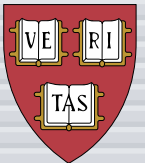
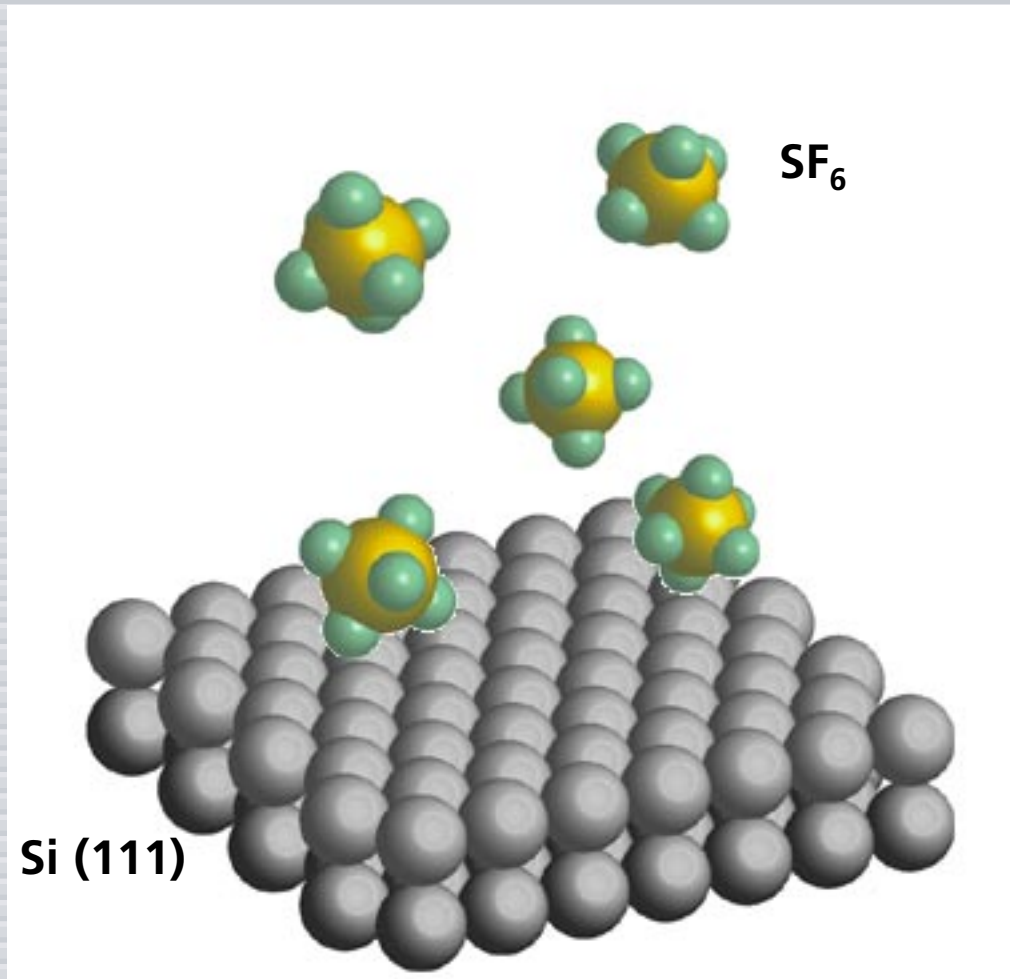


Femtosecond laser-assisted microstructuring of silicon for novel detector, sensing, and display technologies

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

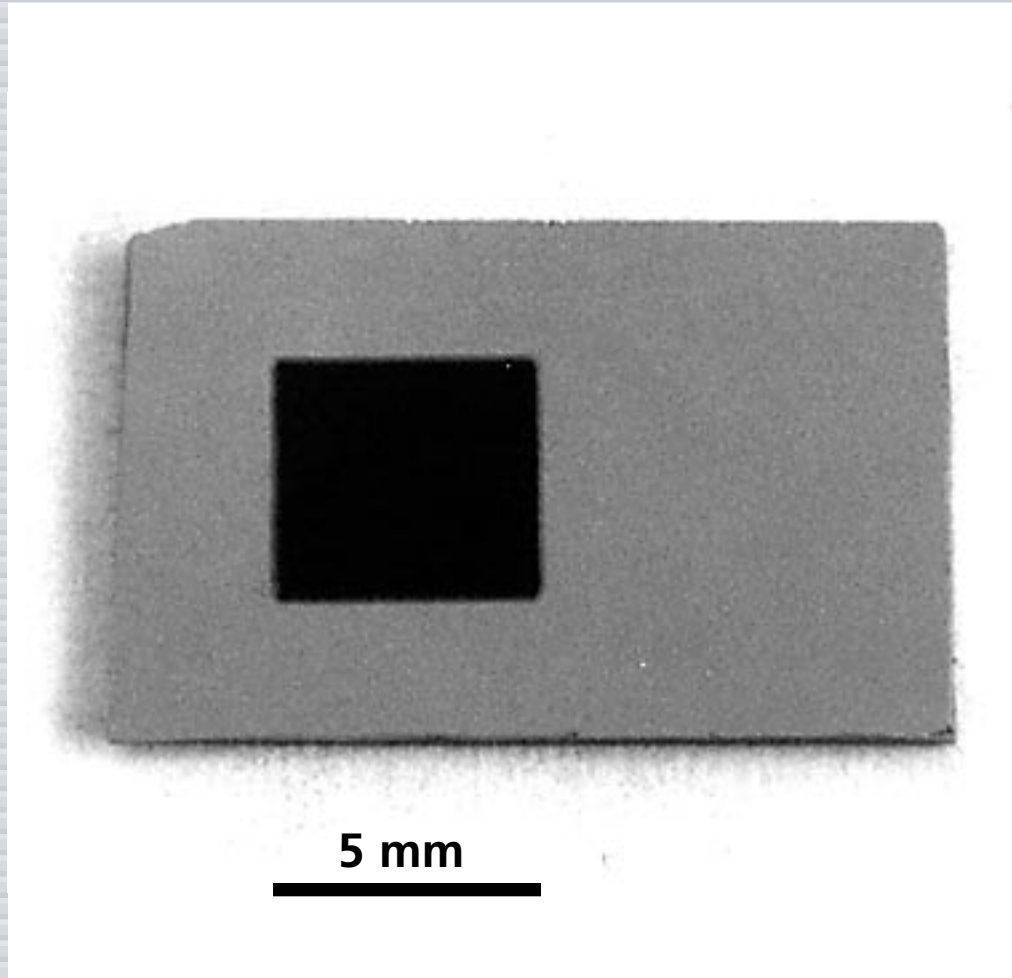


Introduction



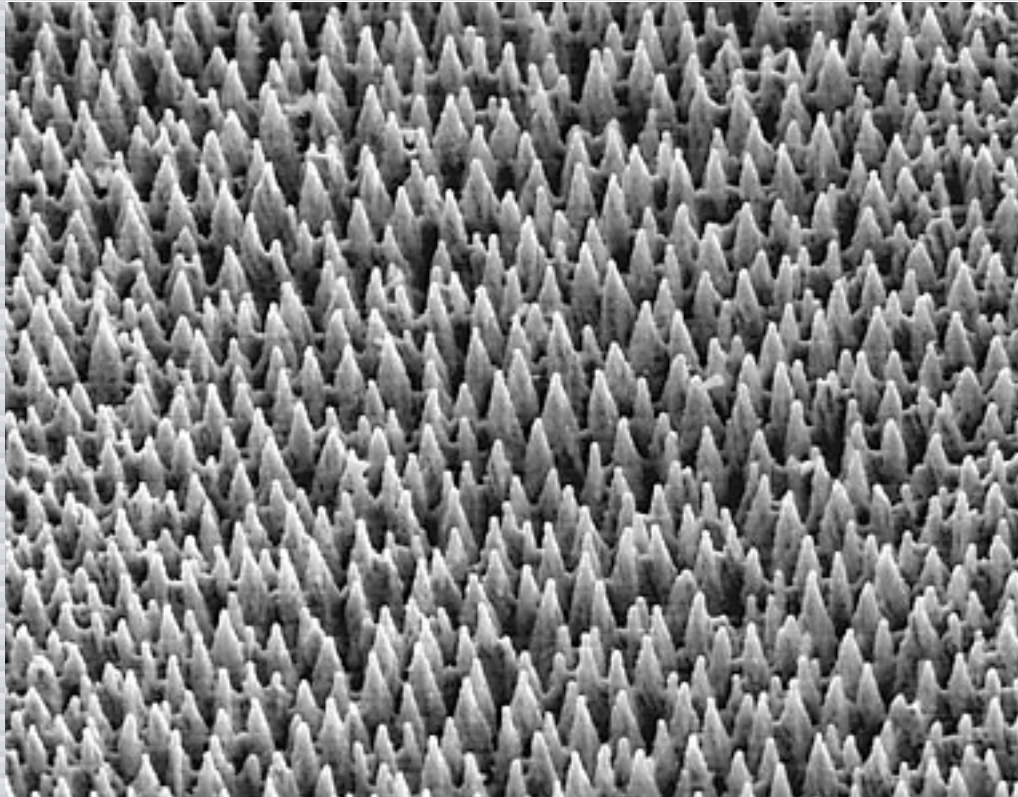
irradiate with 100-fs 10 kJ/m^2 pulses

Introduction



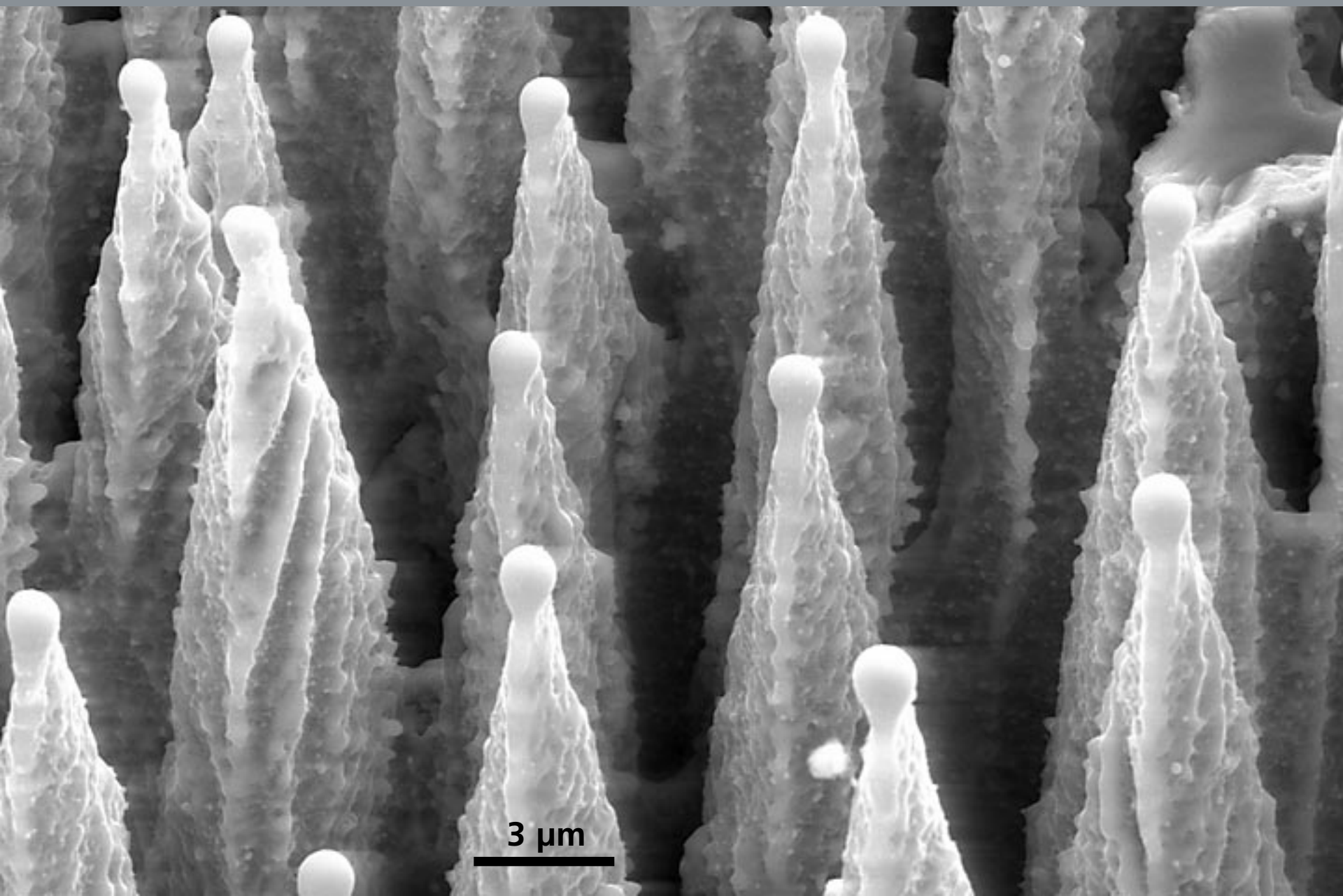
"black silicon"

Introduction

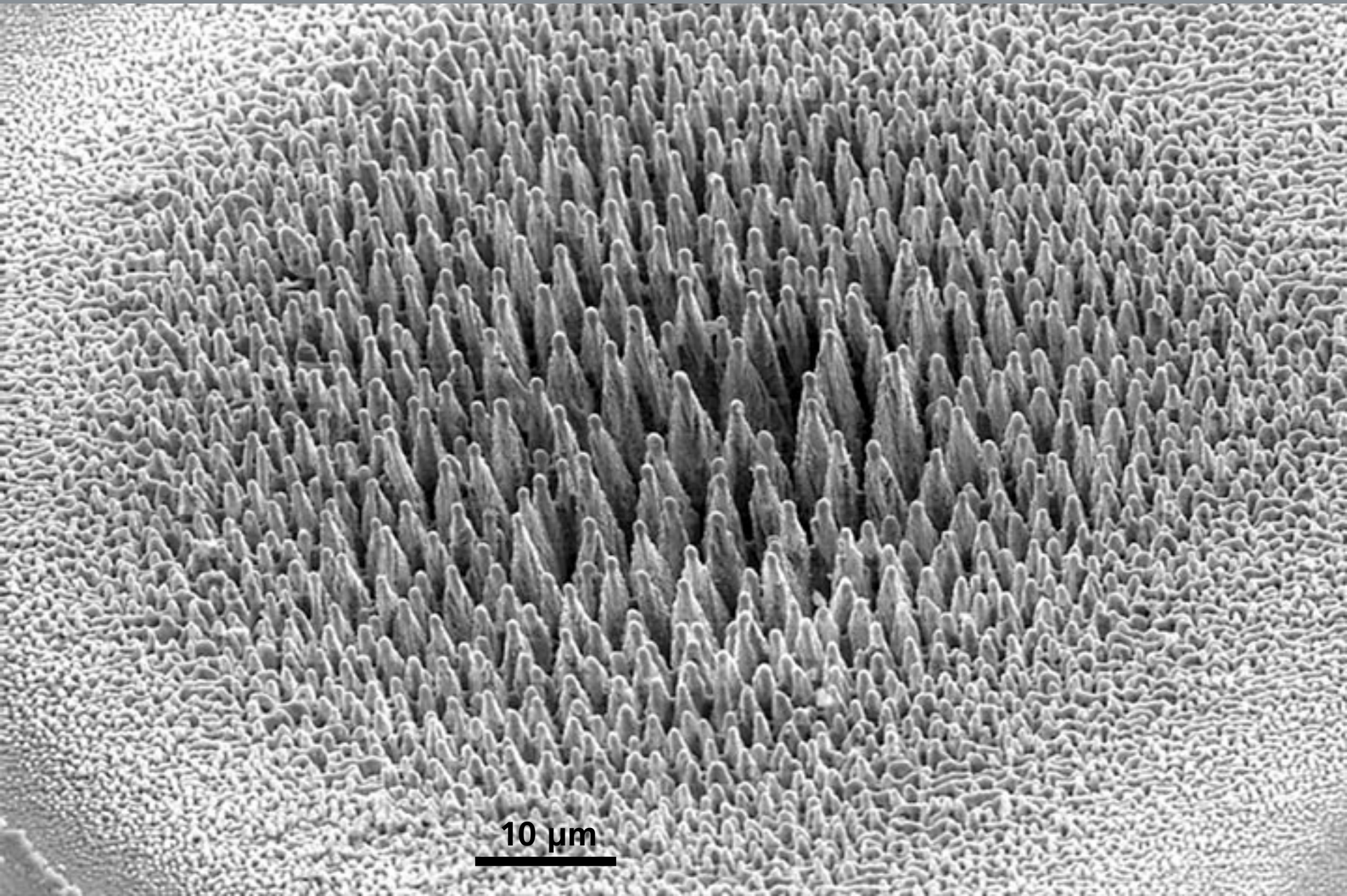


20 μm

Introduction

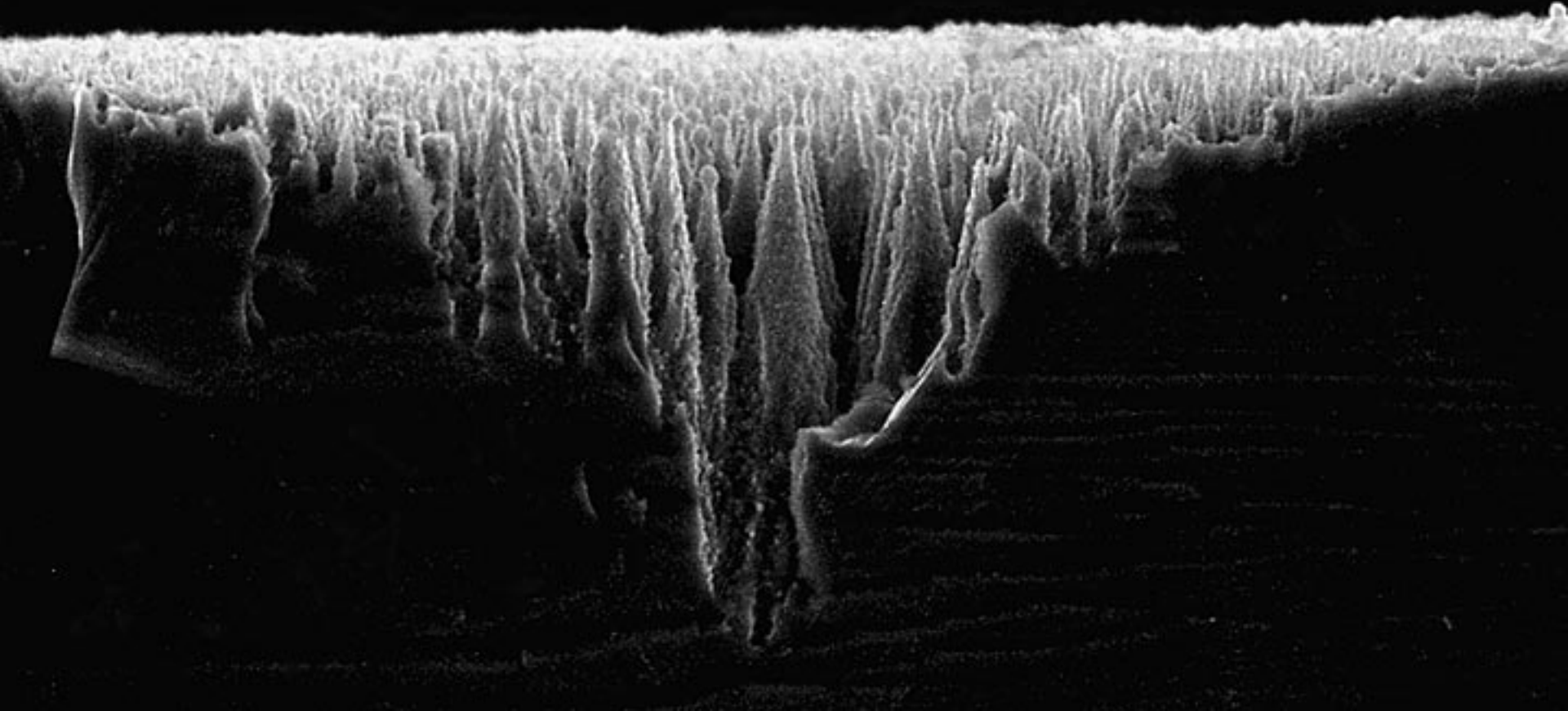


Introduction



10 μm

Introduction



Introduction

Introduction

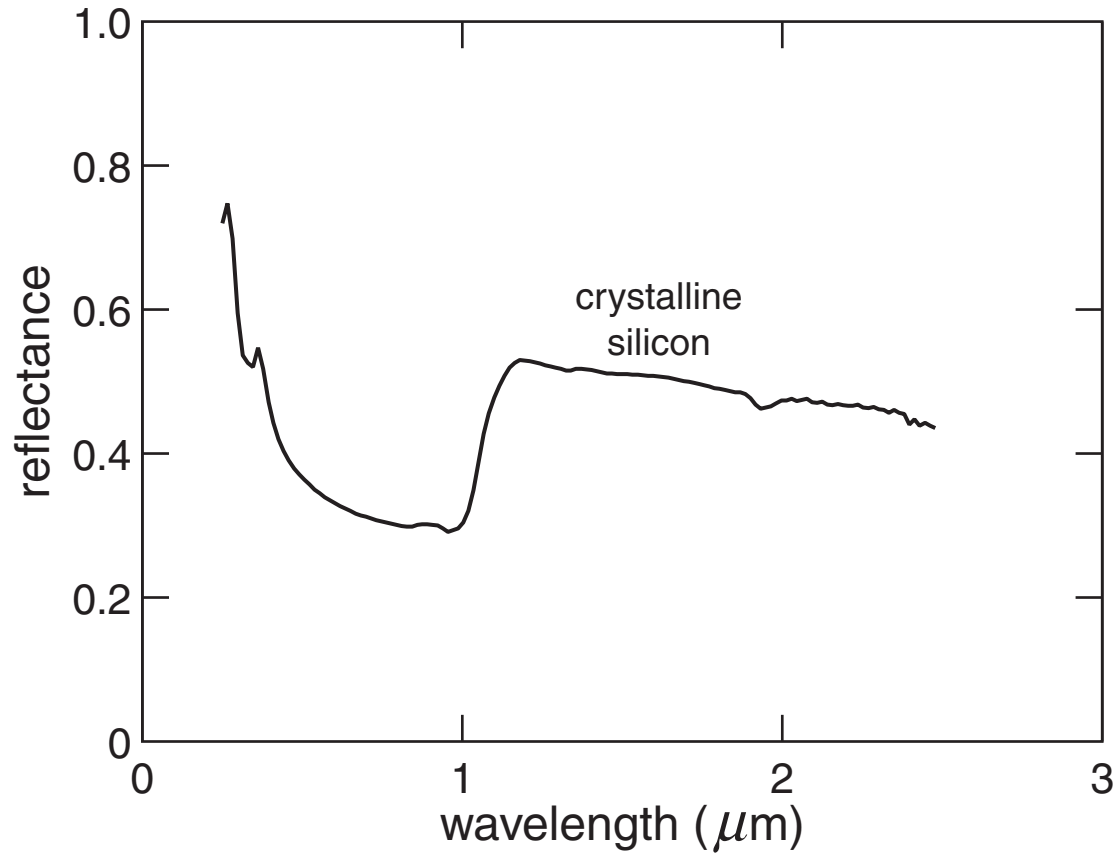
- ▶ **maskless etching process**
- ▶ **self-organized, tall, sharp structures**
- ▶ **nanoscale structure on spikes**

Outline

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

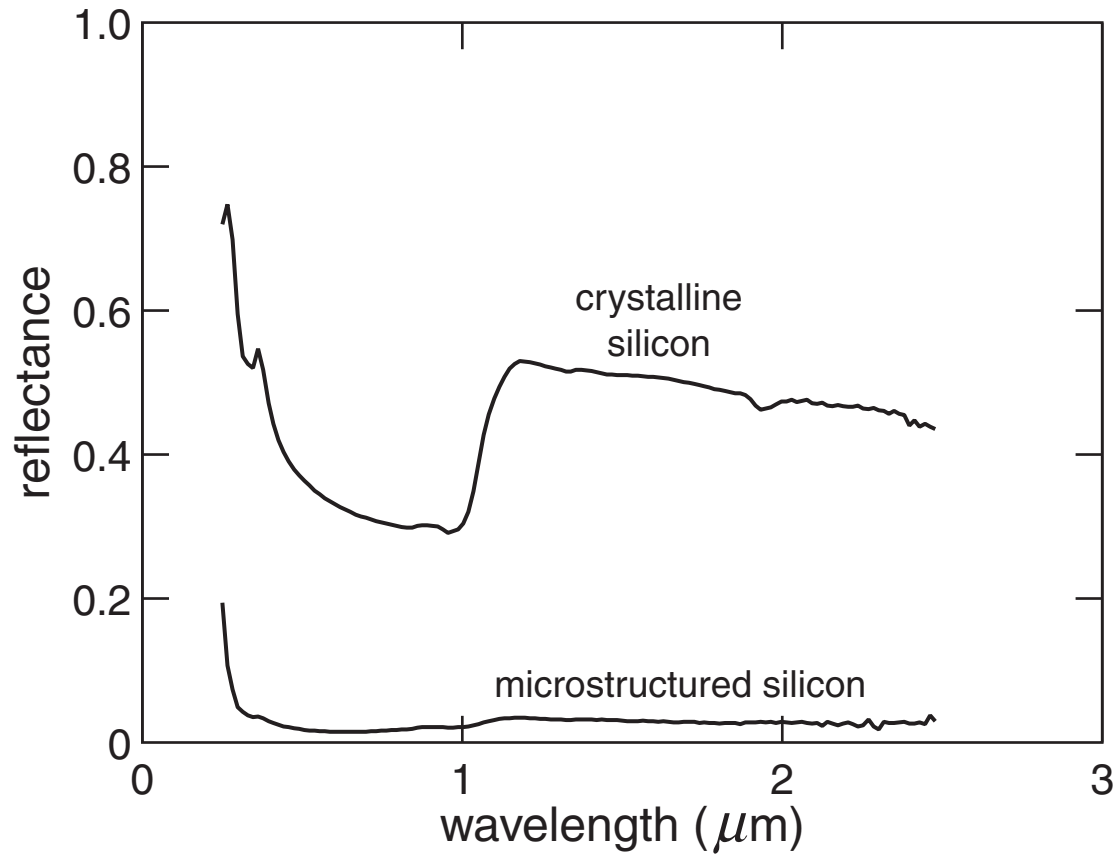
Properties

reflectance (integrating sphere)



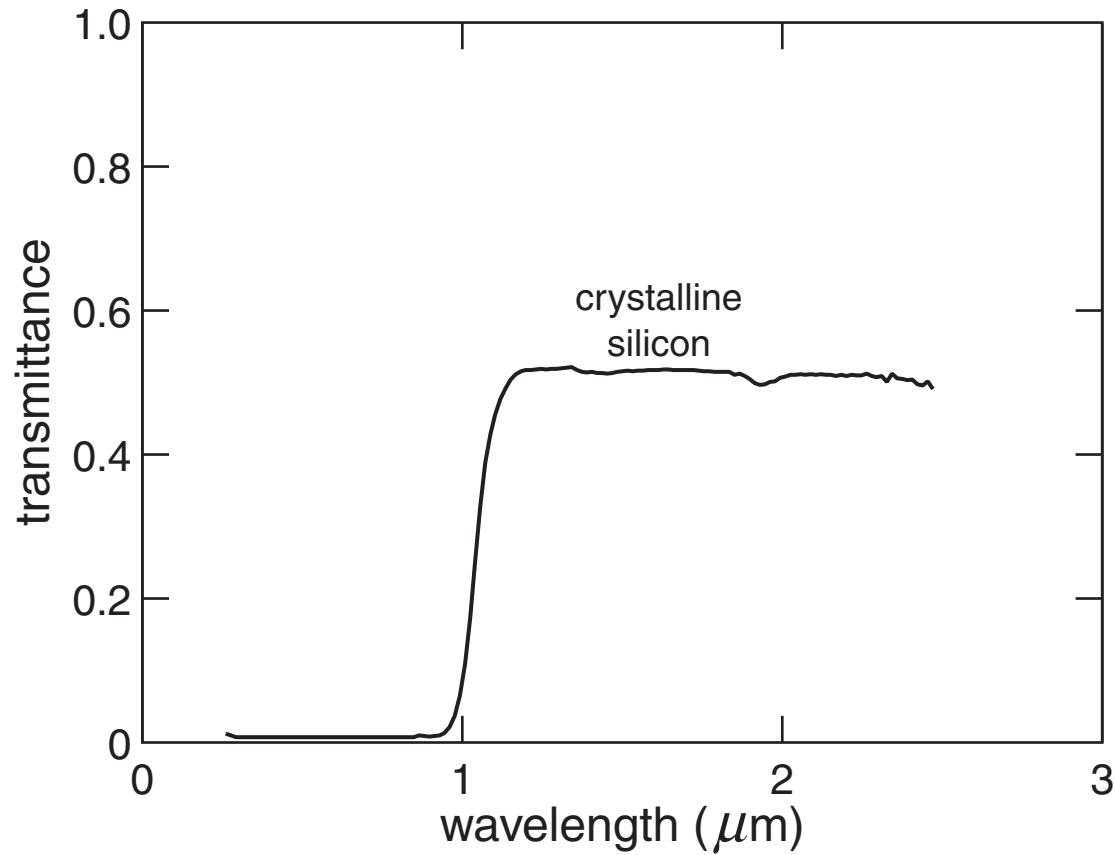
Properties

reflectance (integrating sphere)



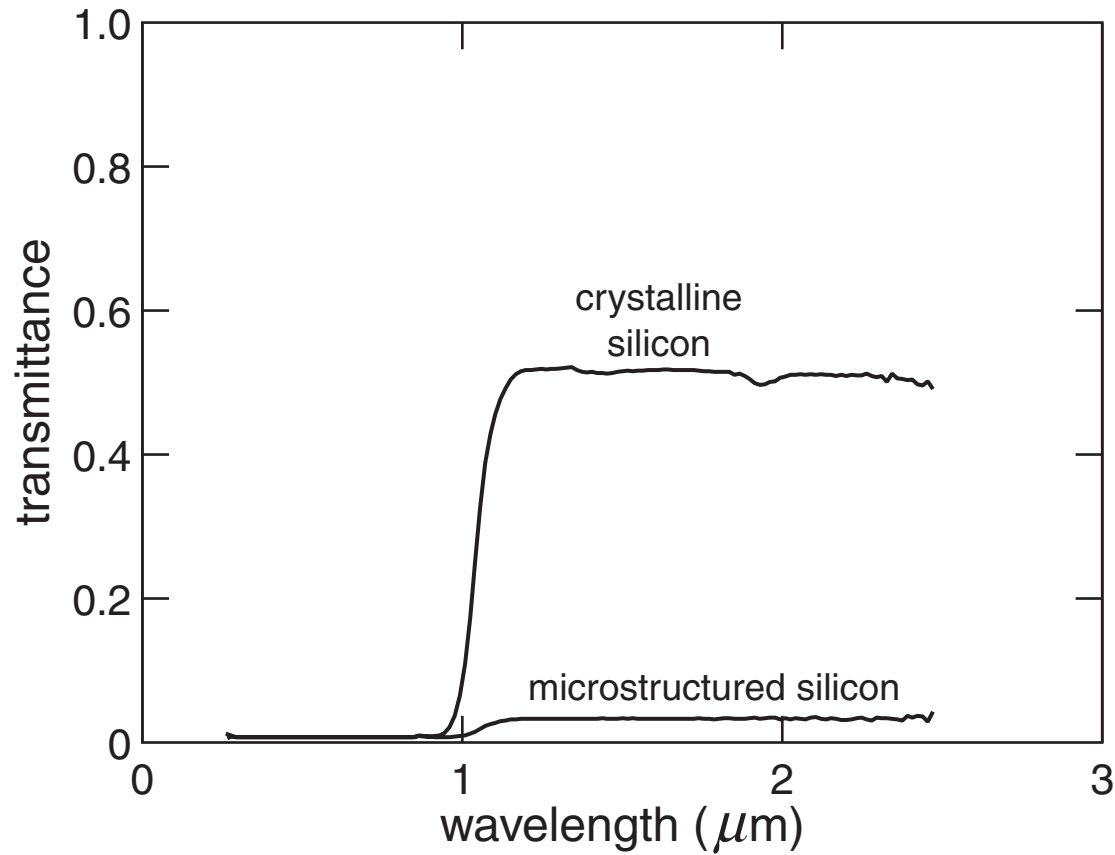
Properties

transmittance (integrating sphere)



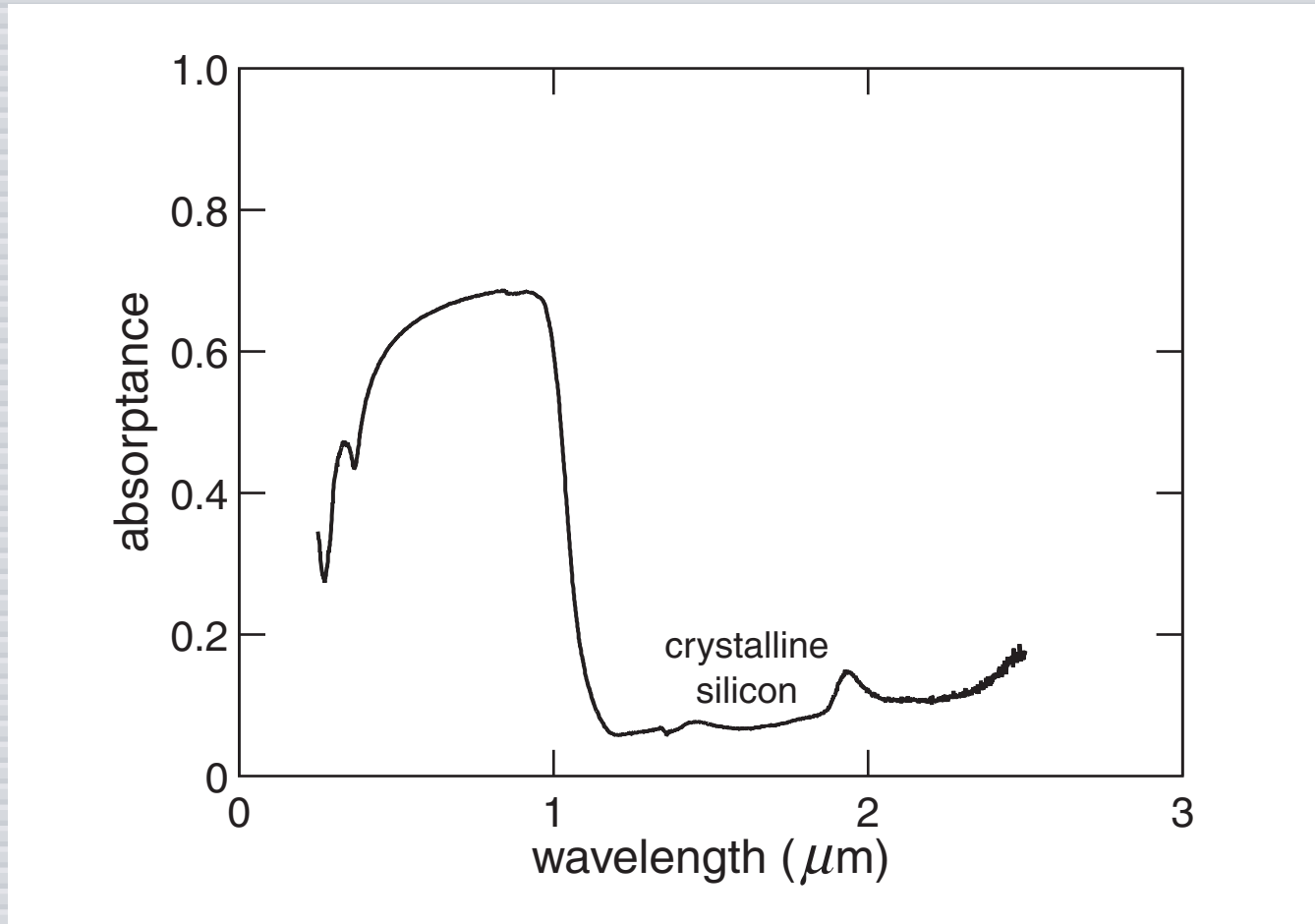
Properties

transmittance (integrating sphere)



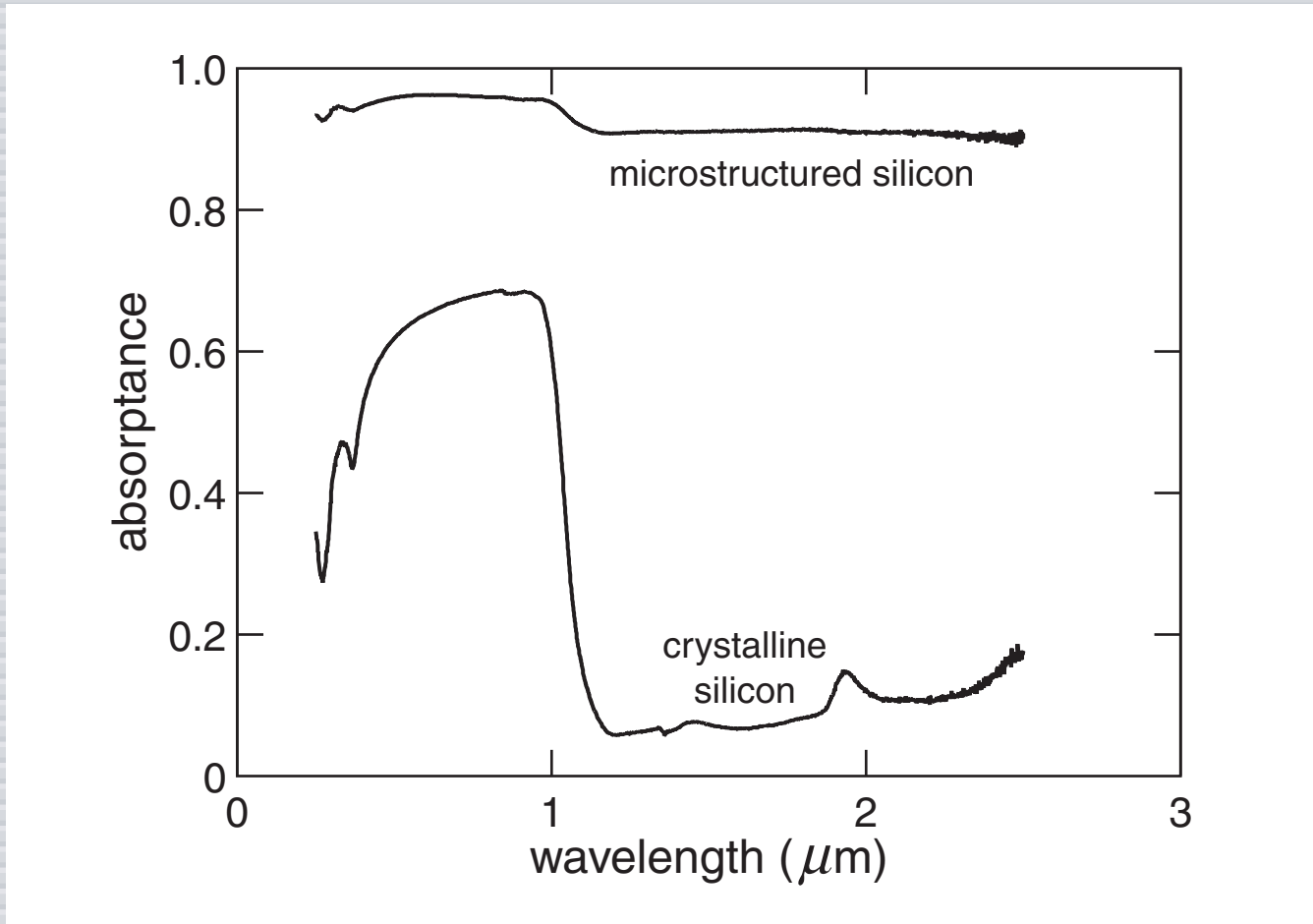
Properties

absorptance ($1 - R - T$)



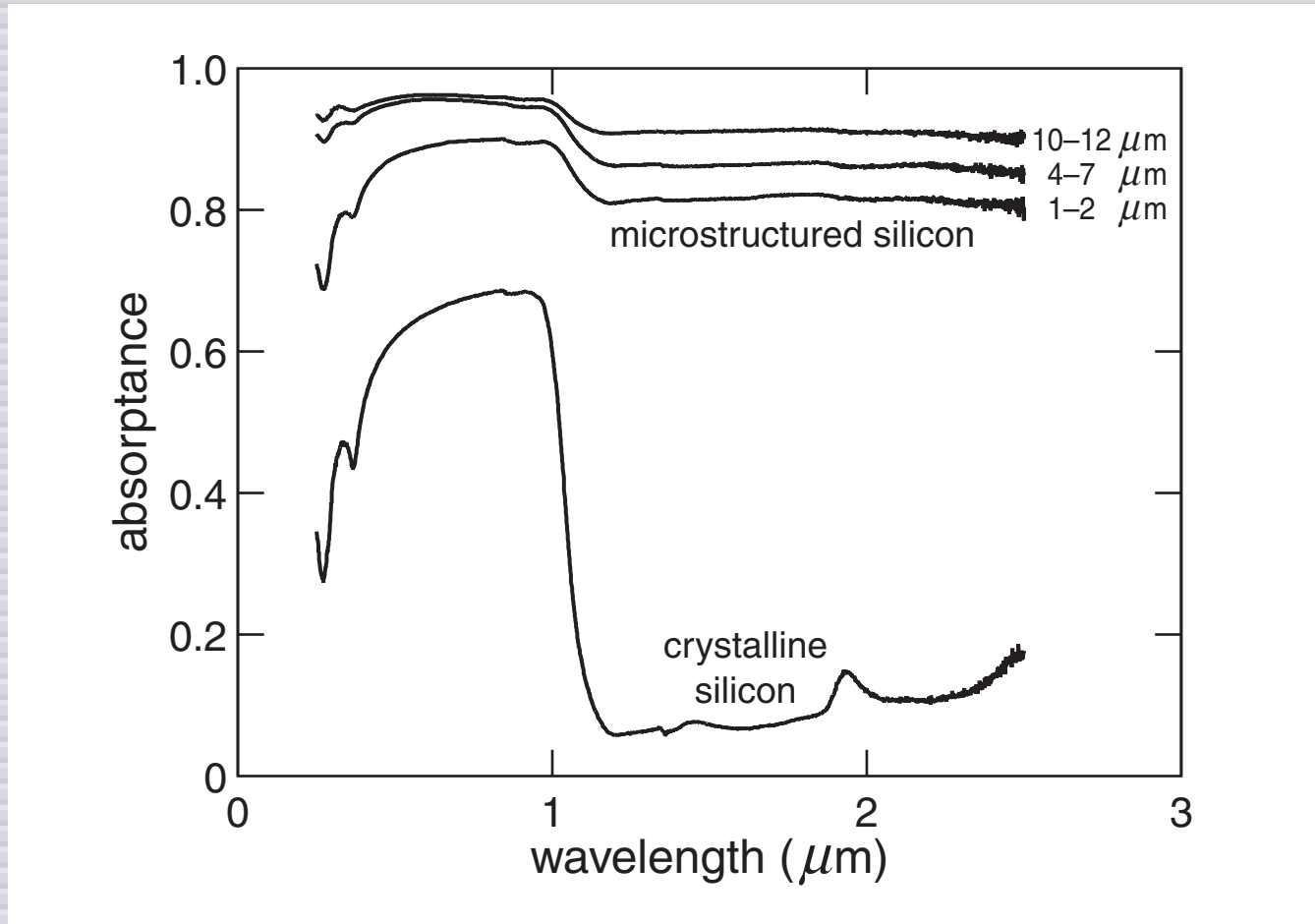
Properties

absorptance ($1 - R - T$)



Properties

absorptance ($1 - R - T$)



Properties

field emission setup



Properties

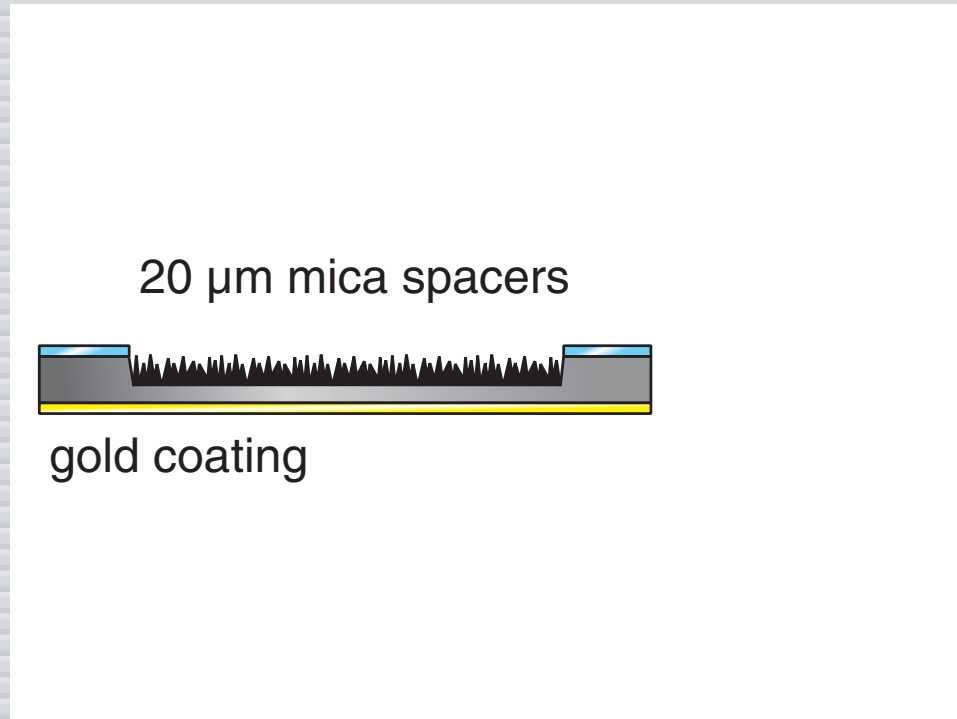
field emission setup



gold coating

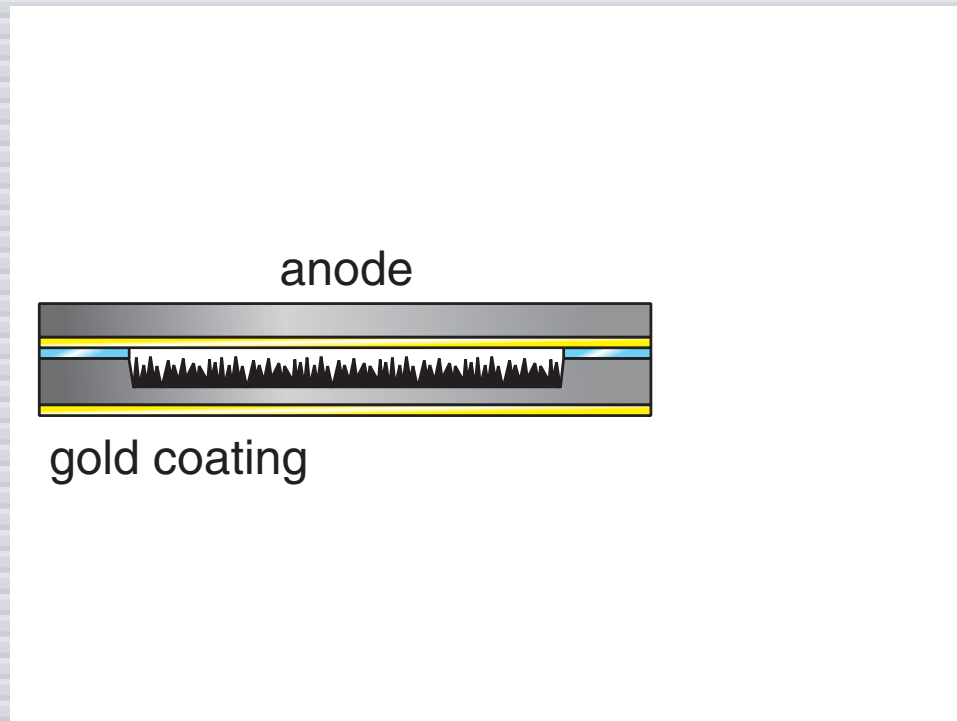
Properties

field emission setup



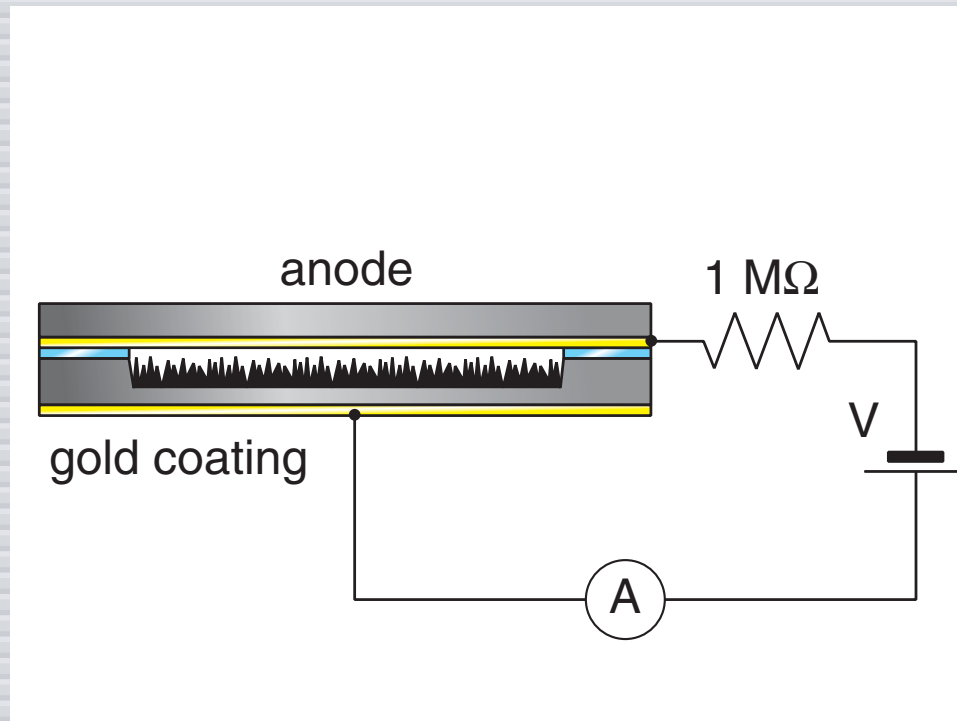
Properties

field emission setup

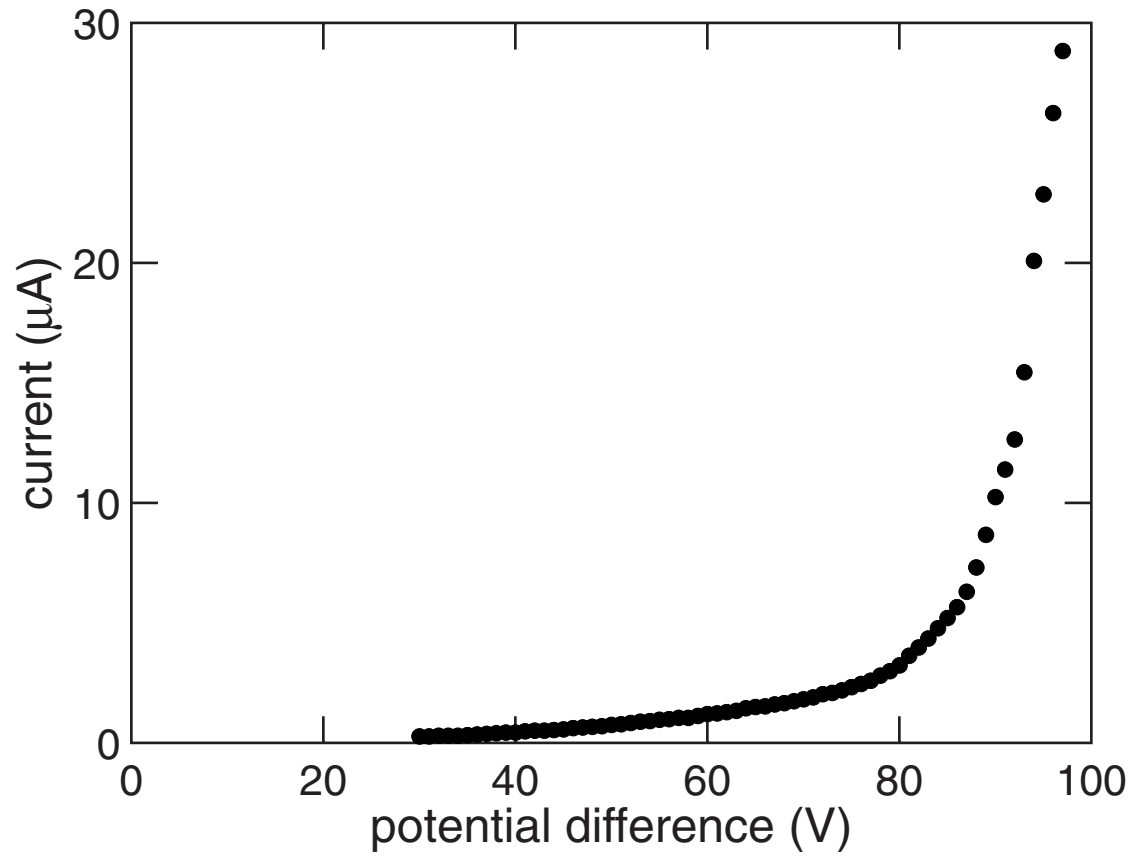


Properties

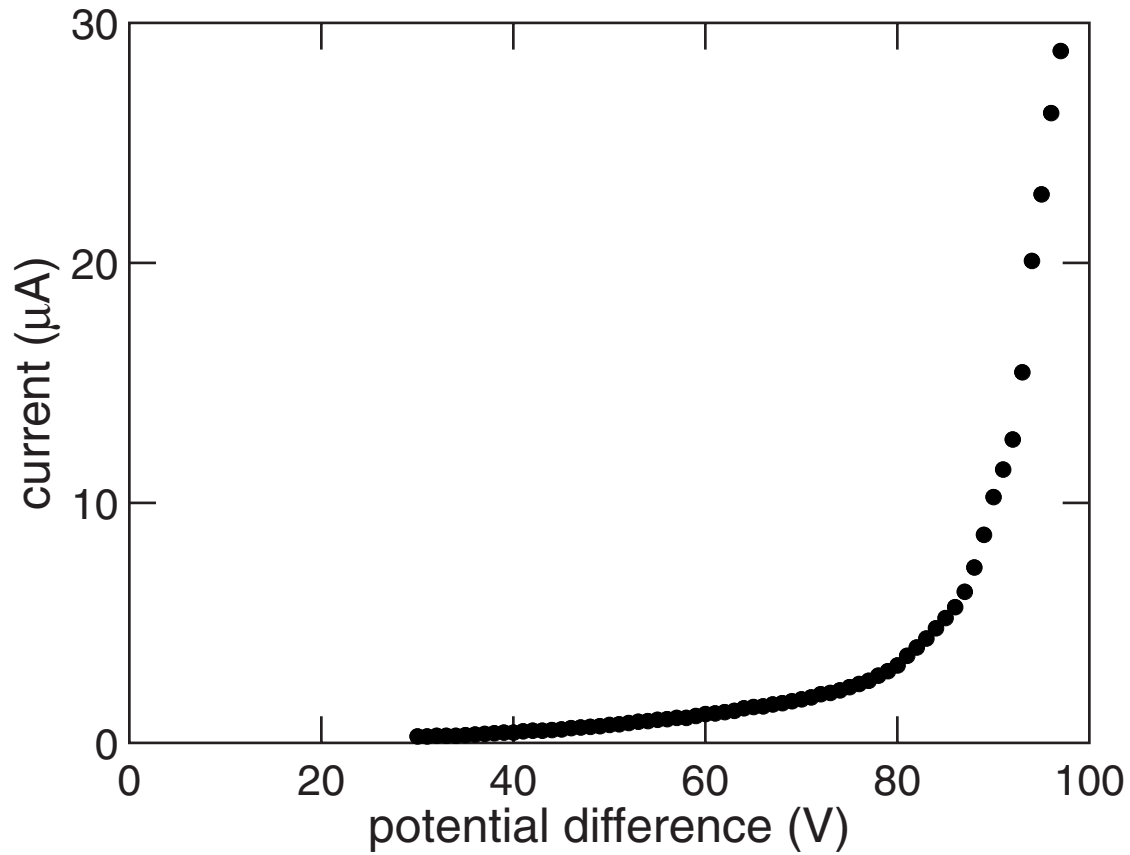
field emission setup



Properties

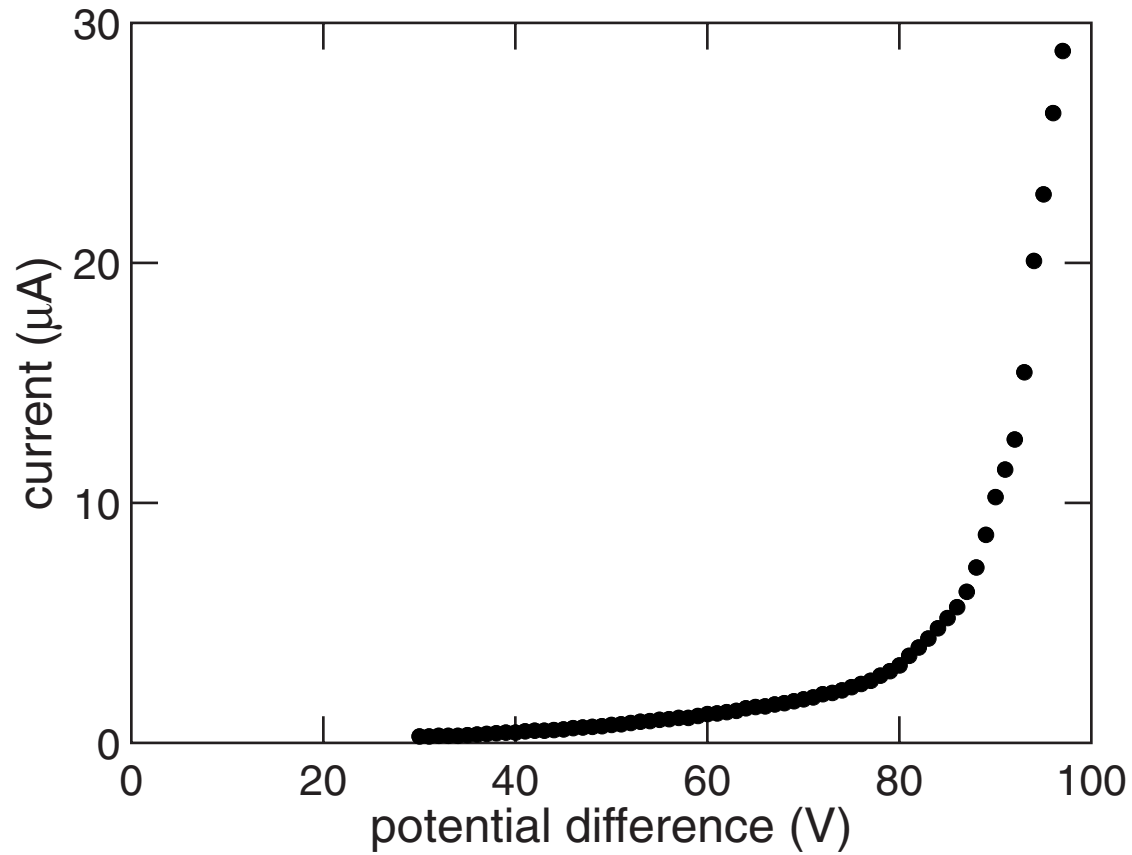


Properties



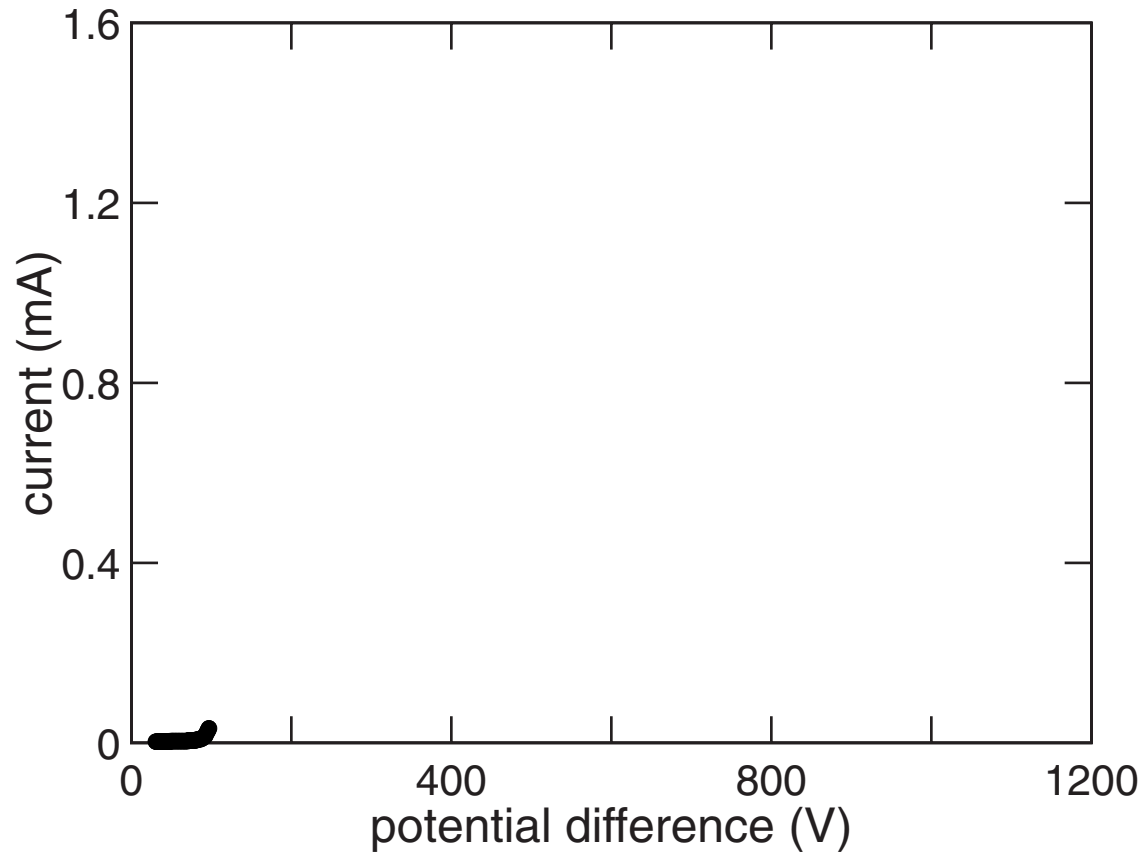
turn-on field ($1 \mu\text{A}/\text{cm}^2$): $1.2 \text{ V}/\mu\text{m}$

Properties

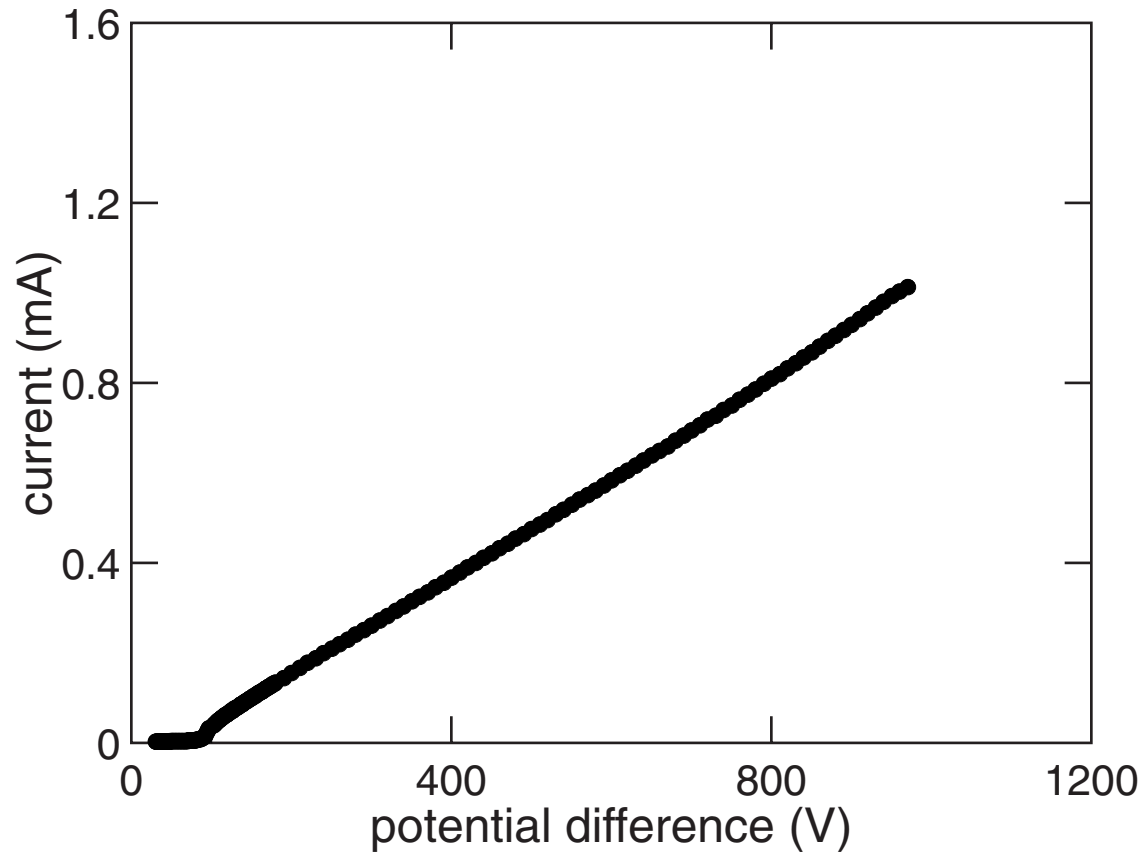


threshold field ($10 \mu\text{A}/\text{cm}^2$): $2.1 \text{ V}/\mu\text{m}$

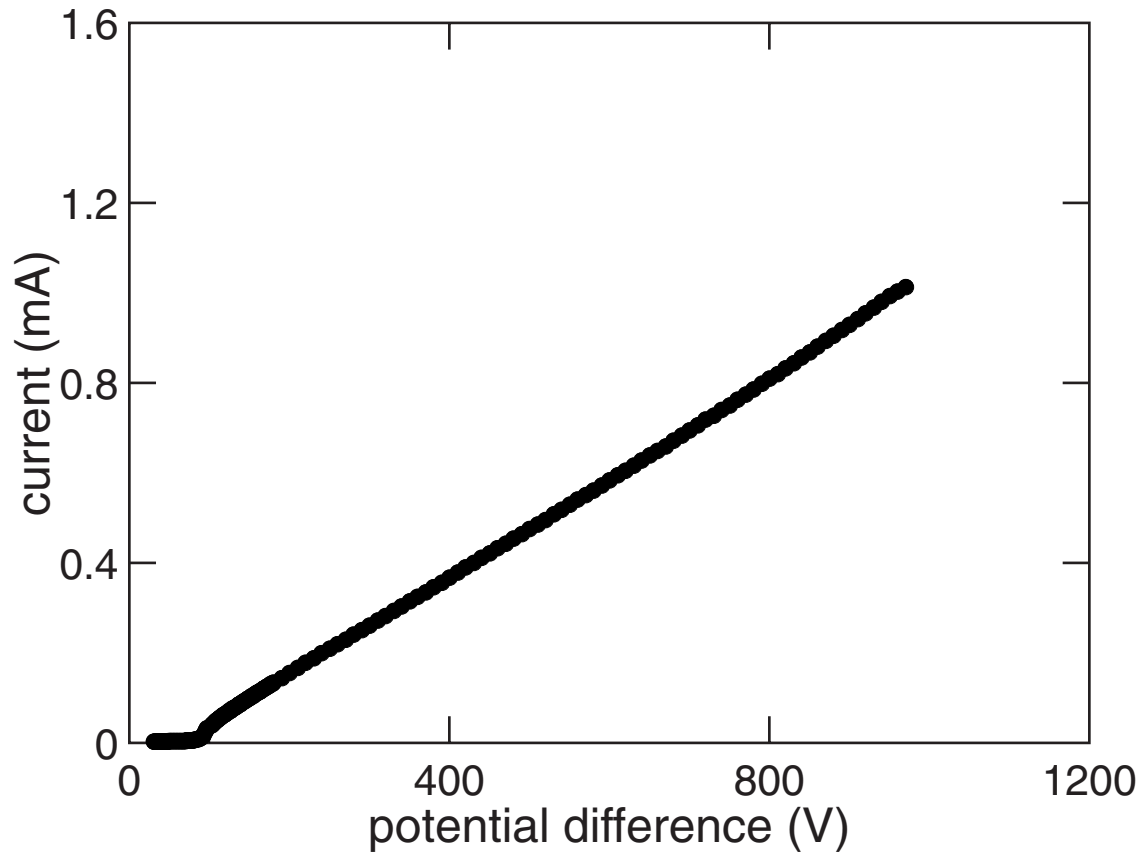
Properties



Properties



Properties



maximum current: 20 mA (4 mm² sample)

Properties

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

Structural and chemical analysis

1 μm

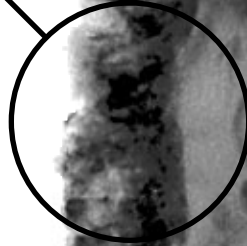


cross-sectional TEM (F. Génin, M. Wall, LLNL)

Structural and chemical analysis

1 μm

porous "fuzz"



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

Structural and chemical analysis

1 μm



nanocrystallites

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

Structural and chemical analysis

1 μm

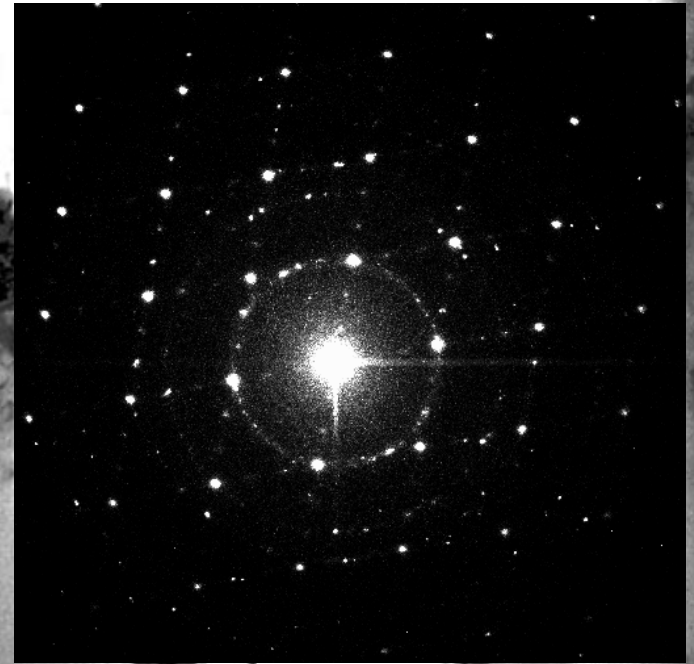


crystalline Si

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

Structural and chemical analysis

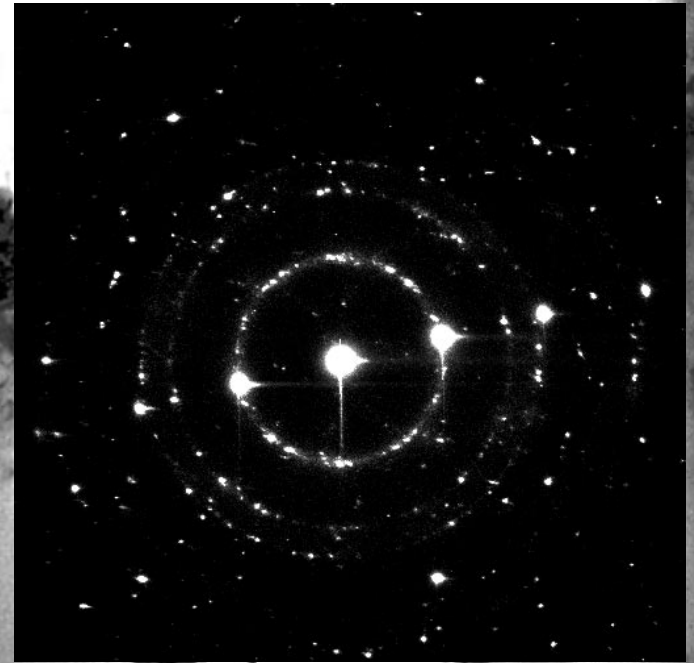
1 μm



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

Structural and chemical analysis

1 μm



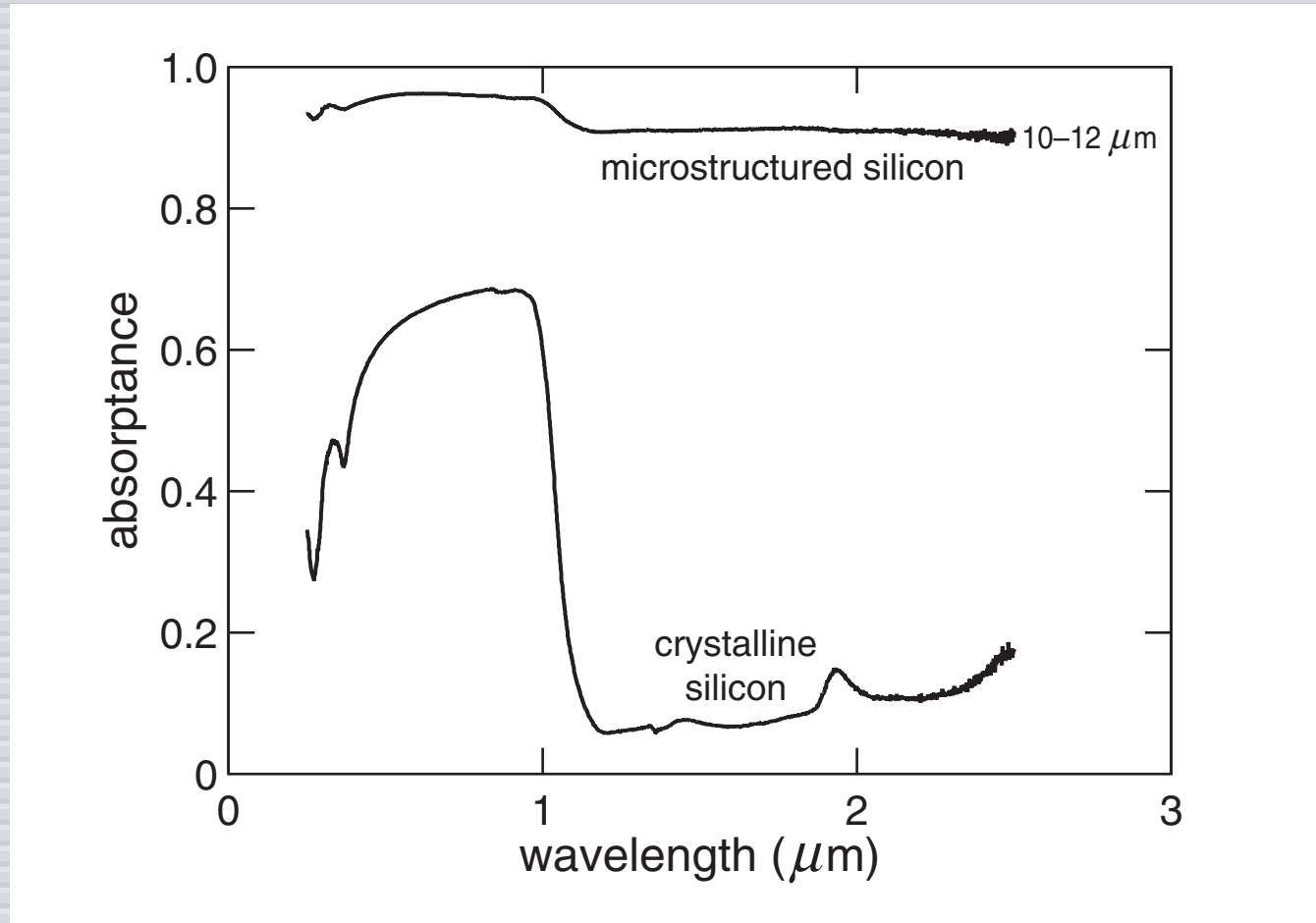
electron diffraction (F. Génin, M. Wall, LLNL)

cross-sectional TEM:

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

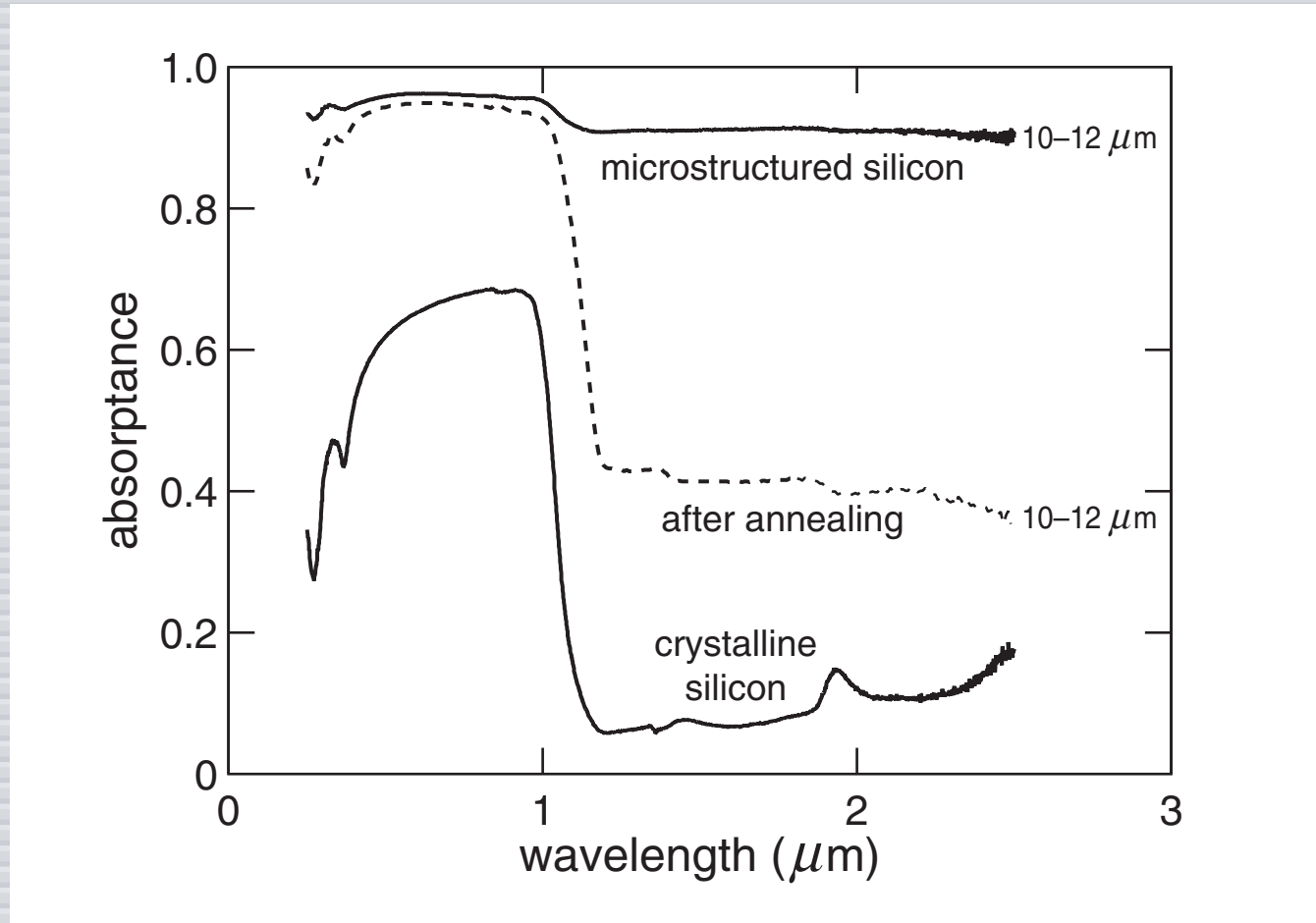
Structural and chemical analysis

anneal 4 hours at 1200 K



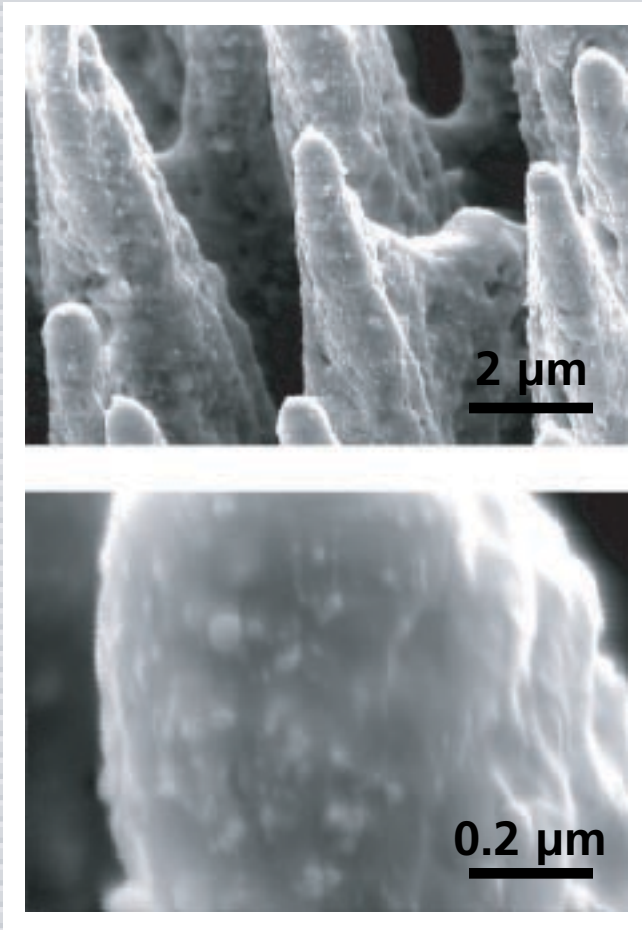
Structural and chemical analysis

anneal 4 hours at 1200 K



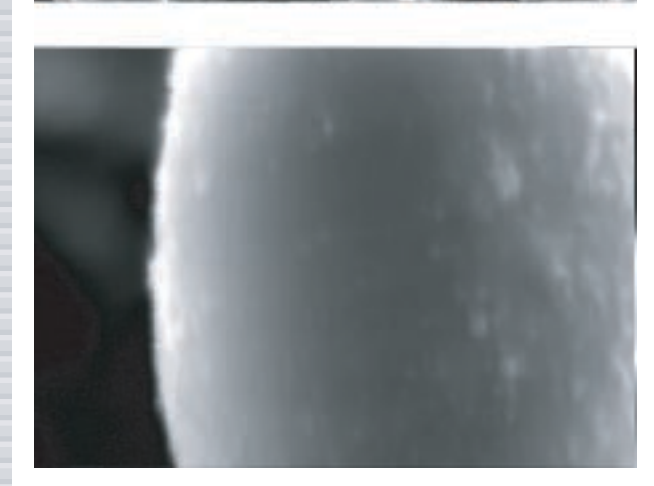
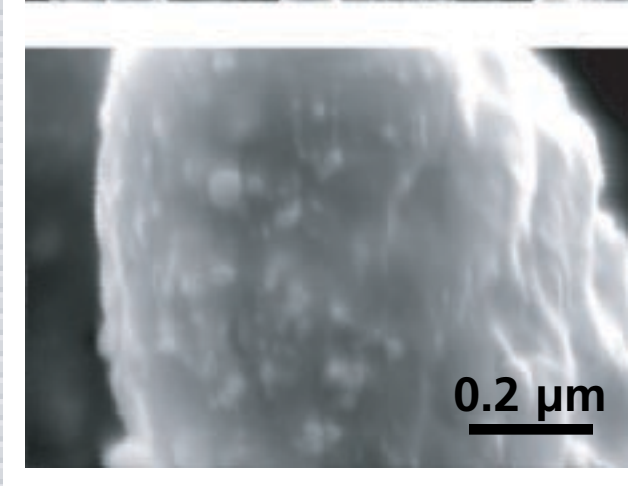
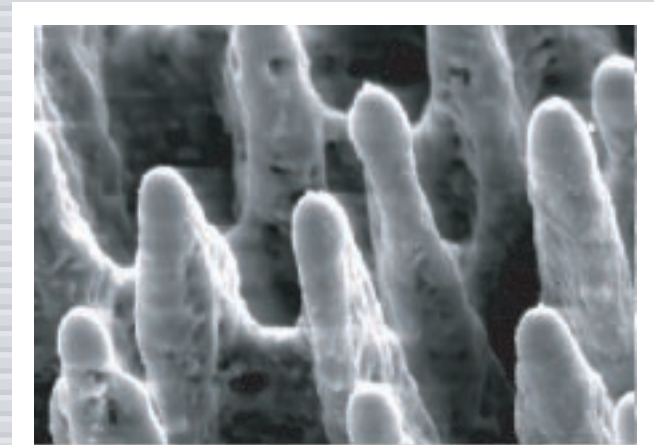
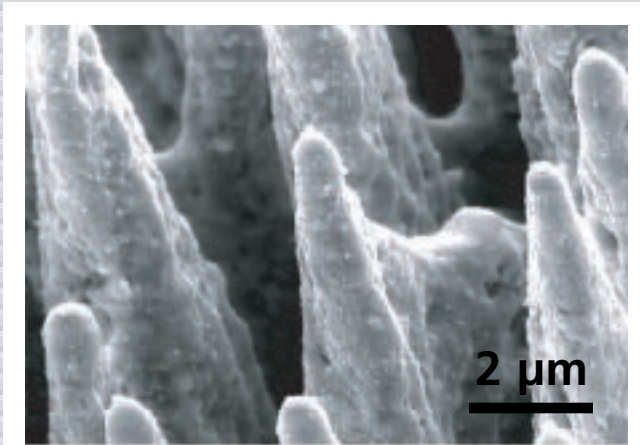
Structural and chemical analysis

anneal 4 hours at 1200 K



Structural and chemical analysis

anneal 4 hours at 1200 K



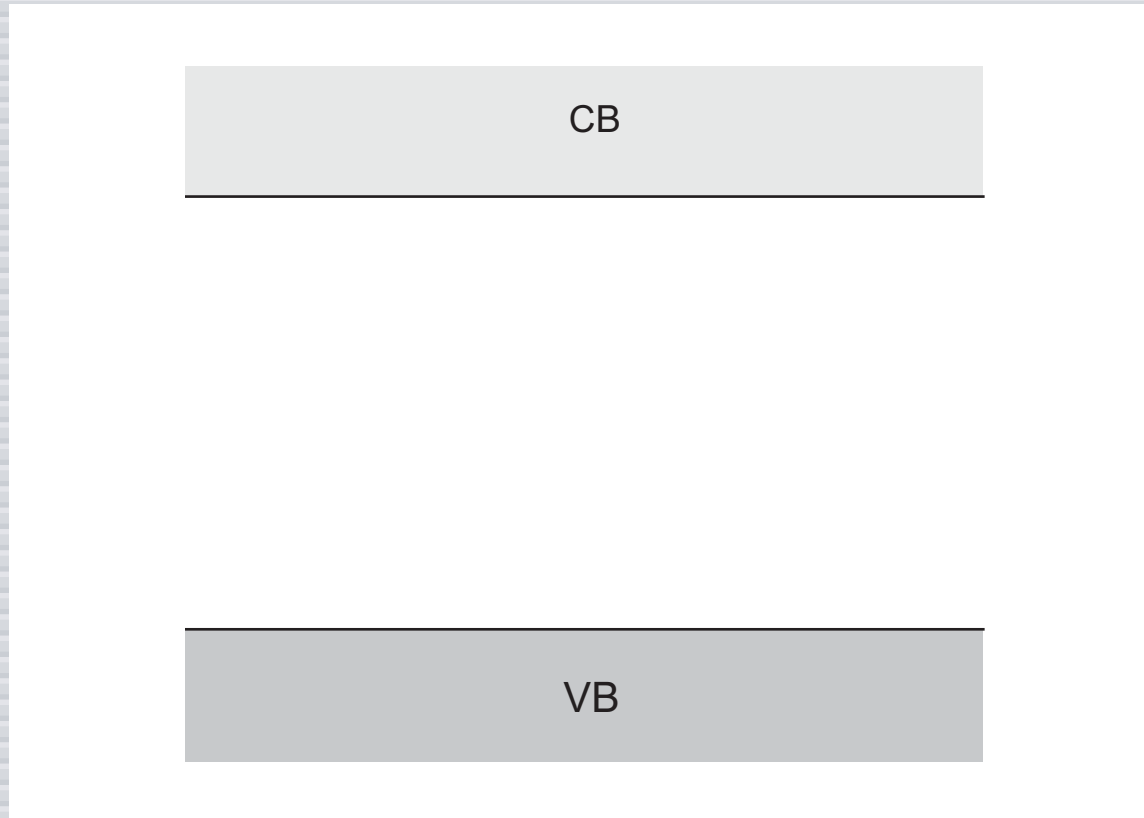
Structural and chemical analysis

Effects of annealing:

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

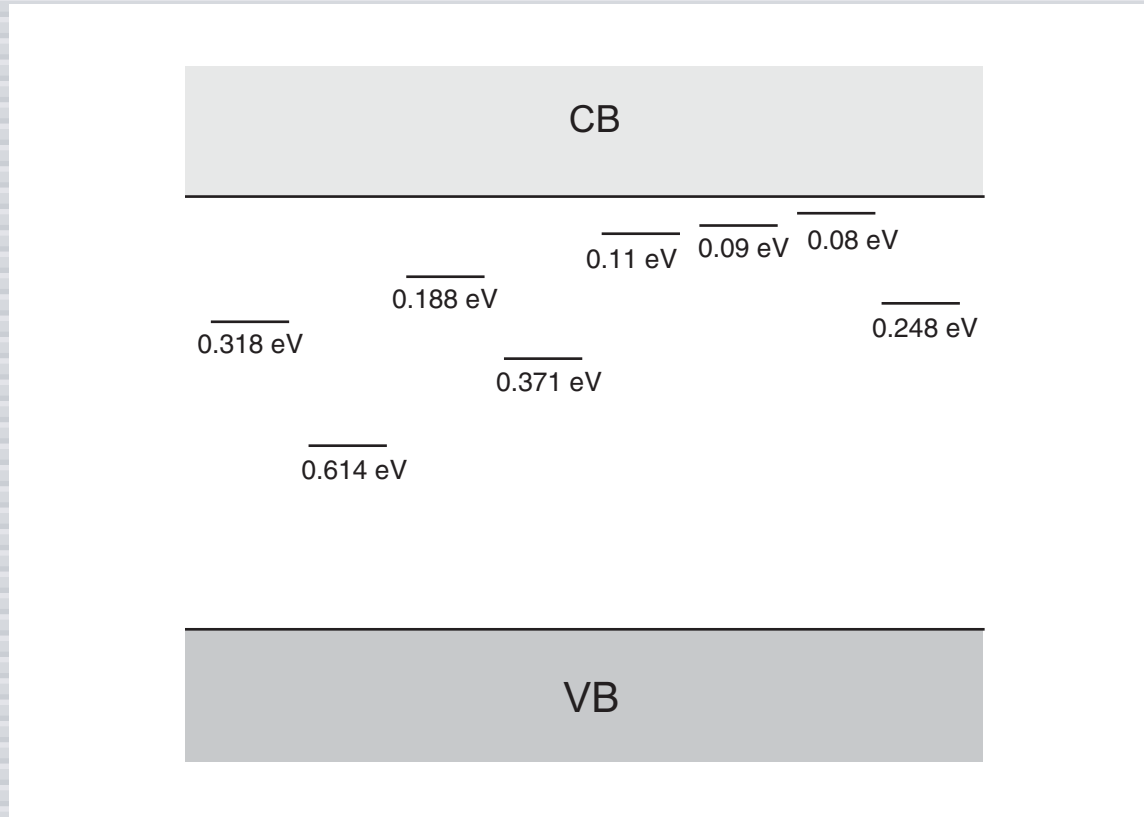
Structural and chemical analysis

sulfur introduces states in the gap



Structural and chemical analysis

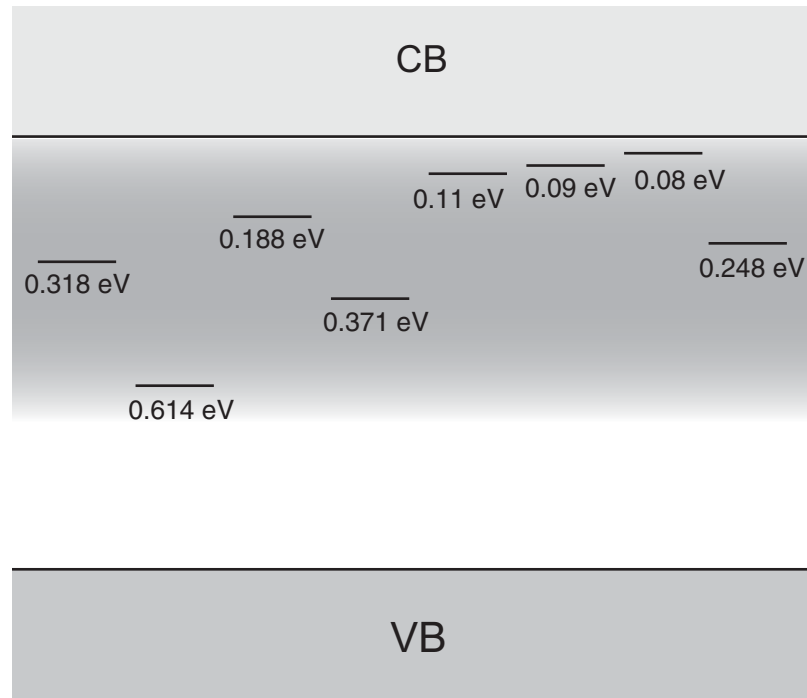
sulfur introduces states in the gap



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

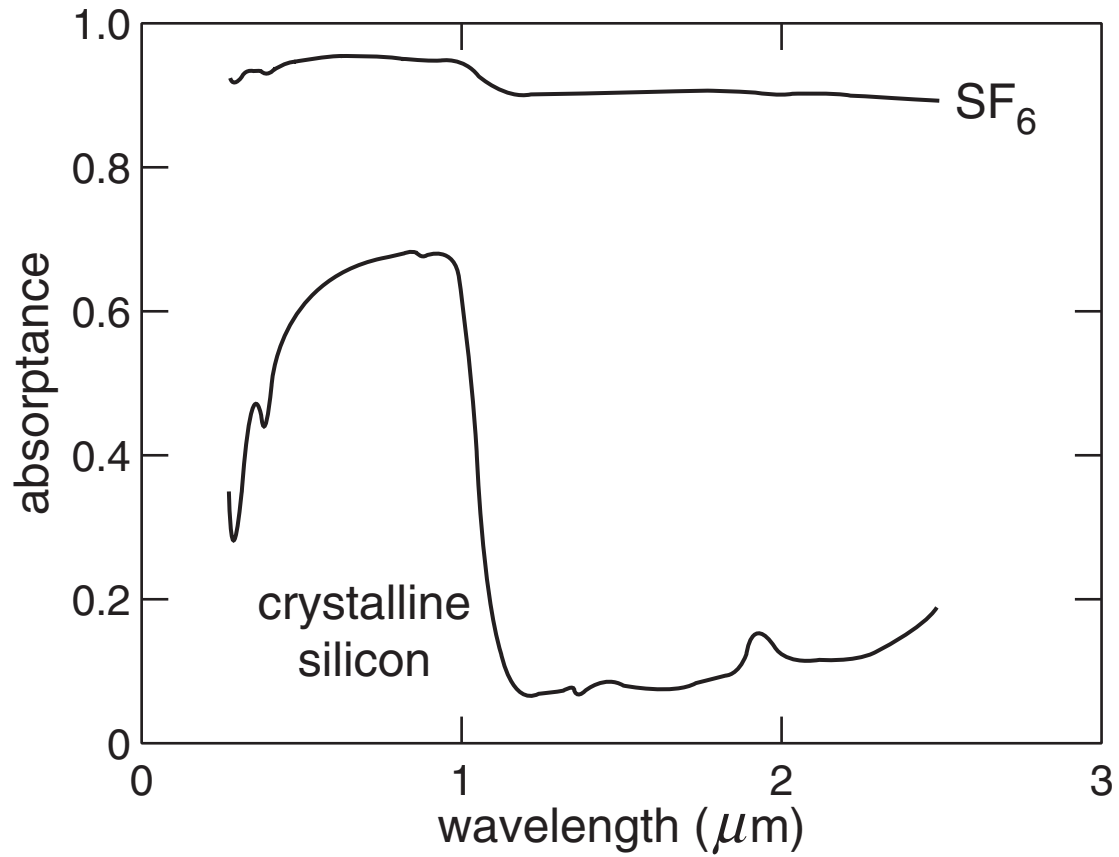
Structural and chemical analysis

states broaden into a band



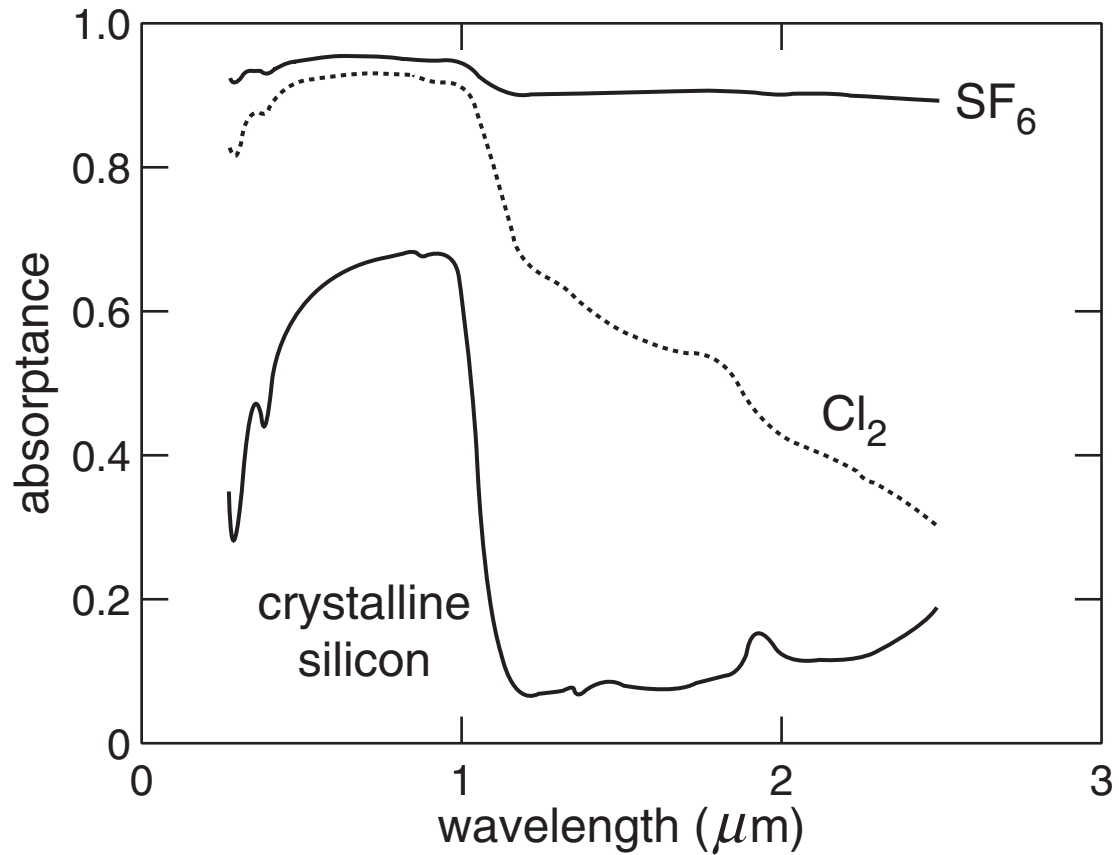
Structural and chemical analysis

effect of ambient gas on absorptance



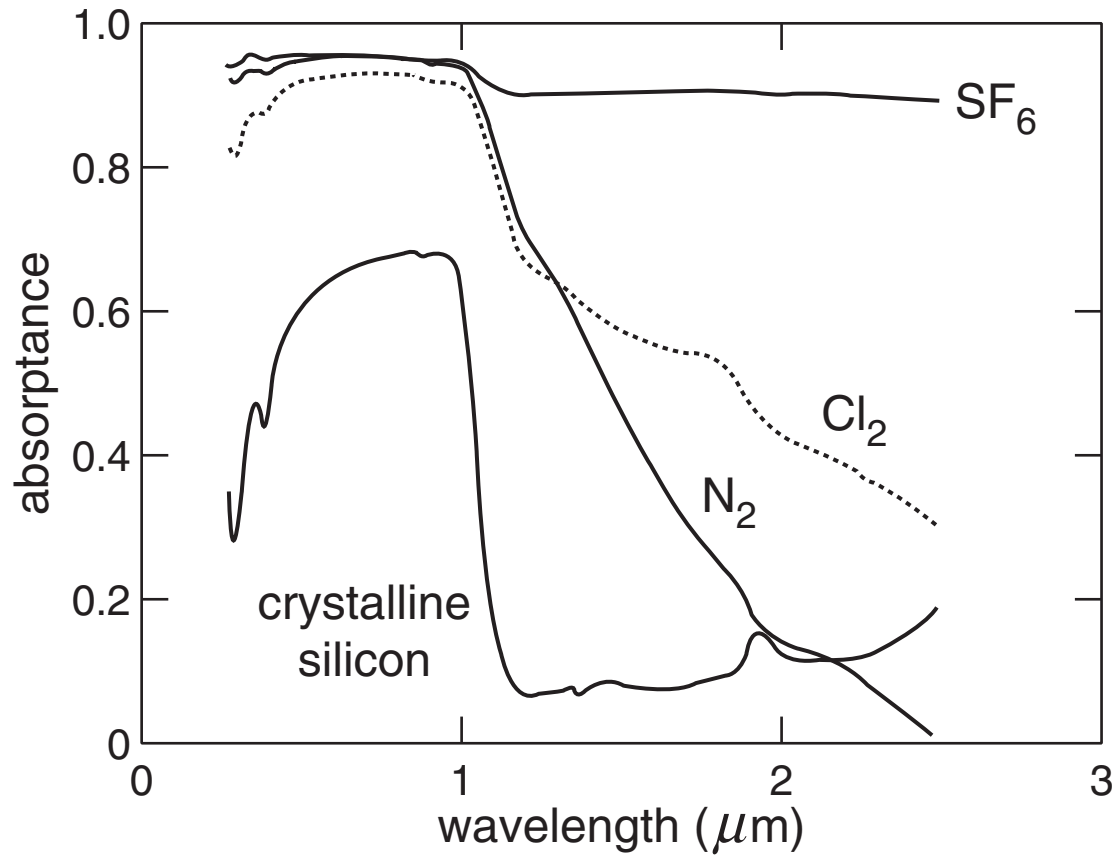
Structural and chemical analysis

effect of ambient gas on absorptance



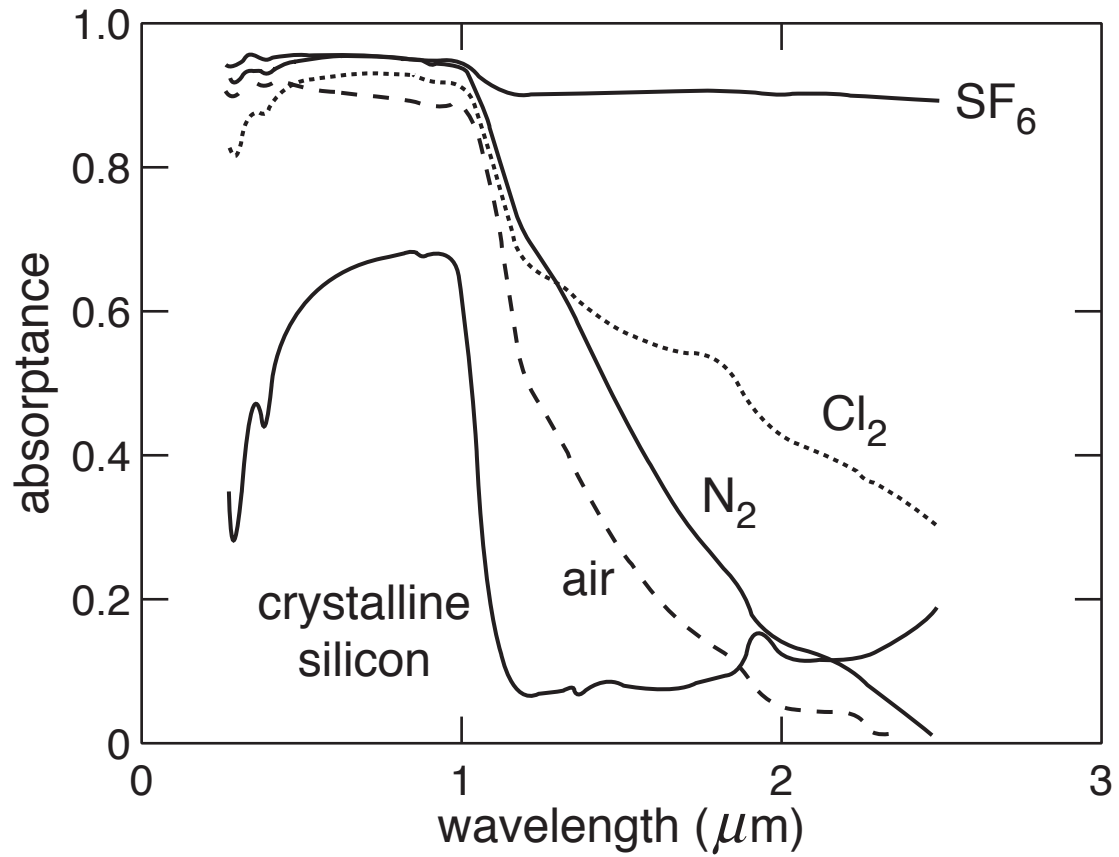
Structural and chemical analysis

effect of ambient gas on absorptance



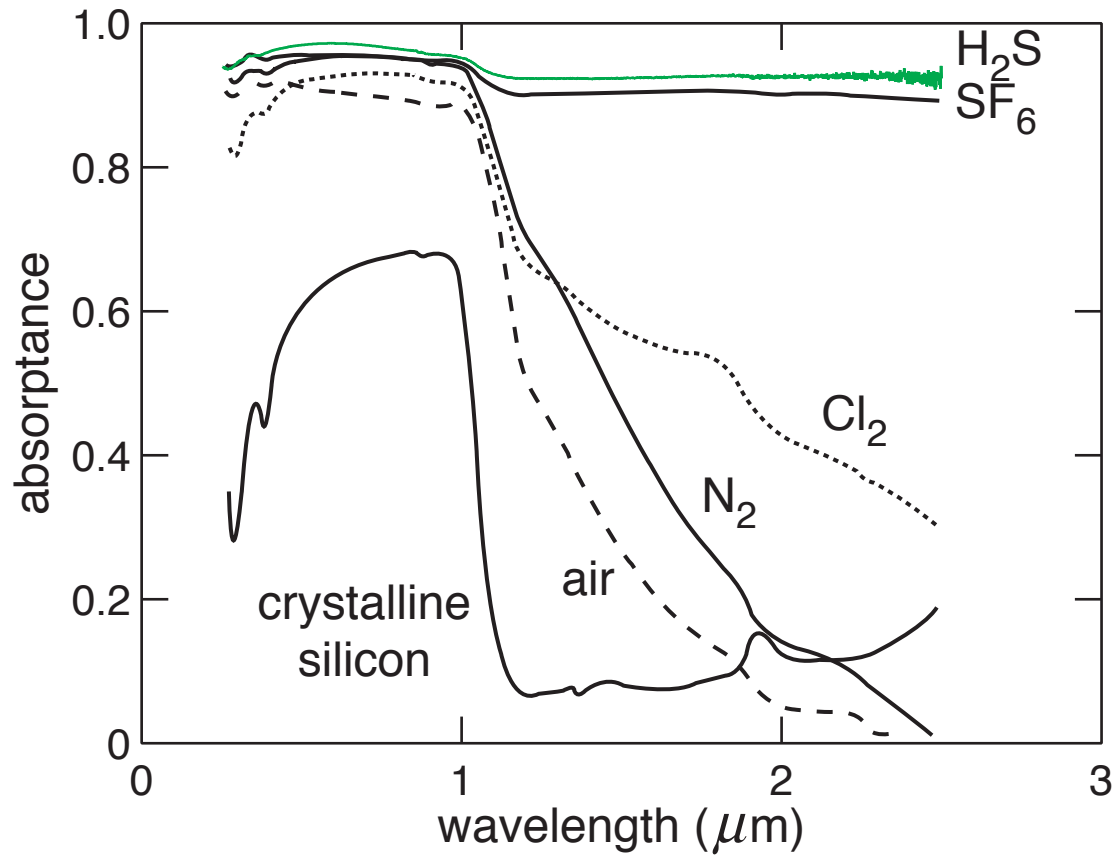
Structural and chemical analysis

effect of ambient gas on absorptance



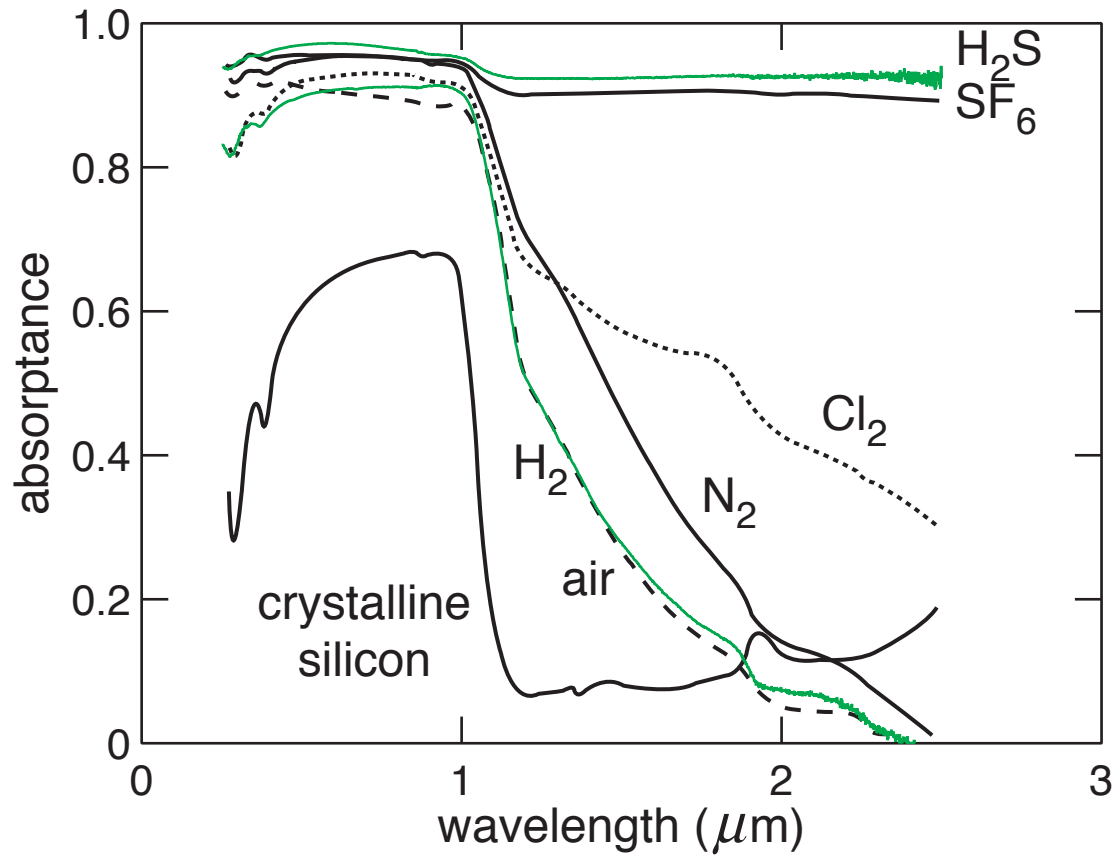
Structural and chemical analysis

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

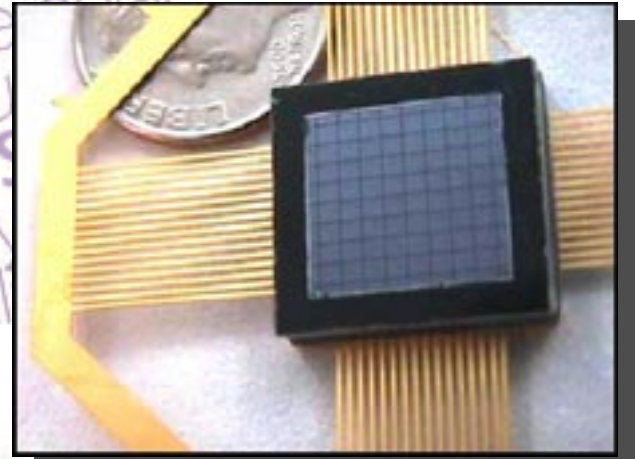
semiconductors with a powerful laser. In the early 1990s, Mazur's was the first academic lab in the world to get its hands on a femtosecond laser. This device produces pulses of light that are hundreds of times brighter than the Sun. and extremely

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 SF₆ would do it and then the fluorine would so with the silicon," Mazur explains. "I was more than

Outlook

▶ detector technology

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



TALL, DARK AND STRANGER

We'll all love stories of sci-fi. This is a story to look back on in time when a legend is born. It's a story of a life. It's a story of a life when

semiconductors with a powerful laser. In the early 1960s, Matar's was the first academic lab in the world to do so. It was a hard-core attempt to build a laser. It was a hard-core attempt to build a laser. It was a hard-core attempt to build a laser. It was a hard-core attempt to build a laser.

around the laboratory. He claims that it was a great time. He claims that it was a great time. He claims that it was a great time. He claims that it was a great time. He claims that it was a great time.

Outlook

- ▶ detector technology
- ▶ solar cells

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



TALL, DARK AND STRANGER

We'll all agree that it's weird. This man to look back to a time when a single ... of a fifty ... when

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

around the "invention," he claims. "Well, it was a great time to make ... their lives" ... but it was ... into a path and ... will attack a ... thought ... through ... would ... the silicon. Most ex ...

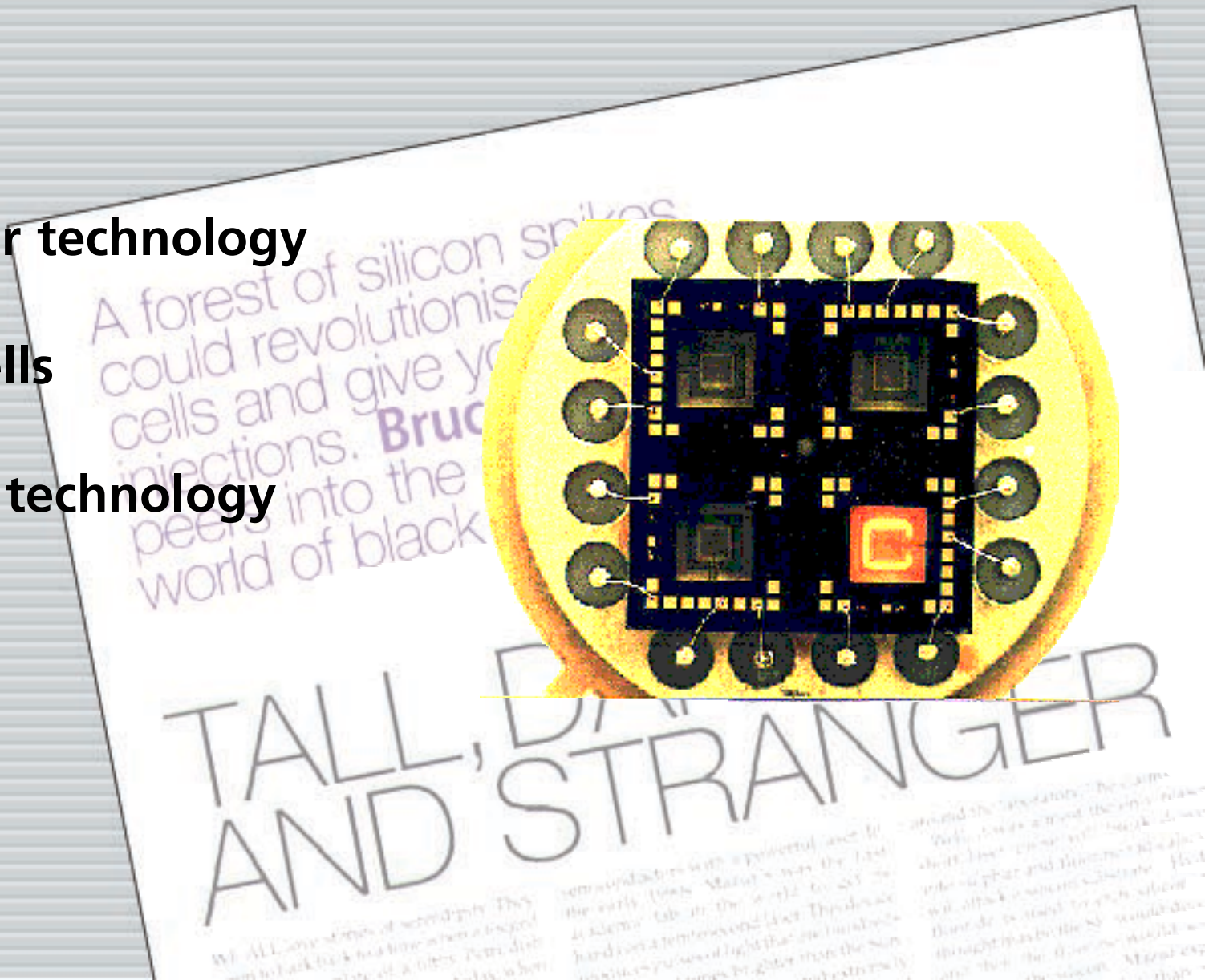
Outlook

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



Outlook

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



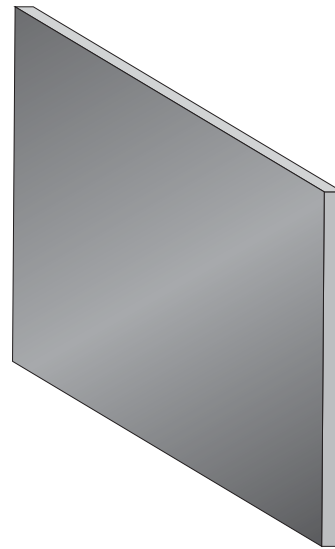
Outlook

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

Outlook

can ordering of spikes be improved by using a grid?

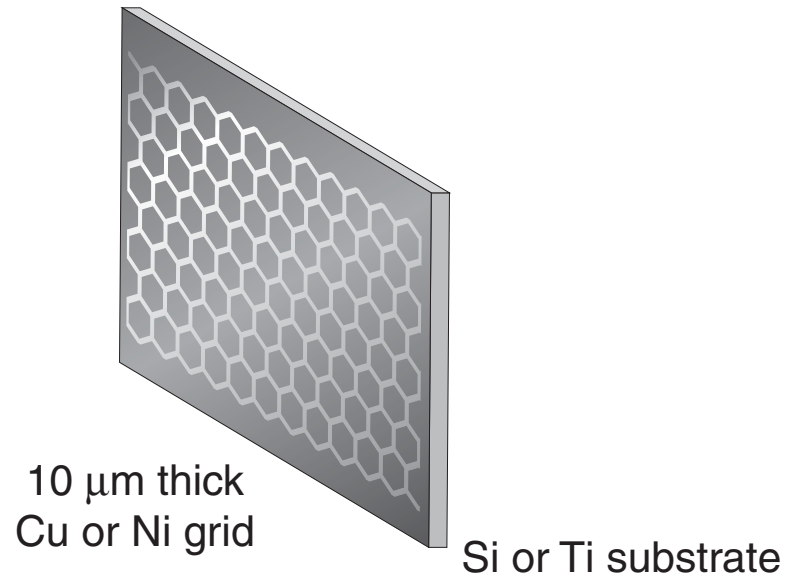
Outlook



Si or Ti substrate

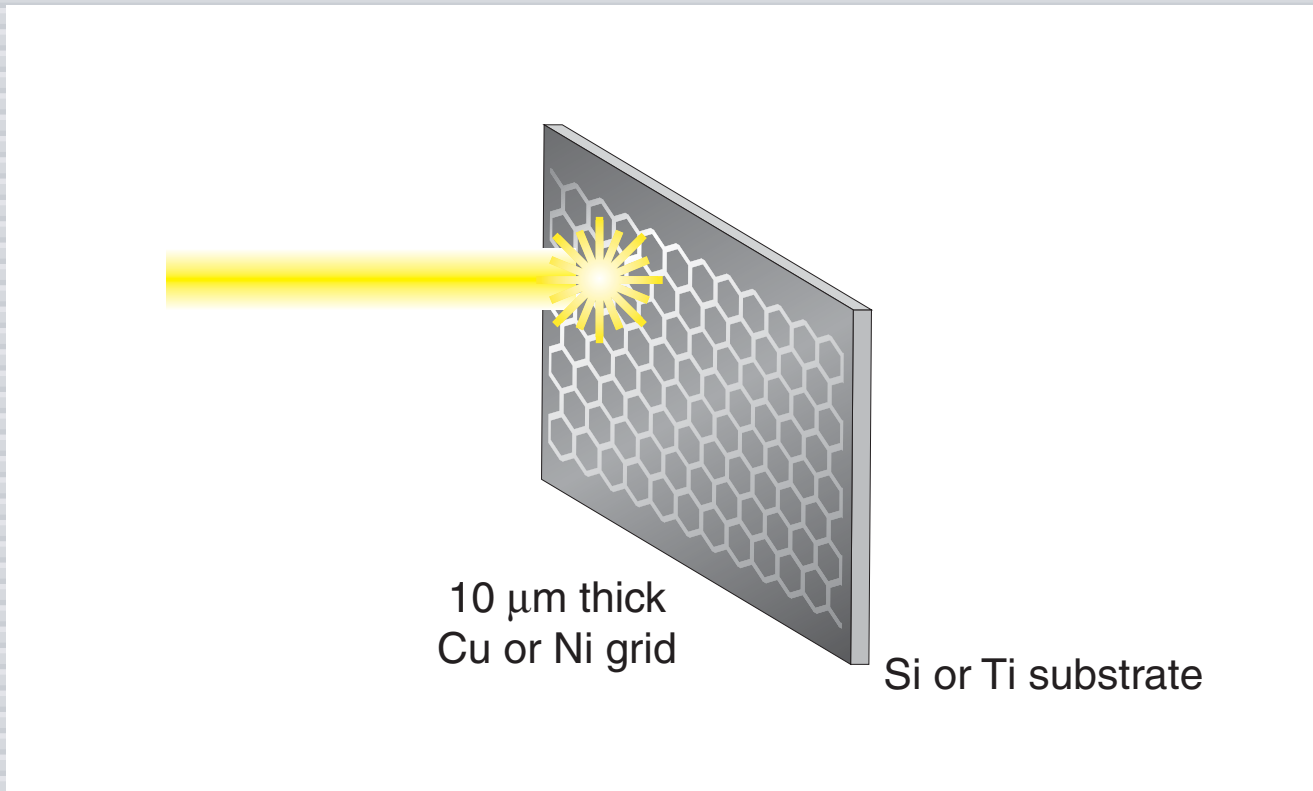
Outlook

place grid in front of substrate



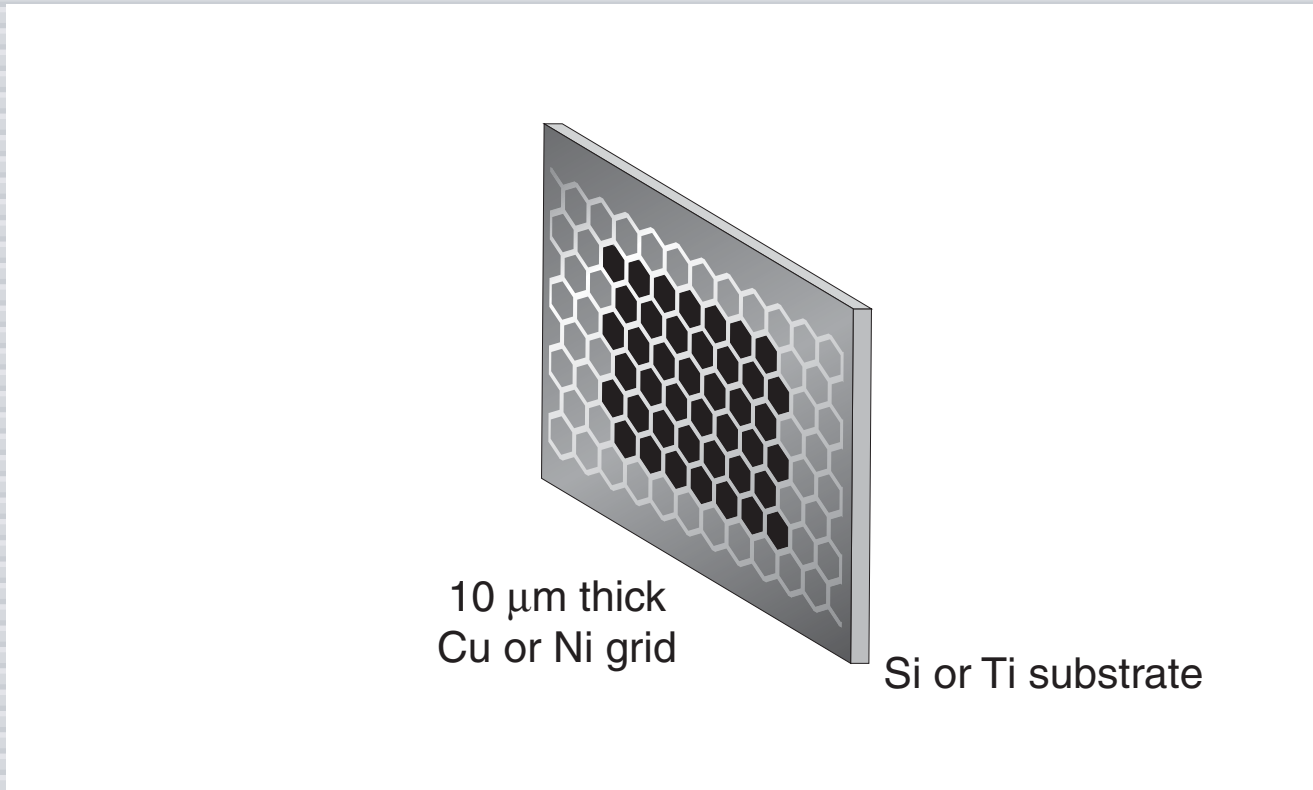
Outlook

scan laser beam



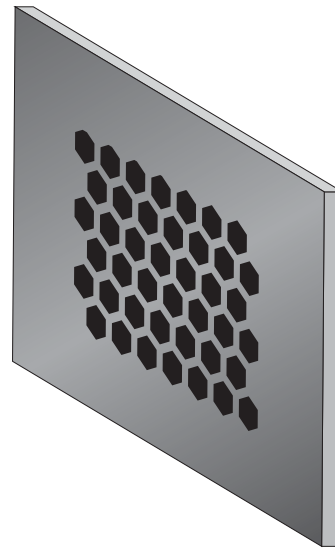
Outlook

scan laser beam

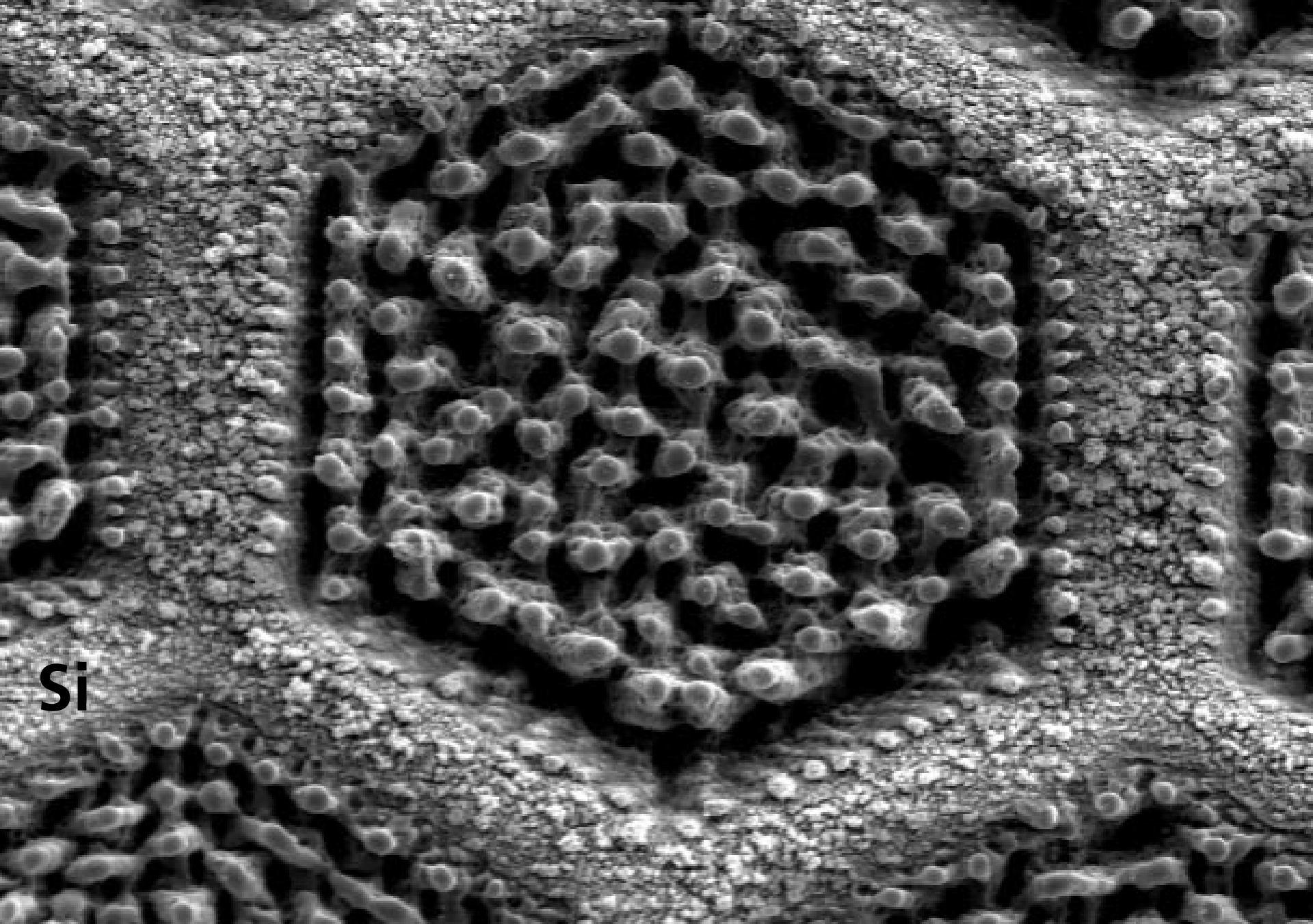


Outlook

remove grid



Si or Ti substrate

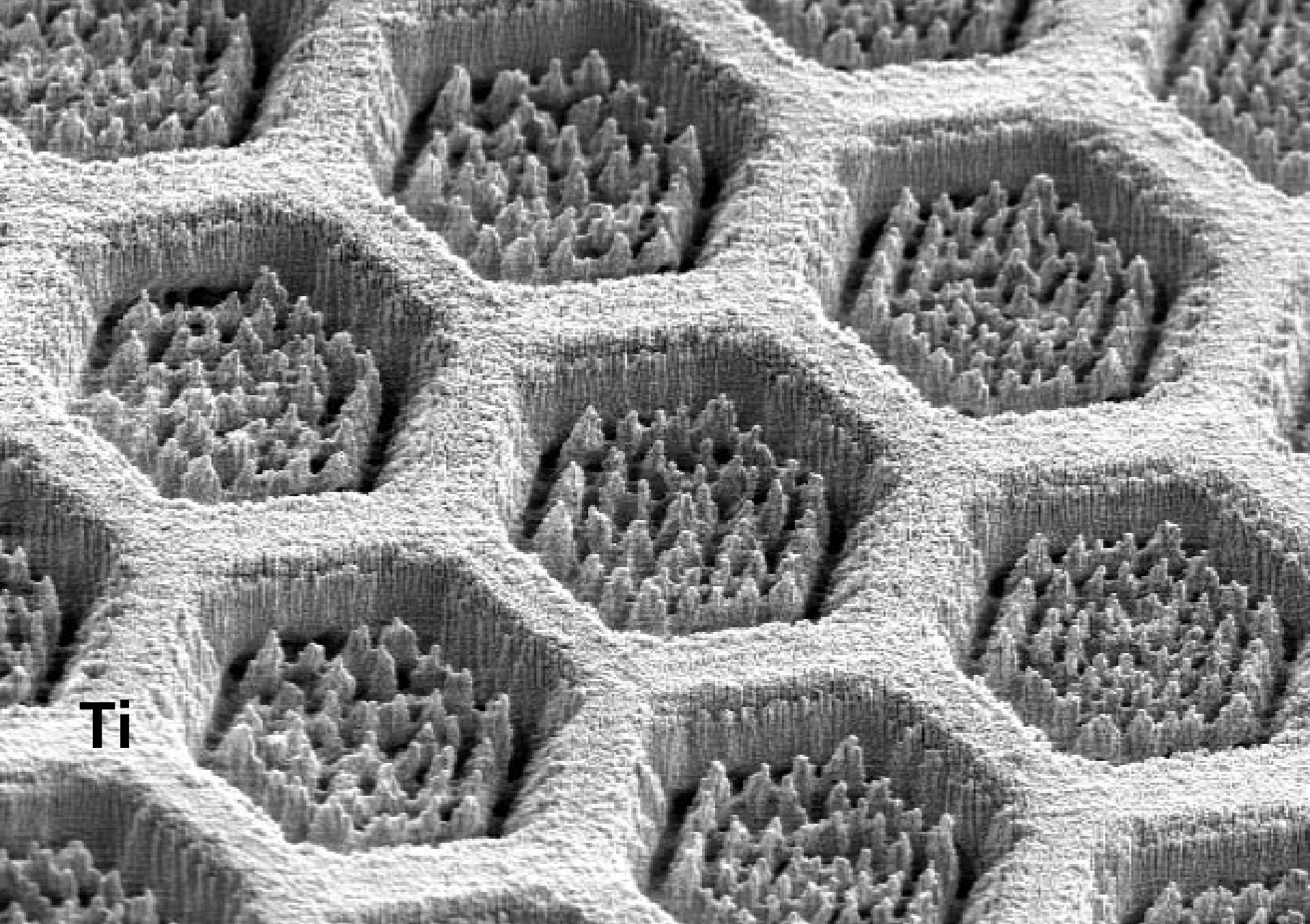


Si

x2000
512 x 480

20 μm

5kV 24mm
H300.TIF

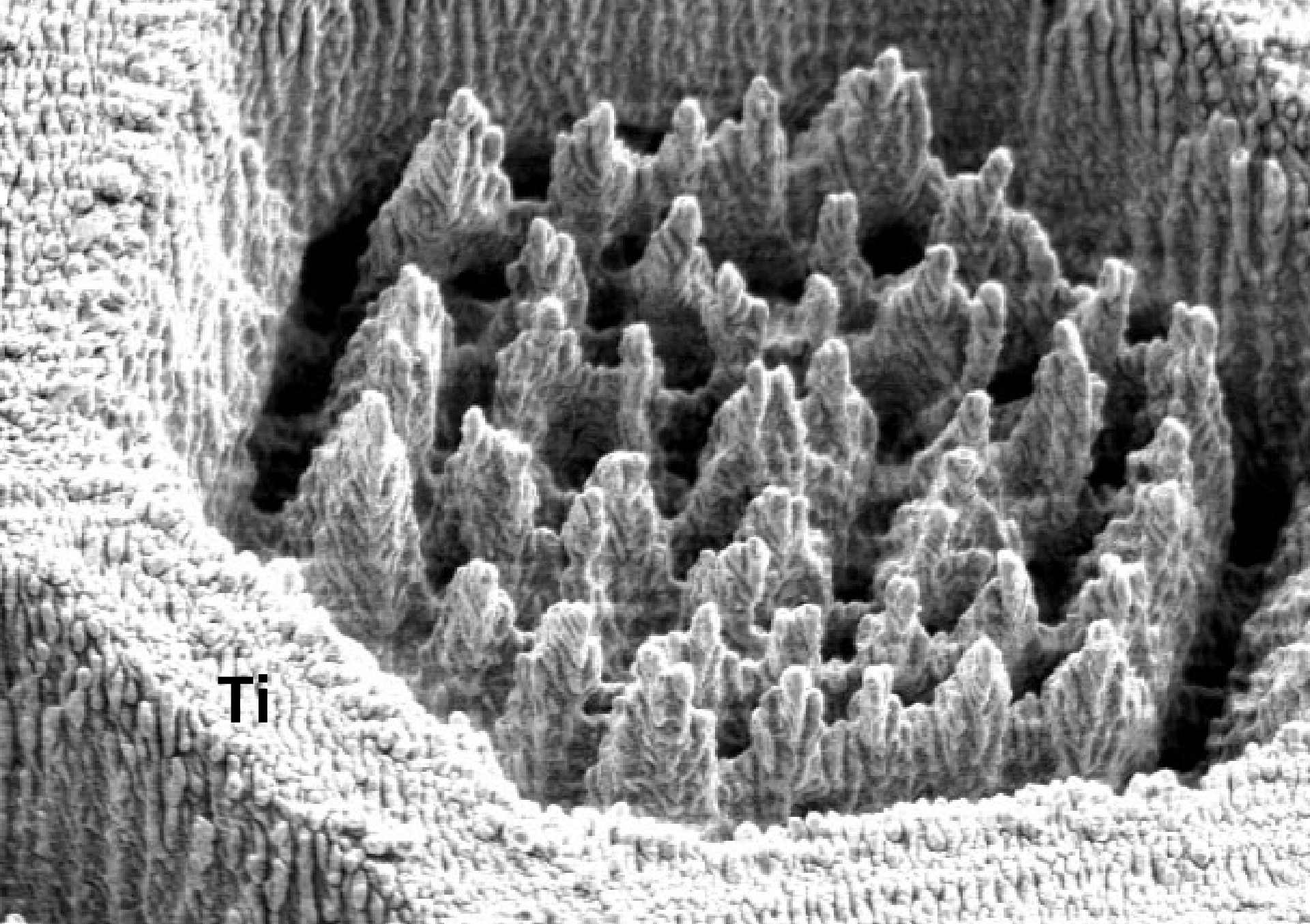


Ti

20 μ m

5kV

17mm



Ti

10 μ m

5kV

17mm

Outlook

Summary

Microstructured silicon

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

Summary

Microstructured silicon

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

Microstructured silicon

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

Summary

Microstructured silicon

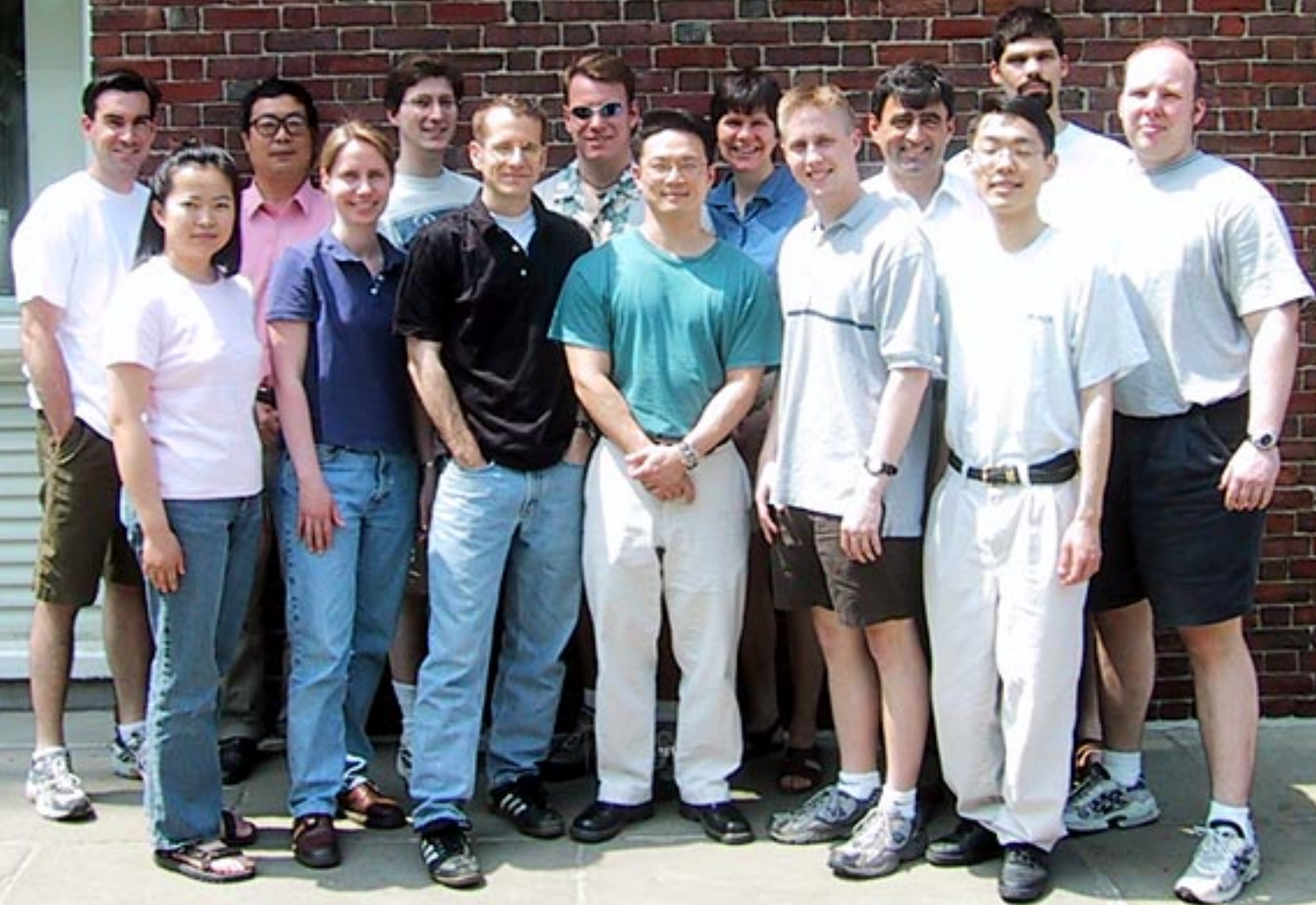
- ▶ **fabricated by simple, maskless process**
- ▶ **can be integrated with microelectronics**
- ▶ **generates IR photocurrent**
- ▶ **provides stable, high field emission current**

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. Arie 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

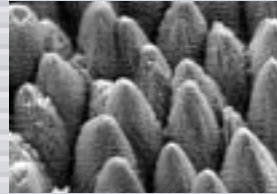
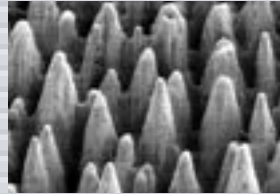
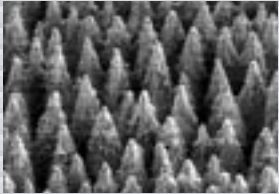
Cl₂

N₂

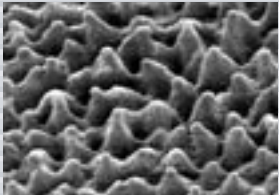
air

vacuum

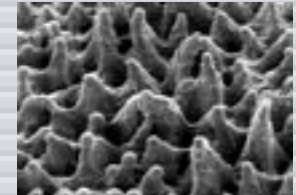
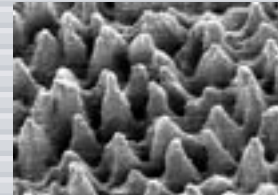
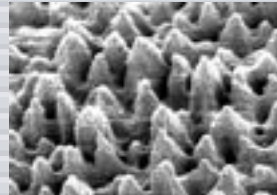
Si



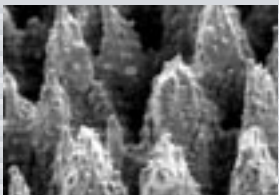
Ti



reacts



Only in SF₆:



Ge

InP

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

Materials

SF₆

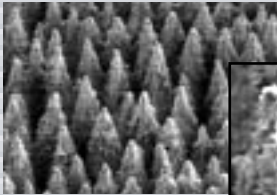
Cl₂

N₂

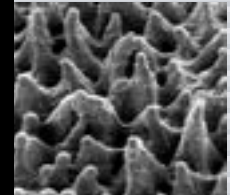
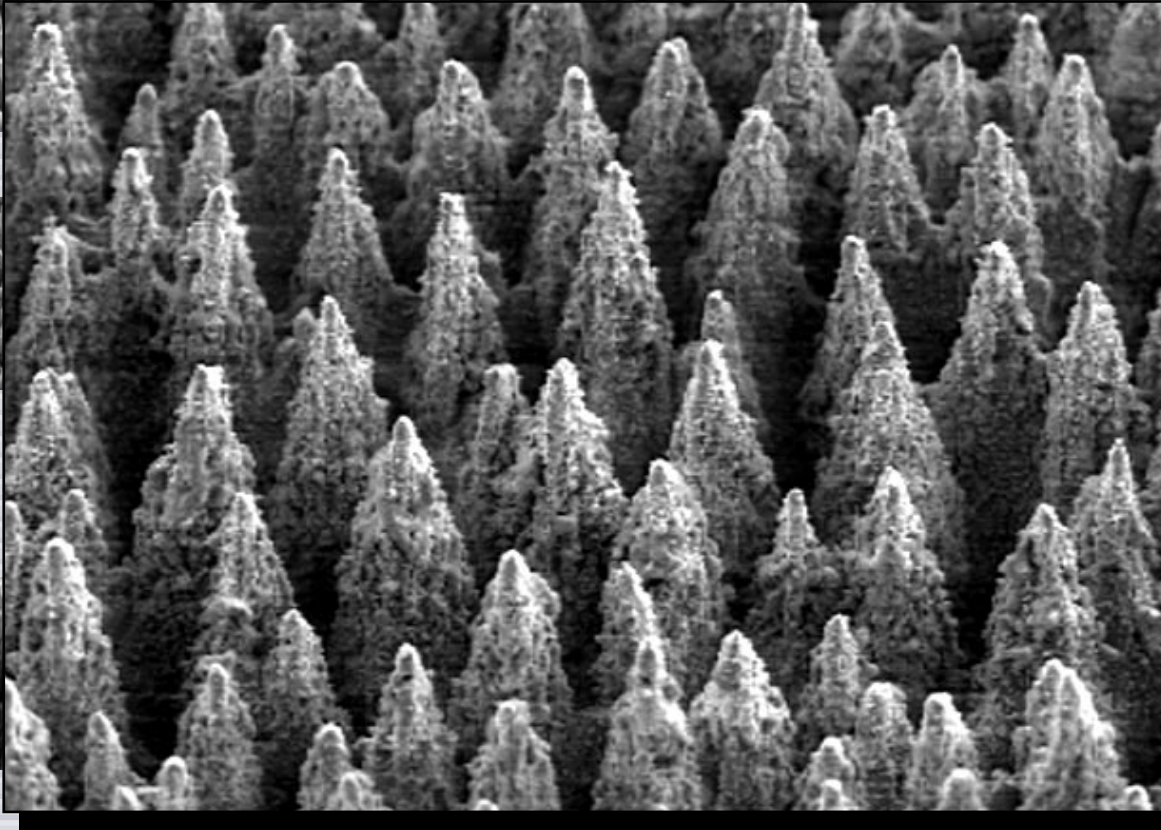
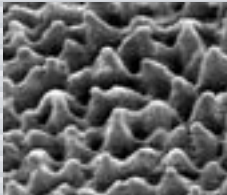
air

vacuum

Si

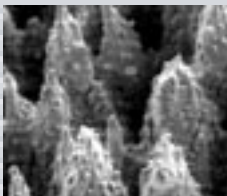


Ti



Only in SF₆

Ge



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

Materials

SF₆

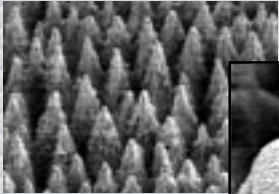
Cl₂

N₂

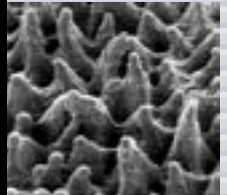
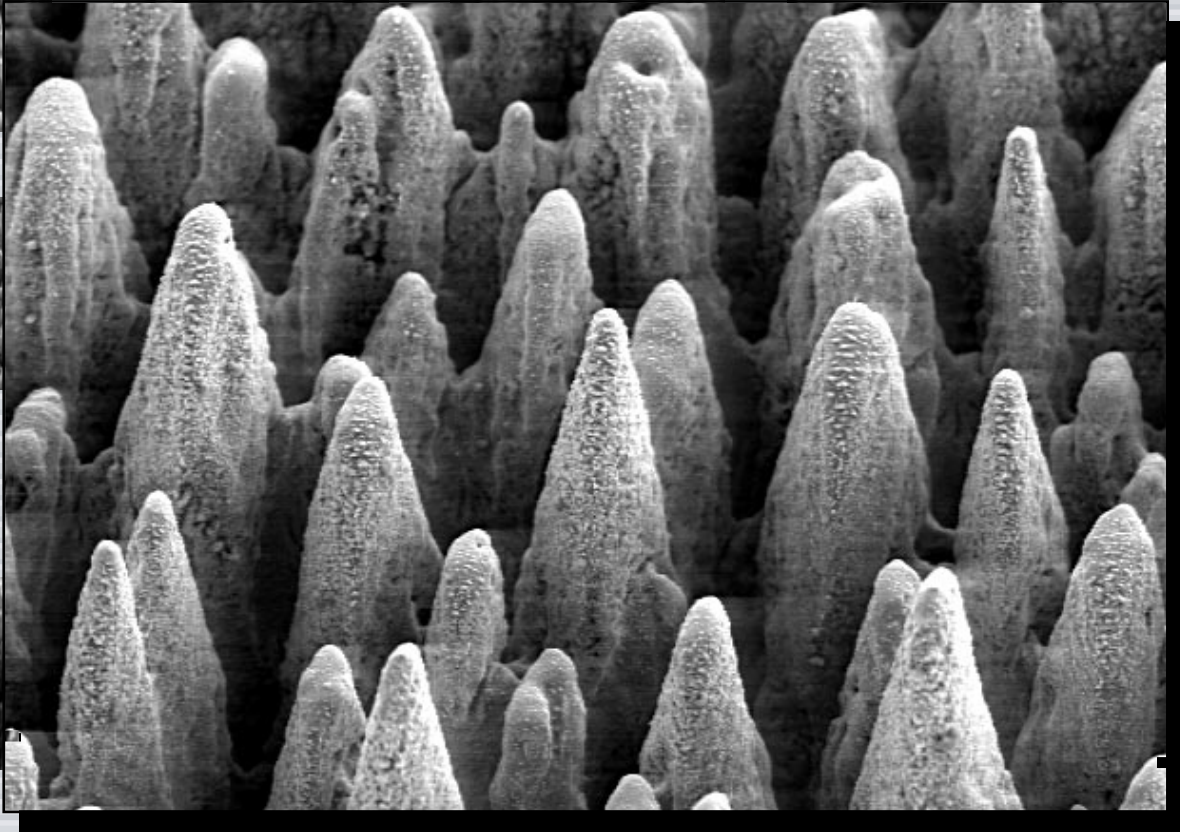
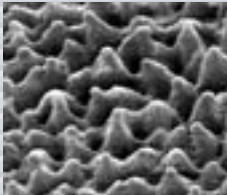
air

vacuum

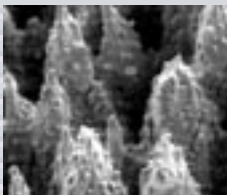
Si



Ti



Only in SF₆



Ge

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

Materials

SF₆

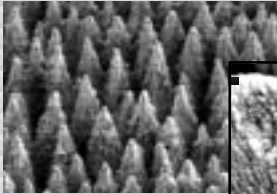
Cl₂

N₂

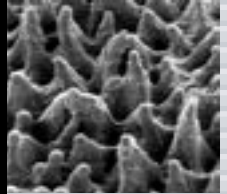
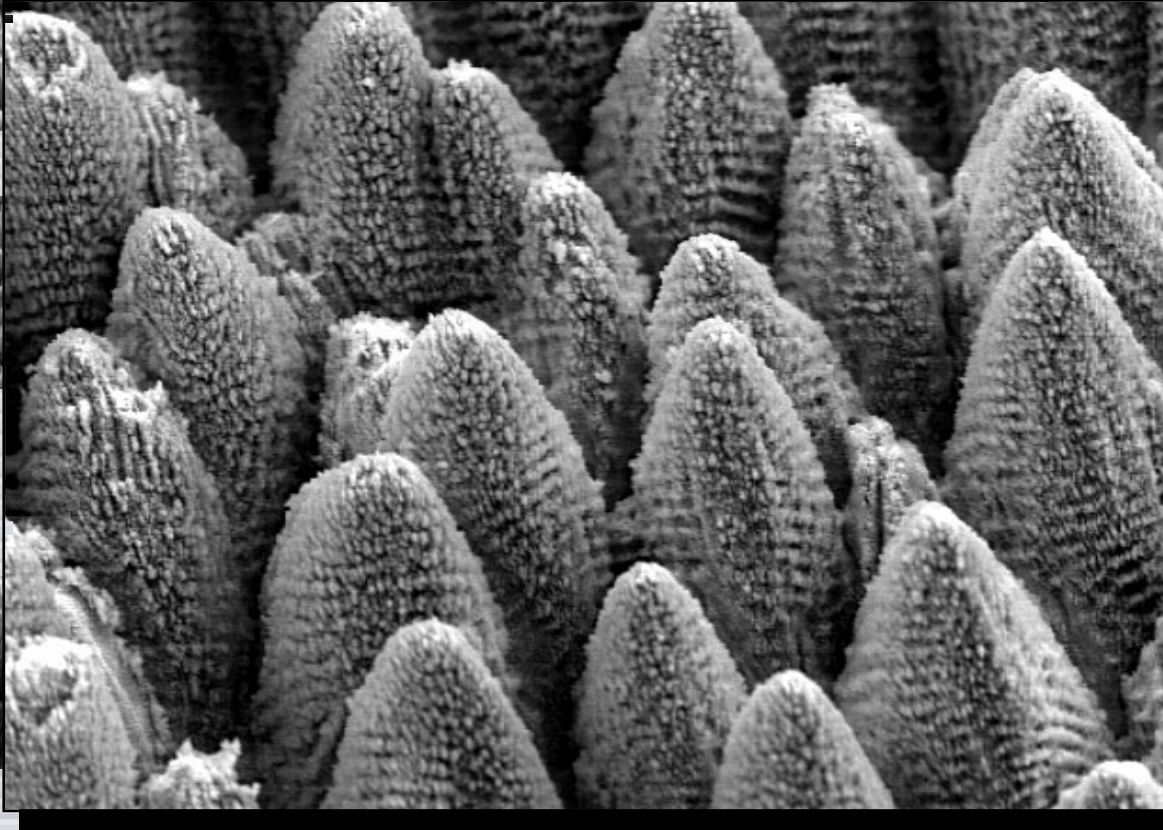
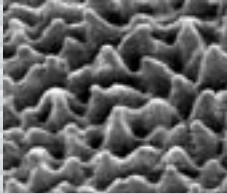
air

vacuum

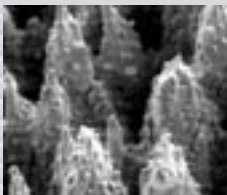
Si



Ti



Only in SF₆



Ge

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

Materials

SF₆

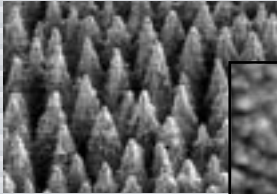
Cl₂

N₂

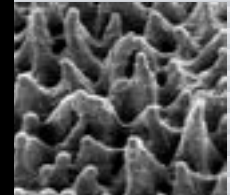
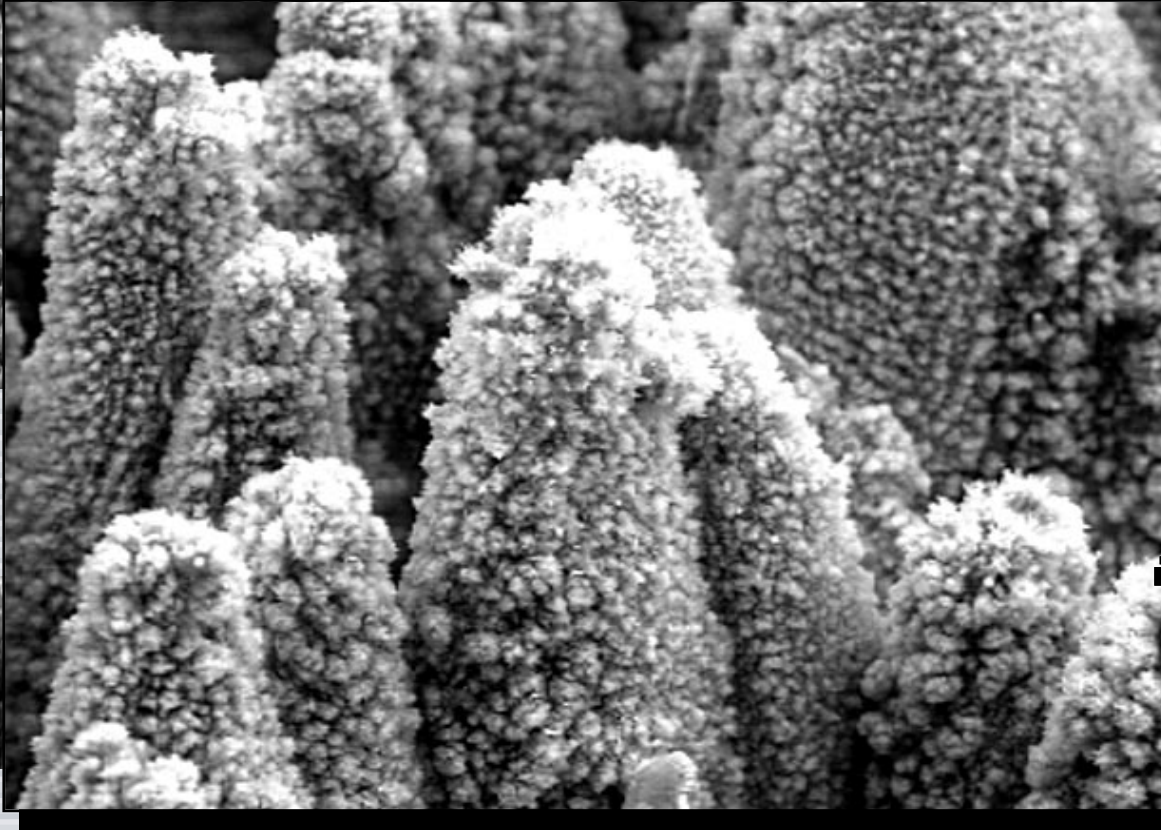
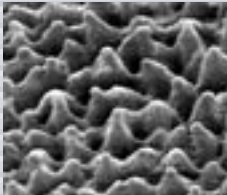
air

vacuum

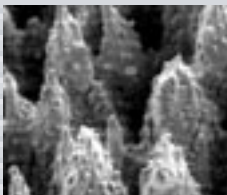
Si



Ti



Only in SF₆



Ge

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

Materials

SF₆

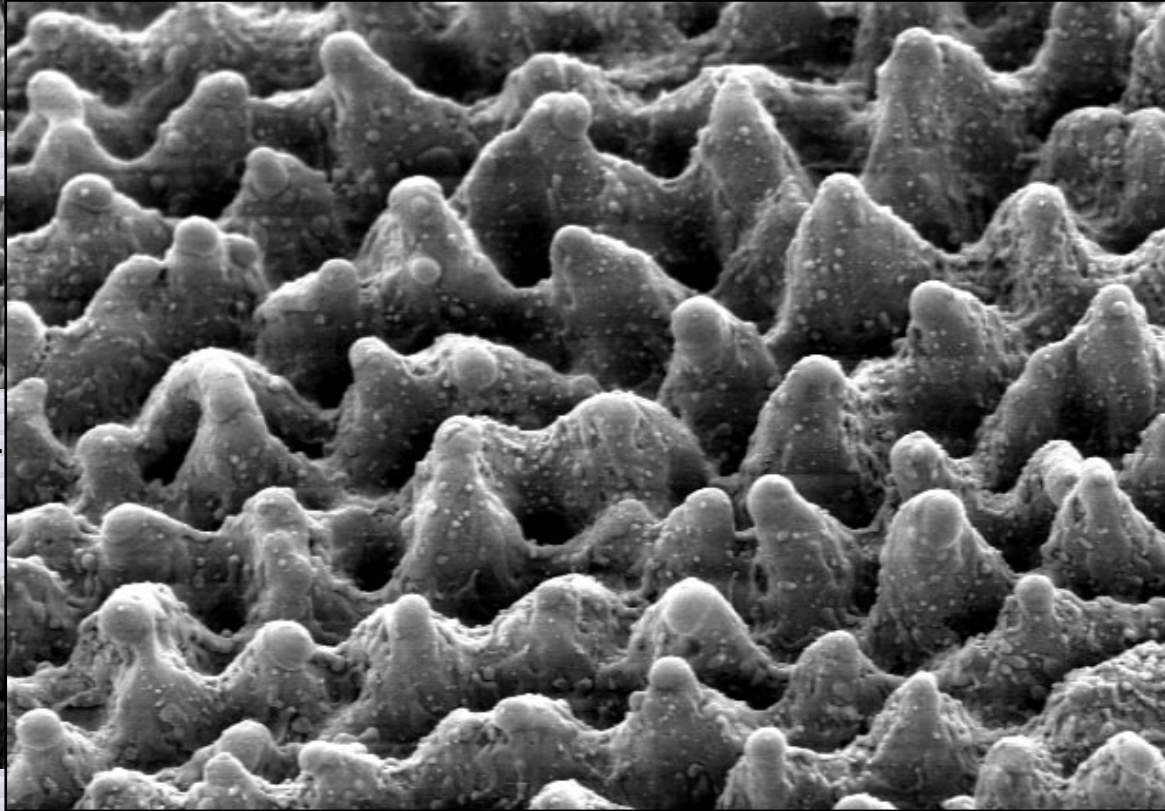
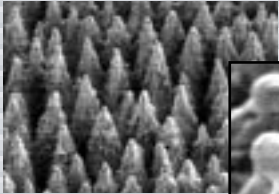
Cl₂

N₂

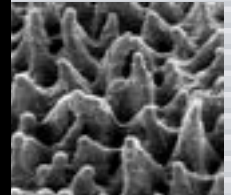
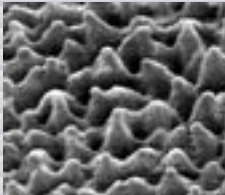
air

vacuum

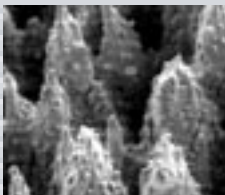
Si



Ti



Only in SF₆



Ge

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

Materials

SF₆

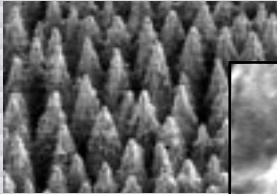
Cl₂

N₂

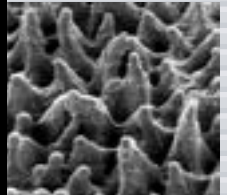
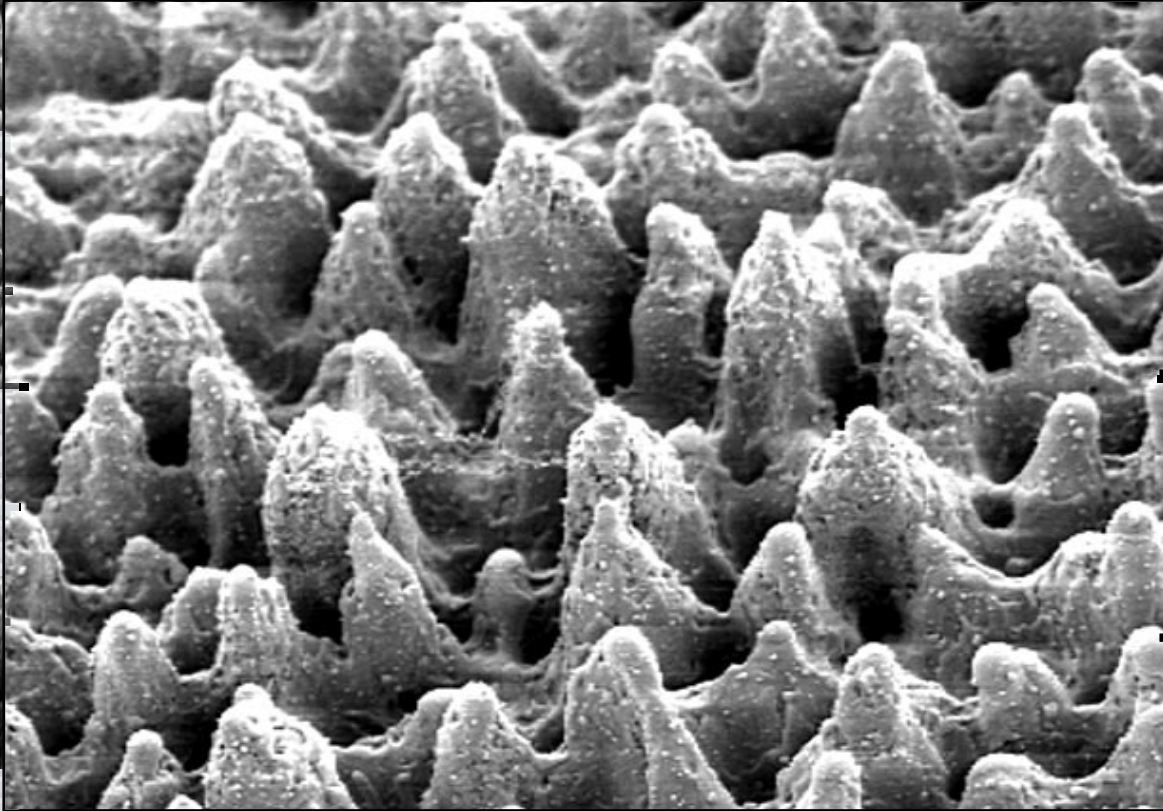
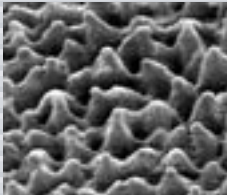
air

vacuum

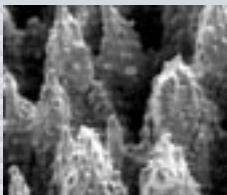
Si



Ti



Only in SF₆



Ge

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

Materials

SF₆

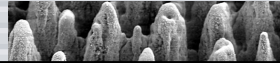
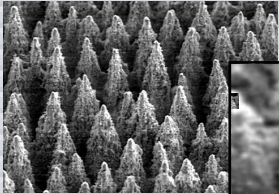
Cl₂

N₂

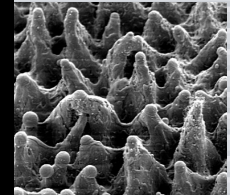
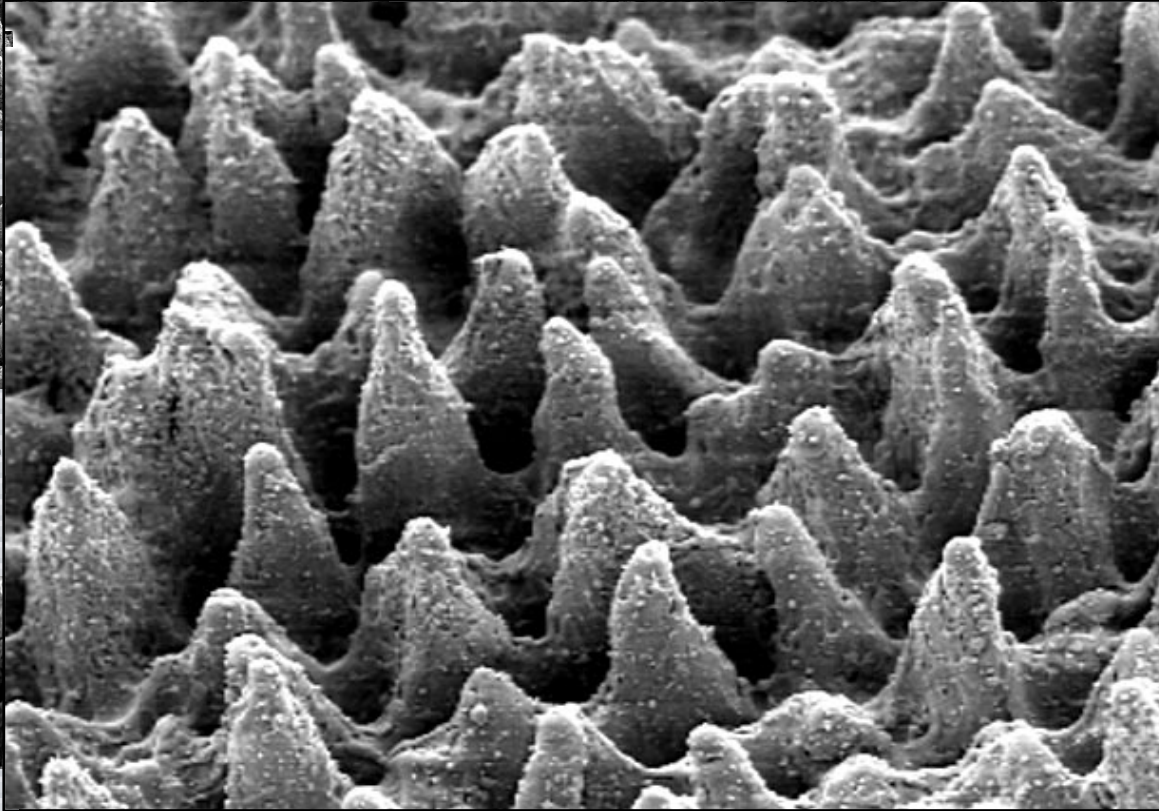
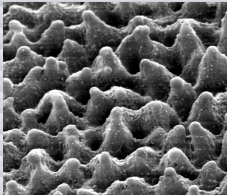
air

vacuum

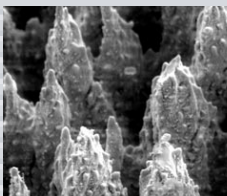
Si



Ti



Only in SF₆



Ge

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

Materials

SF₆

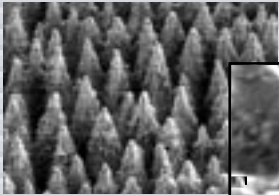
Cl₂

N₂

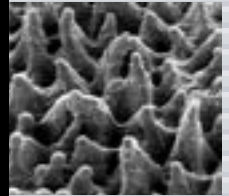
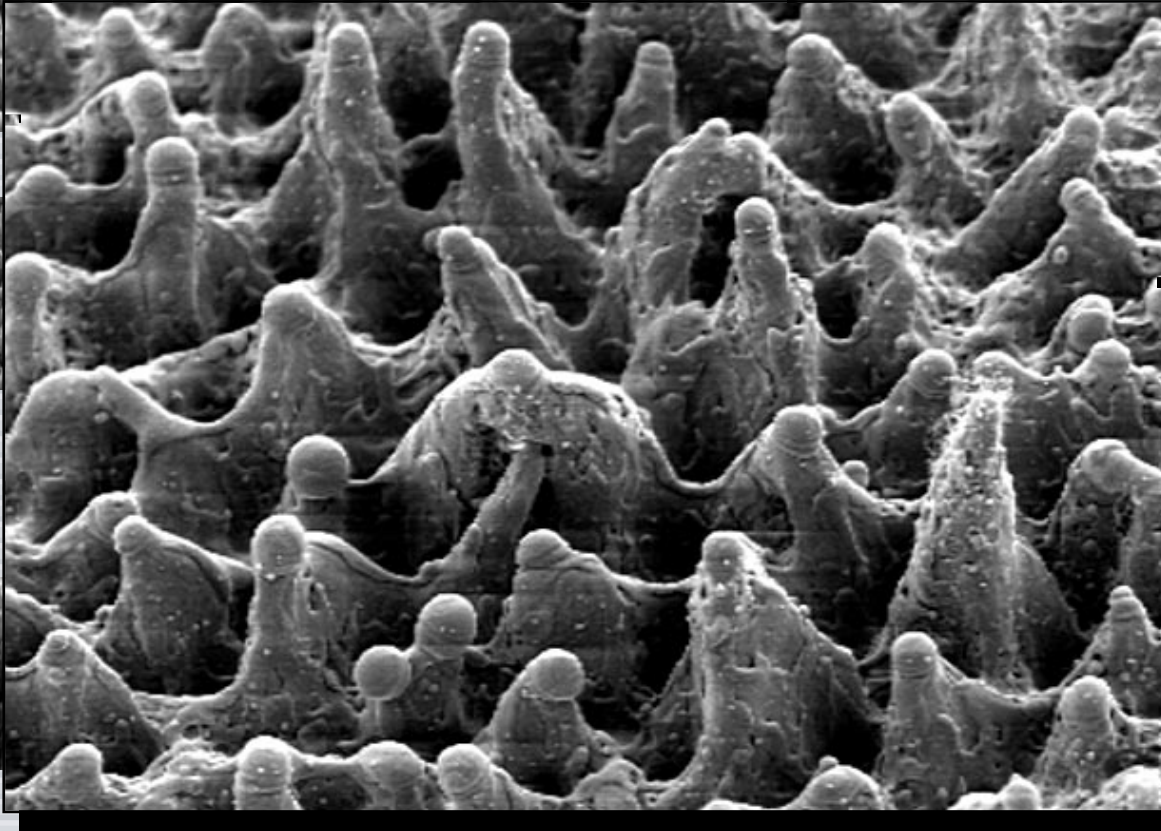
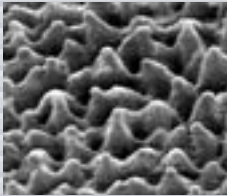
air

vacuum

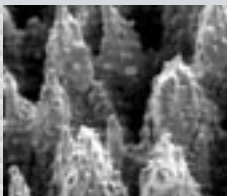
Si



Ti



Only in SF₆



Ge

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

Materials

SF₆

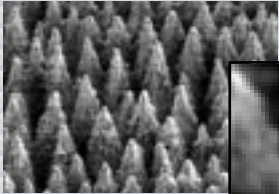
Cl₂

N₂

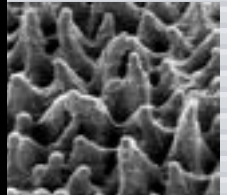
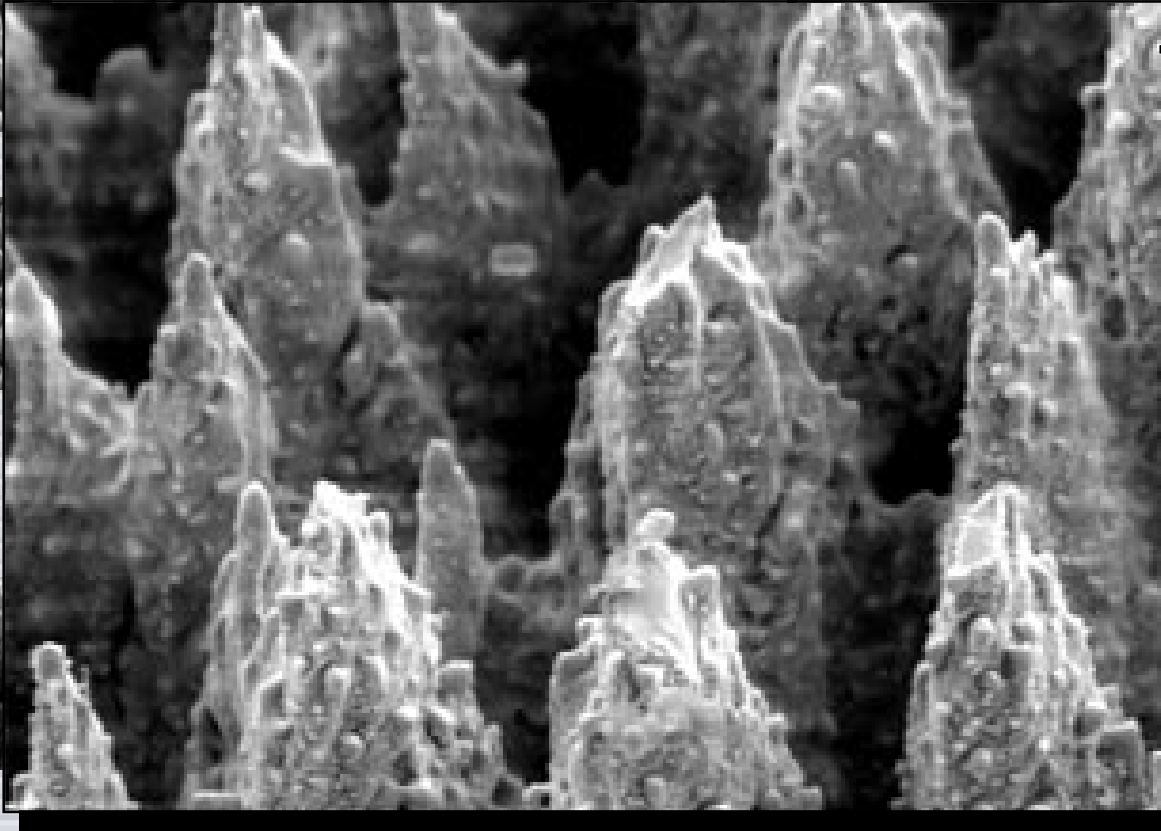
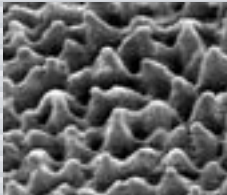
air

vacuum

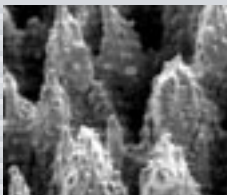
Si



Ti



Only in SF₆



Ge

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

Materials

SF₆

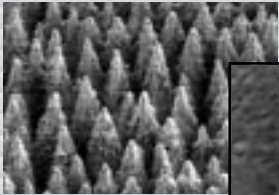
Cl₂

N₂

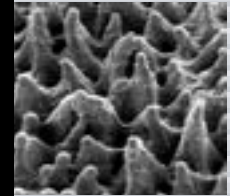
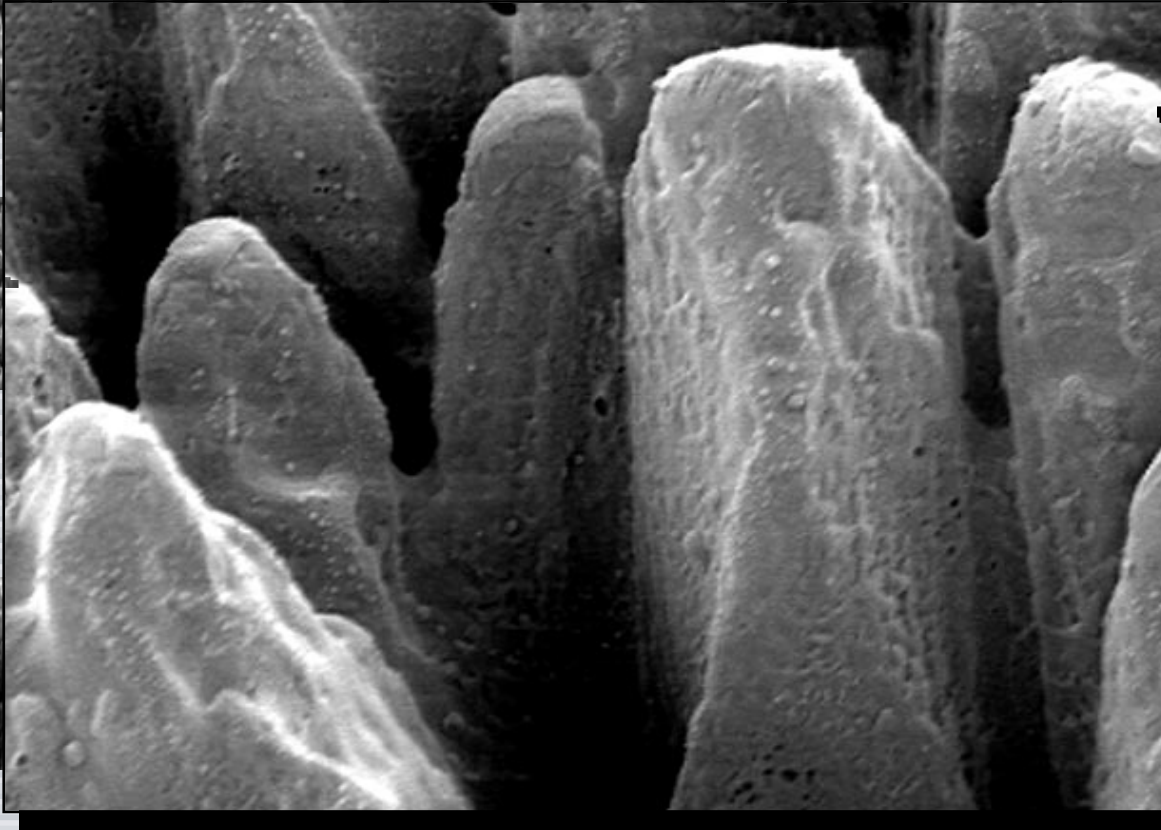
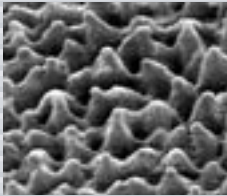
air

vacuum

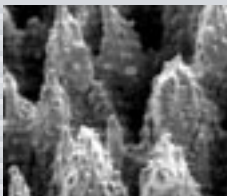
Si



Ti



Only in SF₆



Ge

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