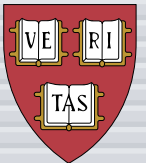
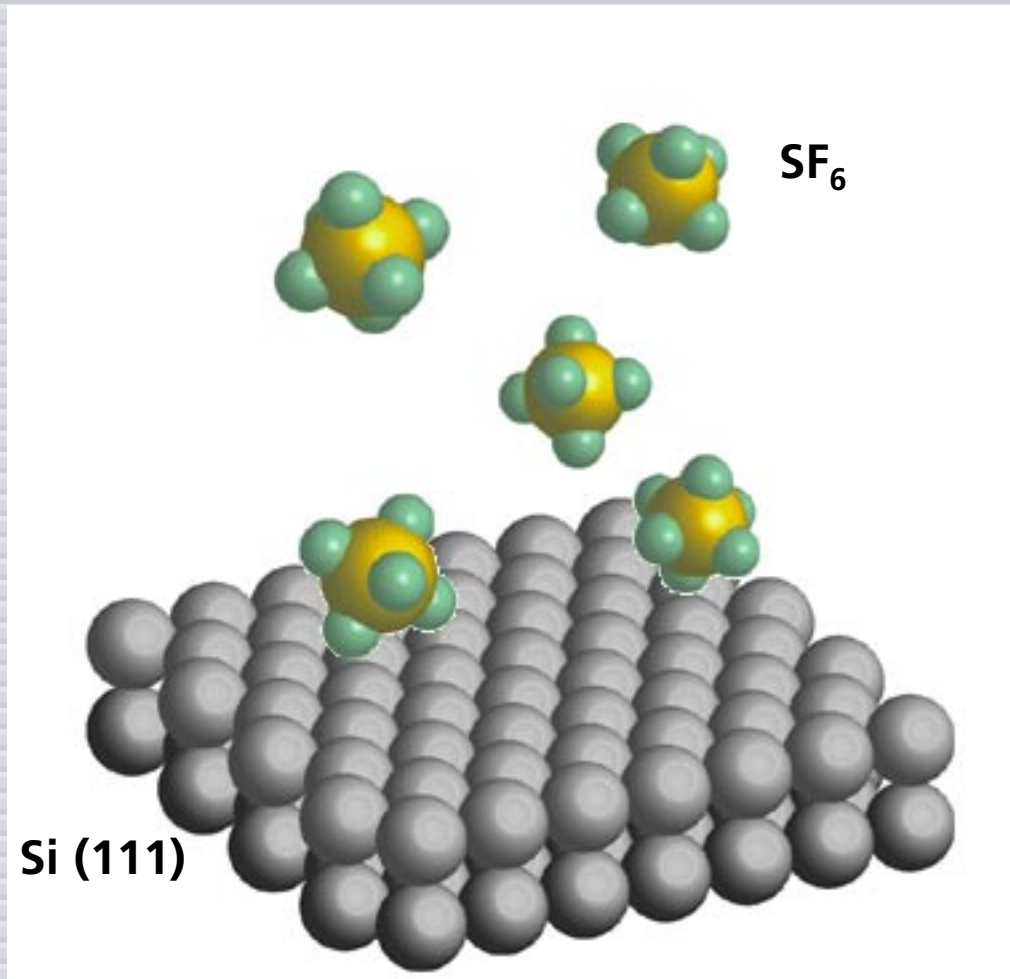


# **Femtosecond laser-assisted microstructuring of silicon surfaces for novel detector, sensing, and display technologies**

**Eric Mazur  
Jim Carey  
Mikey Sheehy  
Catherine Crouch  
Meng Yan Shen  
Harvard University**

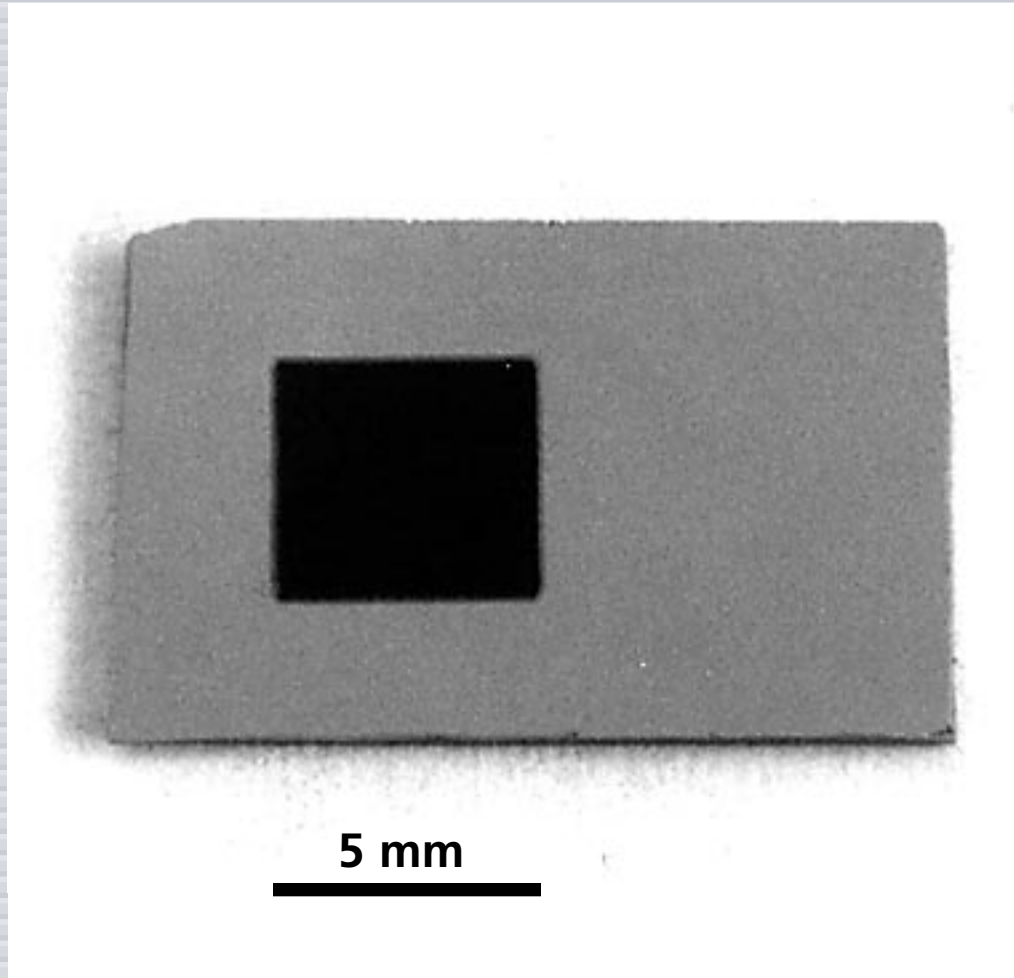


# Introduction



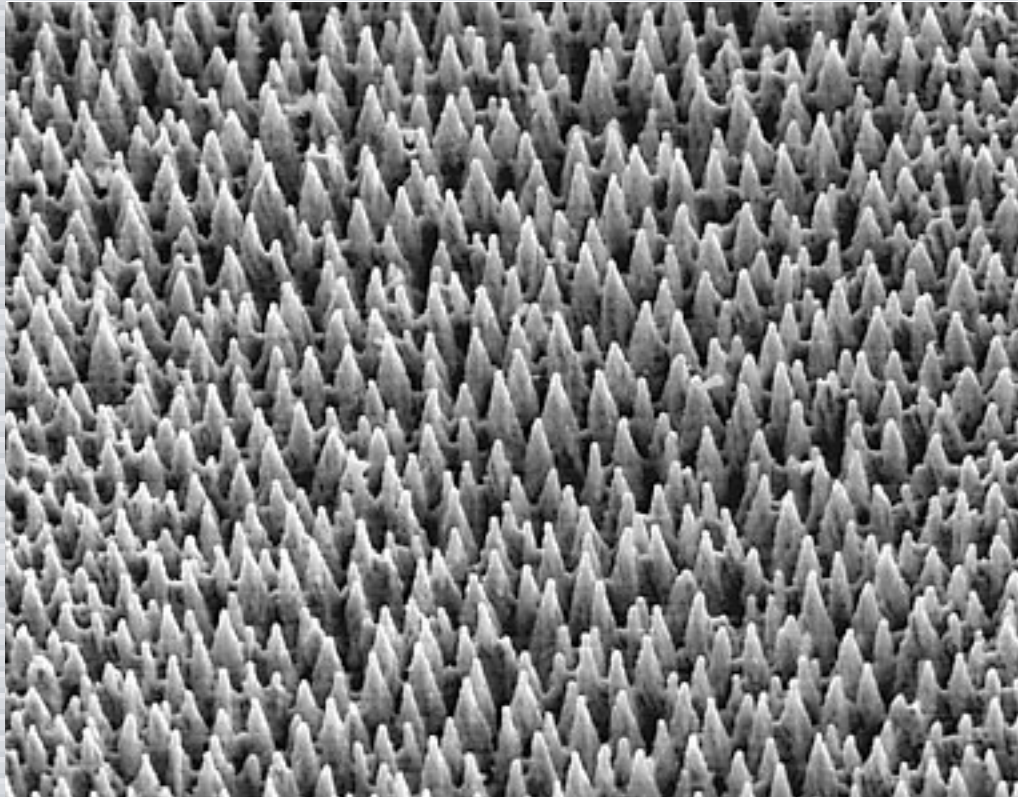
irradiate with 100-fs 10 kJ/m<sup>2</sup> pulses

# *Introduction*



**"black silicon"**

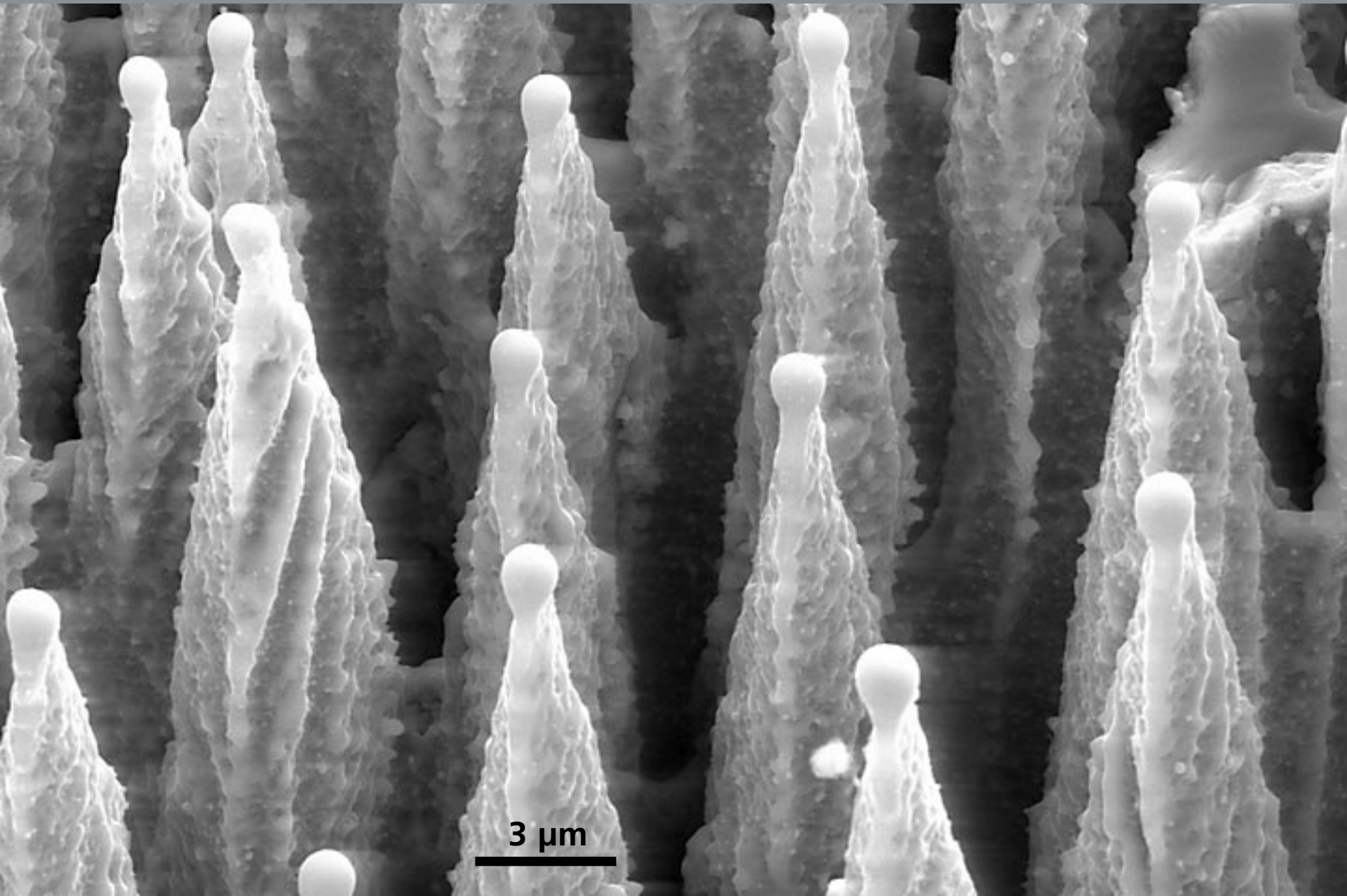
# *Introduction*



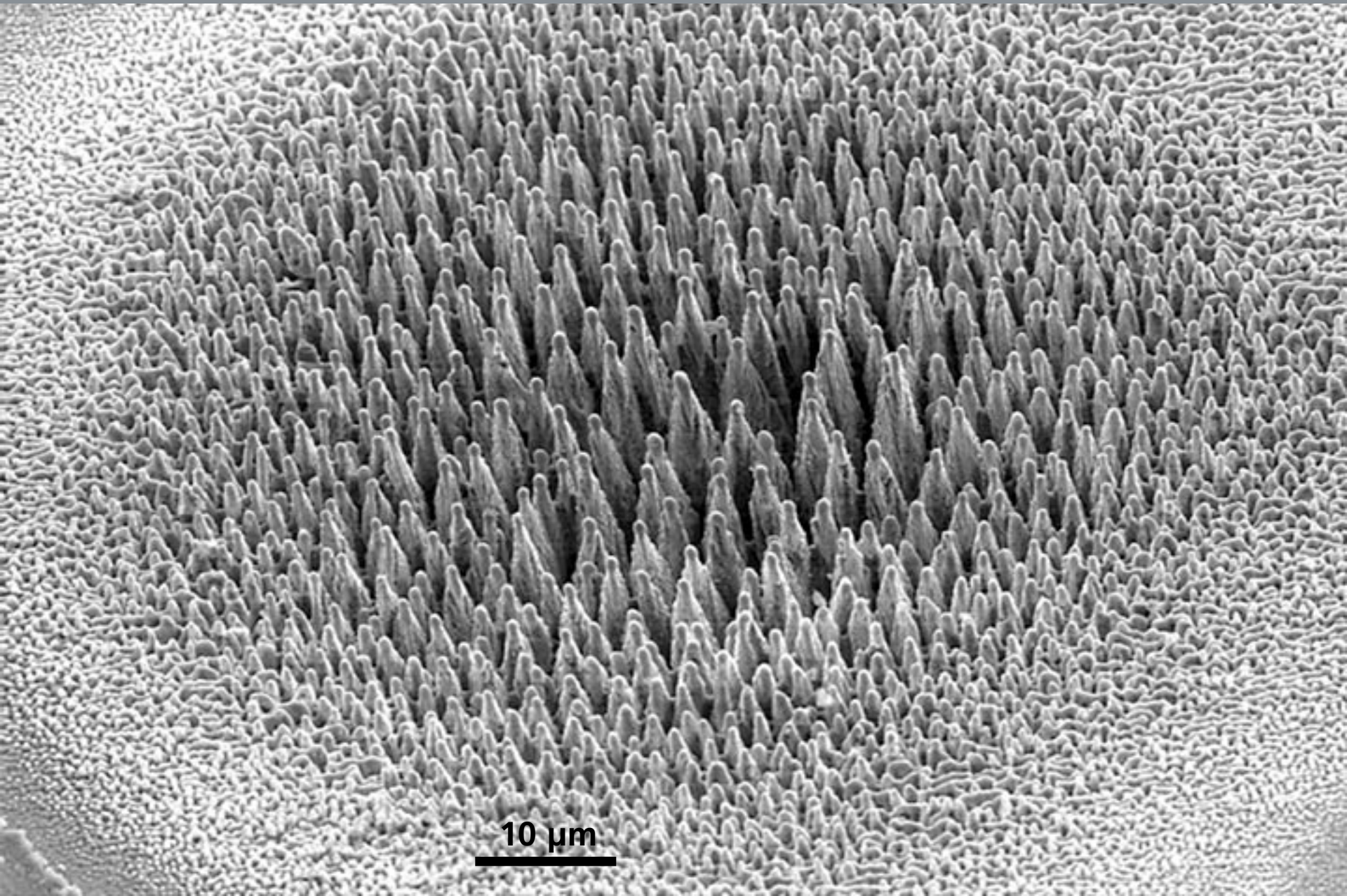
**20  $\mu\text{m}$**



# *Introduction*



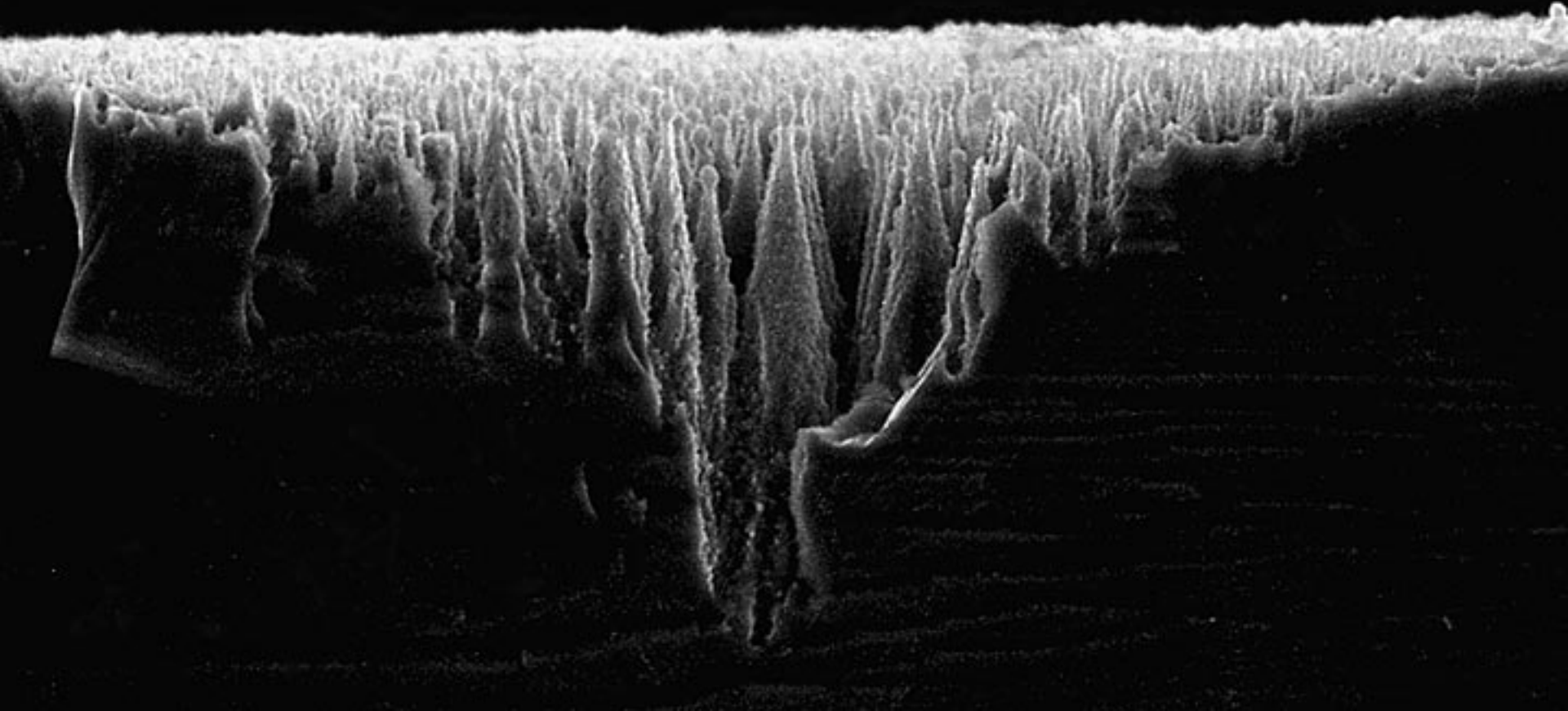
# *Introduction*



10  $\mu\text{m}$

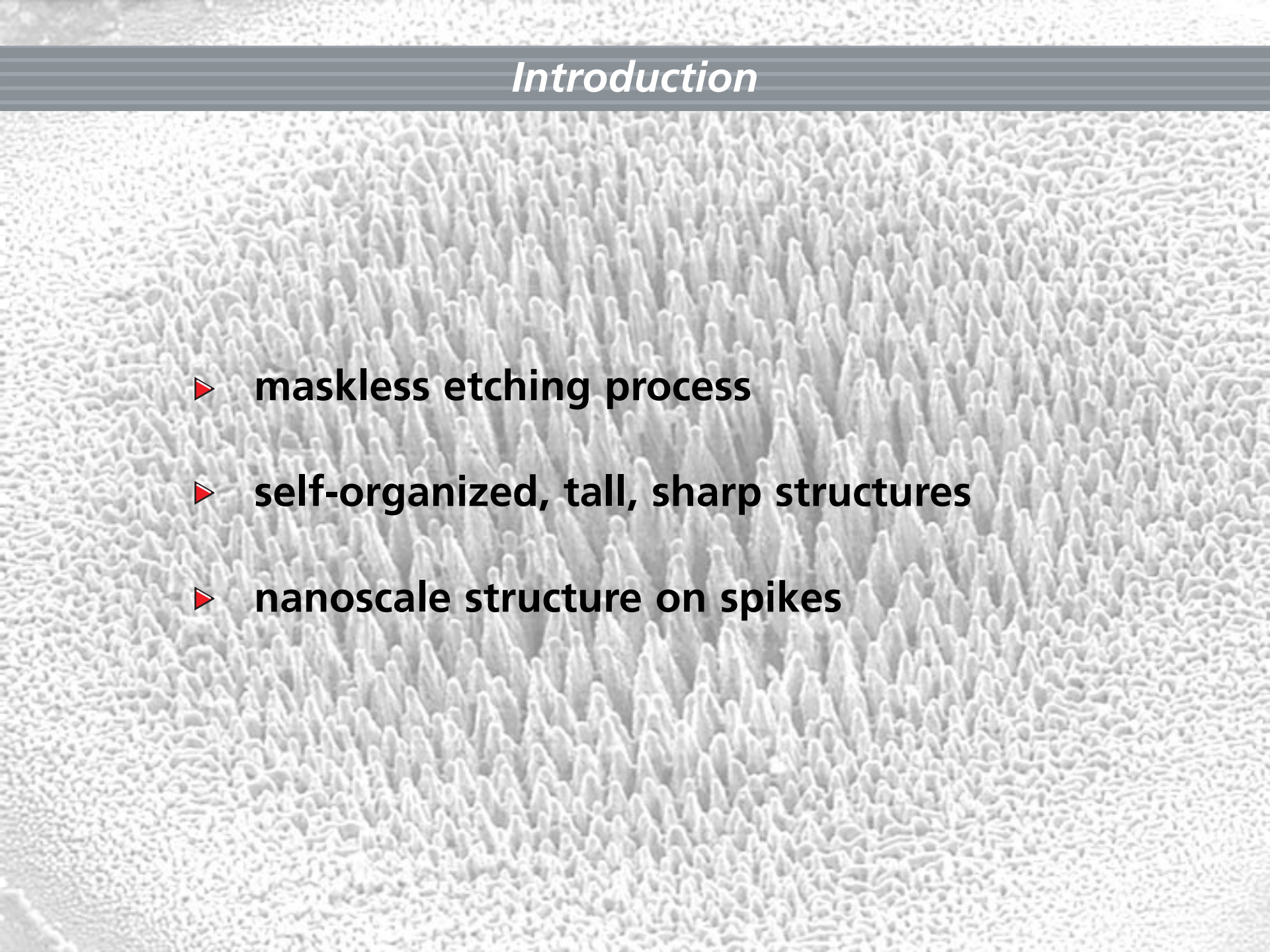


# *Introduction*



# *Introduction*

# *Introduction*

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

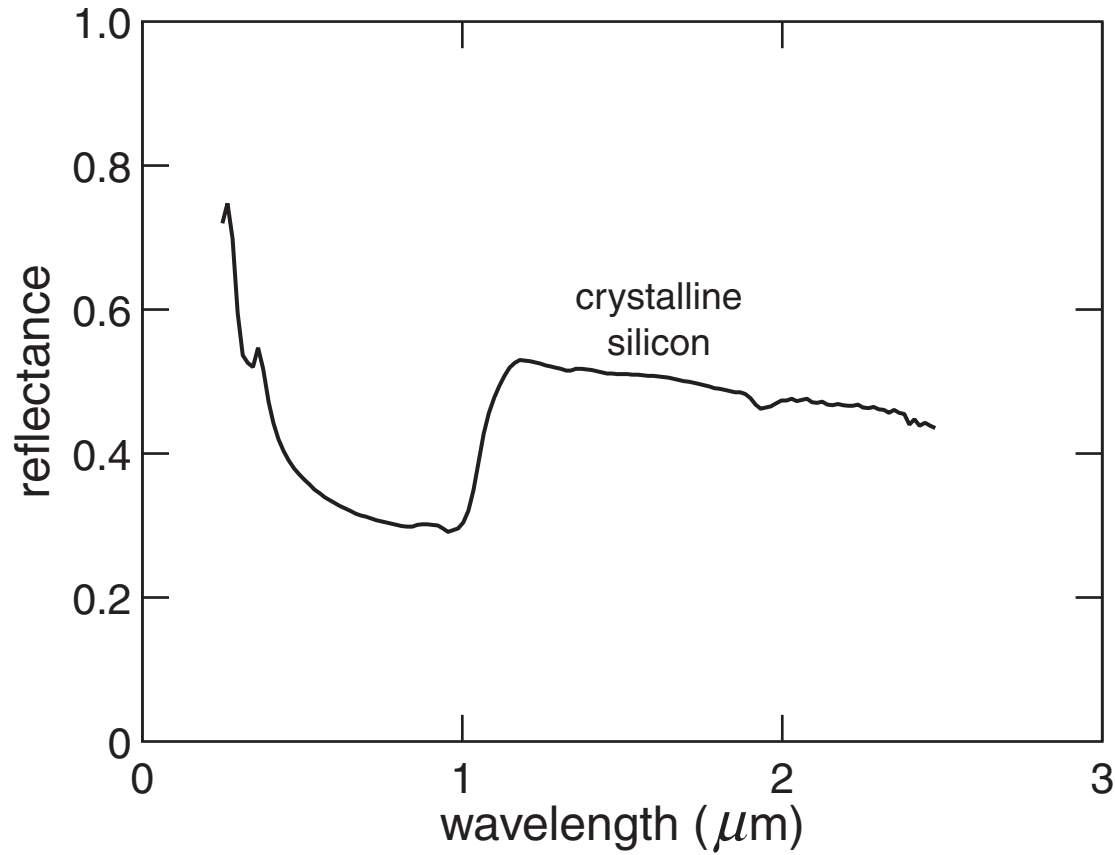


# Outline

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

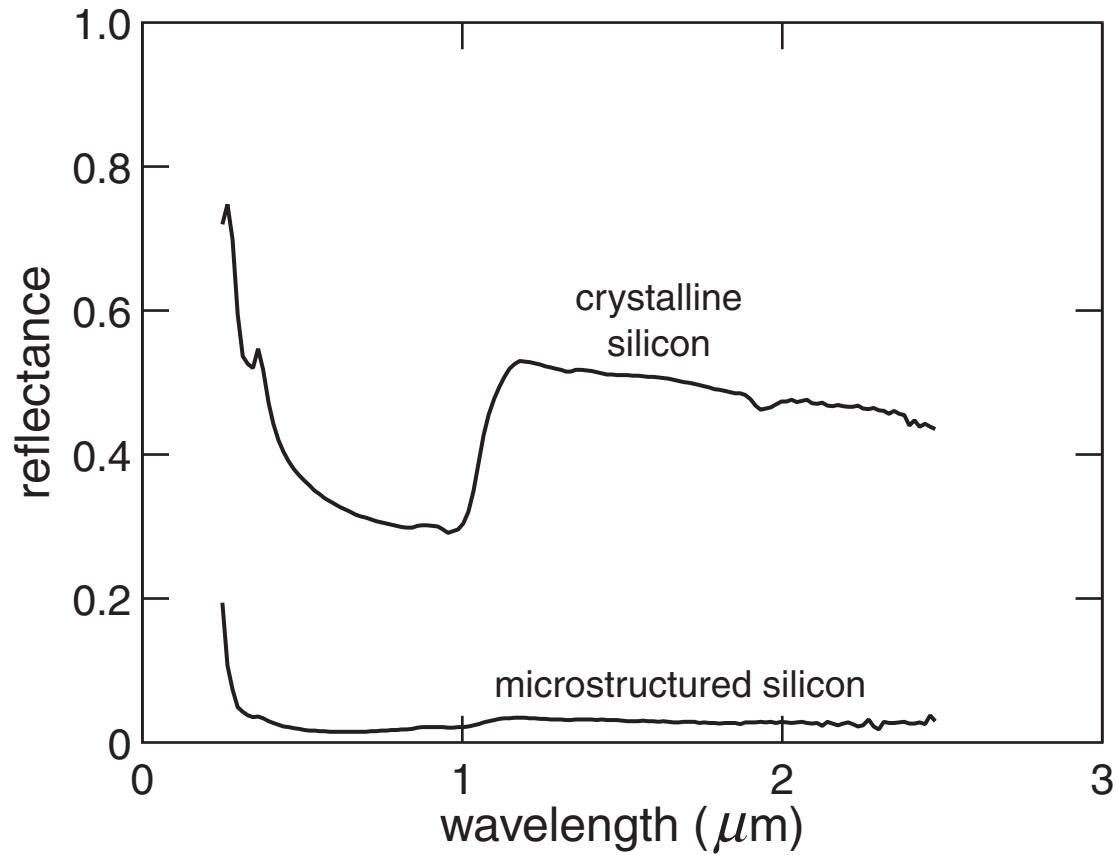
# *Properties*

## reflectance (integrating sphere)



# Properties

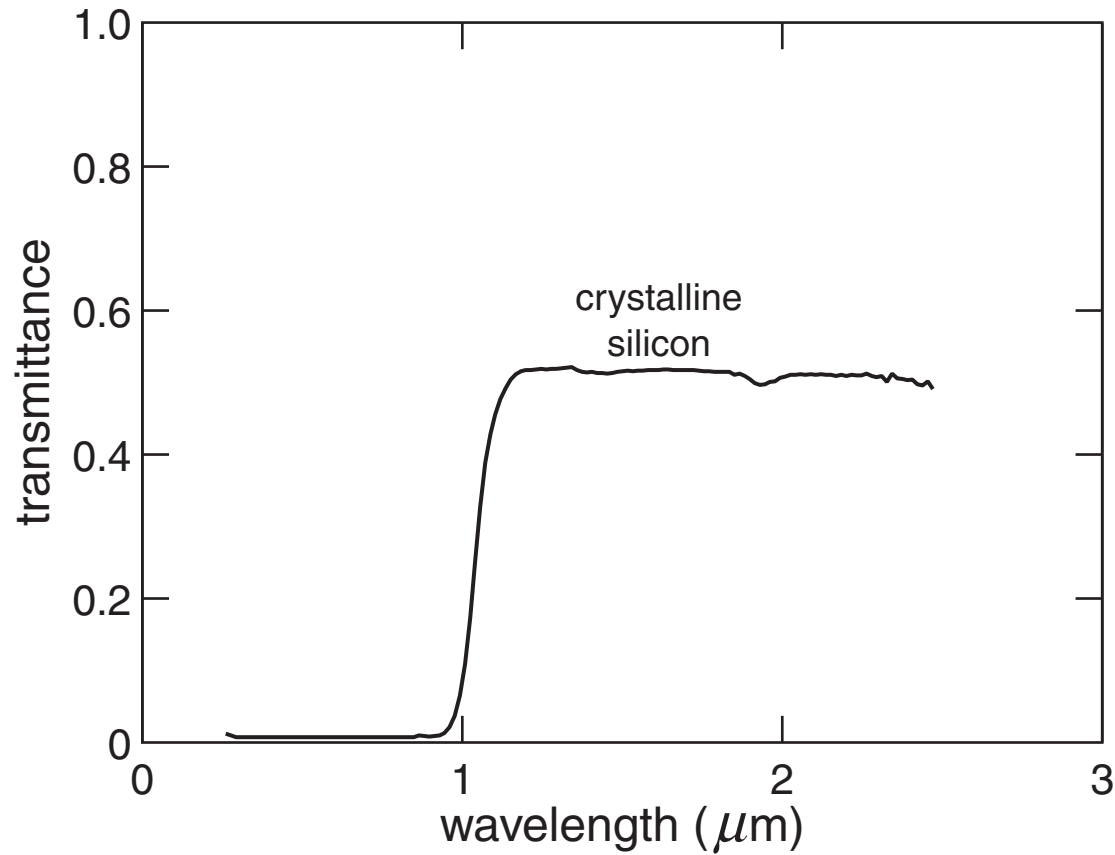
## reflectance (integrating sphere)





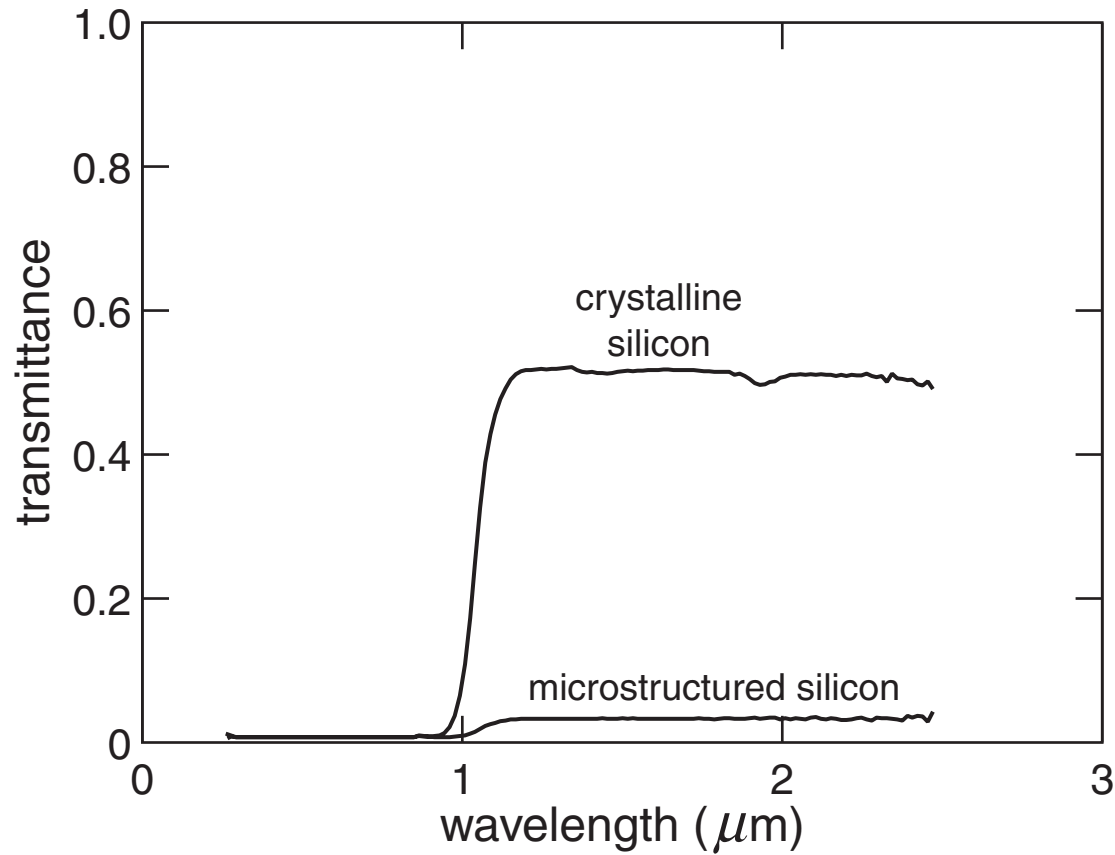
# Properties

## transmittance (integrating sphere)



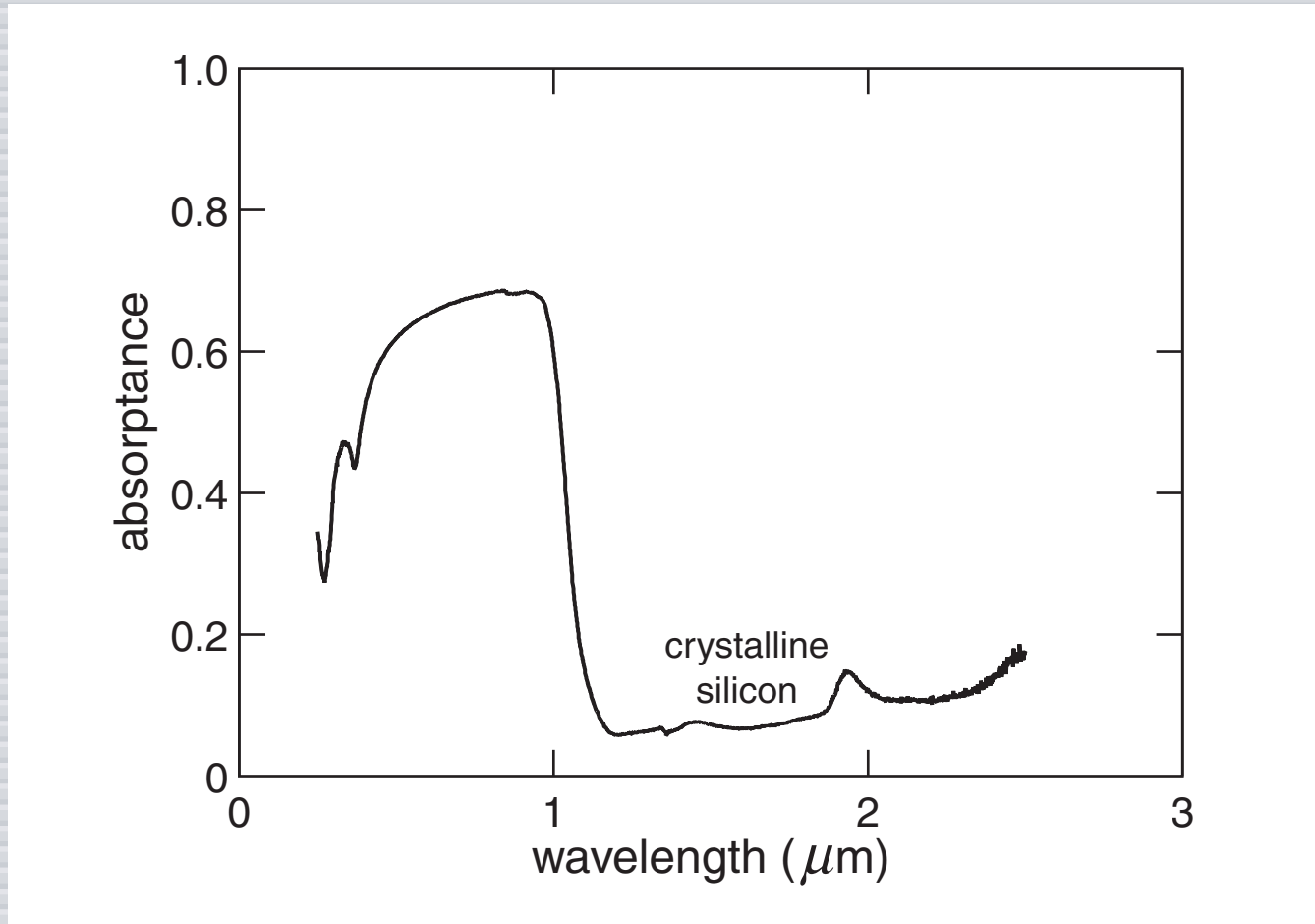
# Properties

## transmittance (integrating sphere)



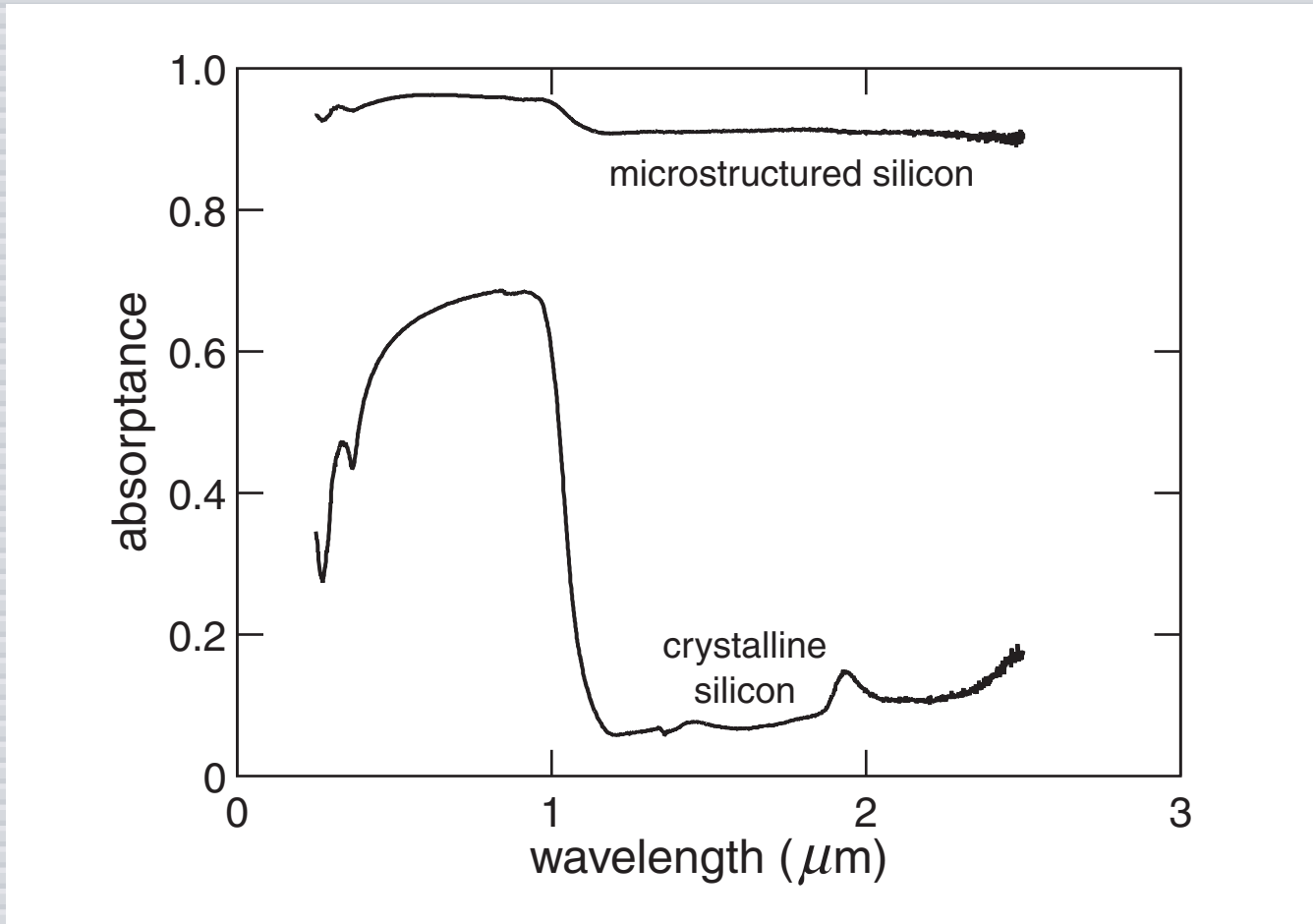
# Properties

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



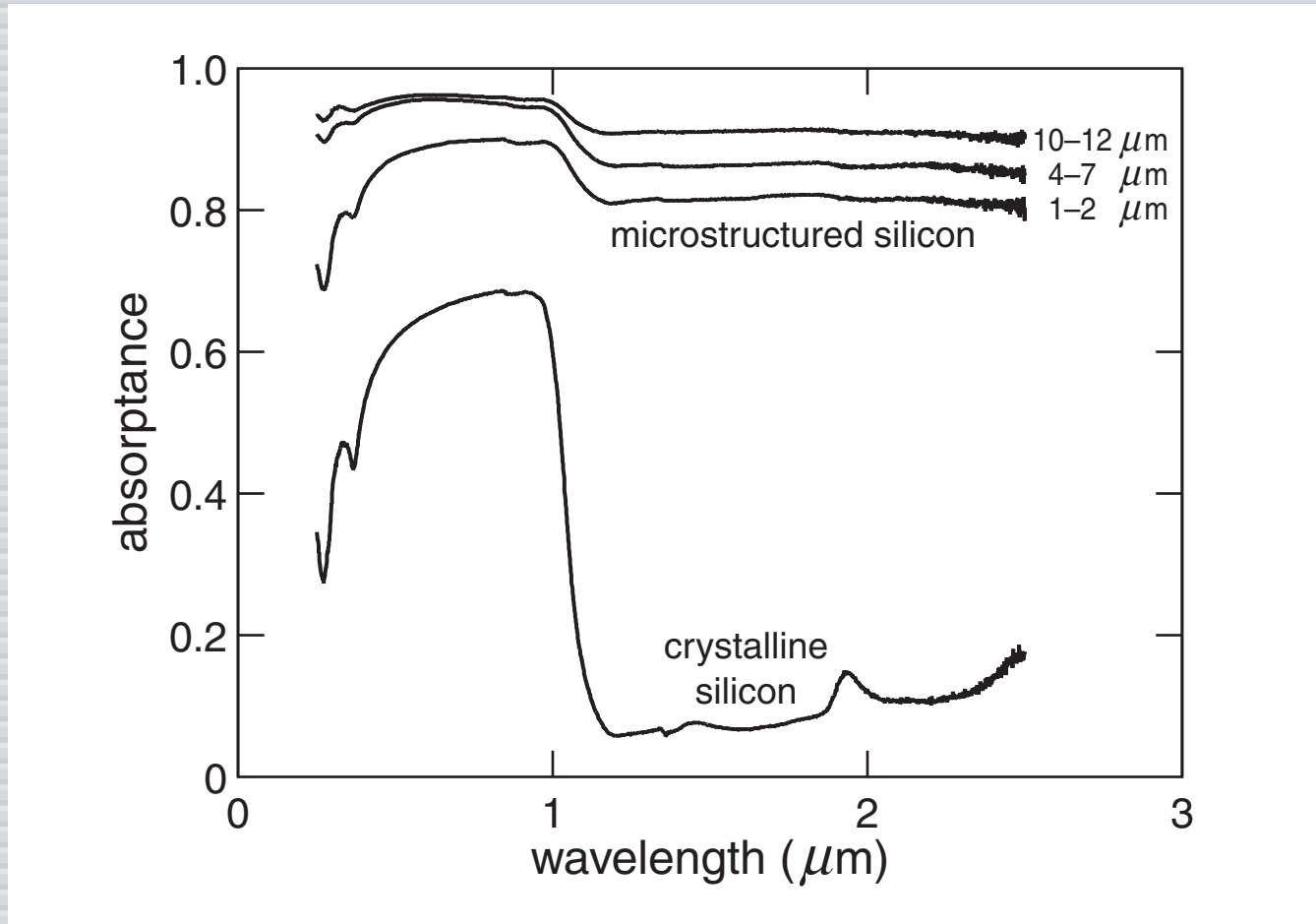
# Properties

absorptance ( $1 - R - T$ )



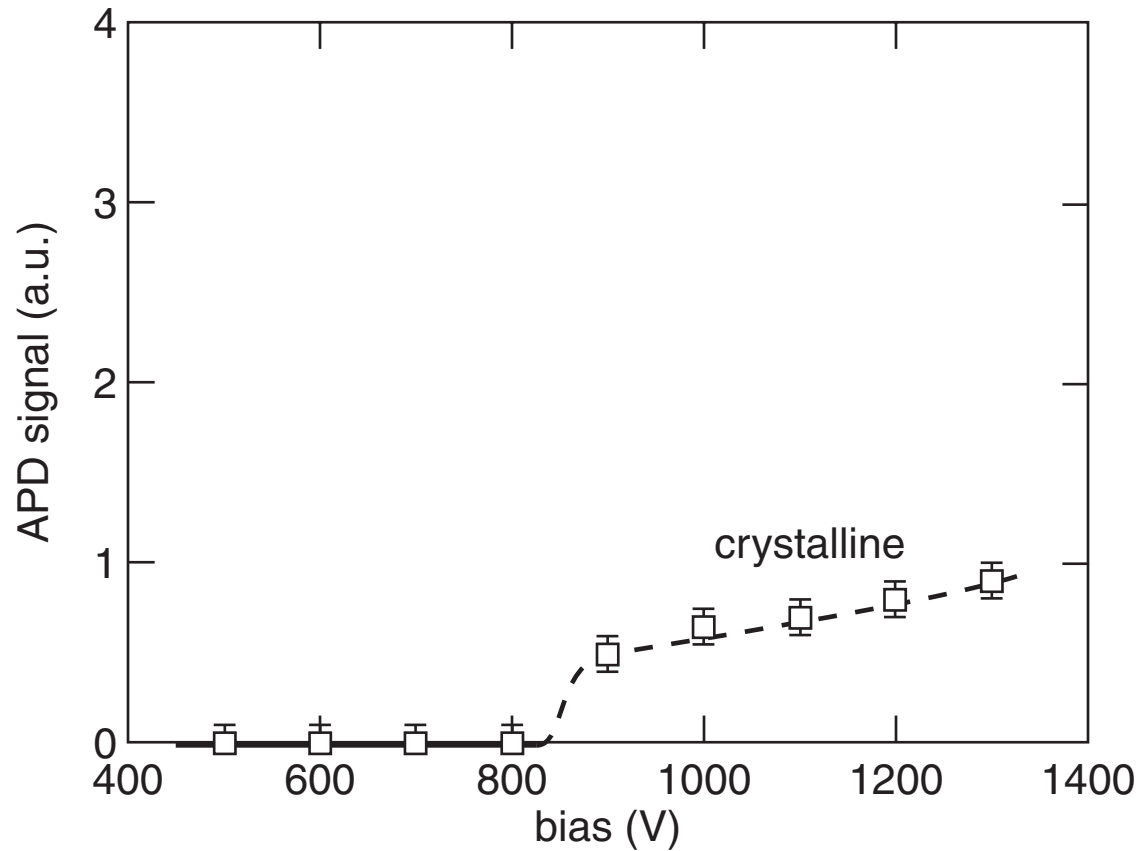
# Properties

absorptance ( $1 - R - T$ )



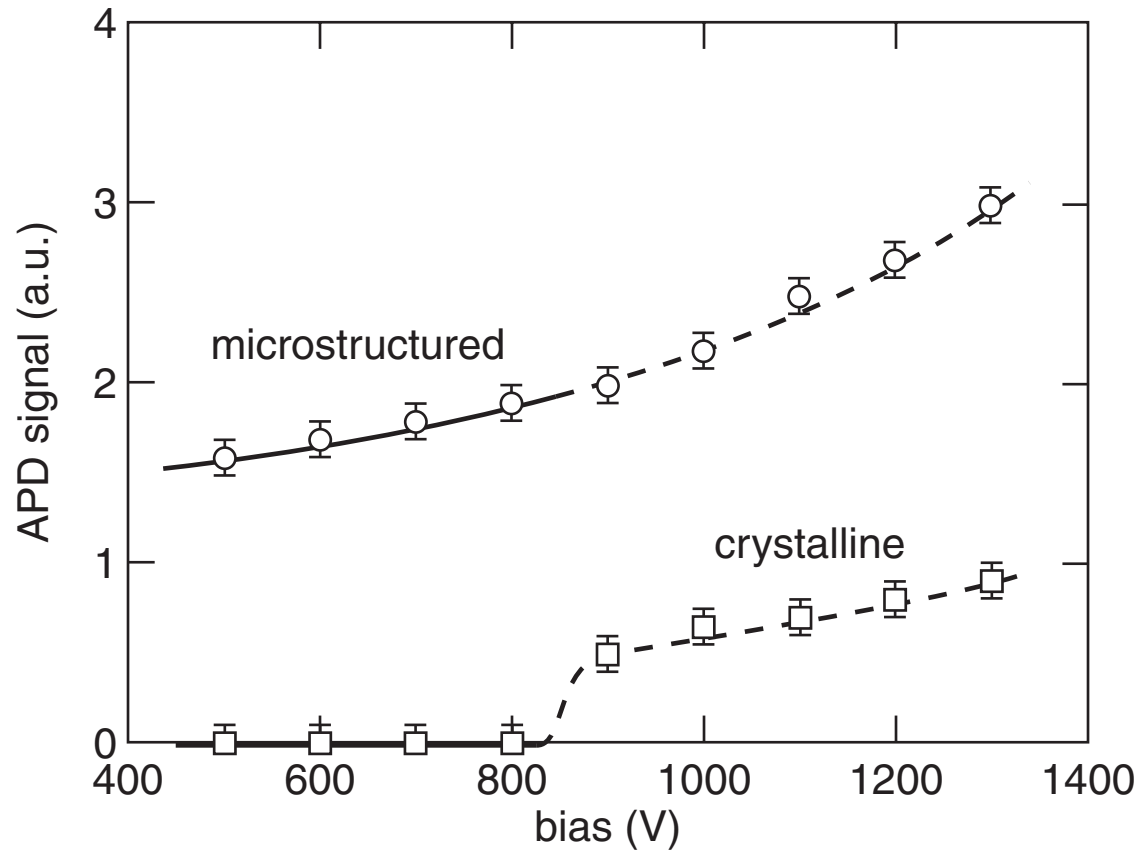
# Properties

## avalanche photodiode response at $1.3 \mu\text{m}$



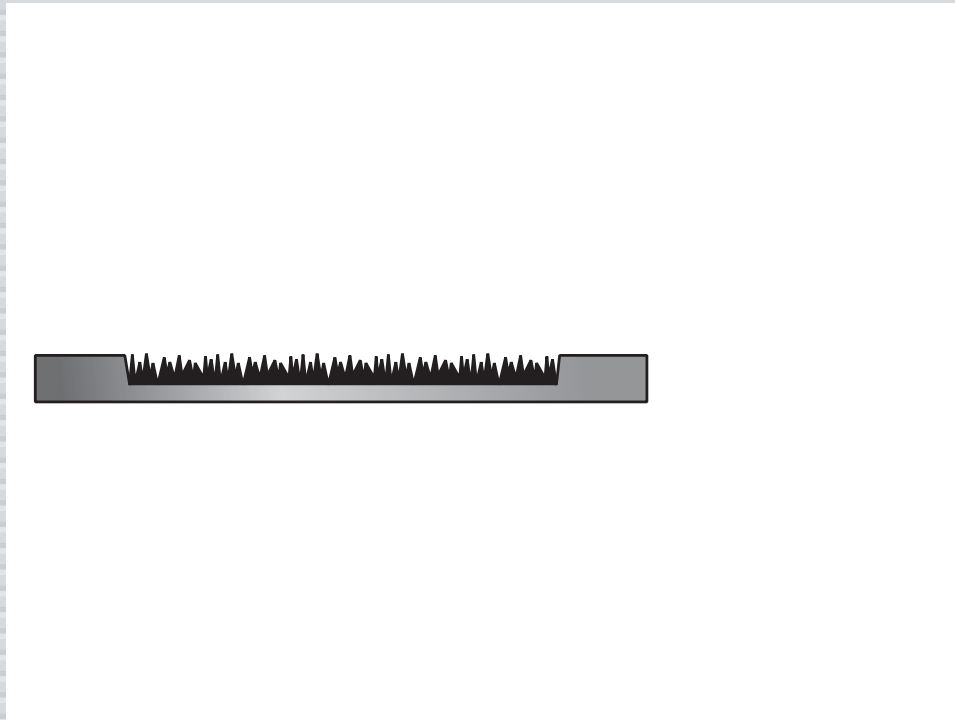
# Properties

## avalanche photodiode response at $1.3 \mu\text{m}$



# *Properties*

## **field emission setup**





# *Properties*

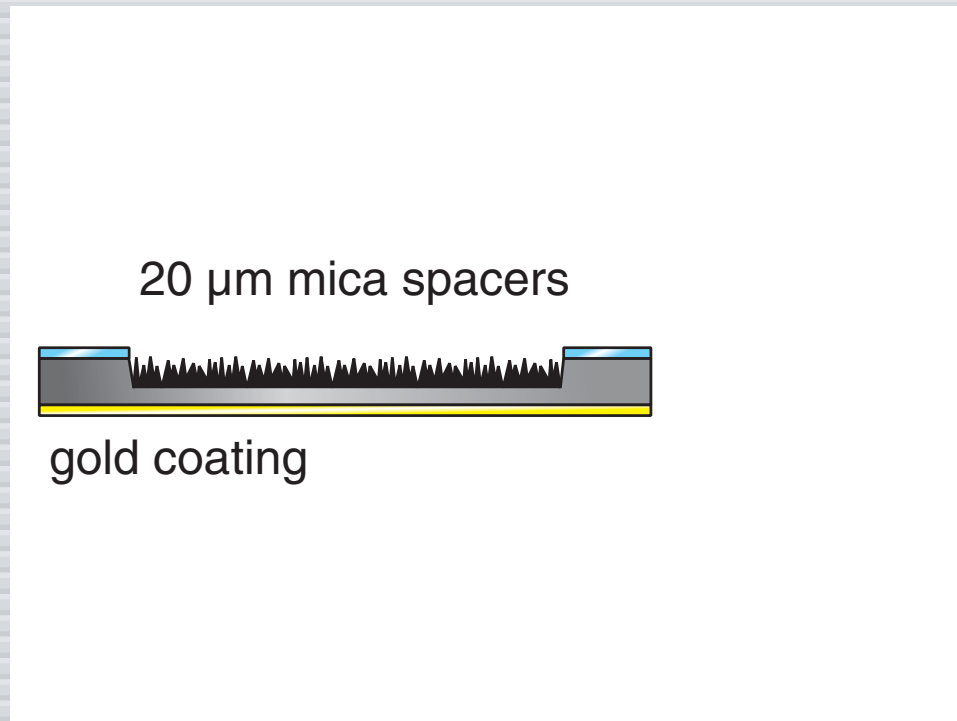
## **field emission setup**



gold coating

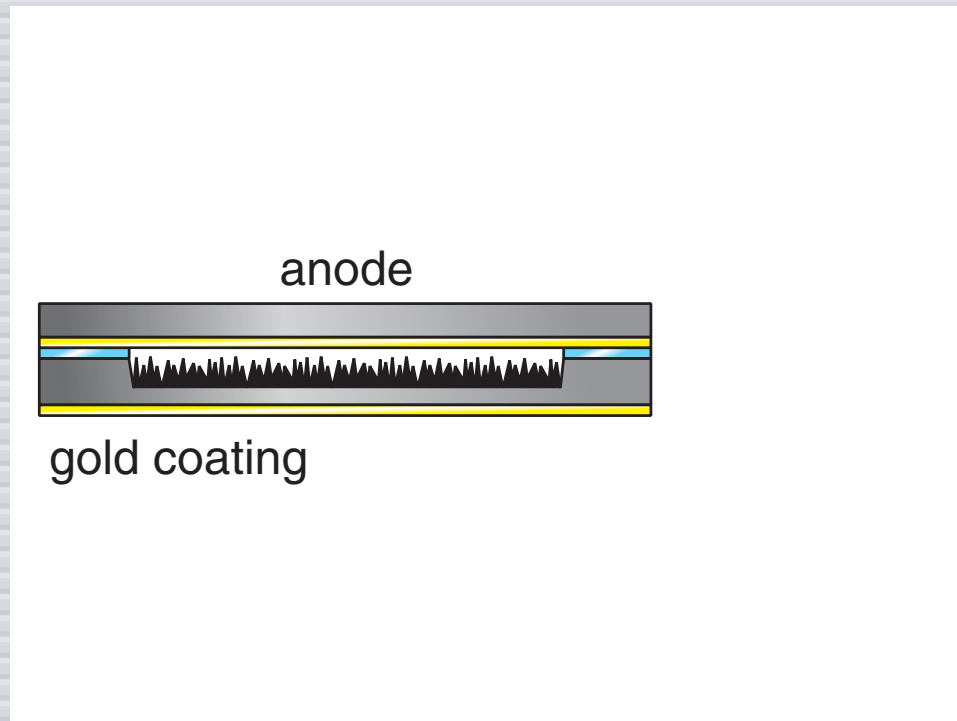
# *Properties*

## field emission setup



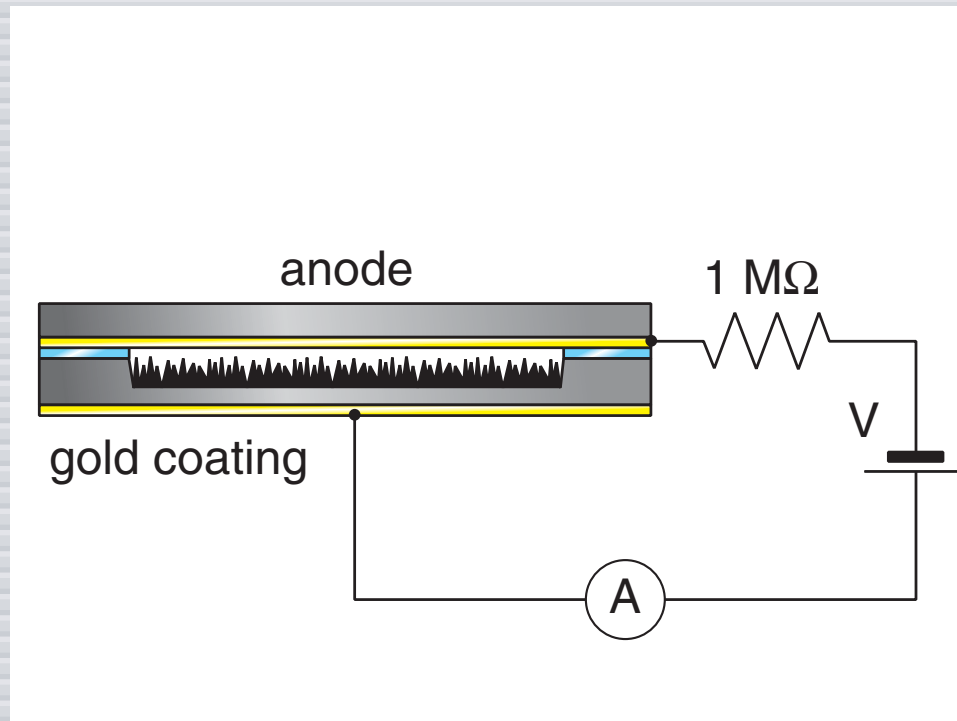
# *Properties*

## field emission setup

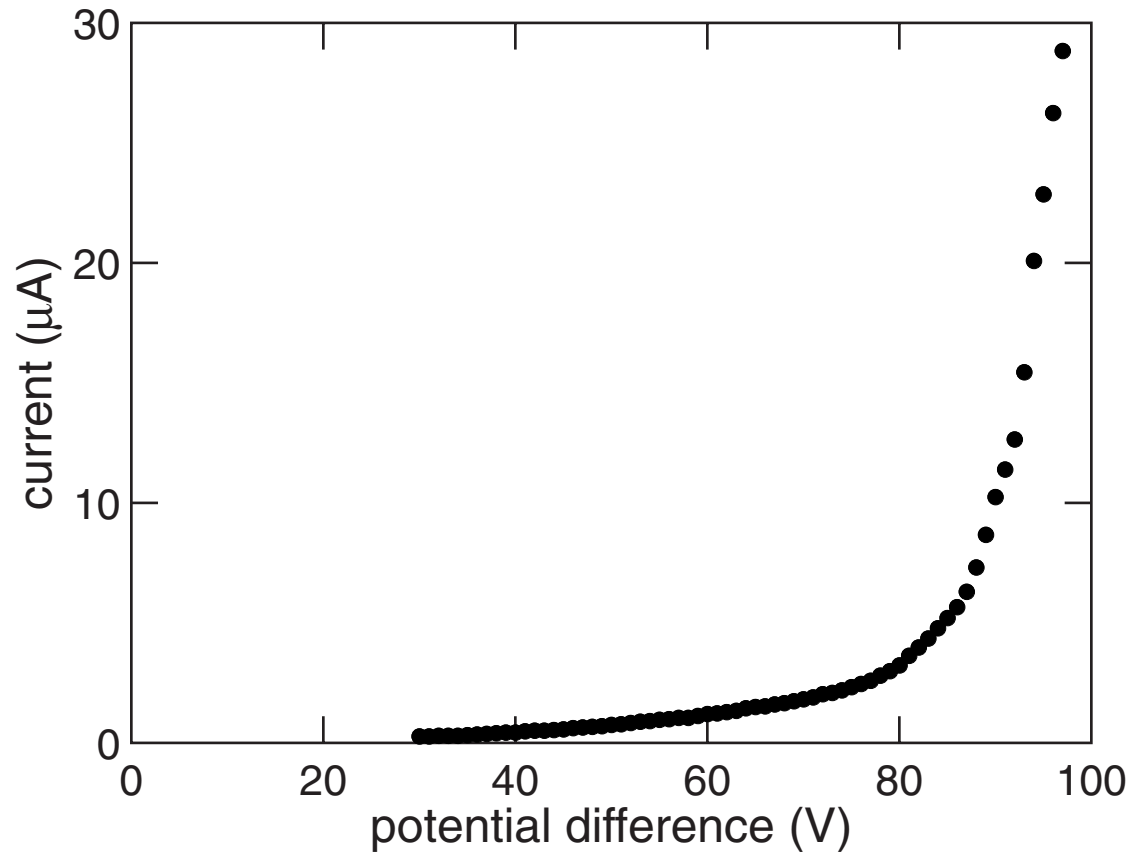


# *Properties*

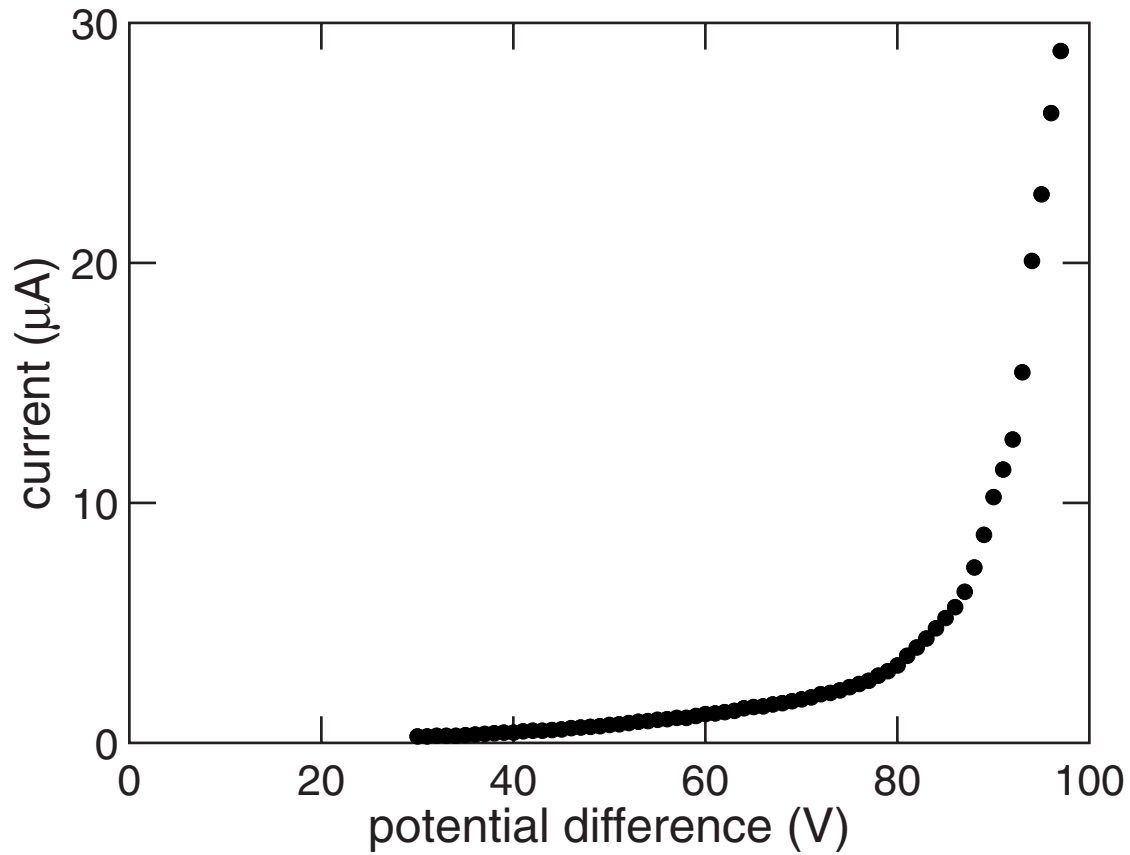
## field emission setup



# Properties

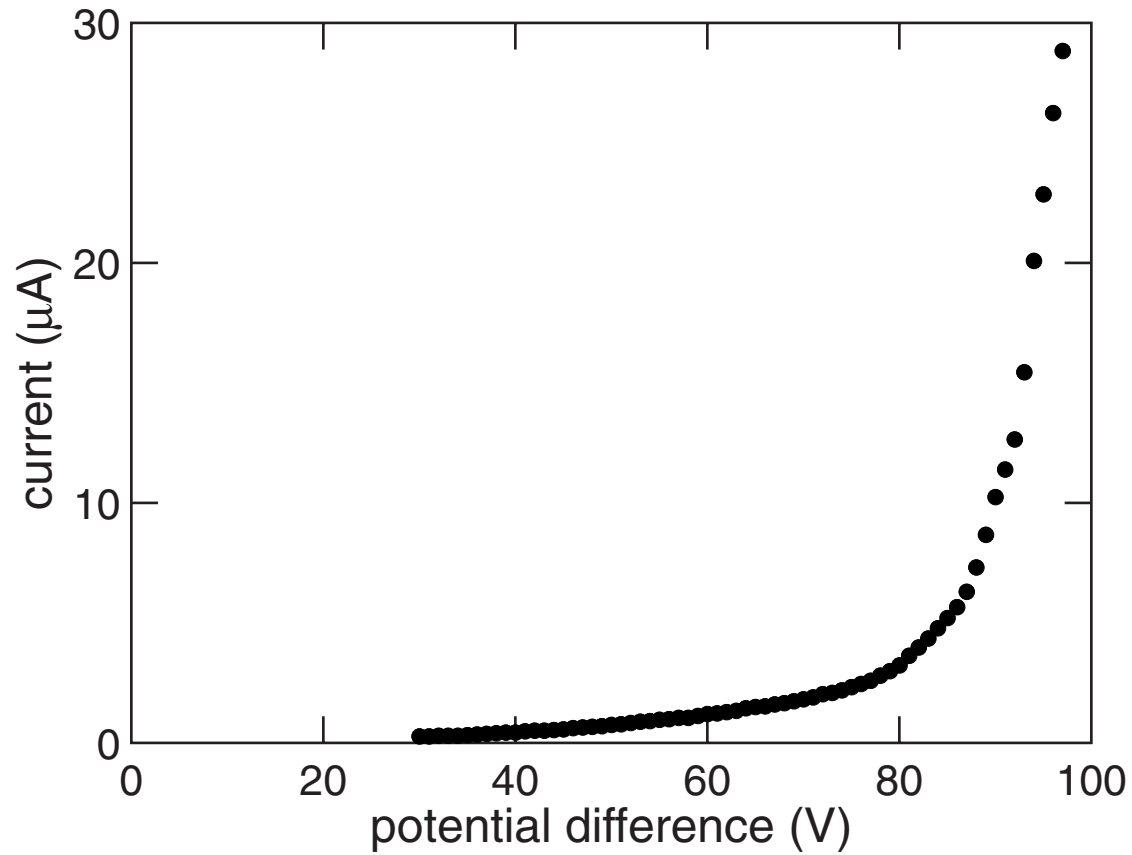


# Properties



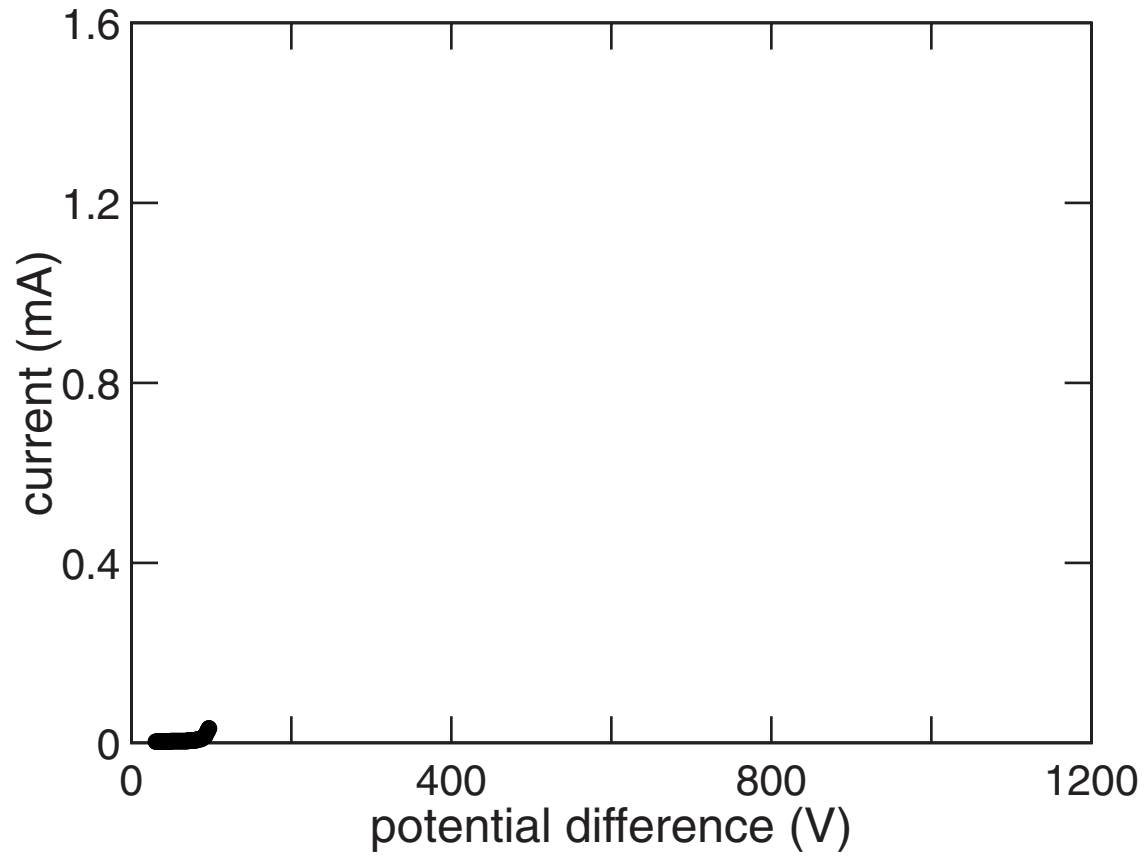
**turn-on field ( $1 \mu\text{A}/\text{cm}^2$ ):  $1.2 \text{ V}/\mu\text{m}$**

# Properties



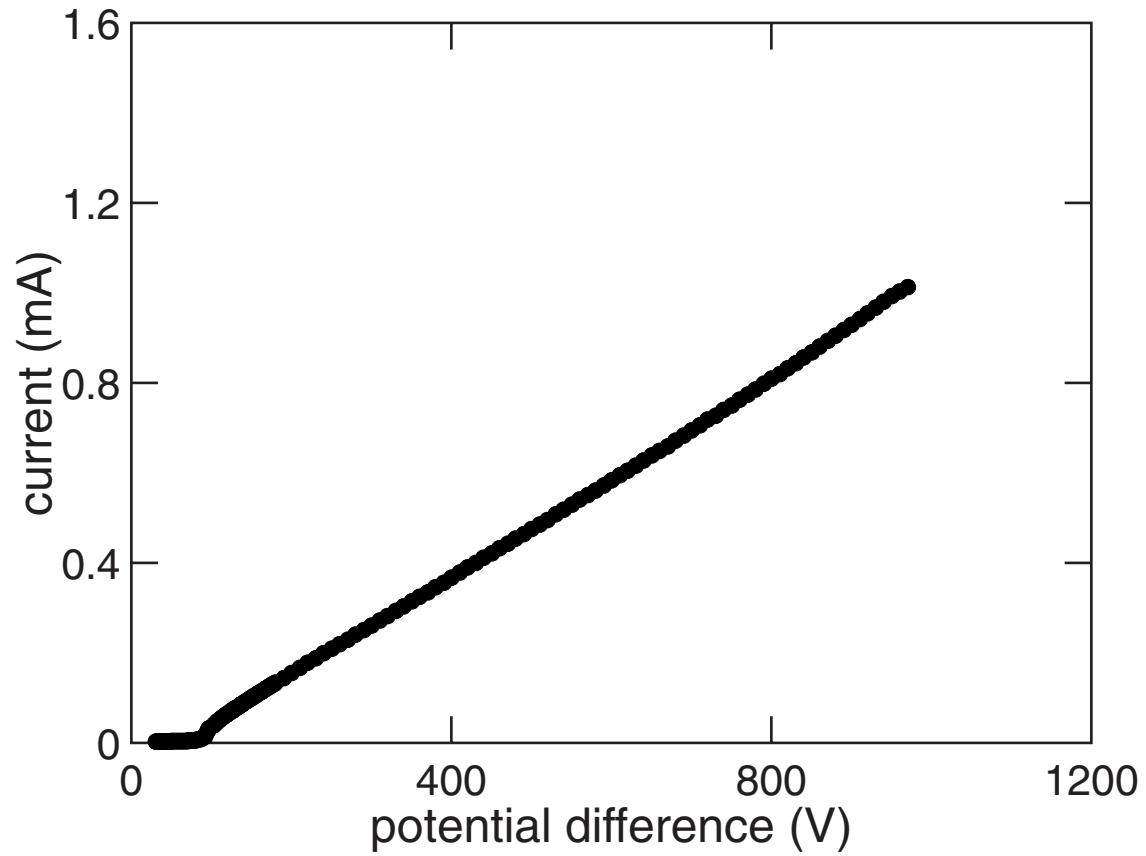
**threshold field ( $10 \mu\text{A}/\text{cm}^2$ ):  $2.1 \text{ V}/\mu\text{m}$**

# Properties

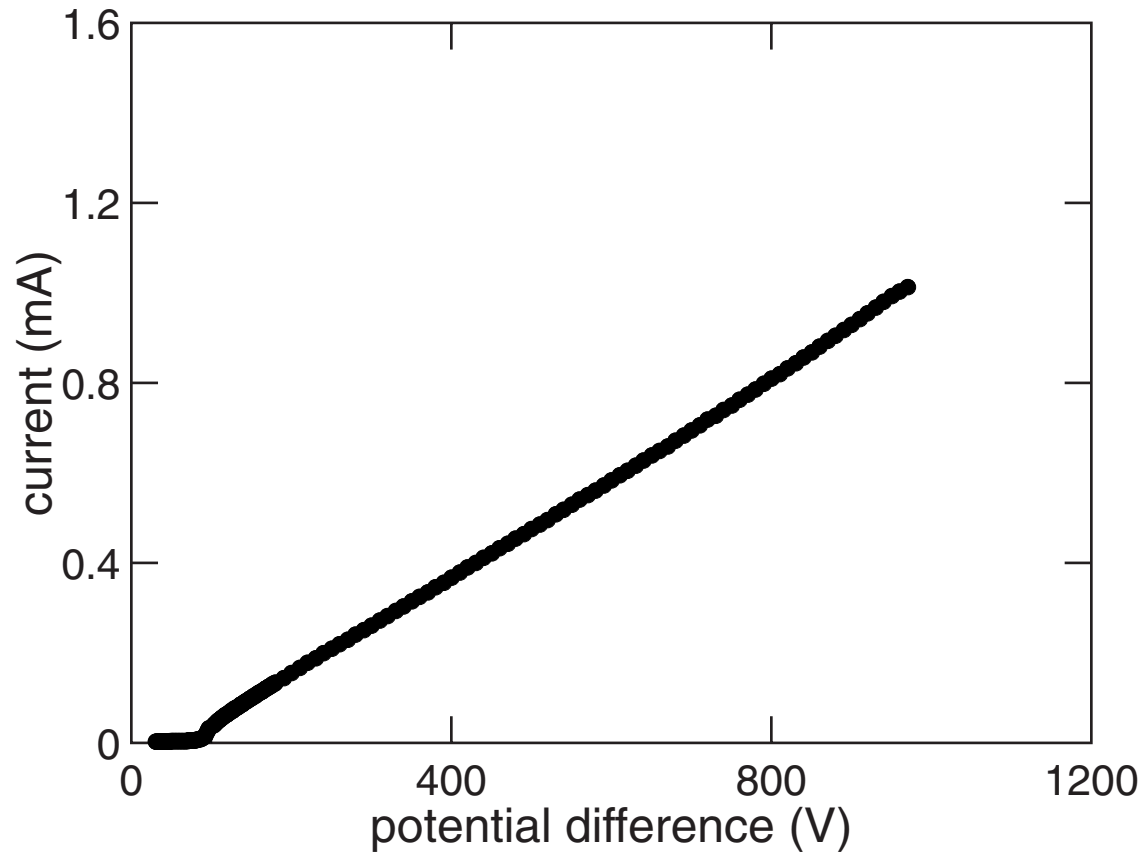




# Properties



# Properties



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

# *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?**

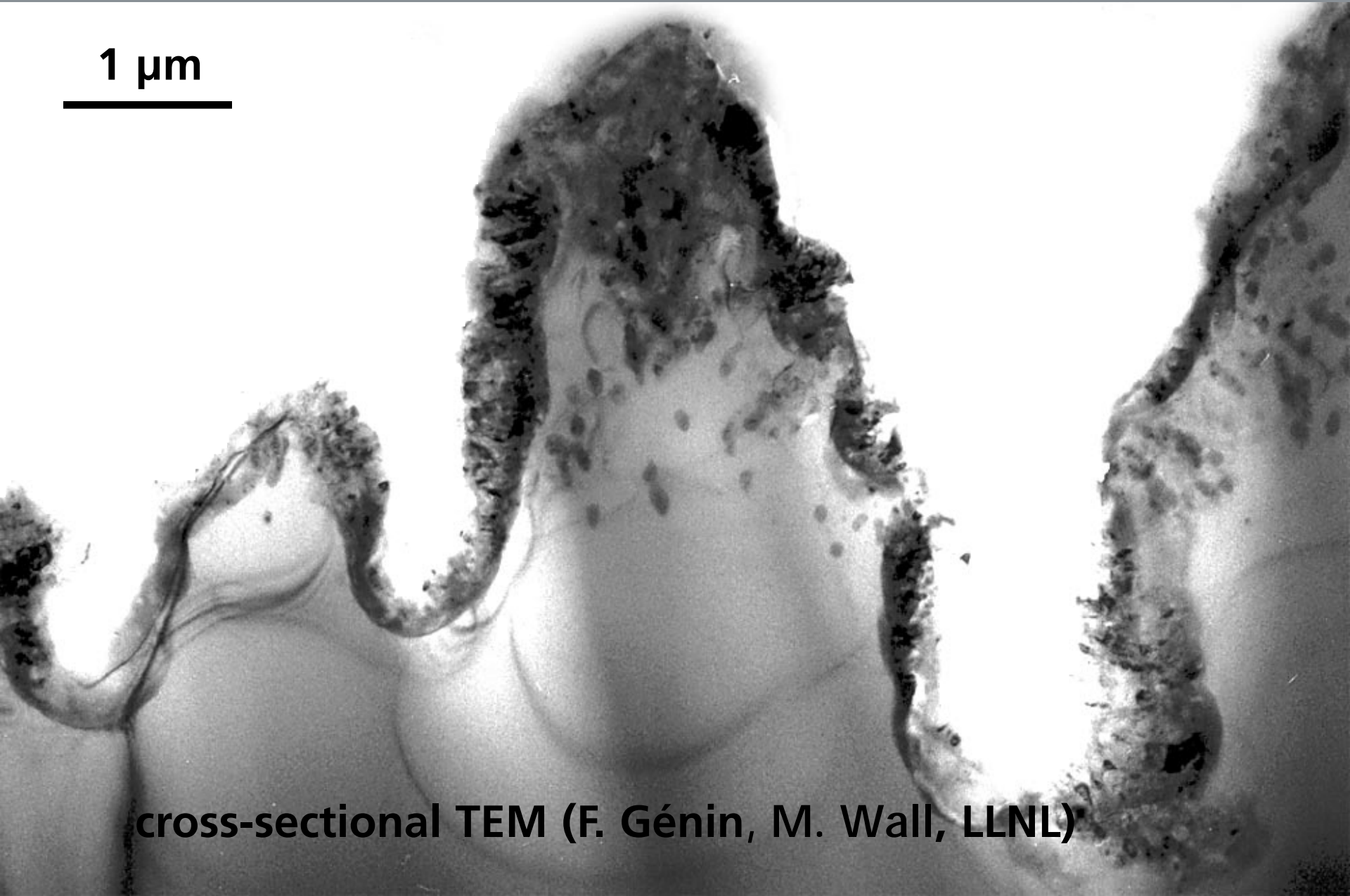
## **Secondary ion mass spectrometry:**

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

*Structural and chemical analysis*

**1  $\mu\text{m}$**

---



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

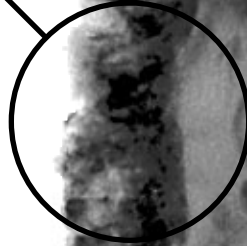


# *Structural and chemical analysis*

**1  $\mu\text{m}$**

---

**porous "fuzz"**



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



# *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  $\mu\text{m}$**

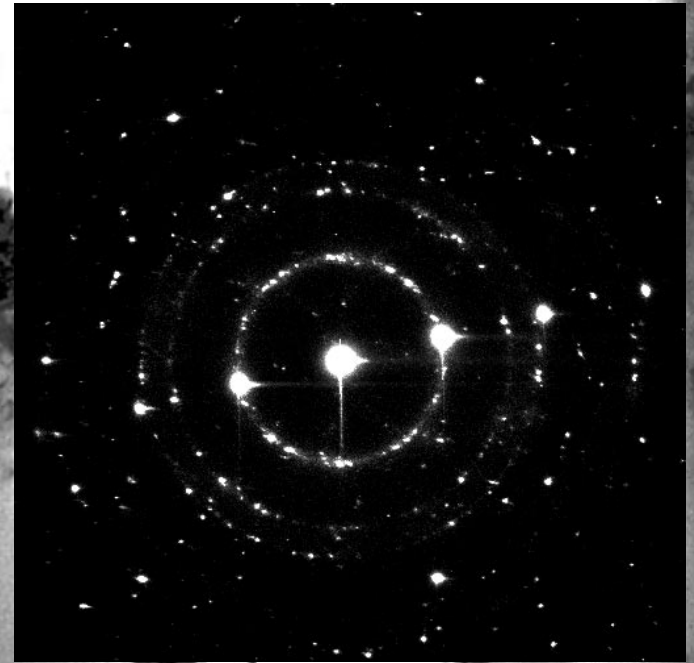
The image is a transmission electron micrograph (TEM) showing a biological specimen, possibly a cross-section of a plant stem or root. The specimen has a central, lighter-colored region surrounded by darker, more textured layers. A scale bar in the top left corner indicates a length of 1 micrometer.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

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



# *Structural and chemical analysis*

1  $\mu\text{m}$

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".

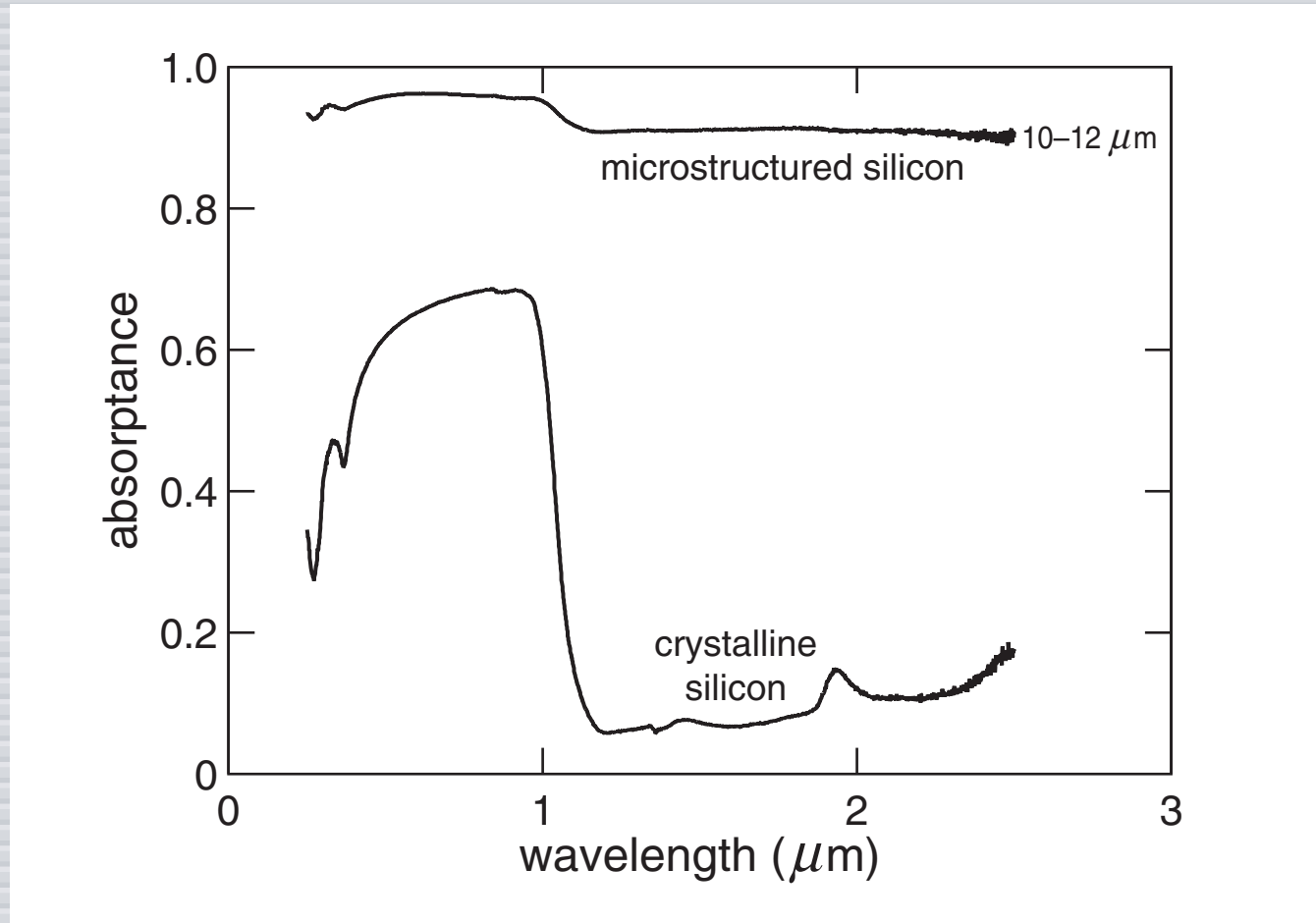
electron diffraction (F. Génin, M. Wall, LLNL)

**cross-sectional TEM:**

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

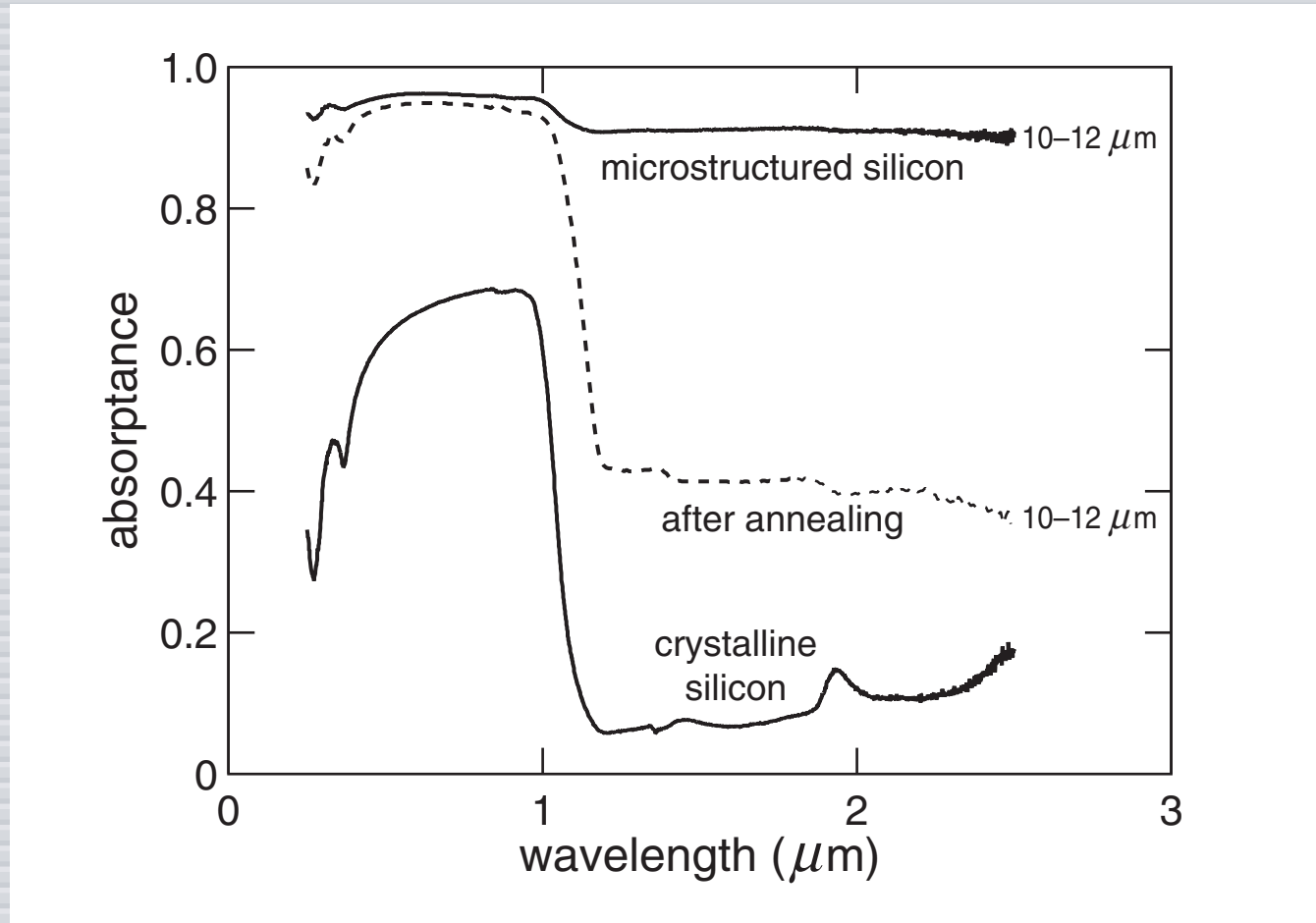
# Structural and chemical analysis

anneal 4 hours at 1200 K



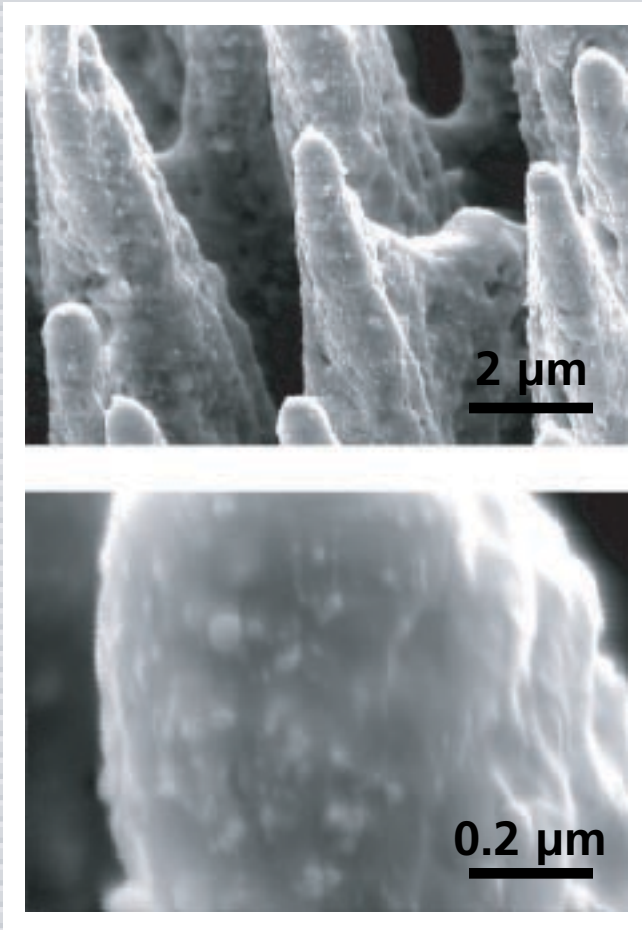
# Structural and chemical analysis

anneal 4 hours at 1200 K



# *Structural and chemical analysis*

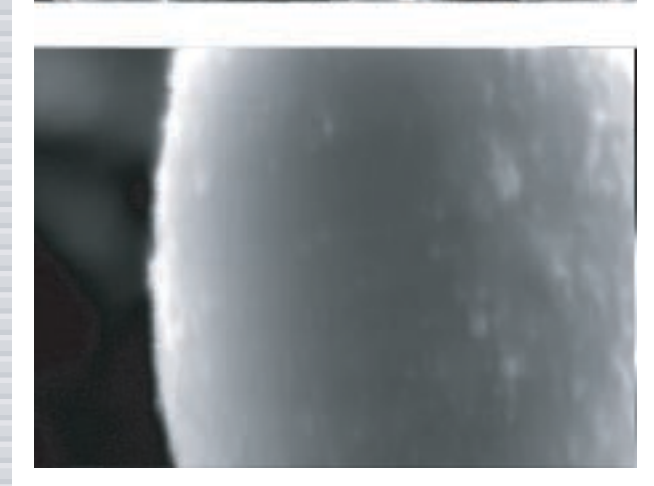
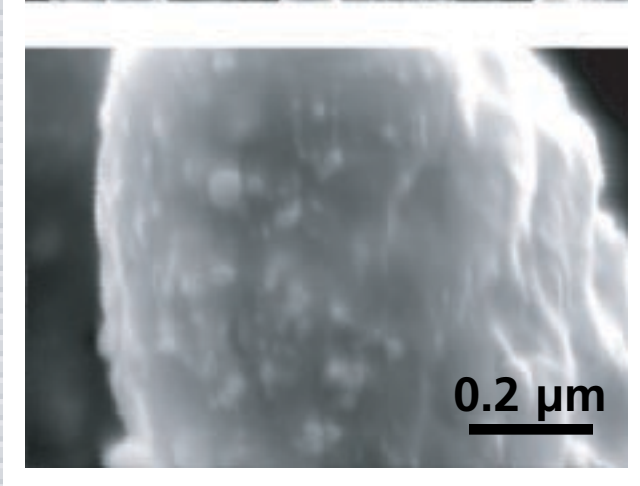
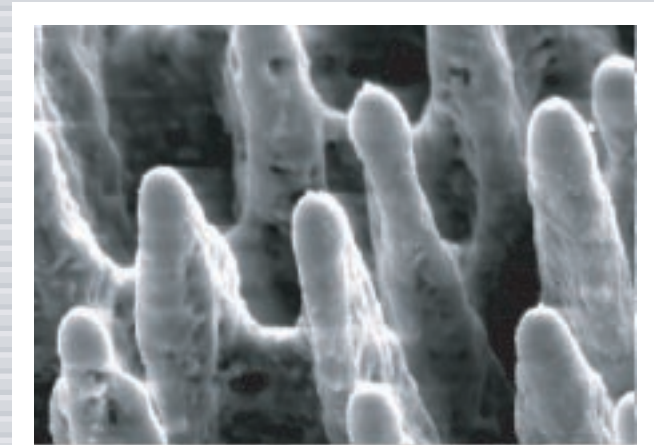
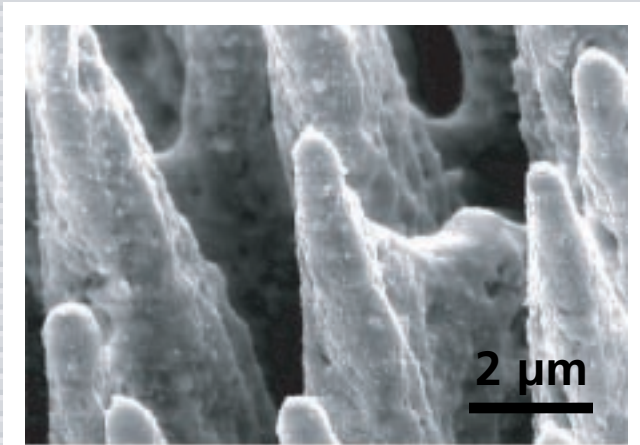
**anneal 4 hours at 1200 K**





# *Structural and chemical analysis*

**anneal 4 hours at 1200 K**



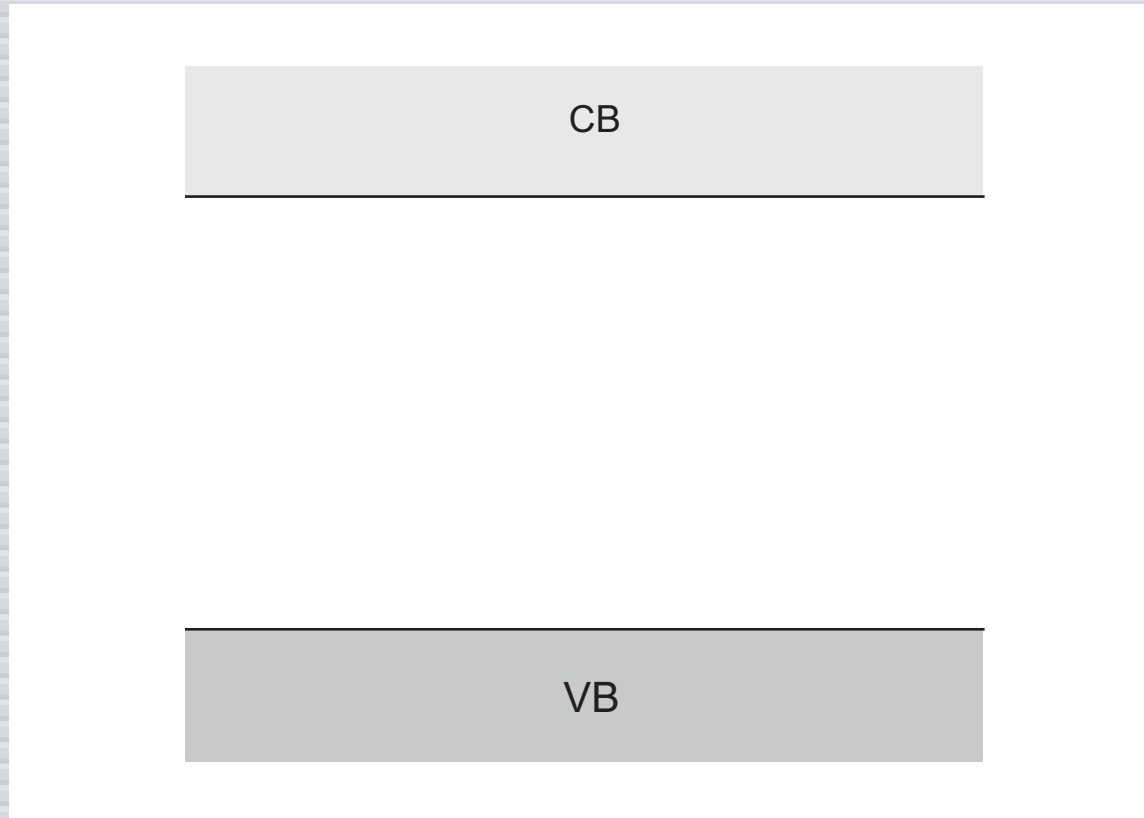
# *Structural and chemical analysis*

## **Effects of annealing:**

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

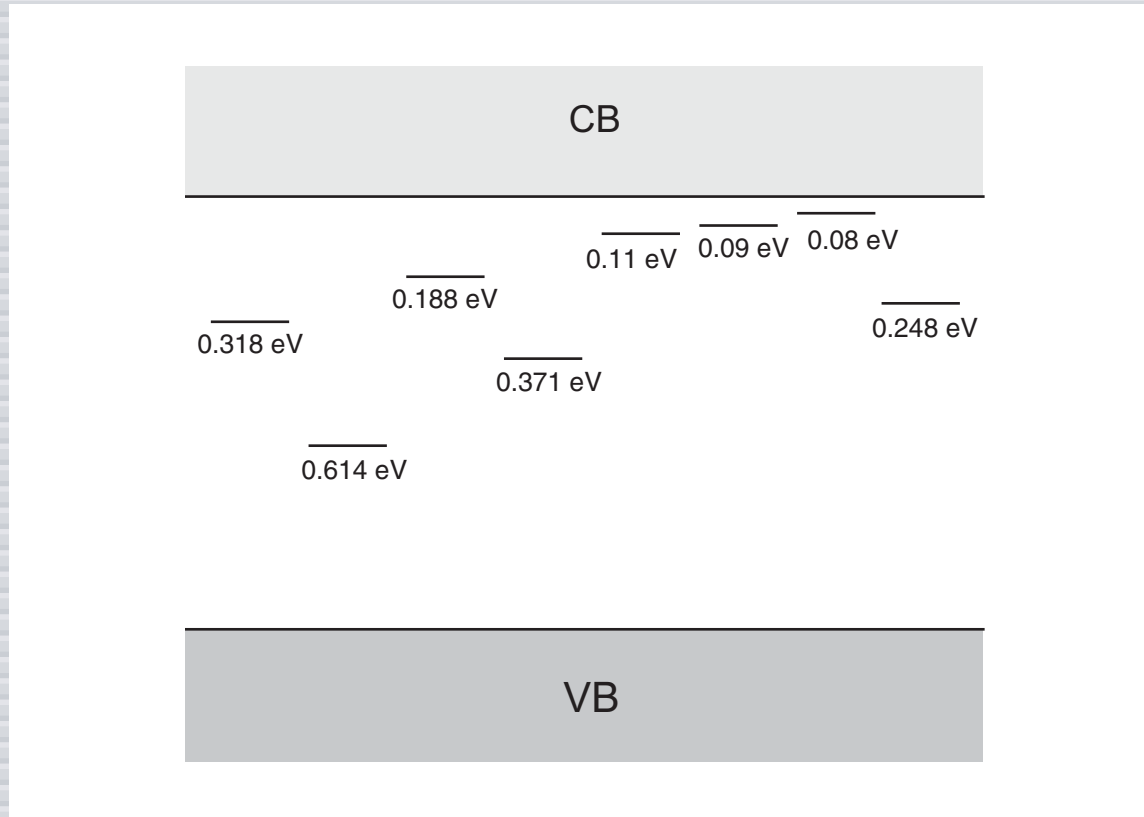
# *Structural and chemical analysis*

**sulfur introduces states in the gap**



# Structural and chemical analysis

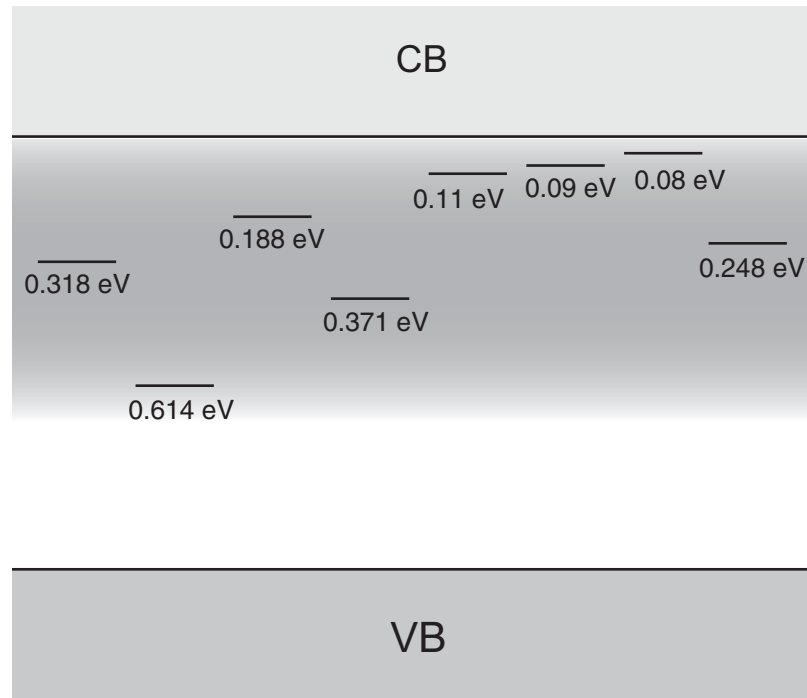
## sulfur introduces states in the gap



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

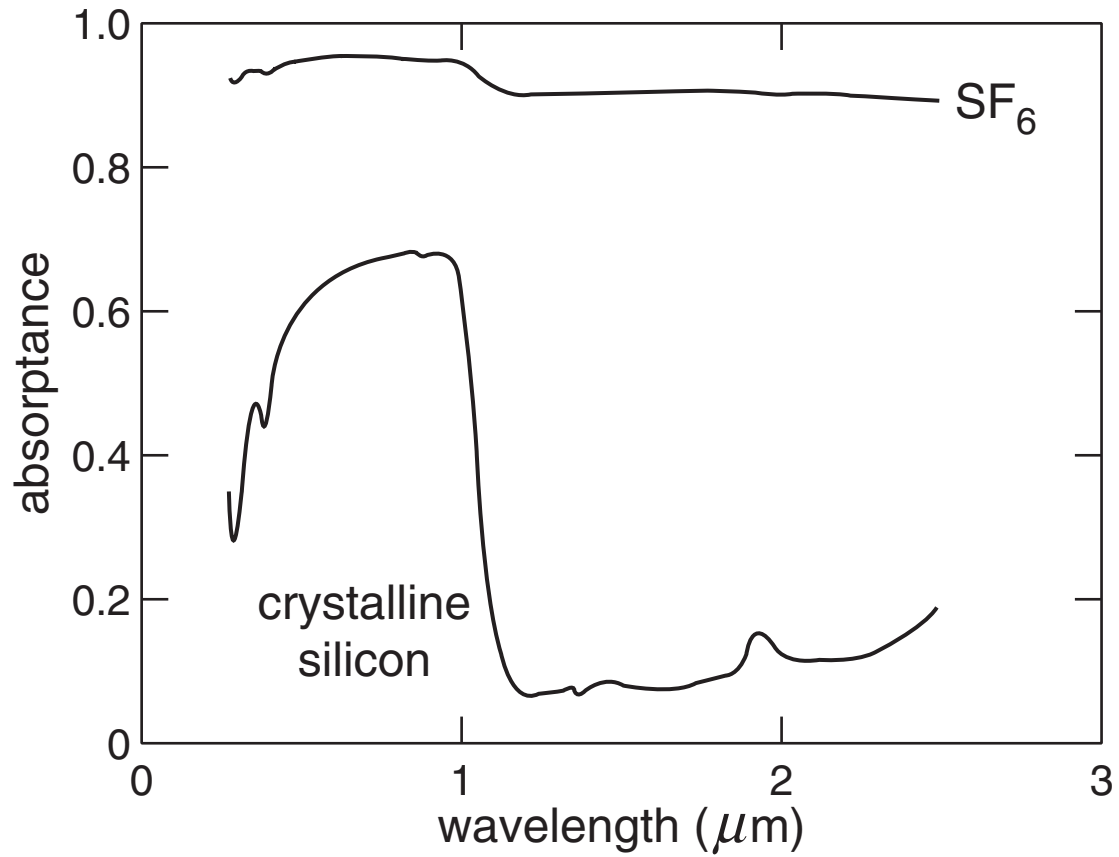
# Structural and chemical analysis

states broaden into a band



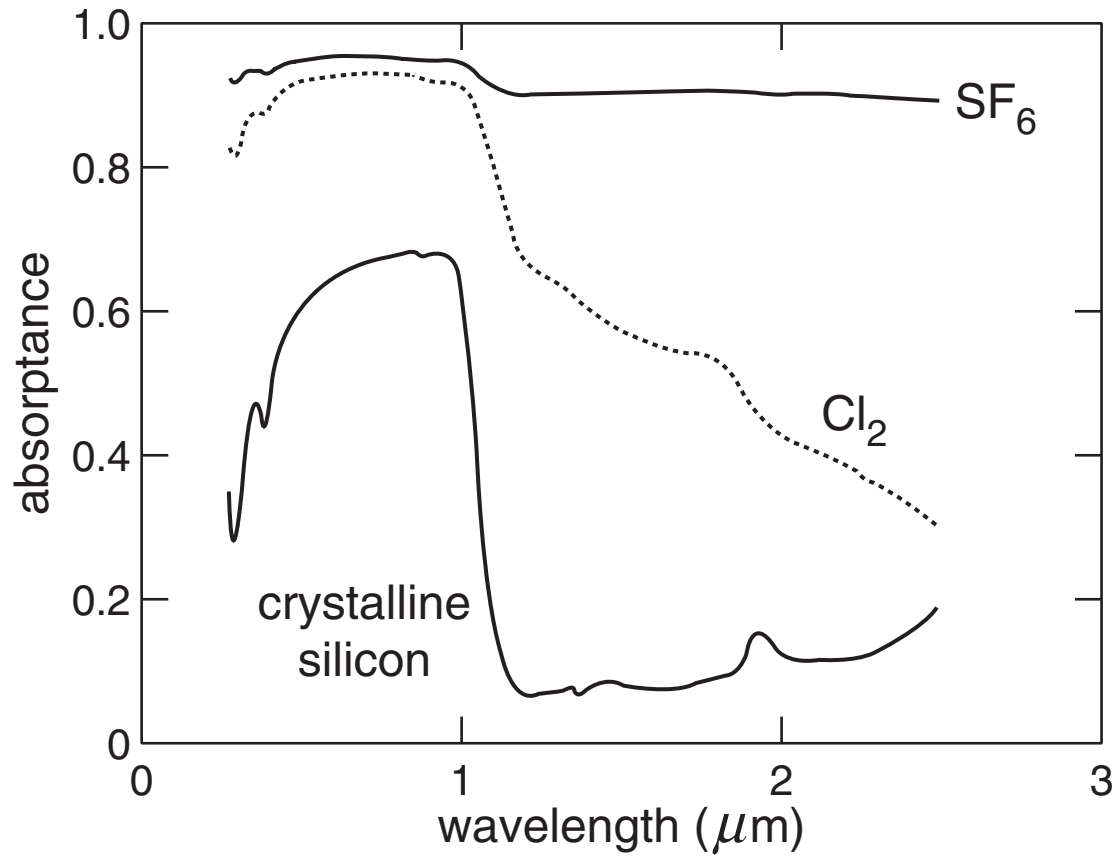
# *Structural and chemical analysis*

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



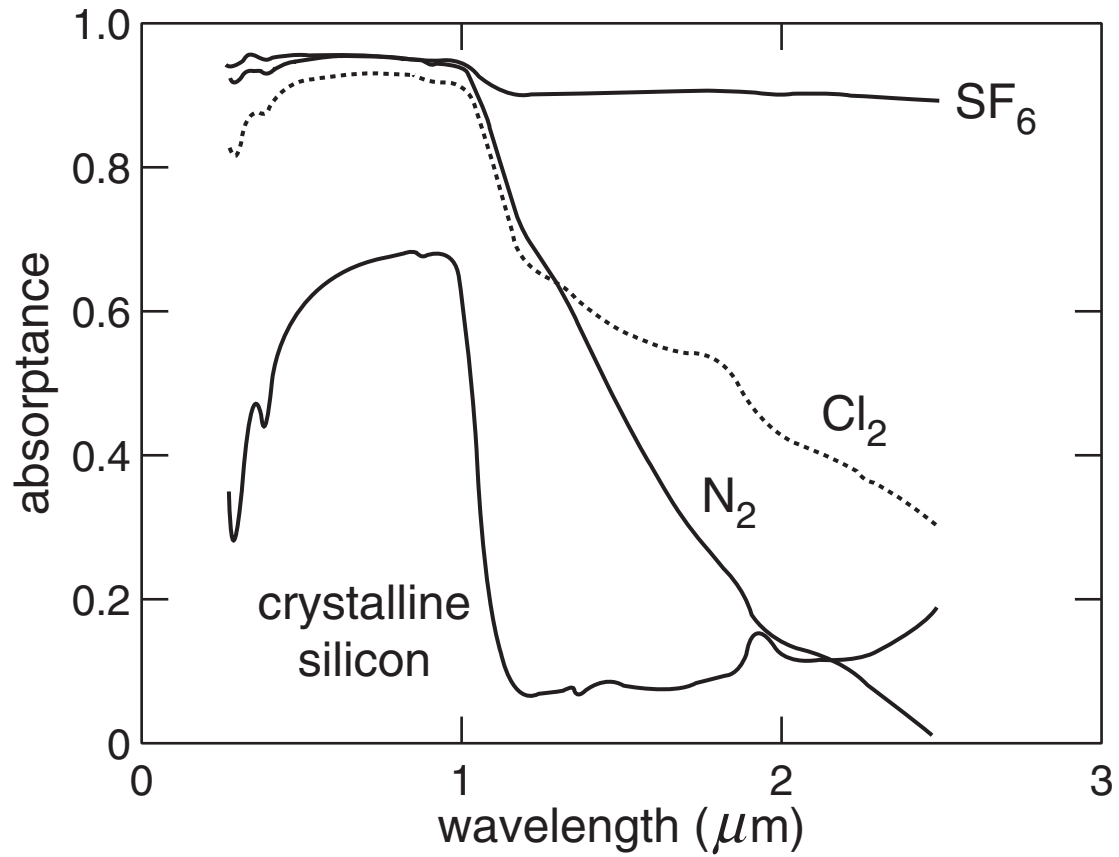
# *Structural and chemical analysis*

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



# Structural and chemical analysis

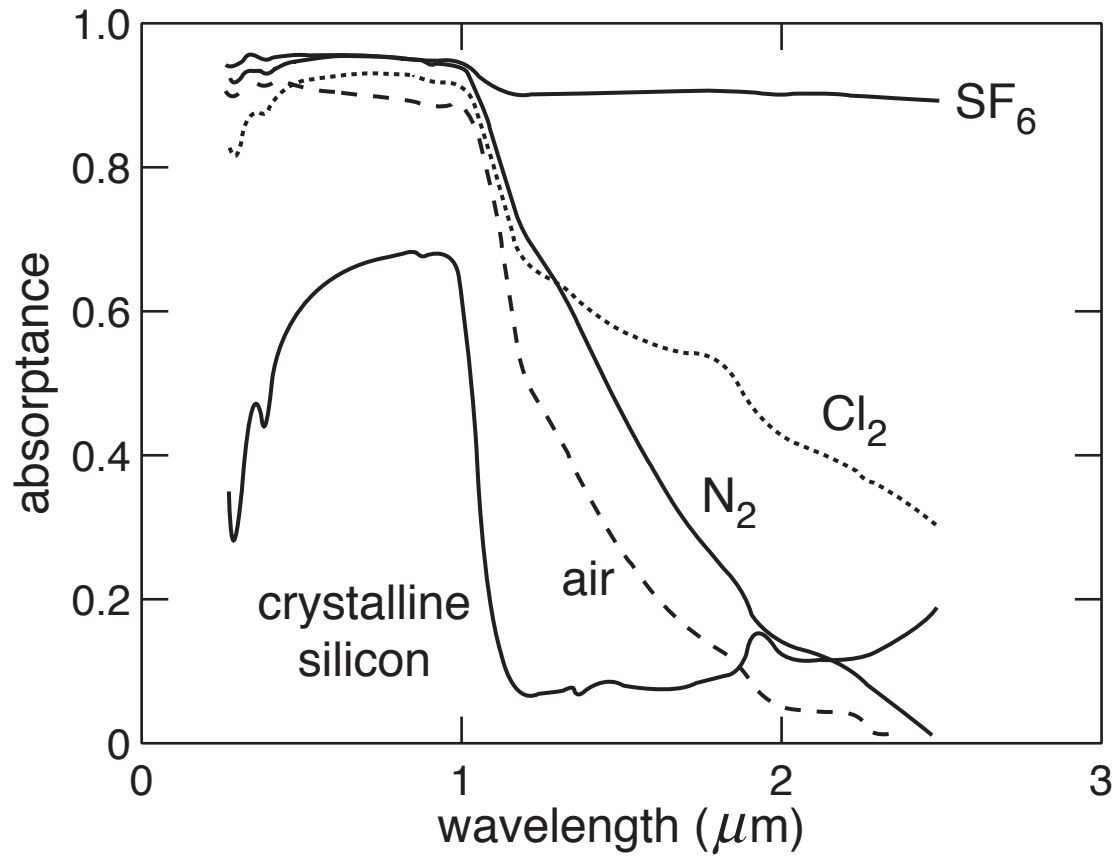
## effect of ambient gas on absorptance





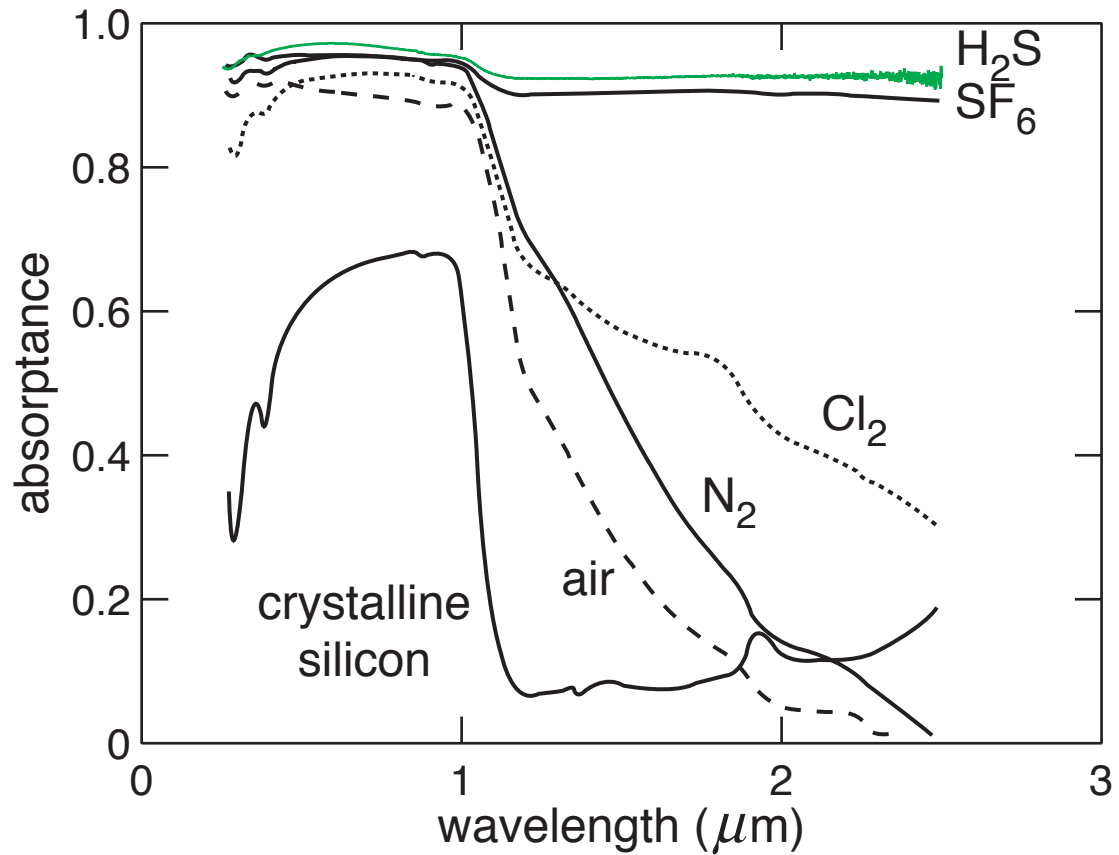
# *Structural and chemical analysis*

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



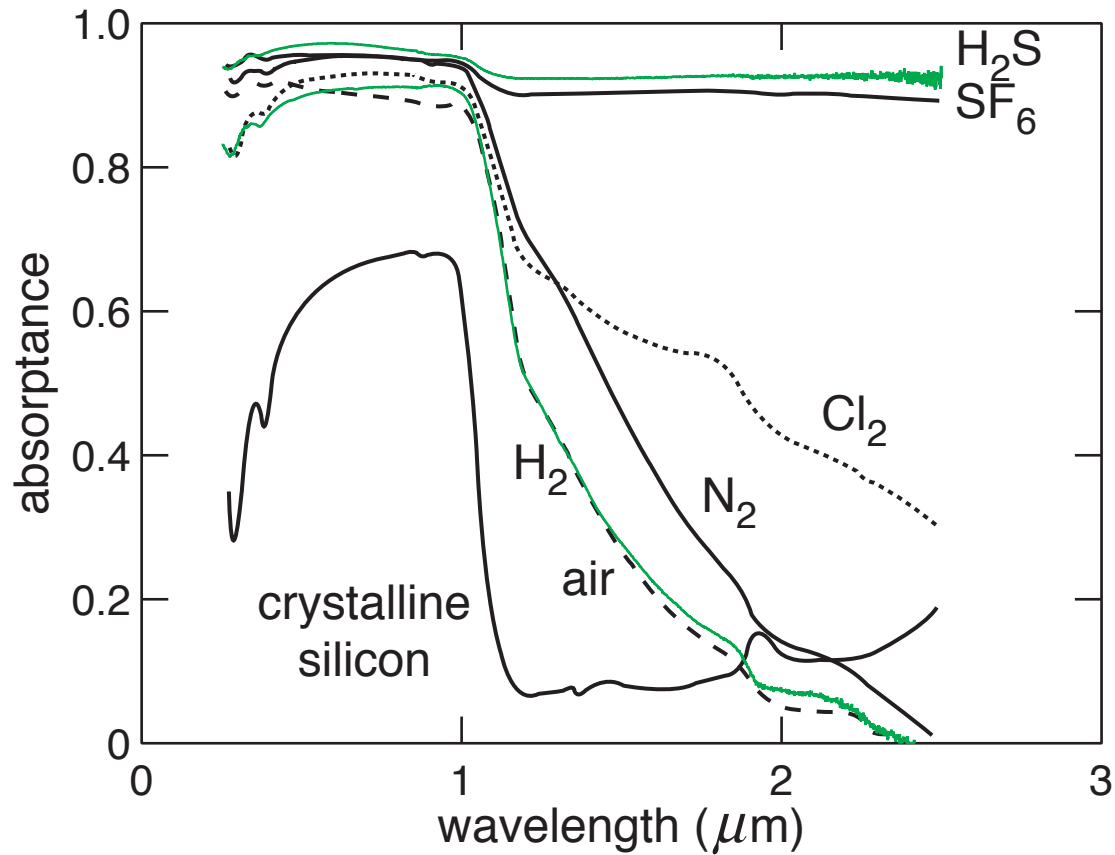
# Structural and chemical analysis

## effect of ambient gas on absorptance



# Structural and chemical analysis

## effect of ambient gas on absorptance



## *Structural and chemical analysis*

- ▶ **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

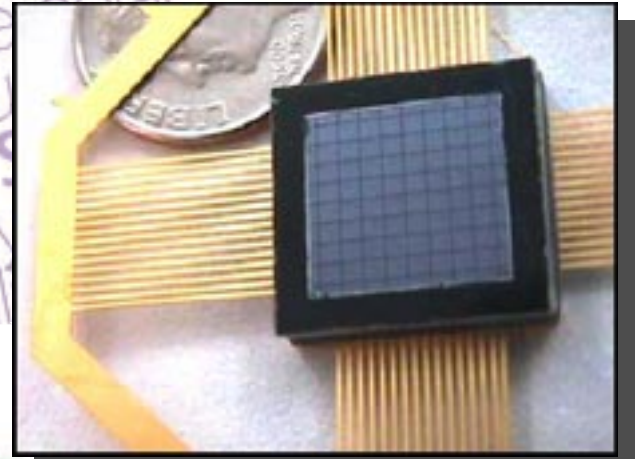
around the laboratory," he claims. Well, it was almost the only reason a short laser pulse will break down into sulphur and fluorine radicals, which will attack a silicon substrate. "Hydrogen fluoride is used to etch silicon. I thought maybe the SF<sub>6</sub> would do it and then the fluorine would so... 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 have stories of weird days. They seem to lack back to the time when a dog bit a child or a fire broke out in a room when

semiconductors with a powerful laser. In the early 1960s, Major's was the first academic lab in the world to do so. It was a hard-core attempt to see if there were any uses for the light that the sun sends down on us every day. It was extremely

around the laboratory. "He claims that it was a great idea to make a laser that would break down into sulphur and fluorine radicals. That's the way to make a solar cell. But there's a problem. It would be a thought that the silicon would be more than 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. Myers peers into the mysterious world of black silicon



## TALL, DARK AND STRANGER

WE ALL love stories of scientific discovery. They seem to ask for a headline when a scientist discovers a new way of doing things, or when

somebody does with a powerful laser. In the early 1990s, Myers was the first to create a lab in the world to study hard-to-control light that included wavelengths brighter than the Sun and extremely

around the laboratory," he claims. "While it was a great time to be a scientist, it was also a time to be a scientist who was not a scientist. He had thought that he would do something that would be a breakthrough in the silicon. Myers ex-

# Outlook

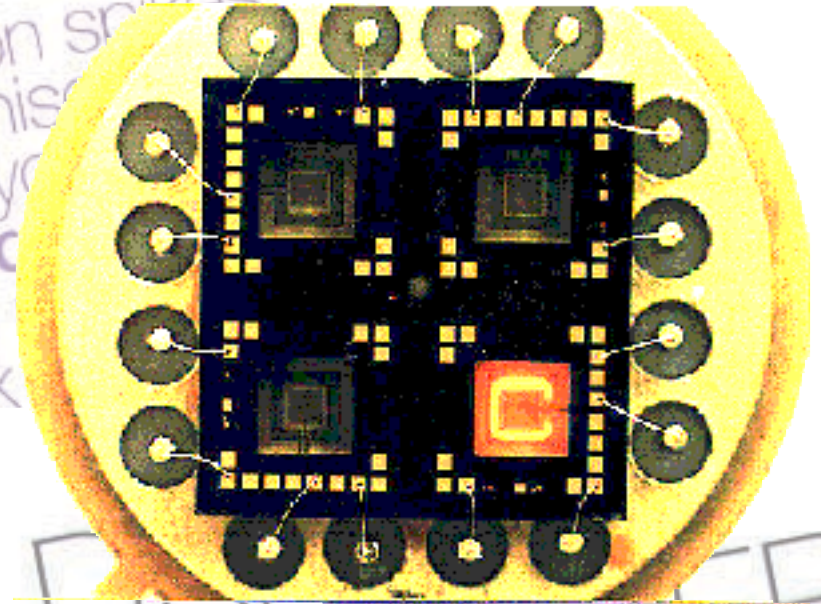
- ▶ detector technology
- ▶ solar cells
- ▶ display technology



# 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 days. This  
one to ask for a headline when a legend  
of a life's time dies.

semiconductors with a potential use for  
the early 1960s. Major's was the first  
academic lab in the world to do so.  
hard-core computer work. This was  
analogous to the way of light that included  
computer chips lighter than the Sun  
and extremely

around the laboratory," he claims.  
While it was a great time to make  
about 1960, it was not until 1962  
into silicon and fluorine. The  
will attack a silicon wafer. But  
there is a need to cut silicon  
through the silicon. It would  
and then the silicon would  
the silicon. Most ex-

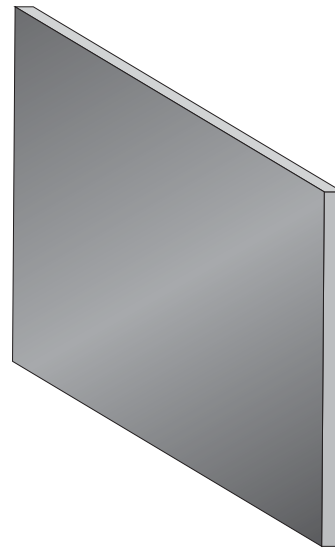
# *Outlook*

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

# *Outlook*

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

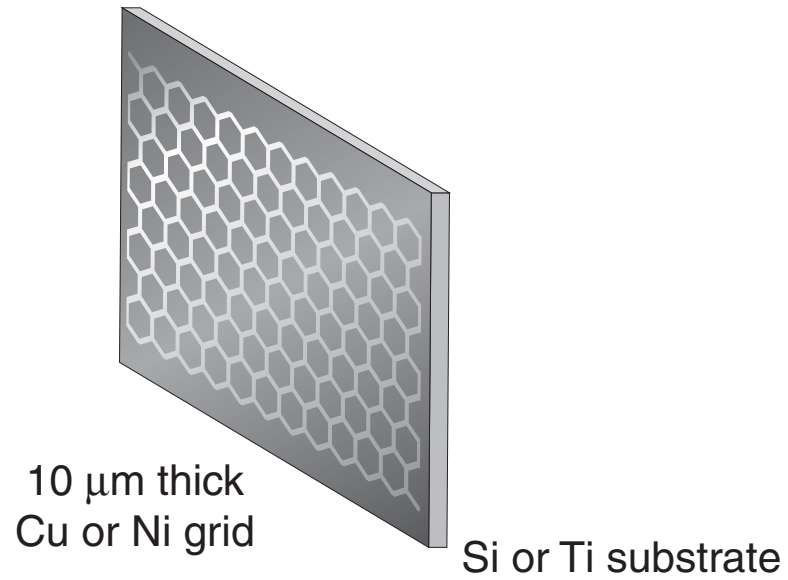
# Outlook



Si or Ti substrate

# Outlook

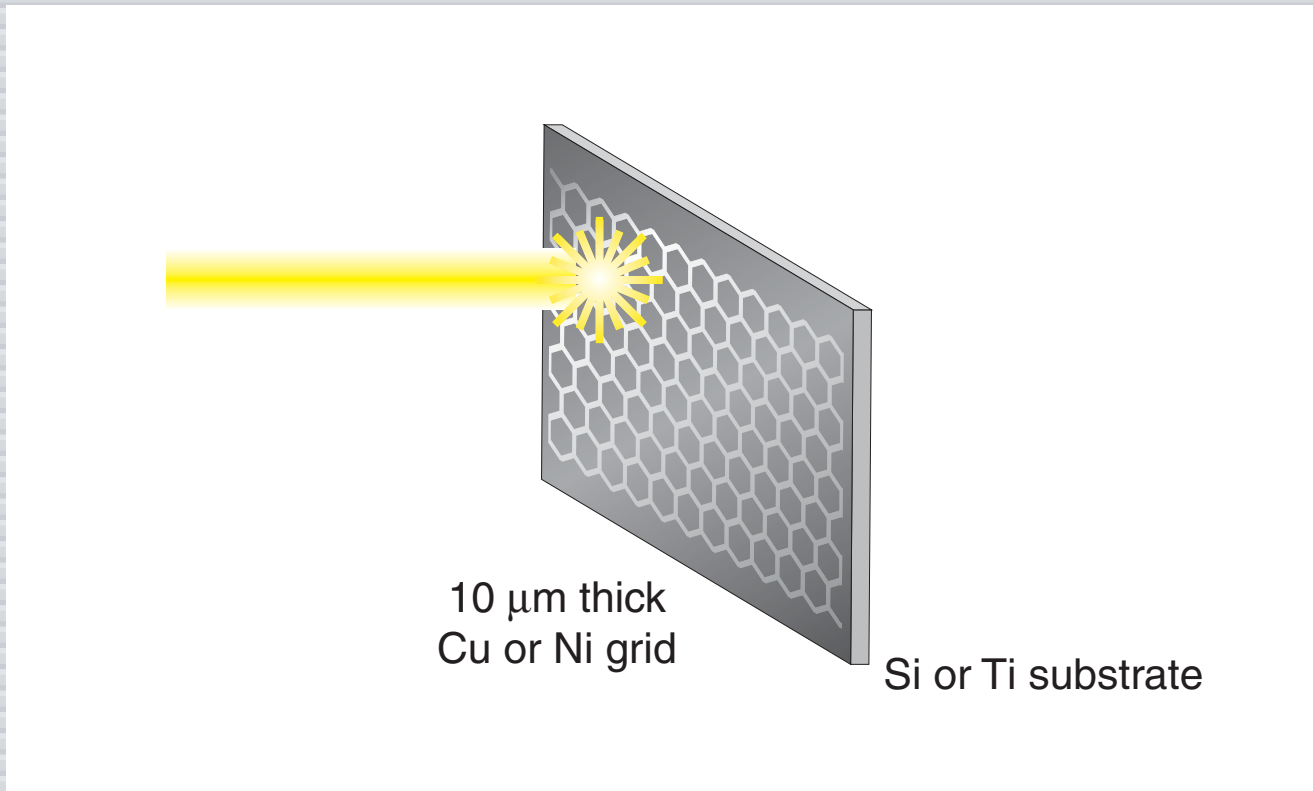
**place grid in front of substrate**





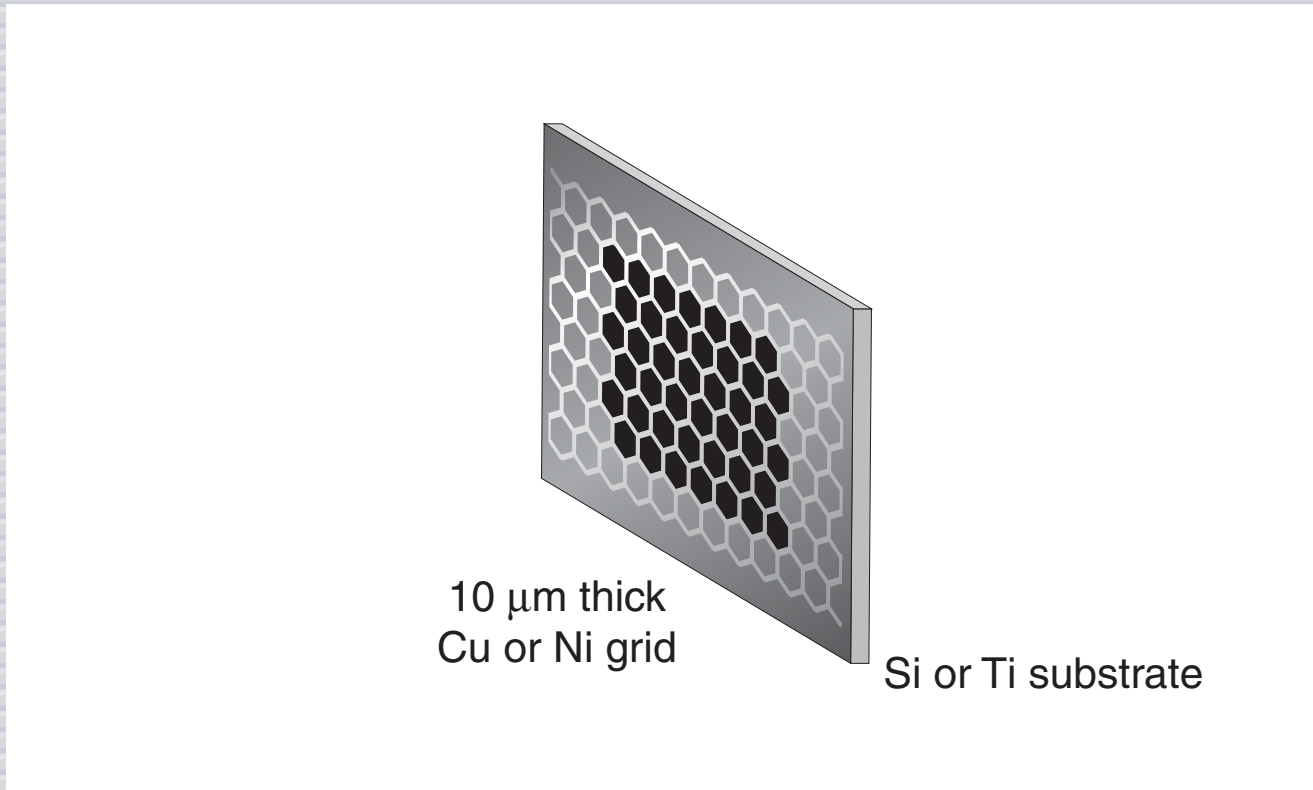
# Outlook

## scan laser beam



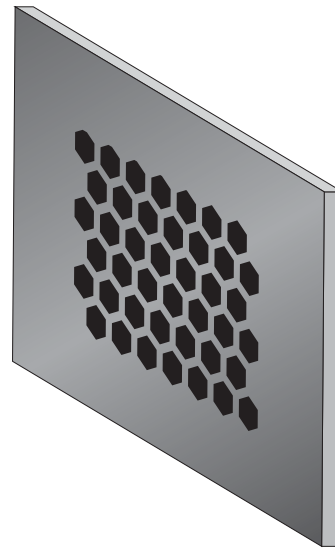
# Outlook

## scan laser beam

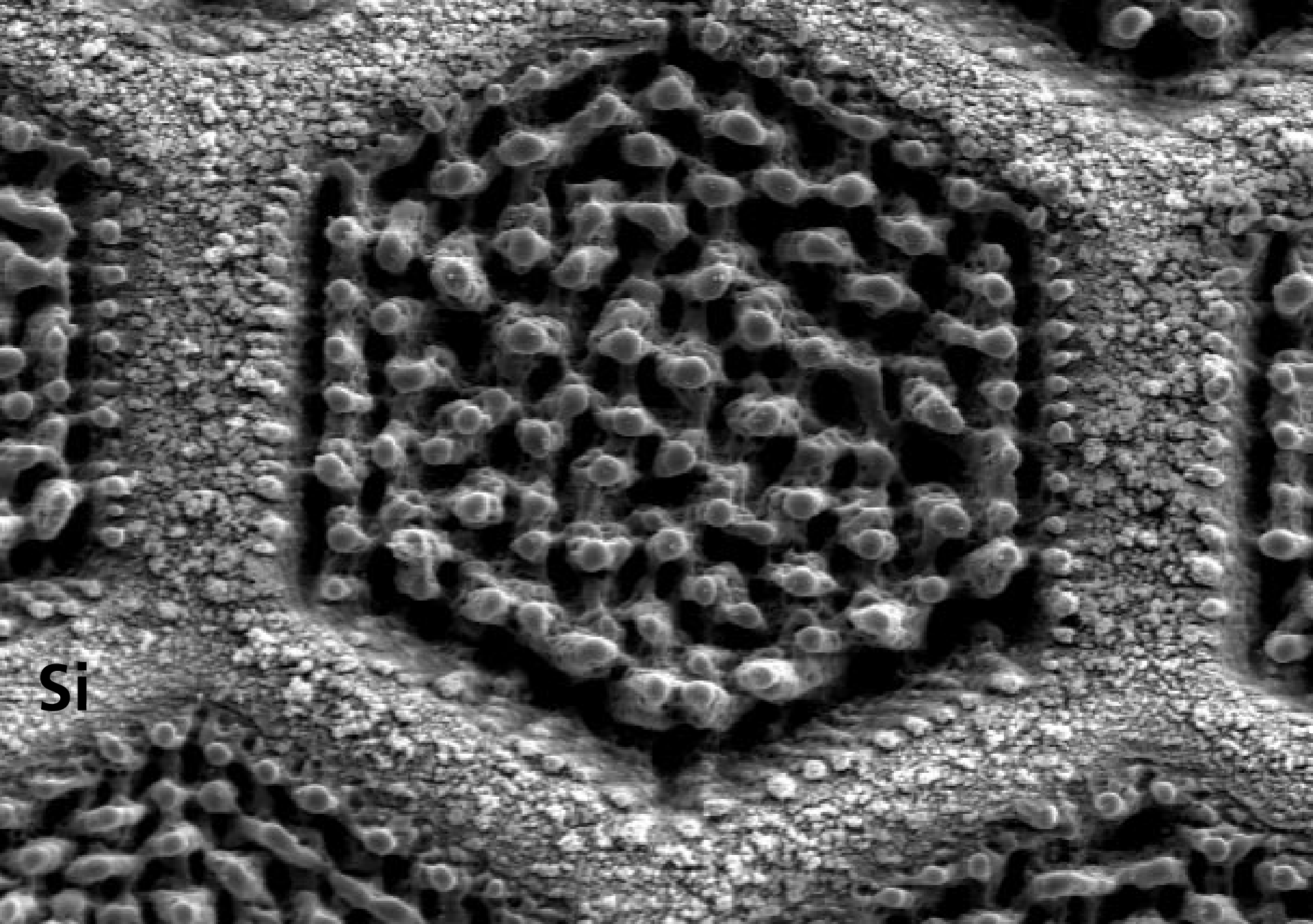


# *Outlook*

**remove grid**



Si or Ti substrate

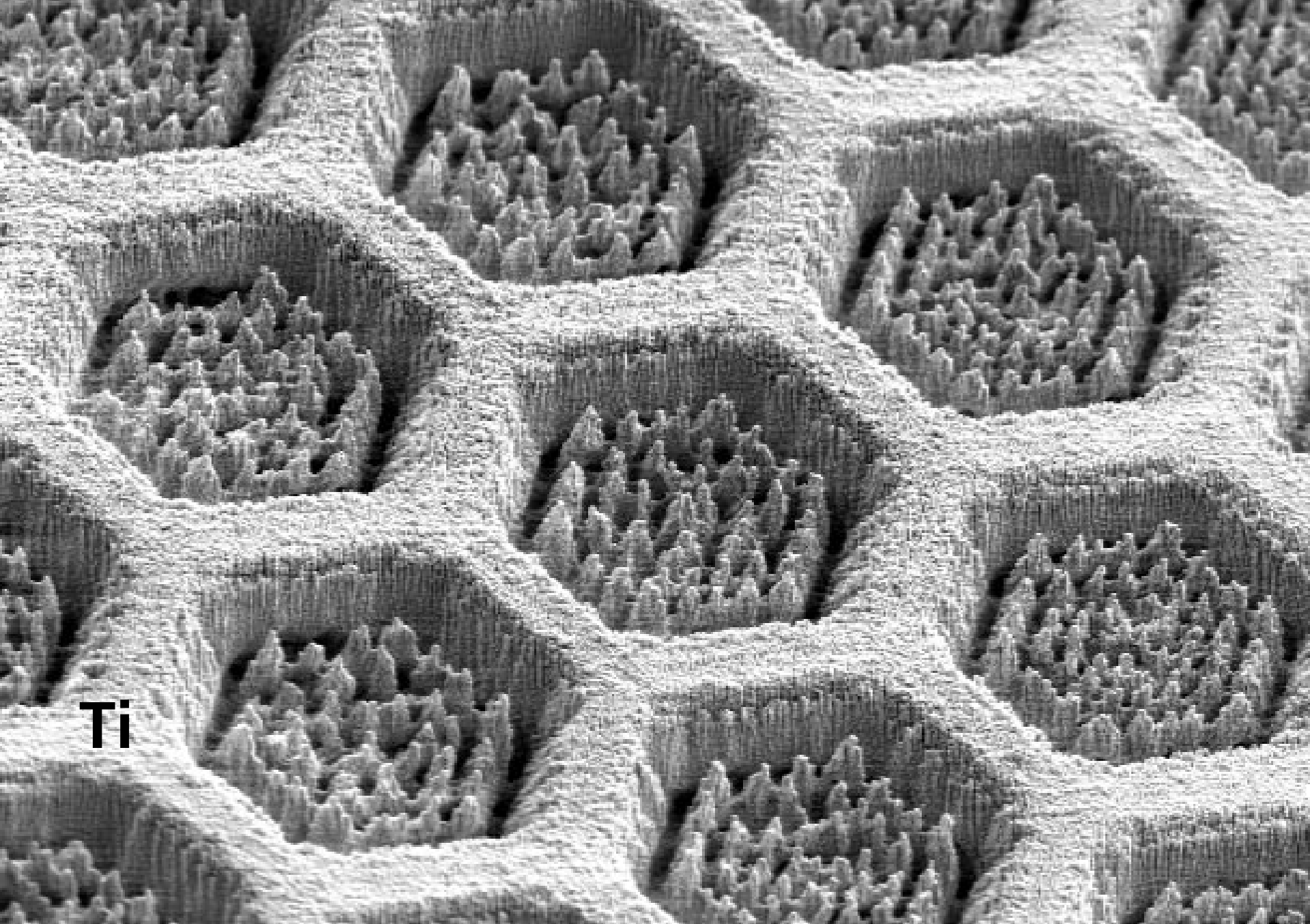


Si

x2000  
512 x 480

20  $\mu$ m

5kV 24mm  
H300 .TIF

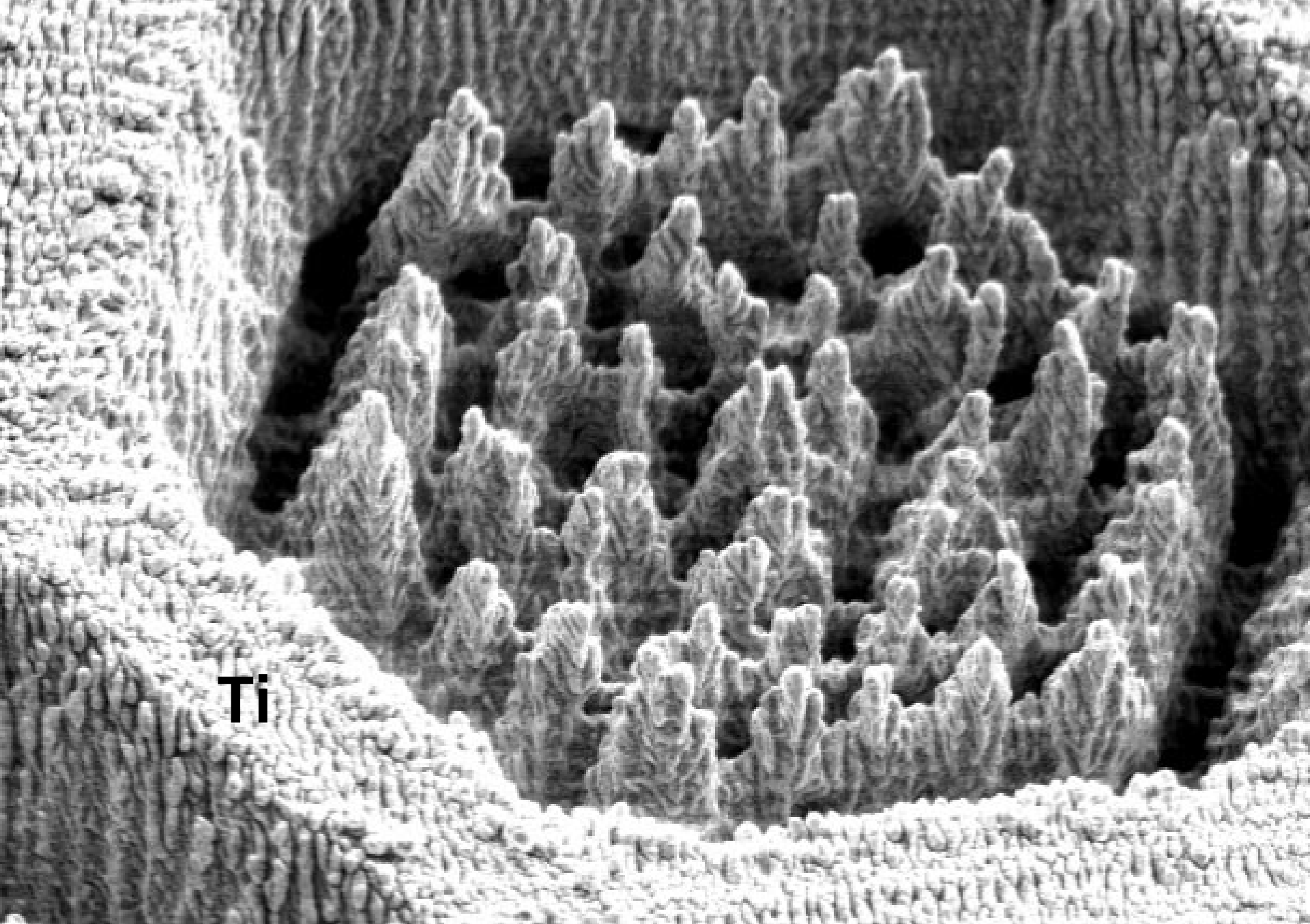


Ti

20  $\mu$ m

5kV

17mm



Ti

10  $\mu$ 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**

## **Microstructured silicon**

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

# *Summary*

## **Microstructured silicon**

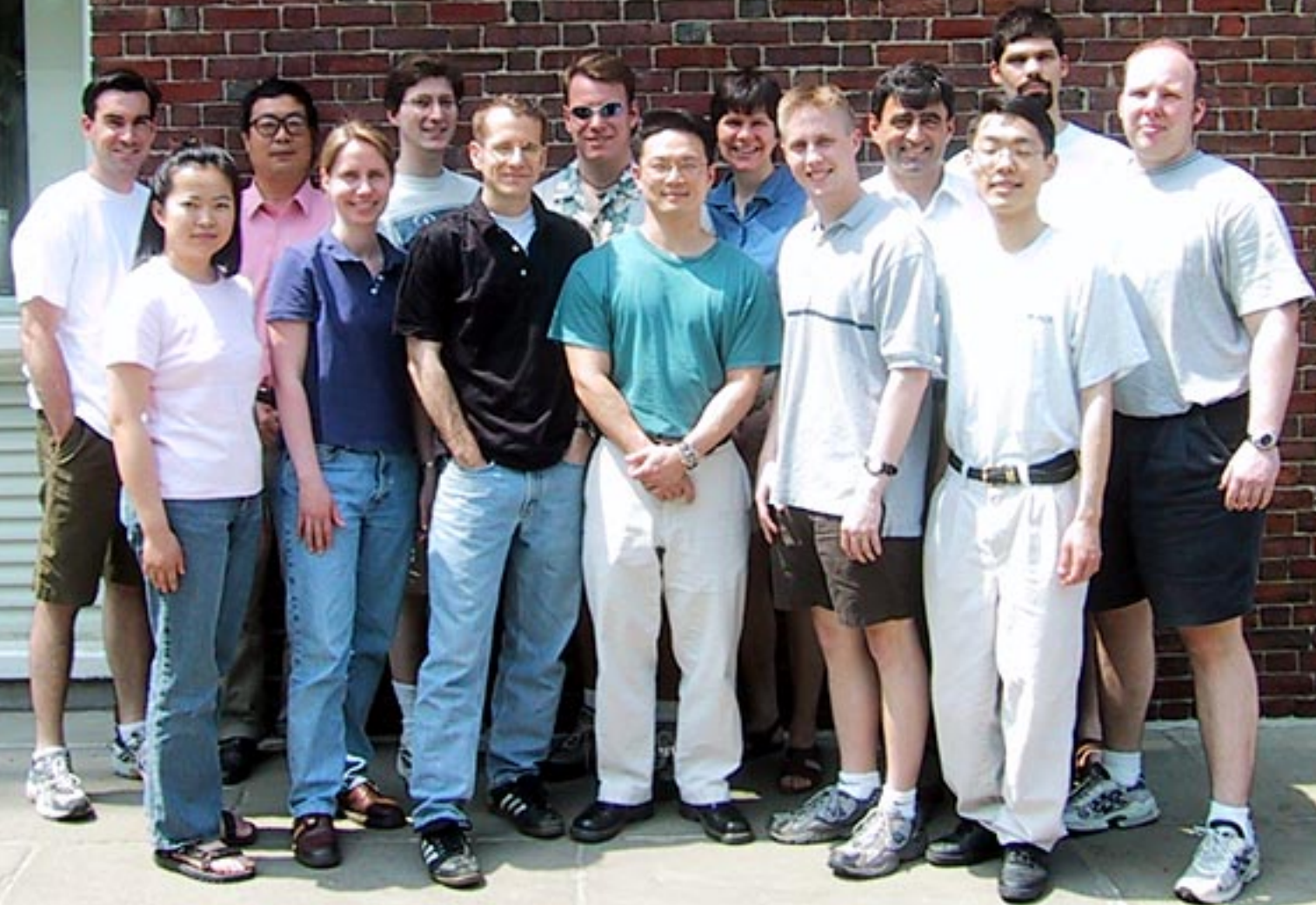
- ▶ **fabricated by simple, maskless process**
- ▶ **can be integrated with microelectronics**
- ▶ **generates IR photocurrent**
- ▶ **provides stable, high field emission current**

# *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>

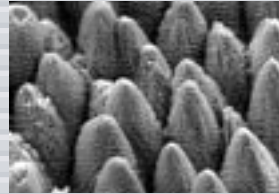
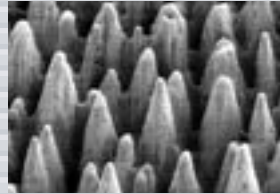
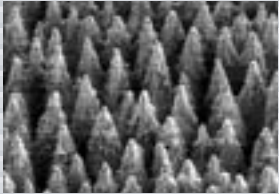
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N<sub>2</sub>

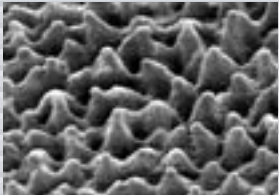
air

vacuum

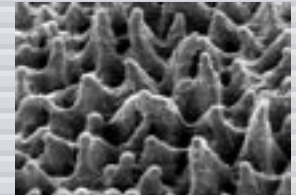
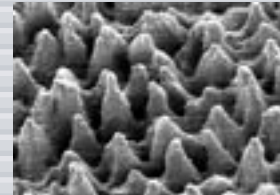
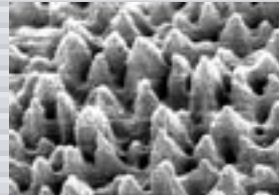
Si



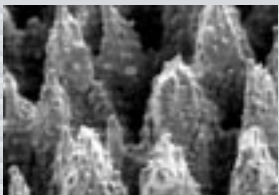
Ti



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

SF<sub>6</sub>

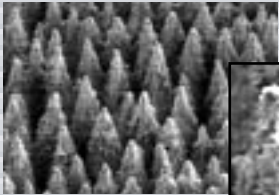
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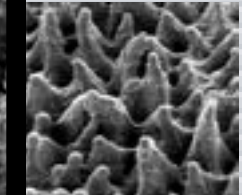
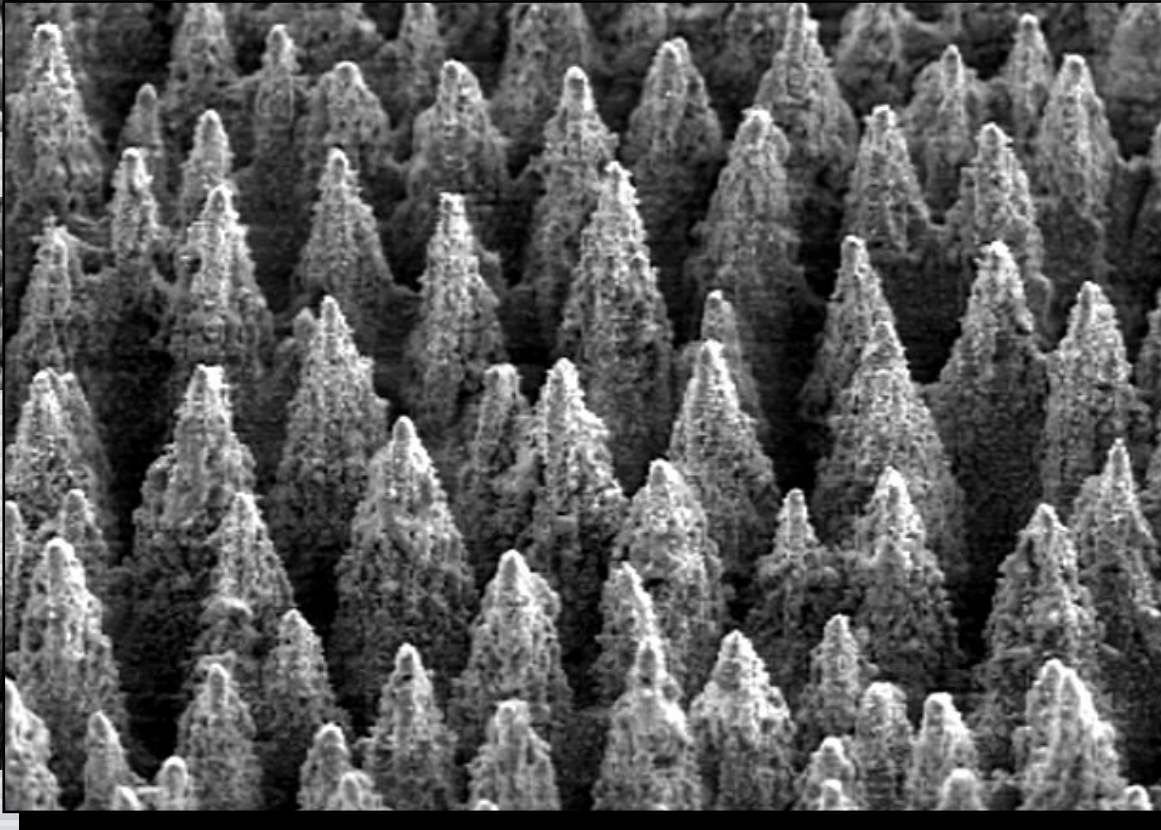
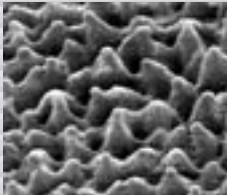
air

vacuum

Si

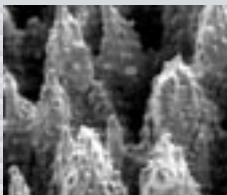


Ti



Only in SF<sub>6</sub>

Ge



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# Materials

SF<sub>6</sub>

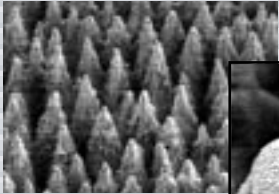
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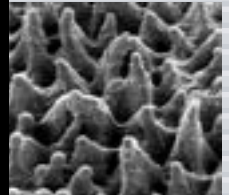
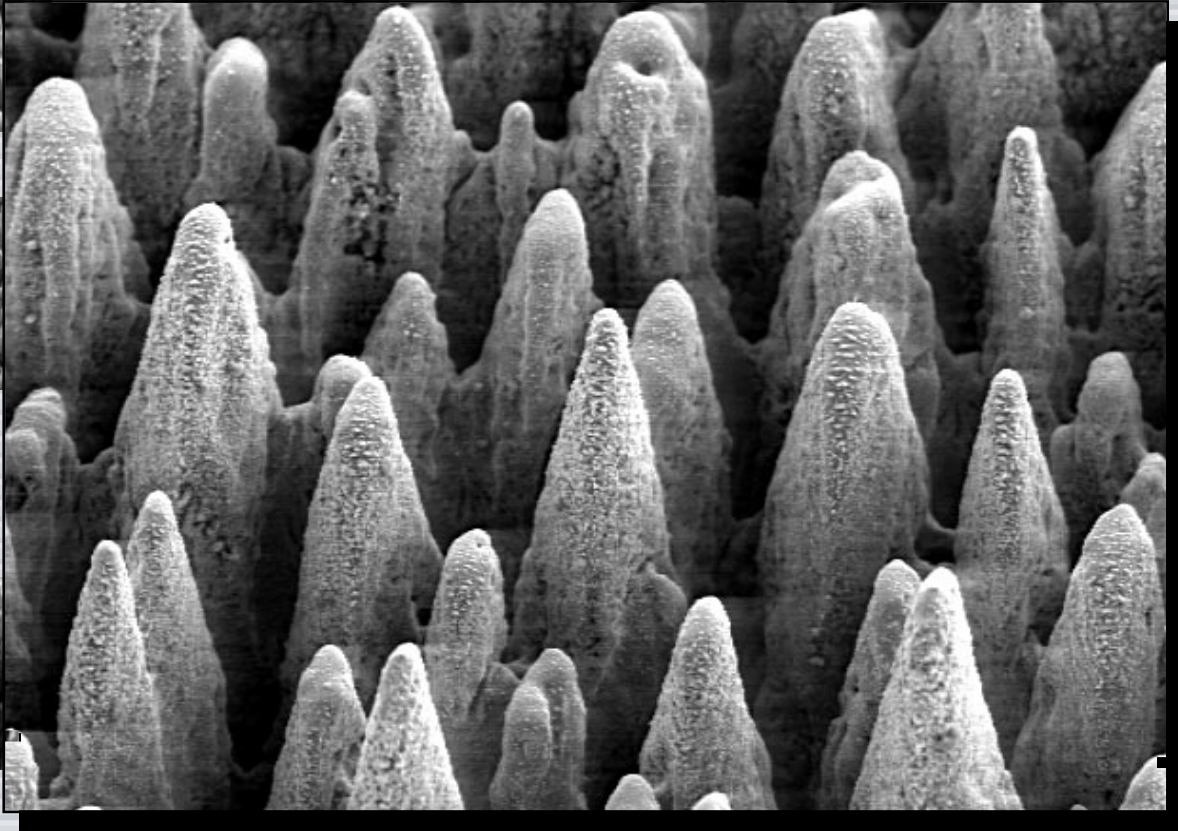
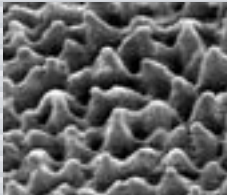
air

vacuum

Si



Ti



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# Materials

SF<sub>6</sub>

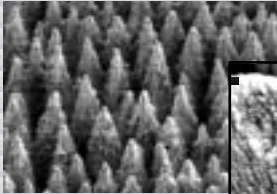
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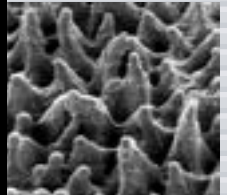
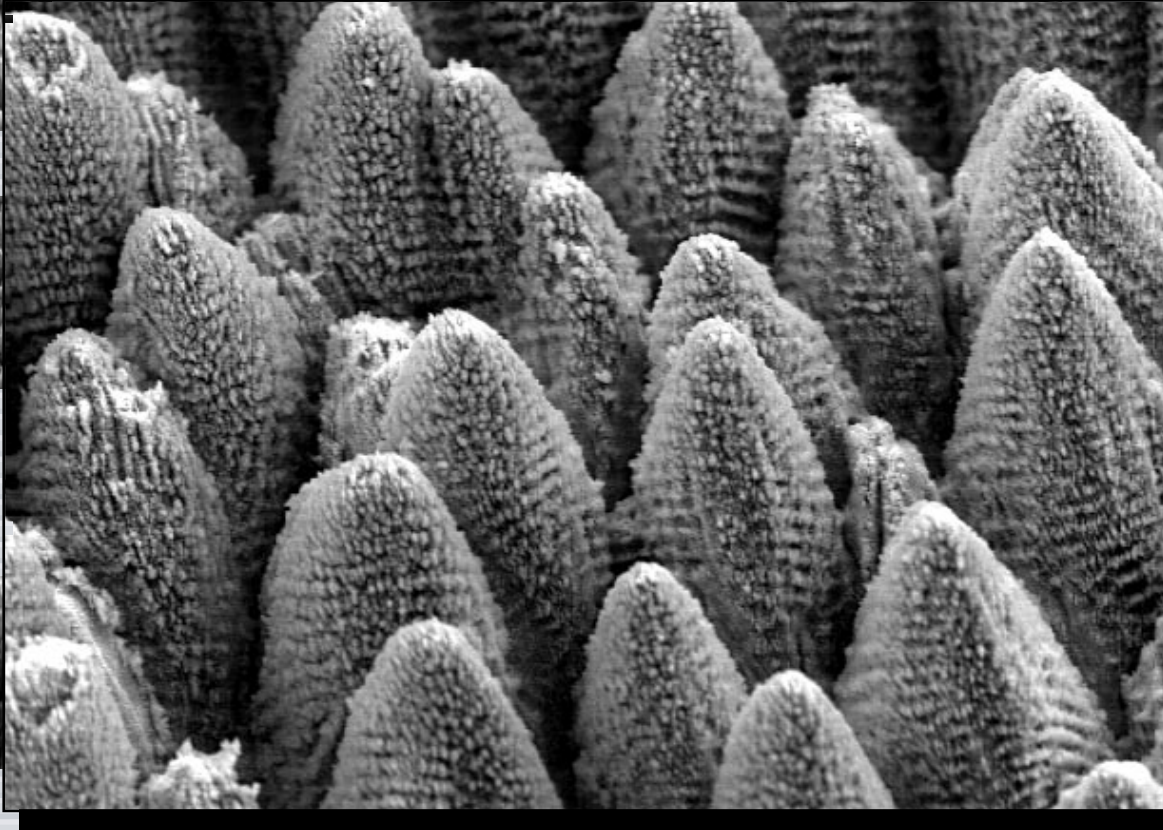
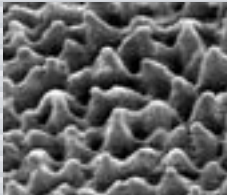
air

vacuum

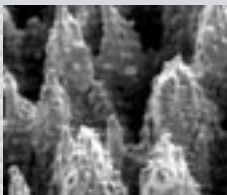
Si



Ti



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# Materials

SF<sub>6</sub>

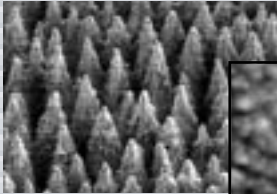
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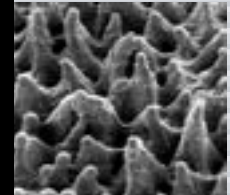
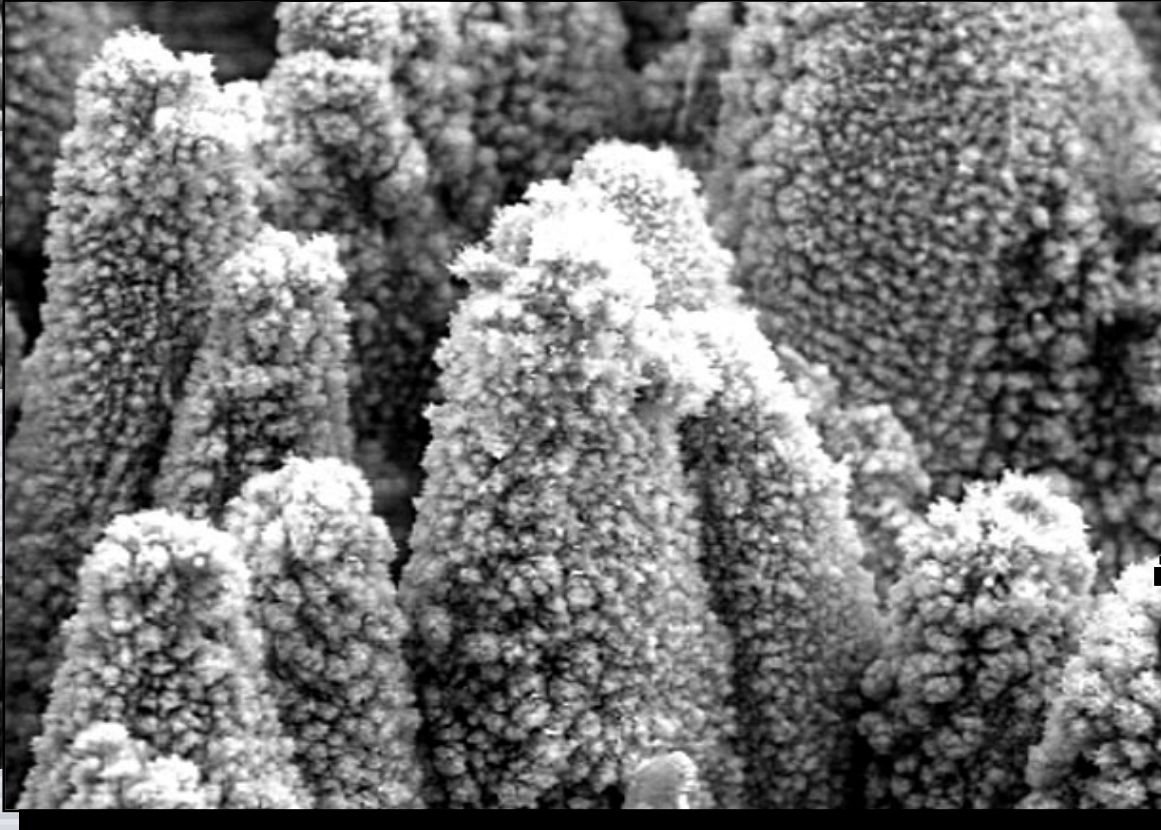
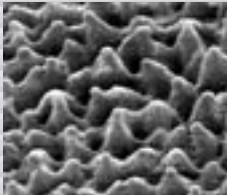
air

vacuum

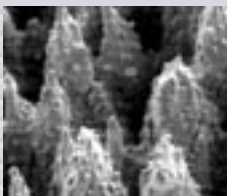
Si



Ti



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# Materials

SF<sub>6</sub>

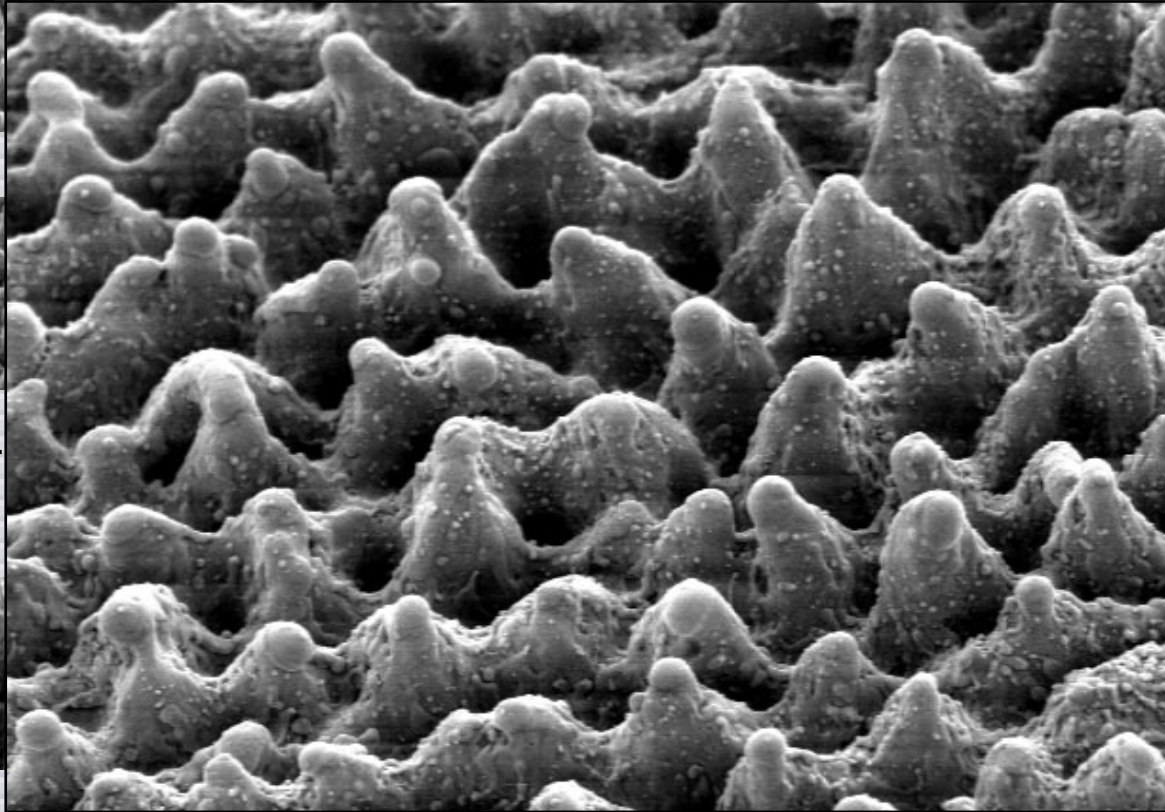
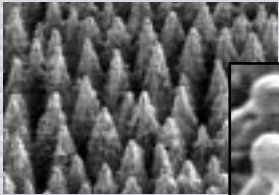
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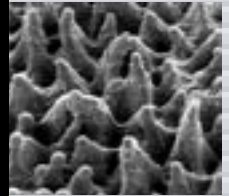
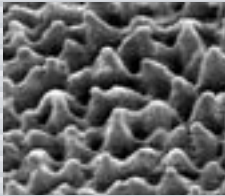
air

vacuum

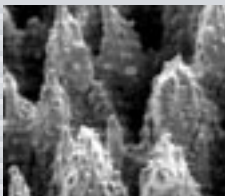
Si



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# Materials

SF<sub>6</sub>

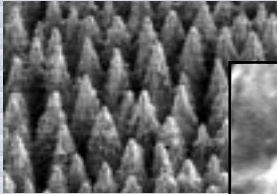
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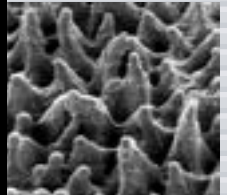
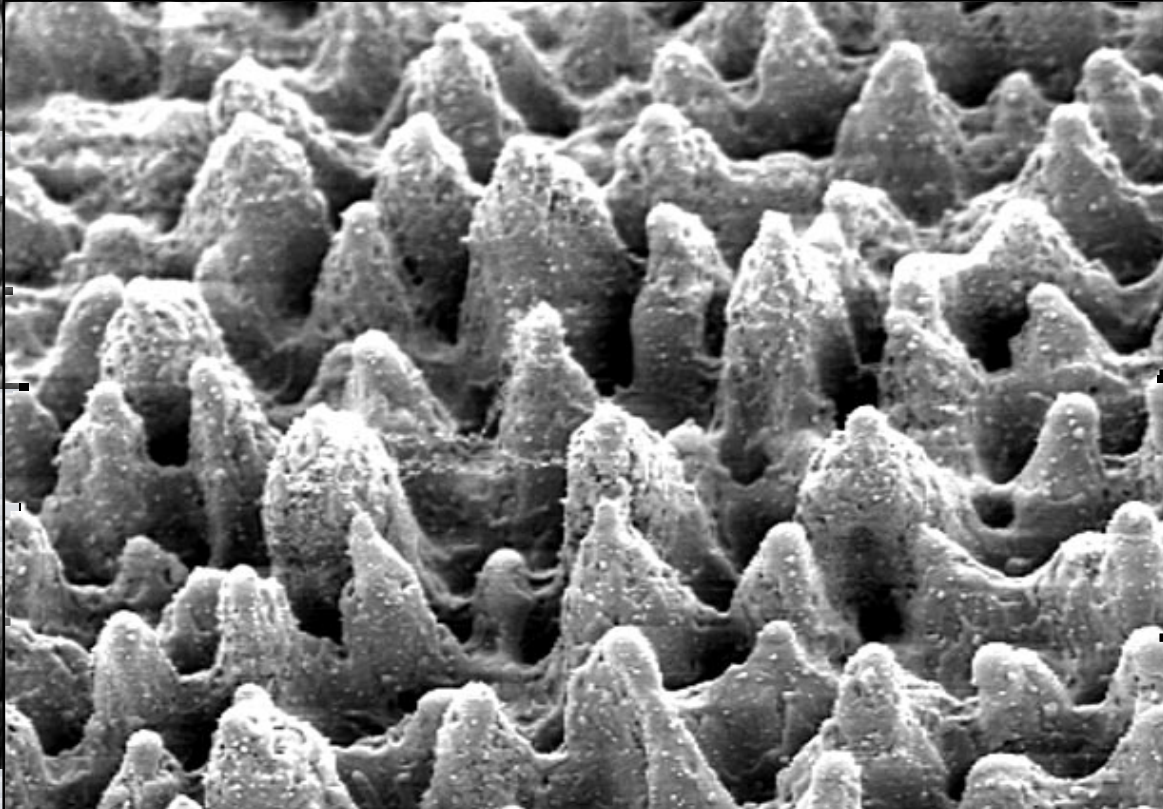
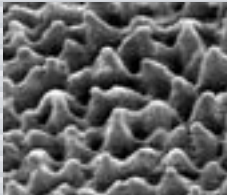
air

vacuum

Si

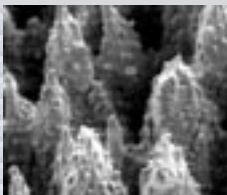


Ti



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# Materials

SF<sub>6</sub>

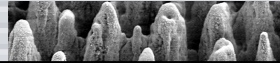
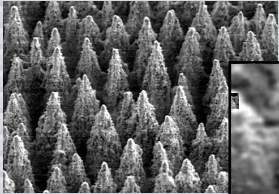
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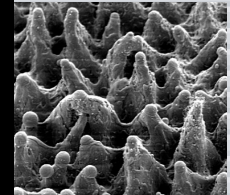
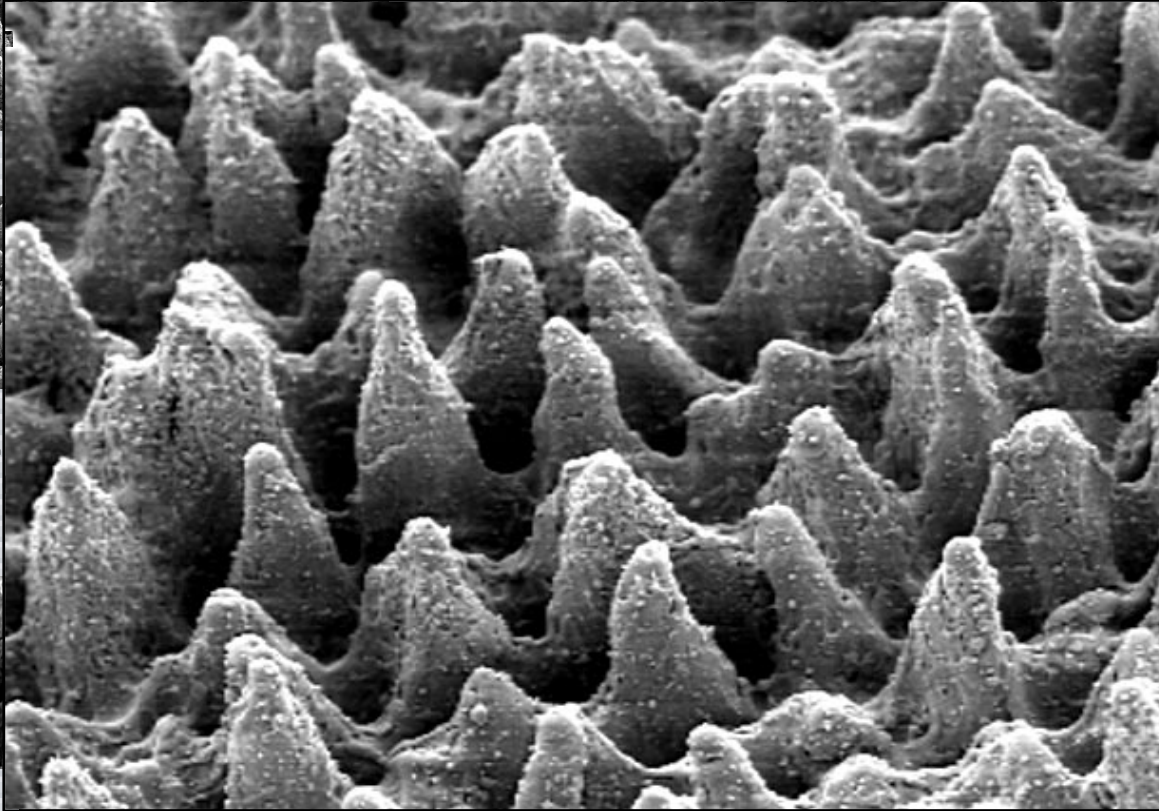
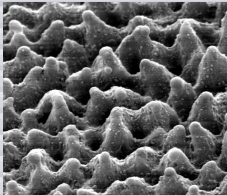
air

vacuum

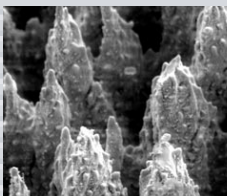
Si



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# Materials

SF<sub>6</sub>

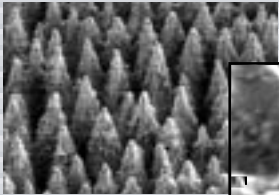
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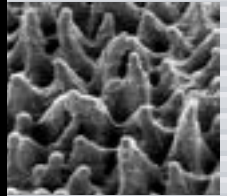
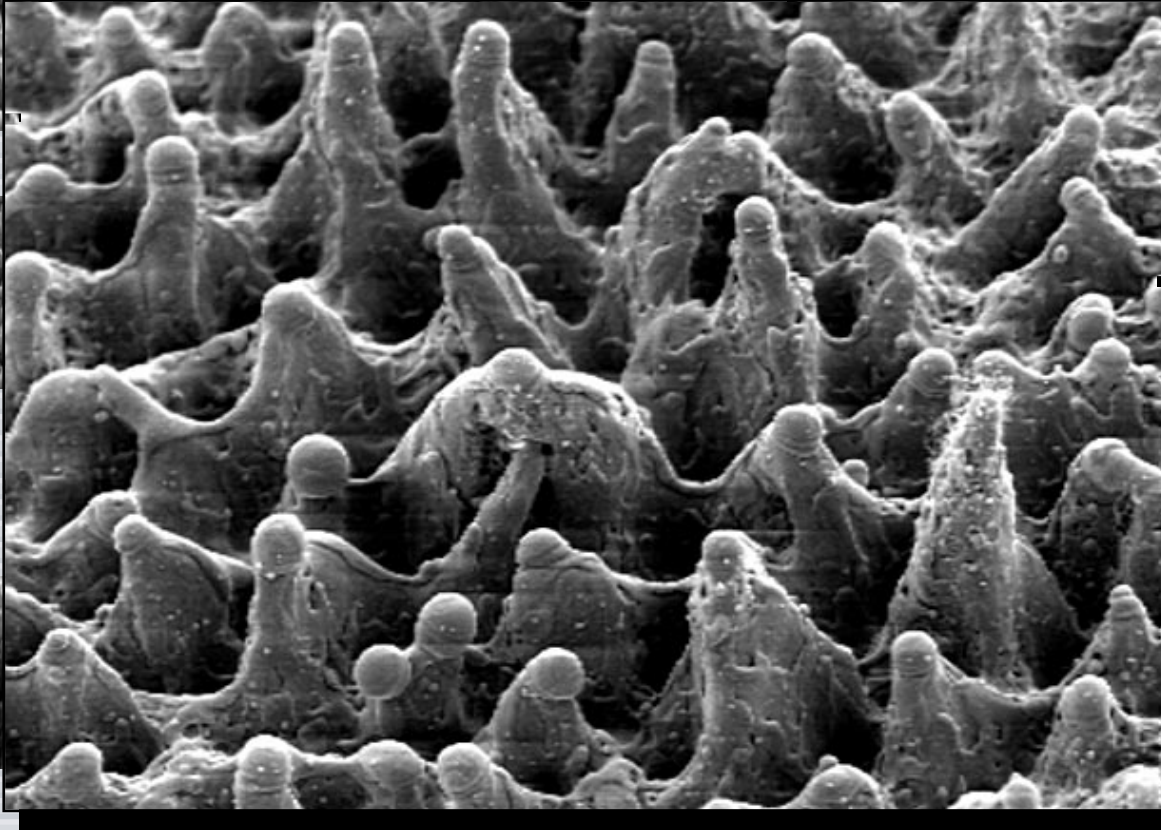
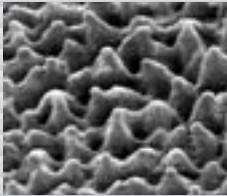
air

vacuum

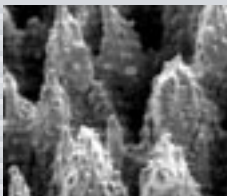
Si



Ti



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# Materials

SF<sub>6</sub>

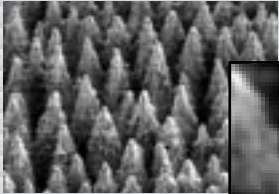
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N<sub>2</sub>

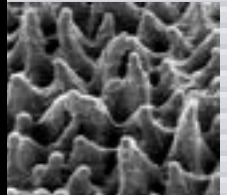
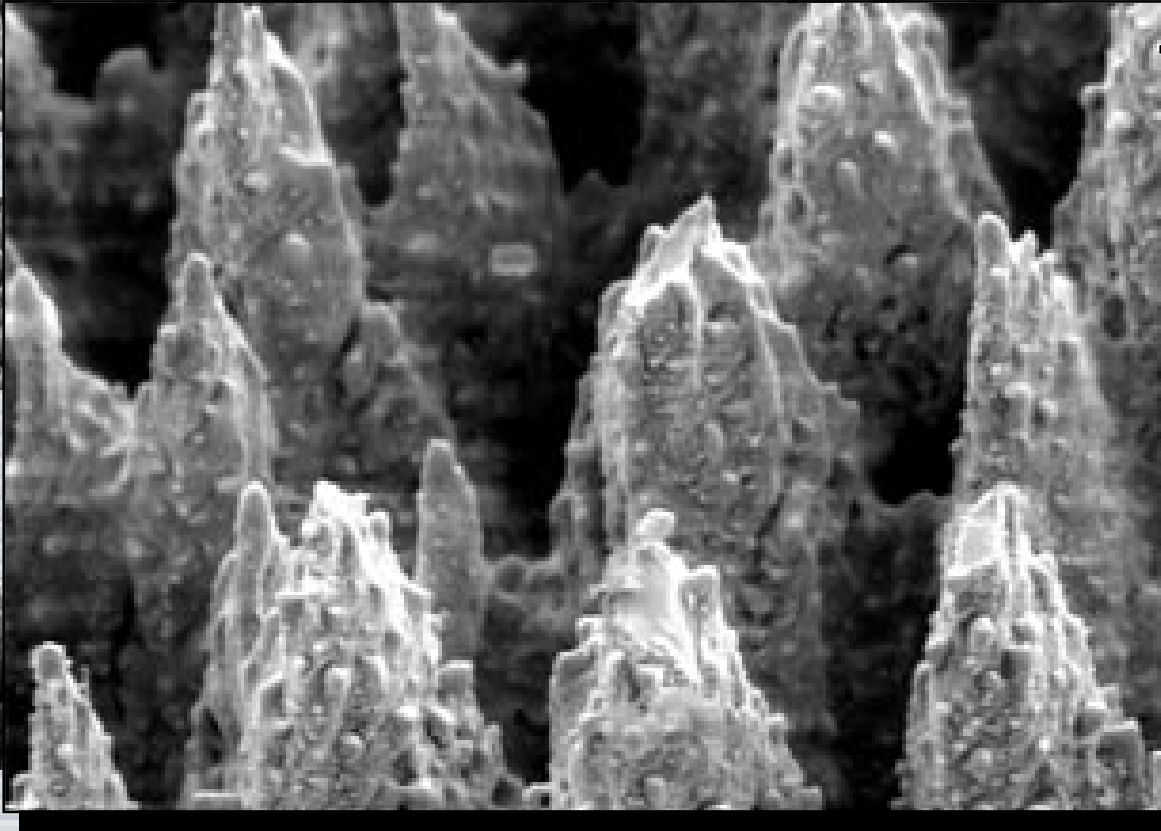
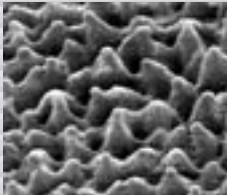
air

vacuum

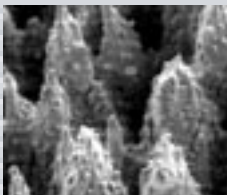
Si



Ti



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# Materials

SF<sub>6</sub>

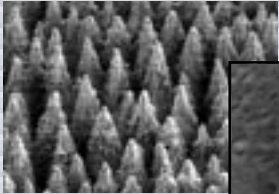
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N<sub>2</sub>

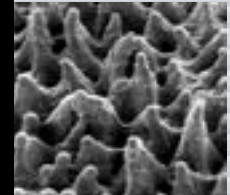
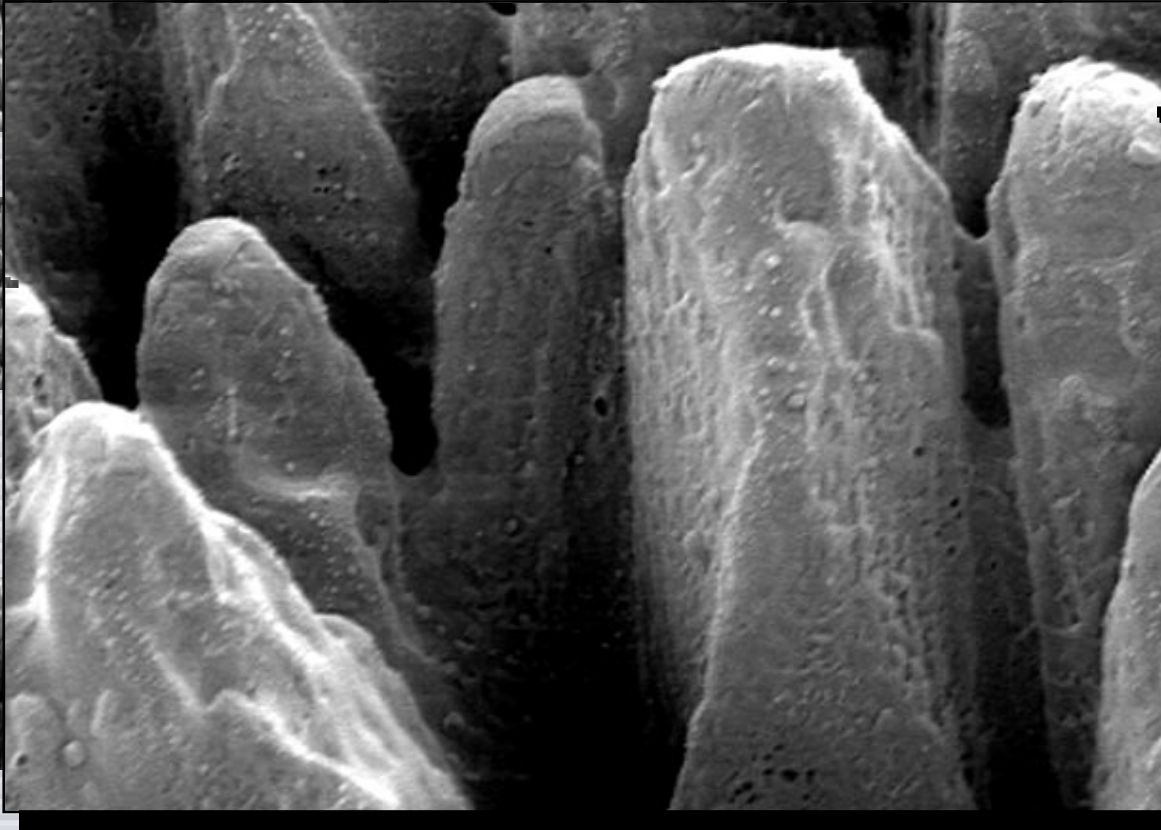
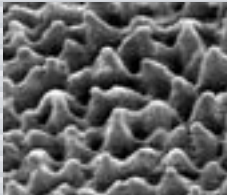
air

vacuum

Si

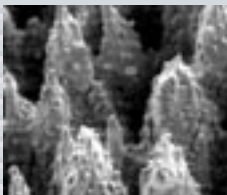


Ti



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Ge



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