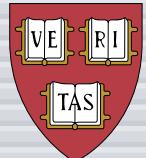
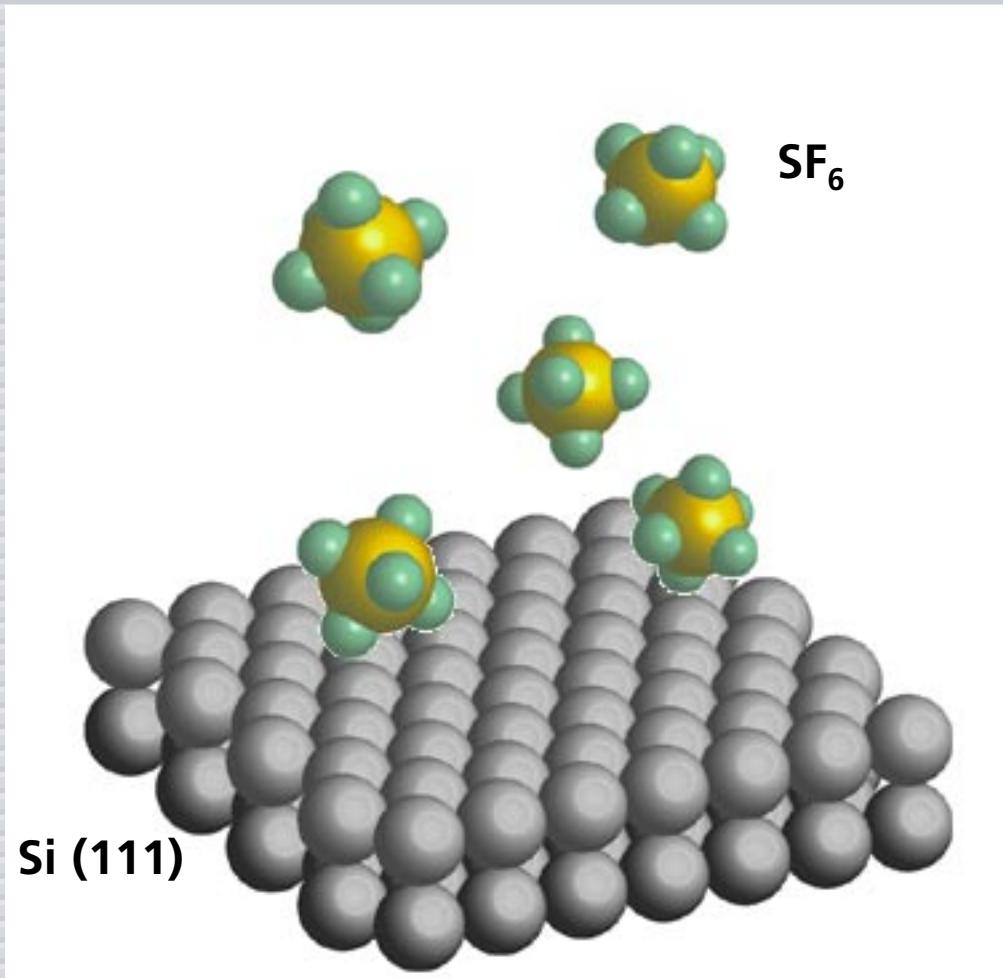


Femtosecond laser-assisted microstructuring of silicon for novel detector, sensing, and display technologies

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

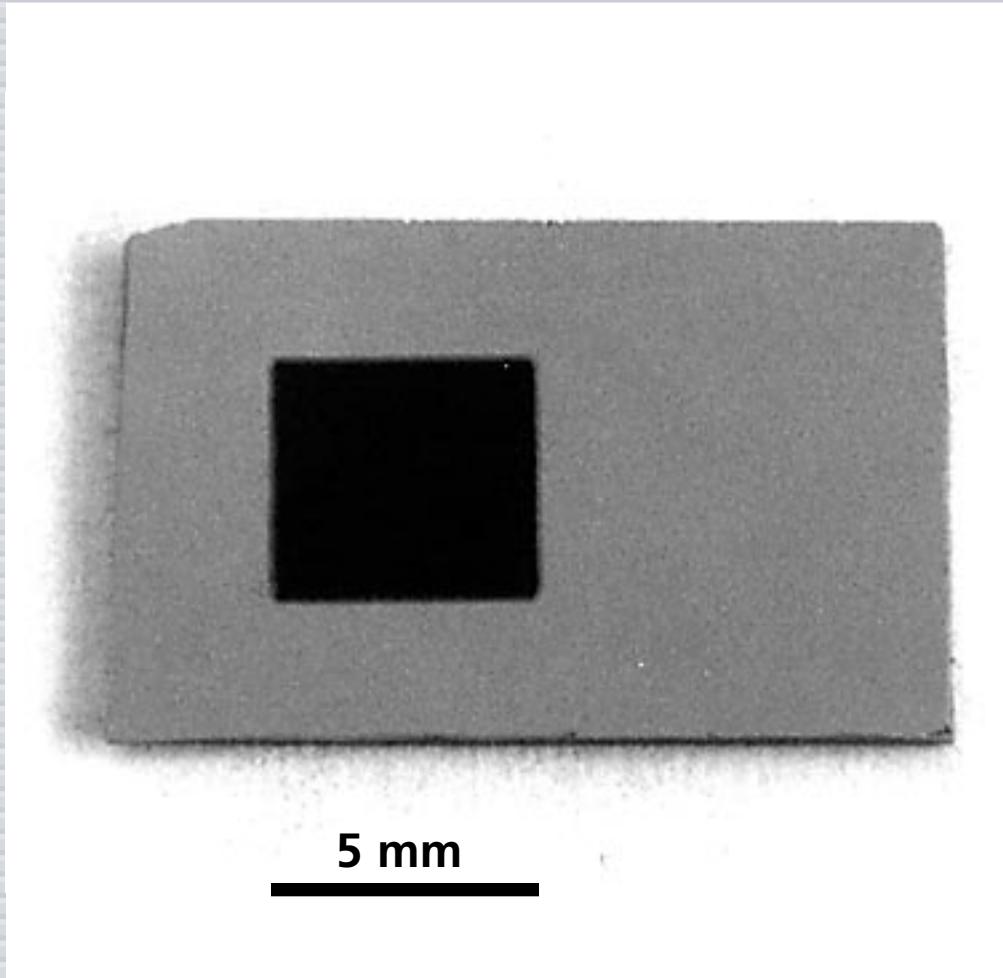


Introduction



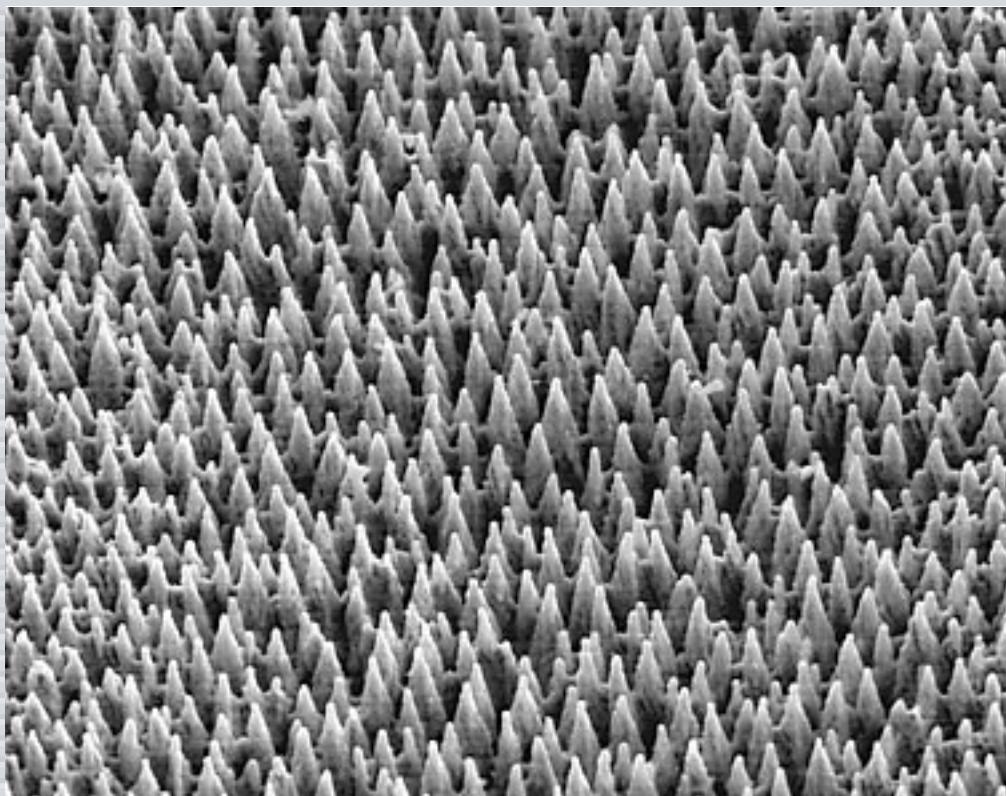
irradiate with 100-fs 10 kJ/m² pulses

Introduction



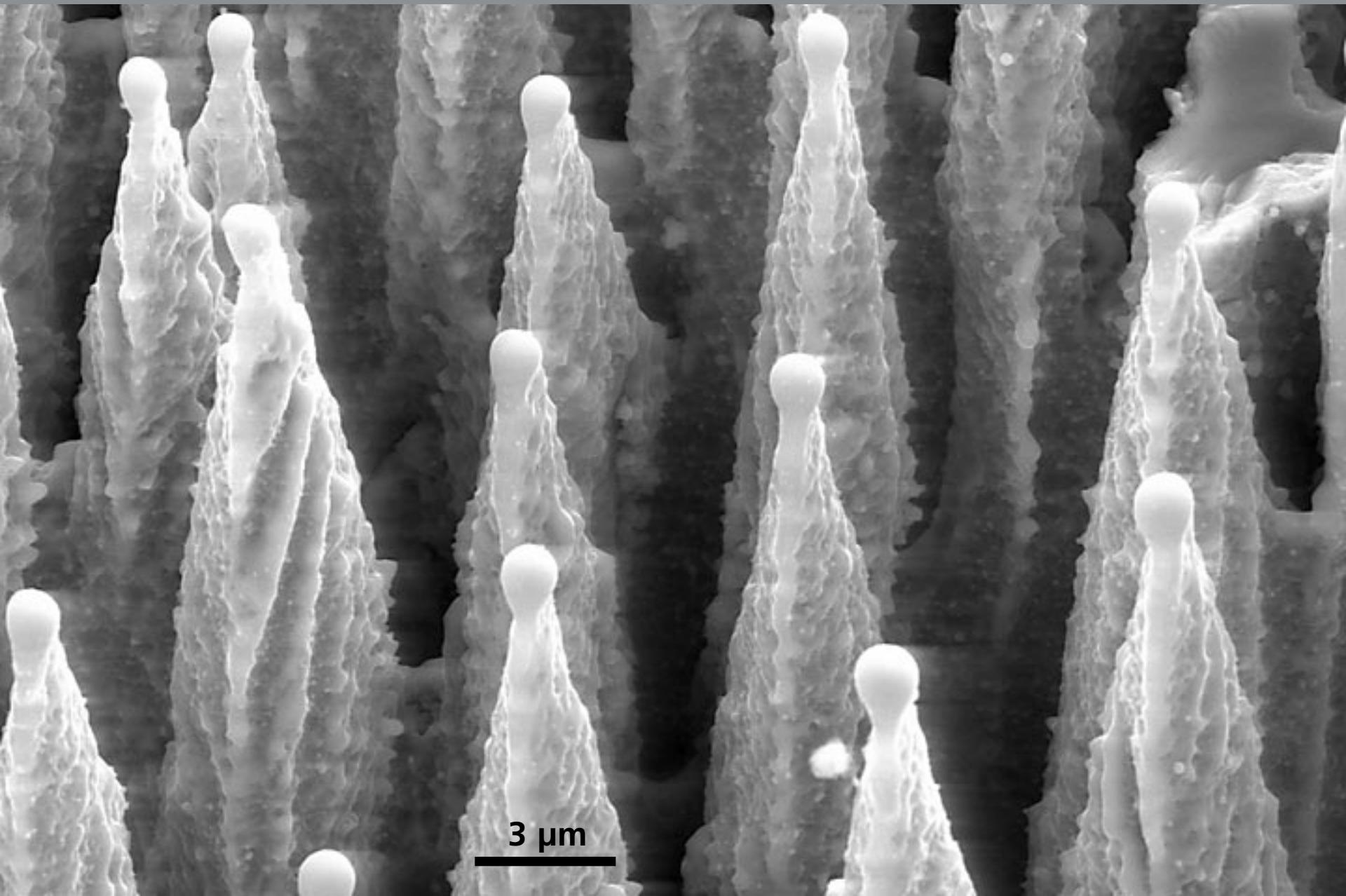
"black silicon"

Introduction

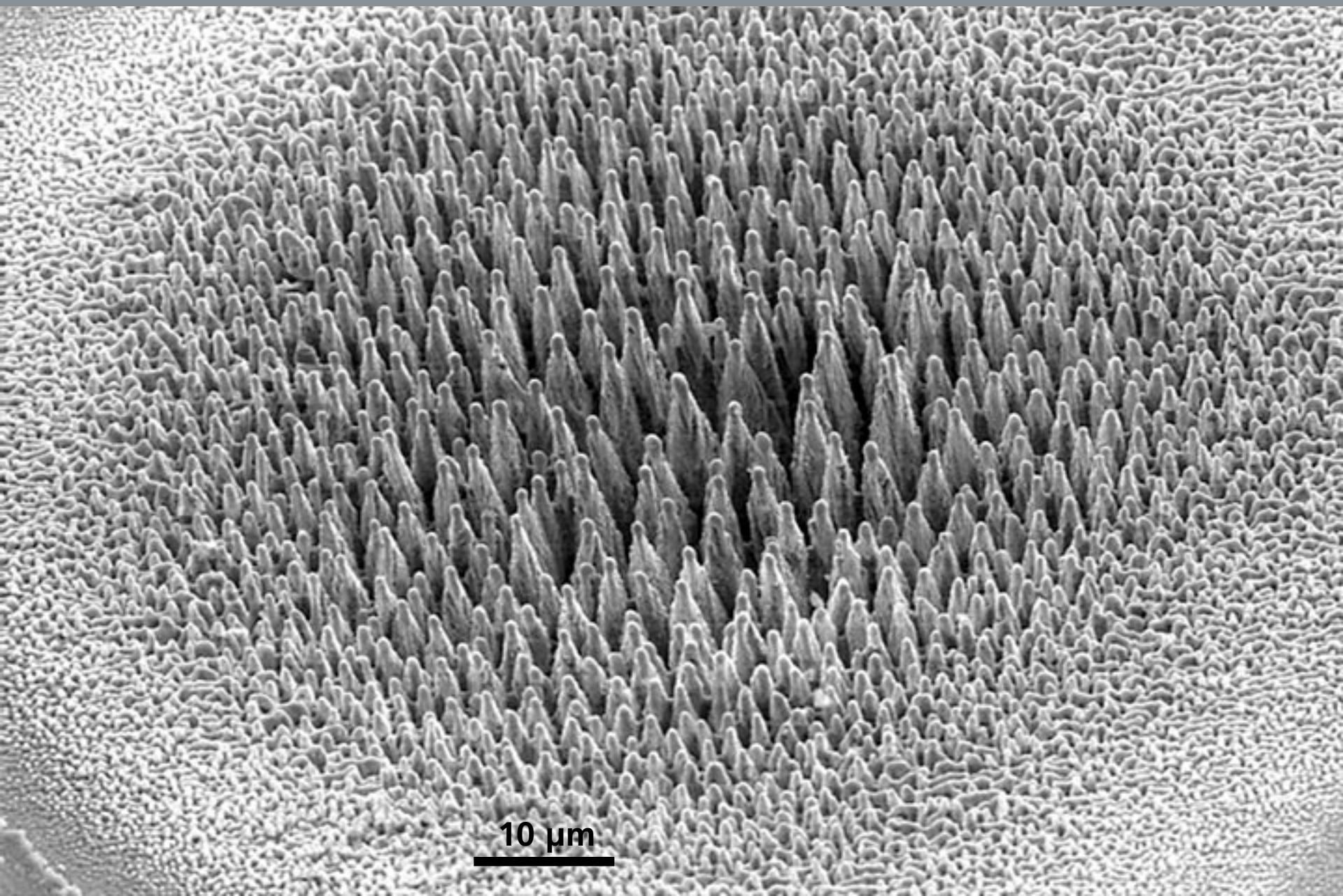


20 μm

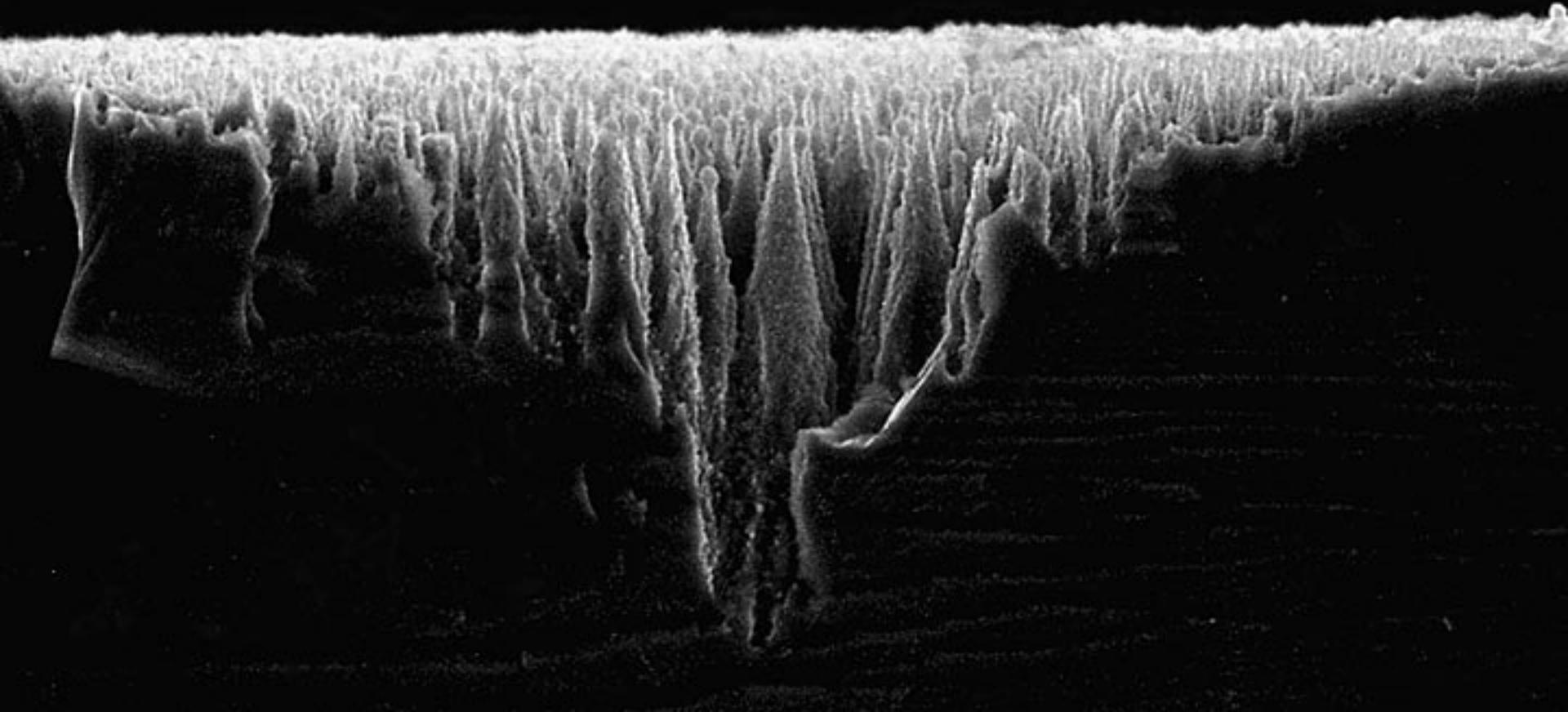
Introduction



Introduction



Introduction



Introduction

Introduction

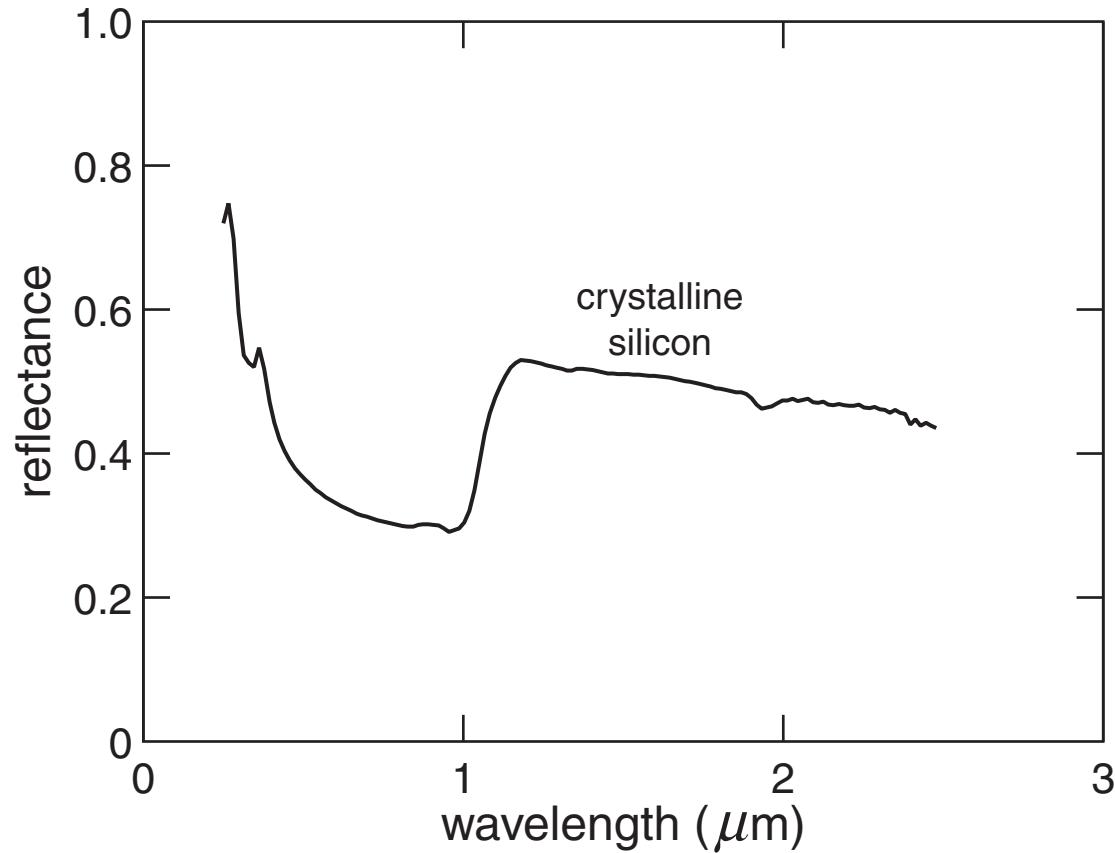
- ▶ **maskless etching process**
- ▶ **self-organized, tall, sharp structures**
- ▶ **nanoscale structure on spikes**

Outline

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

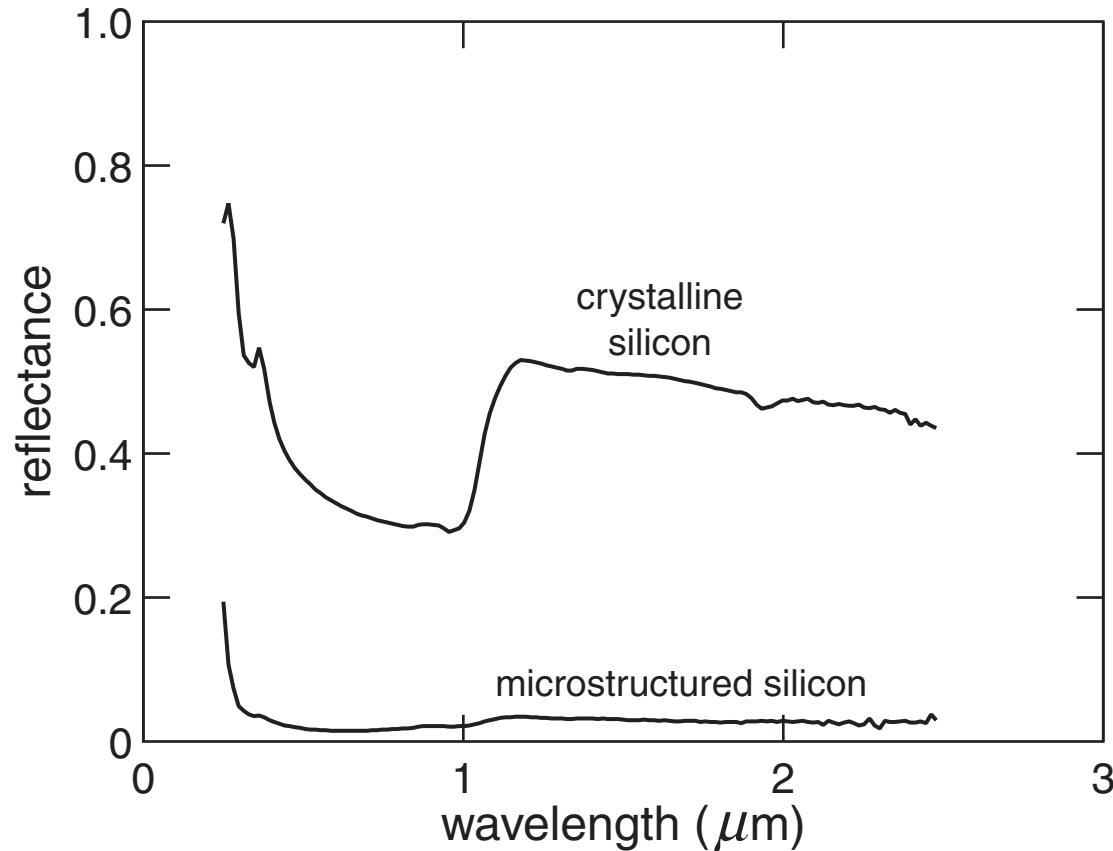
Properties

reflectance (integrating sphere)



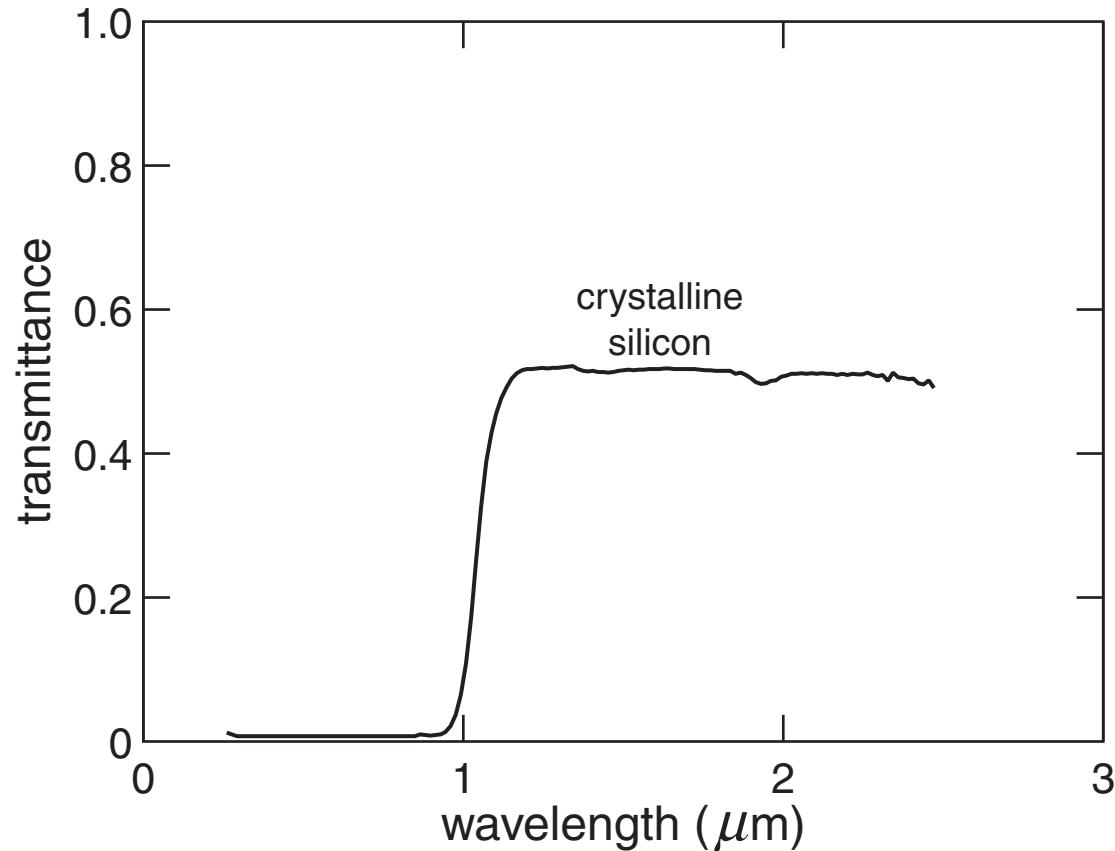
Properties

reflectance (integrating sphere)



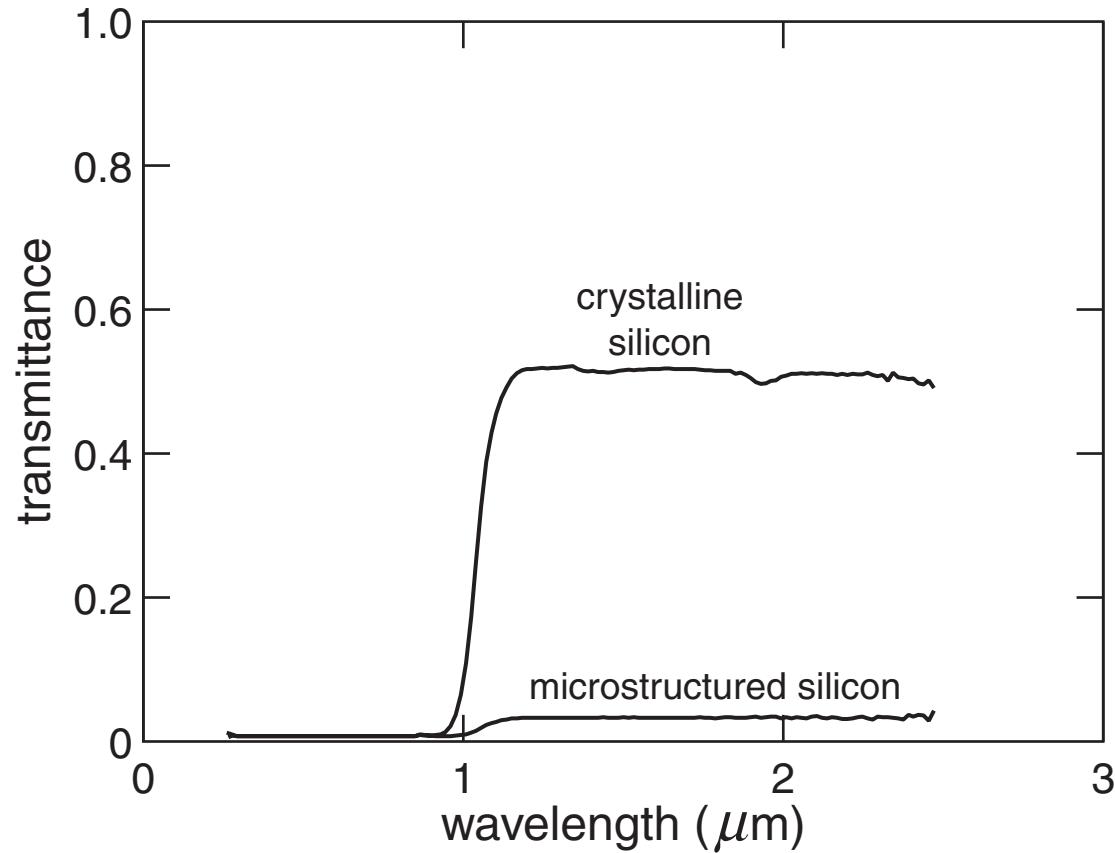
Properties

transmittance (integrating sphere)



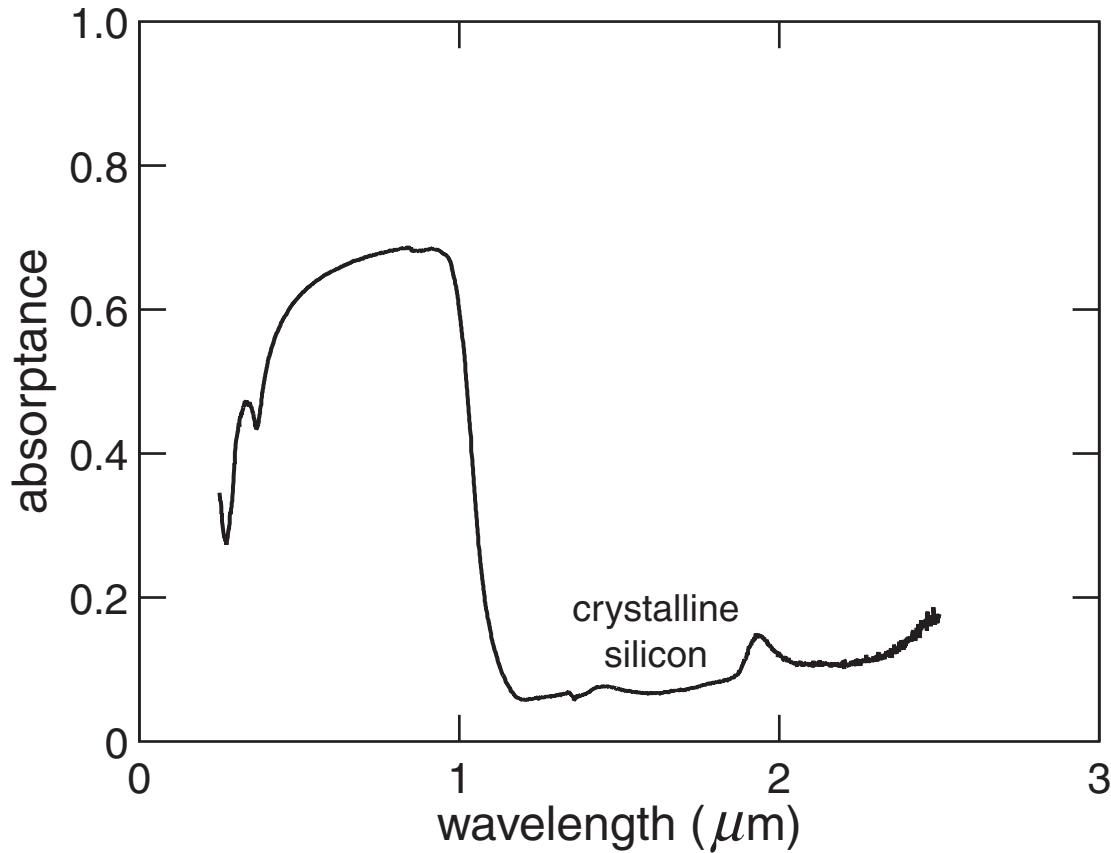
Properties

transmittance (integrating sphere)



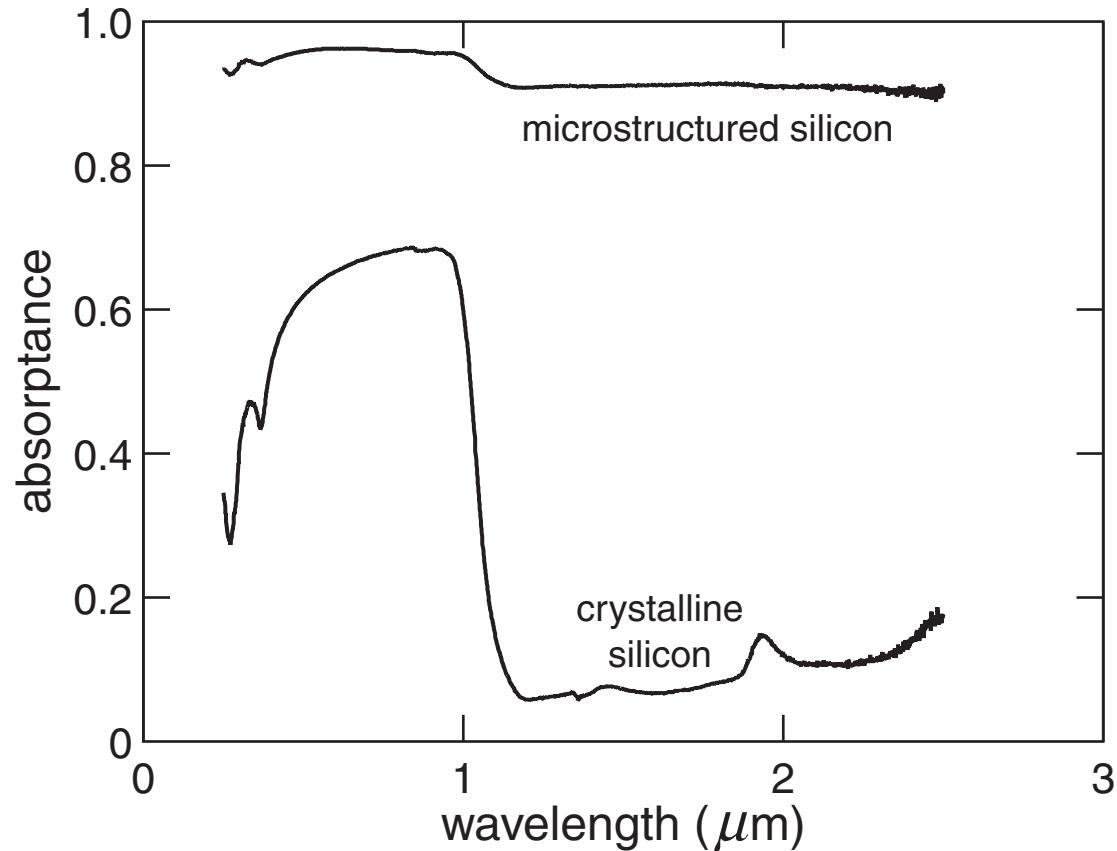
Properties

absorptance ($1 - R - T$)



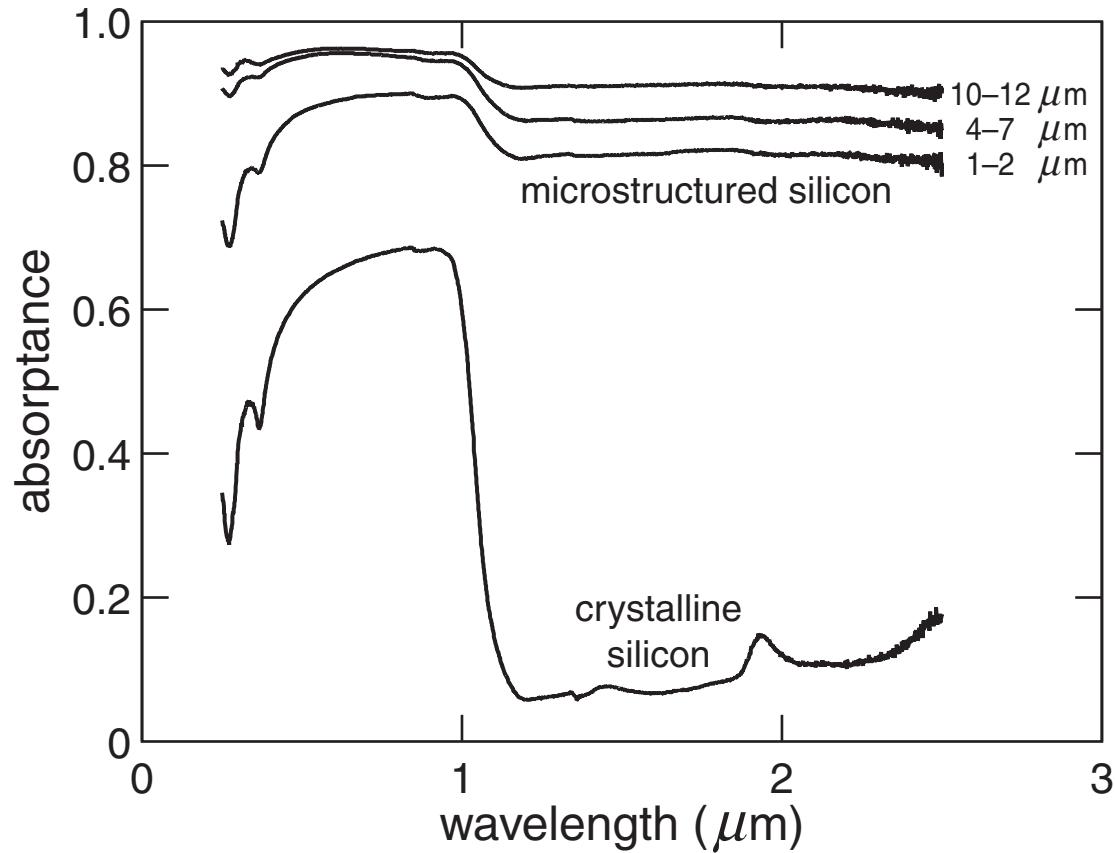
Properties

absorptance ($1 - R - T$)



Properties

absorptance ($1 - R - T$)



Properties

field emission setup



Properties

field emission setup



gold coating

Properties

field emission setup

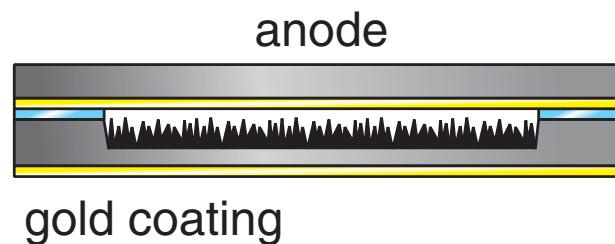
20 μm mica spacers



gold coating

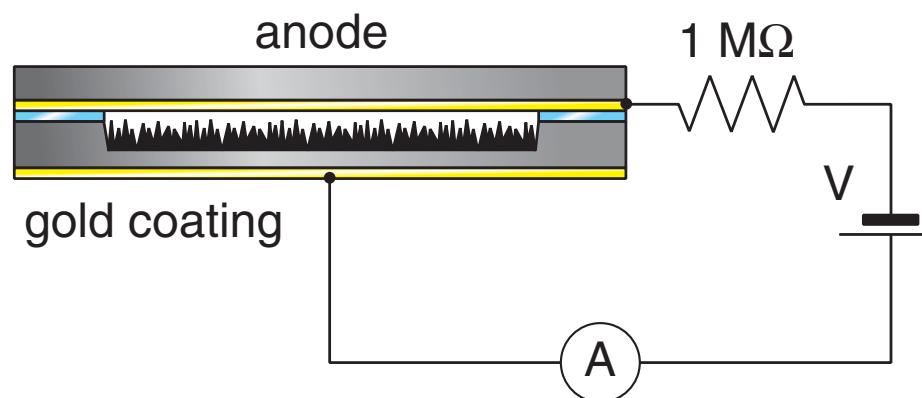
Properties

field emission setup

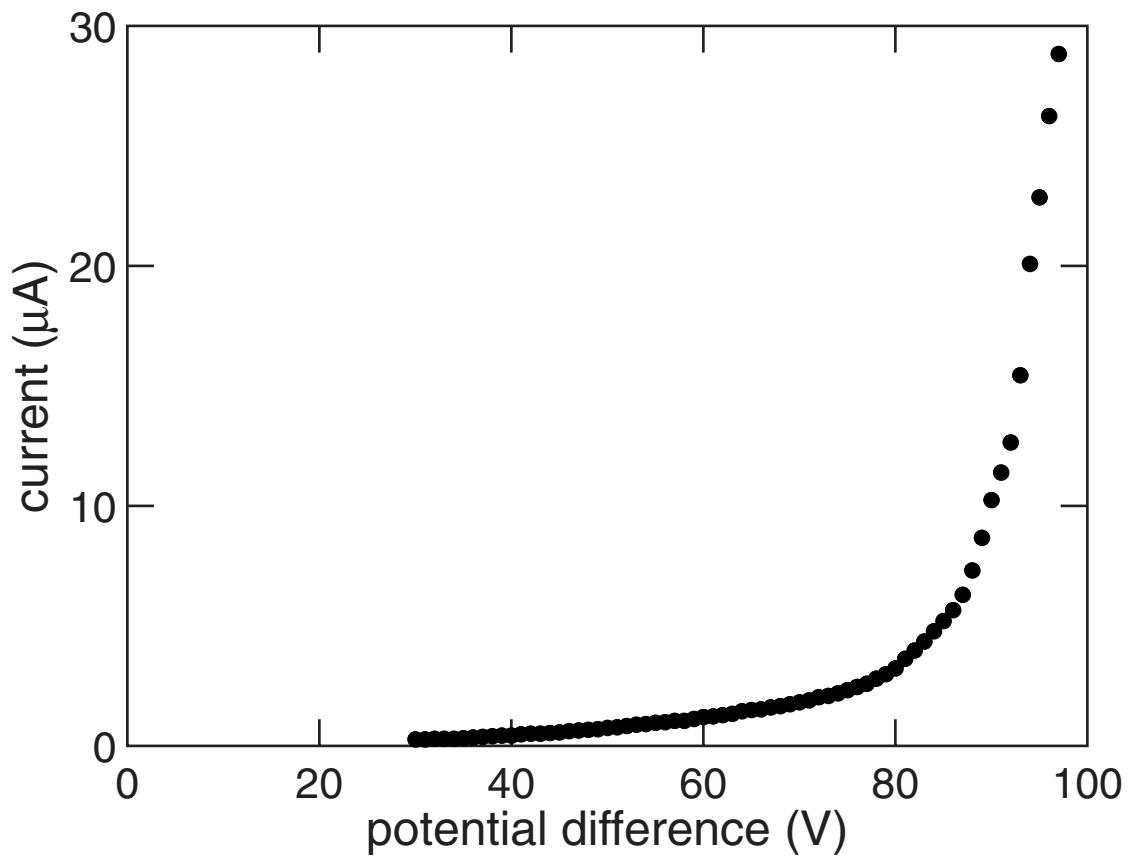


Properties

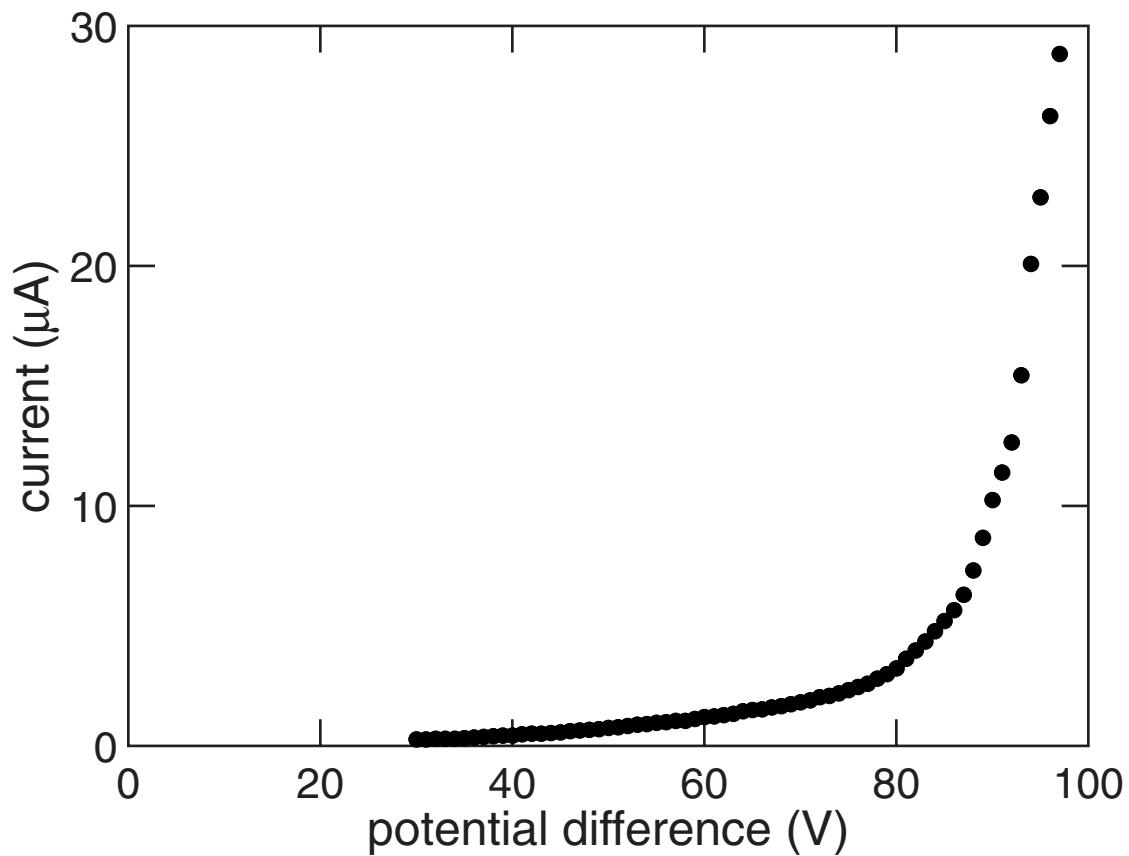
field emission setup



Properties

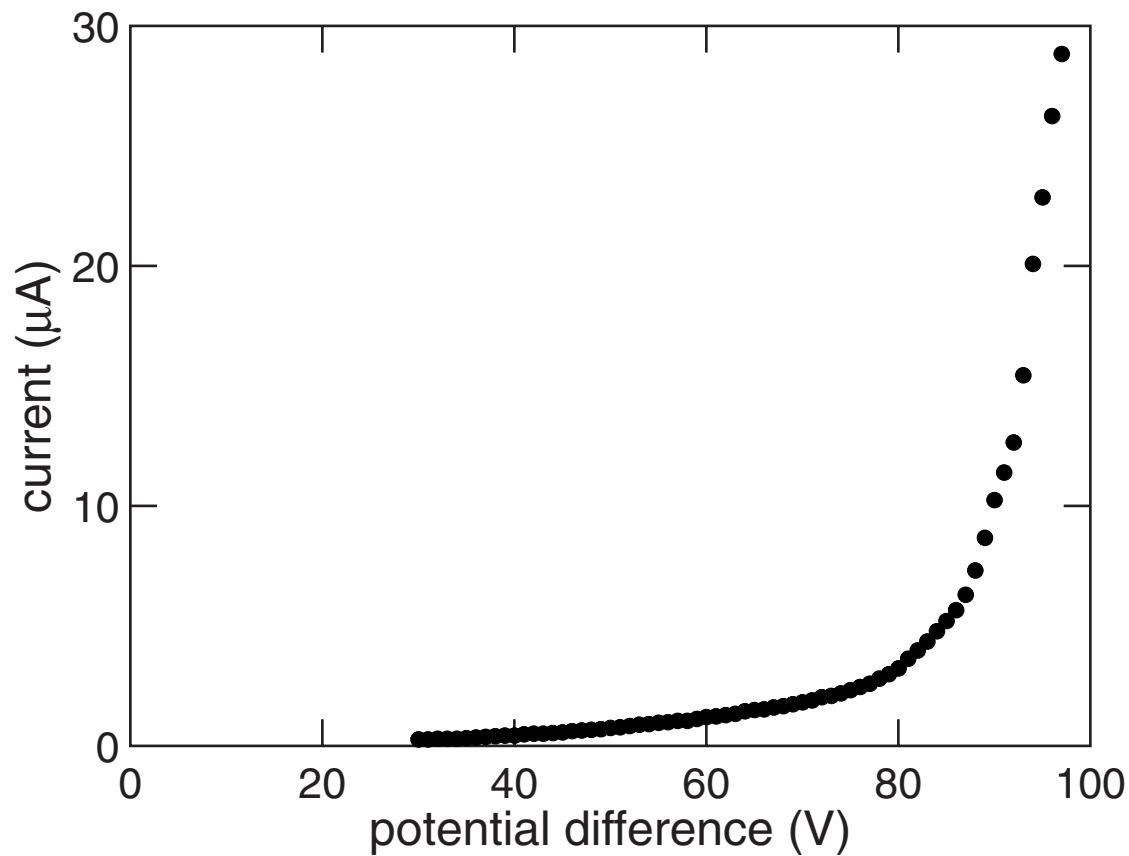


Properties



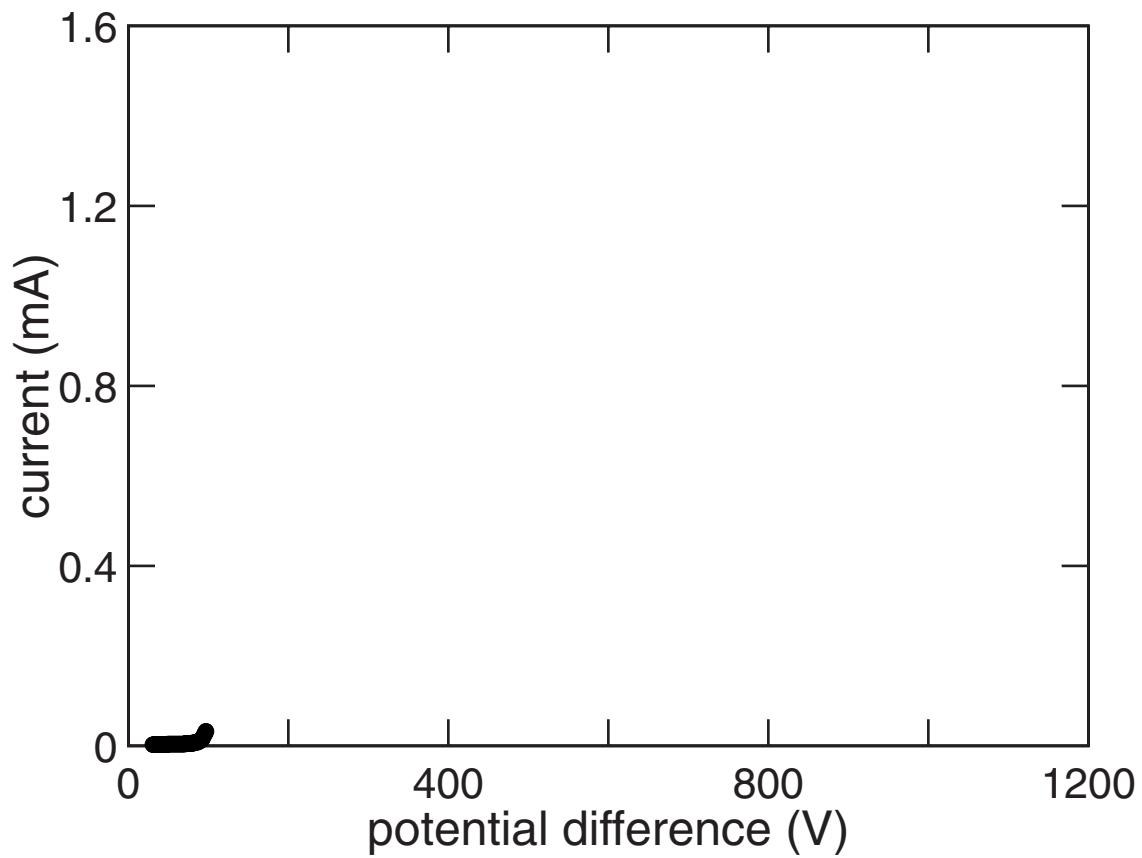
turn-on field ($1 \mu\text{A}/\text{cm}^2$): $1.2 \text{ V}/\mu\text{m}$

Properties

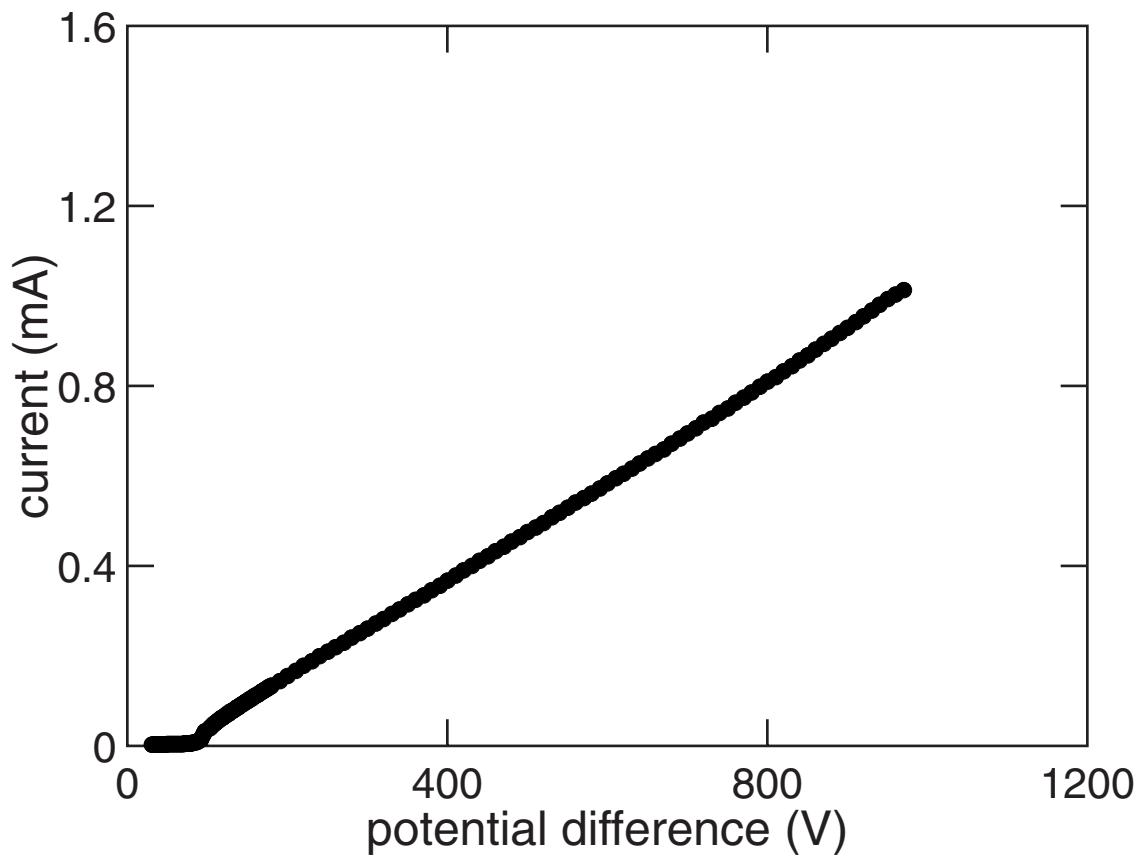


threshold field ($10 \mu\text{A}/\text{cm}^2$): $2.1 \text{ V}/\mu\text{m}$

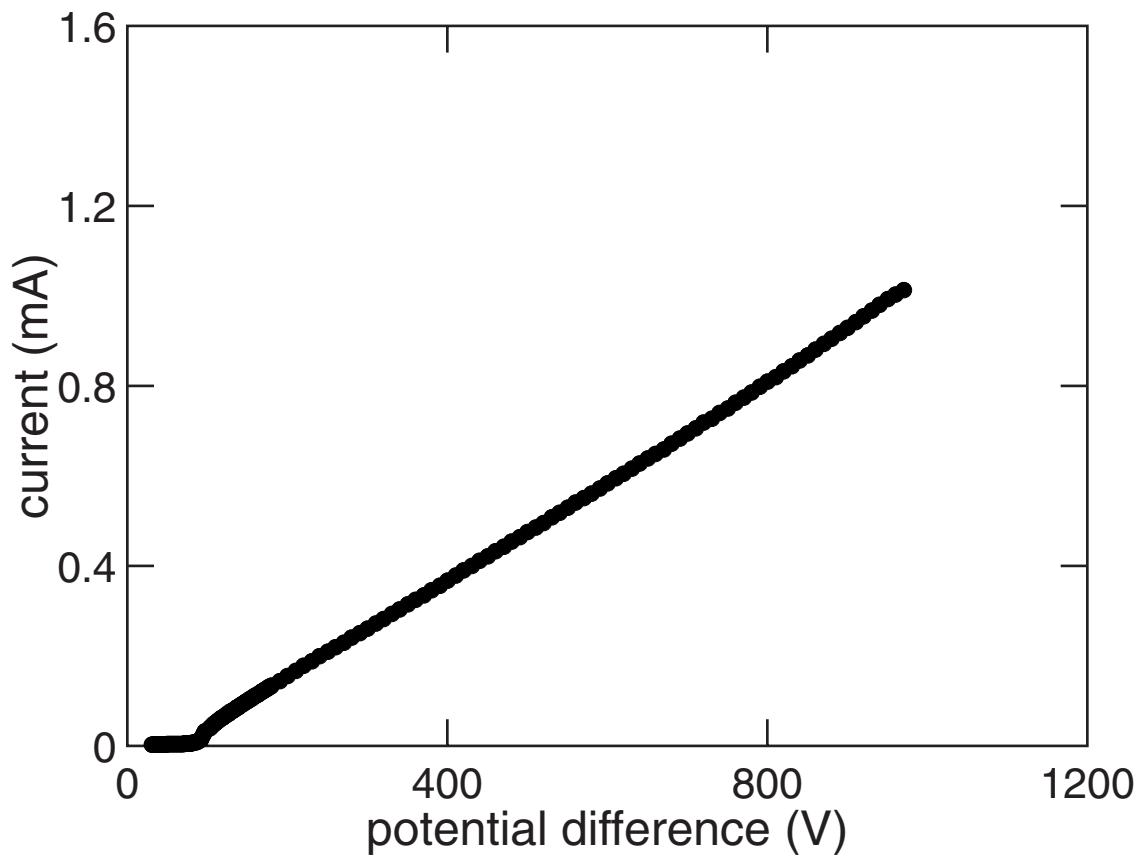
Properties



Properties



Properties



maximum current: 20 mA (4 mm² 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?**

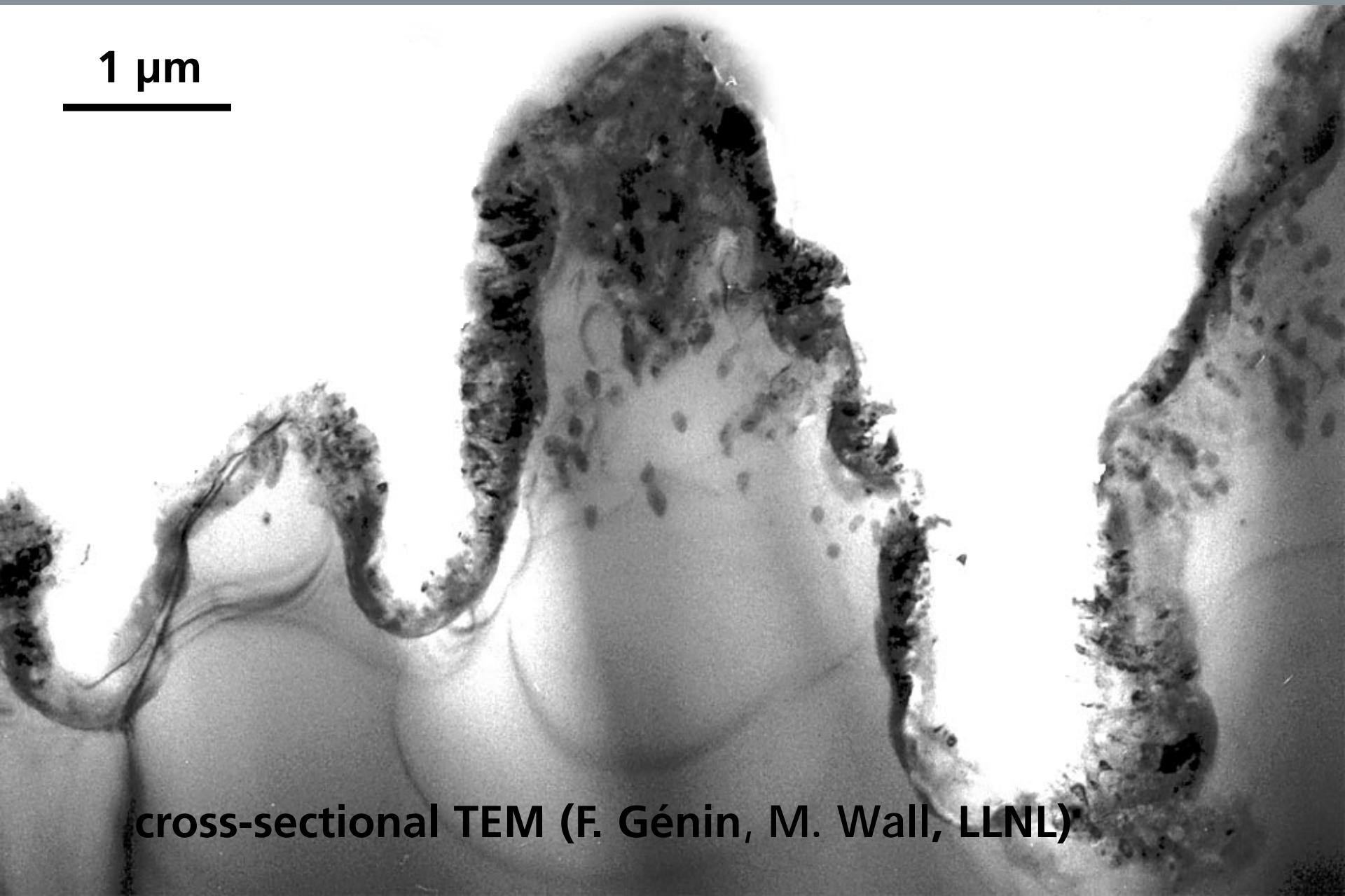
Structural and chemical analysis

Secondary ion mass spectrometry:

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

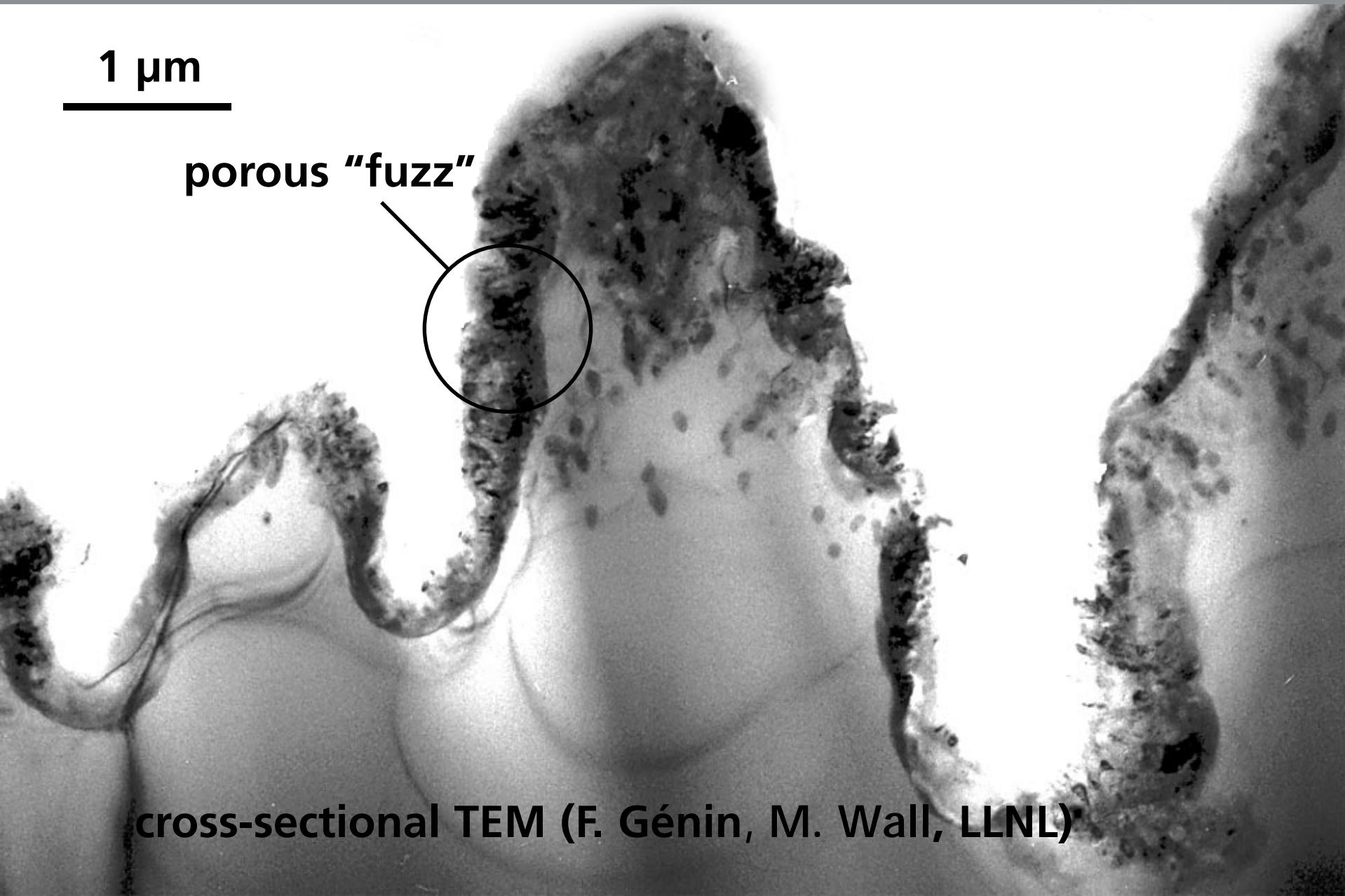
Structural and chemical analysis

1 μm



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

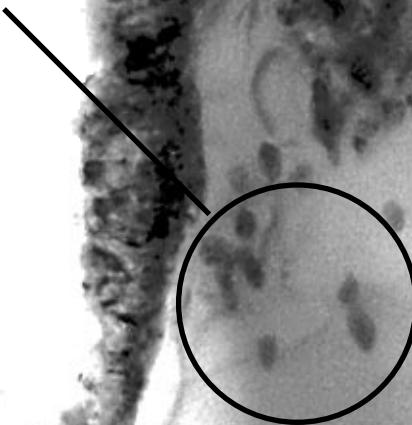
Structural and chemical analysis



Structural and chemical analysis

1 μm

nanocrystallites

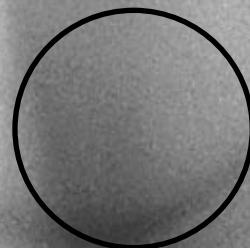


cross-sectional TEM (F. Génin, M. Wall, LLNL)

Structural and chemical analysis

1 μm

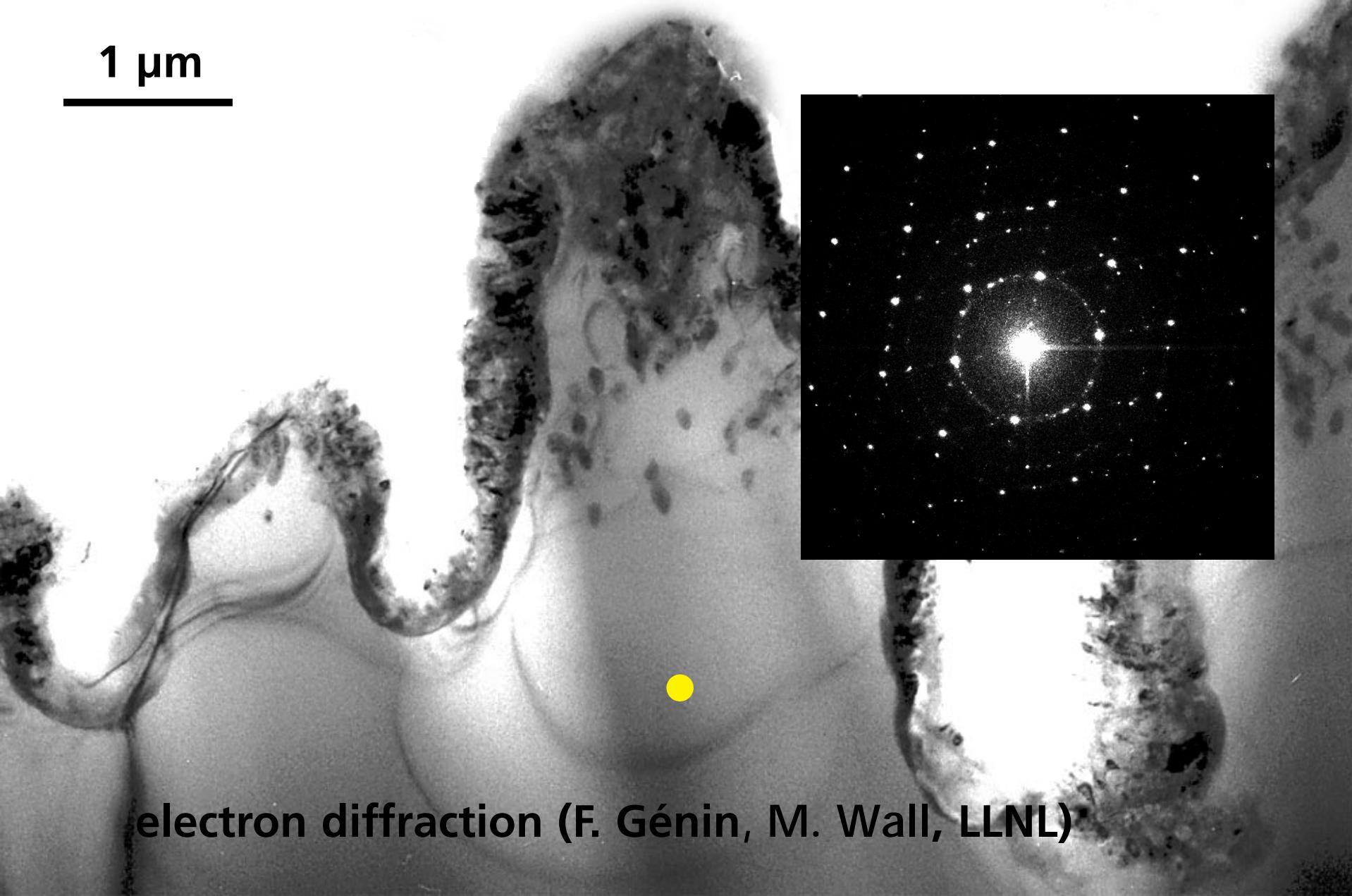
crystalline Si



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

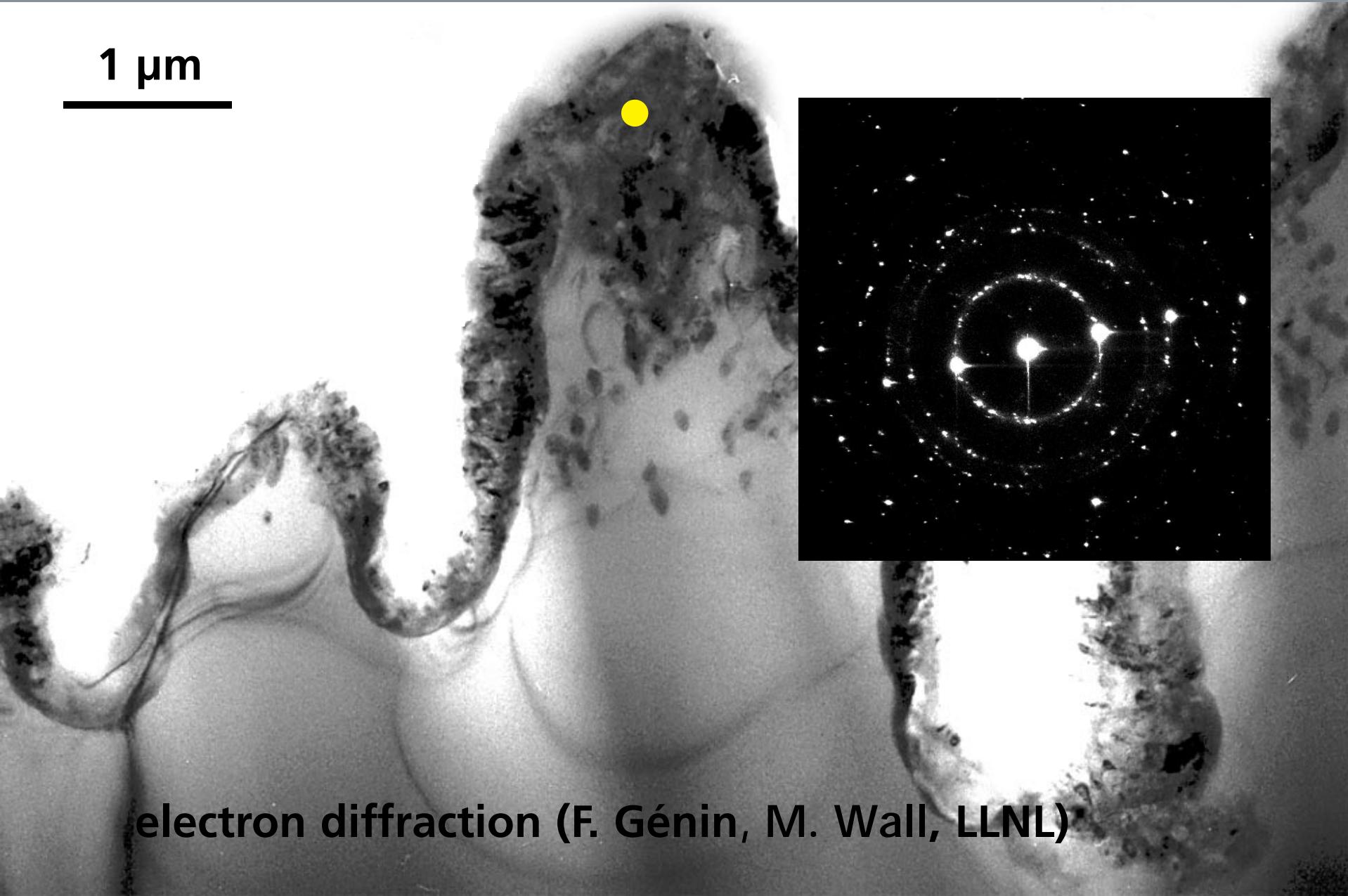
Structural and chemical analysis

1 μm



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

Structural and chemical analysis



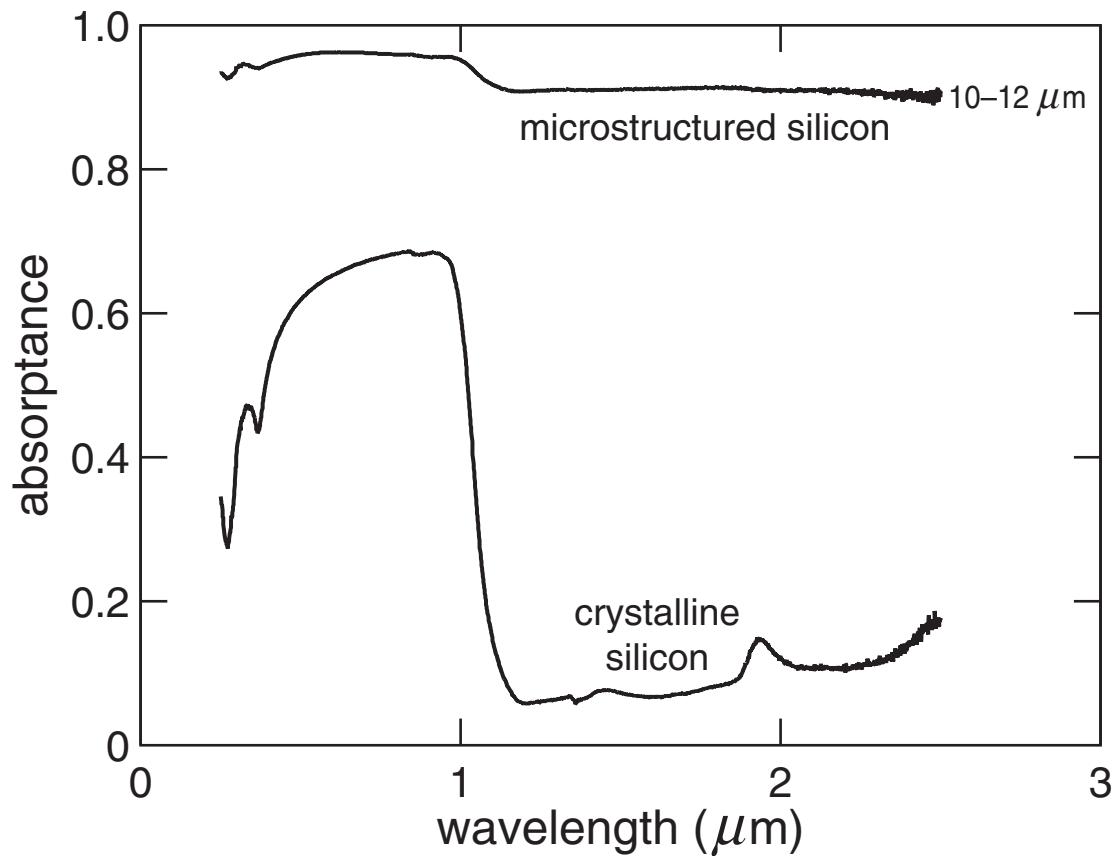
Structural and chemical analysis

cross-sectional TEM:

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

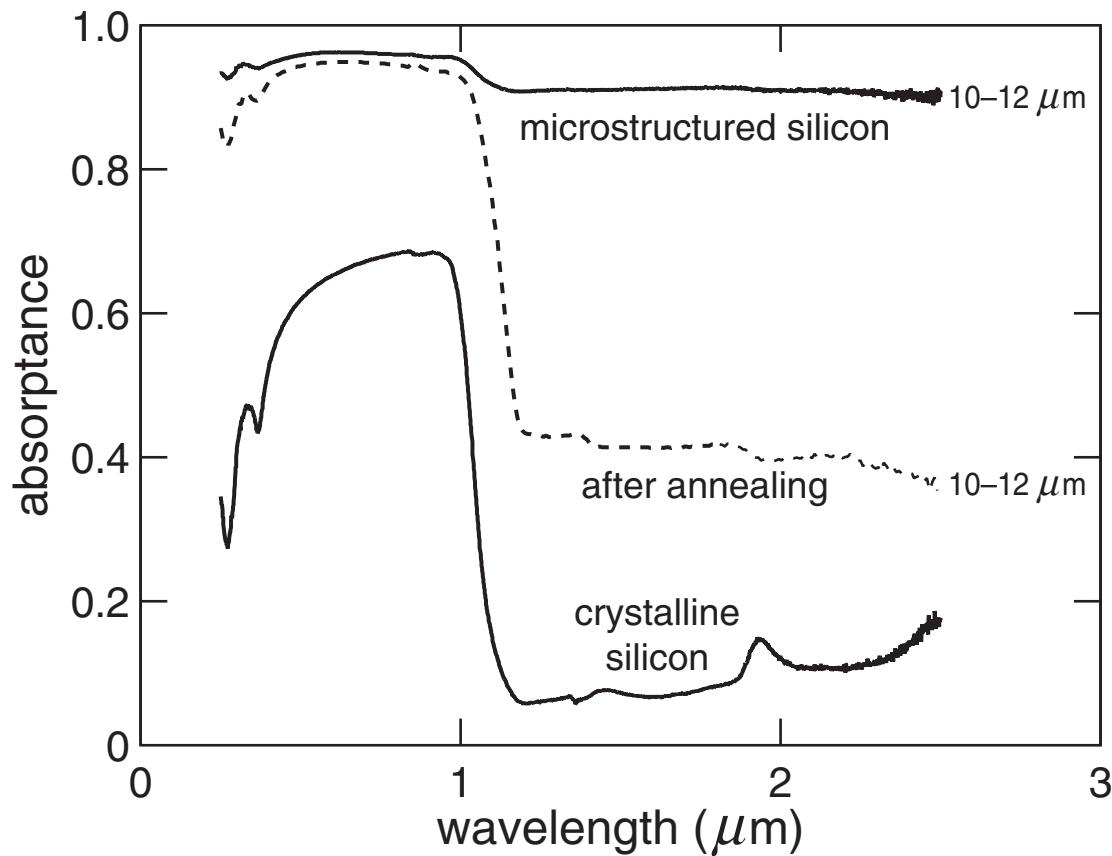
Structural and chemical analysis

anneal 4 hours at 1200 K



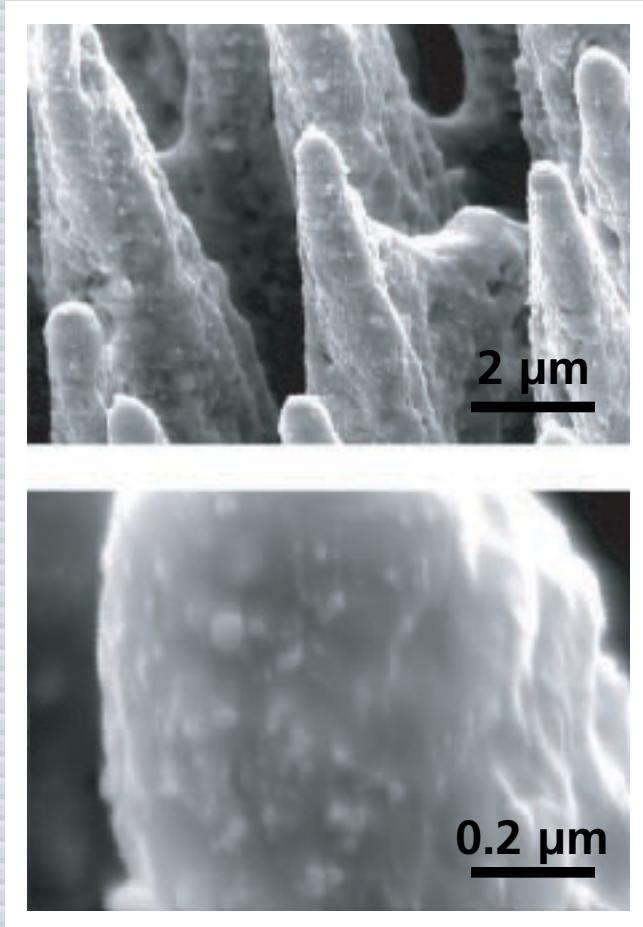
Structural and chemical analysis

anneal 4 hours at 1200 K



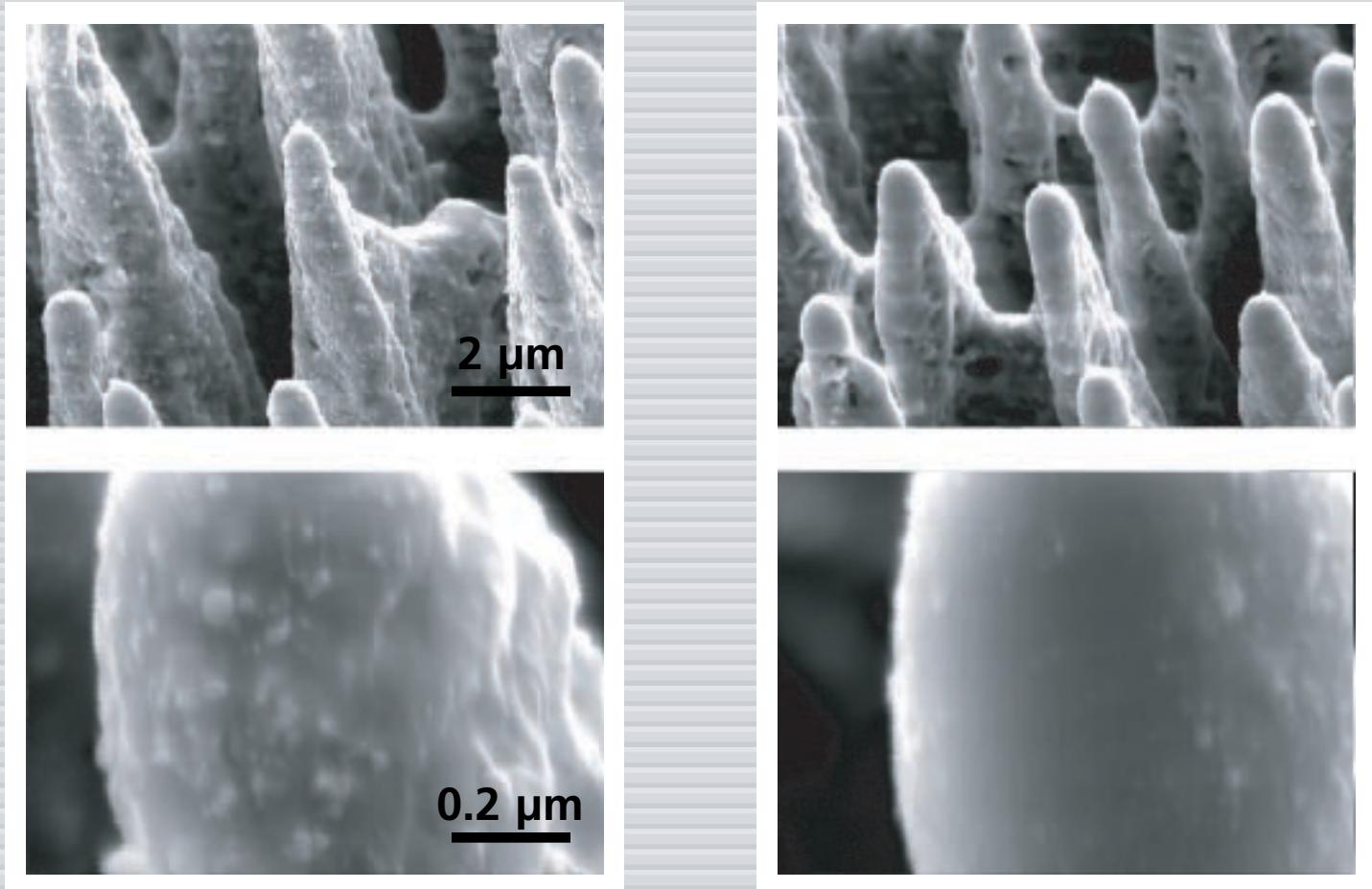
Structural and chemical analysis

anneal 4 hours at 1200 K



Structural and chemical analysis

anneal 4 hours at 1200 K



Structural and chemical analysis

Effects of annealing:

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

Structural and chemical analysis

sulfur introduces states in the gap

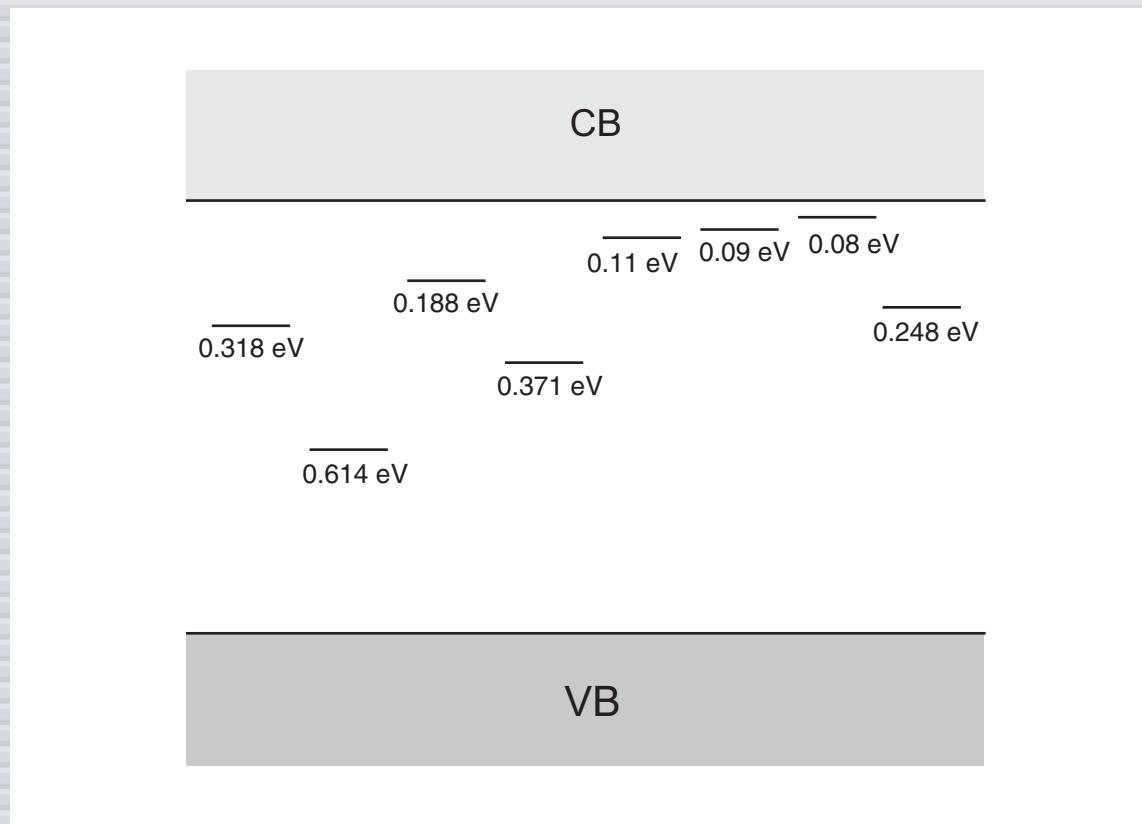
CB

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

VB

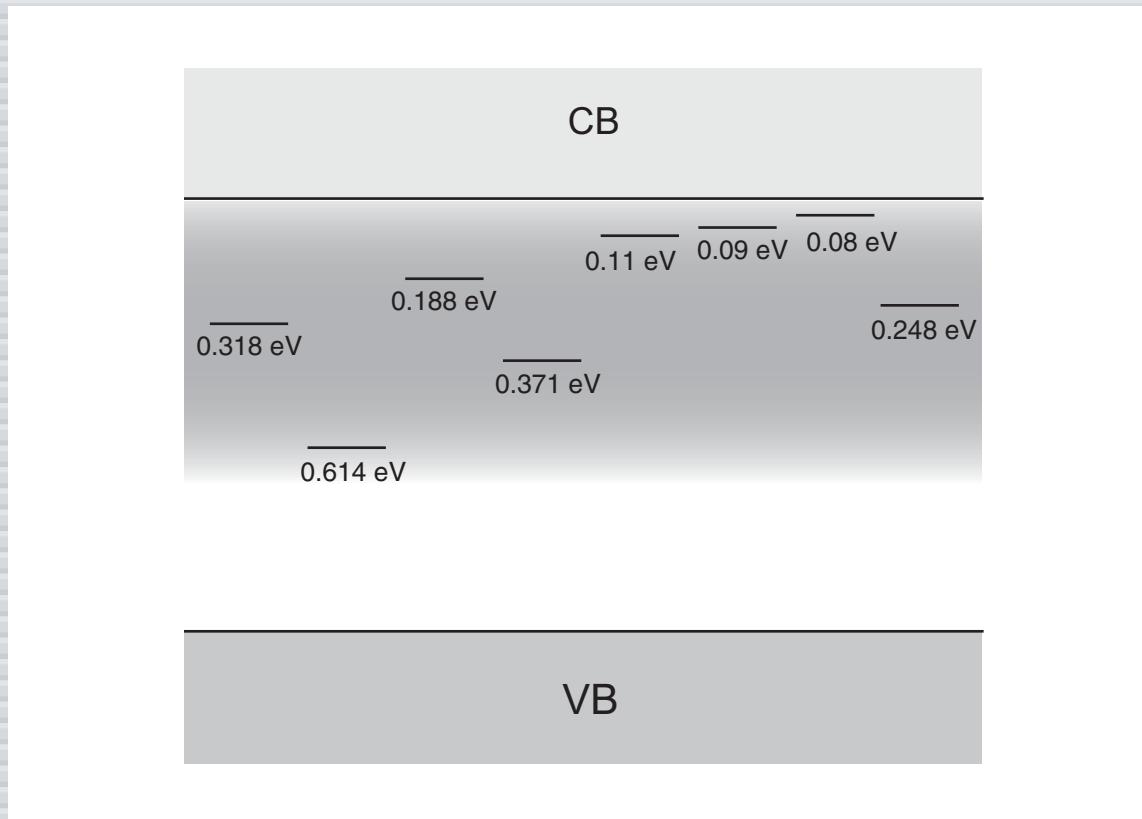
Structural and chemical analysis

sulfur introduces states in the gap



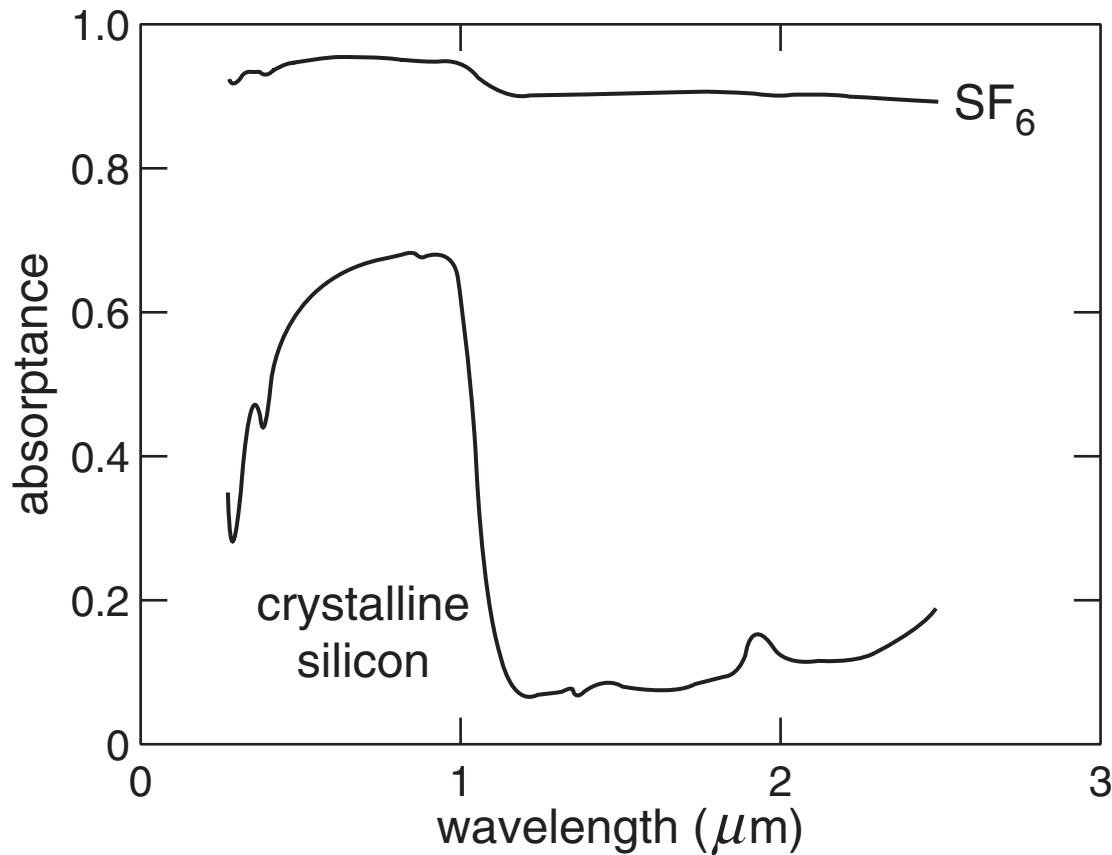
Structural and chemical analysis

states broaden into a band



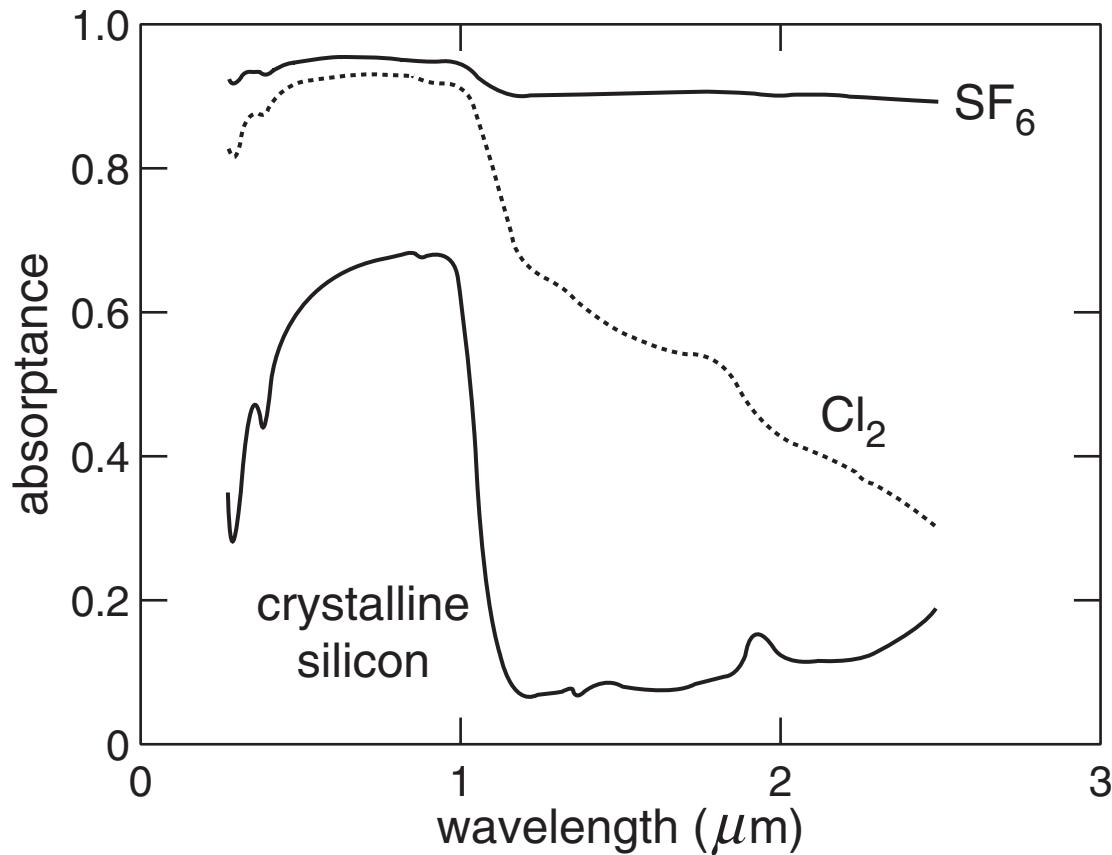
Structural and chemical analysis

effect of ambient gas on absorptance



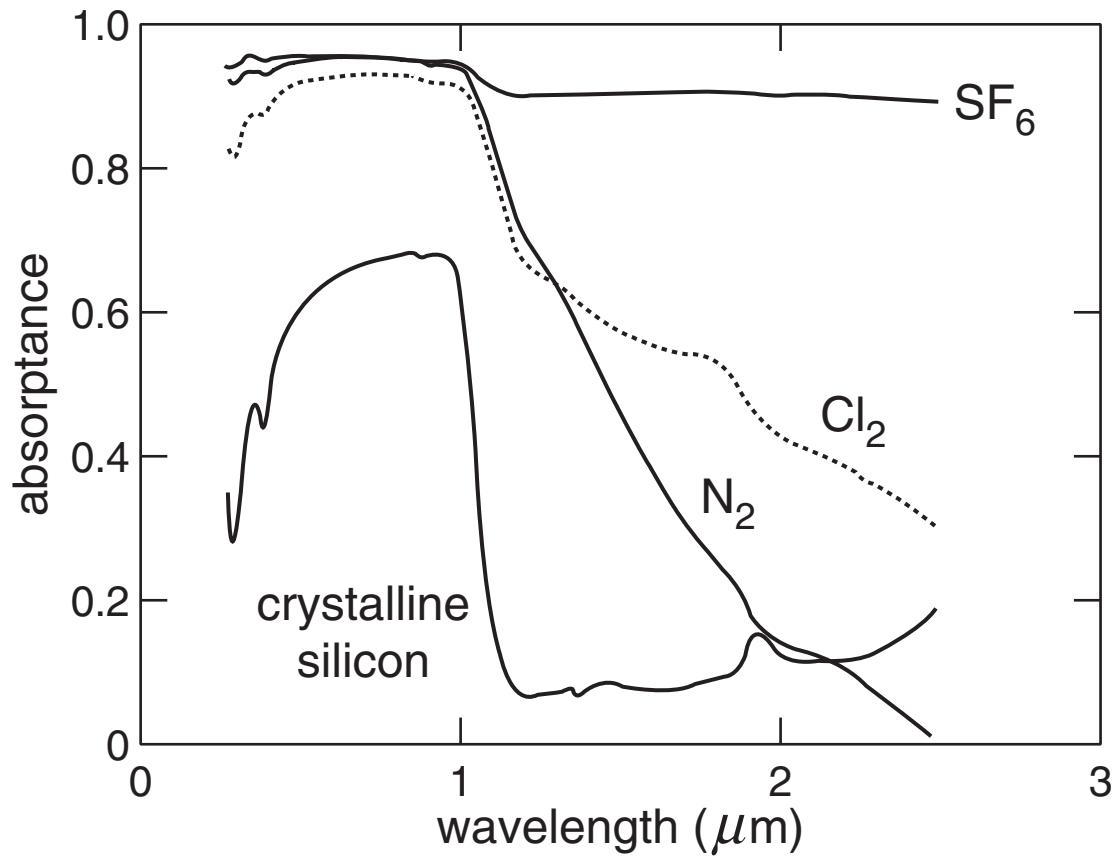
Structural and chemical analysis

effect of ambient gas on absorptance



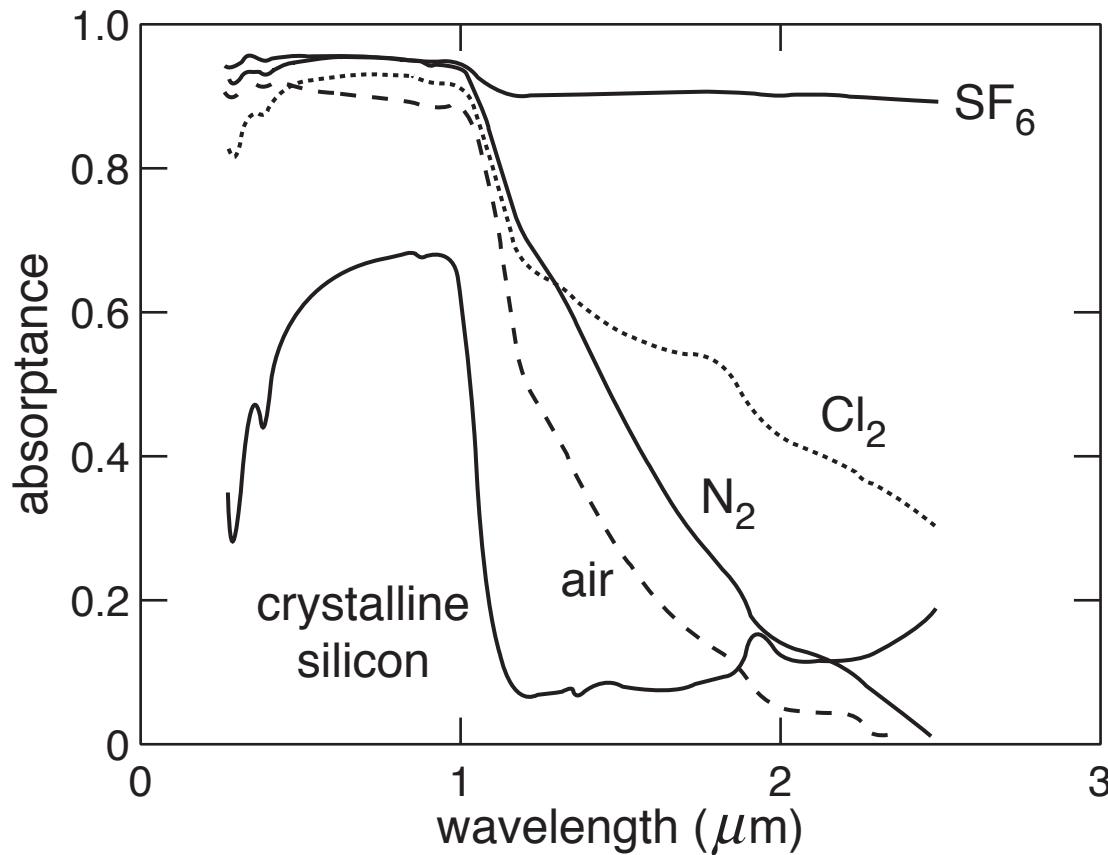
Structural and chemical analysis

effect of ambient gas on absorptance



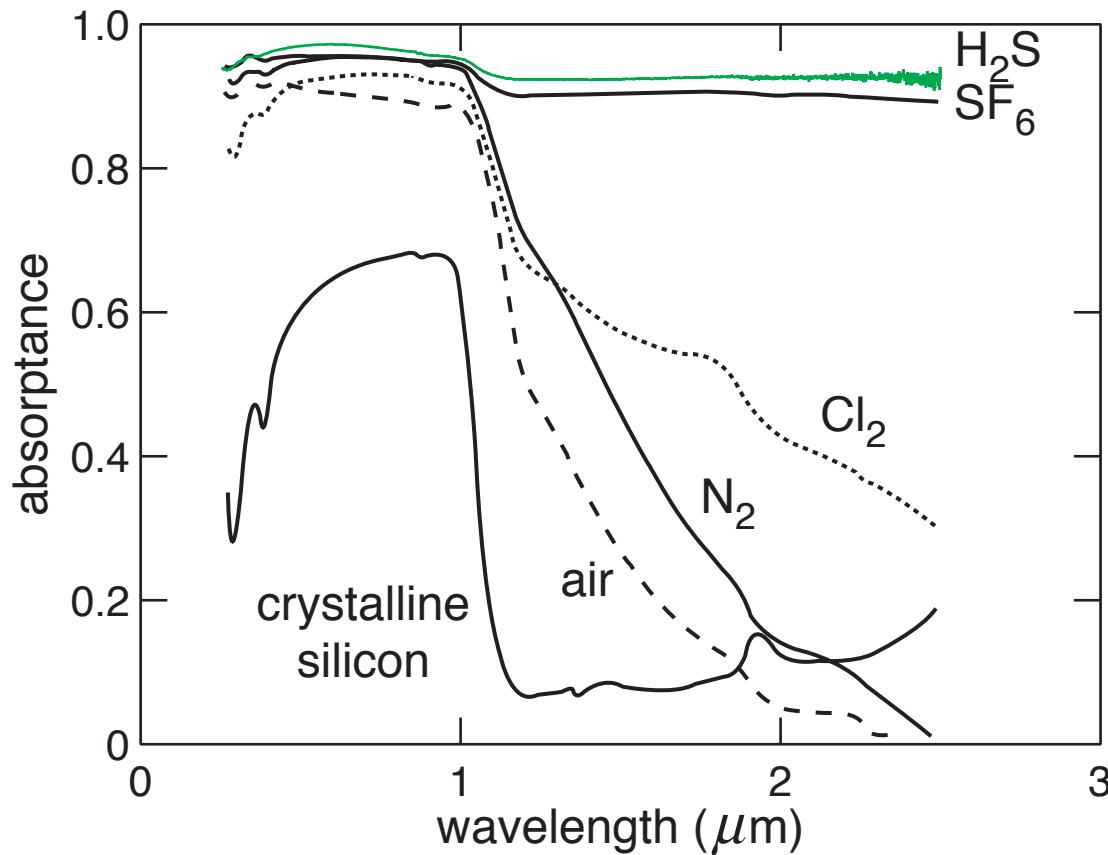
Structural and chemical analysis

effect of ambient gas on absorptance



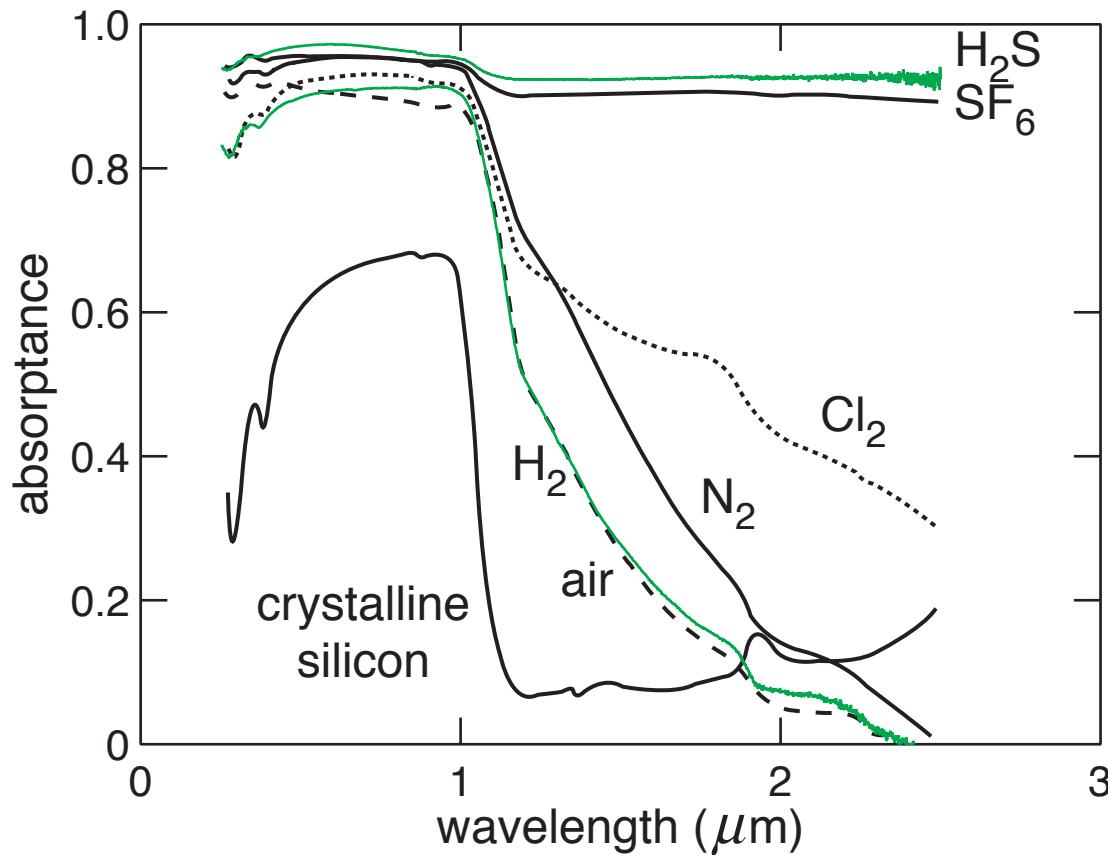
Structural and chemical analysis

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 microscope or a filthy Petri dish

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

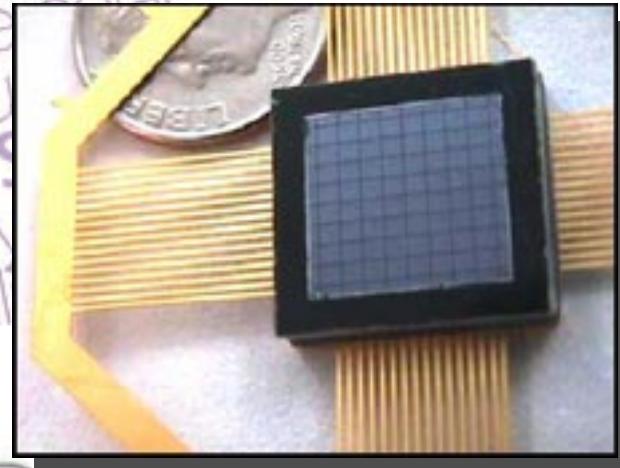
of times brighter than the Sun and extremely short laser pulse will break down around the laboratory," he claims.

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

Outlook

► **detector technology**

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



TALL, DARK AND STRANGER

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

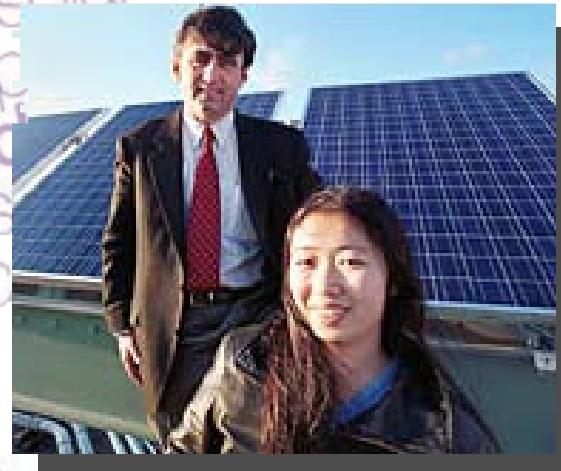
semiconductors with a powerful base to the early 1980s. Moxtek's was the first academic lab in the world to do so, based on a temperature-based threshold voltage that is so low that it can measure 20 times better than the best

around the "strange" base. It's also the first to make the only truly short-base device for high-current applications that can measure 10 times better than the best. And the most interesting part is that the new technology may be the key to a whole new generation of sensors. Moxtek esti-

Outlook

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

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



TALL, DARK AND STRANGER

We ALL know stories of weirdness. They come back to us from time to time when a friend or relative tells us of a little-known secret. It's always when we least expect it, when we're least prepared for it. And it's always something that we didn't expect. Like a forest of silicon spikes that could revolutionise solar cells and give you pain-free injections. Or a mysterious world of black silicon that peers into the unknown.

Silicon is a semiconductor with a powerful base. In the early 1950s, Mervin K. Mizell's was the first academic lab in the world to grow single-crystal silicon on a temperature-controlled furnace. This device can convert solar energy into electricity more efficiently than any other material. It's also extremely durable and can withstand temperatures up to 1,000 degrees Celsius without melting. This makes it ideal for use in space applications where temperatures can fluctuate greatly. In fact, it's so durable that it can even withstand the impact of a meteorite hitting Earth at speeds of up to 10 km per second!

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

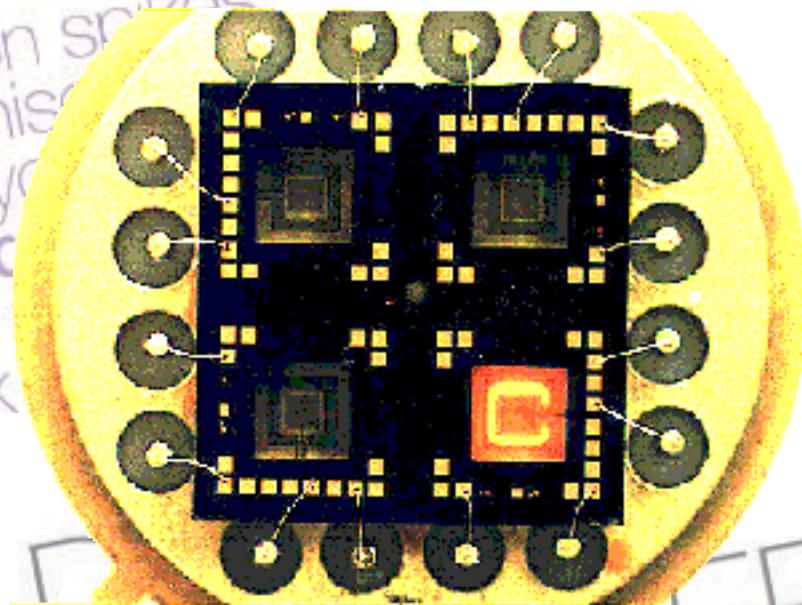
semiconductors with a powerful base to around the "unconscious" becomes a Park. It's not a word the only reason that I can't believe those words back to me. I'm not a scientist, but I do know that and there are no aliens who will attack a species called "Homo Sapiens" as they are too much like us. And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



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

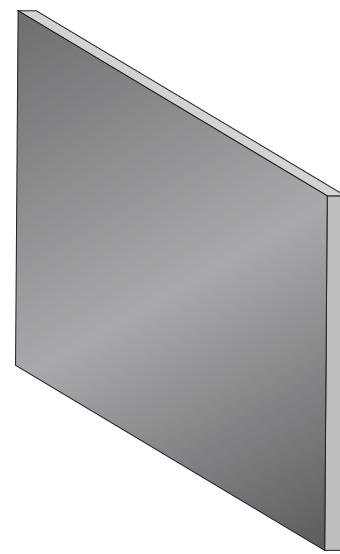
Outlook

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

Outlook

can ordering of spikes be improved by using a grid?

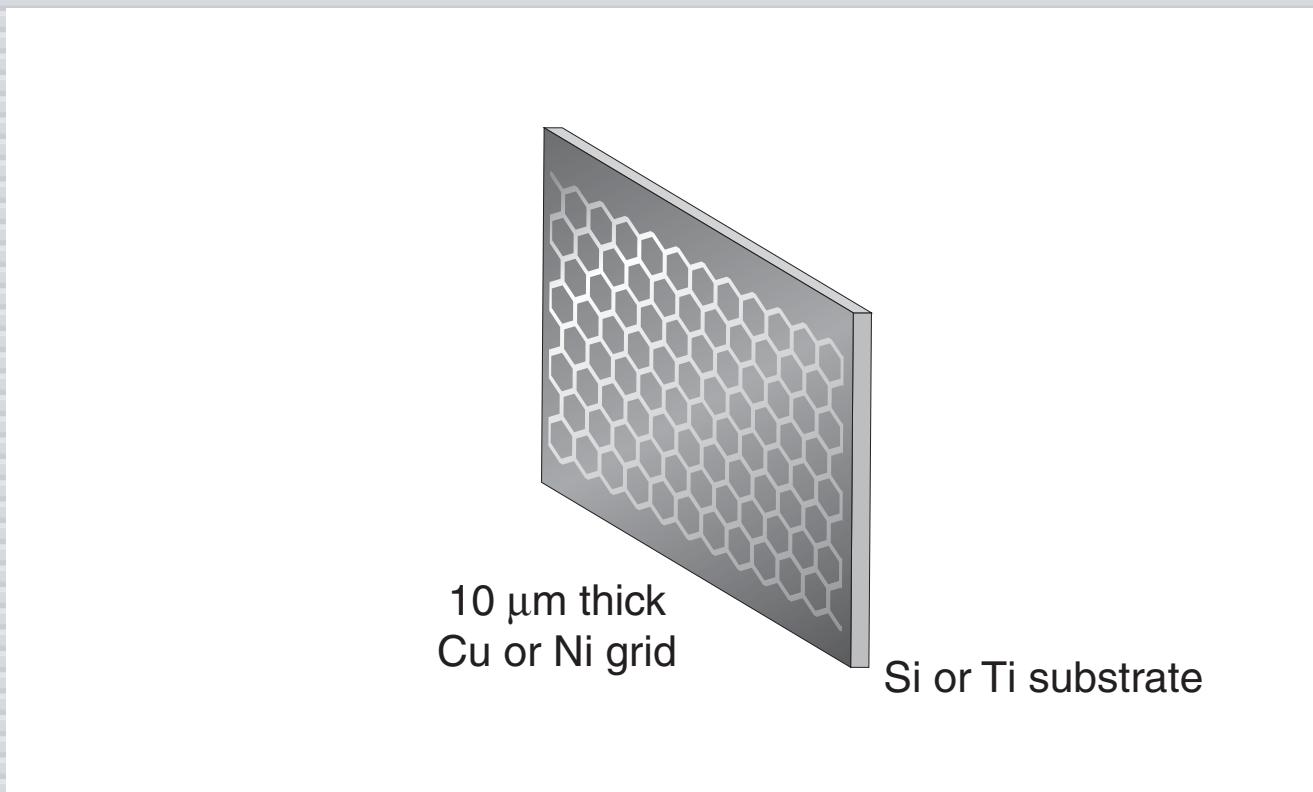
Outlook



Si or Ti substrate

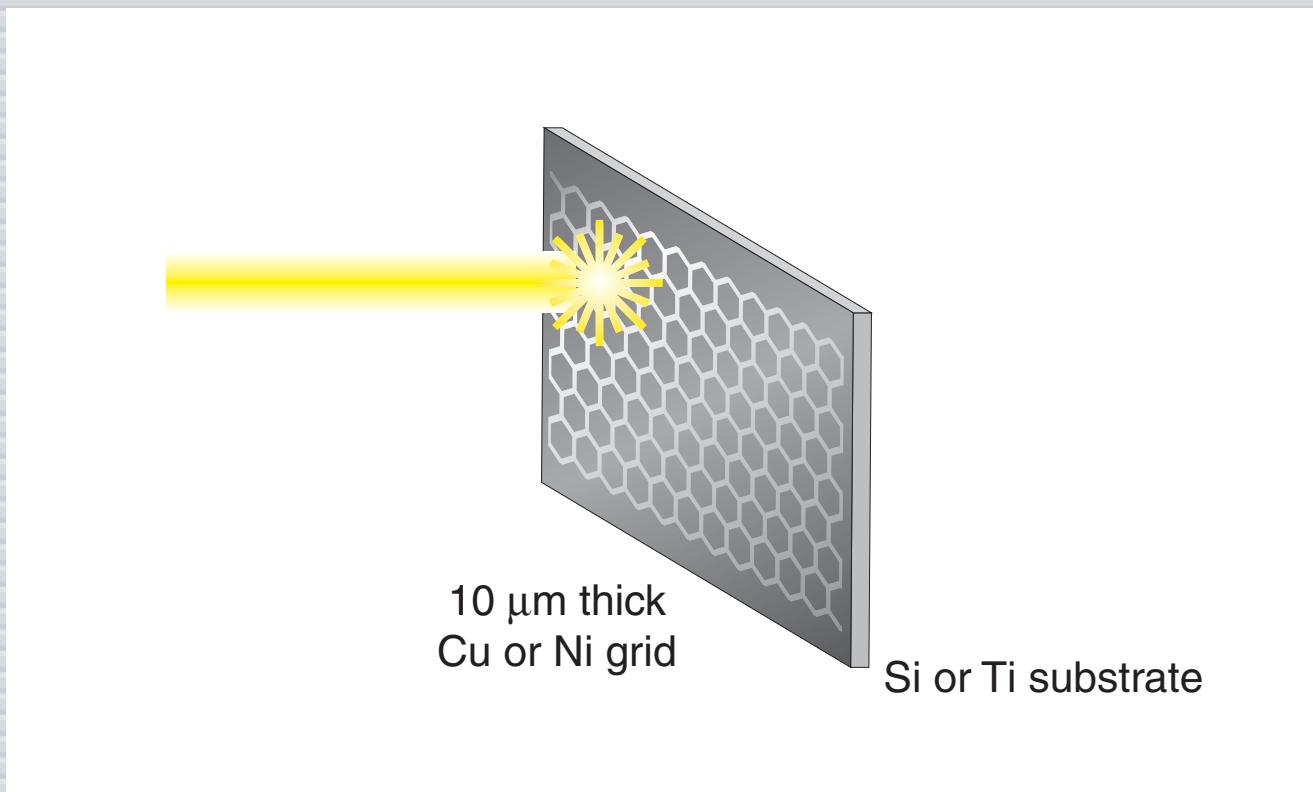
Outlook

place grid in front of substrate



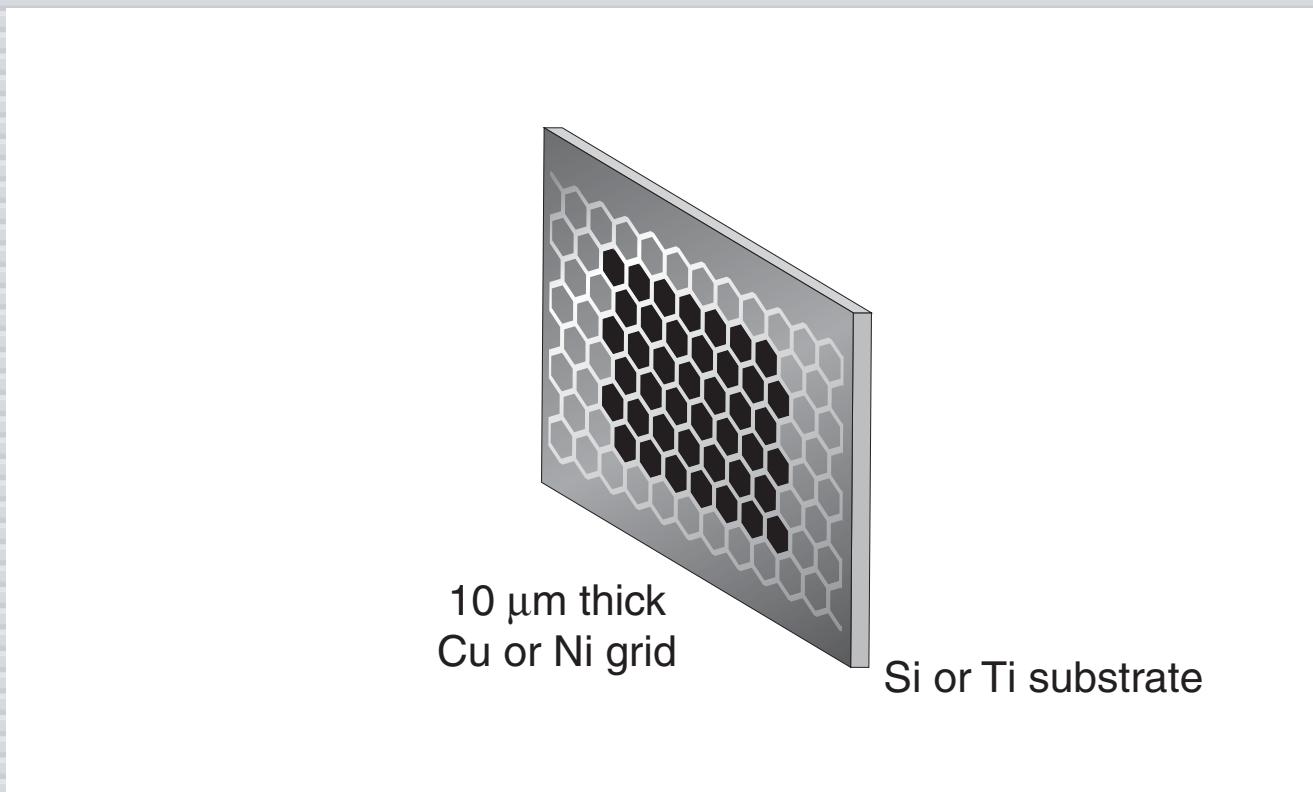
Outlook

scan laser beam



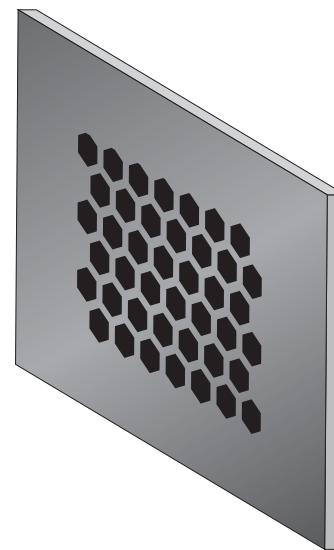
Outlook

scan laser beam

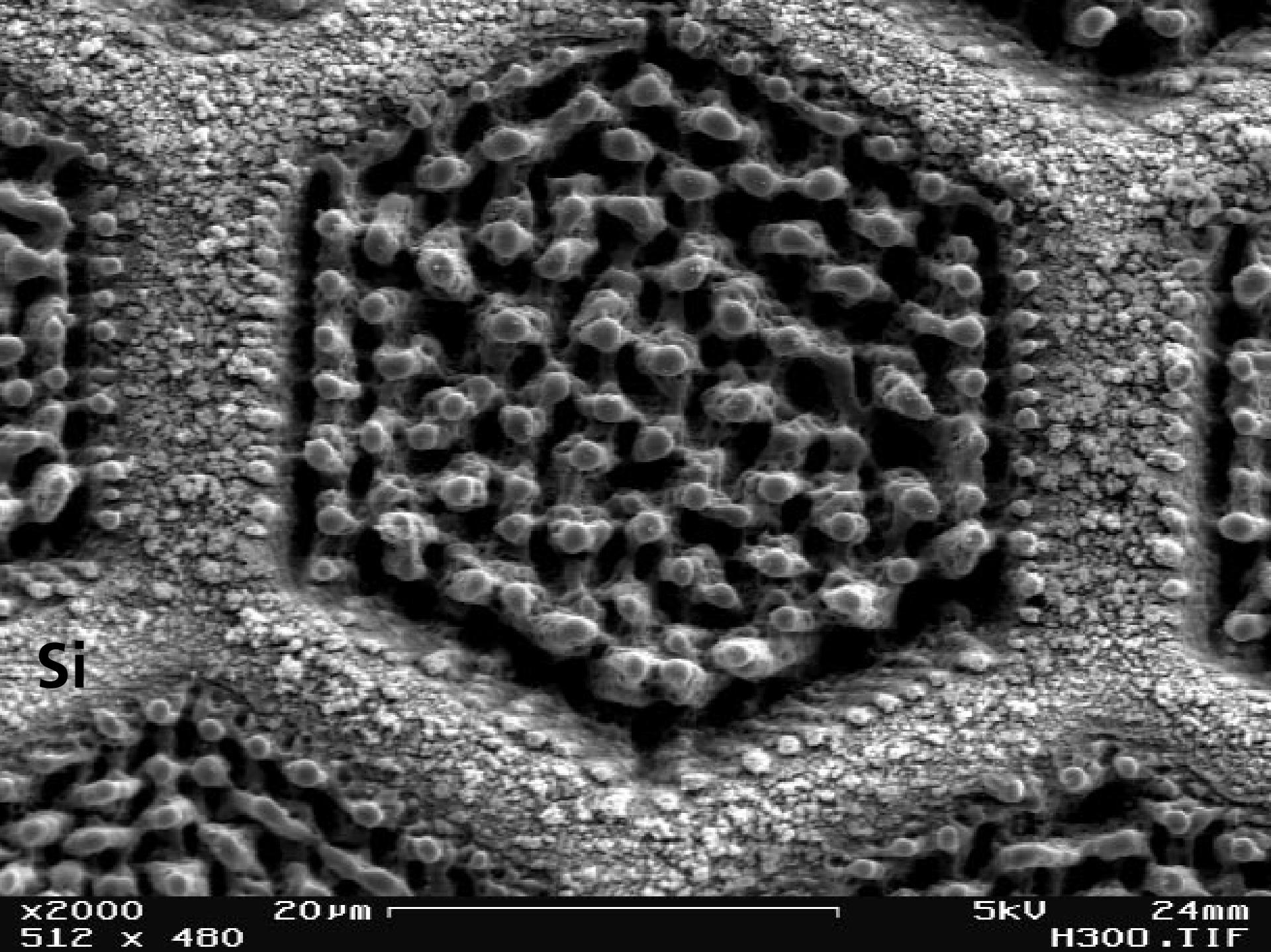


Outlook

remove grid



Si or Ti substrate



x2000

512 x 480

20 μm

5kV

24mm
H300.TIF

Ti

20 μm

5kV 17mm

Ti

10 μm

5kV

17mm

Outlook

Summary

Microstructured silicon

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

Summary

Microstructured silicon

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

Summary

Microstructured silicon

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

Summary

Microstructured silicon

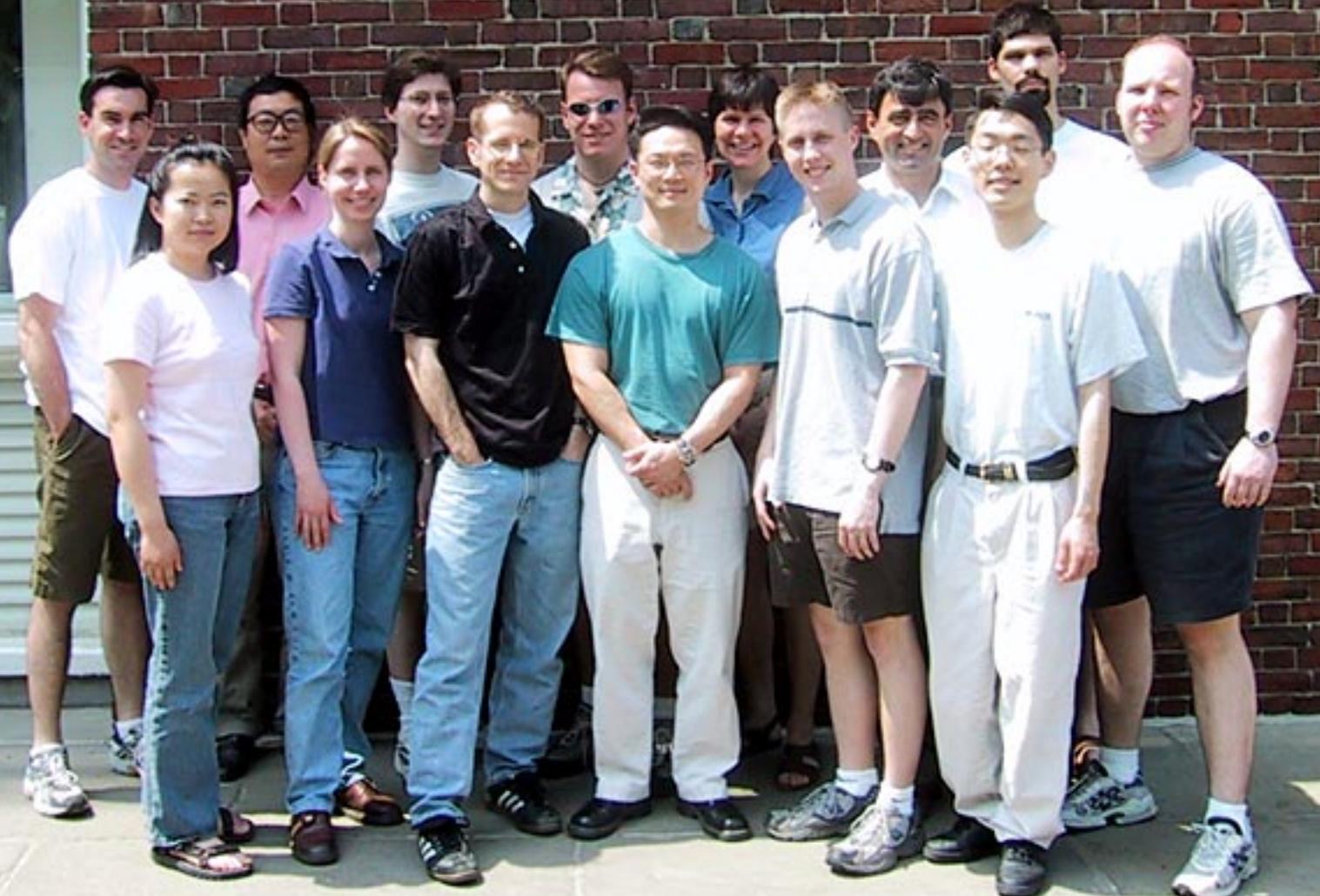
- ▶ **fabricated by simple, maskless process**
- ▶ **can be integrated with microelectronics**
- ▶ **generates IR photocurrent**
- ▶ **provides stable, high field emission current**

Summary

Microstructured silicon

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

CORDON MCKAY
LABORATORY OF
APPLIED SCIENCE



Funding: ARO, DoE, NDSEG

Acknowledgments:

Dr. François Génin (LLNL)

Dr. Arieh Karger (Radiation Monitoring Devices)

Dr. Alf Bjørseth (Scanwafer)

Dr. Tom Mates (UCSB)

Dr. John Chervinsky (Harvard University)

Prof. Cynthia Friend (Harvard University)

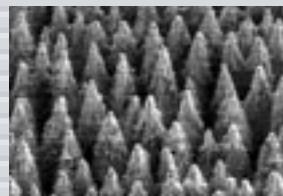
Prof. Mike Aziz (Harvard University)

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

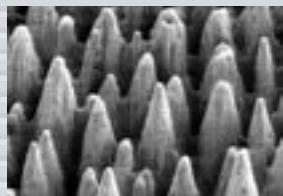
<http://mazur-www.harvard.edu>

Materials

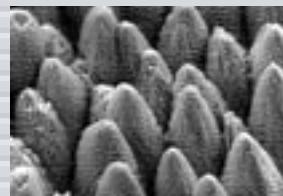
SF₆



Cl₂



N₂

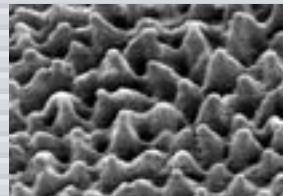


air



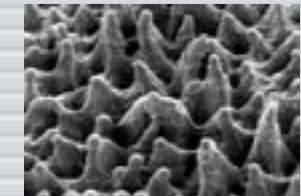
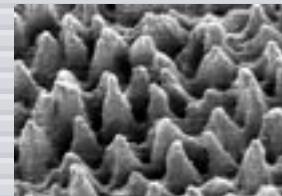
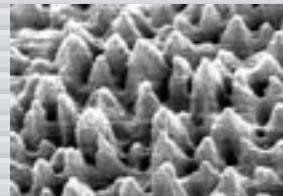
vacuum

Si

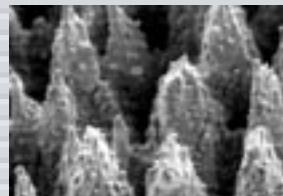


Ti

reacts



Only in SF₆:



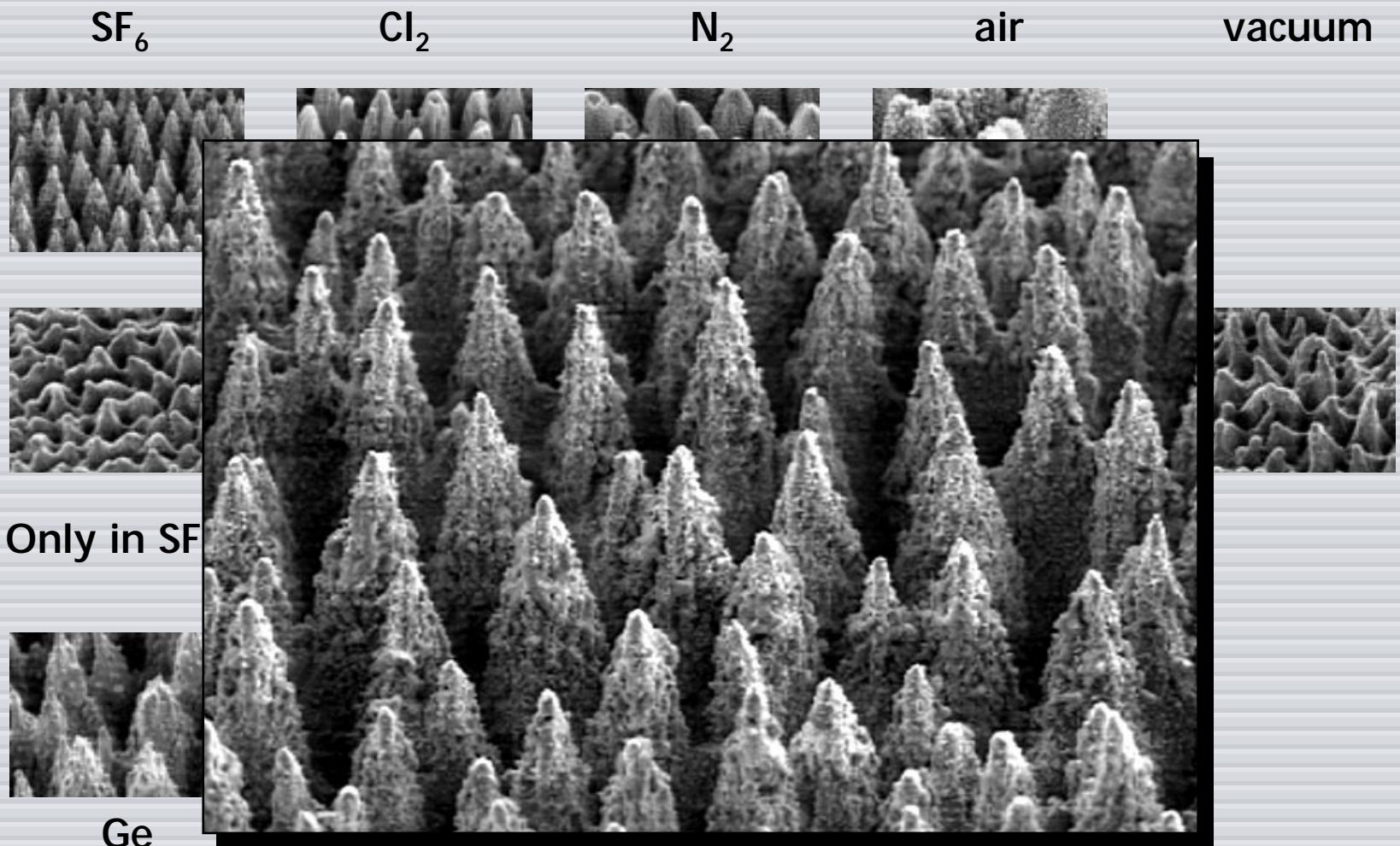
Ge



InP

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

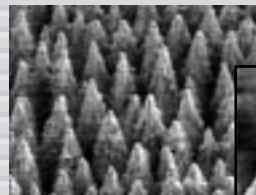
Materials



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

Materials

SF₆



Cl₂



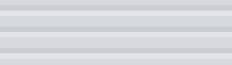
N₂



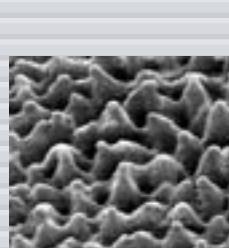
air



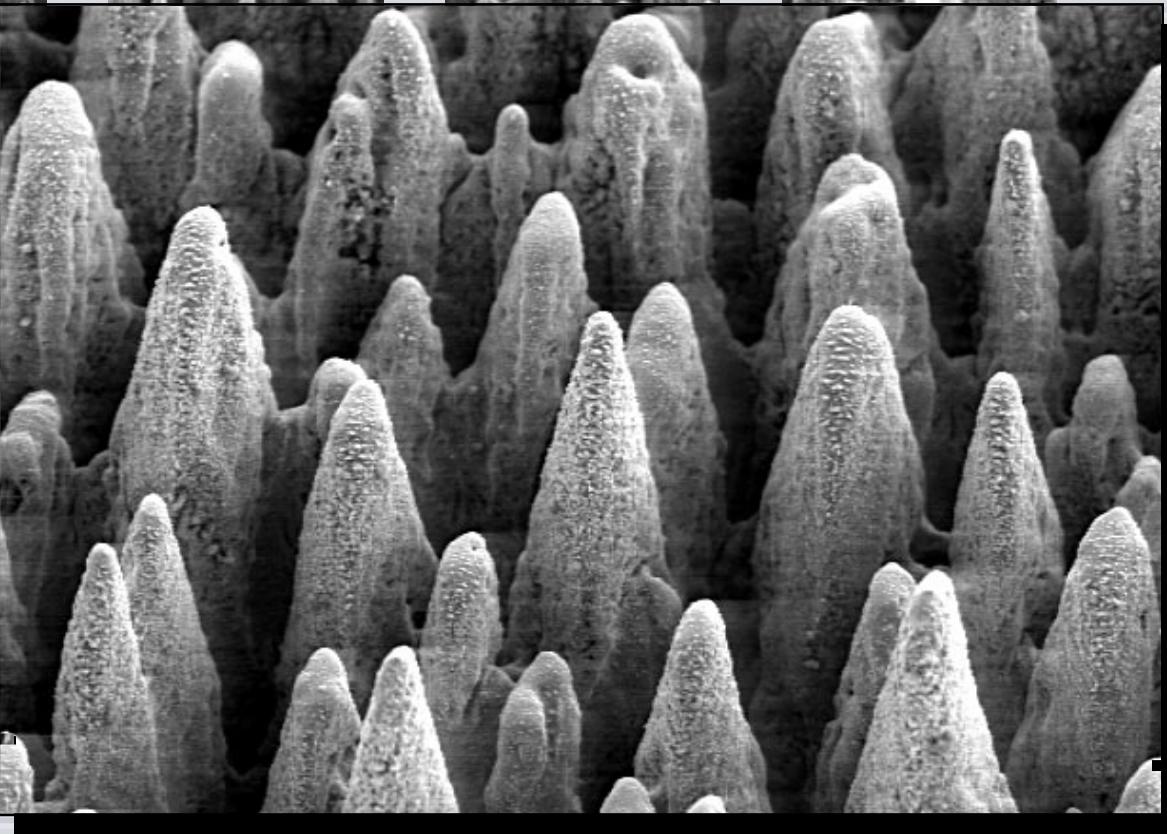
vacuum



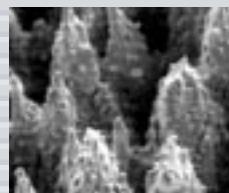
Si



Ti



Only in SF₆

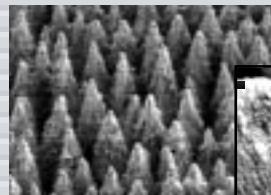


Ge

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

Materials

SF₆



Cl₂



N₂

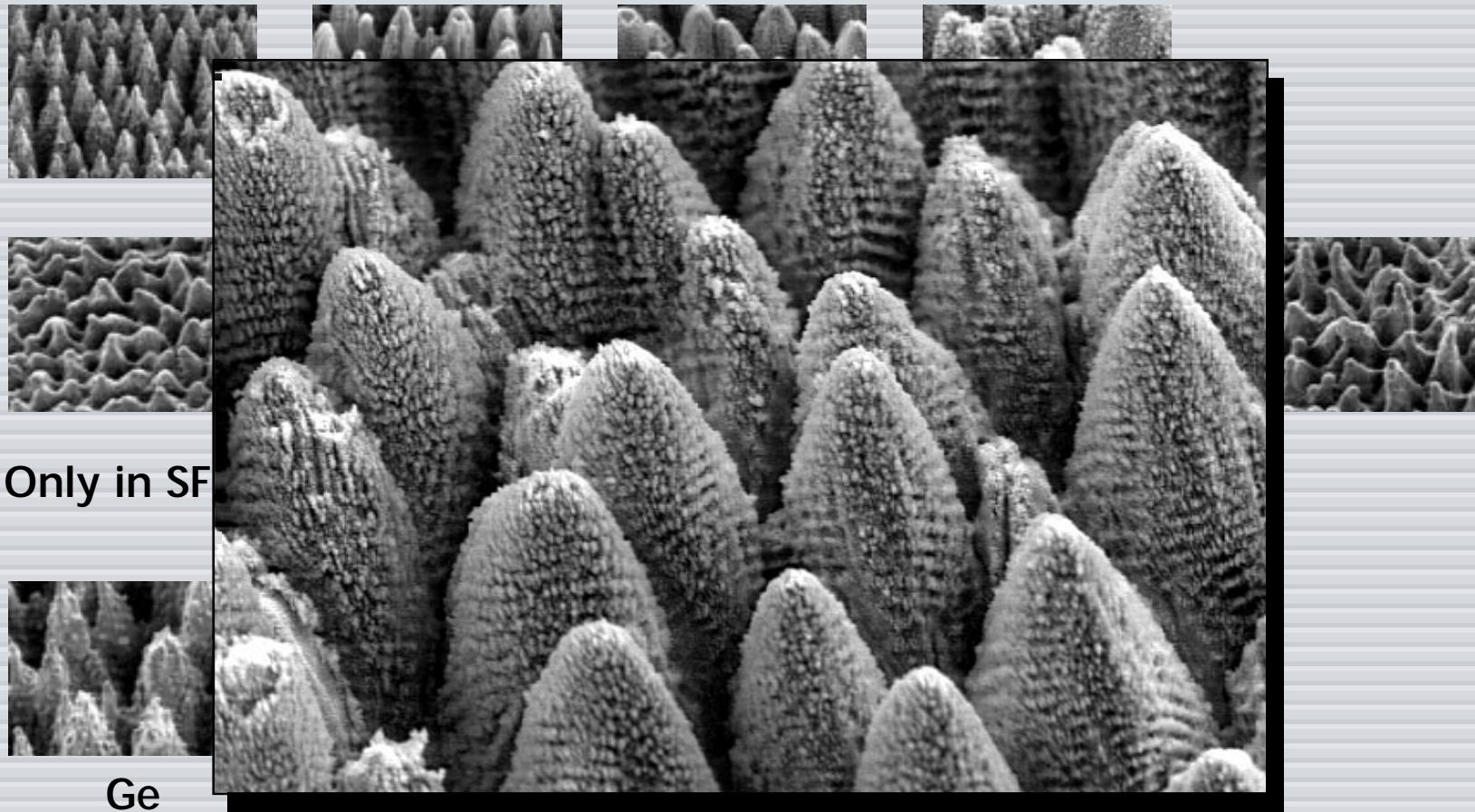


air

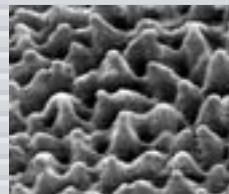


vacuum

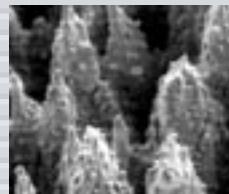
Si



Ti



Only in SF₆

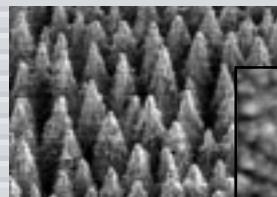


Ge

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

Materials

SF₆



Cl₂



N₂



air

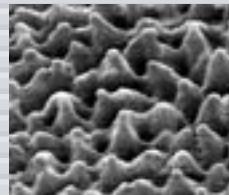


vacuum

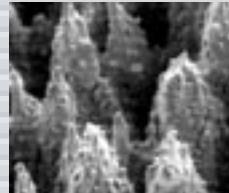
Si



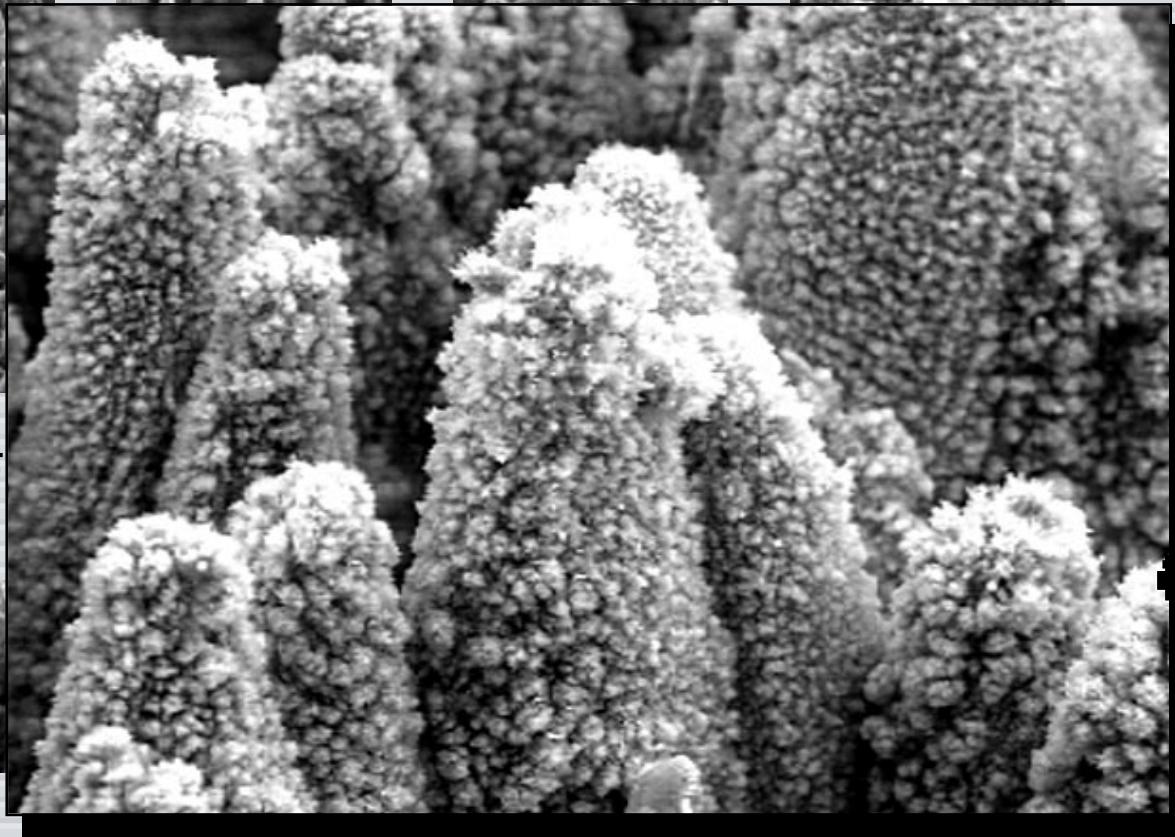
Ti



Only in SF₆



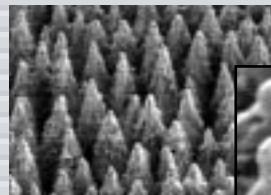
Ge



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

Materials

SF₆



Cl₂



N₂

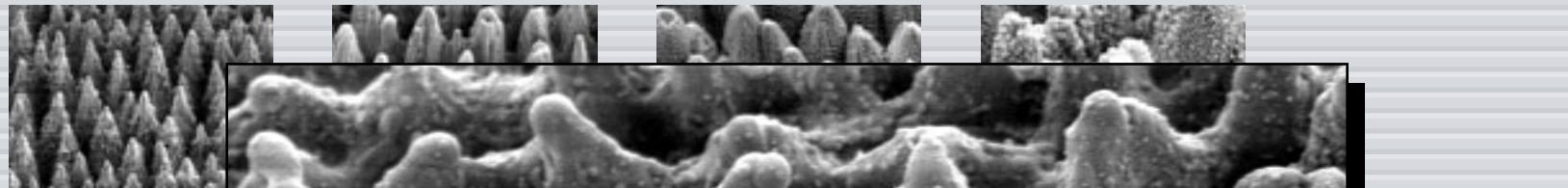


air

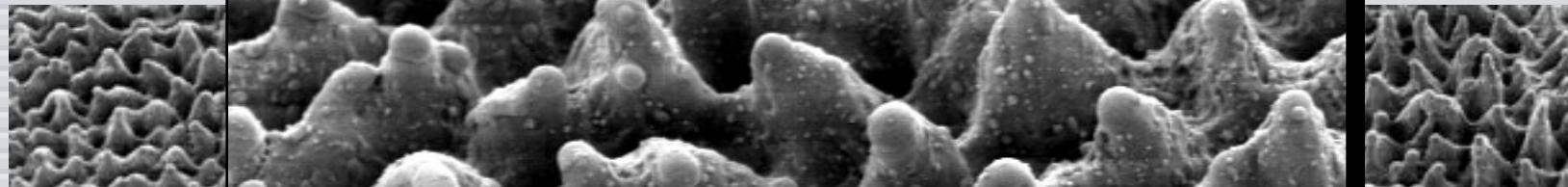


vacuum

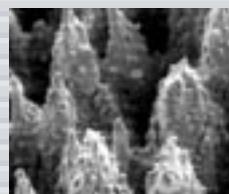
Si



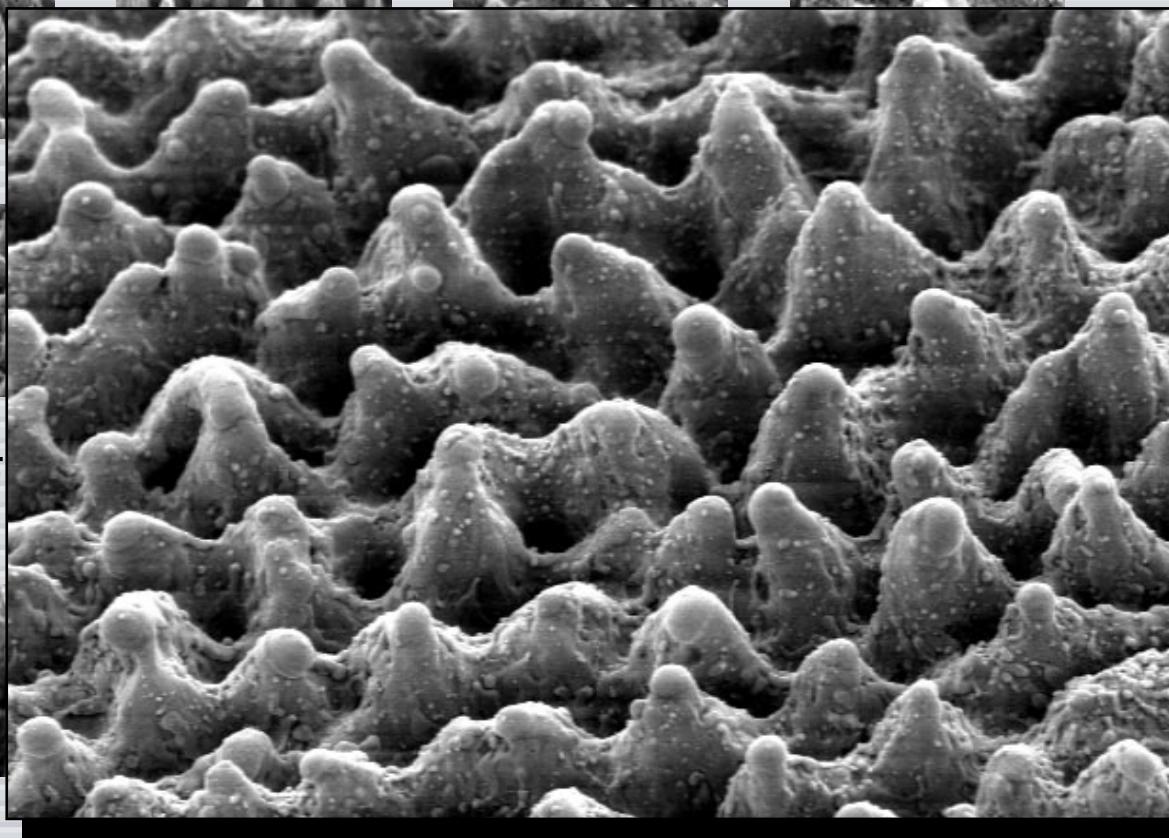
Ti



Only in SF₆

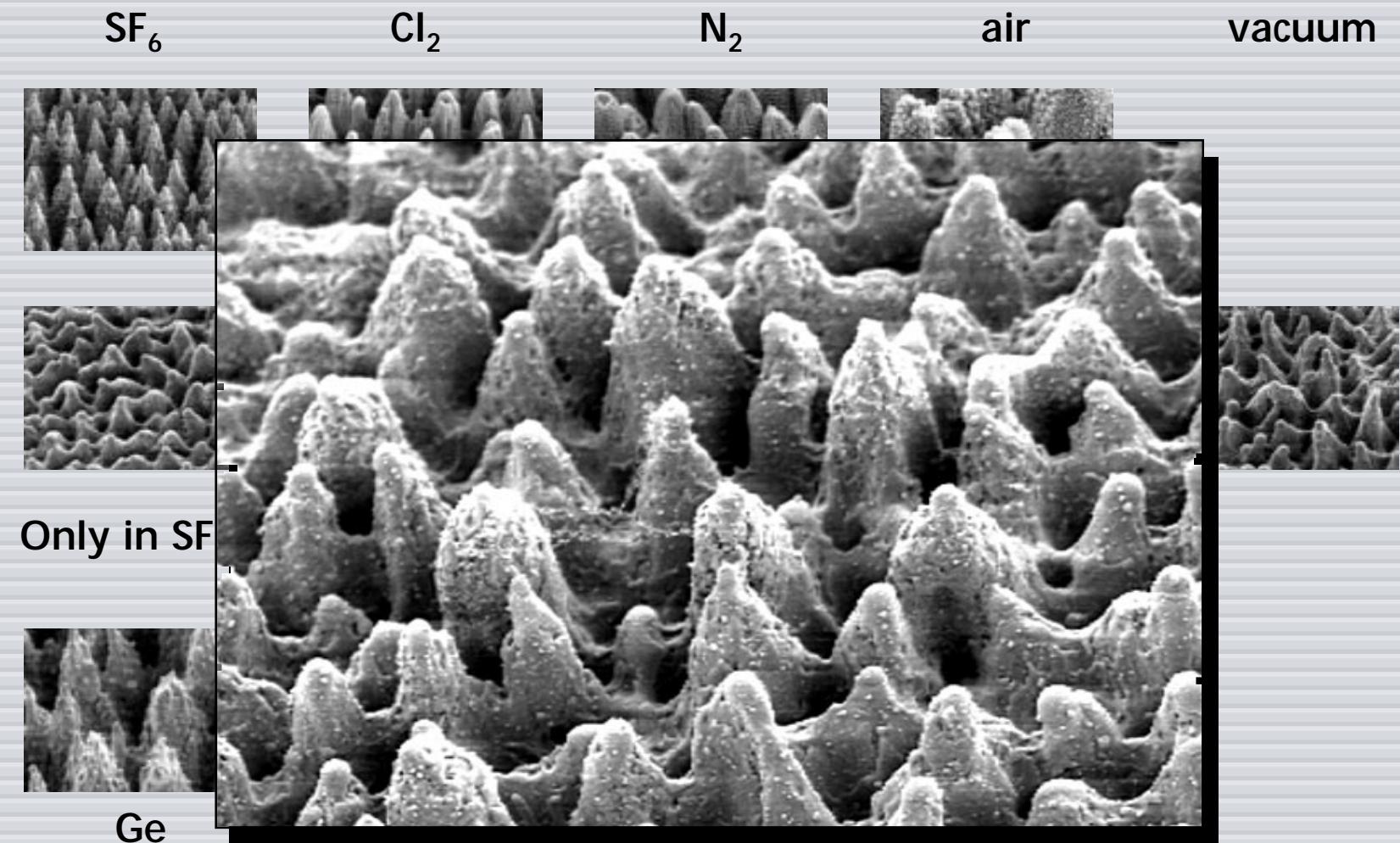


Ge



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

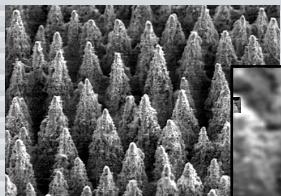
Materials



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

Materials

SF₆



Cl₂



N₂

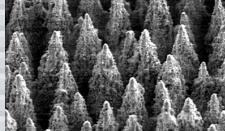


air

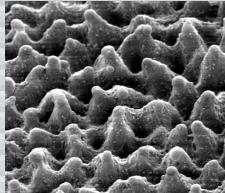


vacuum

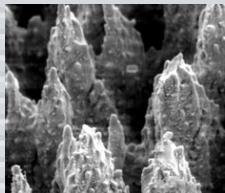
Si



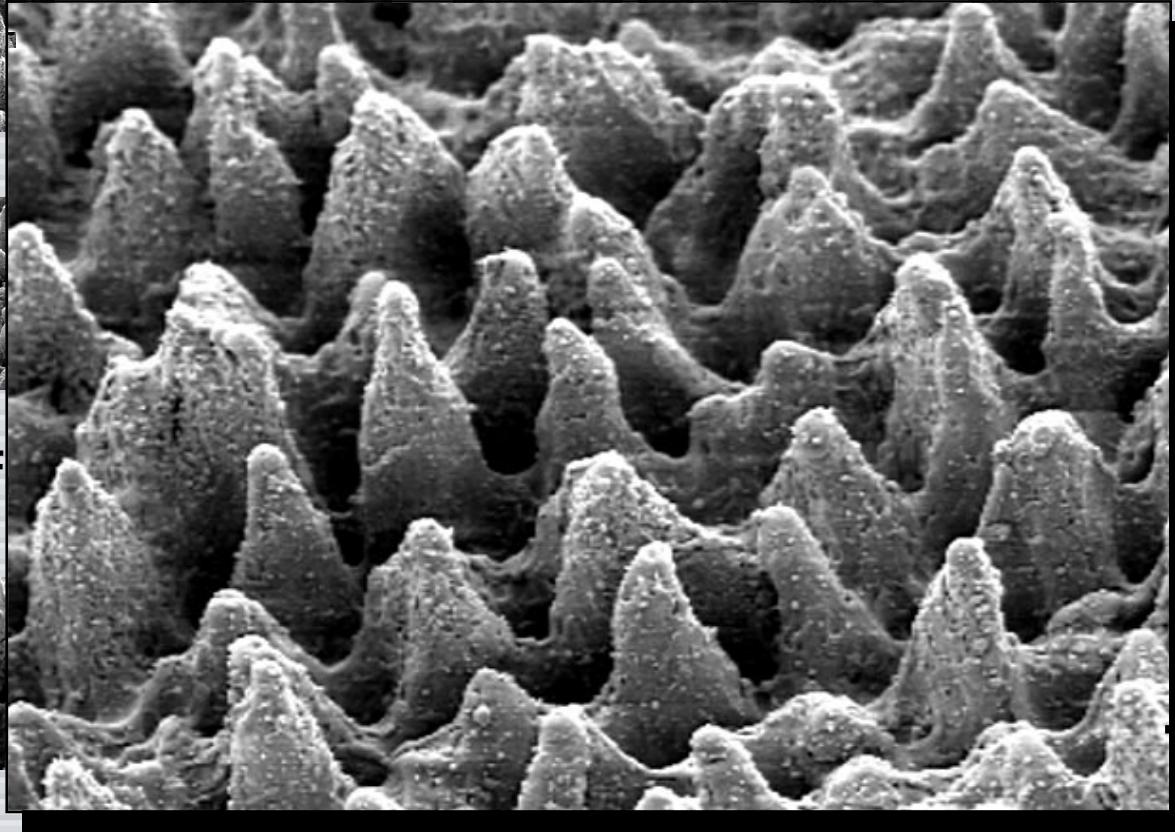
Ti



Only in SF₆



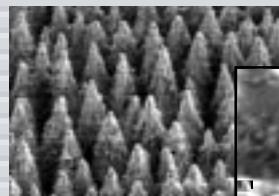
Ge



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

Materials

SF₆



Cl₂



N₂

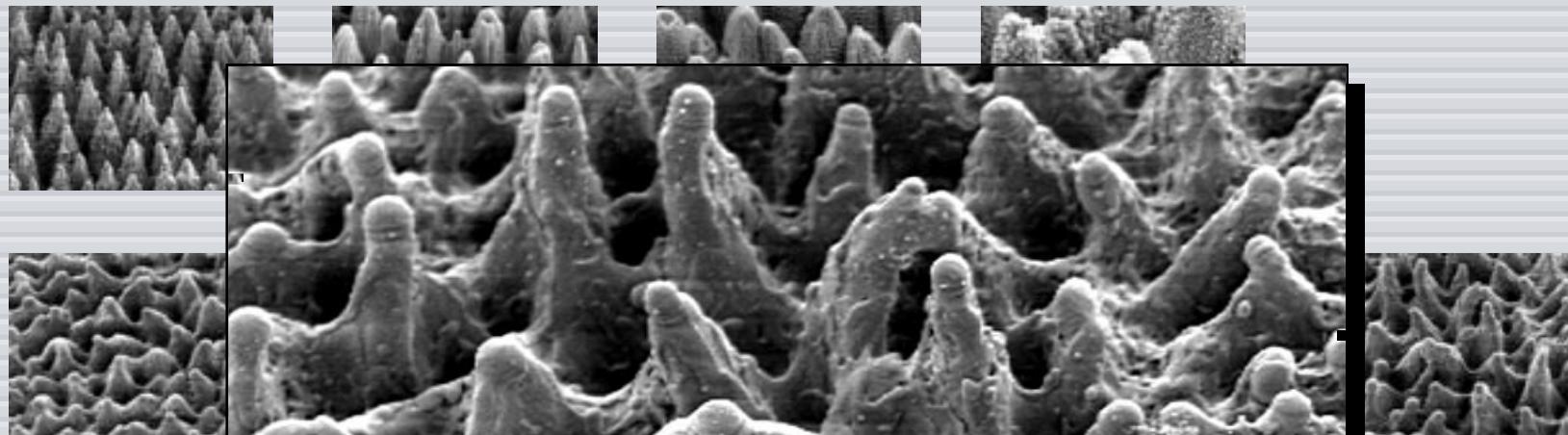


air

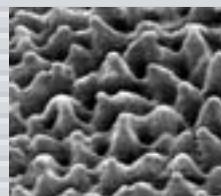


vacuum

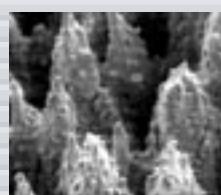
Si



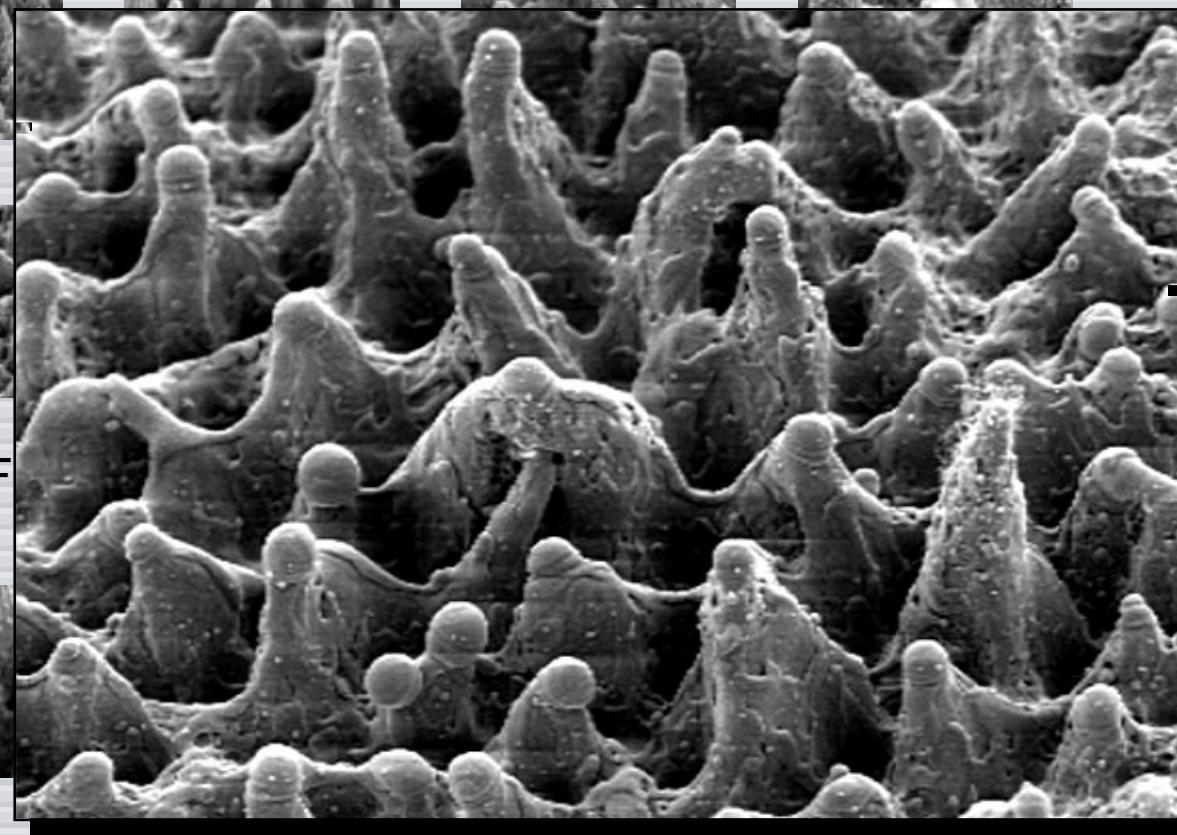
Ti



Only in SF₆



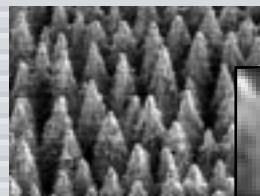
Ge



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

Materials

SF₆



Cl₂



N₂

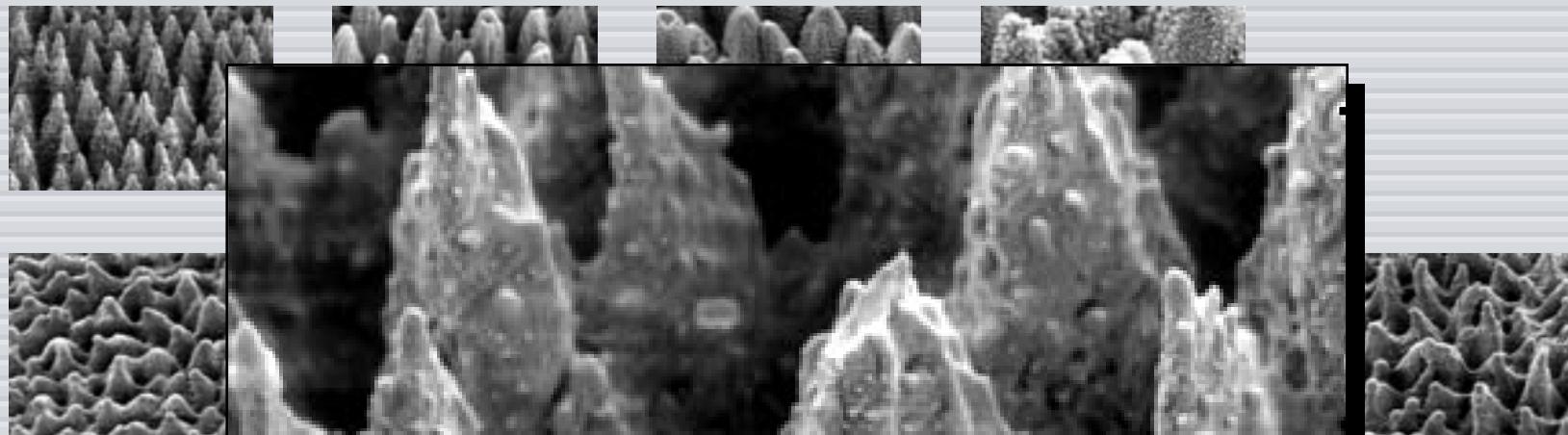


air

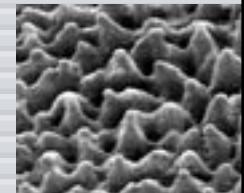


vacuum

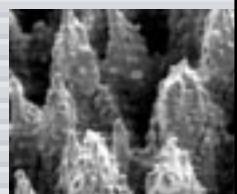
Si



Ti



Only in SF₆

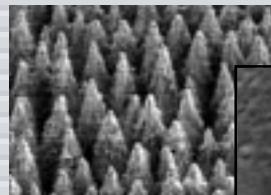


Ge

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

Materials

SF₆



Cl₂



N₂

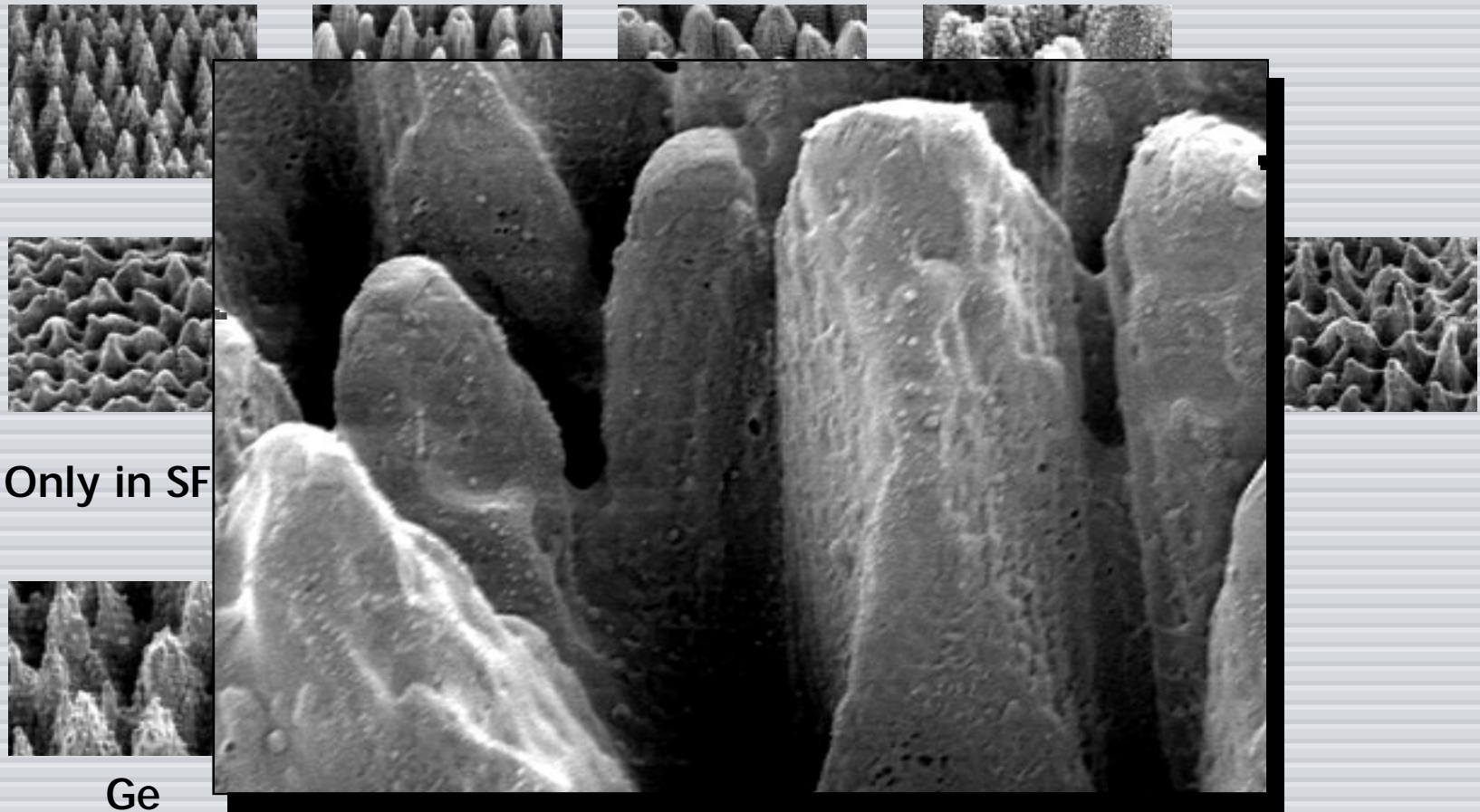


air

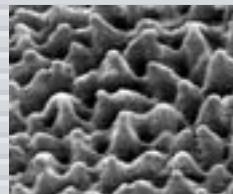


vacuum

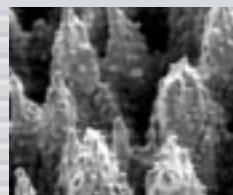
Si



Ti



Only in SF₆



Ge

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