

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



The 41st Annual SES Technical Meeting
Lincoln, NE, 11 October 2004





Eric Mazur



Jim Carey



Brian Tull



Eric Diebold

and also....

Dr. Tsing-Hua Her

Dr. Shrenik Deliwala

Dr. Richard Finlay

Dr. Michael Sheehy

Dr. Jeffrey Warrander

Dr. Claudia Wu

Dr. Rebecca Younkin

Prof. Catherine Crouch

Prof. Mengyan Shen

Dr. John Chervinsky

Dr. Joshua Levinson

Dr. François Génin (LLNL)

Dr. Richard Farrell

Dr. Arieh Karger (RMD)

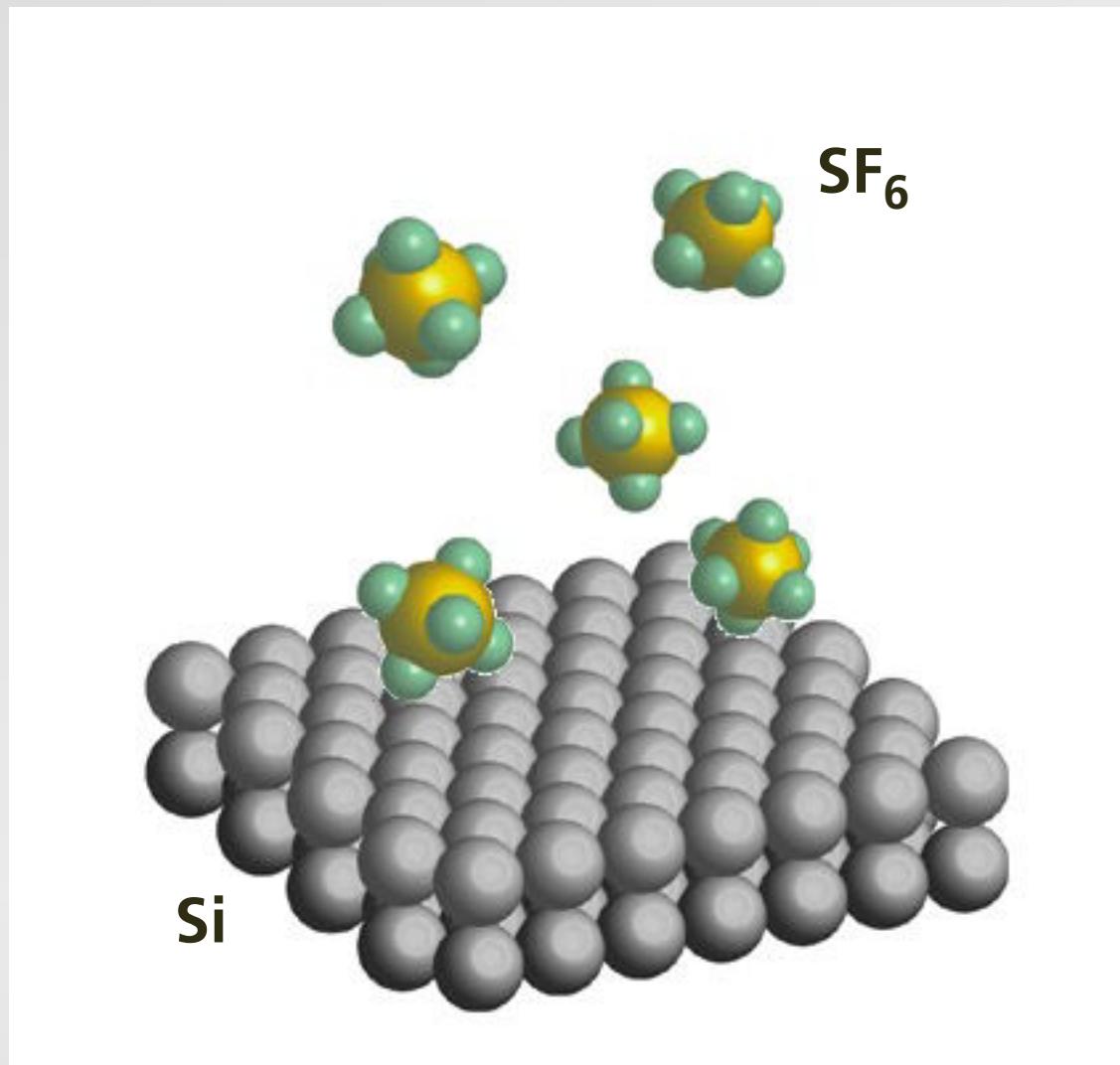
Dr. Richard Meyers (RMD)

Prof. Michael Aziz

Prof. Cynthia Friend

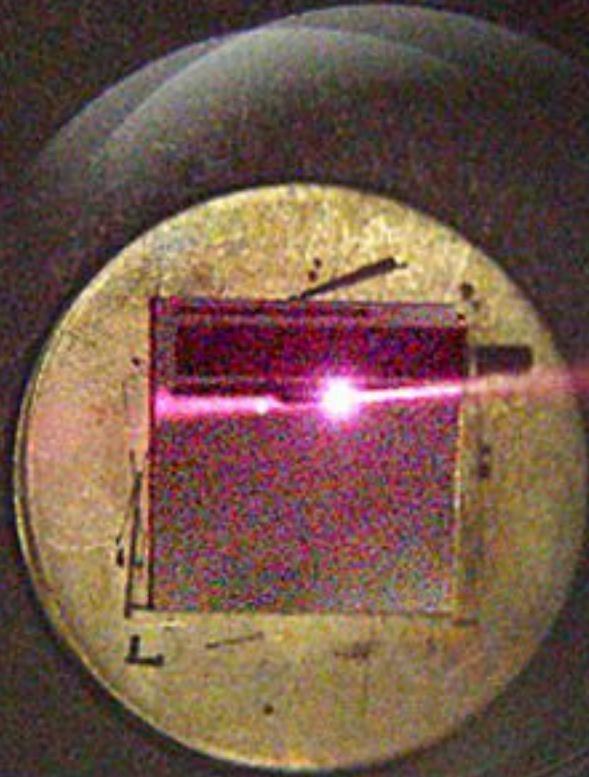
Prof. Li Zhao (Fudan)

Introduction

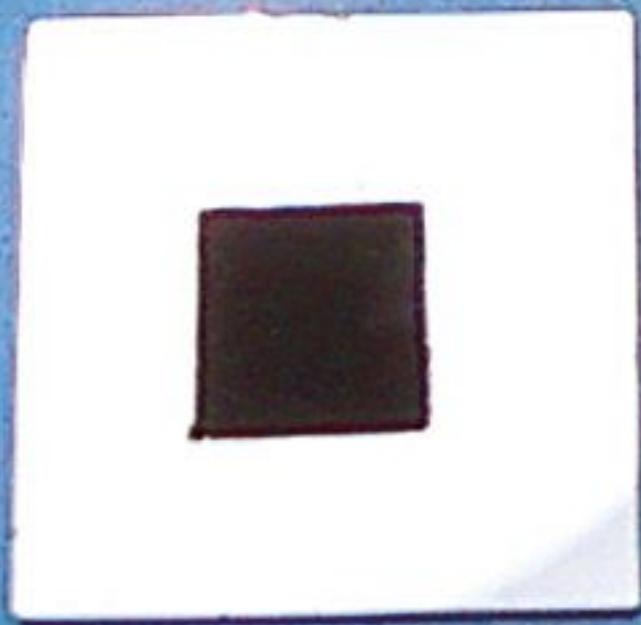


irradiate with 100-fs 10 kJ/m² pulses

Introduction



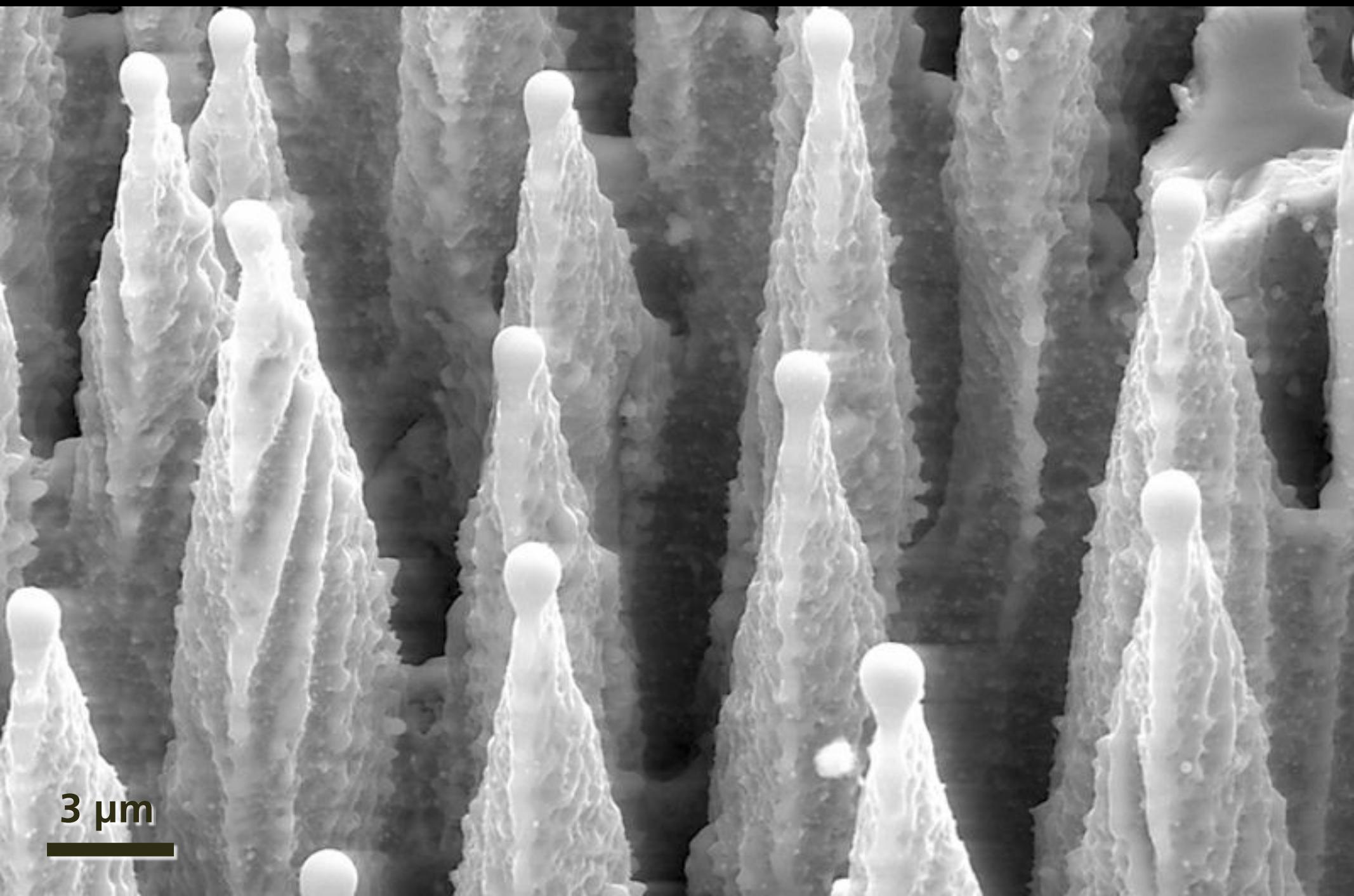
Introduction



“black silicon”

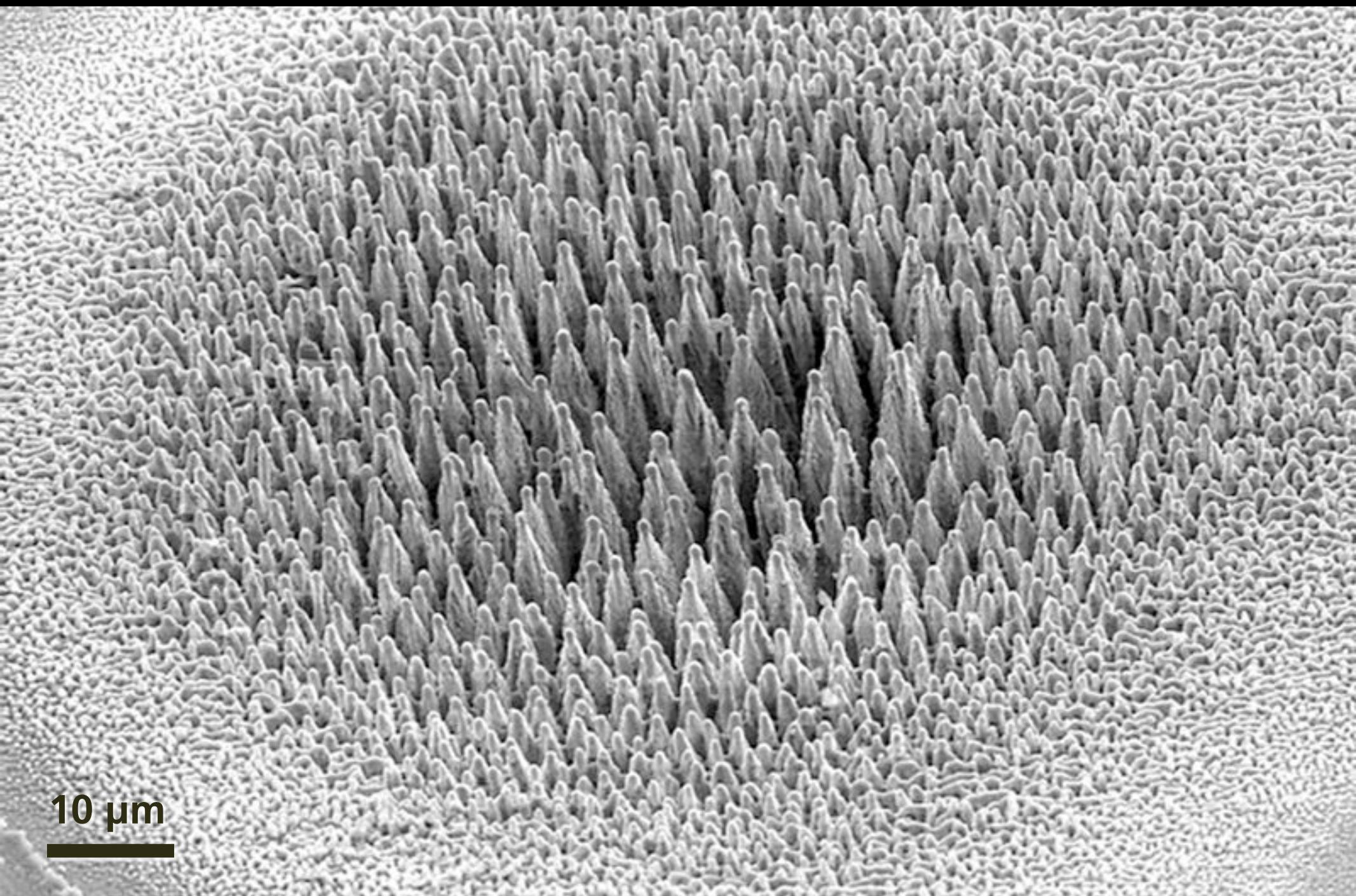


Introduction



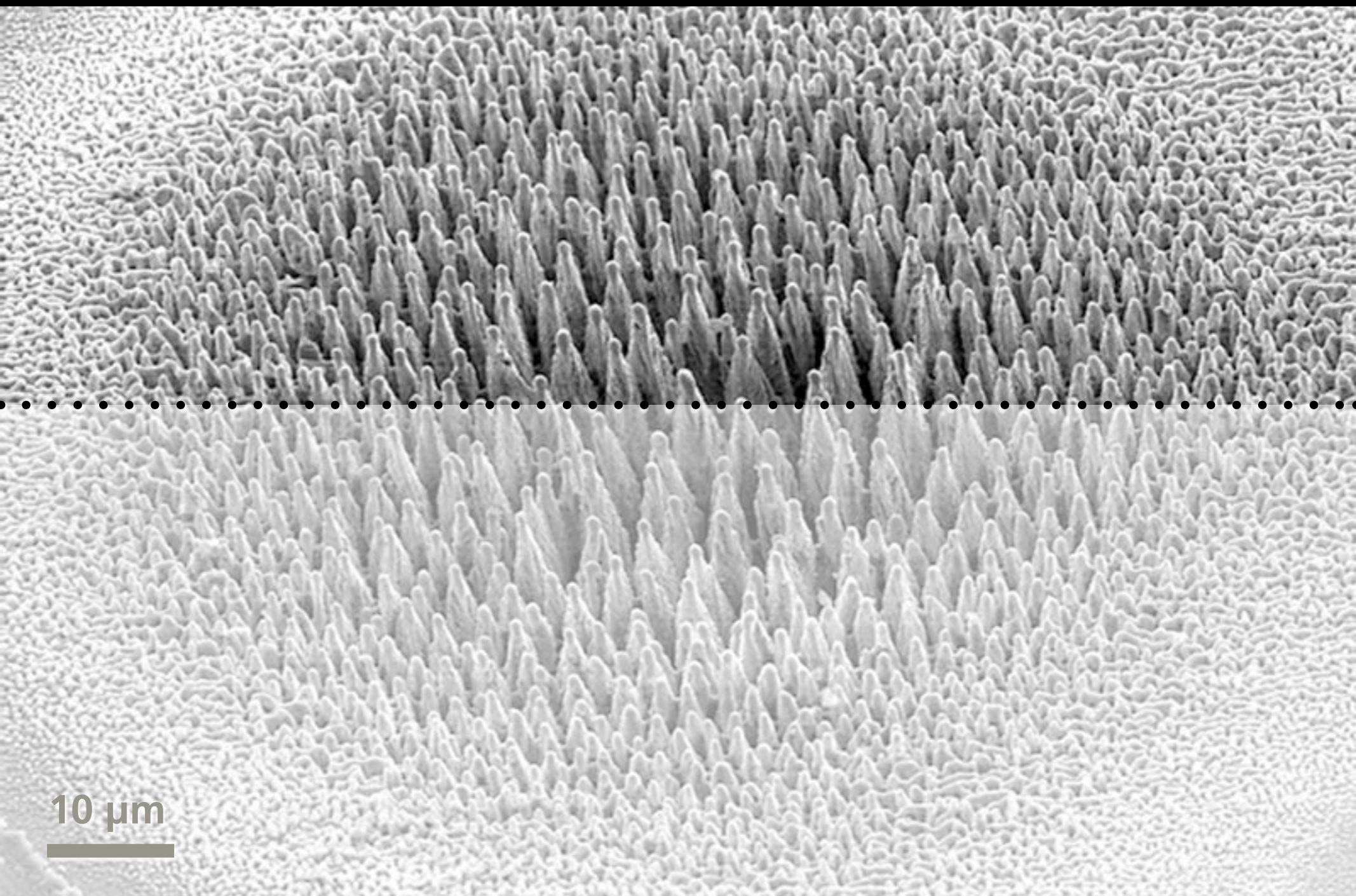
3 μm

Introduction

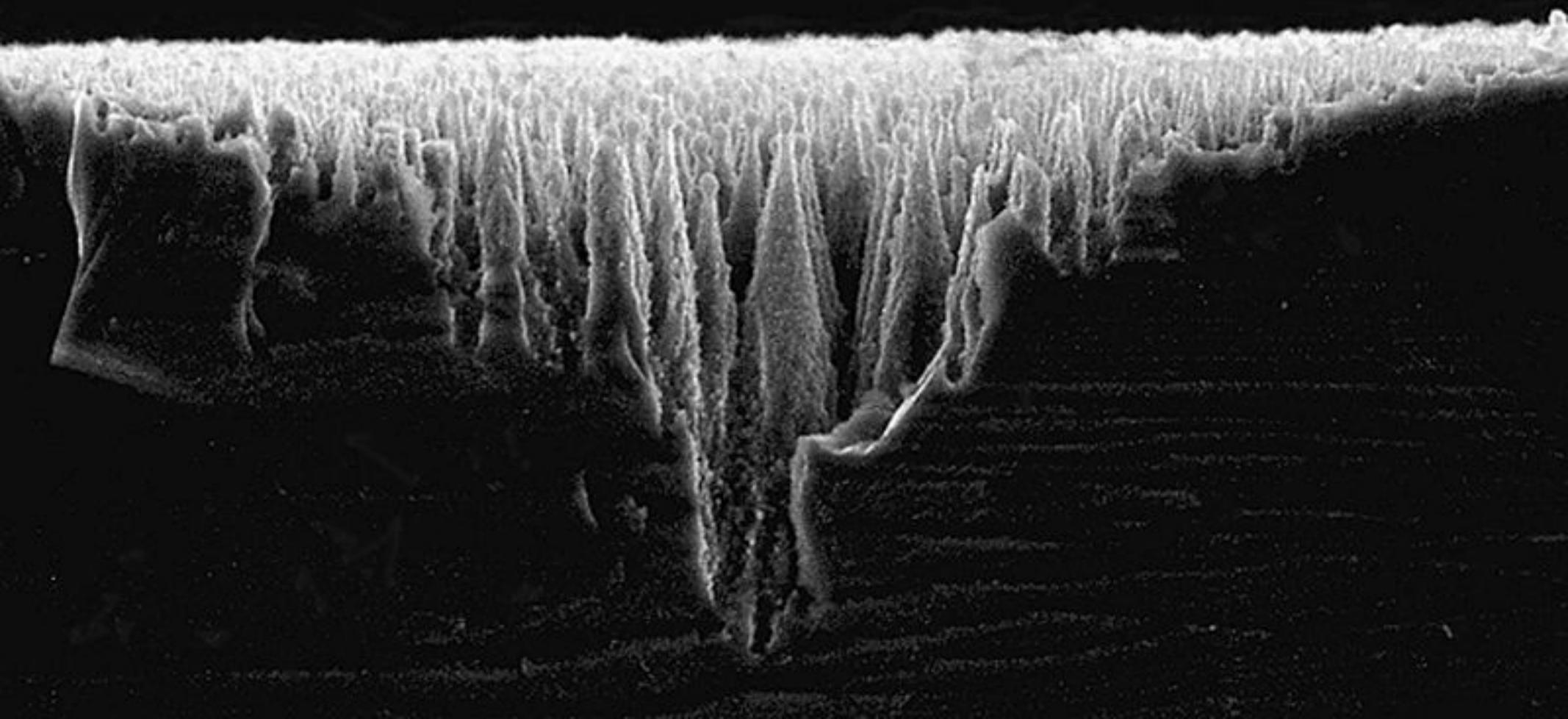


10 μm

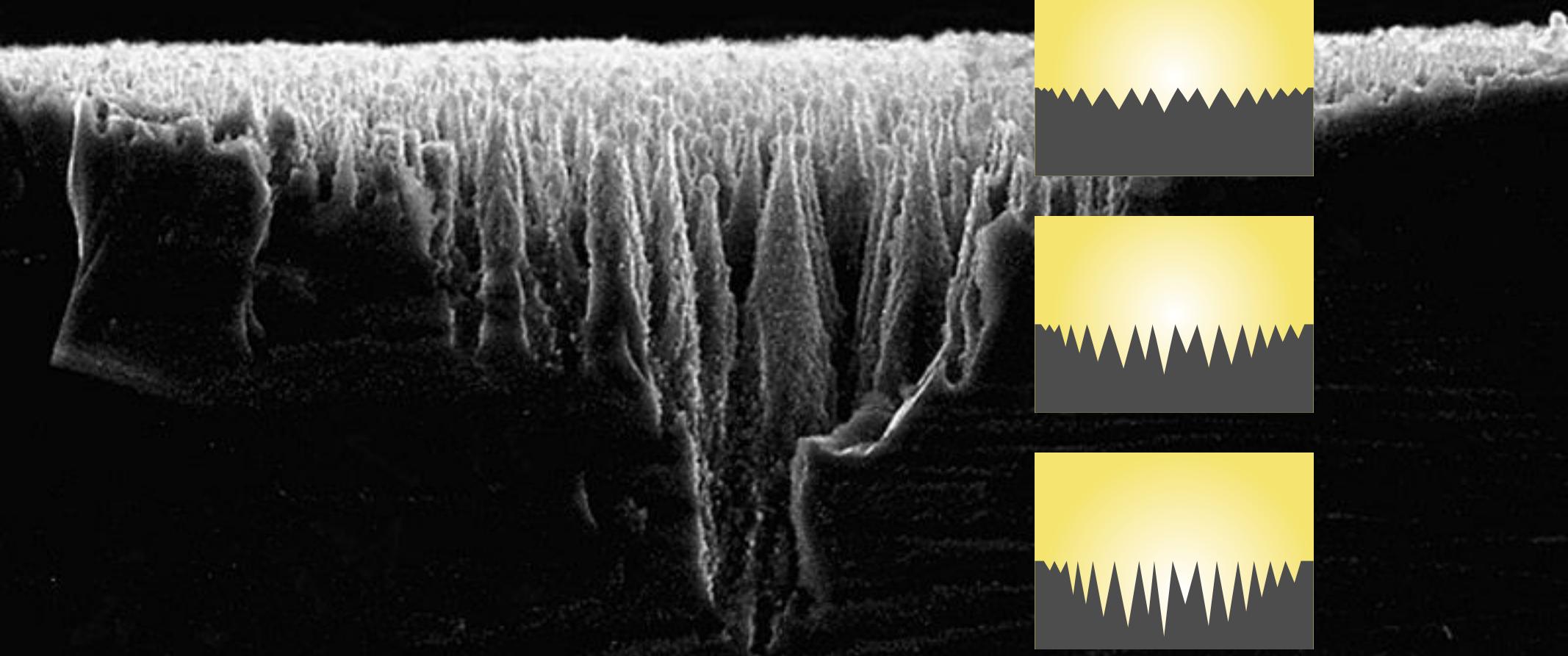
Introduction



Introduction



Introduction



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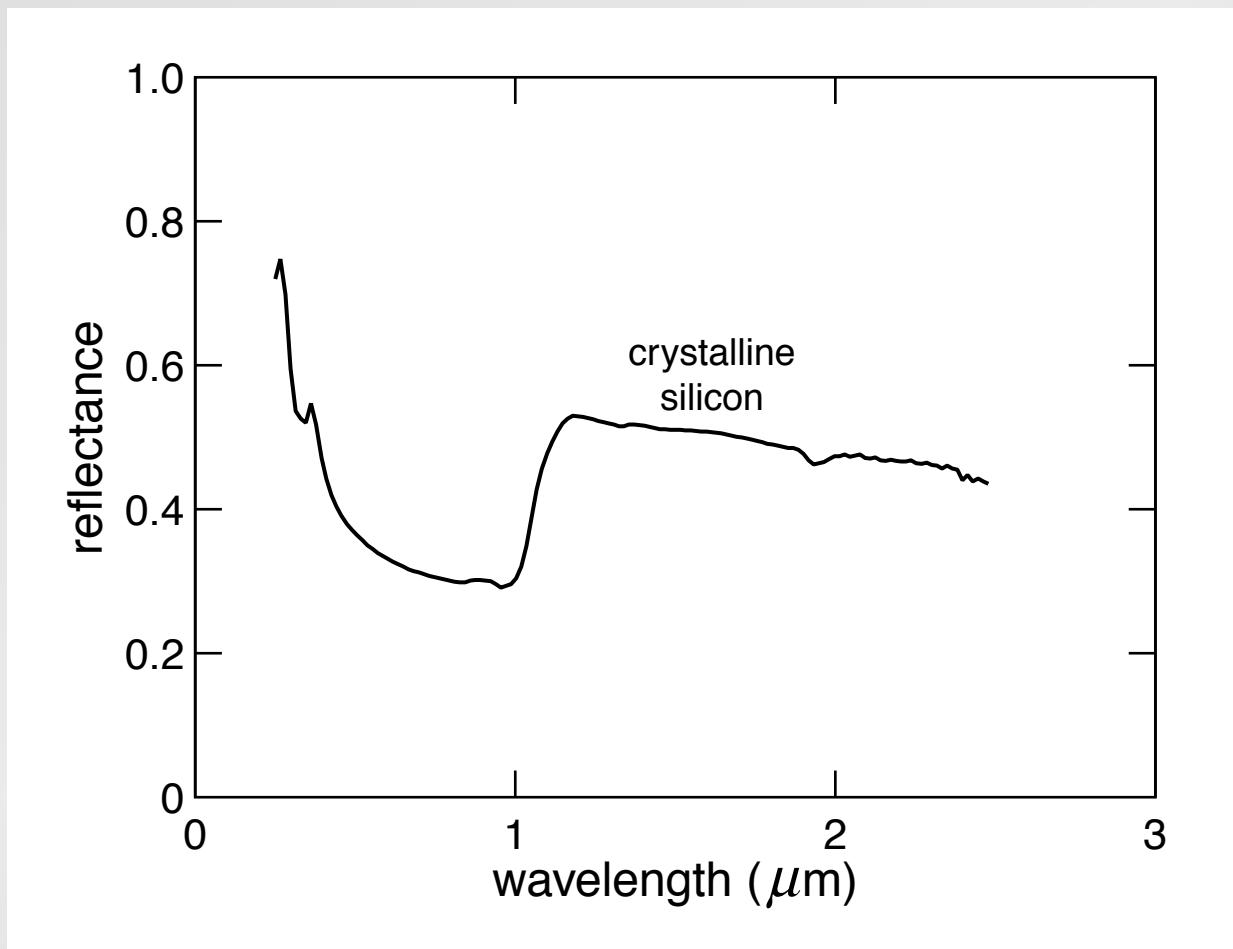
- maskless etching process
- self-organized, tall microstructures
- highly light absorbing

Outline

- properties
- structural and chemical analysis
- detectors
- outlook

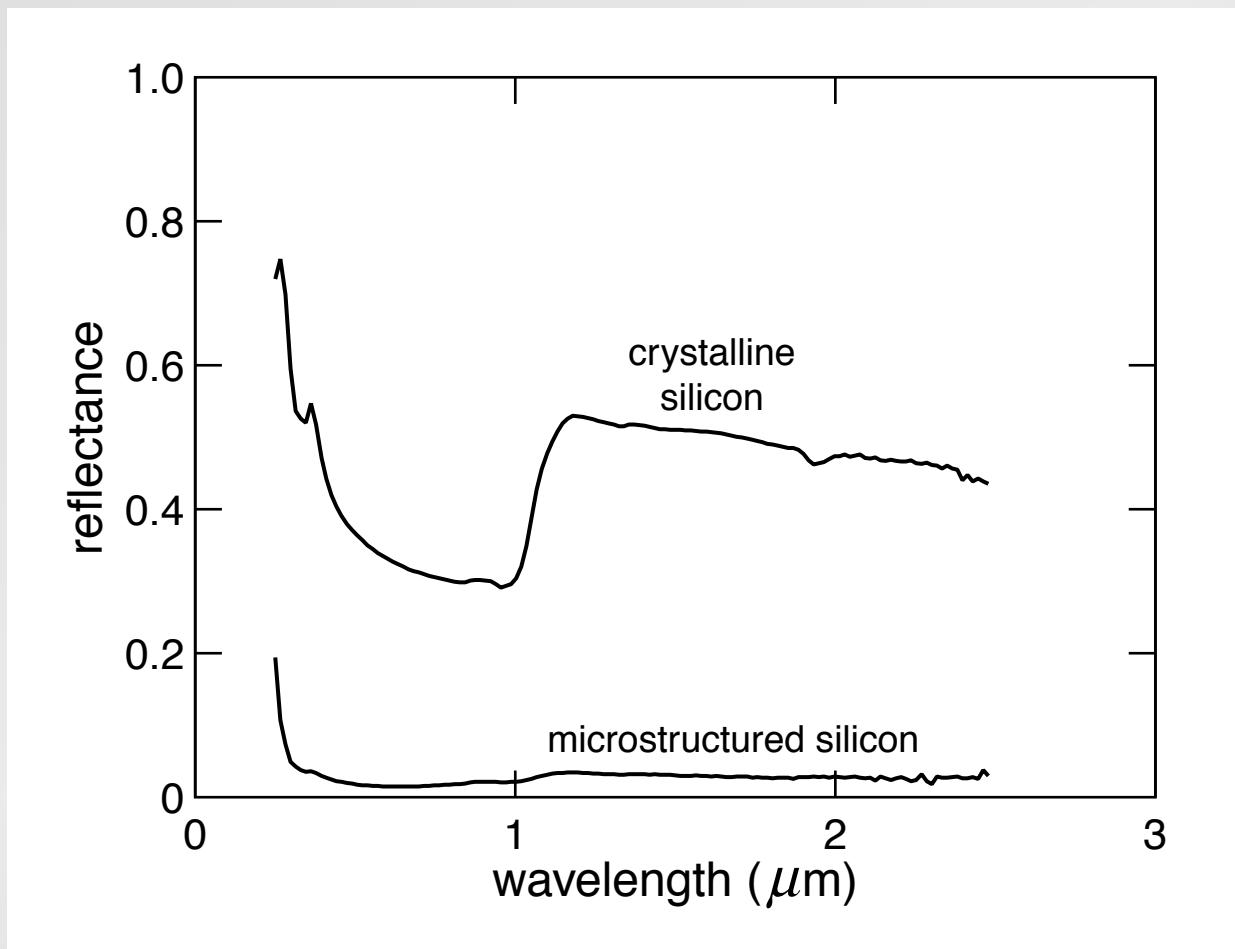
Properties

reflectance (integrating sphere)



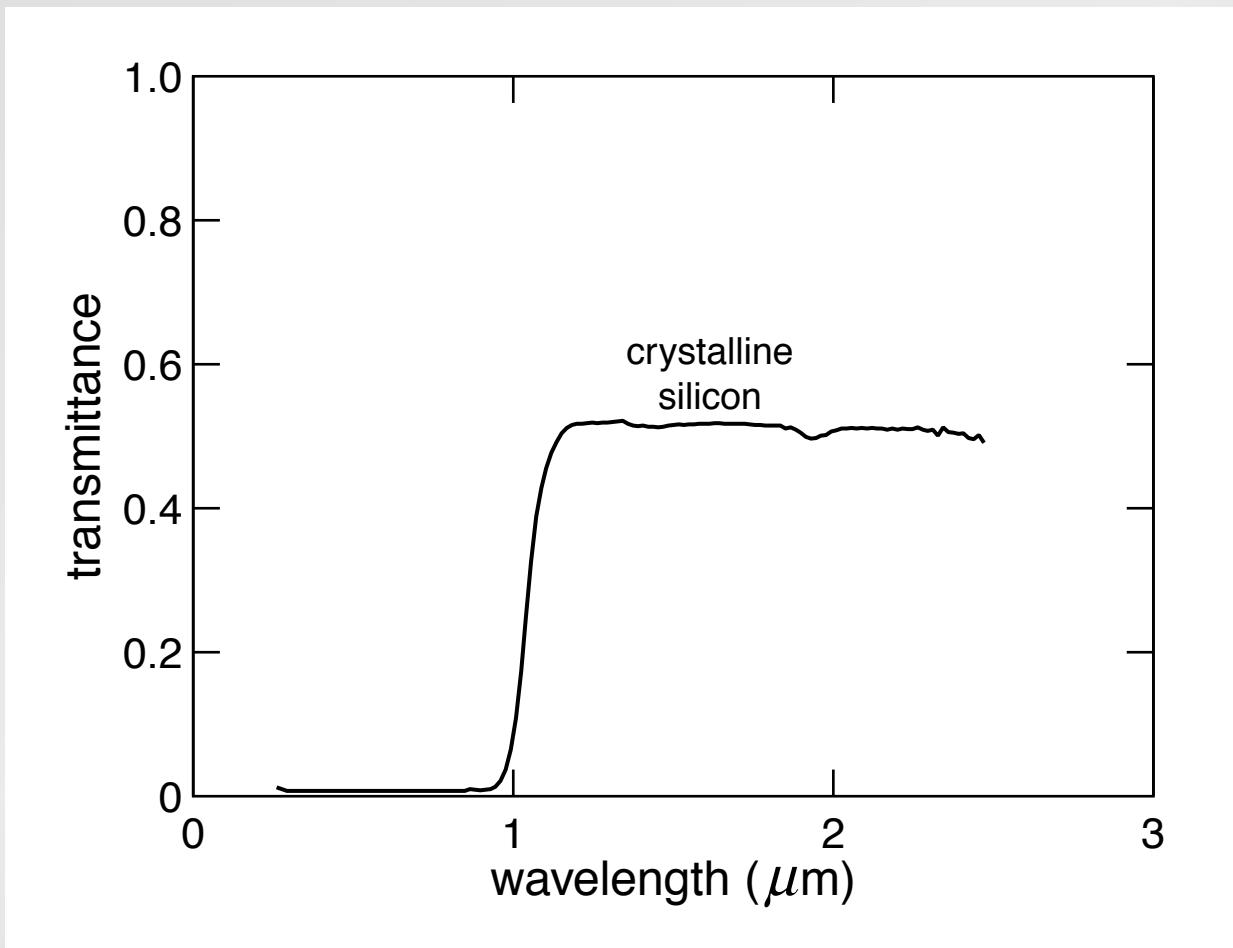
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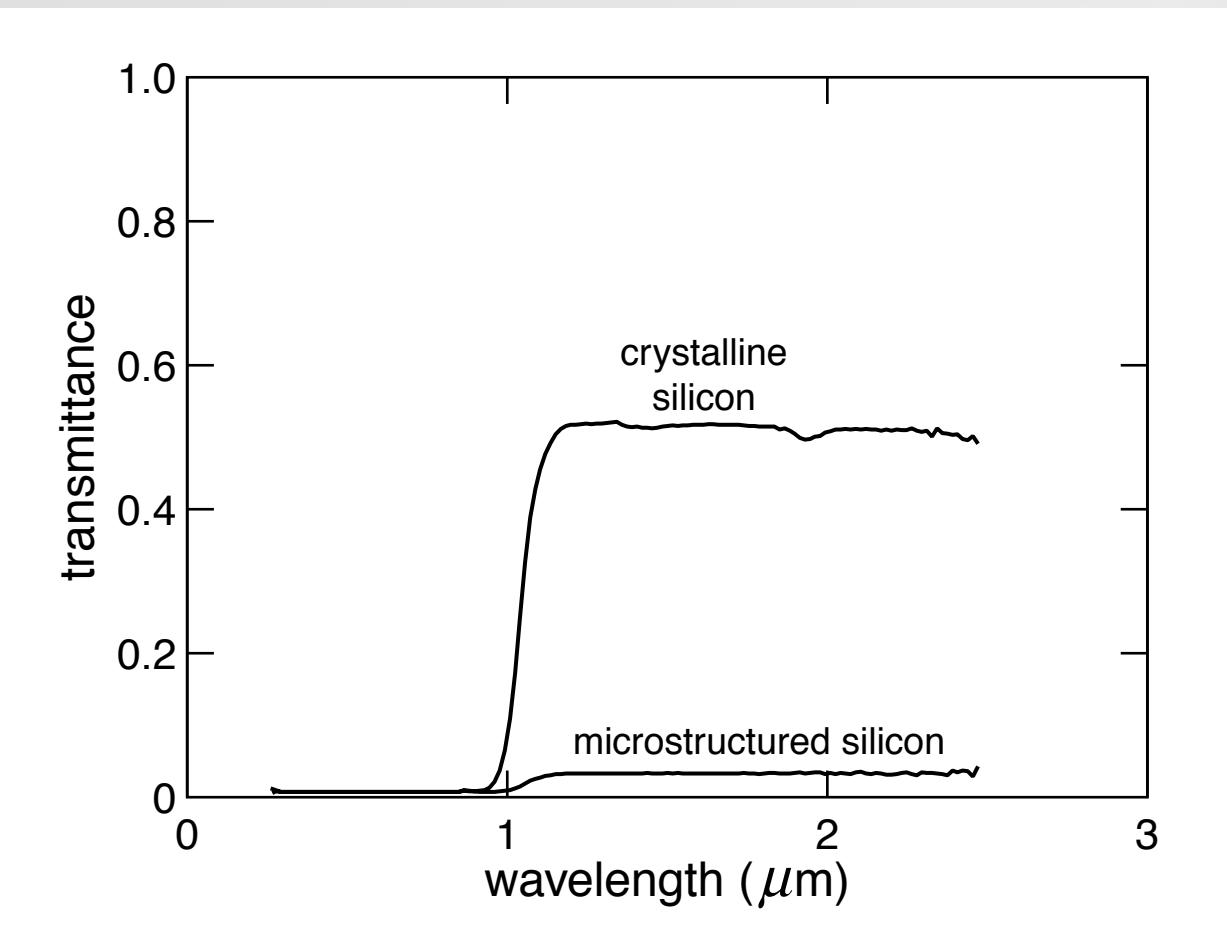
Properties

transmittance (integrating sphere)



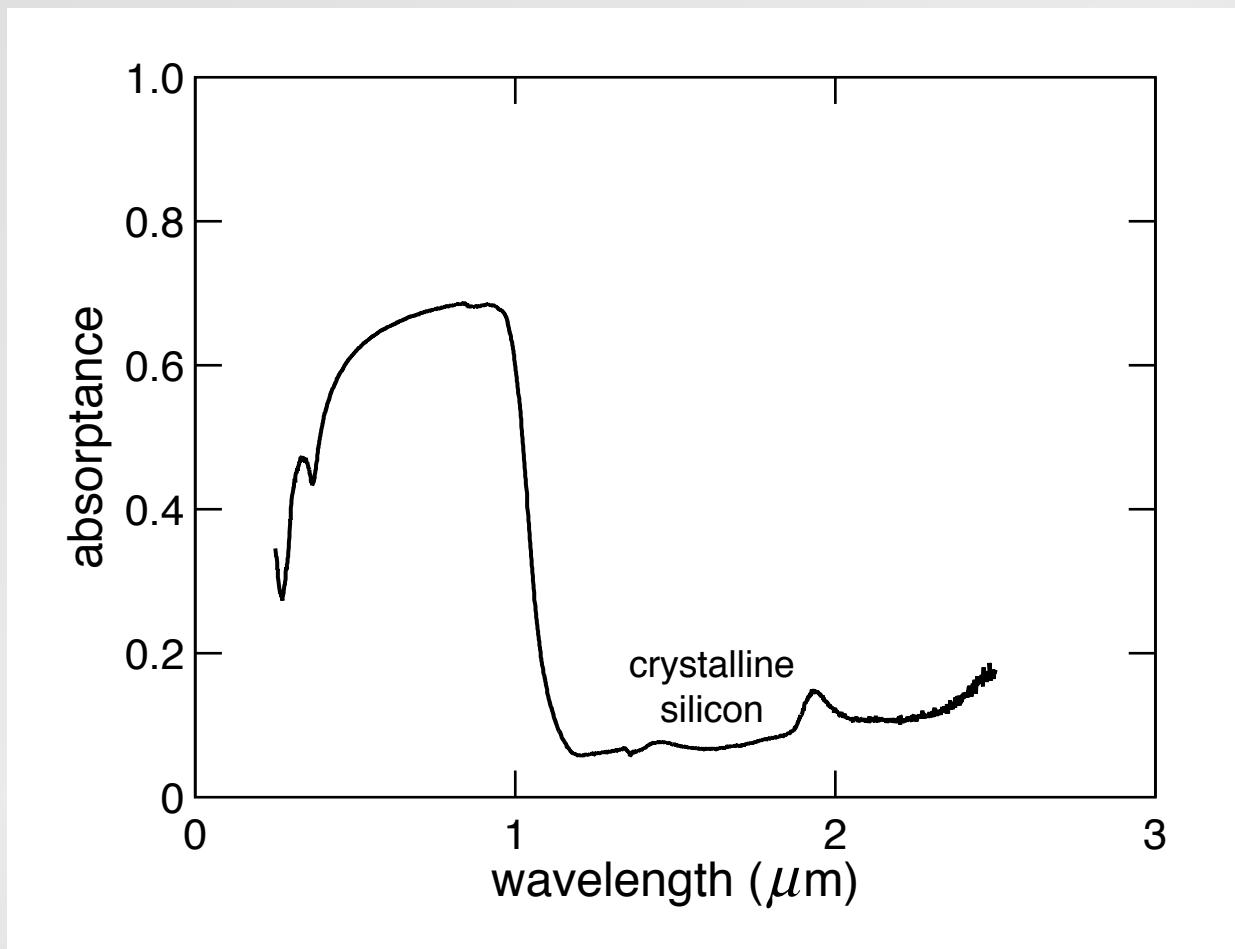
Properties

transmittance (integrating sphere)



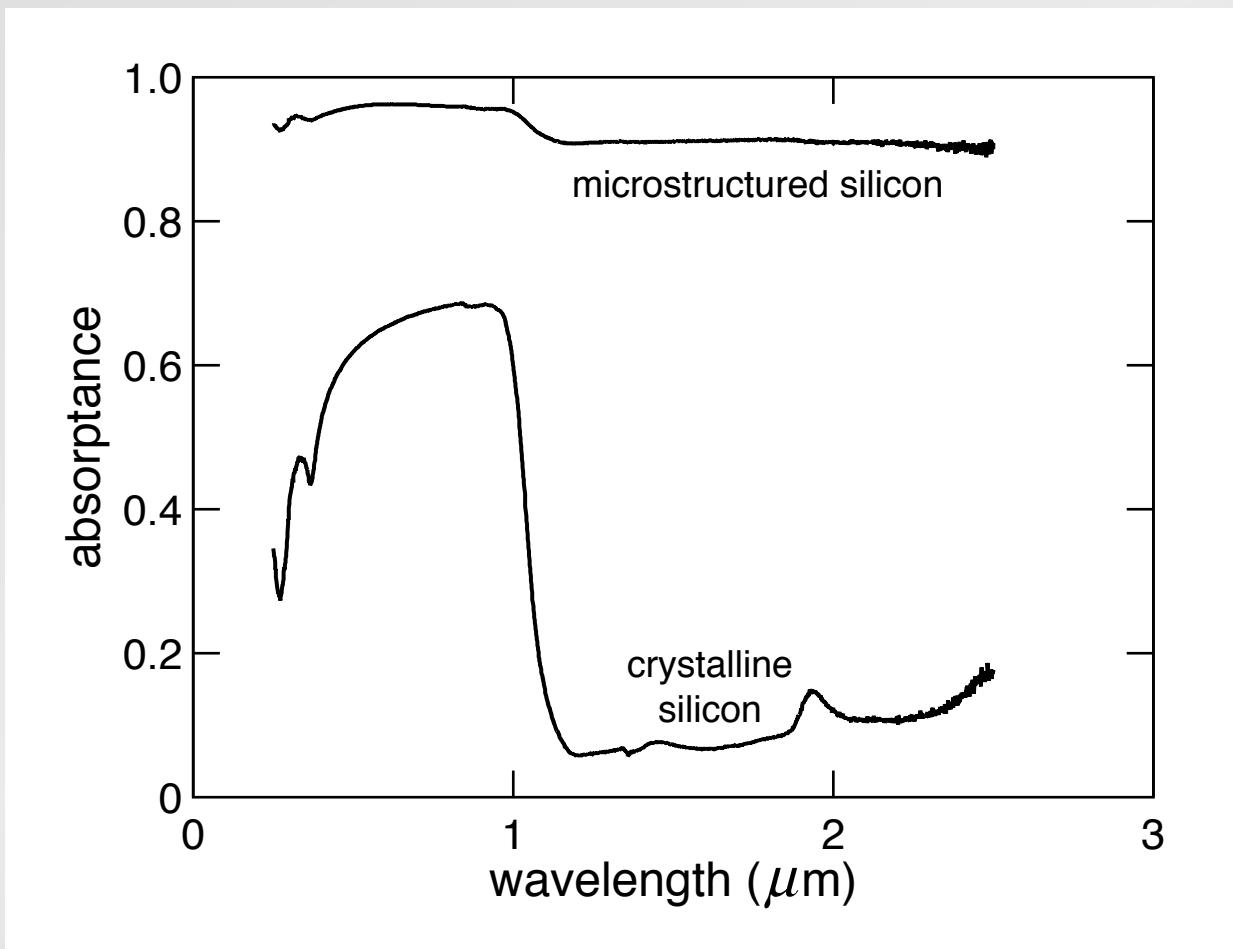
Properties

absorptance ($1 - R - T$)



Properties

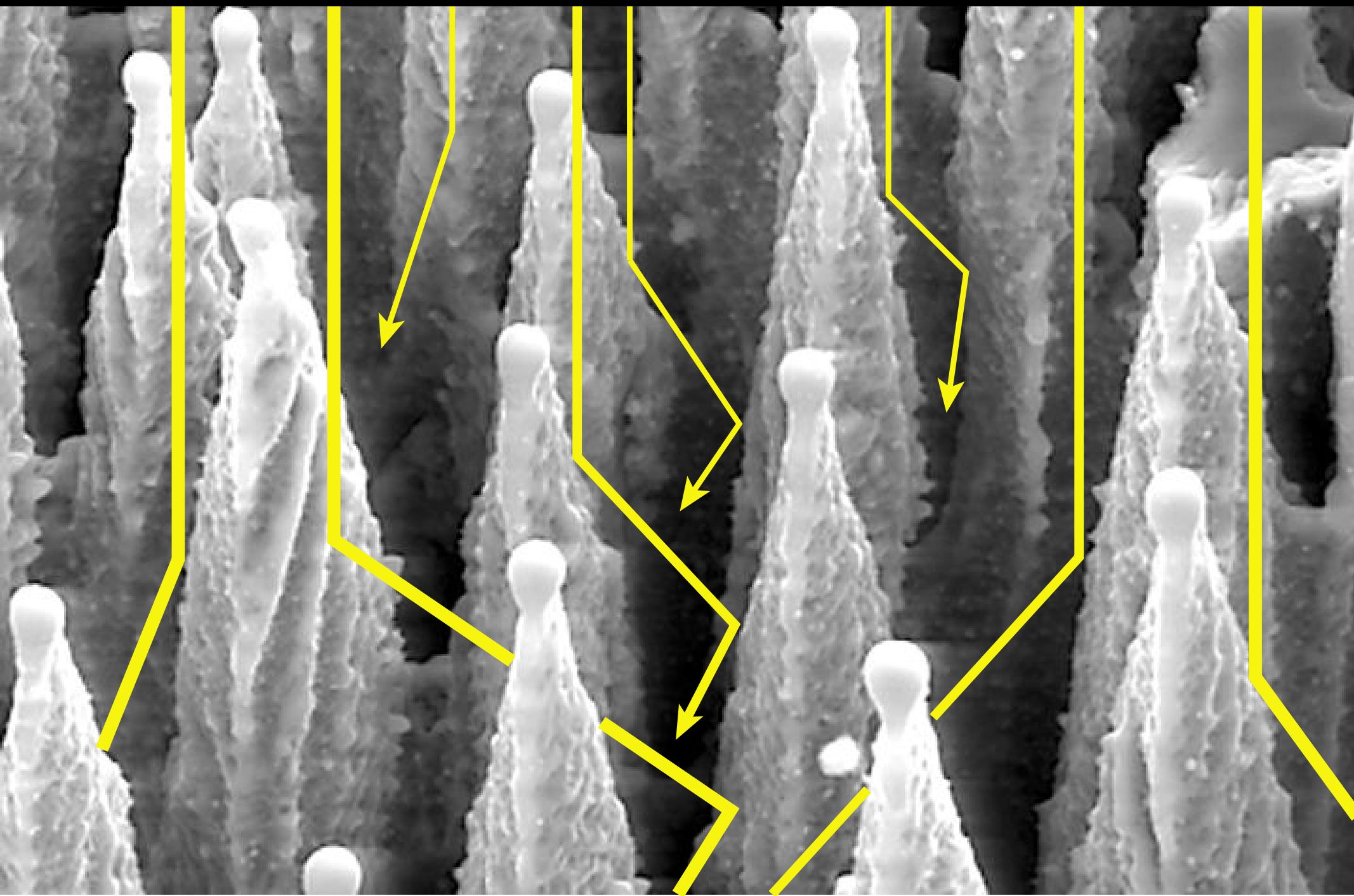
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Properties

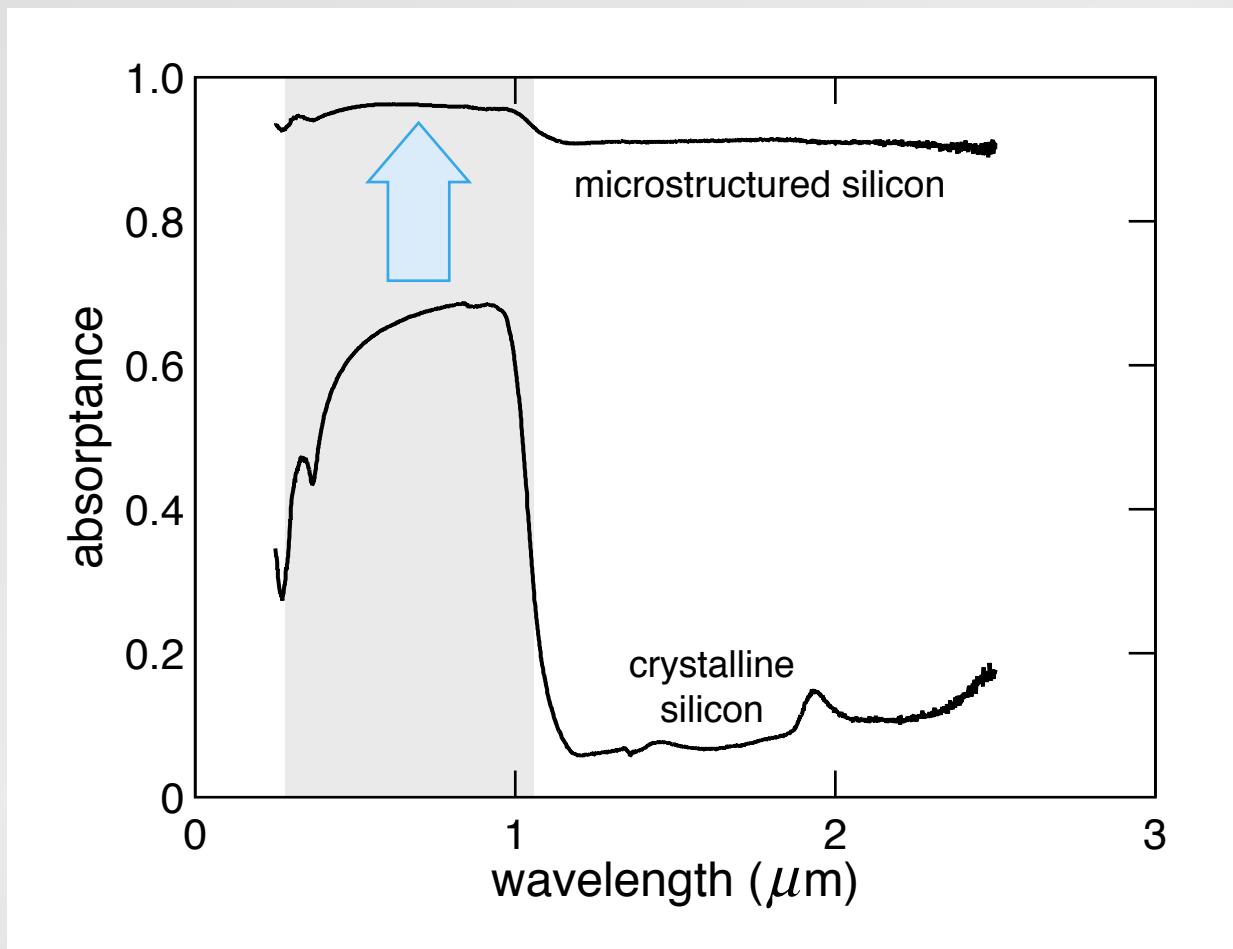
What causes the near-unity absorptance?

Properties



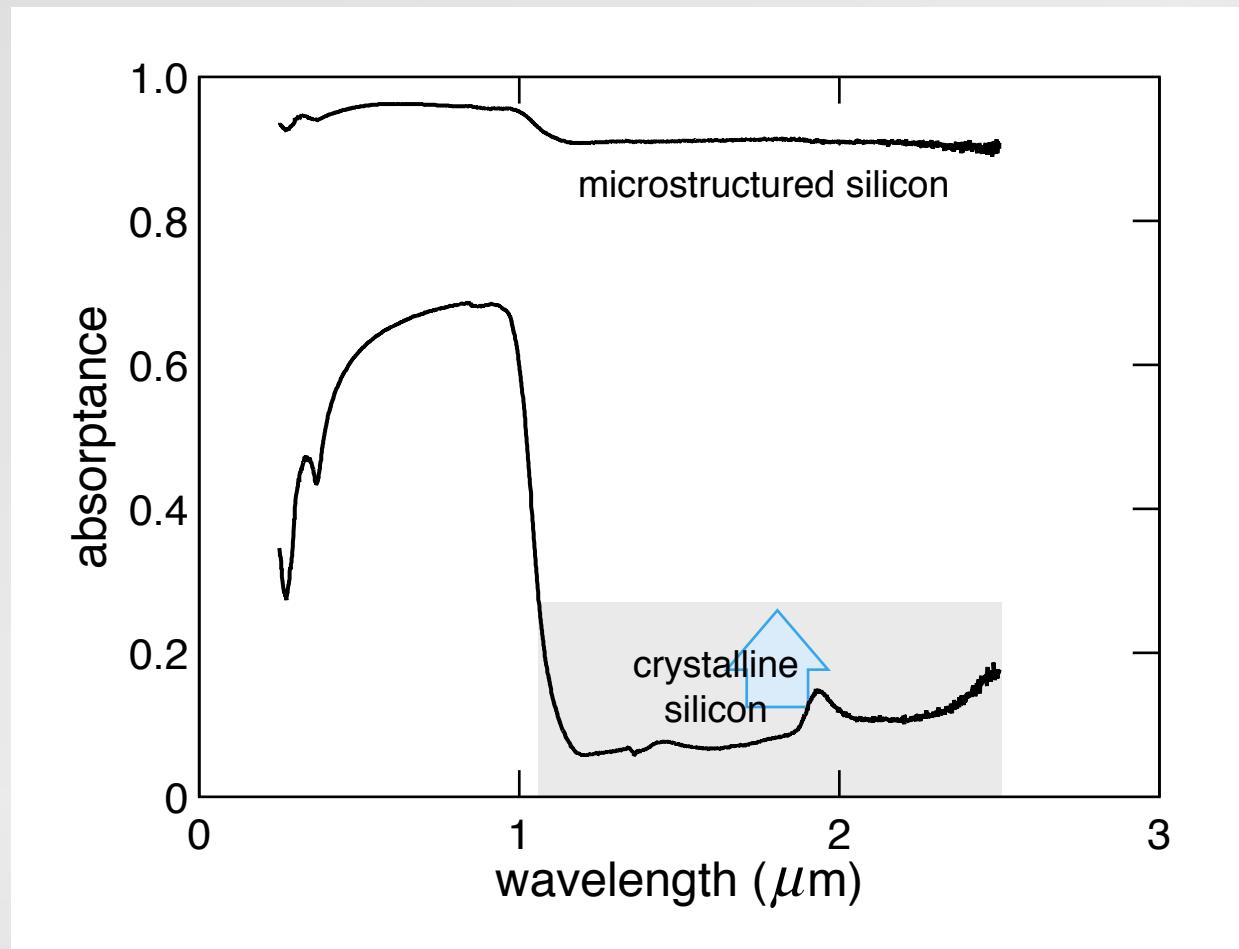
Properties

multiple reflections enhance absorption



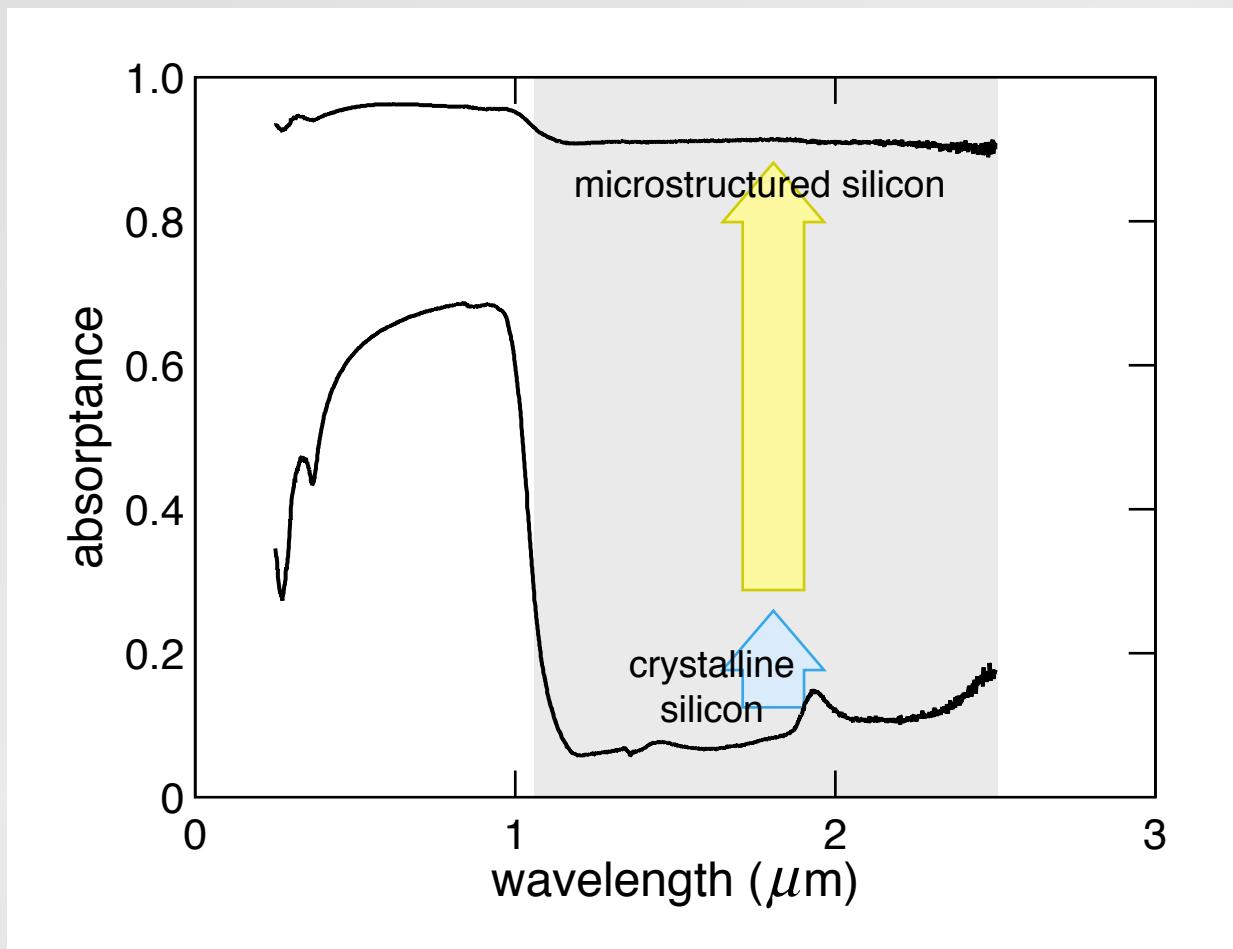
Properties

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

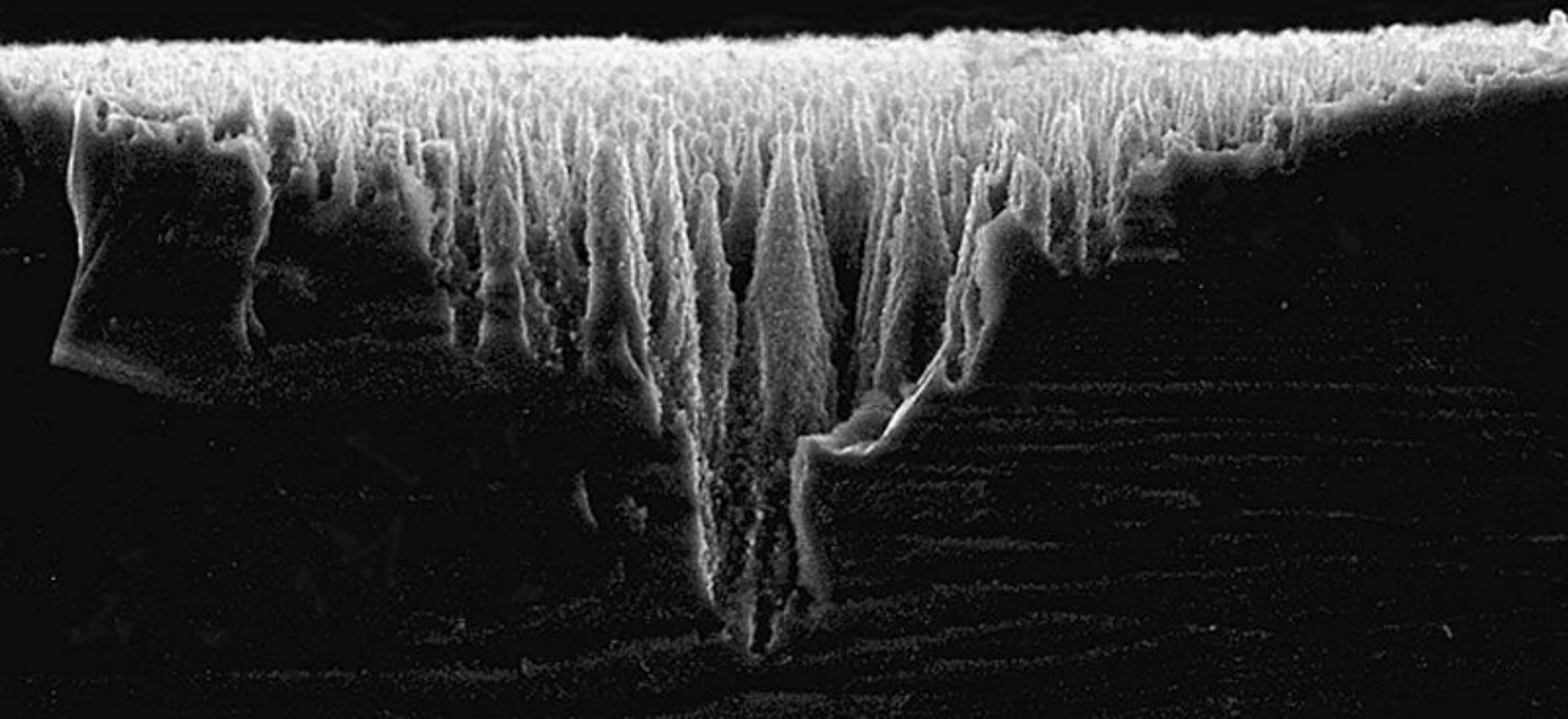
Outline

- properties
- structural and chemical analysis
- detectors
- outlook

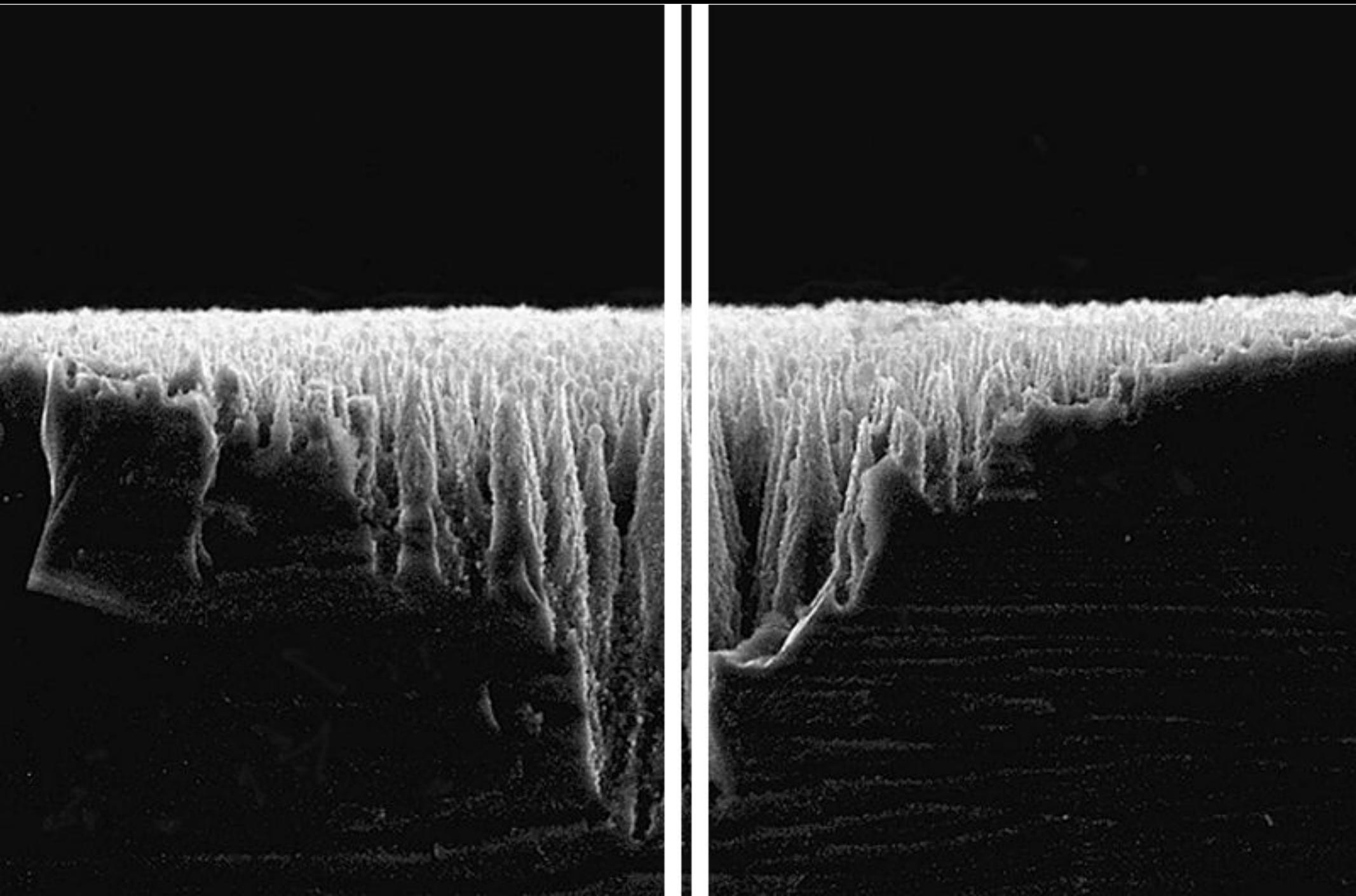
Structural and chemical analysis

Band structure changes: defects and/or impurities

Structural and chemical analysis



Structural and chemical analysis



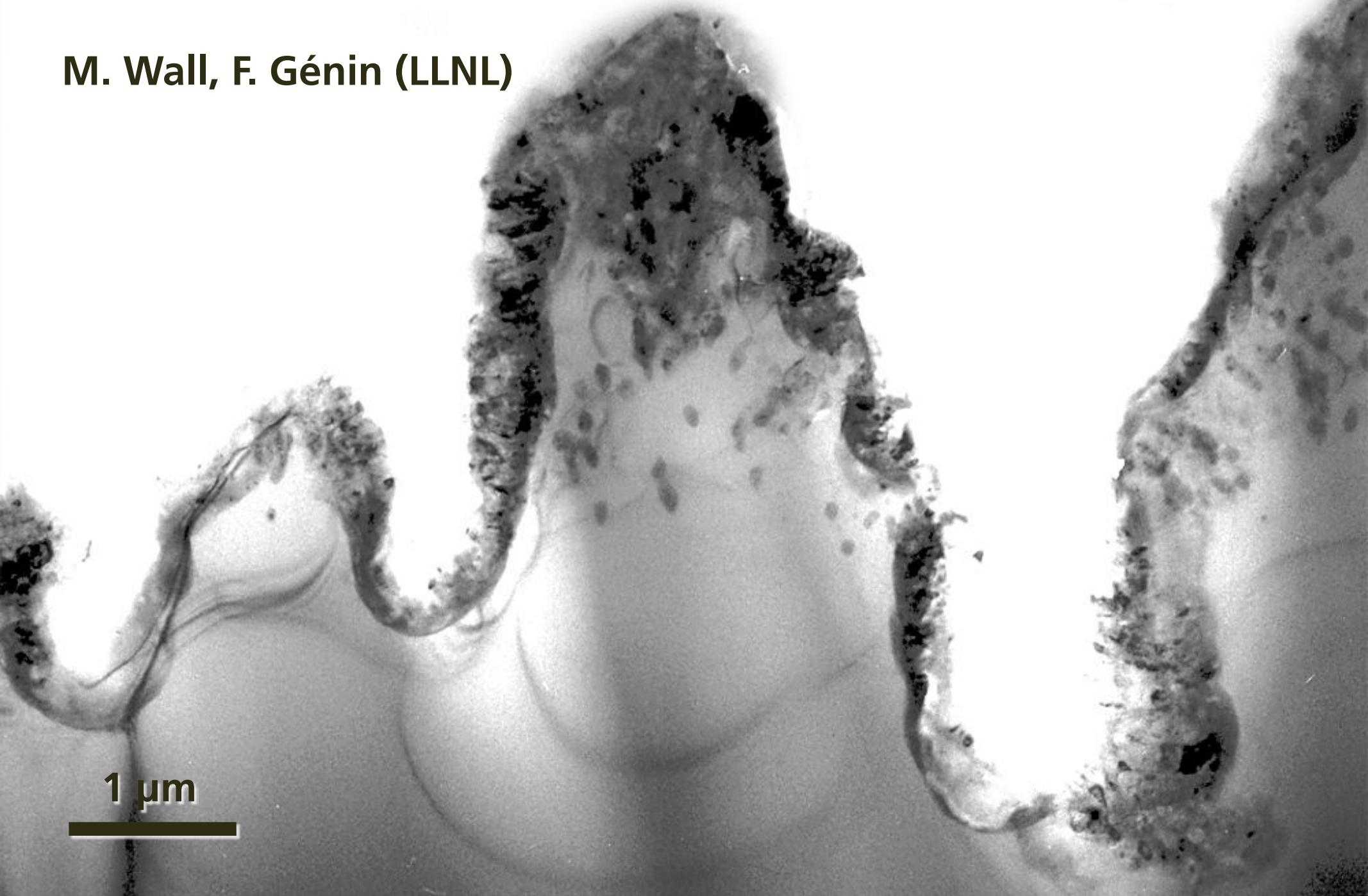
Structural and chemical analysis

**cross-sectional
Transmission Electron
Microscopy**



Structural and chemical analysis

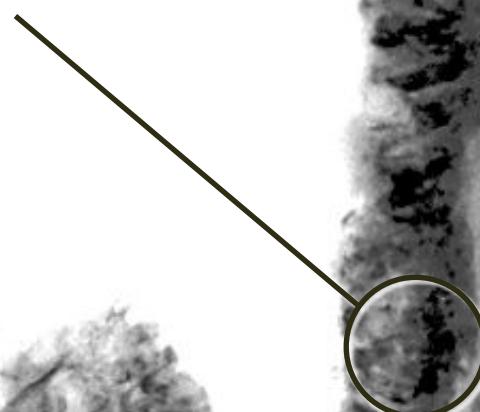
M. Wall, F. Génin (LLNL)



1 μm

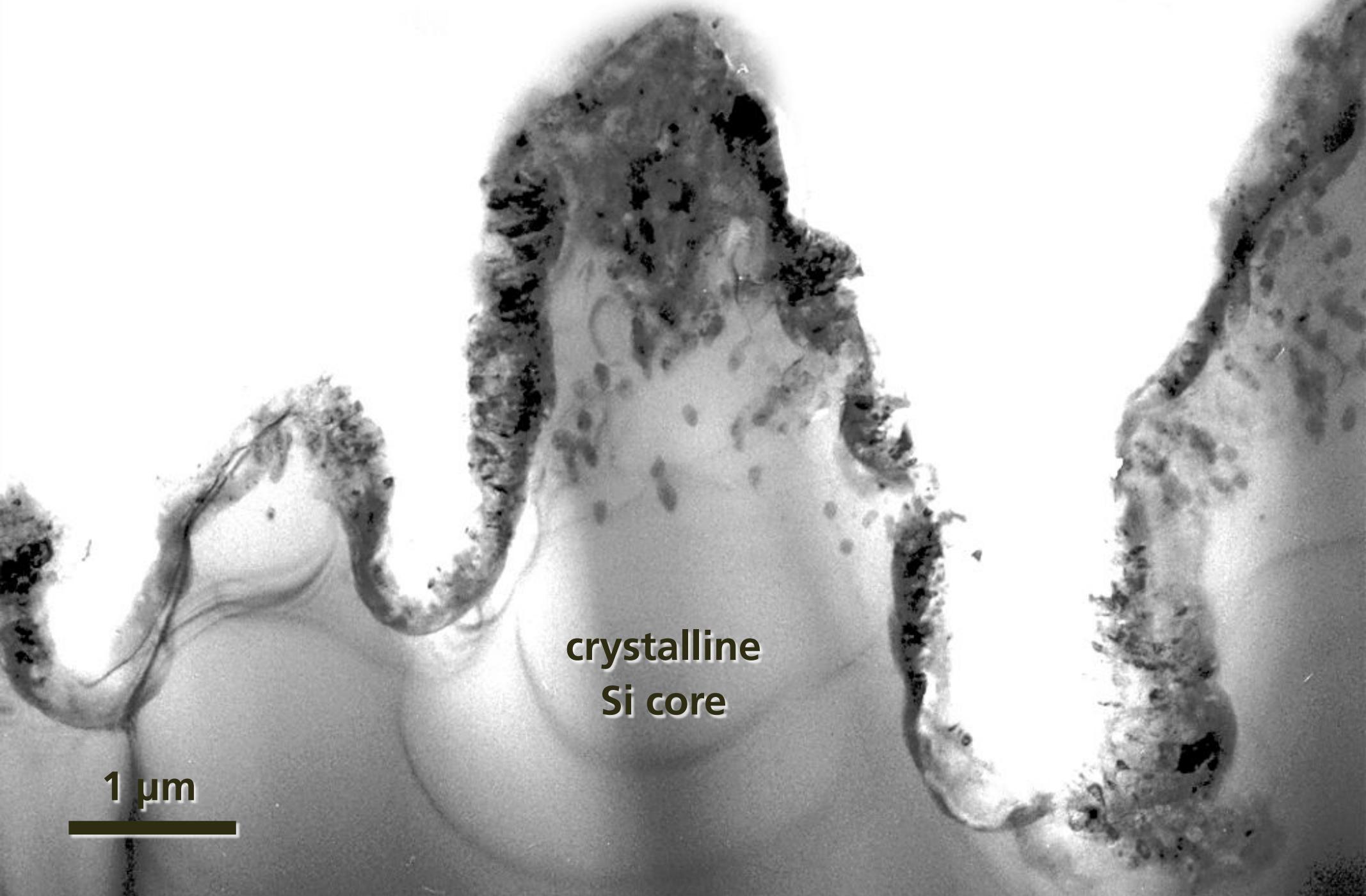
Structural and chemical analysis

disordered
surface layer



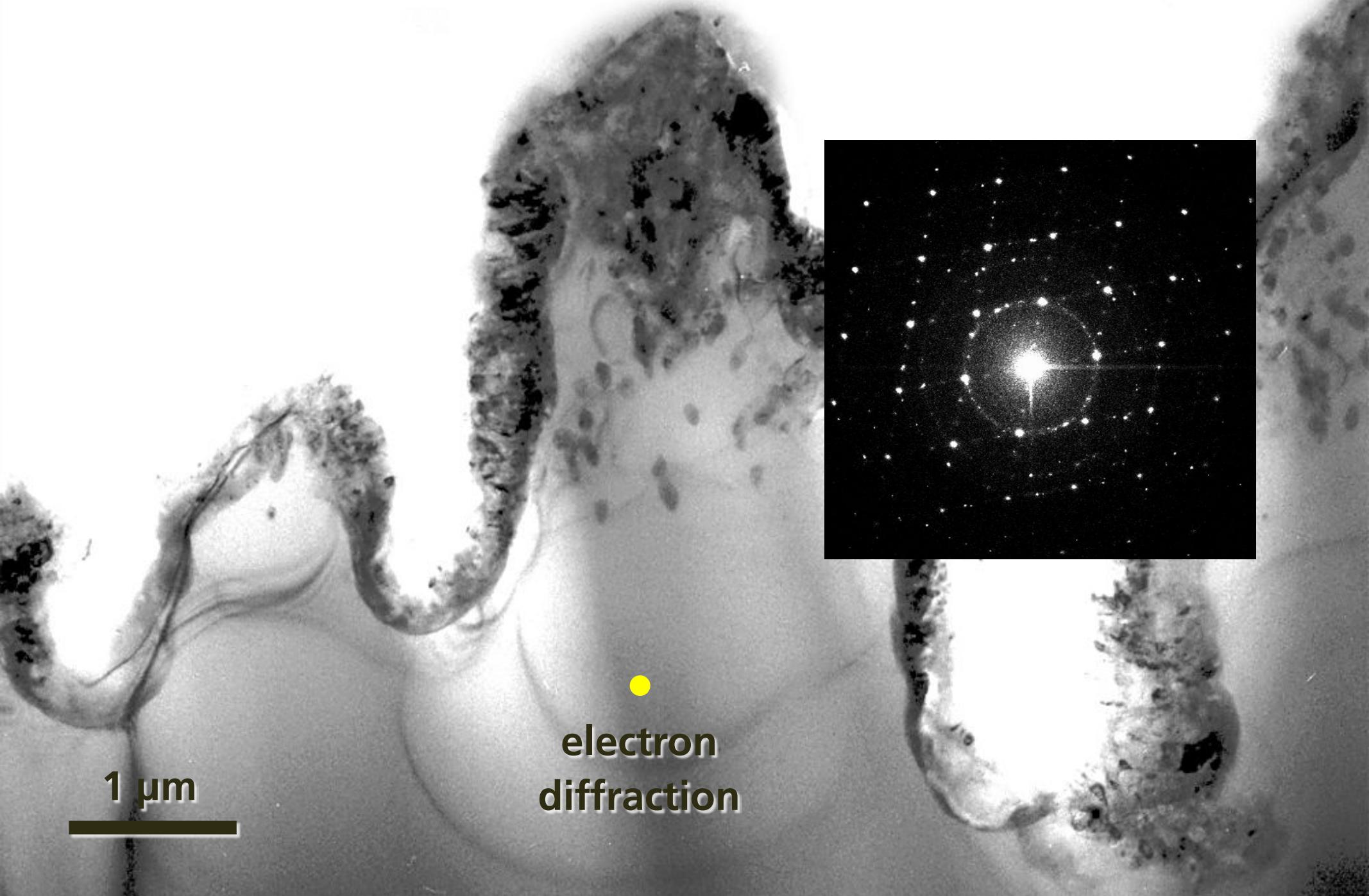
1 μm

Structural and chemical analysis



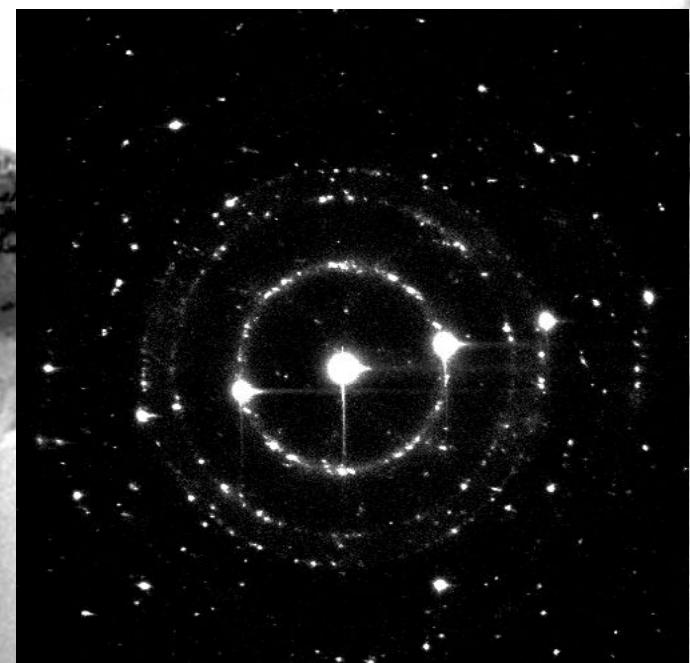
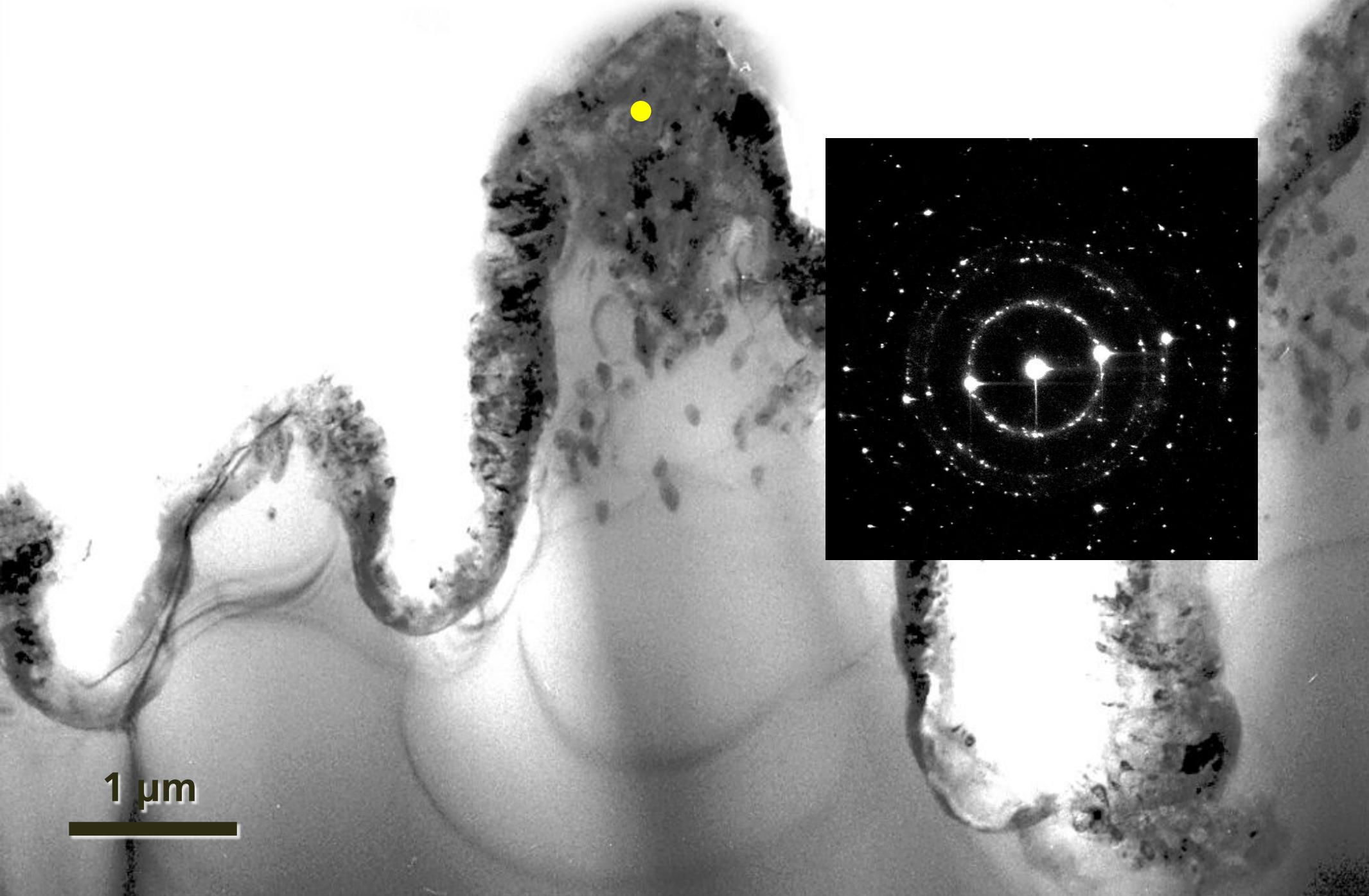
1 μm

Structural and chemical analysis



electron
diffraction

Structural and chemical analysis



Structural and chemical analysis

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

1 μm

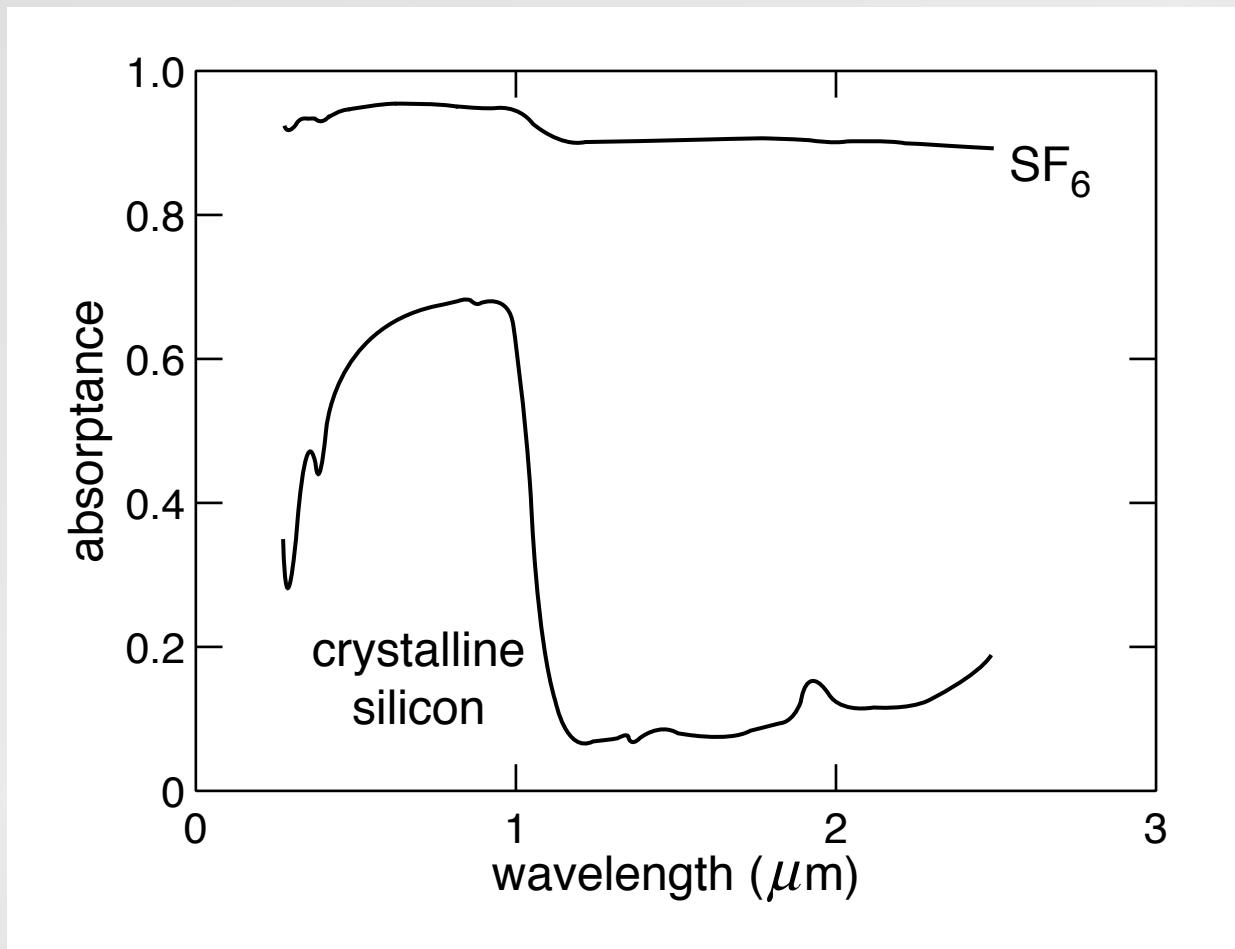
Structural and chemical analysis

Microstructure with different gases:

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

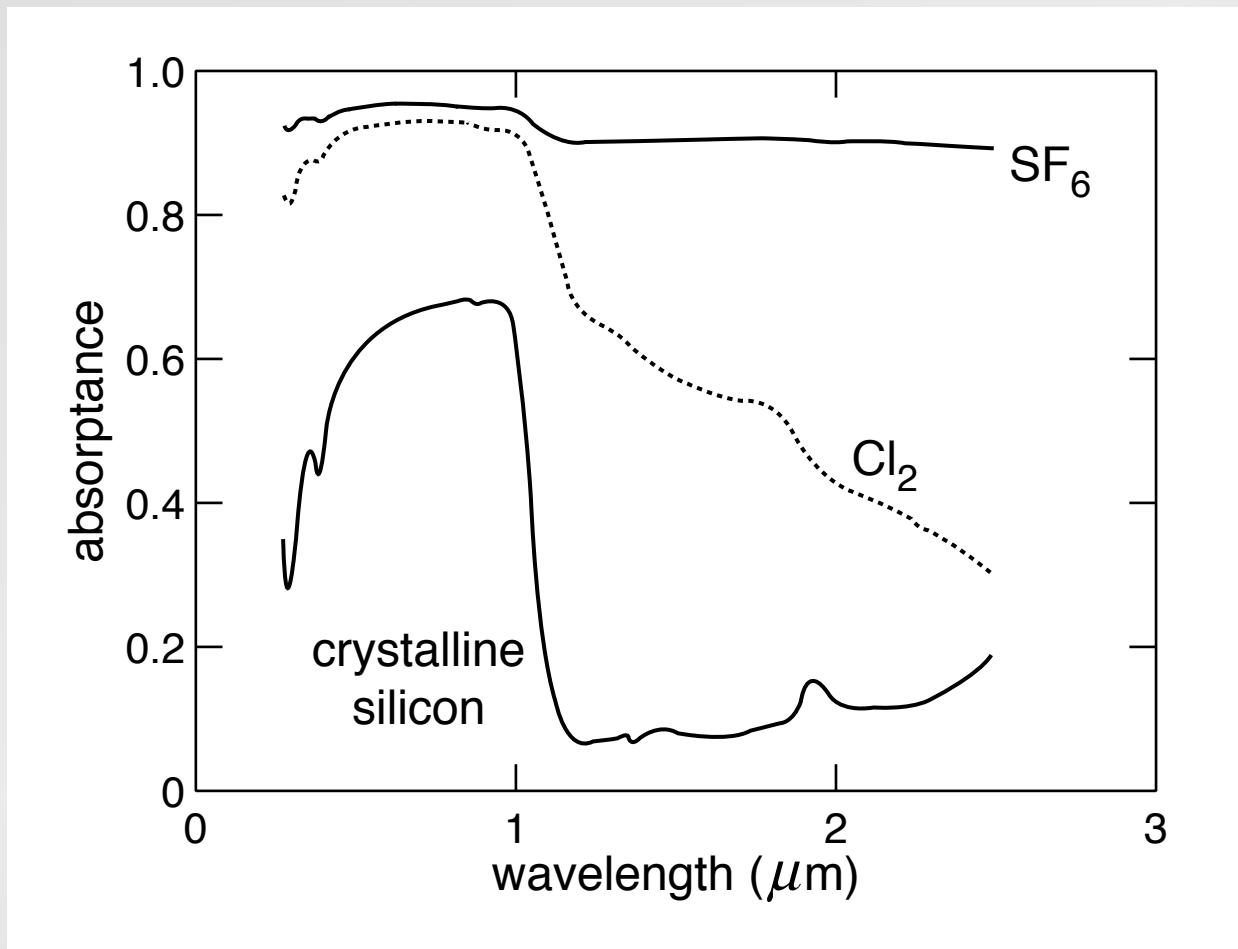
Structural and chemical analysis

microstructure with different gases



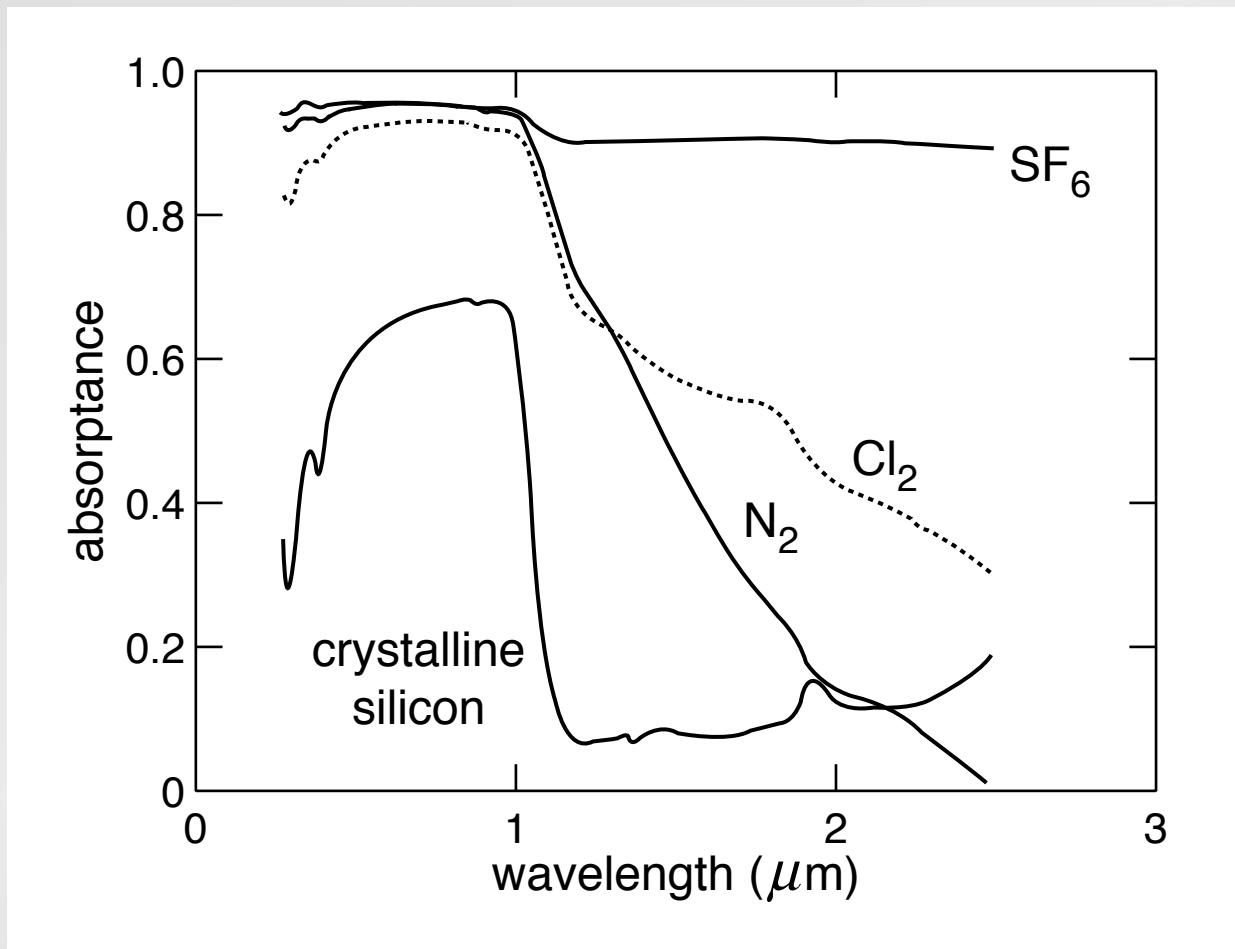
Structural and chemical analysis

microstructure with different gases



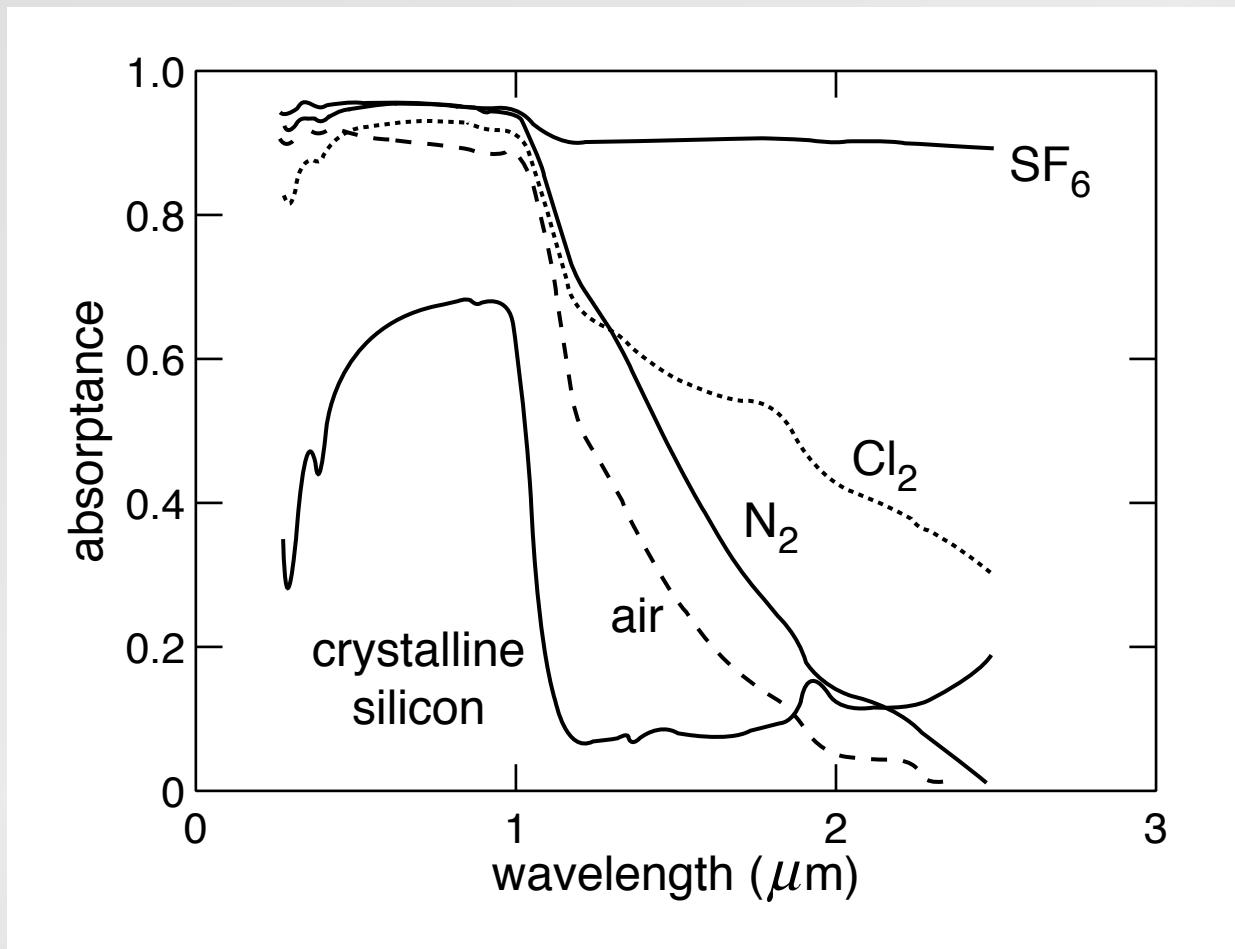
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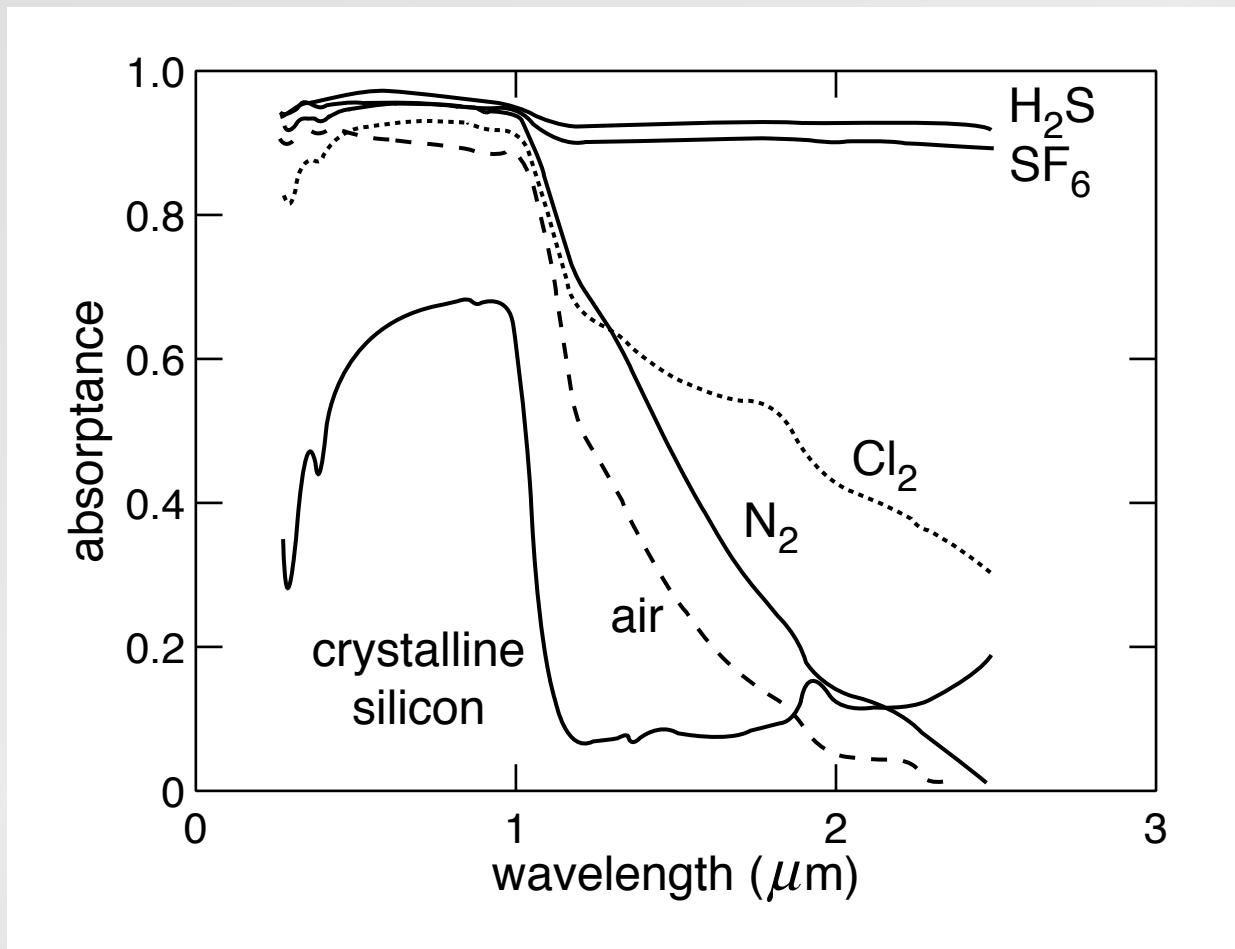
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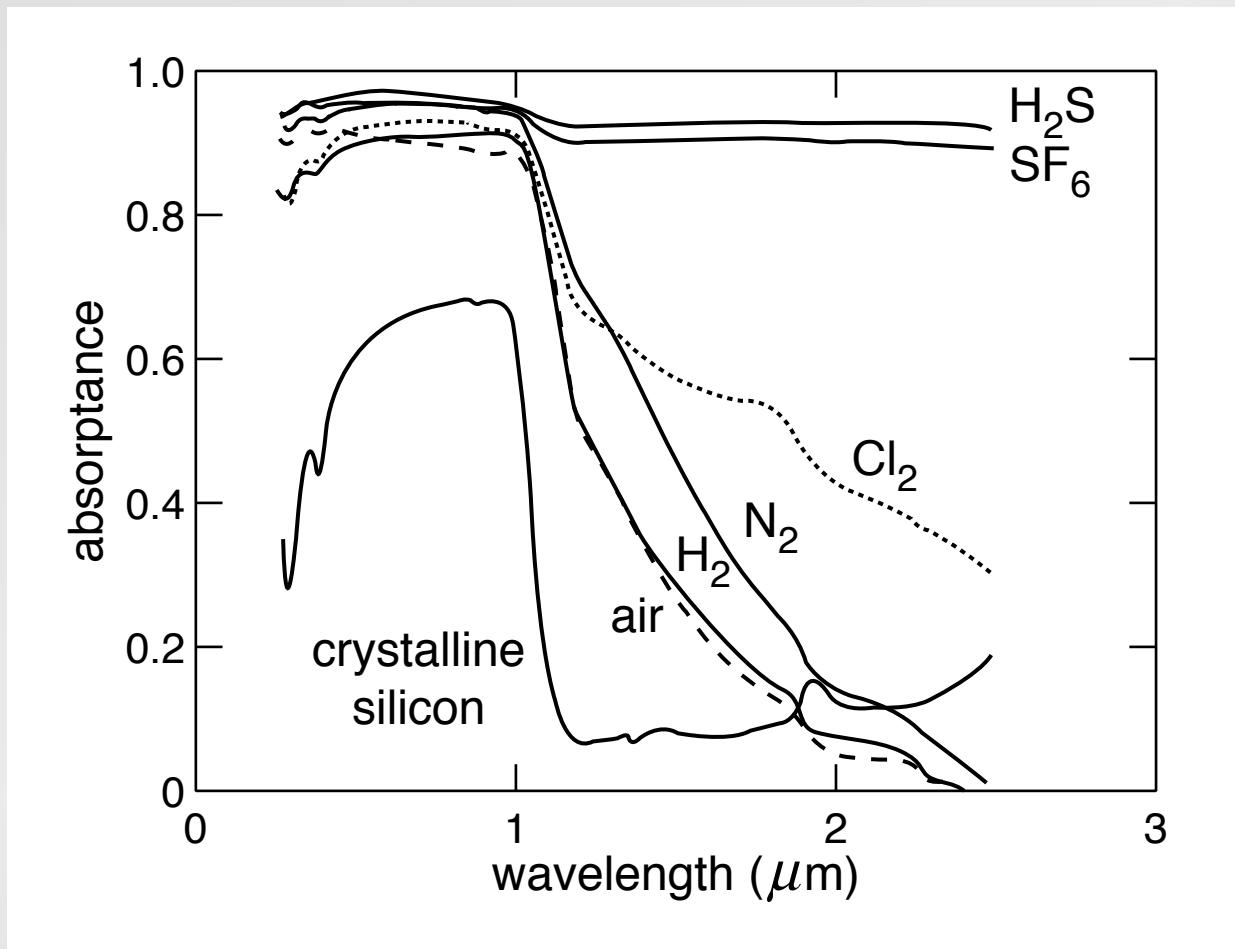
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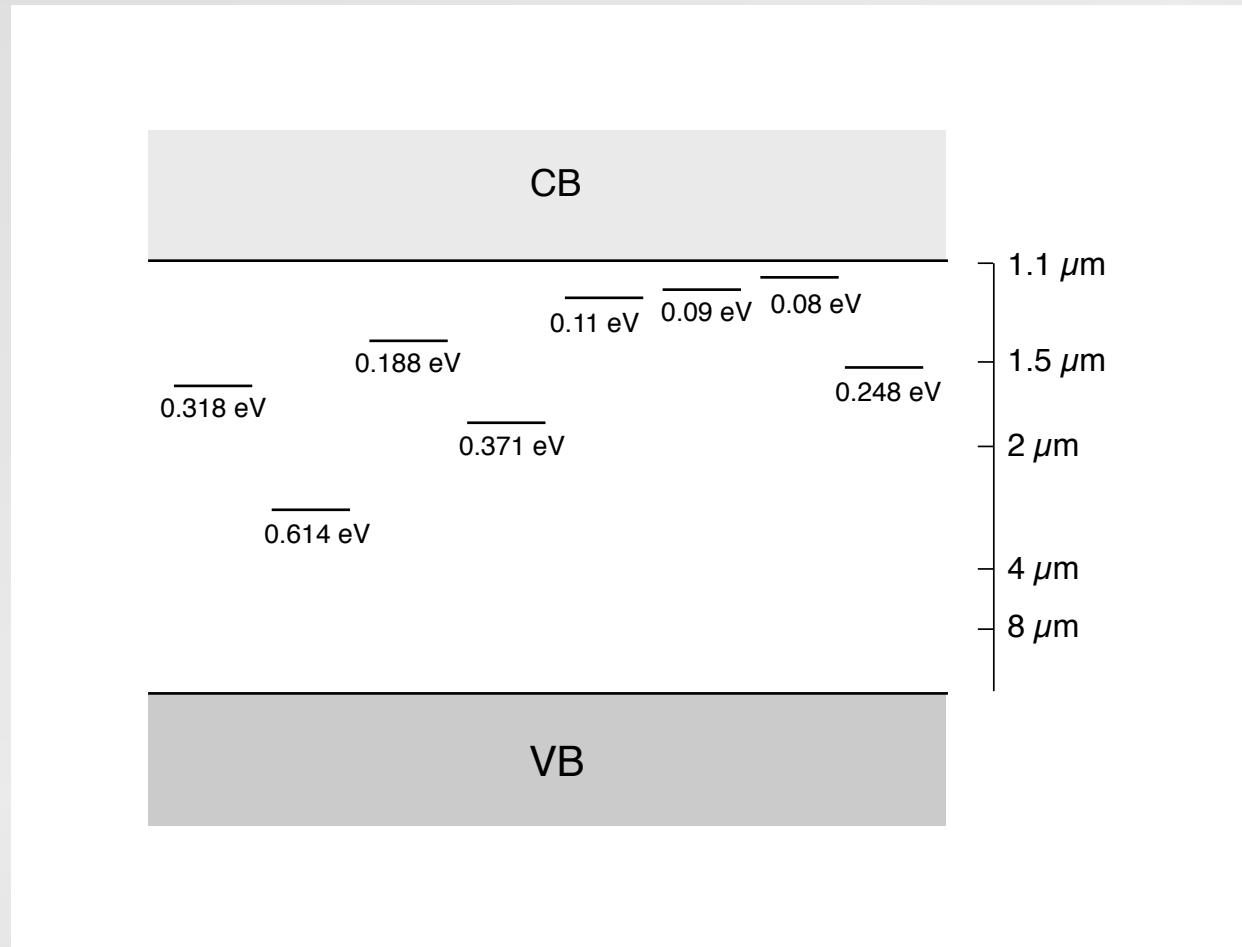
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microstructure with different gases



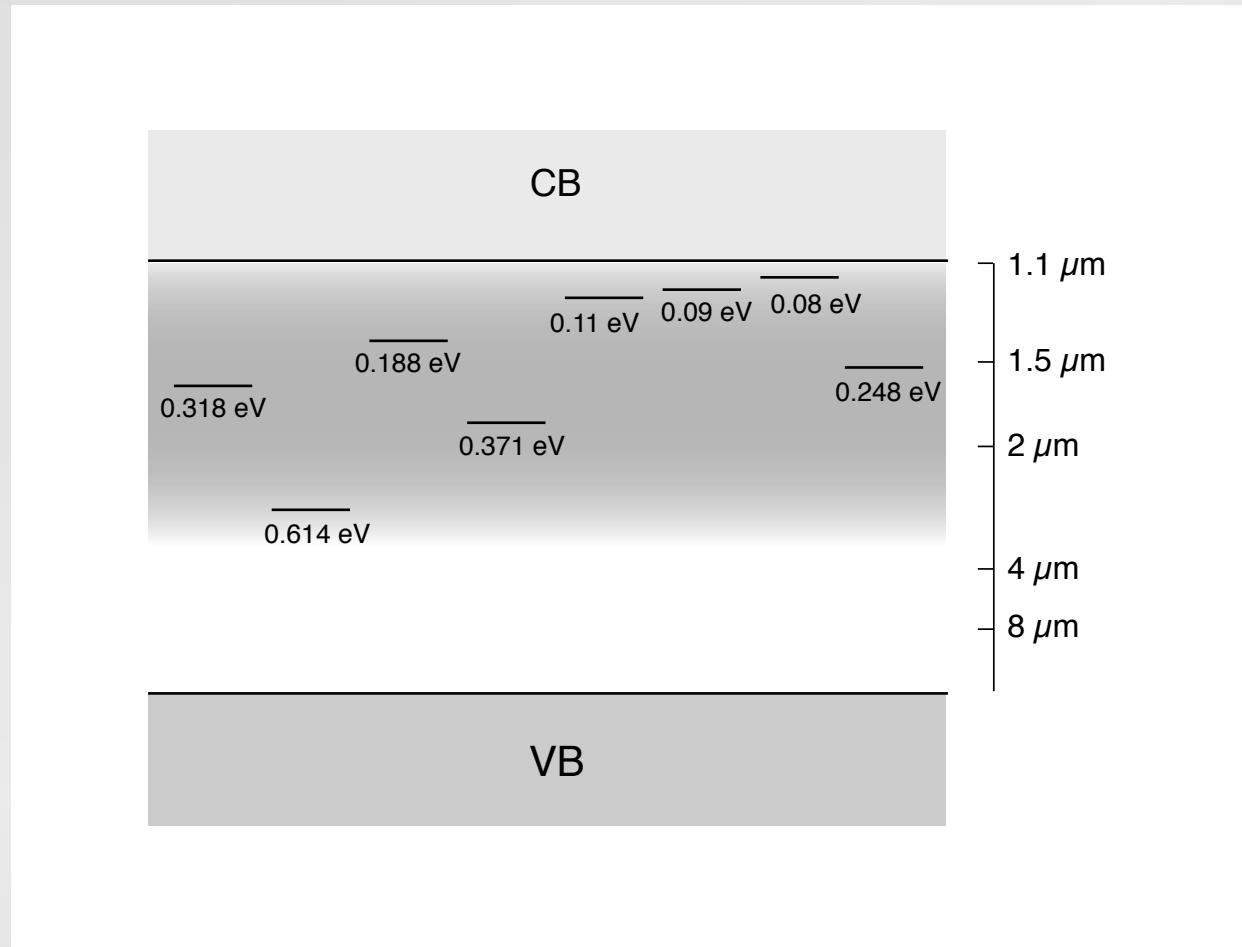
Structural and chemical analysis

1 part in 10^6 sulfur introduces states in gap



Structural and chemical analysis

at high concentration states broaden into band

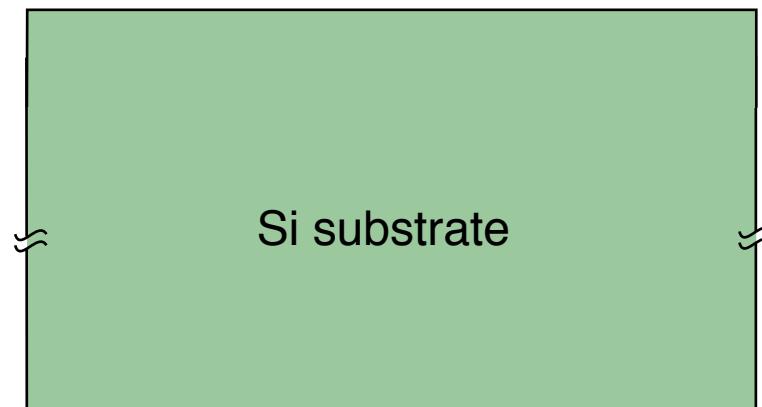


Outline

- properties
- structural and chemical analysis
- detectors
- outlook

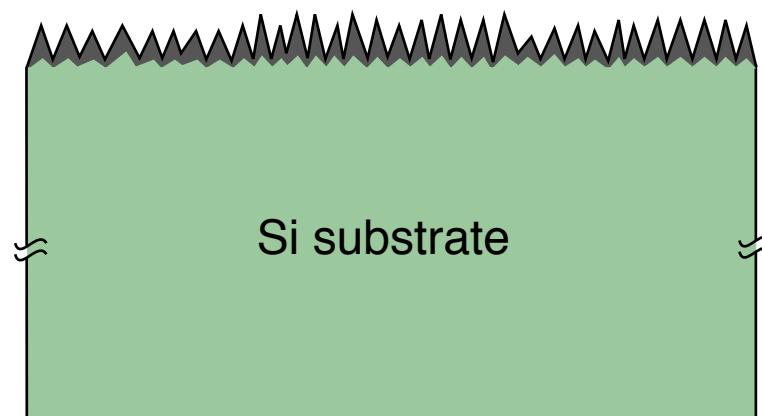
Detectors

black silicon/silicon junction



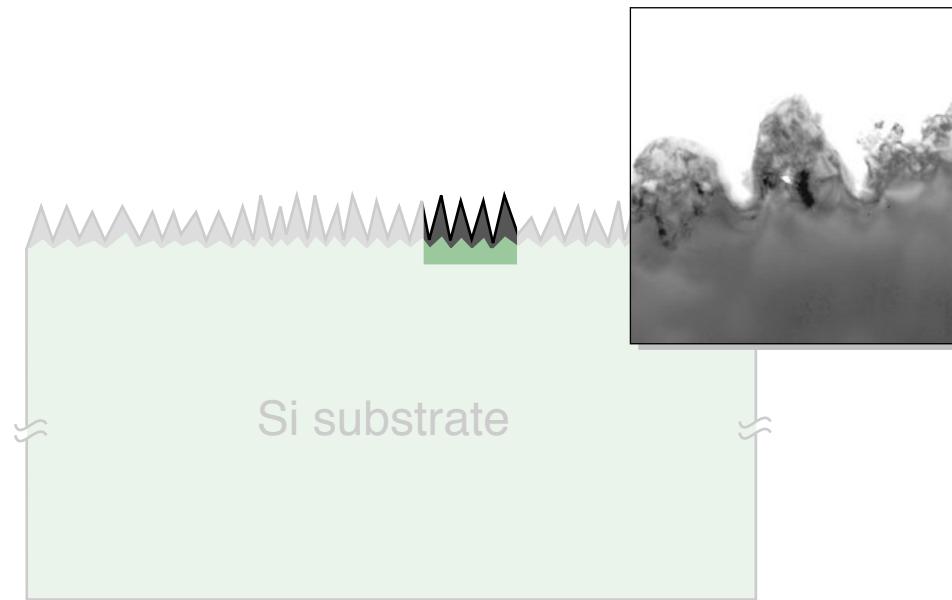
Detectors

black silicon/silicon junction



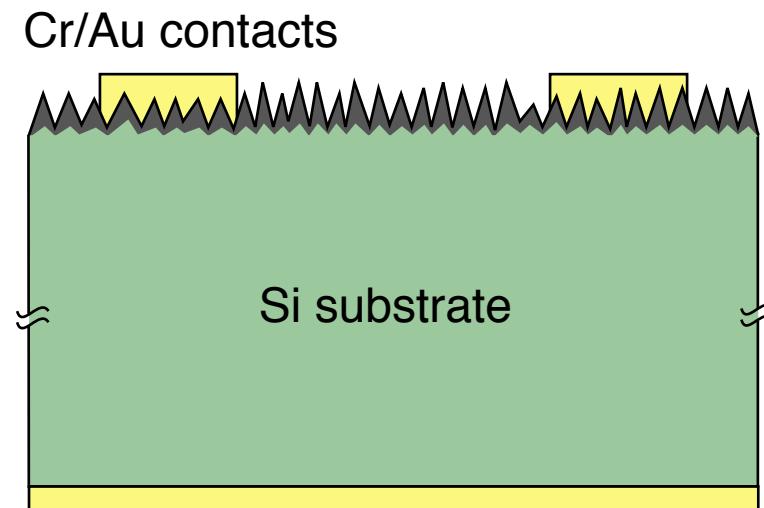
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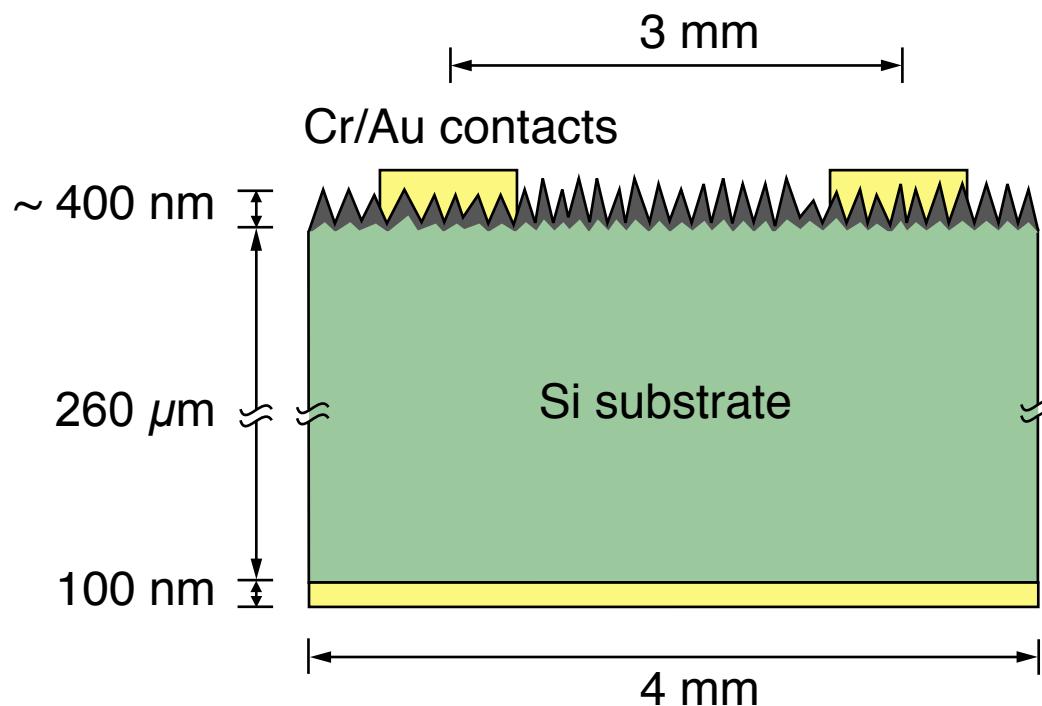
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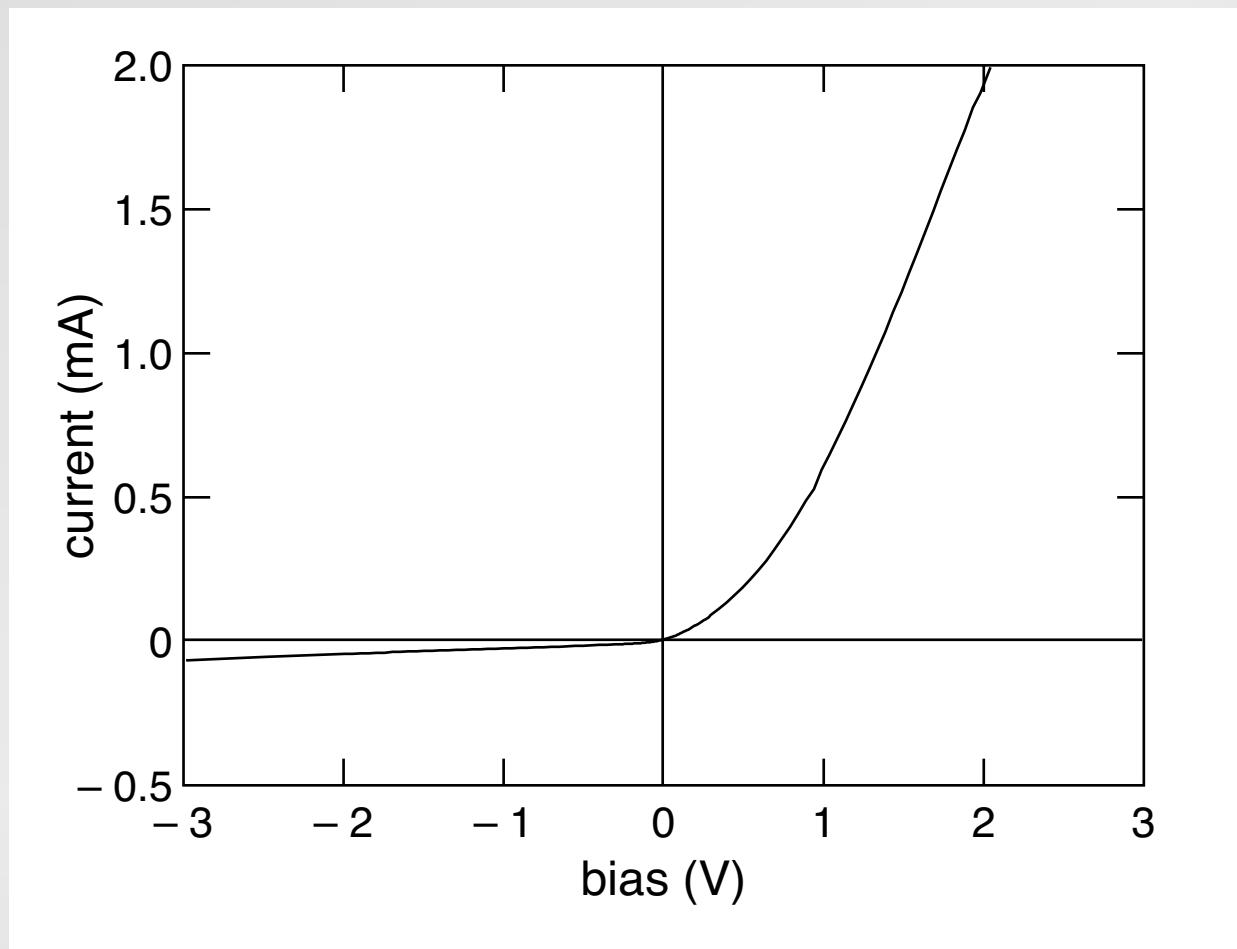
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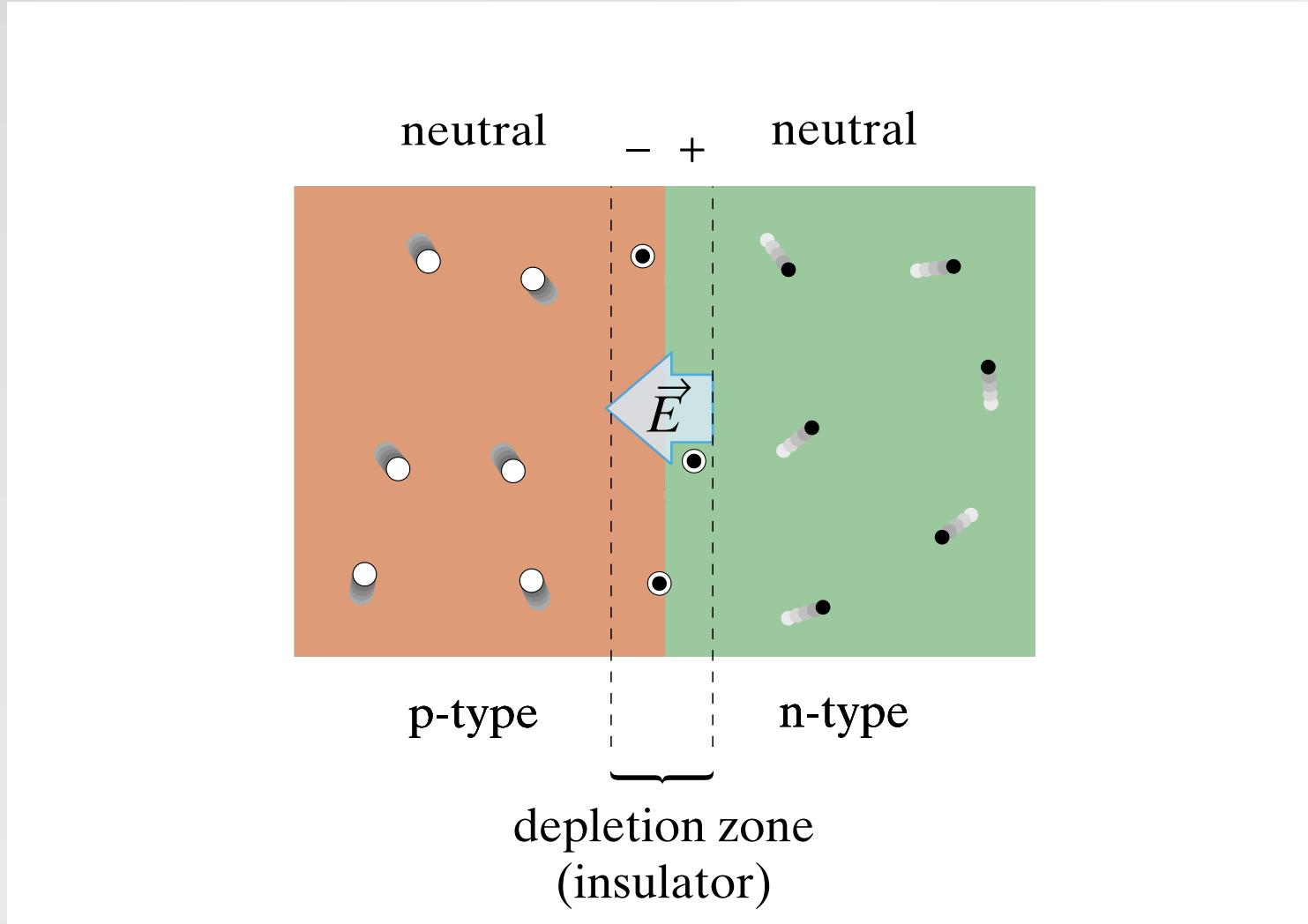


Detectors

I/V characteristics

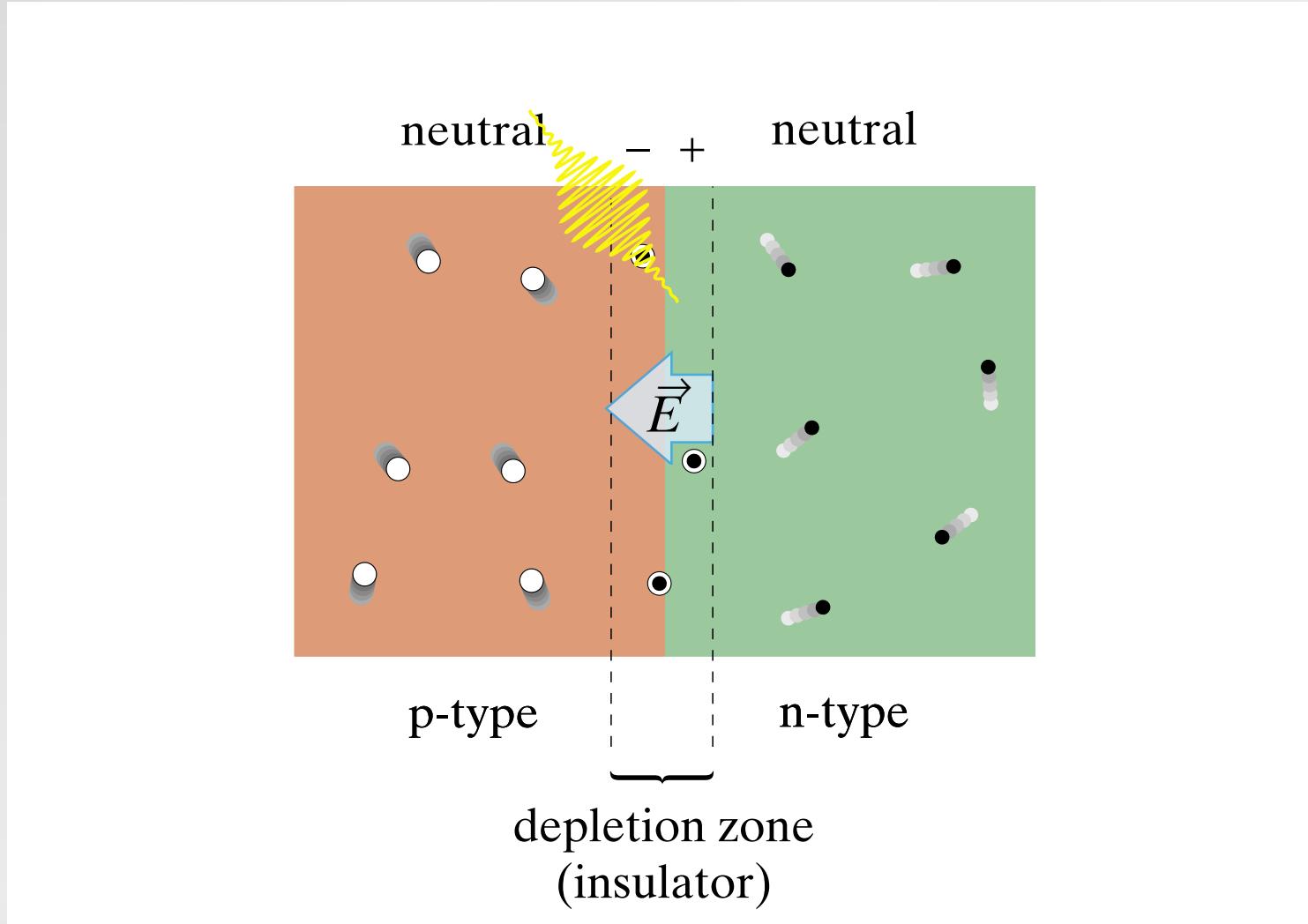


Detectors



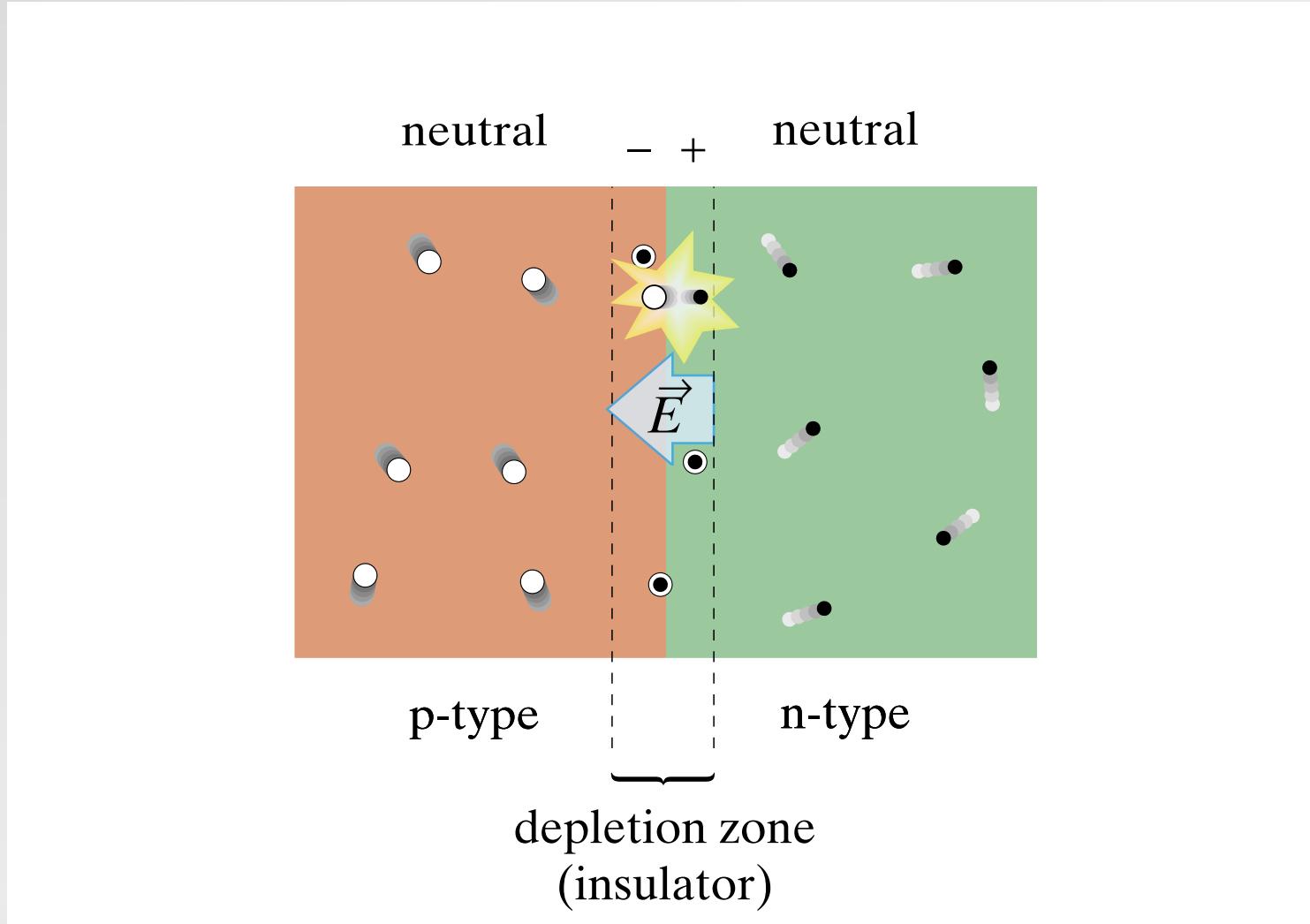
depletion layer can convert light into electric energy

Detectors



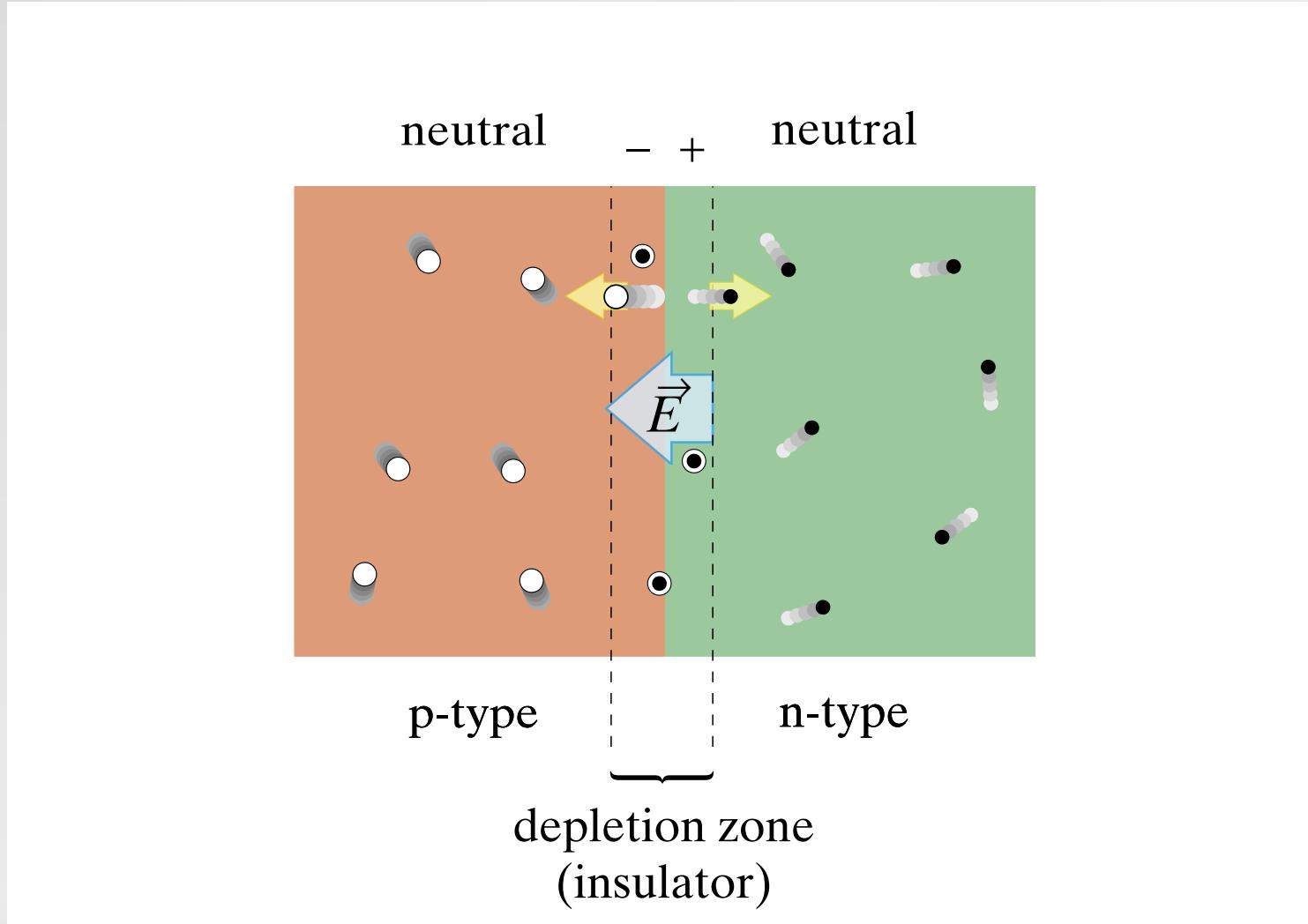
incident photon knocks out electron...

Detectors



...creating an electron-hole pair

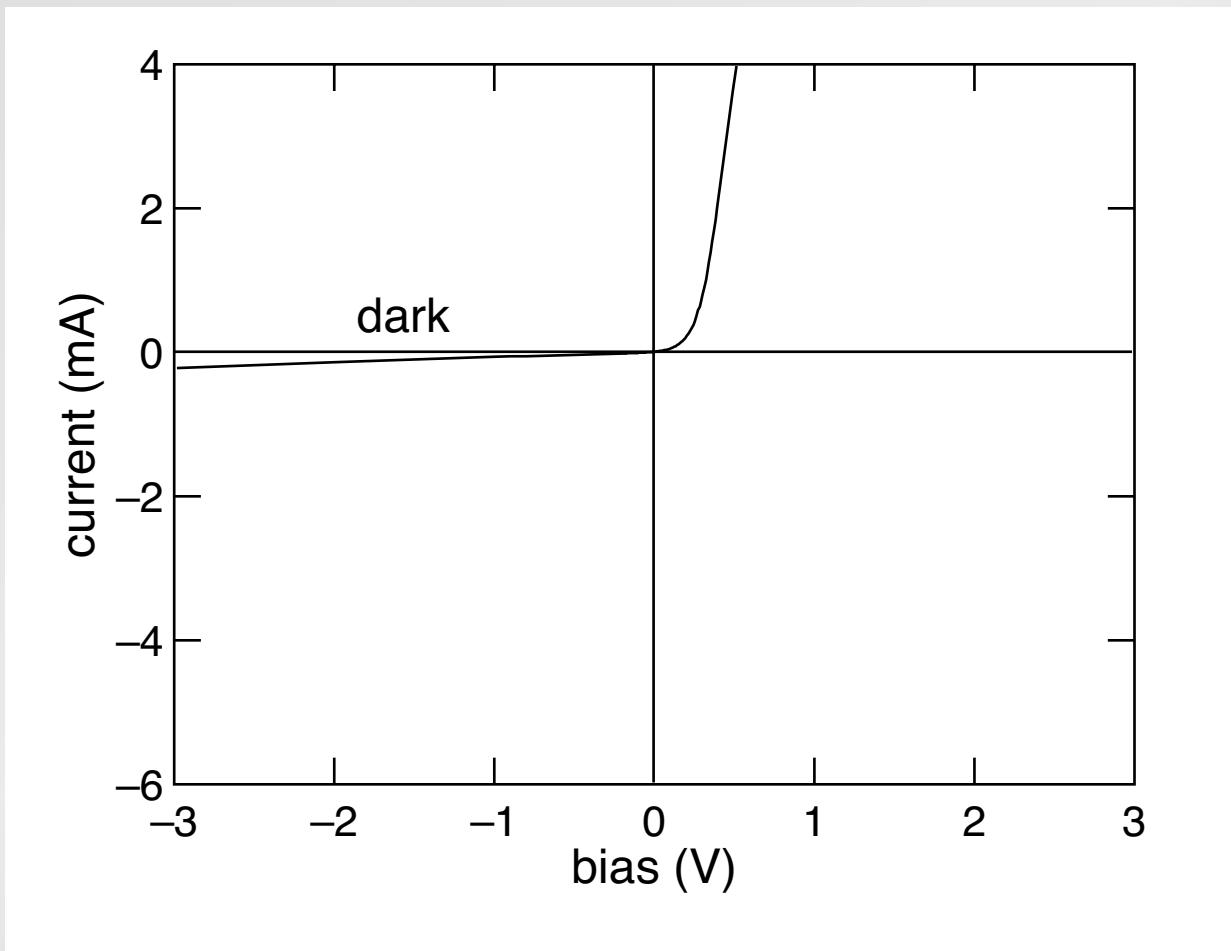
Detectors



E-field separates eh-pair, causing current

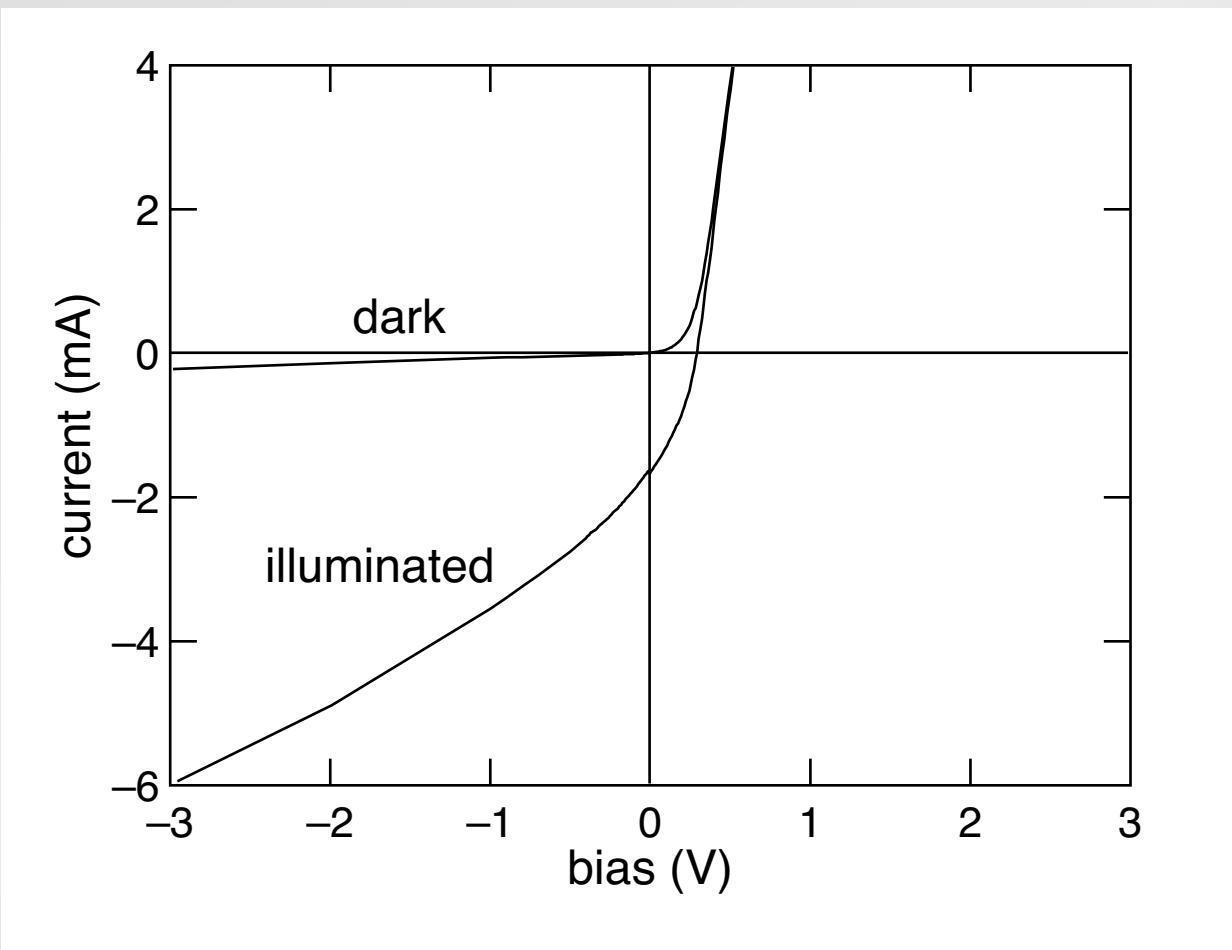
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I/V characteristics



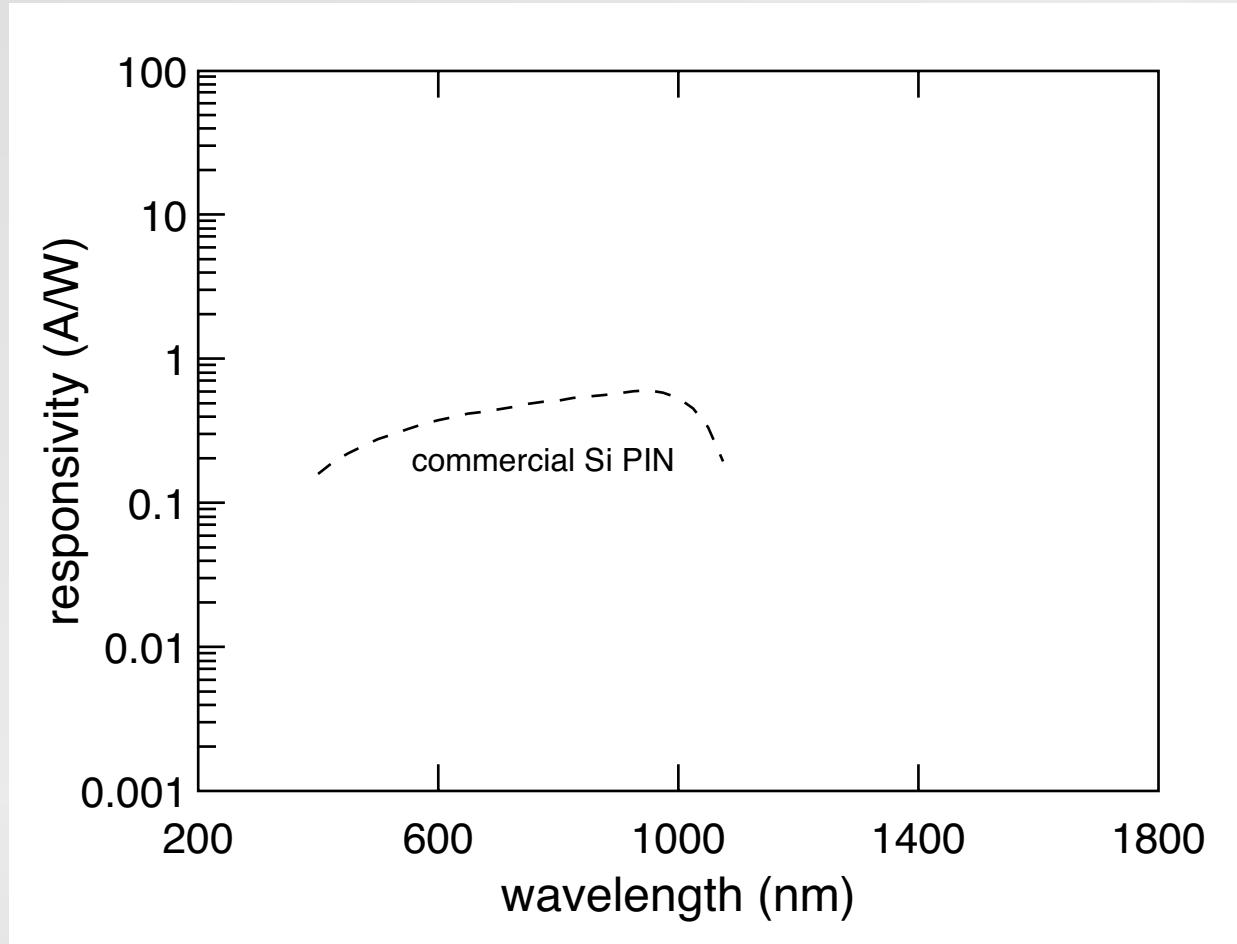
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I/V characteristics



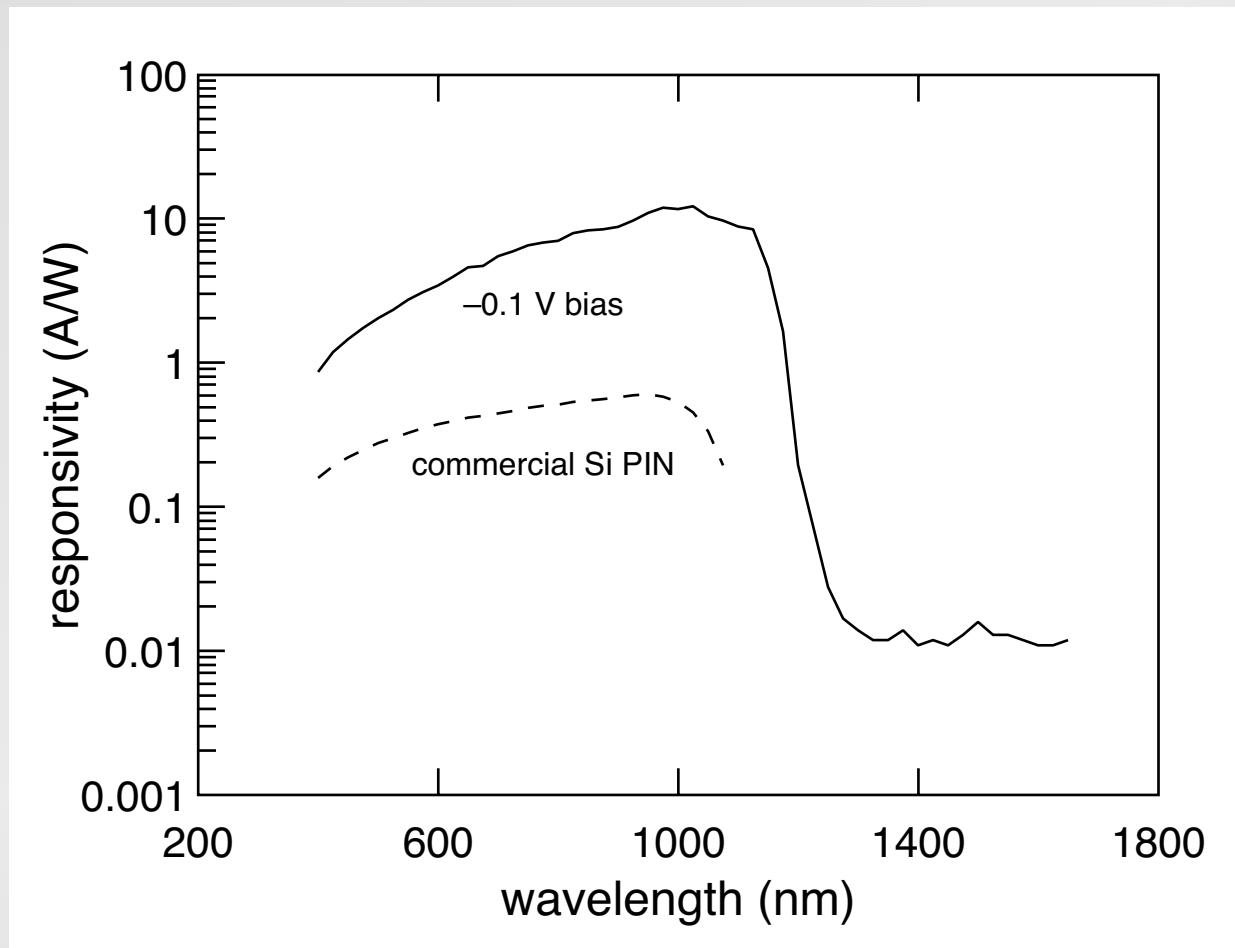
Detectors

responsivity



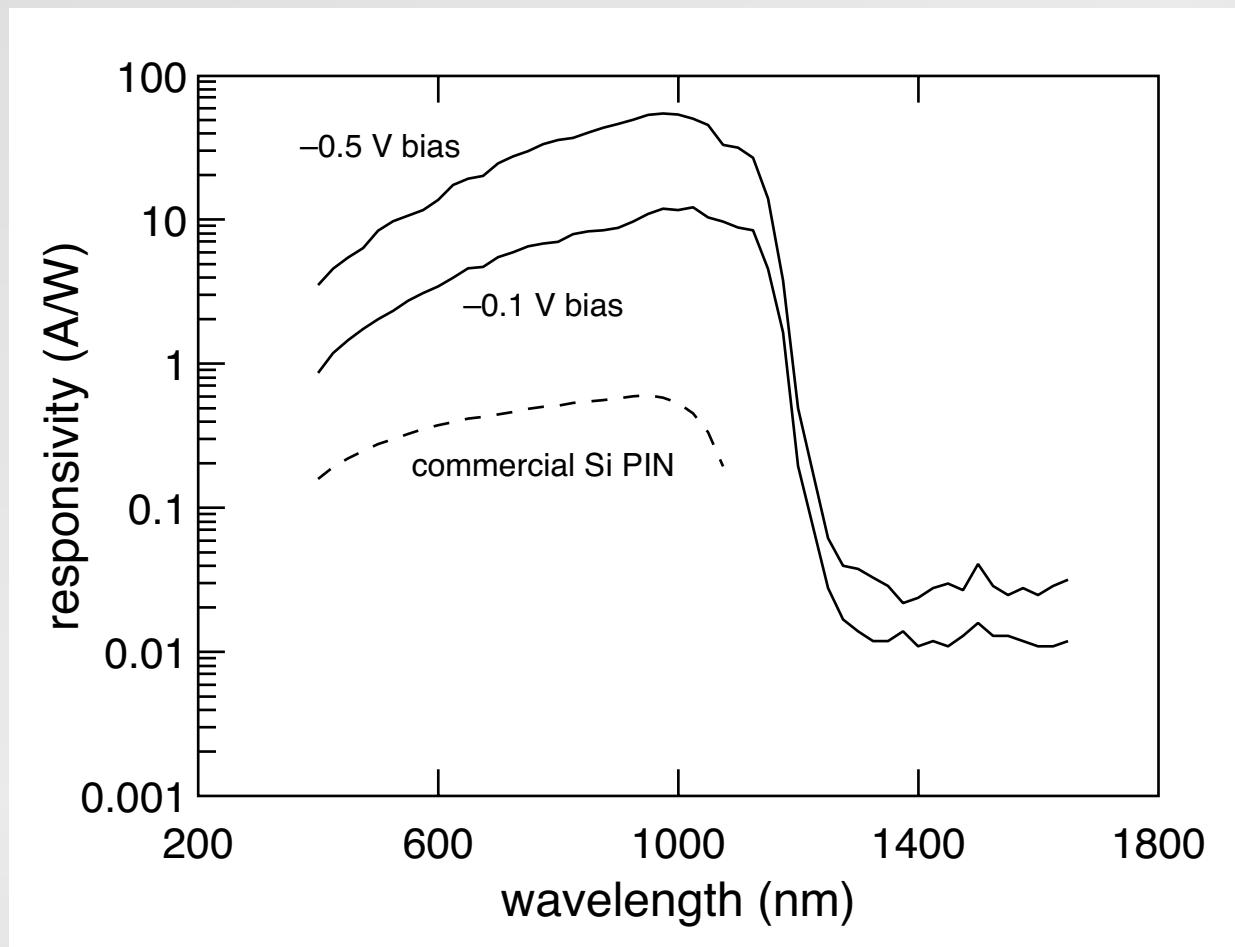
Detectors

responsivity



Detectors

responsivity



Detectors

Black silicon photodiode (at 0.5 V bias):

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

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 Harvard University is a new form of silicon soot. What started life as

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 California, had been wondering for years what

around the laboratory," he claims. Well, it was almost the only reason. A short laser pulse will break down SF₆ into sulphur and fluorine radicals, which will attack a silicon substrate. "Hydrogen fluoride is used to etch silicon. So we thought maybe the SF₆ would decompose and then the fluorine would somehow react with the silicon," Mazur explains.

With no clearer idea than this, the researchers began firing 100-femtosecond pulses of laser light through the windows of their chamber, through the shiny silicon wafer. After firing about 100 pulses they cracked the window of the chamber and removed the wafer. They saw a tiny black spot at the focal point of the laser beam. A burn, perhaps.

"You can get silicon oxide, but

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Outlook

• detector technology

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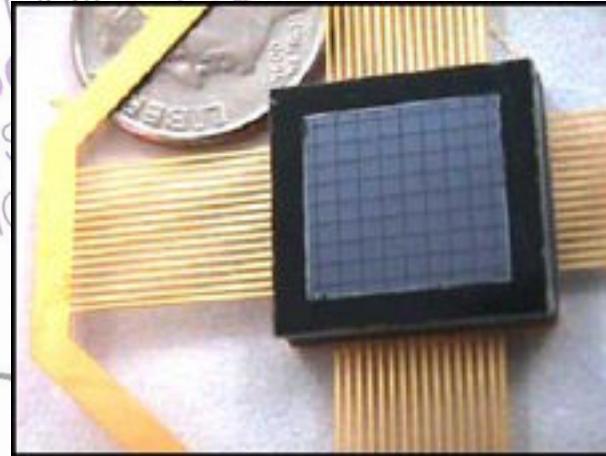
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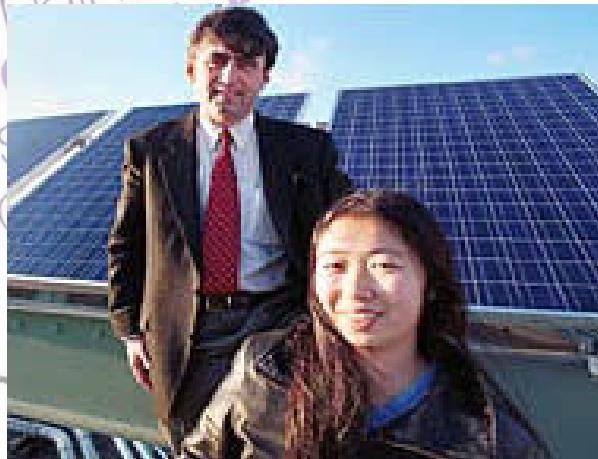
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Outlook

- detector technology
- solar cells

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



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Outlook

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- solar cells
- display technology

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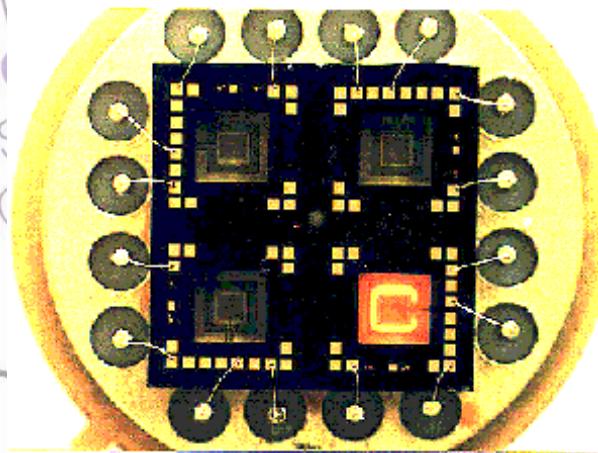


Outlook

- detector technology
- solar cells
- display technology
- biosensing

New Scientist 13, 34 (2001)

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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

CORDON MCKAY
LABORATORY OF
APPLIED SCIENCE





Funding:

Army Research Office

DARPA

Department of Energy

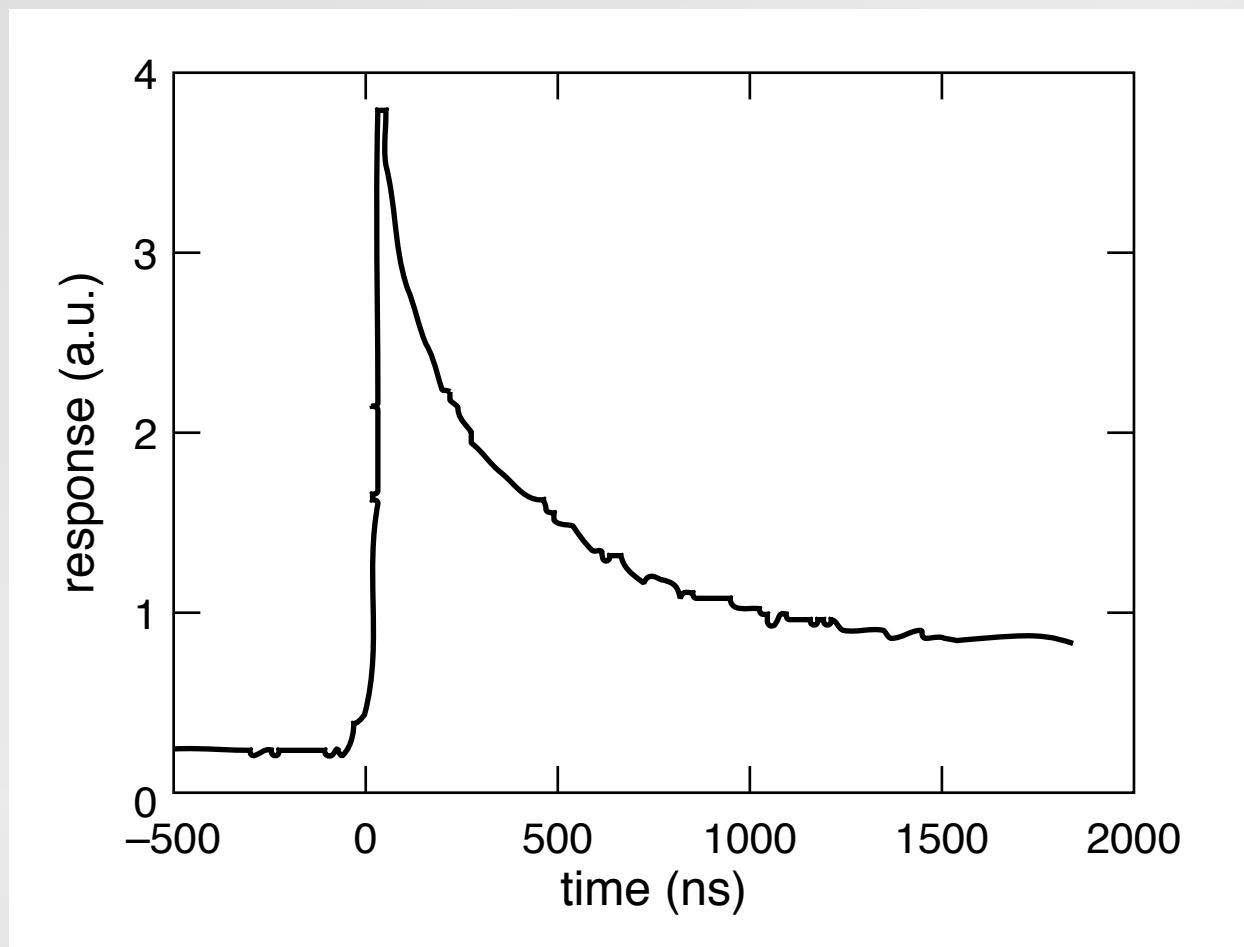
NDSEG

for a copy of this presentation:

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

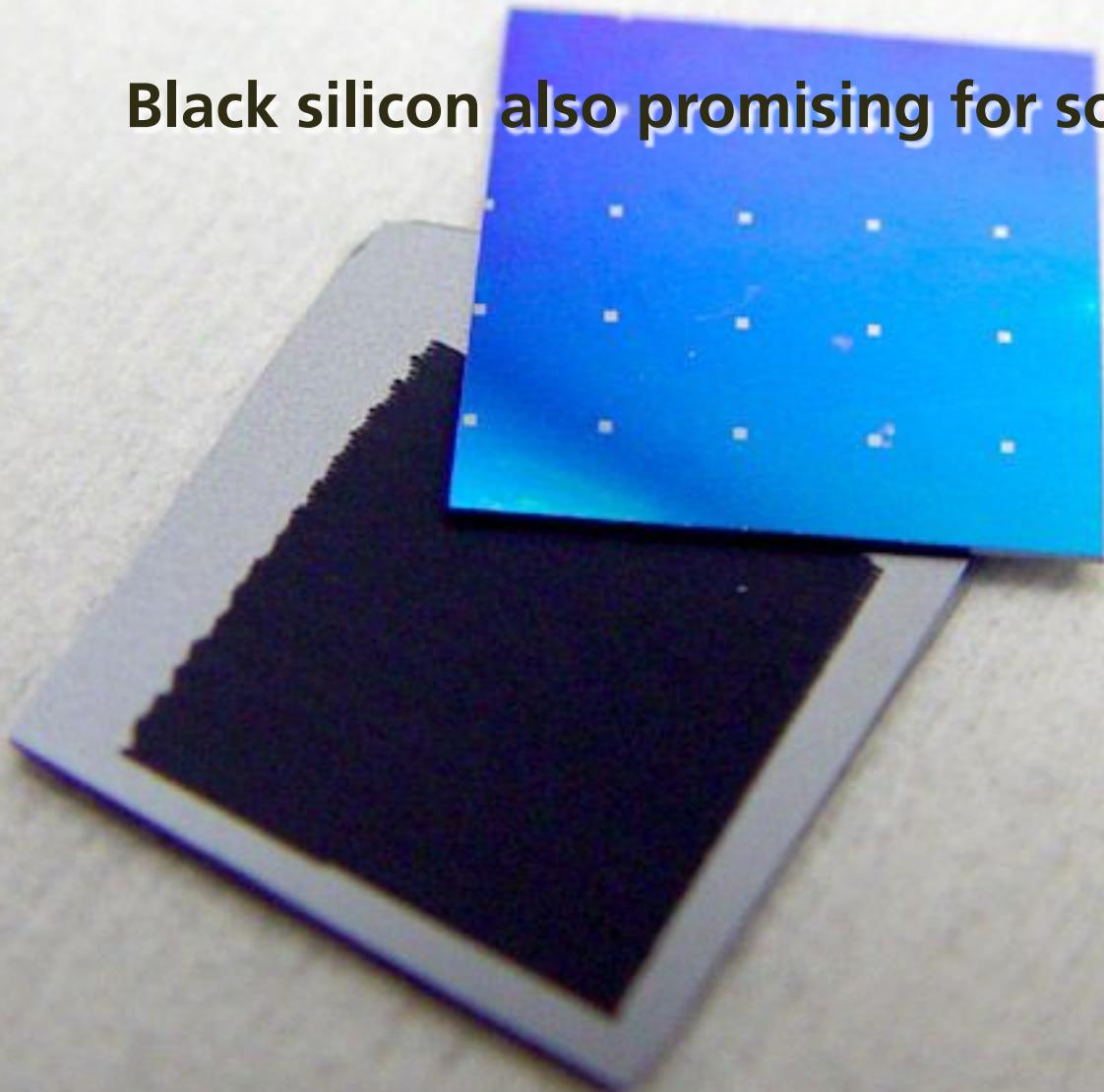
Detectors

response: 35-ns rise, 350-ns fall

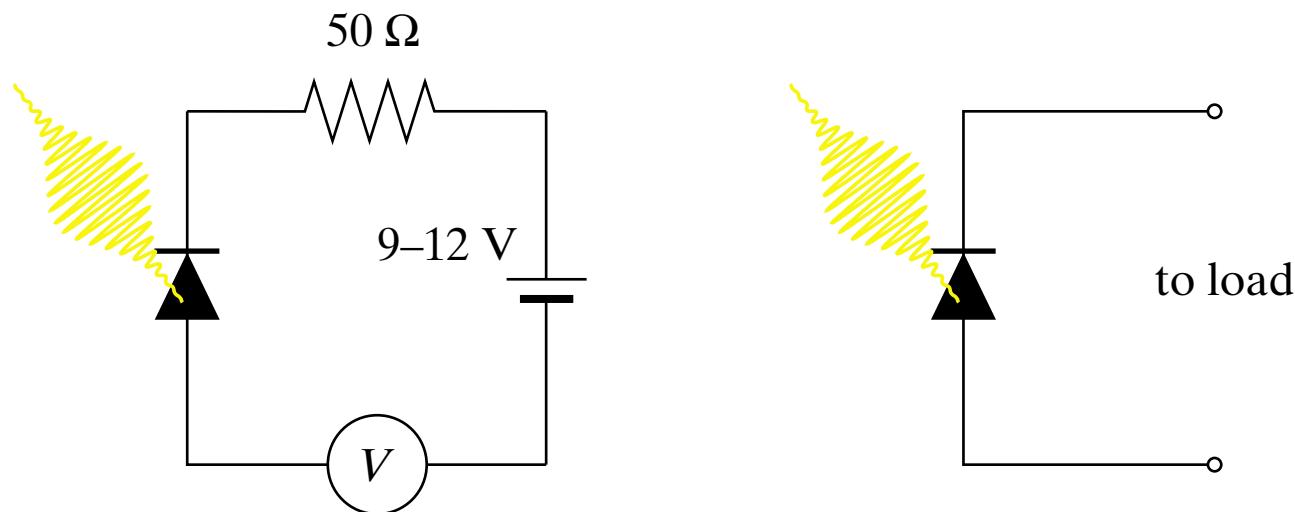


Detectors

Black silicon also promising for solar cells

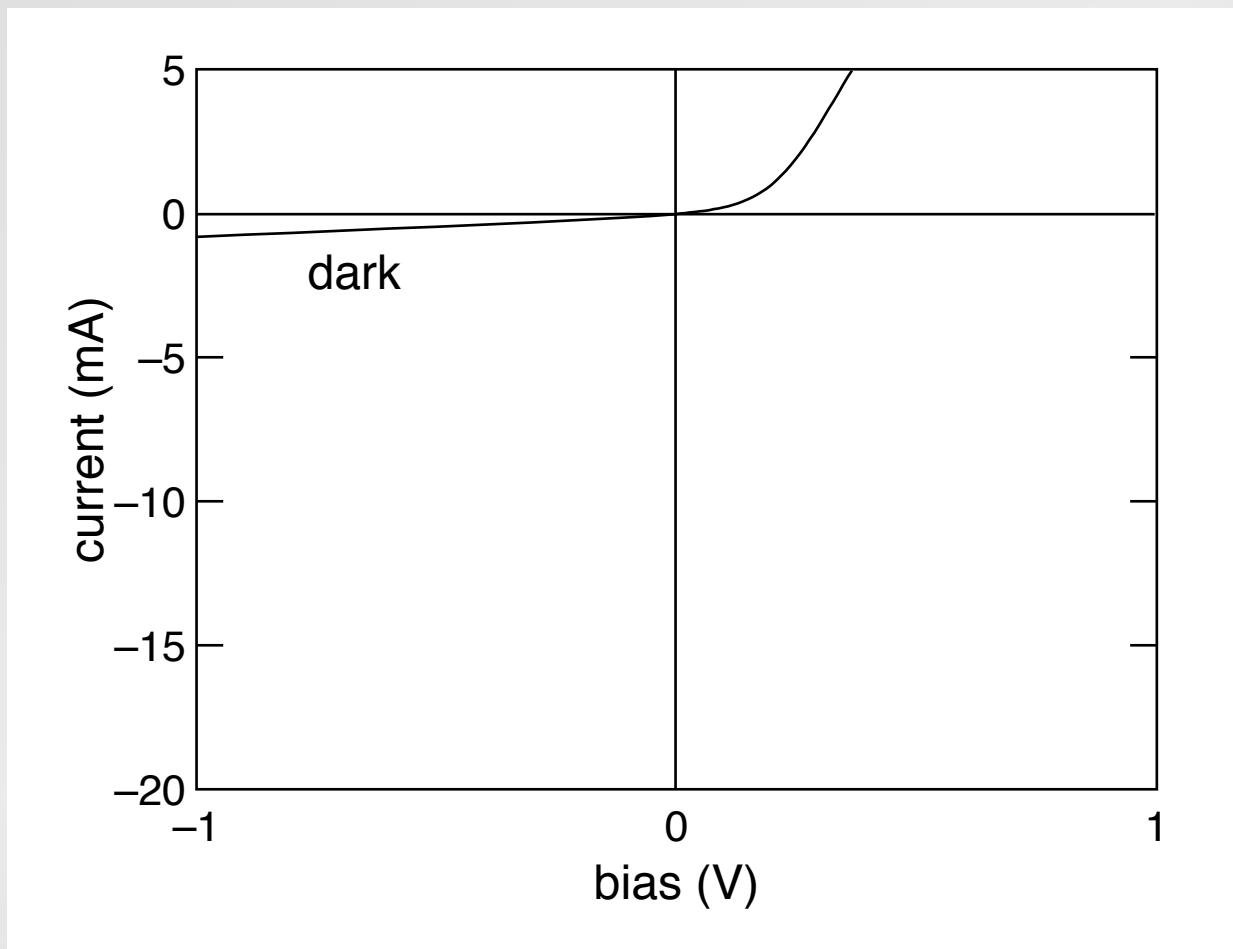


Detectors



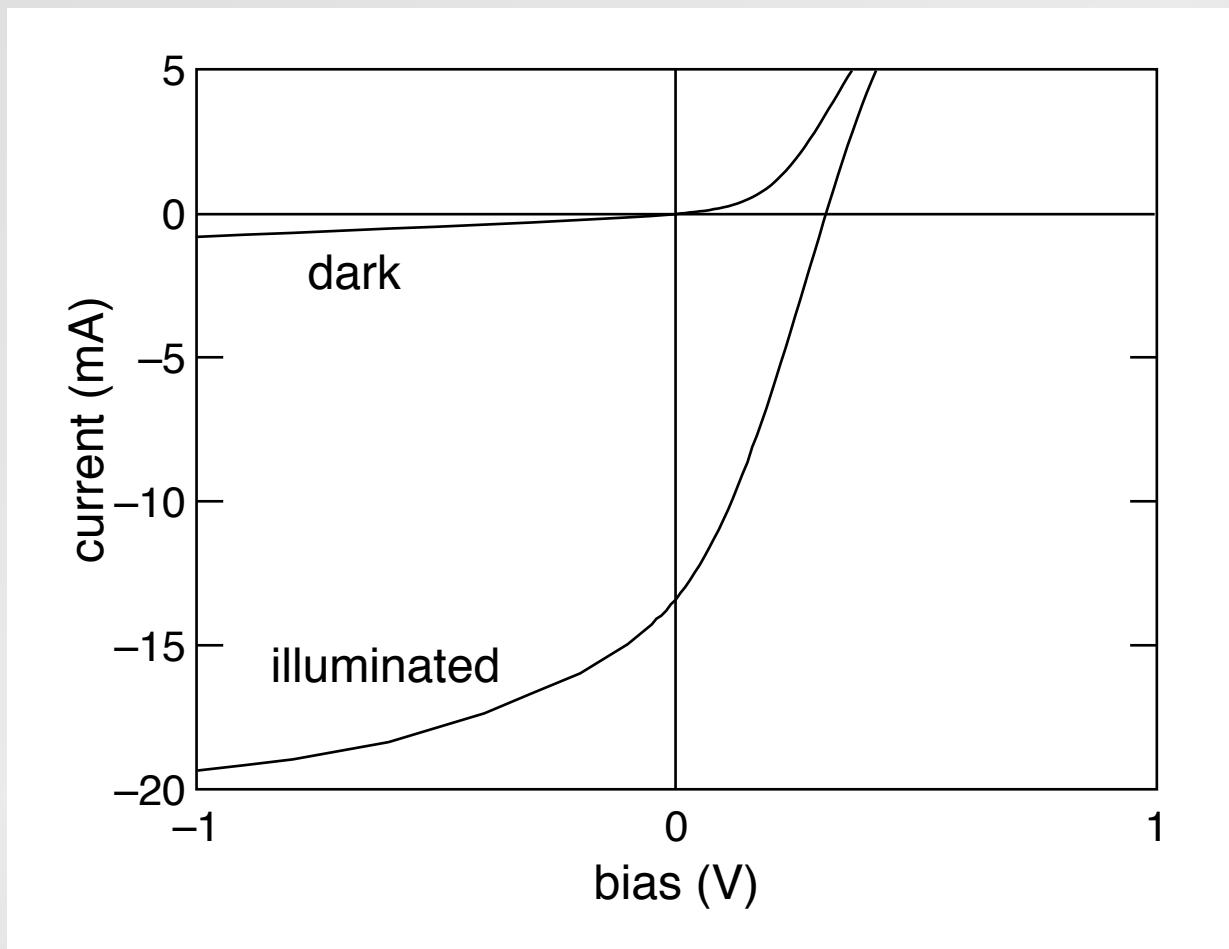
Detectors

I/V characteristics



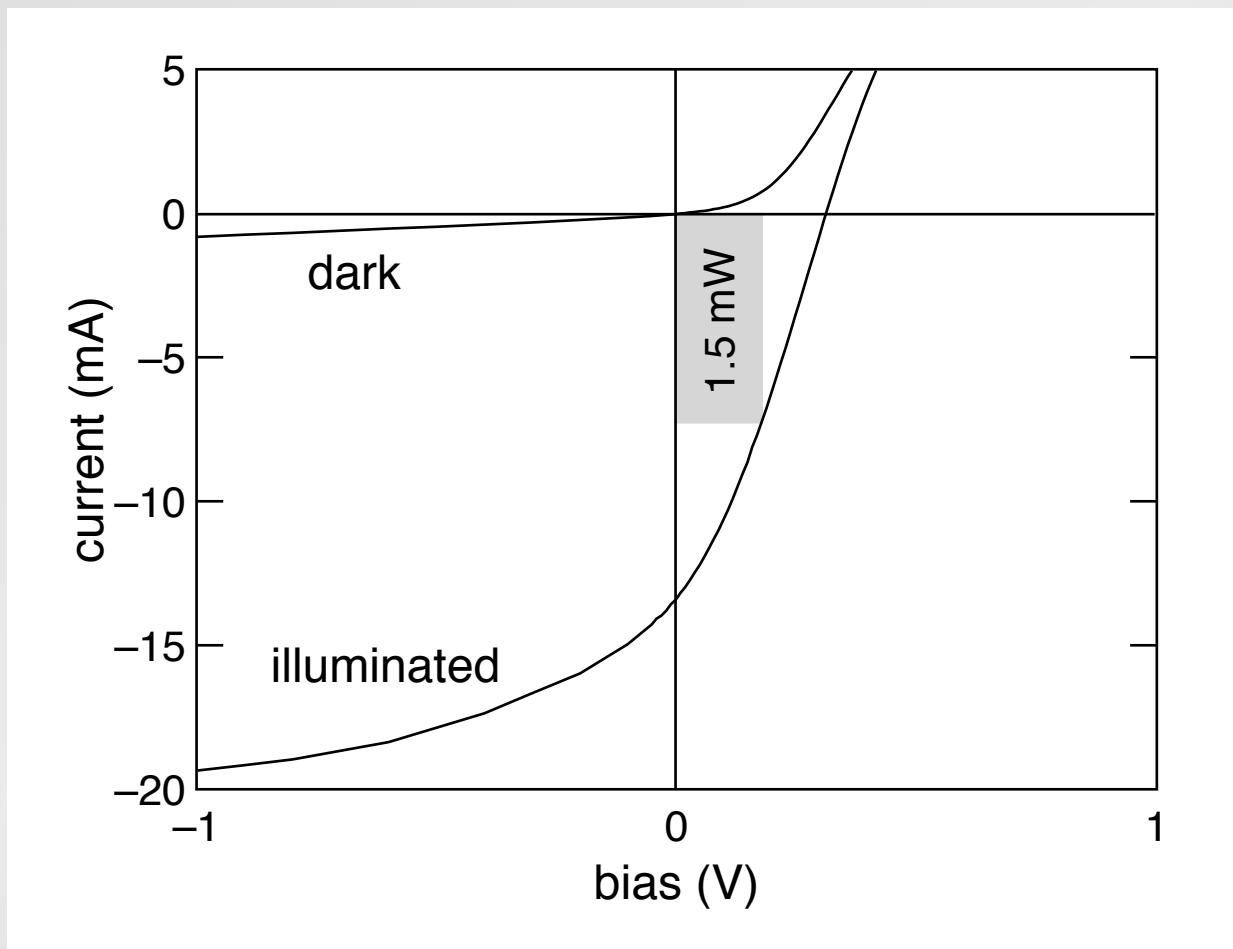
Detectors

I/V characteristics



Detectors

I/V characteristics



Detectors

Black silicon solar cell (preliminary):

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