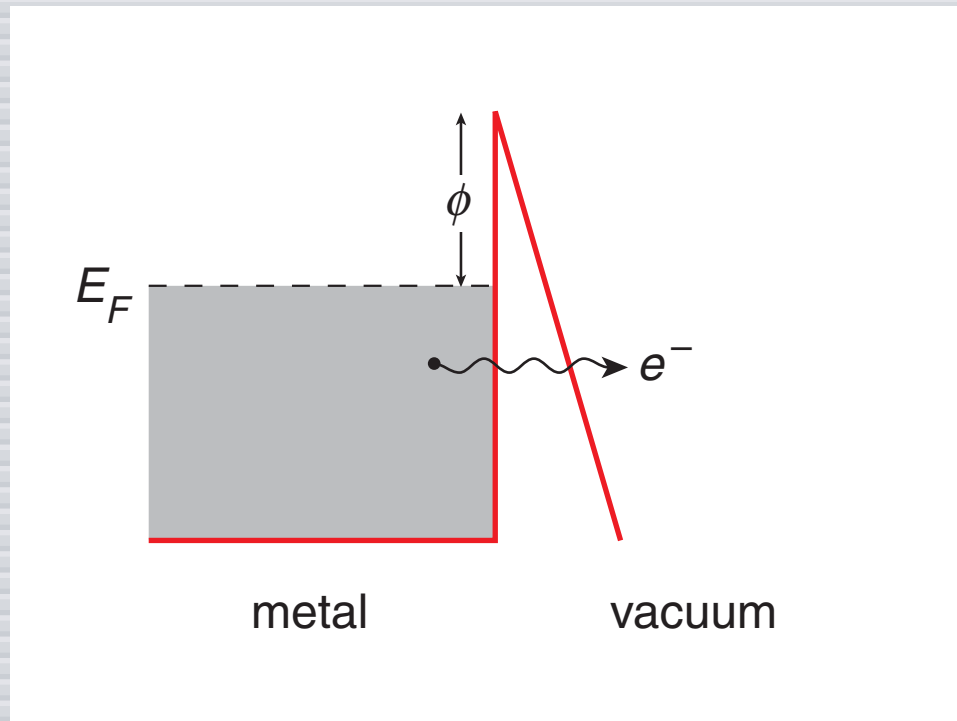
Structural and chemical analysis



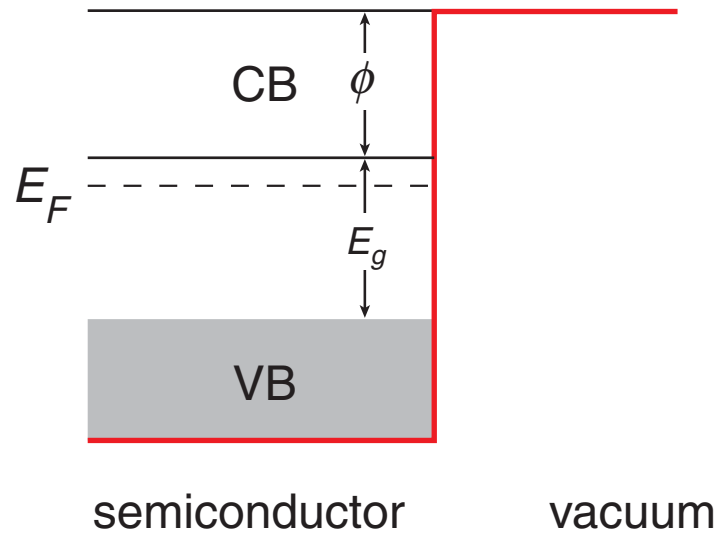
Structural and chemical analysis



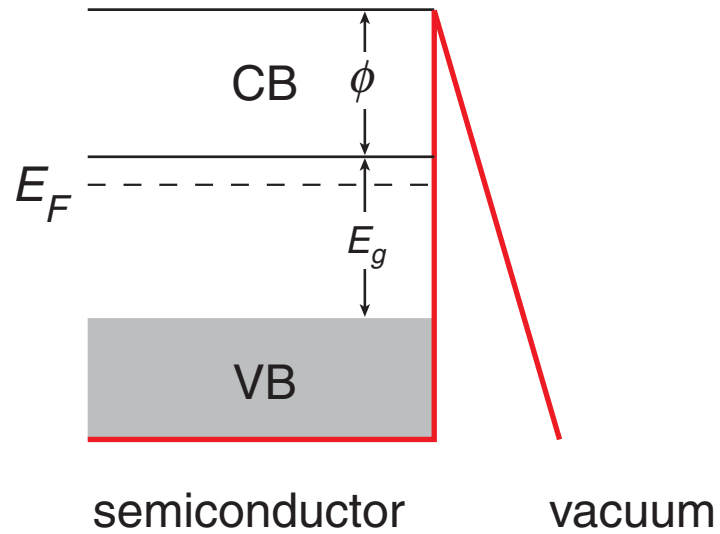
Structural and chemical analysis



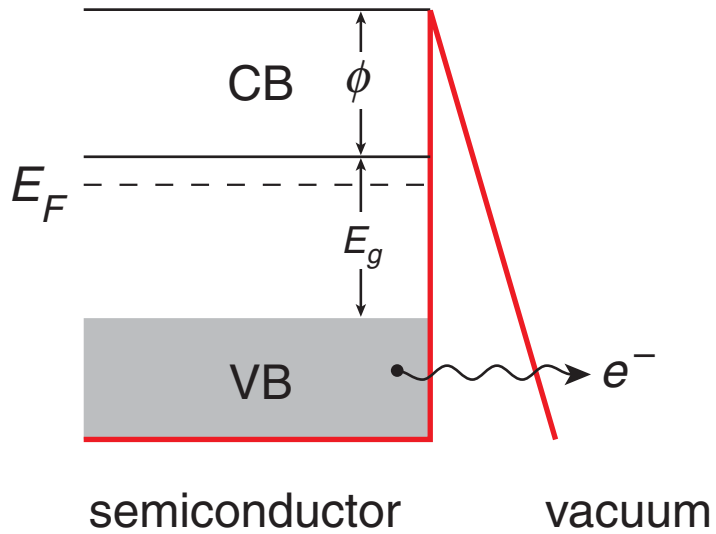
Structural and chemical analysis



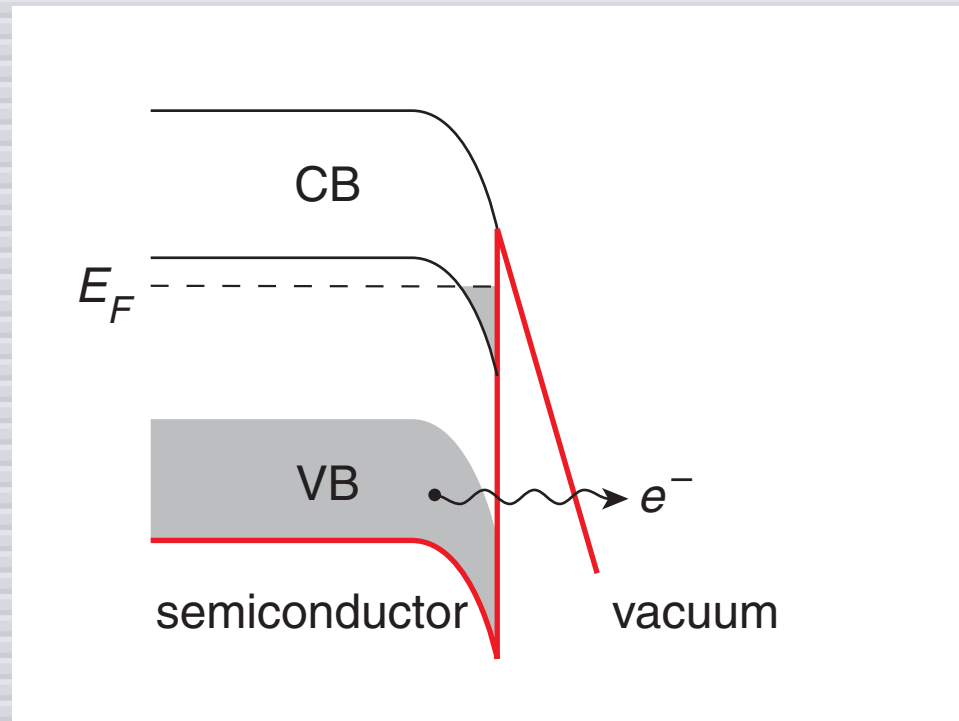
Structural and chemical analysis



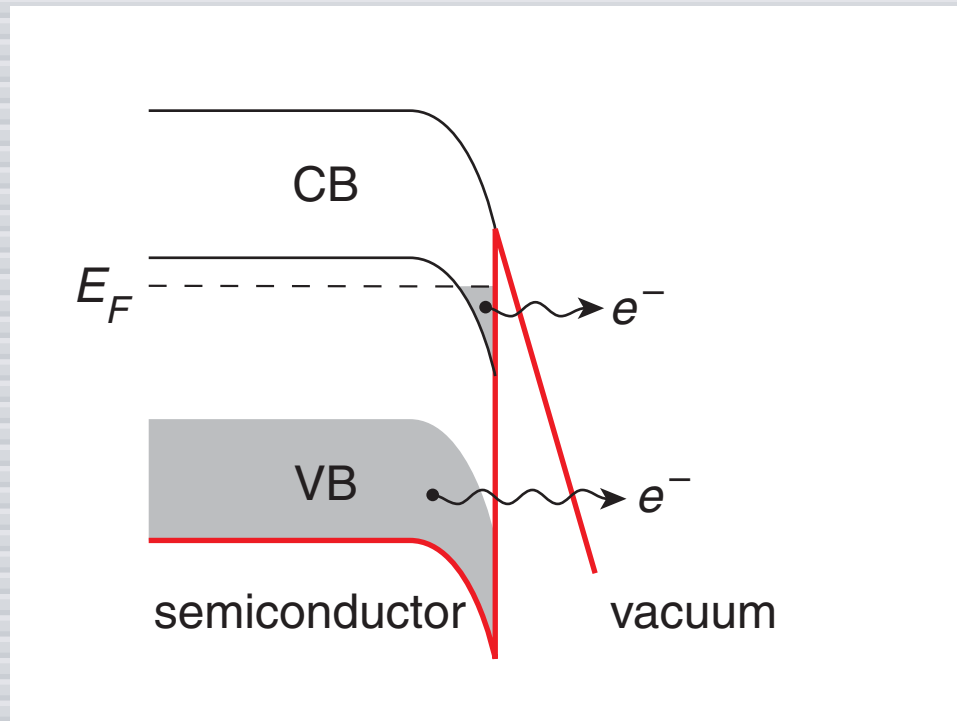
Structural and chemical analysis



Structural and chemical analysis

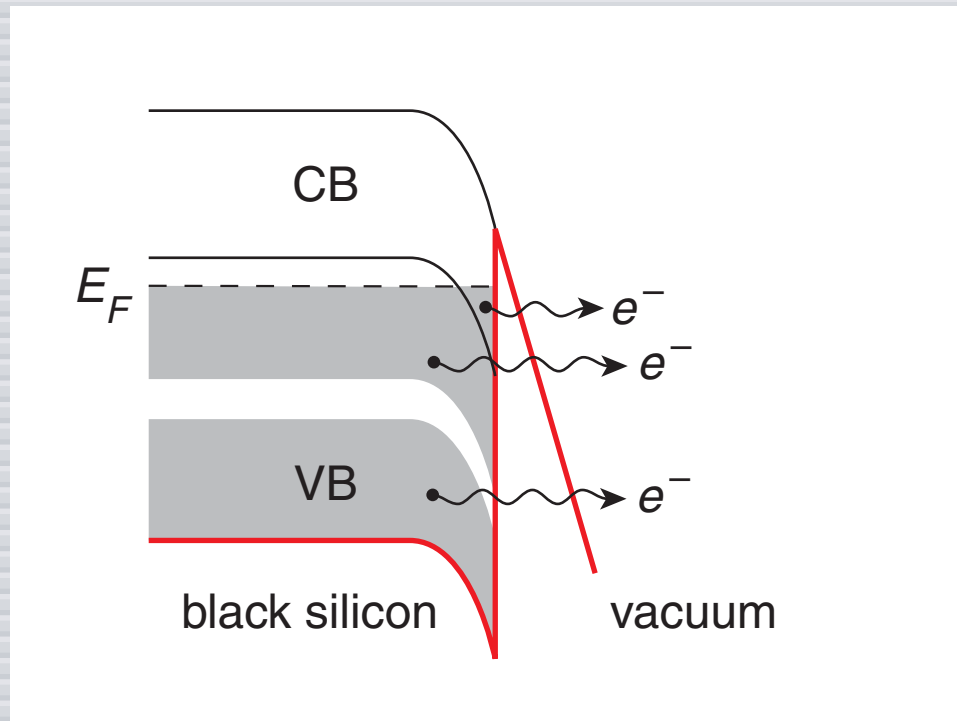


Structural and chemical analysis



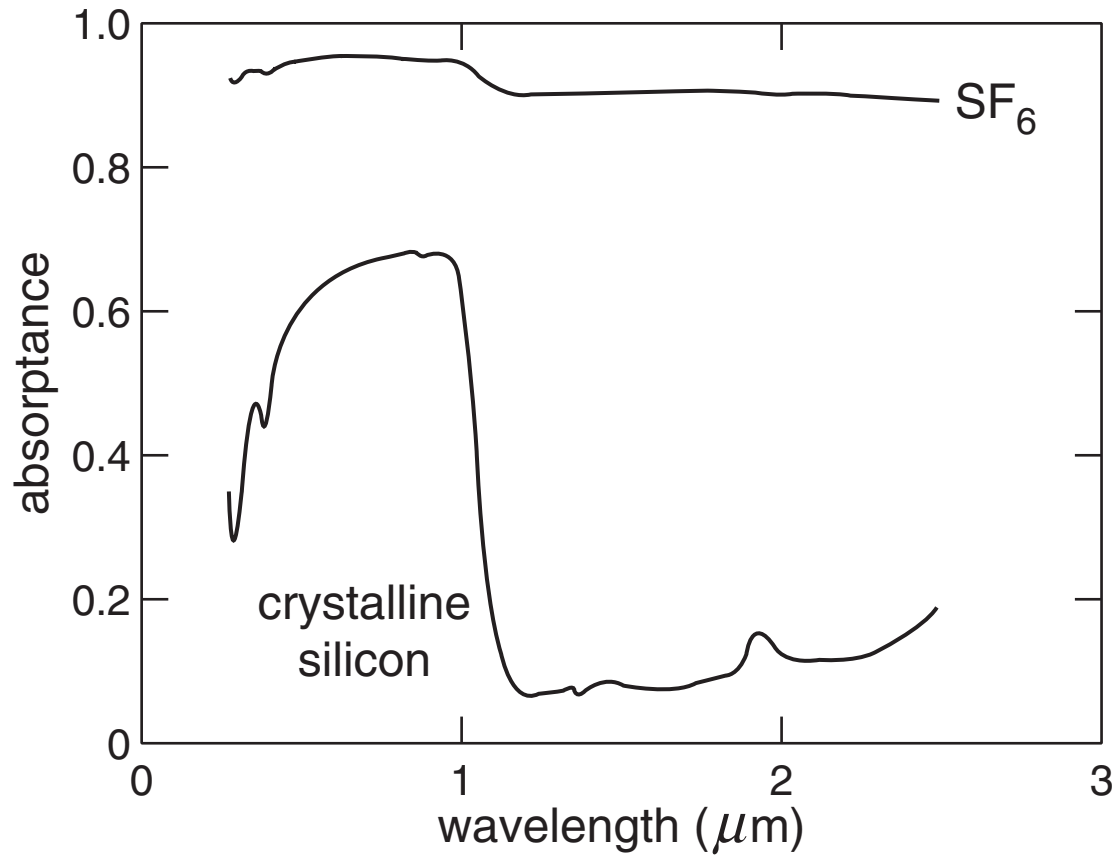
Structural and chemical analysis

sulfur band provides additional electrons



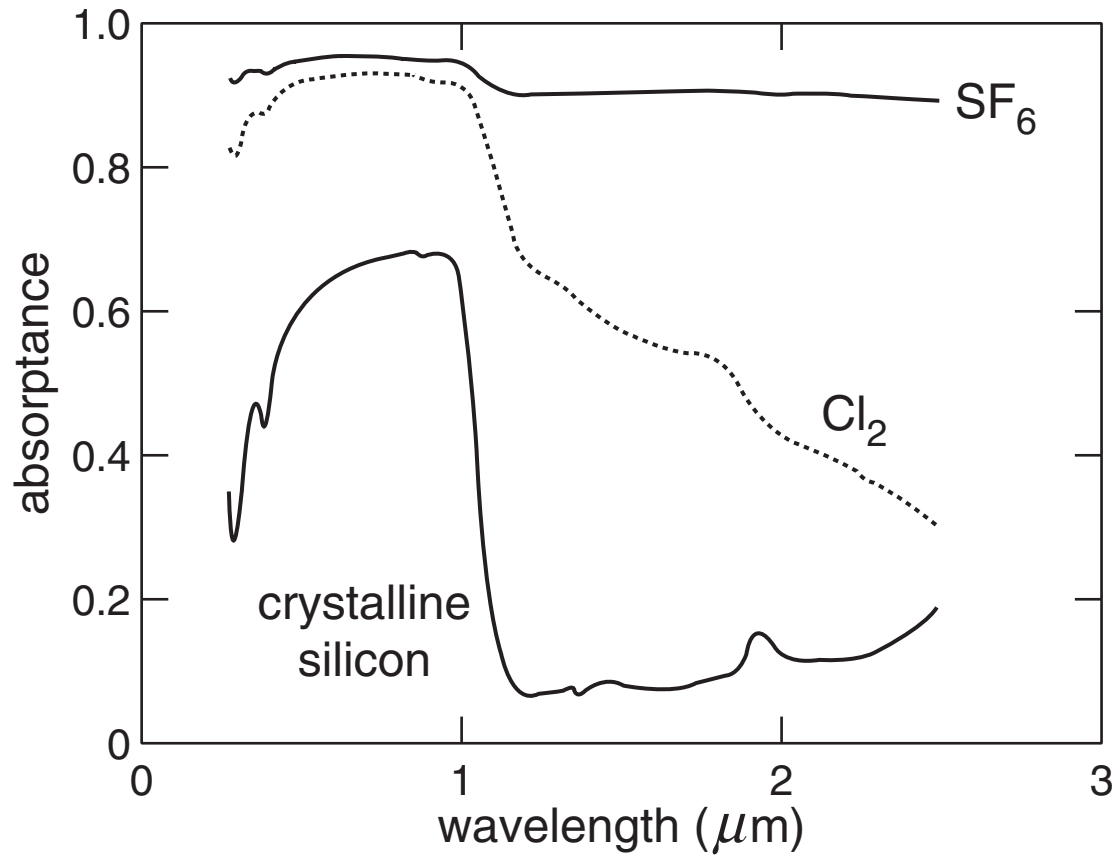
Structural and chemical analysis

effect of ambient gas on absorptance



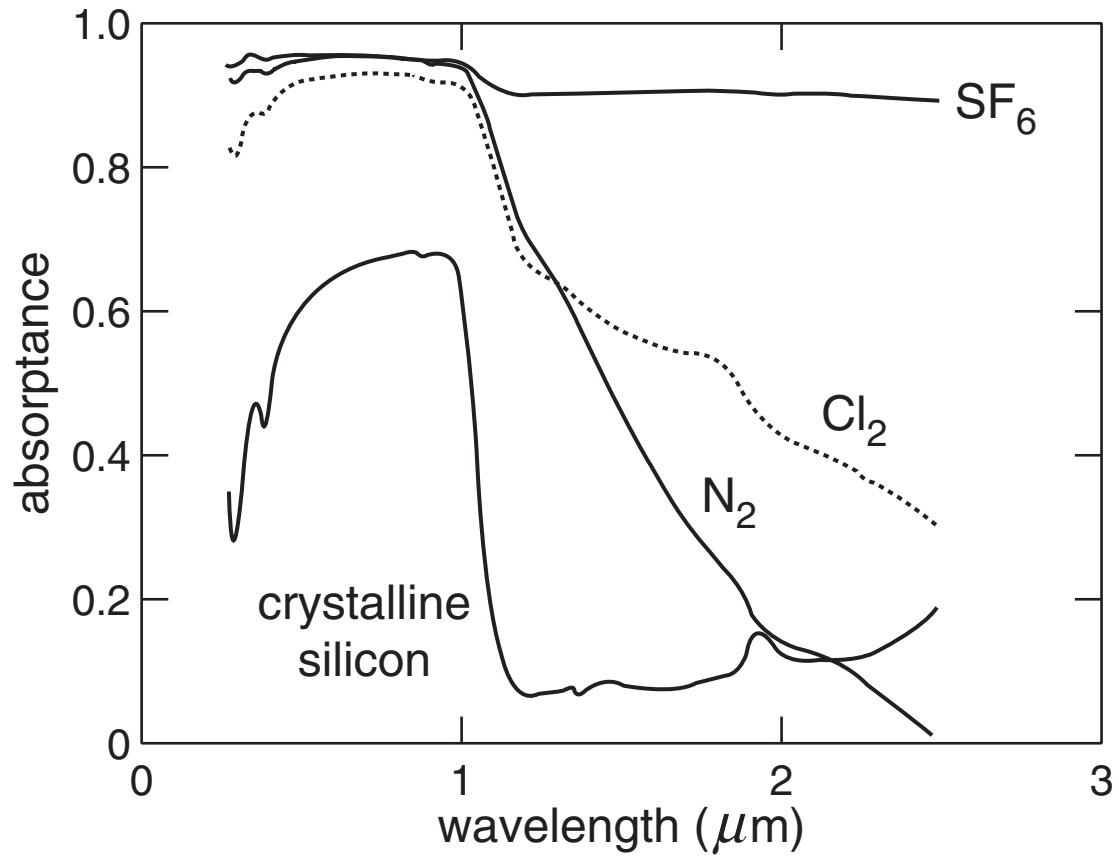
Structural and chemical analysis

effect of ambient gas on absorptance



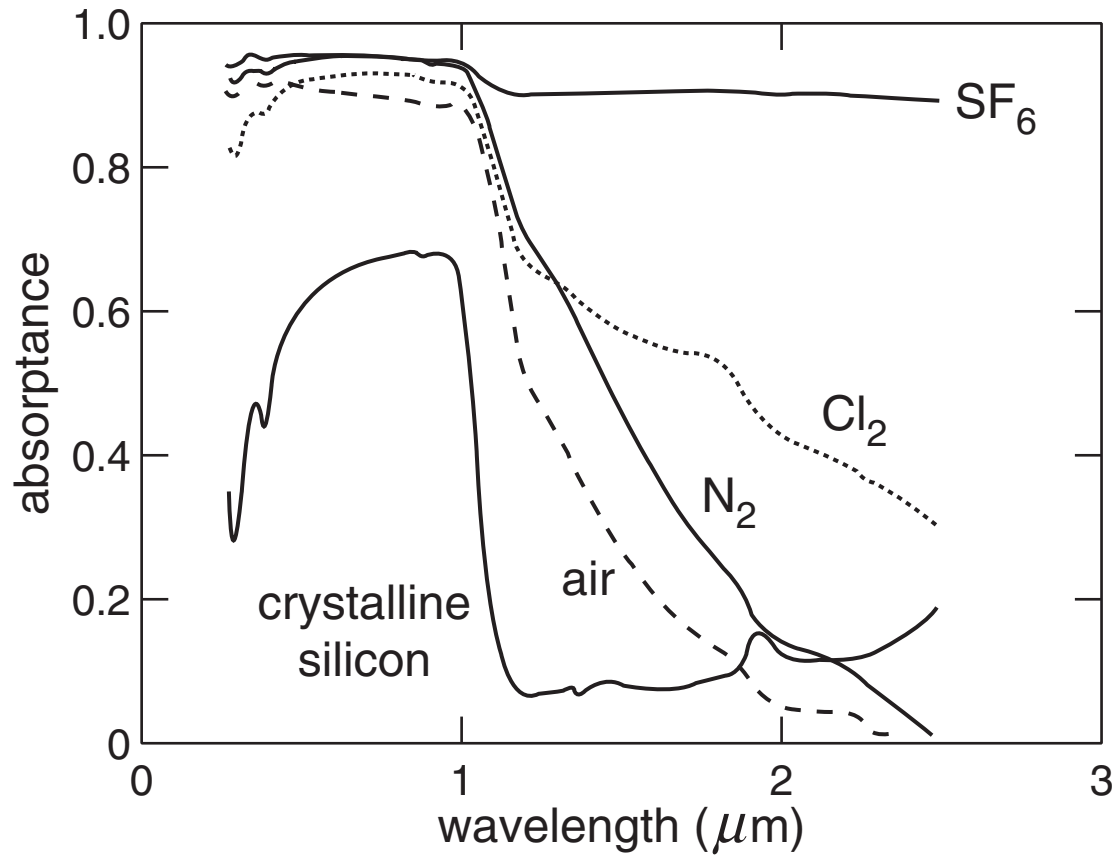
Structural and chemical analysis

effect of ambient gas on absorptance



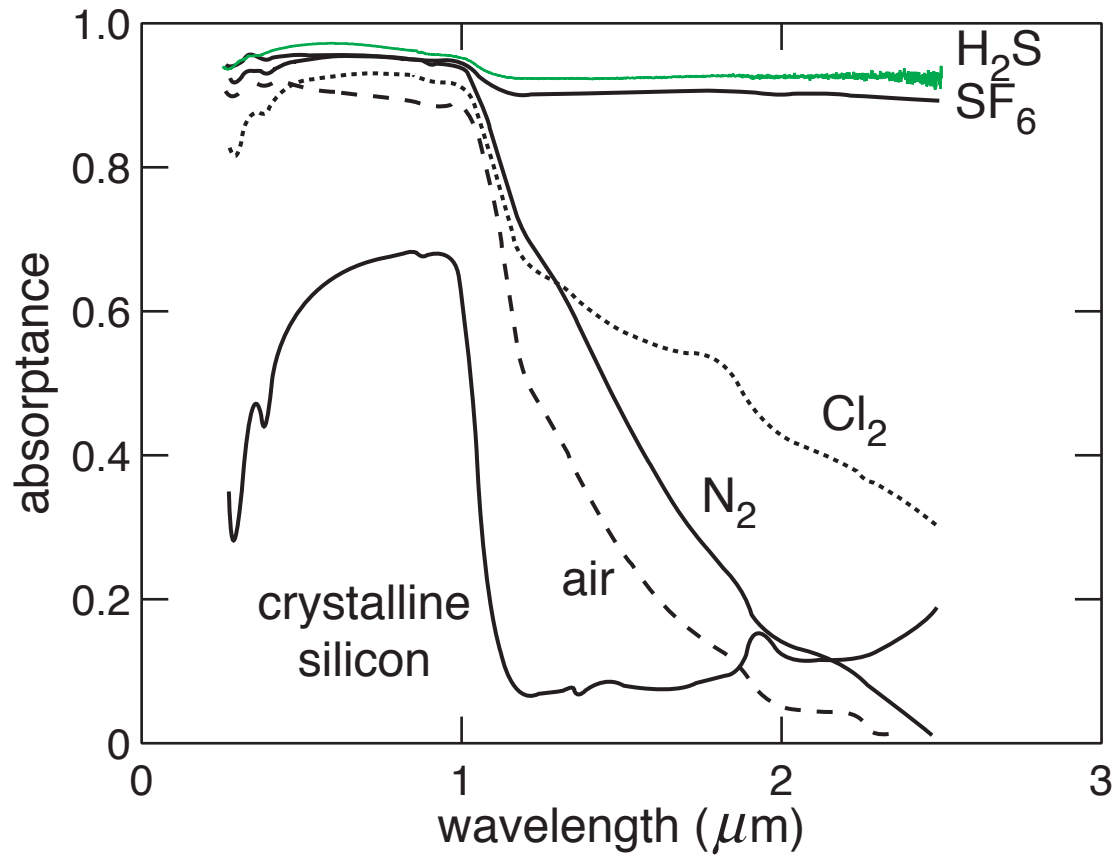
Structural and chemical analysis

effect of ambient gas on absorptance



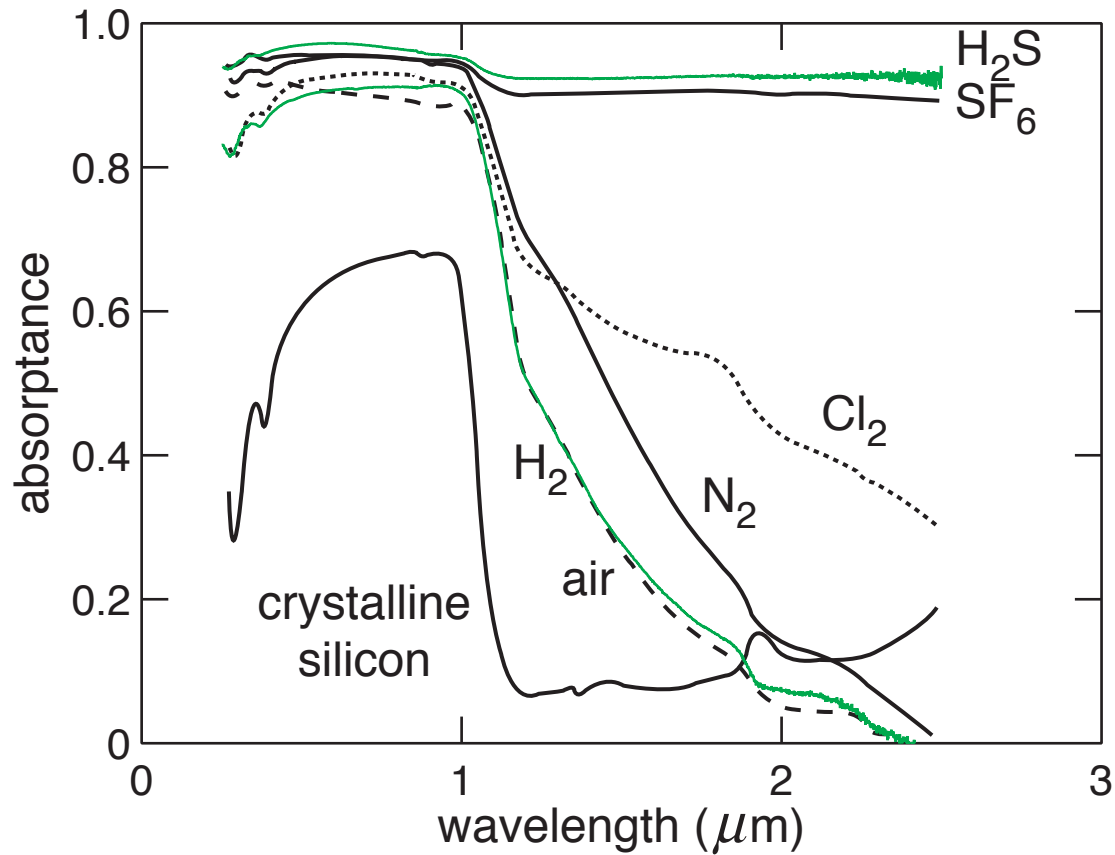
Structural and chemical analysis

effect of ambient gas on absorptance



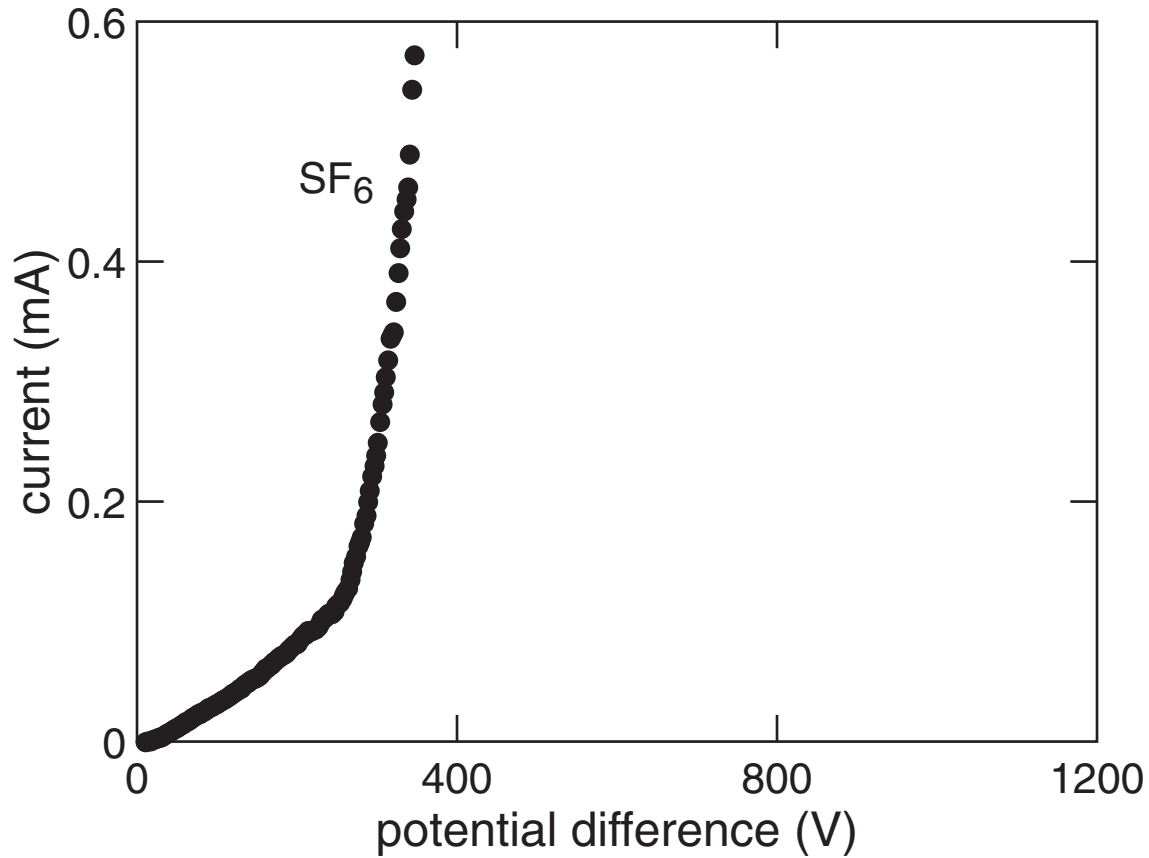
Structural and chemical analysis

effect of ambient gas on absorptance



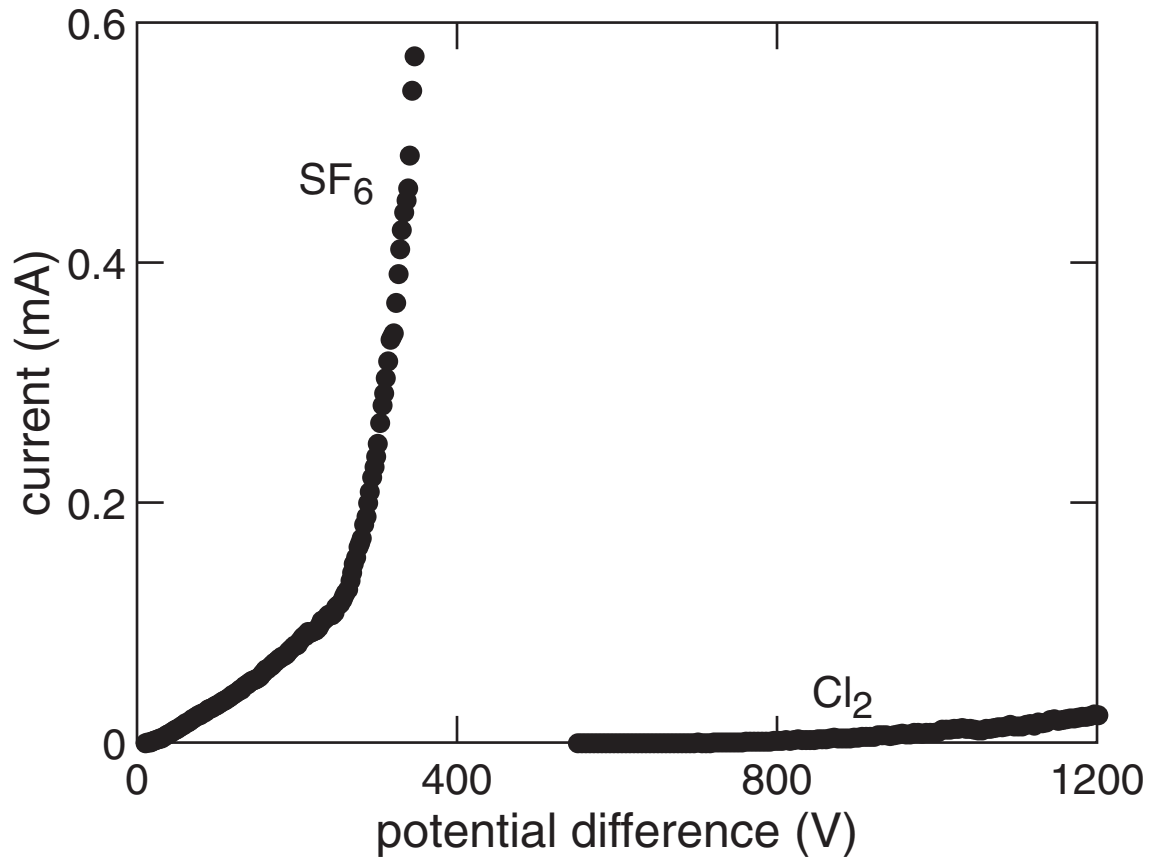
Structural and chemical analysis

effect of ambient gas on field emission



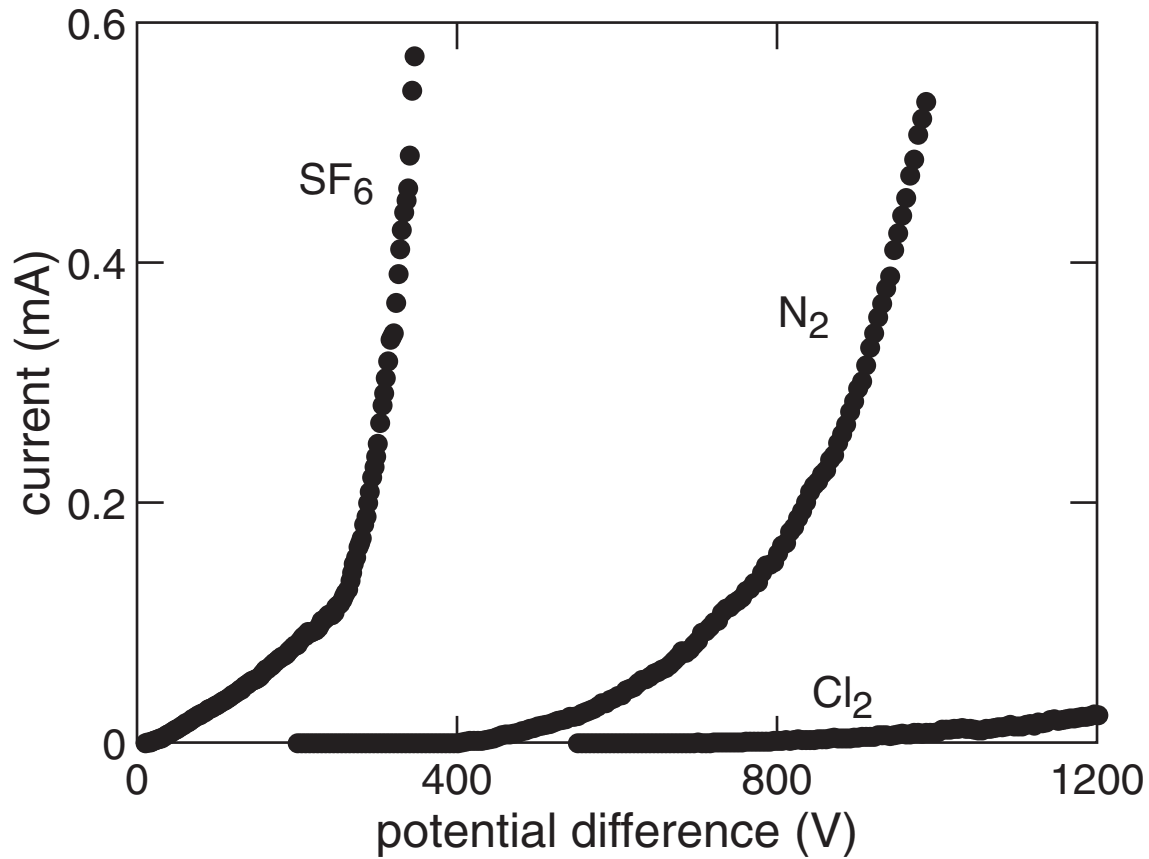
Structural and chemical analysis

effect of ambient gas on field emission



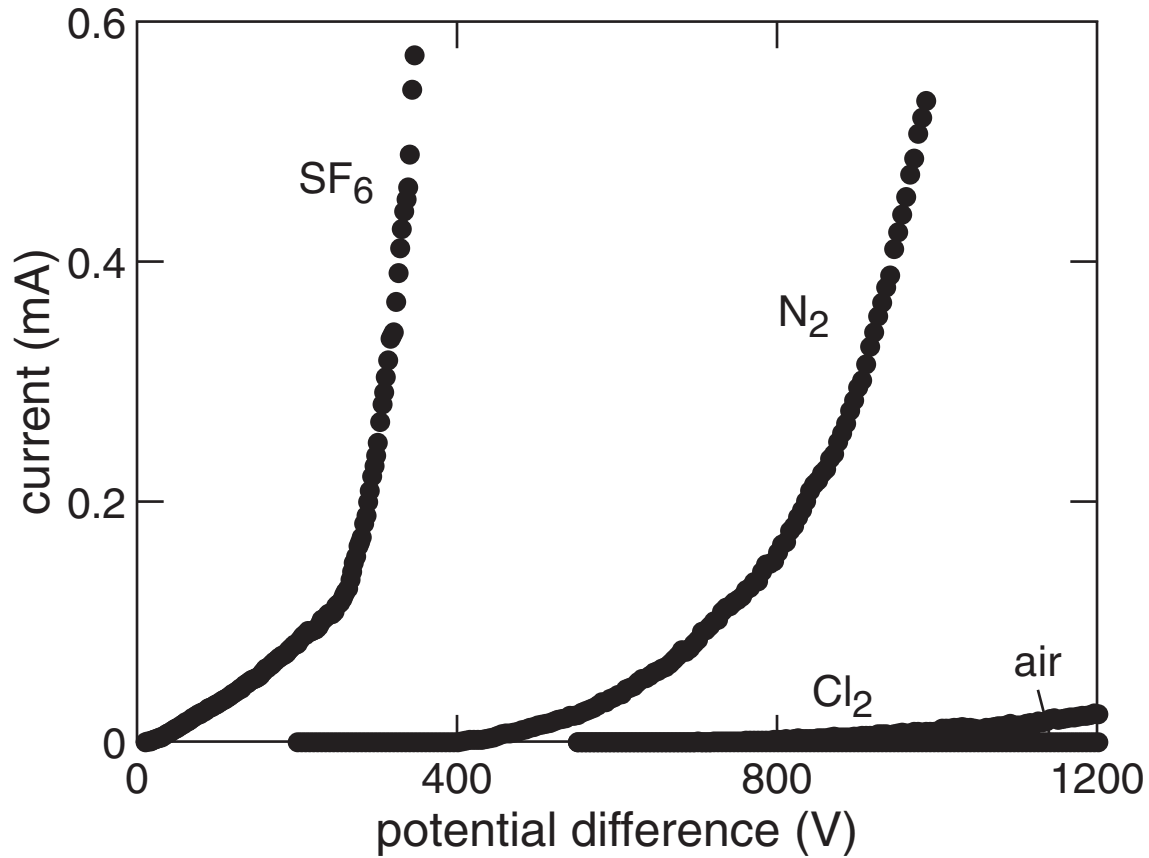
Structural and chemical analysis

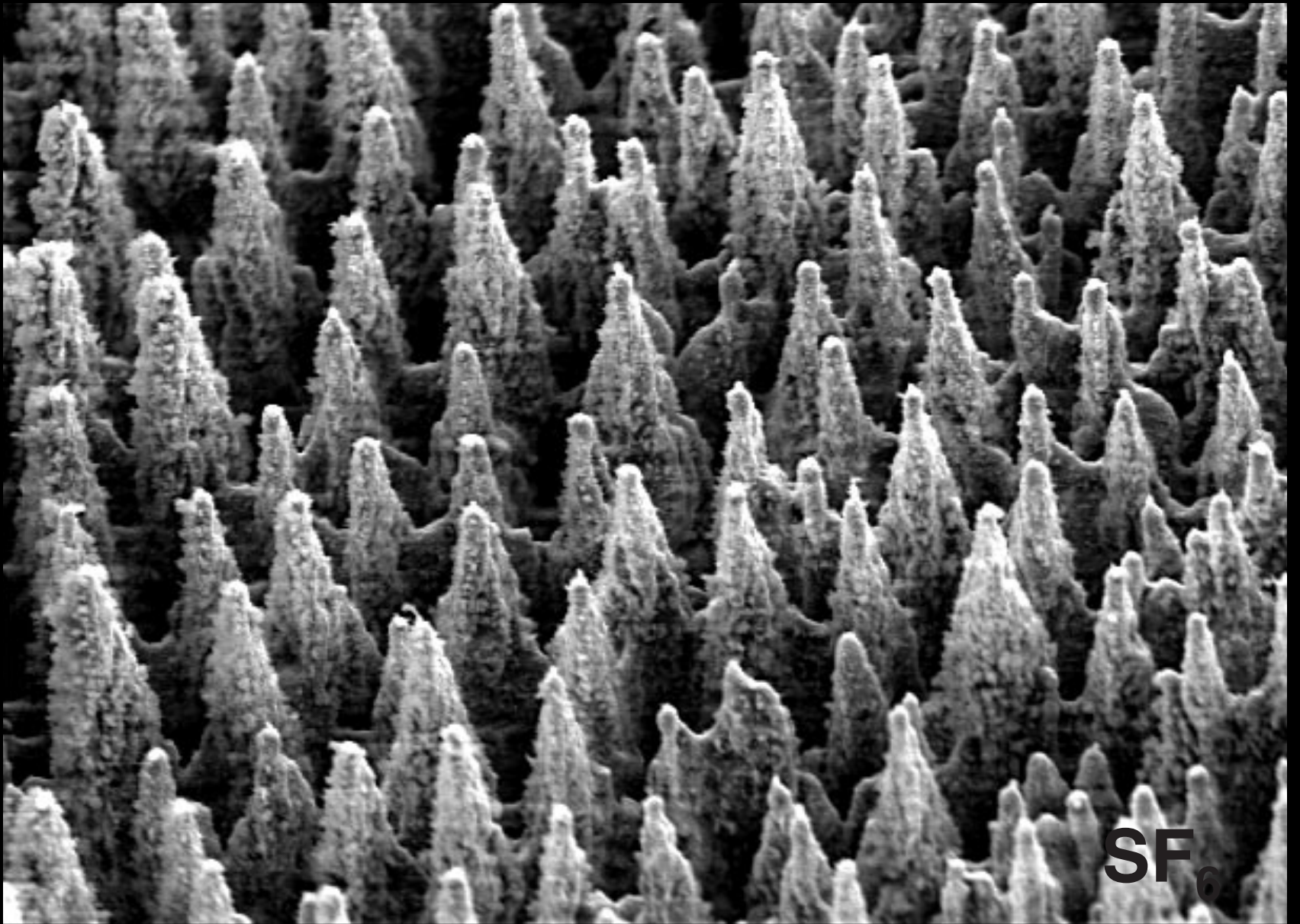
effect of ambient gas on field emission



Structural and chemical analysis

effect of ambient gas on field emission



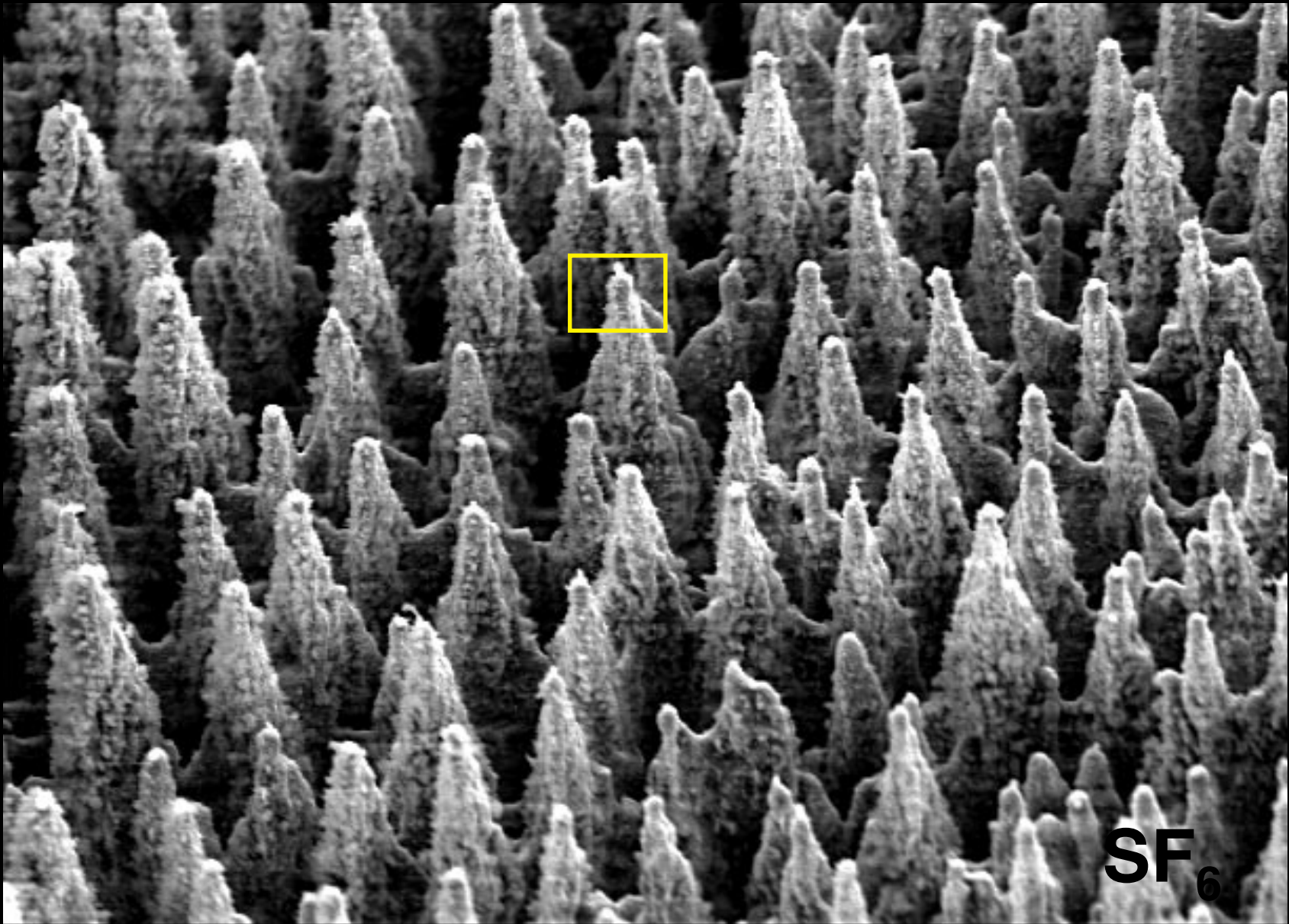


x3000
#240

10 μ m
SF6

5kV

14mm



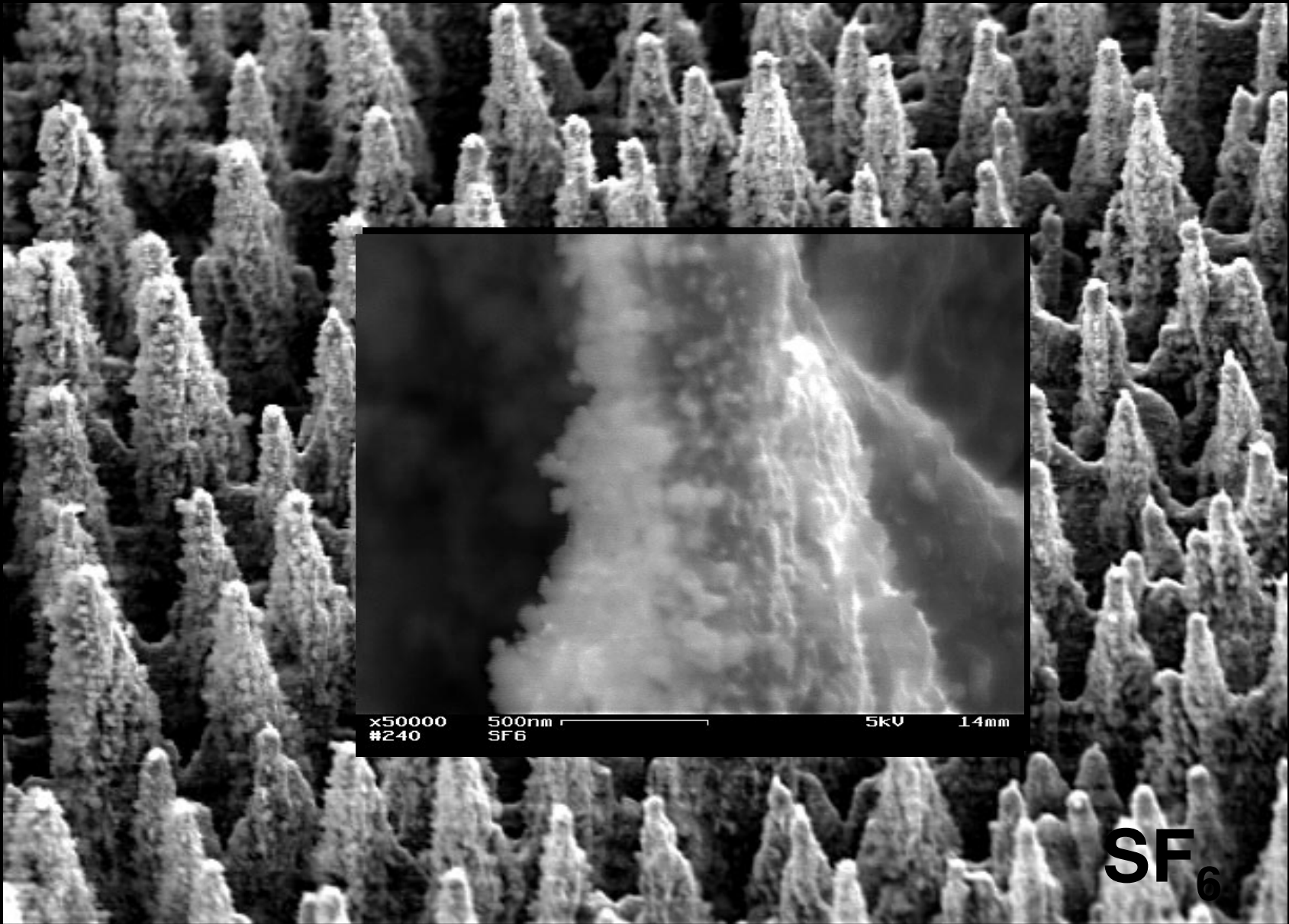
SF₆

x3000
#240

10 μm
SF6

5kV

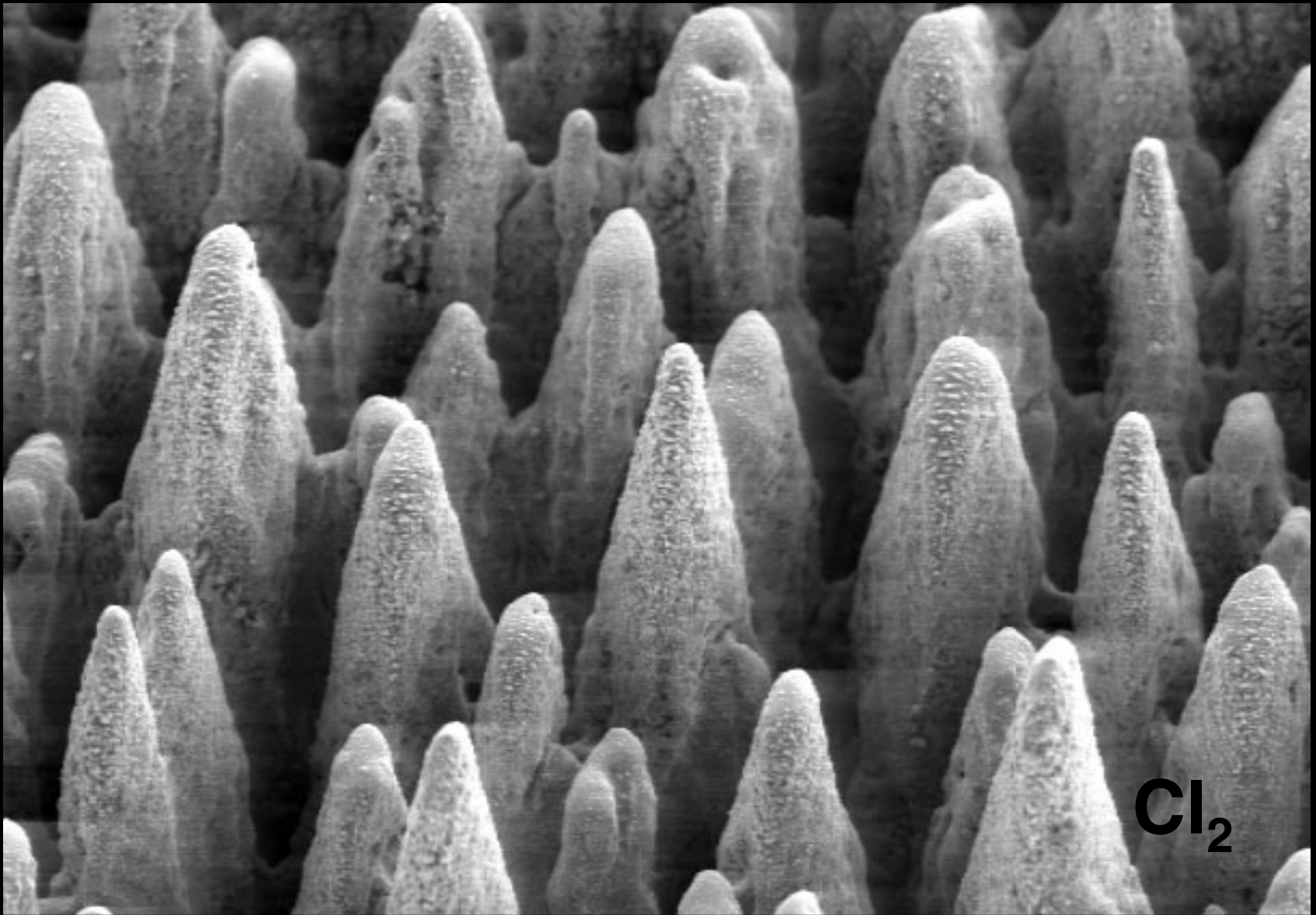
14mm



x50000 500nm 5kV 14mm
#240 SF6

SF₆

x3000 10µm 5kV 14mm
#240 SF6

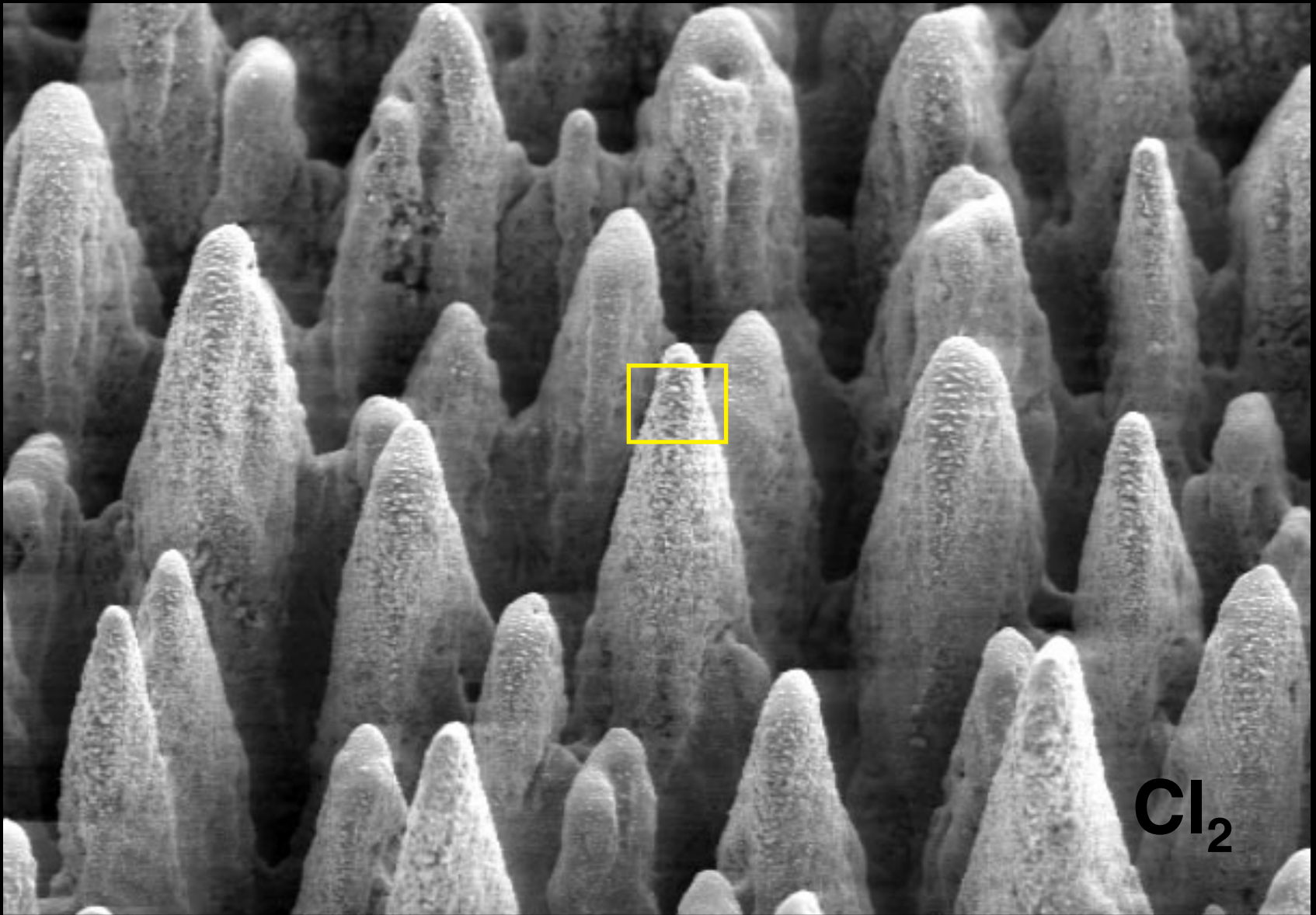


Cl₂

x3000
#34
512 x 480

10 μm
10/18 Cl2 #3

4.00kV
11/6/00
CL2#3-1.TIF
12mm

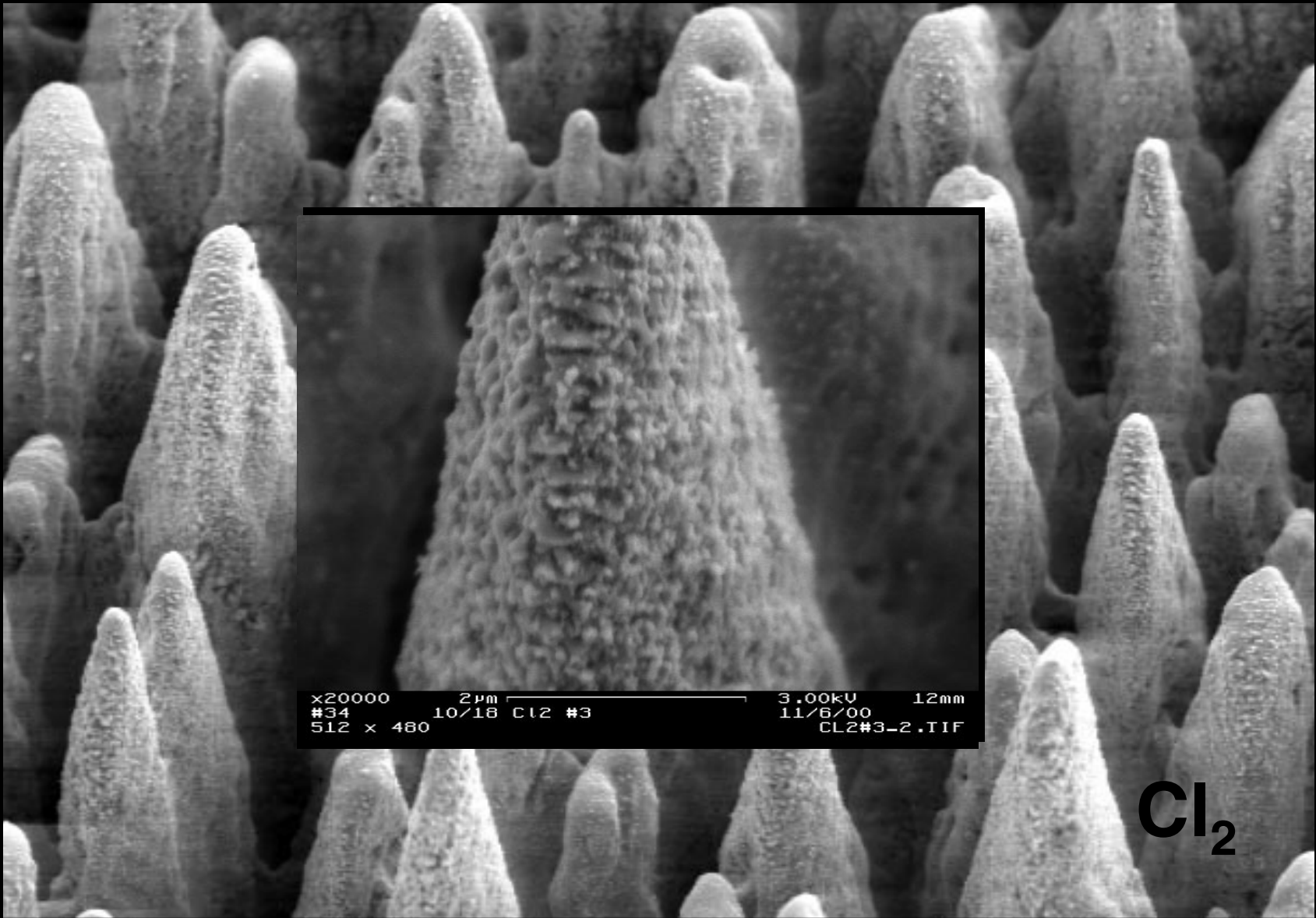


Cl₂

x3000
#34
512 x 480

10 μm
10/18 Cl2 #3

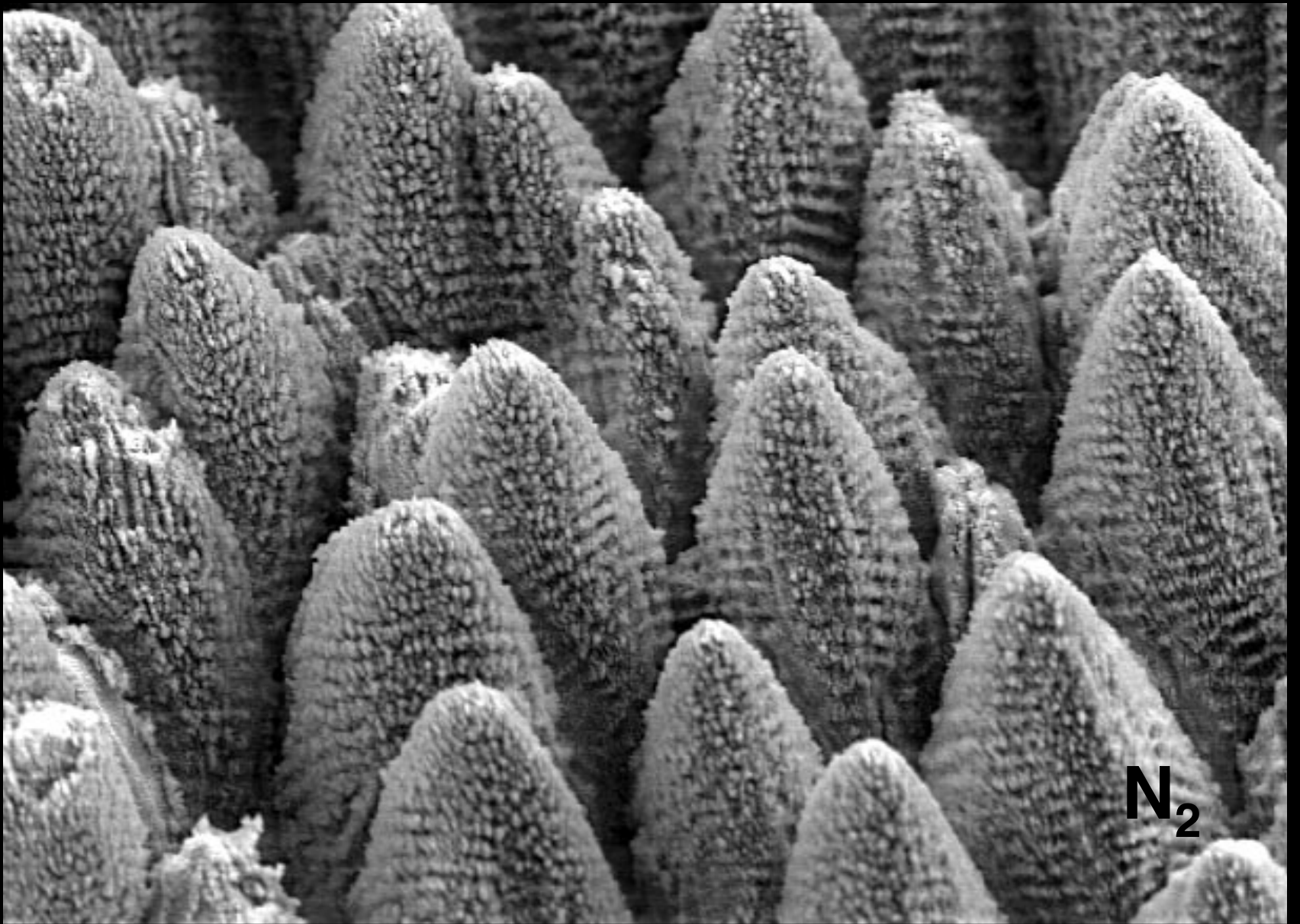
4.00kV
11/6/00
CL2#3-1.TIF
12mm



x20000 2 μm 3.00kV 12mm
 #34 10/18 Cl2 #3 11/6/00
 512 x 480 CL2#3-2.TIF

Cl₂

x3000 10 μm 4.00kV 12mm
 #34 10/18 Cl2 #3 11/6/00
 512 x 480 CL2#3-1.TIF



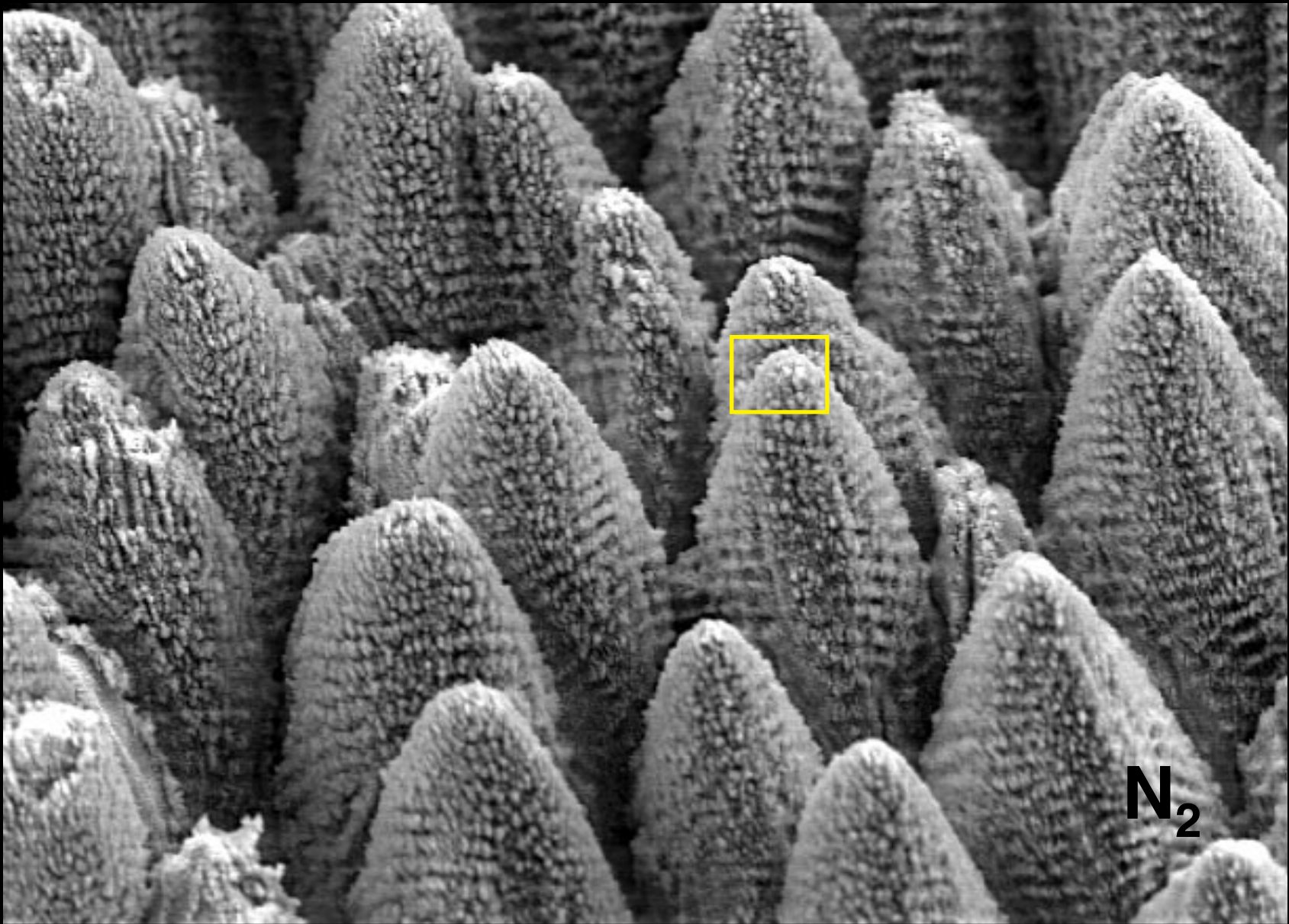
N_2

x3000
#240

10 μ m

5kV

14mm



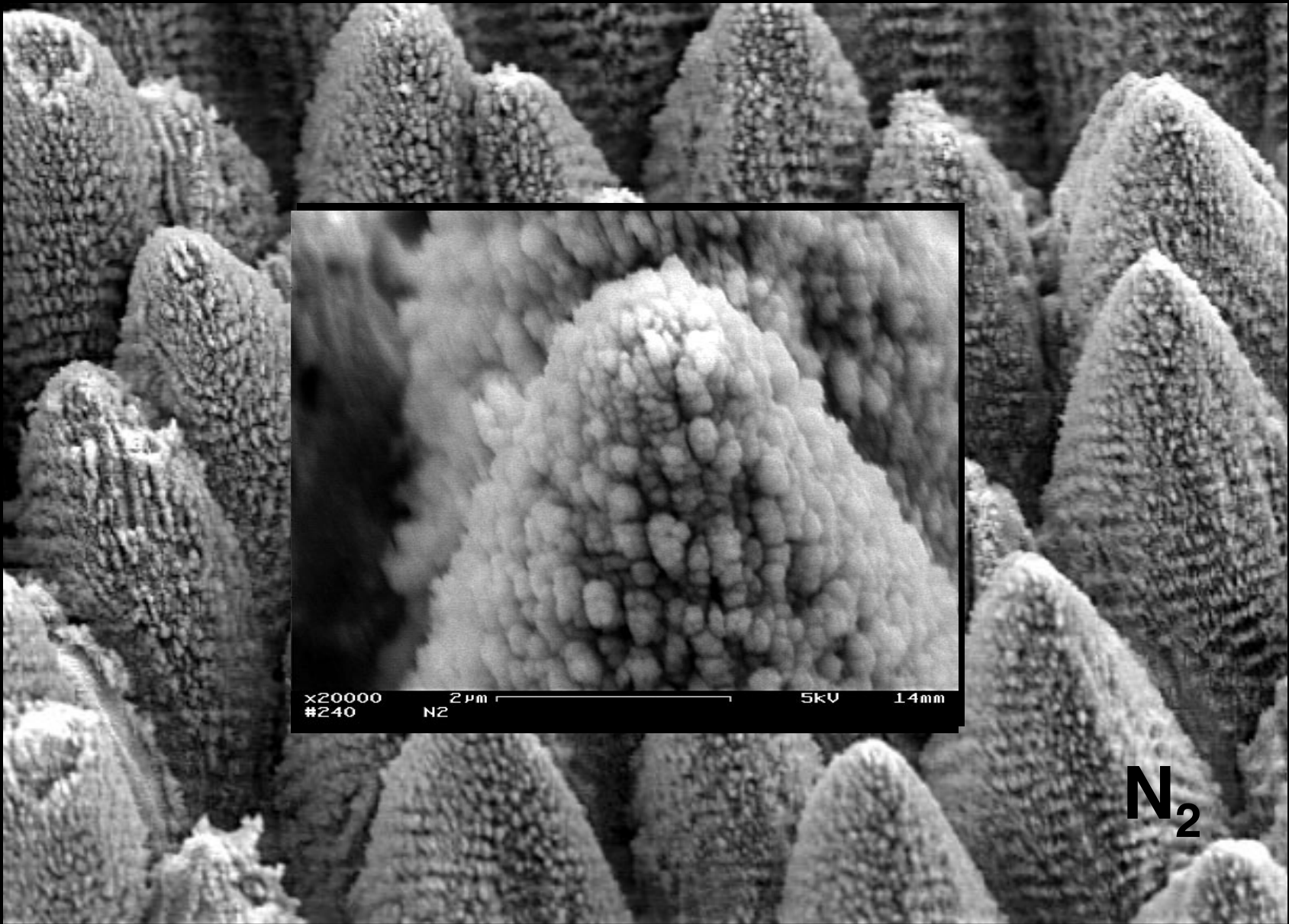
N_2

x3000
#240

10 μ m

5kV

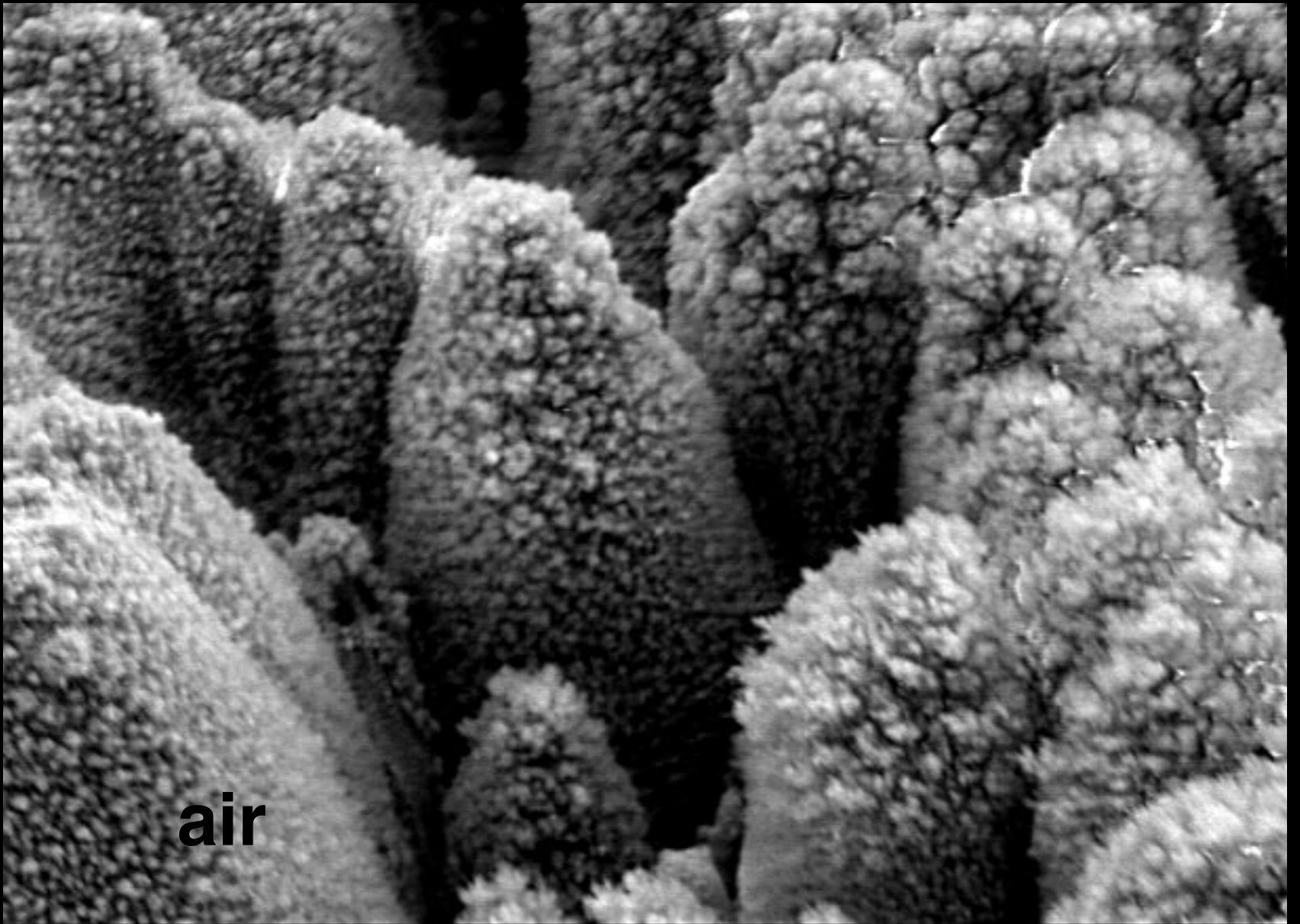
14mm



x20000 2µm 5kV 14mm
#240 N2

N₂

x3000 10µm 5kV 14mm
#240 N2



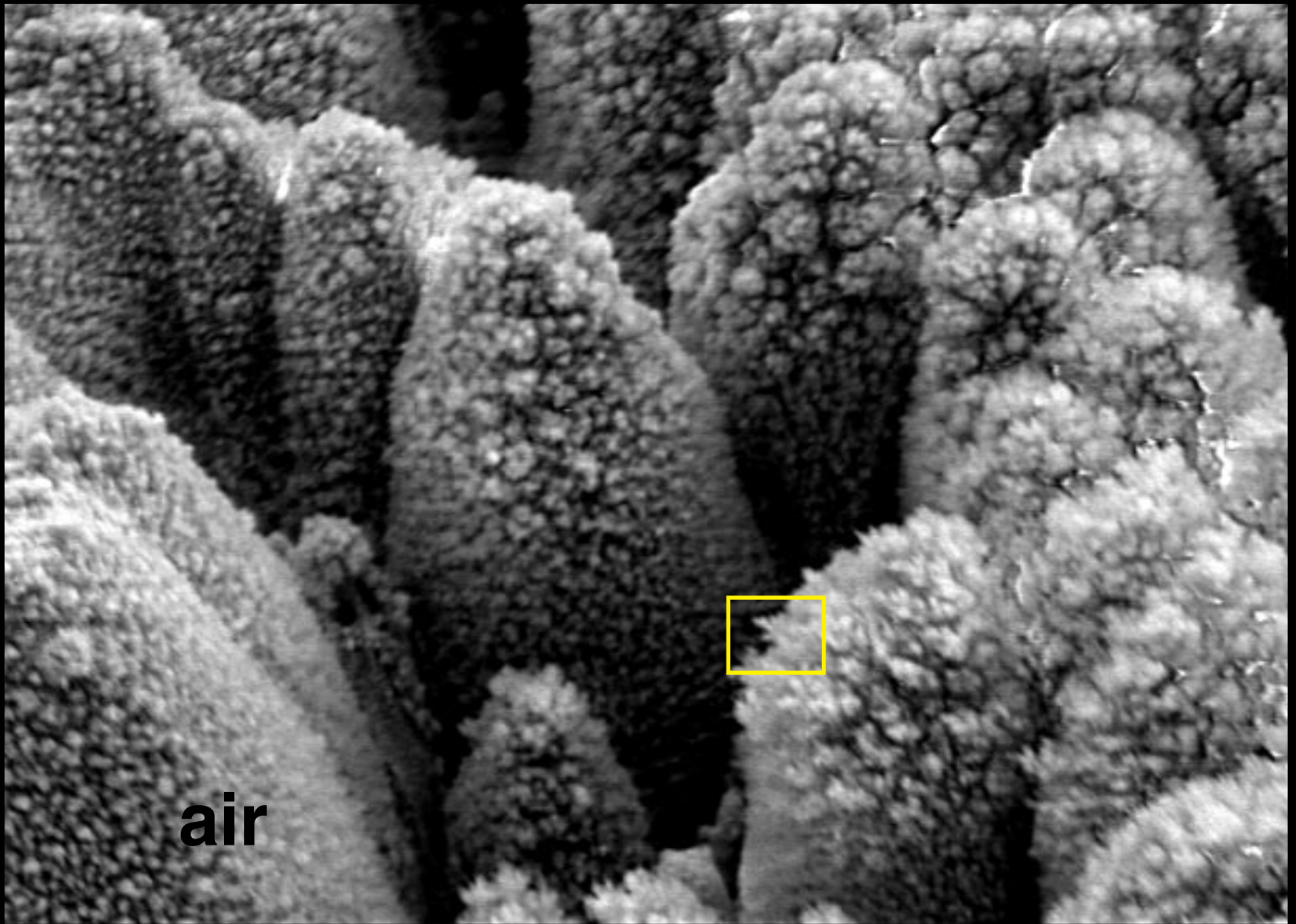
air

x3000
#240

10 μ m
SF6

5kV

14mm

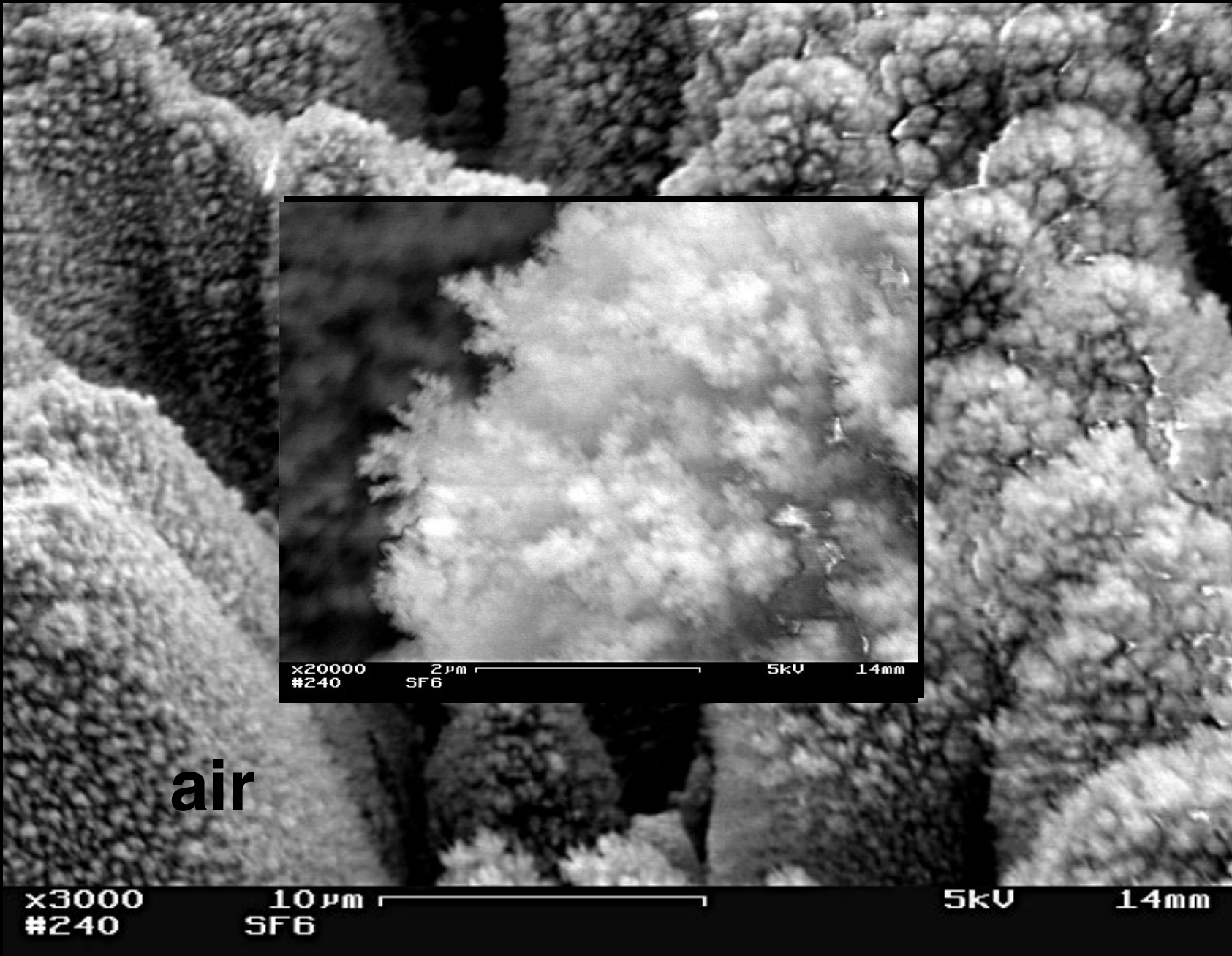


x3000
#240

10 μ m
SF6

5kV

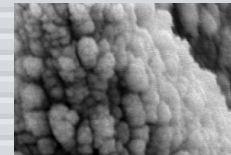
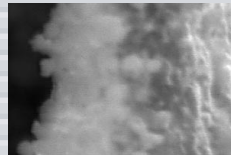
14mm



Structural and chemical analysis

	SF₆	Cl₂	N₂	air
IR absorption	high	medium	low	low
field emission	high	low	medium	low
SIMS	high S	?	?	high O

nanostucture



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 plate or a filthy Petri dish today, when

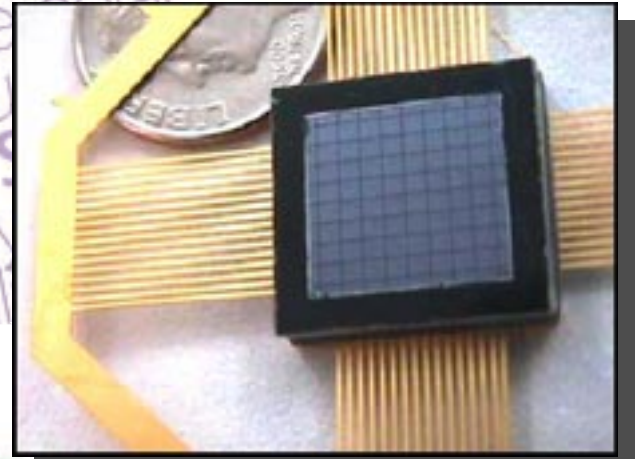
semiconductors with a powerful laser. In the early 1990s, Mazur's was the first academic lab in the world to get its hands on a femtosecond laser. This device produces pulses of light that are hundreds of times brighter than the Sun. and extremely

around the laboratory," he claims. Well, it was almost the only reason a short laser pulse will break down into sulphur and fluorine radicals, which will attack a silicon substrate. "Hydrogen fluoride is used to etch silicon. I thought maybe the SF₆ would do it and then the fluorine would so with the silicon," Mazur explains. than

Outlook

▶ detector technology

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



TALL, DARK AND STRANGER

We'll all love stories of sci-fi... This...
...to look back to a time when a single...
...of a life's journey when...

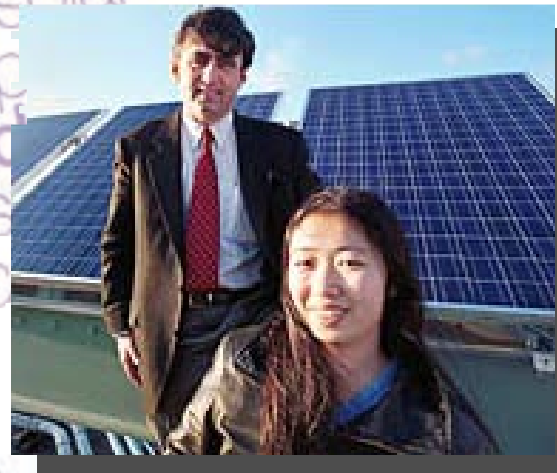
semiconductors with a powerful laser...
the early 1960s. Major's was the first...
academic lab in the world to do so...
hard over a ten-year period. This...
...as a source of light that included...
...times brighter than the Sun...
...and extremely

around the laboratory," he claims...
"Well, it was a great time to be...
...the sun and the moon...
...with a lot of...
...thought that the...
...the silicon. Most ex...

Outlook

- ▶ detector technology
- ▶ solar cells

A forest of silicon spikes could revolutionise solar cells and give you free energy injections. Bruce S. Ziegler peers into the mysterious world of black silicon



TALL, DARK AND STRANGER

We'll all agree that it's weird. This man to look back to a time when a single site of a city's power distribution system when

semiconductors with a potential use for the early 1960s. Major's was the first academic lab in the world to do so. hard over a ten-year period. This device produces a glow of light that is much brighter than the Sun and extremely

around the "invention," he claims. "While it was a great step, the only mistake I see is that it was not built to be used in a practical and efficient way. It will attack a silicon substrate. But there is a need to create silicon through a process that would allow the silicon. Most ex-

Outlook

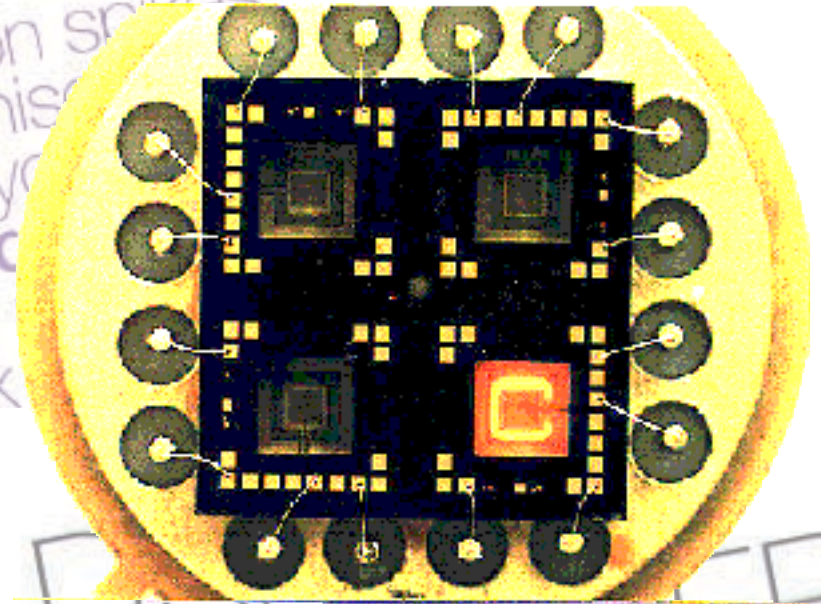
- ▶ detector technology
- ▶ solar cells
- ▶ display technology



Outlook

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

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



TALL, DARK
AND STRANGER

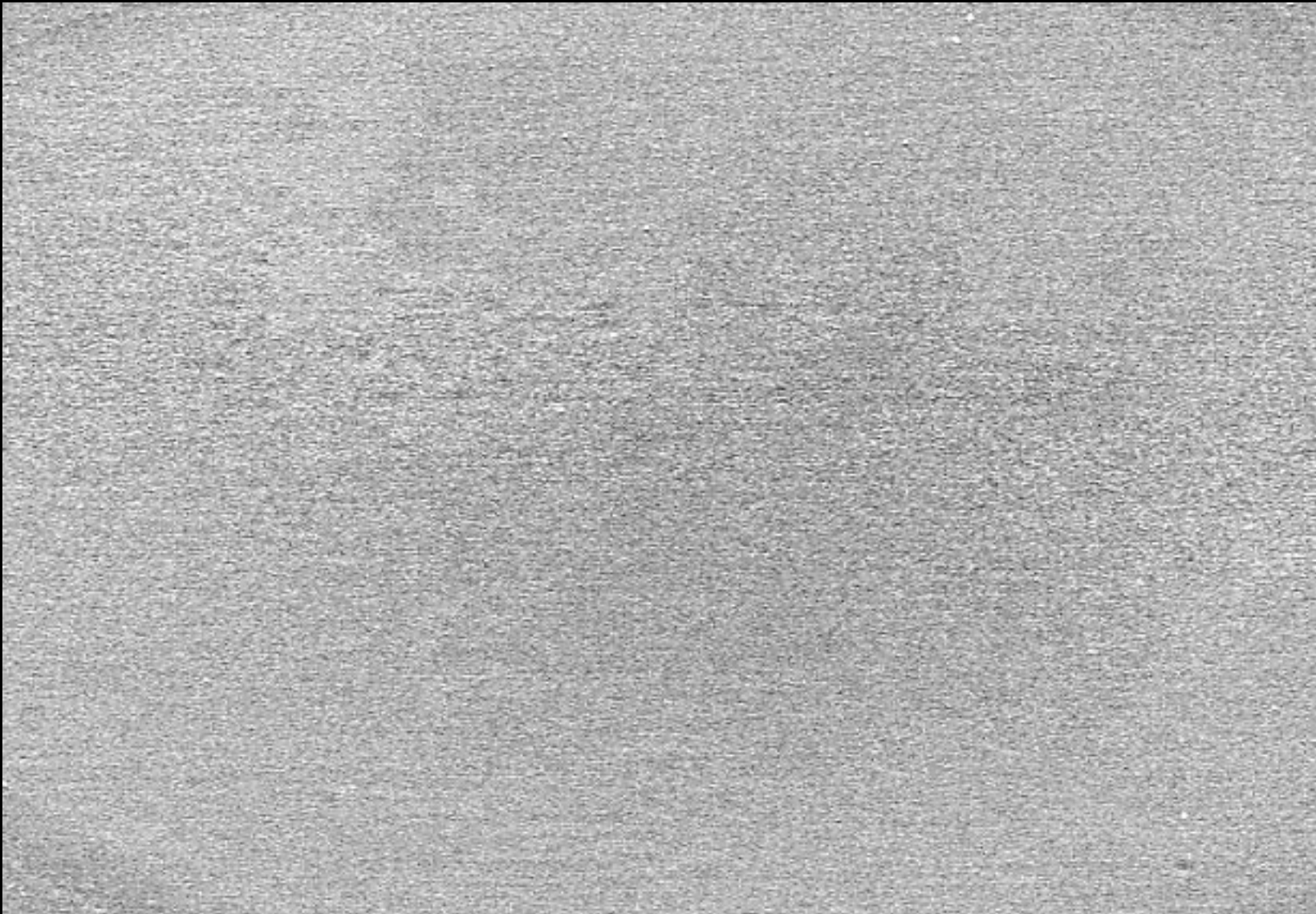
We'll all have stories of weird jobs. This
one to ask for a long time when a legend
of a life's time. You don't
only when

semiconductors with a potential use for
the early 1960s. Major's was the first
academic lab in the world to do so.
hard over a ten-year period. This was
an idea as far as light that included
a lamp brighter than the Sun
and extremely

around the laboratory," he claims.
While it was a great idea, it was
short-lived. "I was not happy to see
it go up and down the road. Had
it not been for the silicon, it would
have been a failure. It would have
been the silicon. Most ex-

Outlook

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



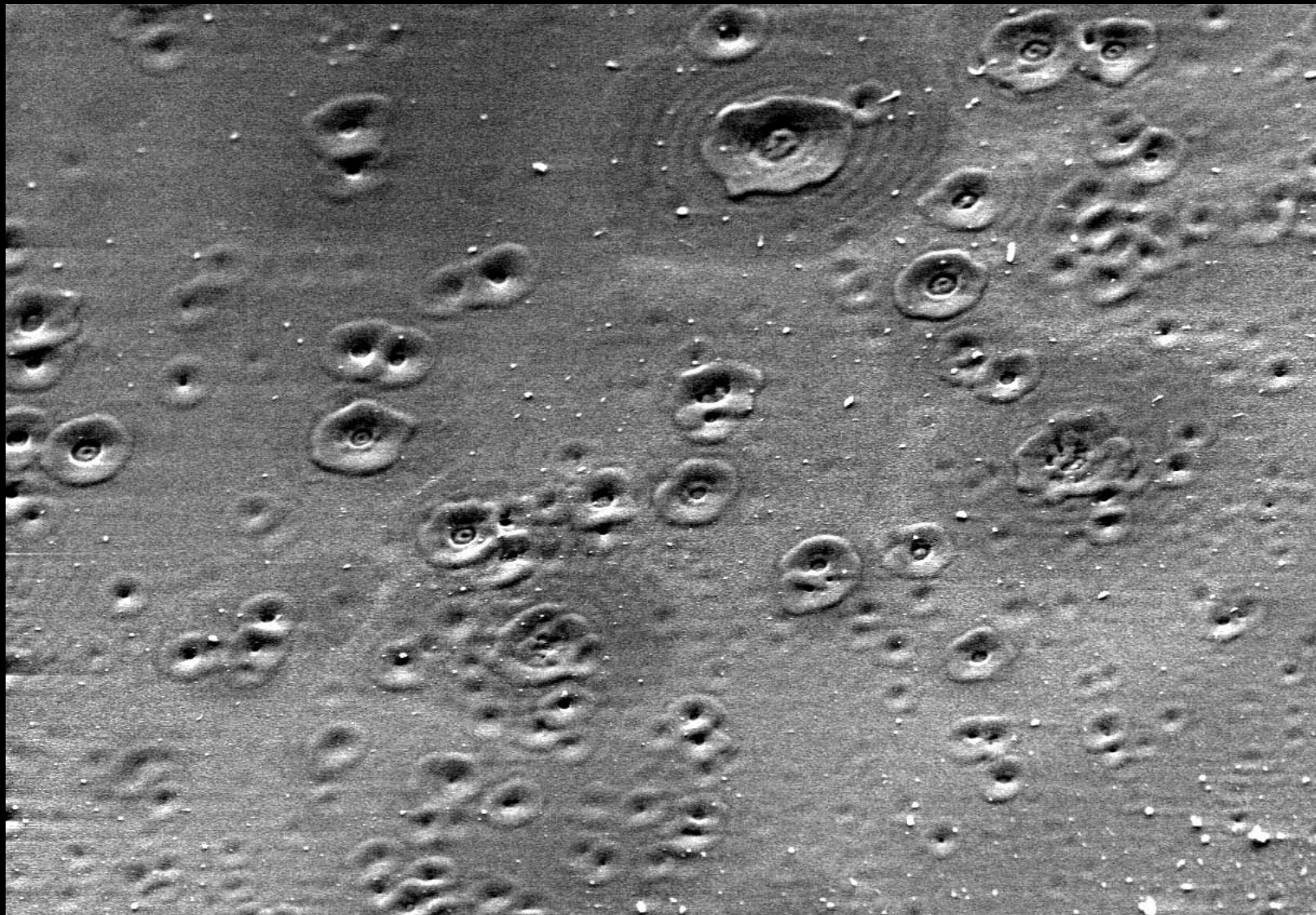
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0000



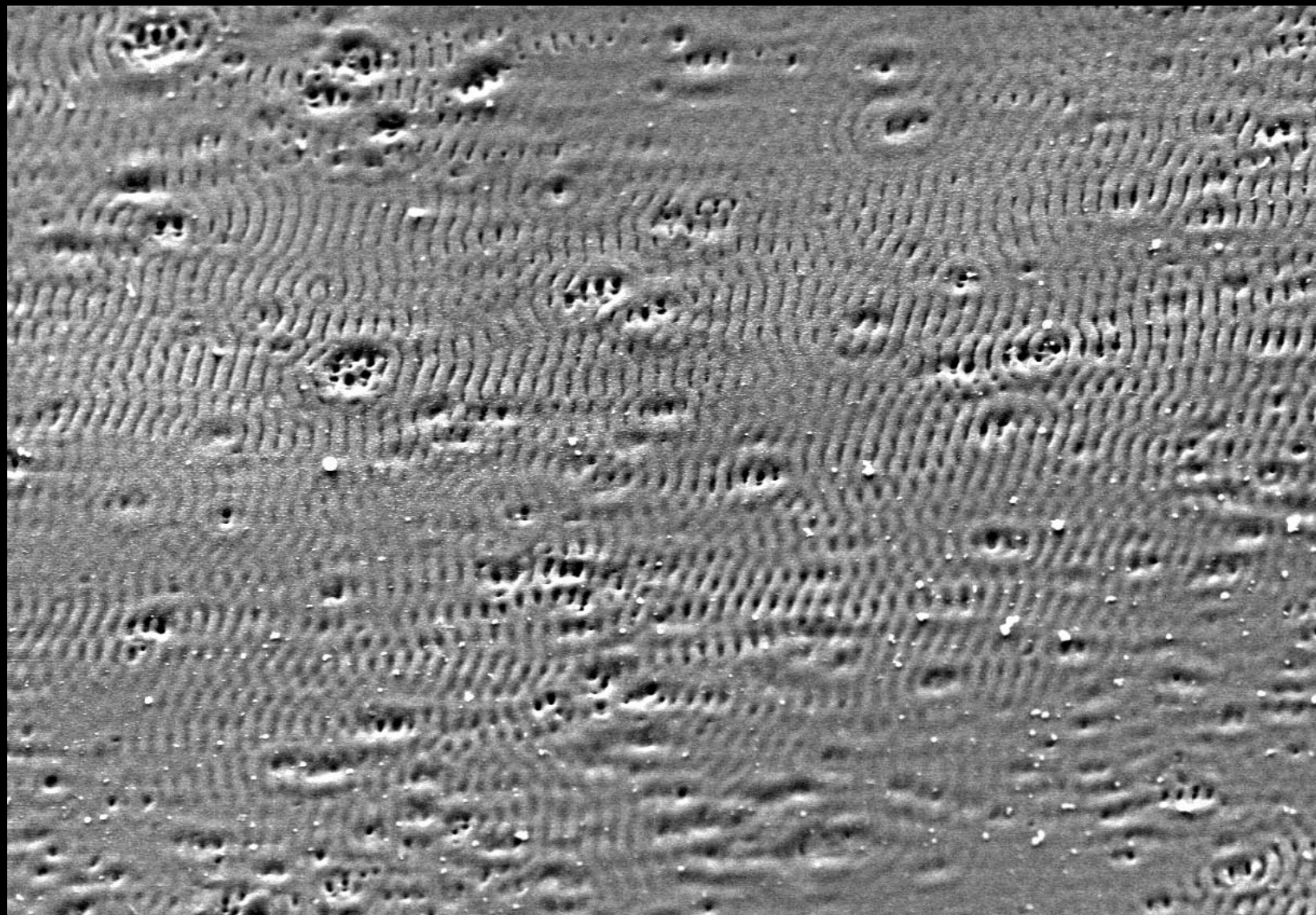
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#3548
512 x 480

20 μ m

10kV

15mm

0001



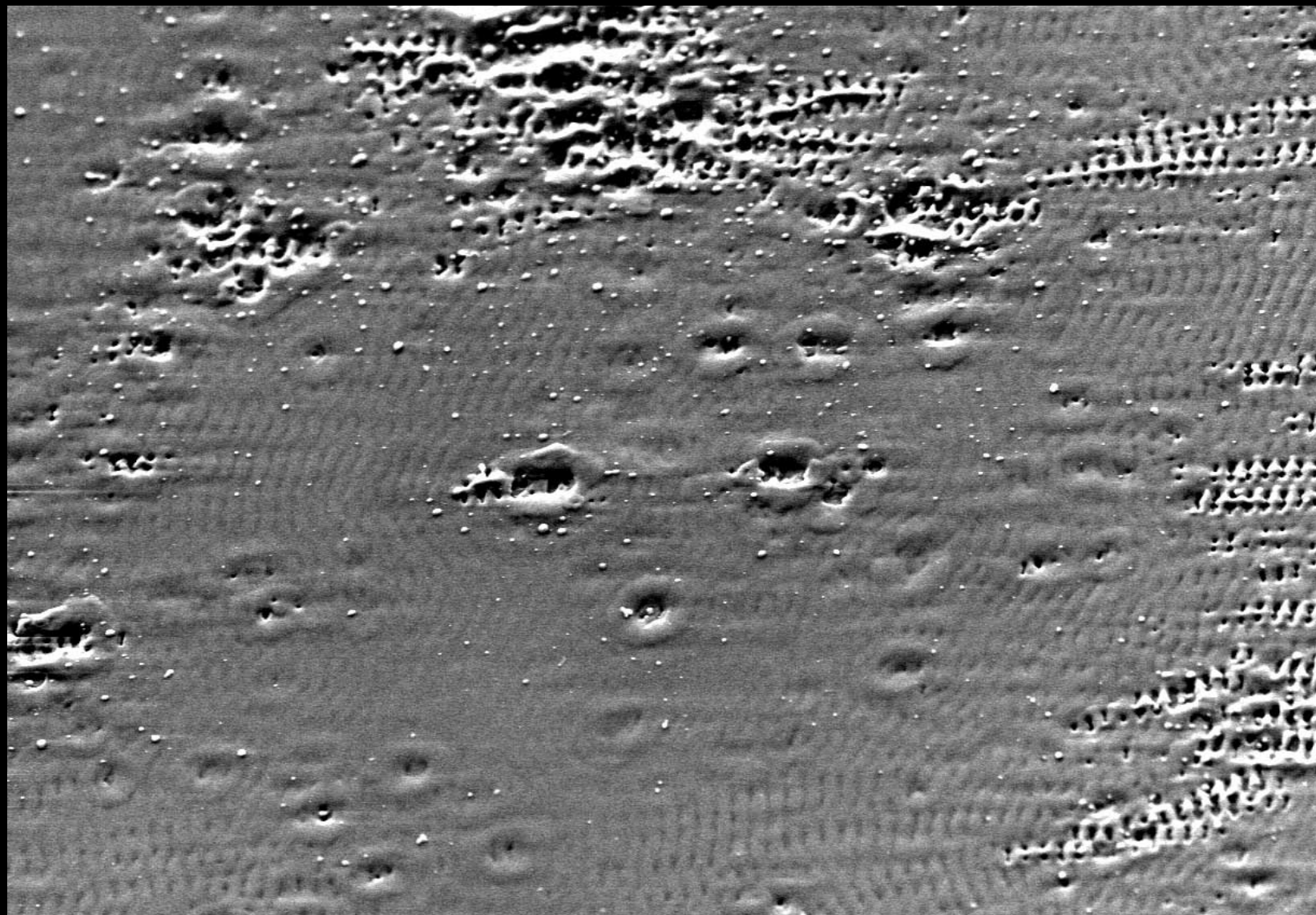
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512 x 480

20 μ m

10kV

15mm

0002



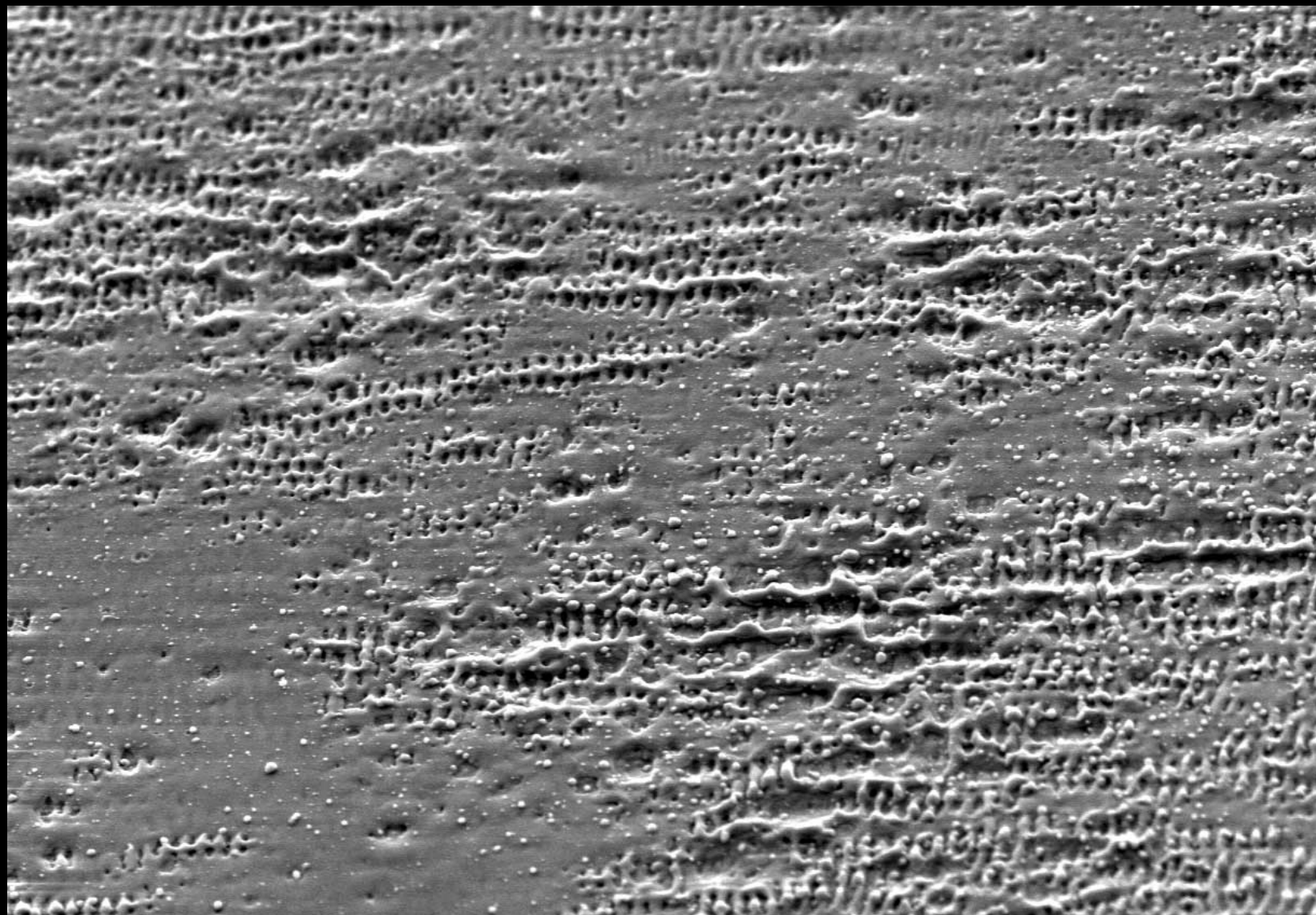
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20 μ m

10kV

15mm

0003



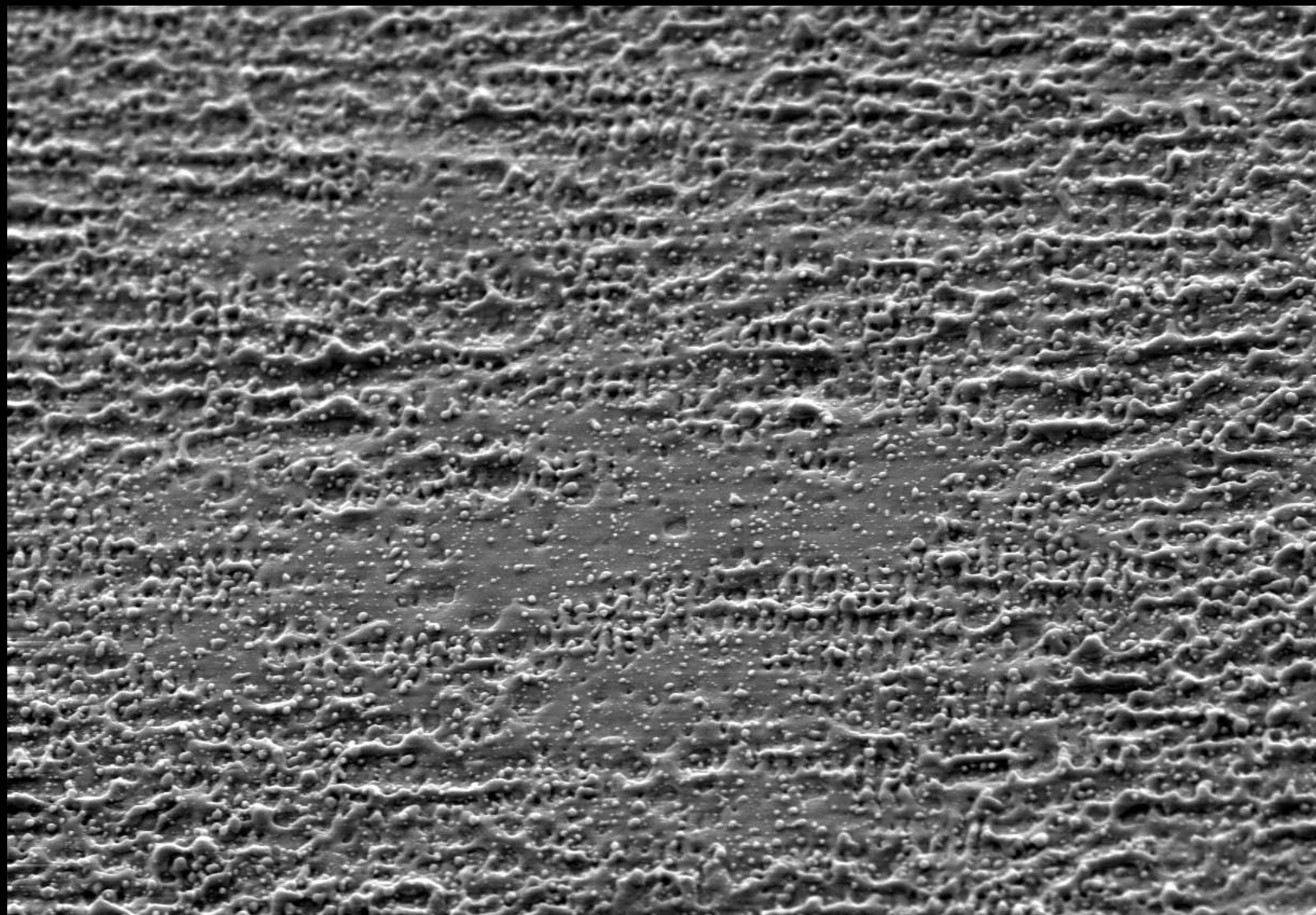
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512 x 480

20 μm

10kV

15mm

0004



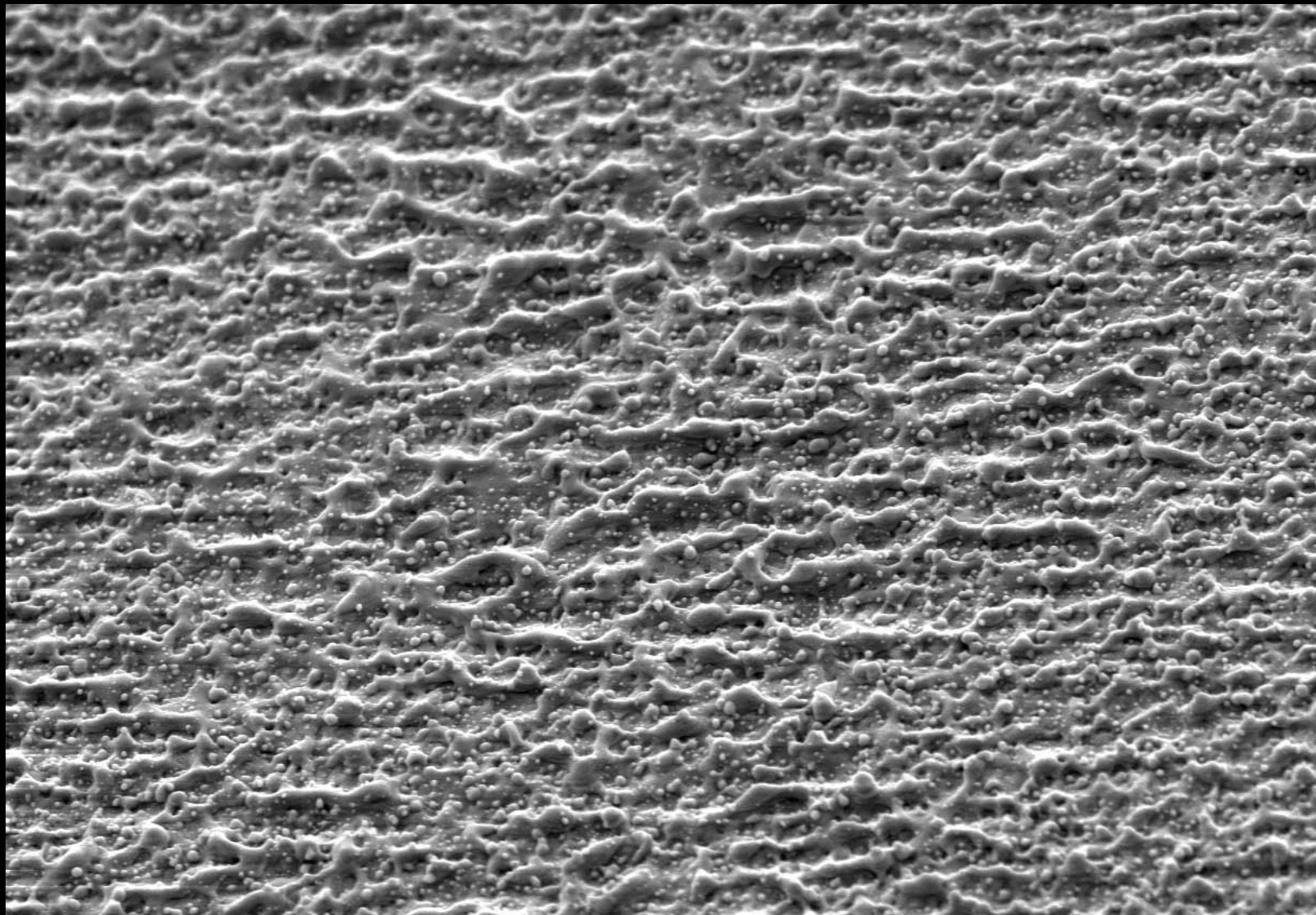
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512 x 480

20 μm

10kV

15mm

0005



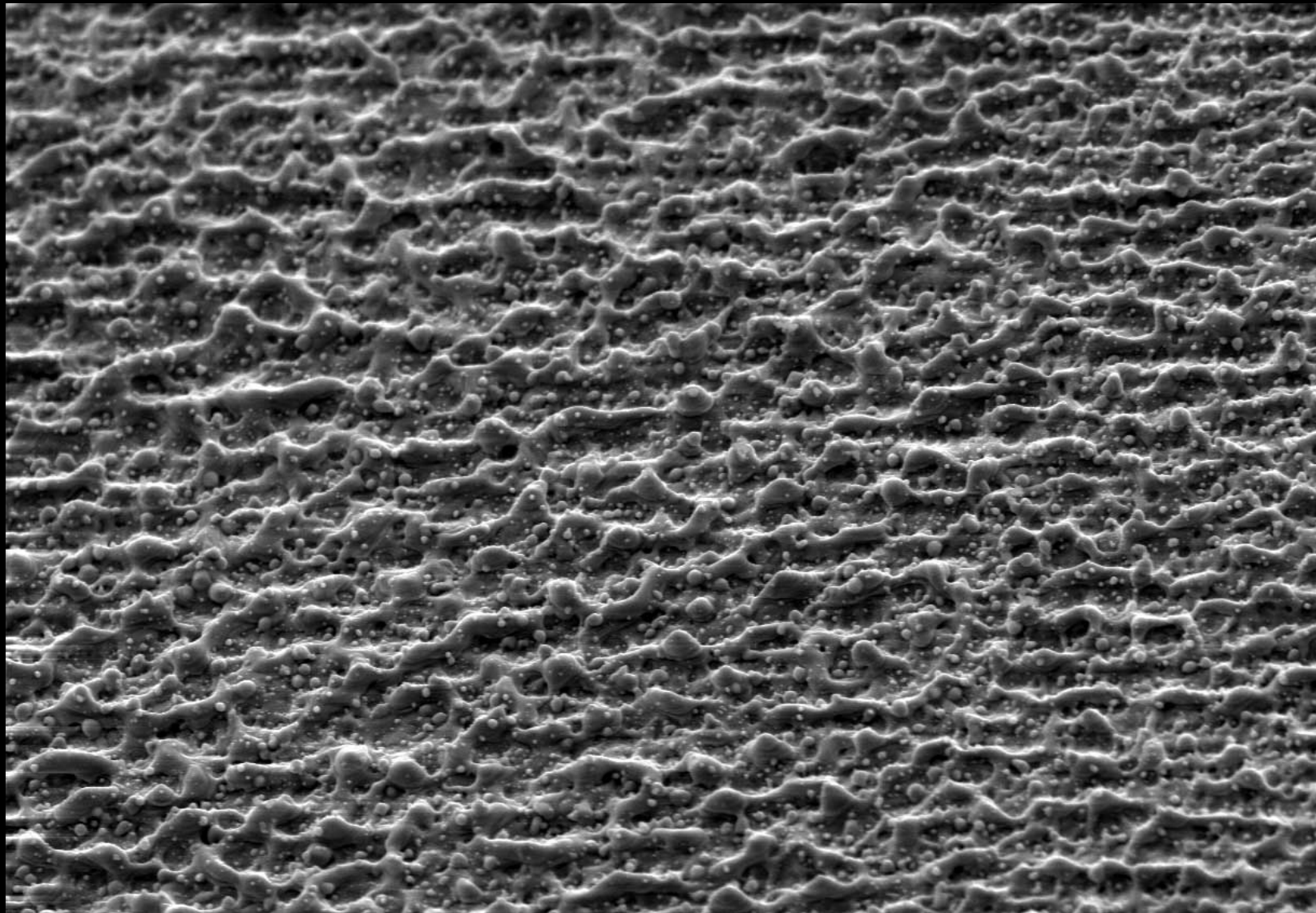
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20 μ m

10kV

15mm

0006



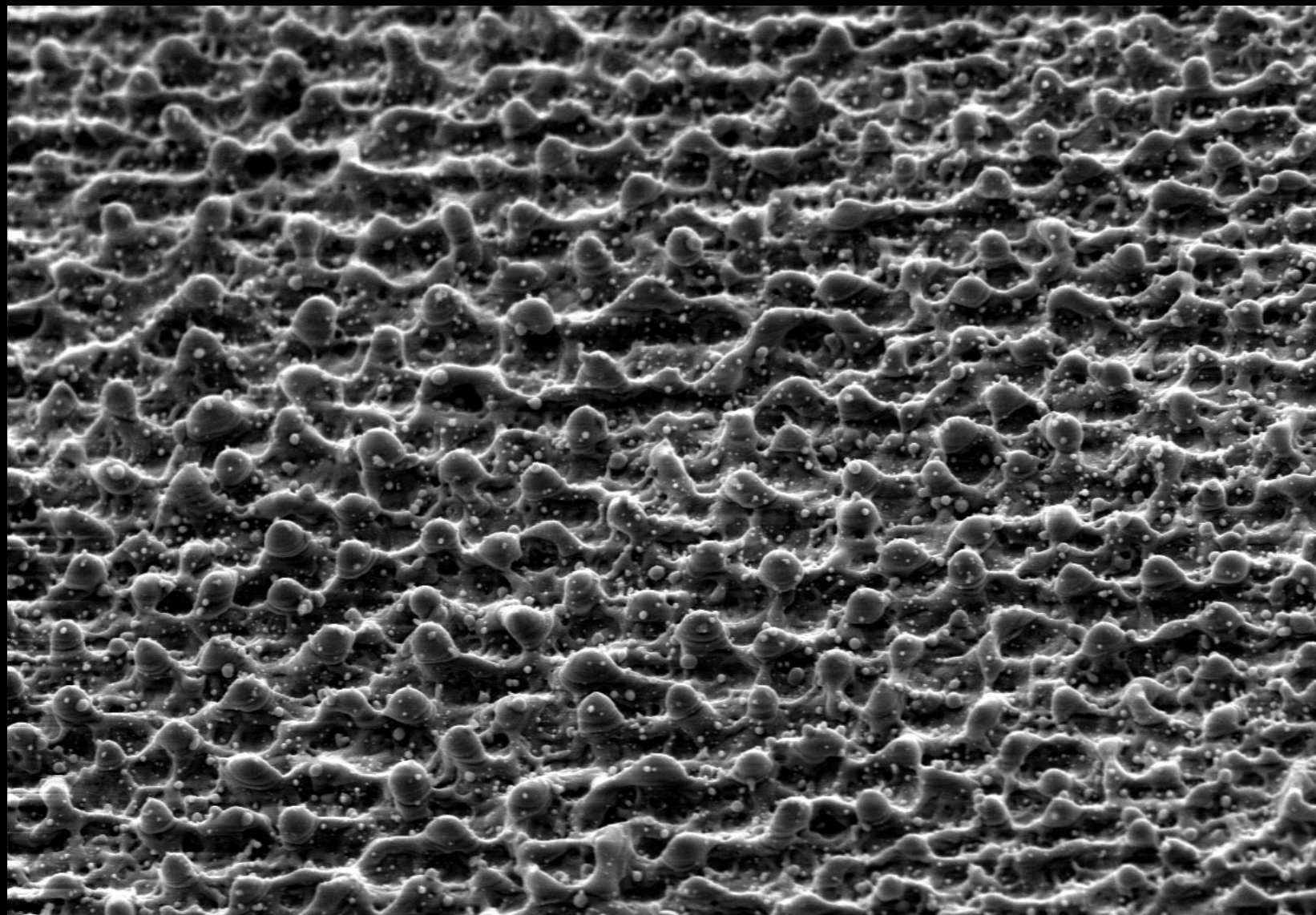
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20 μ m

10kV

15mm

0008



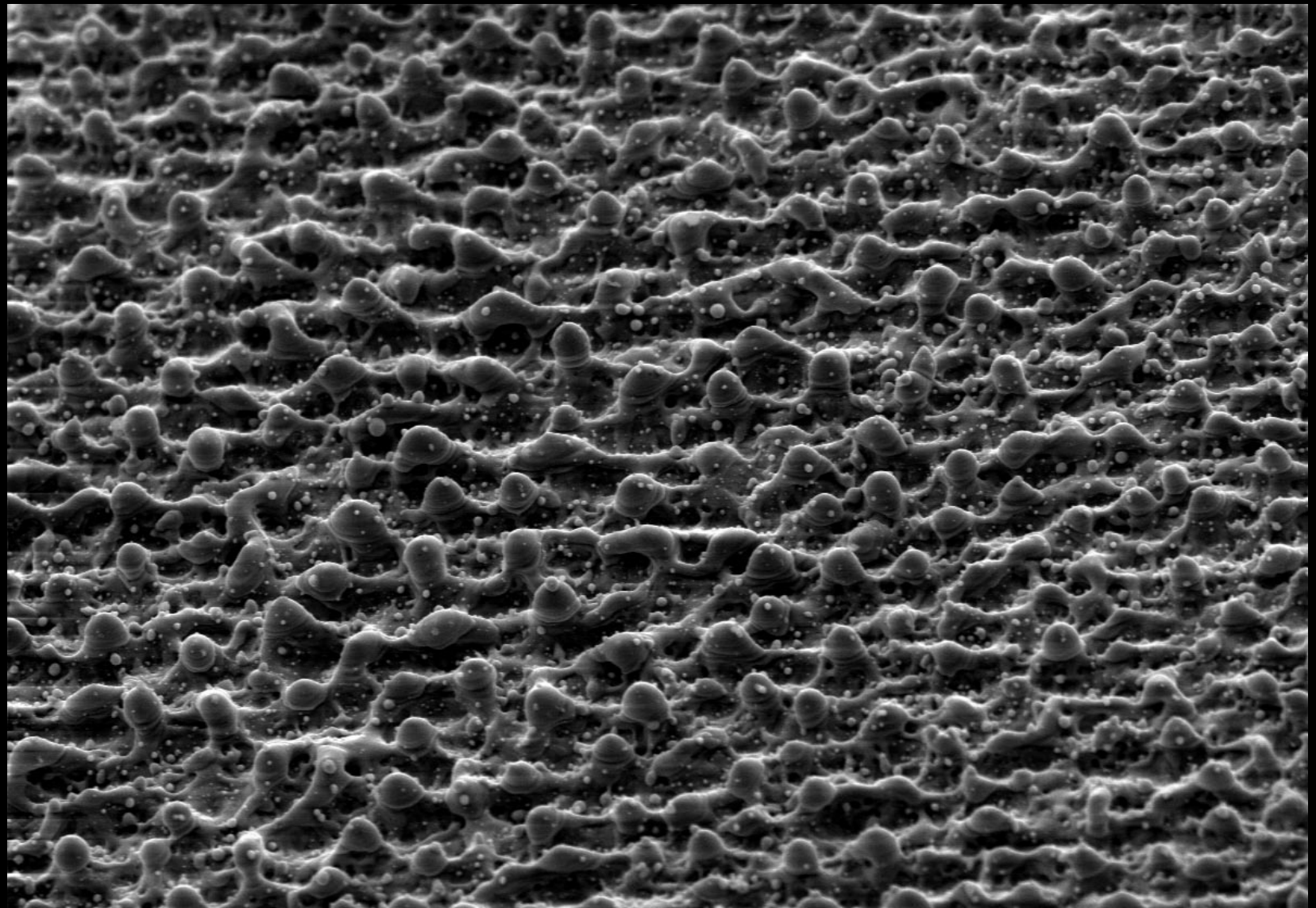
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#3548
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20 μ m

10kV

15mm

0010



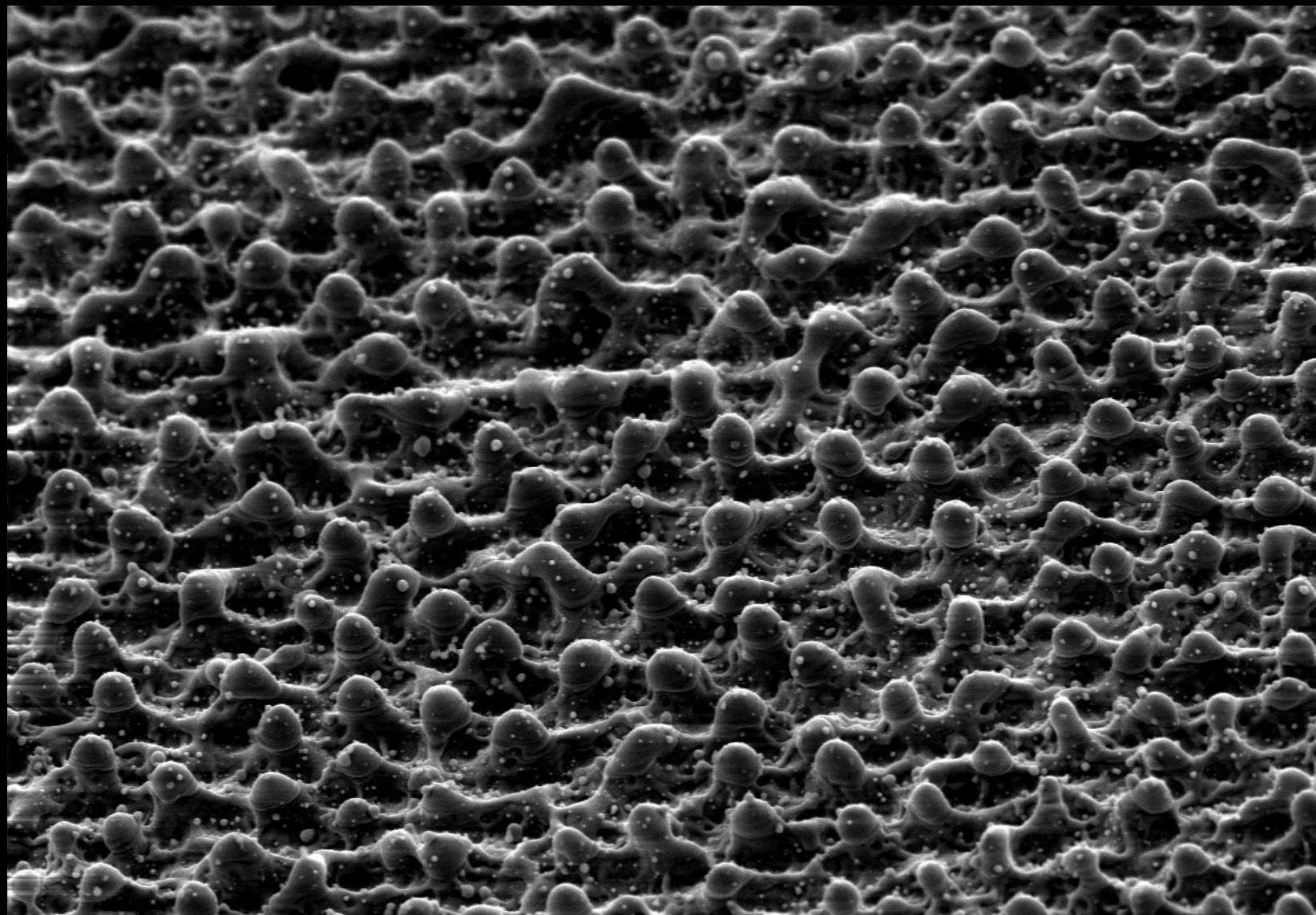
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0012



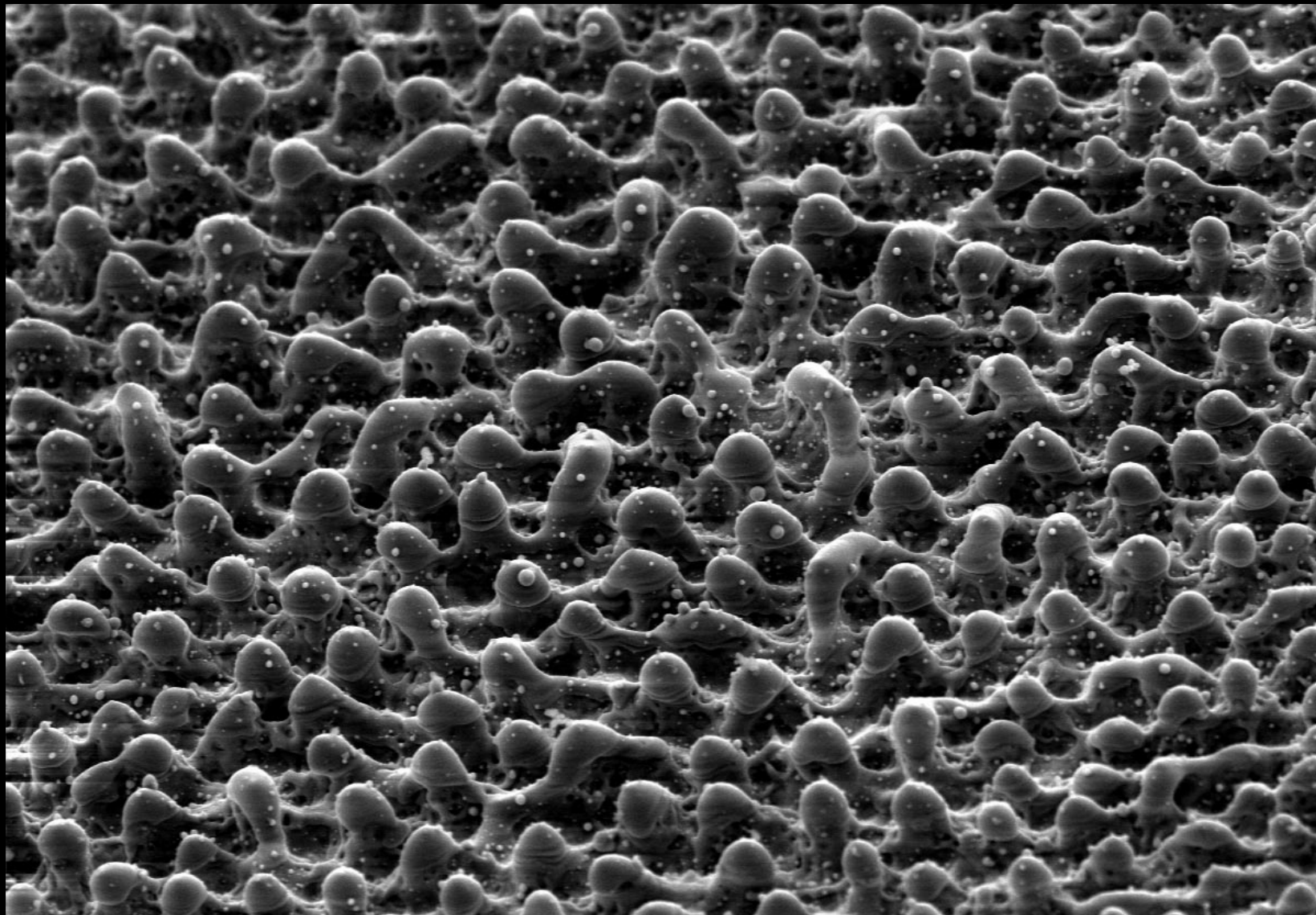
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0015



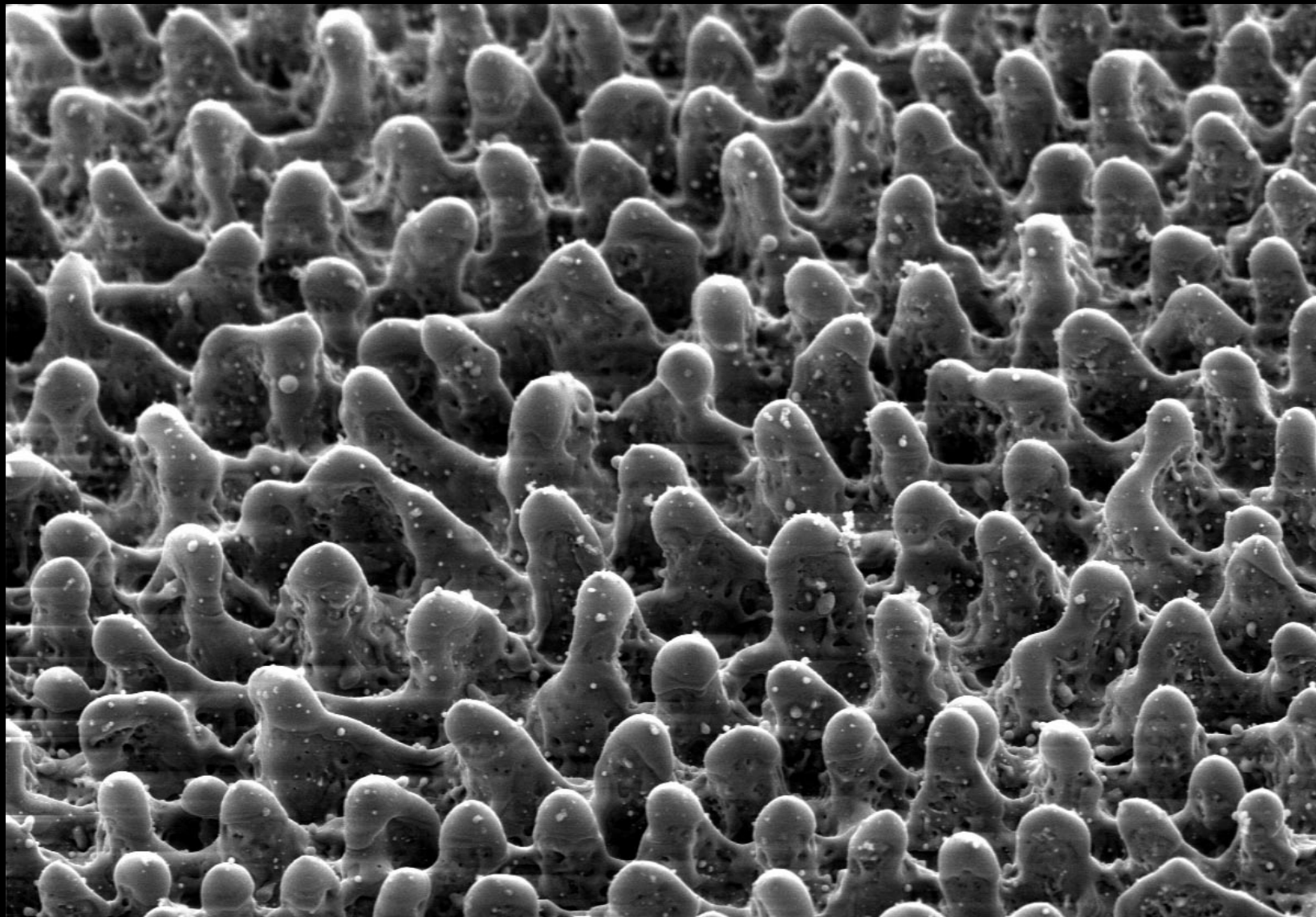
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20 μ m

10kV

15mm

0020



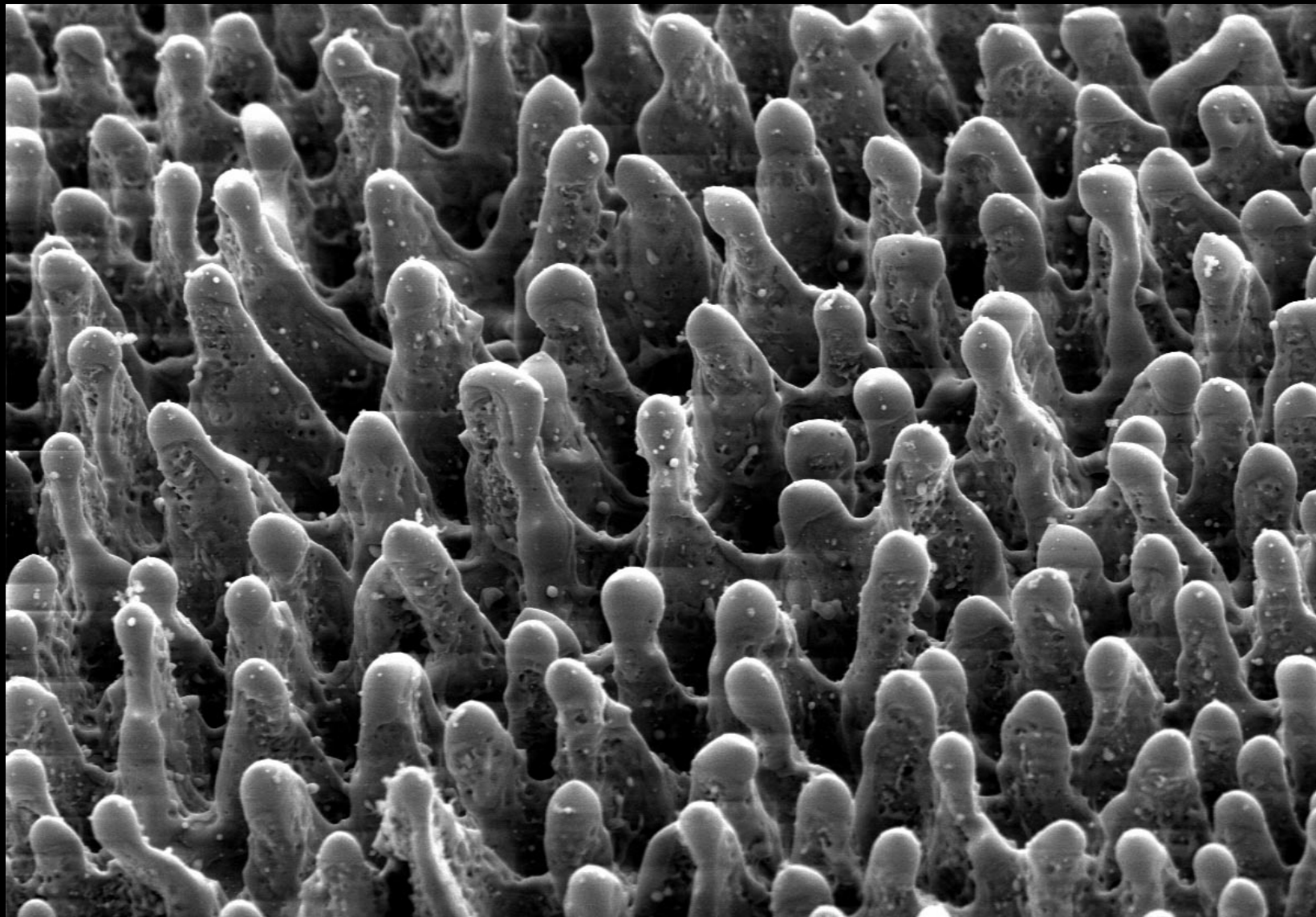
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#3548
512 x 480

20 μ m

10kV

15mm

0030



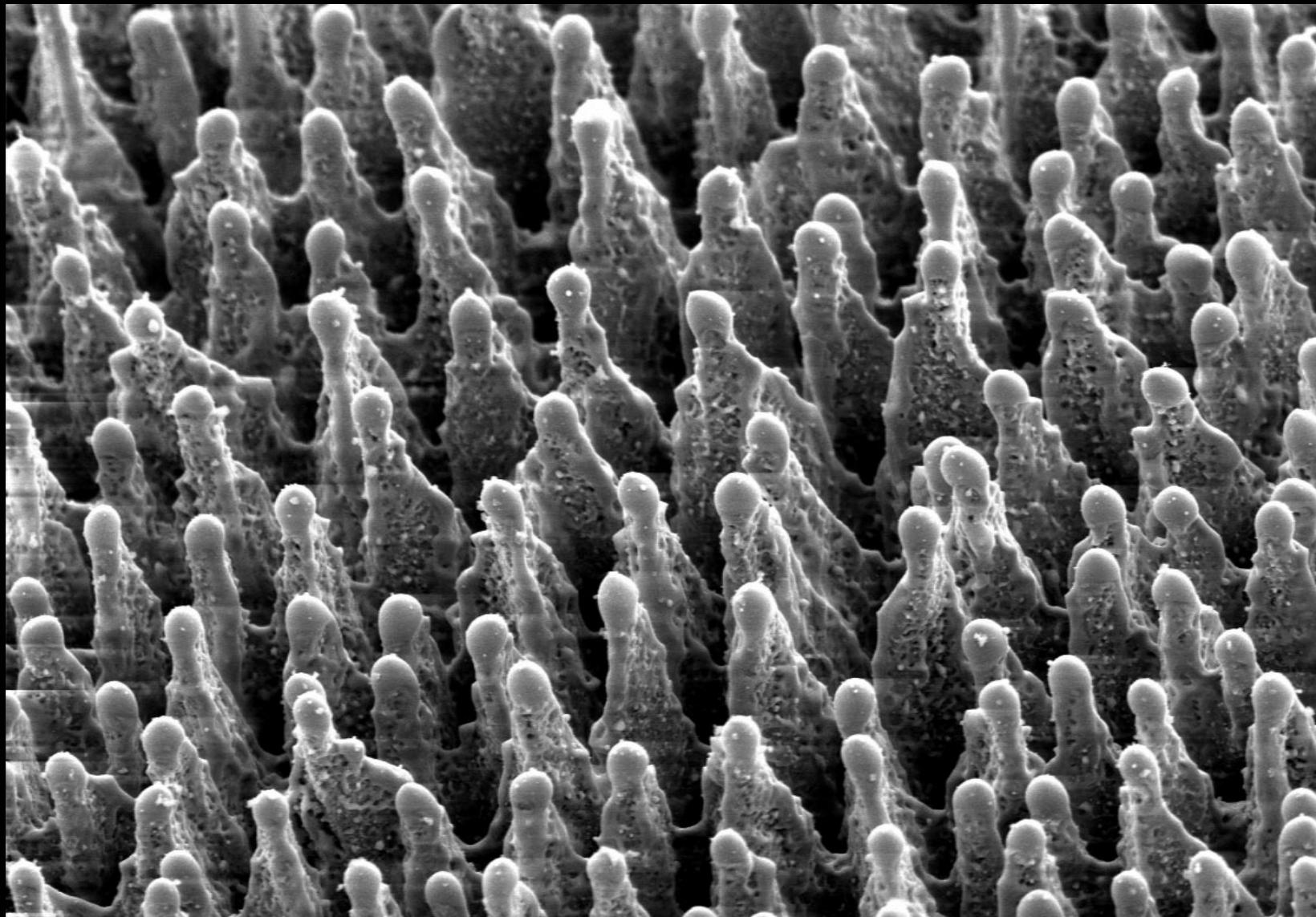
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#3548
512 x 480

20 μ m

10kV

15mm

0050



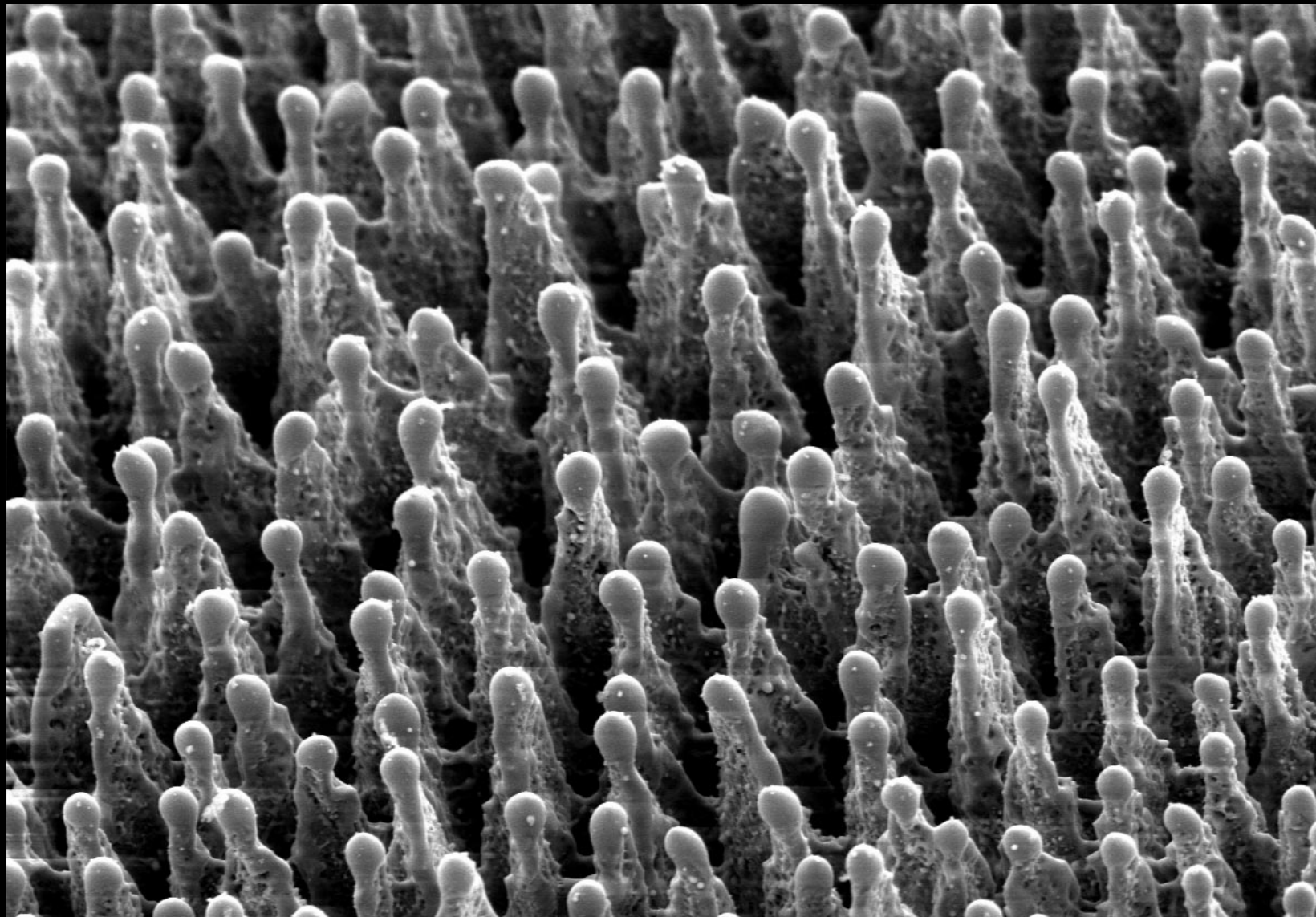
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0070



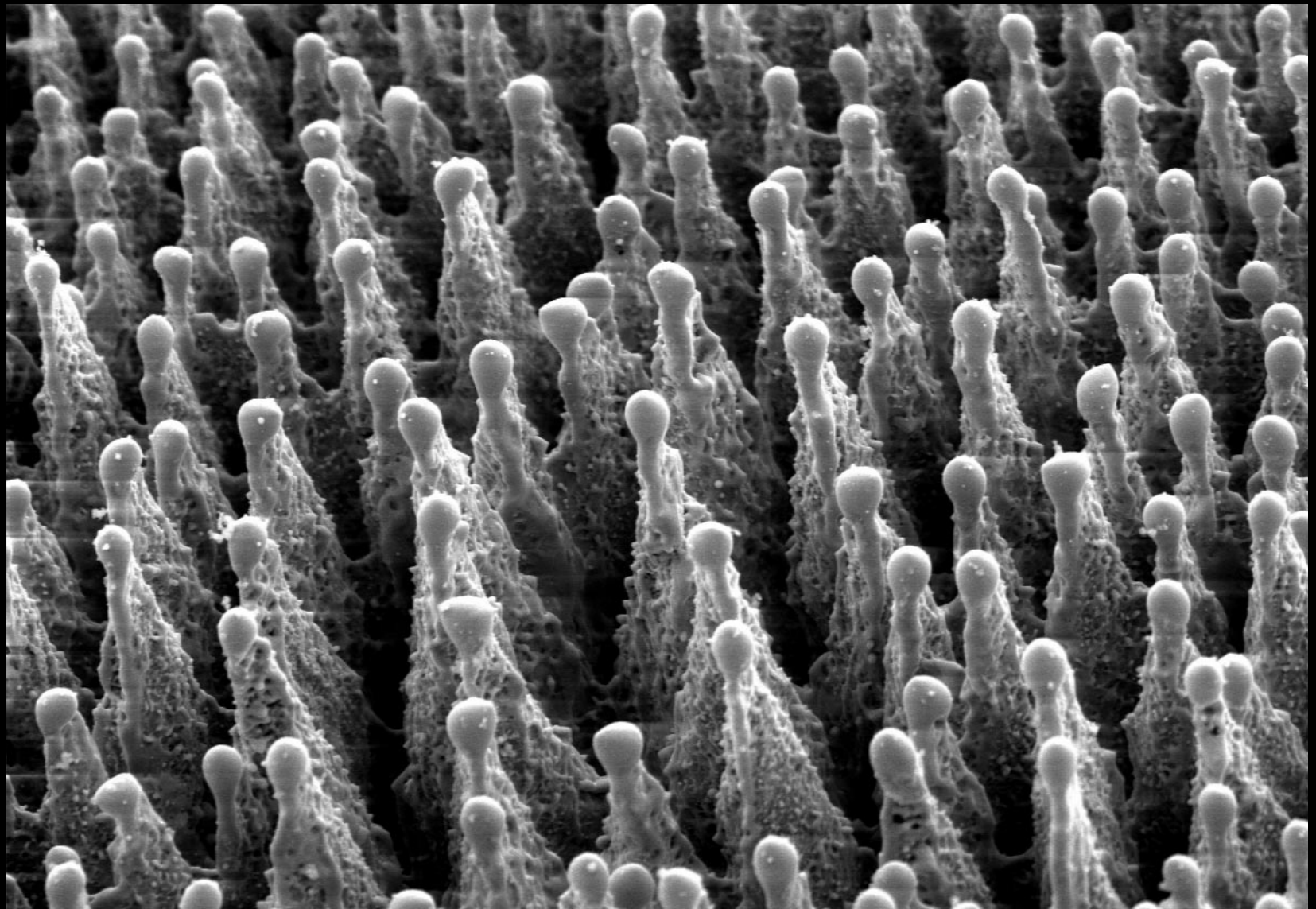
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0100



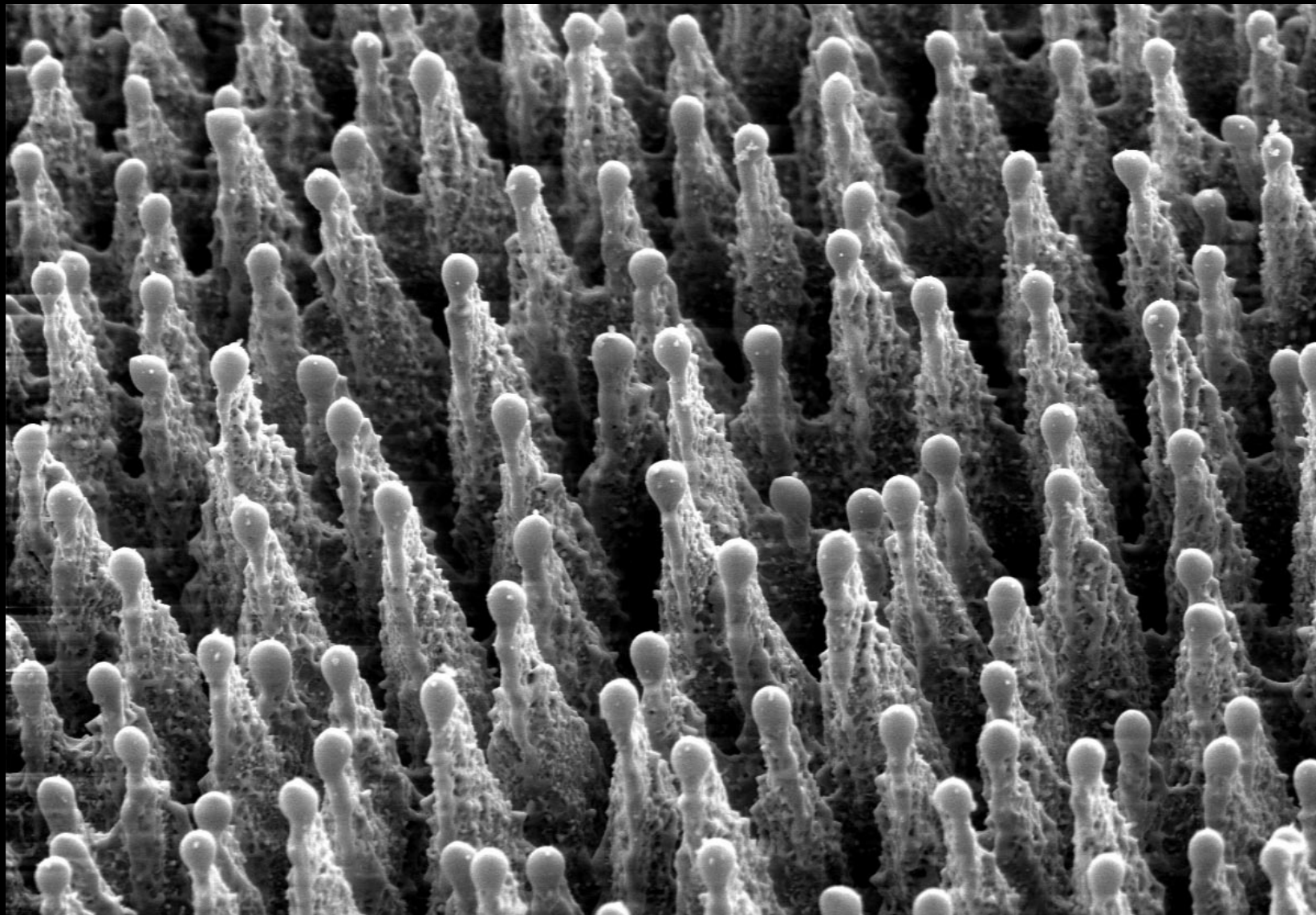
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512 x 480

20 μ m

10kV

15mm

0200



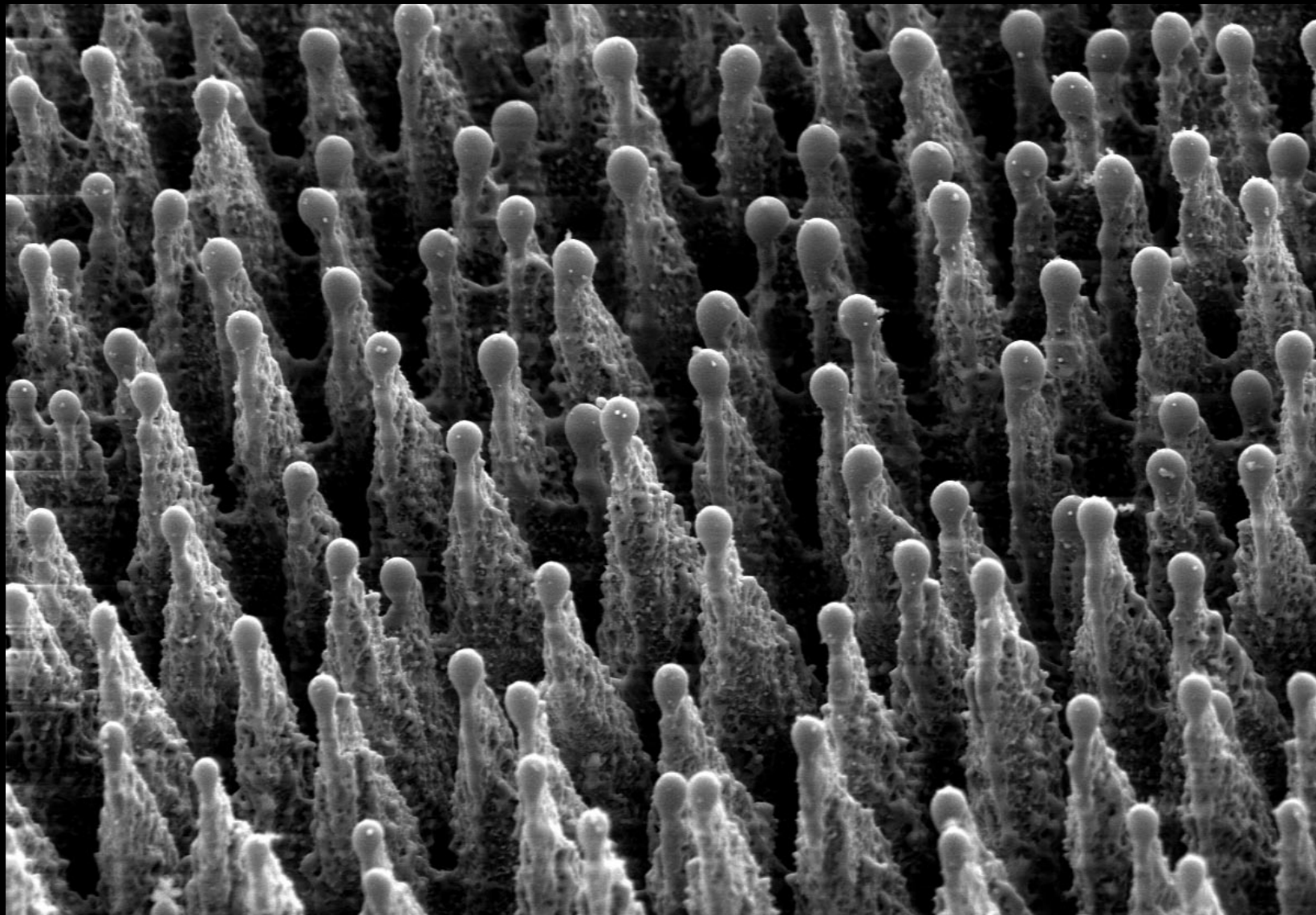
x2000
#3548
512 x 480

20 μ m

10kV

15mm

0400



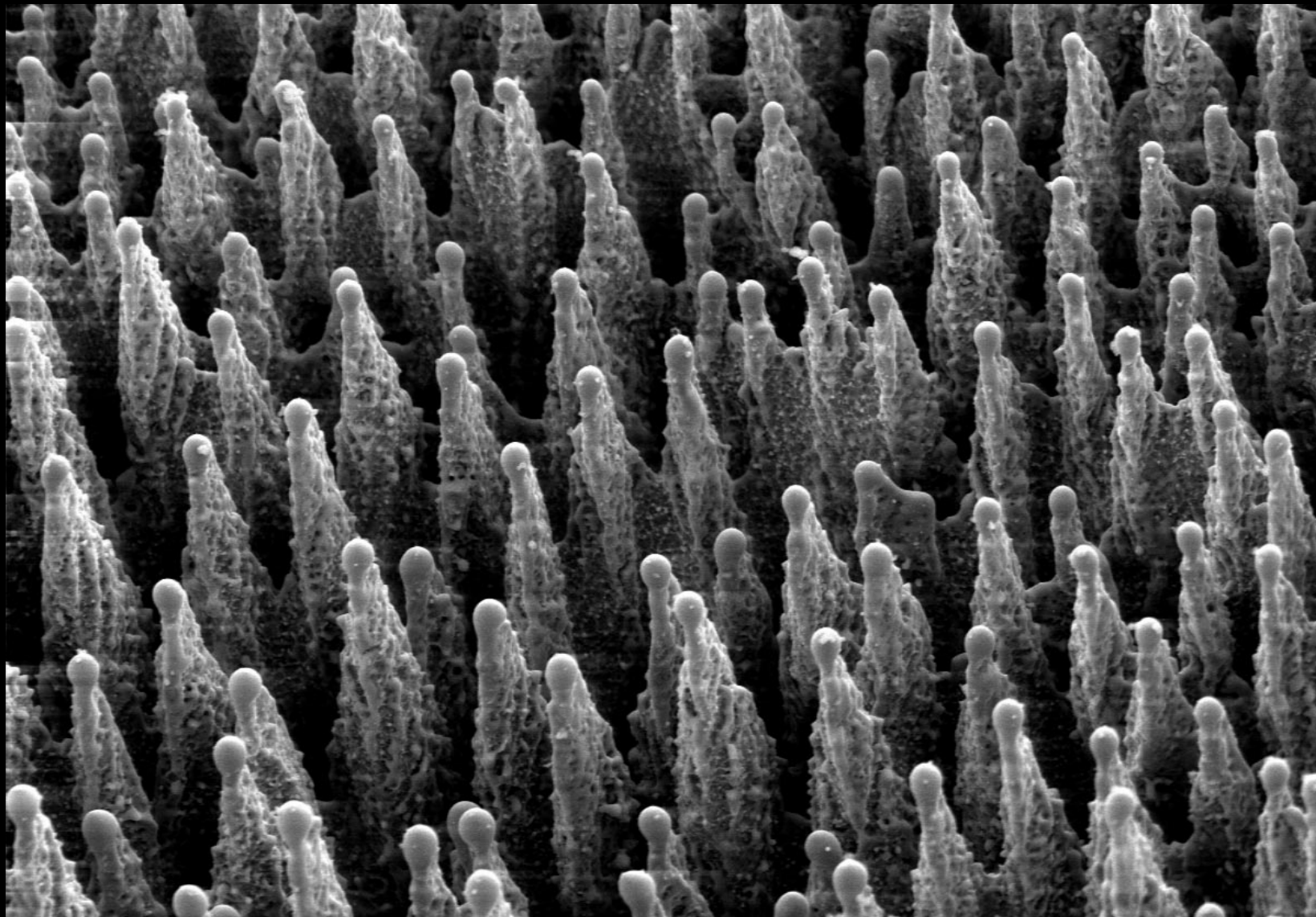
x2000
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512 x 480

20 μ m

10kV

15mm

0600



x2000
#3548
512 x 480

20 μ m

10kV

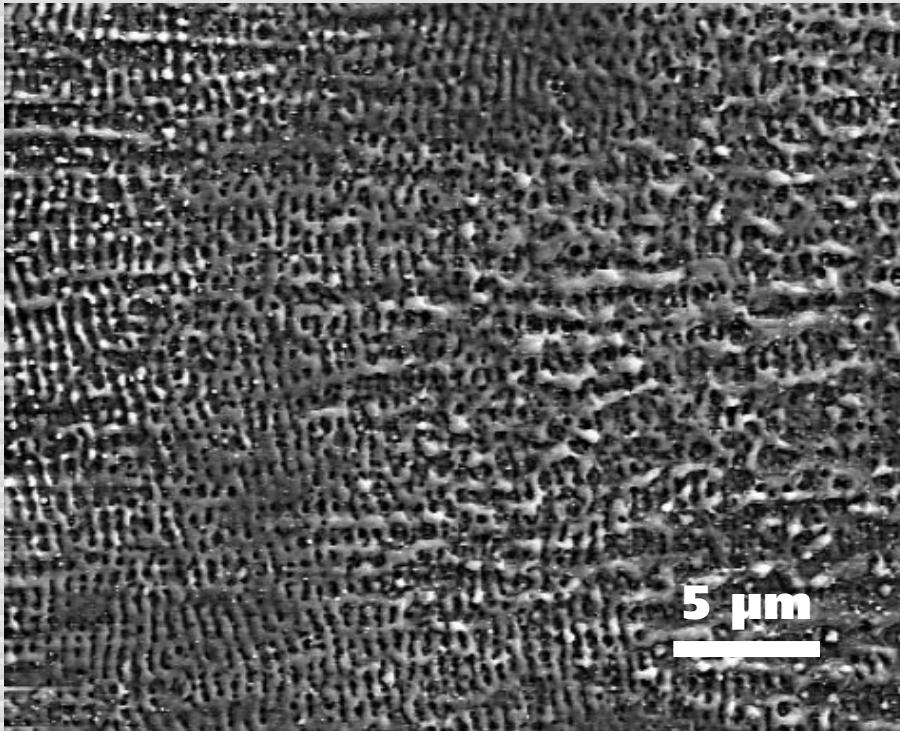
15mm

1000

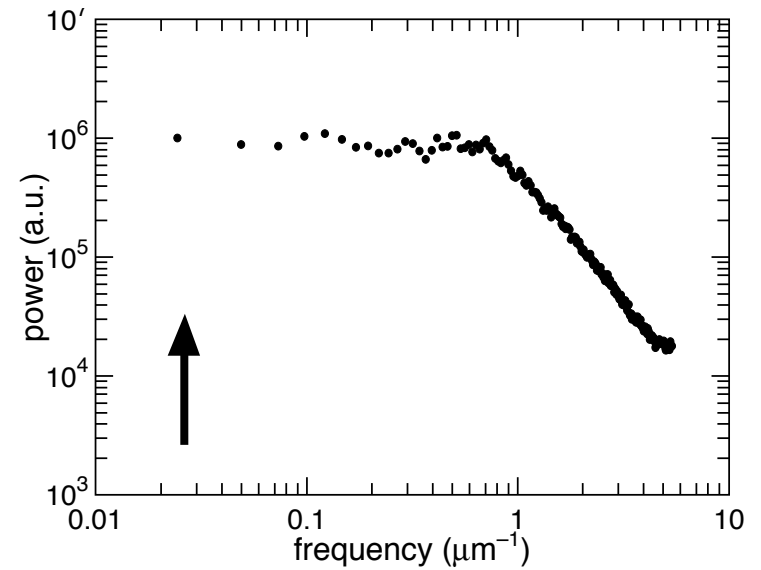
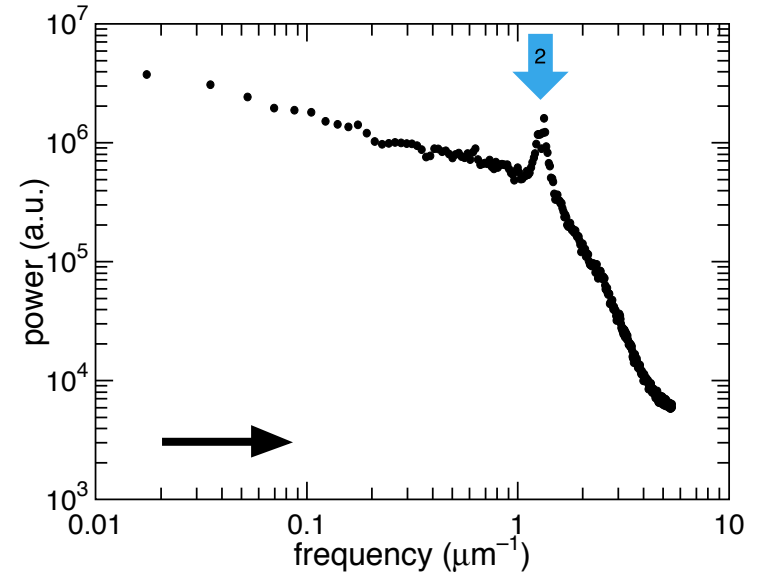
Formation

SF_6

2 pulses



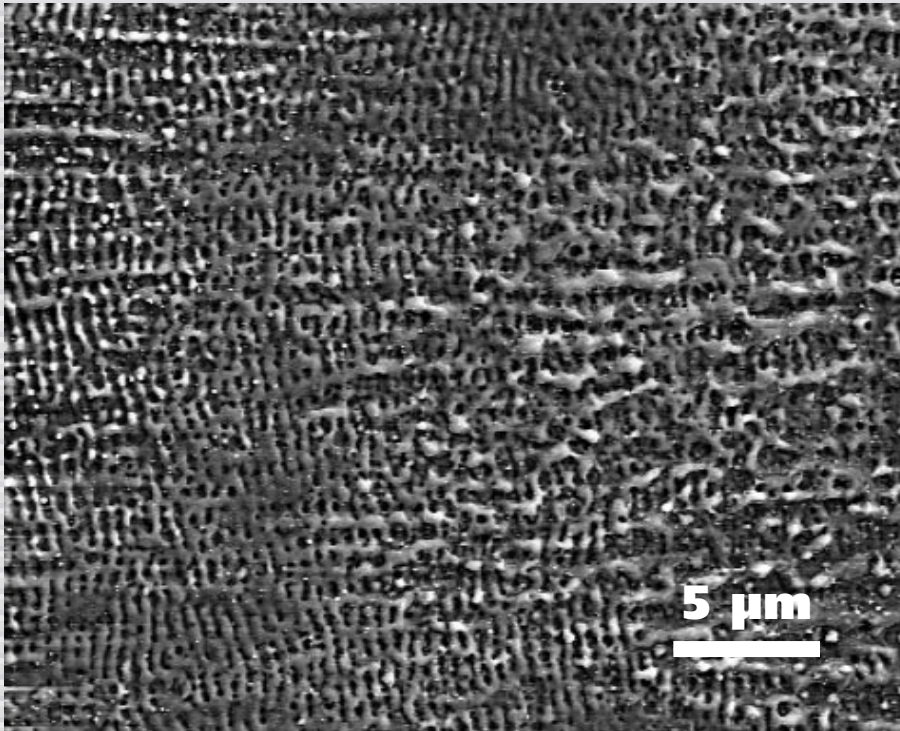
laser polarization



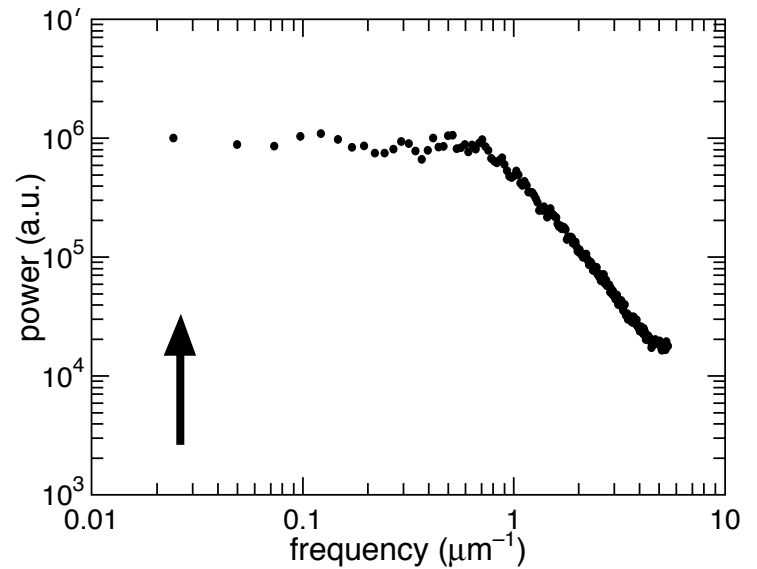
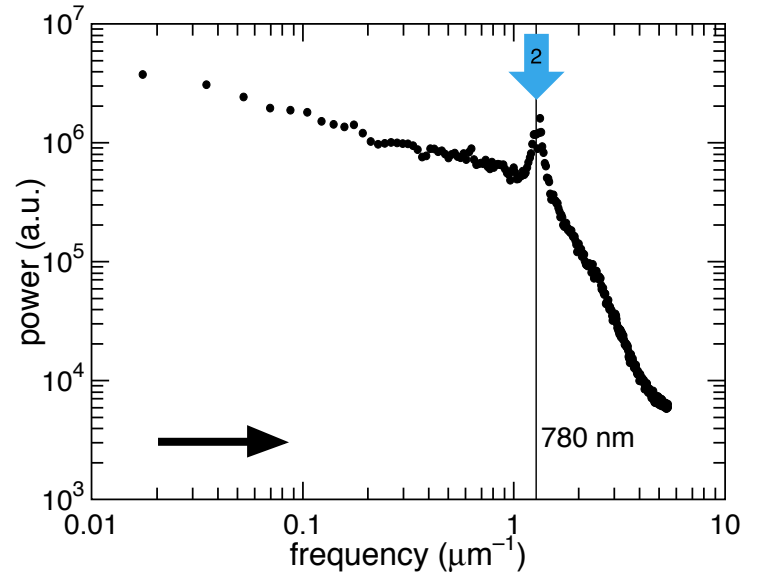
Formation

SF₆

2 pulses



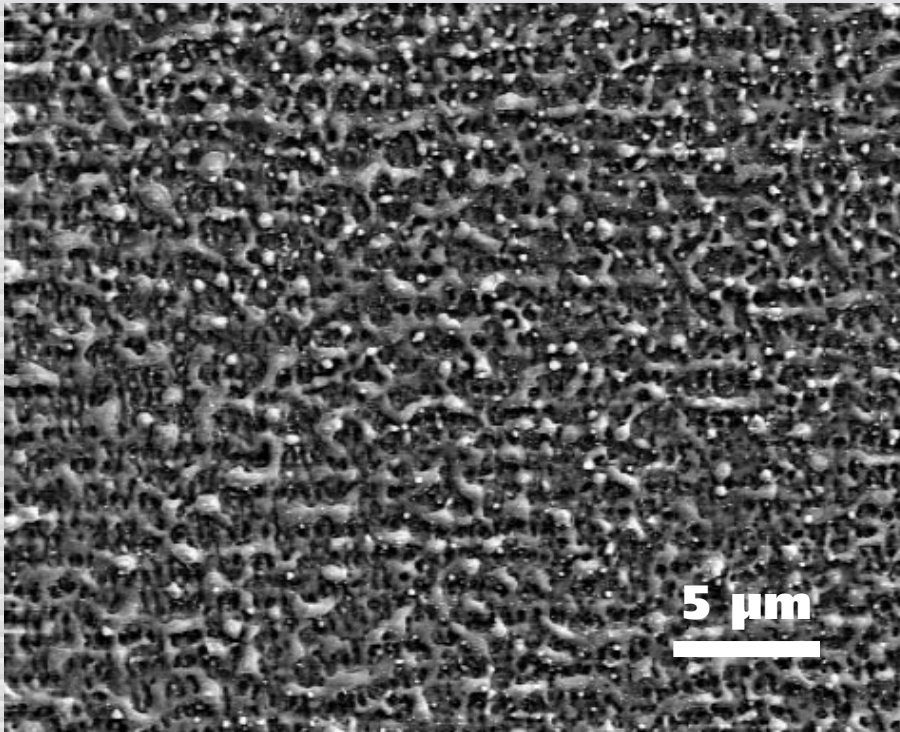
laser polarization



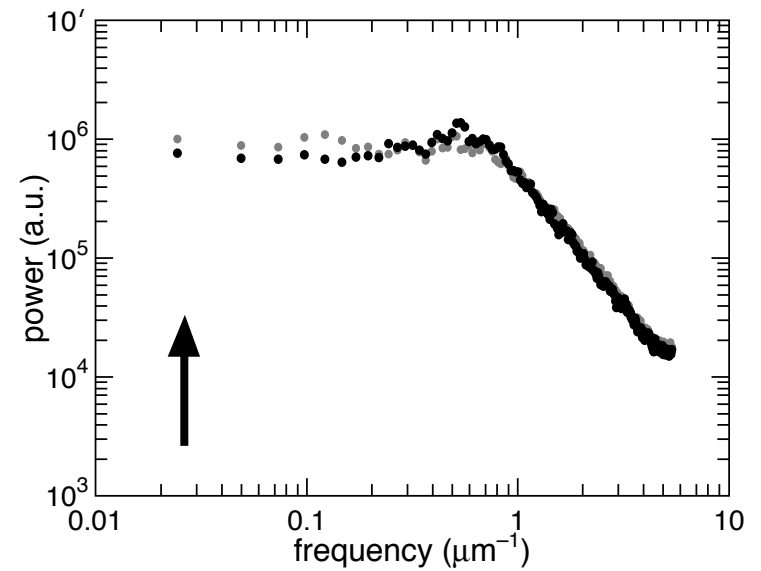
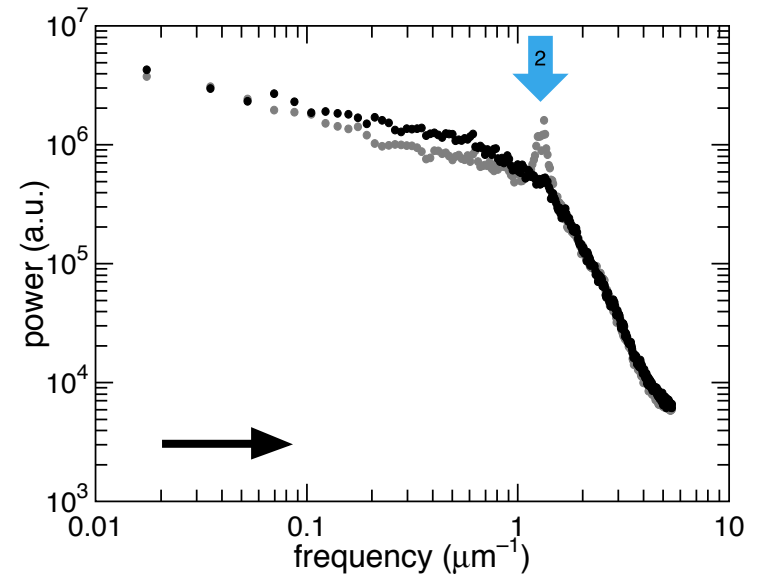
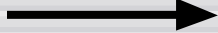
Formation

SF_6

3 pulses



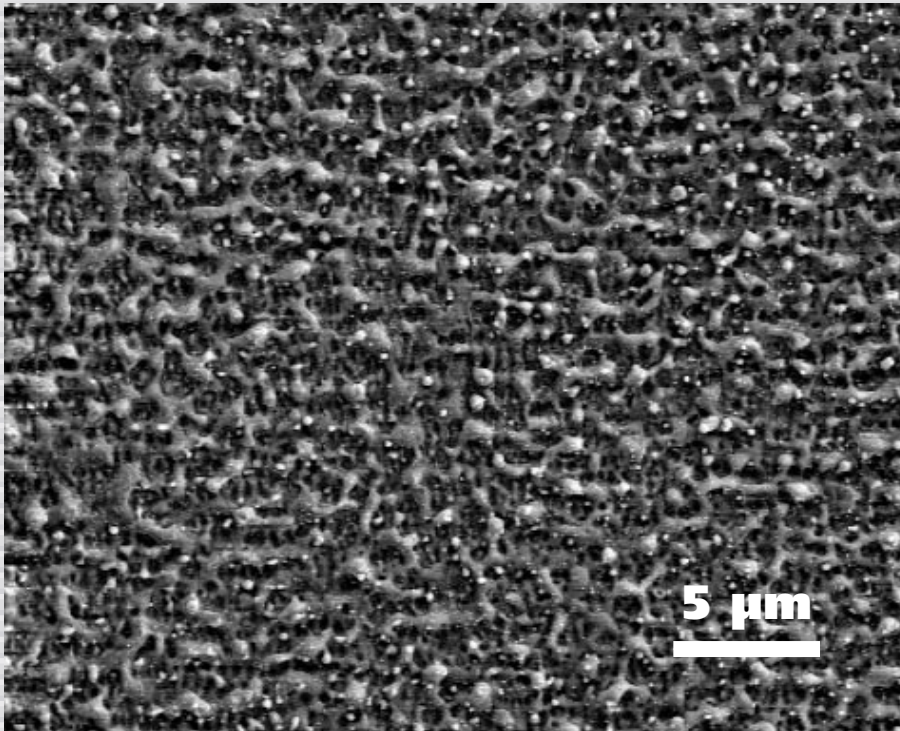
laser polarization



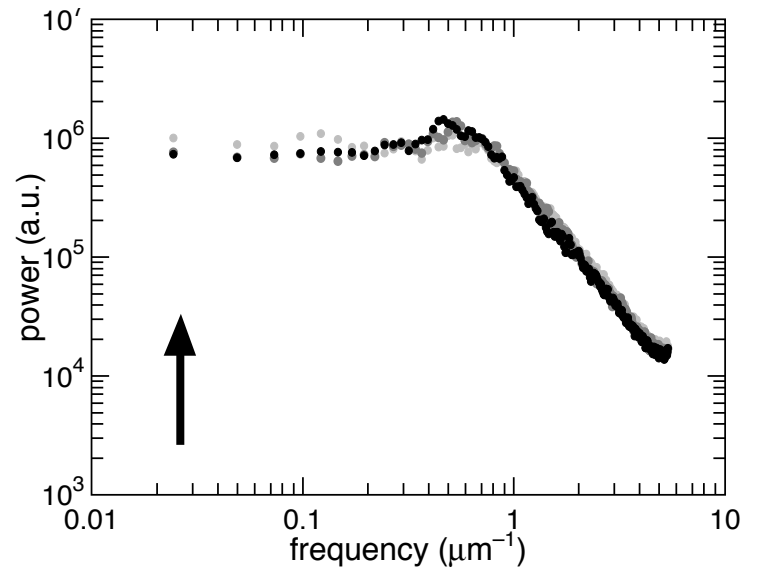
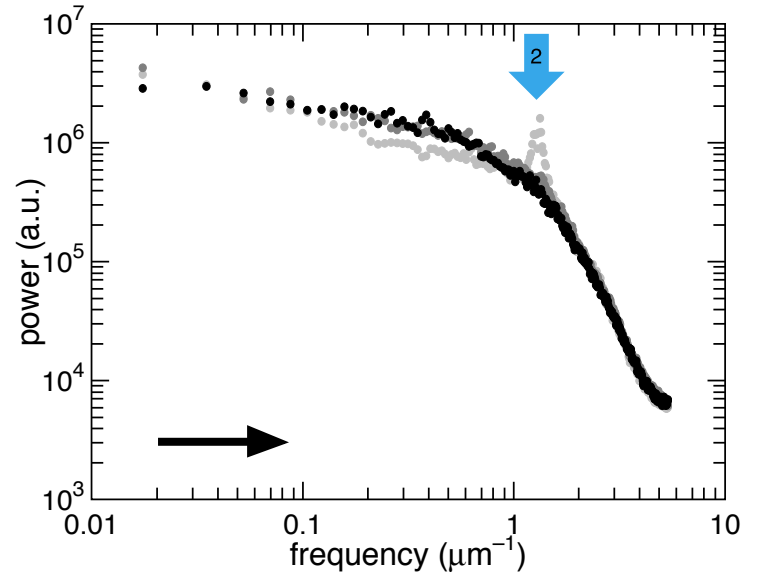
Formation

SF_6

4 pulses



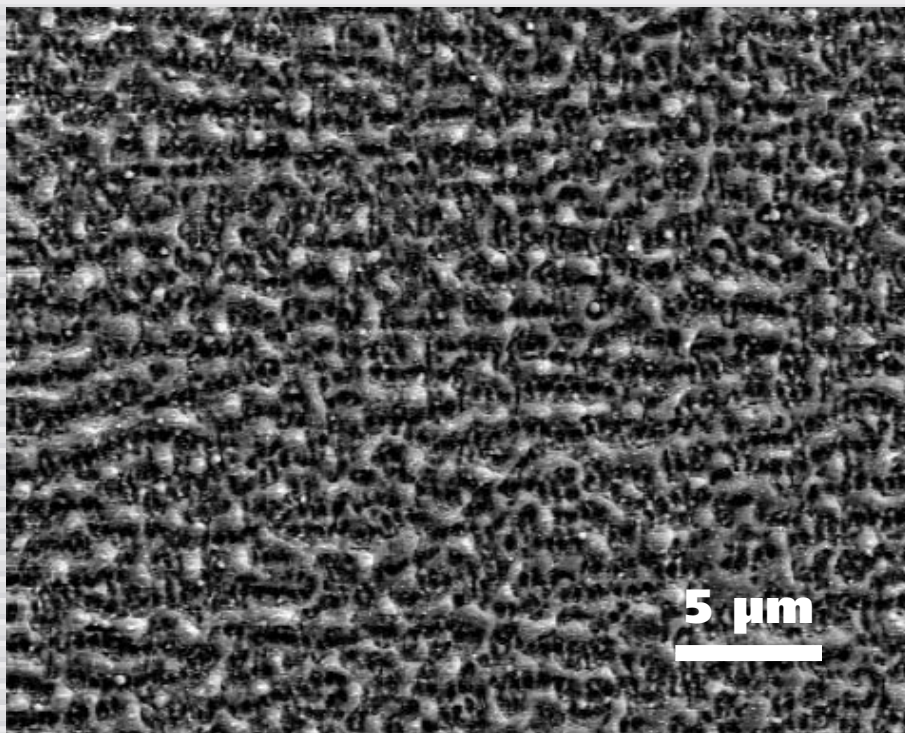
laser polarization



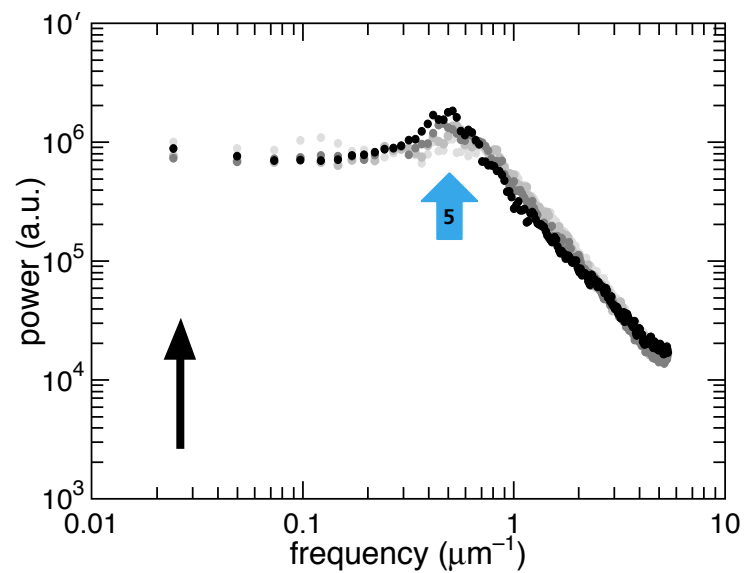
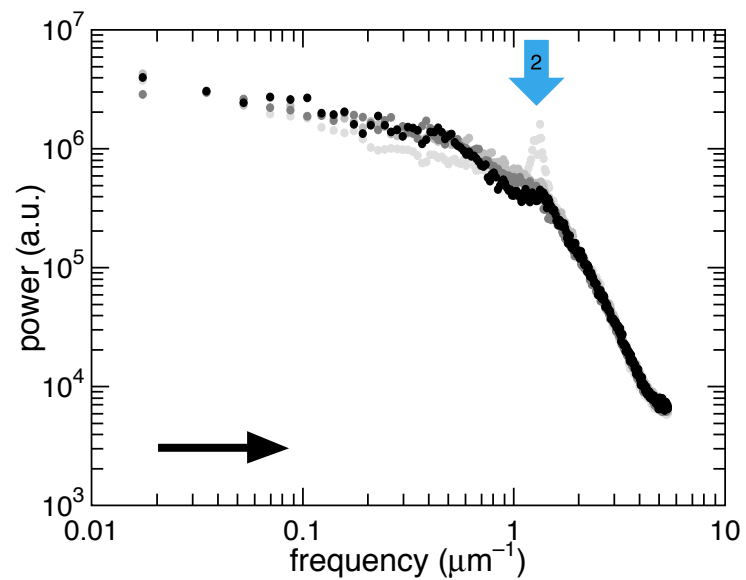
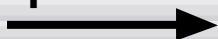
Formation

SF_6

5 pulses



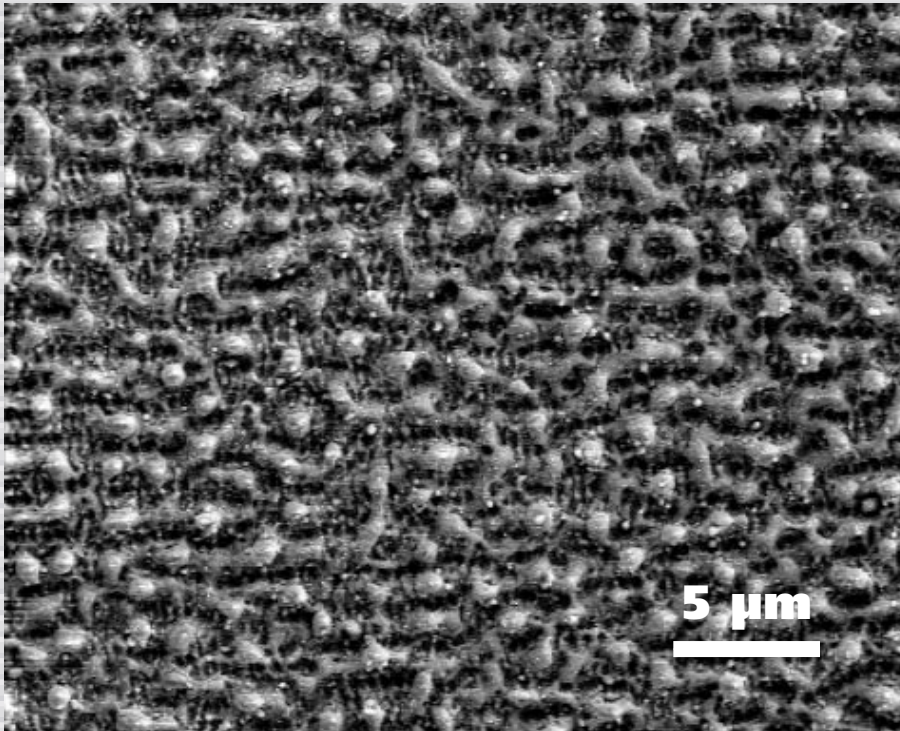
laser polarization



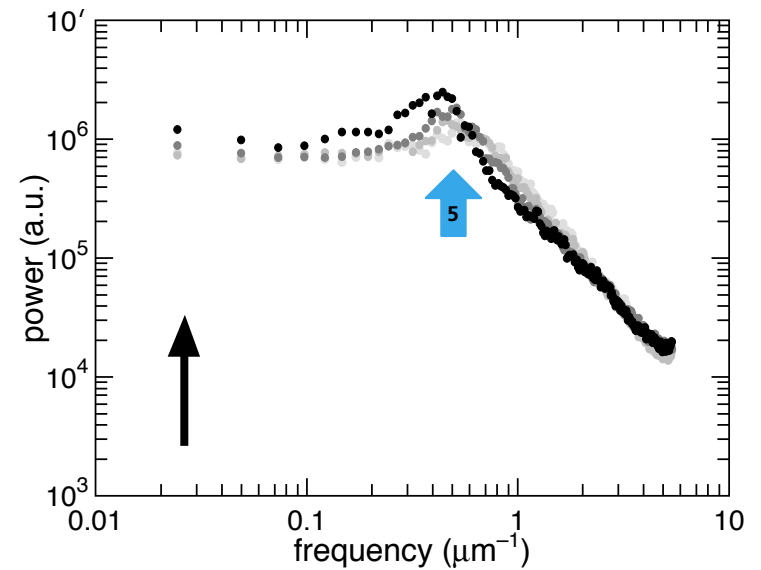
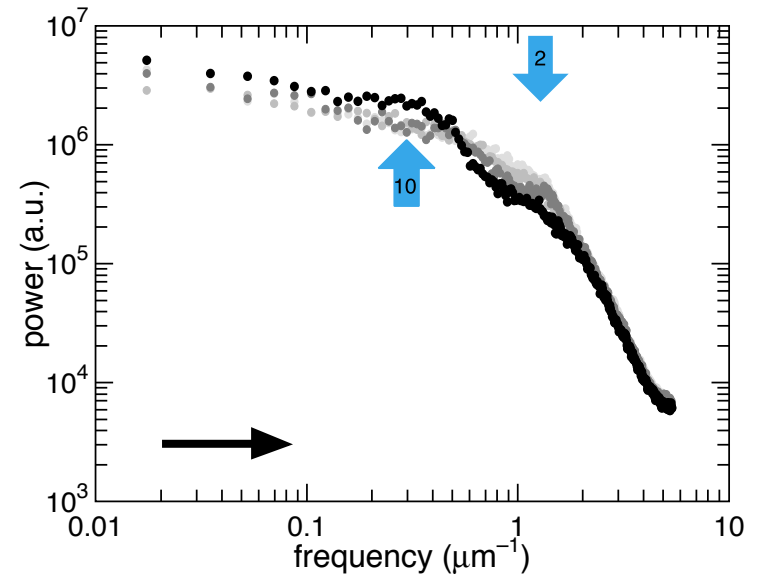
Formation

SF₆

10 pulses



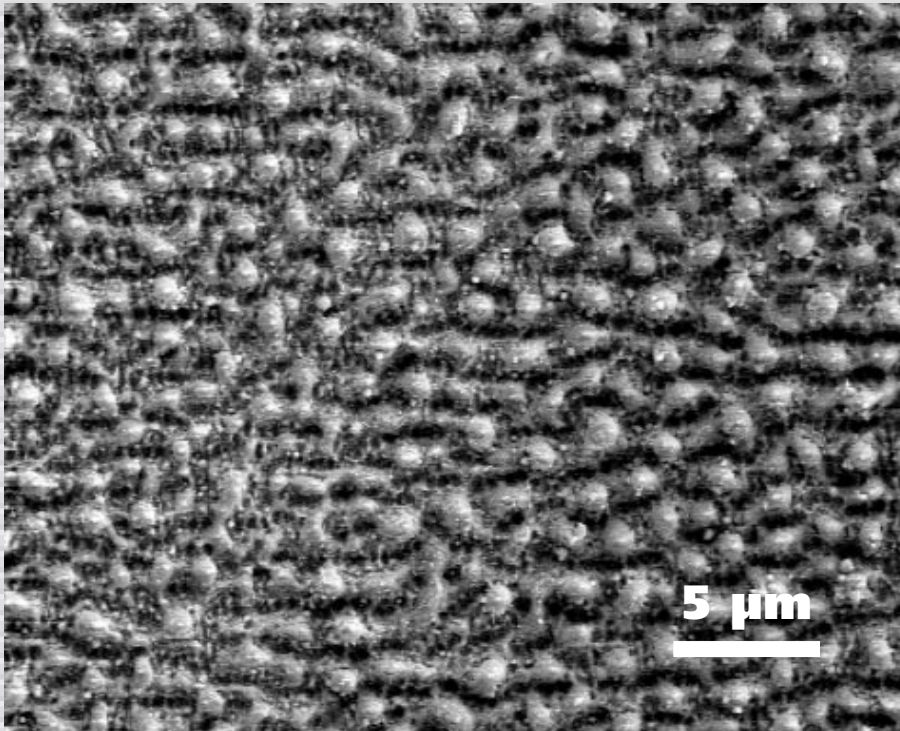
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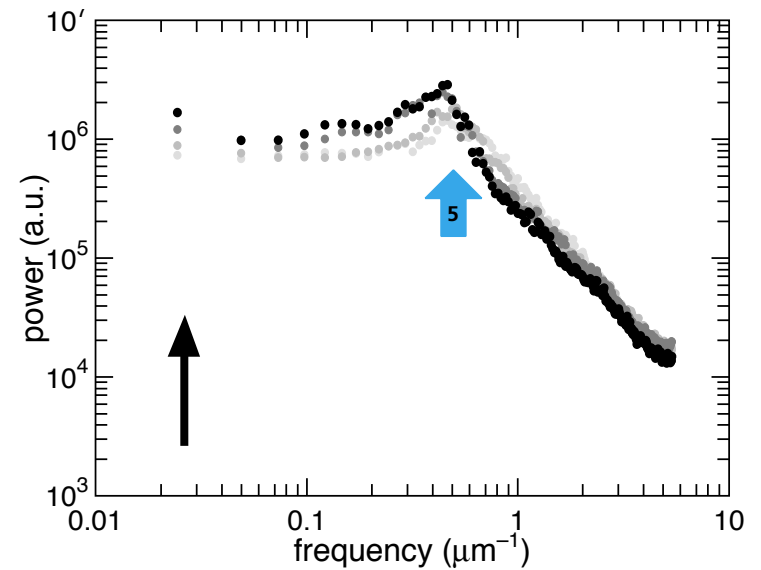
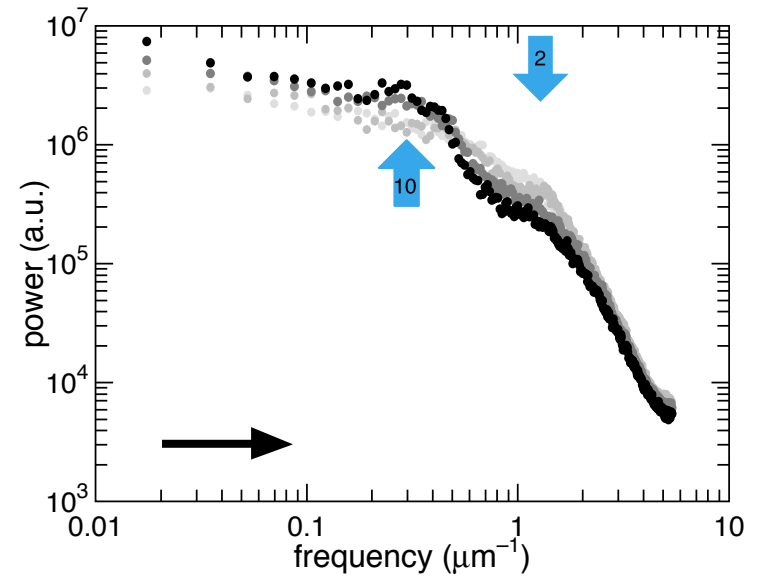
Formation

SF_6

15 pulses



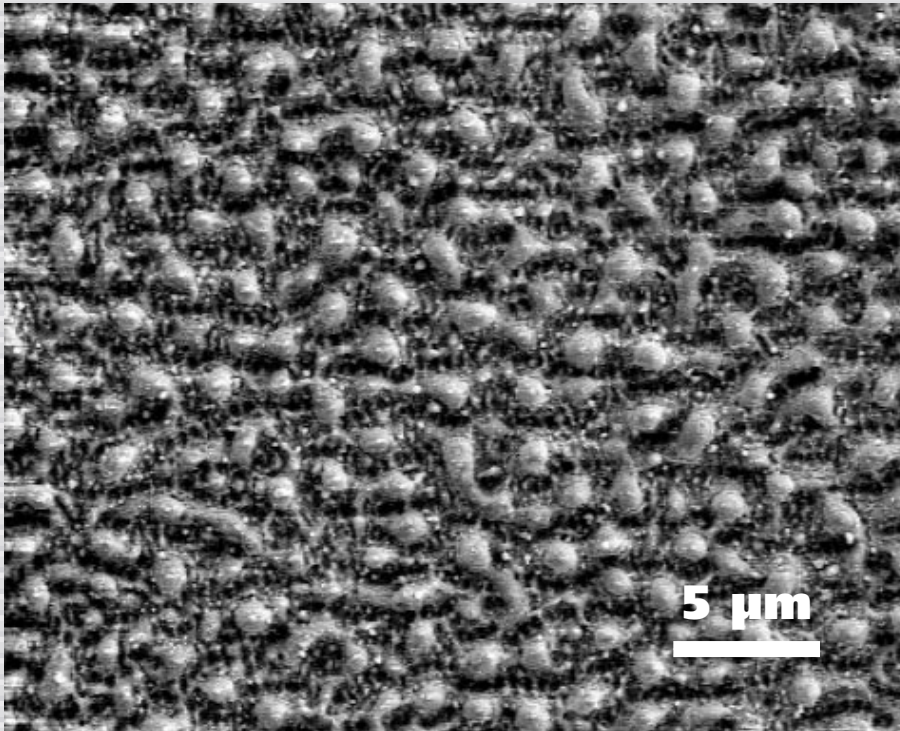
laser polarization



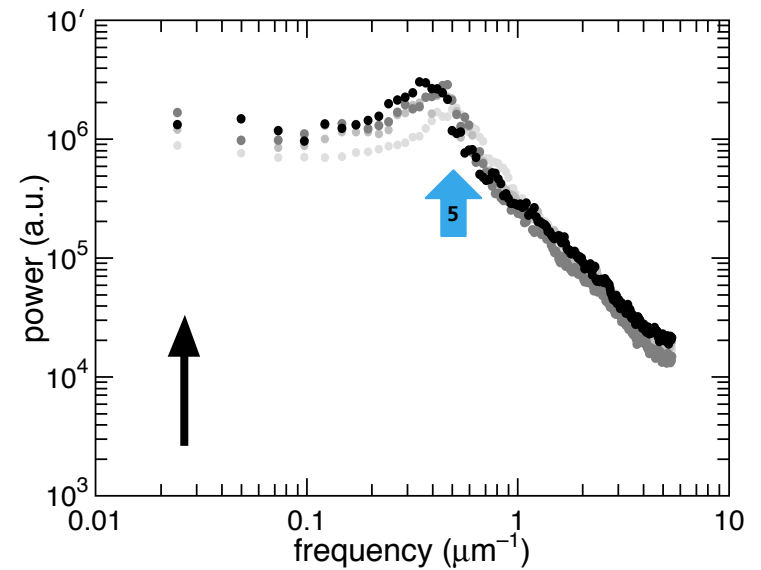
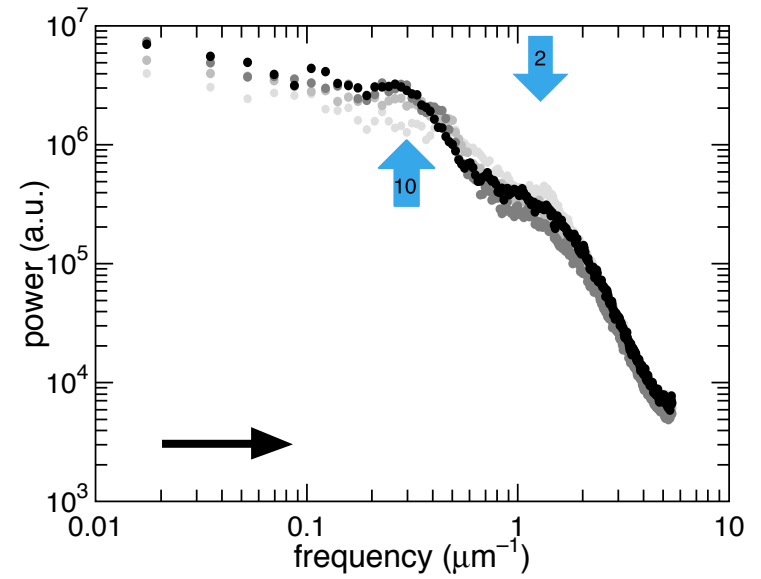
Formation

SF_6

20 pulses



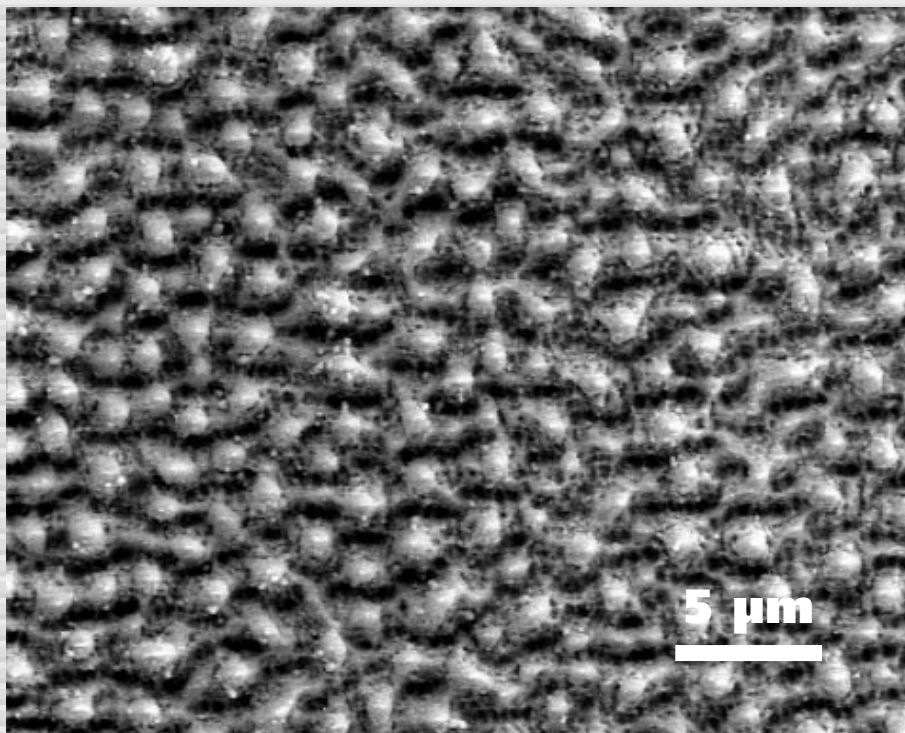
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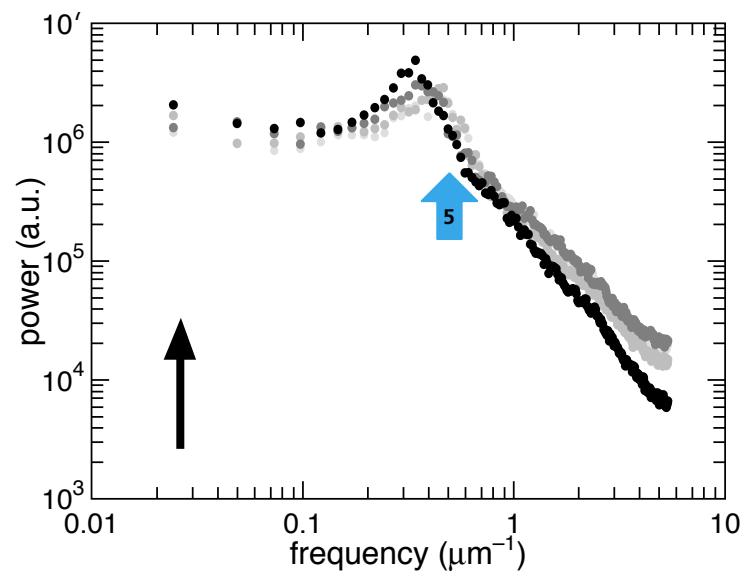
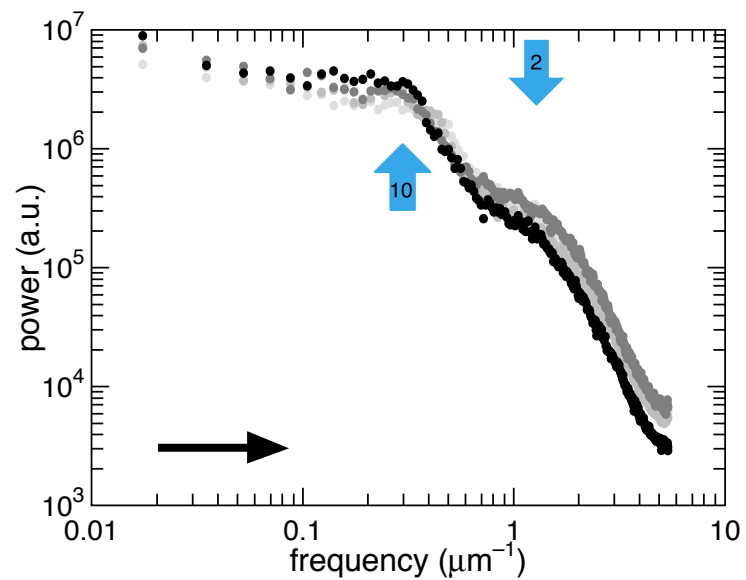
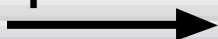
Formation

SF_6

50 pulses



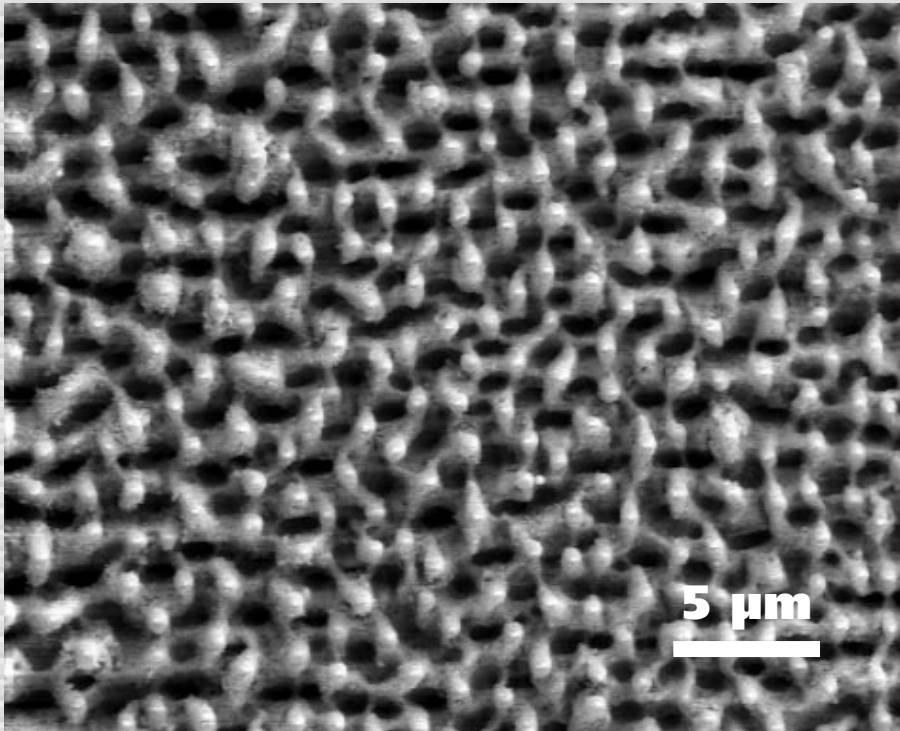
laser polarization



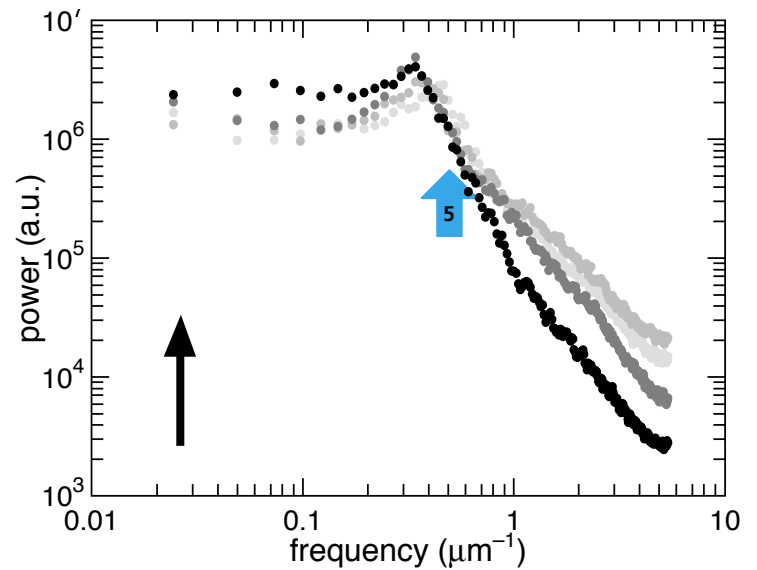
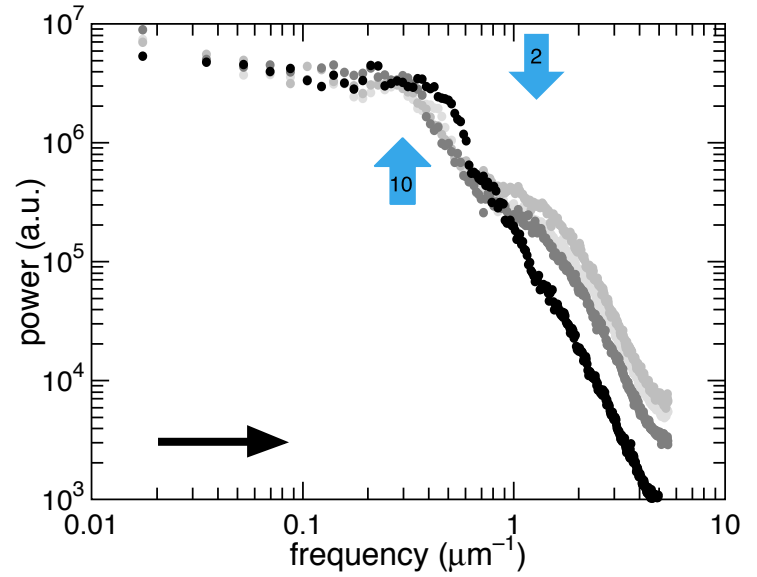
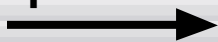
Formation

SF_6

200 pulses



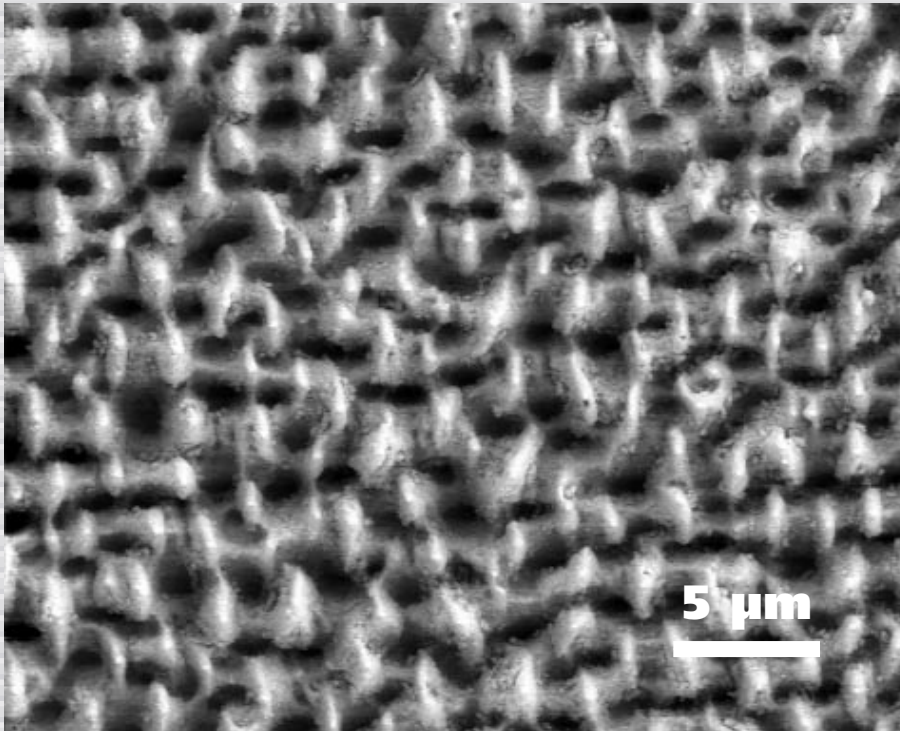
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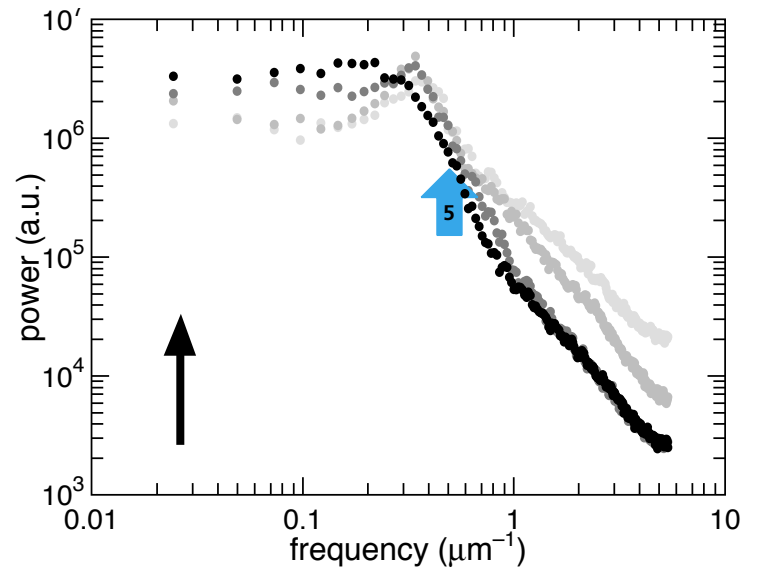
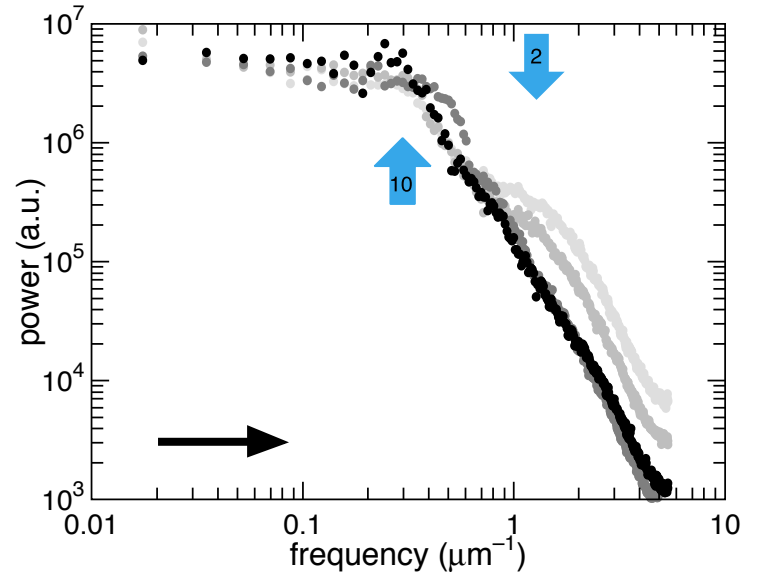
Formation

SF₆

500 pulses



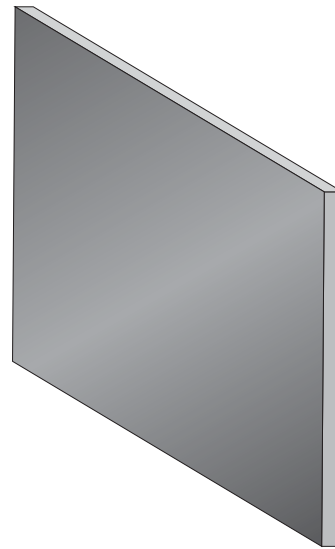
laser polarization



Outlook

can ordering of spikes be improved by using a grid?

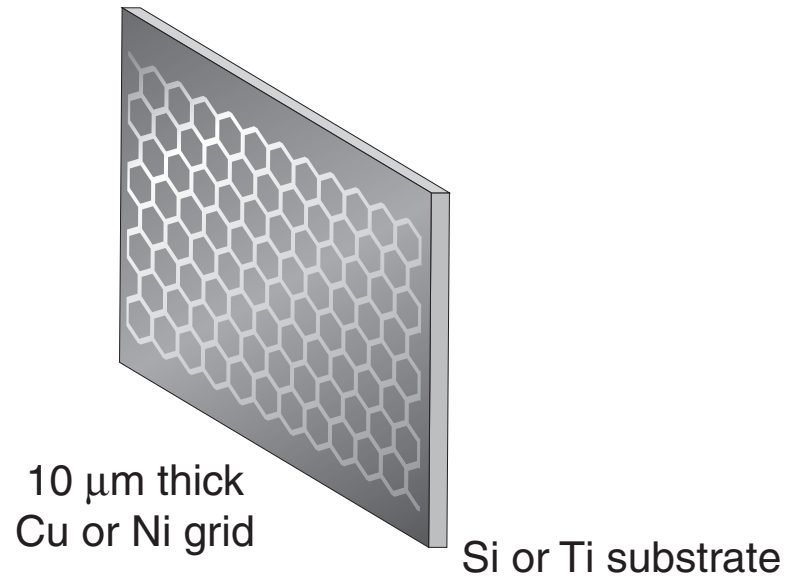
Outlook



Si or Ti substrate

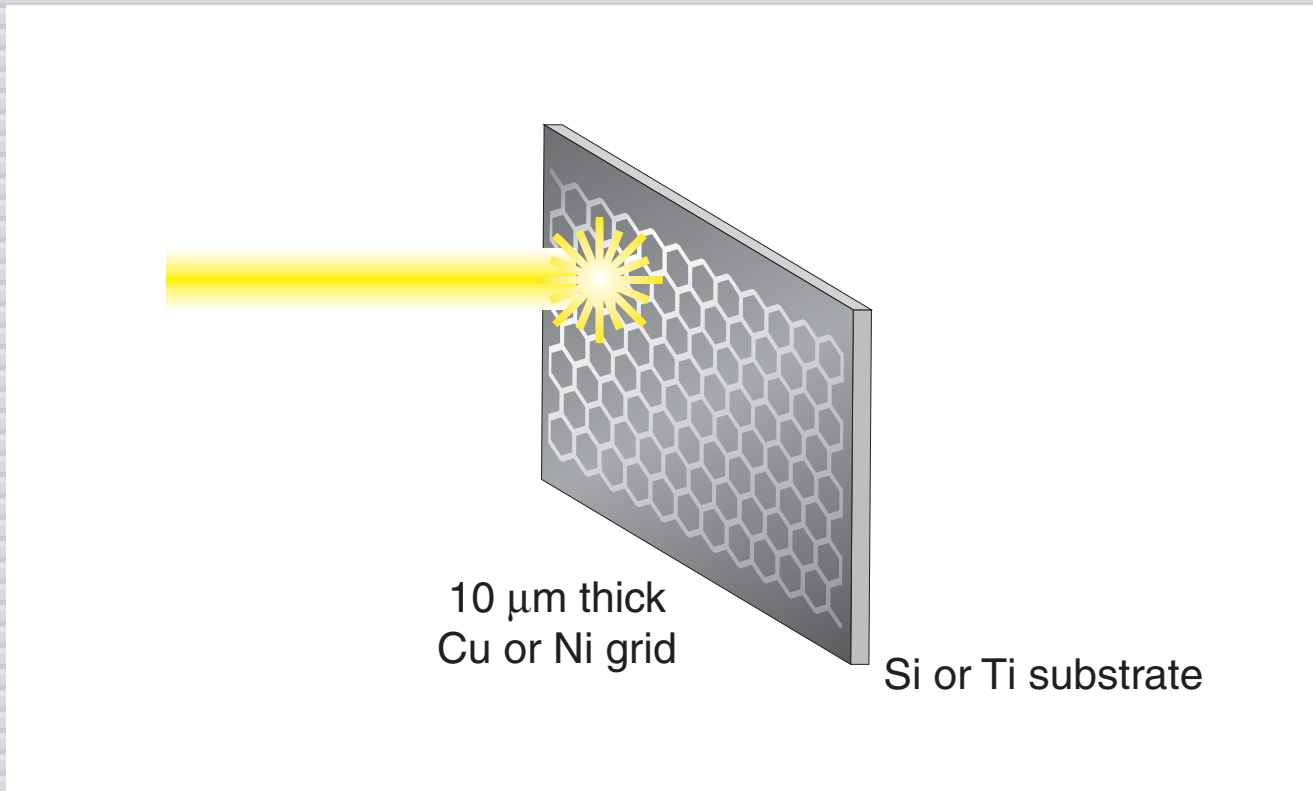
Outlook

place grid in front of substrate



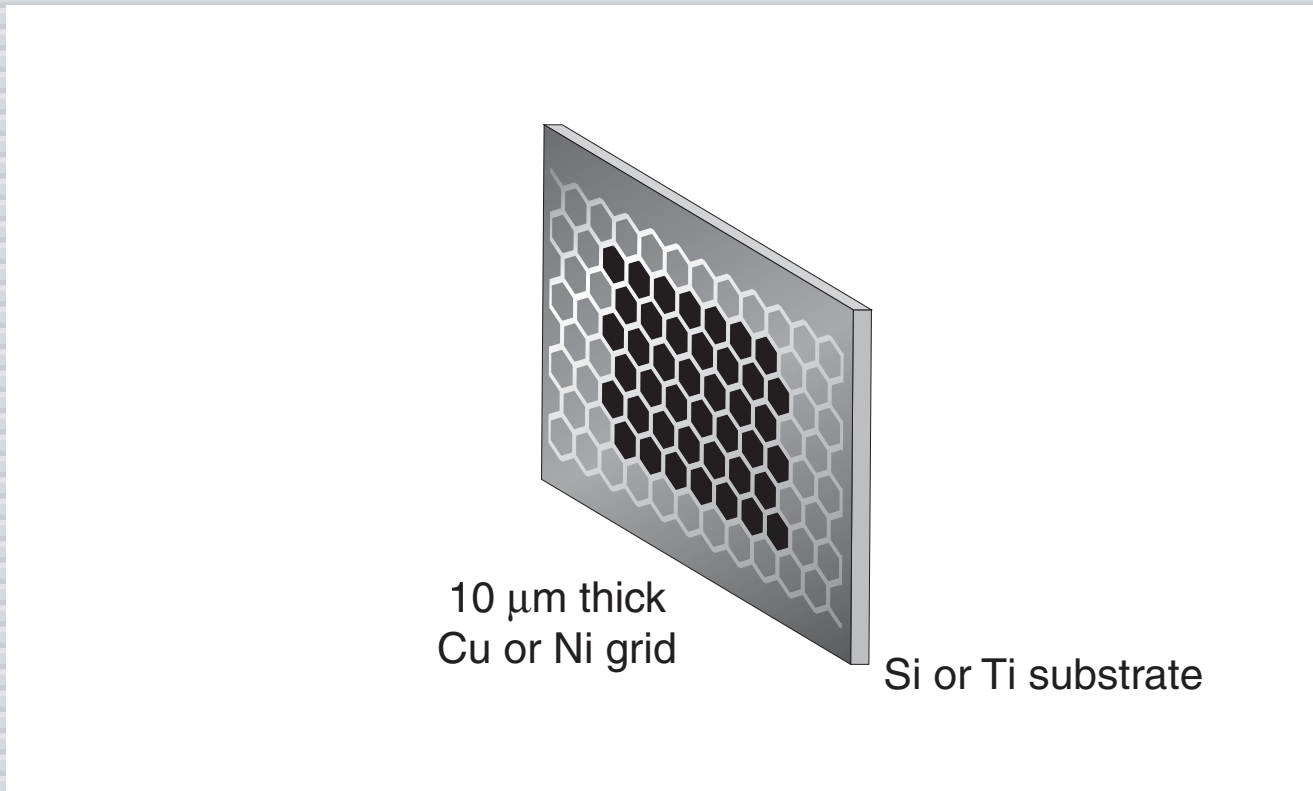
Outlook

scan laser beam



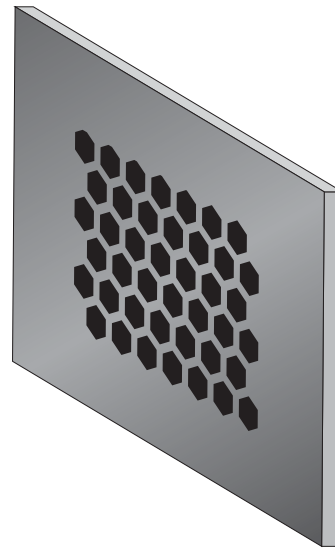
Outlook

scan laser beam

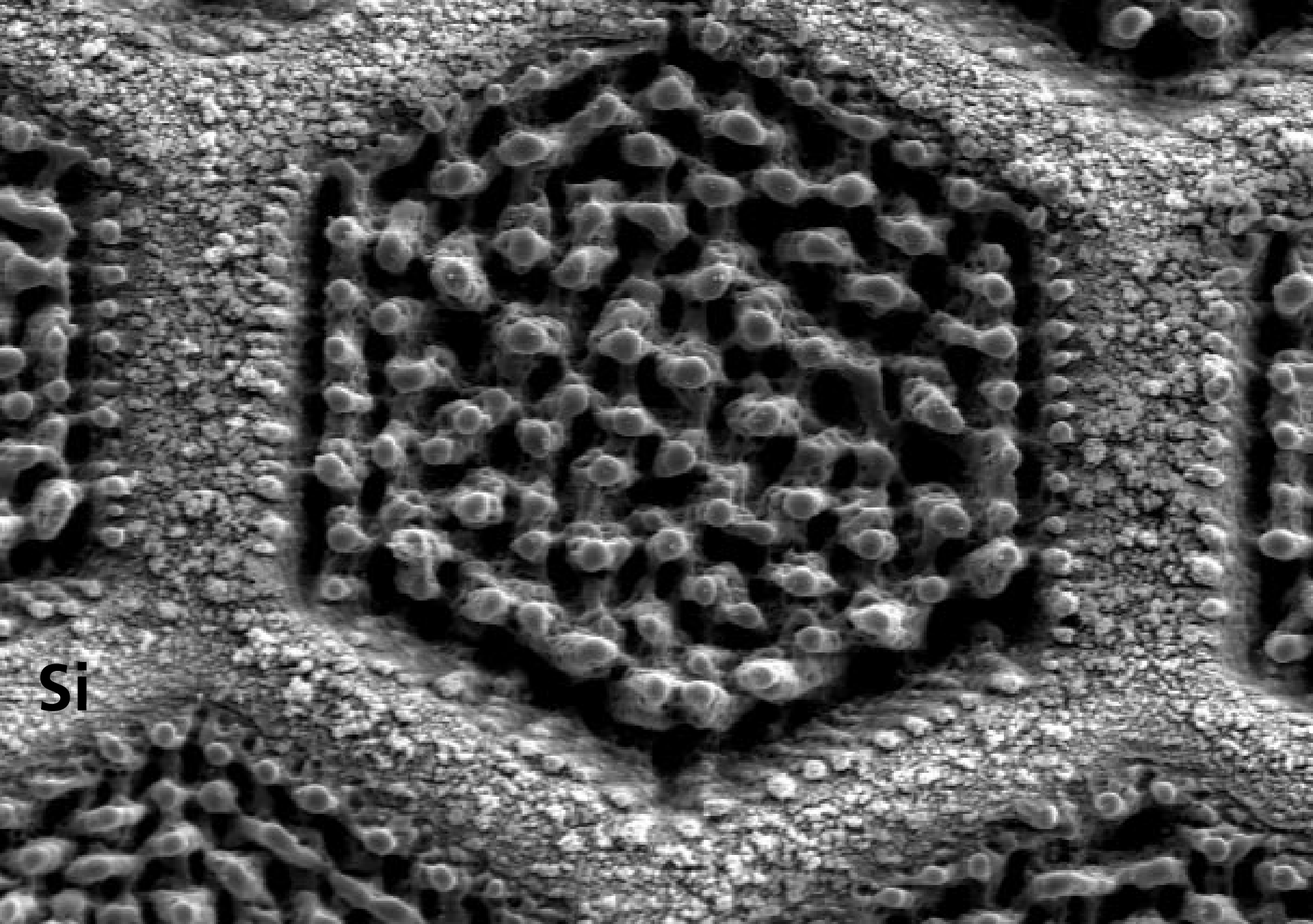


Outlook

remove grid



Si or Ti substrate

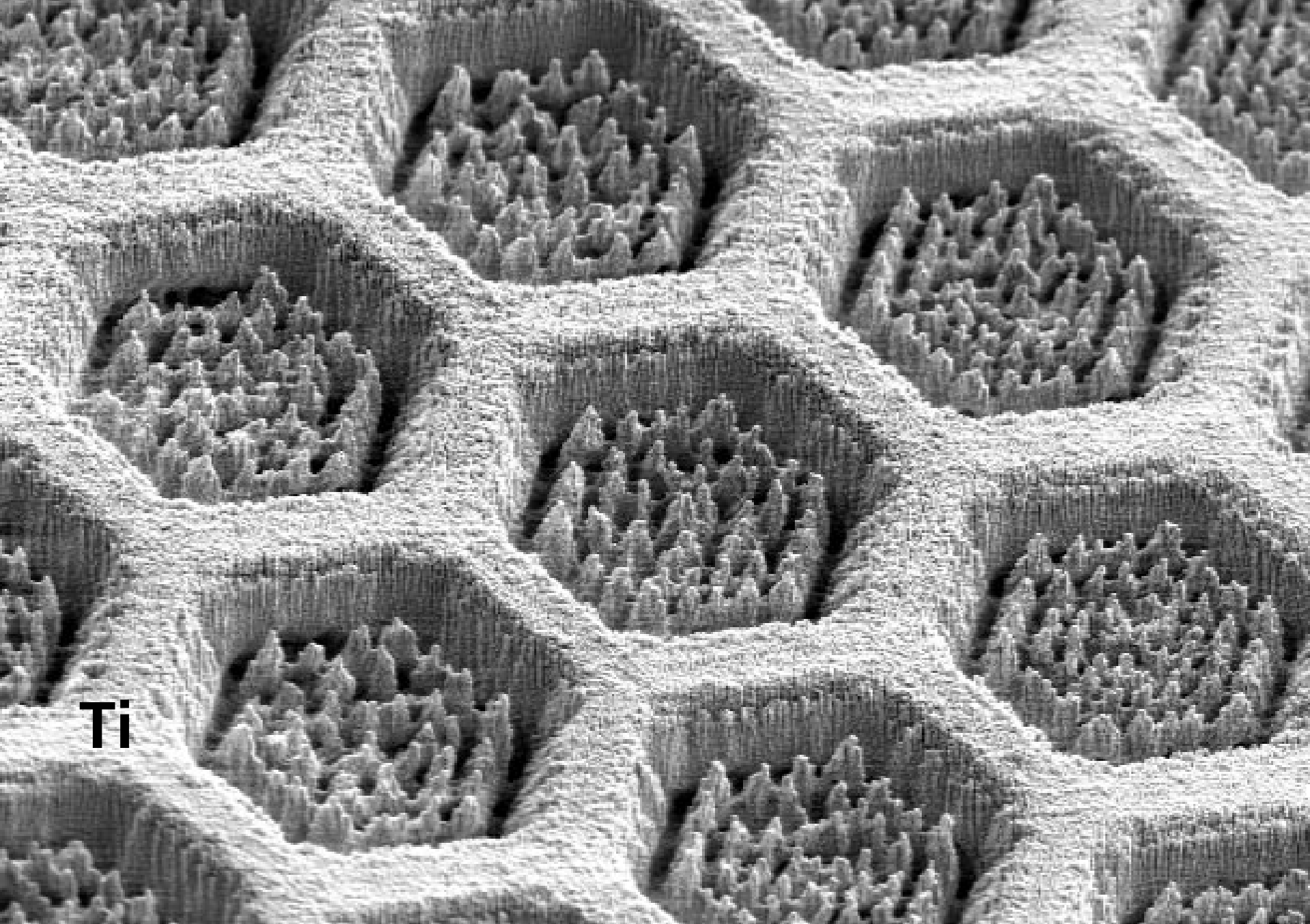


Si

x2000
512 x 480

20 μ m

5kV 24mm
H300.TIF

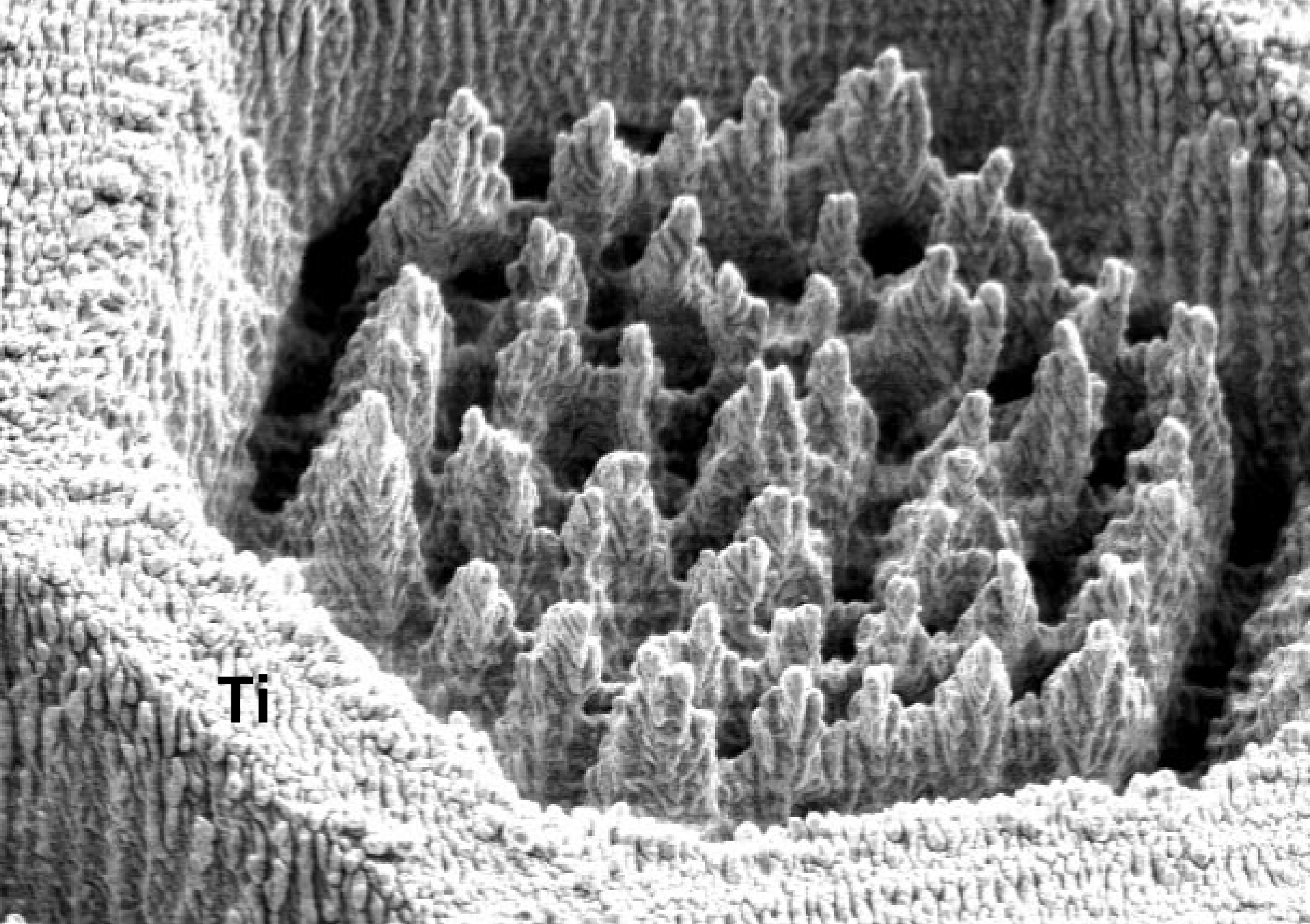


Ti

20 μ m

5kV

17mm



Ti

10 μ m

5kV

17mm

Outlook

Summary

Microstructured silicon

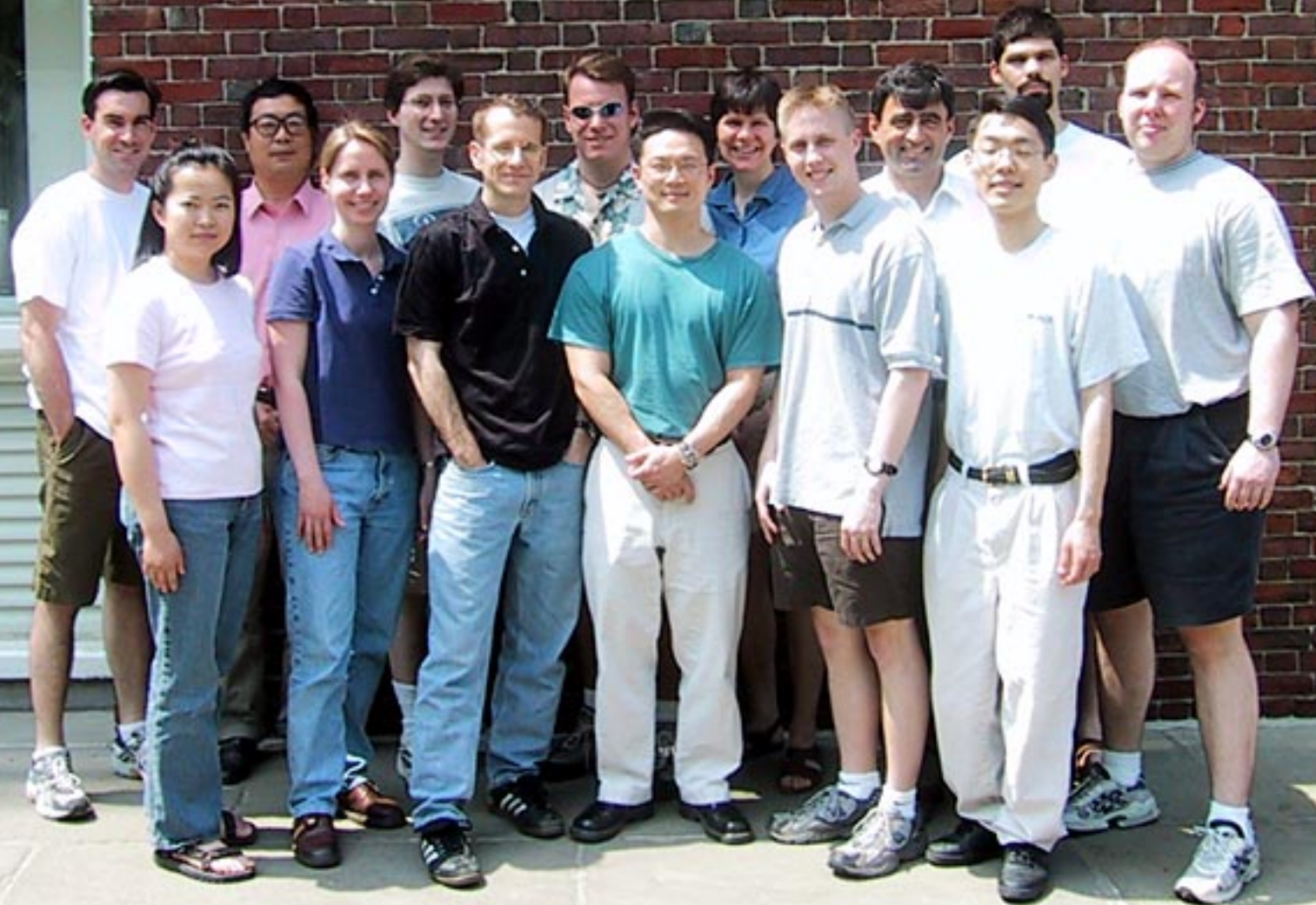
- ▶ **fabricated by simple, maskless process**

Summary

Microstructured silicon

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

CORDON MCKAY
LABORATORY OF
APPLIED SCIENCE



Funding: ARO, DoE, NDSEG

Acknowledgments:

Dr. François Génin (LLNL)

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Dr. Alf Bjørseth (Scanwafer)

Dr. Tom Mates (UCSB)

Dr. John Chervinsky (Harvard University)

Prof. Mike Aziz (Harvard University)

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

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

Materials

SF₆

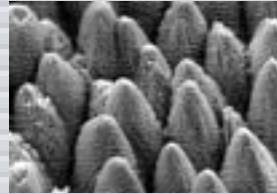
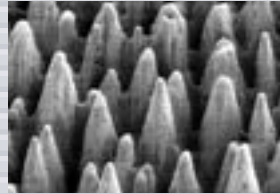
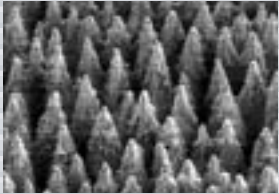
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N₂

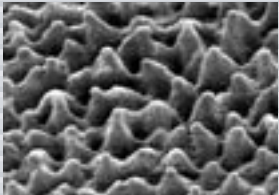
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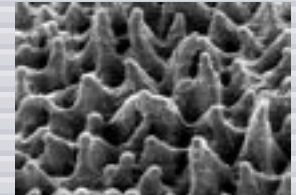
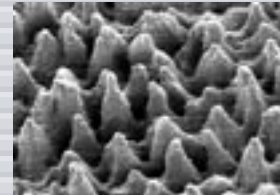
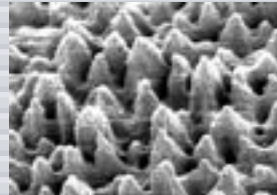
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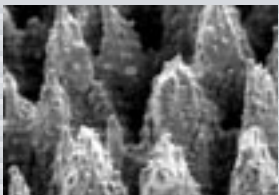
Ti



reacts



Only in SF₆:



Ge

InP

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

Materials

SF₆

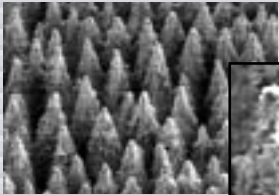
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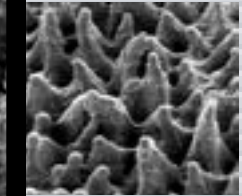
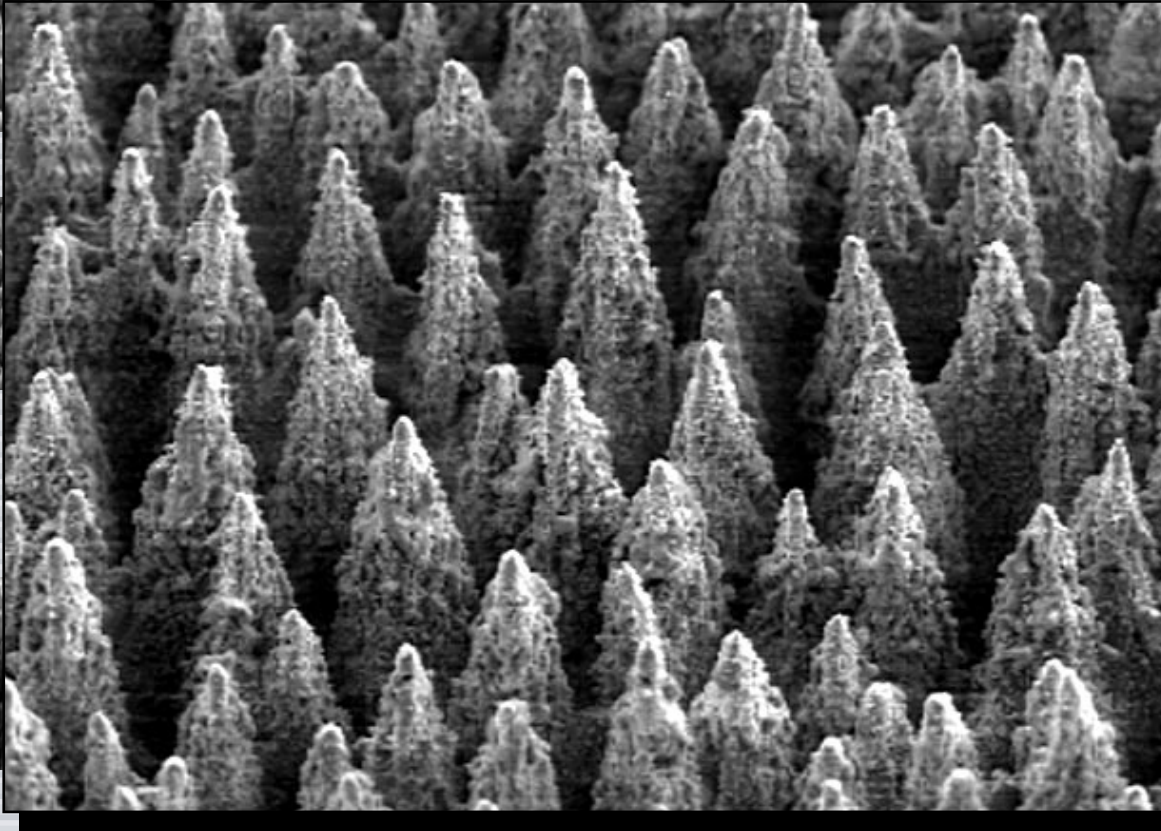
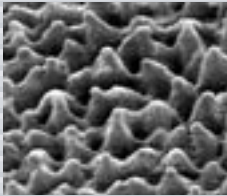
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vacuum

Si

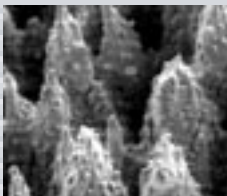


Ti



Only in SF₆

Ge



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Materials

SF₆

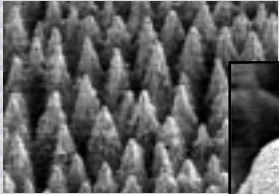
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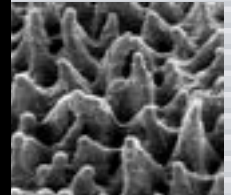
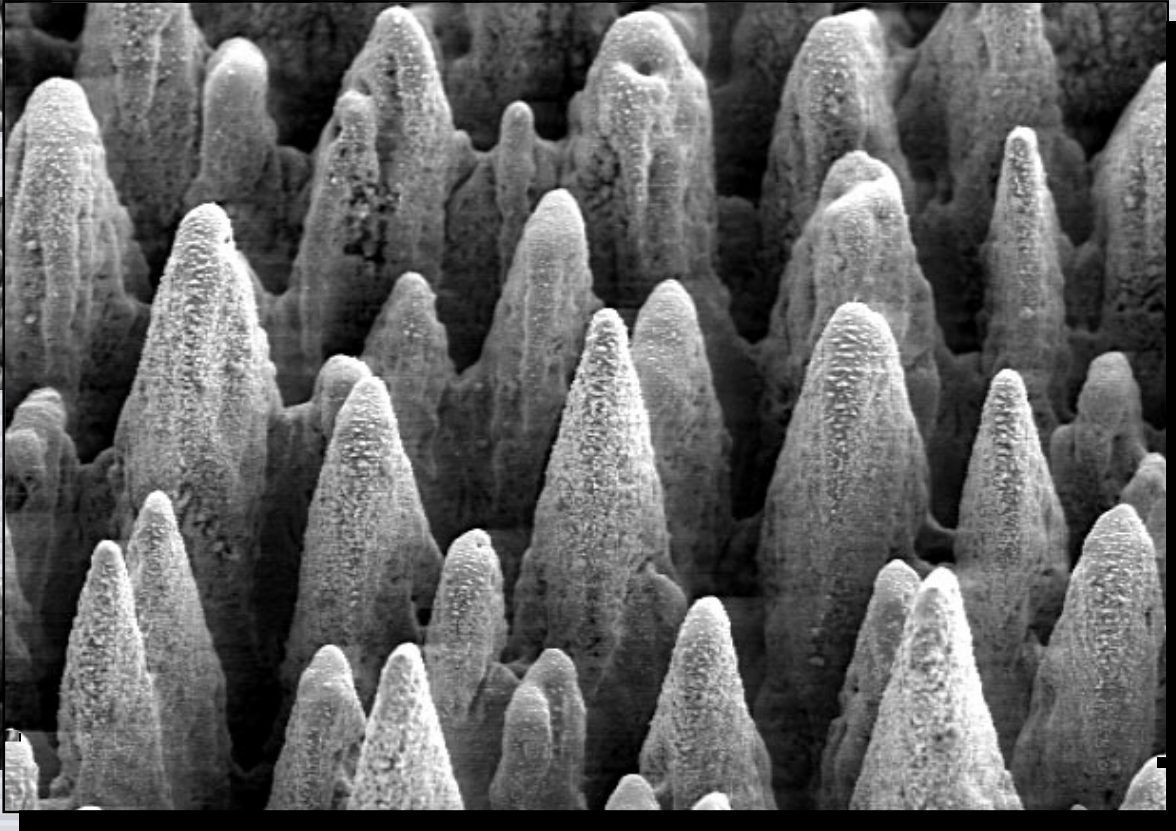
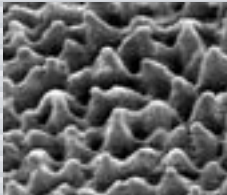
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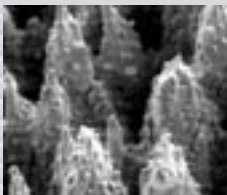
Si



Ti



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SF₆

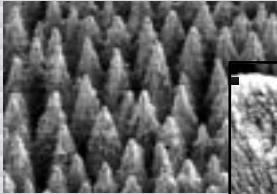
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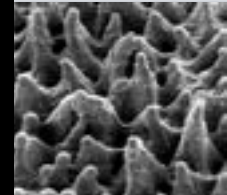
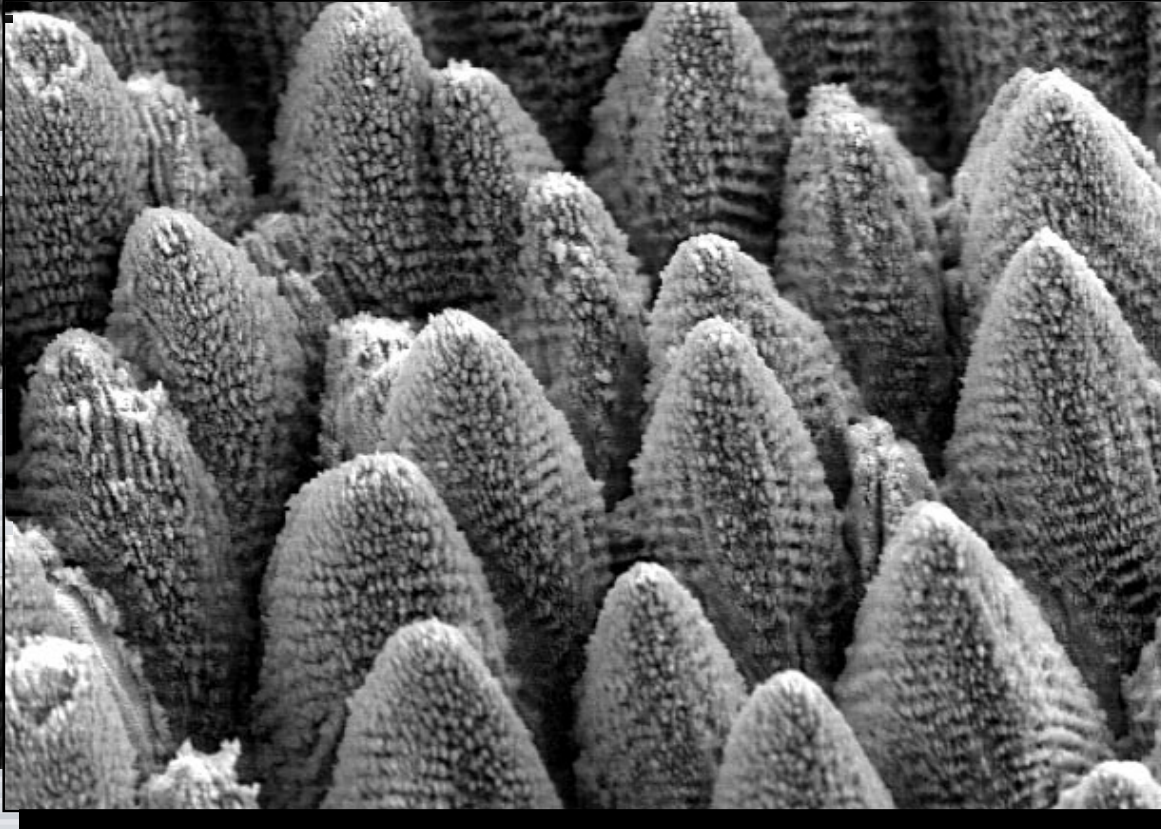
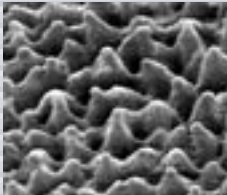
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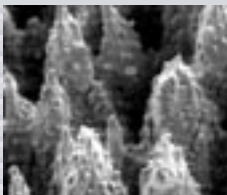


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SF₆

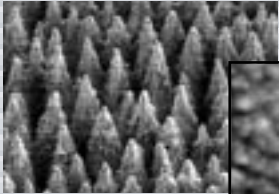
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N₂

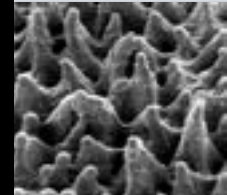
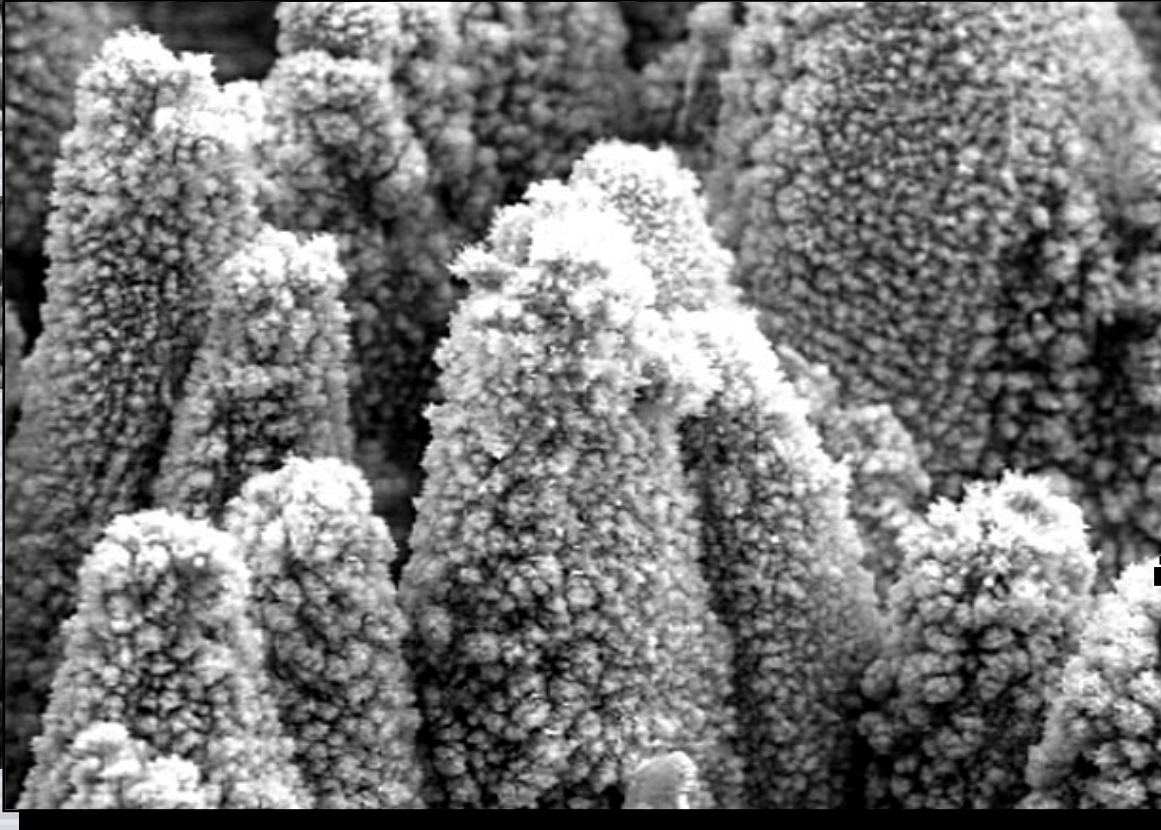
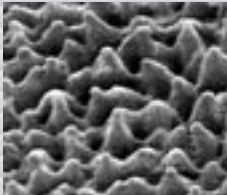
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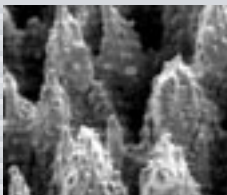
Si



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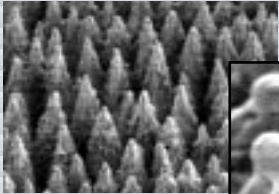
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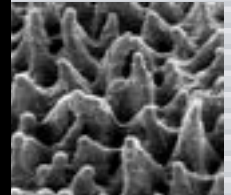
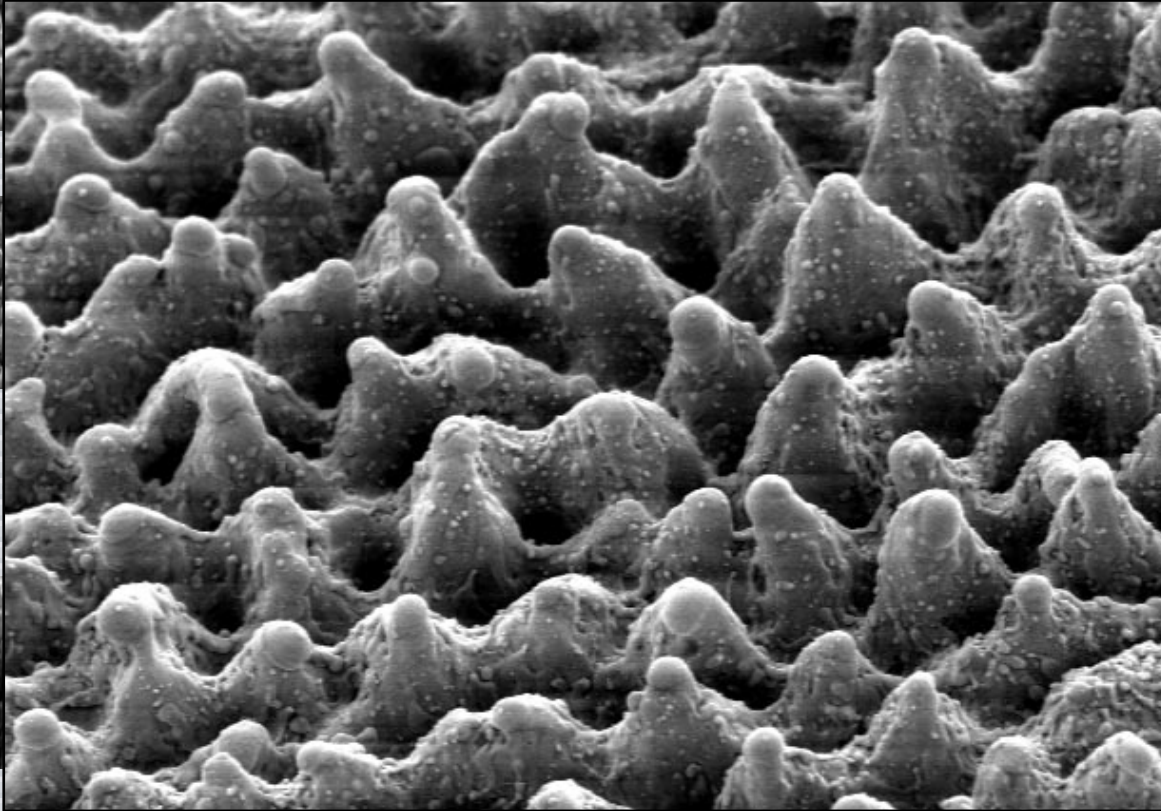
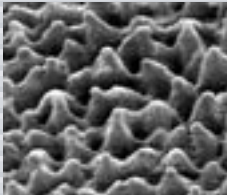
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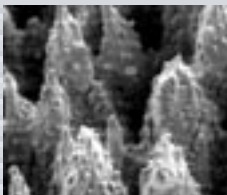


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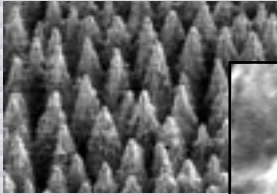
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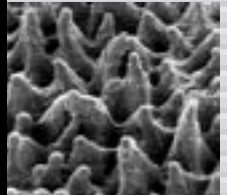
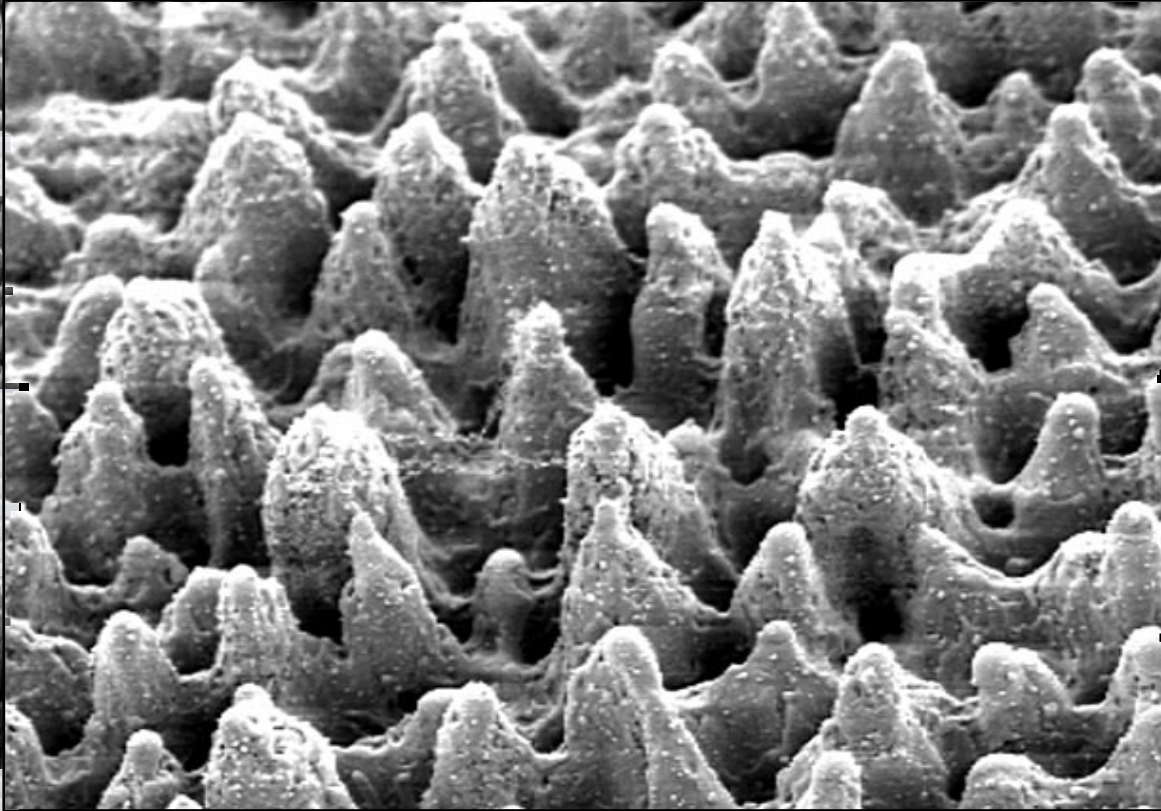
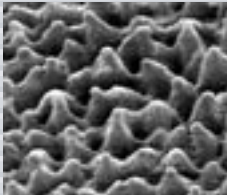
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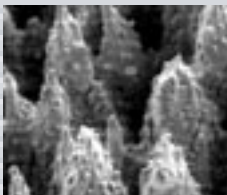
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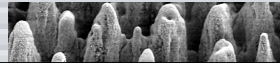
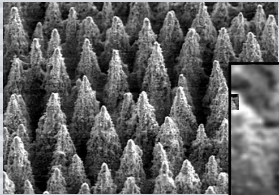
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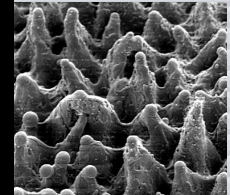
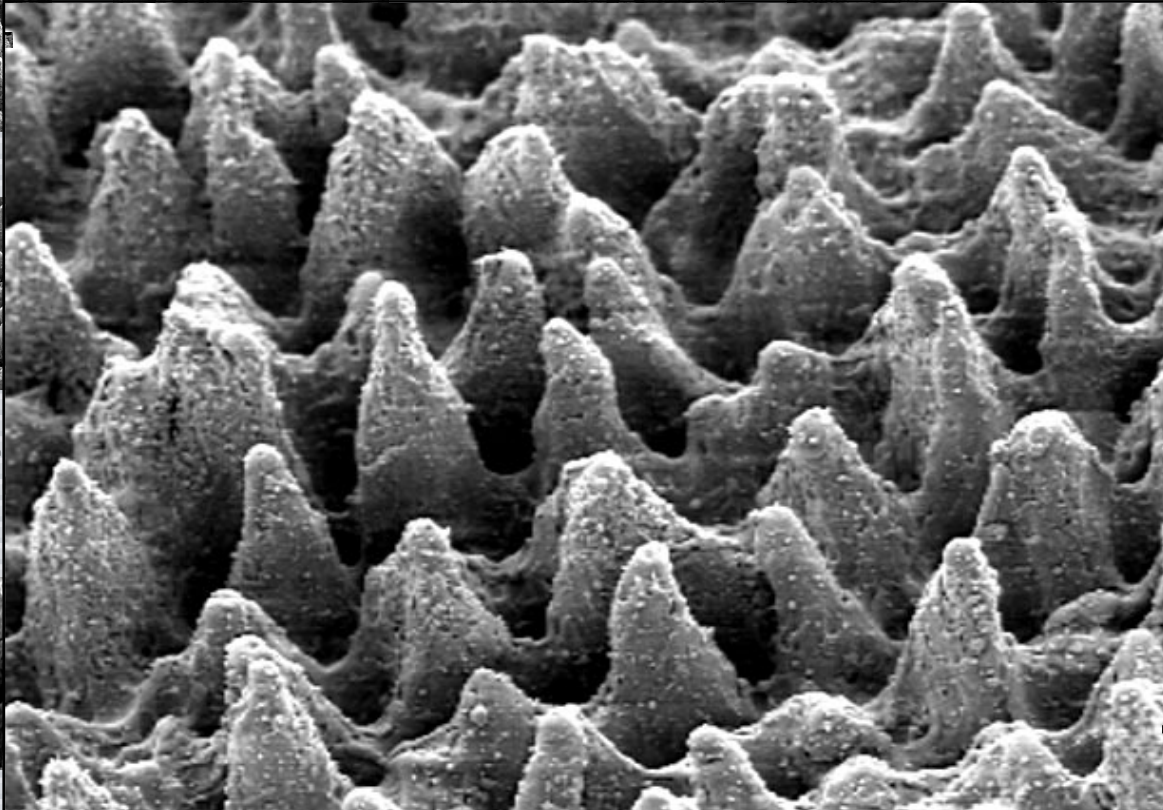
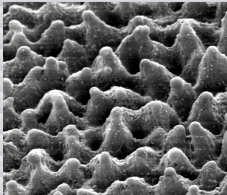
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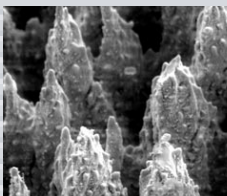
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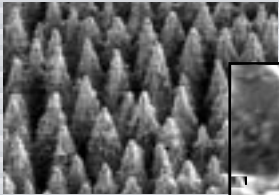
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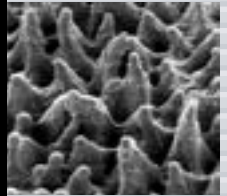
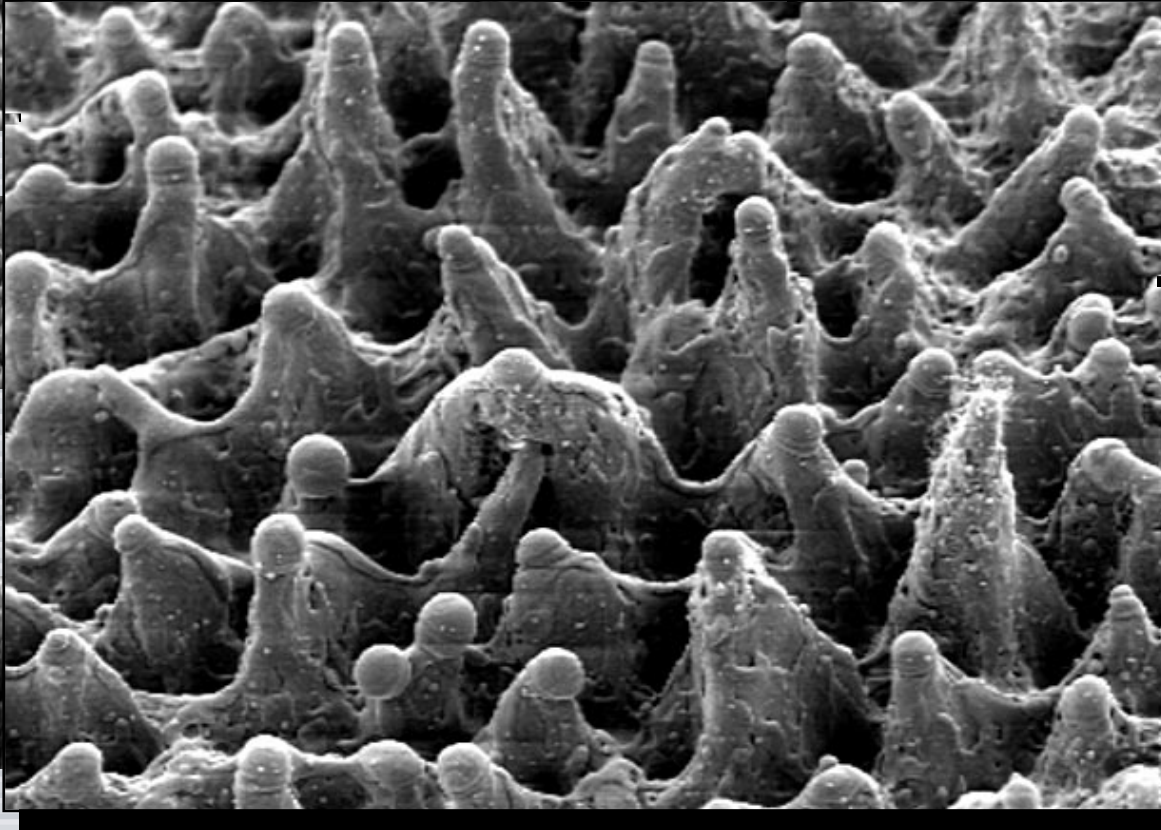
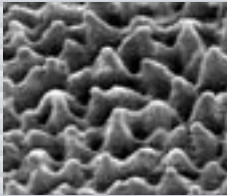
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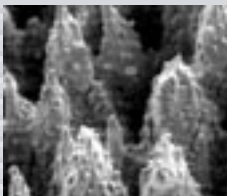
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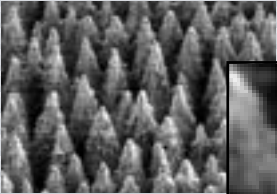
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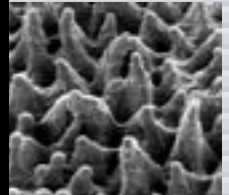
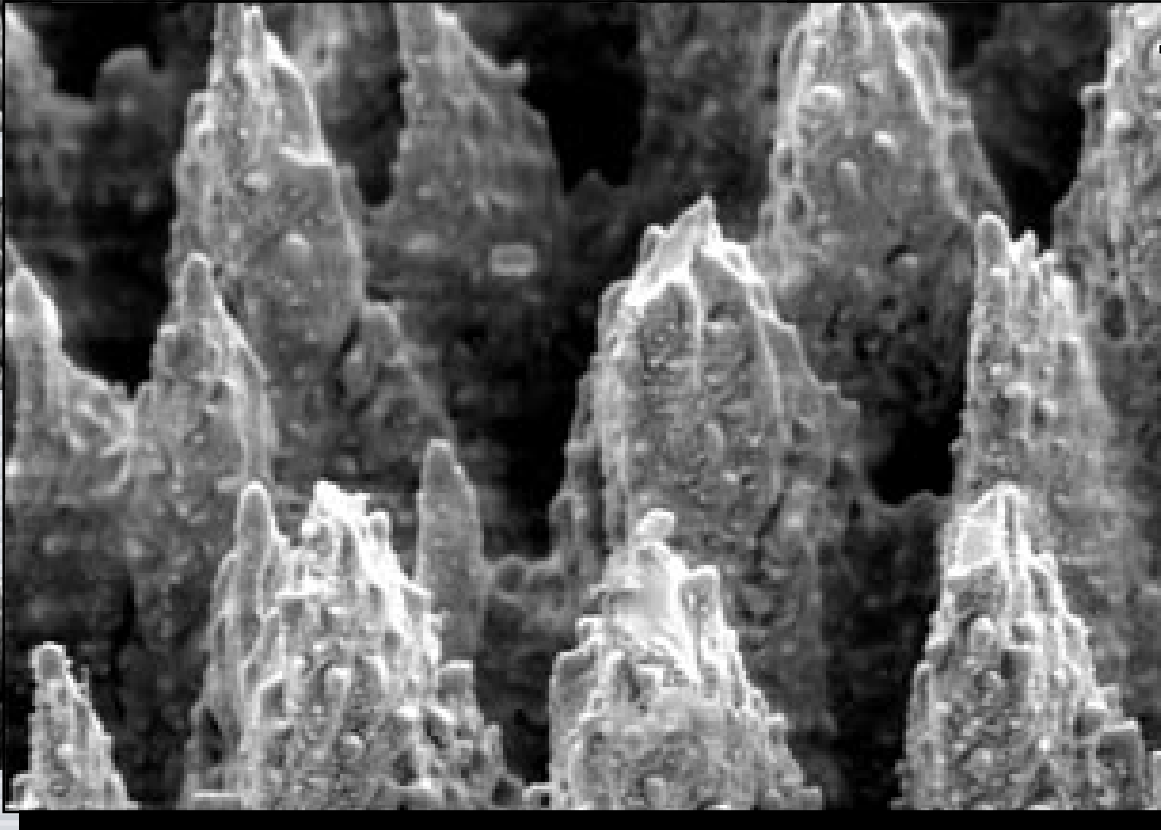
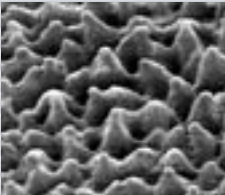
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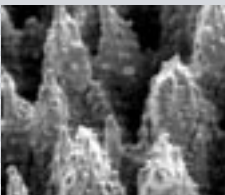
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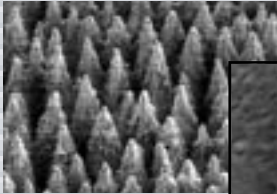
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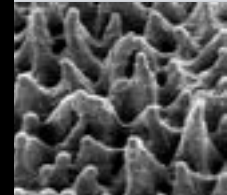
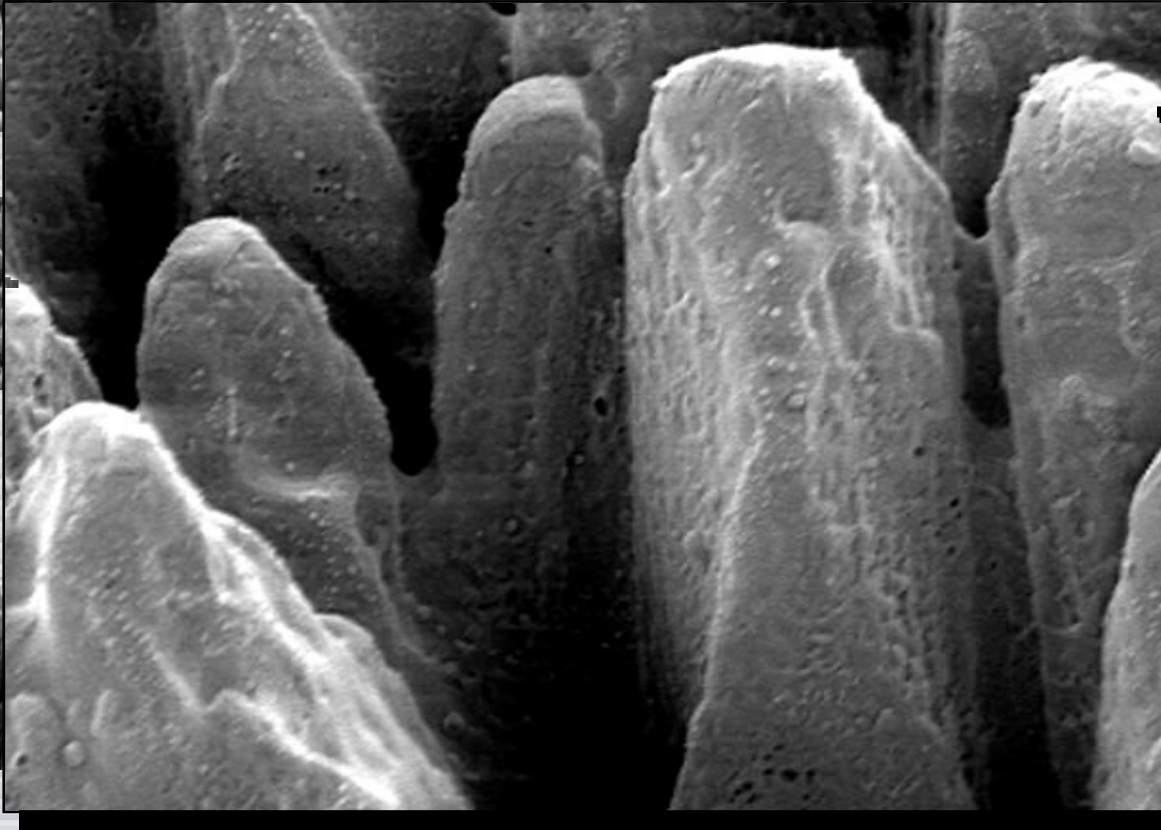
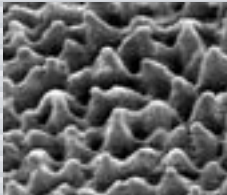
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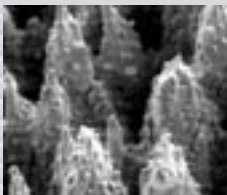
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