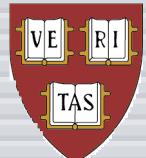
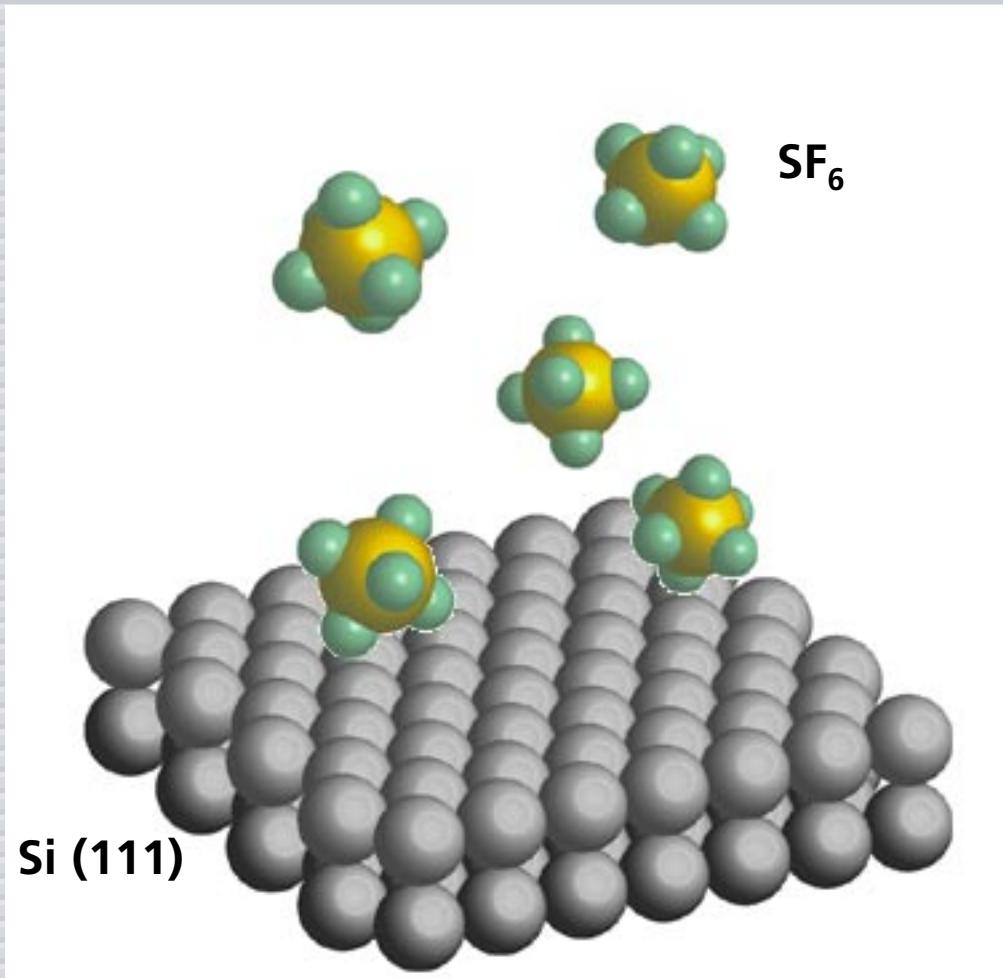


# **Ultrafast laser microstructuring of silicon for optoelectronic devices**

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

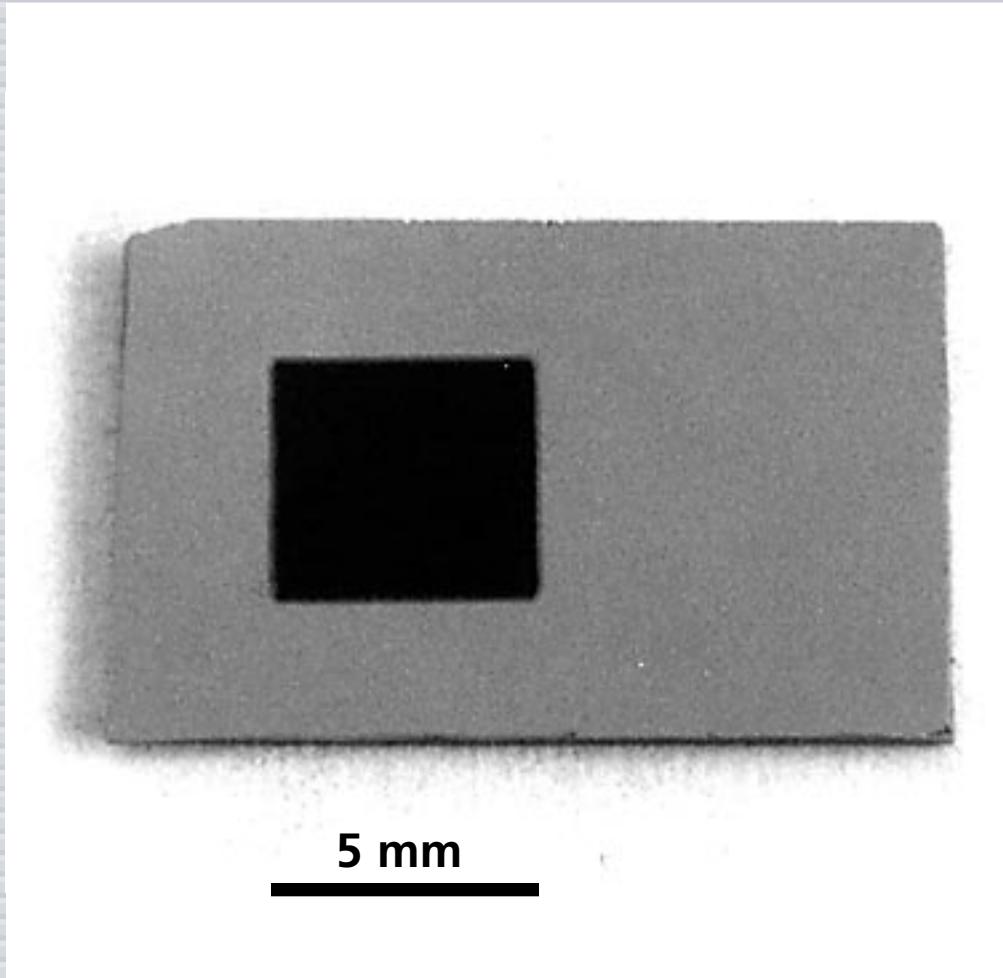


# *Introduction*



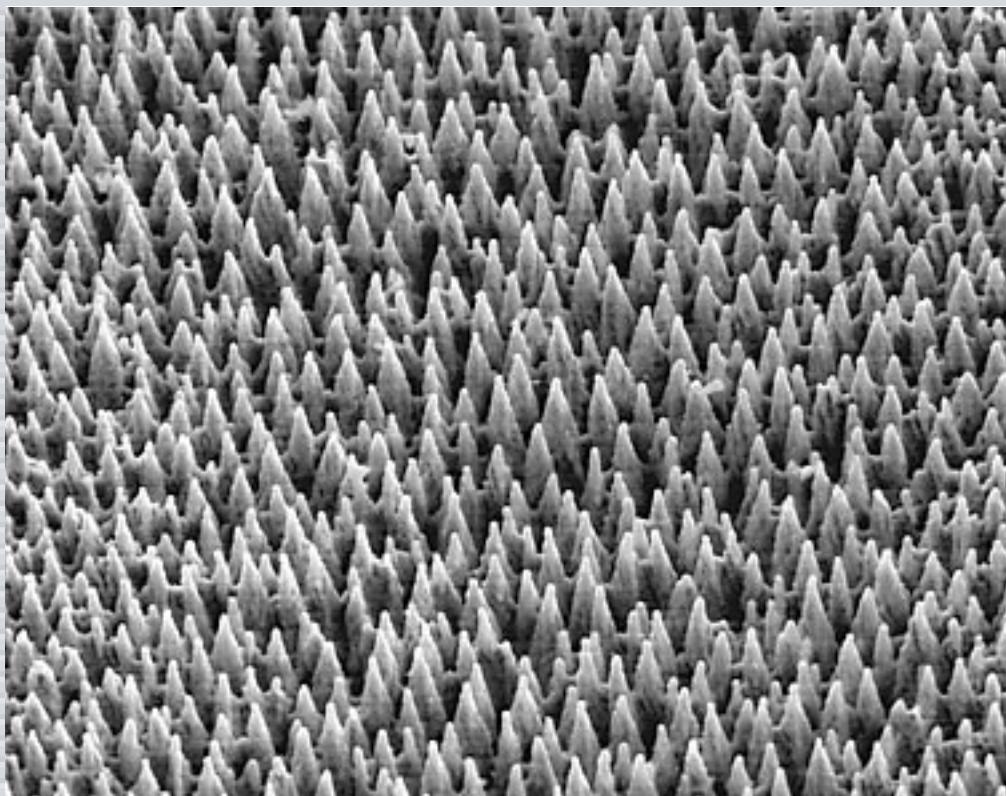
**irradiate with 100-fs  $10 \text{ kJ/m}^2$  pulses**

# *Introduction*



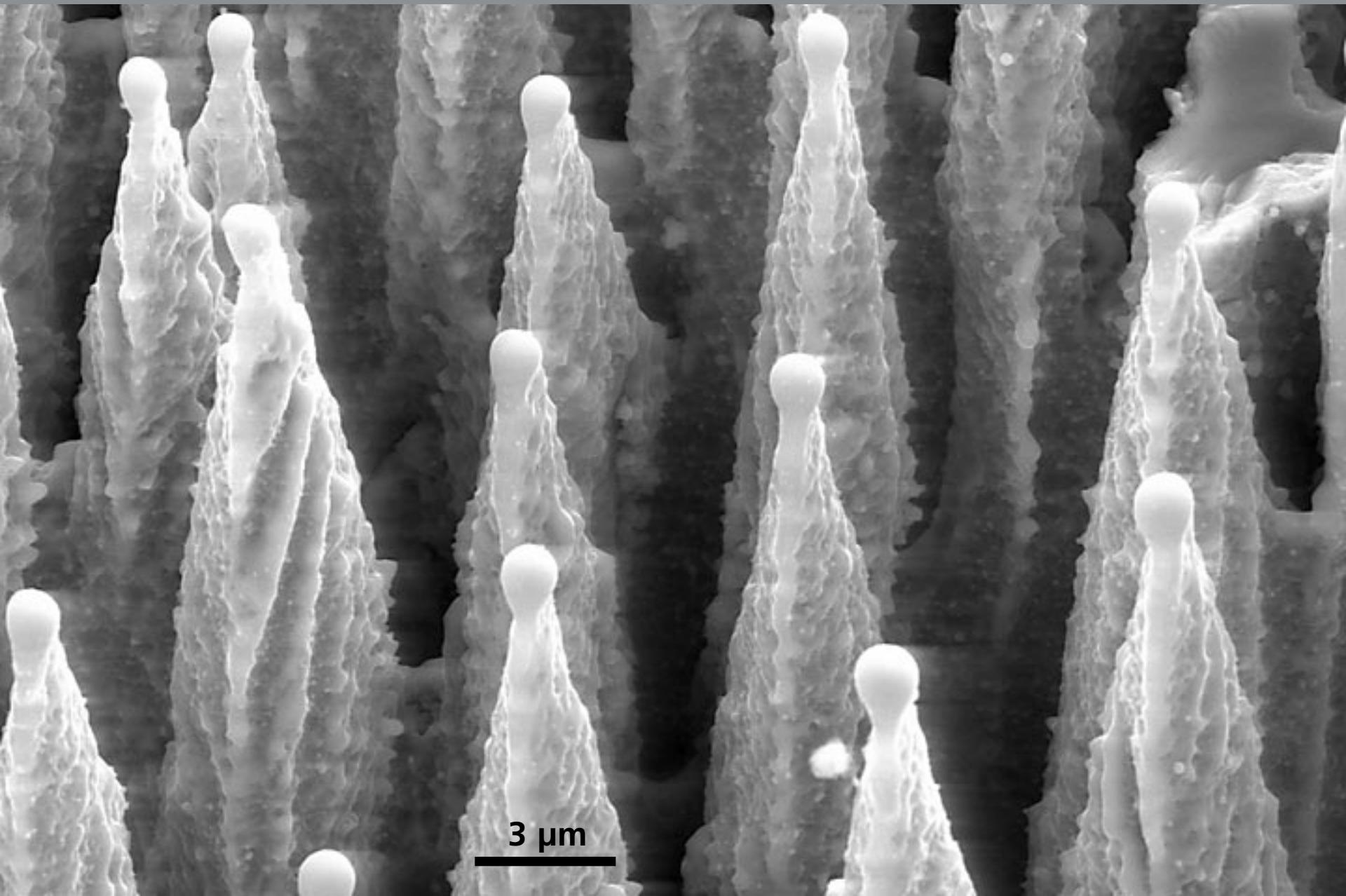
**"black silicon"**

# *Introduction*

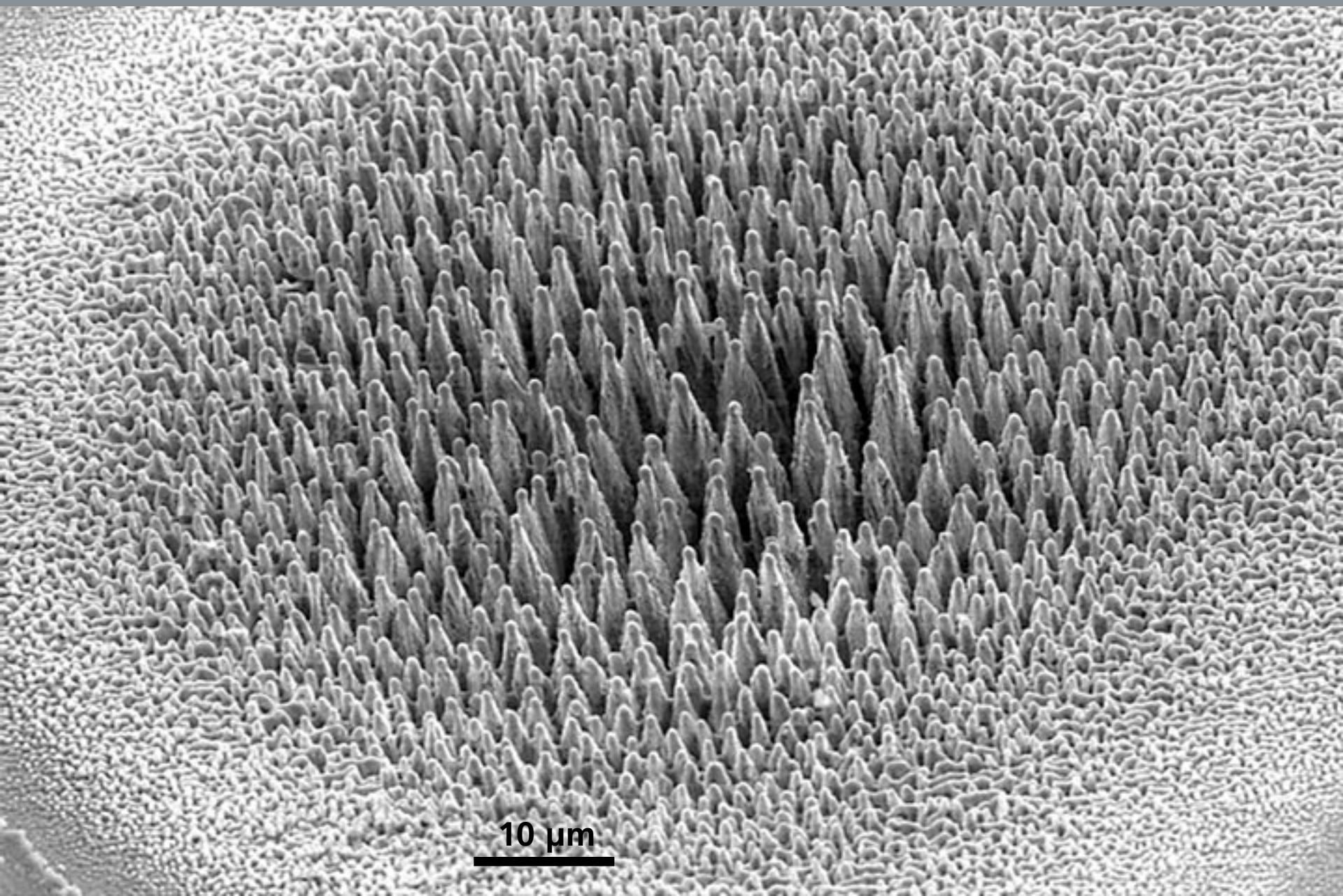


20  $\mu\text{m}$

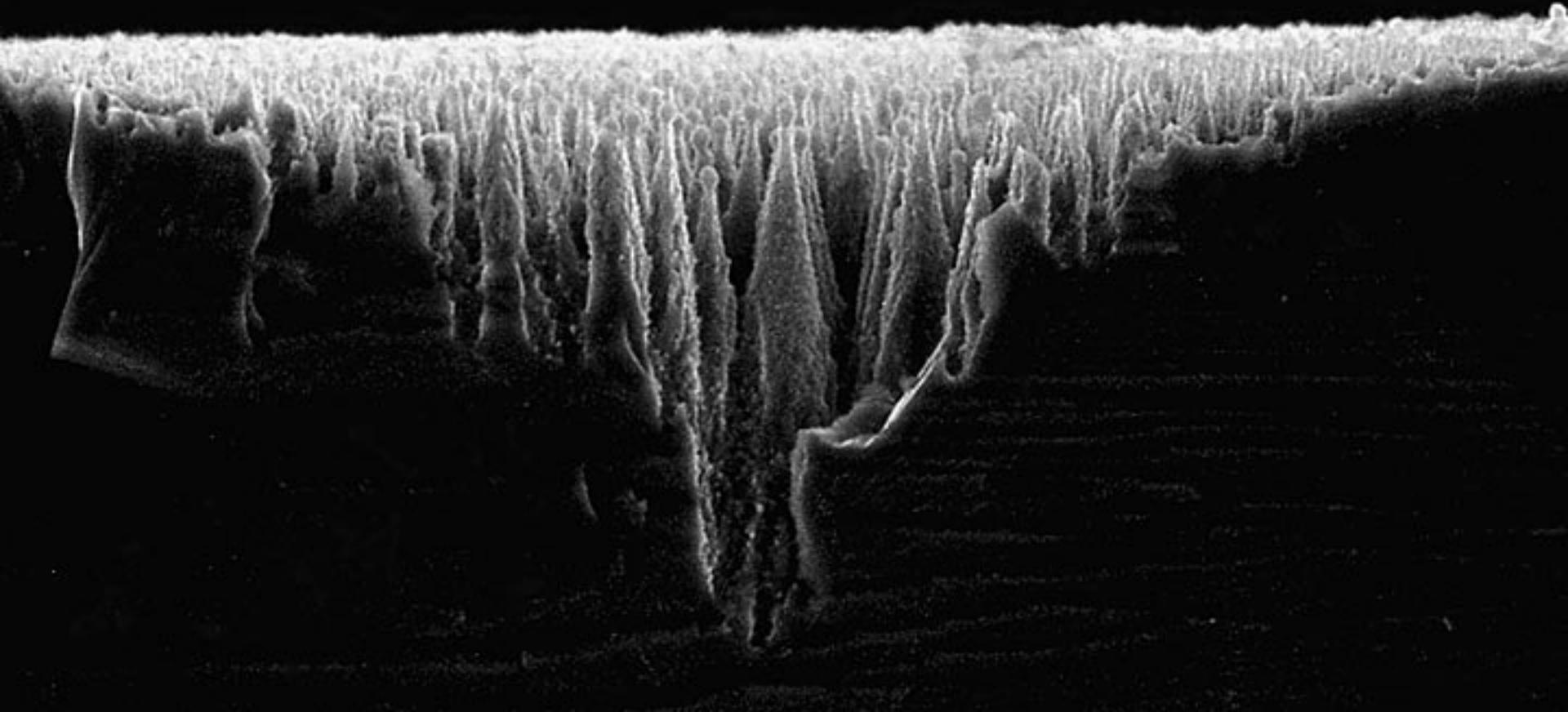
## *Introduction*



## *Introduction*



# *Introduction*



# *Introduction*

## *Introduction*

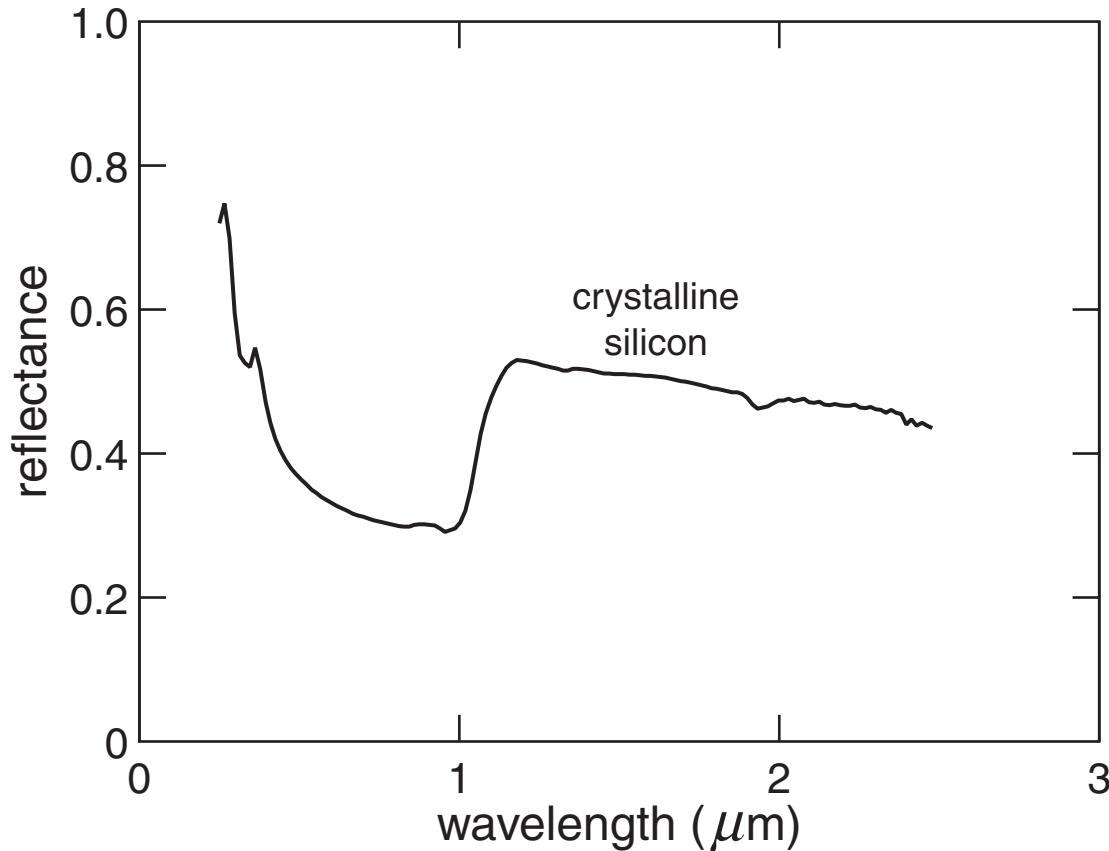
- ▶ **maskless etching process**
- ▶ **self-organized, tall, sharp structures**
- ▶ **nanoscale structure on spikes**

# *Outline*

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

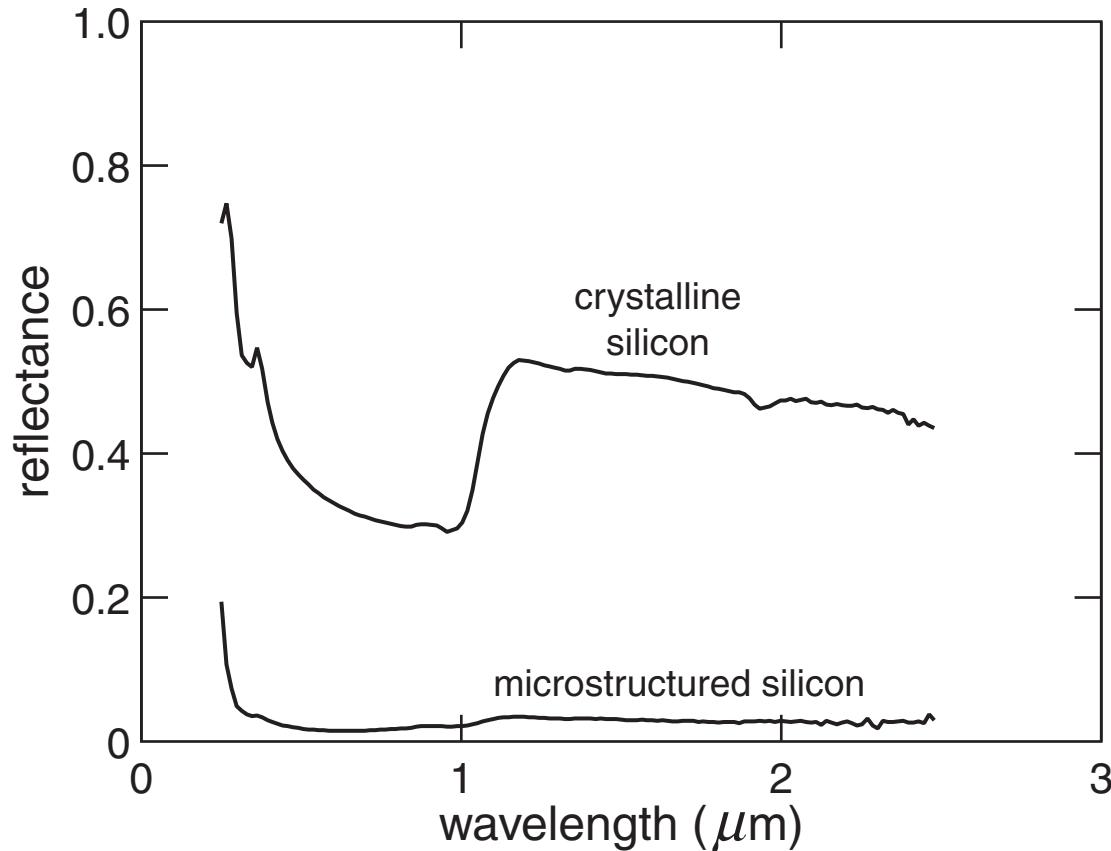
# *Properties*

## reflectance (integrating sphere)



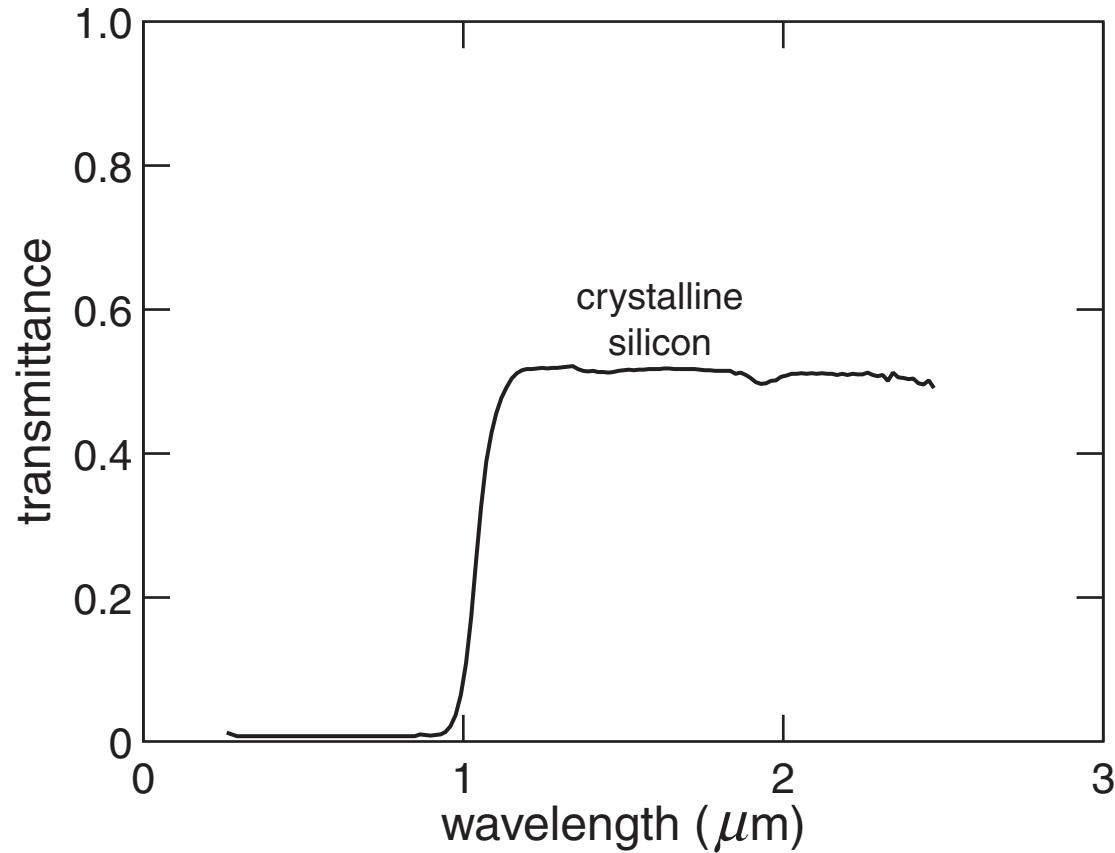
# *Properties*

## reflectance (integrating sphere)



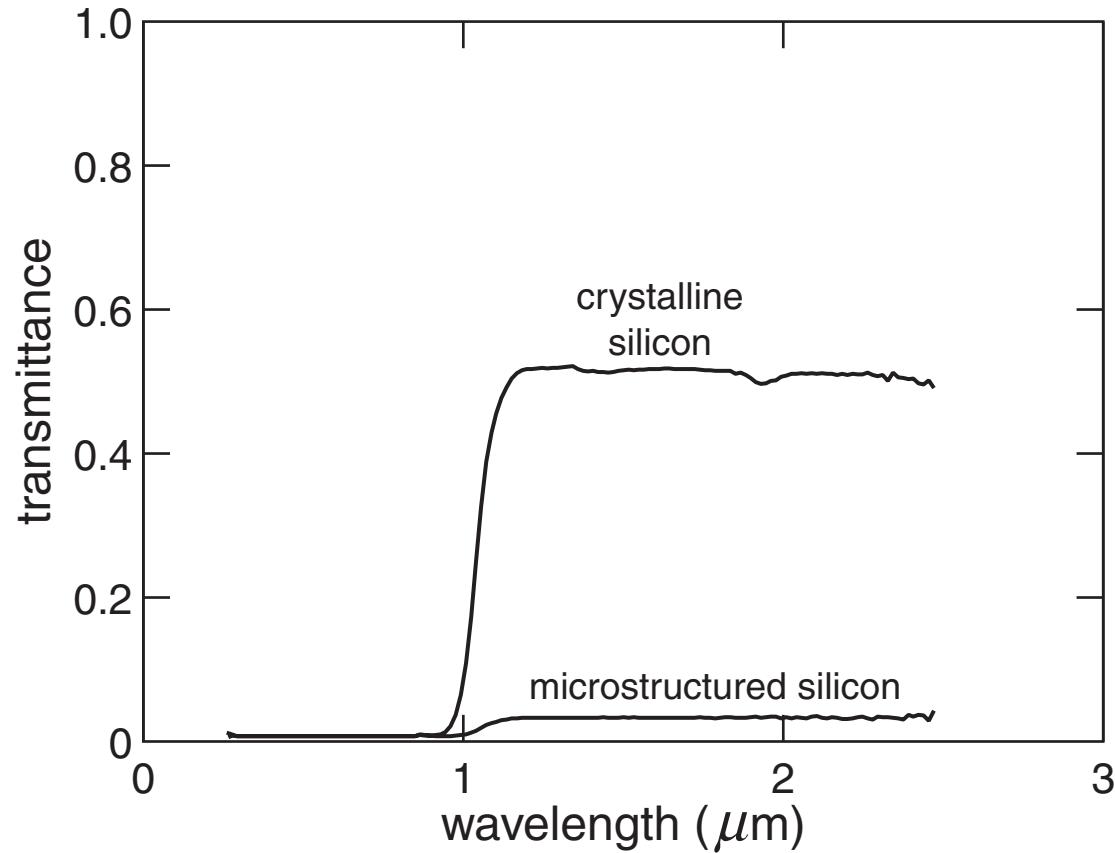
# *Properties*

## transmittance (integrating sphere)



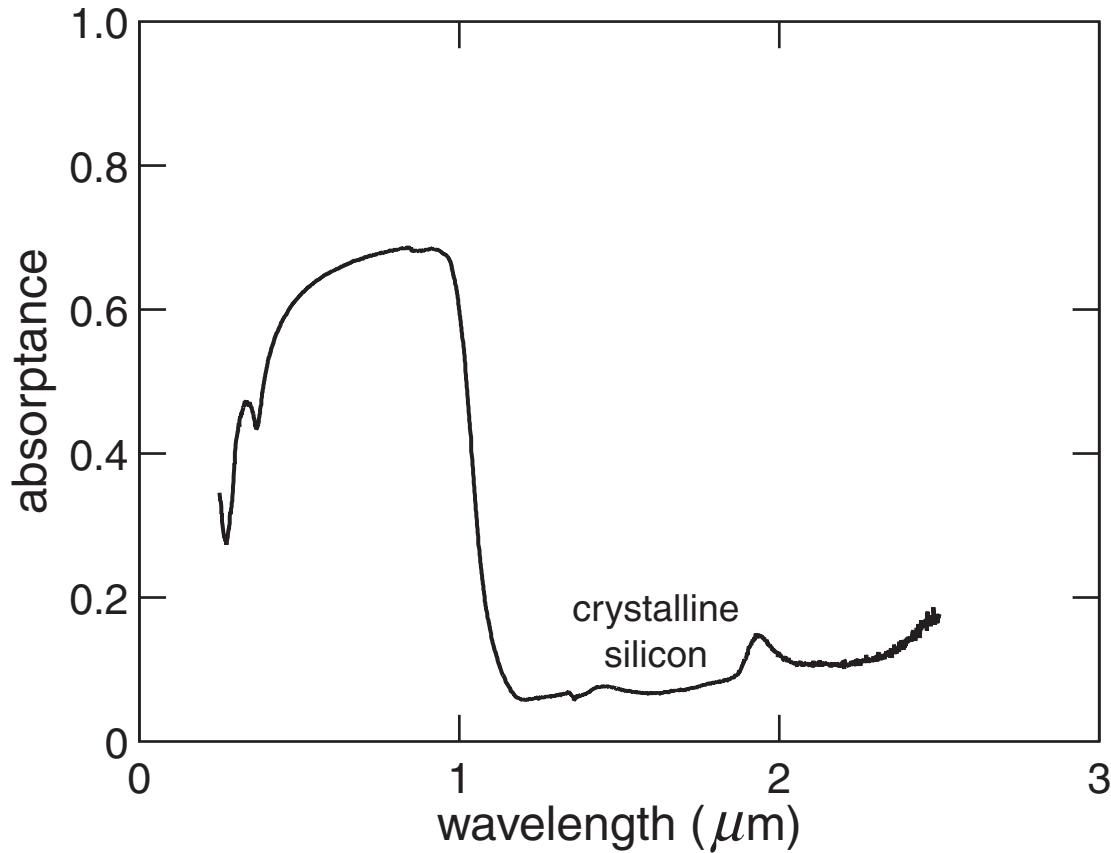
# *Properties*

## transmittance (integrating sphere)



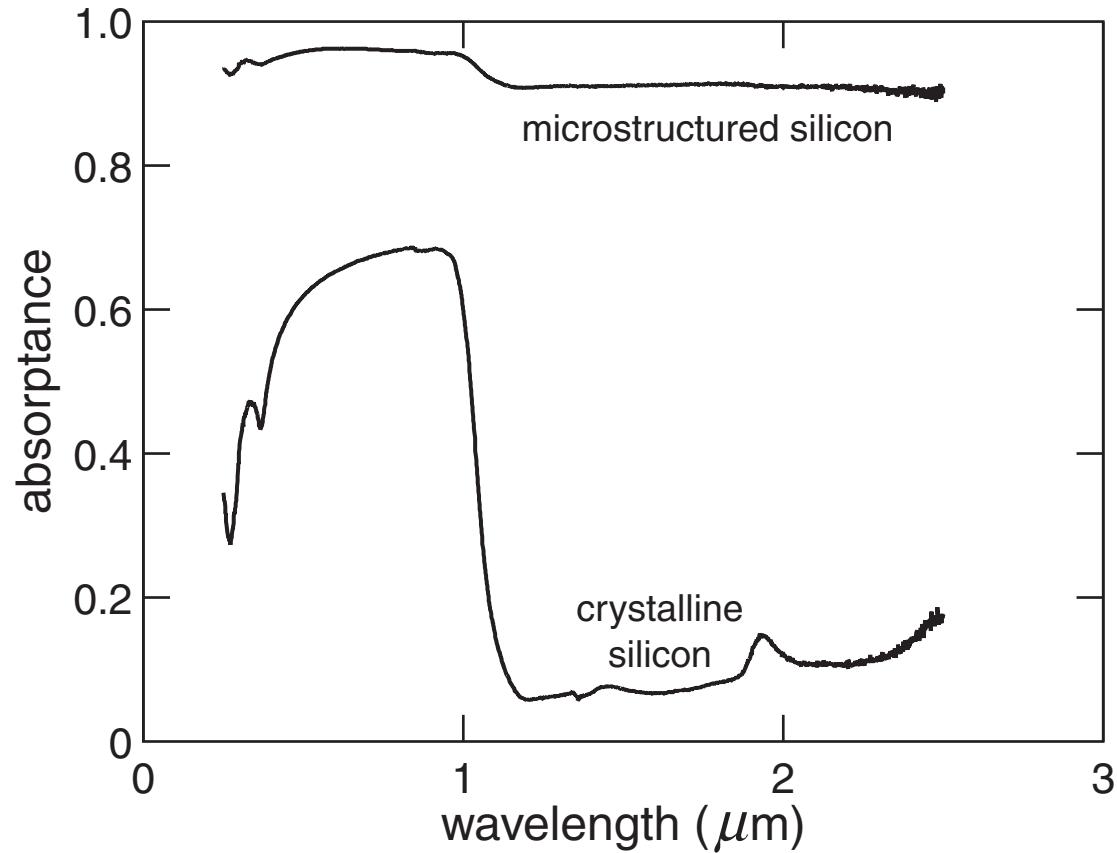
# *Properties*

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



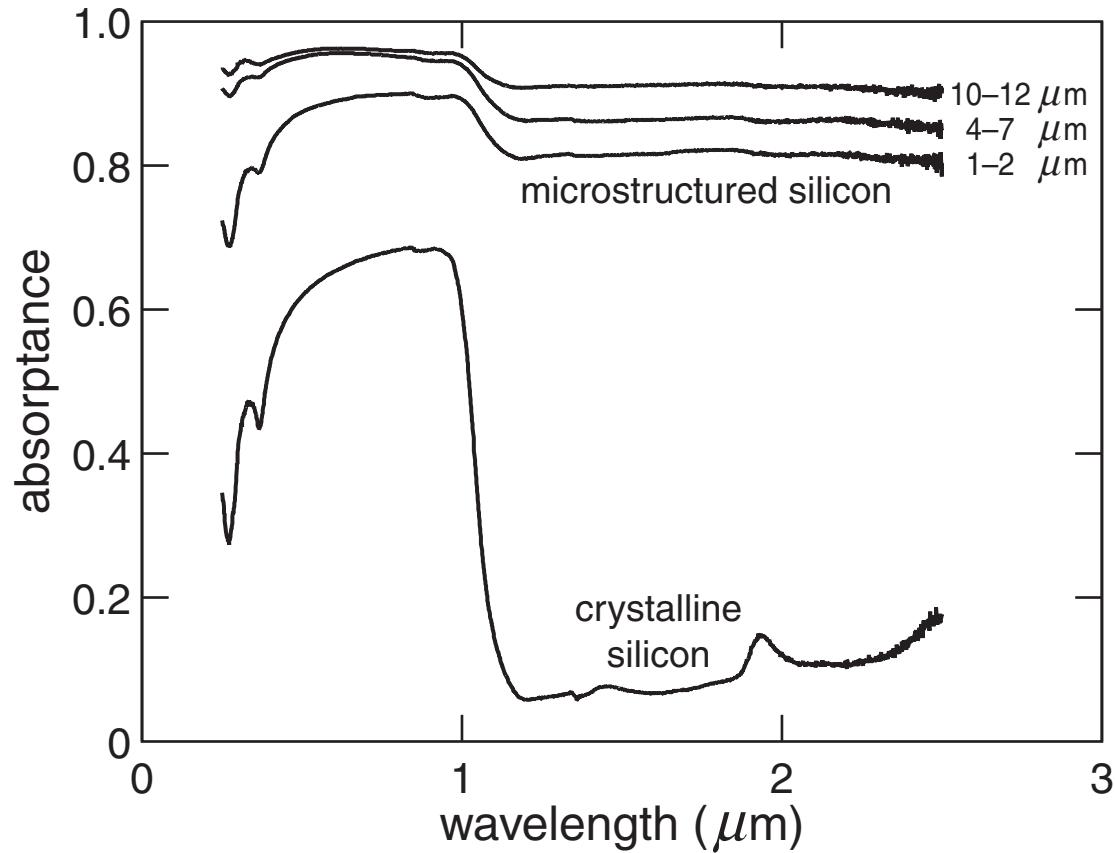
# *Properties*

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



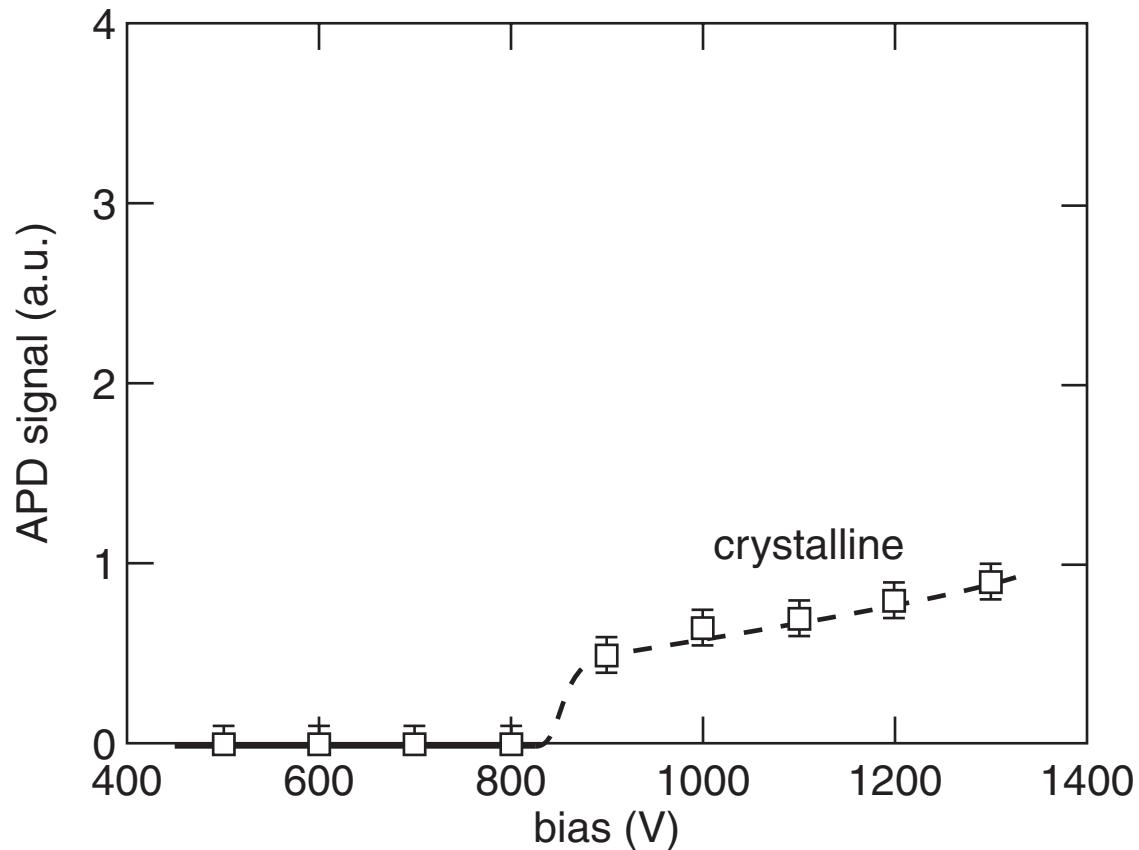
# *Properties*

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



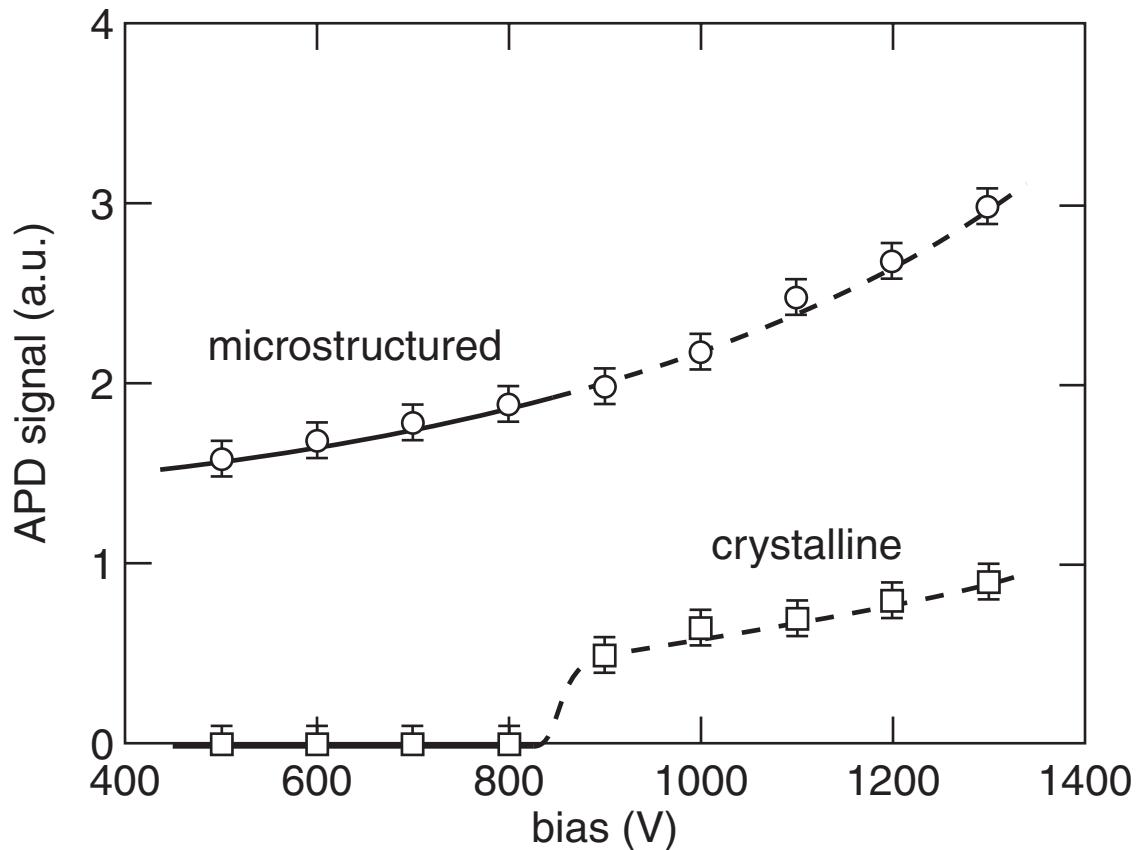
# *Properties*

## avalanche photodiode response at 1.3 $\mu$ m



# *Properties*

## avalanche photodiode response at 1.3 $\mu$ m



# *Properties*

## **field emission setup**



# *Properties*

## **field emission setup**



gold coating

# *Properties*

## field emission setup

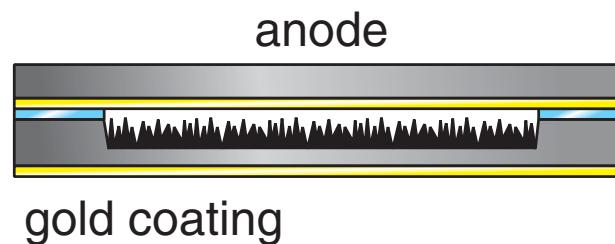
20 µm mica spacers



gold coating

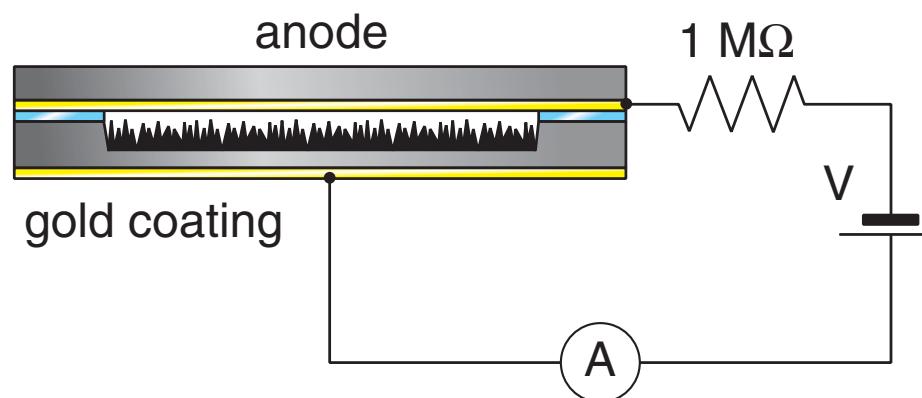
# *Properties*

## **field emission setup**

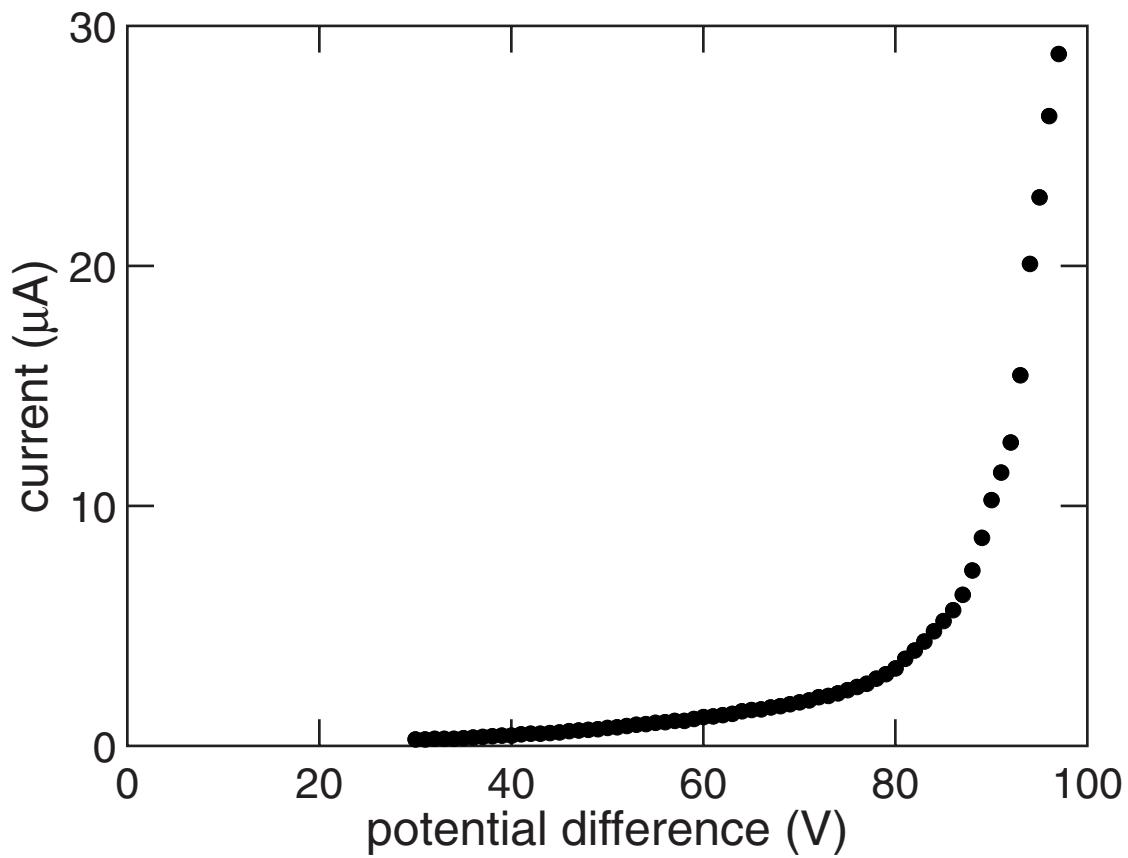


# *Properties*

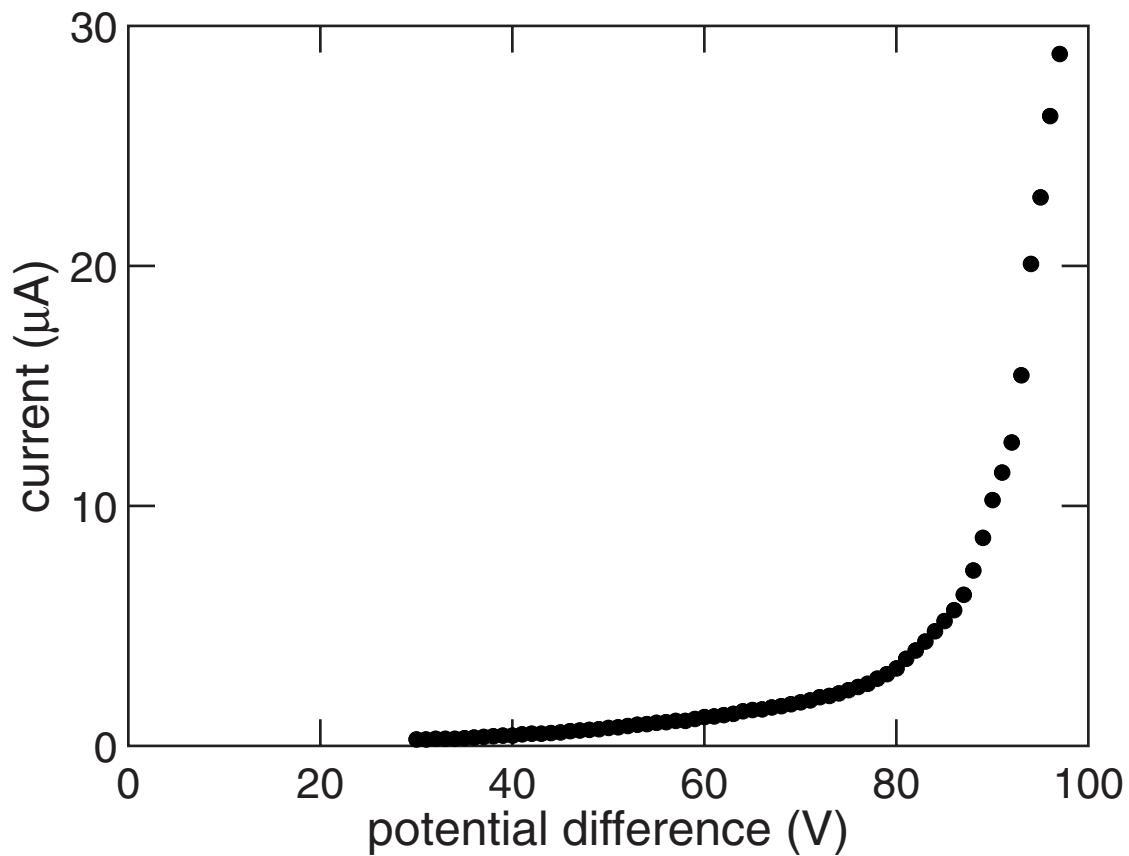
## field emission setup



# *Properties*

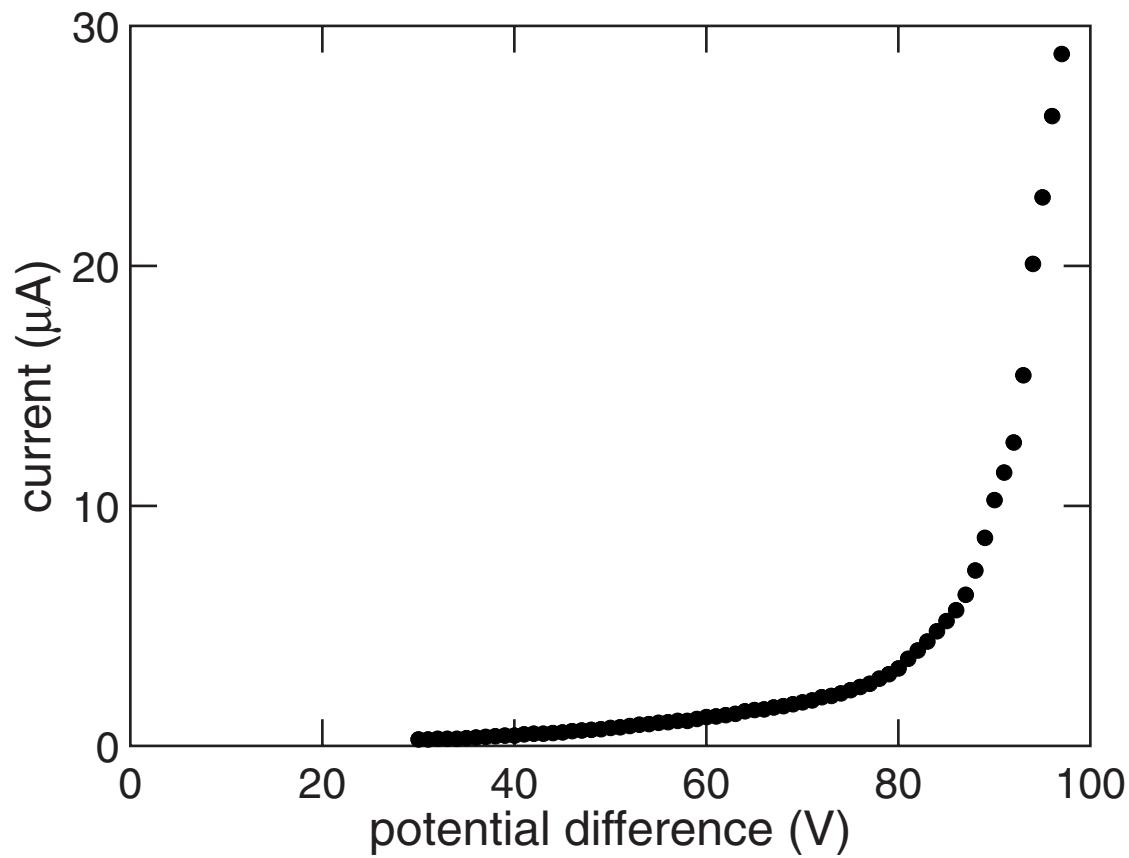


## *Properties*



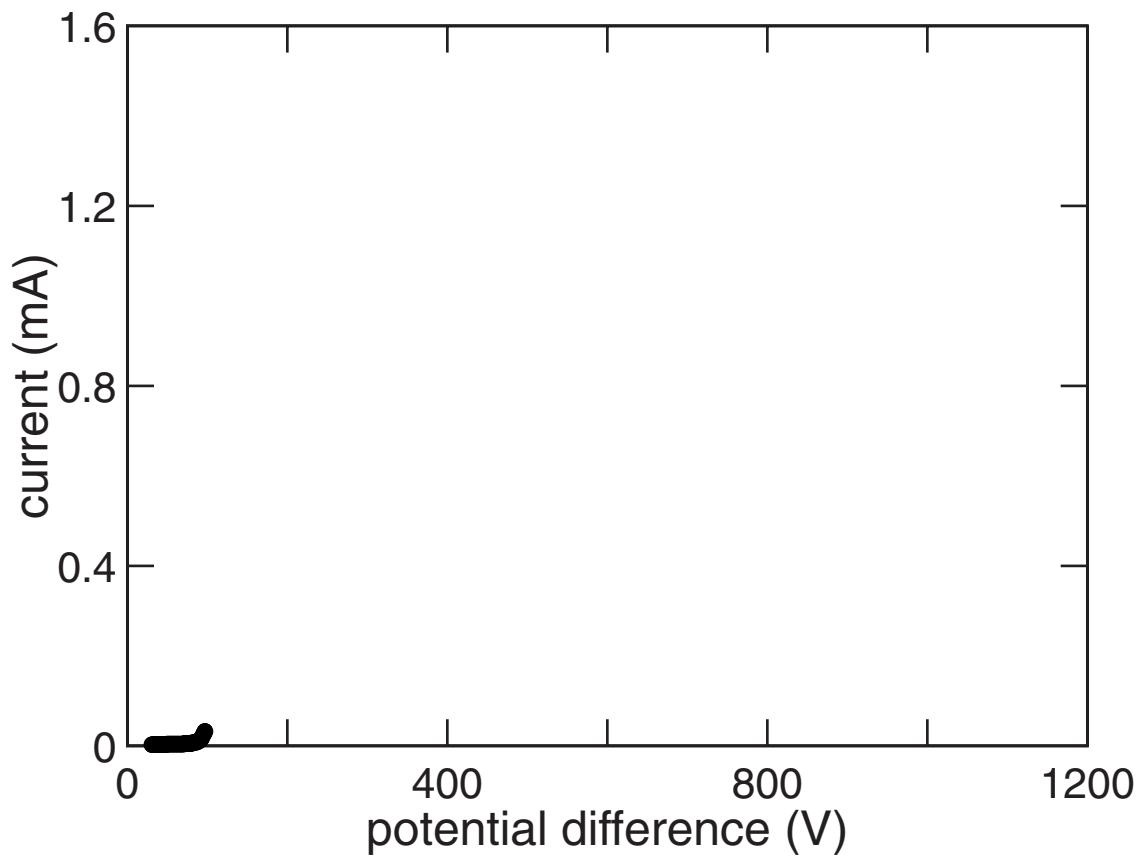
**turn-on field (1  $\mu$ A/cm $^2$ ): 1.2 V/ $\mu$ m**

# *Properties*

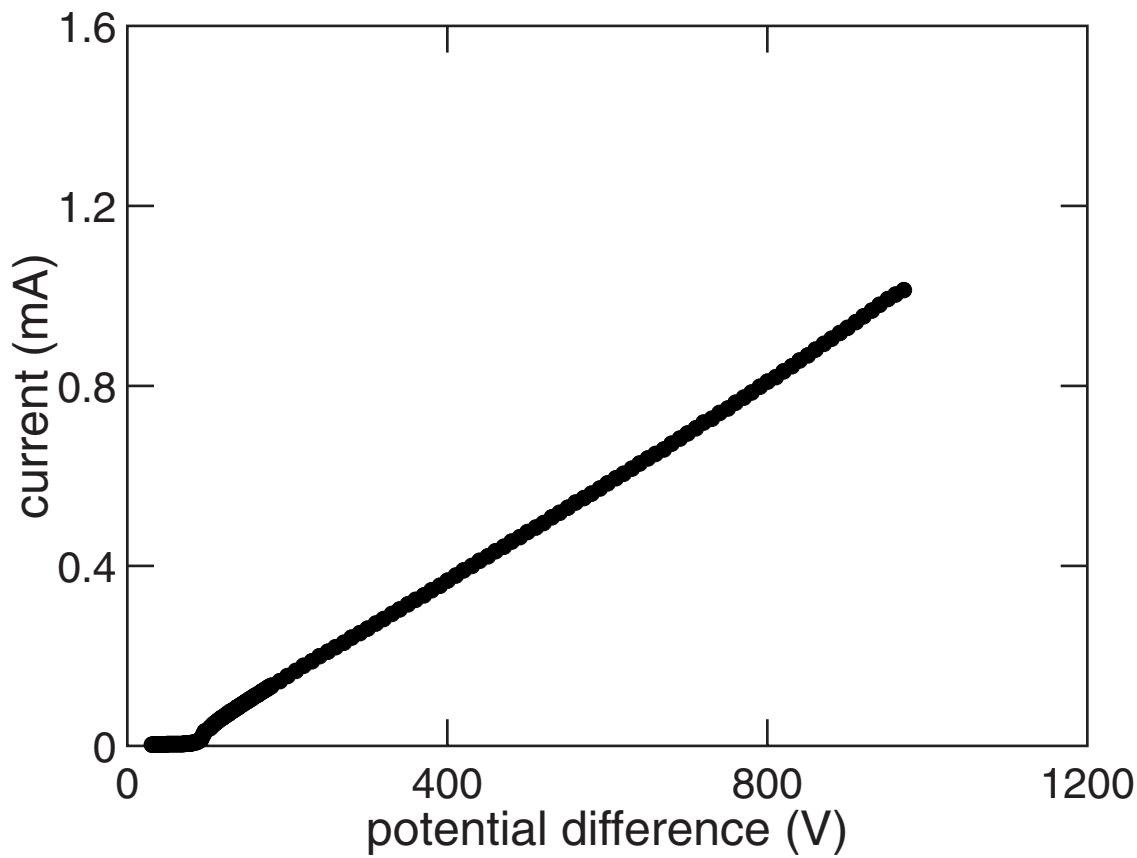


**threshold field ( $10 \mu\text{A}/\text{cm}^2$ ):  $2.1 \text{ V}/\mu\text{m}$**

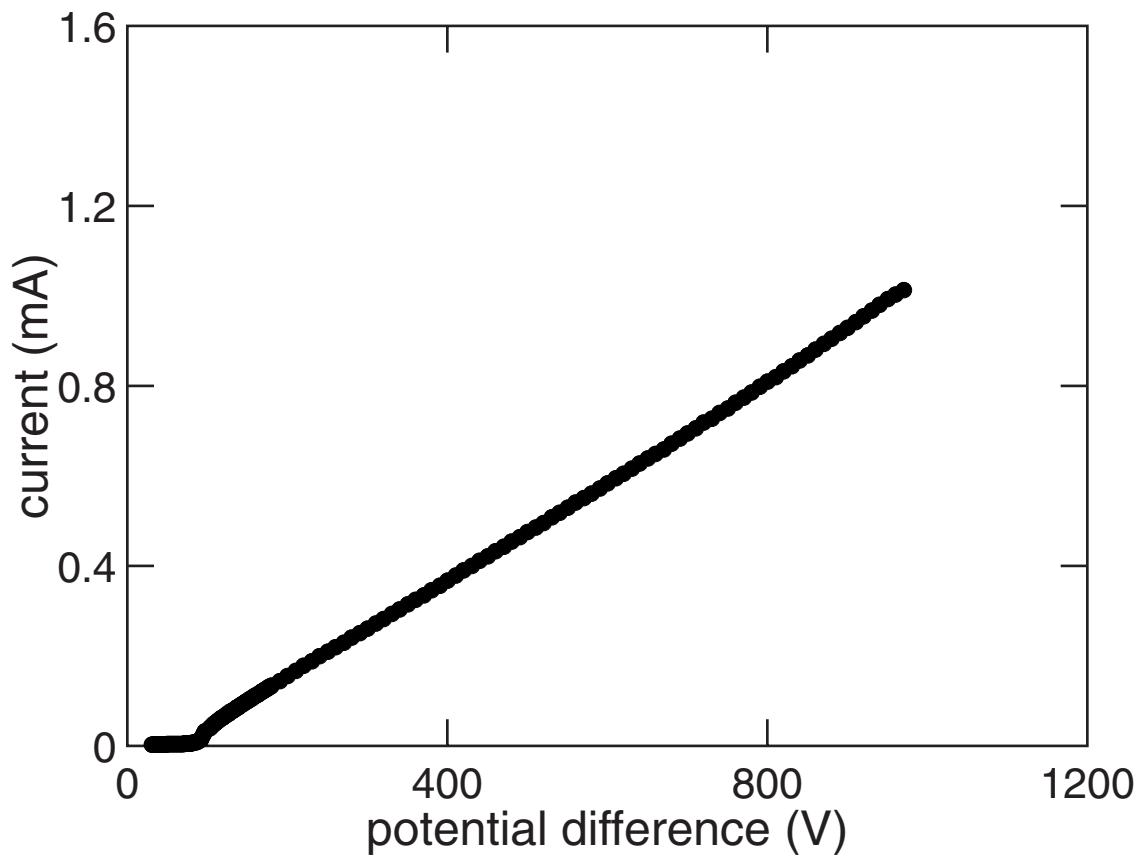
# *Properties*



# *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?**

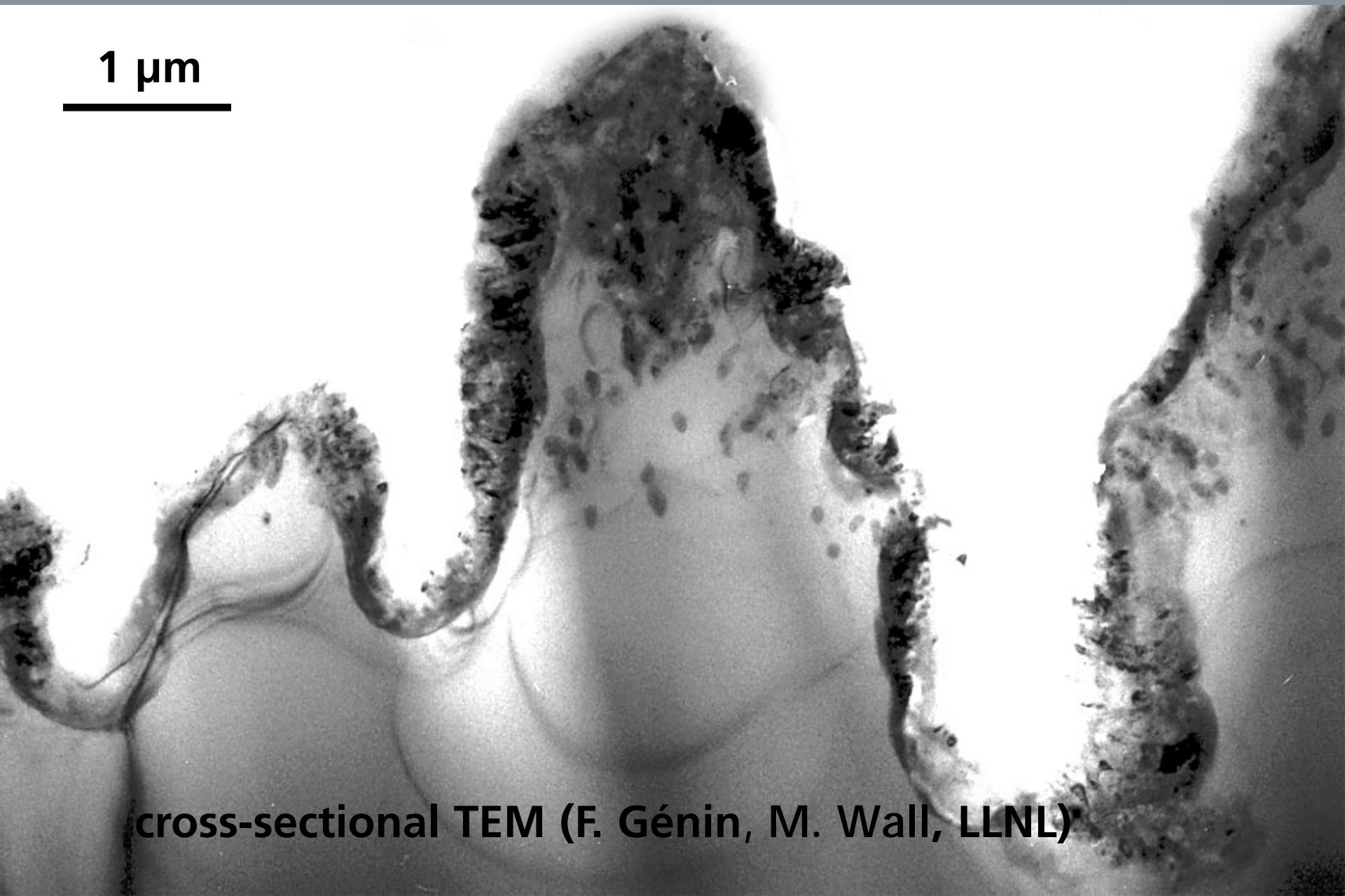
## *Structural and chemical analysis*

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

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

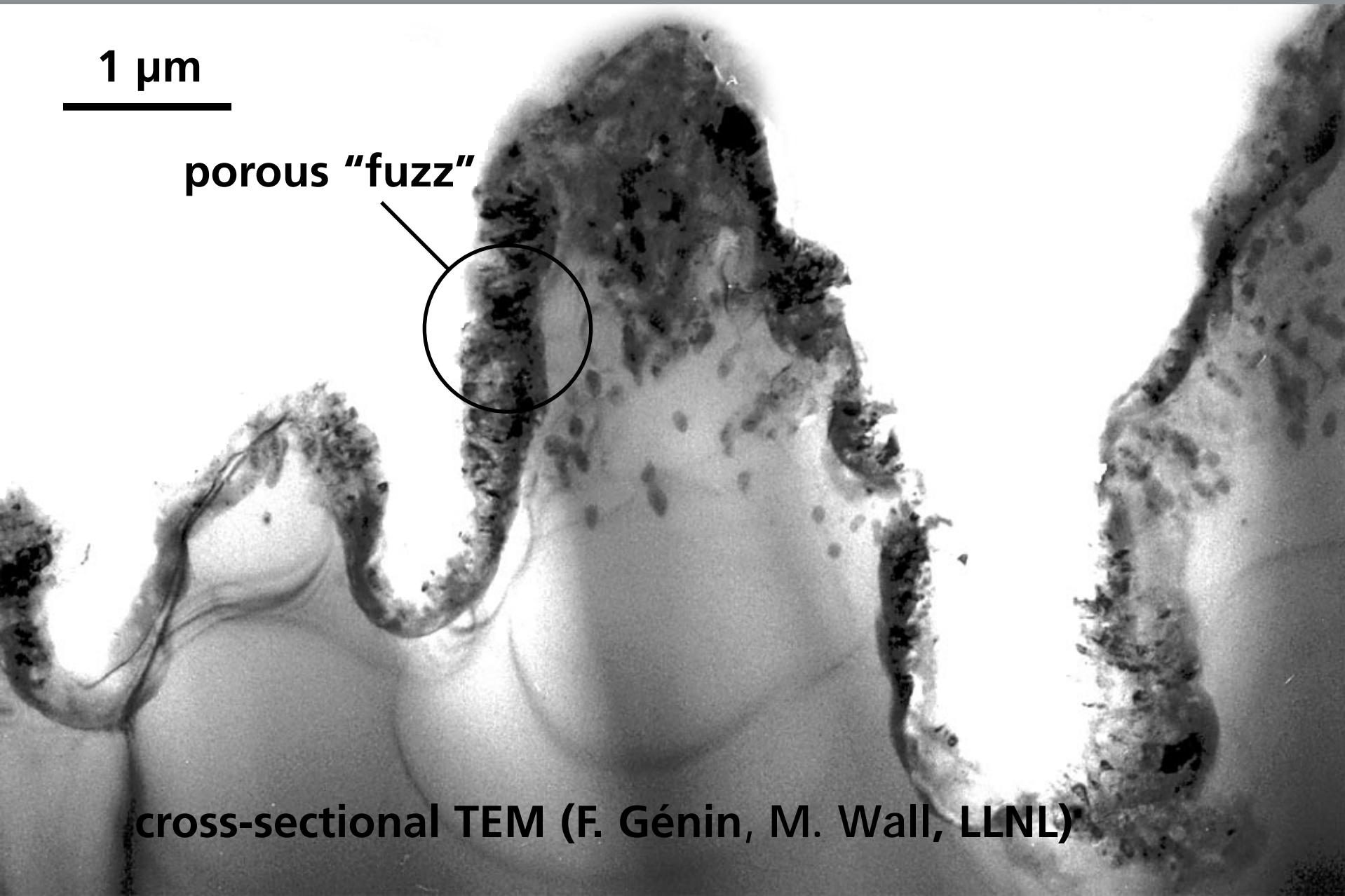
## *Structural and chemical analysis*

1  $\mu\text{m}$



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

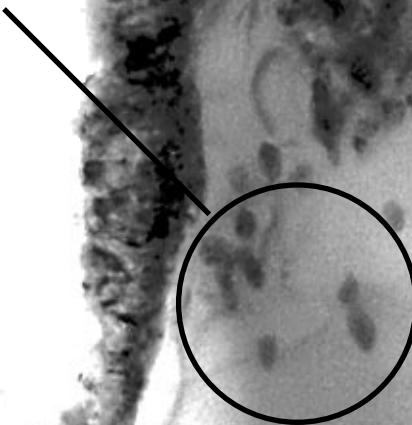
## *Structural and chemical analysis*



## *Structural and chemical analysis*

1  $\mu\text{m}$

nanocrystallites

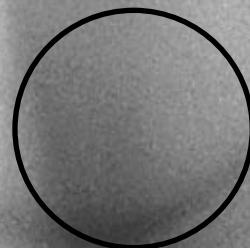


cross-sectional TEM (F. Génin, M. Wall, LLNL)

## *Structural and chemical analysis*

1  $\mu\text{m}$

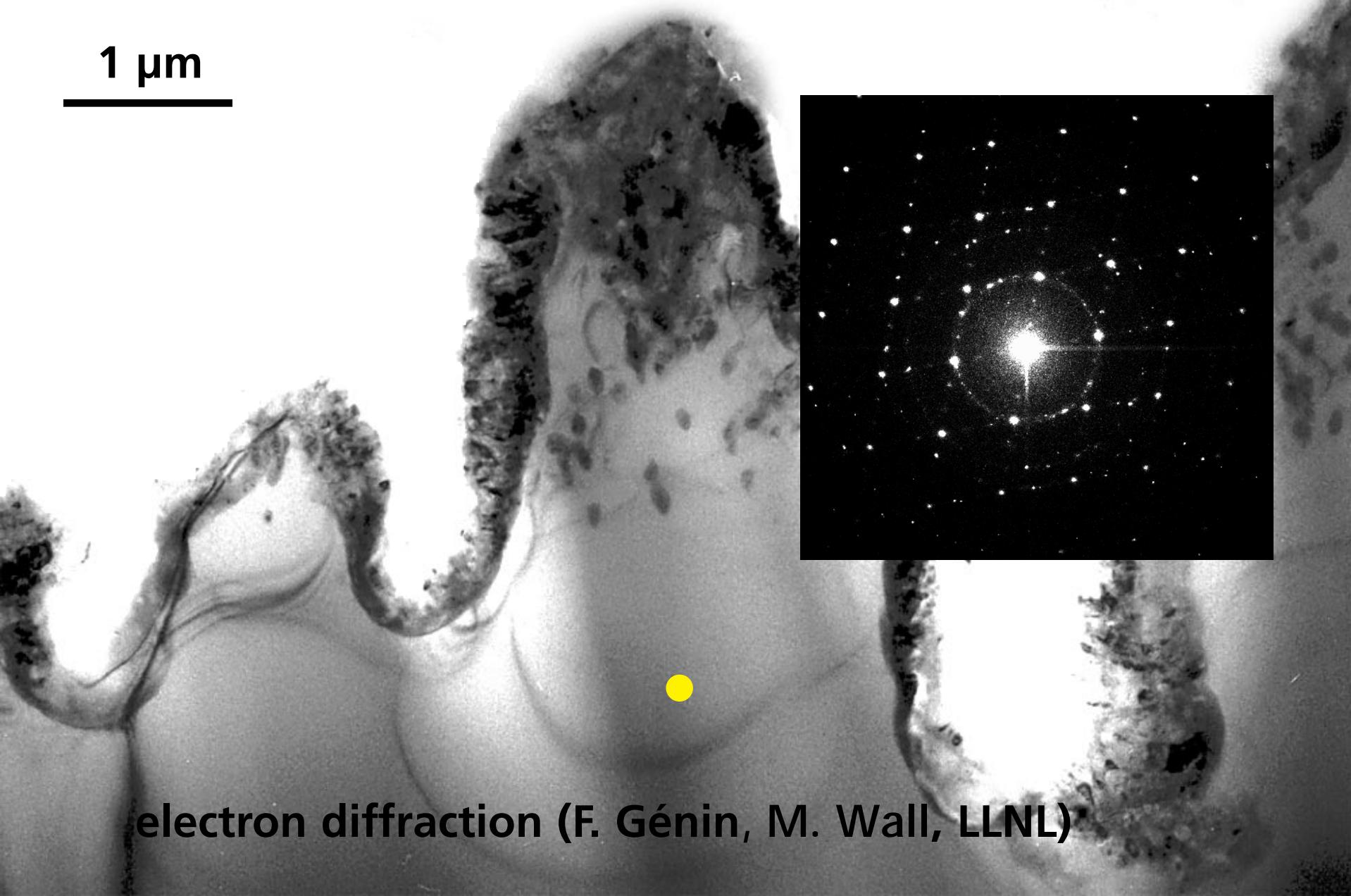
crystalline Si



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

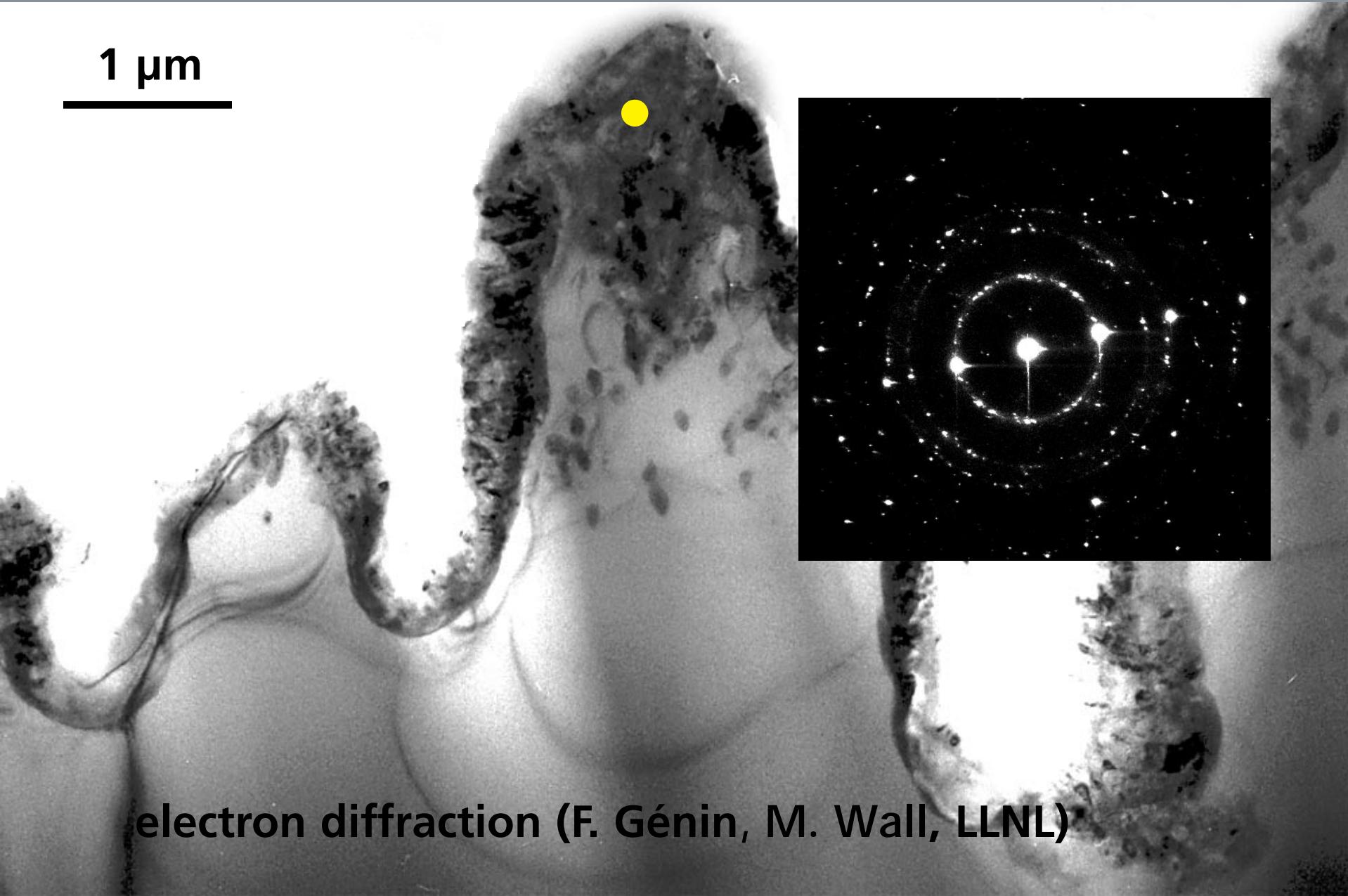
## *Structural and chemical analysis*

1  $\mu\text{m}$



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

## *Structural and chemical analysis*



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

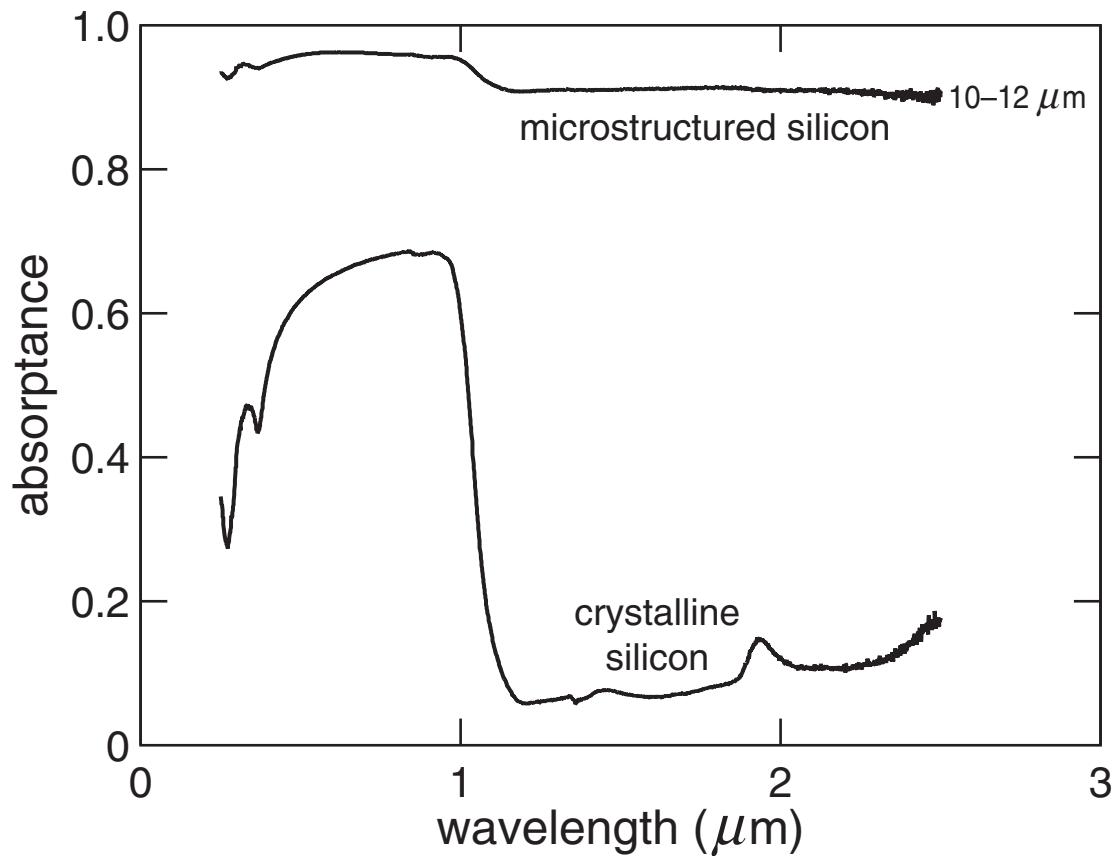
## *Structural and chemical analysis*

**cross-sectional TEM:**

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

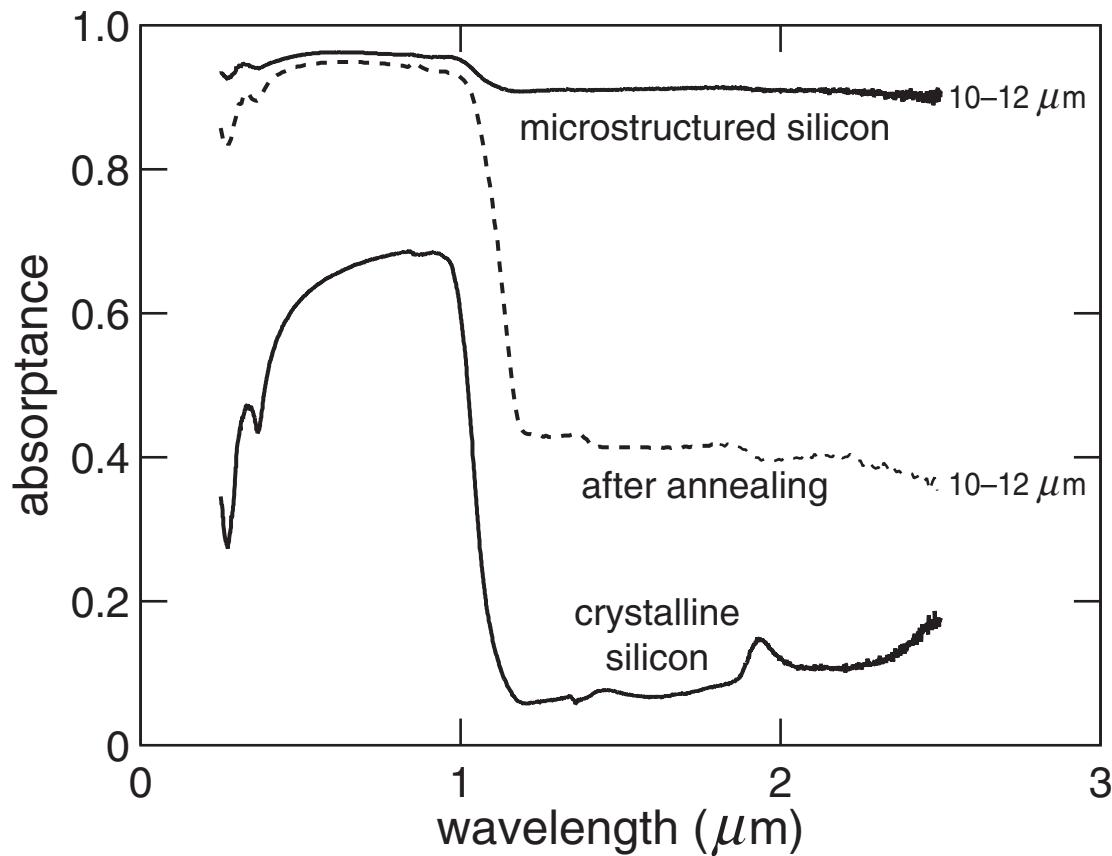
## *Structural and chemical analysis*

**anneal 4 hours at 1200 K**



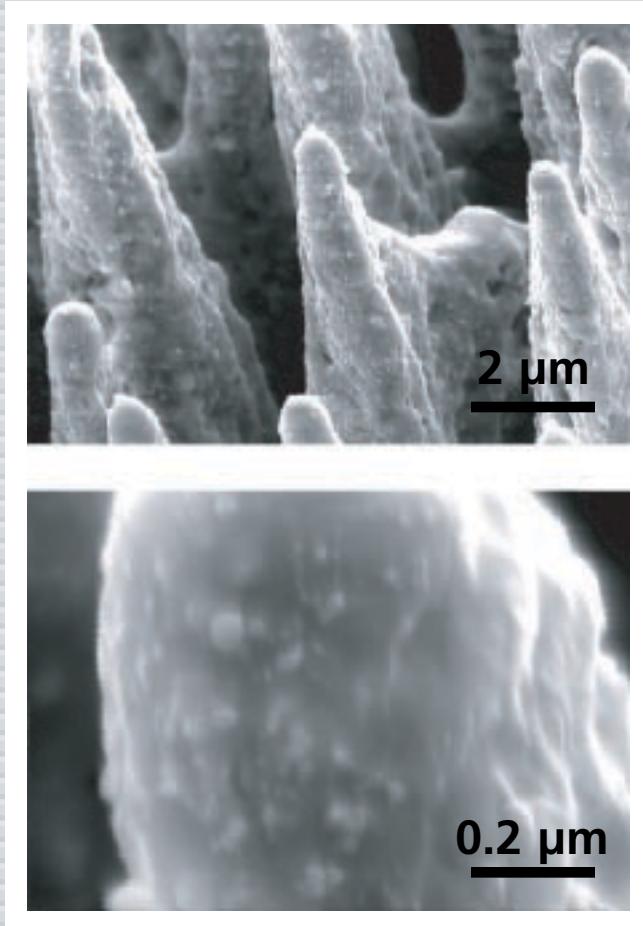
## *Structural and chemical analysis*

anneal 4 hours at 1200 K



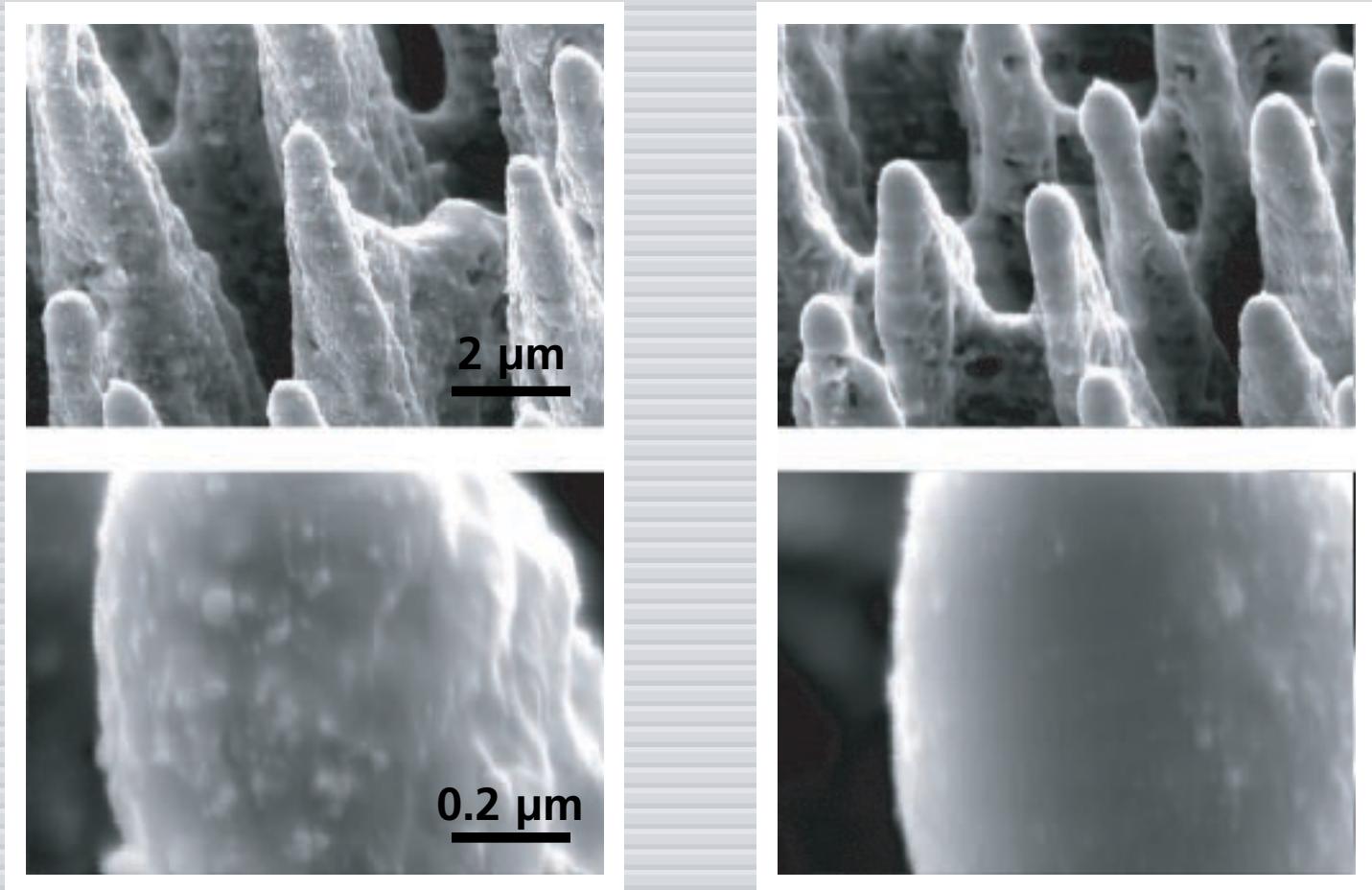
## *Structural and chemical analysis*

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**

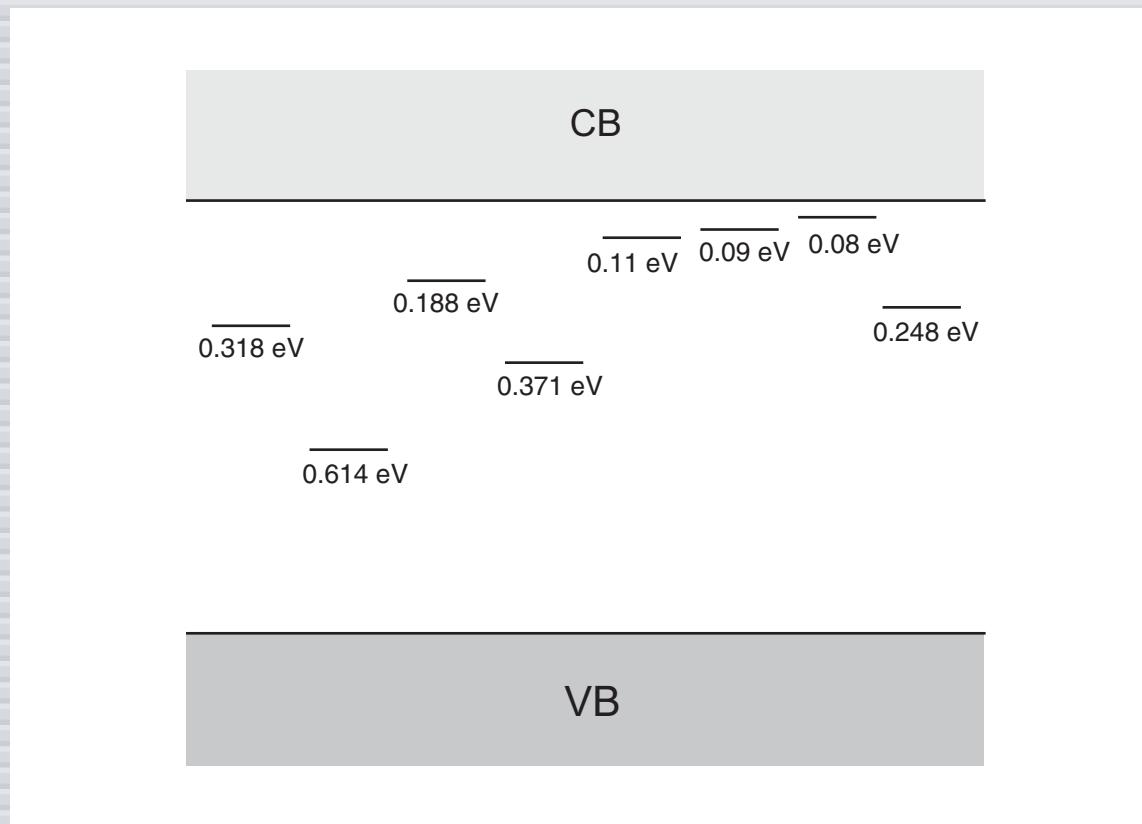
CB

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

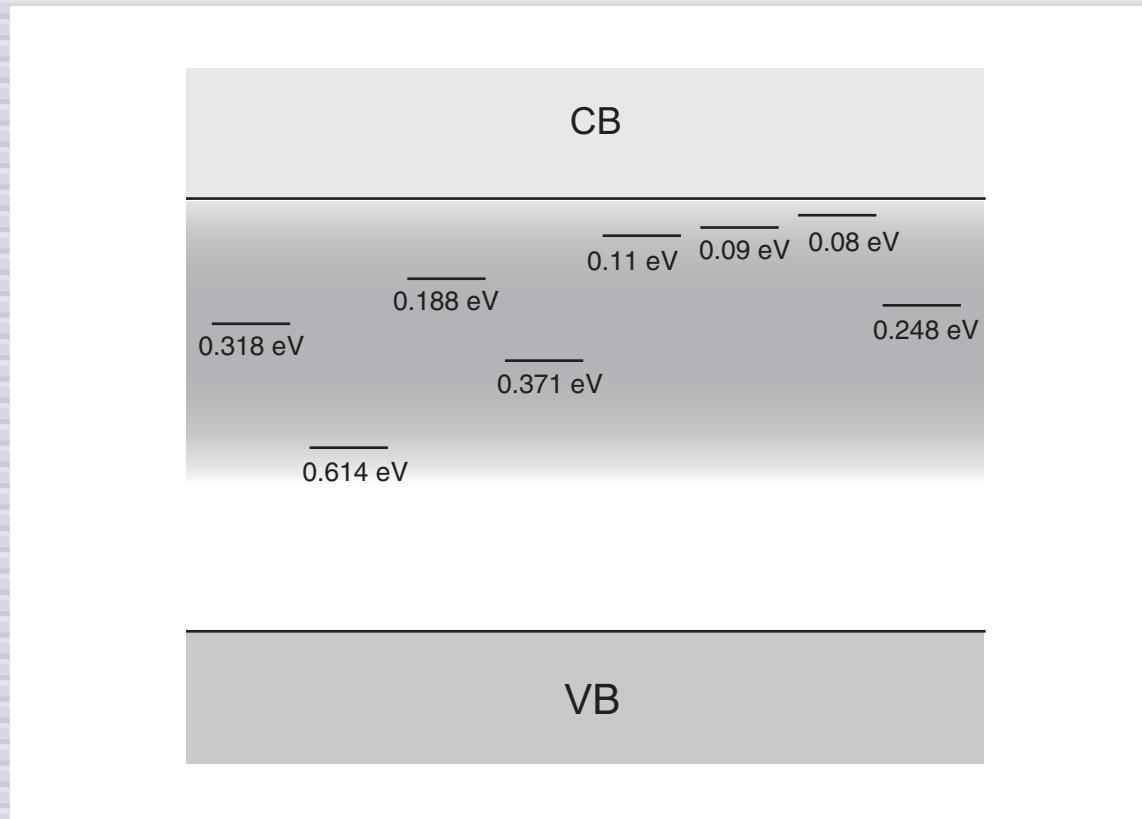
# *Structural and chemical analysis*

**sulfur introduces states in the gap**



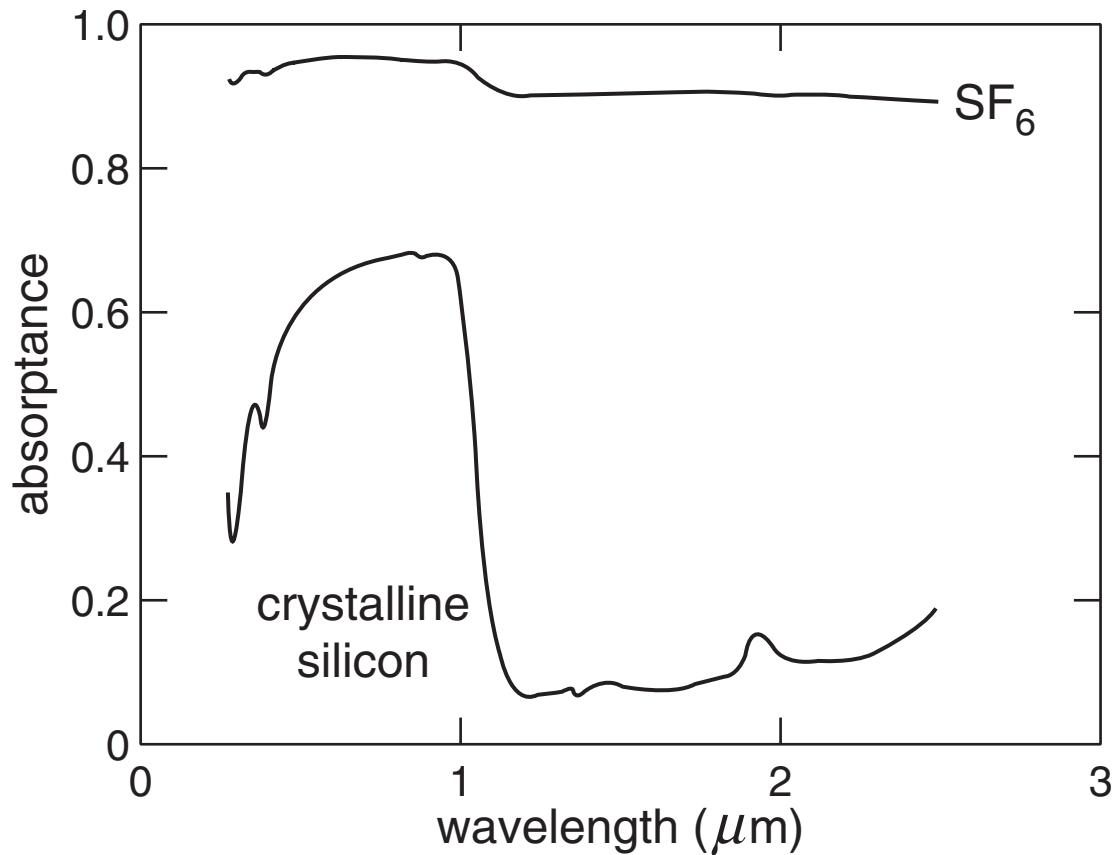
# *Structural and chemical analysis*

**states broaden into a band**



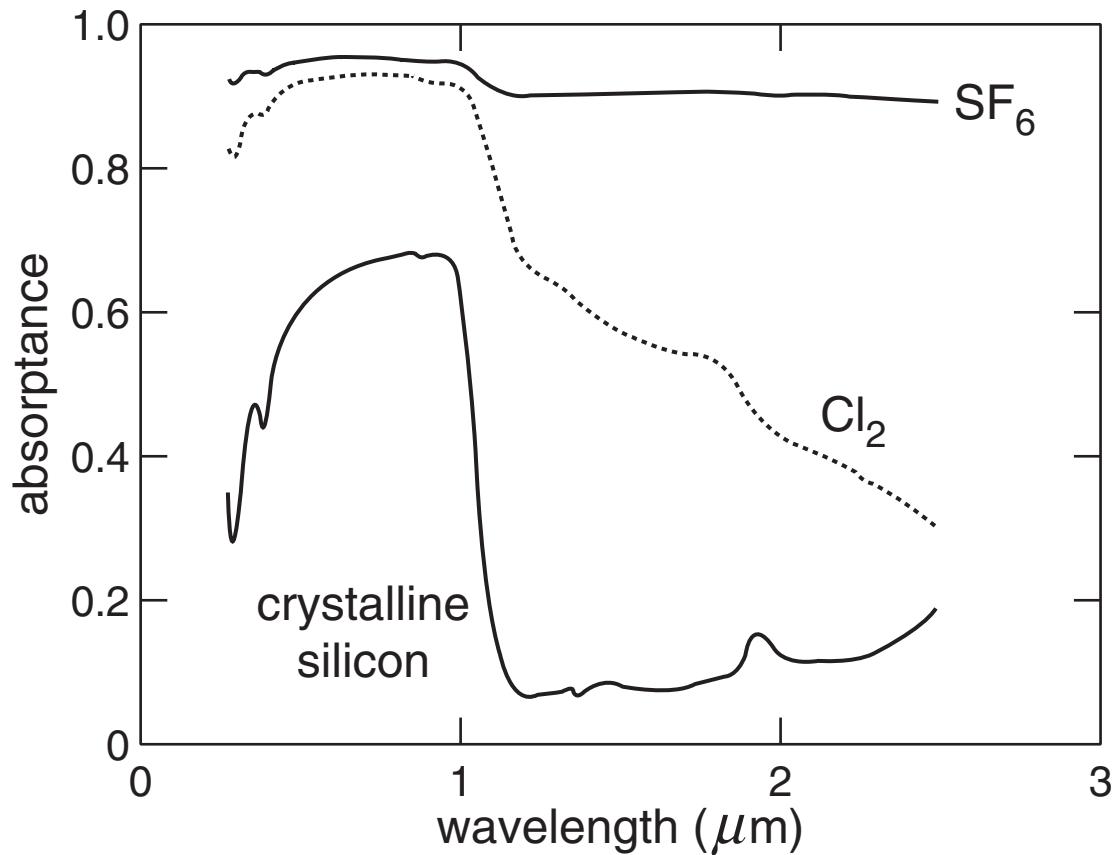
# *Structural and chemical analysis*

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



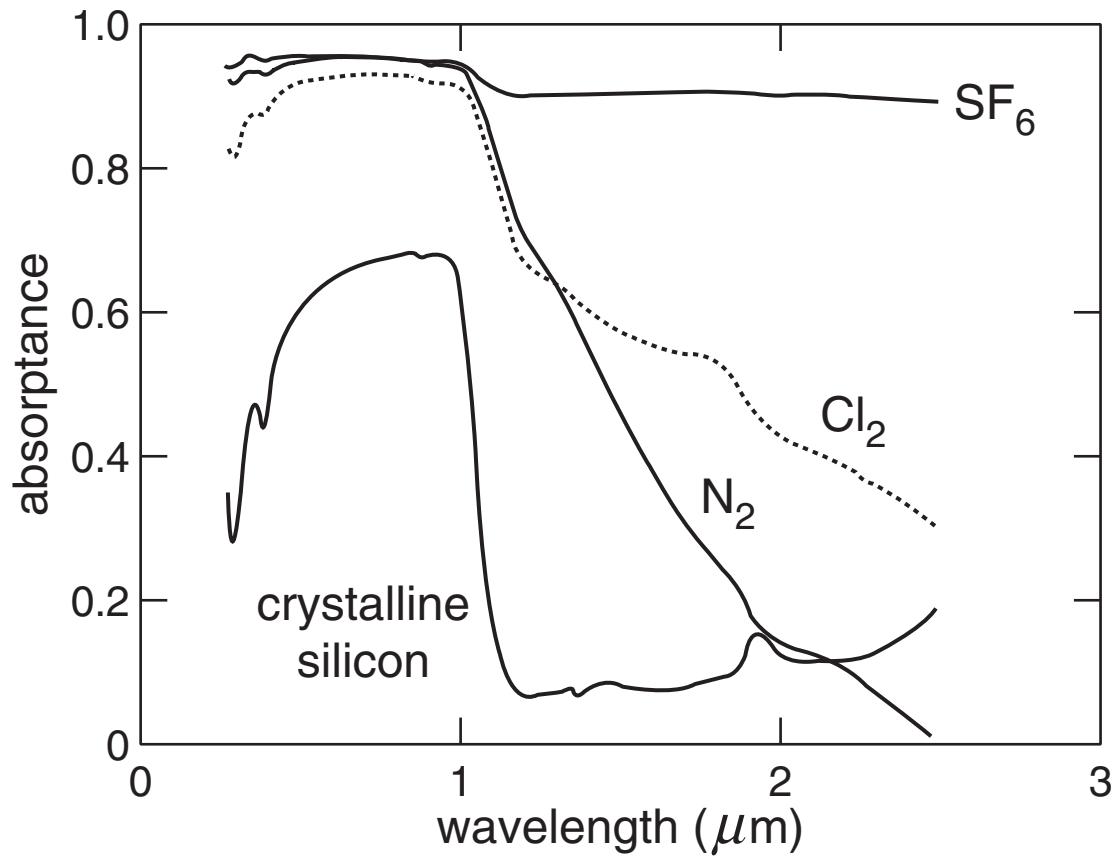
# *Structural and chemical analysis*

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



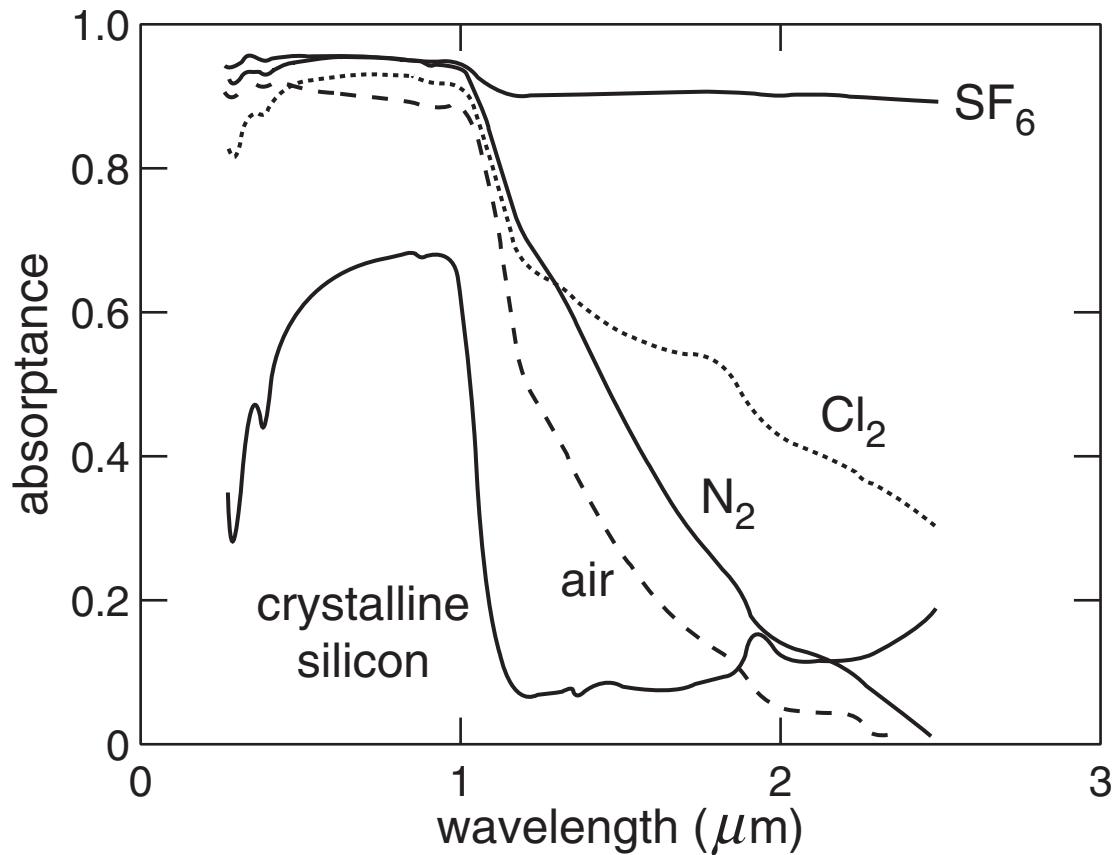
# *Structural and chemical analysis*

## **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 microscope or a filthy Petri dish

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

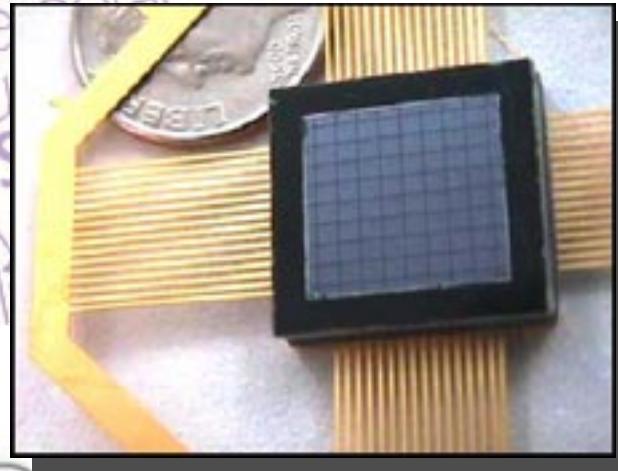
of times brighter than the Sun and extremely short laser pulse will break down around the laboratory," he claims.

Well, it was almost the only reason into sulphur and fluorine radicals, which will attack a silicon substrate. "Hydrogen fluoride is used to etch silicon. I thought maybe the SF<sub>6</sub> would decompose the silicon," Mazur says.

# *Outlook*

## ► detector technology

A forest of silicon spikes could revolutionise cells and give you injections. **Bruce S** peers into the 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 1960s, Marzai's was the last academic lab in the world to do so.

Marzai's work has now been taken over by the US company Microelectronics and Computer Technology Corporation (Metc), which has developed a new type of silicon that can conduct electricity at temperatures up to 200°C.

The new silicon is made from a mixture of silicon and carbon, and is extremely

# *Outlook*

- ▶ detector technology
  - ▶ solar cells

**technology**

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





# TALL, DARK AND STRANGER

# *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

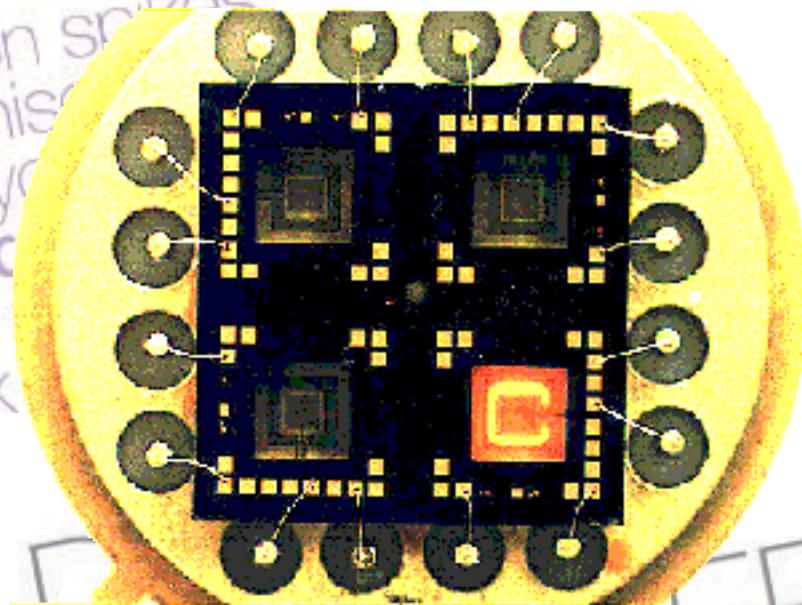
semiconductors with a powerful base to around the "unconscious" becomes a Park. It's not a word the only reason that I can't tell you much about it is that it's not a word that anyone has ever heard of. But if you do, then you will attack a specific culture. And that's why the Sun is so bright, because it's so hot, and extremely



# *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

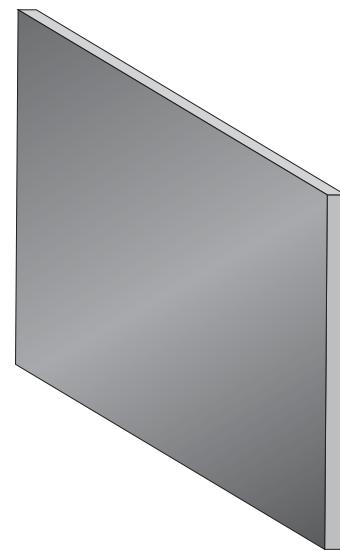
## *Outlook*

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

## *Outlook*

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

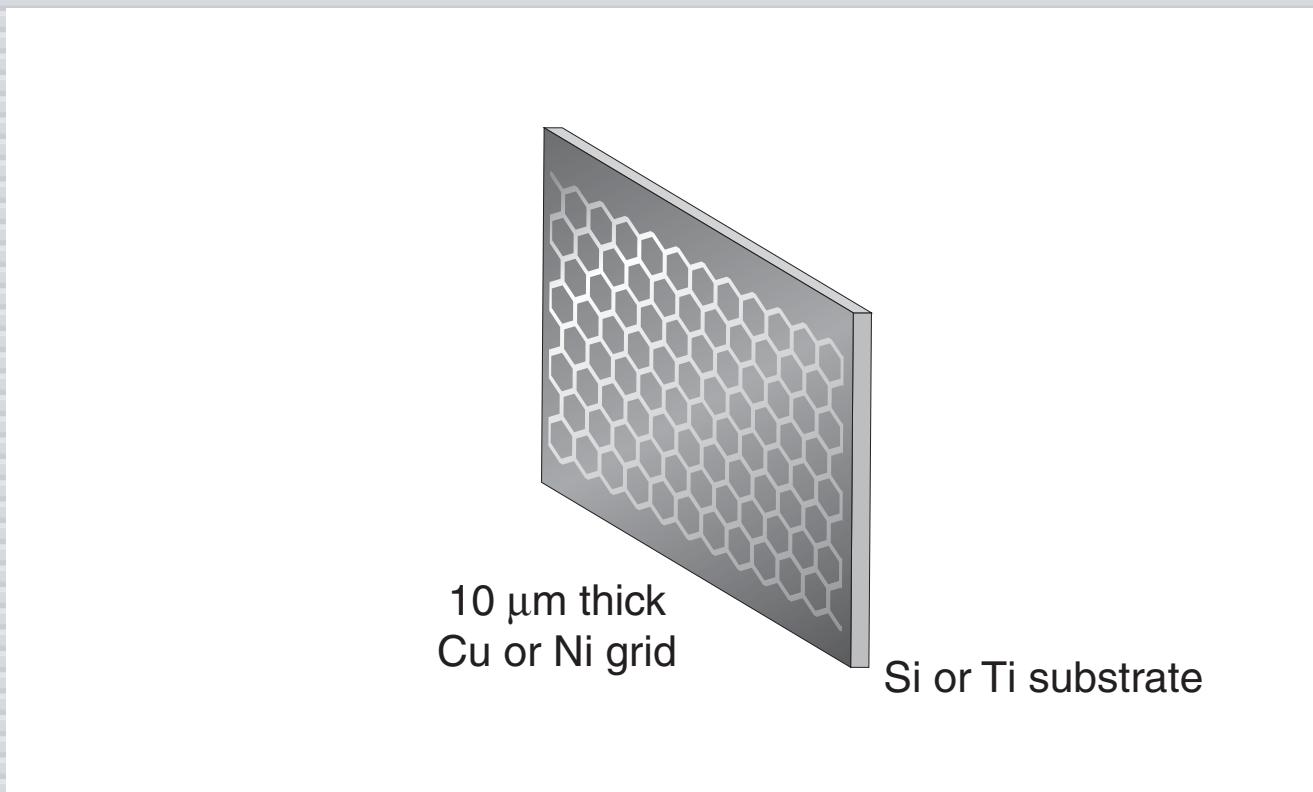
# *Outlook*



Si or Ti substrate

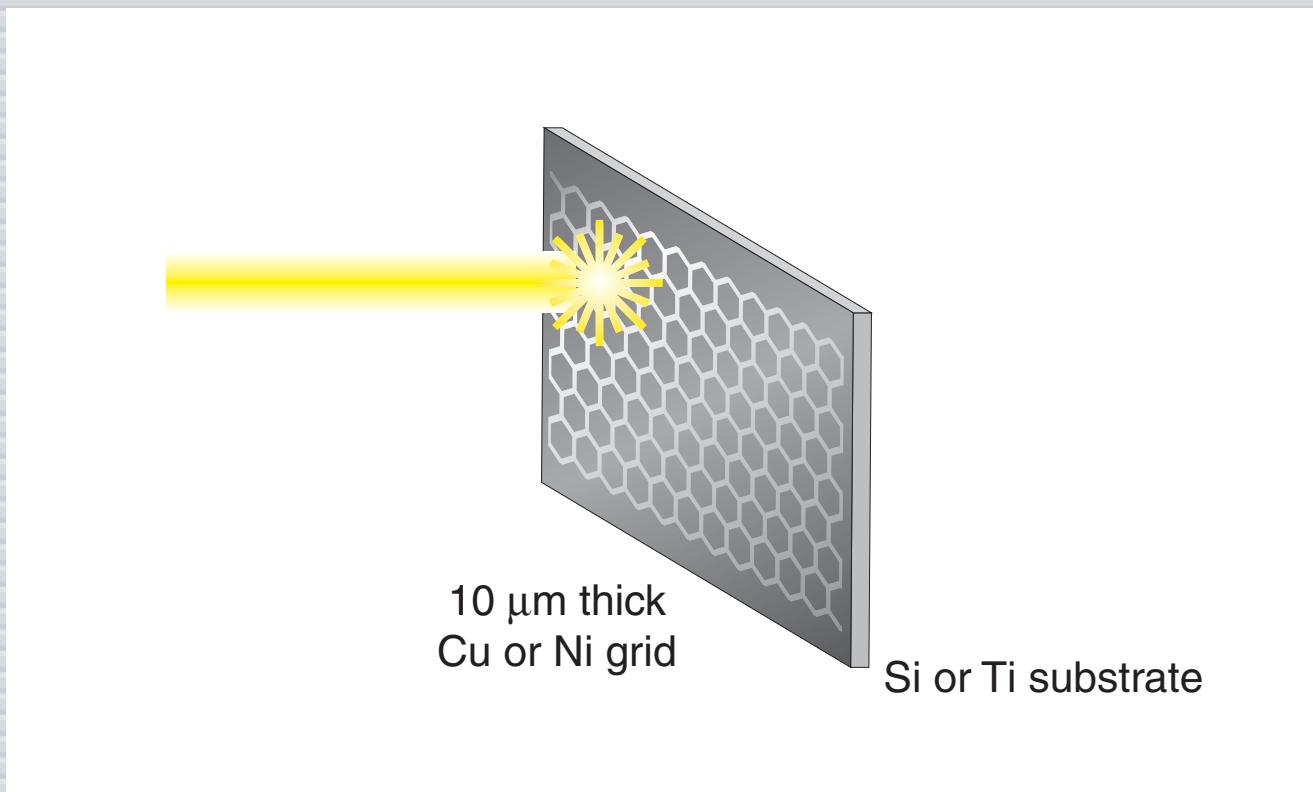
# *Outlook*

**place grid in front of substrate**



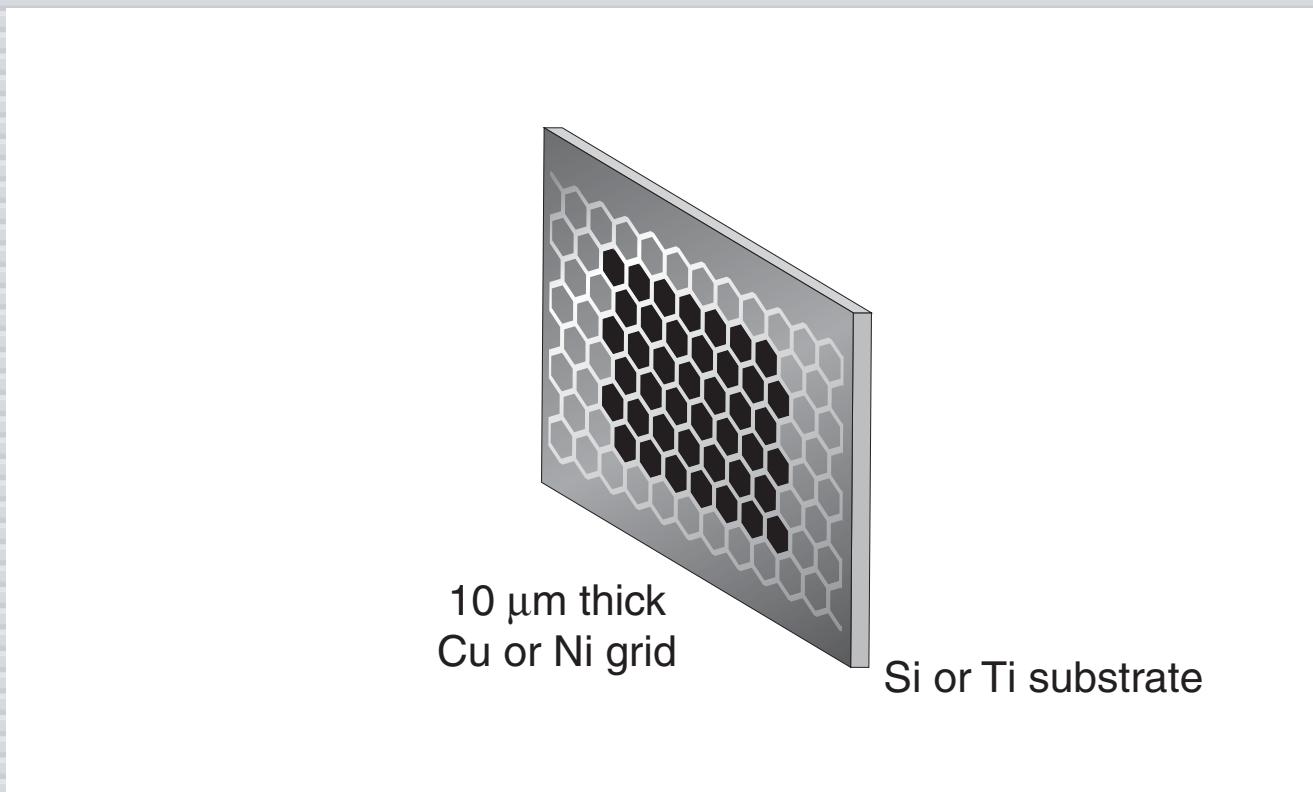
# *Outlook*

## scan laser beam



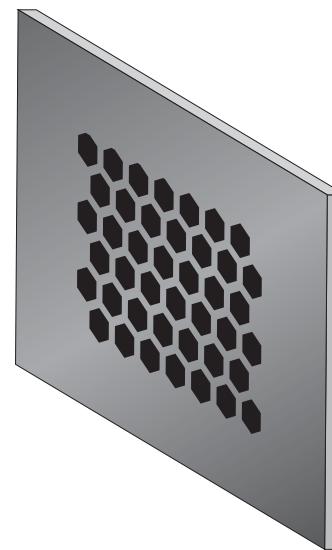
# *Outlook*

**scan laser beam**

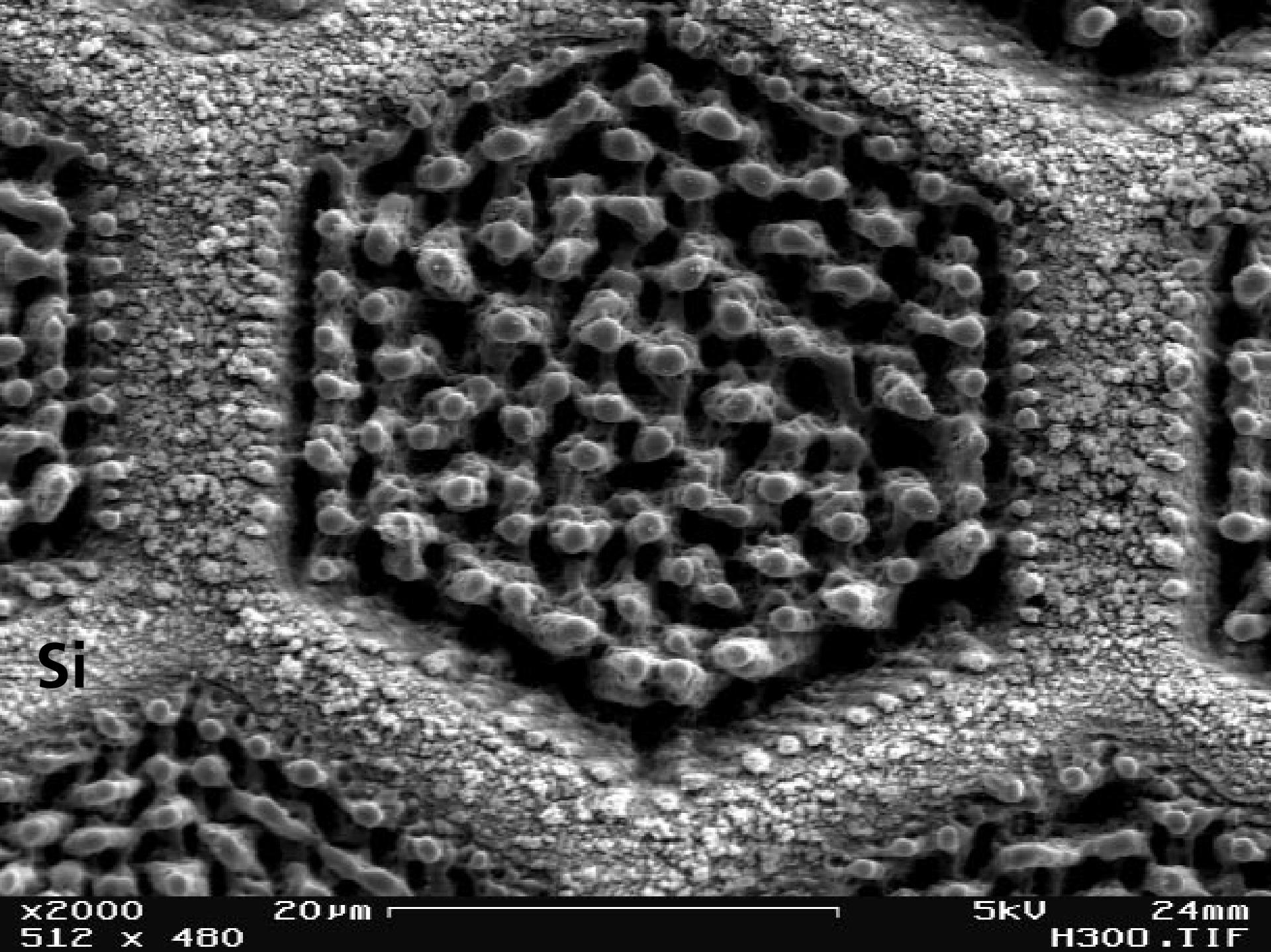


# *Outlook*

**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**

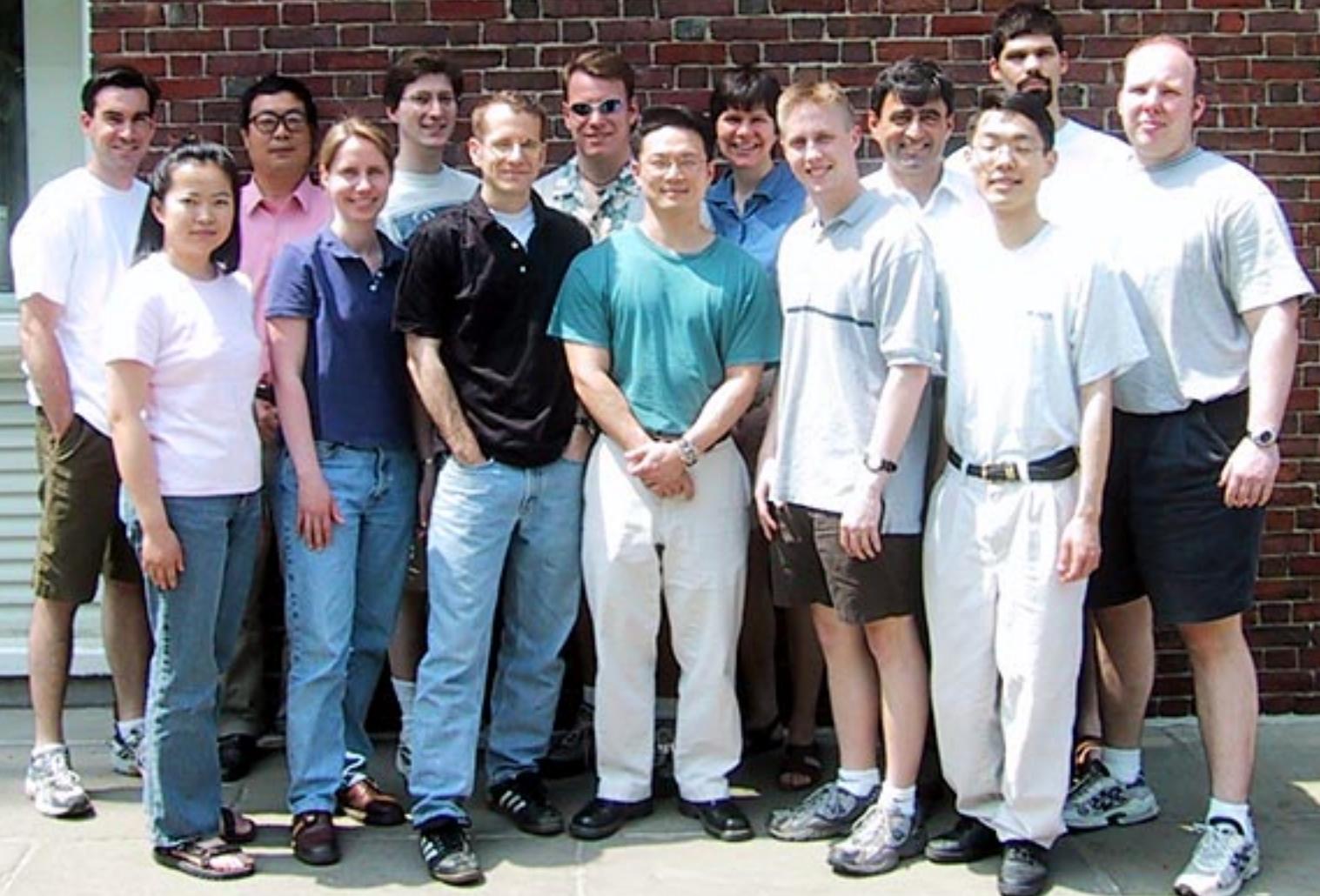
- ▶ **fabricated by simple, maskless process**

## *Summary*

### **Microstructured silicon**

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

CORDON MCKAY  
LABORATORY OF  
APPLIED SCIENCE



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**Dr. Alf Bjørseth (Scanwafer)**

**Dr. Tom Mates (UCSB)**

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

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

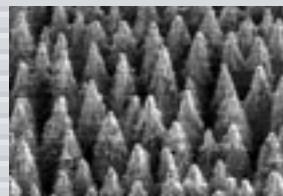
**Prof. Mike Aziz (Harvard University)**

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

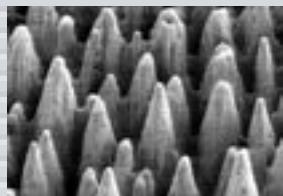
**<http://mazur-www.harvard.edu>**

# *Materials*

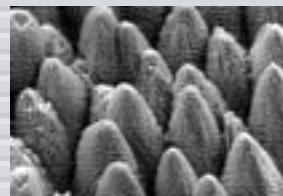
SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>

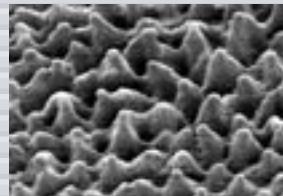


air



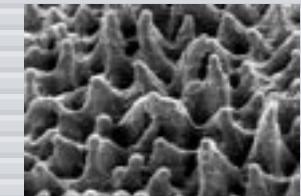
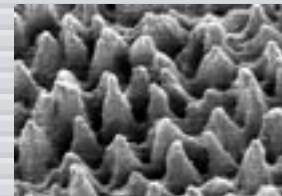
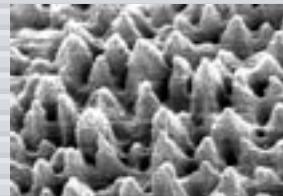
vacuum

Si

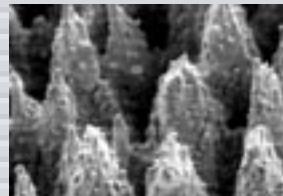


Ti

reacts



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



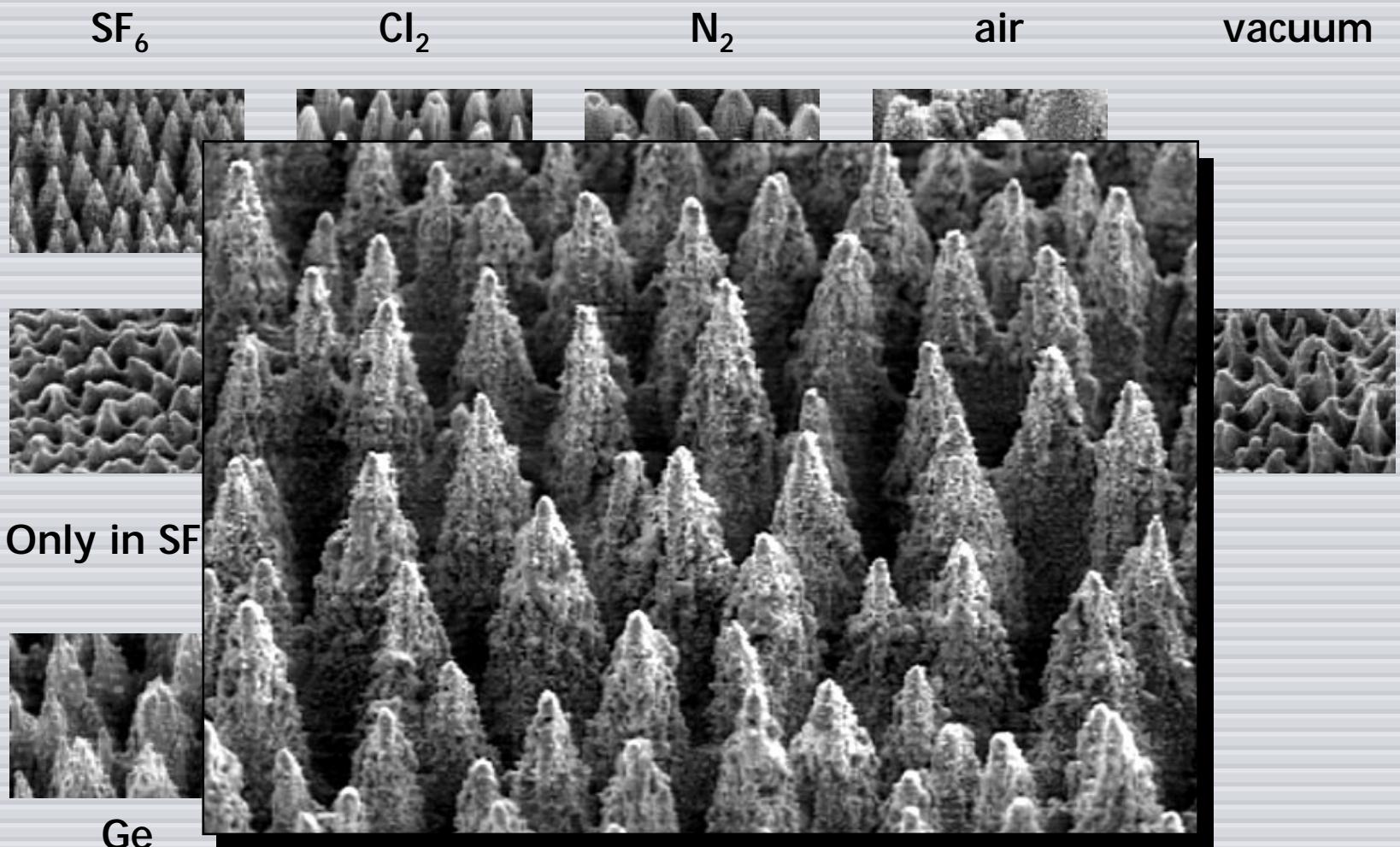
Ge



InP

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

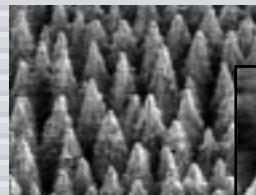
# *Materials*



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>



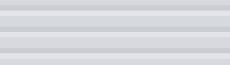
N<sub>2</sub>



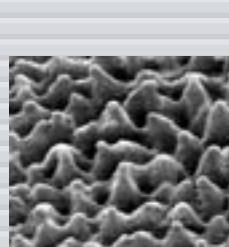
air



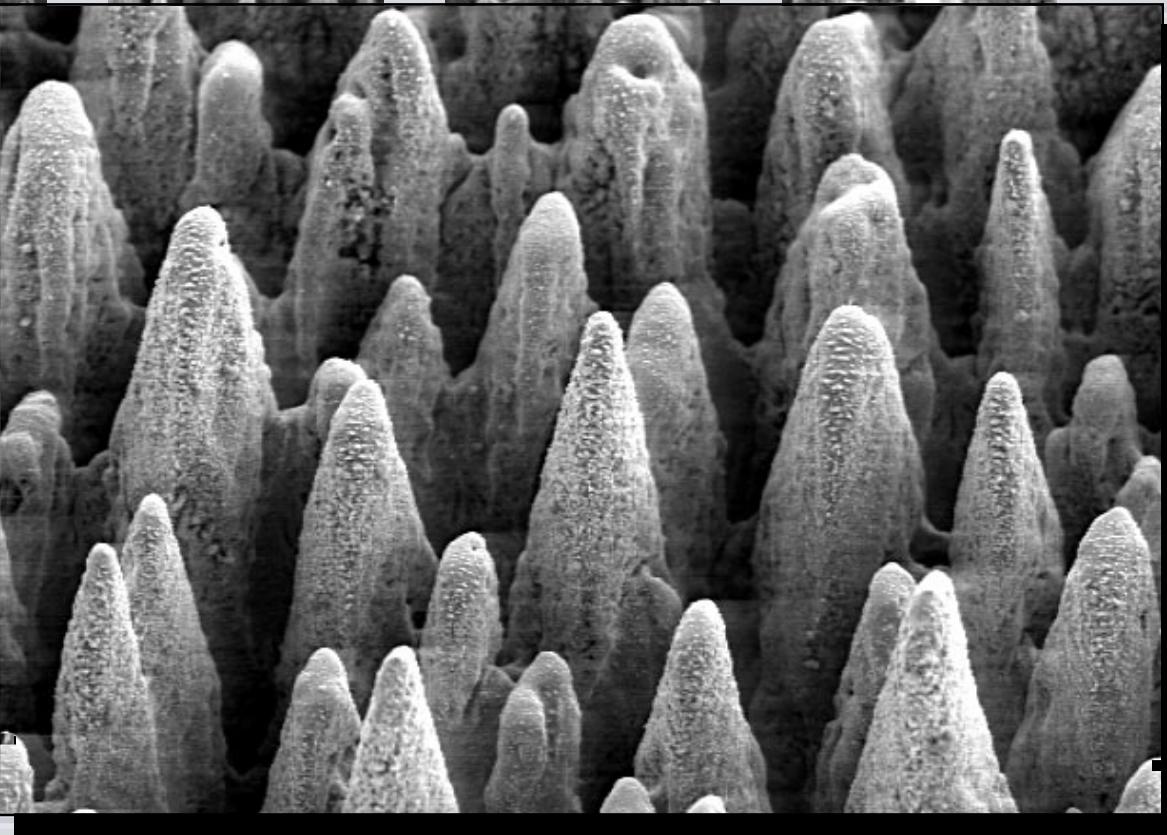
vacuum



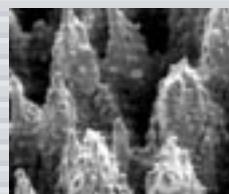
Si



Ti



Only in SF<sub>6</sub>

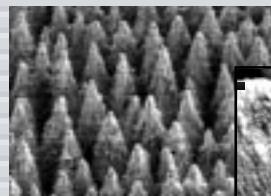


Ge

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>

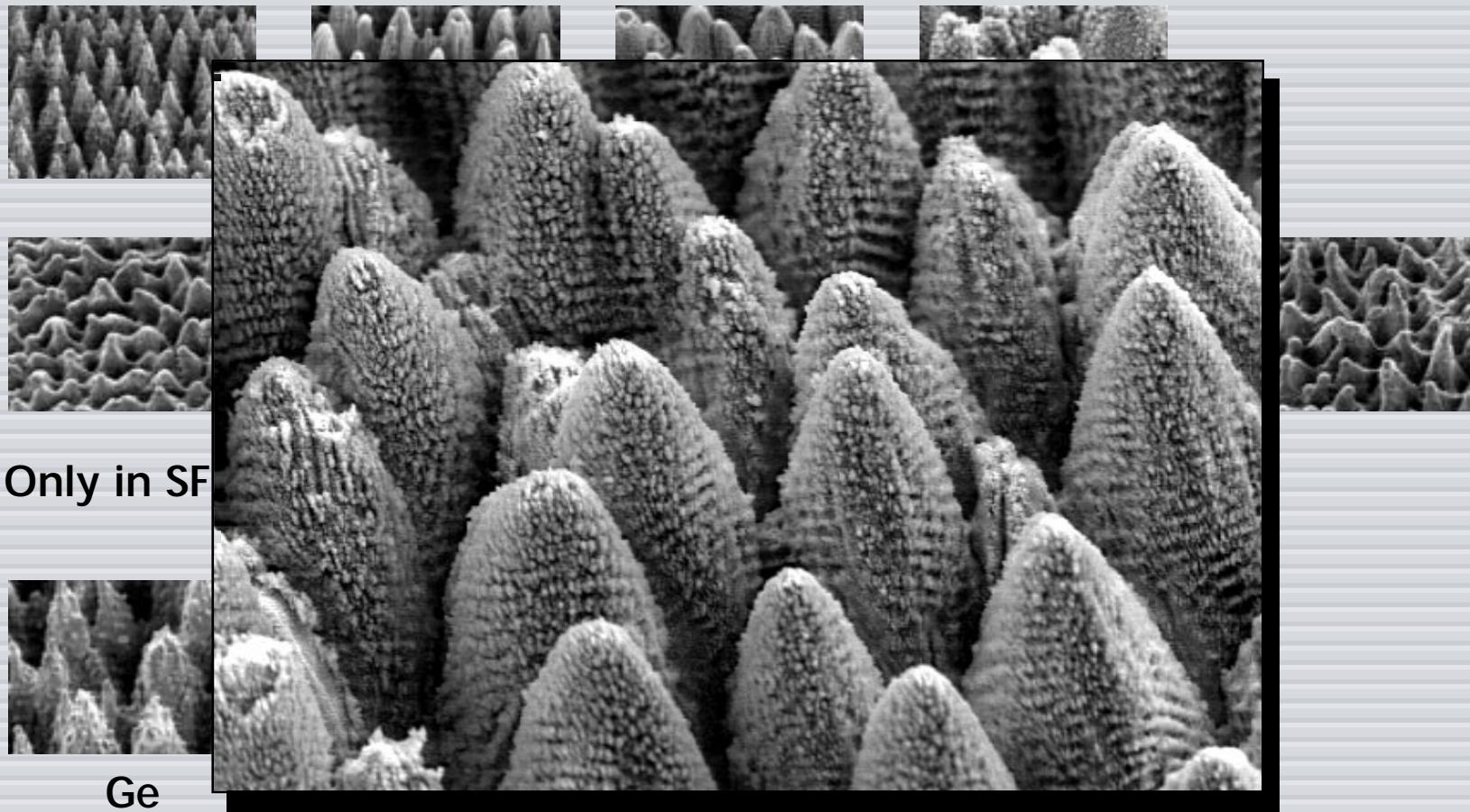


air

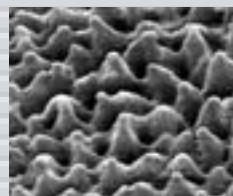


vacuum

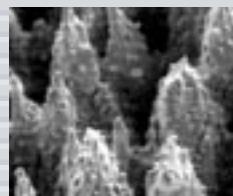
Si



Ti



Only in SF<sub>6</sub>

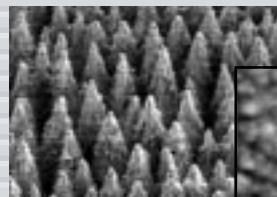


Ge

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# *Materials*

SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>



air

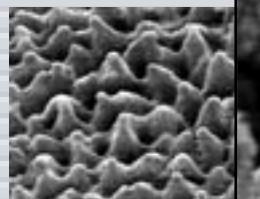


vacuum

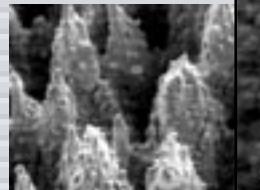
Si



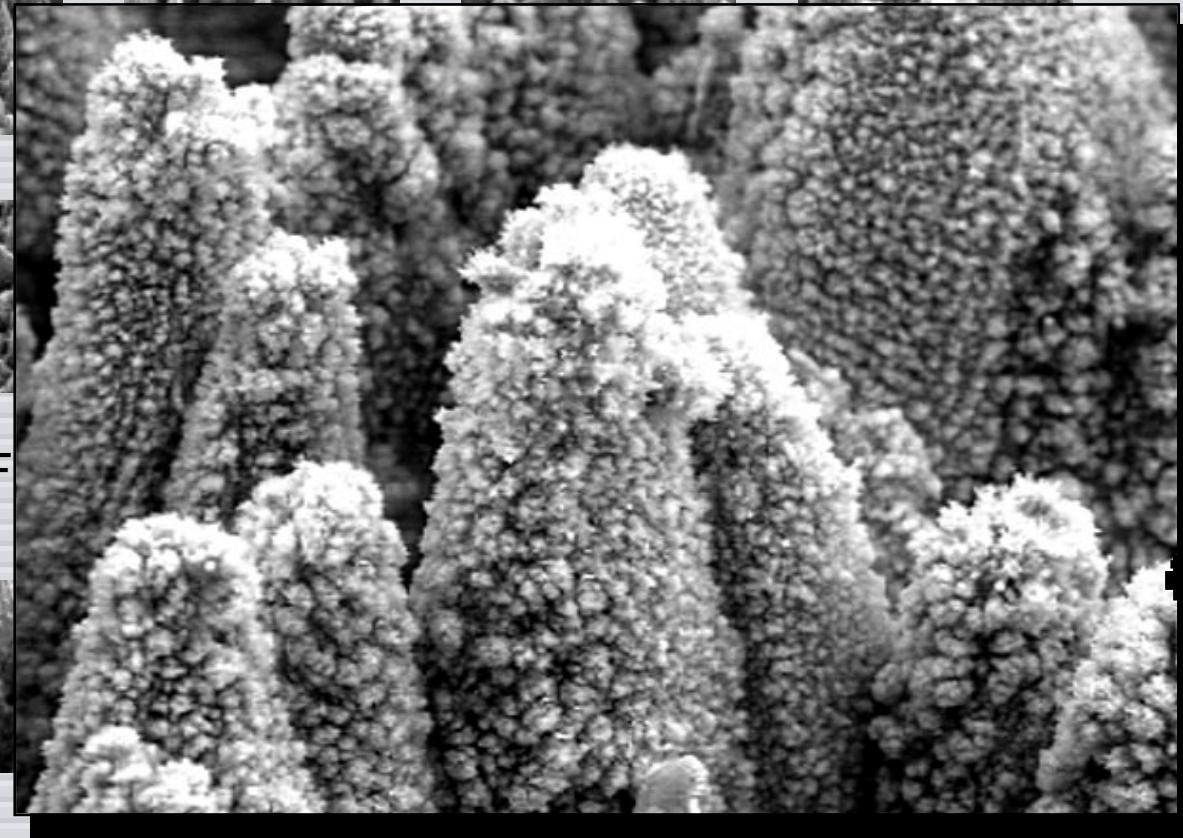
Ti



Only in SF<sub>6</sub>



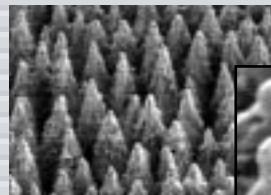
Ge



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# *Materials*

SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>

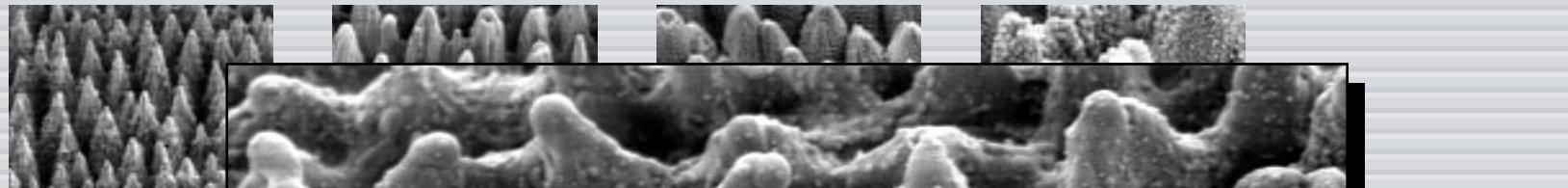


air

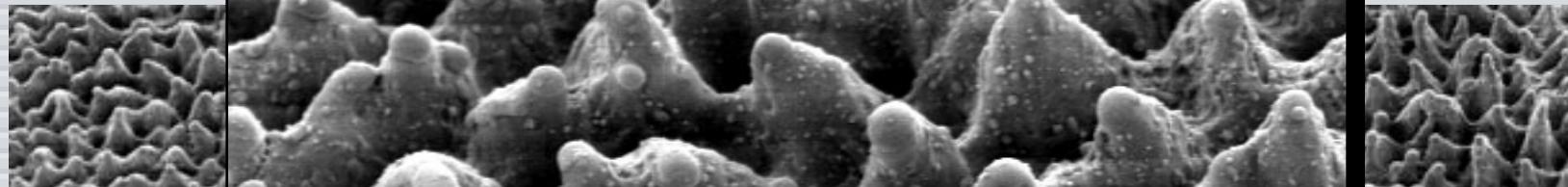


vacuum

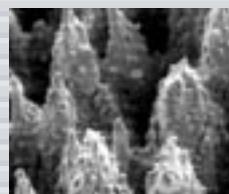
Si



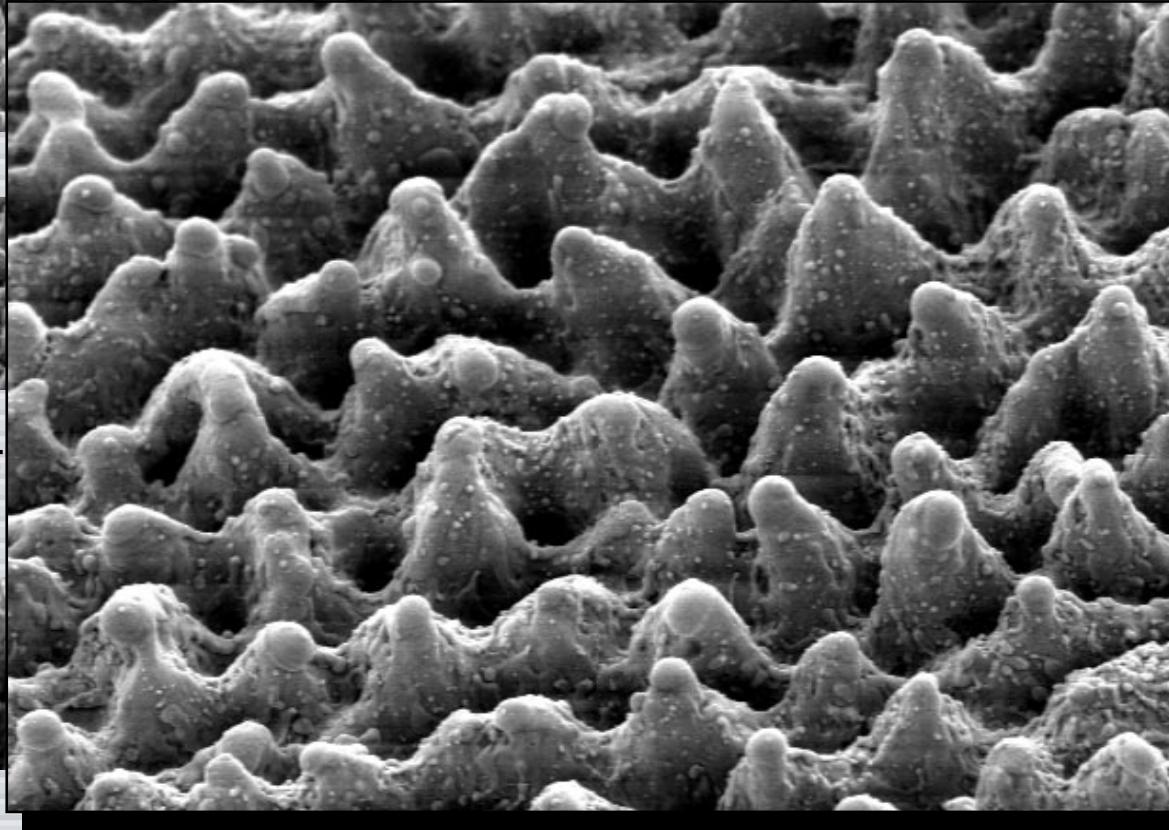
Ti



Only in SF<sub>6</sub>

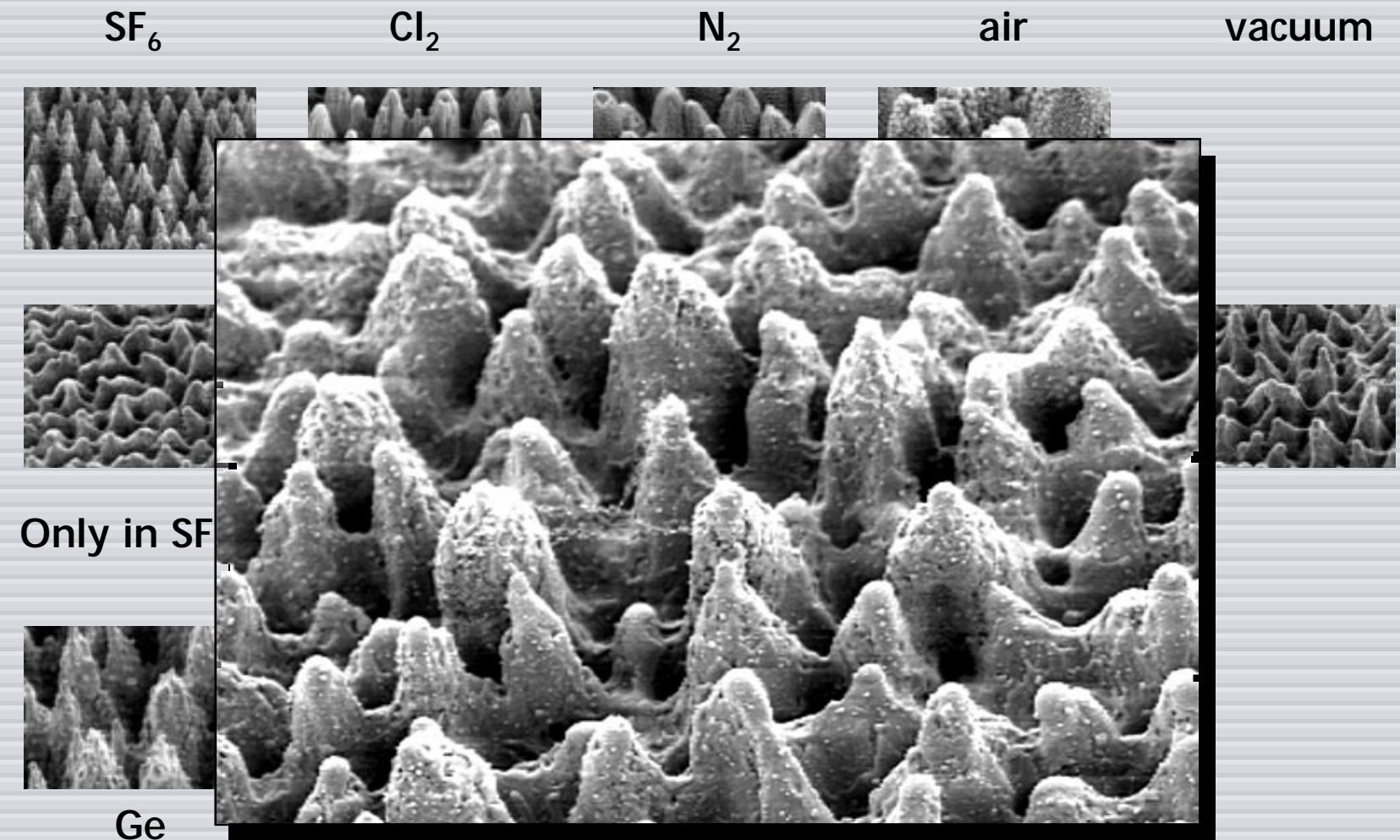


Ge



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

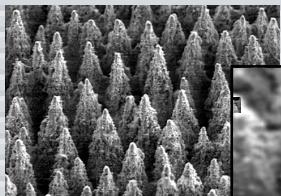
# *Materials*



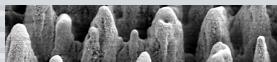
No spikes in SF<sub>6</sub>: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

# *Materials*

SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>

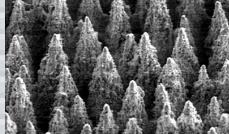


air

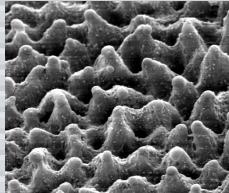


vacuum

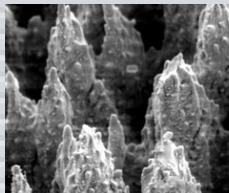
Si



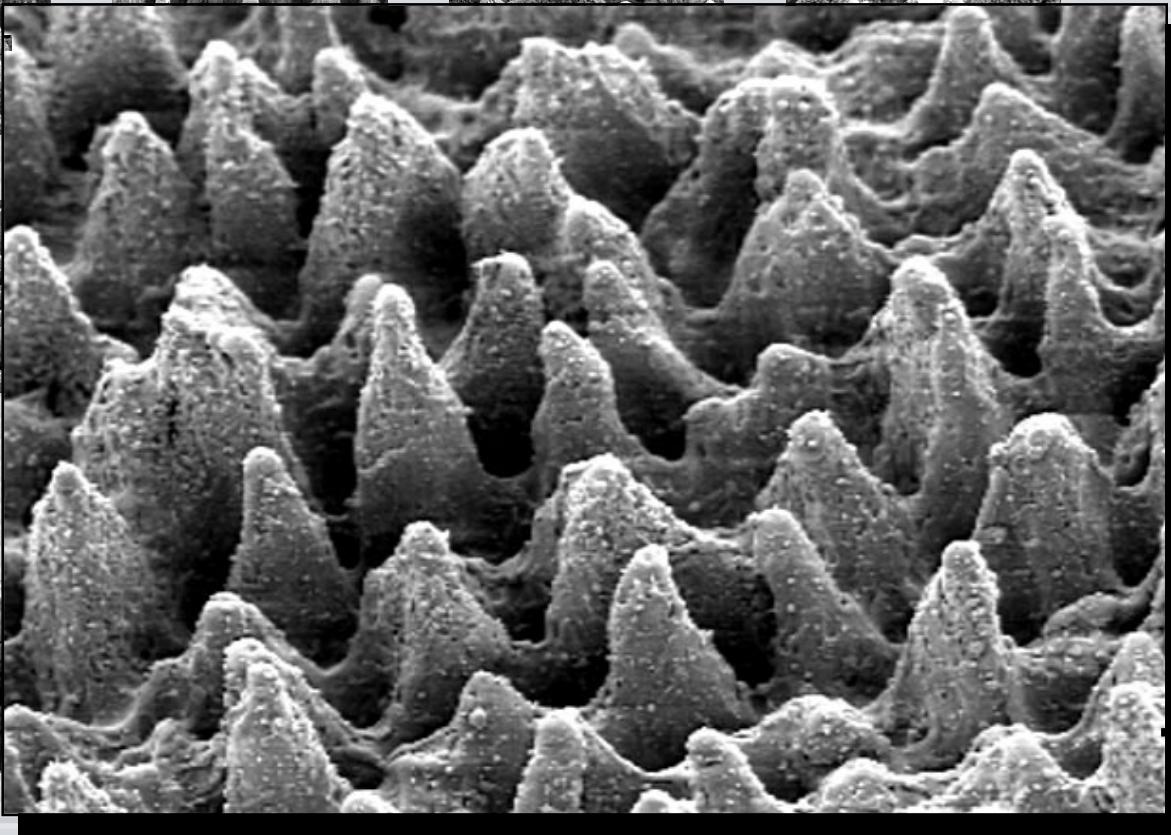
Ti



Only in SF<sub>6</sub>



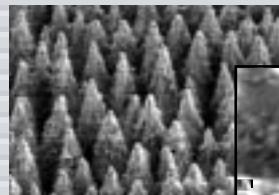
Ge



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>

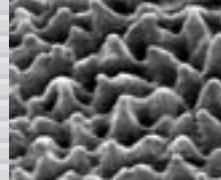


air

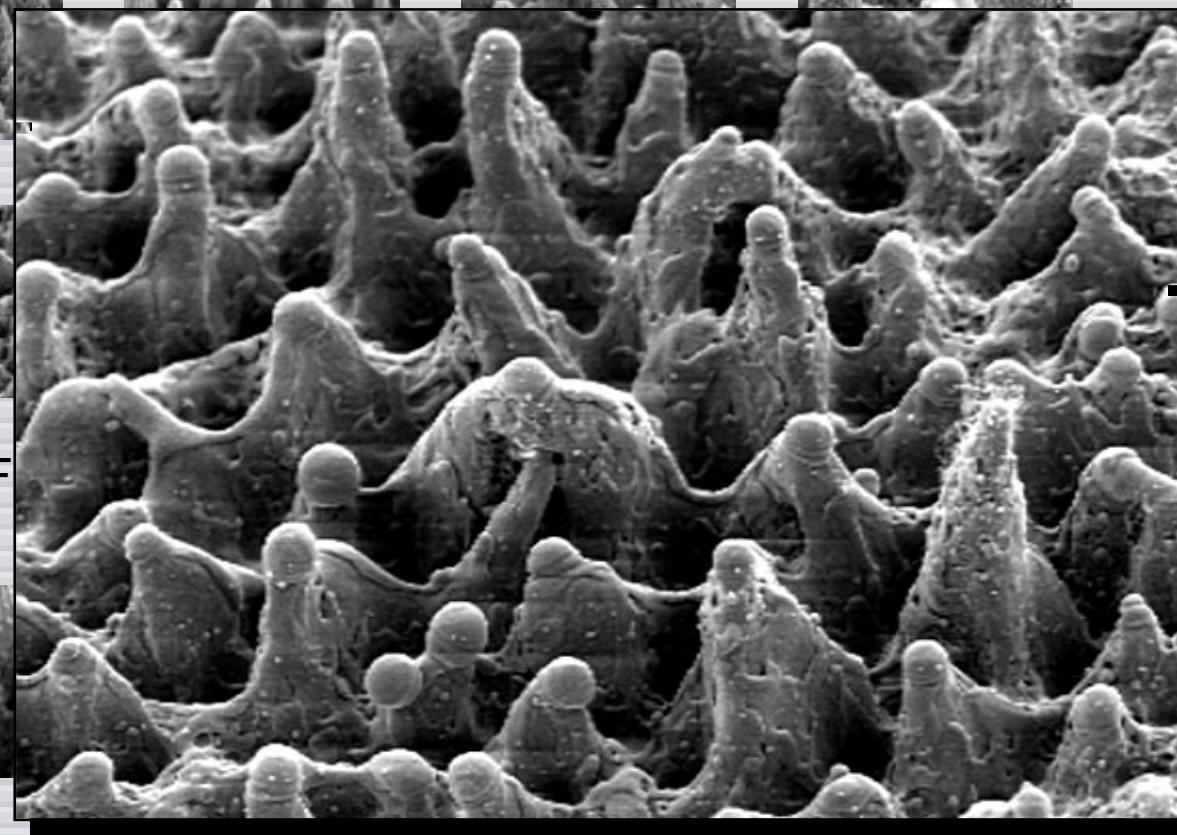


vacuum

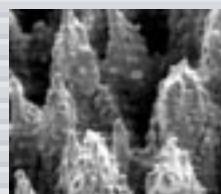
Si



Ti



Only in SF<sub>6</sub>

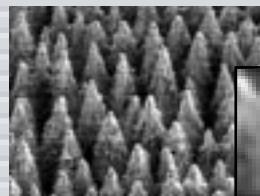


Ge

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

# *Materials*

SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>

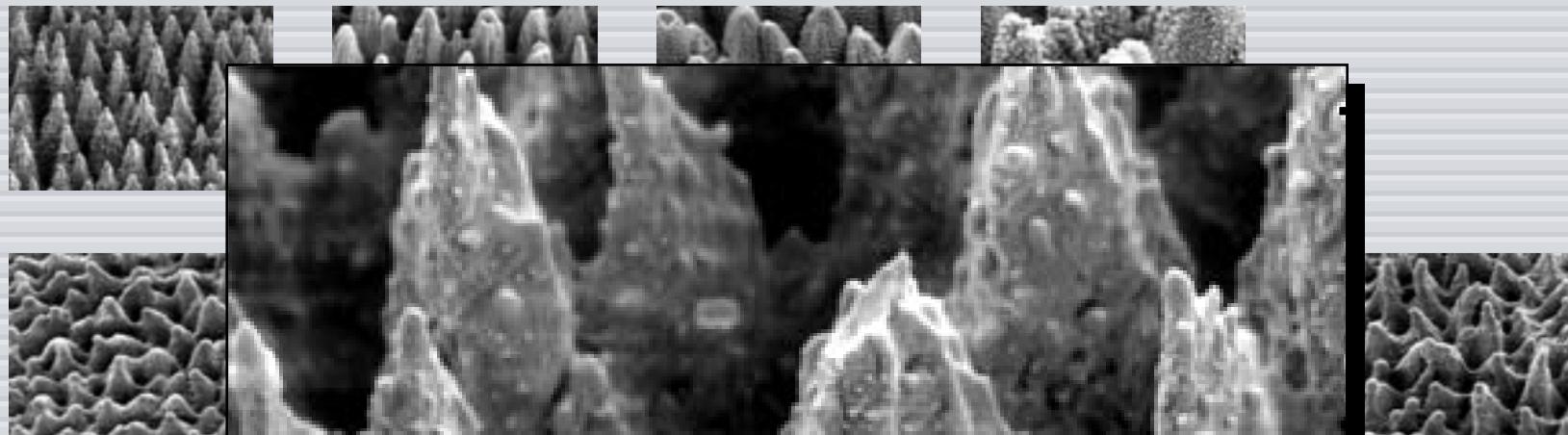


air

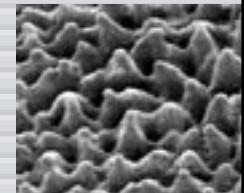


vacuum

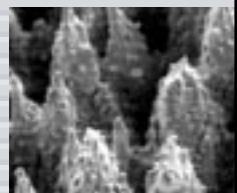
Si



Ti



Only in SF<sub>6</sub>

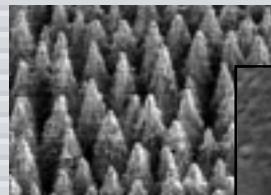


Ge

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# *Materials*

SF<sub>6</sub>



Cl<sub>2</sub>



N<sub>2</sub>

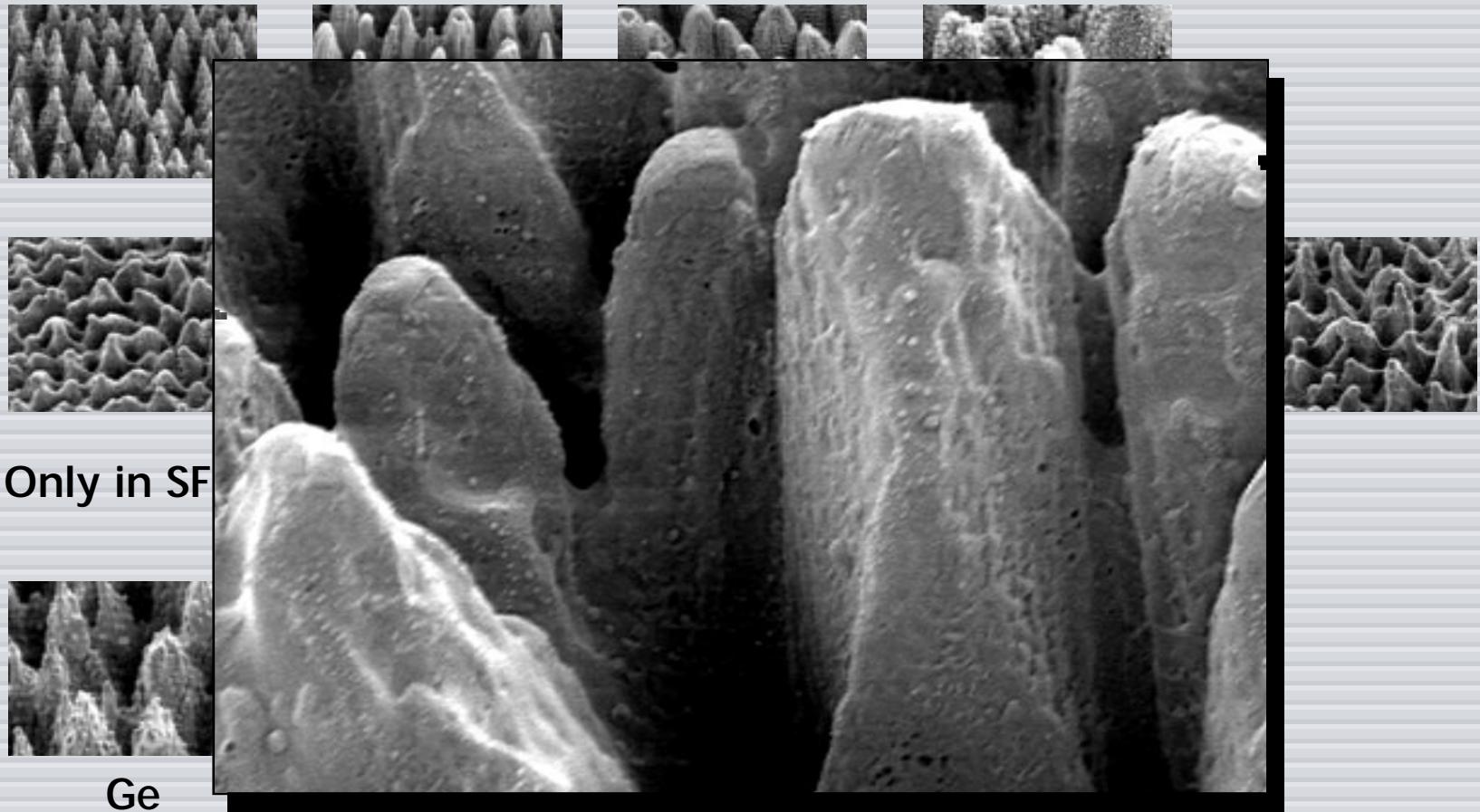


air

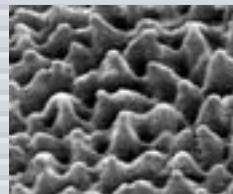


vacuum

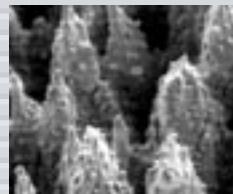
Si



Ti



Only in SF<sub>6</sub>



Ge

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