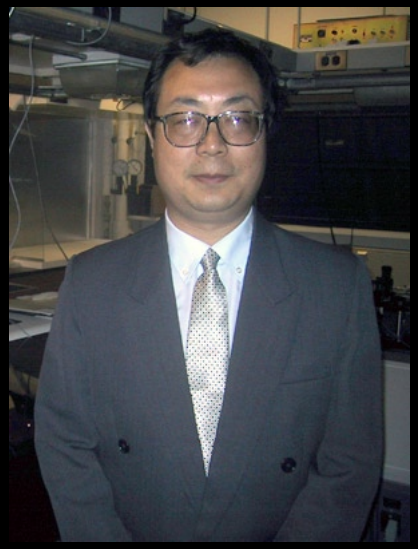
Femtosecond laser-assisted microstructuring of silicon for novel detector, sensing and display technologies

University of Massachusetts Lowell
Lowell, MA, 10 March 2004

Eric Mazur

Jim Carey

Catherine Crouch



Mengyan Shen

and also....

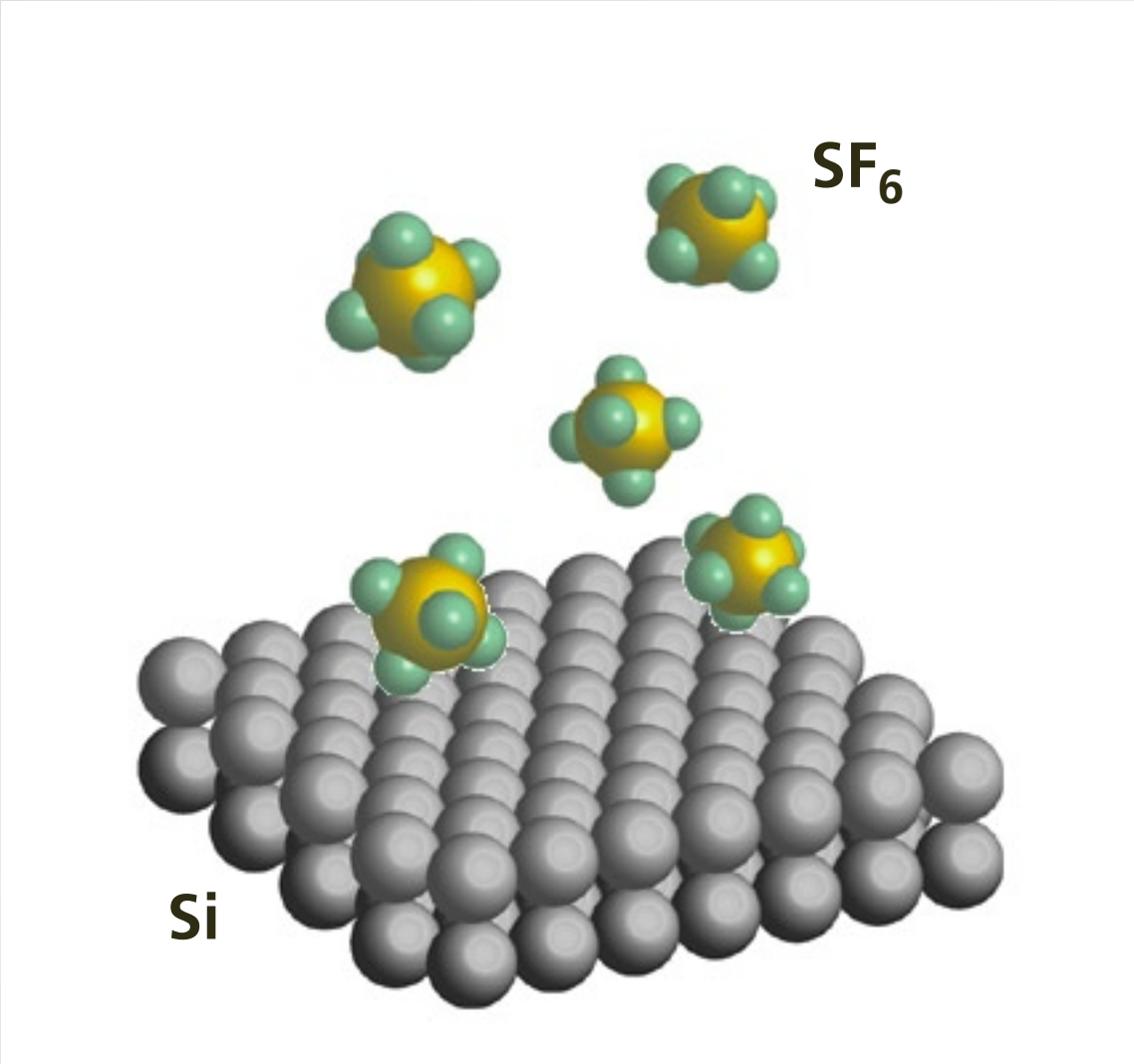
Tsing-Hua Her
Shrenik Deliwala
Richard Finlay
Michael Sheehy
Brian Tull
Jeffrey Warrander
Claudia Wu
Rebecca Younkin

Dr. John Chervinsky
Dr. Joshua Levinson

Dr. François Génin (LLNL)
Dr. Richard Farrell
Dr. Arieh Karger (RMD)
Dr. Richard Meyers (RMD)

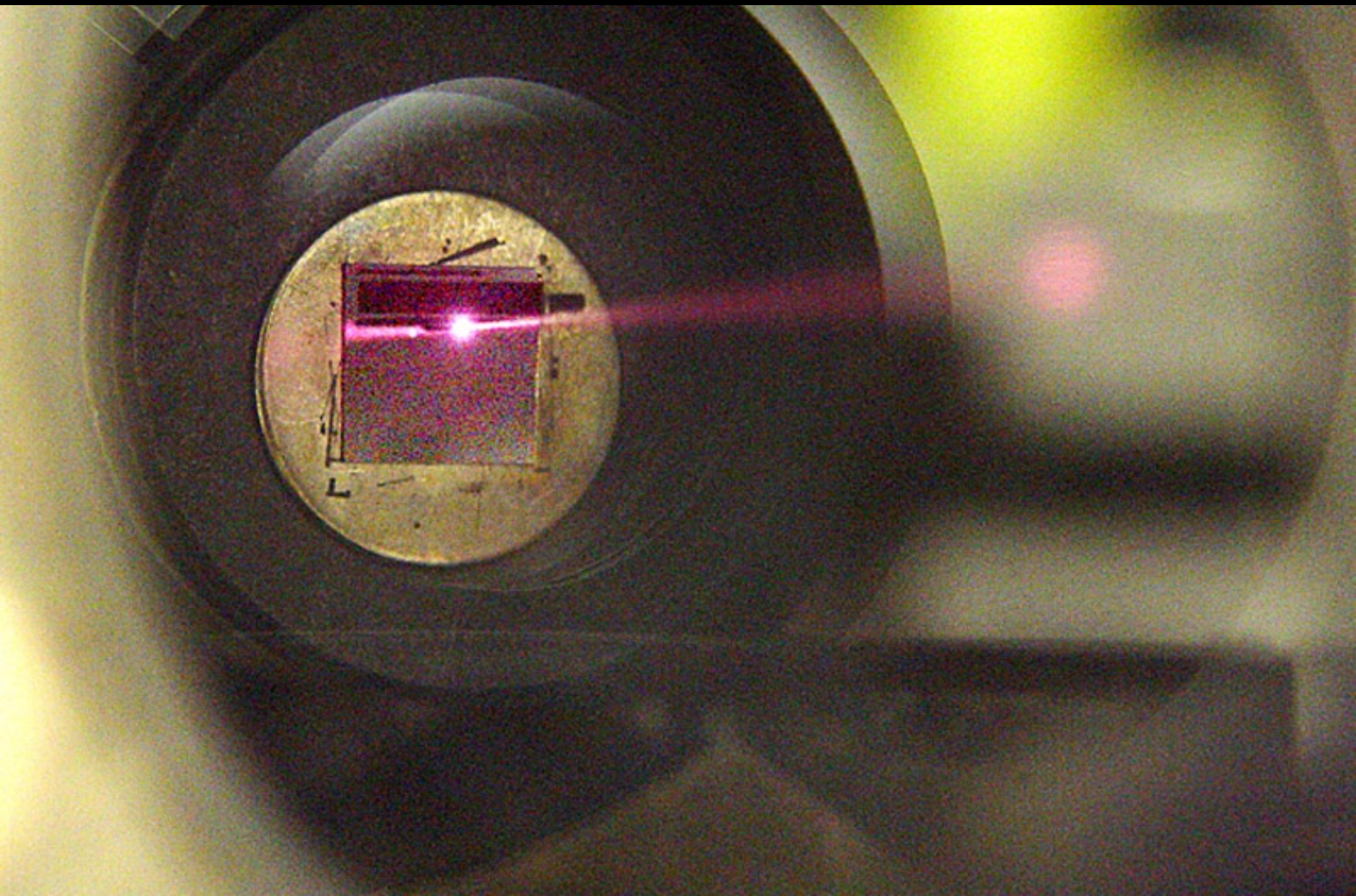
Prof. Michael Aziz
Prof. Cynthia Friend
Prof. Li Zhao (Fudan)

Introduction



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

Introduction



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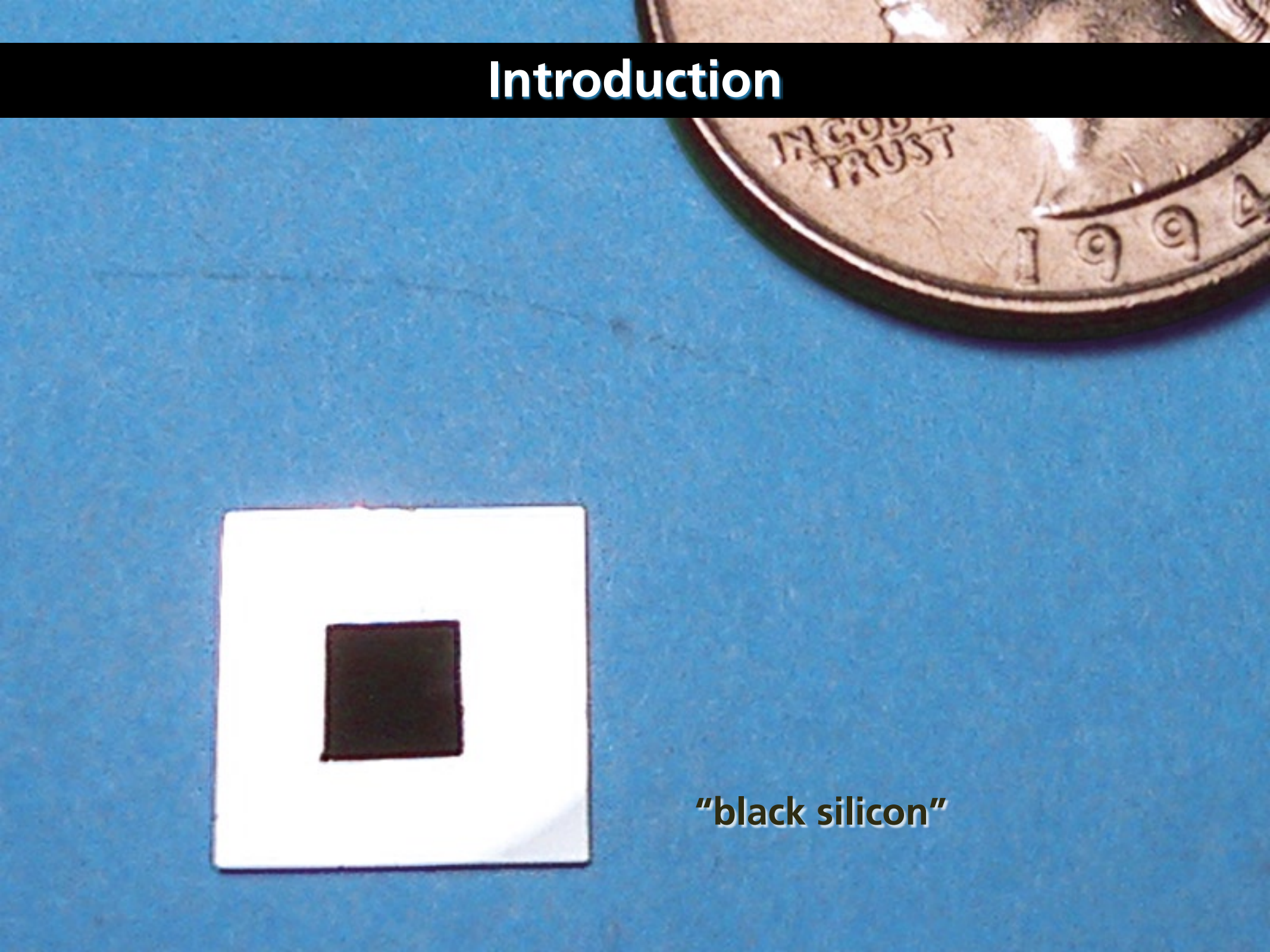
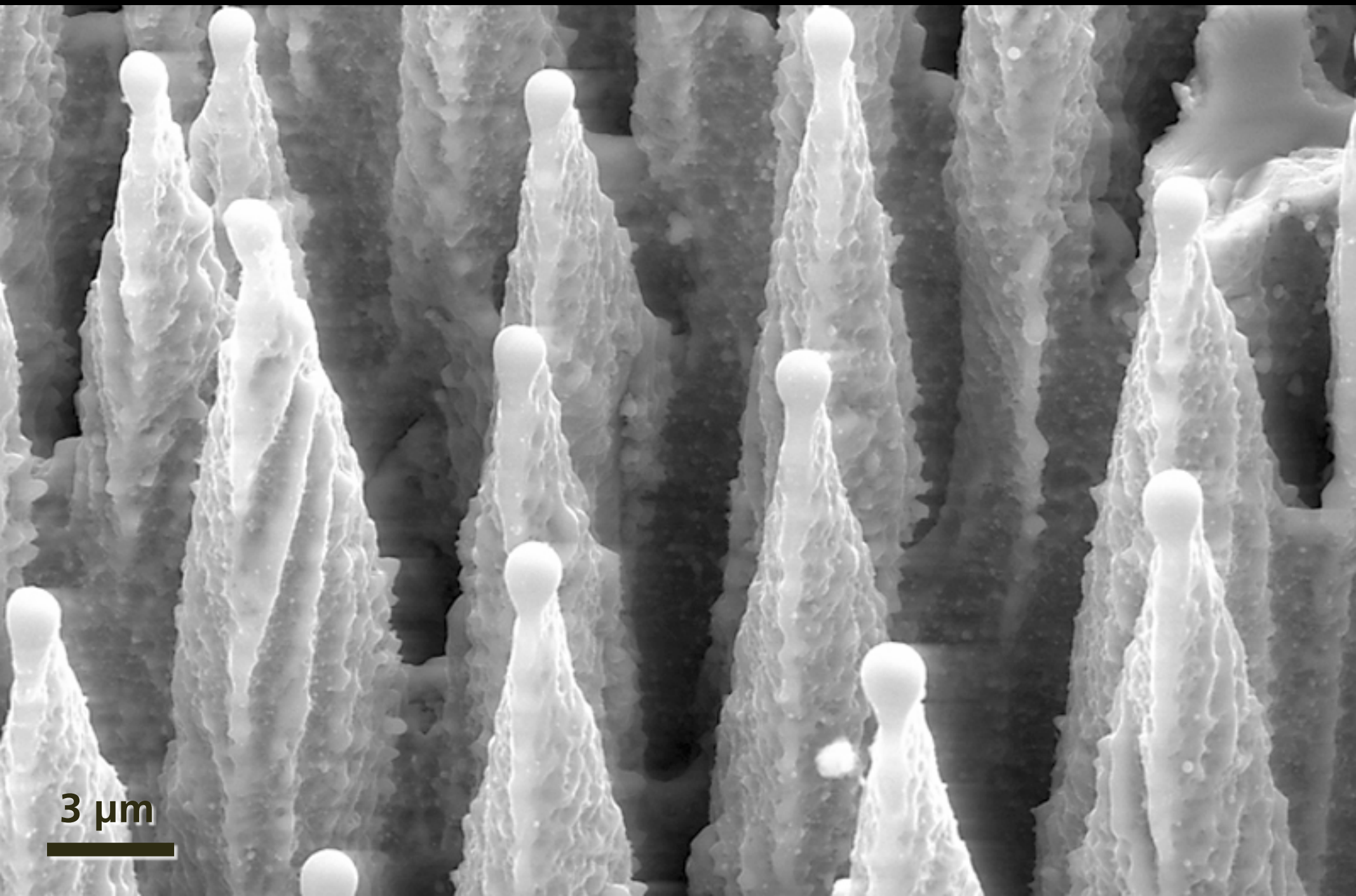


“black silicon”

Introduction



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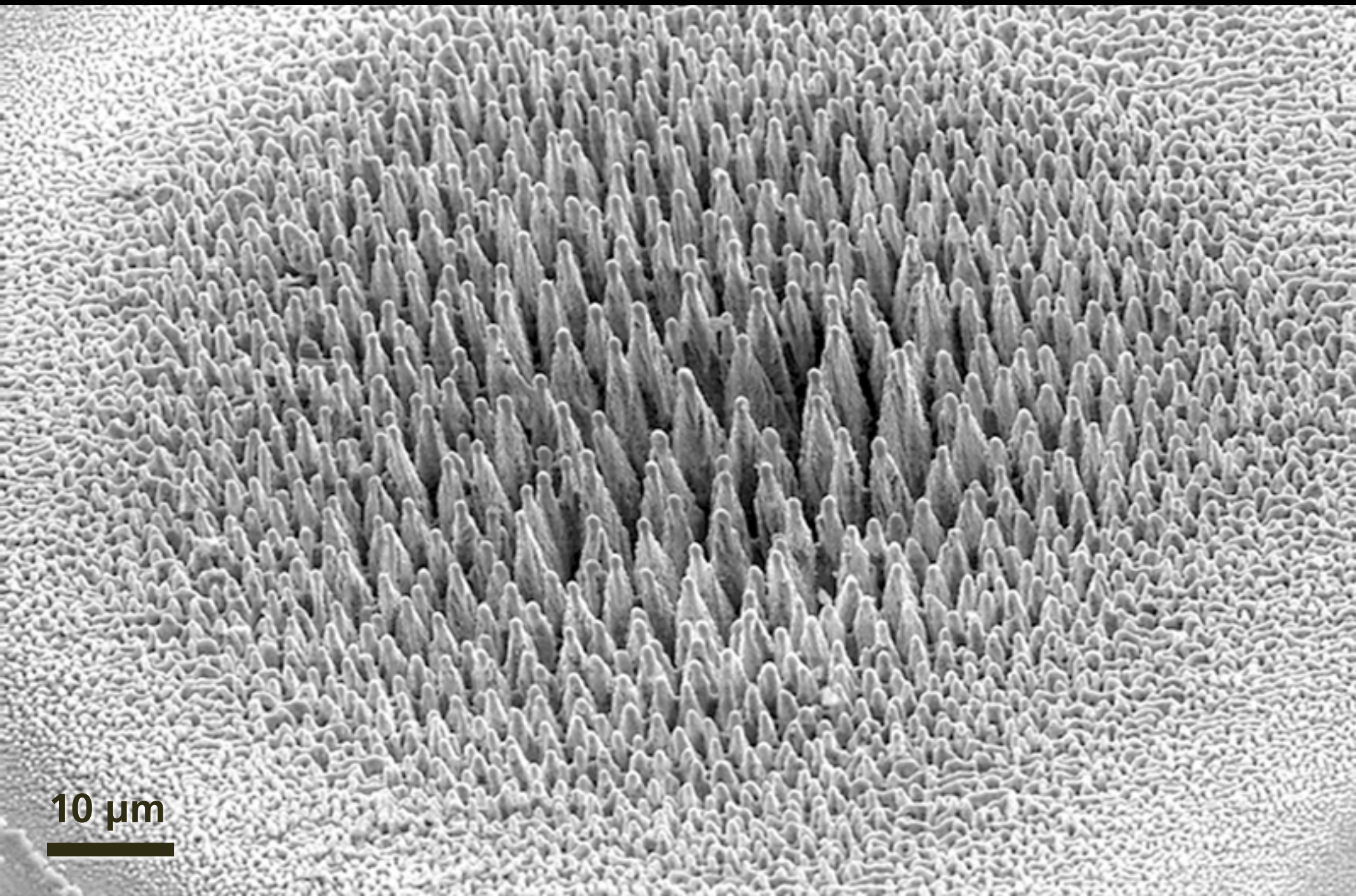

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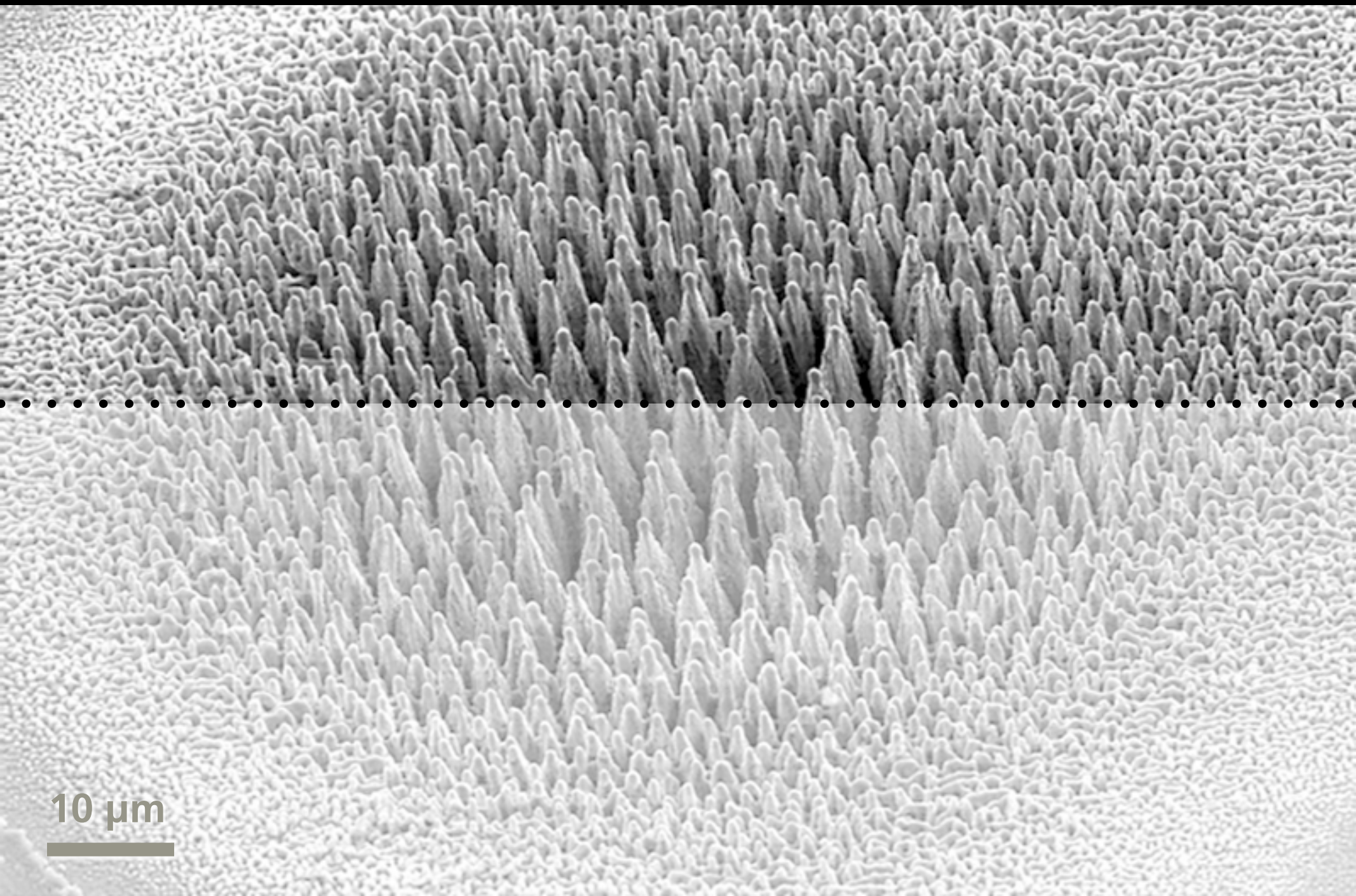

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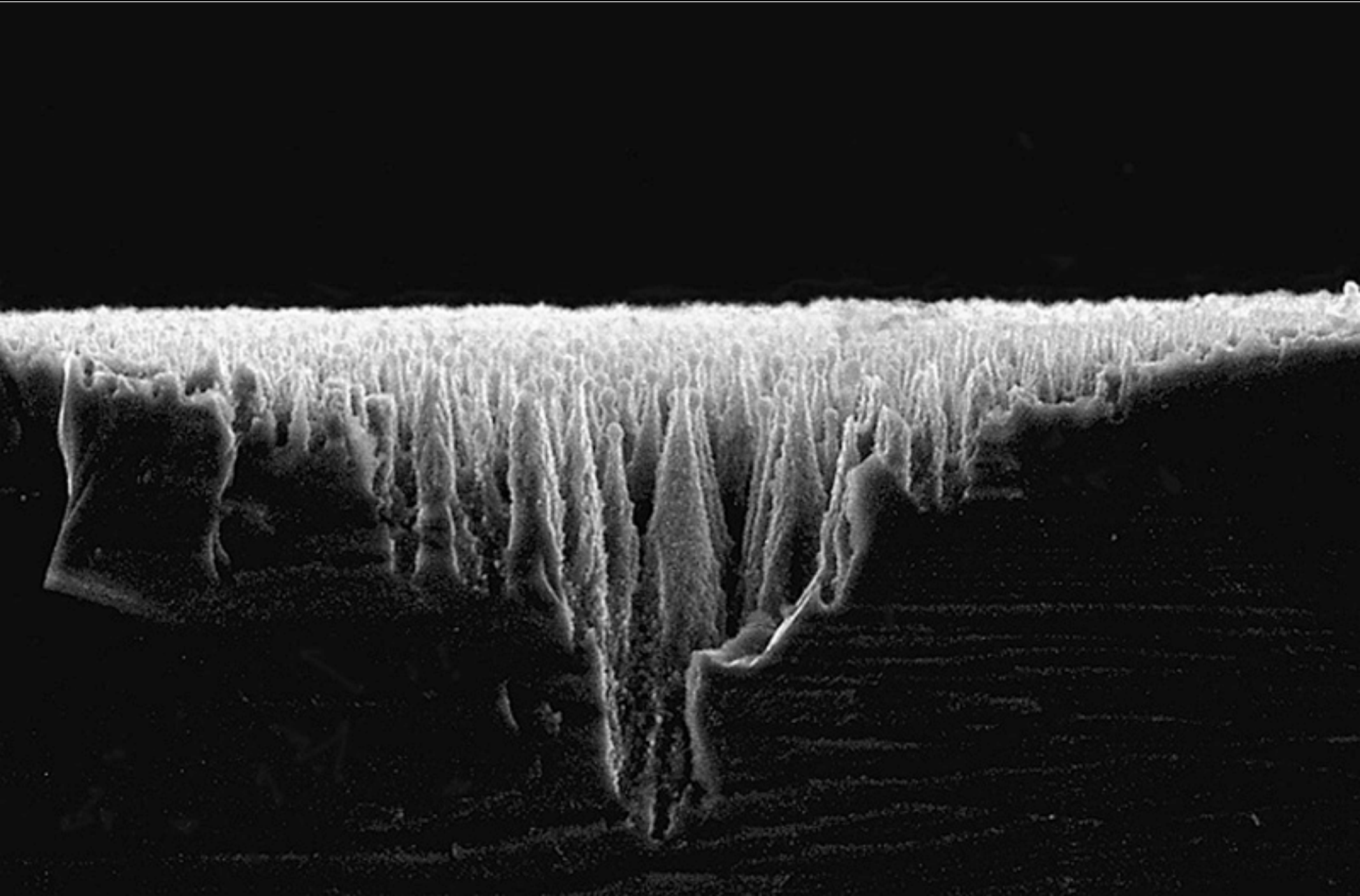

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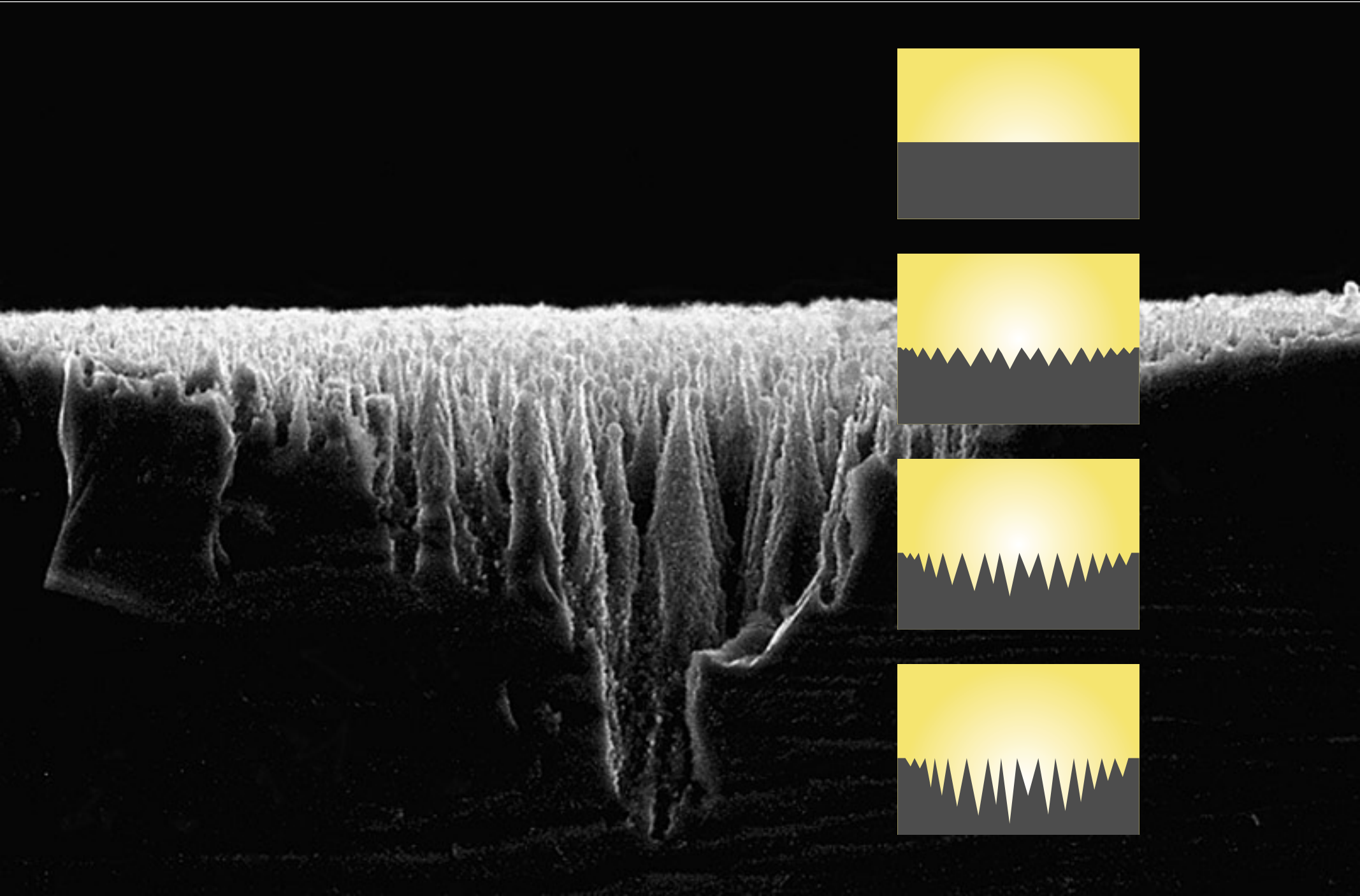


Introduction

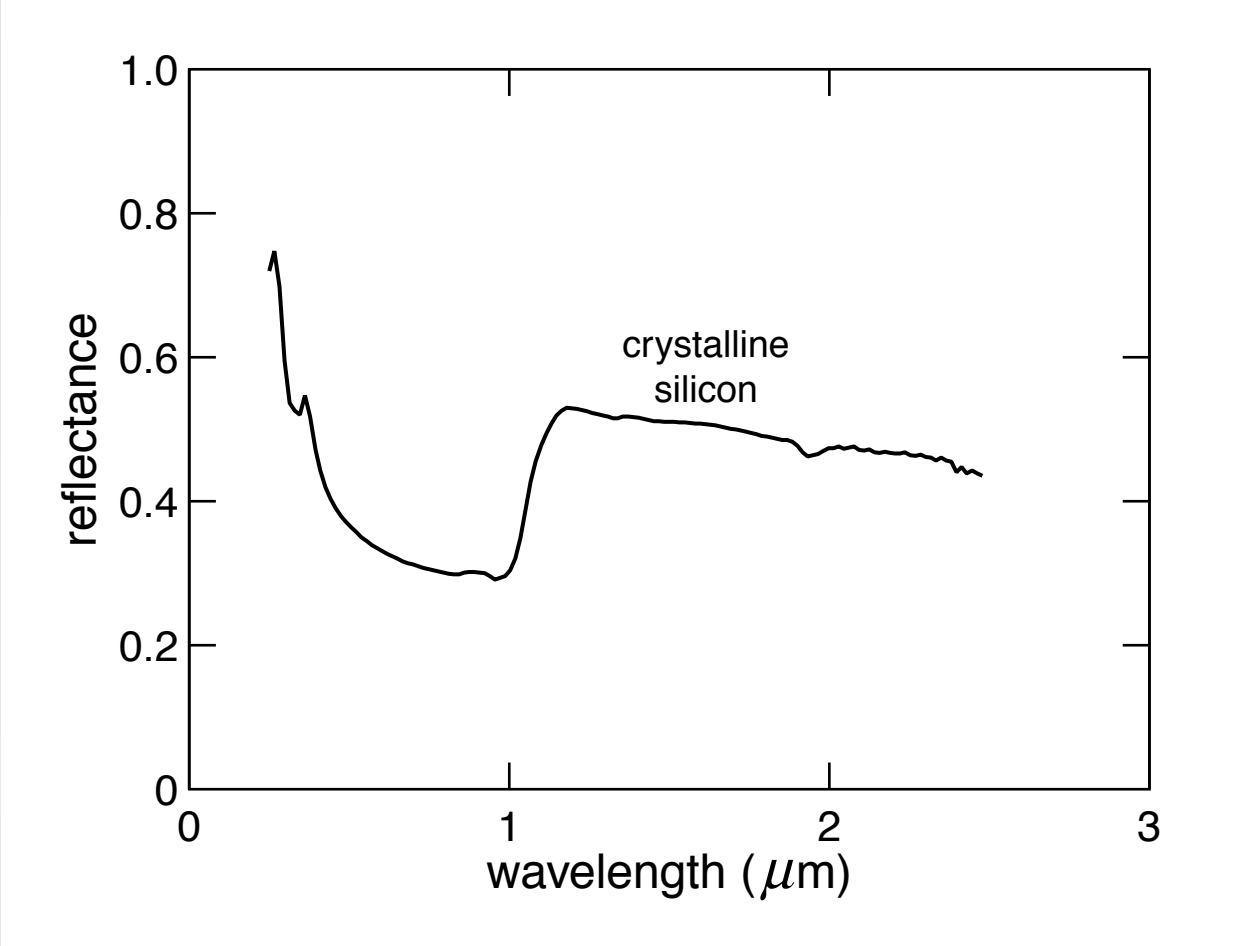
- maskless etching process
- self-organized, tall microstructures
- highly light absorbing

Outline

- properties
- structural and chemical analysis
- detectors
- outlook

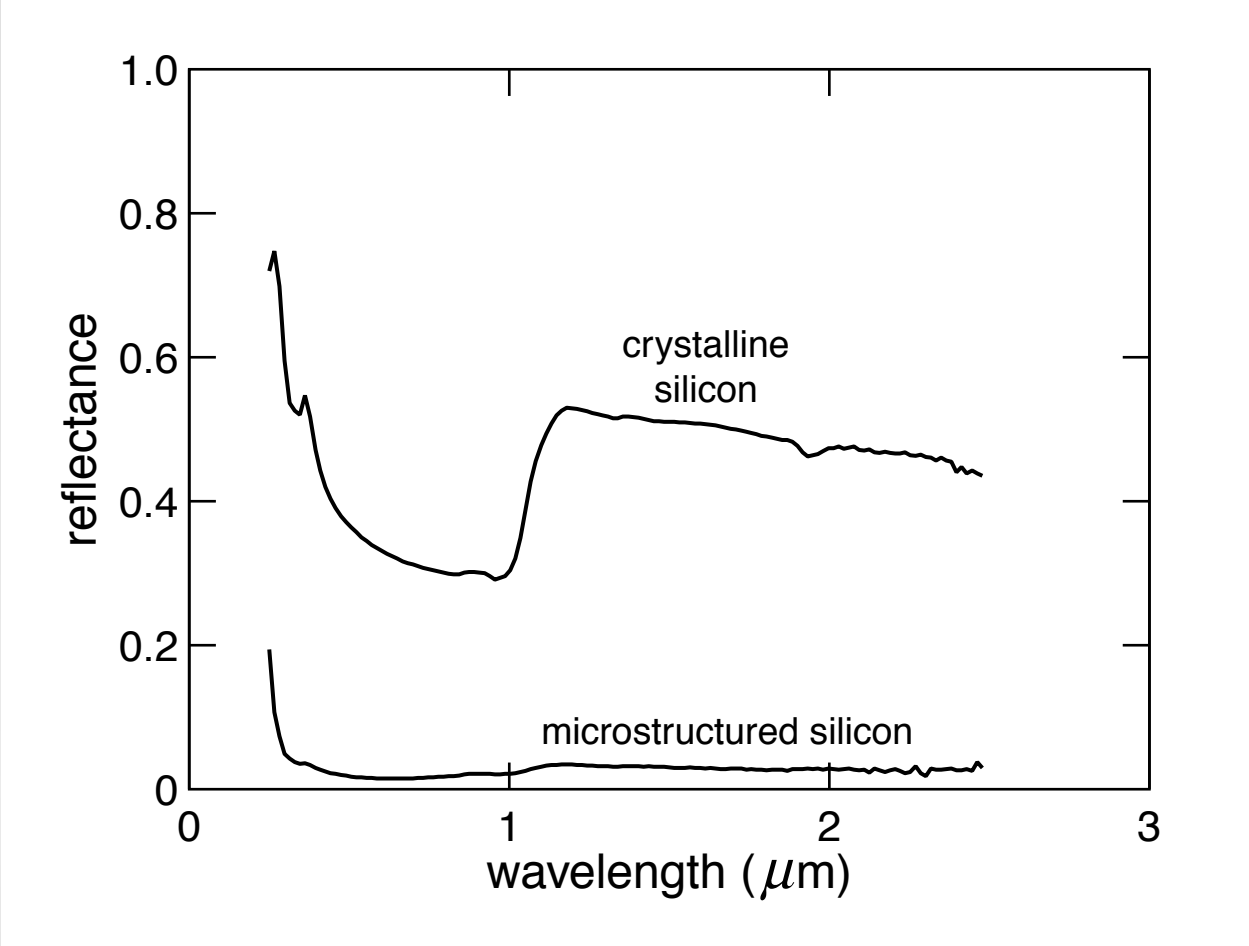
Properties

reflectance (integrating sphere)



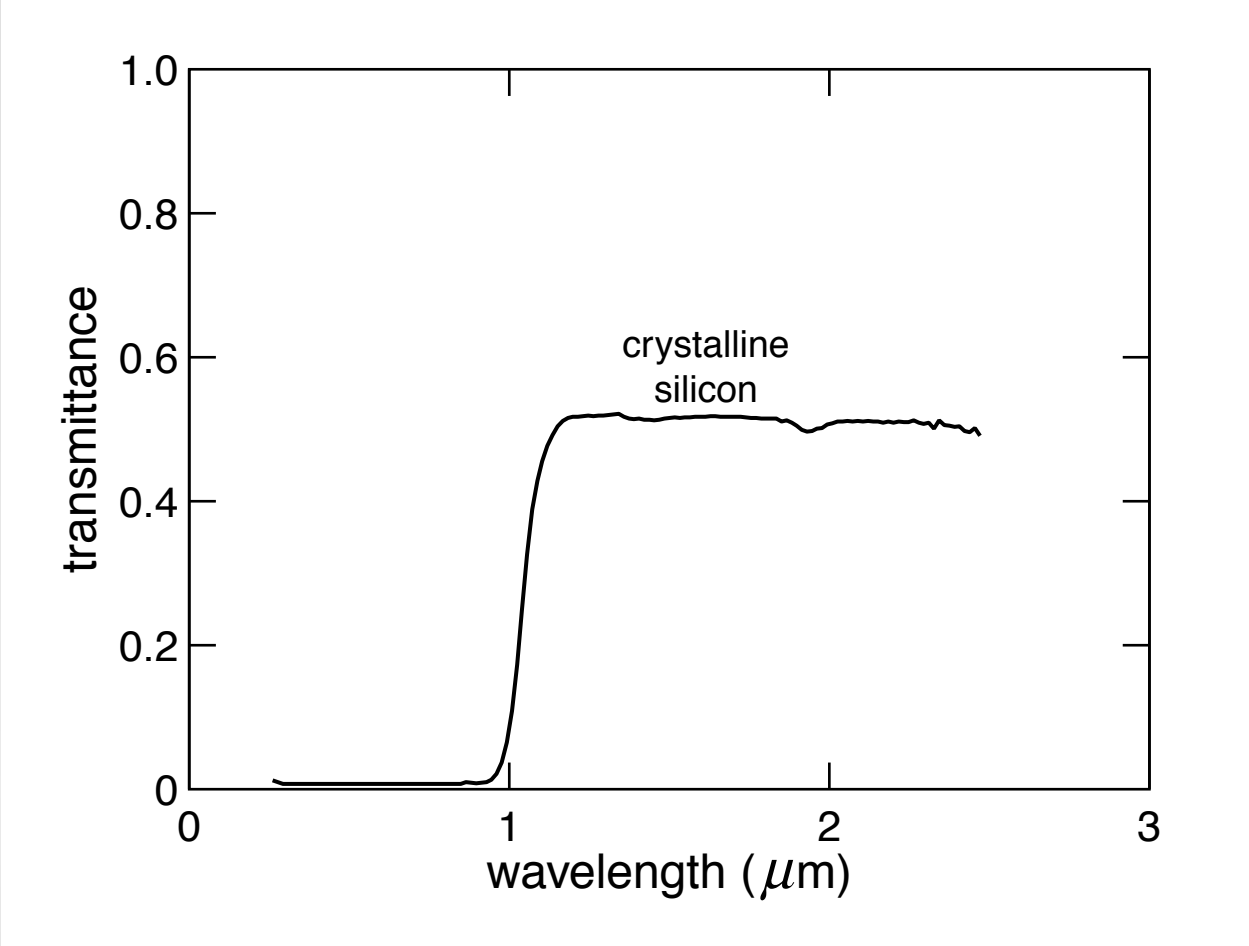
Properties

reflectance (integrating sphere)



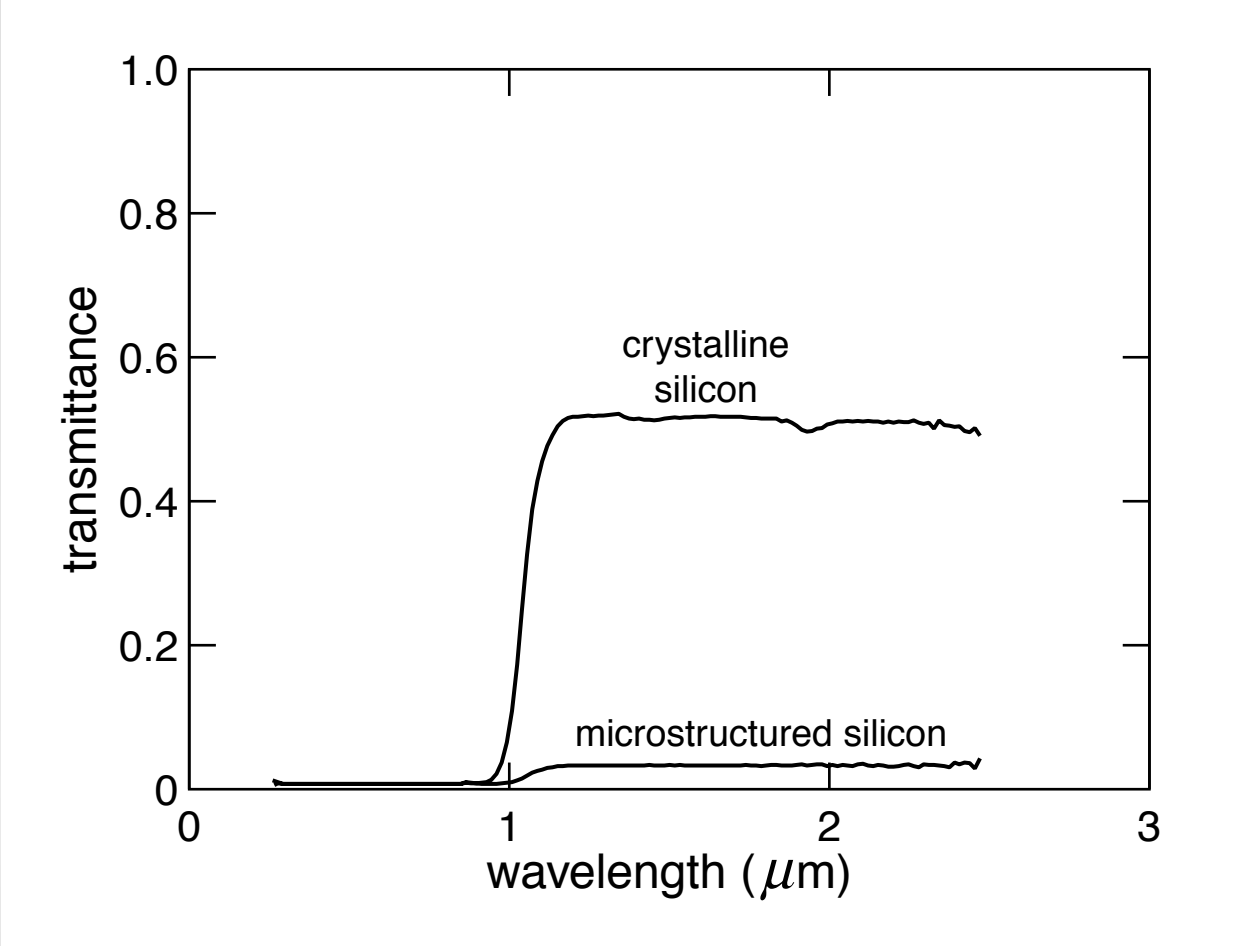
Properties

transmittance (integrating sphere)



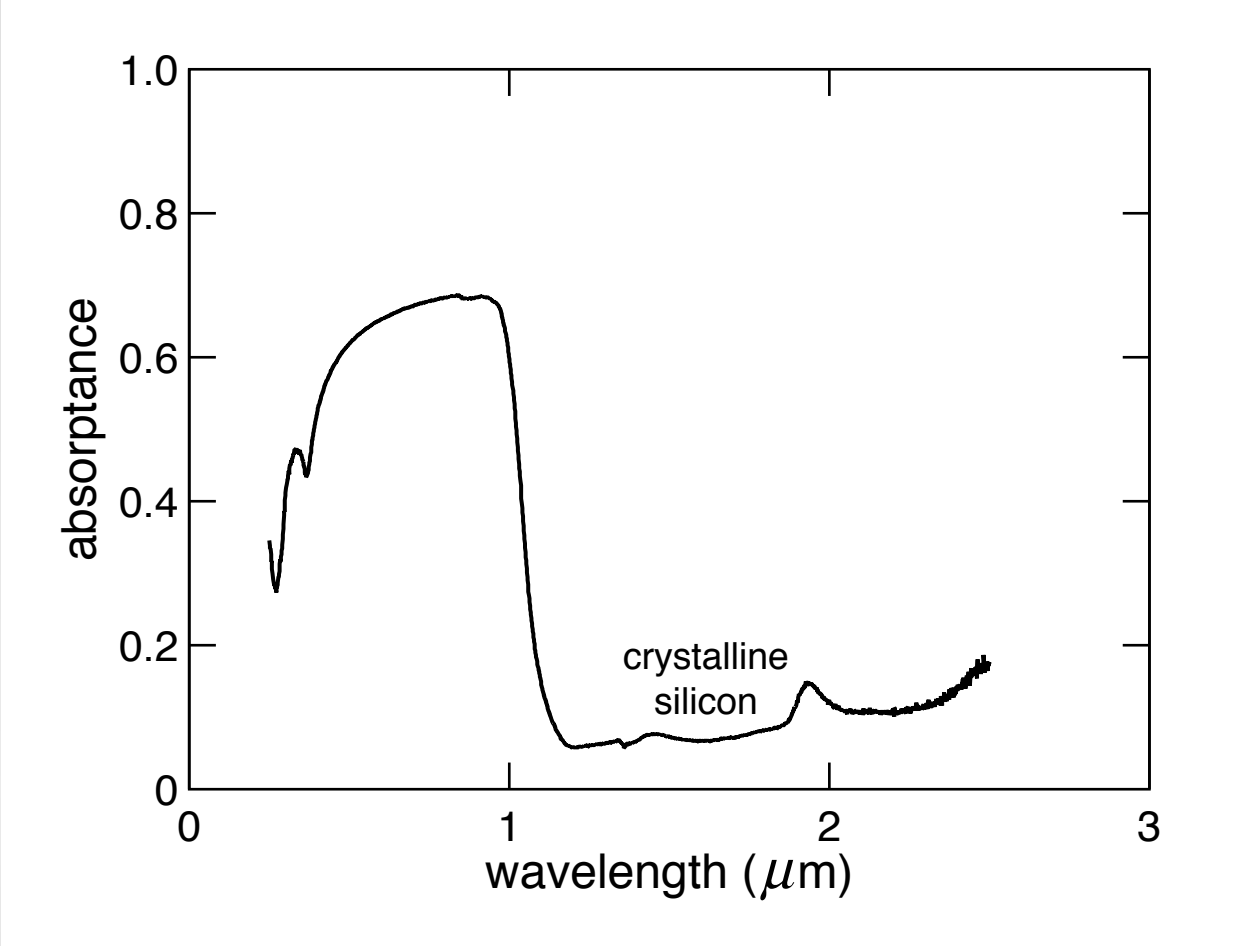
Properties

transmittance (integrating sphere)



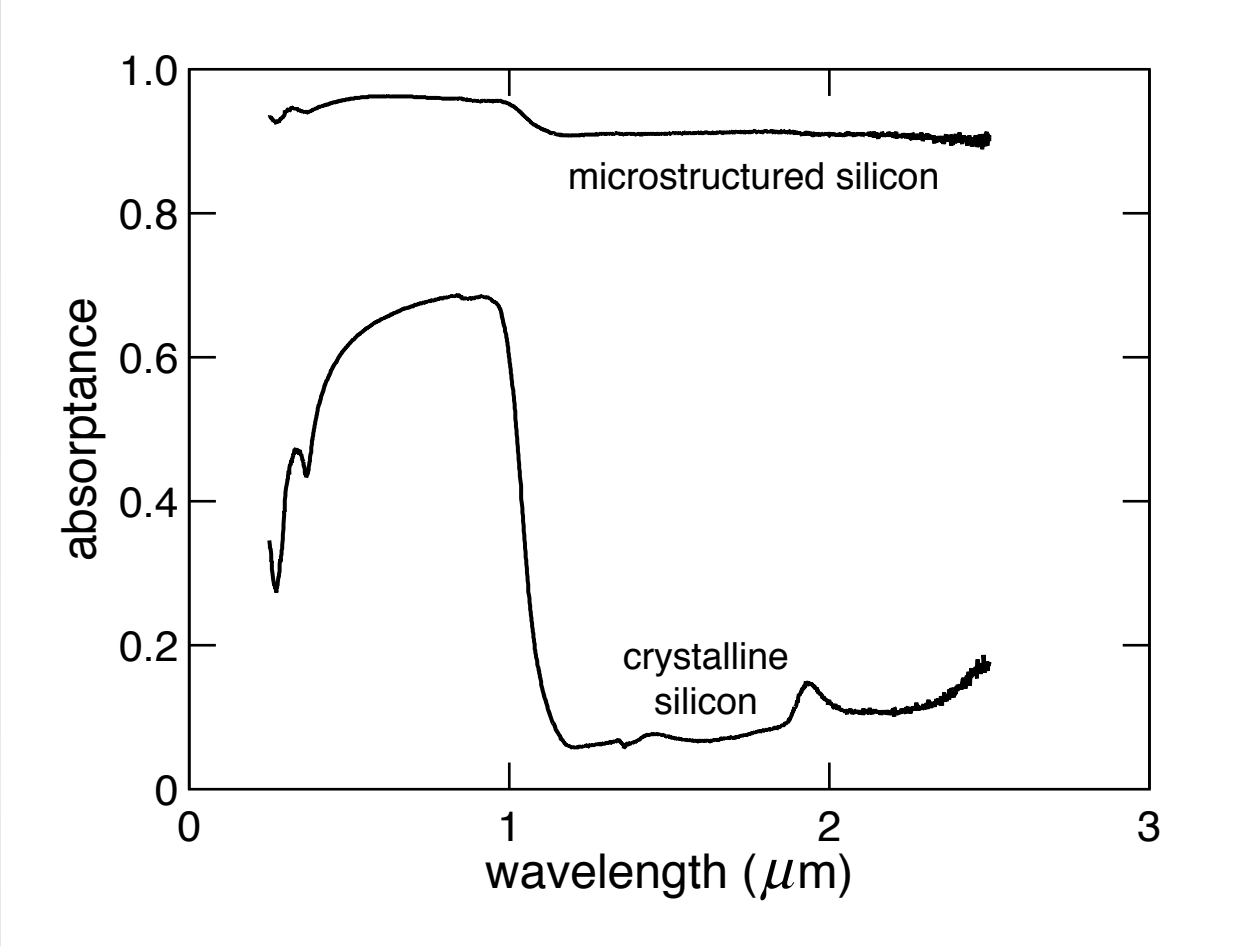
Properties

absorptance (1 – *R* – *T*)



Properties

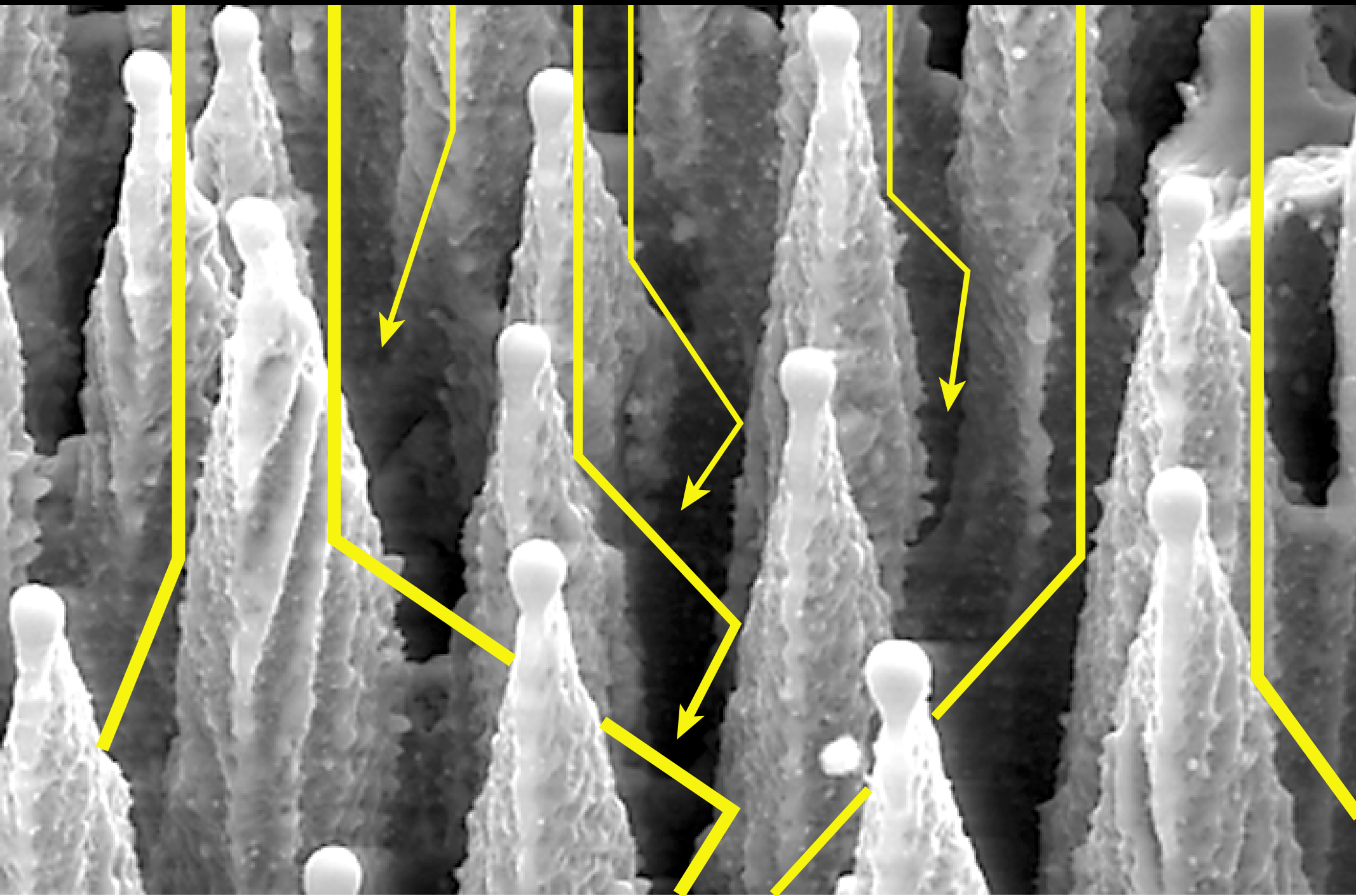
absorptance (1 – *R* – *T*)



Properties

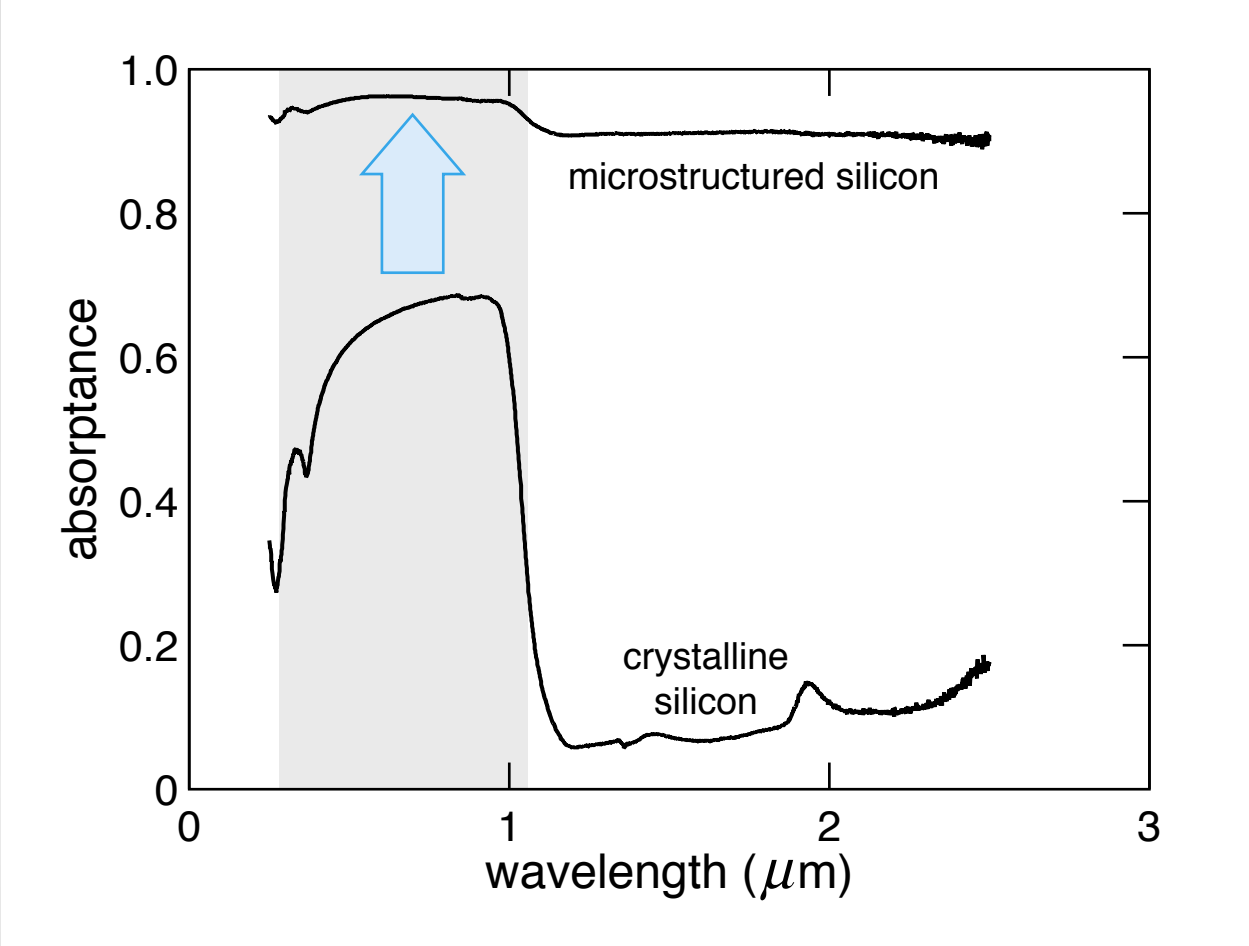
What causes the near-unity absorptance?

Properties



Properties

multiple reflections enhance absorption



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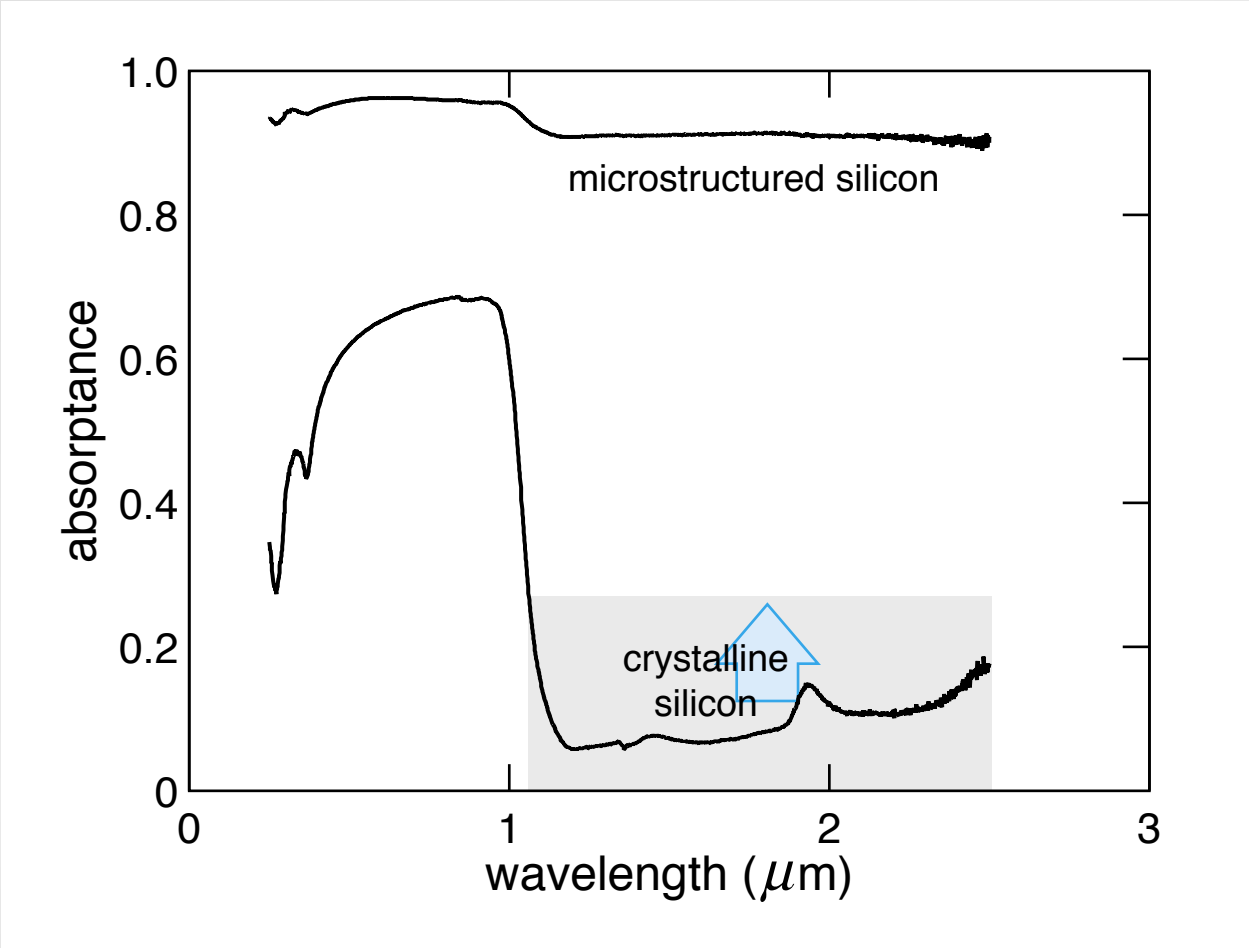
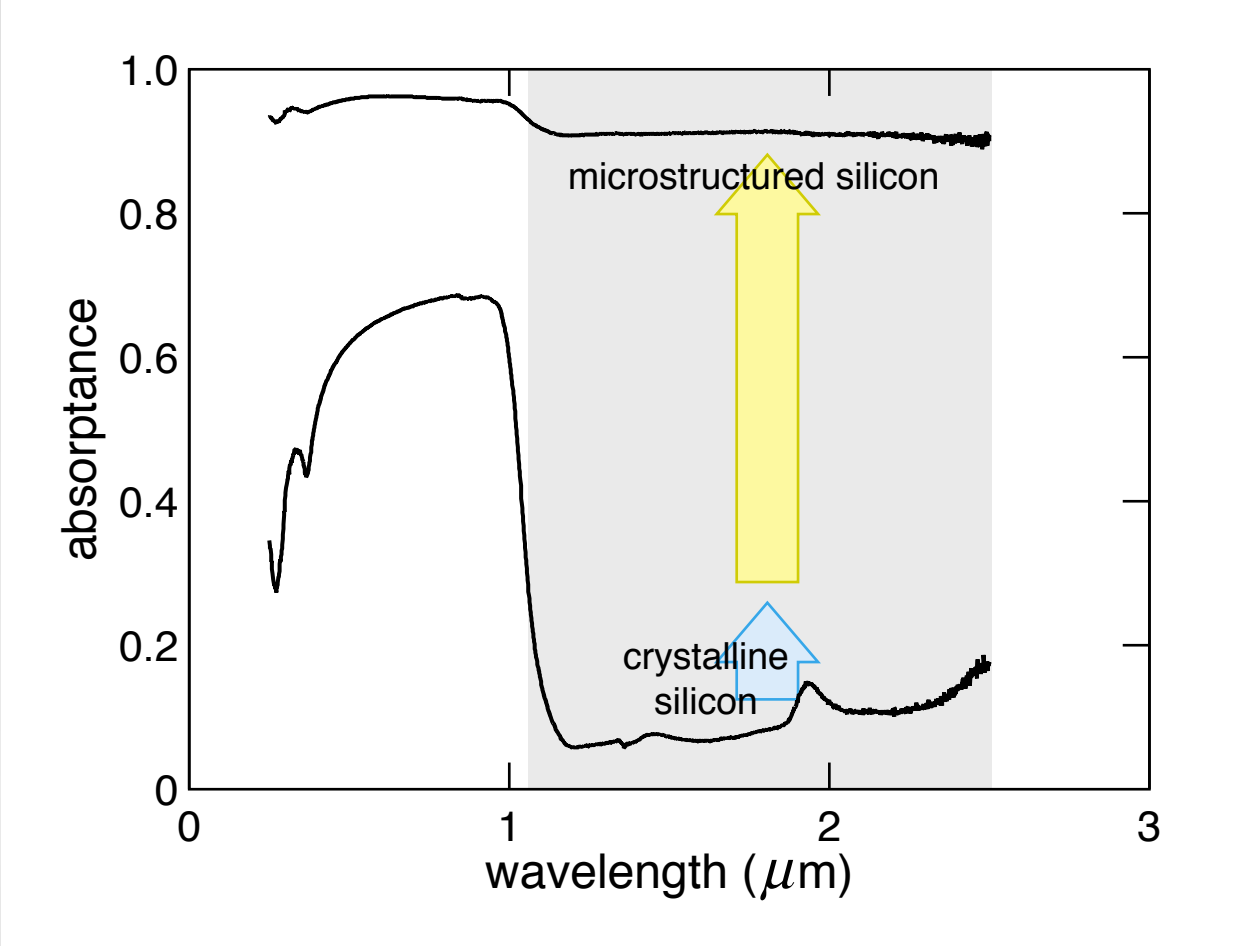
multiple reflections enhance absorption



Properties

electronic band structure changes



Properties

- enhanced absorption in visible
- enhanced photoelectron generation in visible
- near unity absorption in IR
- visible photoluminescence
- strong field emission

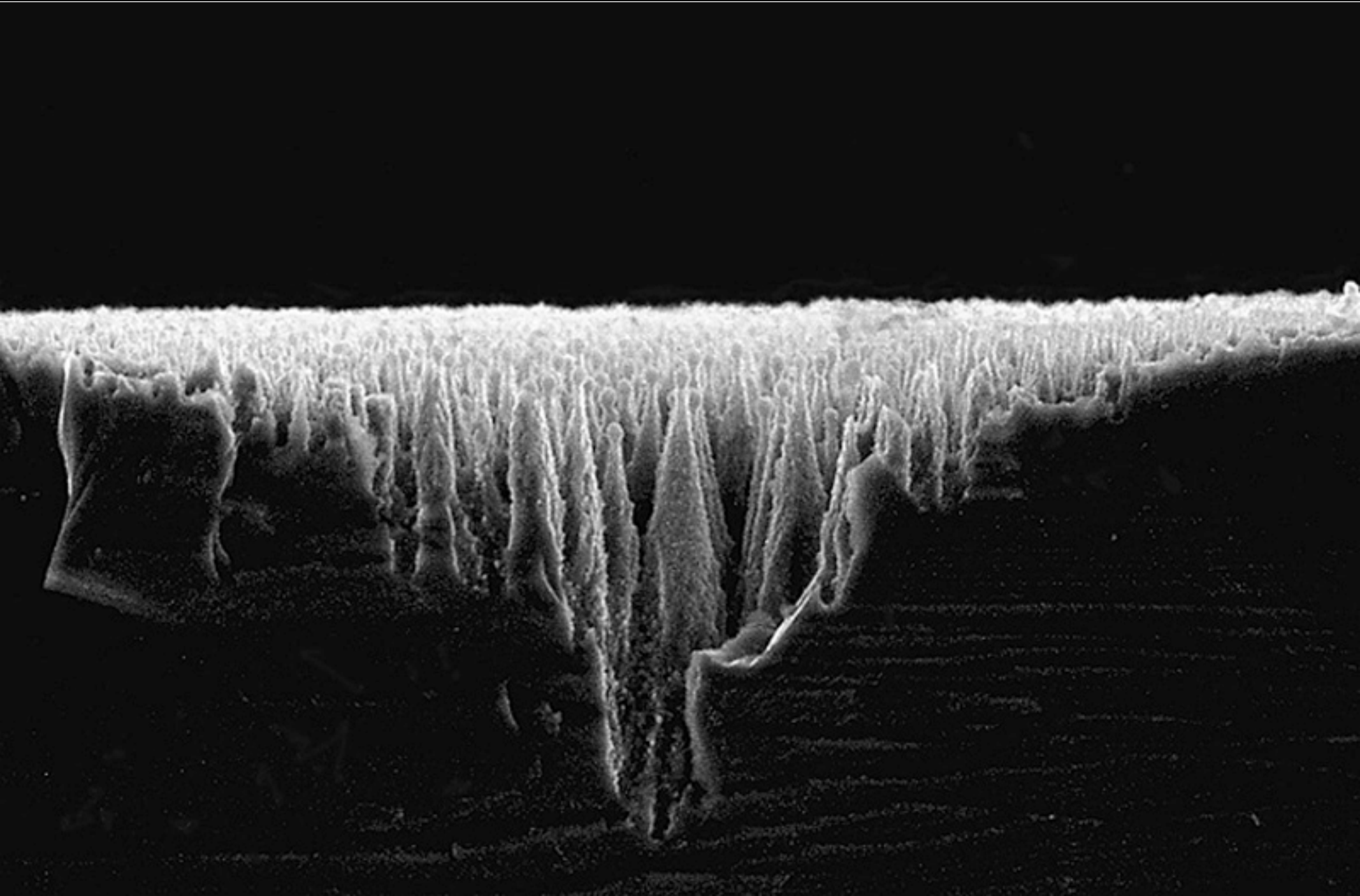
Outline

- properties
- **structural and chemical analysis**
- detectors
- outlook

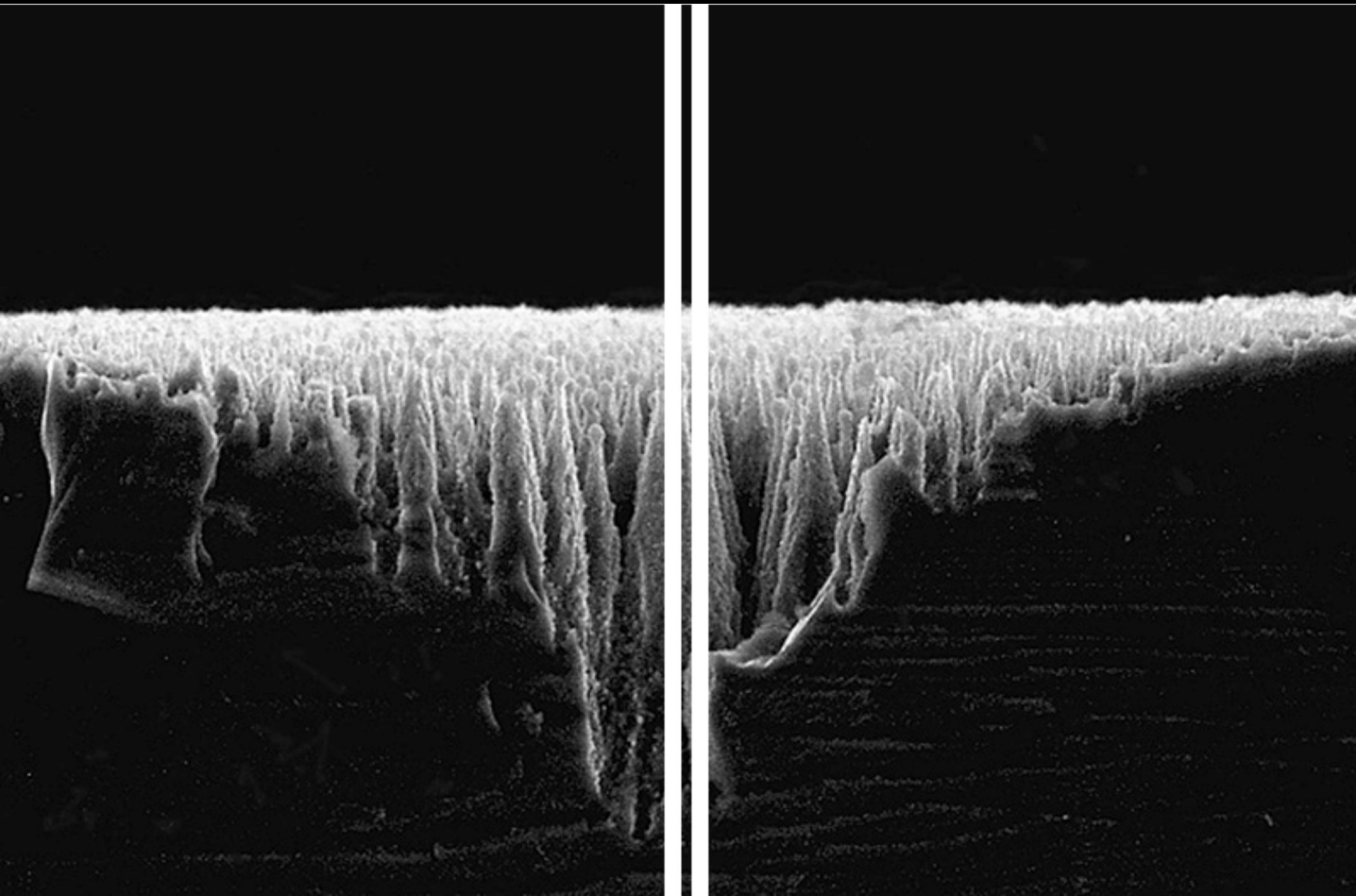
Structural and chemical analysis

Band structure changes: defects and/or impurities

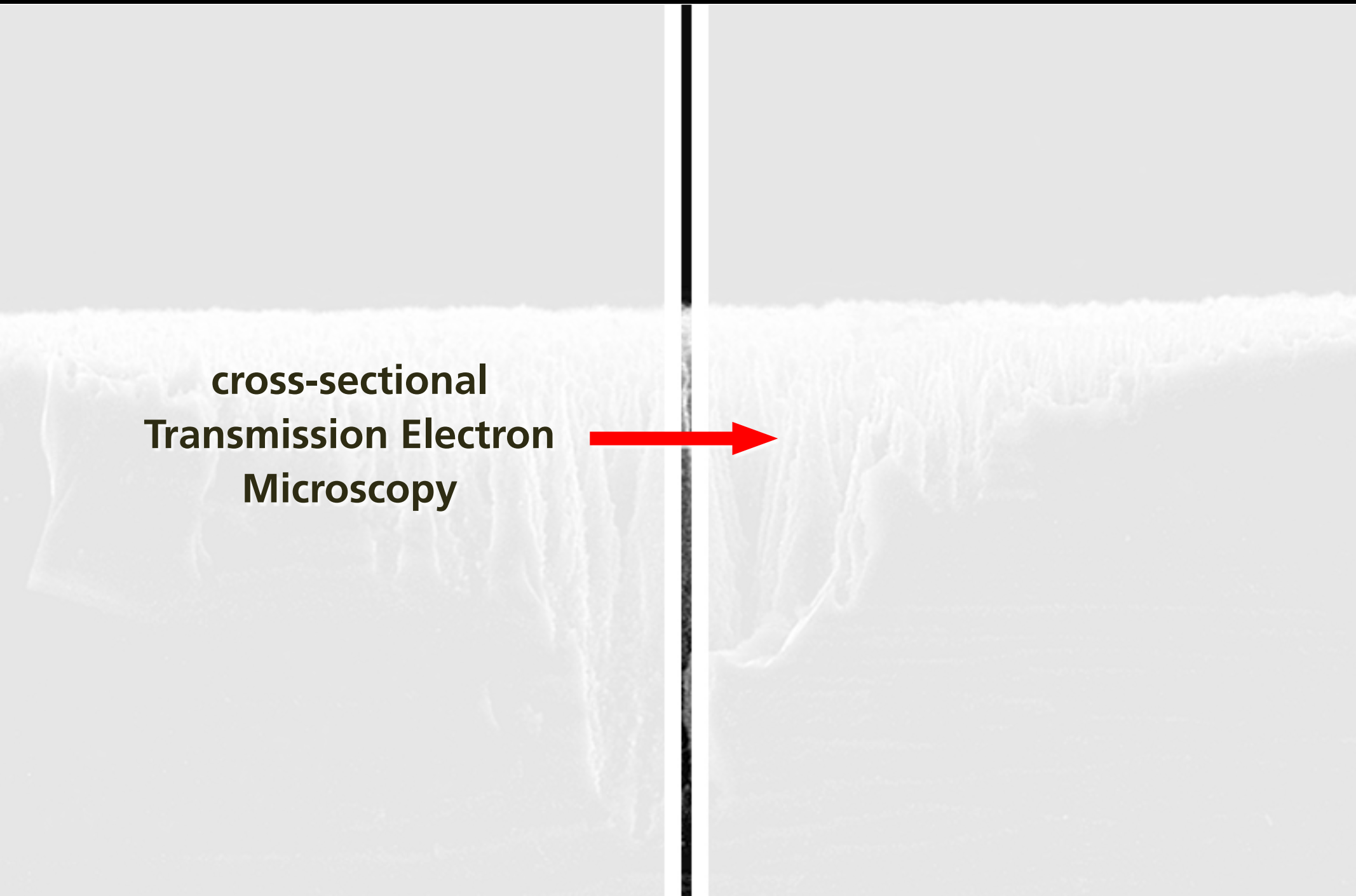
Structural and chemical analysis



Structural and chemical analysis

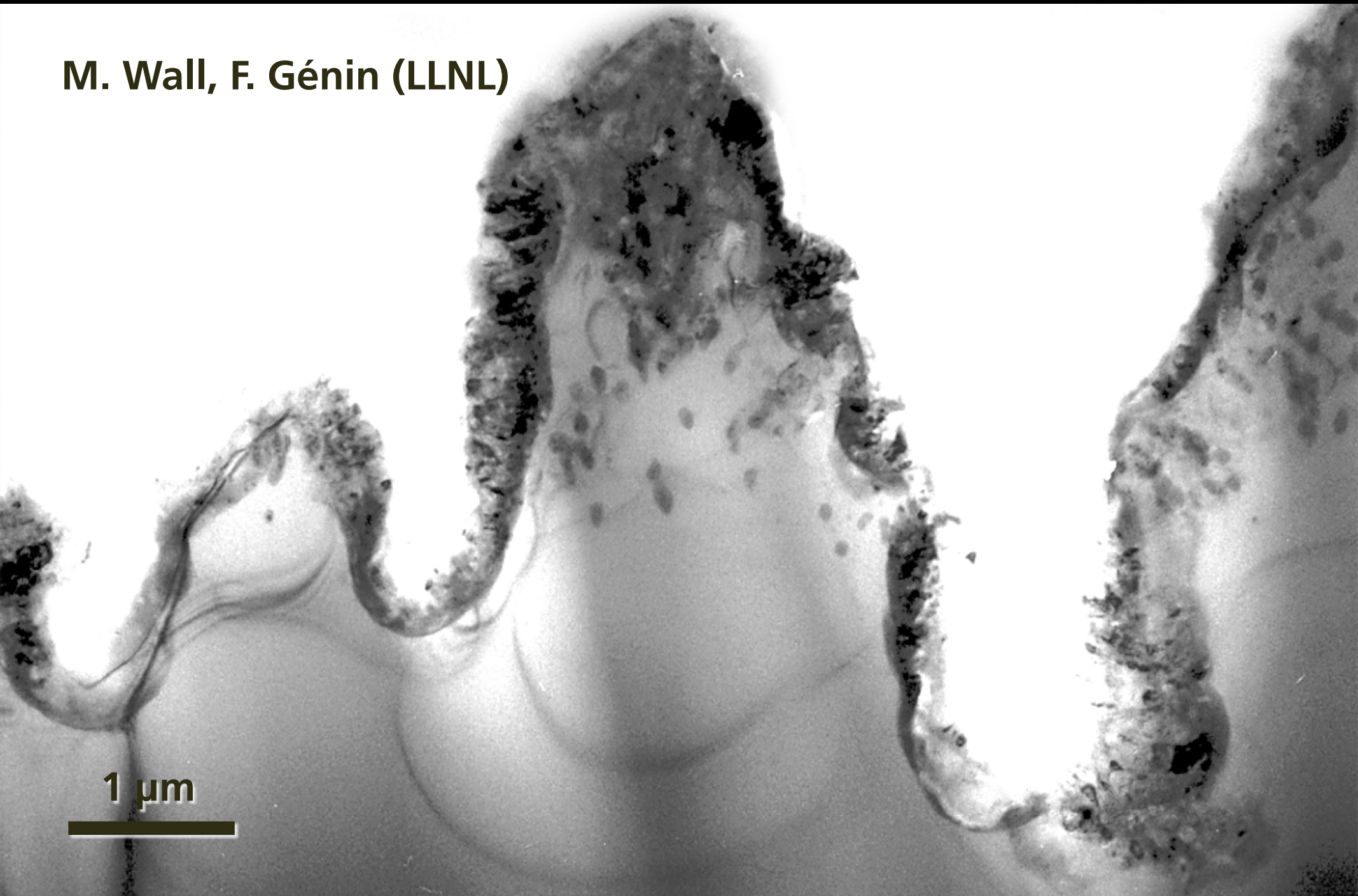


Structural and chemical analysis

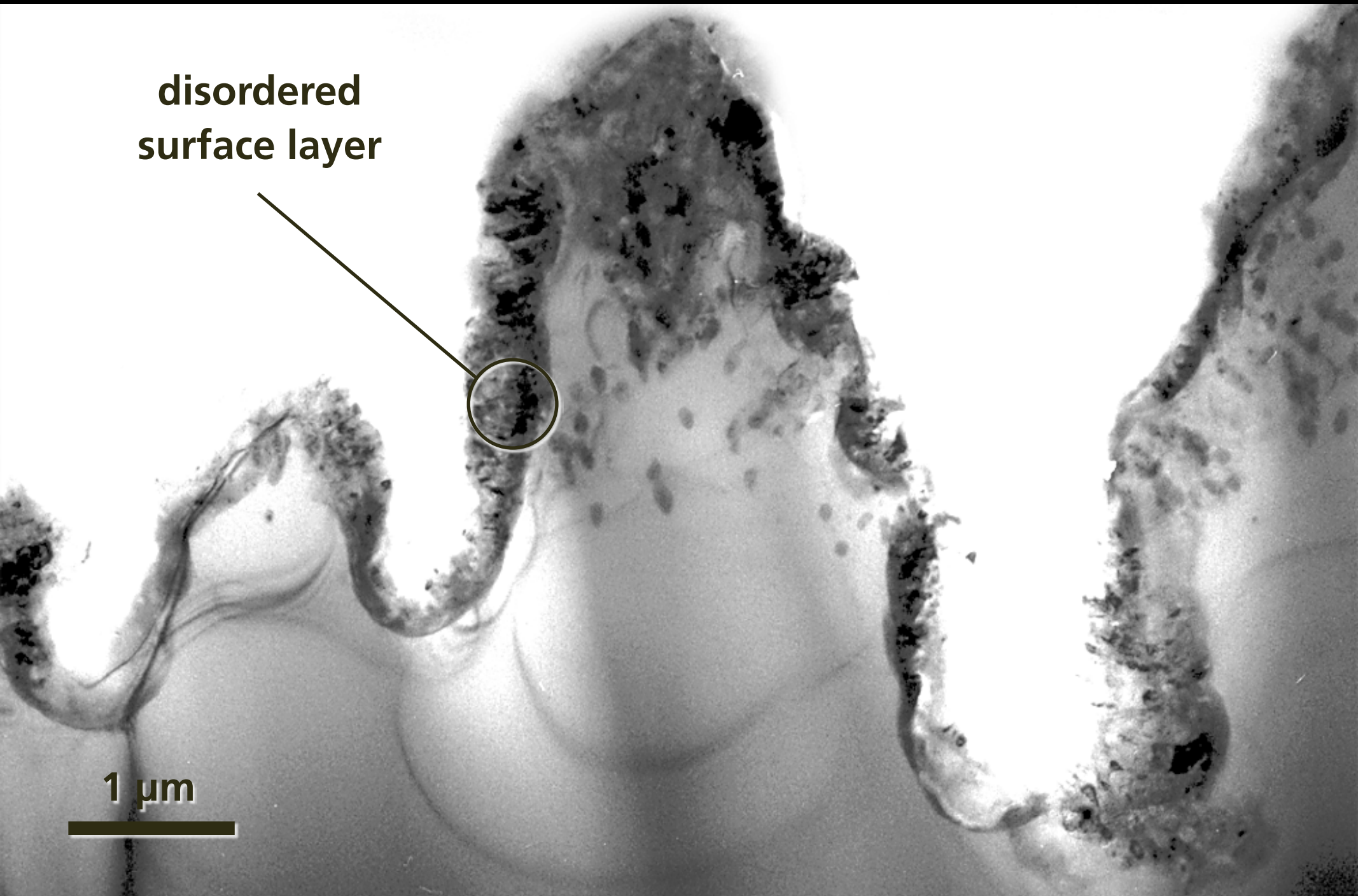


Structural and chemical analysis

M. Wall, F. Génin (LLNL)



Structural and chemical analysis



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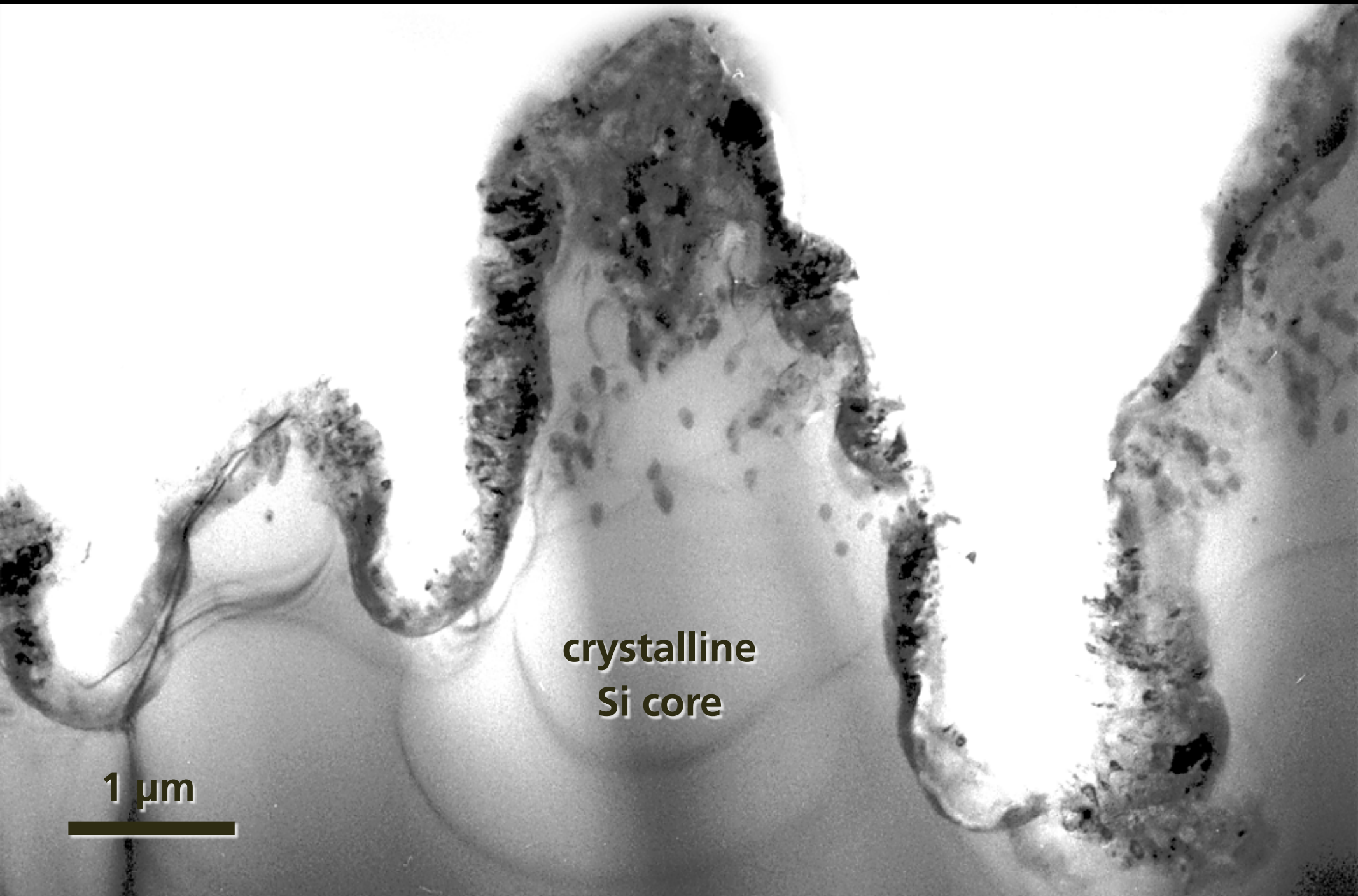
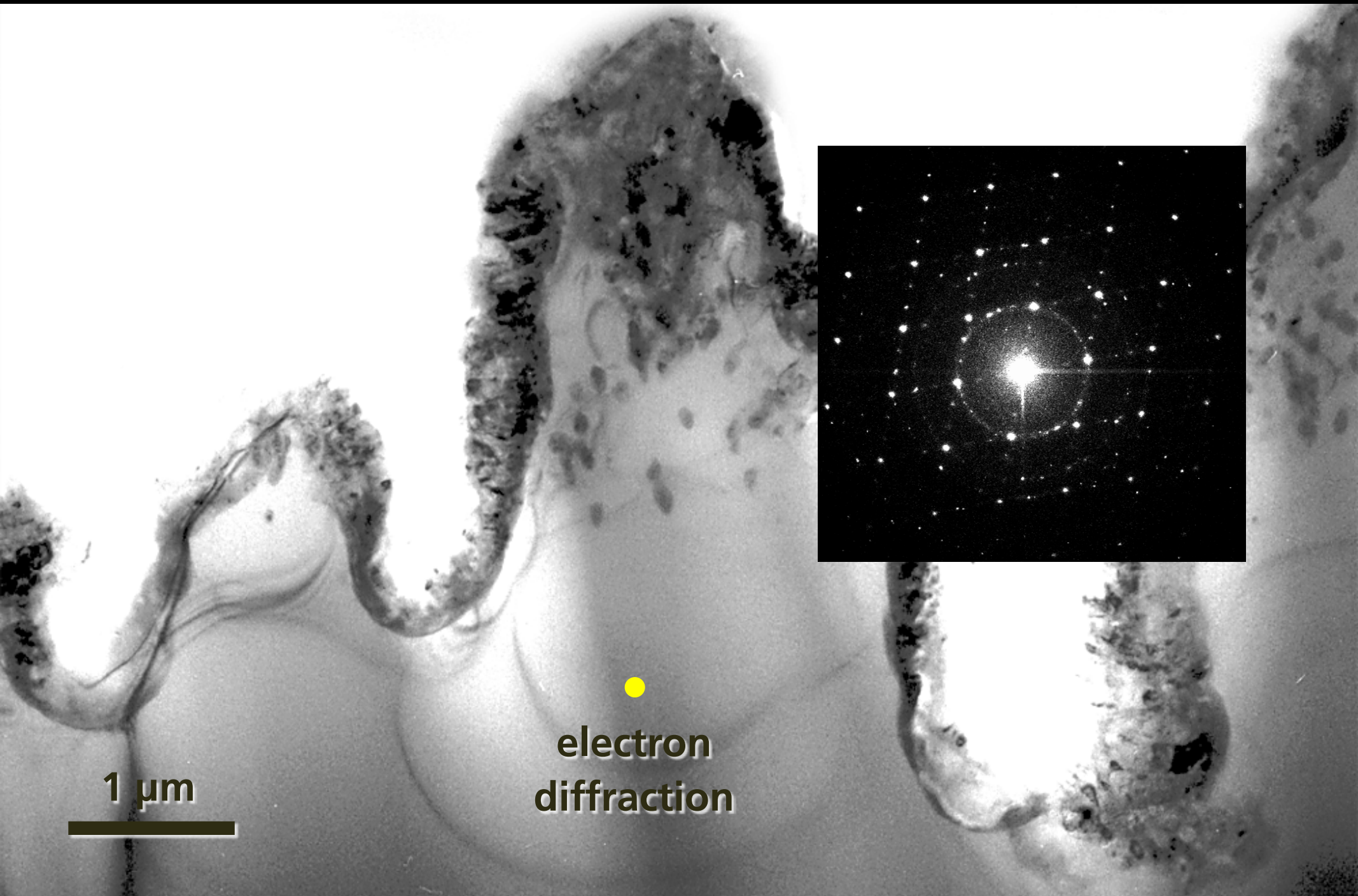


Structural and chemical analysis



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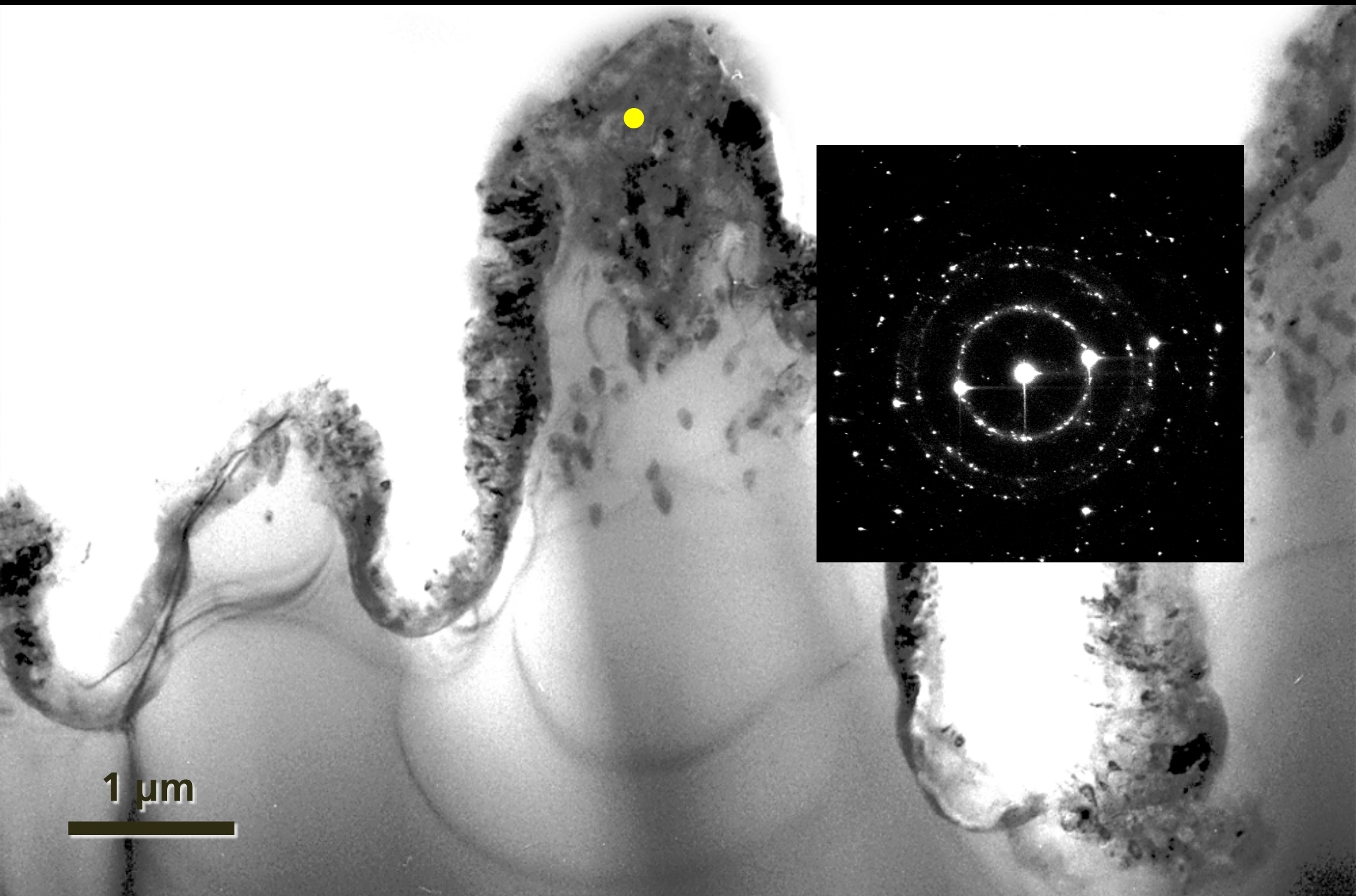
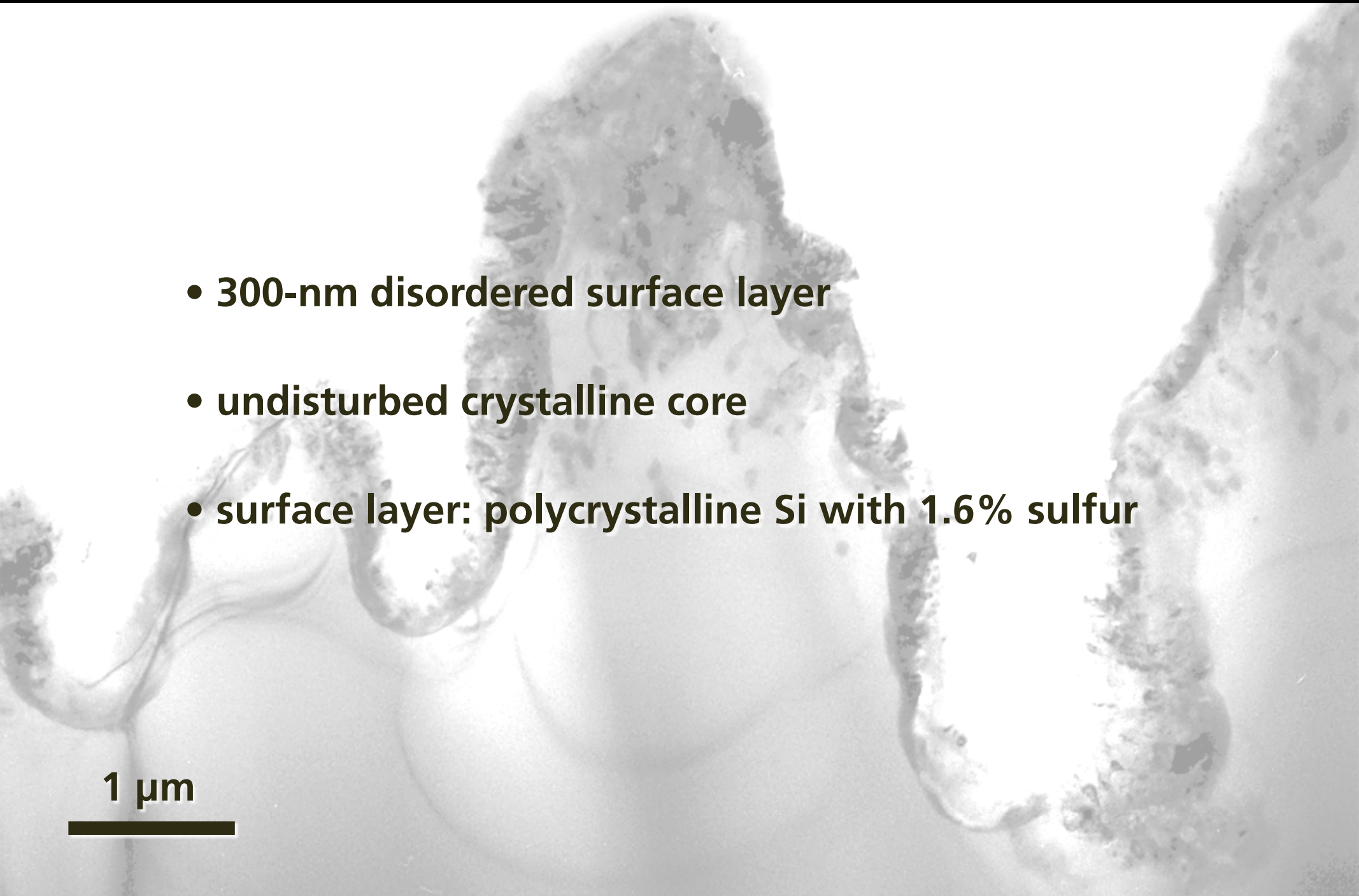


Structural and chemical analysis



- 300-nm disordered surface layer
- undisturbed crystalline core
- surface layer: polycrystalline Si with 1.6% sulfur

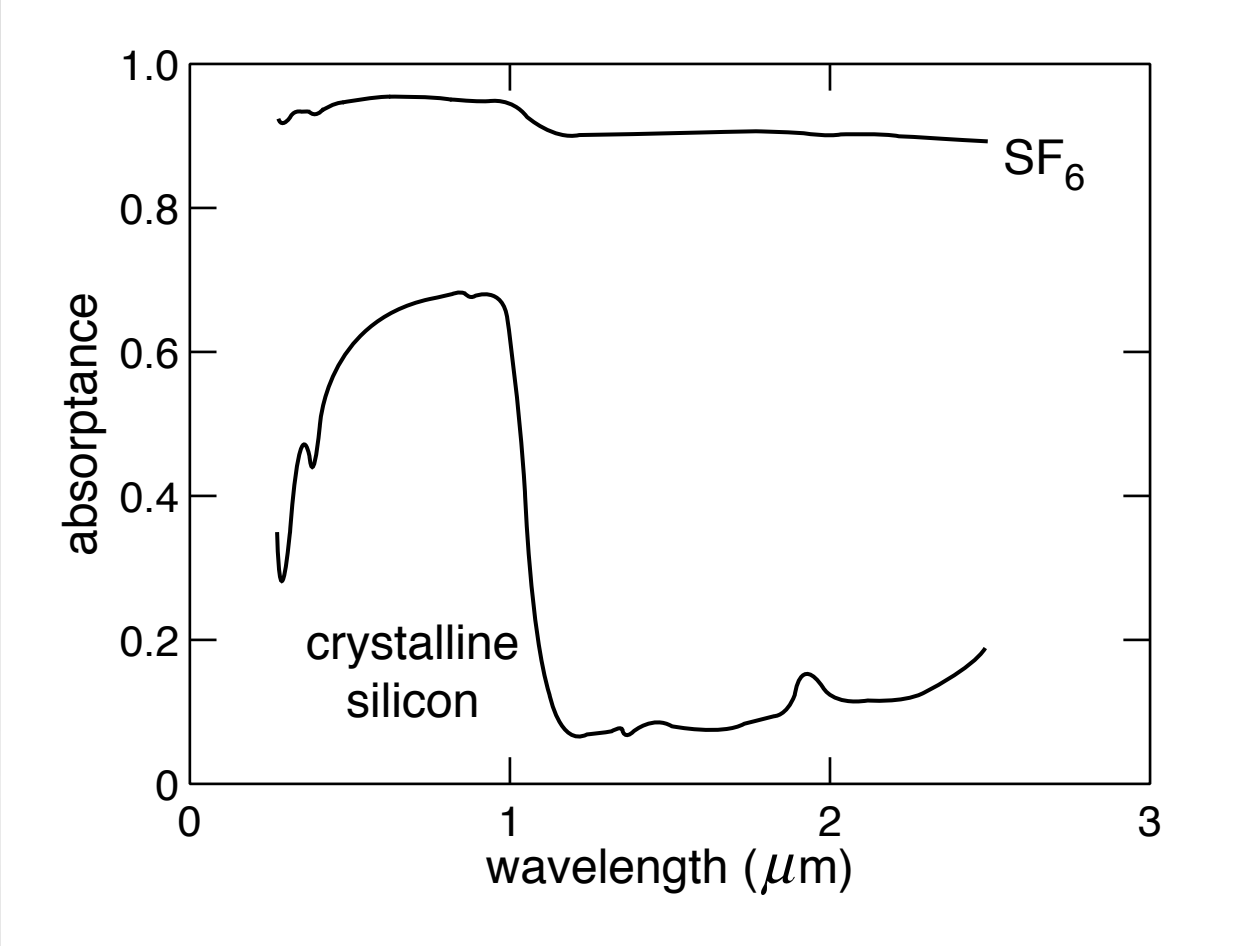
Structural and chemical analysis

Microstructure with different gases:

- gas species incorporated into surface layer
- sulfur required for below band gap absorption

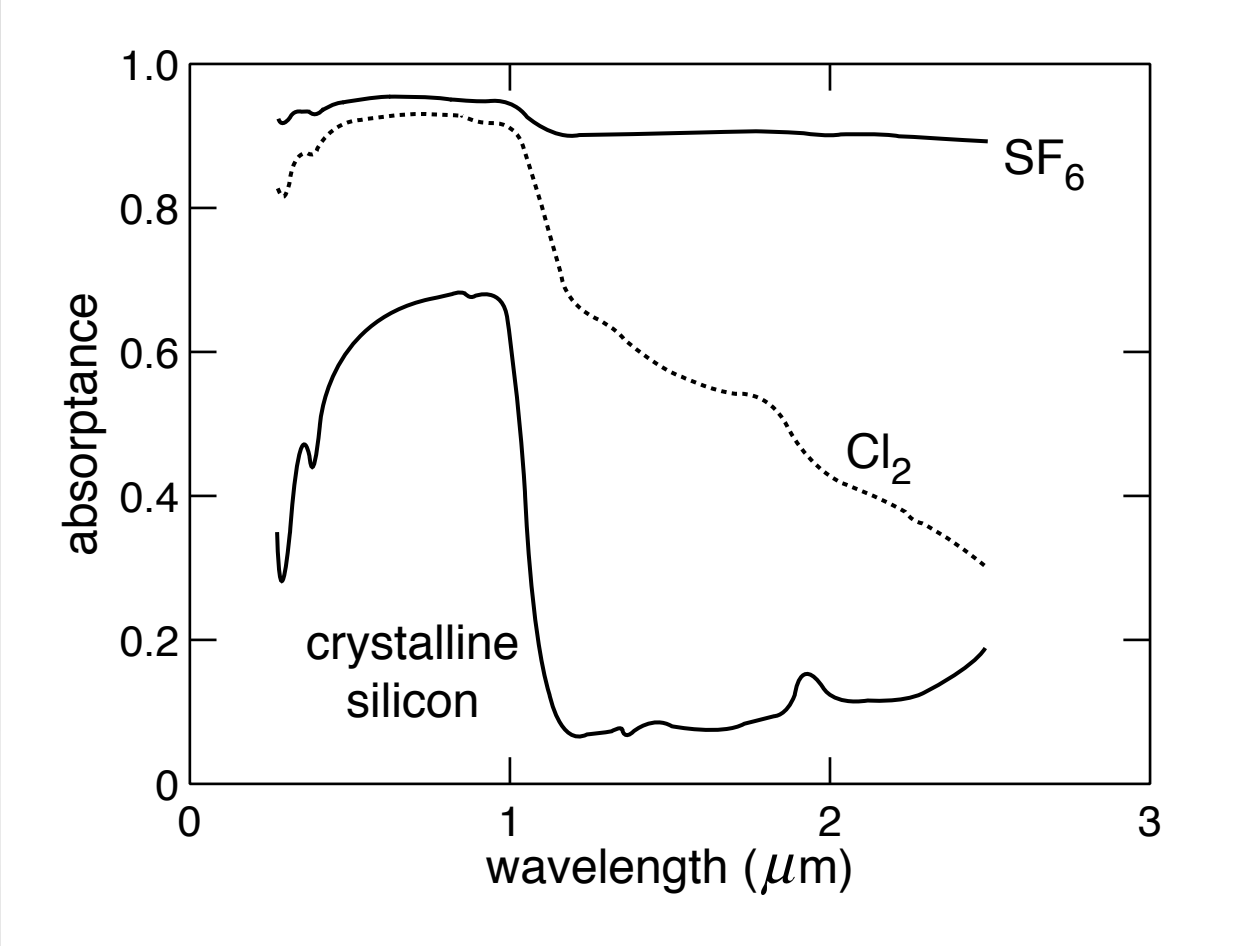
Structural and chemical analysis

microstructure with different gases



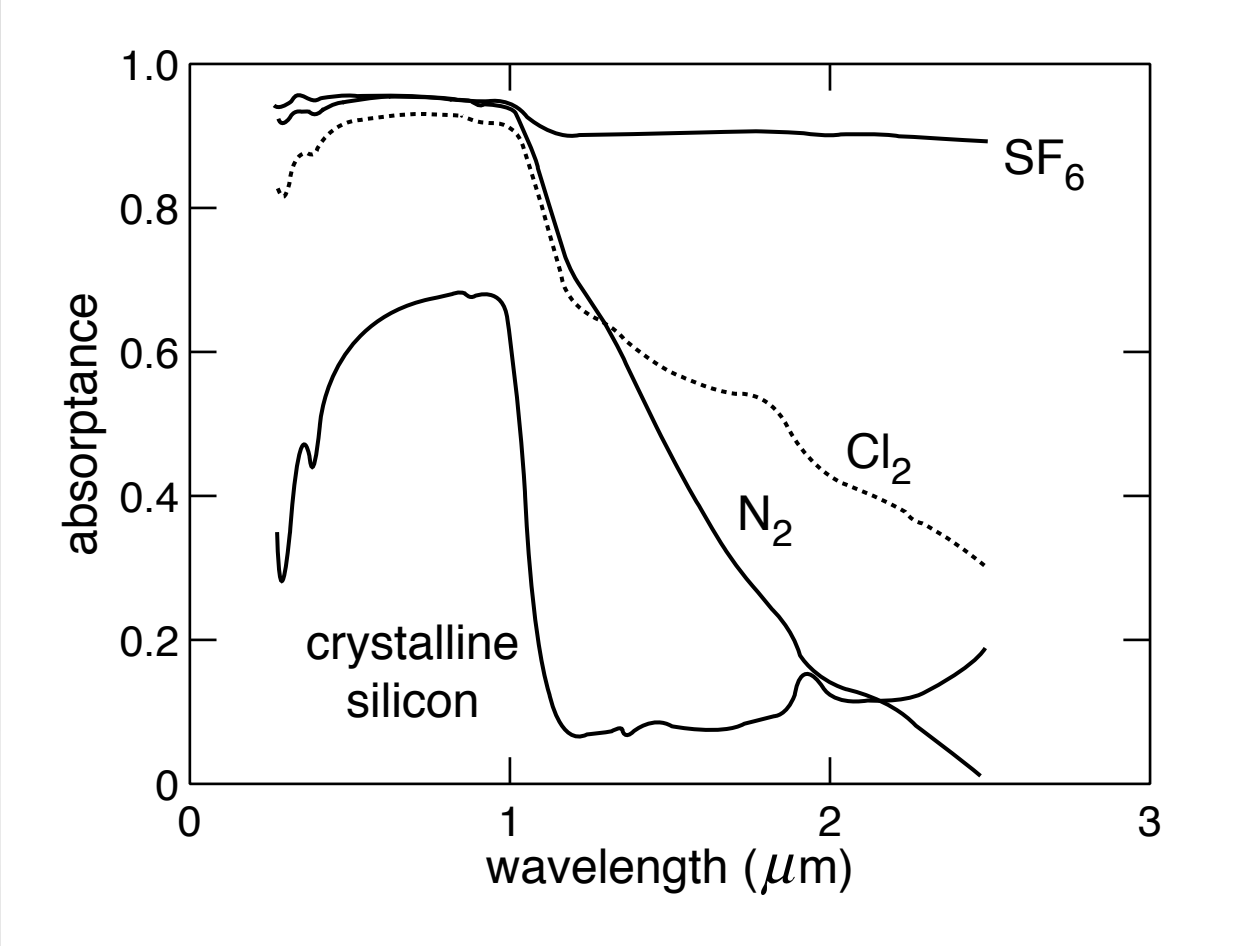
Structural and chemical analysis

microstructure with different gases



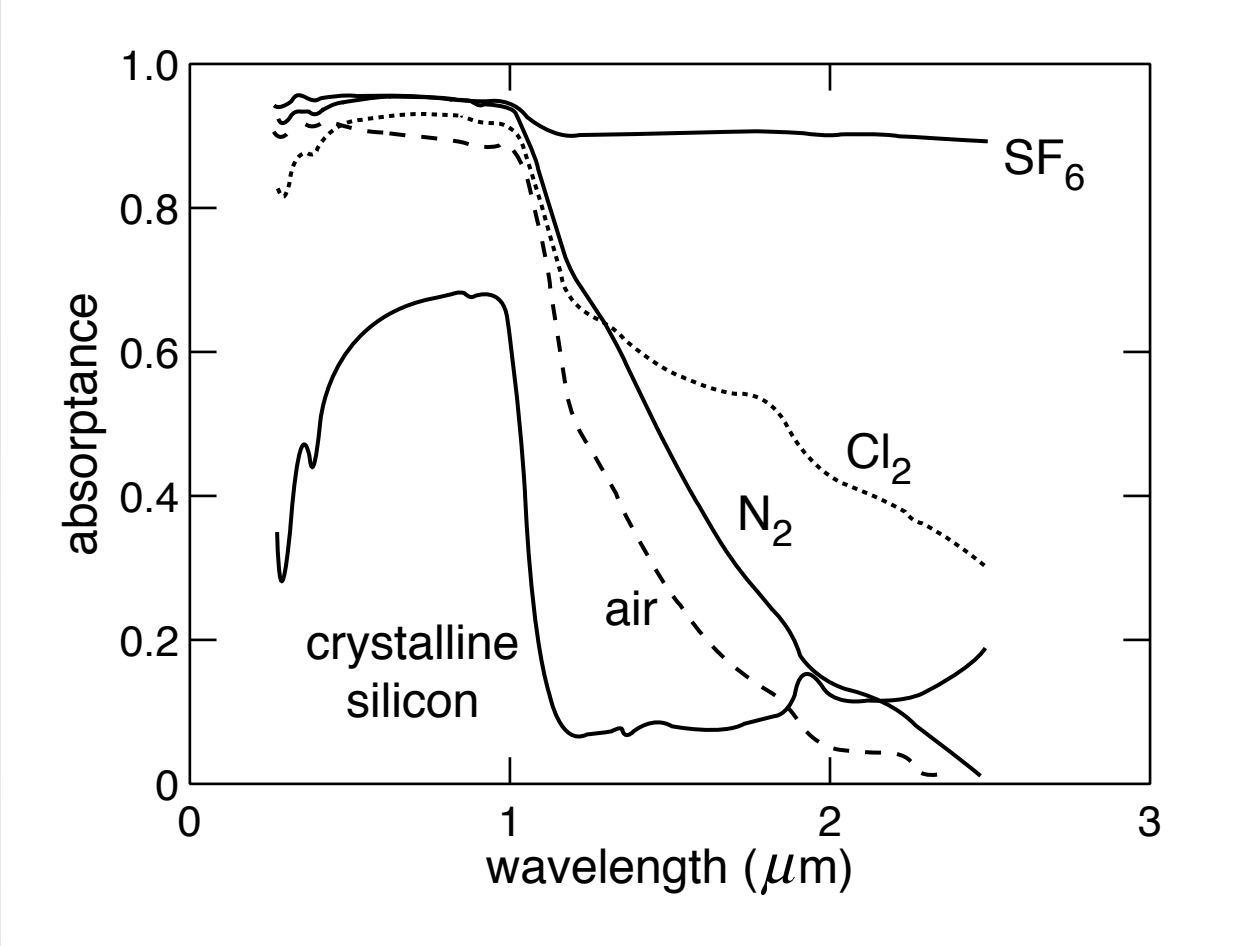
Structural and chemical analysis

microstructure with different gases



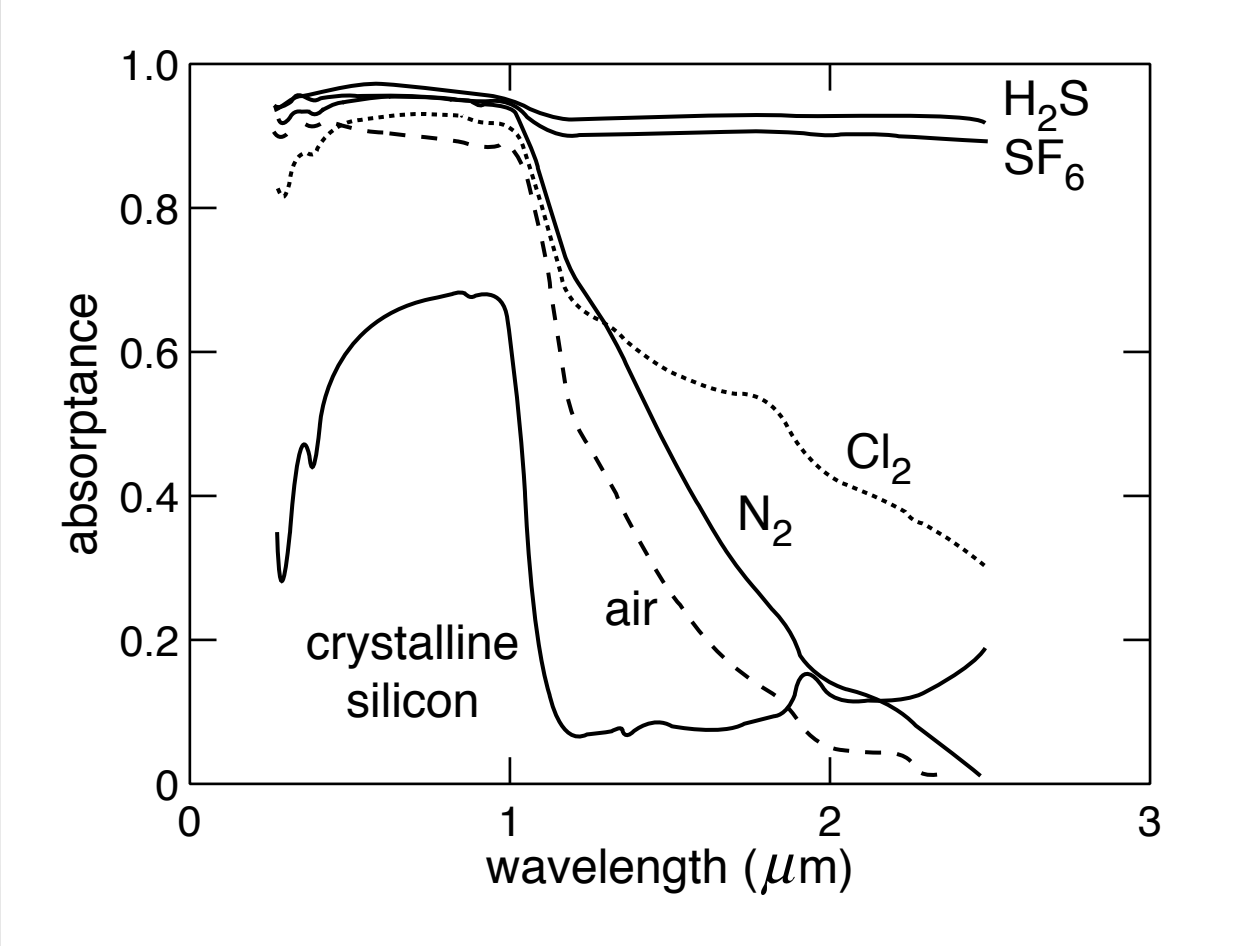
Structural and chemical analysis

microstructure with different gases



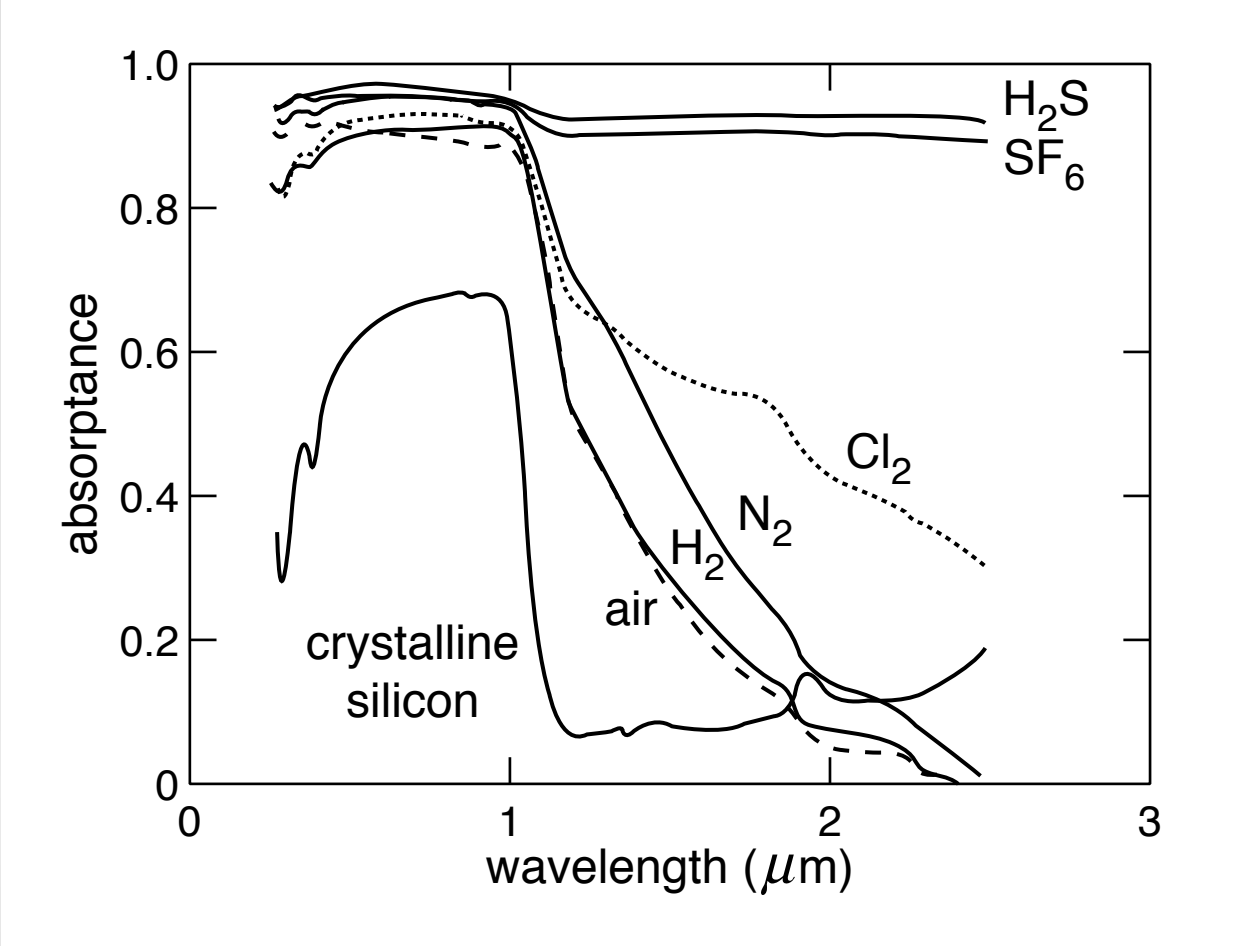
Structural and chemical analysis

microstructure with different gases



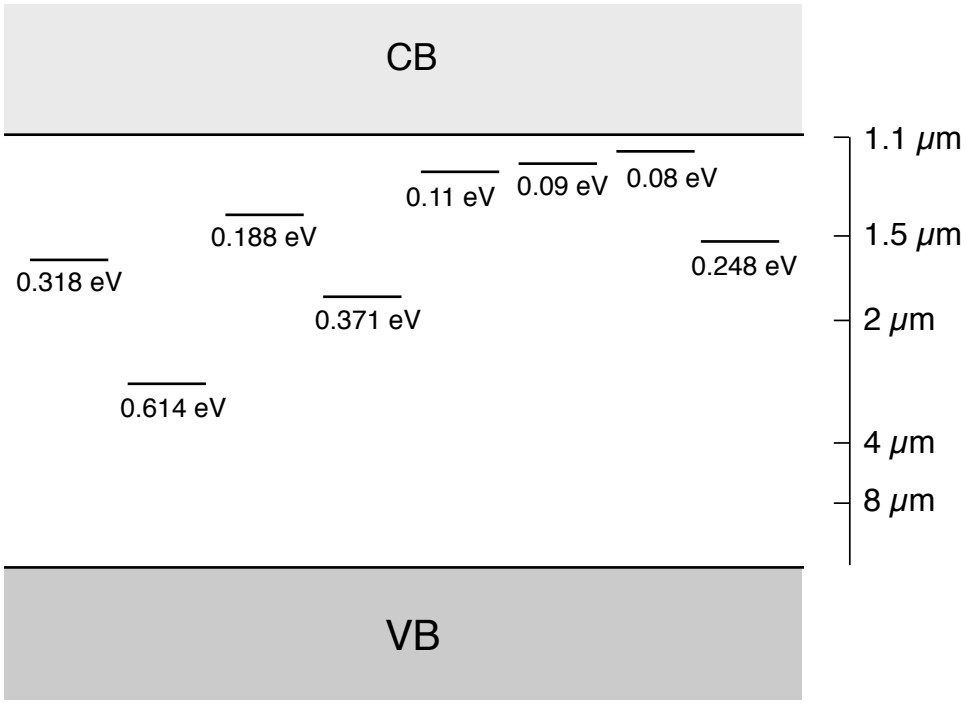
Structural and chemical analysis

microstructure with different gases



Structural and chemical analysis

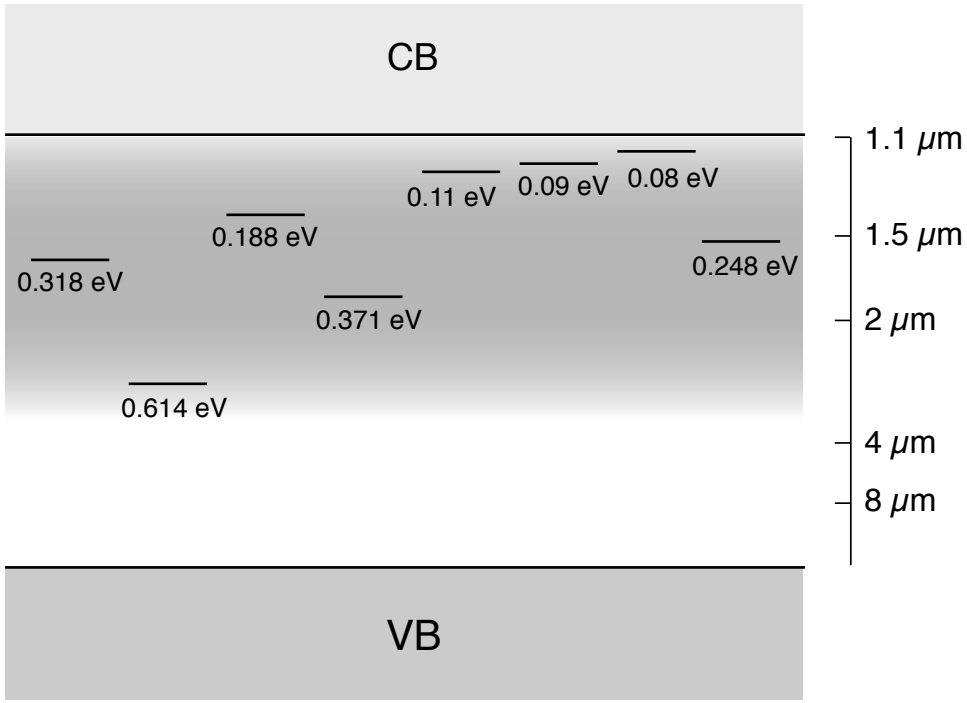
1 part in 10^6 sulfur introduces states in gap



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

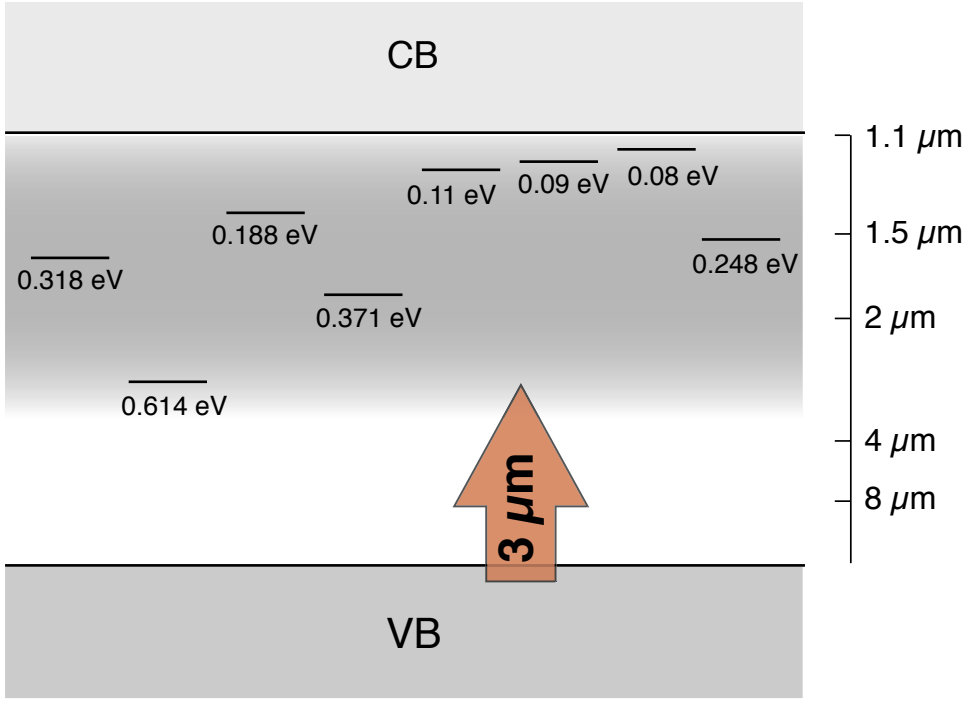
Structural and chemical analysis

at high concentration states broaden into band



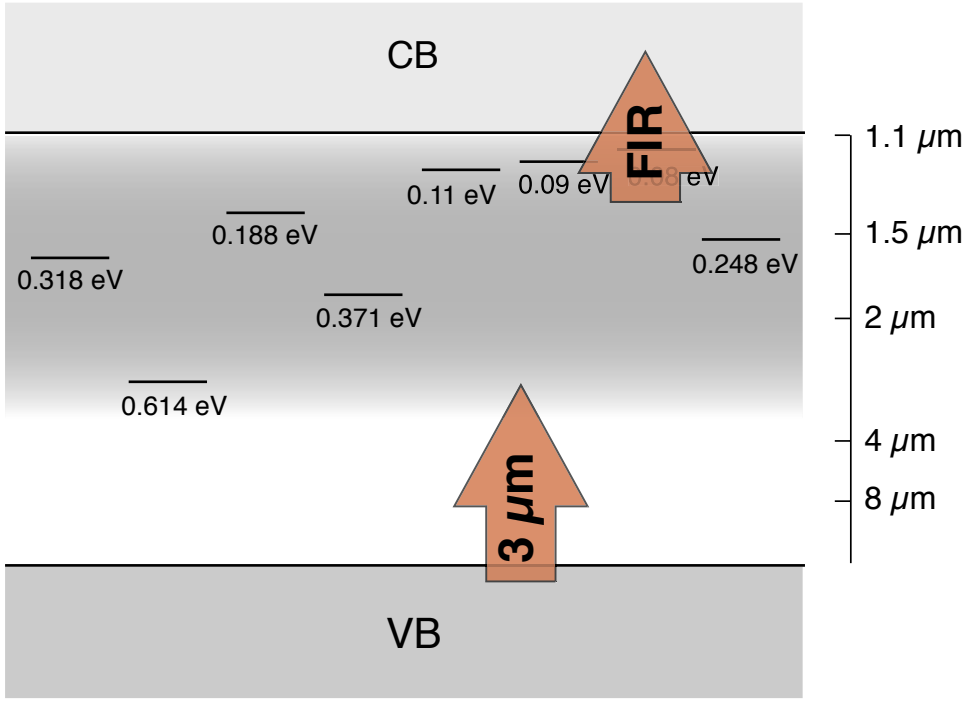
Structural and chemical analysis

absorption extends into infrared



Structural and chemical analysis

sulfur has 6 valence electrons: donor states?



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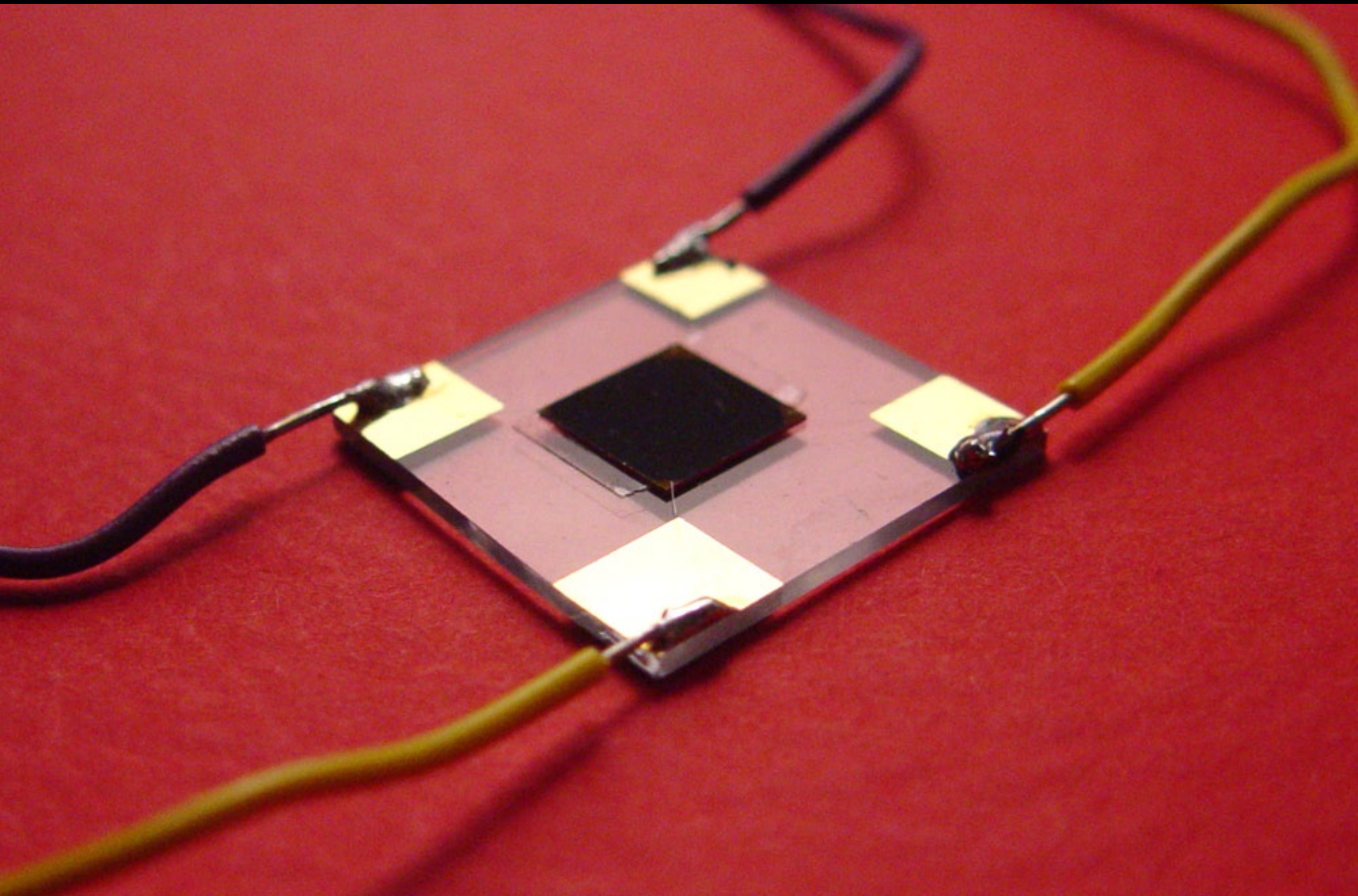
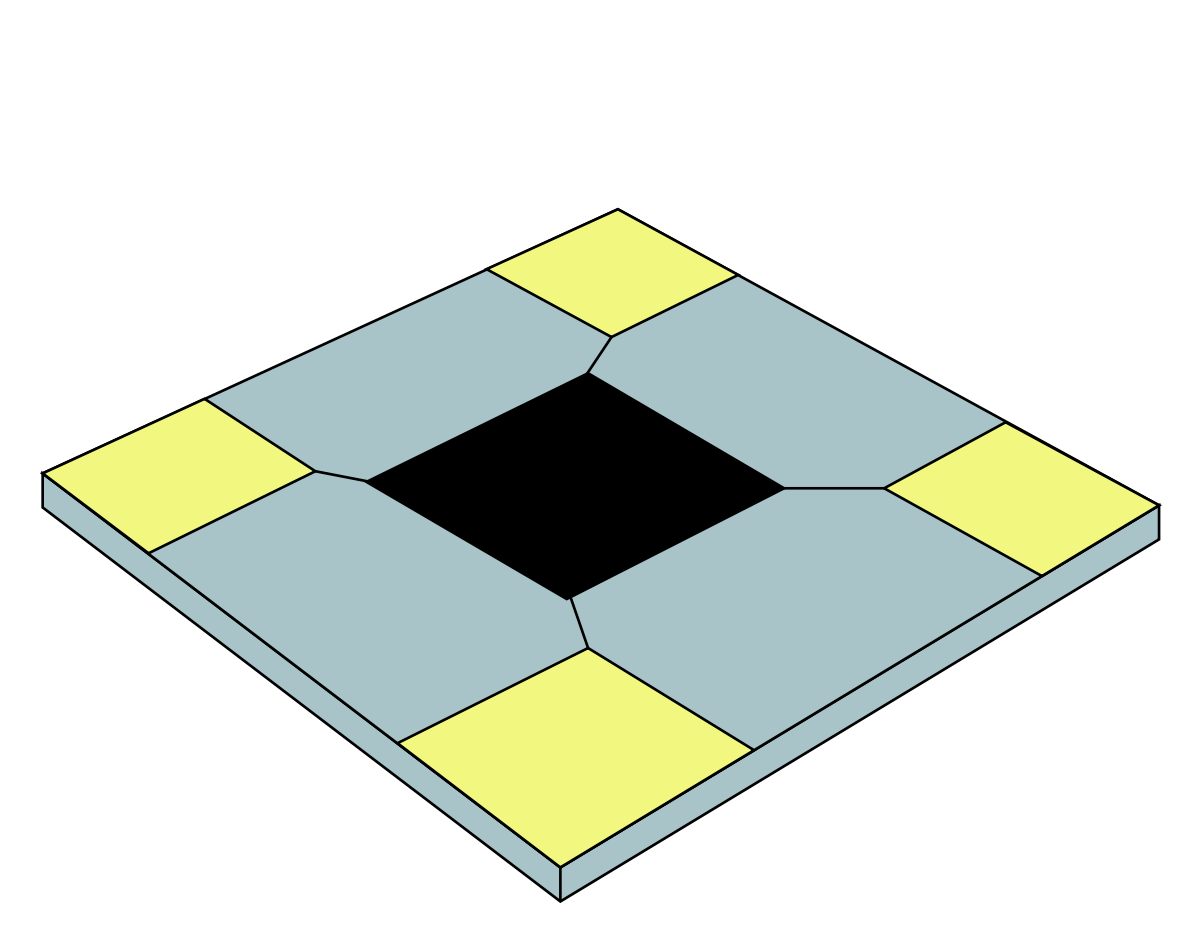


Structural and chemical analysis

Hall measurement



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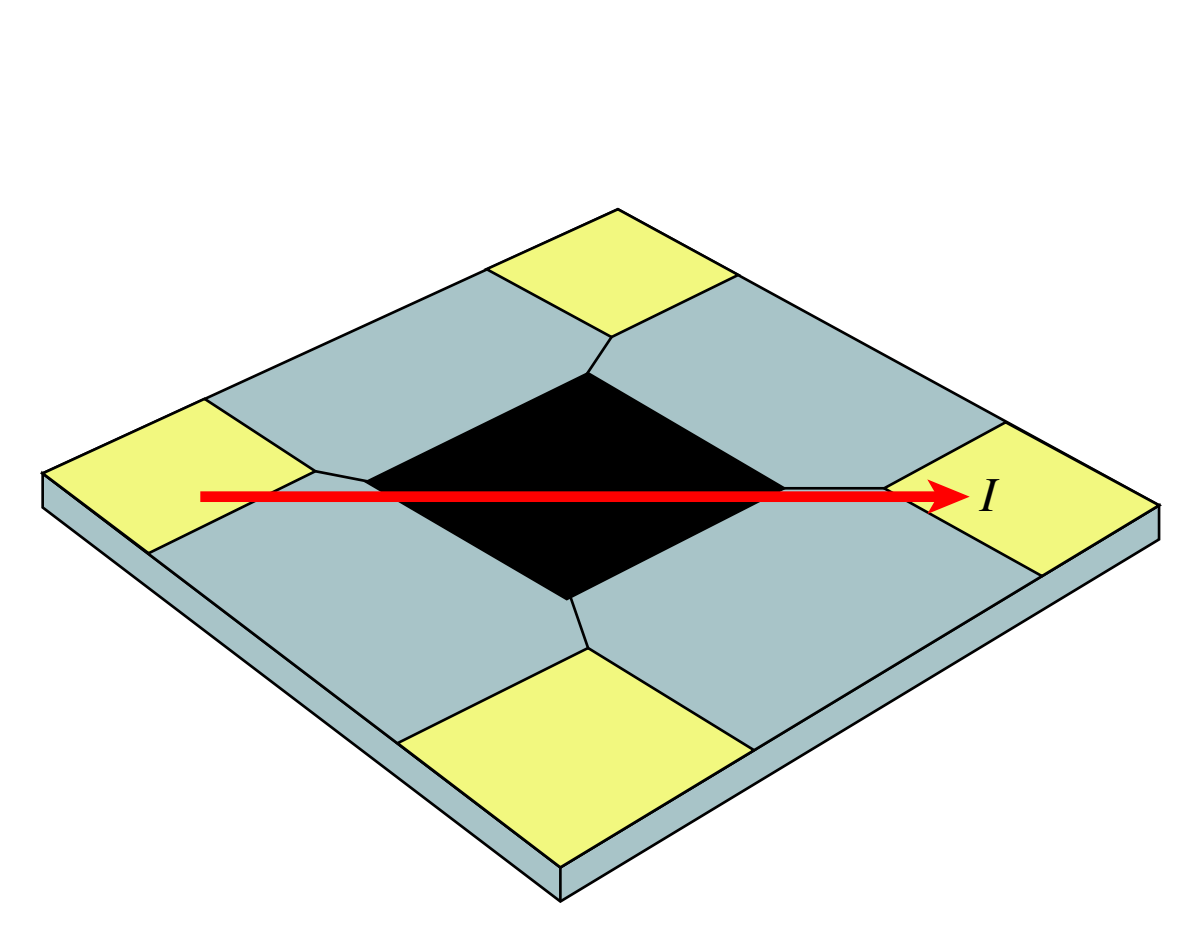

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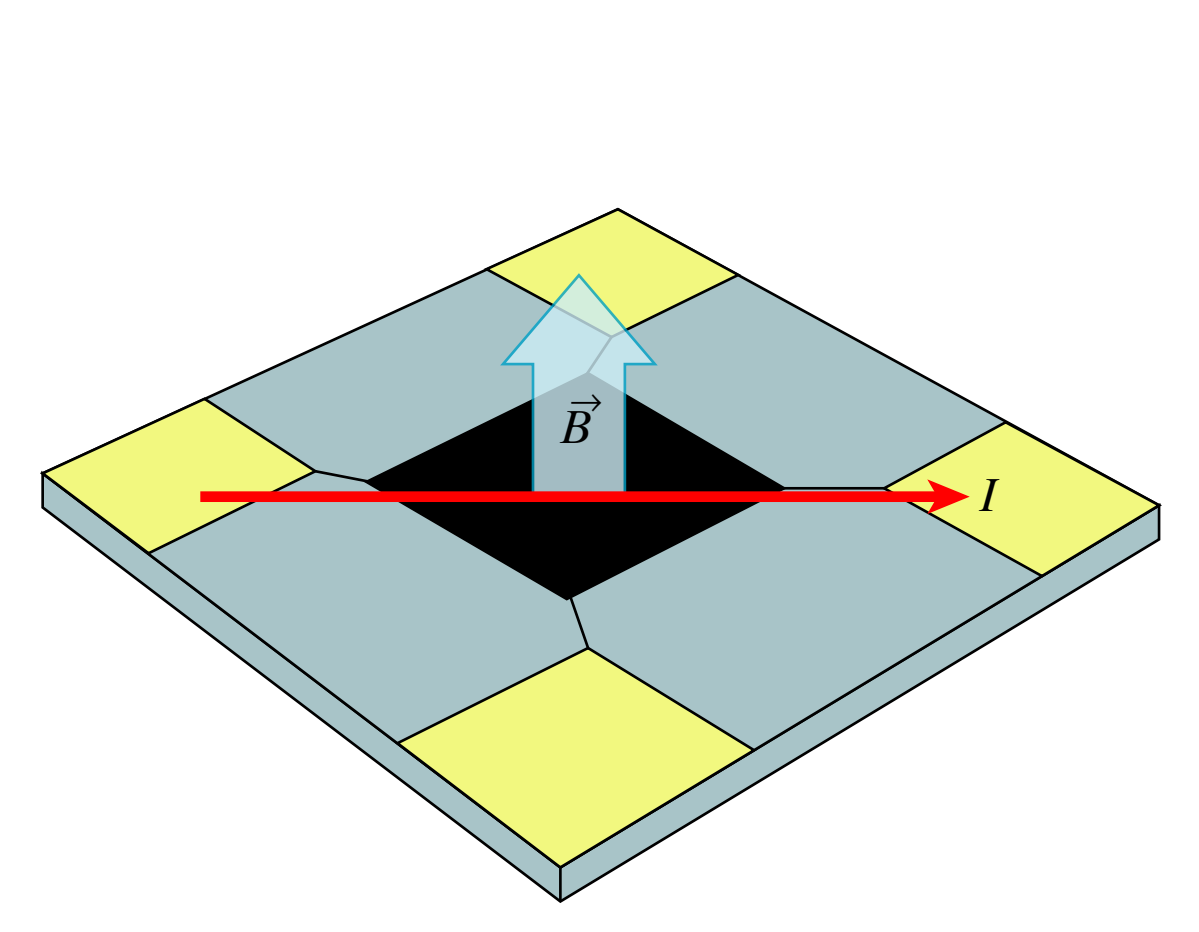

Structural and chemical analysis

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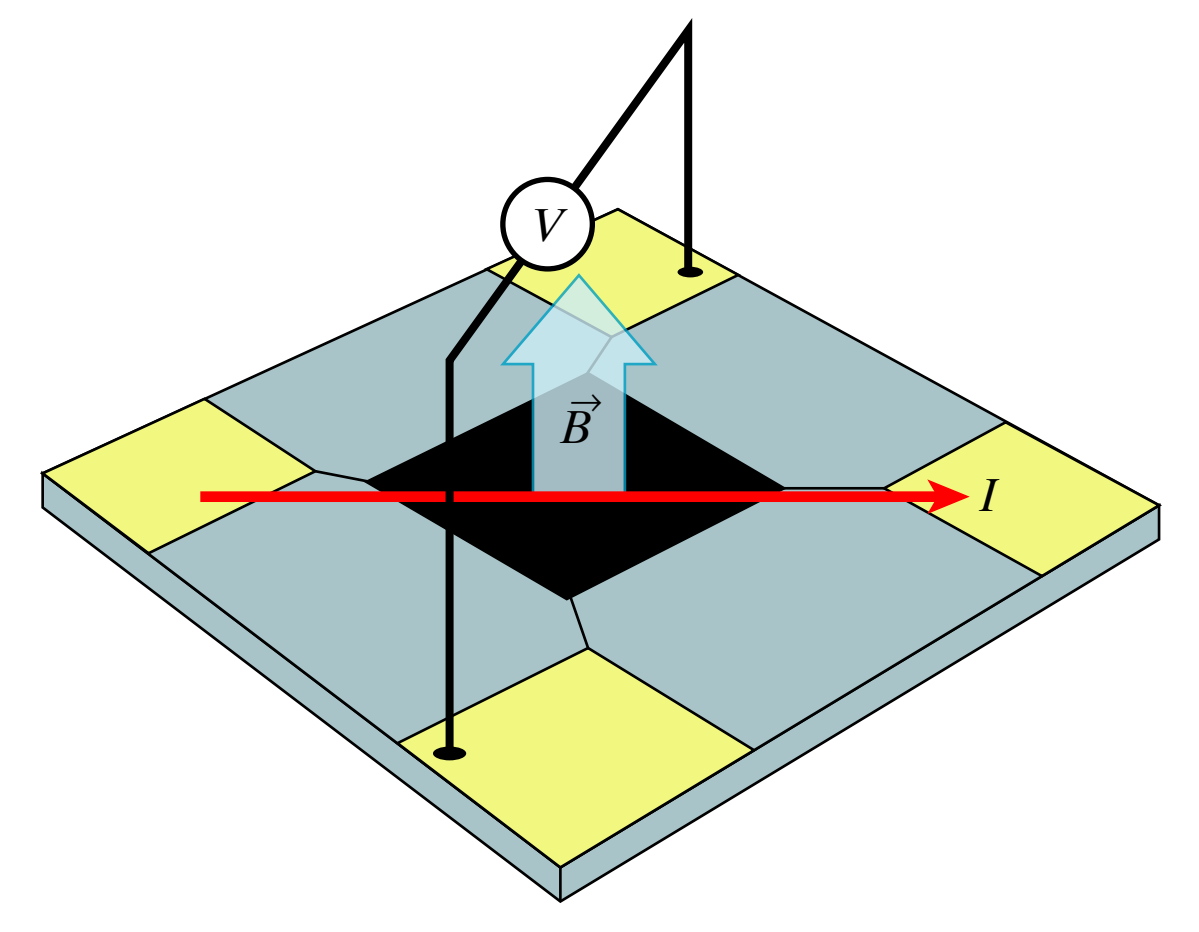


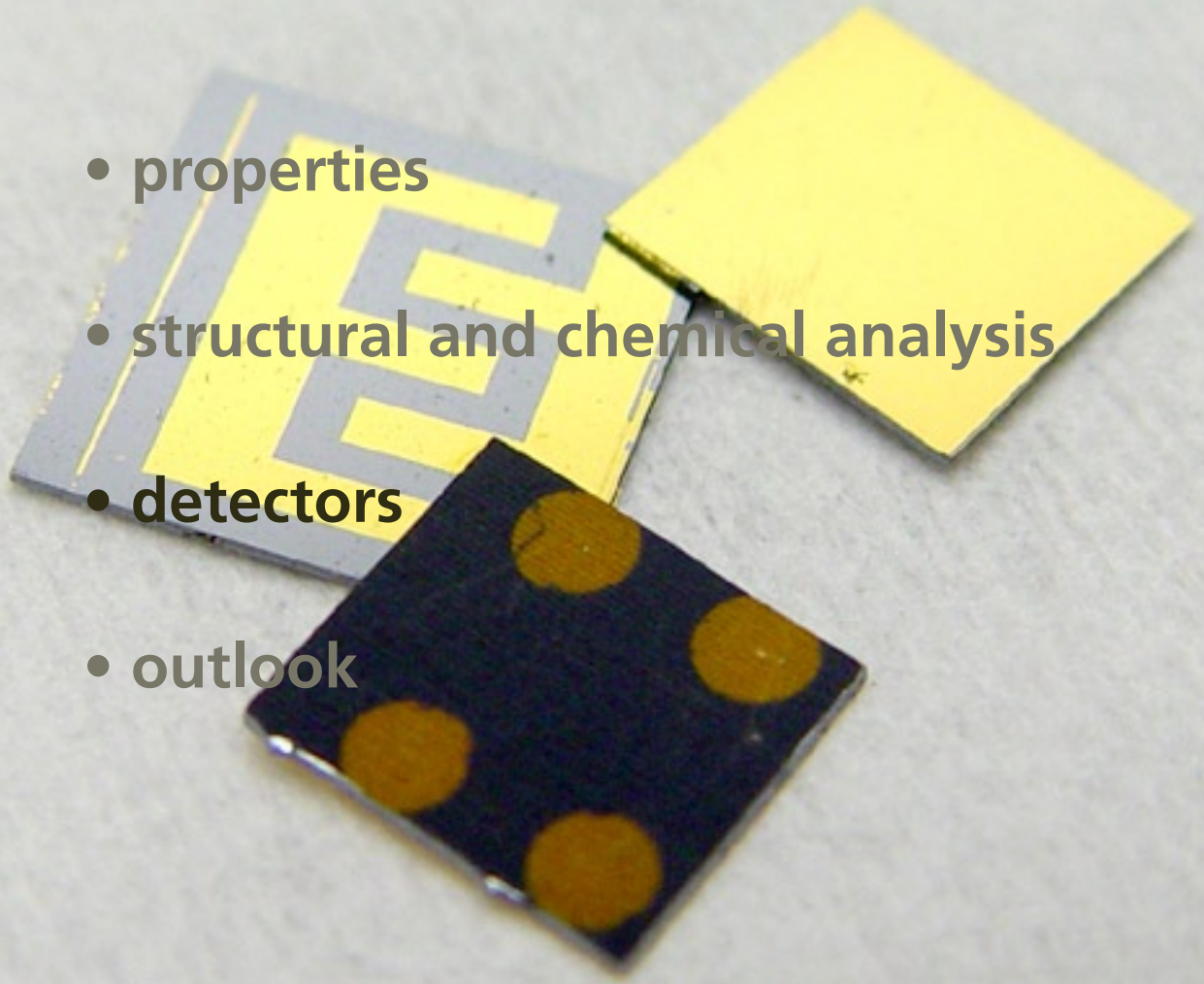
Structural and chemical analysis

Hall measurements:

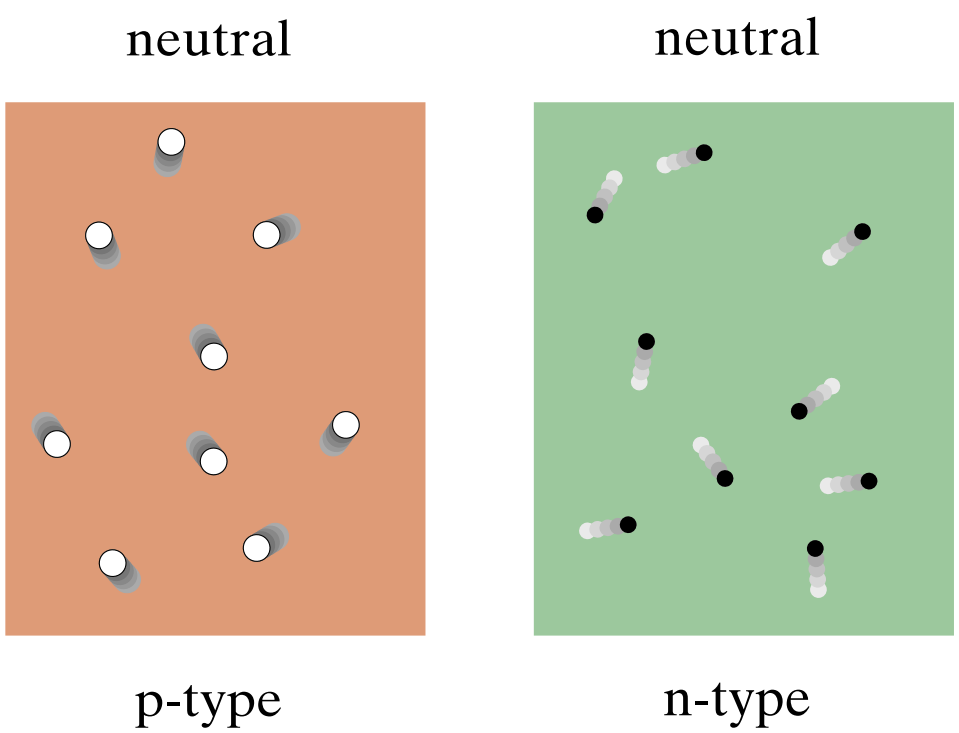
- microstructuring causes moderate n-doping
- annealing greatly increases donor concentration

Outline

- properties
- structural and chemical analysis
- detectors
- outlook

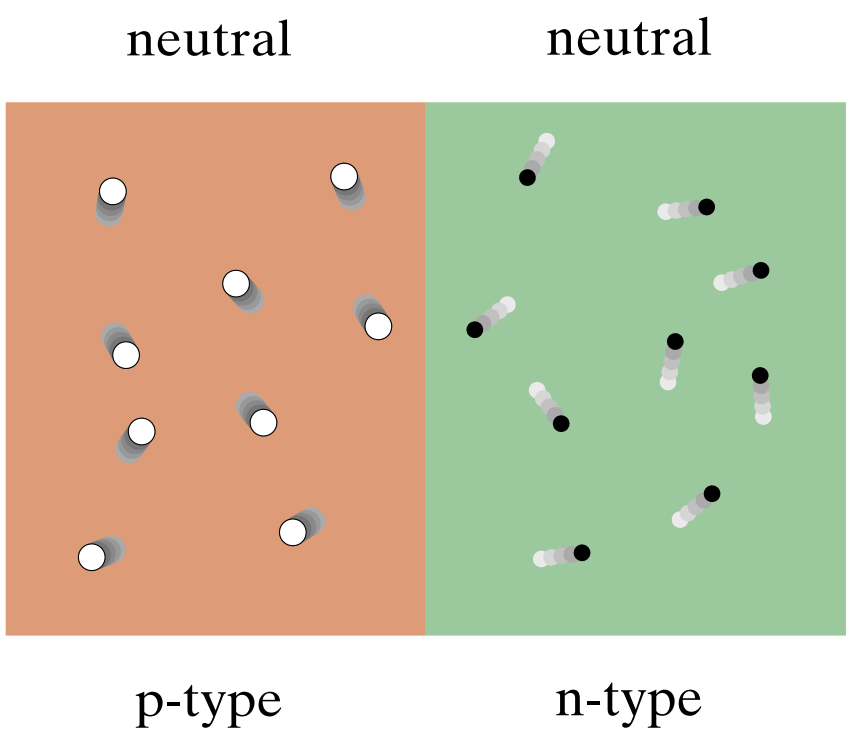


Detectors



join acceptor and donor type Si…

Detectors



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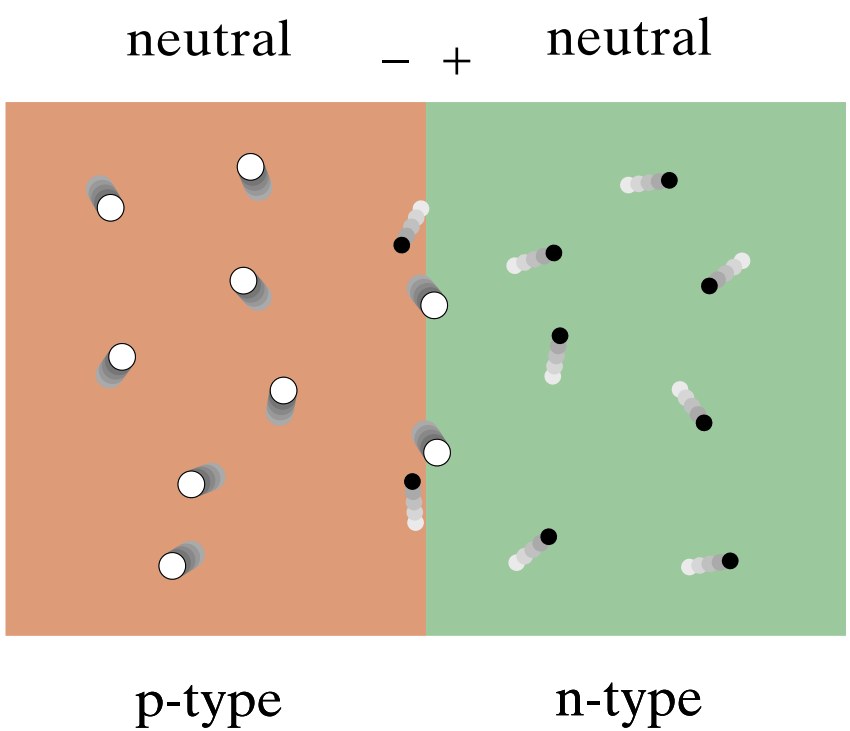
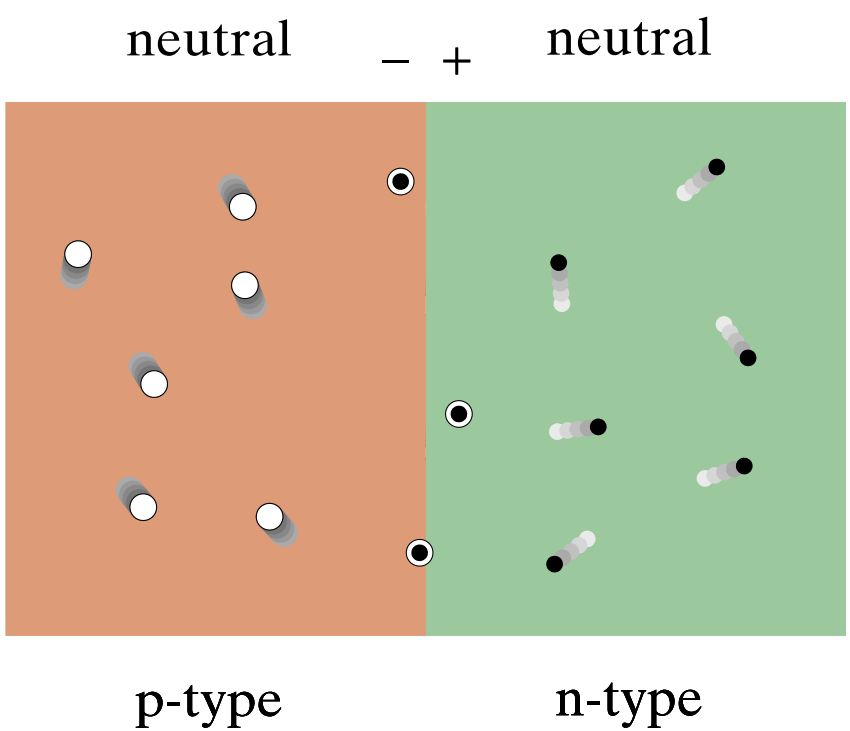


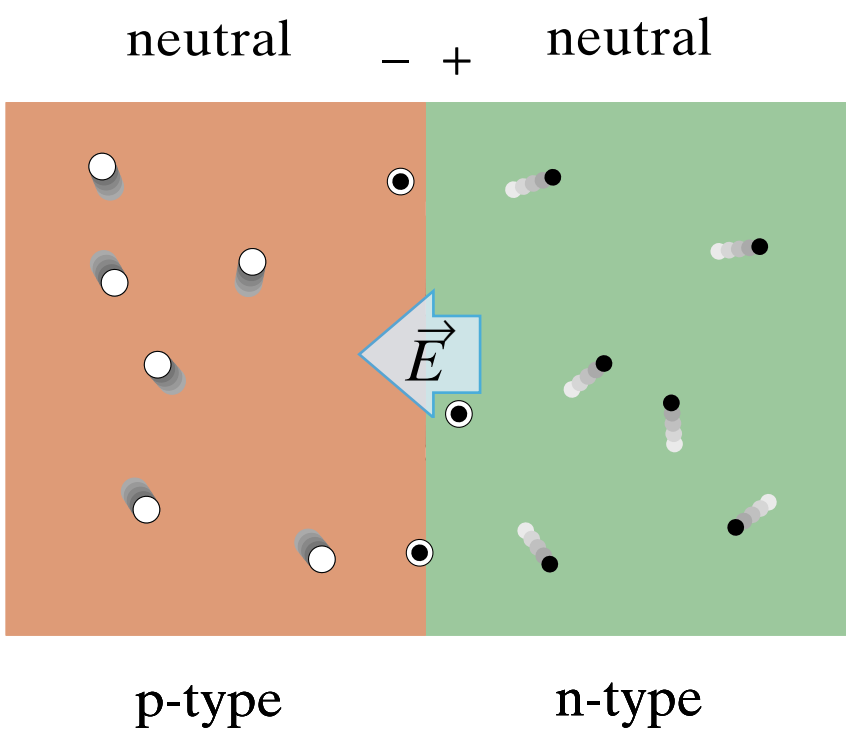
electrons and holes diffuse across junction…

Detectors



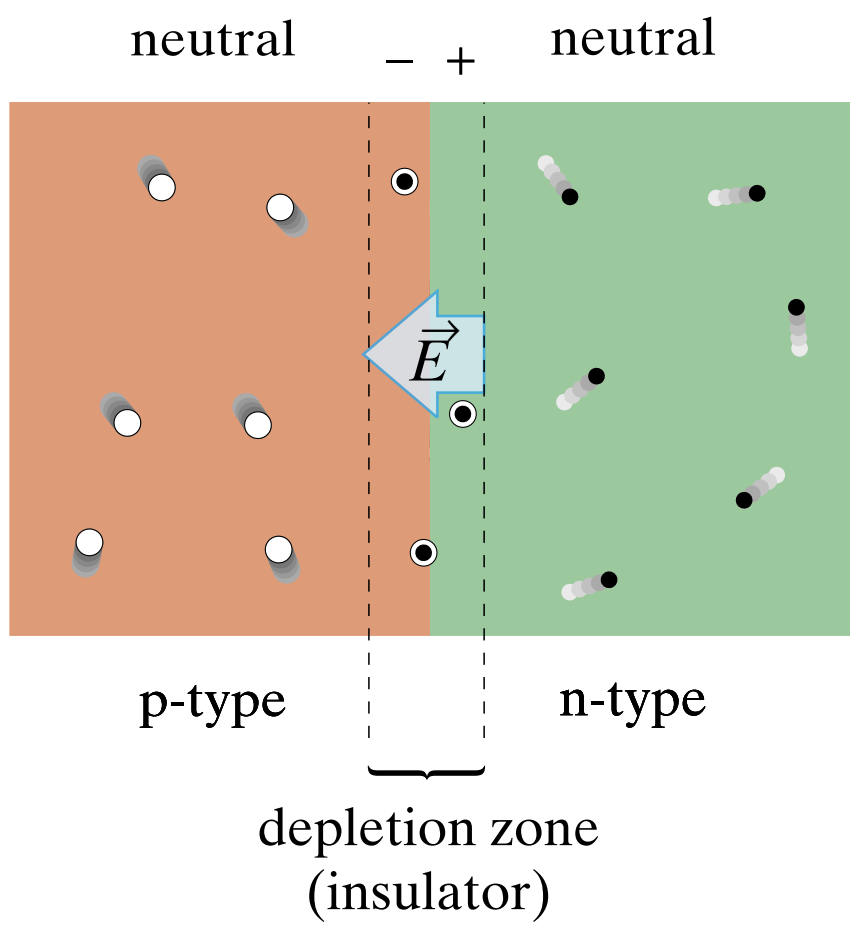
…and get ‘trapped’ after they combine

Detectors



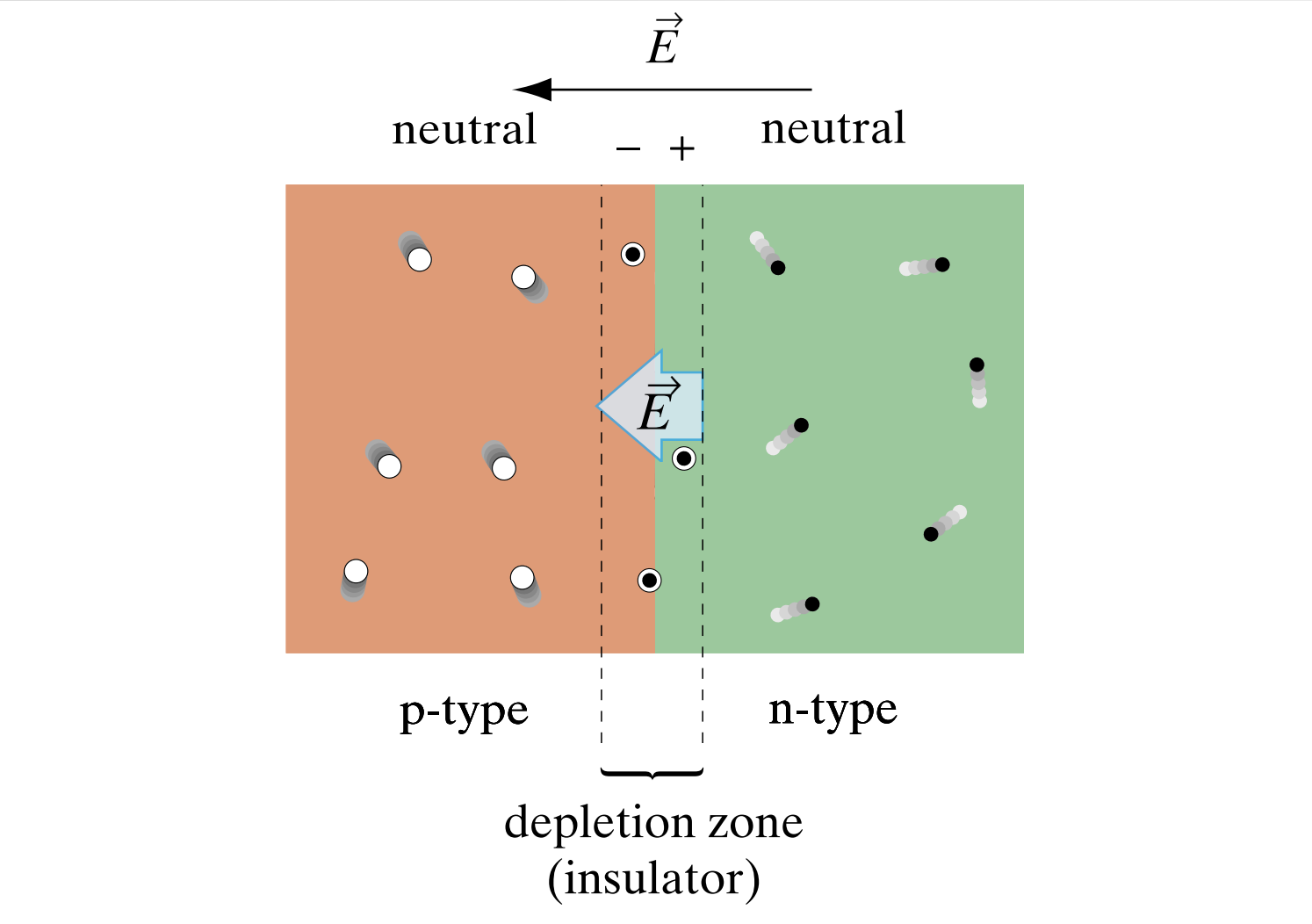
build-up of charge leads to electric field that stops diffusion

Detectors



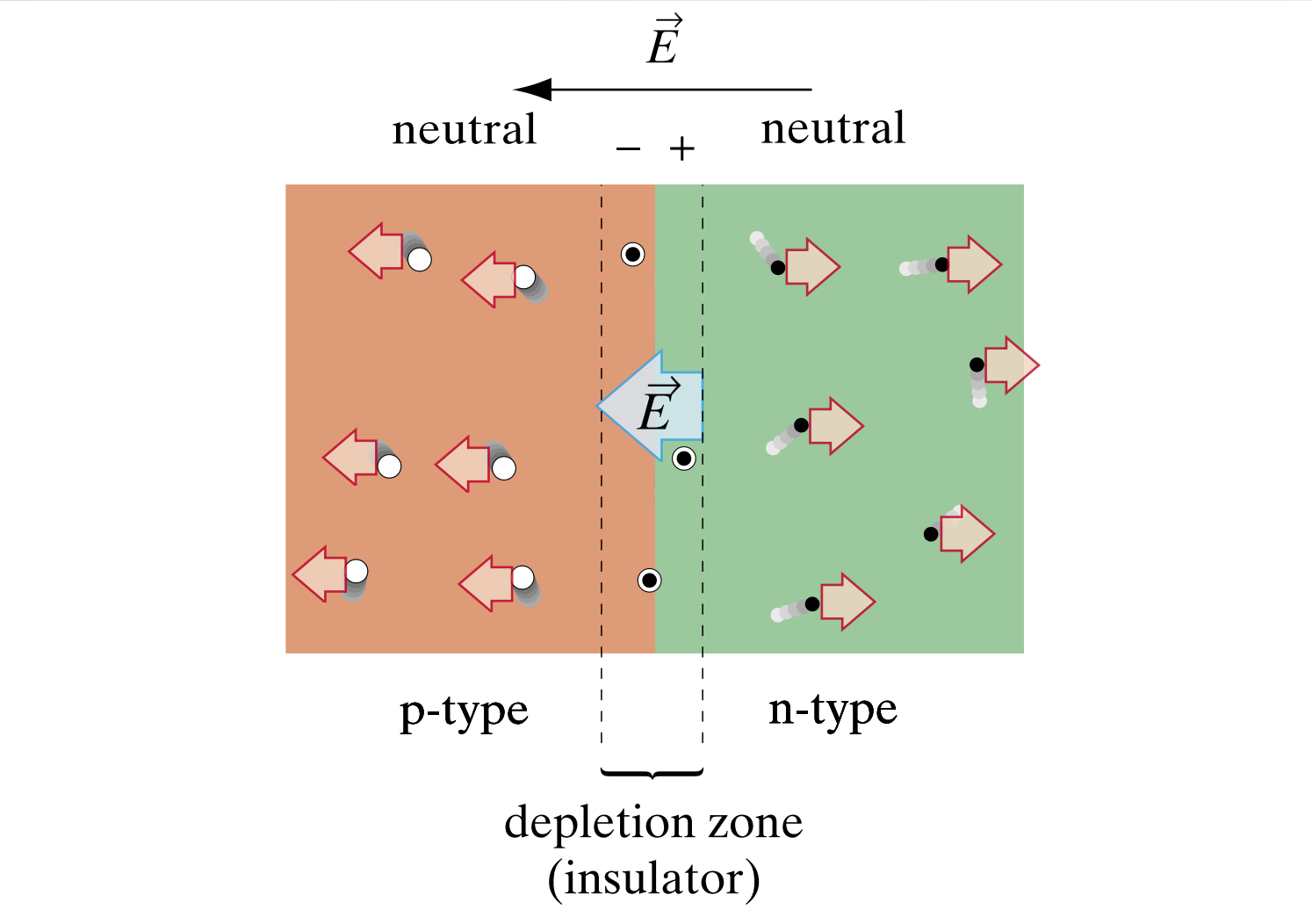
non-conducting layer at junction

Detectors



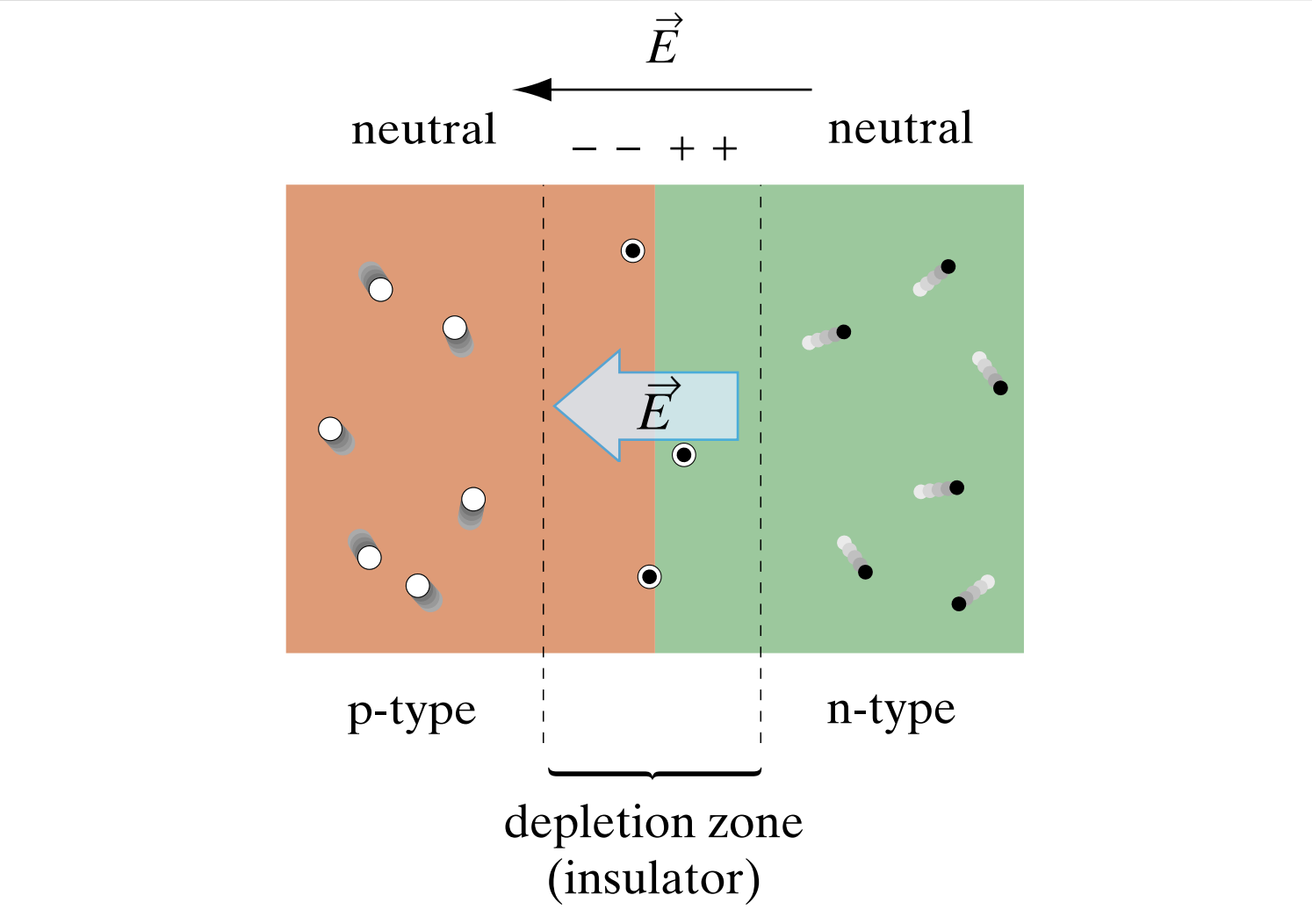
apply electric field…

Detectors



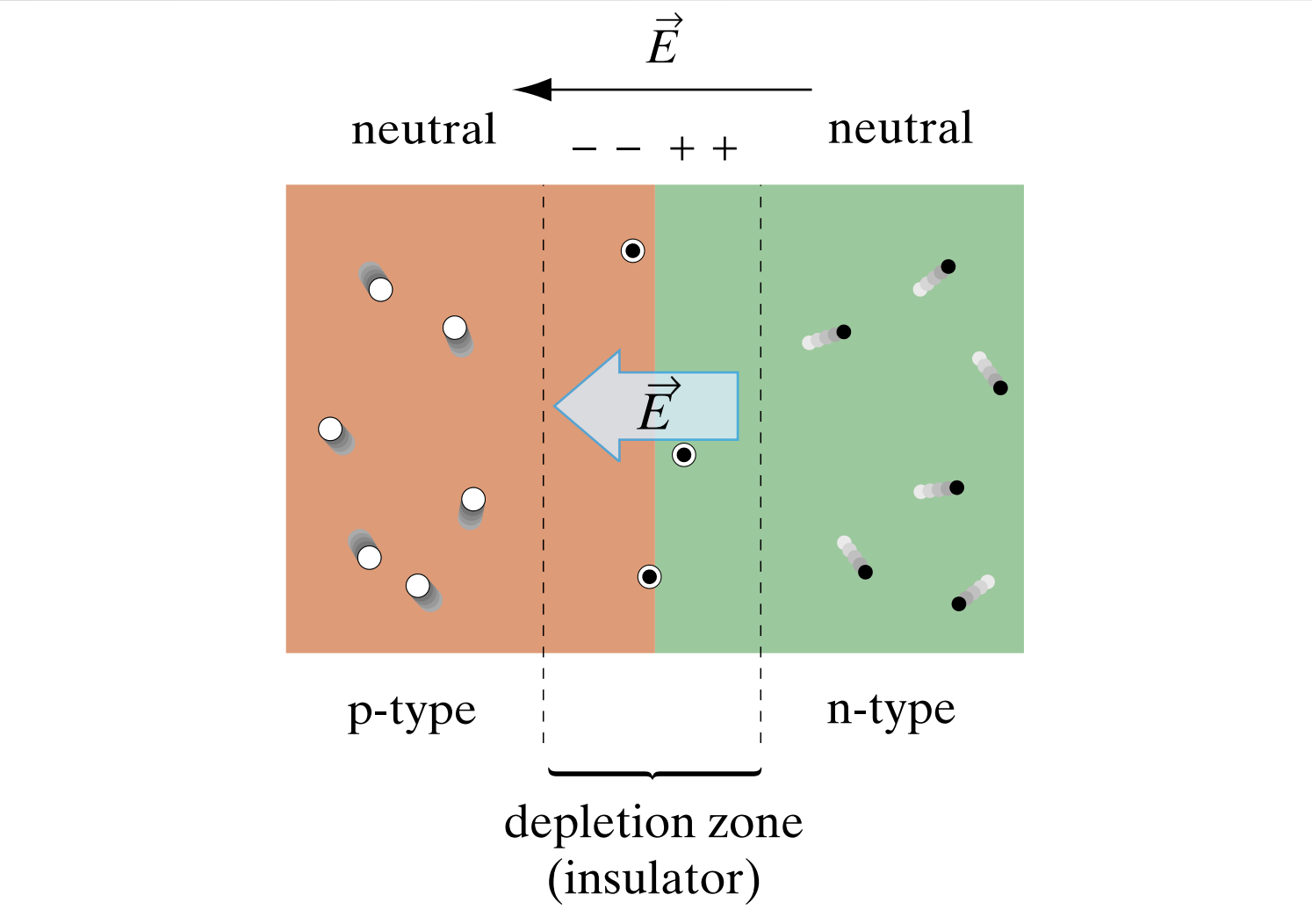
…holes pushed to left, electrons to right…

Detectors



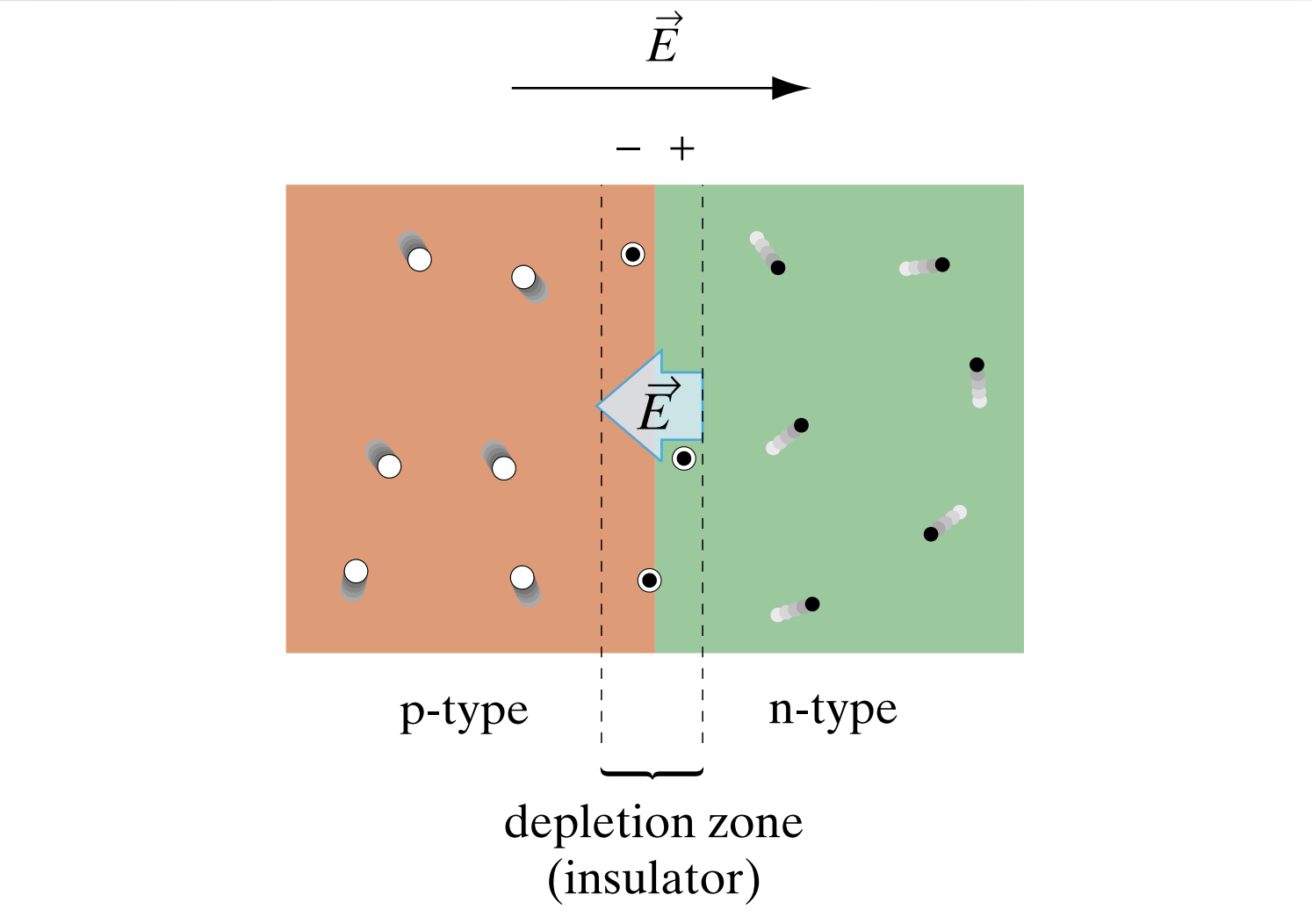
…and so depletion zone expands

Detectors



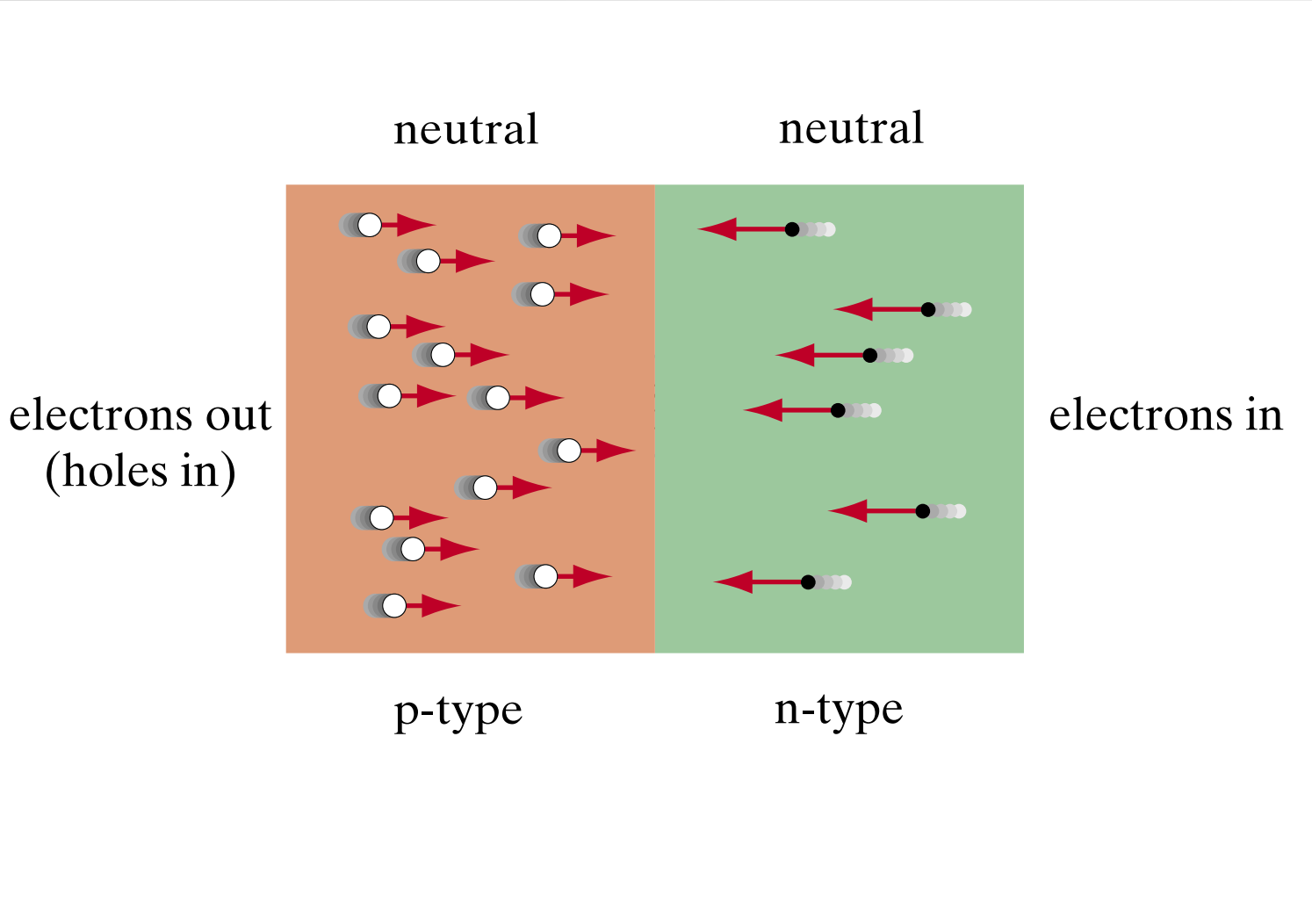
NO conduction

Detectors



reverse electric field…

Detectors



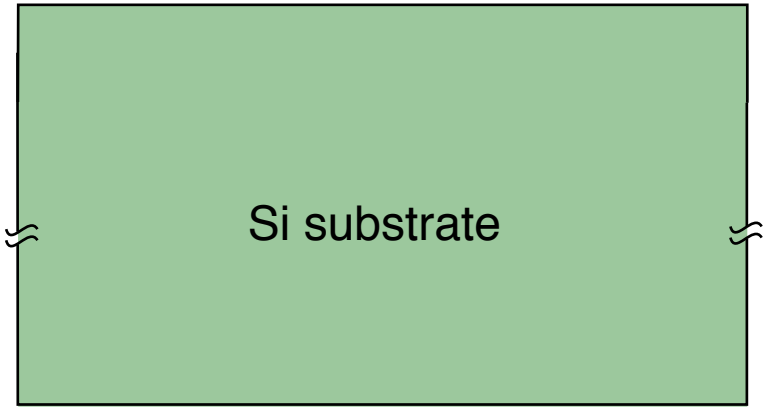
…depletion zone shrinks and current flows

pn-junctions

so *pn*-junction like one-way valve for charge flow

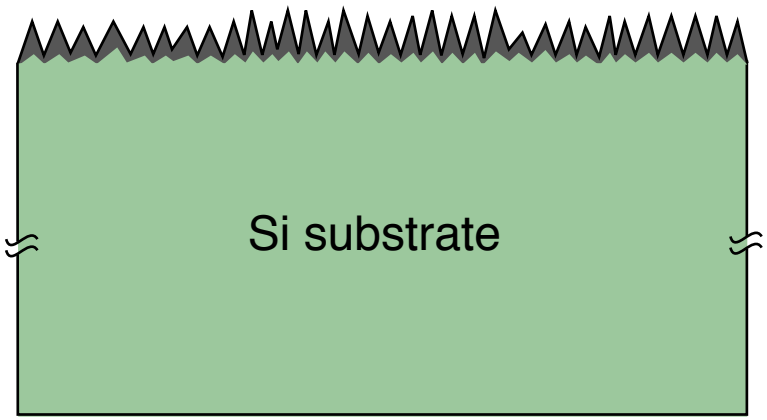
Detectors

black silicon/silicon junction



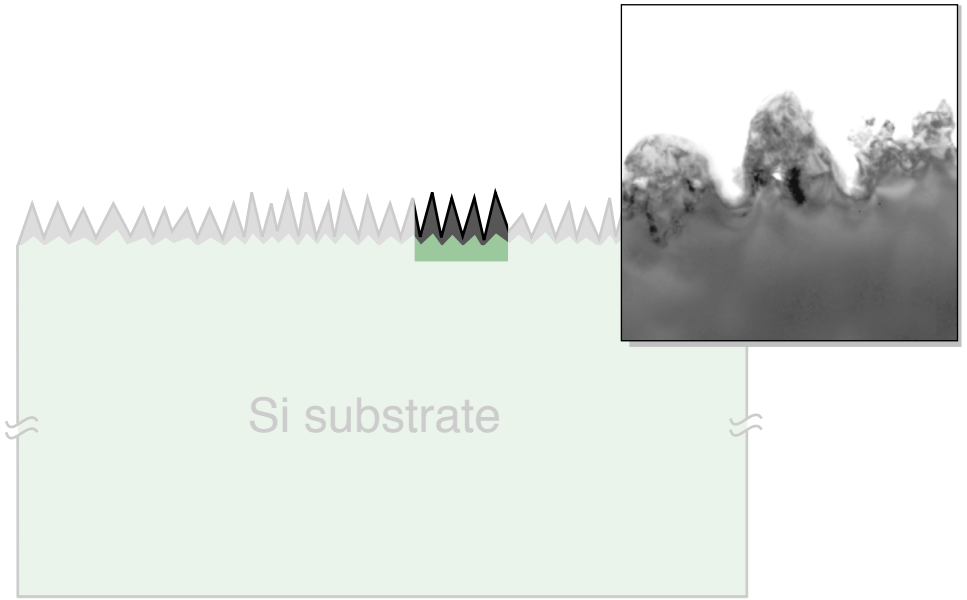
Detectors

black silicon/silicon junction



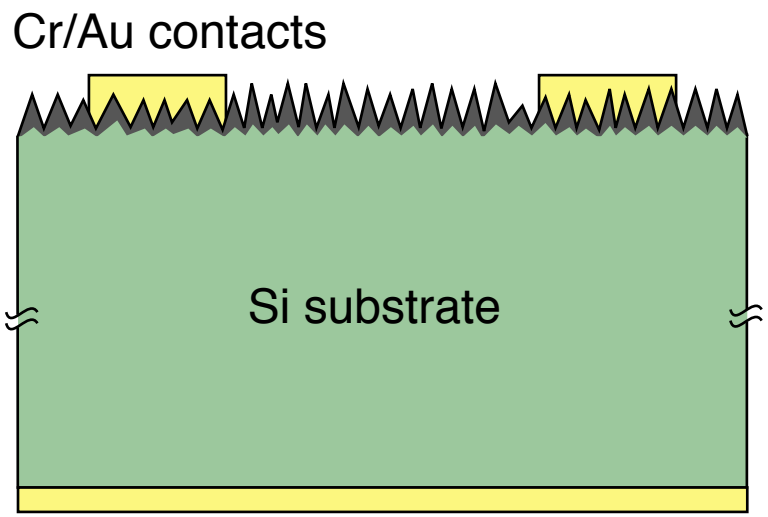
Detectors

black silicon/silicon junction



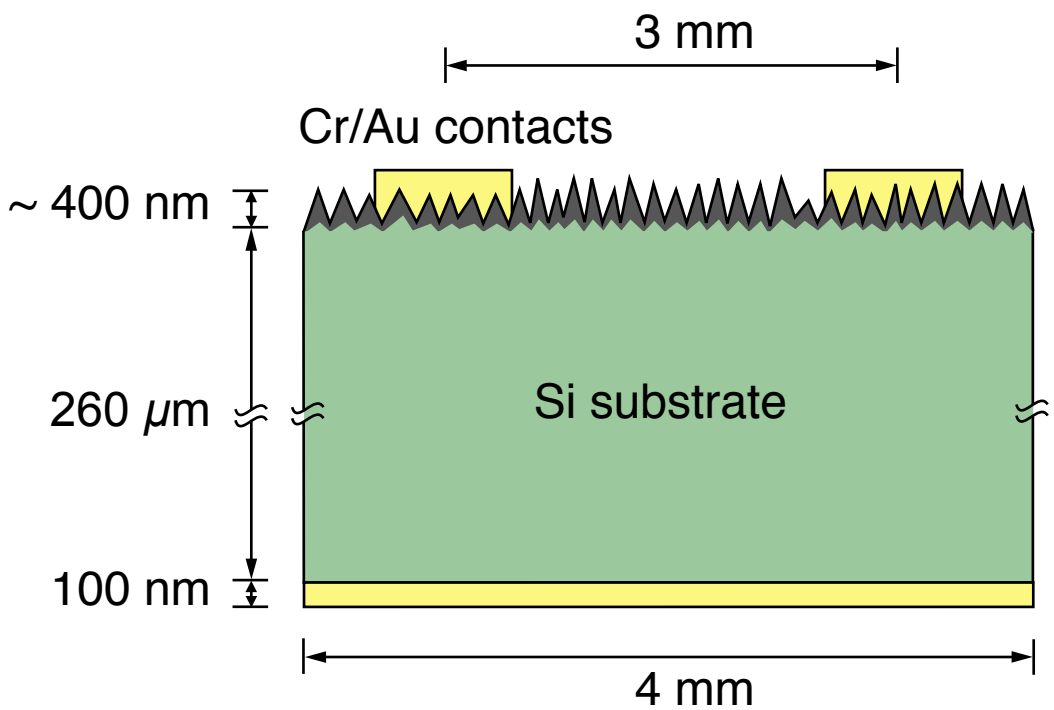
Detectors

black silicon/silicon junction



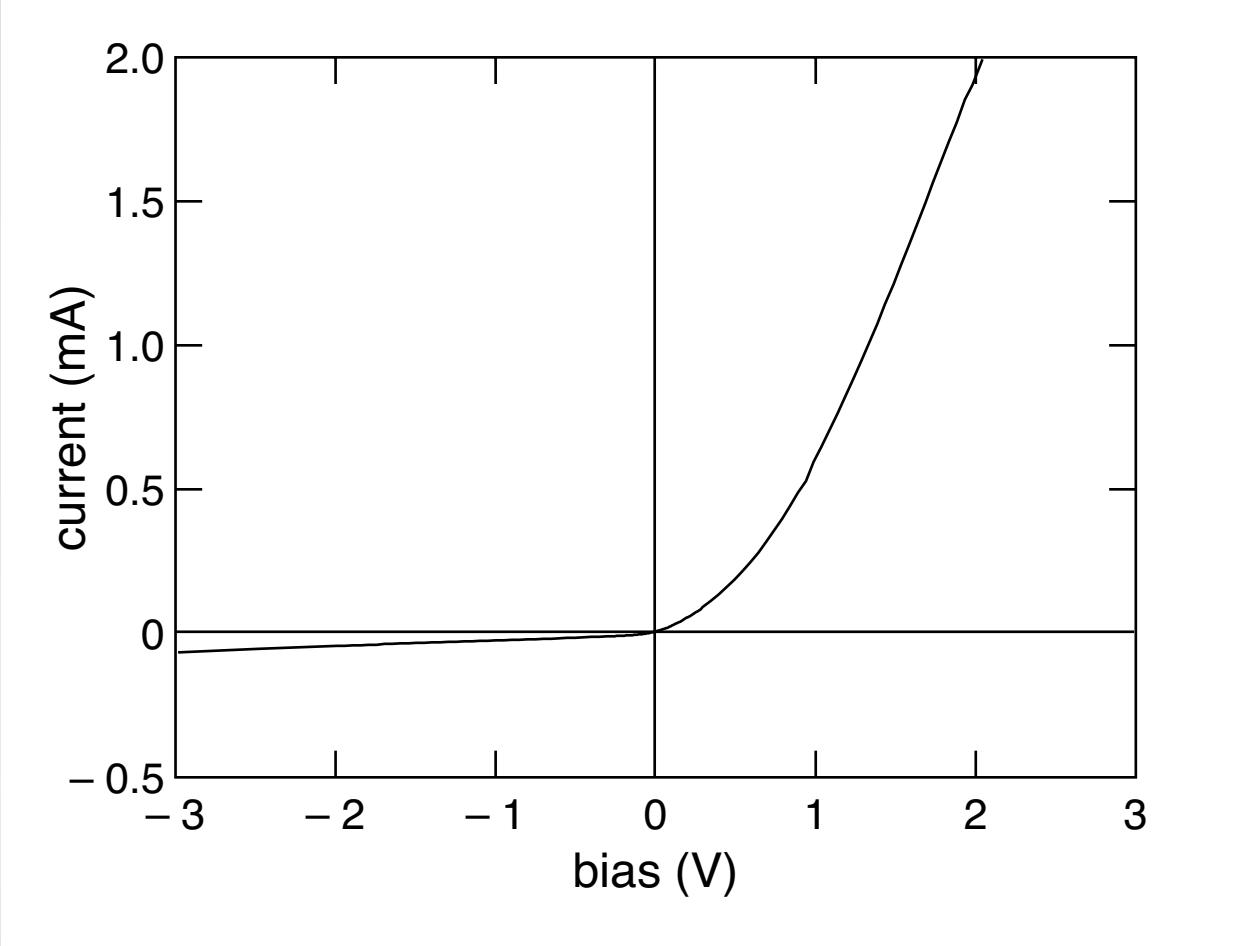
Detectors

black silicon/silicon junction

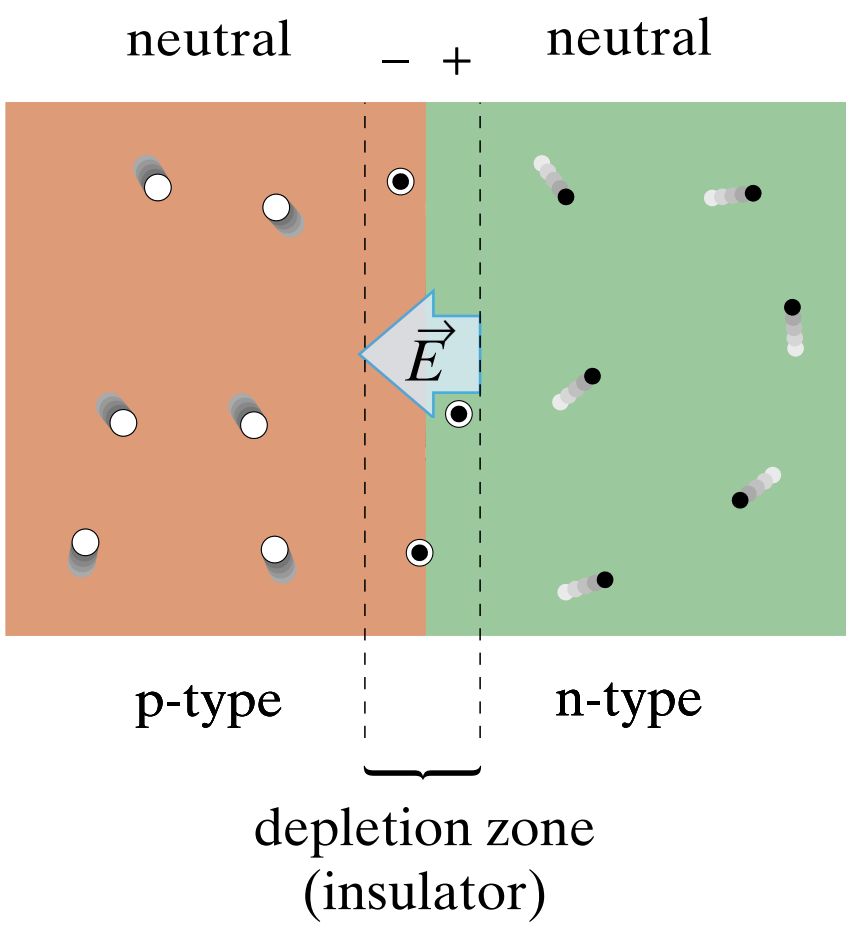


Detectors

IV characteristics

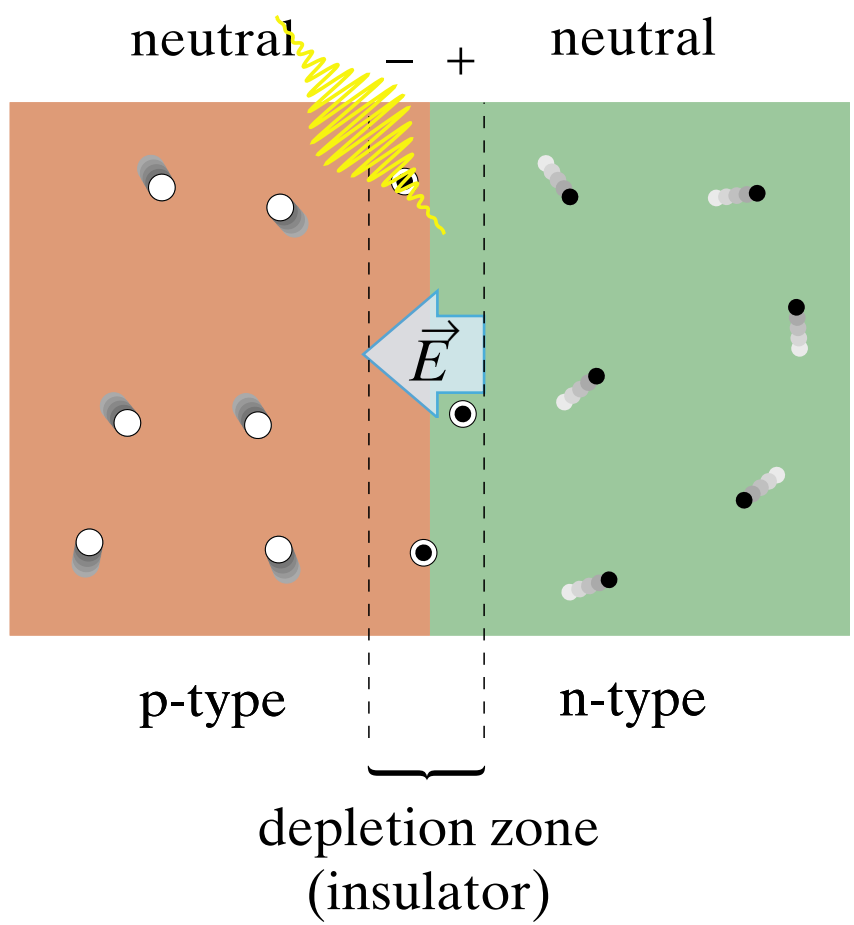


Detectors



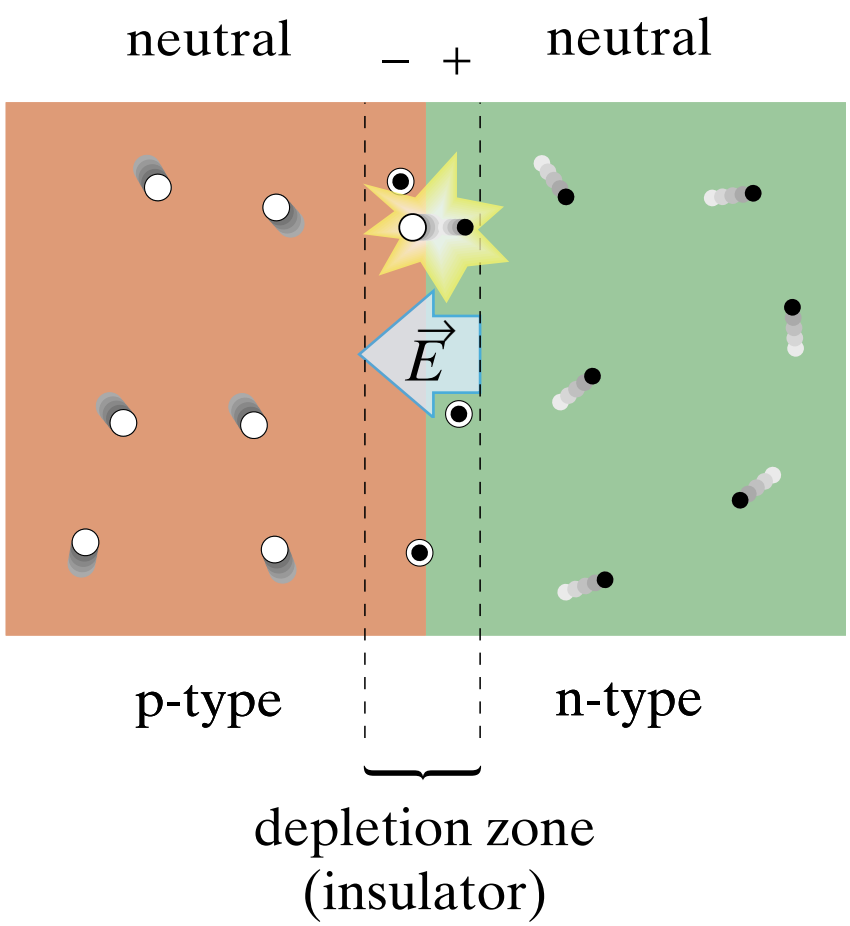
depletion layer can convert light into electric energy

Detectors



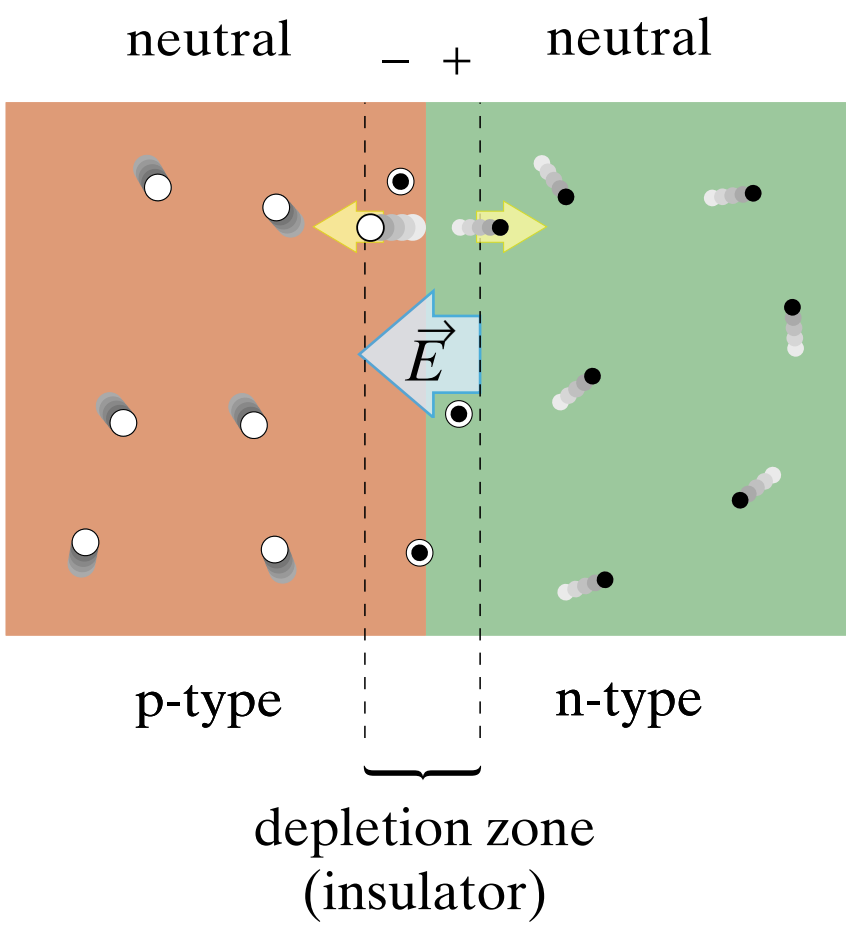
incident photon knocks out electron…

Detectors



…creating an electron-hole pair

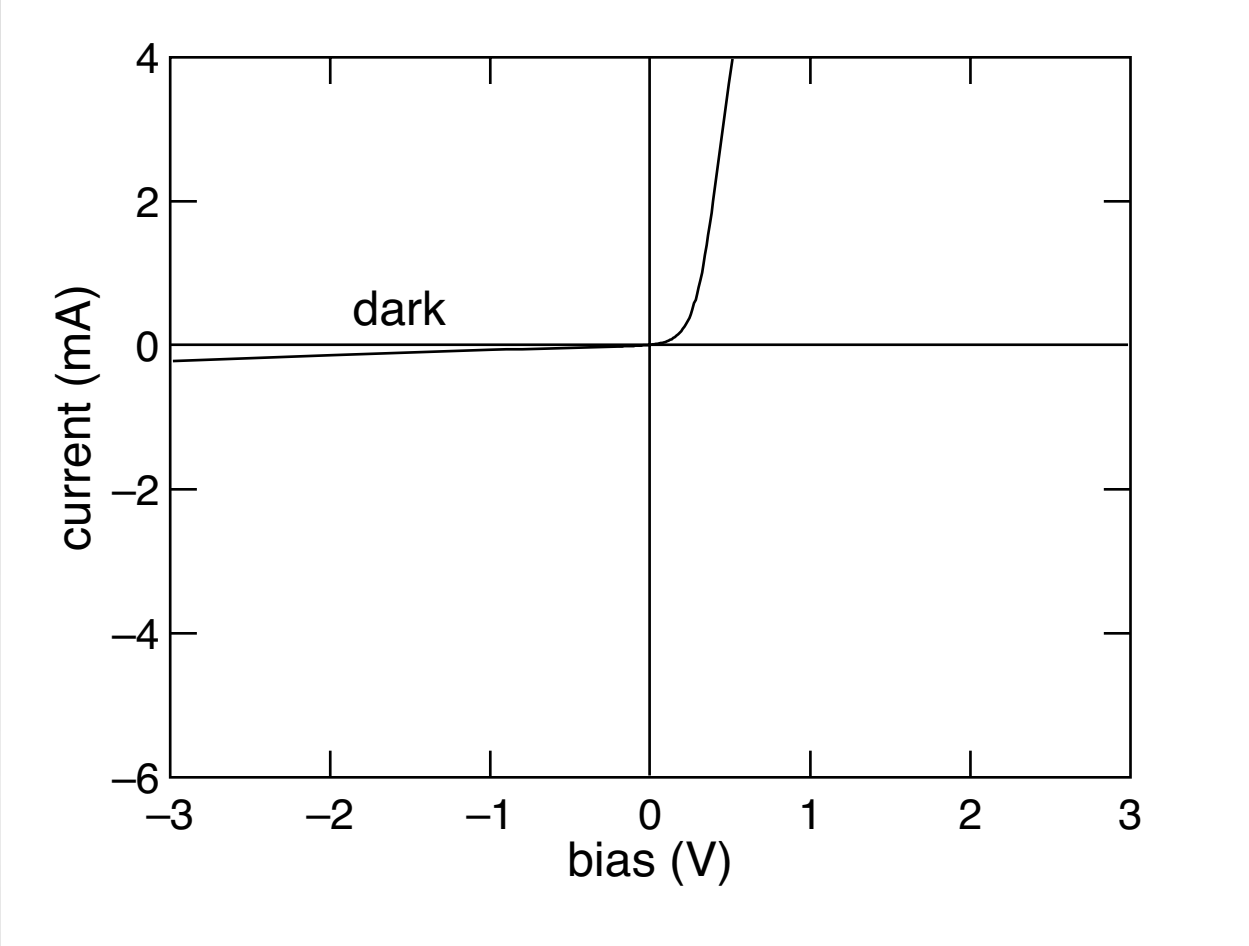
Detectors



E-field separates eh-pair, causing current

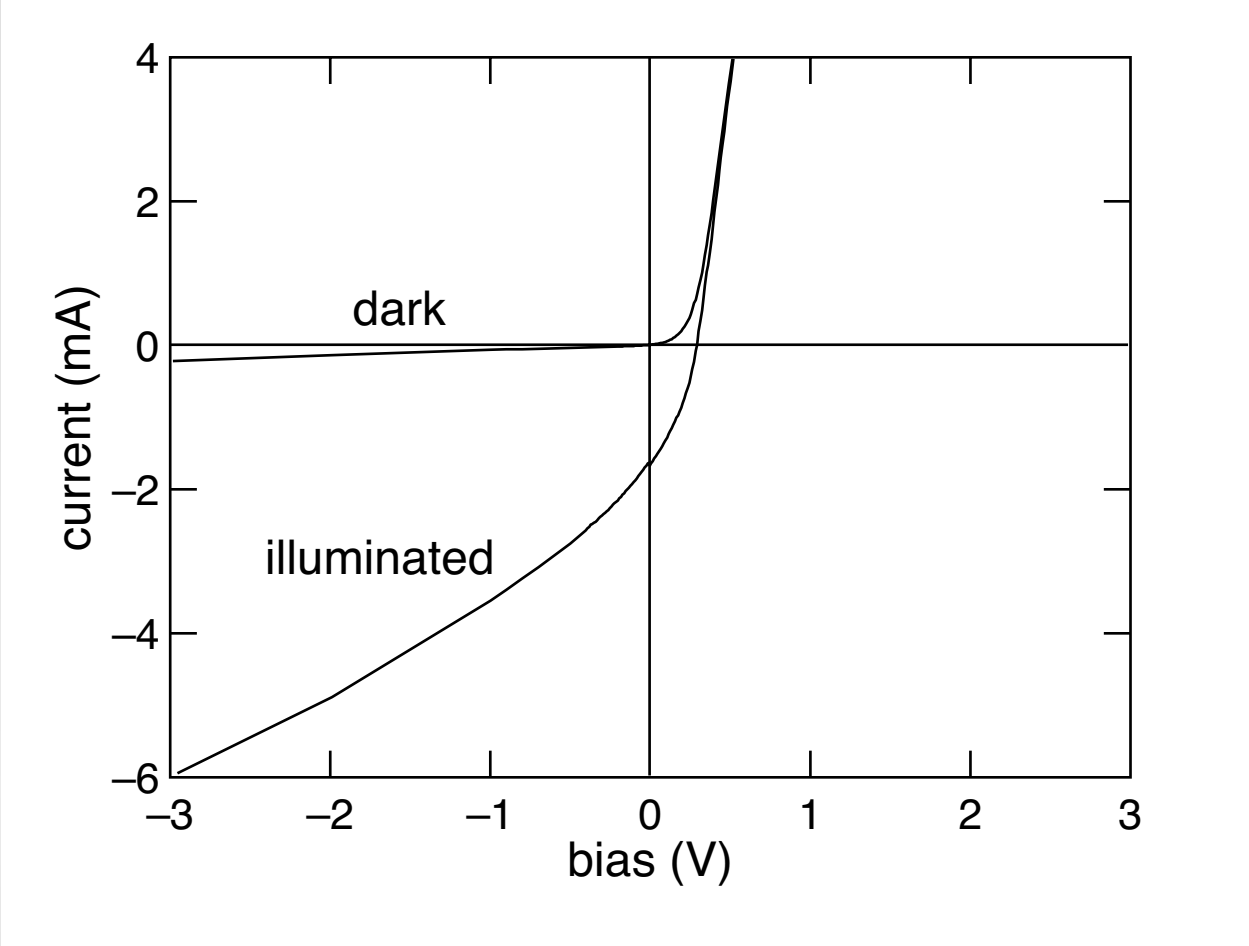
Detectors

IV characteristics



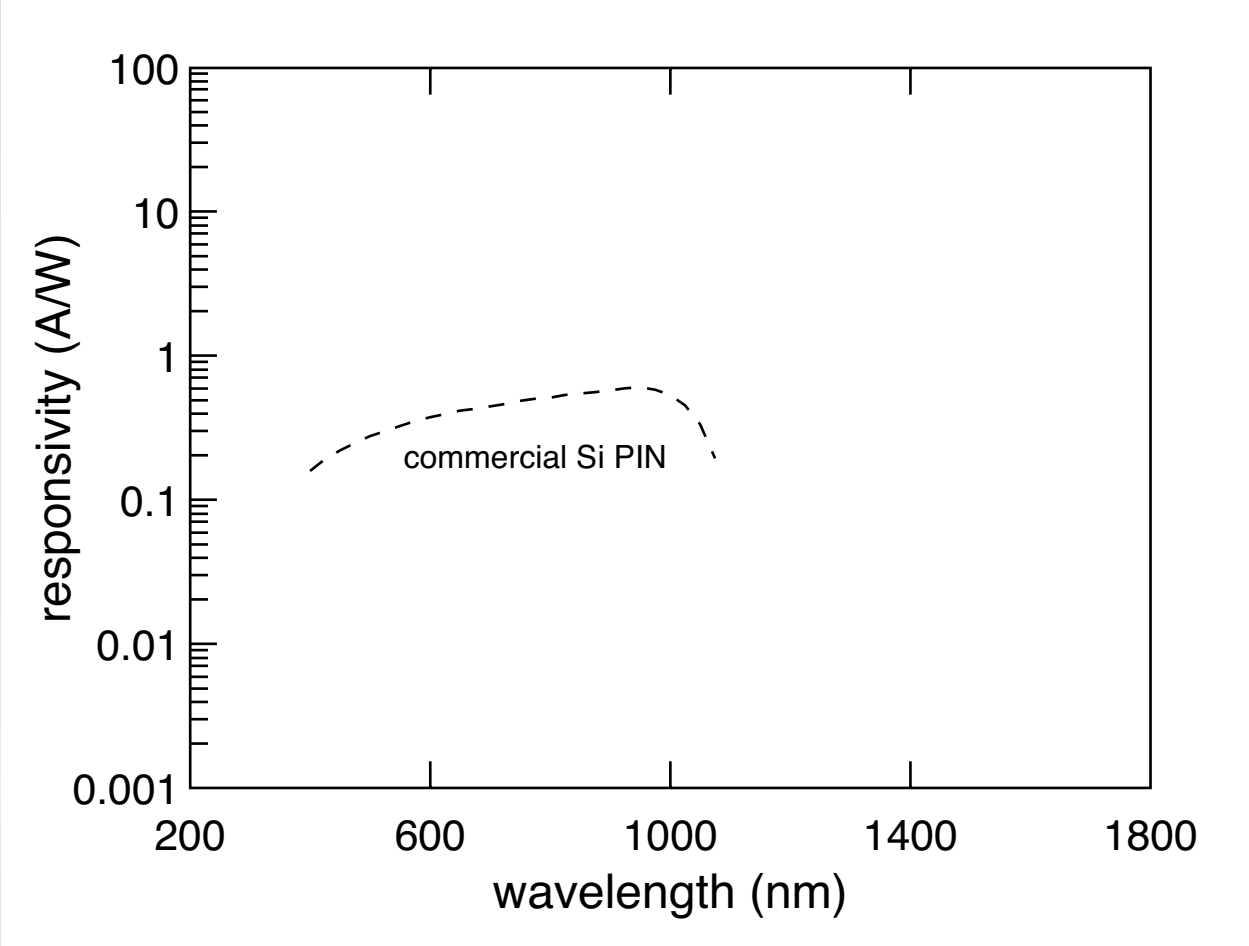
Detectors

IV characteristics



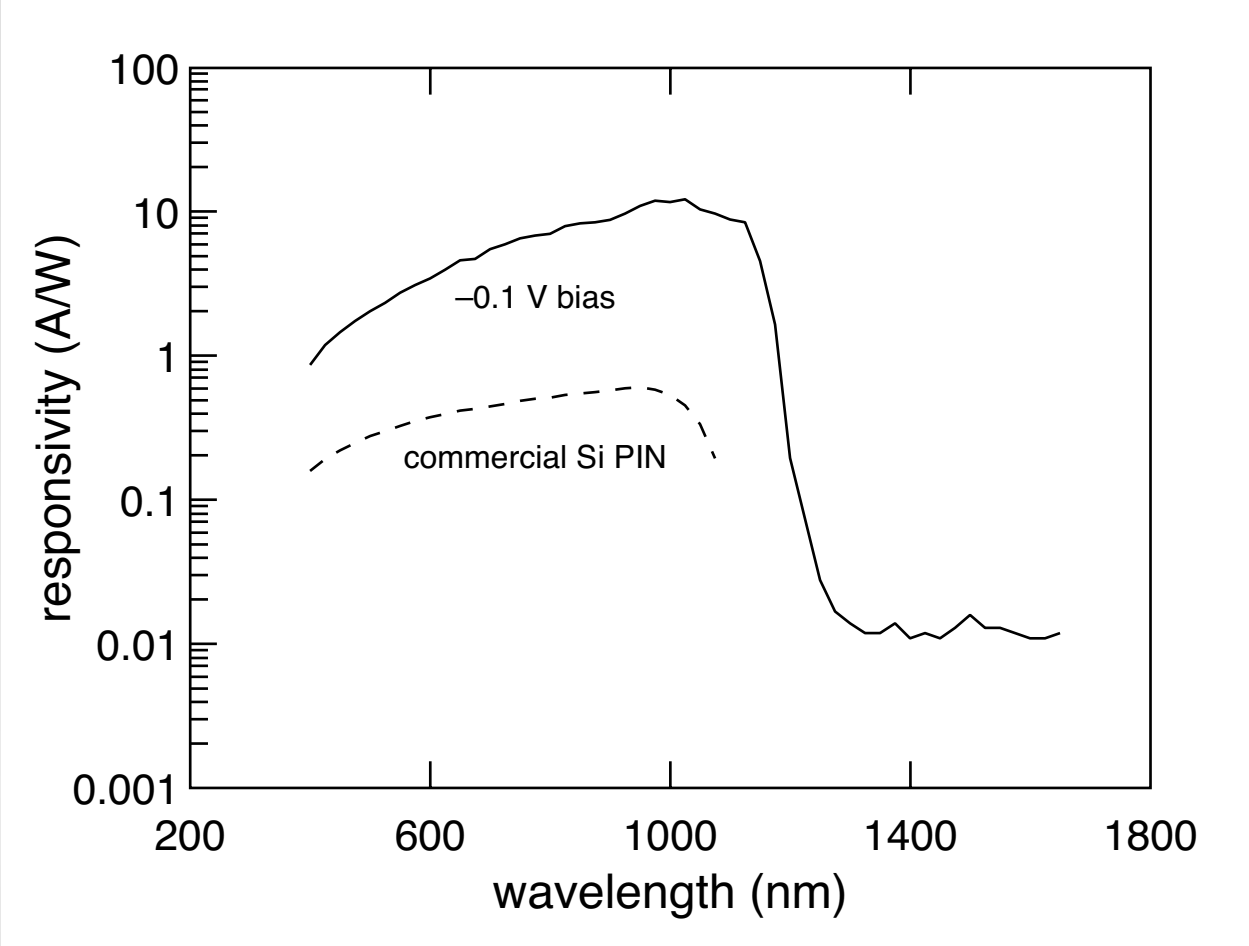
Detectors

responsivity



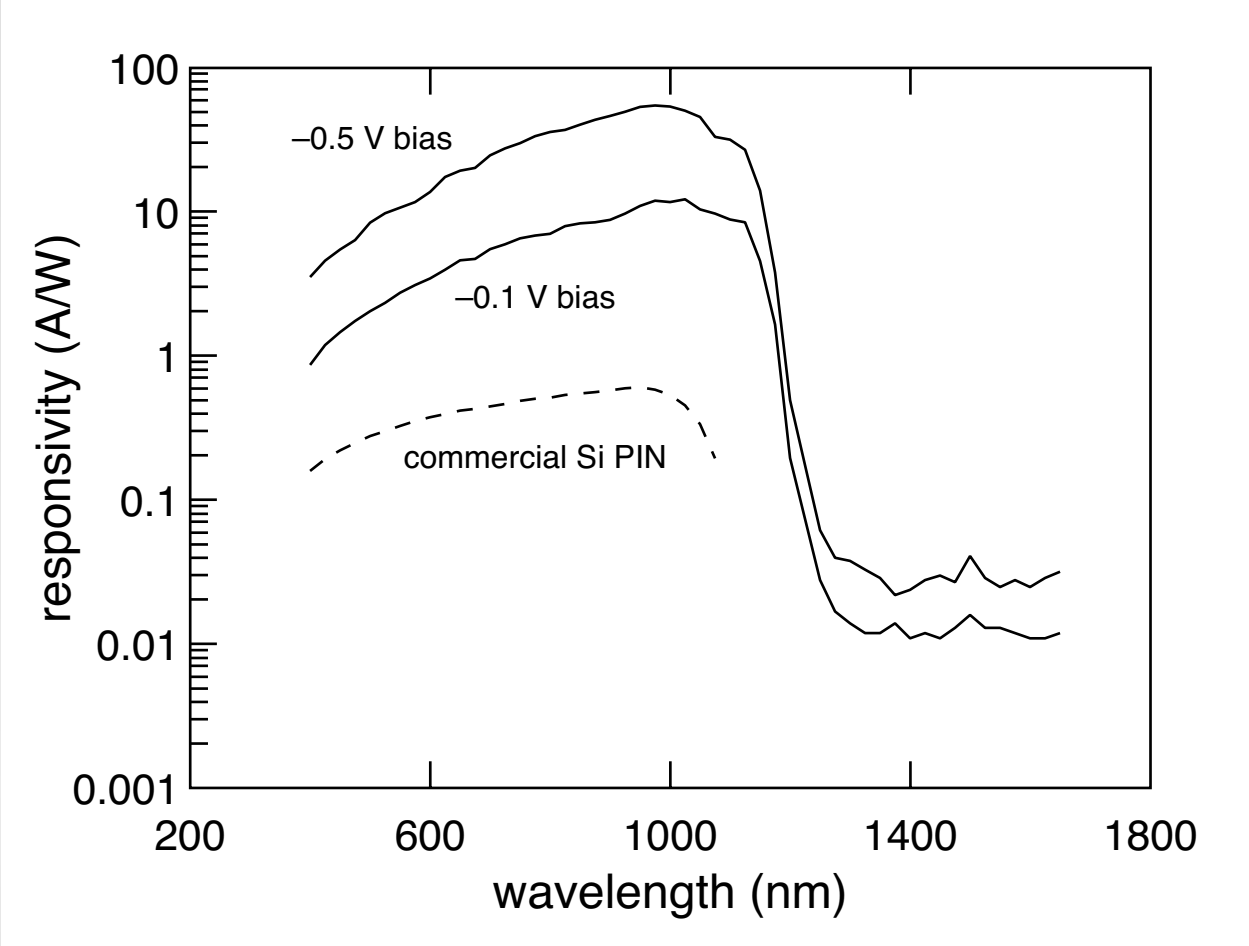
Detectors

responsivity



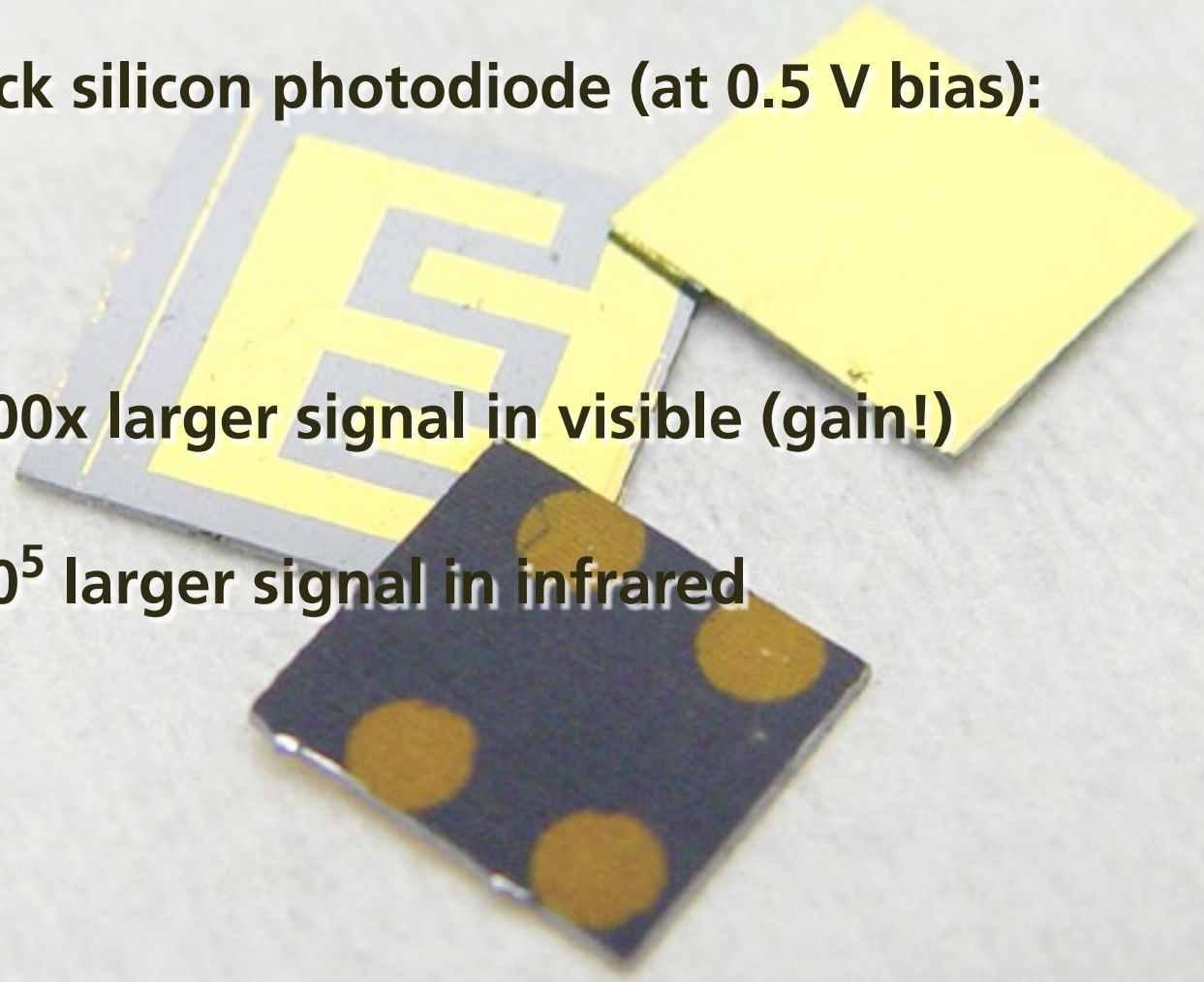
Detectors

responsivity



Detectors

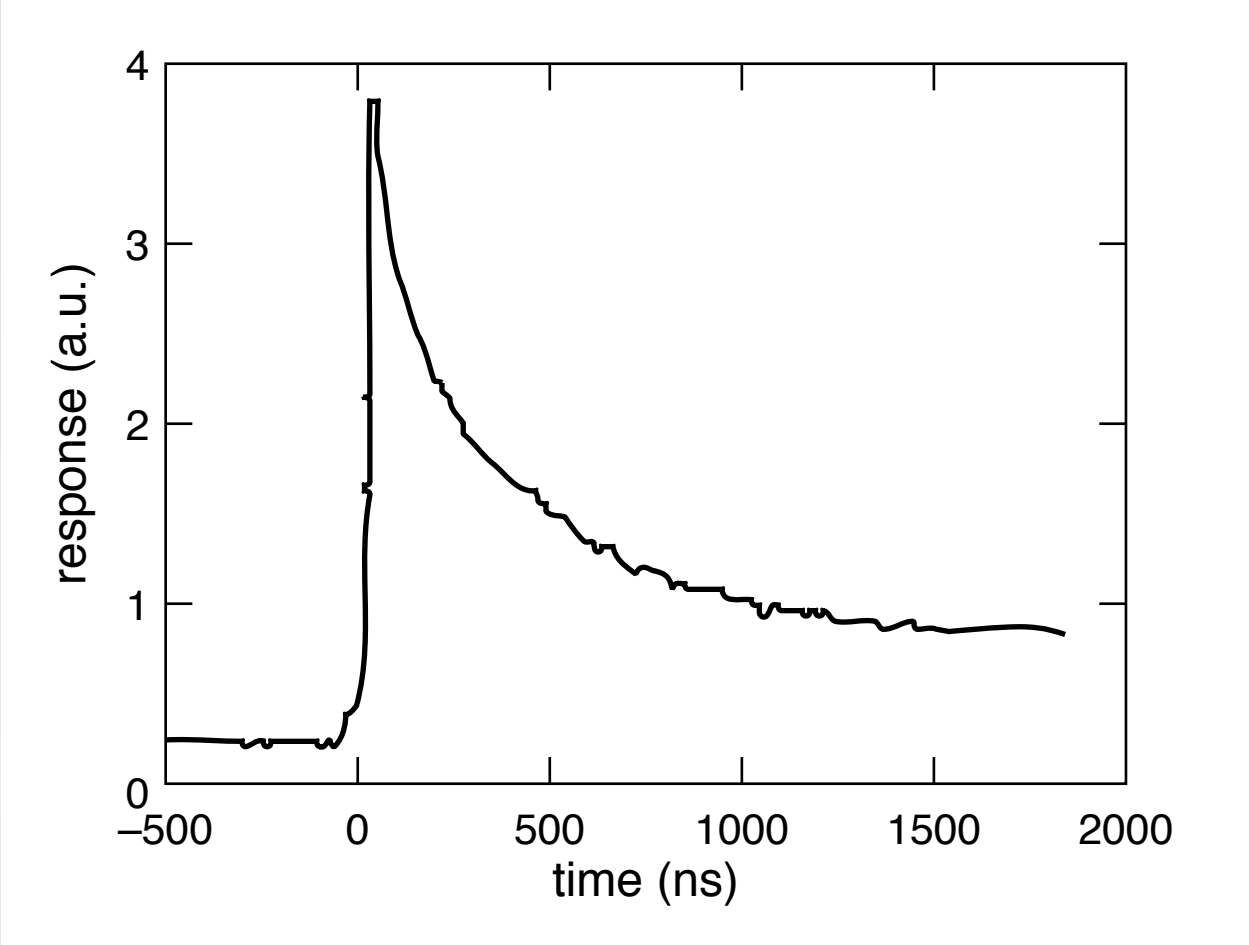
Black silicon photodiode (at 0.5 V bias):



- 100x larger signal in visible (gain!)
- 10^5 larger signal in infrared

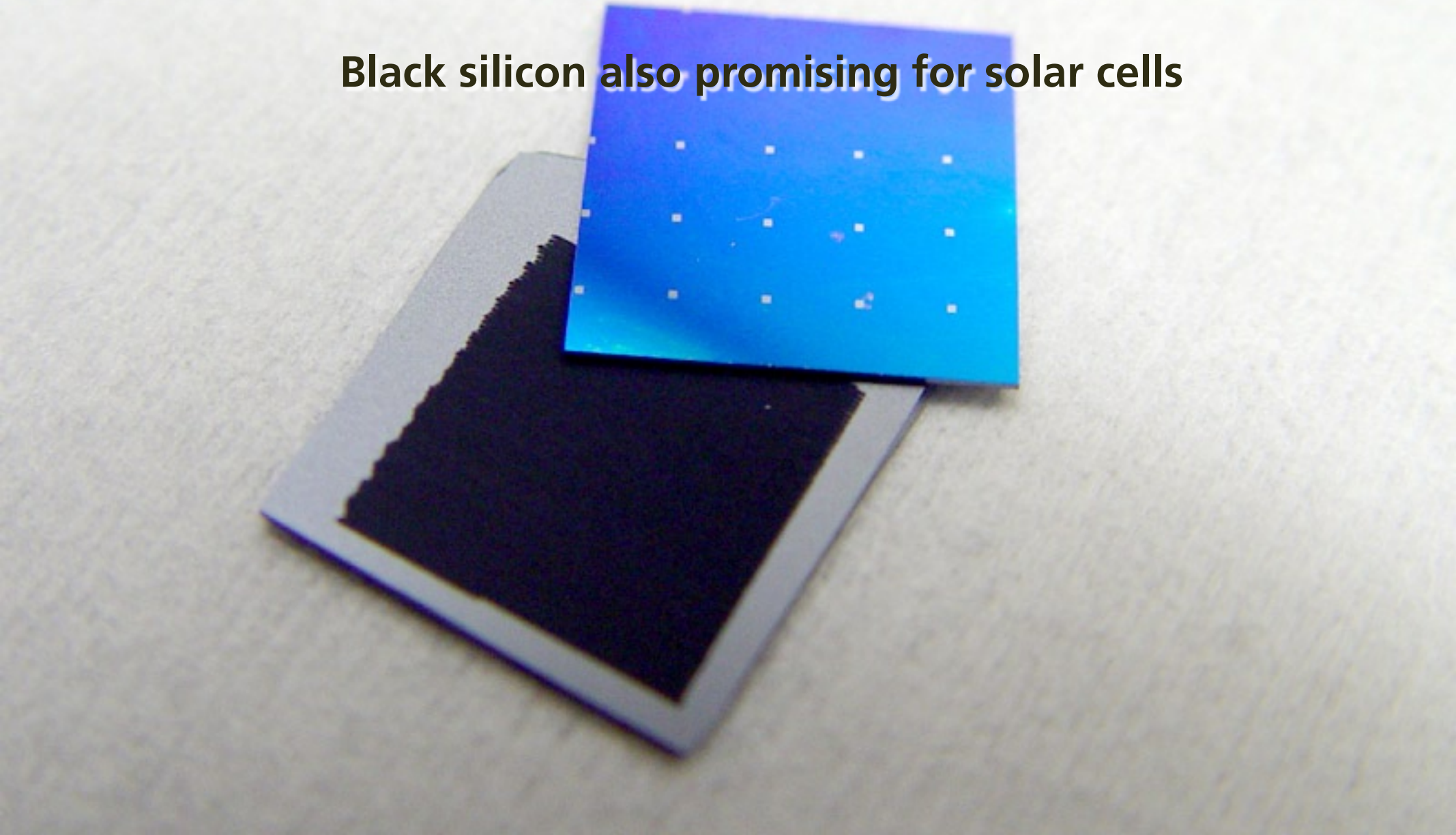
Detectors

response: 35-ns rise, 350-ns fall

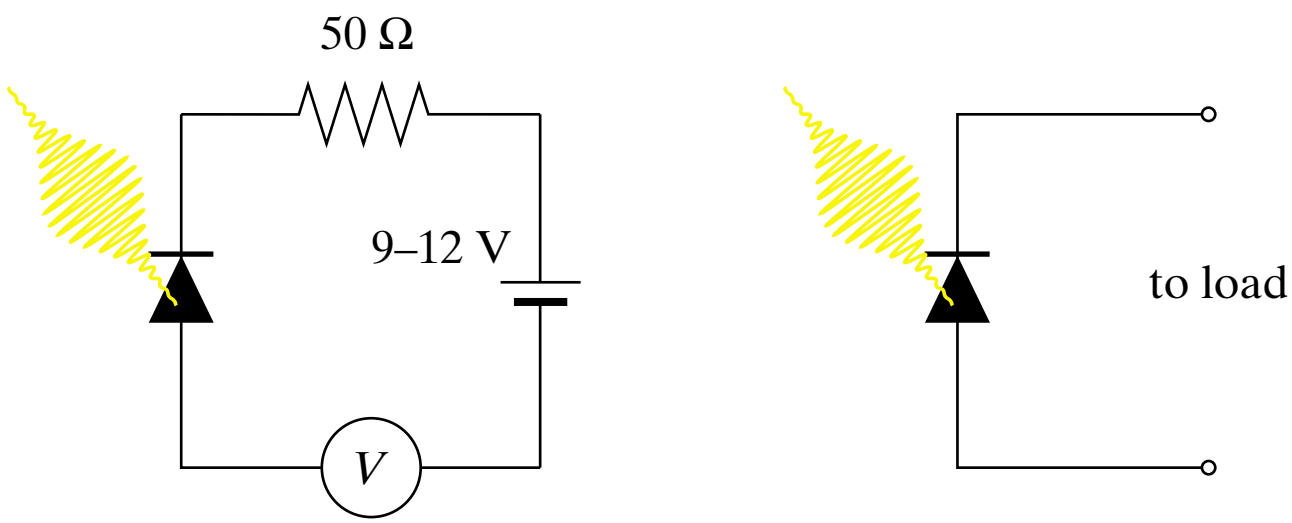


Detectors

Black silicon also promising for solar cells

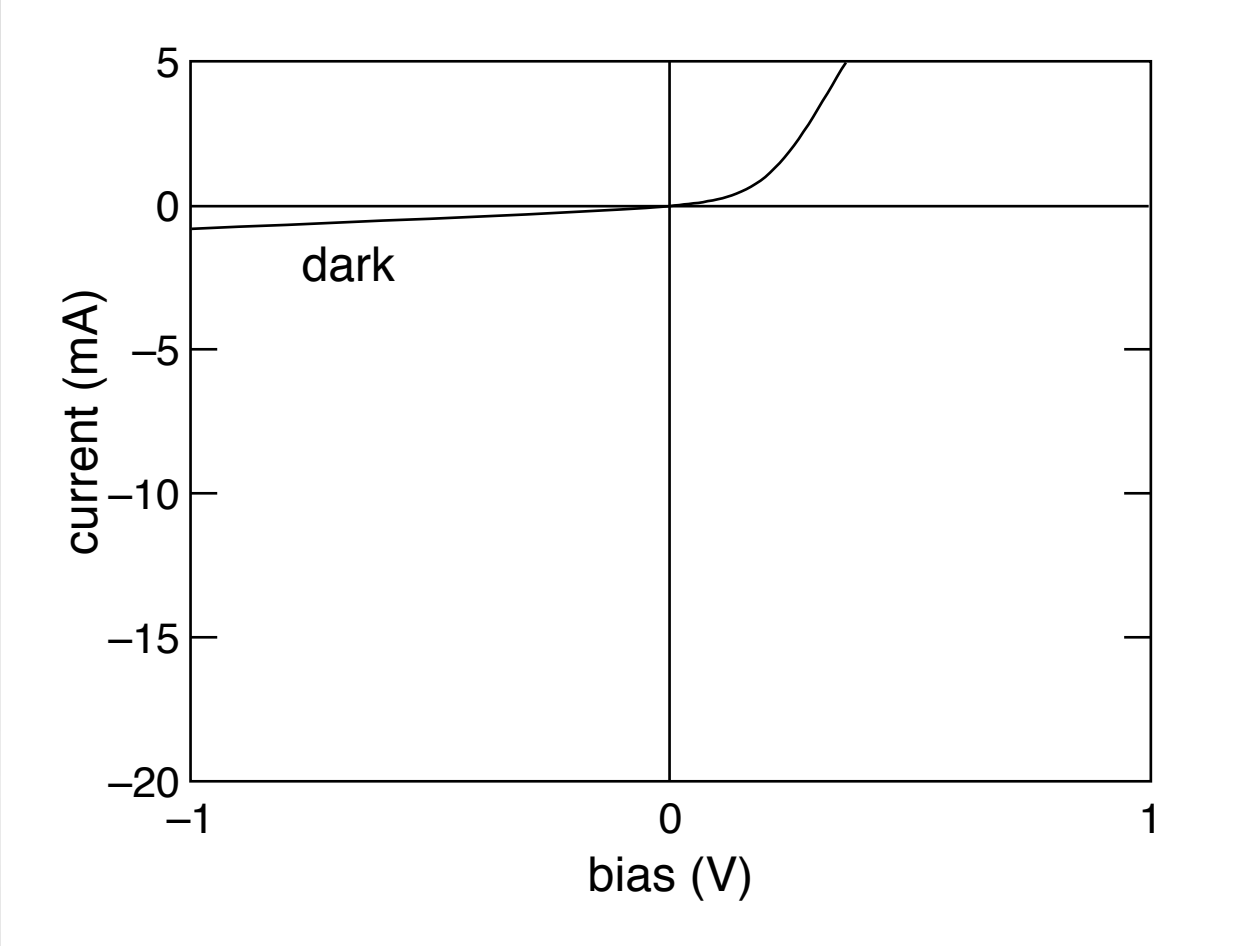


Detectors



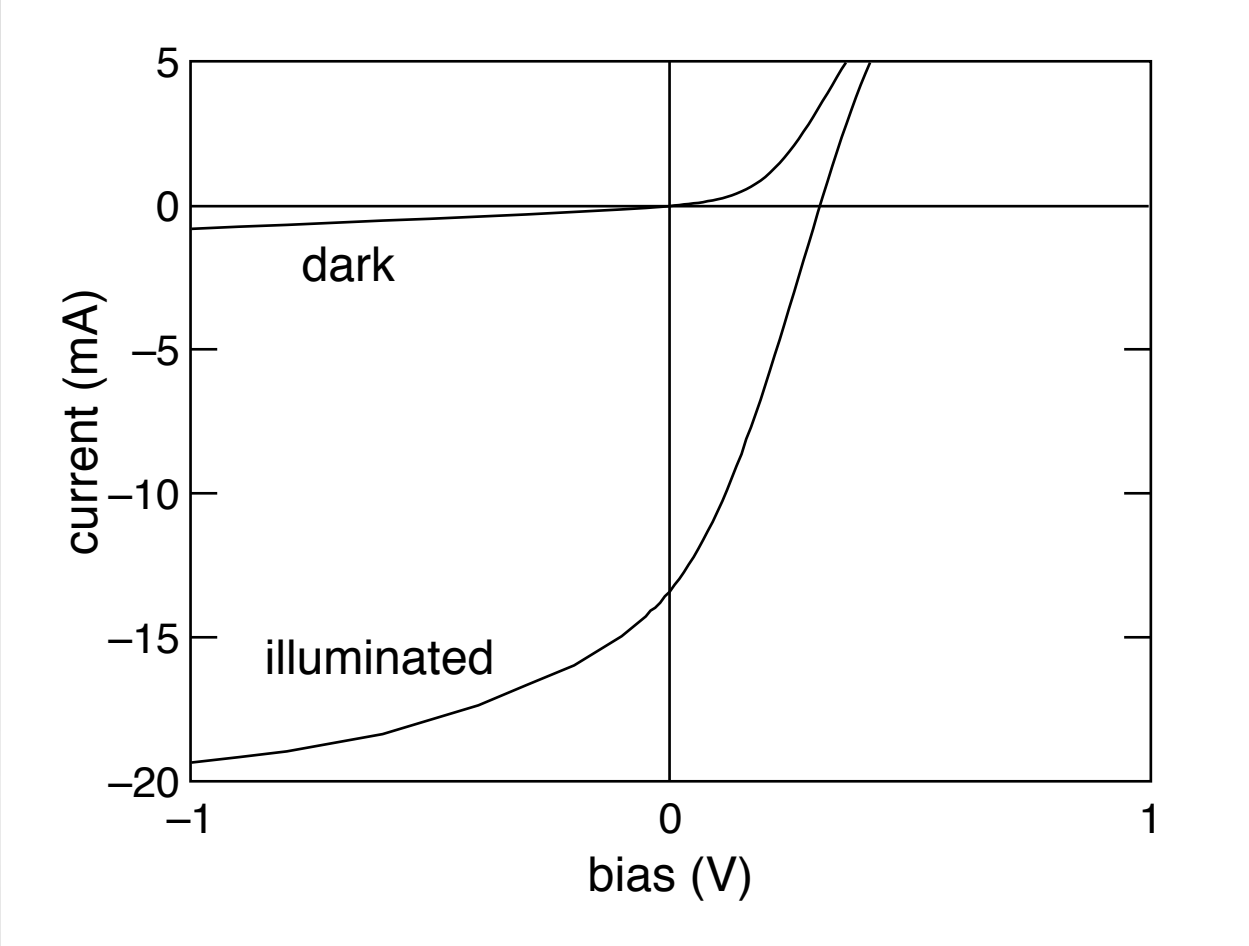
Detectors

IV characteristics



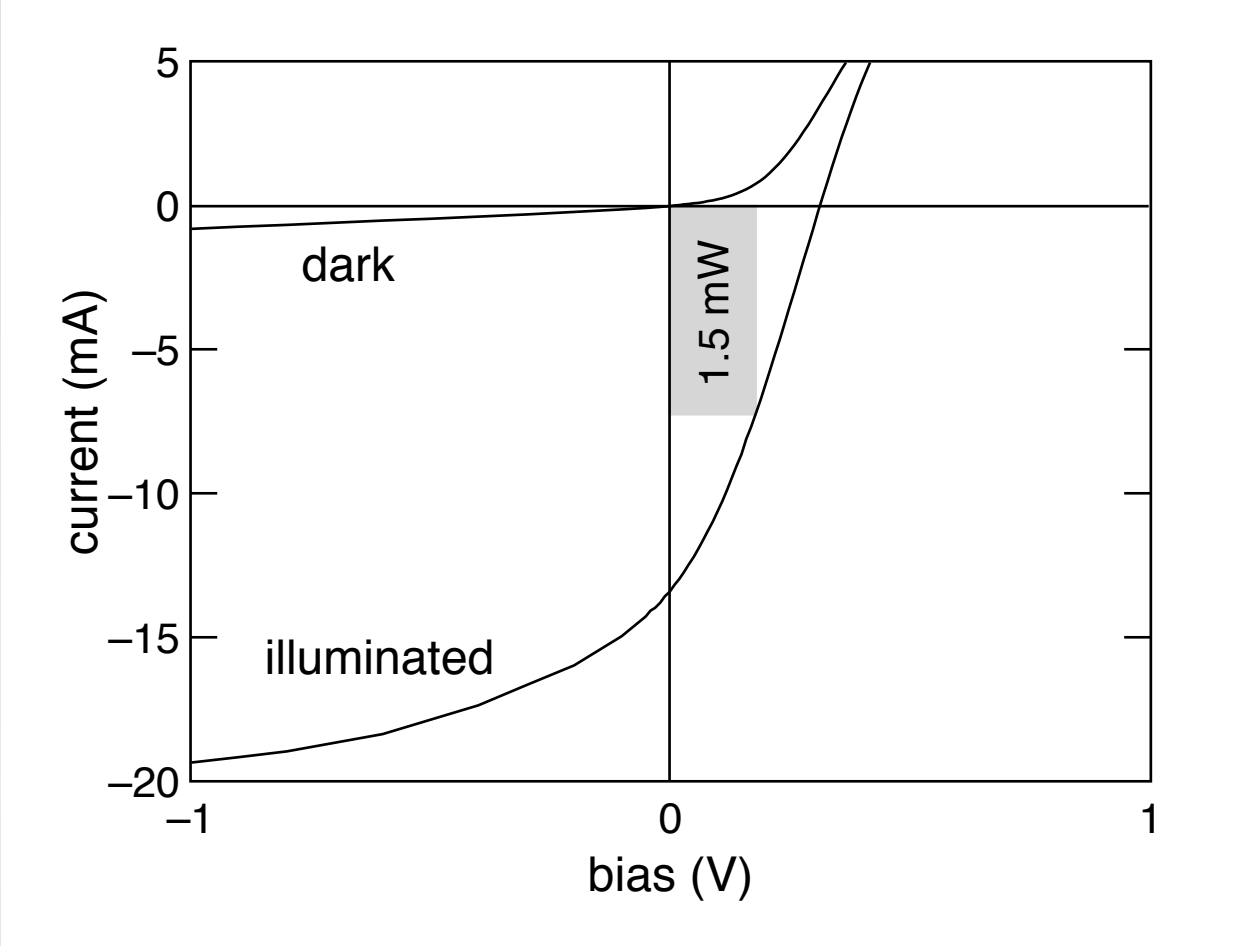
Detectors

IV characteristics



Detectors

IV characteristics



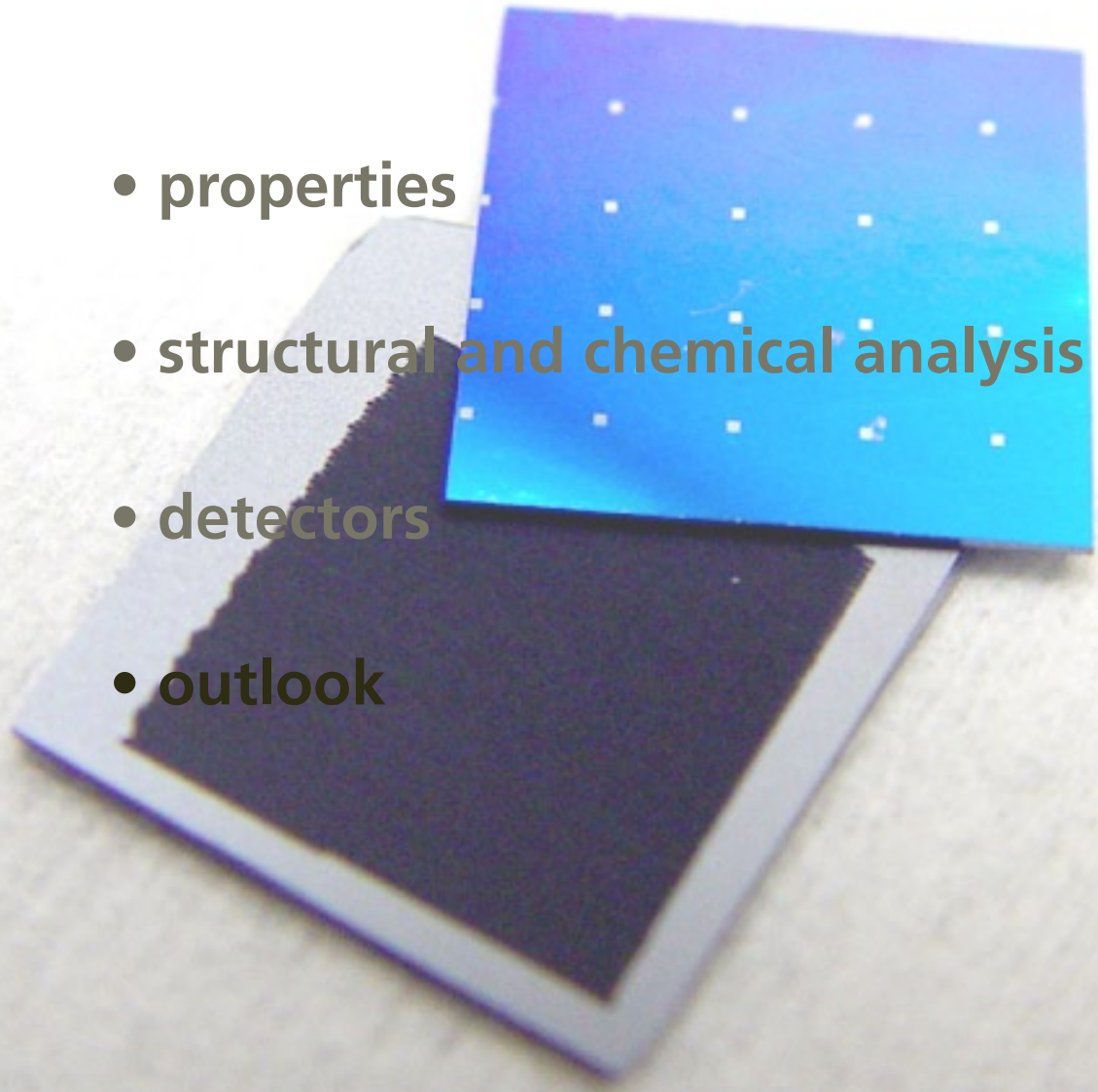
Detectors

Black silicon solar cell (preliminary):

- 2–3% efficiency
- photocurrent generated in thin layer

Outline

- properties
- structural and chemical analysis
- detectors
- outlook



Outlook

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 photographic plate or a filthy Petri dish could change the world. Even today, when financial constraints keep the role of chance to a minimum, science is still sometimes a spontaneous act, a freelance exploration of the unknown. It often starts in front of a blackboard when one scientist says, "I wonder what would happen if . . .", and the other one replies, "Let's give it a try."

The result of one such conversation two years ago in Eric Mazur's laboratory at [illegible]ard University is a new form of sil[illegible] soot. What started life as [illegible] now has patents be[illegible]

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 billions of times brighter than the Sun. Its immense power is delivered extremely quickly: each pulse lasts a mere fraction of a trillionth of a second.

These flashes of laser light have provided researchers with a new way to probe the characteristics of many materials (*New Scientist*, 19 February 2000, p 34). Mazur's group was using the powerful femtosecond pulses to study the surface chemistry of metals. But Her, who is now at the Lawrence Livermore Laboratory in Calif[illegible]nia, had been wondering for years what [illegible]uld do to semiconductors like [illegible]r tried it, so there

around the laboratory," he claims.

Well, it was almost the only reason. A short laser pulse will break down SF_6 into sulphur and fluorine radicals, which will attack a silicon substrate. "Hydrogen fluoride is used to etch silicon. So we thought maybe the SF_6 would decompose and then the fluorine would somehow react with the silicon," Mazur explains.

With no clearer idea than this, th[illegible] researchers began firing 100-femtosecon[illegible] pulses of laser light through the windo[illegible] of their chamber, through the SF_6 gas a[illegible] onto the shiny silicon wafer. After fi[illegible] about 100 pulses they cracked the se[illegible] the chamber and removed the wafer. [illegible] saw a tiny black spot at the focal p[illegible] the laser beam. A burn, perhaps. [illegible] that Mazur knew that silicon doesn[illegible] "You can get silicon oxide, but [illegible] black," he says. So what was goi[illegible]

New Scientist 13, 34 (2001)

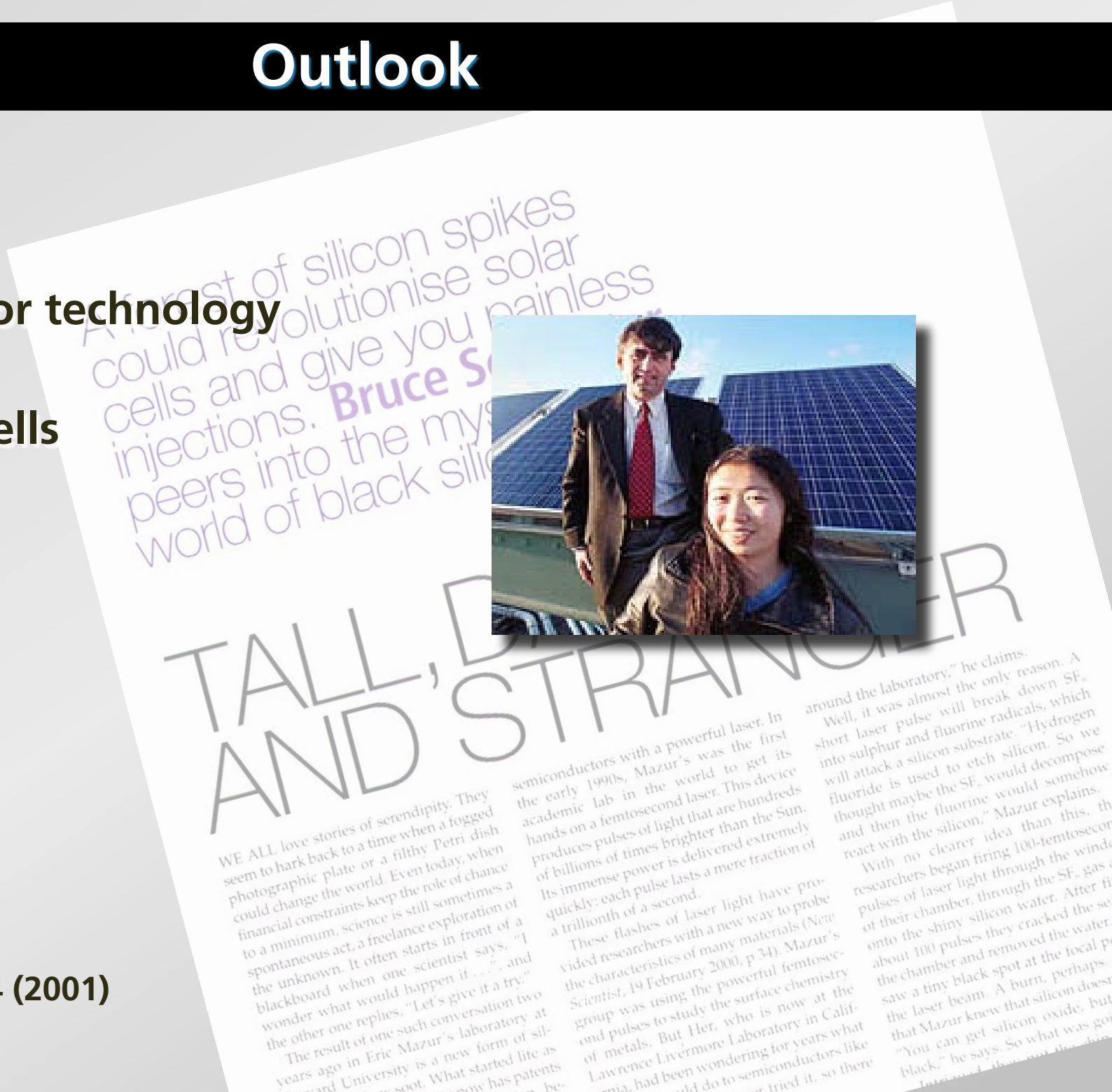
Outlook

- **detector technology**

New Scientist 13, 34 (2001)

Outlook

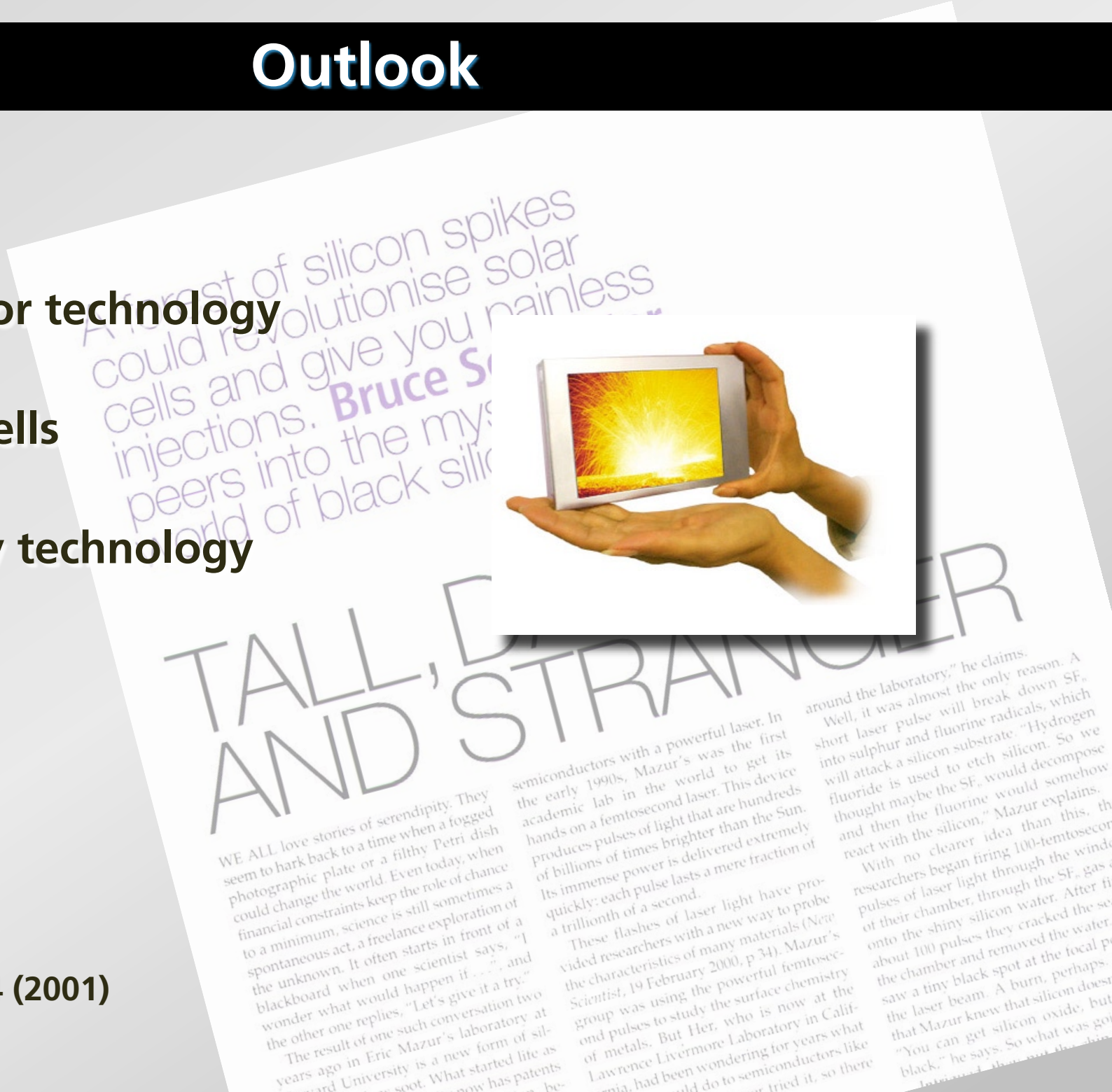
- detector technology
- solar cells



New Scientist 13, 34 (2001)

Outlook

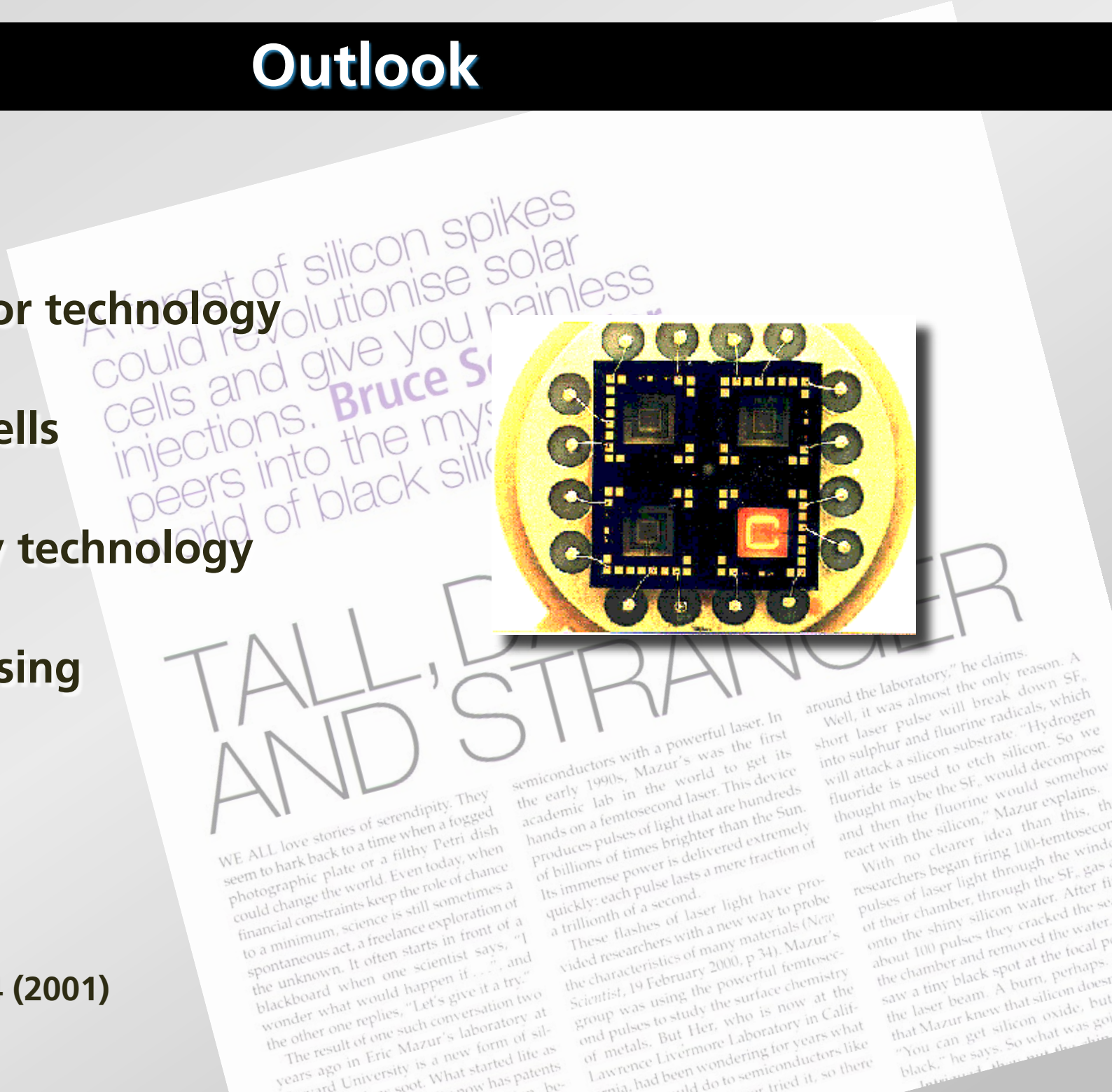
- detector technology
- solar cells
- display technology



New Scientist 13, 34 (2001)

Outlook

- detector technology
- solar cells
- display technology
- biosensing

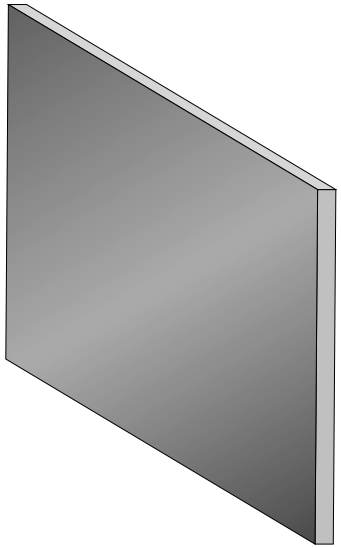


New Scientist 13, 34 (2001)

Outlook

Can we control ordering and placement of spikes?

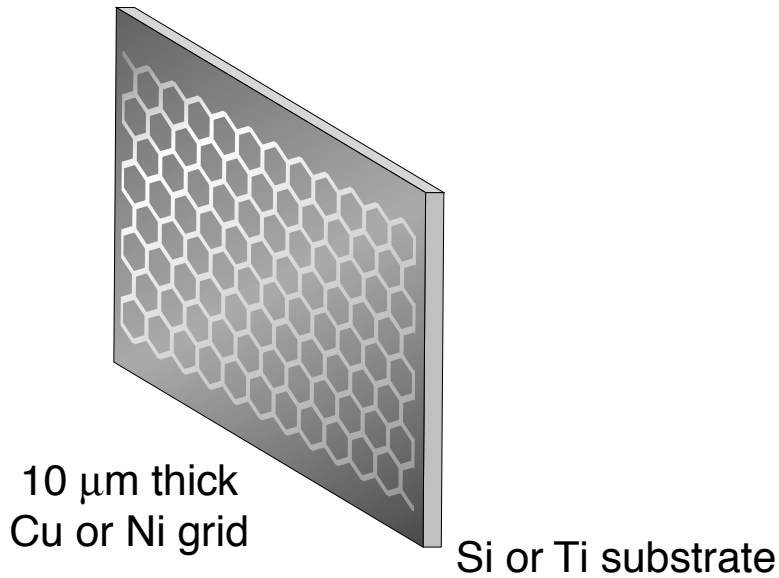
Outlook



Si or Ti substrate

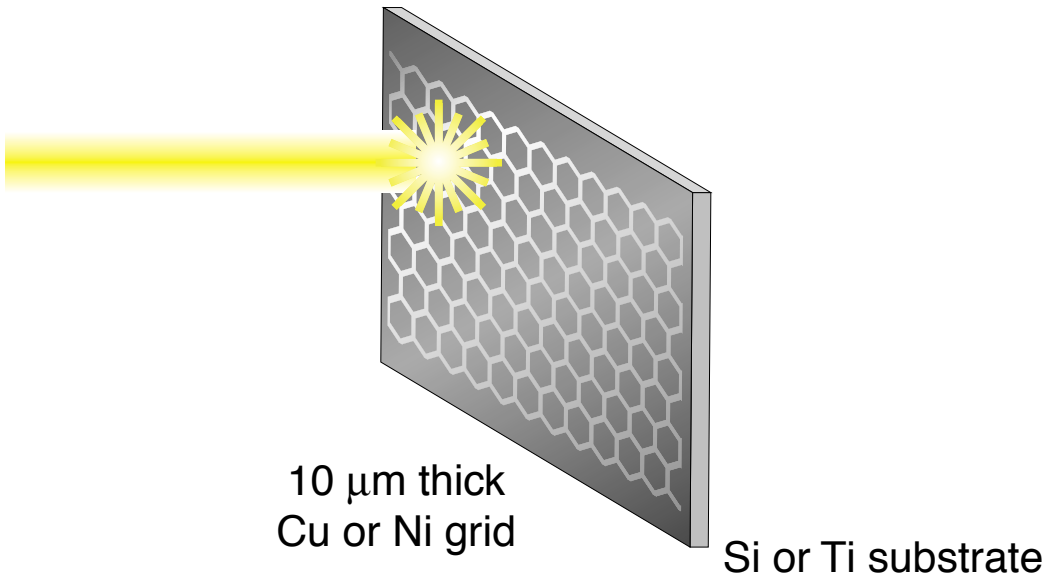
Outlook

place grid in front of sample



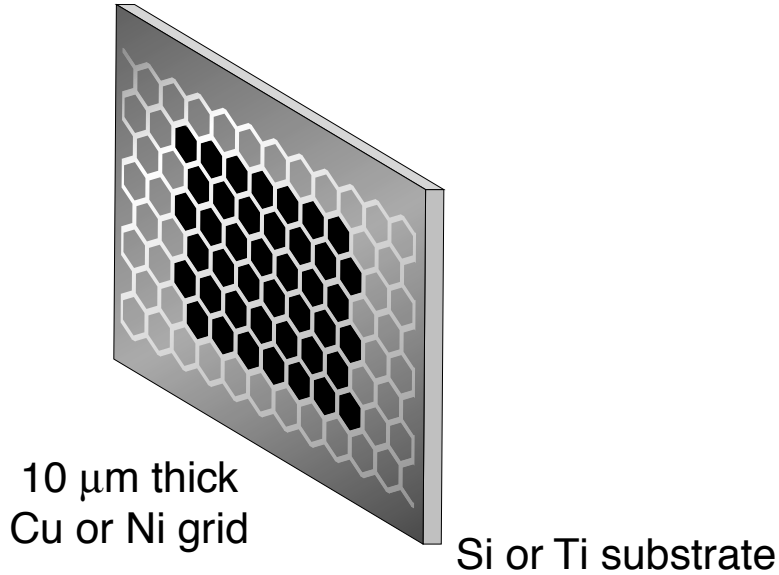
Outlook

scan laser beam



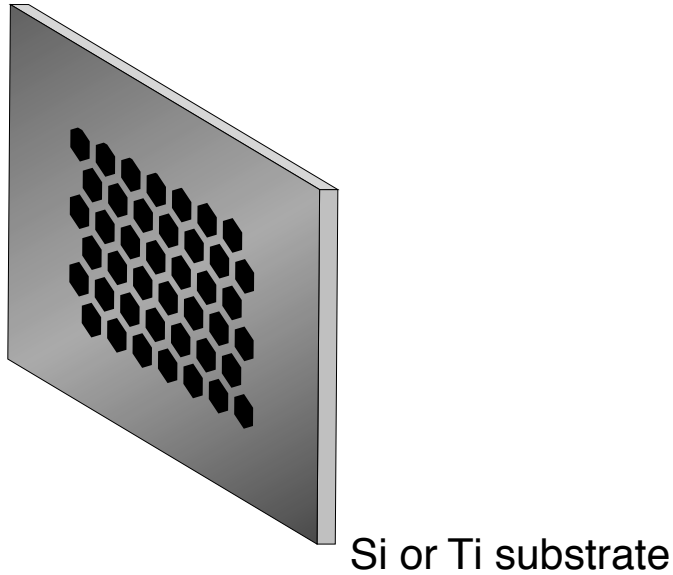
Outlook

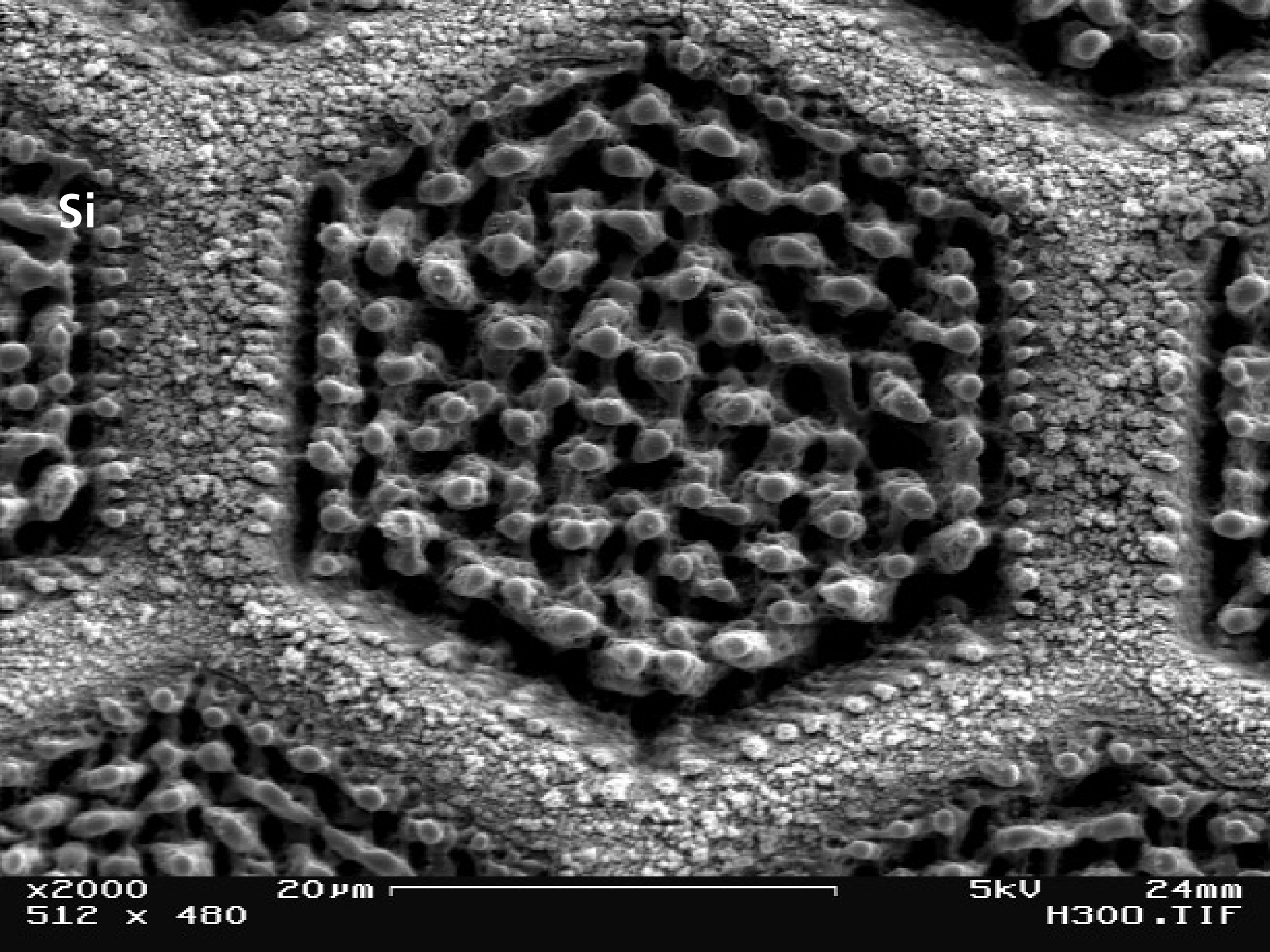
scan laser beam



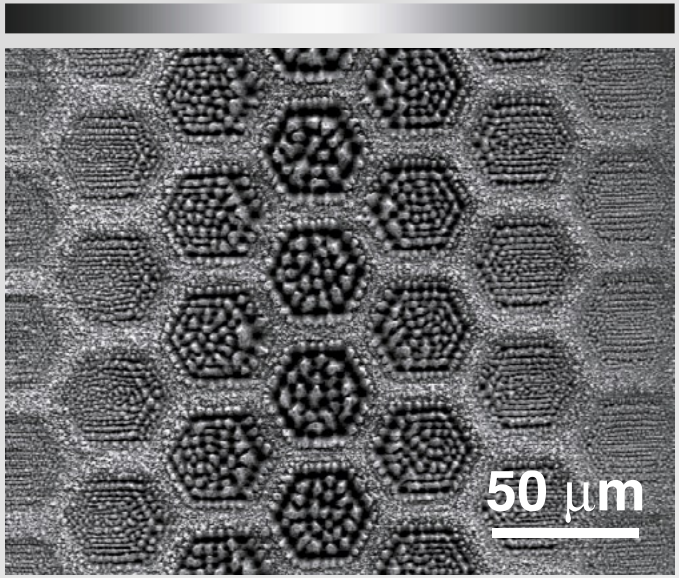
Outlook

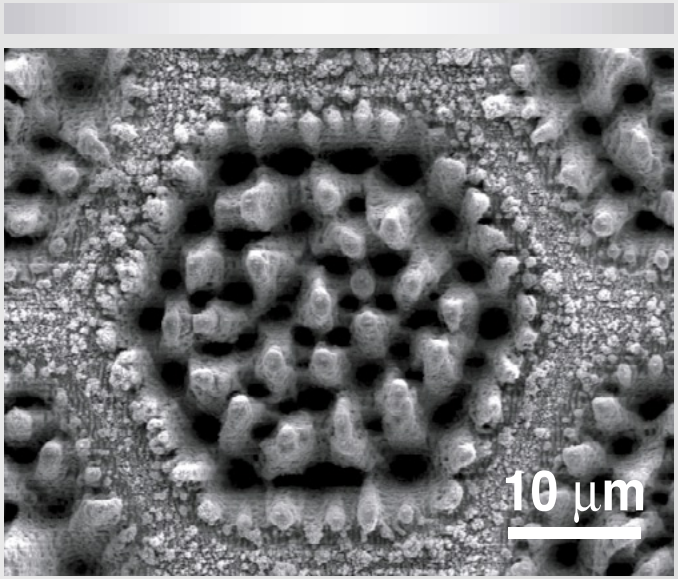
remove grid

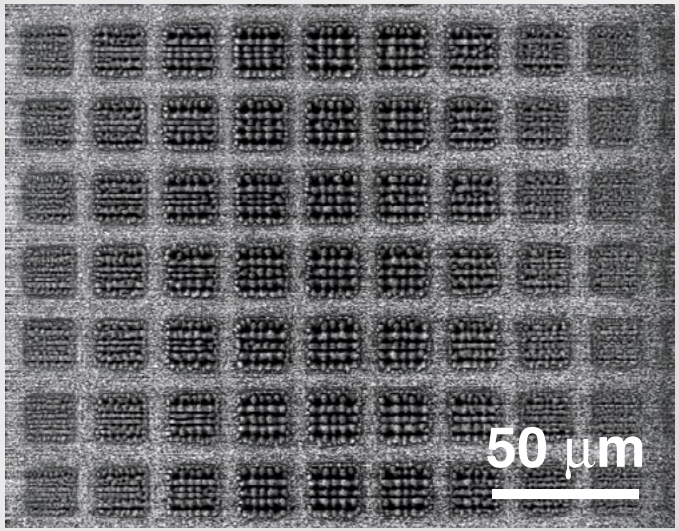


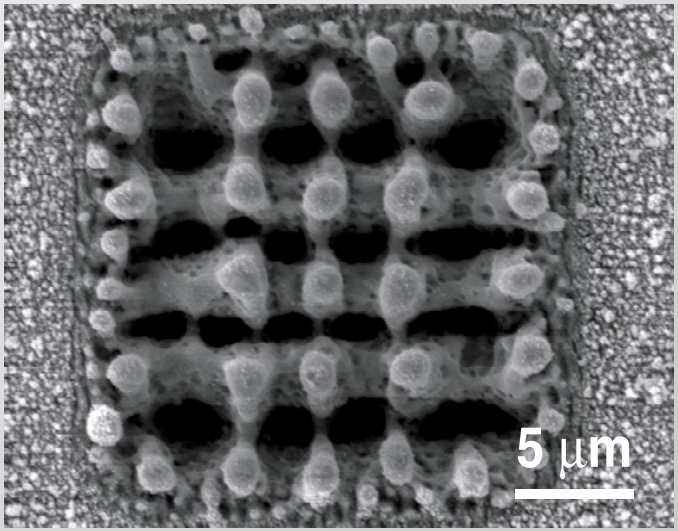

Si
x2000
20μm
5kV
24mm
512 x 480
H30D.TIF

Outlook





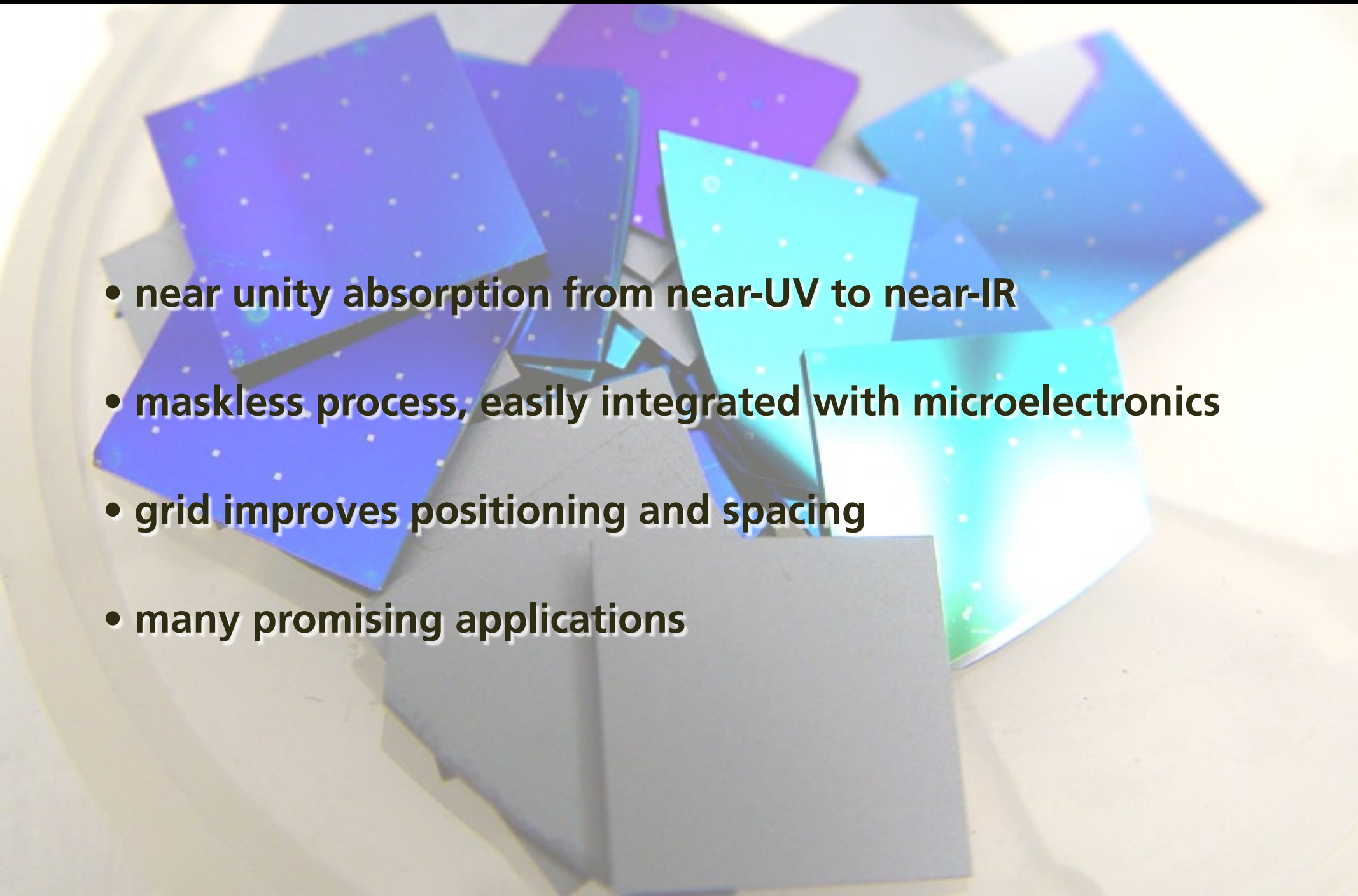




Appl. Phys. Lett., **82**, 1715 (2003)

Summary

Summary



- near unity absorption from near-UV to near-IR
- maskless process, easily integrated with microelectronics
- grid improves positioning and spacing
- many promising applications


GORDON McKAY
LABORATORY OF
APPLIED SCIENCE

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DARPA
Department of Energy
NDSEG

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