

# Black silicon: Engineering an intermediate band in silicon for sensing and energy harvesting



Nanophotonics and Plasmonic Technologies Workshop  
Harvard University  
Cambridge, MA, 7 May 2010

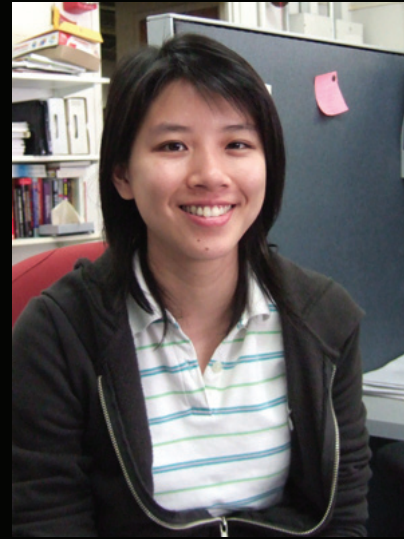




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**Yu-Ting Lin**



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William Whitney  
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Dr. Jim Carey  
Prof. Tsing-Hua Her  
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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  
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Prof. Howard Stone**

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Prof. Silvija Gradecak (MIT)  
Dr. Bonna Newman (MIT)  
Joe Sullivan (MIT)  
Matthew Smith (MIT)**

**Prof. Augustinus Asenbaum (Vienna)**

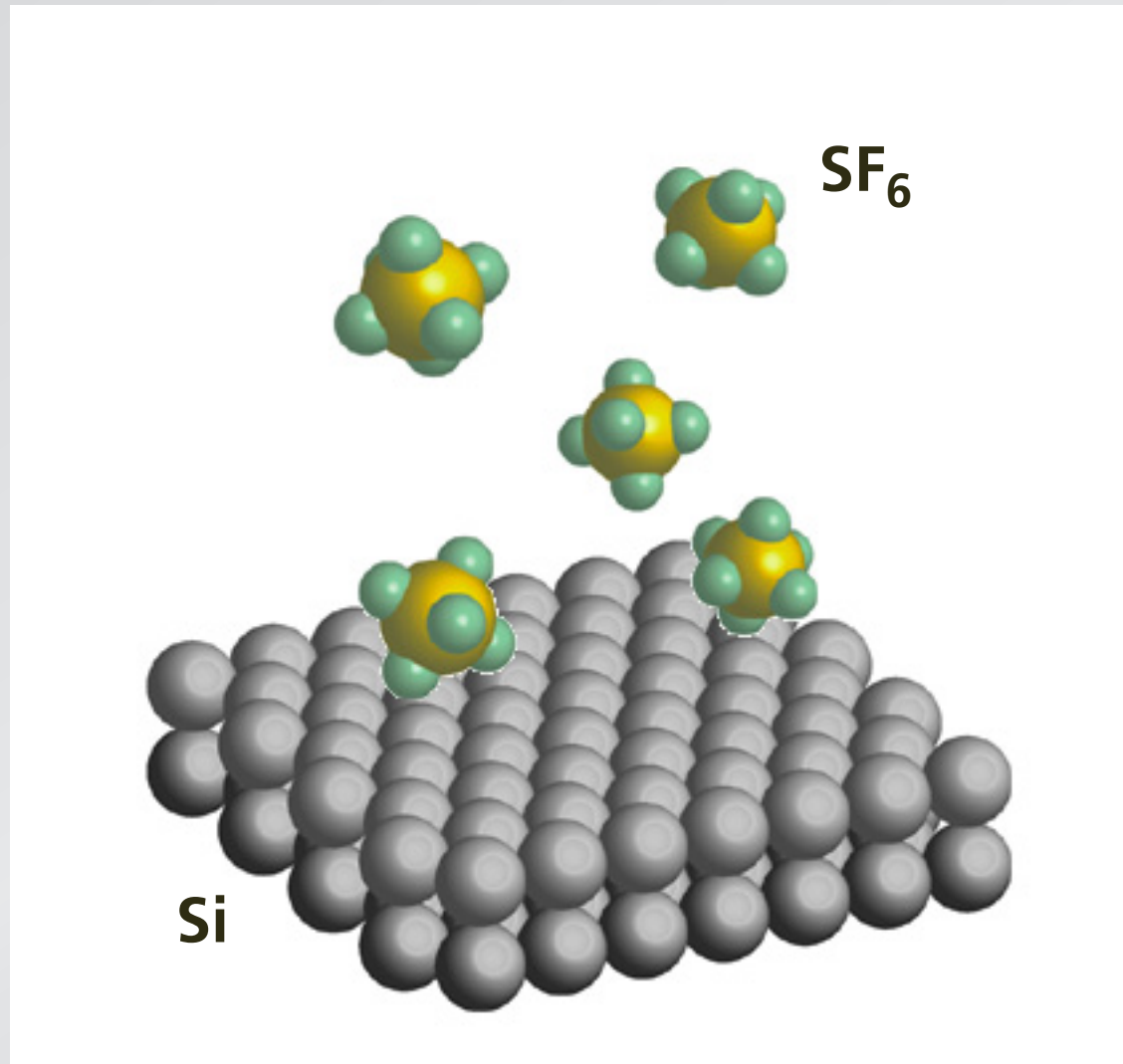
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Mark Wall (LLNL)**

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

**Dr. Pat Maloney (NVSED)**

**Dr. Jeffrey Warrander (ARDEC)**

# Introduction



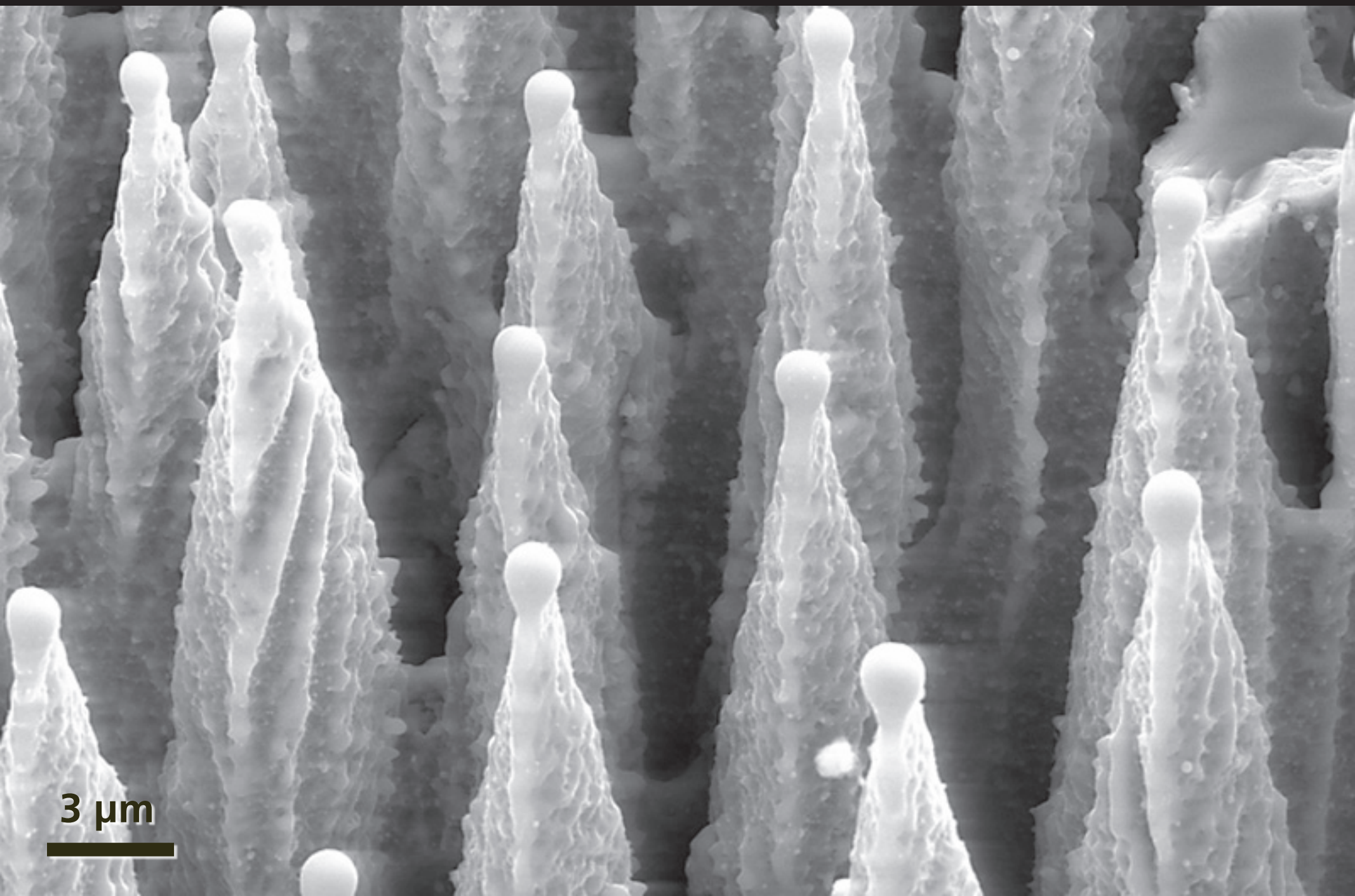
irradiate with 100-fs 10 kJ/m<sup>2</sup> pulses

# Introduction



**"black silicon"**

# Introduction



# Introduction

**Since first publication (1998):**

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- **optoelectronic properties (2001)**



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- **(super)hydrophobic properties (2006)**

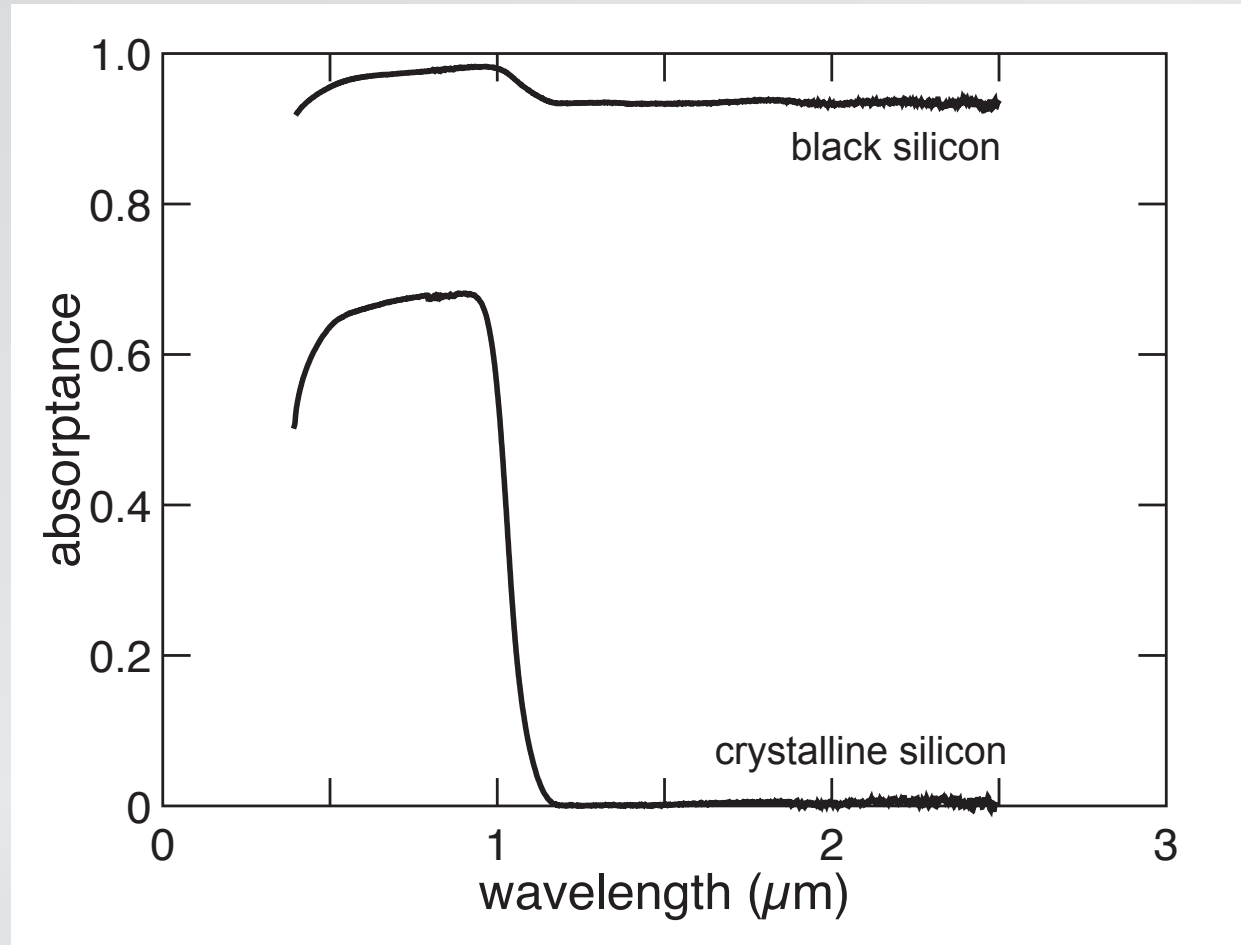
# Introduction

**Since first publication (1998):**

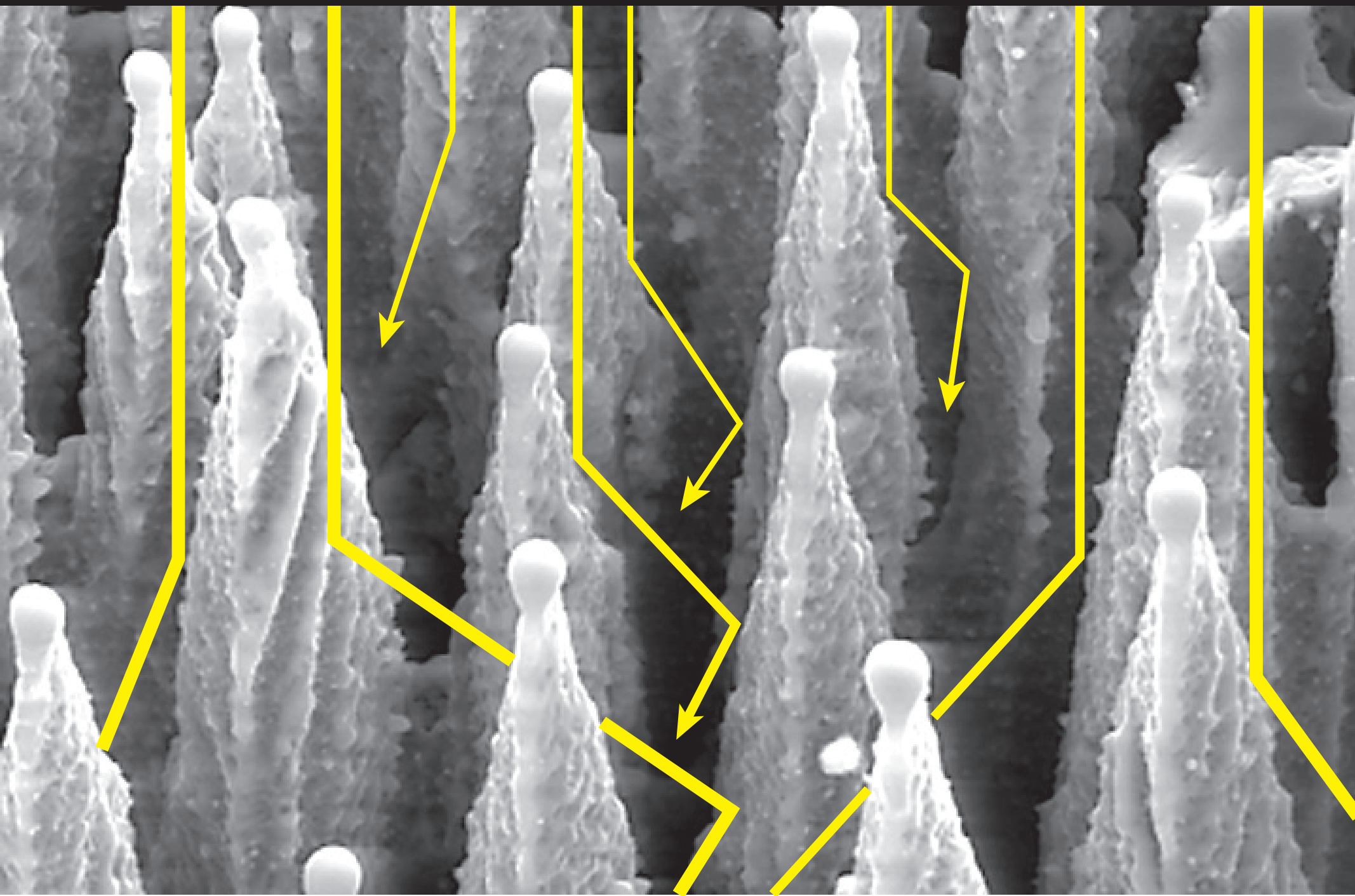
- **optoelectronic properties (2001)**
- **field emission (2001)**
- **structuring of metals and other materials (2001)**
- **(super)hydrophobic properties (2006)**
- **field enhancement properties (2009)**

# Introduction

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

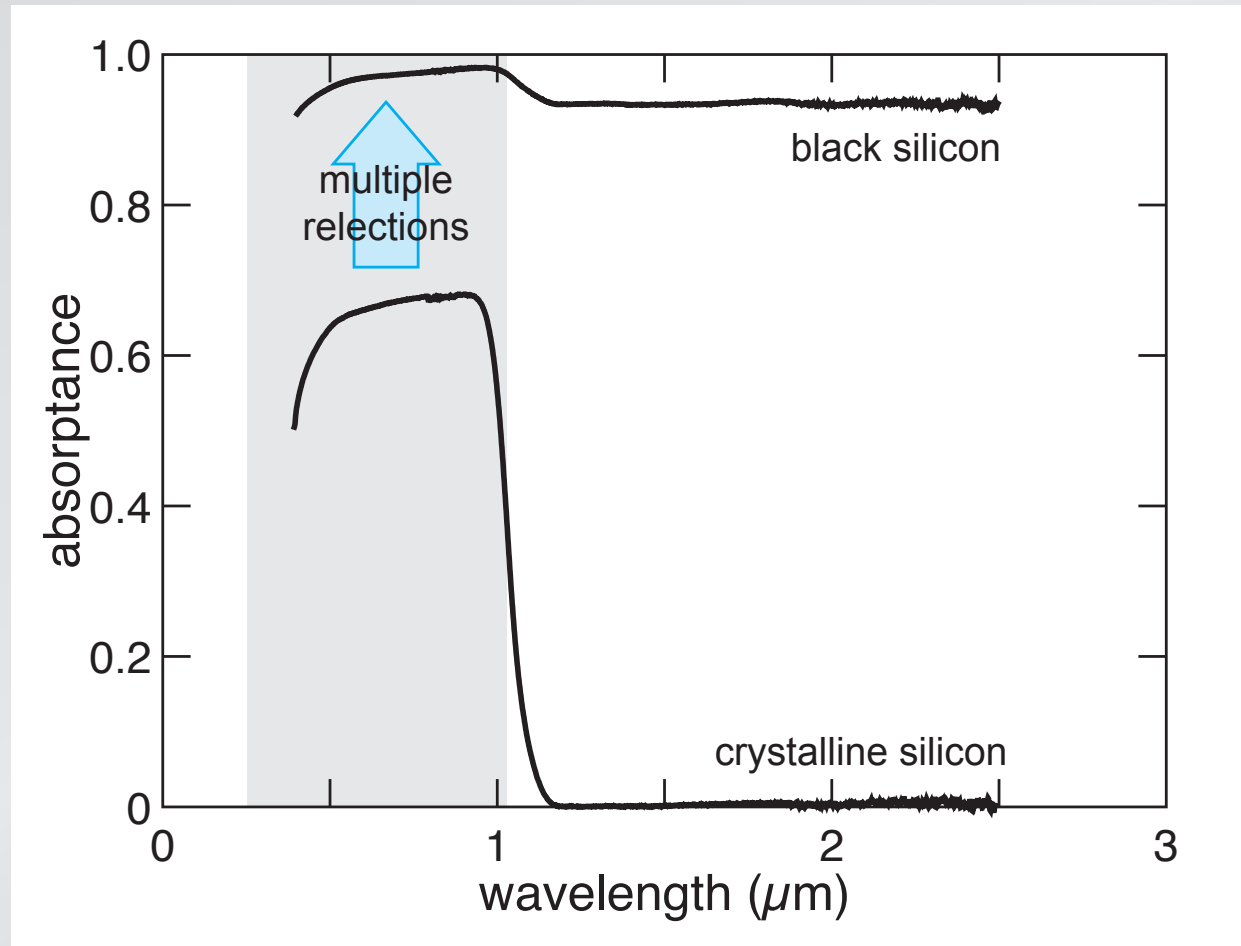


# Introduction



# 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  
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responsivity  
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gap  
impurity band  
transitions

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

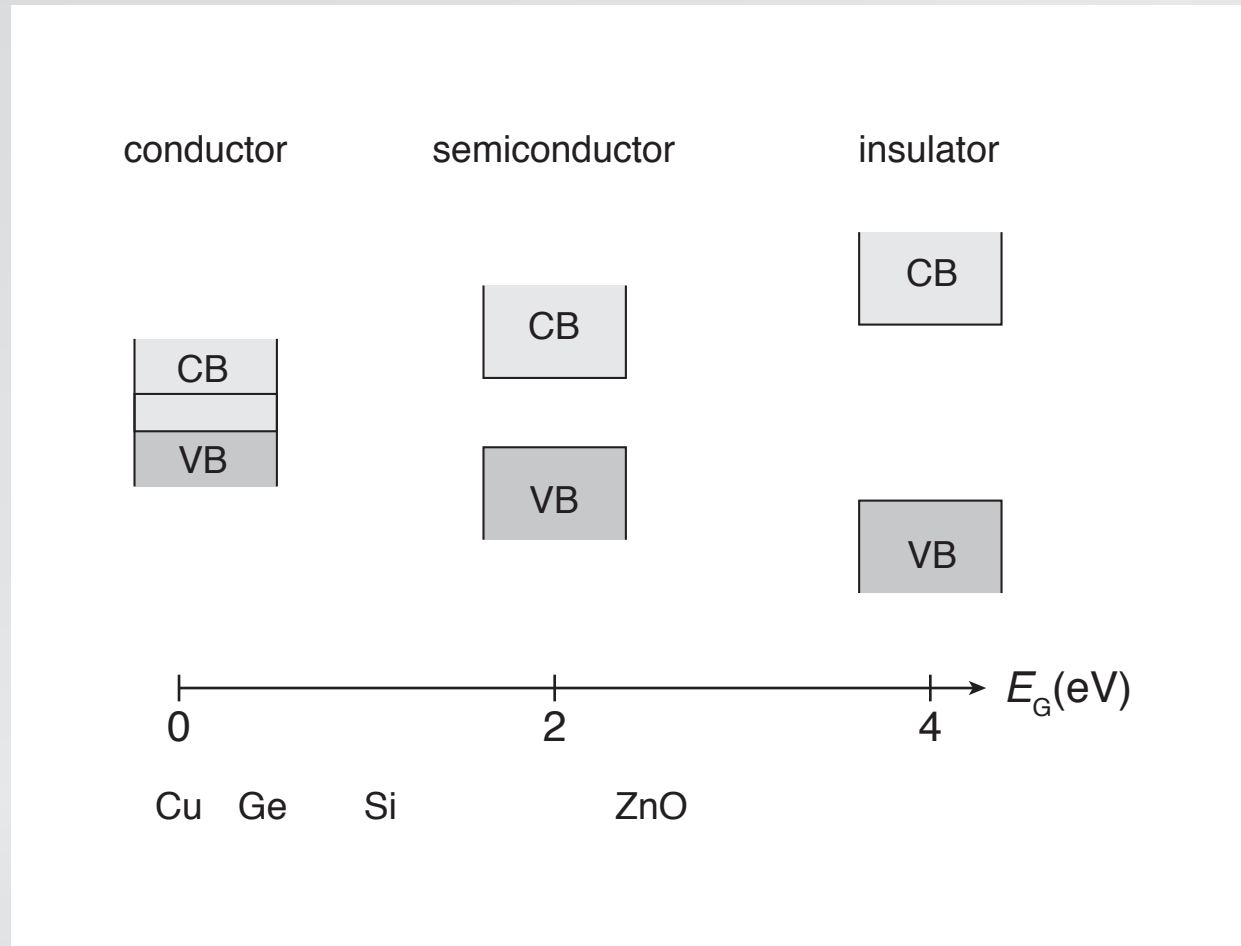
# Introduction

## a decade of research

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

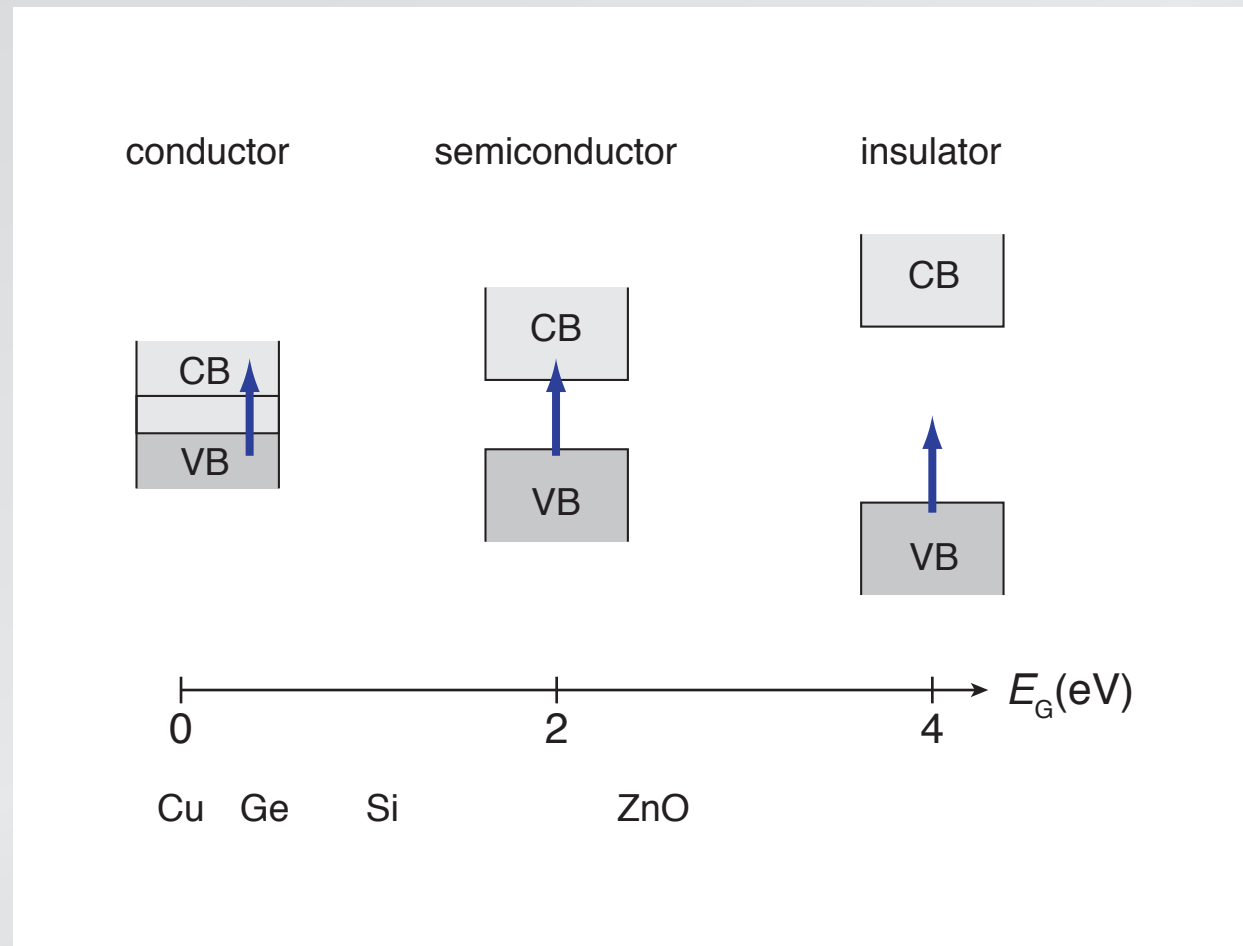
# Introduction

new process & new class of material!



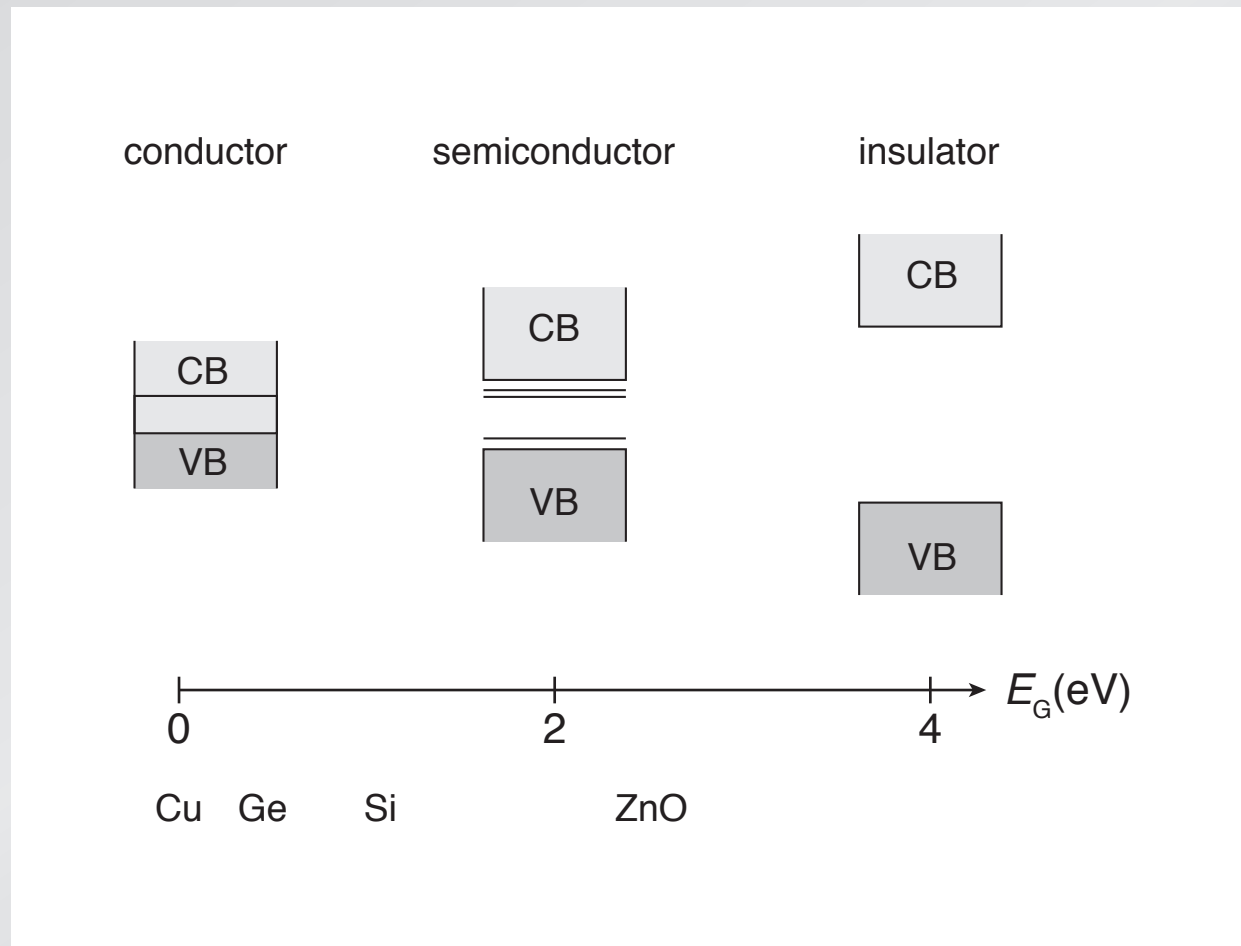
# Introduction

gap determines optical and electronic properties



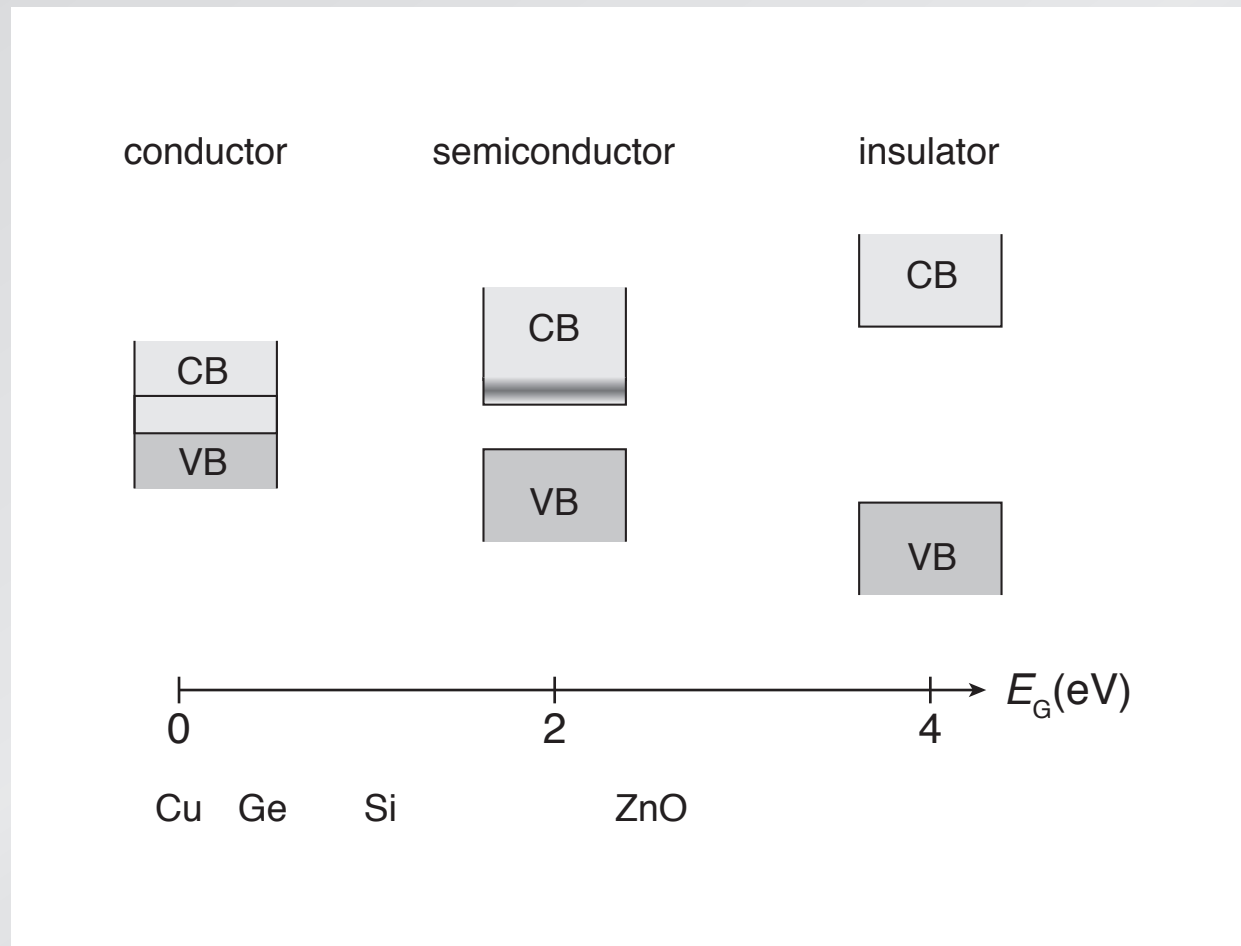
# Introduction

shallow-level dopants control electronic properties



# Introduction

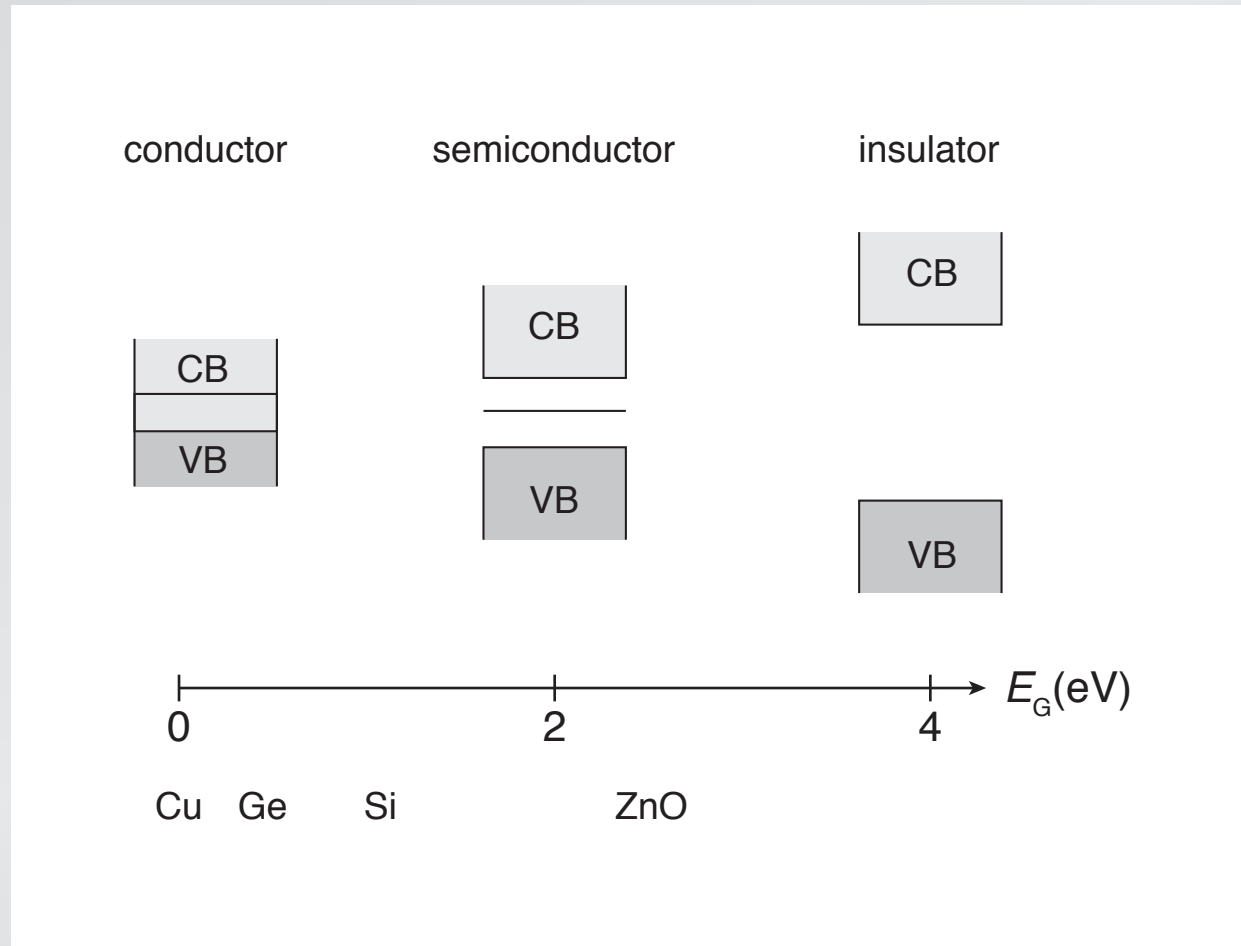
shallow-level dopants control electronic properties





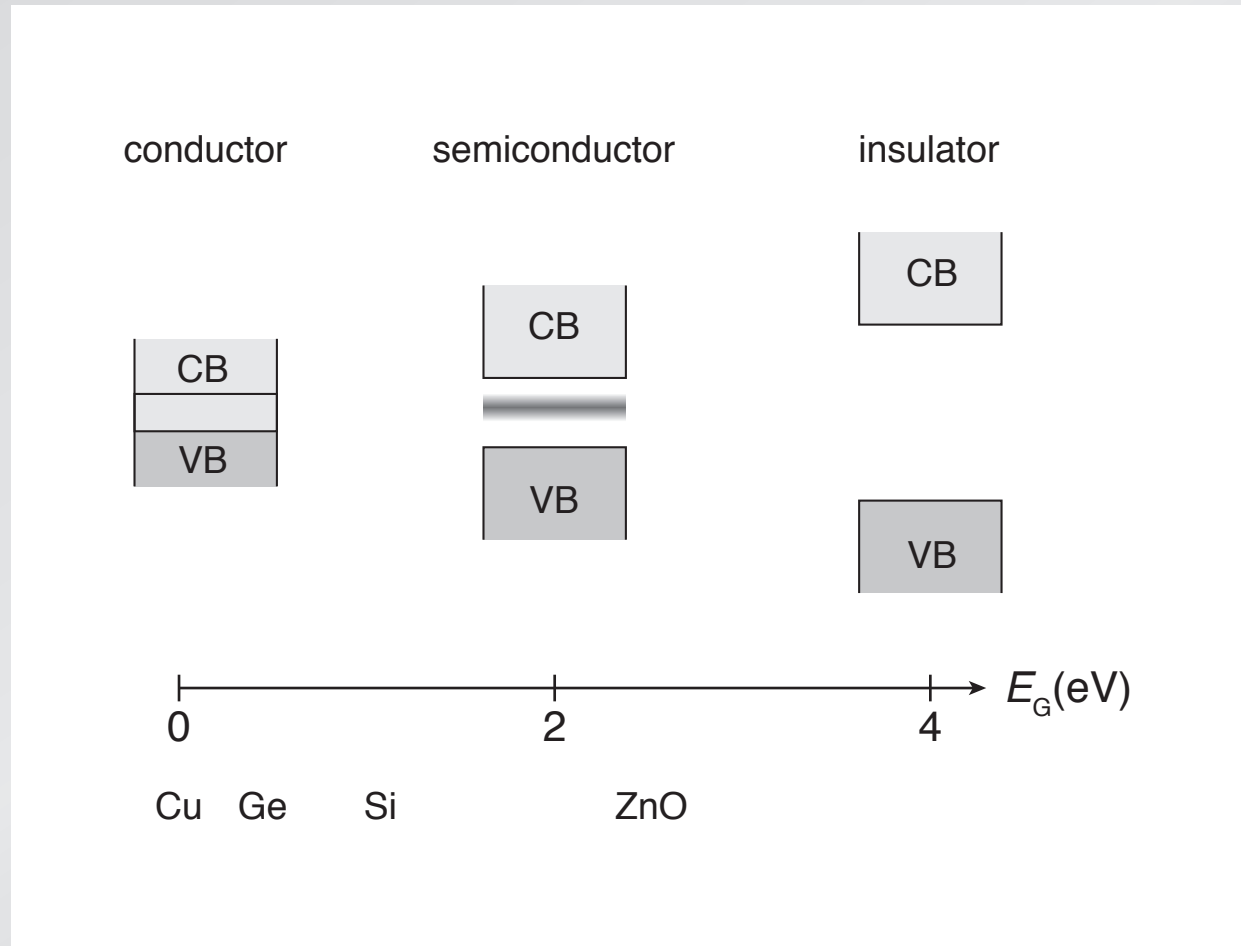
# Introduction

deep-level dopants typically avoided



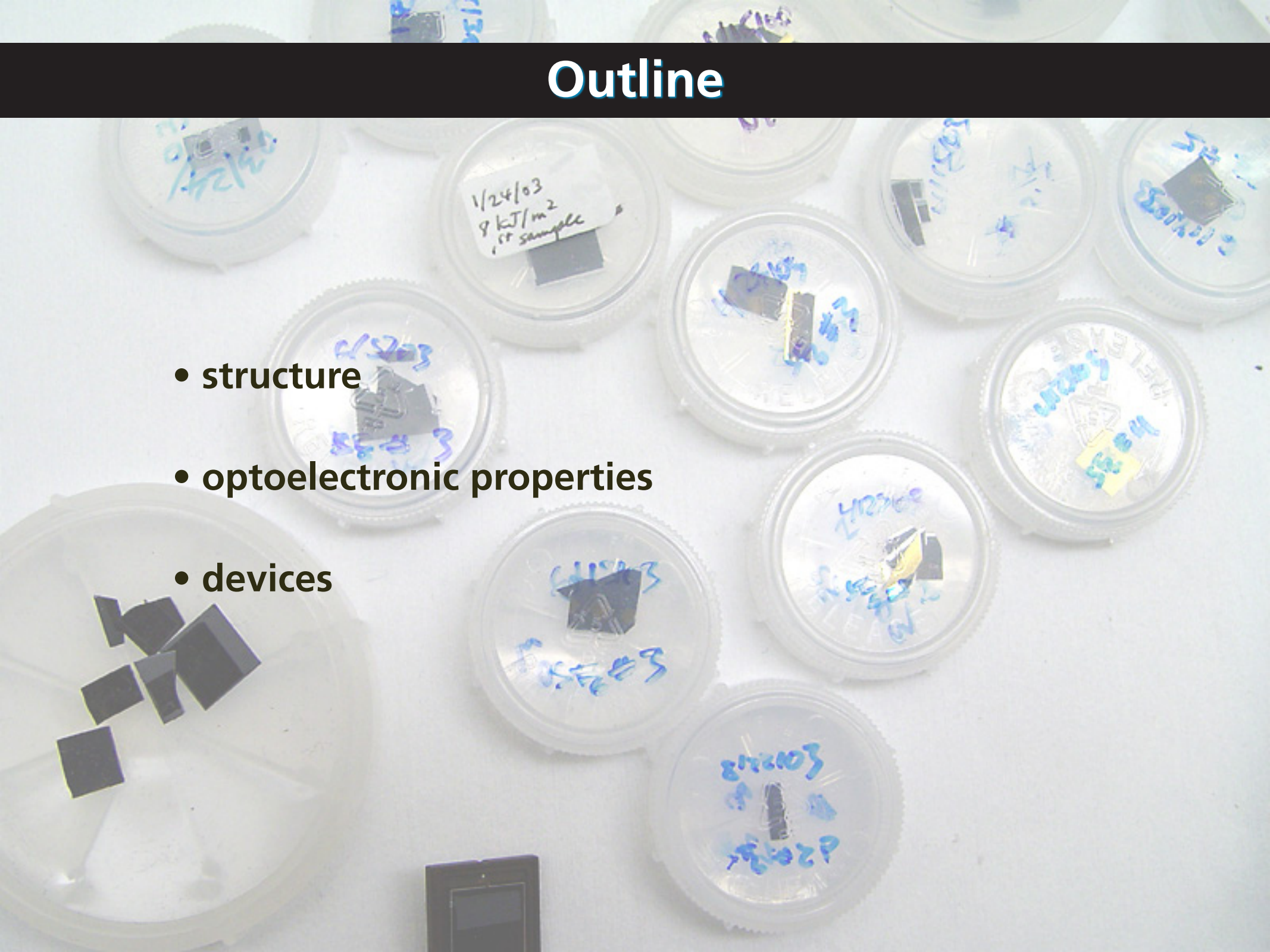
# Introduction

femtosecond laser-doping gives rise to intermediate band

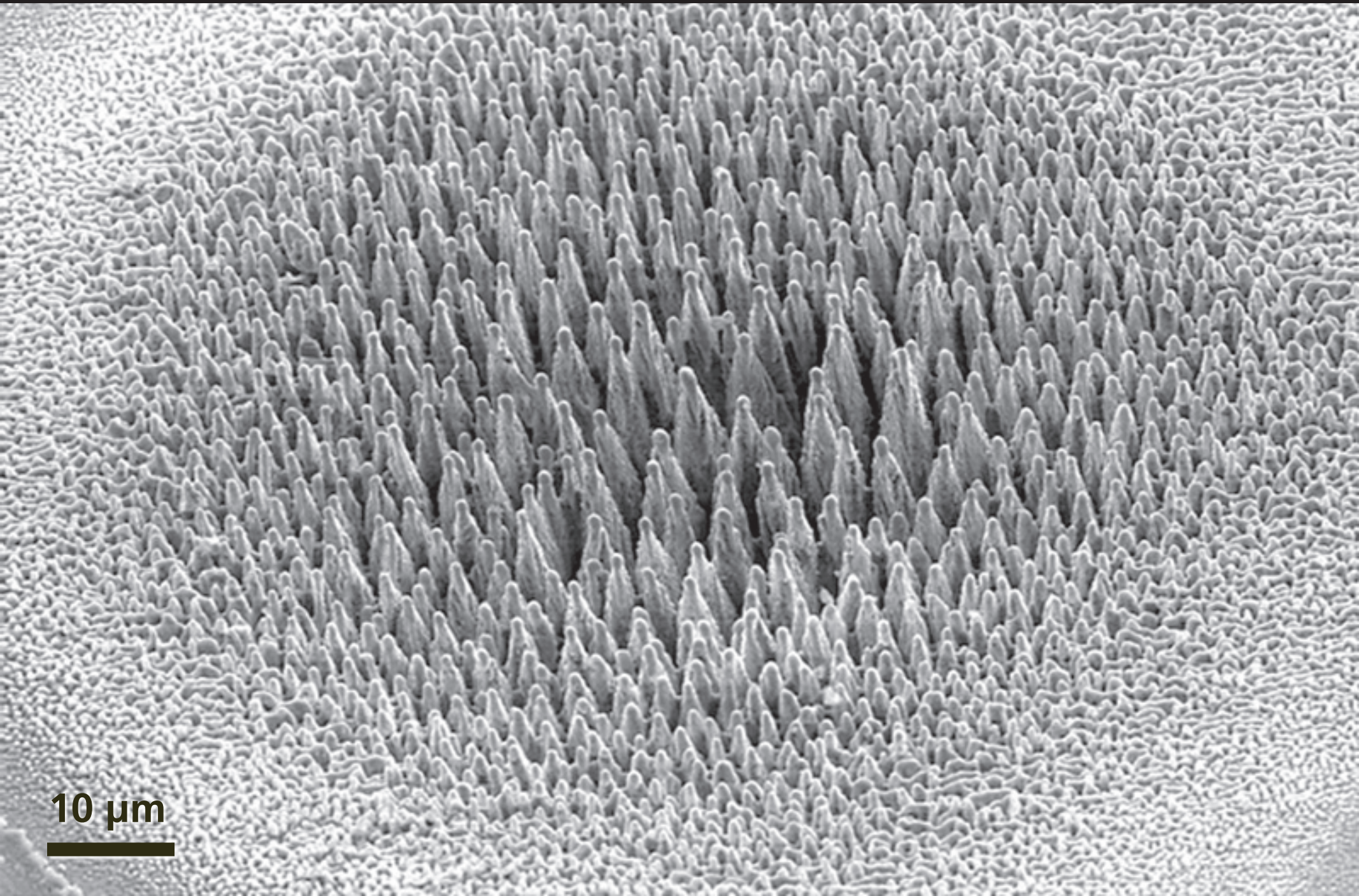


# Outline

- structure
- optoelectronic properties
- devices



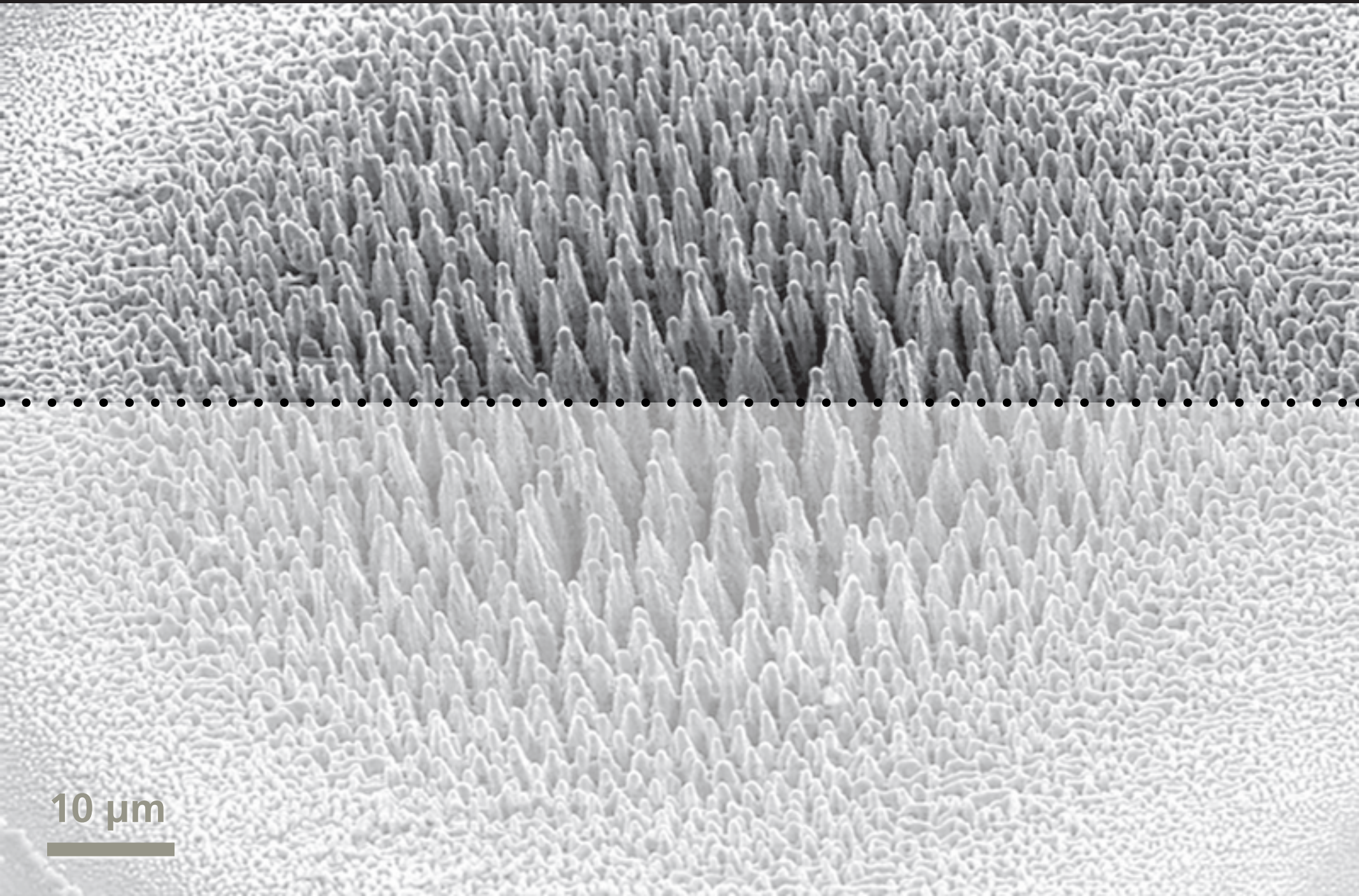
# Structure



10  $\mu\text{m}$

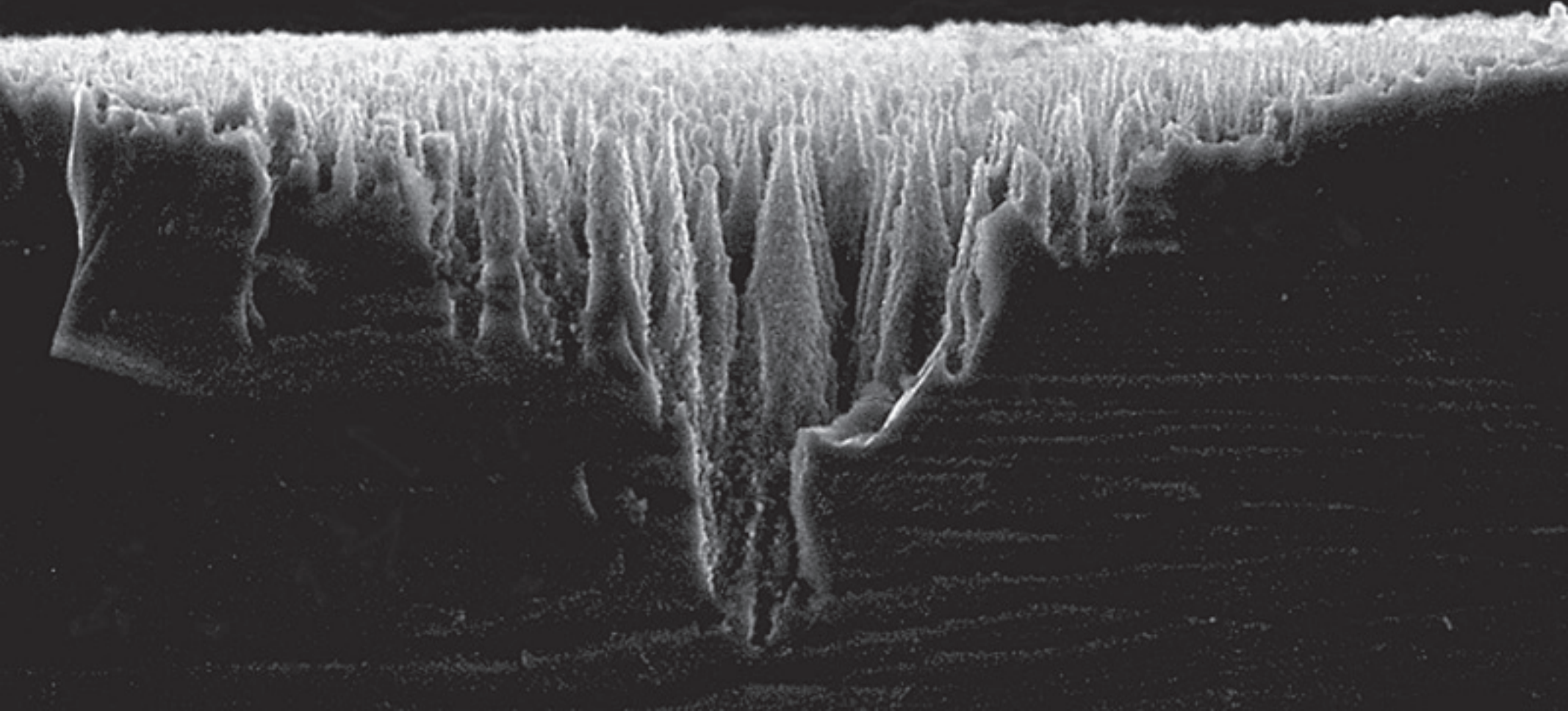


# Structure

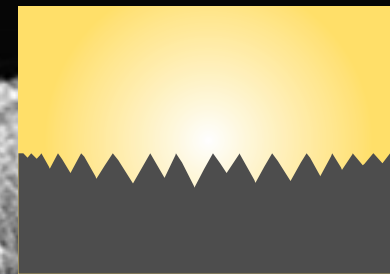
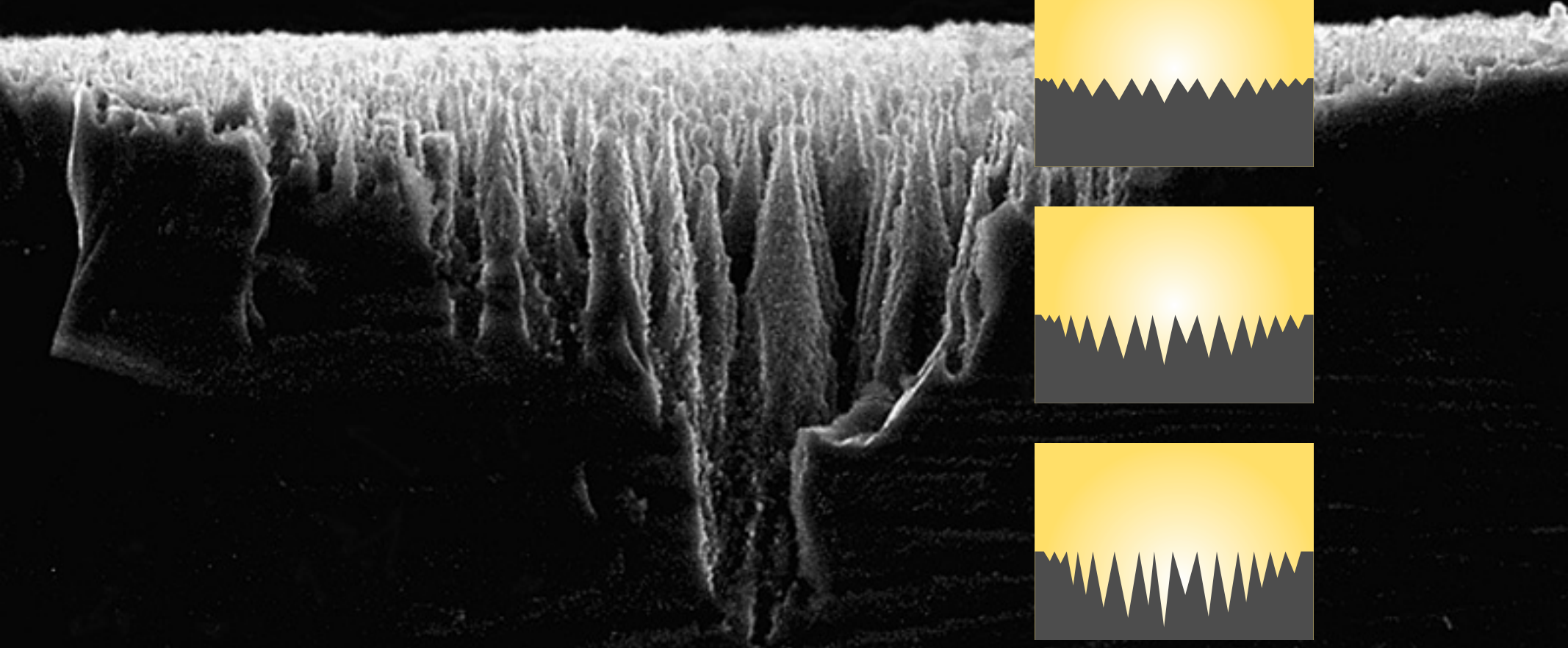


10 μm

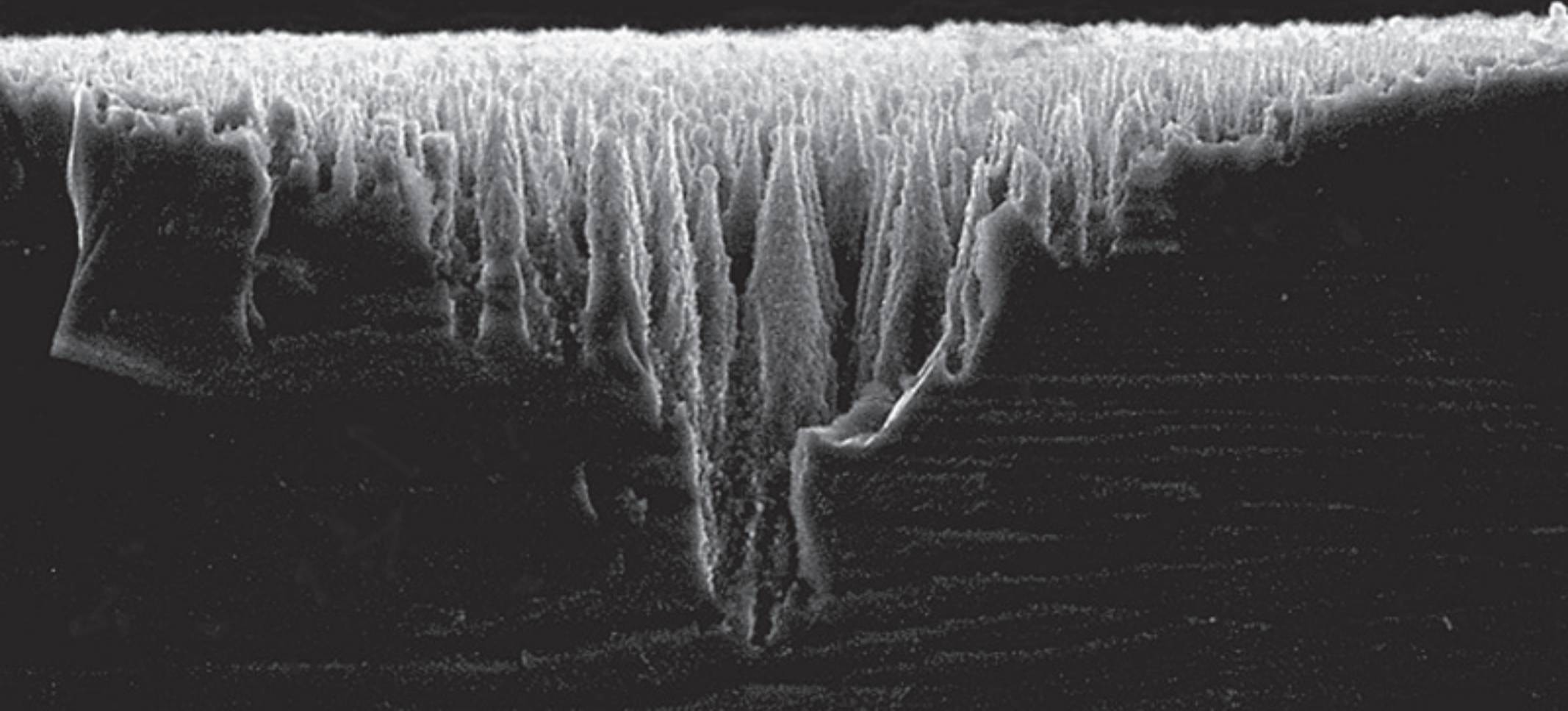
# Structure



# Structure

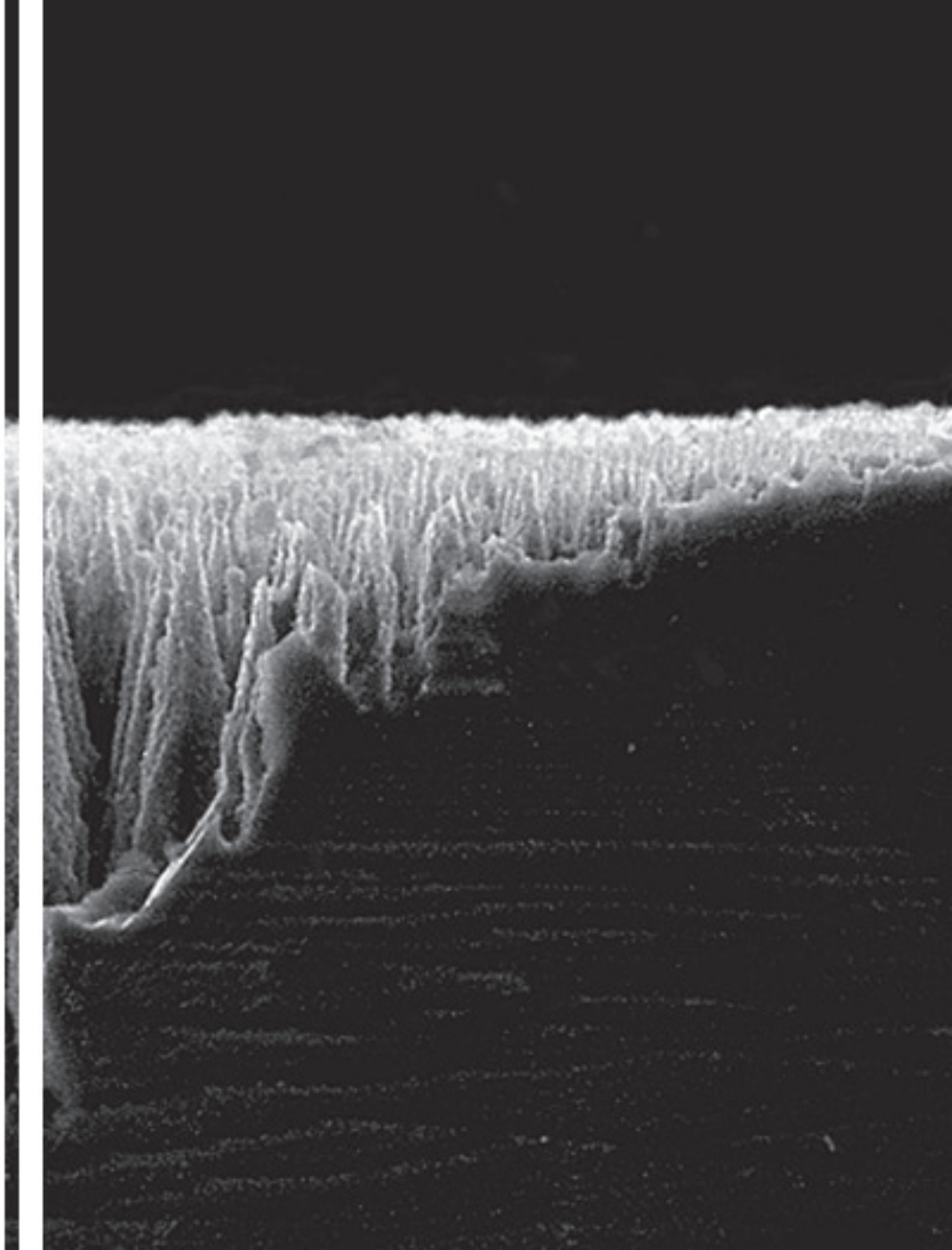
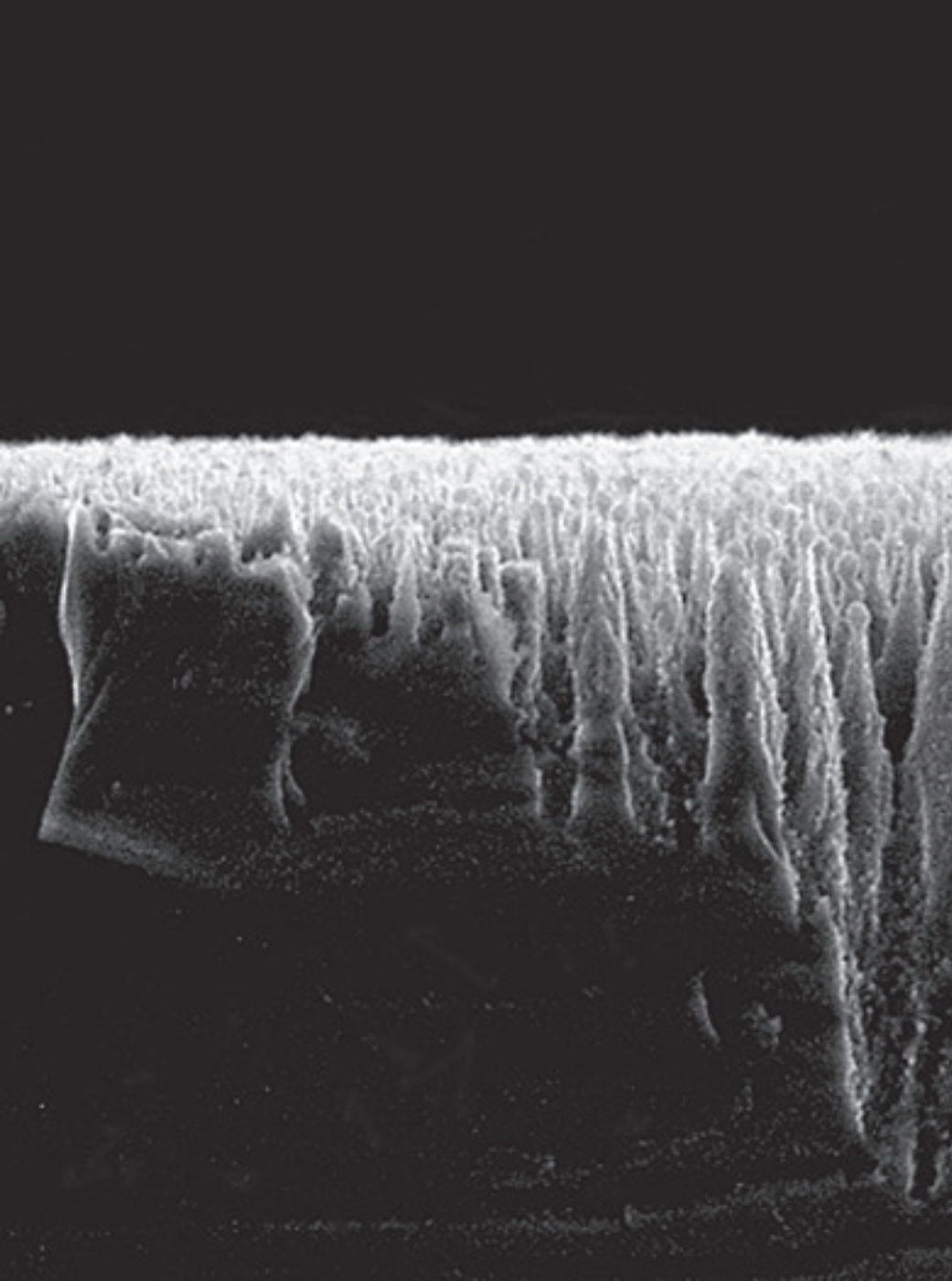


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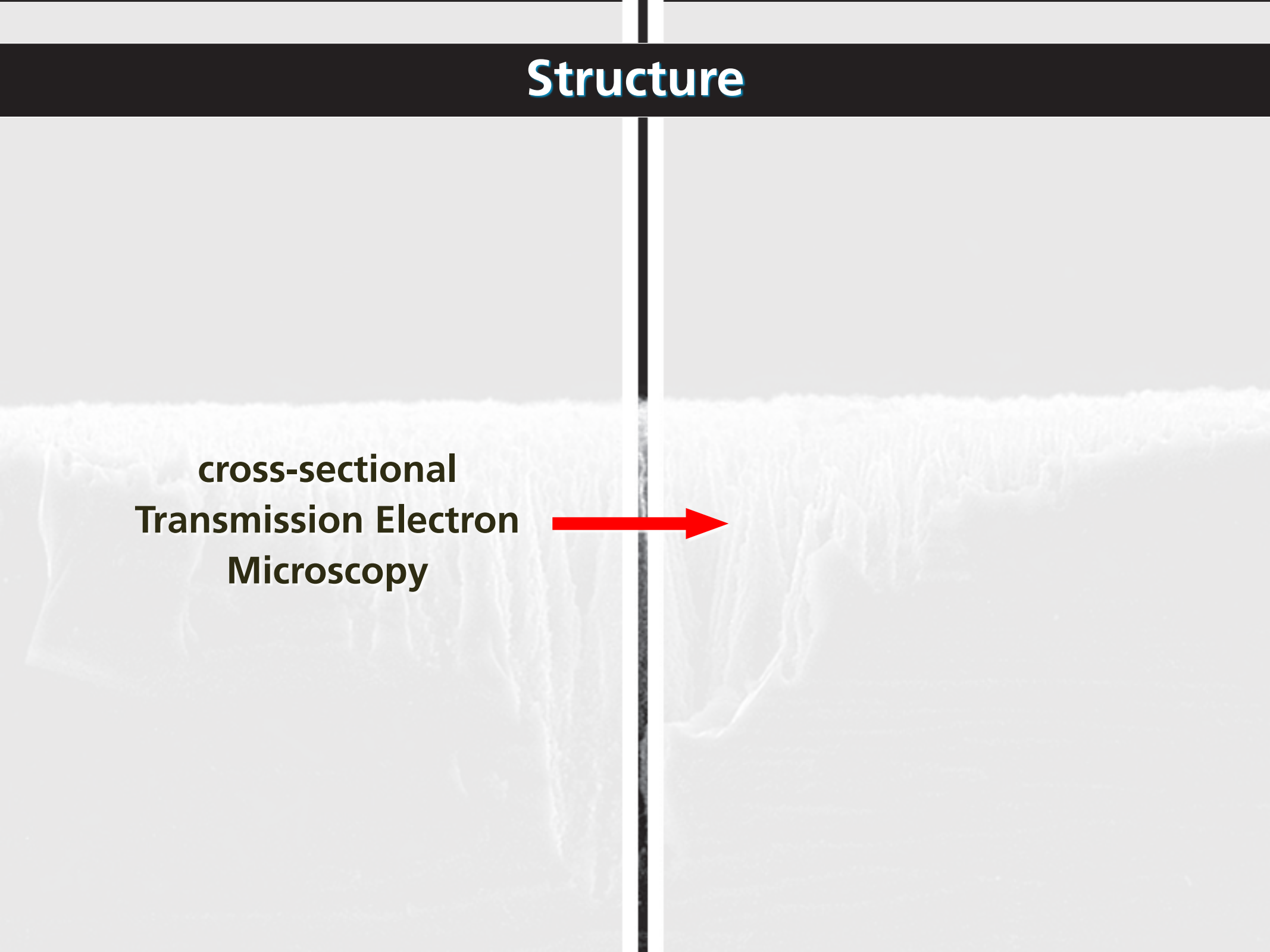


# Structure



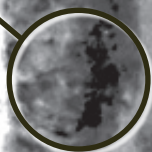
# Structure

**cross-sectional  
Transmission Electron  
Microscopy**



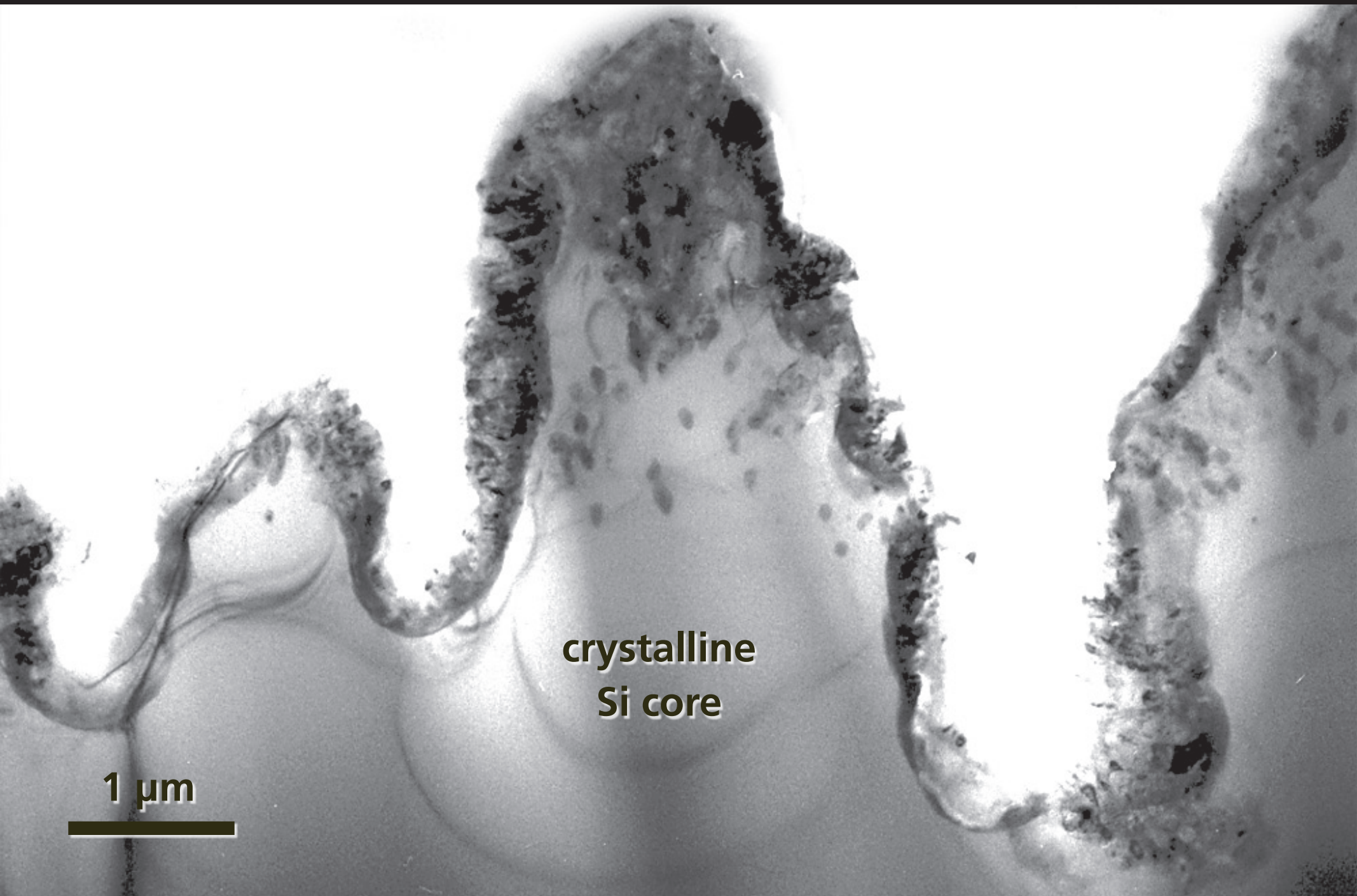
# Structure

disordered  
surface layer



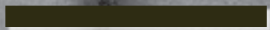
1  $\mu\text{m}$

# Structure



crystalline  
Si core

1  $\mu\text{m}$



# Structure

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

1  $\mu\text{m}$

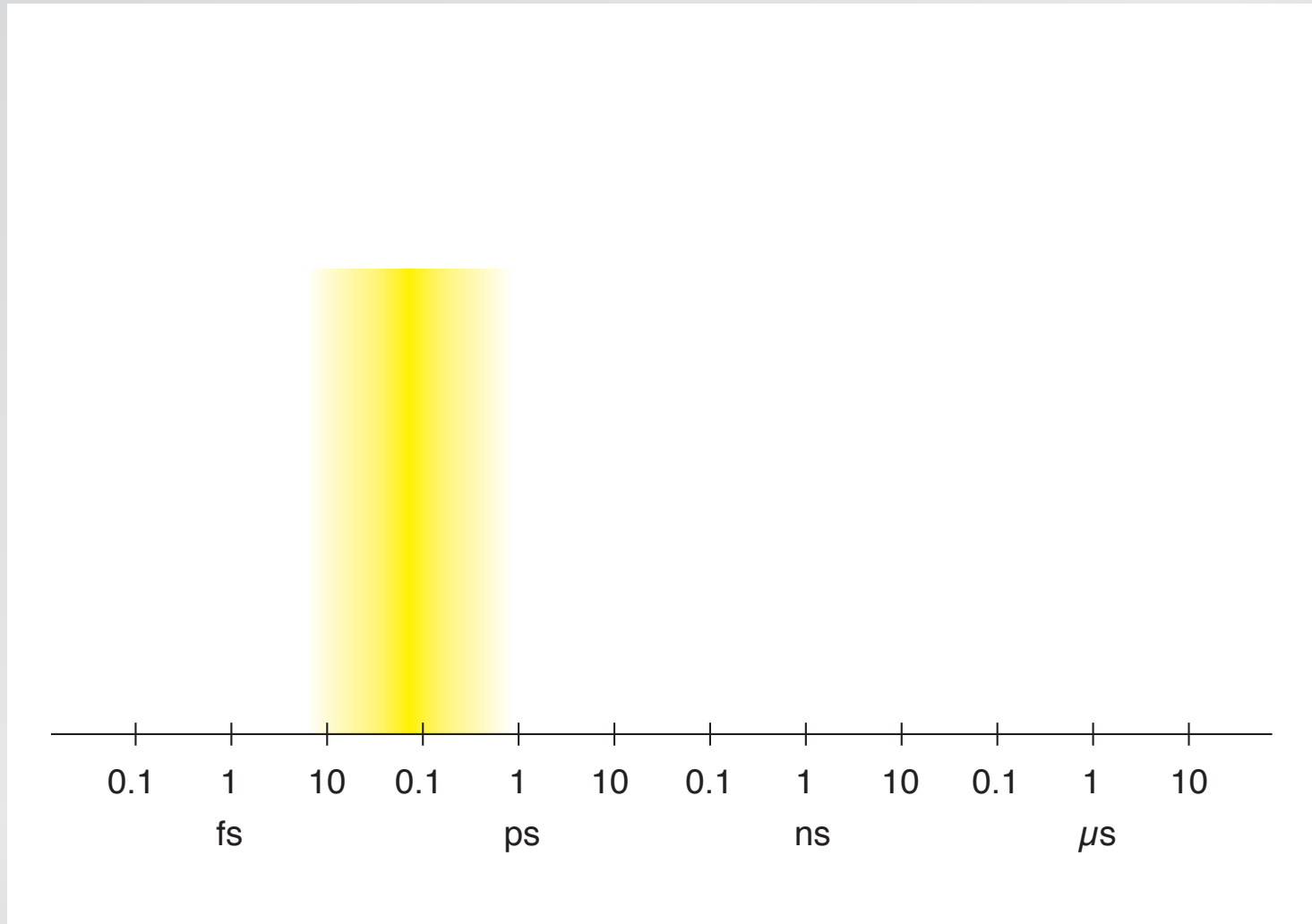
A grayscale micrograph showing several elongated, finger-like structures. Each structure has a darker, textured outer layer and a lighter, smoother inner core. The structures are interconnected and appear to be part of a larger network. A scale bar at the bottom left indicates a length of 1 micrometer.

# Structure

**two processes: melting and ablation**

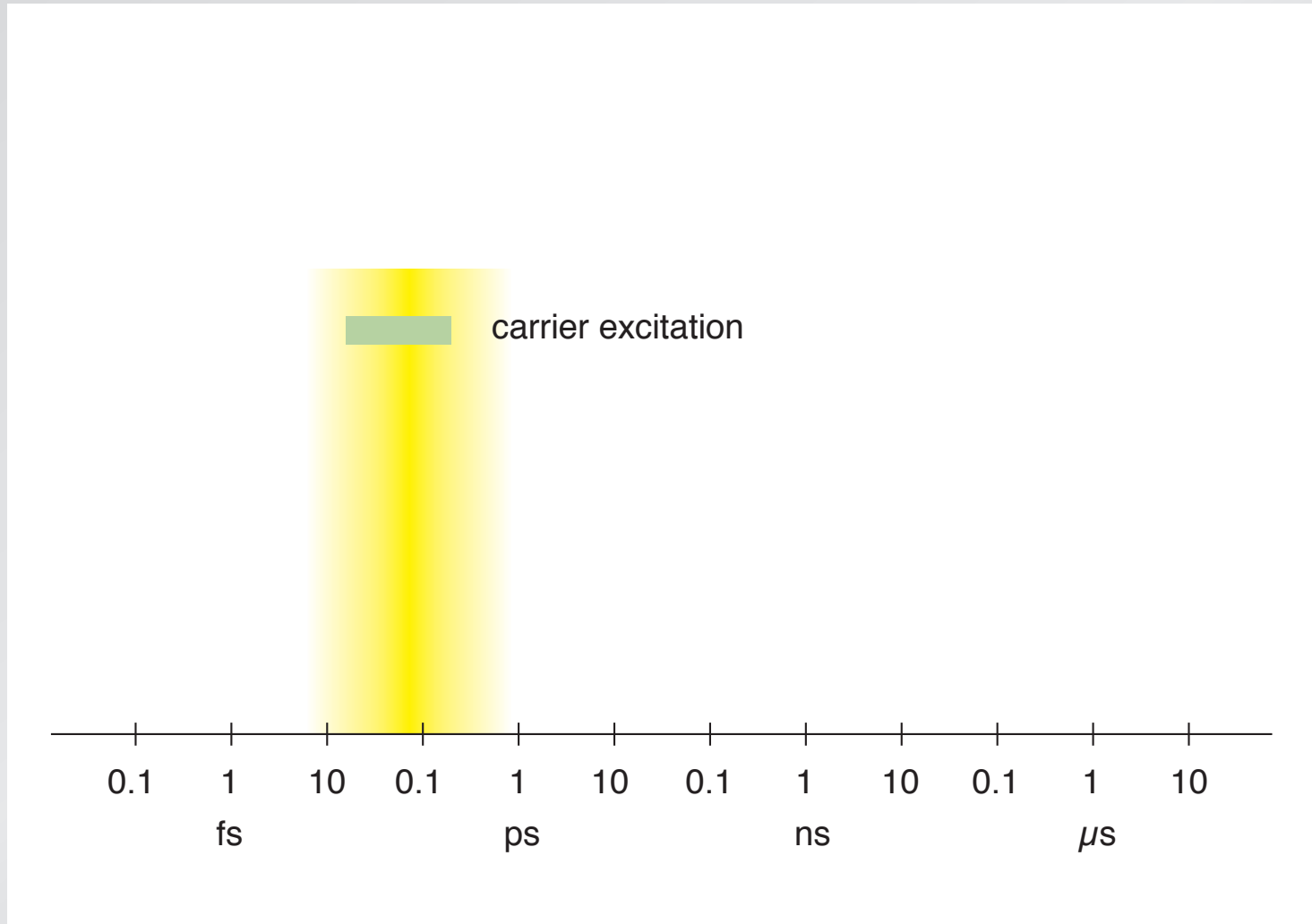
# Structure

relevant time scales



# Structure

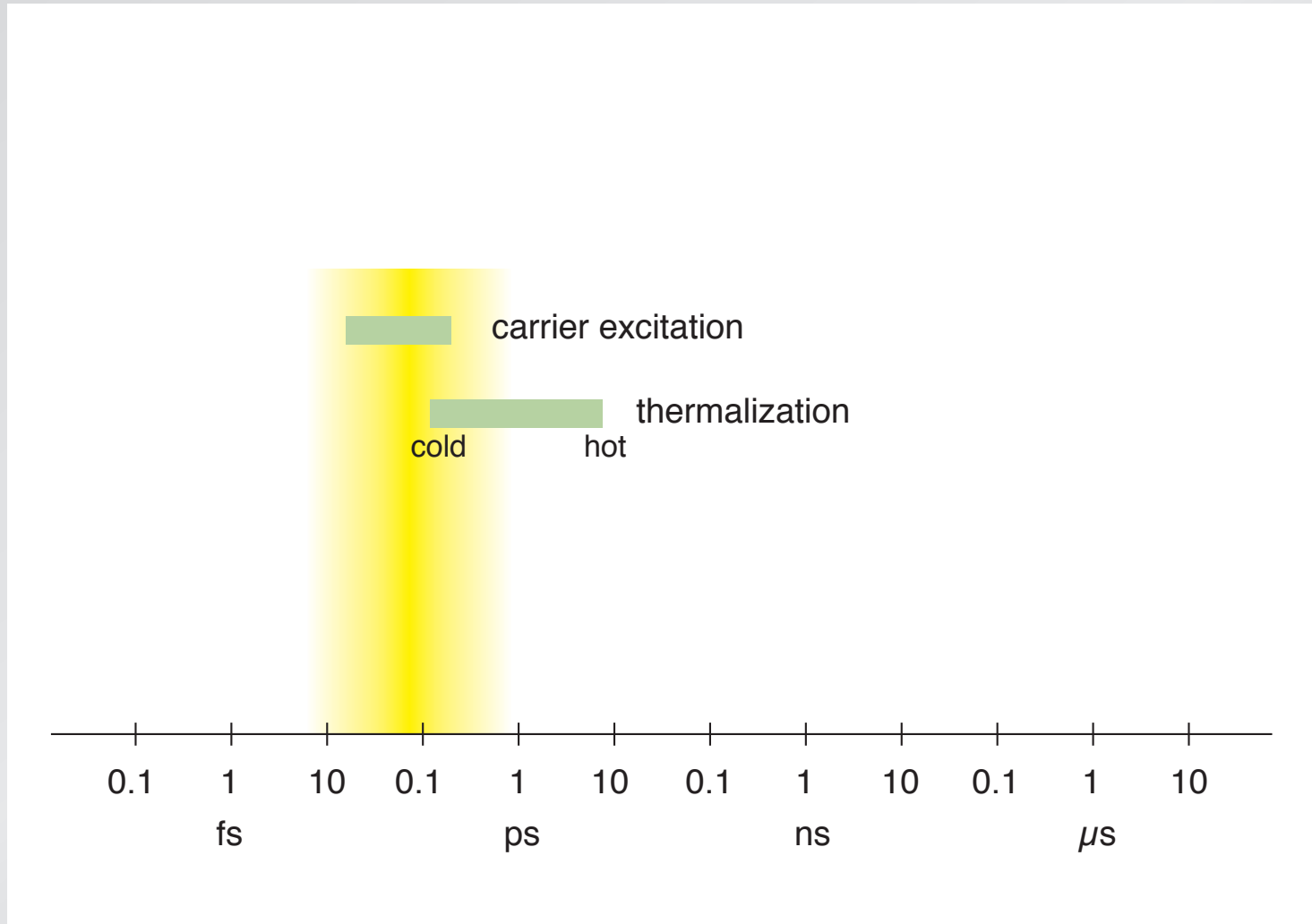
## relevant time scales





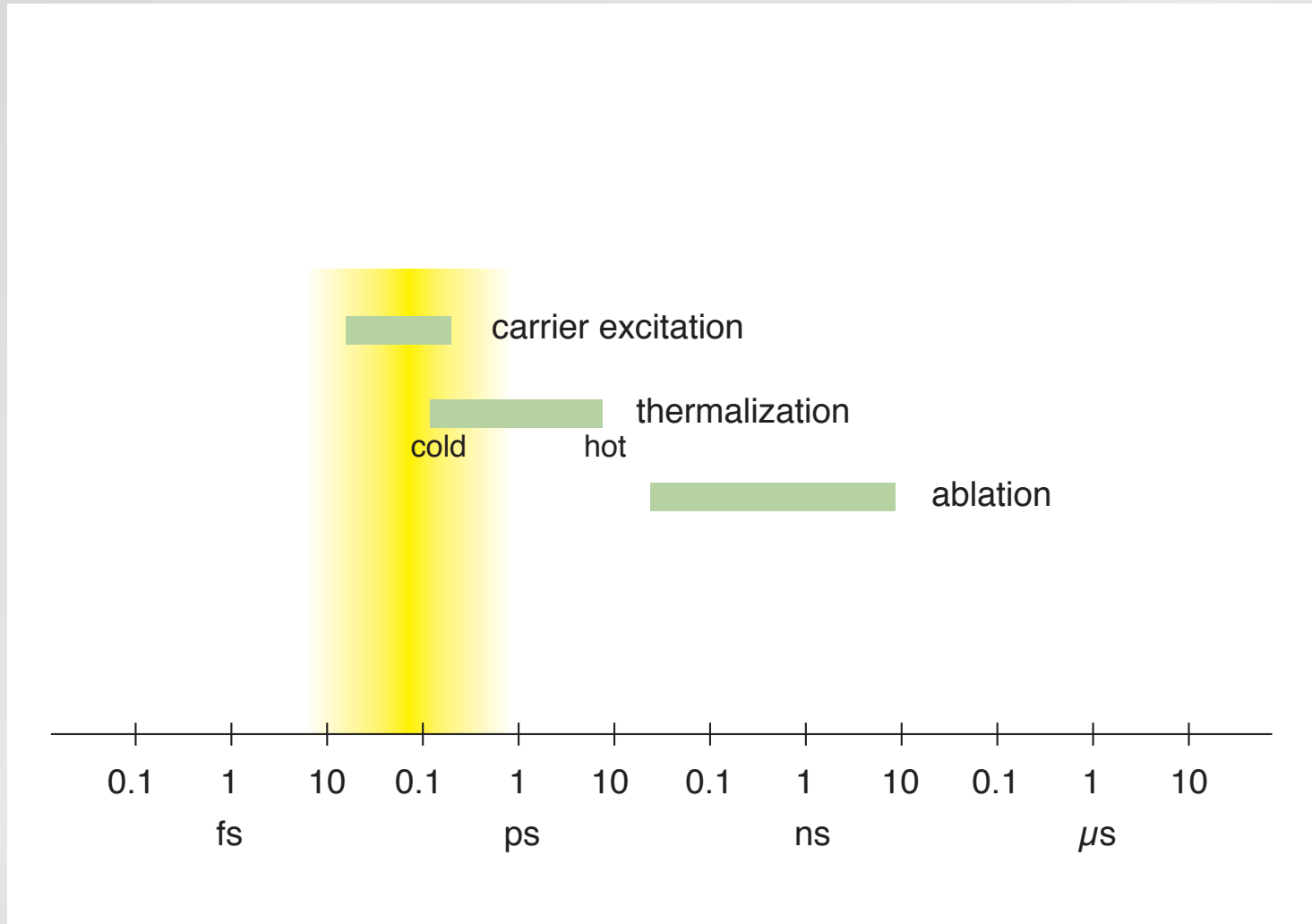
# Structure

## relevant time scales



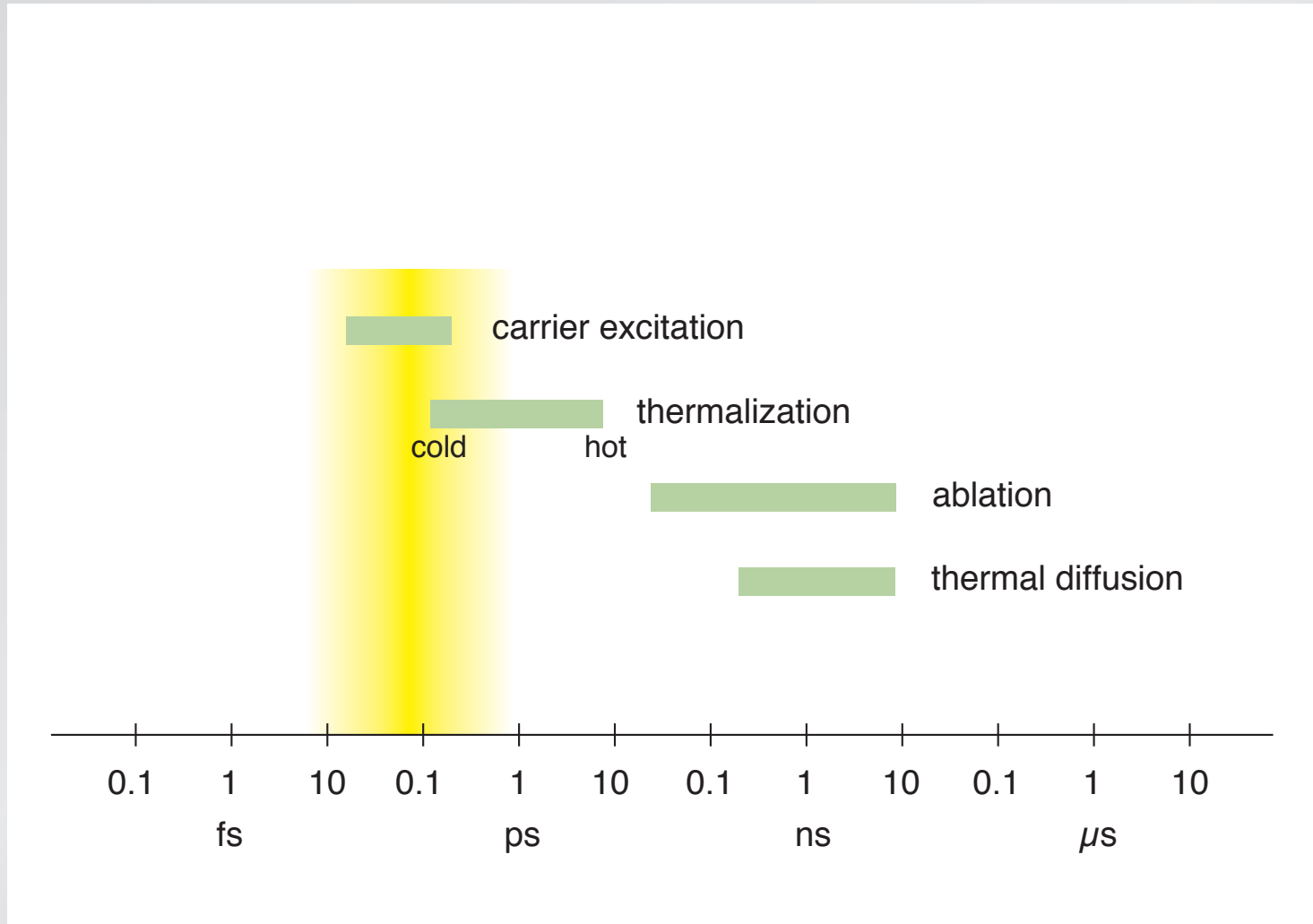
# Structure

## relevant time scales



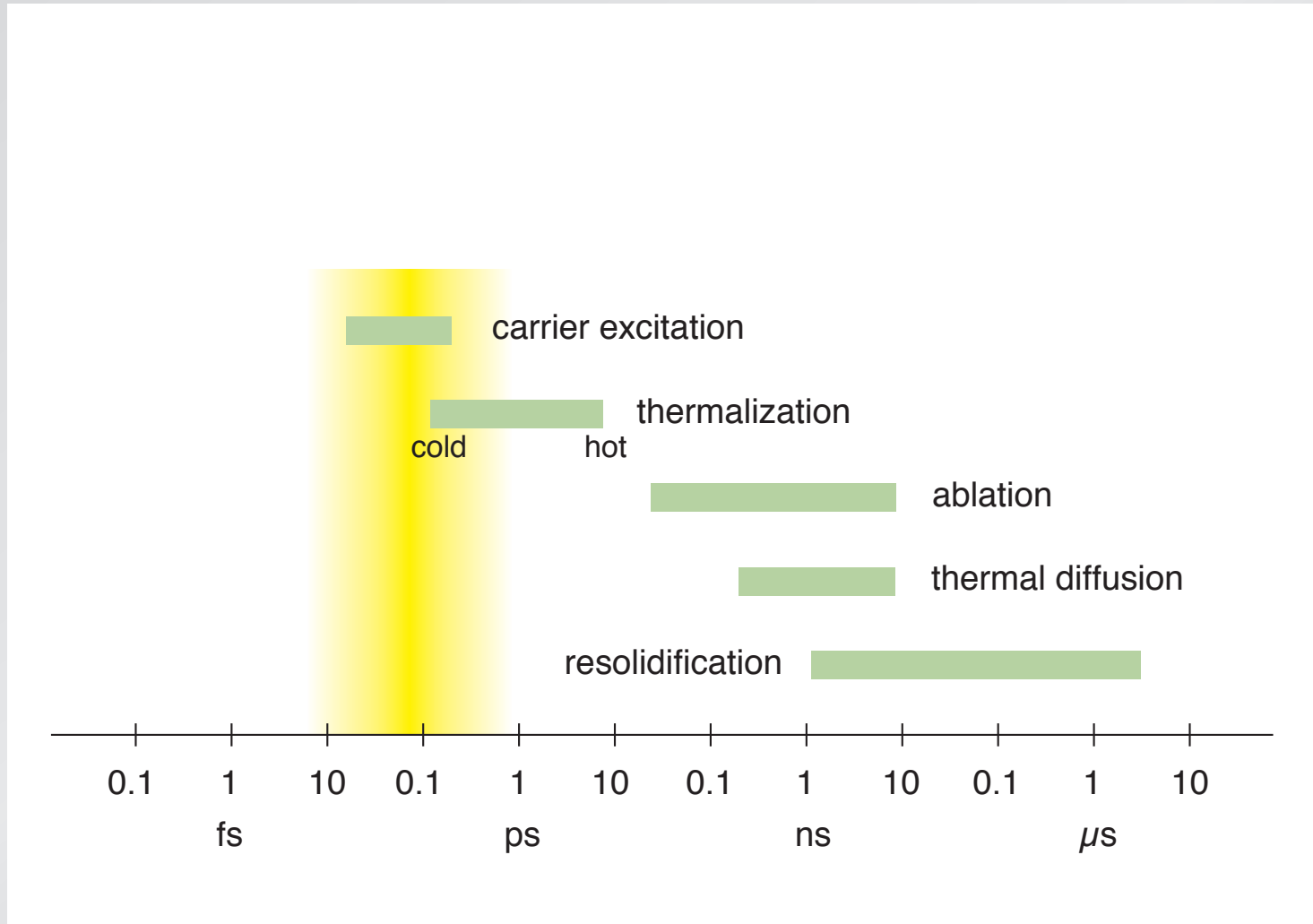
# Structure

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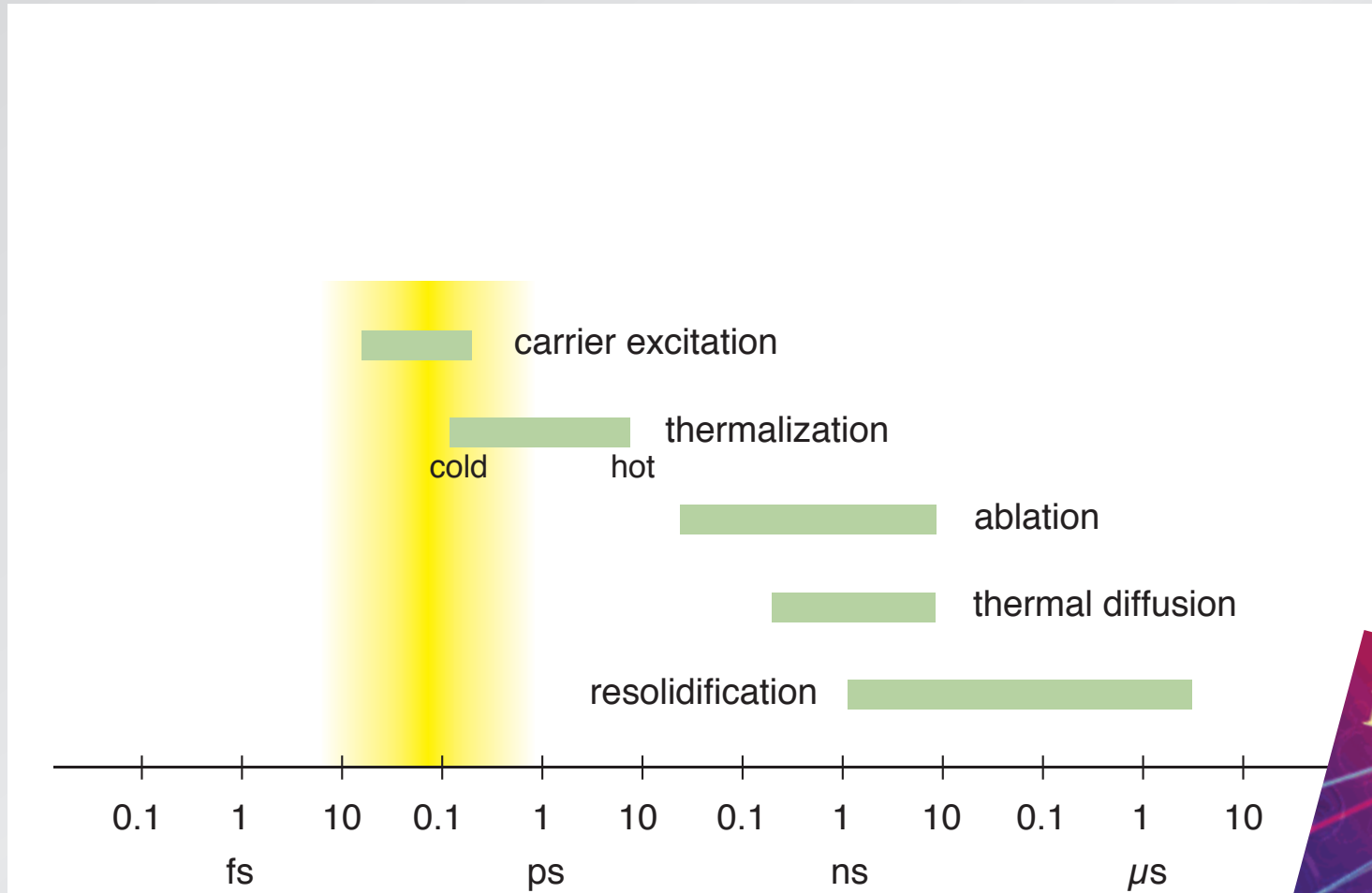
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## relevant time scales

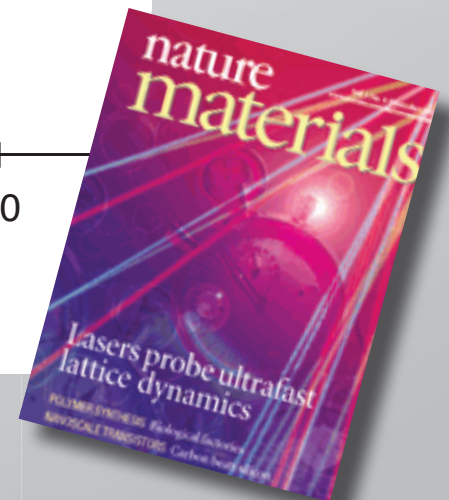


# Structure

## relevant time scales

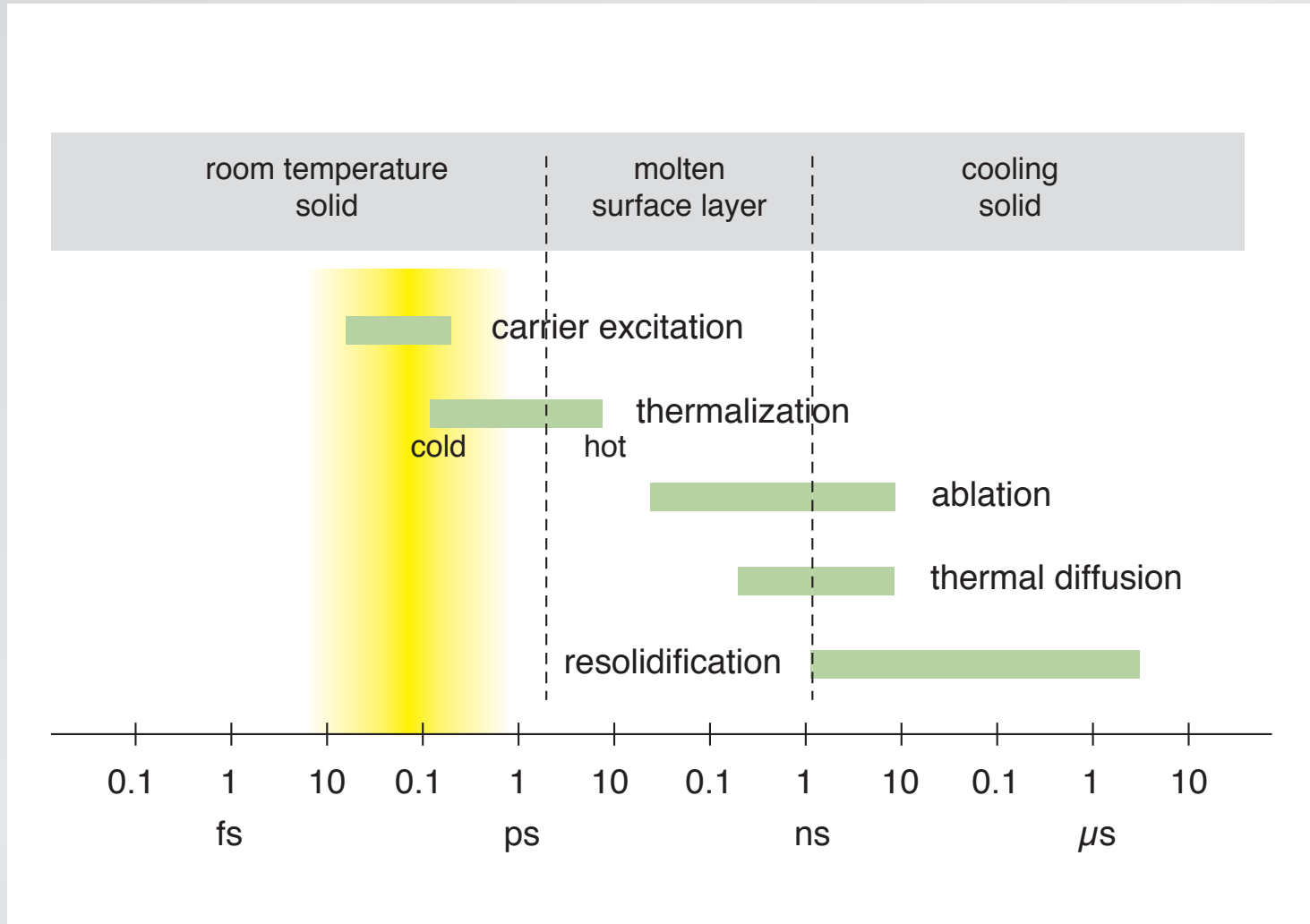


*Nature Materials* 1, 217 (2002)



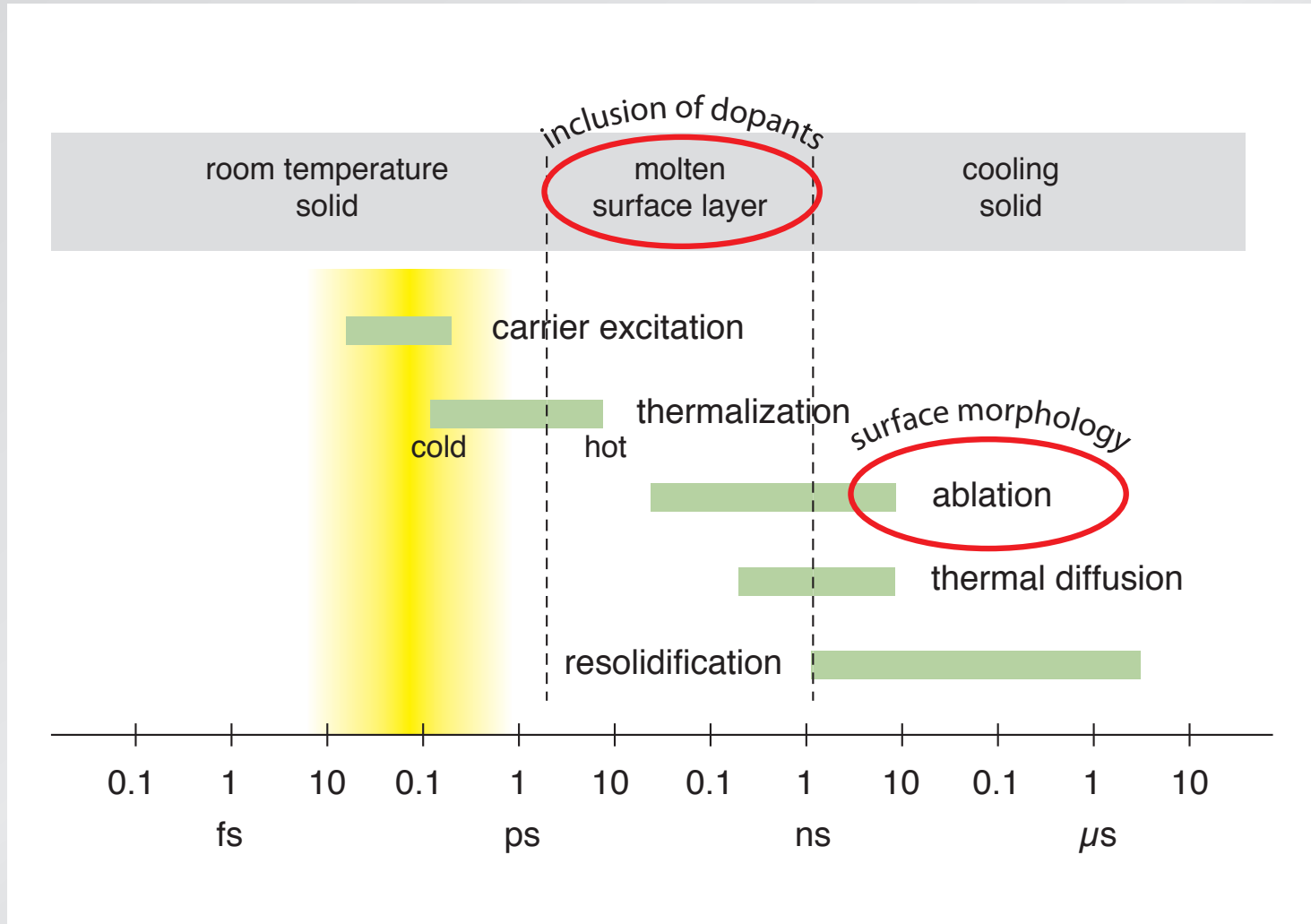
# Structure

## relevant time scales



# Structure

## relevant time scales



# Structure

**different thresholds:**

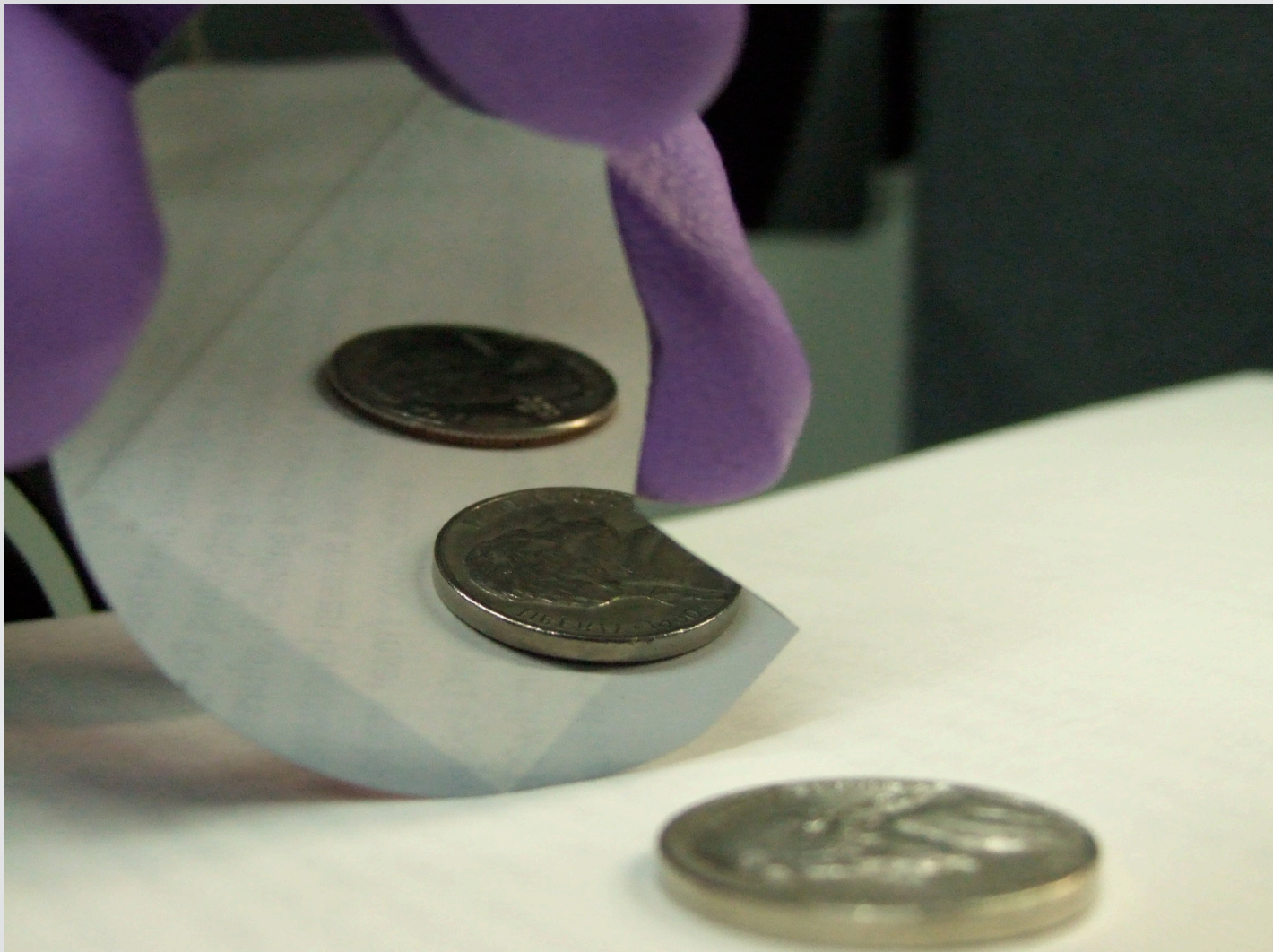
**melting: 1.5 kJ/m<sup>2</sup>**

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



# Structure

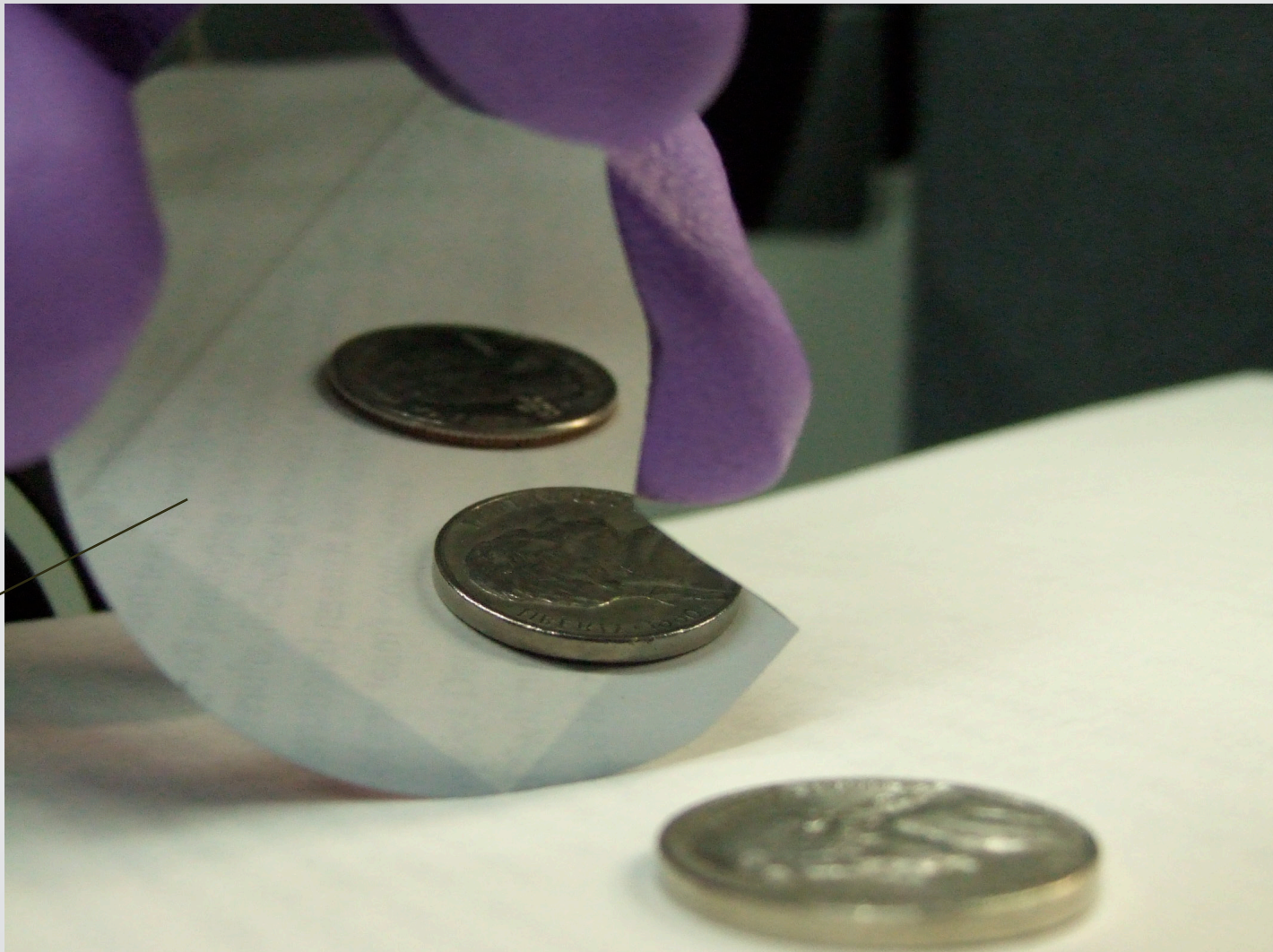
decouple ablation from melting



# Structure

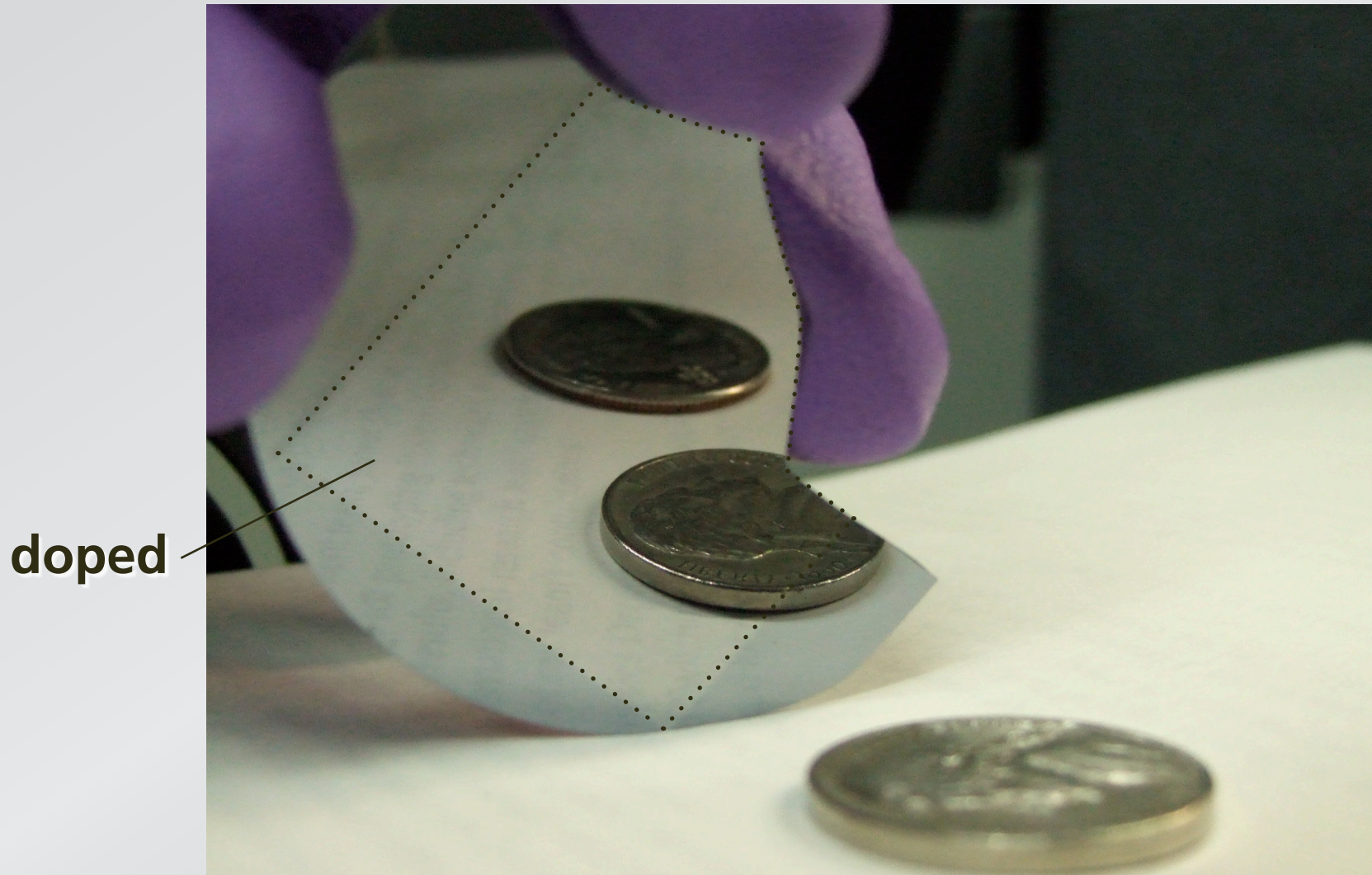
decouple ablation from melting

doped



# Structure

decouple ablation from melting

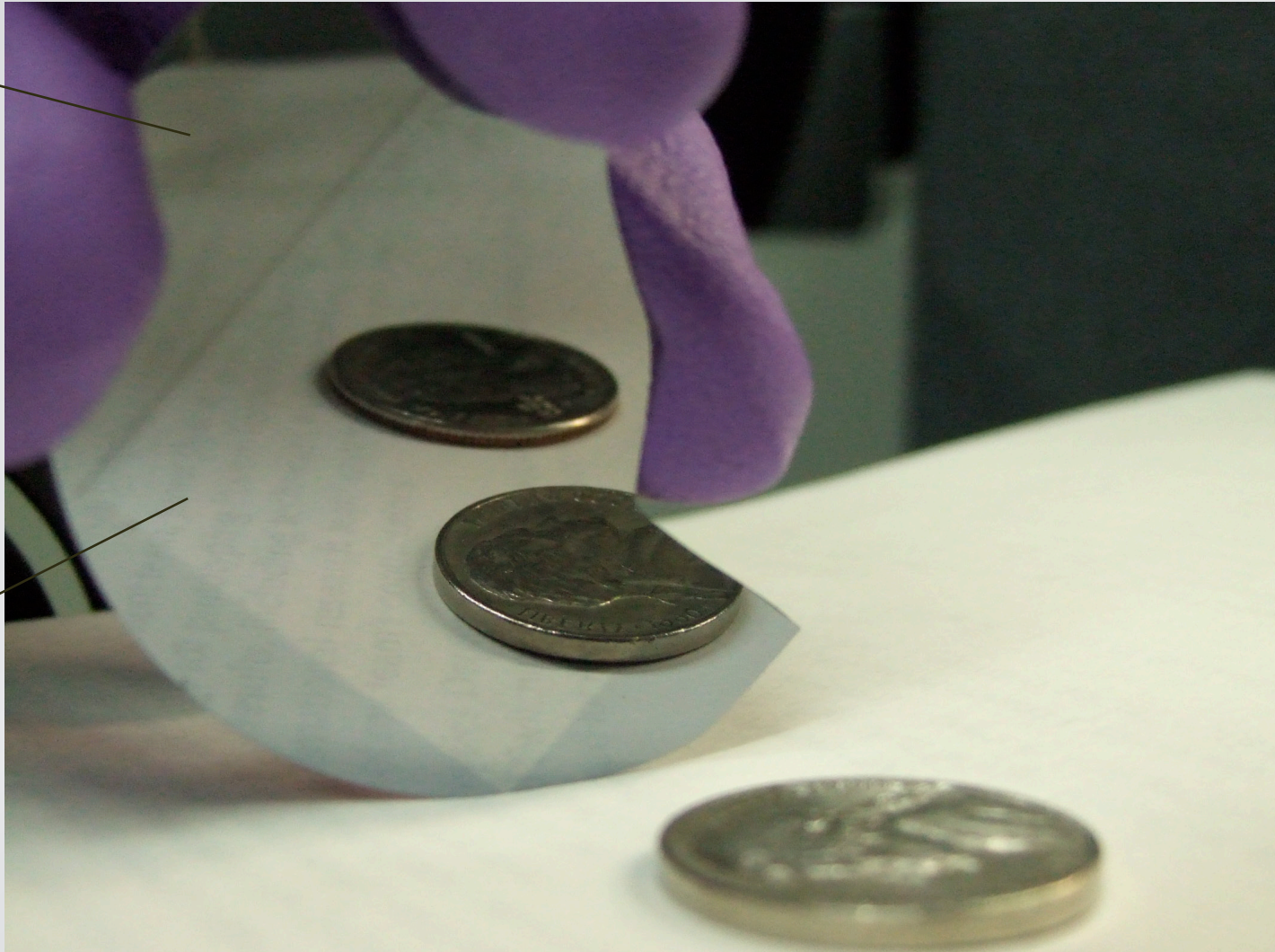


# Structure

decouple ablation from melting

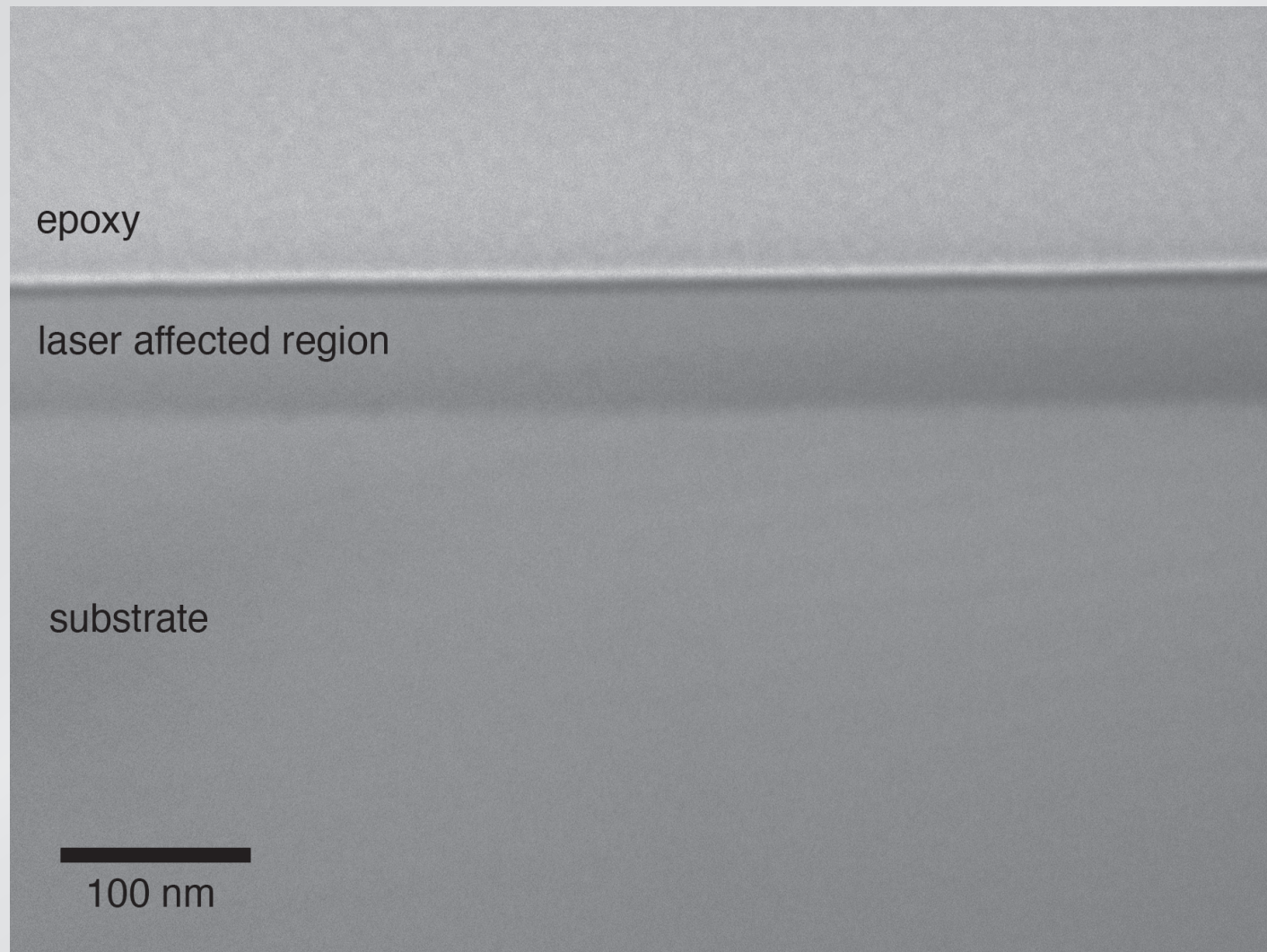
undoped

doped



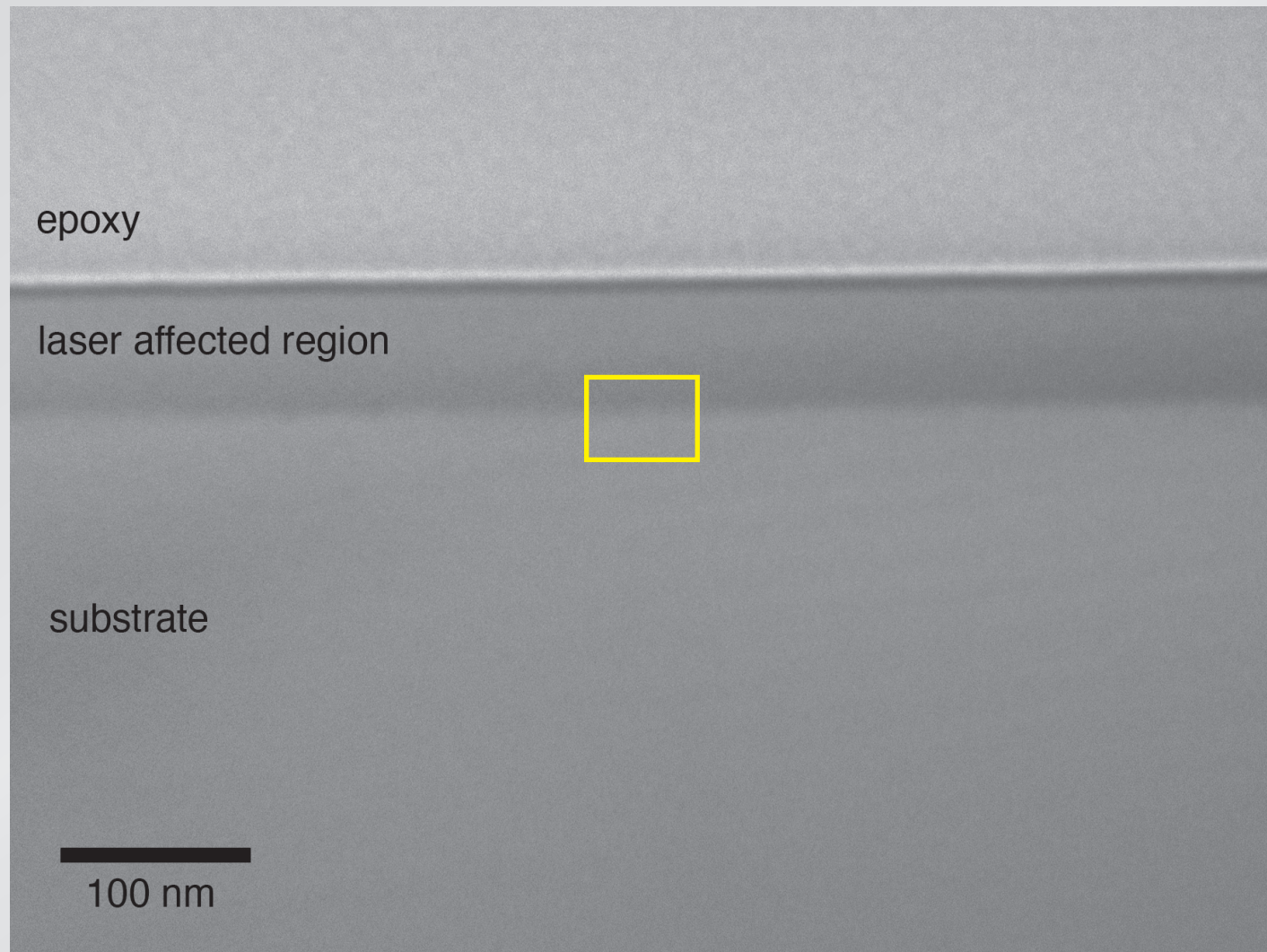
# Structure

decouple ablation from melting



# Structure

decouple ablation from melting



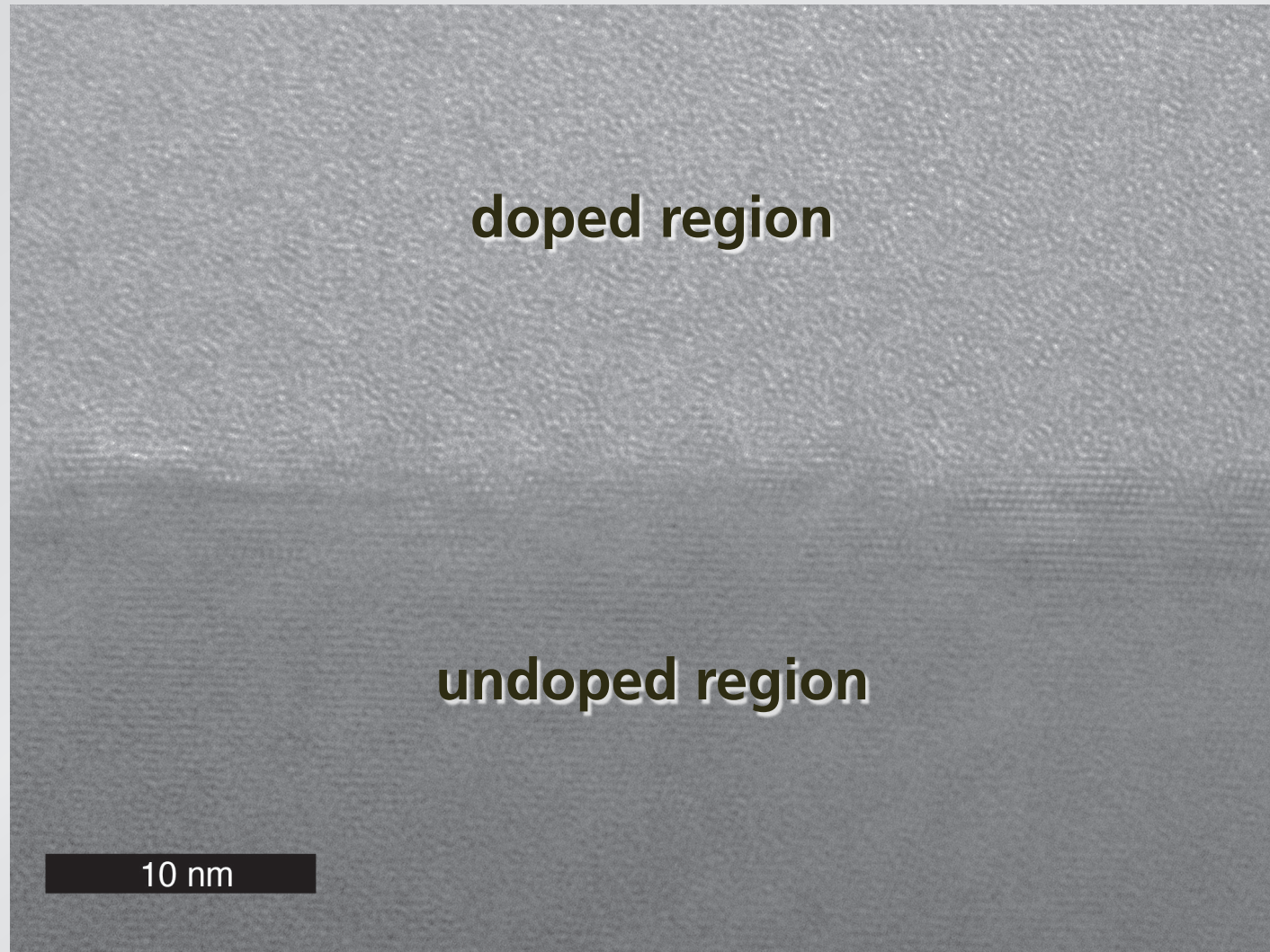
# Structure

decouple ablation from melting



# Structure

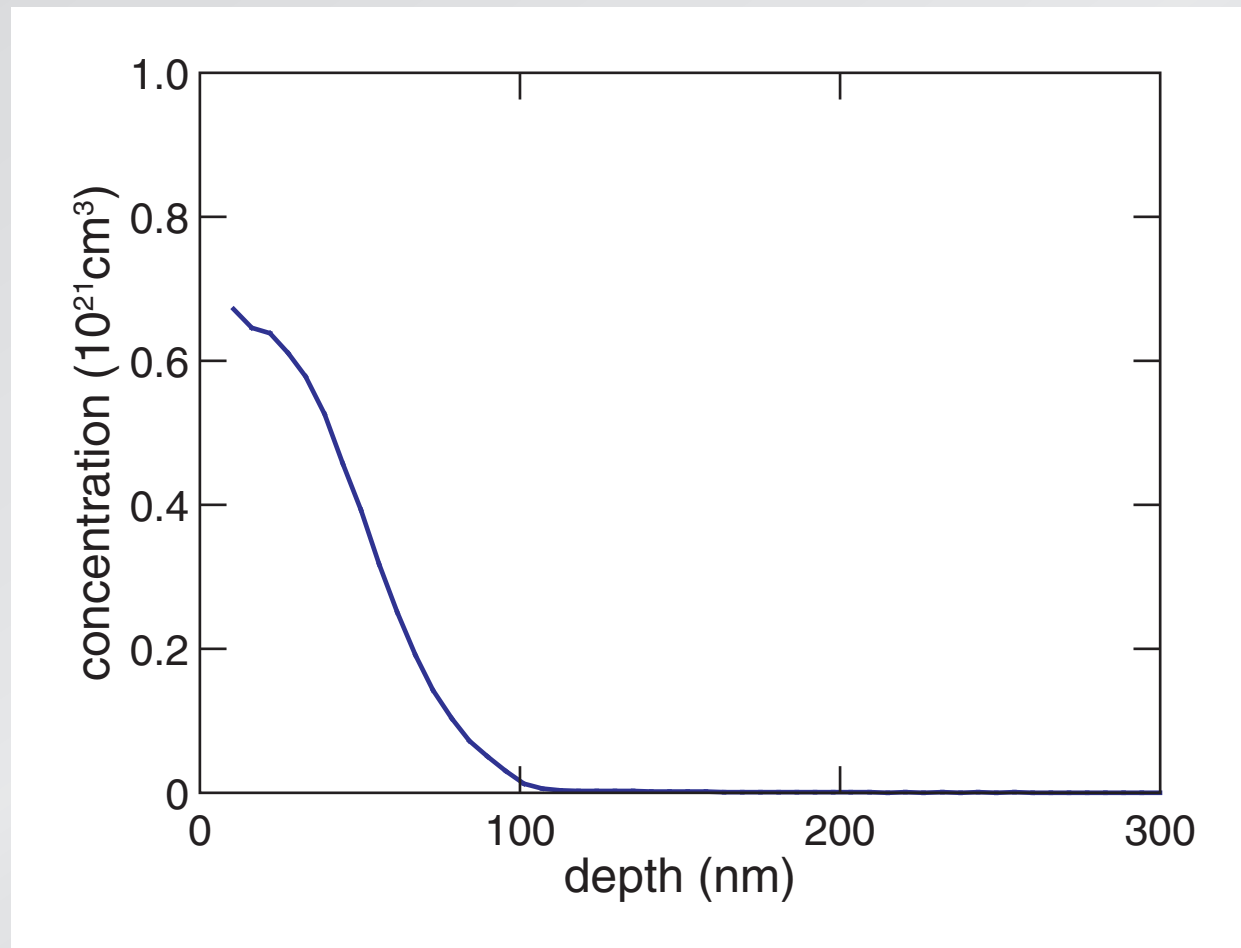
decouple ablation from melting





# Structure

## secondary ion mass spectrometry



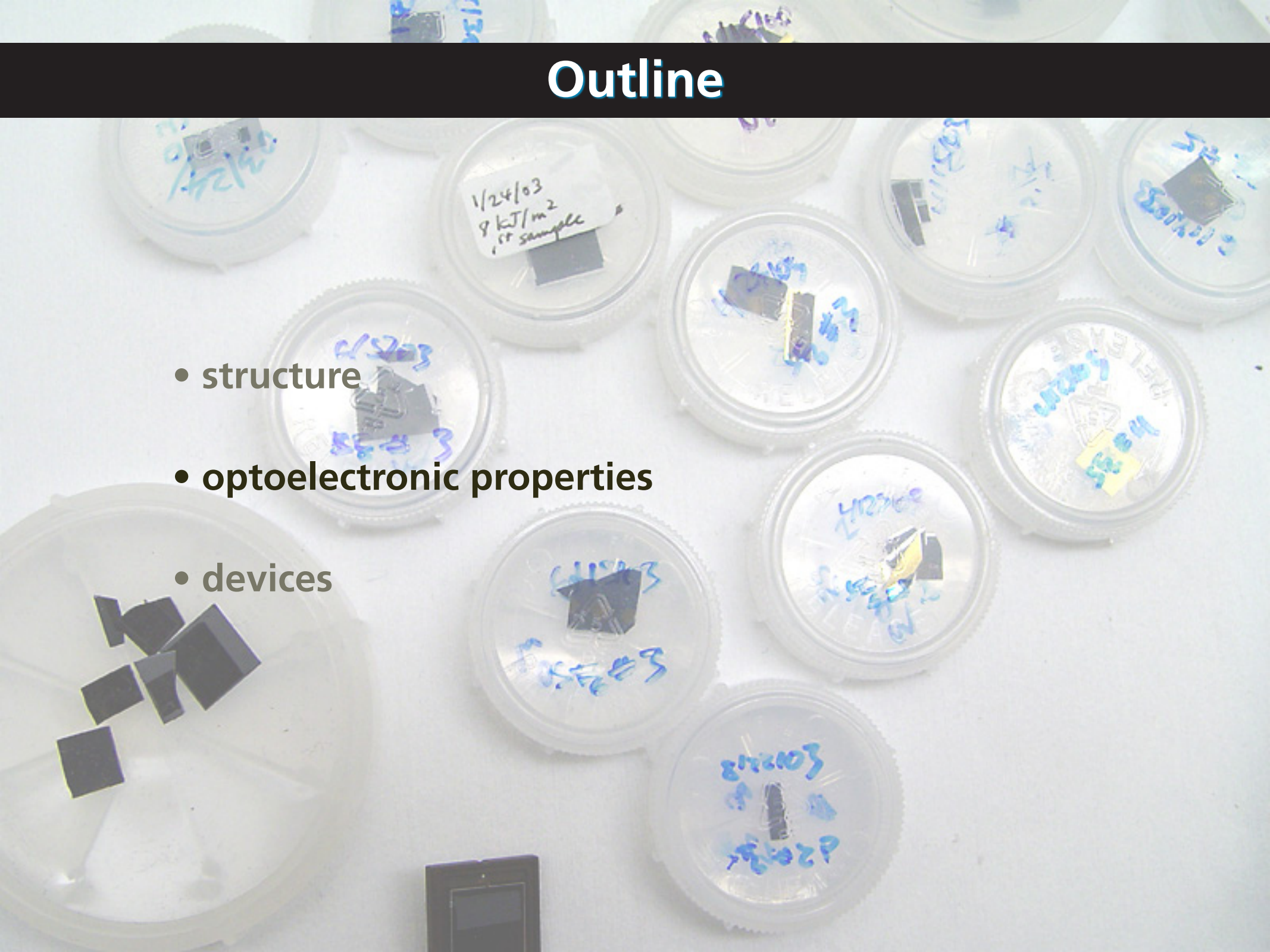
# Structure

## 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

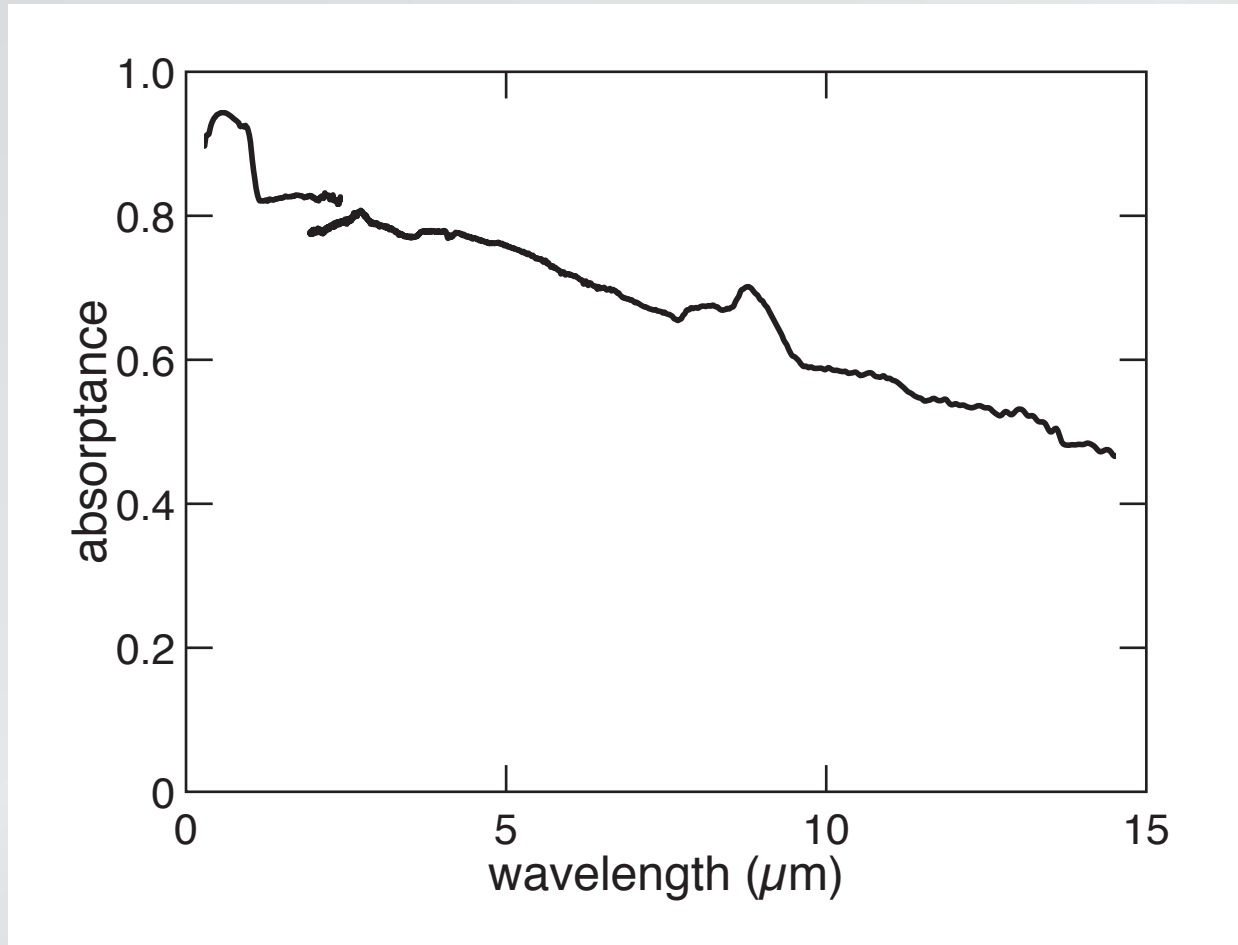
# Outline

- structure
- optoelectronic properties
- devices



# Optoelectronic properties

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

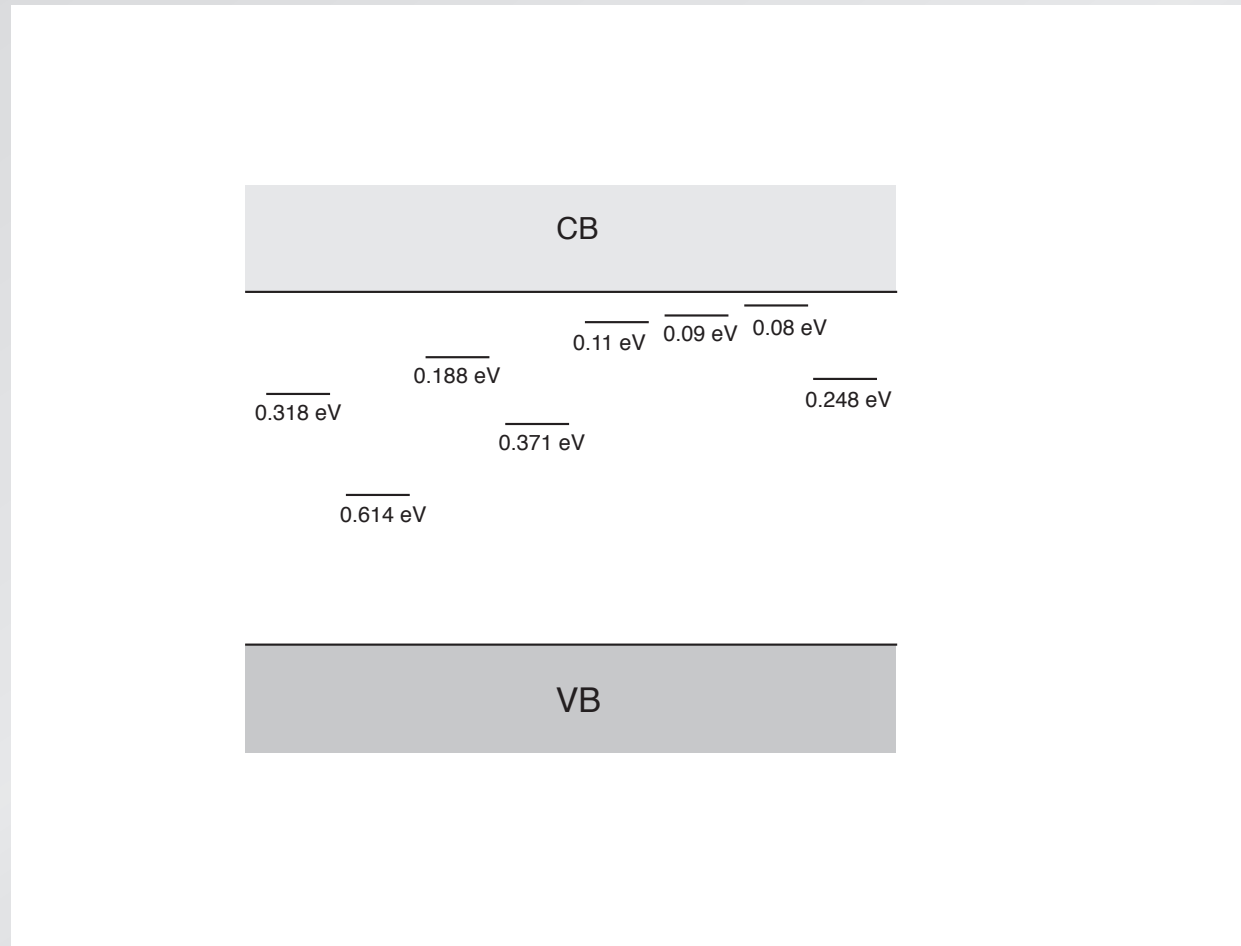


# Optoelectronic properties

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

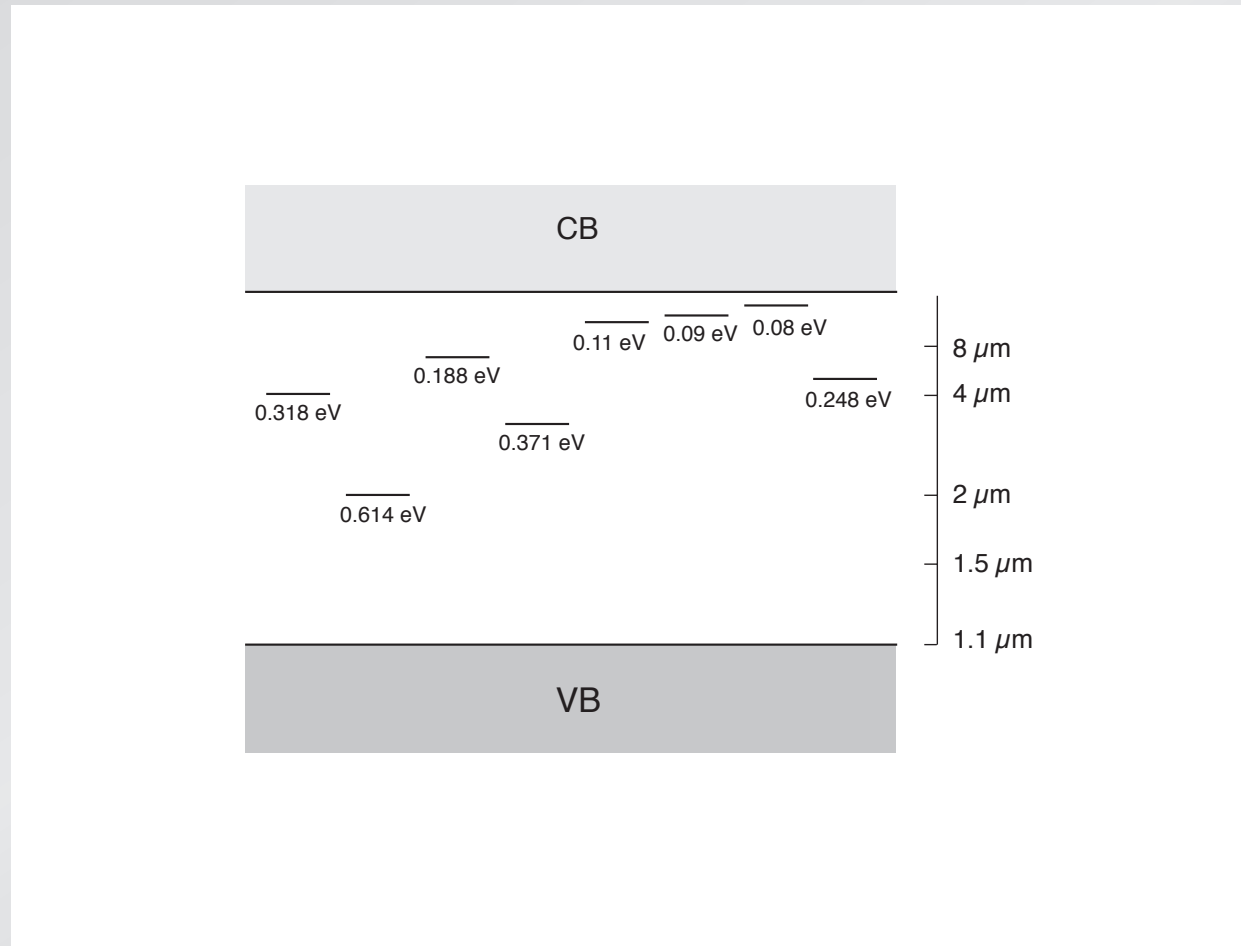
# Optoelectronic properties

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



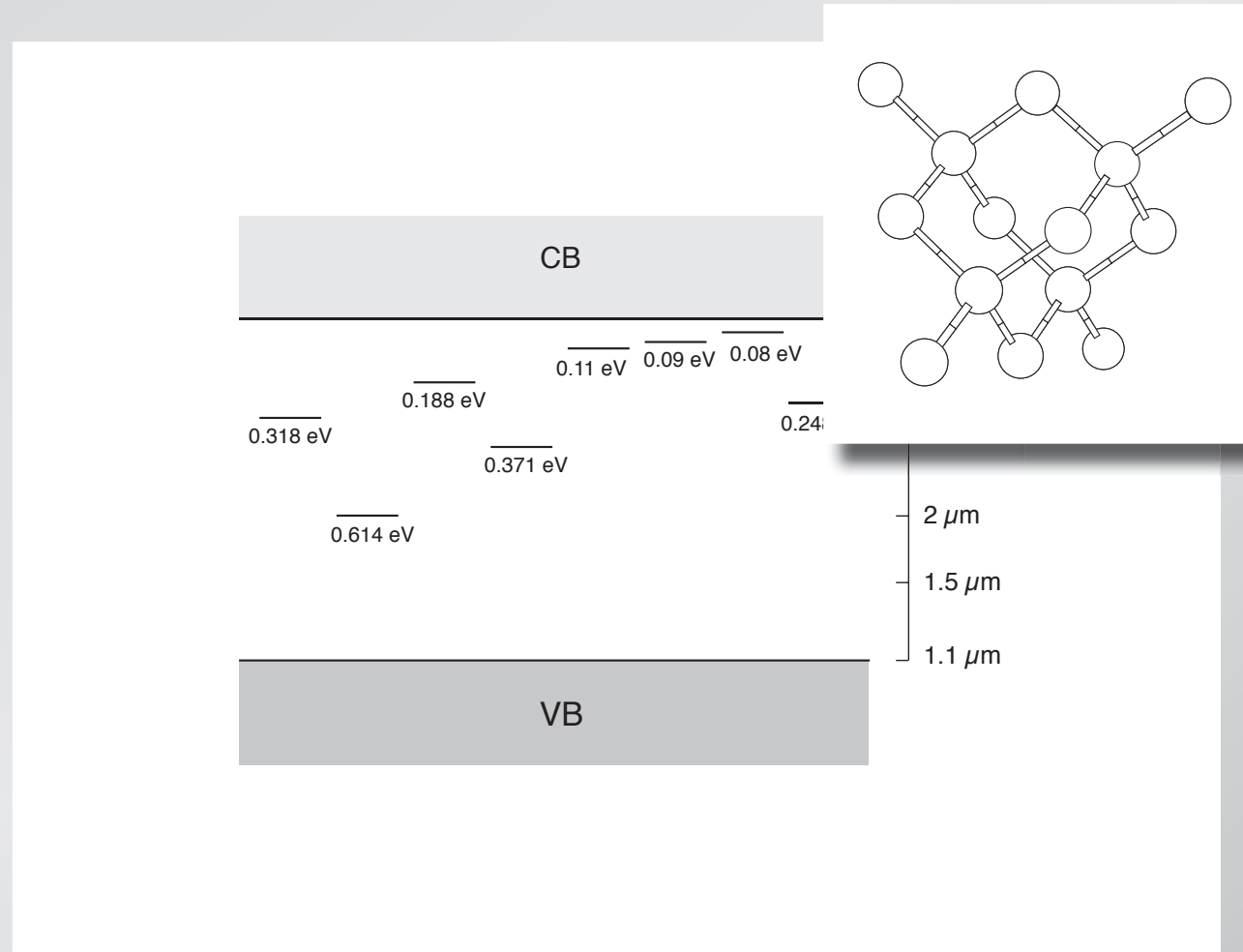
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# Optoelectronic properties

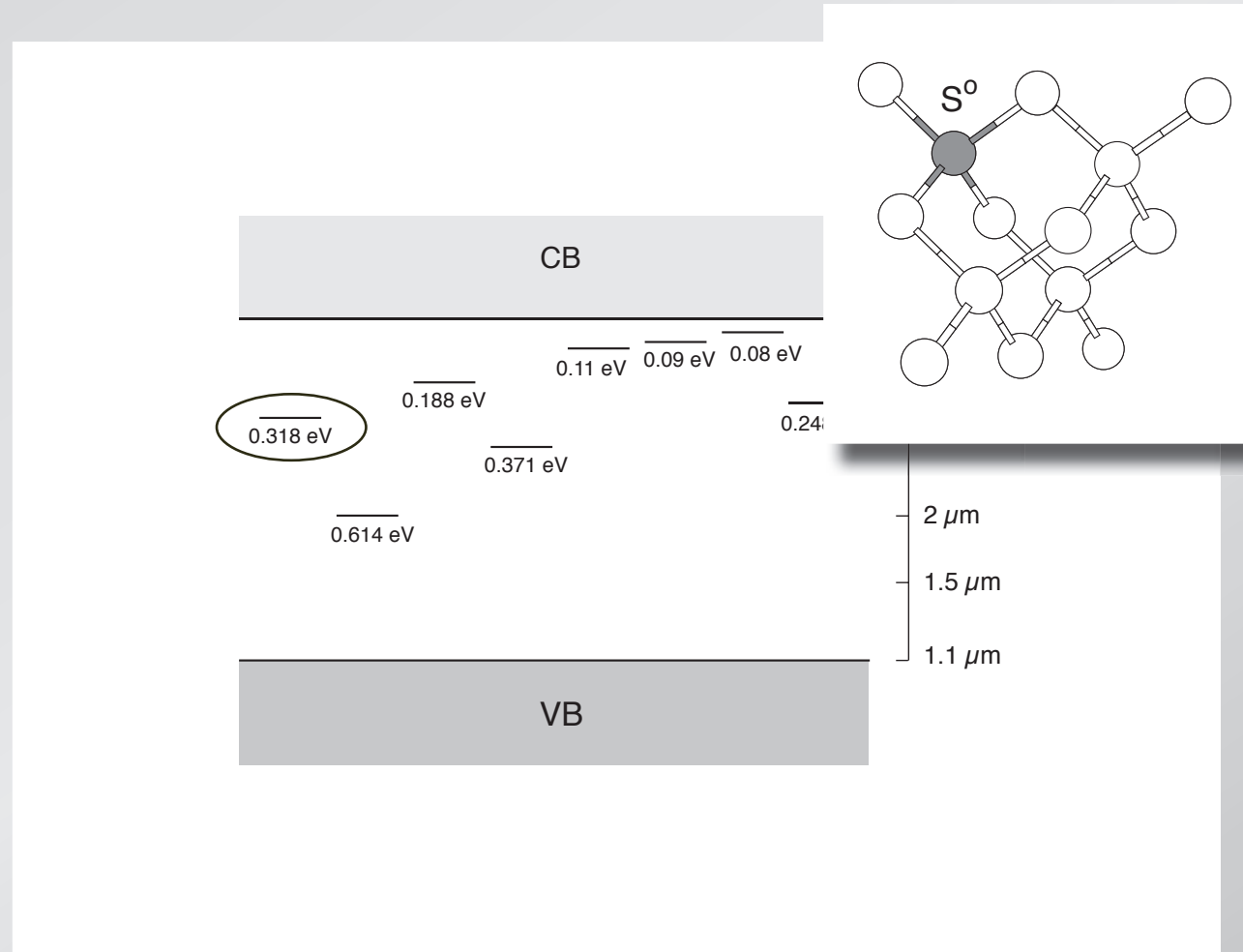
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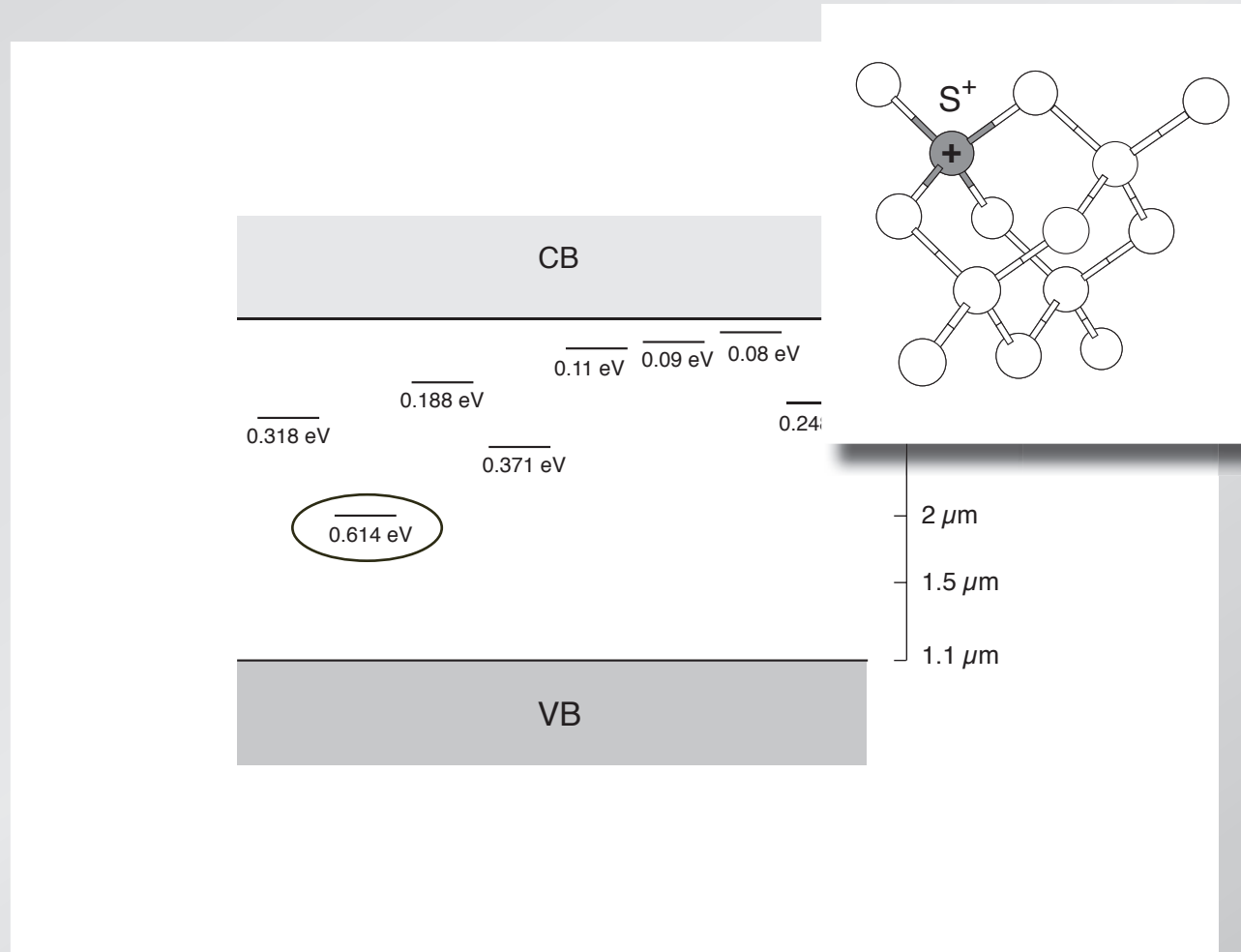
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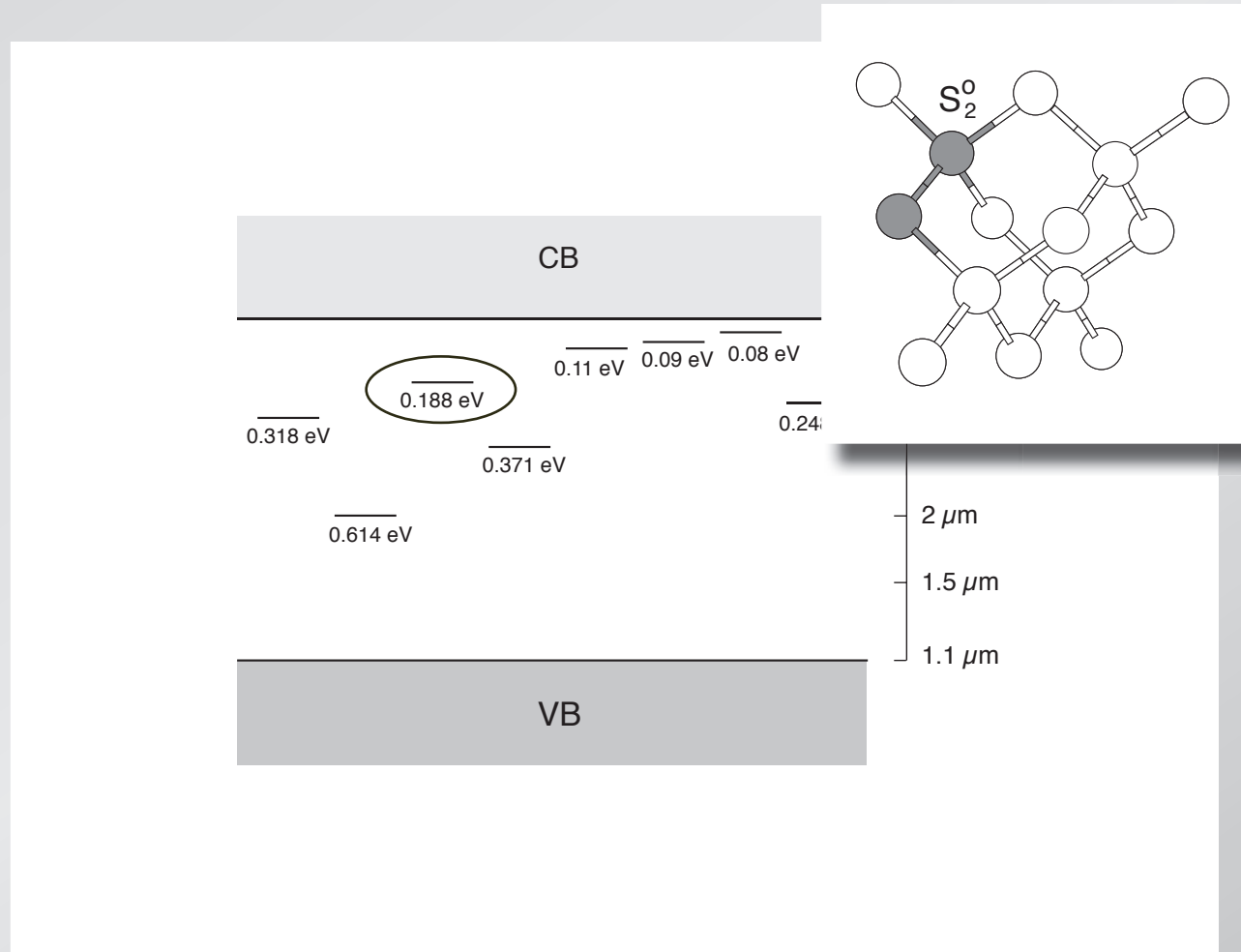
# Optoelectronic properties

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



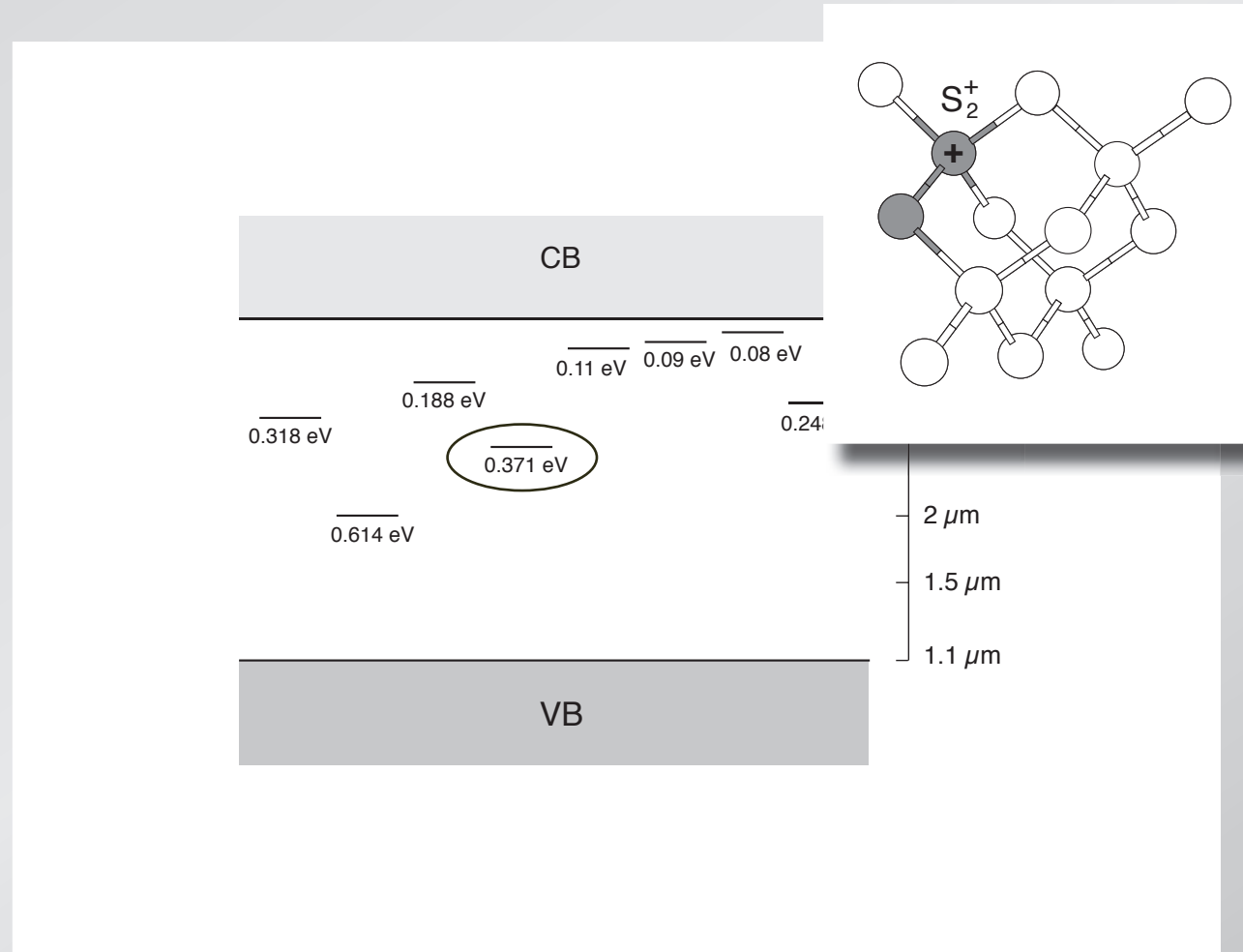
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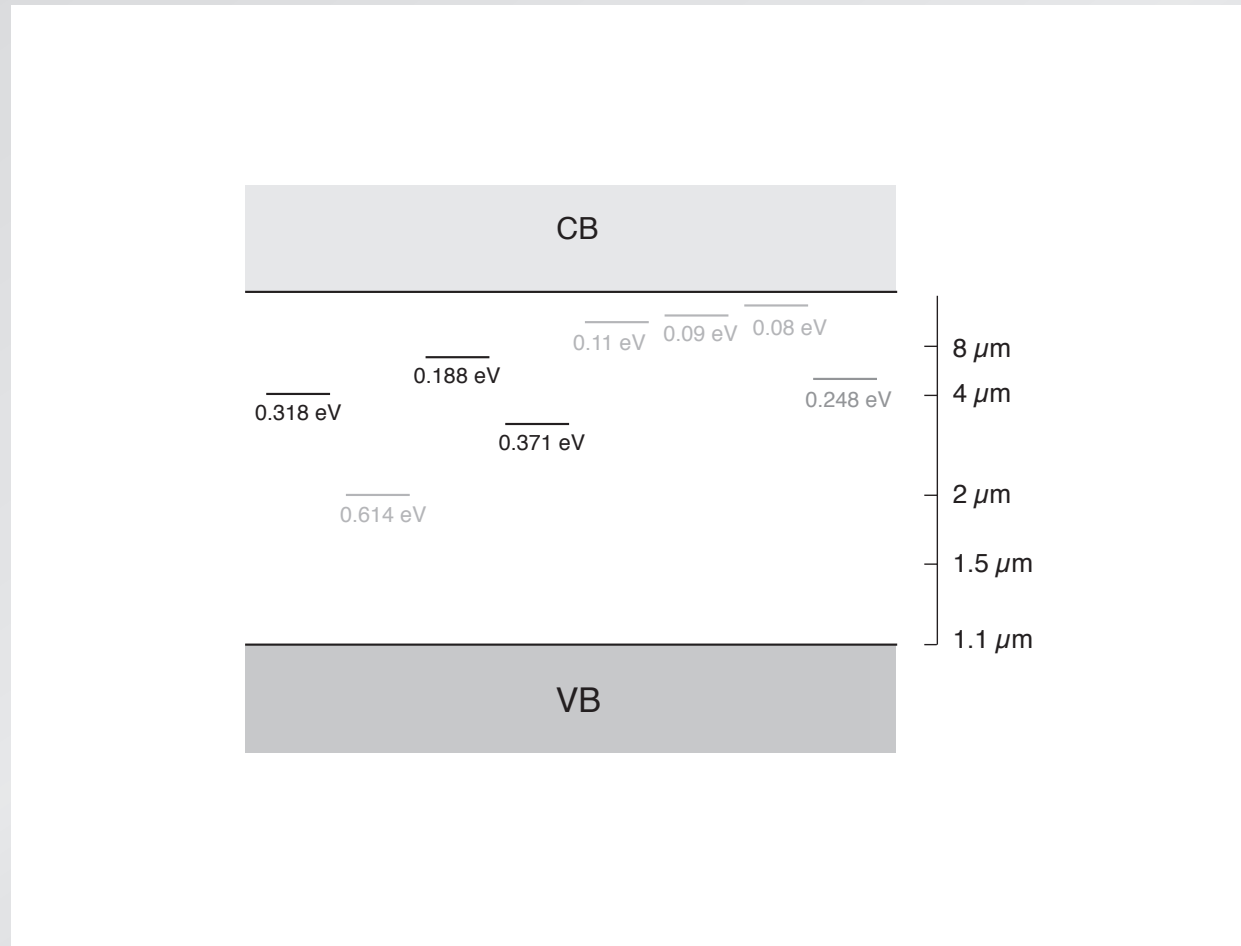
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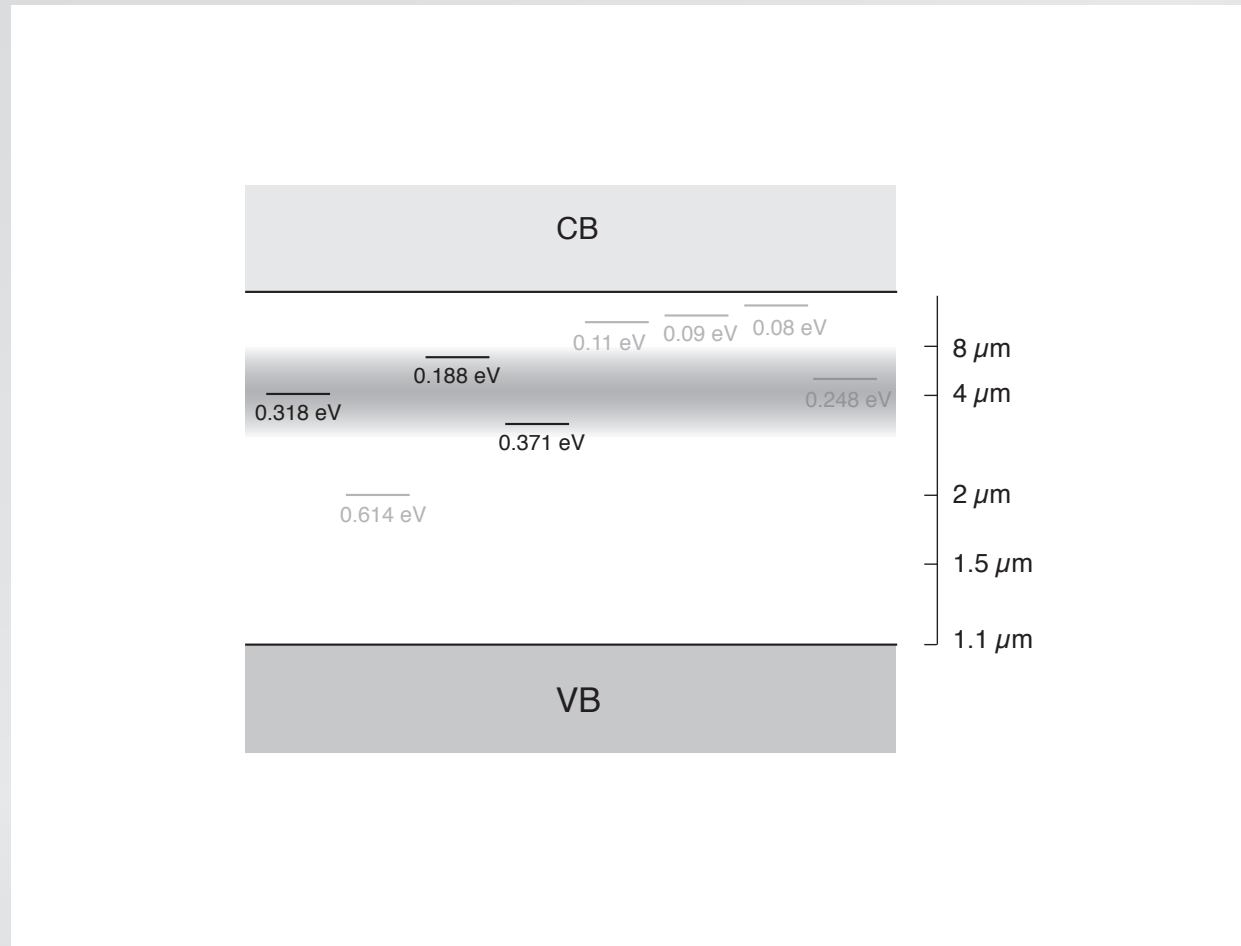
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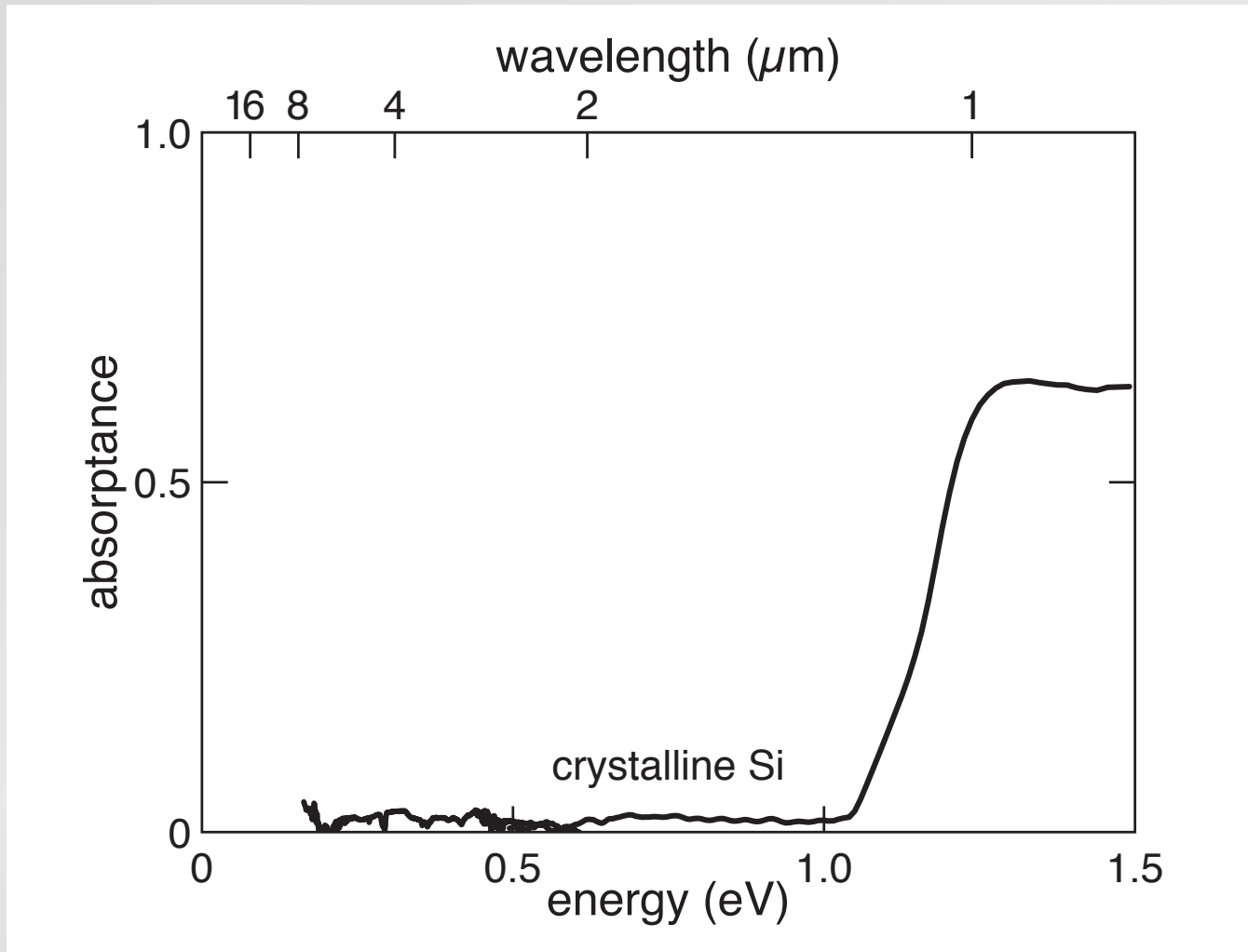
# Optoelectronic properties

at high concentration states broaden into band



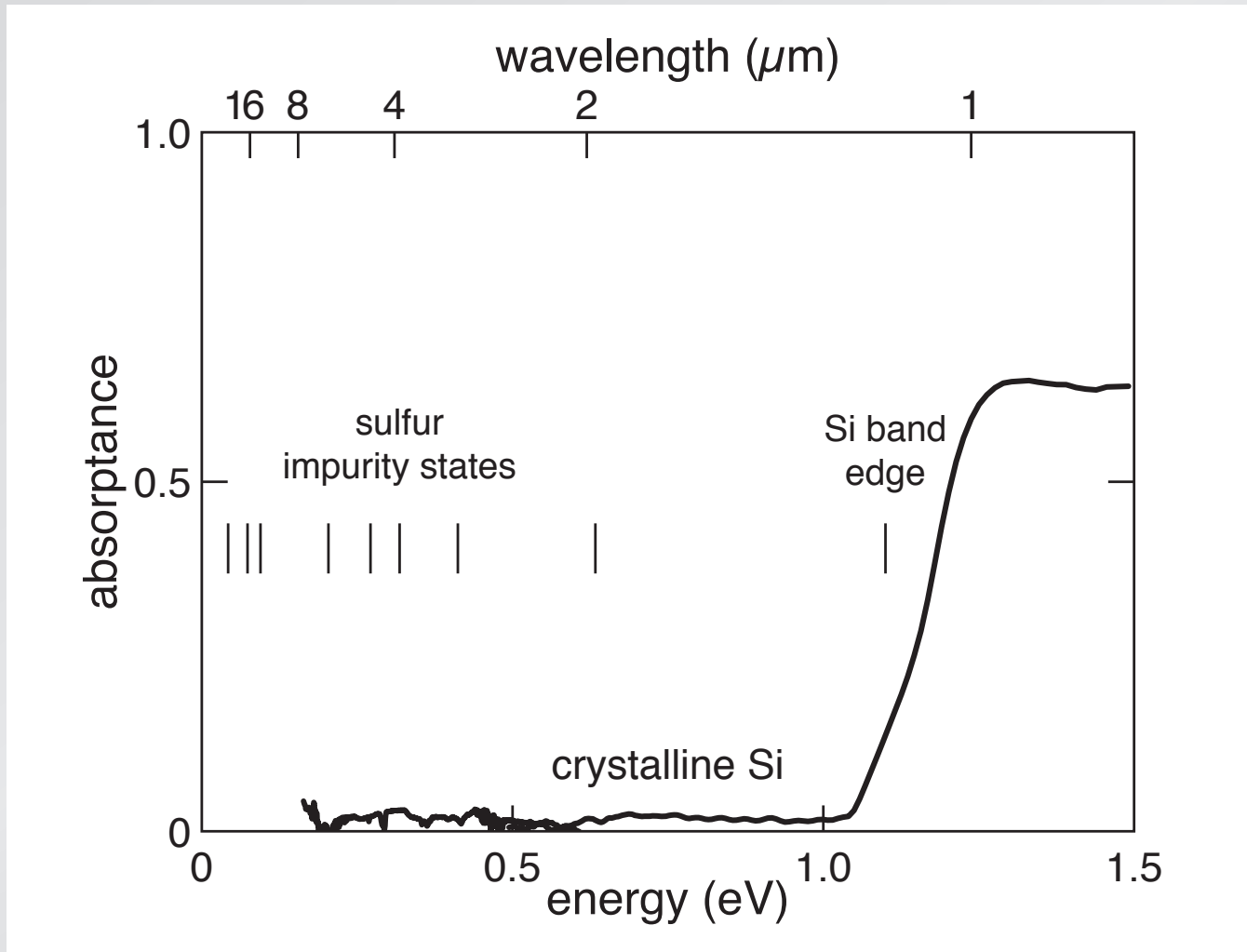
# Optoelectronic properties

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



# Optoelectronic properties

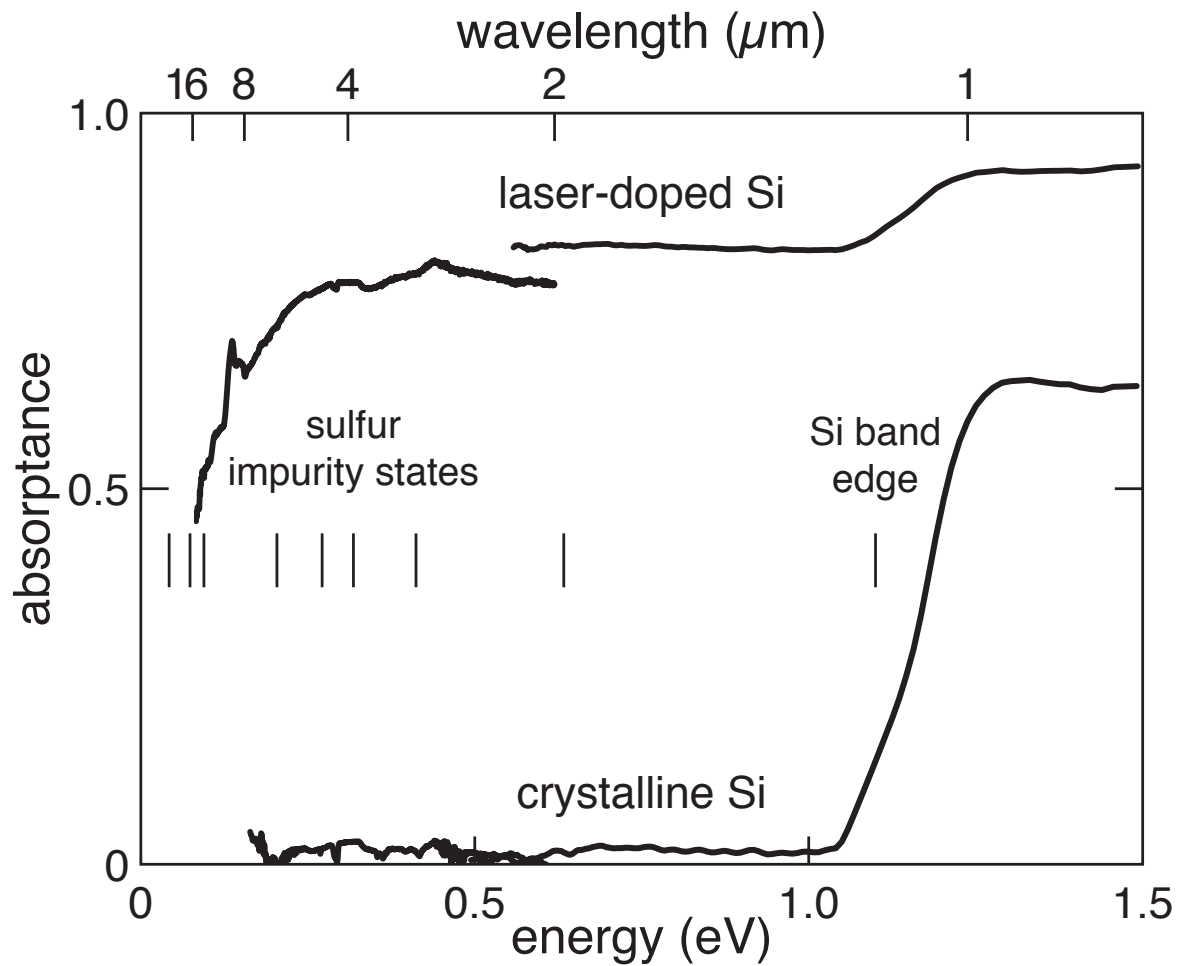
## $10^{-6}$ sulfur doping





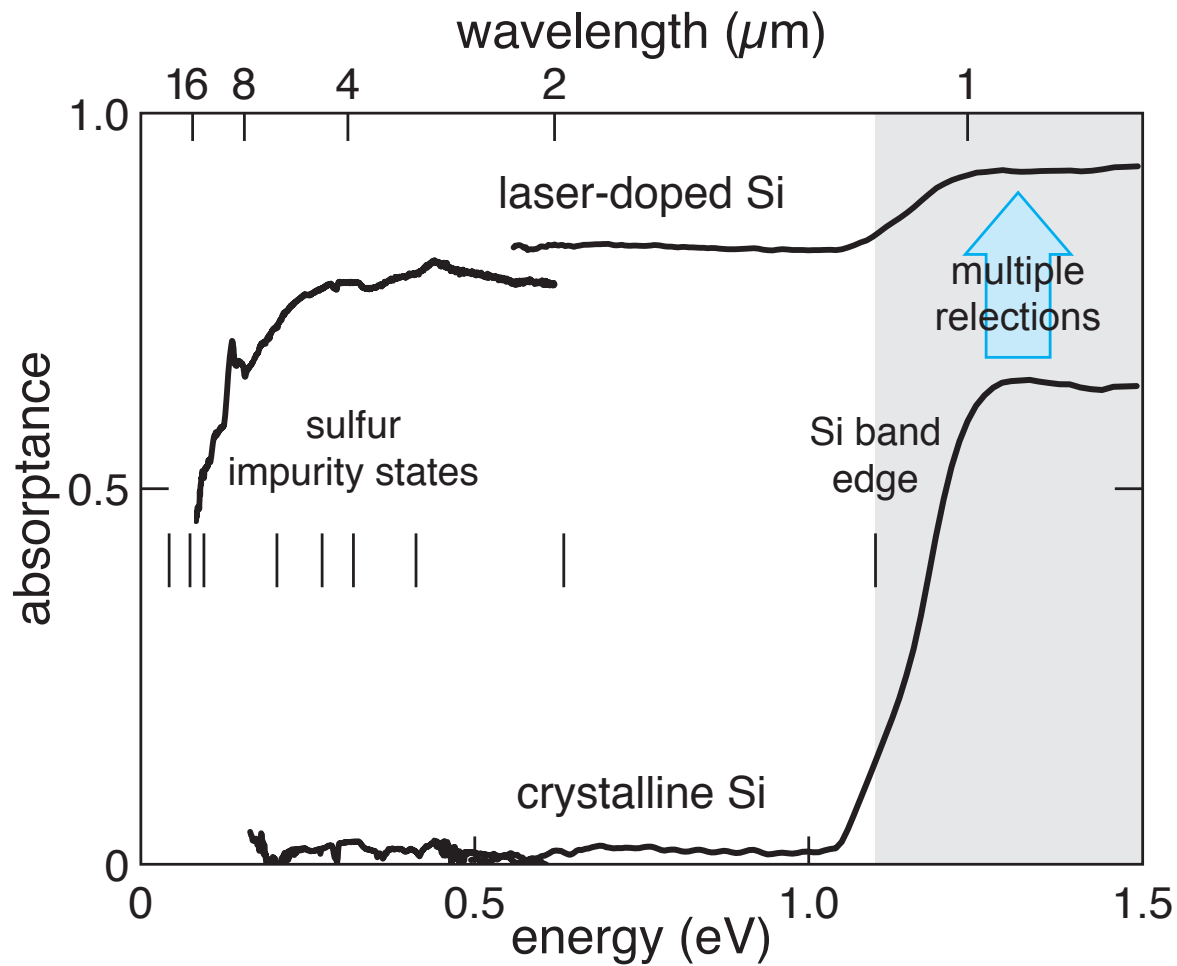
# Optoelectronic properties

## laser-doped S:Si



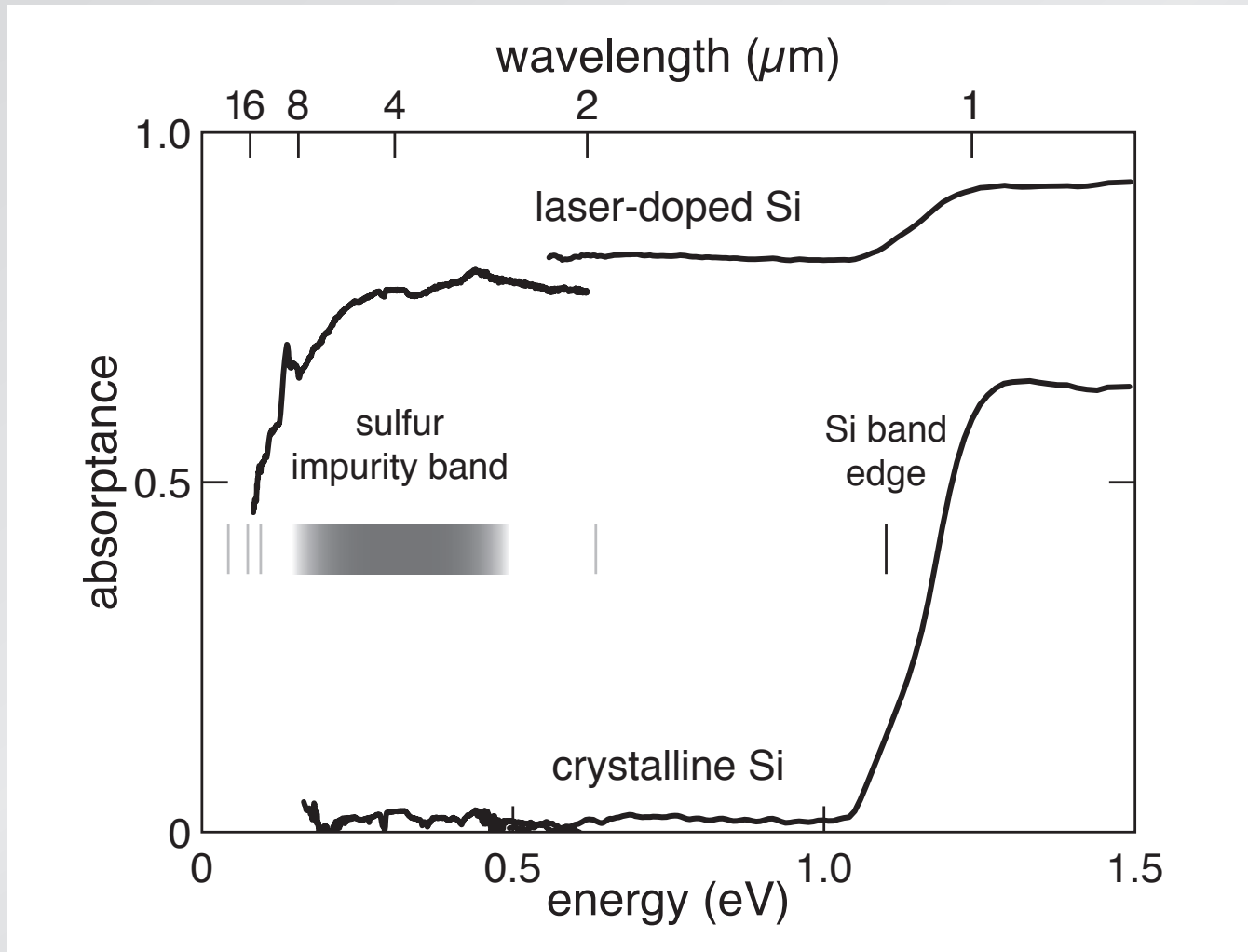
# Optoelectronic properties

## laser-doped S:Si



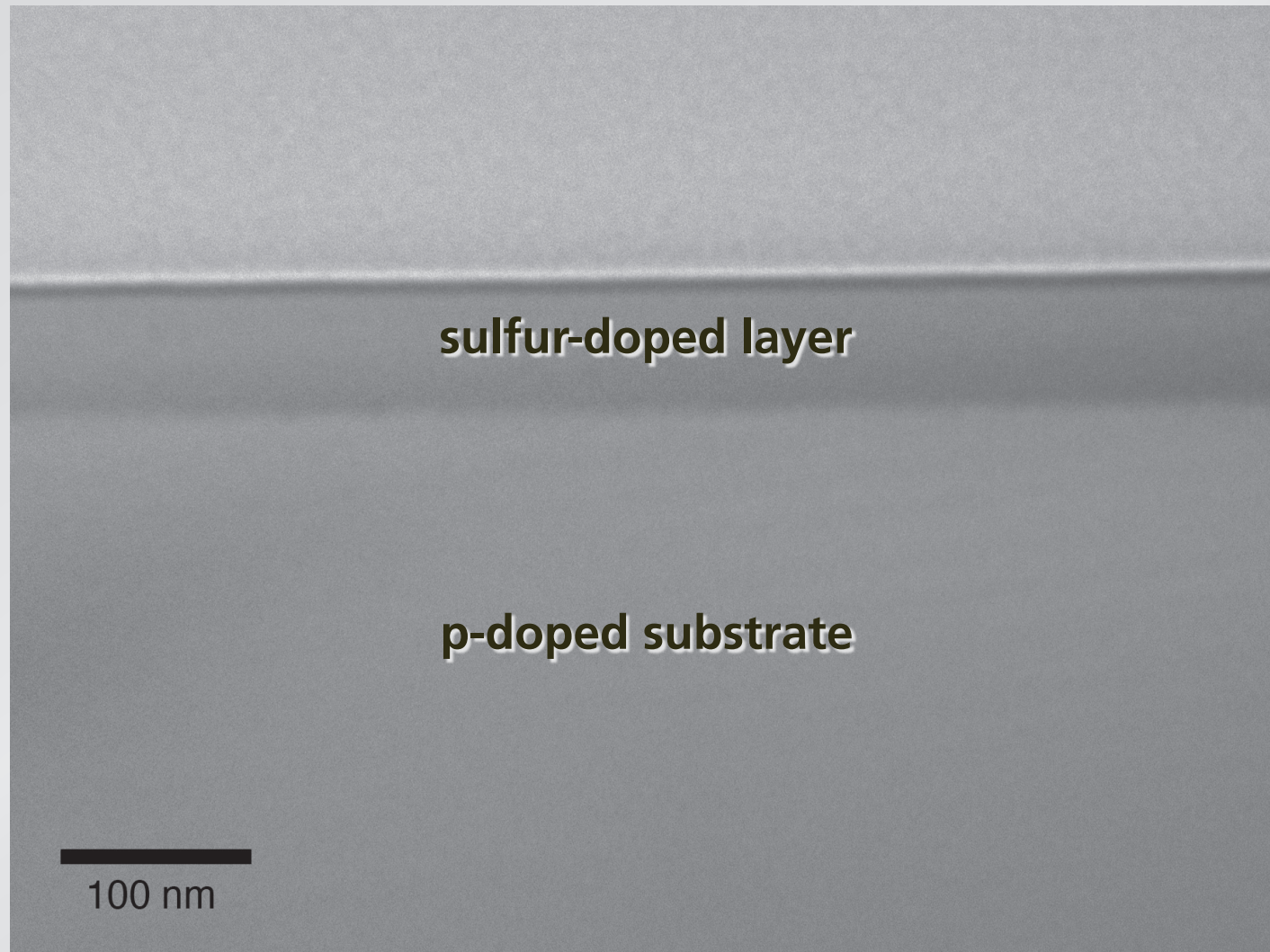
# Optoelectronic properties

## laser-doped S:Si



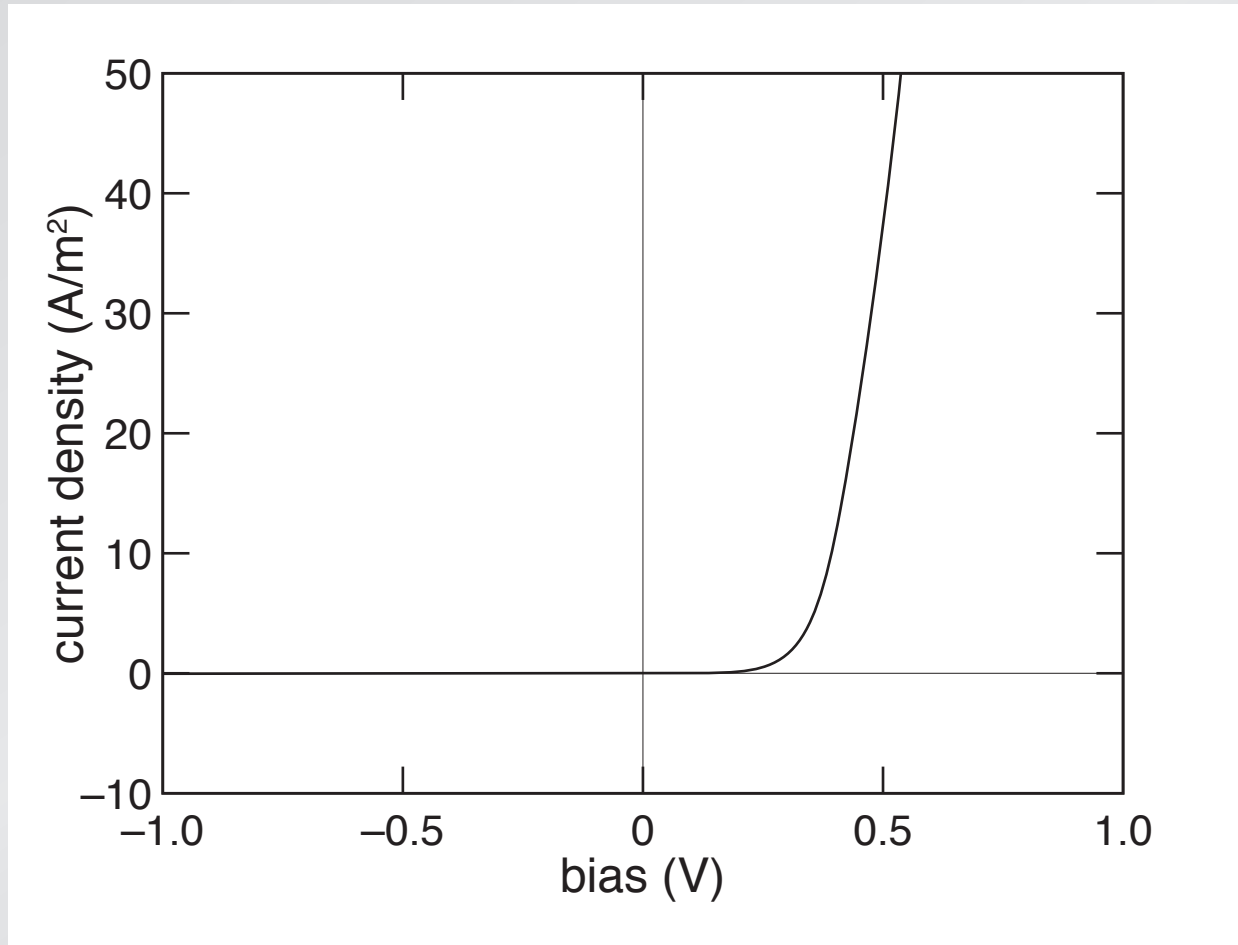
# Optoelectronic properties

should have shallow junction below surface



# Optoelectronic properties

excellent rectification (after annealing)

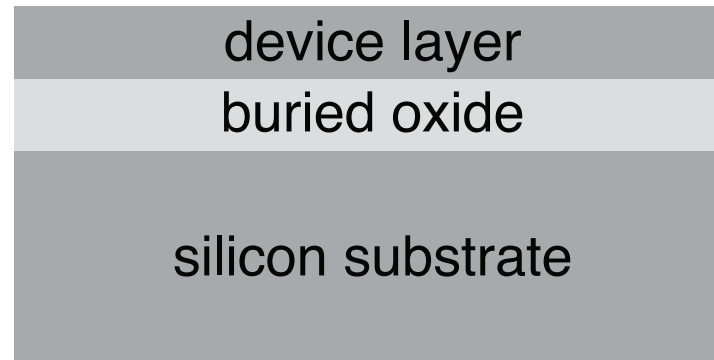


# Optoelectronic properties

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

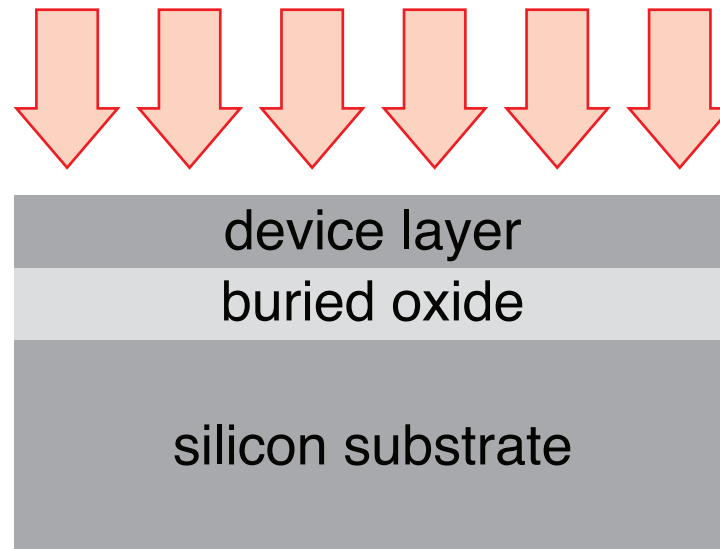
# Optoelectronic properties

isolate surface layer for Hall measurements



# Optoelectronic properties

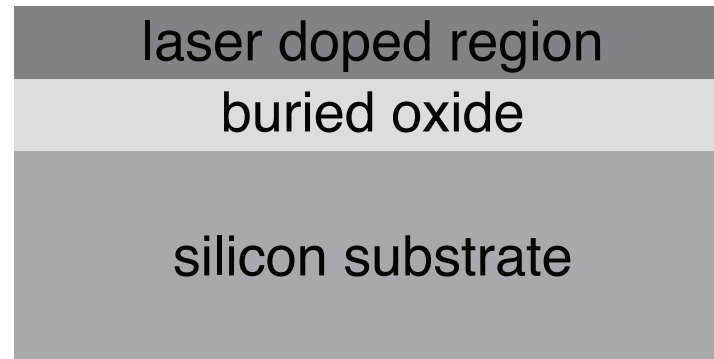
isolate surface layer for Hall measurements





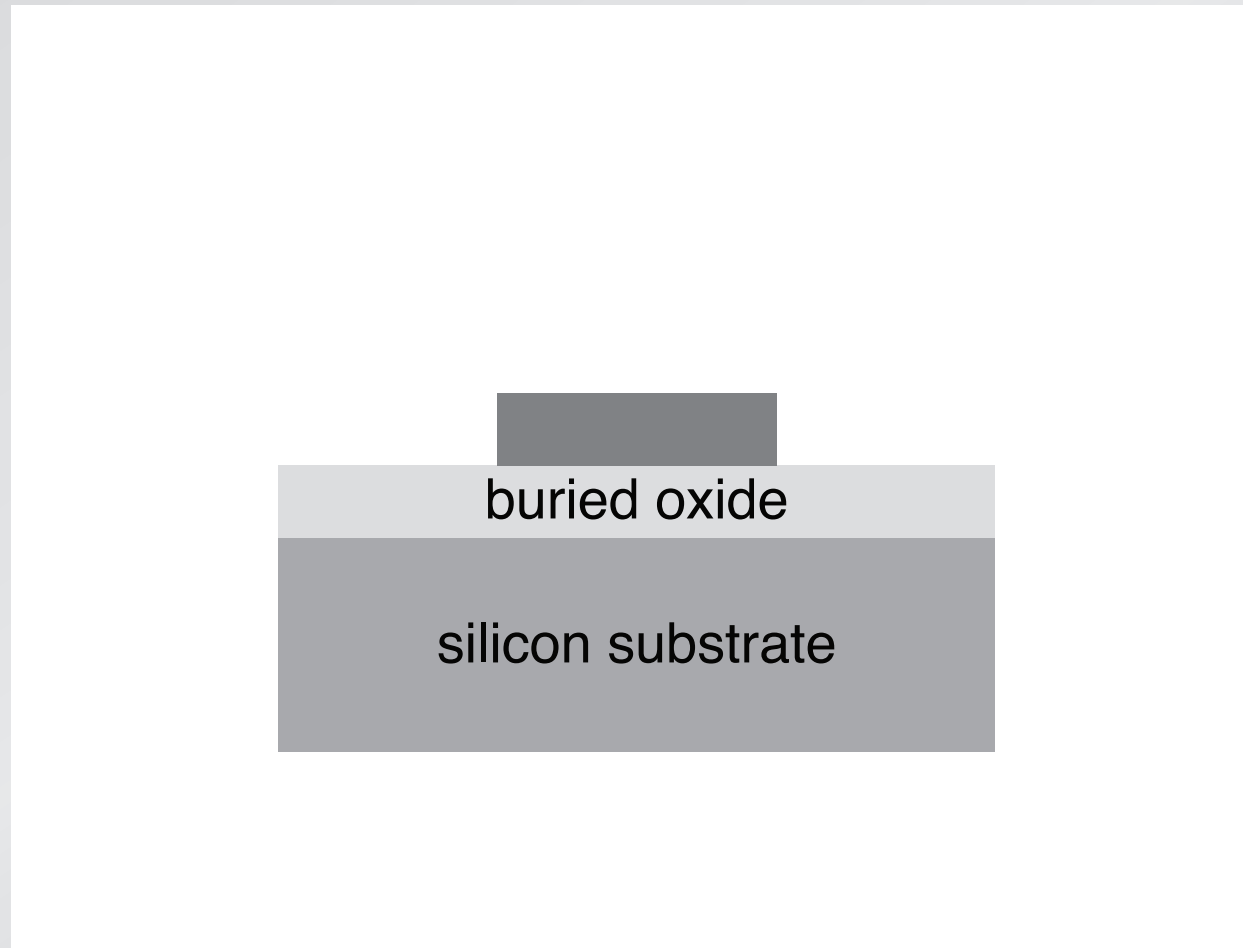
# Optoelectronic properties

isolate surface layer for Hall measurements



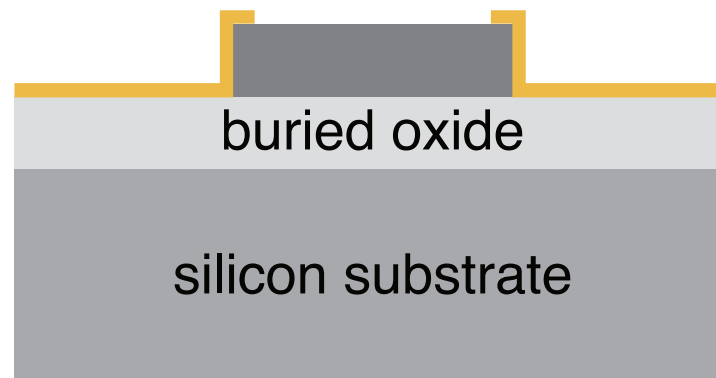
# Optoelectronic properties

isolate surface layer for Hall measurements

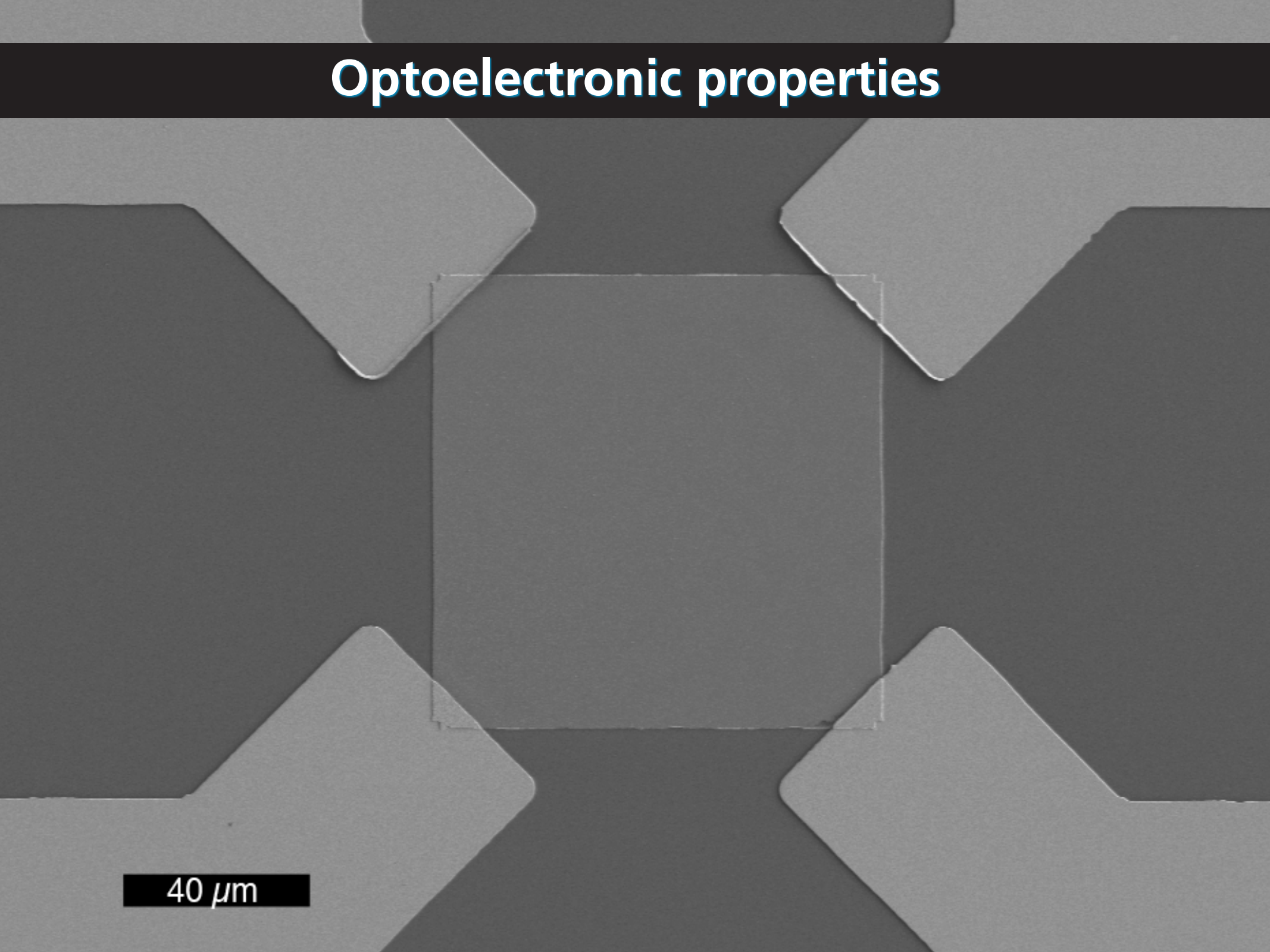


# Optoelectronic properties

isolate surface layer for Hall measurements



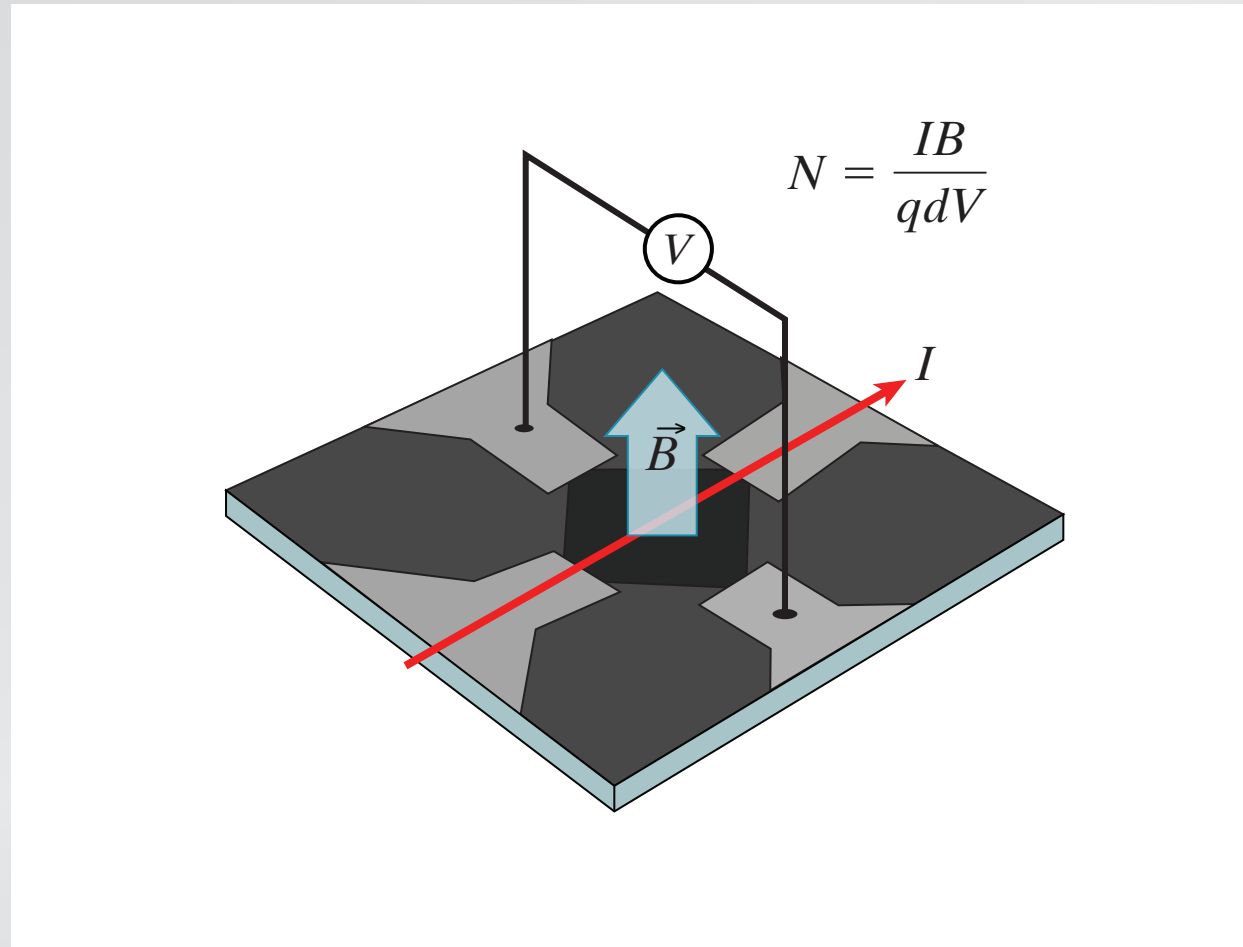
# Optoelectronic properties



40  $\mu\text{m}$

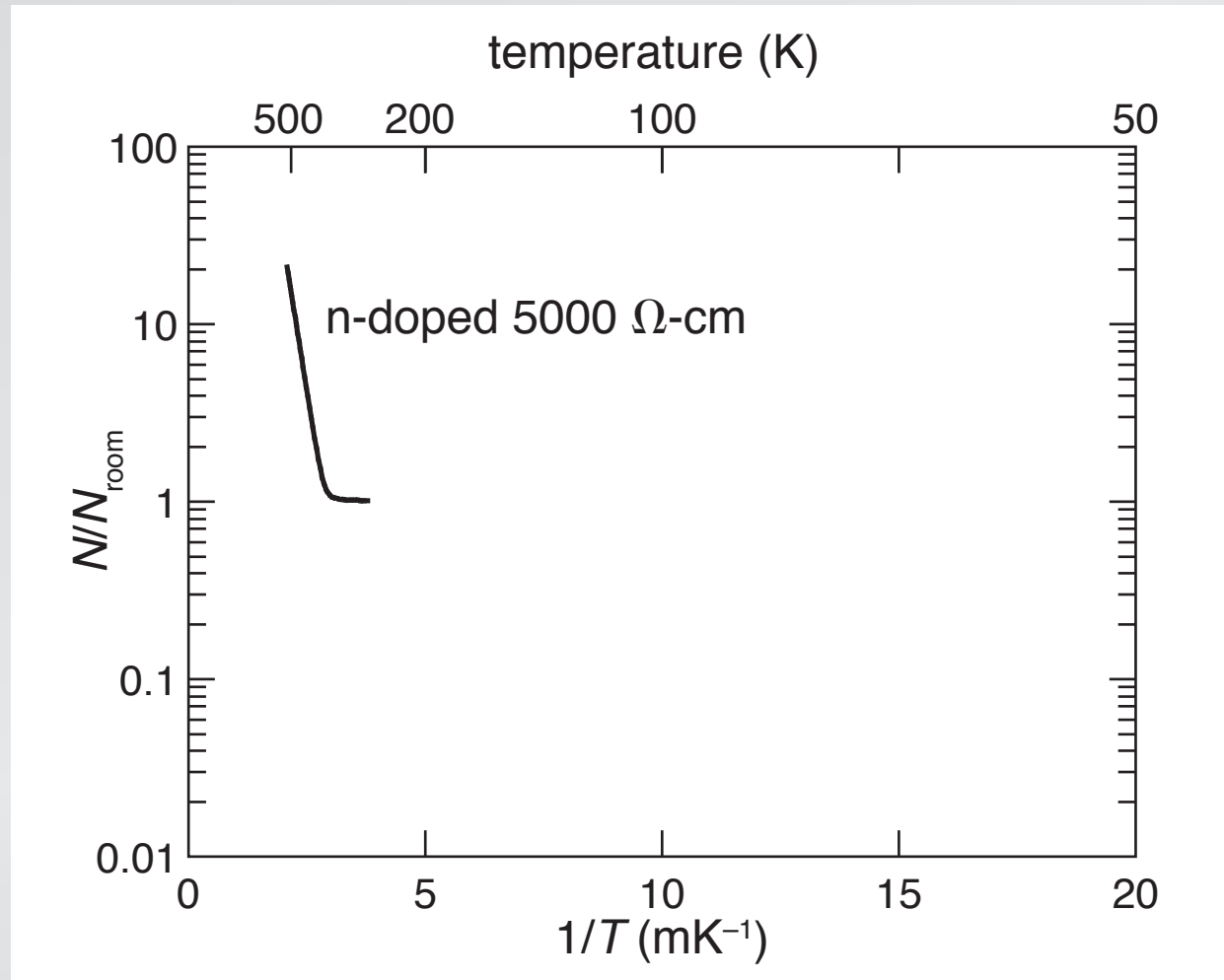
# Optoelectronic properties

## Hall measurements



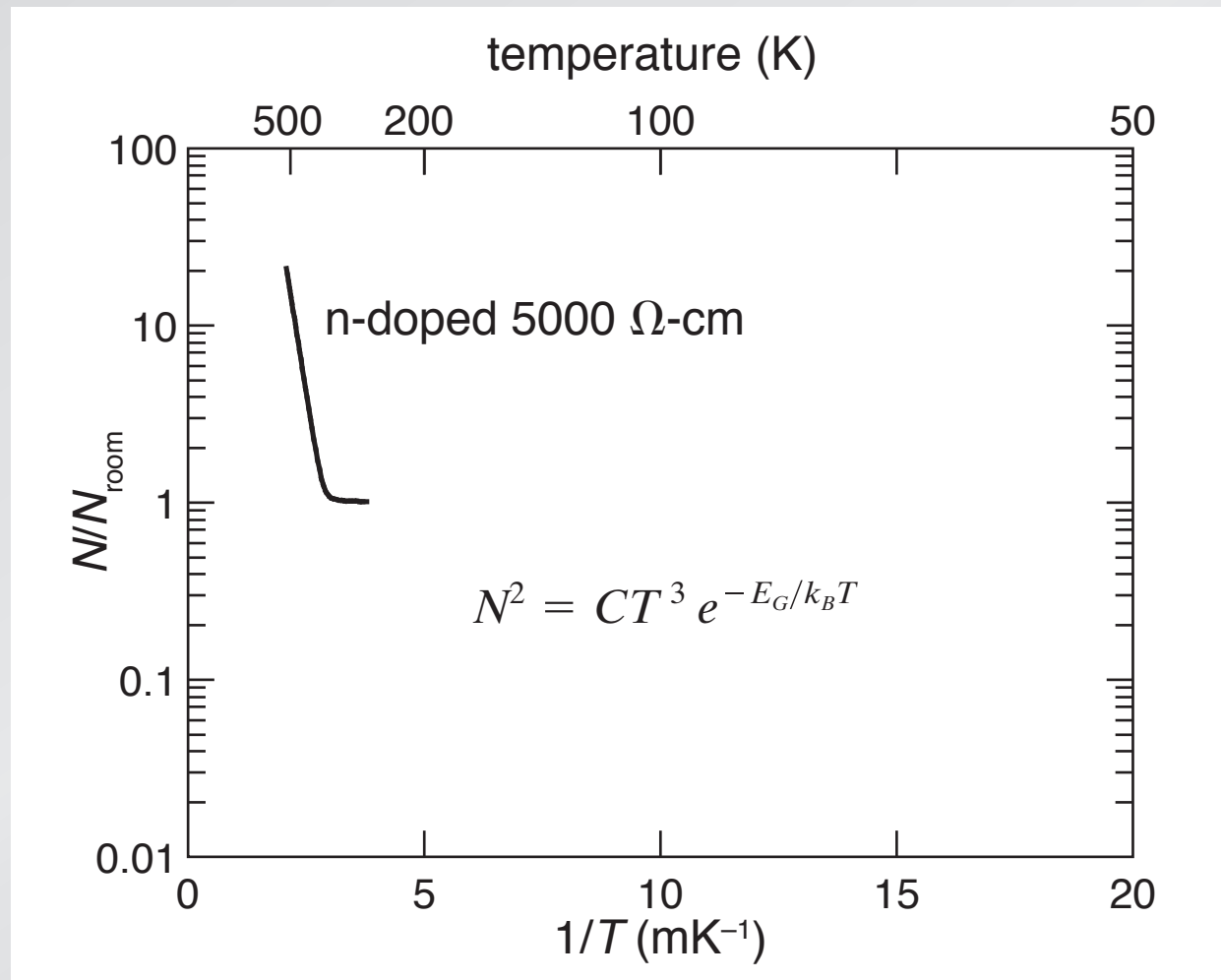
# Optoelectronic properties

## Hall measurements



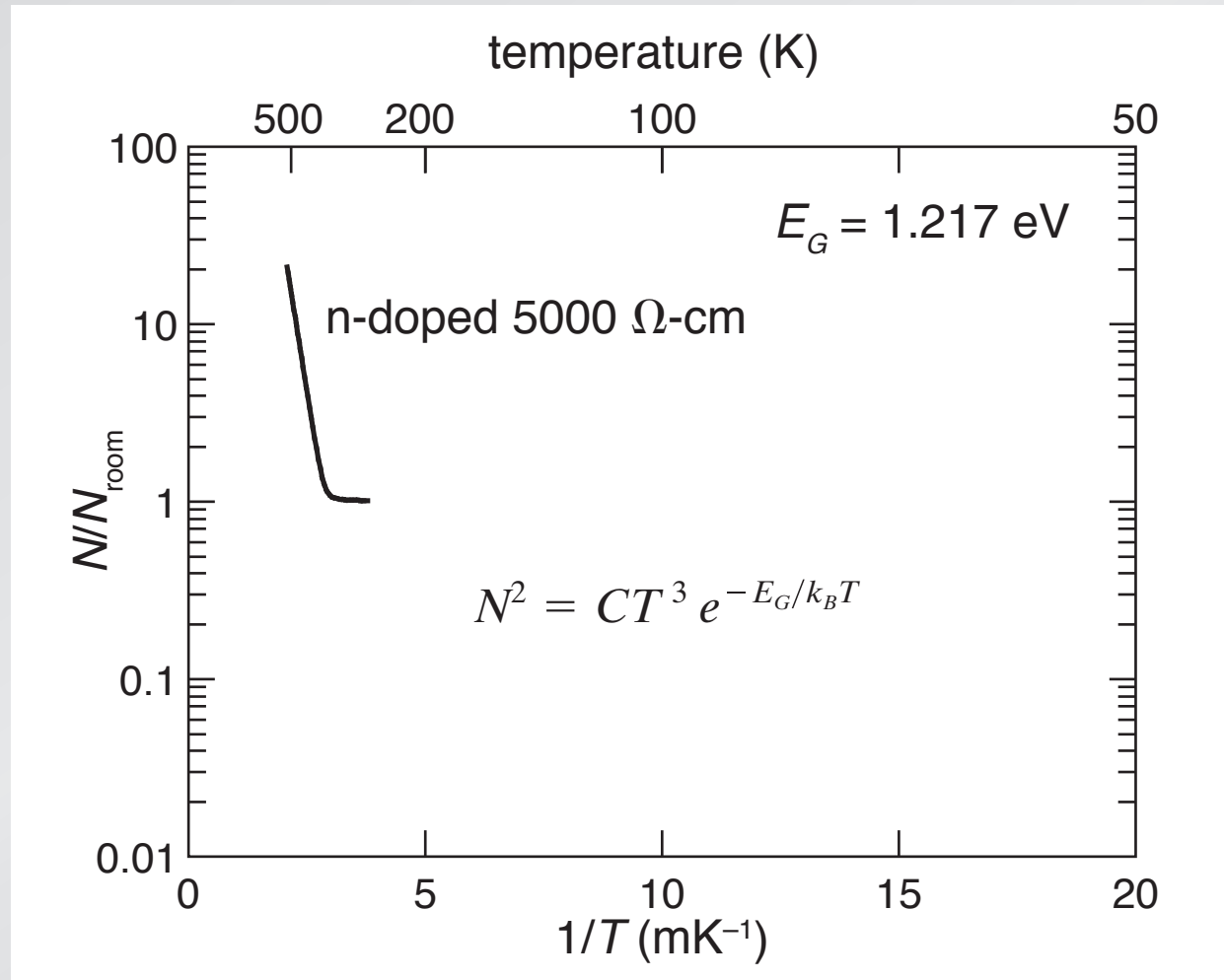
# Optoelectronic properties

## Hall measurements



# Optoelectronic properties

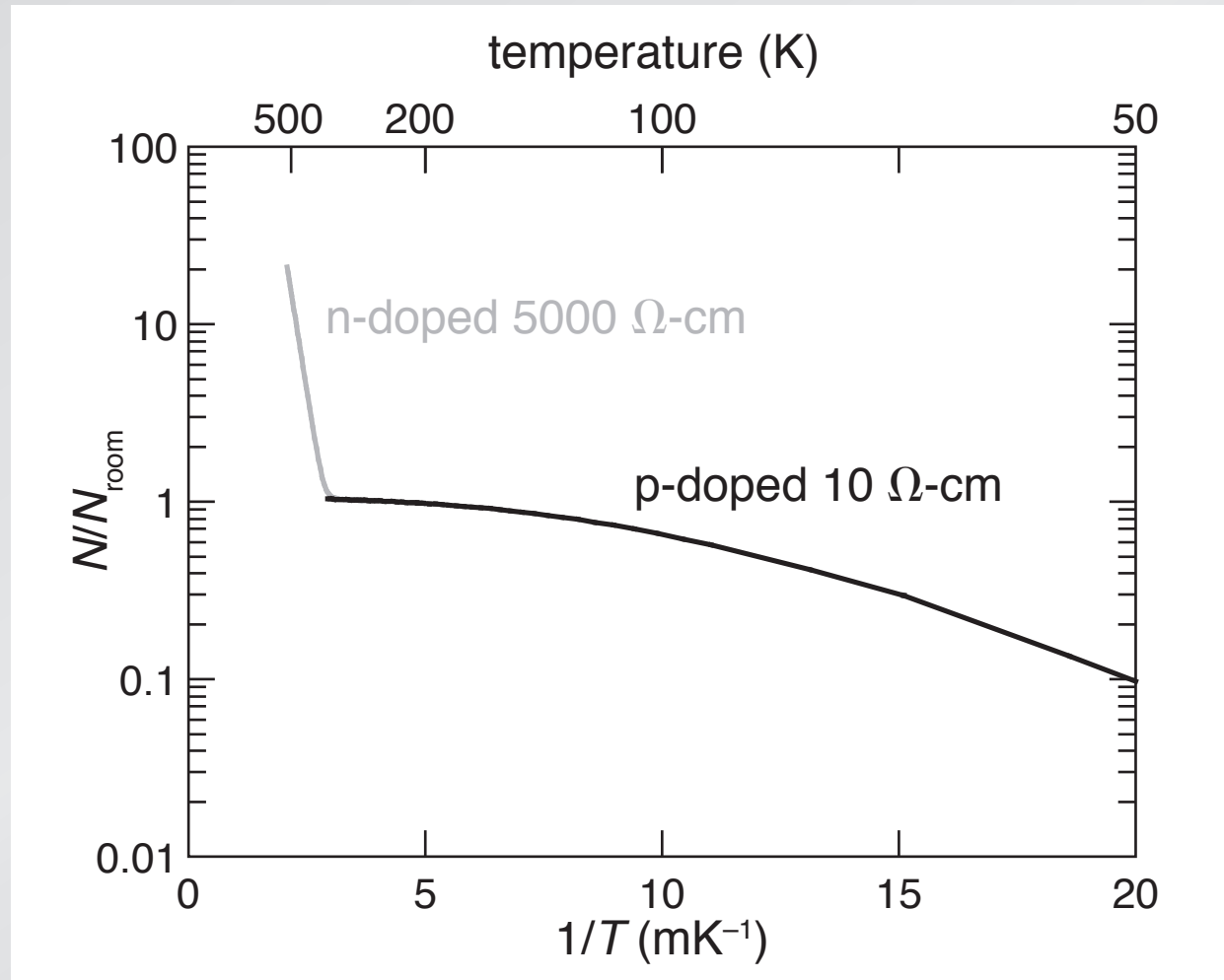
## Hall measurements





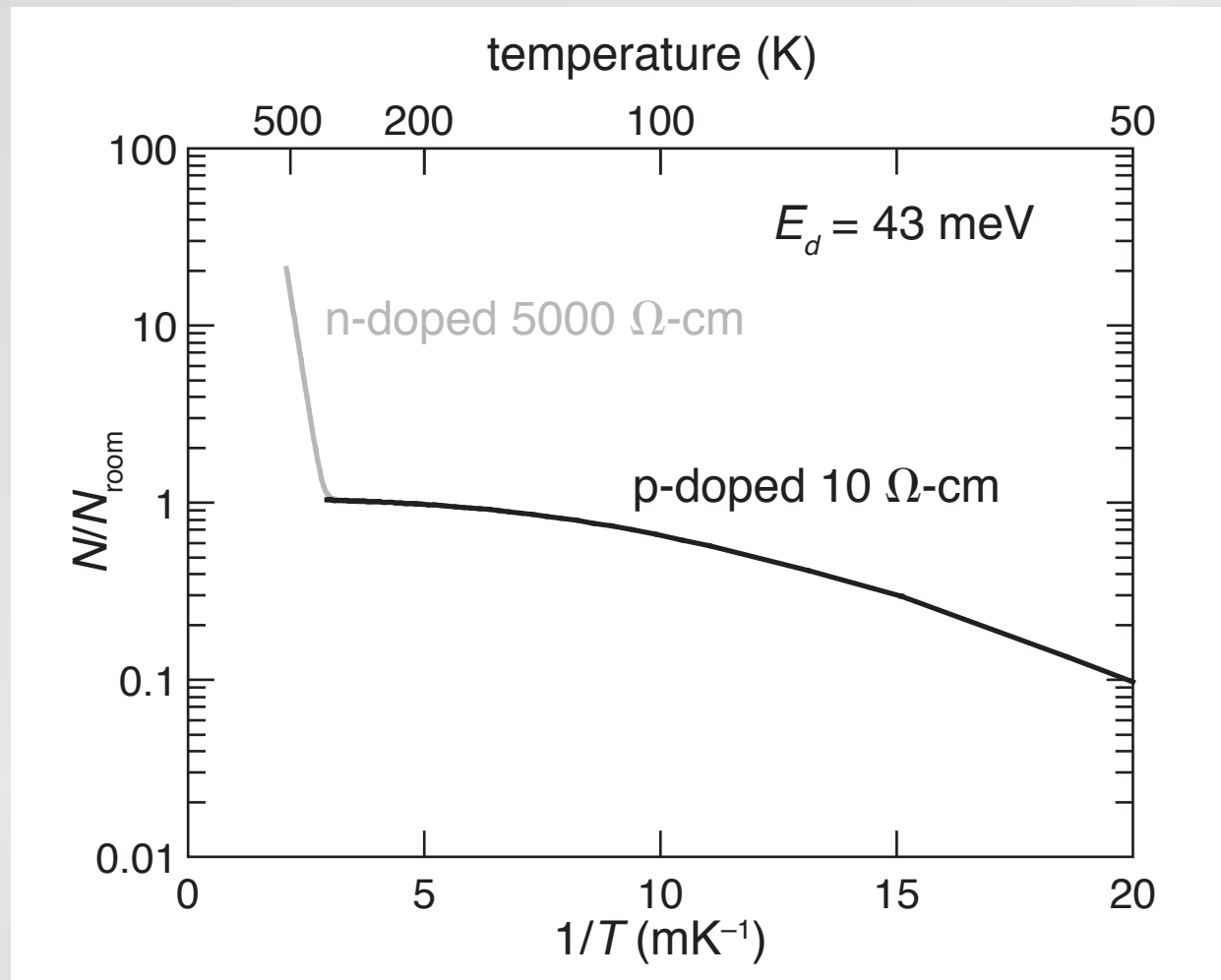
# Optoelectronic properties

## Hall measurements



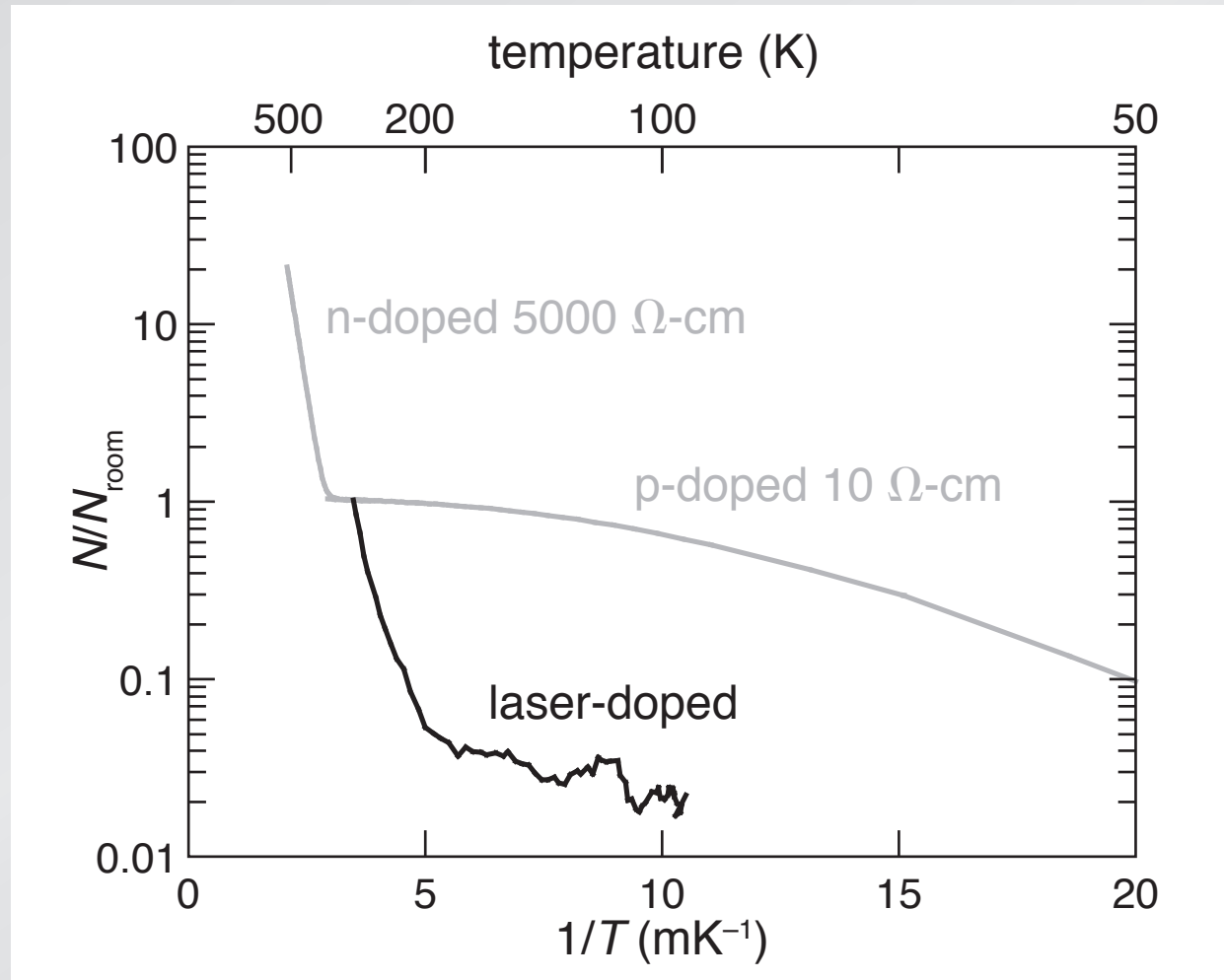
# Optoelectronic properties

## Hall measurements



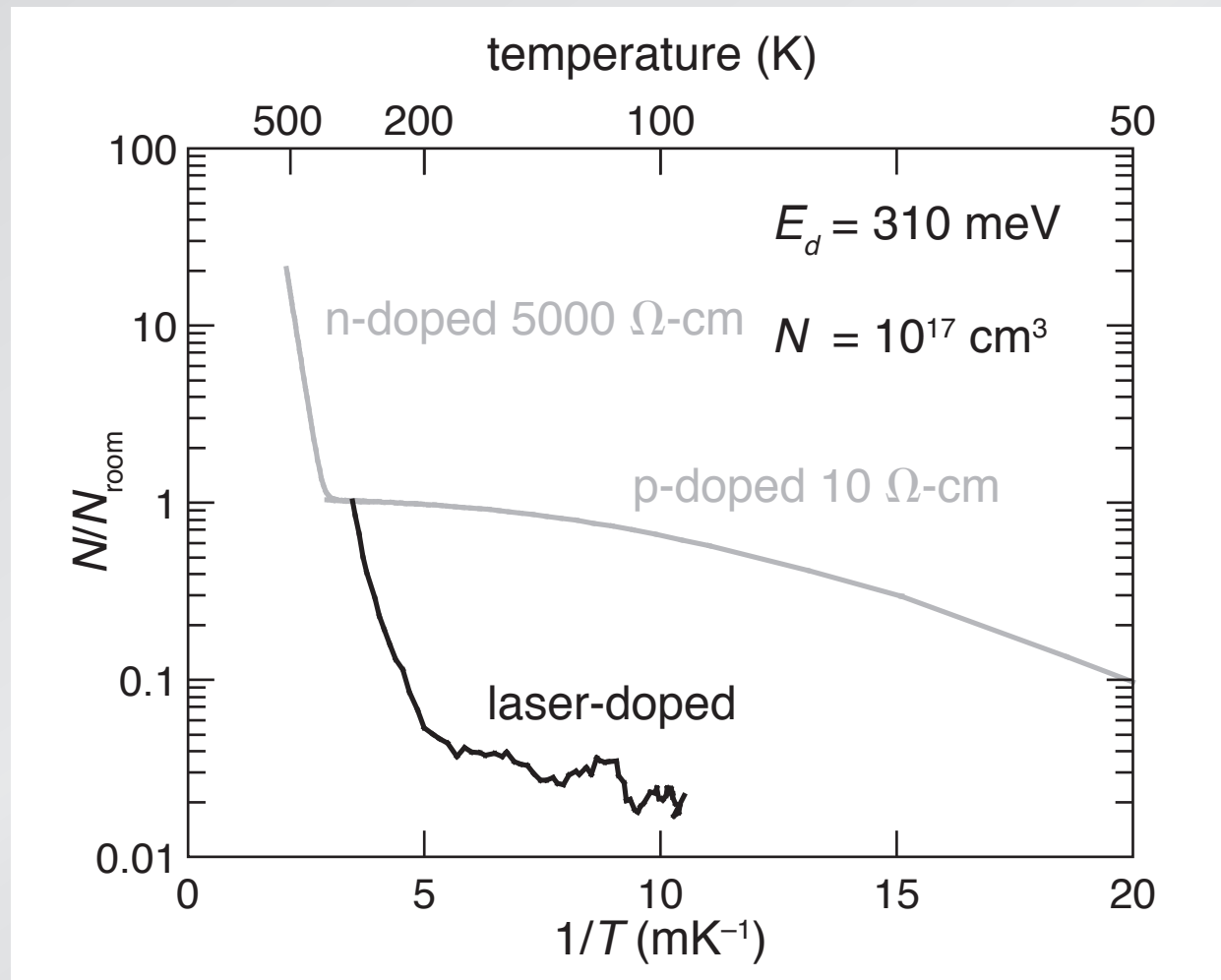
# Optoelectronic properties

## Hall measurements



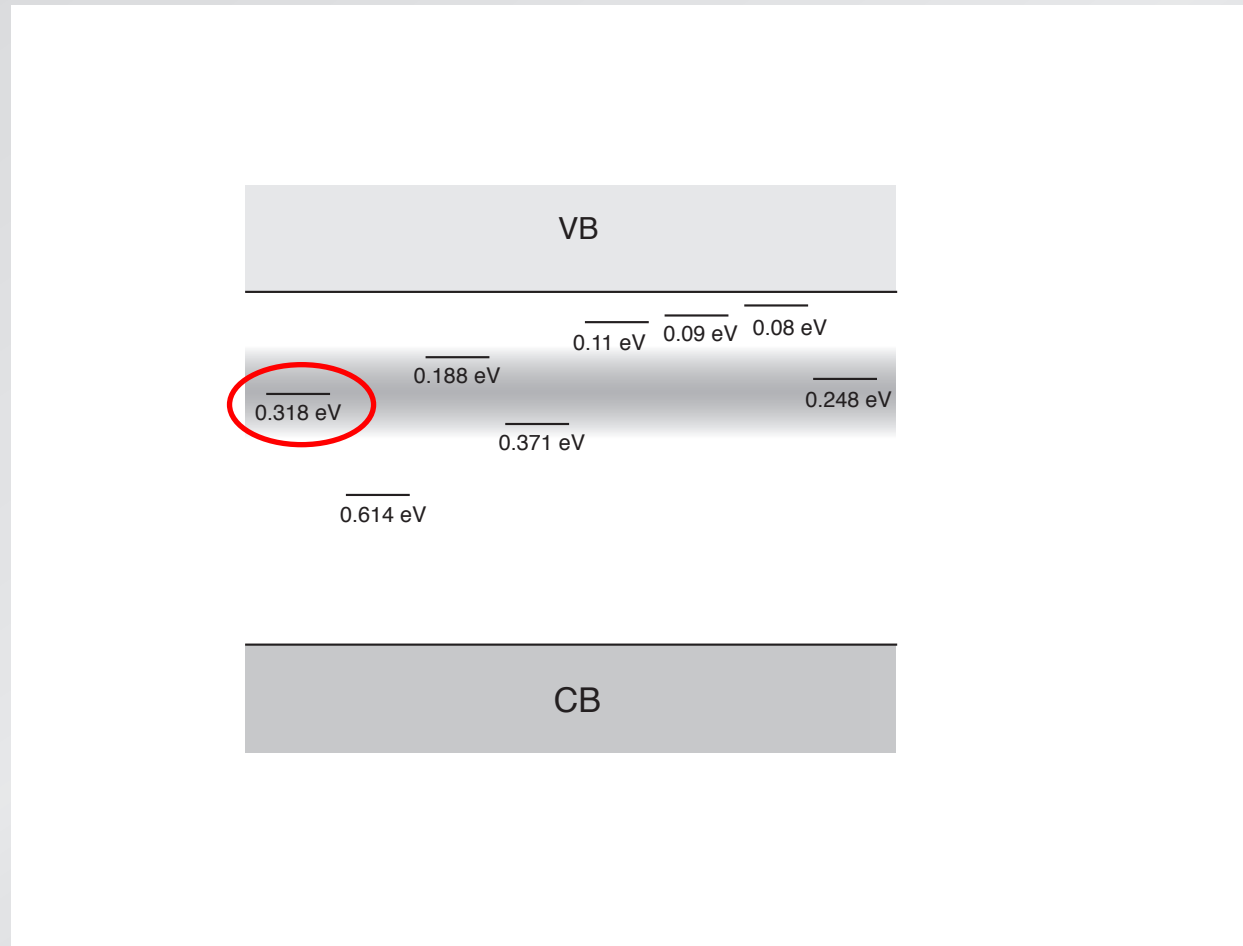
# Optoelectronic properties

## Hall measurements



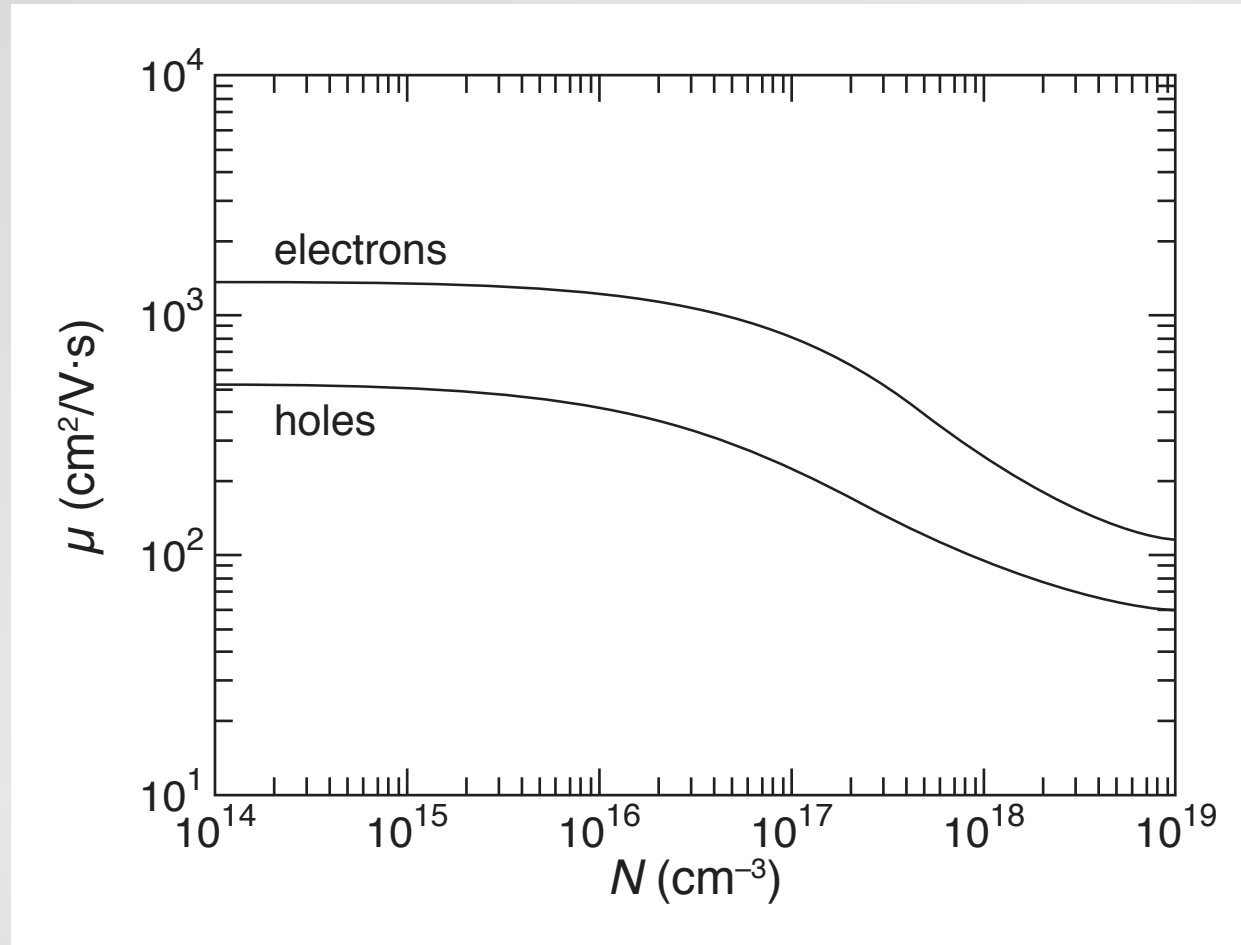
# Optoelectronic properties

impurity (donor) band centered at 310 meV



# Optoelectronic properties

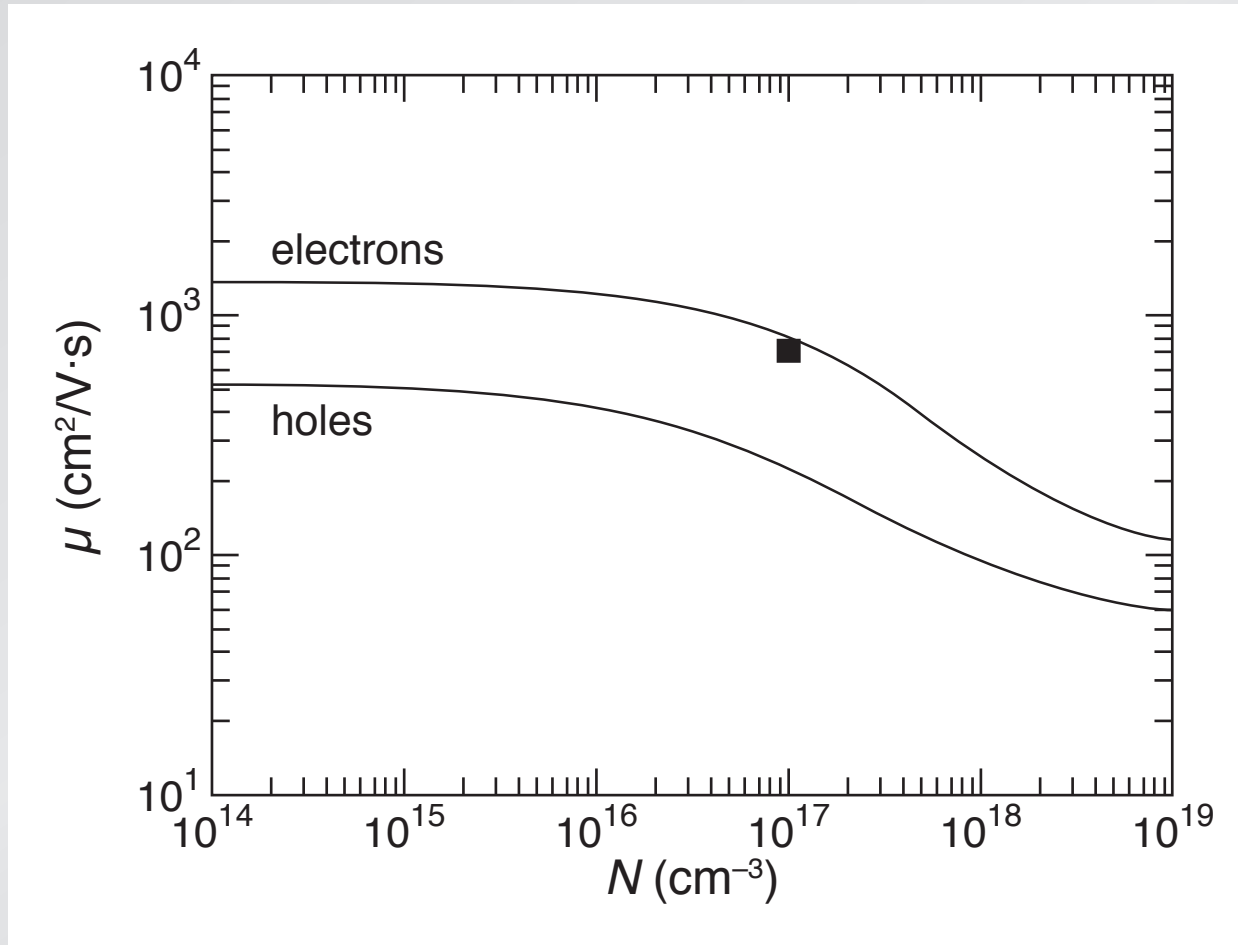
## majority carrier mobility



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

# Optoelectronic properties

## majority carrier mobility



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

# Optoelectronic properties

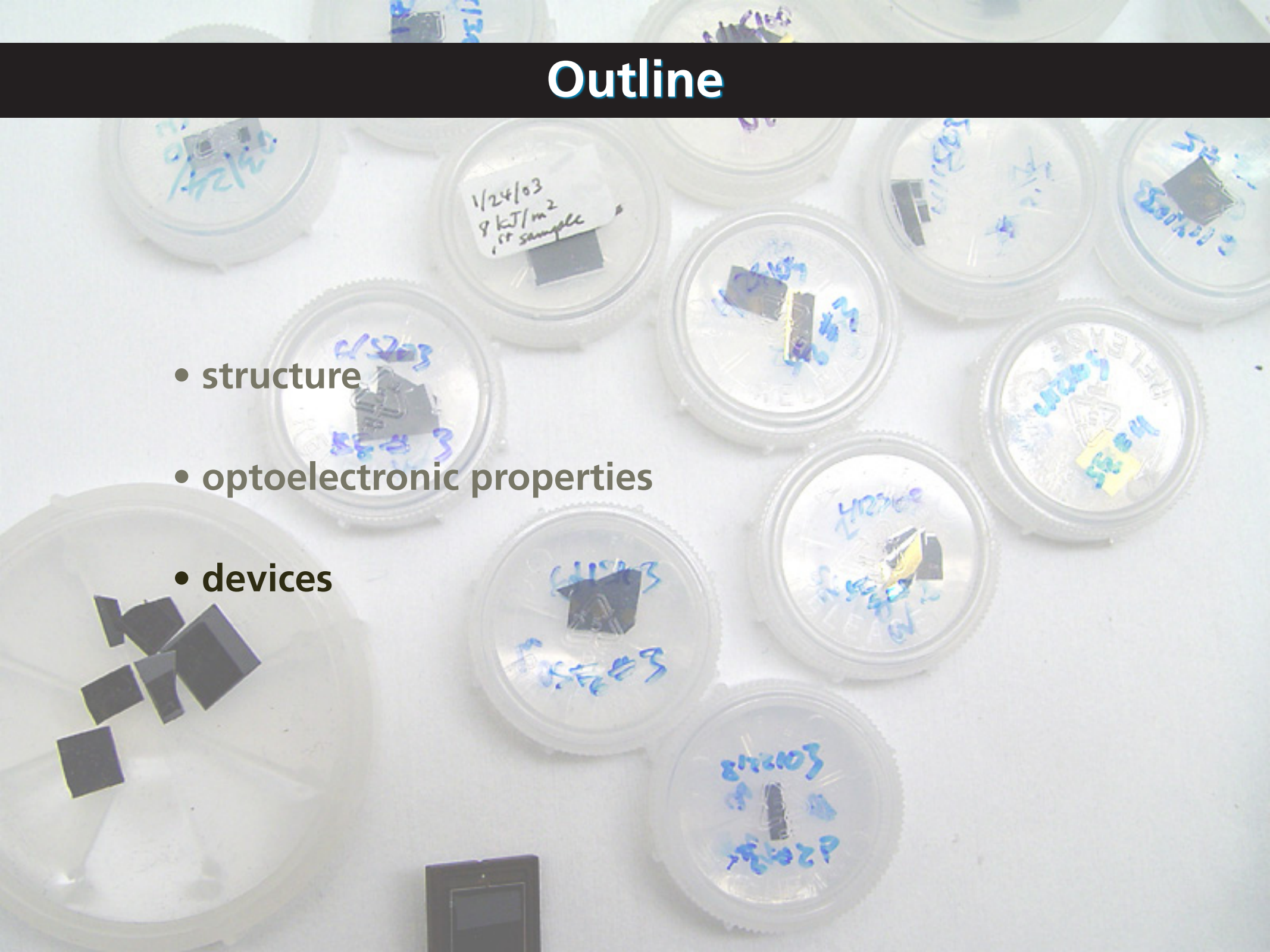
## Things to keep in mind

- 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



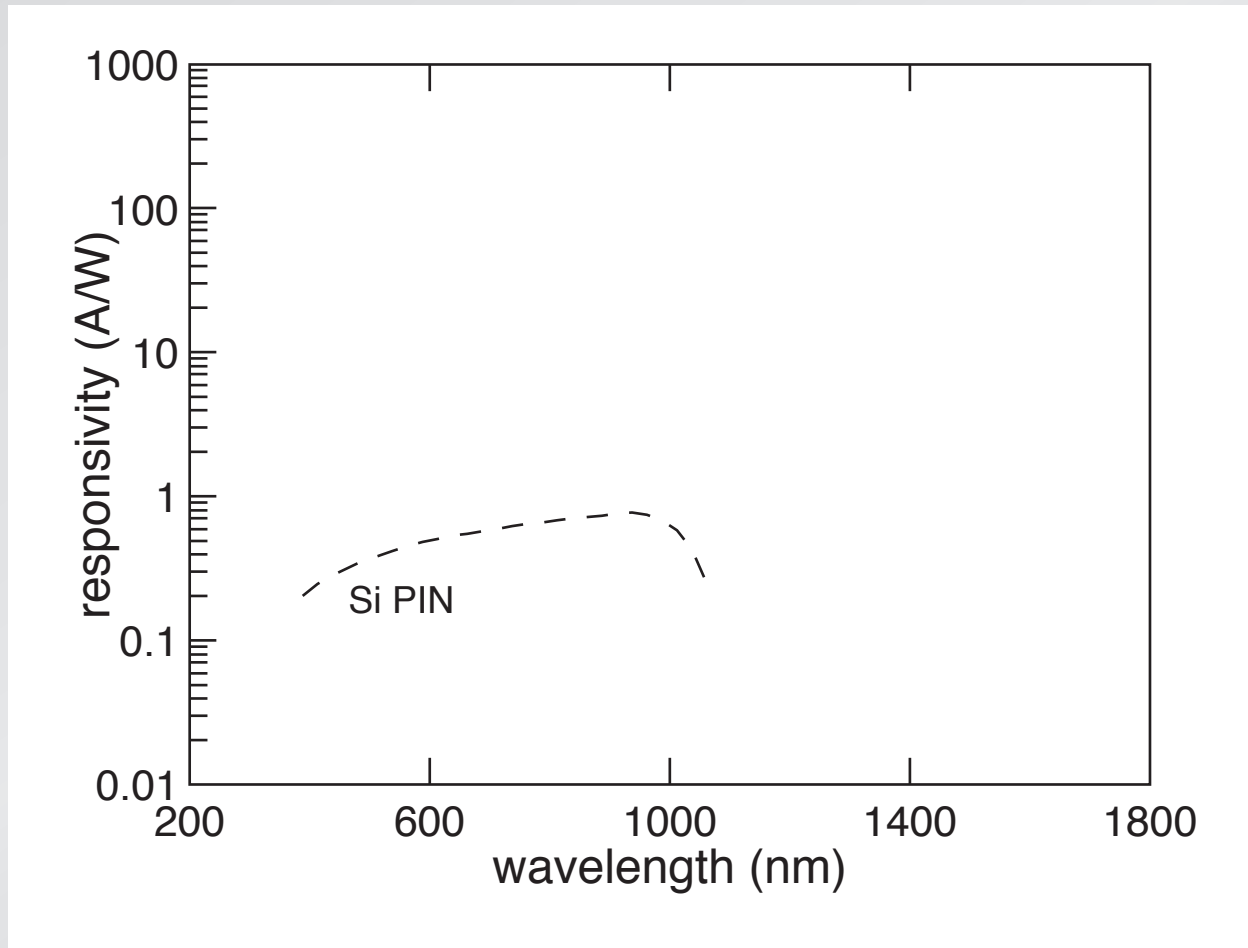
# Outline

- structure
- optoelectronic properties
- devices



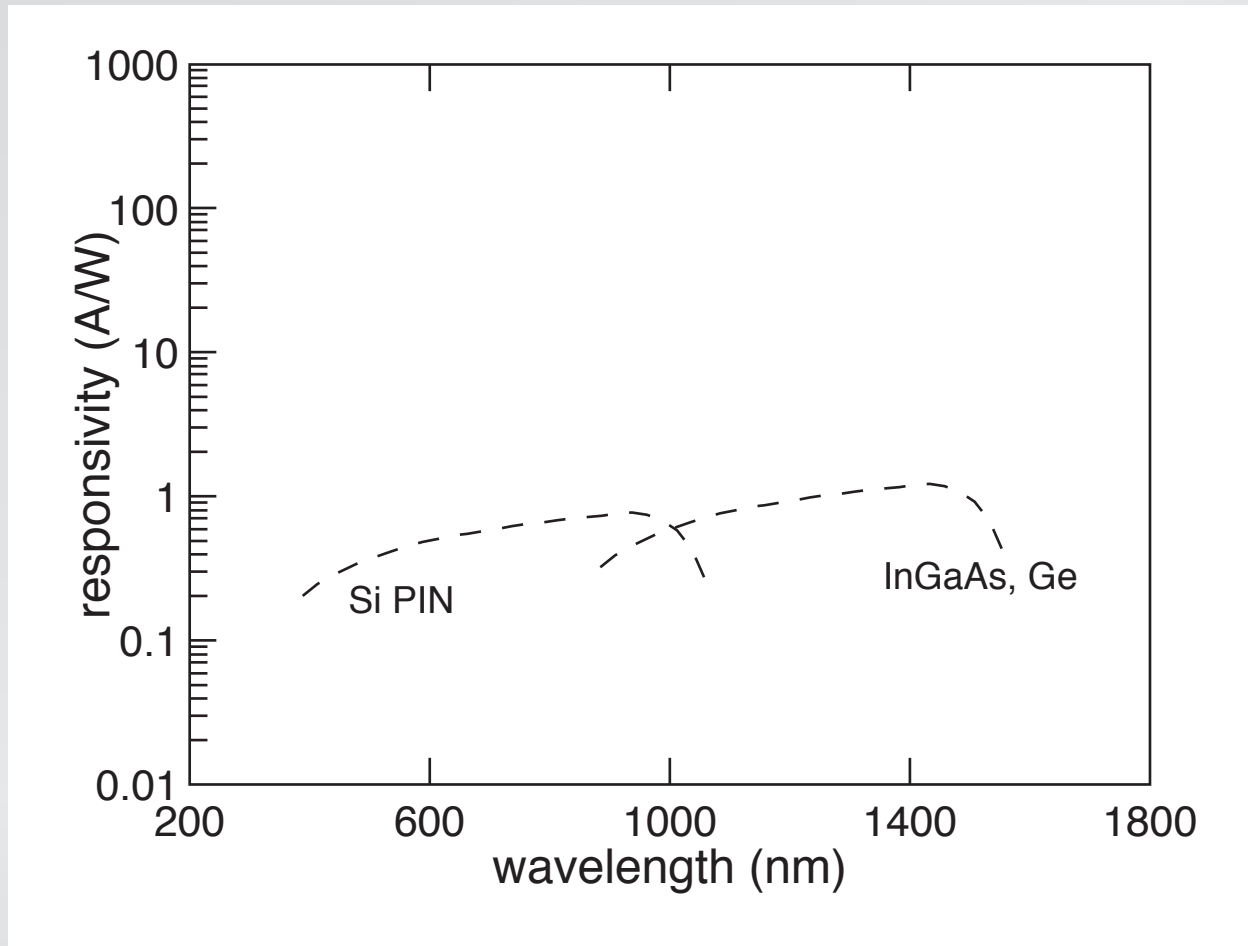
# Devices

## responsivity



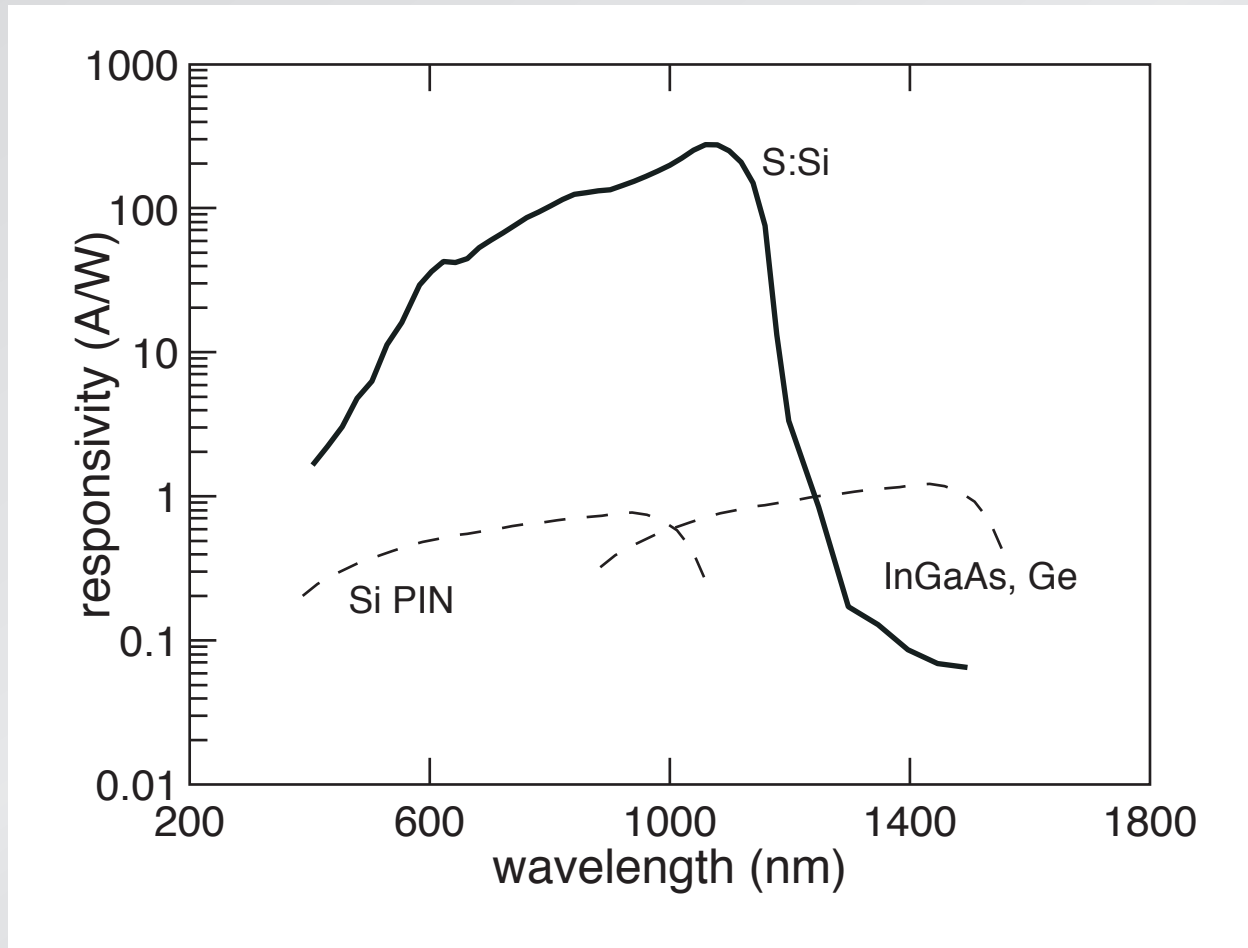
# Devices

## responsivity



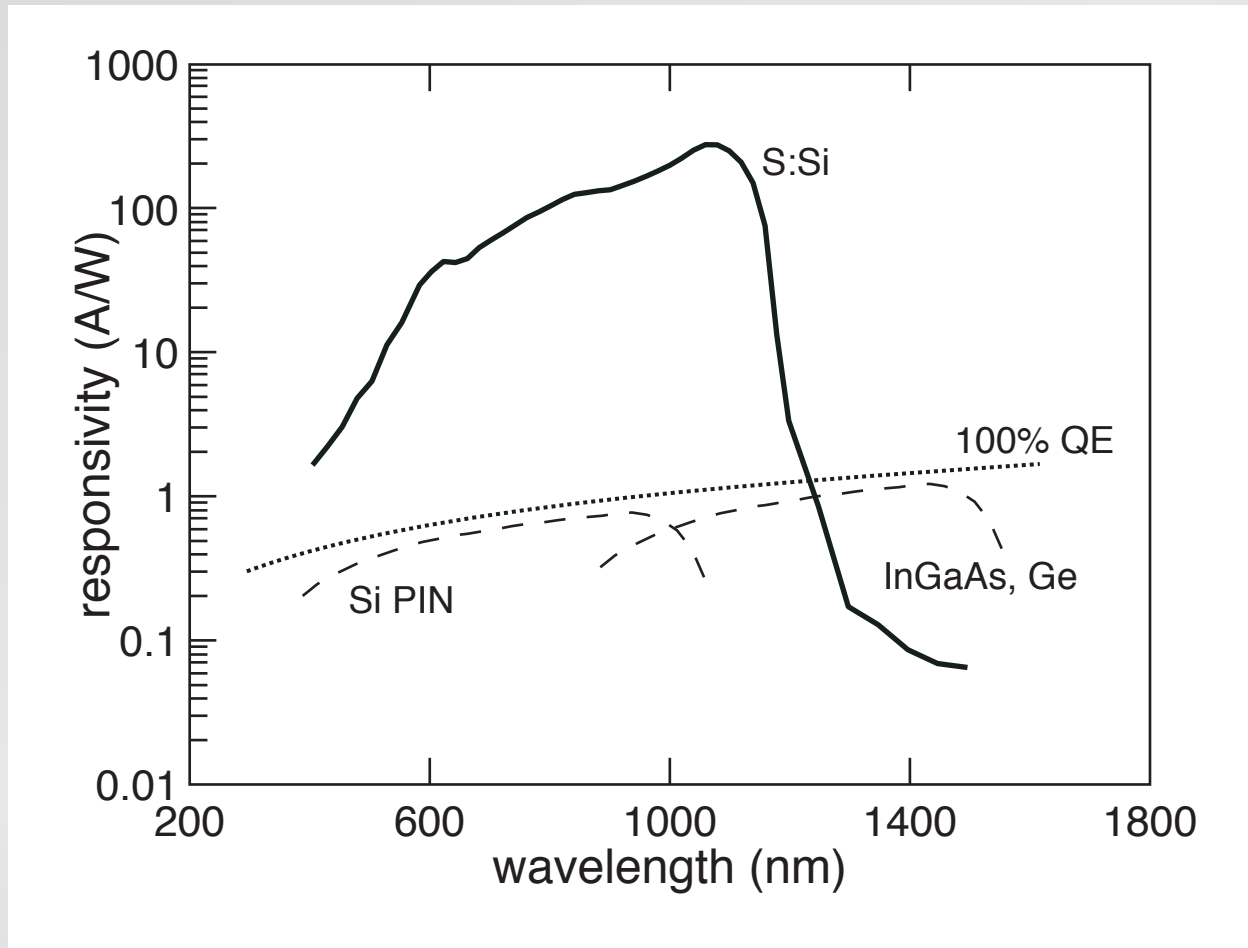
# Devices

## responsivity



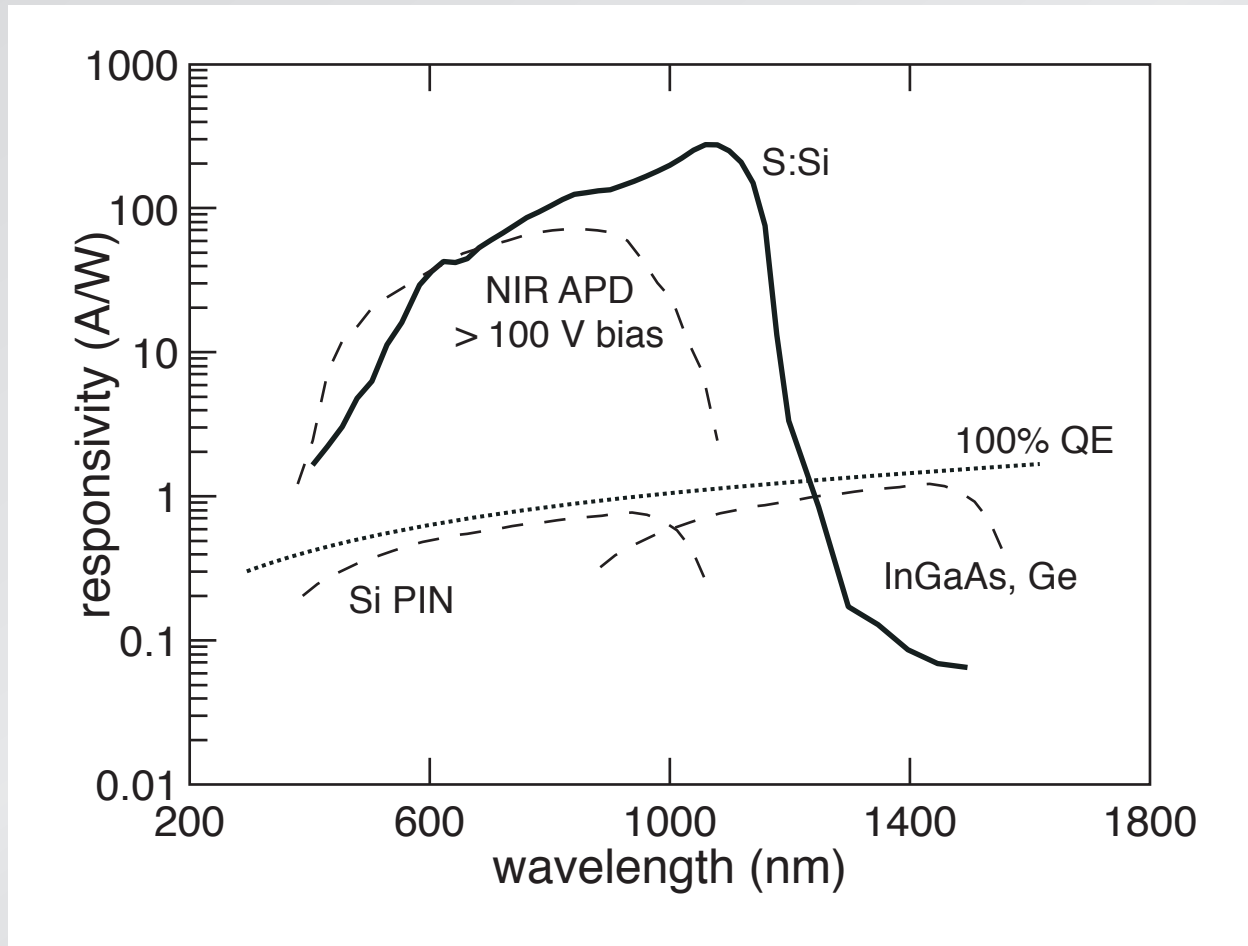
# Devices

## responsivity



# Devices

## responsivity



# Devices

**What causes gain?**

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

# Devices

## 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>

# 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, purple, and cyan, with some featuring small white stars and dots. The scraps are of different sizes and are partially overlapping each other. 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**

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