

# Transforming the optical properties of silicon using femtosecond laser pulses



Keio-Harvard Workshop  
Horizons of Nanophotonics and Nanoelectronics  
Cambridge, MA, 20 December 2010

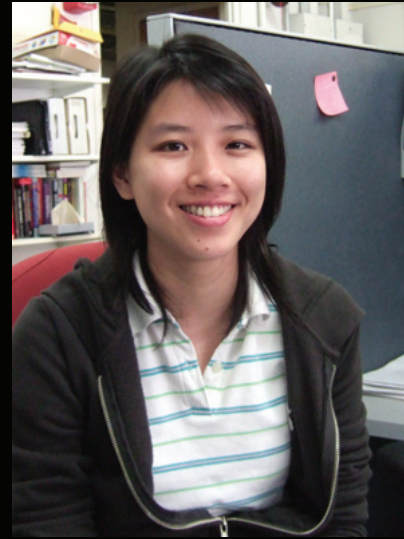




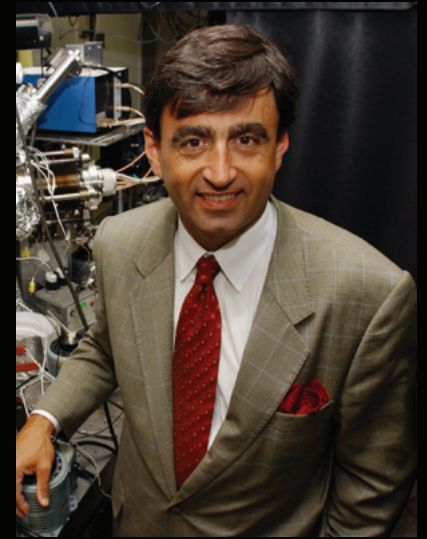
**Mark Winkler**



**Renee Sher**



**Yu-Ting Lin**



**Eric Mazur**

**and also....**

**Eric Diebold  
Haifei Albert Zhang  
William Whitney  
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)  
Matthew Smith (MIT)**

**Prof. Augustinus Asenbaum (Vienna)**

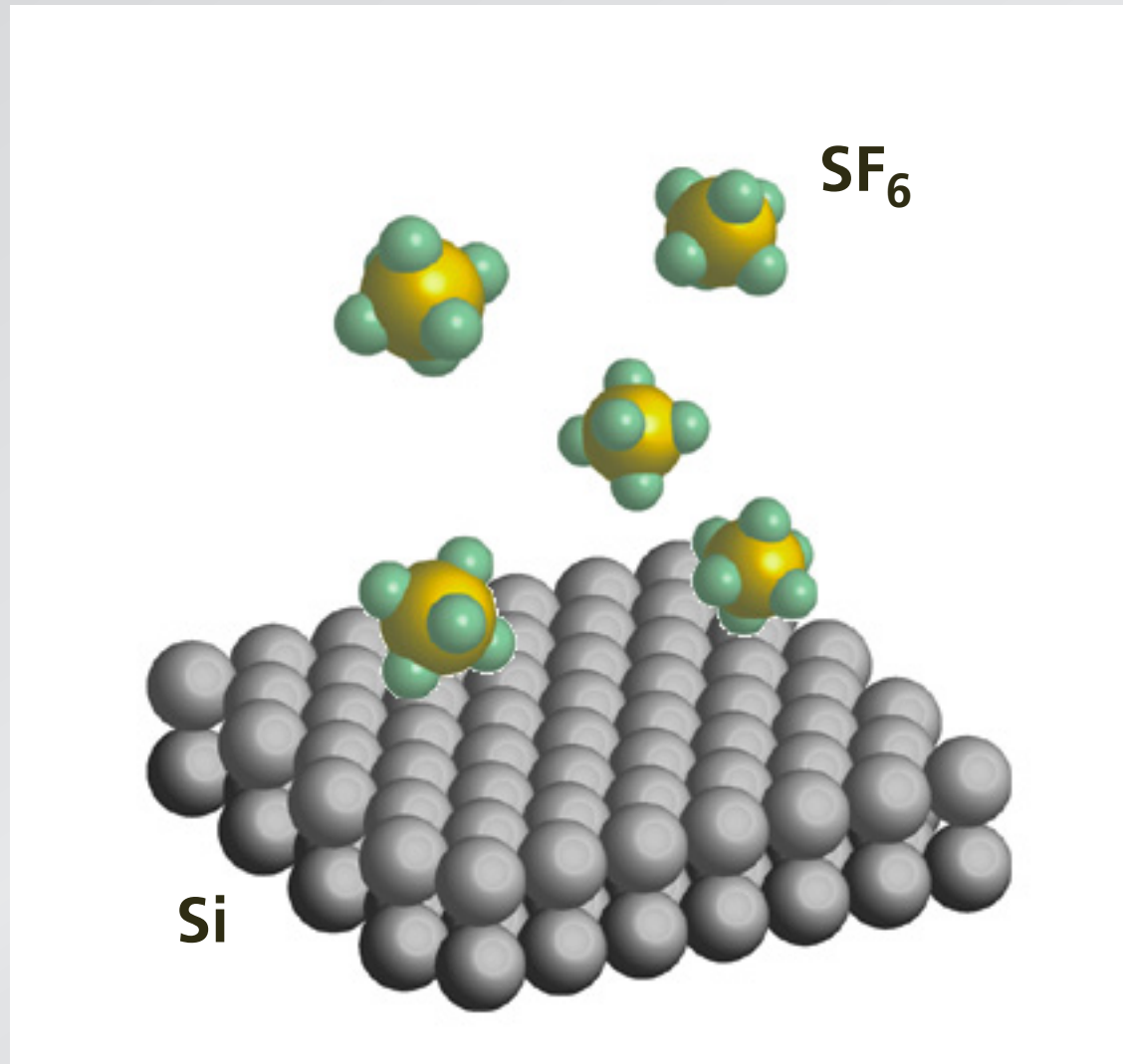
**Dr. François Génin (LLNL)  
Mark Wall (LLNL)**

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

**Dr. Pat Maloney (NVSED)**

**Dr. Jeffrey Warrander (ARDEC)**

# Introduction



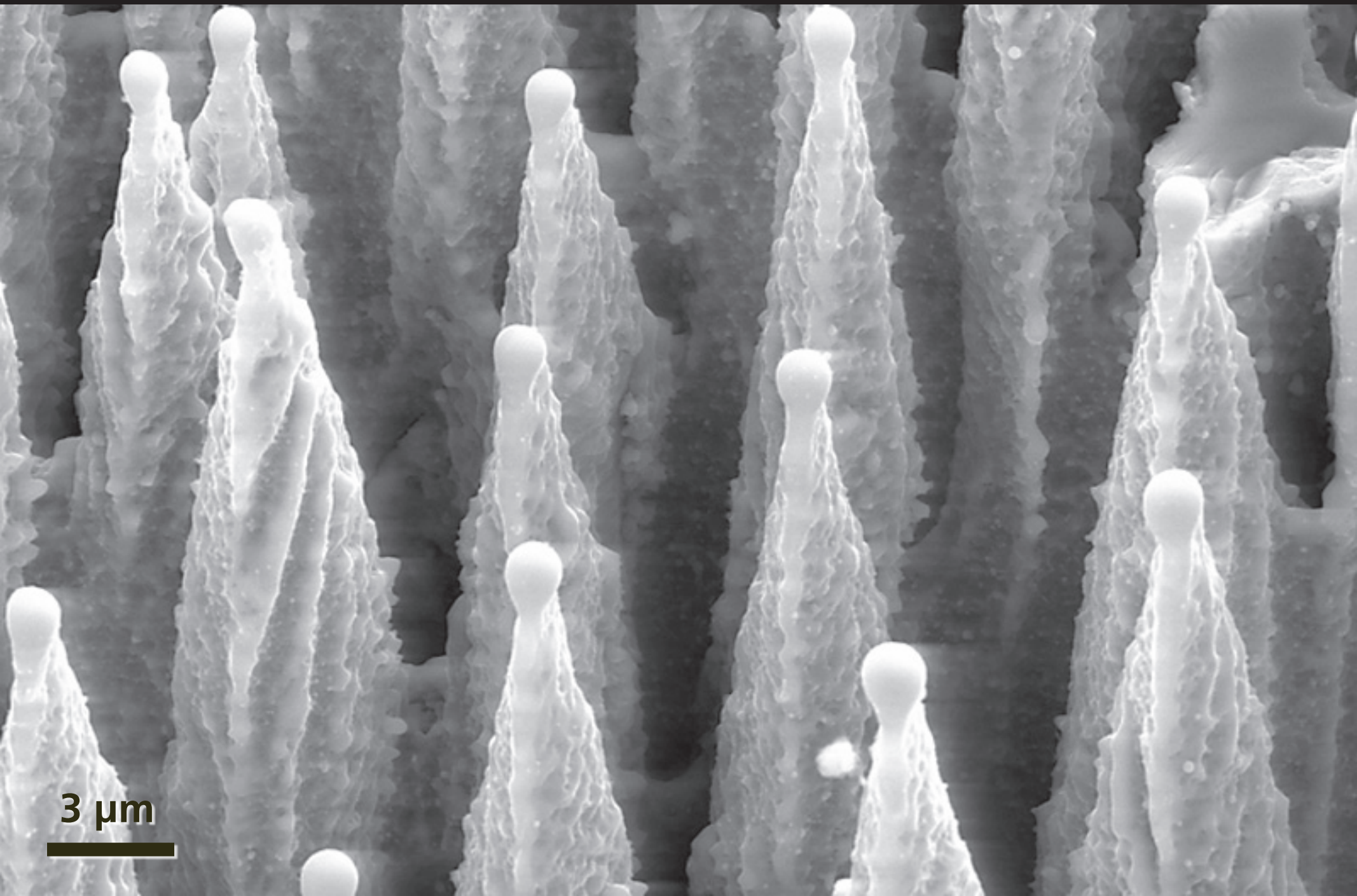
irradiate with 100-fs 10 kJ/m<sup>2</sup> pulses

# Introduction



**"black silicon"**

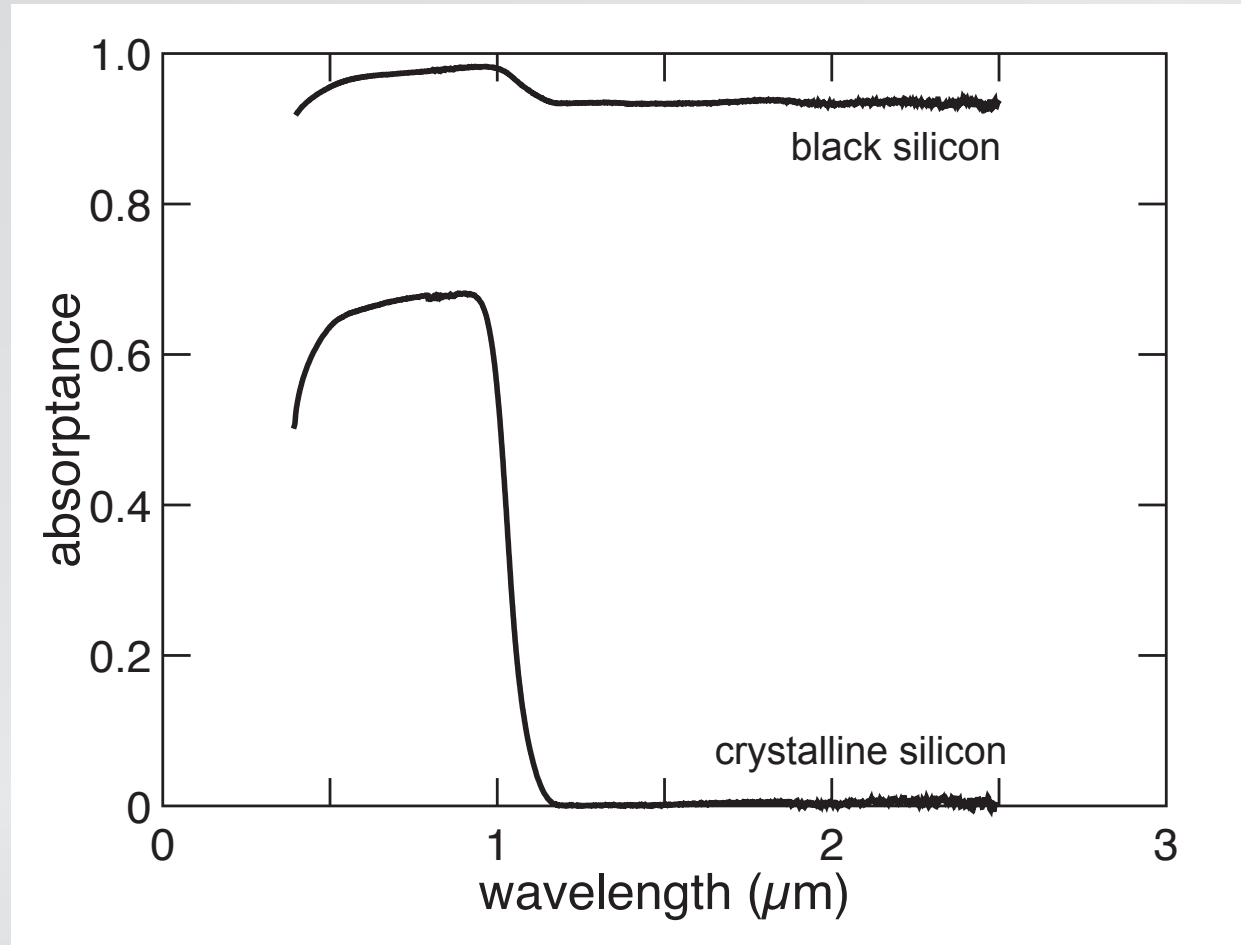
# Introduction



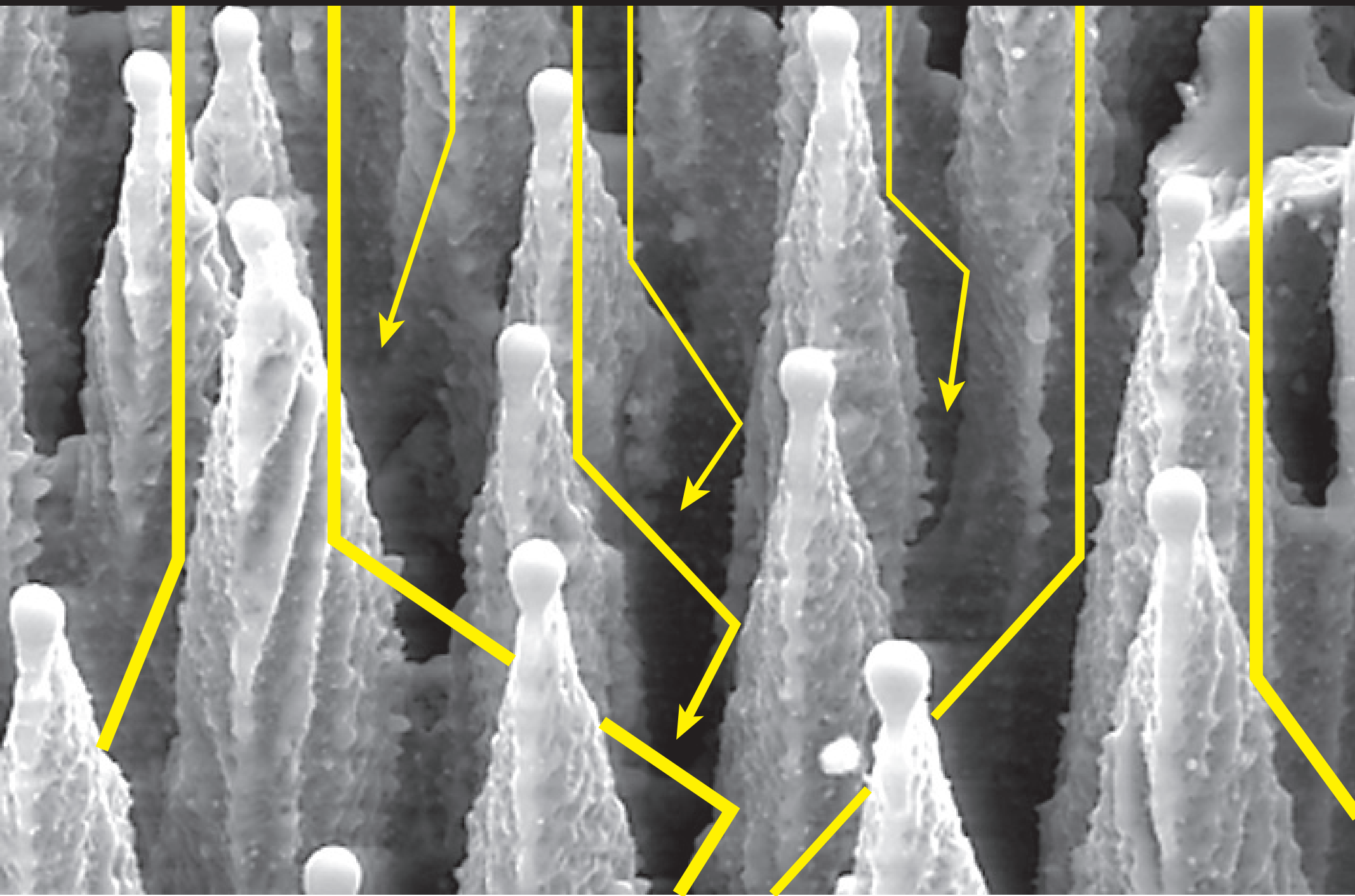
3  $\mu\text{m}$

# Introduction

absorptance ( $1 - R_{int} - T_{int}$ )



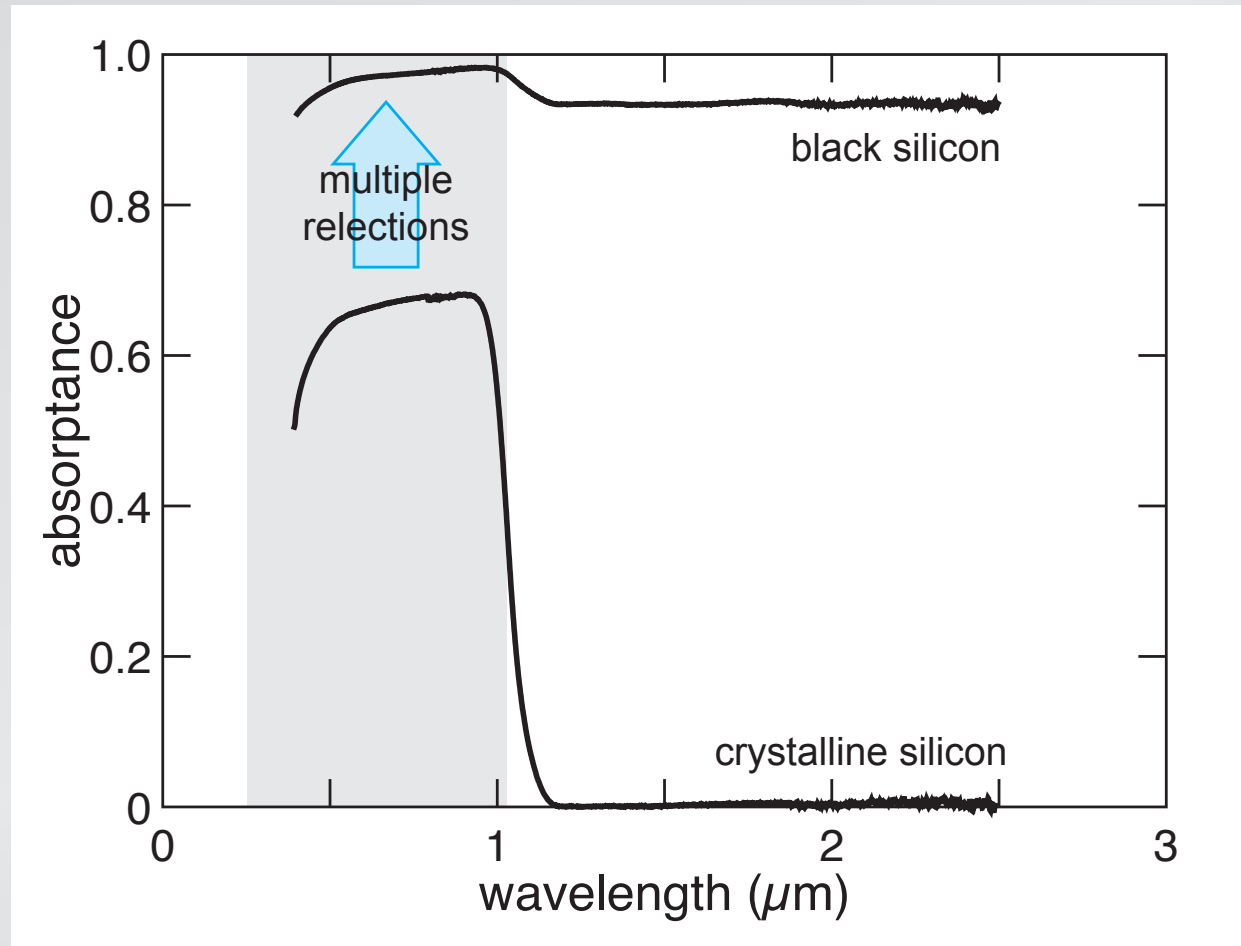
# Introduction





# Introduction

absorptance ( $1 - R_{int} - T_{int}$ )



# Introduction

**band structure changes: defects and/or impurities**

# Introduction

## a decade of research

### OPTICAL

UV-VIS-NIR  
FTIR  
photoluminescence  
PTD spectroscopy  
UPS  
XPS

responsivity  
photoconductivity

### ELECTRONIC

Hall measurements  
conductivity  
IV rectification  
c-AFM

### STRUCTURAL

SEM  
TEM  
EDX  
SAD  
EXAFS  
AFM  
SIMS  
RBS  
ion channeling

# Introduction

## a decade of research

### OPTICAL

UV-VIS-NIR  
FTIR  
photoluminescence  
PTD spectroscopy  
UPS  
XPS

responsivity  
photoconductivity

gap  
impurity band  
transitions

### ELECTRONIC

Hall measurements  
conductivity  
IV rectification  
c-AFM

### STRUCTURAL

SEM  
TEM  
EDX  
SAD  
EXAFS  
AFM  
SIMS  
RBS  
ion channeling

# Introduction

## a decade of research

OPTICAL	ELECTRONIC	STRUCTURAL
UV-VIS-NIR	Hall measurements	SEM
FTIR	conductivity	TEM
photoluminescence	IV rectification	EDX
PTD spectroscopy	c-AFM	SAD
UPS		EXAFS
XPS		AFM
	responsivity	SIMS
	photoconductivity	RBS
		ion channeling
gap	carrier concentration	
impurity band	mobilities	
transitions	junction properties	

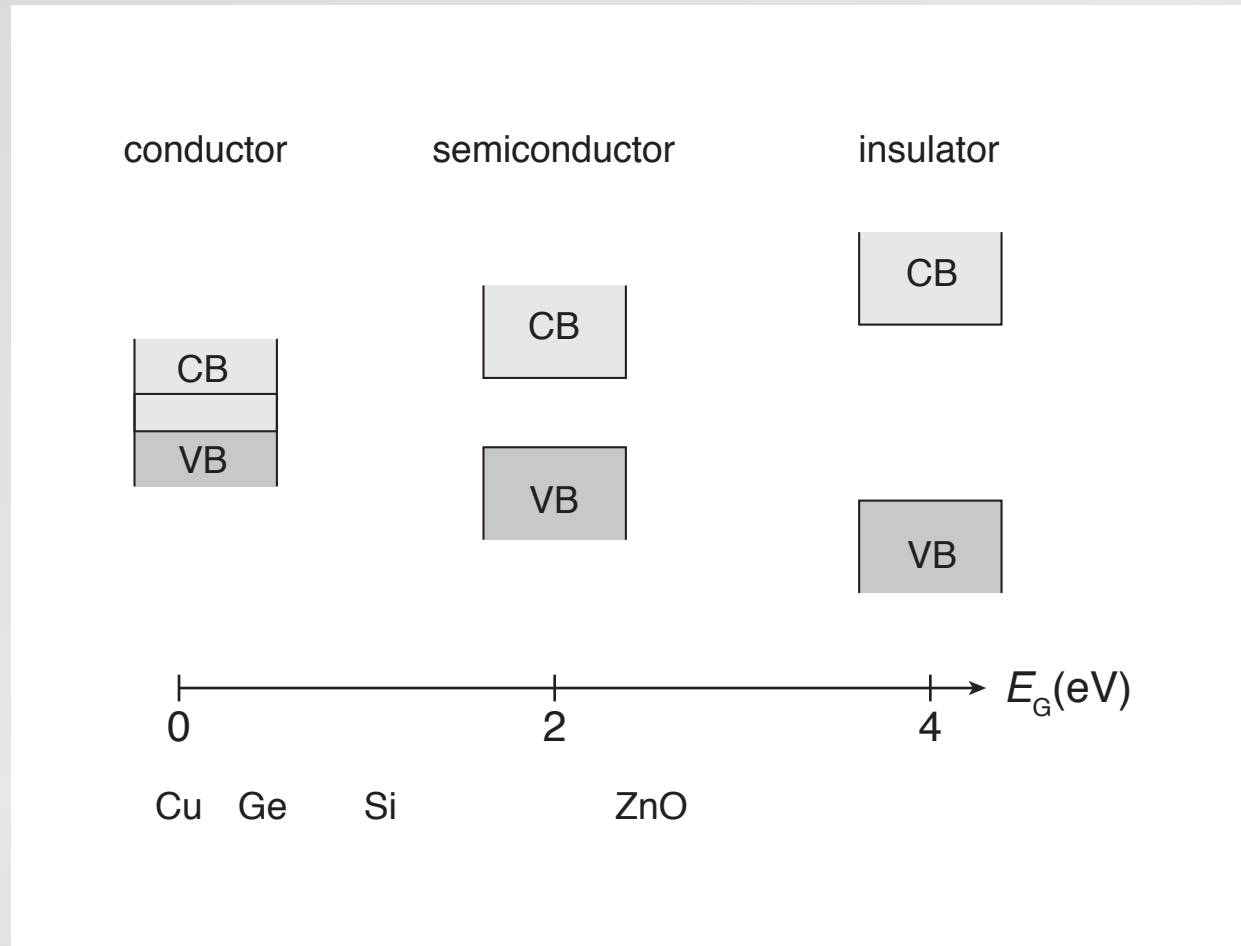
# Introduction

## a decade of research

OPTICAL	ELECTRONIC	STRUCTURAL
UV-VIS-NIR	Hall measurements	SEM
FTIR	conductivity	TEM
photoluminescence	IV rectification	EDX
PTD spectroscopy	c-AFM	SAD
UPS		EXAFS
XPS		AFM
	responsivity	SIMS
	photoconductivity	RBS
		ion channeling
gap	carrier concentration	morphology
impurity band	mobilities	composition
transitions	junction properties	atomic structure

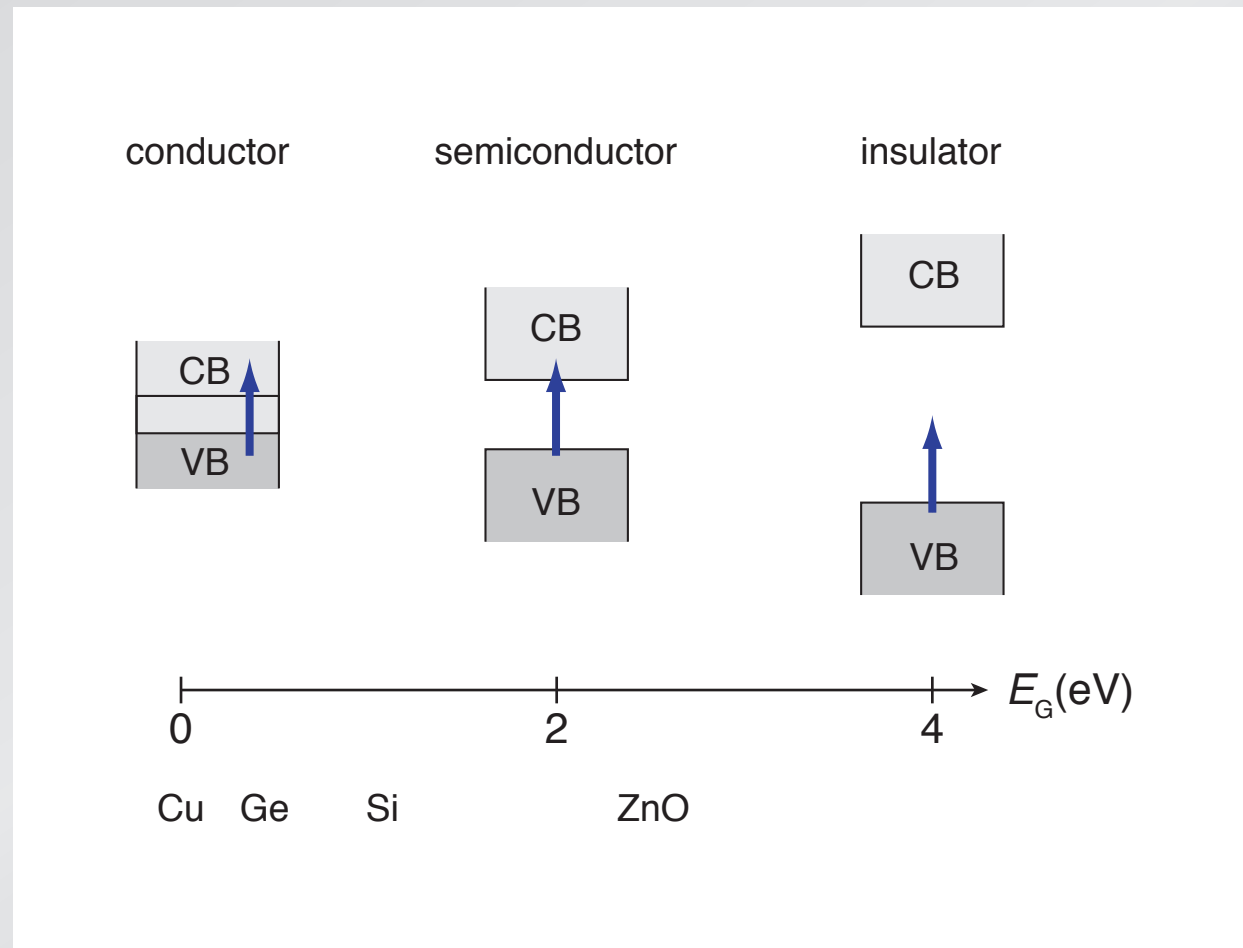
# Introduction

new process & new class of material!



# Introduction

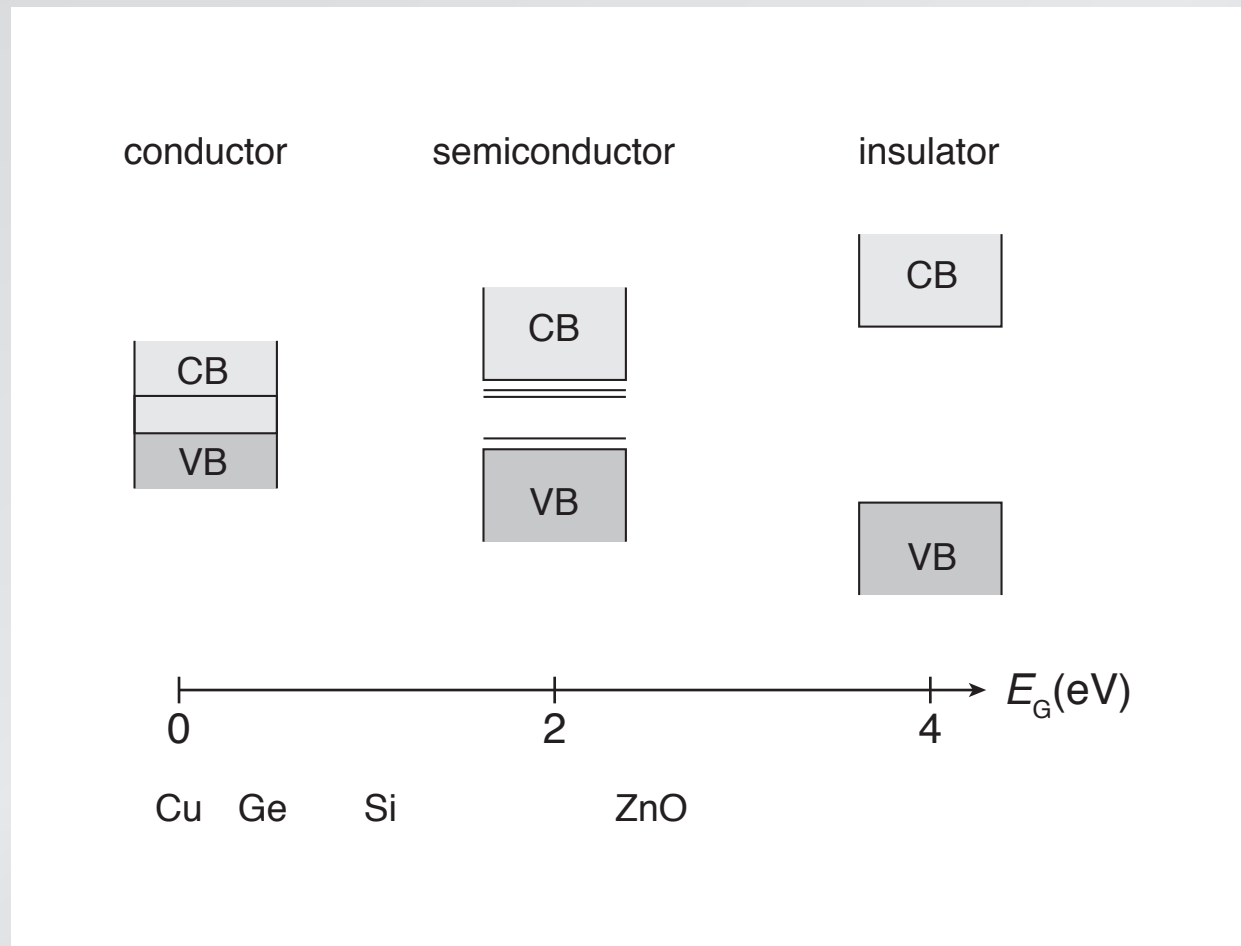
gap determines optical and electronic properties





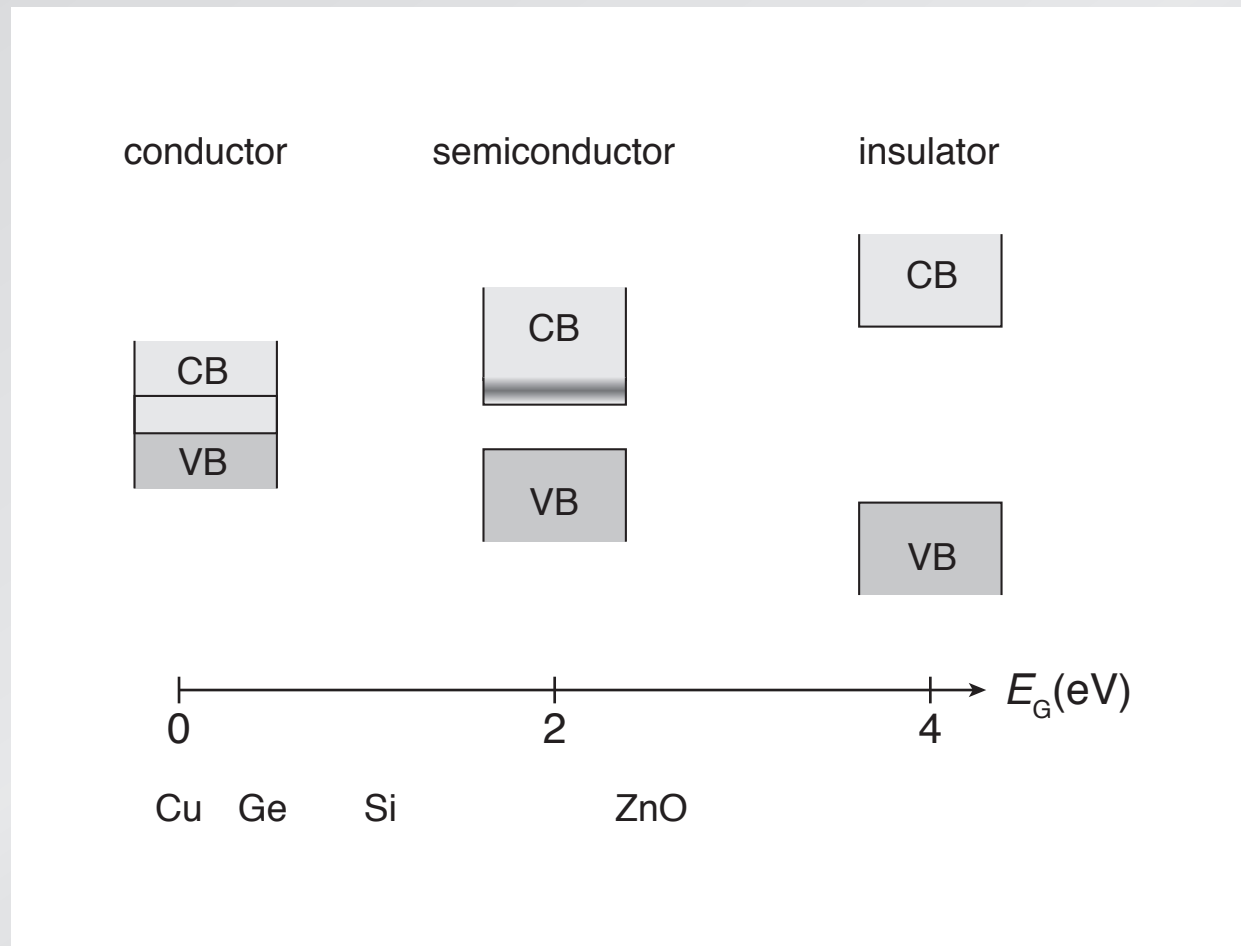
# Introduction

shallow-level dopants control electronic properties



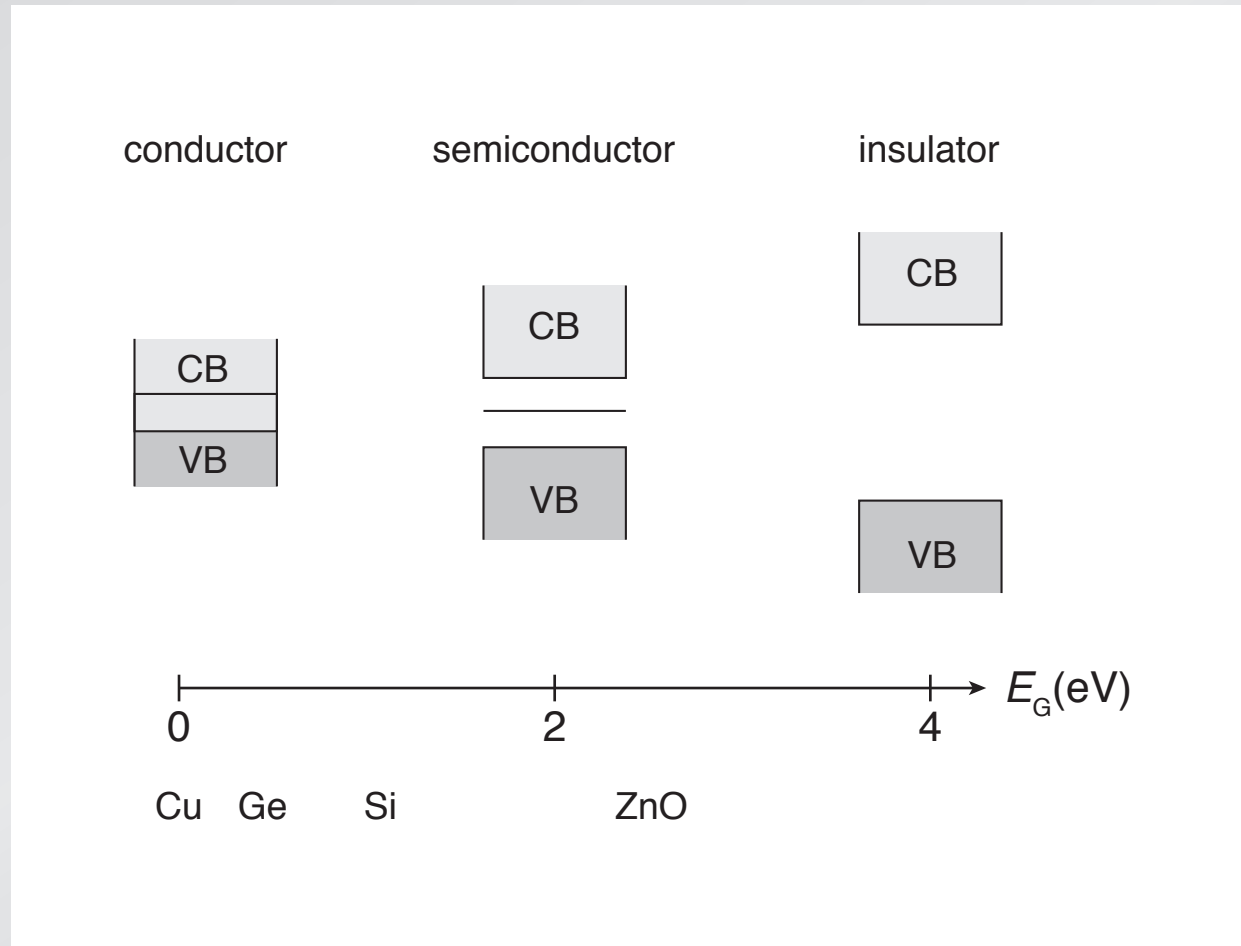
# Introduction

shallow-level dopants control electronic properties



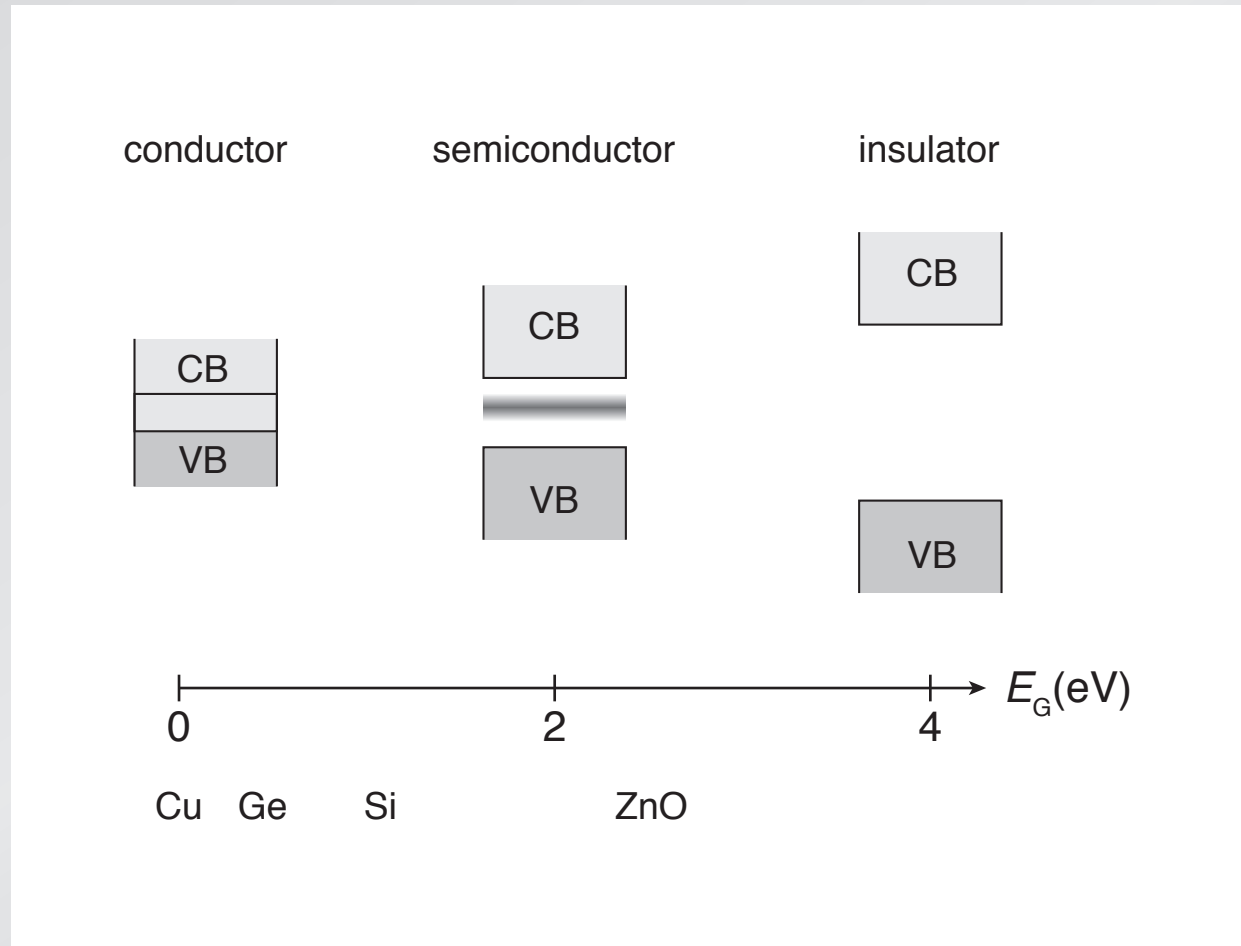
# Introduction

deep-level dopants typically avoided



# Introduction

femtosecond laser-doping gives rise to intermediate band



# Introduction

## substrate/dopant combinations

dopants:

N	O	F
P	S	Cl
	Se	
Sb	Te	

# Introduction

## substrate/dopant combinations

**dopants:**

N	O	F
P	S	Cl
	Se	
Sb	Te	

**substrates:**

Si    Ge    ZnO    InP    GaAs

Ti    Ag    Al    Cu    Pd    Rh    Ta    Pt

# Introduction

focus on chalcogen-doped silicon

dopants:

N	O	F
P	S	Cl
	Se	
Sb	Te	

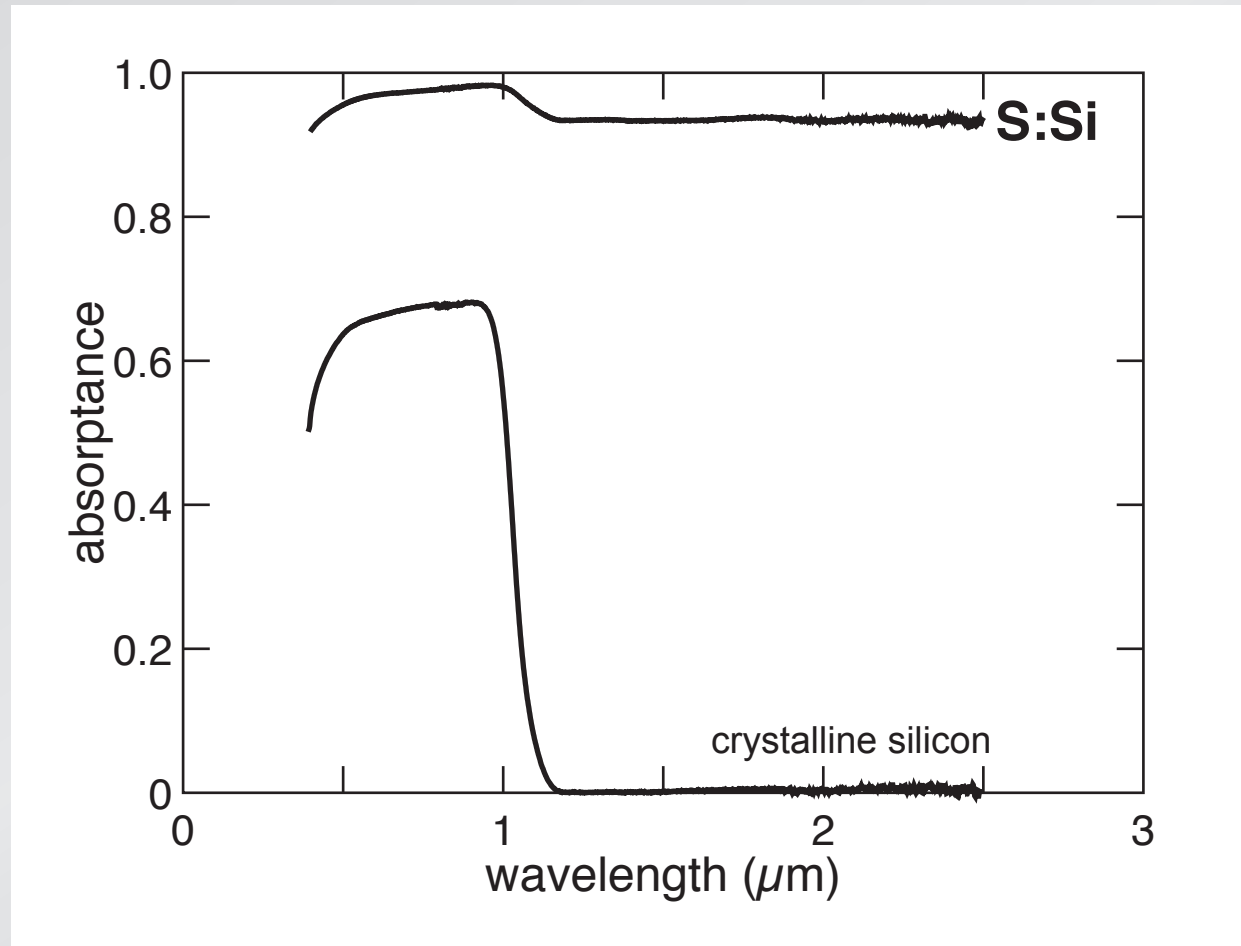
substrates:

Si Ge ZnO InP GaAs

Ti Ag Al Cu Pd Rh Ta Pt

# Introduction

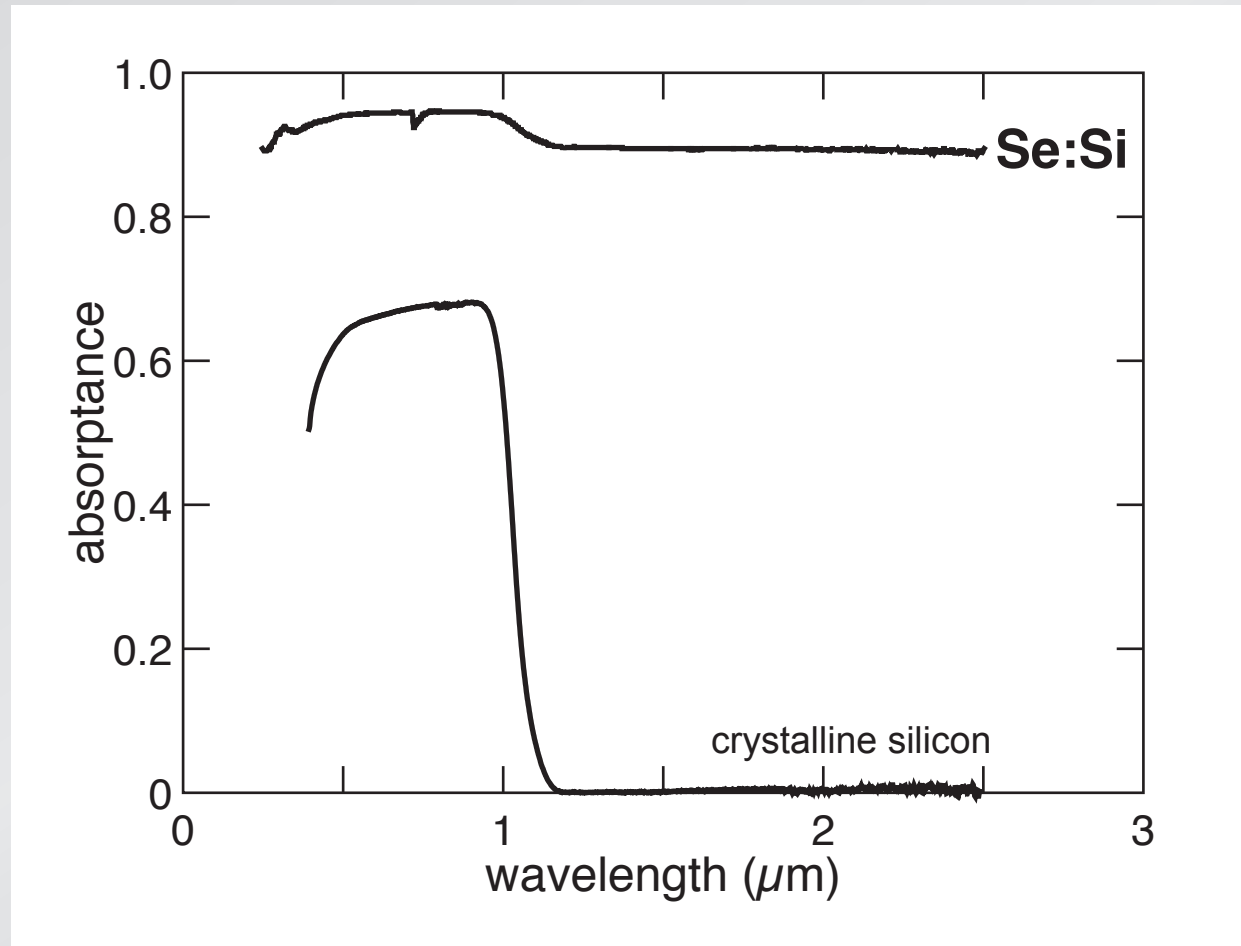
focus on chalcogen-doped silicon





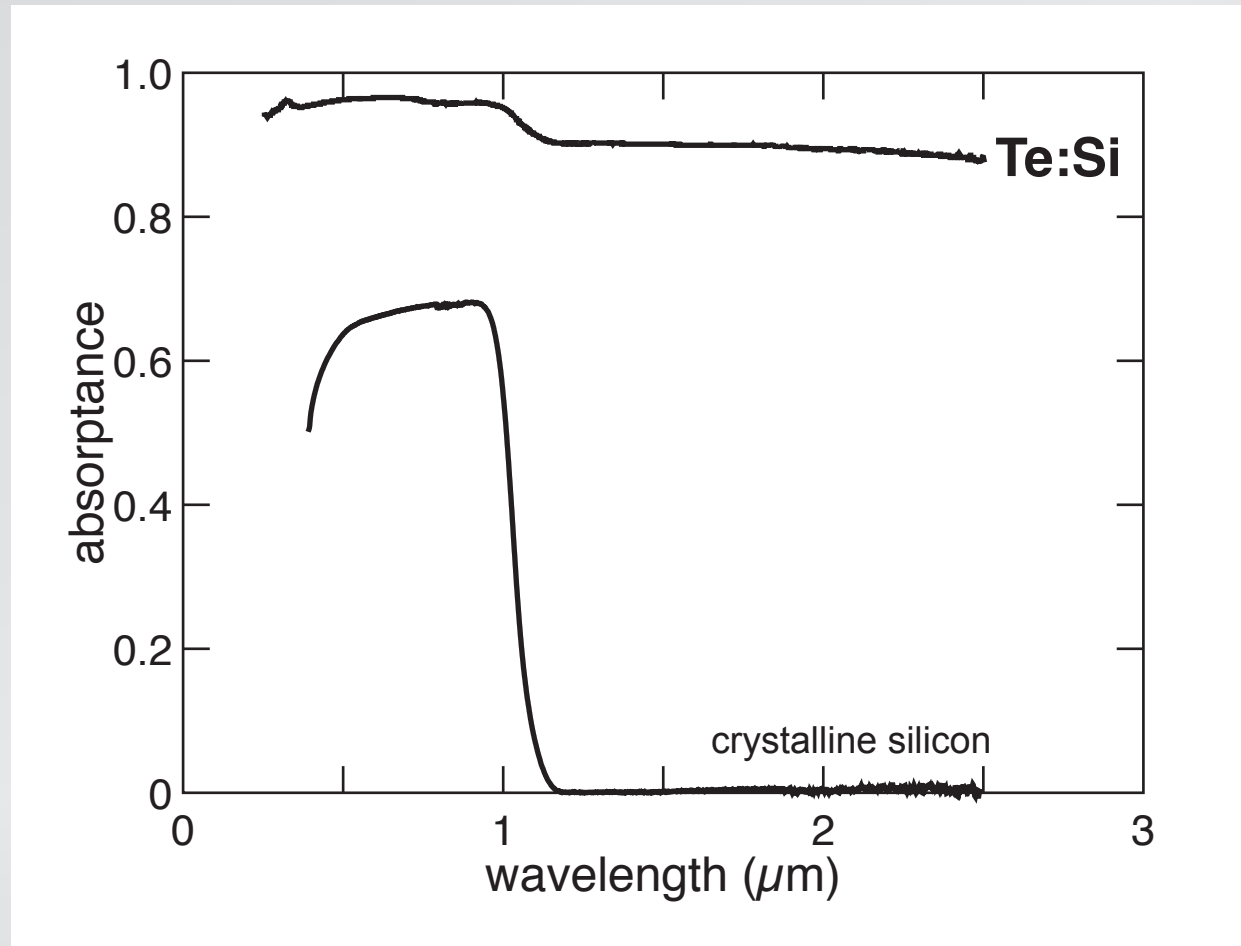
# Introduction

focus on chalcogen-doped silicon



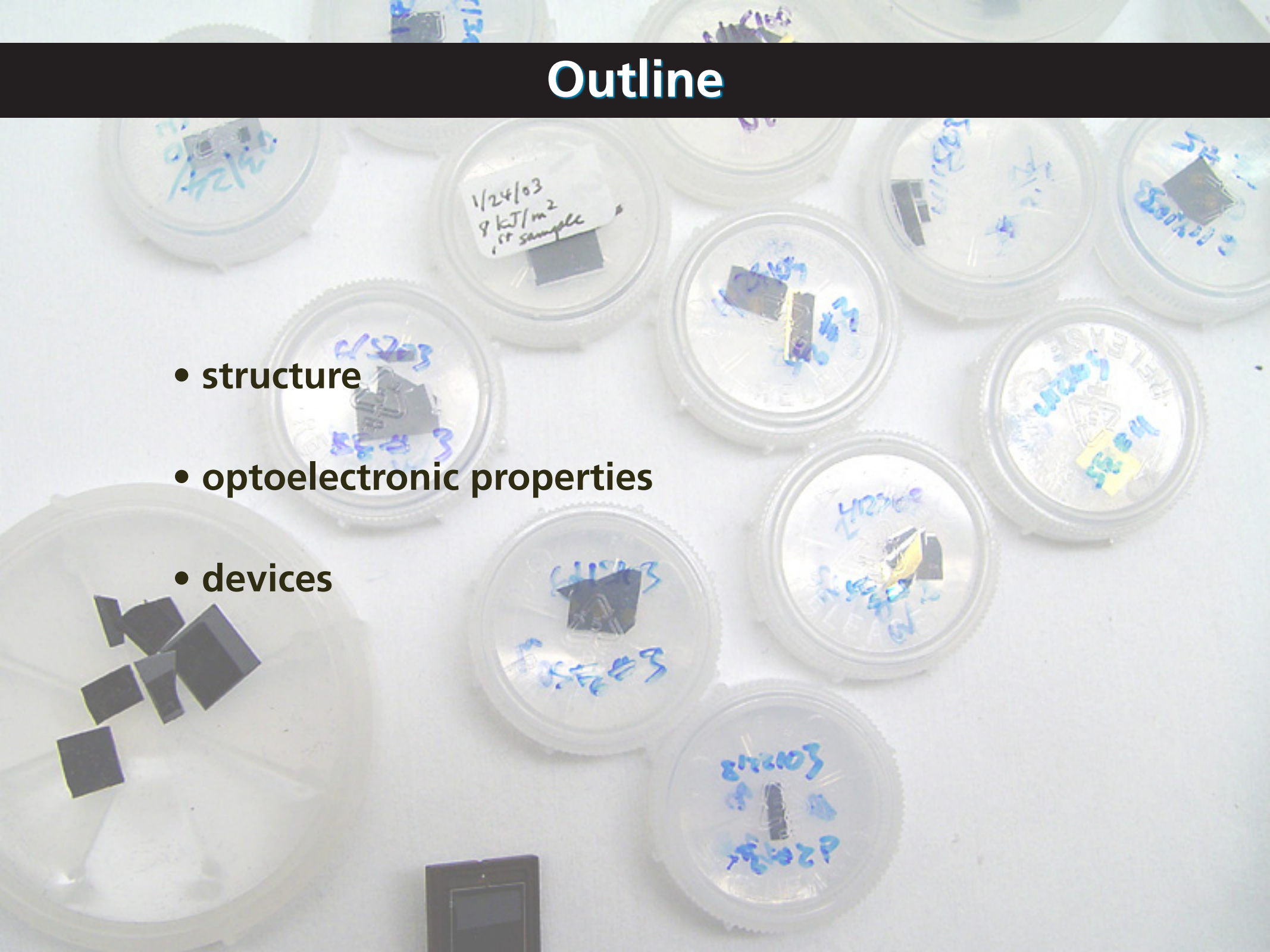
# Introduction

focus on chalcogen-doped silicon

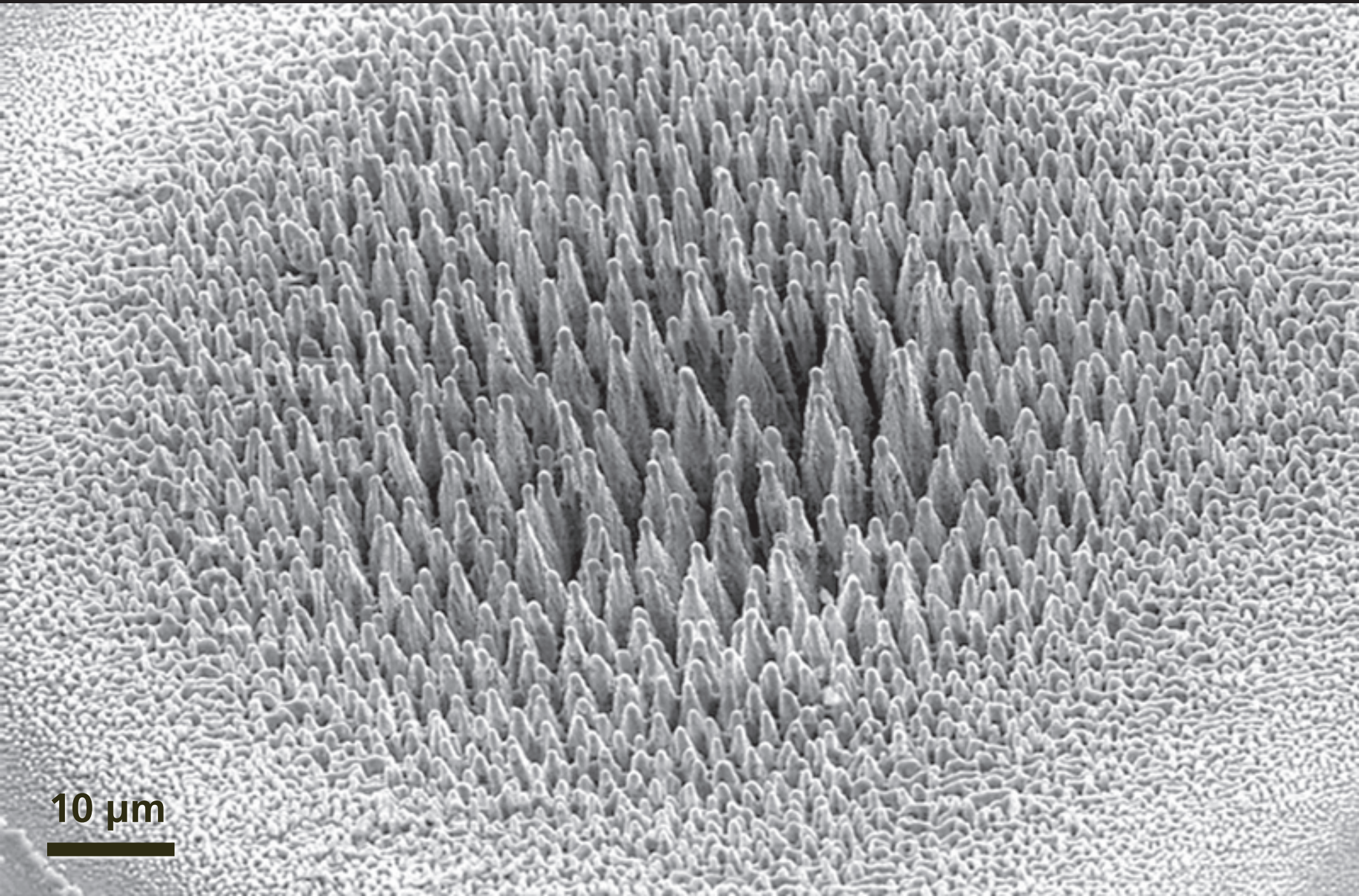


# Outline

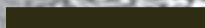
- structure
- optoelectronic properties
- devices



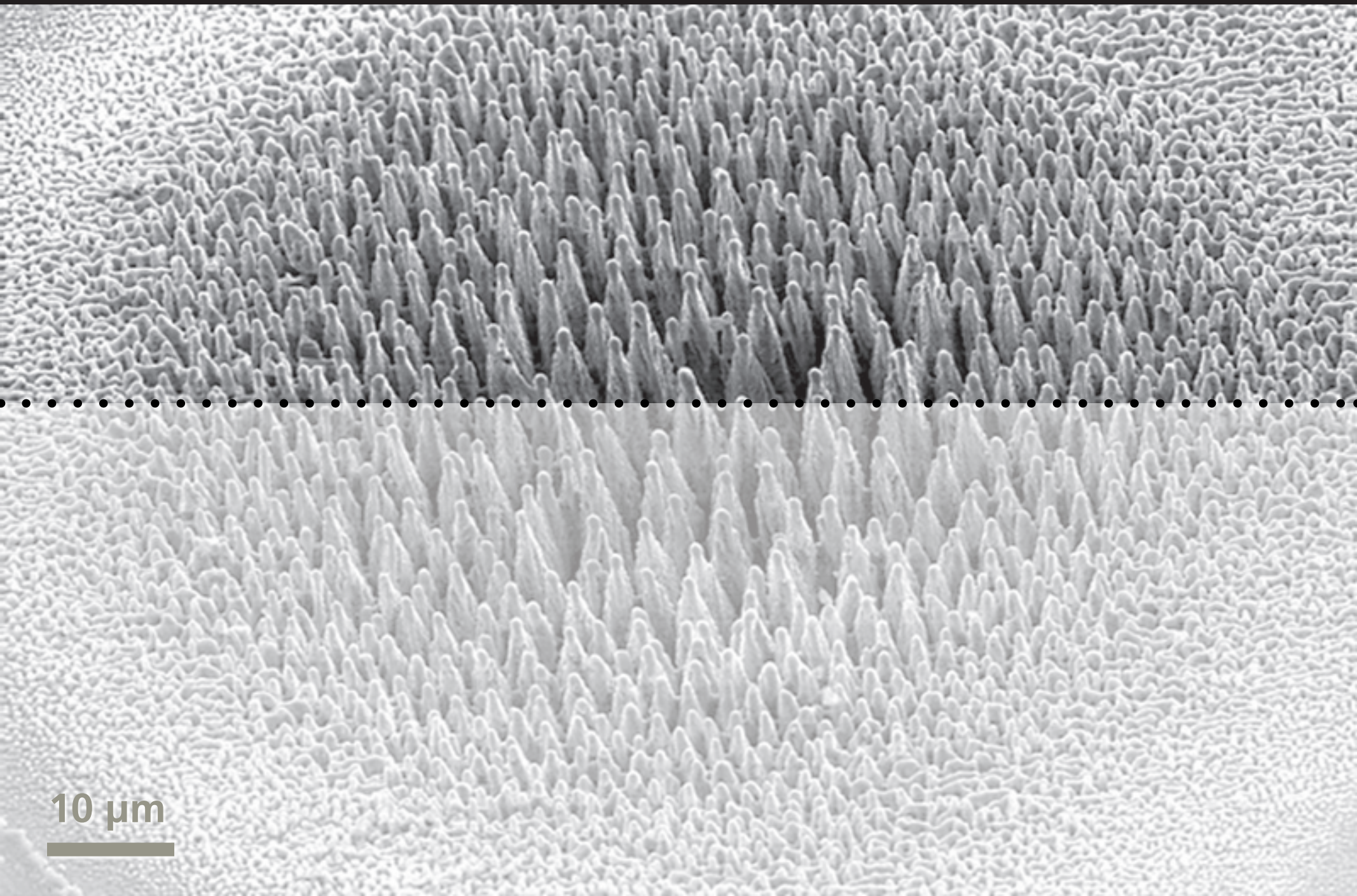
# Structure



10  $\mu\text{m}$



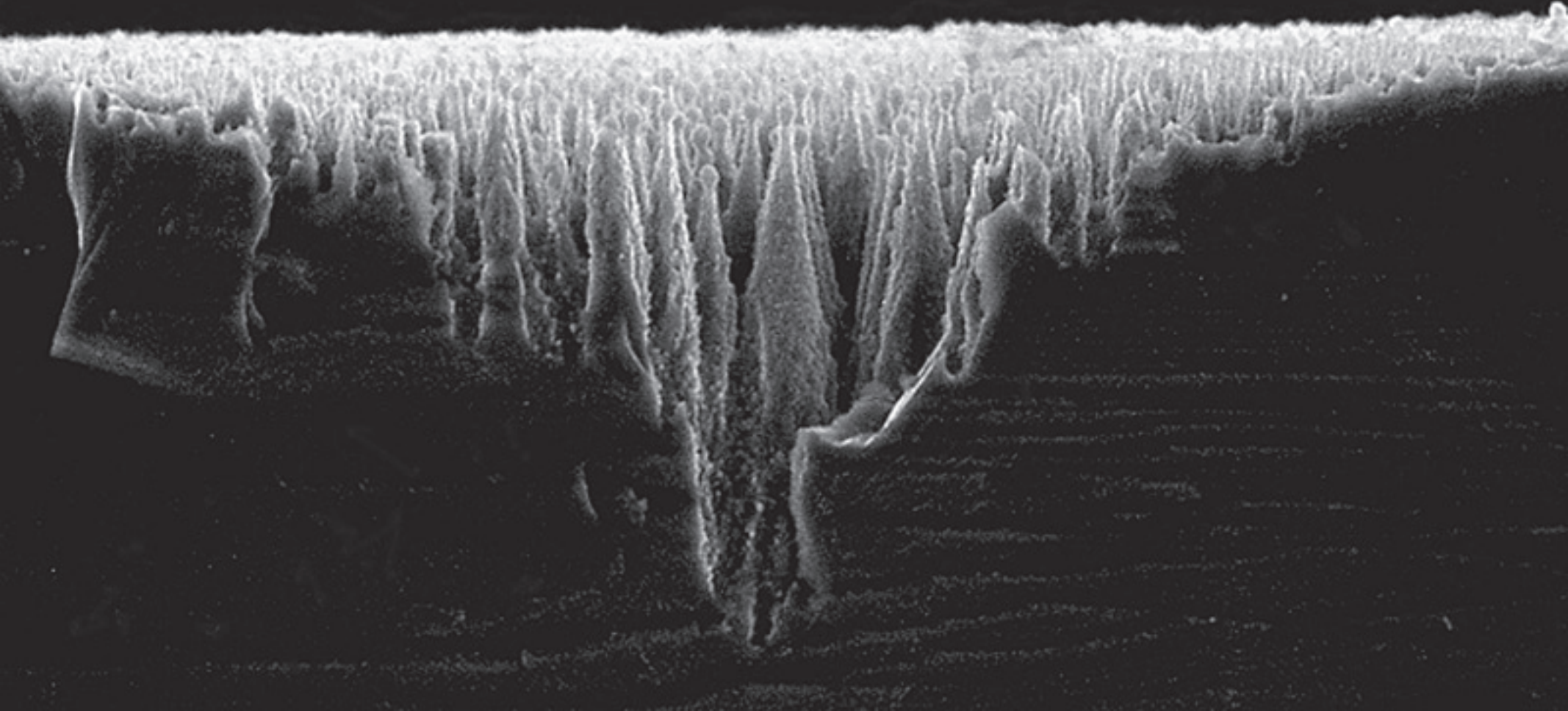
# Structure



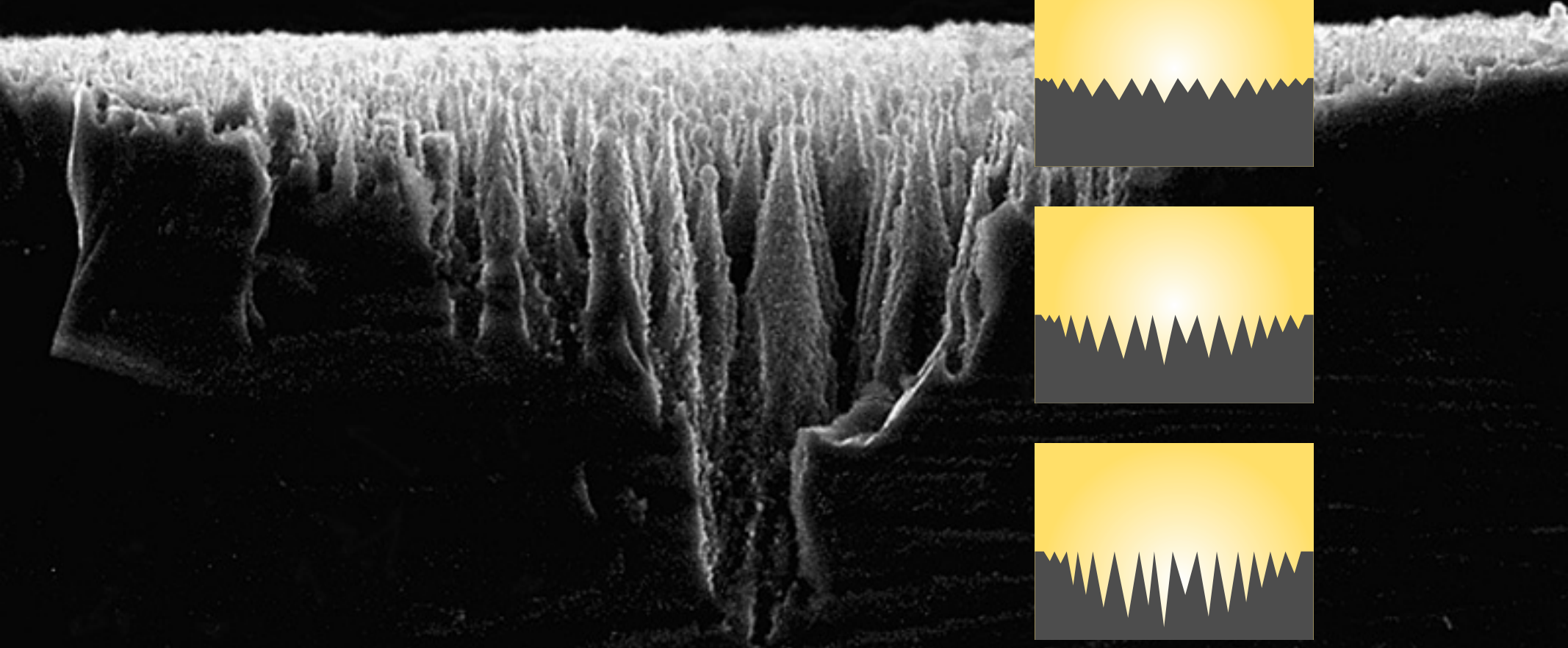
10  $\mu\text{m}$



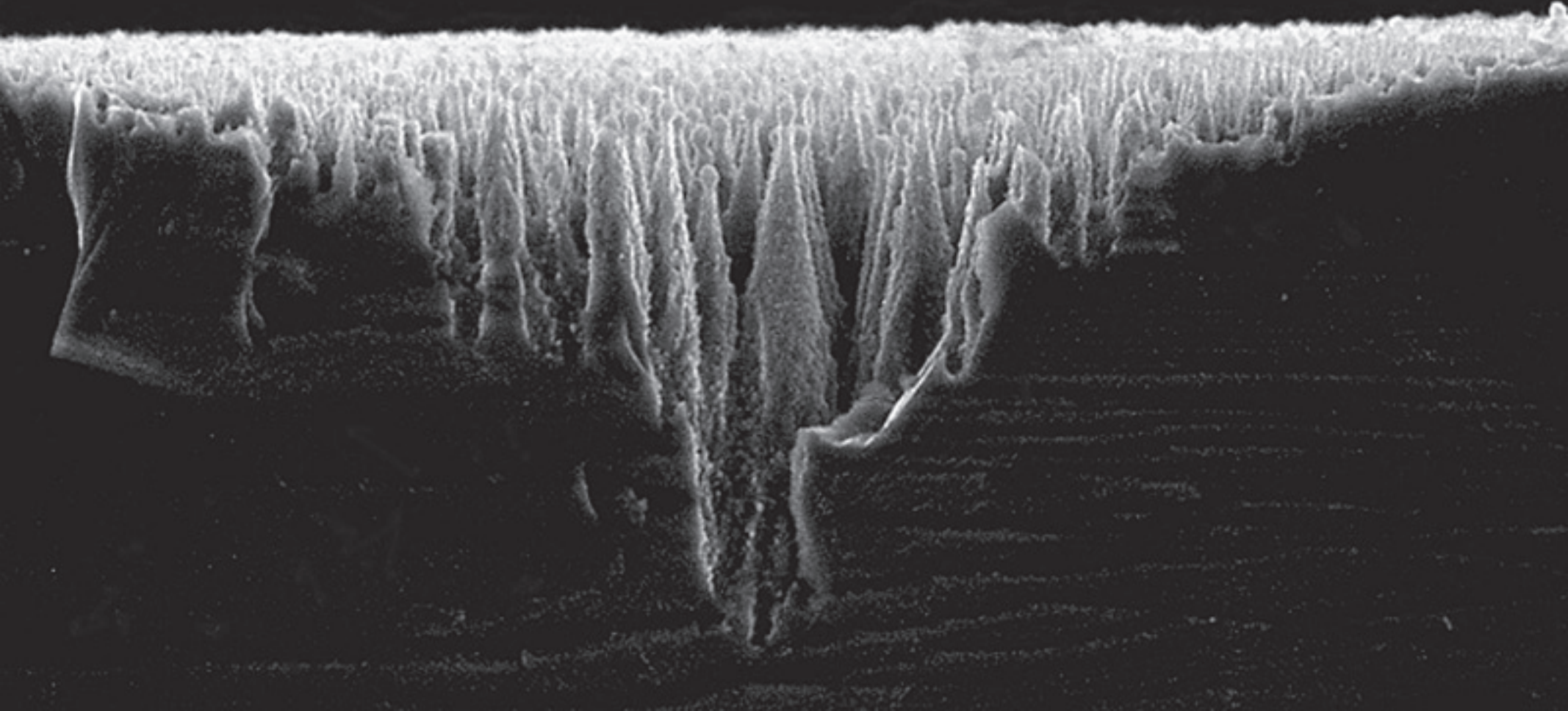
# Structure



# Structure

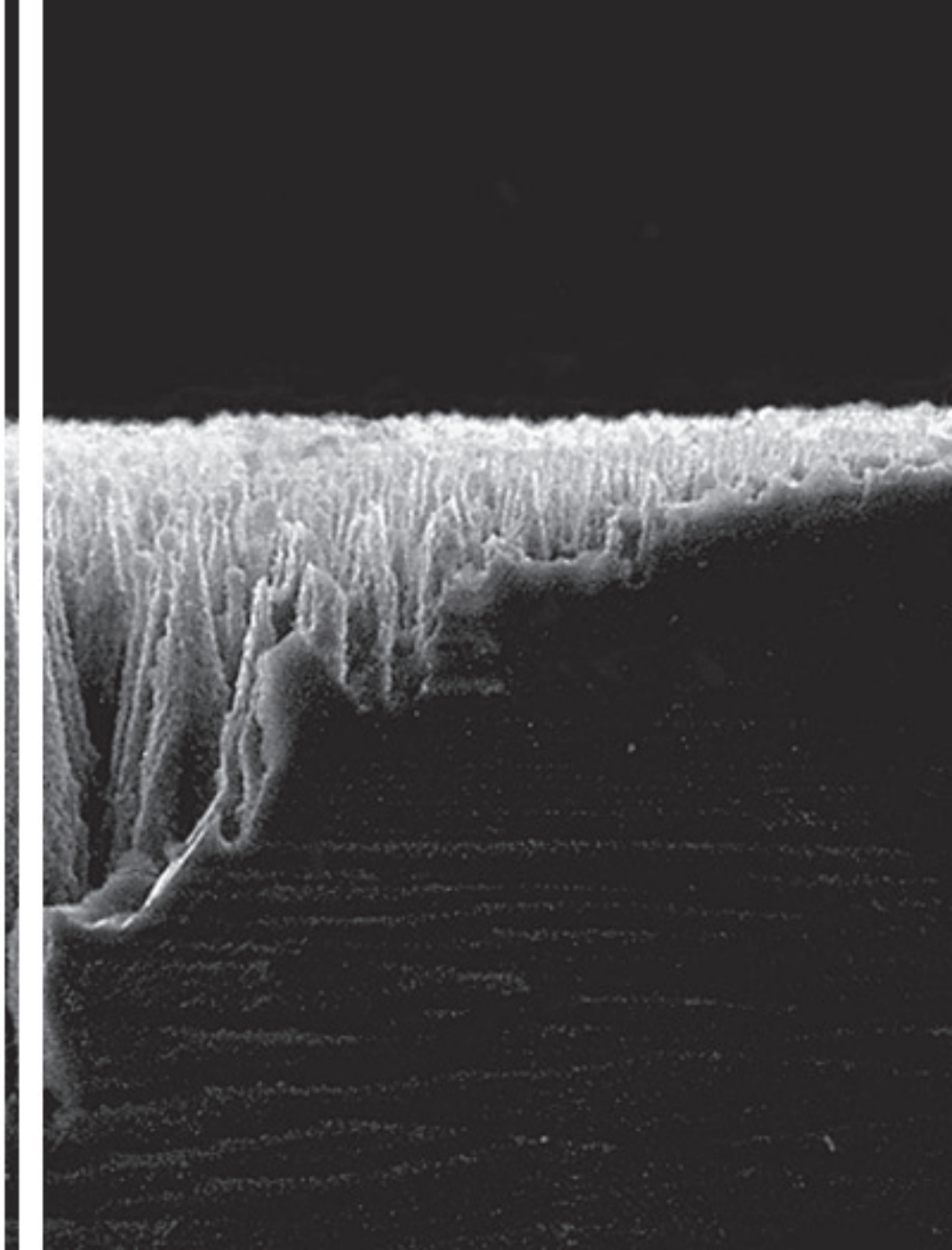
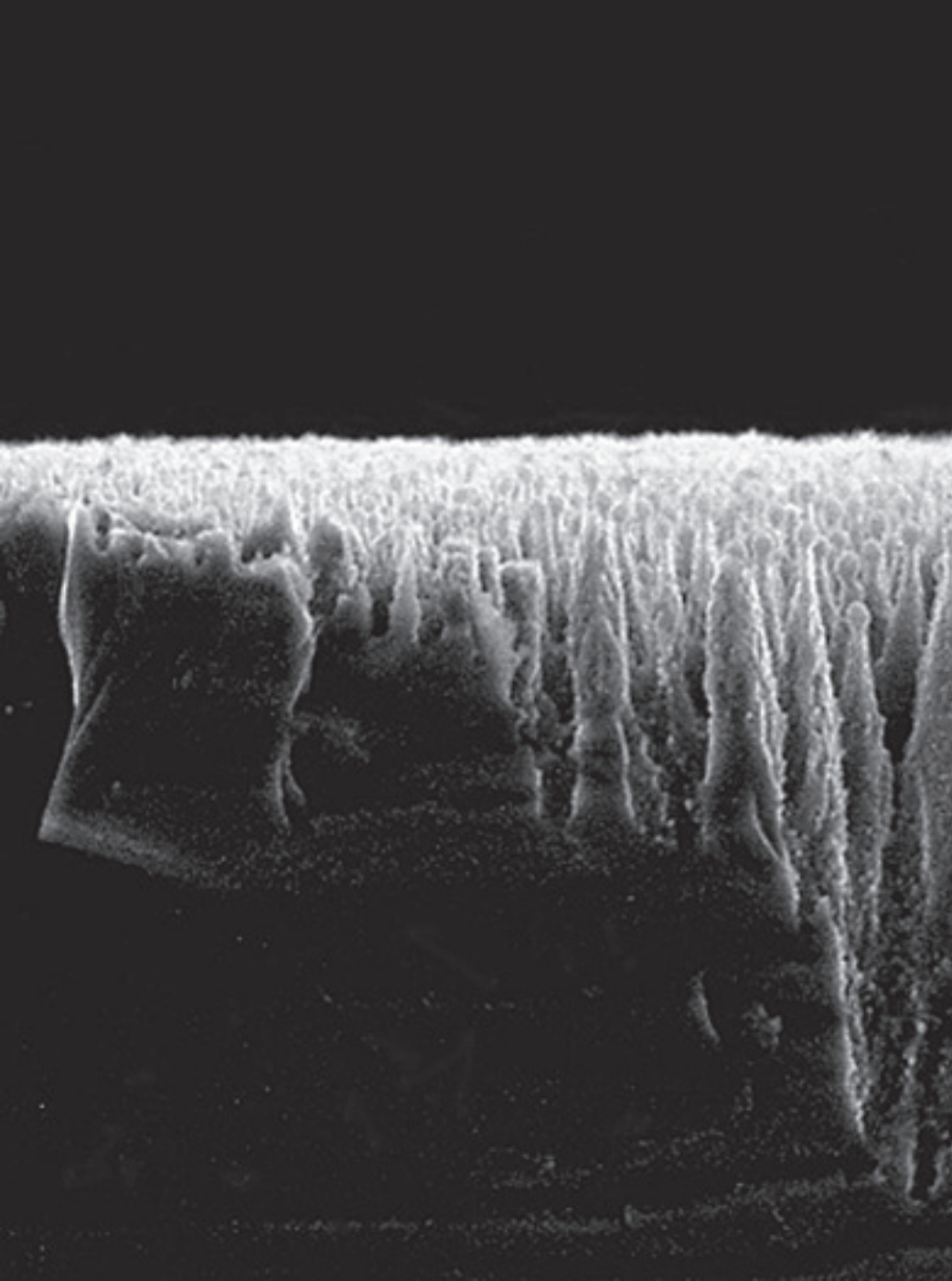


# Structure



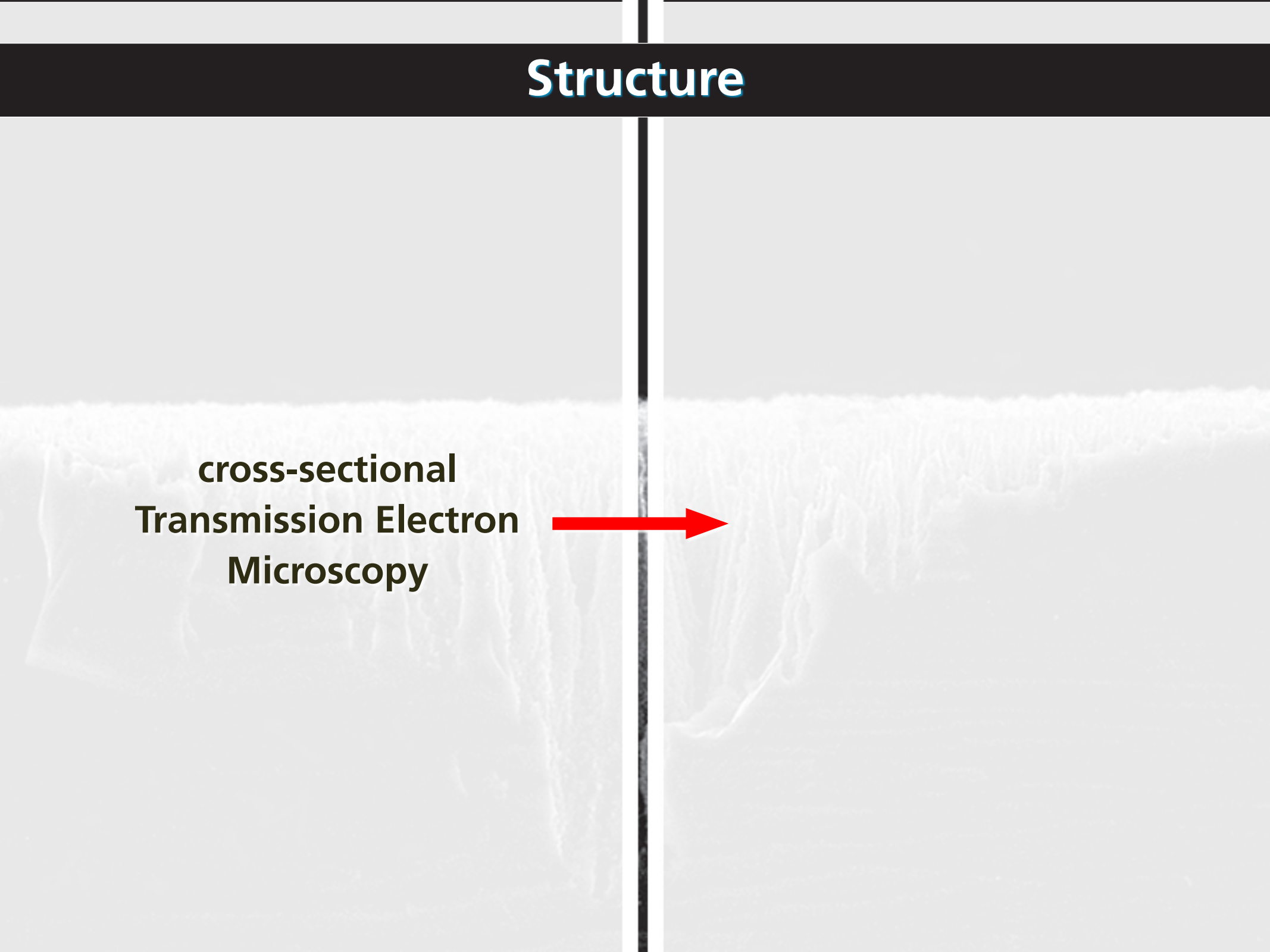


# Structure



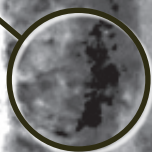
# Structure

**cross-sectional  
Transmission Electron  
Microscopy**



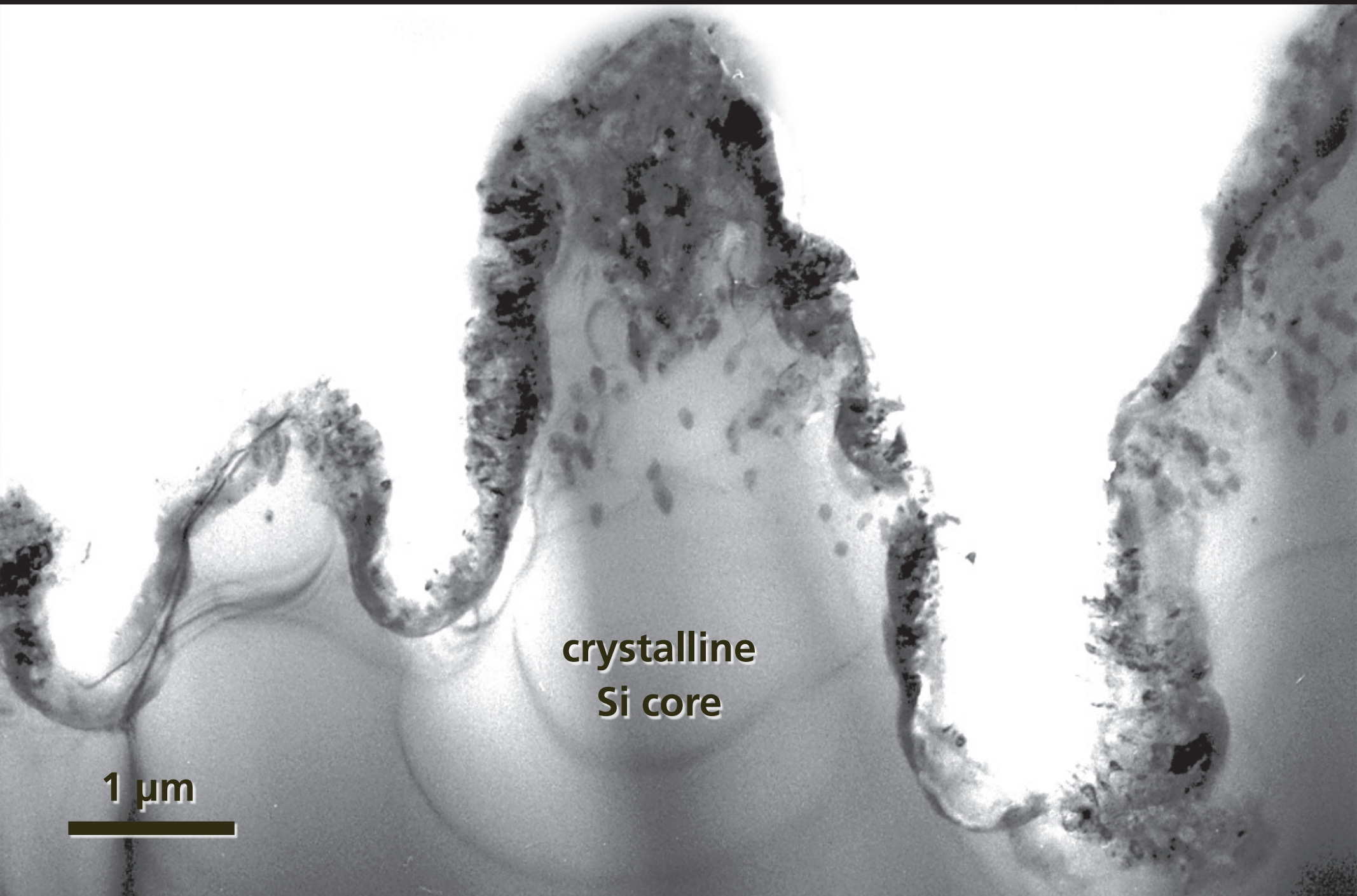
# Structure

disordered  
surface layer



1  $\mu\text{m}$

# Structure



crystalline  
Si core

1 μm

# Structure

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

1  $\mu\text{m}$

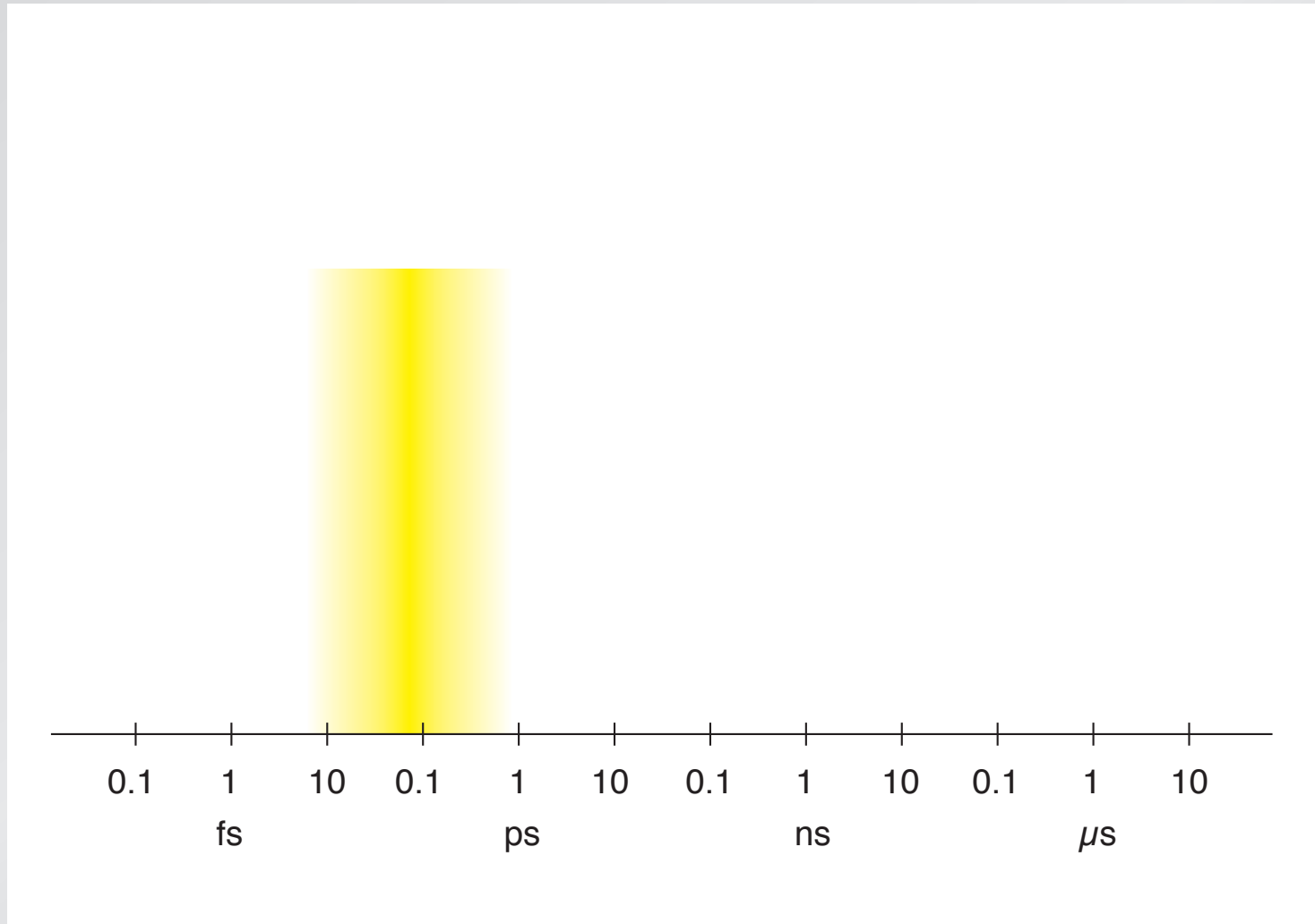
A grayscale micrograph showing several elongated, finger-like structures. Each structure has a darker, textured outer layer and a lighter, smoother inner core. The structures are interconnected and appear to be part of a larger network. A scale bar at the bottom left indicates a length of 1 micrometer.

# Structure

**two processes: melting and ablation**

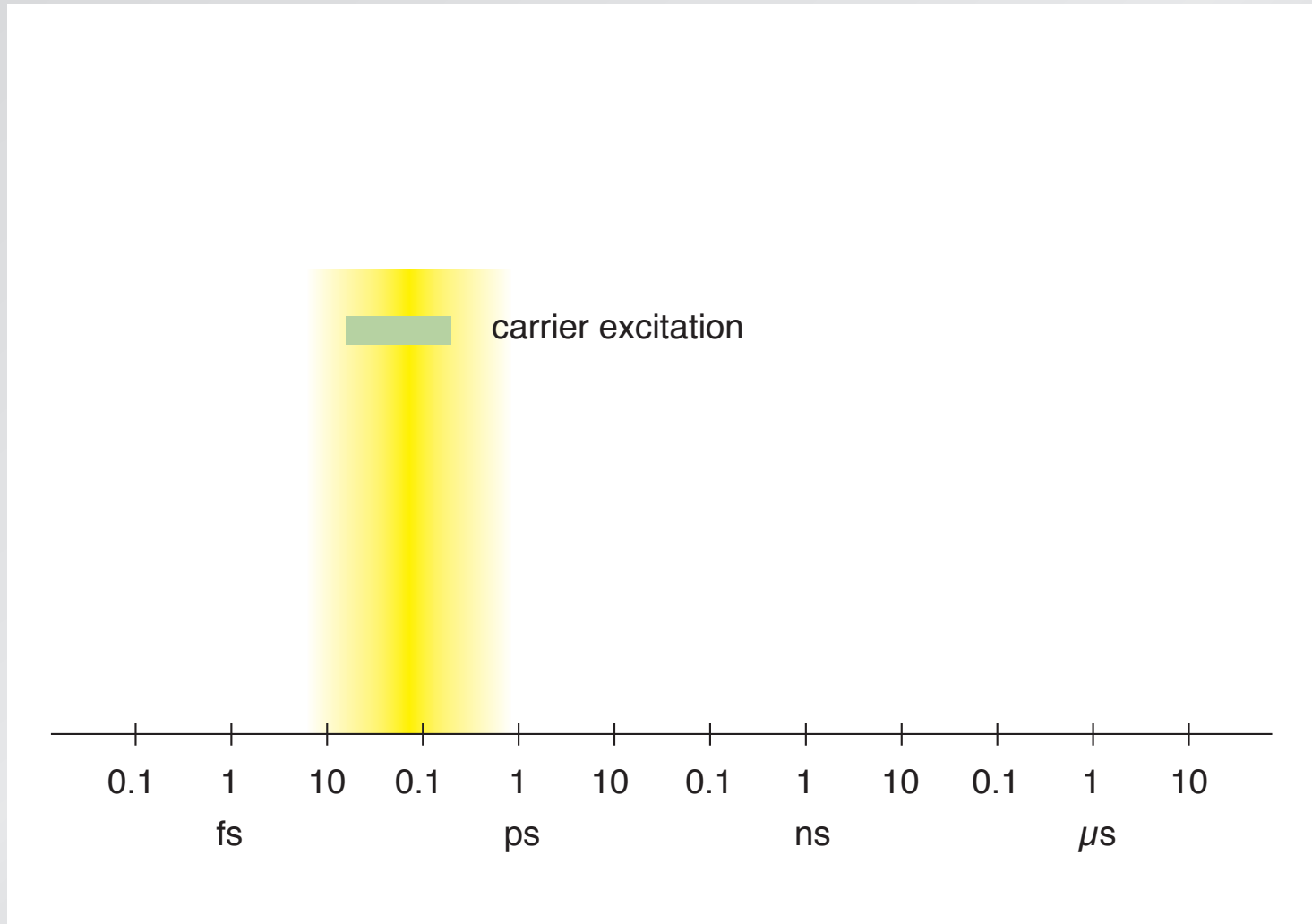
# Structure

relevant time scales



# Structure

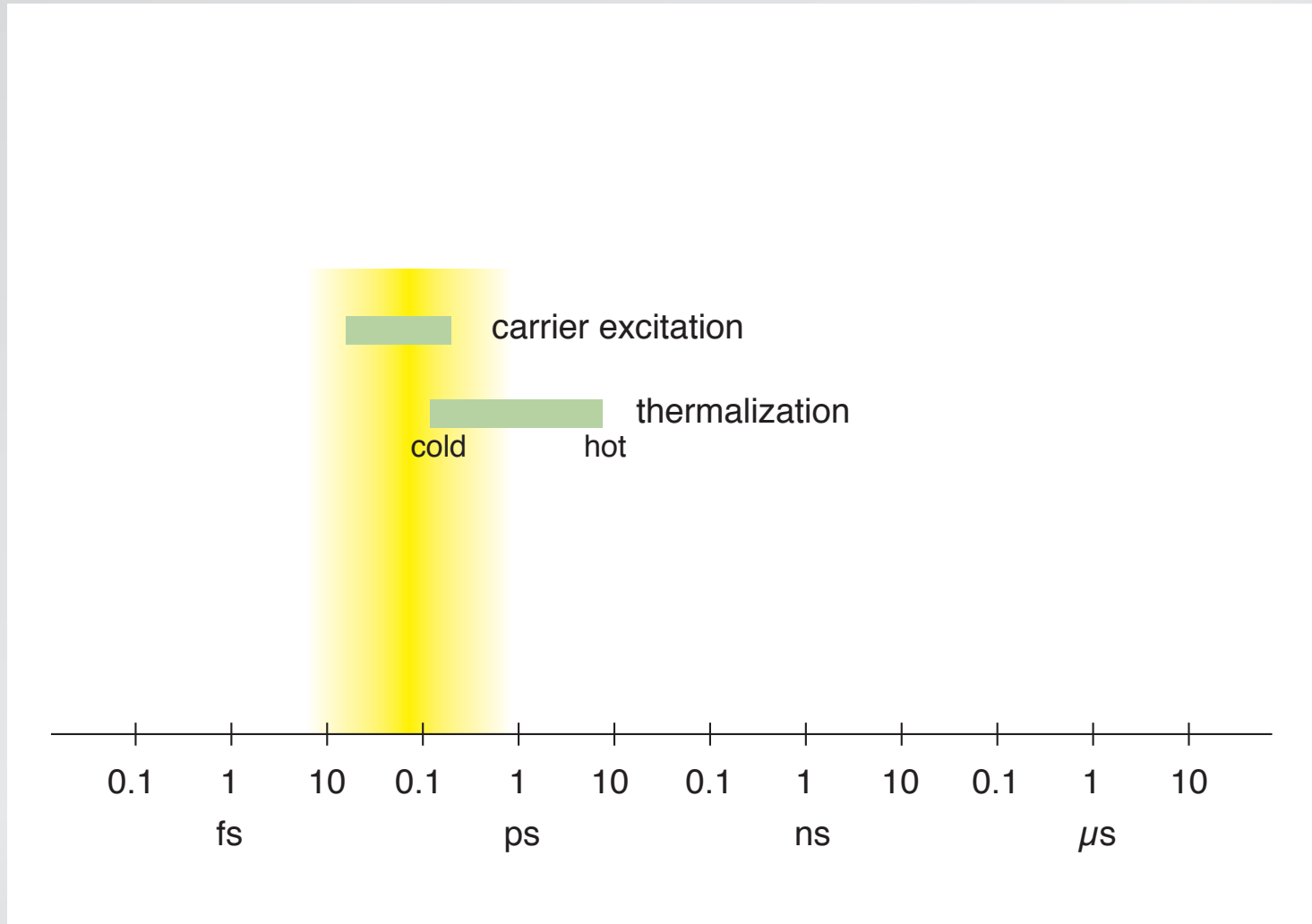
## relevant time scales





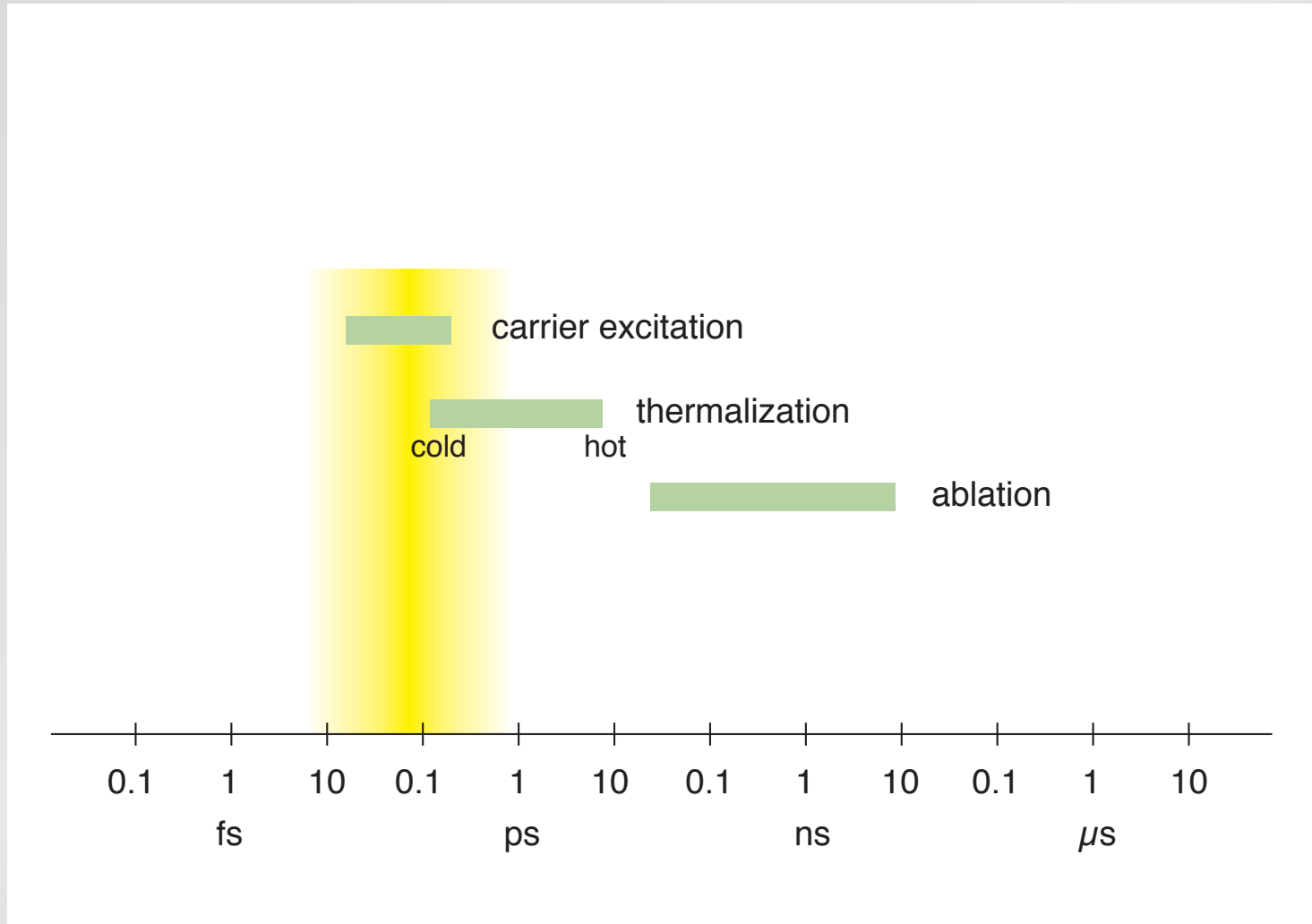
# Structure

## relevant time scales



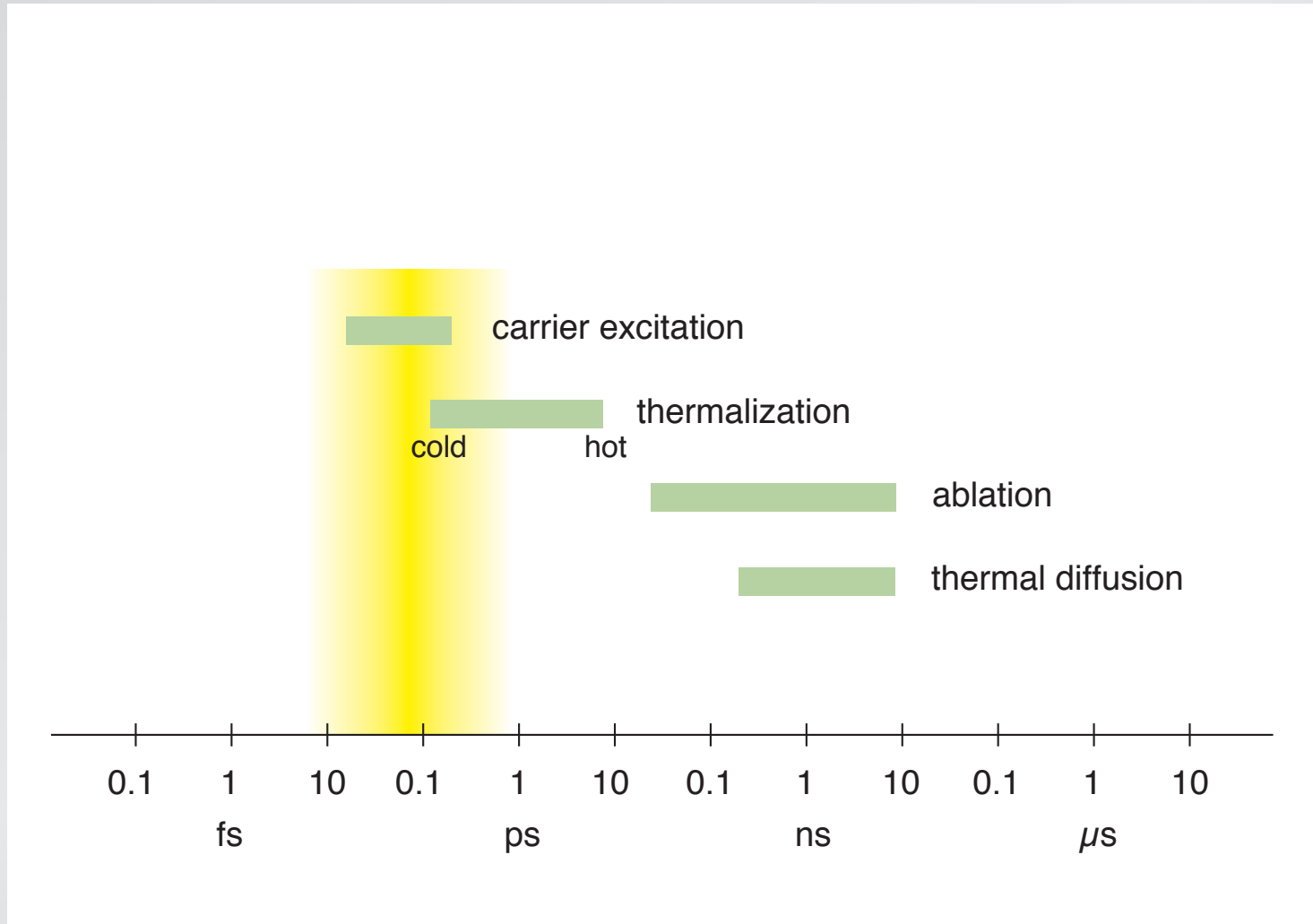
# Structure

## relevant time scales



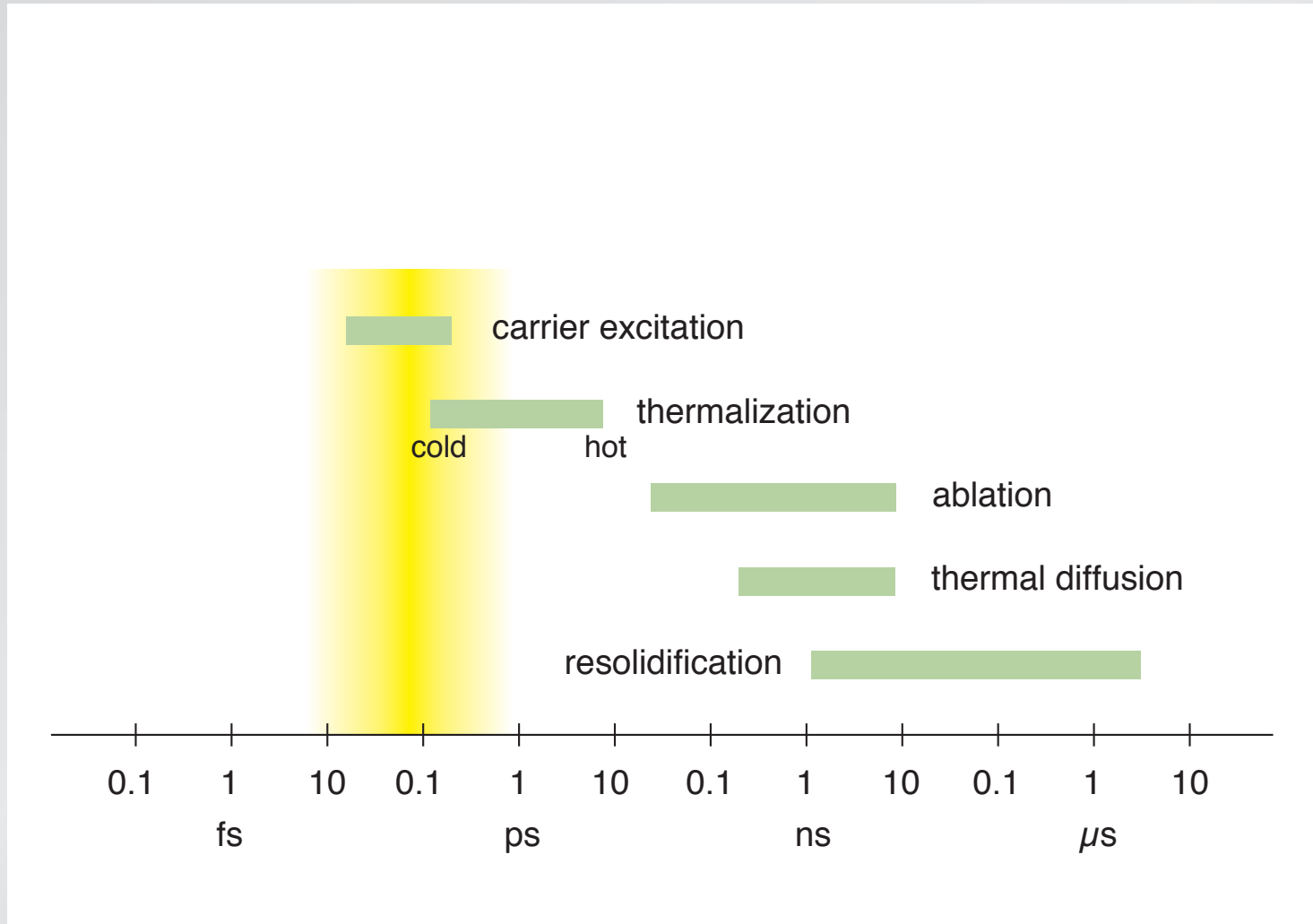
# Structure

## relevant time scales



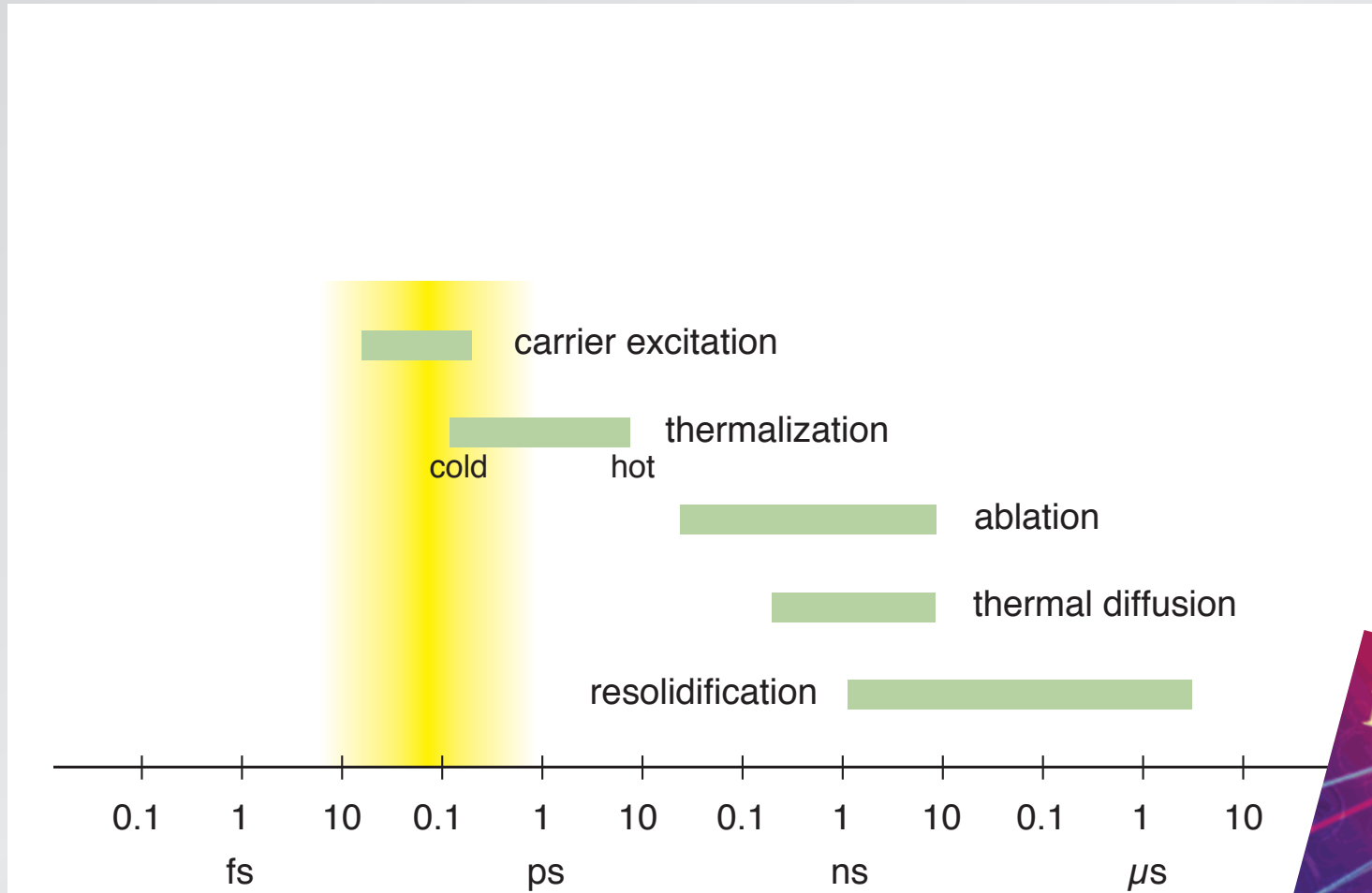
# Structure

## relevant time scales

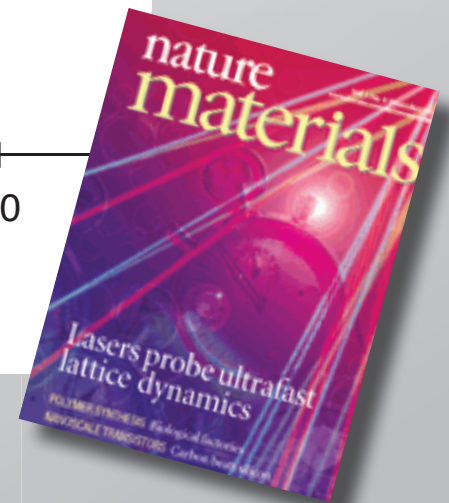


# Structure

## relevant time scales

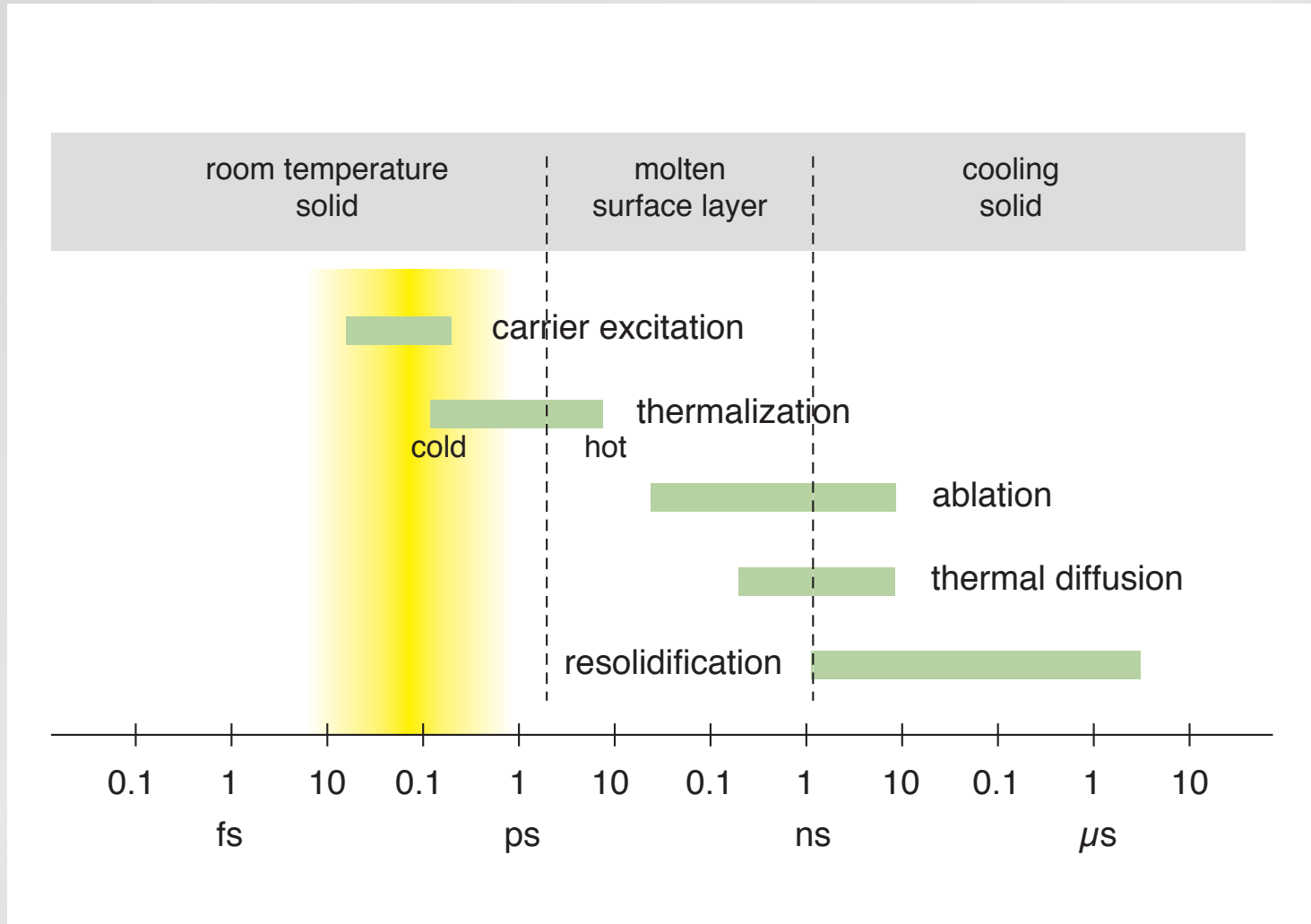


*Nature Materials* 1, 217 (2002)



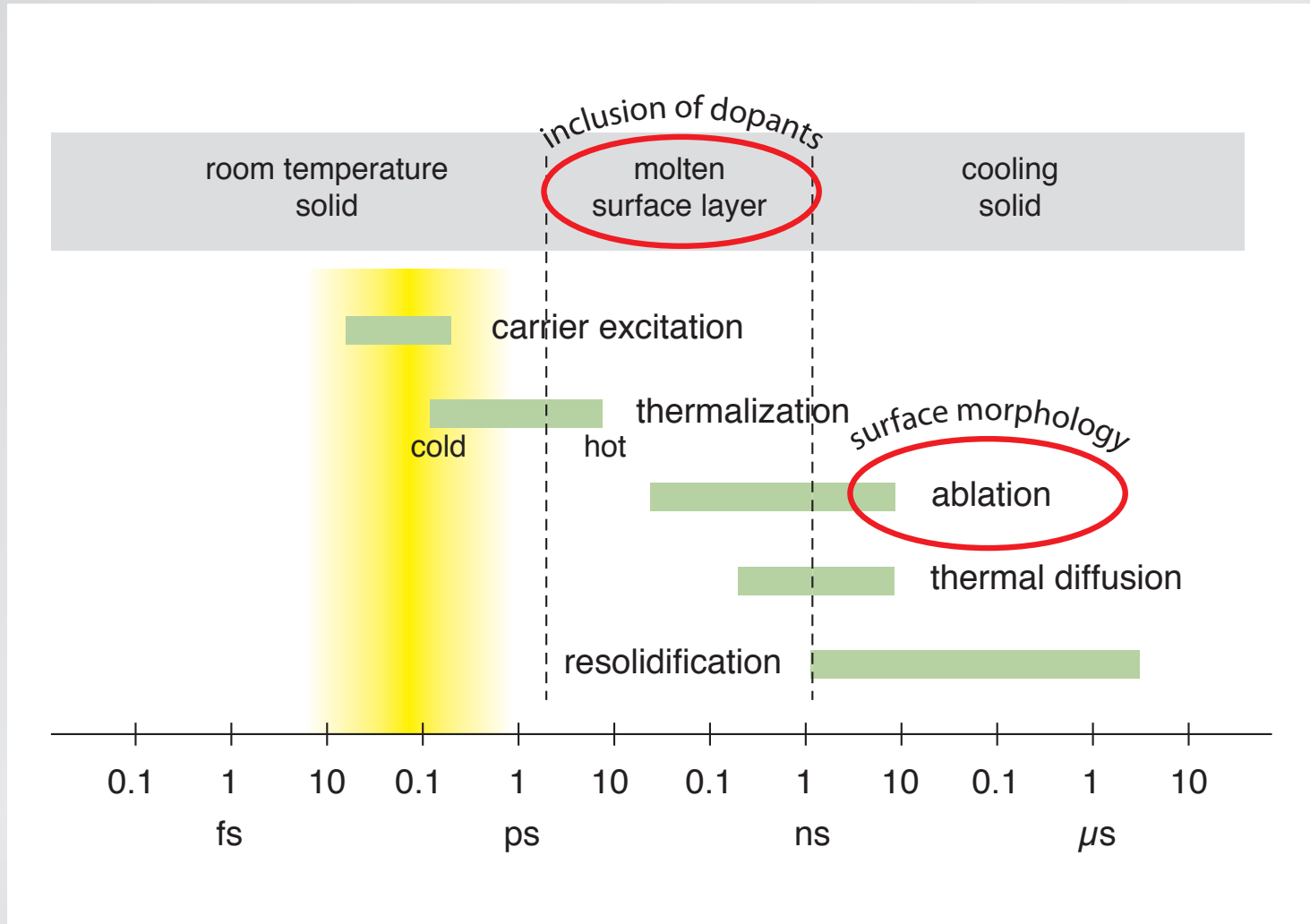
# Structure

## relevant time scales



# Structure

## relevant time scales



# Structure

**different thresholds:**

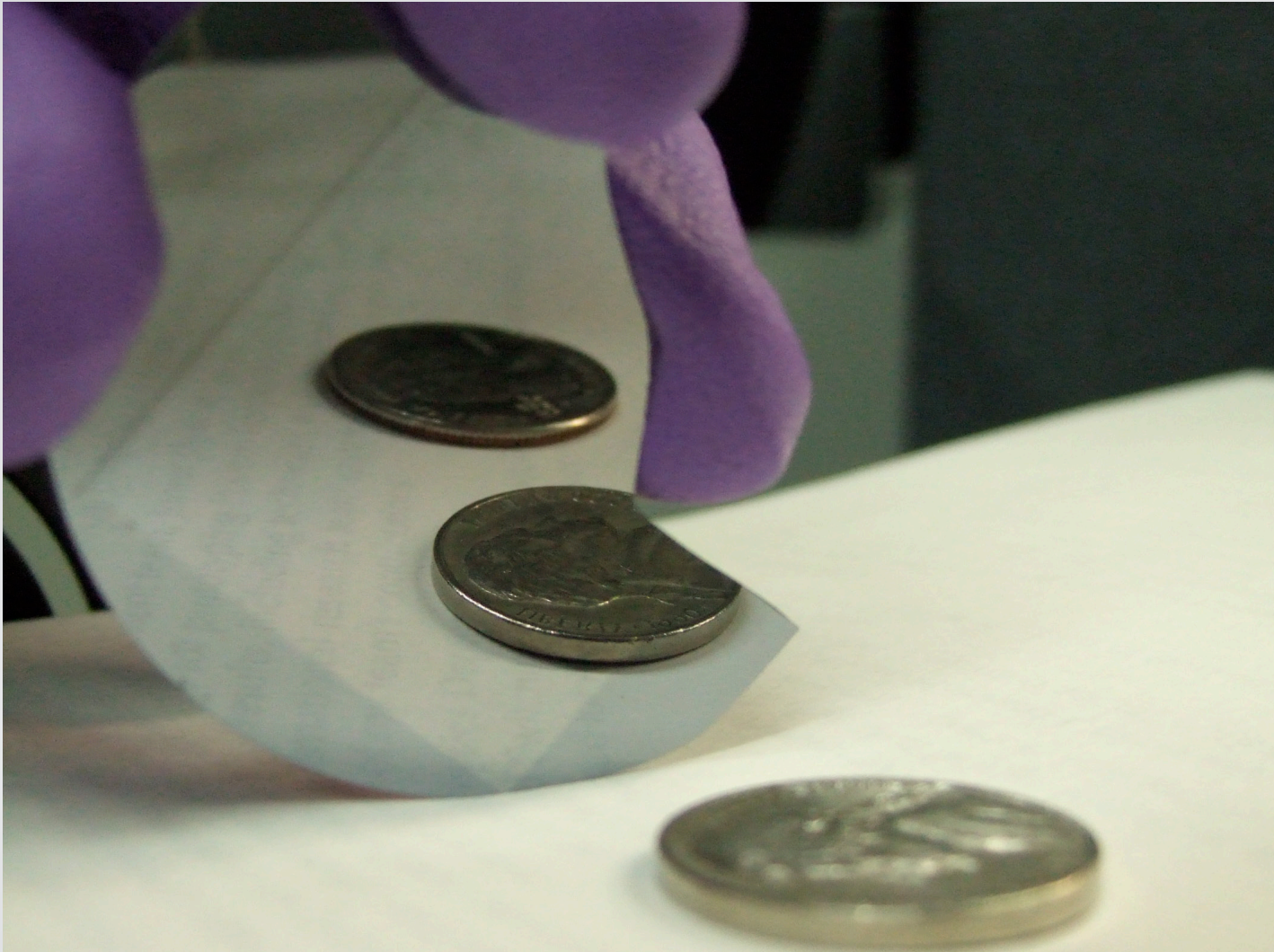
**melting: 1.5 kJ/m<sup>2</sup>**

**ablation: 3.1 kJ/m<sup>2</sup>**



# Structure

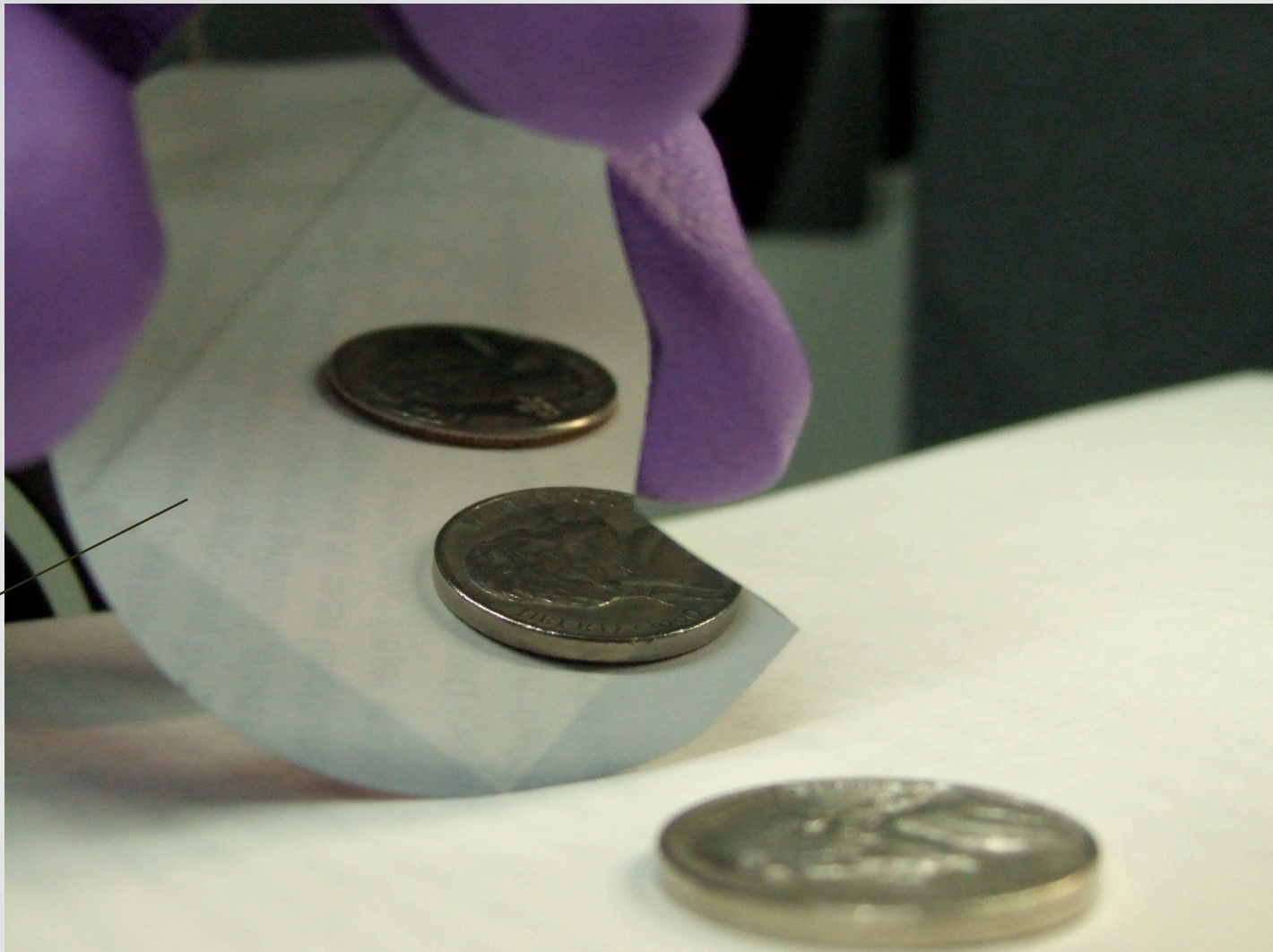
decouple ablation from melting



# Structure

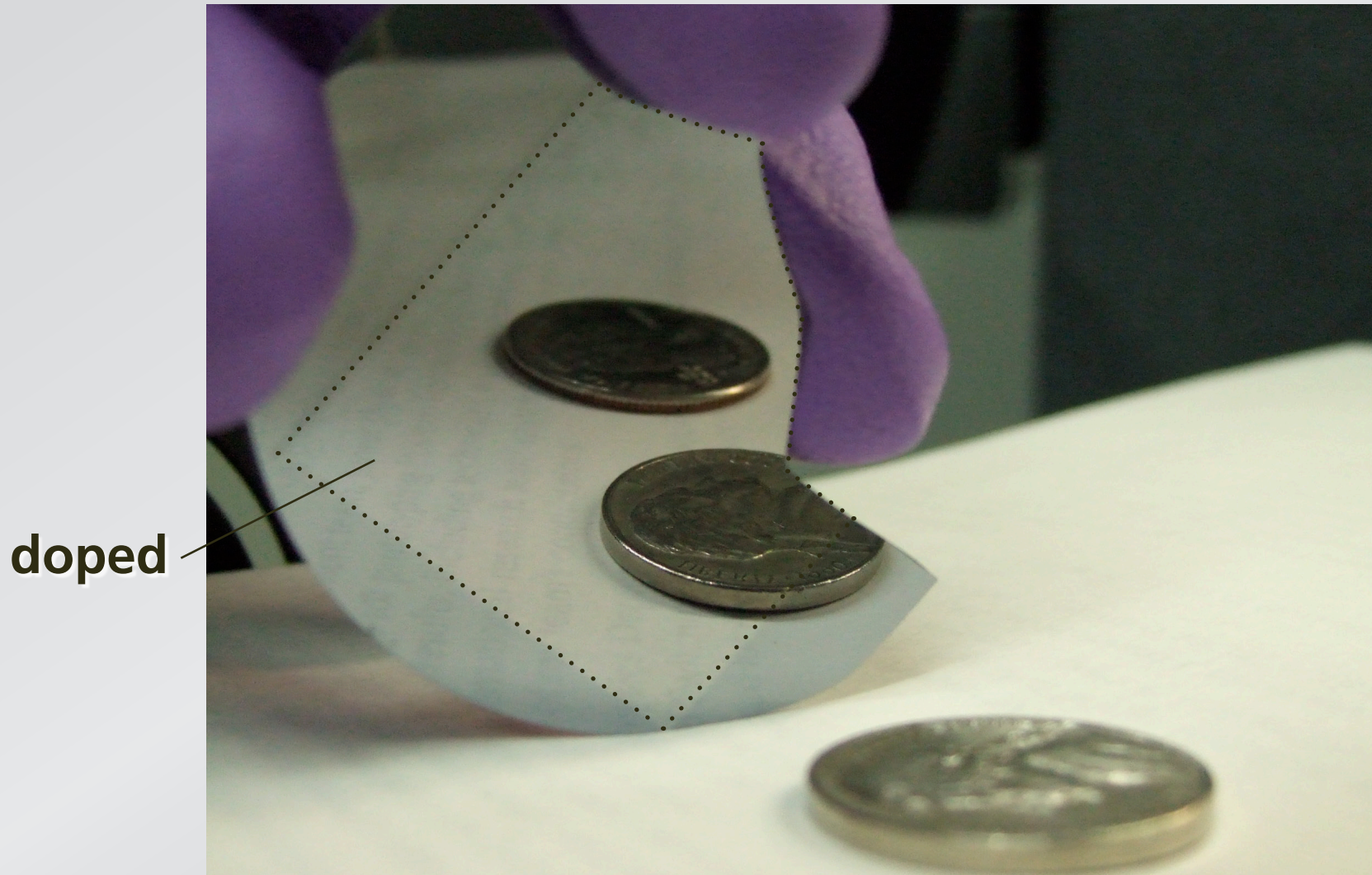
decouple ablation from melting

doped



# Structure

decouple ablation from melting

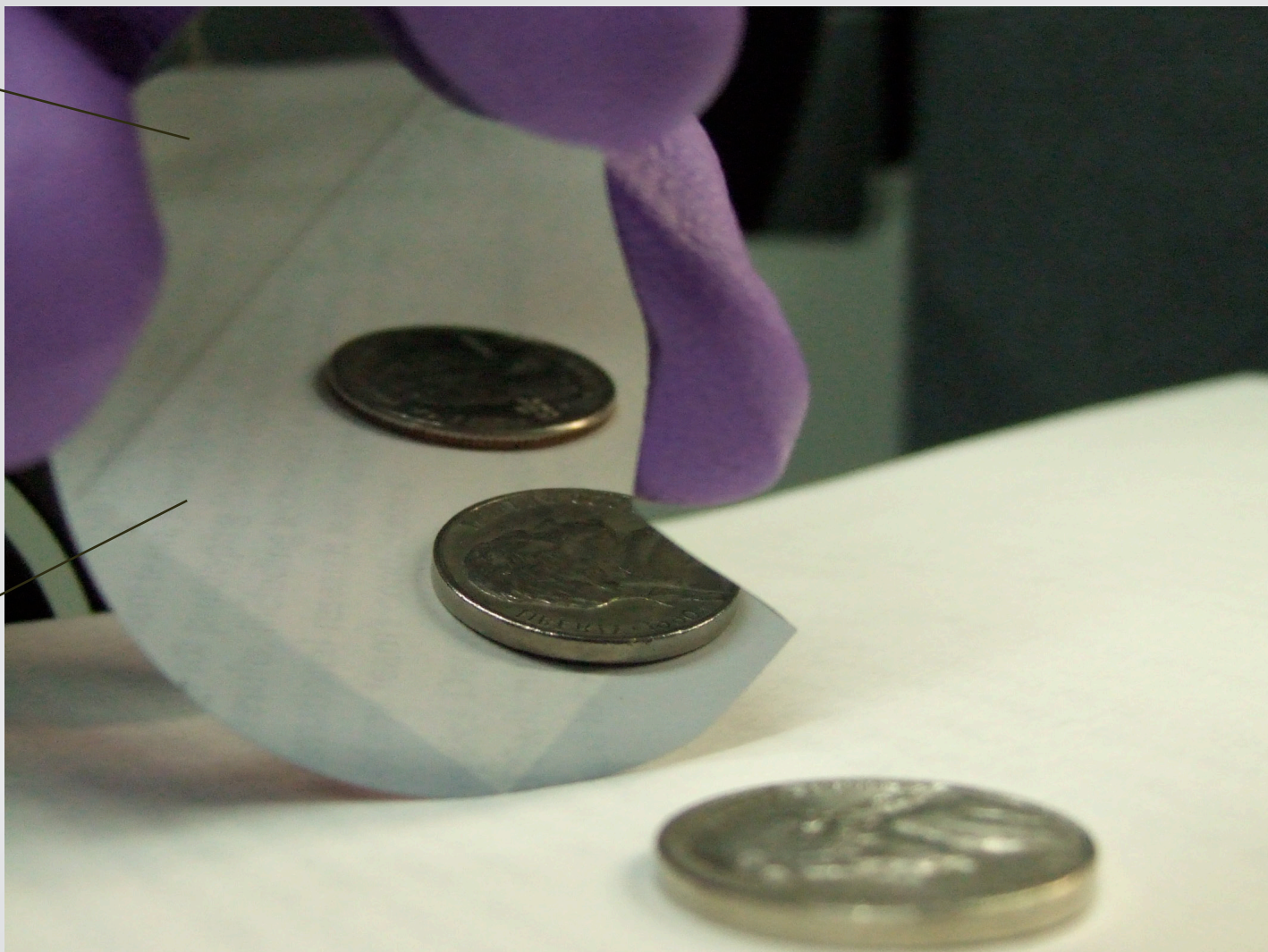


# Structure

decouple ablation from melting

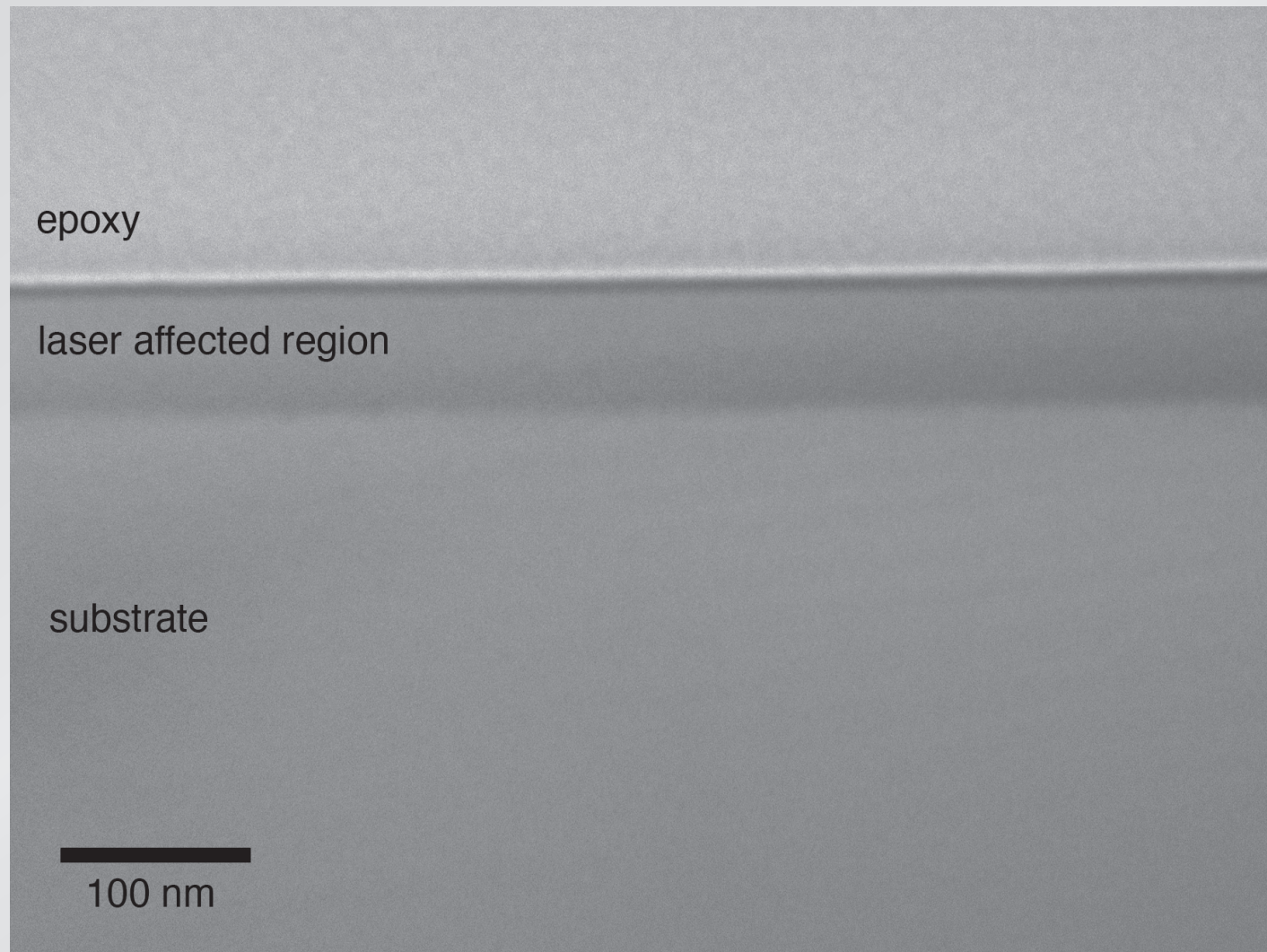
undoped

doped



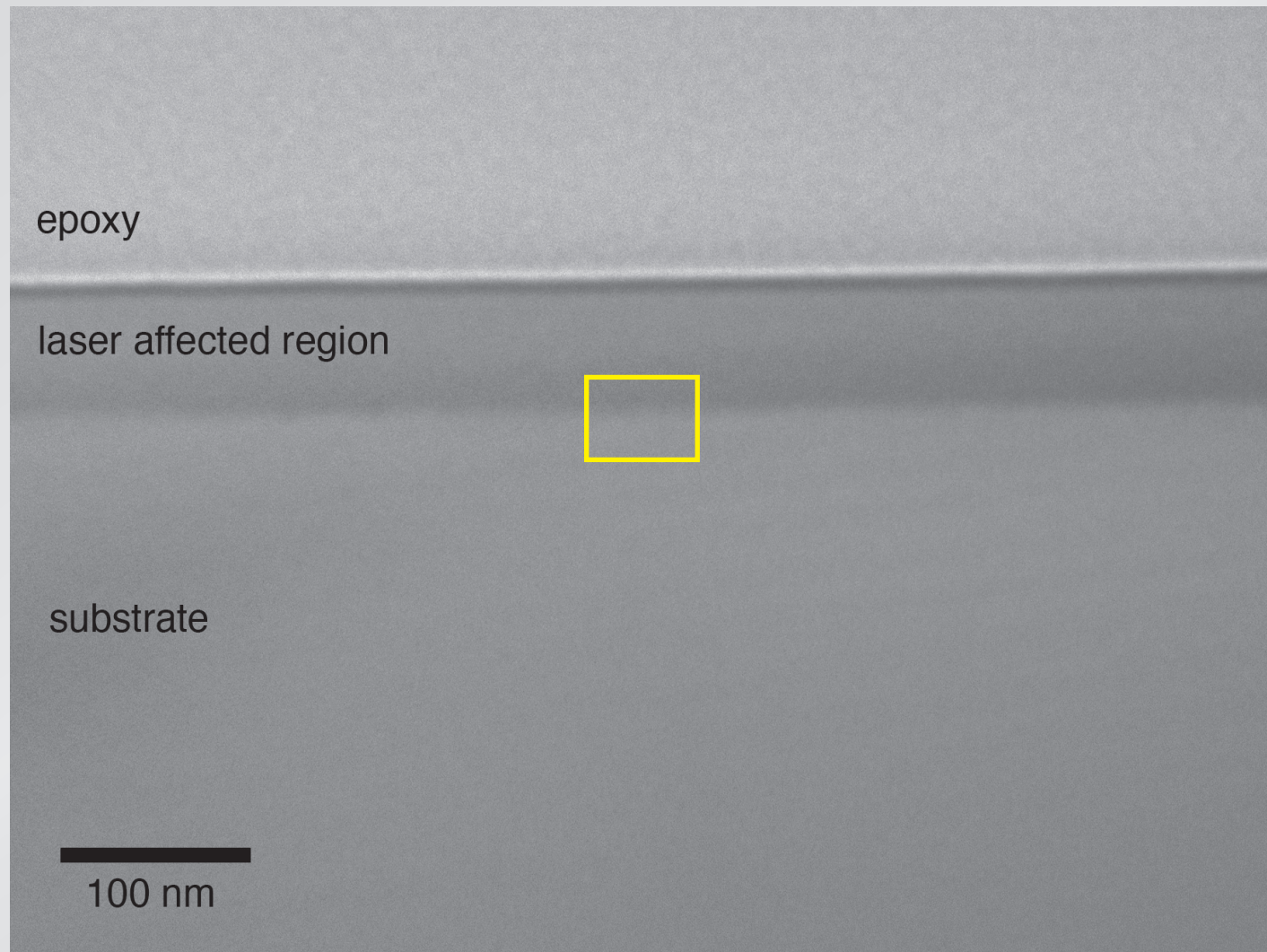
# Structure

decouple ablation from melting



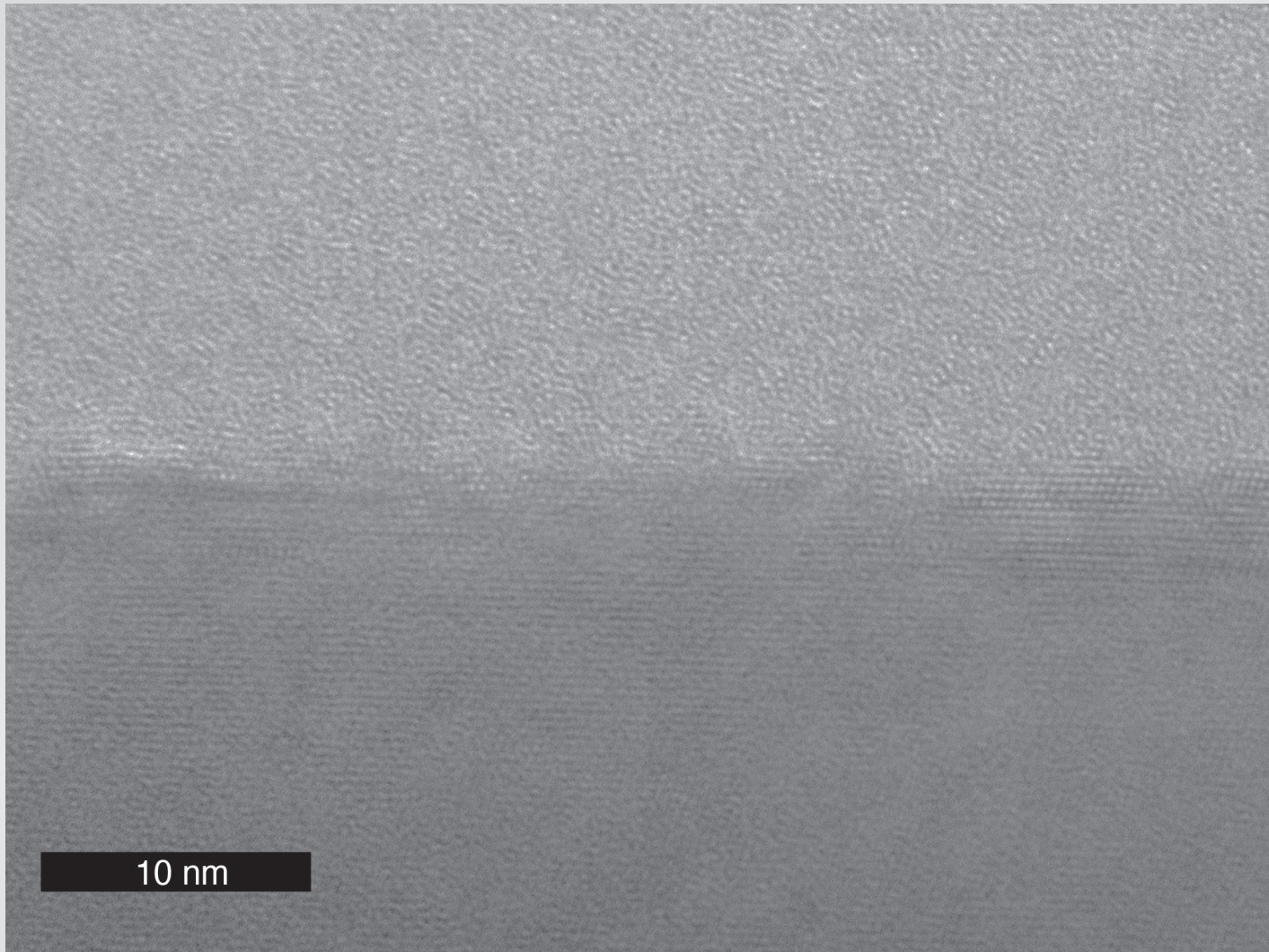
# Structure

decouple ablation from melting



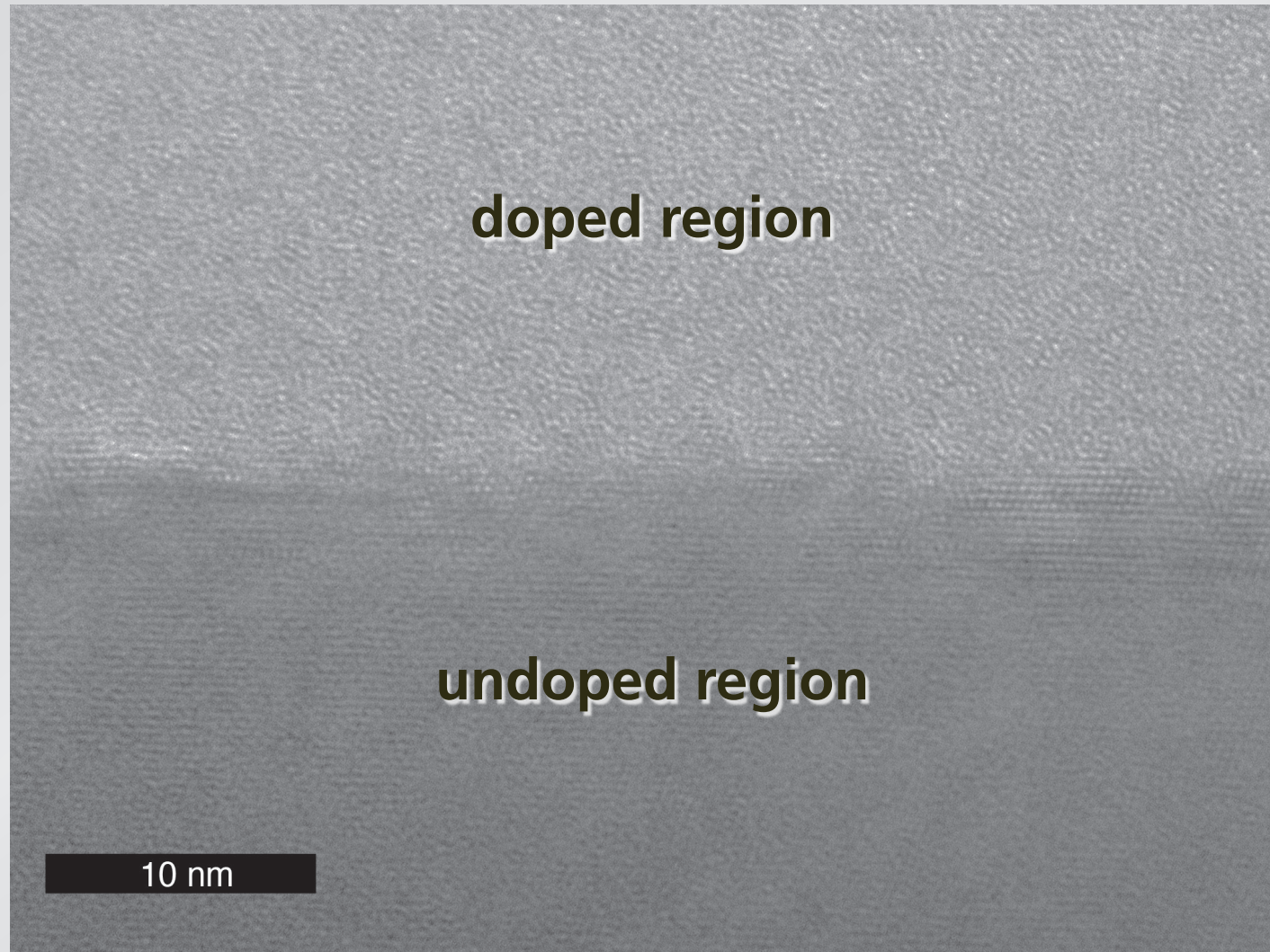
# Structure

decouple ablation from melting



# Structure

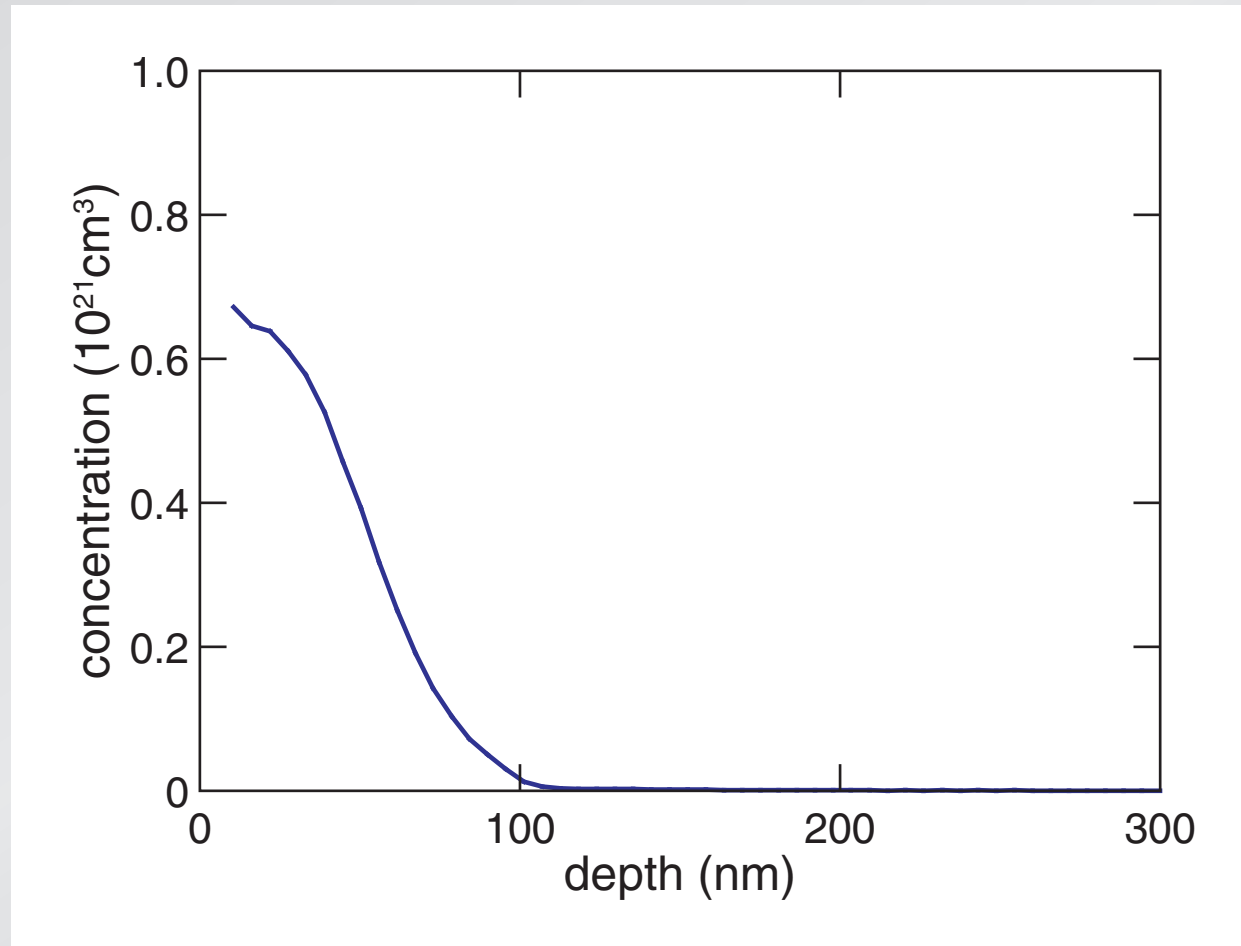
decouple ablation from melting





# Structure

## secondary ion mass spectrometry



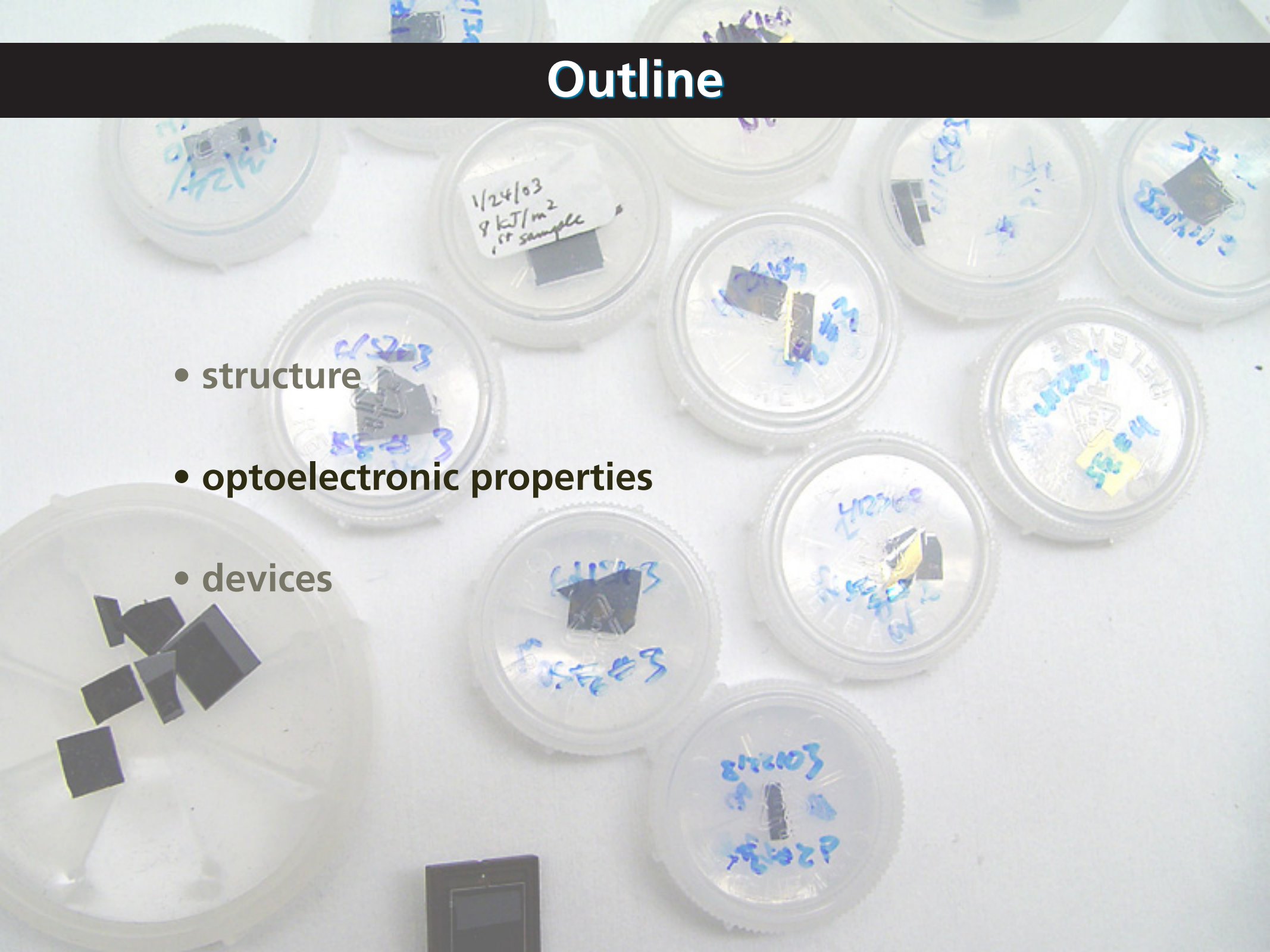
# Structure

## Things to keep in mind

- rapid melting and resolidification causes doping
- ablation causes morphology changes
- about 1% impurity in 100-nm thick surface layer
- annealing changes impurity coordination

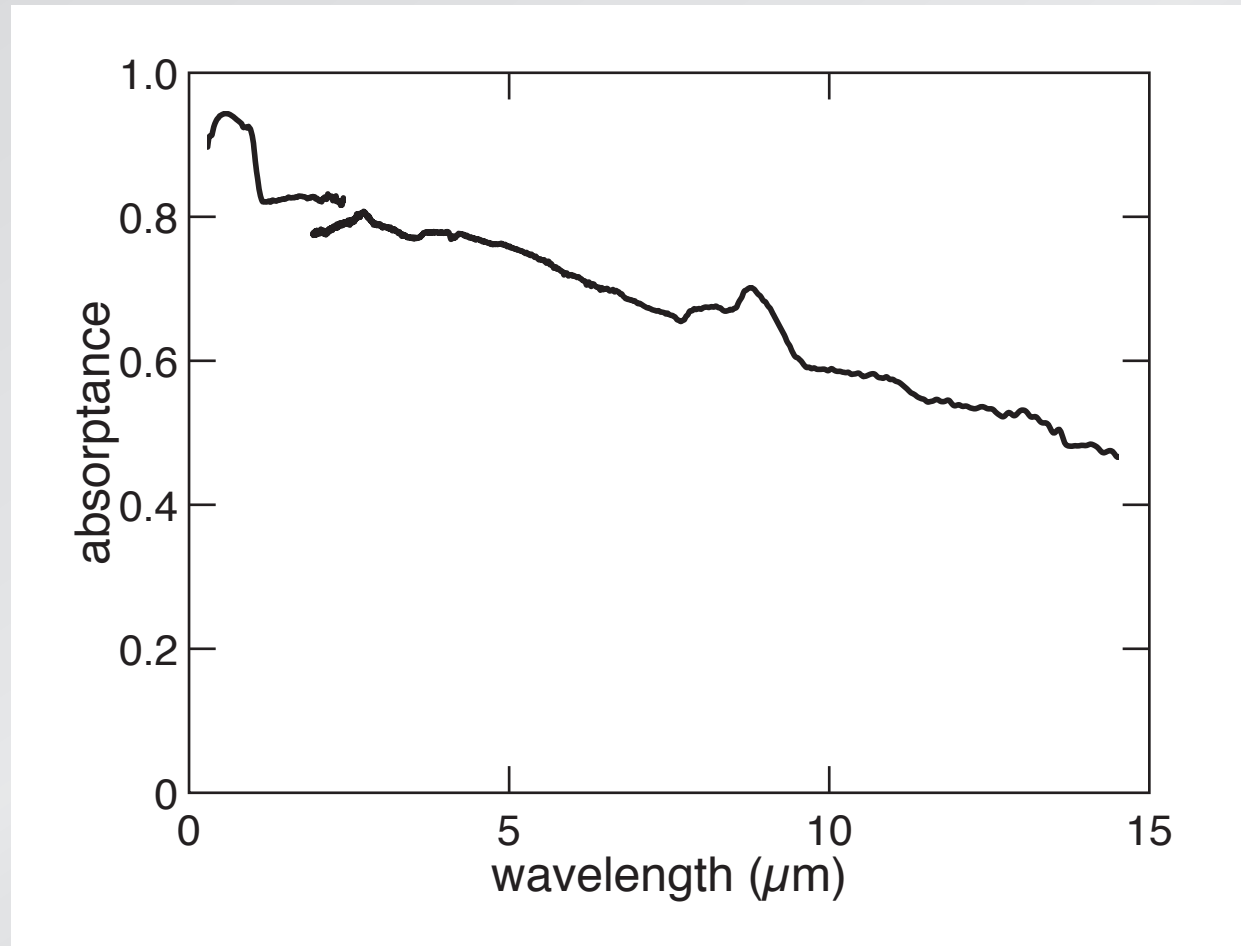
# Outline

- structure
- optoelectronic properties
- devices



# Optoelectronic properties

absorptance ( $1 - R_{int} - T_{int}$ )

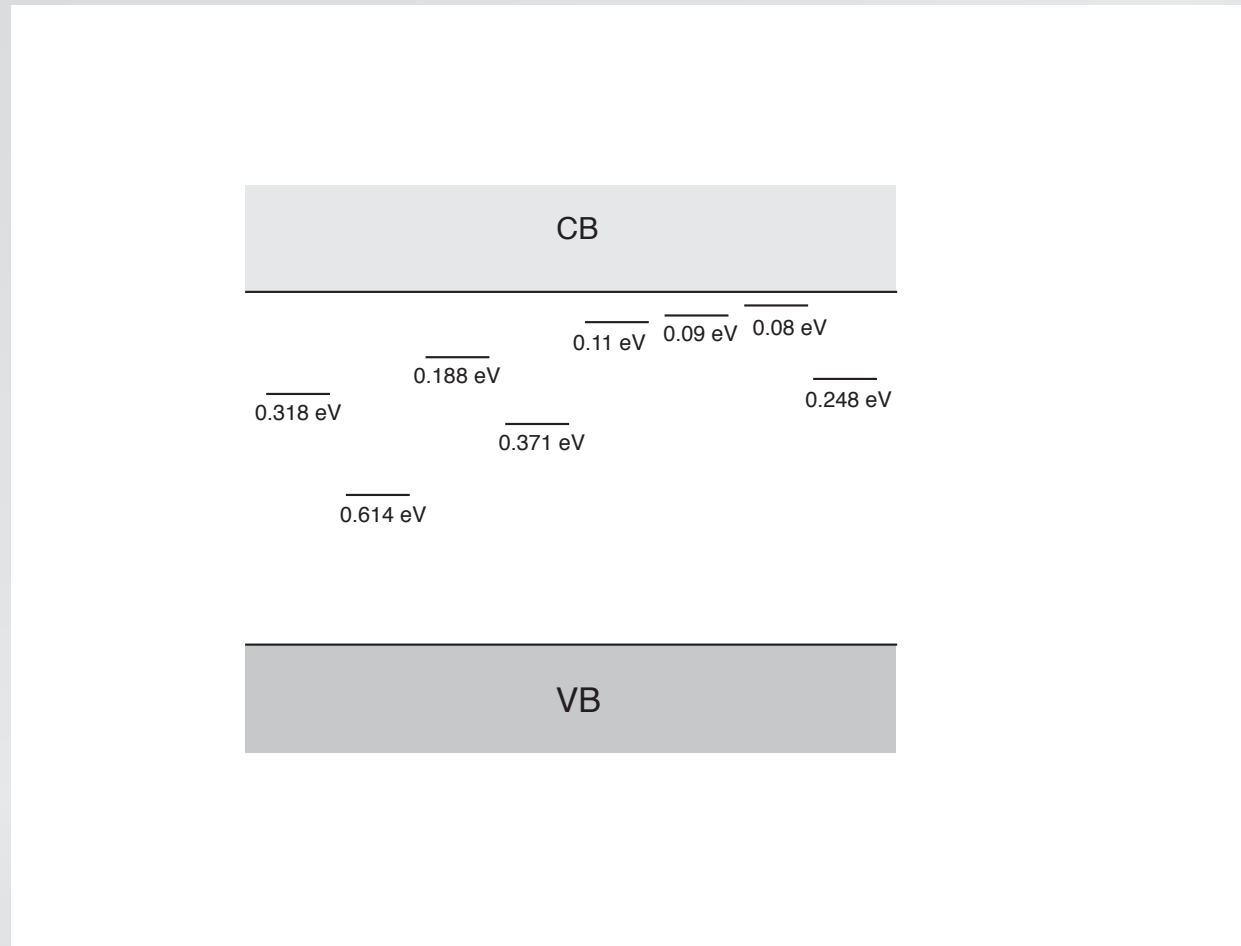


# Optoelectronic properties

**what dopant states/bands cause IR absorption?**

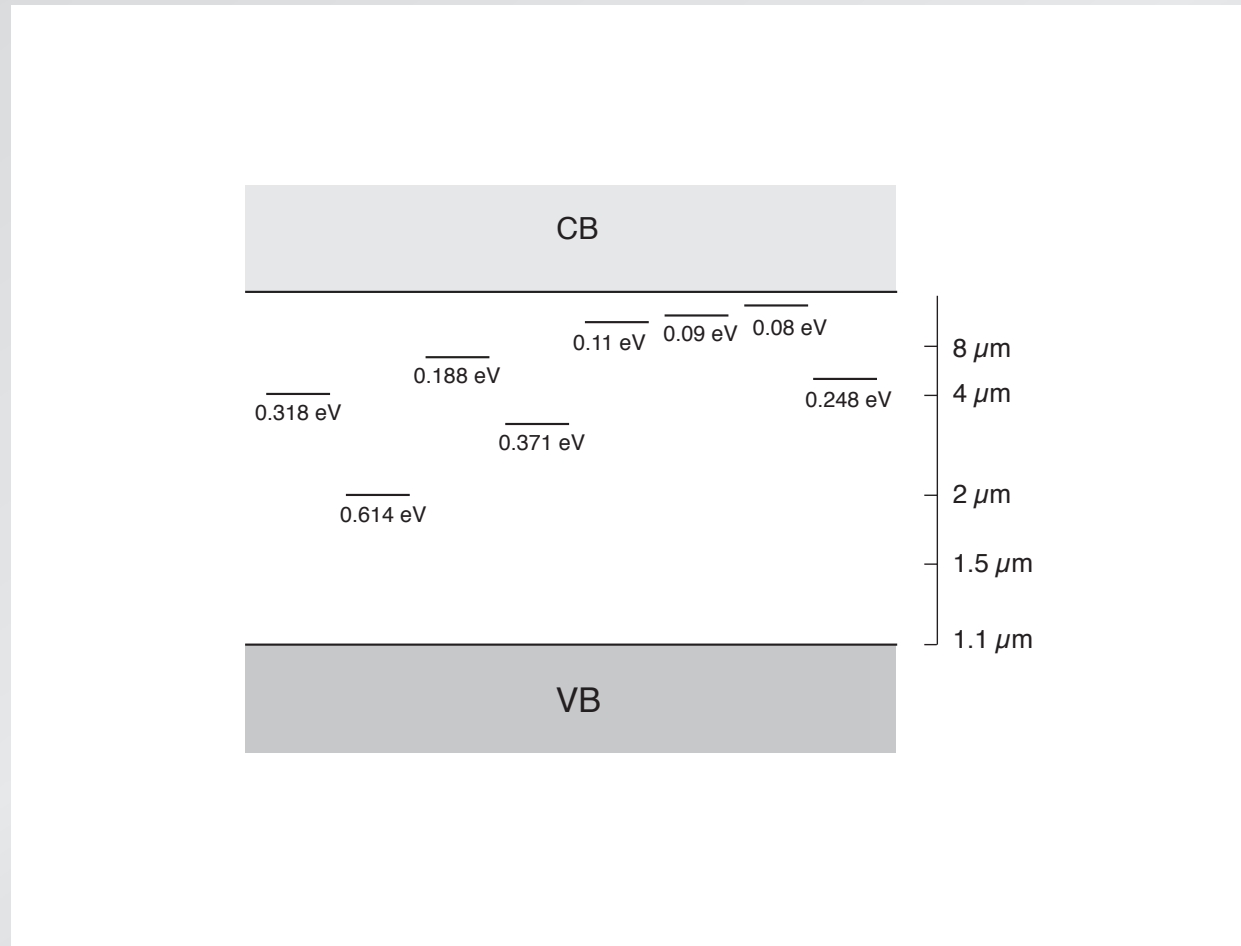
# Optoelectronic properties

1 part in  $10^6$  sulfur introduces donor states in gap



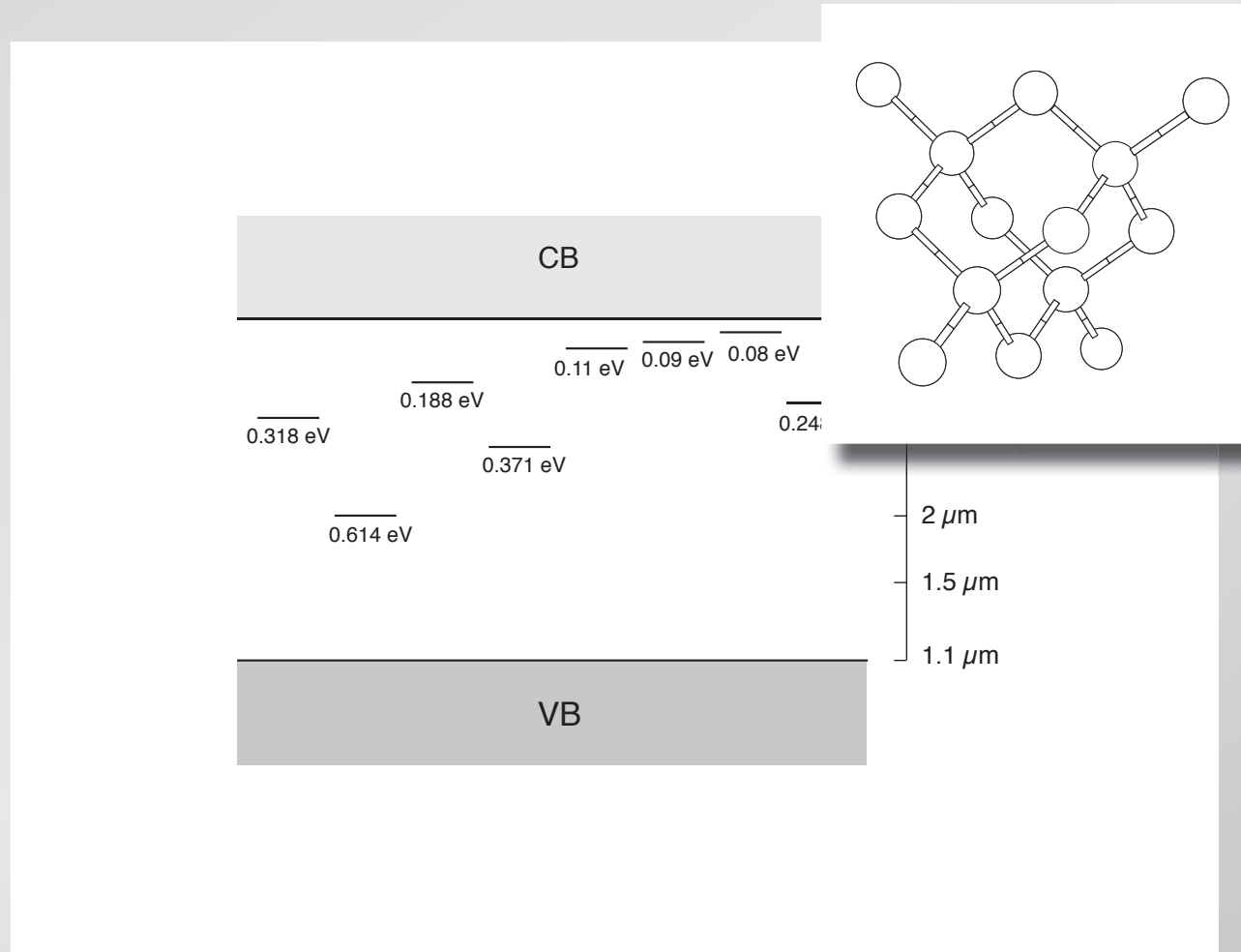
# Optoelectronic properties

1 part in  $10^6$  sulfur introduces donor states in gap



# Optoelectronic properties

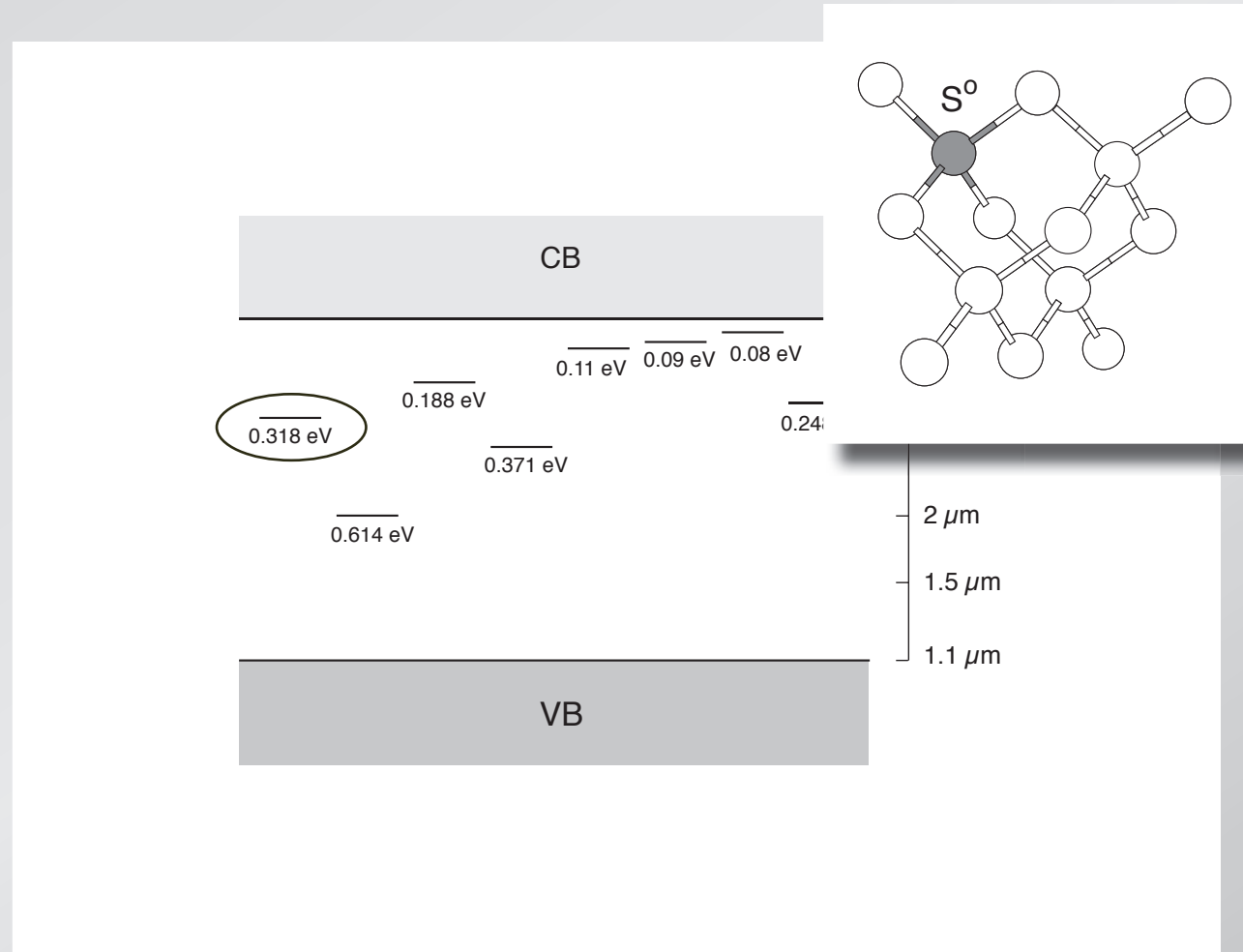
1 part in  $10^6$  sulfur introduces donor states in gap





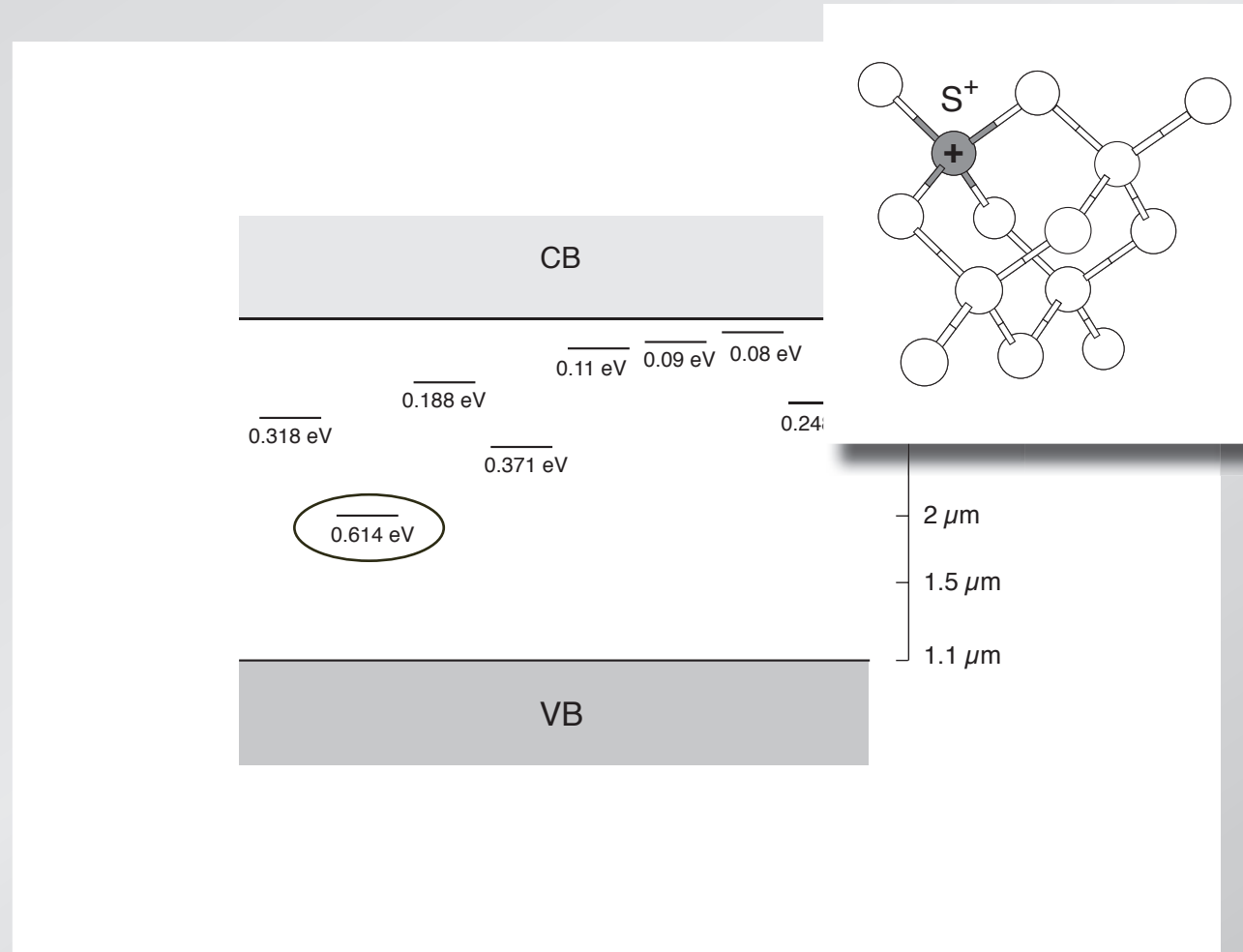
# Optoelectronic properties

1 part in  $10^6$  sulfur introduces donor states in gap



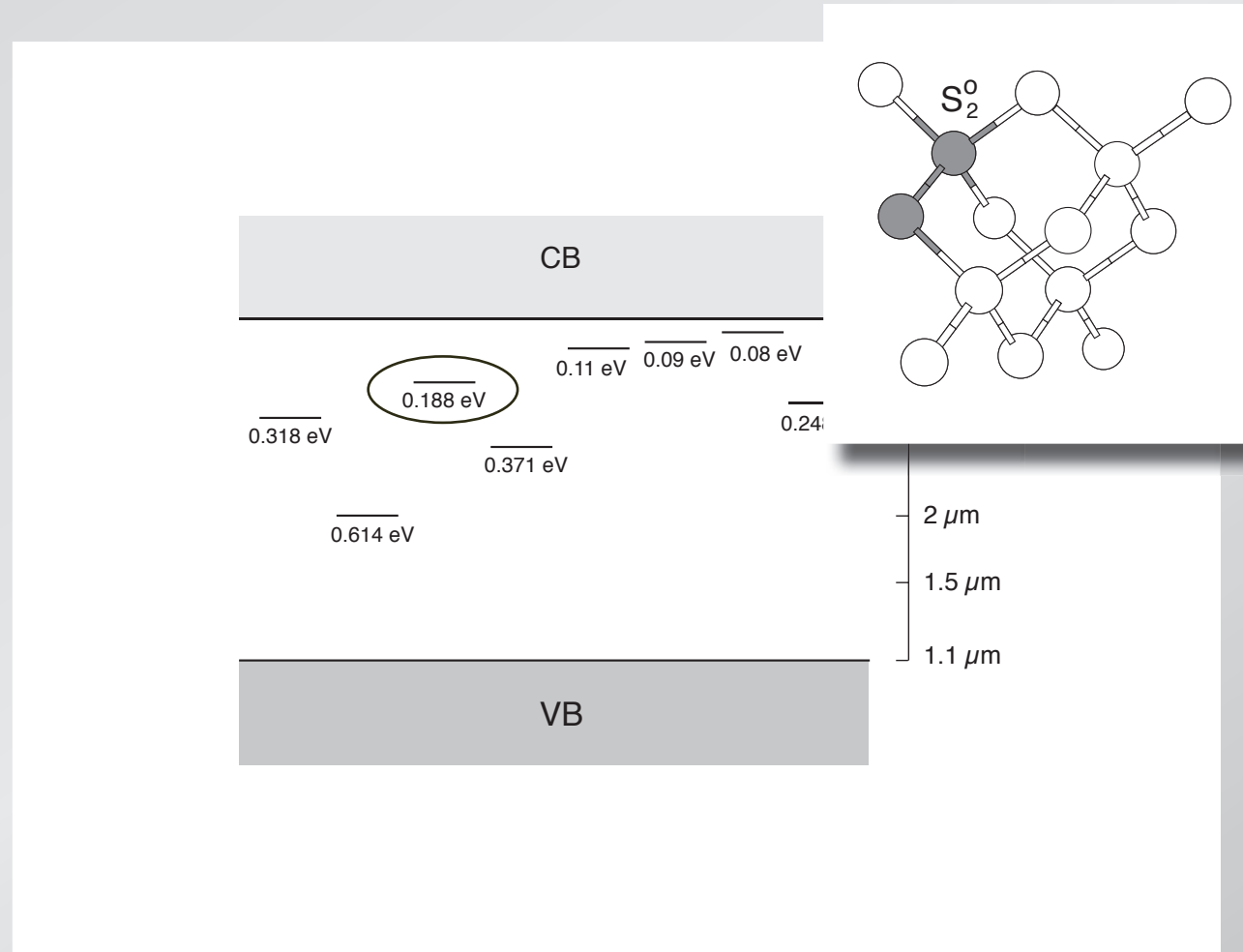
# Optoelectronic properties

1 part in  $10^6$  sulfur introduces donor states in gap



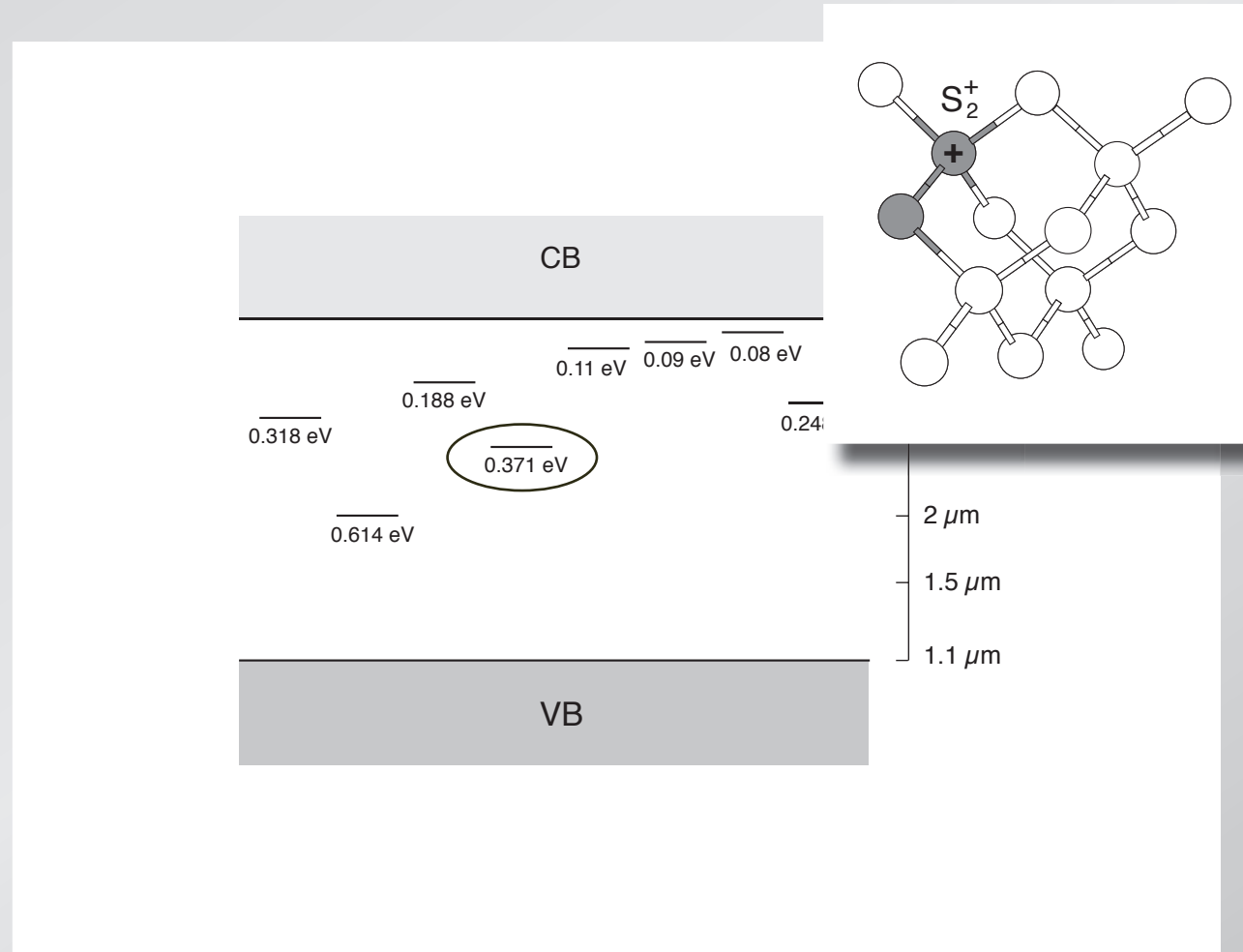
# Optoelectronic properties

1 part in  $10^6$  sulfur introduces donor states in gap



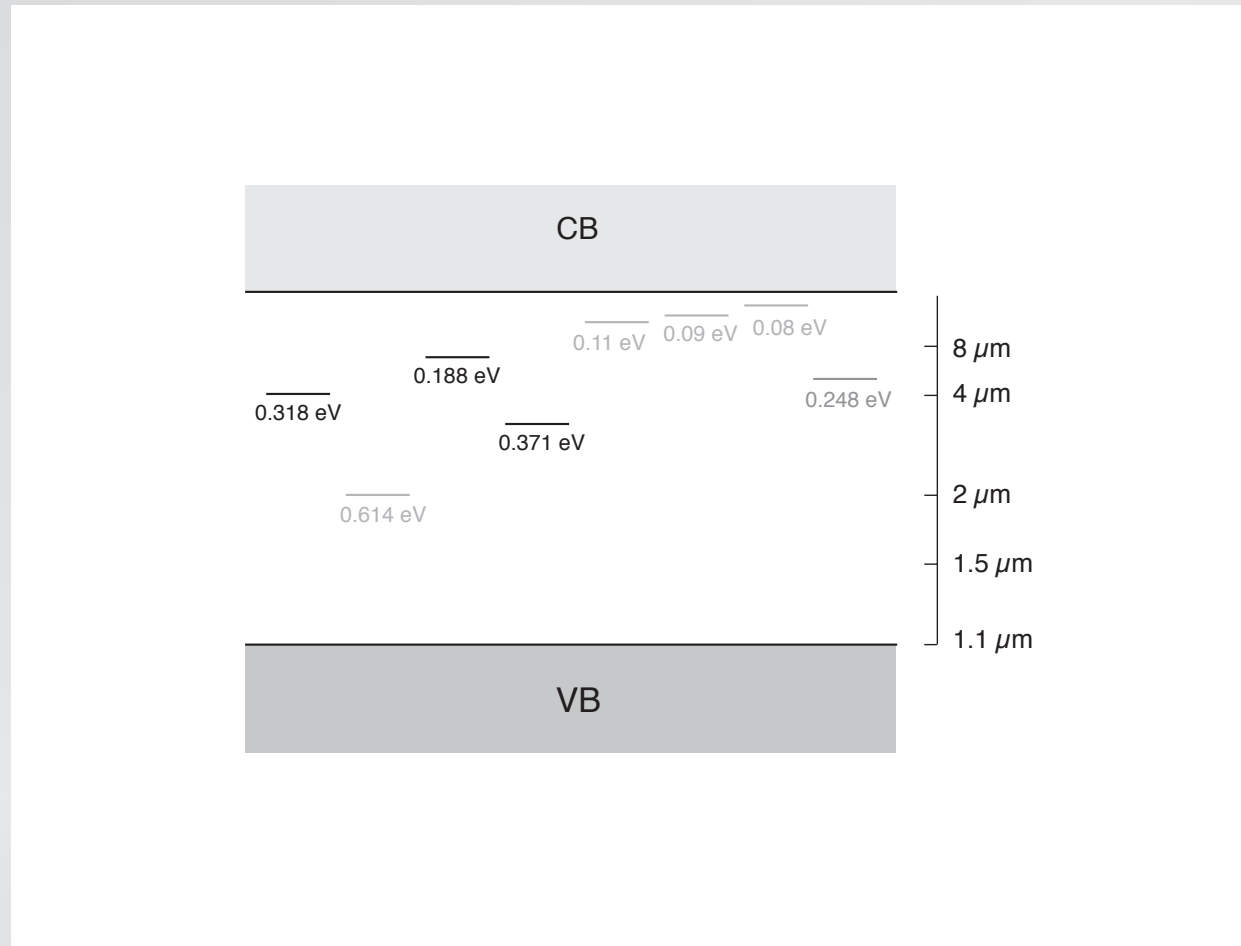
# Optoelectronic properties

1 part in  $10^6$  sulfur introduces donor states in gap



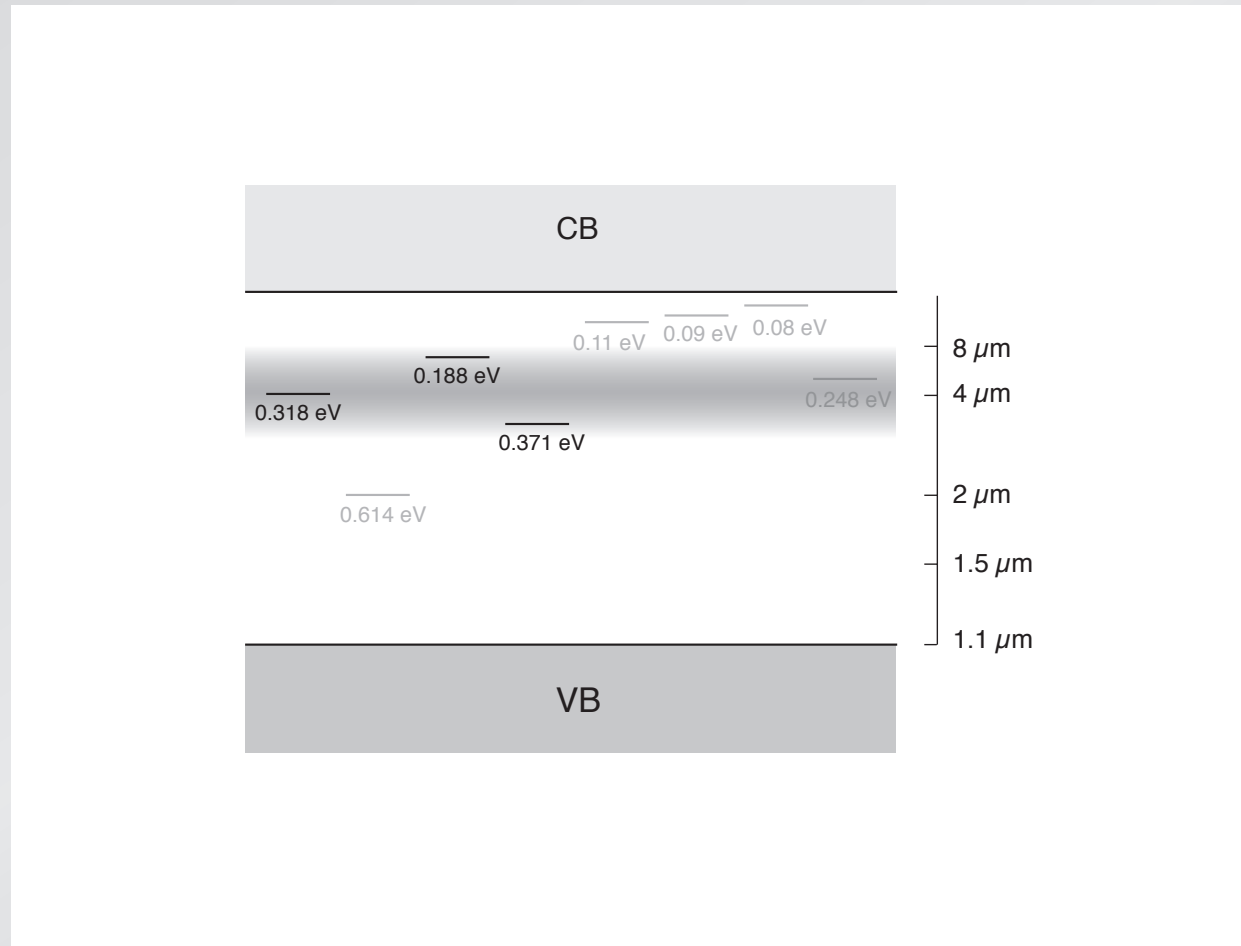
# Optoelectronic properties

1 part in  $10^6$  sulfur introduces donor states in gap



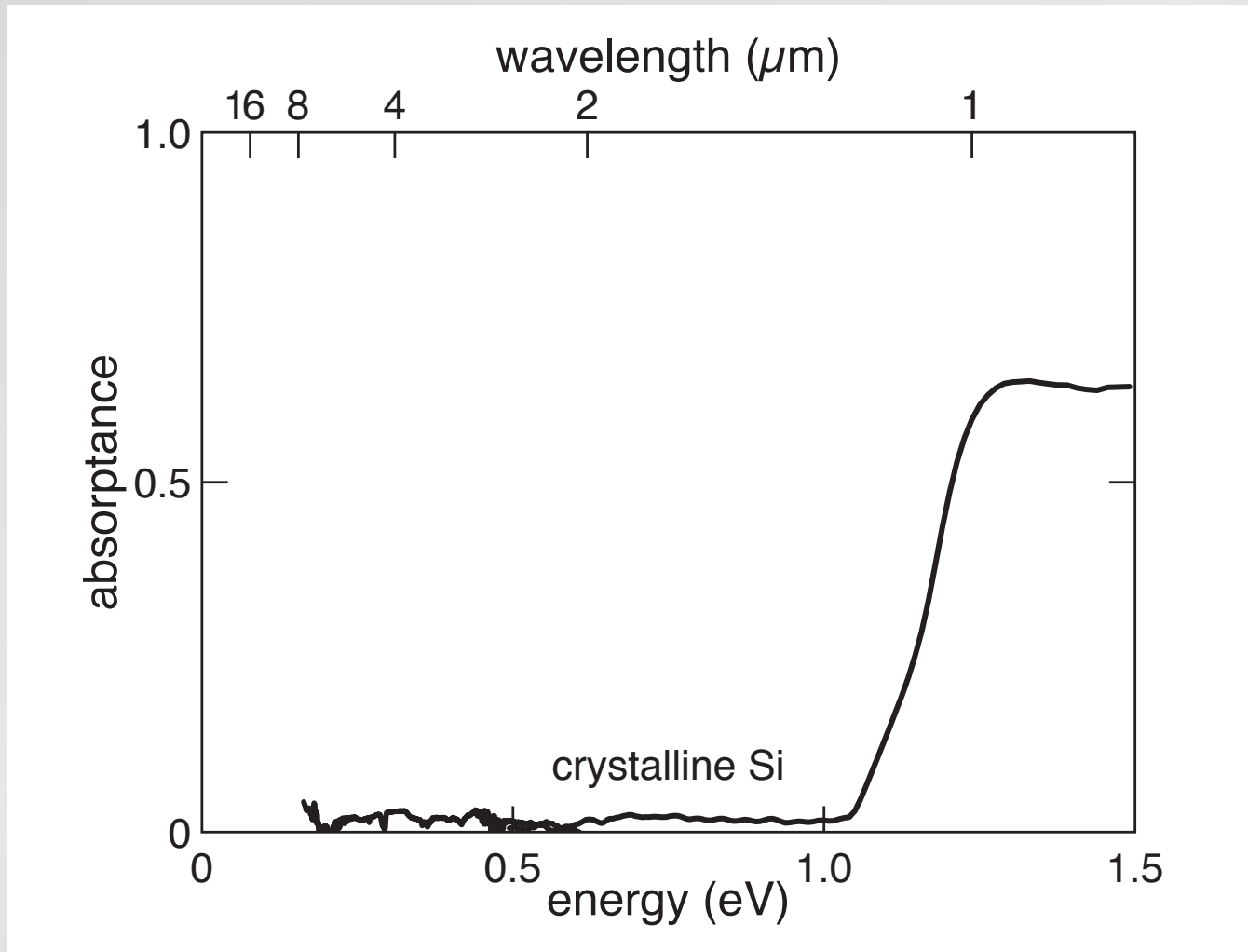
# Optoelectronic properties

at high concentration states broaden into band



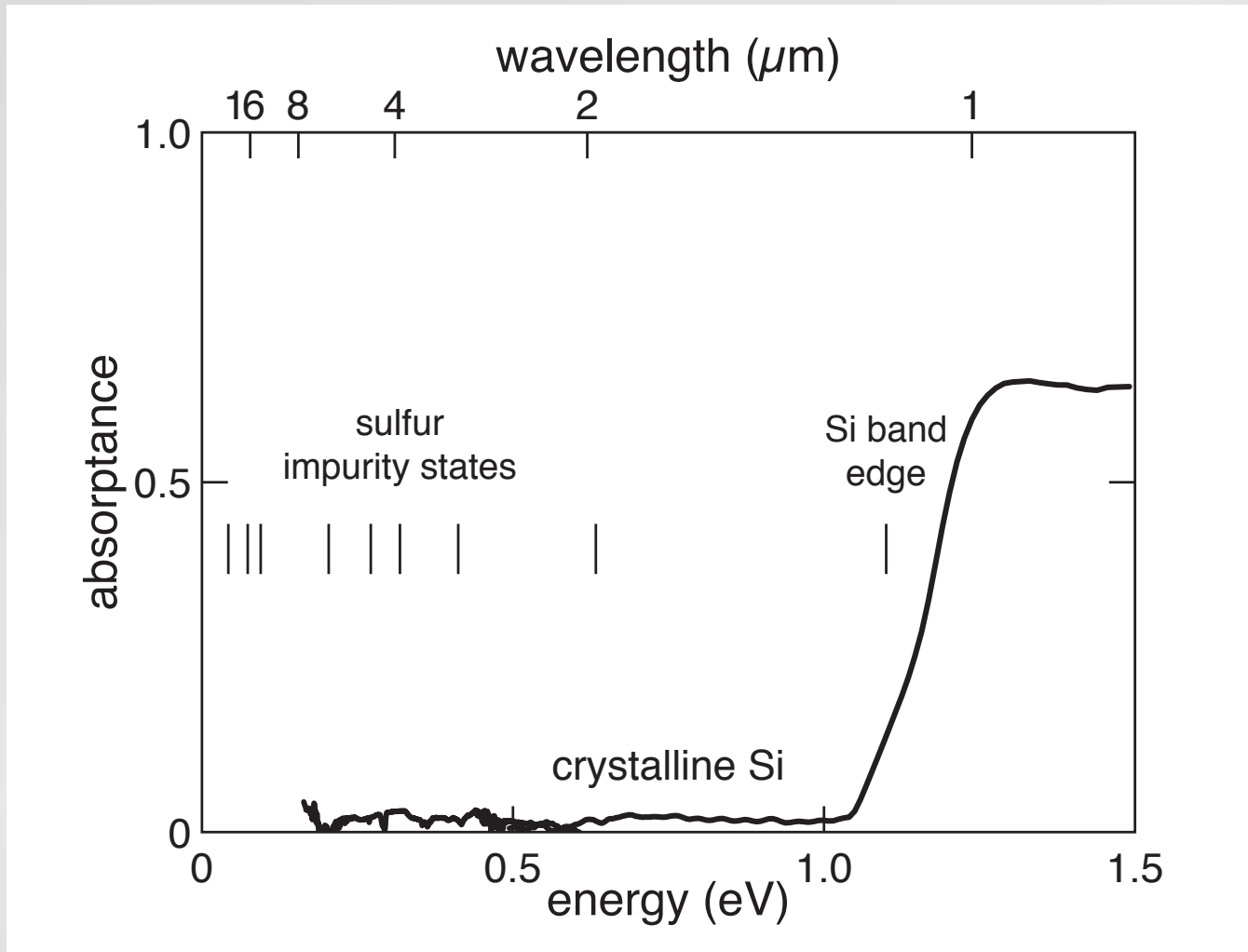
# Optoelectronic properties

absorptance ( $1 - R_{int} - T_{int}$ )



# Optoelectronic properties

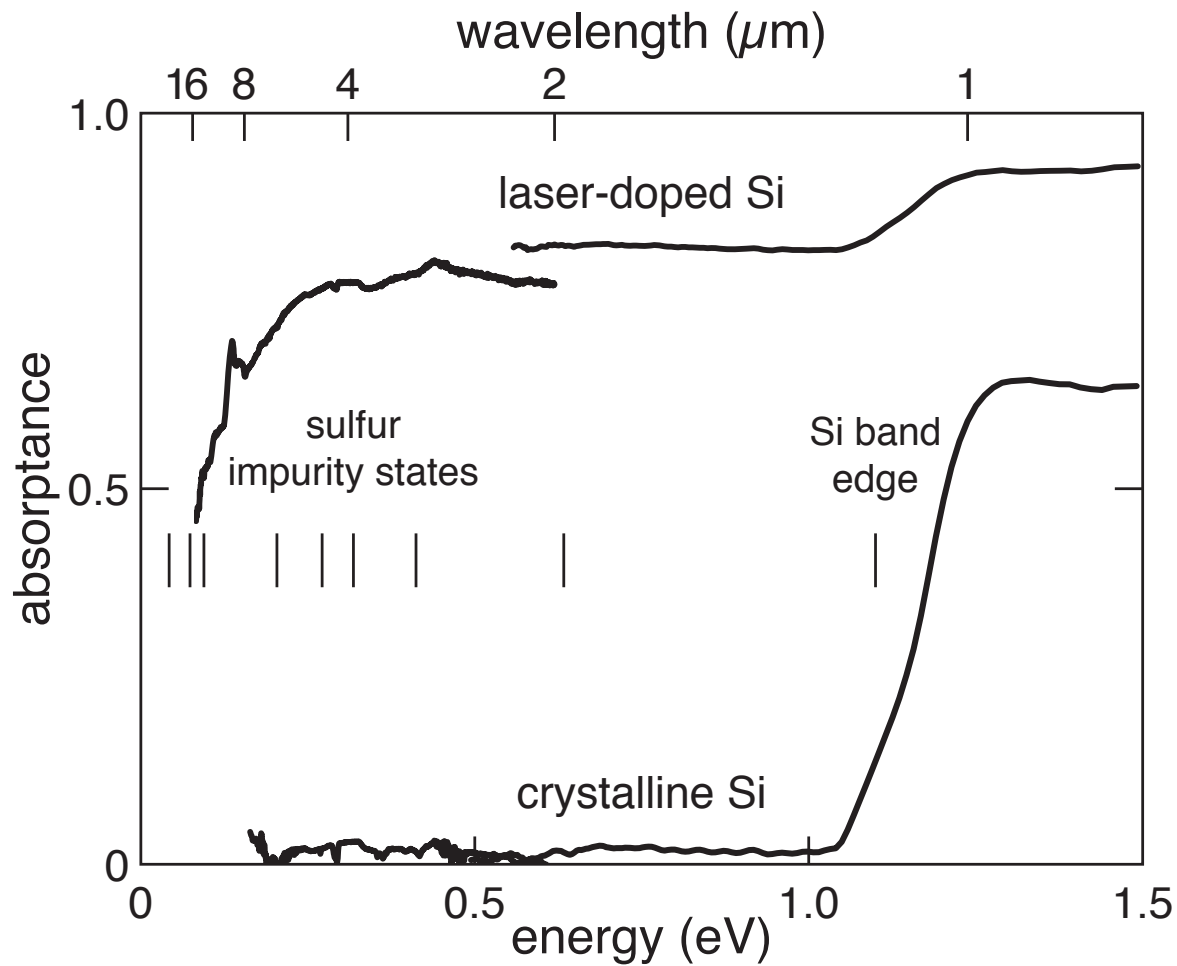
## $10^{-6}$ sulfur doping





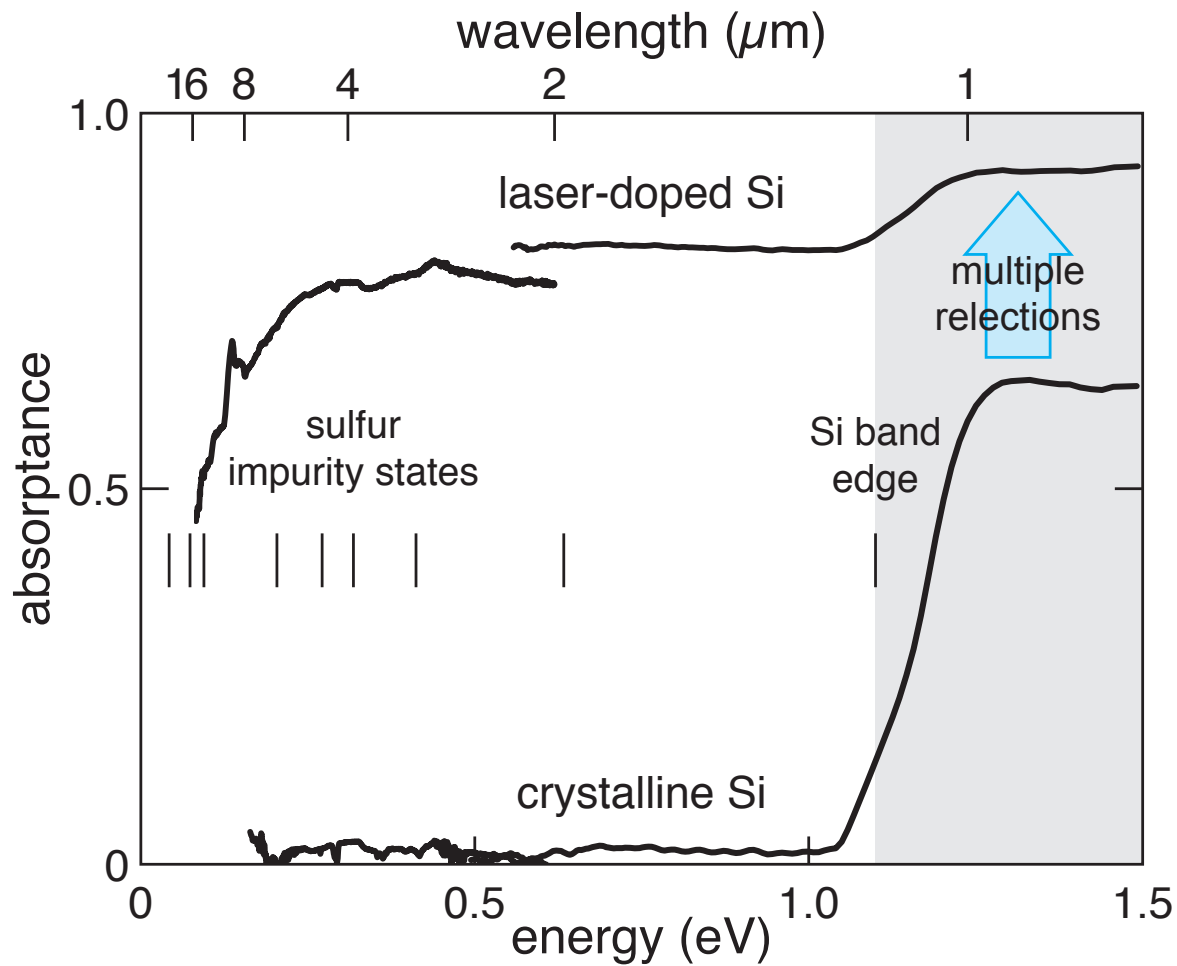
# Optoelectronic properties

## laser-doped S:Si



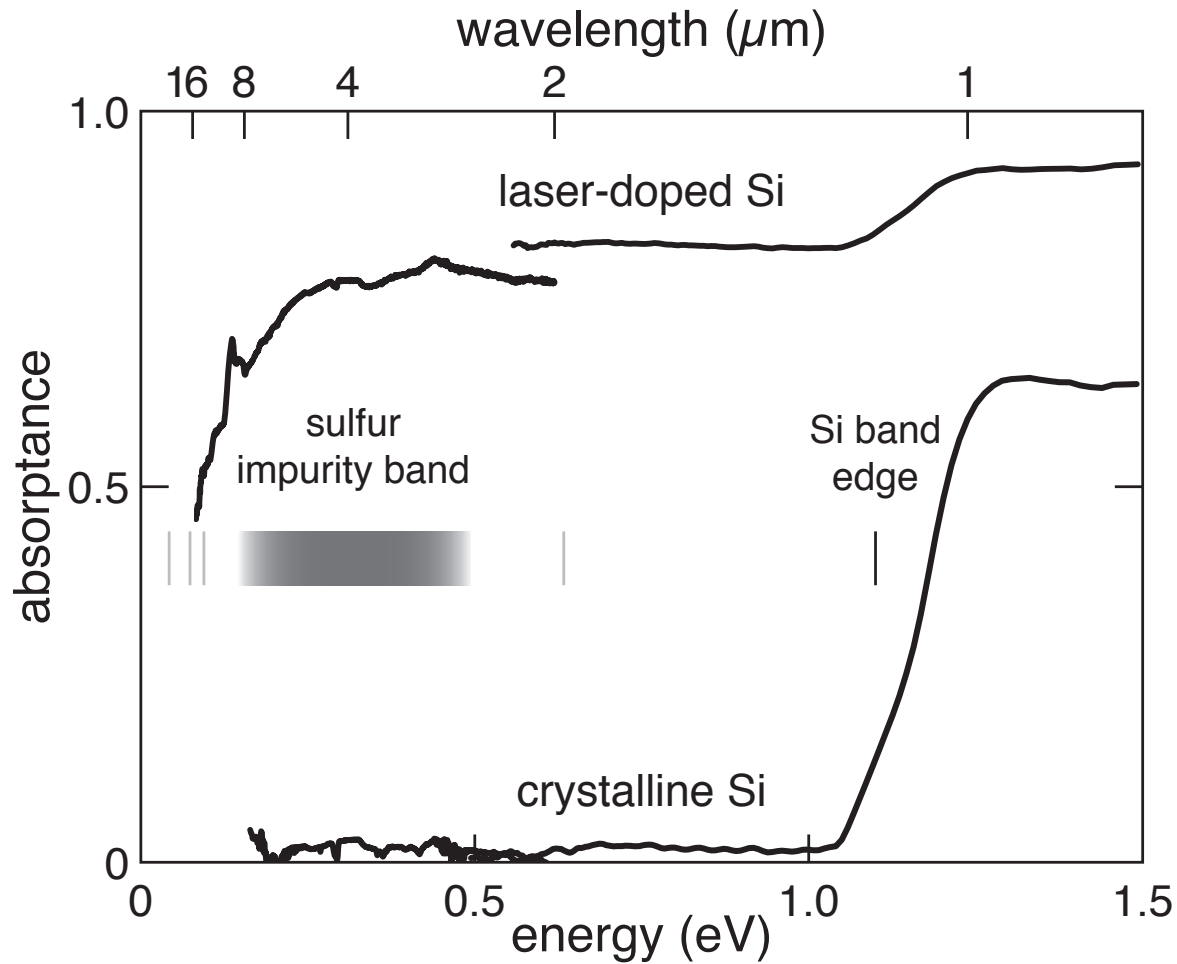
# Optoelectronic properties

## laser-doped S:Si



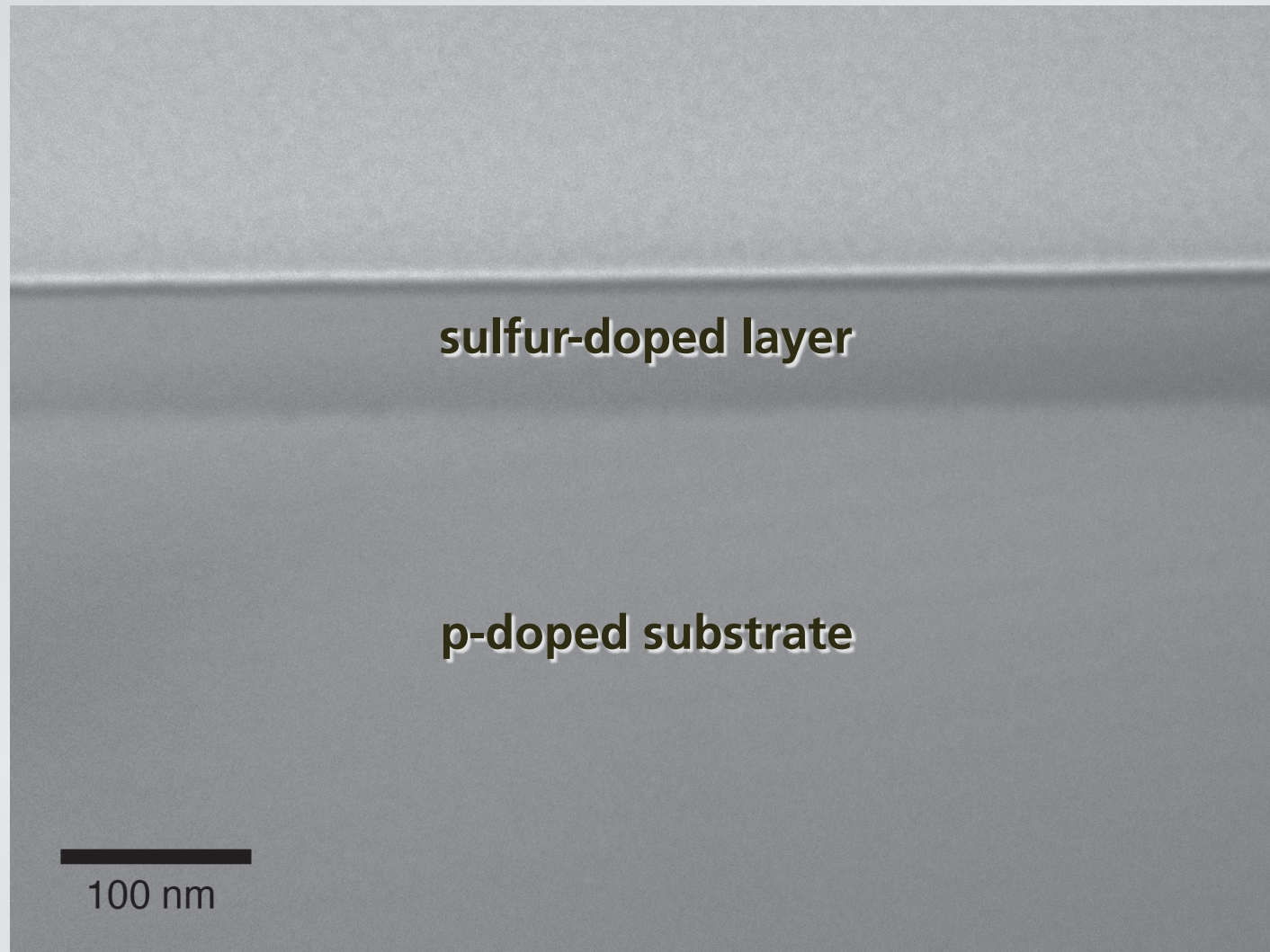
# Optoelectronic properties

## laser-doped S:Si



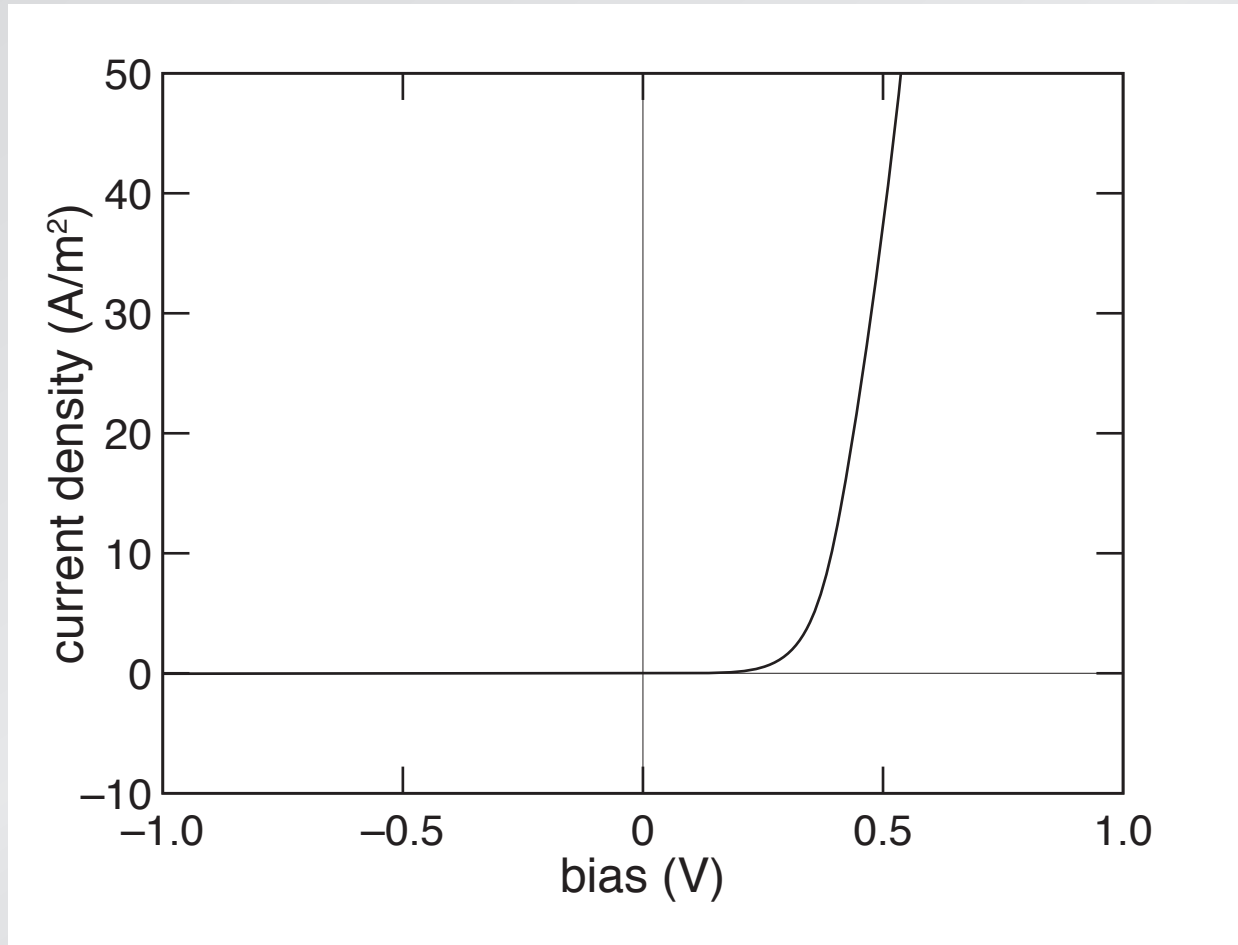
# Optoelectronic properties

should have shallow junction below surface



# Optoelectronic properties

excellent rectification (after annealing)

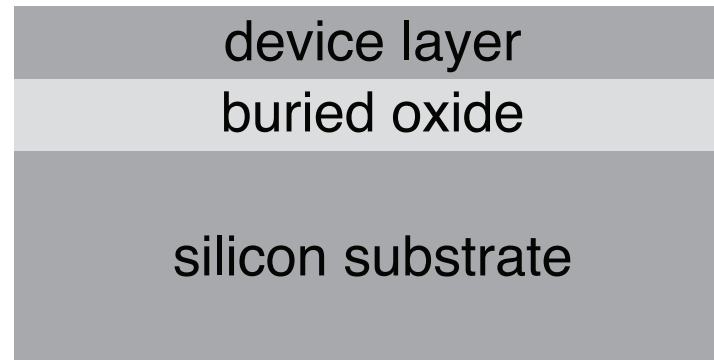


# Optoelectronic properties

***I*/V behavior consistent with  
impurity band between 200 and 400 meV**

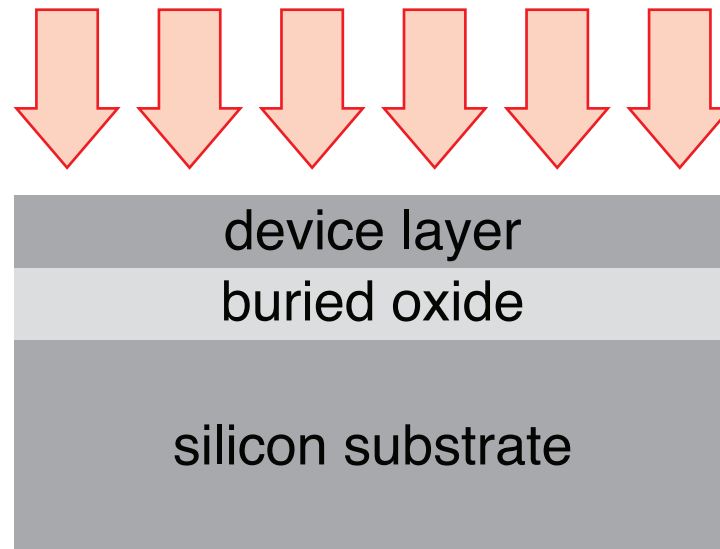
# Optoelectronic properties

isolate surface layer for Hall measurements



# Optoelectronic properties

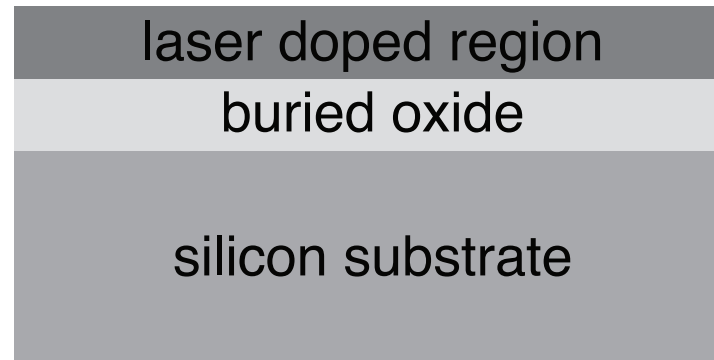
isolate surface layer for Hall measurements





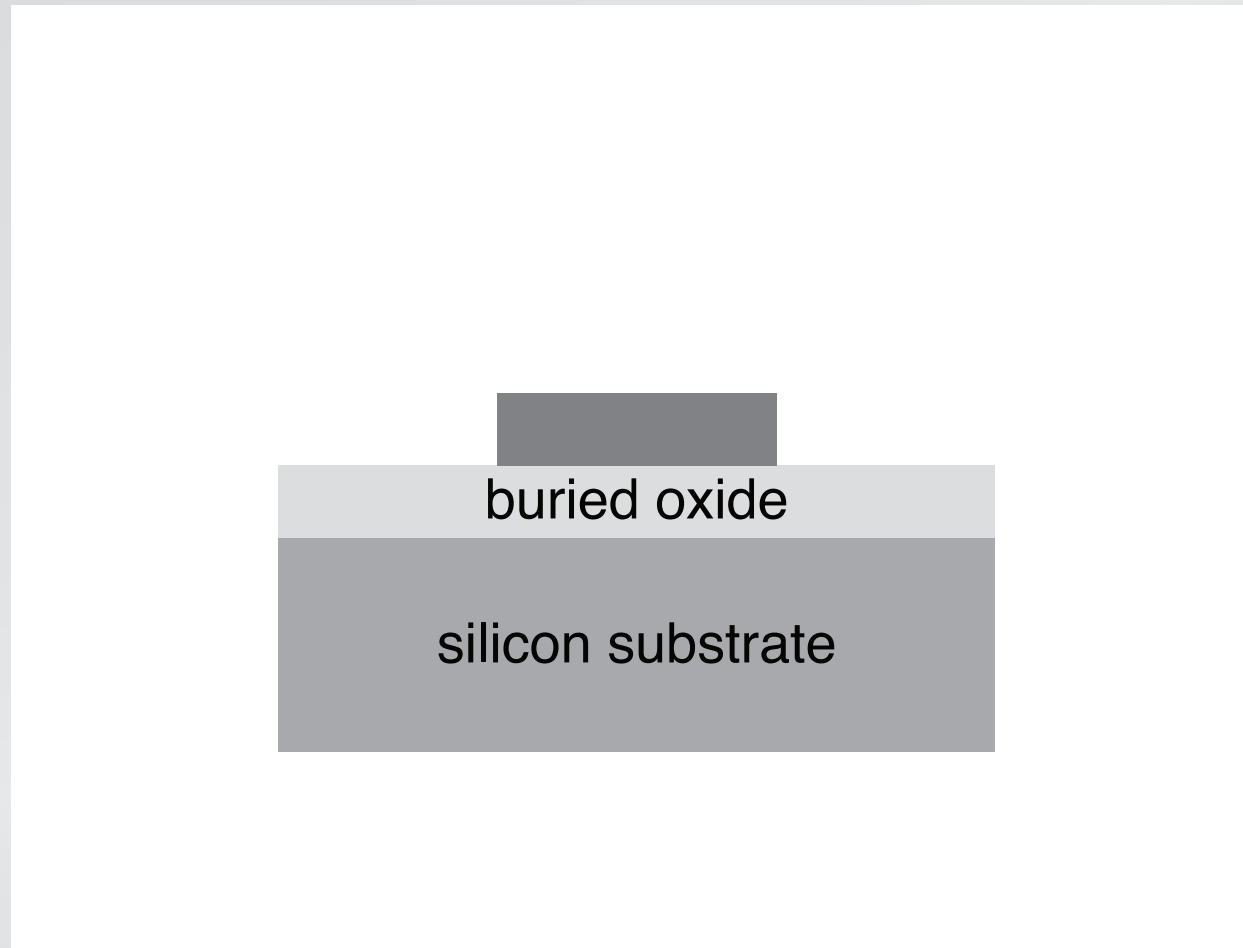
# Optoelectronic properties

isolate surface layer for Hall measurements



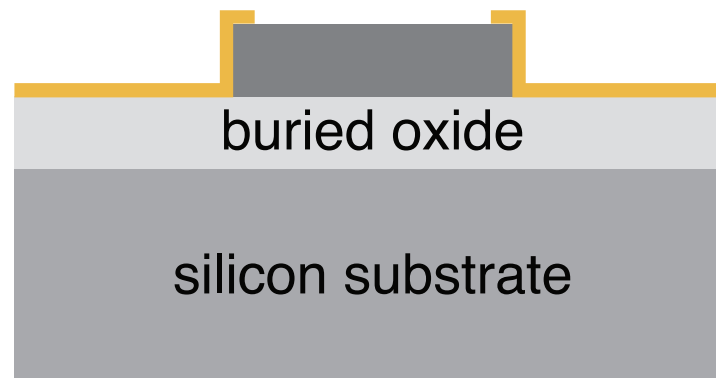
# Optoelectronic properties

isolate surface layer for Hall measurements



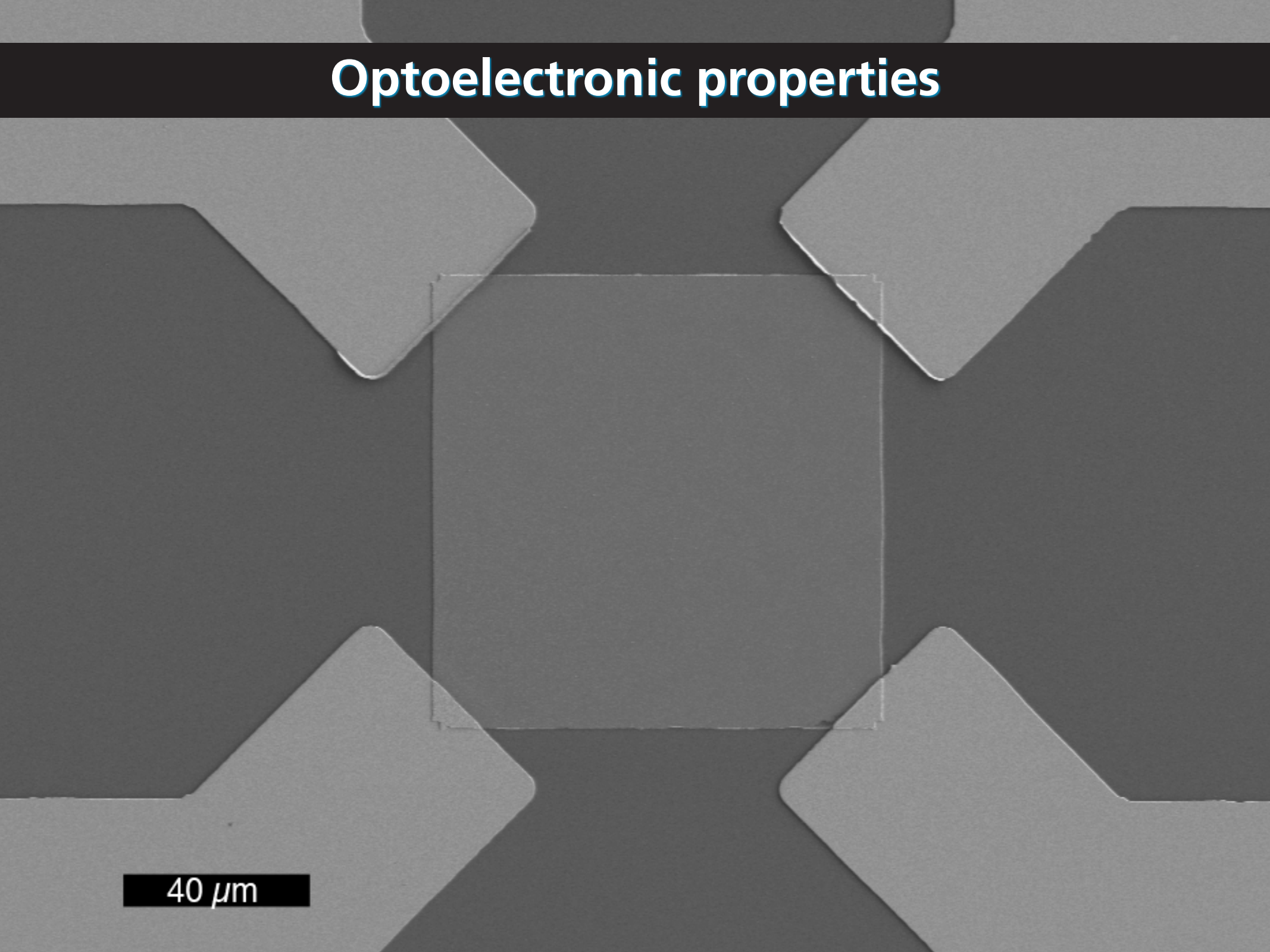
# Optoelectronic properties

isolate surface layer for Hall measurements



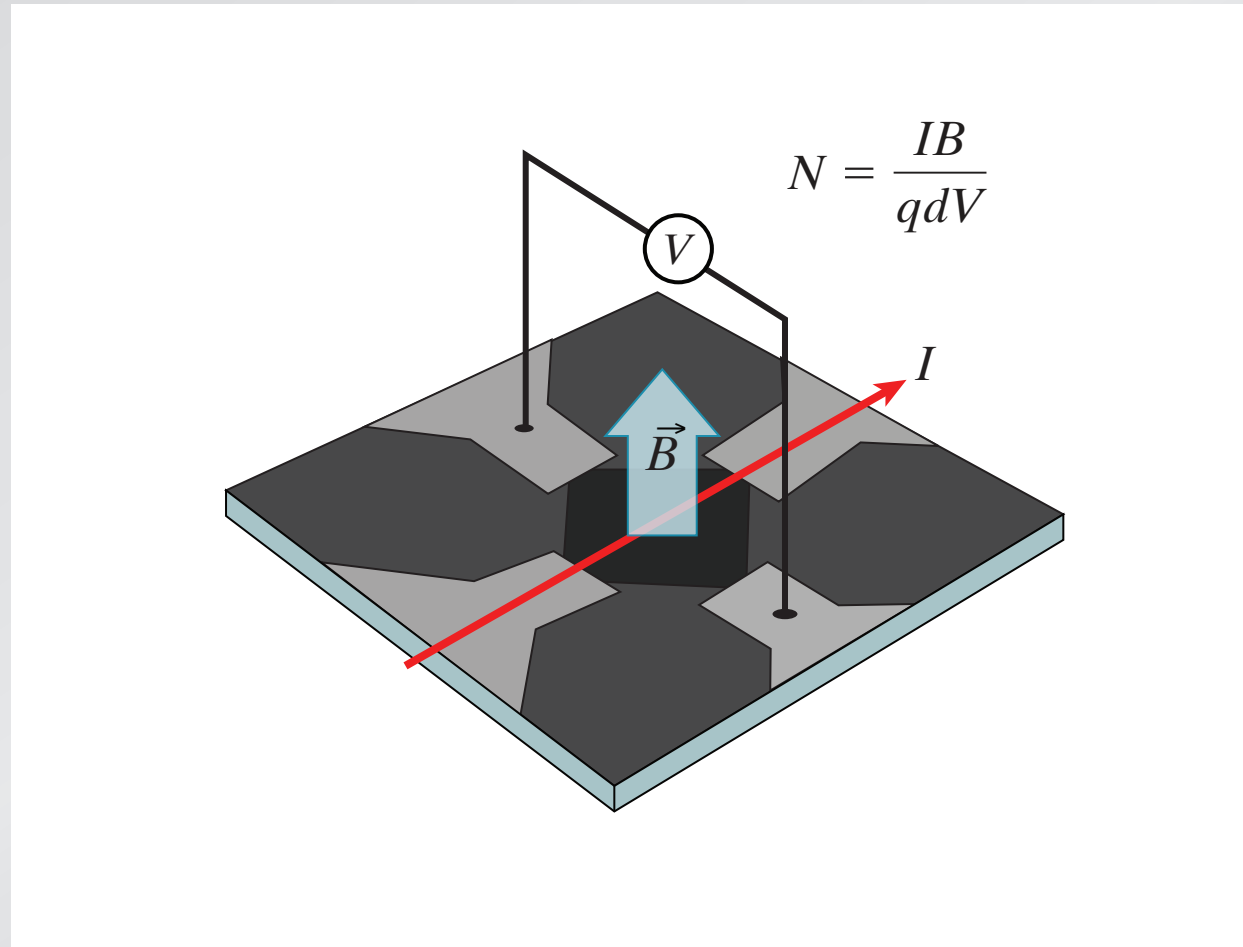
# Optoelectronic properties

40  $\mu\text{m}$

A grayscale micrograph showing a central square region surrounded by four trapezoidal regions. The central square is outlined with a thin white border. The trapezoidal regions are positioned at the top-left, top-right, bottom-left, and bottom-right corners relative to the central square. A scale bar in the bottom-left corner indicates a length of 40 micrometers.

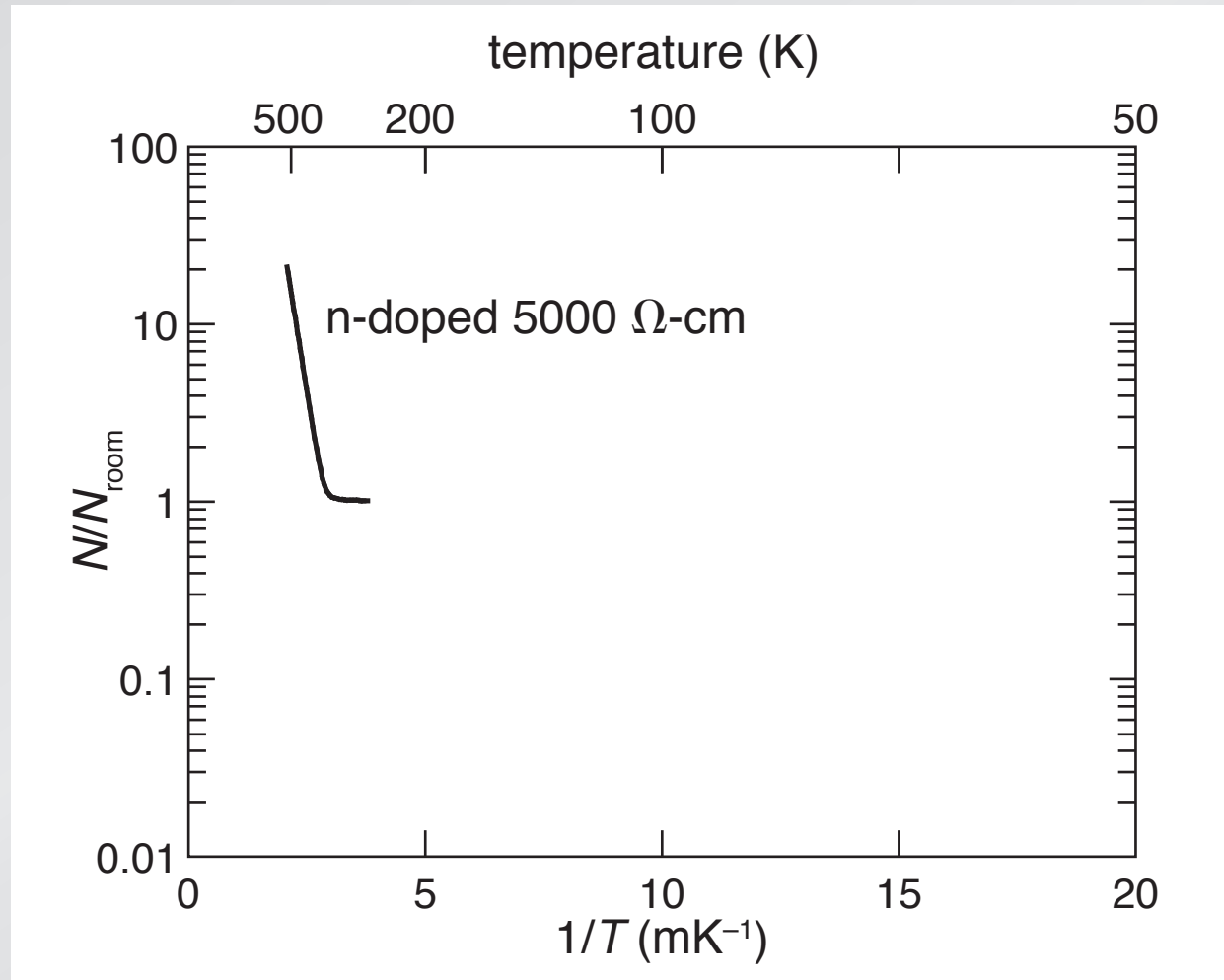
# Optoelectronic properties

## Hall measurements



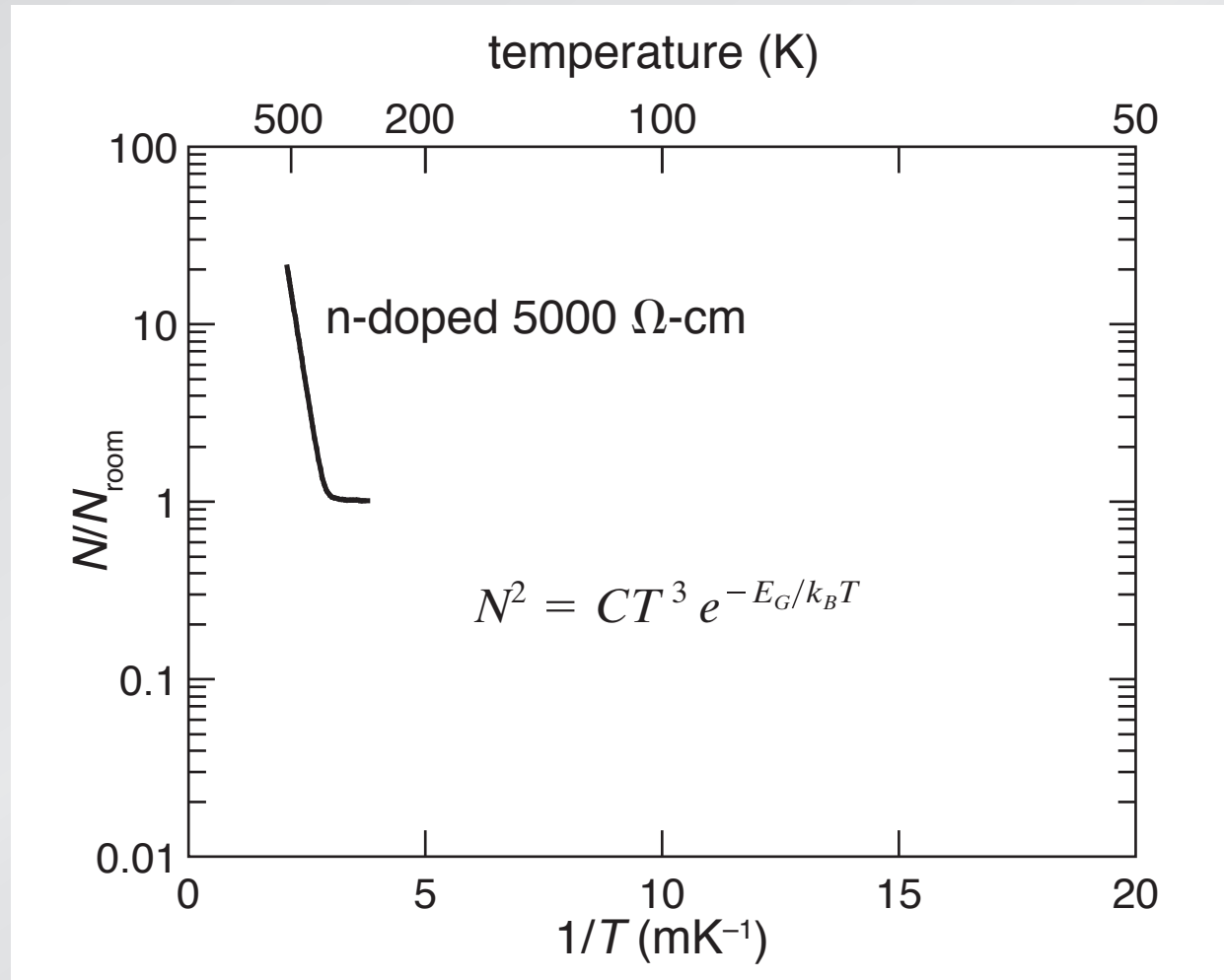
# Optoelectronic properties

## Hall measurements



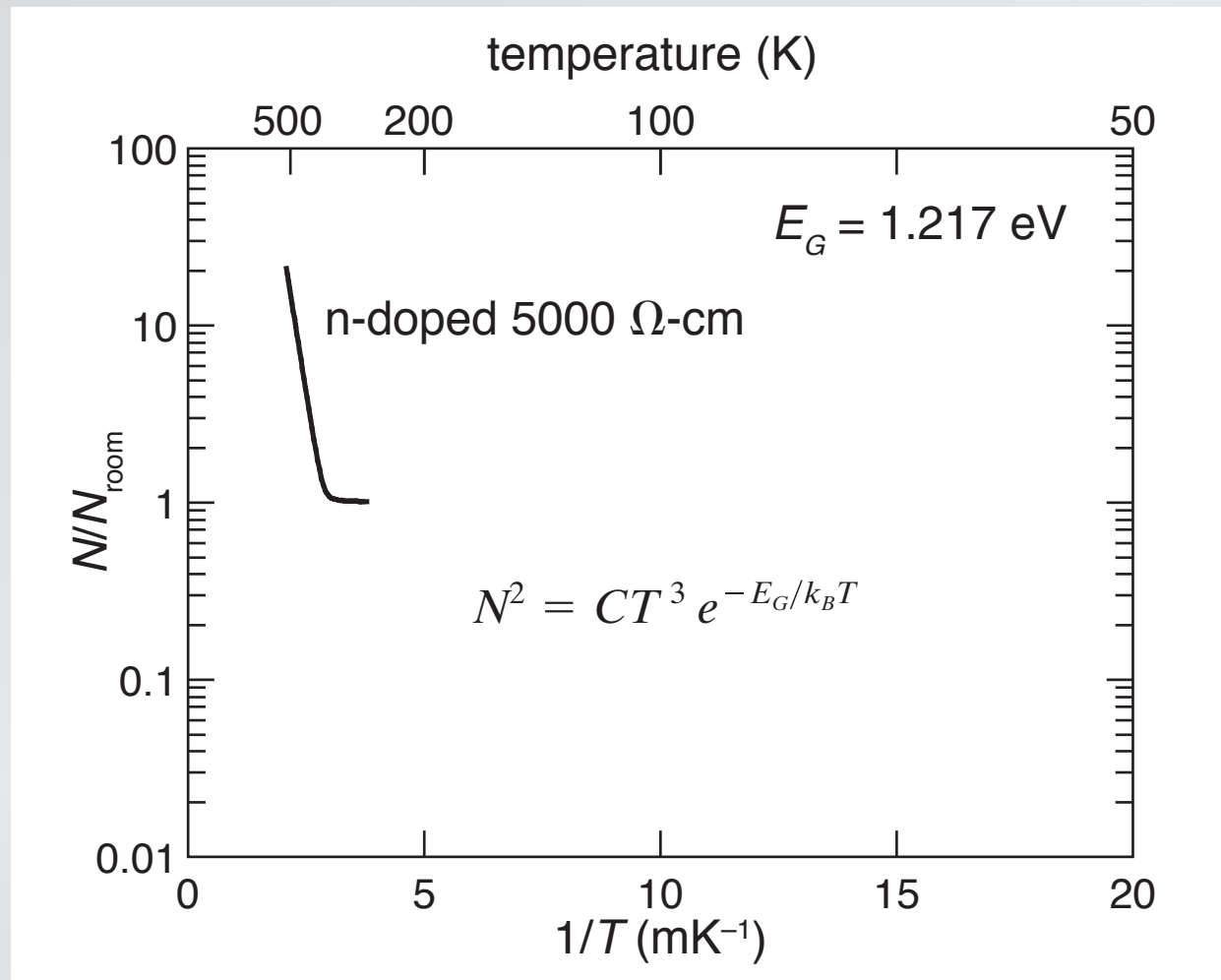
# Optoelectronic properties

## Hall measurements



# Optoelectronic properties

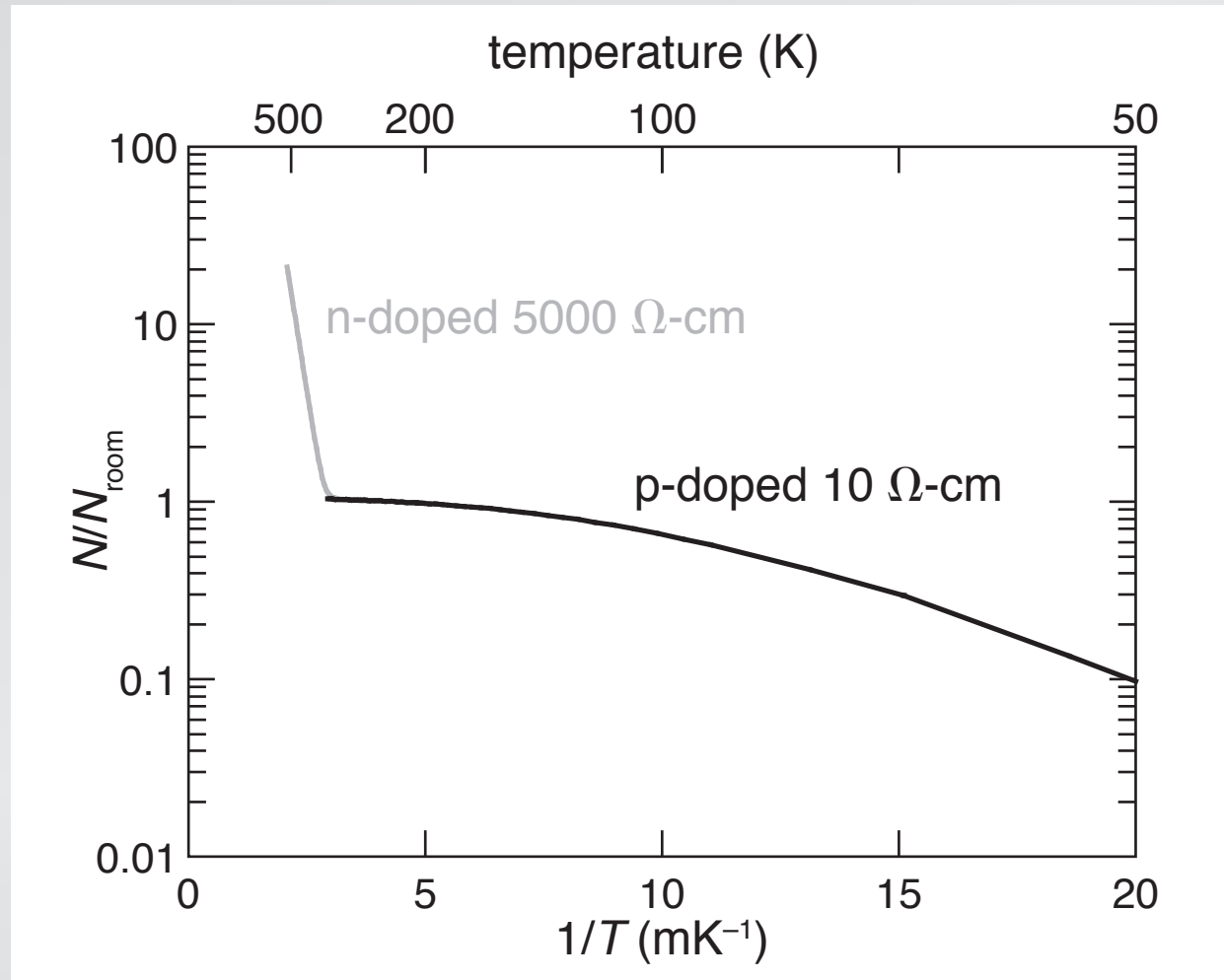
## Hall measurements





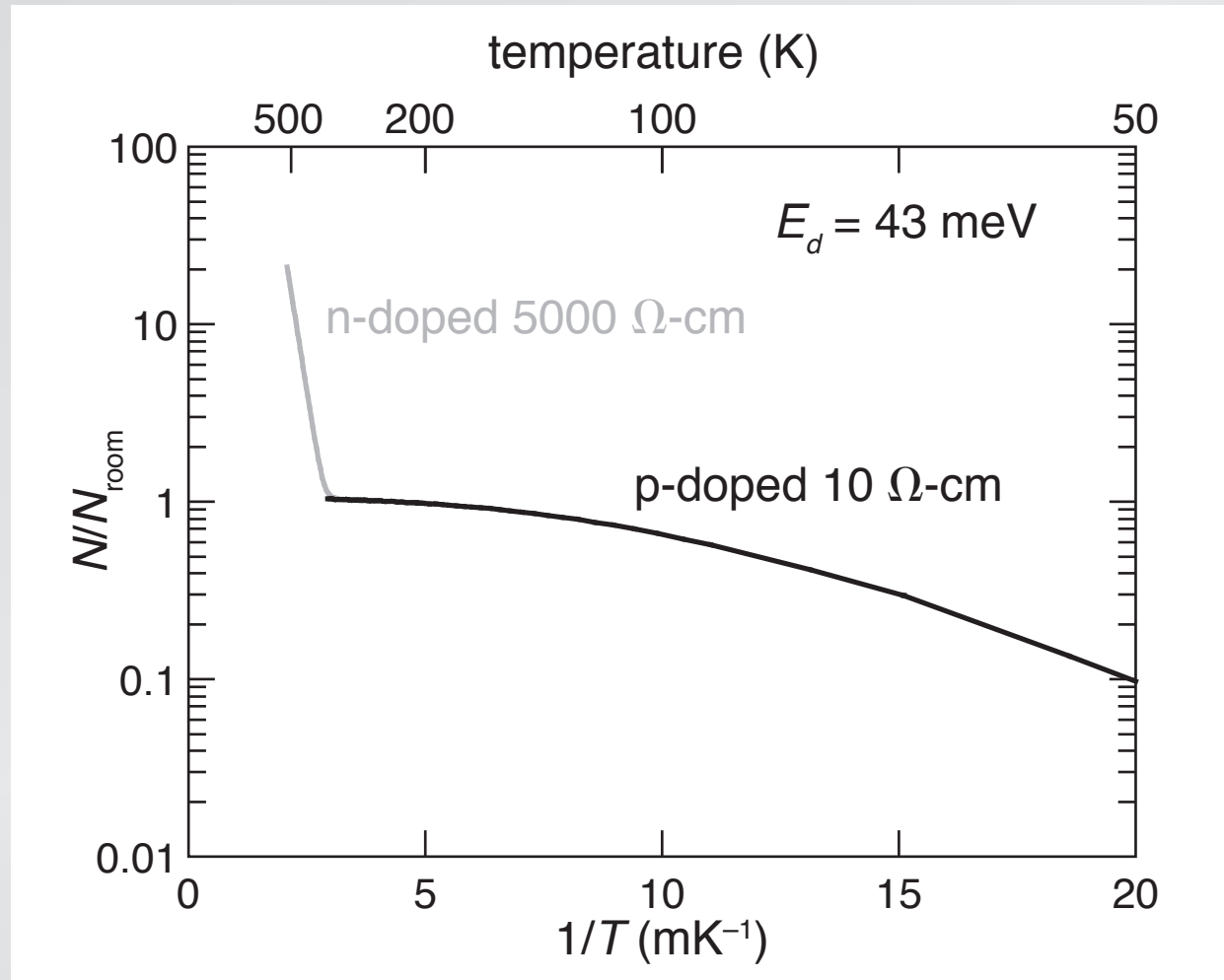
# Optoelectronic properties

## Hall measurements



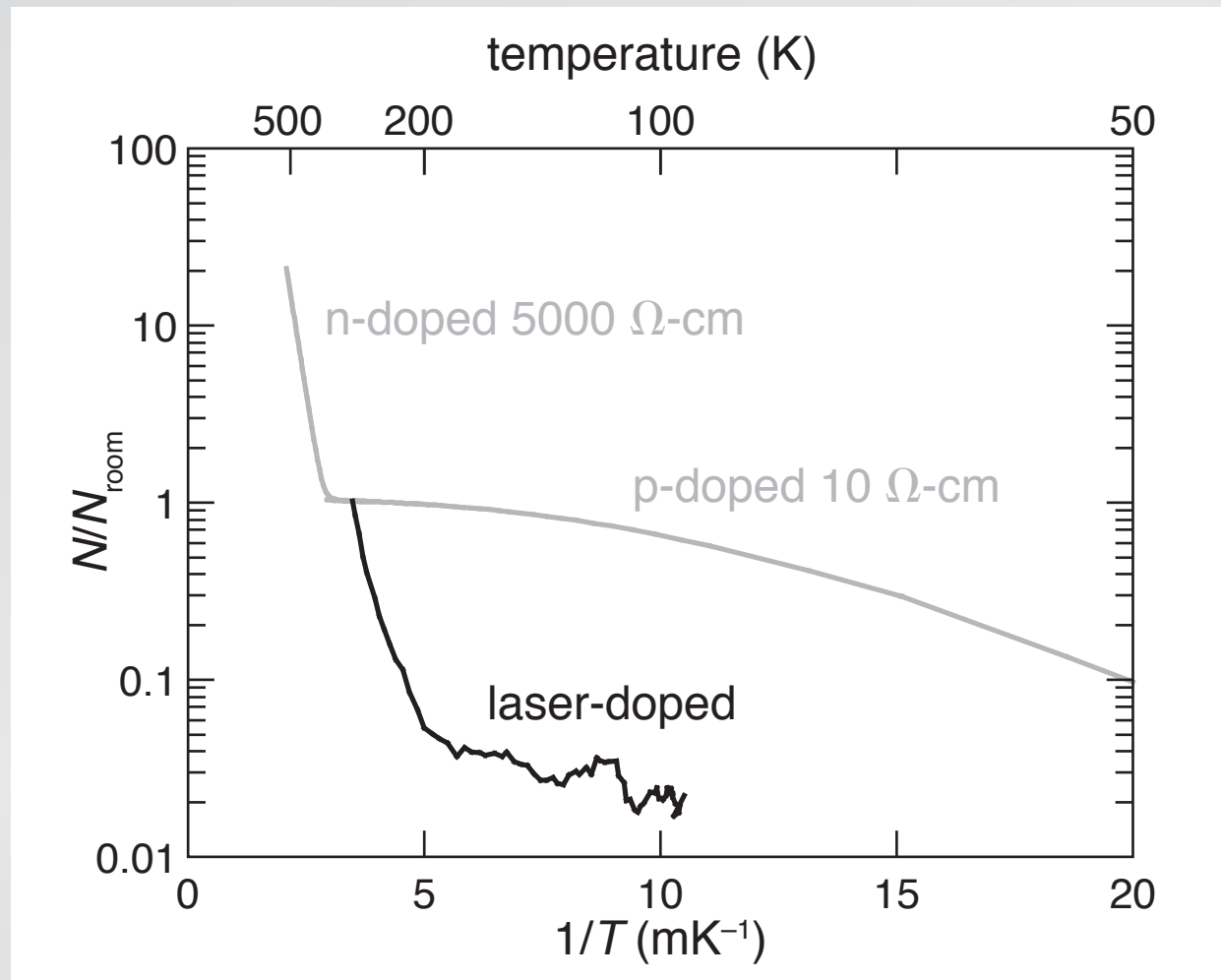
# Optoelectronic properties

## Hall measurements



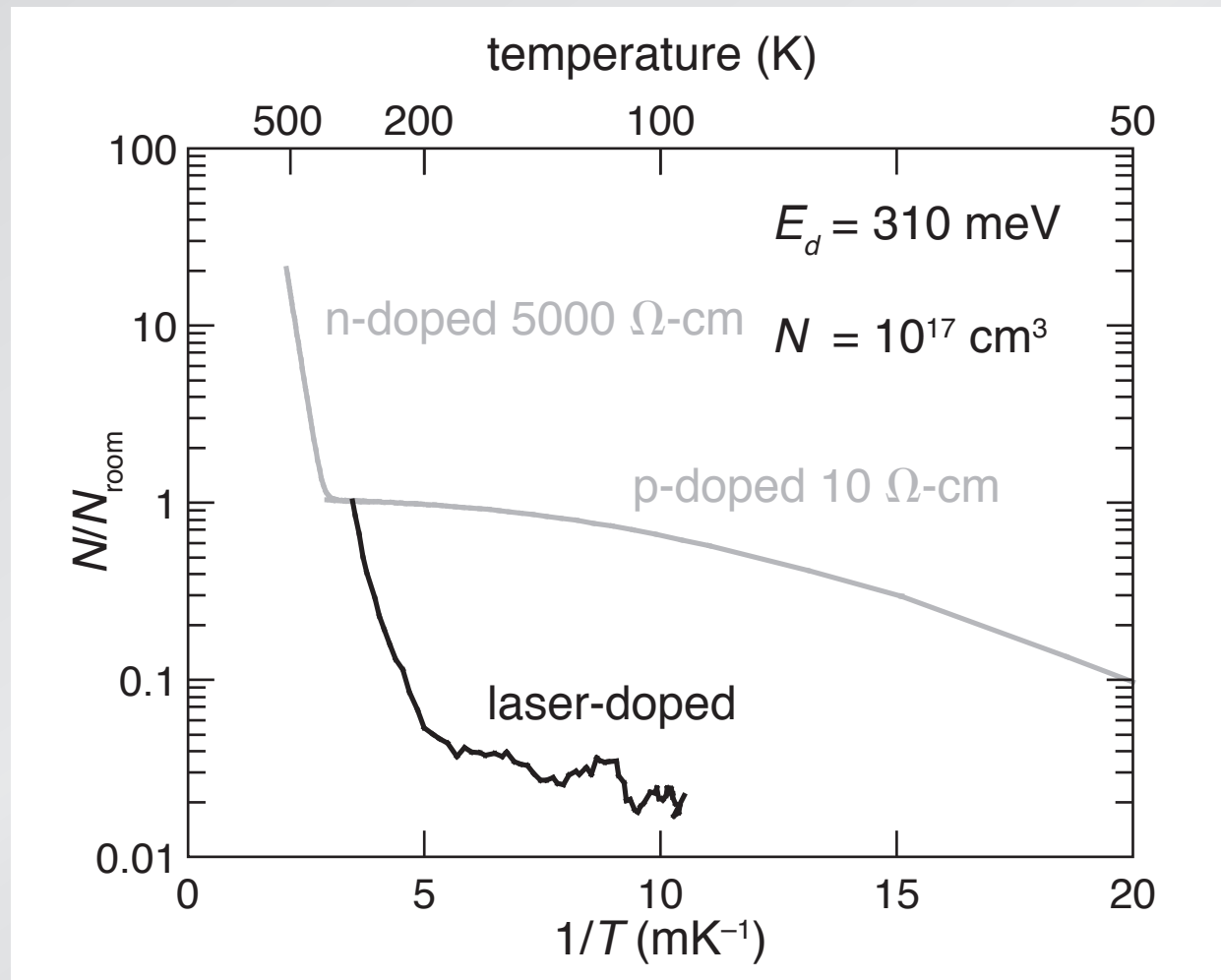
# Optoelectronic properties

## Hall measurements



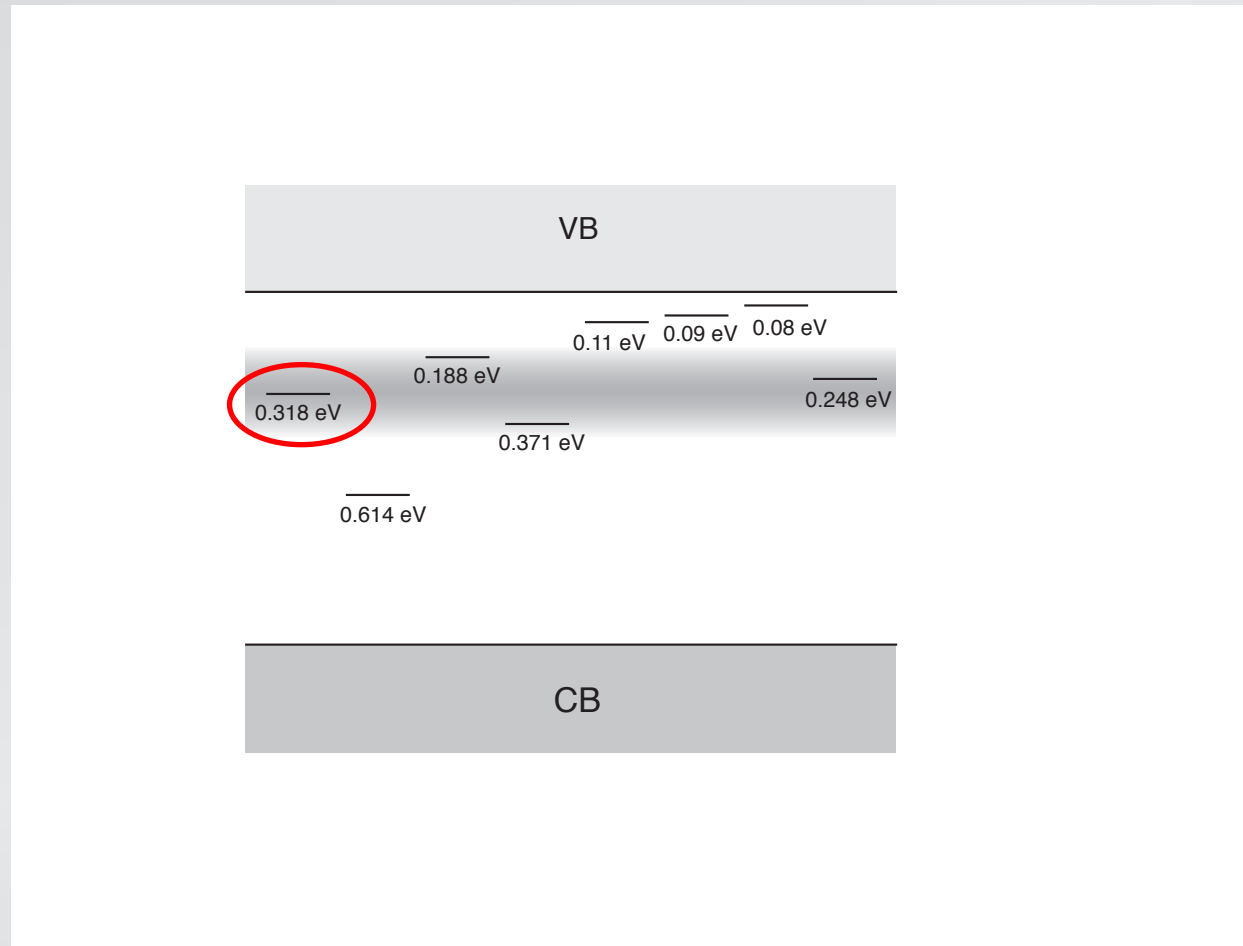
# Optoelectronic properties

## Hall measurements



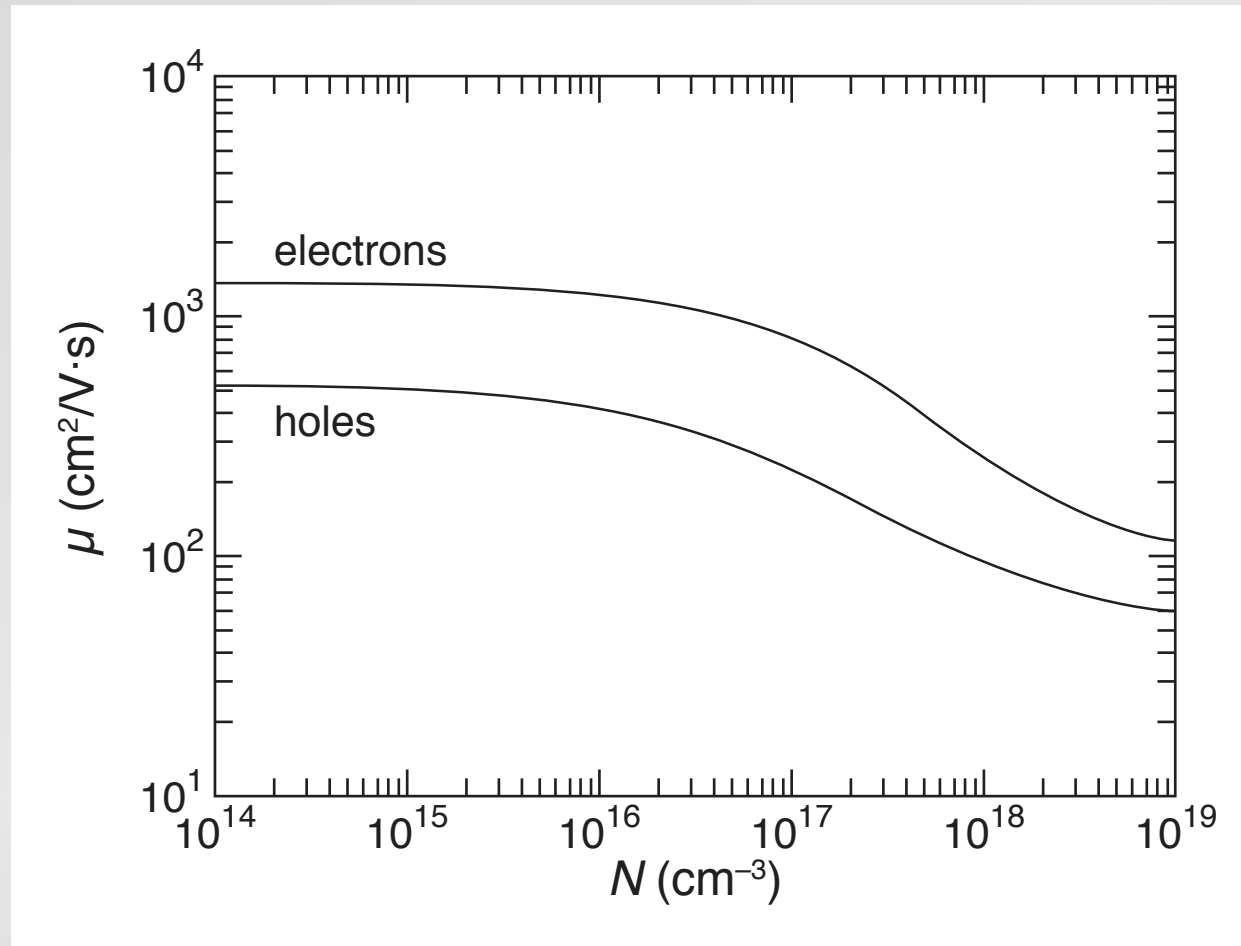
# Optoelectronic properties

impurity (donor) band centered at 310 meV



# Optoelectronic properties

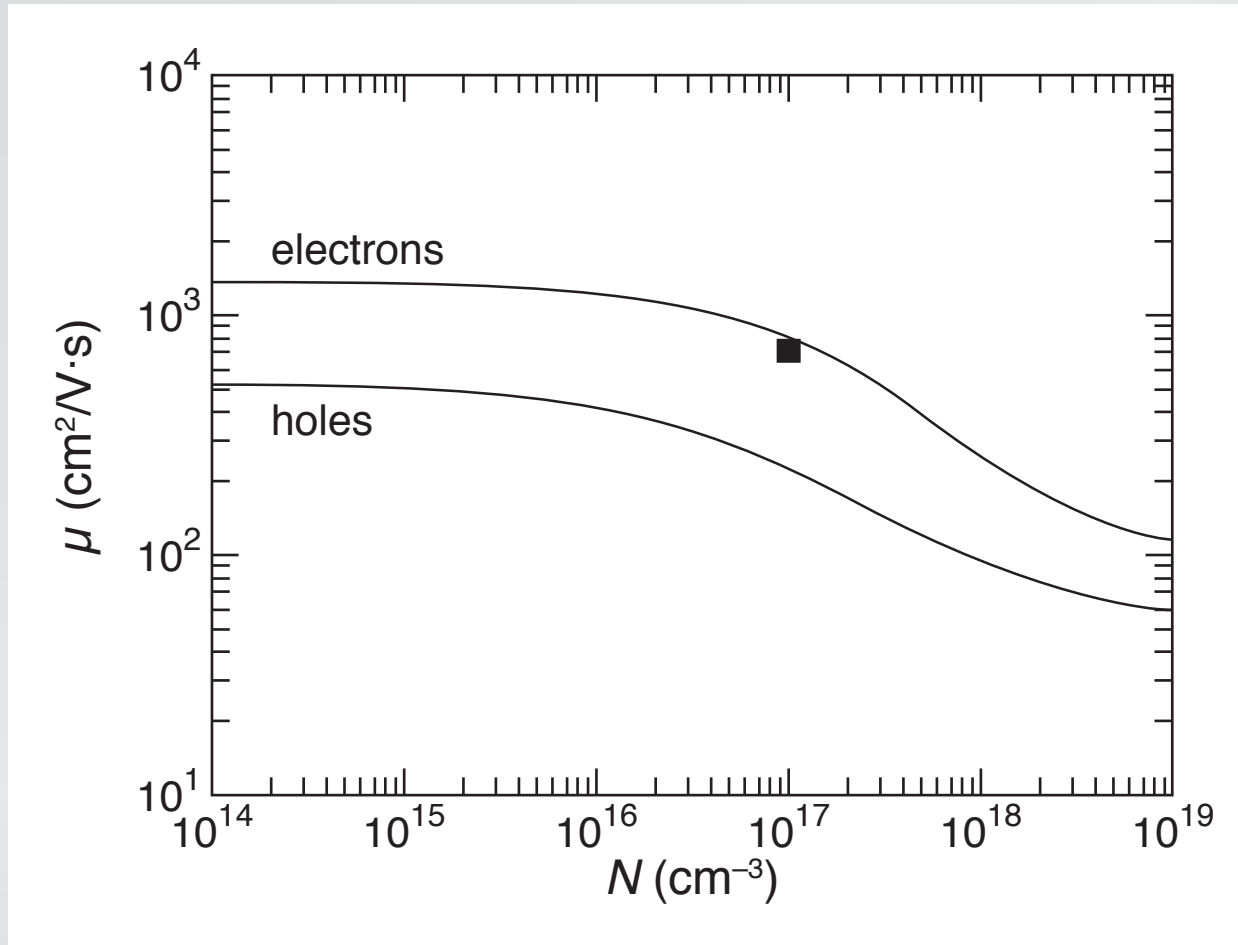
## majority carrier mobility



Caughey *et al.*, Proc. IEEE 55, 2192 (1967)

# Optoelectronic properties

## majority carrier mobility



Caughey *et al.*, Proc. IEEE 55, 2192 (1967)

# Optoelectronic properties

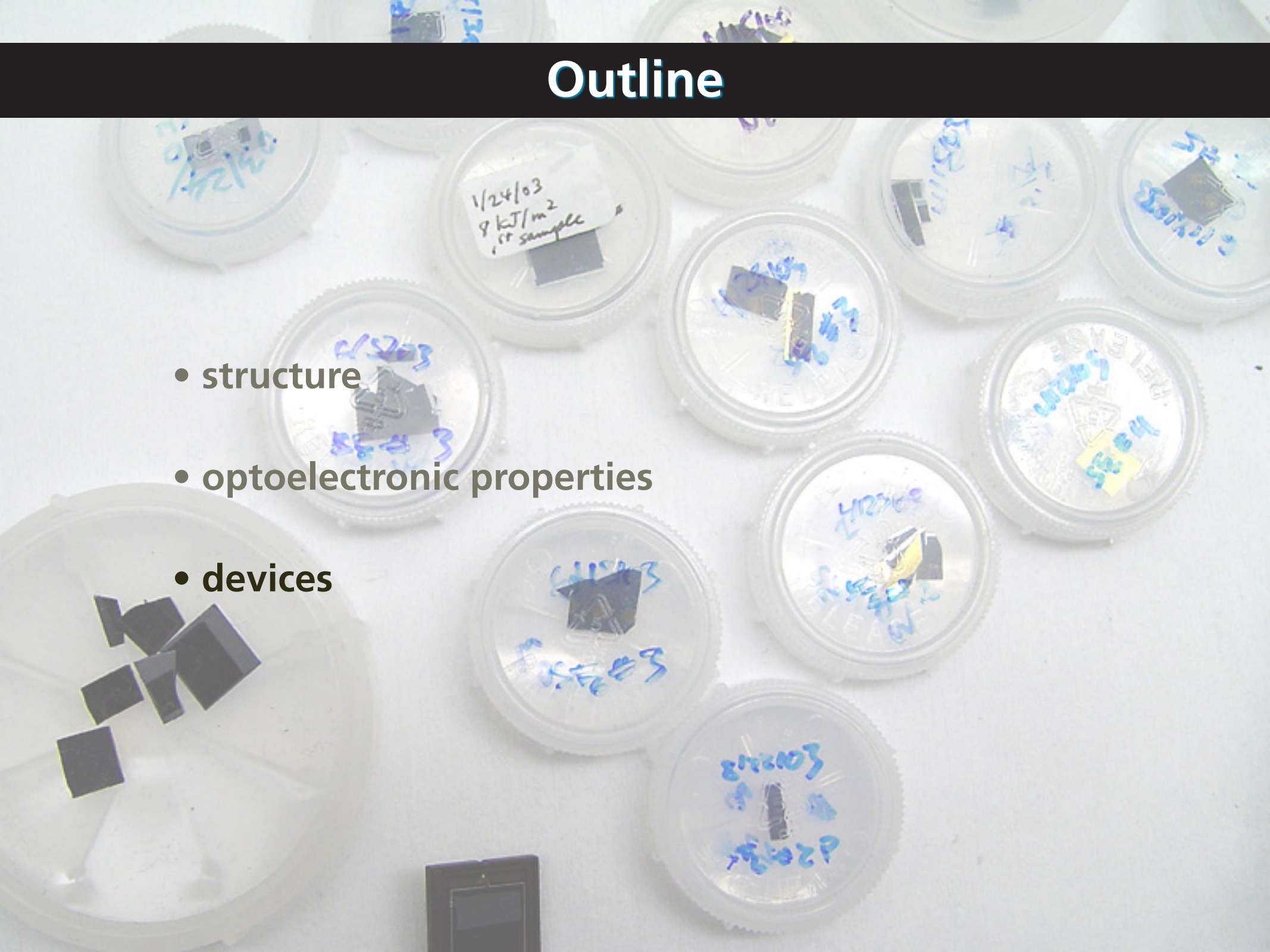
## Things to keep in mind

- IR absorption rolls off around 8  $\mu\text{m}$
- 1 in  $10^3$  sulfur atoms are ionized donors at 300 K
- all data indicate these S donors are substitutional



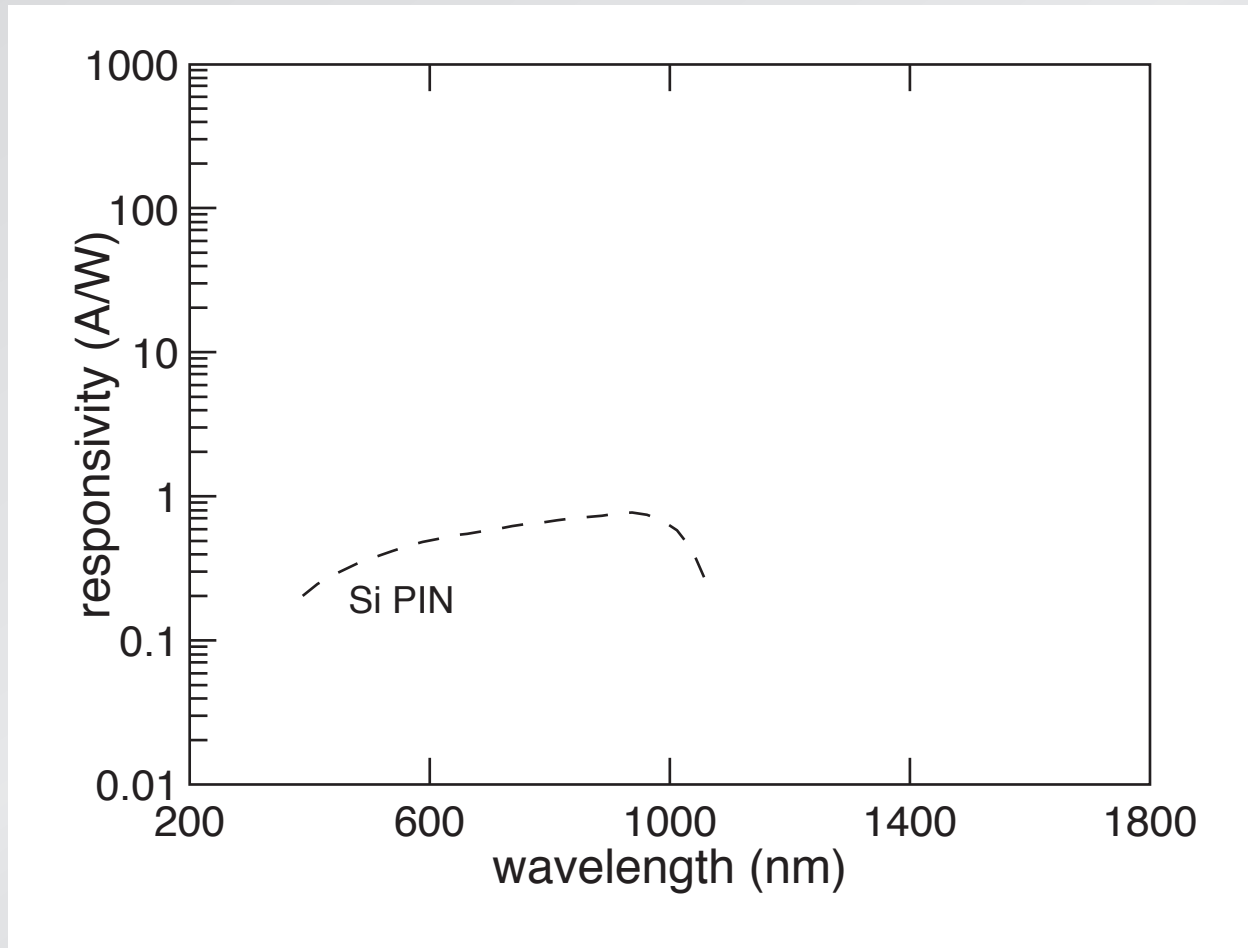
# Outline

- structure
- optoelectronic properties
- devices



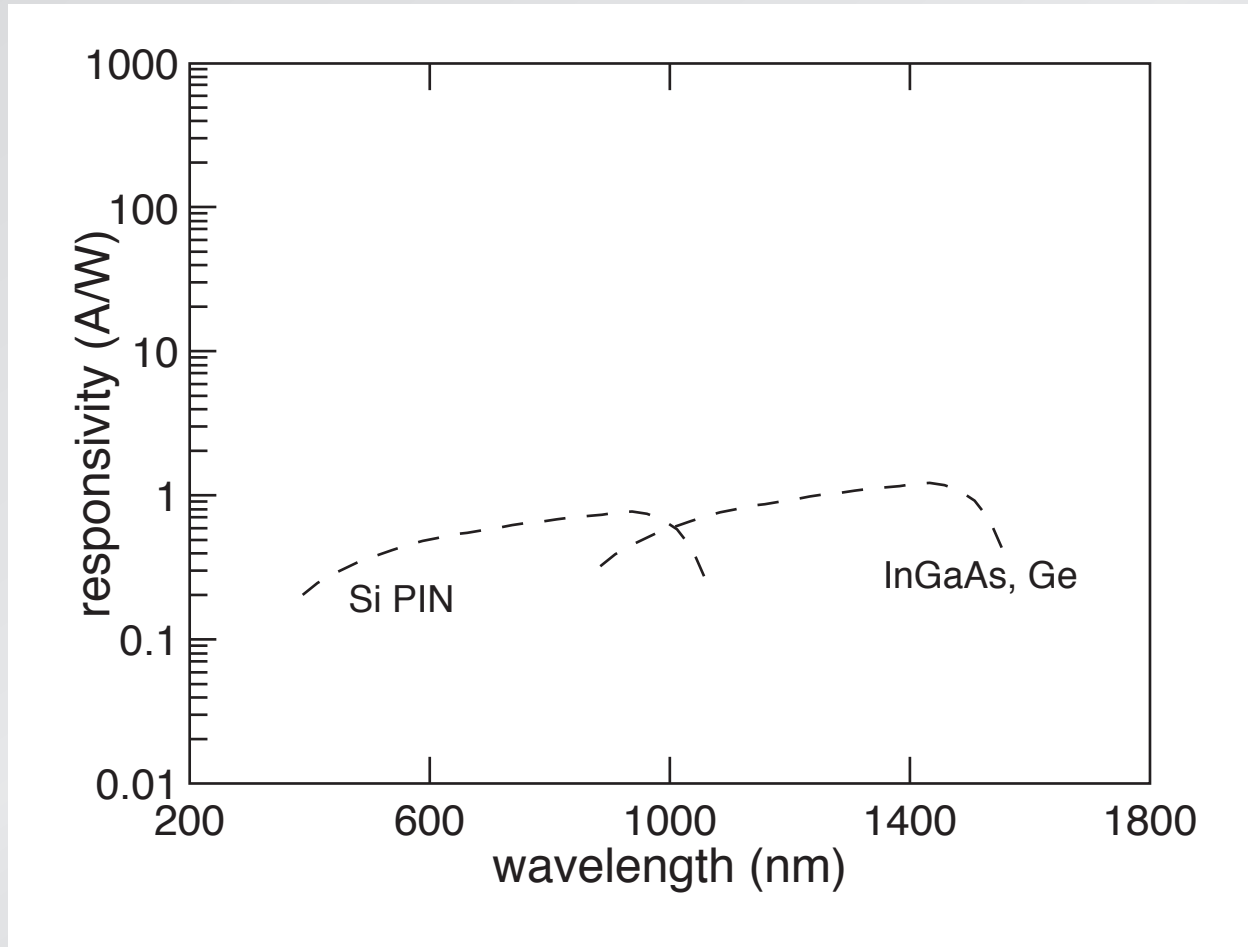
# Devices

## responsivity



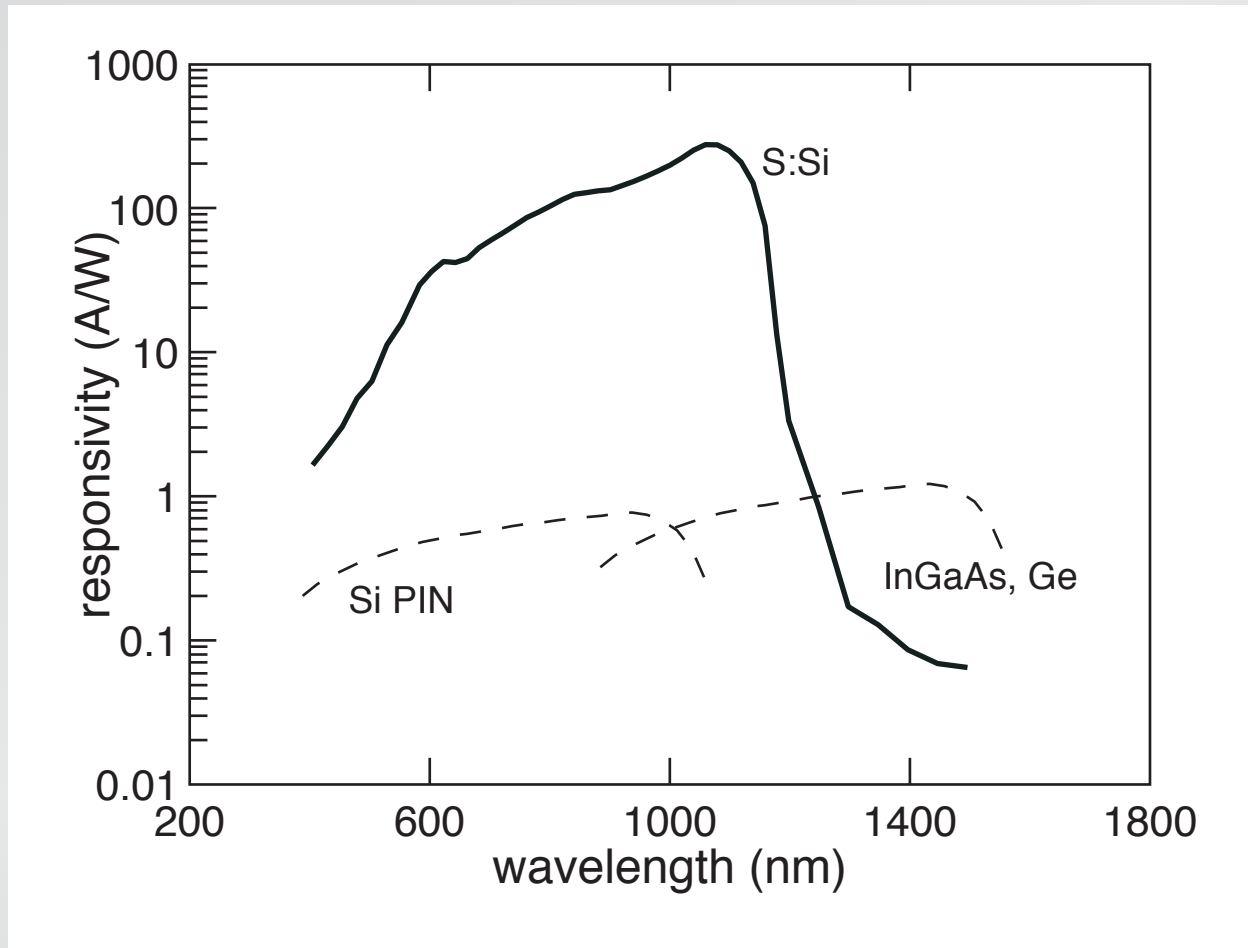
# Devices

## responsivity



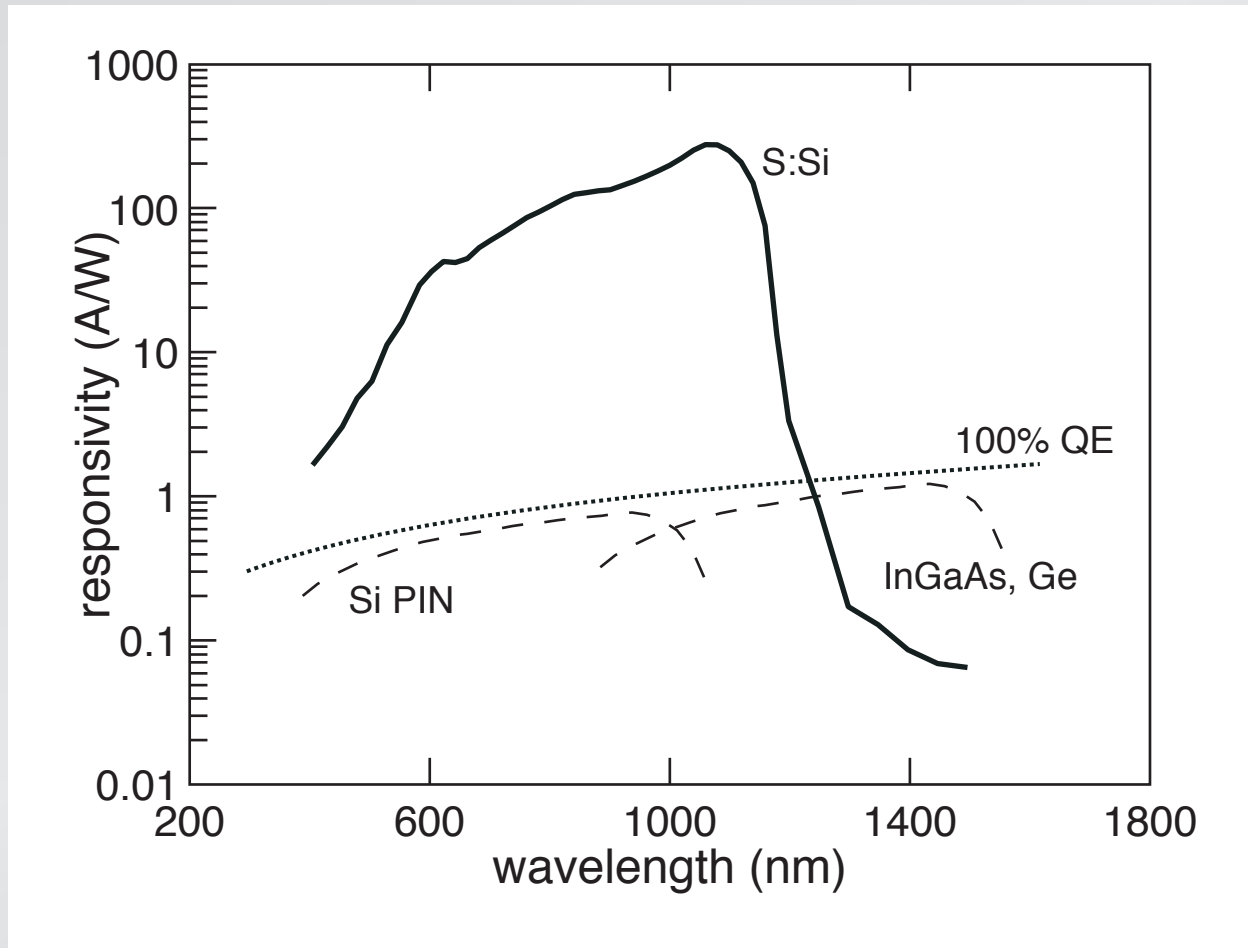
# Devices

## responsivity



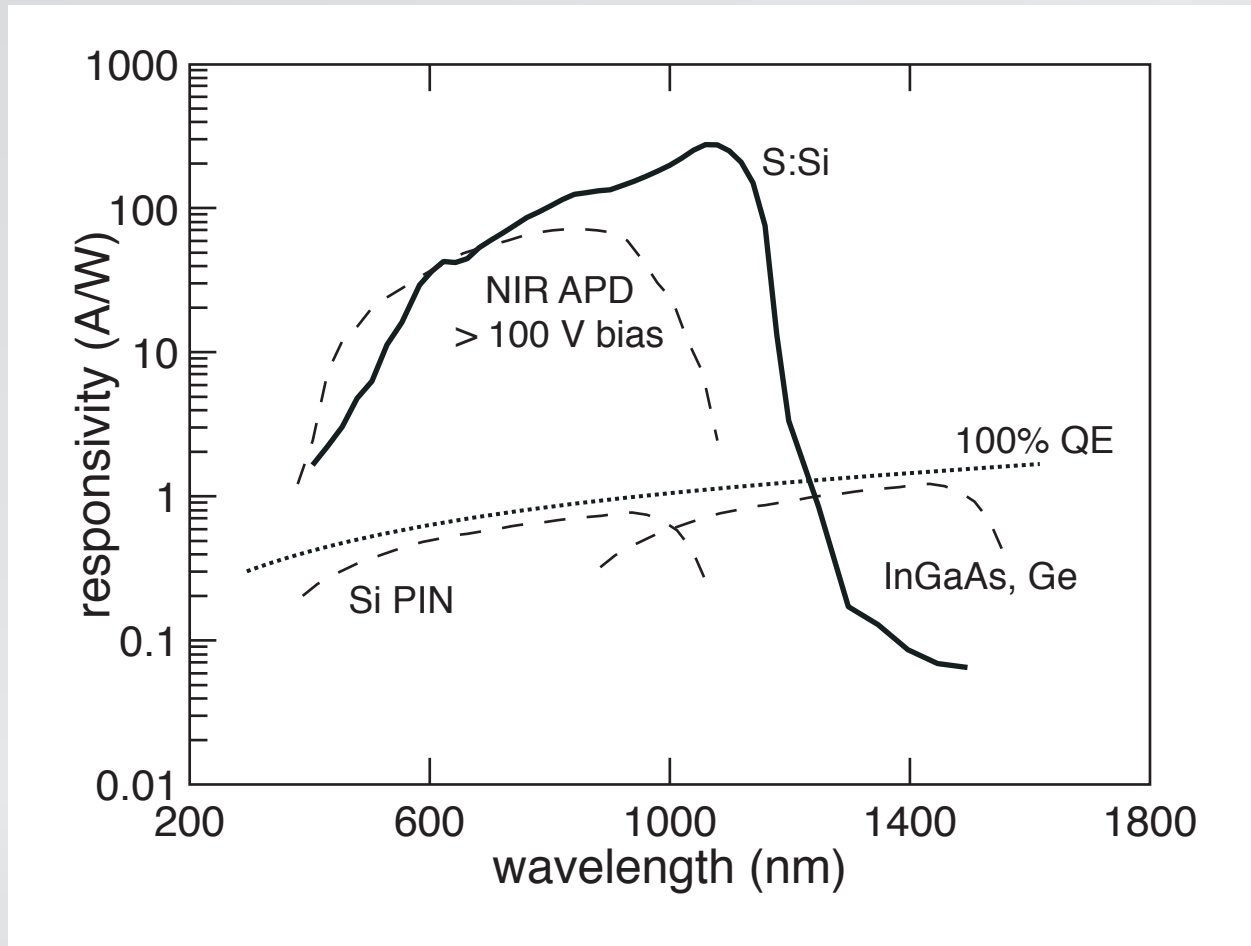
# Devices

## responsivity



# Devices

## responsivity

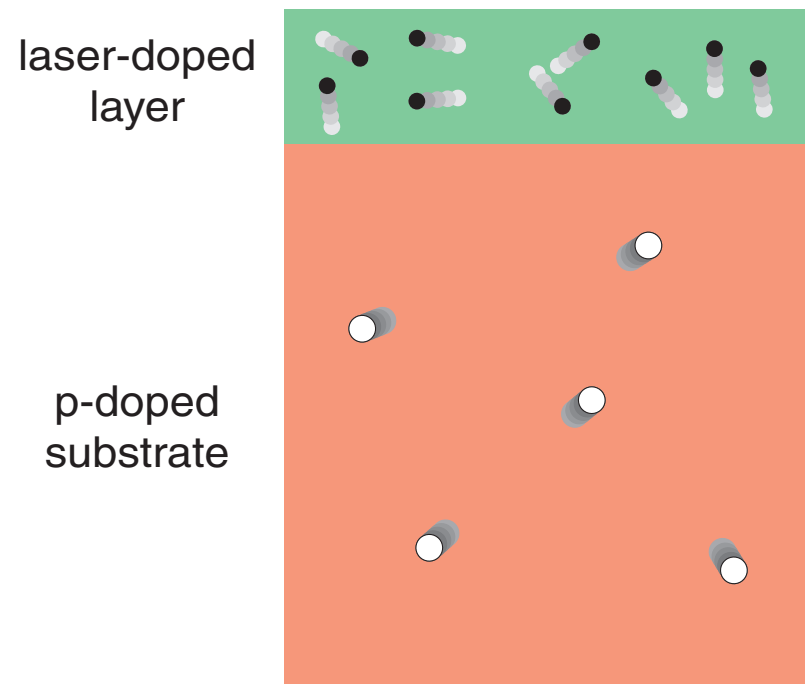


# Devices

**What causes gain?**

- **impact excitation (avalanching)**
- **carrier lifetime  $\gg$  transit time (photoconductive gain)**
- **some other mechanism**

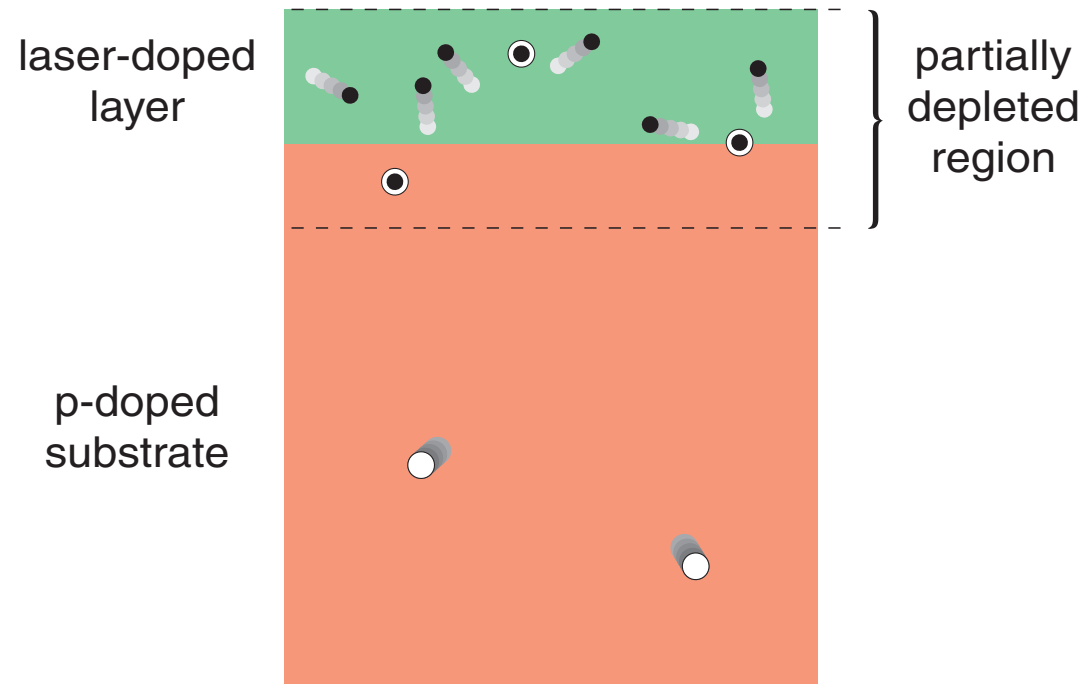
# Devices



**"pl junction"**

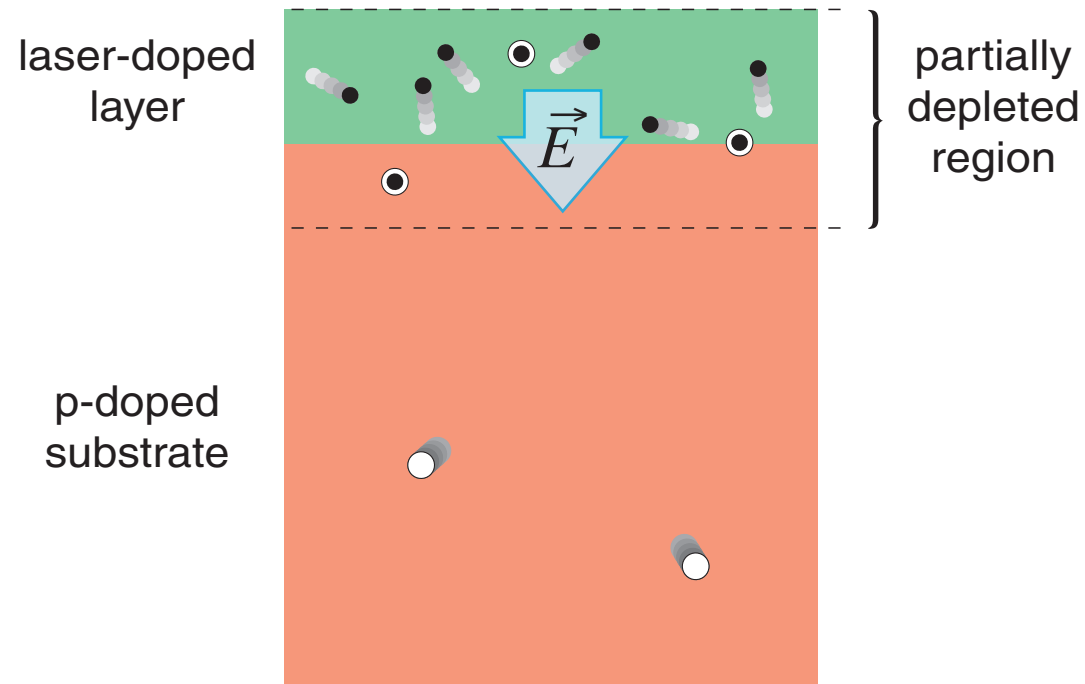


# Devices



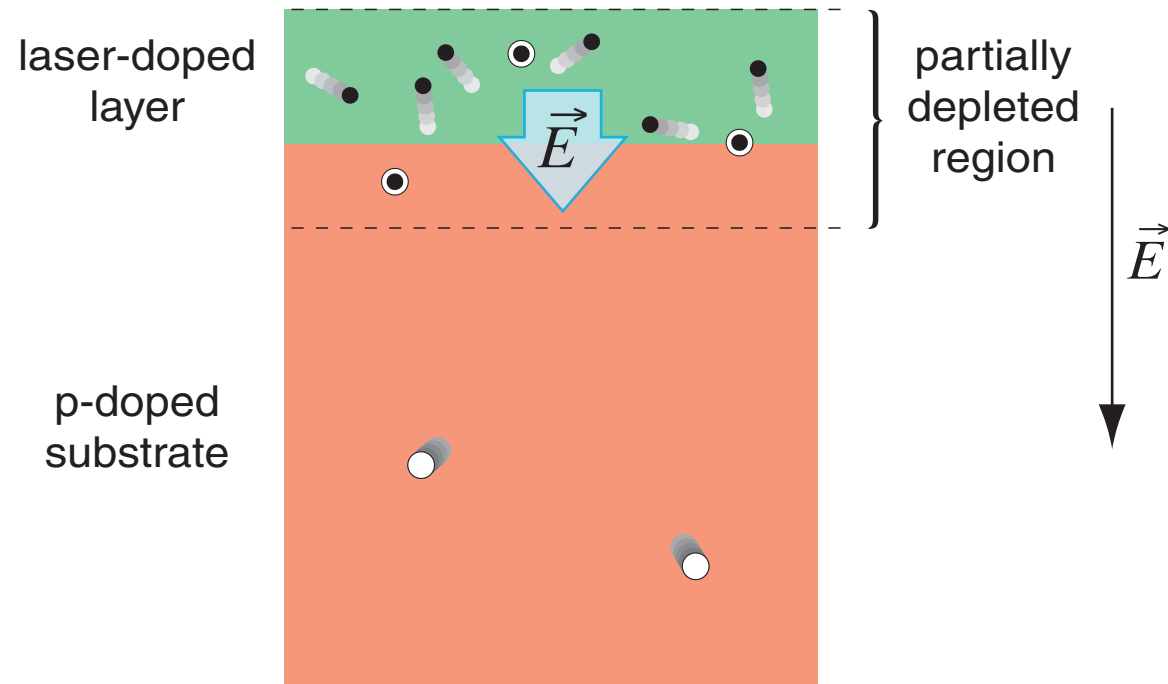
**formation of partially depleted region**

# Devices



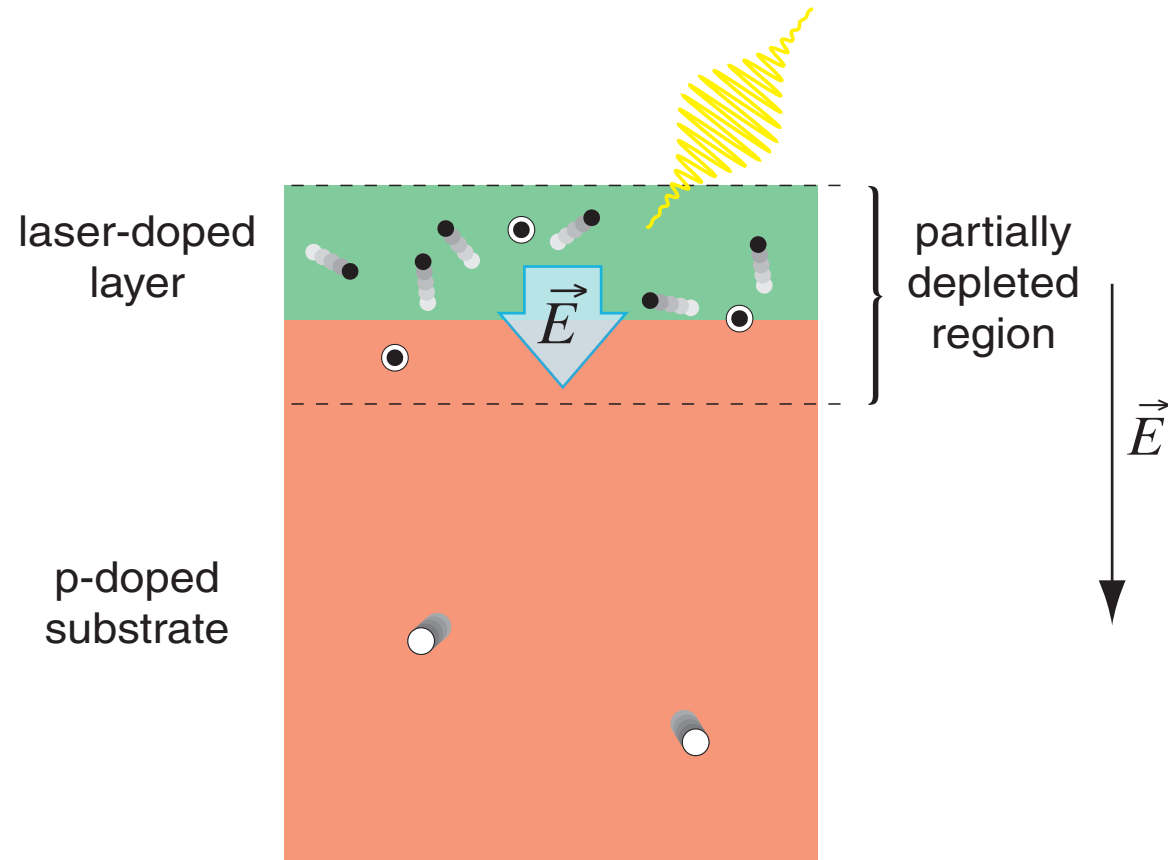
**formation of partially depleted region**

# Devices



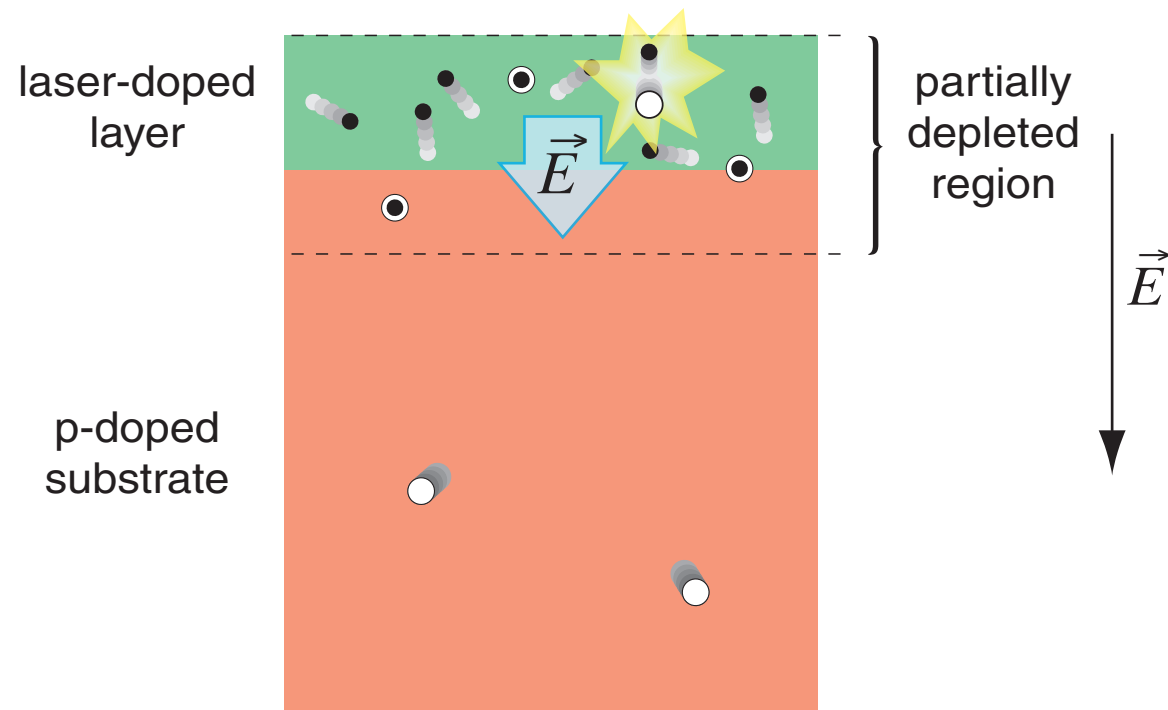
apply backward bias...

# Devices



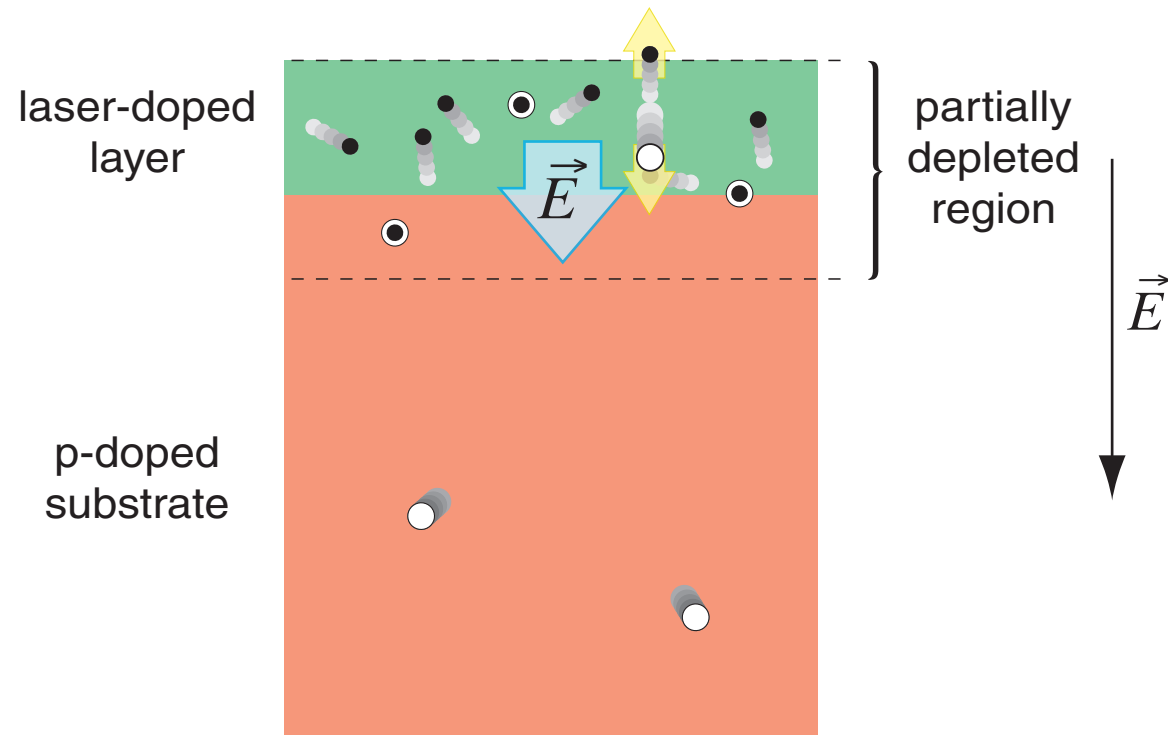
...incident photon generates electron-hole pair...

# Devices



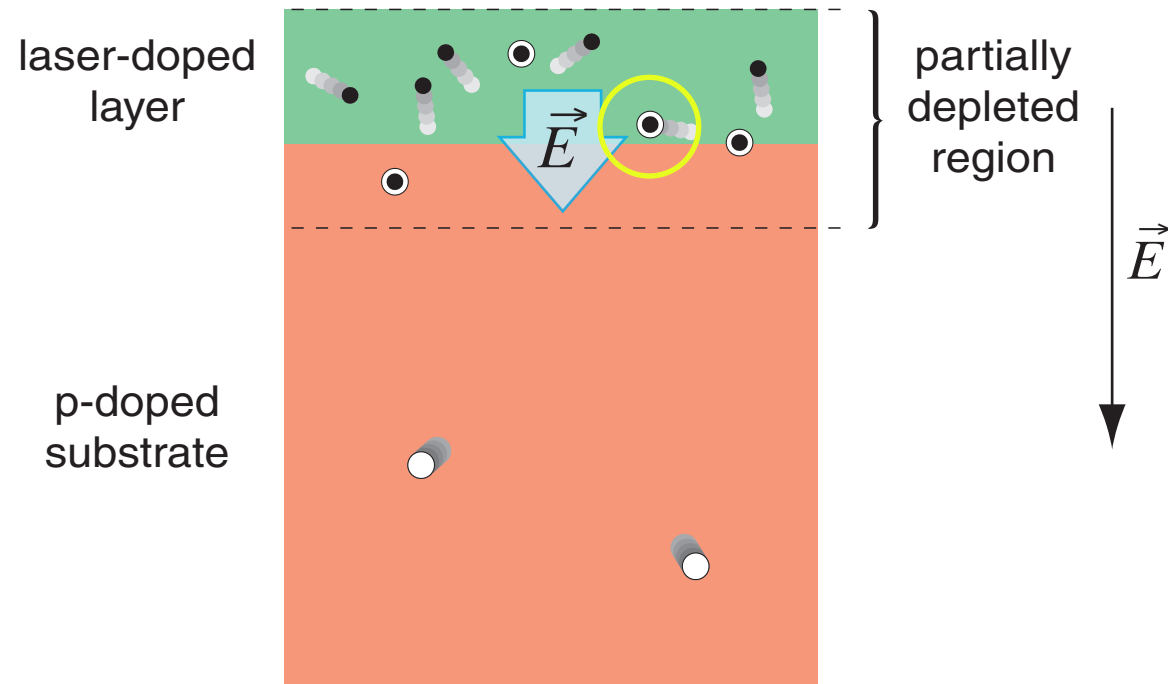
...incident photon generates electron-hole pair...

# Devices



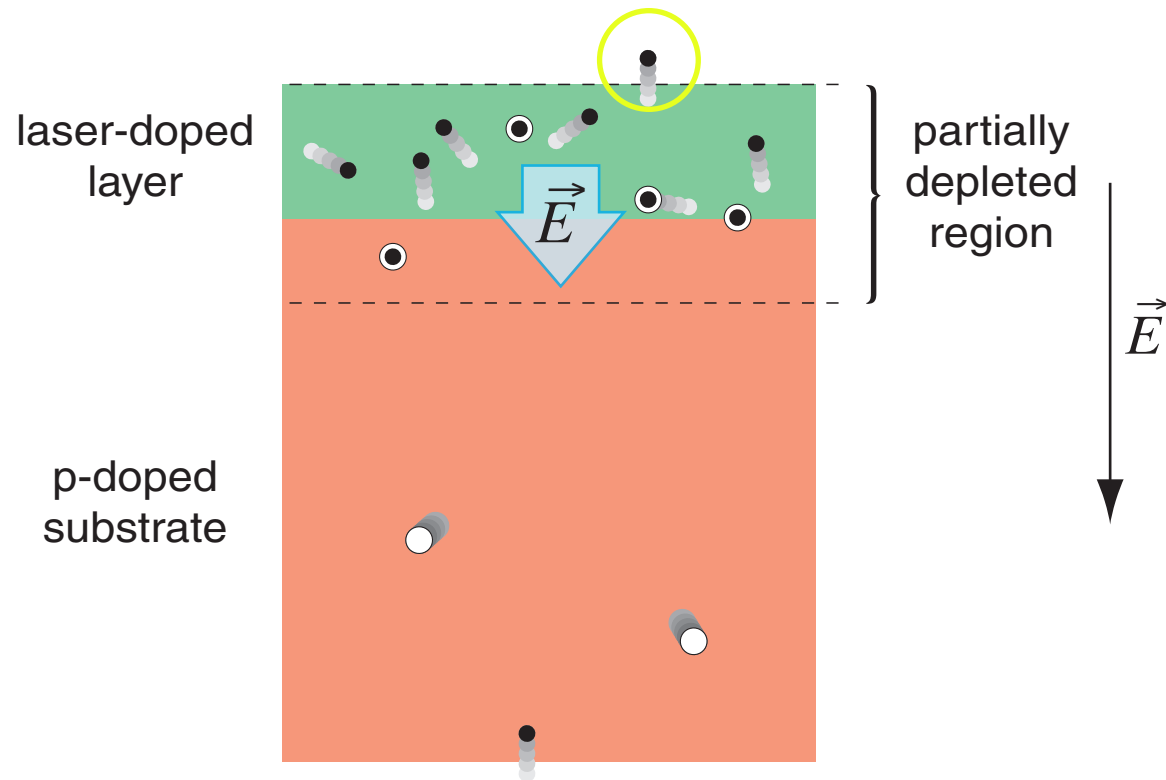
...carriers accelerate away from each other...

# Devices



**...hole is trapped**

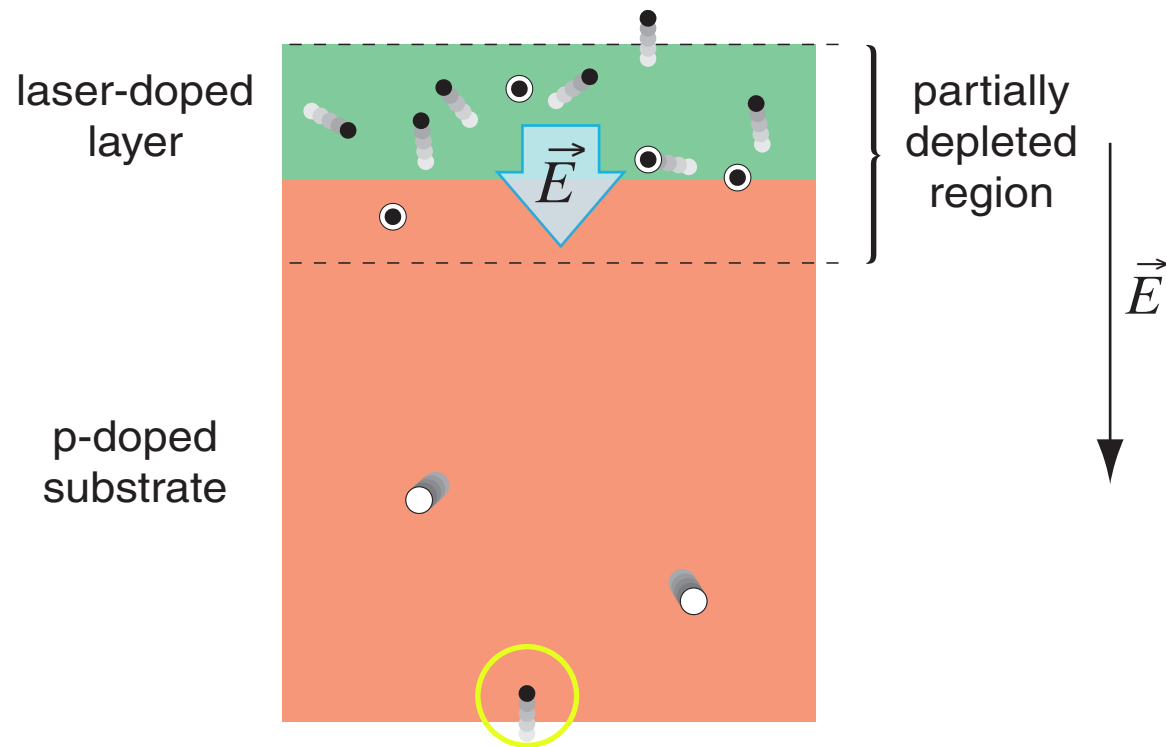
# Devices



meanwhile electron exits sample...



# Devices



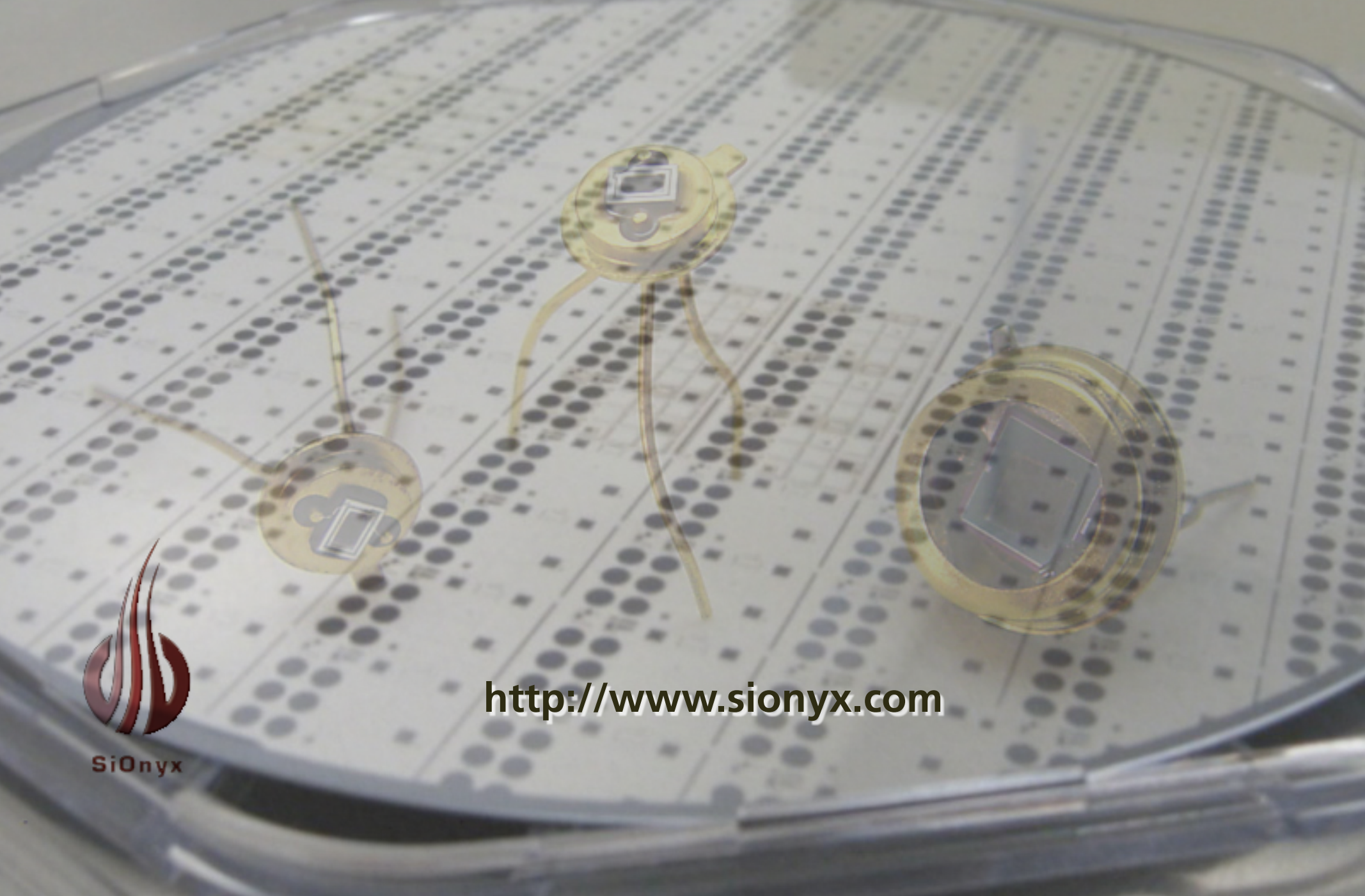
...and source provides new electron

# Devices

## Things to keep in mind

- can turn absorption into carrier generation
- very high responsivity in VIS and IR
- phenomenal photoconductive gain

# Devices



SiOnyx

<http://www.sionyx.com>

# Devices

## Potential benefits for photovoltaics

- surface structure
- absorption in submicrometer layer
- extended IR absorption
- intermediate band

# Conclusion

- **new doping process**
- **new class of material**
- **new types of (silicon-based) devices**

# Conclusion

**What is different about this process?**

A collection of colorful, star-patterned paper scraps is scattered on a white surface. The scraps are in various shades of blue, cyan, and purple, with some featuring small white stars. The scraps are arranged in a somewhat circular pattern, with some overlapping. The background is a plain, light-colored surface.

# Conclusion

**Compare femtosecond laser doping to:**

- **inclusion during growth**
- **thermal diffusion**
- **ion implantation**

**Funding:**

**Army Research Office**

**DARPA**

**Department of Energy**

**NDSEG**

**National Science Foundation**

**for more information and a copy of this presentation:**

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

**Follow me!**



**eric\_mazur**



Google™

Google Search

I'm Feeling Lucky

Google™

mazur

Google Search

I'm Feeling Lucky

# Google™

mazur

Google Search

I'm Feeling Lucky

# Google™

Google Search

I'm Feeling Lucky

**Funding:**

**Army Research Office**

**DARPA**

**Department of Energy**

**NDSEG**

**National Science Foundation**

**for more information and a copy of this presentation:**

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

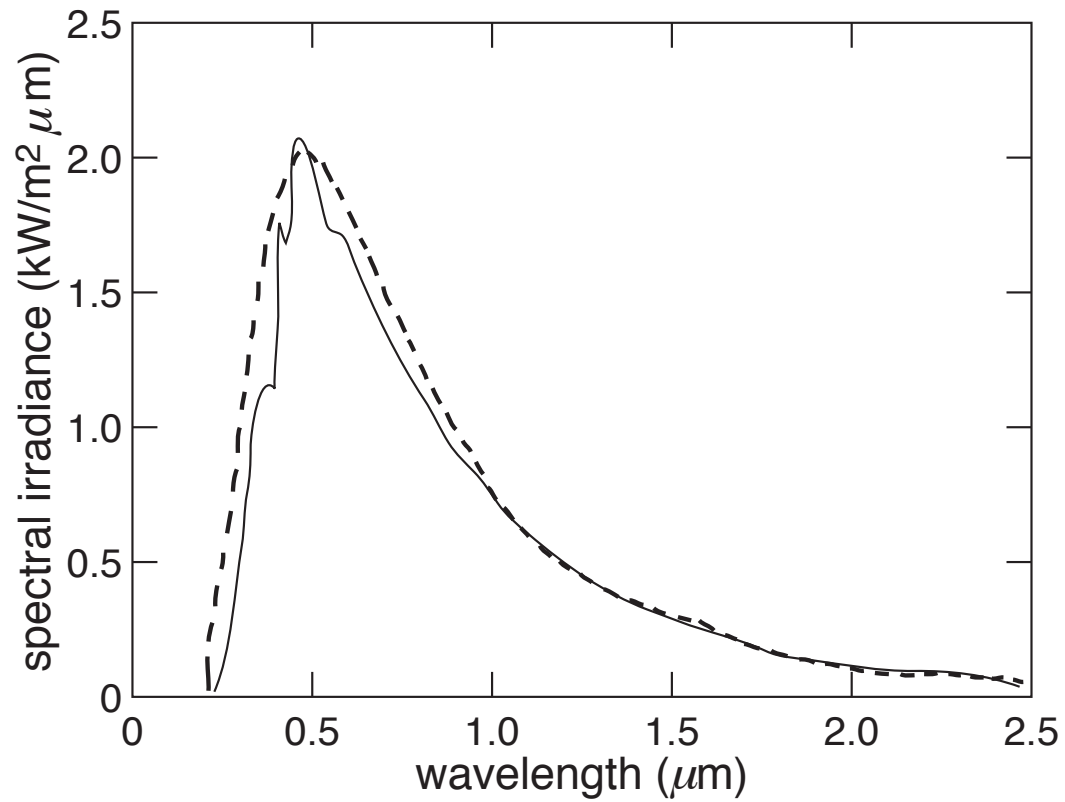
**Follow me!**



**eric\_mazur**

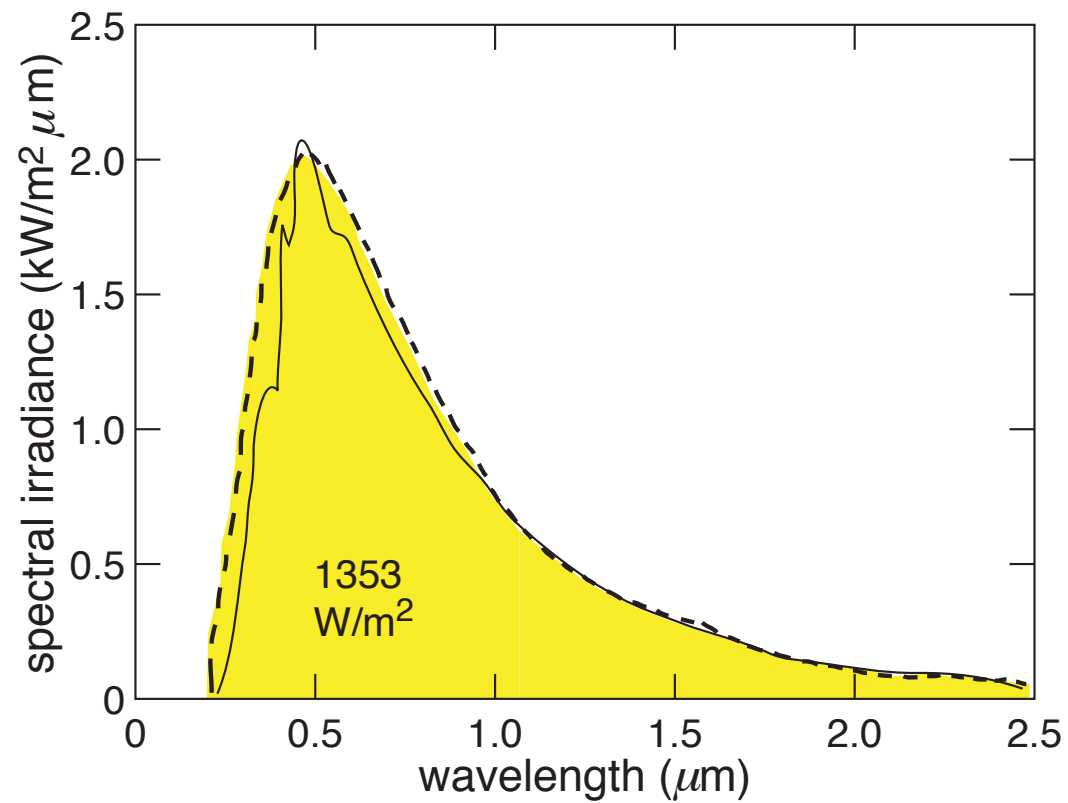
# Devices

## solar spectrum



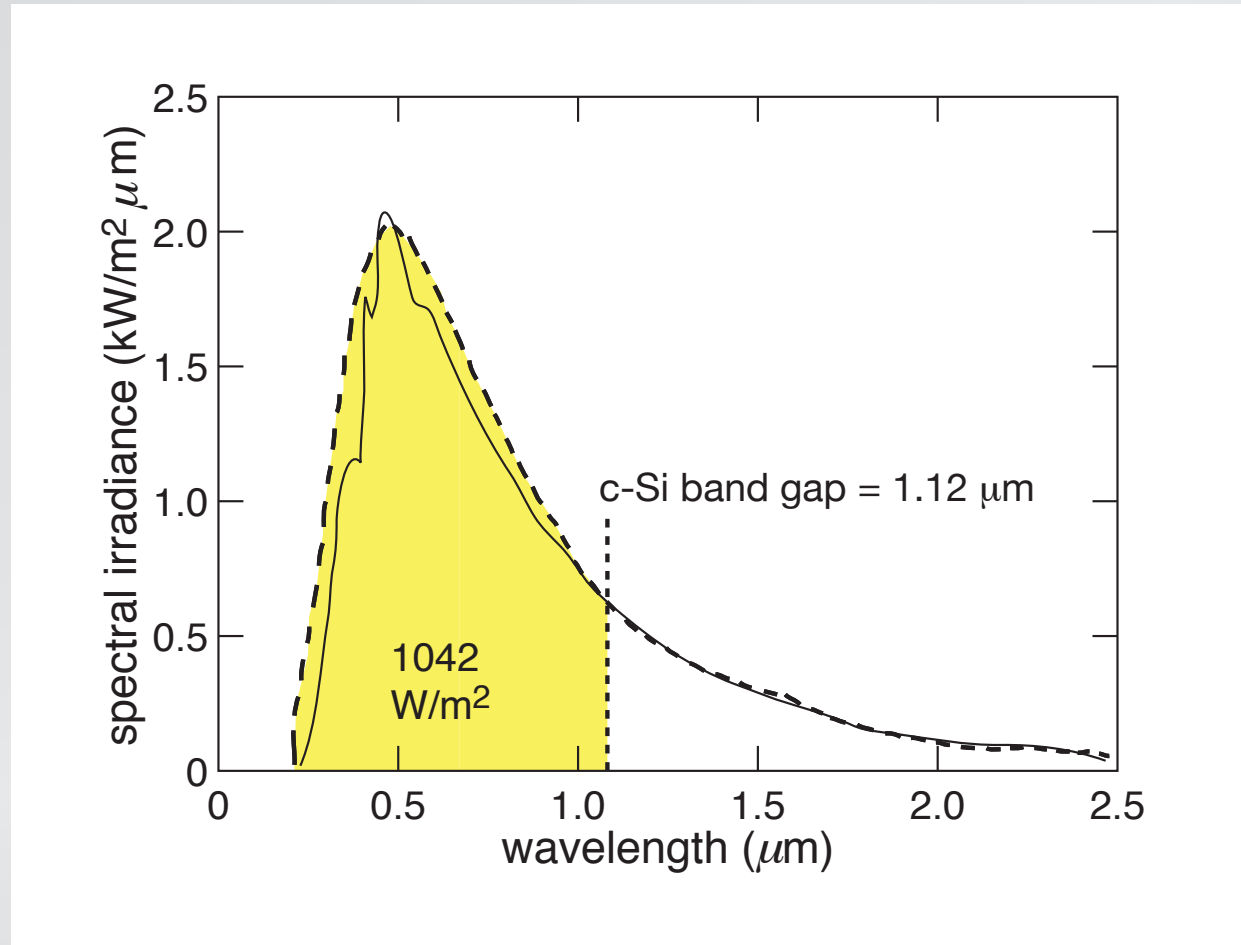
# Devices

## solar spectrum



# Devices

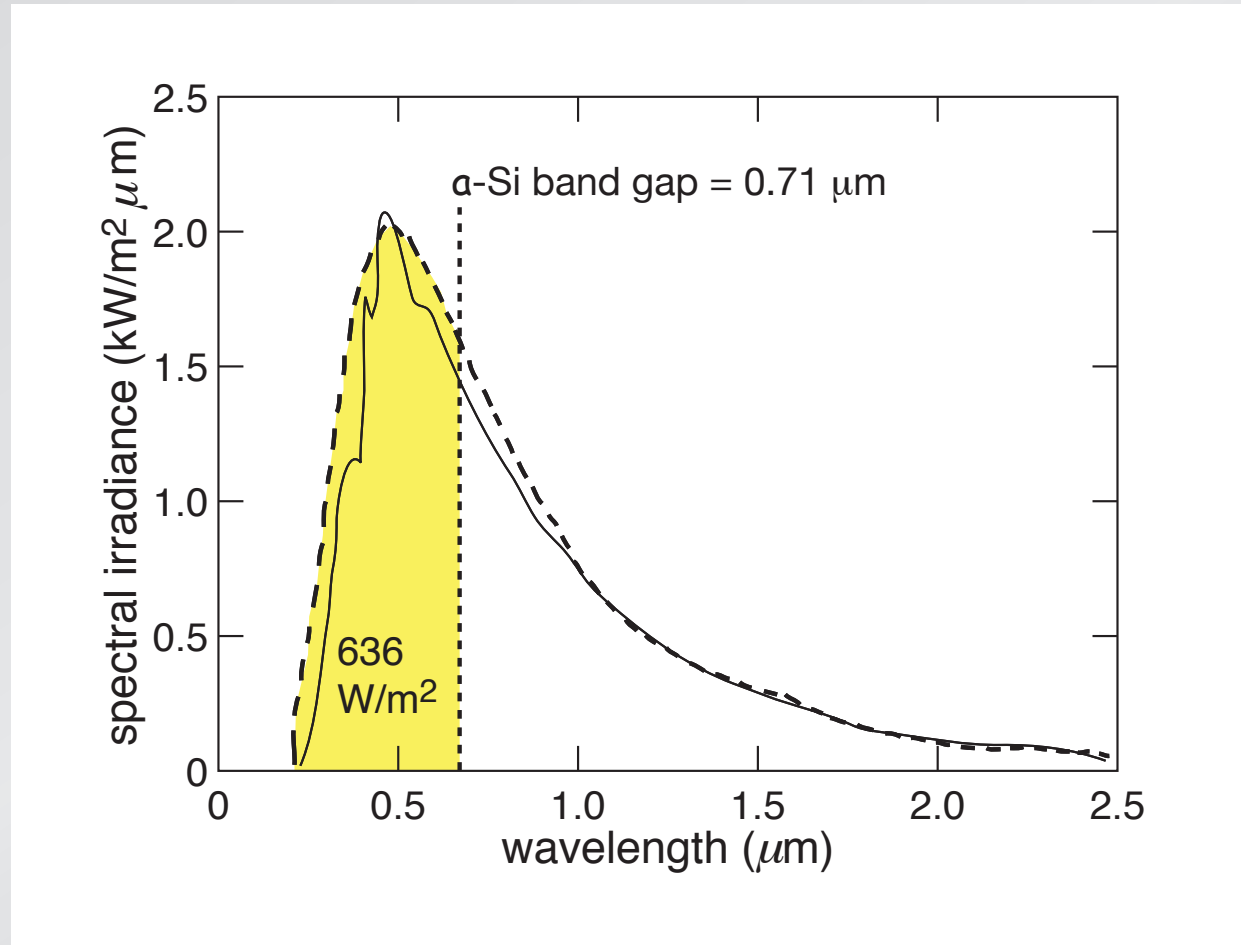
crystalline silicon: transparent to 23% of solar radiation





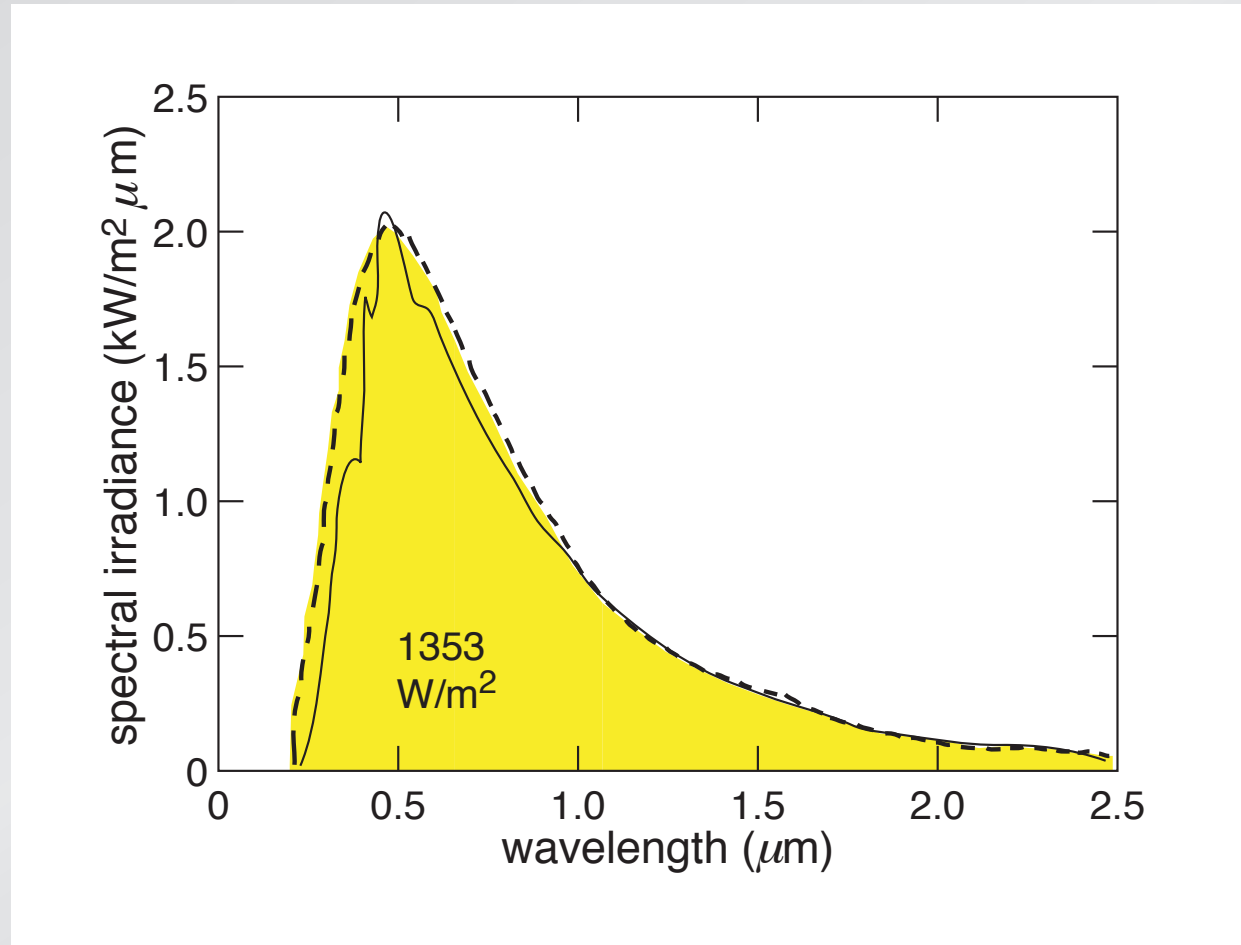
# Devices

amorphous silicon: transparent to 53% of solar radiation



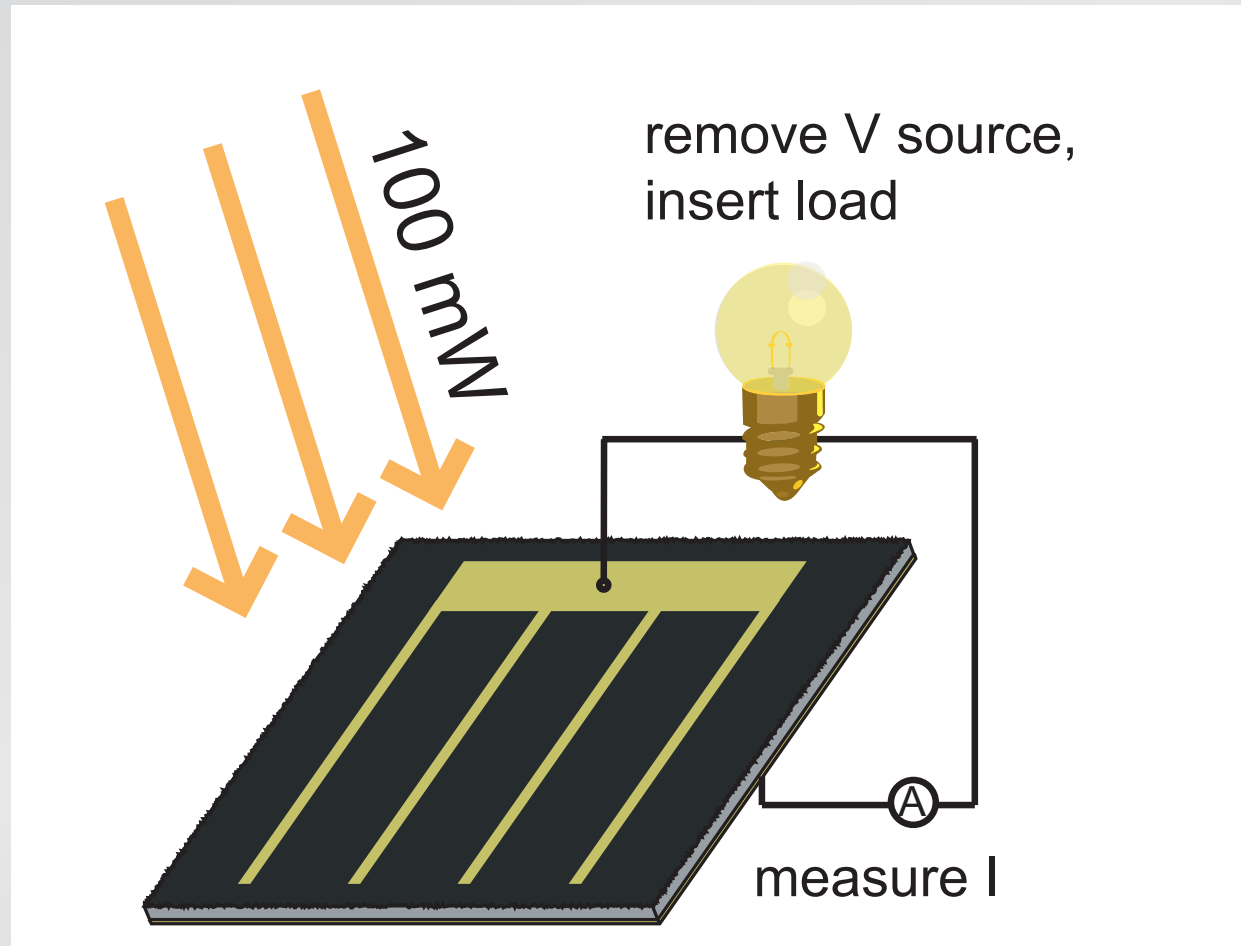
# Devices

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



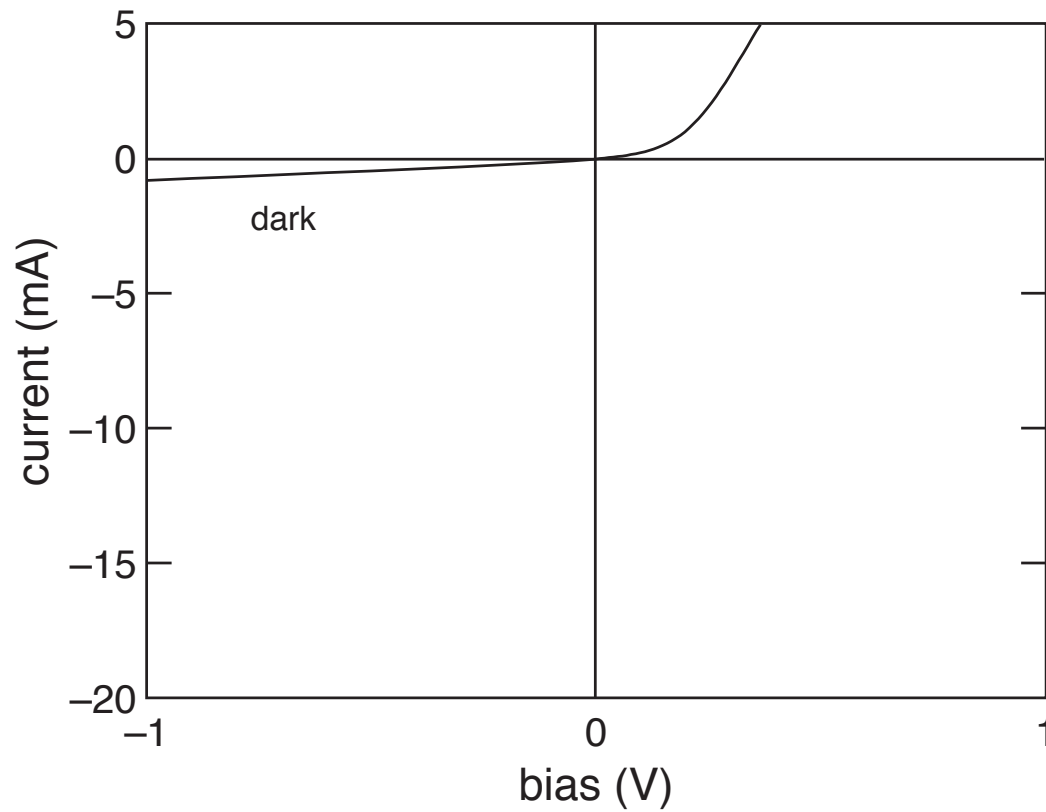
# Devices

very preliminary photovoltaic cell



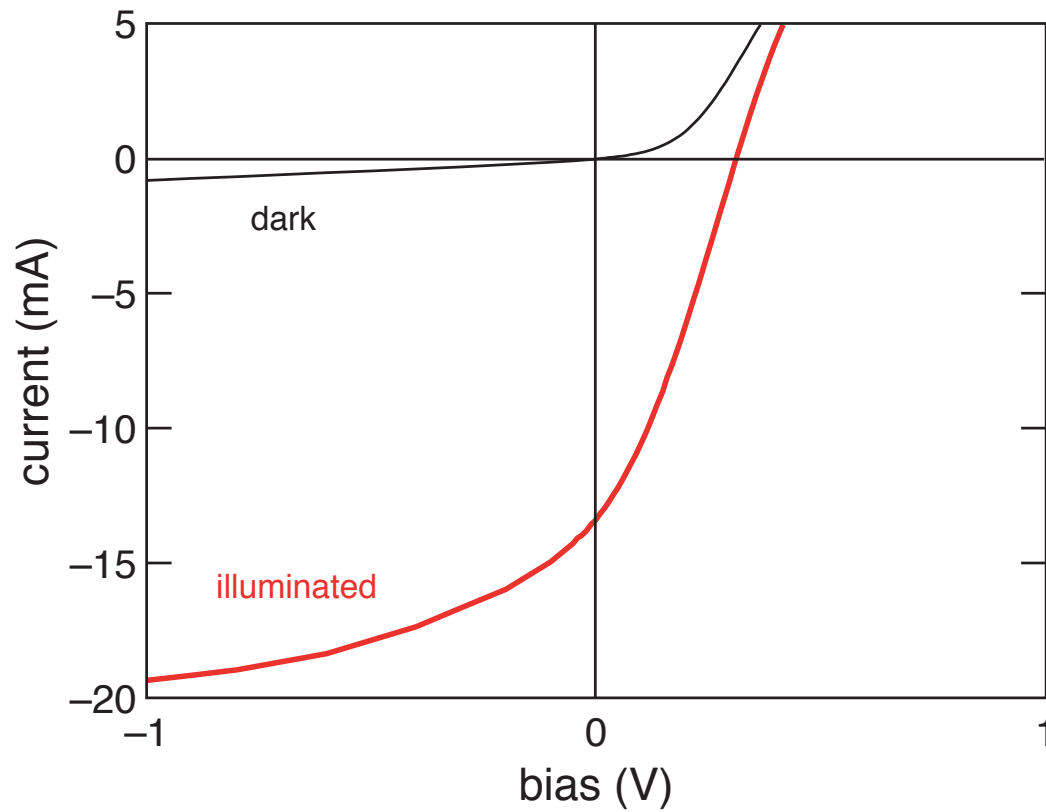
# Devices

very preliminary photovoltaic cell



# Devices

very preliminary photovoltaic cell



# Devices

**1.5% efficiency, a good beginning**

