Ultrafast laser microstructuring of silicon for optoelectronic devices

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Tsing-Hua Her
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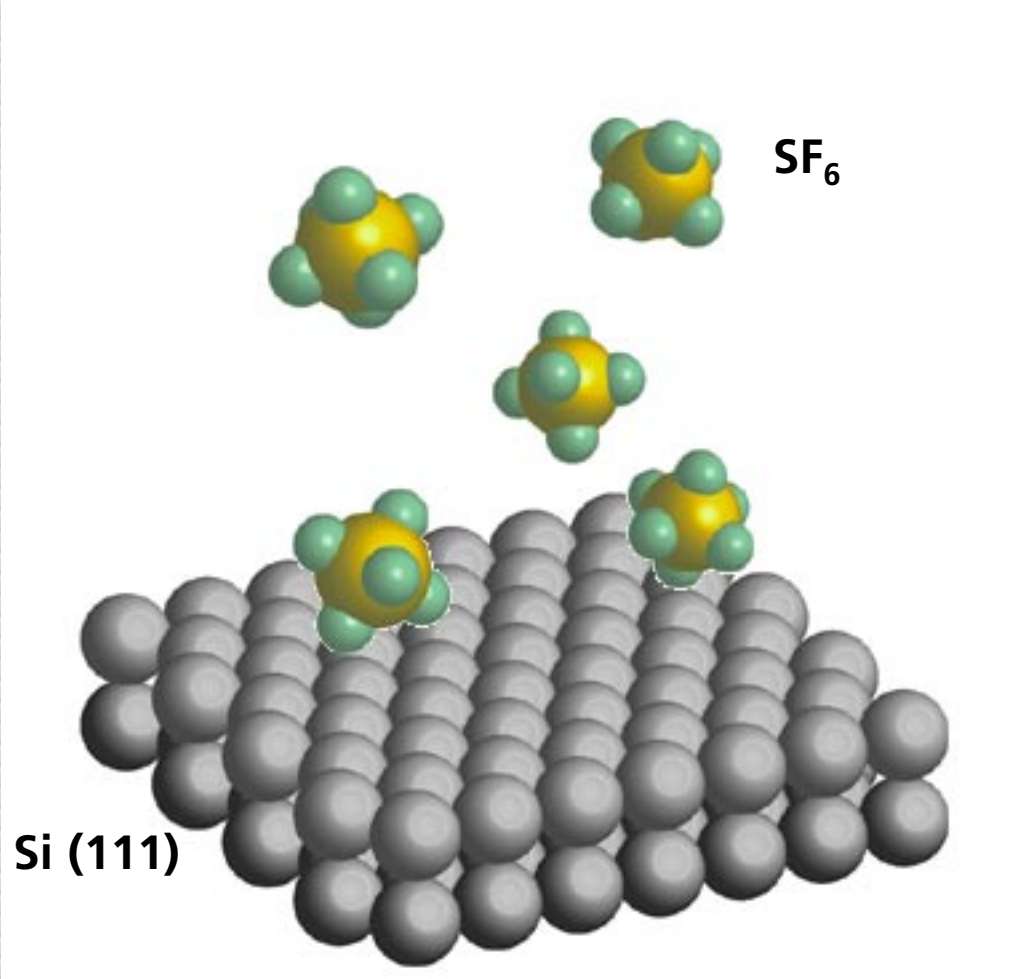
Rebecca Younkin
Catherine Crouch
Meng Yan Shen
Li Zhao

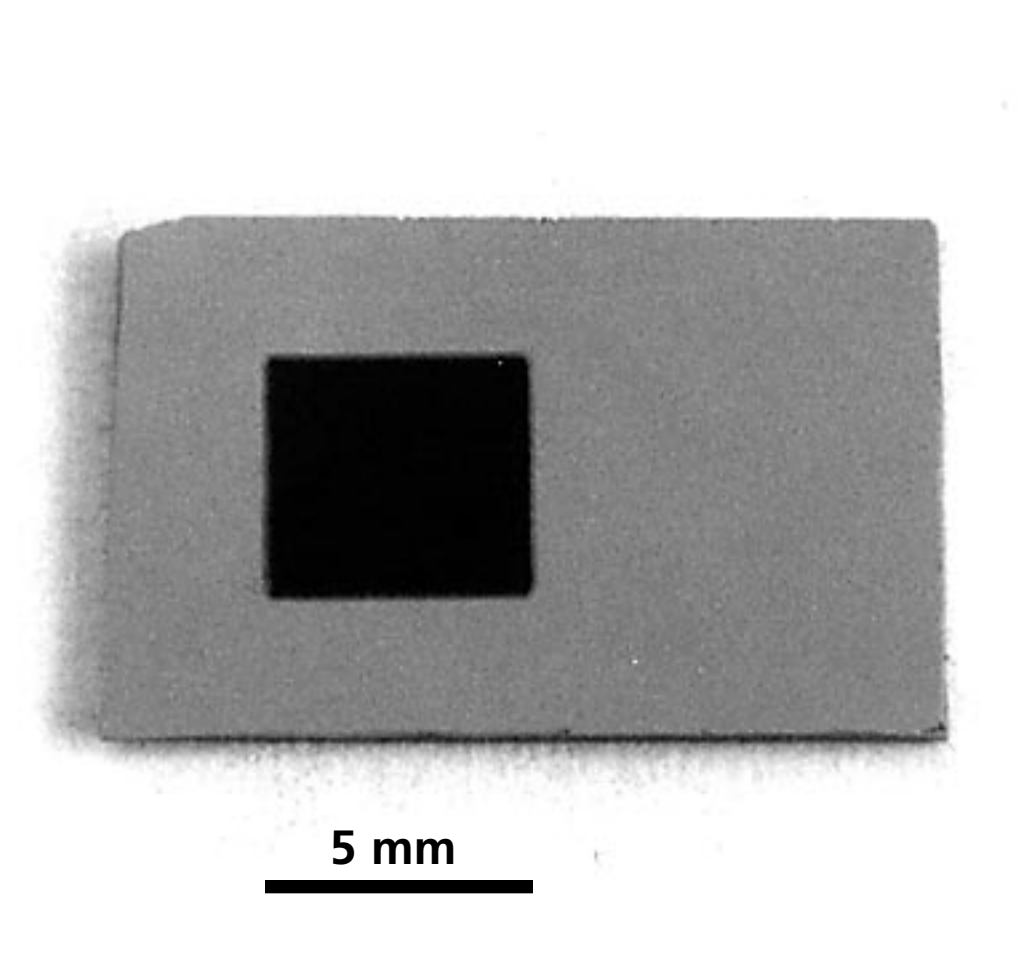
SPIE Photonics West
San Jose, 24 January 2002

Introduction



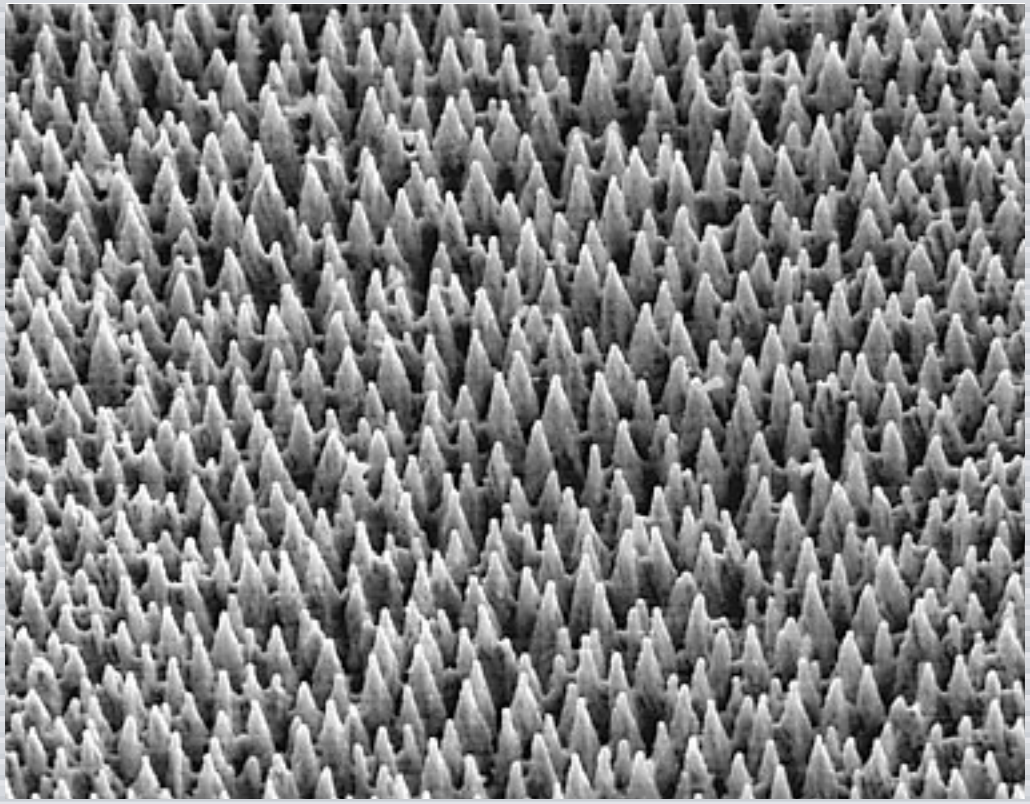
irradiate with 100-fs 10 kJ/m^2 pulses

Introduction



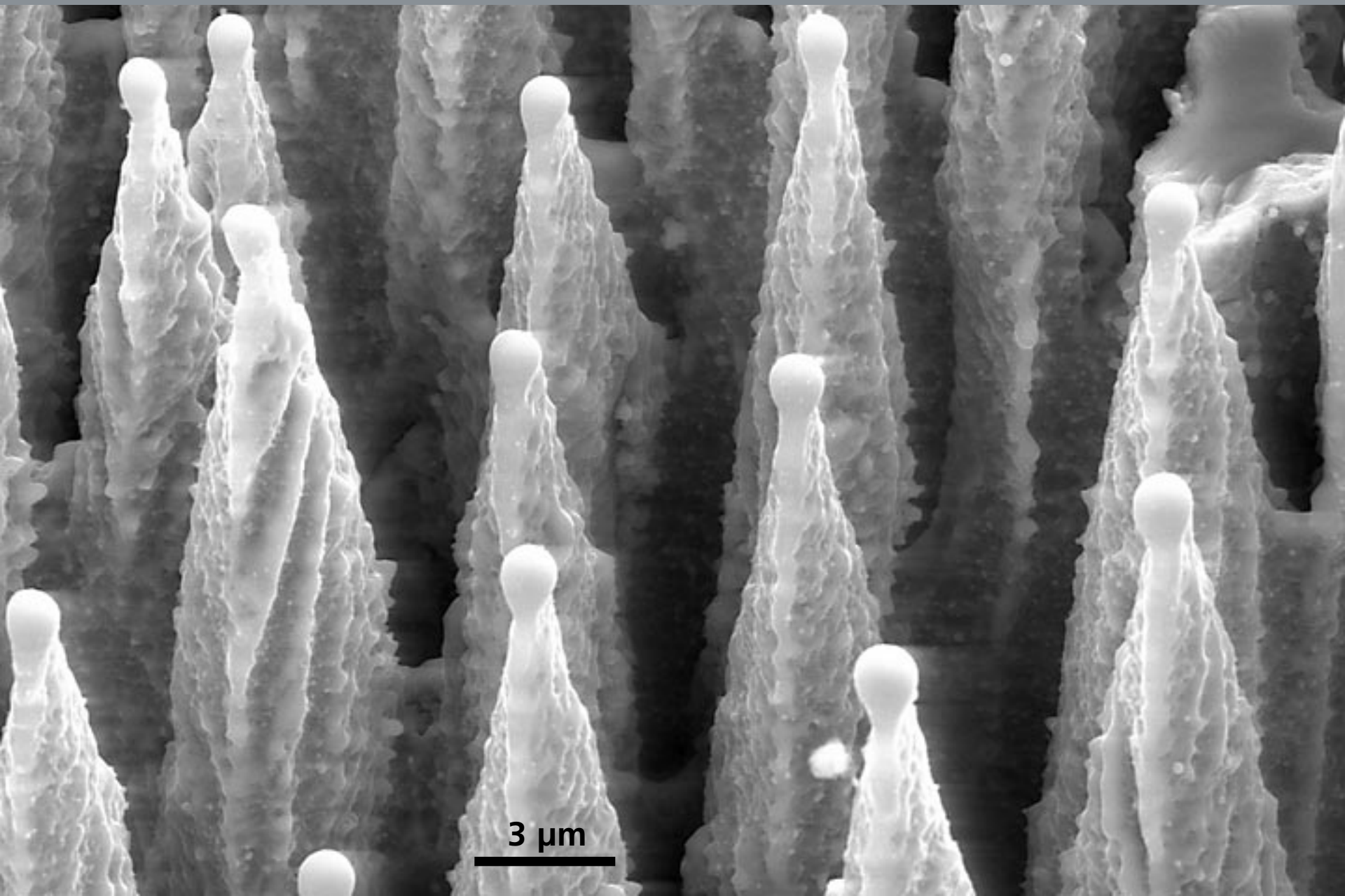
“black silicon”

Introduction



20 μm

Introduction



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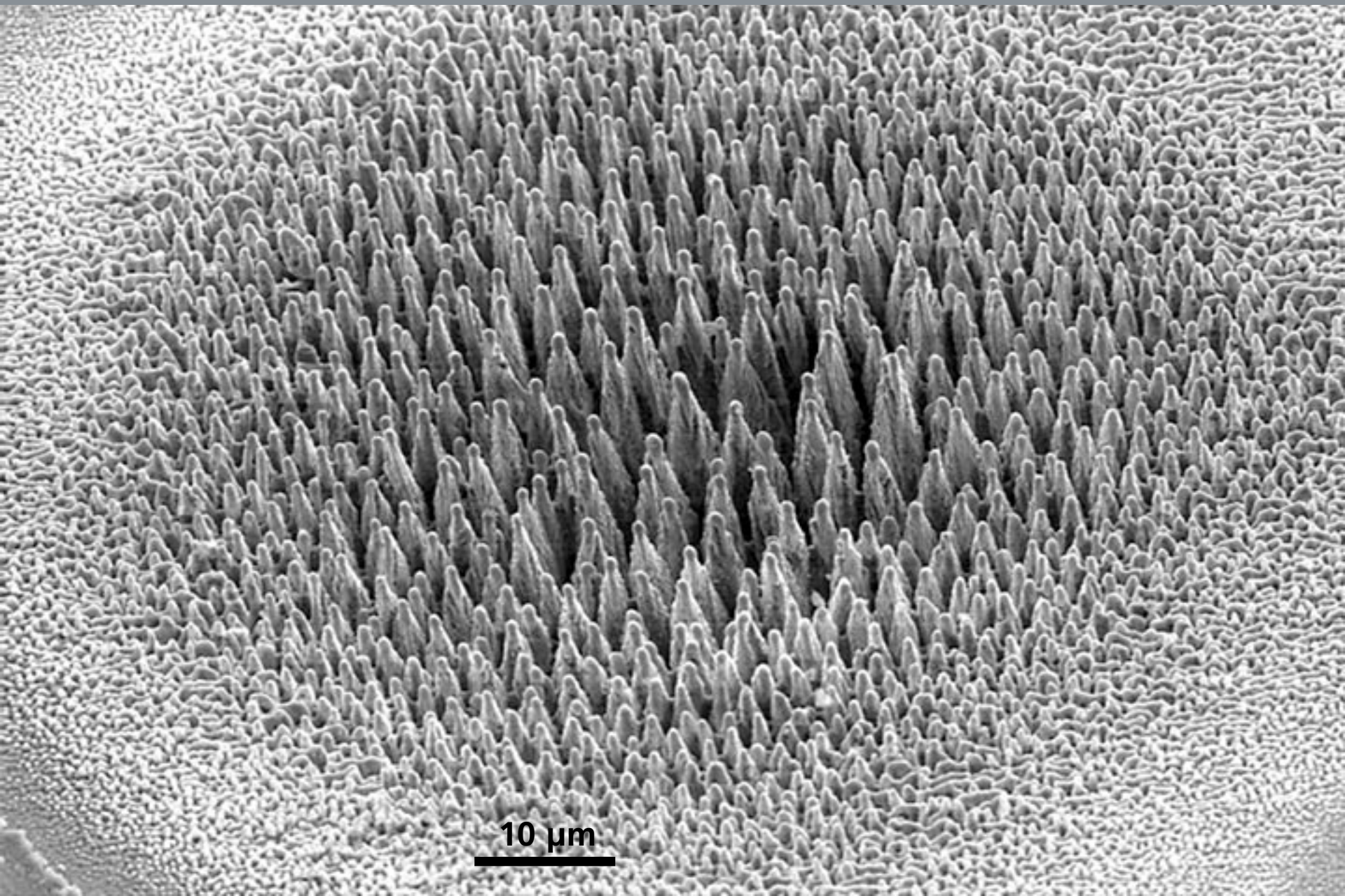

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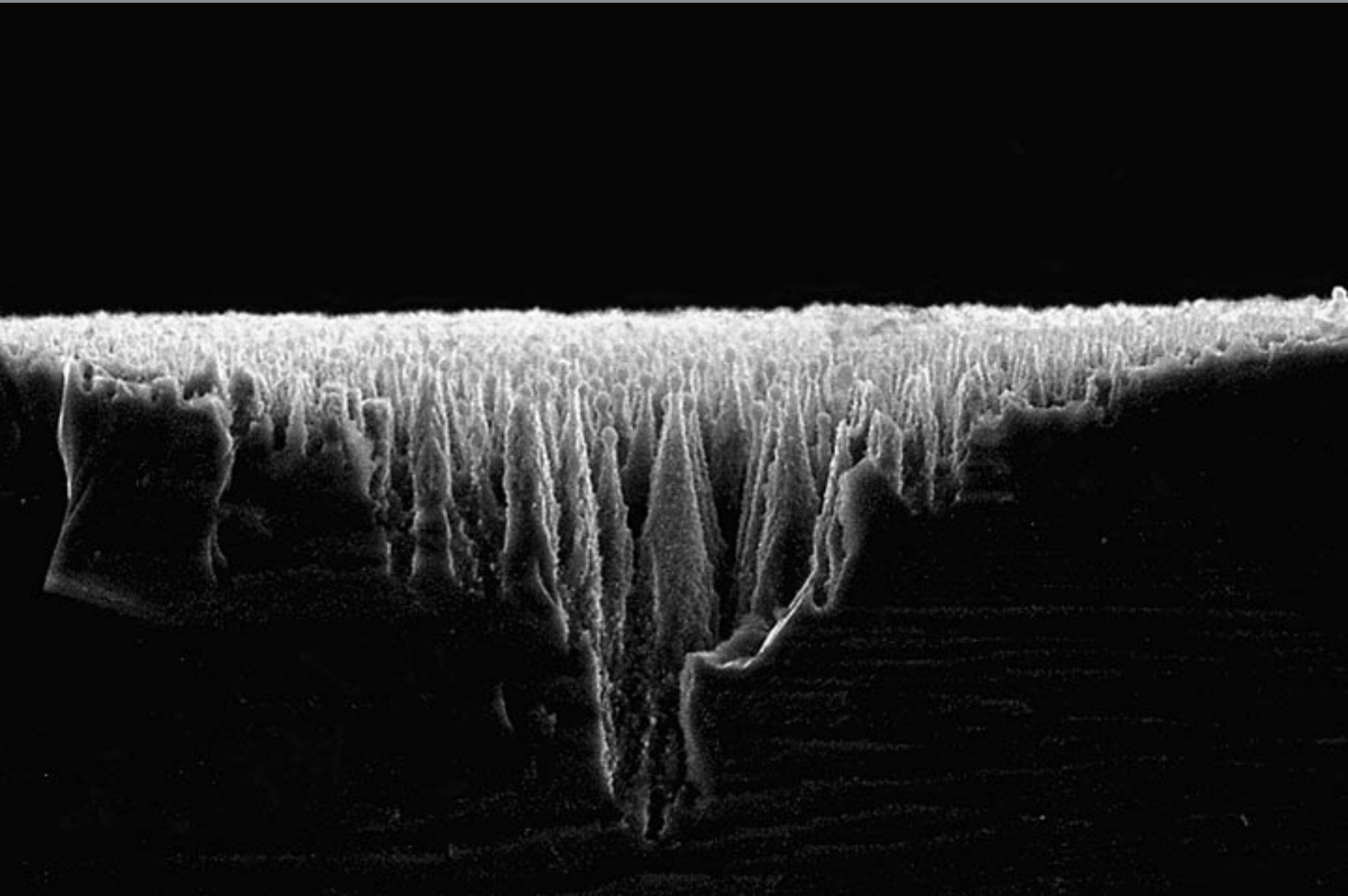


Introduction

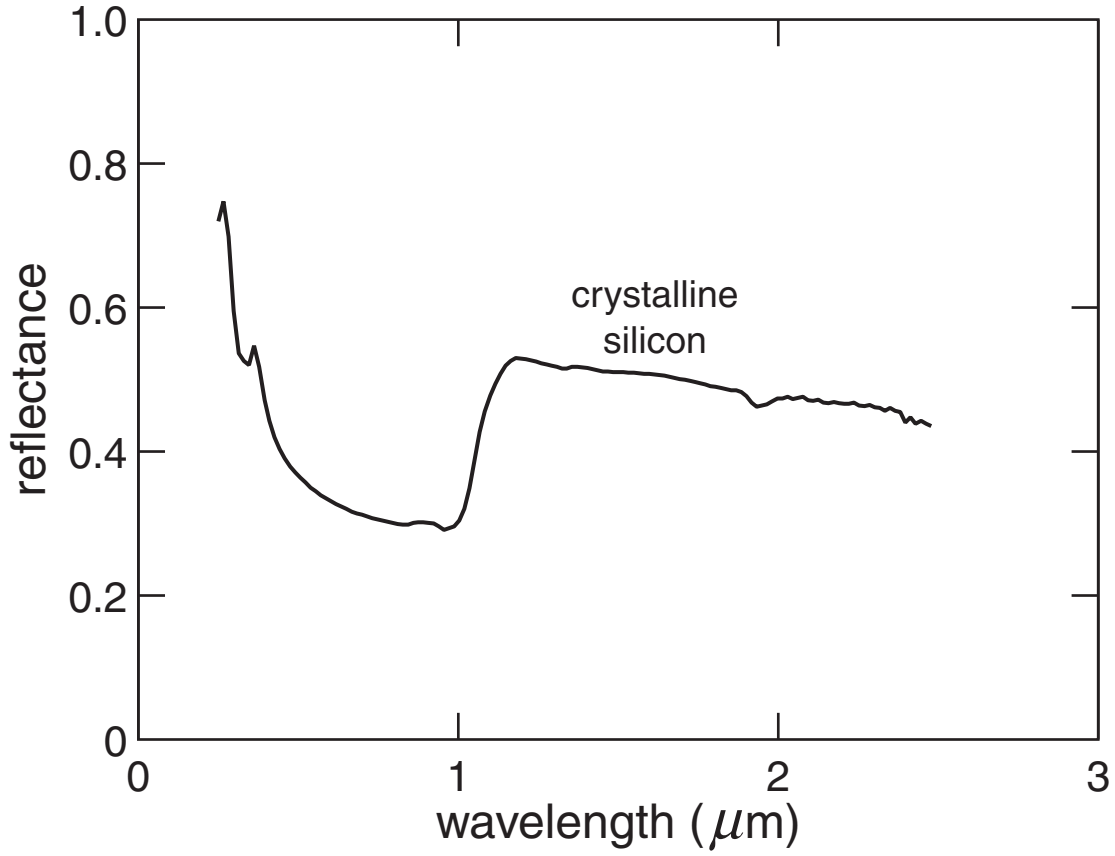
Introduction

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

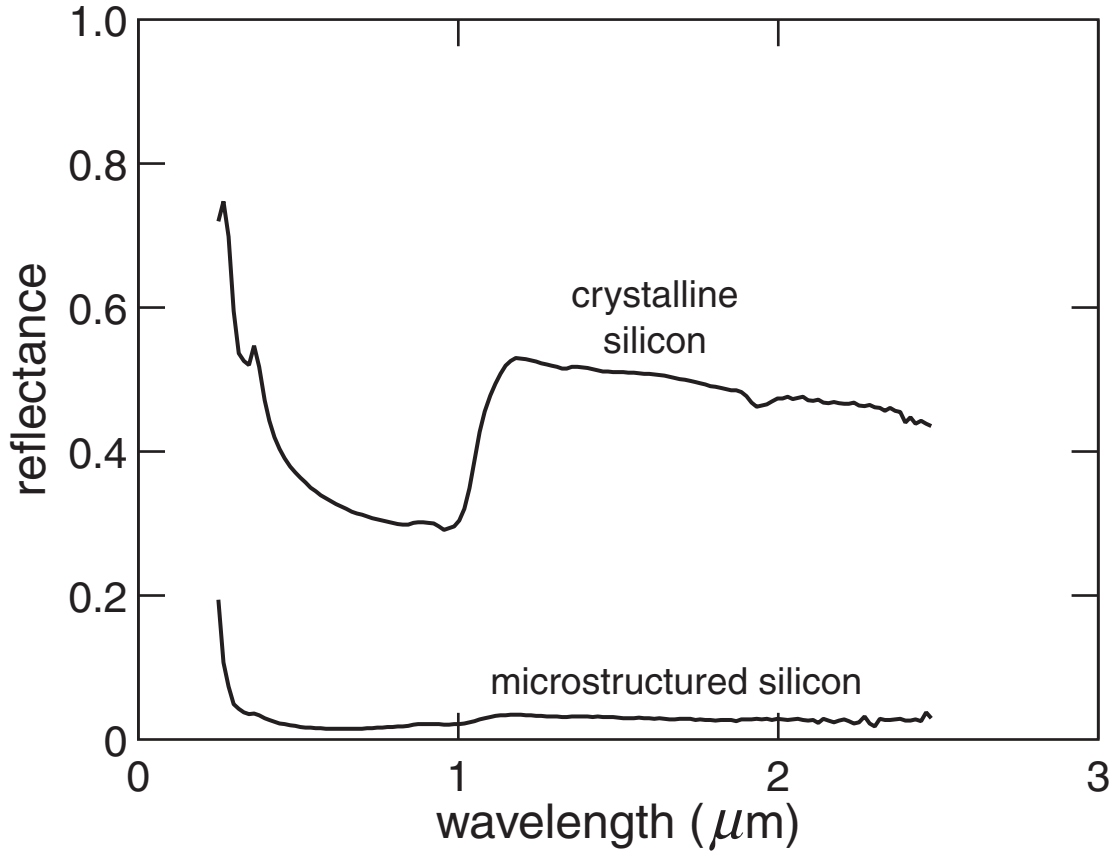
Outline

- Properties
- Structural and chemical analysis
- Outlook

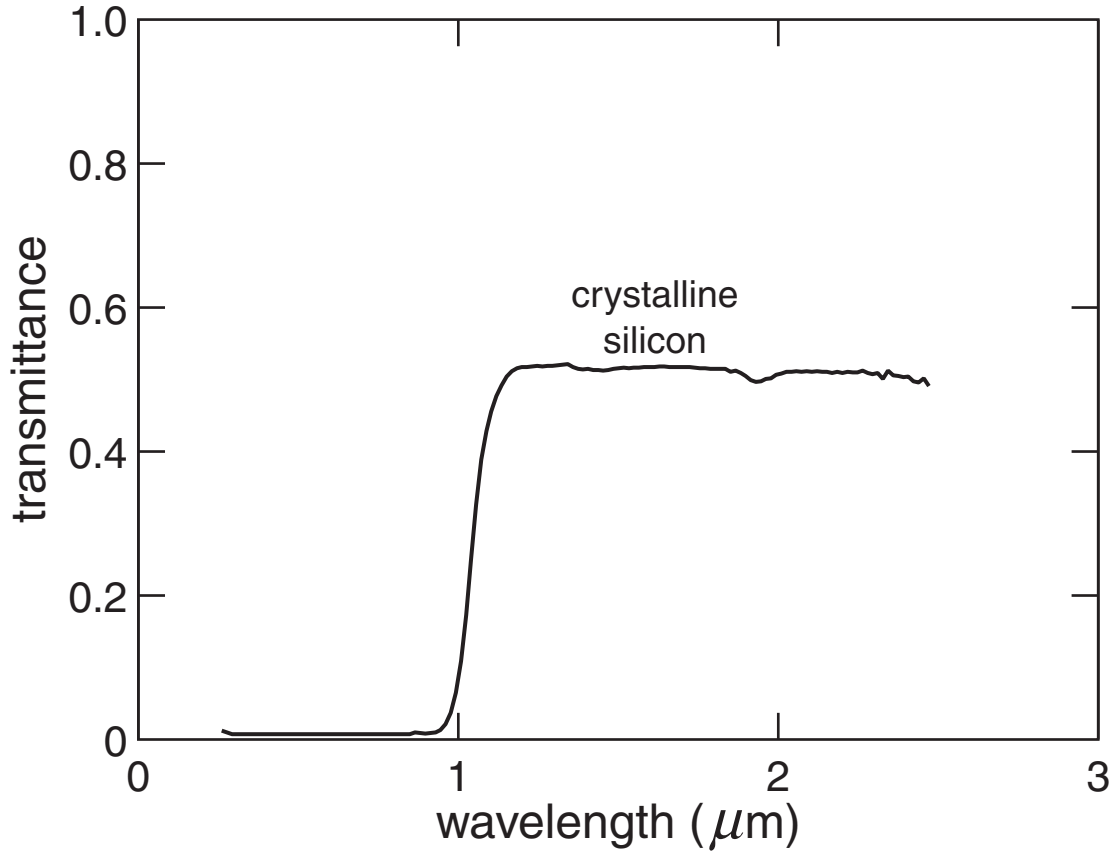
reflectance (integrating sphere)



reflectance (integrating sphere)



transmittance (integrating sphere)



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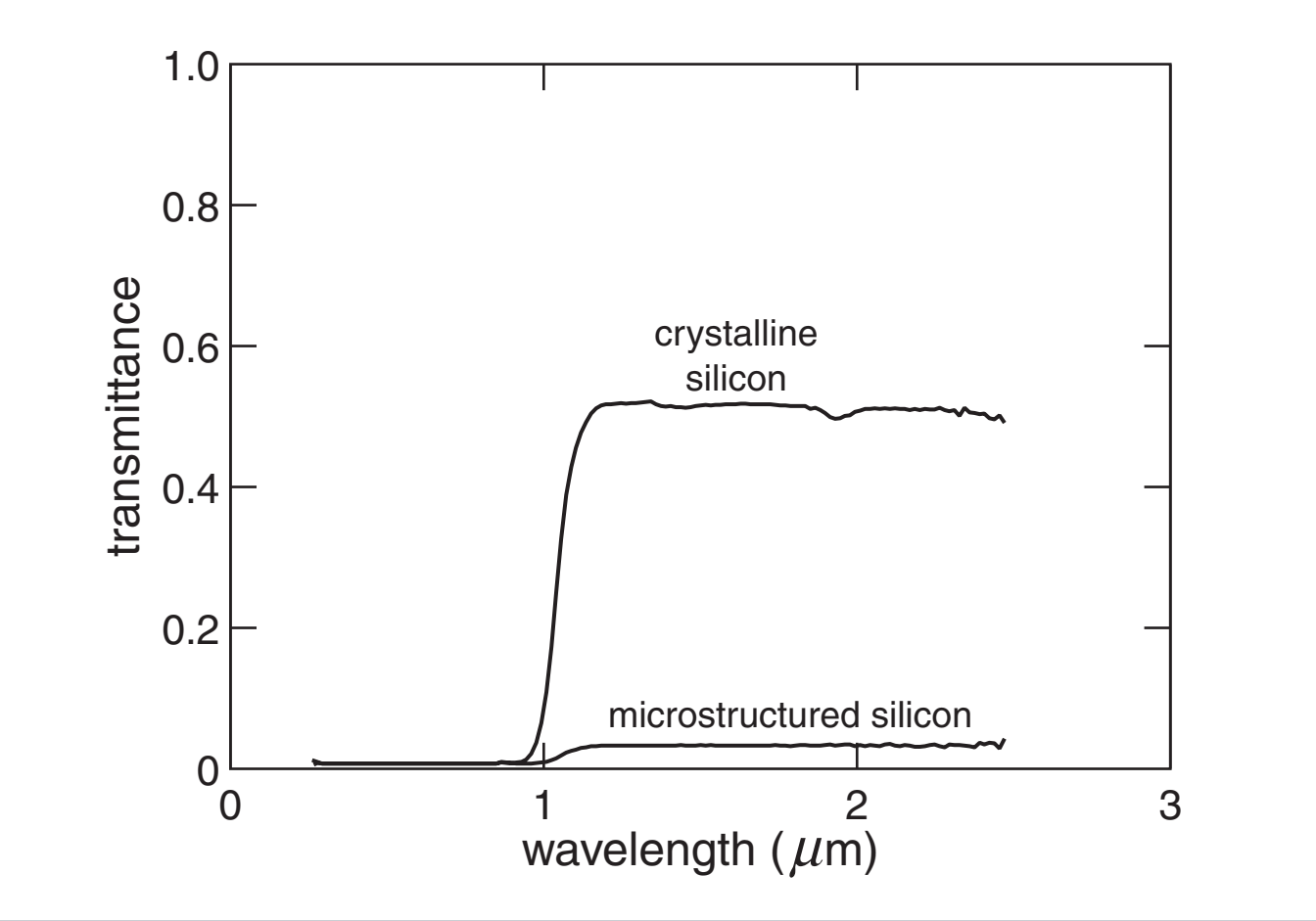
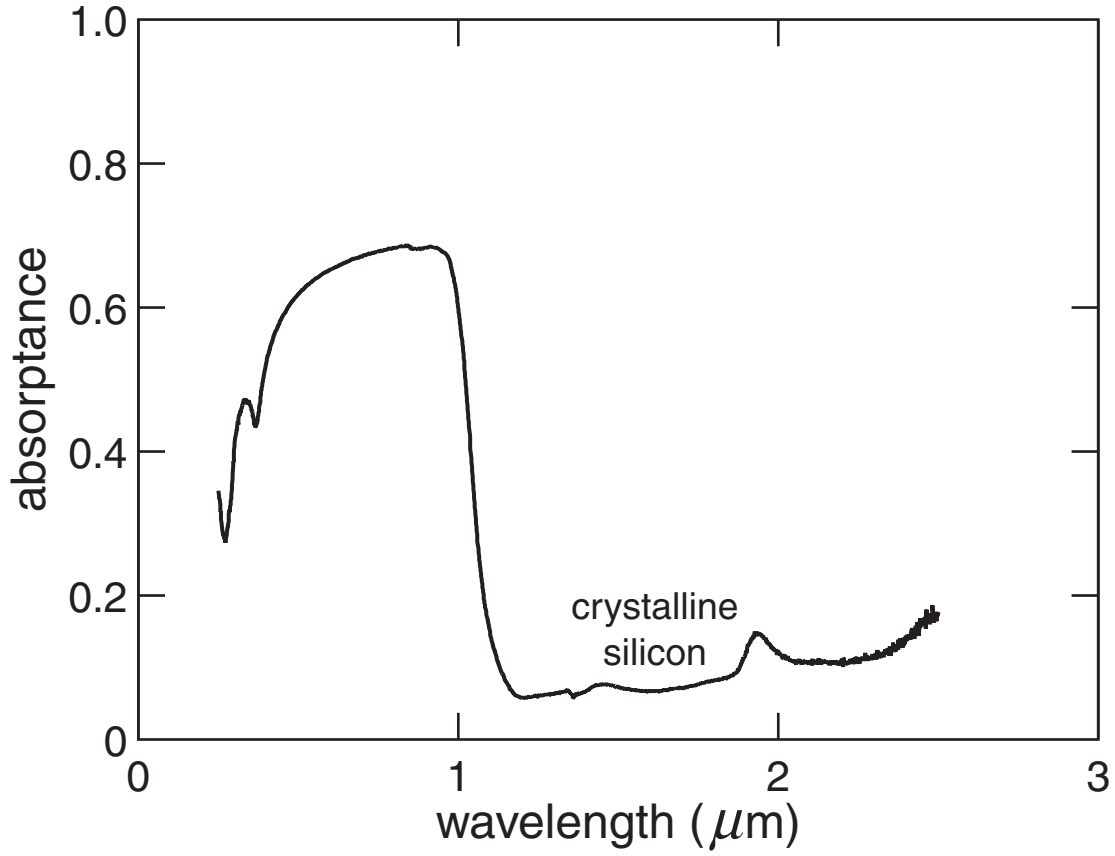
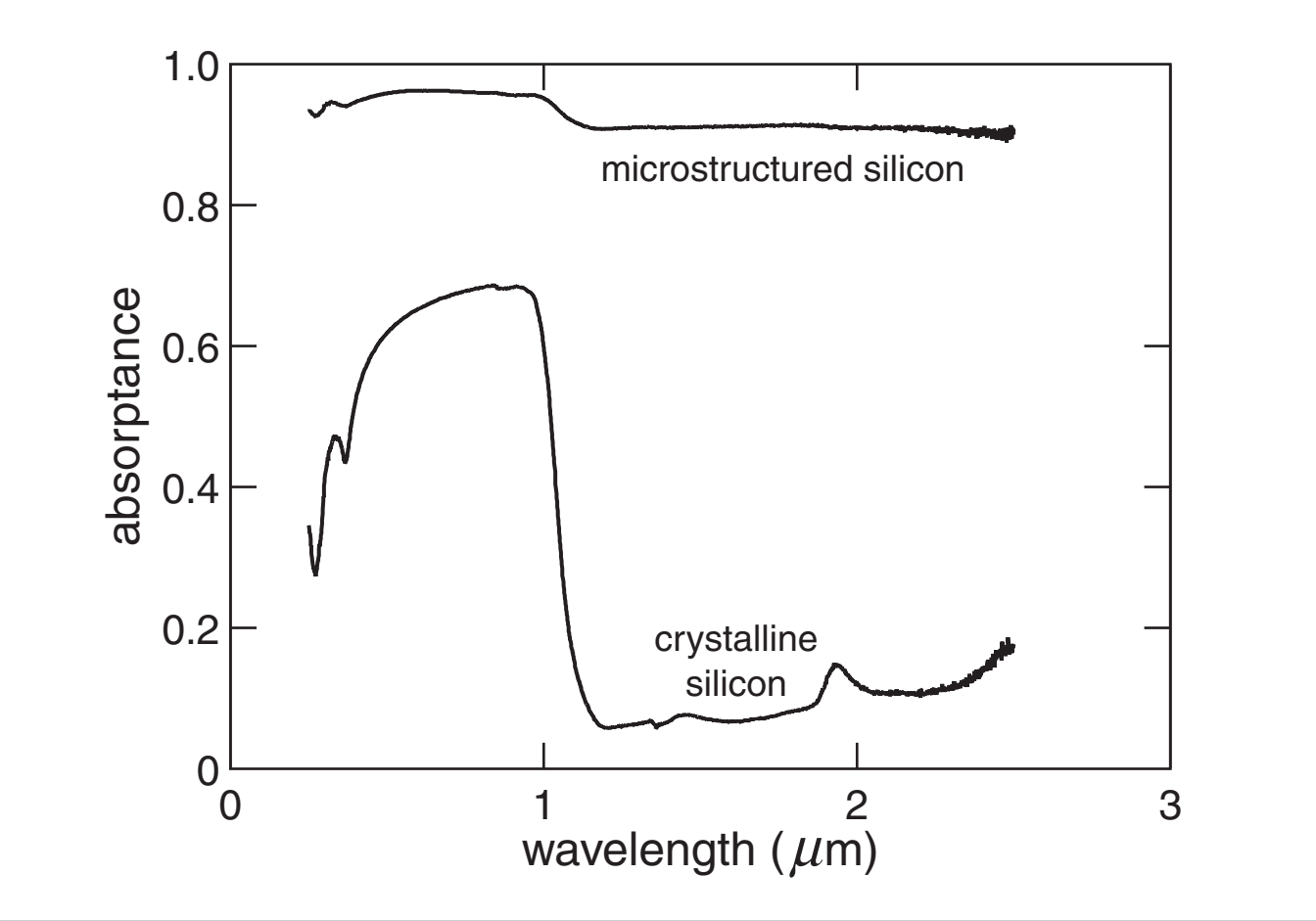


absorptance (1 – *R* – *T*)



Properties

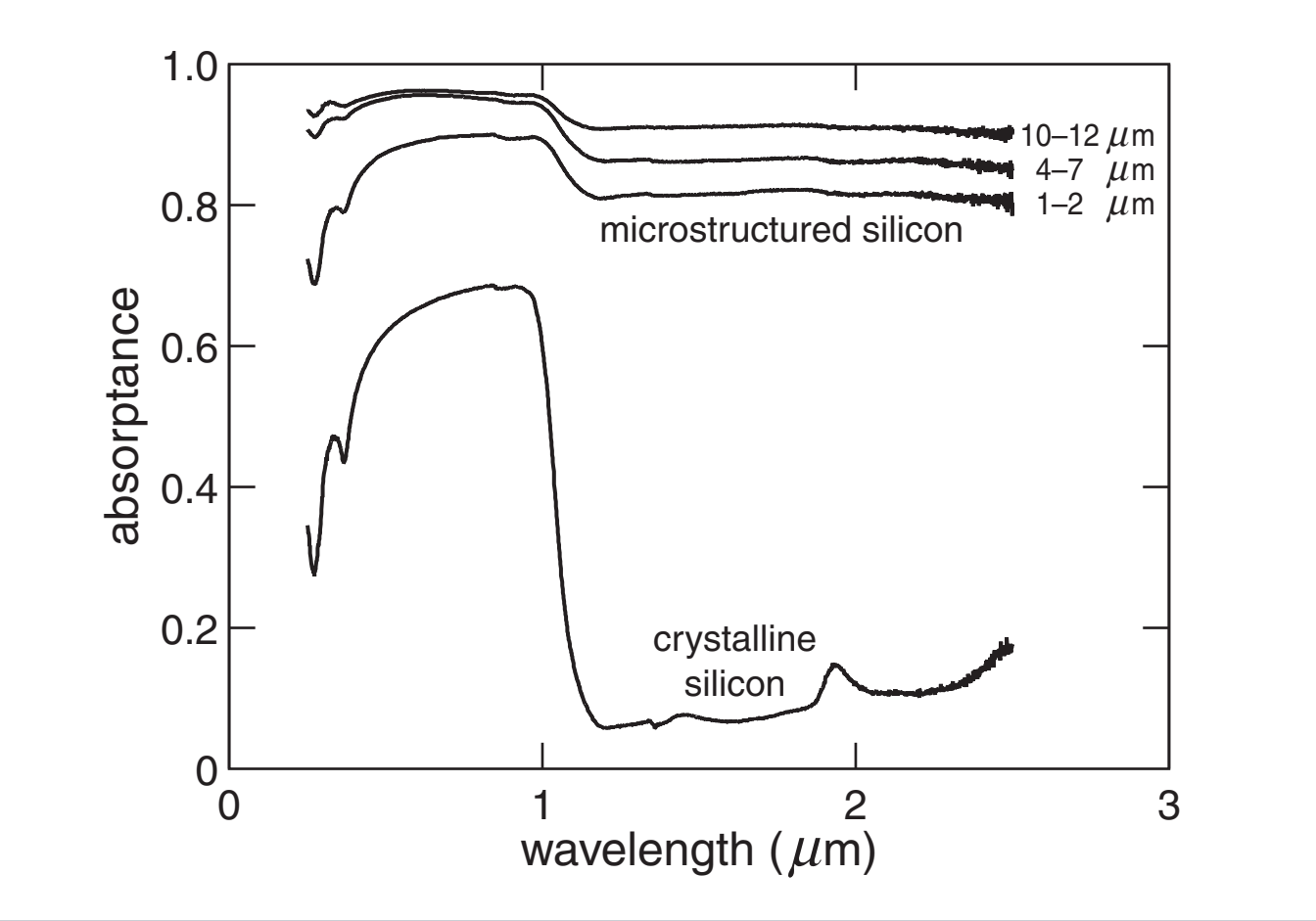
absorptance (1 – *R* – *T*)



Appl. Phys. Lett. **78**, 1850 (2001)

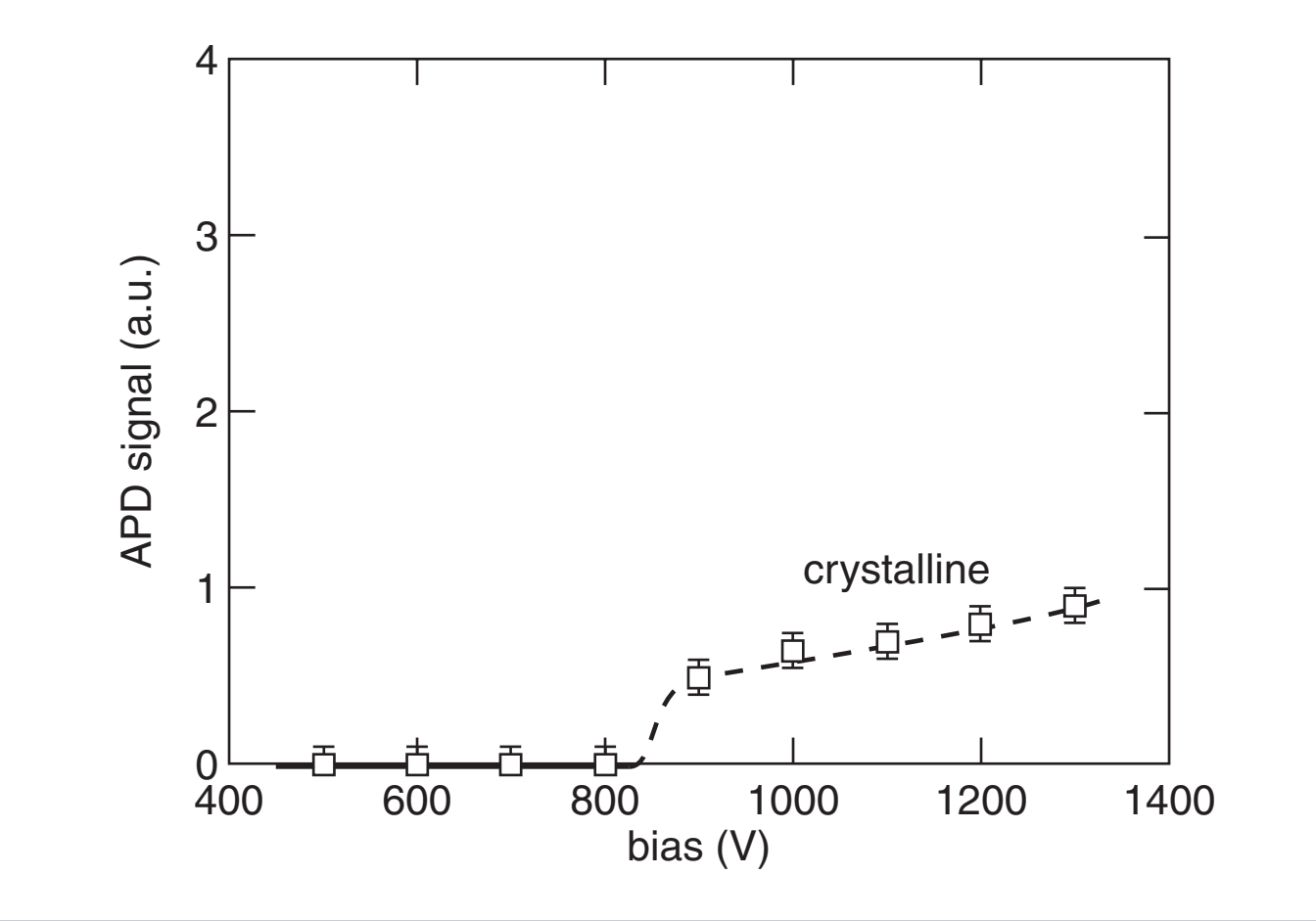
Properties

absorptance (1 – *R* – *T*)



Appl. Phys. Lett. **78,** 1850 (2001)

avalanche photodiode response at 1.3 μm



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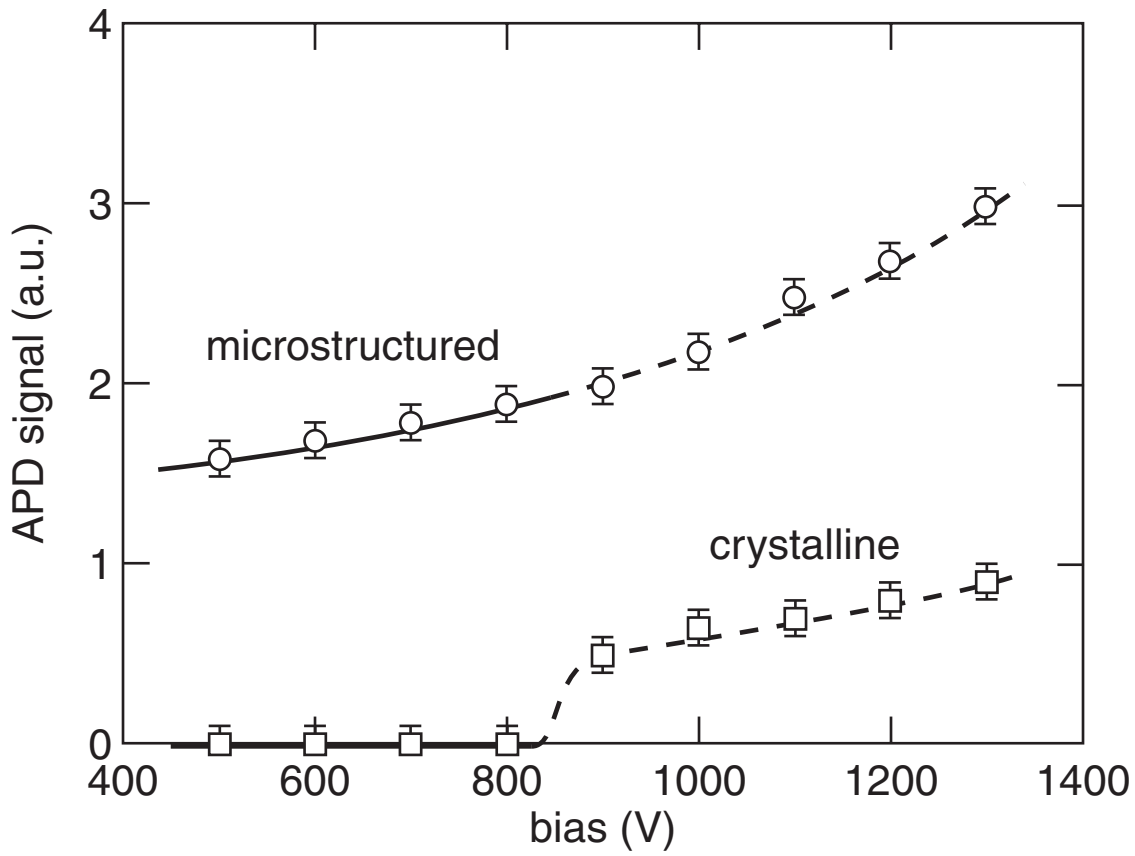


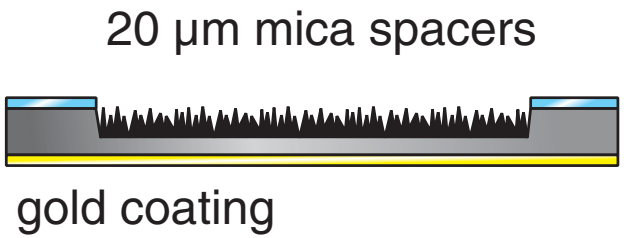
Appl. Phys. Lett. **78, 1850 (2001)**

field emission setup

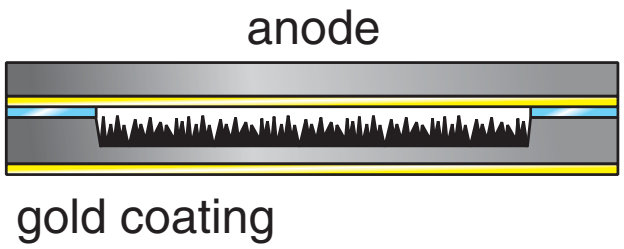
field emission setup

gold coating

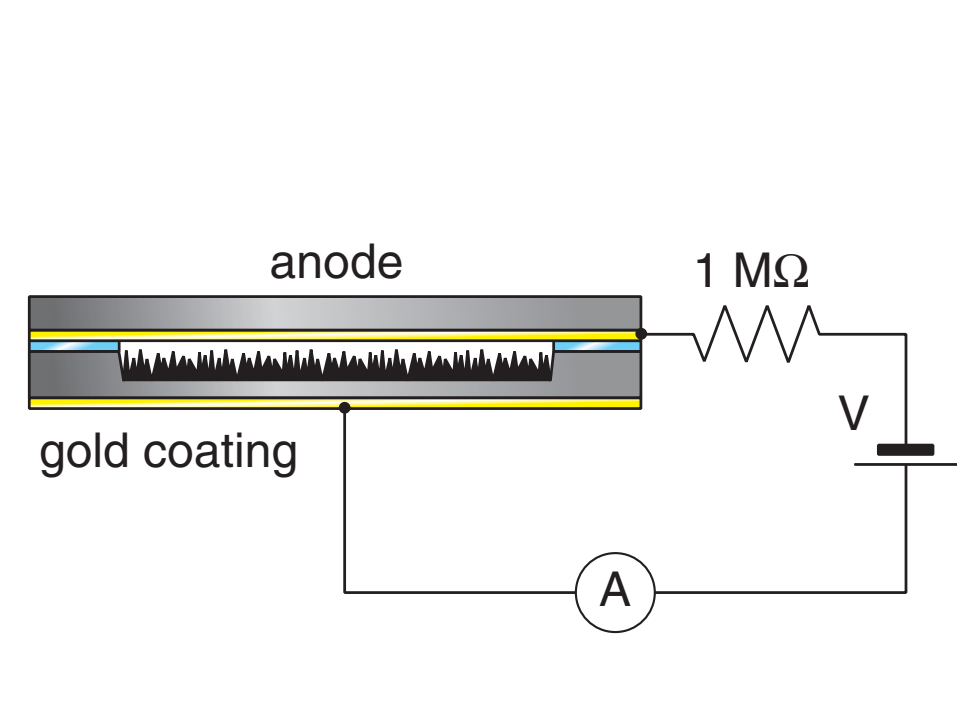
field emission setup



field emission setup



field emission setup



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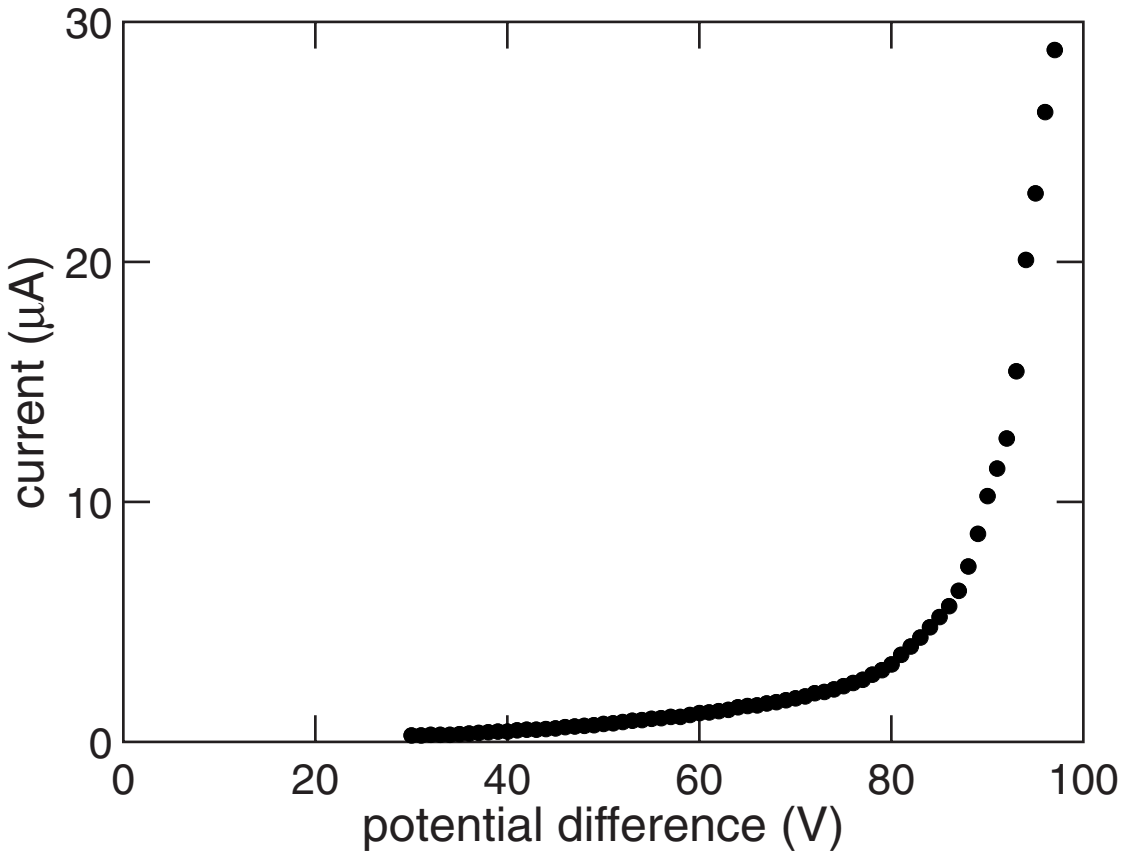

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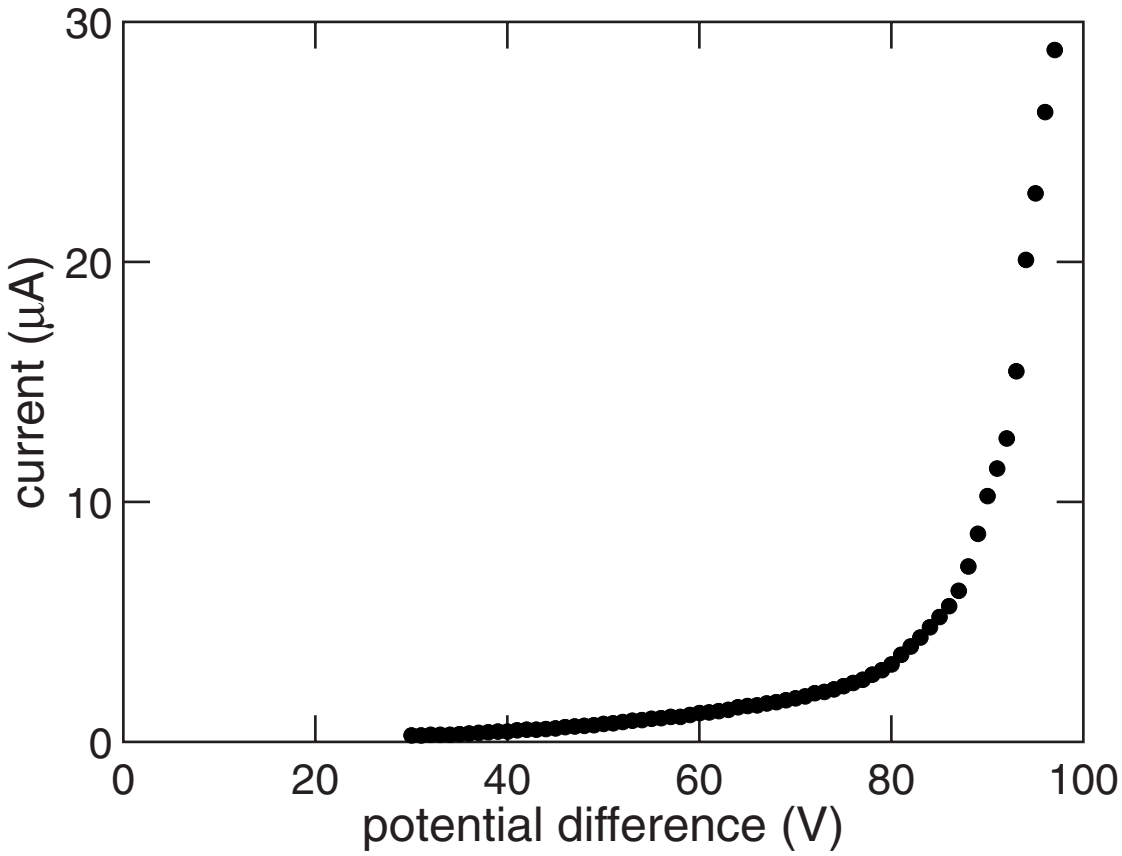
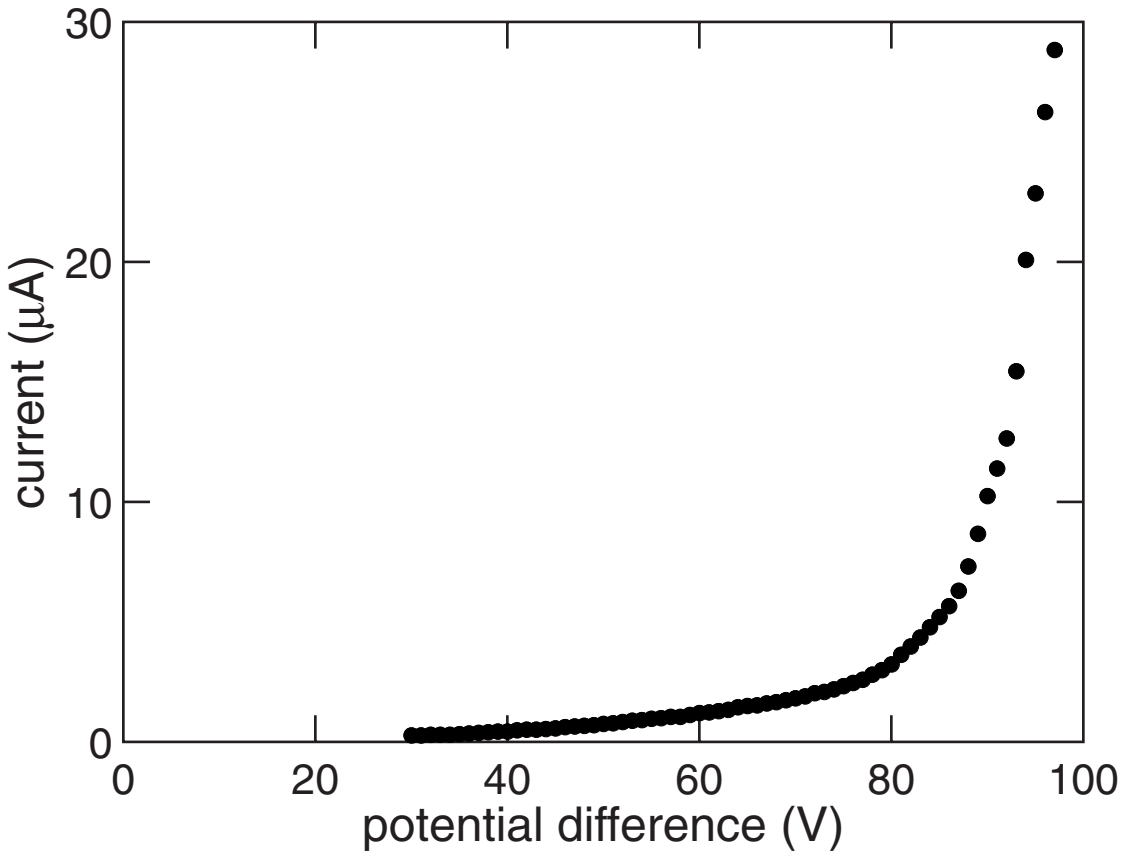


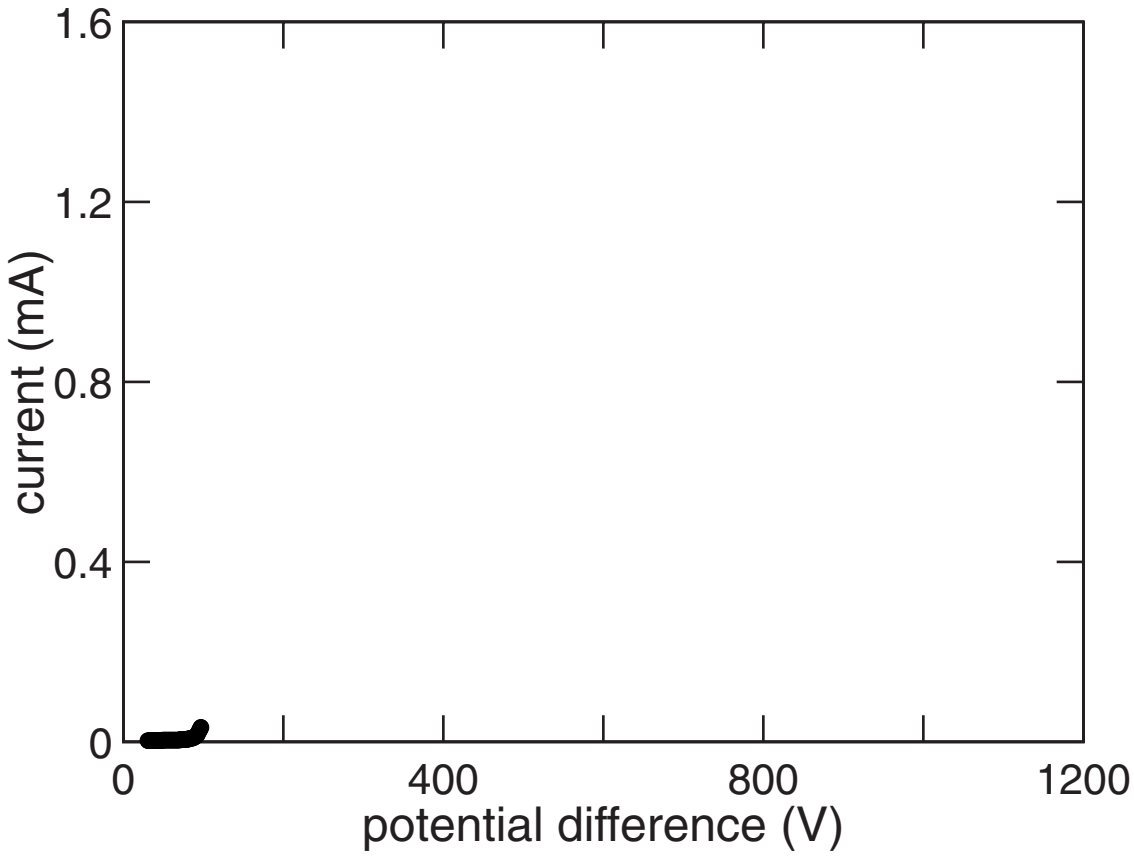
turn-on field (1 μA/cm^2): 1.2 V/μm

Properties

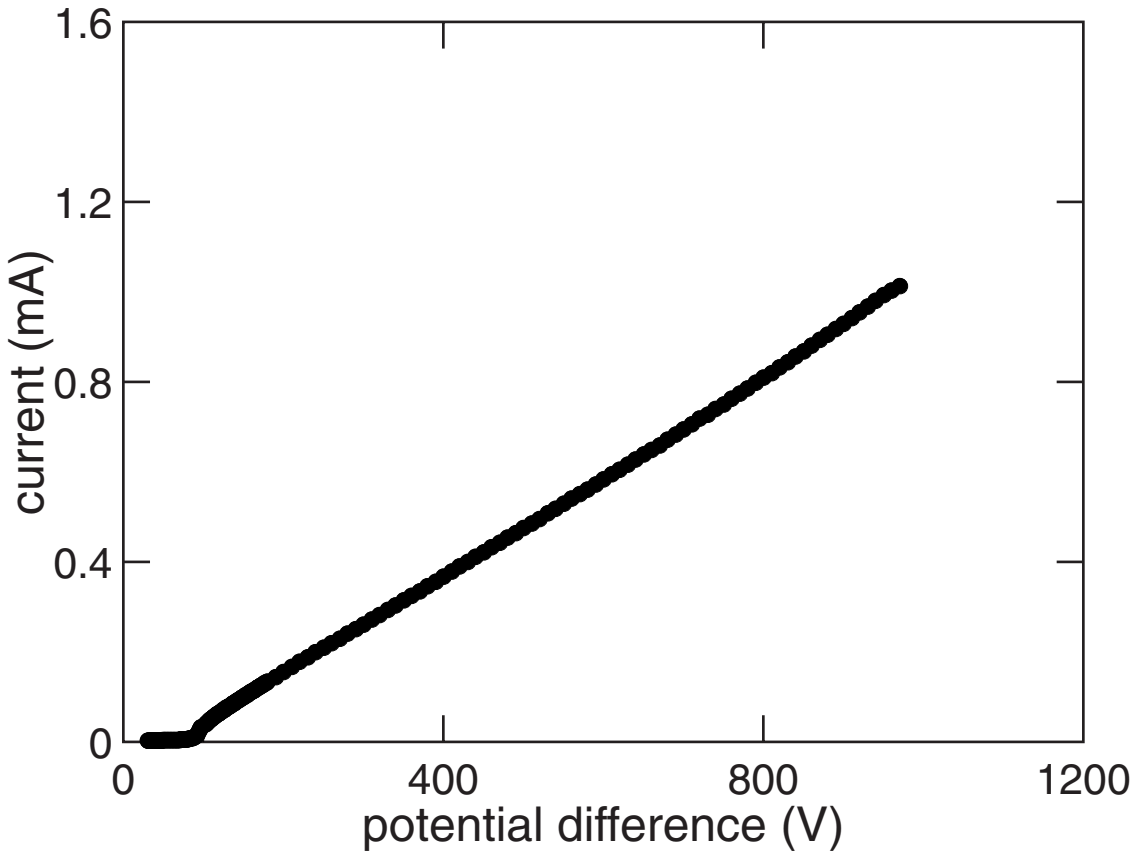


threshold field (10 μA/cm^2): 2.1 V/μm

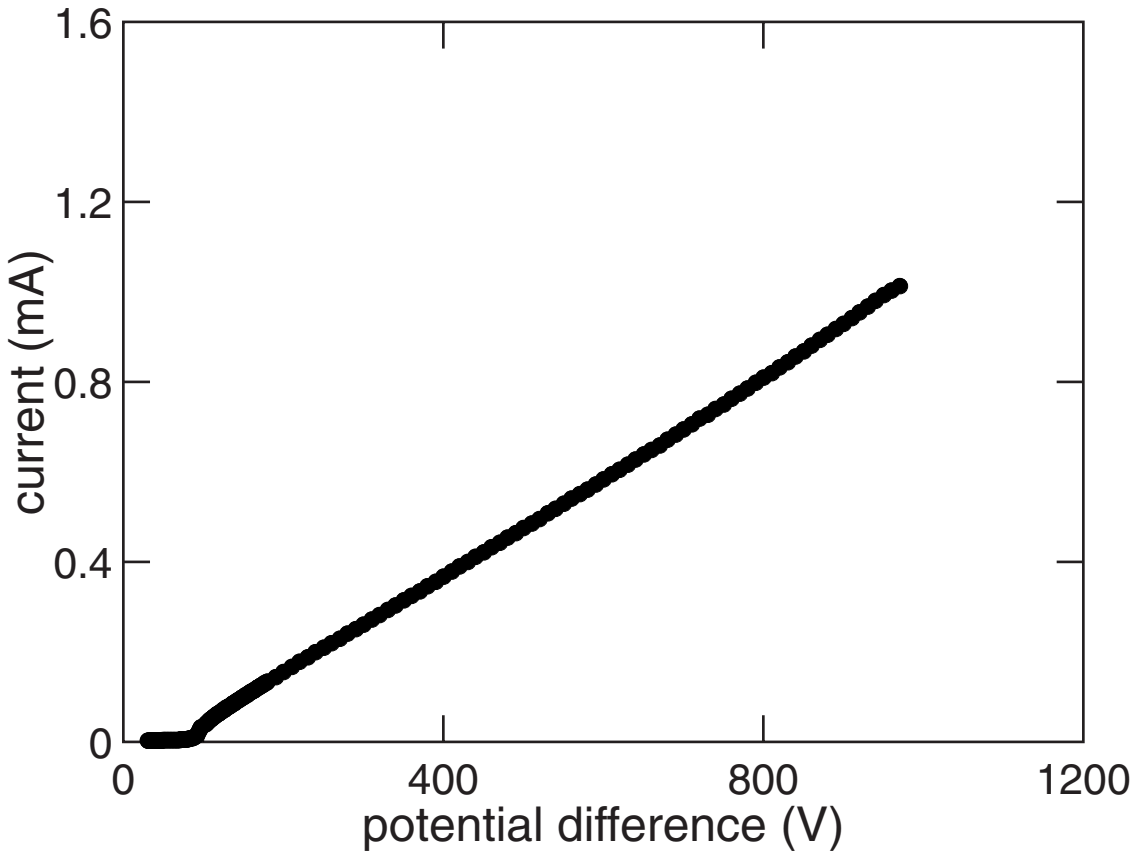
Properties



Properties



Properties



maximum current: 20 mA (4 mm^2 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

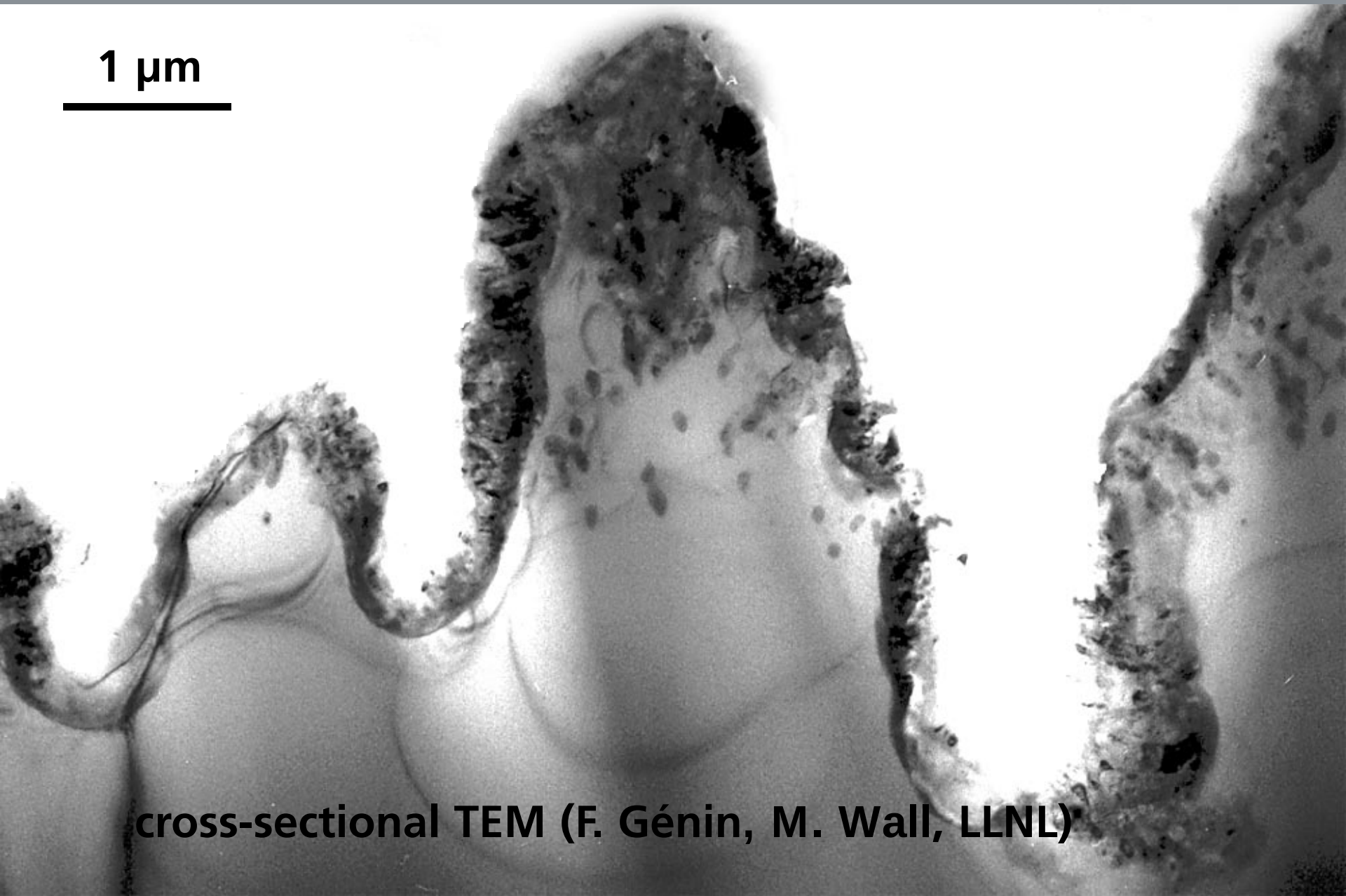
- **What causes these properties?**
- **Other gases?**

Structural and chemical analysis

Secondary ion mass spectrometry:

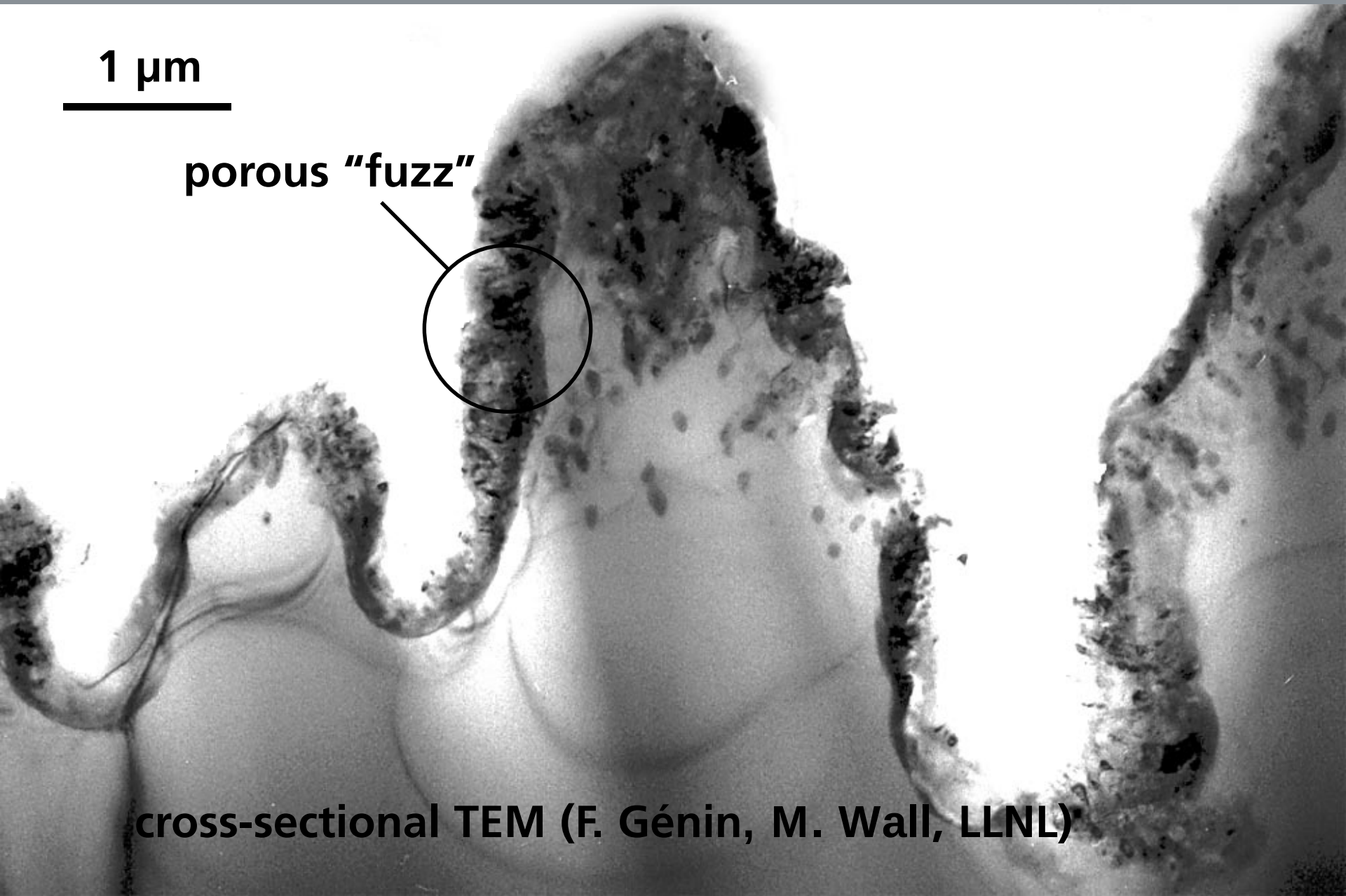
- 10^{20} cm^{-3} sulfur
- 10^{17} cm^{-3} fluorine

Structural and chemical analysis



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

Structural and chemical analysis



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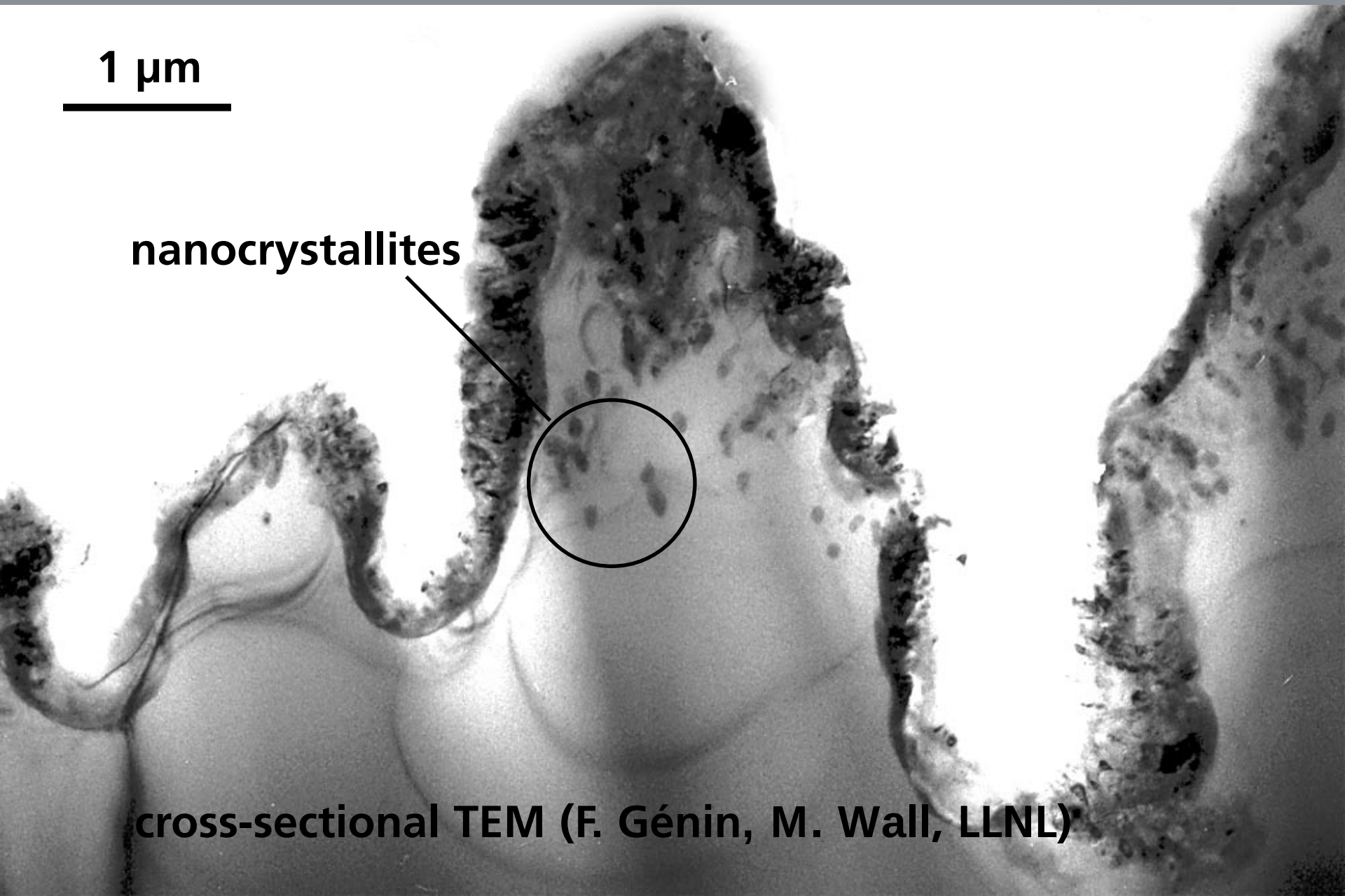

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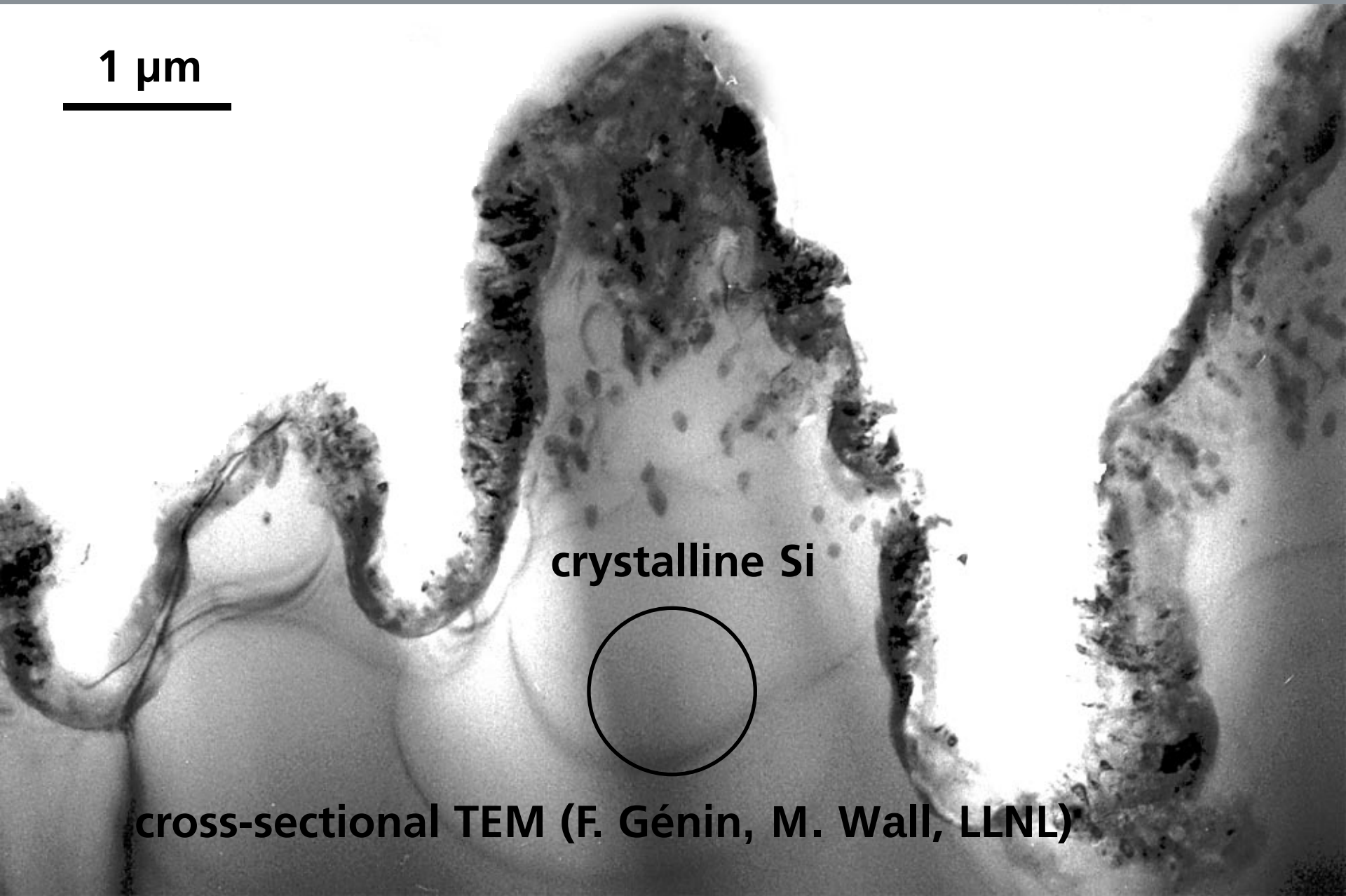

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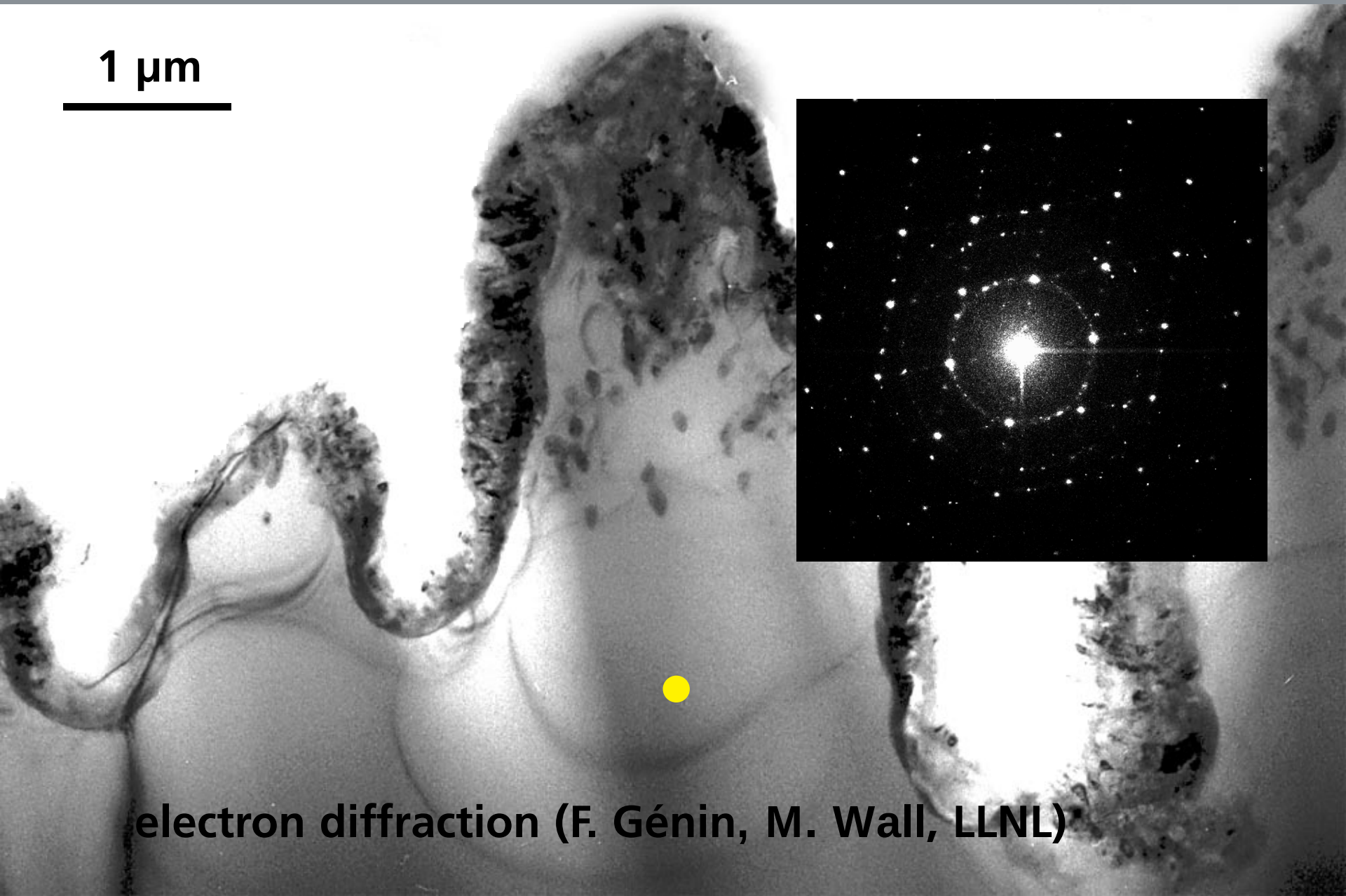
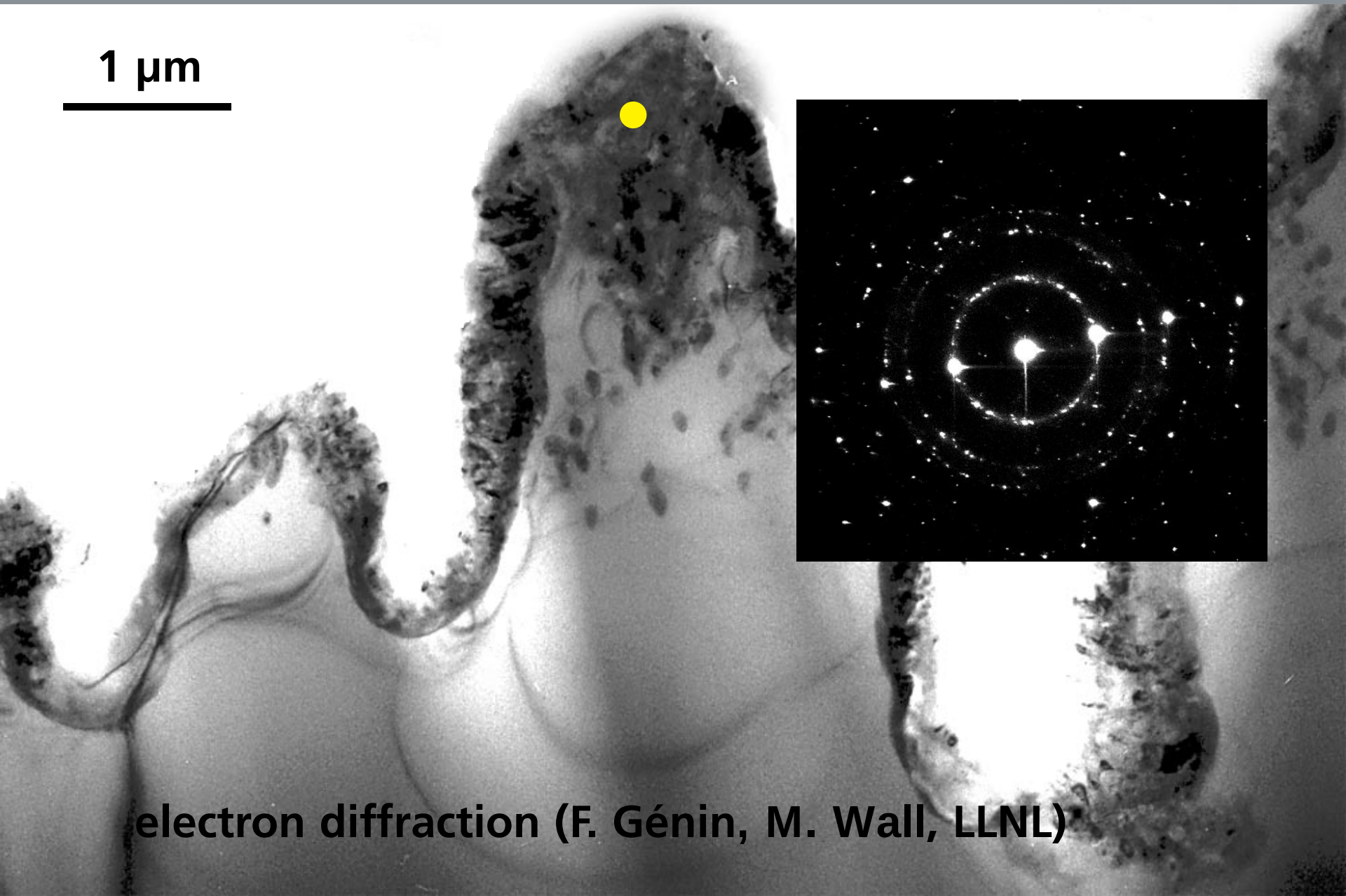


electron diffraction (F. Génin, M. Wall, LLNL)

Structural and chemical analysis



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

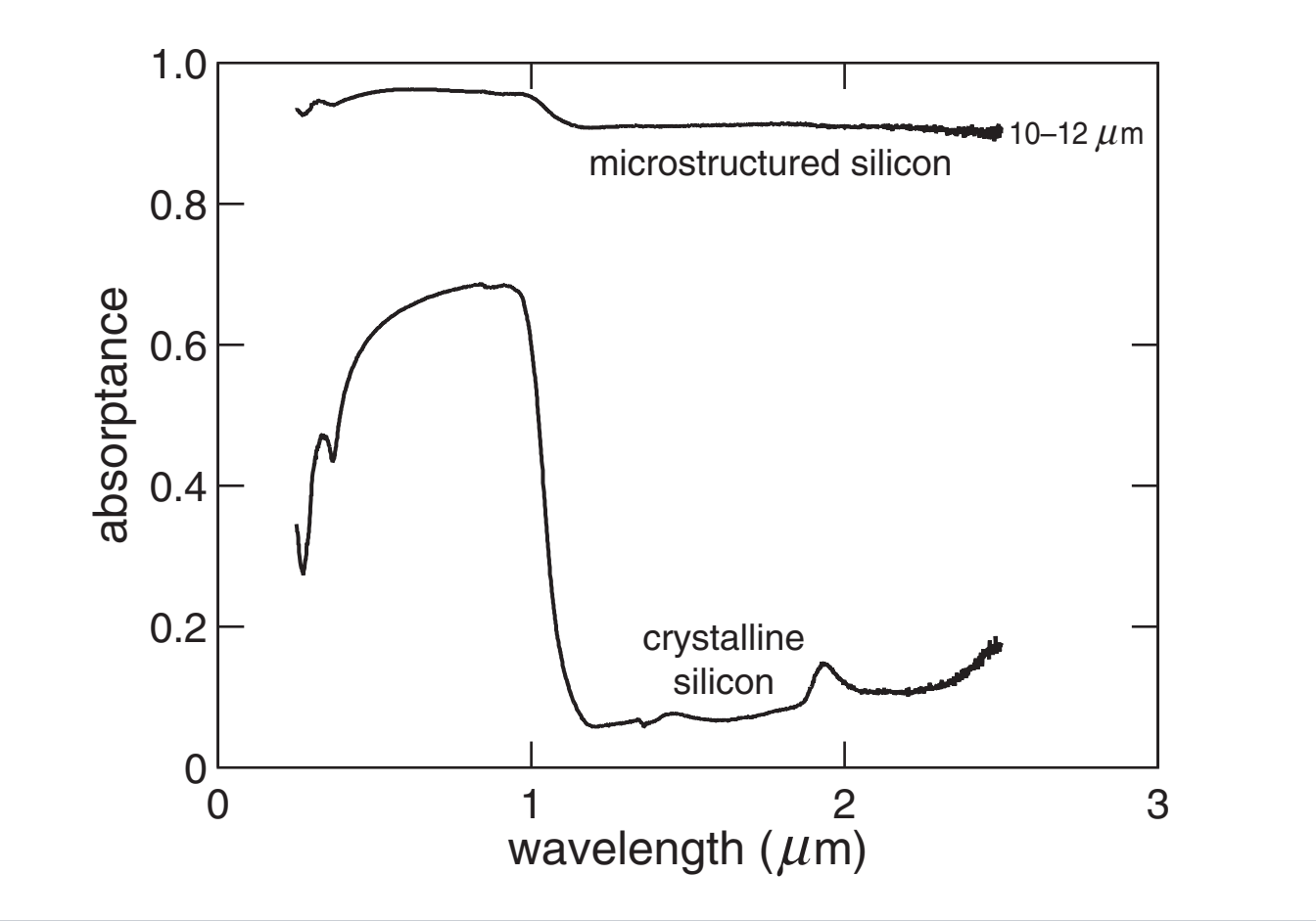
Structural and chemical analysis

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



Appl. Phys. Lett. **78,** 1850 (2001)

Structural and chemical analysis

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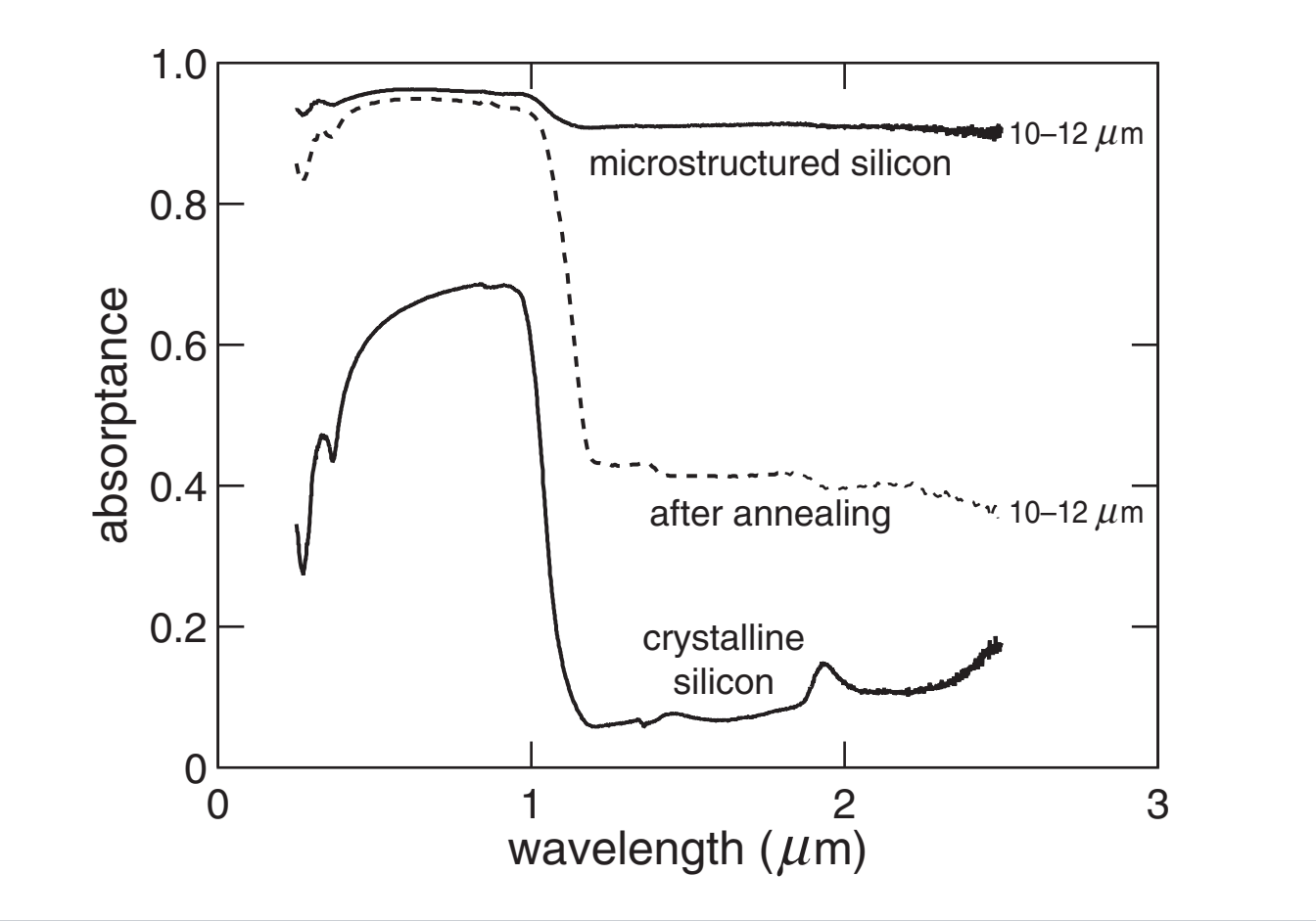

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Structural and chemical analysis

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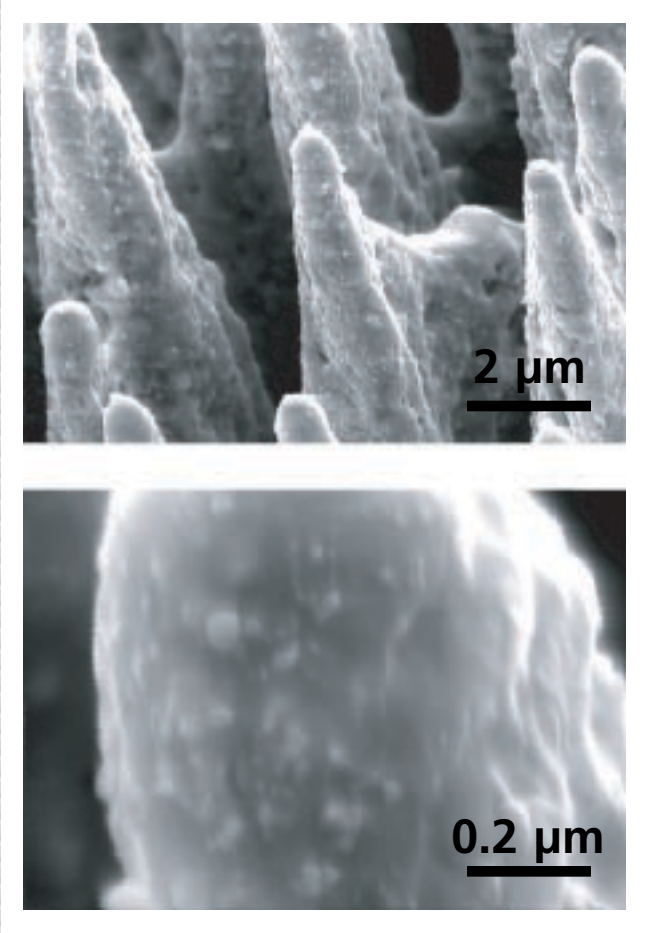

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Structural and chemical analysis

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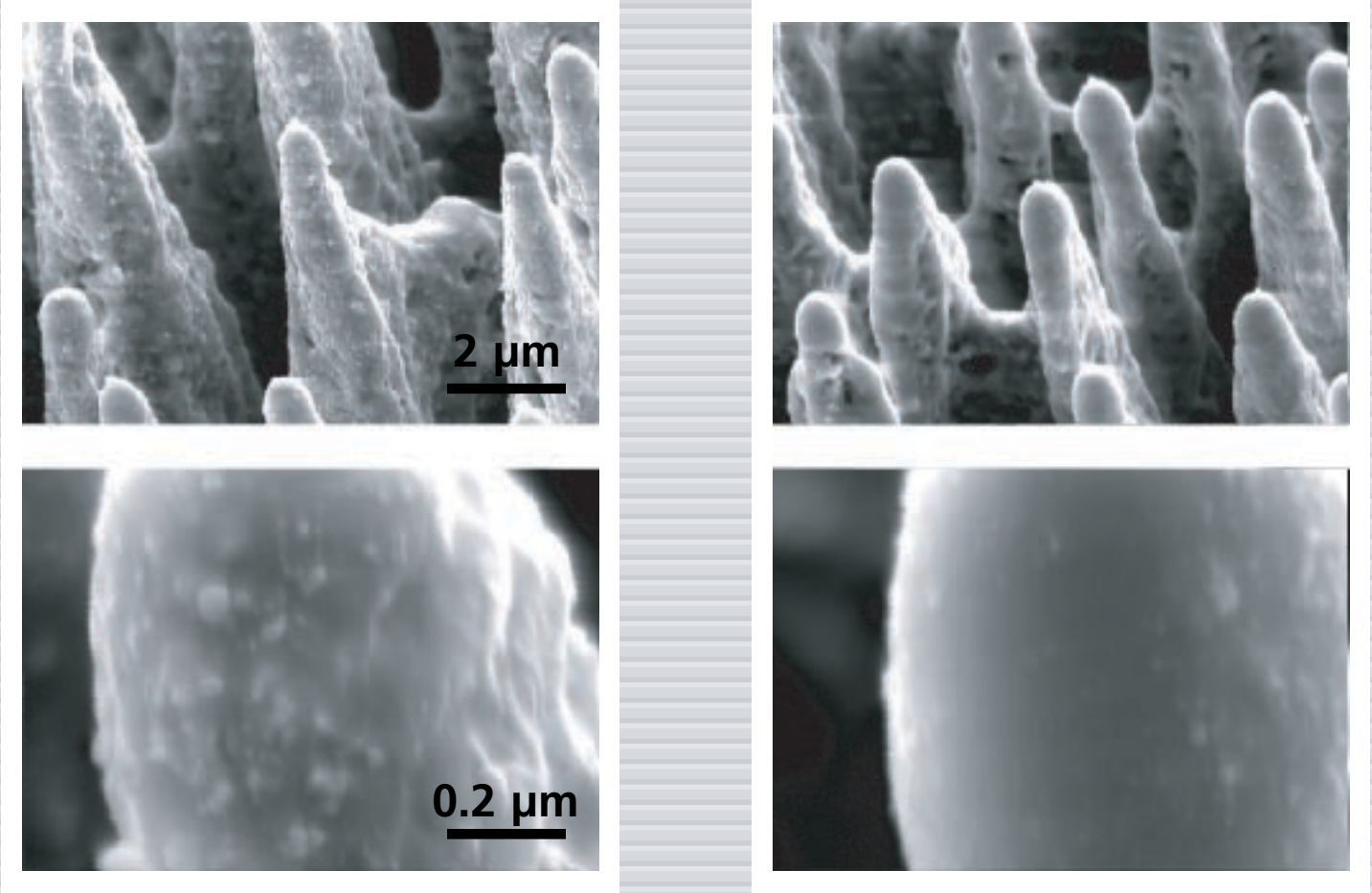


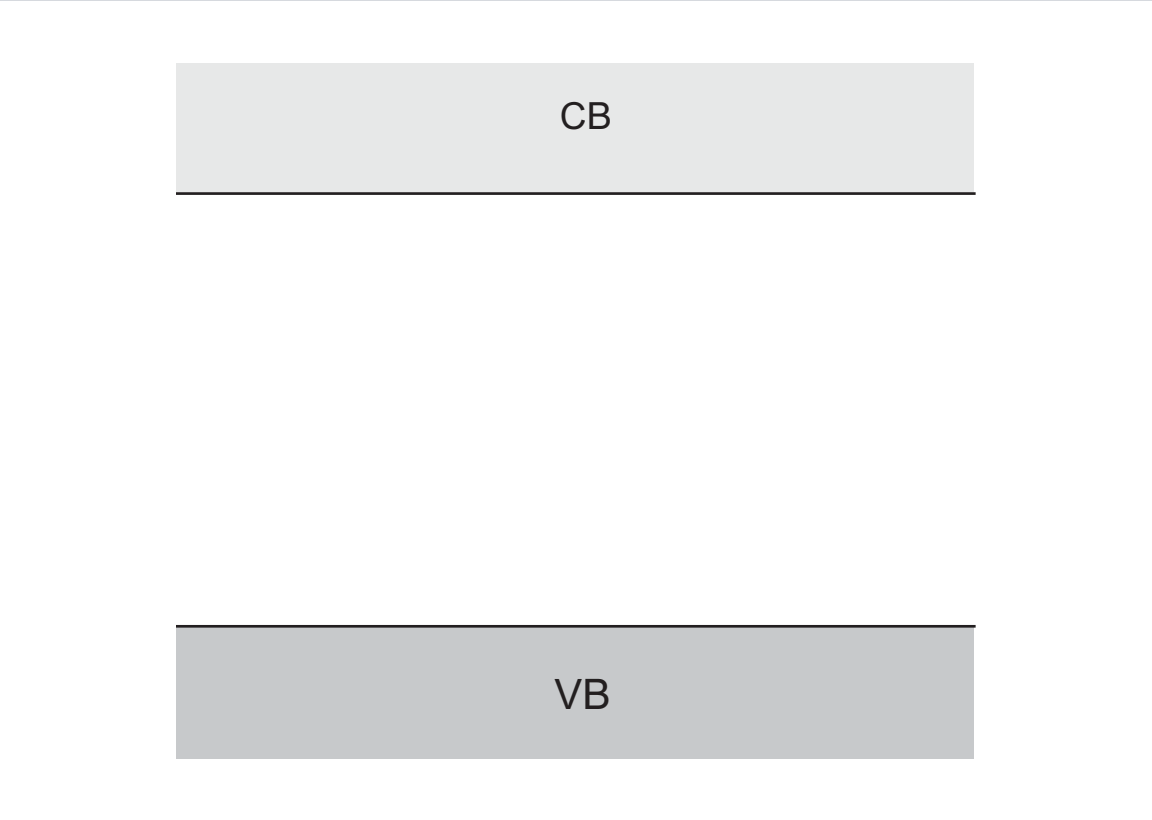
Appl. Phys. Lett. **78**, 1850 (2001)

Structural and chemical analysis

Effects of annealing:

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

sulfur introduces states in the gap



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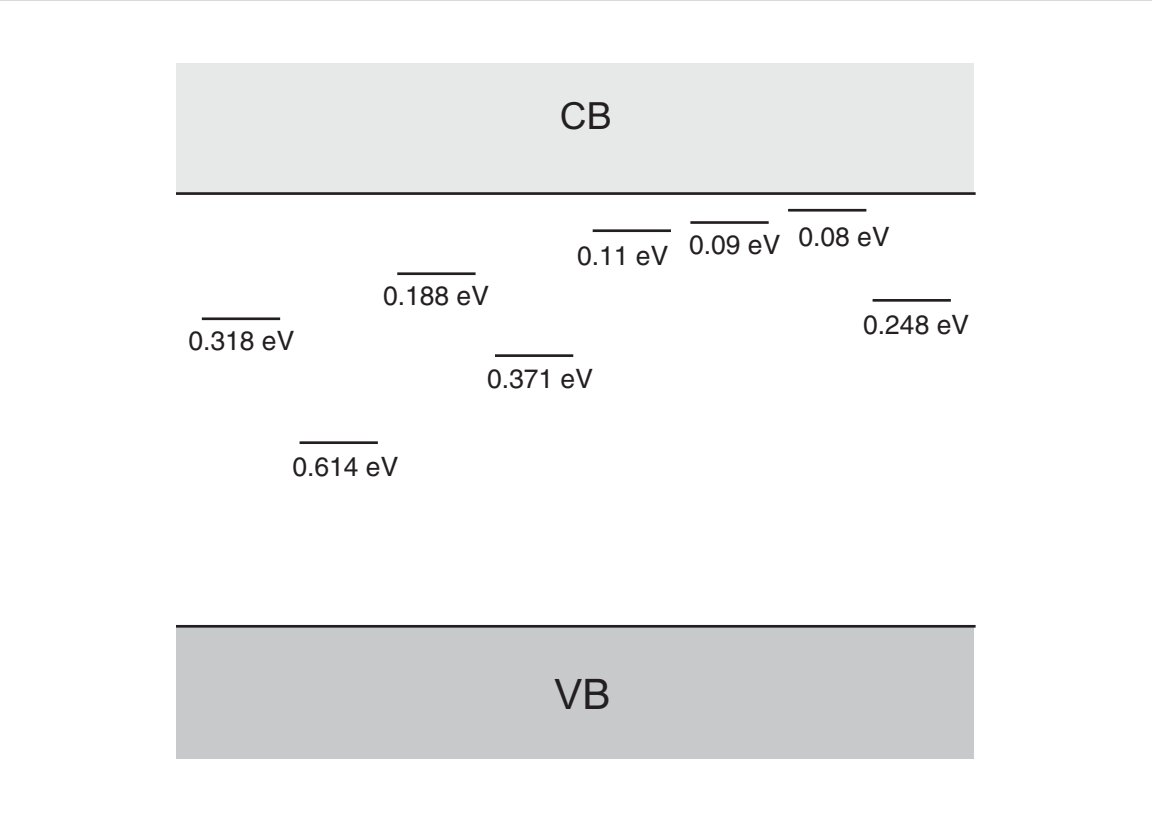
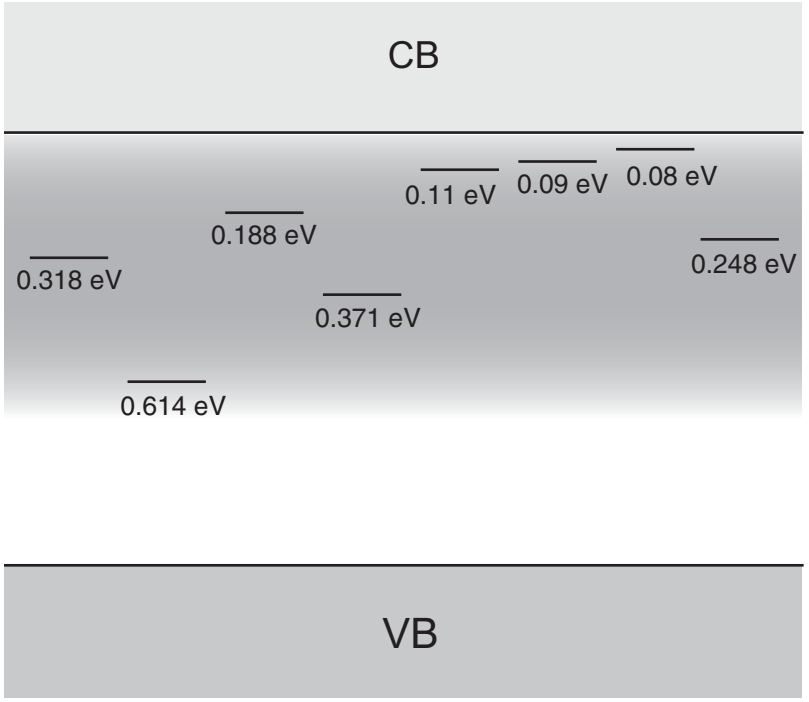
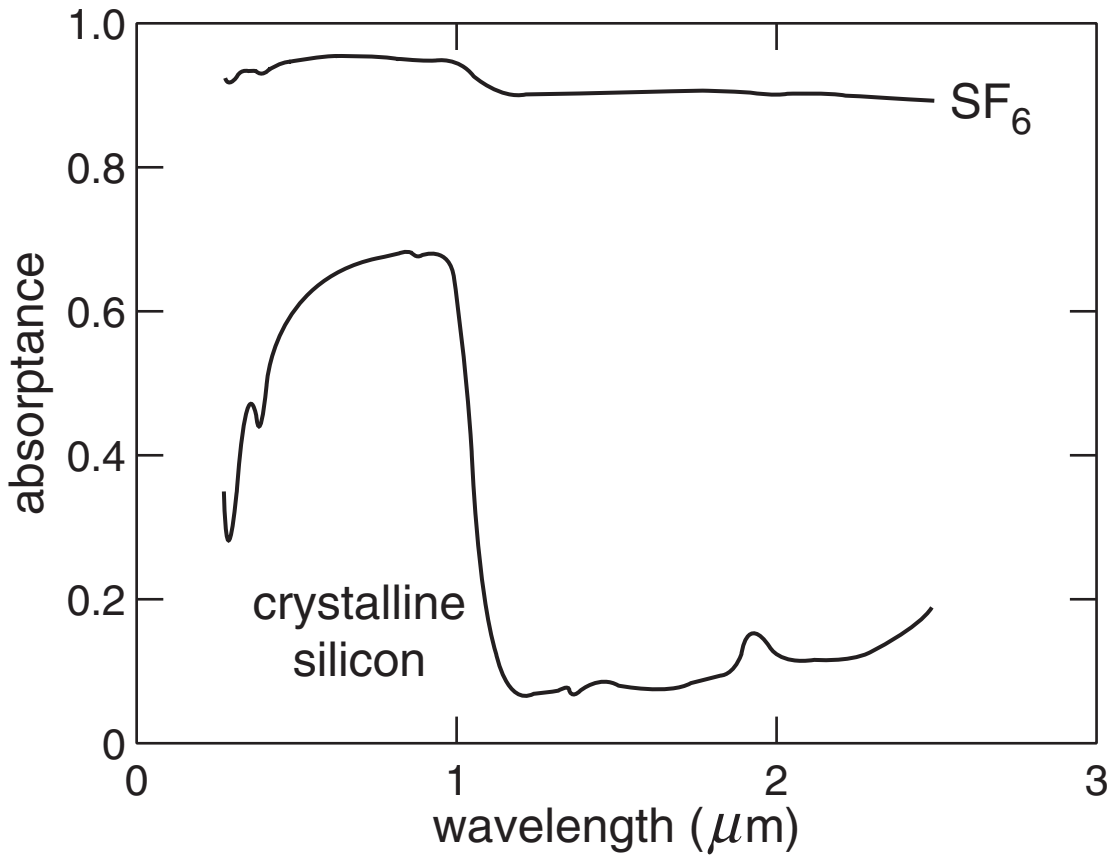


Janzén, *et al.*, *Phys. Rev. B* **29**,1907 (1984)

states broaden into a band



effect of ambient gas on absorptance



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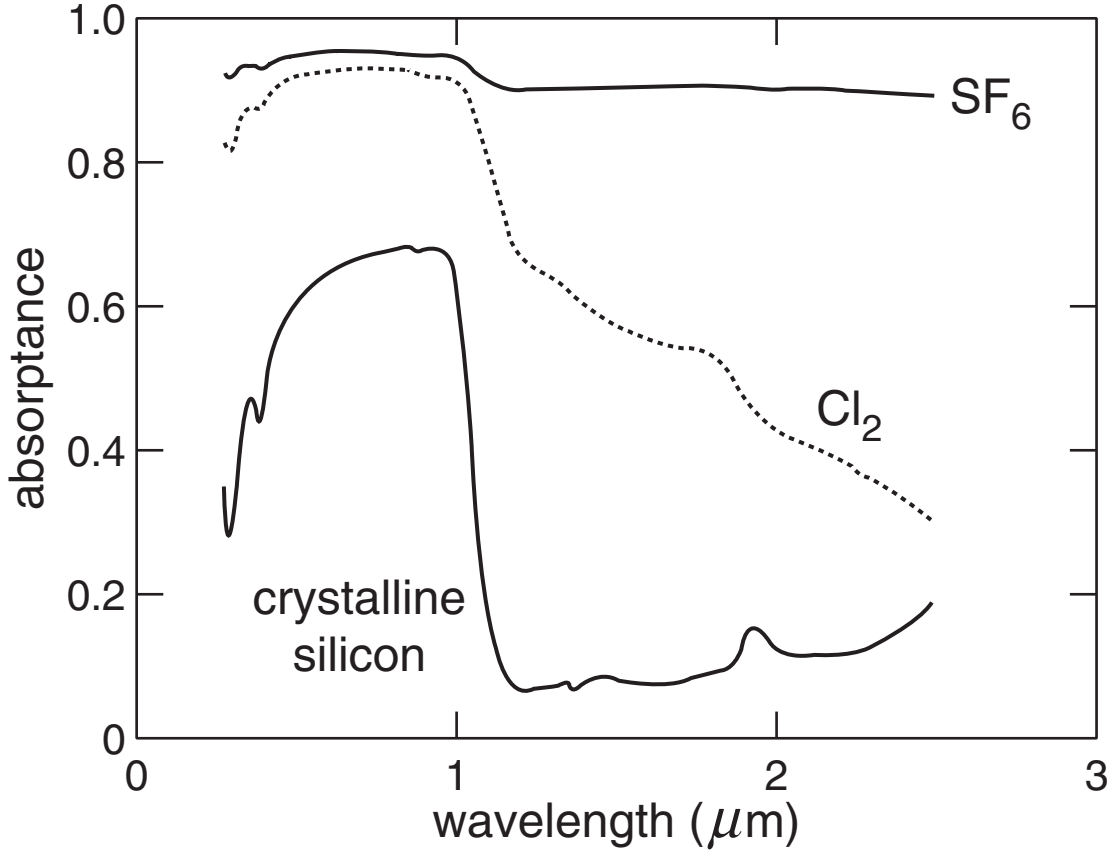

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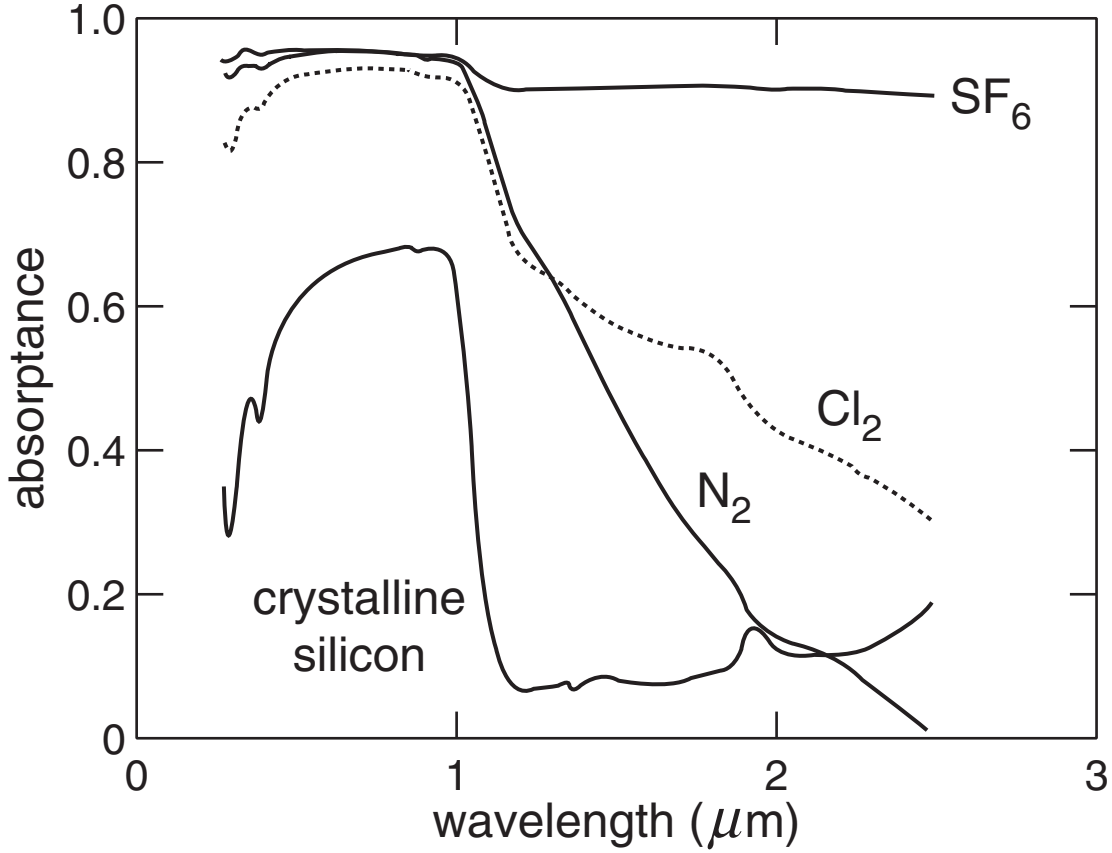

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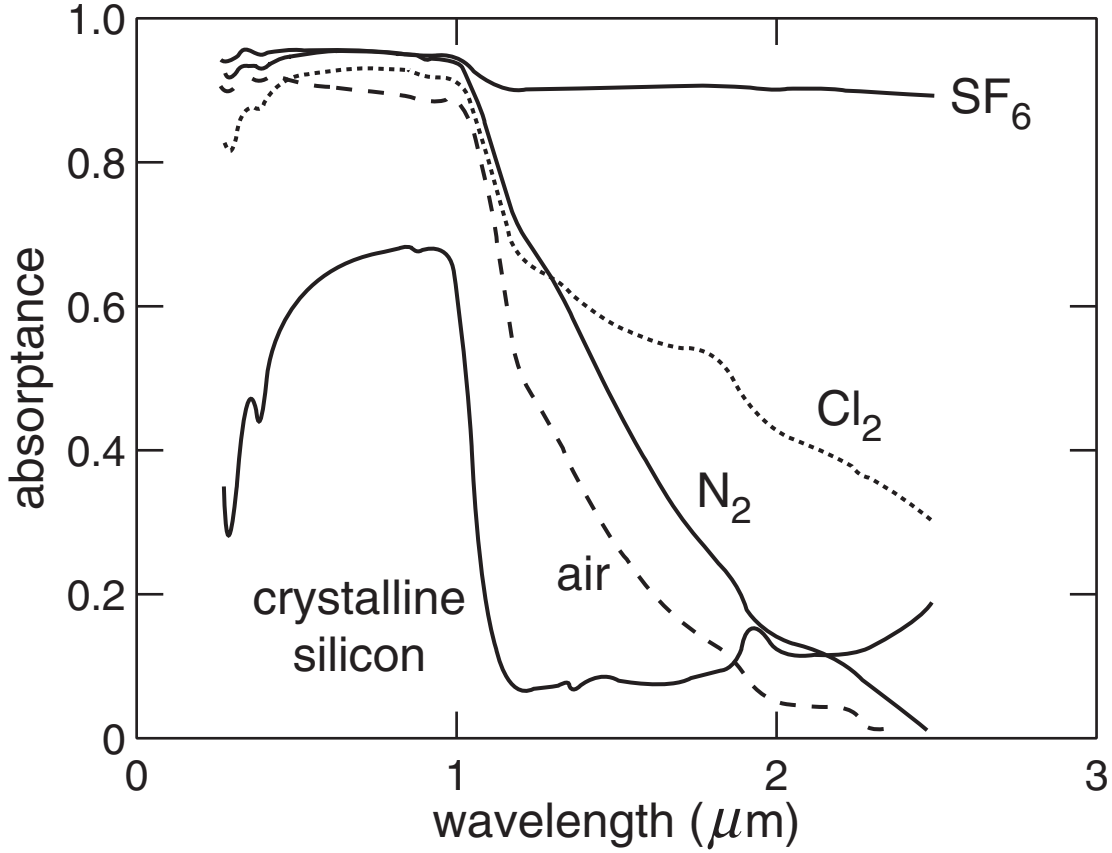


Structural and chemical analysis

- 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

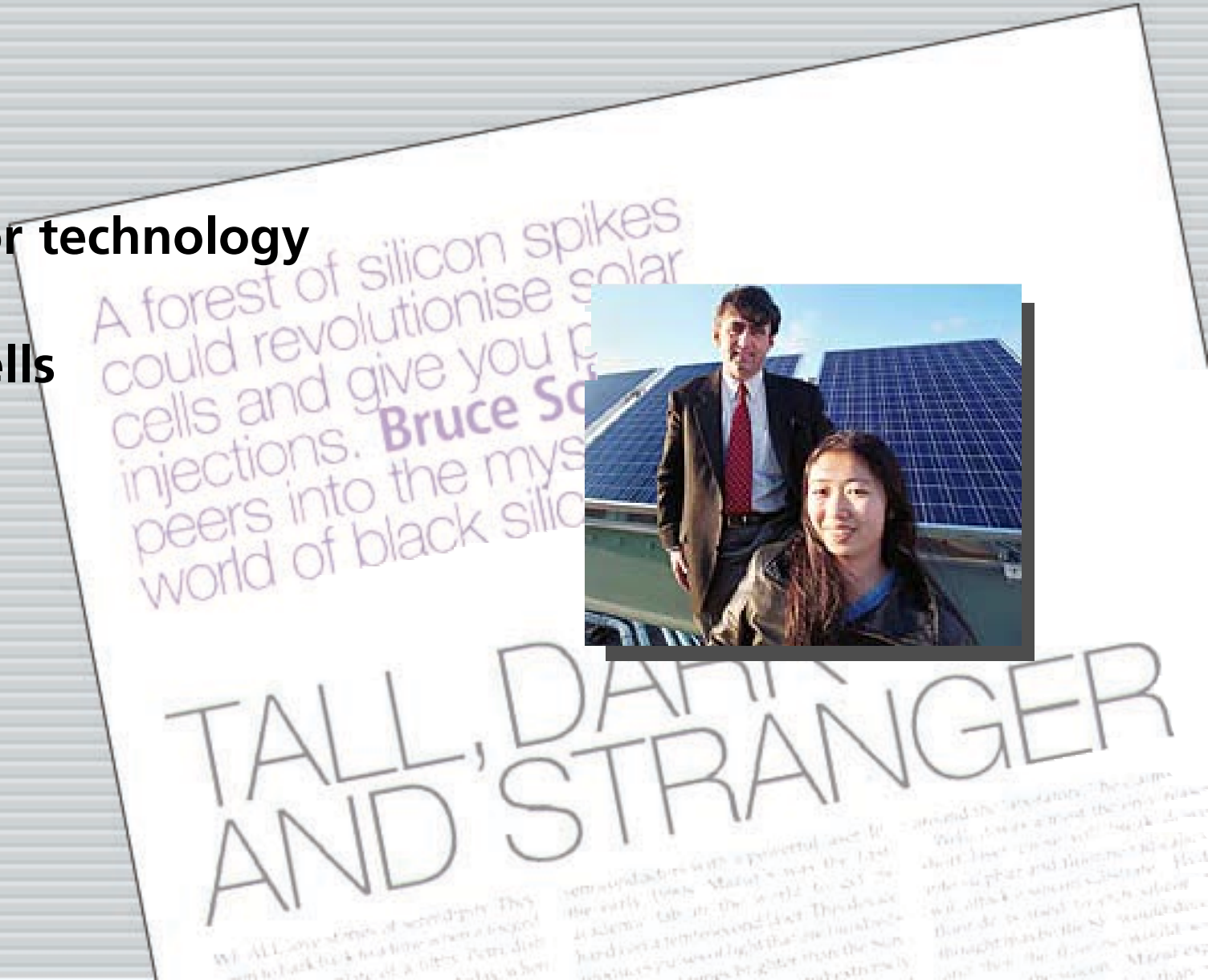
WE ALL love stories of serendipity. They
semiconductors with a powerful laser. In
the early 1990s, Mazur's was the first
academic lab in the world to get its
hands on a femtosecond laser. This device
produces pulses of light that are hundreds
around the laboratory," he claims.
Well, it was almost the only reaso
short laser pulse will break down
into sulphur and fluorine radicals,
will attack a silicon substrate. "Hyd
fluoride is used to etch silicon.
thought maybe the SF_6 would deco
and then the fluorine would so

Outlook

- **detector technology**

Outlook

- detector technology
- solar cells

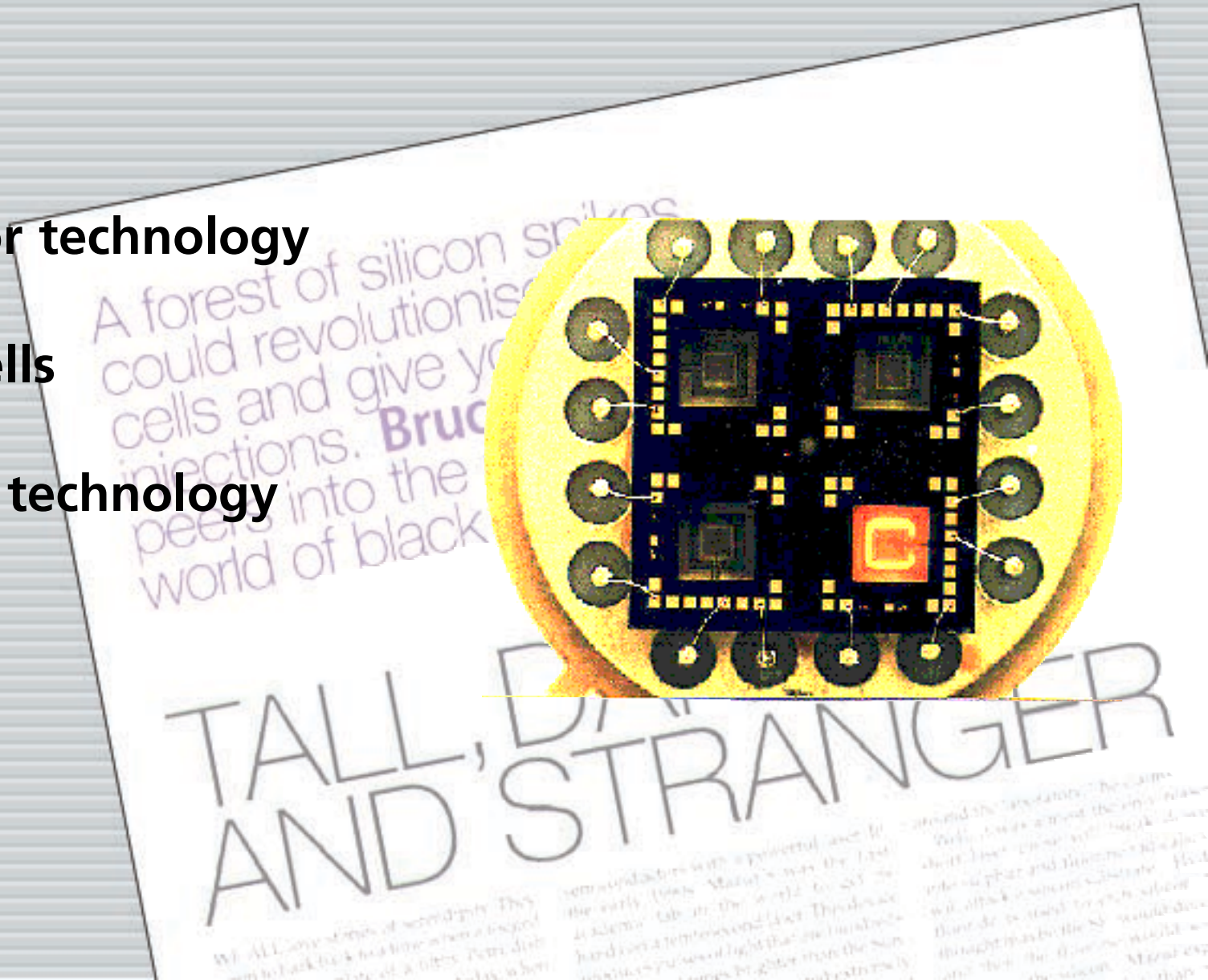


Outlook

- detector technology
- solar cells
- display technology

Outlook

- detector technology
- solar cells
- display technology
- sensors



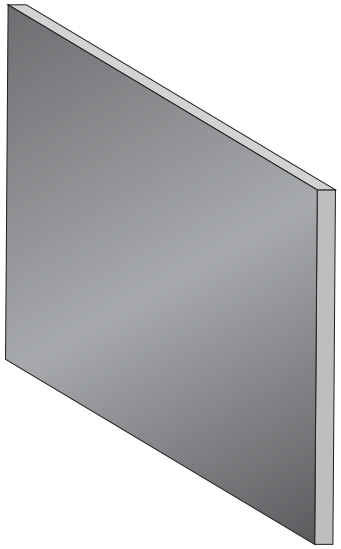
Outlook

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

Outlook

can ordering of spikes be improved by using a grid?

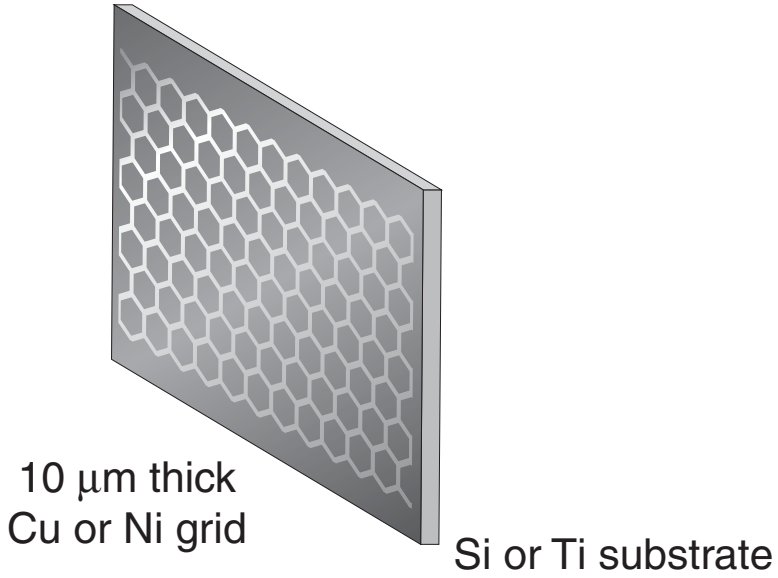
Outlook



Si or Ti substrate

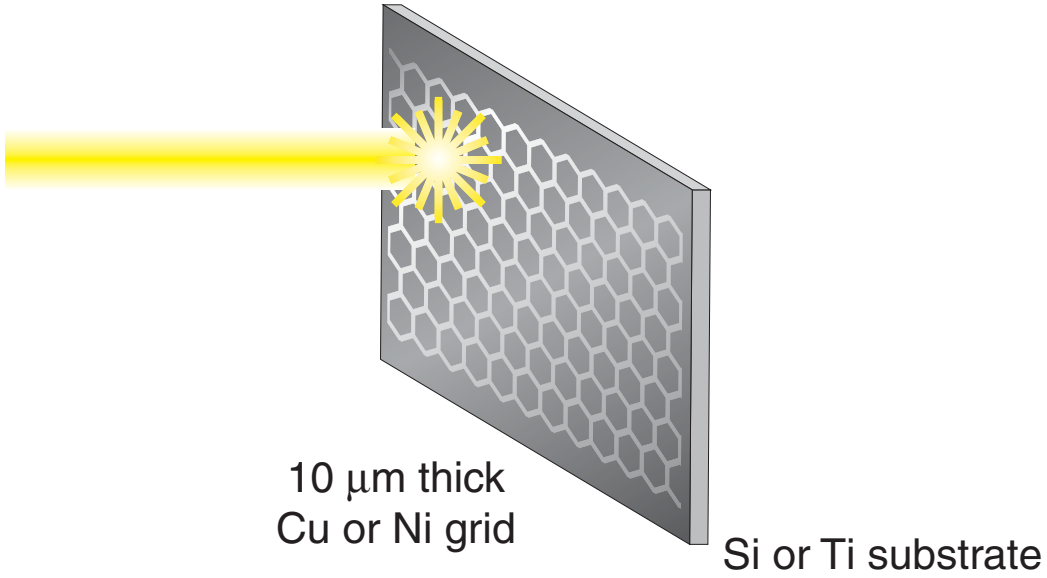
Outlook

place grid in front of substrate



Outlook

scan laser beam



Outlook

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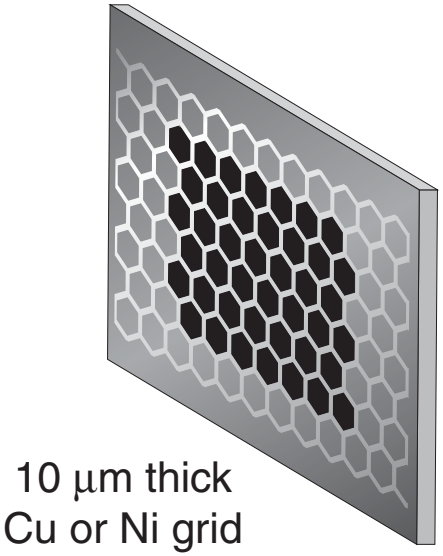
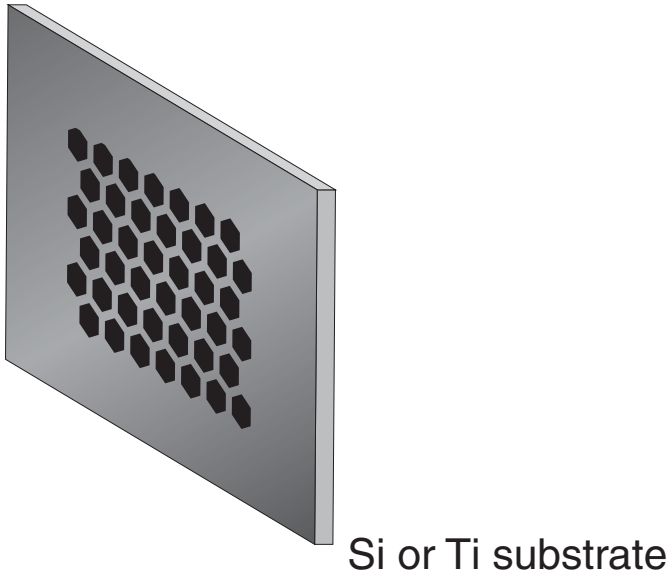
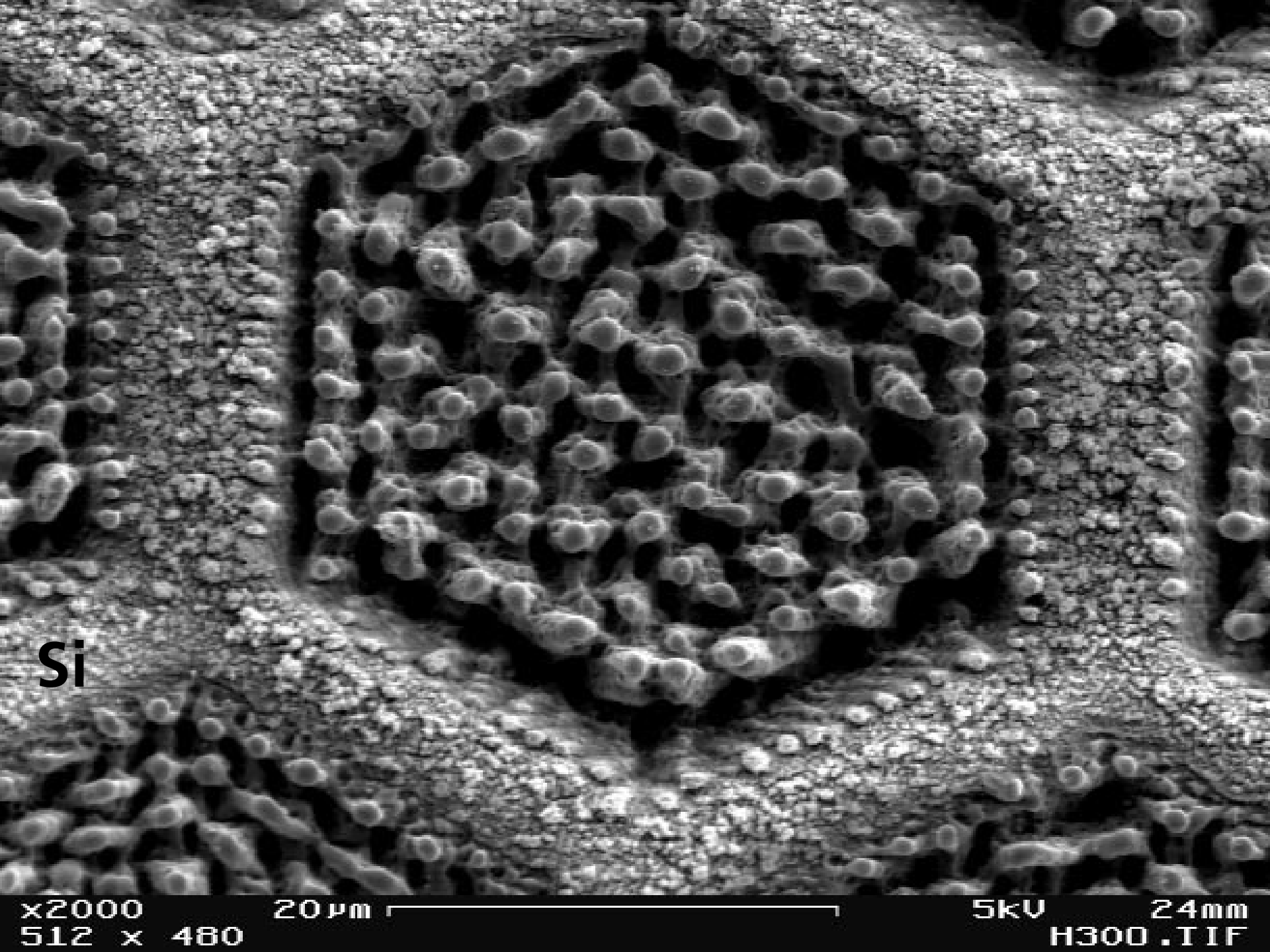
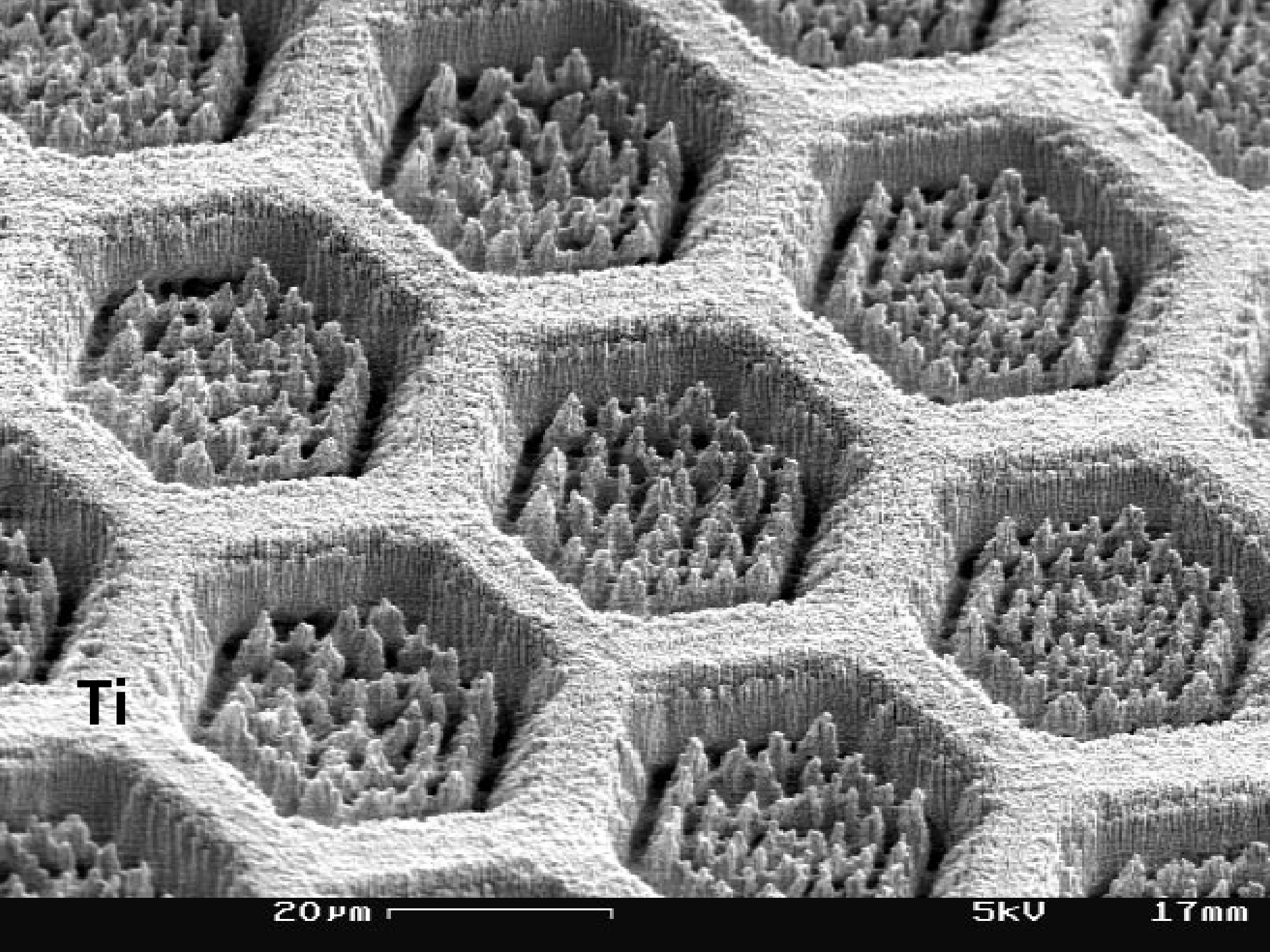


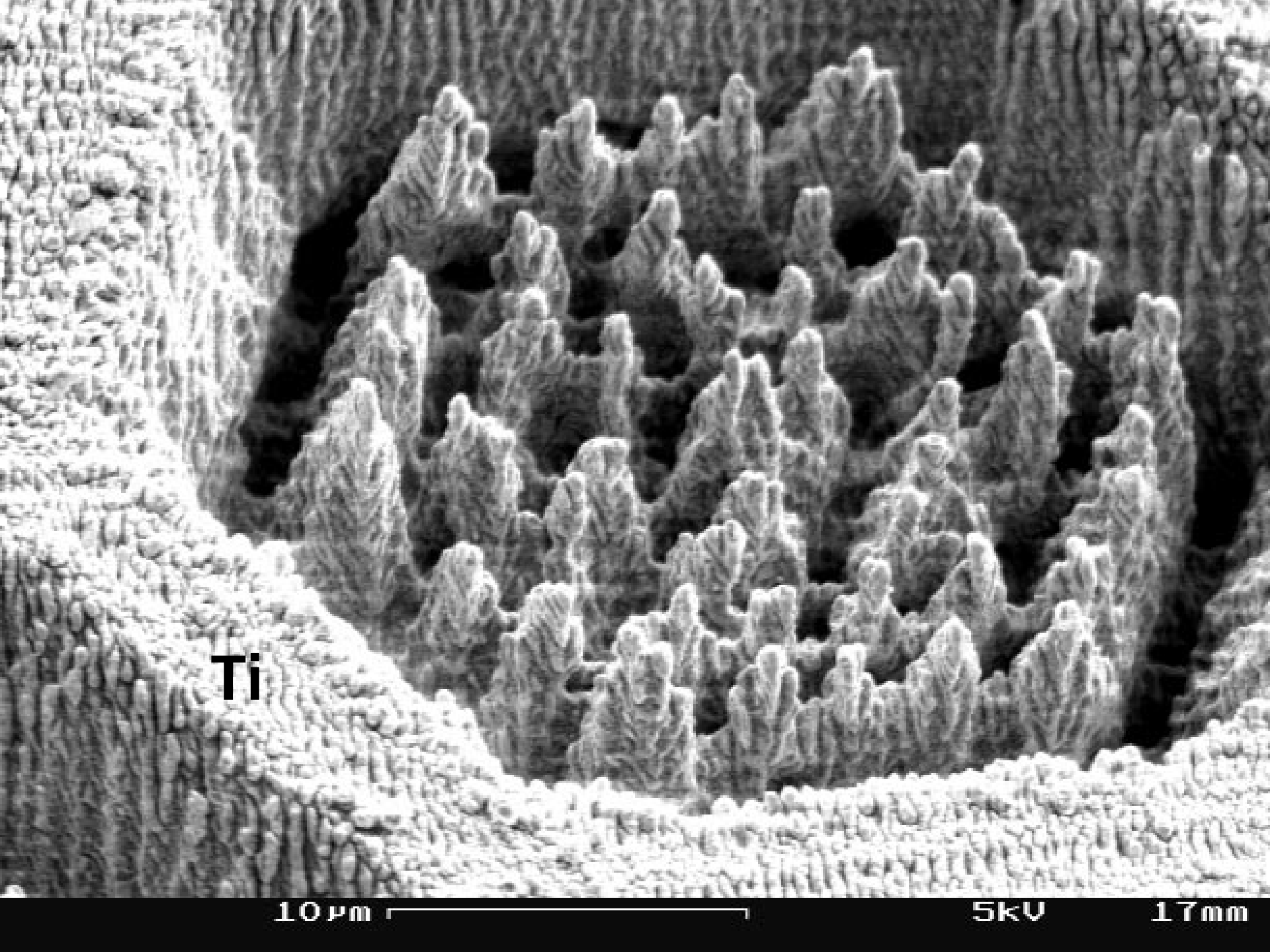
Outlook

remove grid




Si
x2000
20µm
5kV
24mm
512 x 480
H300.TIF


Ti
20μm
5kV
17mm


Ti
10μm
5kV
17mm

Outlook

Summary

Microstructured silicon

- **fabricated by simple, maskless process**

Summary

Microstructured silicon

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


GORDON McKAY
LABORATORY OF
APPLIED SCIENCE

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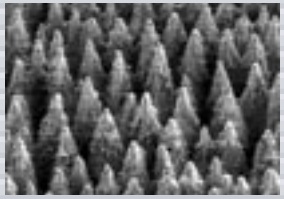
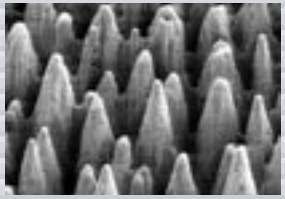
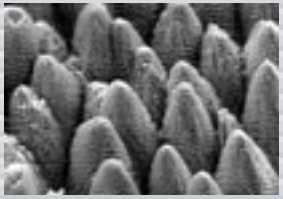
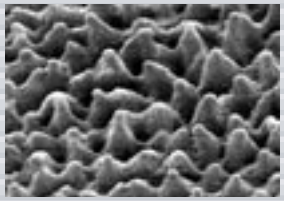
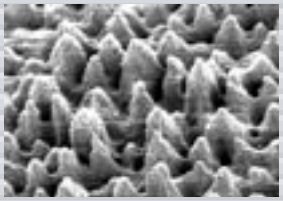
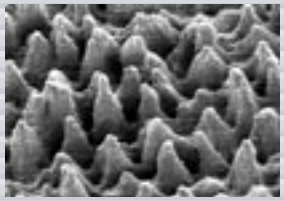
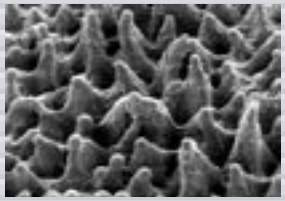
Dr. François Génin (LLNL)
Dr. Arieh Karger (Radiation Monitoring Devices)
Dr. Alf Bjørseth (Scanwafer)
Dr. Tom Mates (UCSB)
Dr. John Chervinsky (Harvard University)
Prof. Cynthia Friend (Harvard University)
Prof. Mike Aziz (Harvard University)

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

http://mazur-www.harvard.edu

Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti		reacts			

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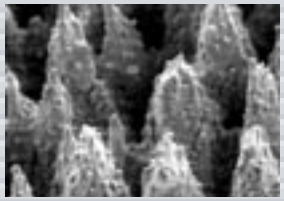

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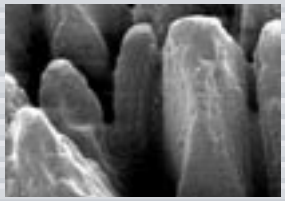
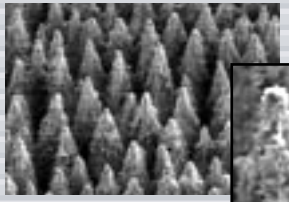
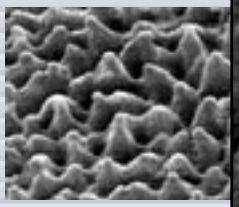
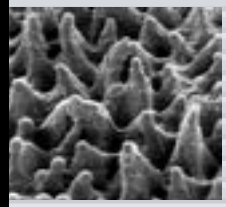
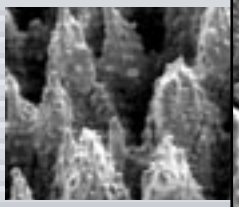


InP

No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					

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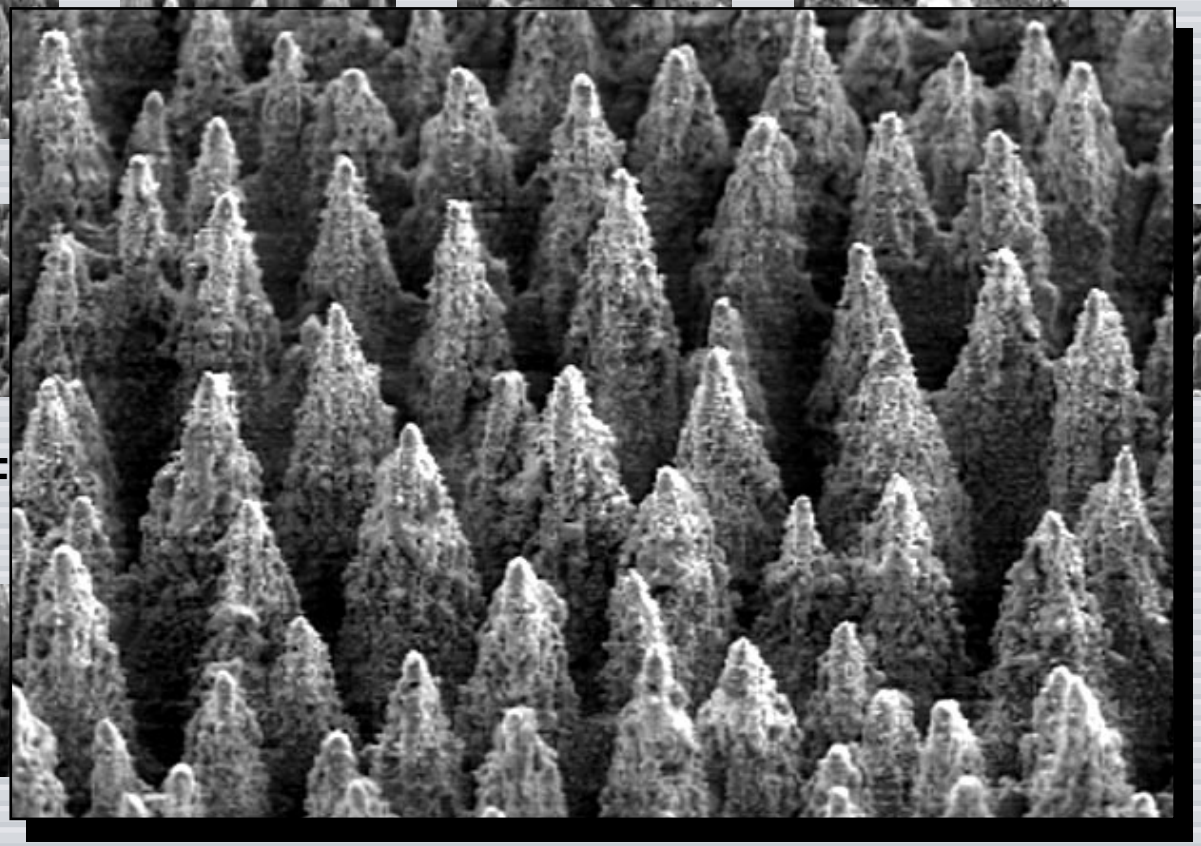

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Materials

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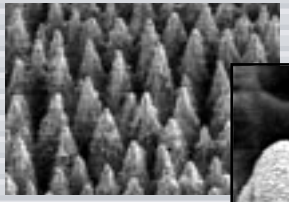
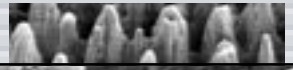
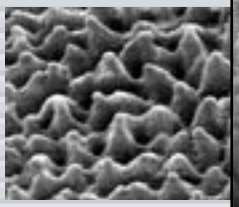
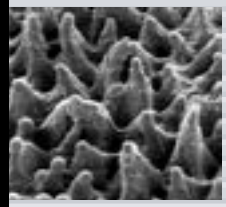
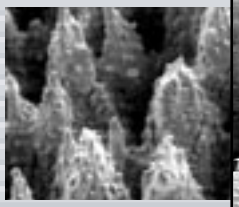
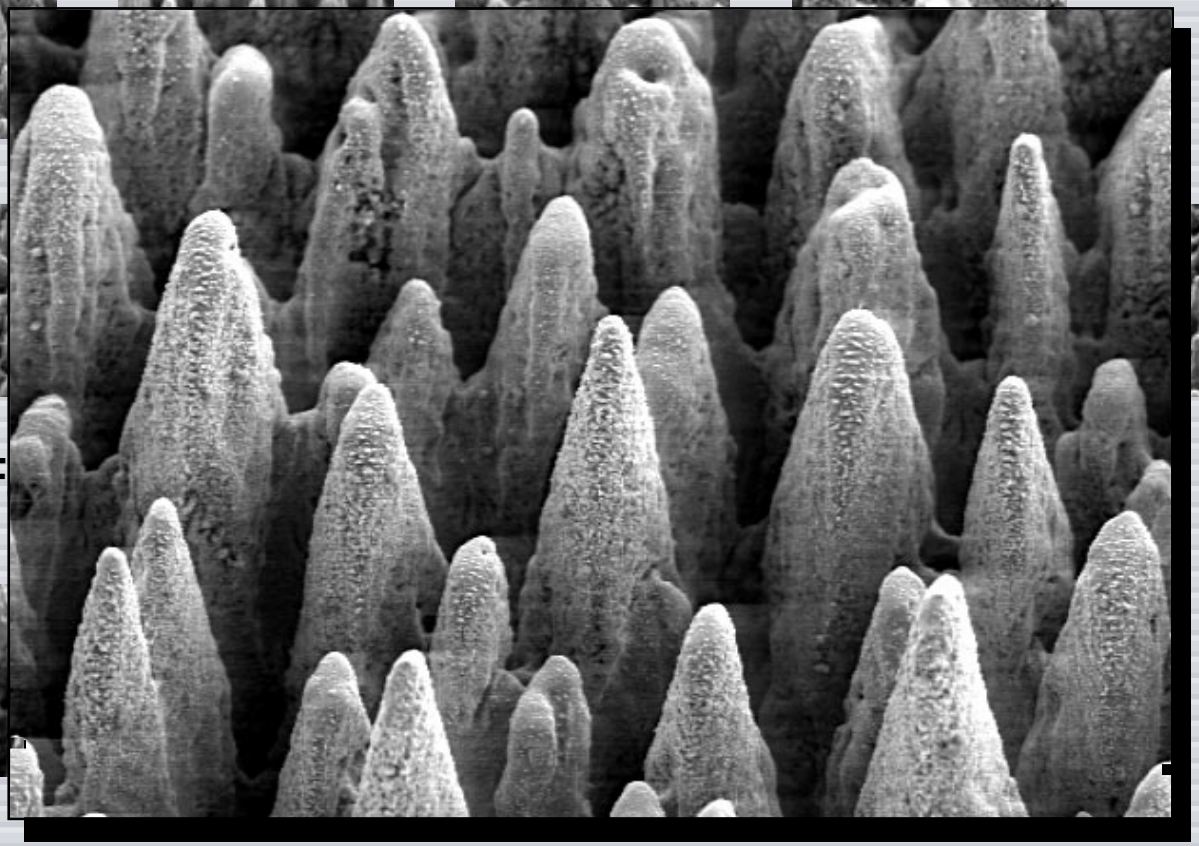
Si					
Ti					
Ge					



Only in SF

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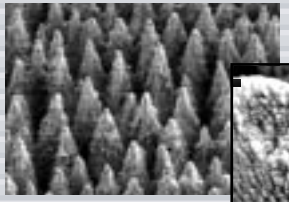
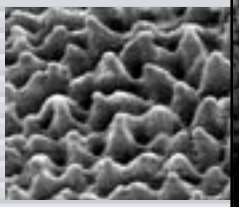
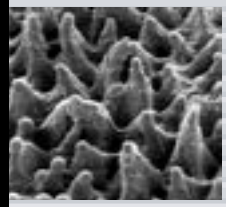
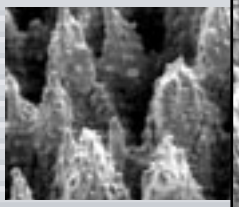
Si					
Ti					
Ge					

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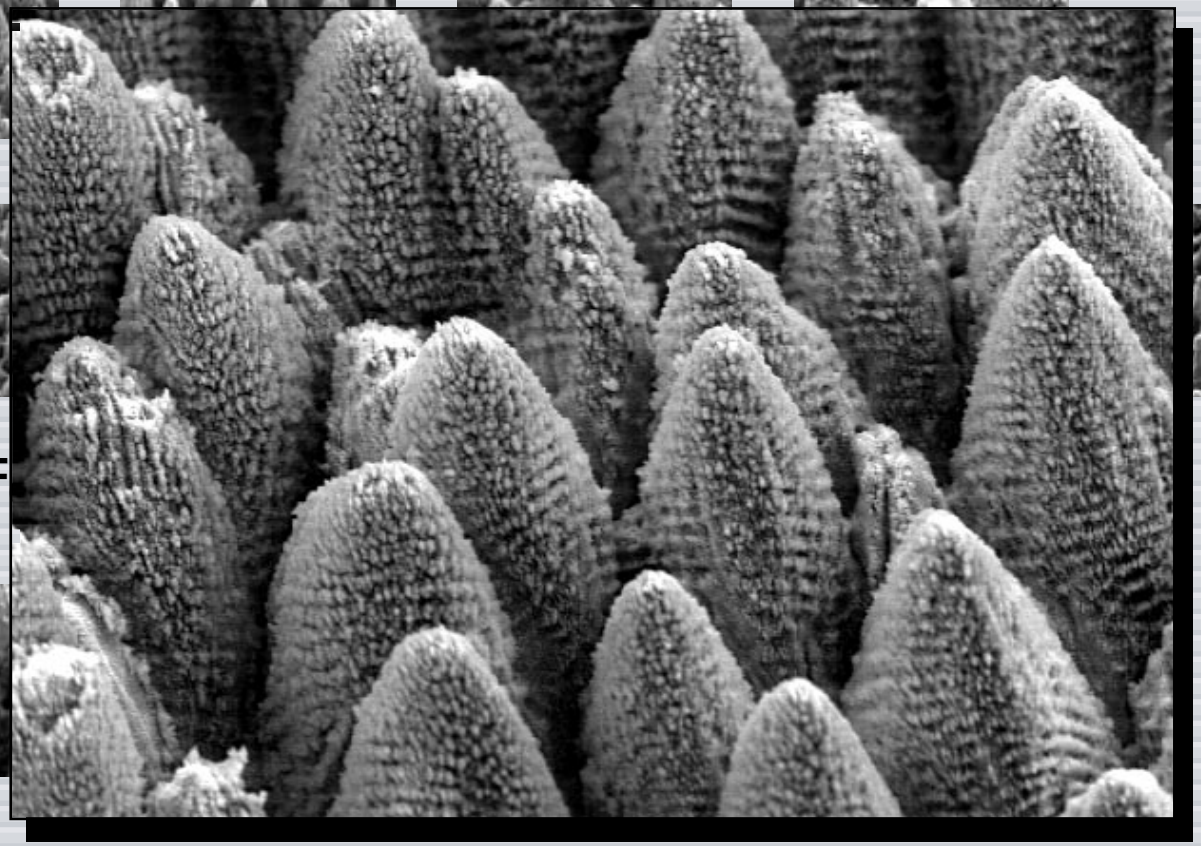

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Materials

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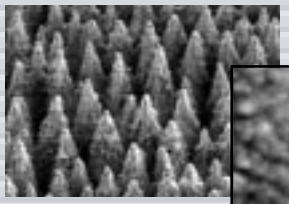
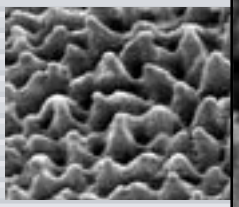
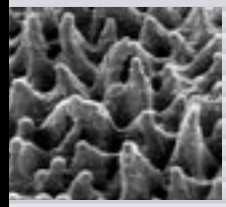
Si					
Ti					
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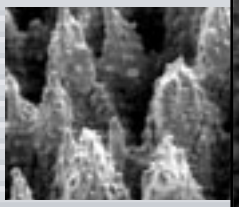
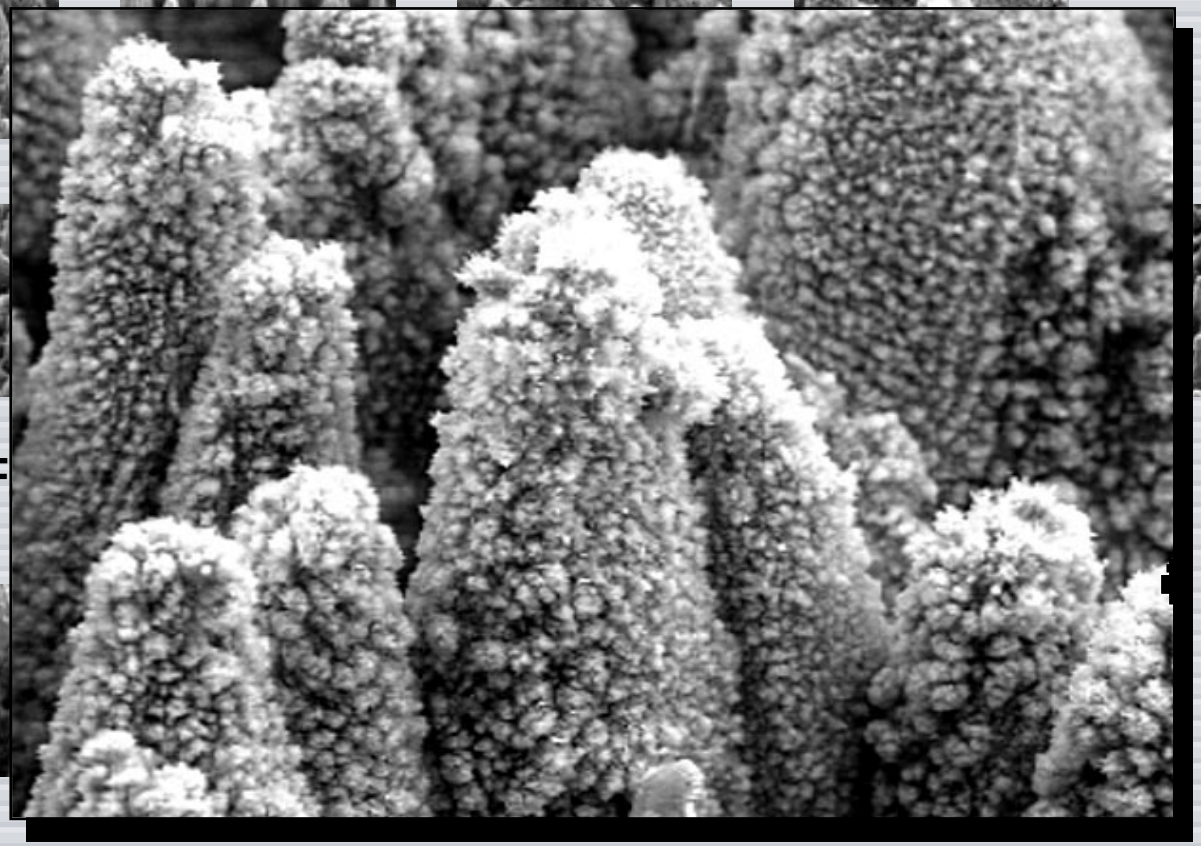
Ge					



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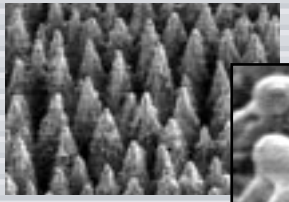
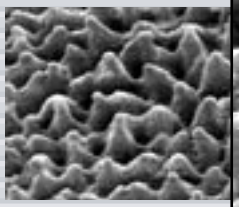
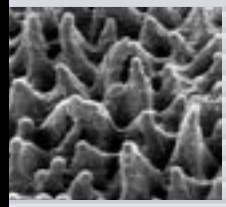
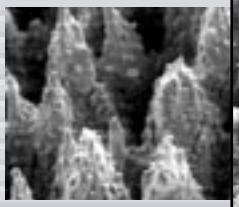
Si					
Ti					
Ge					

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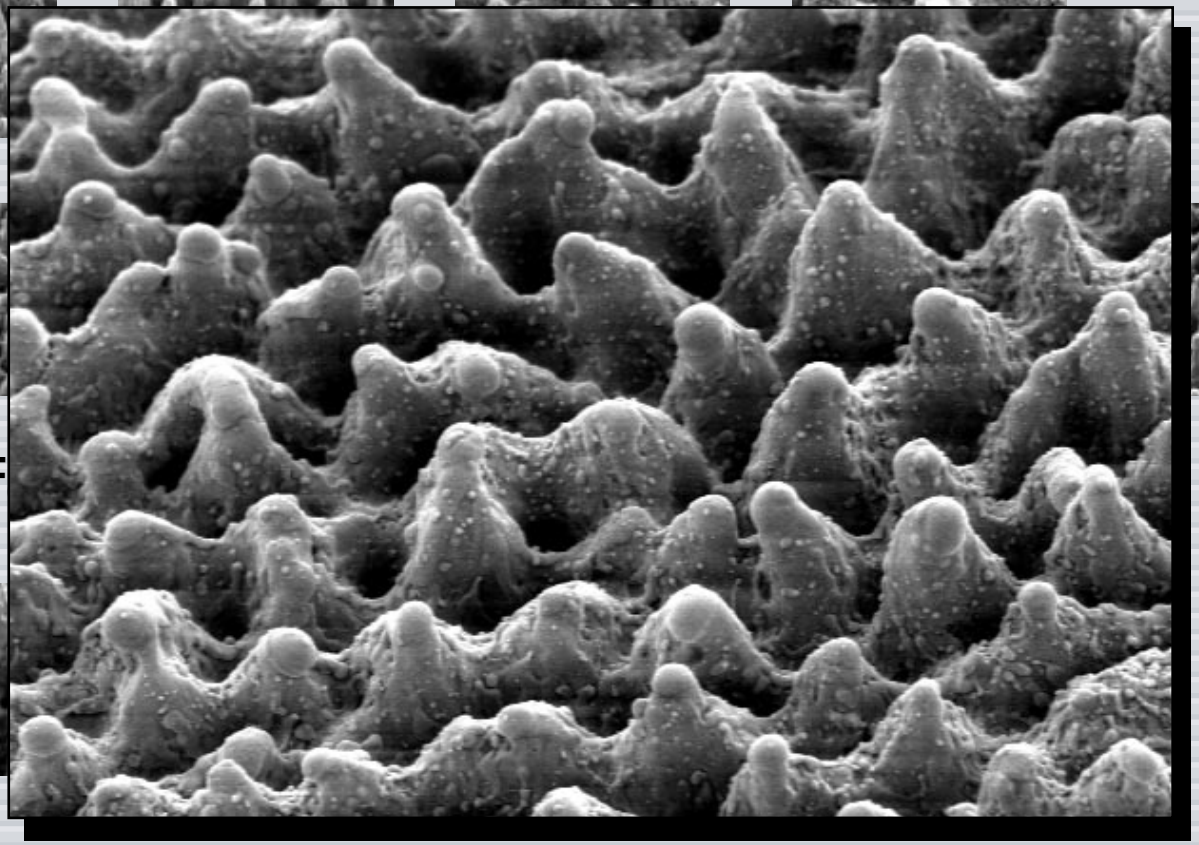

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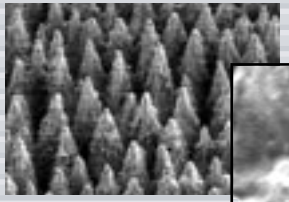
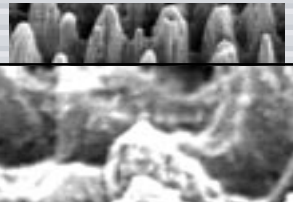
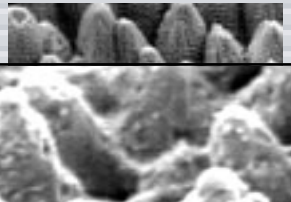
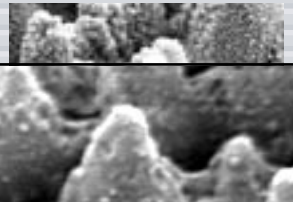
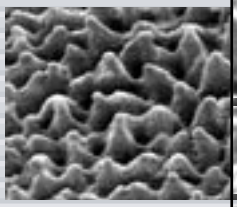
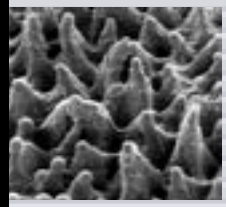
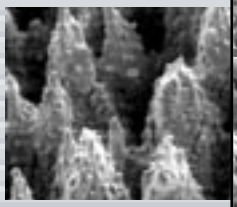
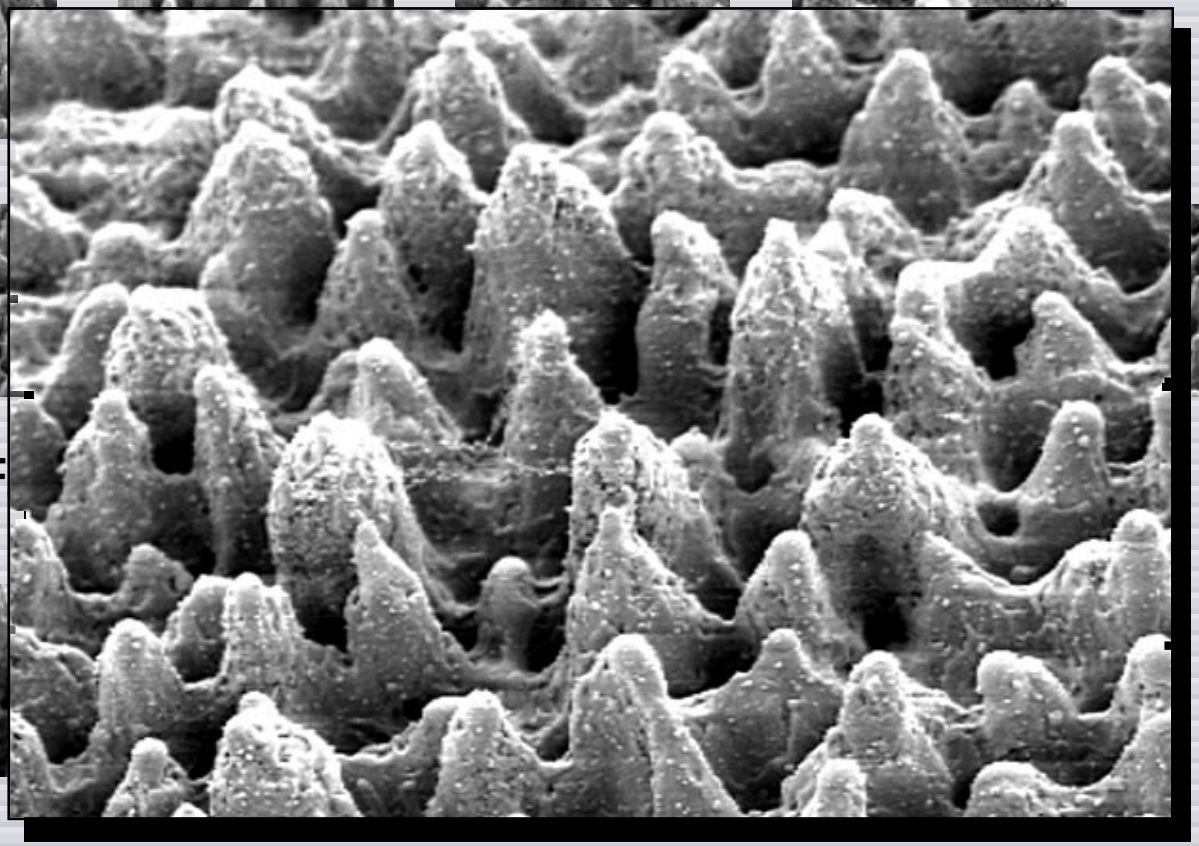
Si					
Ti					
Ge					



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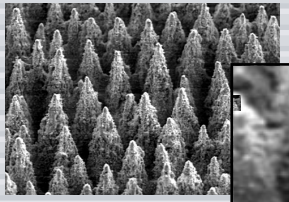
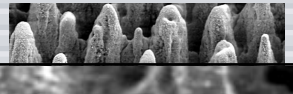
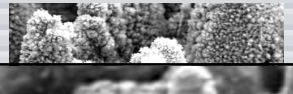
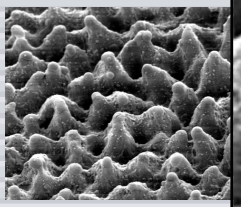
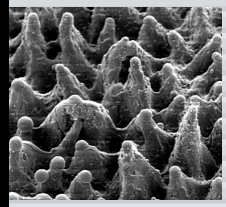
Si					
Ti					
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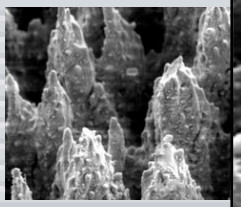
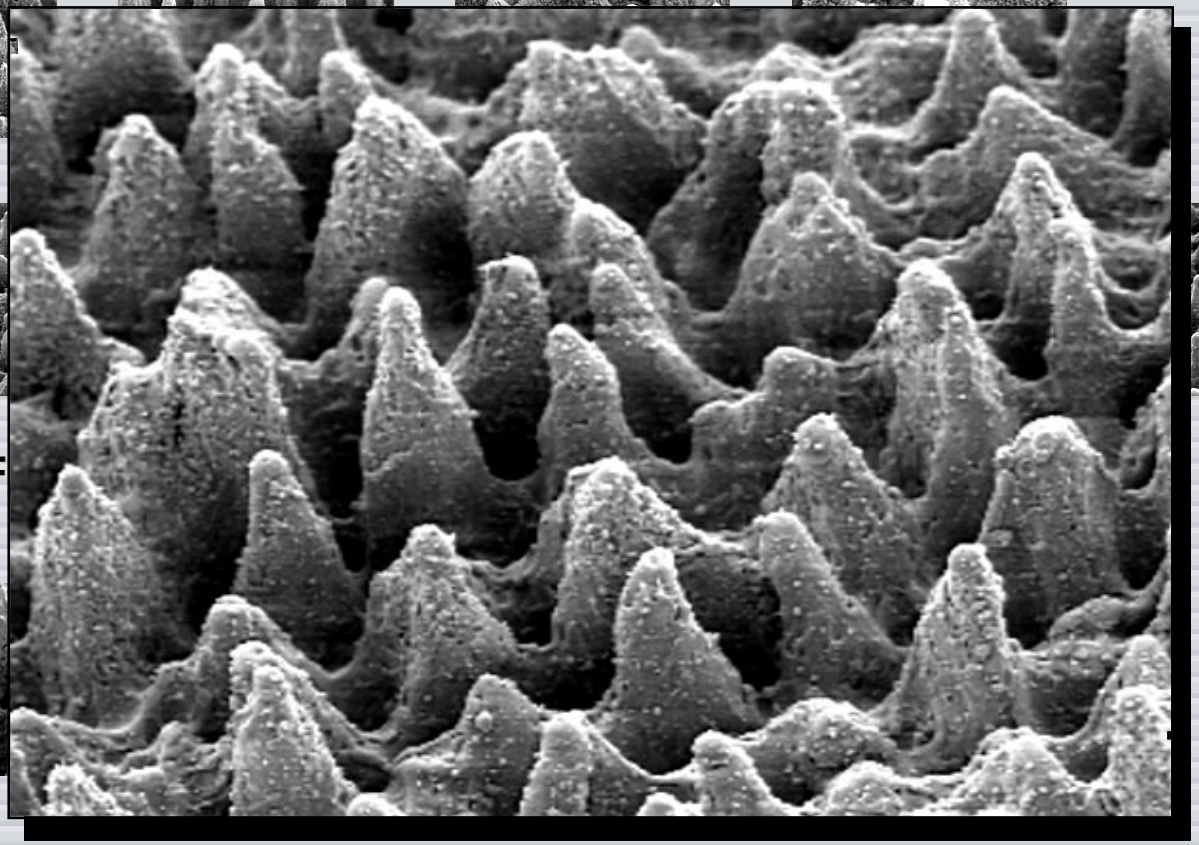
Ge					



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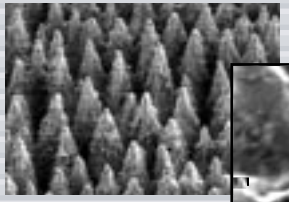
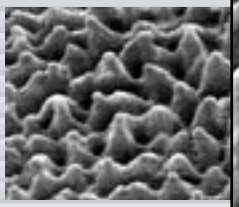
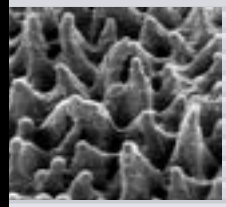
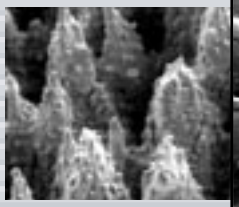
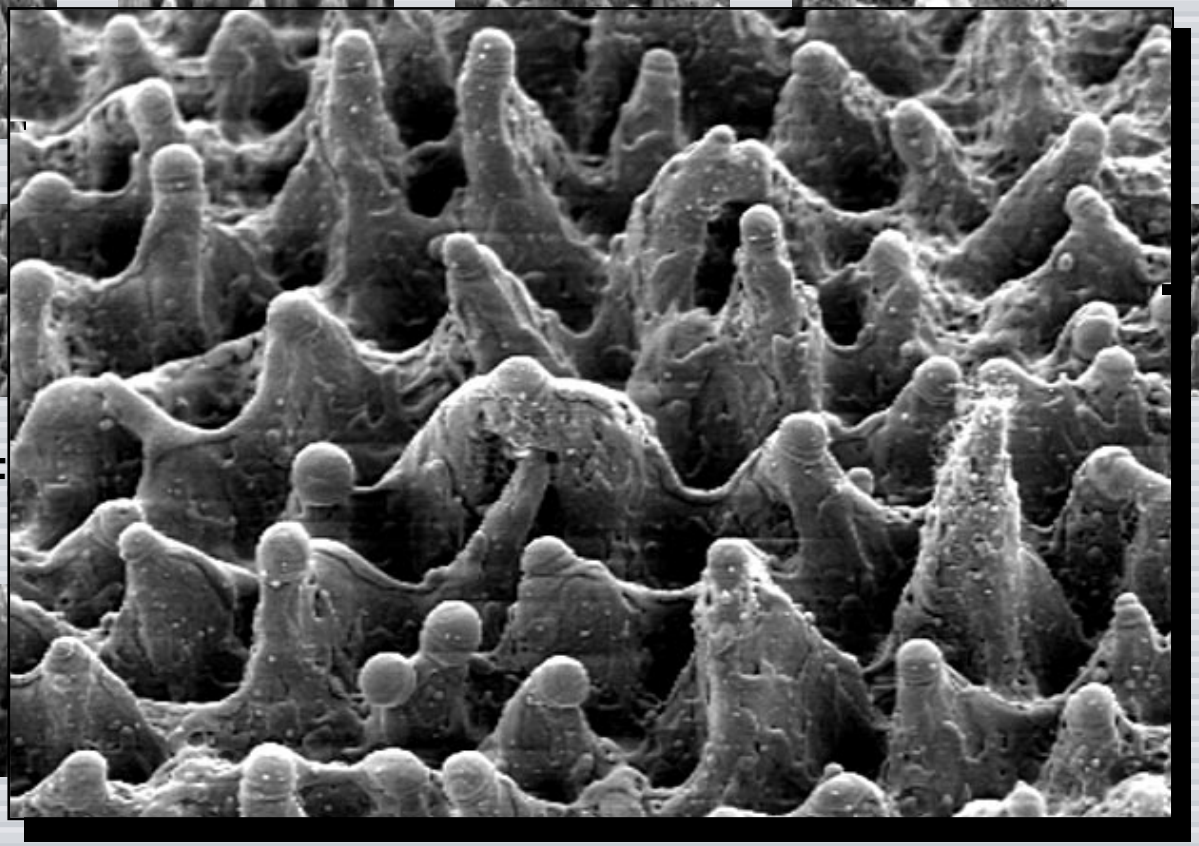
Si					
Ti					
Ge					



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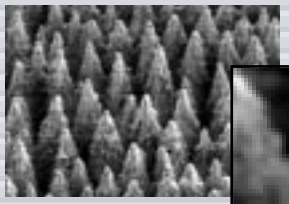
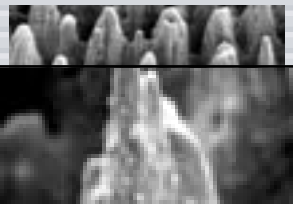
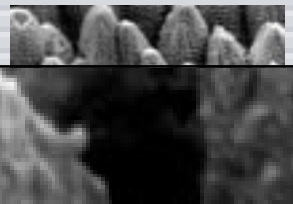
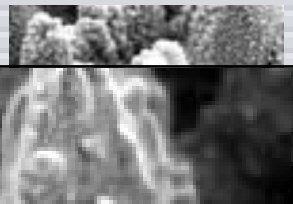
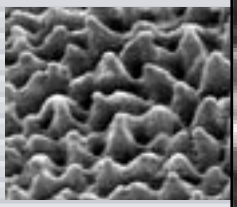
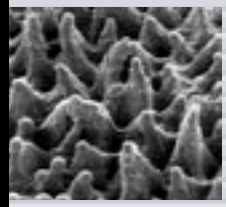
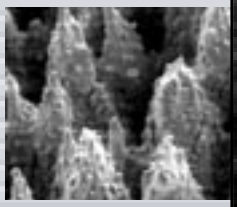
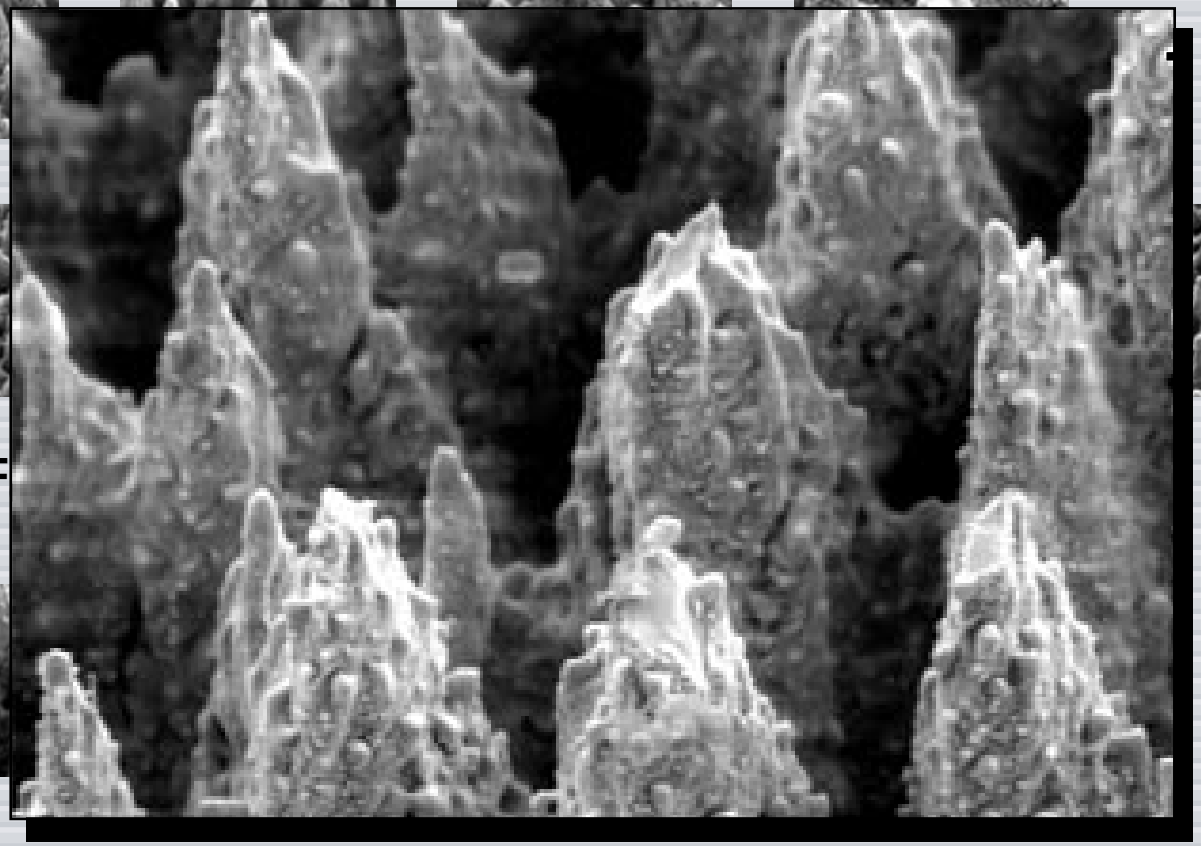
Materials

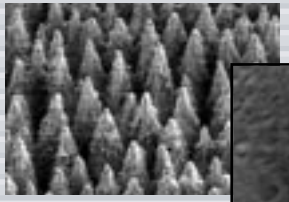
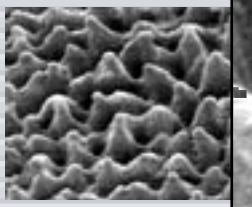
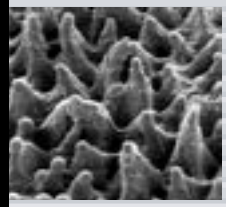
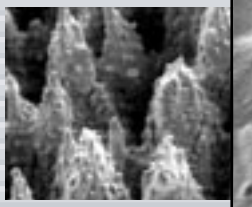
	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					

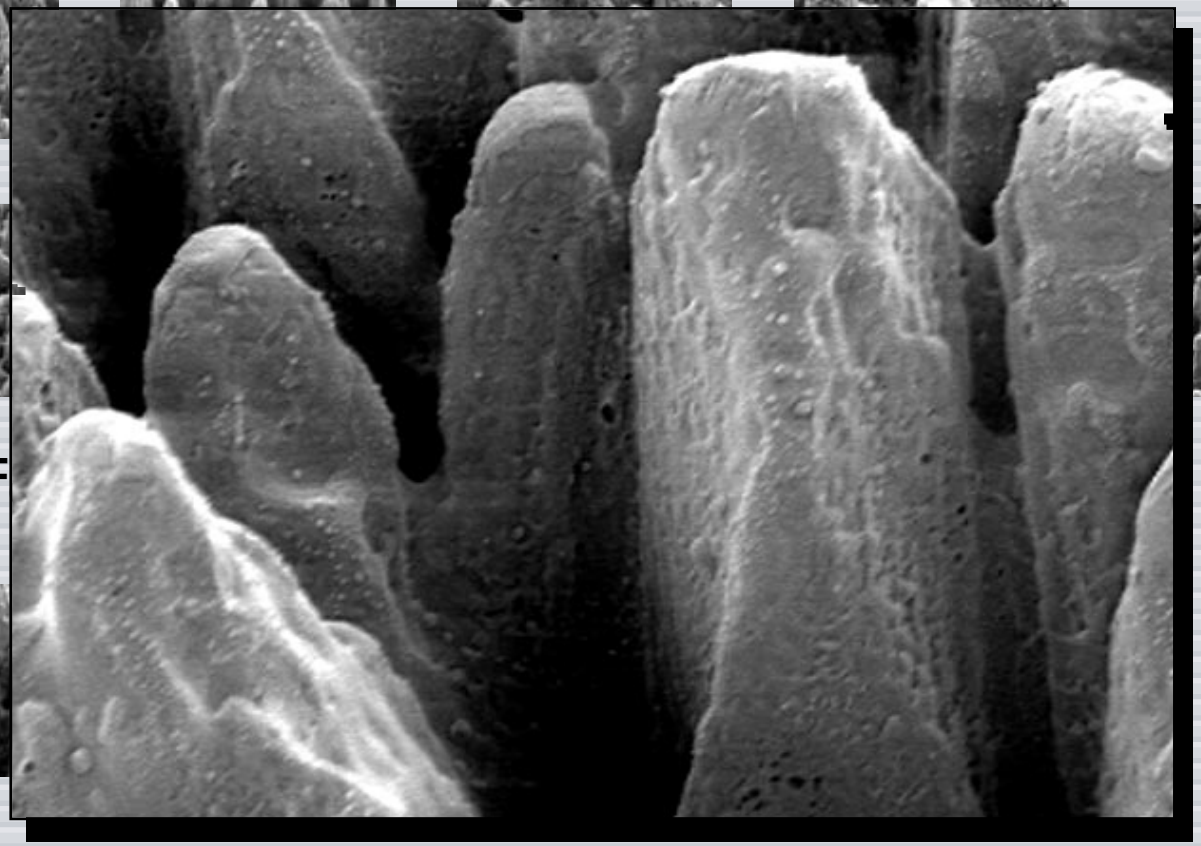


Only in SF

No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs

Materials

	SF_6	Cl_2	N_2	air	vacuum
Si					
Ti					
Ge					



Only in SF

No spikes in SF_6: Ag, Al, Cu, Pd, Pt, Rh, Ta and GaAs