

# Black silicon



Technical University of Denmark  
Copenhagen, Denmark, 16 June 2009

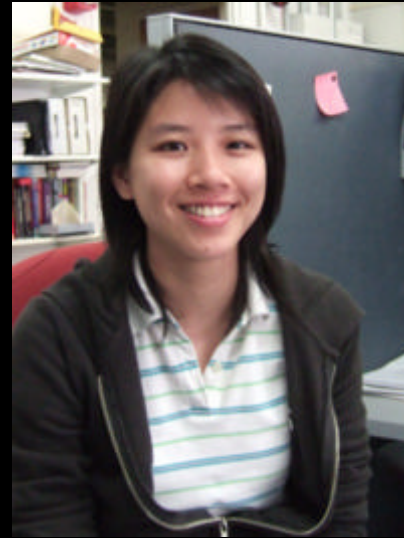




**Mark Winkler**



**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)**

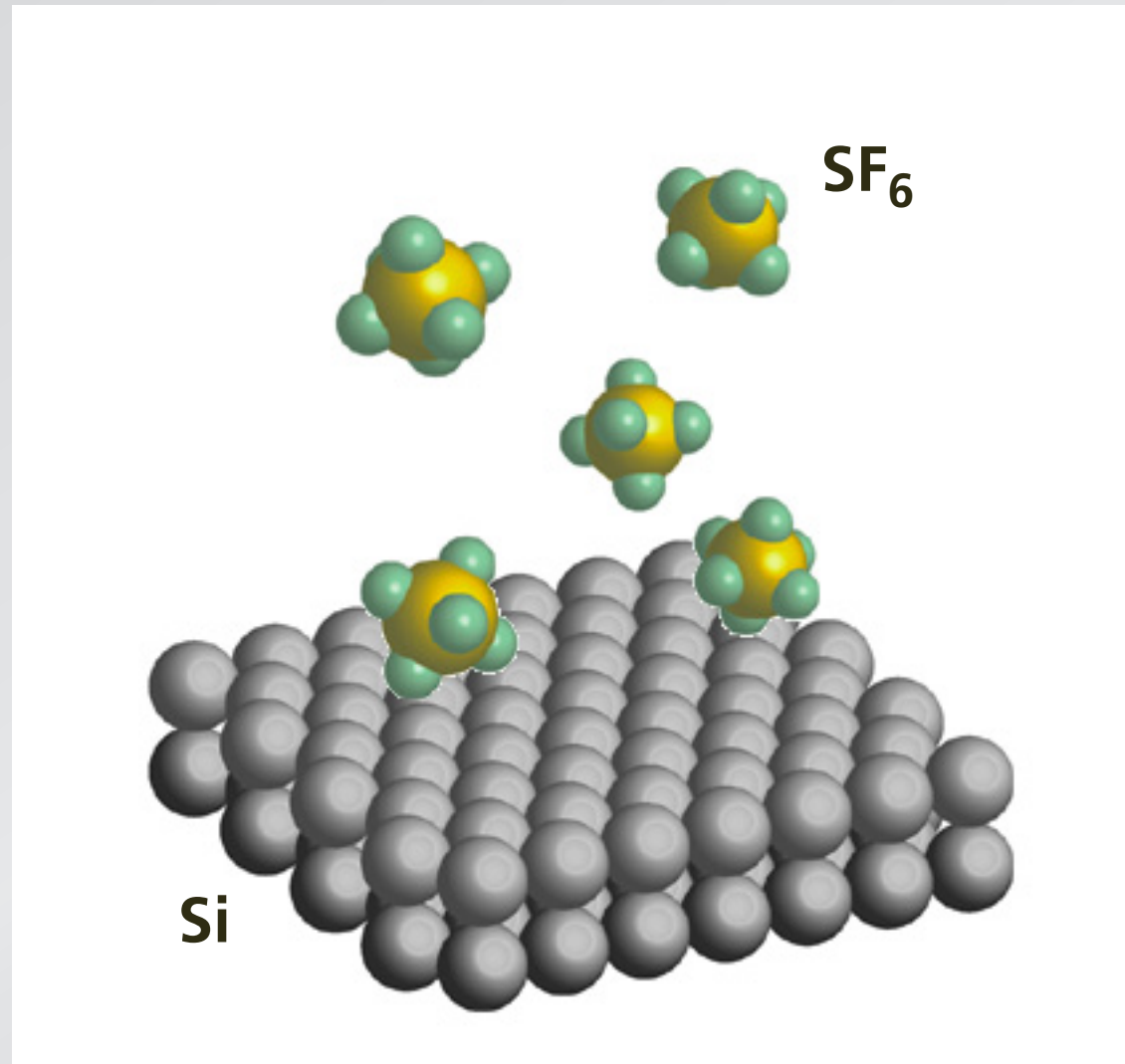
**Dr. François Génin (LLNL)  
Mark Wall (LLNL)**

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

**Dr. Pat Maloney (NVSED)**

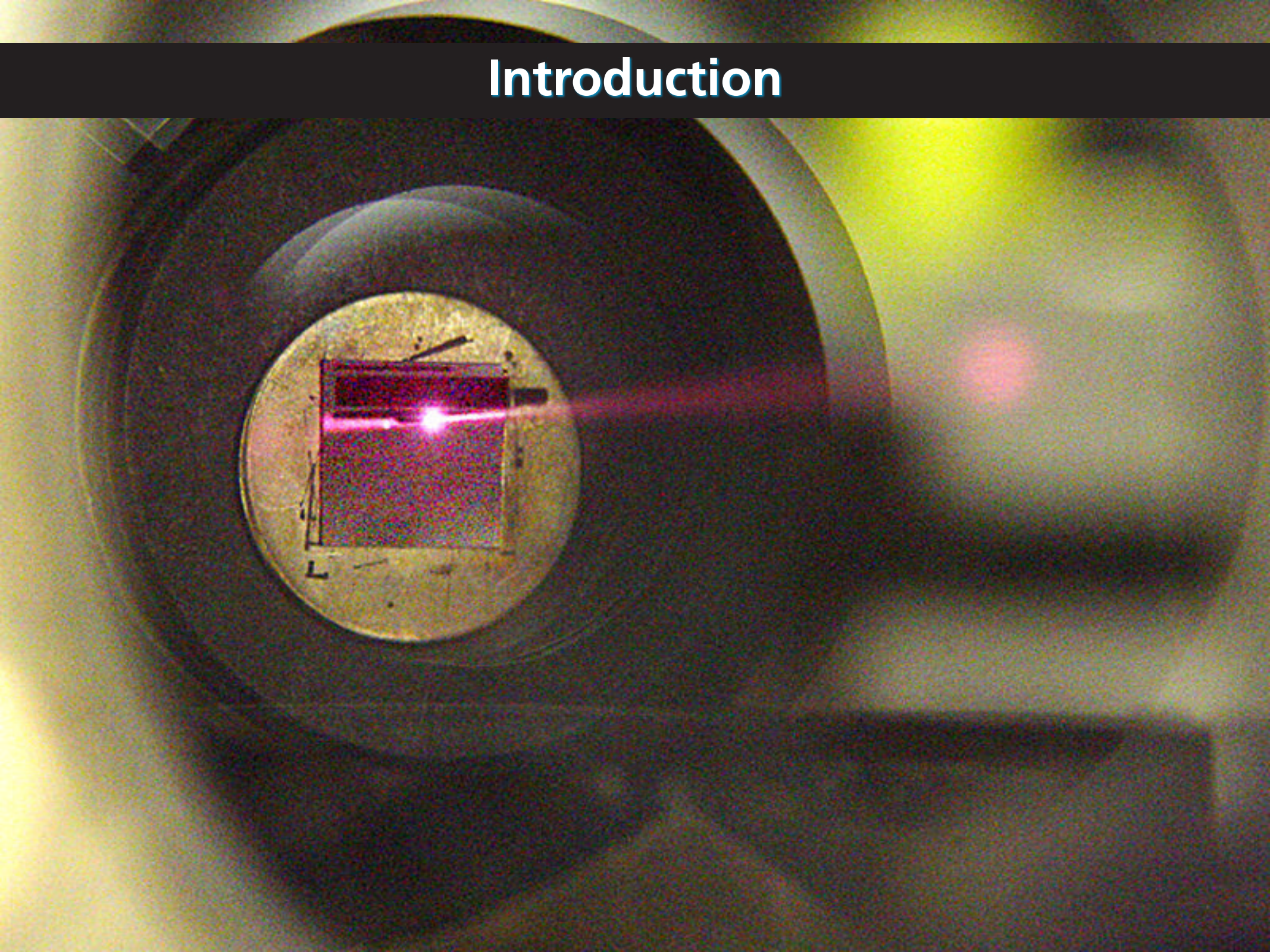
**Dr. Jeffrey Warrander (ARDEC)**

# Introduction



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

# Introduction

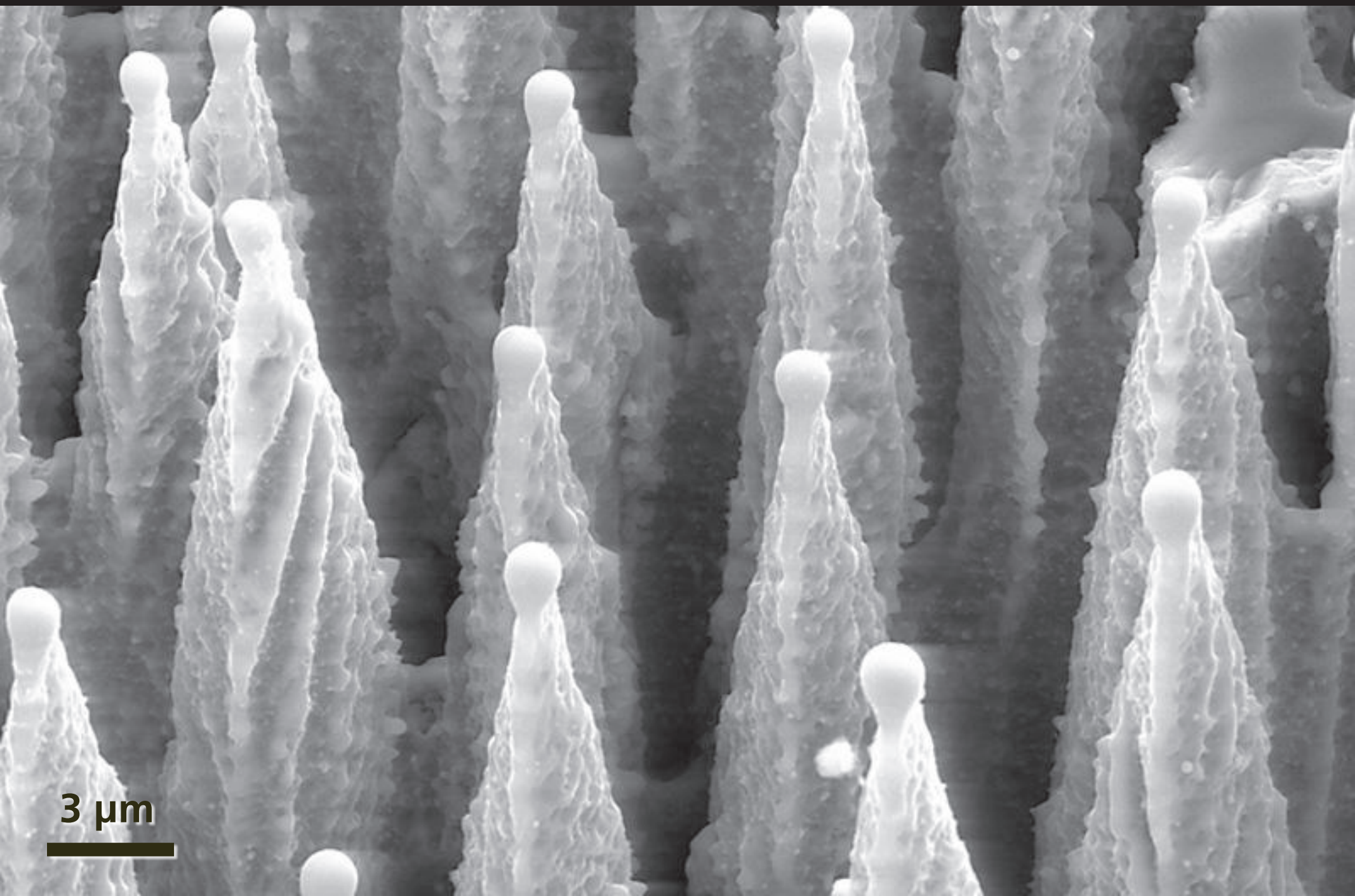


# Introduction



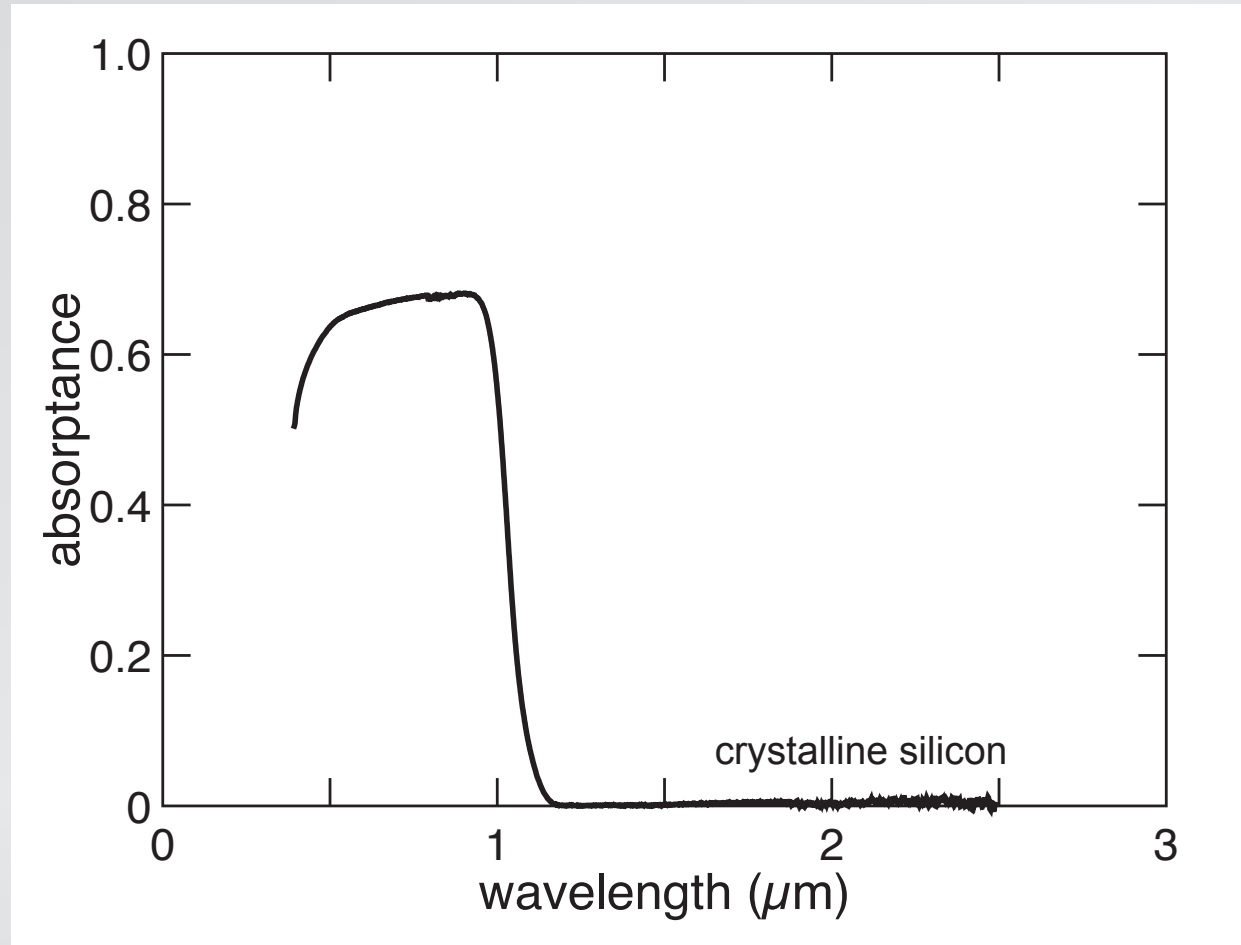
**"black silicon"**

# Introduction



# Introduction

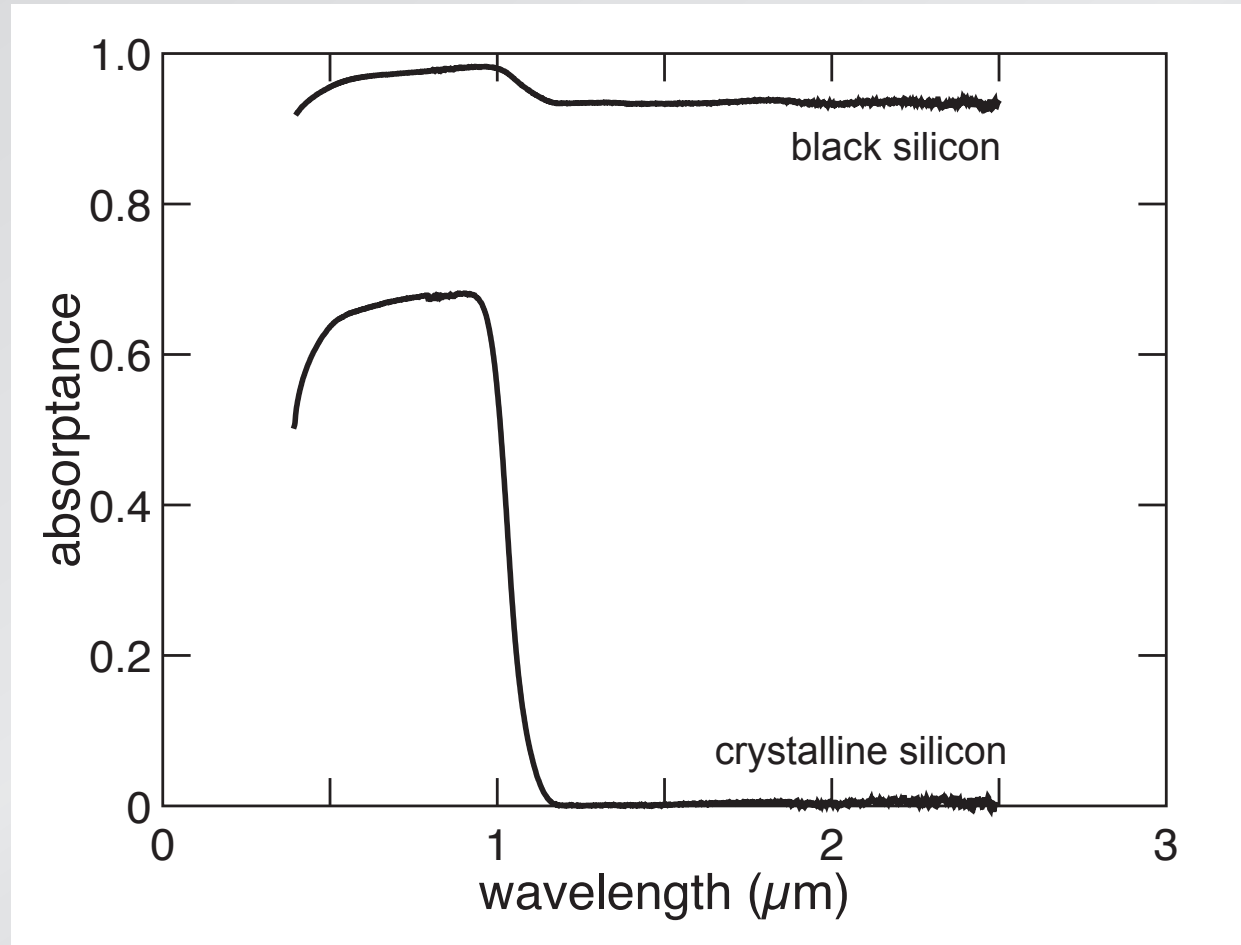
absorptance ( $1 - R_{int} - T_{int}$ )



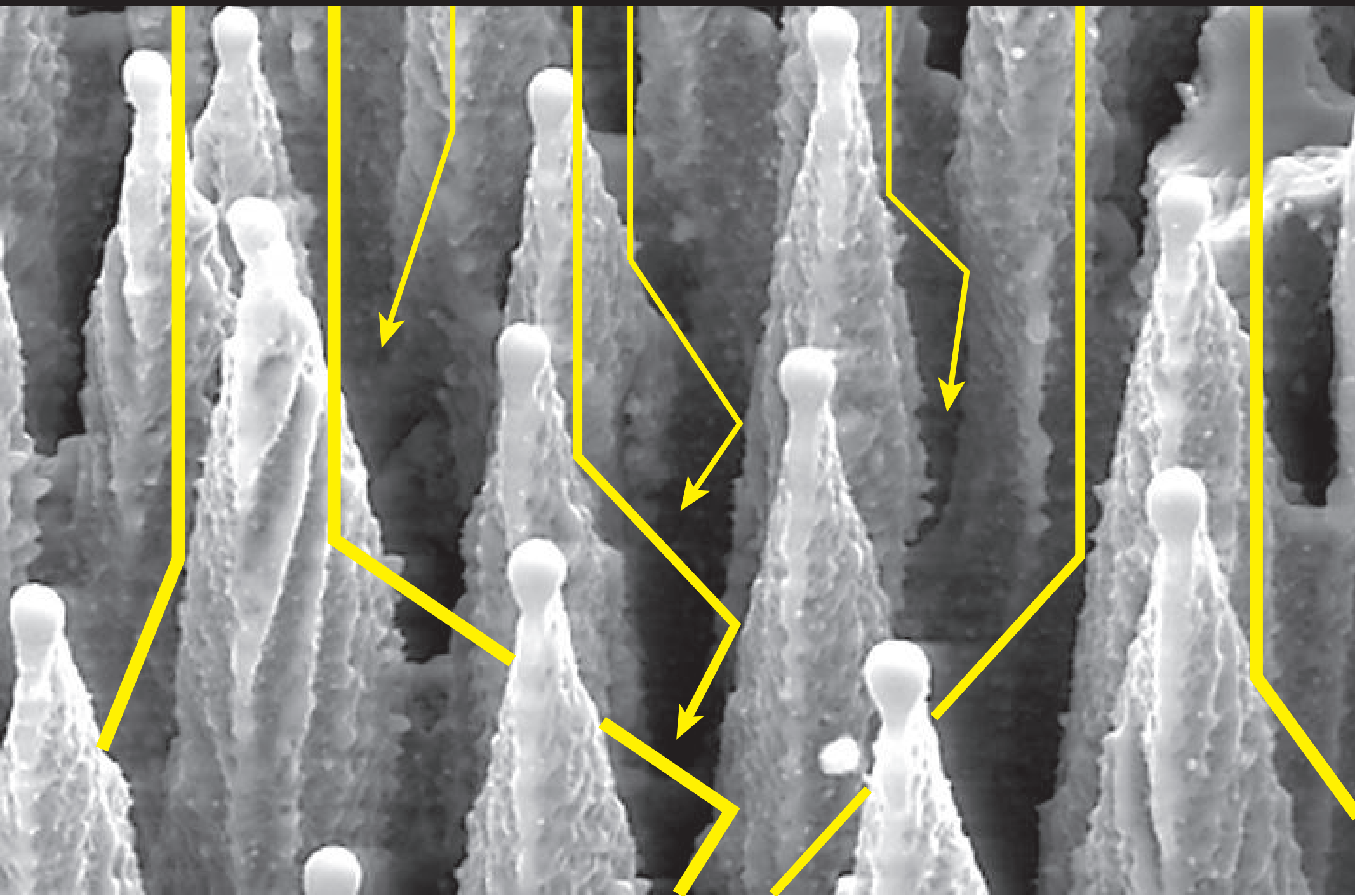


# Introduction

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

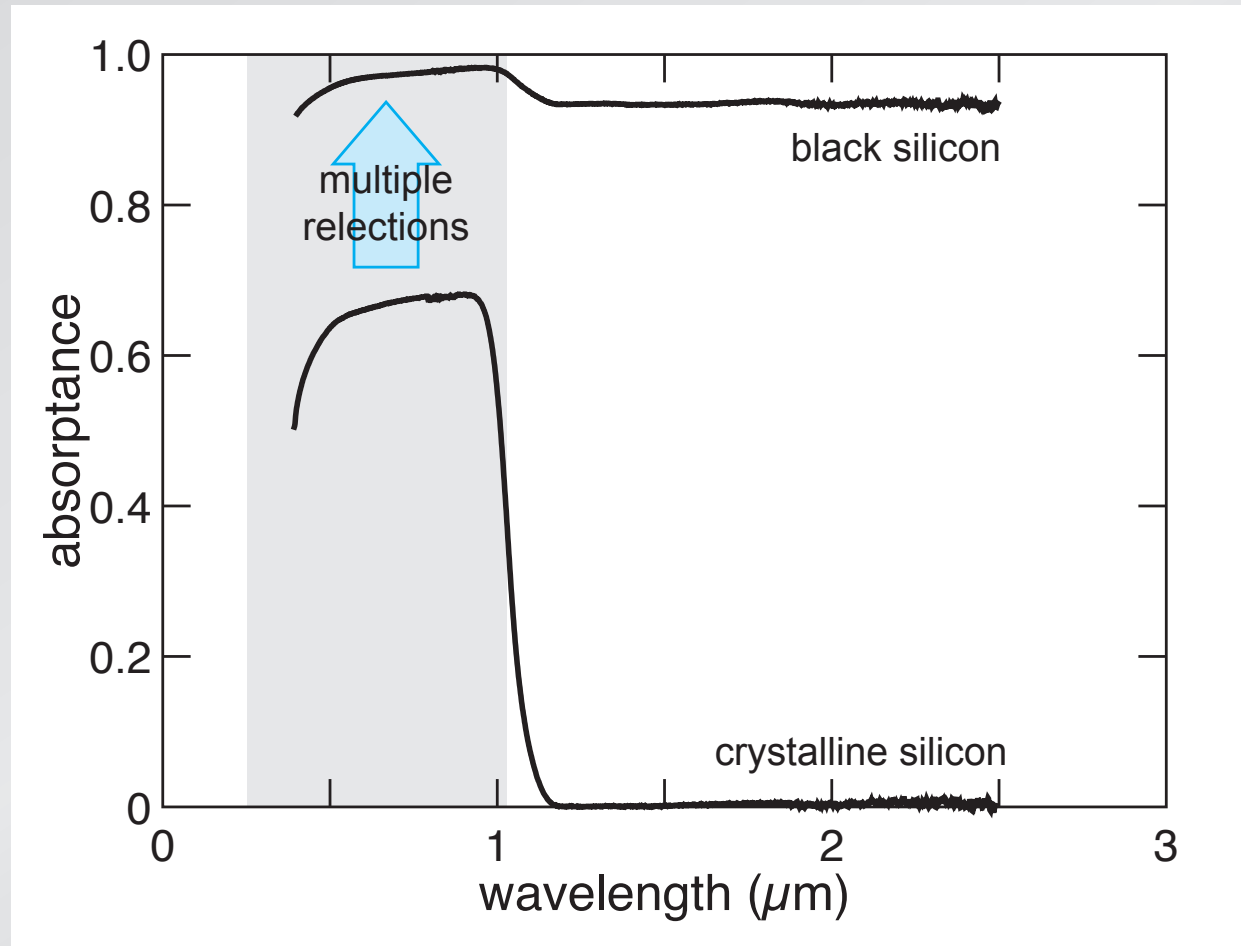


# Introduction



# Introduction

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



# Introduction

silicon transparent in near IR

visible



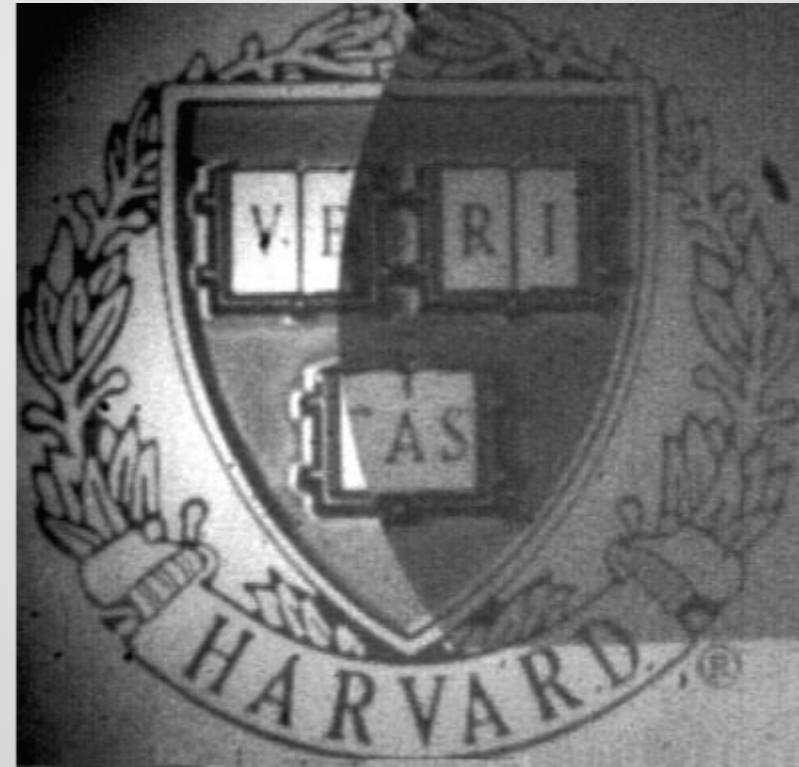
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silicon transparent in near IR

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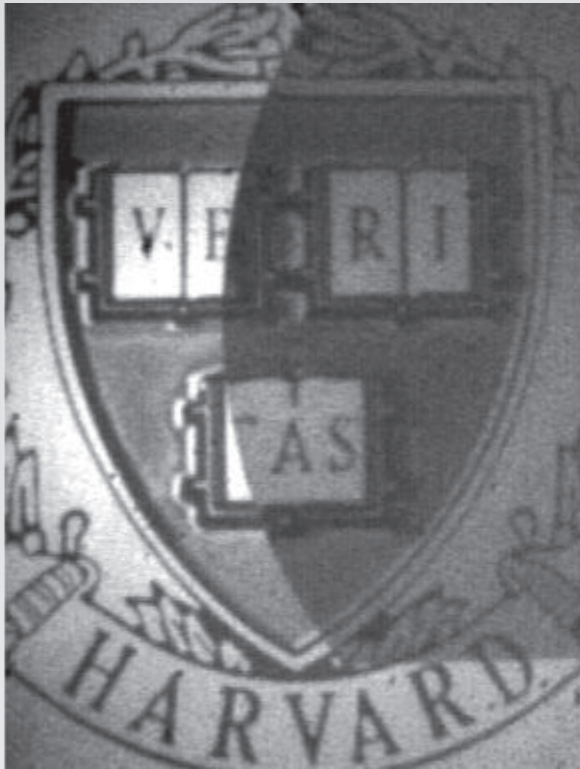
near IR



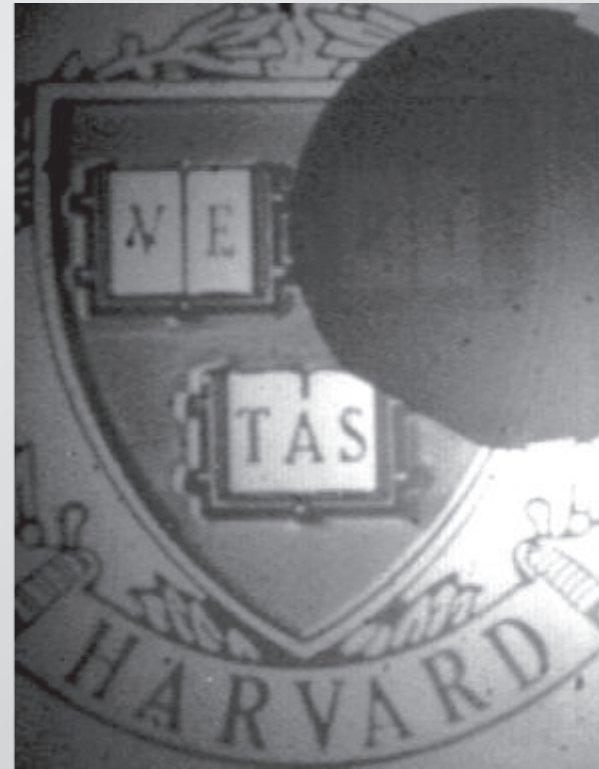
# Introduction

roughening doesn't change IR transmission...

polished



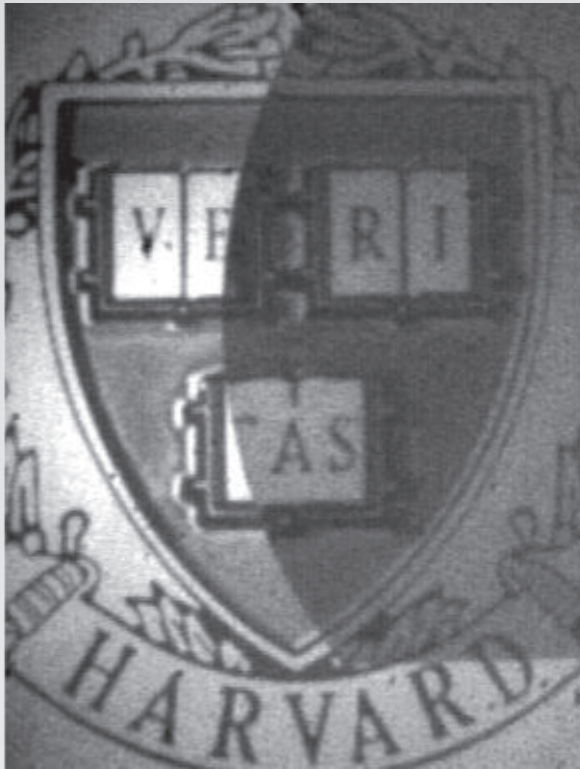
unpolished



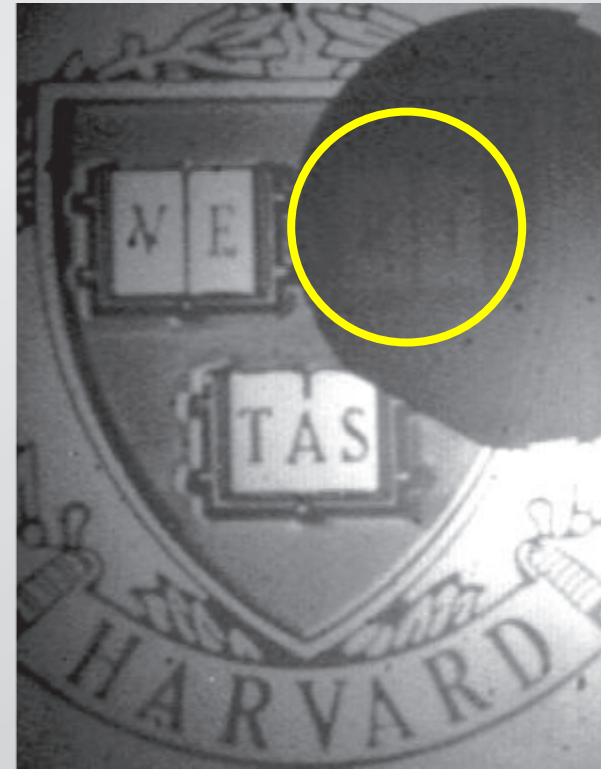
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roughening doesn't change IR transmission...

polished



unpolished



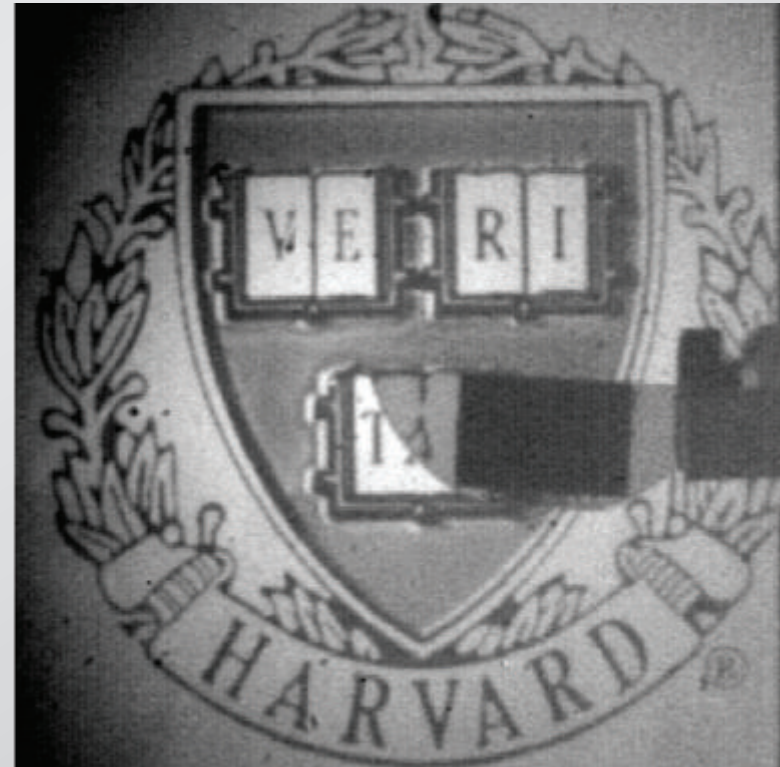
# Introduction

...but black silicon blocks IR completely

visible



near IR

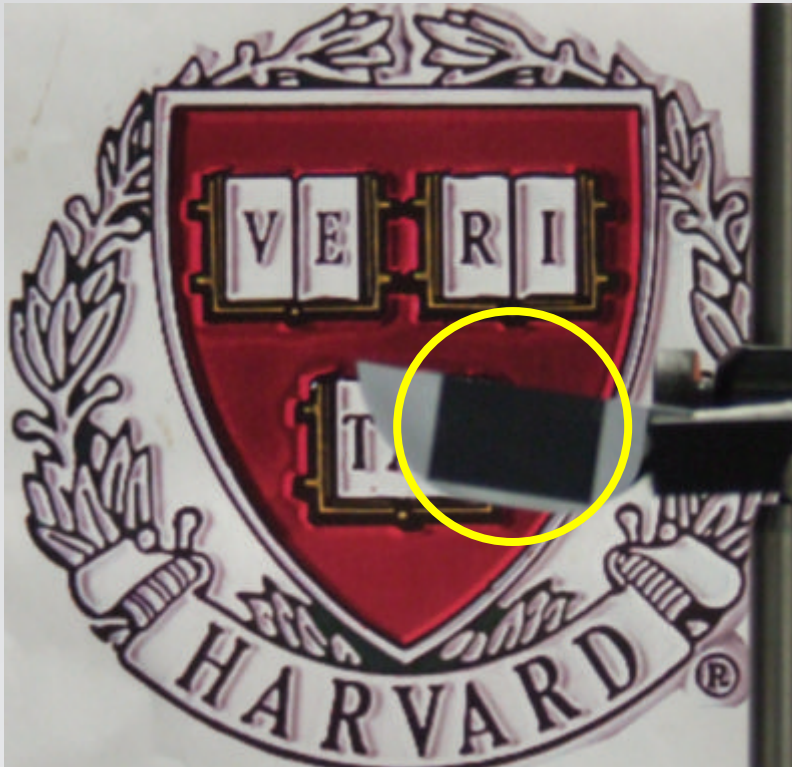




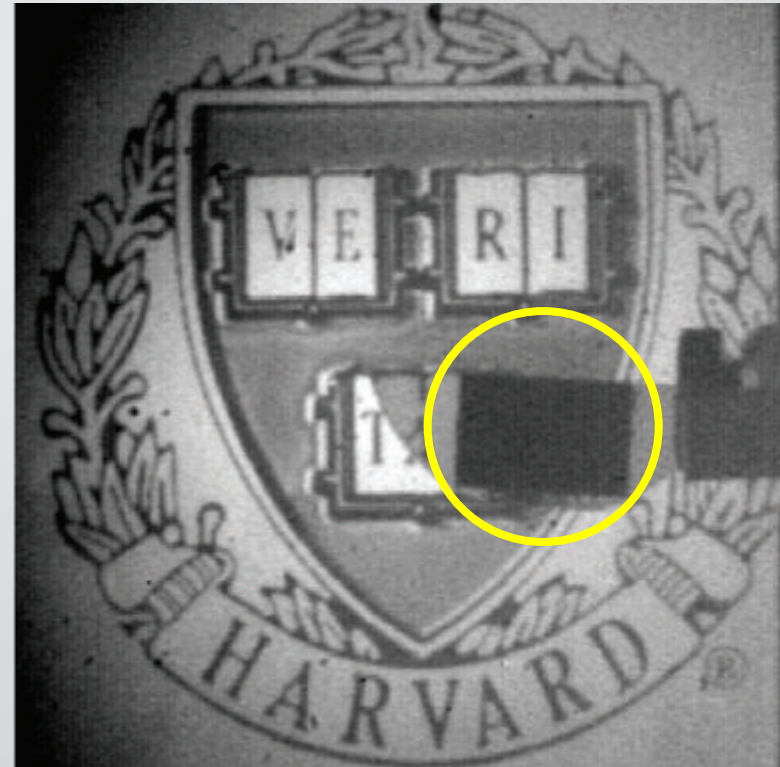
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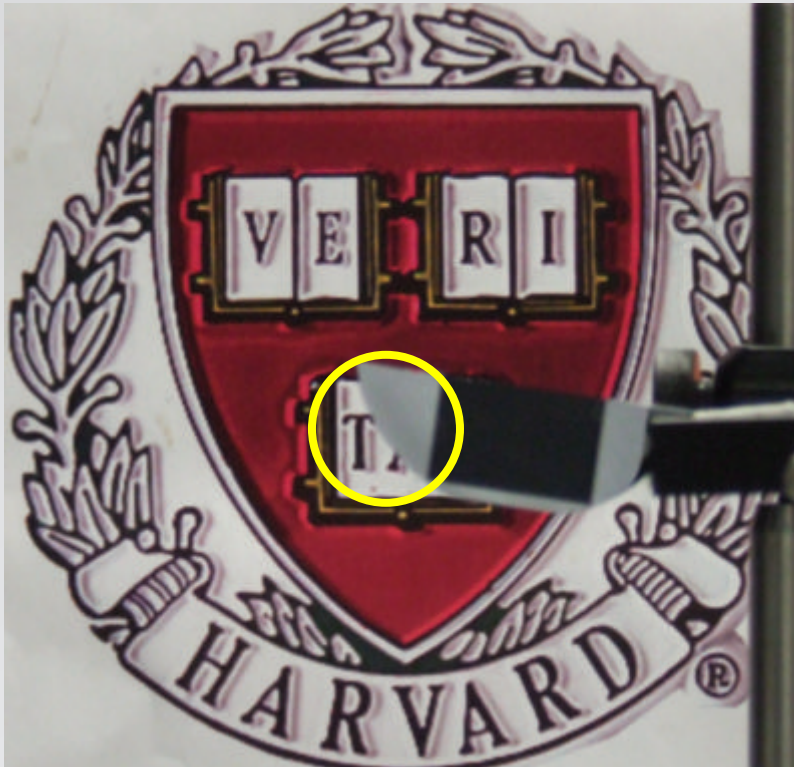
near IR



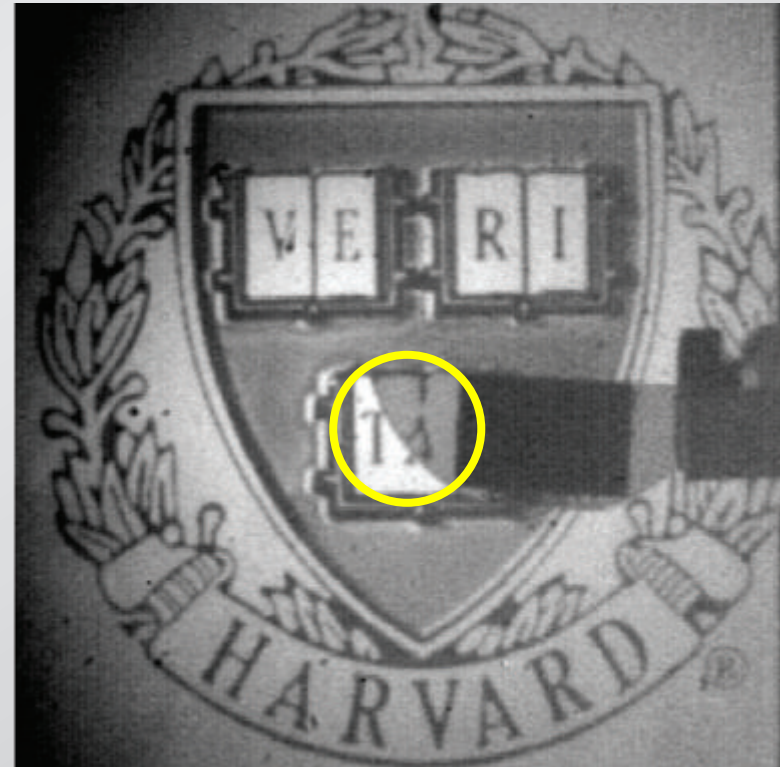
# Introduction

black silicon completely black in IR

visible



near IR



# 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  
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responsivity  
photoconductivity

gap  
impurity band  
transitions

### ELECTRONIC

Hall measurements  
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# Introduction

## a decade of research

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	

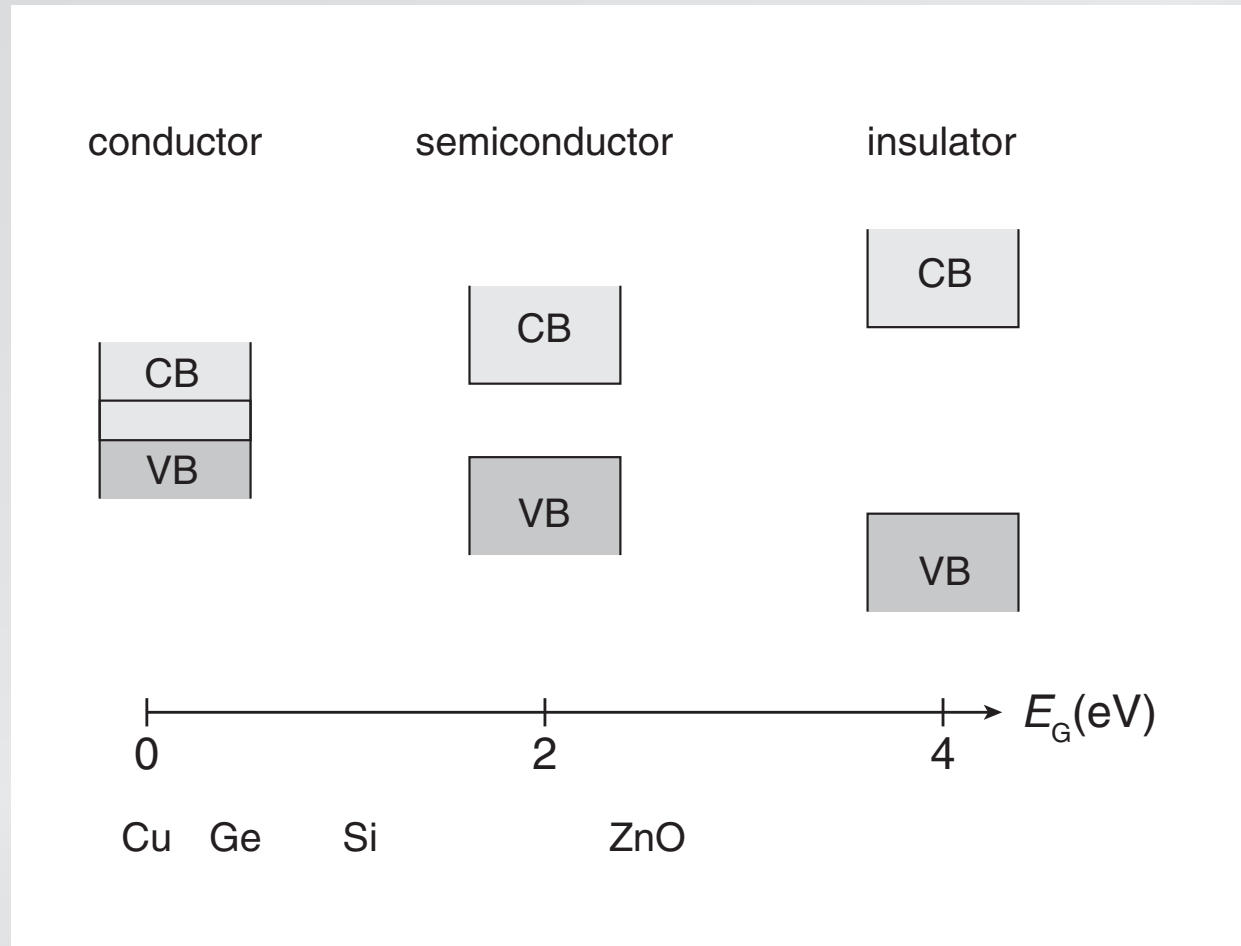
# Introduction

## a decade of research

OPTICAL	ELECTRONIC	STRUCTURAL
UV-VIS-NIR	Hall measurements	SEM
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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

## 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	

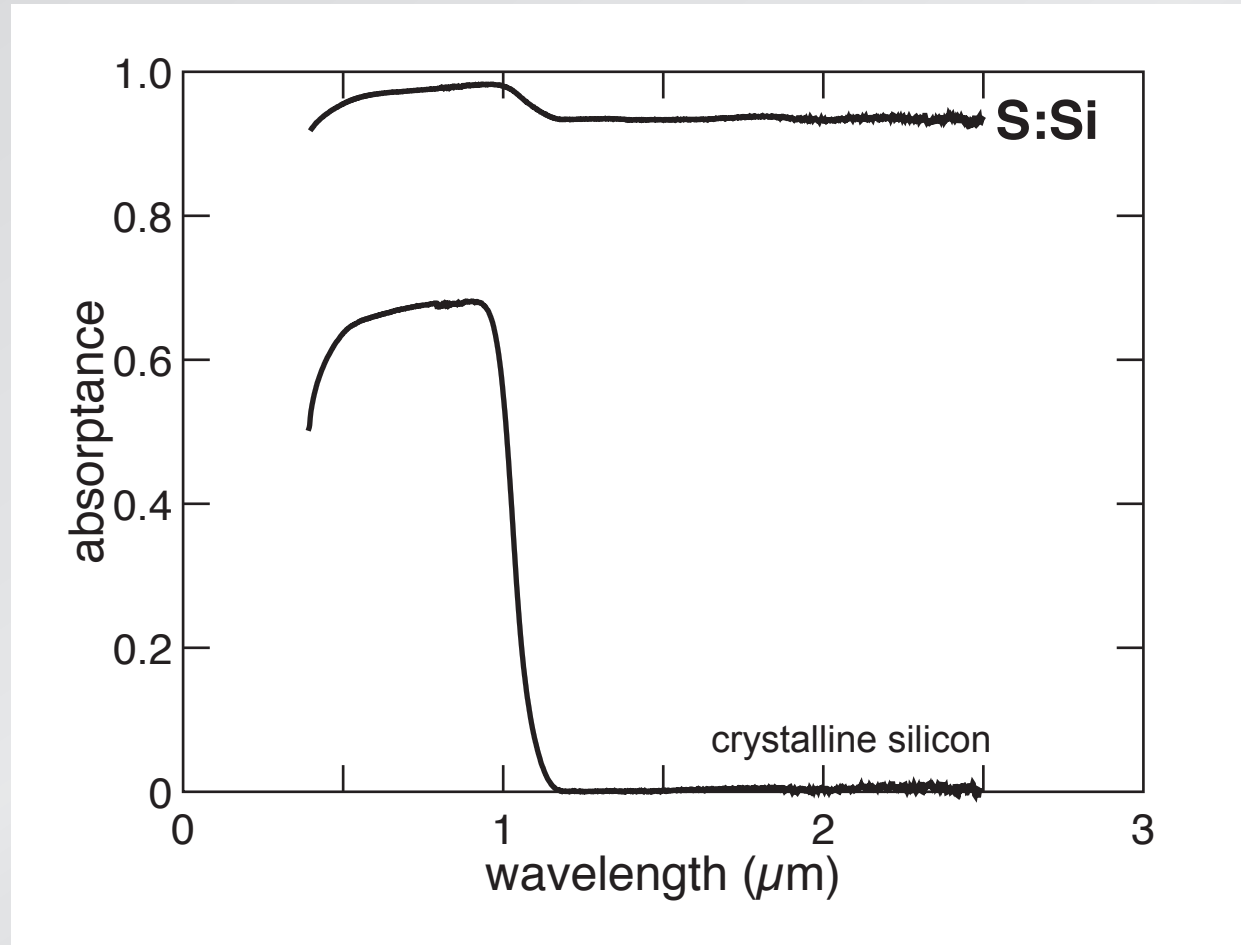
substrates:

Si Ge ZnO InP GaAs

Ti Ag Al Cu Pd Rh Ta Pt

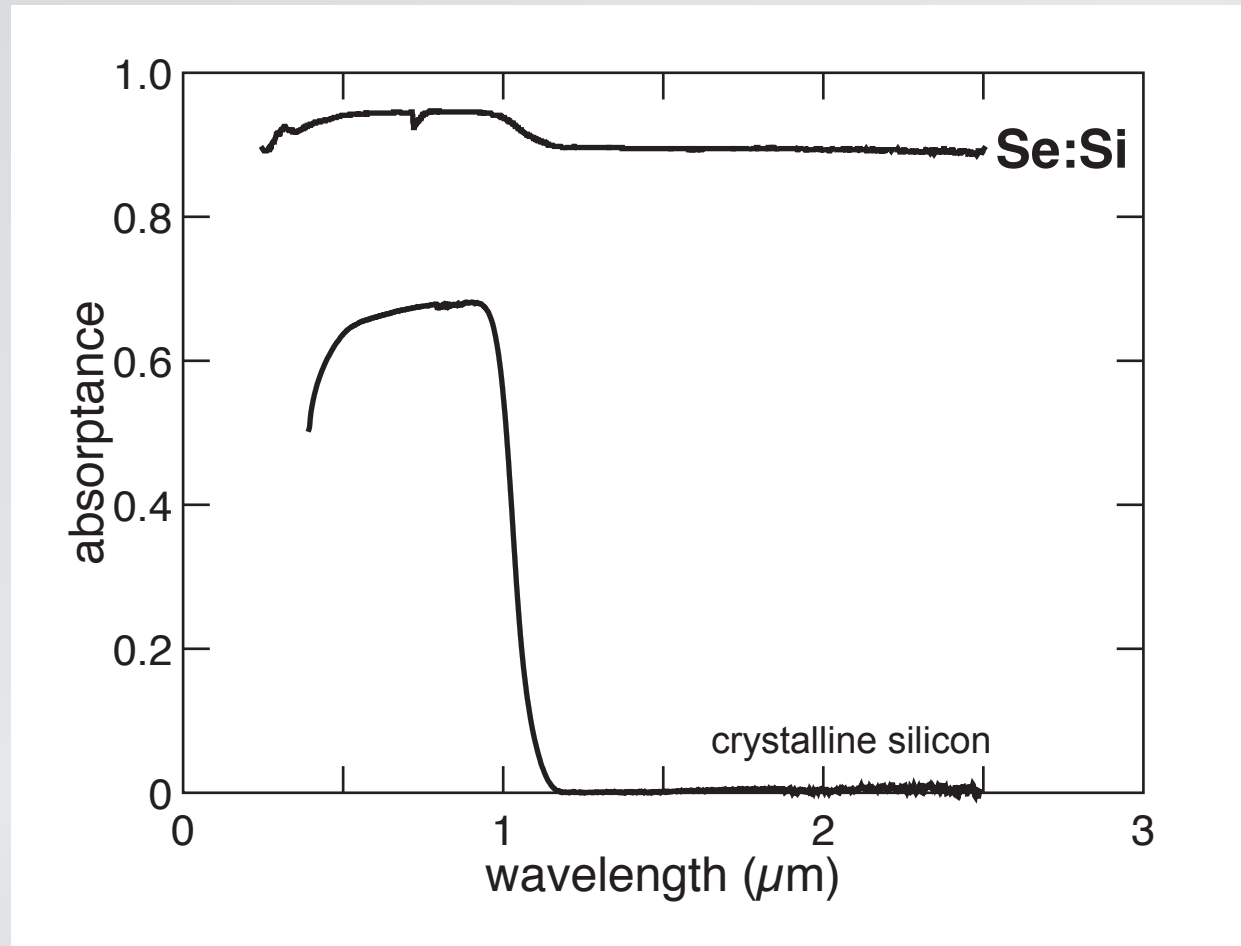
# Introduction

focus on chalcogen-doped silicon



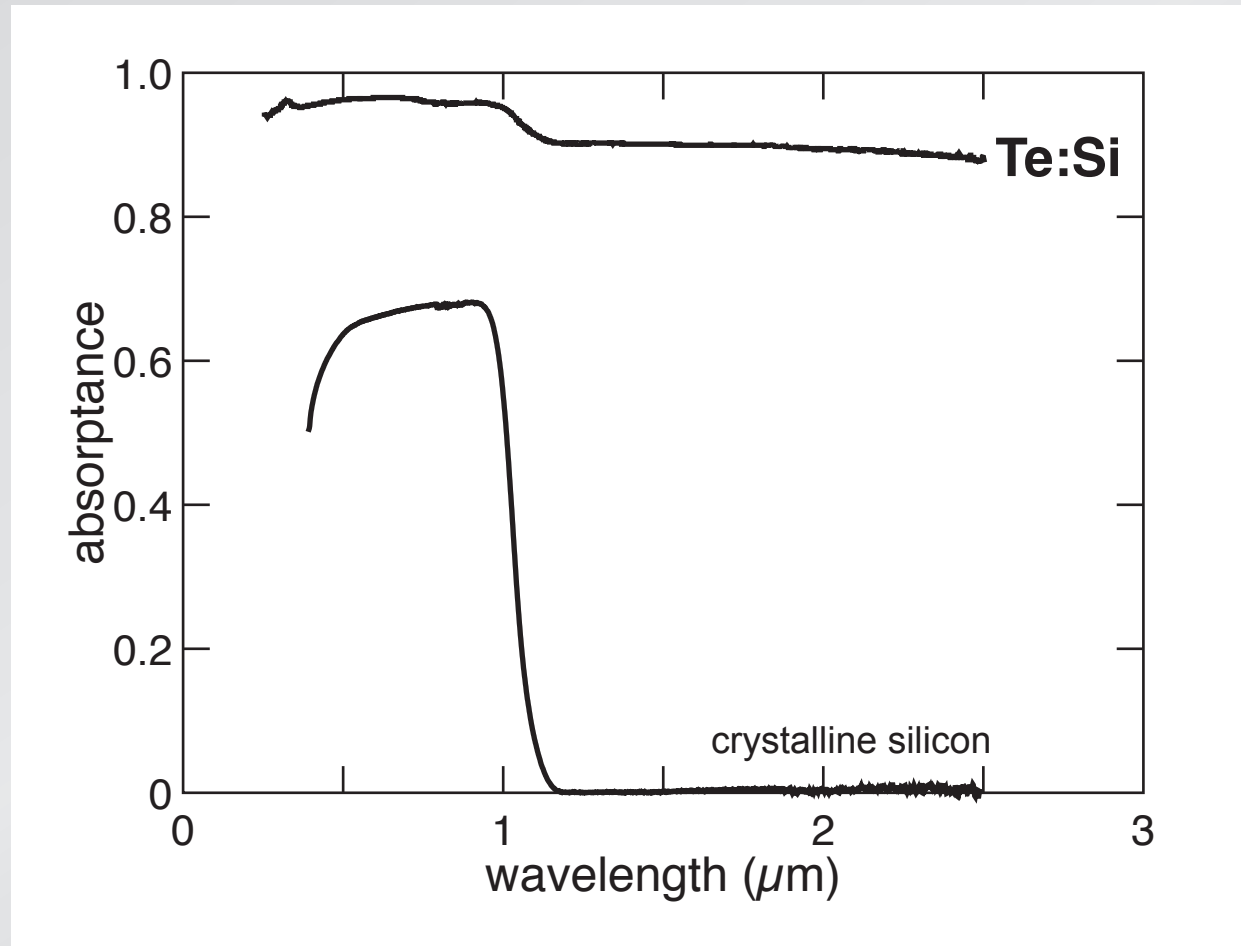
# Introduction

focus on chalcogen-doped silicon



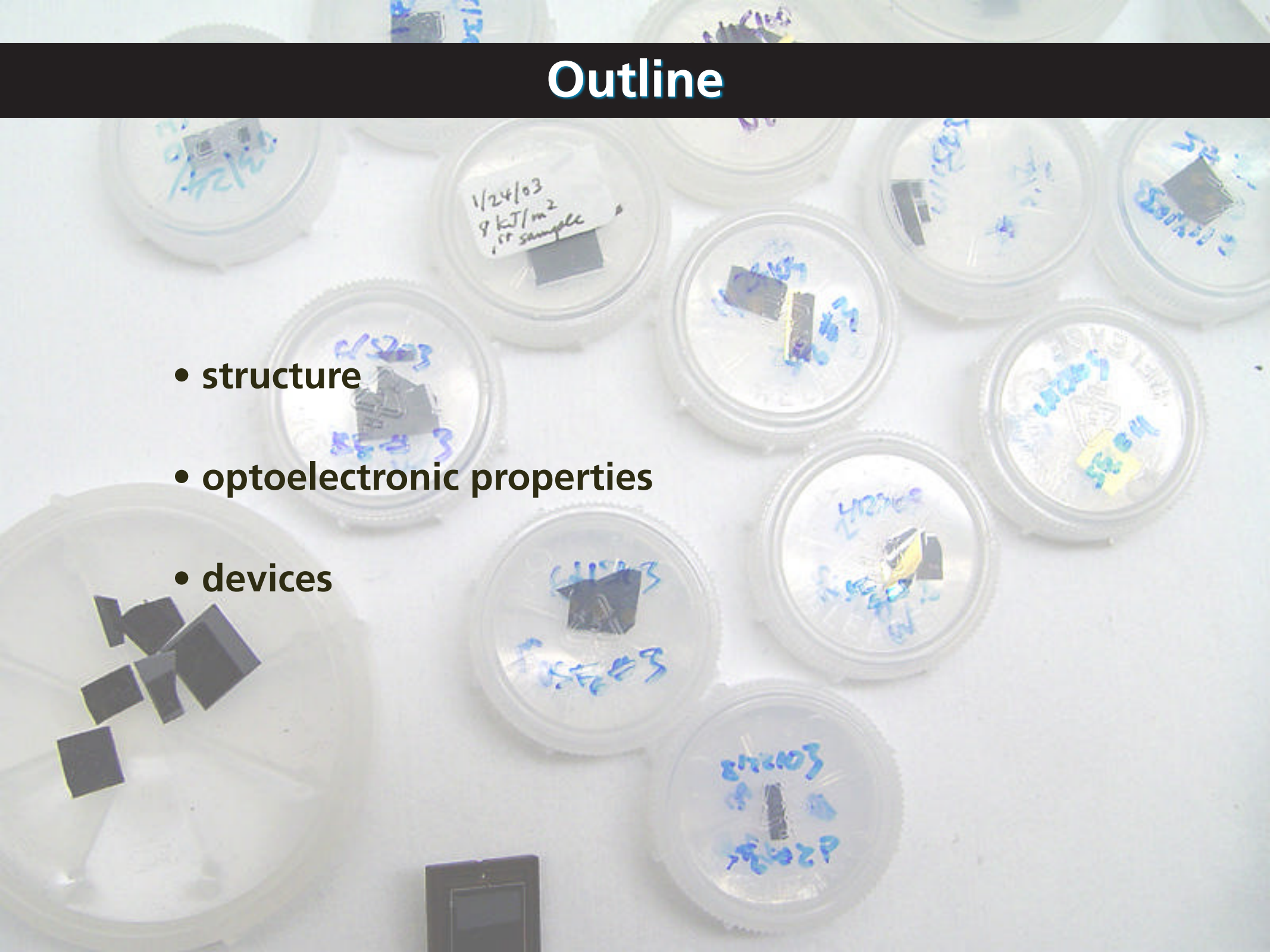
# Introduction

focus on chalcogen-doped silicon

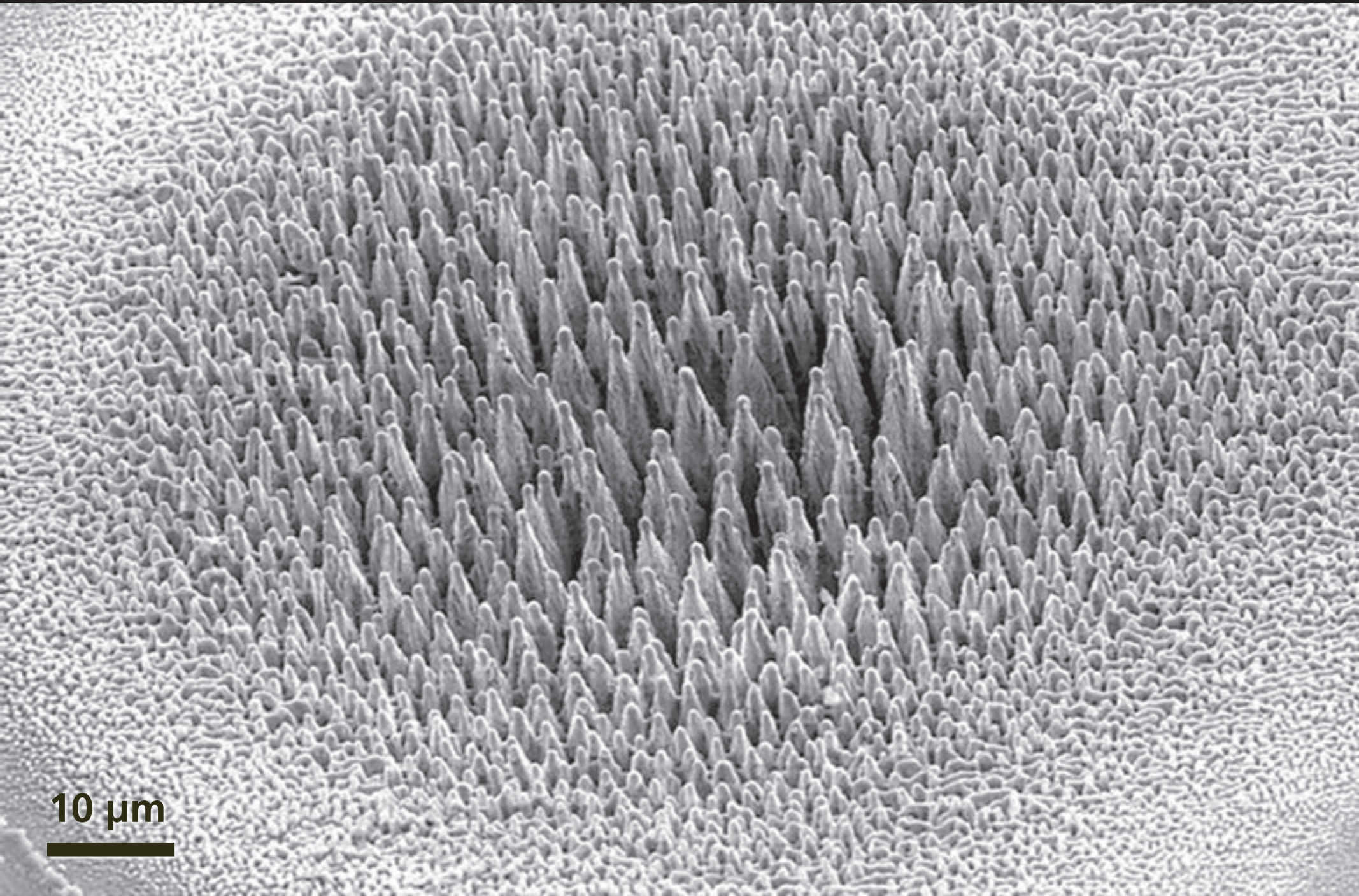


# Outline

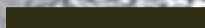
- structure
- optoelectronic properties
- devices



# Structure

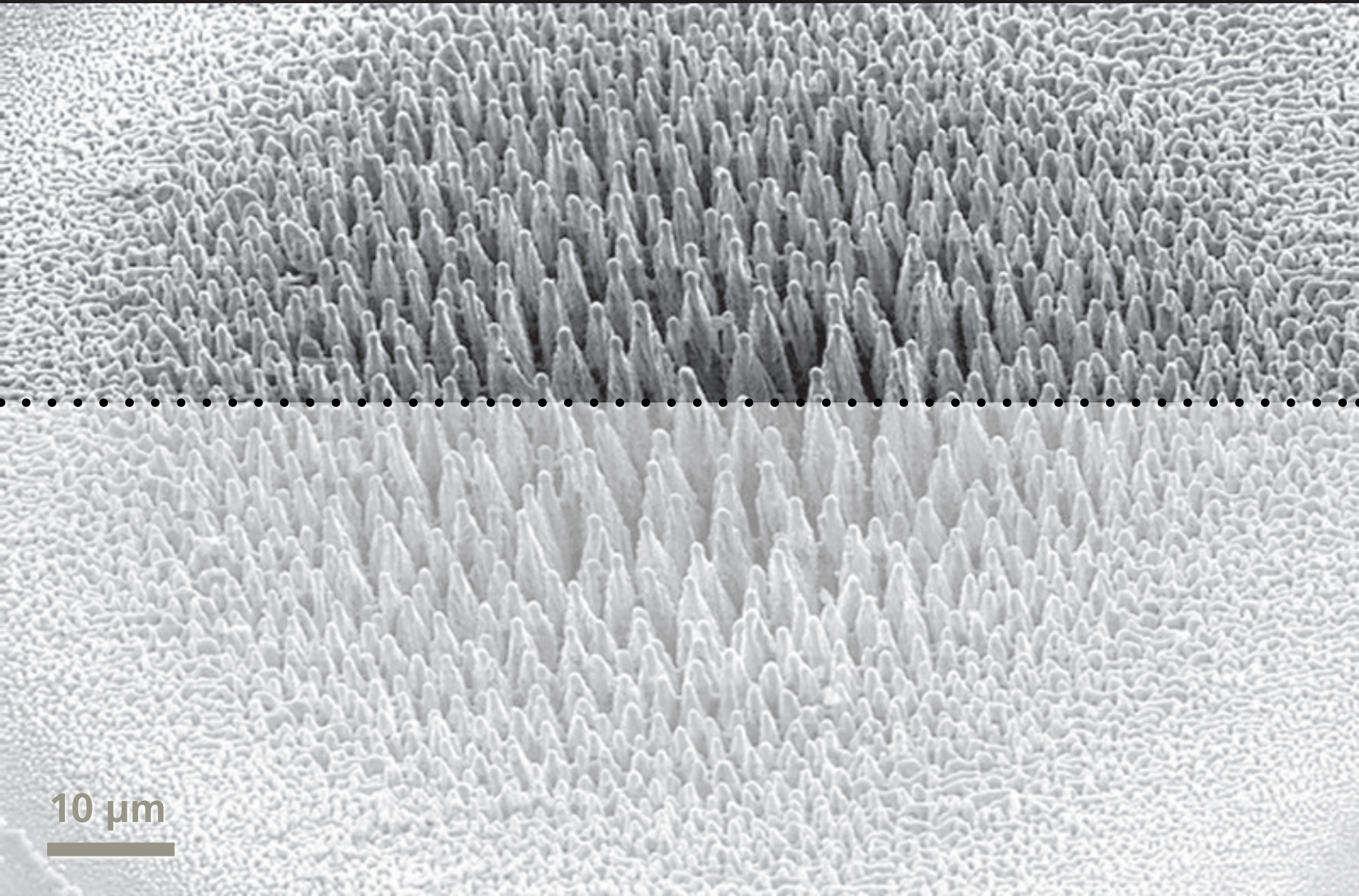


10  $\mu\text{m}$





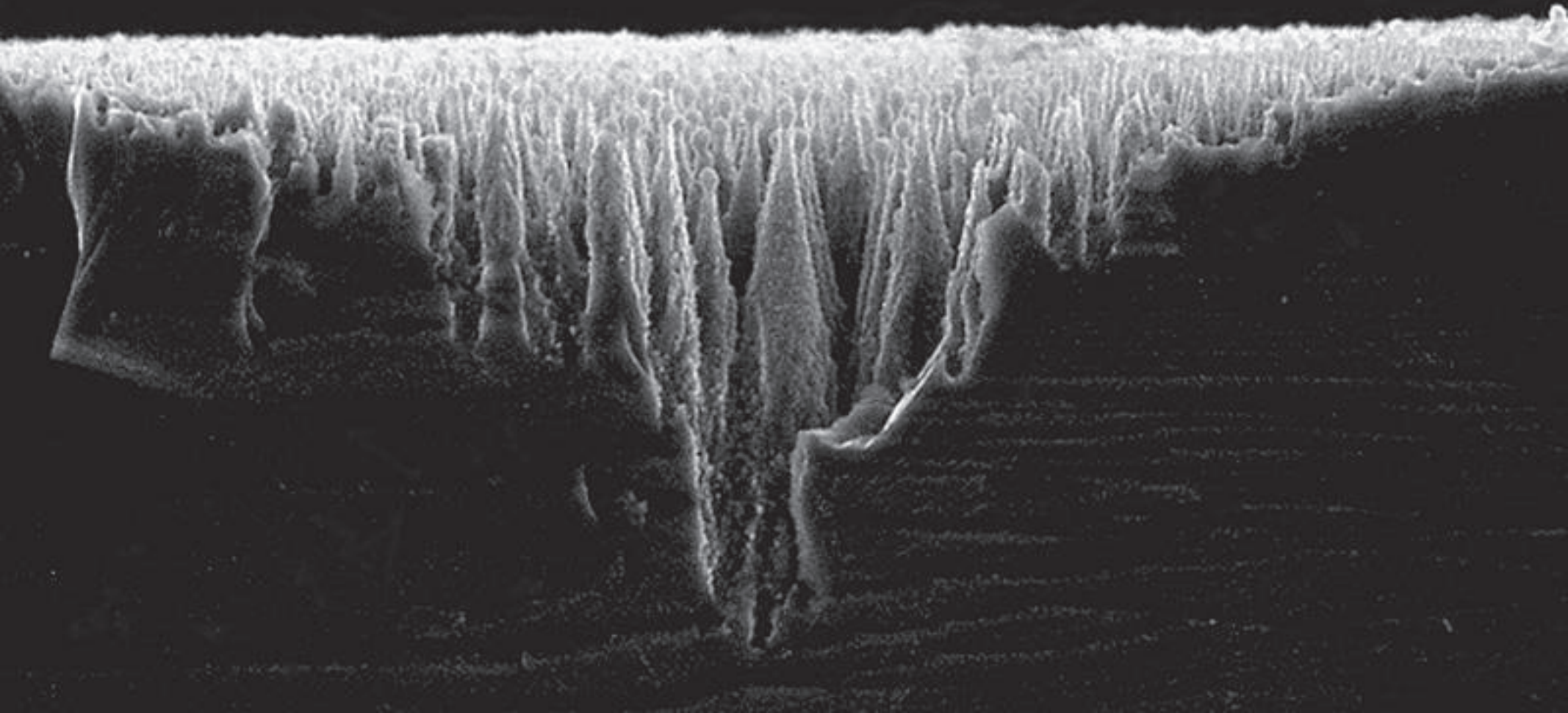
# Structure



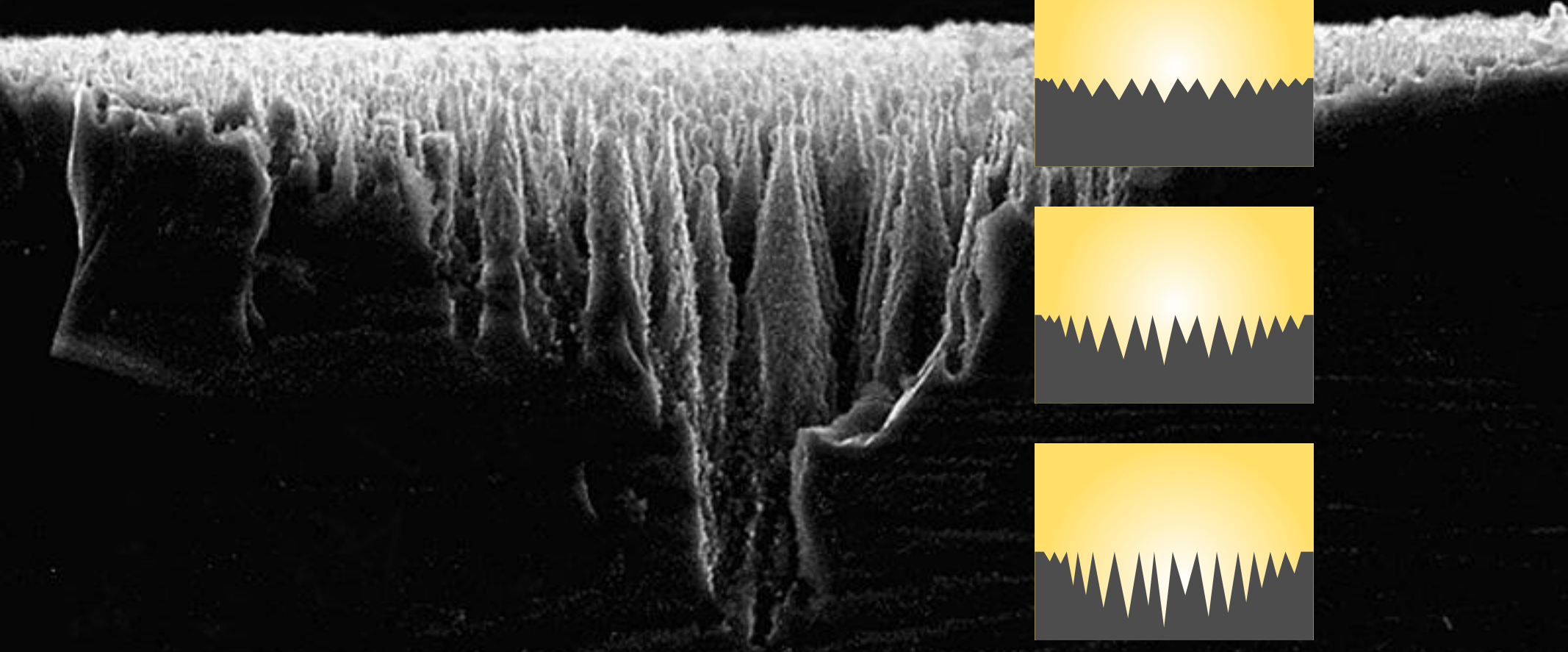
10 μm



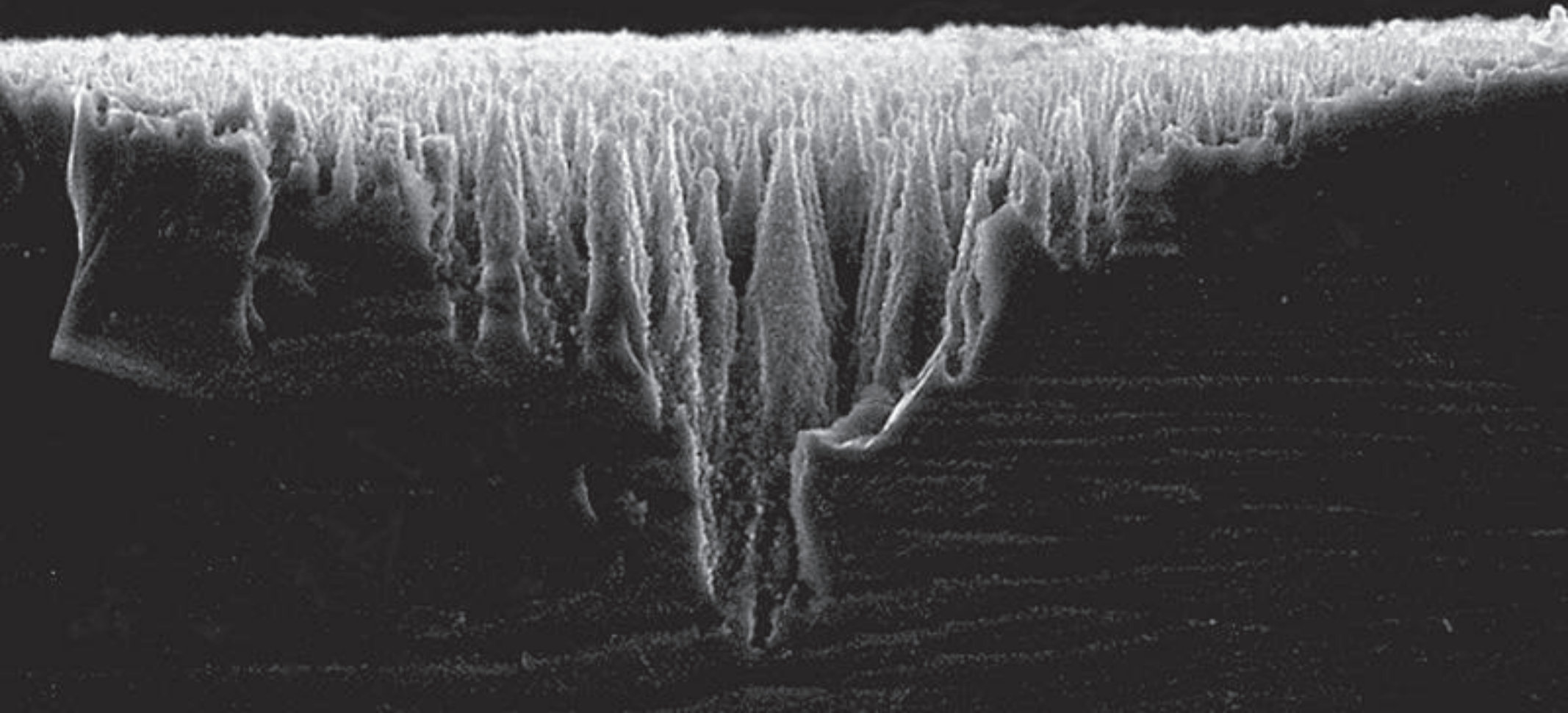
# Structure



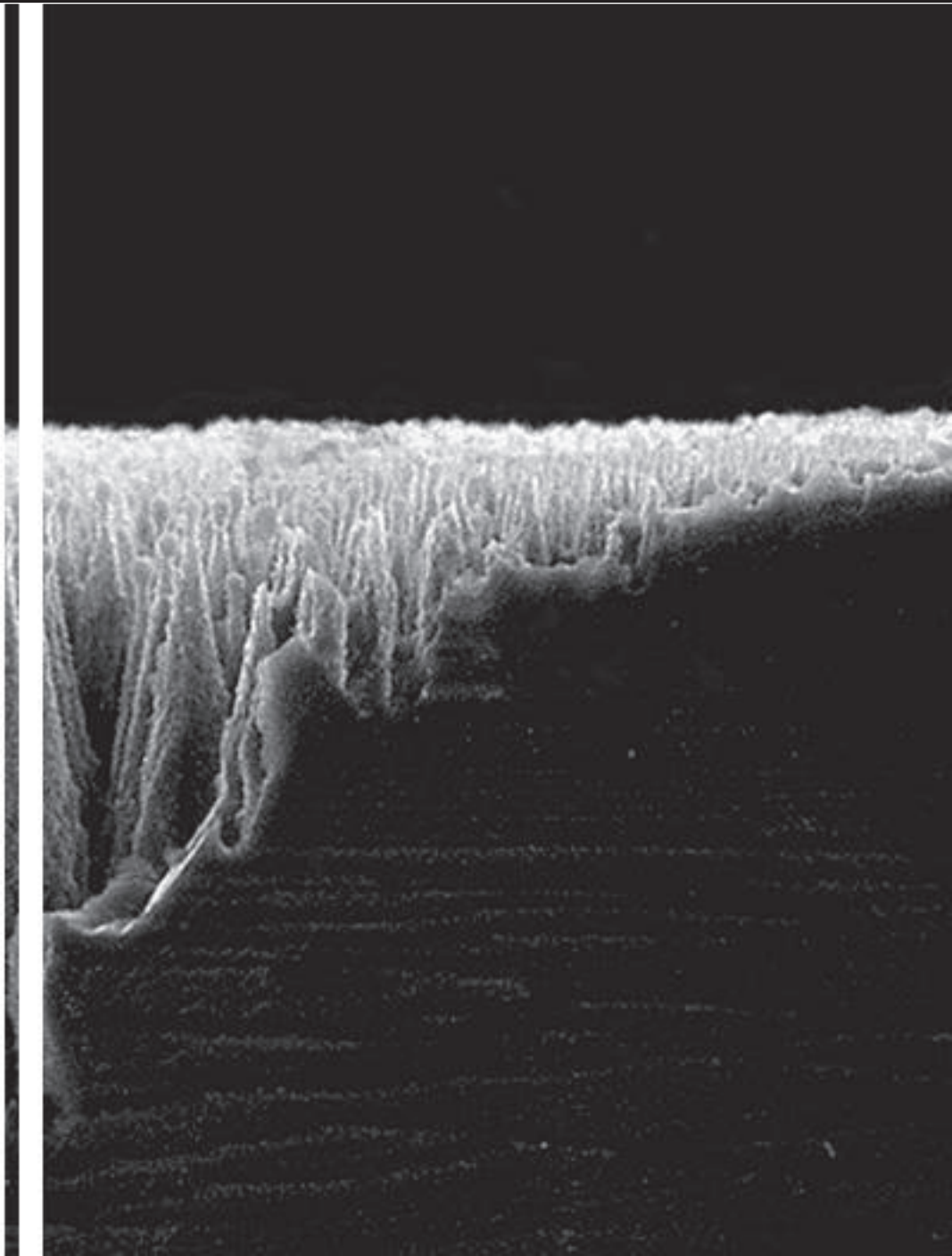
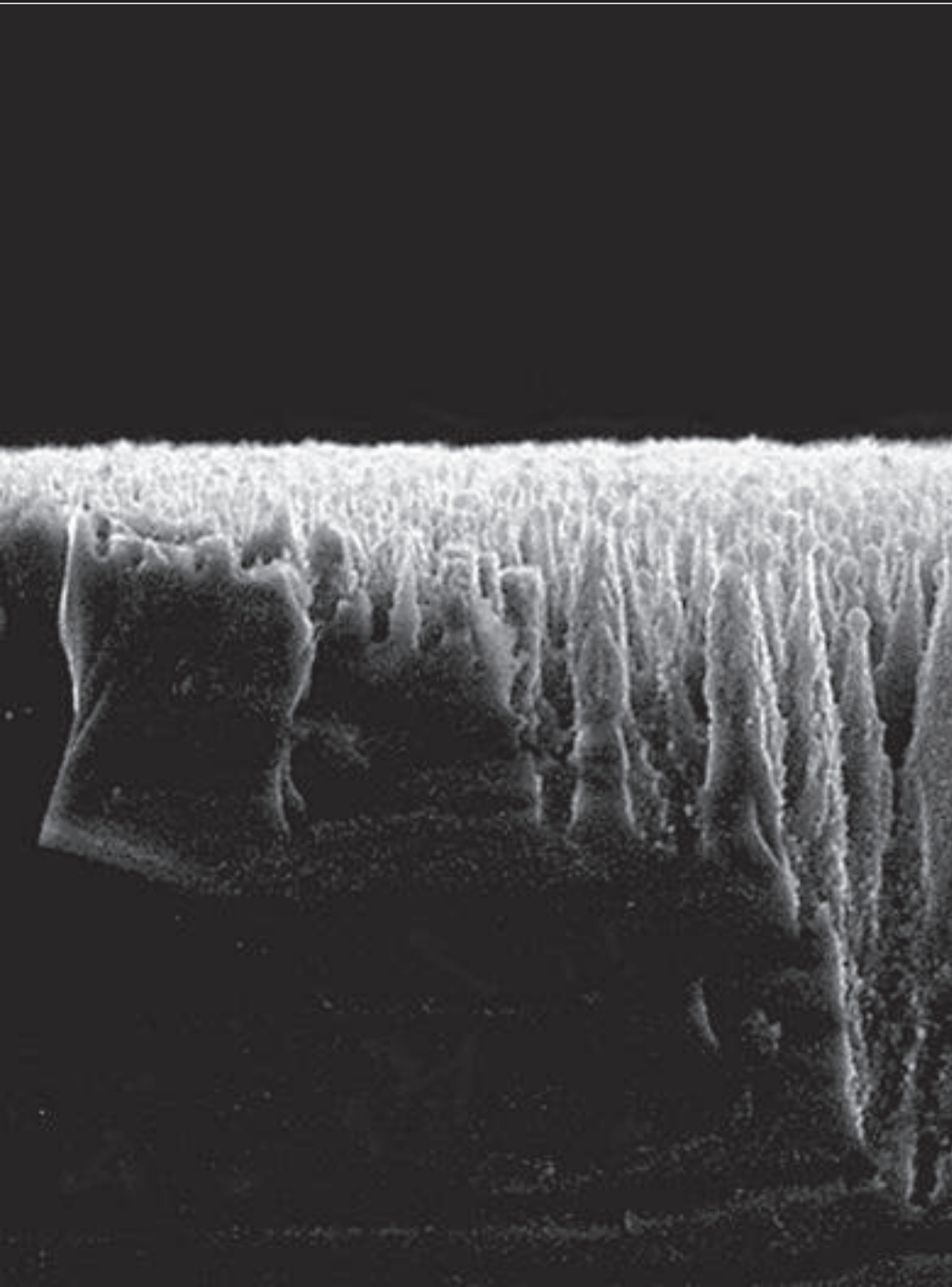
# Structure



# Structure

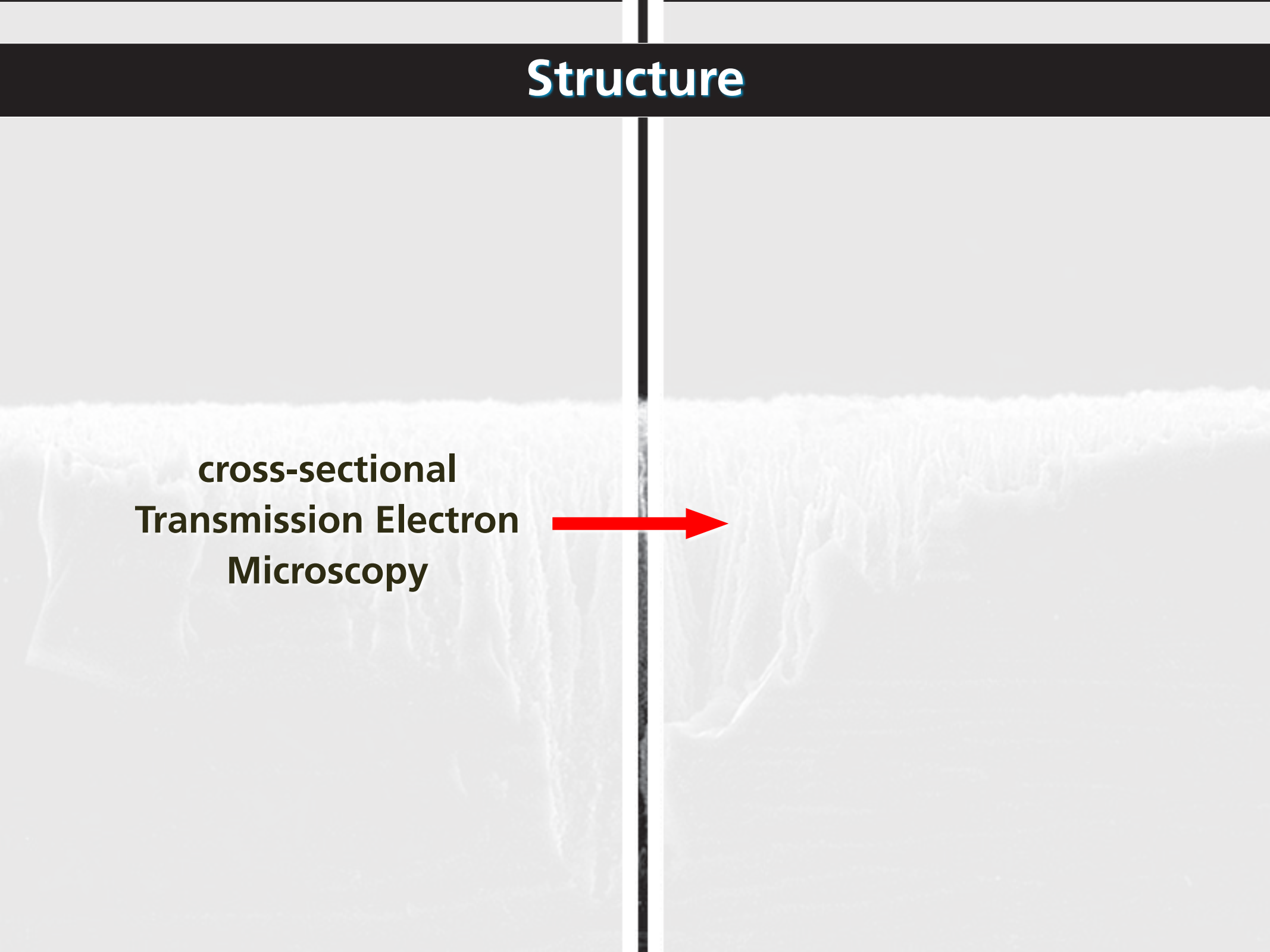


# Structure



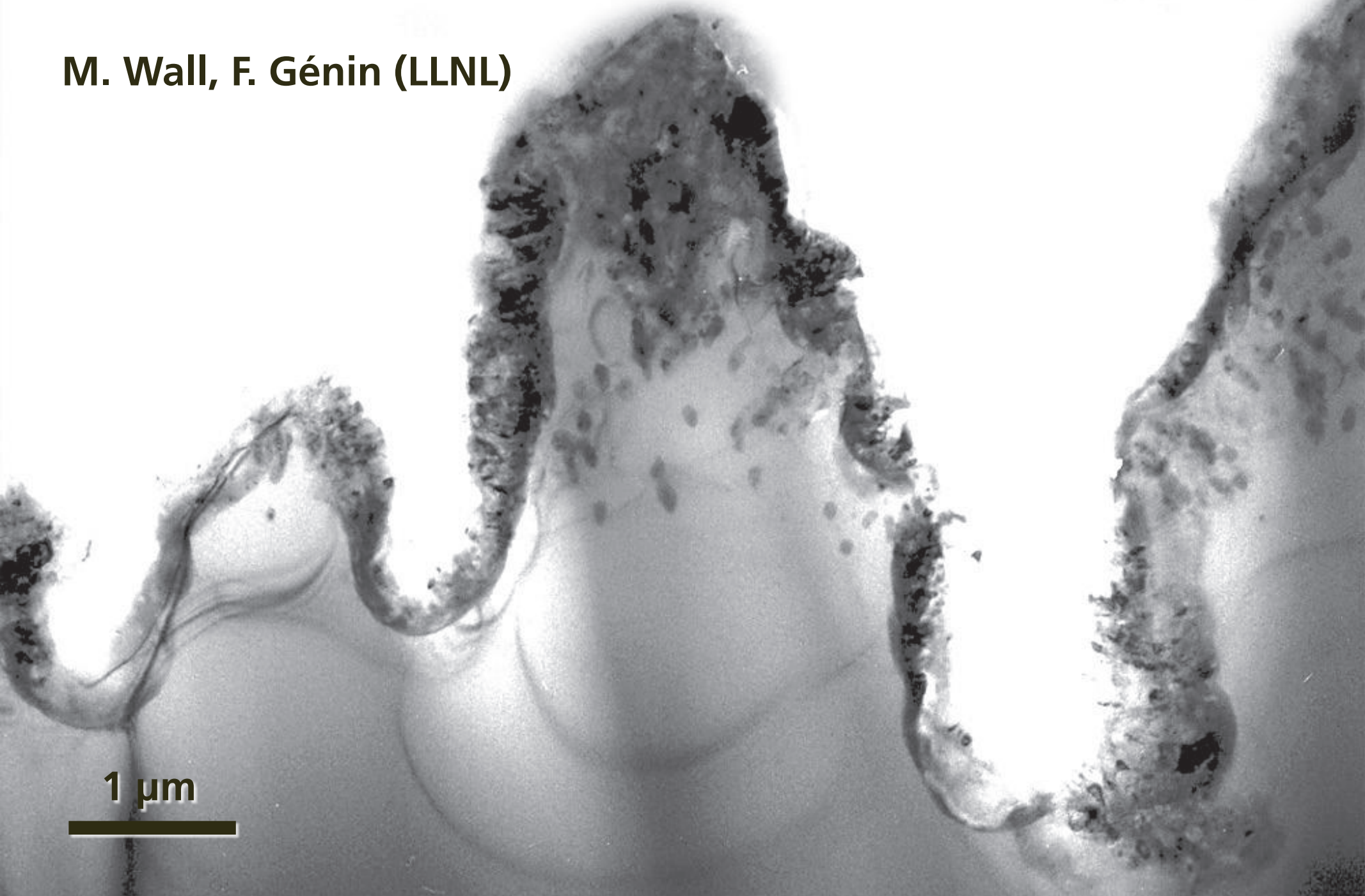
# Structure

**cross-sectional  
Transmission Electron  
Microscopy**



# Structure

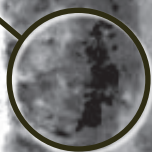
M. Wall, F. Génin (LLNL)



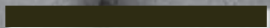
1 μm

# Structure

disordered  
surface layer

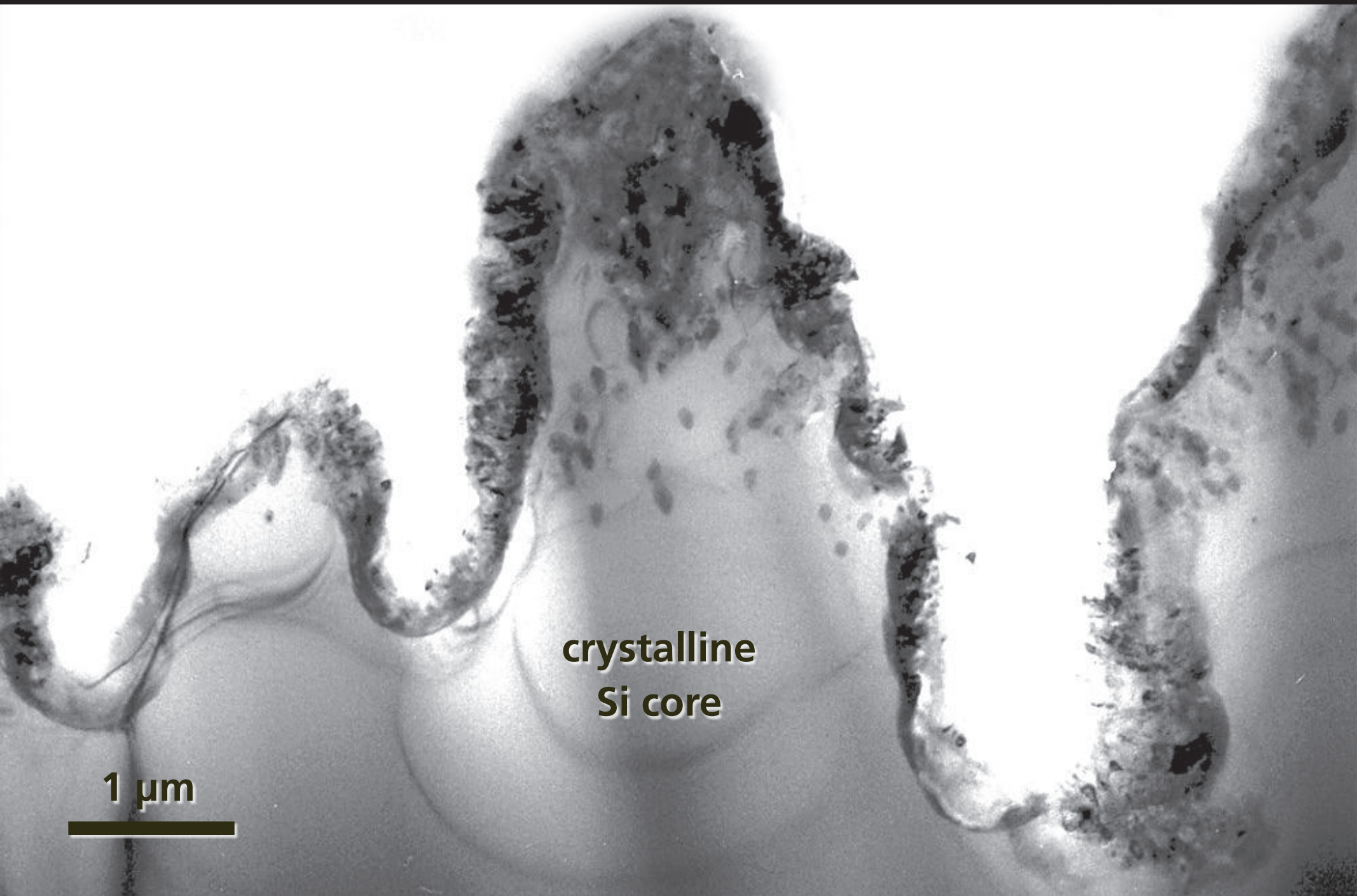


1  $\mu\text{m}$





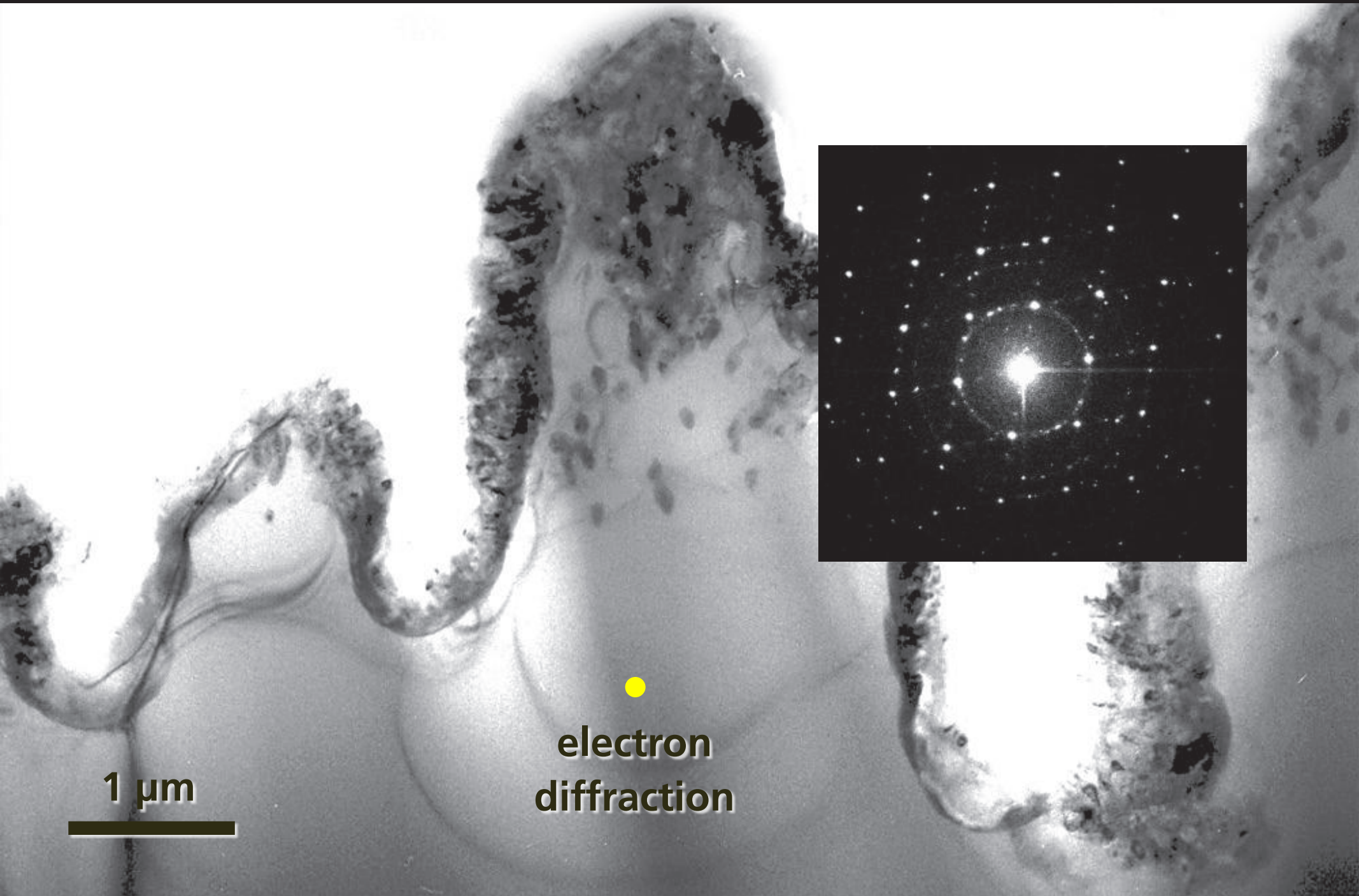
# Structure



crystalline  
Si core

1 μm

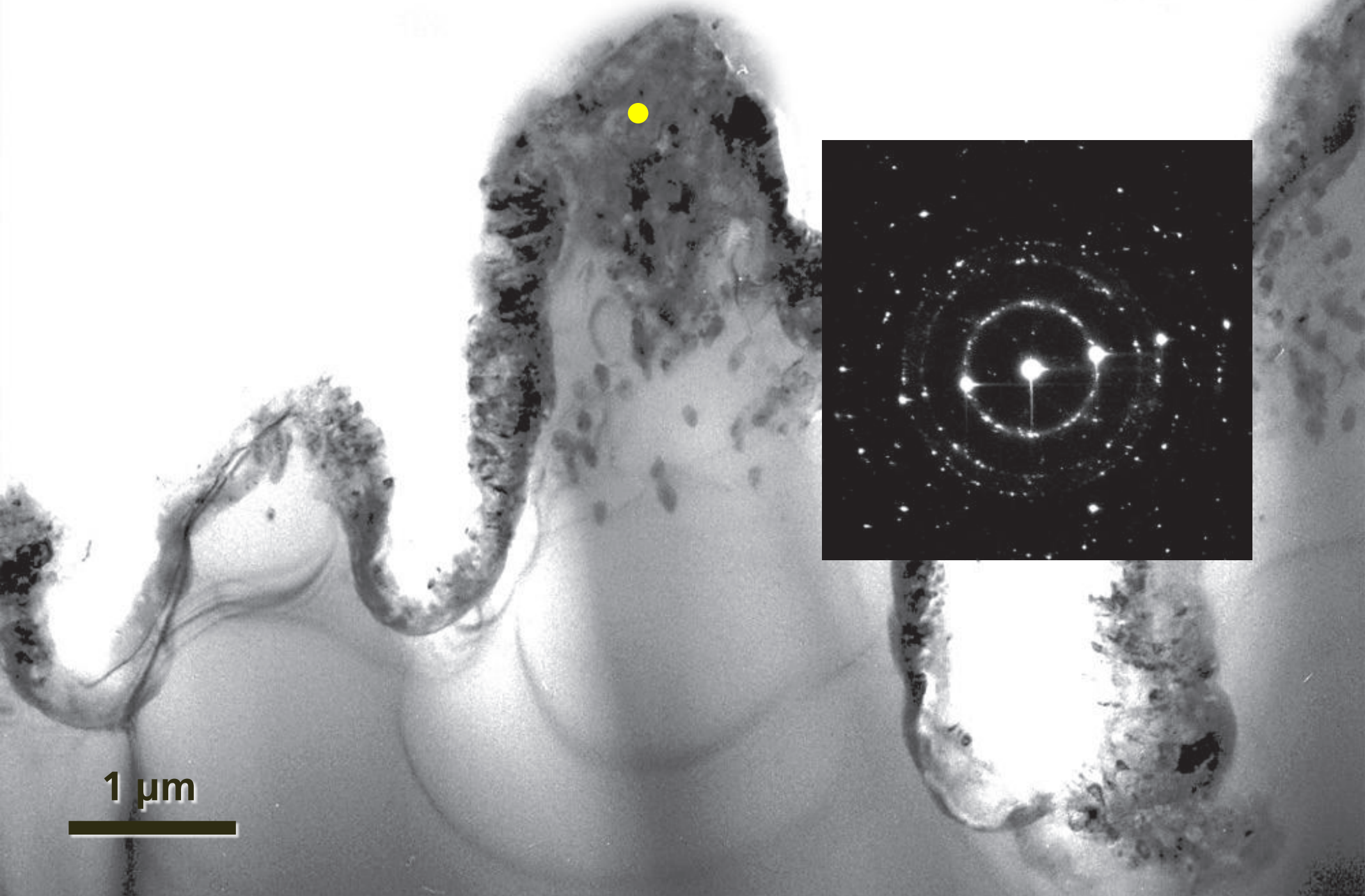
# Structure



1  $\mu\text{m}$

●  
electron  
diffraction

# Structure



# Structure

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

1  $\mu\text{m}$

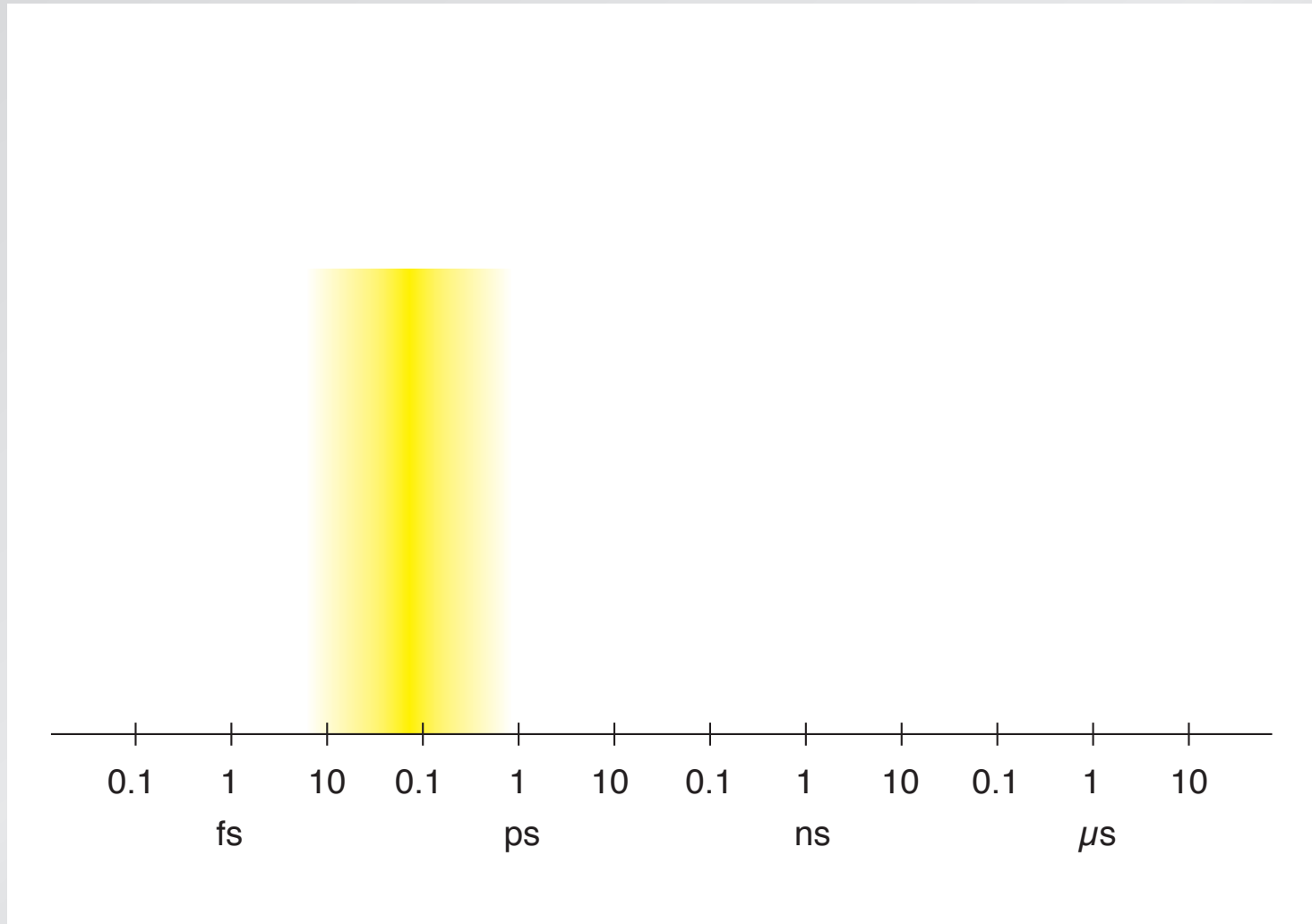
The image is a grayscale micrograph showing several elongated, somewhat irregular structures. Each structure has a darker, more textured outer layer and a lighter, smoother inner core. The structures are arranged in a roughly parallel fashion. In the bottom left corner, there is a horizontal black scale bar with the text "1 μm" above it.

# Structure

**two processes: melting and ablation**

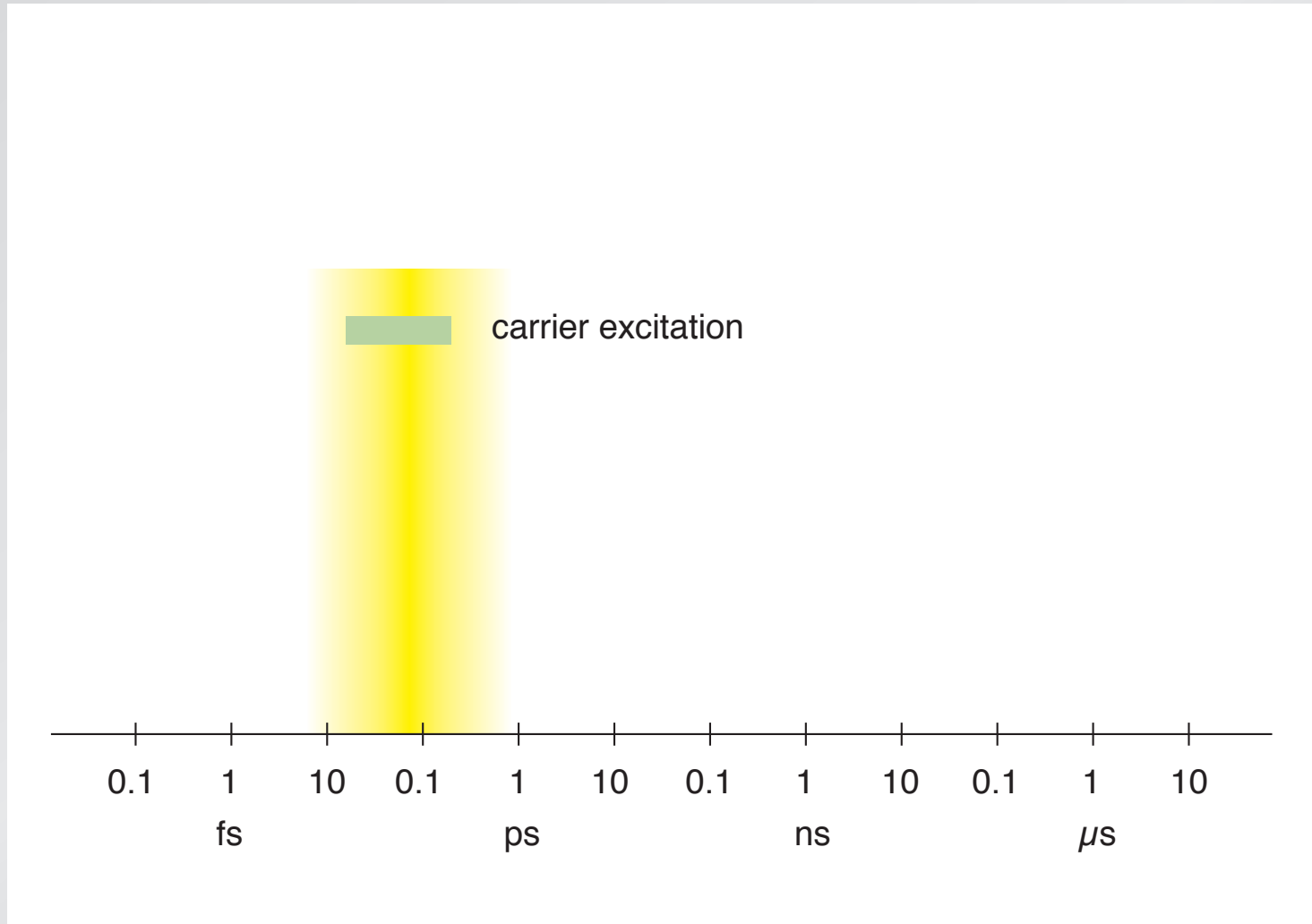
# Structure

relevant time scales



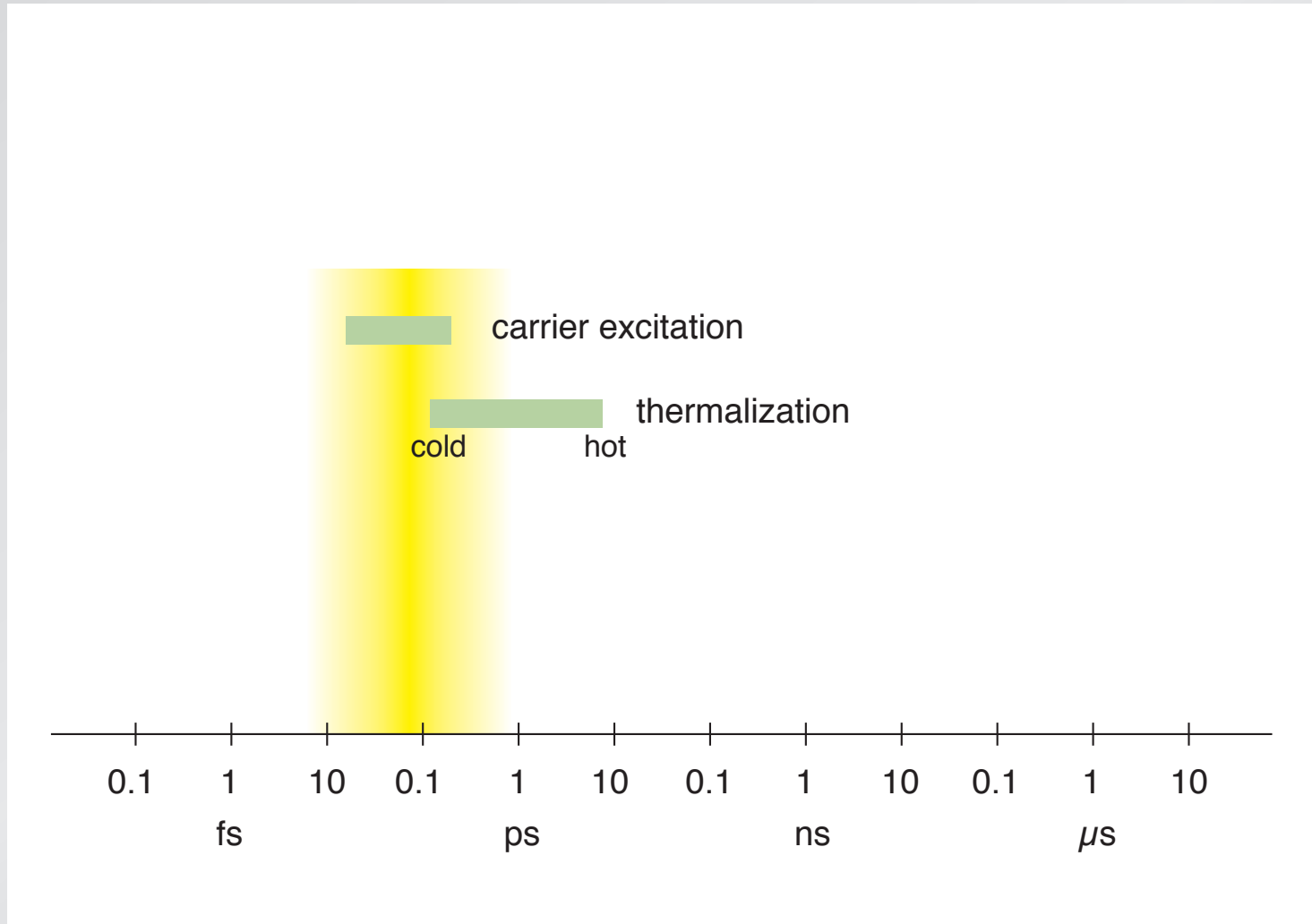
# Structure

## relevant time scales



# Structure

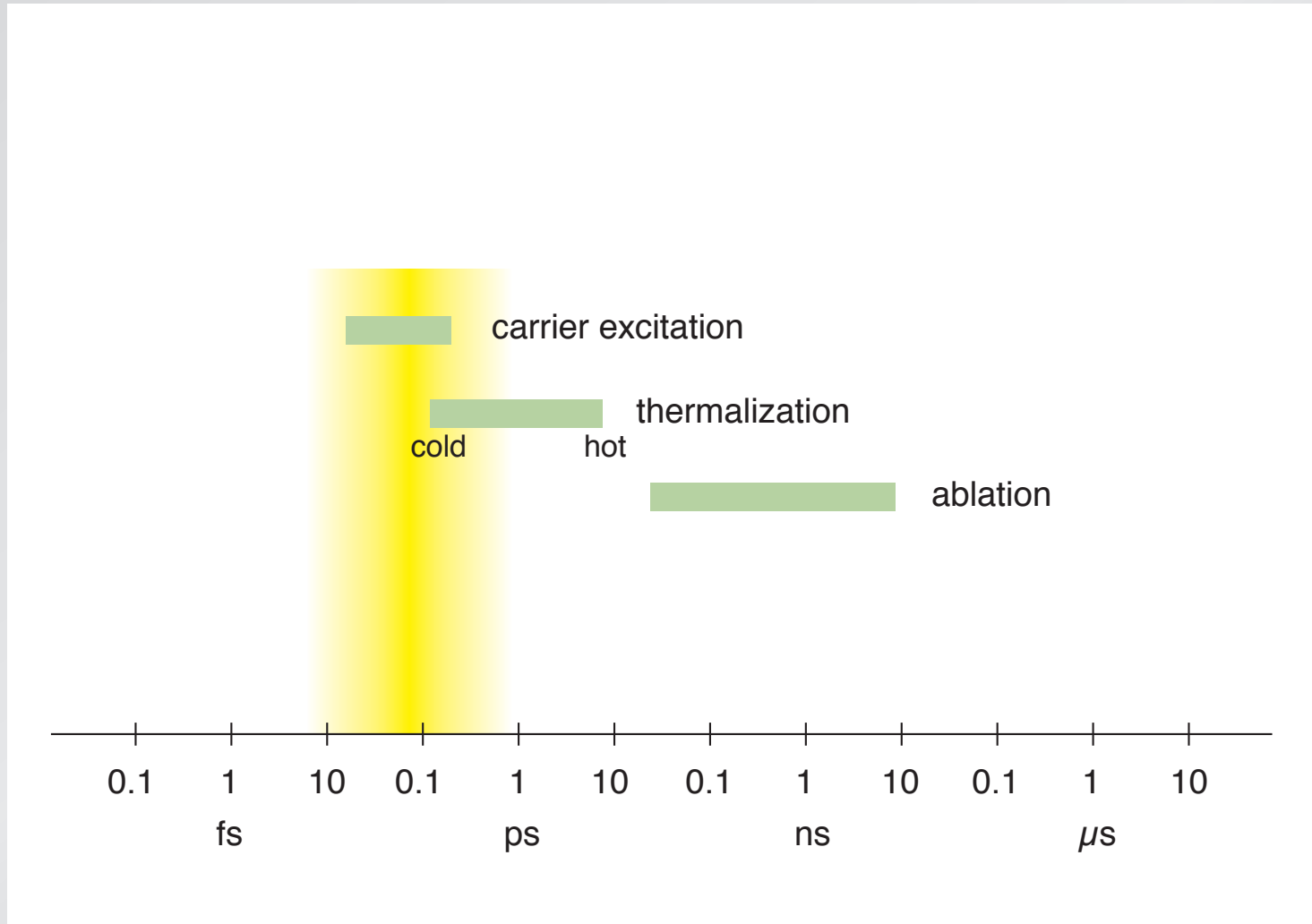
## relevant time scales





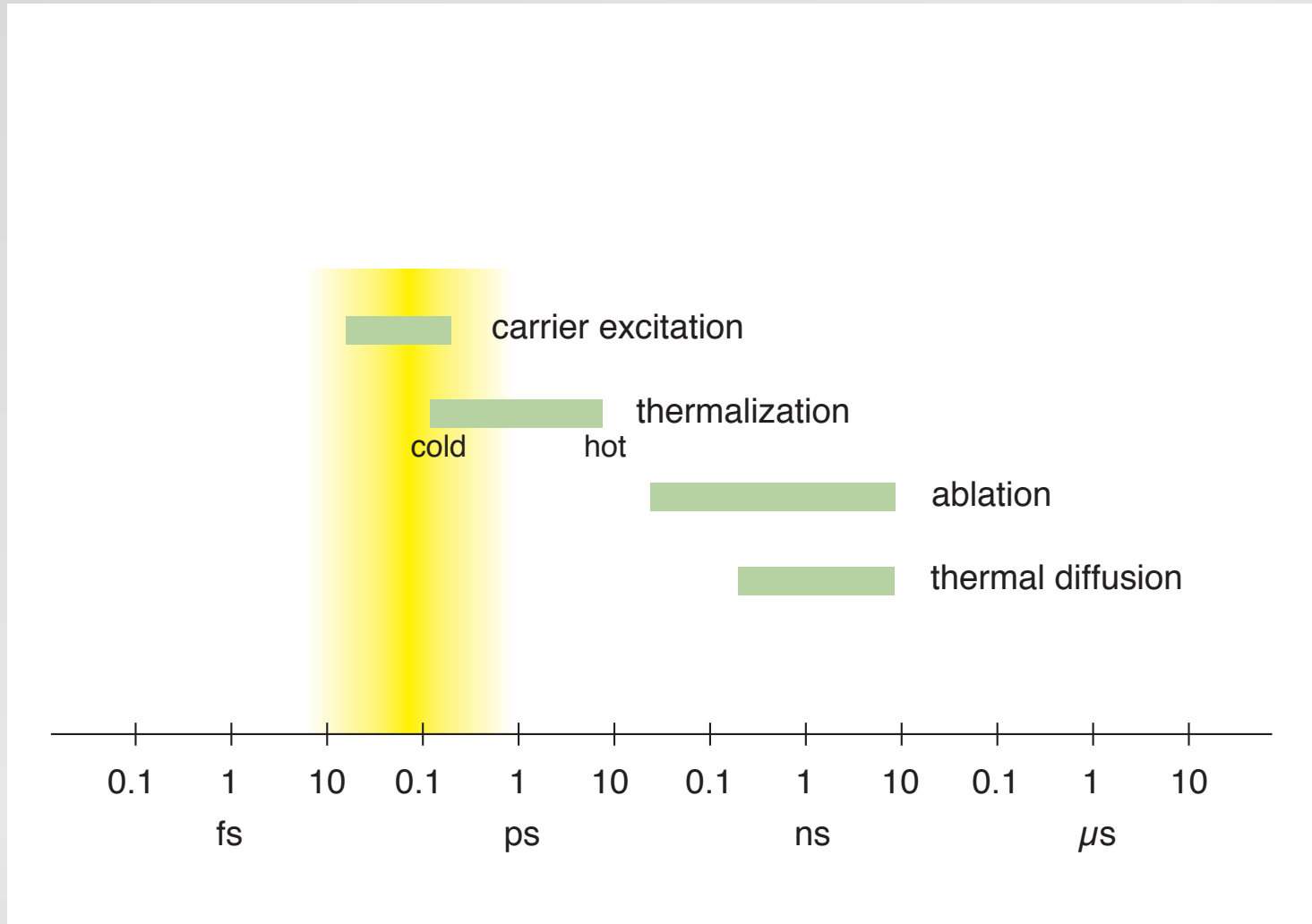
# Structure

## relevant time scales



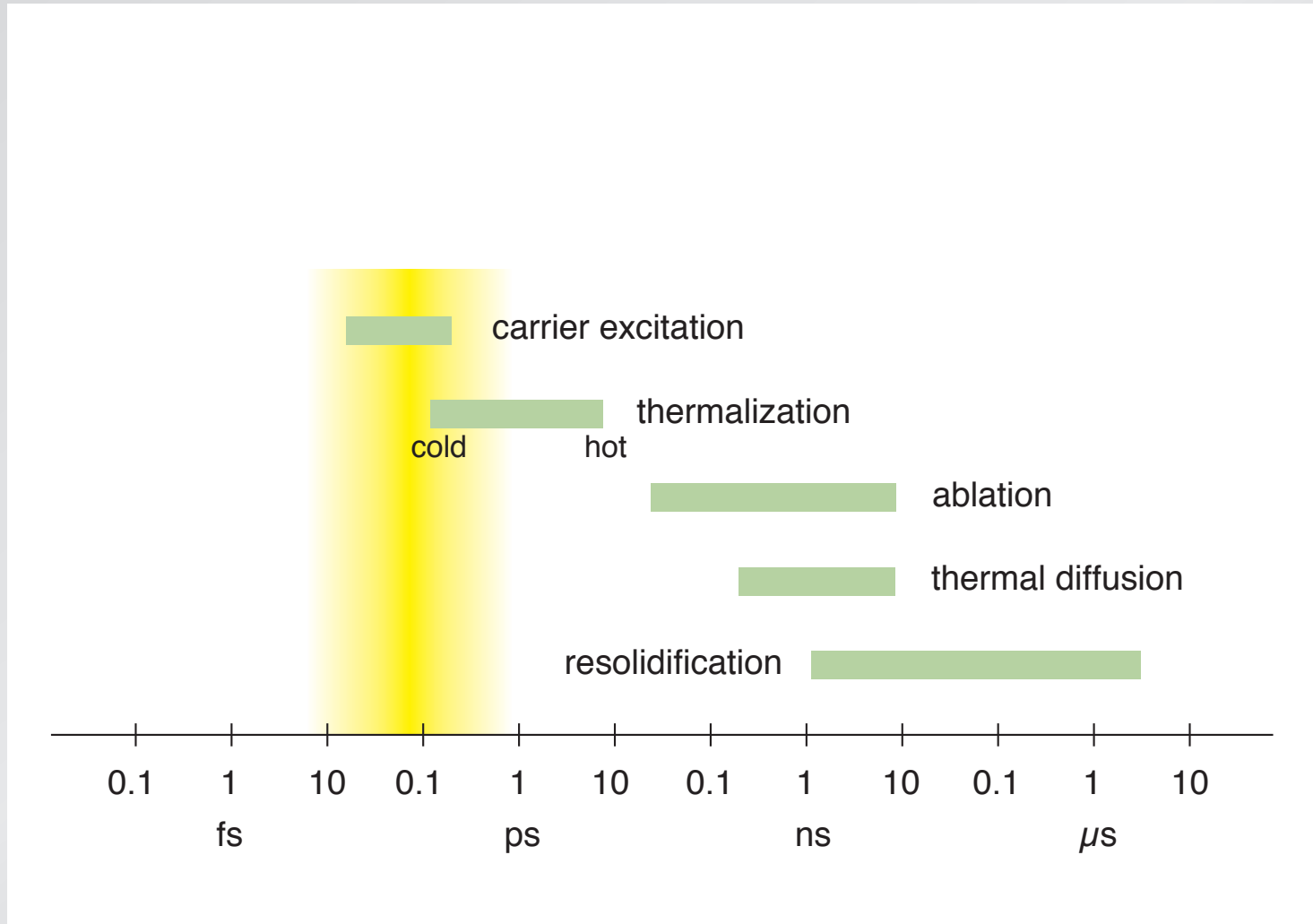
# Structure

## relevant time scales



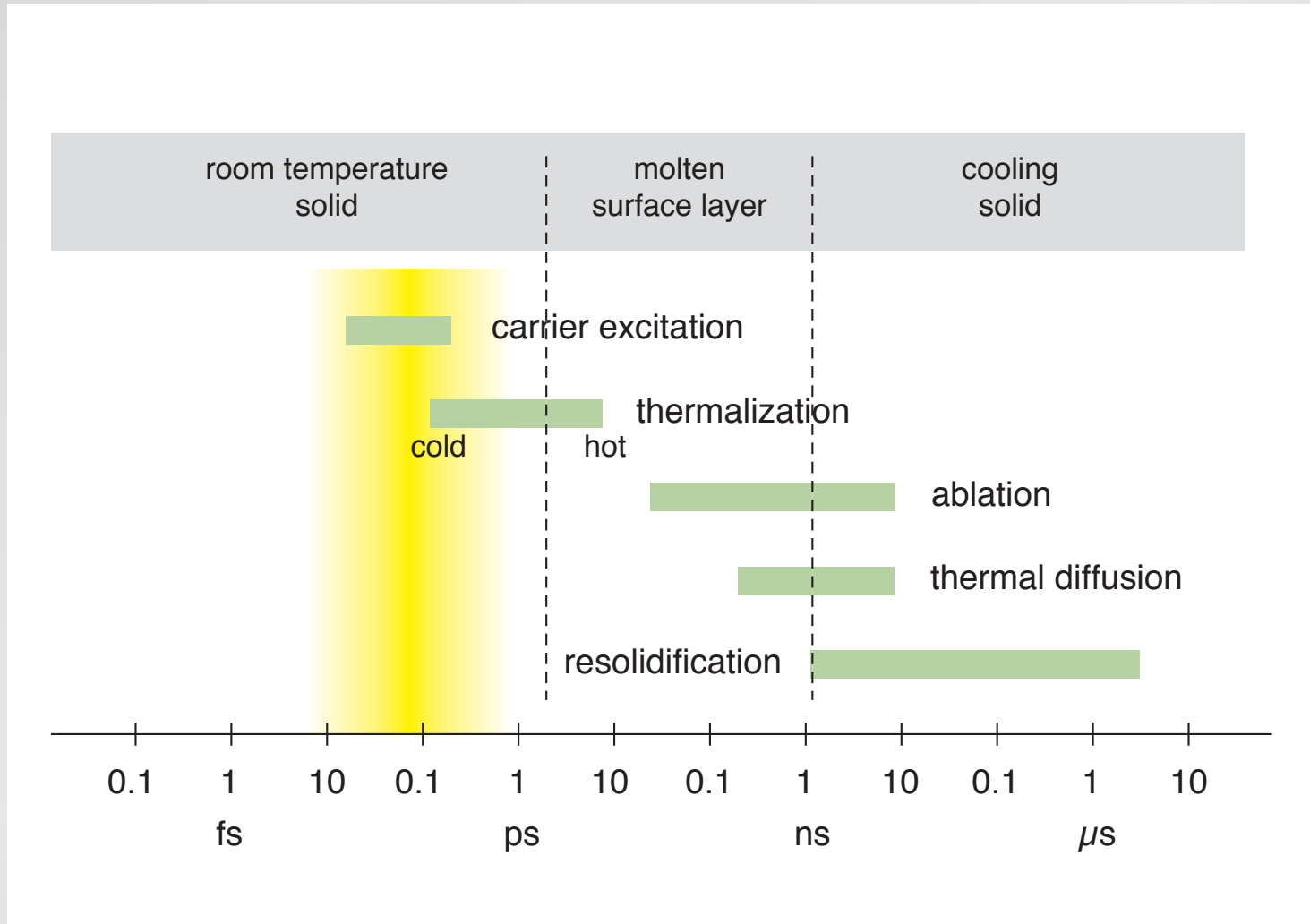
# Structure

## relevant time scales



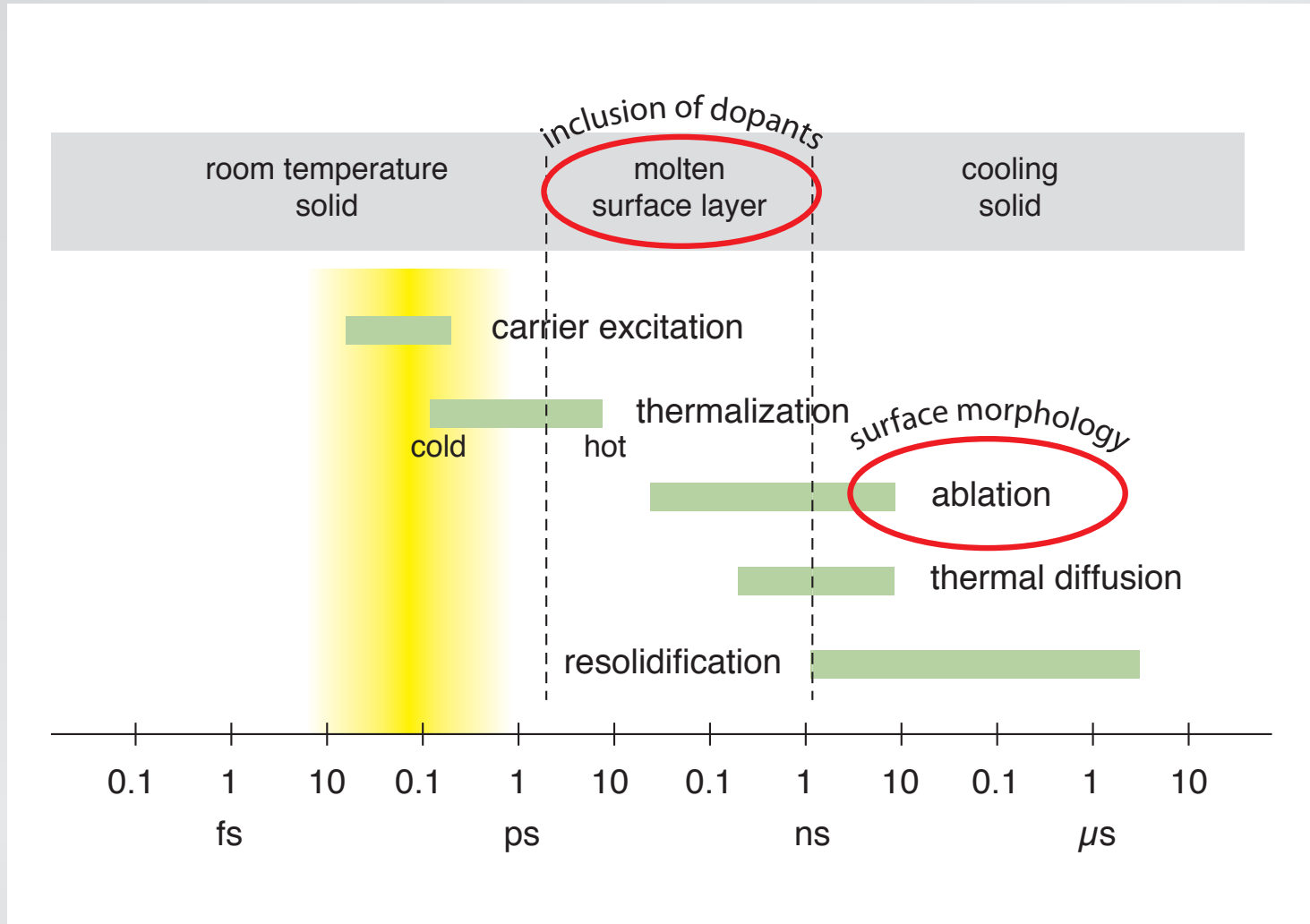
# Structure

## relevant time scales



# Structure

## relevant time scales



# Structure

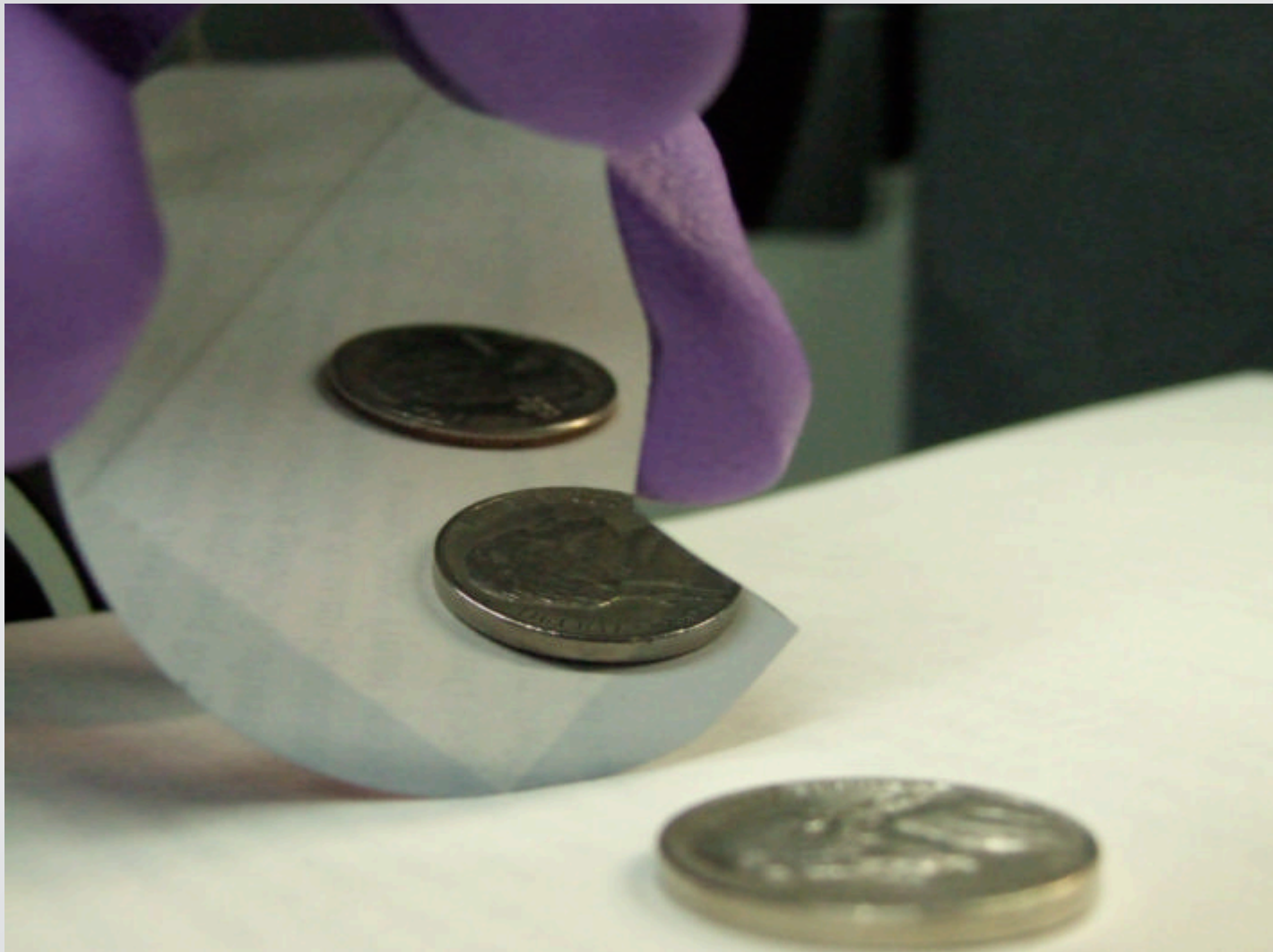
**different thresholds:**

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

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

# Structure

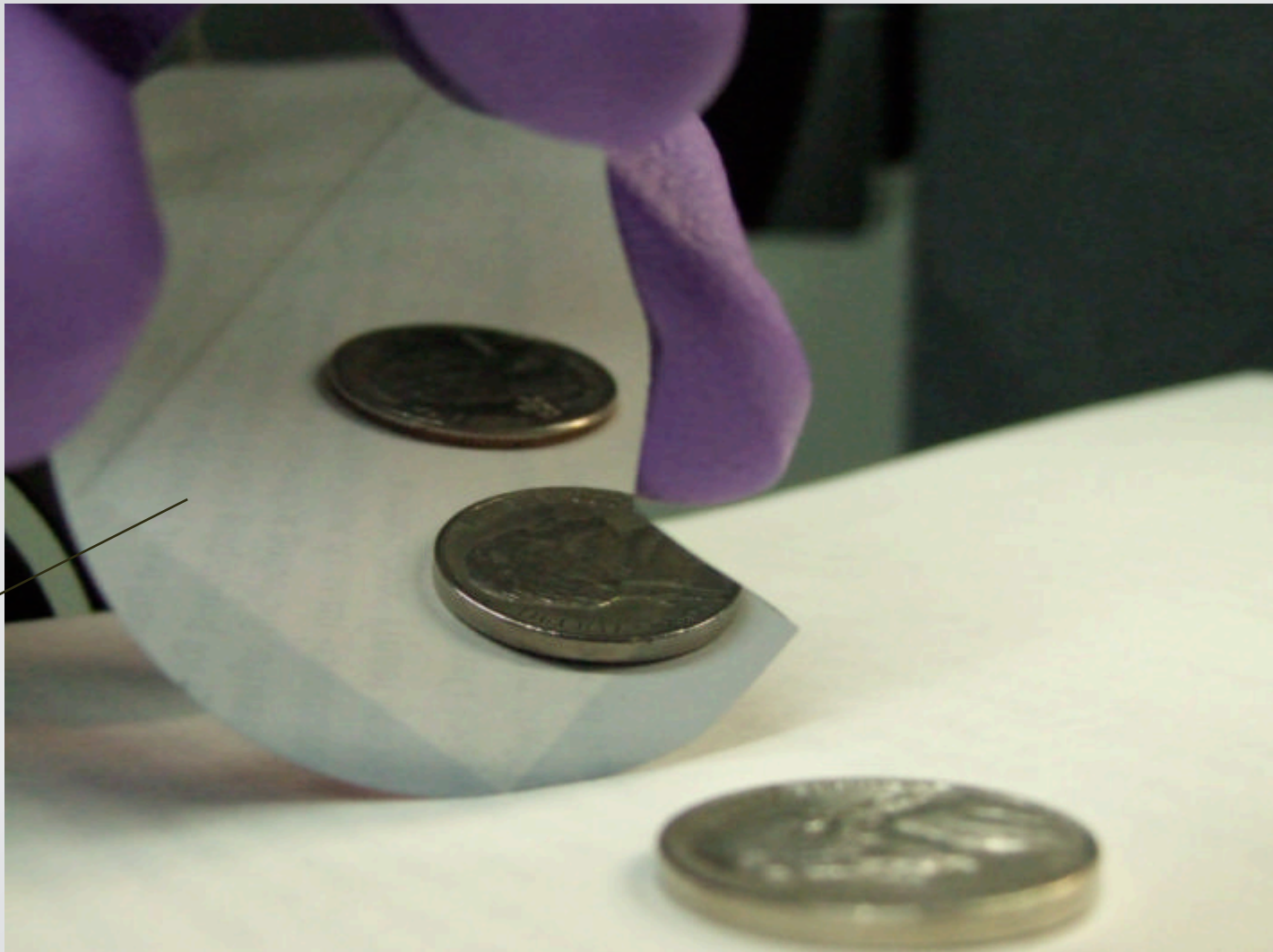
decouple ablation from melting



# Structure

decouple ablation from melting

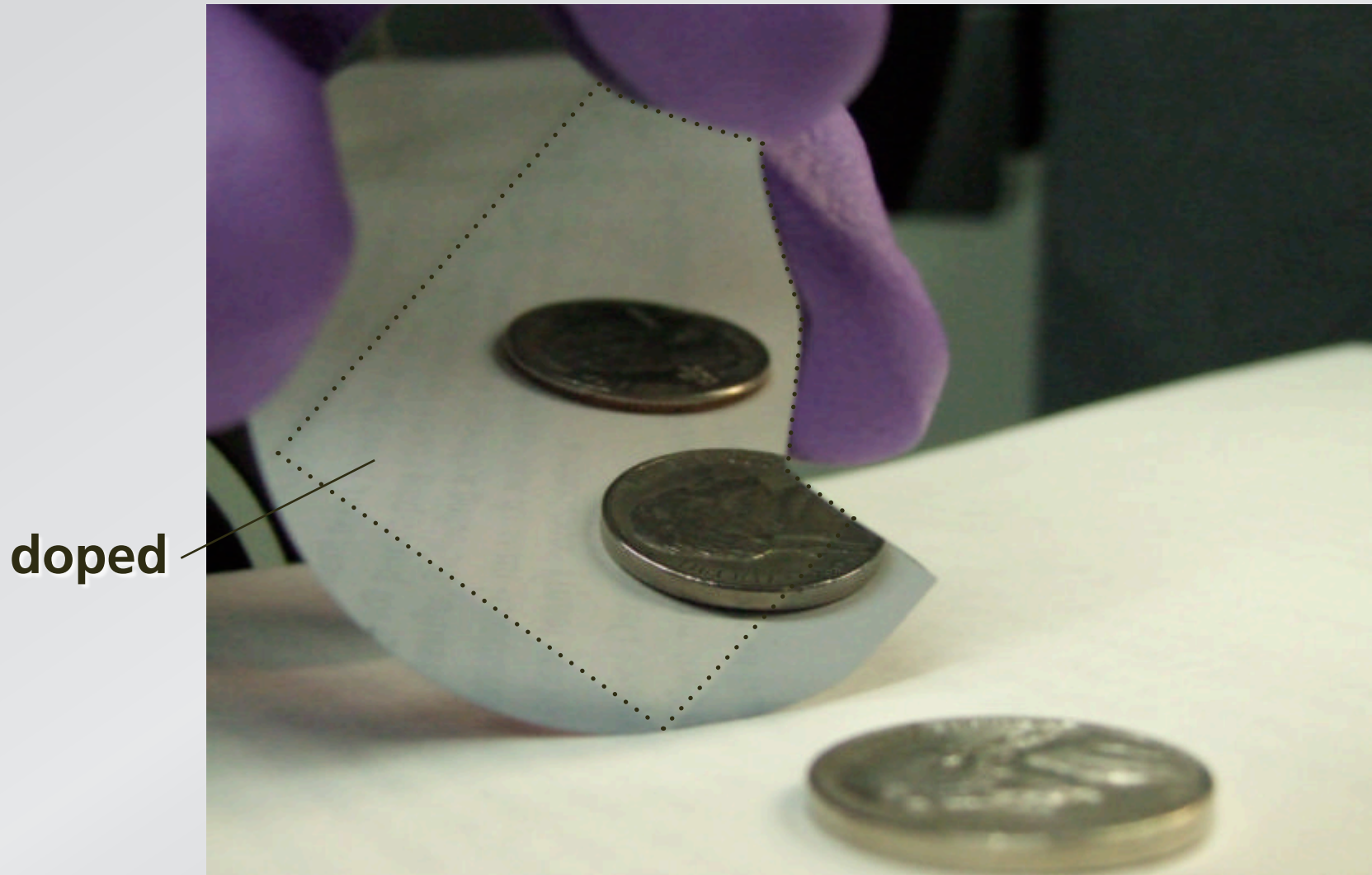
doped





# Structure

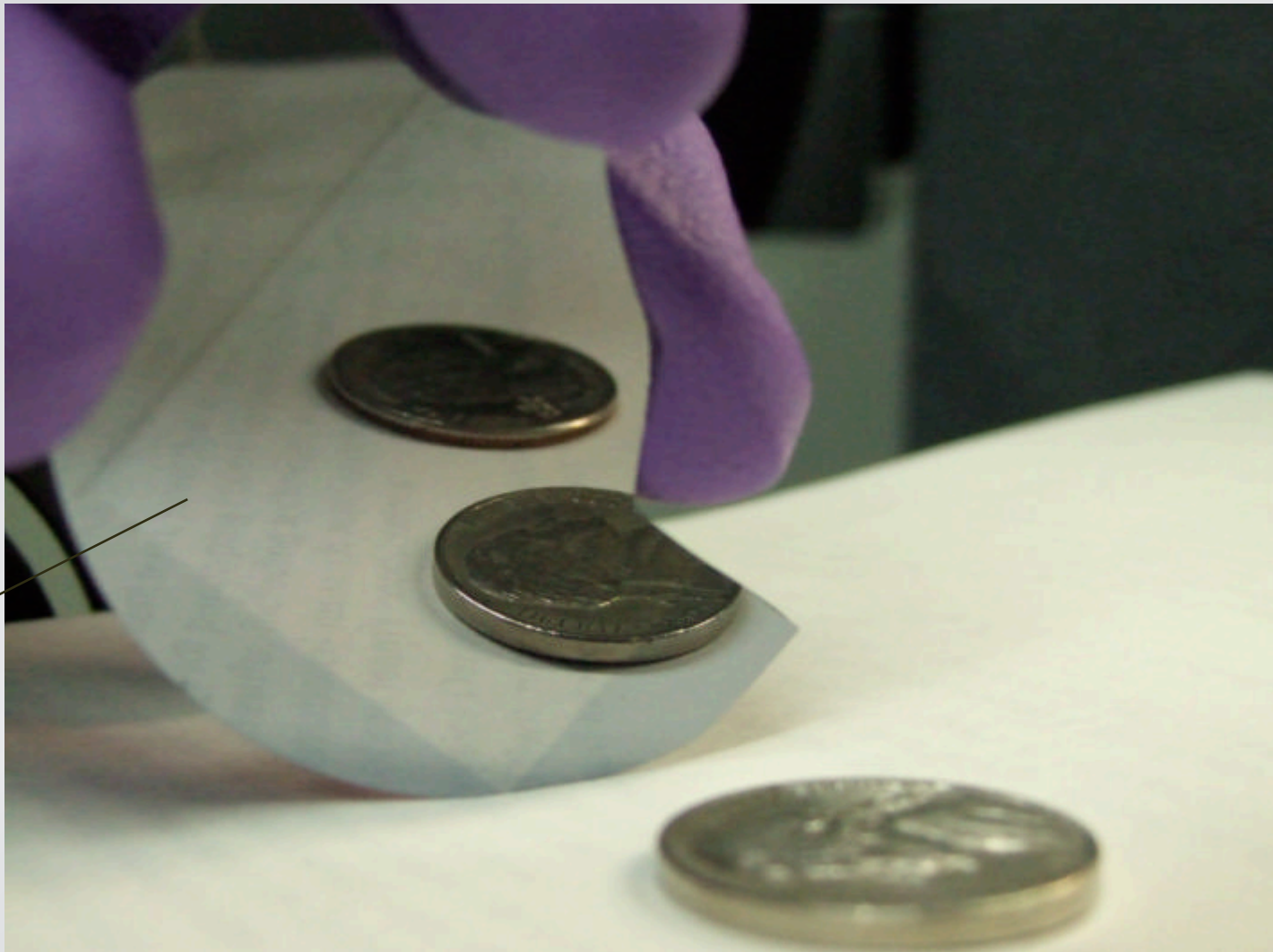
decouple ablation from melting



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decouple ablation from melting

doped

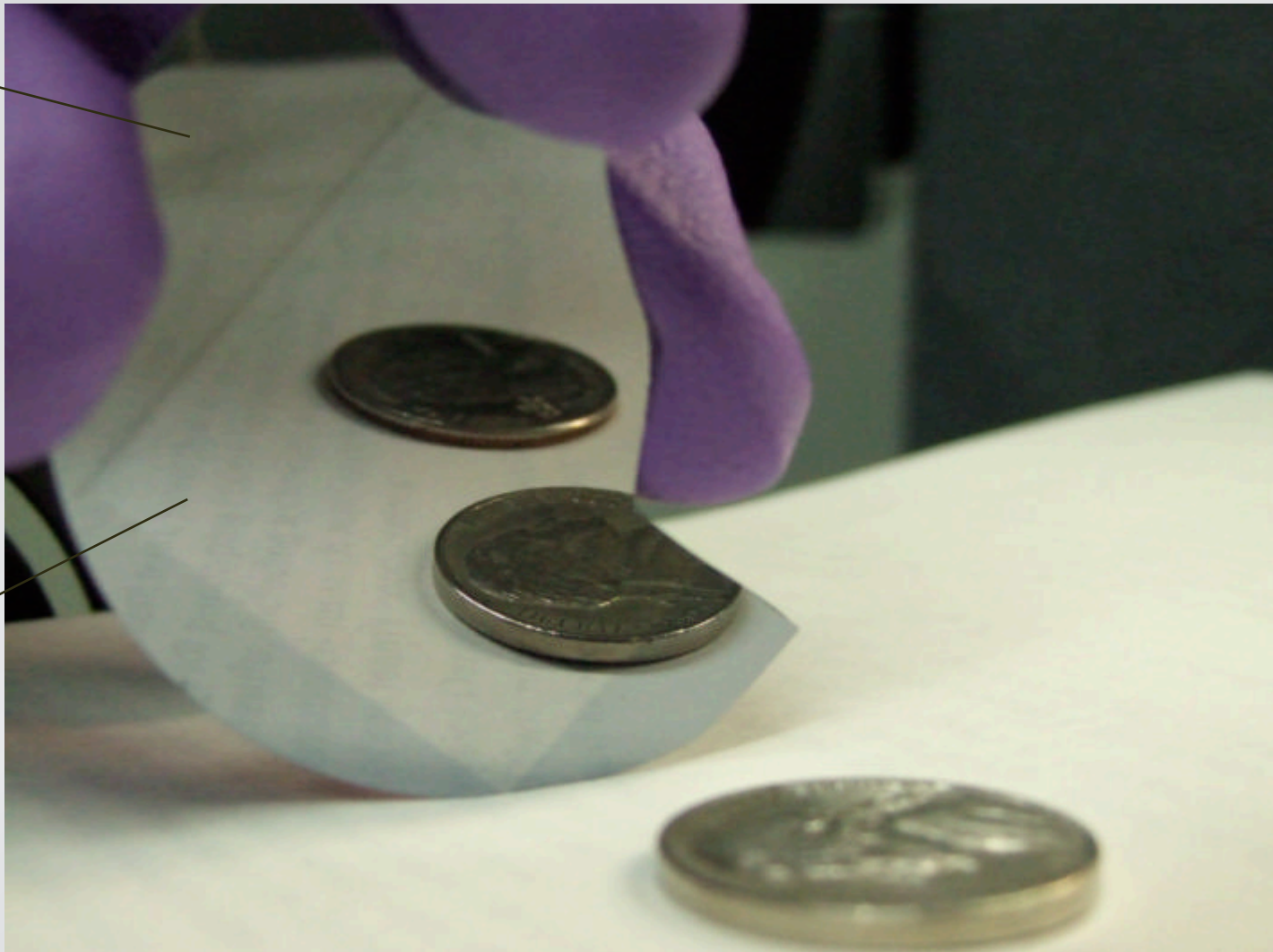


# Structure

decouple ablation from melting

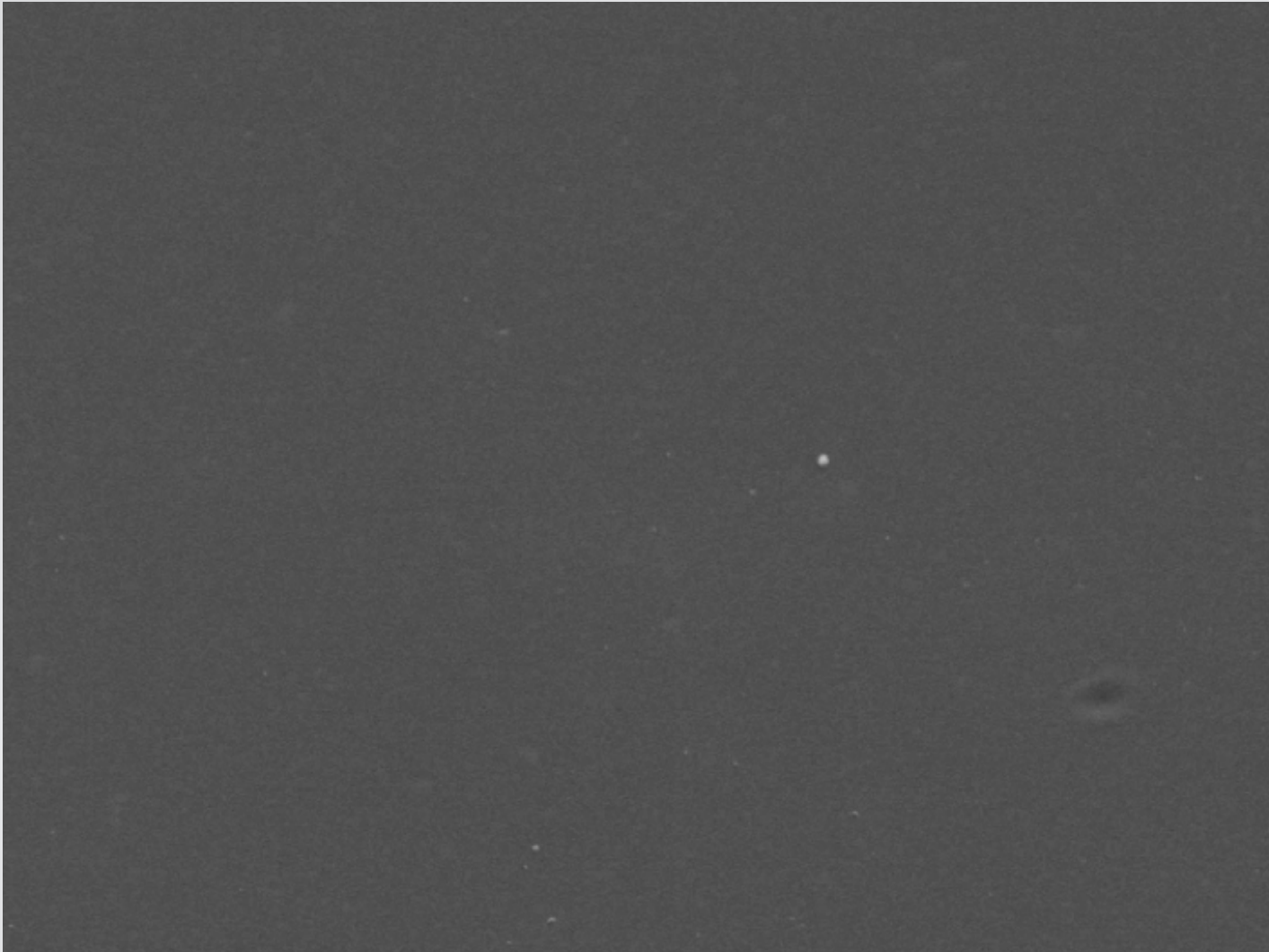
undoped

doped



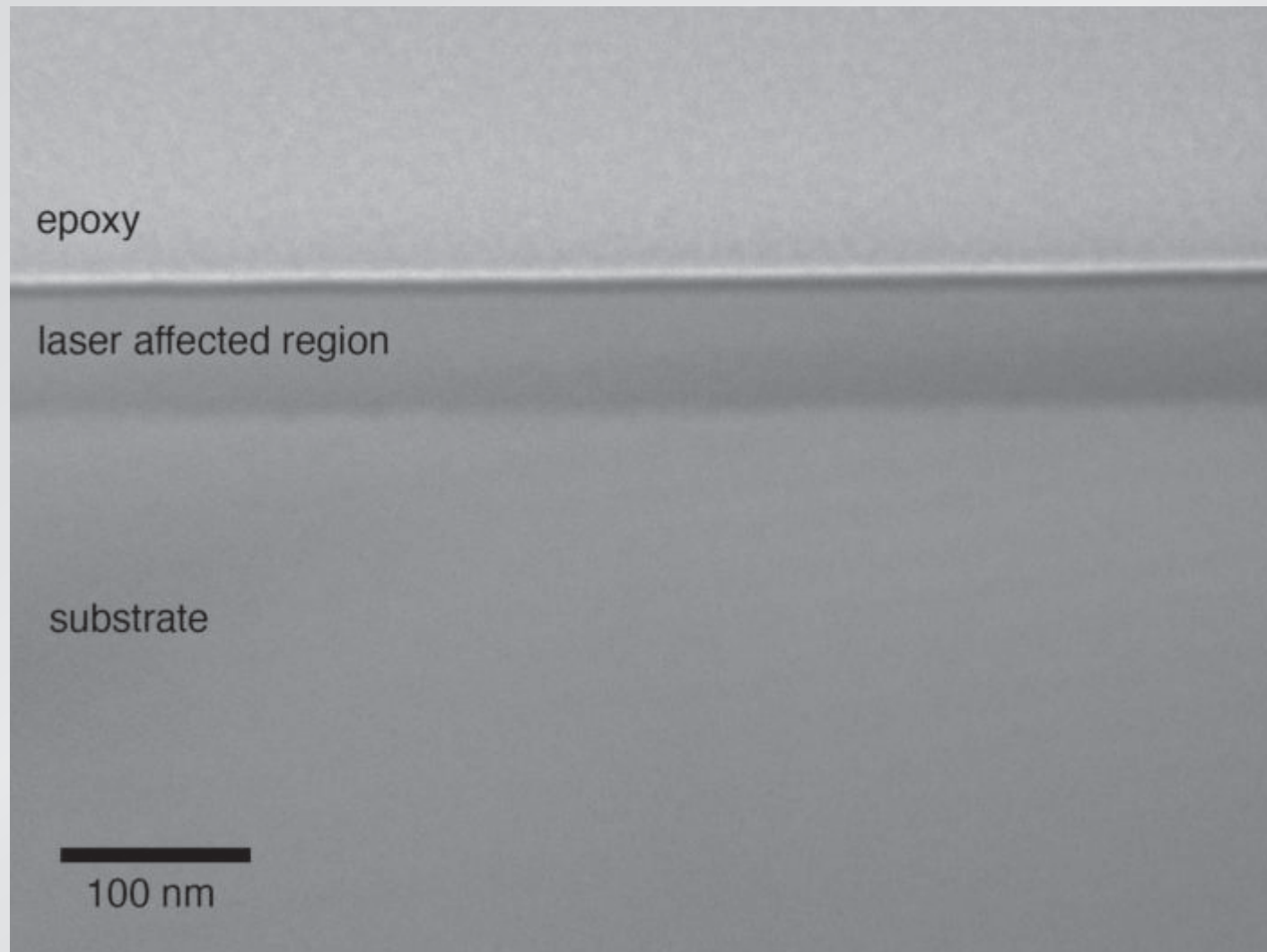
# Structure

decouple ablation from melting



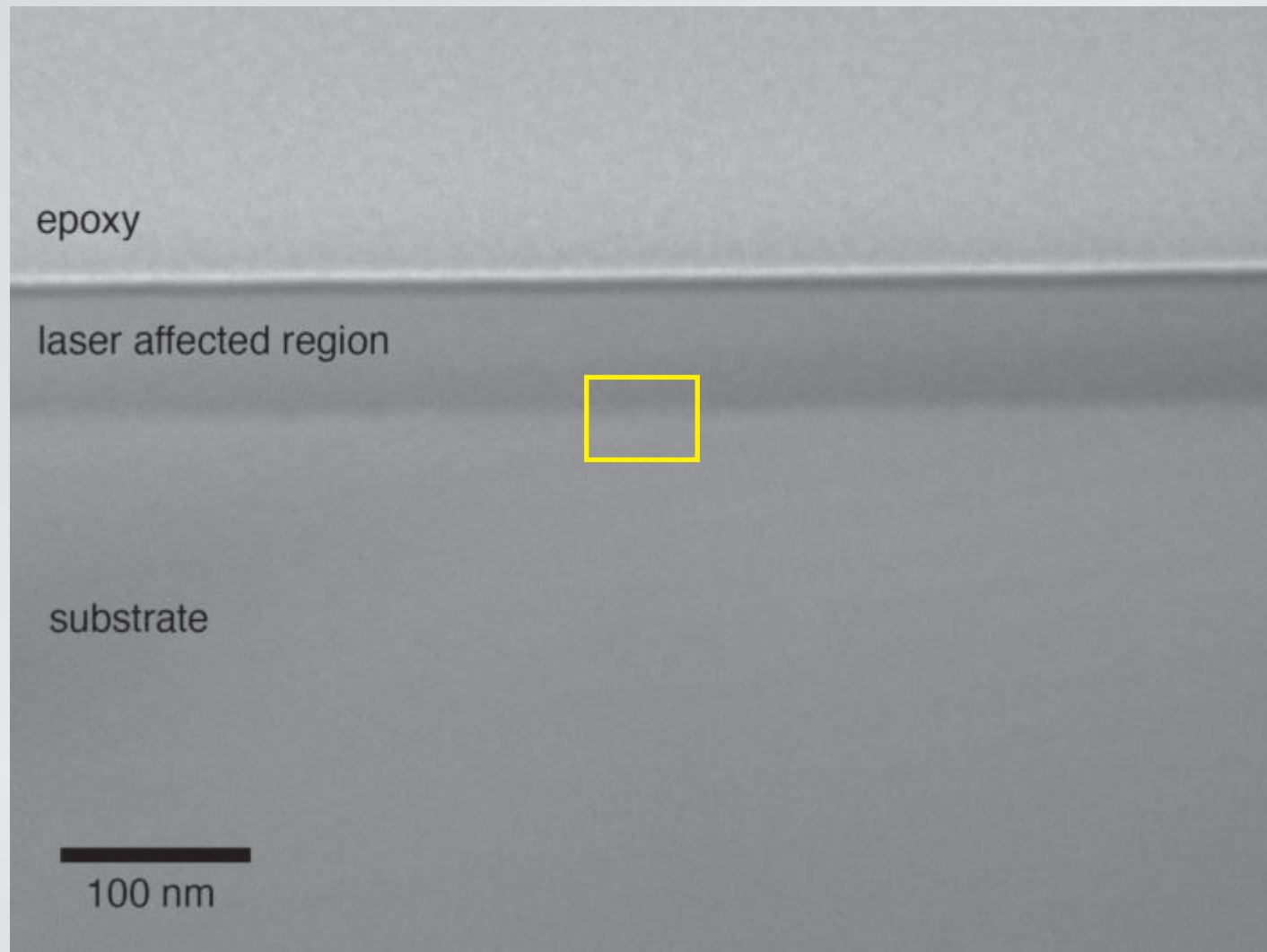
# Structure

decouple ablation from melting



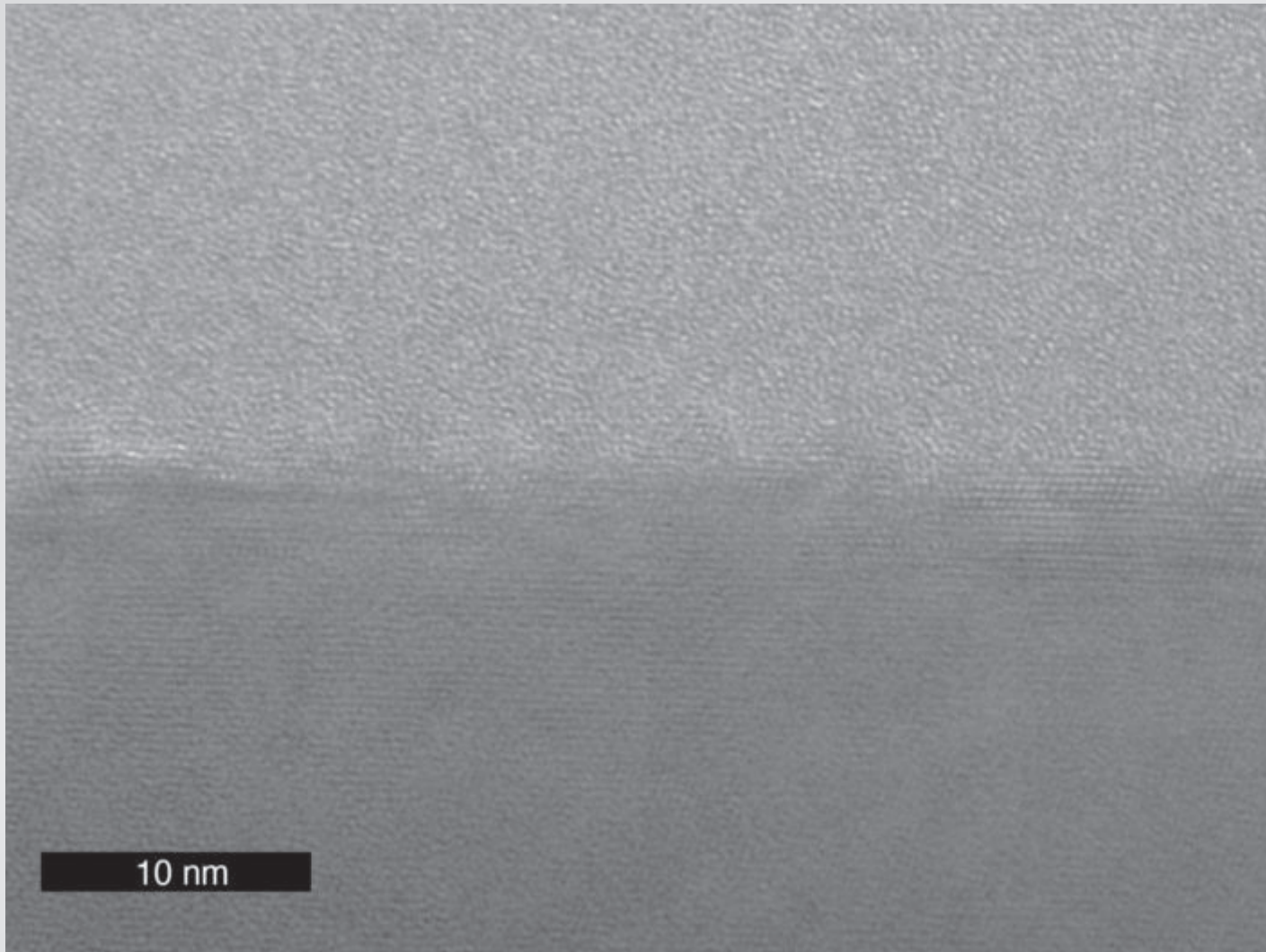
# Structure

decouple ablation from melting



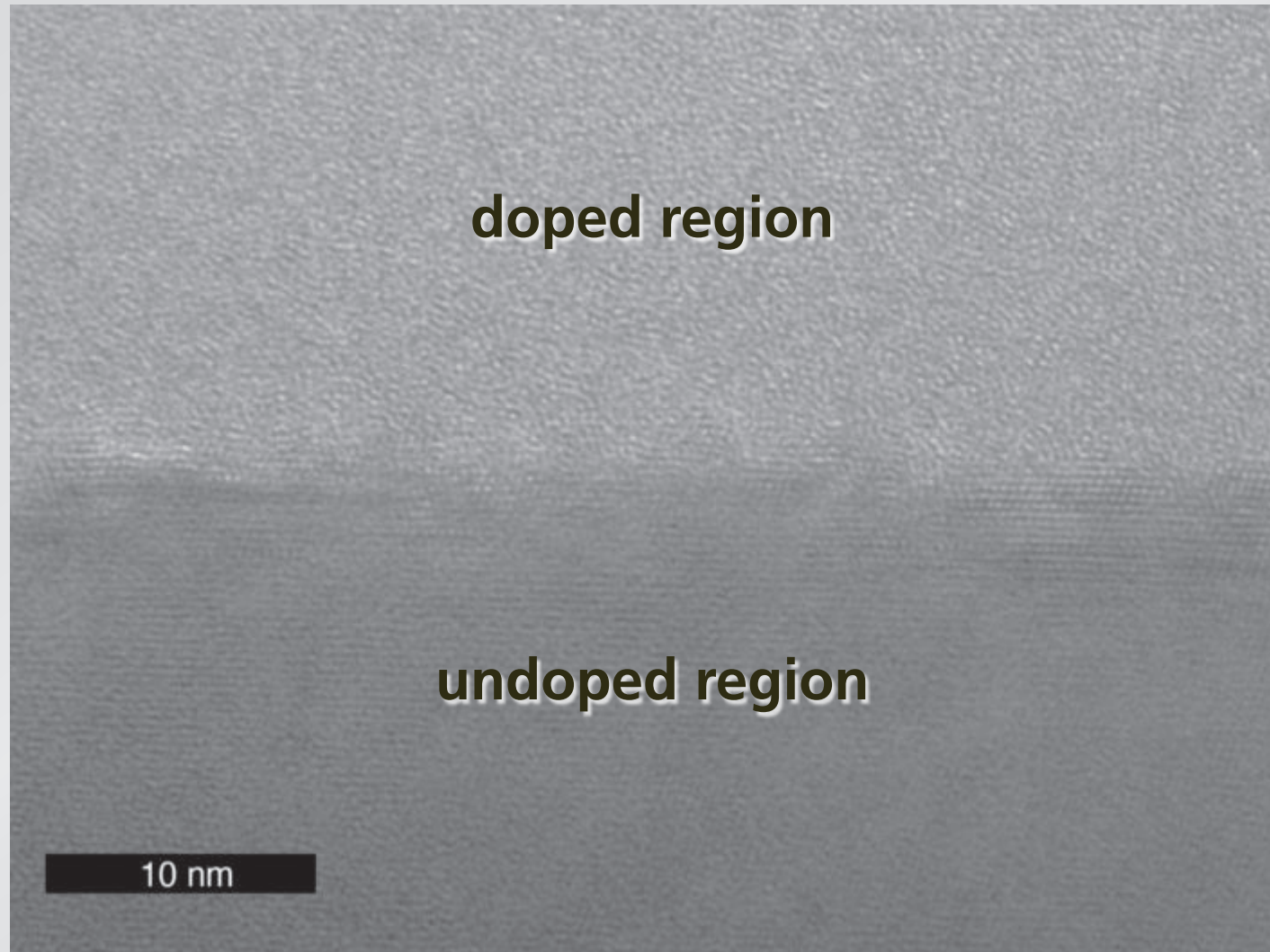
# Structure

decouple ablation from melting



# Structure

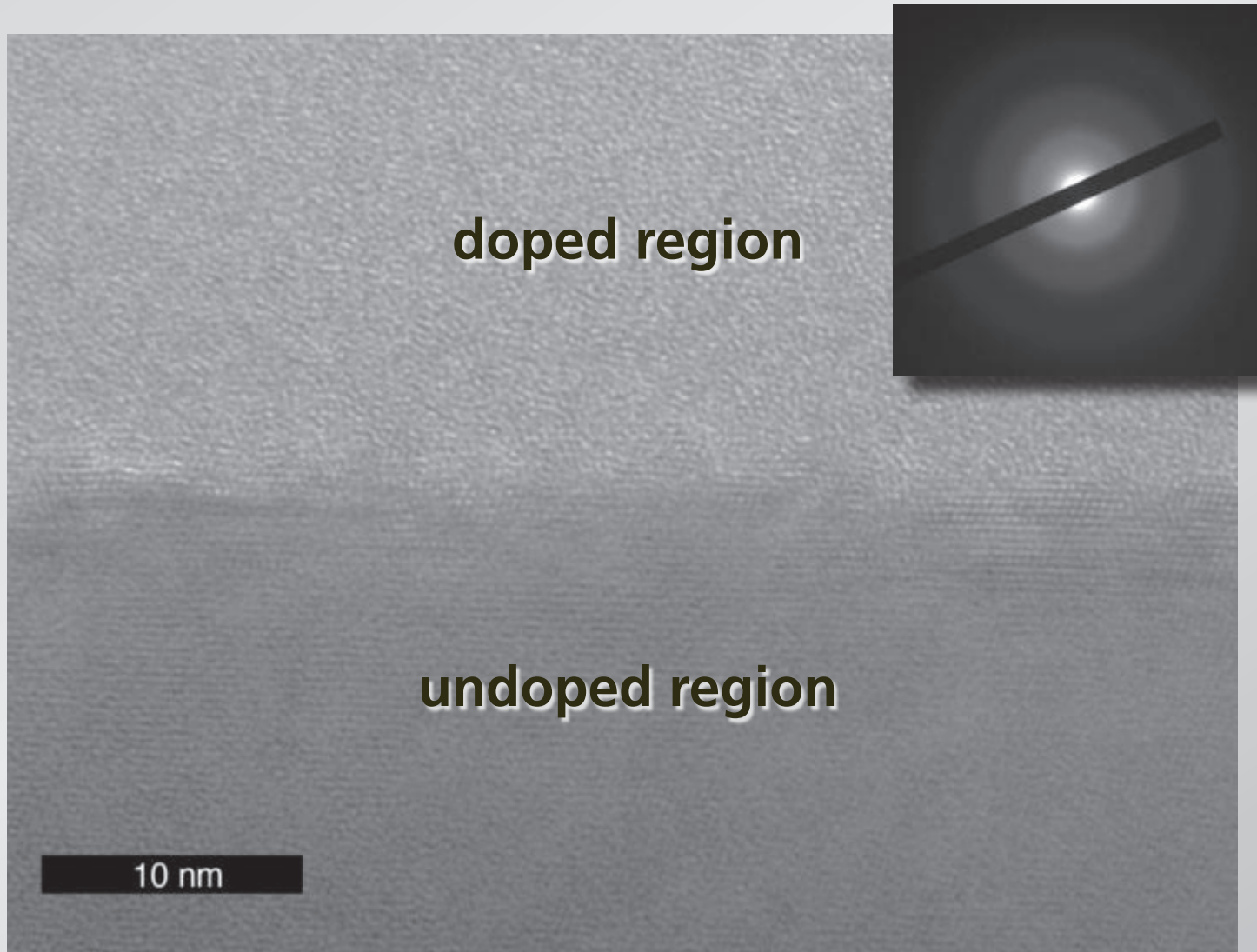
decouple ablation from melting





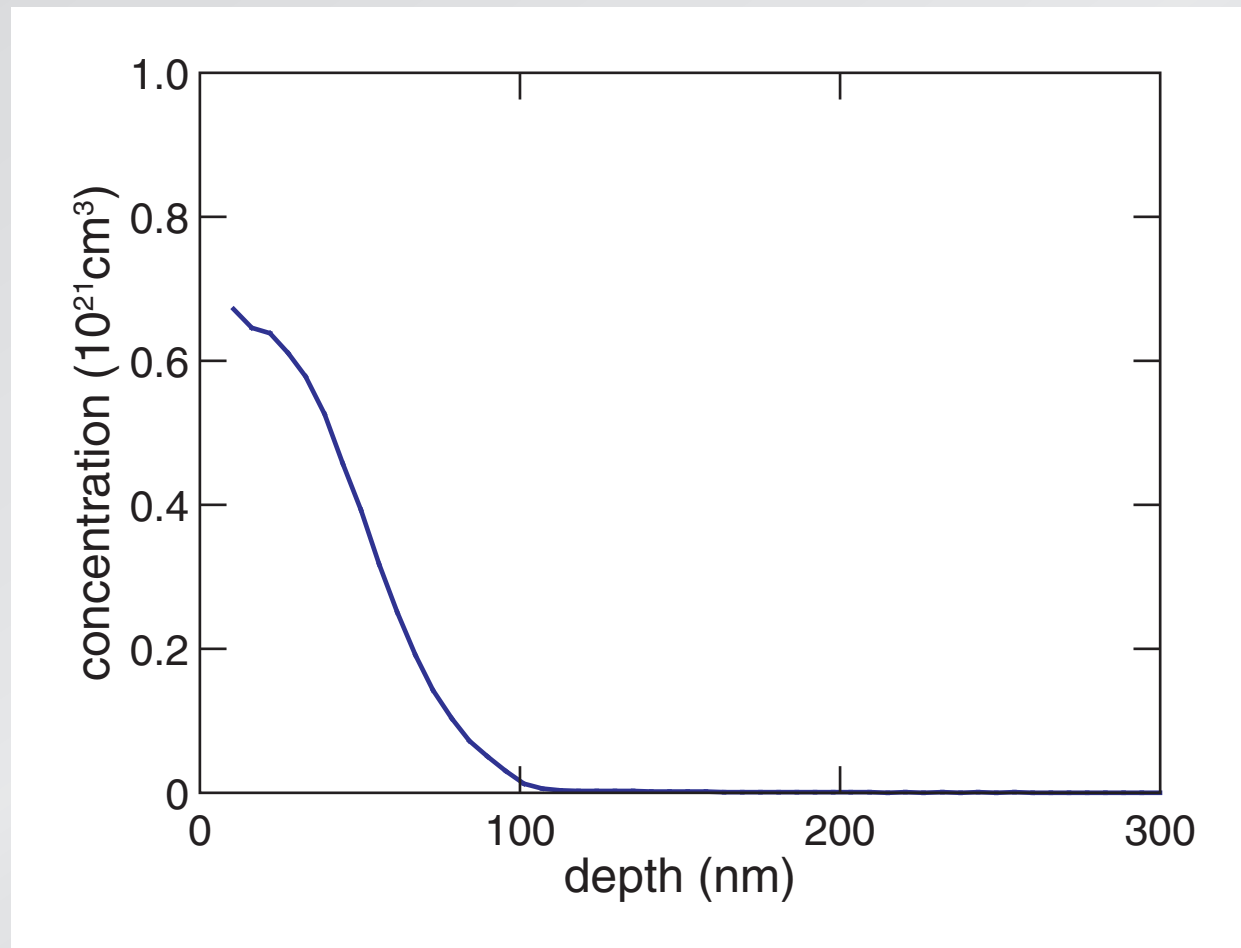
# Structure

decouple ablation from melting

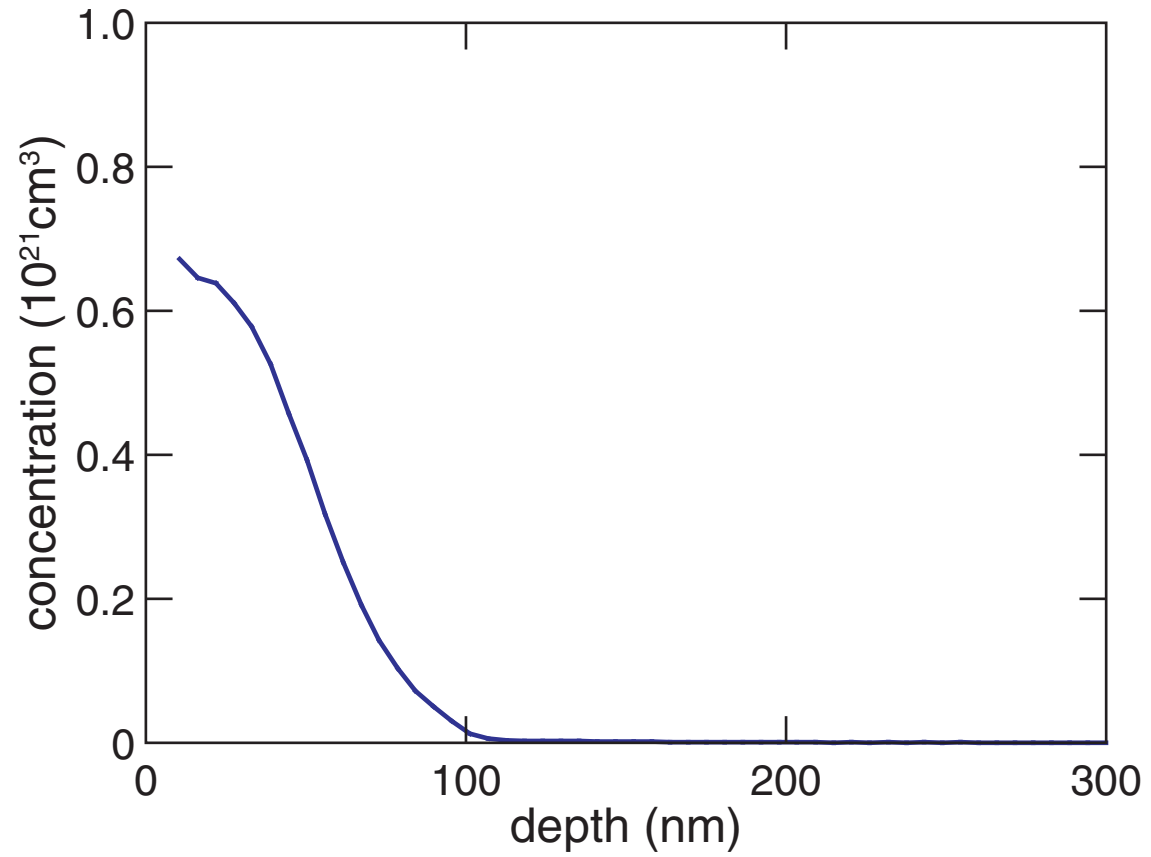


# Structure

## secondary ion mass spectrometry



# Structure



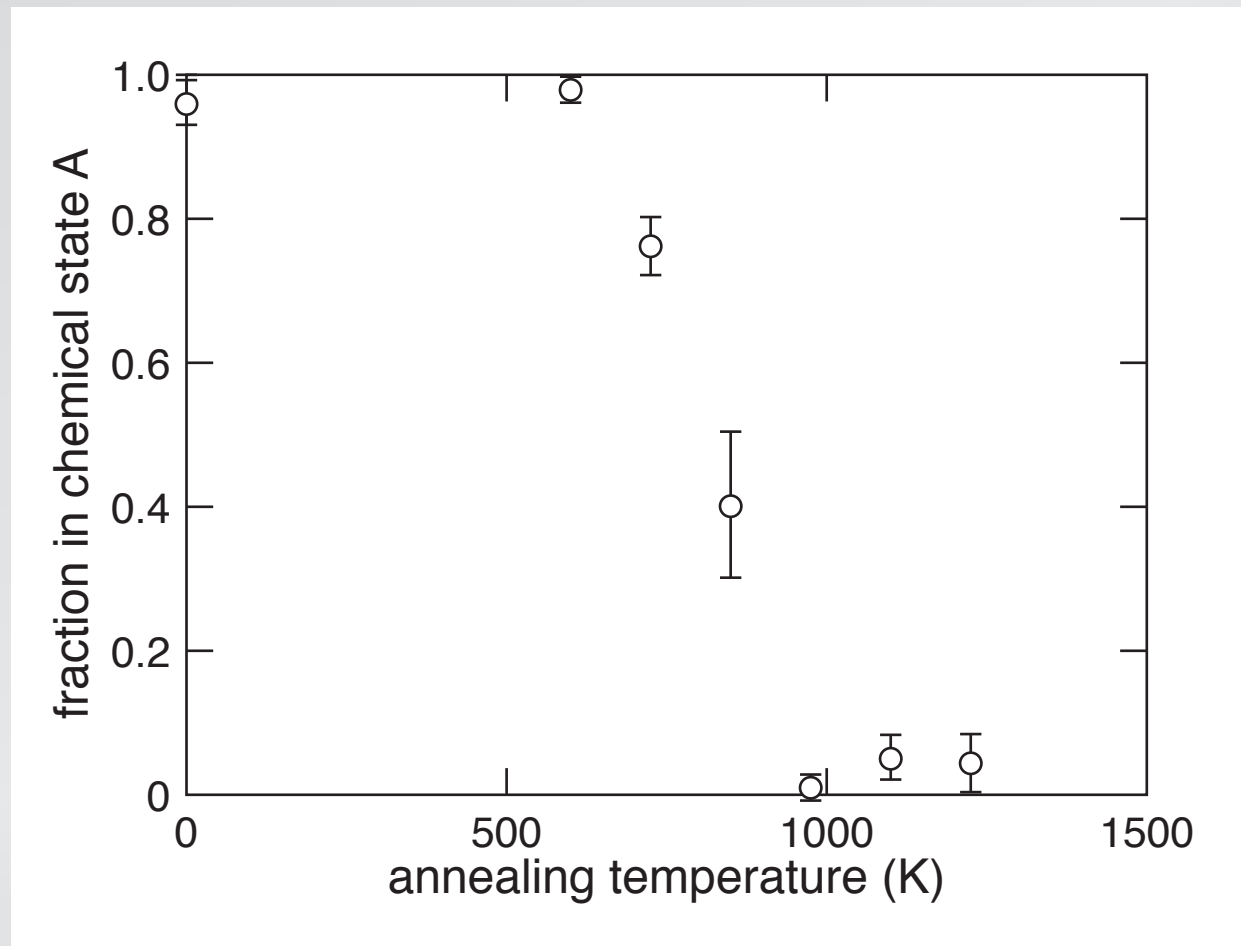
# Structure

**extended x-ray absorption fine structure spectrum:**

**dopant in two different chemical states**

# Structure

annealing changes local coordination



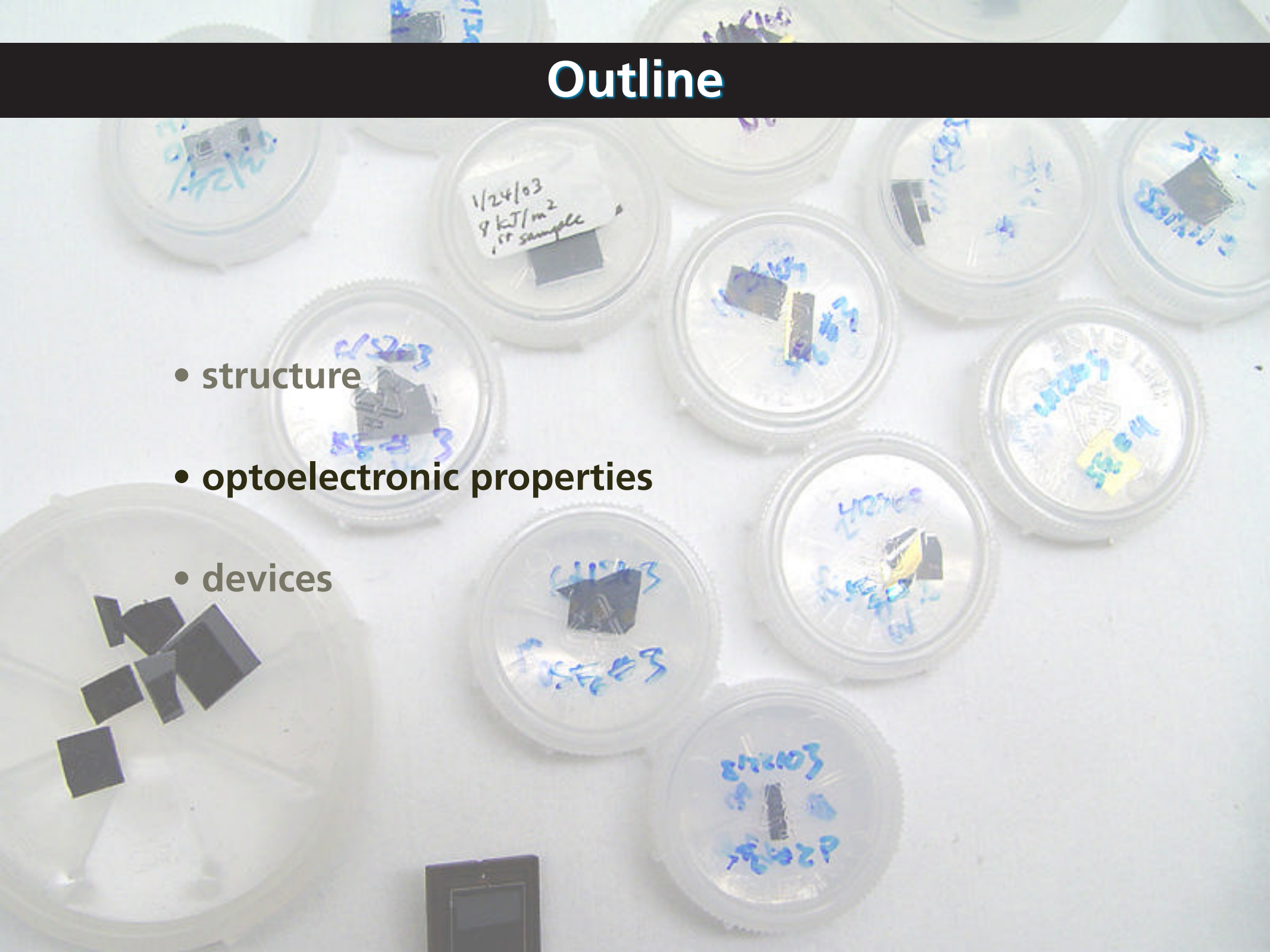
# Structure

## 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

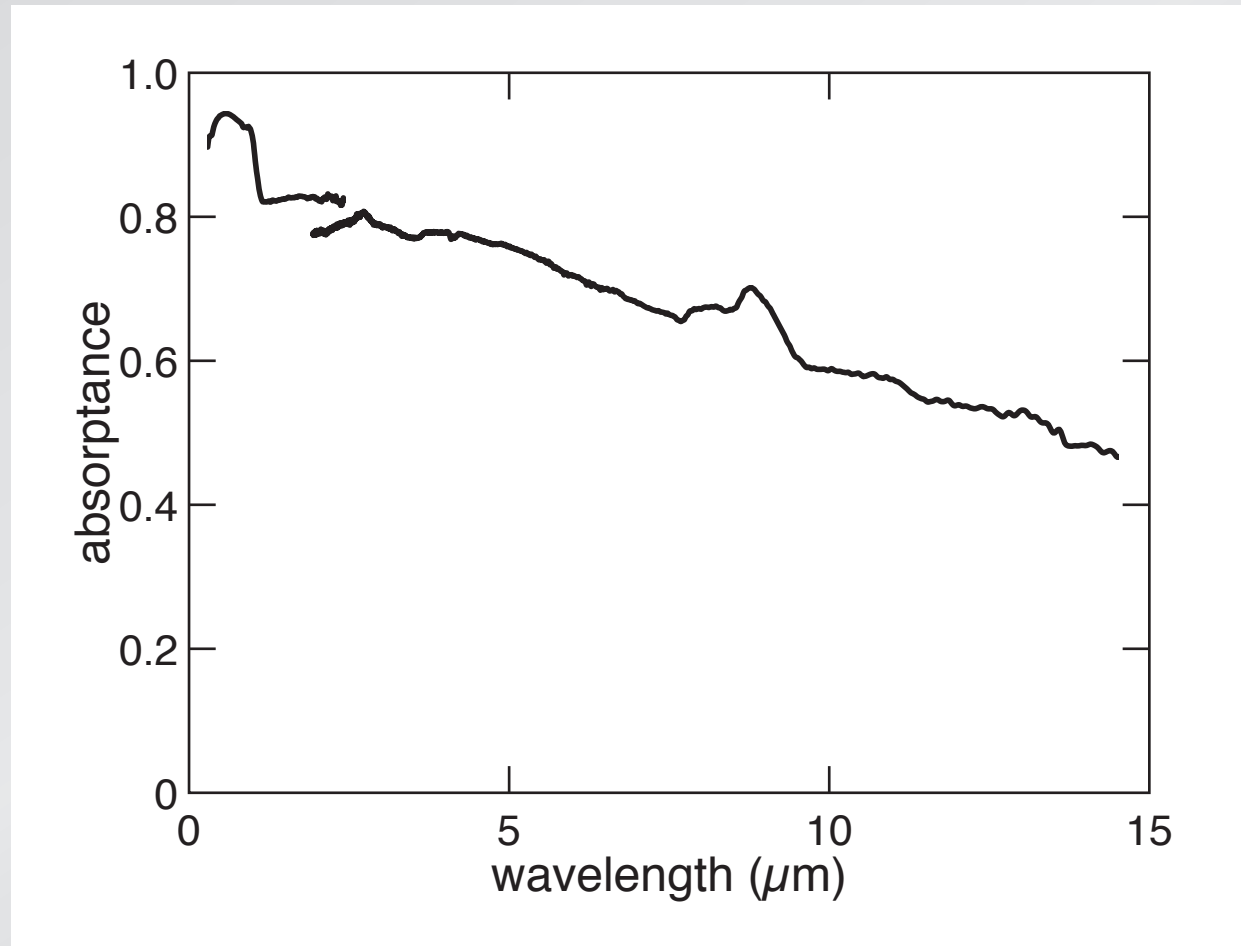
# Outline

- structure
- optoelectronic properties
- devices



# Optoelectronic properties

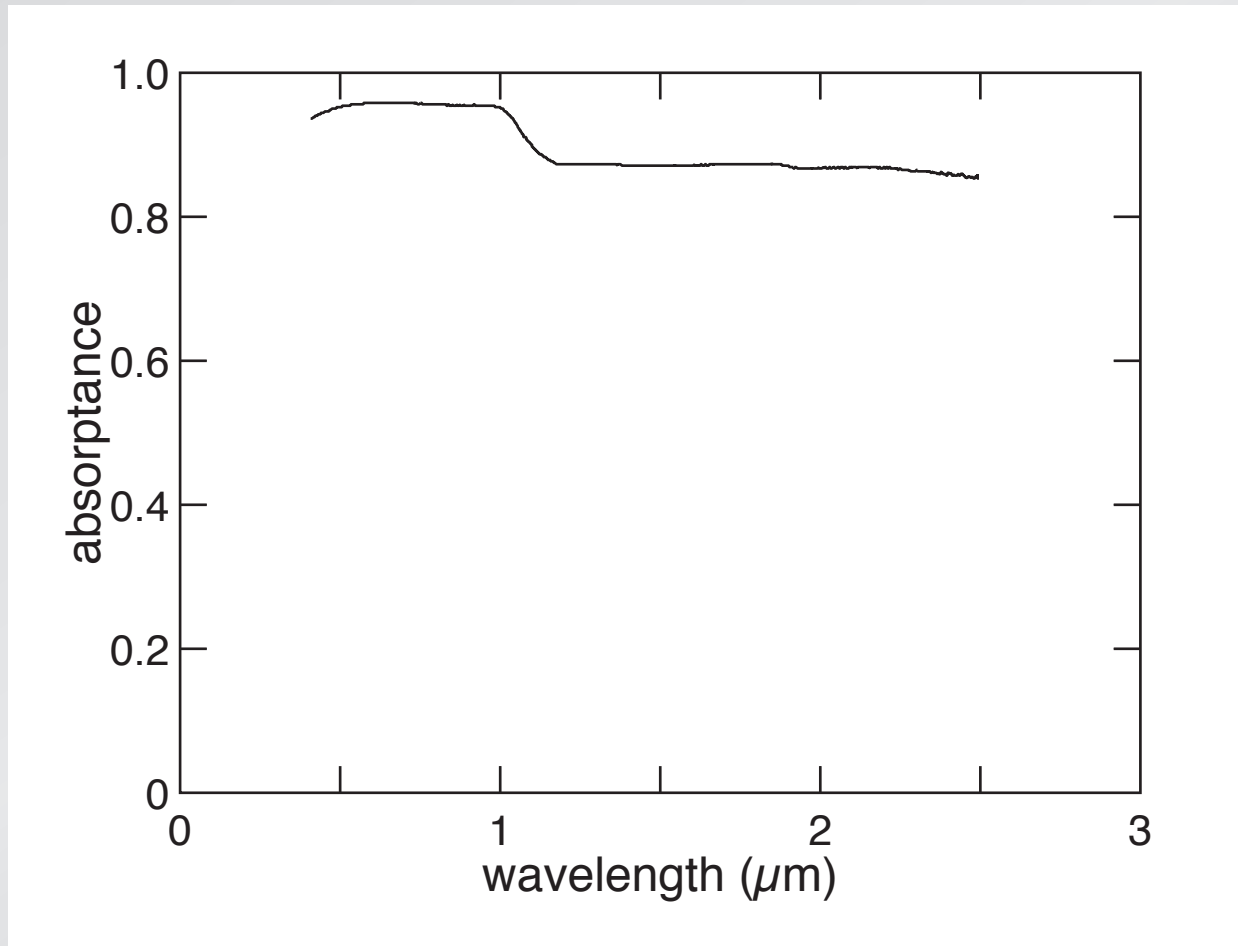
absorptance ( $1 - R_{int} - T_{int}$ )





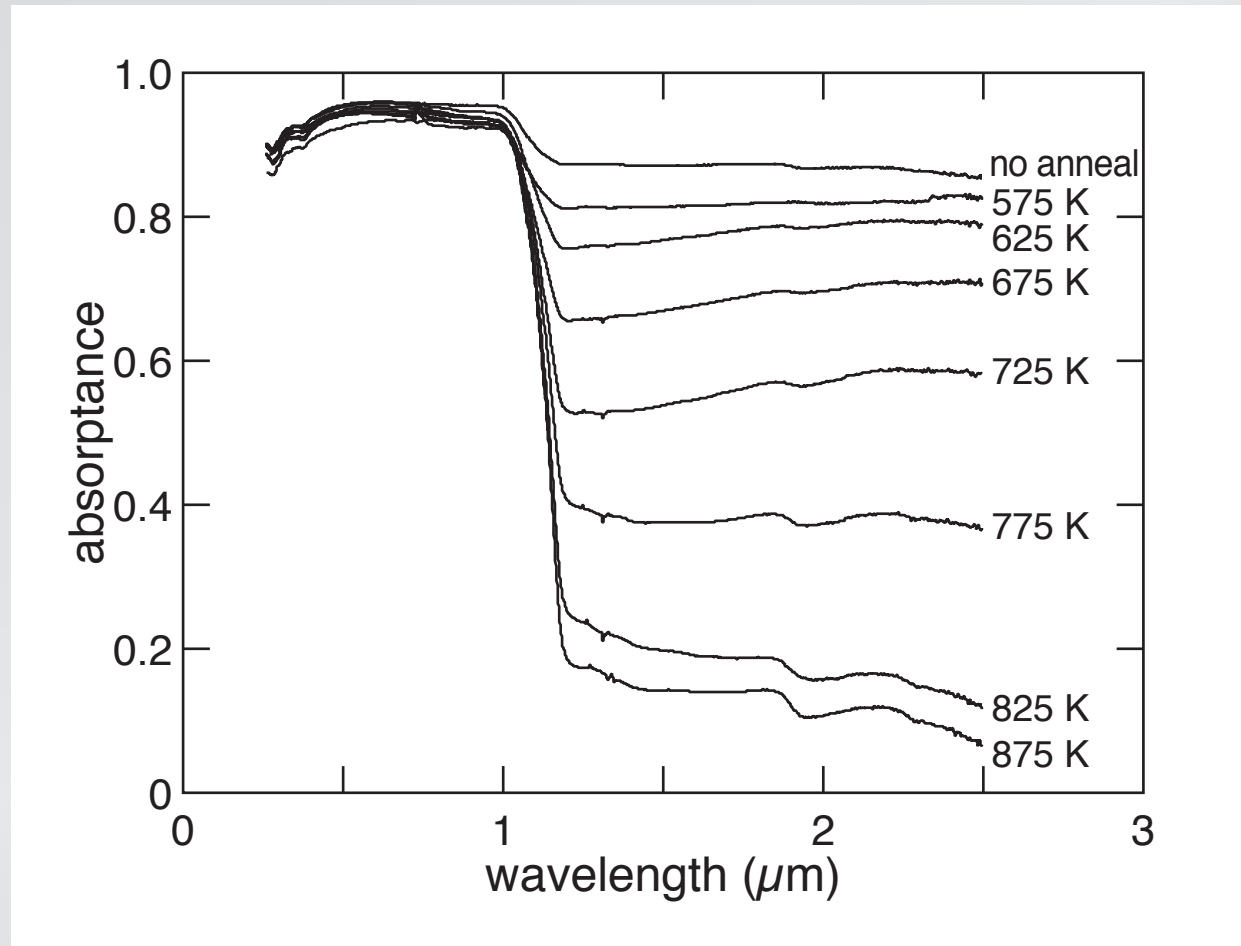
# Optoelectronic properties

effect of annealing on IR absorptance



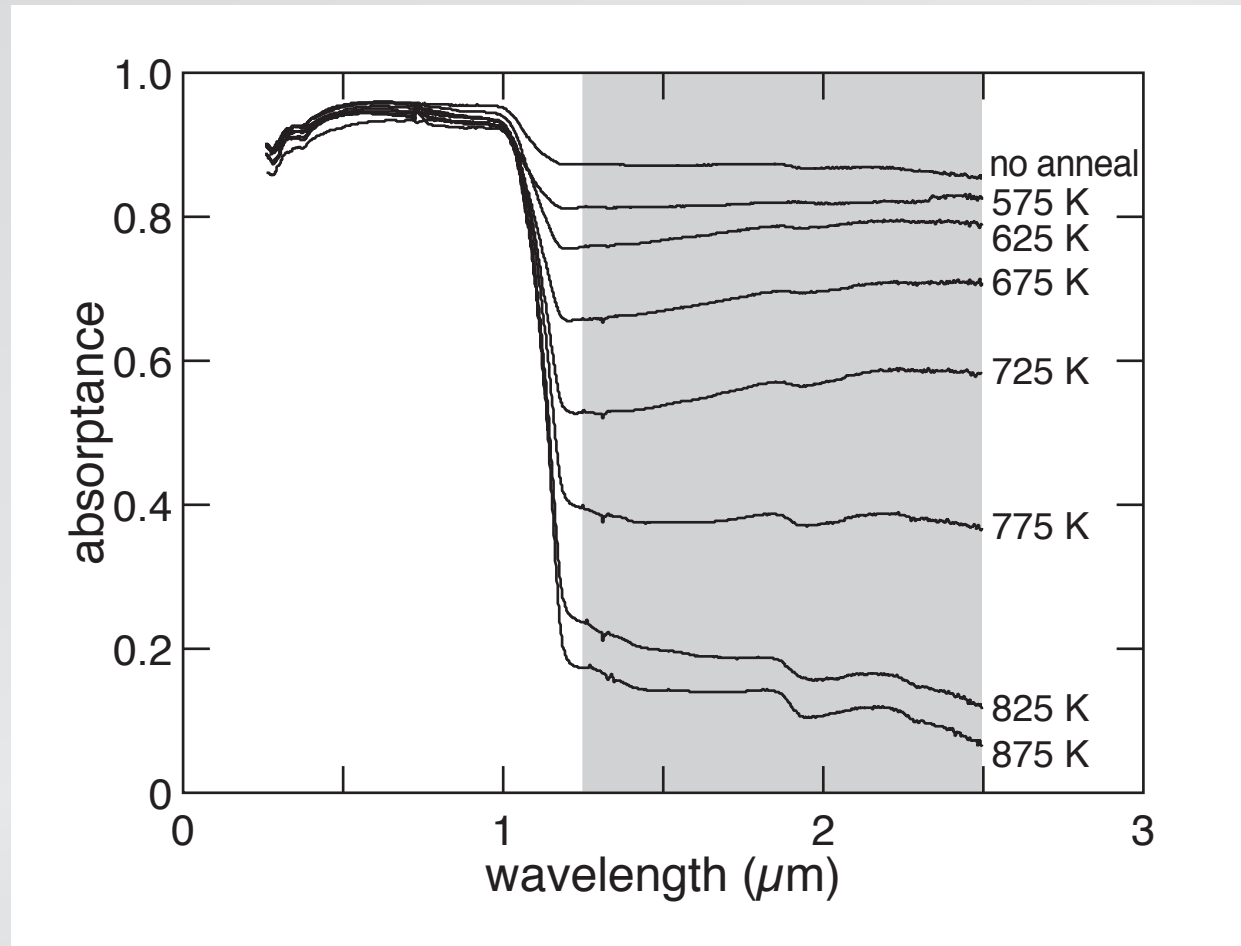
# Optoelectronic properties

effect of annealing on IR absorptance



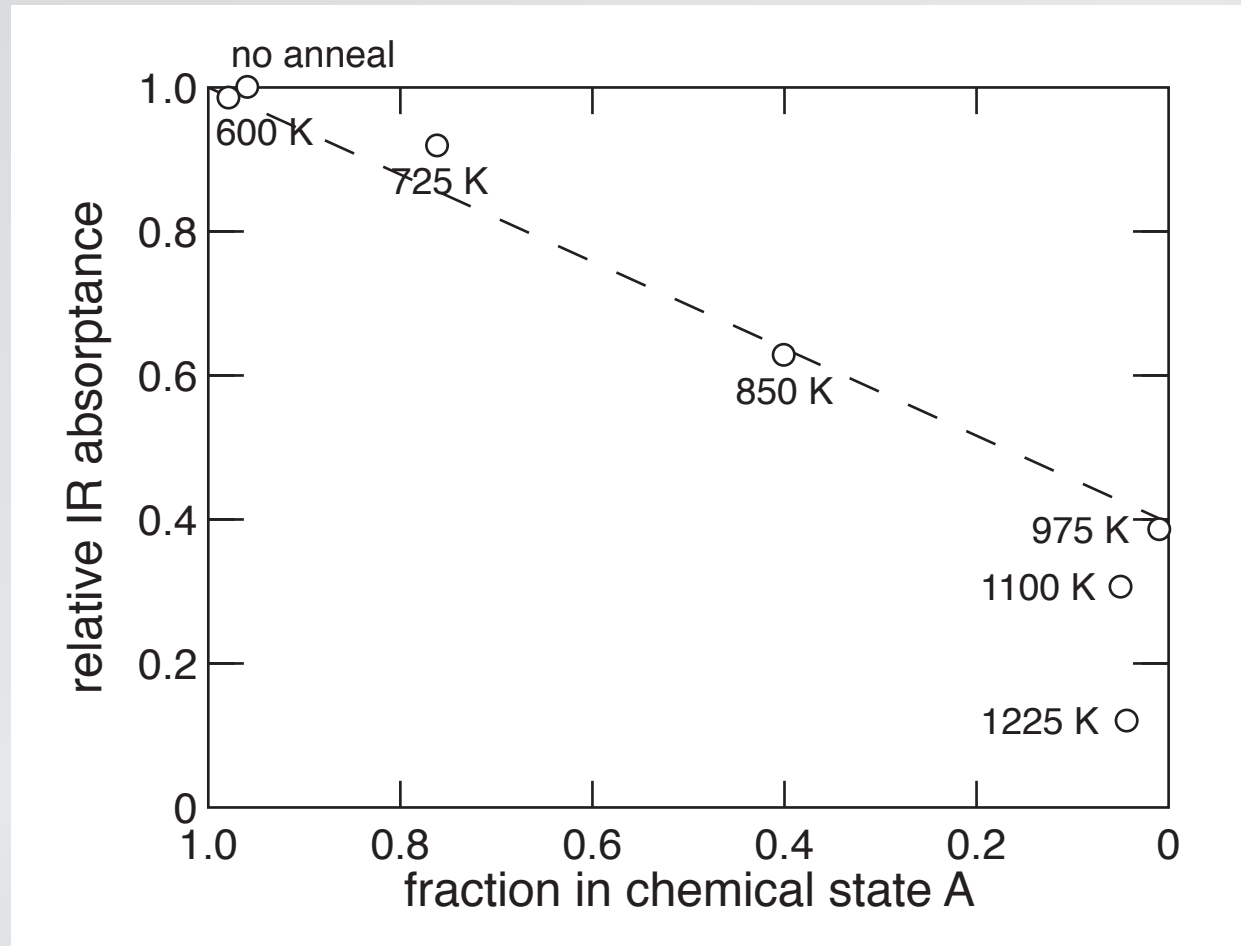
# Optoelectronic properties

effect of annealing on IR absorptance



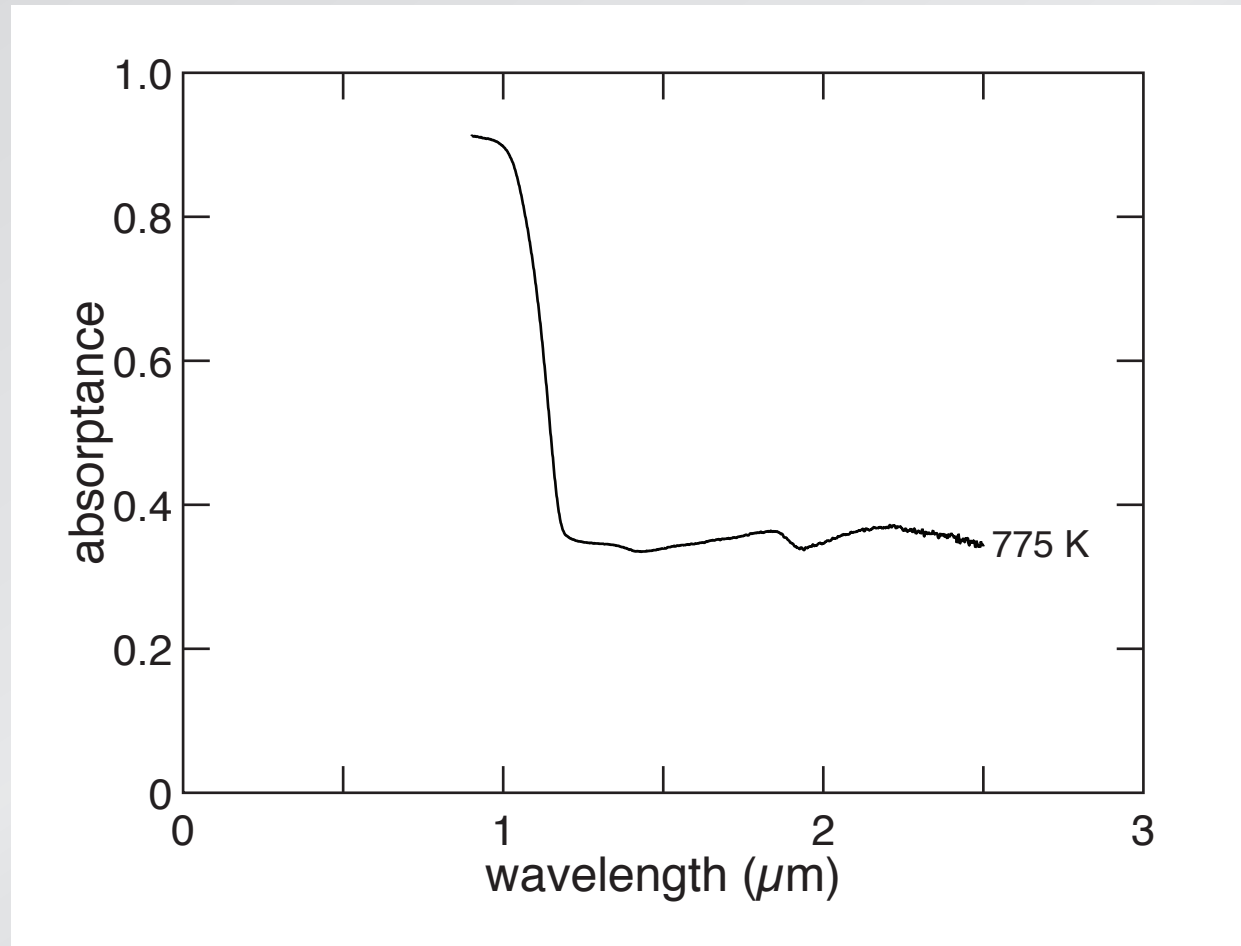
# Optoelectronic properties

correlates with recoordination observed in EXAFS



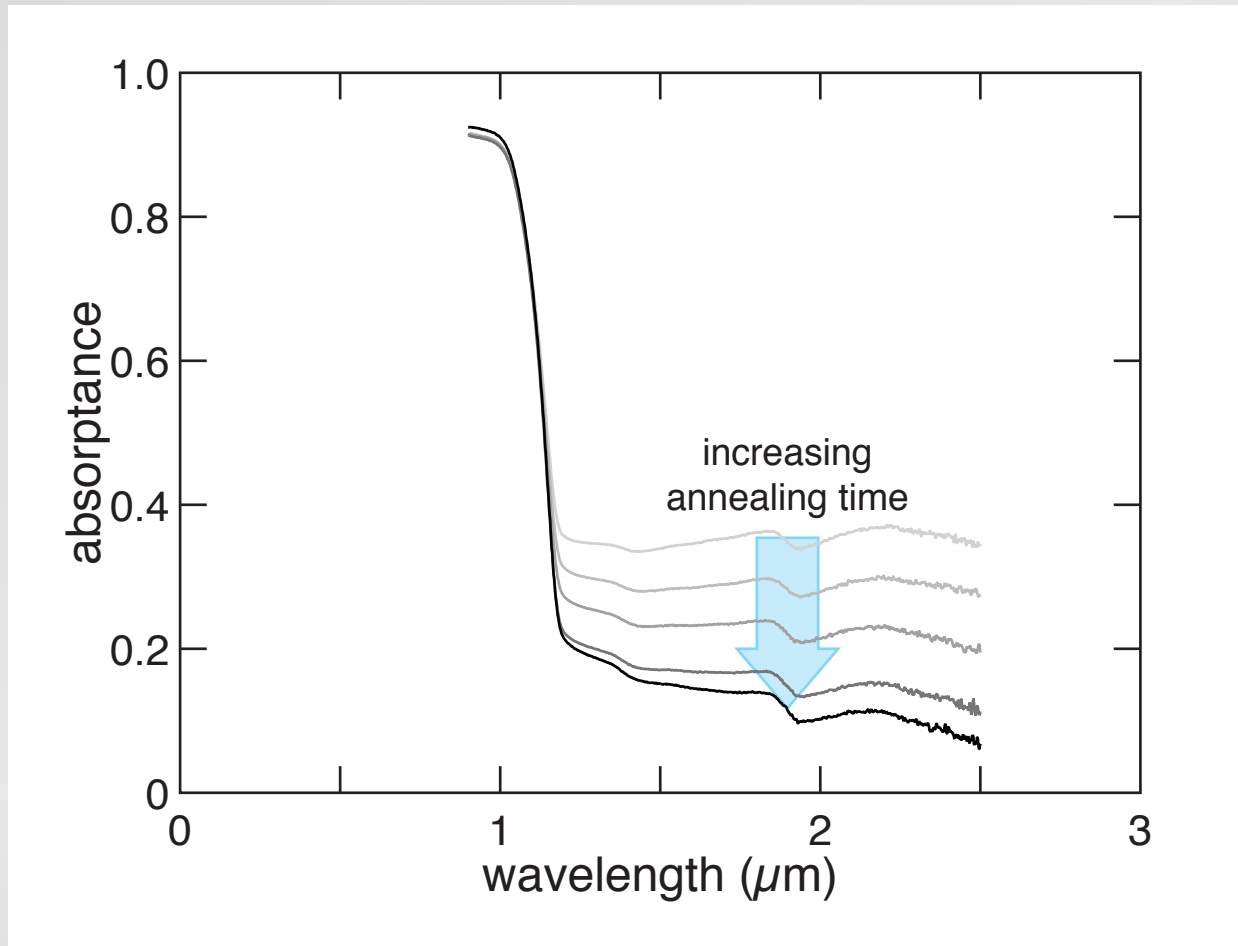
# Optoelectronic properties

vary annealing time



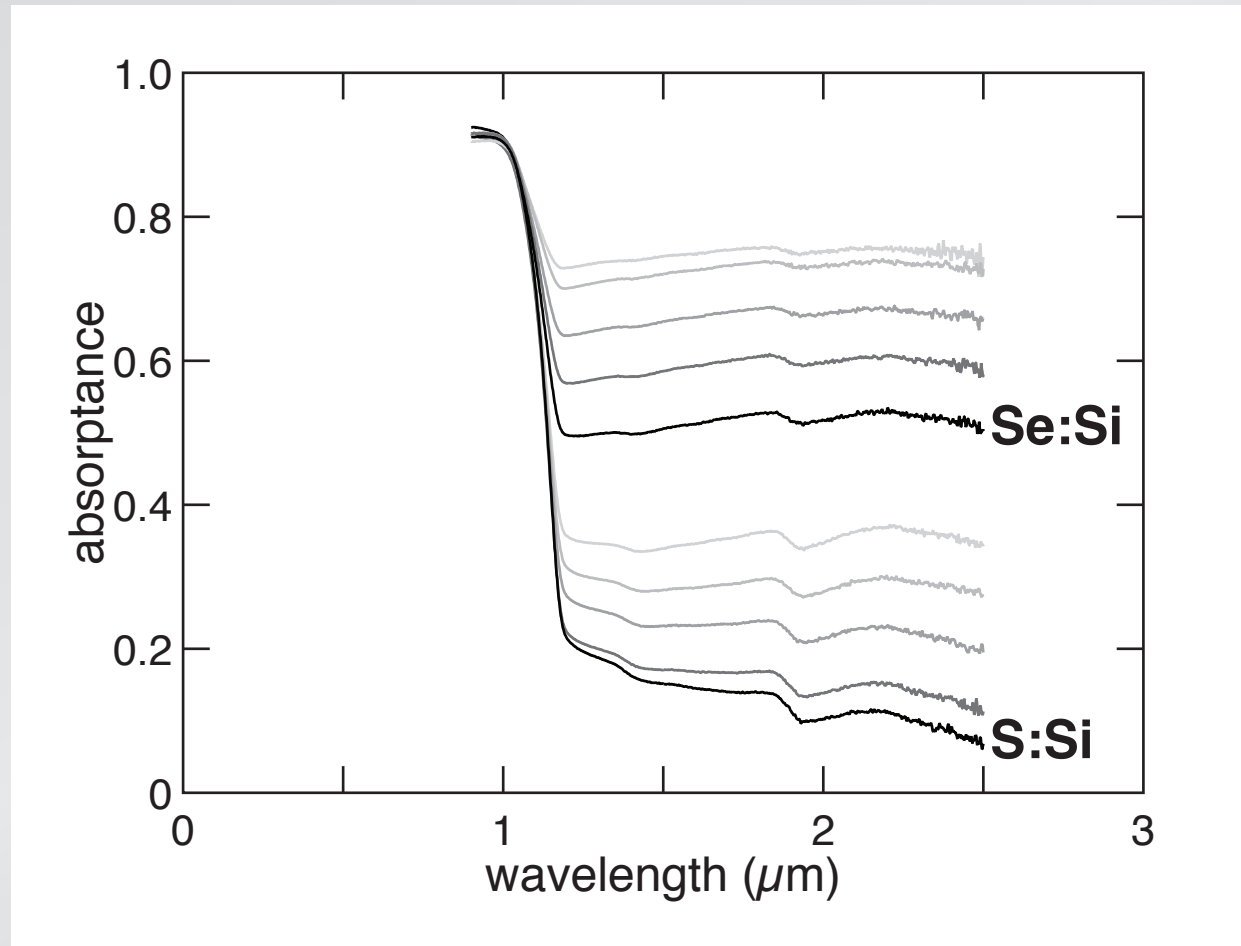
# Optoelectronic properties

longer annealing decreases IR absorptance



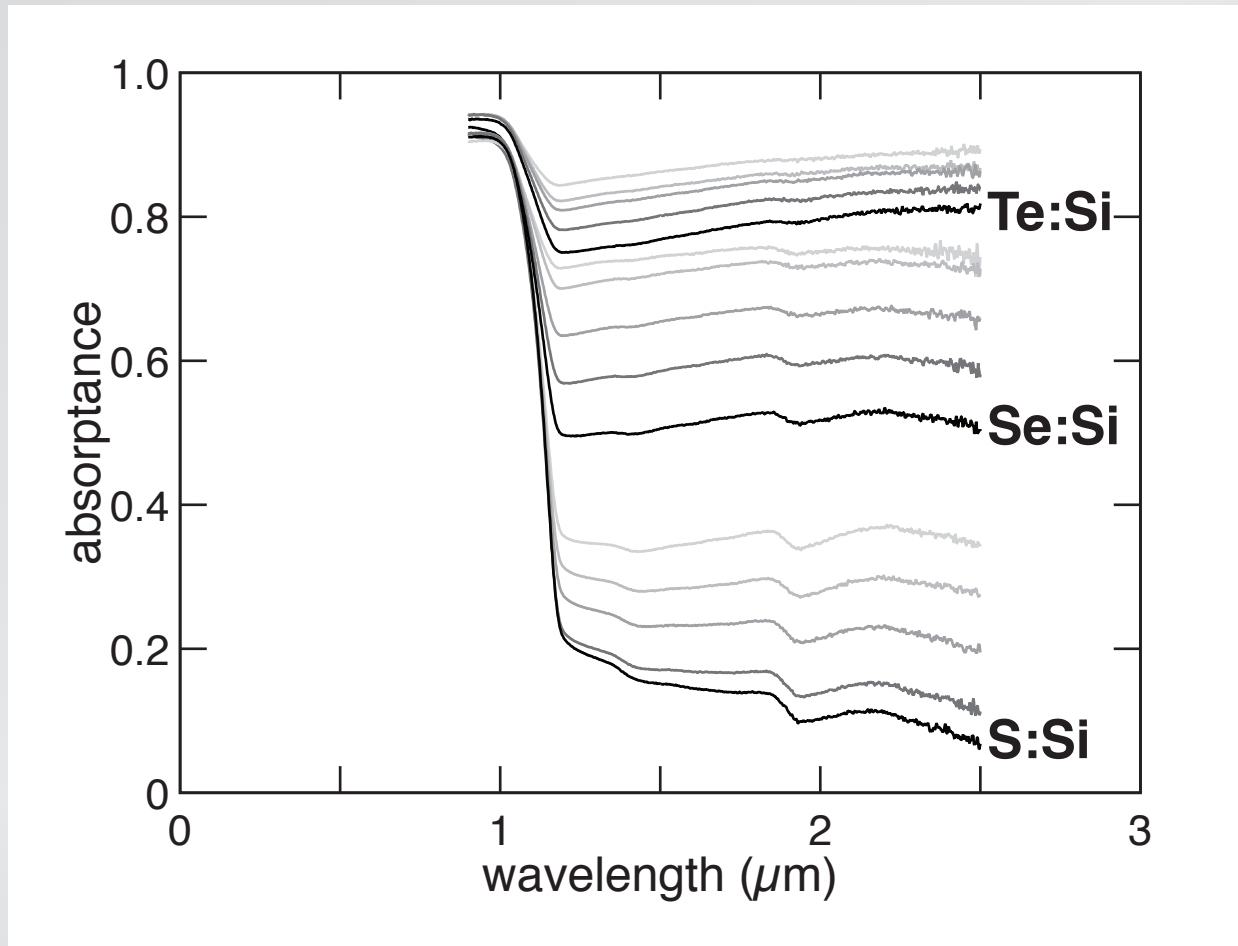
# Optoelectronic properties

IR absorptance decreases less for Se-doped samples...



# Optoelectronic properties

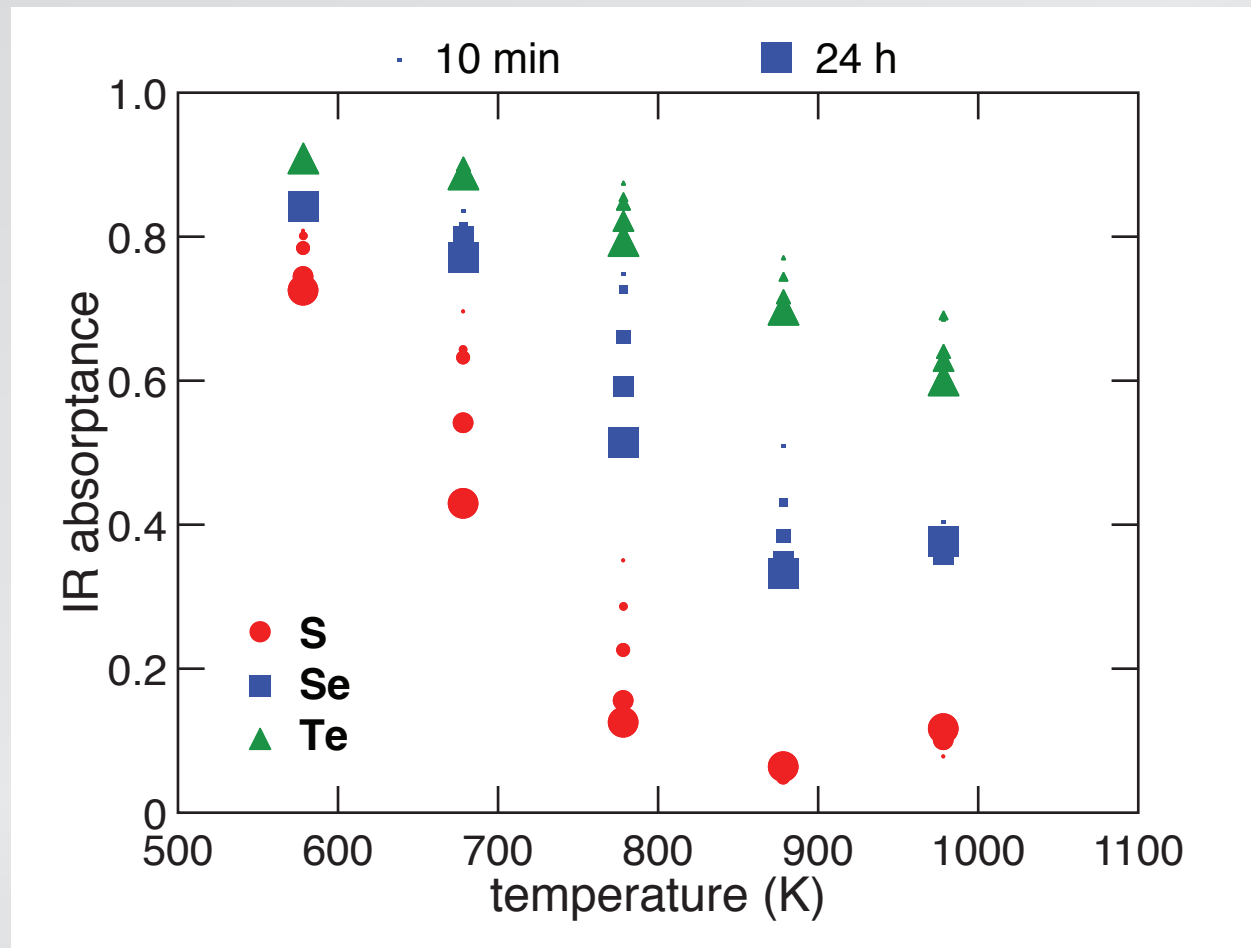
and even less for Te-doped samples...





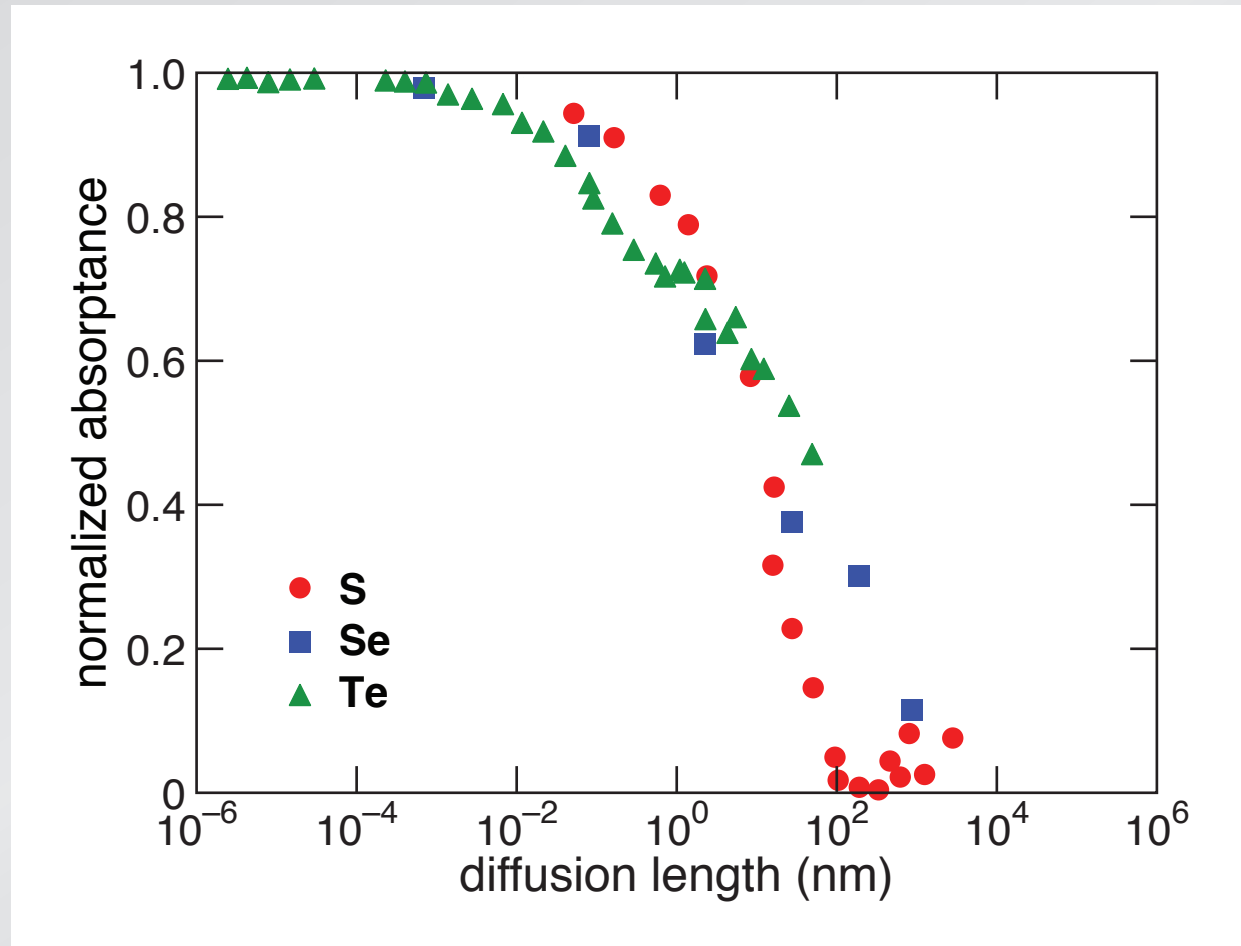
# Optoelectronic properties

IR absorptance function of species,  $T_{\text{anneal}}$ , and  $t_{\text{anneal}}$ ...



# Optoelectronic properties

...but is unique function of diffusion length



# Optoelectronic properties

annealing...

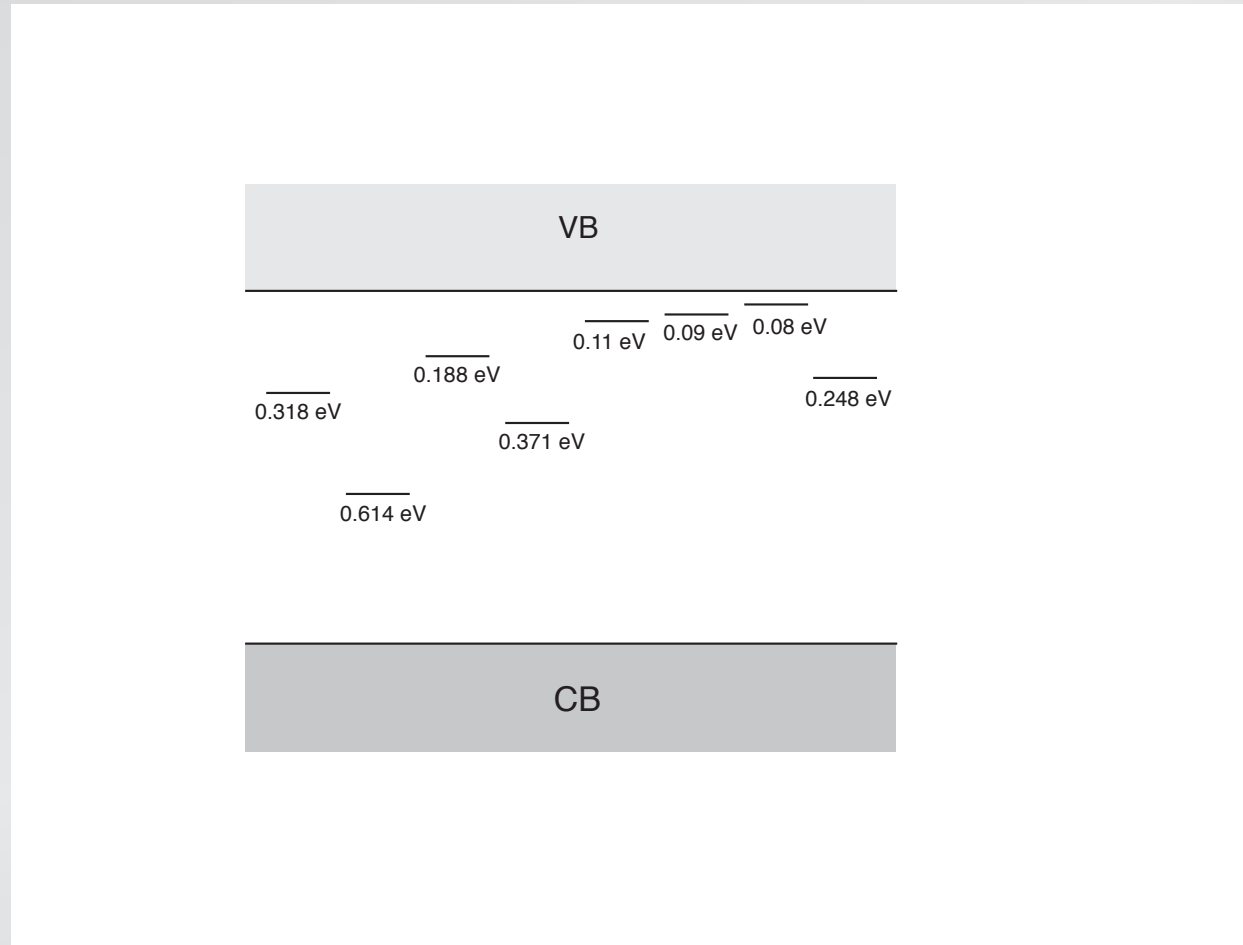
- decreases IR absorptance
- causes recoordination and diffusion of dopants
- IR absorptance reduced by 50% after 20 nm diffusion

# Optoelectronic properties

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

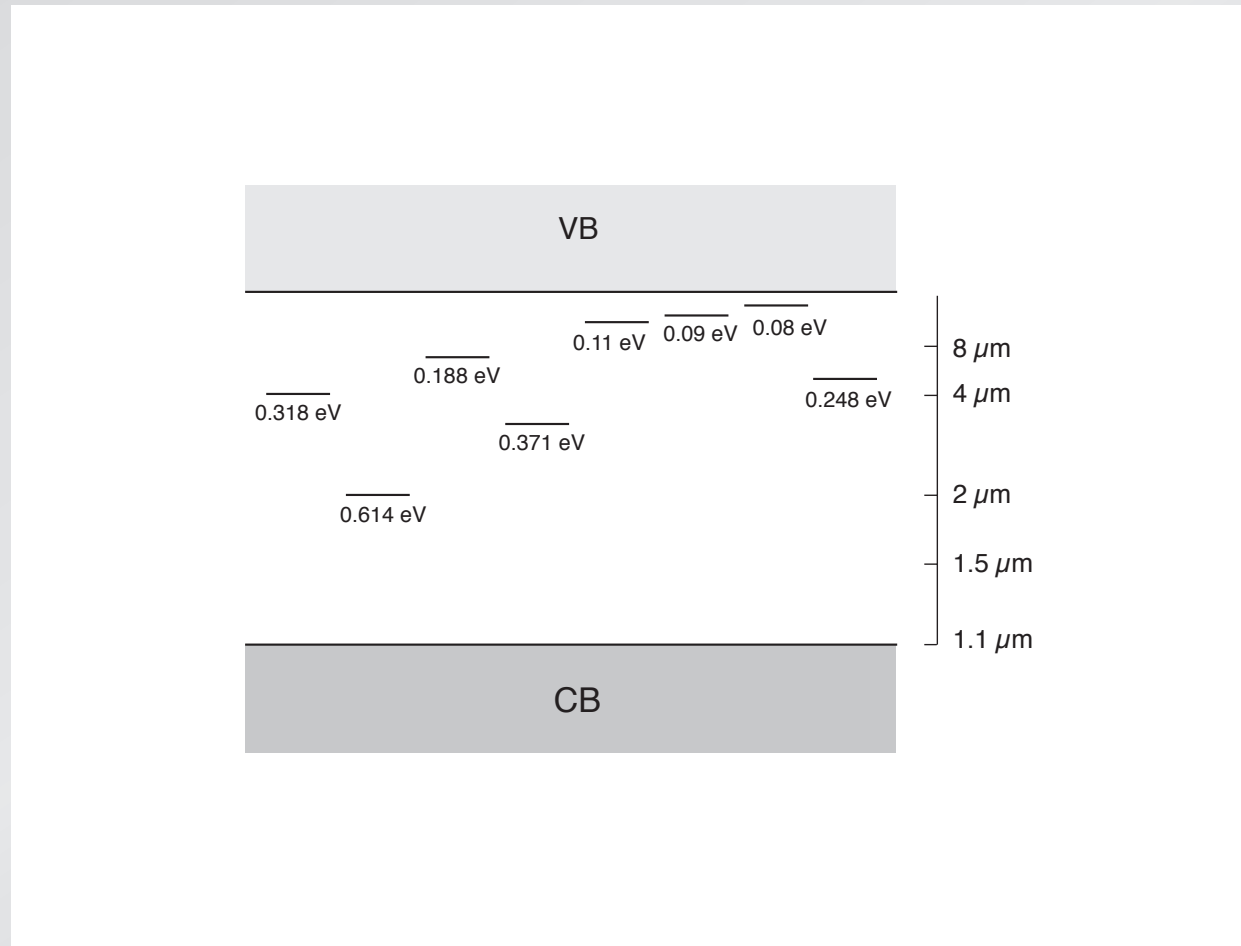
# Optoelectronic properties

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



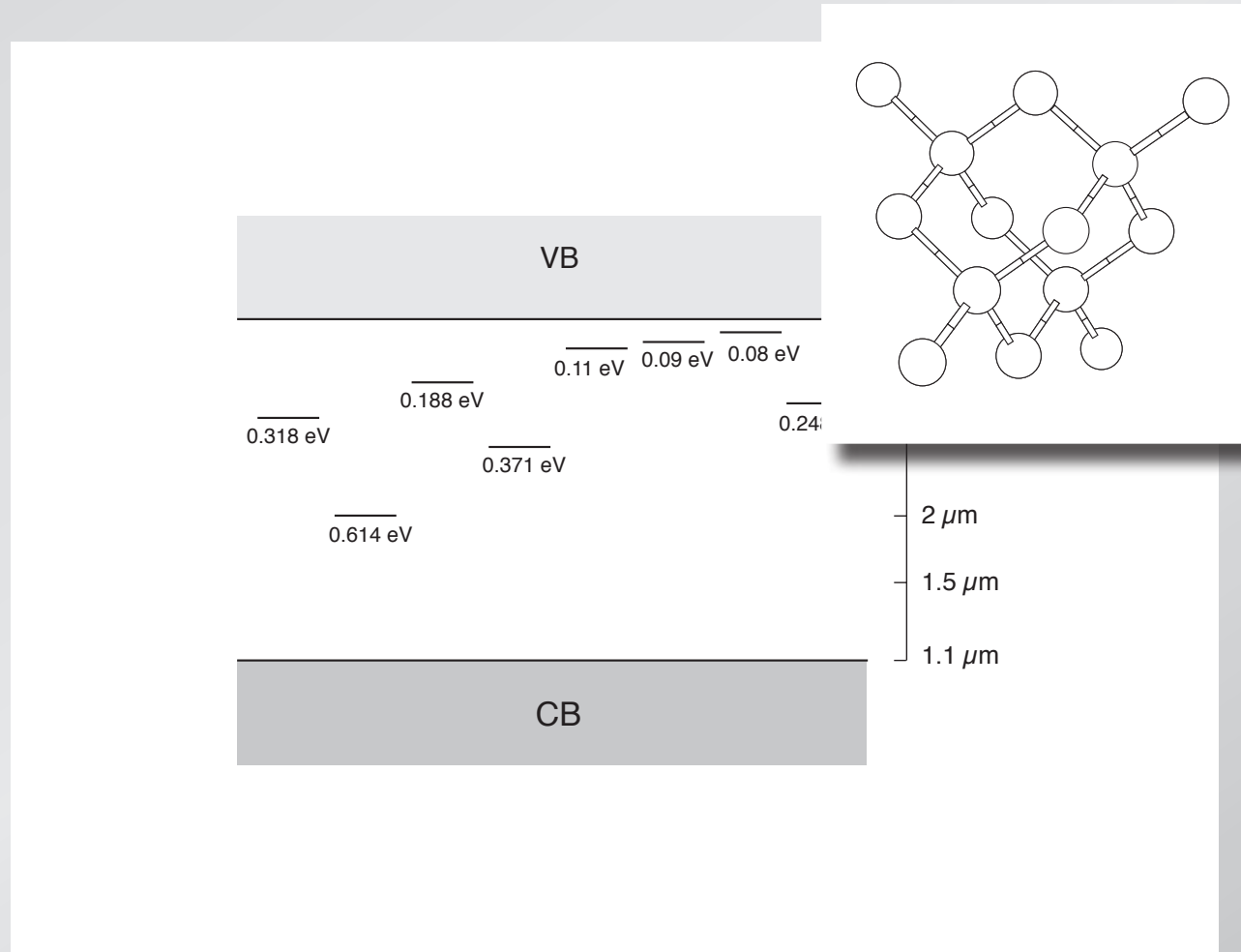
# Optoelectronic properties

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



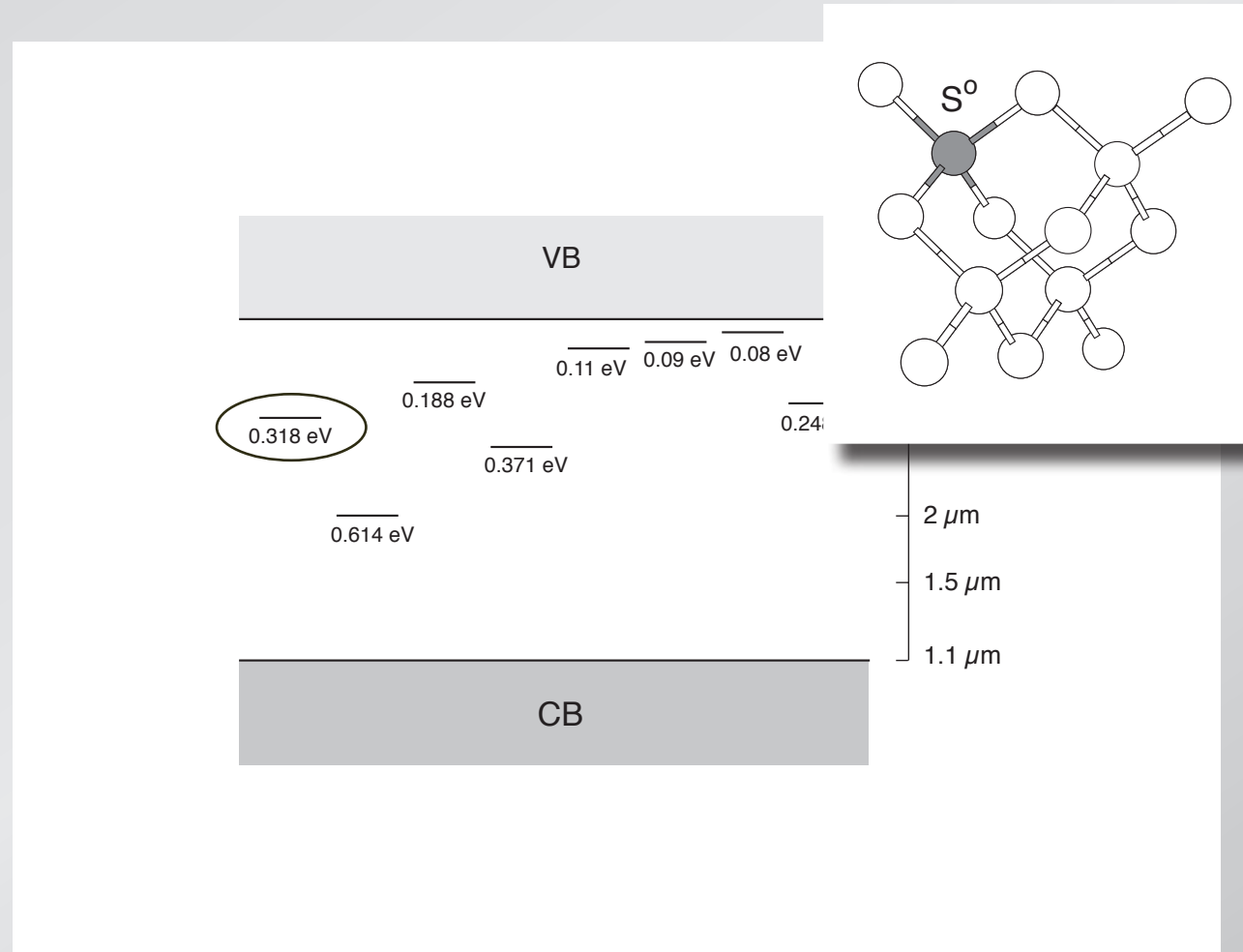
# Optoelectronic properties

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



# Optoelectronic properties

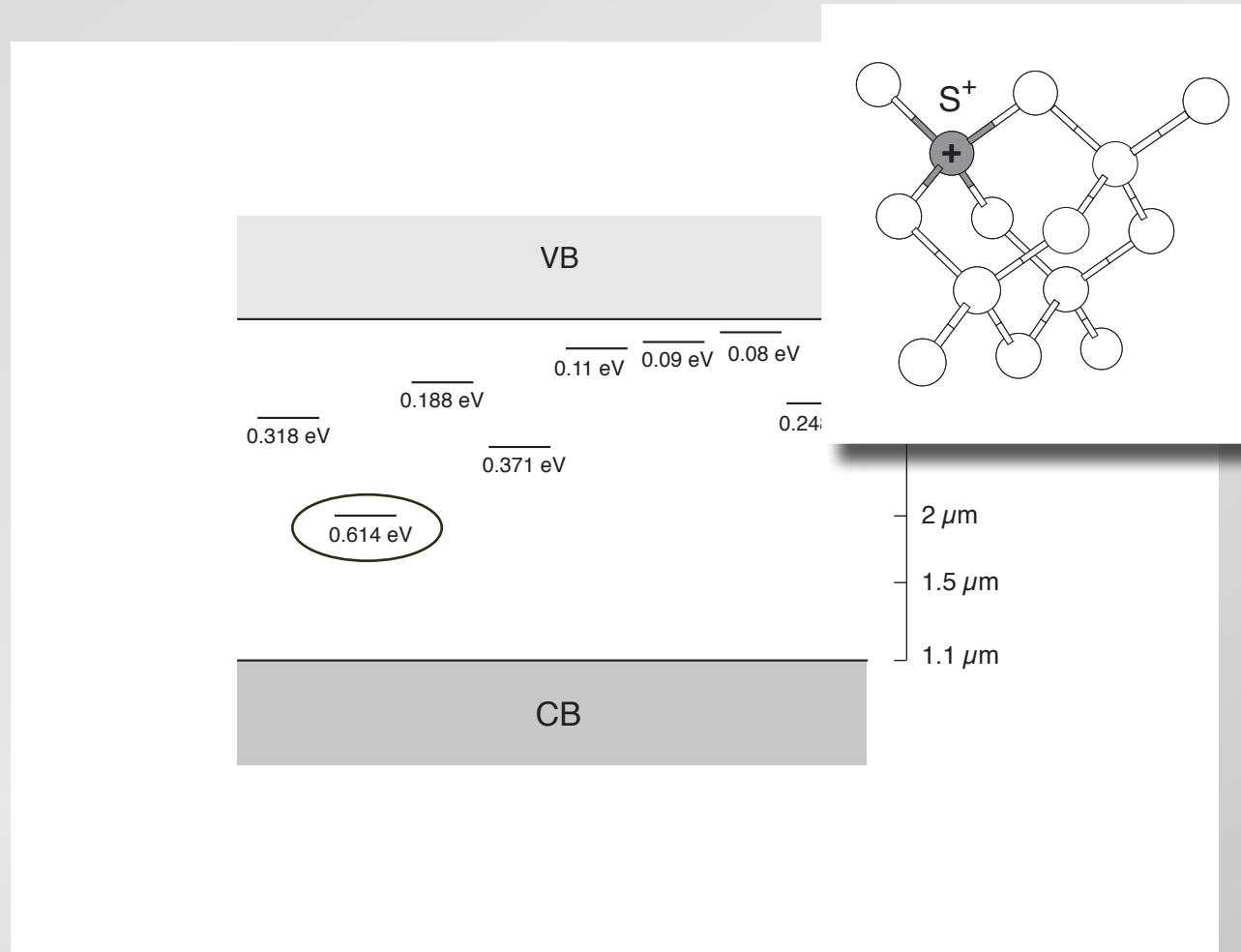
1 part in  $10^6$  sulfur introduces donor states in gap





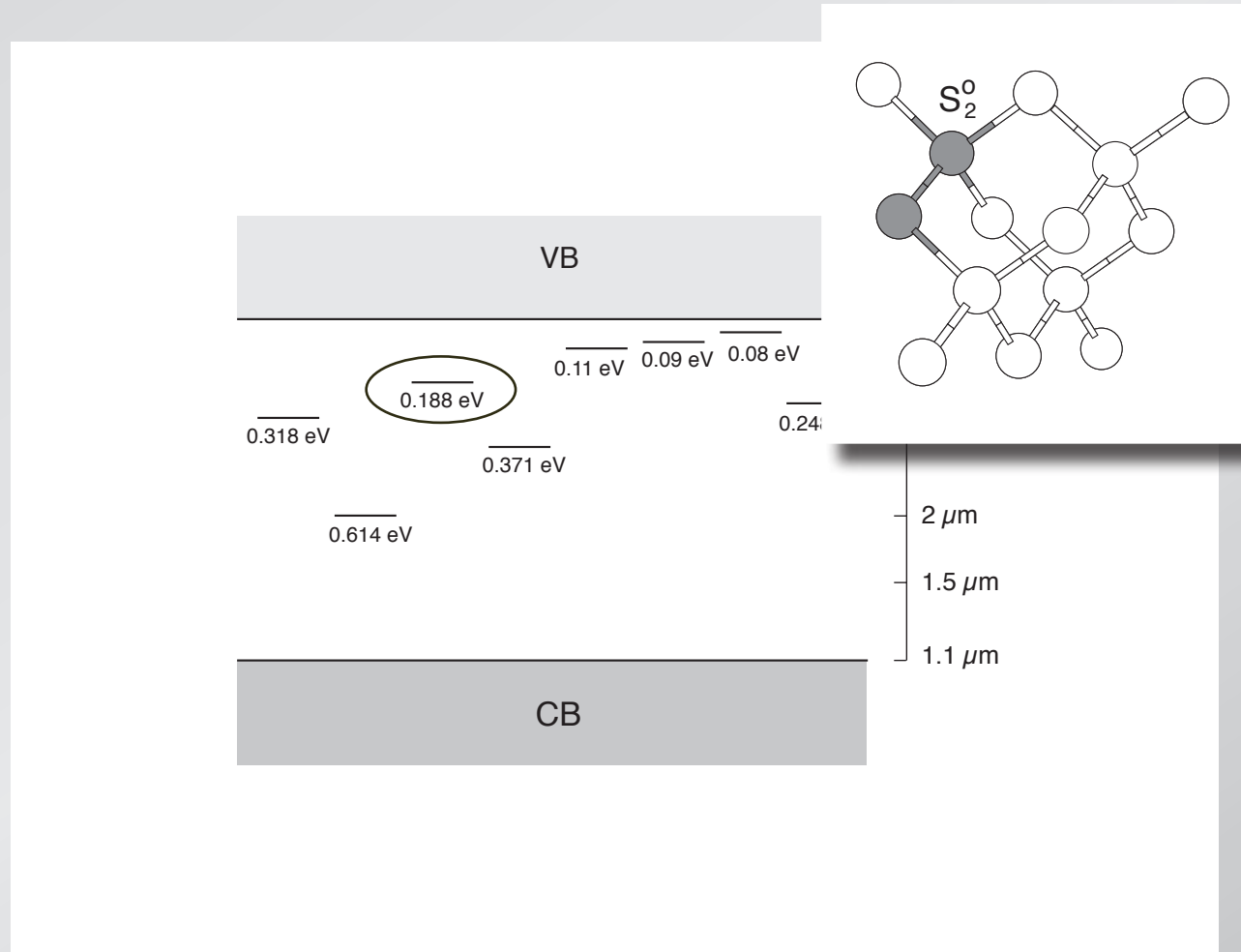
# Optoelectronic properties

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



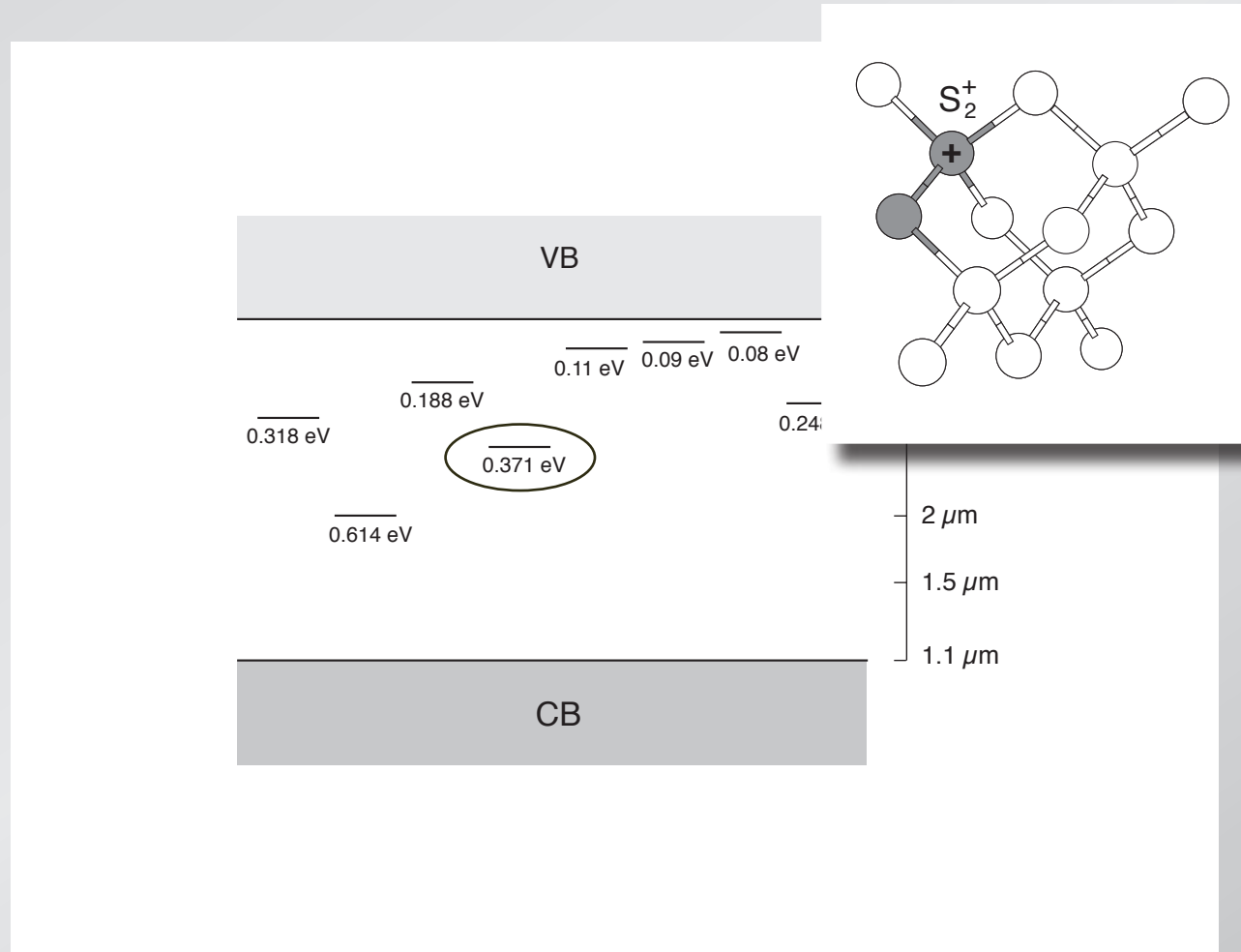
# Optoelectronic properties

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



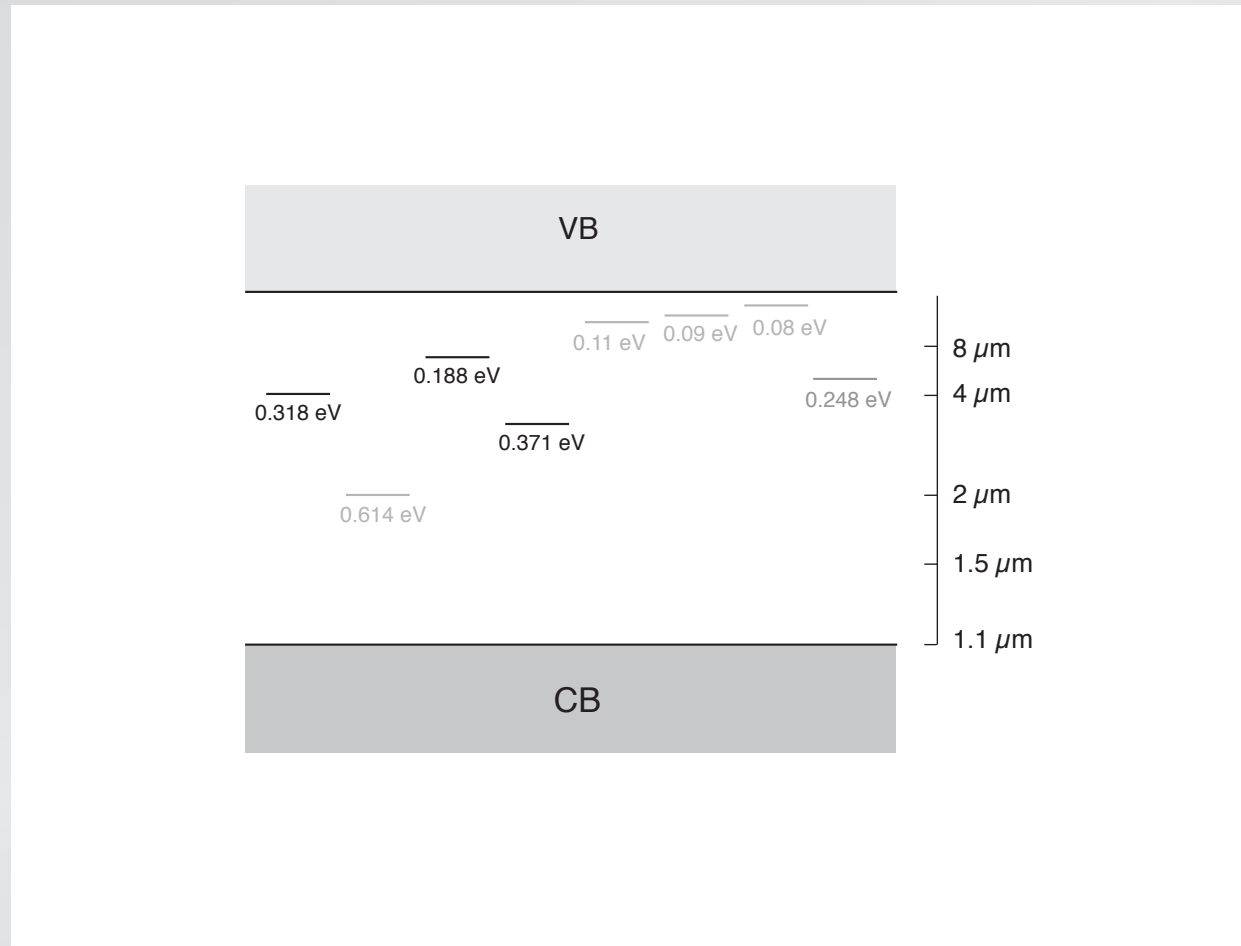
# Optoelectronic properties

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



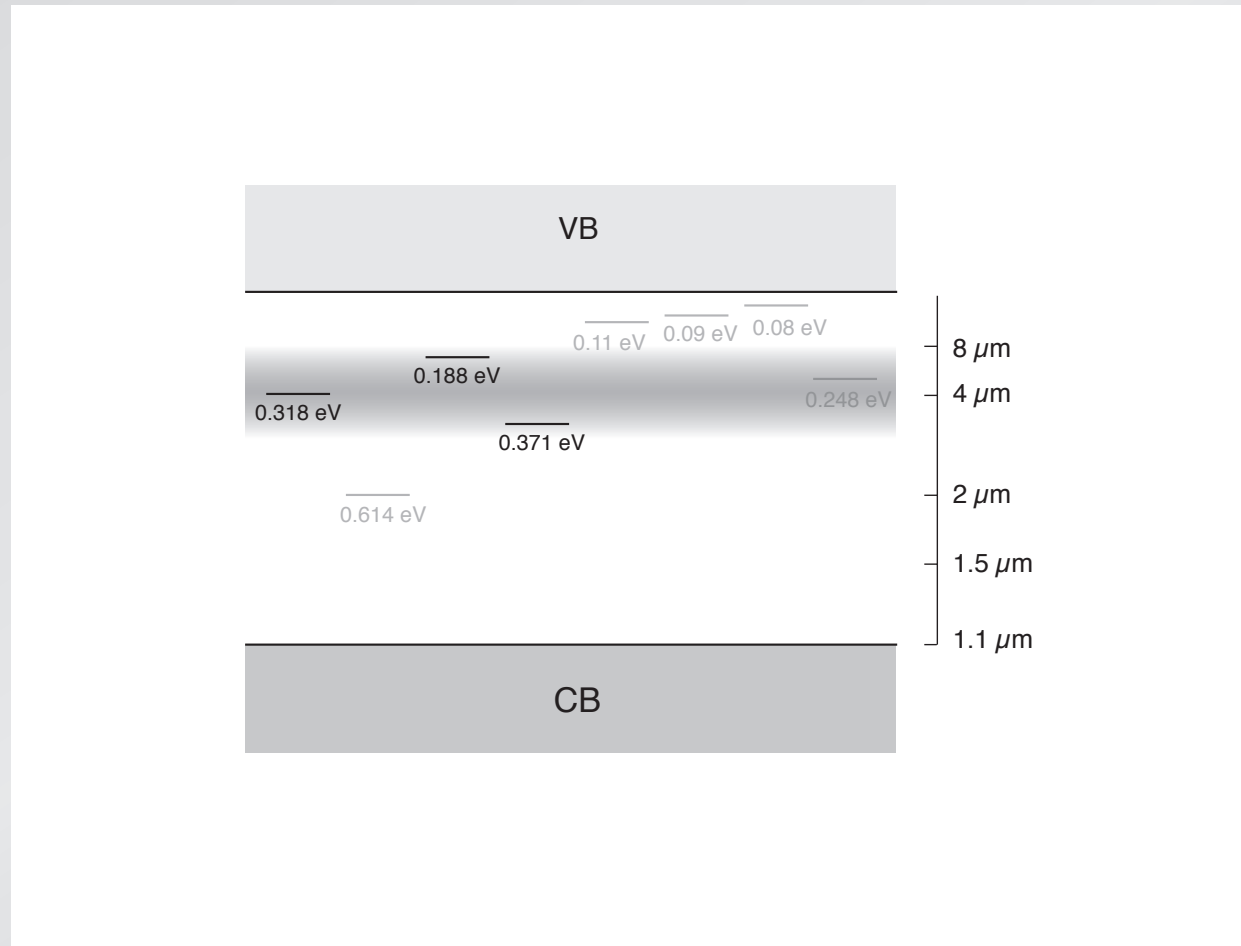
# Optoelectronic properties

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



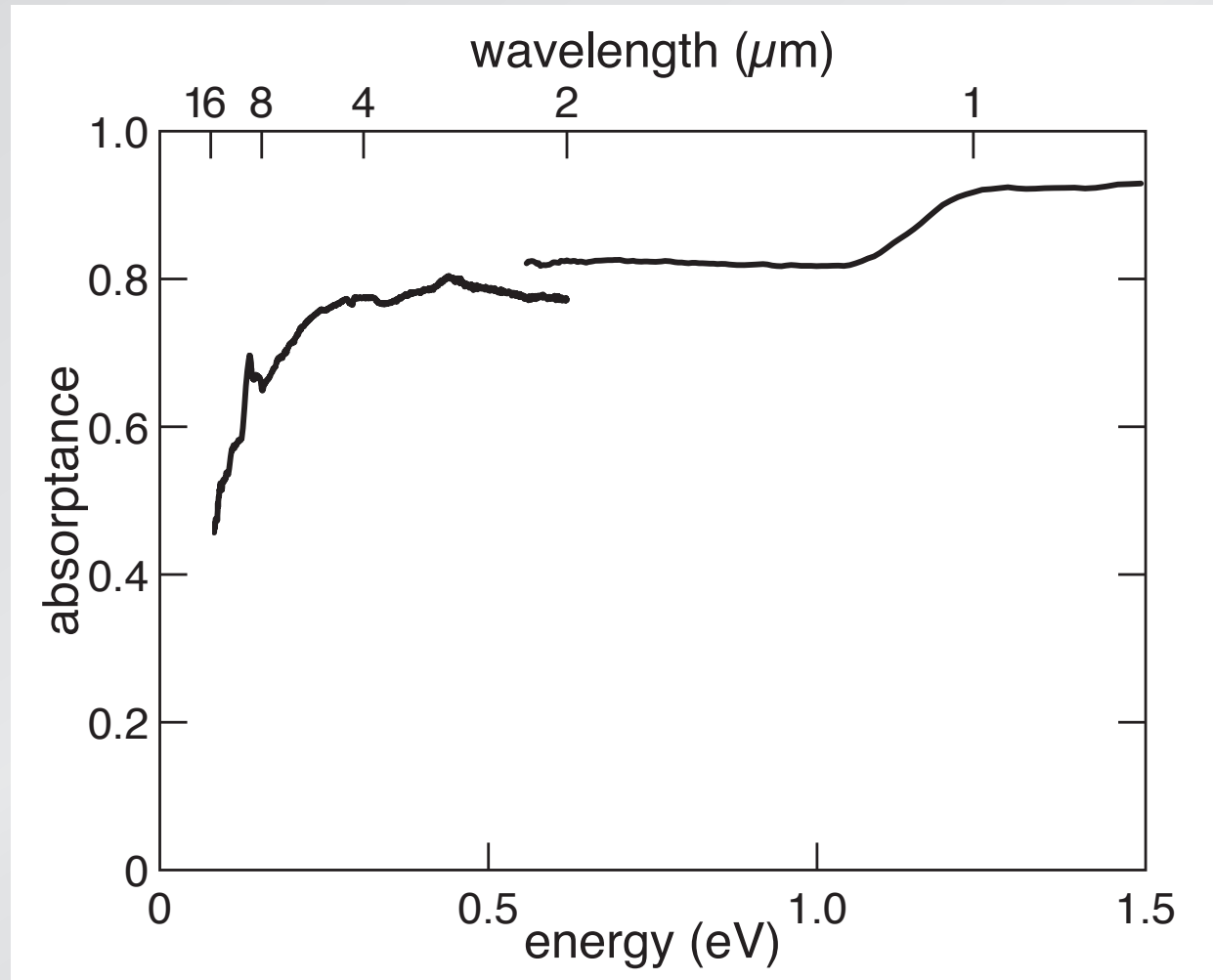
# Optoelectronic properties

at high concentration states broaden into band



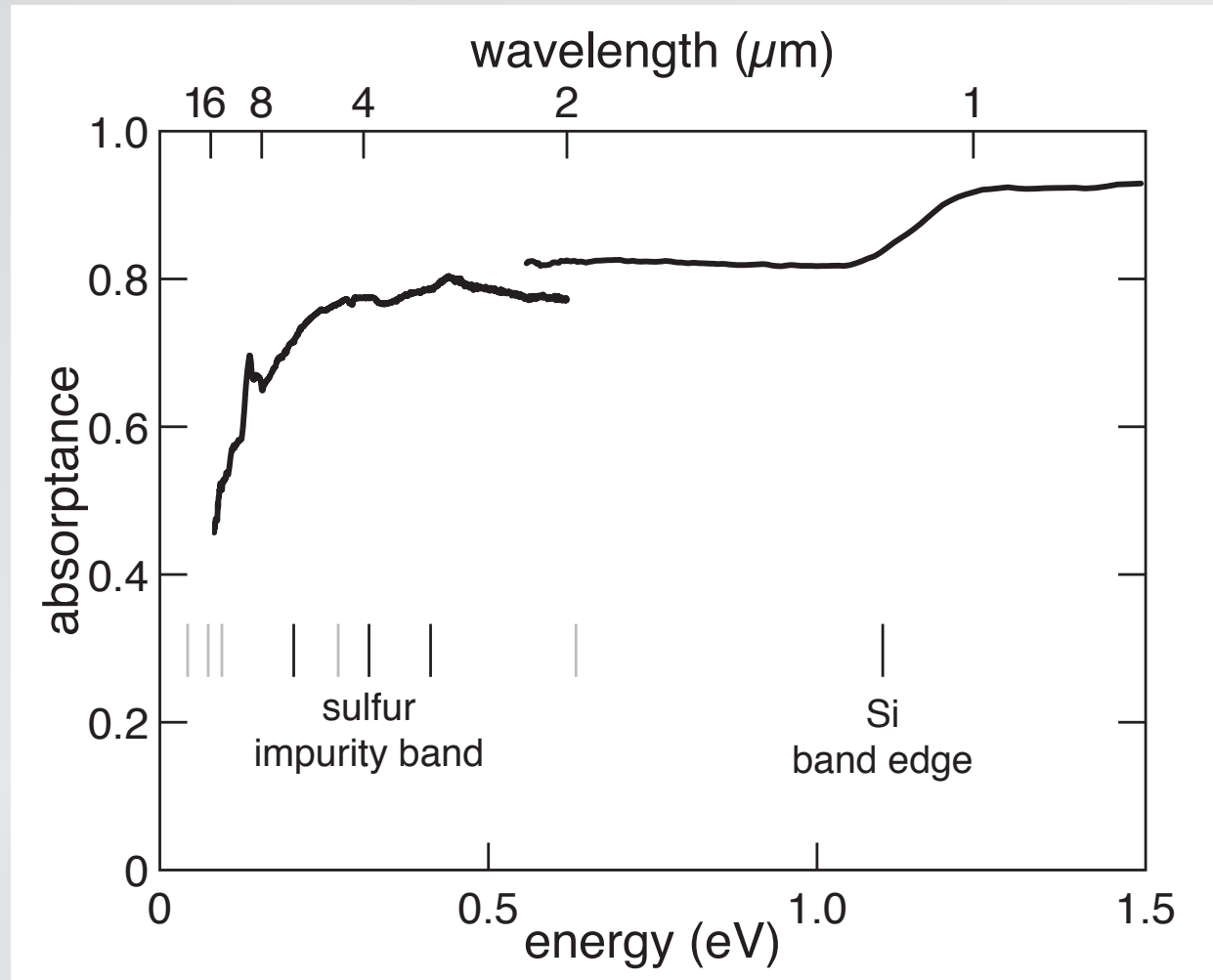
# Optoelectronic properties

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



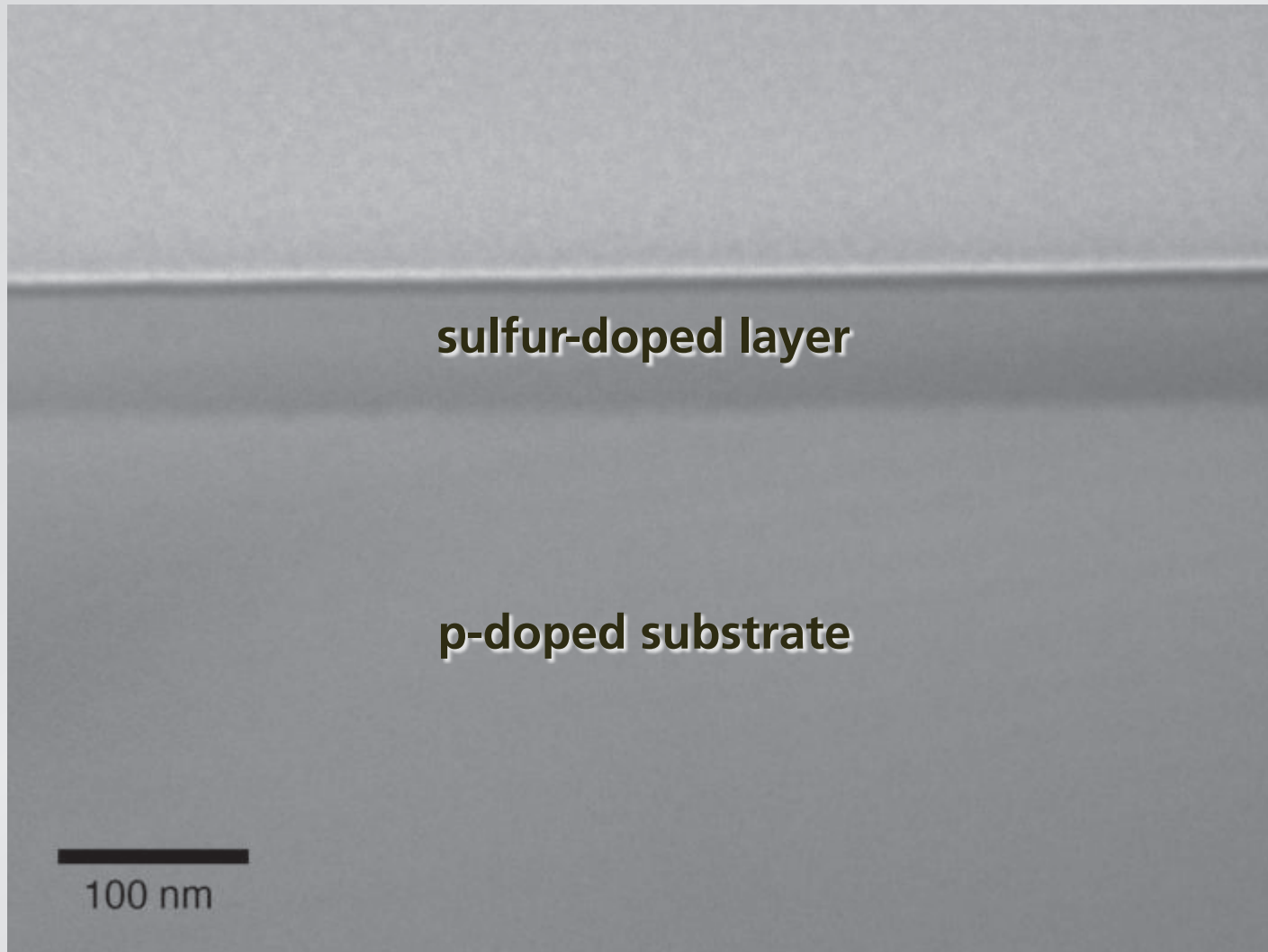
# Optoelectronic properties

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



# Optoelectronic properties

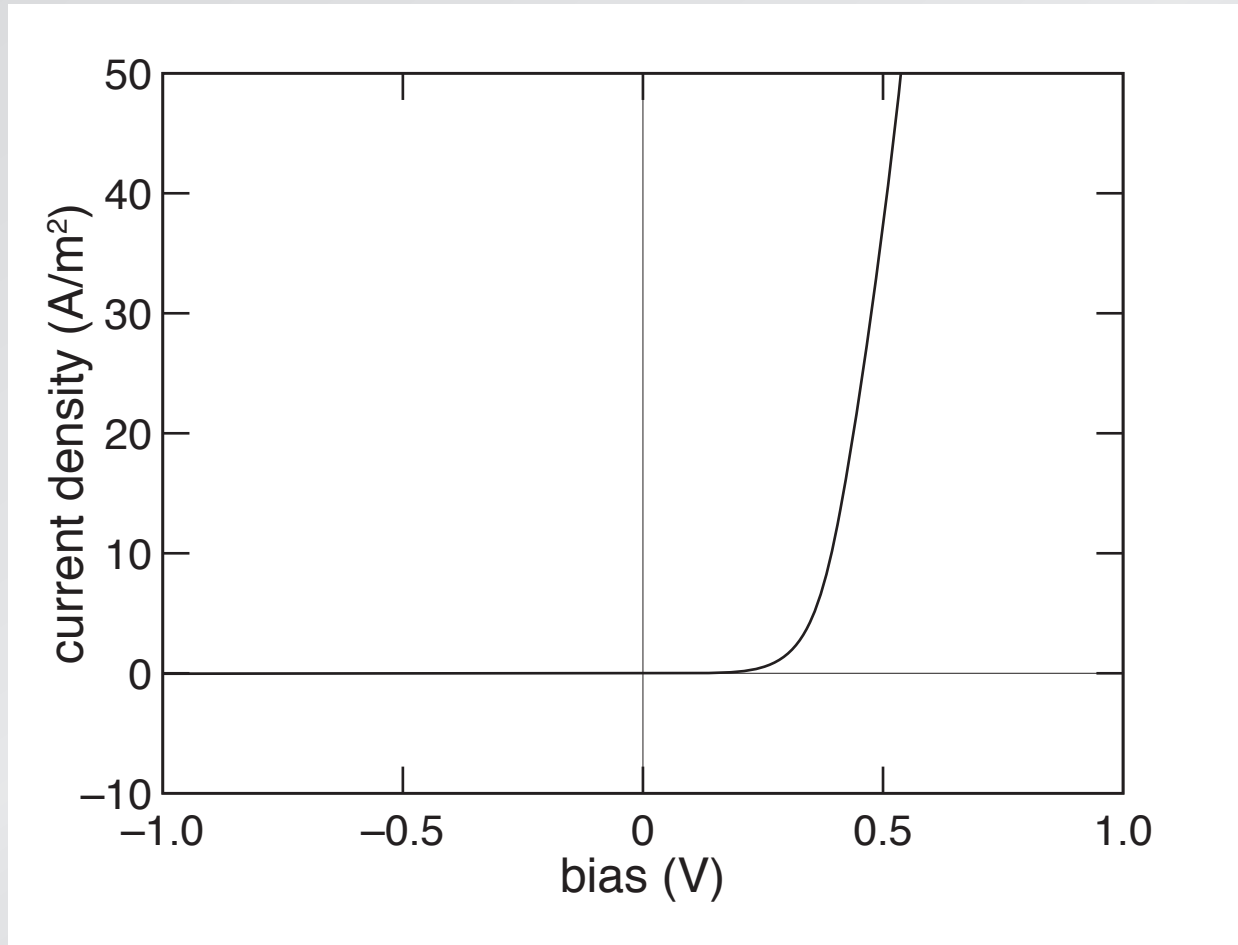
should have shallow junction below surface





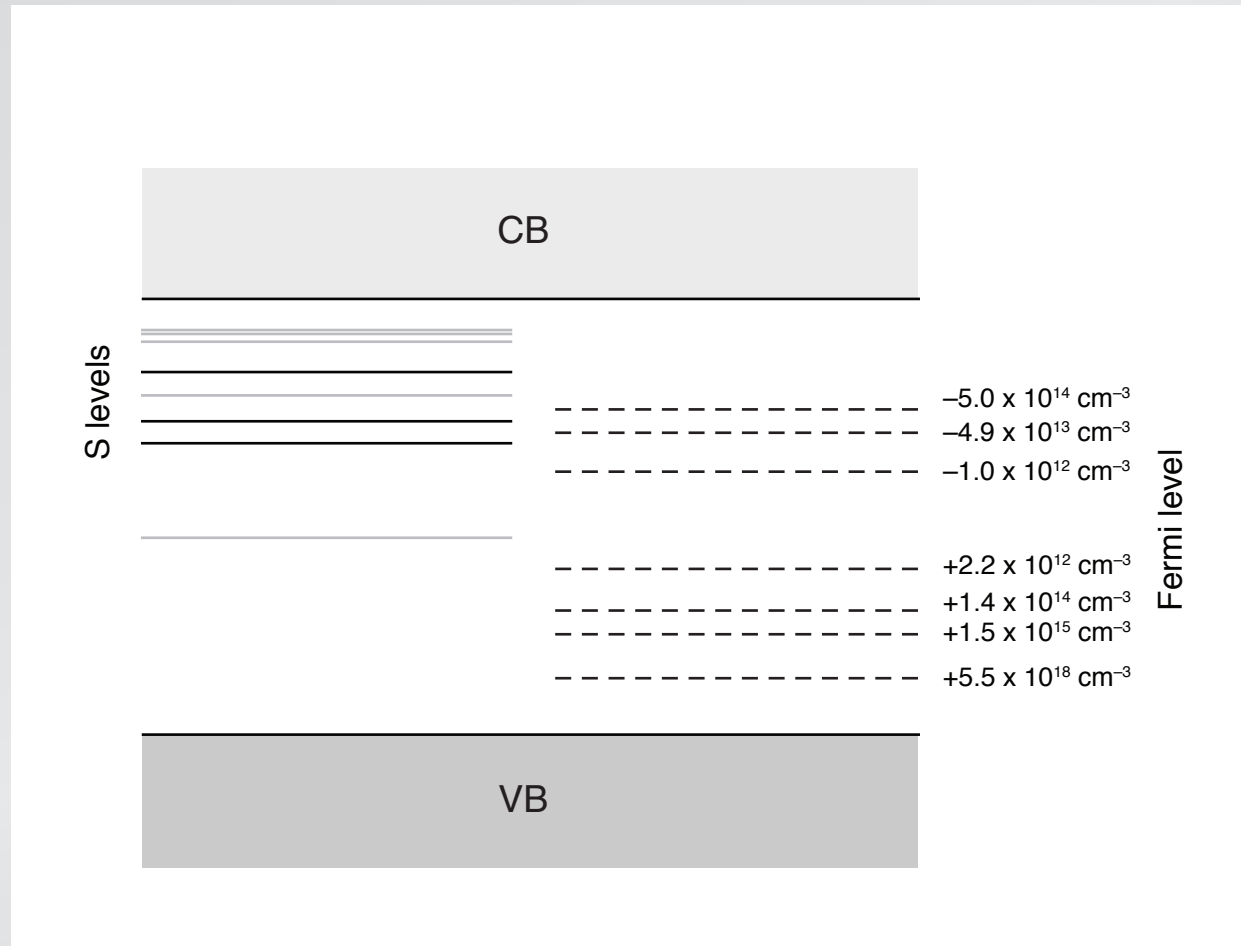
# Optoelectronic properties

excellent rectification (after annealing)



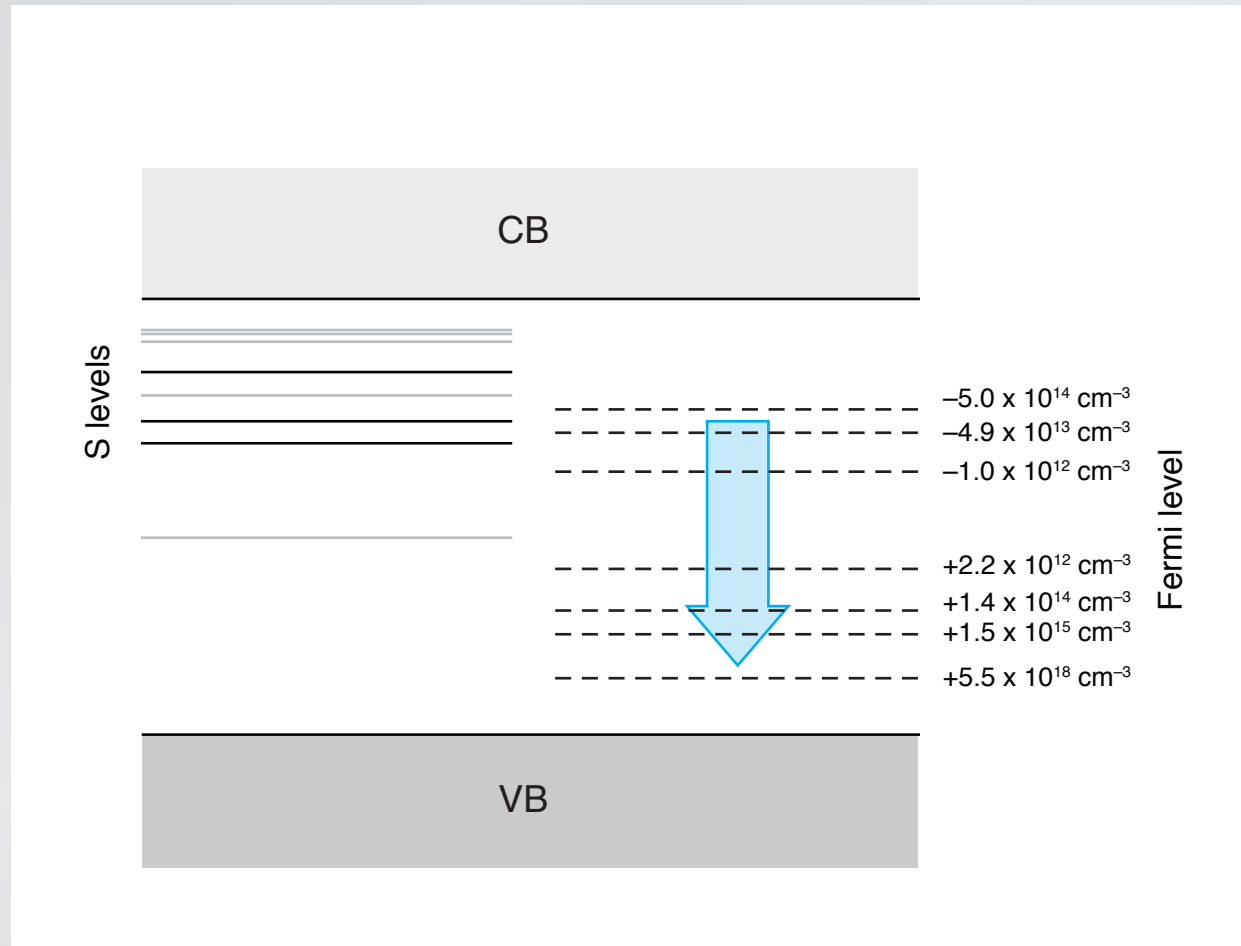
# Optoelectronic properties

probe impurity states by varying Fermi level in substrate



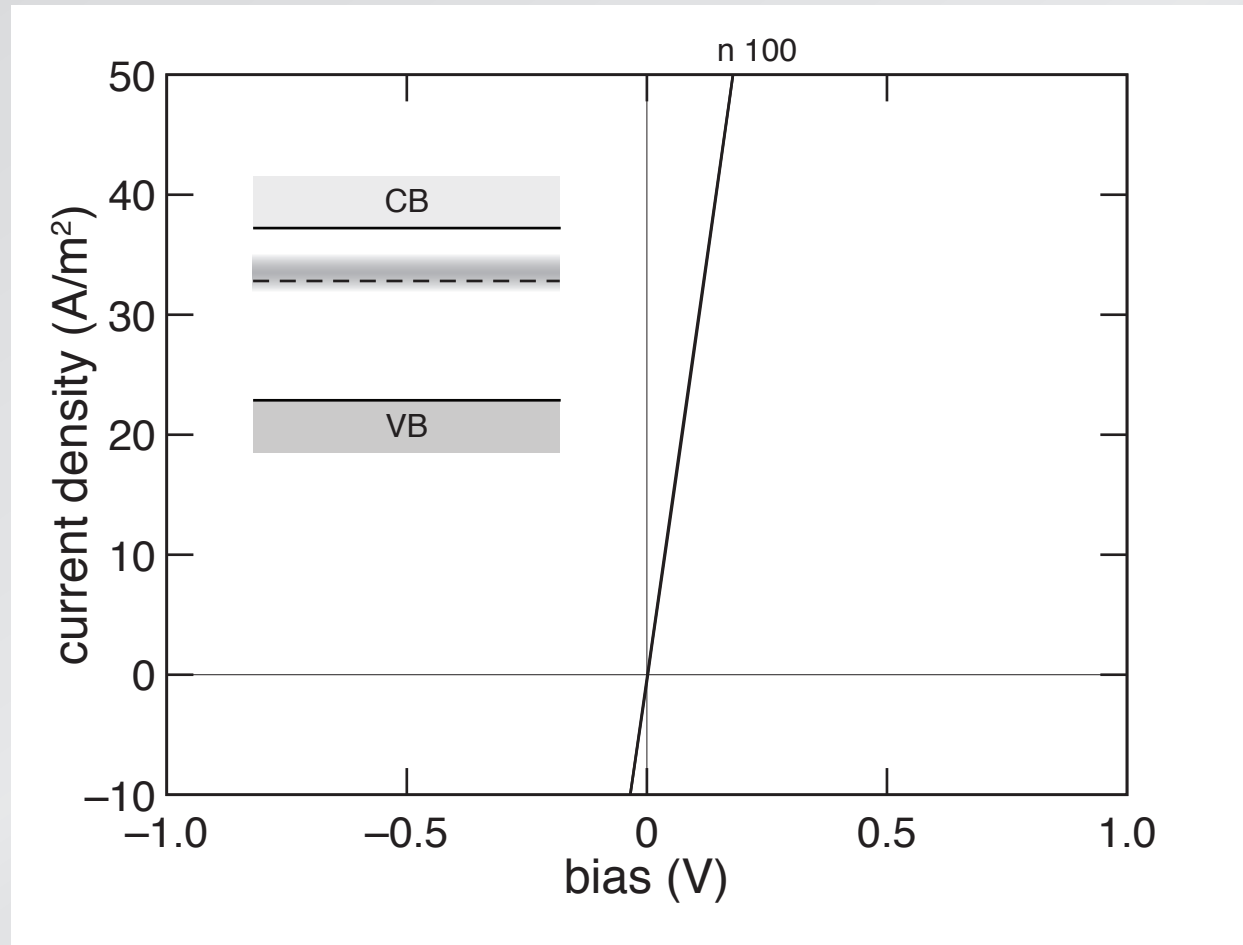
# Optoelectronic properties

probe impurity states by varying Fermi level in substrate



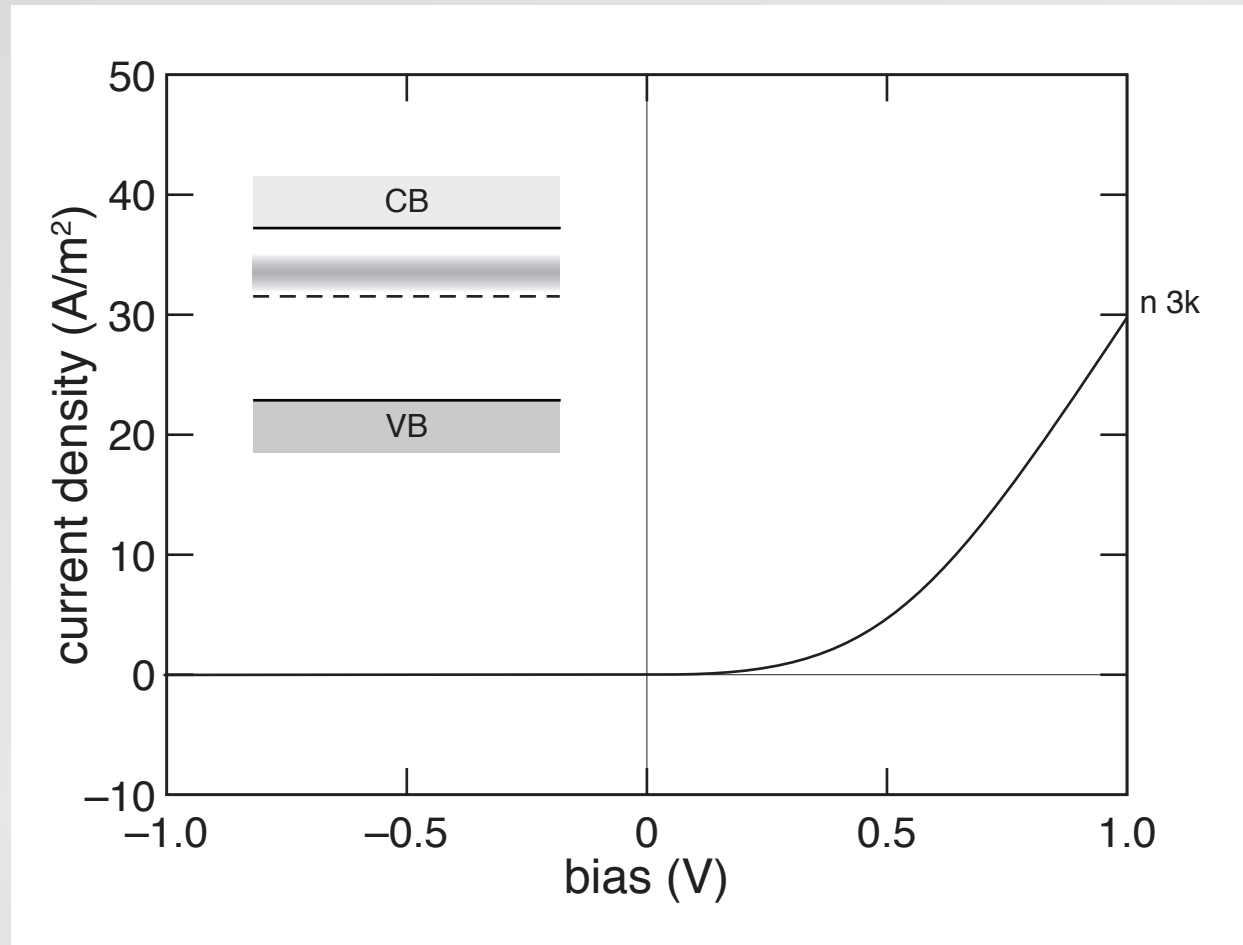
# Optoelectronic properties

vary substrate doping type and resistivity



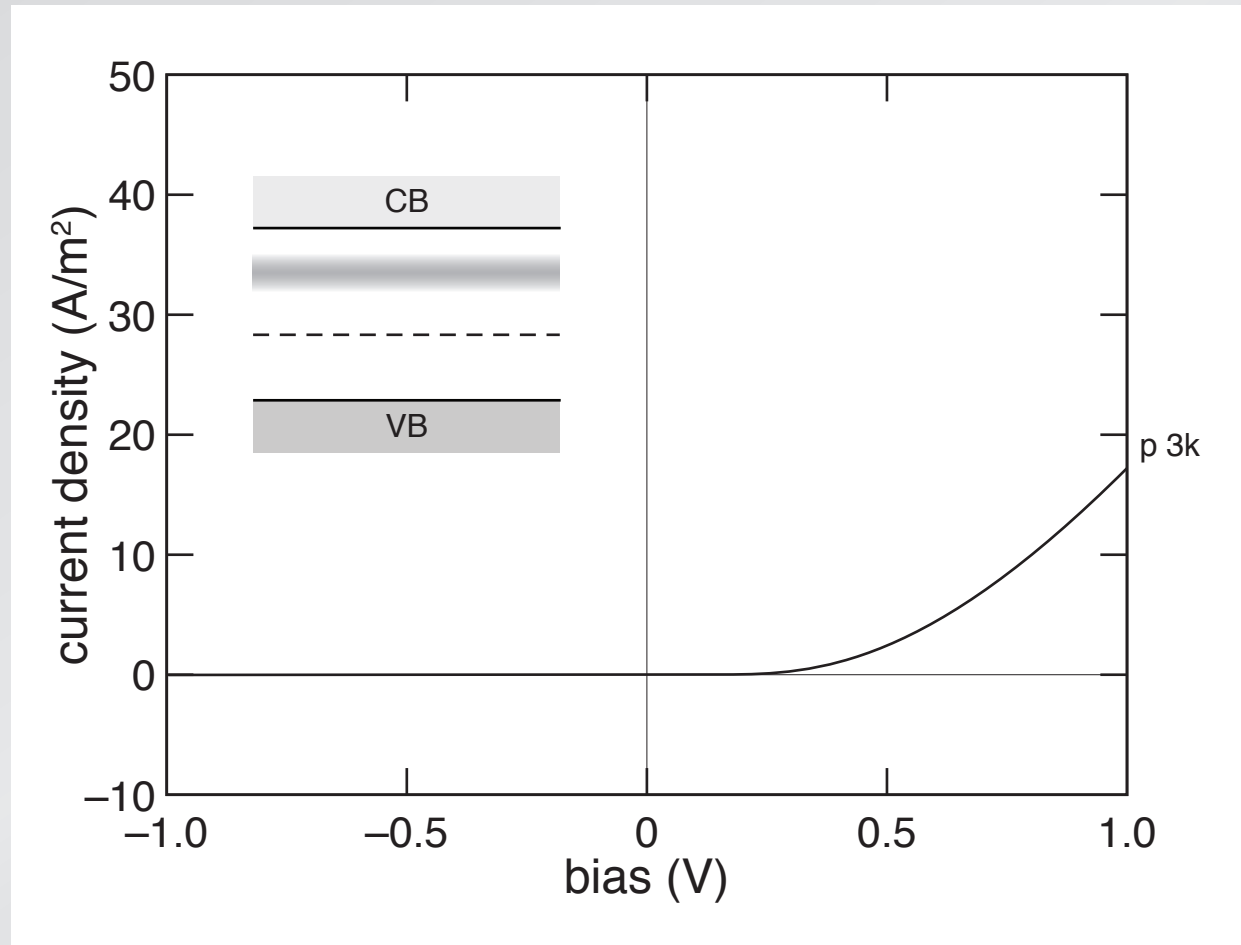
# Optoelectronic properties

vary substrate doping type and resistivity



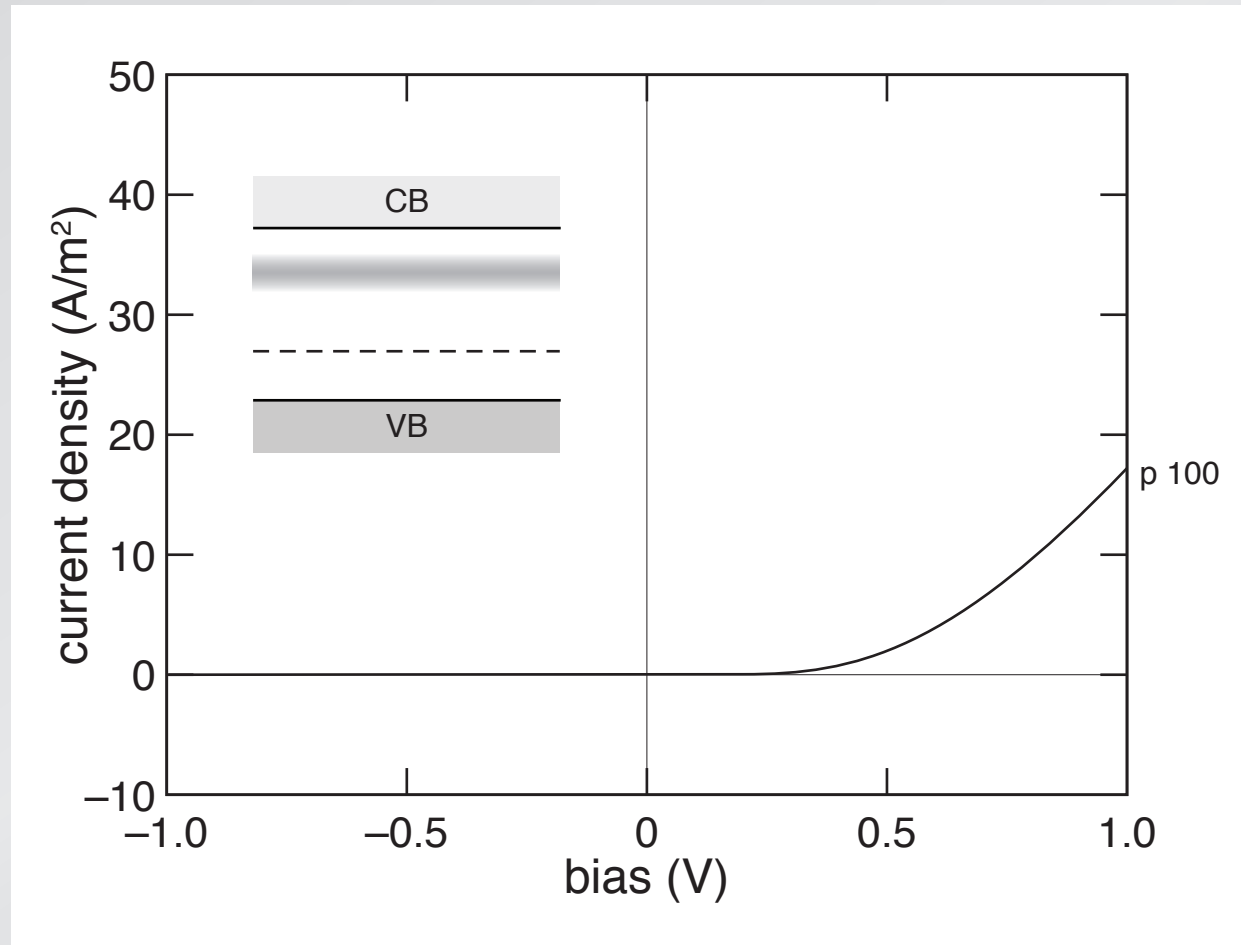
# Optoelectronic properties

vary substrate doping type and resistivity



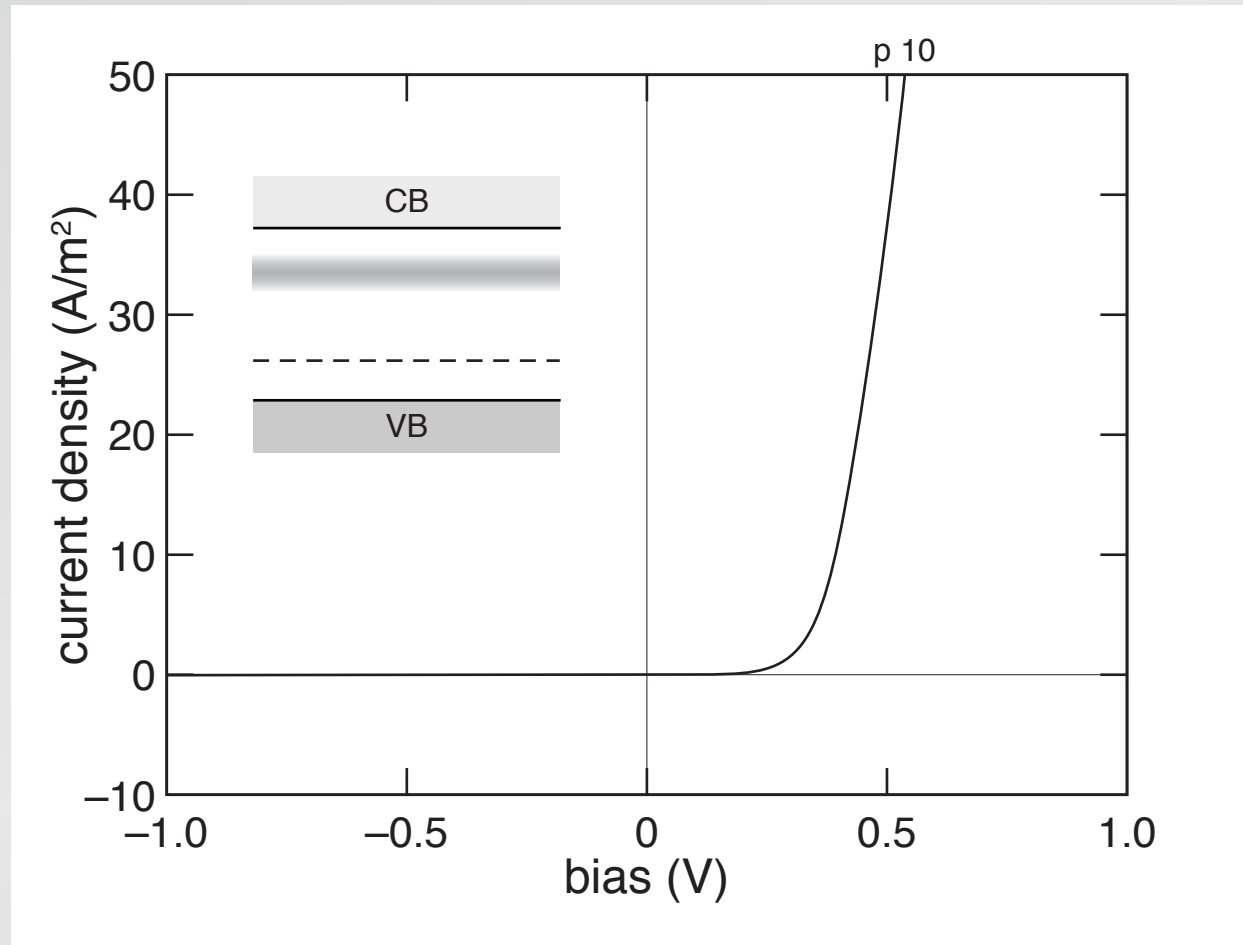
# Optoelectronic properties

vary substrate doping type and resistivity



# Optoelectronic properties

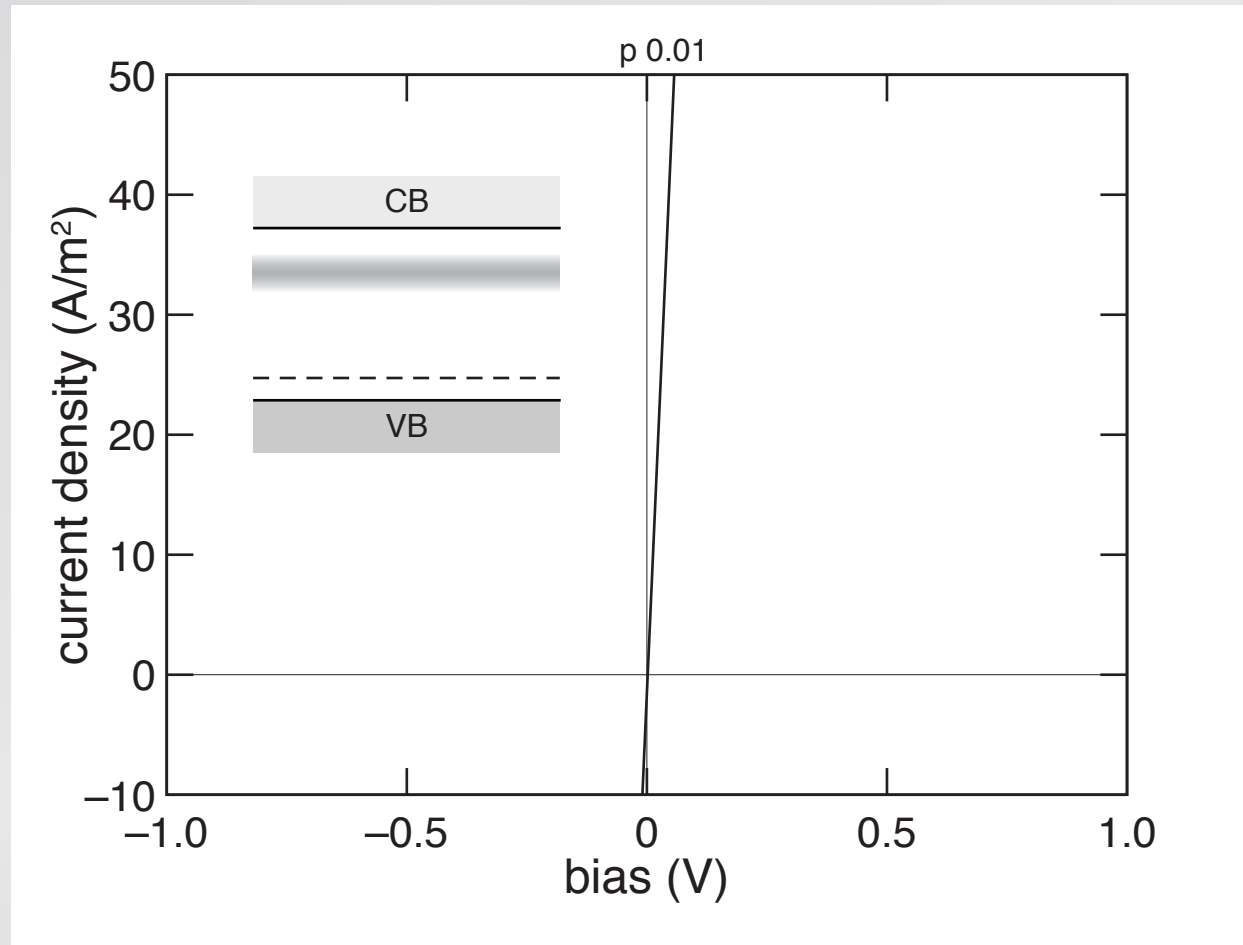
vary substrate doping type and resistivity





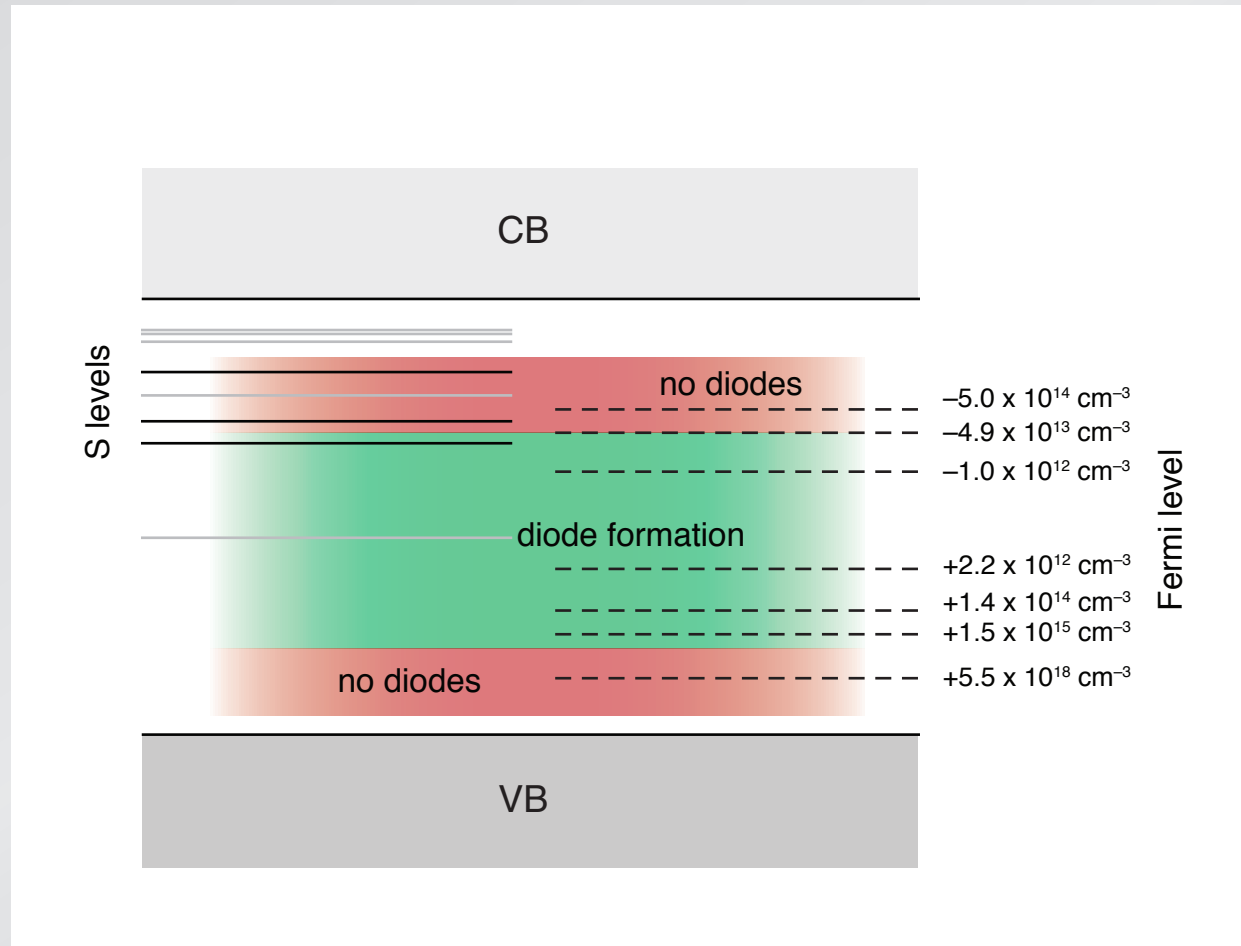
# Optoelectronic properties

vary substrate doping type and resistivity



# Optoelectronic properties

probe impurity states by varying Fermi level in substrate

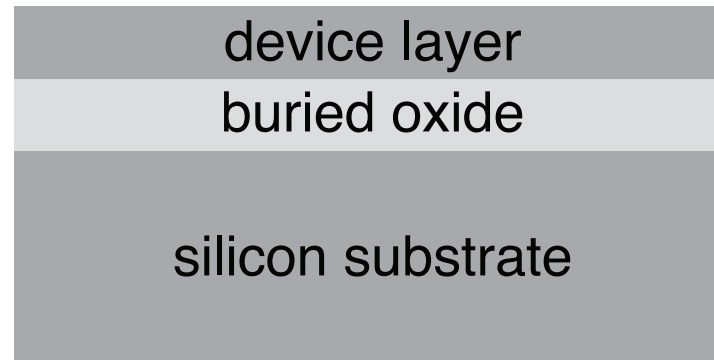


# Optoelectronic properties

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

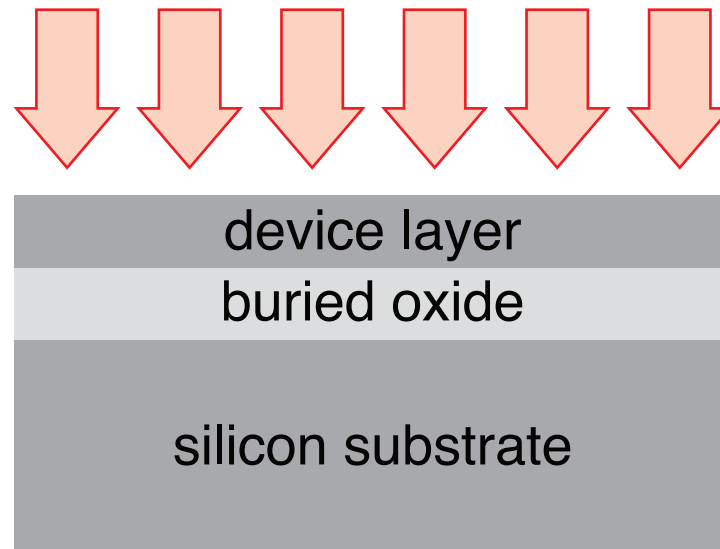
# Optoelectronic properties

isolate surface layer for Hall measurements



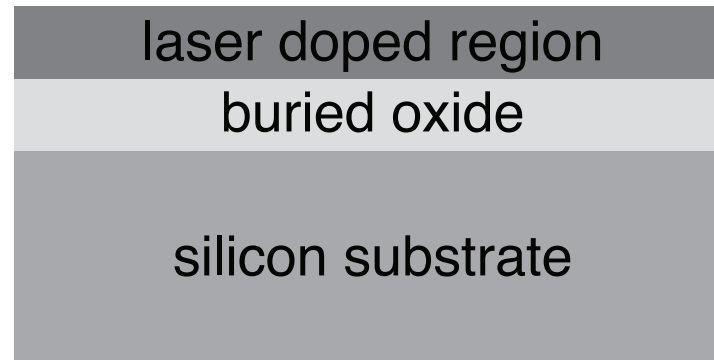
# Optoelectronic properties

isolate surface layer for Hall measurements



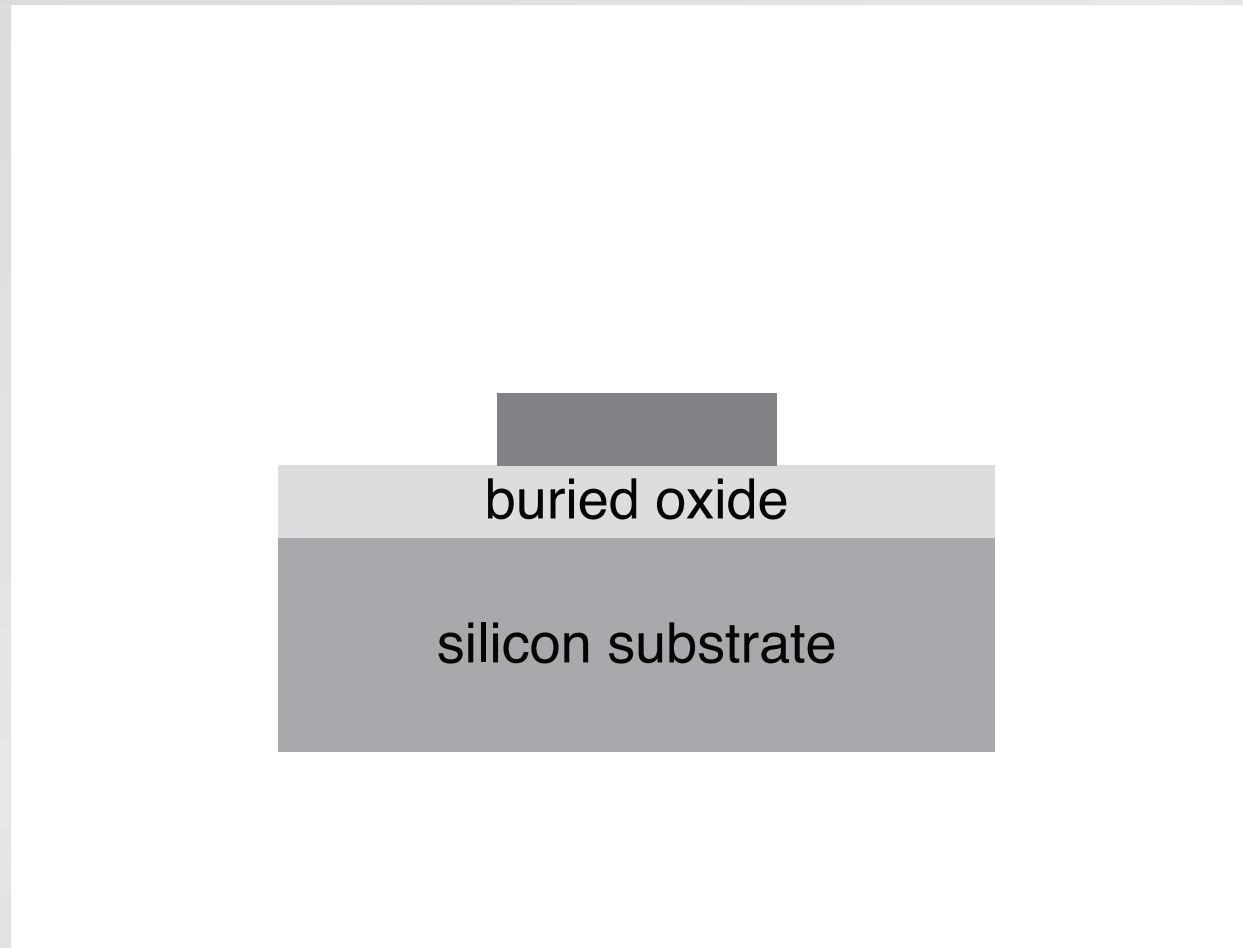
# Optoelectronic properties

isolate surface layer for Hall measurements



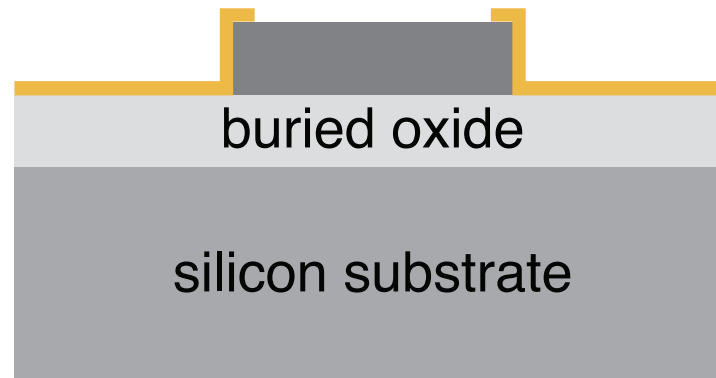
# Optoelectronic properties

isolate surface layer for Hall measurements



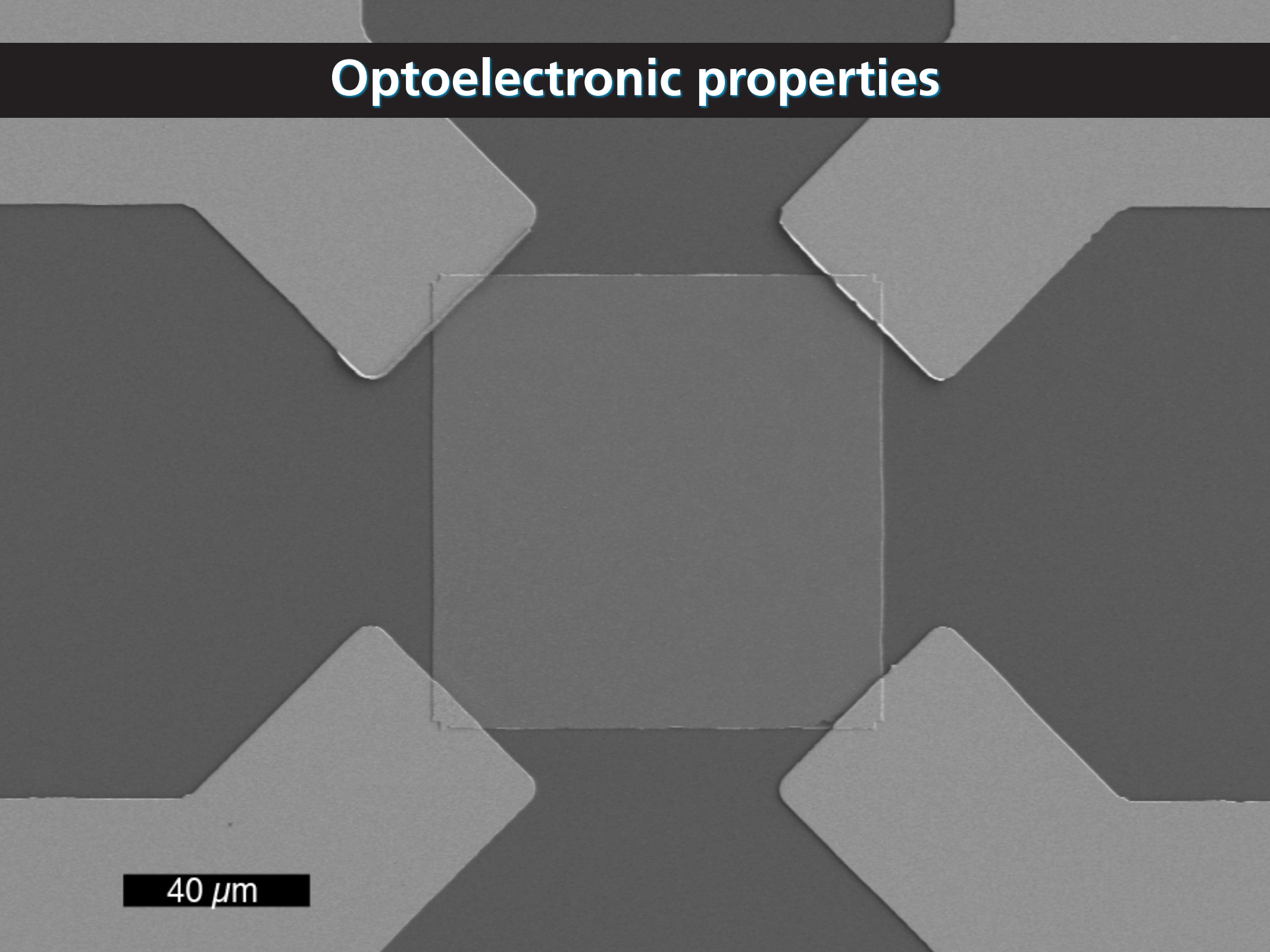
# Optoelectronic properties

isolate surface layer for Hall measurements





# Optoelectronic properties

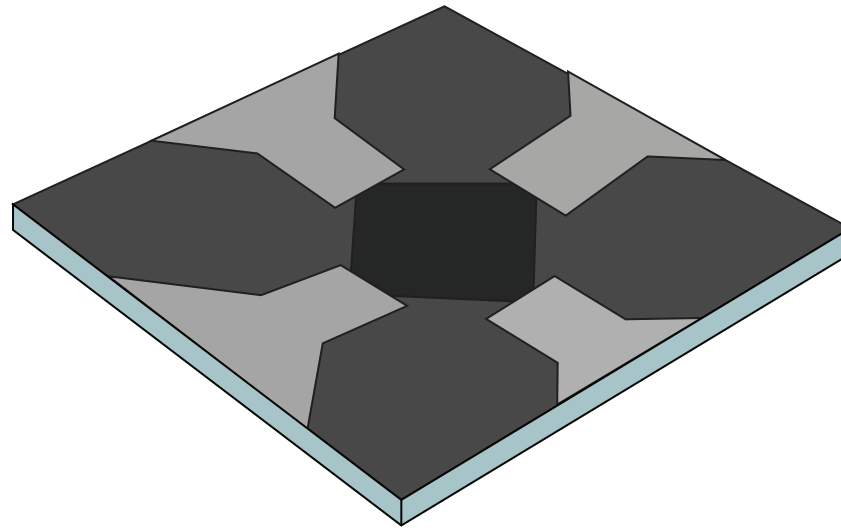


40  $\mu\text{m}$

A grayscale micrograph showing a central square device on a substrate. The device is surrounded by four trapezoidal pads, one in each corner. A scale bar in the bottom left corner indicates a length of 40 micrometers.

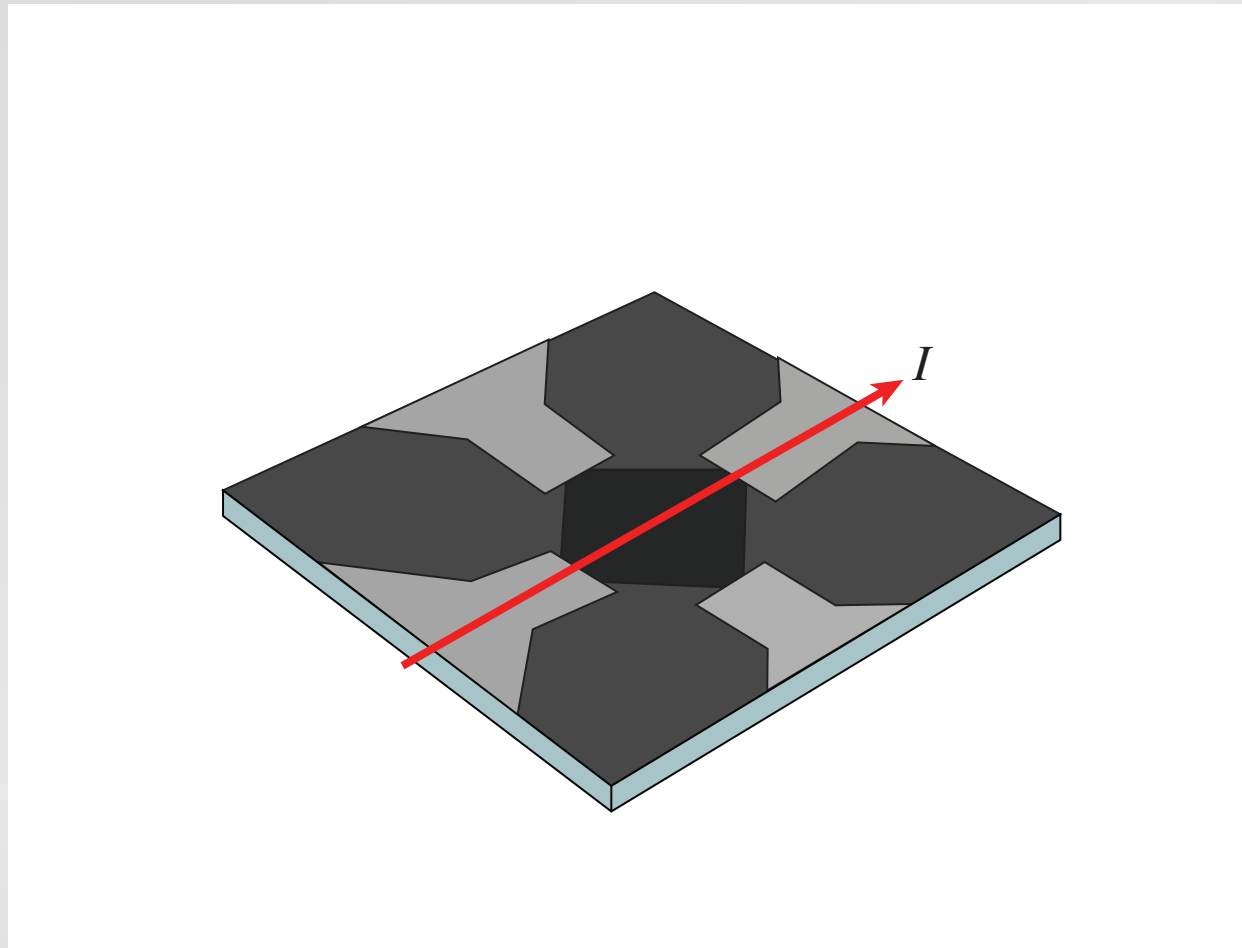
# Optoelectronic properties

## Hall measurements



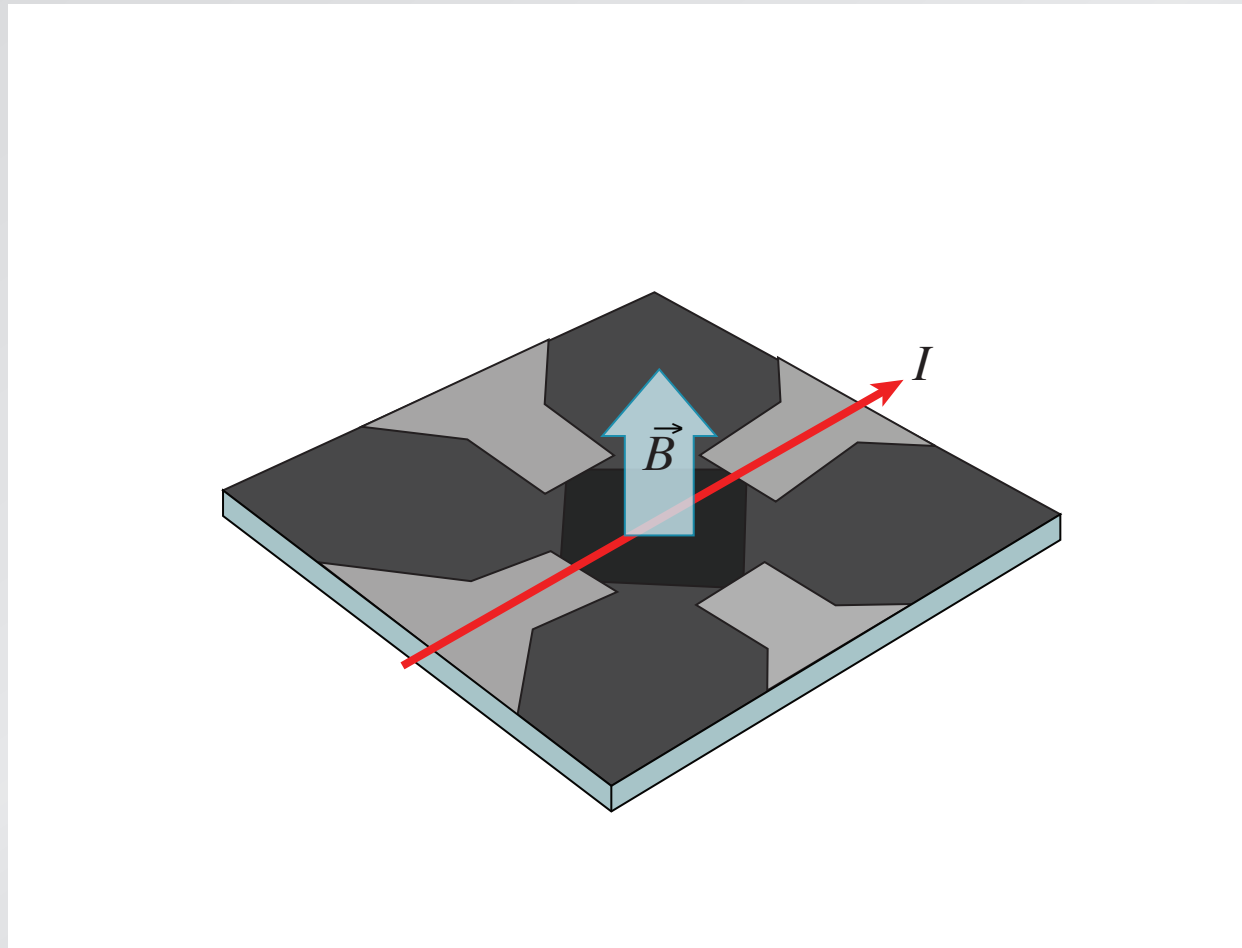
# Optoelectronic properties

## Hall measurements



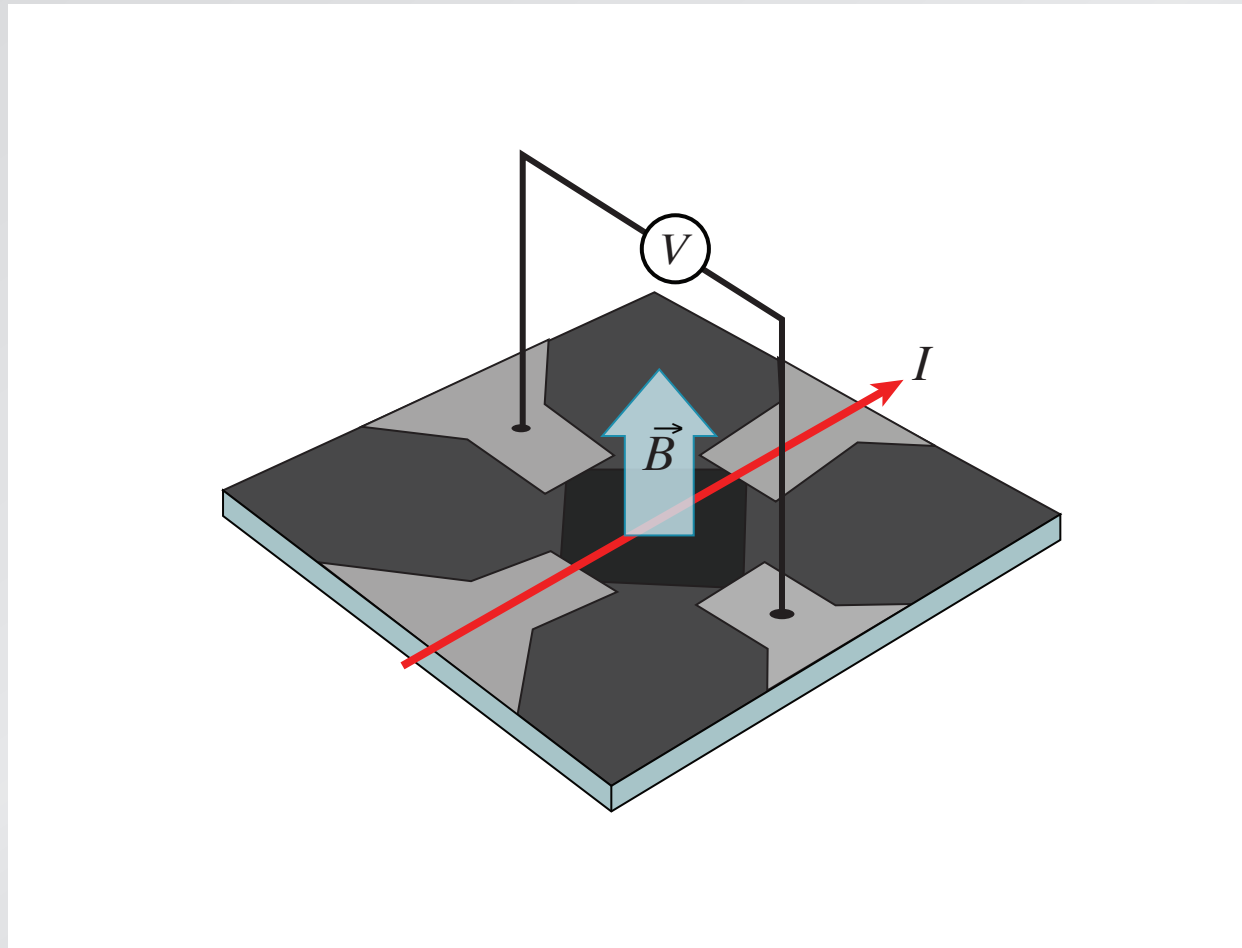
# Optoelectronic properties

## Hall measurements



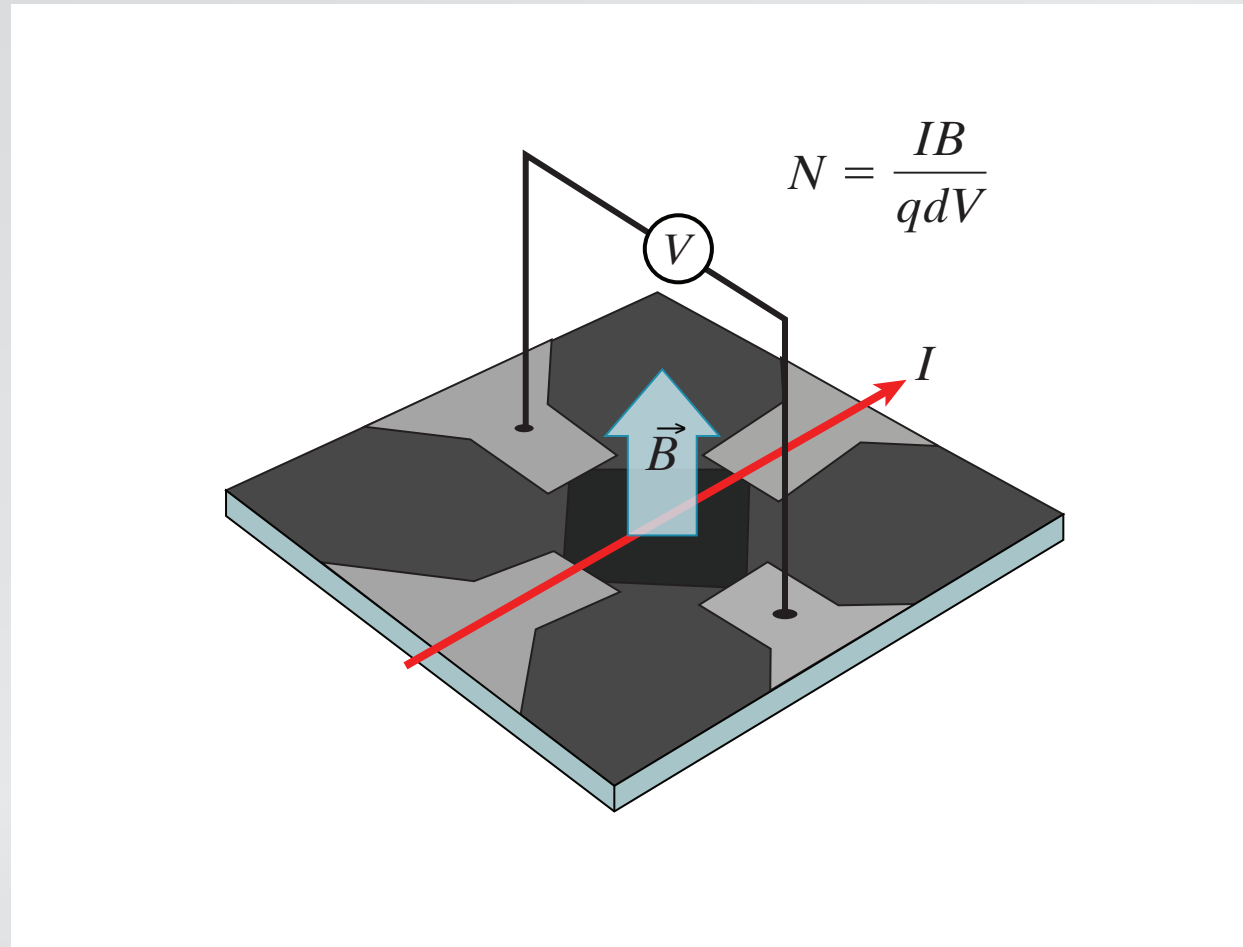
# Optoelectronic properties

## Hall measurements



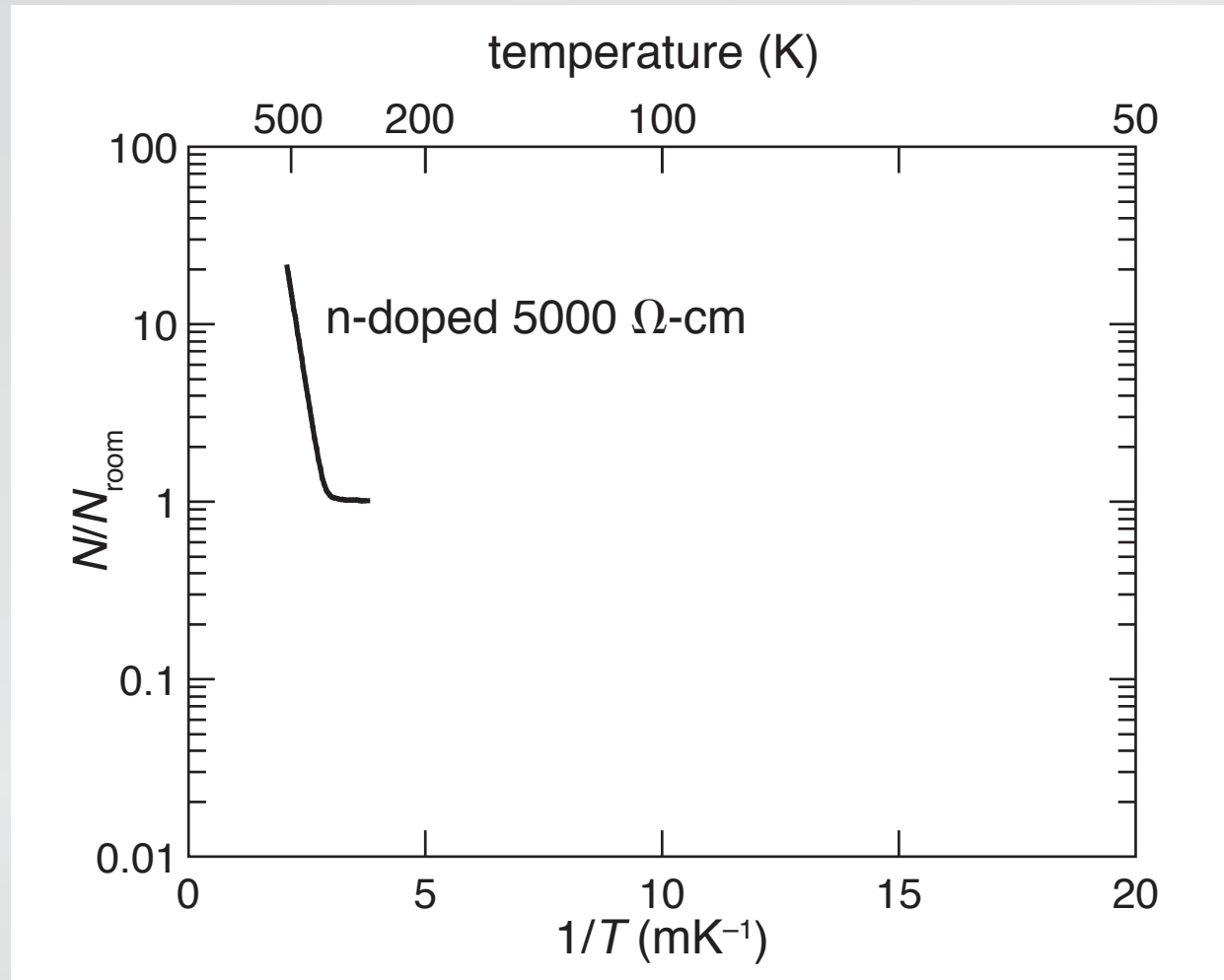
# Optoelectronic properties

## Hall measurements



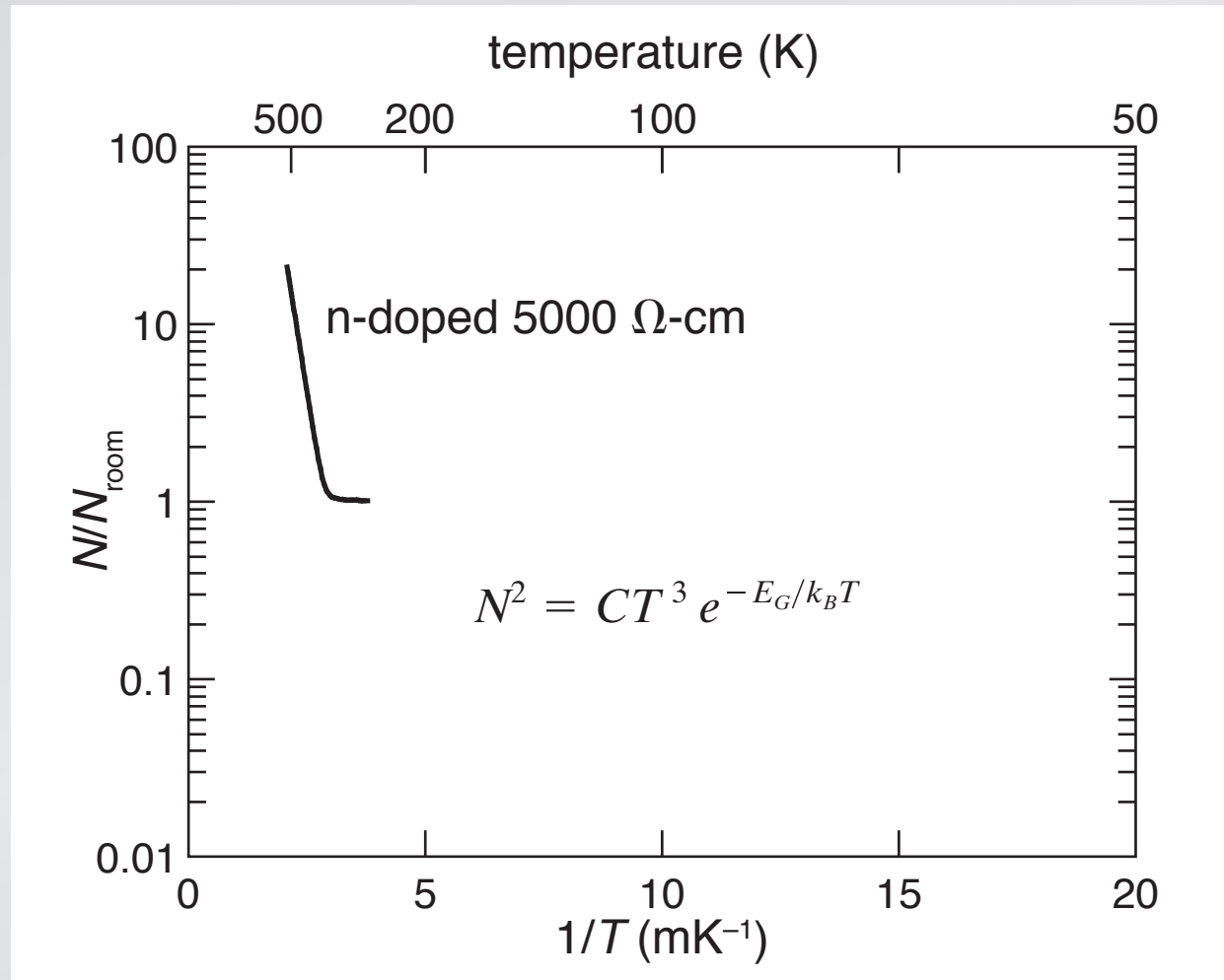
# Optoelectronic properties

## Hall measurements



# Optoelectronic properties

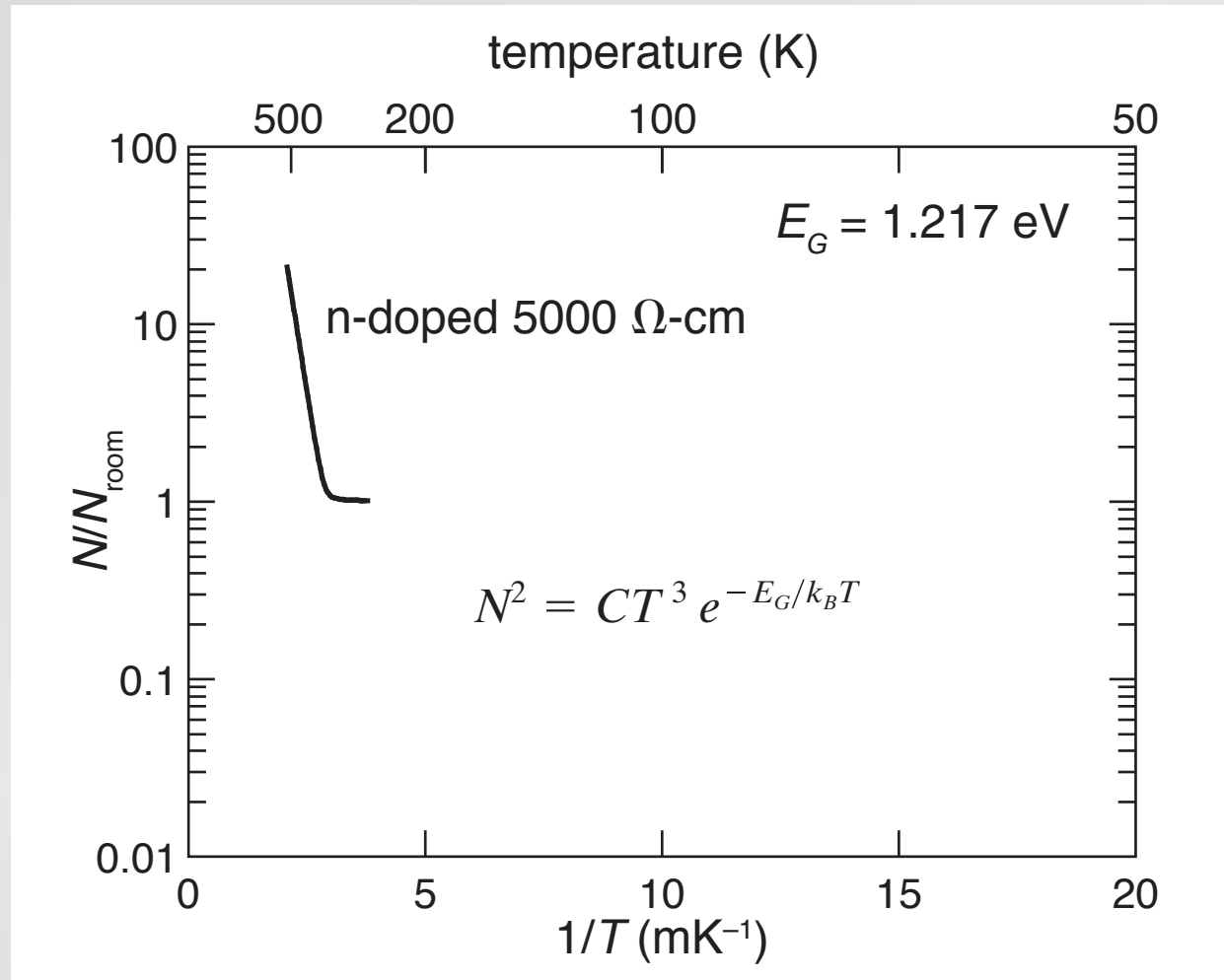
## Hall measurements





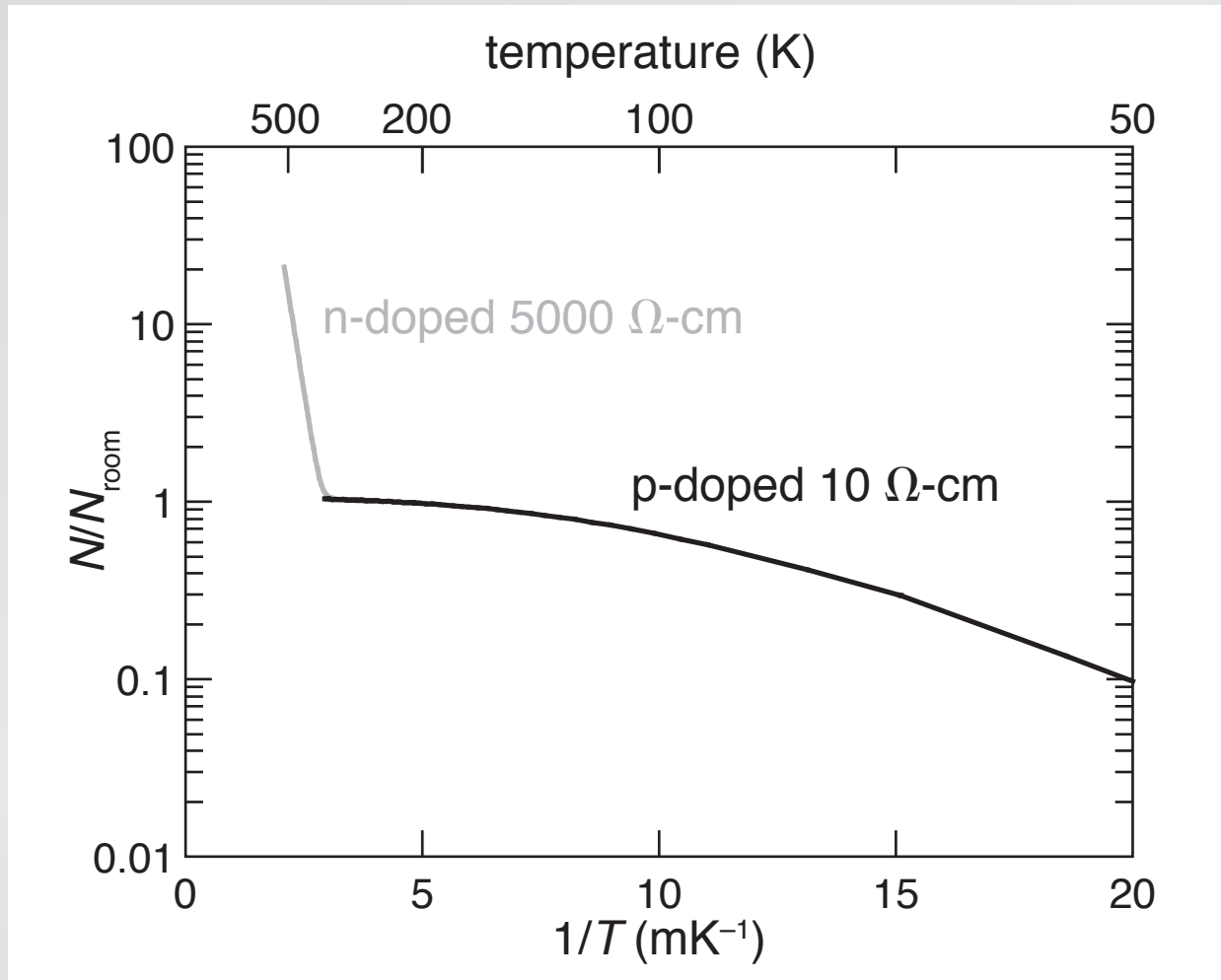
# Optoelectronic properties

## Hall measurements



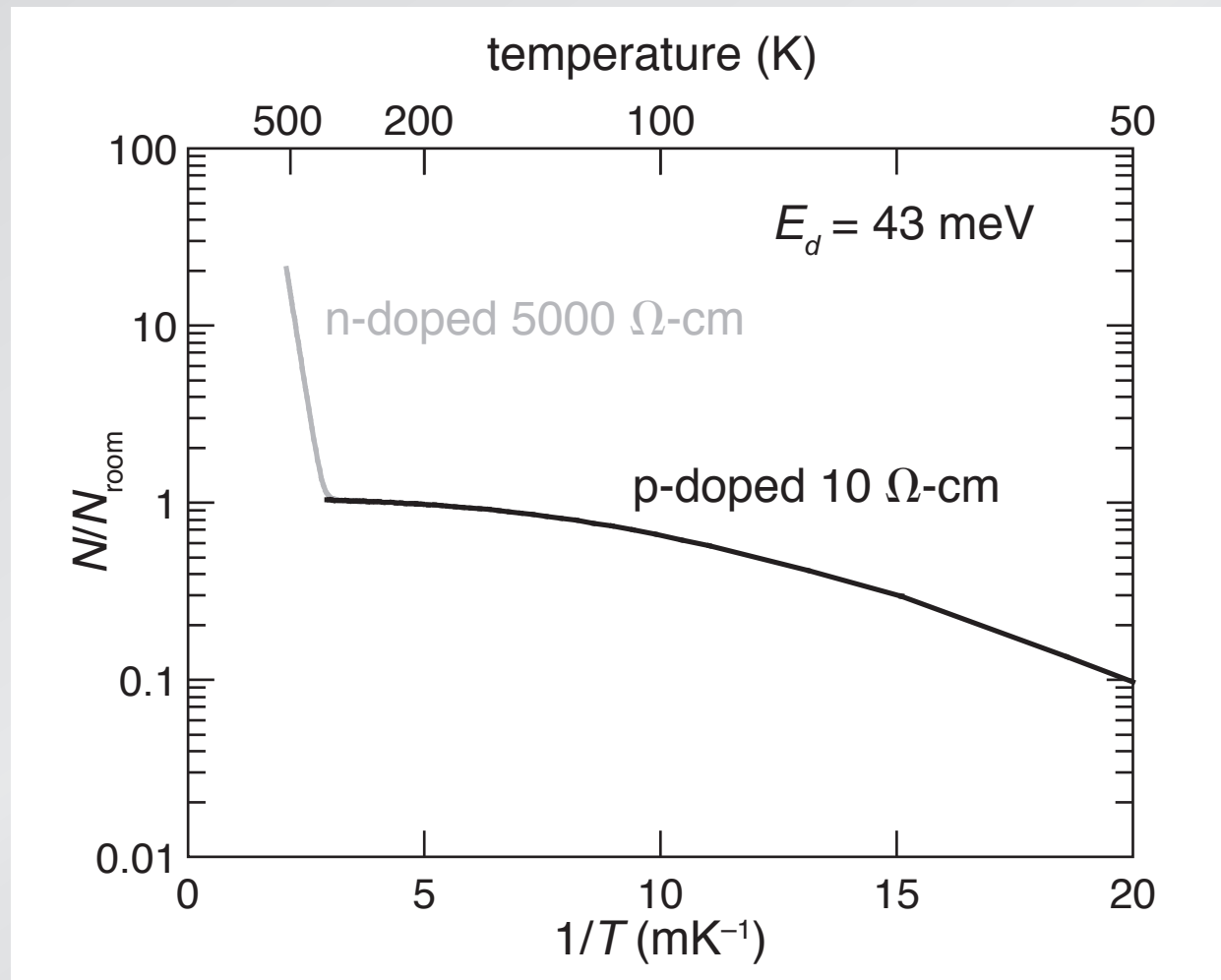
# Optoelectronic properties

## Hall measurements



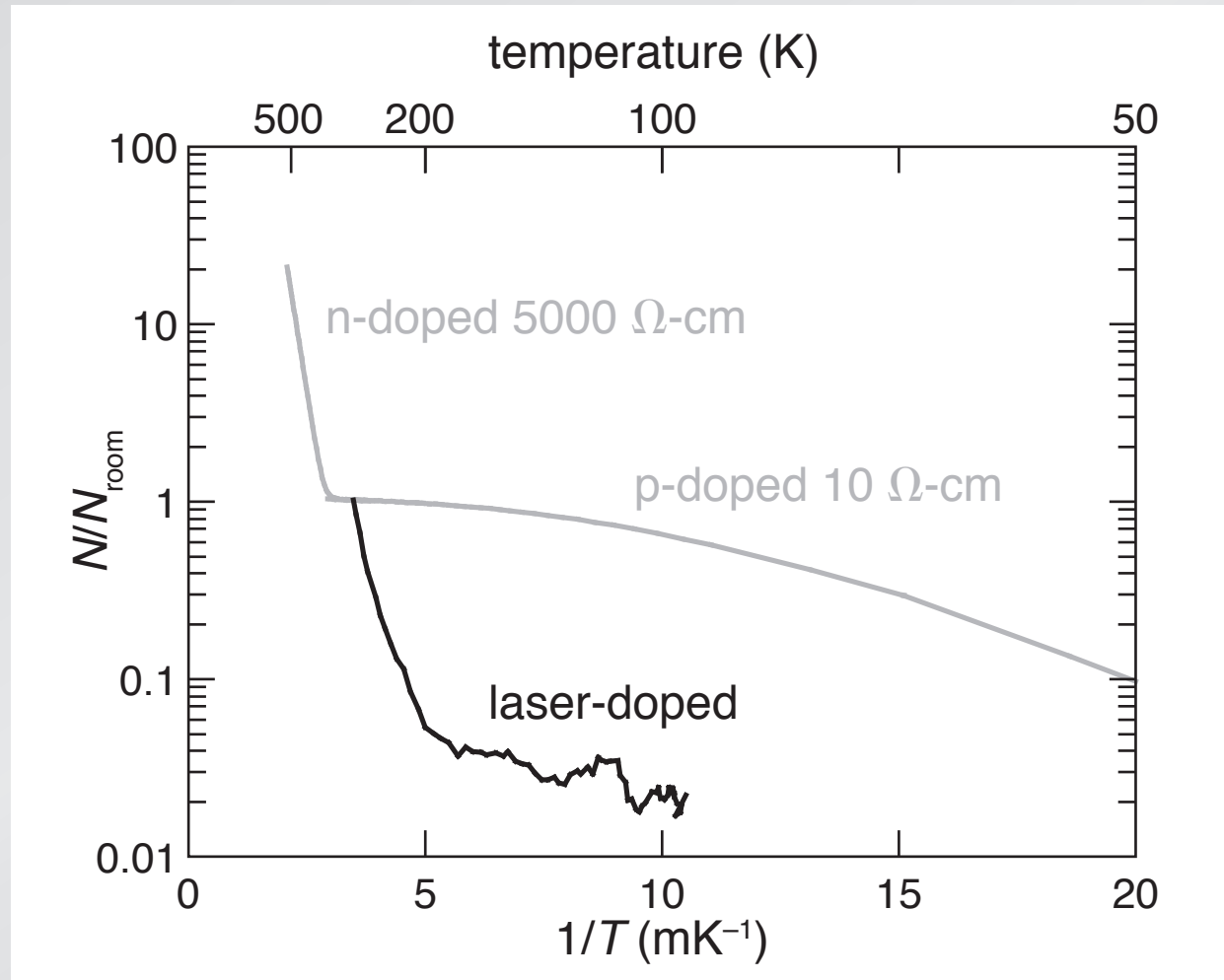
# Optoelectronic properties

## Hall measurements



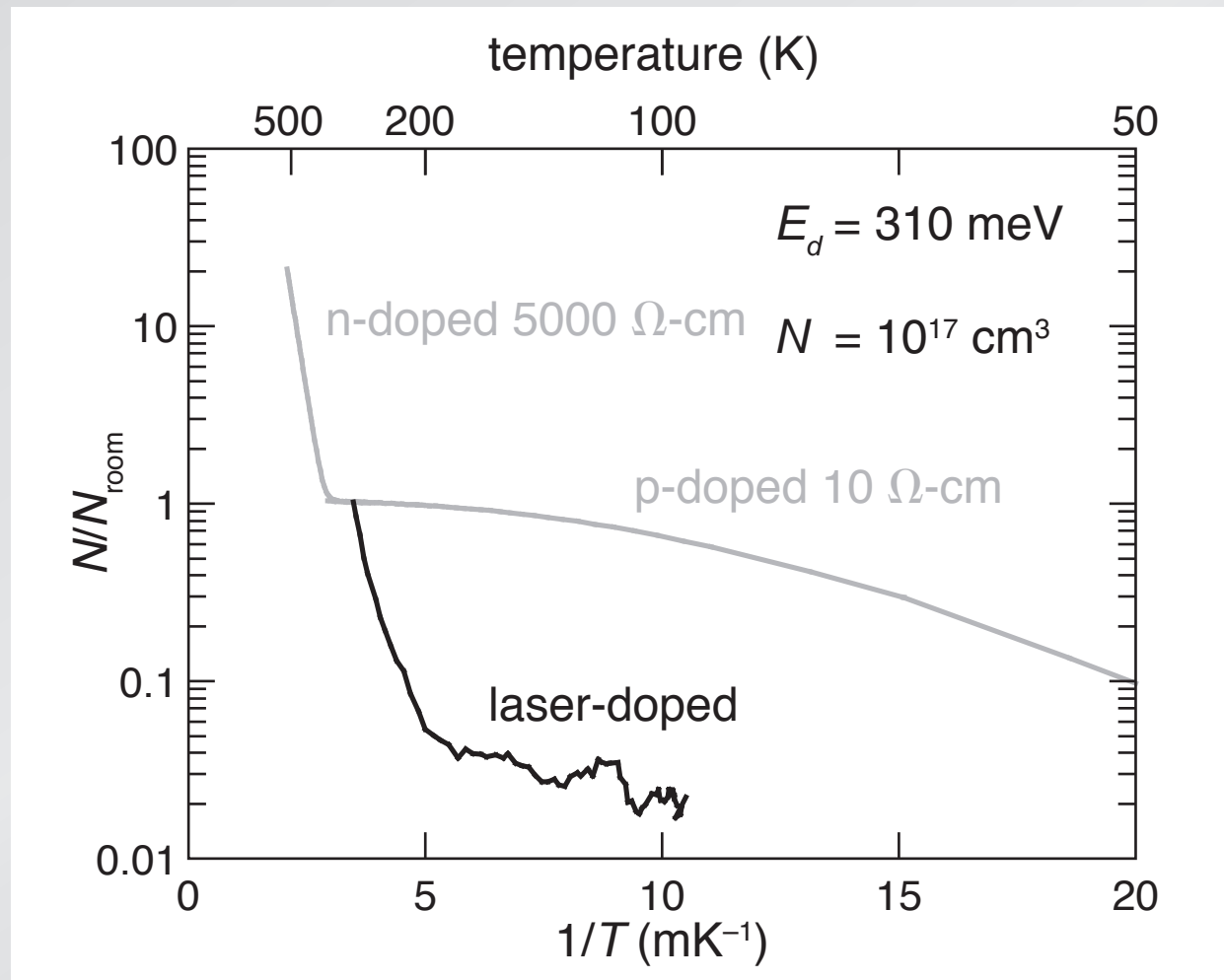
# Optoelectronic properties

## Hall measurements



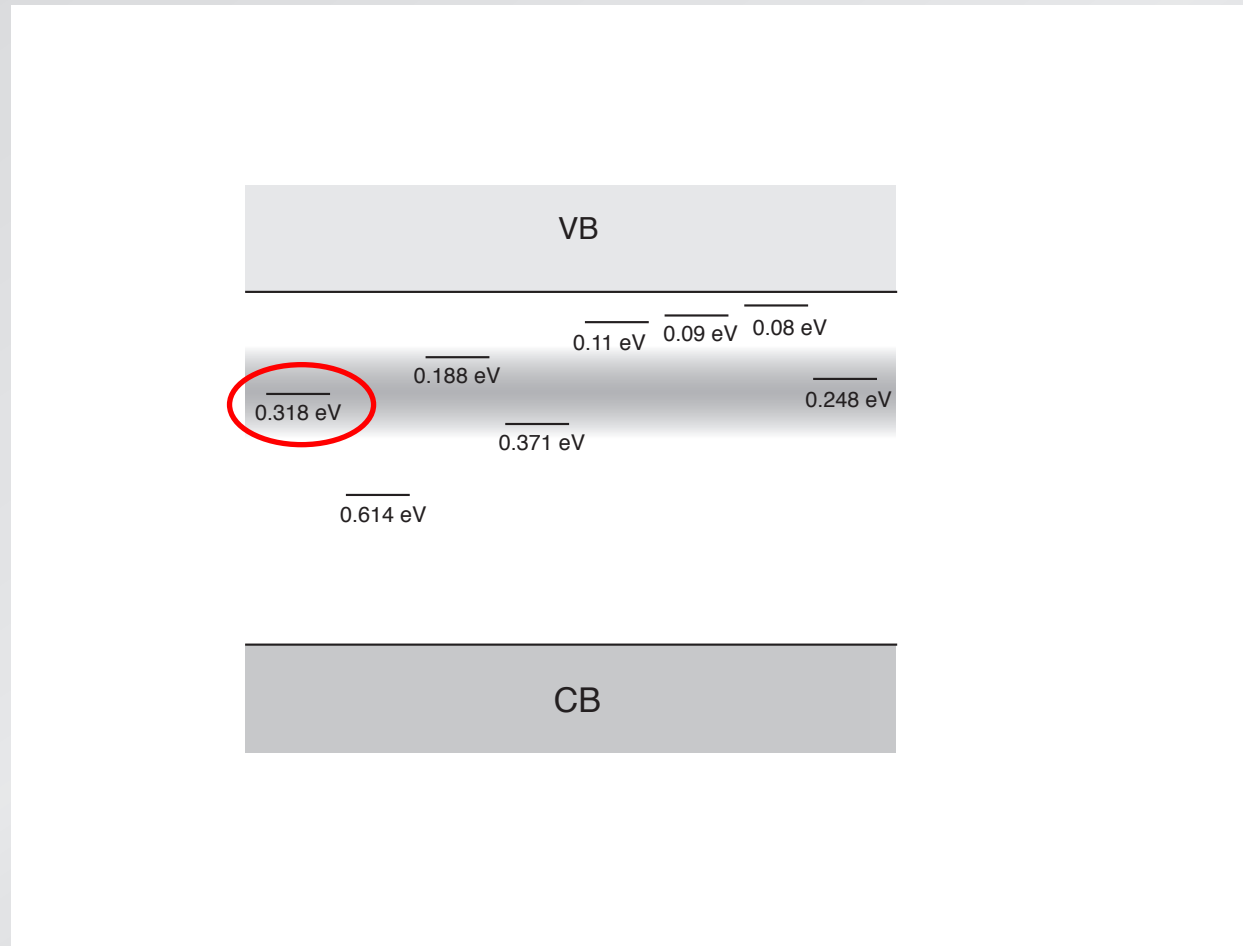
# Optoelectronic properties

## Hall measurements



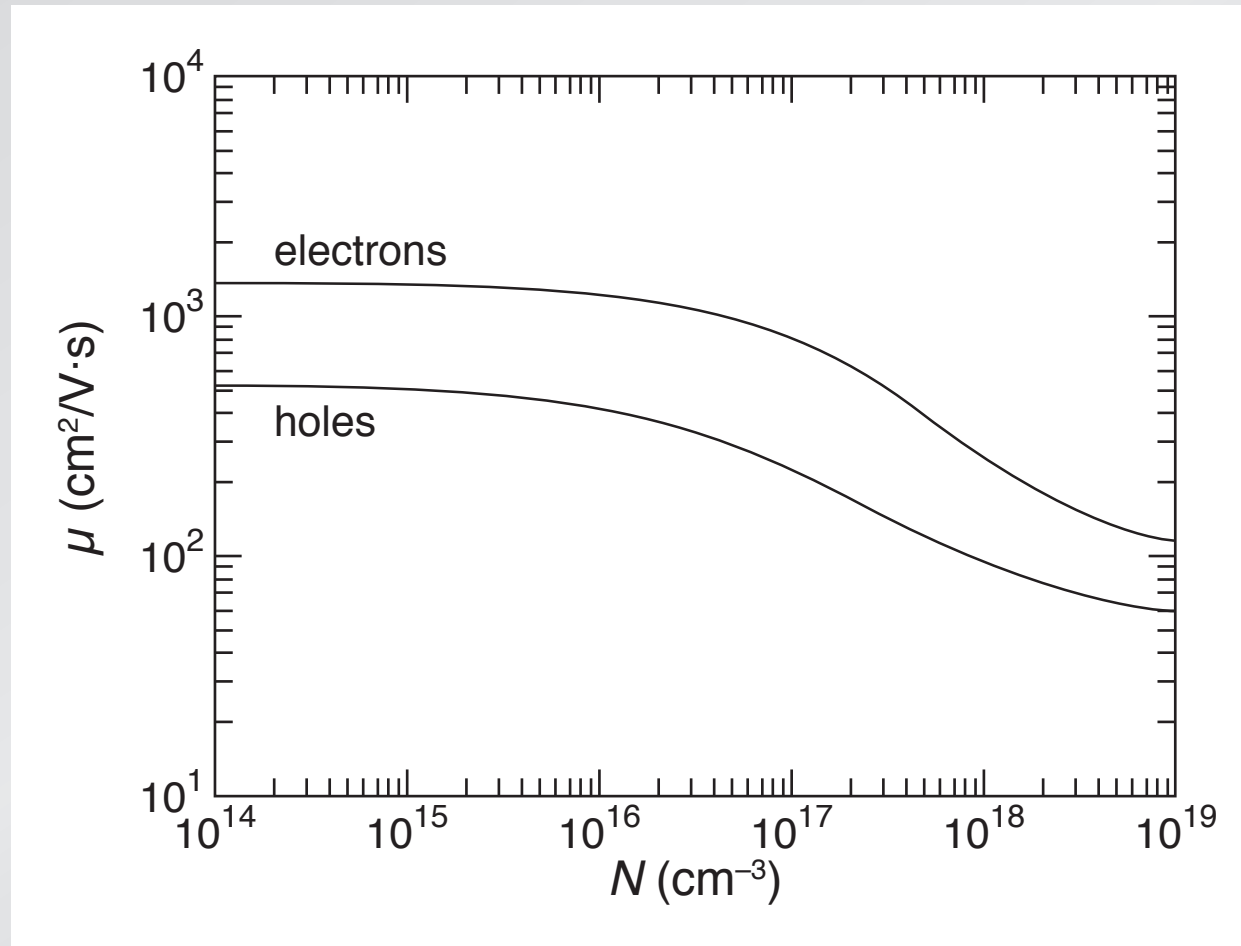
# Optoelectronic properties

impurity (donor) band centered at 310 meV



# Optoelectronic properties

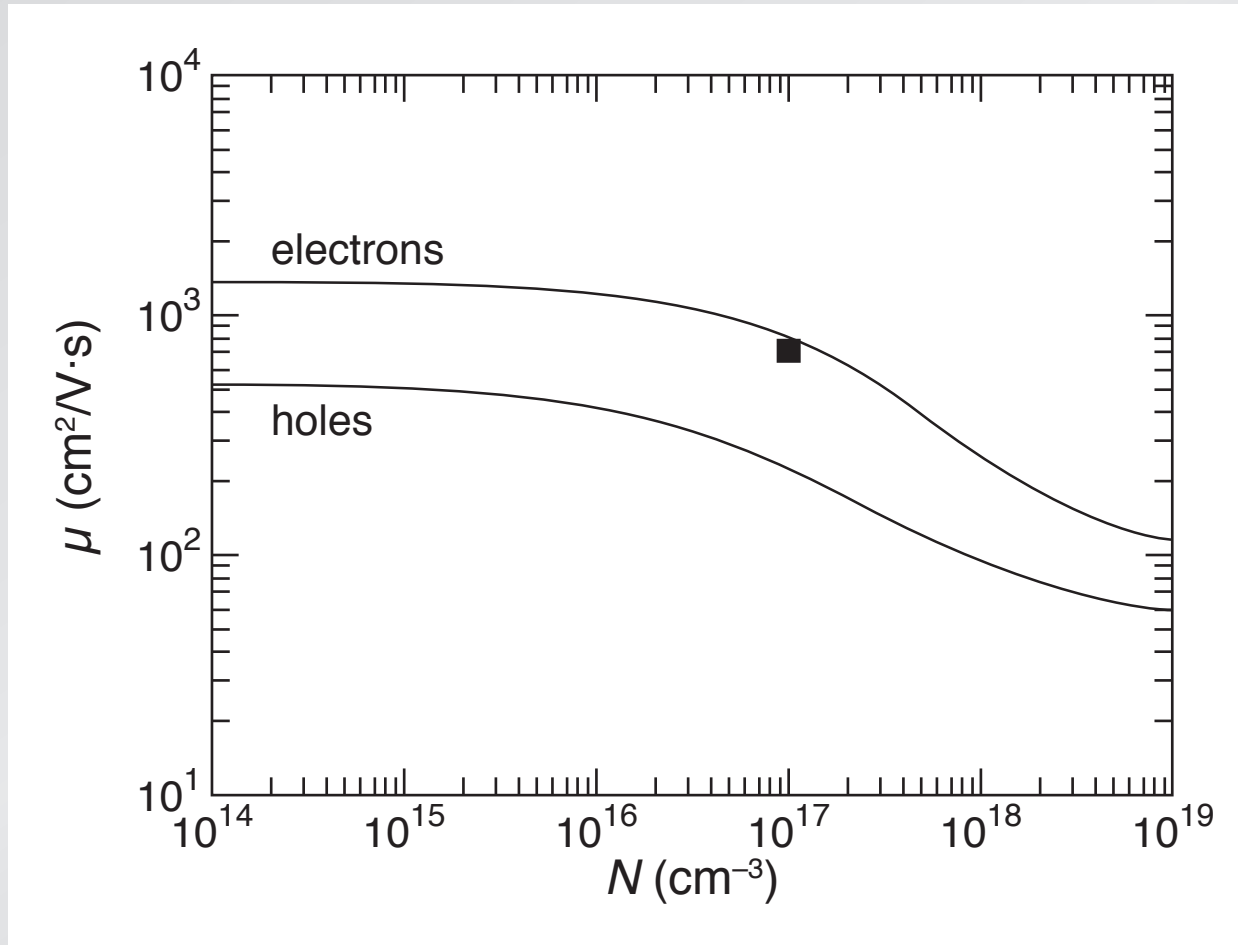
## majority carrier mobility



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

# Optoelectronic properties

## majority carrier mobility



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



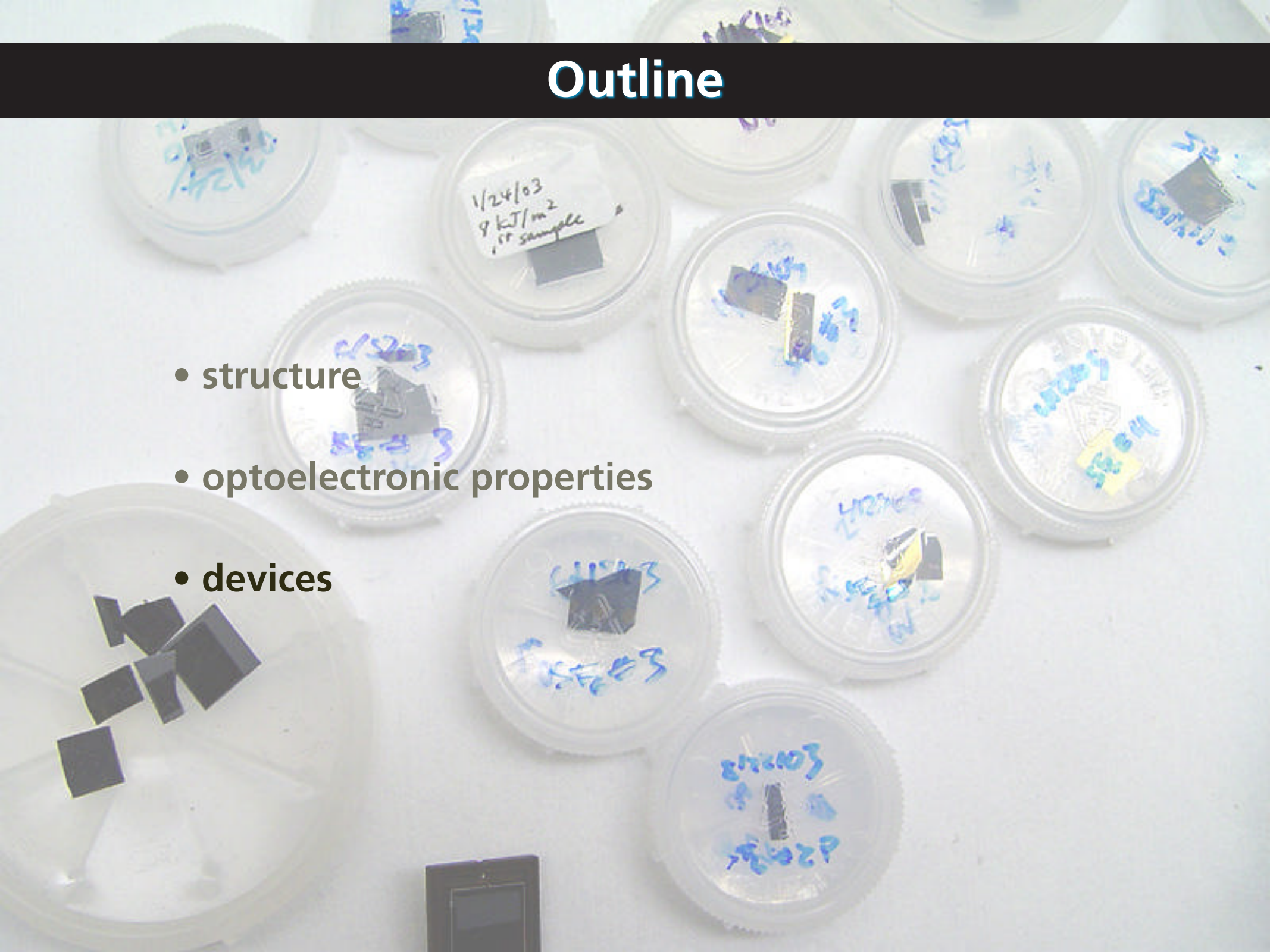
# Optoelectronic properties

## 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

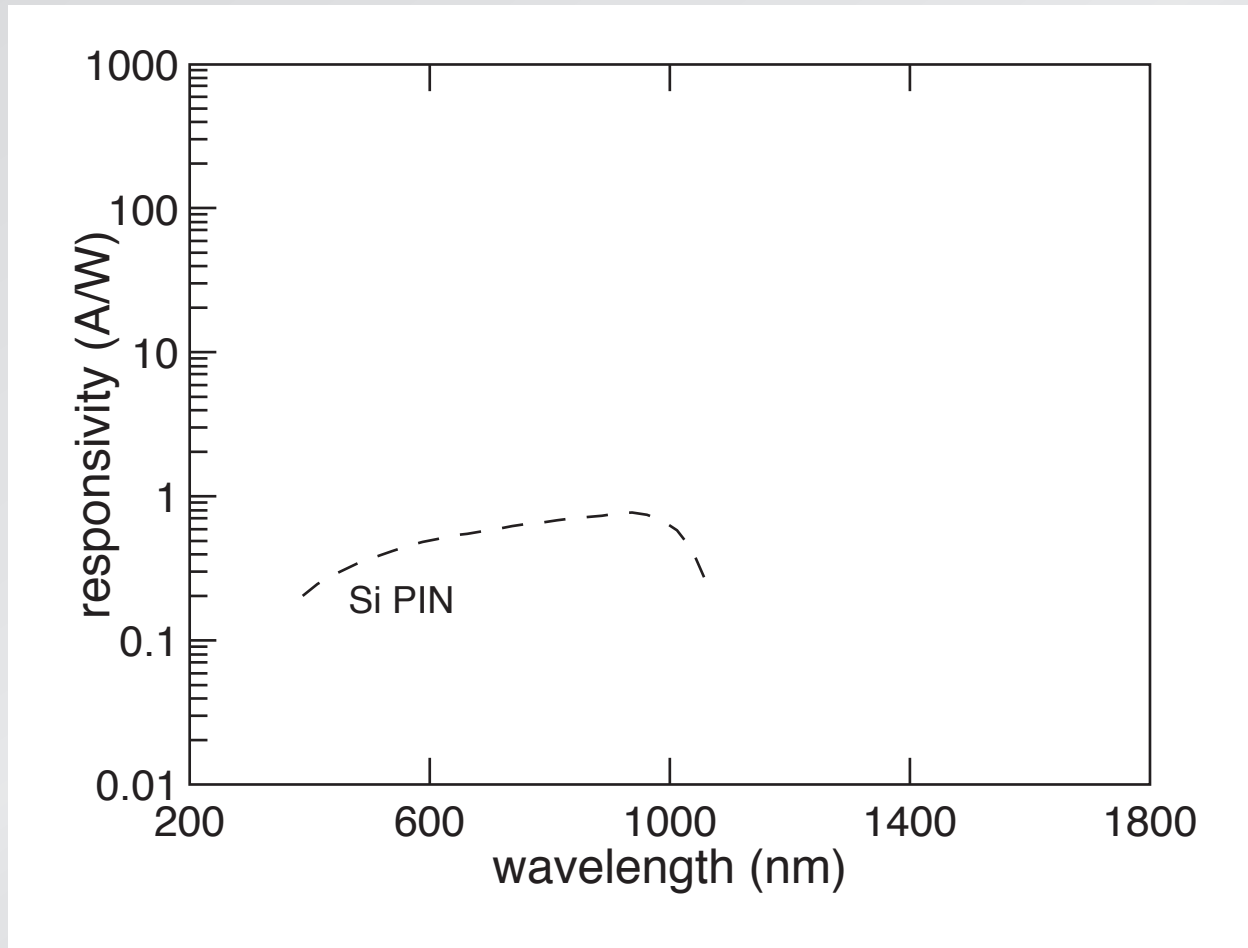
# Outline

- structure
- optoelectronic properties
- devices



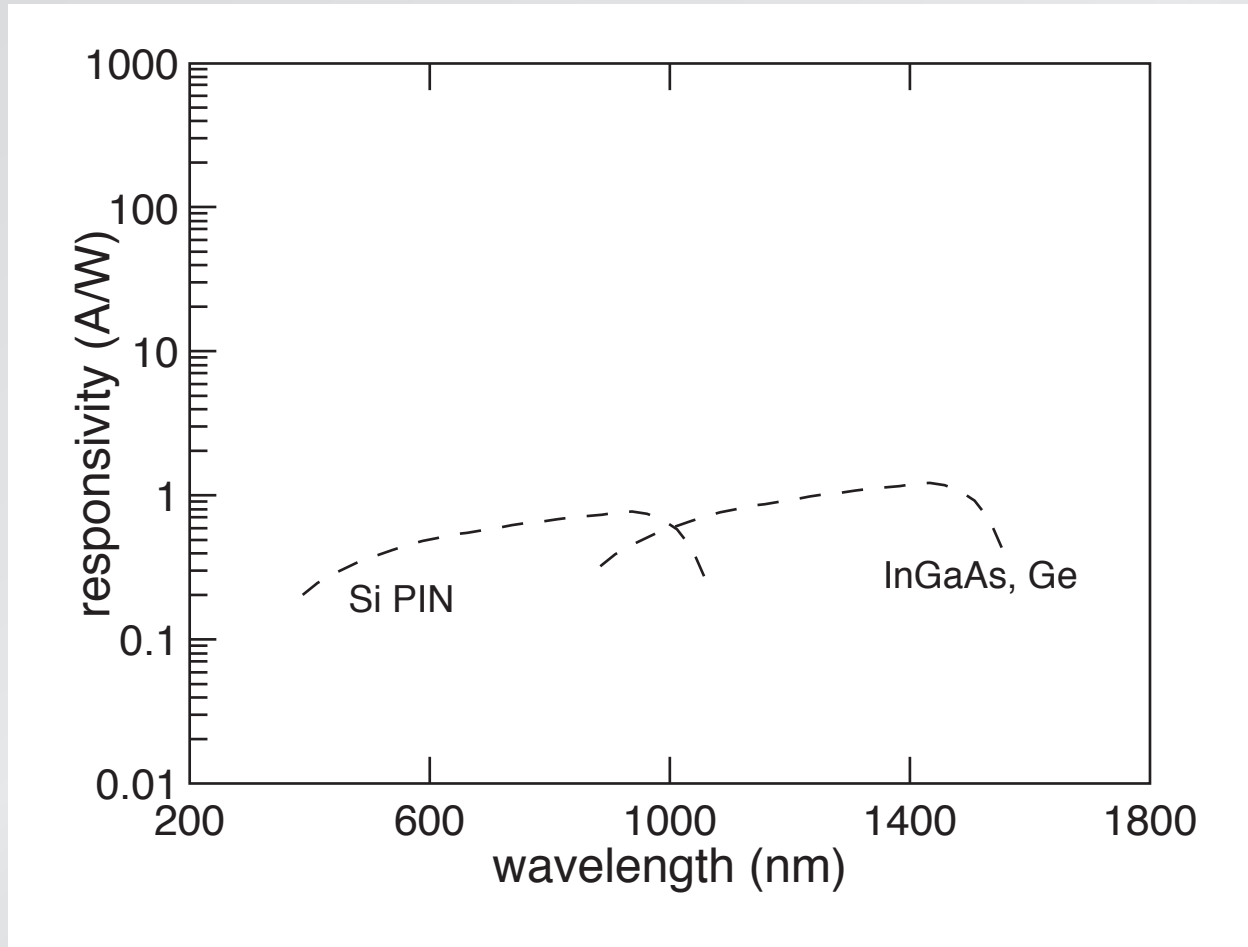
# Devices

## responsivity



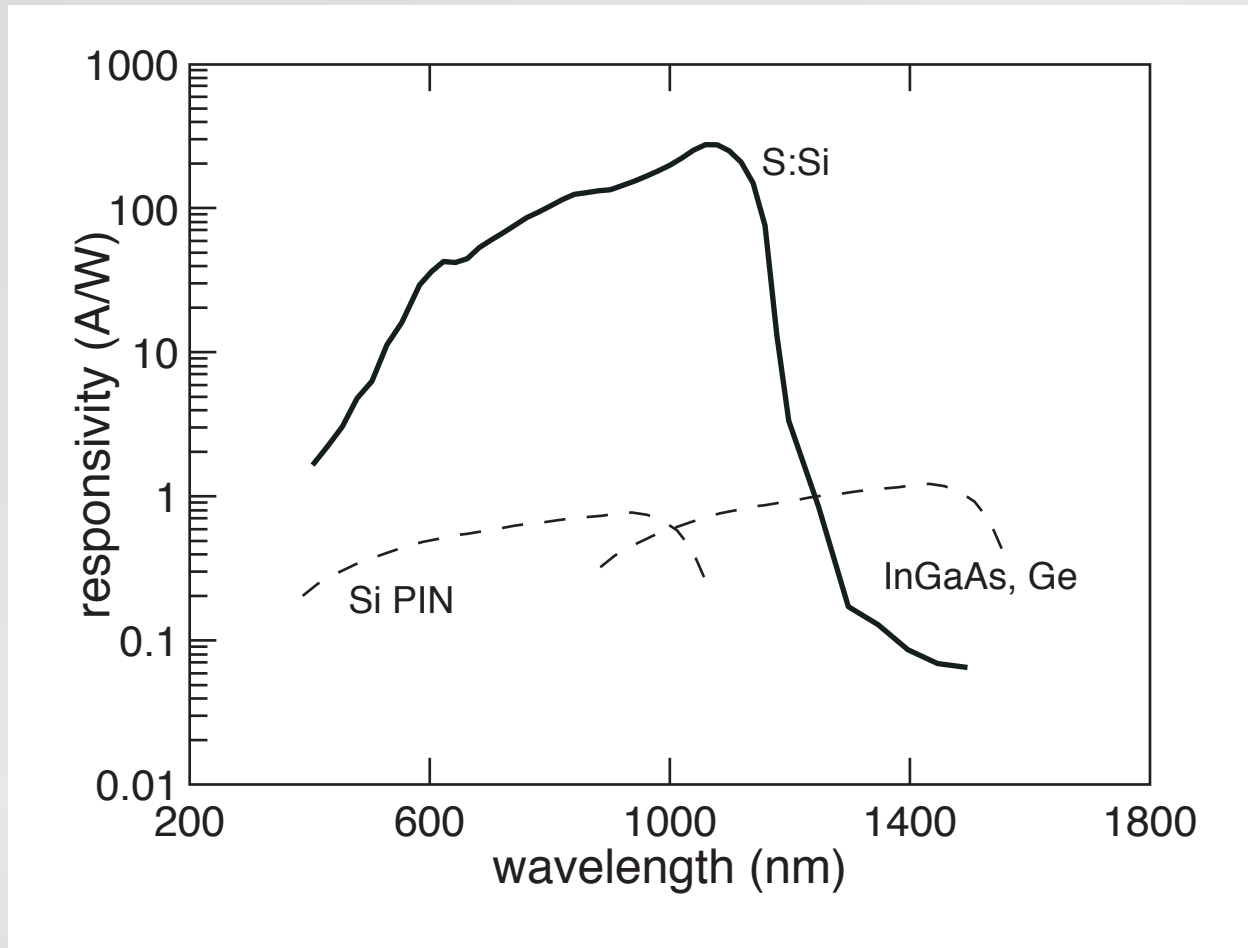
# Devices

## responsivity



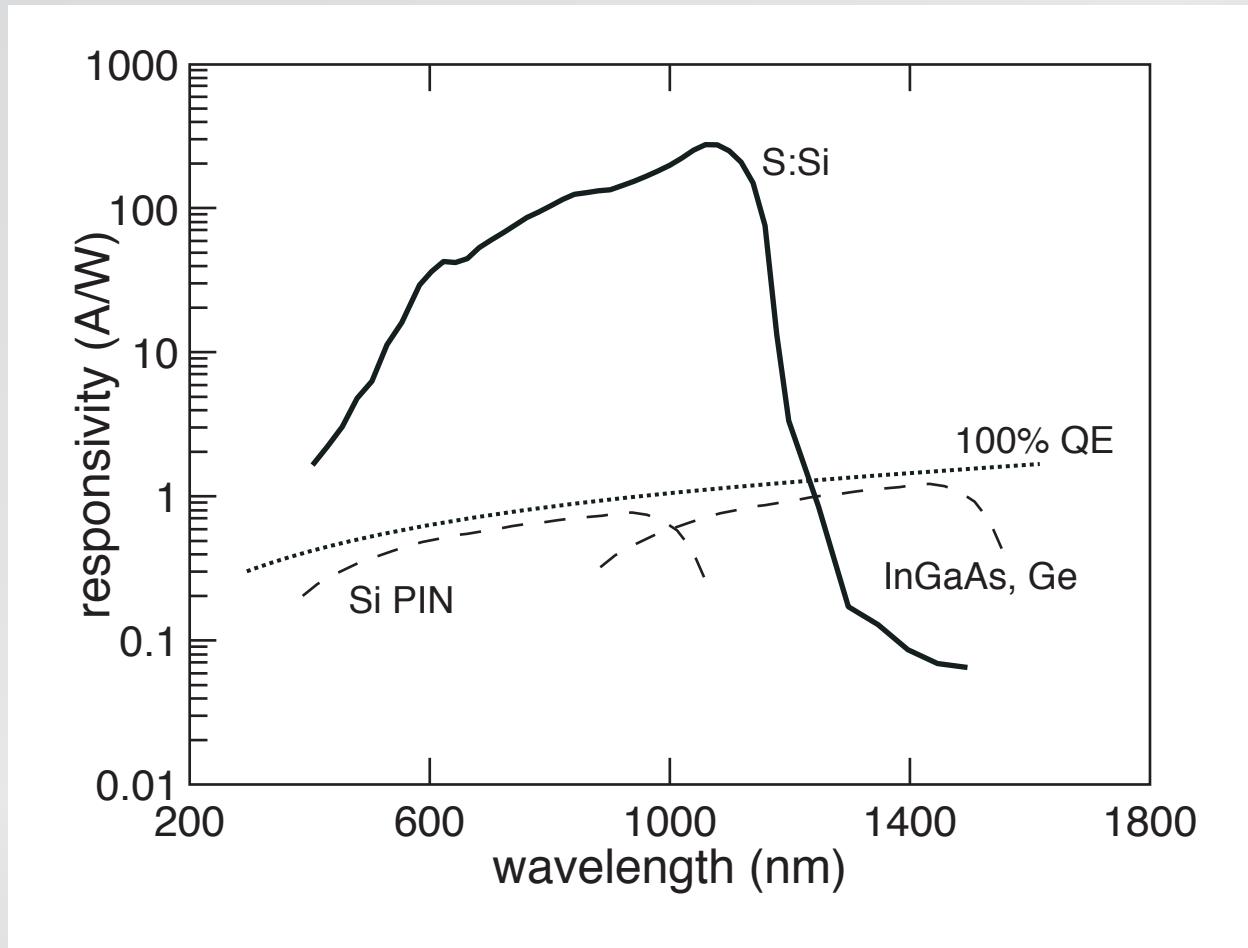
# Devices

## responsivity



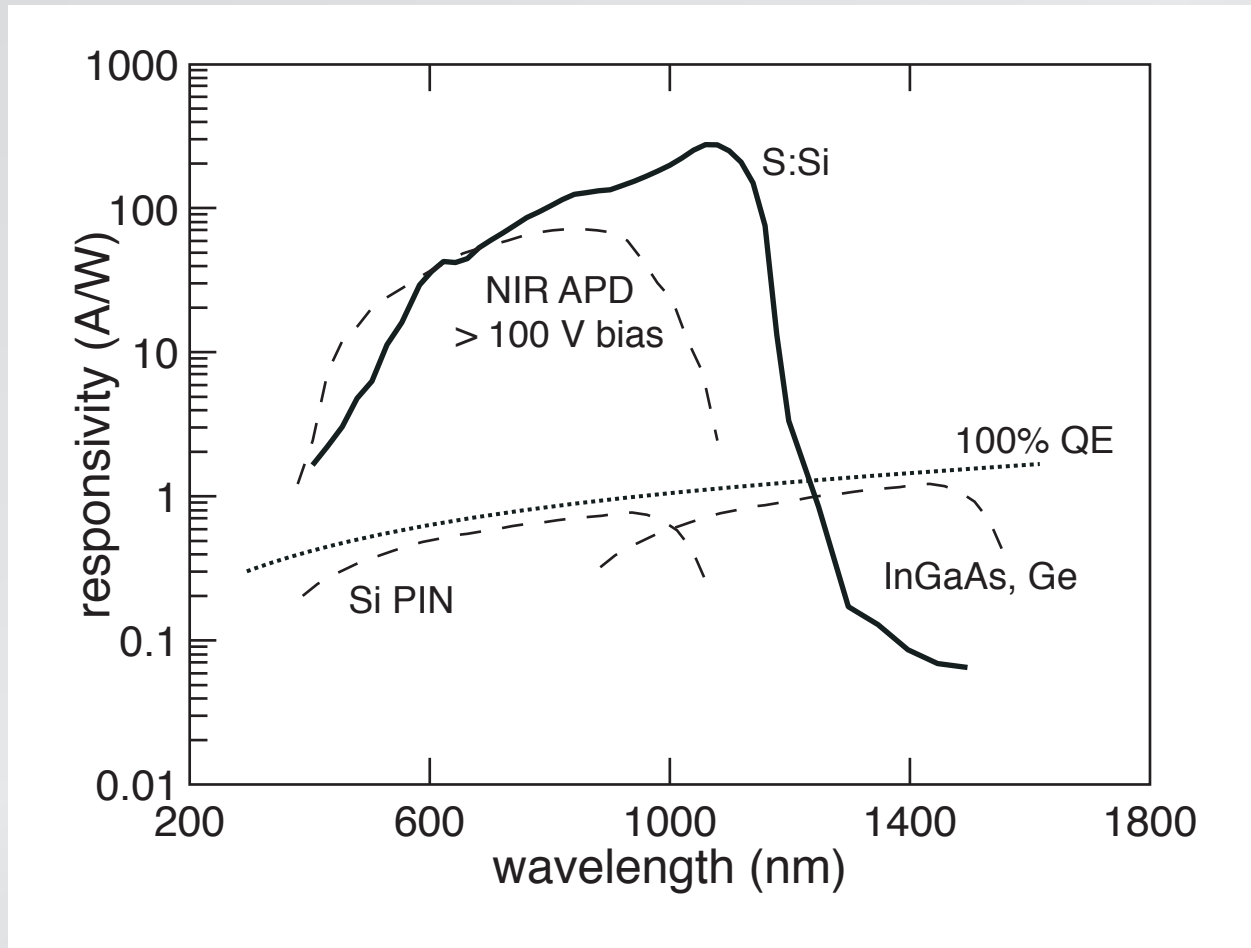
# Devices

## responsivity



# Devices

## responsivity



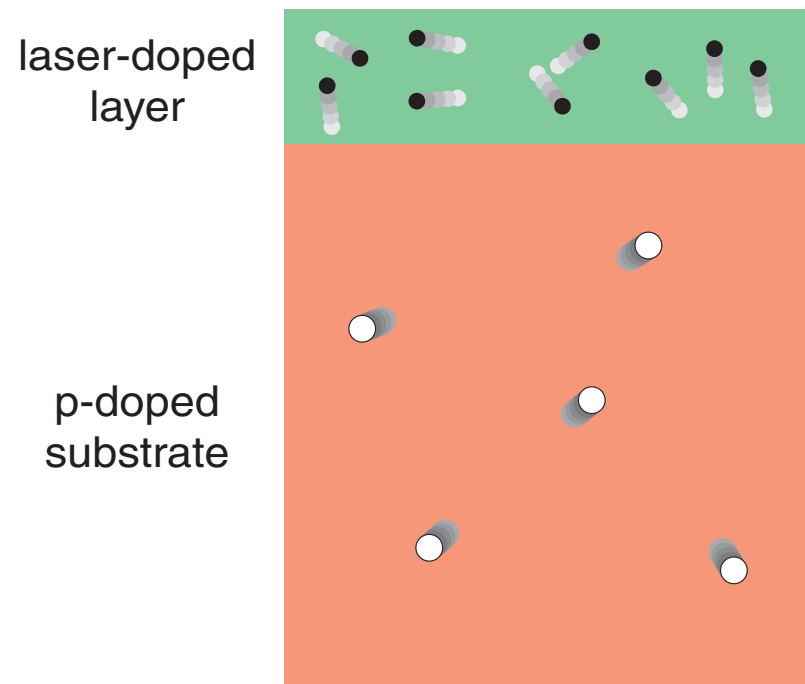
# Devices

**What causes gain?**

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

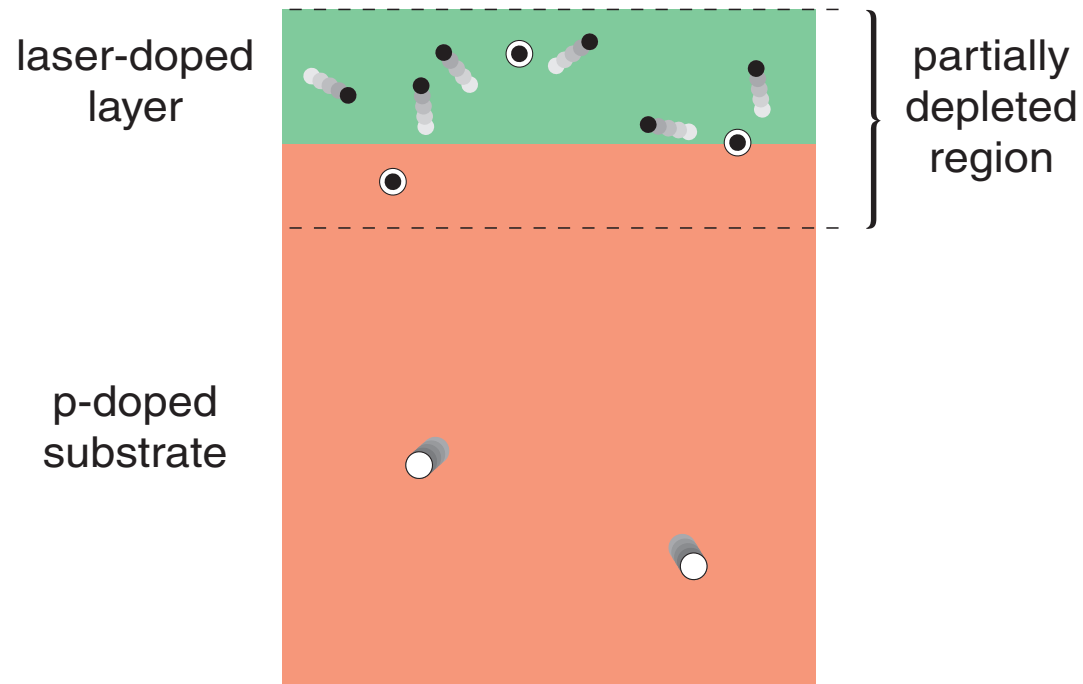


# Devices



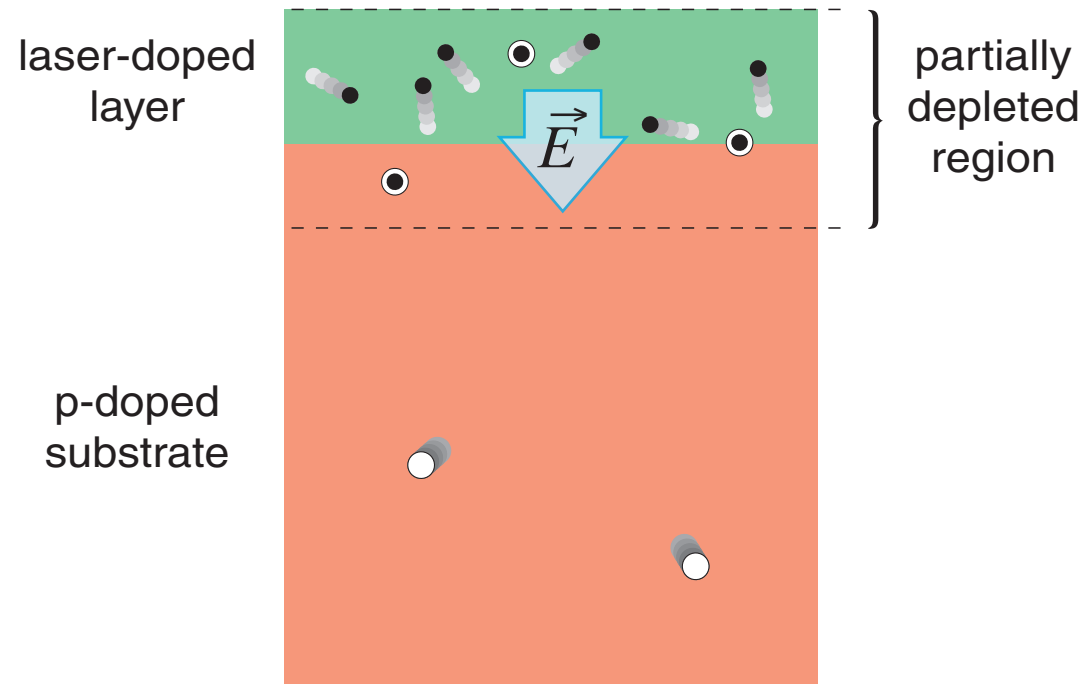
**"pl junction"**

# Devices



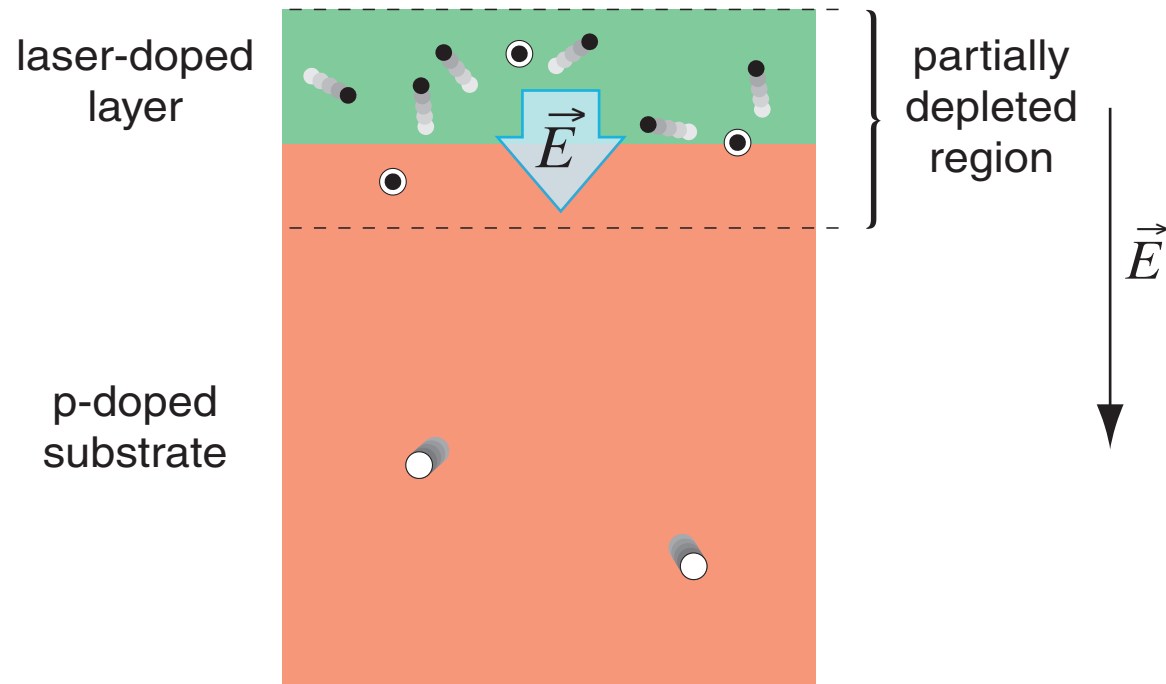
**formation of partially depleted region**

# Devices



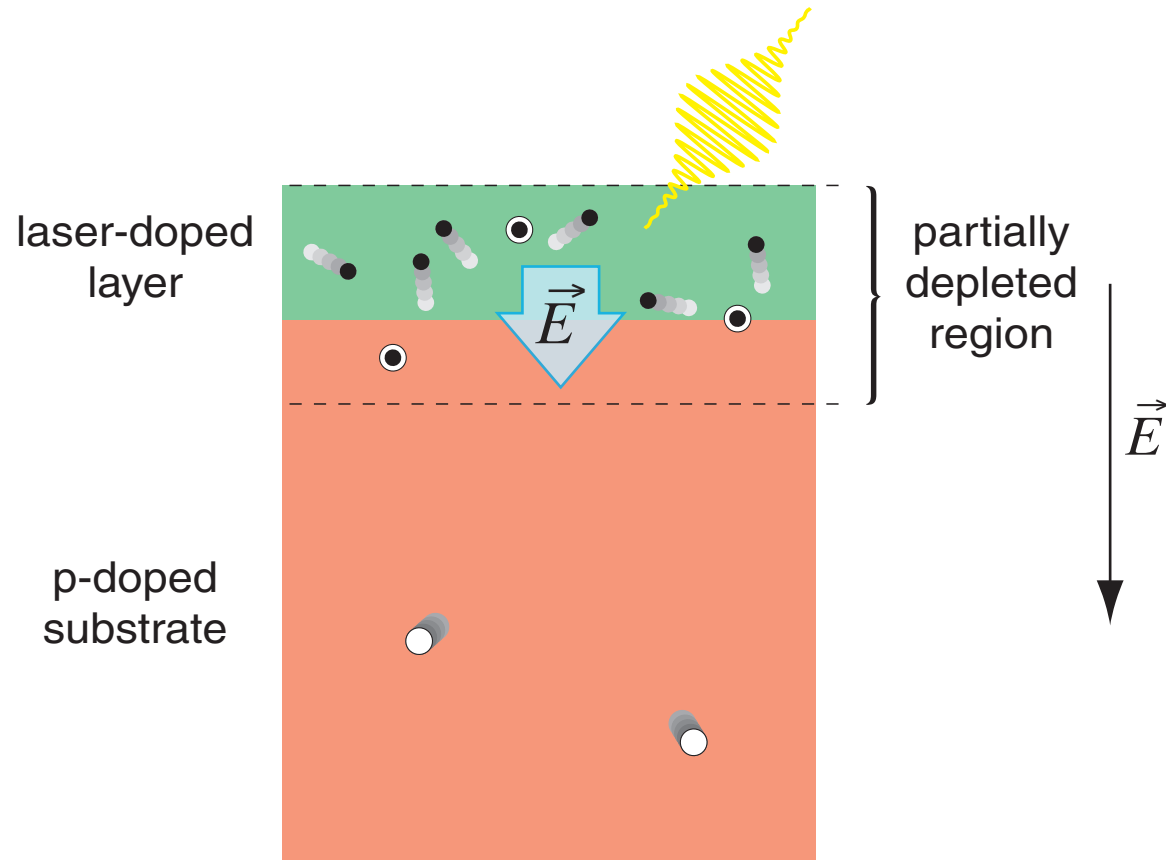
**formation of partially depleted region**

# Devices



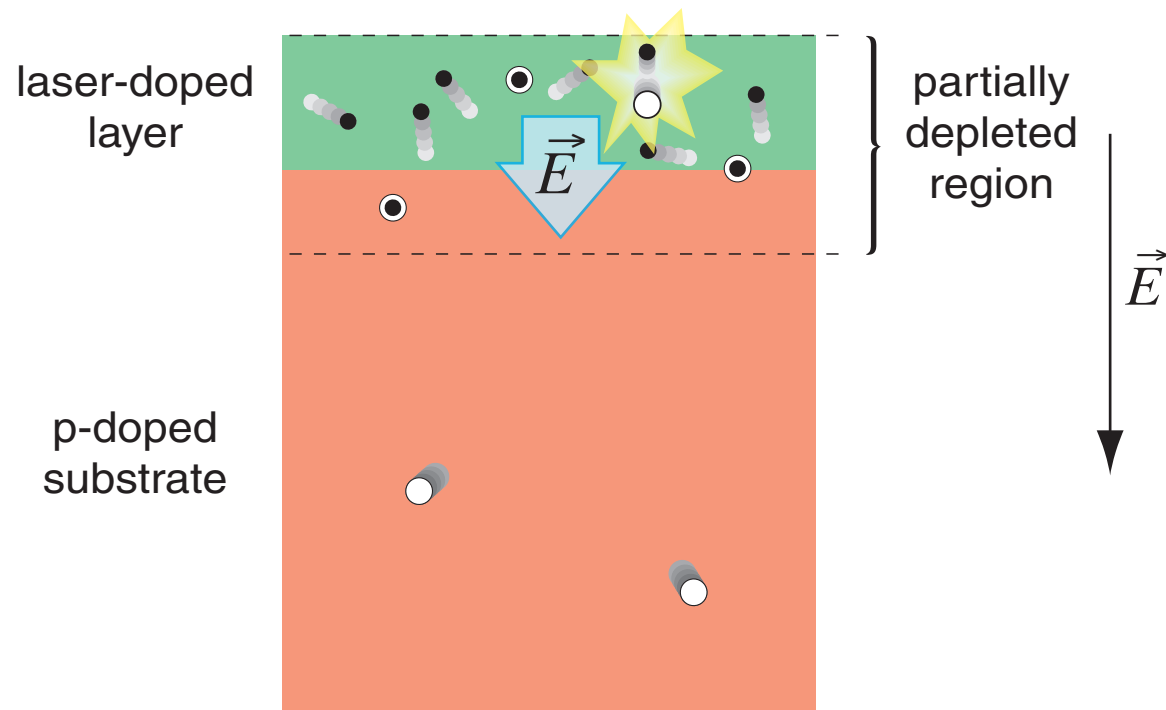
apply backward bias...

# Devices



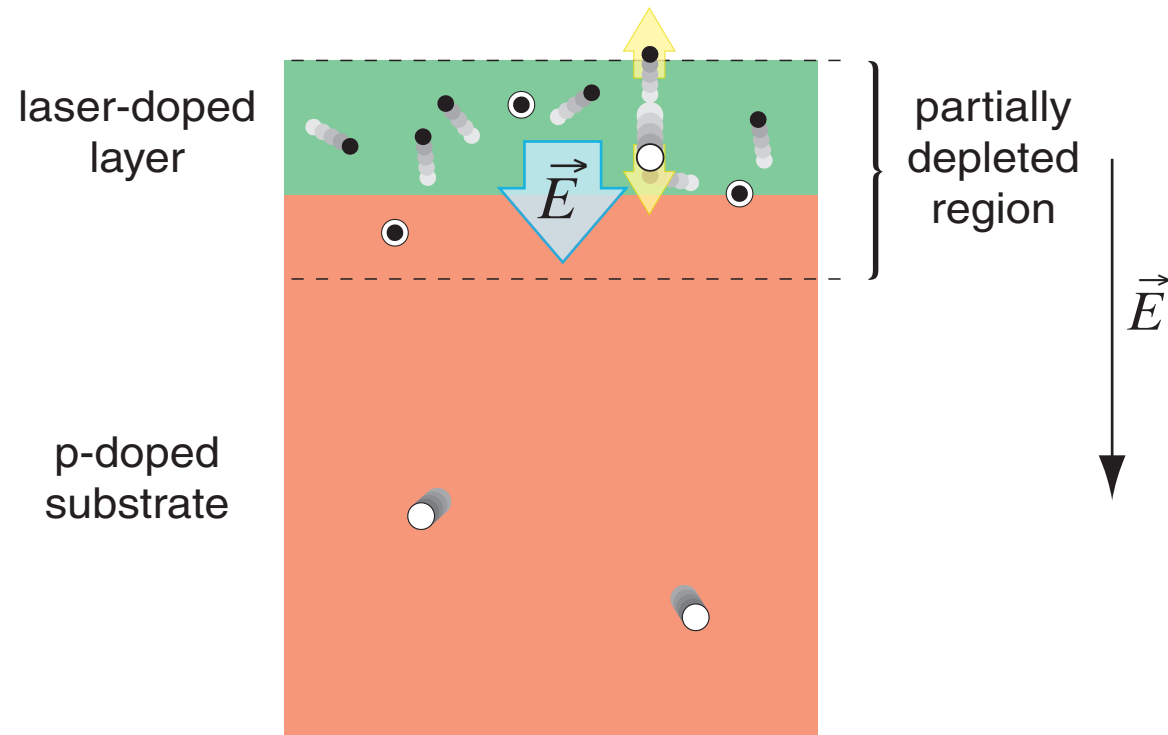
...incident photon generates electron-hole pair...

# Devices



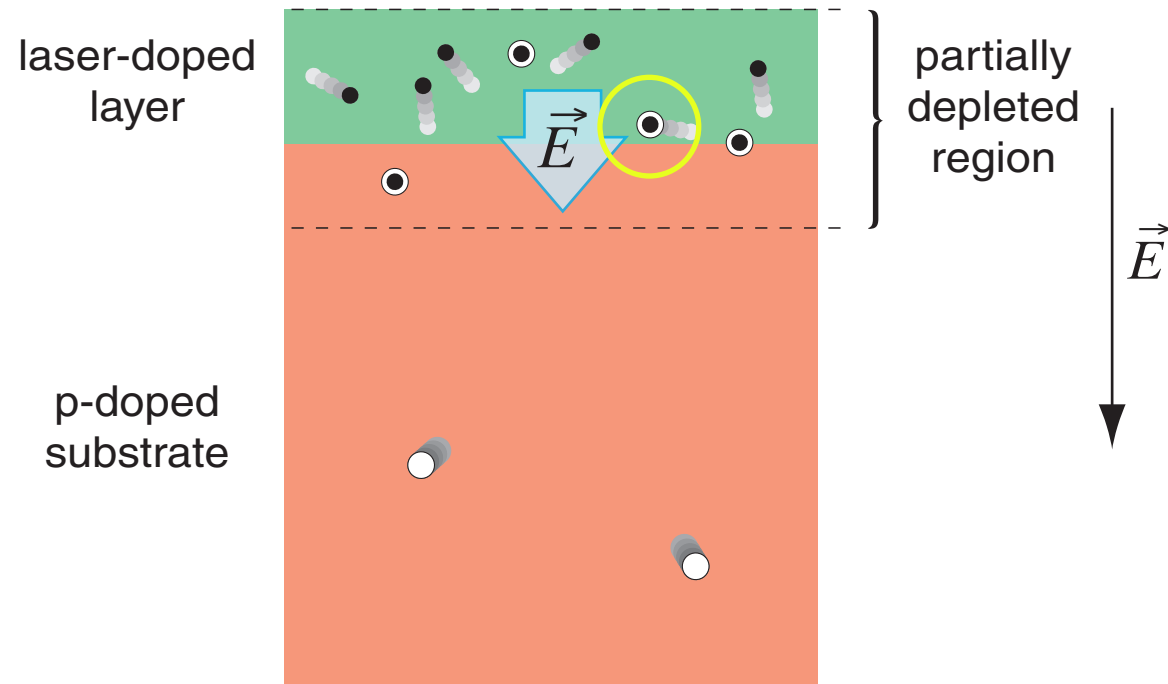
...incident photon generates electron-hole pair...

# Devices



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

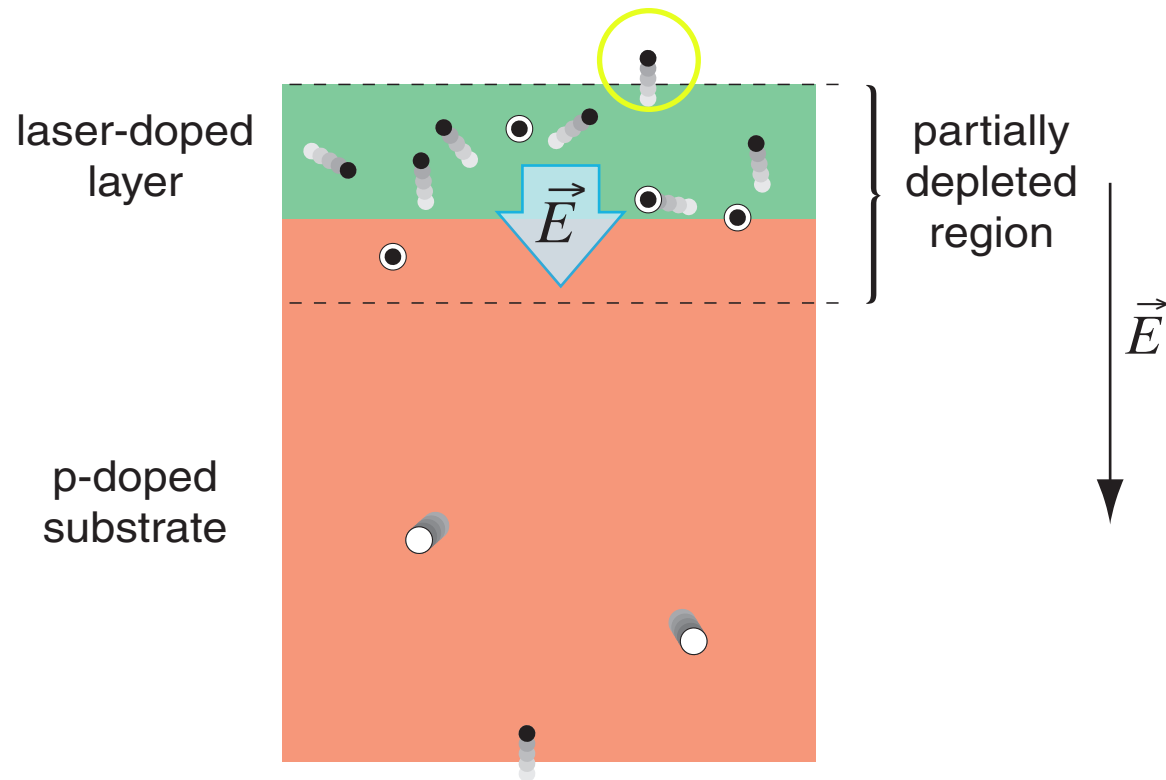
# Devices



**...hole is trapped**

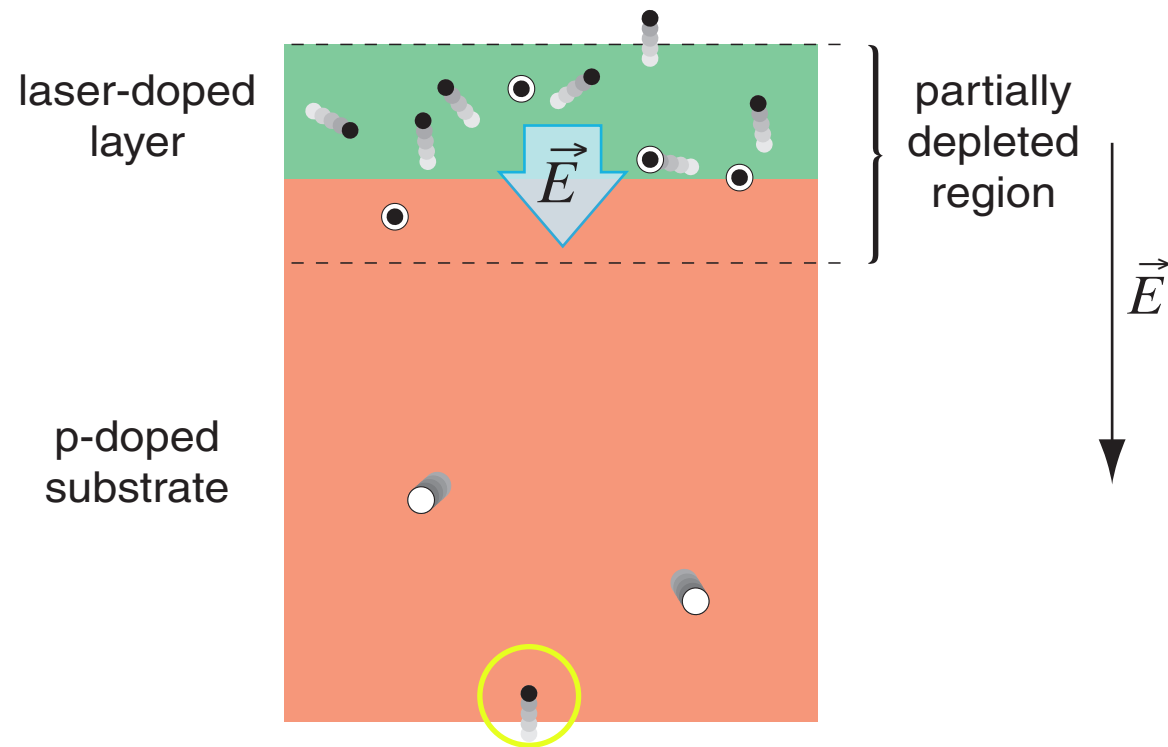


# Devices



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>

# 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. A plain white paper scrap is also visible in the foreground. The background is a light-colored, slightly textured 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:**

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

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