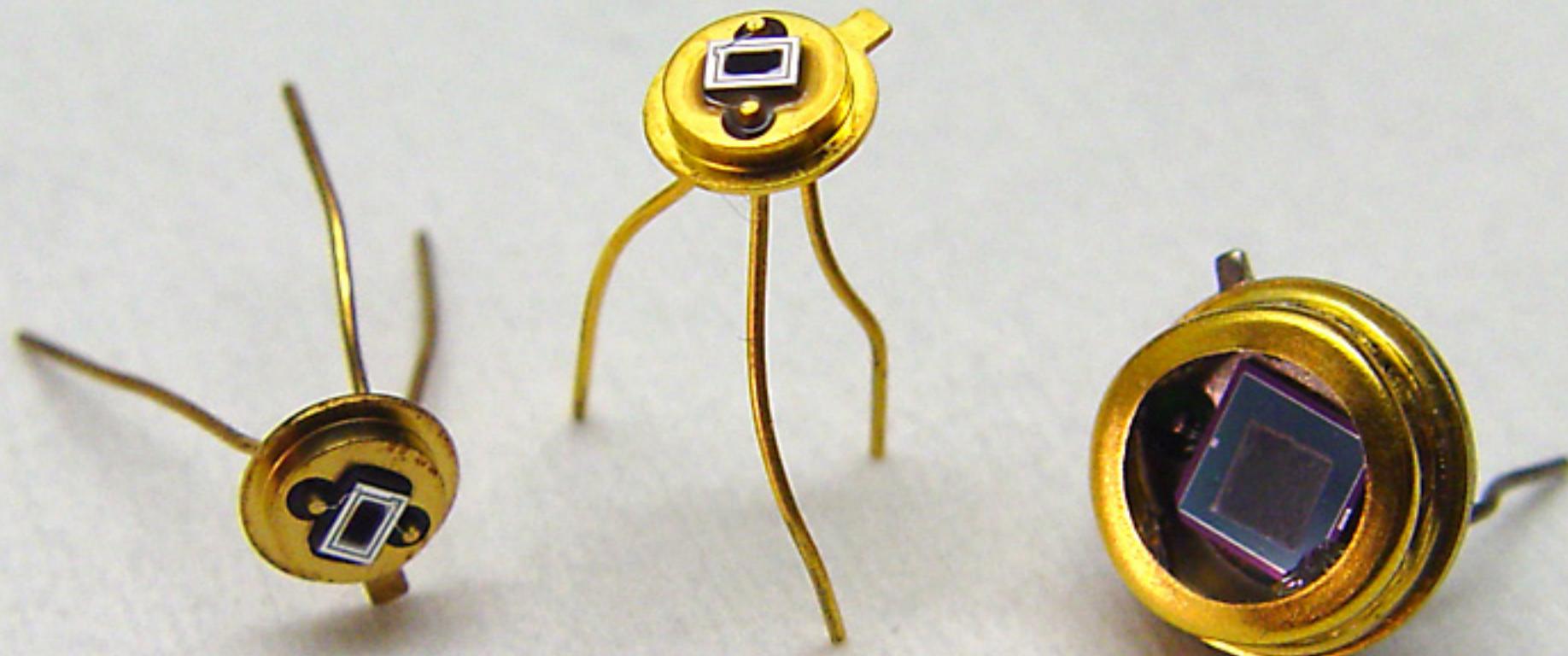
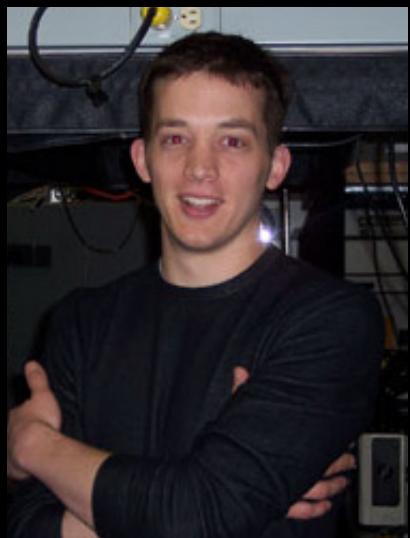


# Black silicon: silicon sees the light



Graduate Consortium on Energy and Environment  
Harvard University  
Cambridge, MA, 17 September 2010





**Mark Winkler**



**Renee Sher**



**Yu-Ting Lin**



**Eric Mazur**

and also....

**Eric Diebold**  
**Haifei Albert Zhang**  
**Dr. Brian Tull**  
**Dr. Jim Carey**  
**Prof. Tsing-Hua Her**  
**Dr. Shrenik Deliwala**  
**Dr. Richard Finlay**  
**Dr. Michael Sheehy**  
**Dr. Claudia Wu**  
**Dr. Rebecca Younkin**  
**Prof. Catherine Crouch**  
**Prof. Mengyan Shen**  
**Prof. Li Zhao**

**Dr. John Chervinsky**  
**Dr. Joshua Levinson**

**Prof. Michael Aziz**  
**Prof. Cynthia Friend**  
**Prof. Howard Stone**

**Prof. Tonio Buonassisi (MIT)**  
**Prof. Silvija Gradecak (MIT)**  
**Dr. Bonna Newman (MIT)**  
**Joe Sullivan (MIT)**

**Prof. Augustinus Asenbaum (Vienna)**

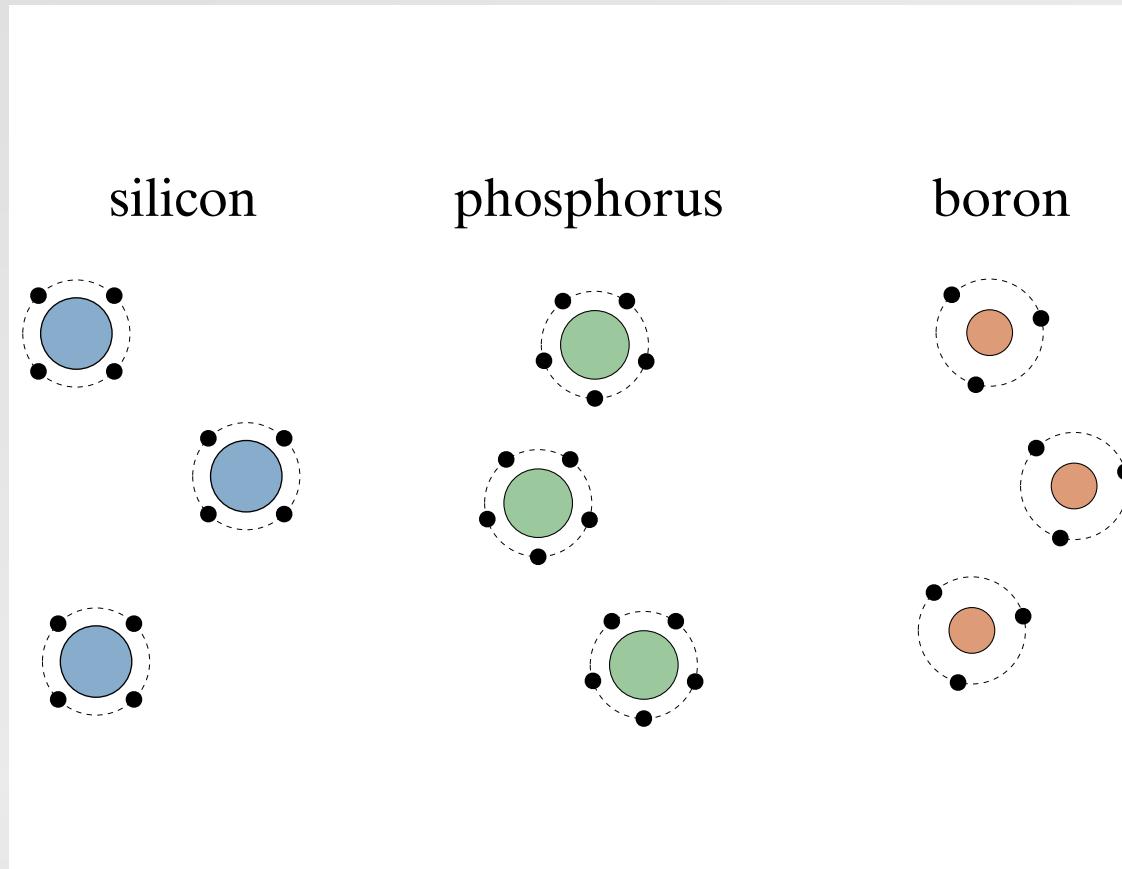
**Dr. François Génin (LLNL)**  
**Mark Wall (LLNL)**

**Dr. Richard Farrell (RMD)**  
**Dr. Arieh Karger (RMD)**  
**Dr. Richard Meyers (RMD)**

**Dr. Pat Maloney (NVSED)**

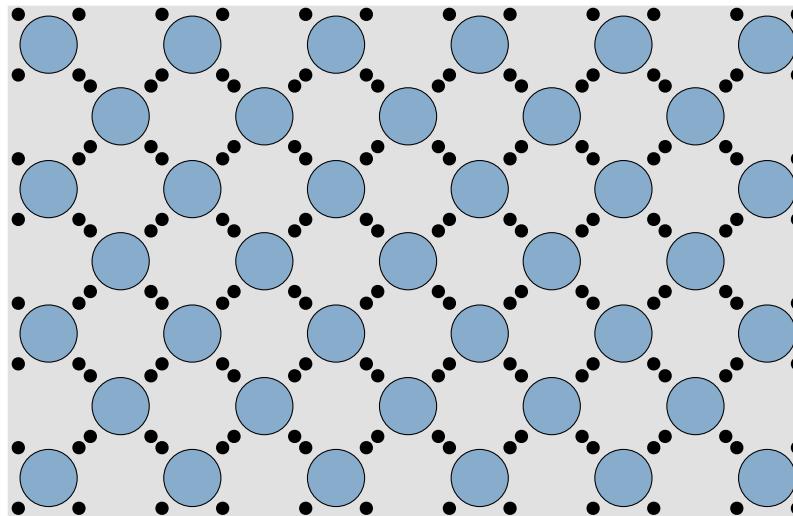
**Dr. Jeffrey Warrander (ARDEC)**

# Introduction



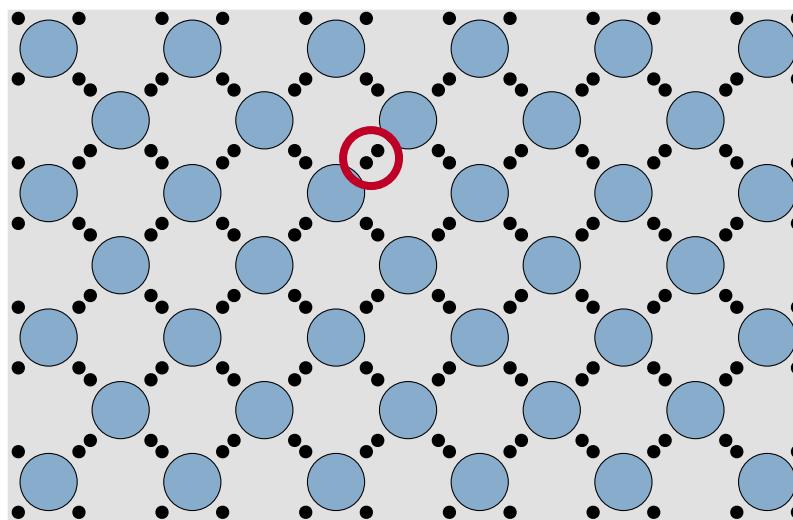
**outer (“valence”) electrons determine electronic properties**

# Introduction



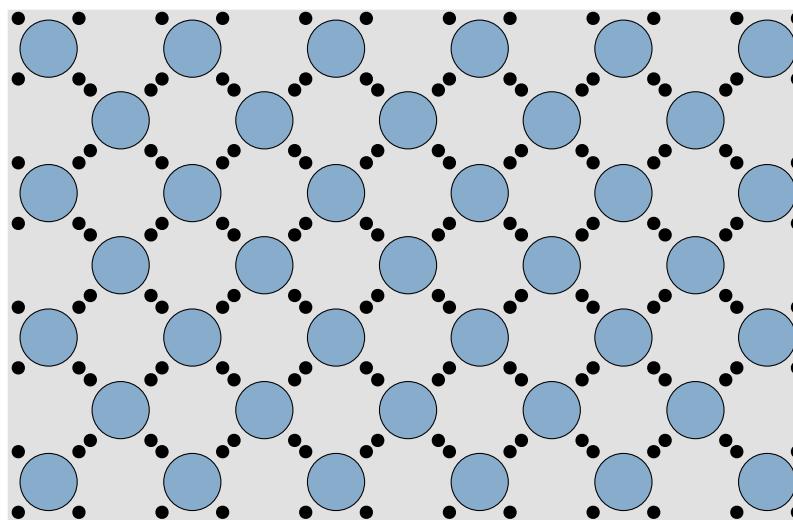
pure ("intrinsic") silicon

# Introduction



**electrons in covalent bond are immobile**

# Introduction

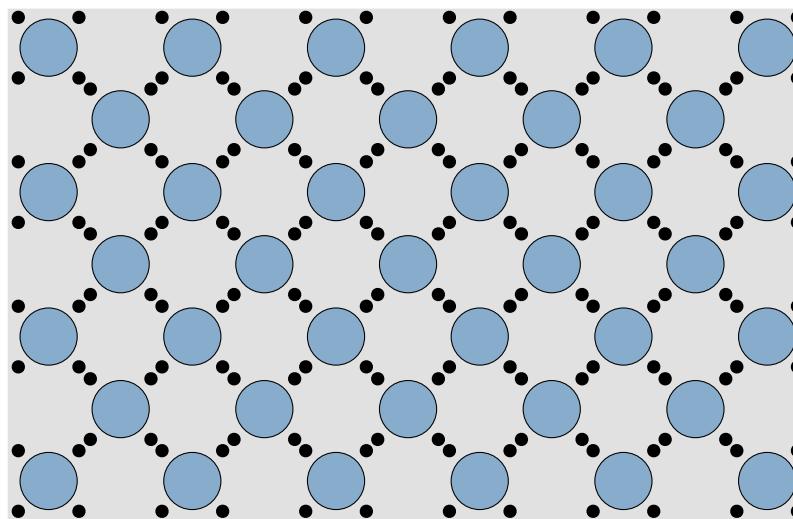


**all electrons bound, so no conduction**

# Outline

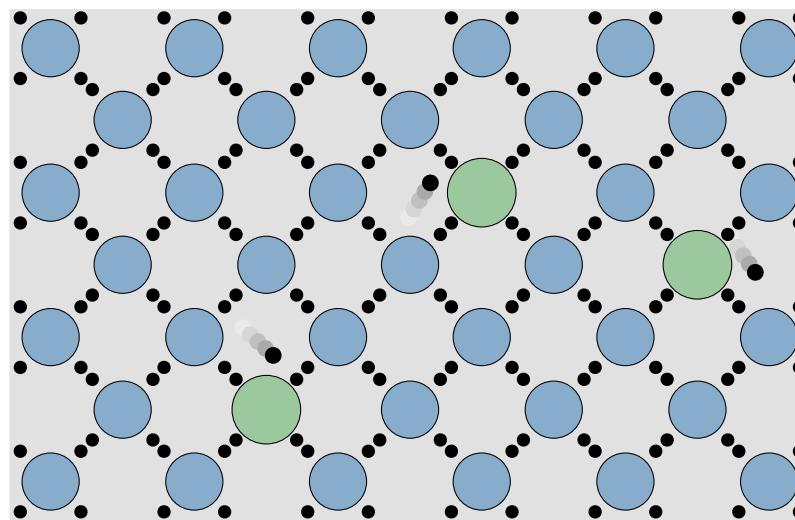
- doped semiconductors
- *pn*-junctions
- black silicon

# Doped semiconductors



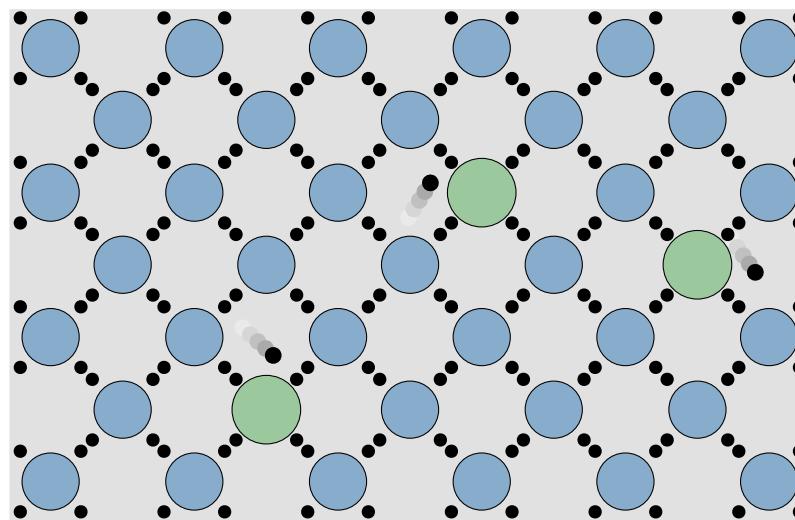
**intrinsic silicon: no conduction**

# Doped semiconductors



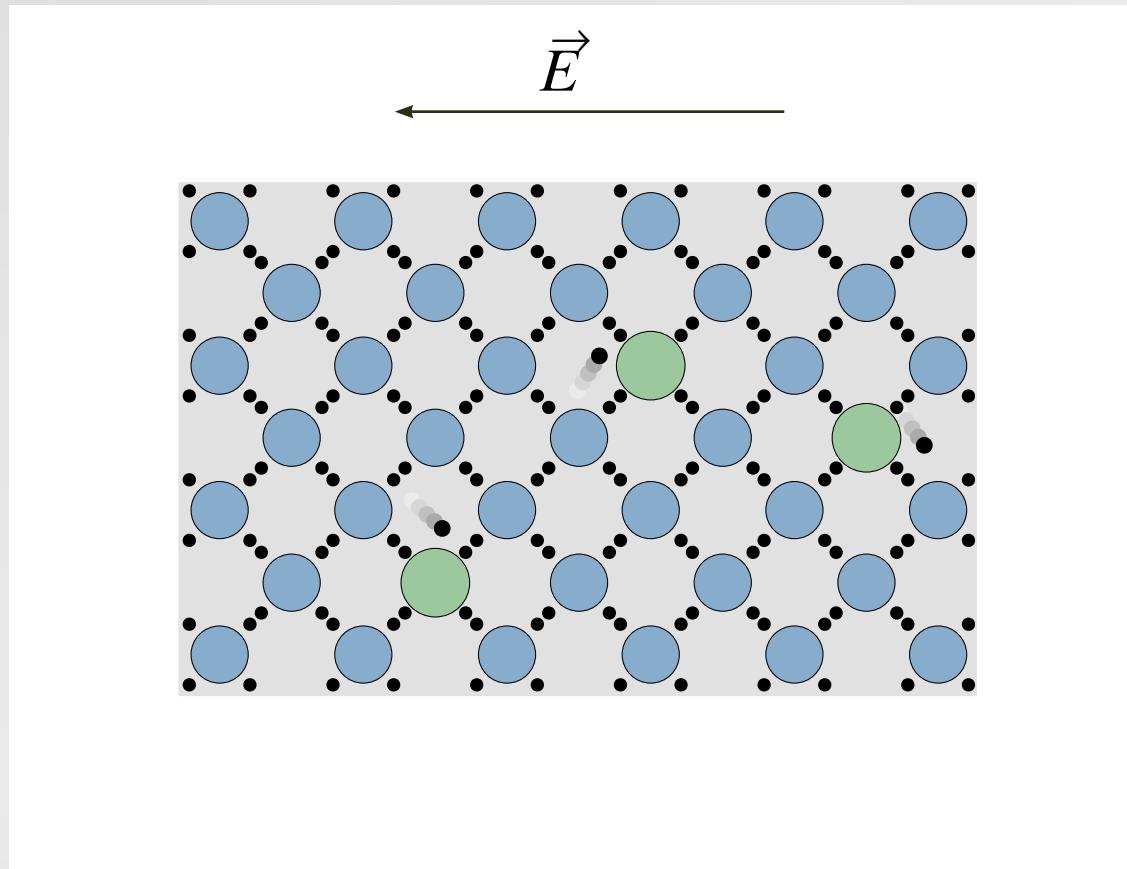
**substitute phosphorous: surplus of (free) electrons**

# Doped semiconductors



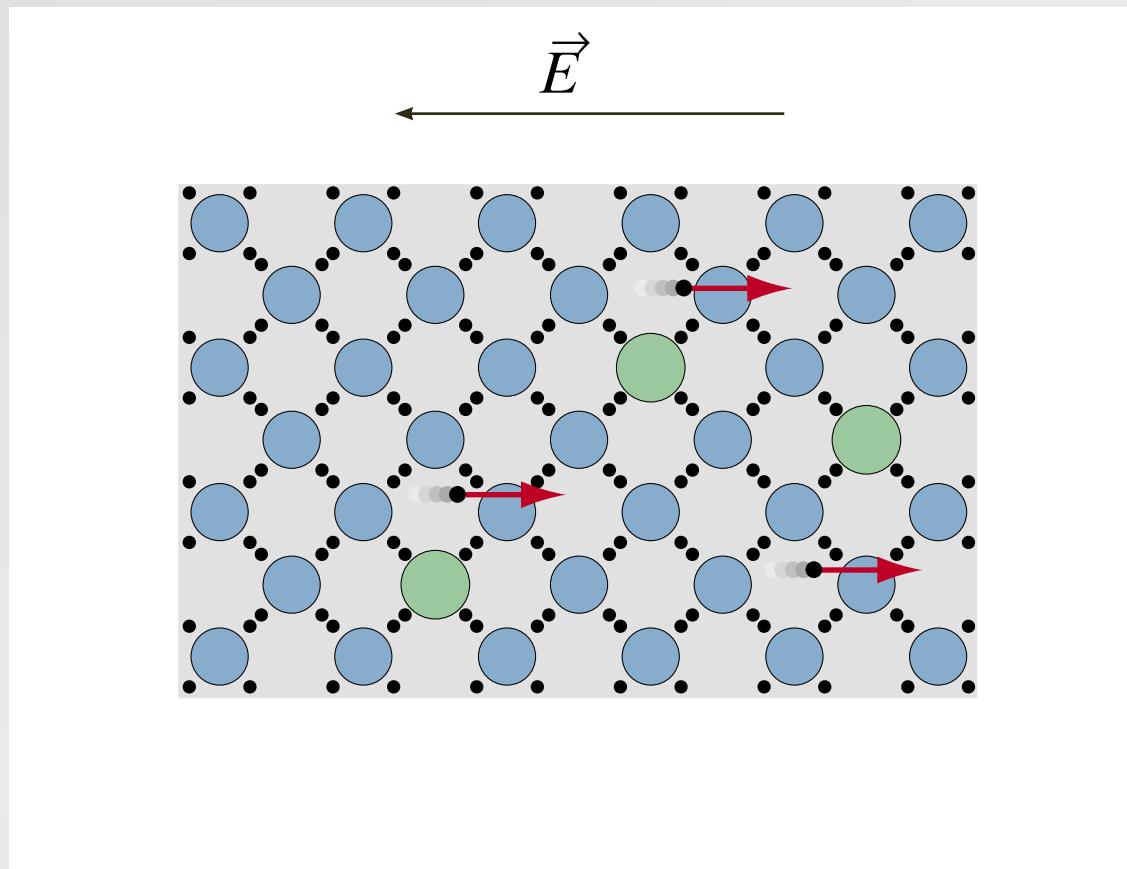
(but material as a whole still neutral!)

# Doped semiconductors



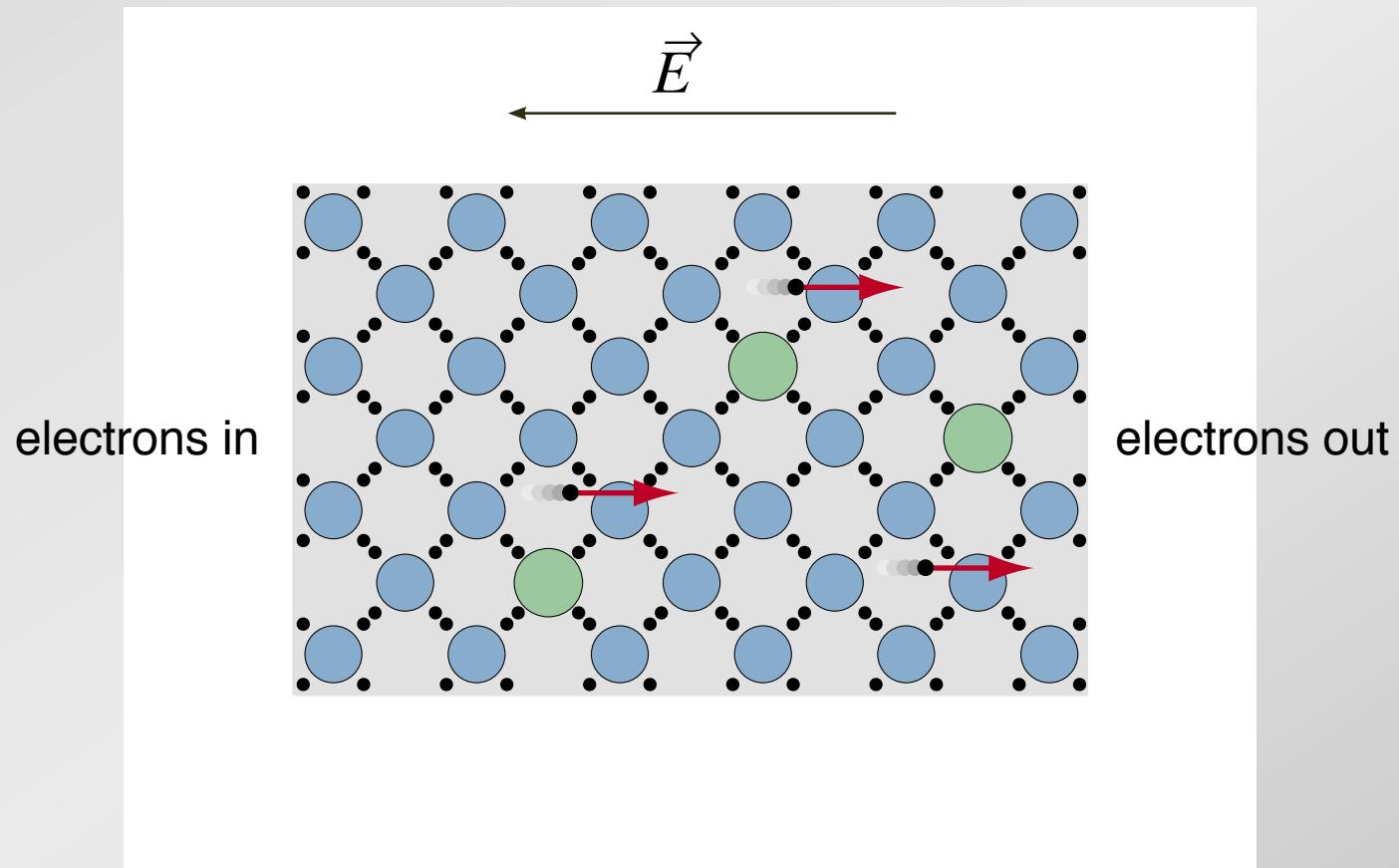
apply electric field...

# Doped semiconductors



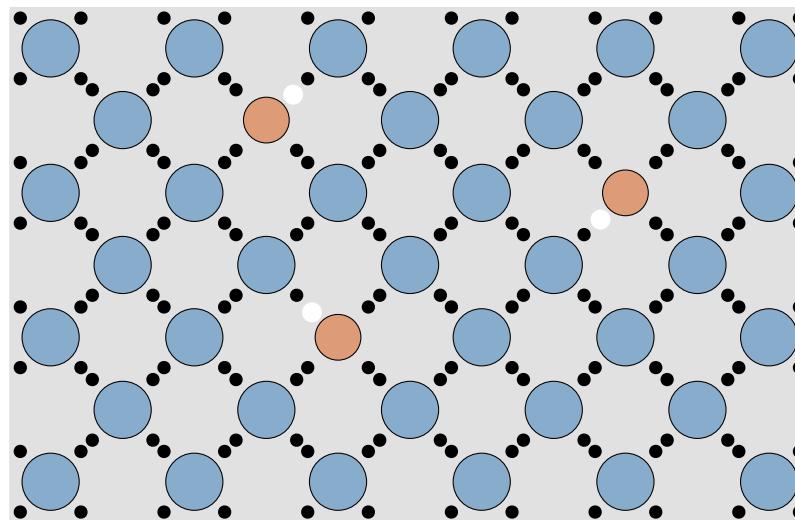
...free electrons lead to conduction

# Doped semiconductors



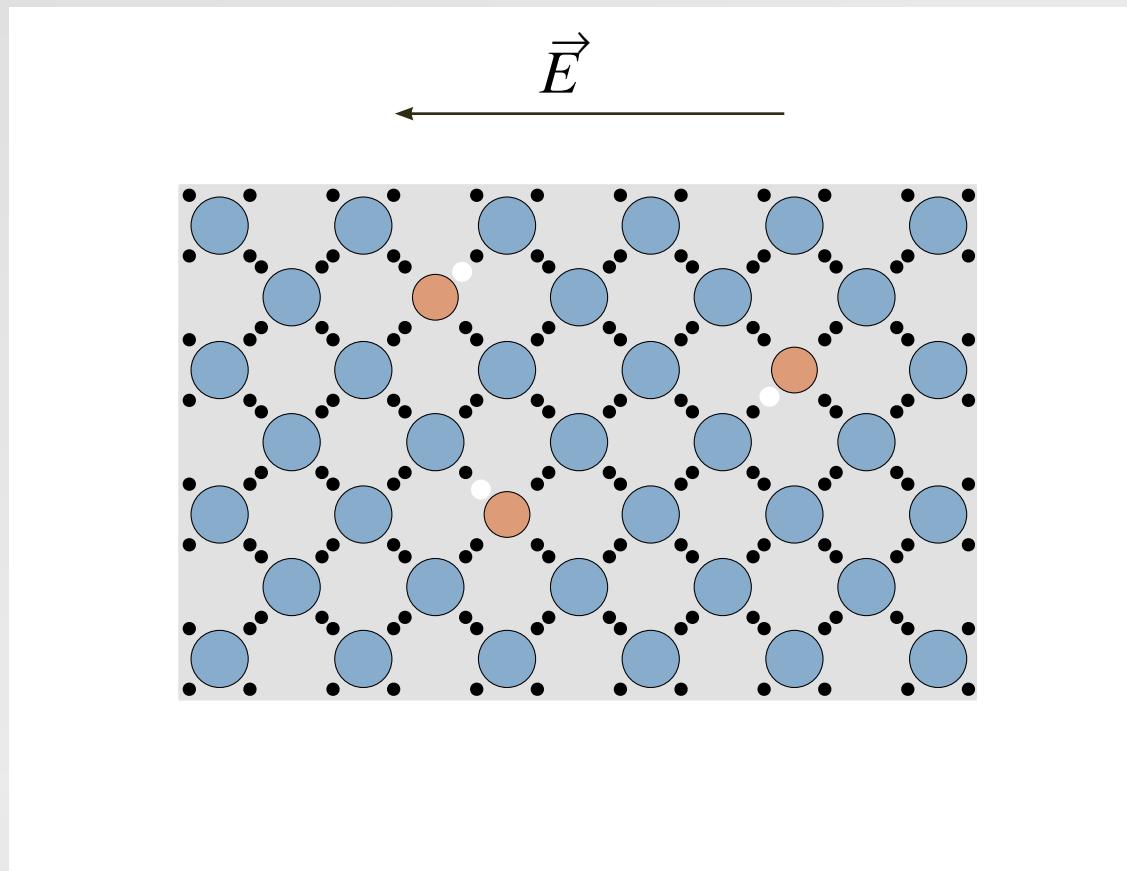
...free electrons lead to conduction

# Doped semiconductors



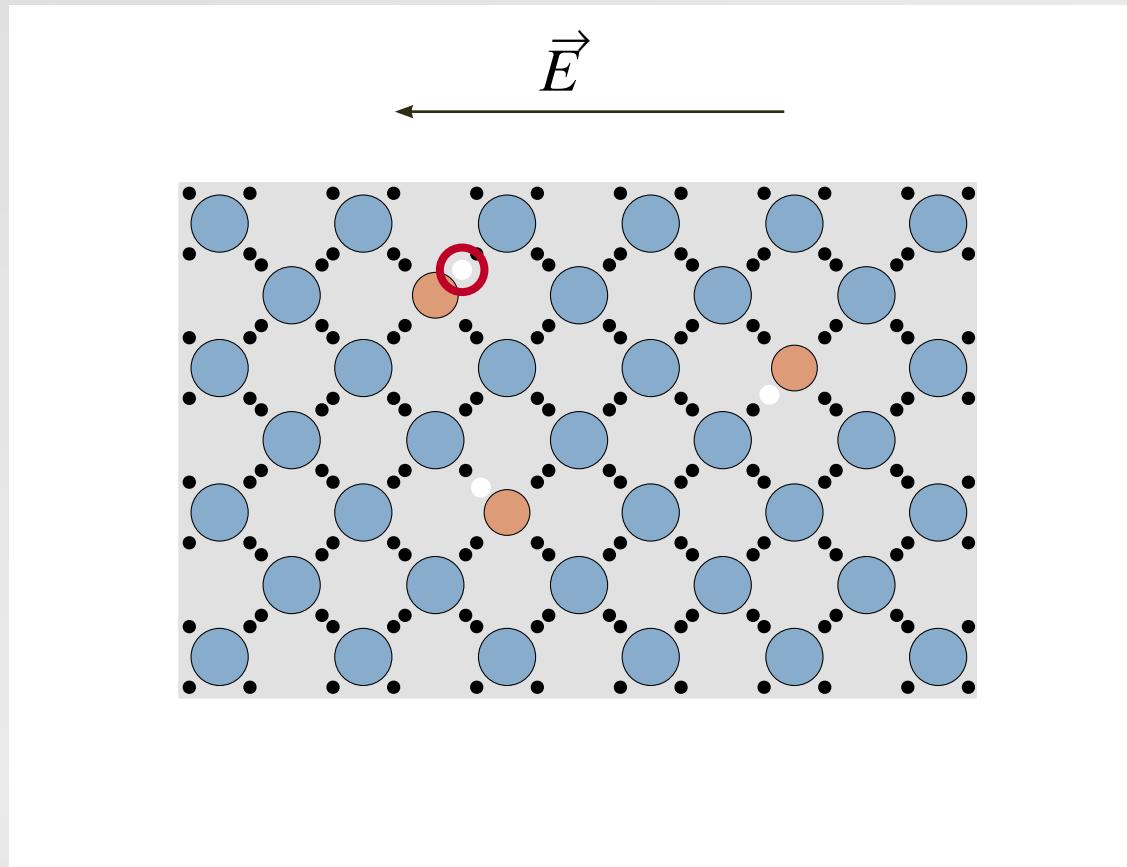
**substitute boron: deficit of electrons leaves "holes"**

# Doped semiconductors



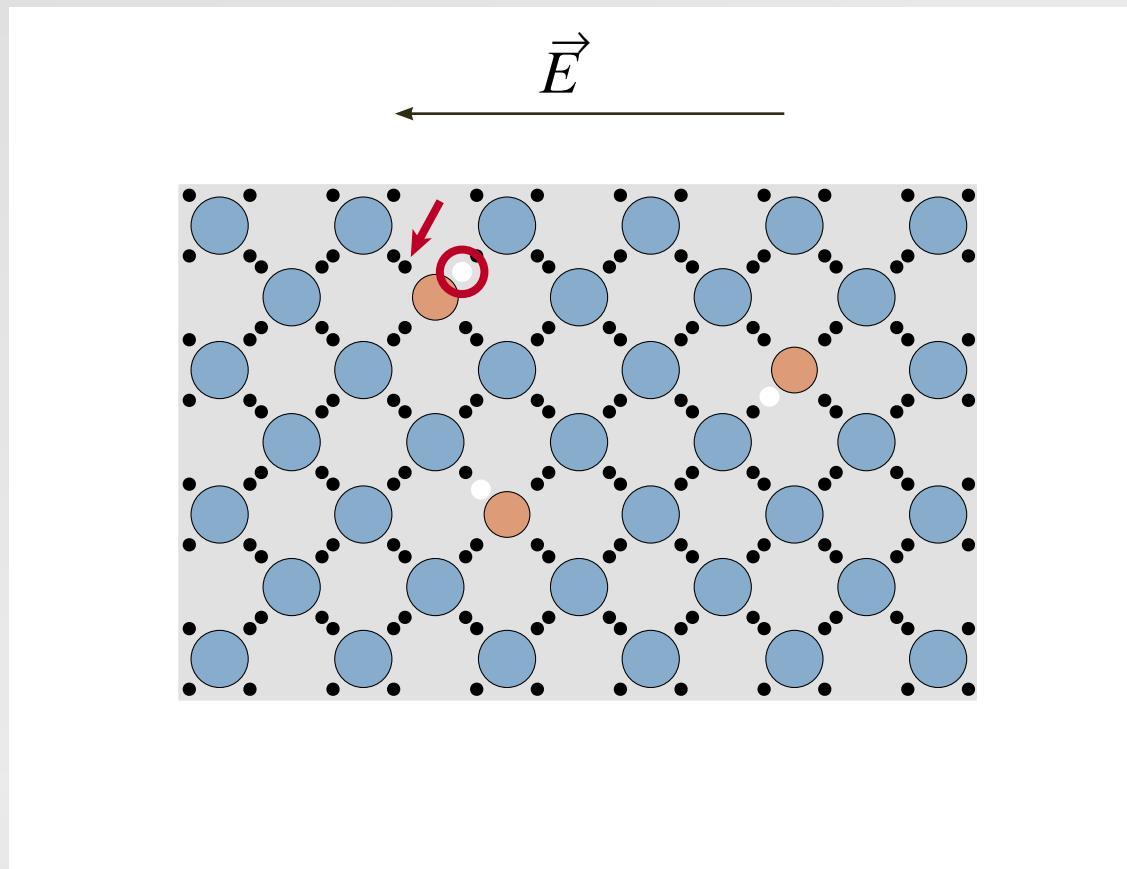
apply electric field...

# Doped semiconductors



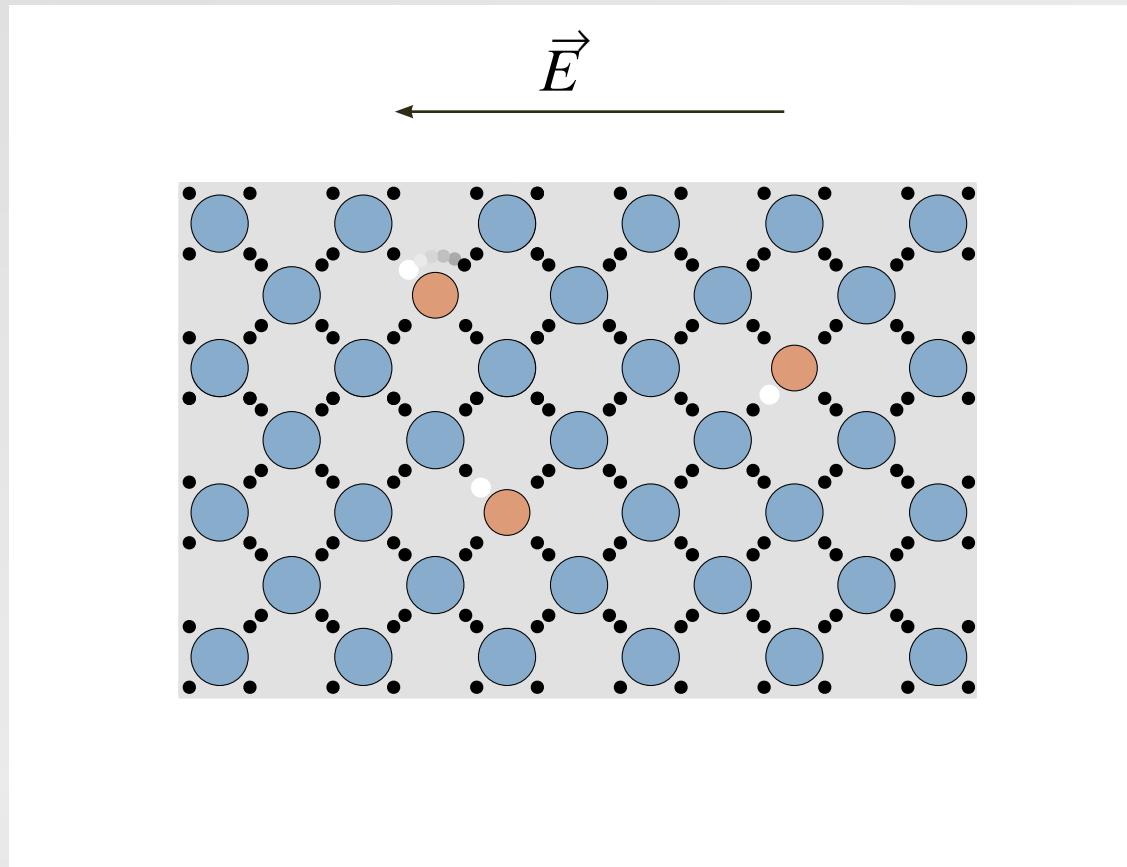
...presence of holes leads to conduction

# Doped semiconductors



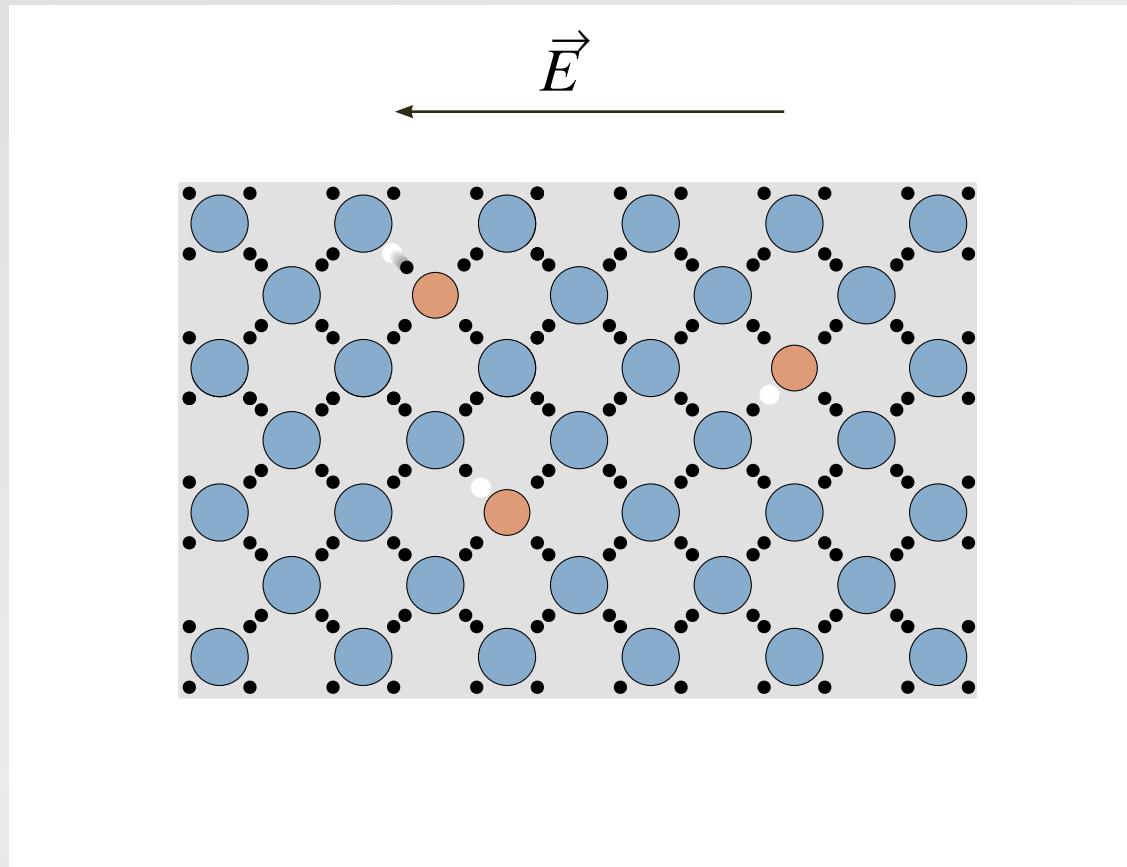
...presence of holes leads to conduction

# Doped semiconductors



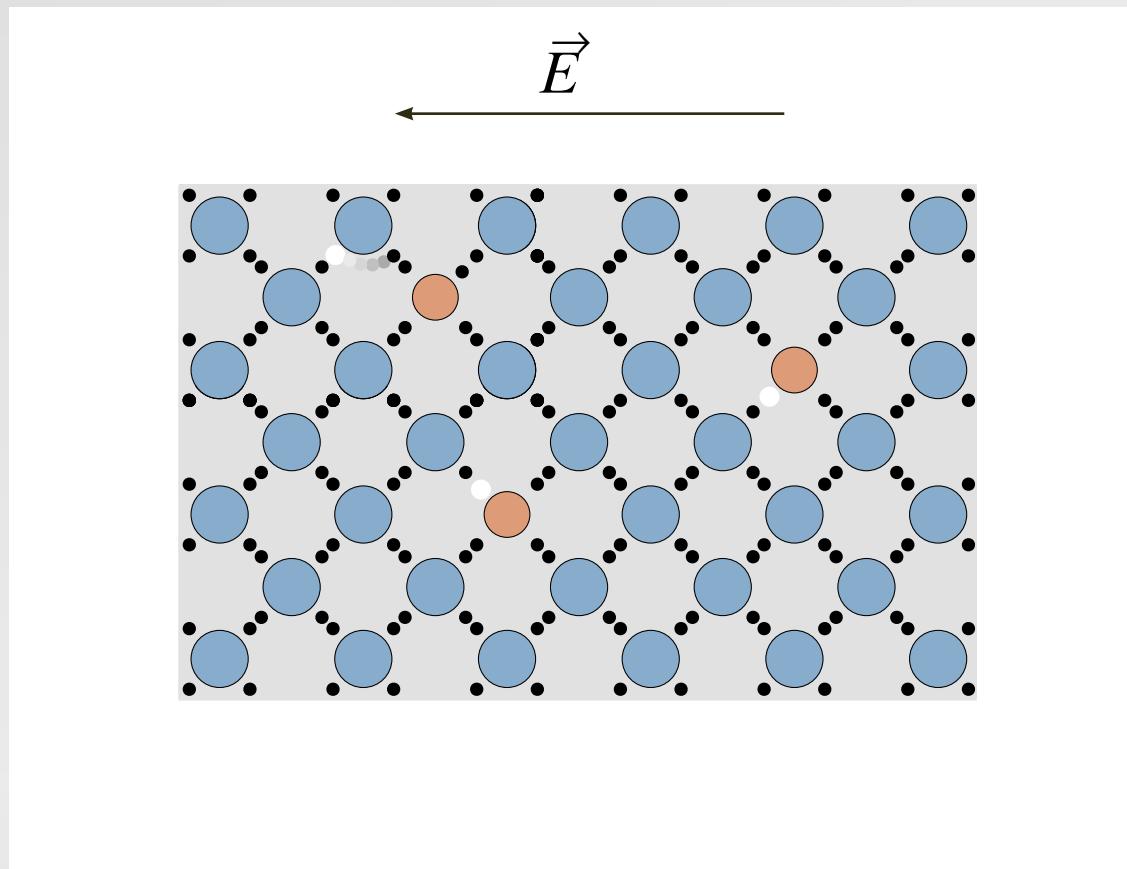
...presence of holes leads to conduction

# Doped semiconductors



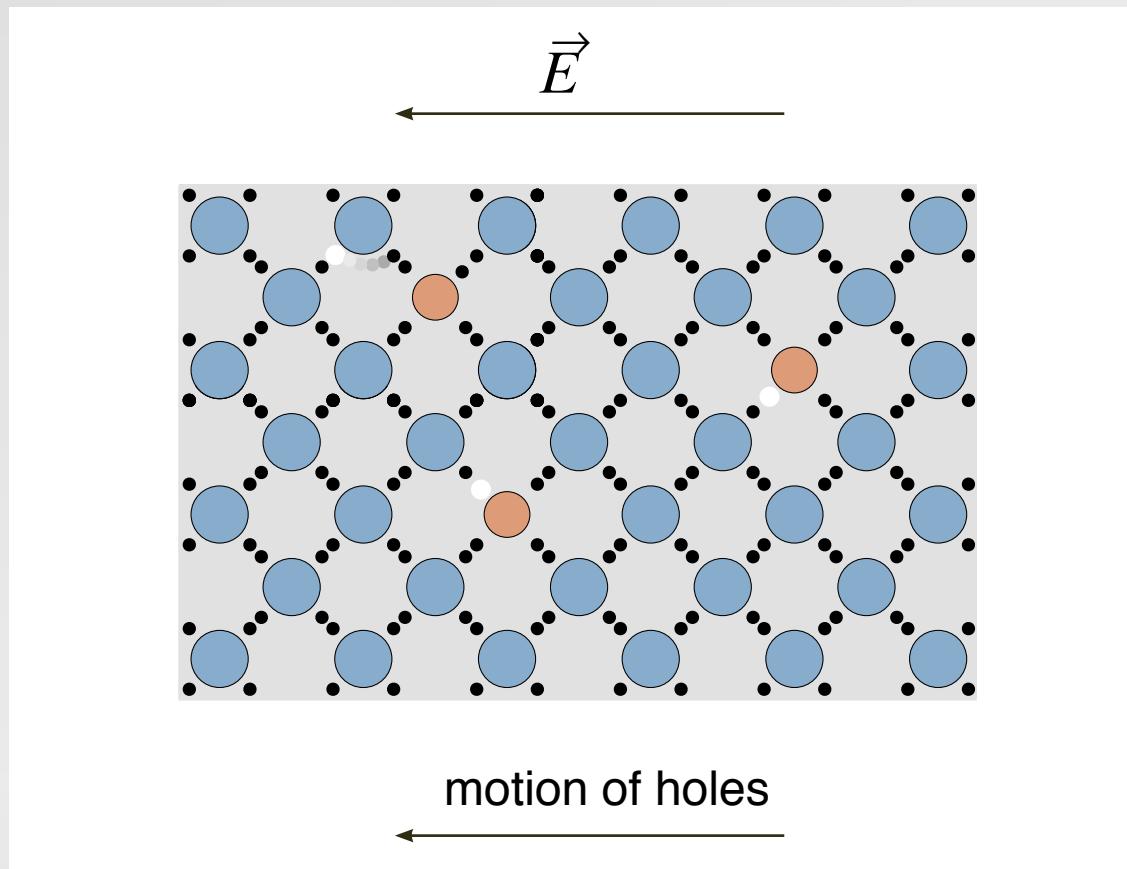
...presence of holes leads to conduction

# Doped semiconductors



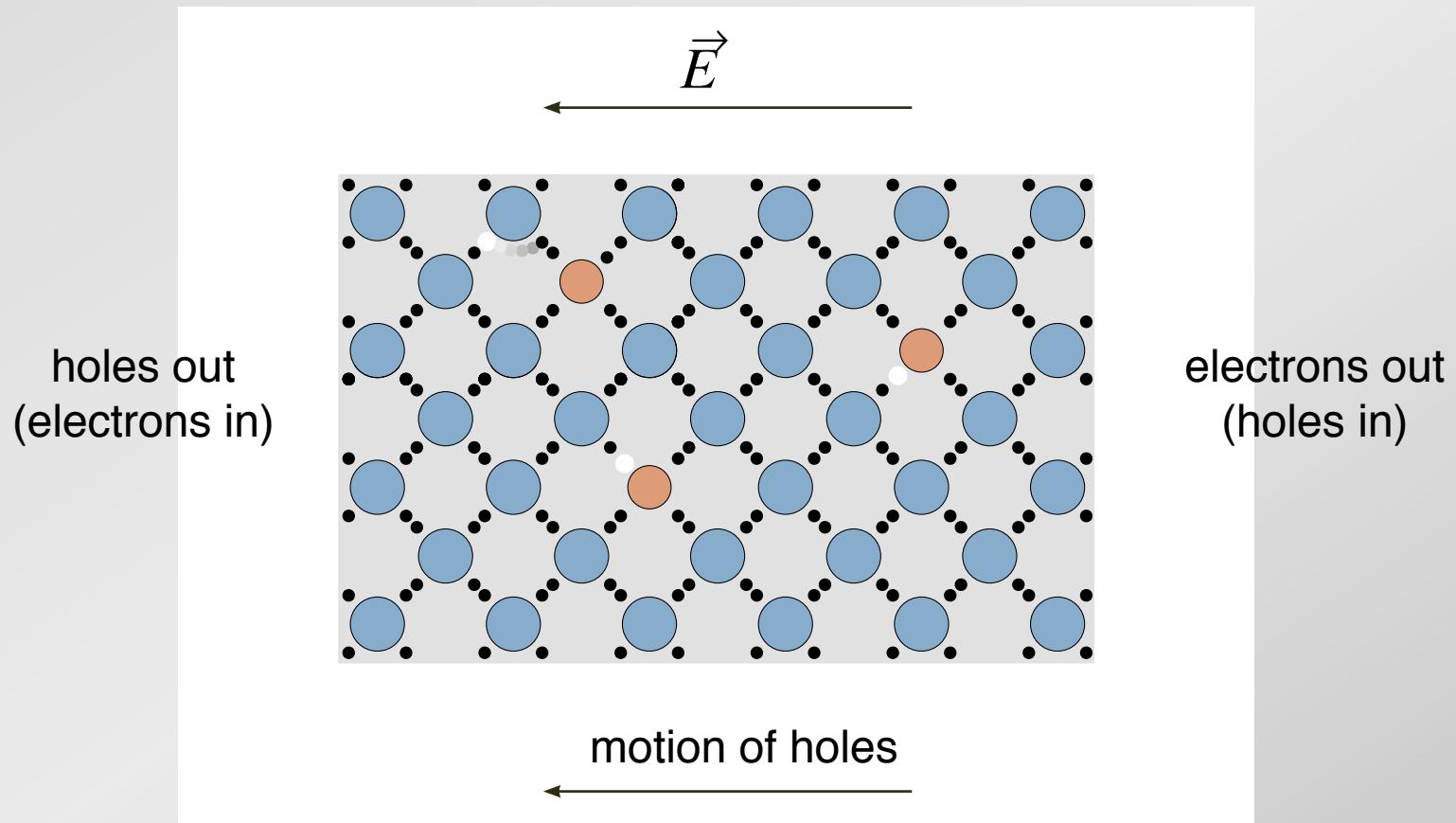
...presence of holes leads to conduction

# Doped semiconductors



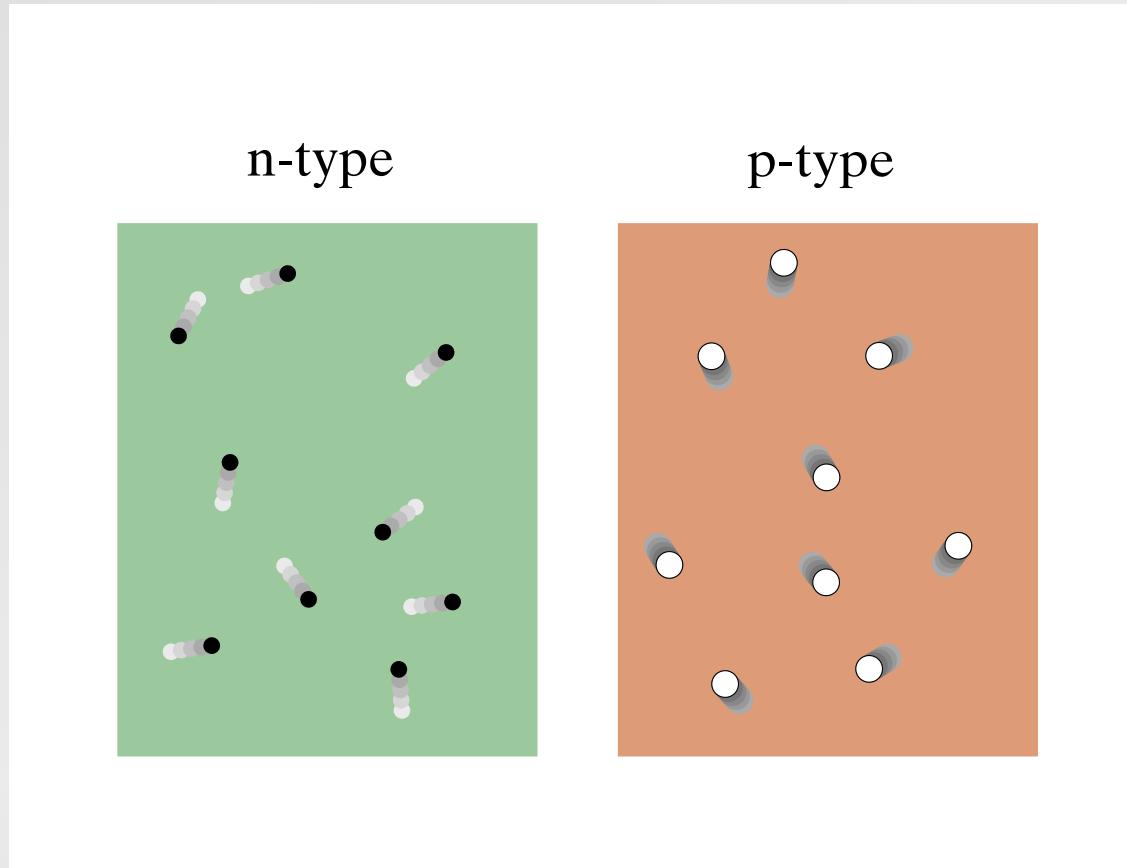
**holes are like positively charged particles**

# Doped semiconductors



**holes are like positively charged particles**

# Doped semiconductors



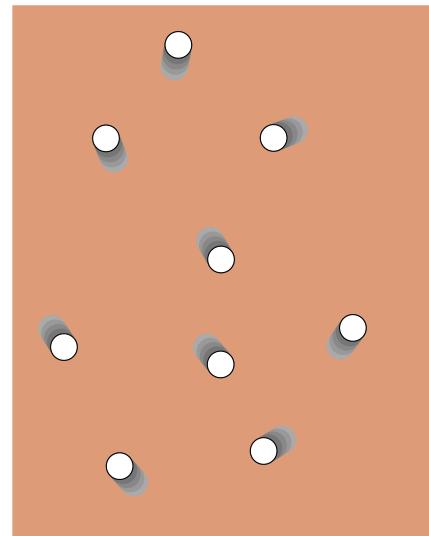
simplify representation

# Outline

- doped semiconductors
- *pn*-junctions
- black silicon

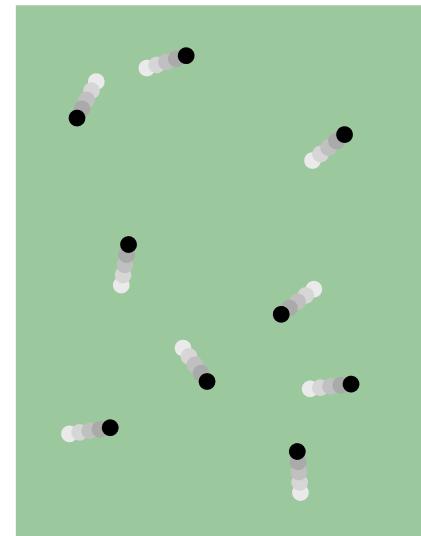
# *pn-junctions*

neutral



p-type

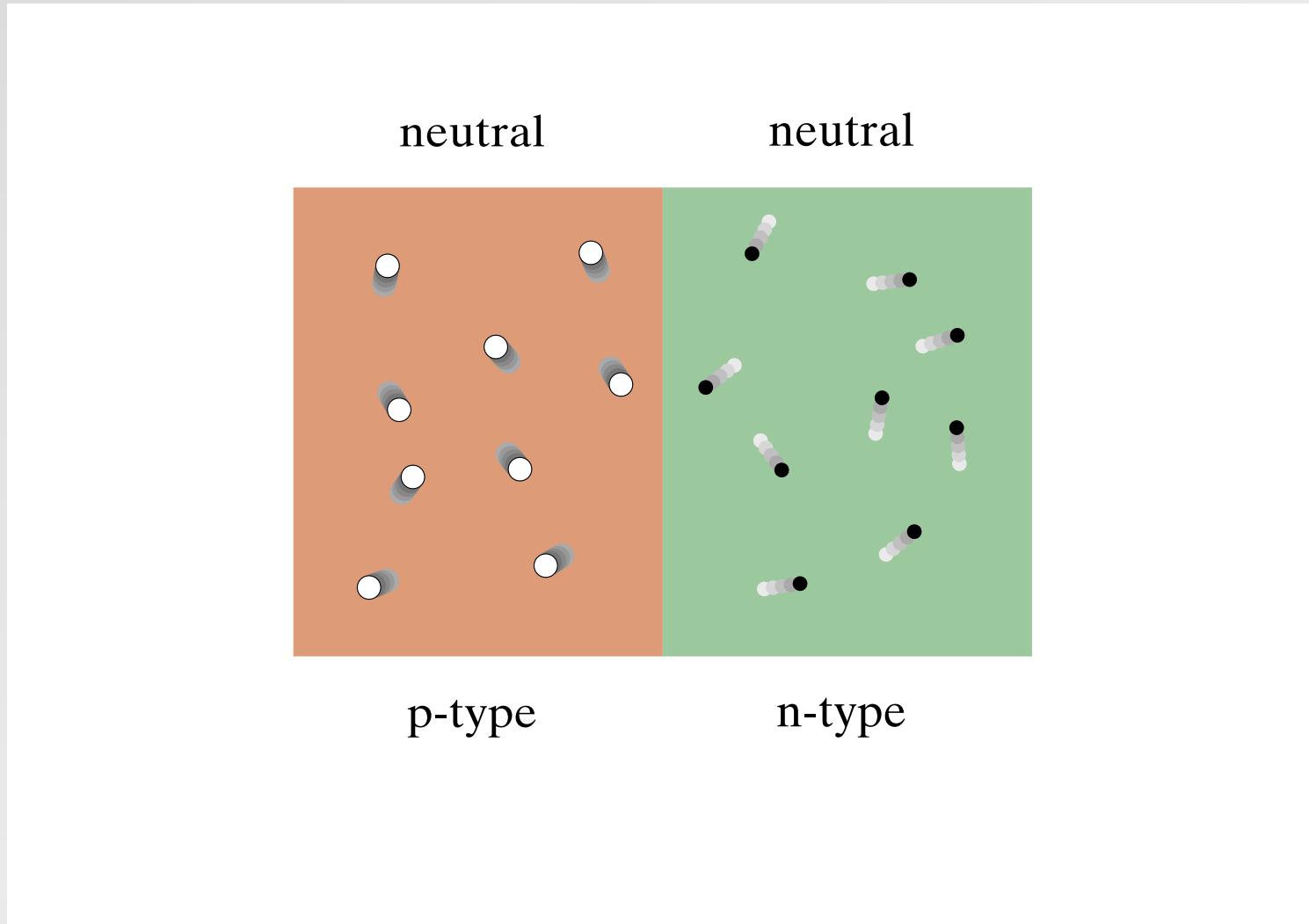
neutral



n-type

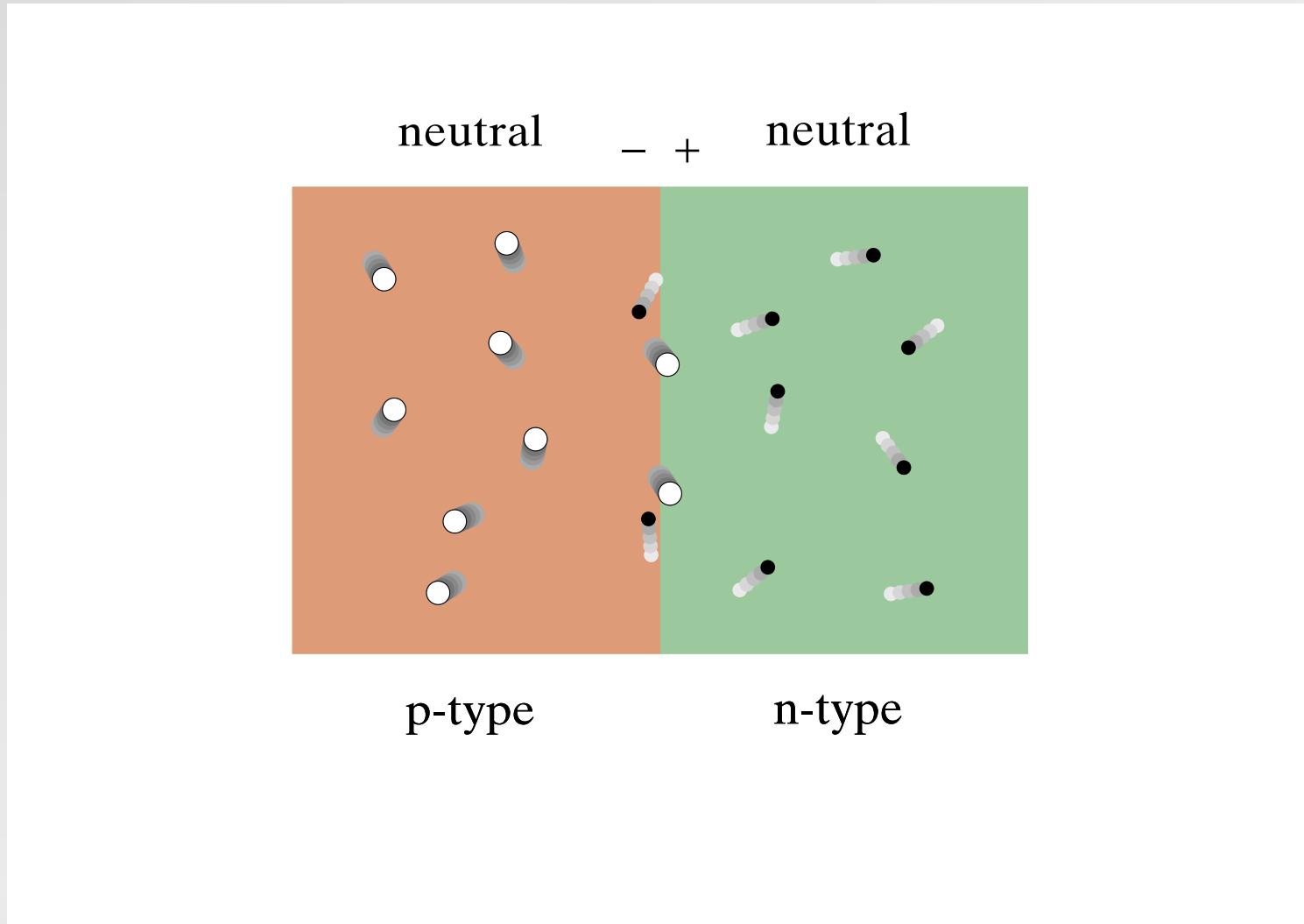
**bring *p* and *n* materials together...**

# *pn-junctions*



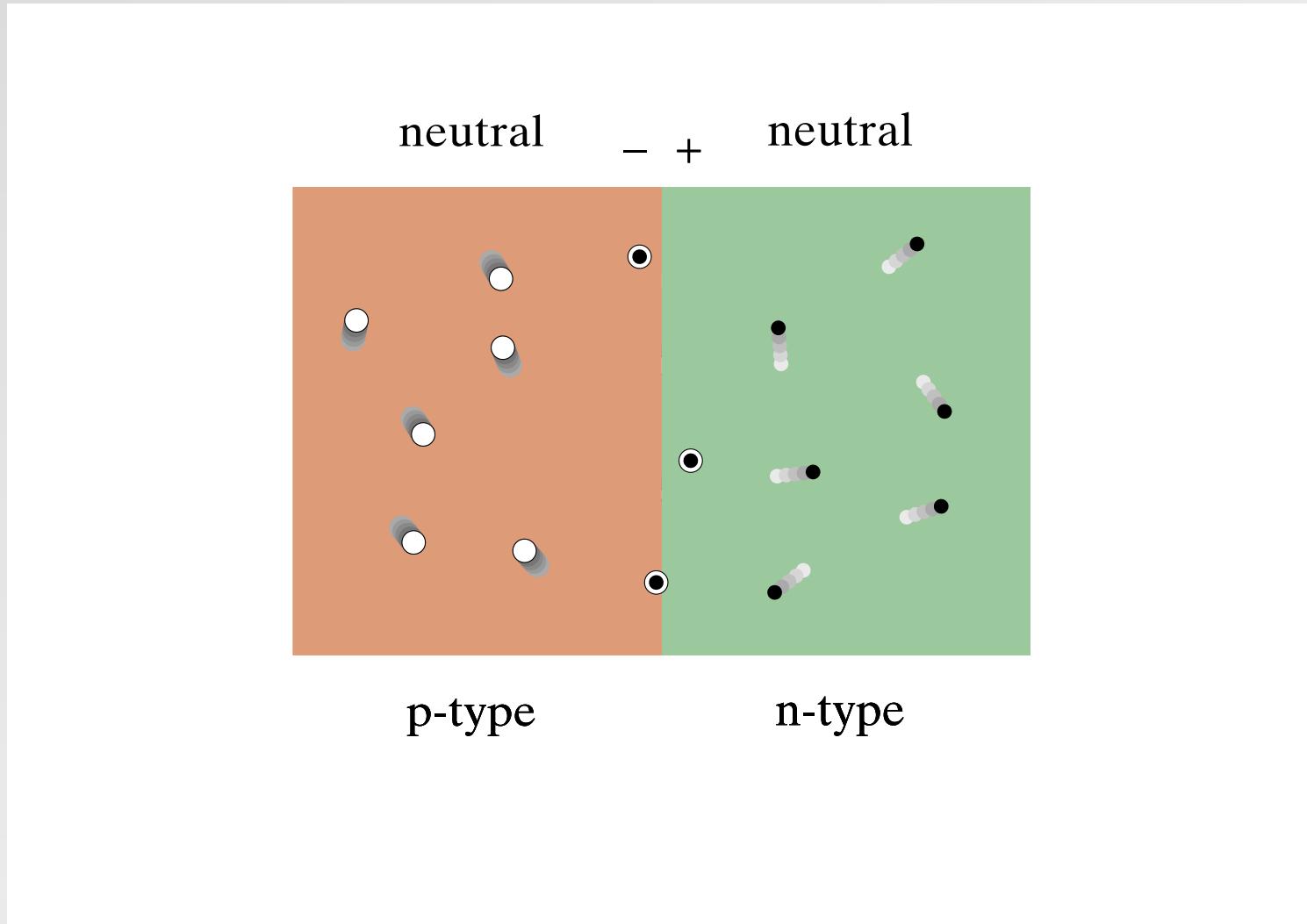
**bring *p* and *n* materials together...**

# *pn-junctions*



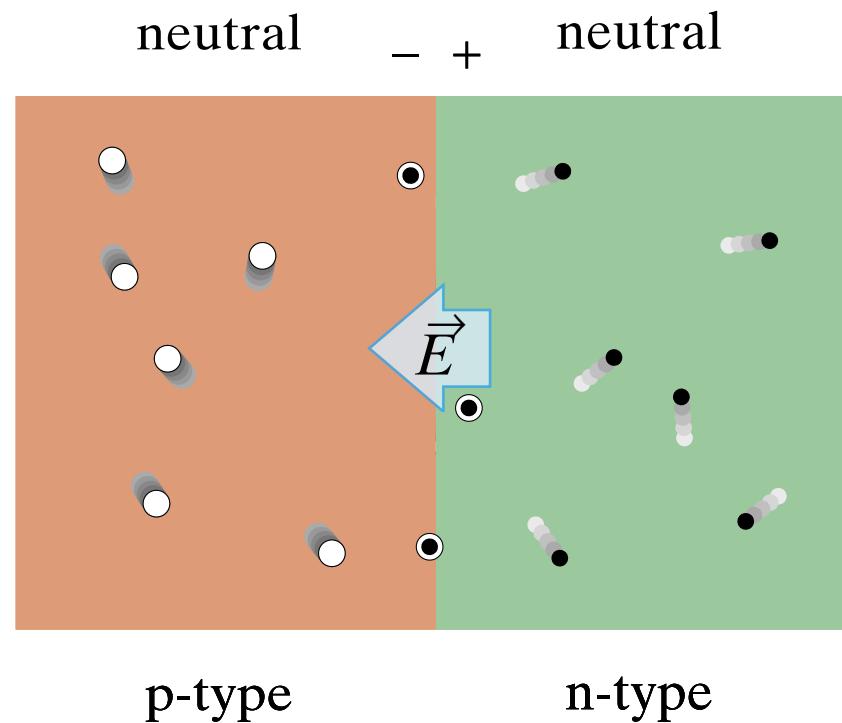
**electrons and holes diffuse across junction...**

# *pn-junctions*



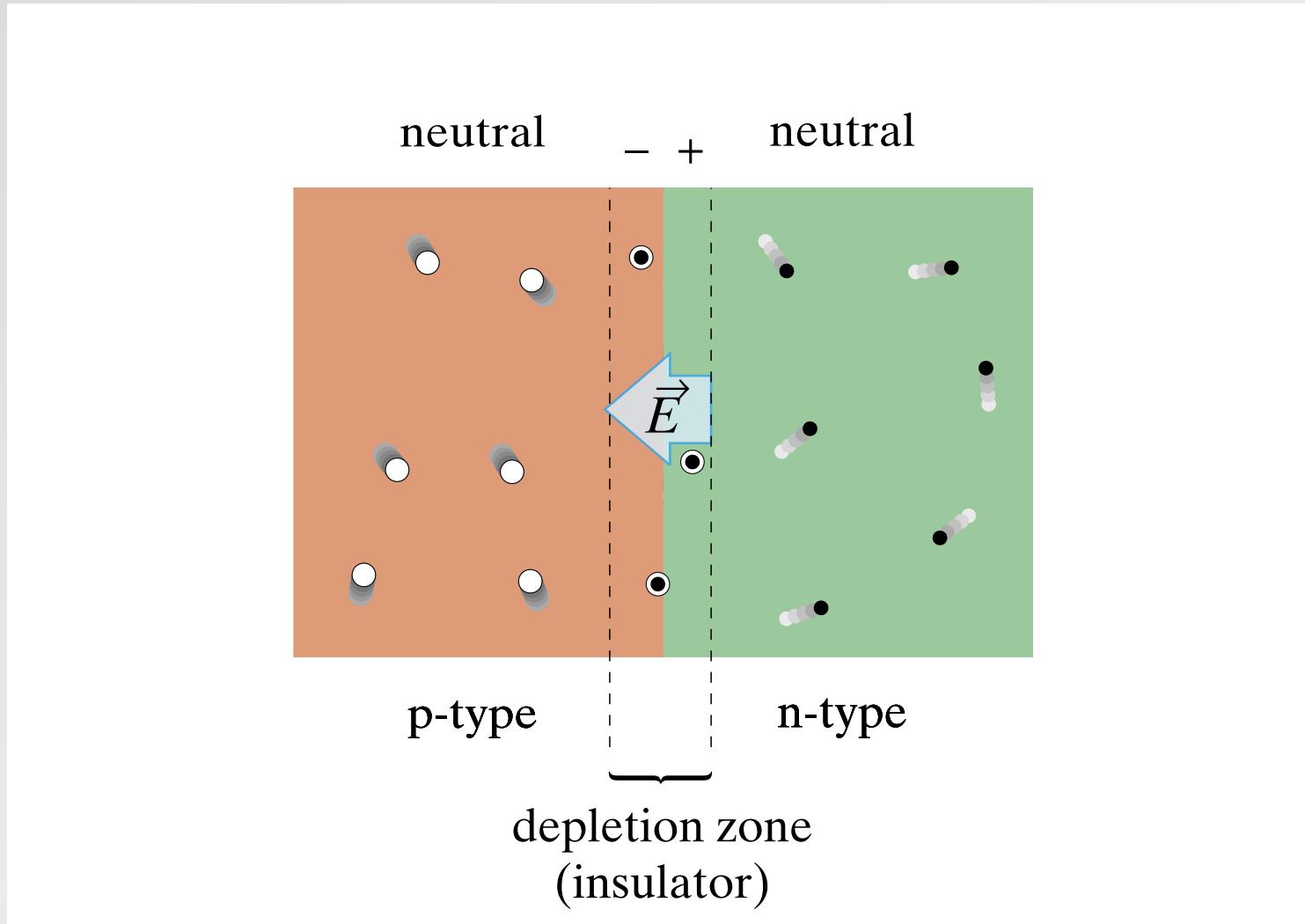
...and get 'trapped' after they combine

# *pn-junctions*



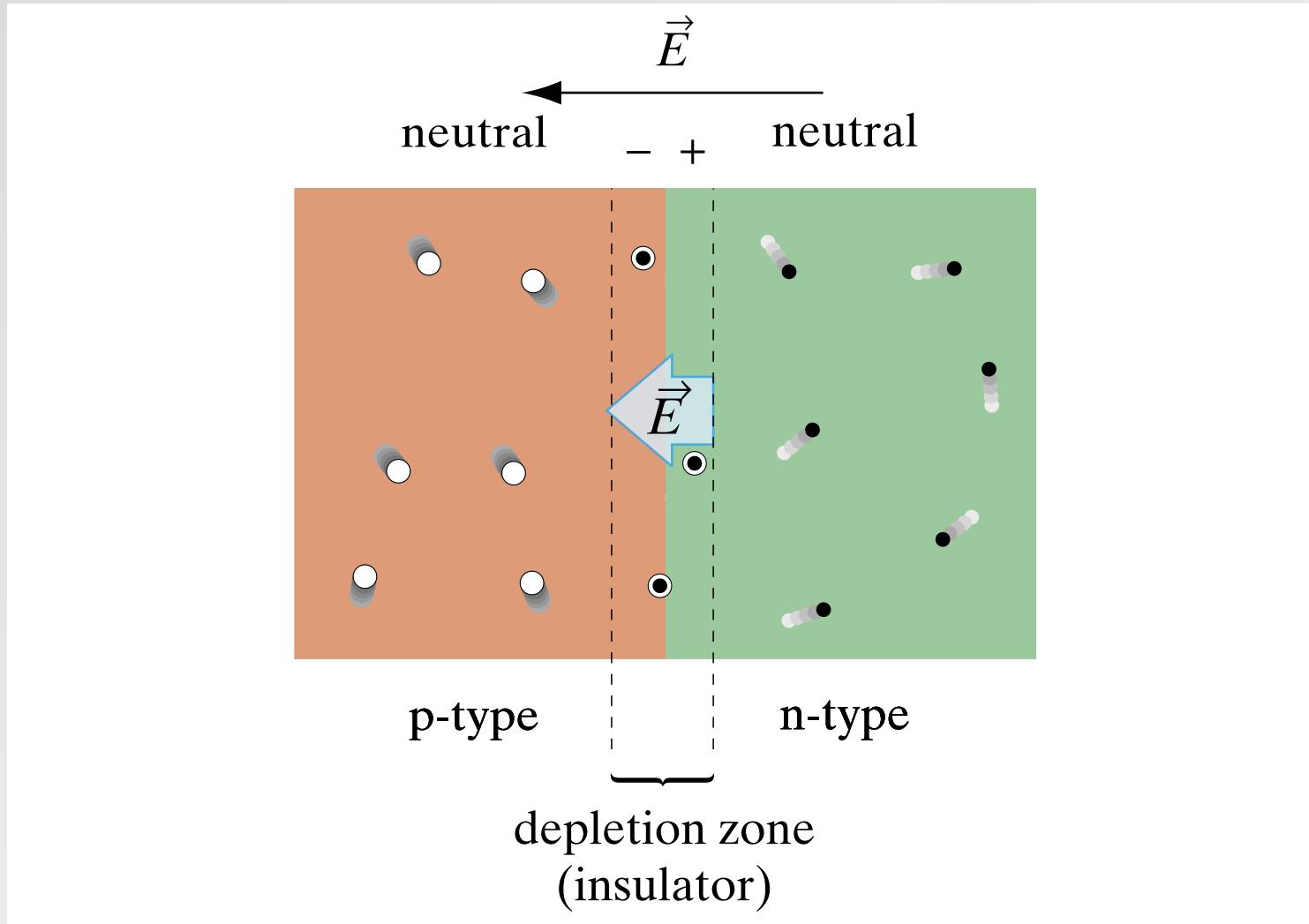
**build-up of charge leads to electric field that stops diffusion**

# *pn-junctions*



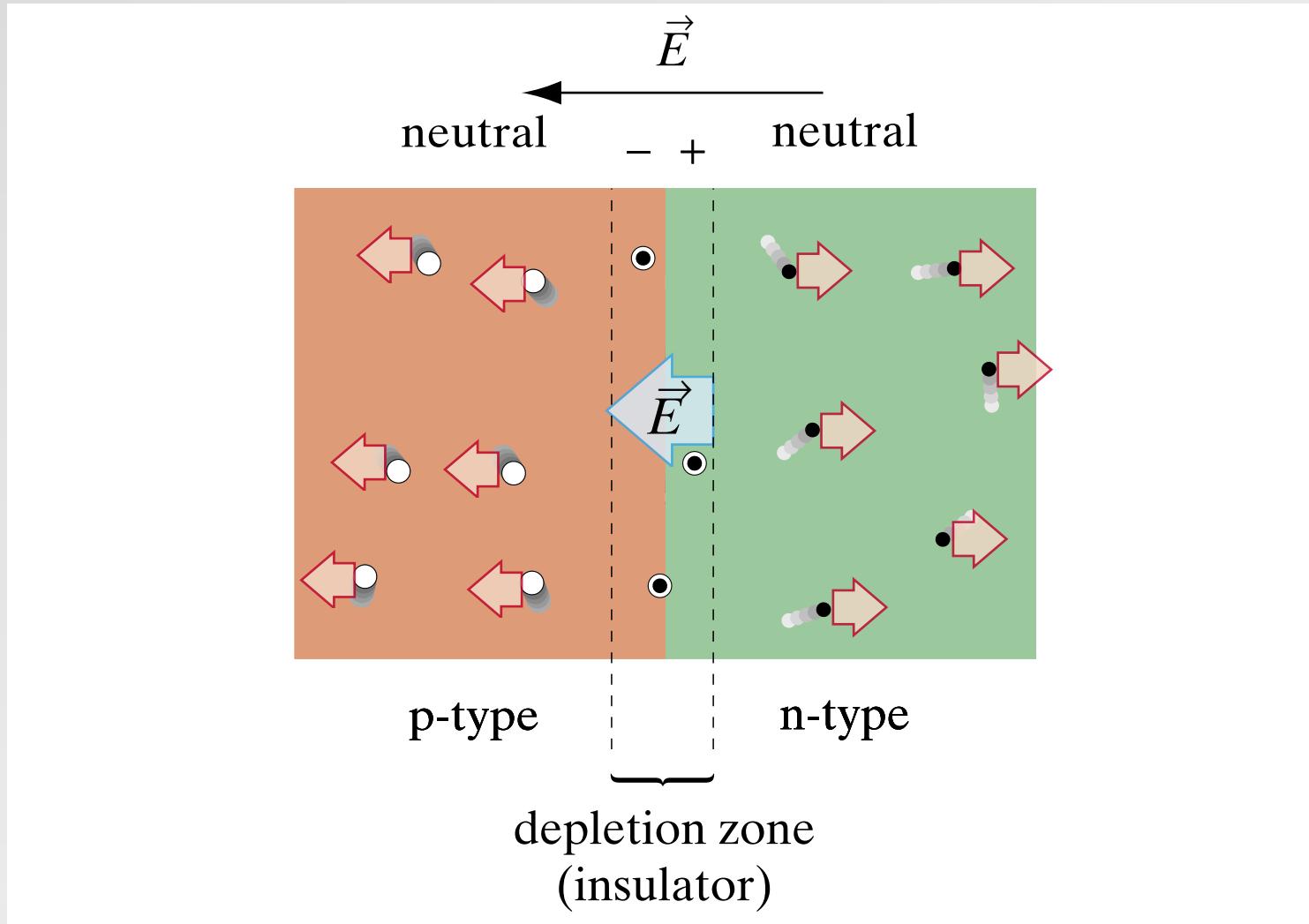
**non-conducting layer at junction**

# *pn-junctions*



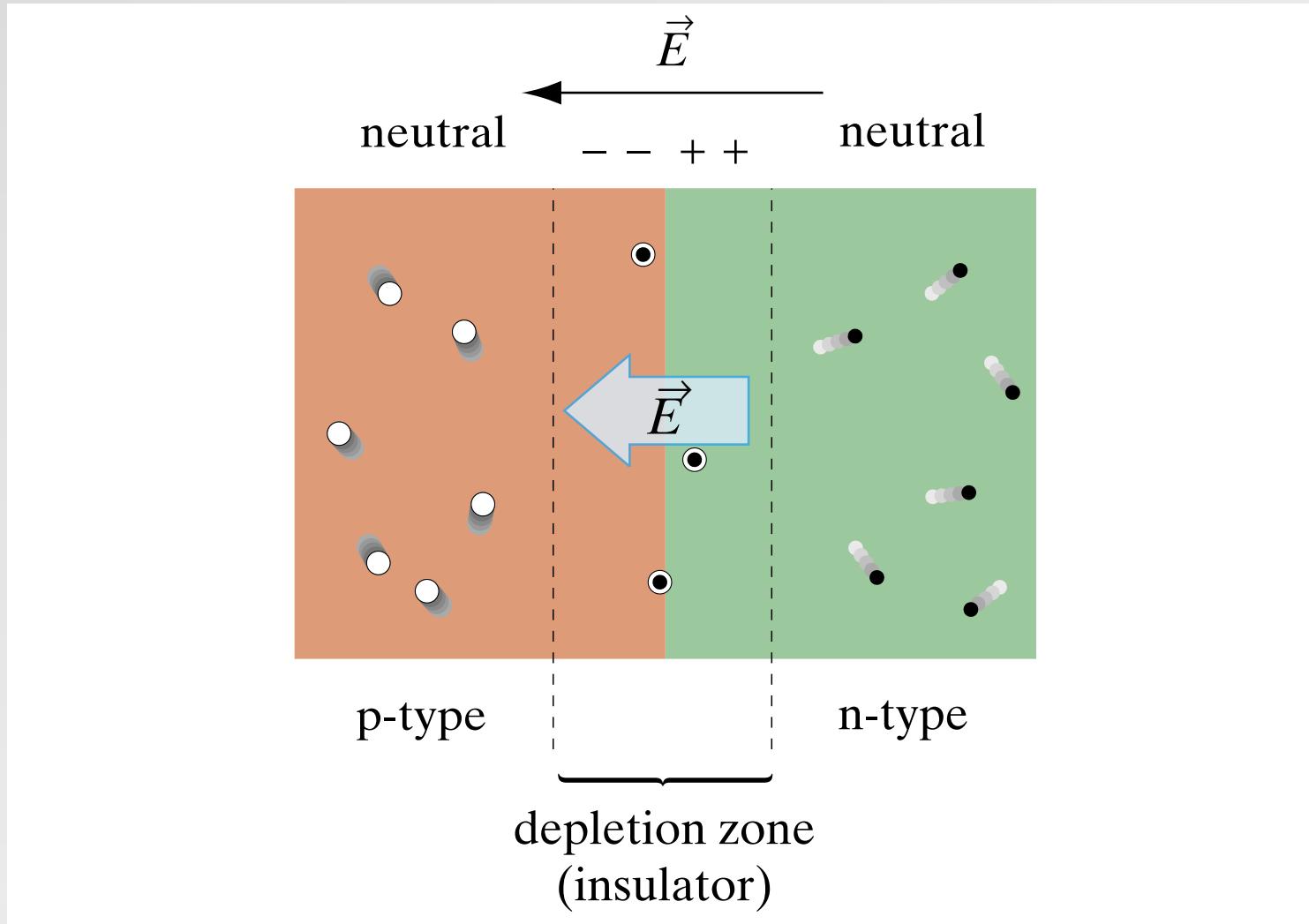
**apply electric field...**

# *pn-junctions*



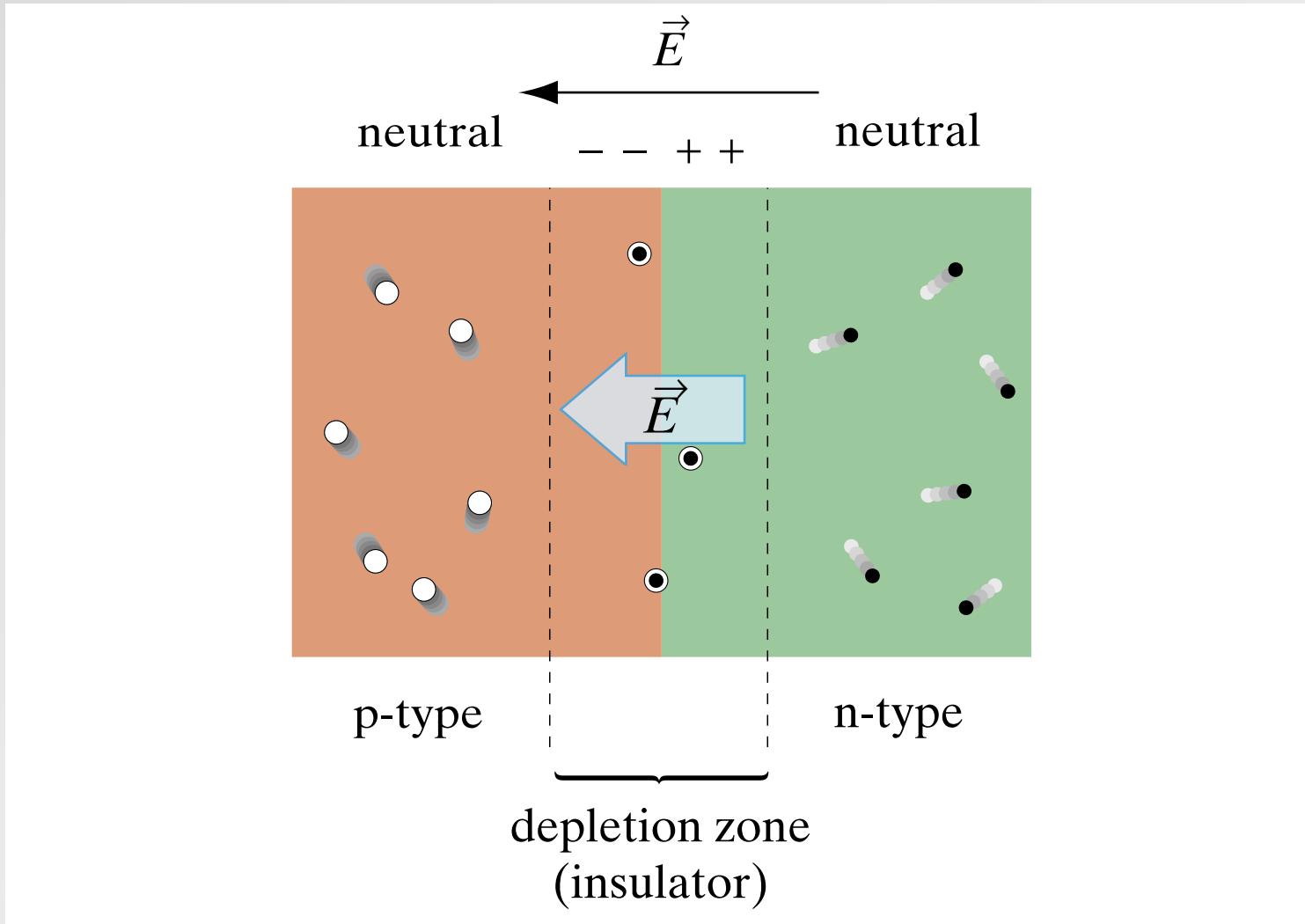
**...holes pushed to left, electrons to right...**

# *pn-junctions*



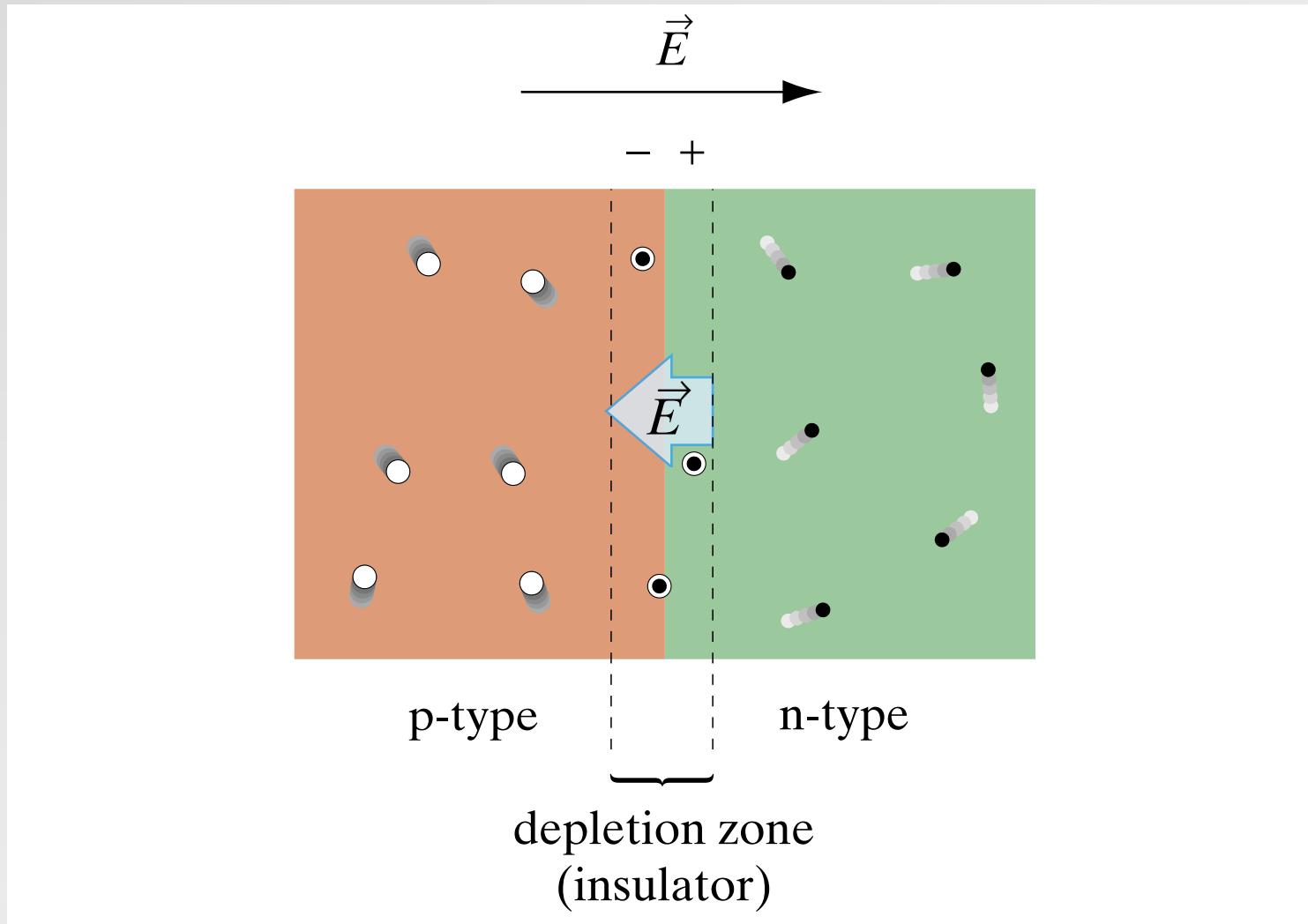
**...and so depletion zone expands**

# *pn-junctions*



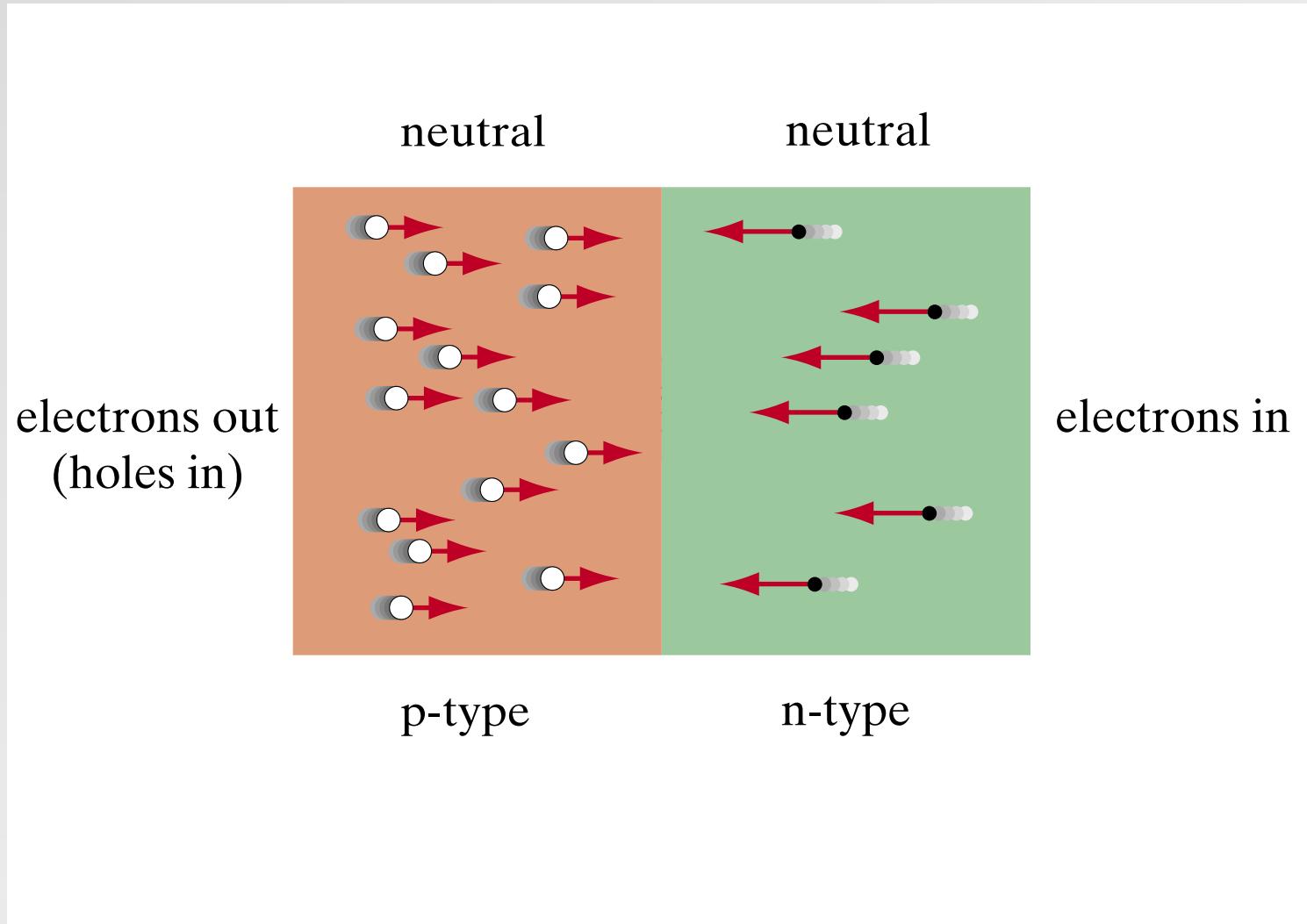
**NO conduction**

# *pn-junctions*



reverse electric field...

# *pn-junctions*



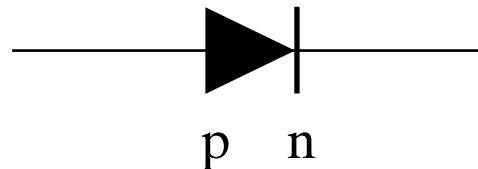
**...depletion zone shrinks and current flows**

# ***pn-junctions***

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

# *pn-junctions*

diode

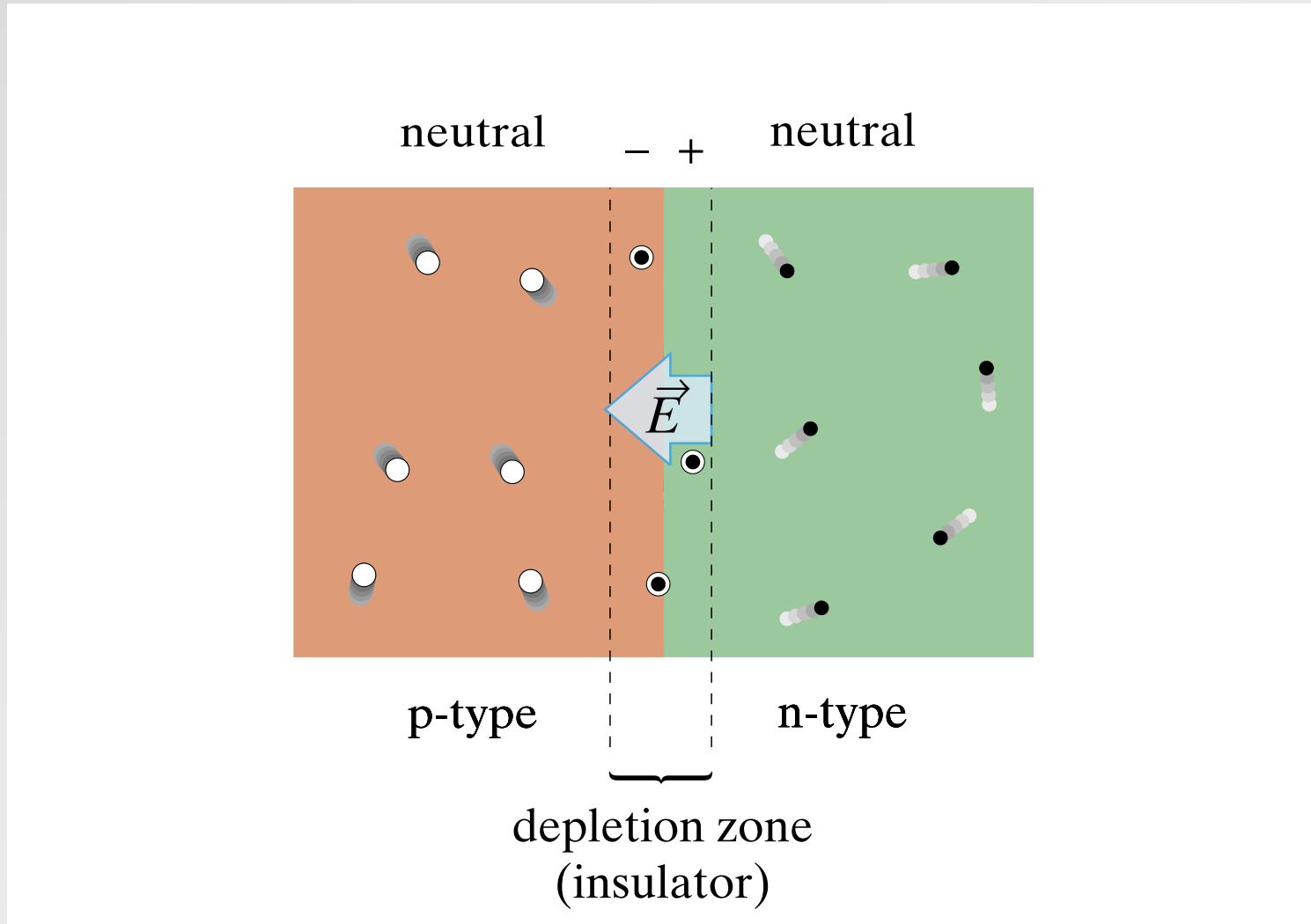


**current flows along arrow only (from *p* to *n*)**

# ***pn-junctions***

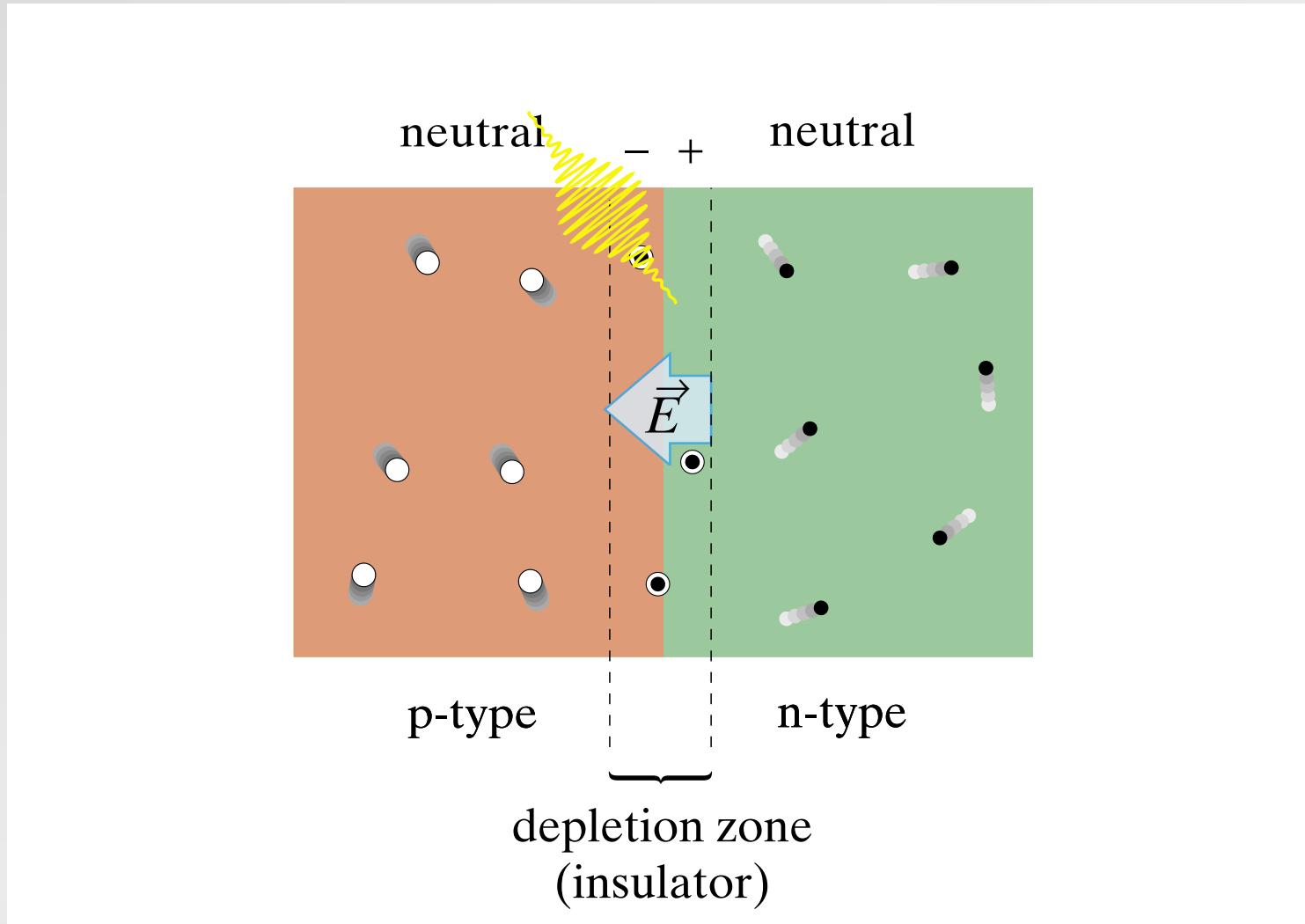
**can also be used as a light detector!**

# *pn-junctions*



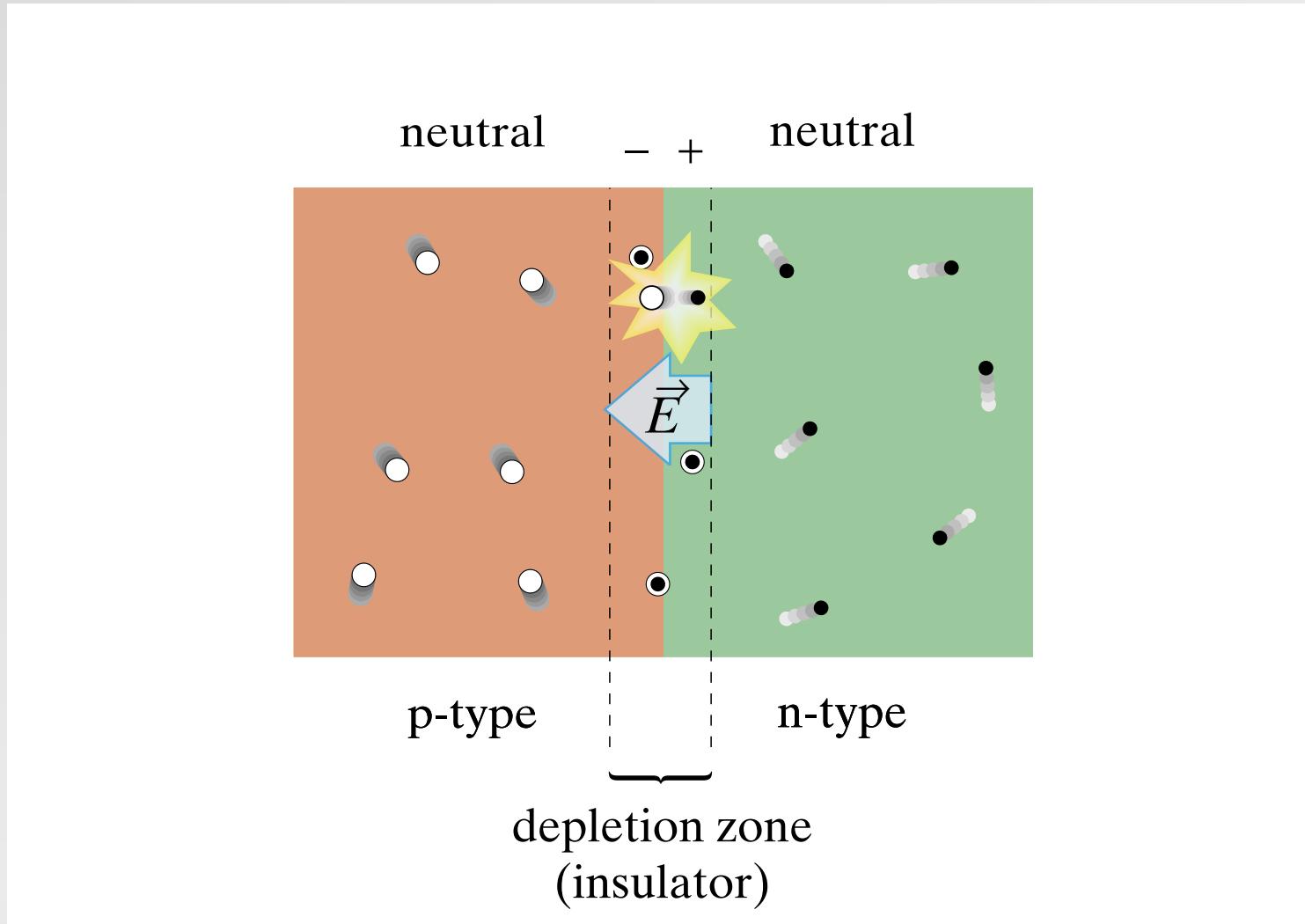
**depletion layer can convert light into electric energy**

# *pn-junctions*



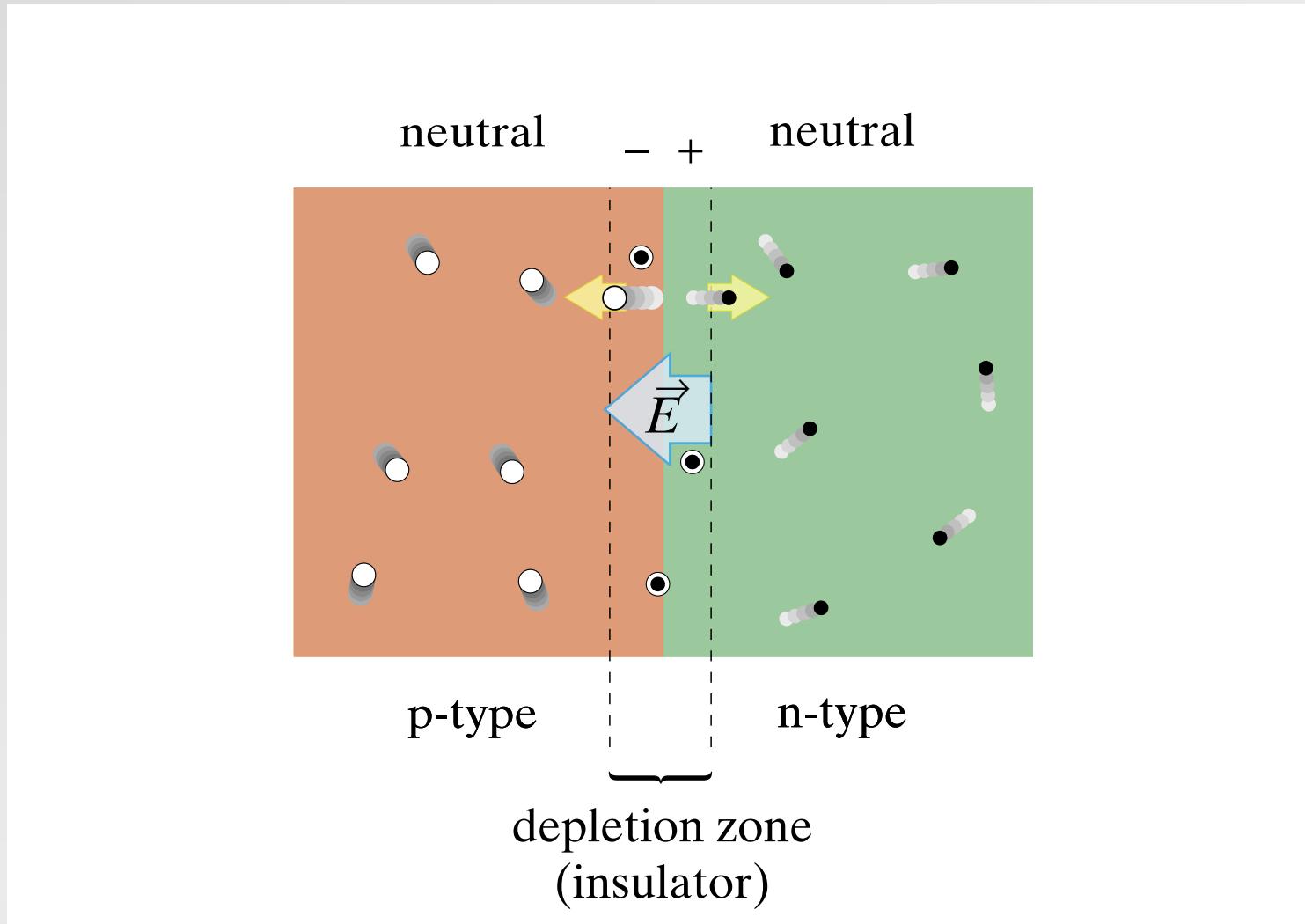
**incident photon knocks out electron...**

# *pn-junctions*



**...creating an electron-hole pair**

# *pn-junctions*

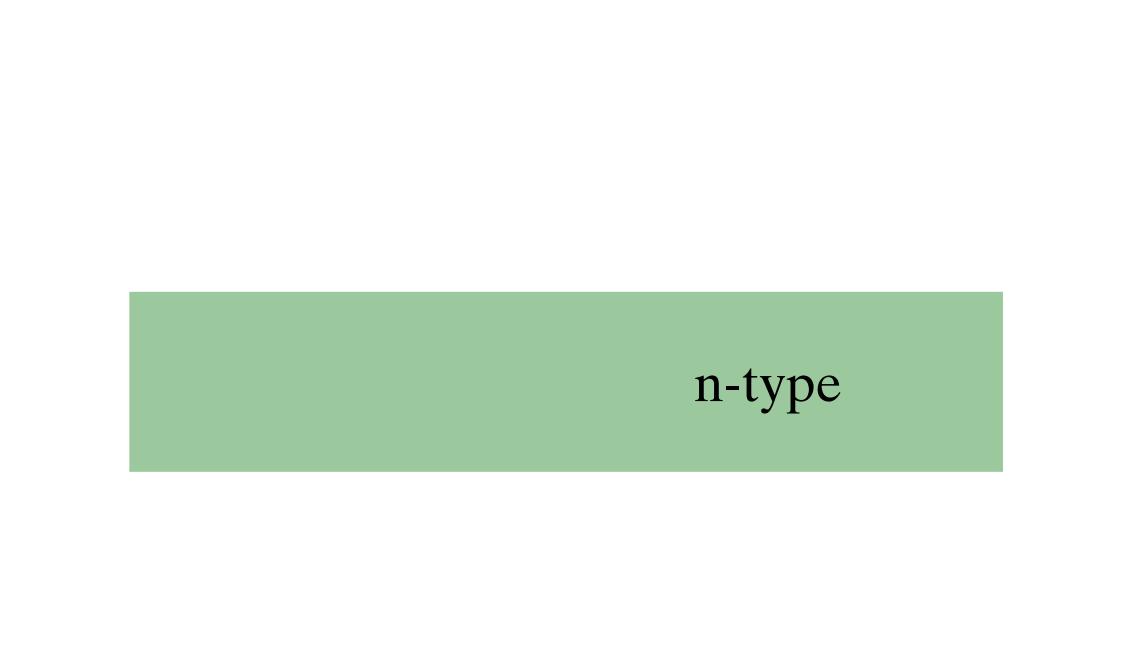


**E-field separates eh-pair, causing current**

# ***pn-junctions***

**how to make a miniature diode on a chip?**

# *pn-junctions*

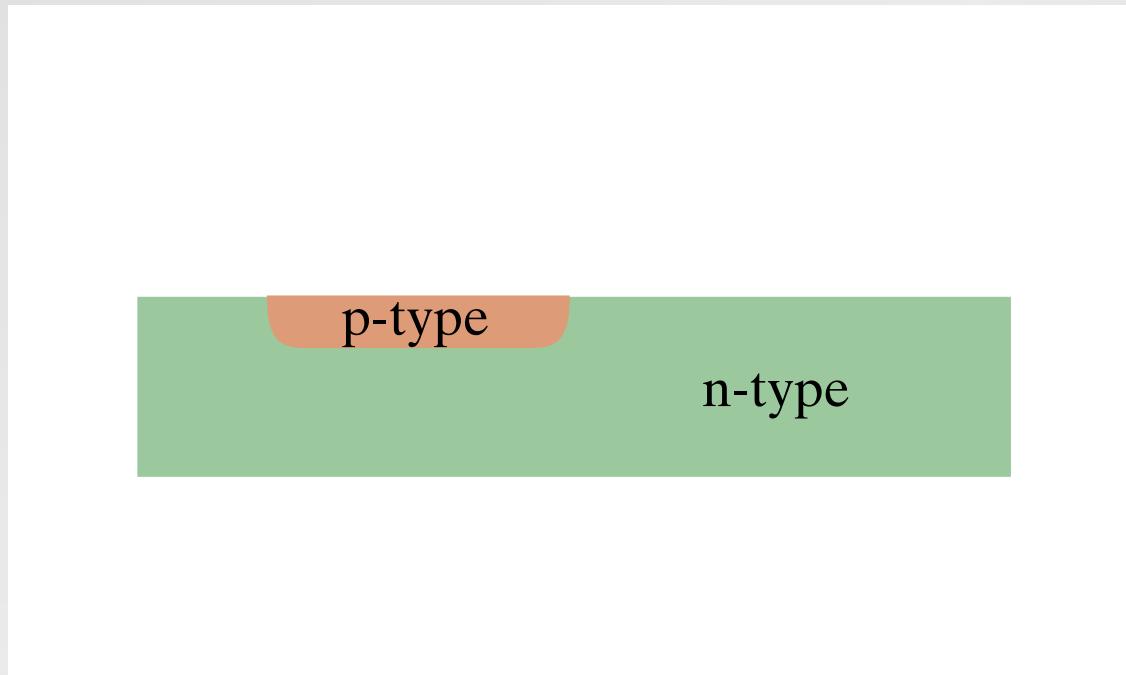


n-type

A diagram showing a white rectangular background with a central green horizontal bar. The word "n-type" is written in white capital letters on the green bar.

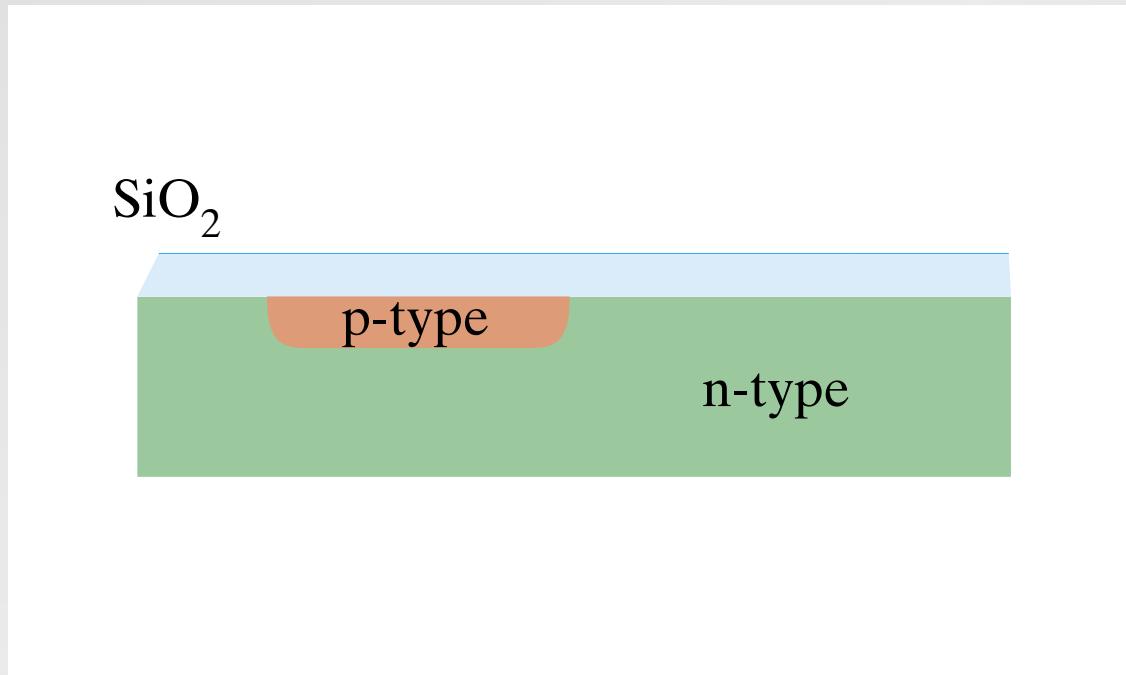
**begin with an *n*-doped wafer**

# *pn-junctions*



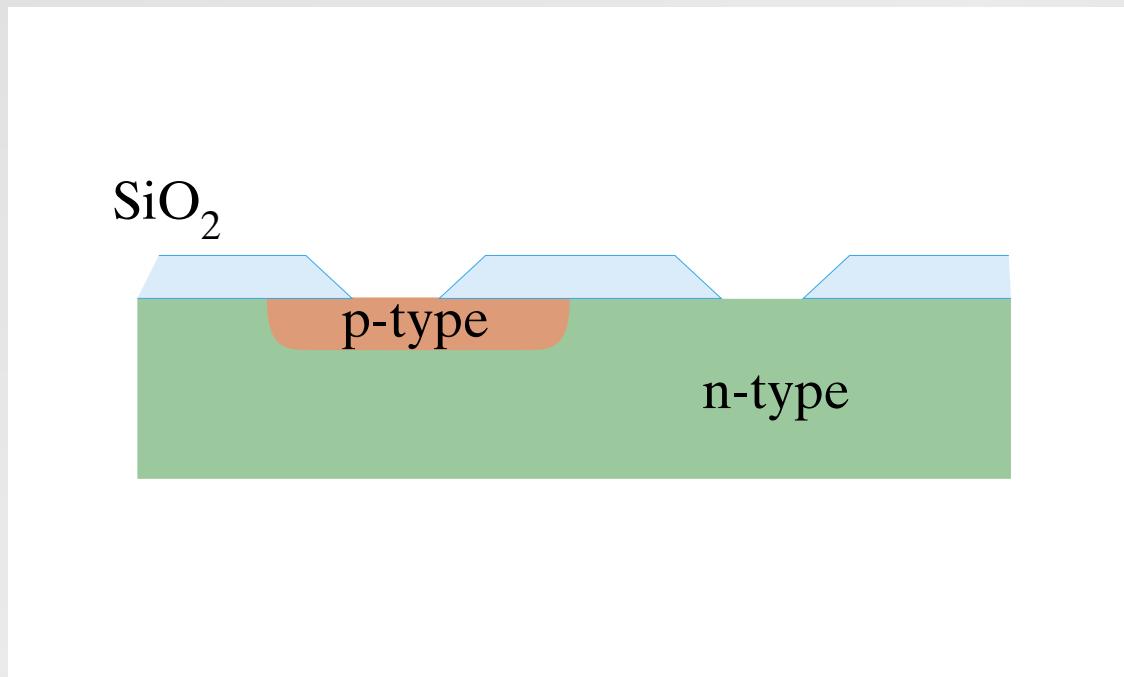
***p-dope small region***

# *pn-junctions*



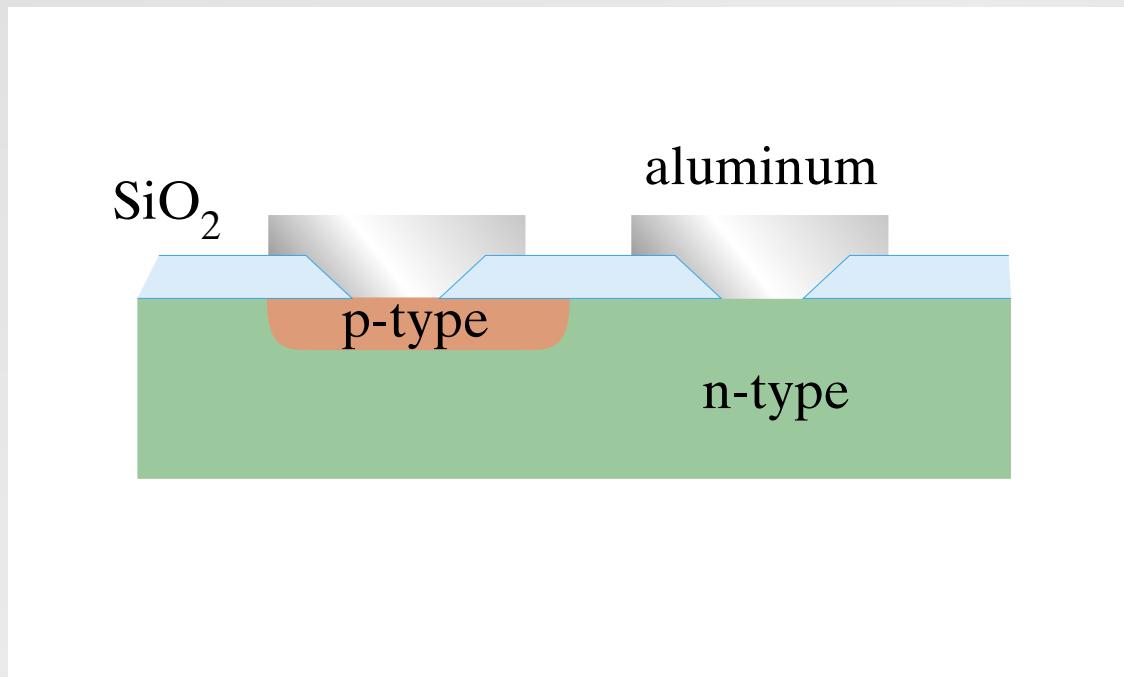
**cover with insulating layer**

# *pn-junctions*



**etch insulating layer**

# *pn-junctions*

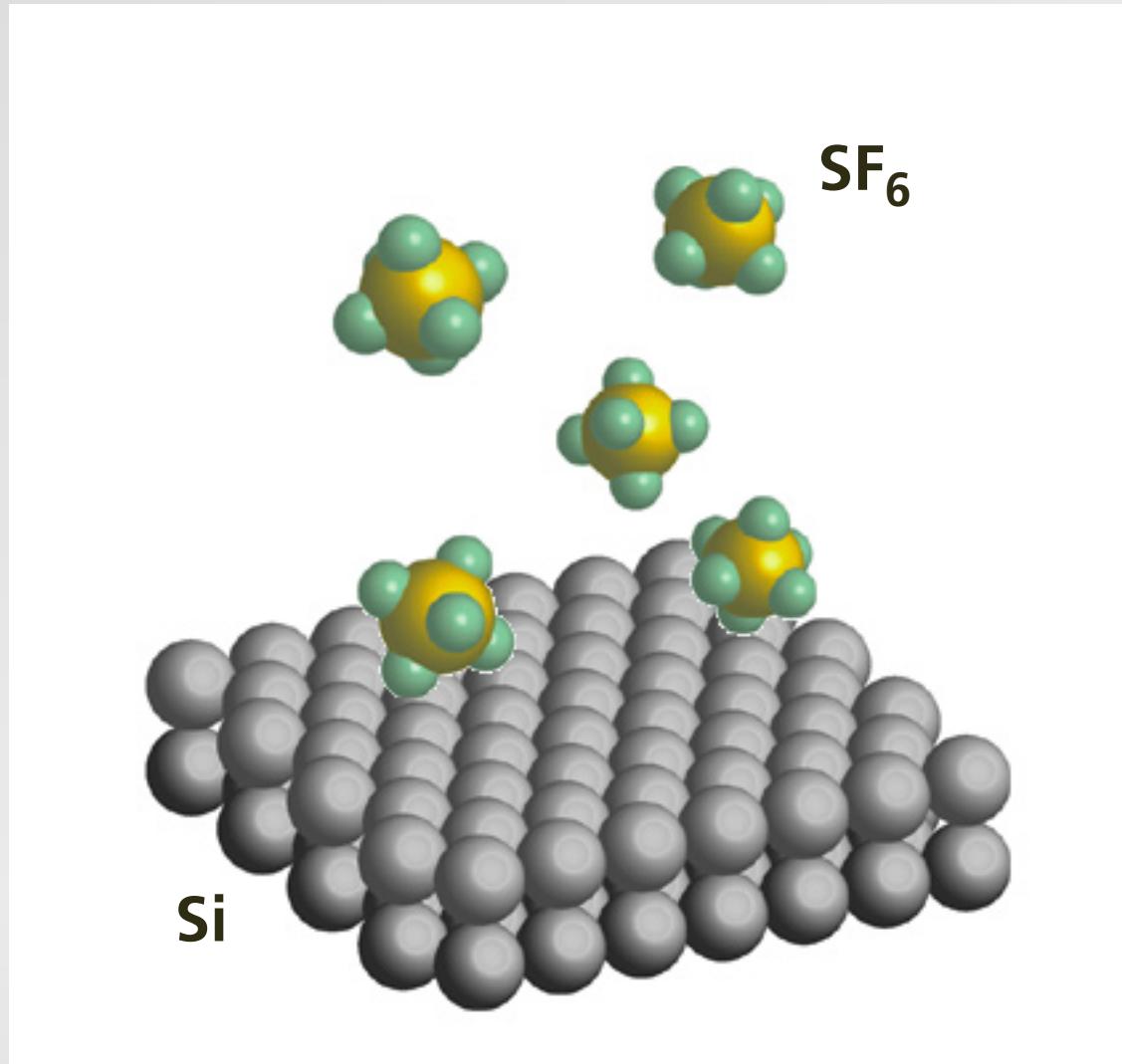


**add aluminum contacts**

# Outline

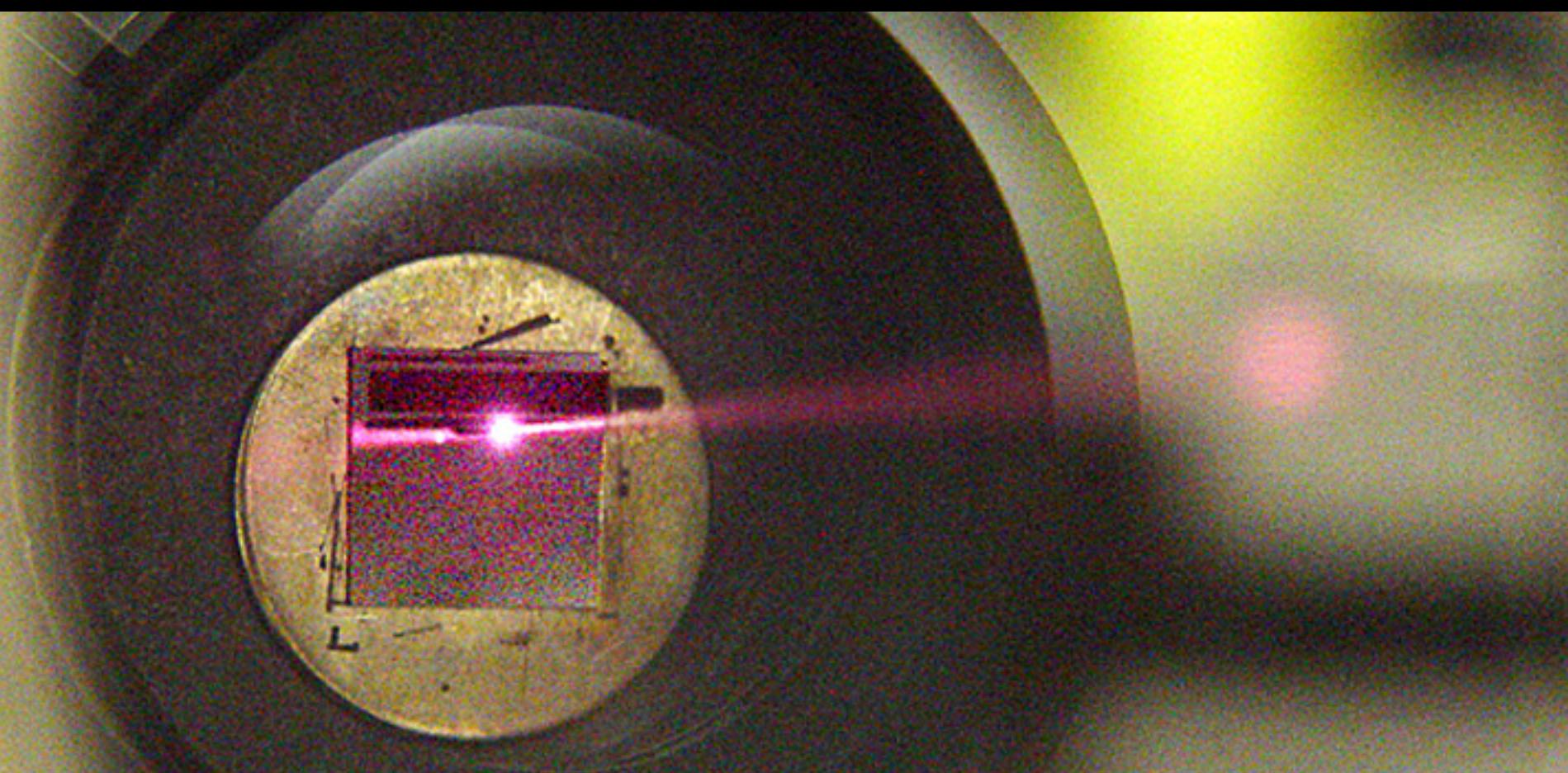
- doped semiconductors
- pn-junctions
- black silicon

# Black silicon

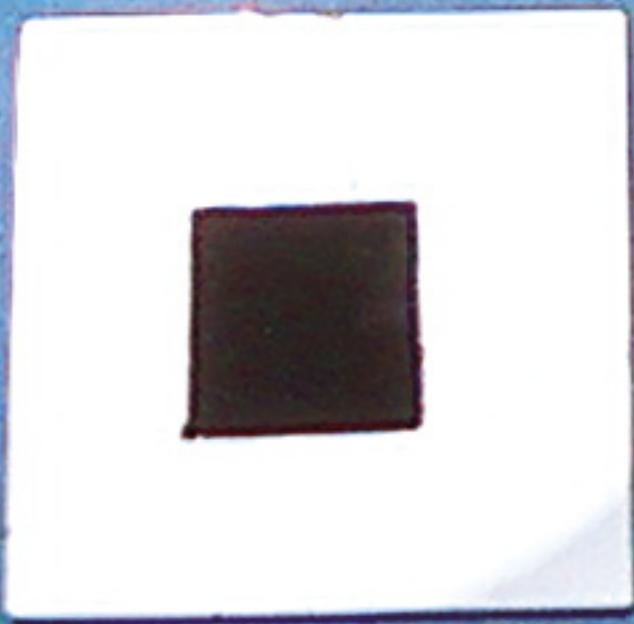


irradiate with 100-fs  $10 \text{ kJ/m}^2$  pulses

# Black silicon



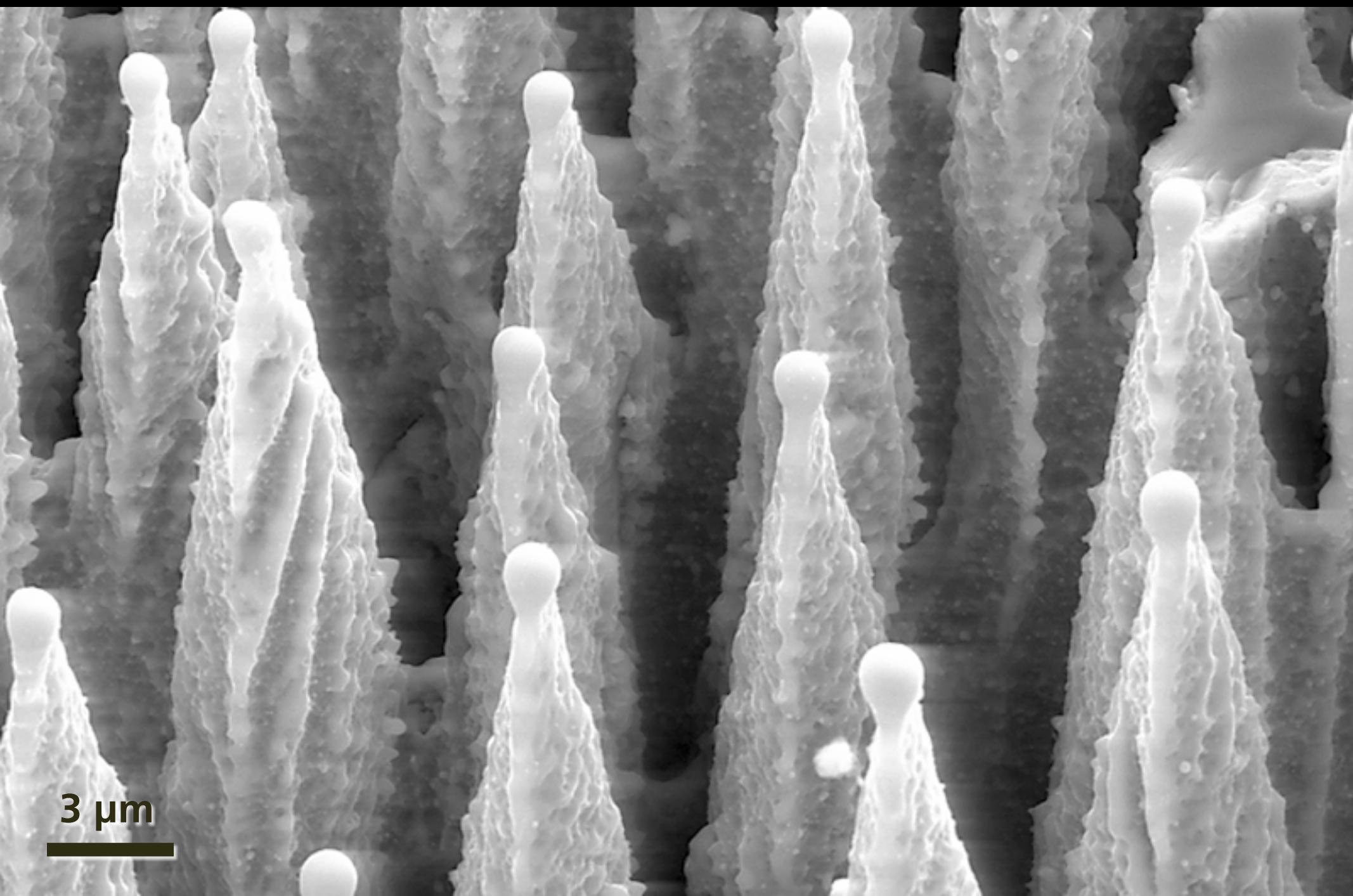
# Black silicon



**"black silicon"**

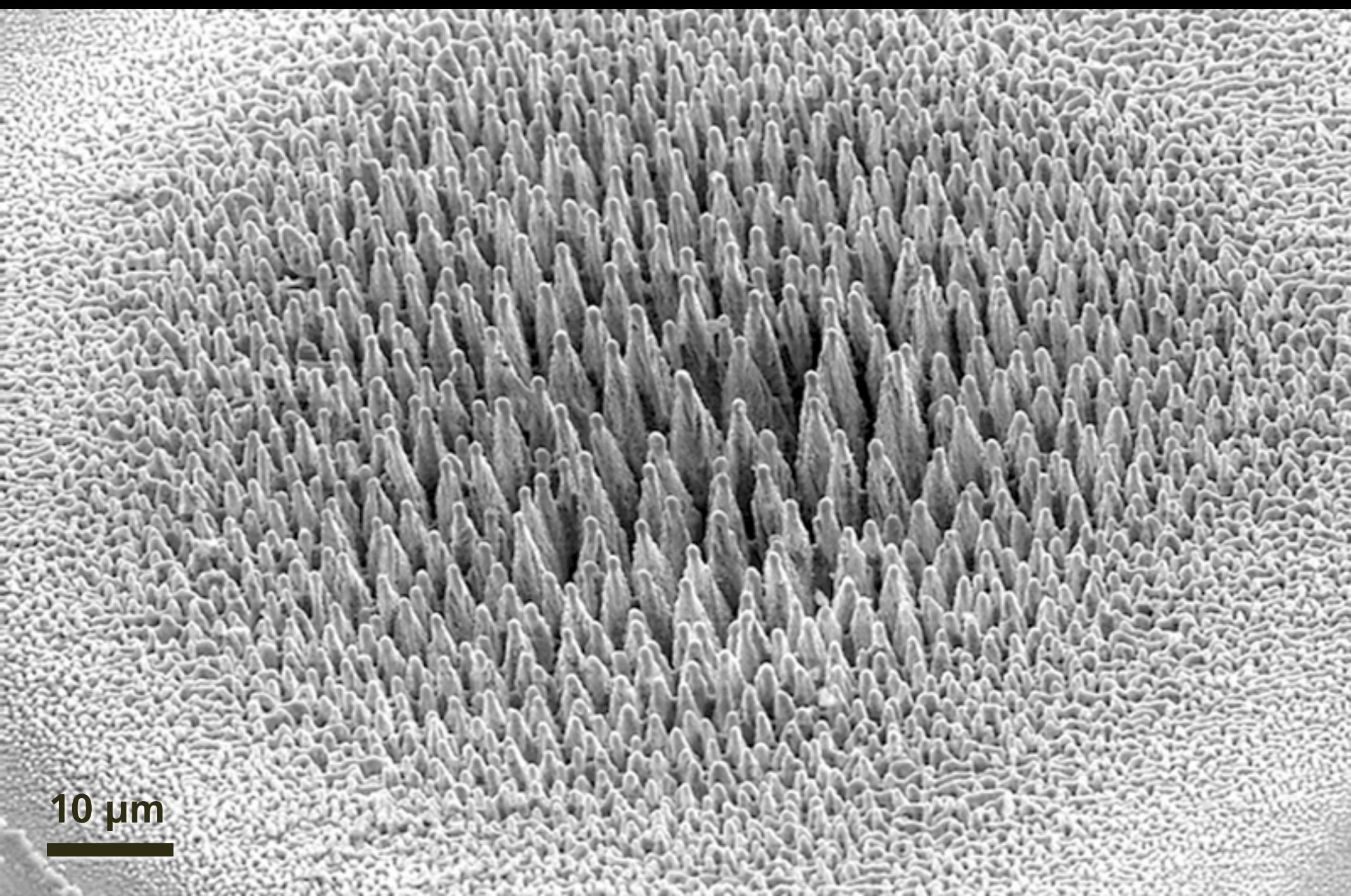


# Black silicon



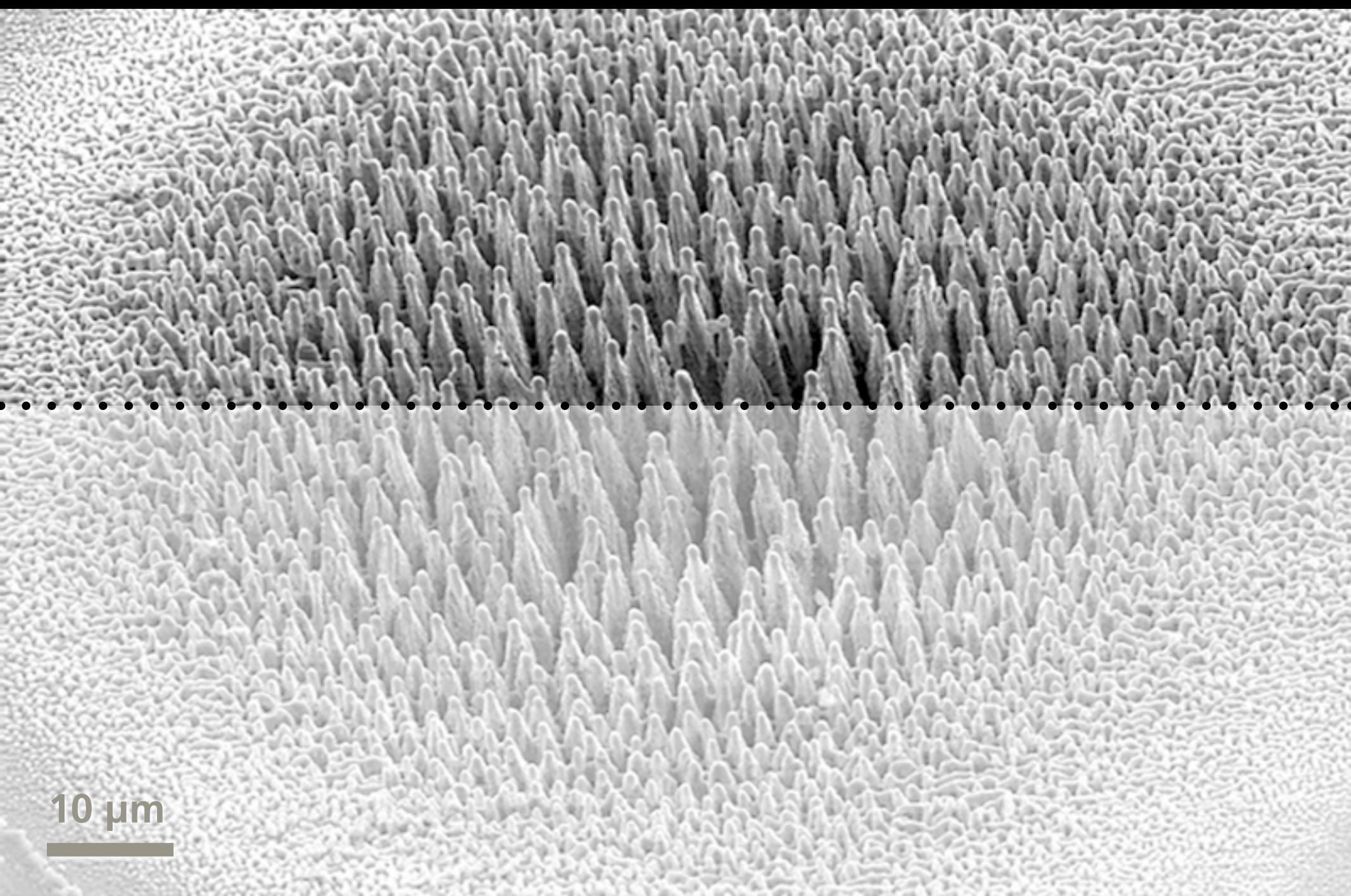
3  $\mu\text{m}$

# Black silicon



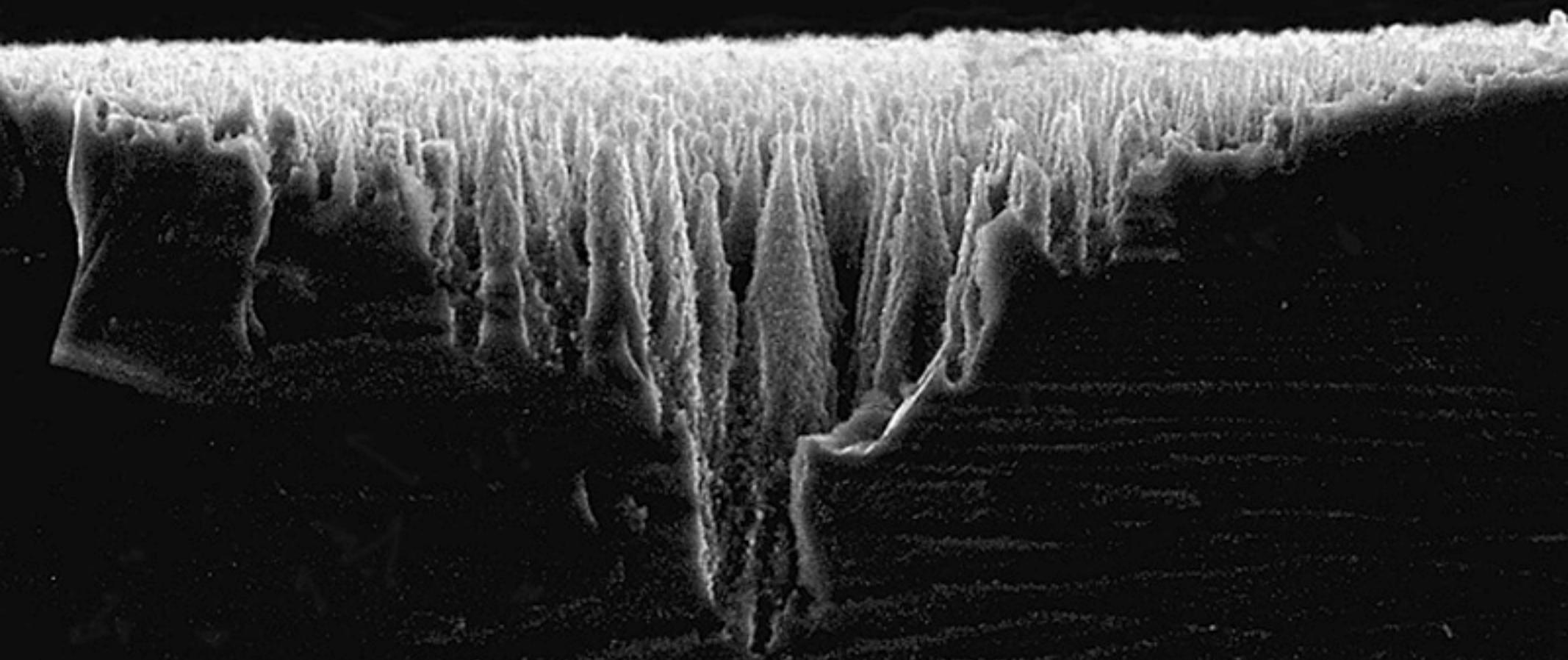
10  $\mu\text{m}$

# Black silicon

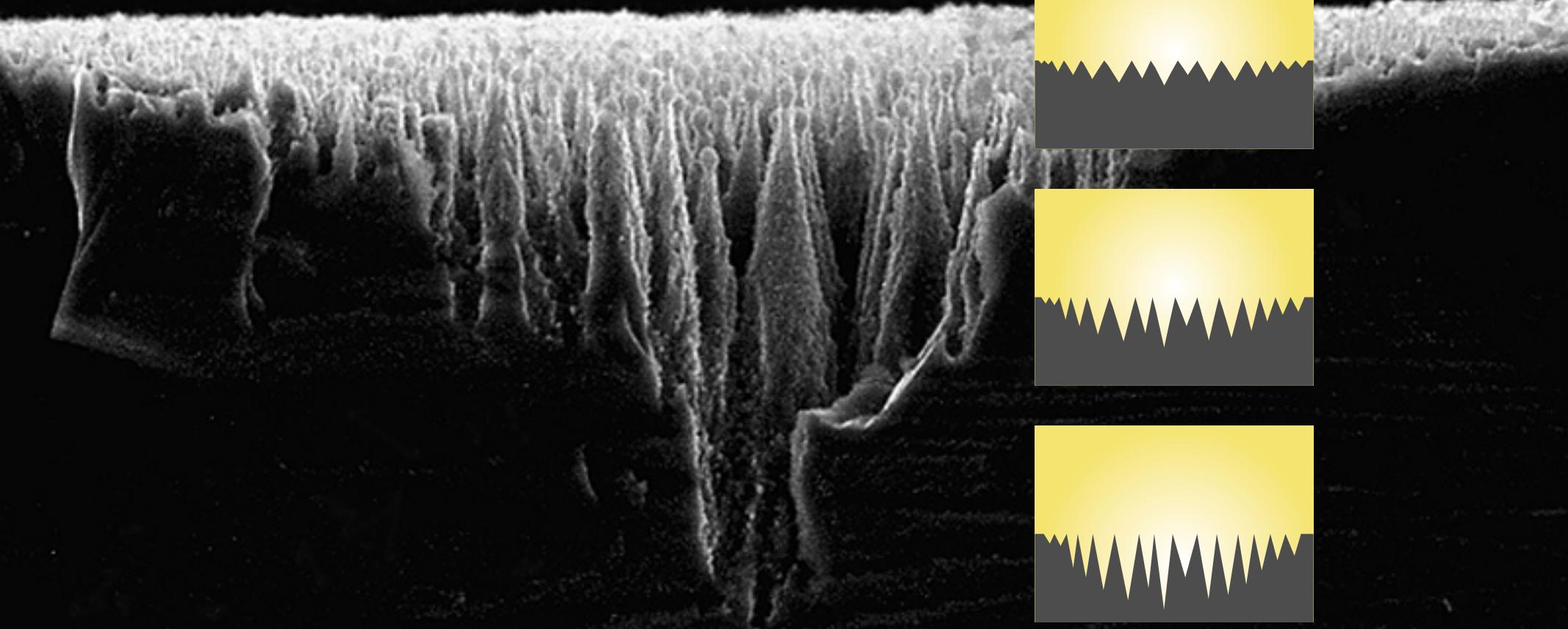


10 µm

# Black silicon

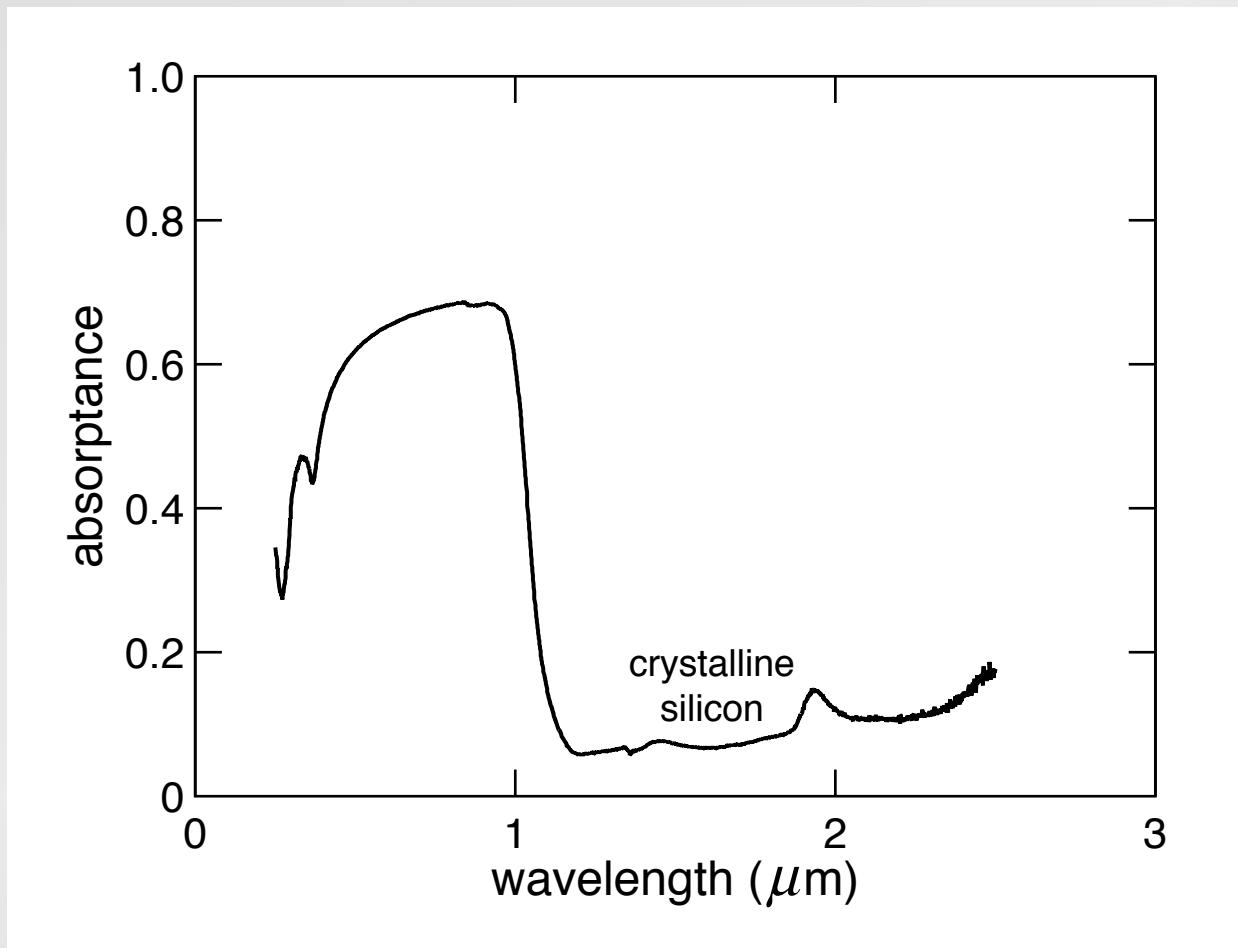


# Black silicon



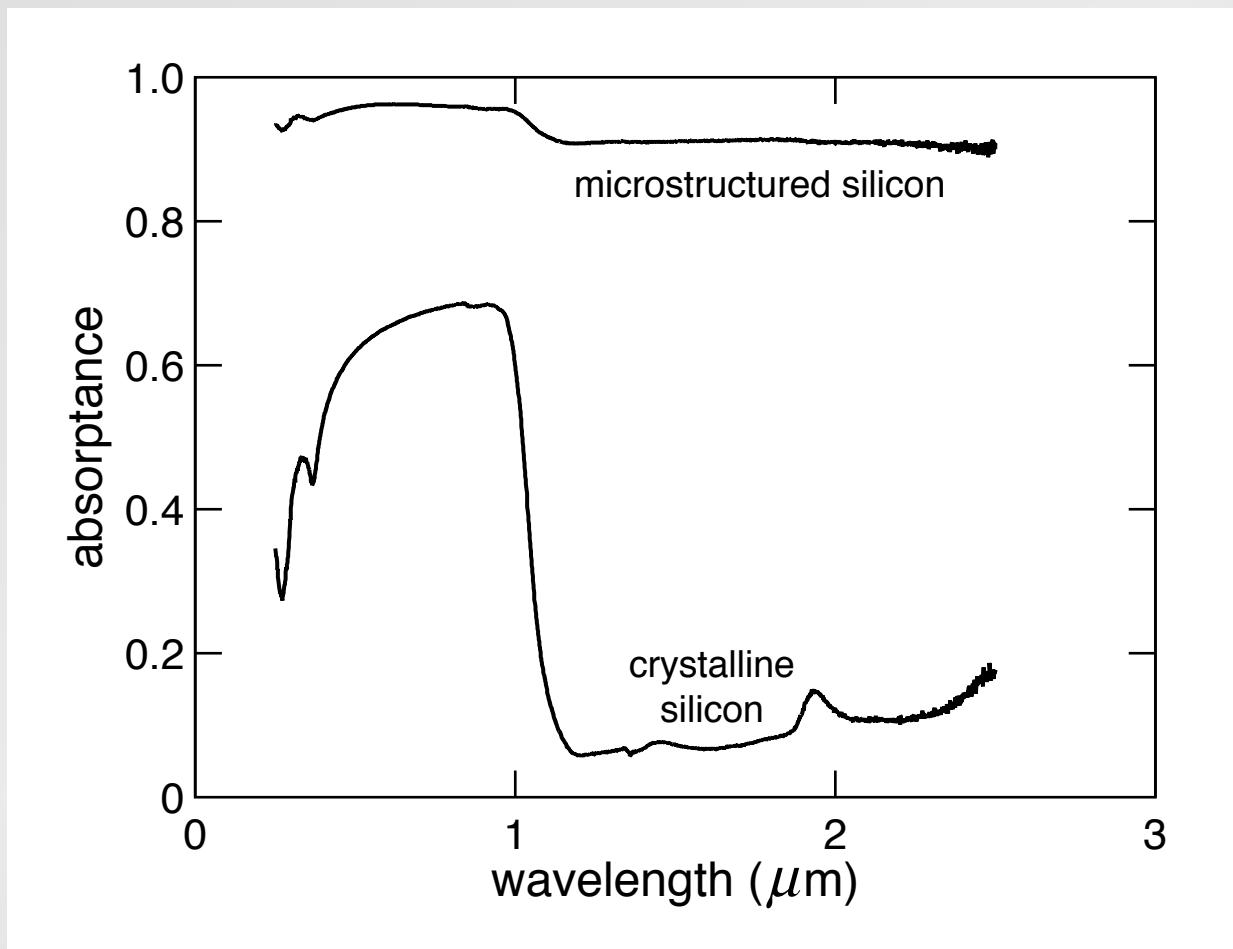
# Black silicon

## absorptance



# Black silicon

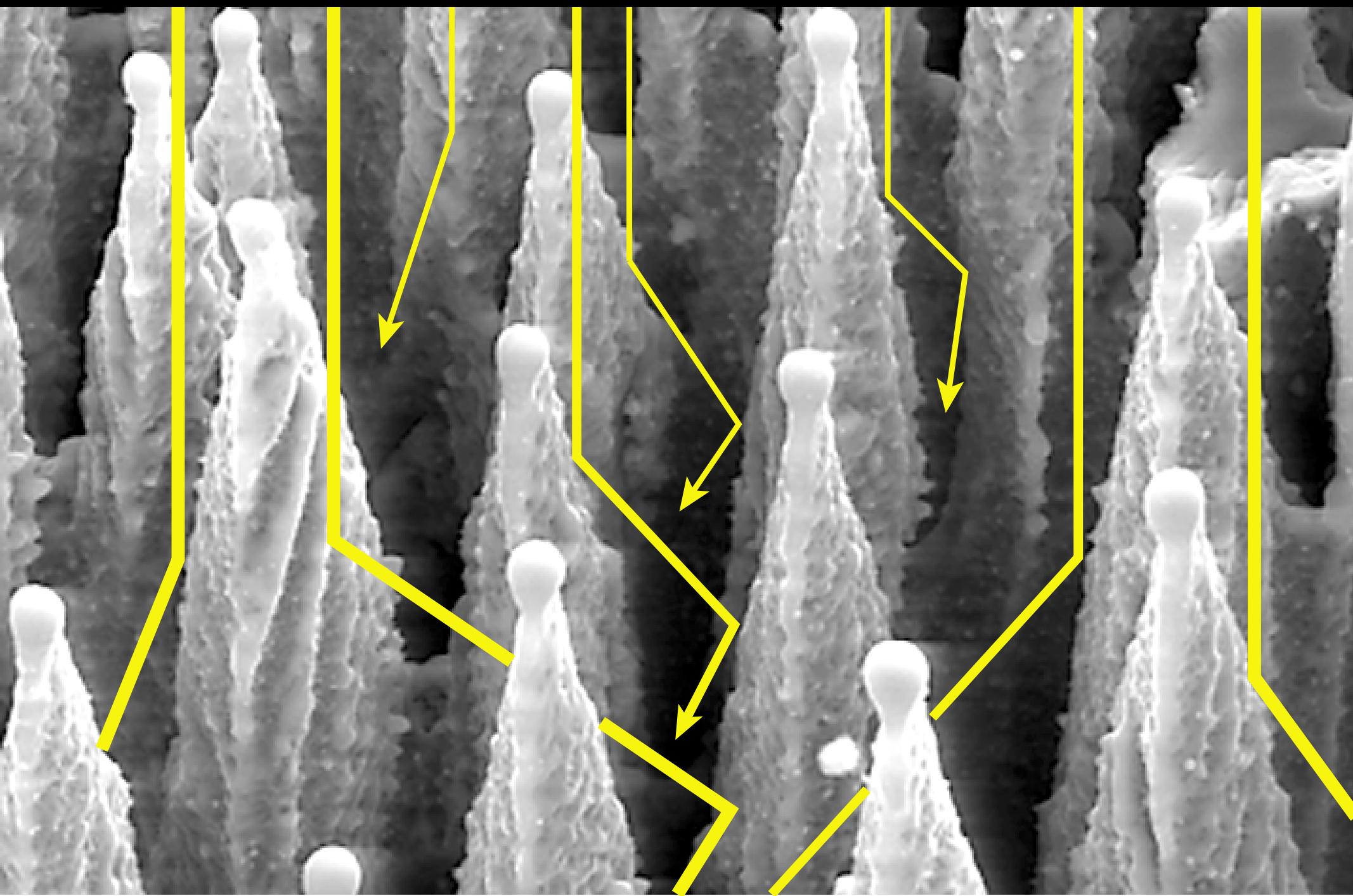
## absorptance



# **Black silicon**

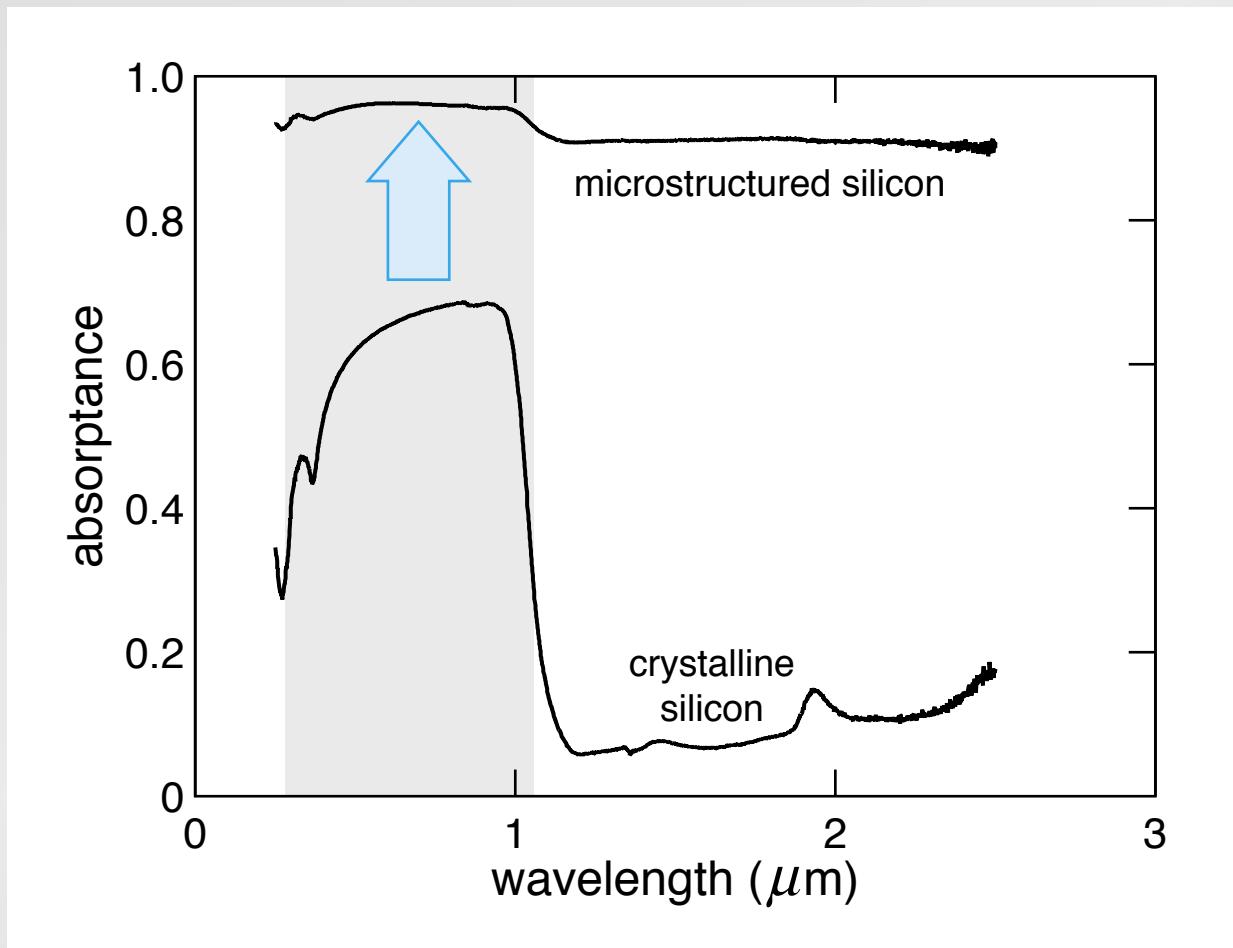
**What causes the near-unity absorptance?**

# Black silicon



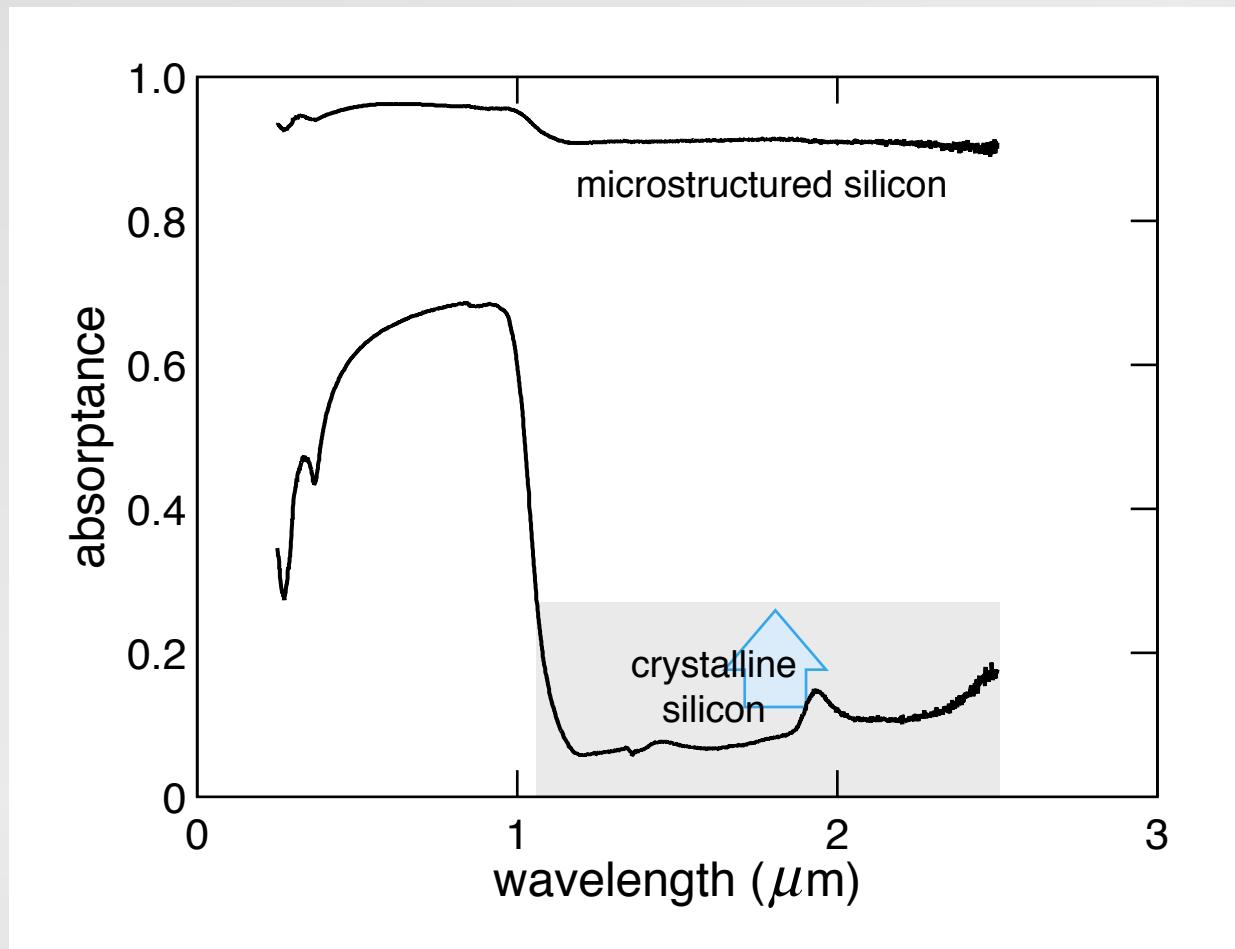
# Black silicon

multiple reflections enhance absorption



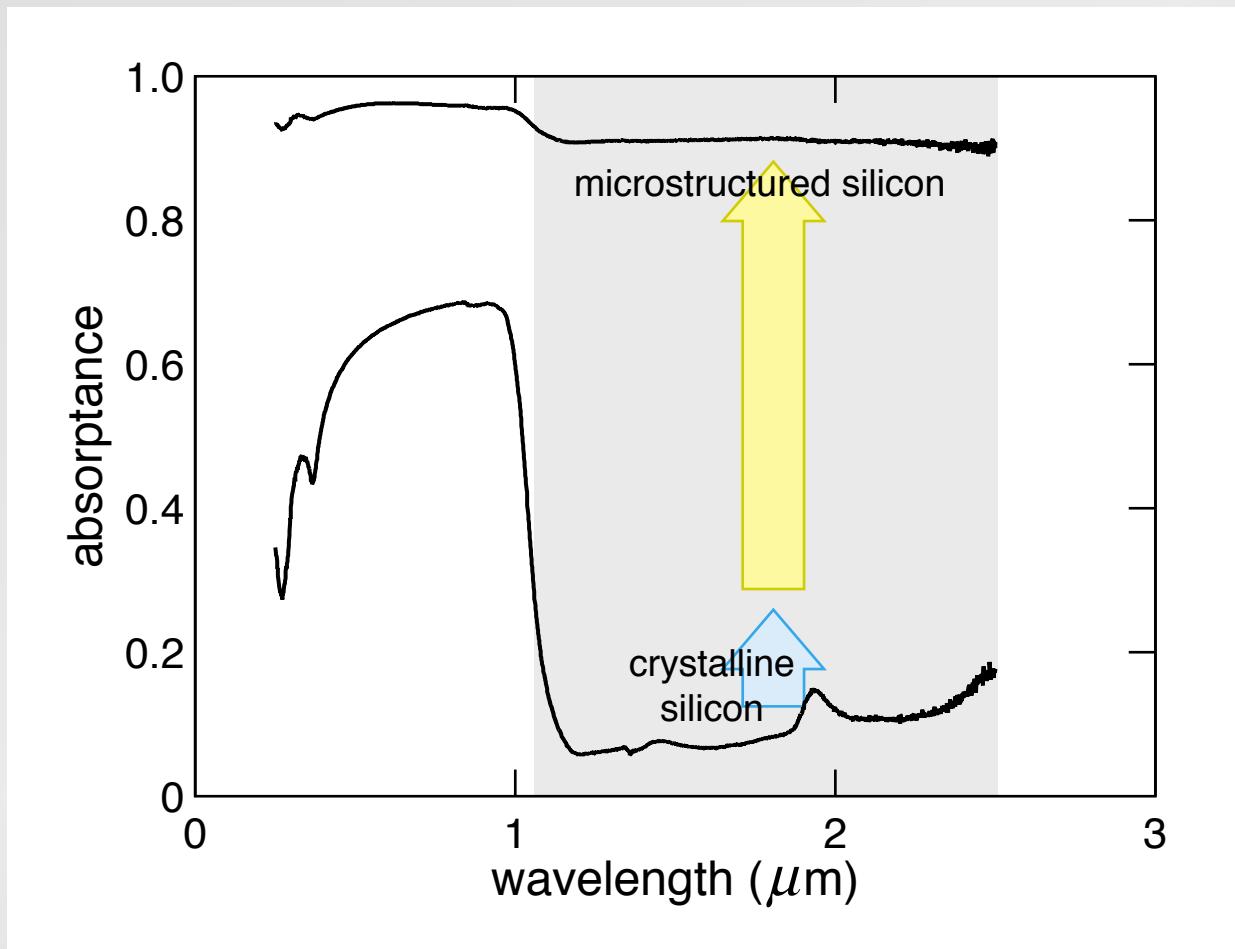
# Black silicon

multiple reflections enhance absorption

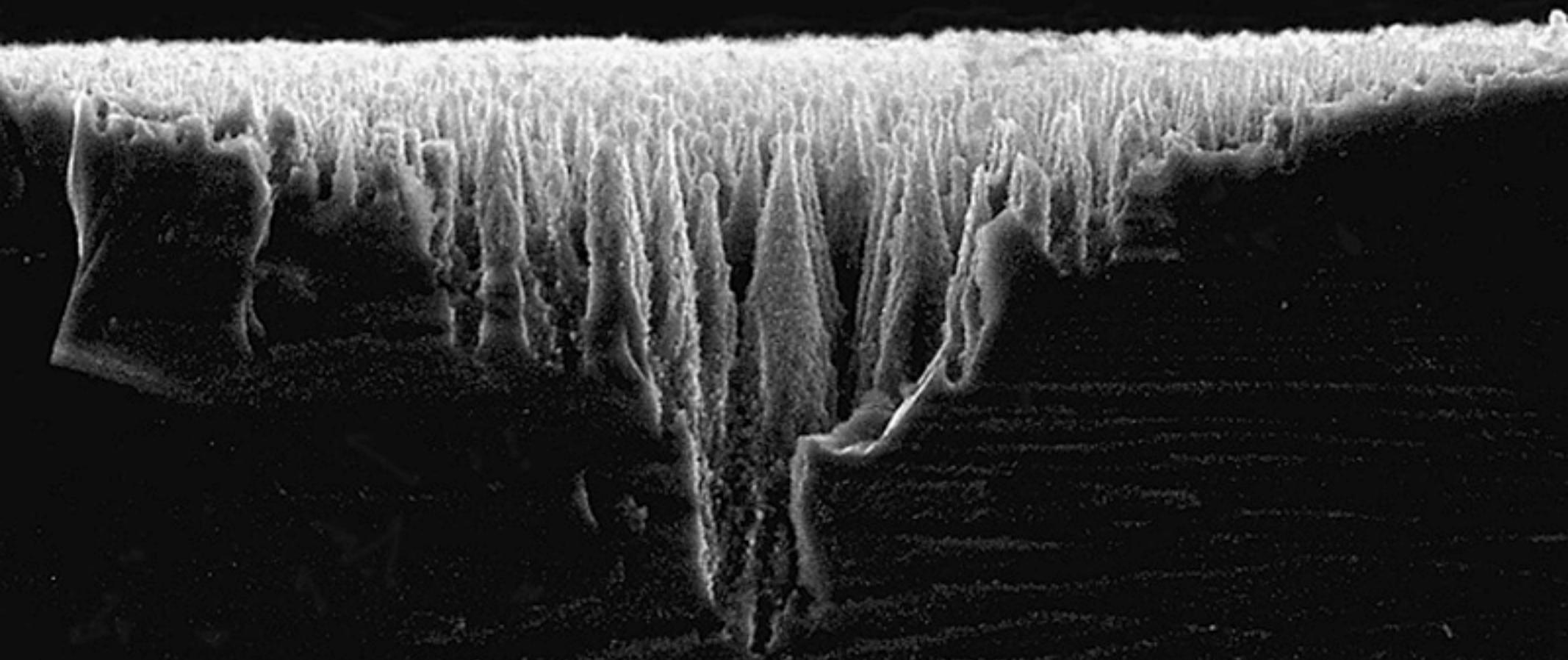


# Black silicon

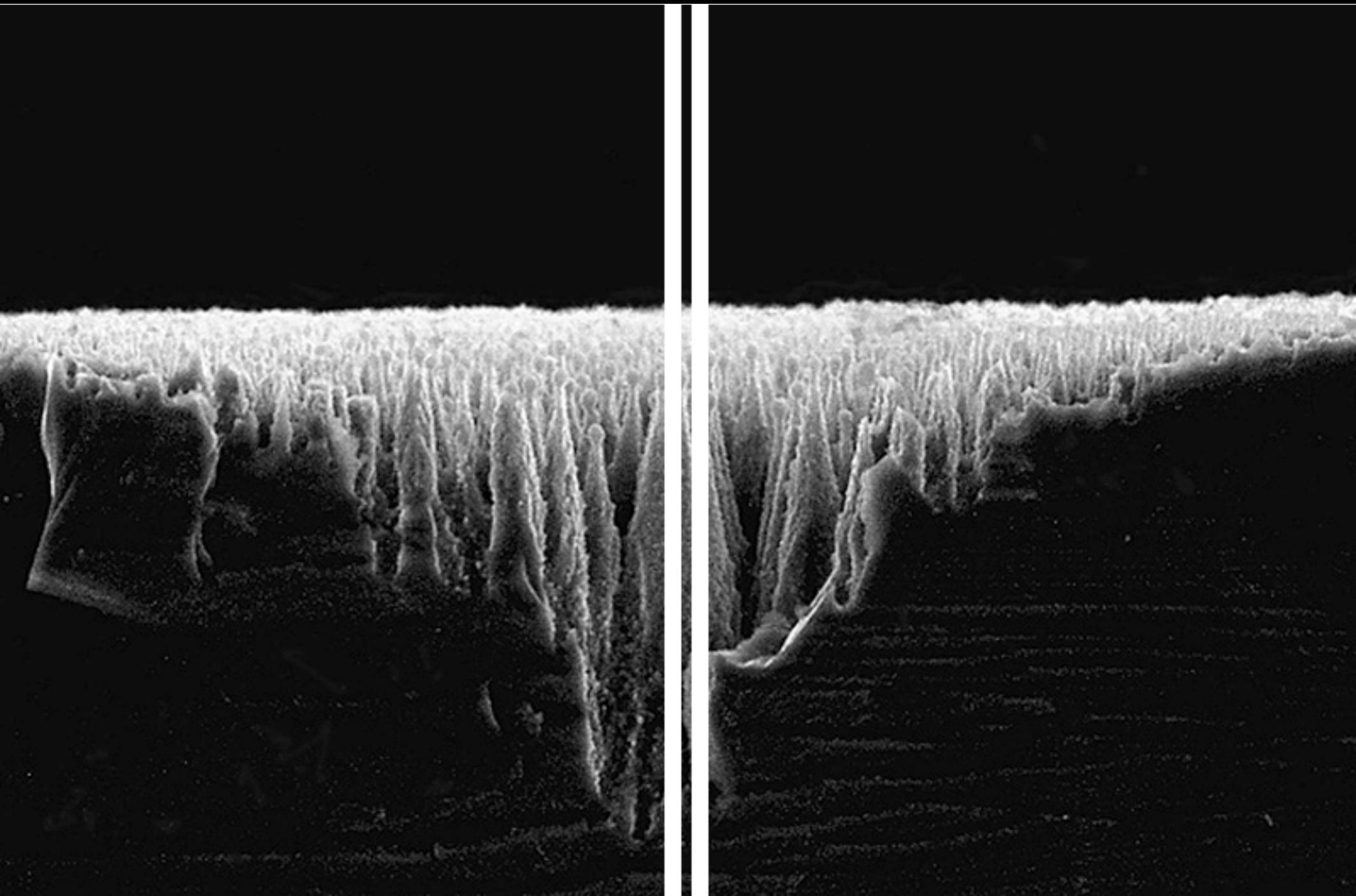
heavy sulfur doping causes infrared absorption



# Black silicon



# Black silicon



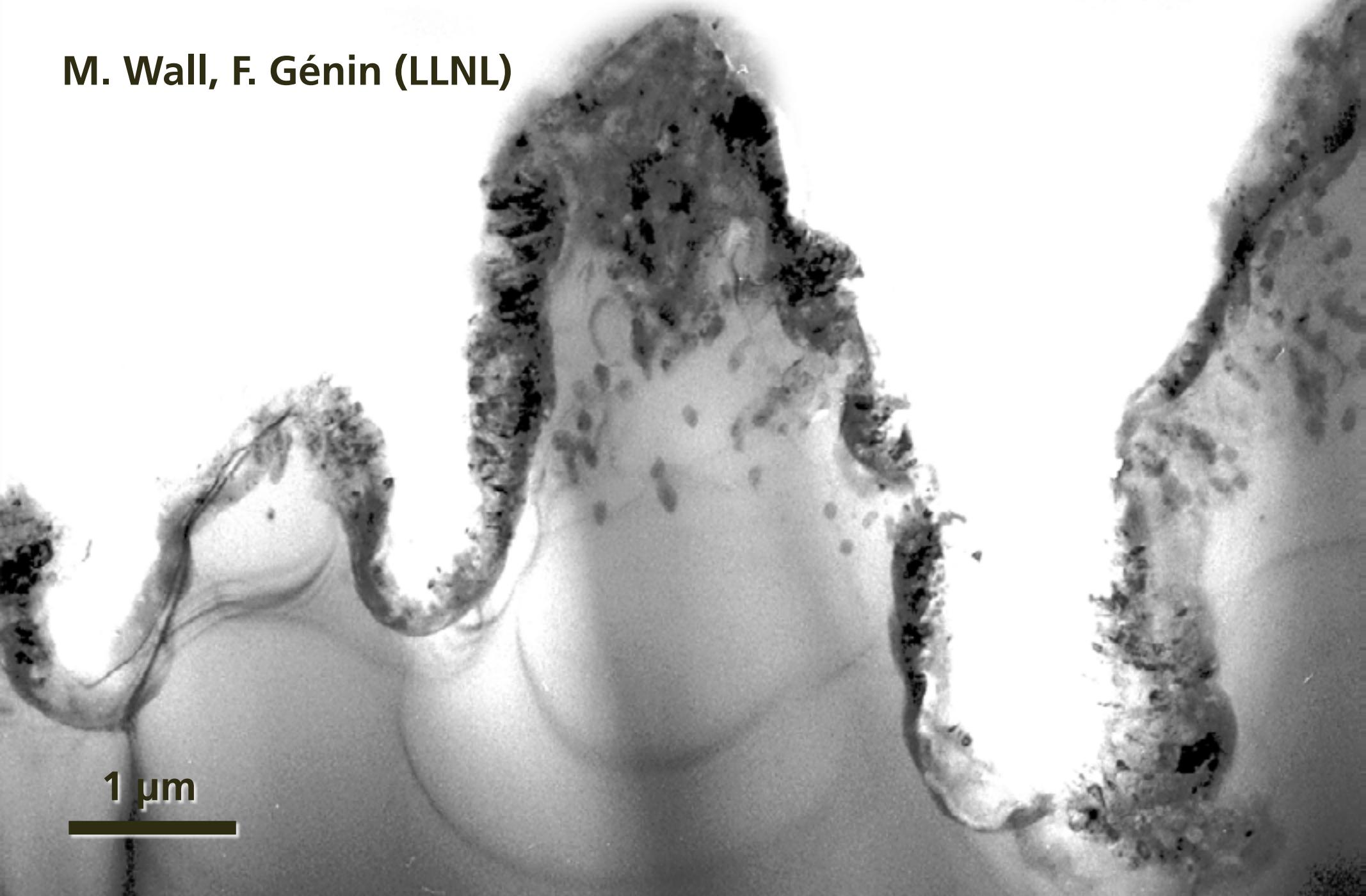
# **Black silicon**

**cross-sectional  
Transmission Electron  
Microscopy**



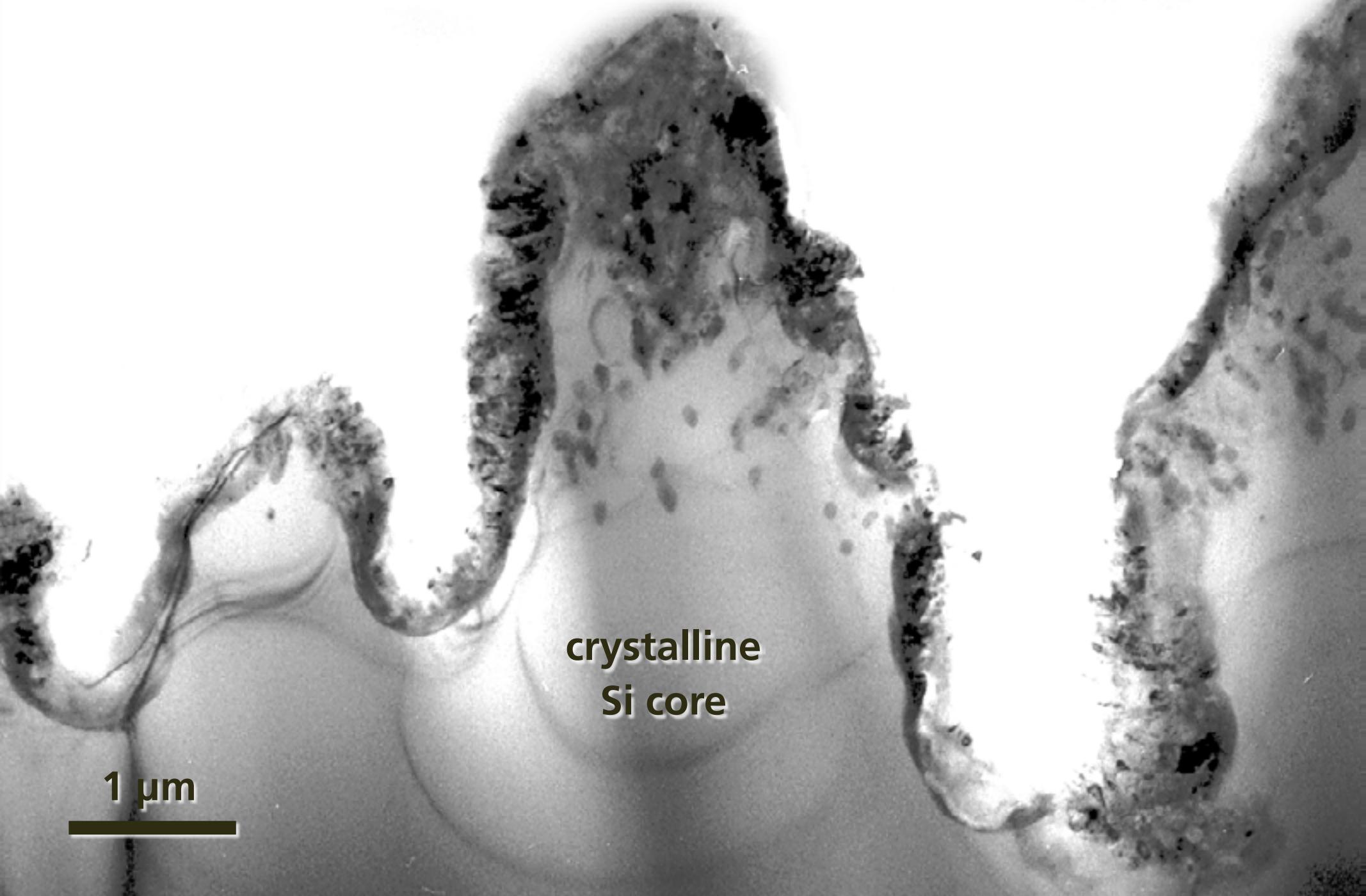
# Black silicon

M. Wall, F. Génin (LLNL)



1  $\mu\text{m}$

# Black silicon

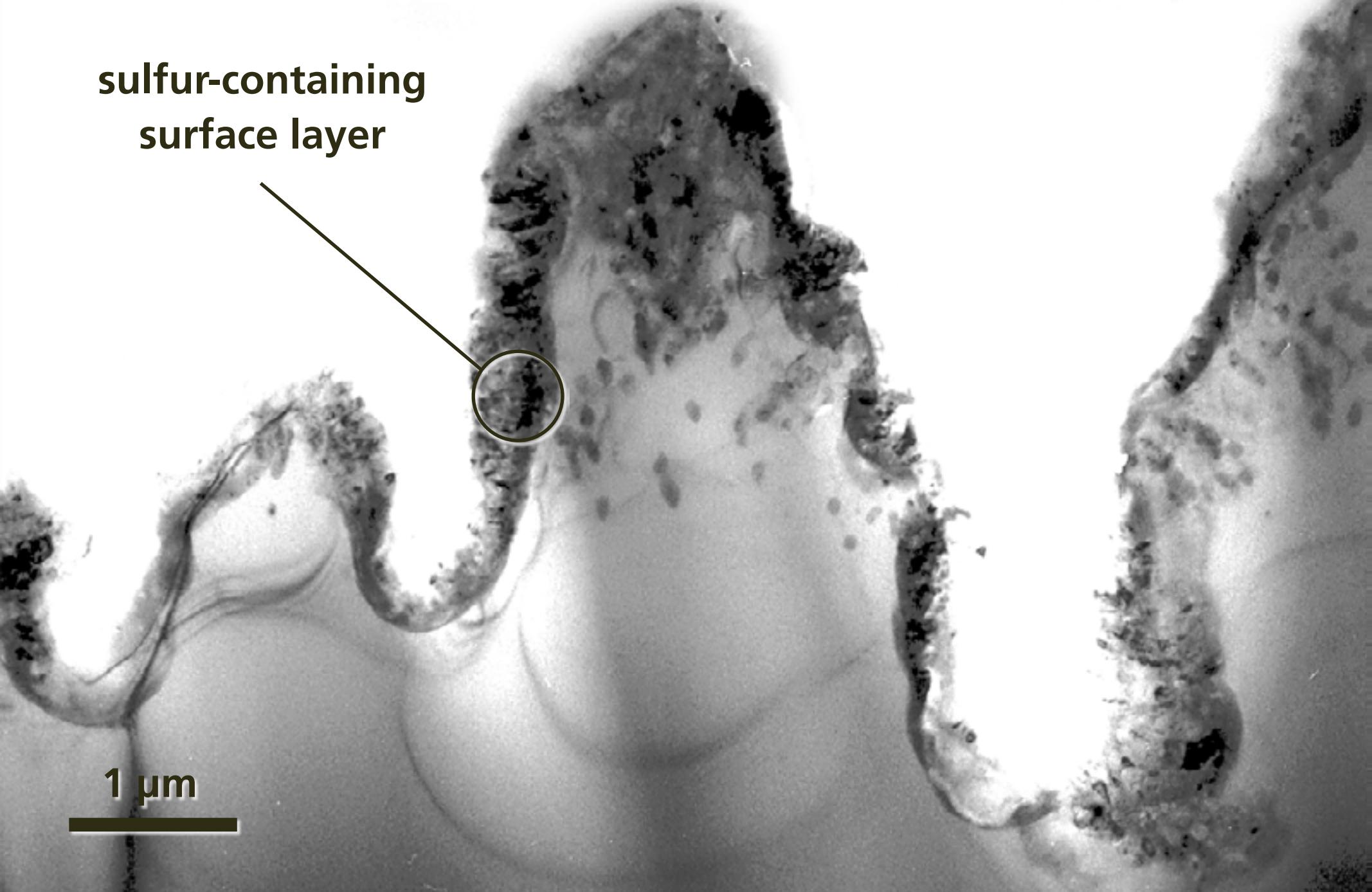


crystalline  
Si core

1  $\mu\text{m}$

# Black silicon

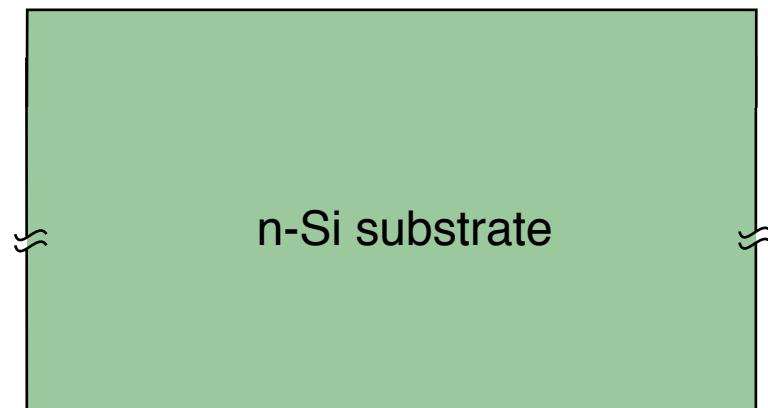
sulfur-containing  
surface layer



1  $\mu\text{m}$

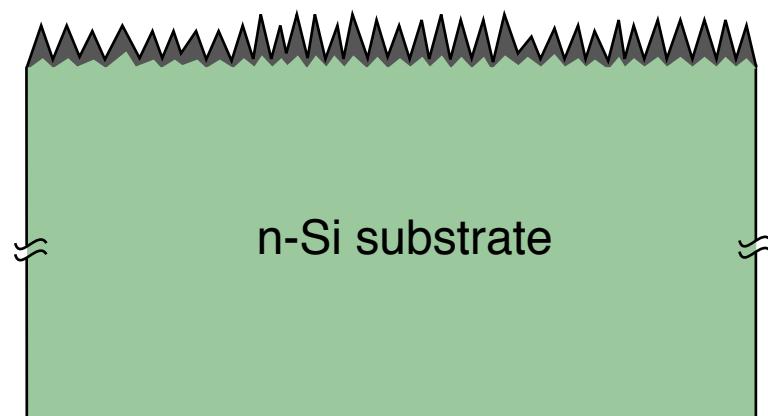
# Black silicon

**black silicon/n-type silicon junction**



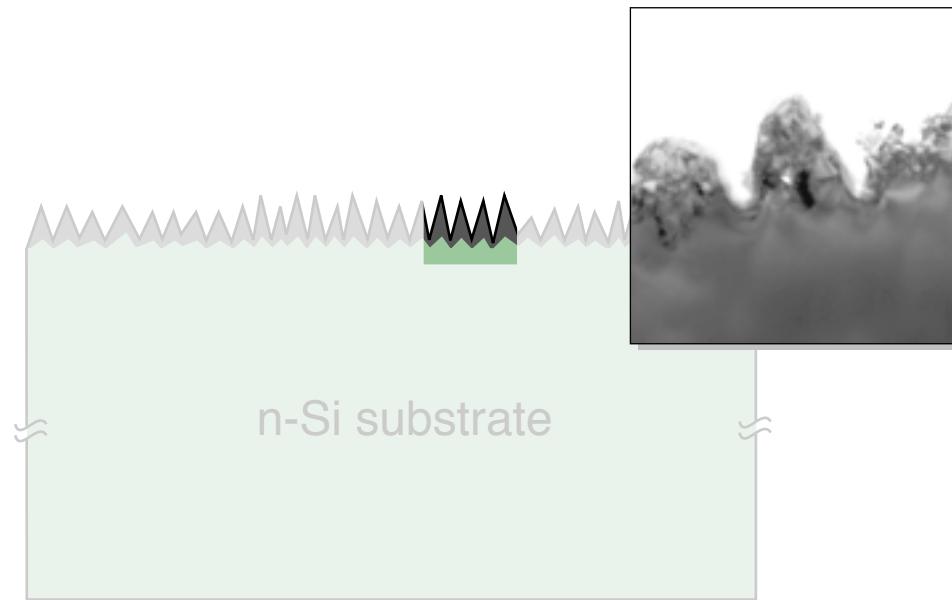
# Black silicon

black silicon/n-type silicon junction



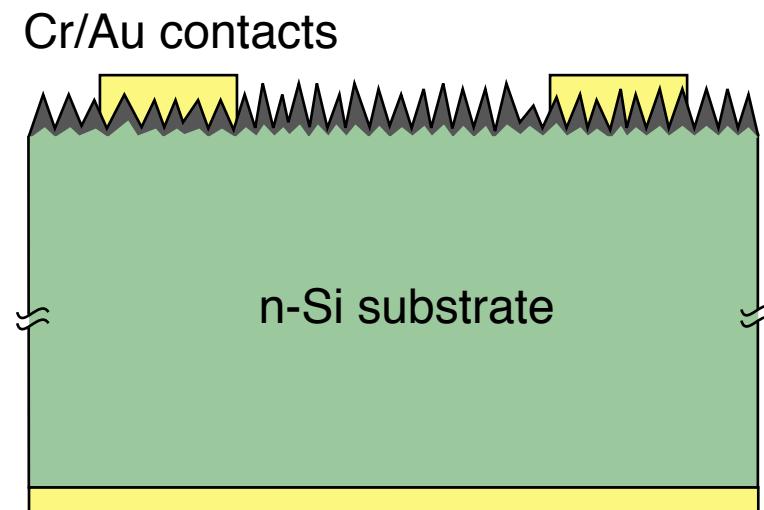
# Black silicon

black silicon/n-type silicon junction



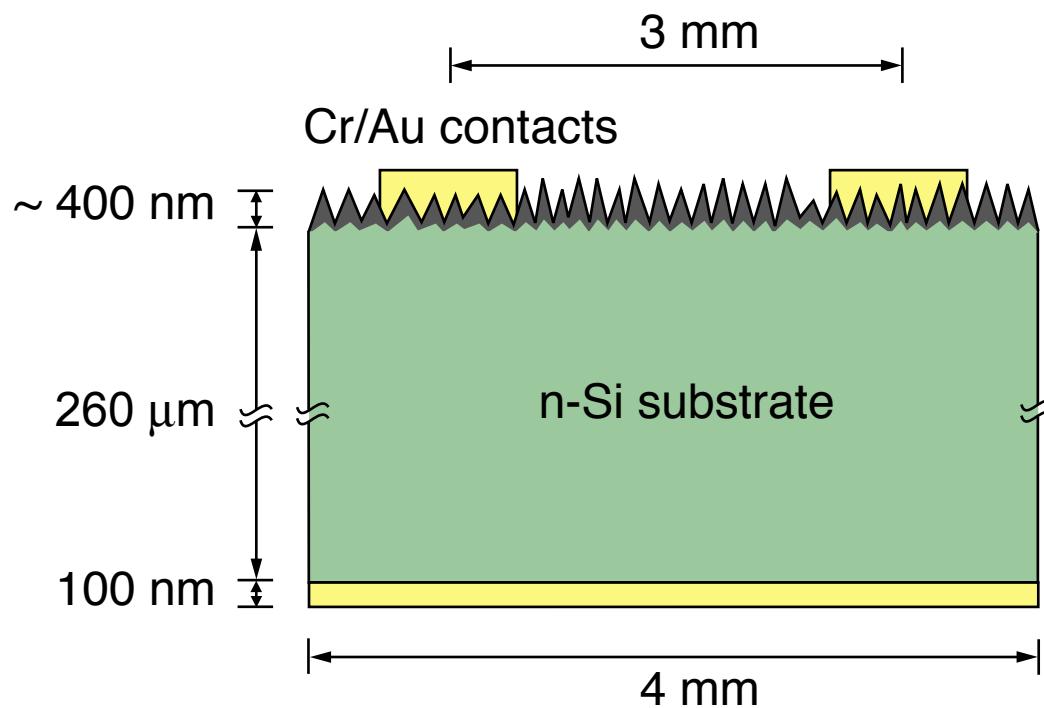
# Black silicon

black silicon/n-type silicon junction



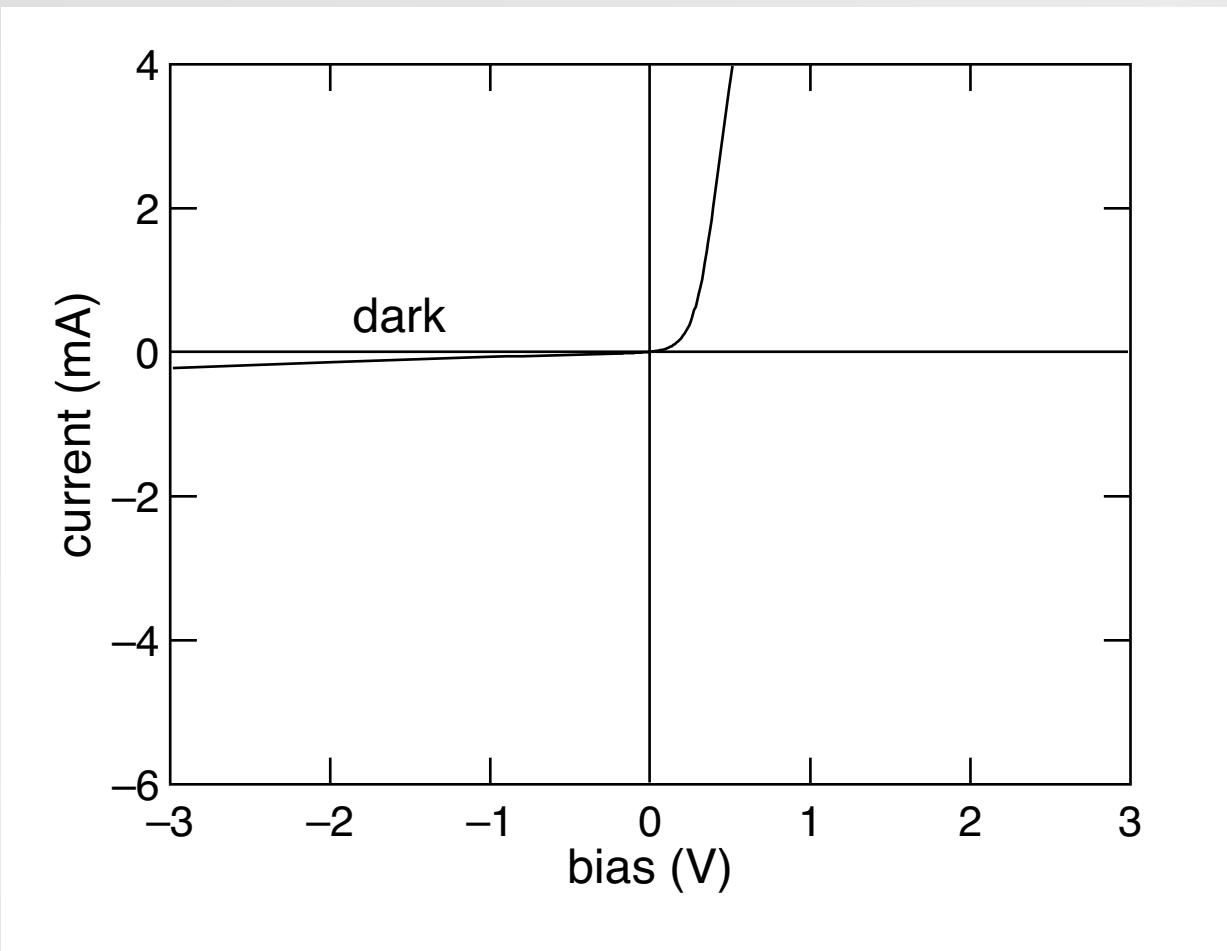
# Black silicon

## black silicon/n-type silicon junction



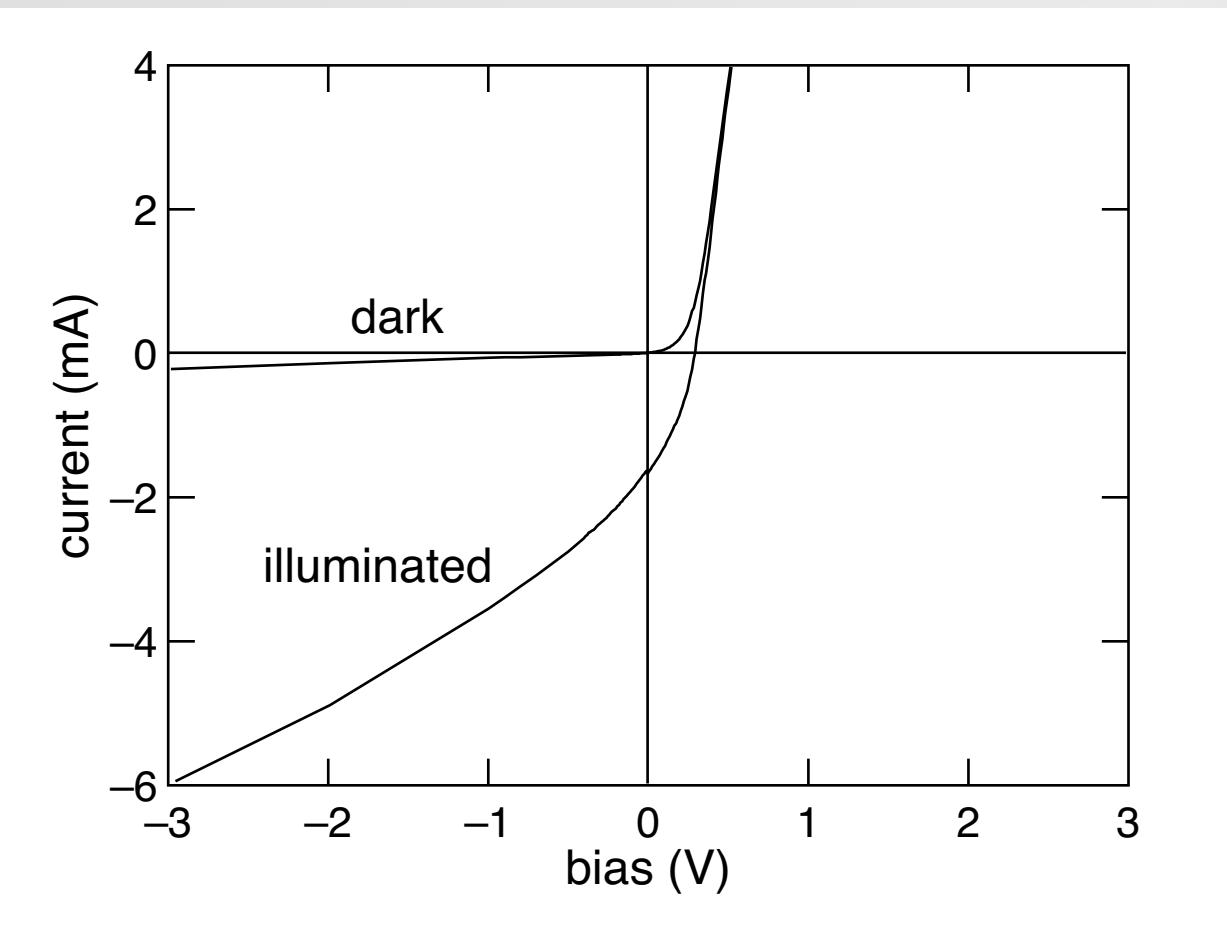
# Black silicon

## *I/V characteristics*



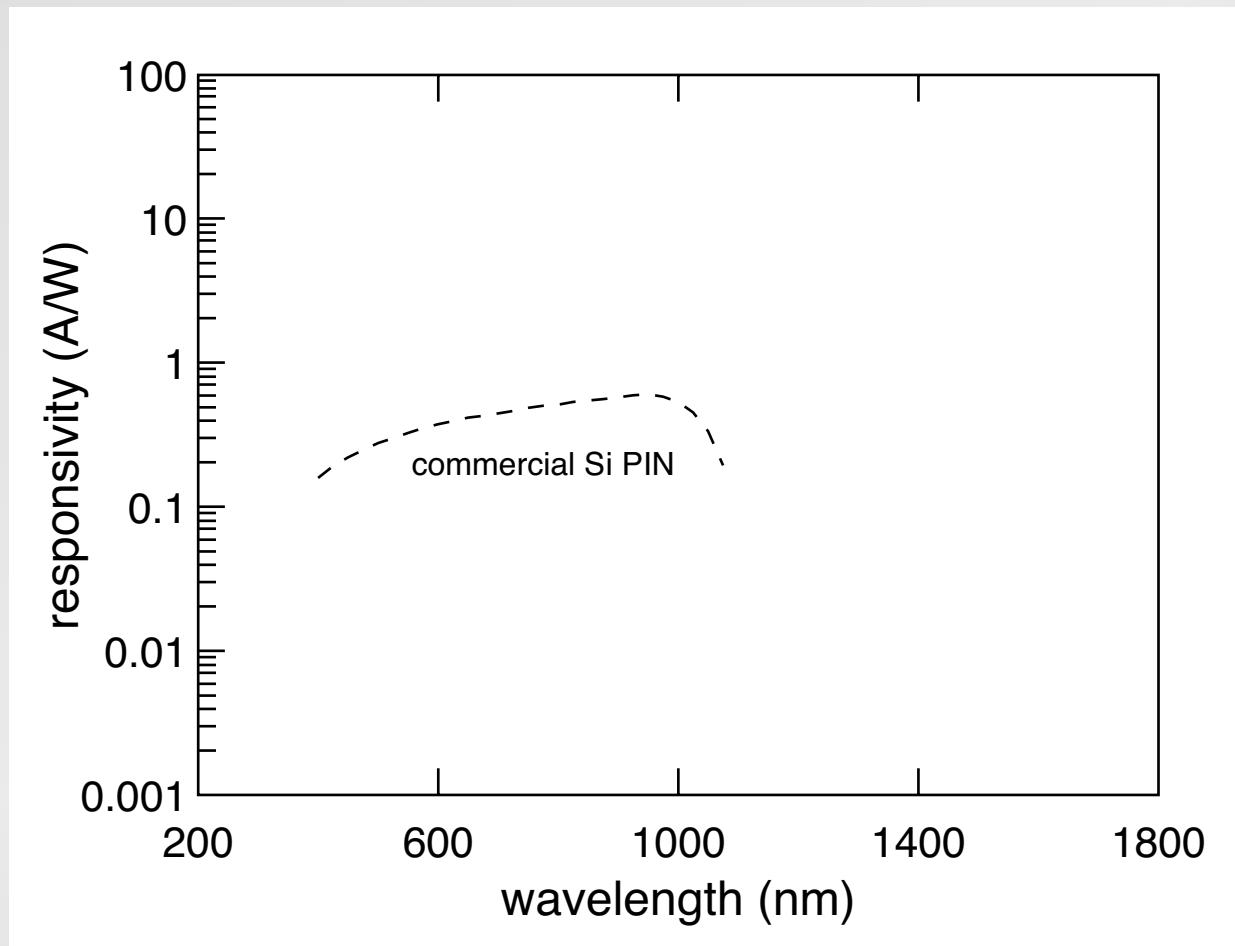
# Black silicon

## *I/V characteristics*



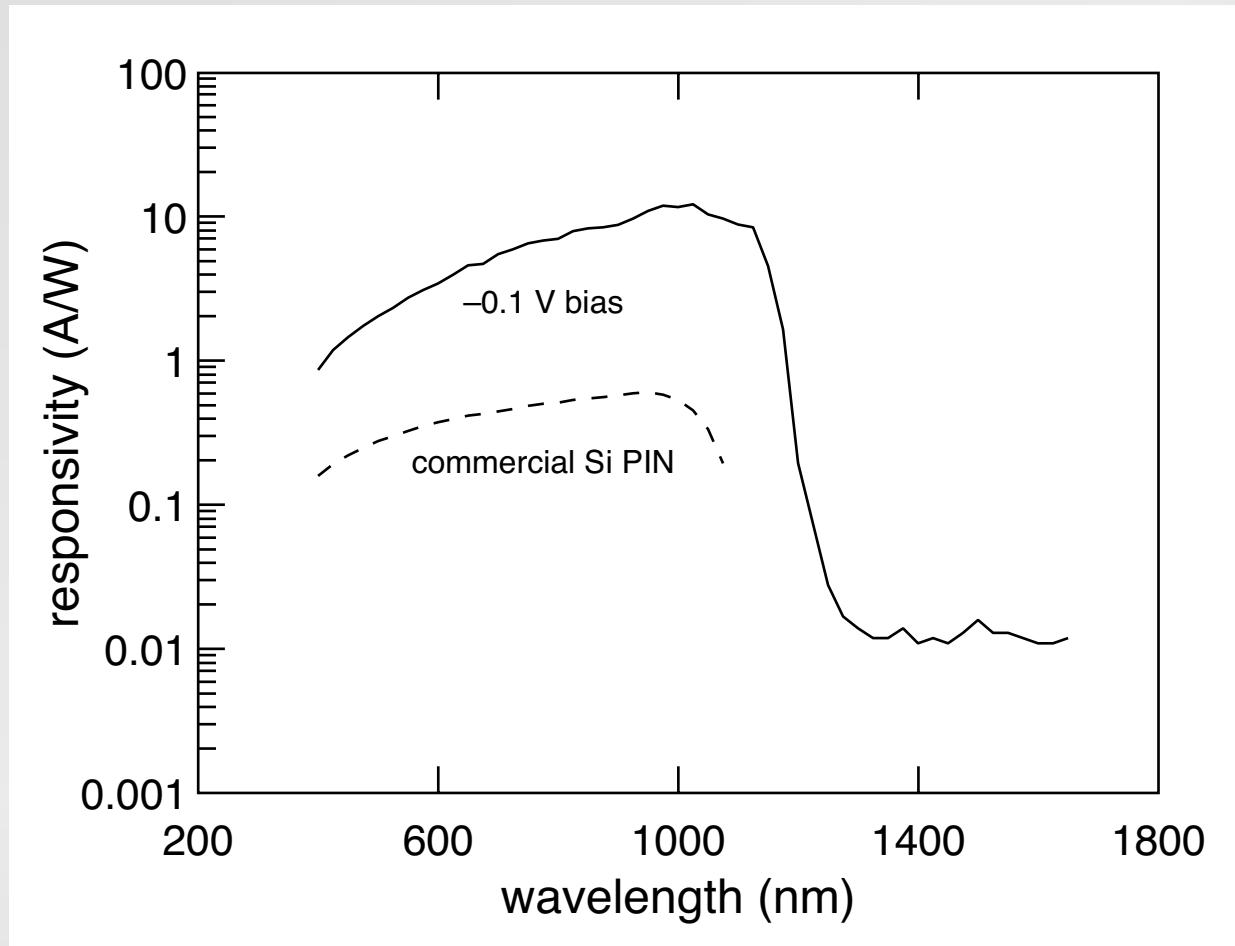
# Black silicon

## responsivity



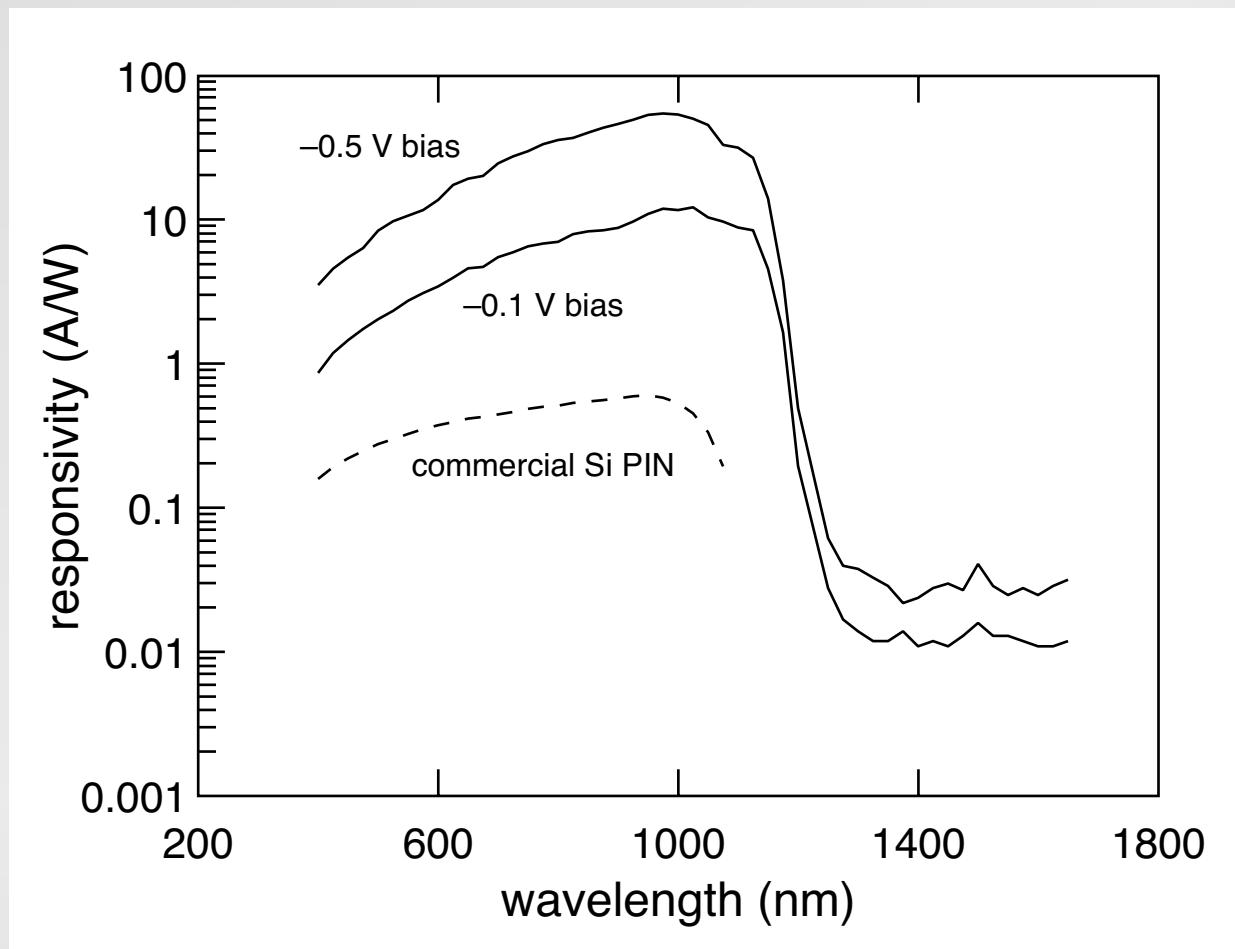
# Black silicon

## responsivity



# Black silicon

## responsivity



# Black silicon

Black silicon photo diode (at 0.5 V bias):

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

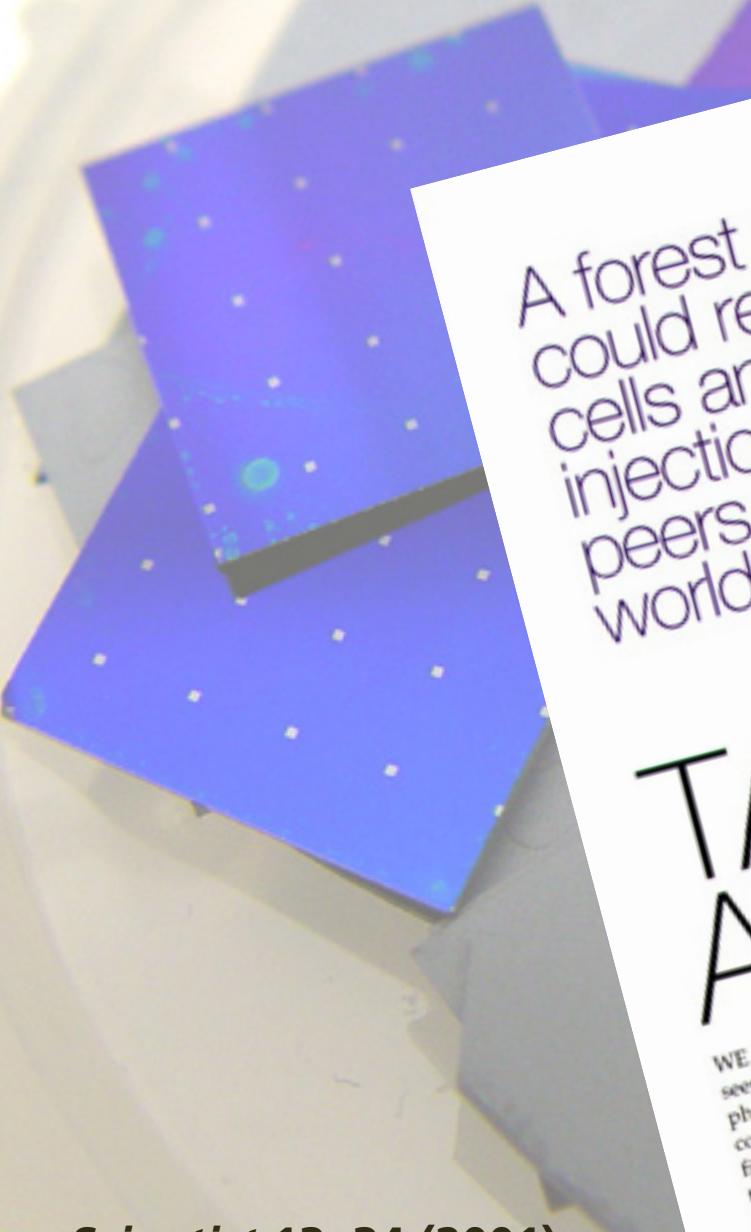
# Devices



SiOnyx

<http://www.sionyx.com>

# Black silicon



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 spout. 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 he

around the laboratory," he claims.

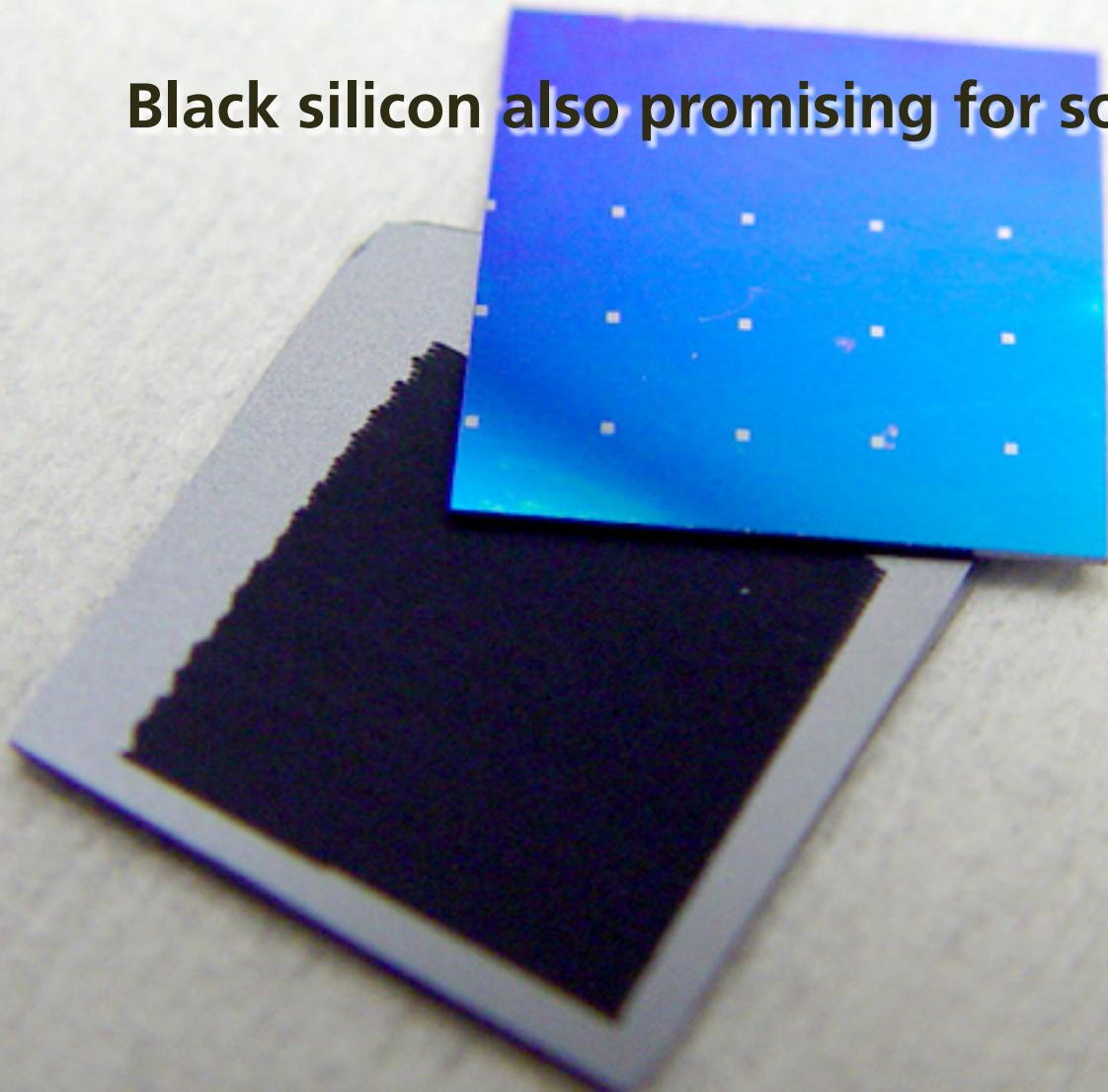
Well, it was almost the only reason. A short laser pulse will break down SF<sub>6</sub> into sulphur and fluorine radicals, which will attack a silicon substrate. Hydrogen fluoride is used to etch silicon. So we thought maybe the SF<sub>6</sub> would decompose and then the fluorine would somehow react 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 SF<sub>6</sub> gas onto the shiny silicon wafer. After firing about 100 pulses they cracked the wafer, the chamber and removed the wafer. He saw a tiny black spot at the focal point of the laser beam. A burn, perhaps. That Mazur knew that silicon doesn't burn.

"You can get silicon oxide, but it's not black," he says. So what was going on?

# **Black silicon**

**Black silicon also promising for solar cells**



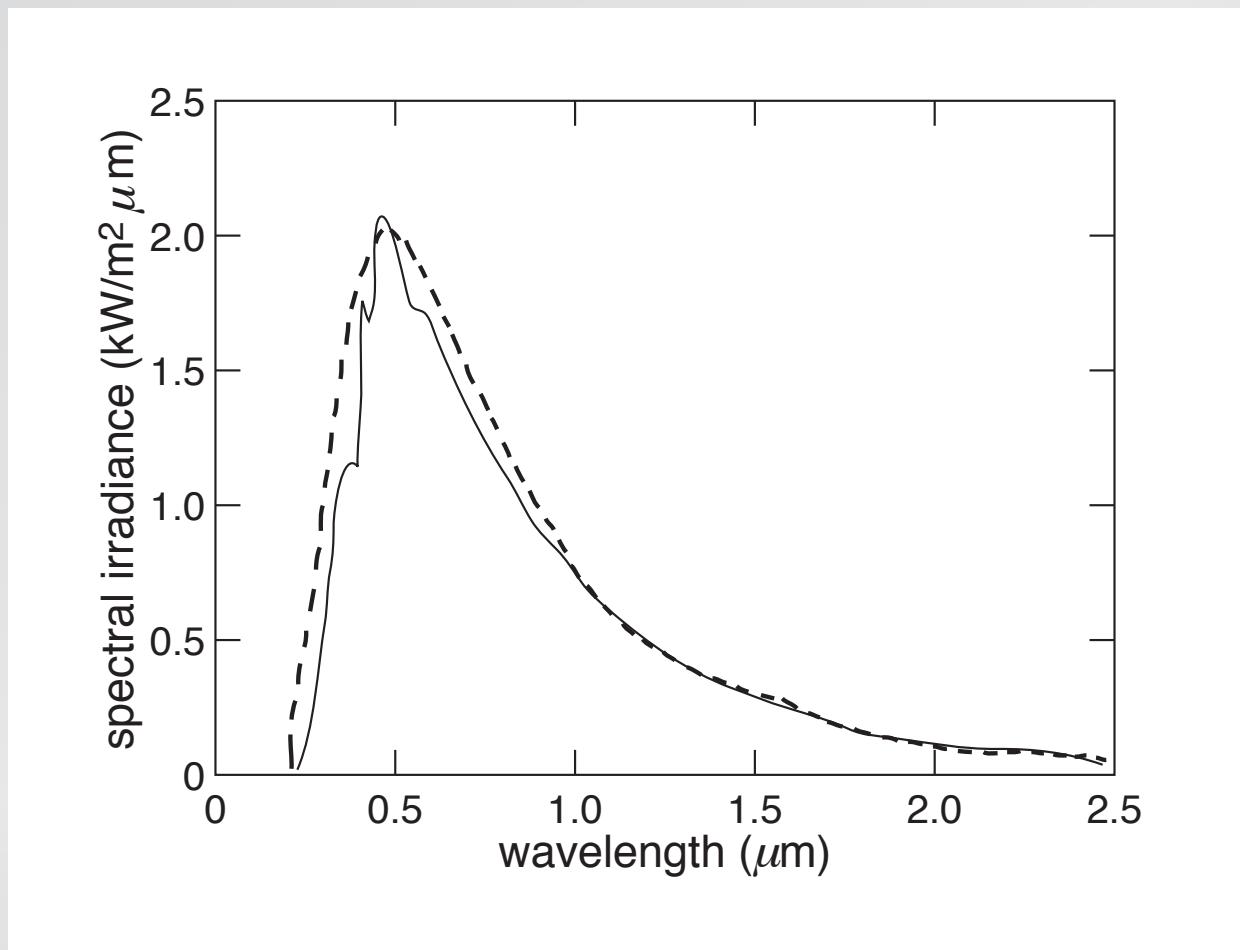
# **Black silicon**

**What causes the large gain?**

**How could black silicon be useful for photovoltaics?**

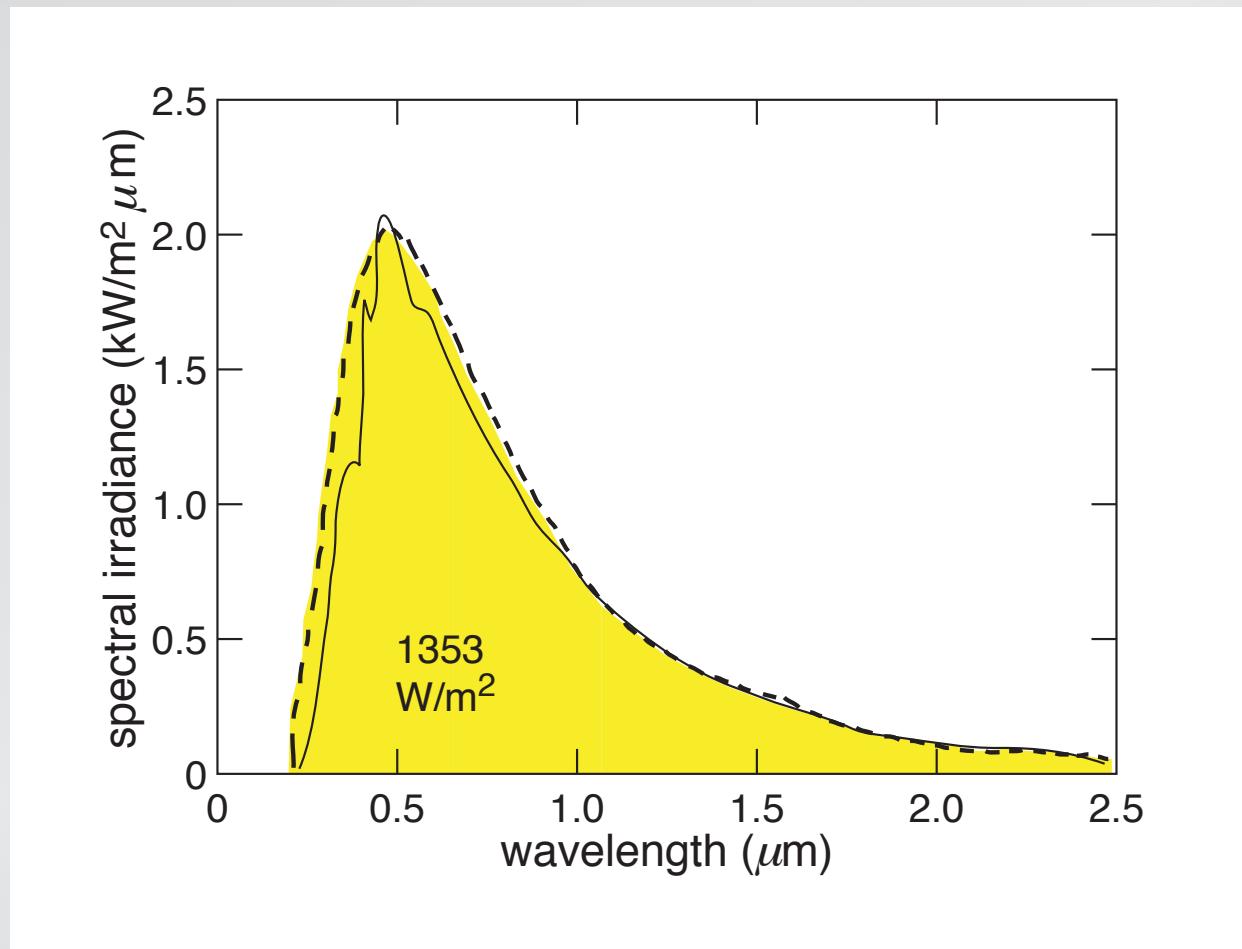
# Devices

## solar spectrum



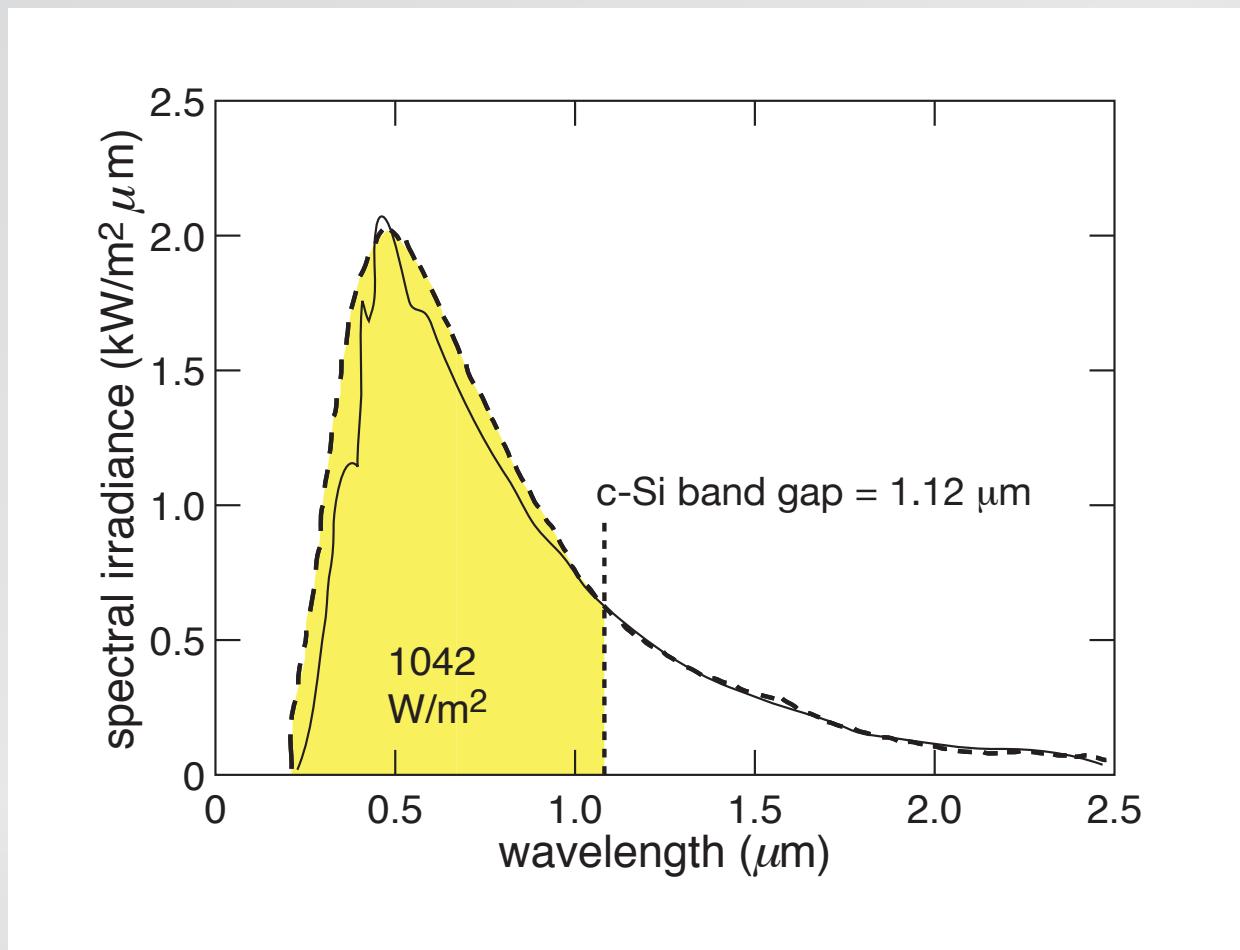
# Devices

## solar spectrum



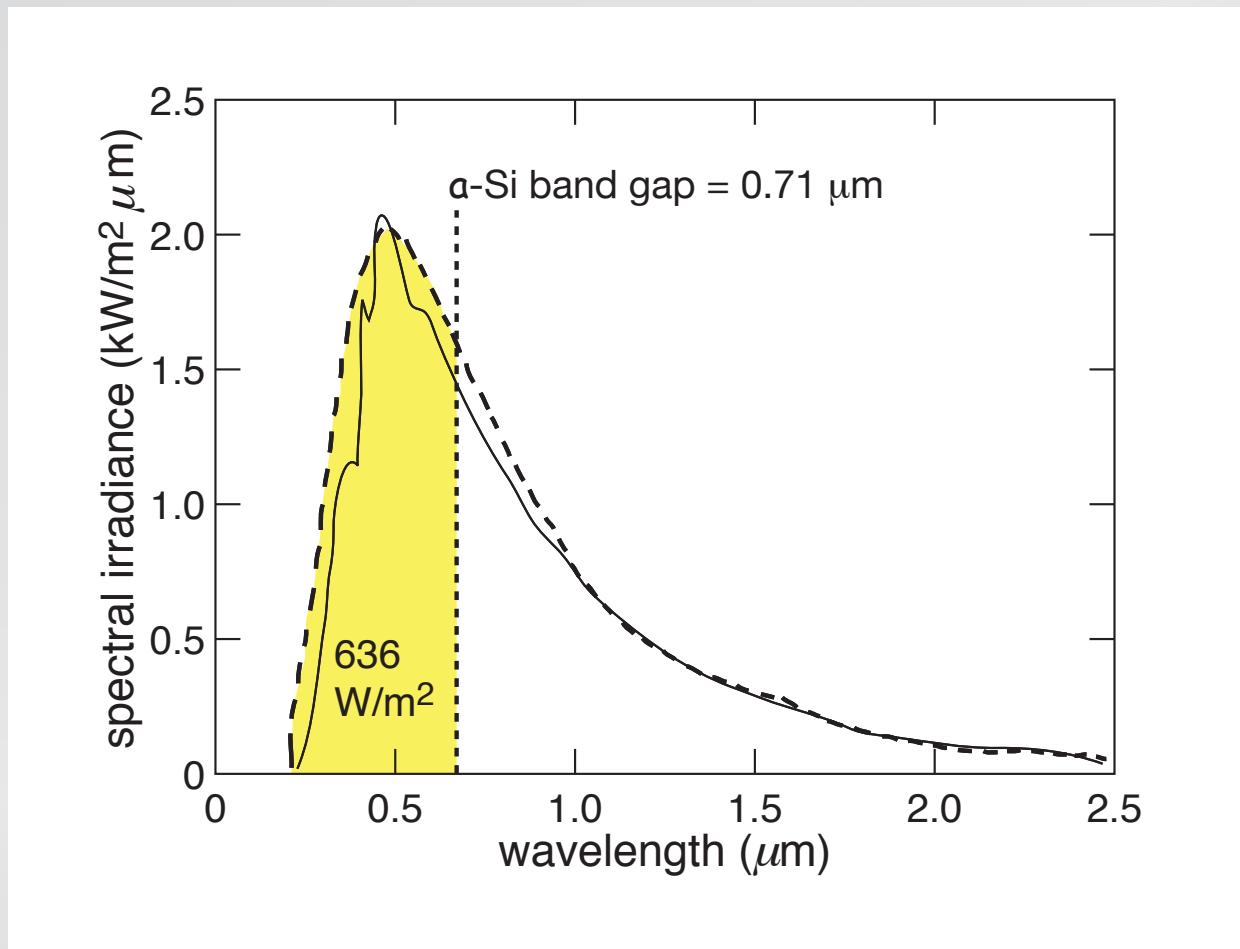
# Devices

crystalline silicon: transparent to 23% of solar radiation



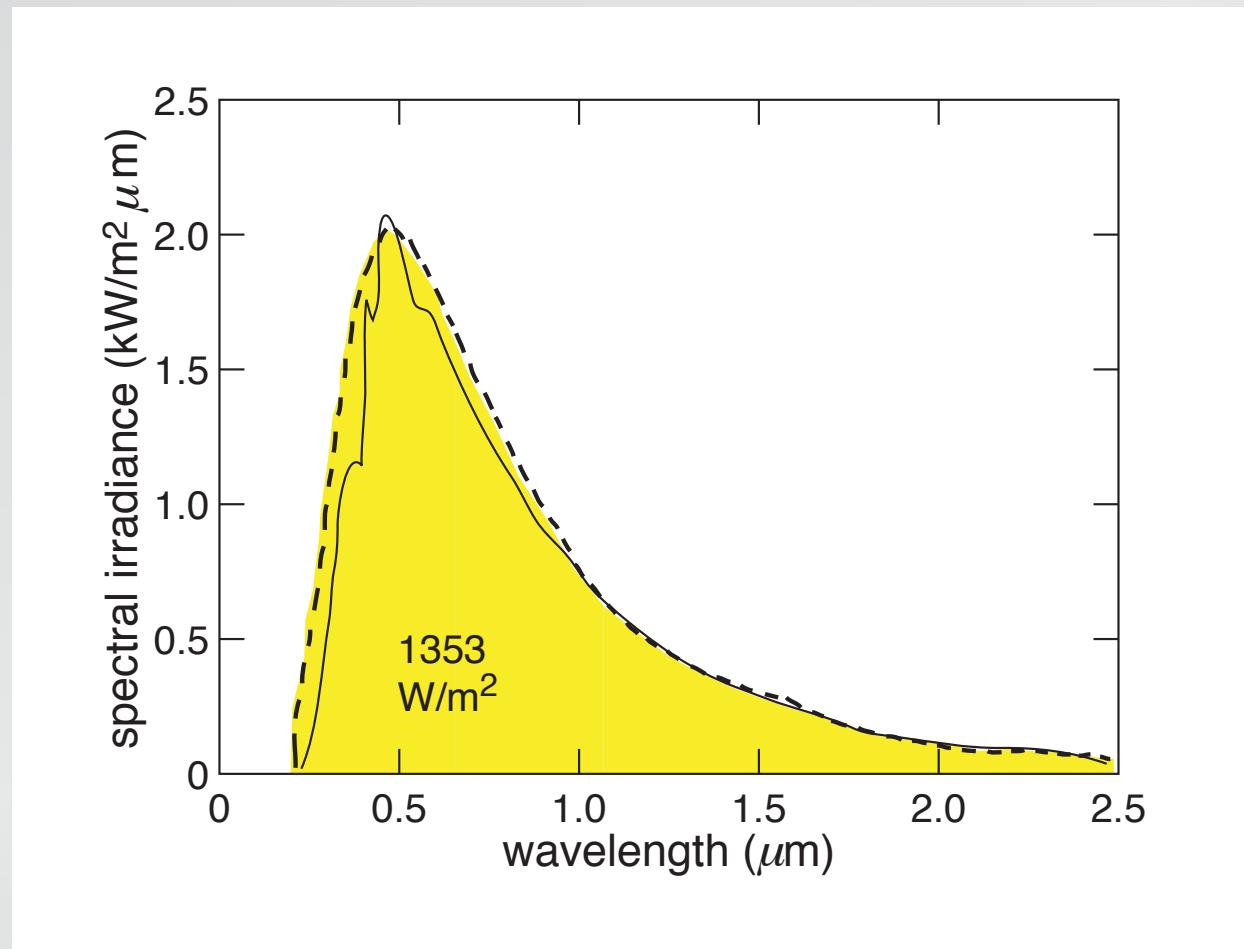
# Devices

**amorphous silicon: transparent to 53% of solar radiation**



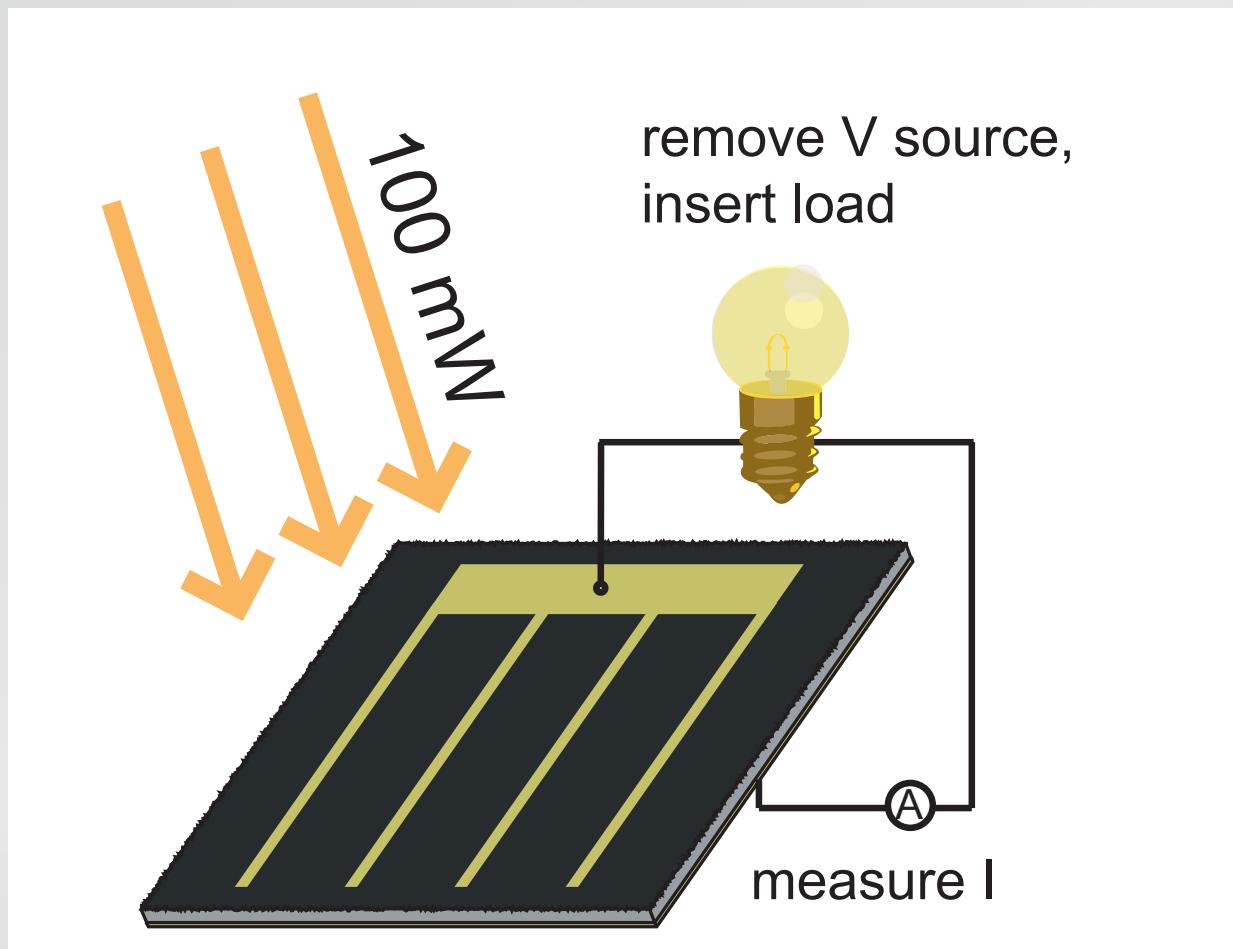
# Devices

**black silicon: potential to recover transmitted energy**



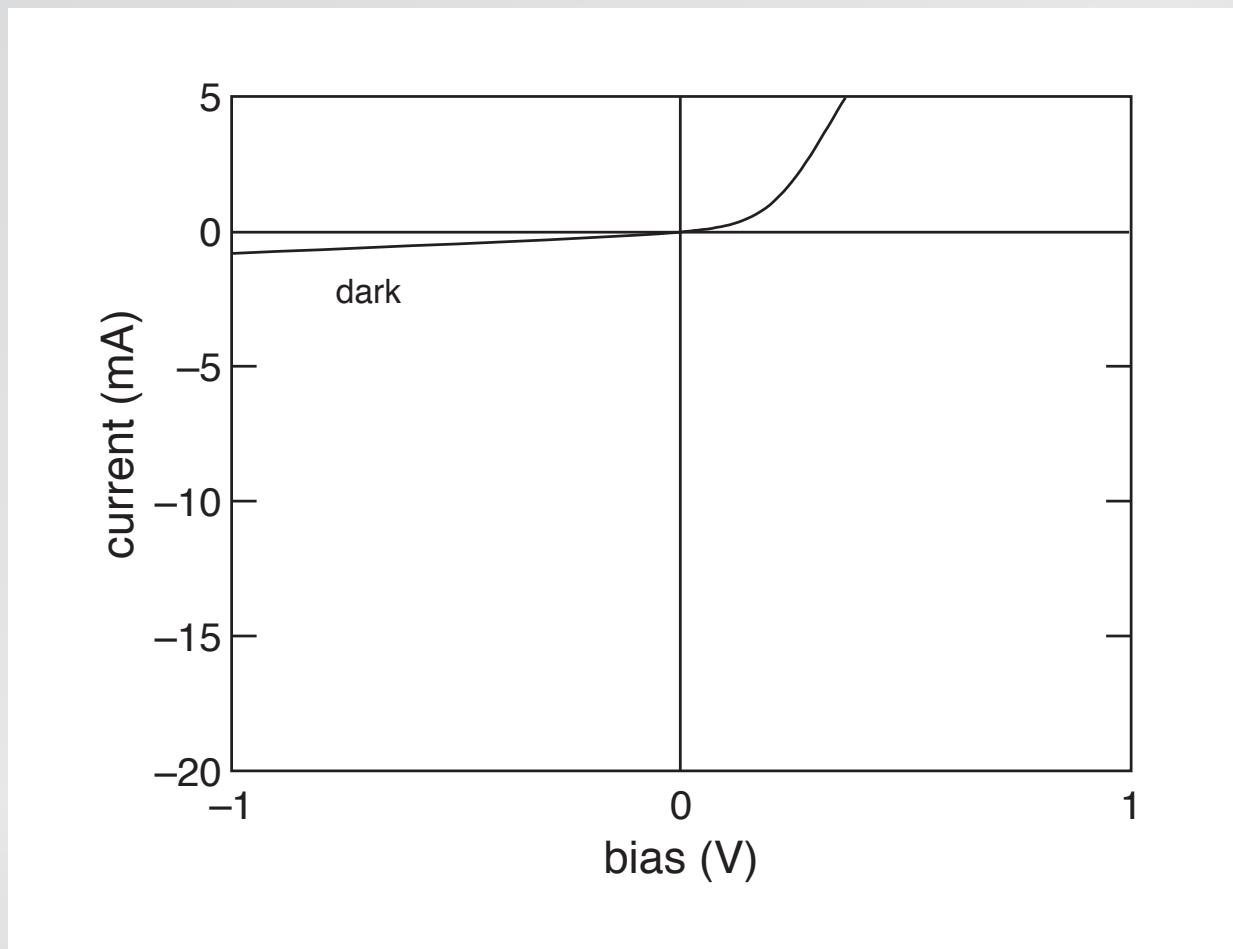
# Devices

## very preliminary photovoltaic cell



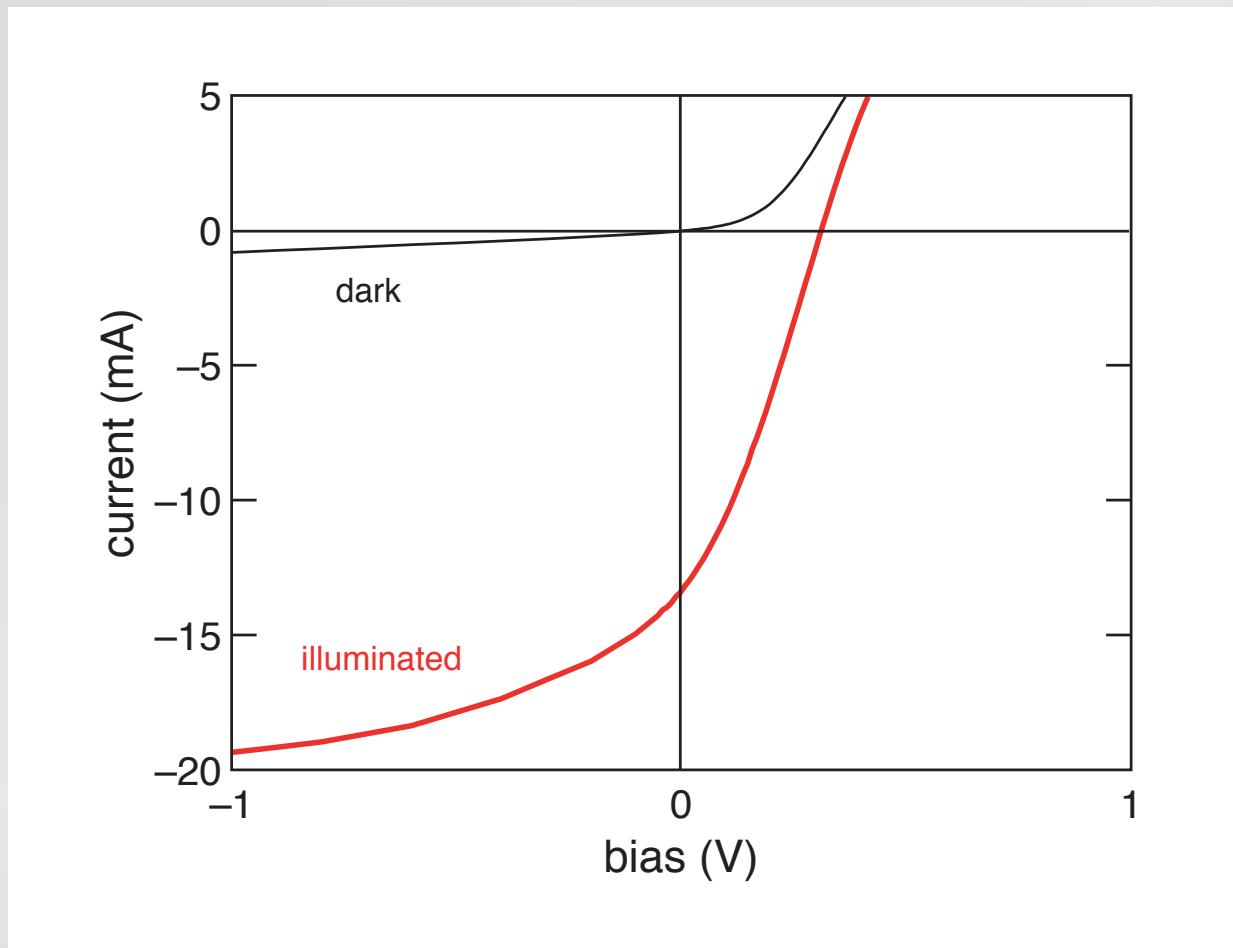
# Devices

very preliminary photovoltaic cell



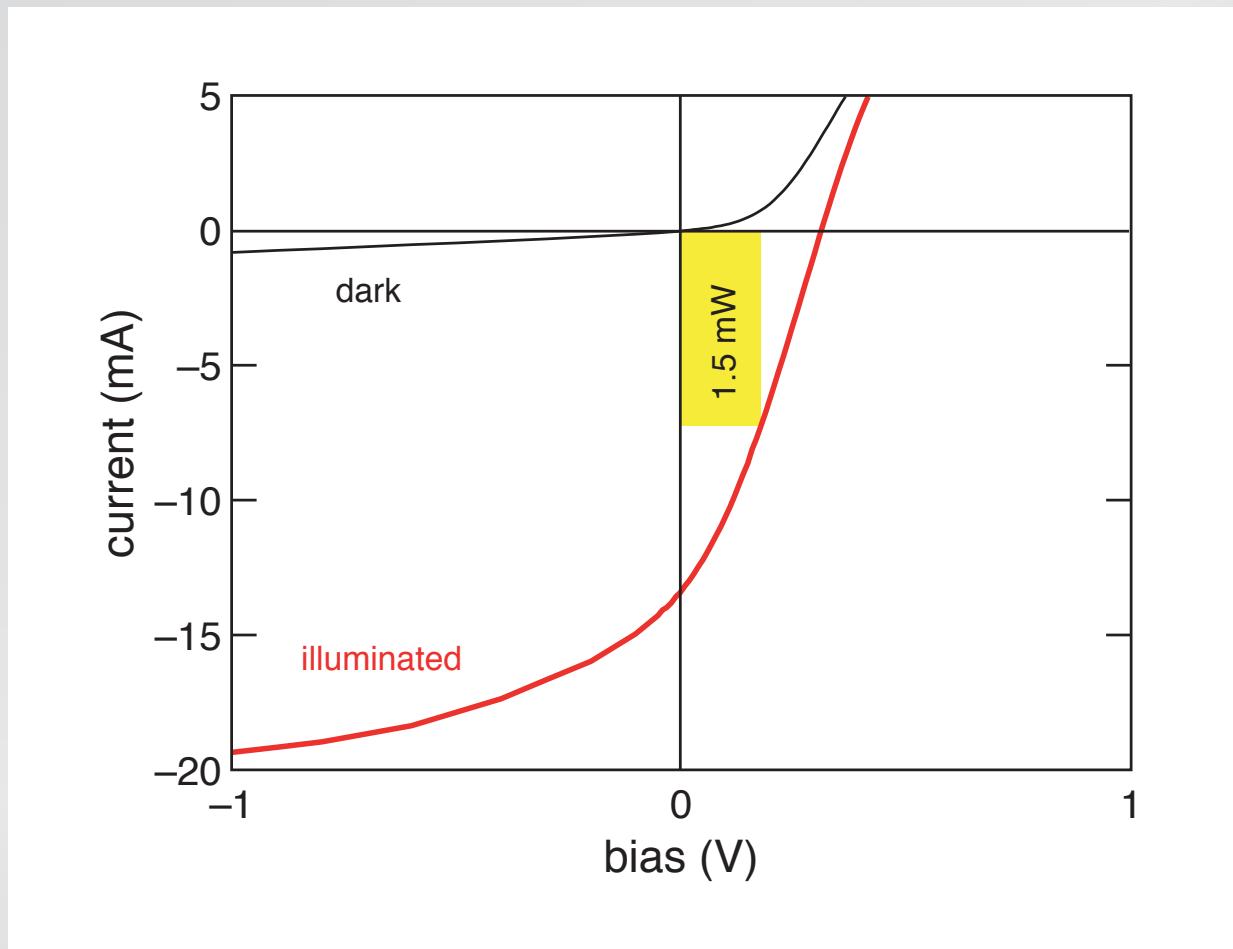
# Devices

very preliminary photovoltaic cell



# Devices

1.5% efficiency, a good beginning







**Funding:**

**Army Research Office**

**DARPA**

**Department of Energy**

**NDSEG**

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