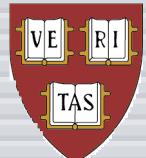


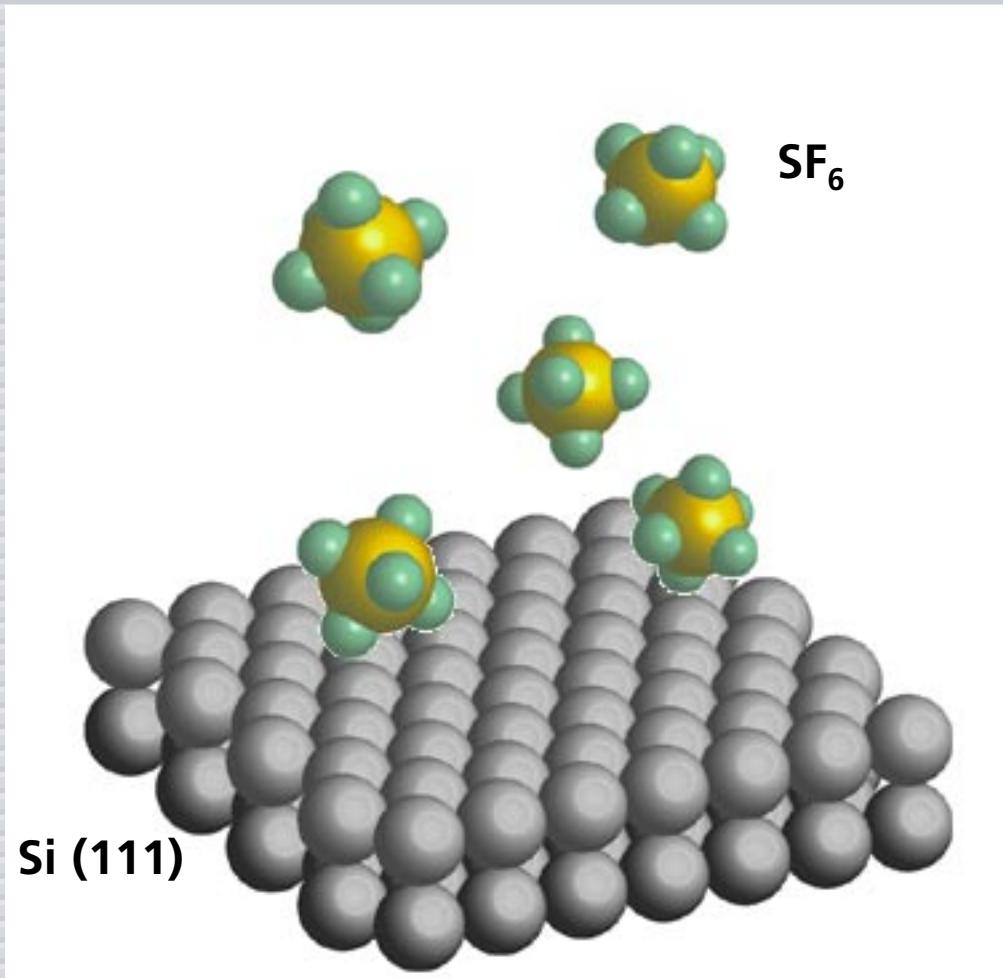
# **Laser-assisted microstructuring of silicon surfaces for novel detector, sensing, and display technologies**

**Jim Carey  
Tsing-Hua Her  
Mike Sheehy  
Claudia Wu  
Rebecca Younkin  
Catherine Crouch  
Meng Yan Shen  
Li Zhao**

**Lawrence Livermore National Laboratory  
Livermore, 16 October 2001**

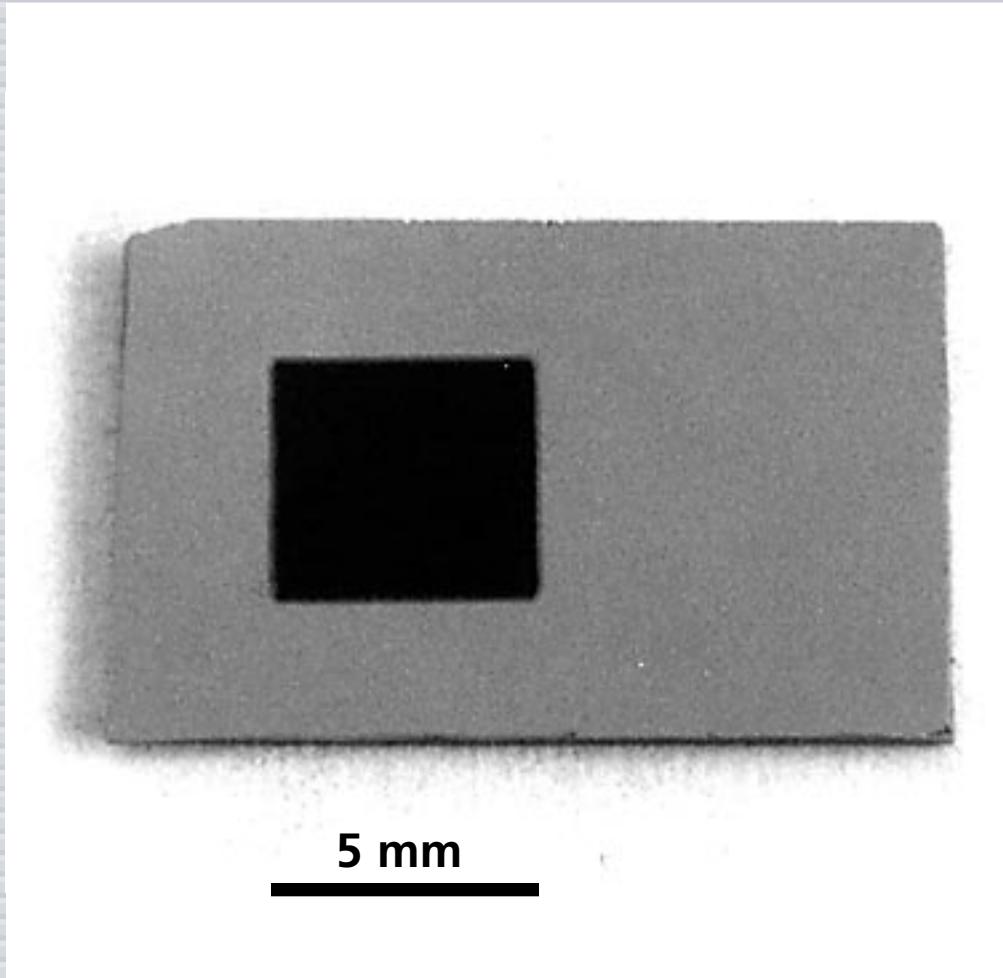


# *Introduction*



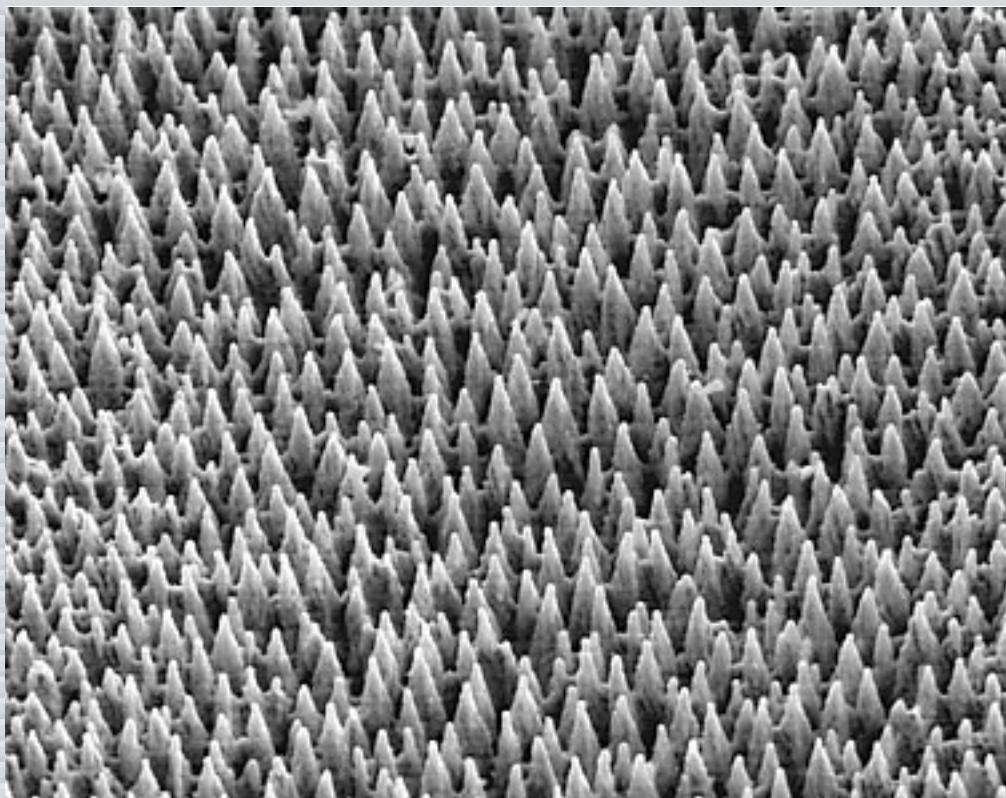
**irradiate with 100-fs  $10 \text{ kJ/m}^2$  pulses**

# *Introduction*



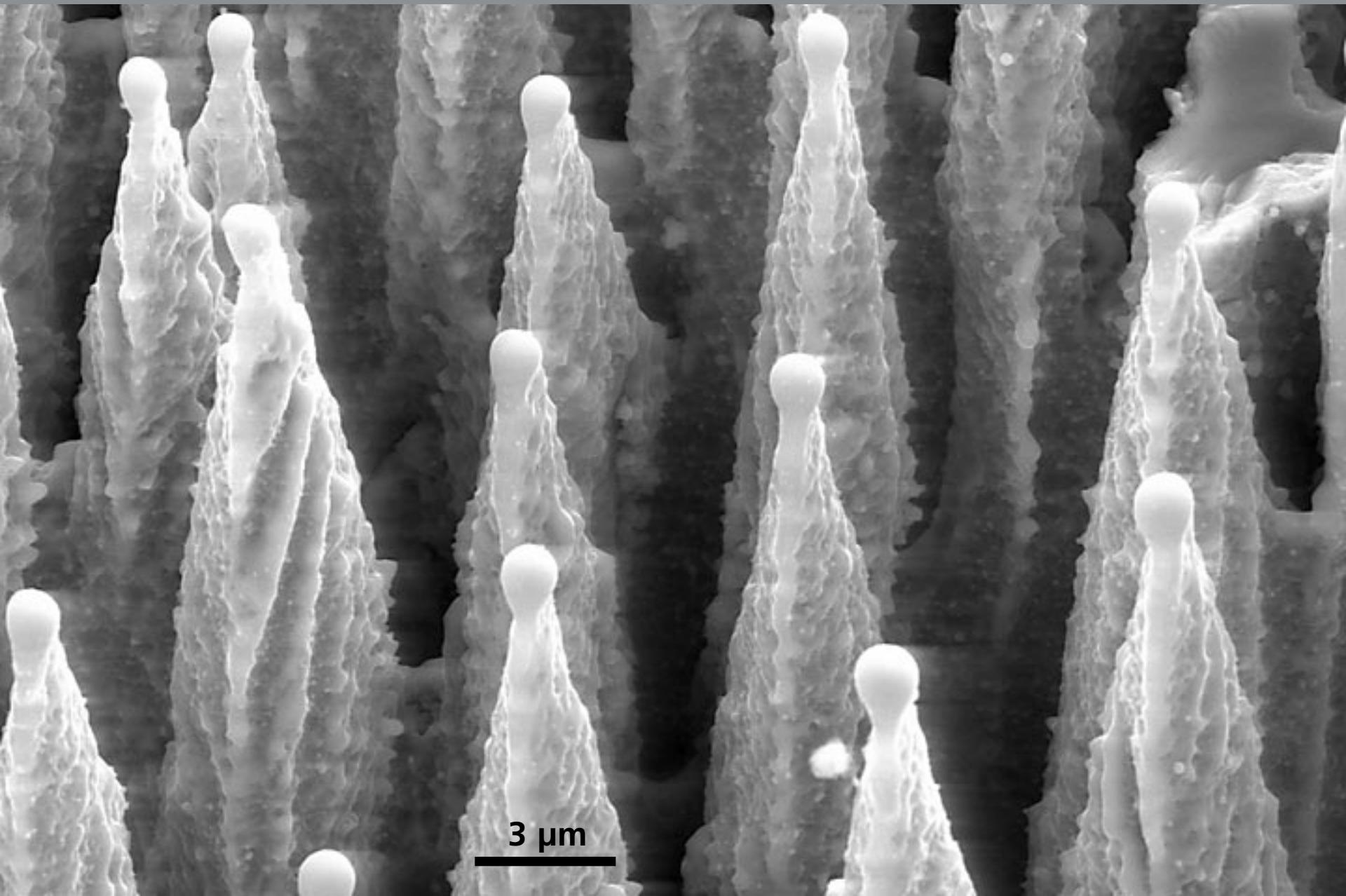
**"black silicon"**

# *Introduction*

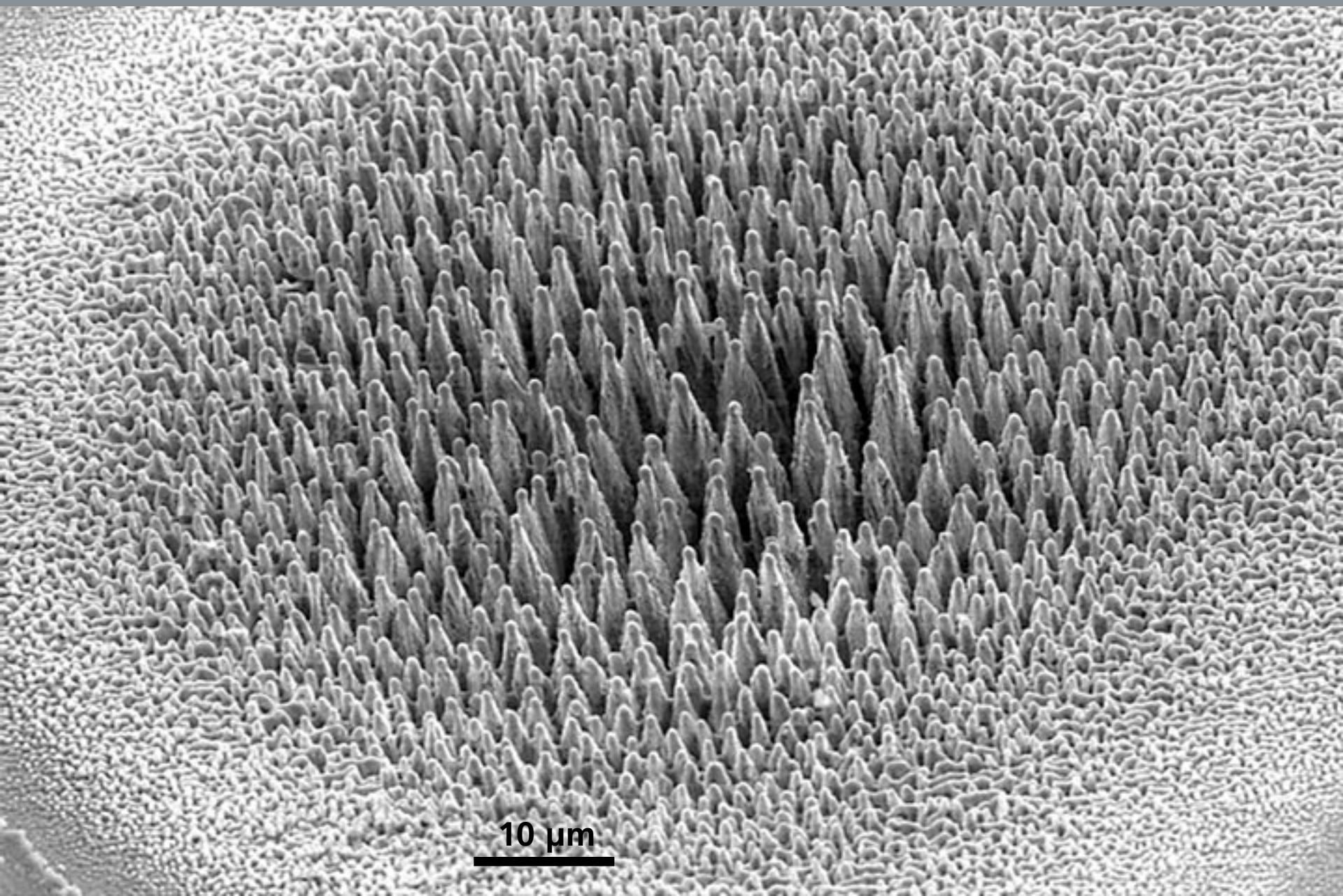


20  $\mu\text{m}$

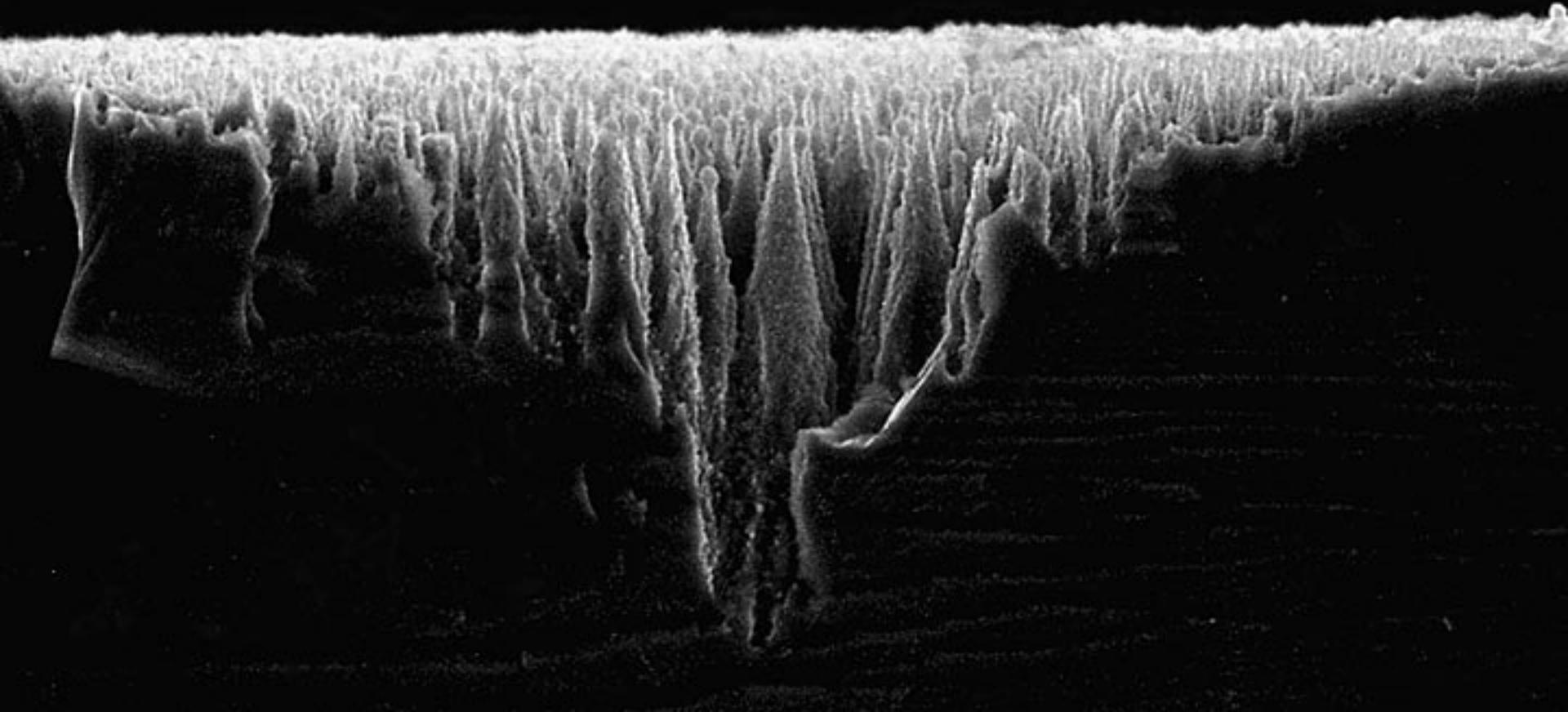
## *Introduction*



## *Introduction*



# *Introduction*



# *Introduction*

## *Introduction*

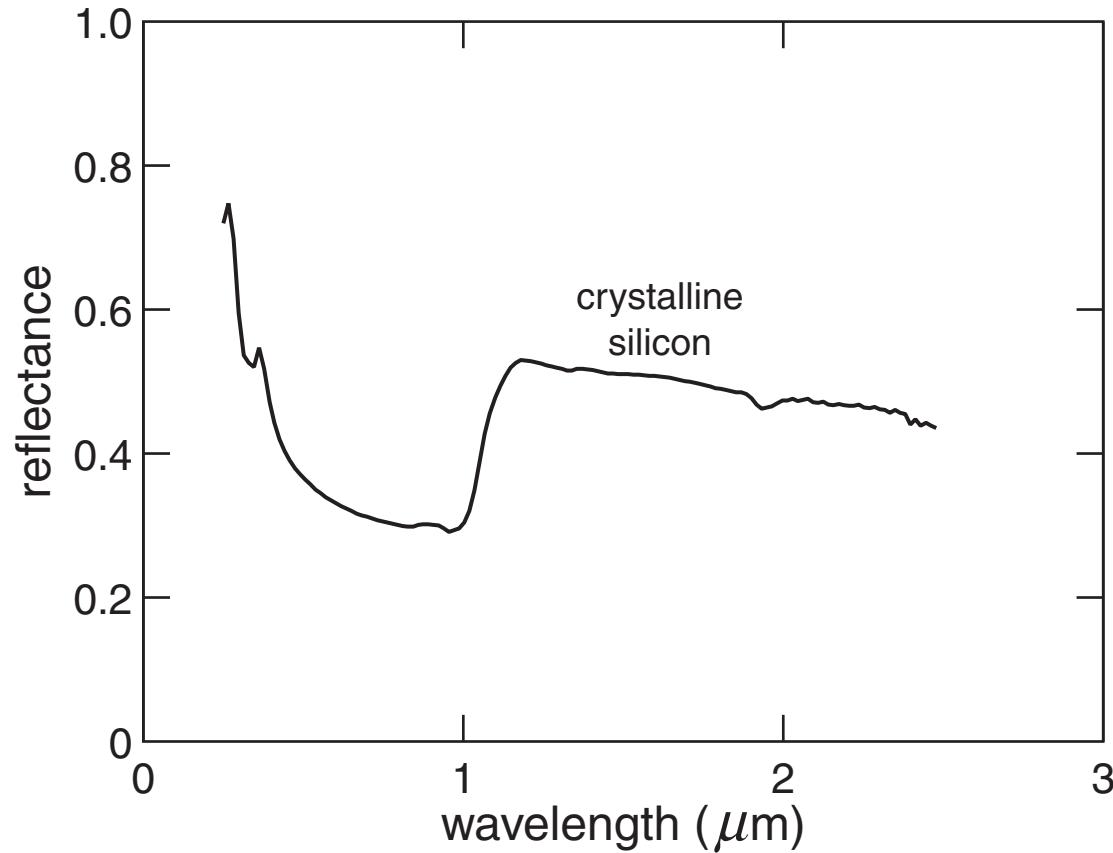
- ▶ **maskless etching process**
- ▶ **self-organized, tall, sharp structures**
- ▶ **nanoscale structure on spikes**

# *Outline*

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

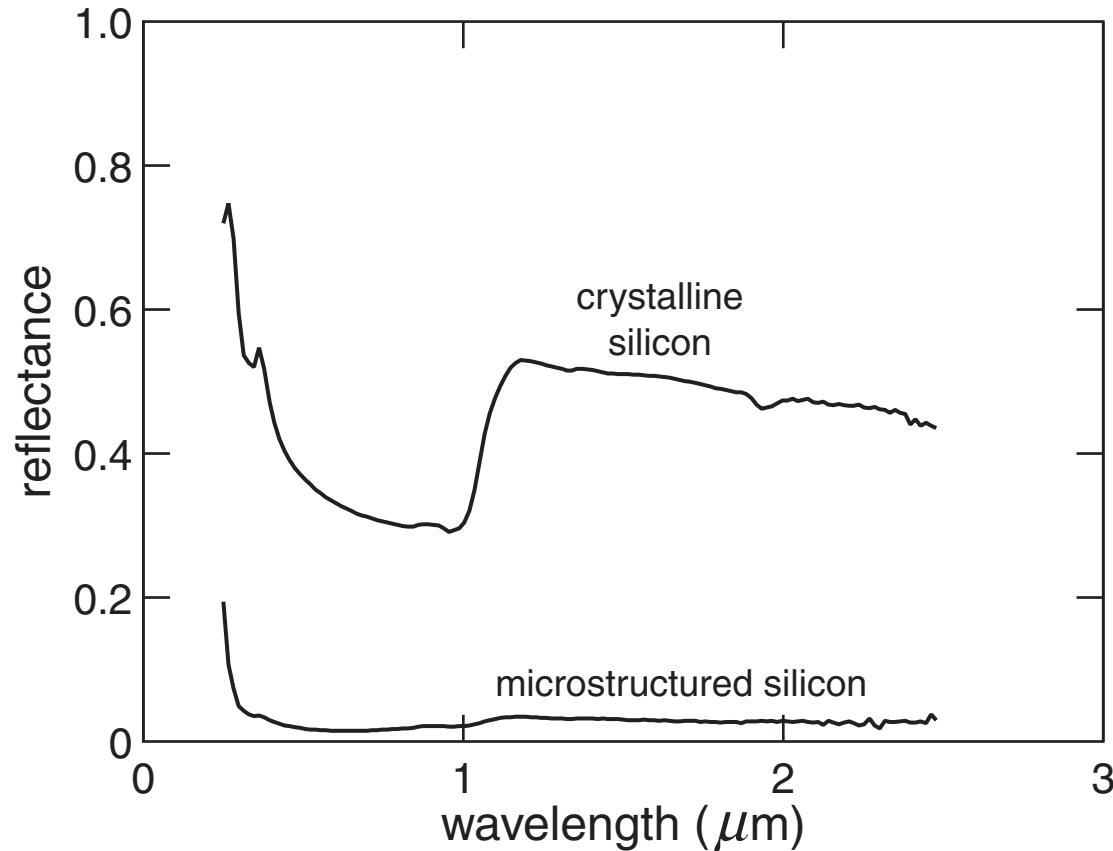
# *Properties*

## reflectance (integrating sphere)



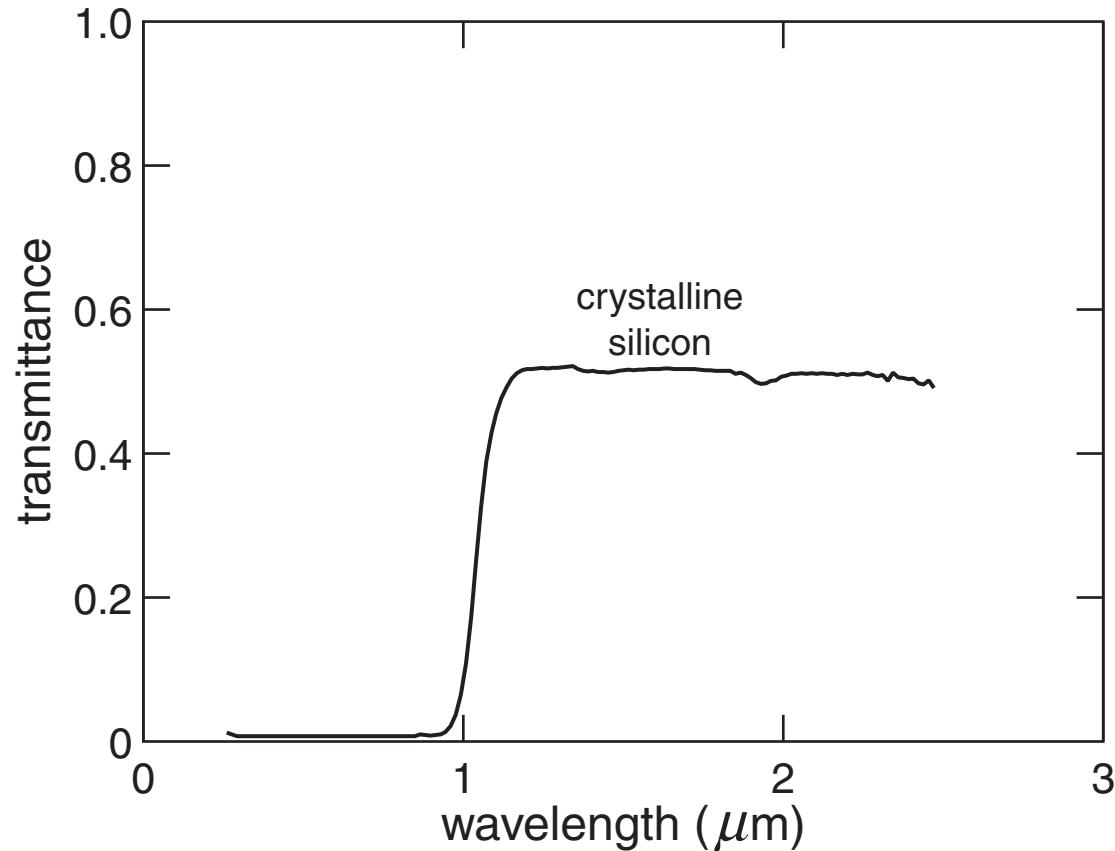
# *Properties*

## reflectance (integrating sphere)



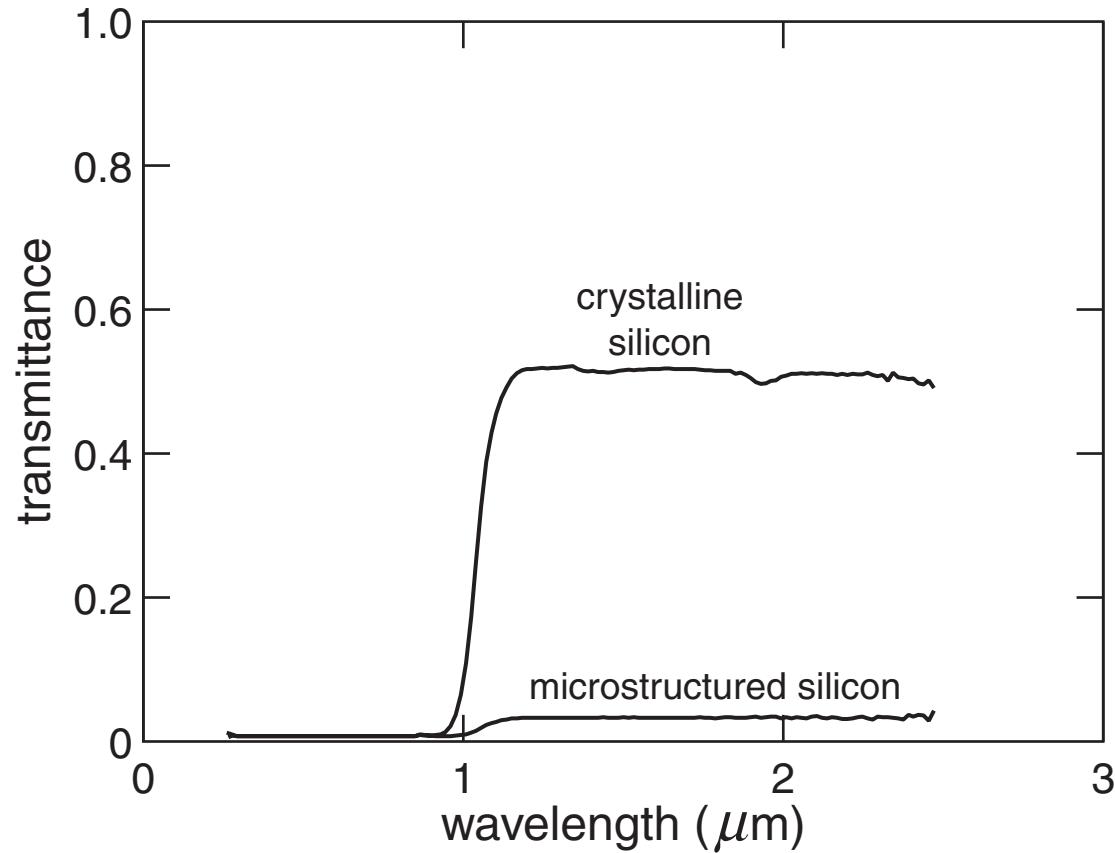
# *Properties*

## transmittance (integrating sphere)



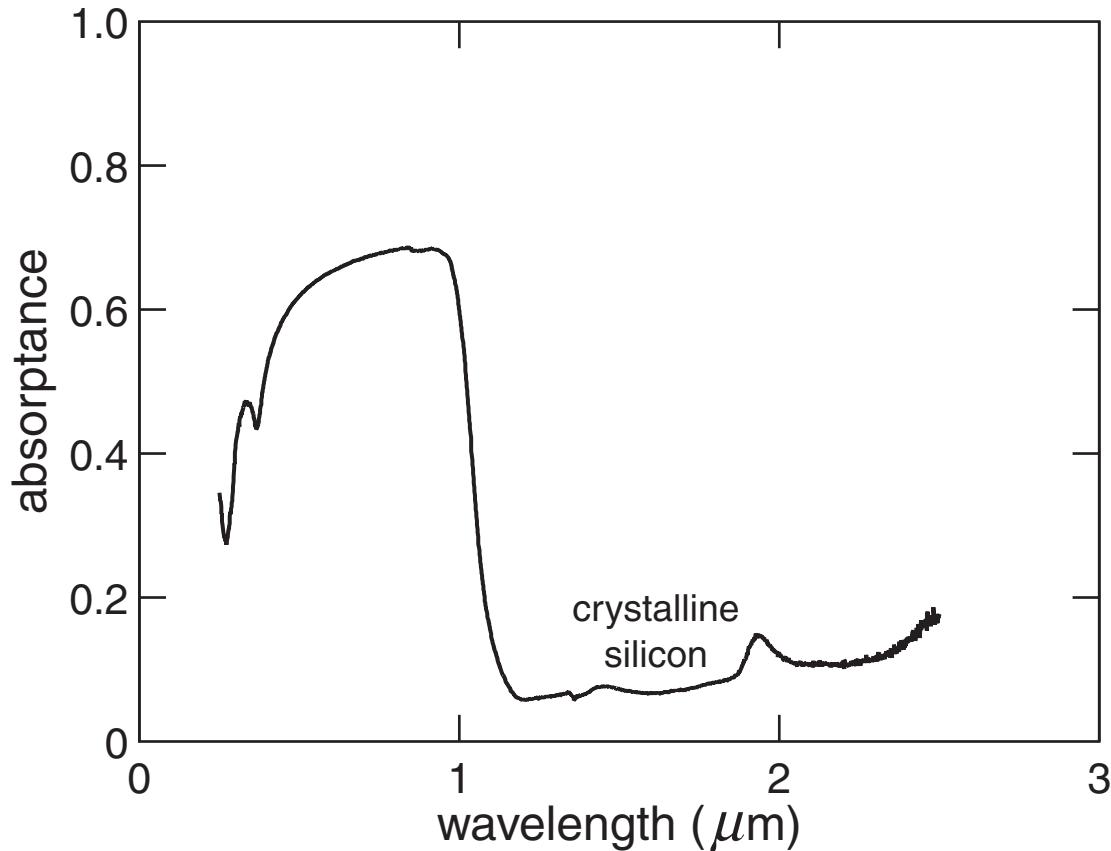
# *Properties*

## transmittance (integrating sphere)



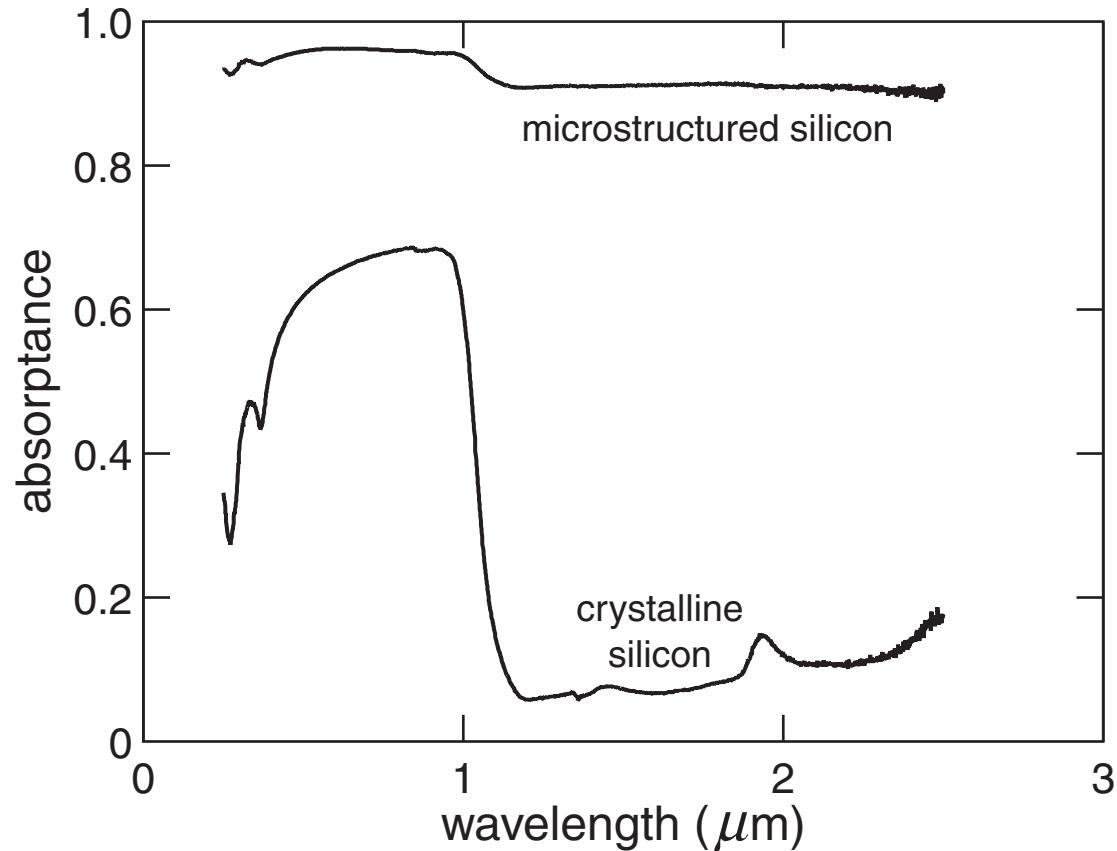
# *Properties*

## **absorptance ( $1 - R - T$ )**



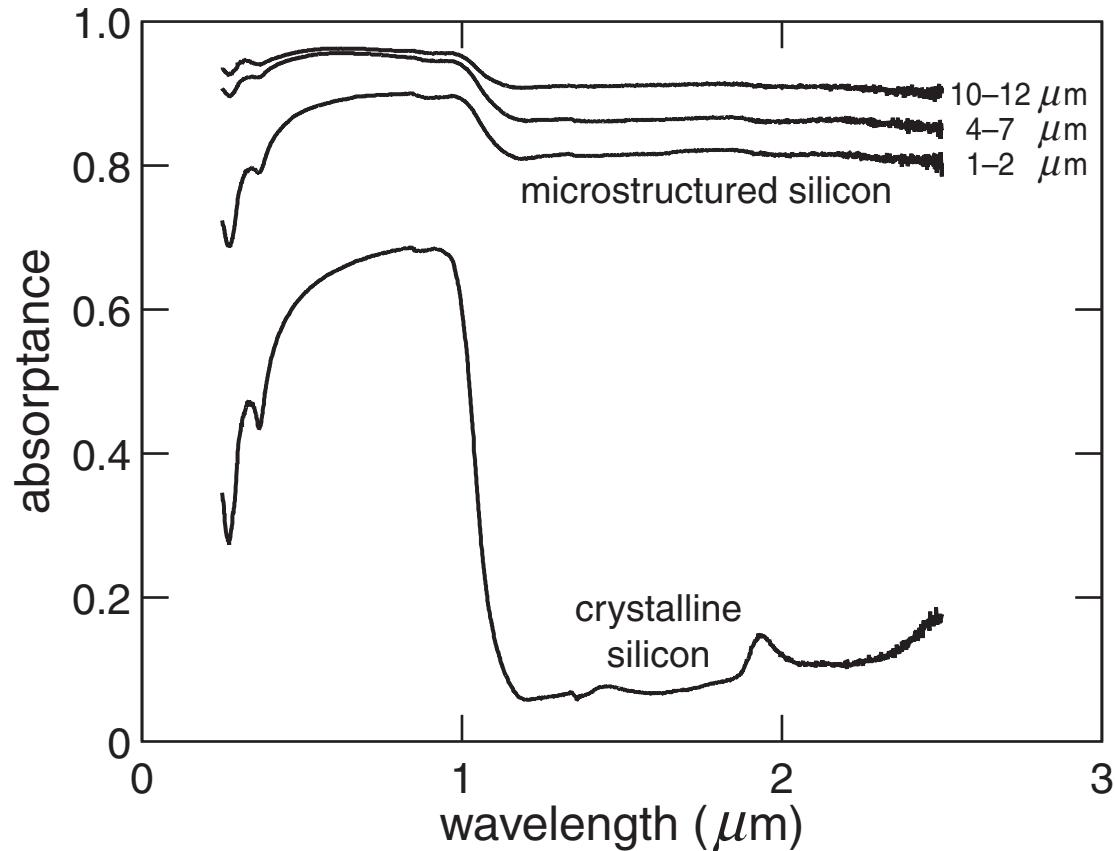
# *Properties*

## absorptance ( $1 - R - T$ )



# *Properties*

## absorptance ( $1 - R - T$ )



# *Properties*

## **field emission setup**



# *Properties*

## **field emission setup**



gold coating

# *Properties*

## field emission setup

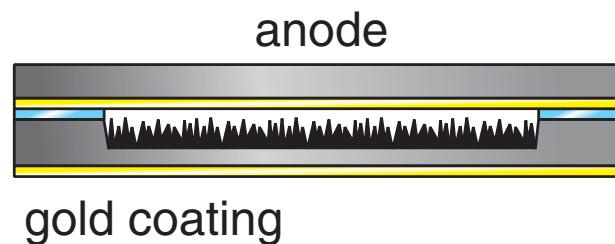
20 µm mica spacers



gold coating

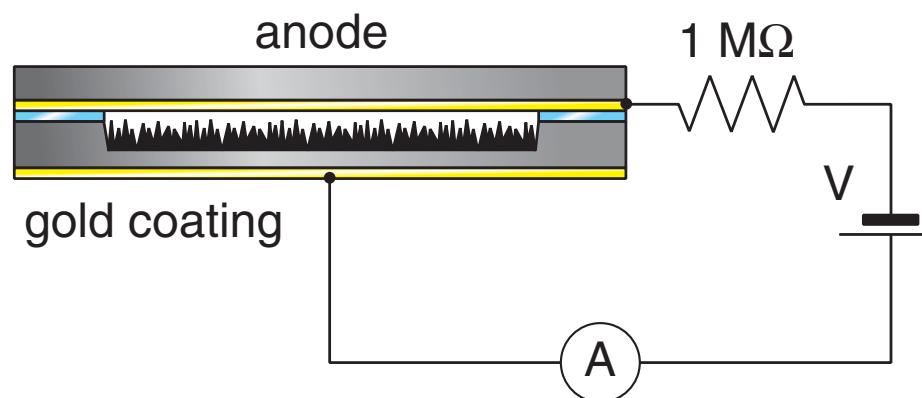
# *Properties*

## **field emission setup**

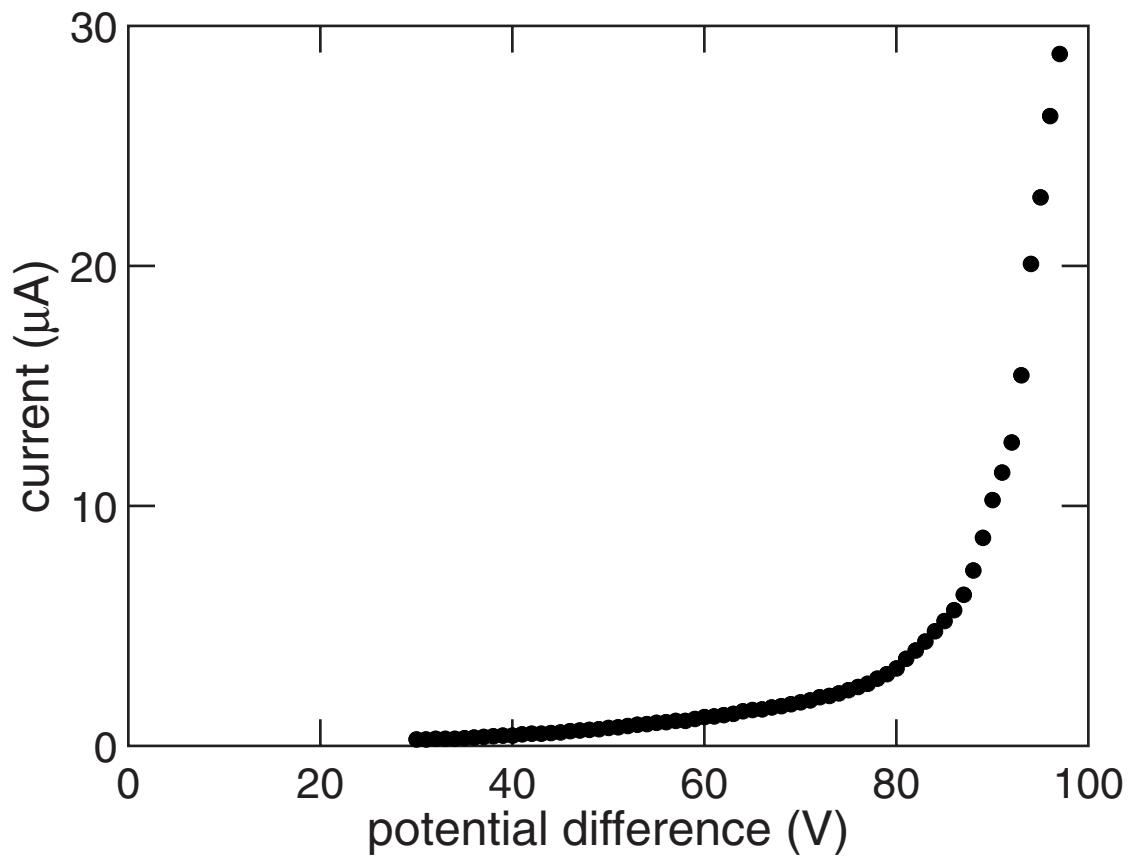


# *Properties*

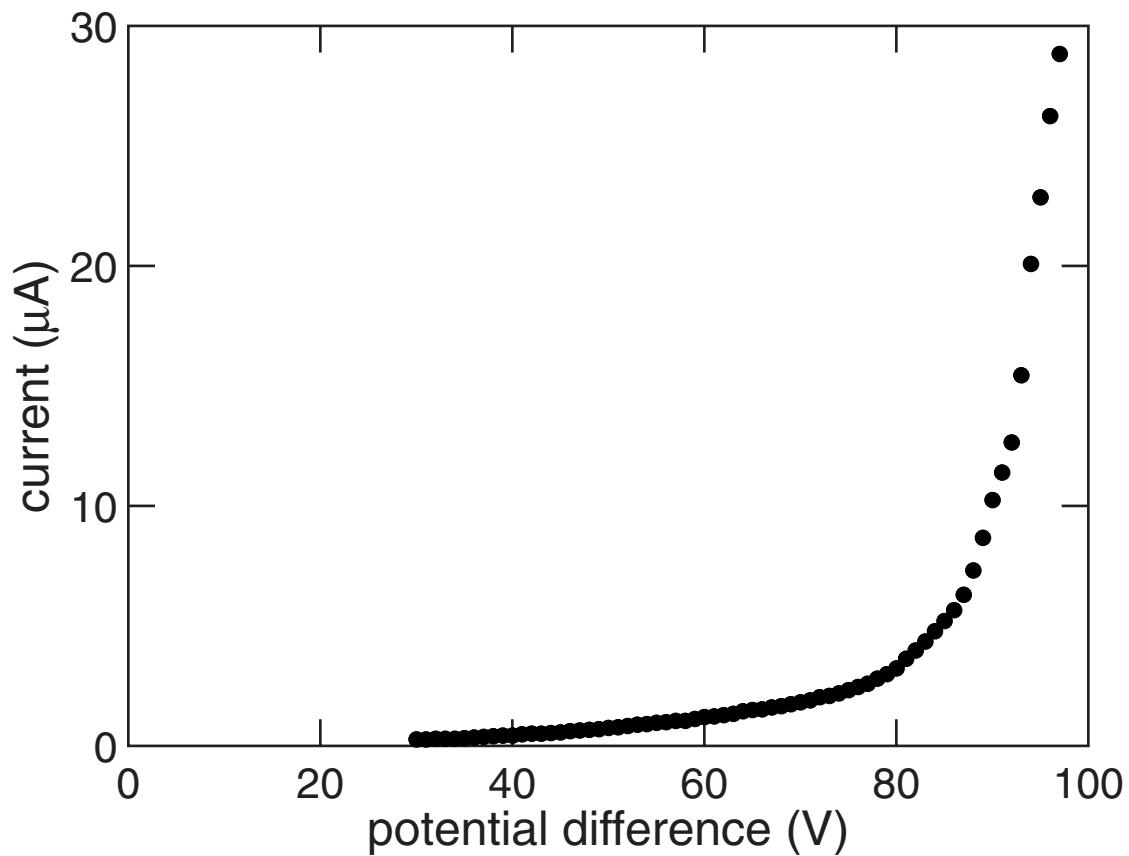
## field emission setup



# *Properties*

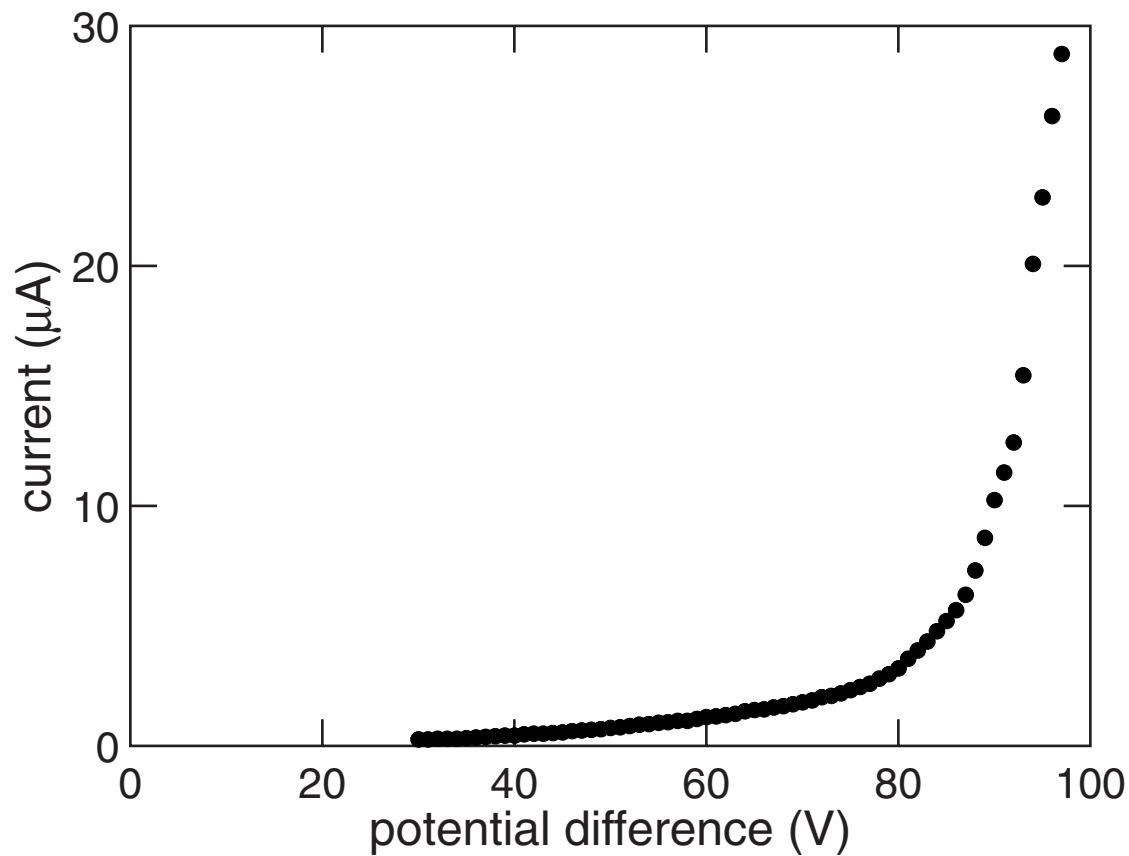


## *Properties*



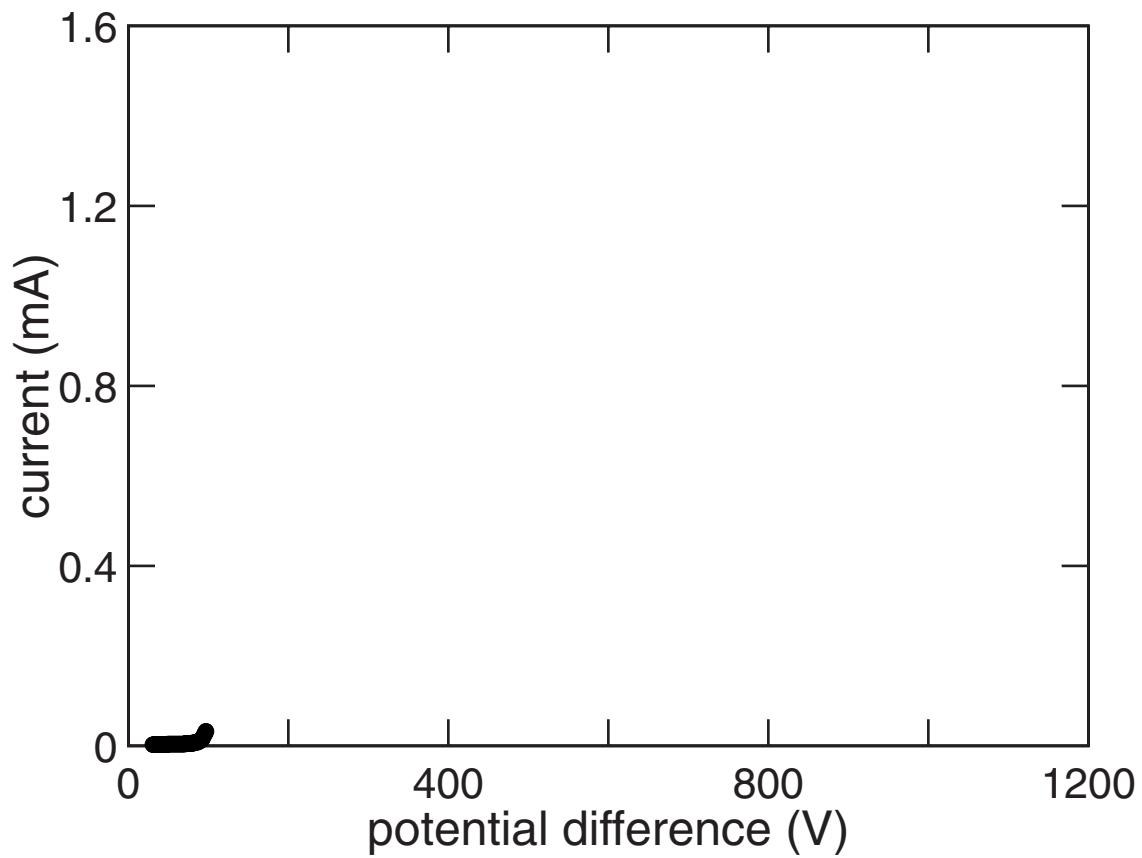
**turn-on field ( $1 \mu\text{A}/\text{cm}^2$ ):  $1.2 \text{ V}/\mu\text{m}$**

# *Properties*

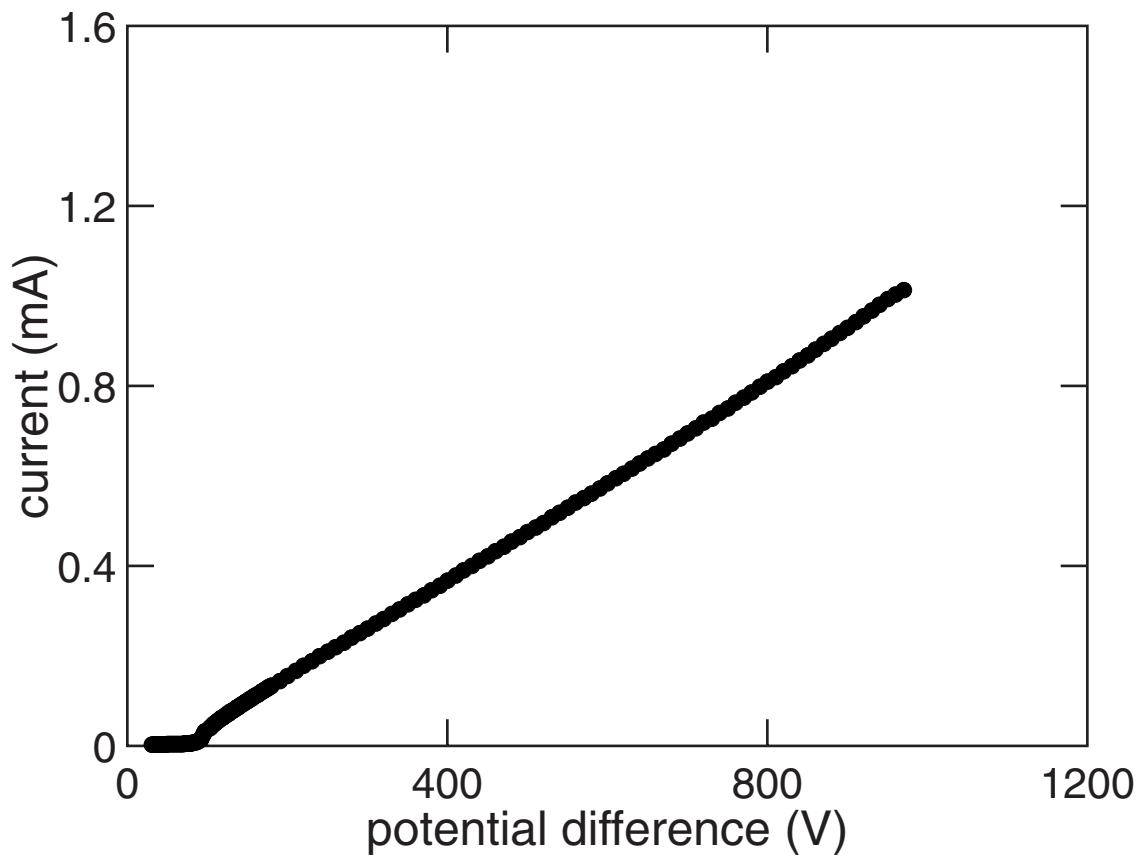


**threshold field ( $10 \mu\text{A}/\text{cm}^2$ ):  $2.1 \text{ V}/\mu\text{m}$**

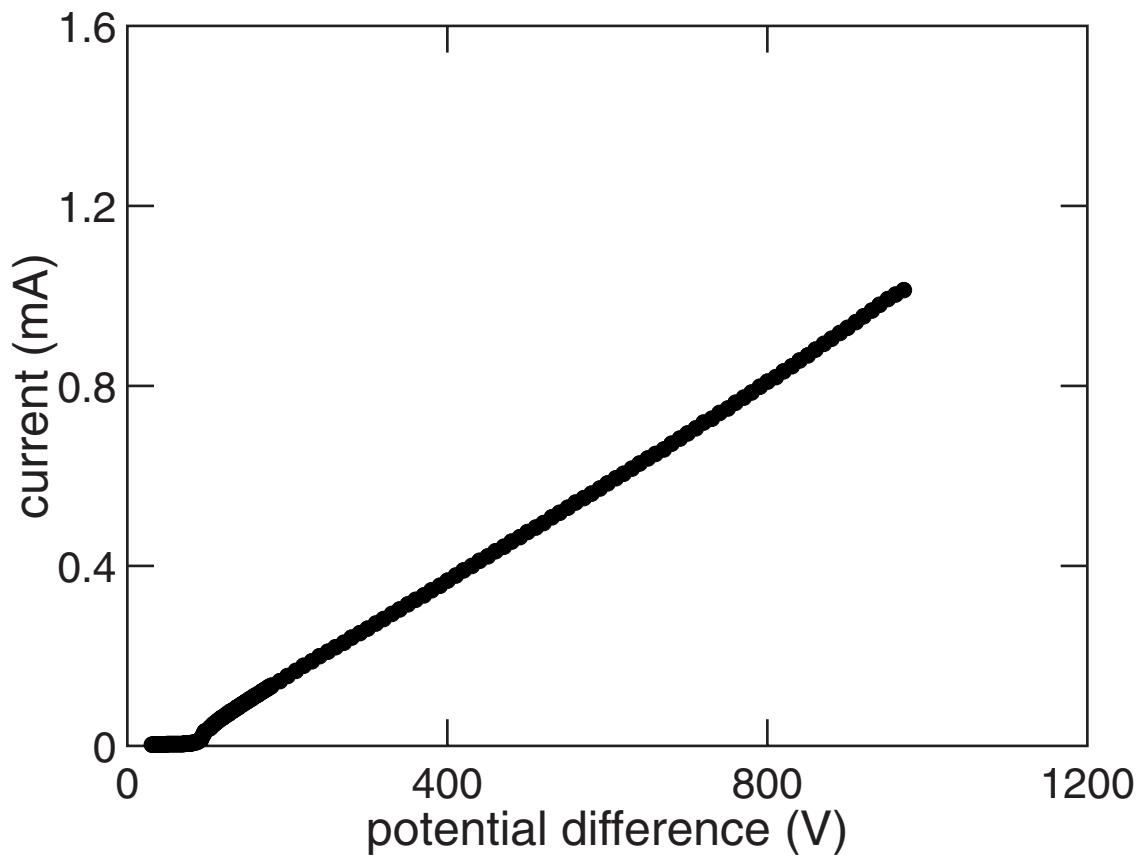
# *Properties*



# *Properties*



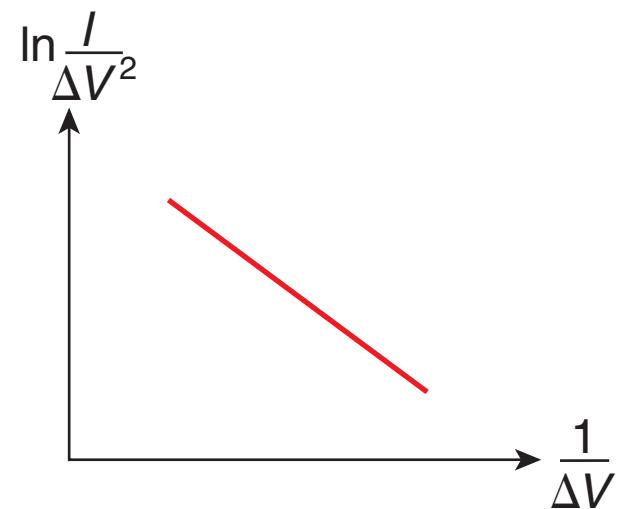
## *Properties*



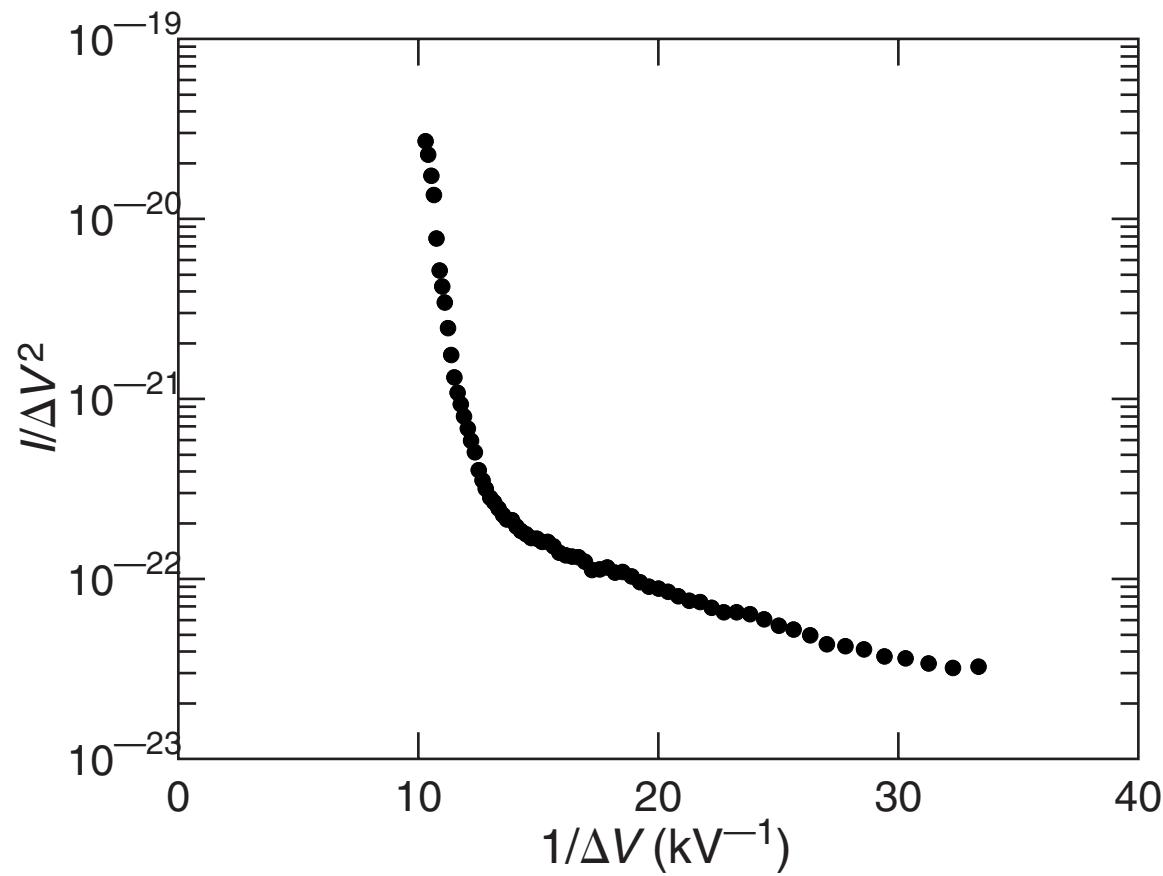
**maximum current: 20 mA (4 mm<sup>2</sup> sample)**

# *Properties*

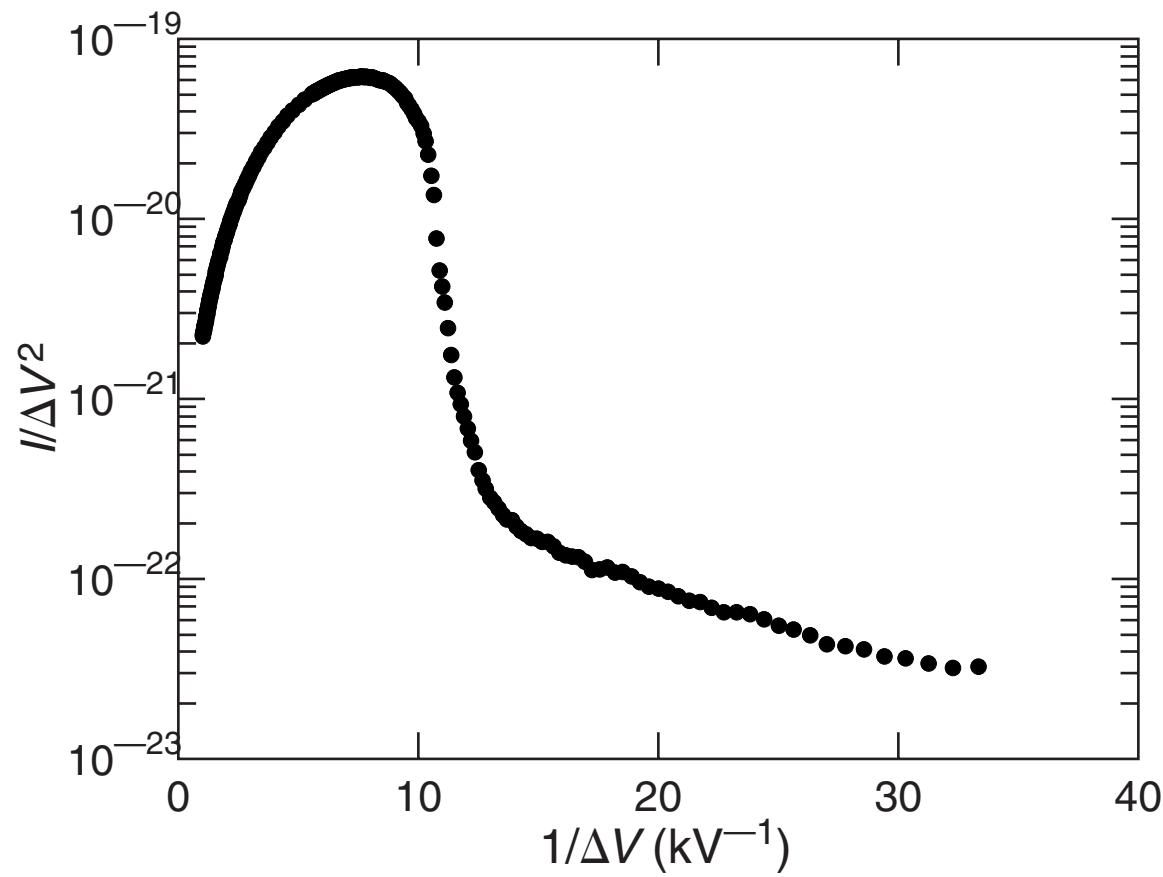
$$\ln \frac{I}{\Delta V^2} = \ln a - b \frac{1}{\Delta V}$$



# *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**

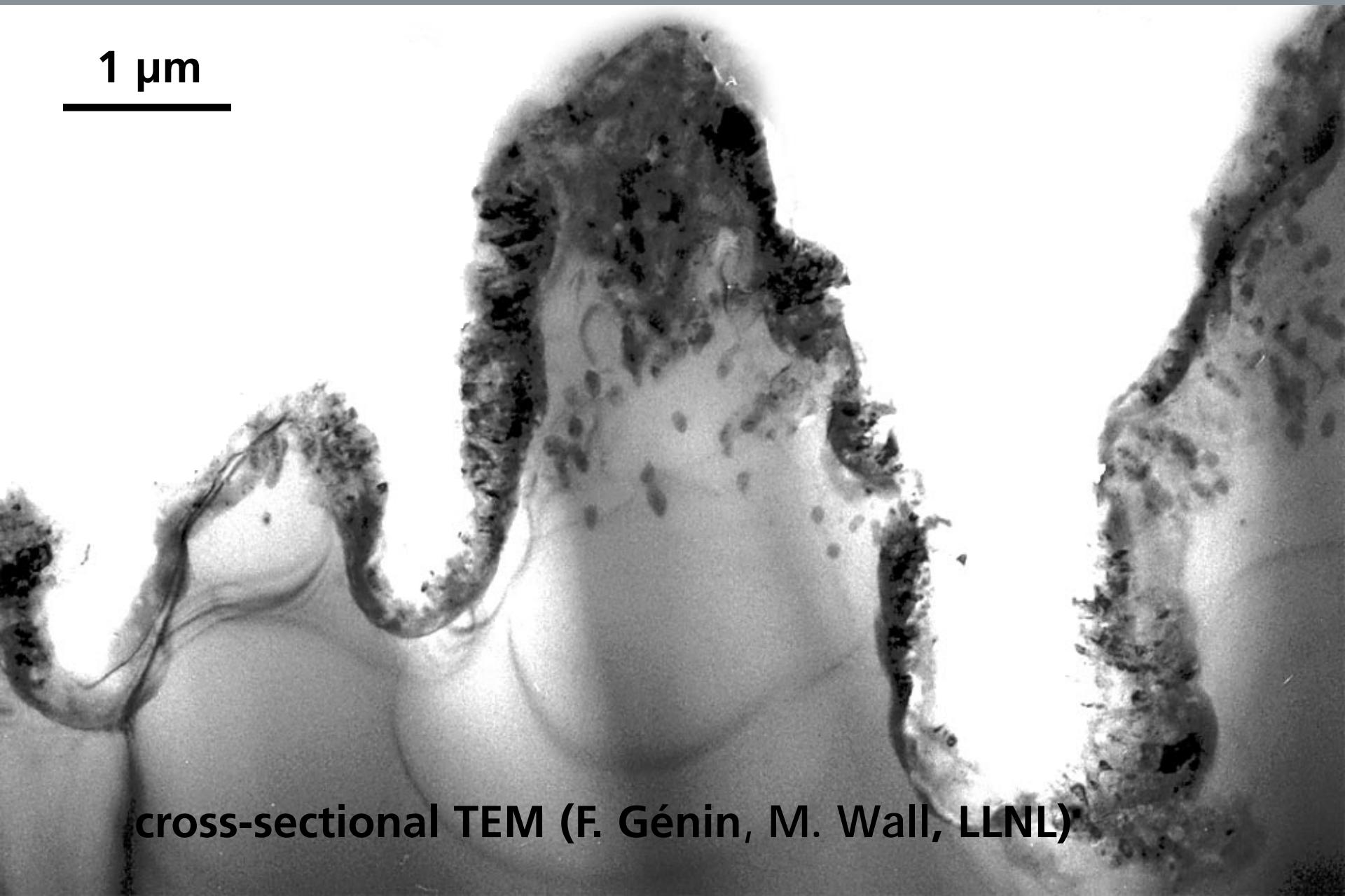
## *Structural and chemical analysis*

### **Secondary ion mass spectrometry:**

- ▶  $10^{20} \text{ cm}^{-3}$  sulfur
  
- ▶  $10^{17} \text{ cm}^{-3}$  fluorine

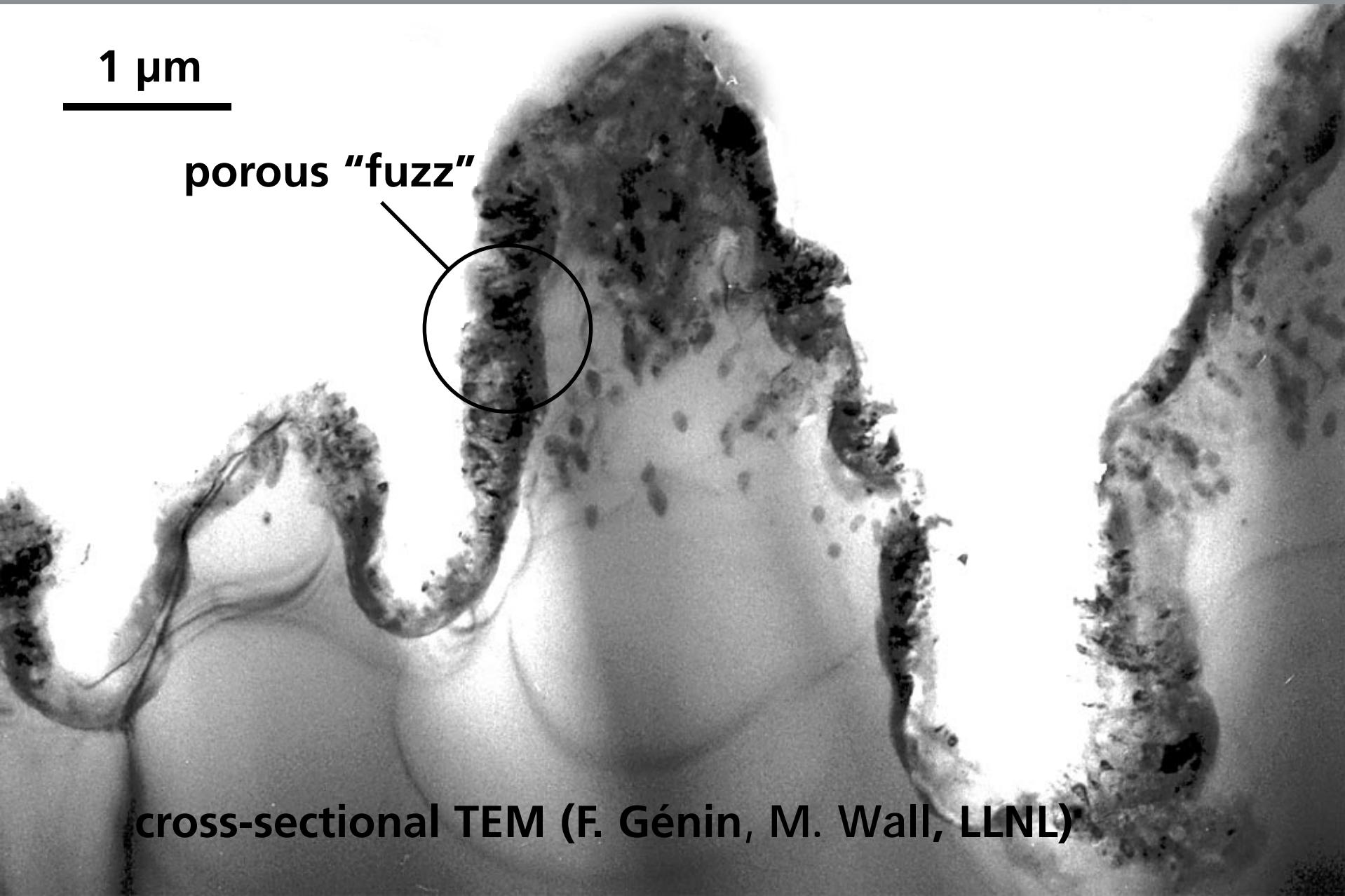
## *Structural and chemical analysis*

1  $\mu\text{m}$



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

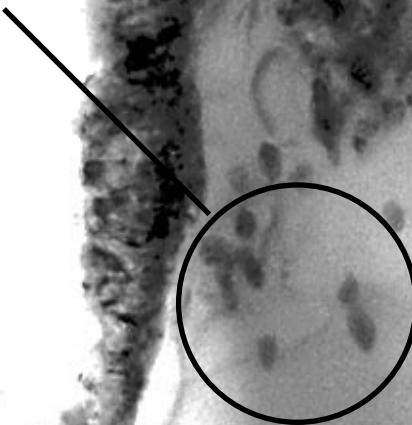
## *Structural and chemical analysis*



## *Structural and chemical analysis*

1  $\mu\text{m}$

nanocrystallites

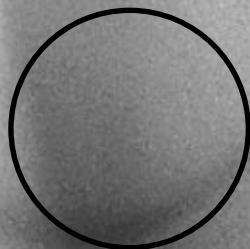


cross-sectional TEM (F. Génin, M. Wall, LLNL)

## *Structural and chemical analysis*

1  $\mu\text{m}$

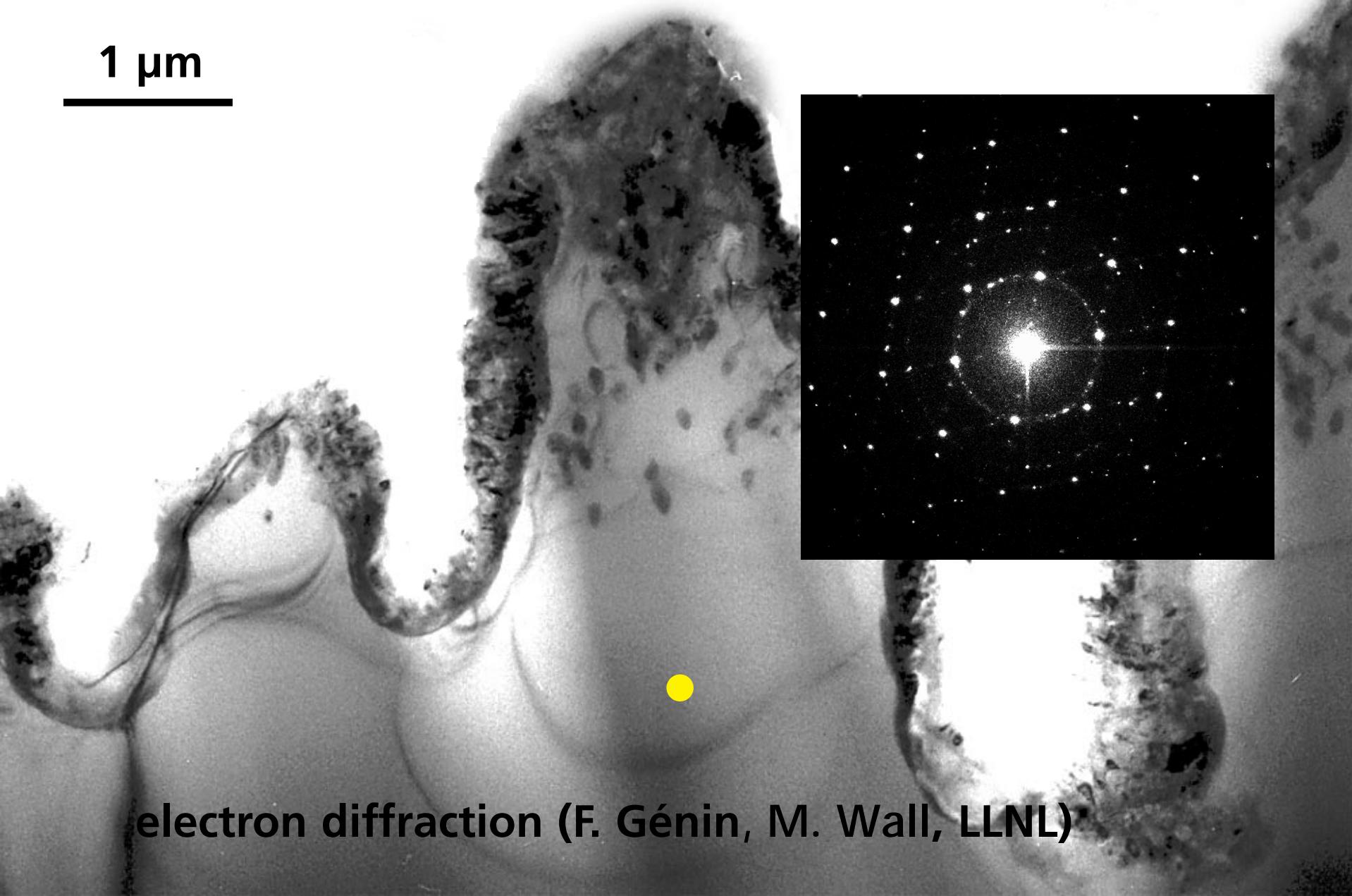
crystalline Si



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

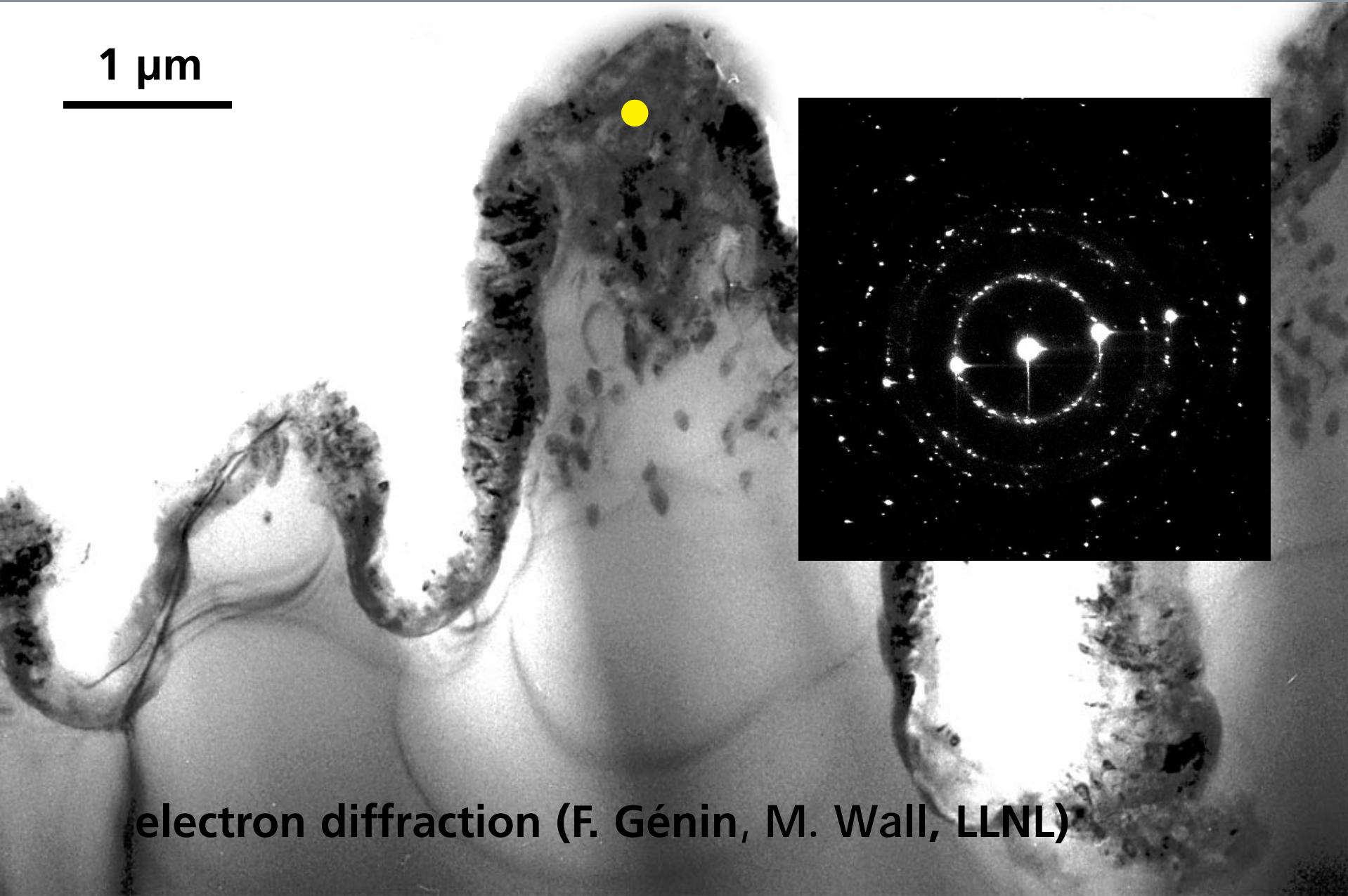
## *Structural and chemical analysis*

1  $\mu\text{m}$



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

## *Structural and chemical analysis*



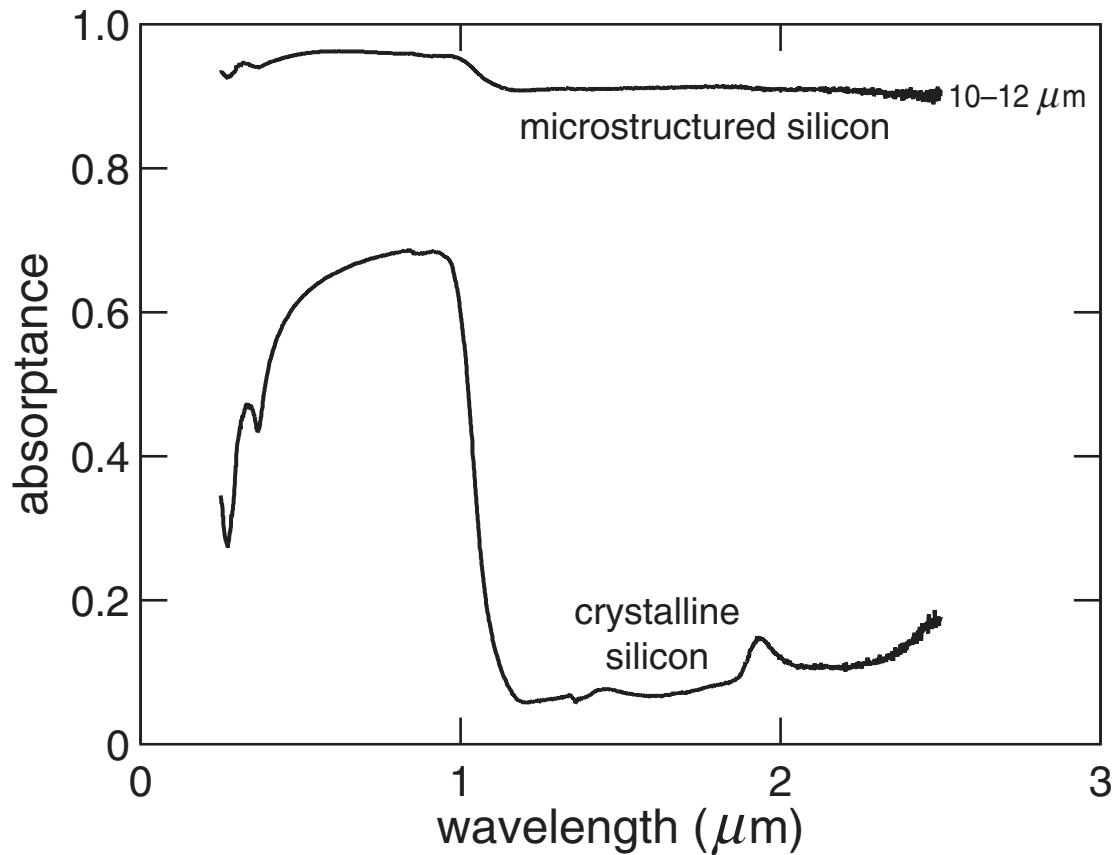
## *Structural and chemical analysis*

**cross-sectional TEM:**

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

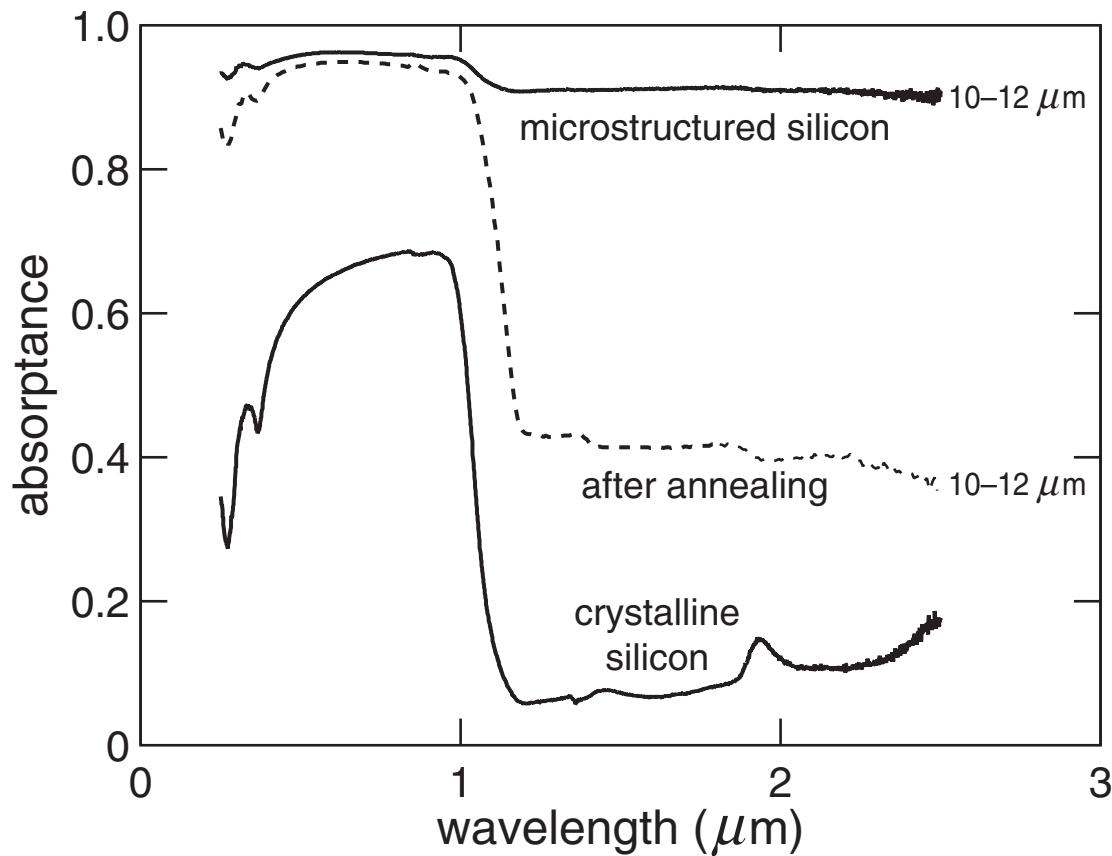
## *Structural and chemical analysis*

**anneal 4 hours at 1200 K**



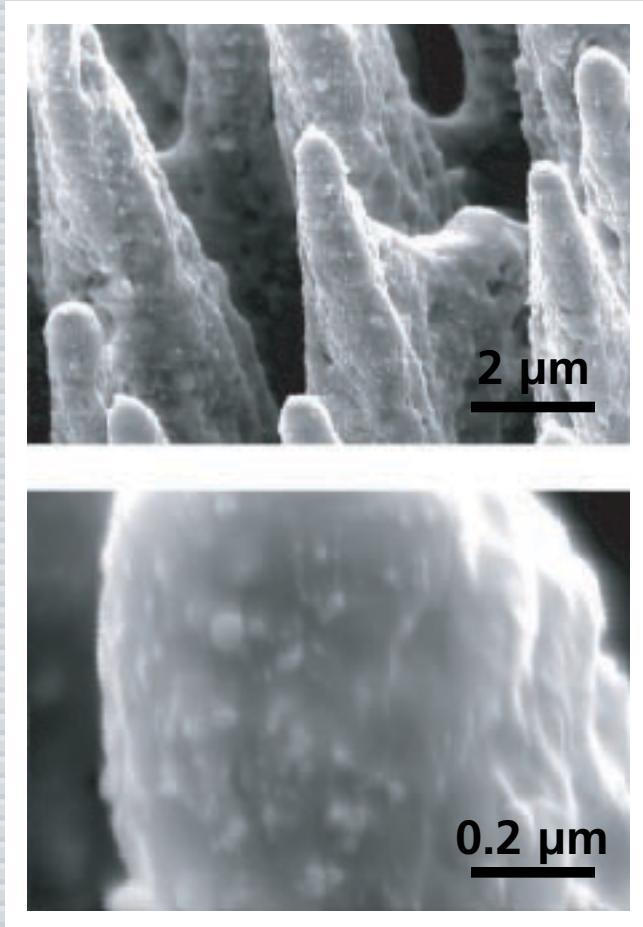
## *Structural and chemical analysis*

anneal 4 hours at 1200 K



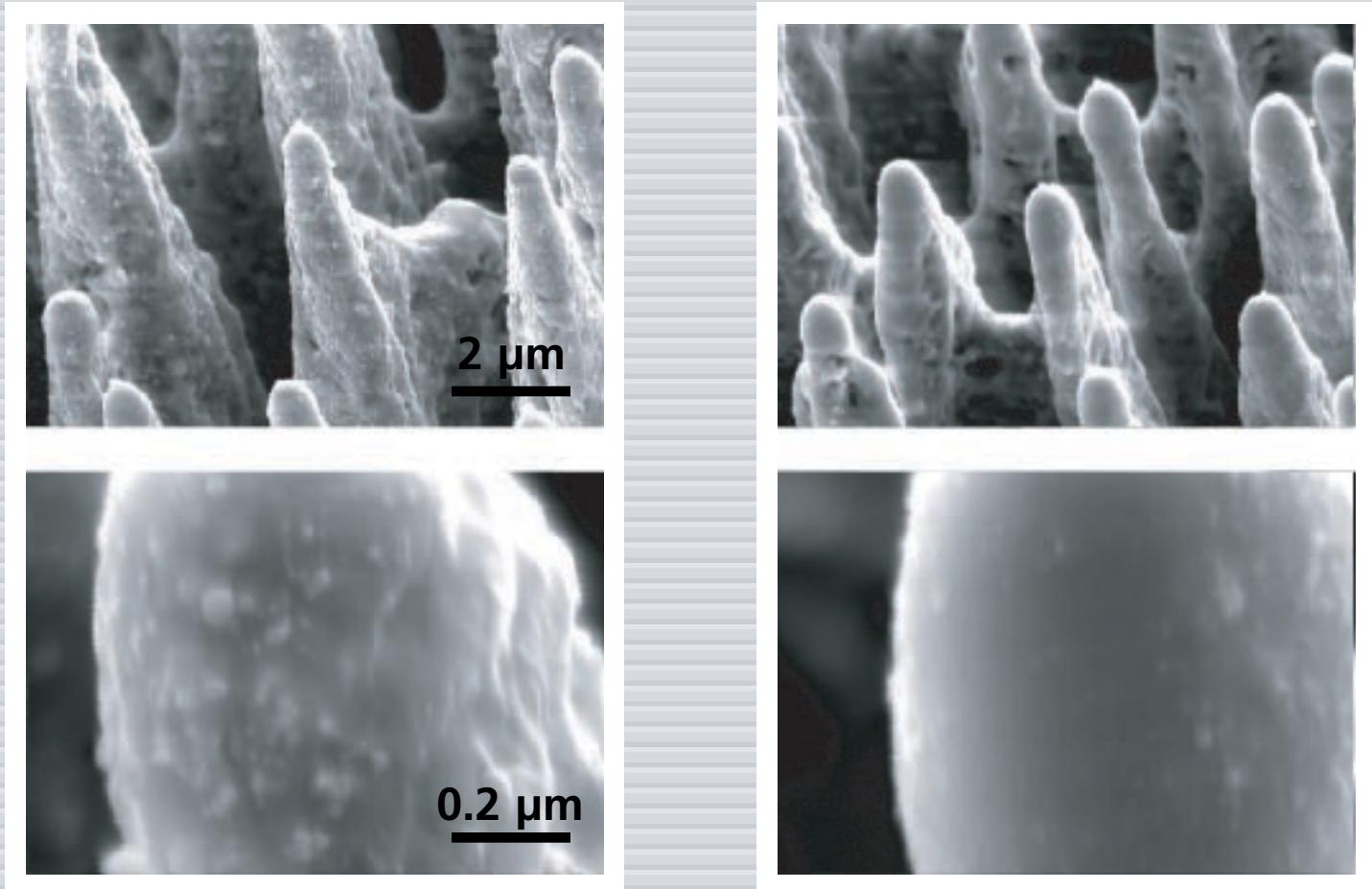
## *Structural and chemical analysis*

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**

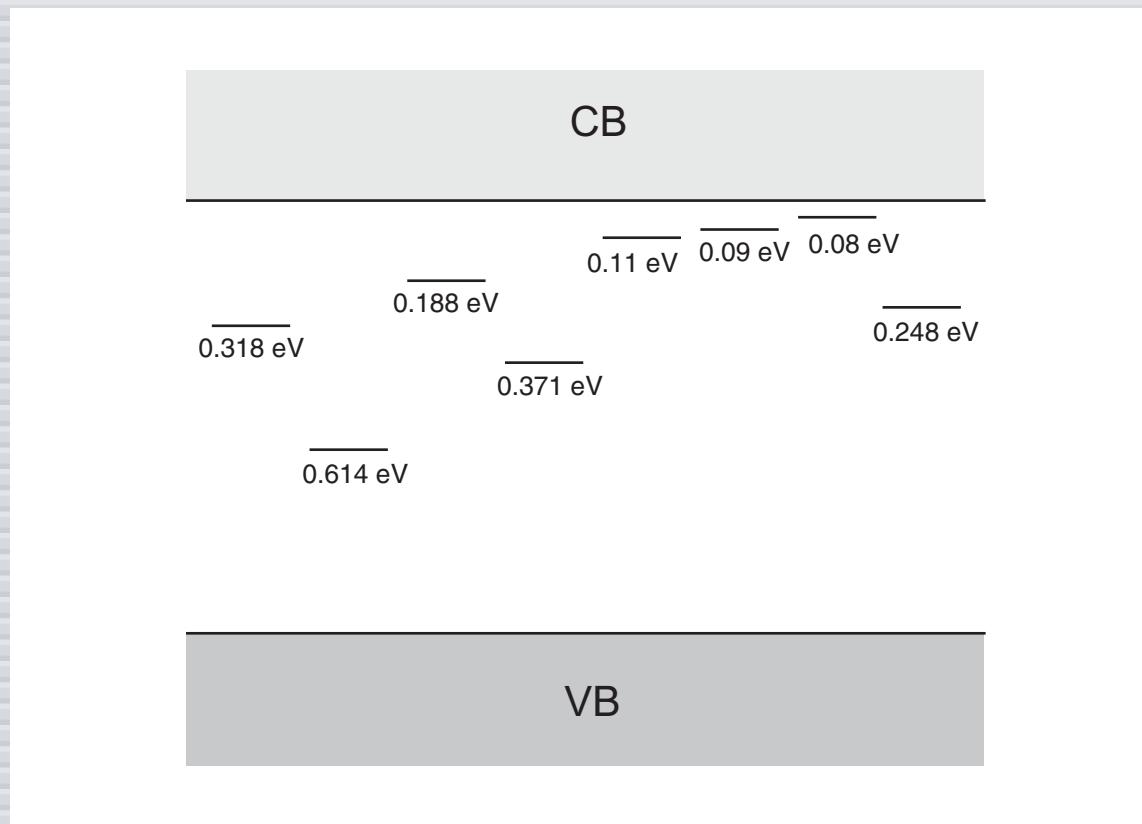
CB

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

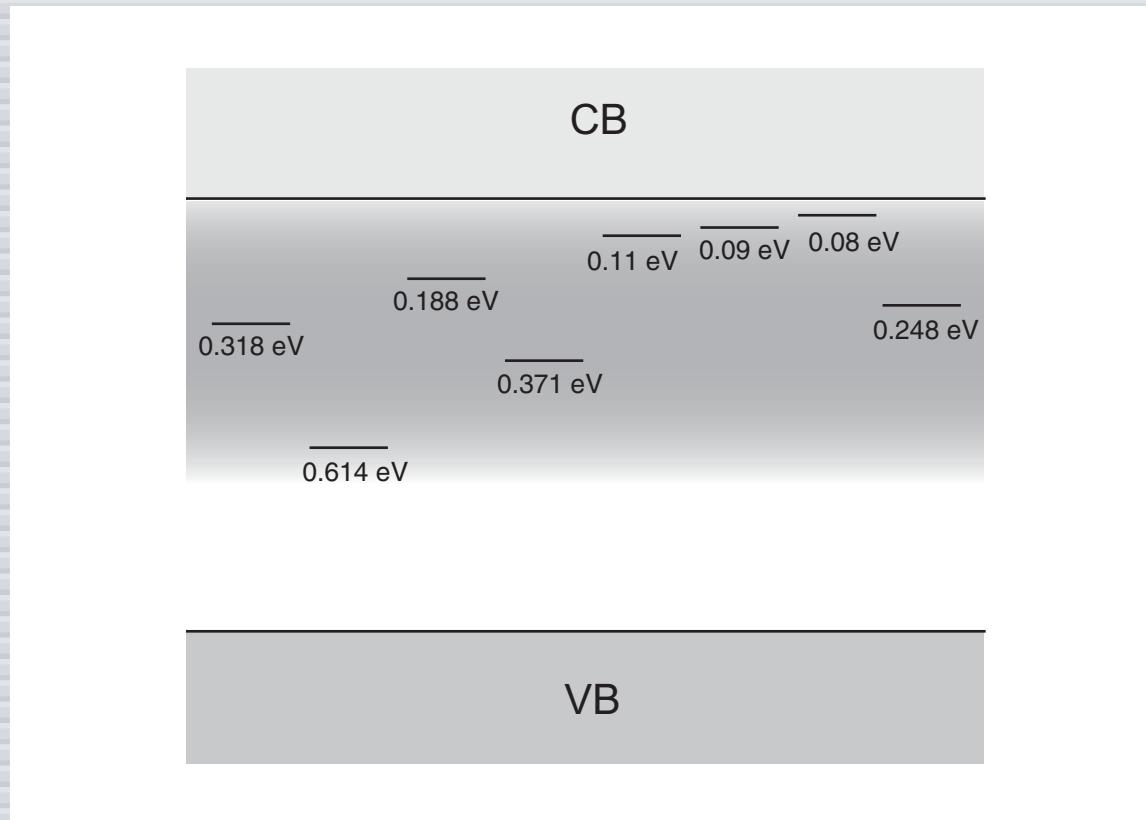
# *Structural and chemical analysis*

**sulfur introduces states in the gap**

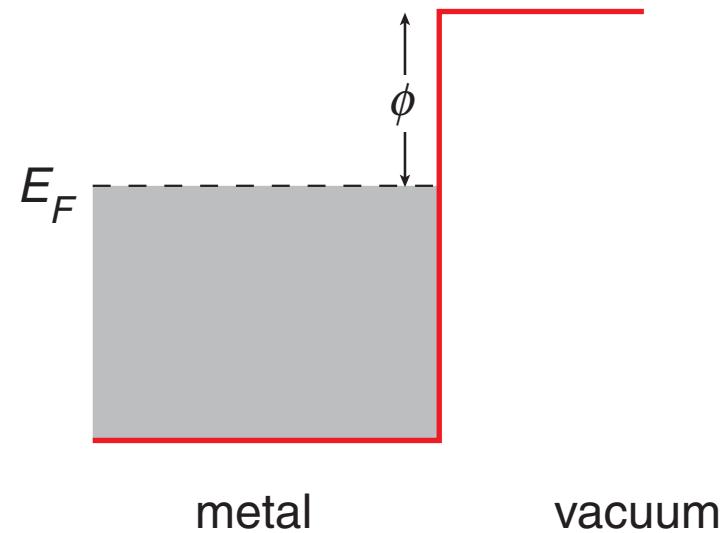


# *Structural and chemical analysis*

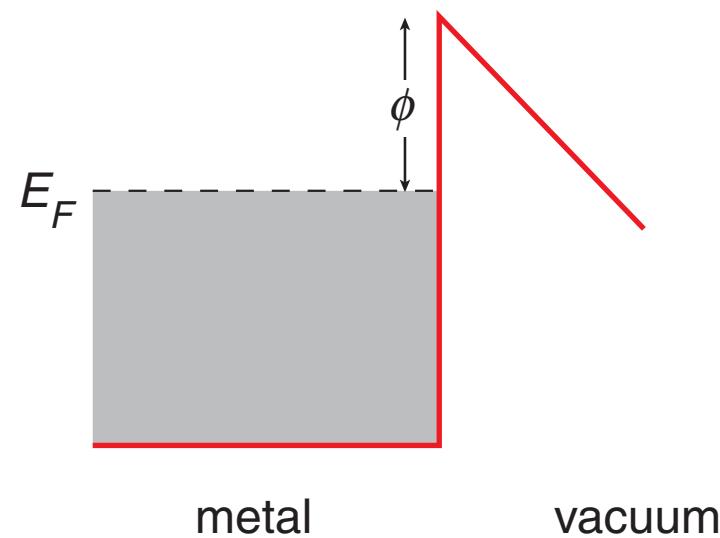
**states broaden into a band**



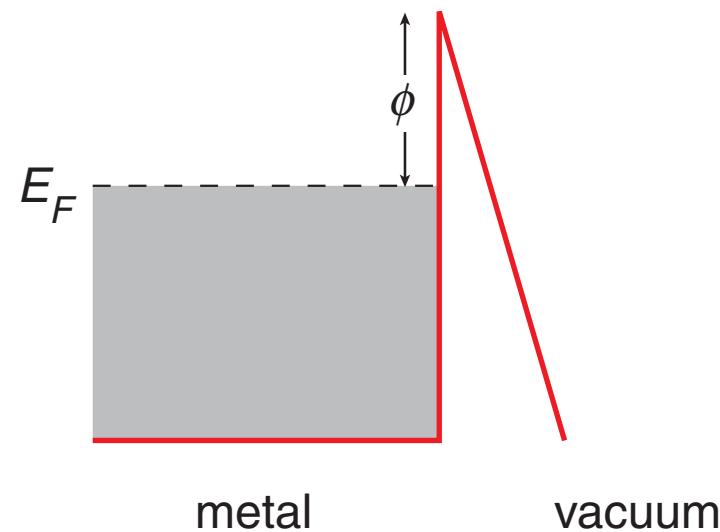
# *Structural and chemical analysis*



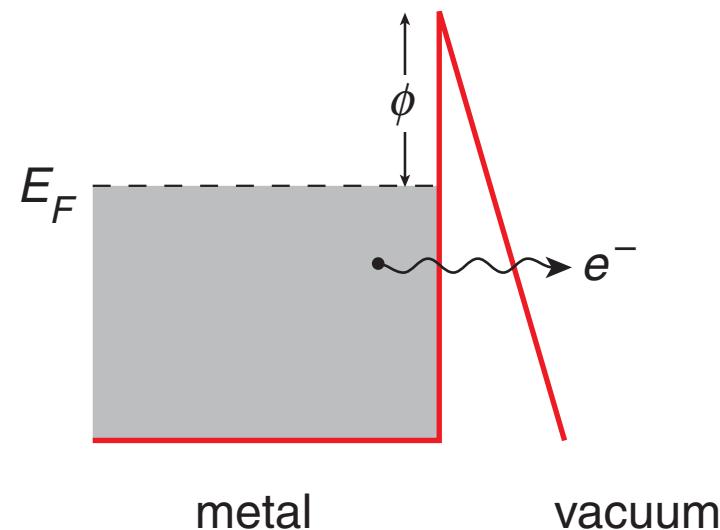
# *Structural and chemical analysis*



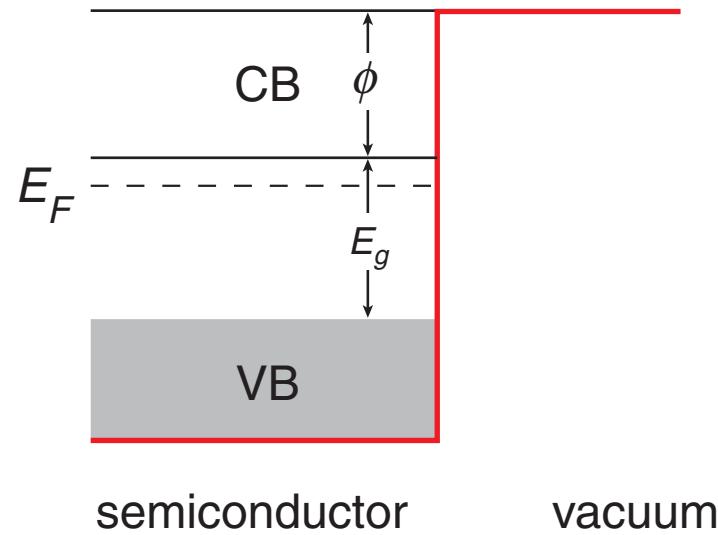
# *Structural and chemical analysis*



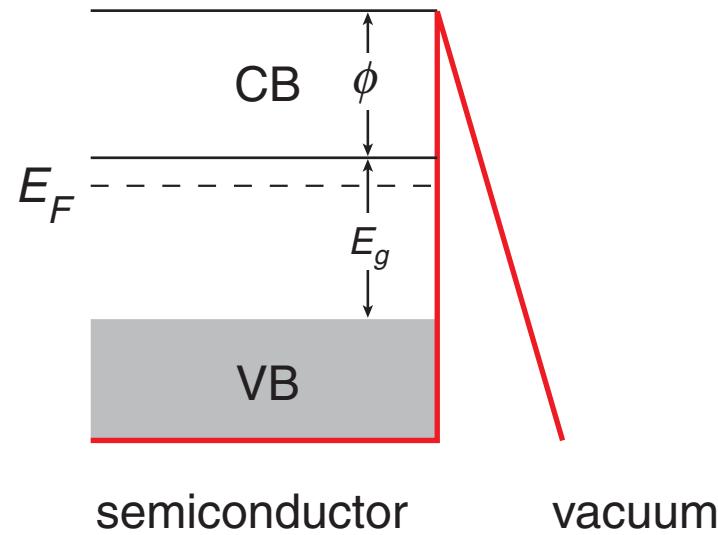
# *Structural and chemical analysis*



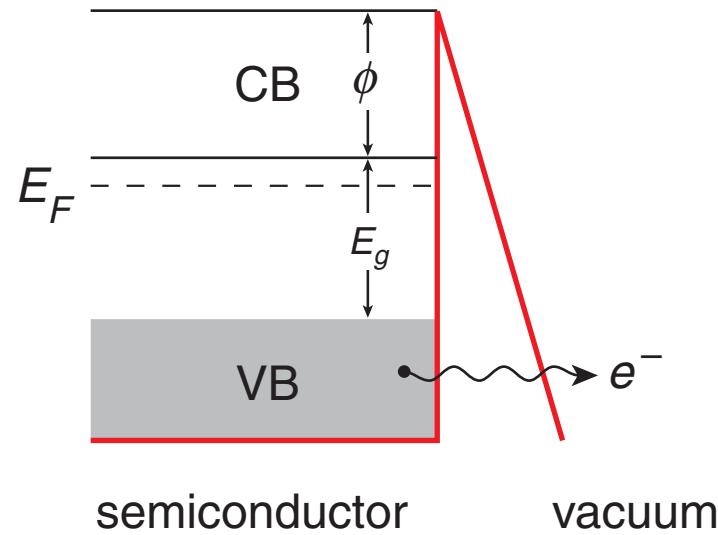
# *Structural and chemical analysis*



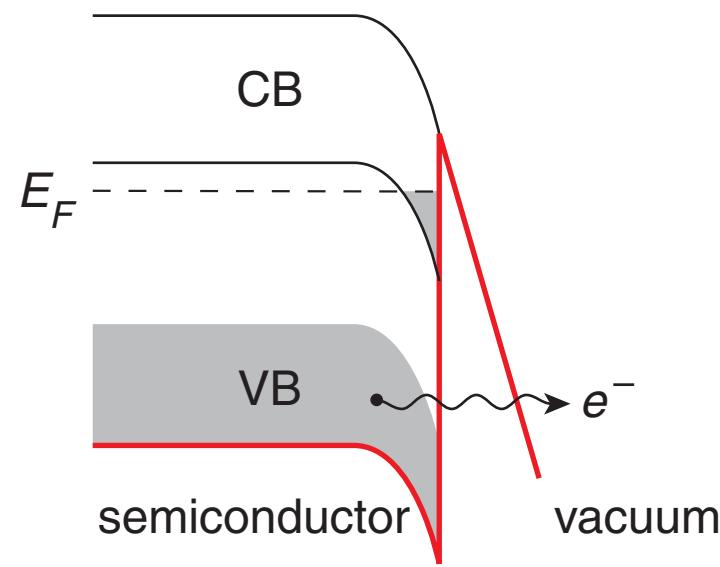
# *Structural and chemical analysis*



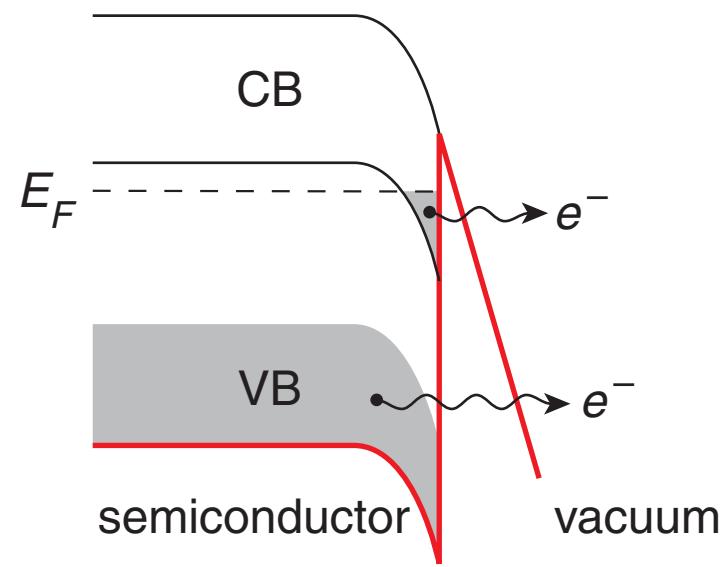
# *Structural and chemical analysis*



# *Structural and chemical analysis*

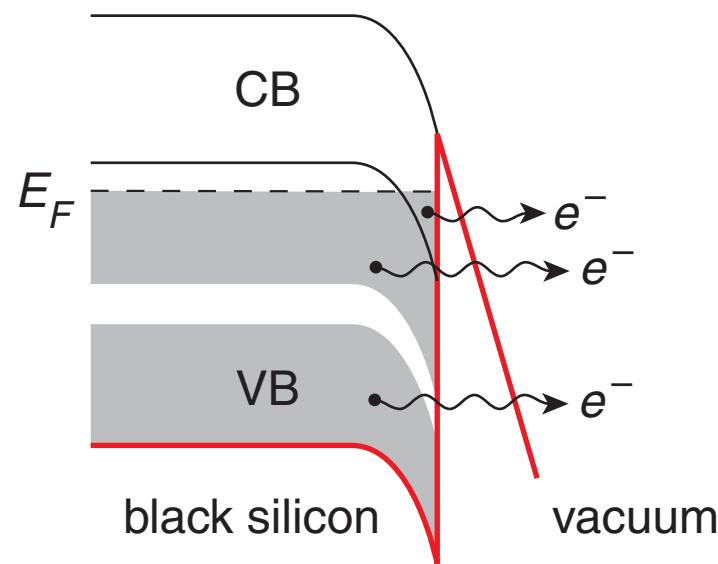


# *Structural and chemical analysis*



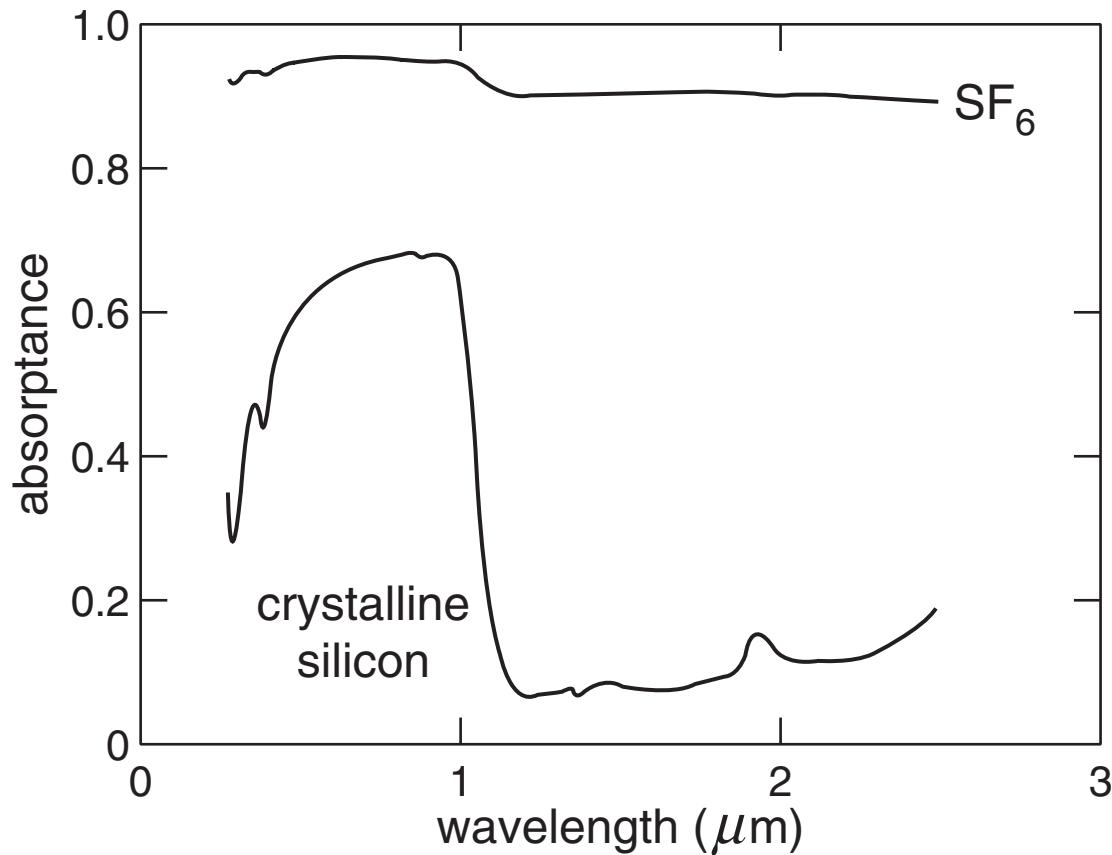
# *Structural and chemical analysis*

**sulfur band provides additional electrons**



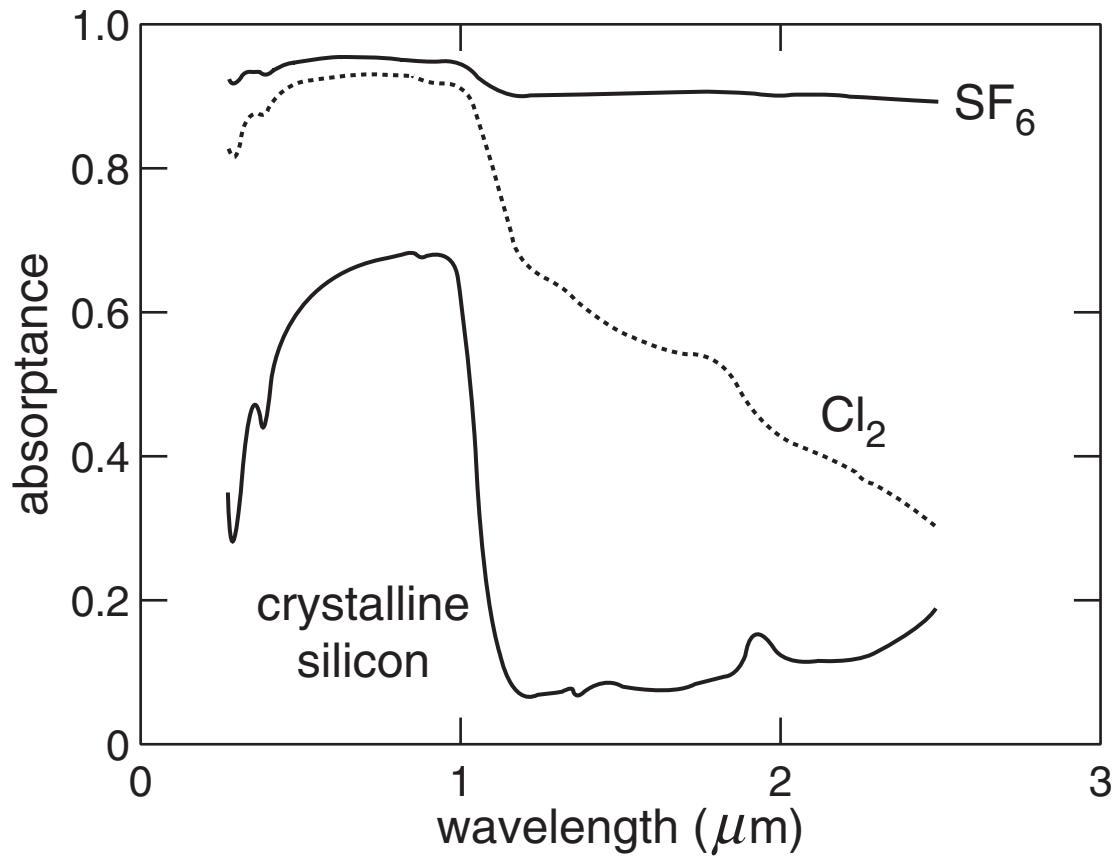
# *Structural and chemical analysis*

## **effect of ambient gas on absorptance**



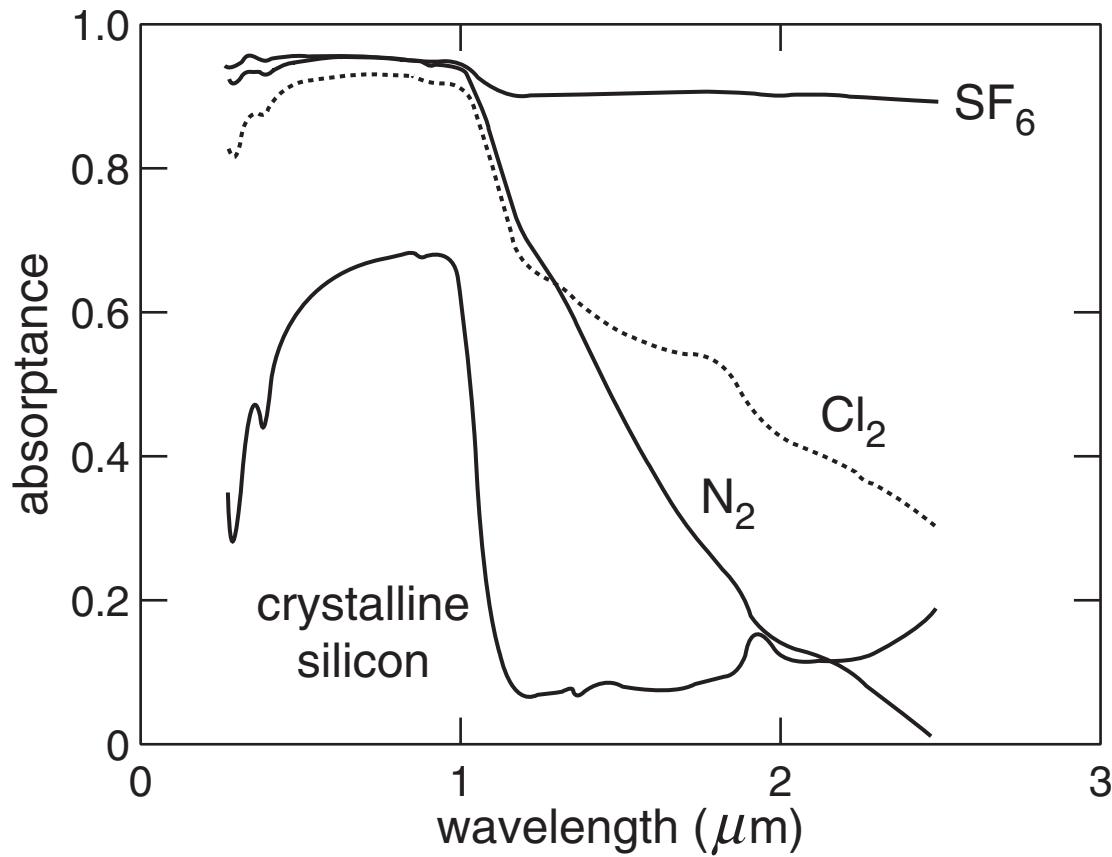
# *Structural and chemical analysis*

## **effect of ambient gas on absorptance**



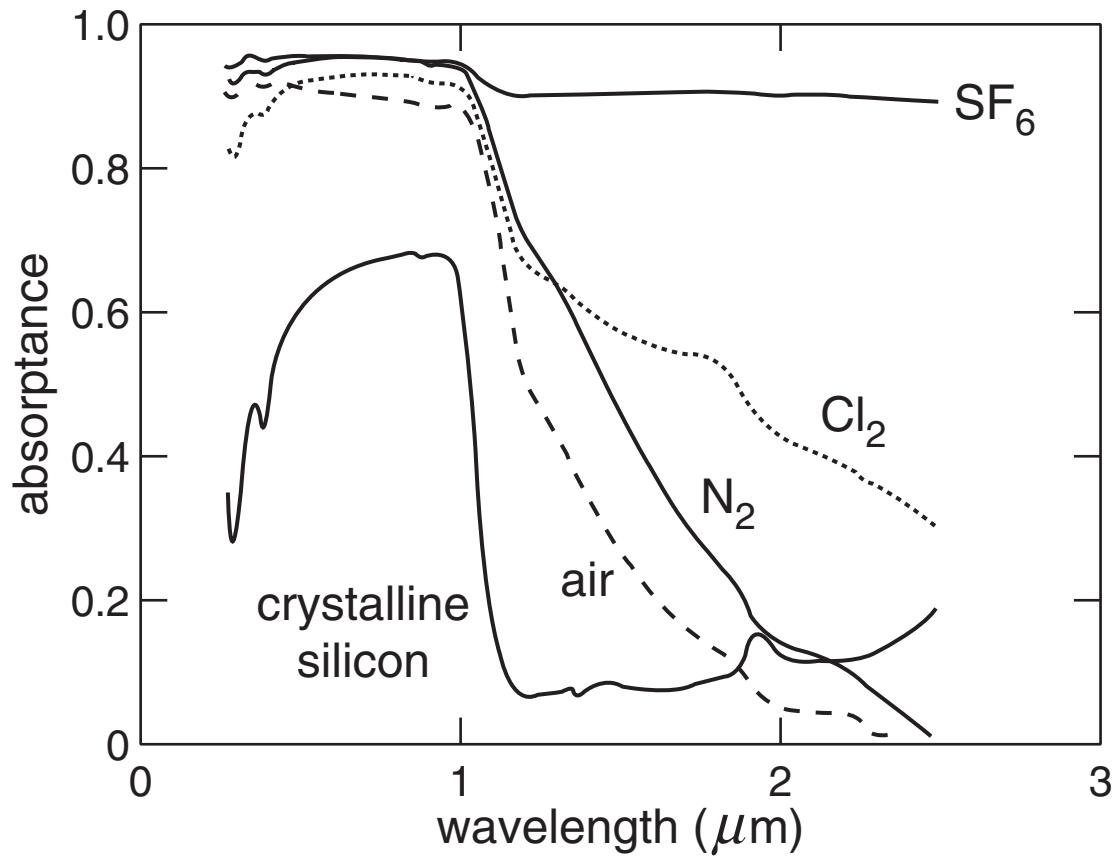
# *Structural and chemical analysis*

## **effect of ambient gas on absorptance**



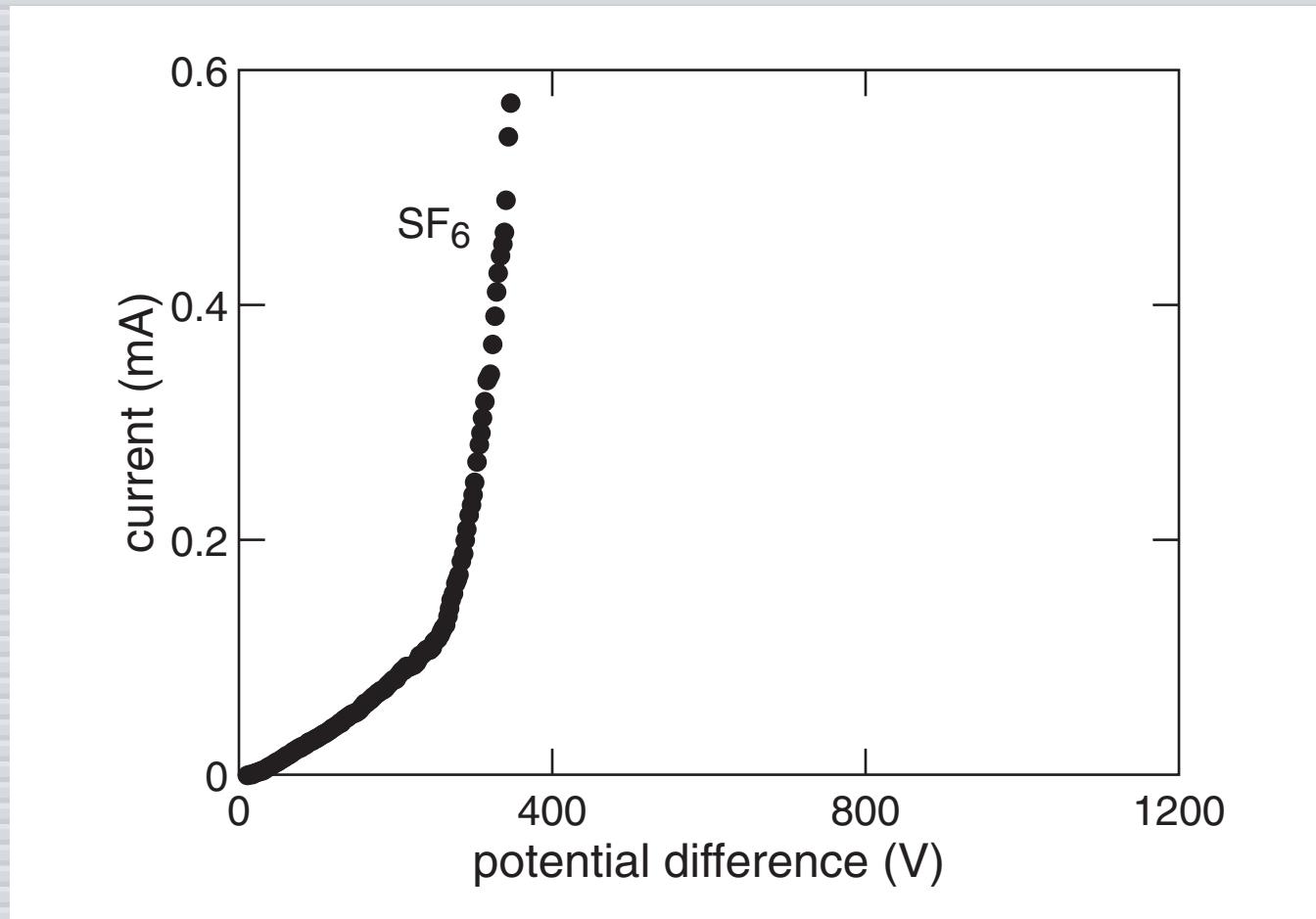
# *Structural and chemical analysis*

## **effect of ambient gas on absorptance**



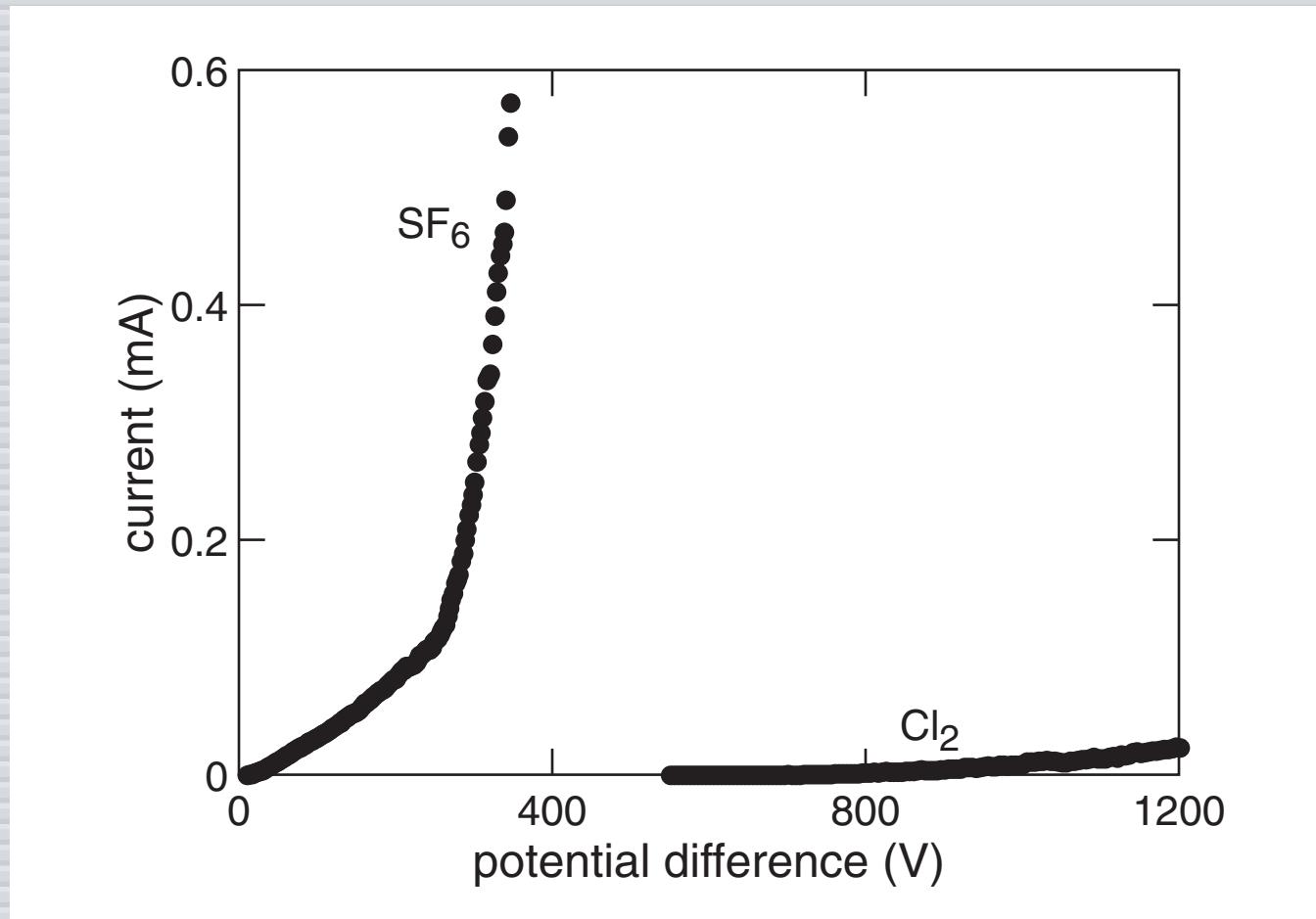
## *Structural and chemical analysis*

### **effect of ambient gas on field emission**



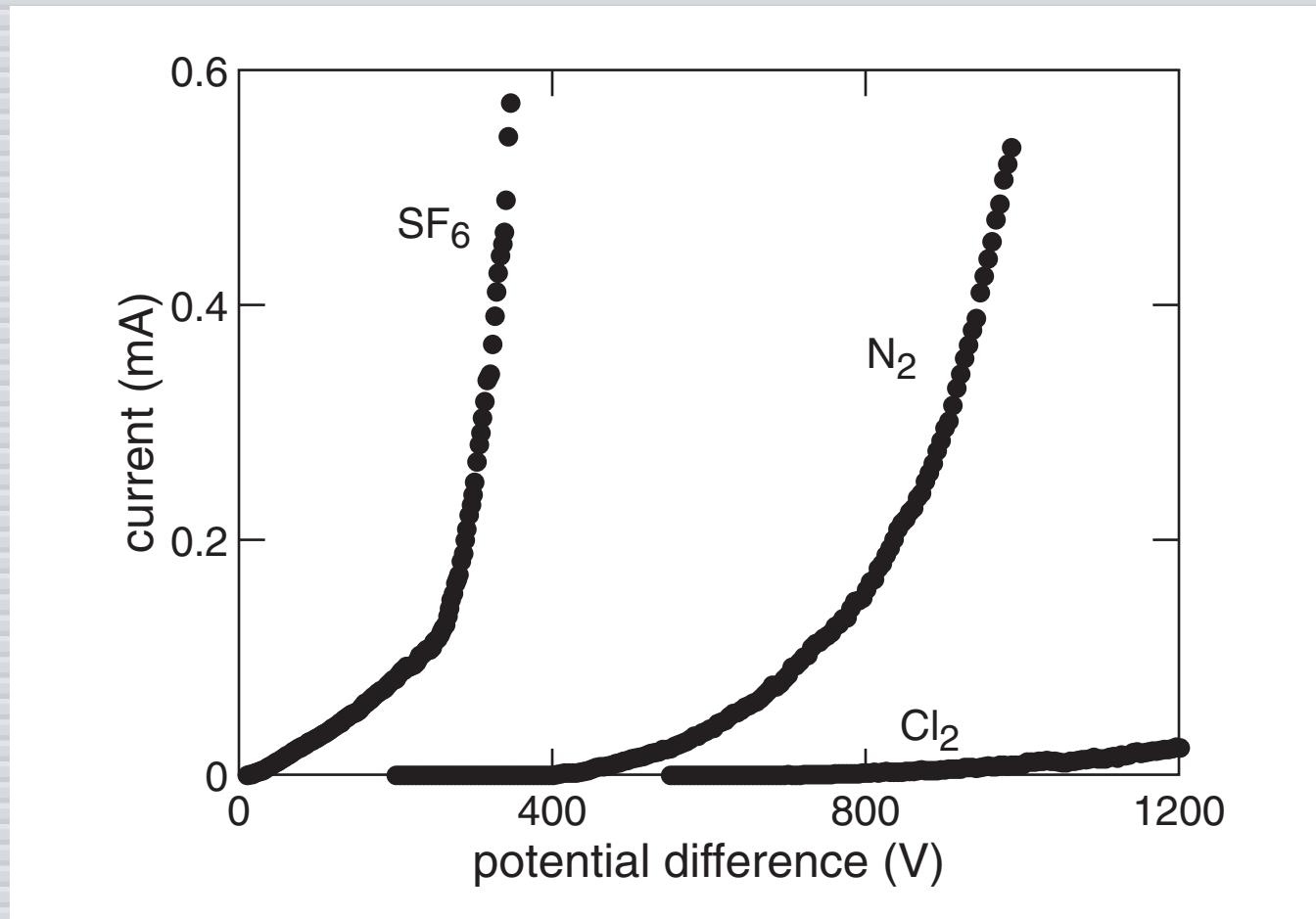
## *Structural and chemical analysis*

### **effect of ambient gas on field emission**



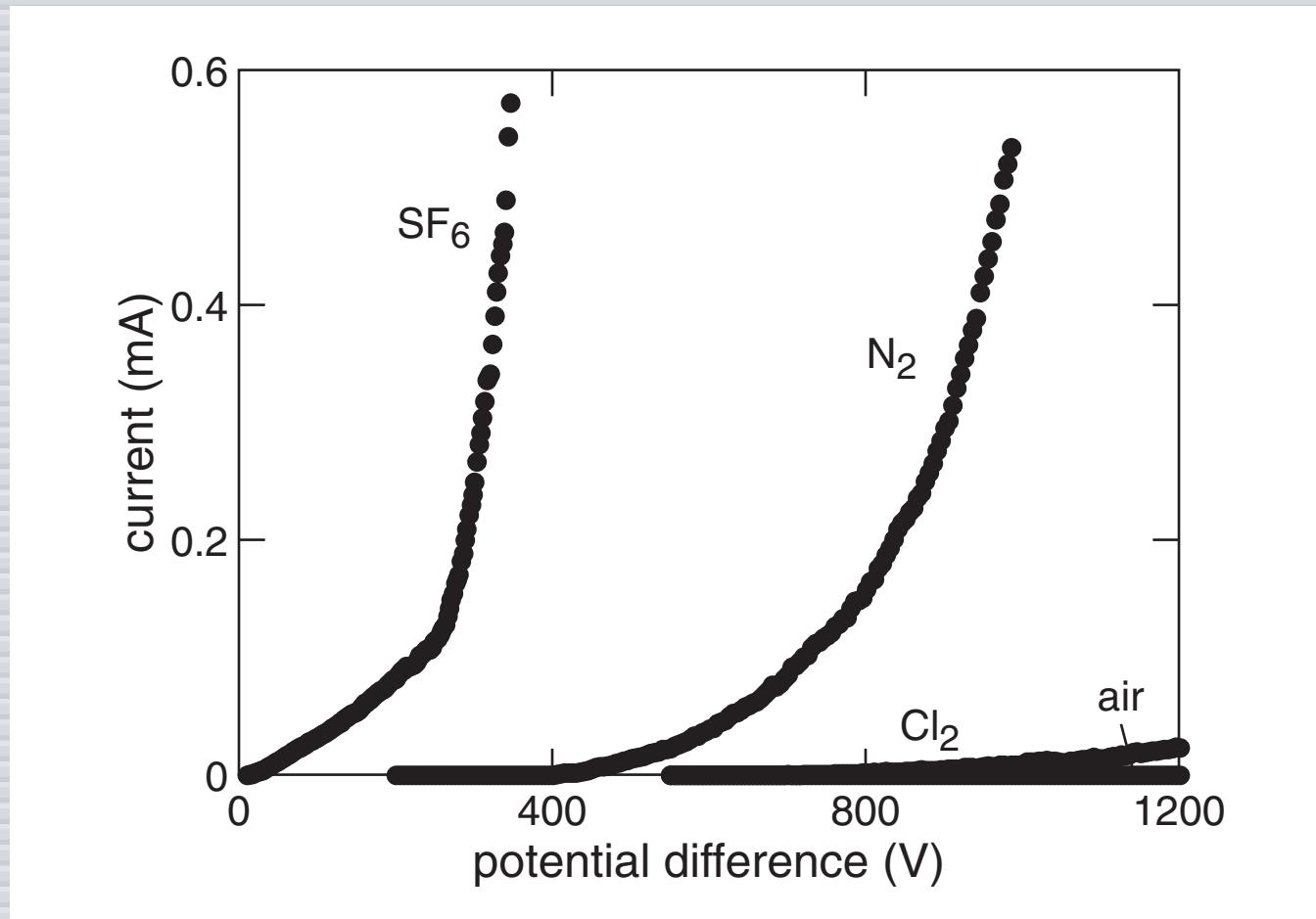
# *Structural and chemical analysis*

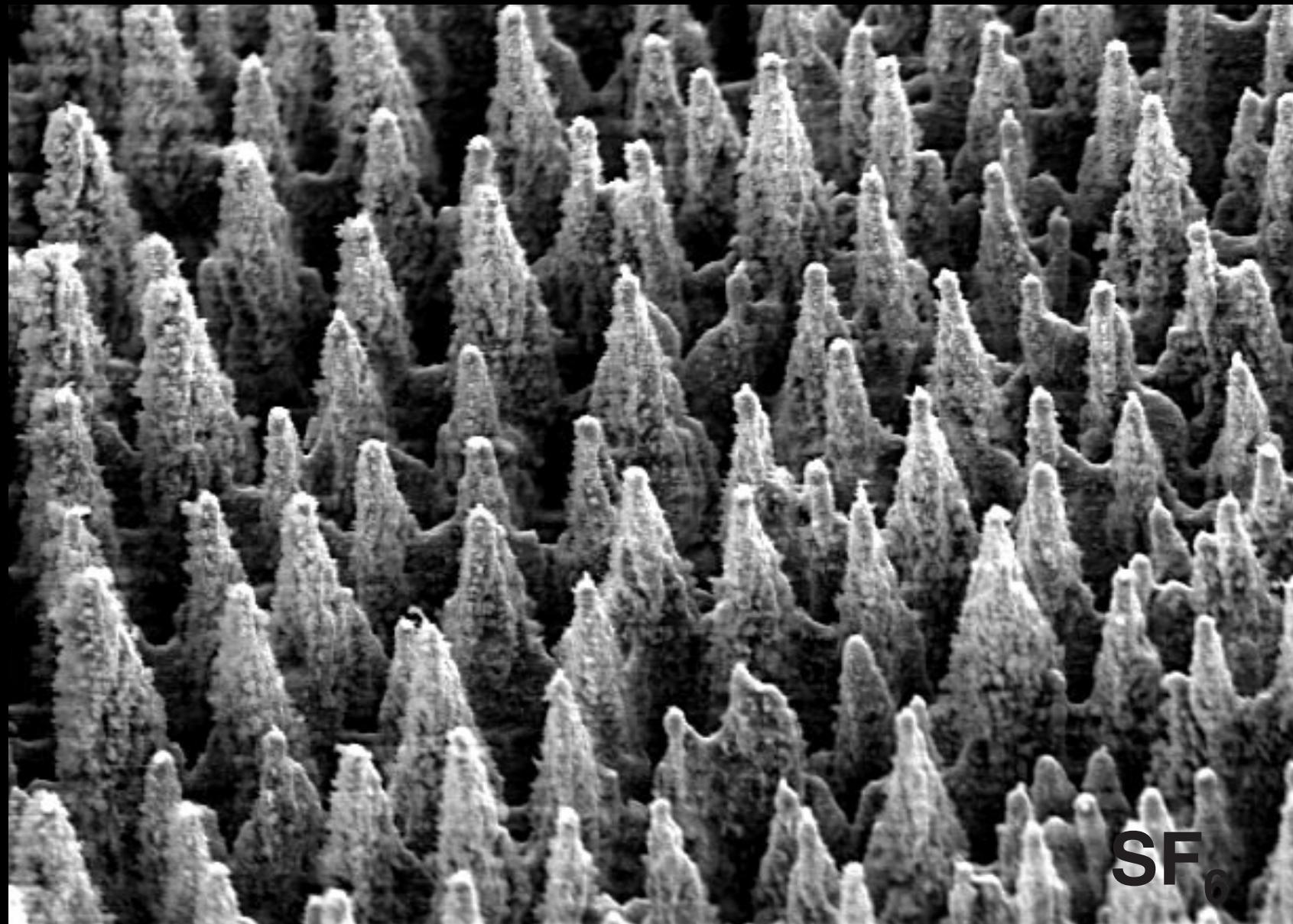
## effect of ambient gas on field emission



# *Structural and chemical analysis*

## effect of ambient gas on field emission



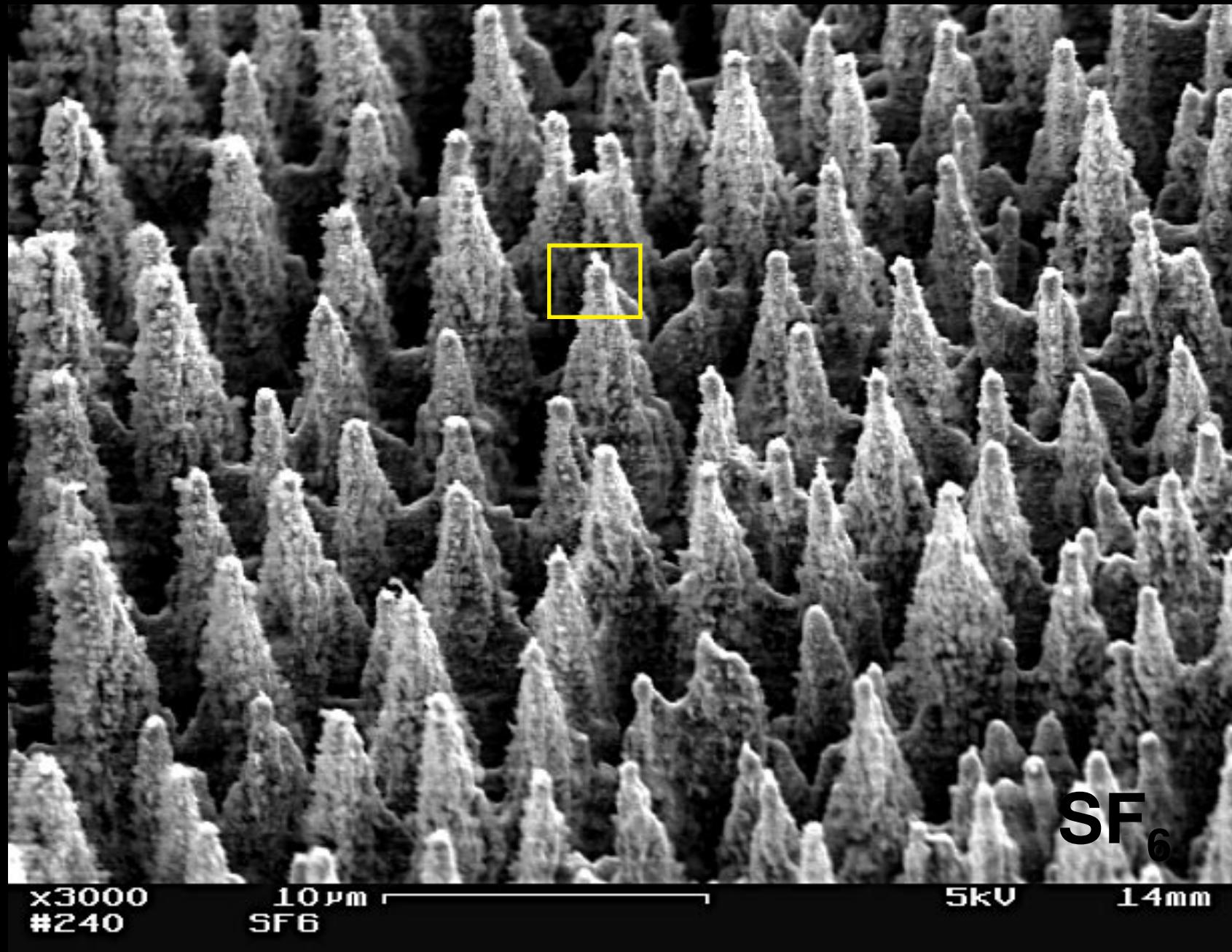


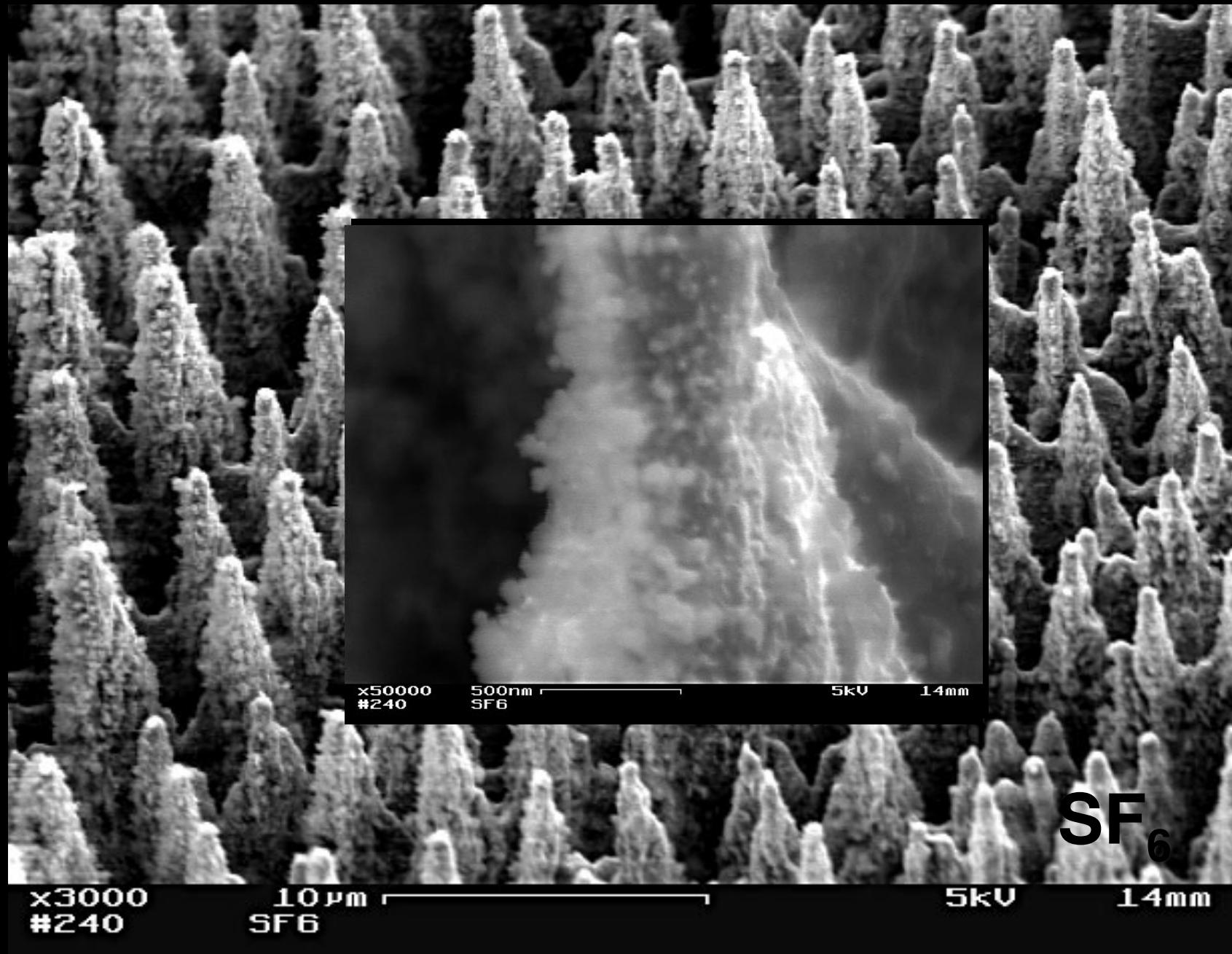
x3000  
#240

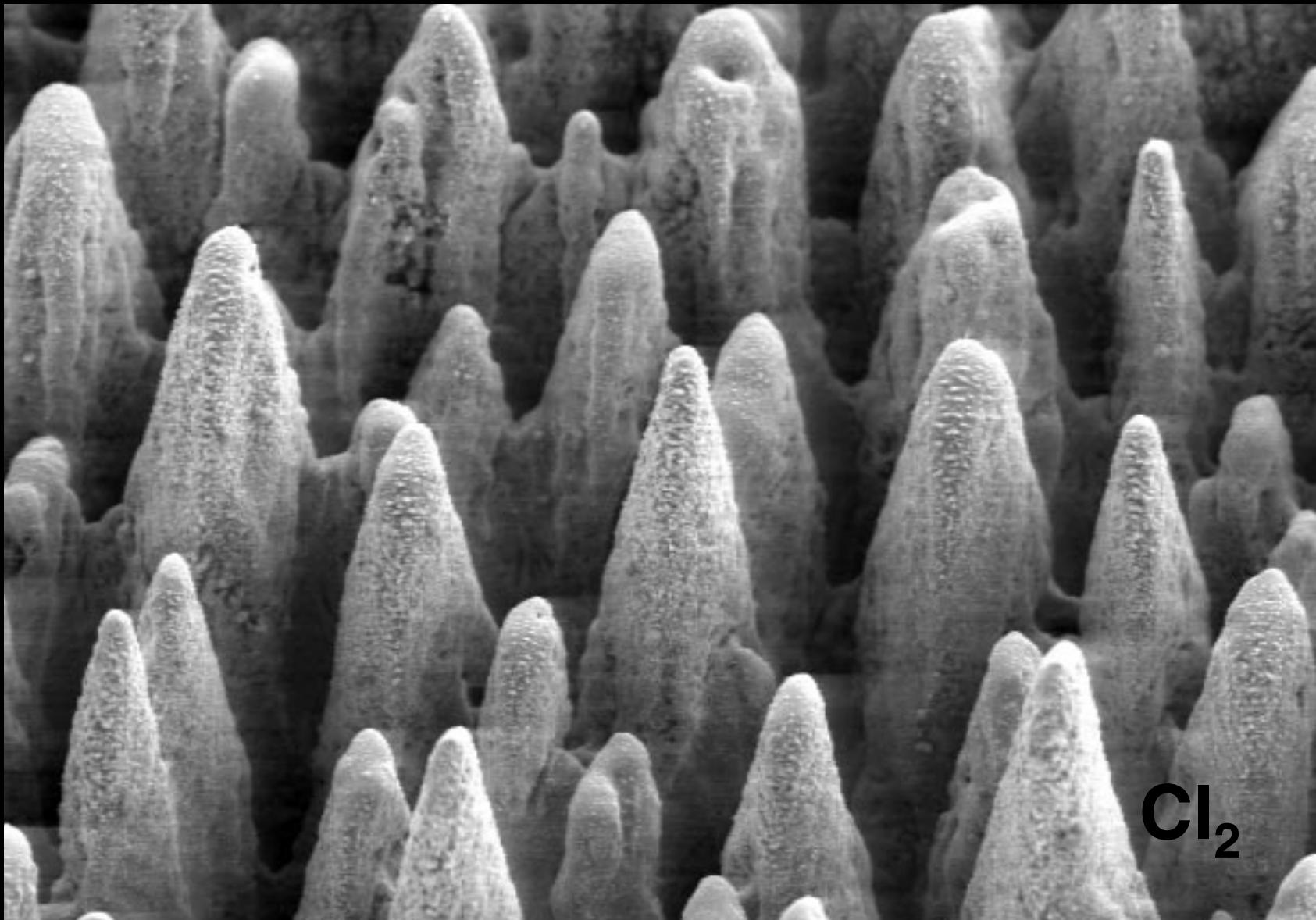
10  $\mu\text{m}$   
SF6

5kV      14mm

SF<sub>6</sub>







**Cl<sub>2</sub>**

x3000

#34

512 x 480

10 μm

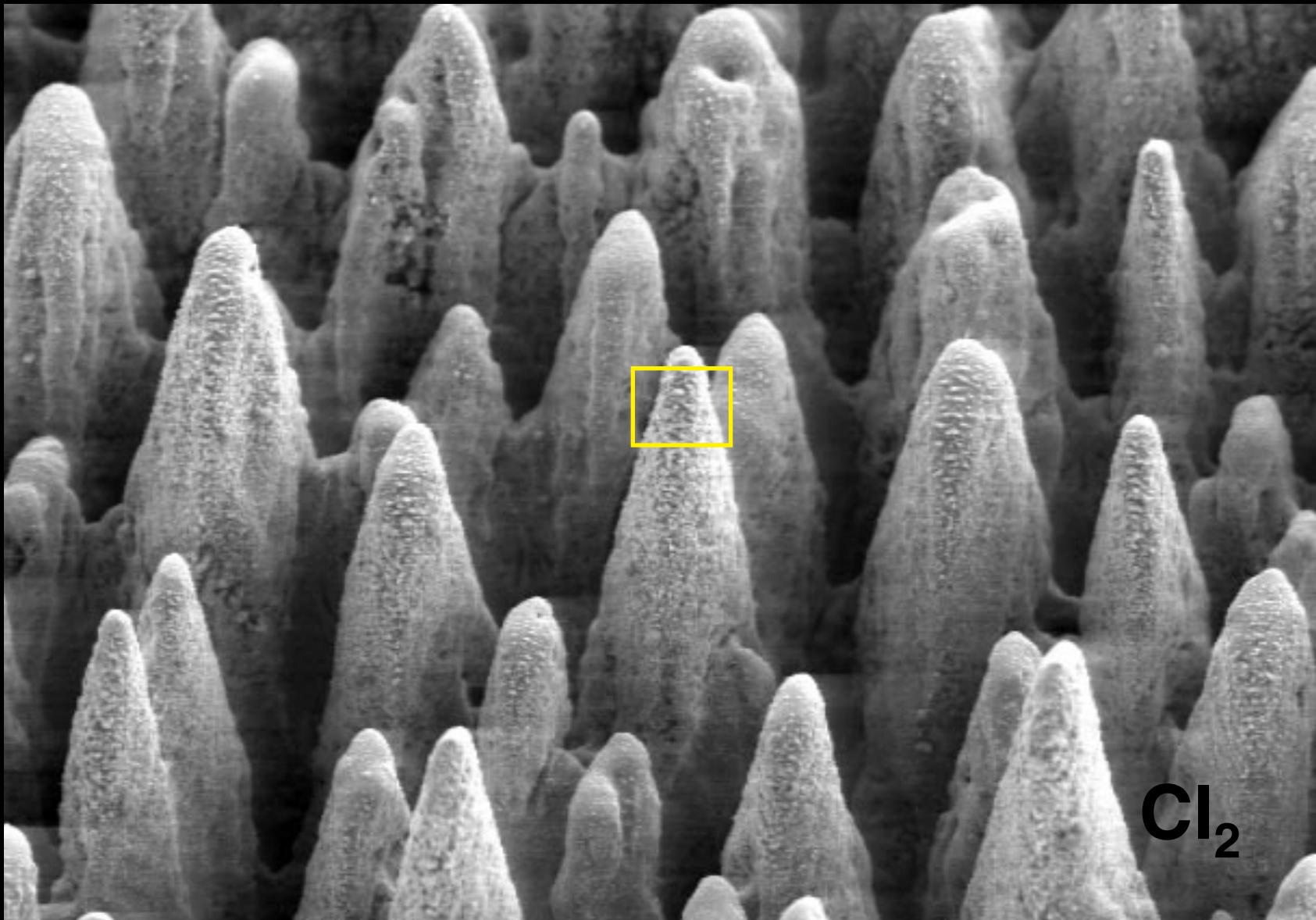
10/18 Cl2 #3

4.00kV

11/6/00

CL2#3-1.TIF

12mm

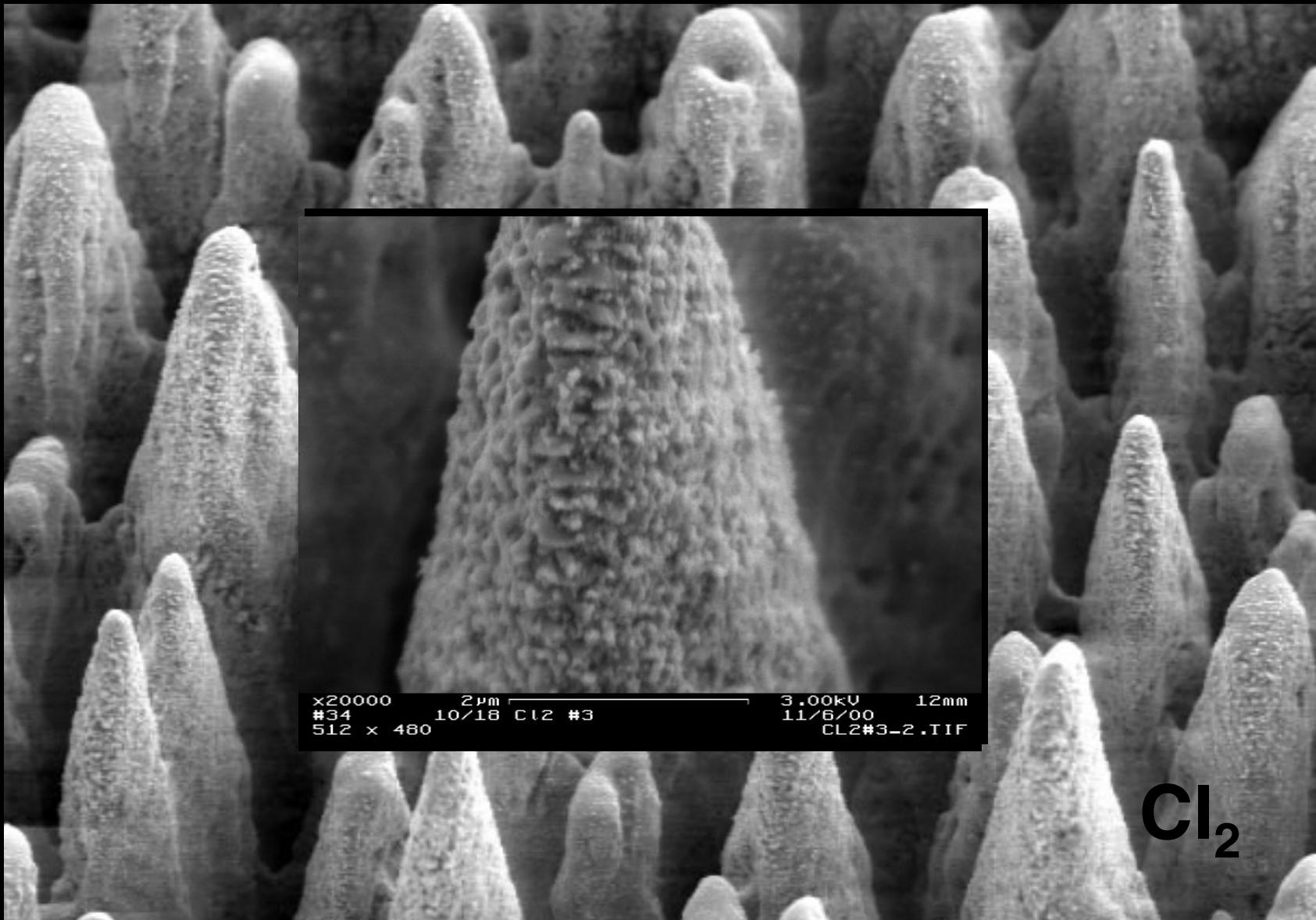


x3000  
#34  
512 x 480

10µm  
10/18 Cl2 #3

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

Cl<sub>2</sub>



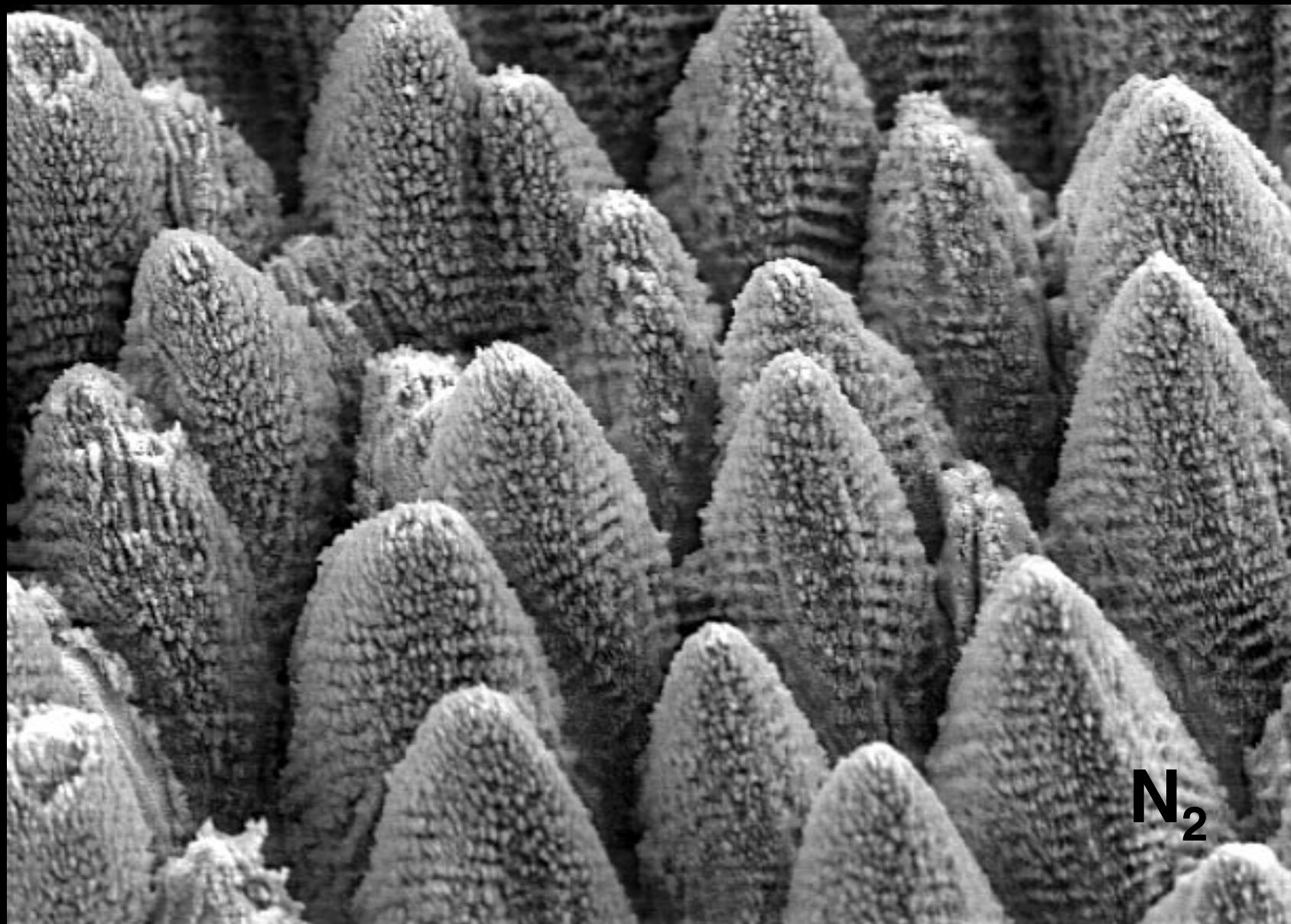
x20000 2 $\mu$ m  
#34 10/18 Cl2 #3  
512 x 480

3.00kV 12mm  
11/6/00 CL2#3-2.TIF

x3000 10 $\mu$ m  
#34 10/18 Cl2 #3  
512 x 480

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

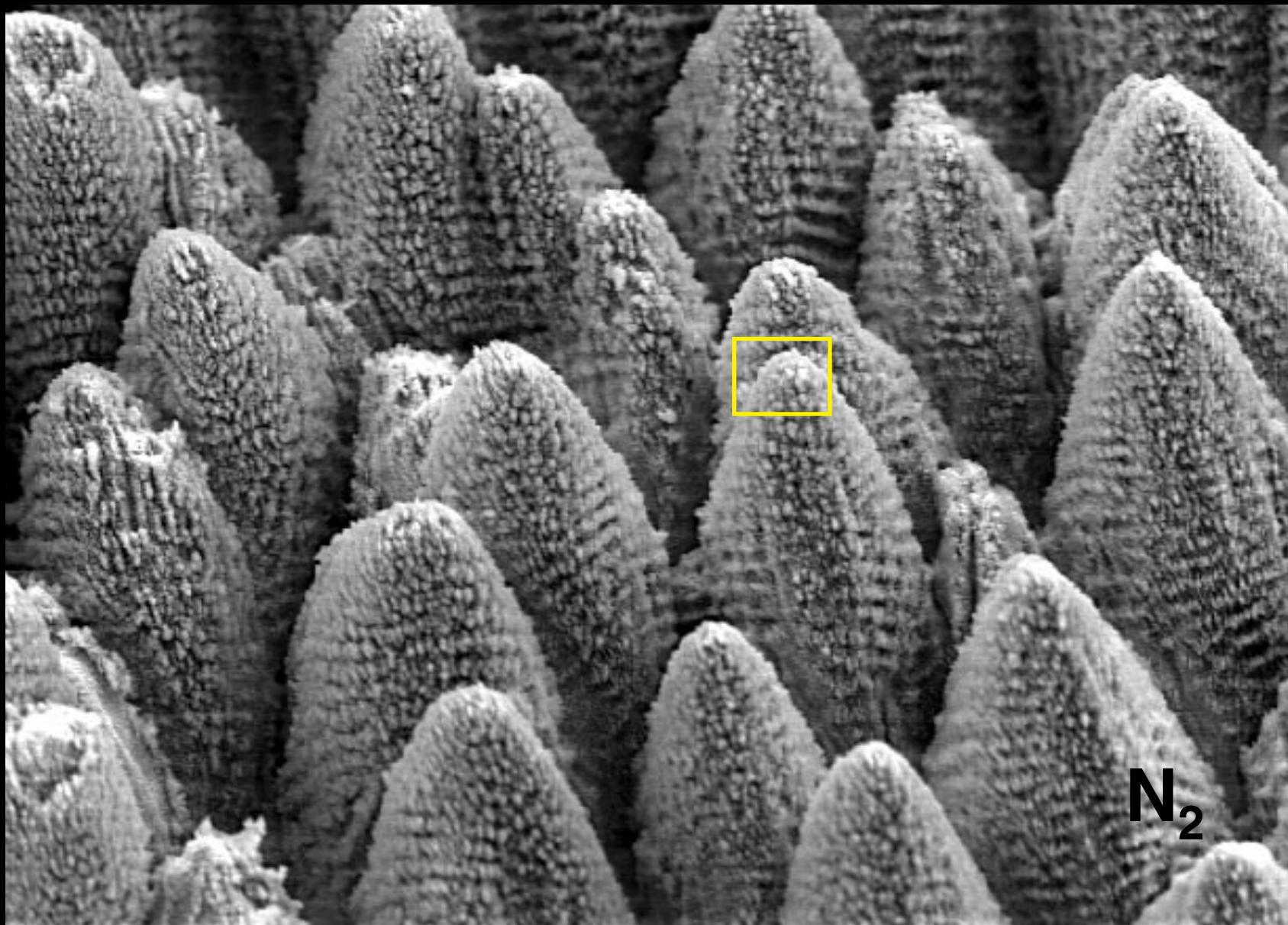
Cl<sub>2</sub>



x3000  
#240

10  $\mu\text{m}$  N<sub>2</sub>

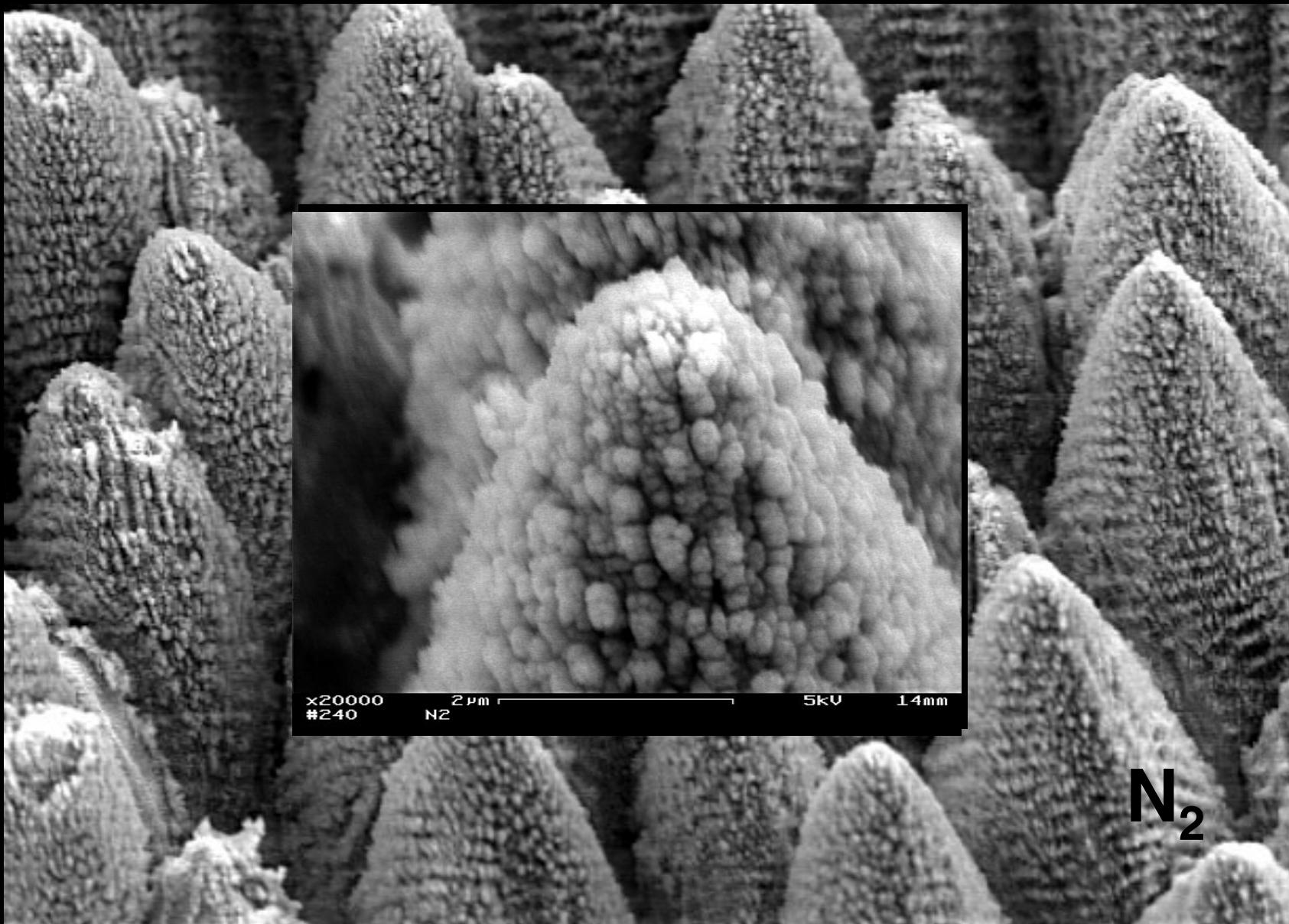
5kV 14mm



x3000  
#240

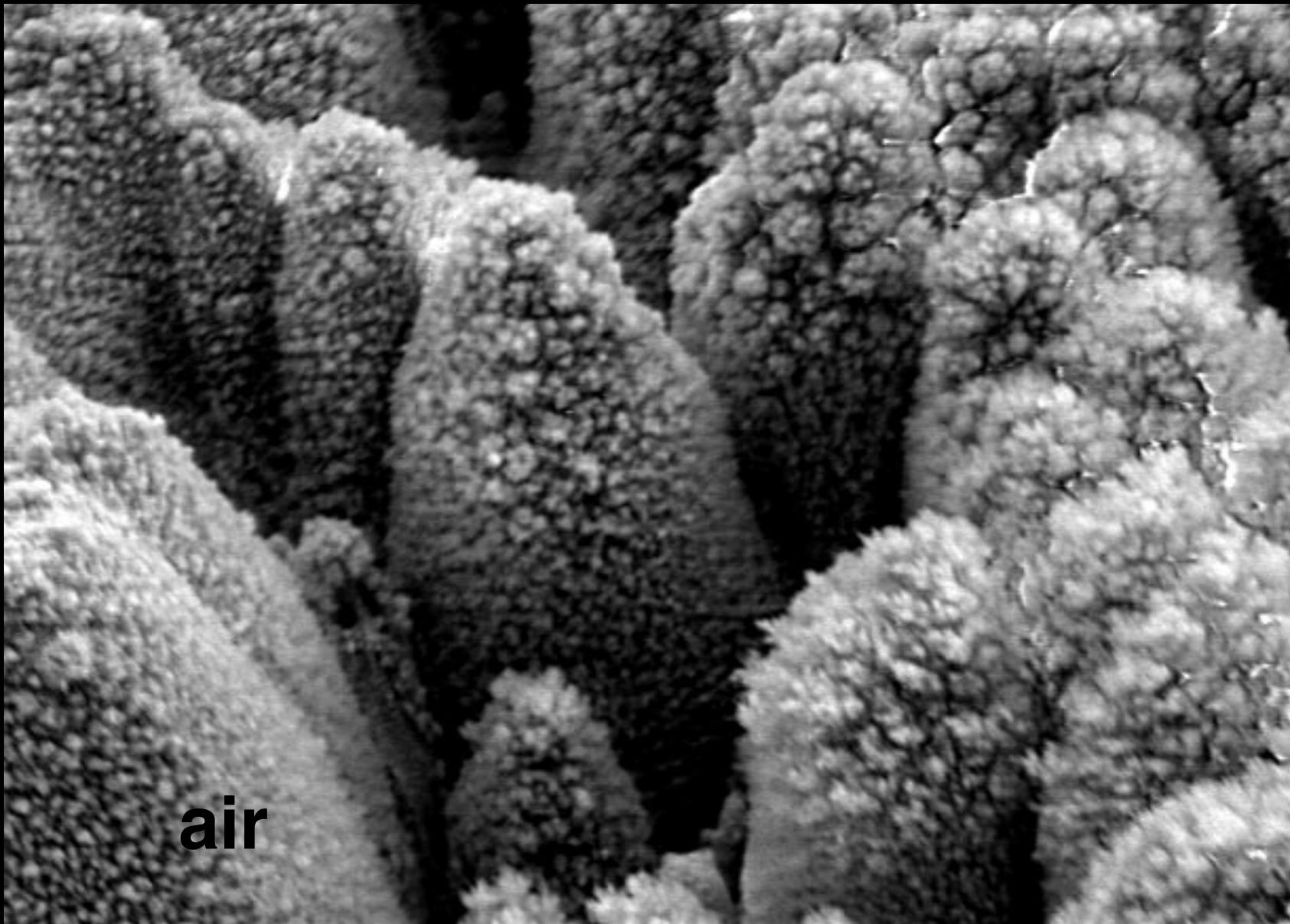
10 μm  
N2

5kV 14mm



x3000      10  $\mu$ m      5kV      14mm  
#240      N2

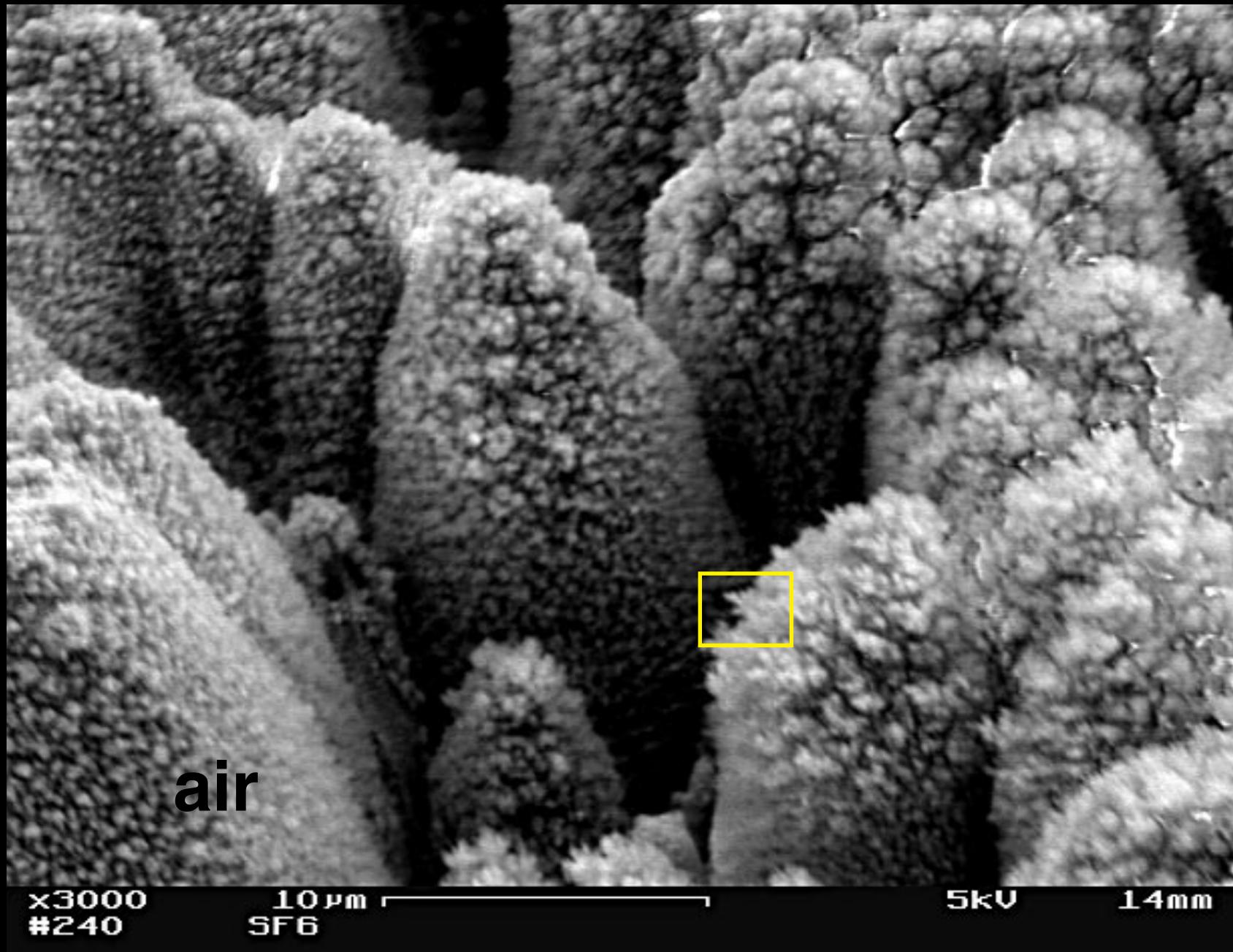
N<sub>2</sub>



x3000  
#240

10  $\mu\text{m}$   
SF6

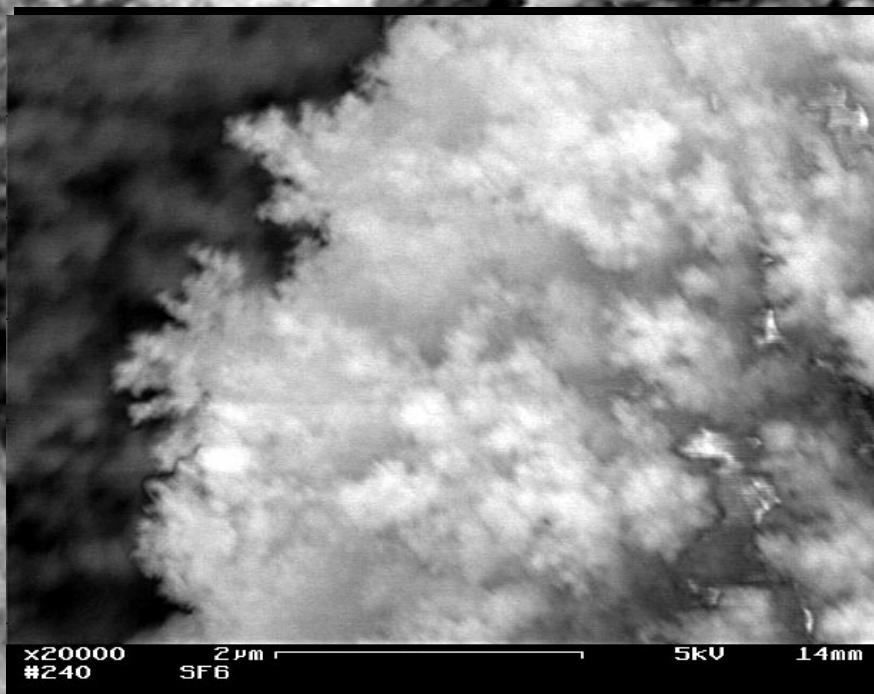
5kV      14mm



x3000  
#240

10  $\mu\text{m}$   
SF6

5kV      14mm



air

x3000  
#240

10 μm  
SF6

5kV 14mm

## *Structural and chemical analysis*

---

	$\text{SF}_6$	$\text{Cl}_2$	$\text{N}_2$	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 could lead to a major discovery. 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

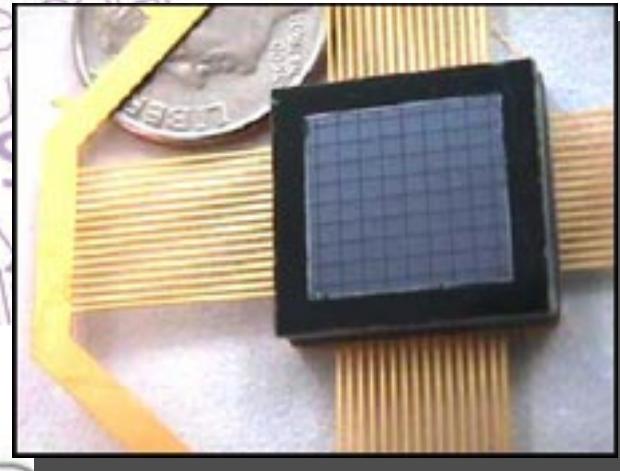
of times brighter than the Sun and extremely short laser pulse will break down around the laboratory," he claims.

Well, it was almost the only reason 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 SF<sub>6</sub> would decompose in 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 weirdality. They come back to us again when a design comes along that's a little bit different. This is when

semiconductors with a powerful base to the early days. Mazzatorta's was the first academic lab in the world to do

hard iron a temperature and threshold-controlled pulsed light that can measure

times 10 faster than the sun

around the "strangeness". But James Park, director of the University of Illinois' Institute for Advanced Materials and Devices, says that the device will attack a specific challenge. He adds:

"Boron is added to the silicon which

quenches the Si around

and then the silicon would

the silicon. Mazzatorta

# *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 again when a legend of a life-time dies.

semiconductors with a powerful base. In the early 1990s, Mizrahi's was the first academic lab in the world to grow the hardest carbon nanotubes ever. This device can withstand temperatures of 1,000 degrees Celsius. It is 20 times harder than the sun's corona and extremely

around the "carbonium". He claims Park's claim to a record breaking material is not true. "There is no such thing as that and there are no such things as will attack a specific carbonate," he said. Mizrahi is fond of such clichés as "black diamonds" because Si is usually white and then the silicon "should be black

# *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

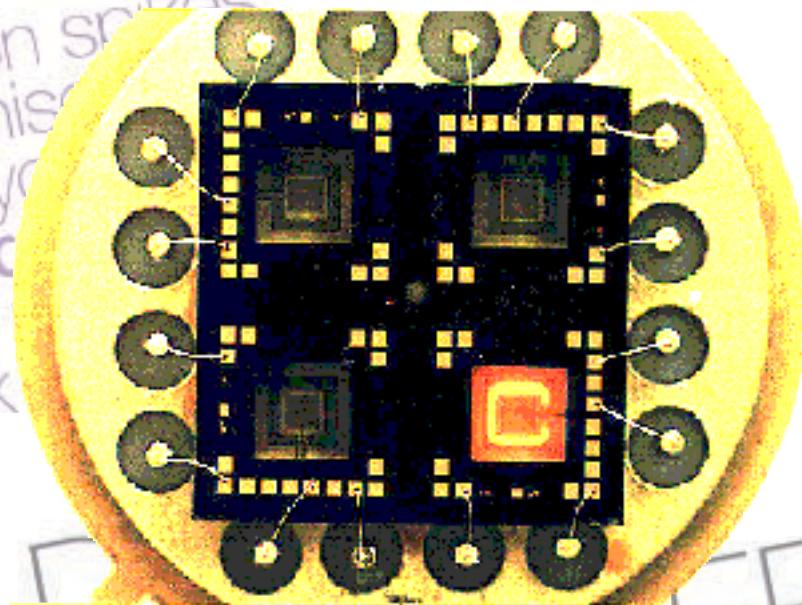
semiconductors with a powerful base to around the "unconscious" becomes a Park. It's not a word the only reason that I can't believe those words back to me. I'm not a scientist, but I do know that and there are no aliens who will attack a species called "Homo Sapiens" as they are too much like us. And I think that it's quite likely that the S. would do the same thing when they found out that



# *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

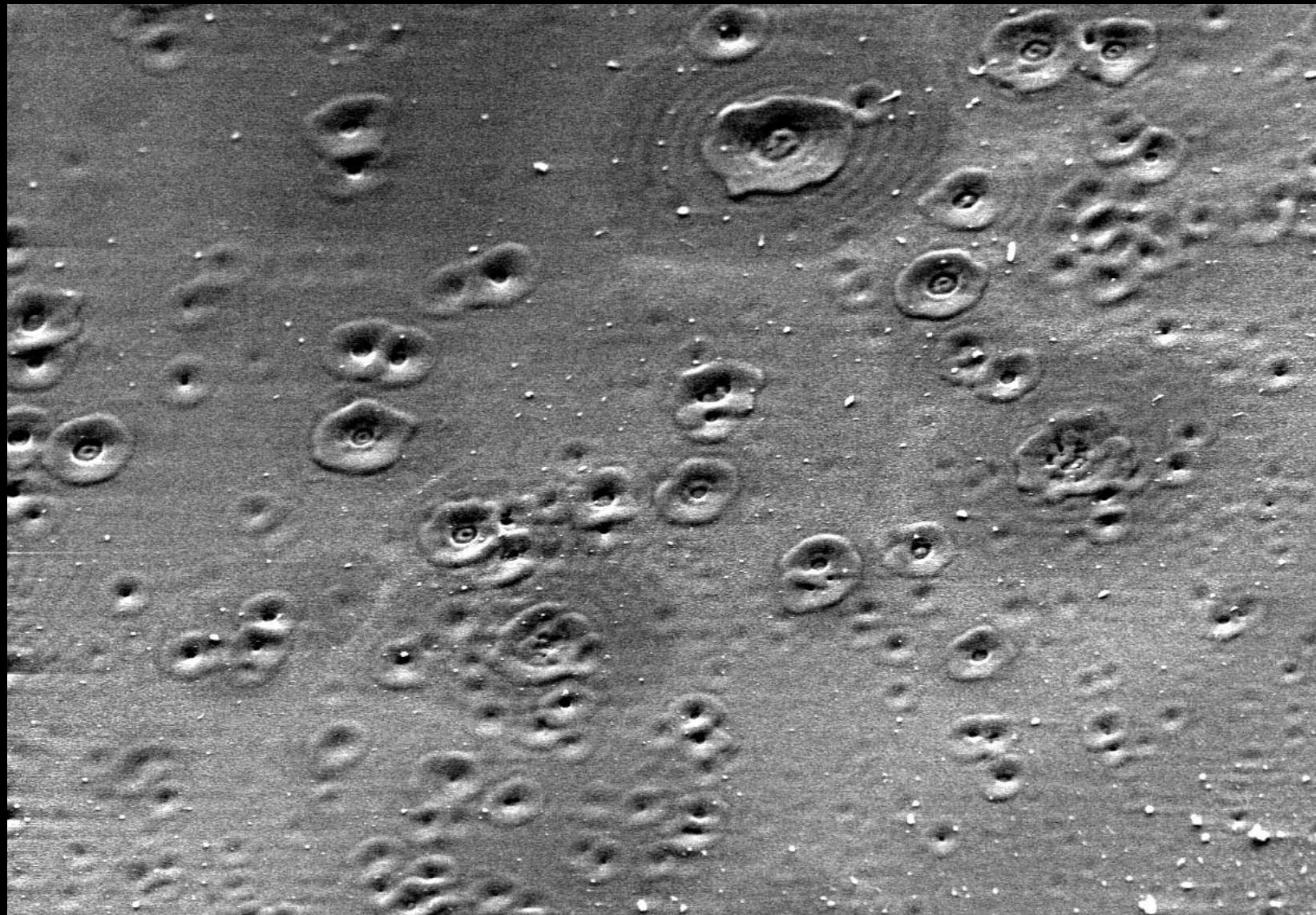
## *Outlook*

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

x2000  
#3548  
512 x 480

20  $\mu$ m

10kV      15mm  
0000



x2000

#3548

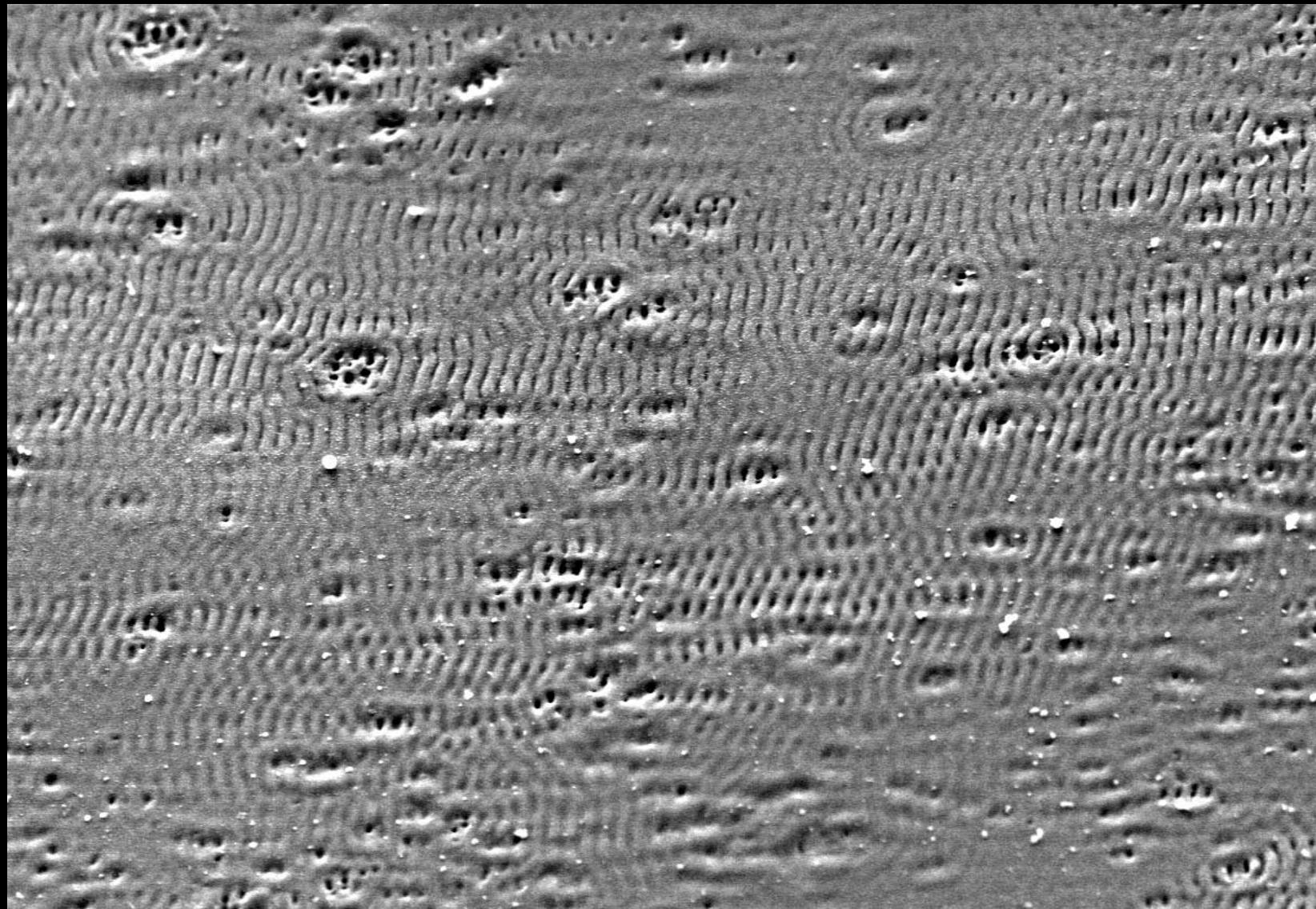
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20  $\mu\text{m}$

10kV

15mm

0001



x2000

20  $\mu\text{m}$

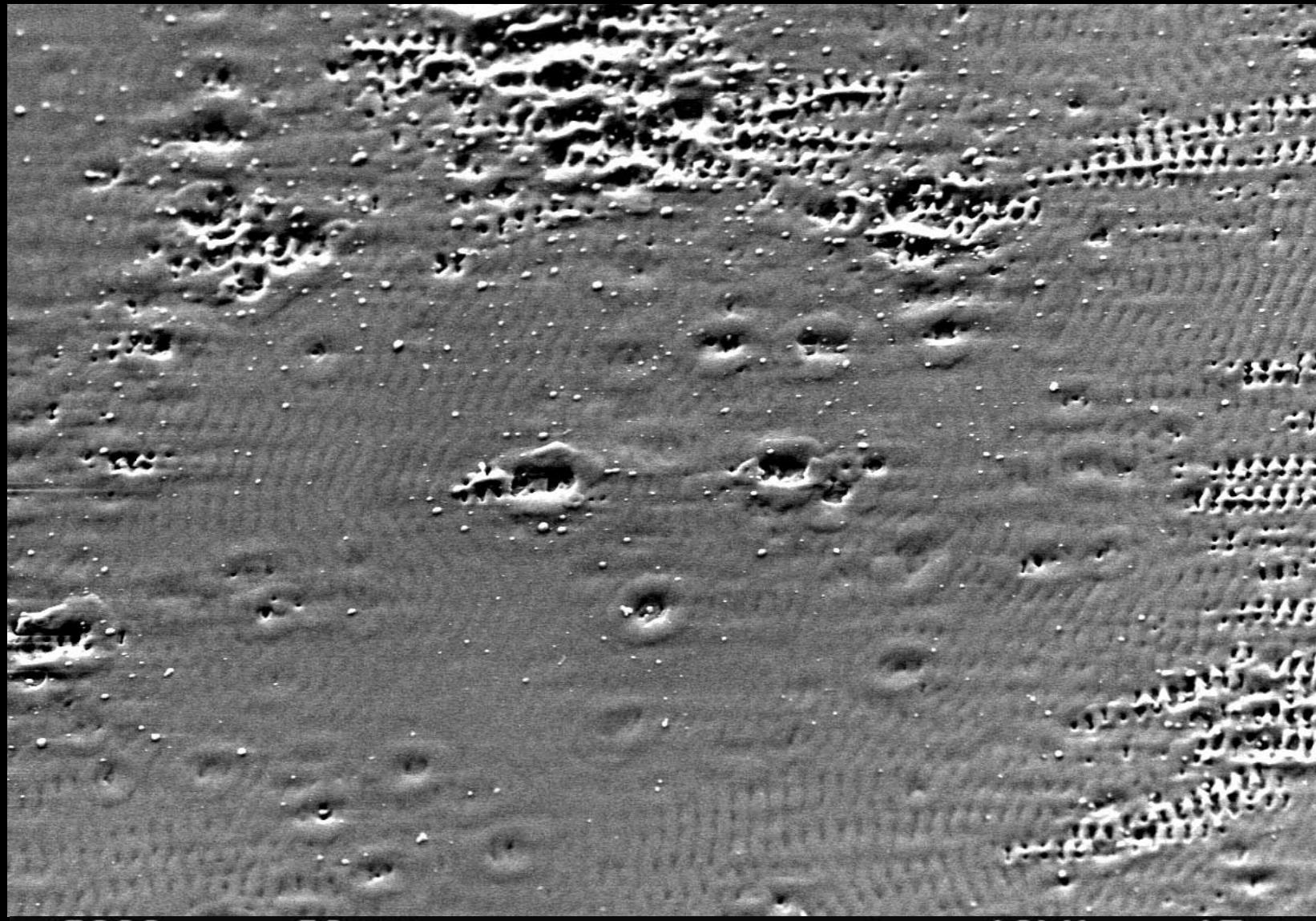
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512 x 480

10kV

15mm

0002



x2000

#3548

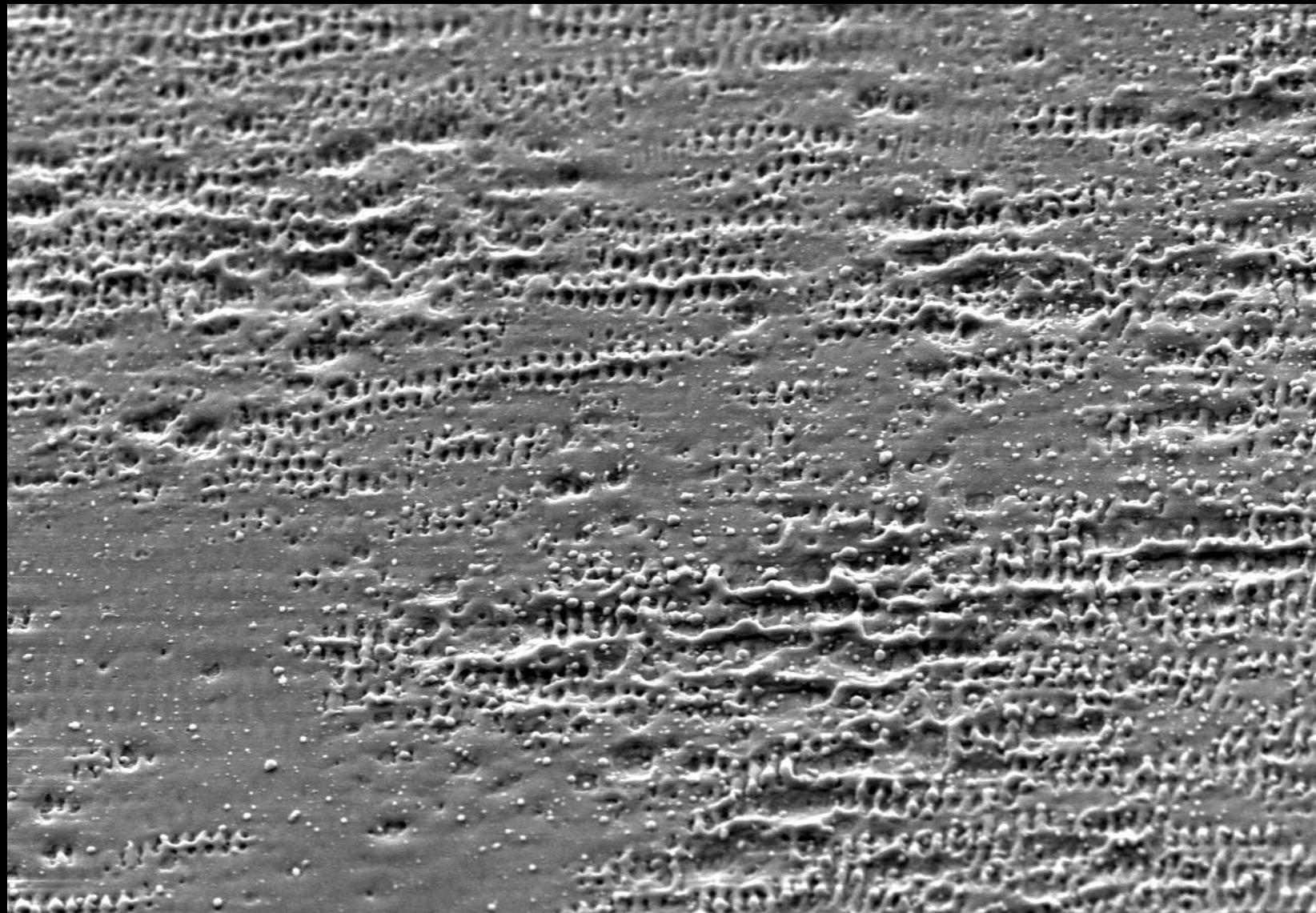
512 x 480

20 μm

10kV

15mm

0003



x2000

#3548

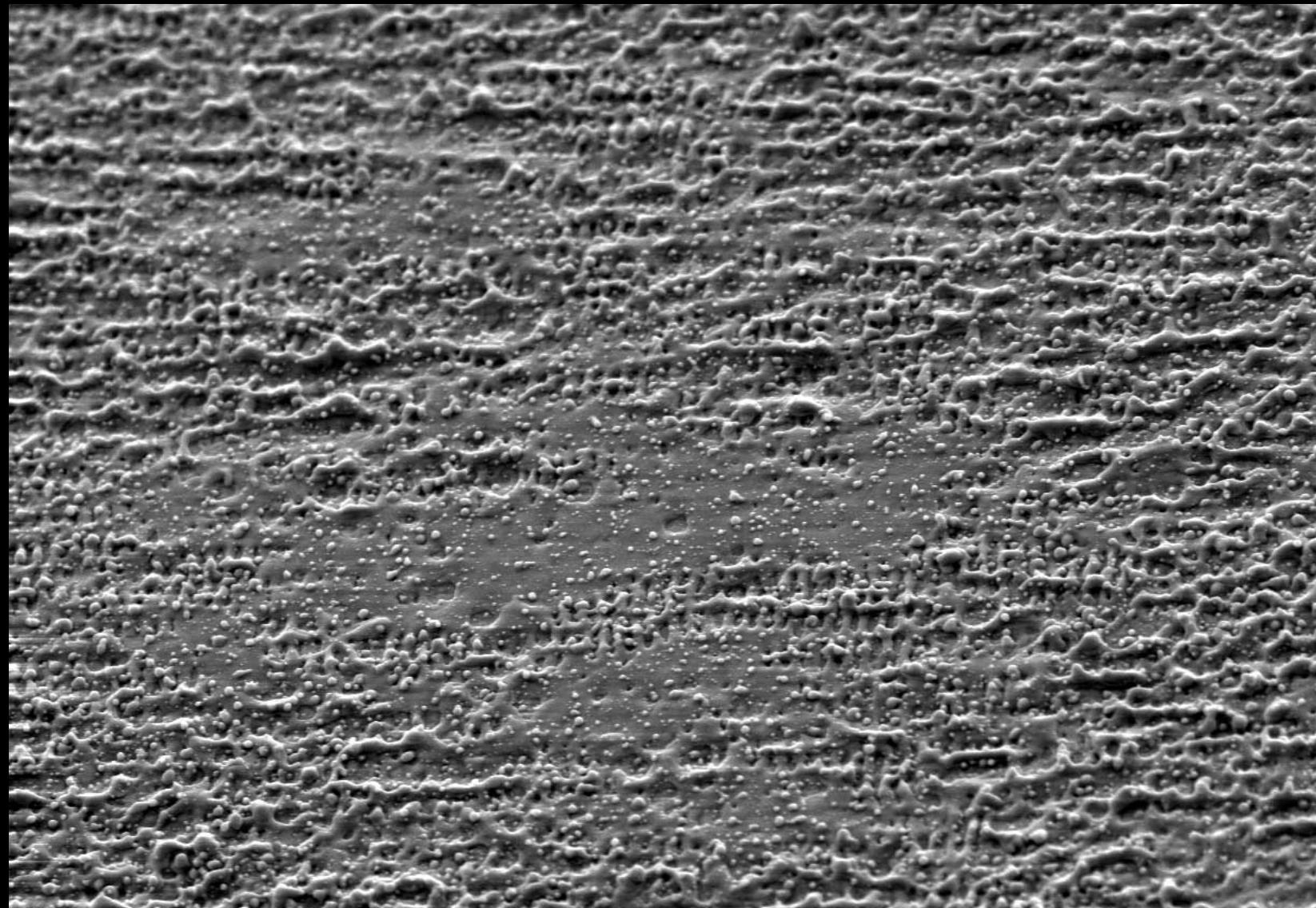
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20  $\mu\text{m}$

10kV

15mm

0004



x2000

#3548

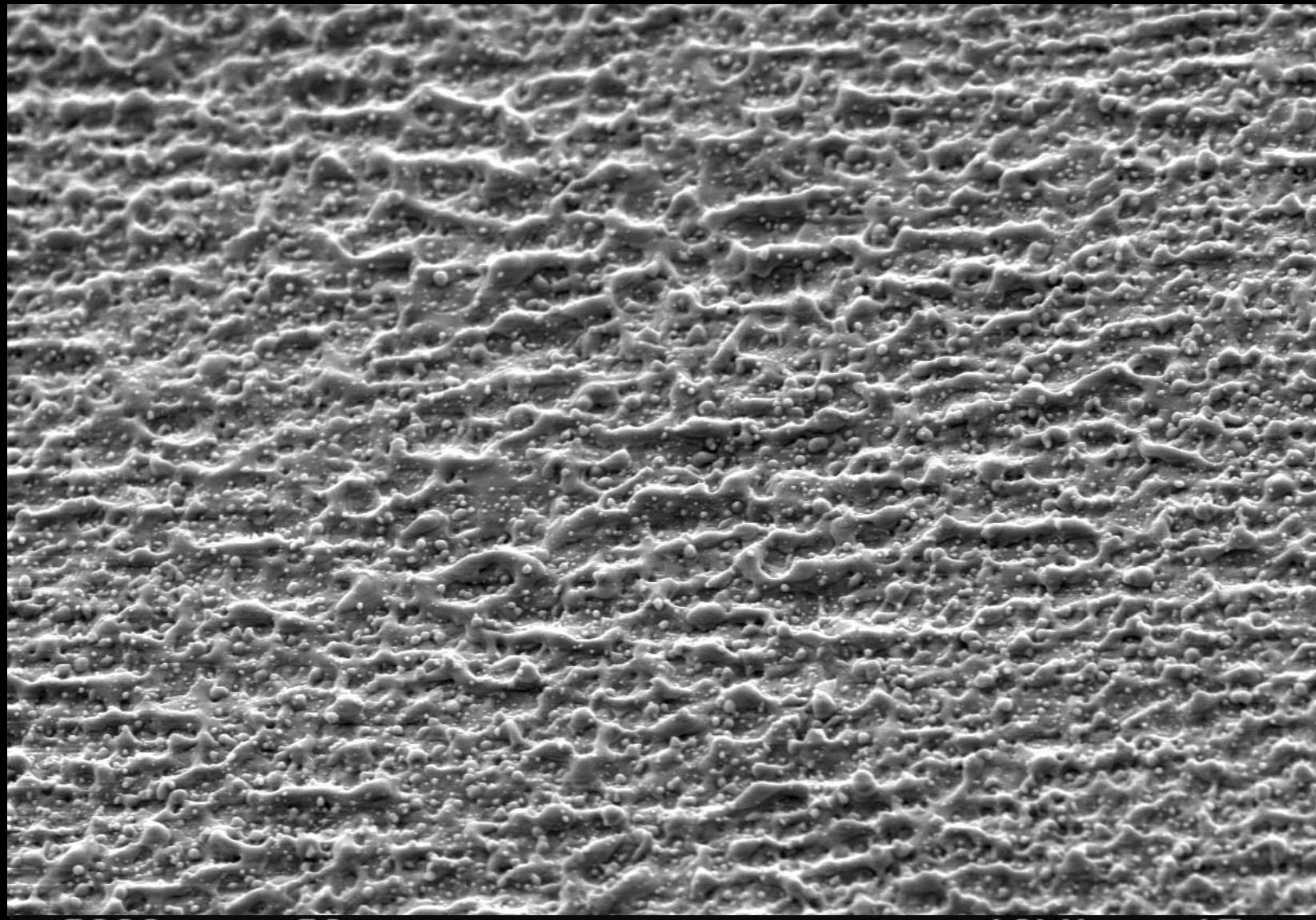
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20  $\mu\text{m}$

10kV

15mm

0005



x2000

#3548

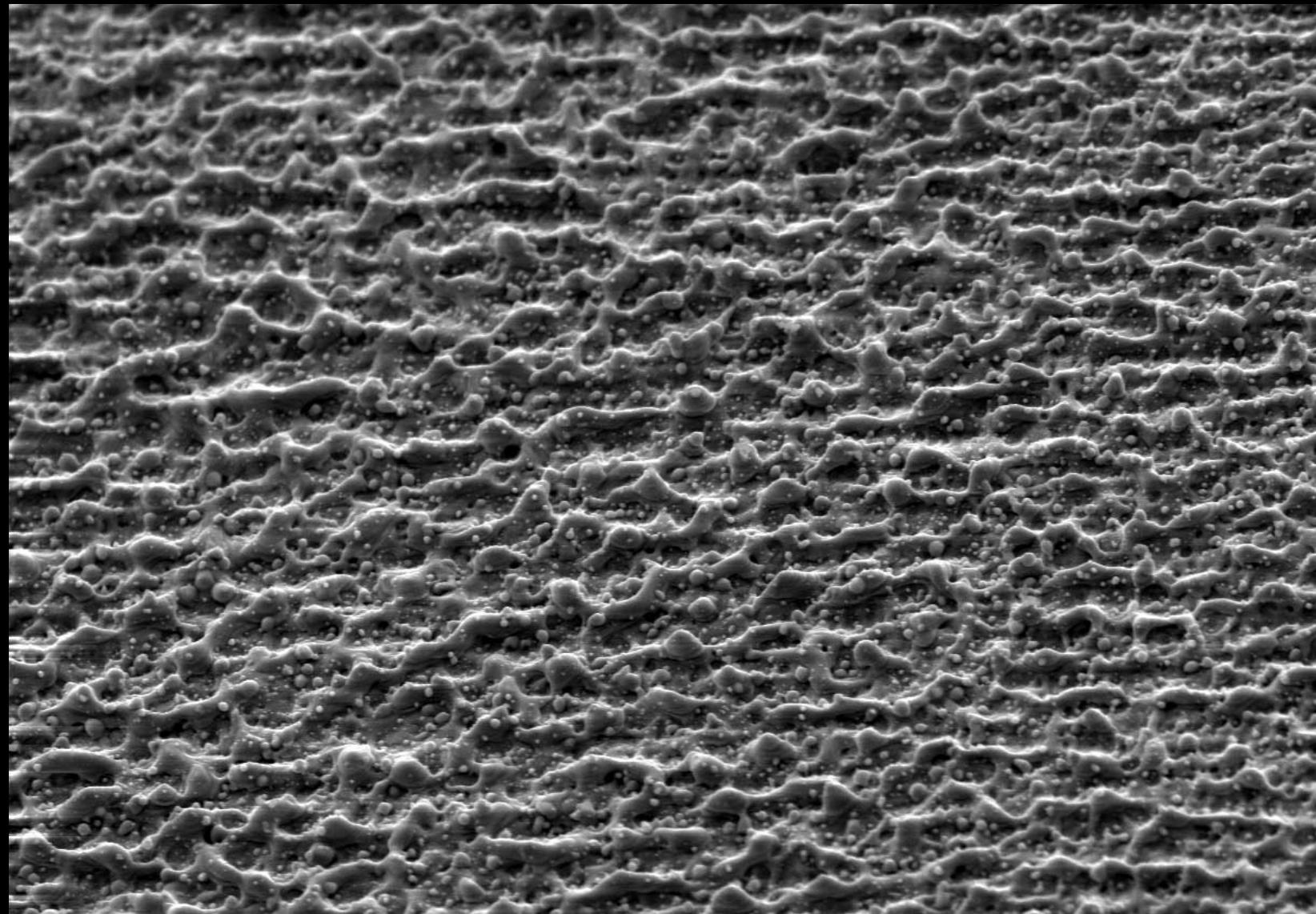
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20 μm

10kV

15mm

0006



x2000

#3548

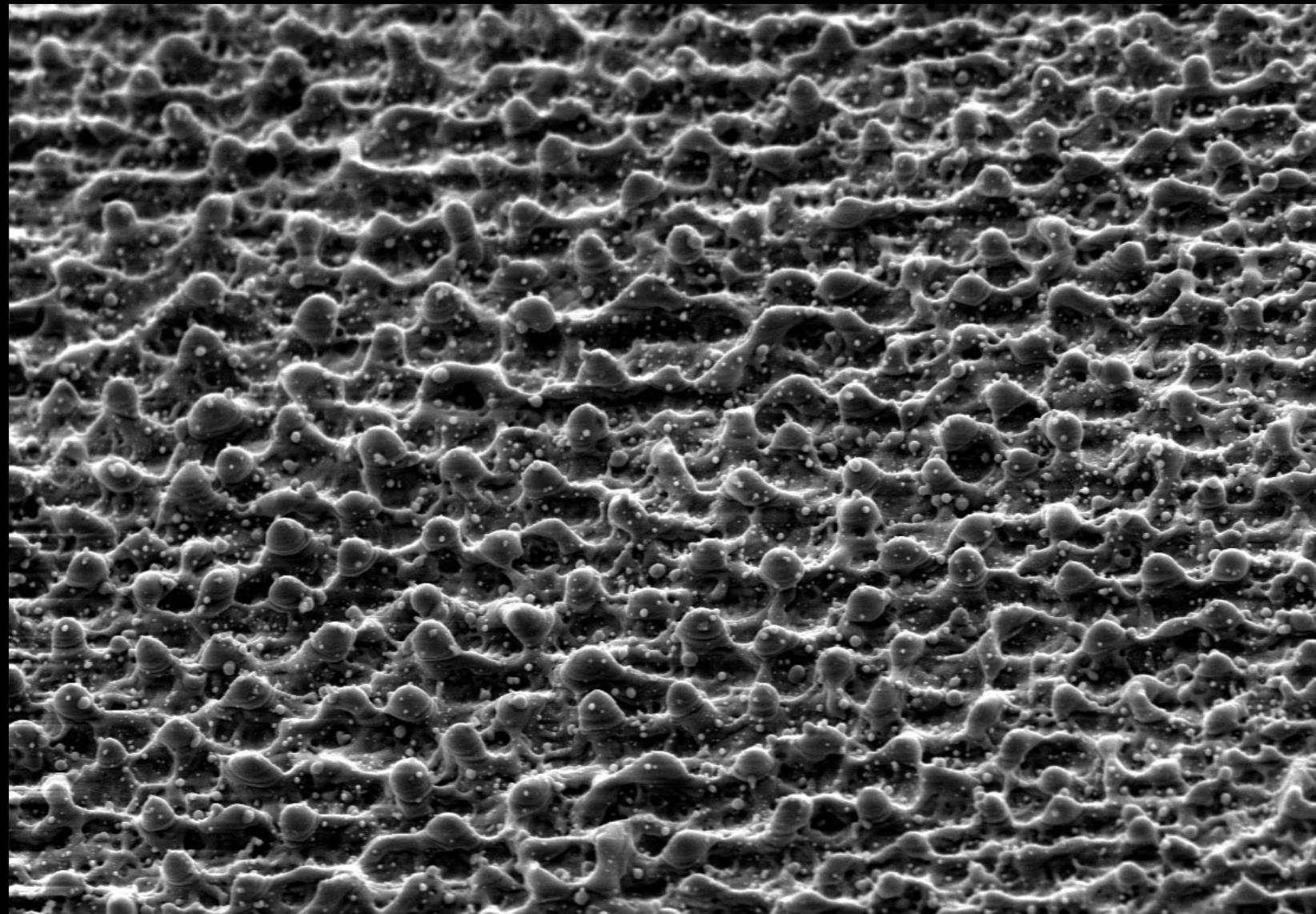
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20  $\mu\text{m}$

10kV

15mm

0008



x2000

#3548

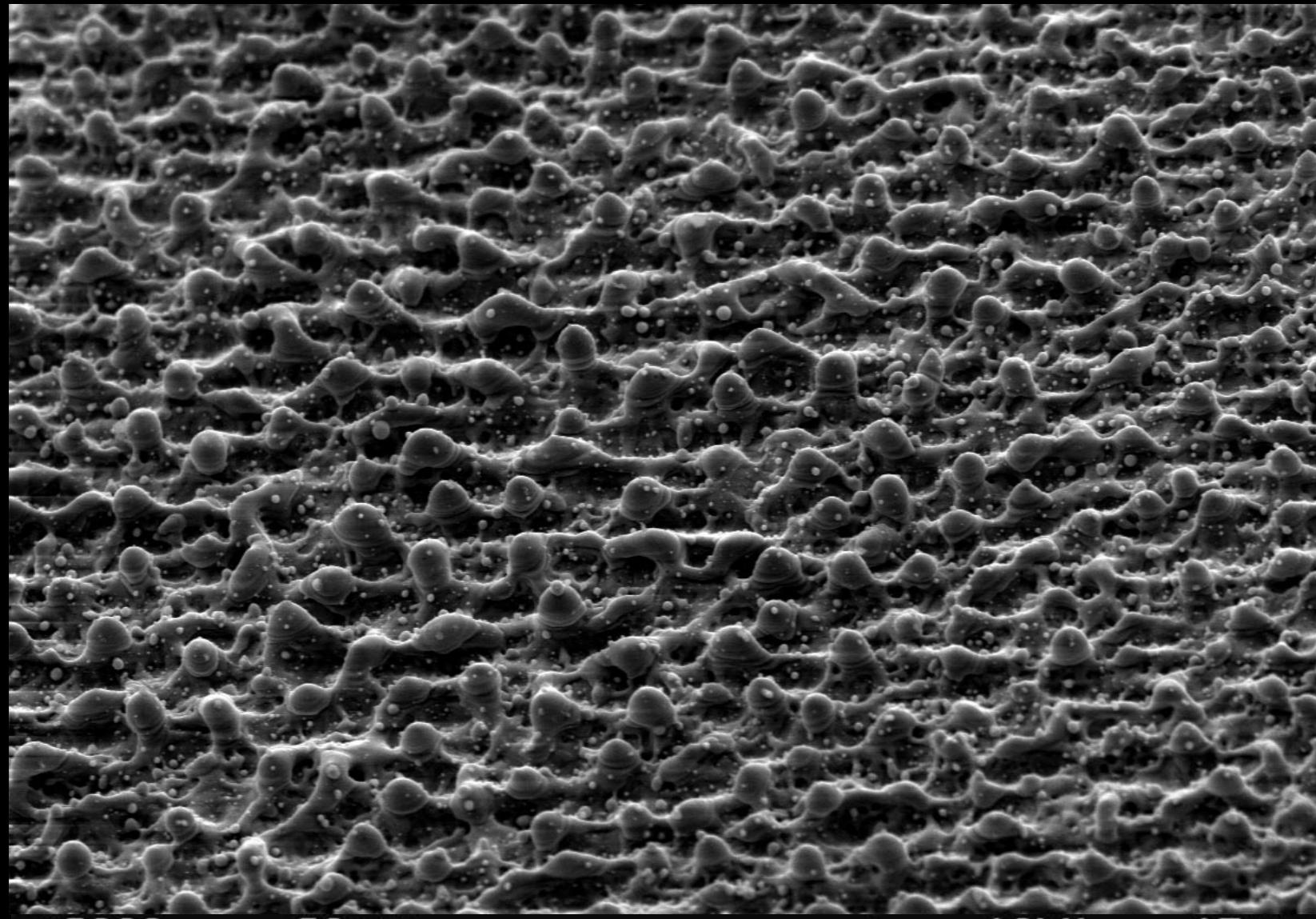
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20  $\mu\text{m}$

10kV

15mm

0010



x2000

#3548

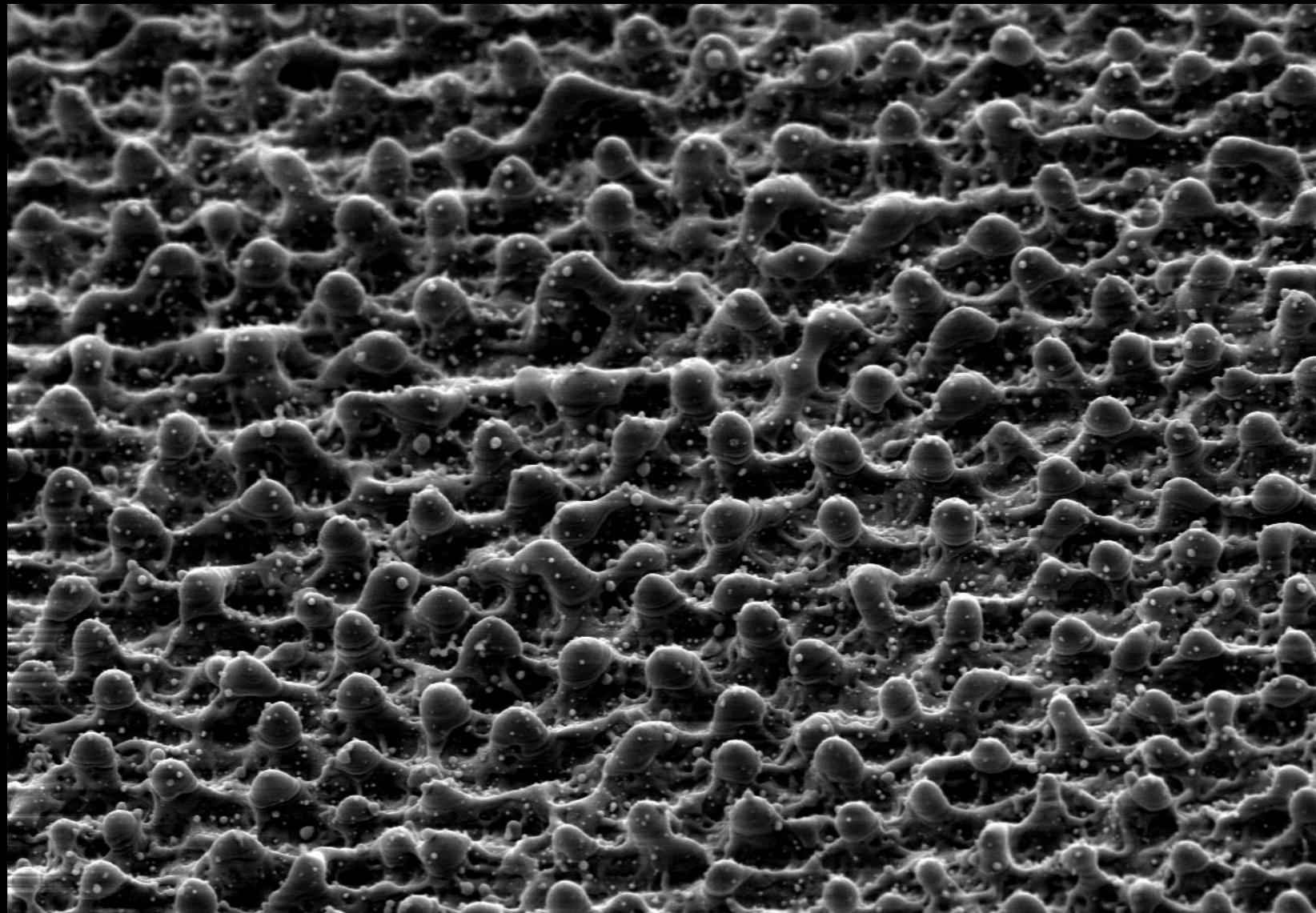
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20  $\mu\text{m}$

10kV

15mm

0012



x2000

#3548

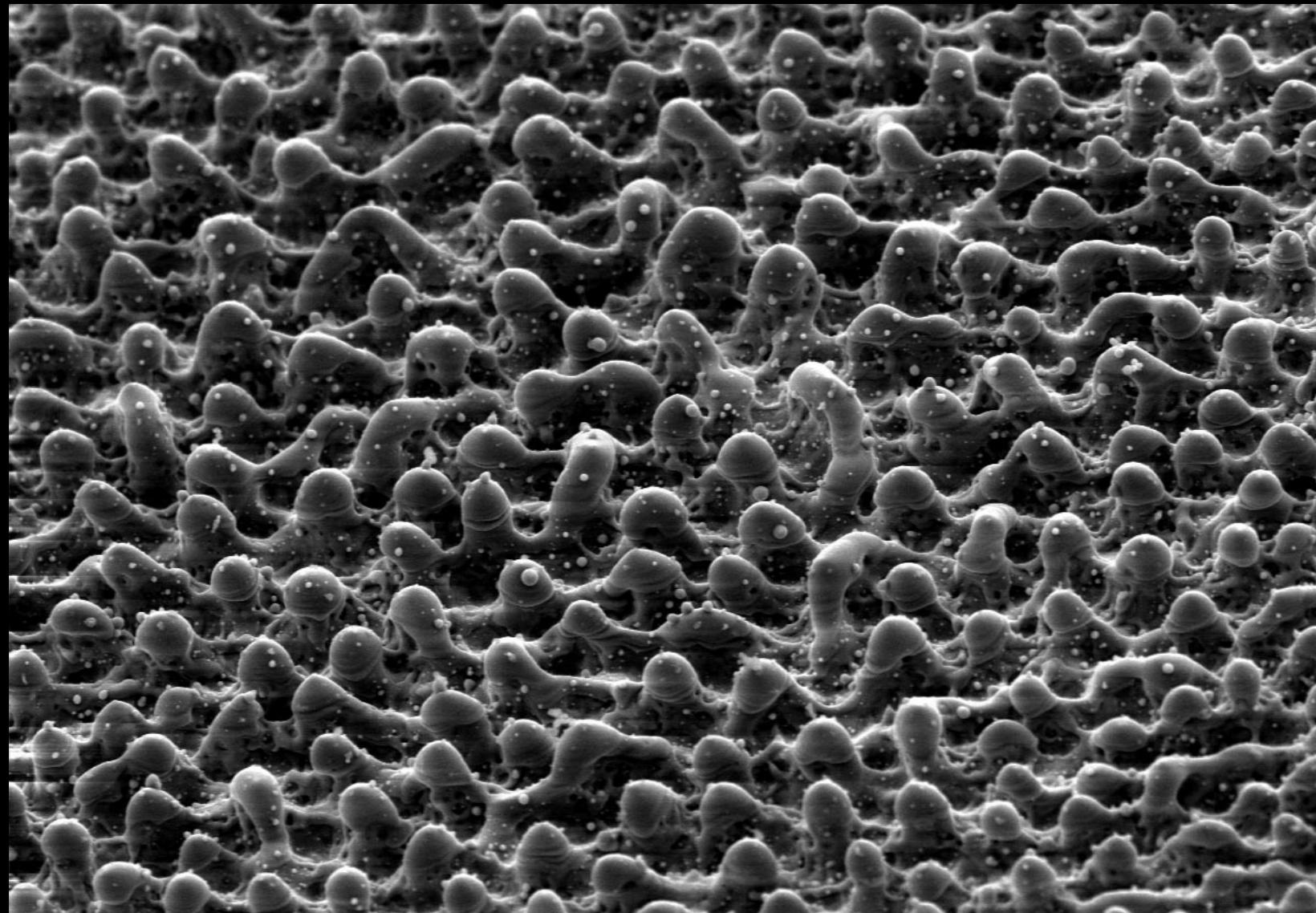
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20  $\mu$ m

10kV

15mm

0015



x2000

#3548

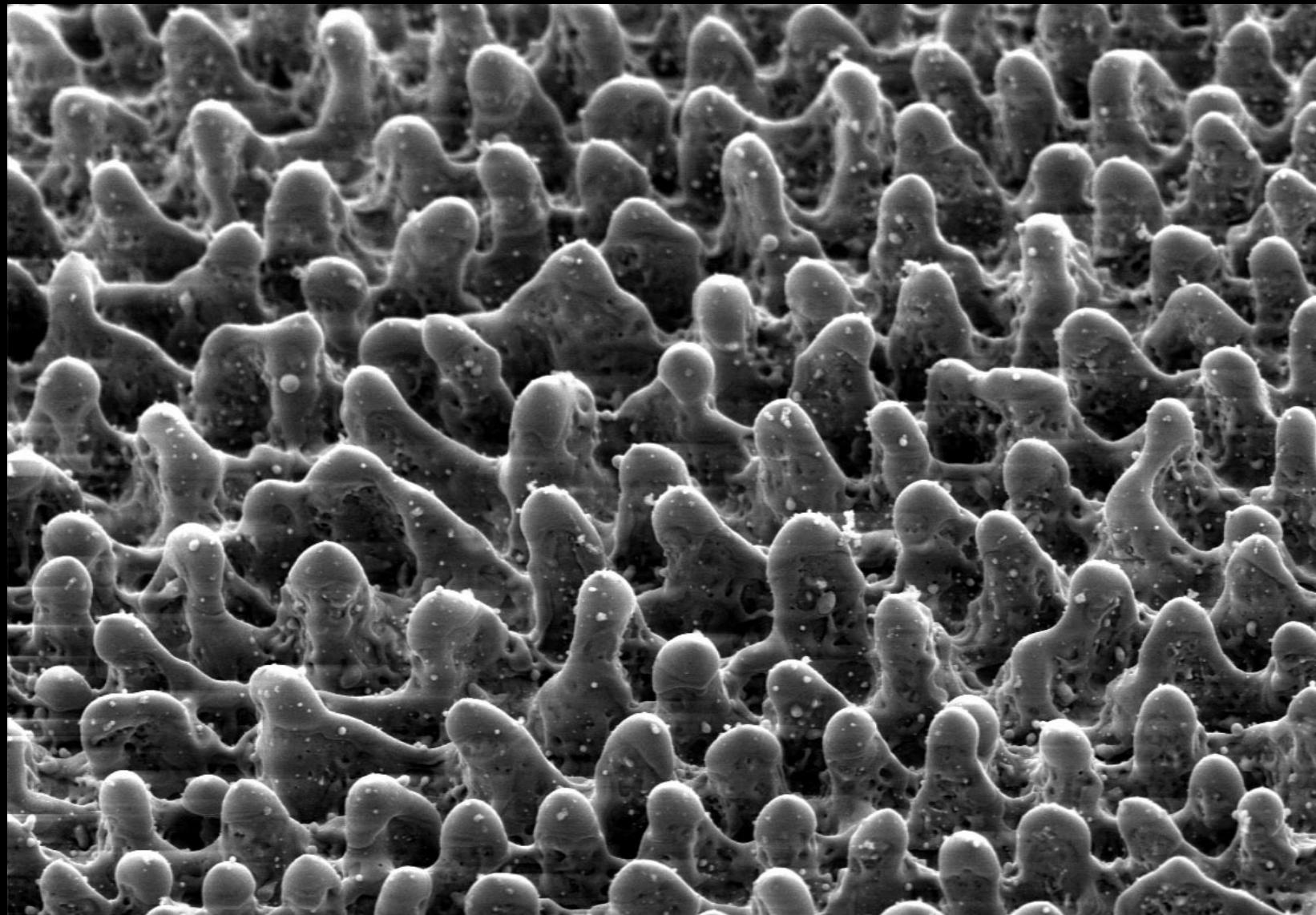
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20  $\mu\text{m}$

10kV

15mm

0020



x2000

#3548

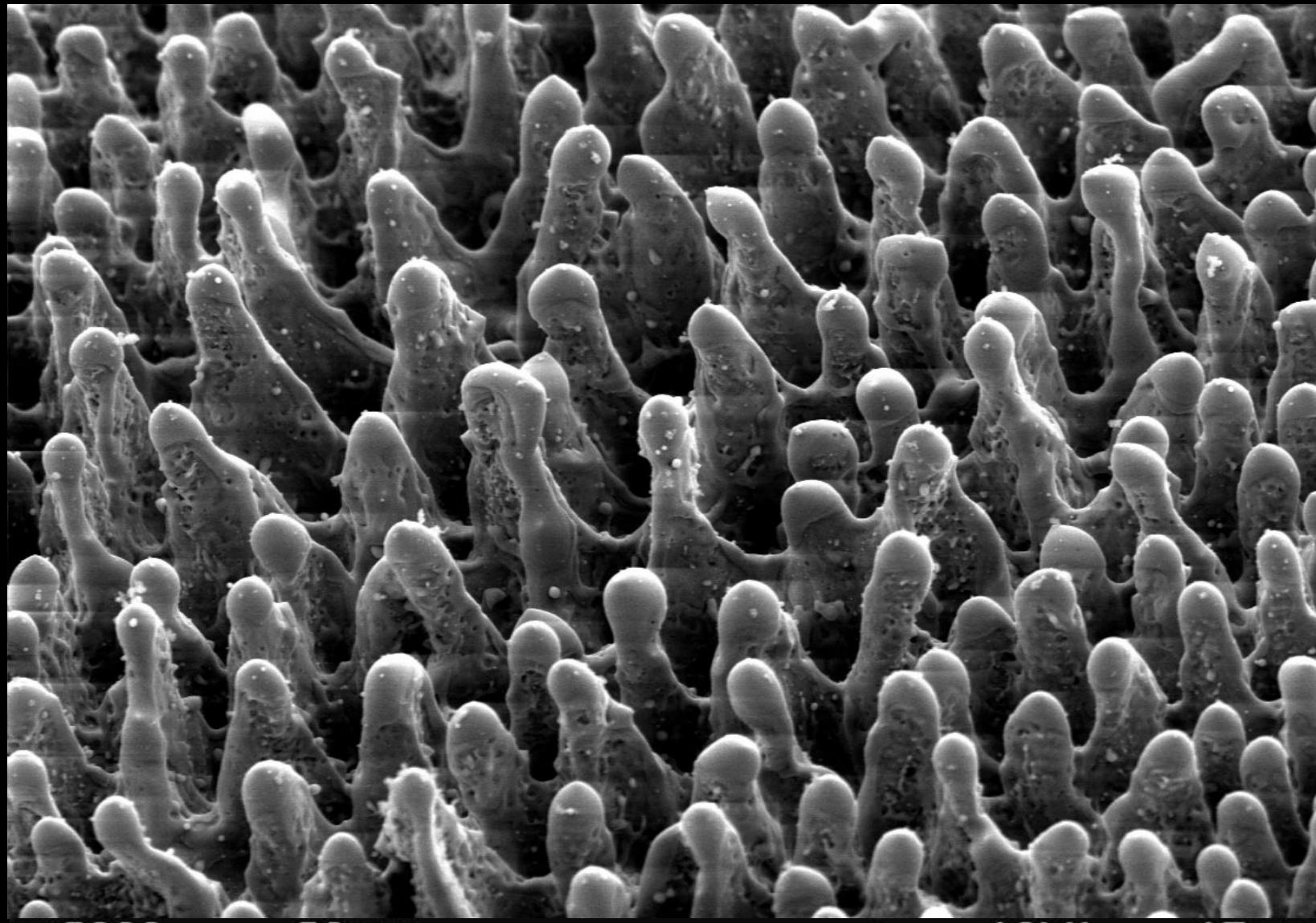
512 x 480

20 μm

10kV

15mm

0030



x2000

#3548

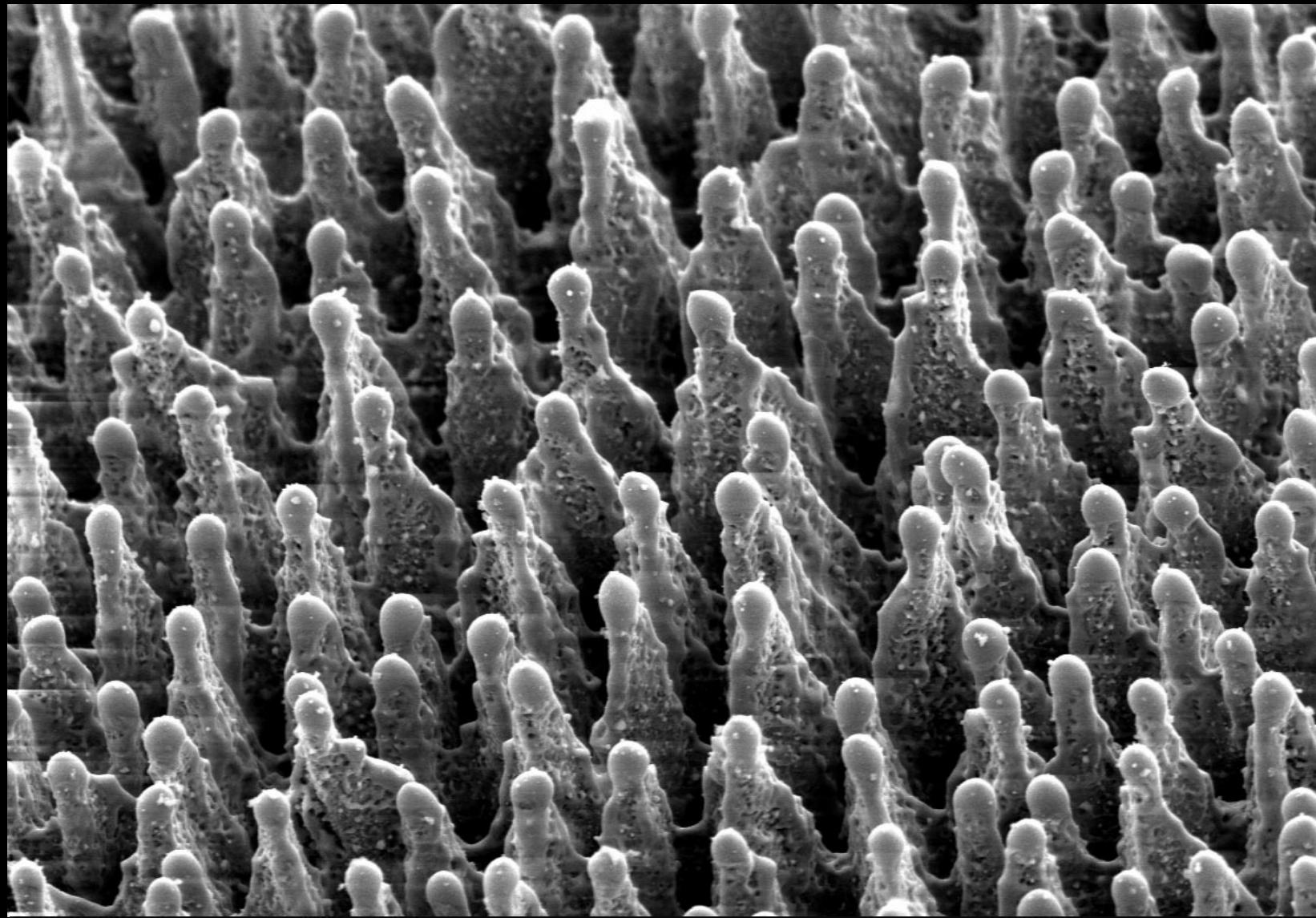
512 x 480

20  $\mu$ m

10kV

15mm

0050



x2000

20  $\mu$ m

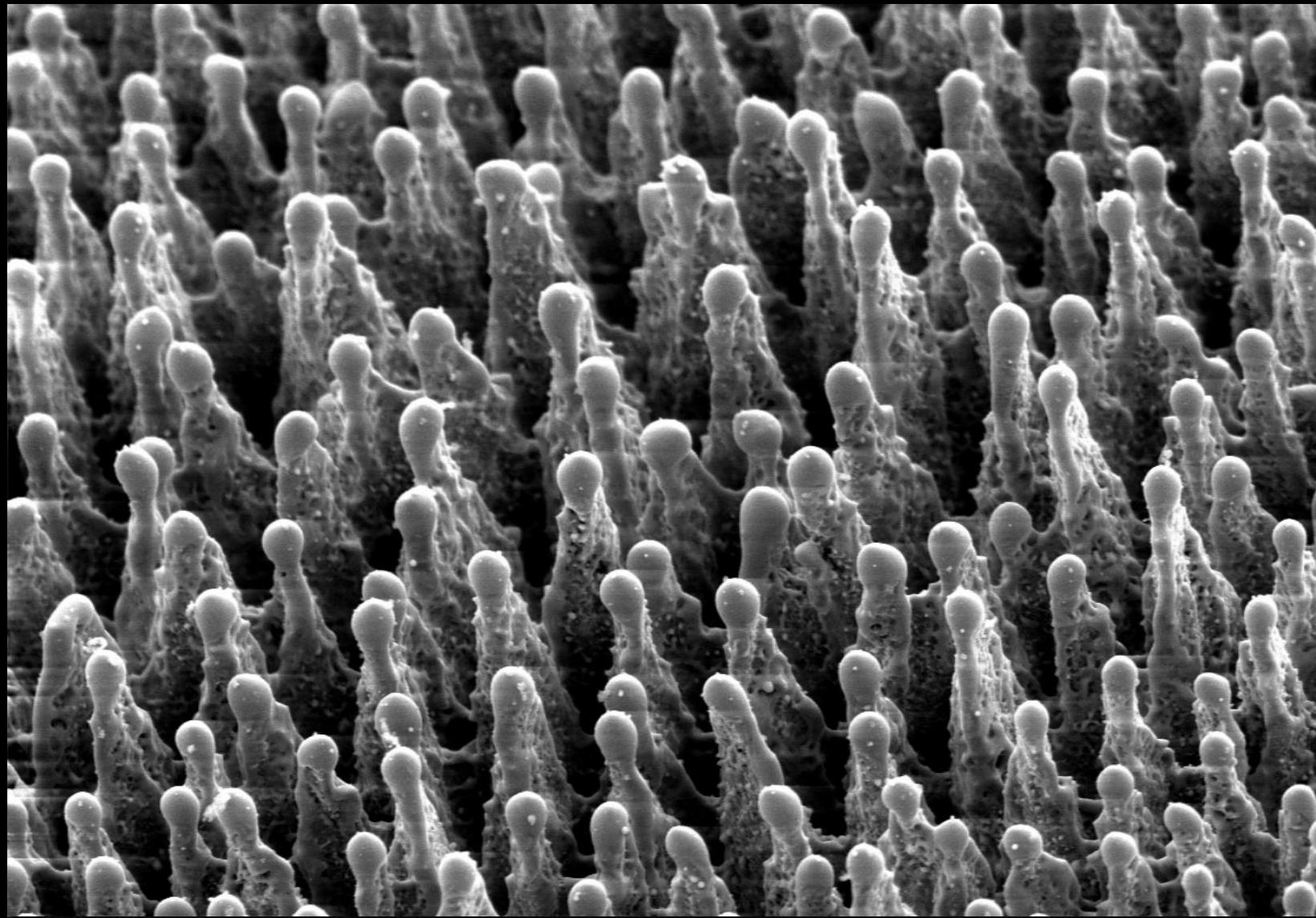
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512 x 480

10kV

15mm

0070



x2000

20  $\mu\text{m}$

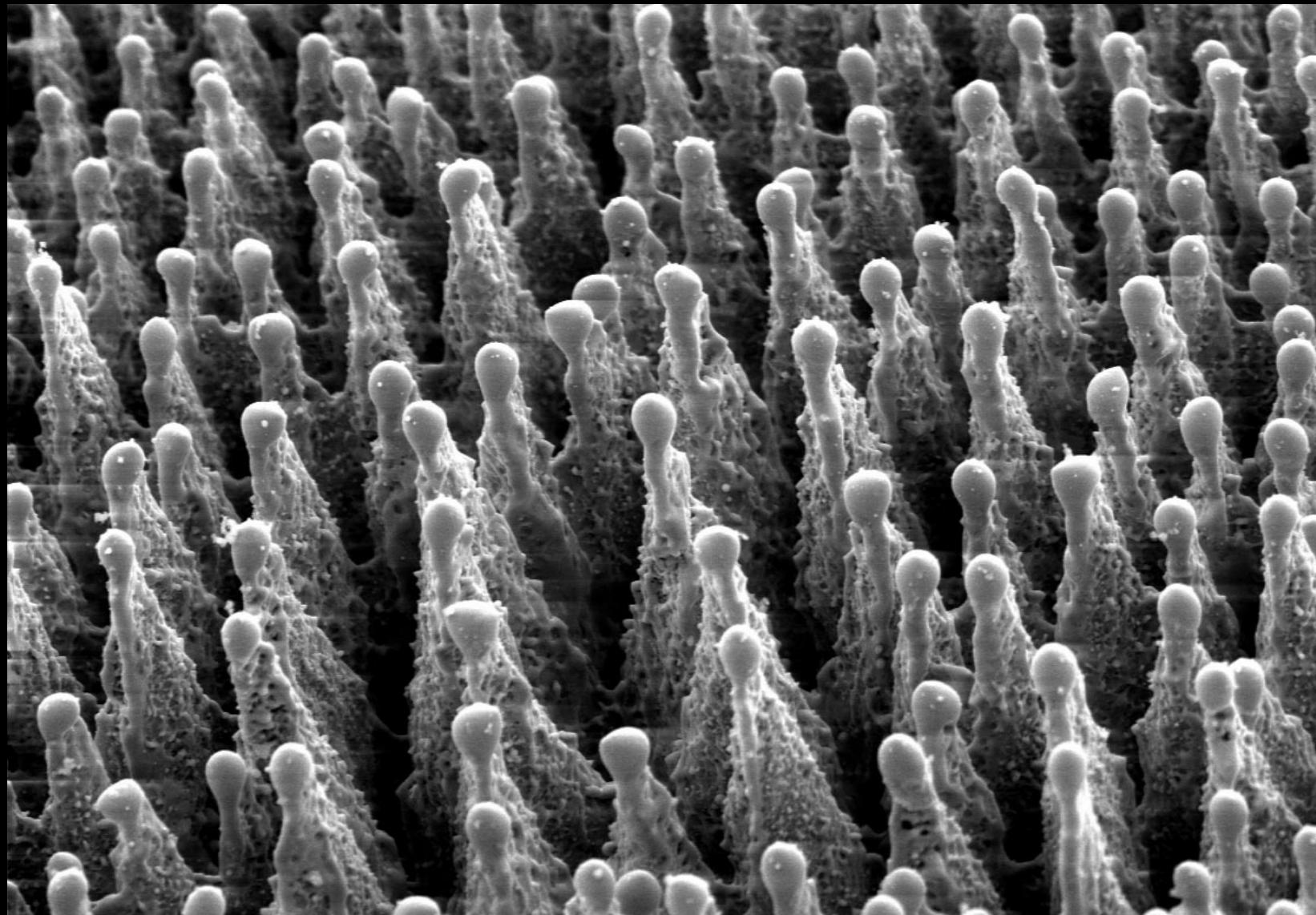
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512 x 480

10kV

15mm

0100



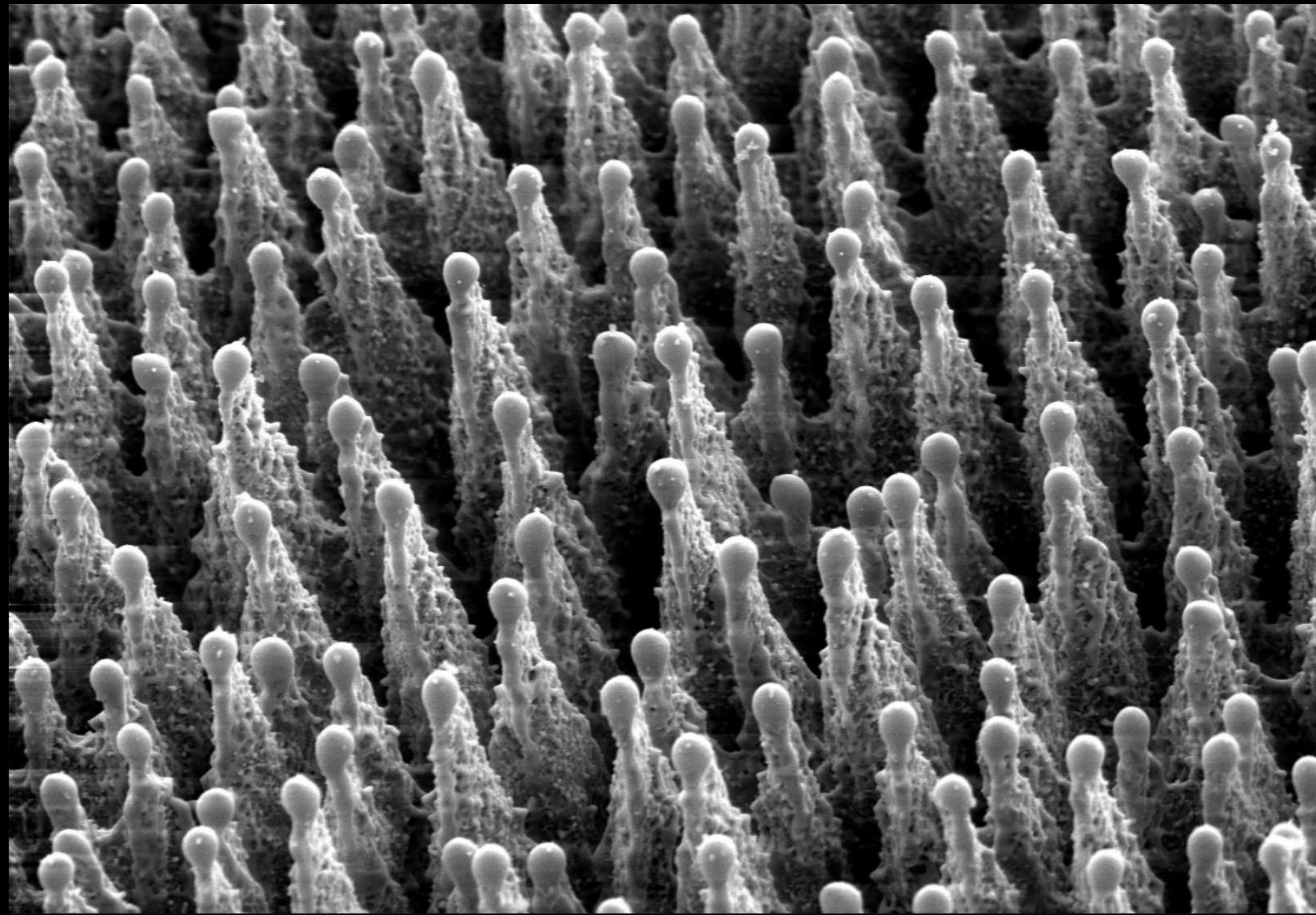
x2000  
#3548  
512 x 480

20  $\mu$ m

10kV

15mm

0200



x2000

20  $\mu\text{m}$

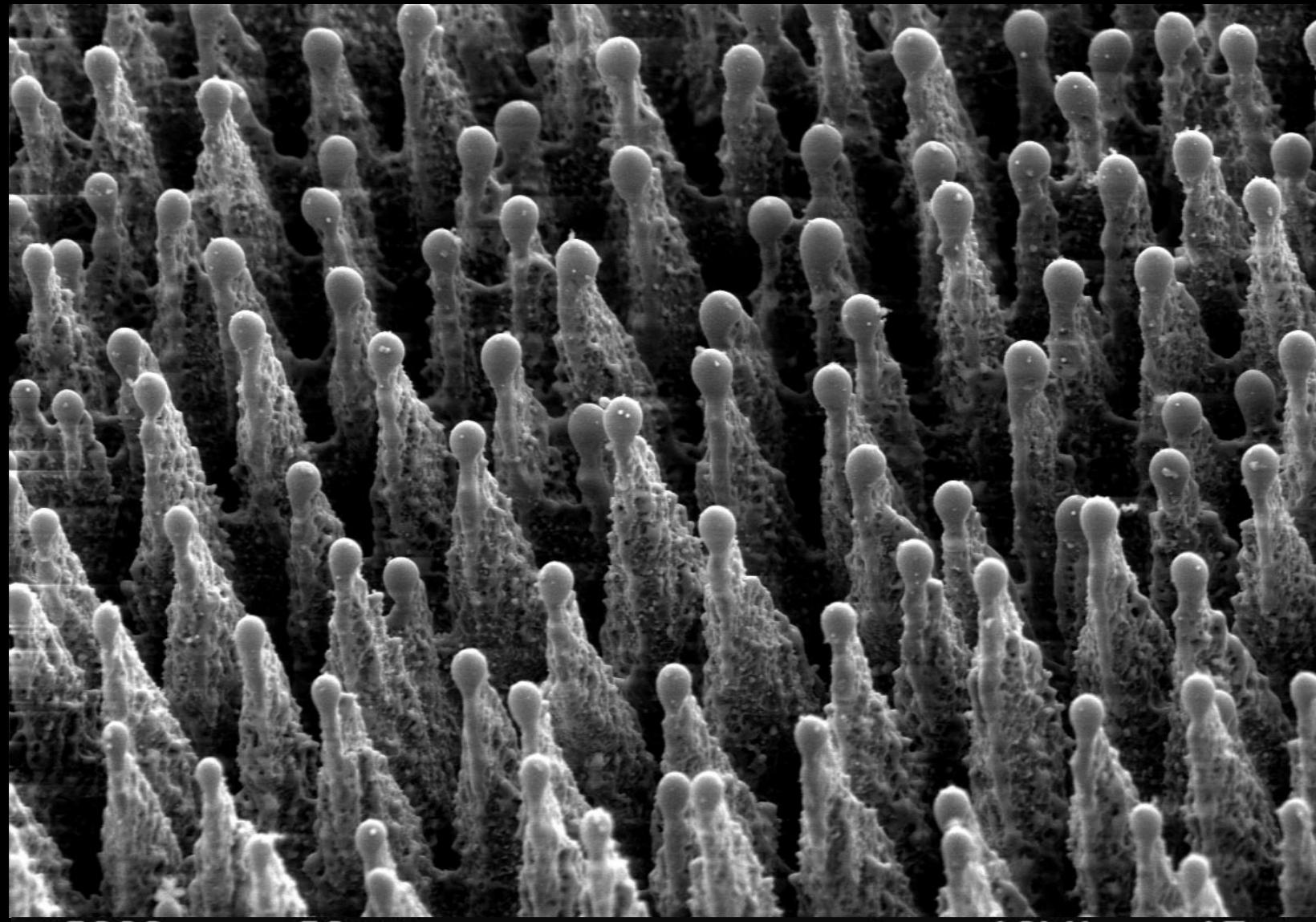
#3548

512 x 480

10kV

15mm

0400



x2000

#3548

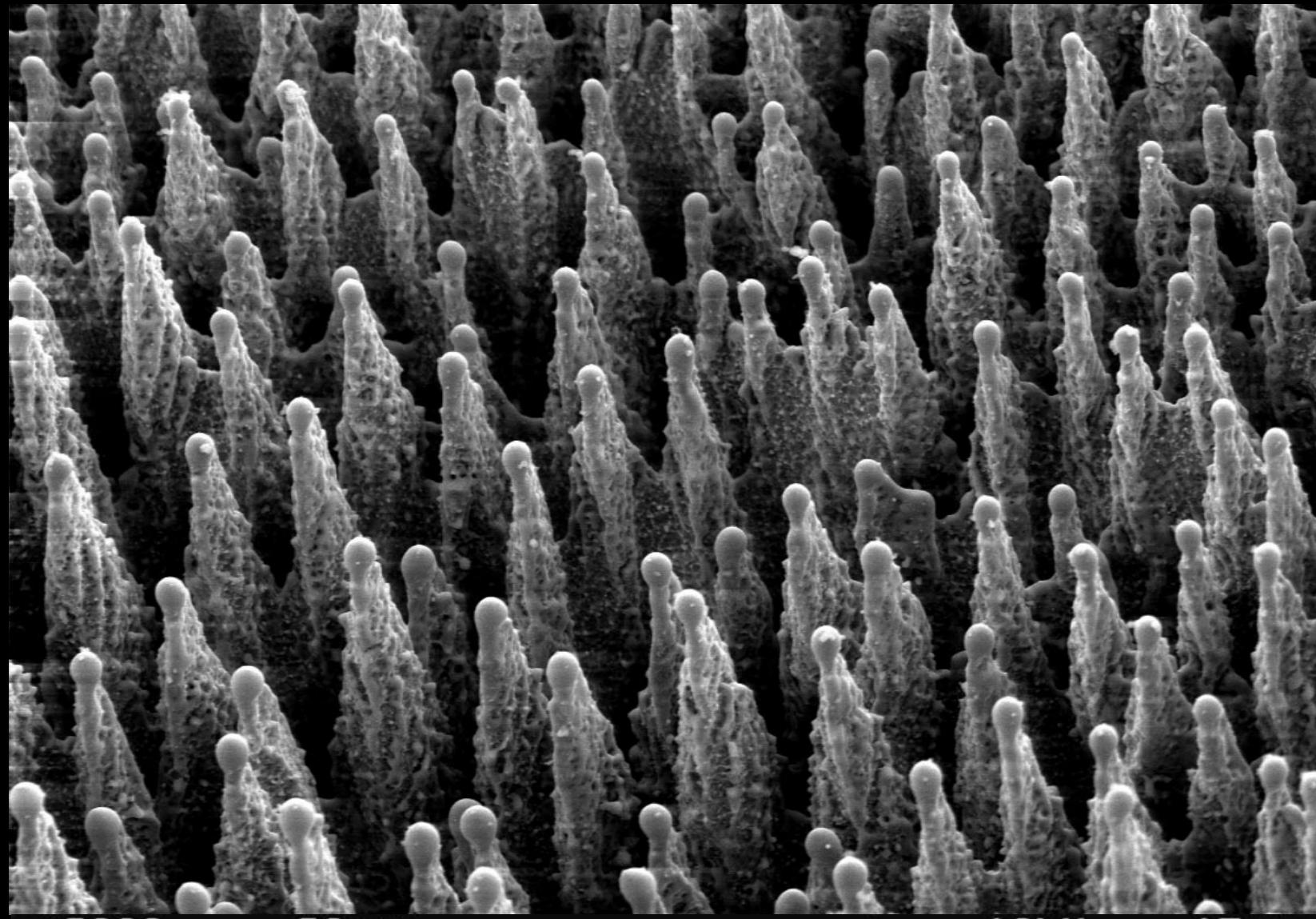
512 x 480

20  $\mu\text{m}$

10kV

15mm

0600



x2000

20  $\mu\text{m}$

#3548

512 x 480

10kV

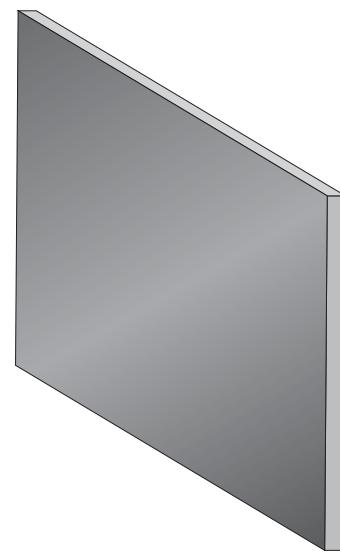
15mm

1000

## *Outlook*

**can ordering of spikes be improved by using a grid?**

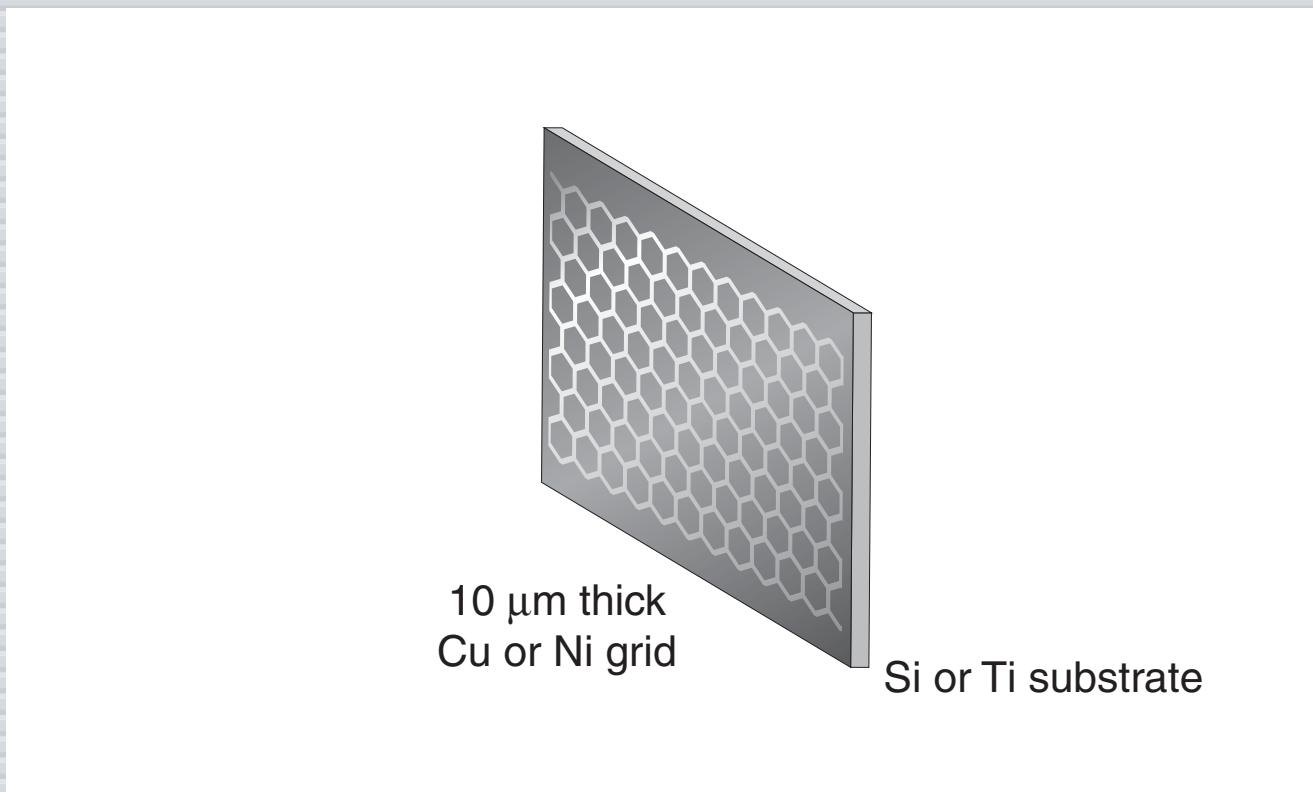
# *Outlook*



Si or Ti substrate

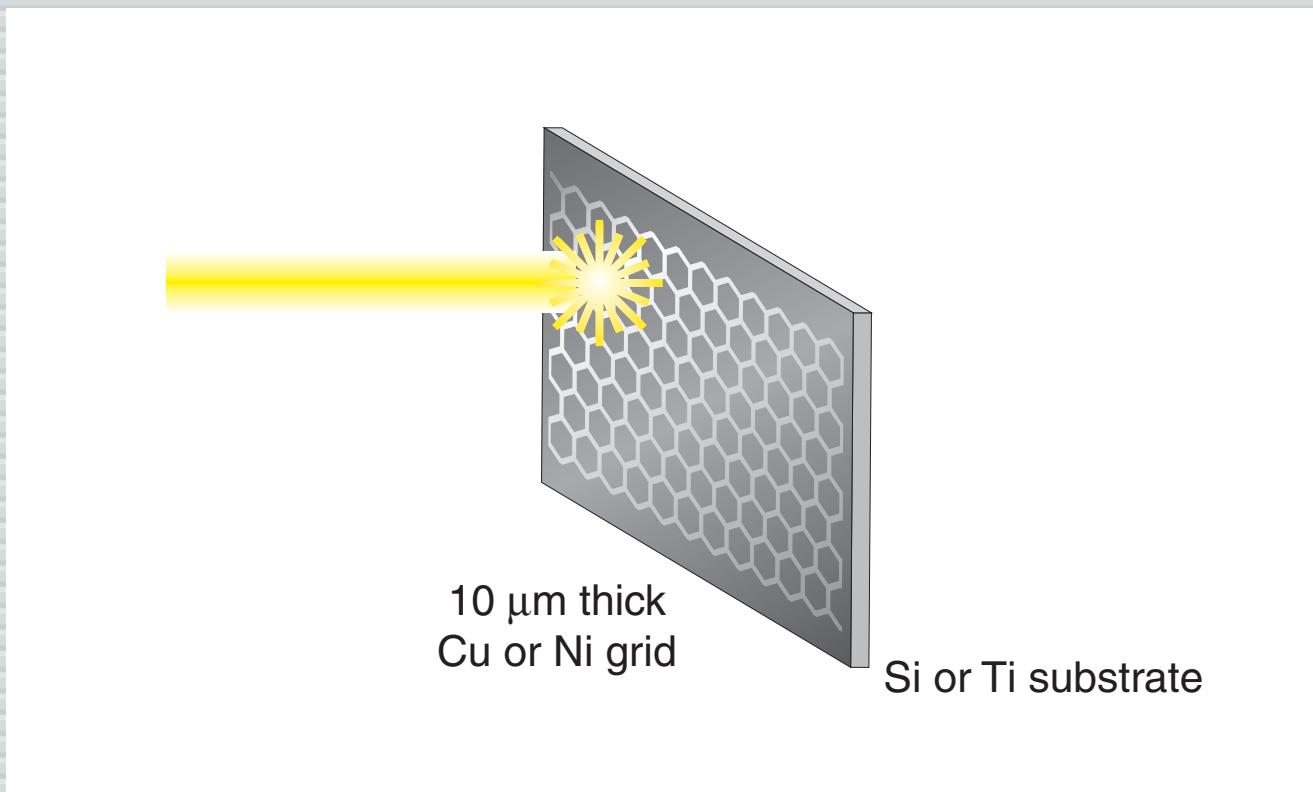
# *Outlook*

**place grid in front of substrate**



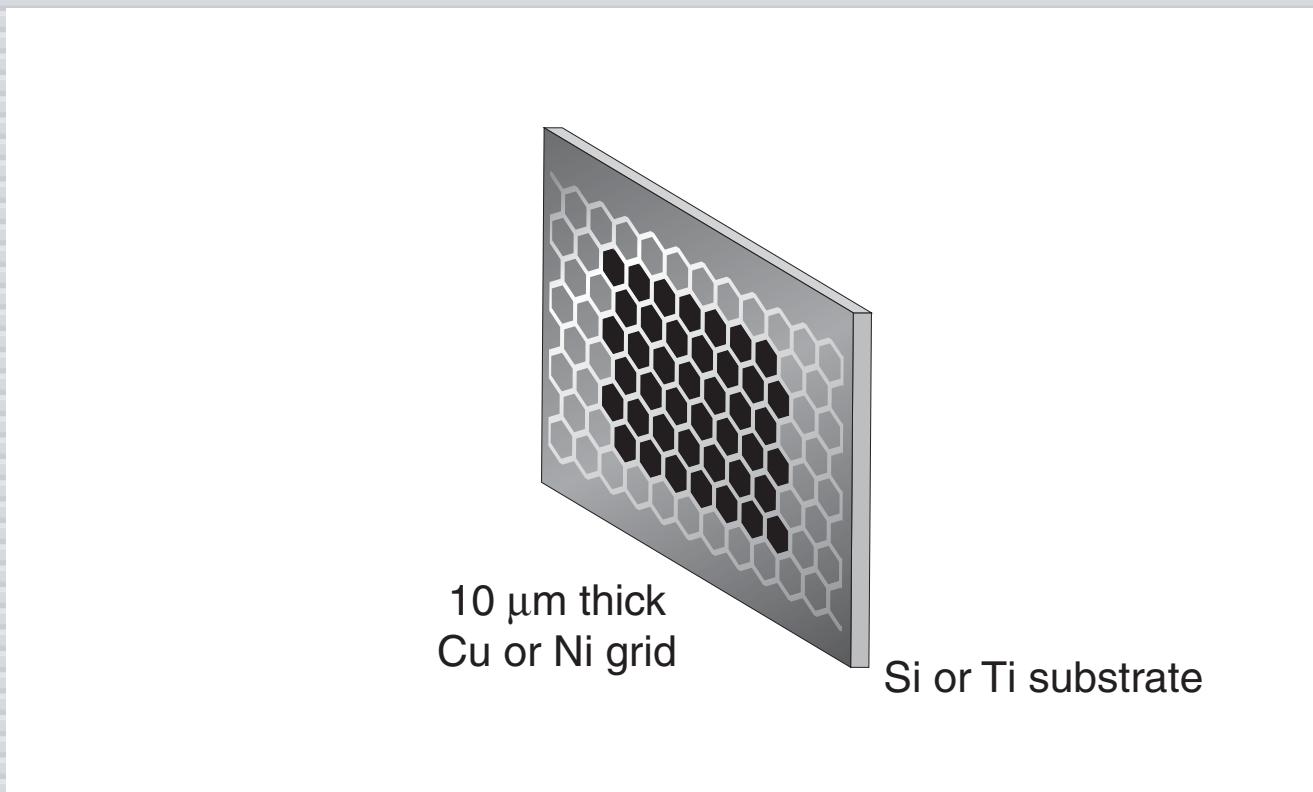
# *Outlook*

## scan laser beam



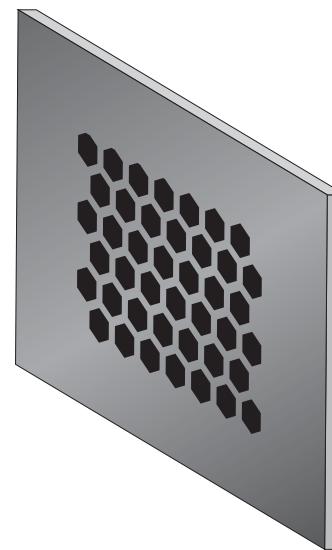
# *Outlook*

**scan laser beam**

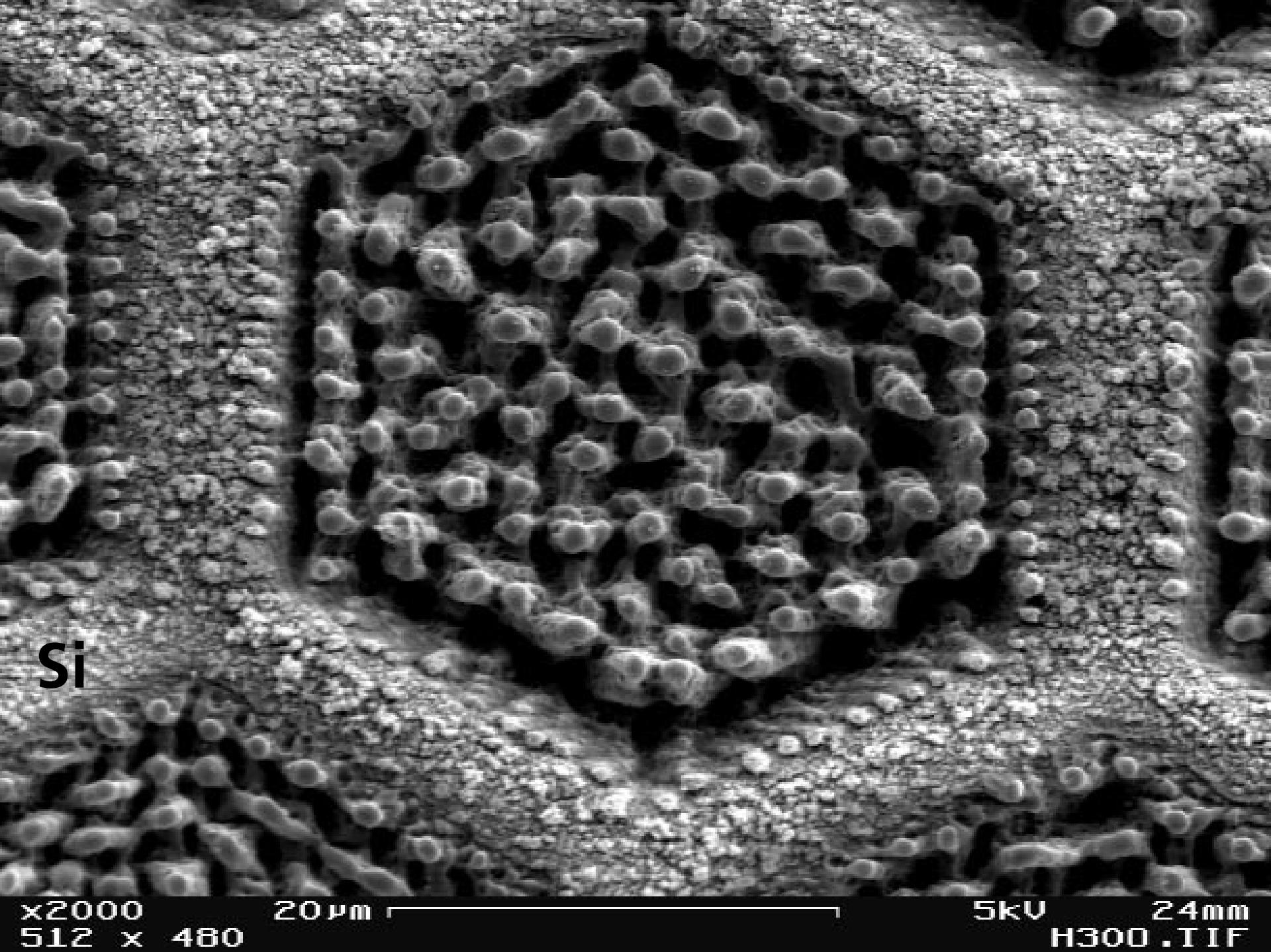


# *Outlook*

**remove grid**



Si or Ti substrate



x2000

512 x 480

20 μm

5kV

24mm  
H300.TIF

Ti

20  $\mu\text{m}$

5kV 17mm

Ti

10  $\mu\text{m}$

5kV

17mm

# *Outlook*

## *Summary*

### **Microstructured silicon**

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

## *Summary*

### **Microstructured silicon**

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

## *Summary*

### **Microstructured silicon**

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

## *Summary*

### **Microstructured silicon**

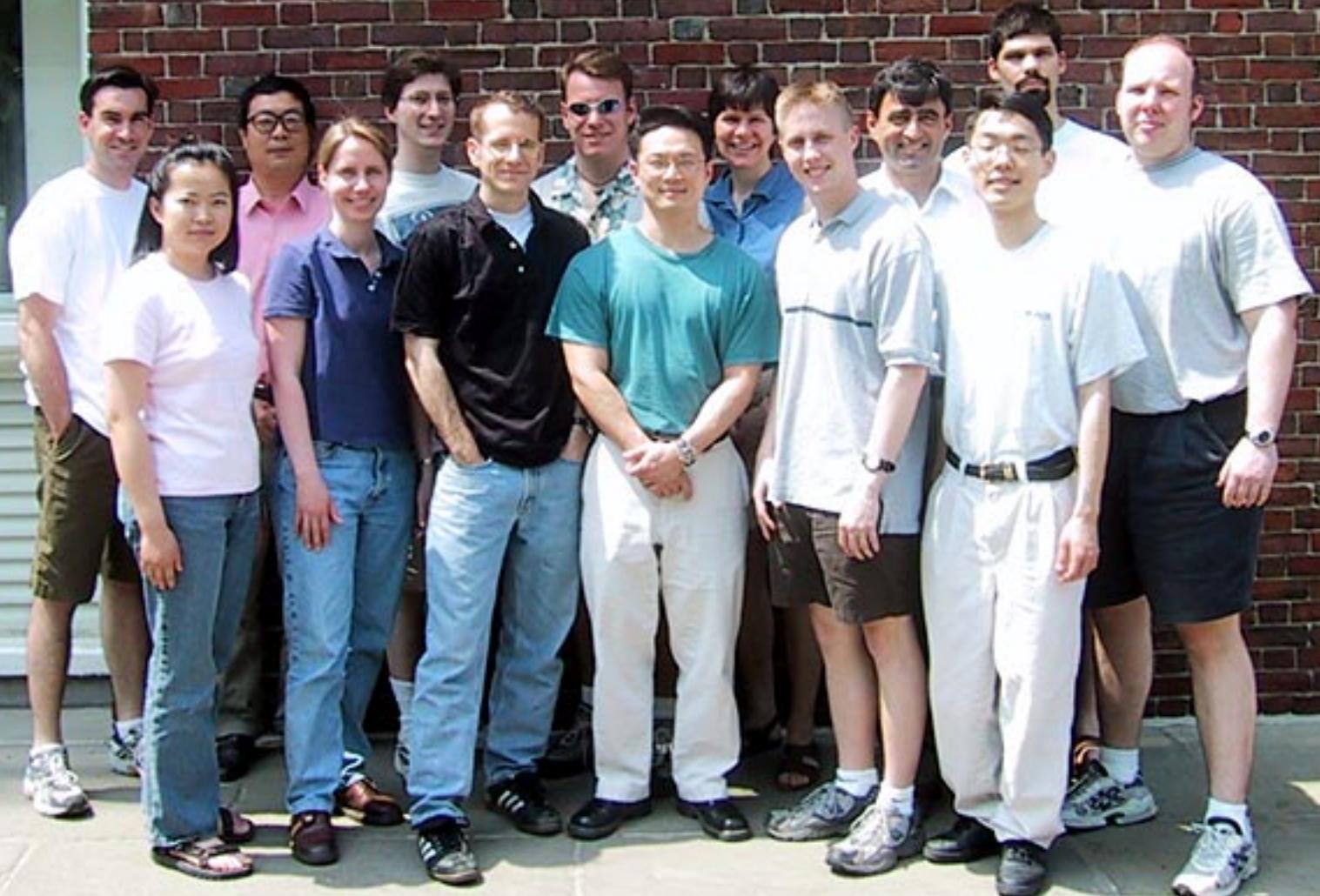
- ▶ **fabricated by simple, maskless process**
- ▶ **can be integrated with microelectronics**
- ▶ **generates IR photocurrent**
- ▶ **provides stable, high field emission current**

## *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. Tom Mates (UCSB)**

**Dr. John Chervinsky (Harvard University)**

**Prof. Cynthia Friend (Harvard University)**

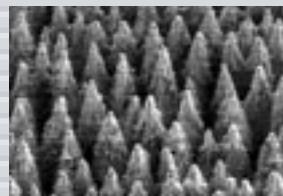
**Prof. Mike Aziz (Harvard University)**

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

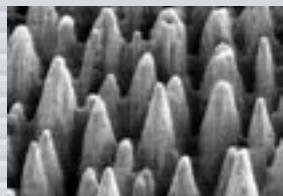
**<http://mazur-www.harvard.edu>**

# *Materials*

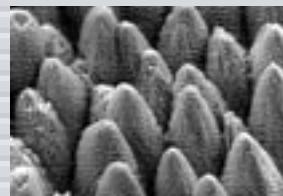
SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>

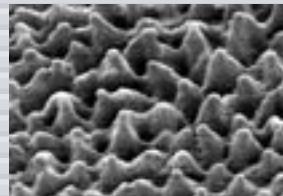


air



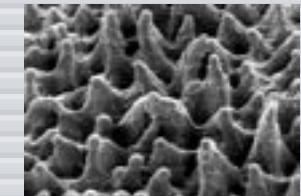
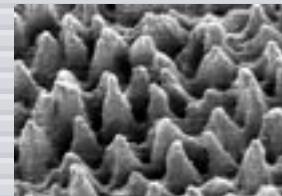
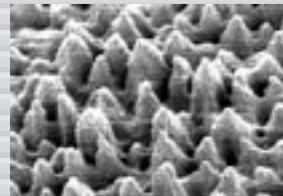
vacuum

Si

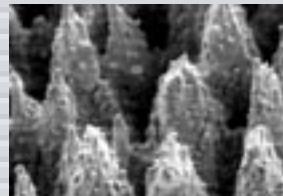


Ti

reacts



Only in SF<sub>6</sub>:



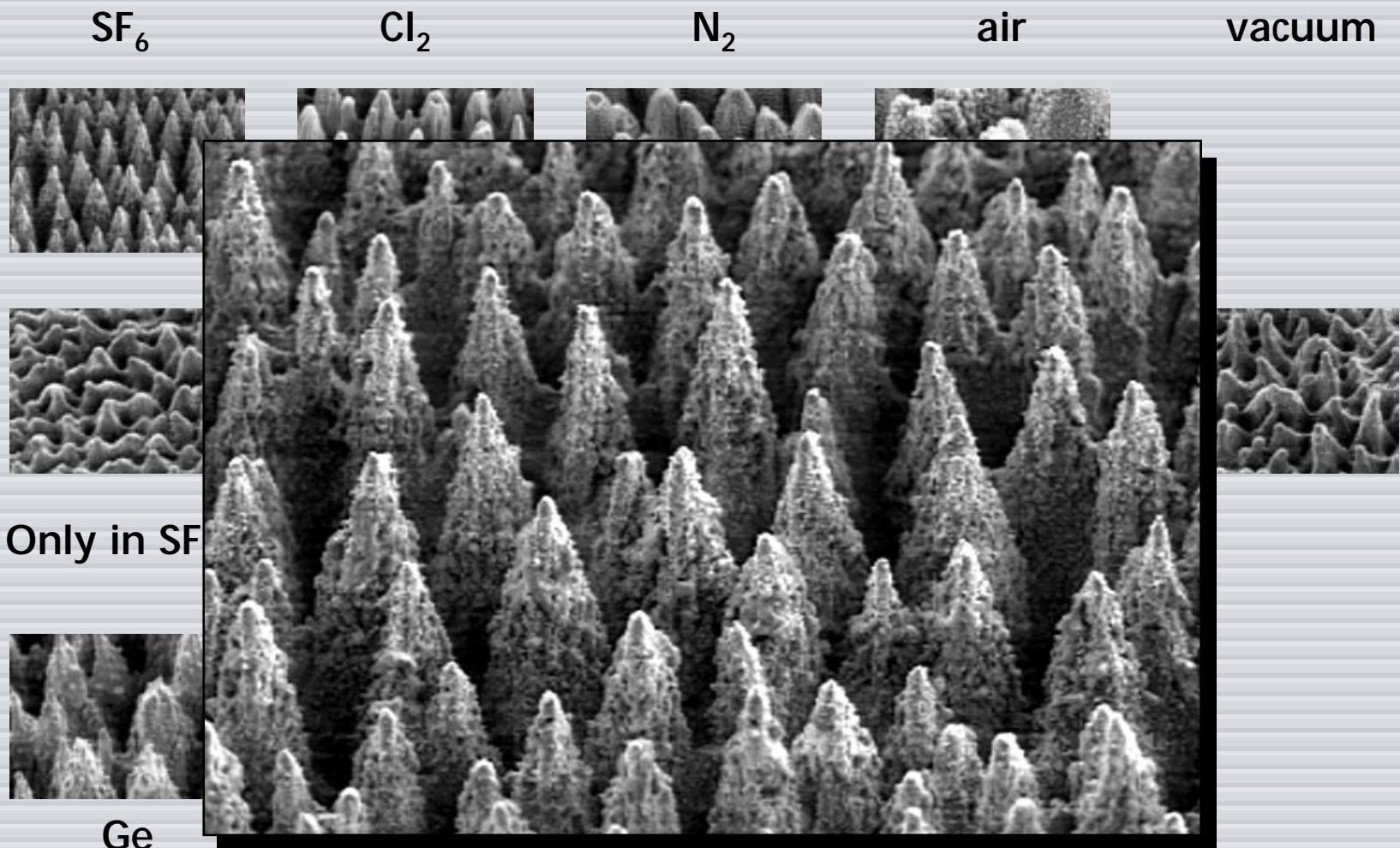
Ge



InP

No spikes in SF<sub>6</sub>: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

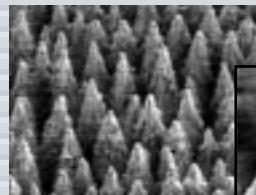
# *Materials*



No spikes in SF<sub>6</sub>: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

# *Materials*

SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>



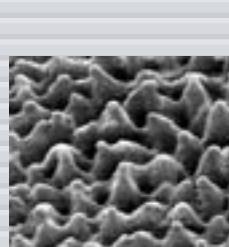
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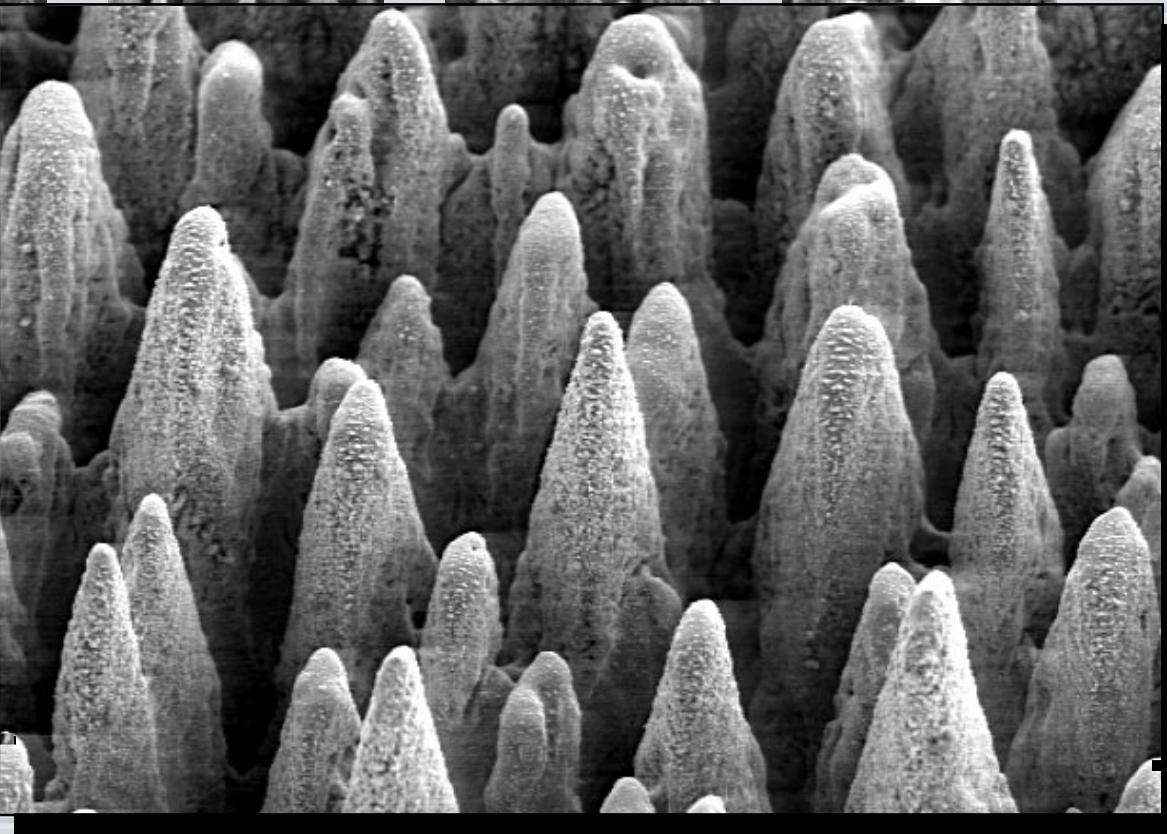
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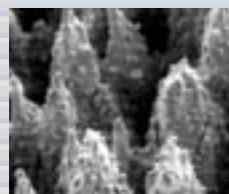
Si



Ti



Only in SF<sub>6</sub>

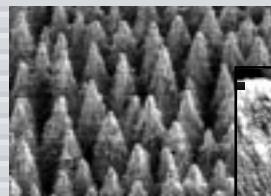


Ge

No spikes in SF<sub>6</sub>: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

# *Materials*

SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>

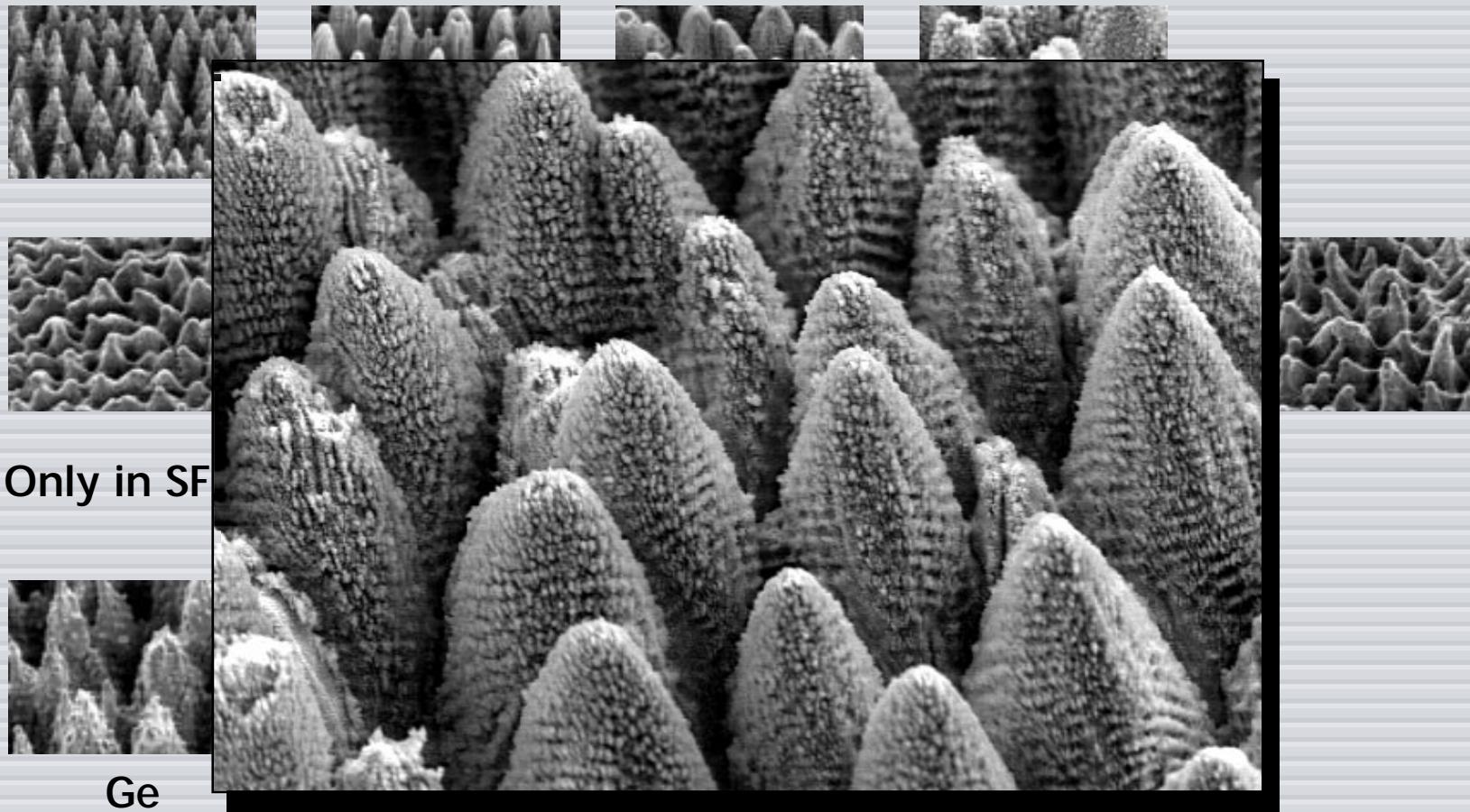


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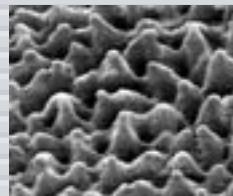


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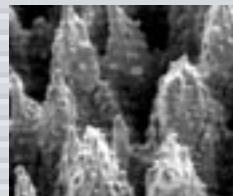
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Ti



Only in SF<sub>6</sub>

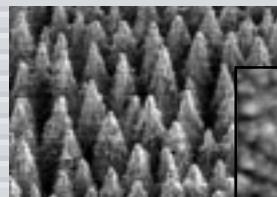


Ge

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# *Materials*

SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>



air

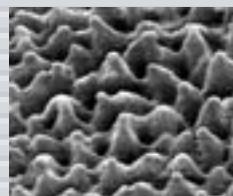


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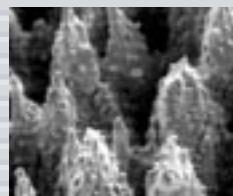
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Ti



Only in SF<sub>6</sub>

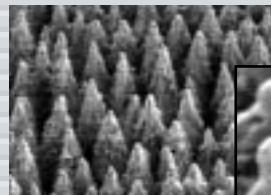


Ge

No spikes in SF<sub>6</sub>: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

# *Materials*

SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>

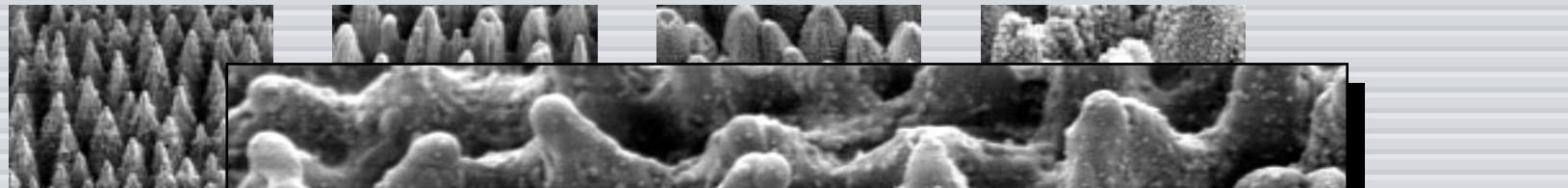


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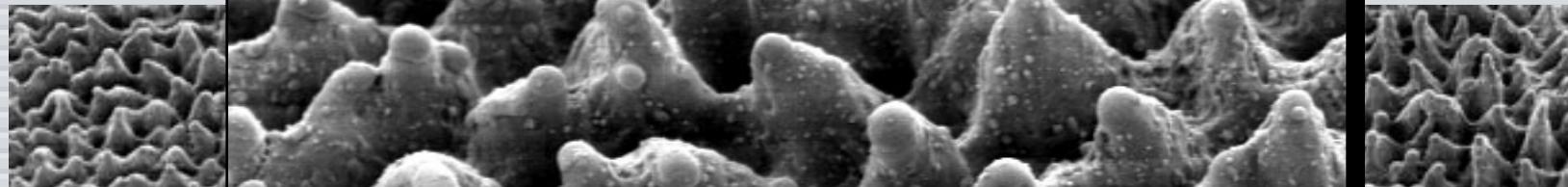


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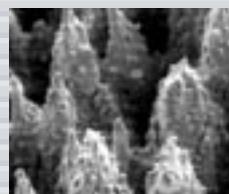
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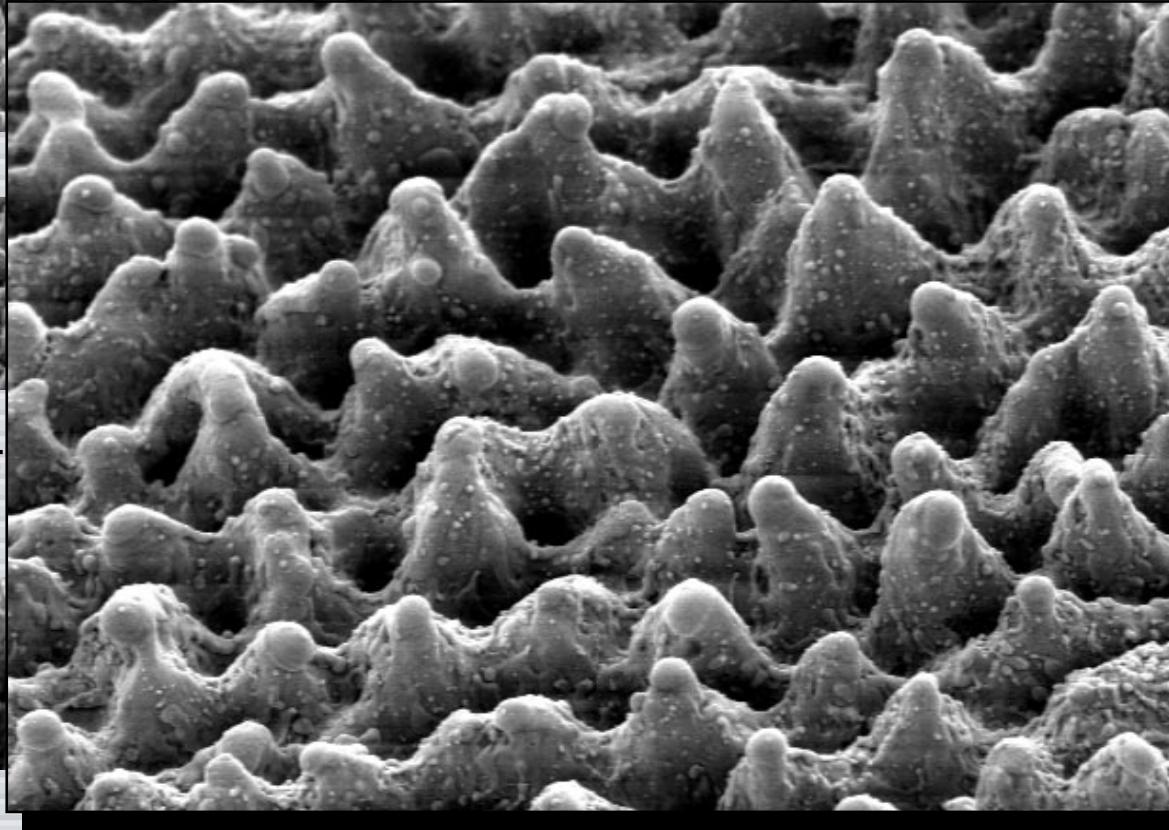
Ti



Only in SF<sub>6</sub>

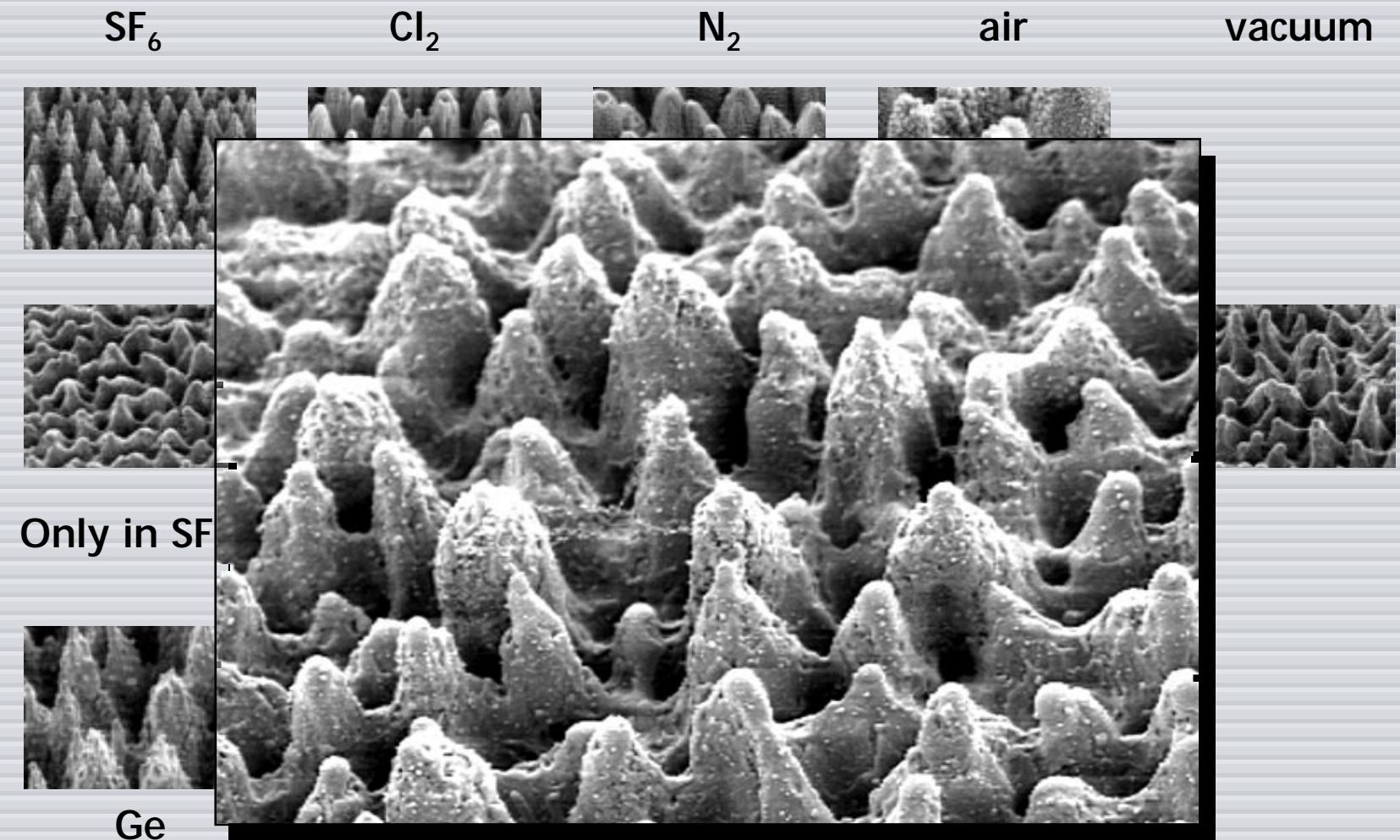


Ge



No spikes in SF<sub>6</sub>: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

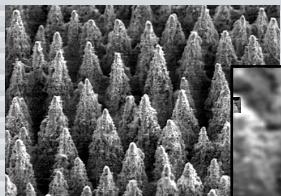
# *Materials*



No spikes in SF<sub>6</sub>: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

# *Materials*

SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>

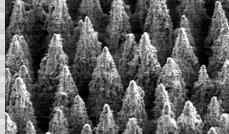


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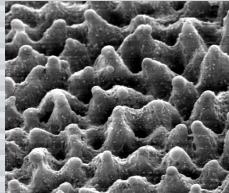


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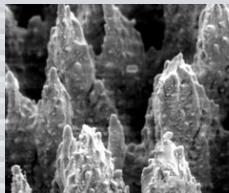
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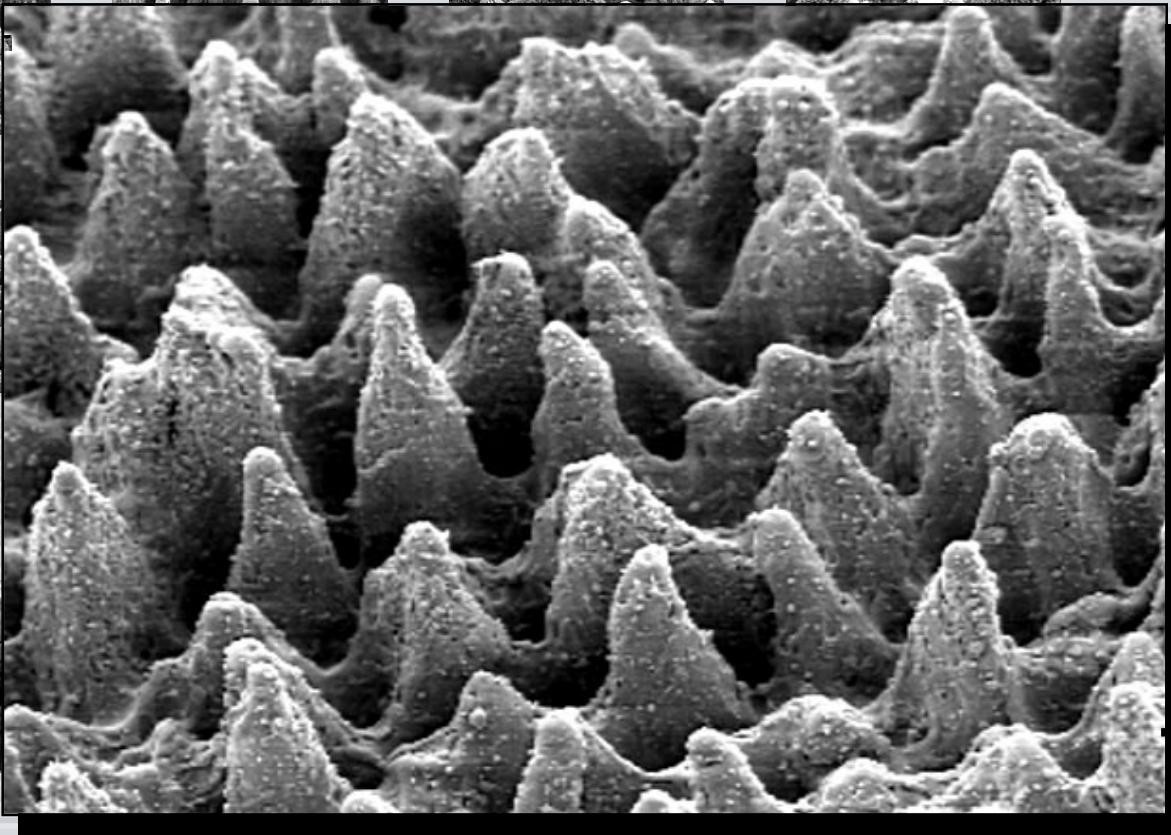
Ti



Only in SF<sub>6</sub>



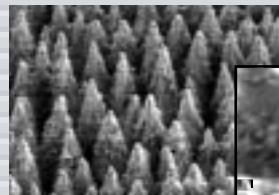
Ge



No spikes in SF<sub>6</sub>: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

# *Materials*

SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>

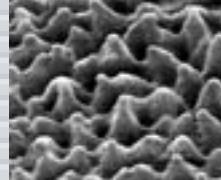


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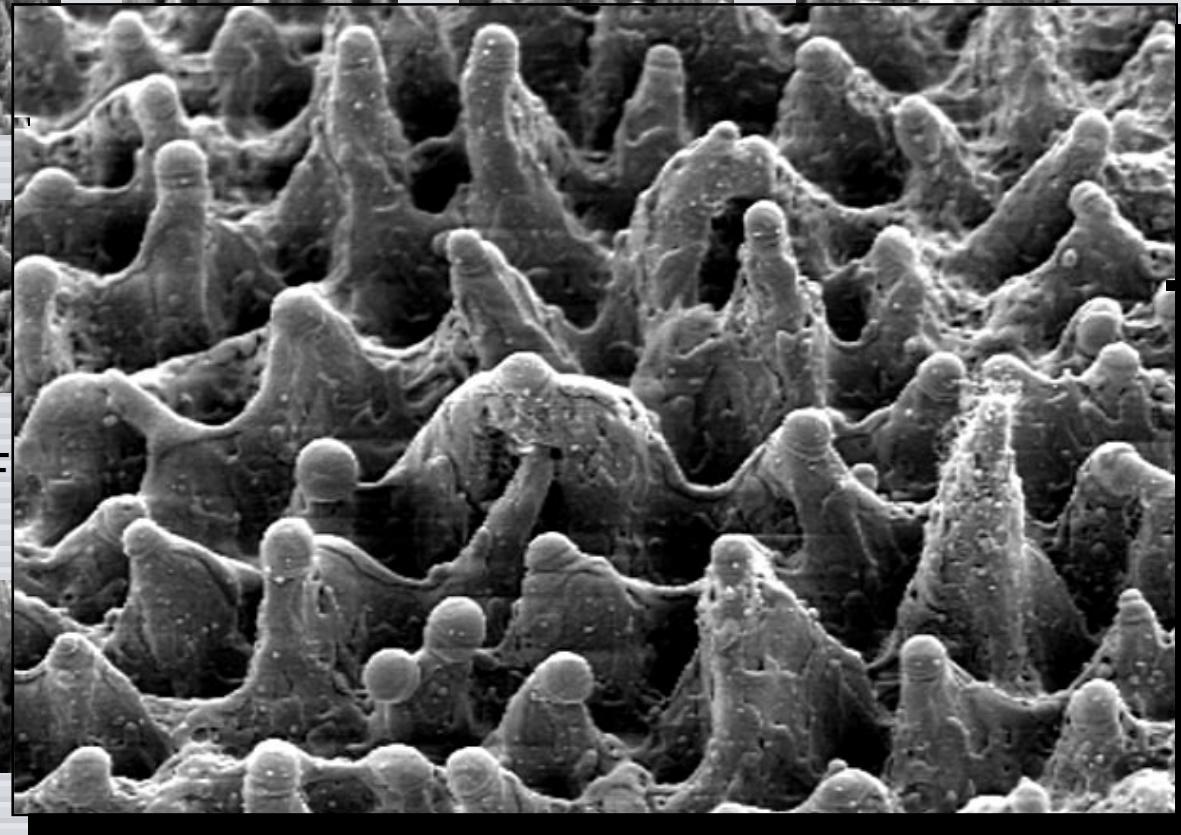


vacuum

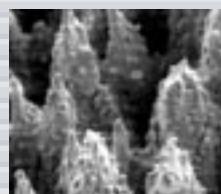
Si



Ti



Only in SF<sub>6</sub>

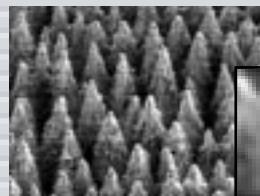


Ge

No spikes in SF<sub>6</sub>: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

# *Materials*

SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>

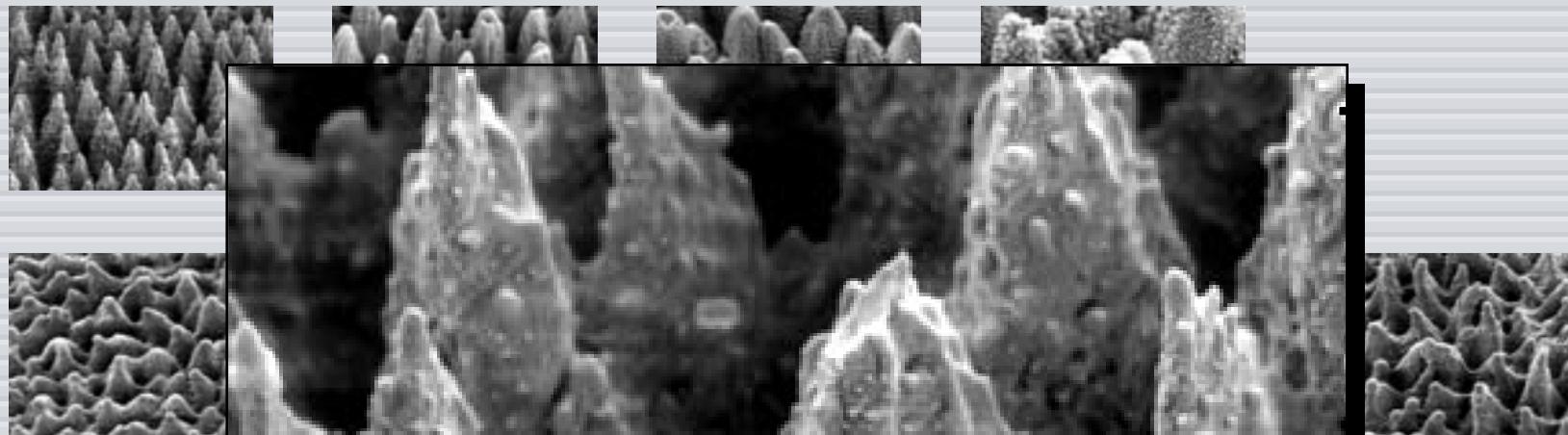


air

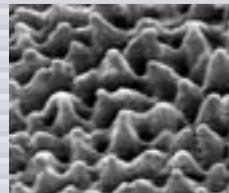


vacuum

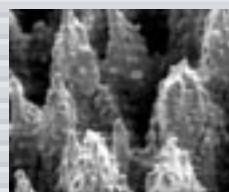
Si



Ti



Only in SF<sub>6</sub>

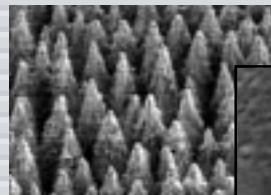


Ge

No spikes in SF<sub>6</sub>: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

# *Materials*

SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>

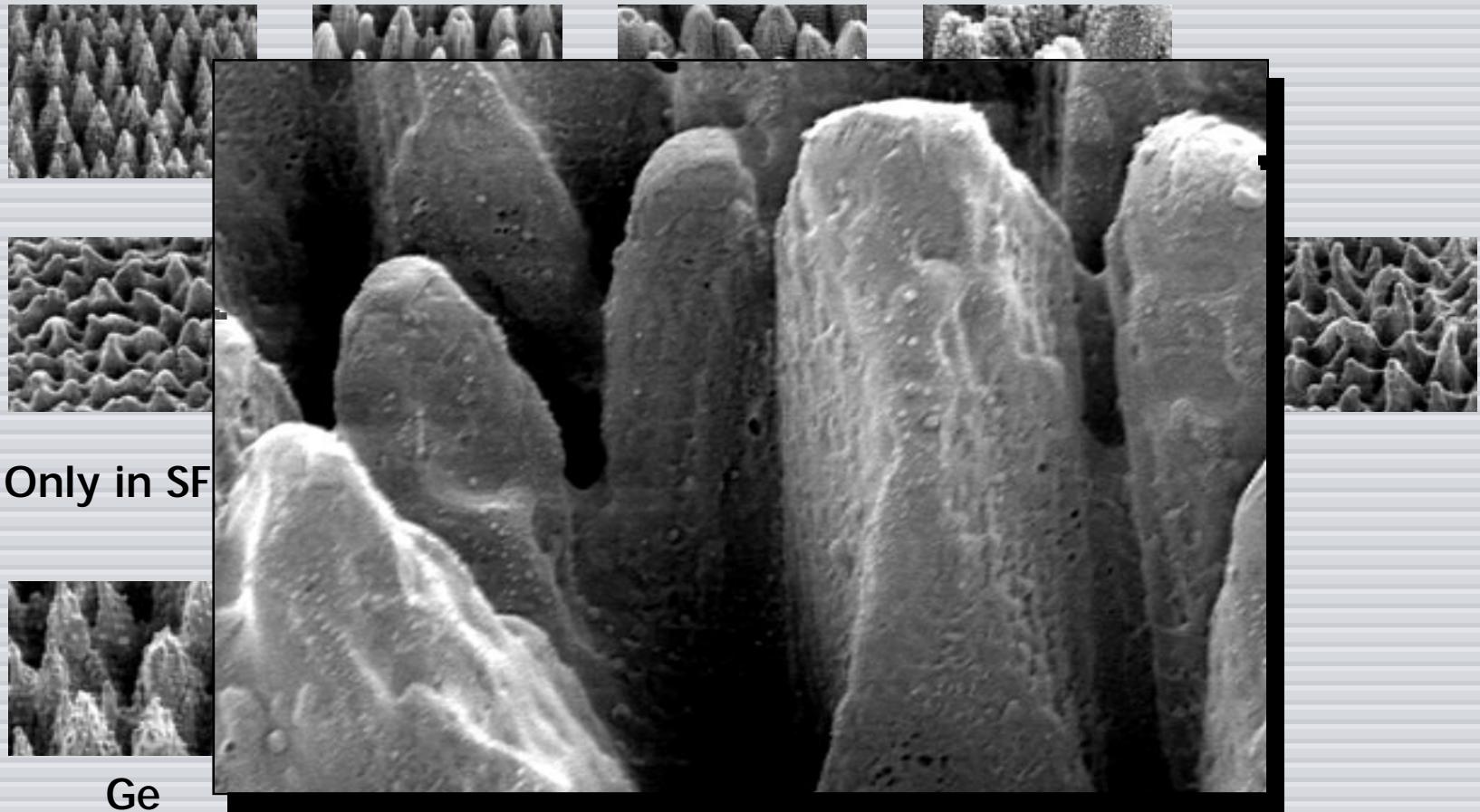


air

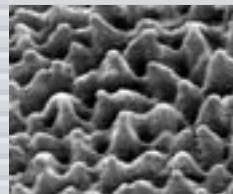


vacuum

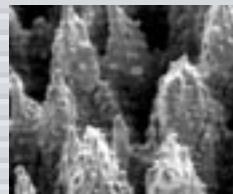
Si



Ti



Only in SF<sub>6</sub>



Ge

No spikes in SF<sub>6</sub>: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs