

# Black silicon



École Polytechnique de Montréal  
Montréal, QC, 19 May 2010

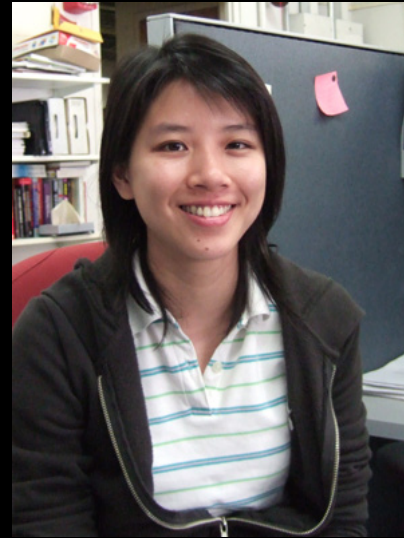




**Mark Winkler**



**Renee Sher**



**Yu-Ting Lin**



**Eric Mazur**

**and also....**

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

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

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

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

**Prof. Augustinus Asenbaum (Vienna)**

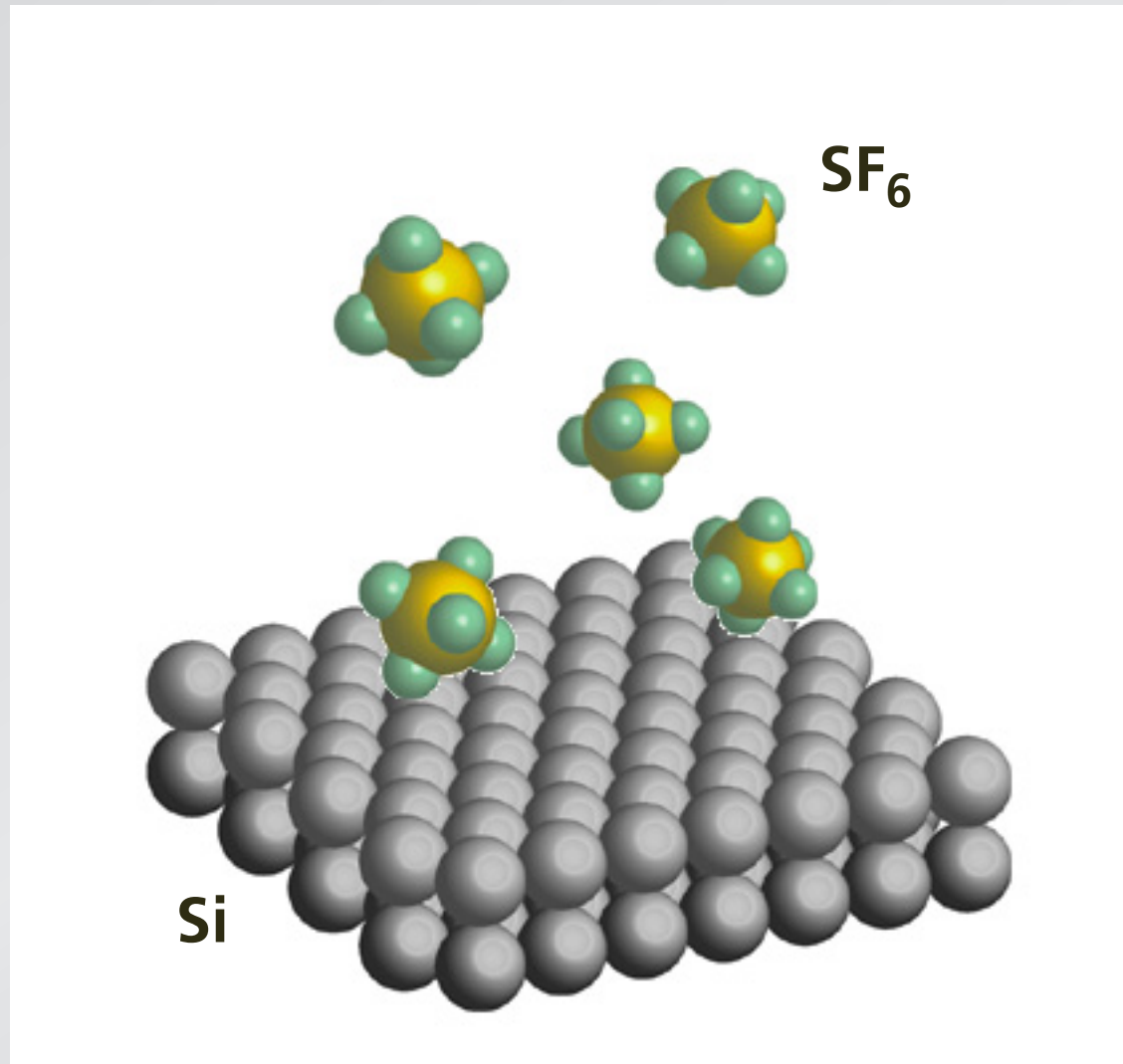
**Dr. François Génin (LLNL)  
Mark Wall (LLNL)**

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

**Dr. Pat Maloney (NVSED)**

**Dr. Jeffrey Warrander (ARDEC)**

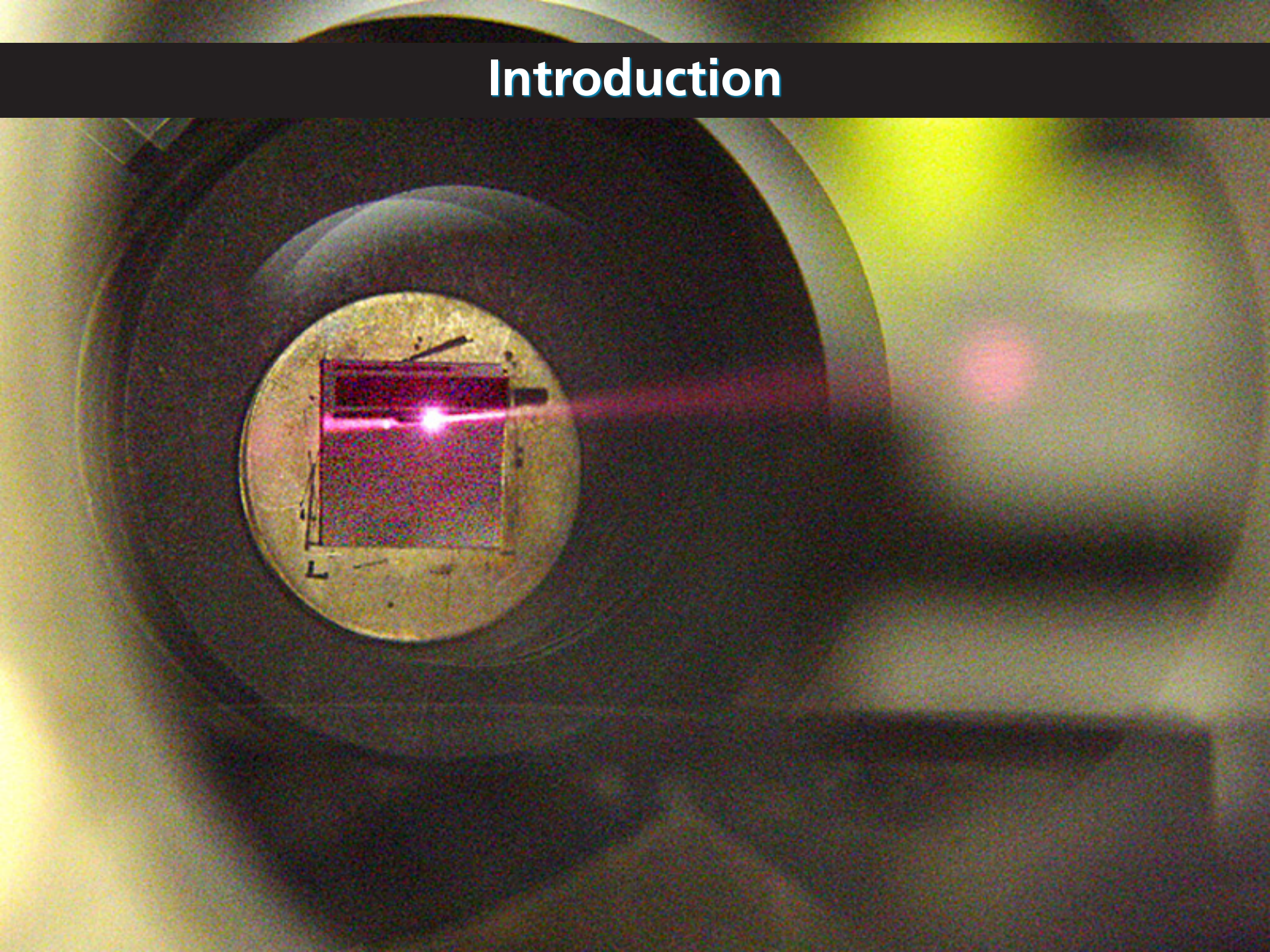
# Introduction



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



# Introduction



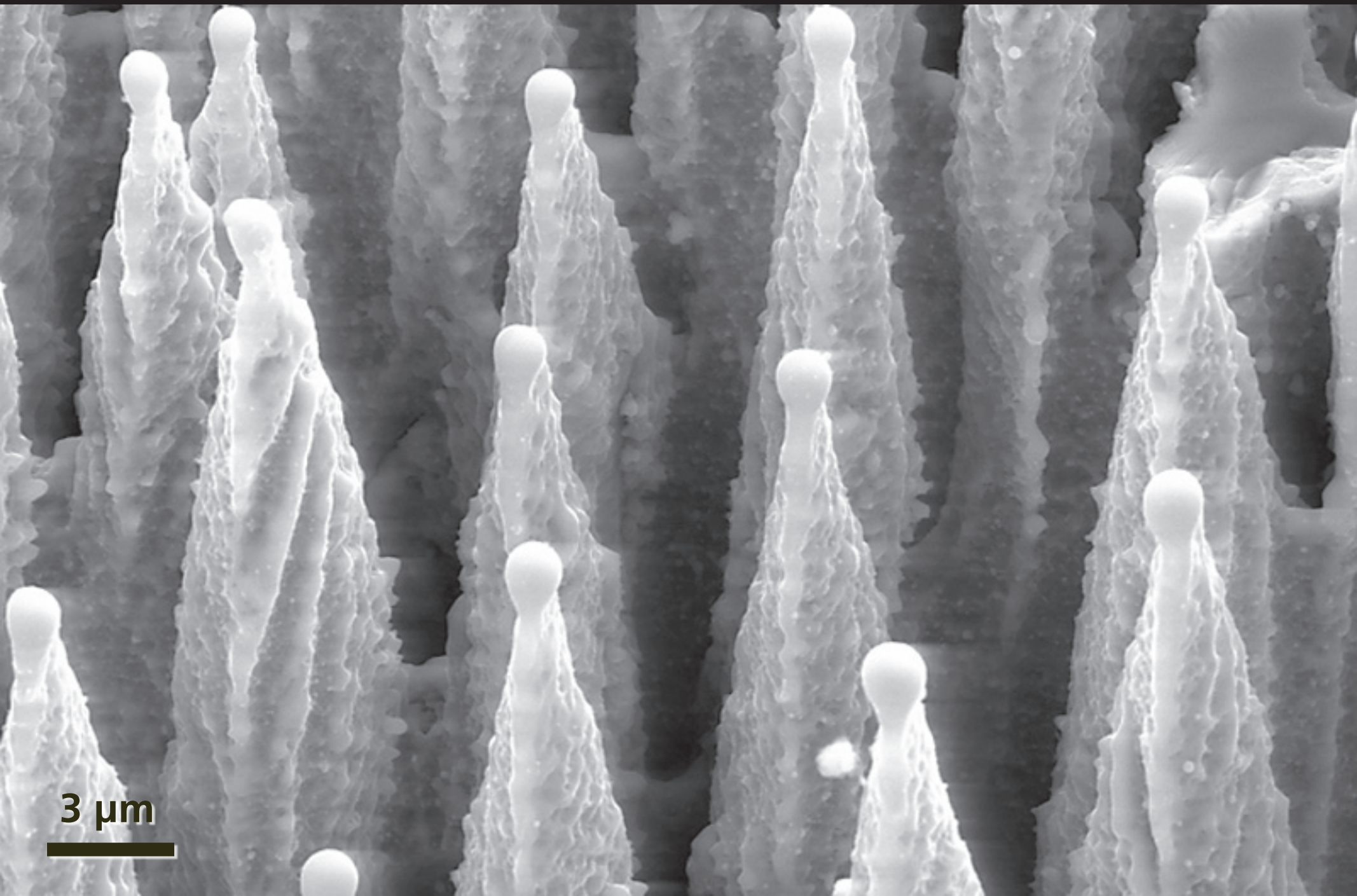


# Introduction



**"black silicon"**

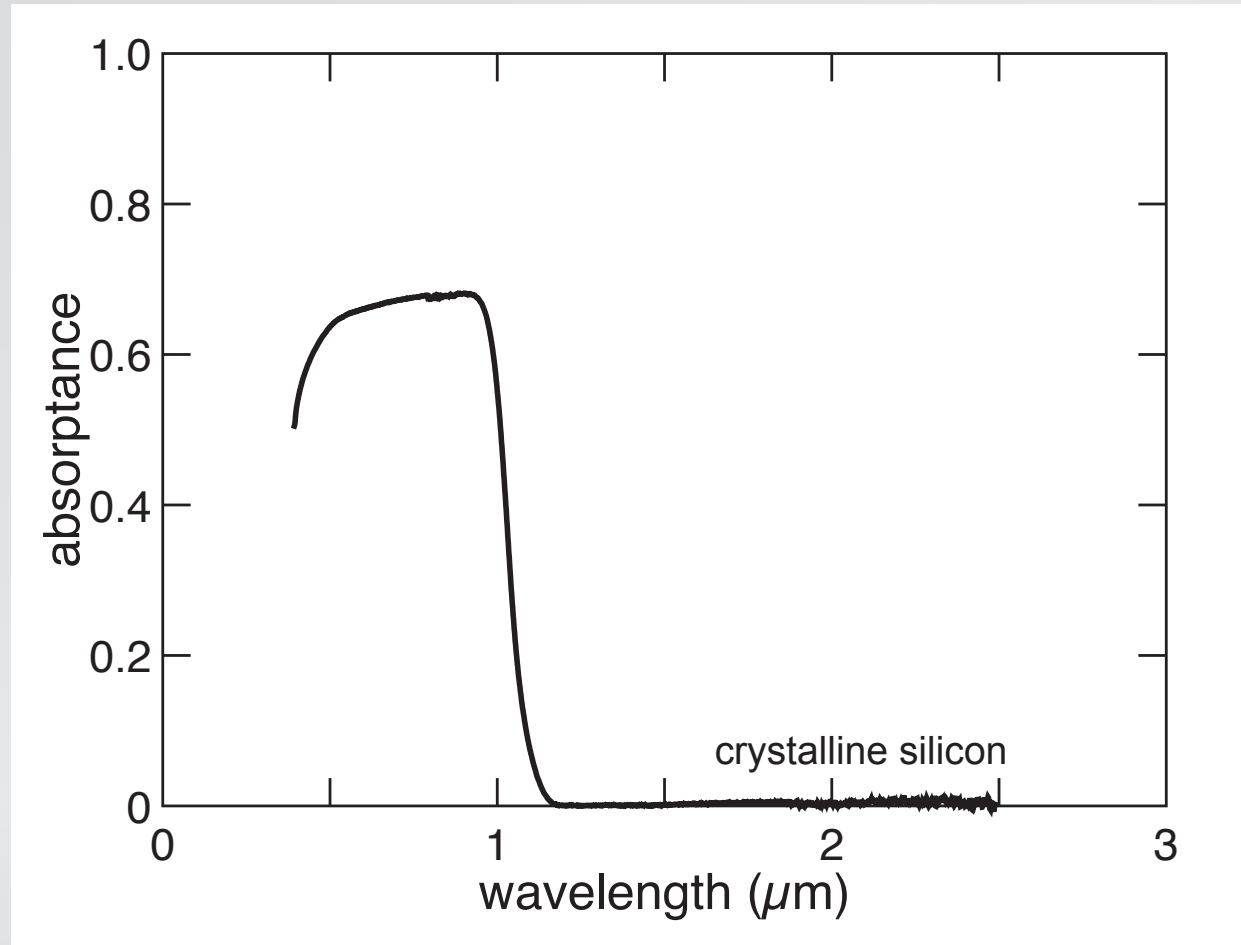
# Introduction



3  $\mu\text{m}$

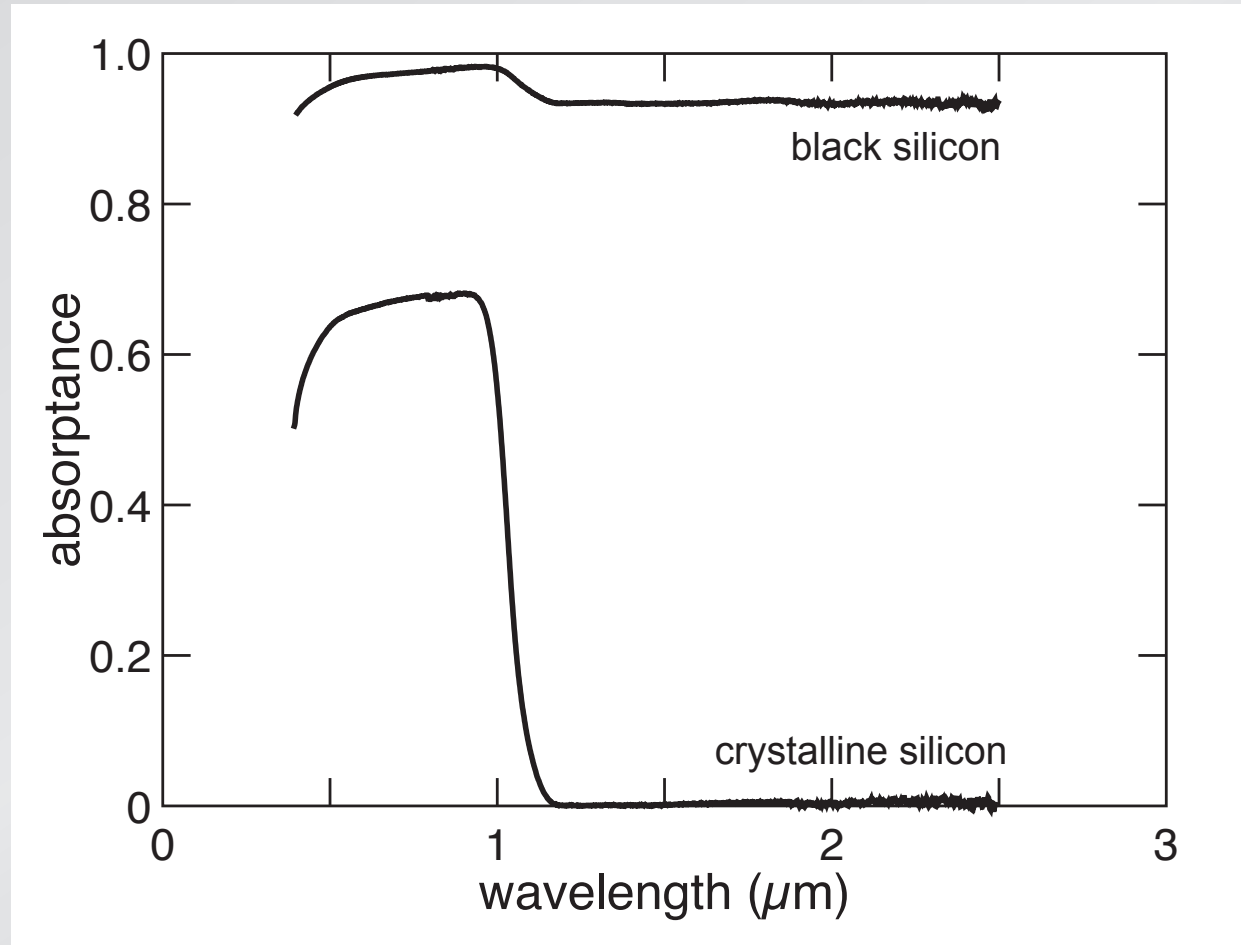
# Introduction

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



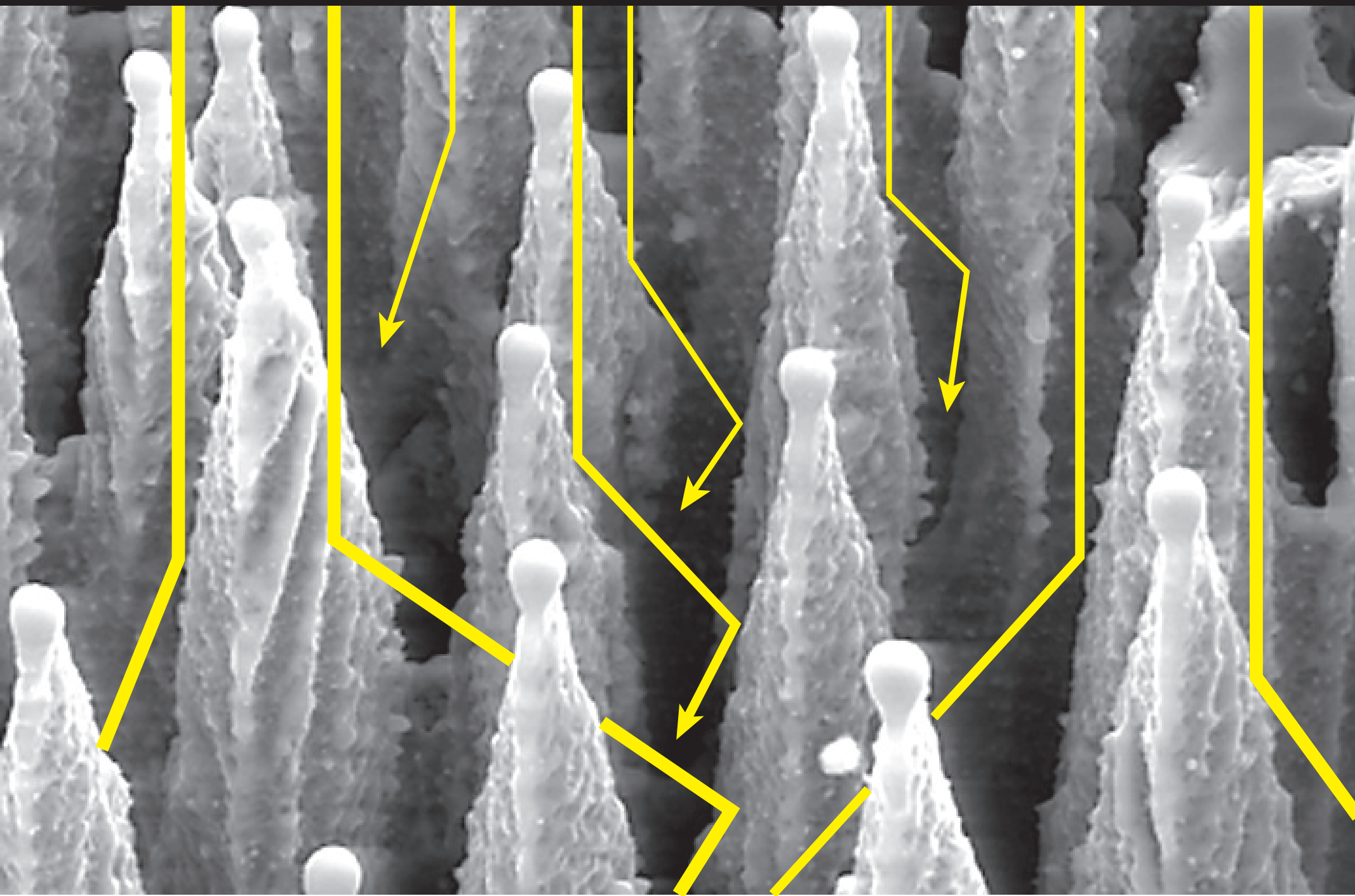
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absorptance ( $1 - R_{int} - T_{int}$ )





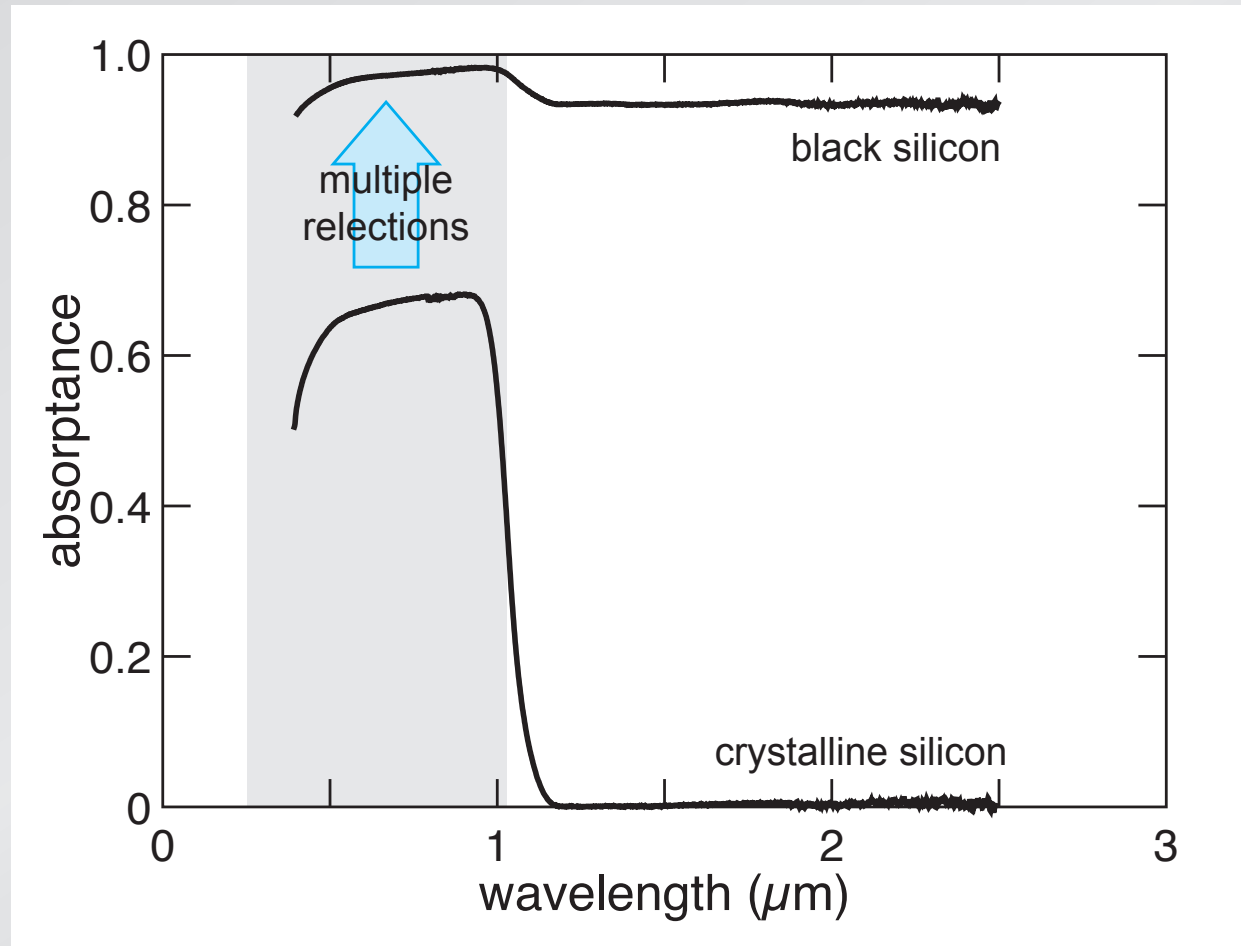
# Introduction





# Introduction

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



# Introduction

silicon transparent in near IR

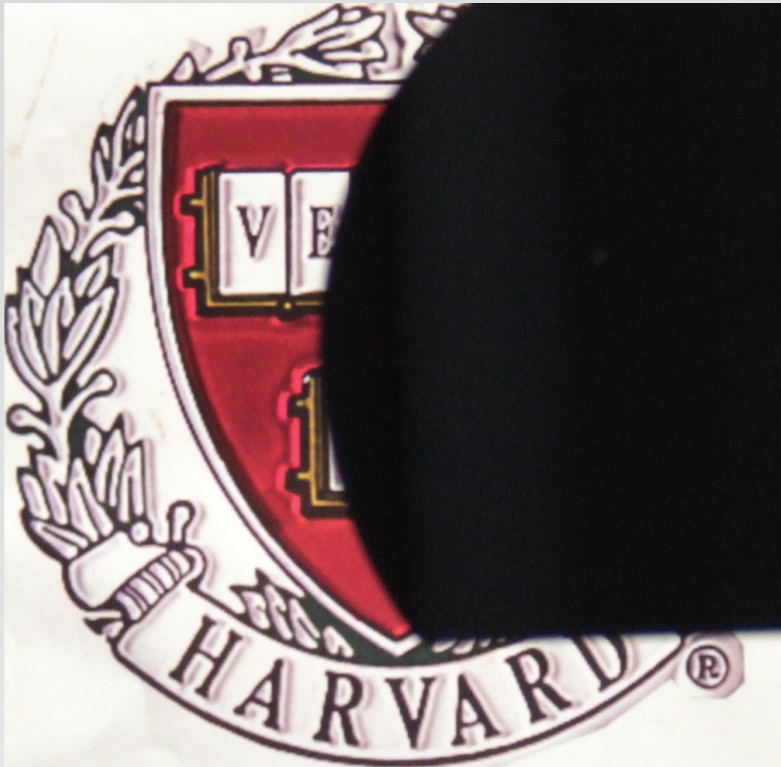
visible



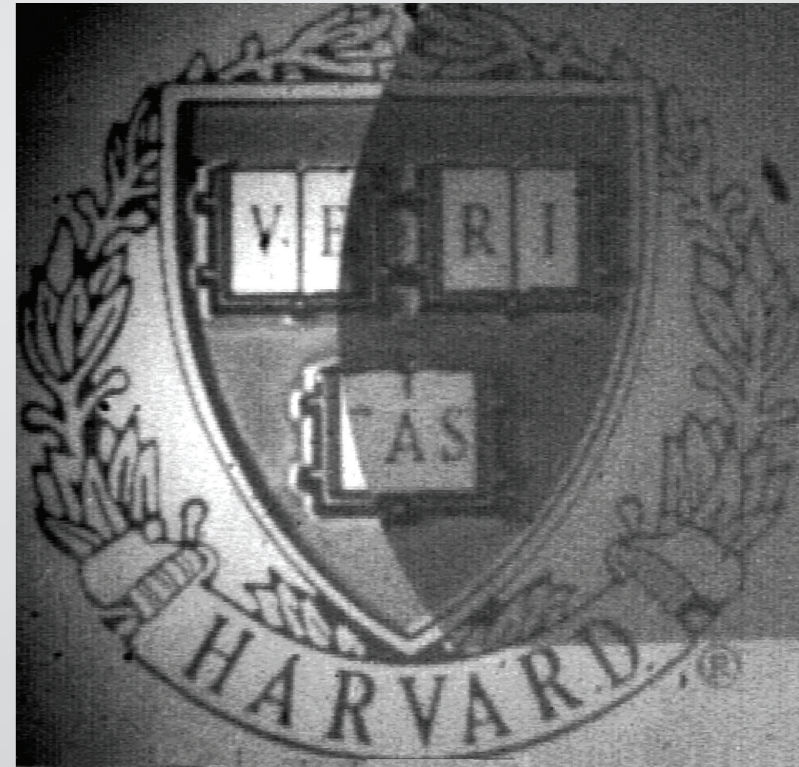
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silicon transparent in near IR

visible



near IR

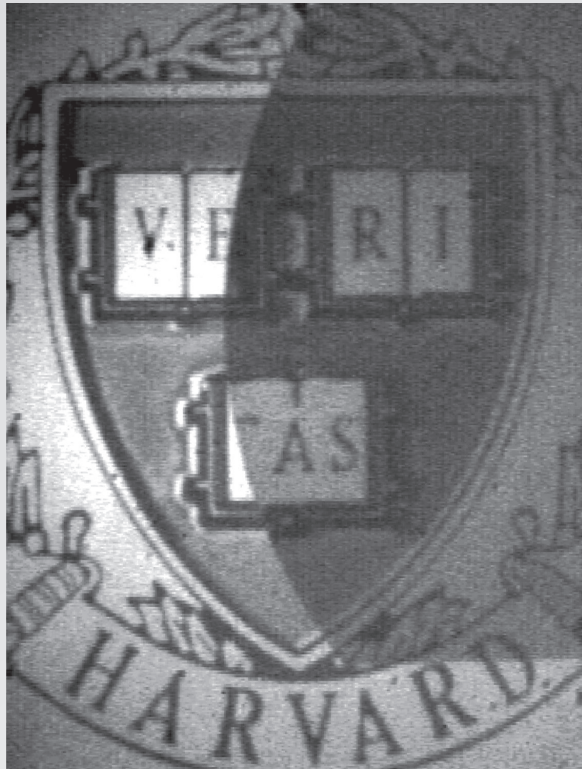




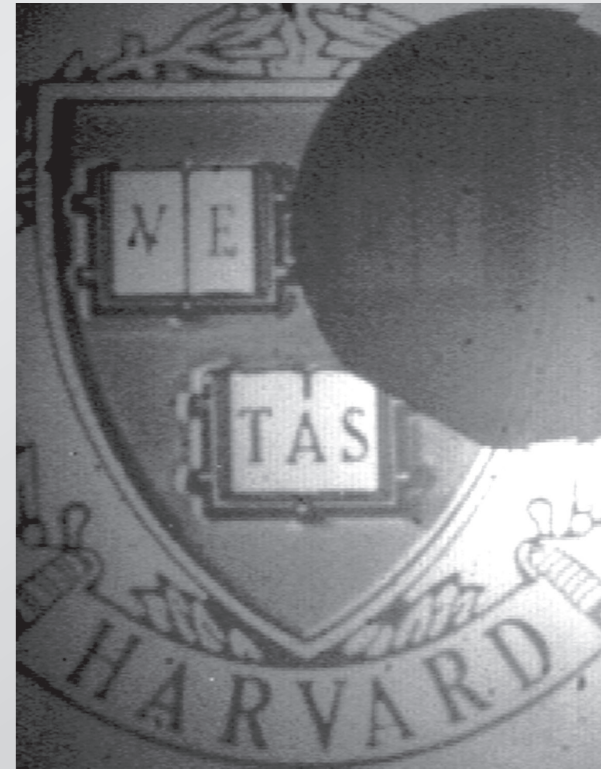
# Introduction

roughening doesn't change IR transmission...

polished



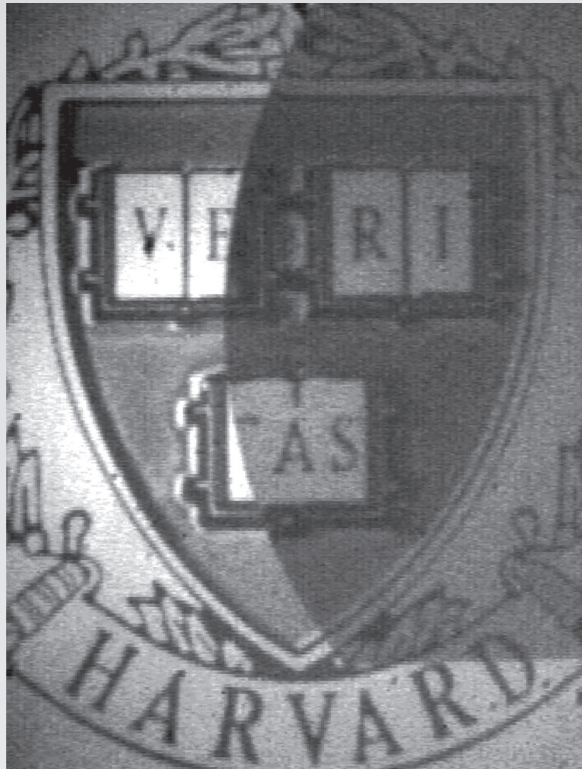
unpolished



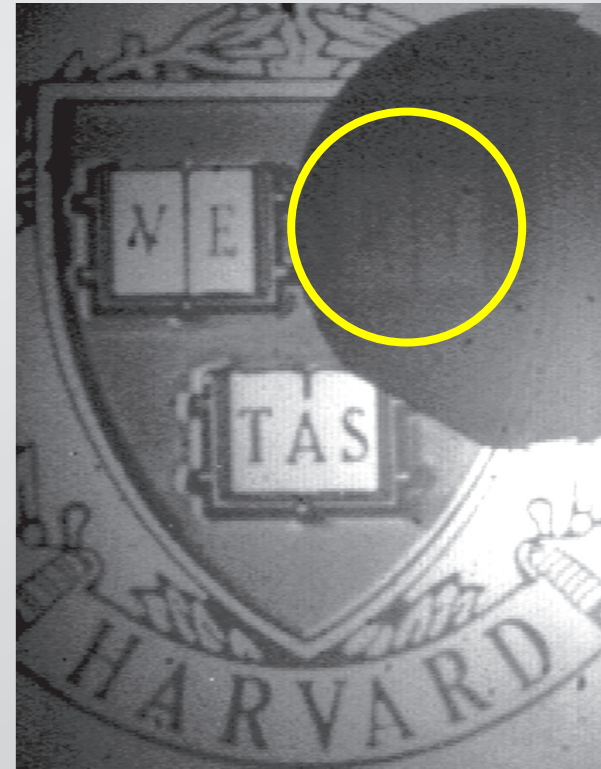
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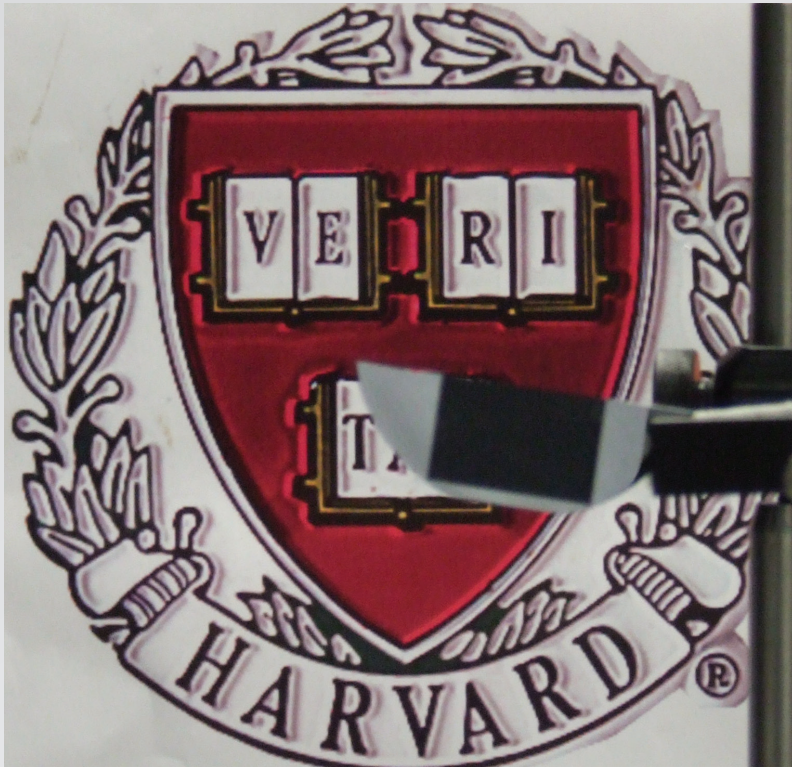




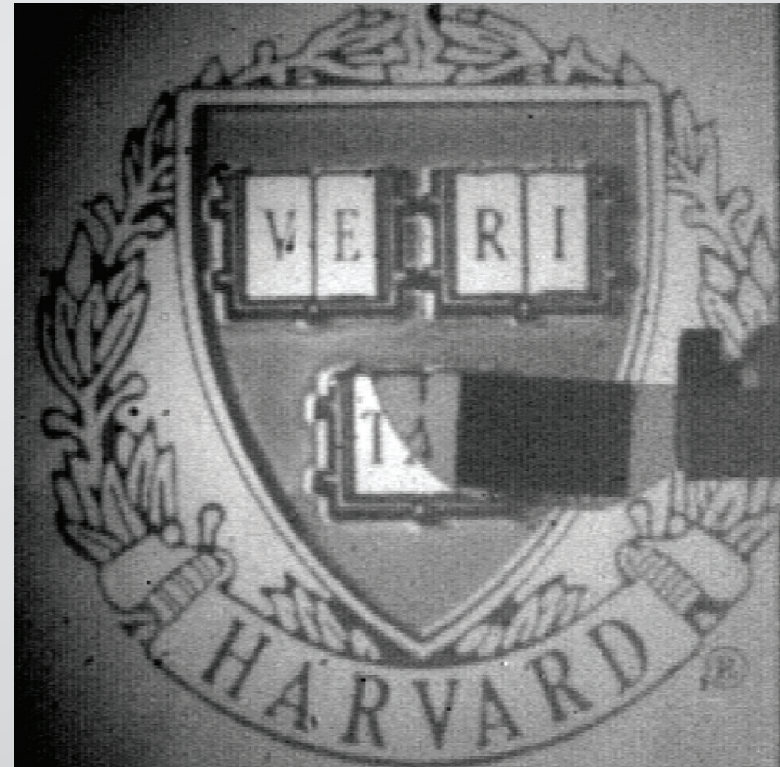
# Introduction

...but black silicon blocks IR completely

visible



near IR

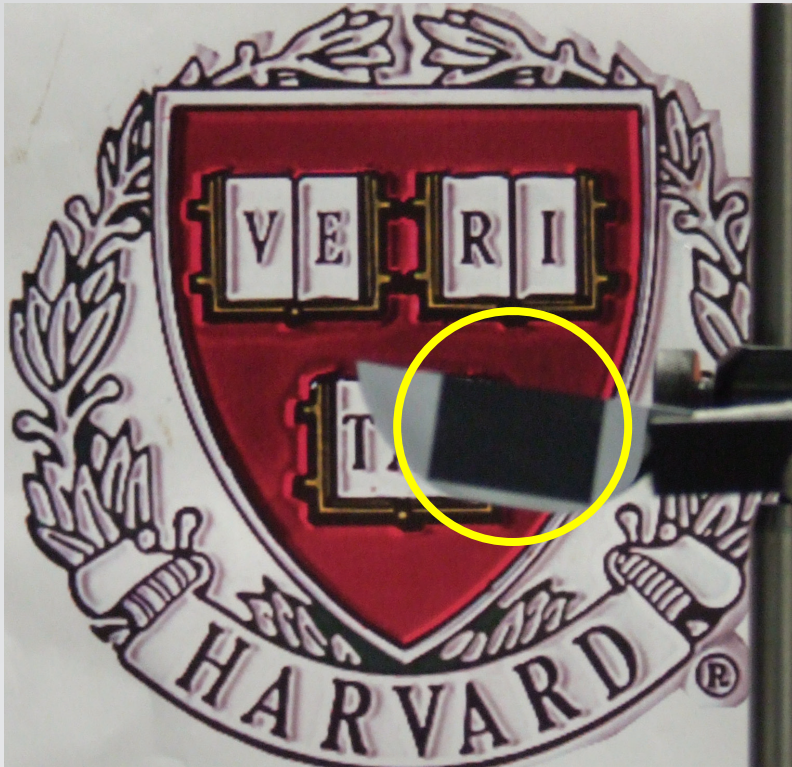




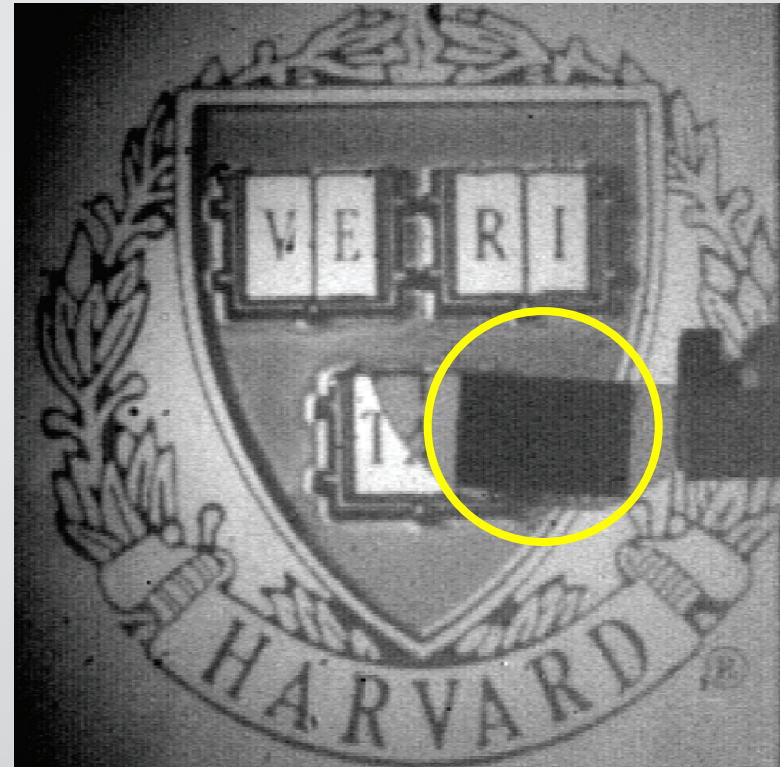
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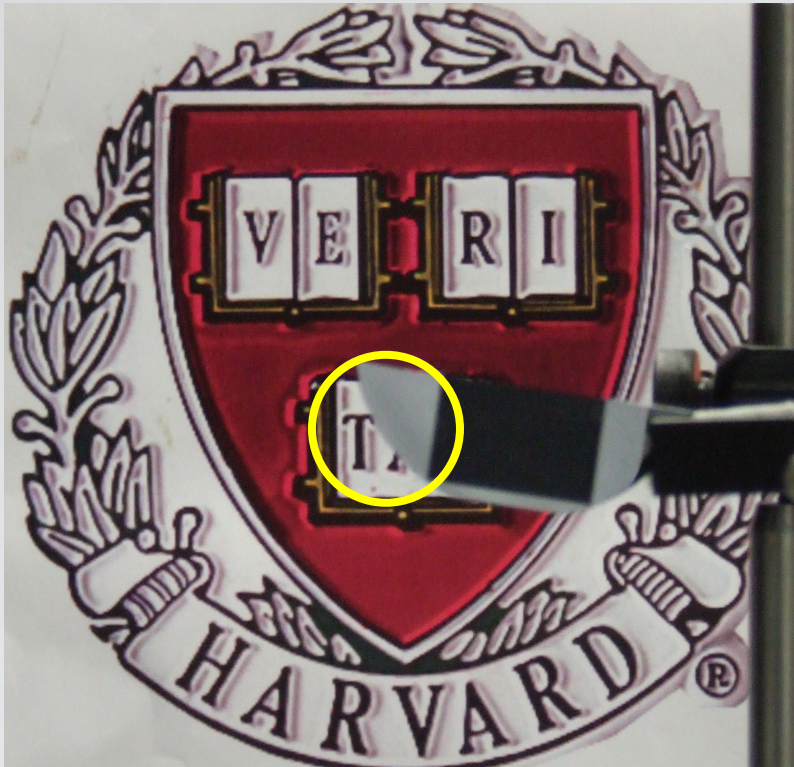
near IR



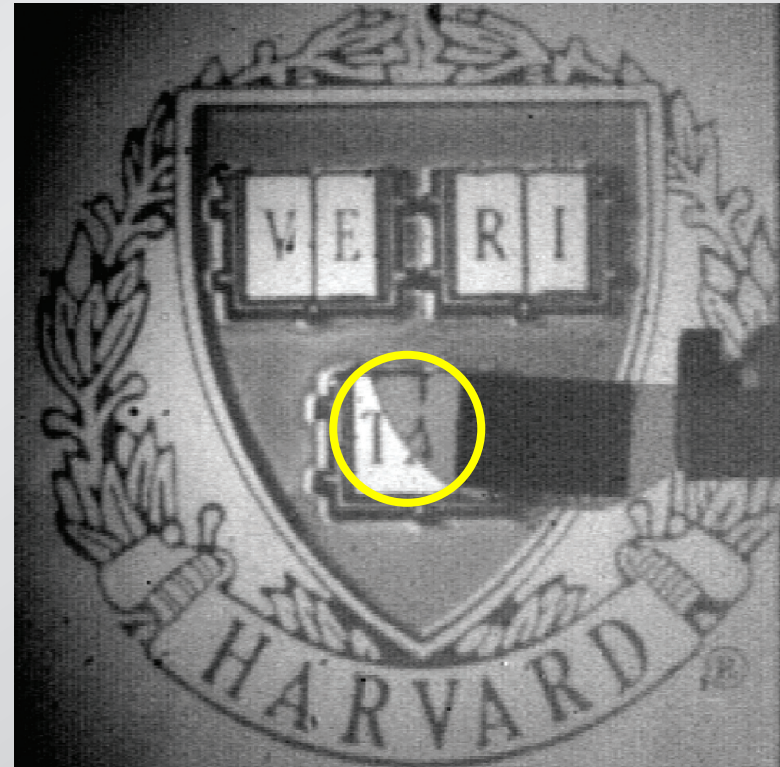
# Introduction

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

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## a decade of research

### OPTICAL

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gap  
impurity band  
transitions

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## 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
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	responsivity	SIMS
	photoconductivity	RBS
		ion channeling
gap	carrier concentration	
impurity band	mobilities	
transitions	junction properties	



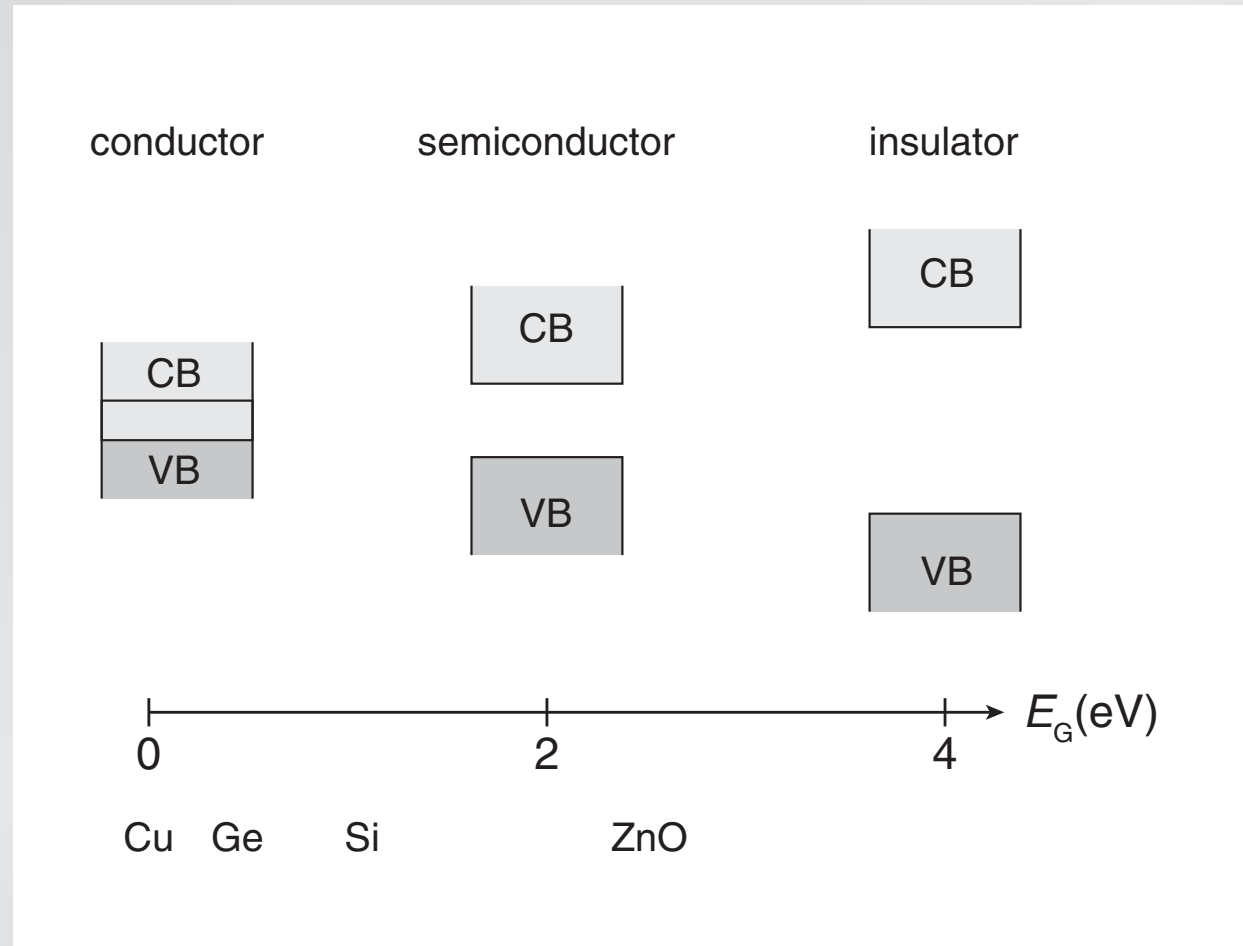
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UV-VIS-NIR	Hall measurements	SEM
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UPS		EXAFS
XPS		AFM
	responsivity	SIMS
	photoconductivity	RBS
		ion channeling
gap	carrier concentration	morphology
impurity band	mobilities	composition
transitions	junction properties	atomic structure

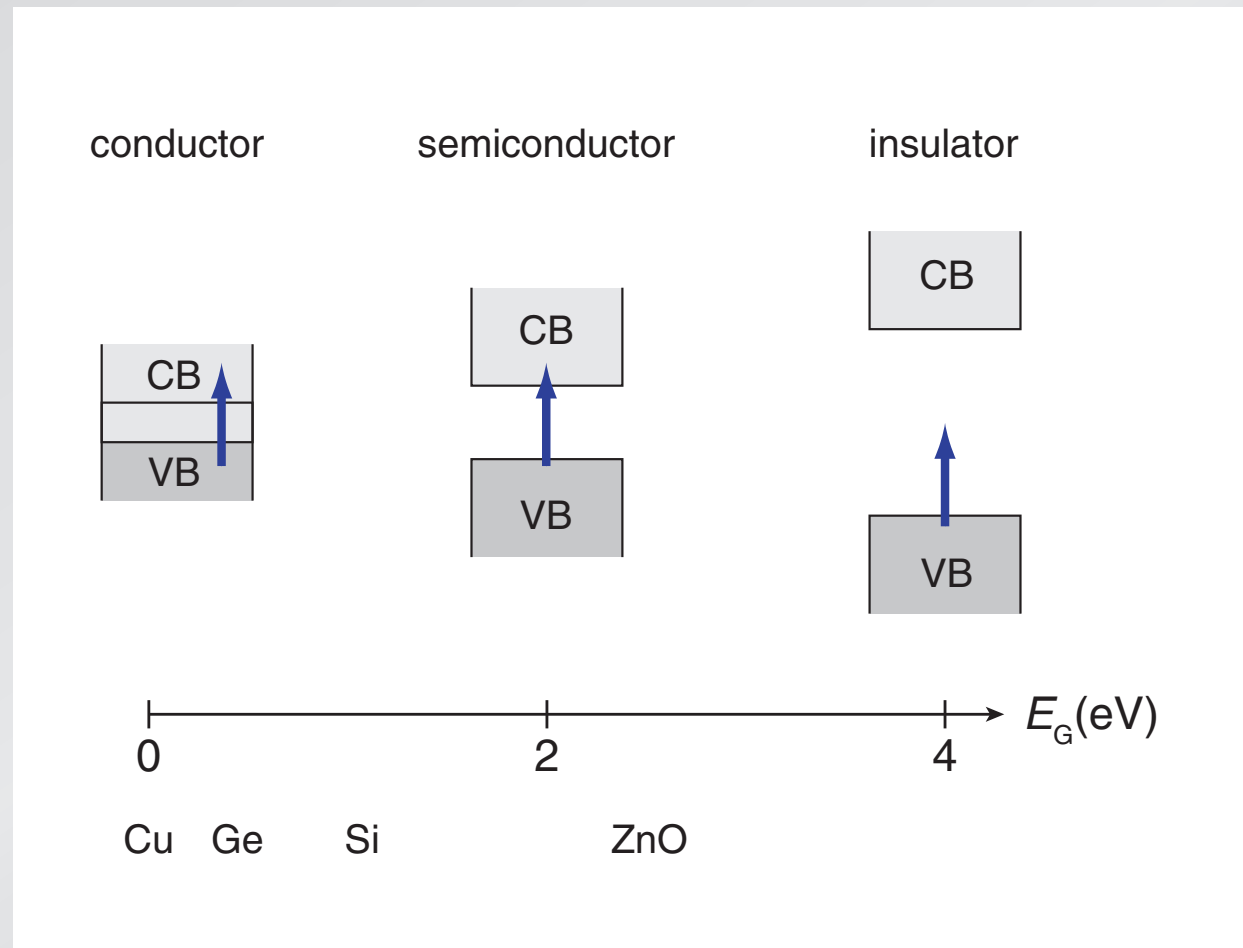
# Introduction

new process & new class of material!



# Introduction

**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:

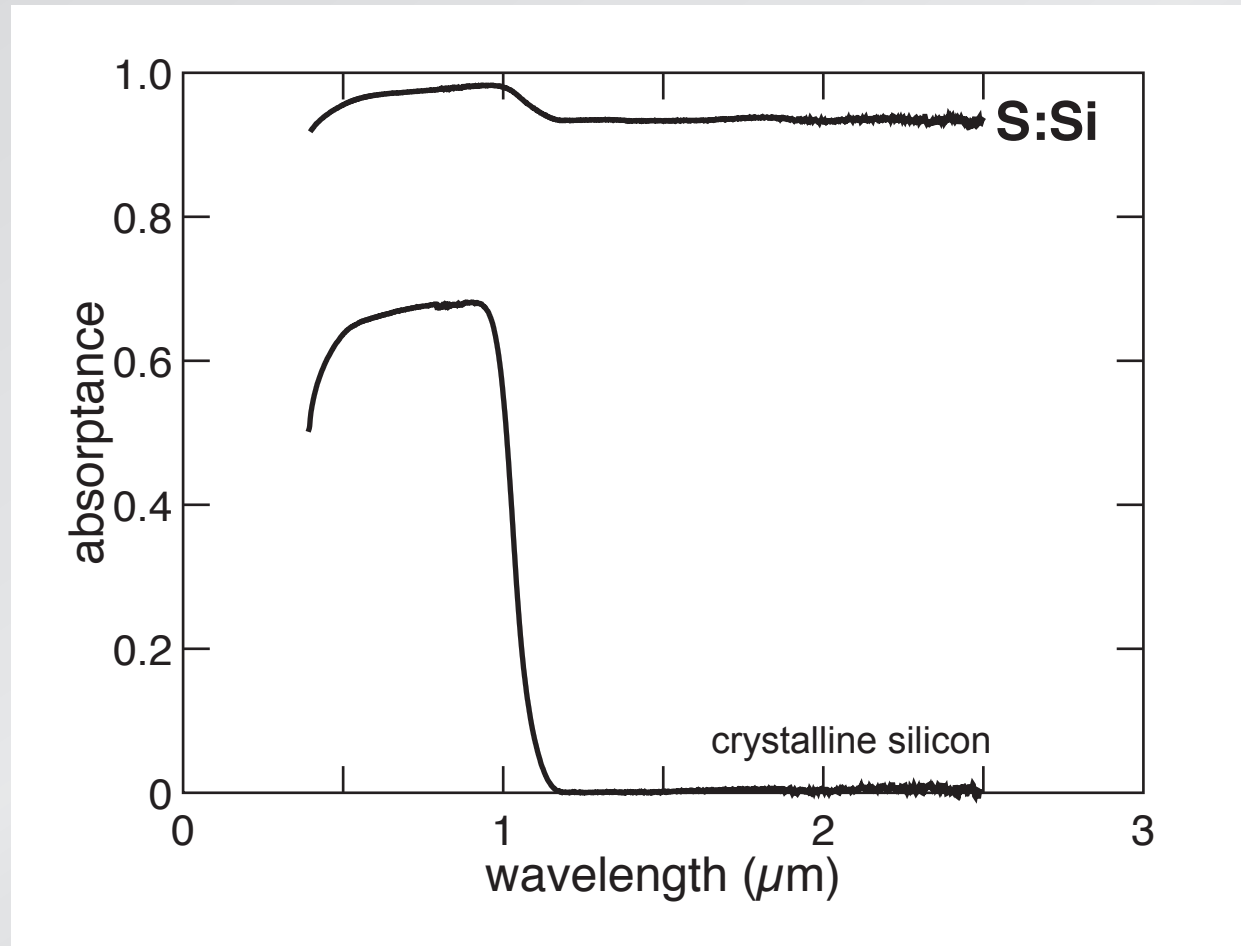
Si Ge ZnO InP GaAs

Ti Ag Al Cu Pd Rh Ta Pt



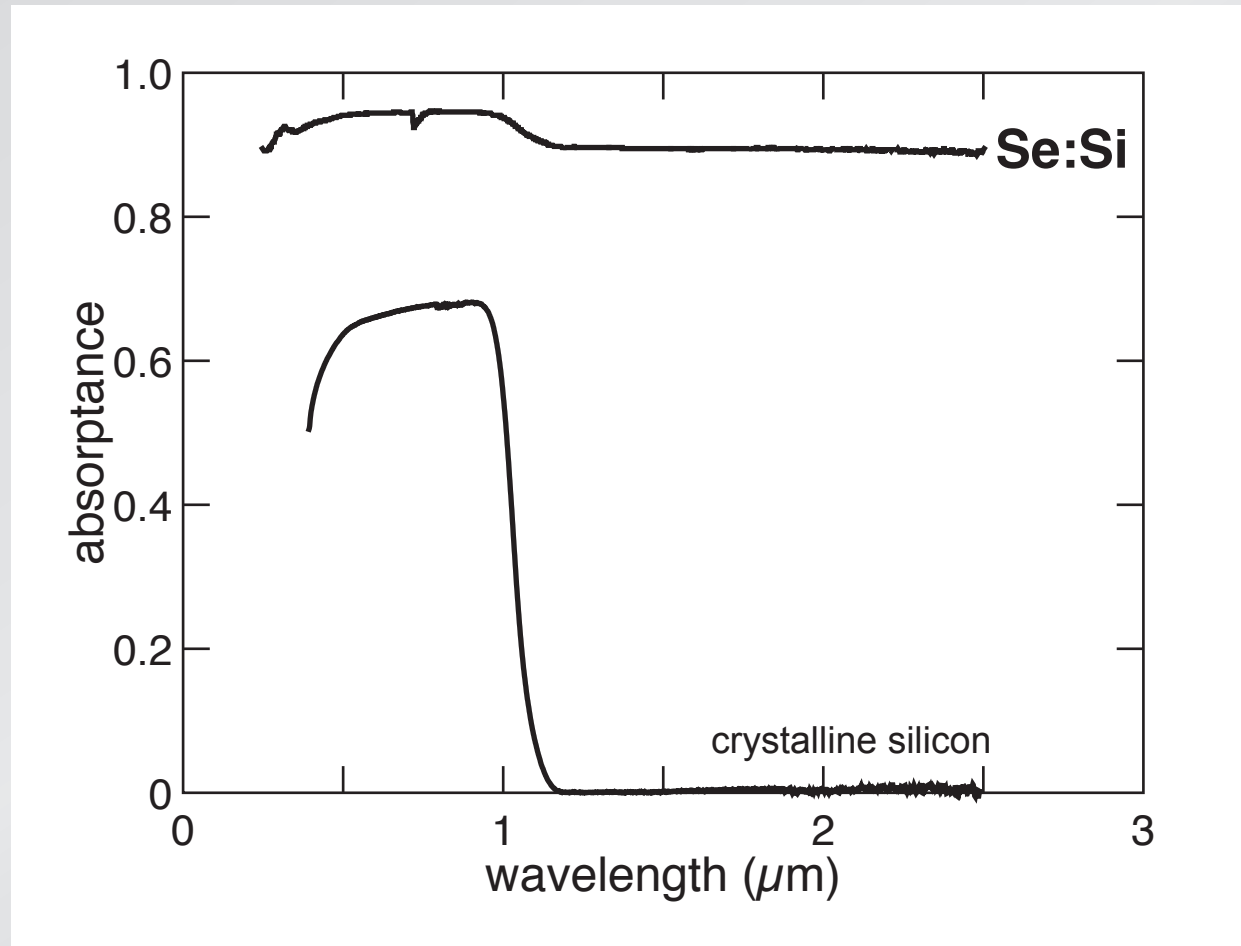
# Introduction

focus on chalcogen-doped silicon



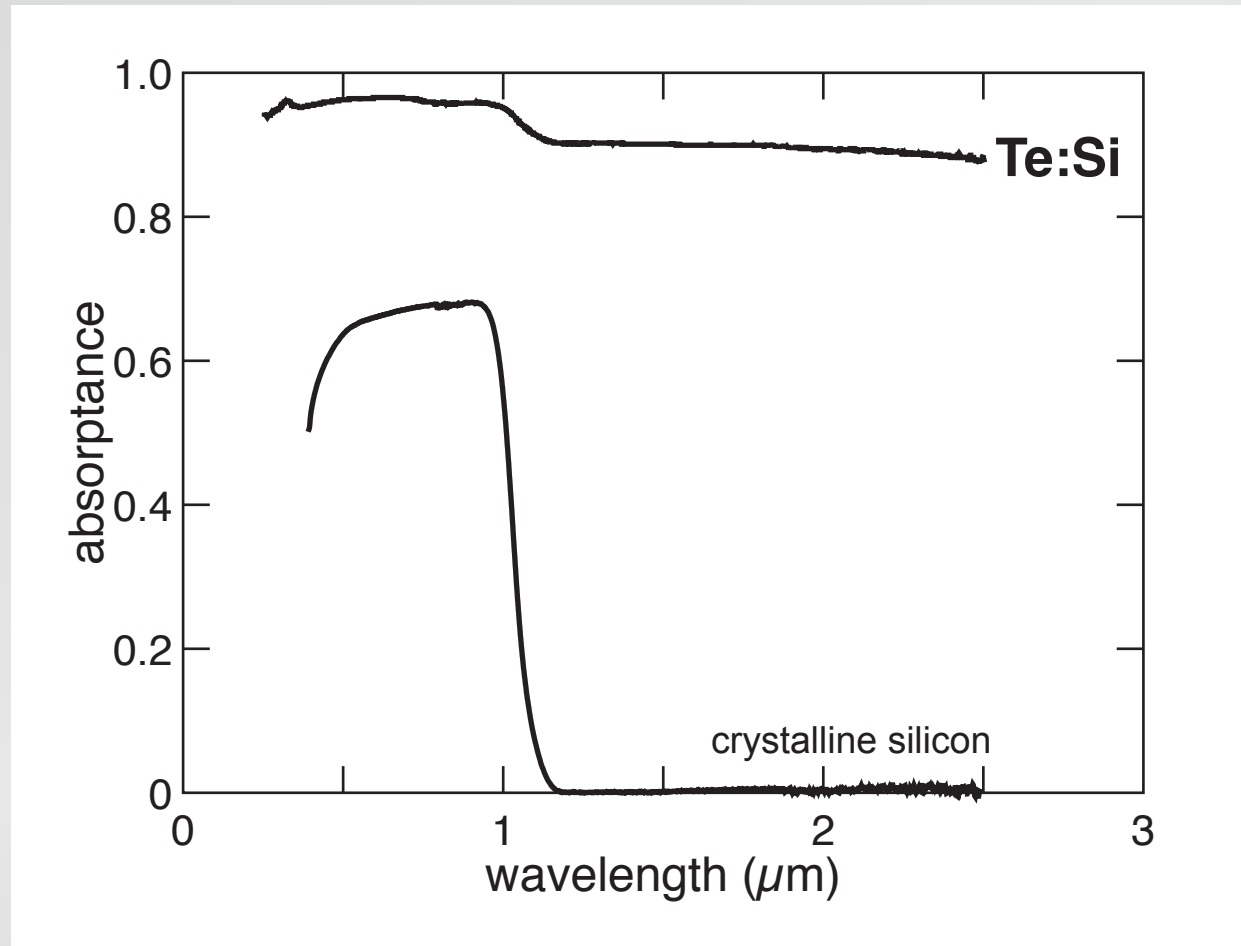
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focus on chalcogen-doped silicon



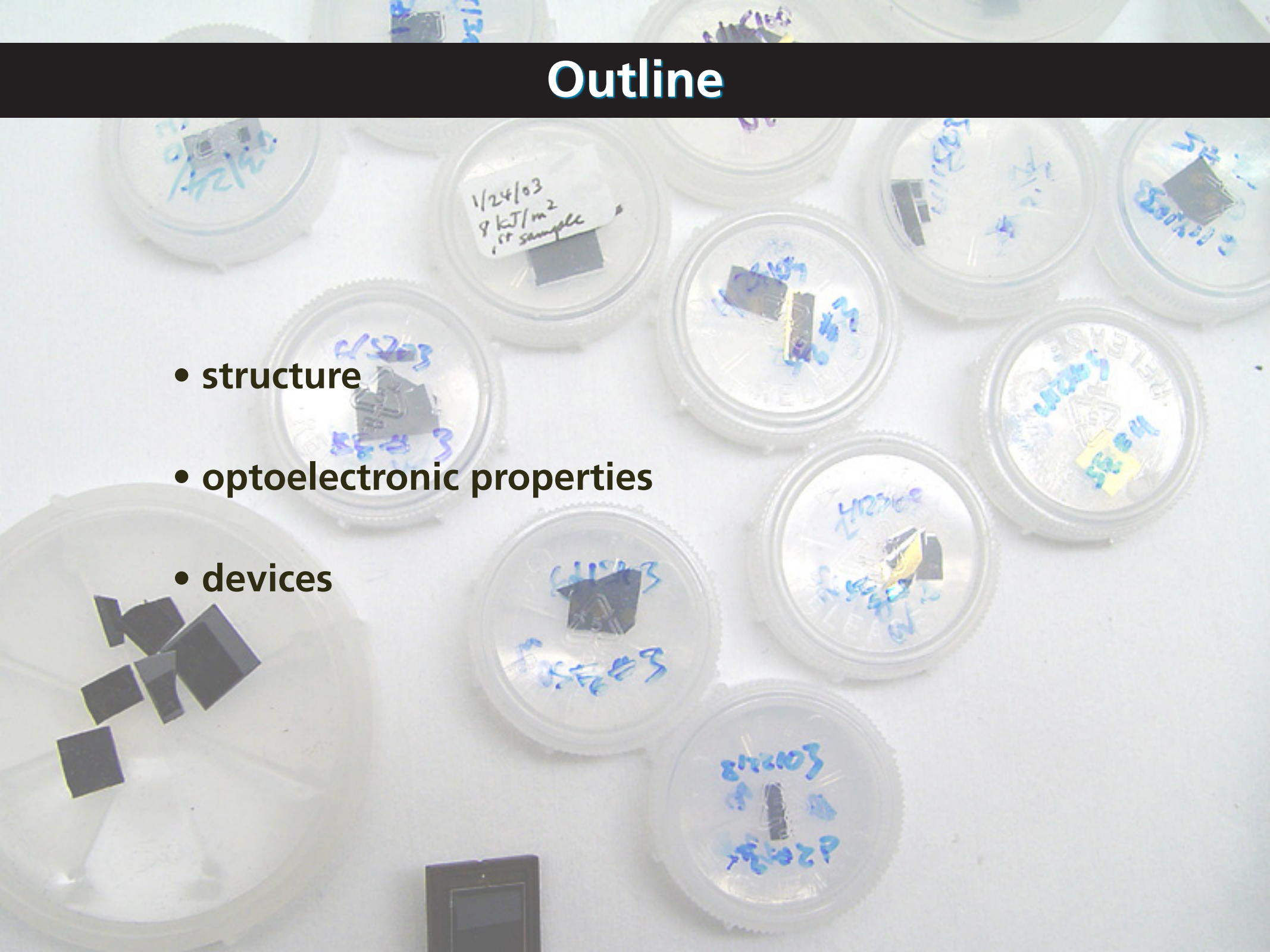
# Introduction

focus on chalcogen-doped silicon



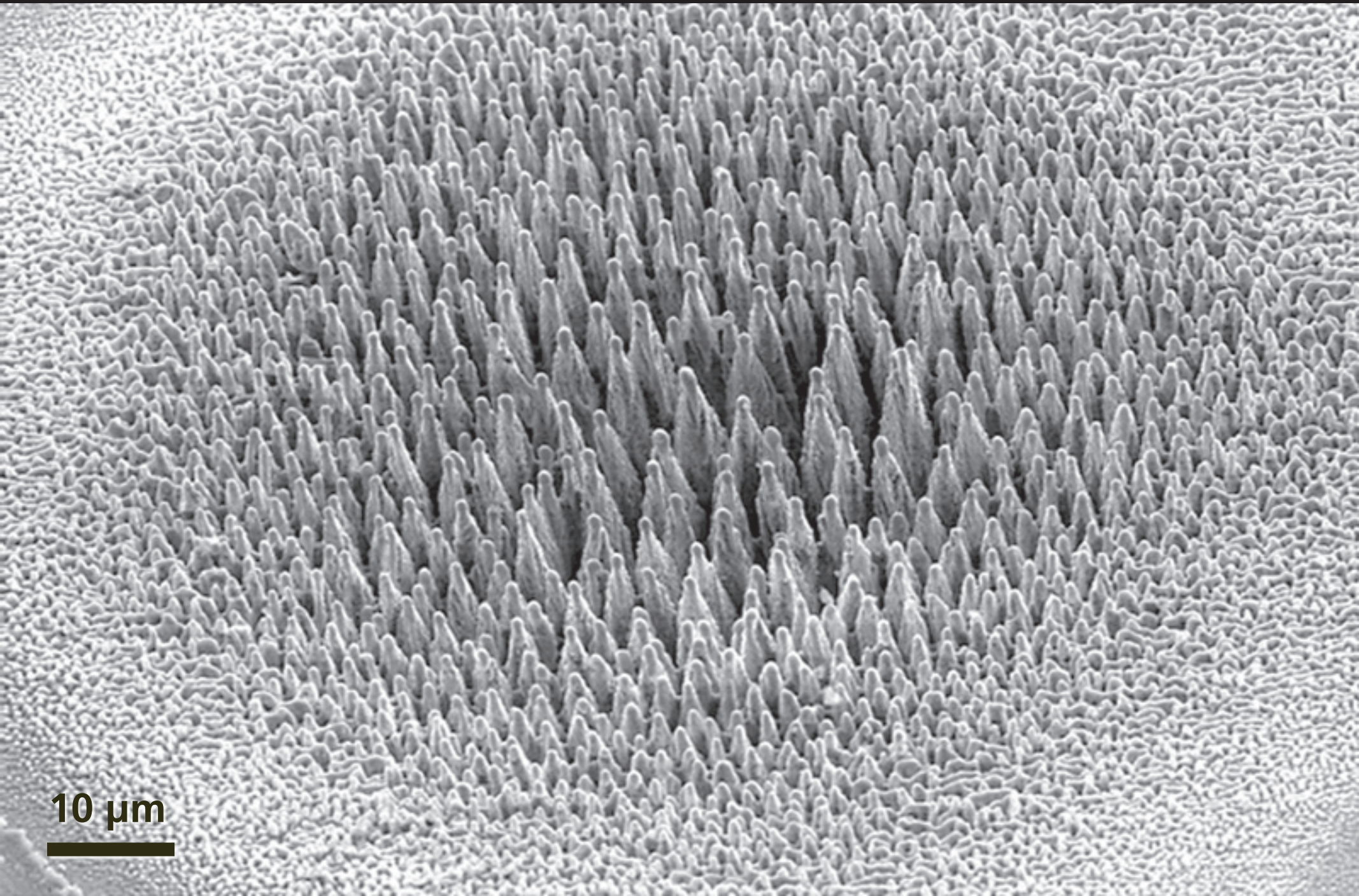
# Outline

- structure
- optoelectronic properties
- devices





# Structure

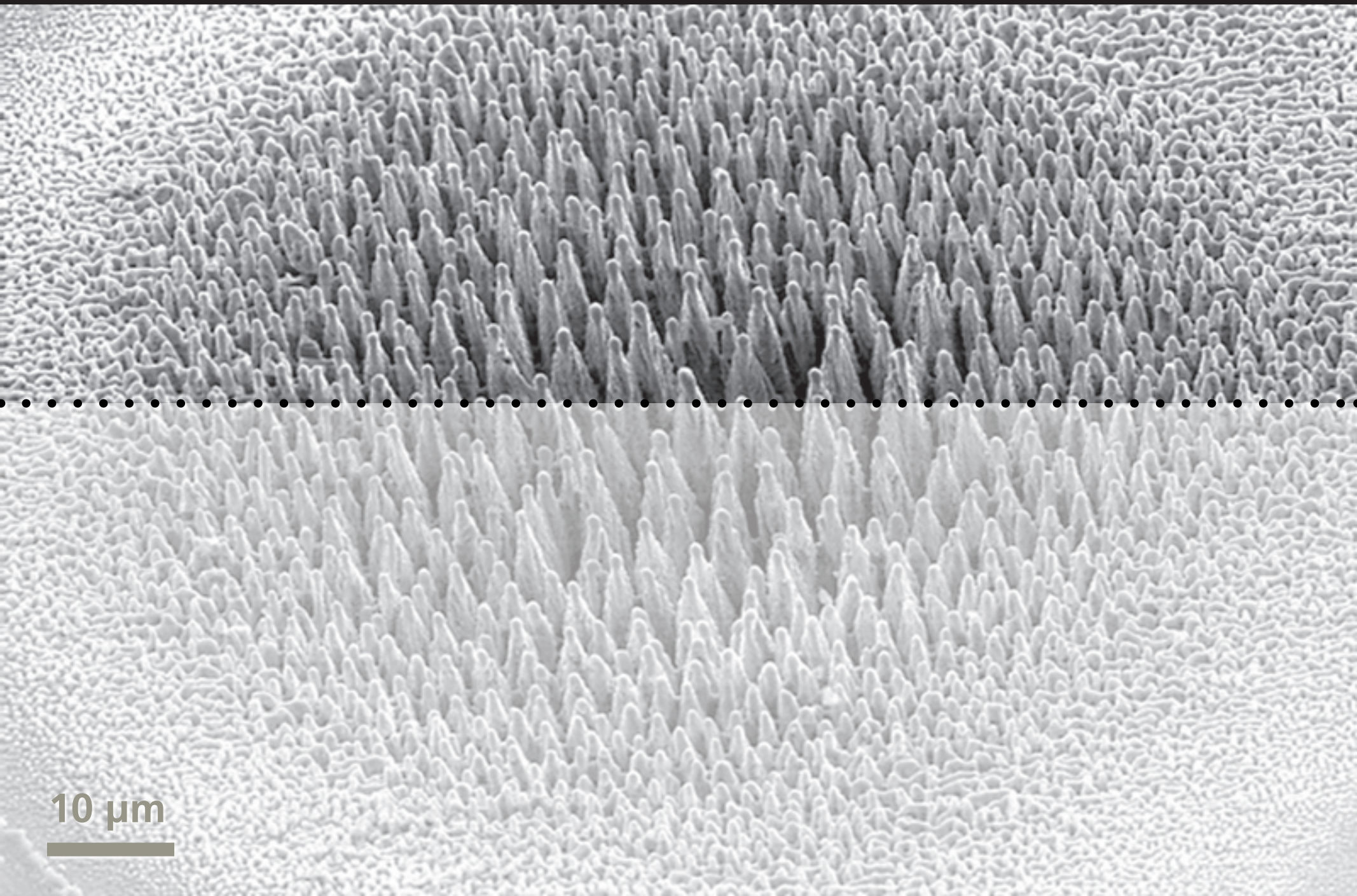


10  $\mu\text{m}$





# Structure

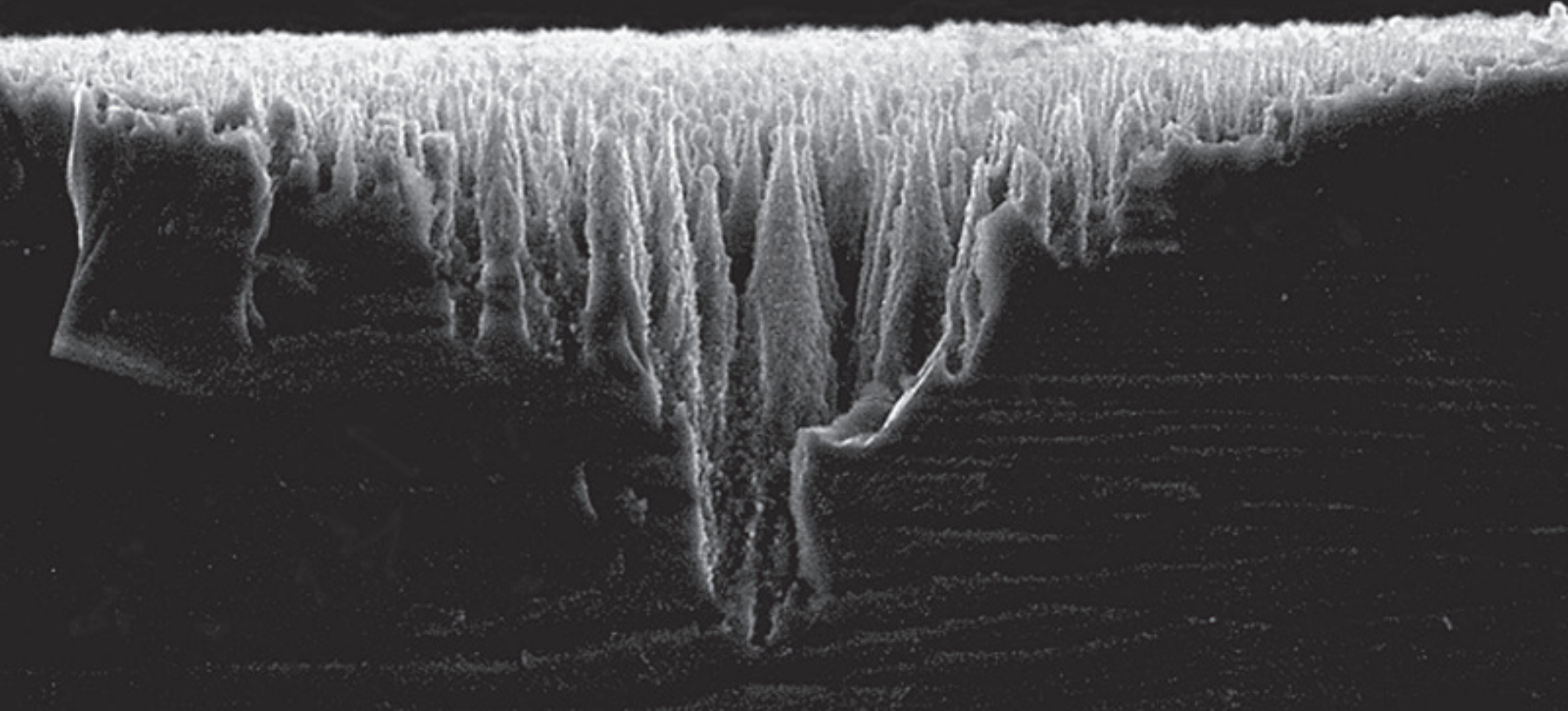


10 μm

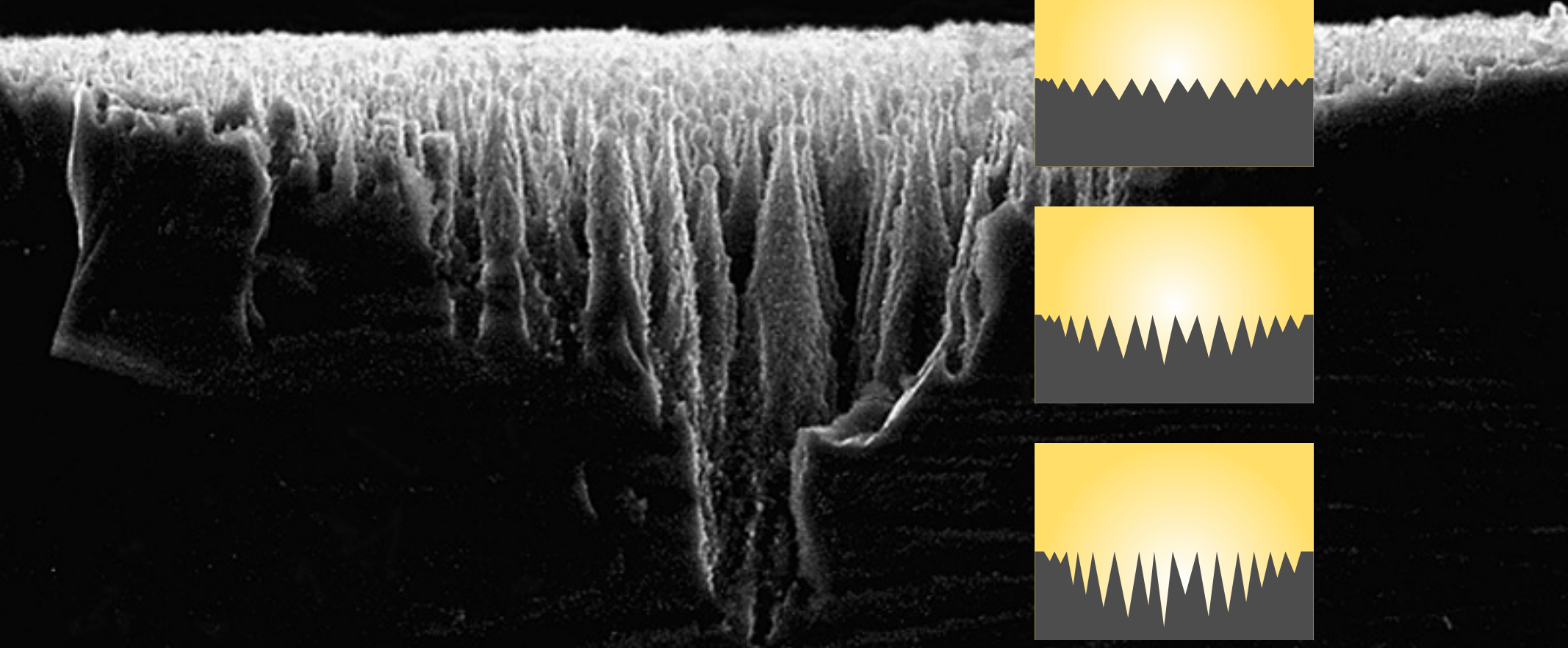




# Structure

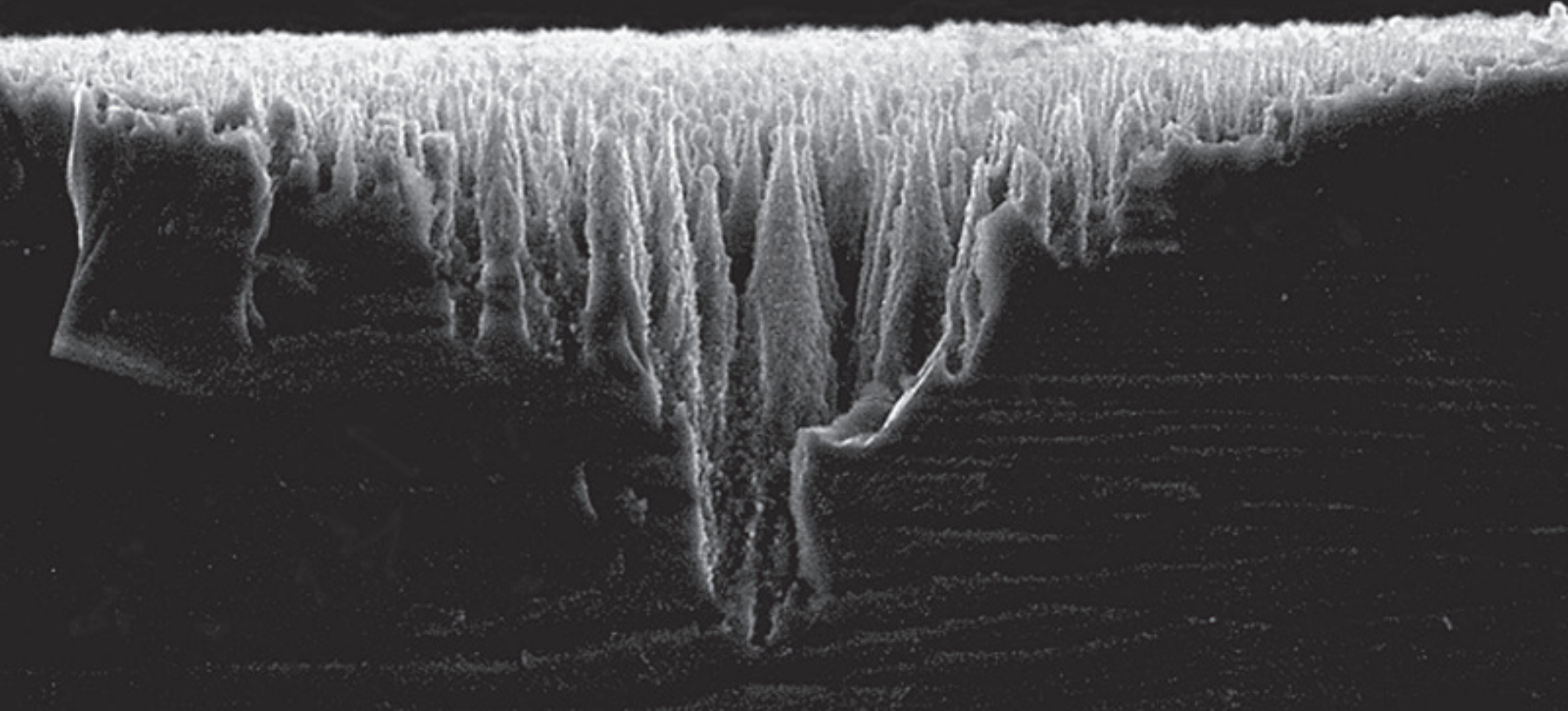


# Structure

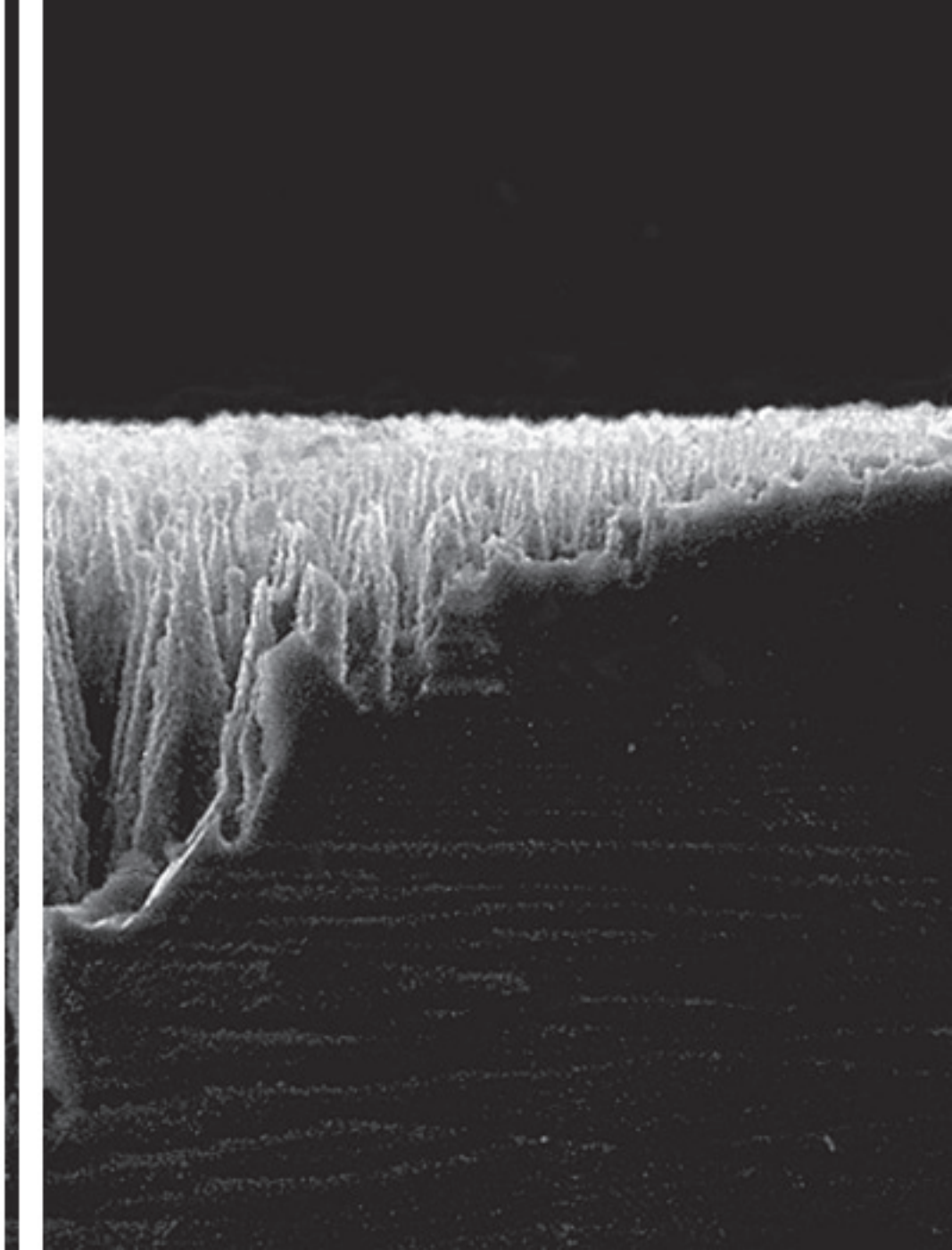
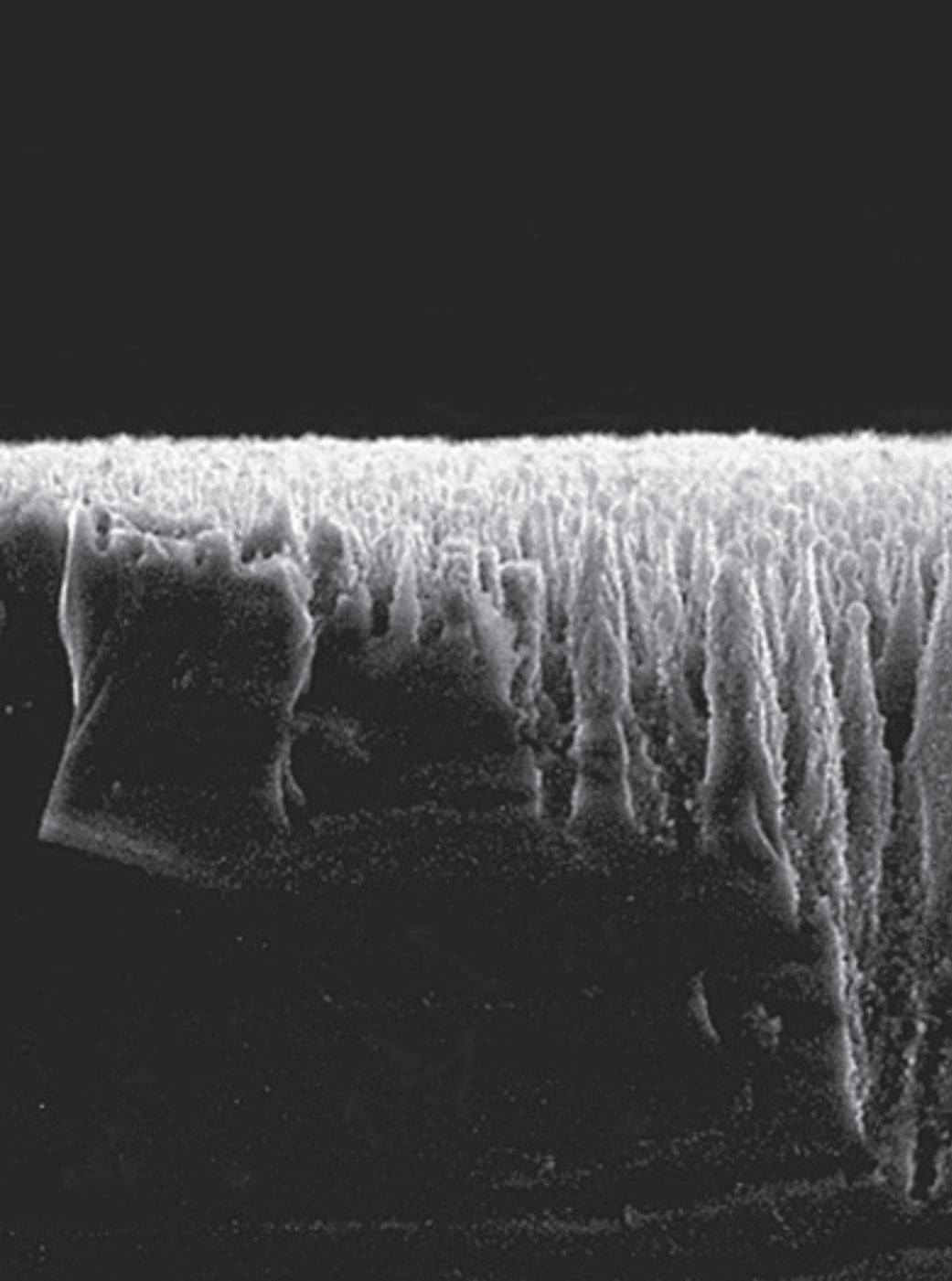




# Structure

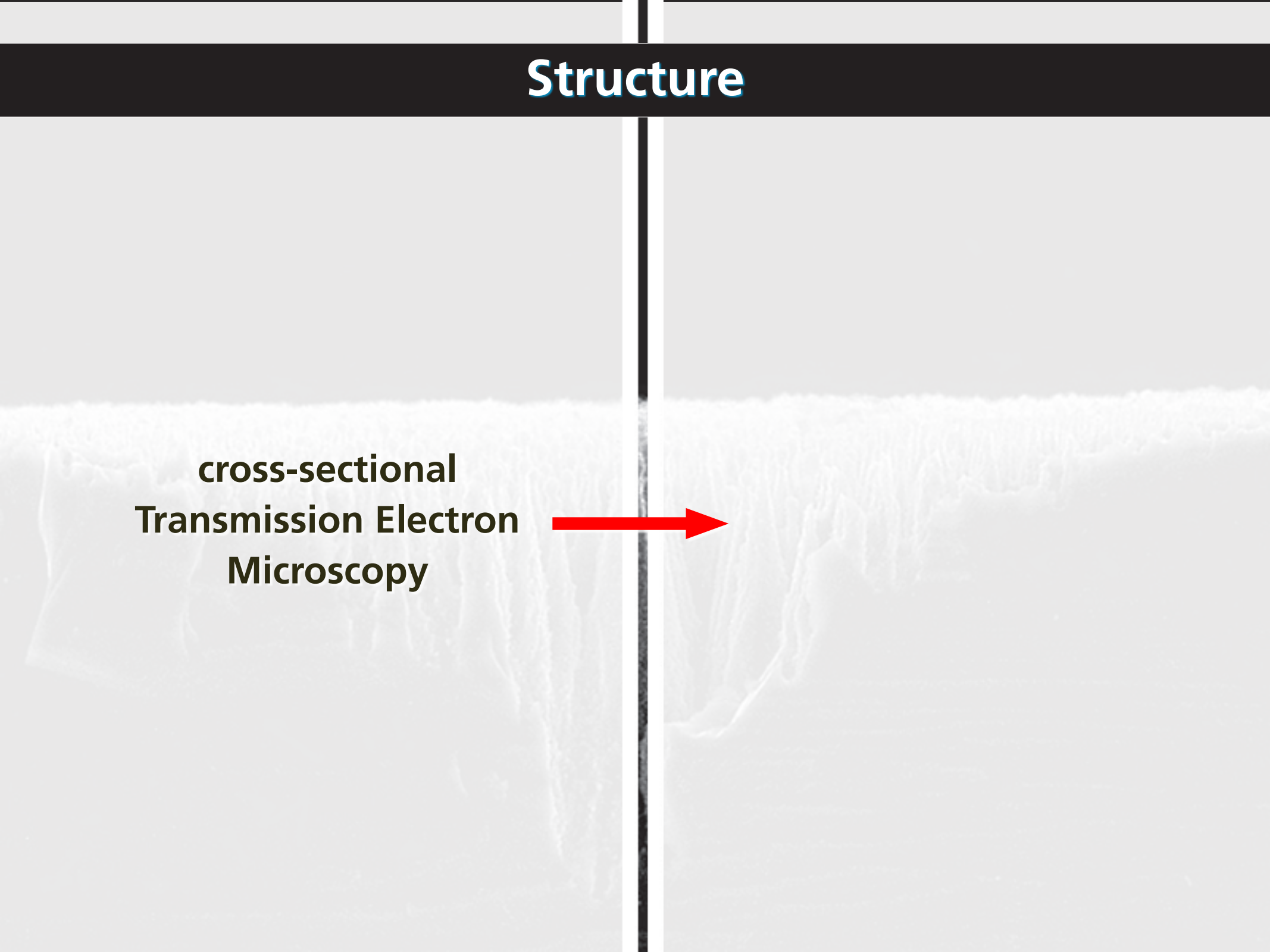


# Structure



# Structure

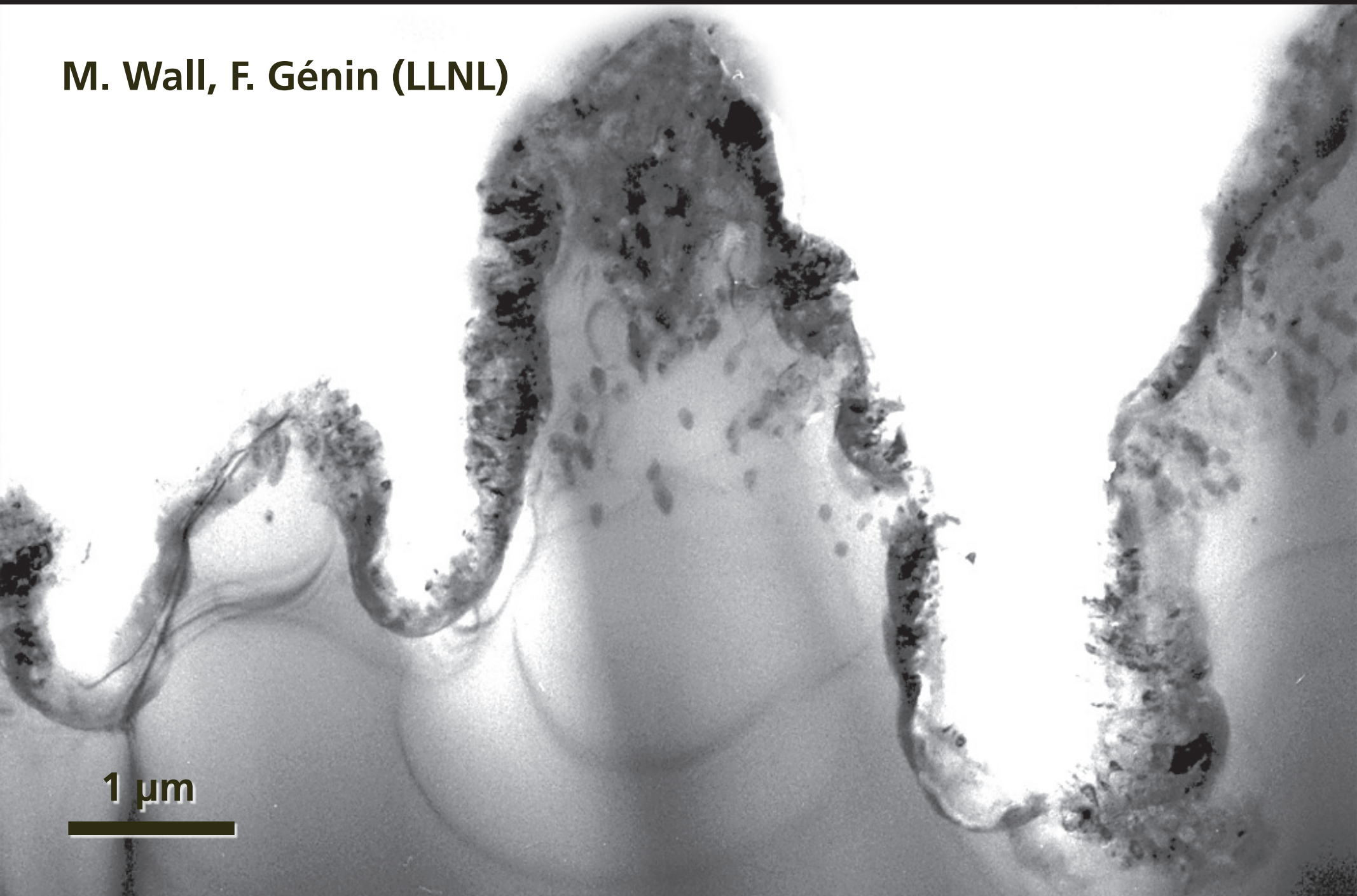
**cross-sectional  
Transmission Electron  
Microscopy**





# Structure

M. Wall, F. Génin (LLNL)

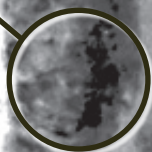


1  $\mu\text{m}$

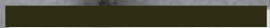


# Structure

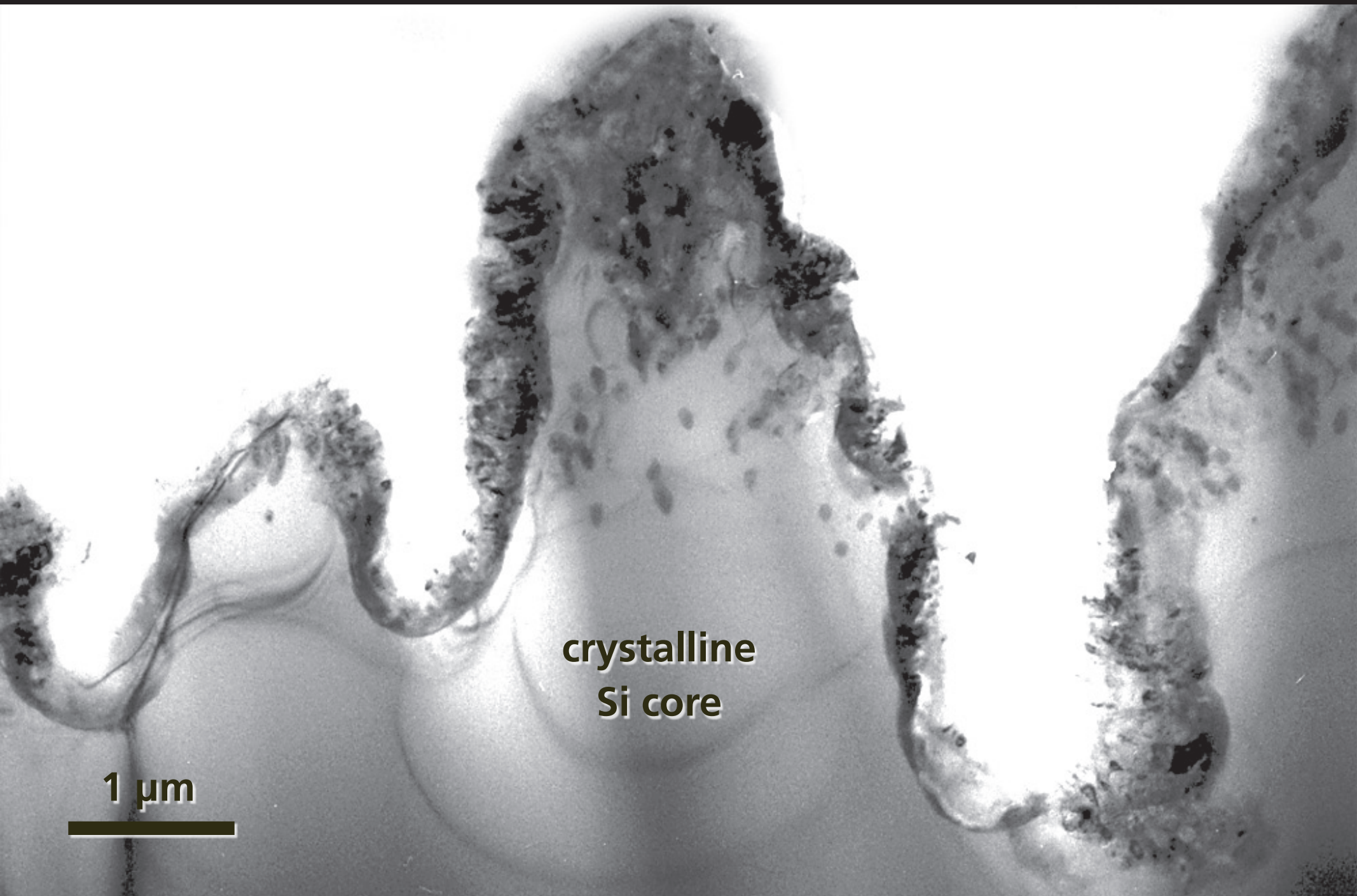
disordered  
surface layer



1  $\mu\text{m}$



# Structure

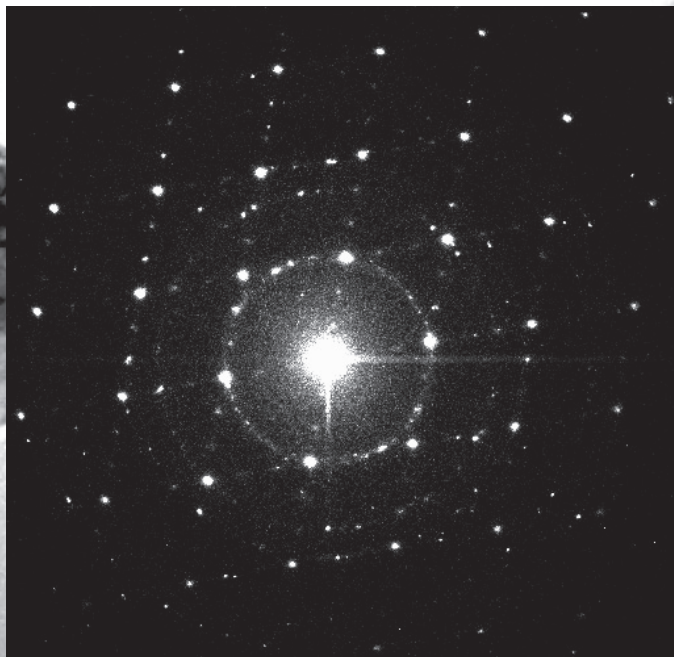
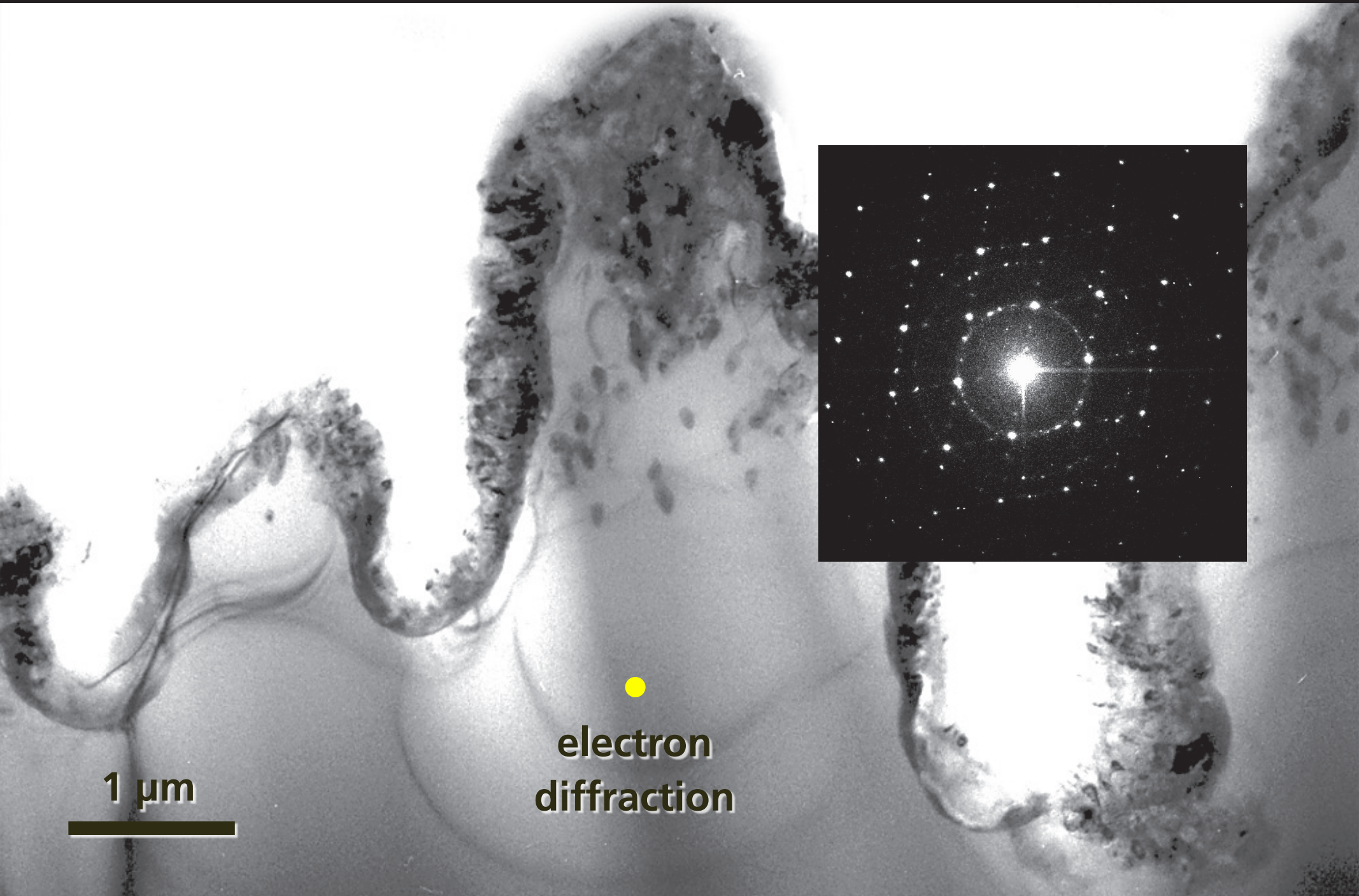


crystalline  
Si core

1 μm

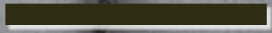


# Structure

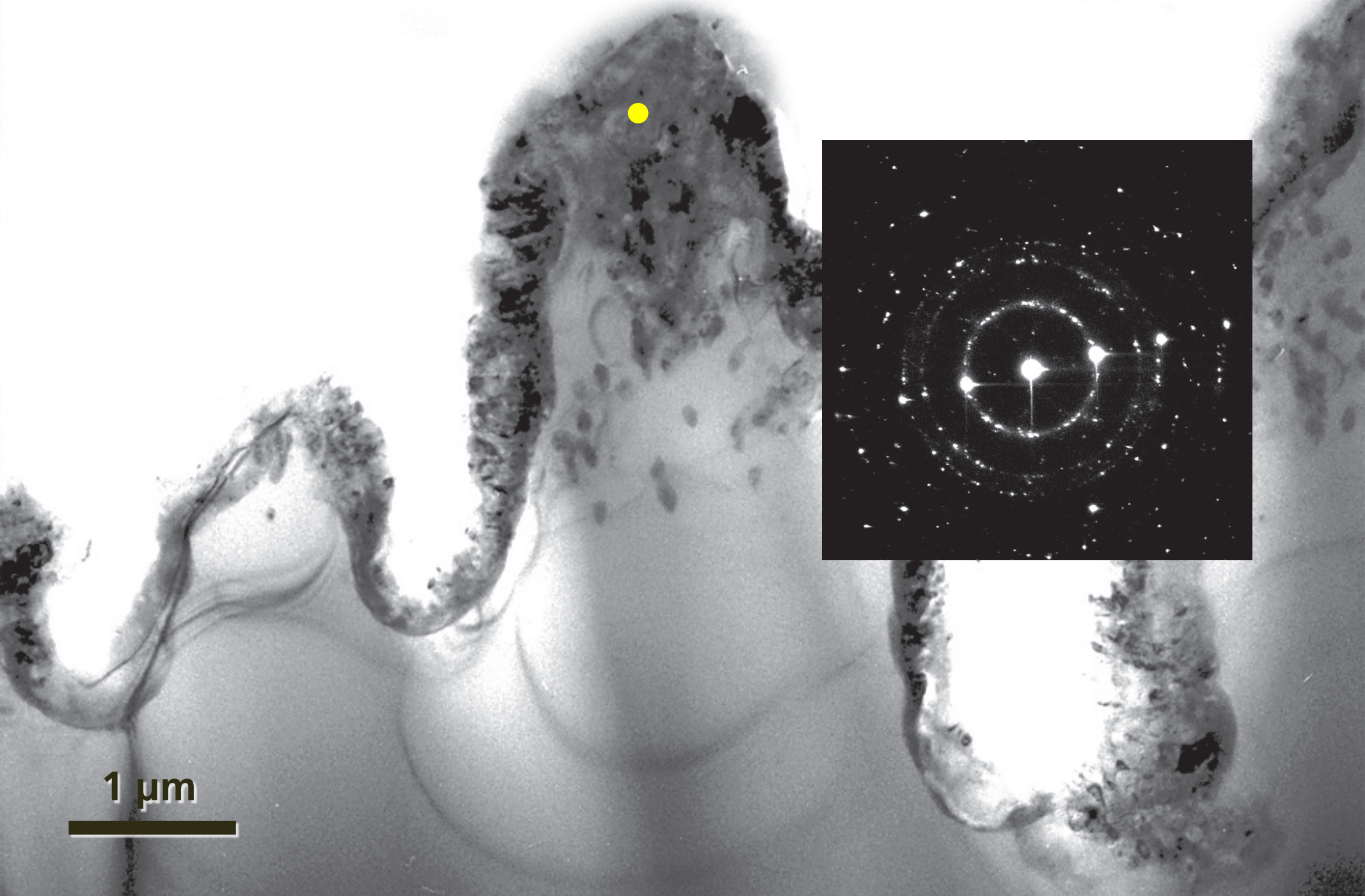


electron  
diffraction

1  $\mu\text{m}$



# Structure





# Structure

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

1  $\mu\text{m}$

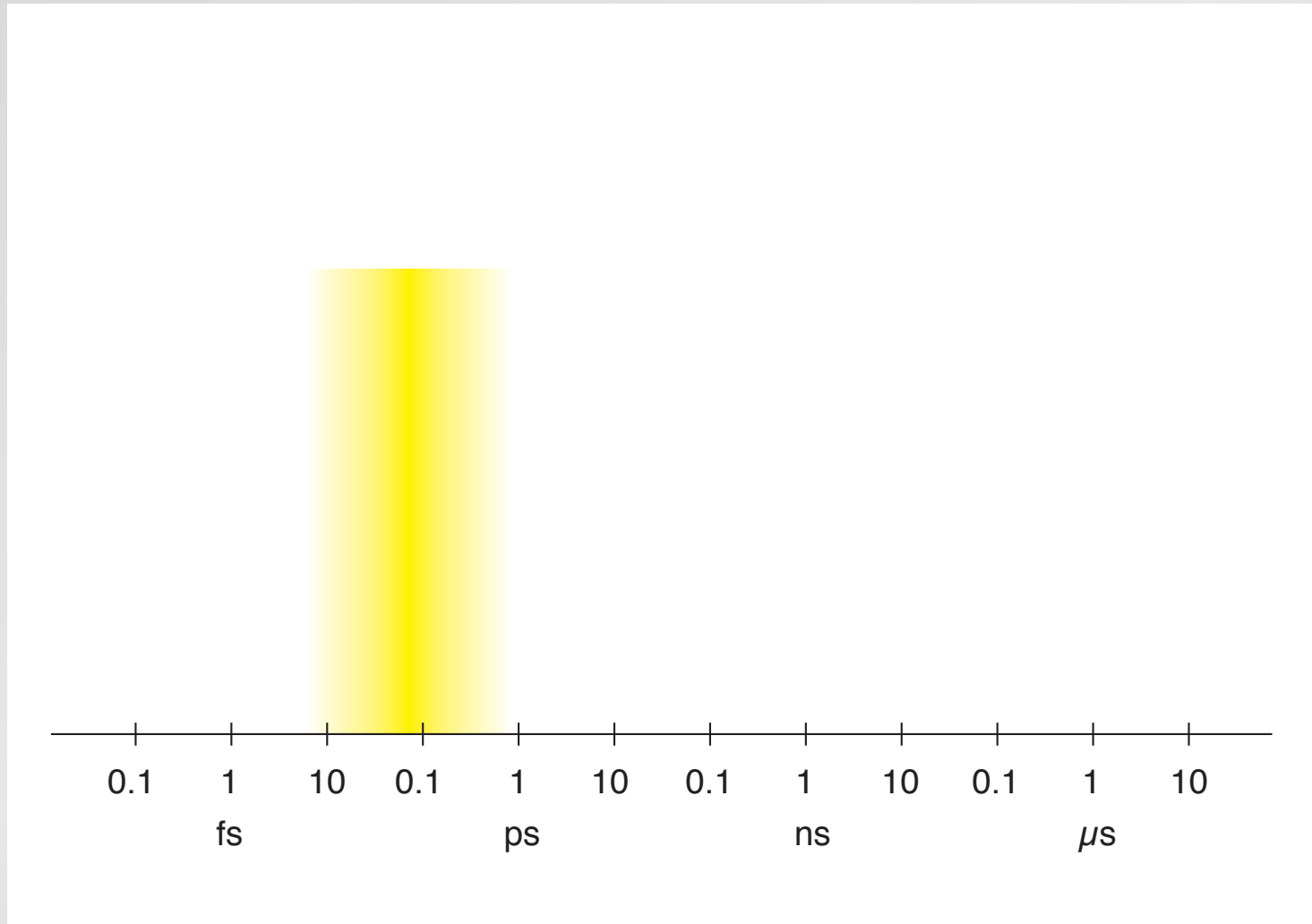
A grayscale micrograph showing several elongated, finger-like structures. Each structure has a darker, textured outer layer and a lighter, smoother inner core. The structures are interconnected and appear to be part of a larger network. A scale bar at the bottom left indicates a length of 1 micrometer.

# Structure

**two processes: melting and ablation**

# Structure

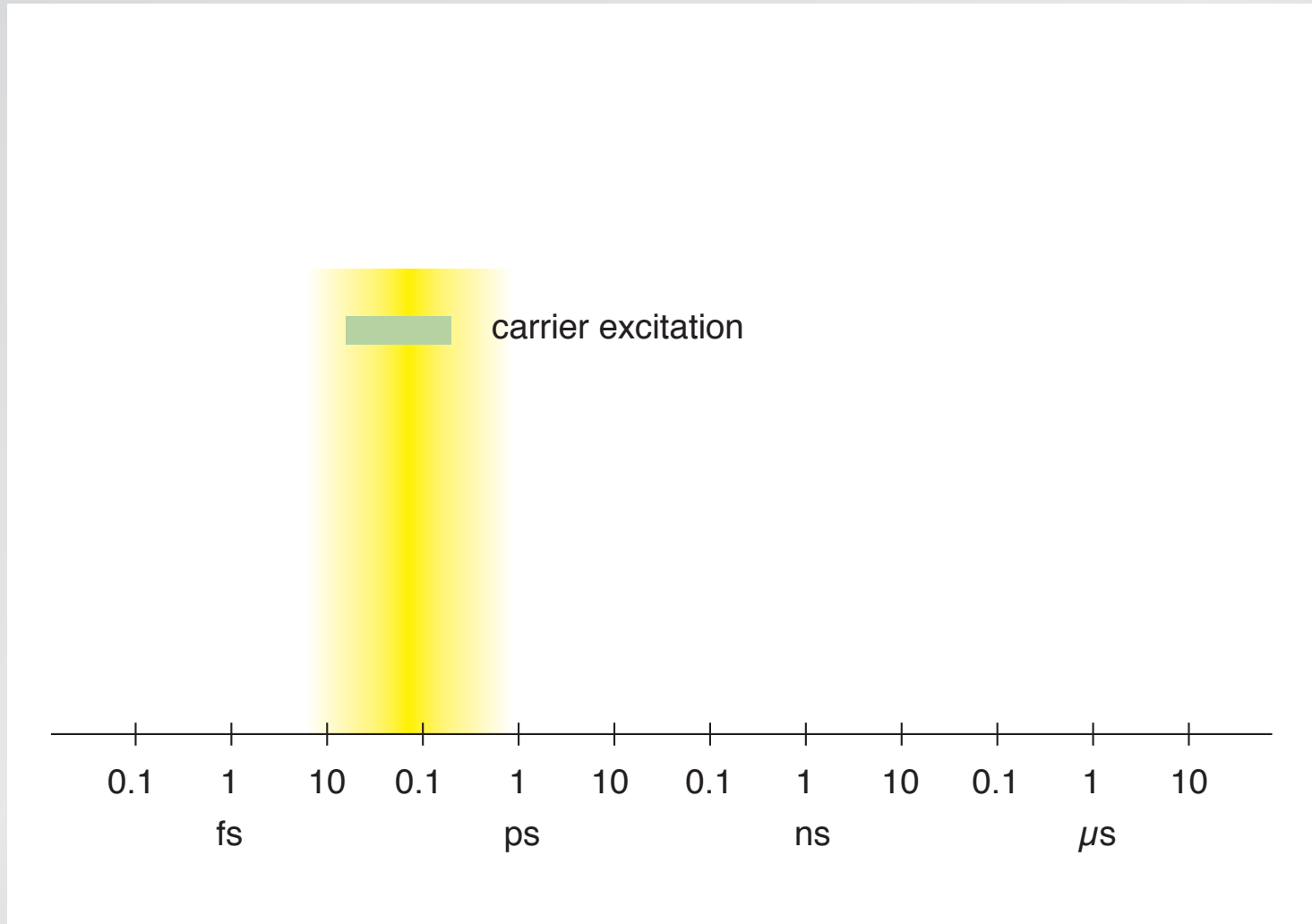
relevant time scales





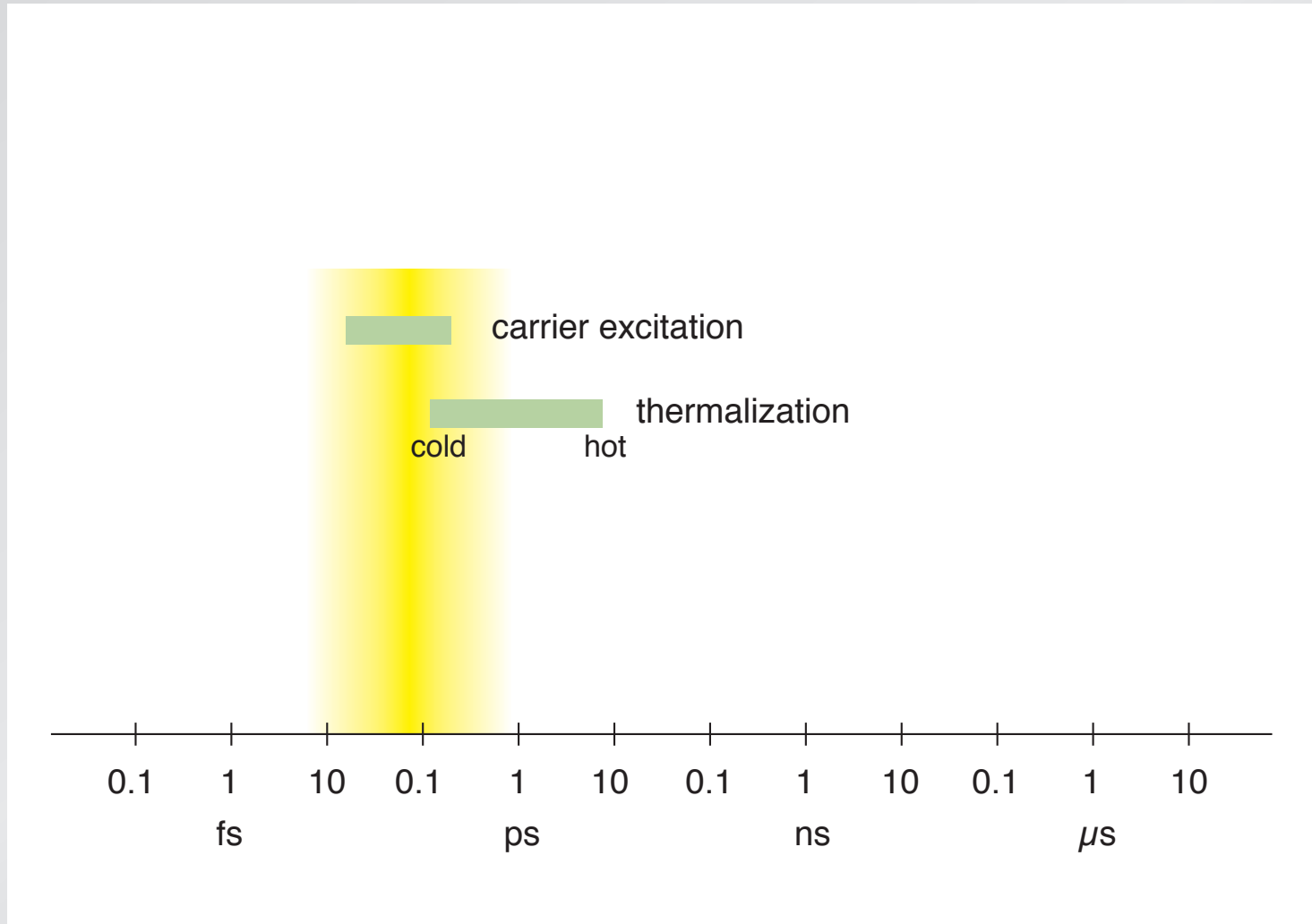
# Structure

## relevant time scales



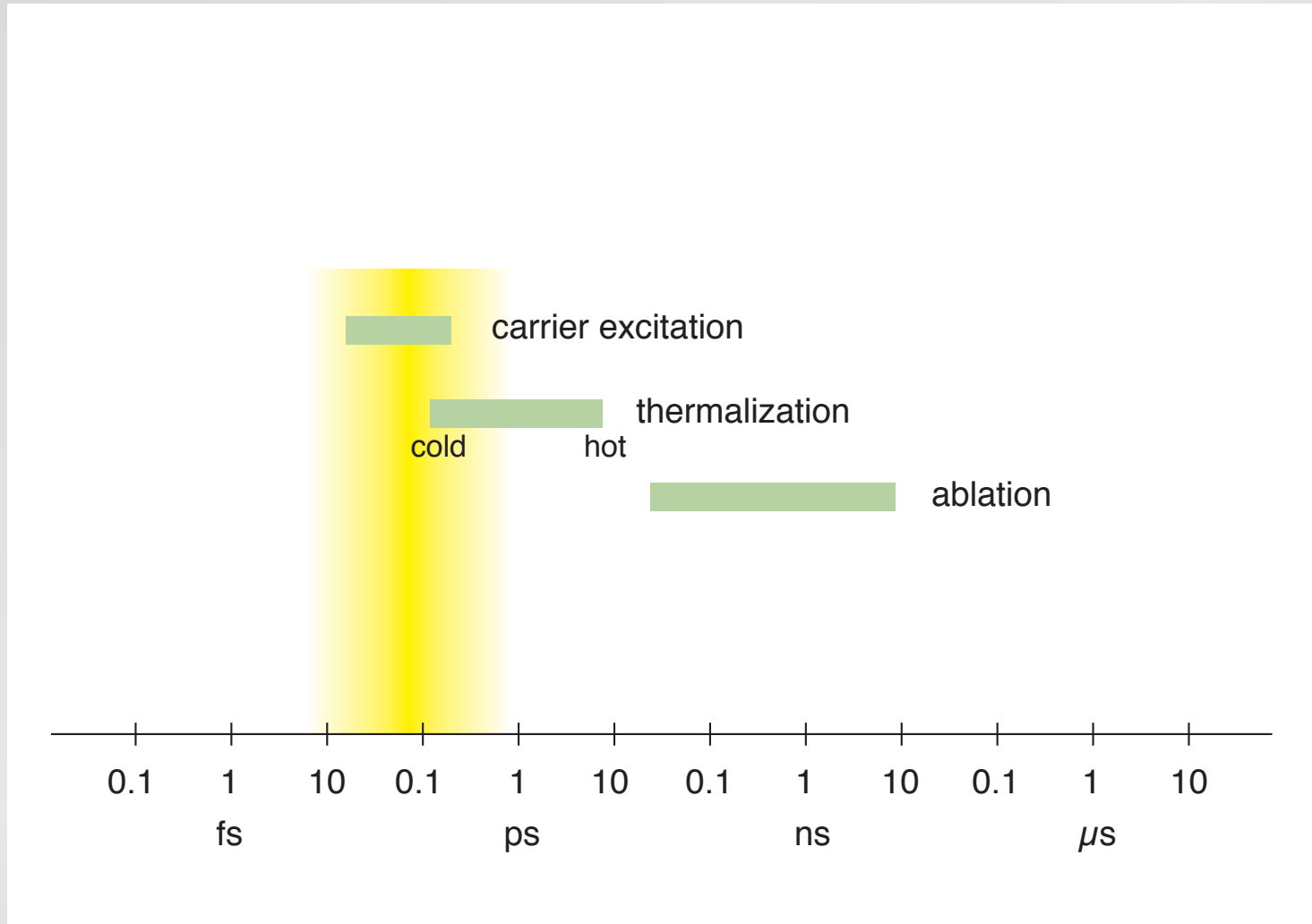
# Structure

## relevant time scales



# Structure

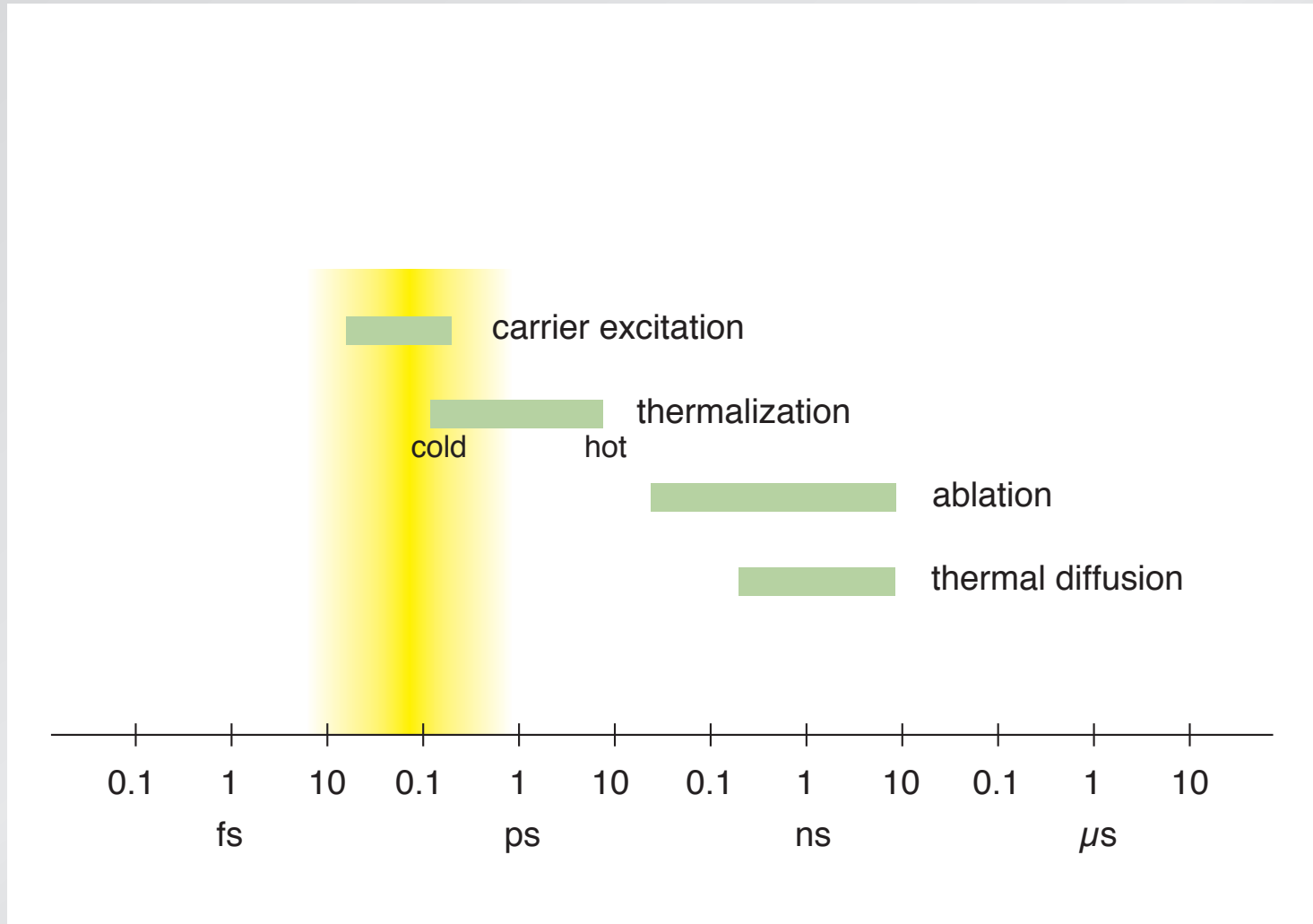
## relevant time scales





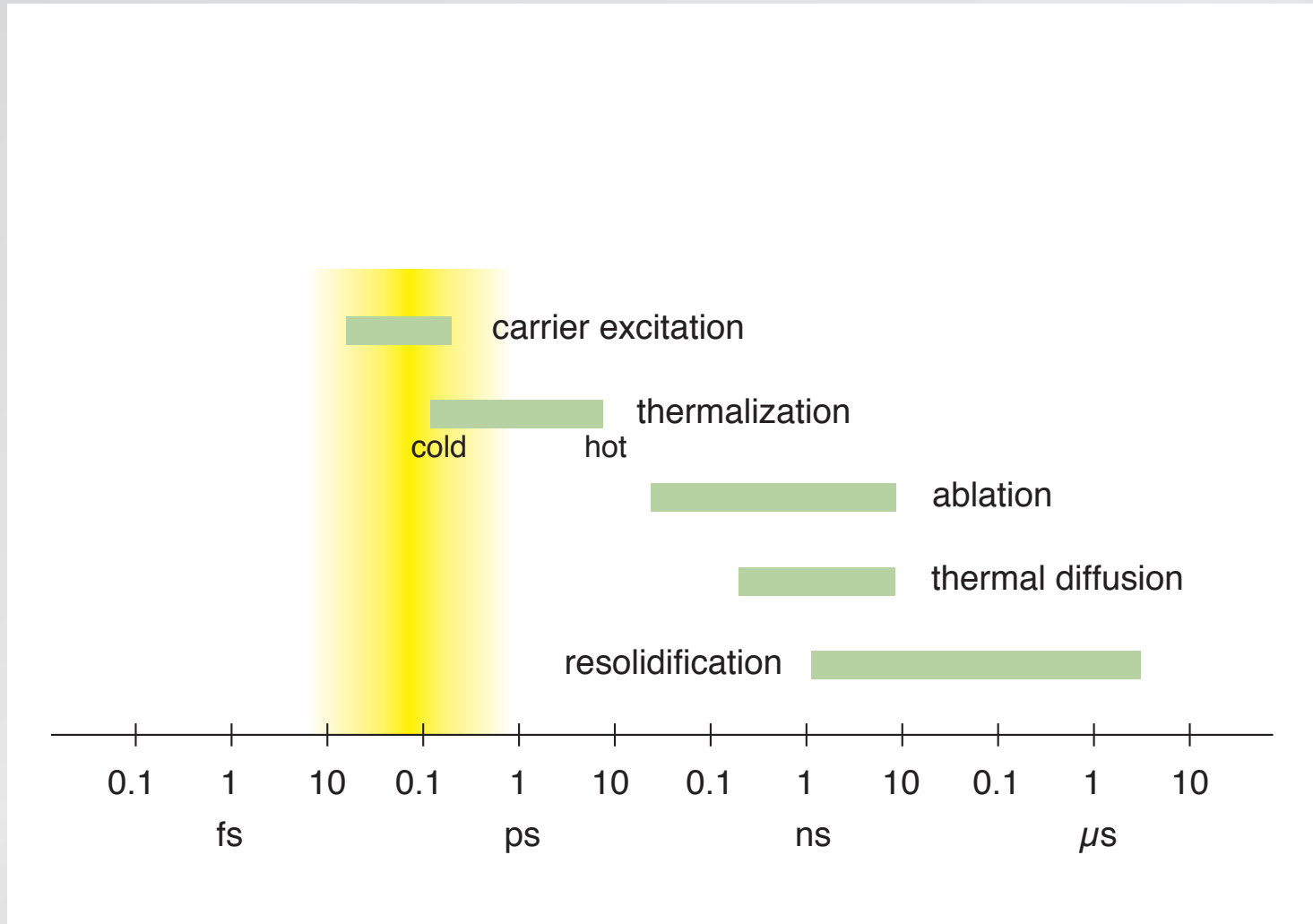
# Structure

## relevant time scales



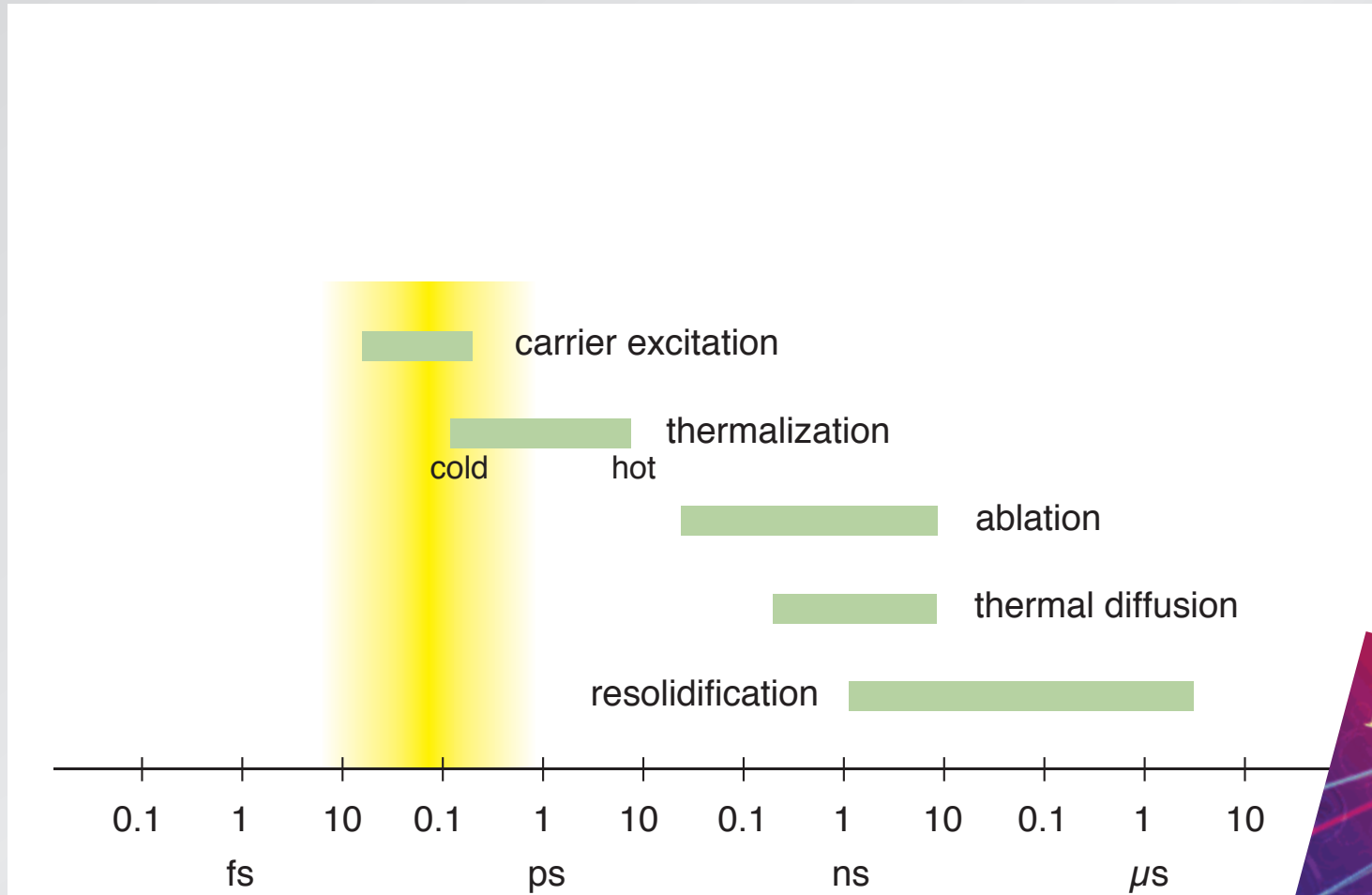
# Structure

## relevant time scales

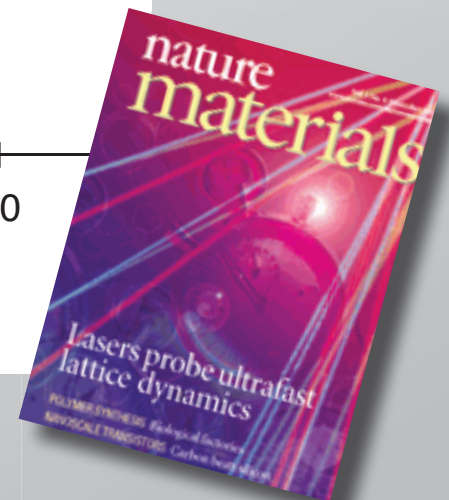


# Structure

## relevant time scales



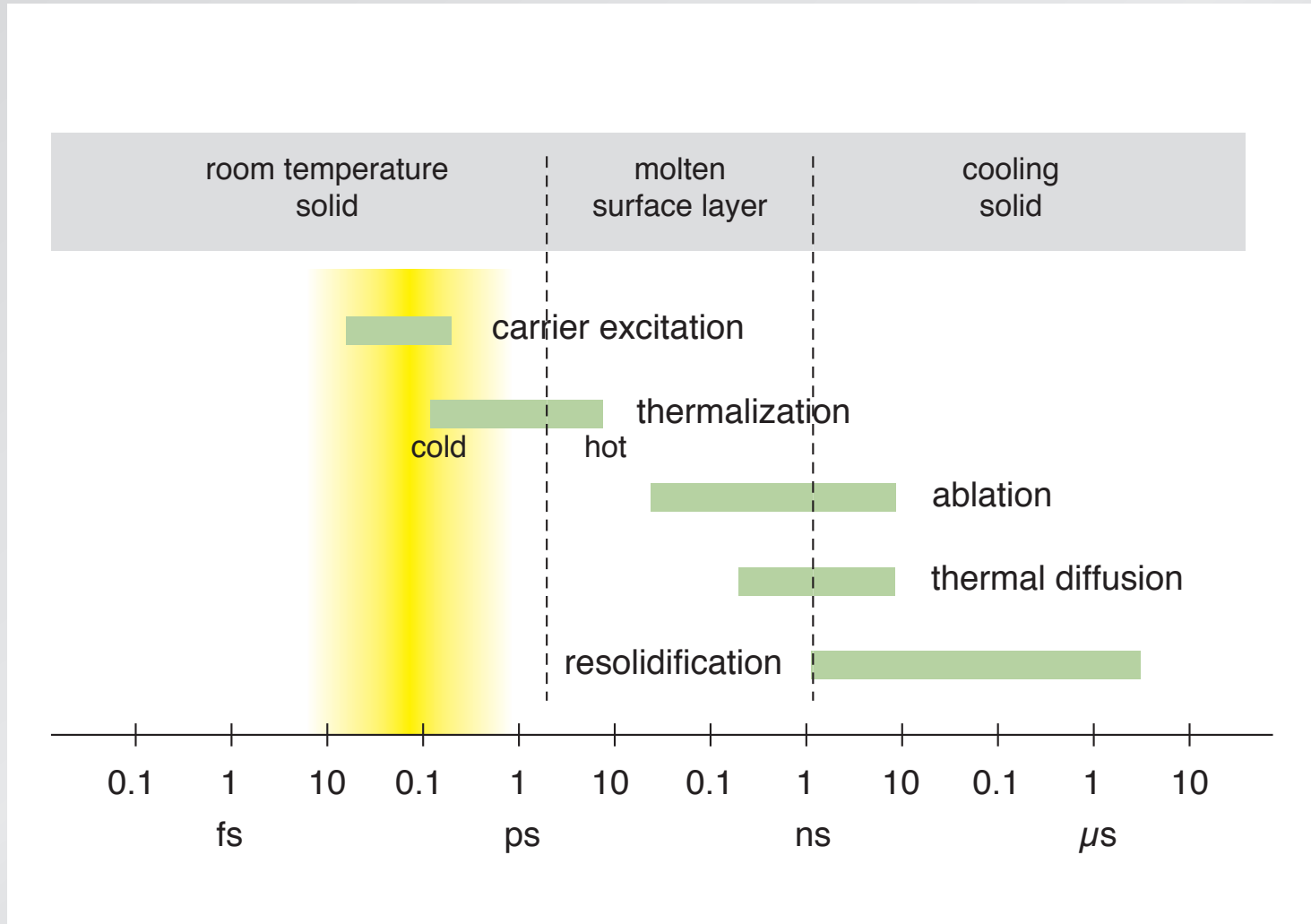
*Nature Materials* 1, 217 (2002)





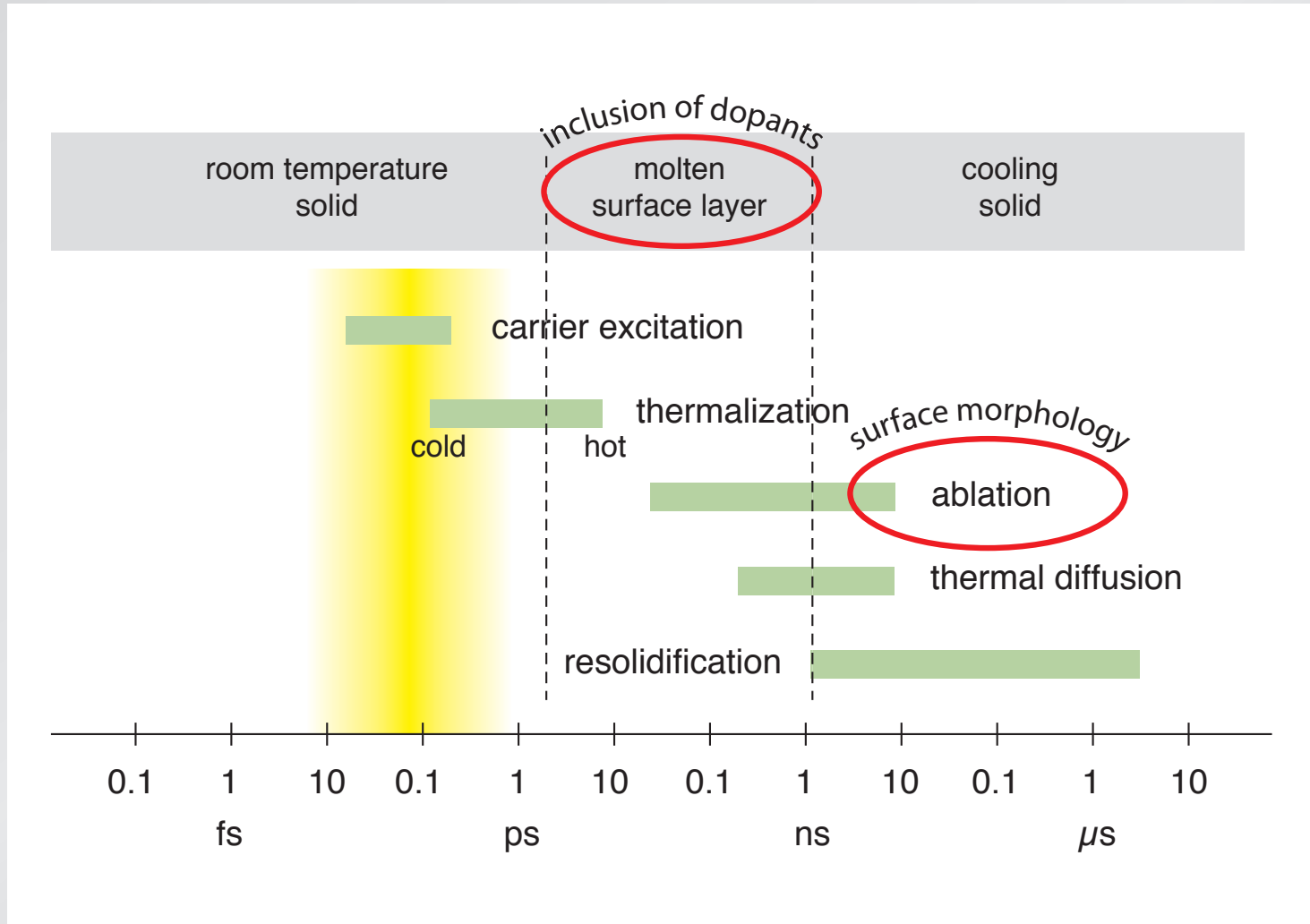
# Structure

## relevant time scales



# Structure

## relevant time scales



# Structure

**different thresholds:**

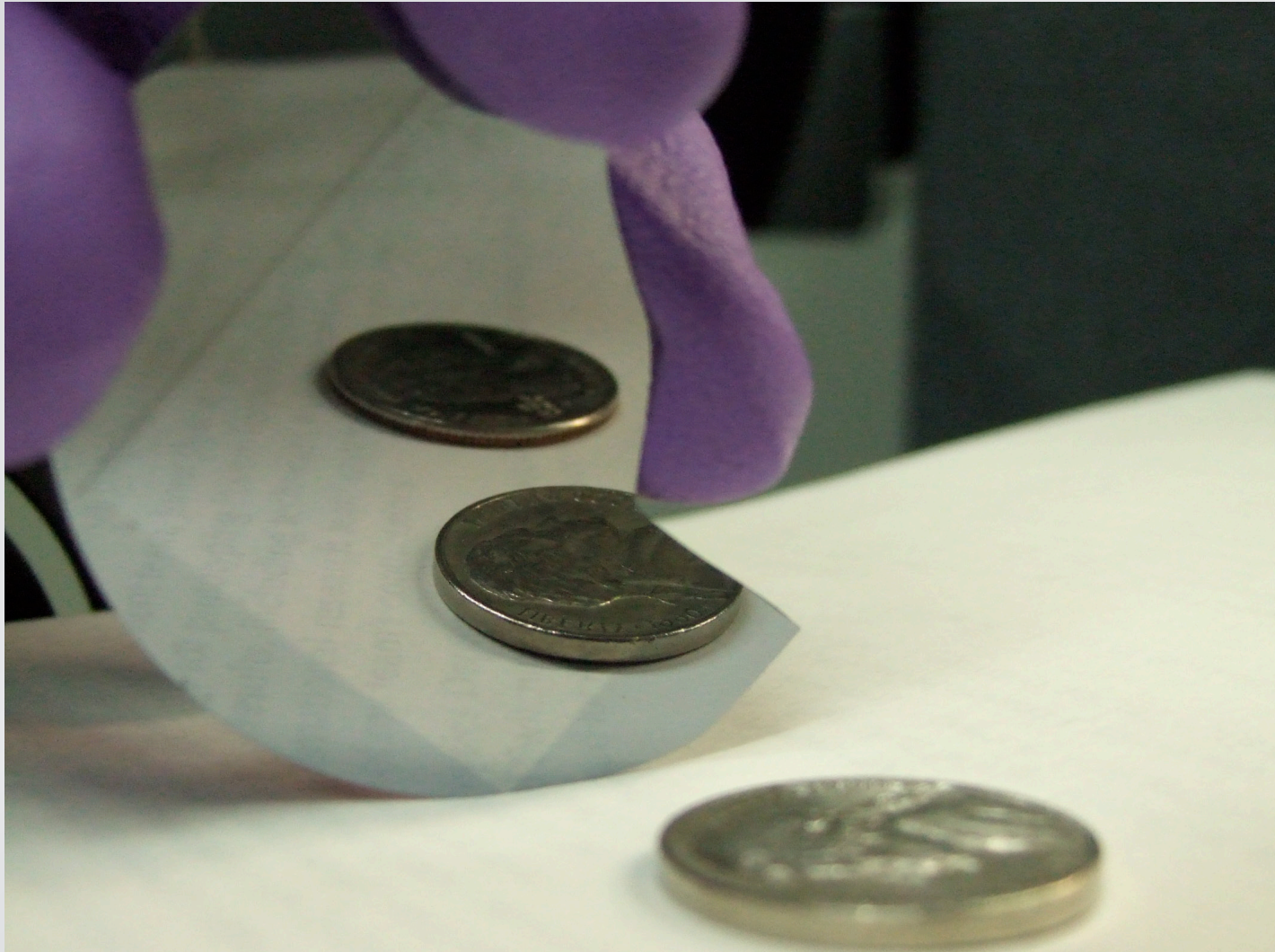
**melting: 1.5 kJ/m<sup>2</sup>**

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



# Structure

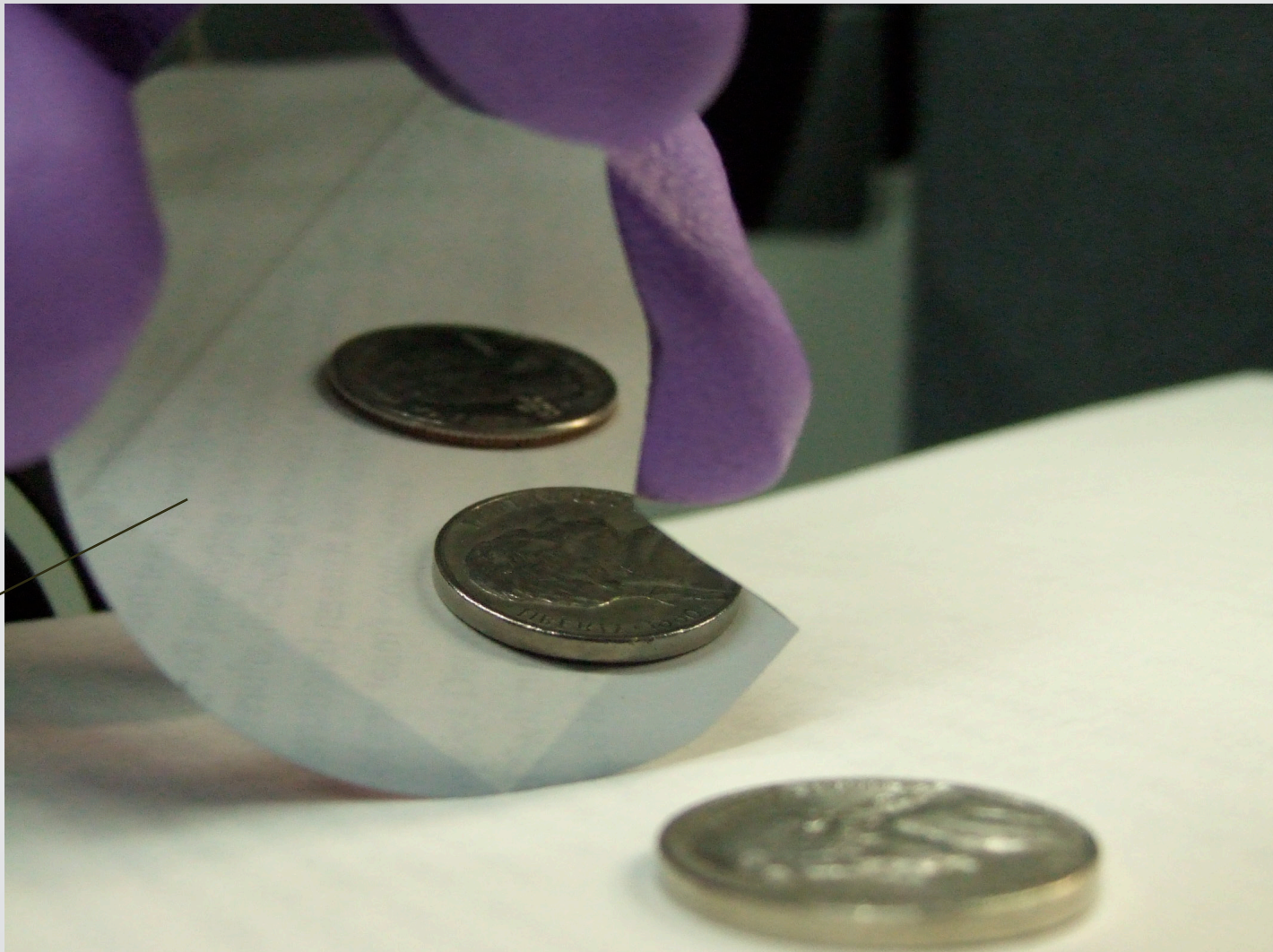
decouple ablation from melting



# Structure

decouple ablation from melting

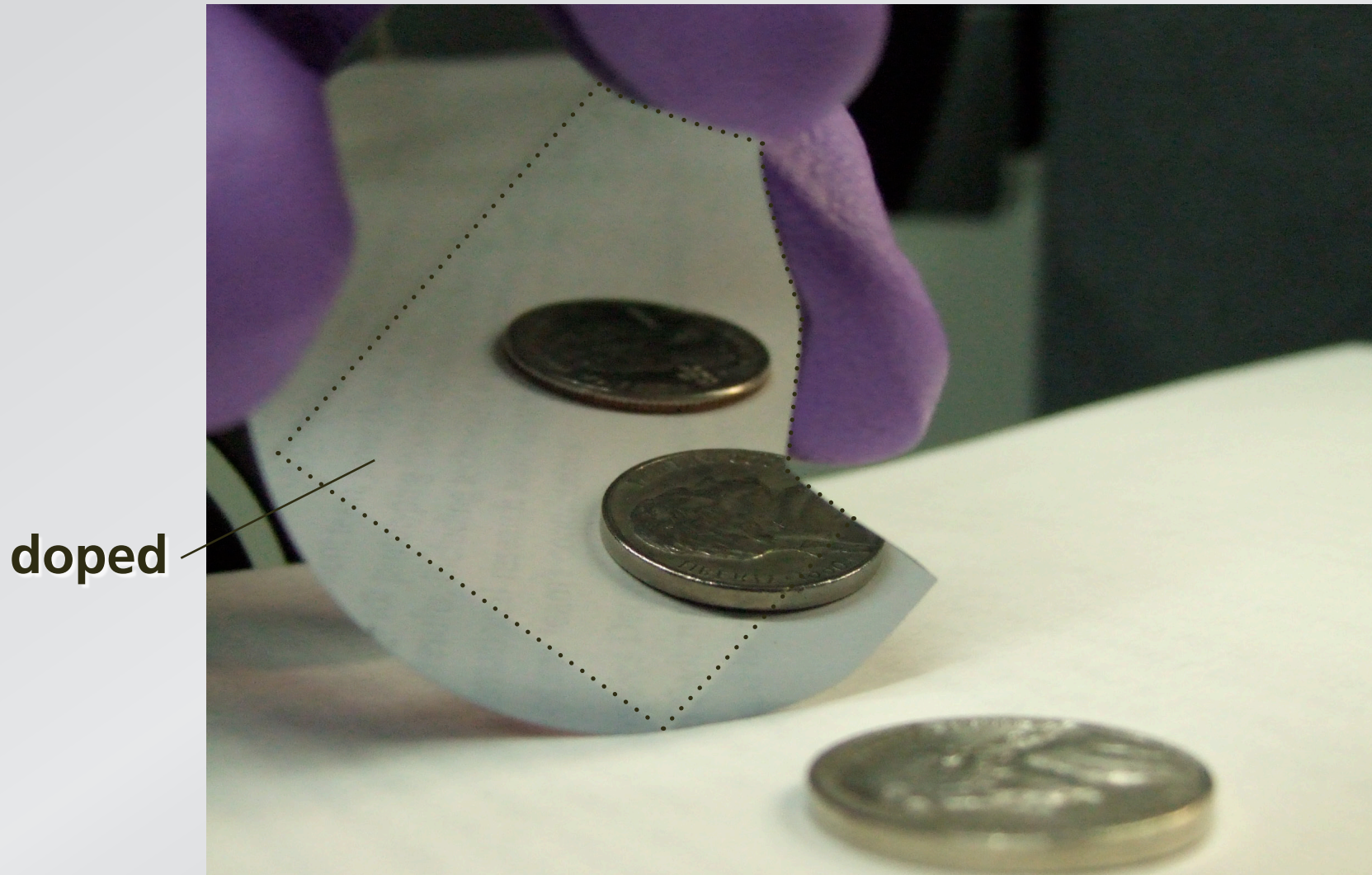
doped





# Structure

decouple ablation from melting

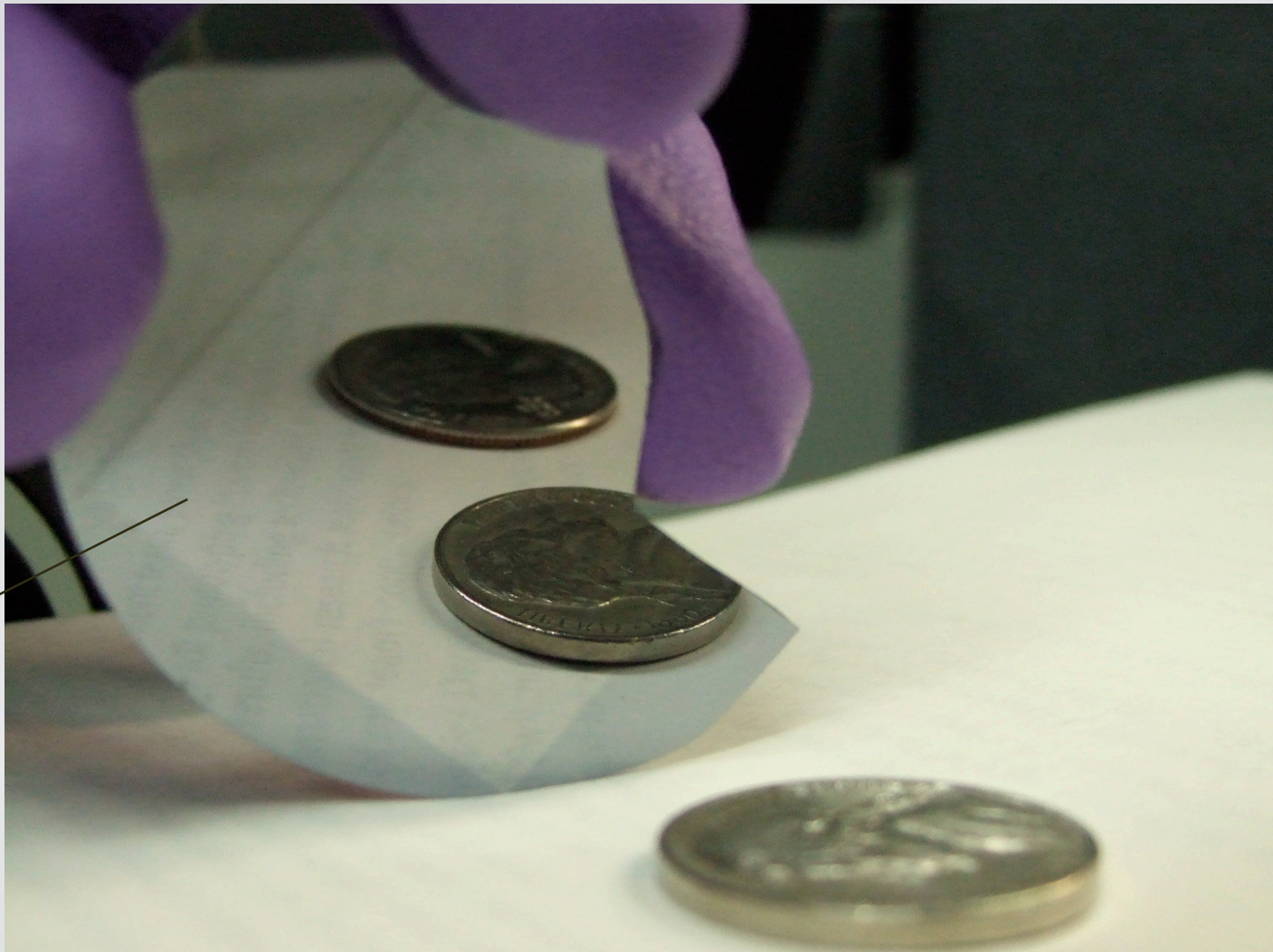




# Structure

decouple ablation from melting

doped

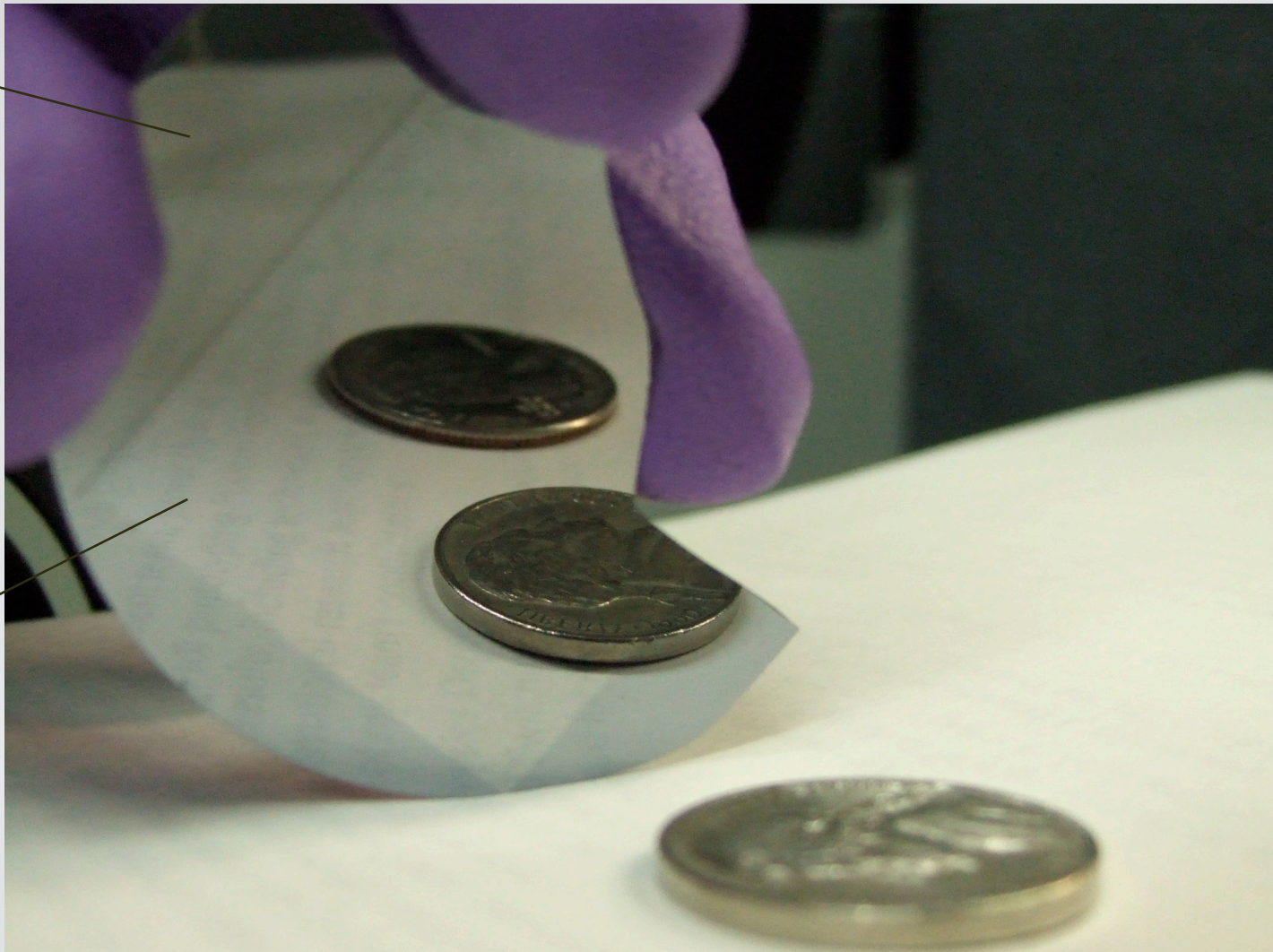


# Structure

decouple ablation from melting

undoped

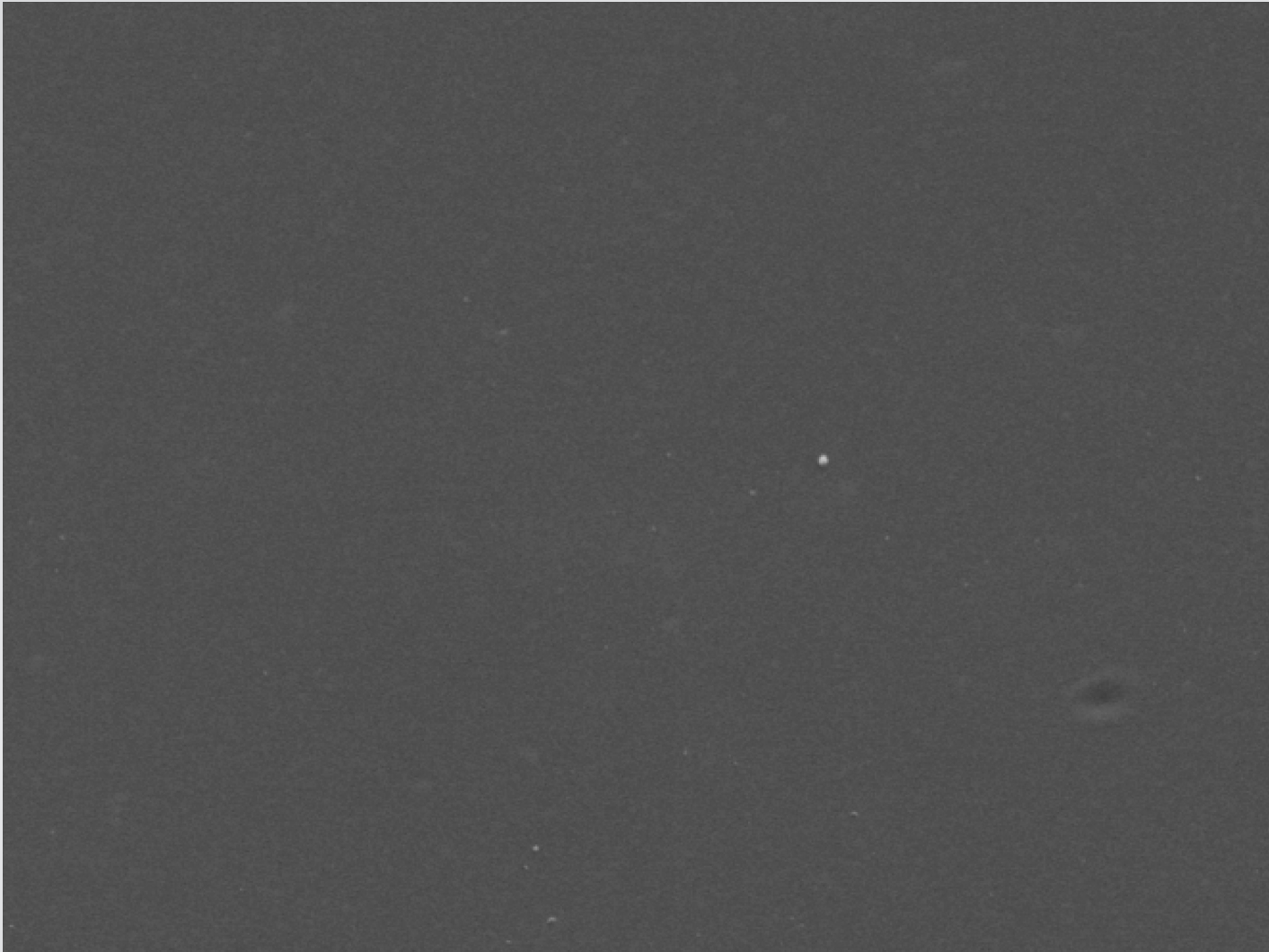
doped





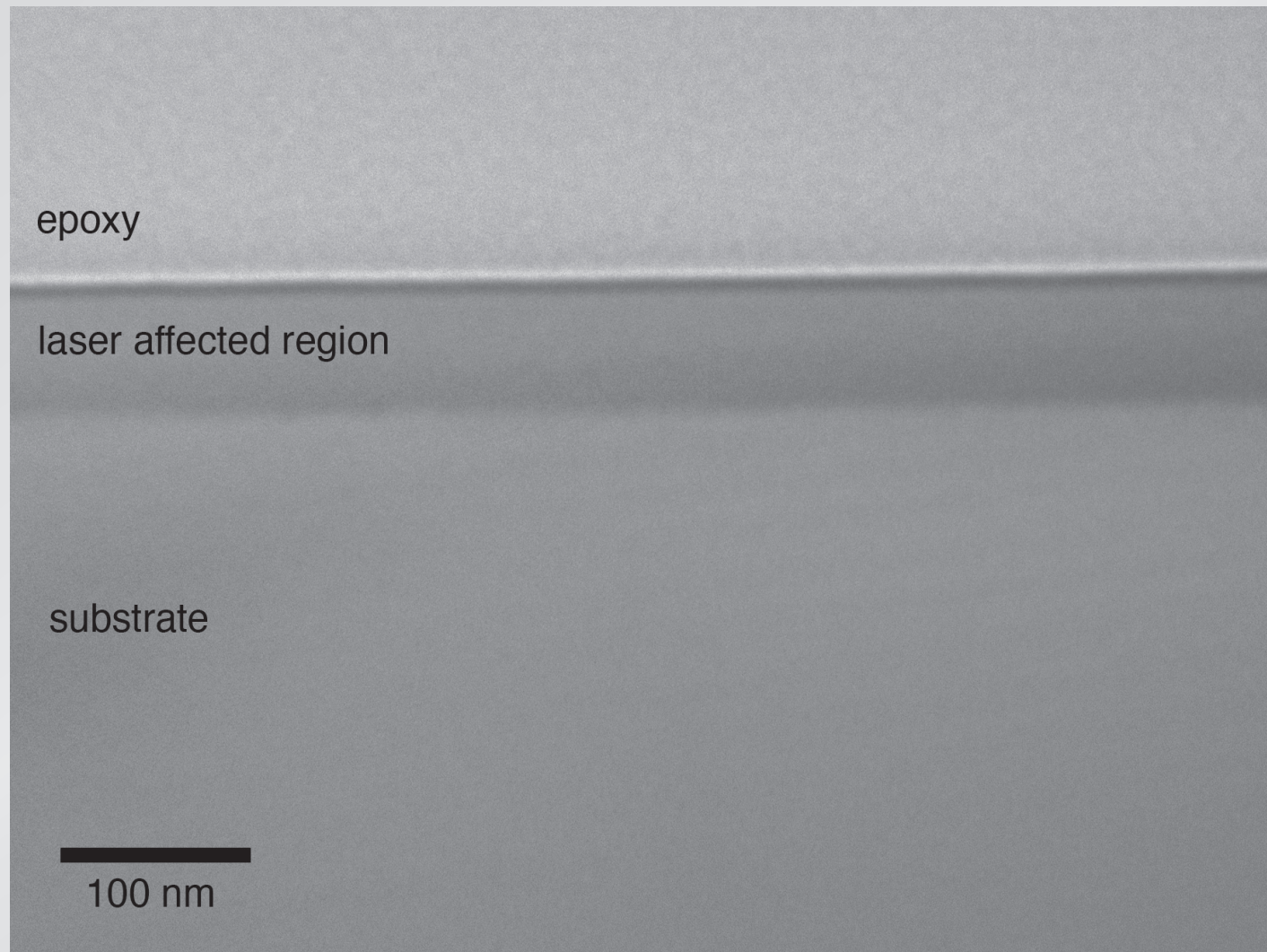
# Structure

decouple ablation from melting



# Structure

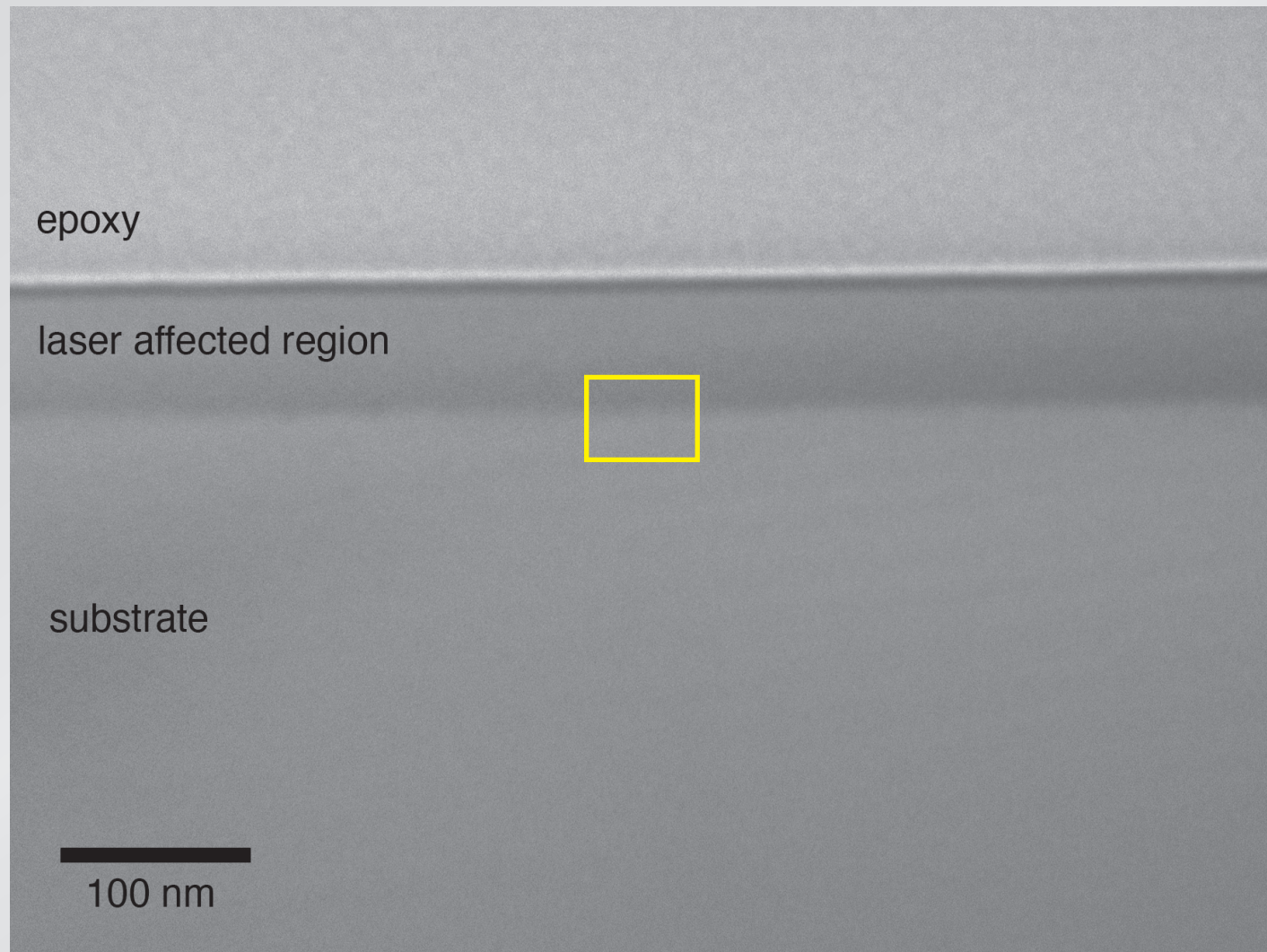
decouple ablation from melting





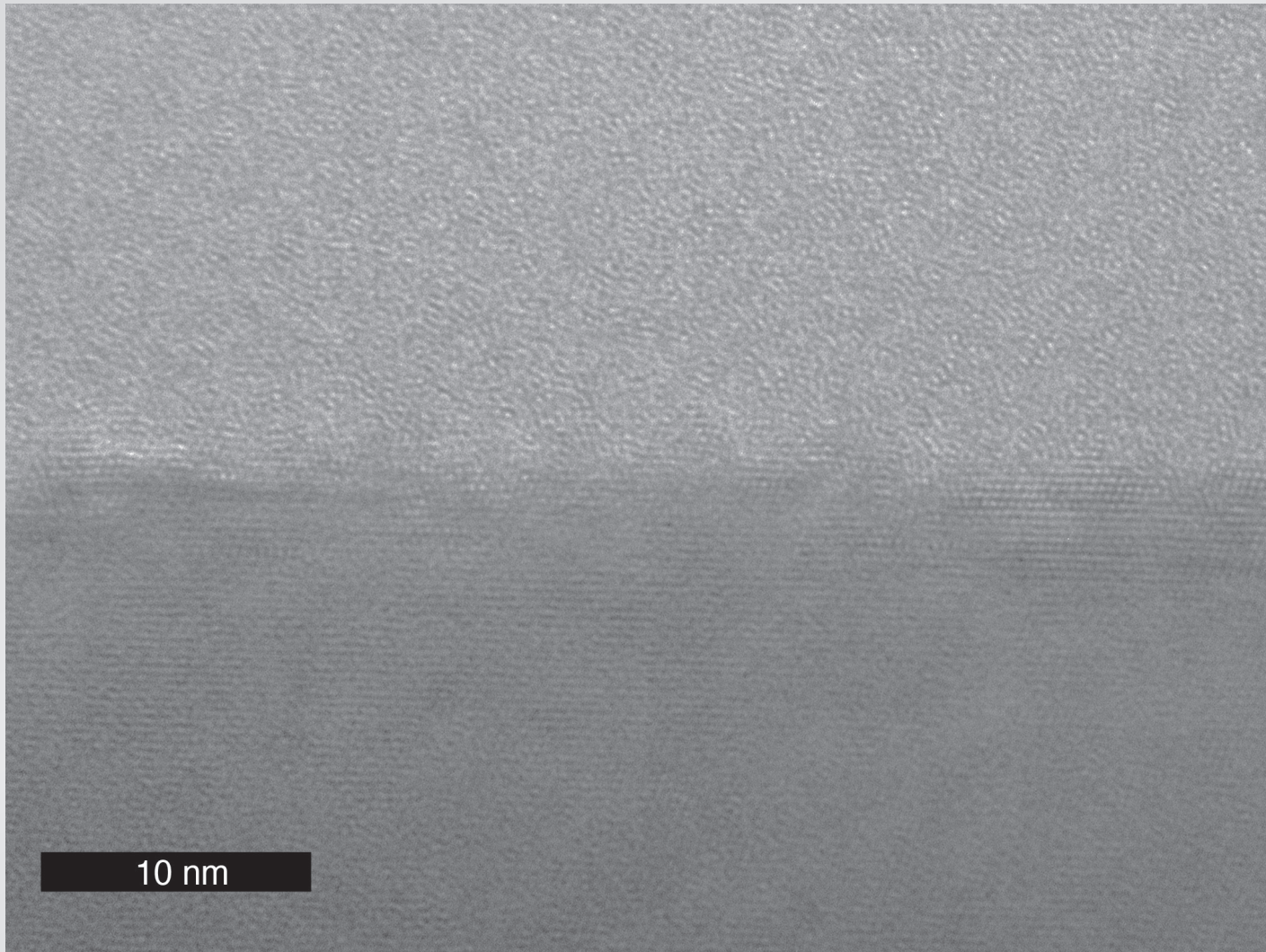
# Structure

decouple ablation from melting



# Structure

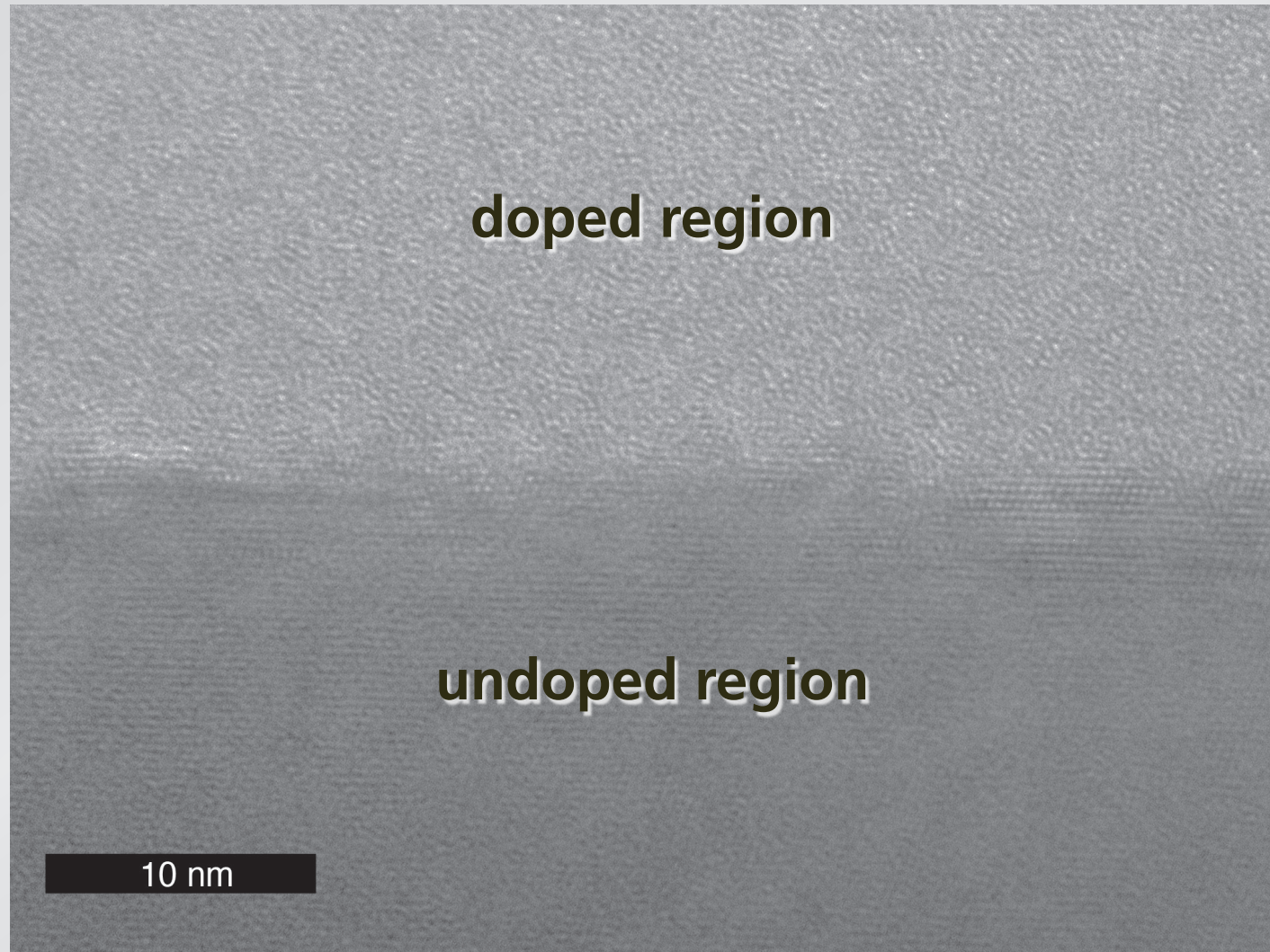
decouple ablation from melting





# Structure

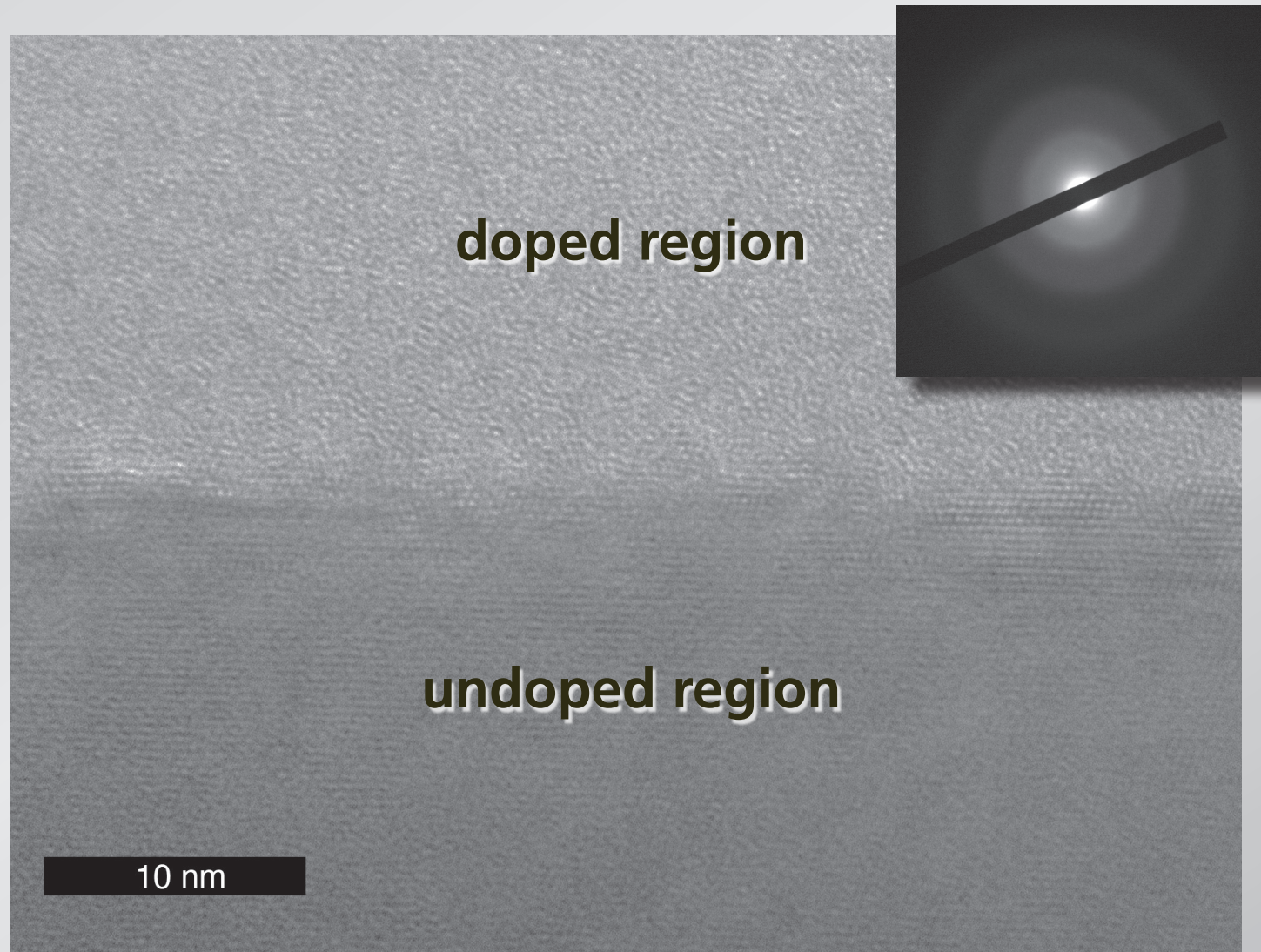
decouple ablation from melting





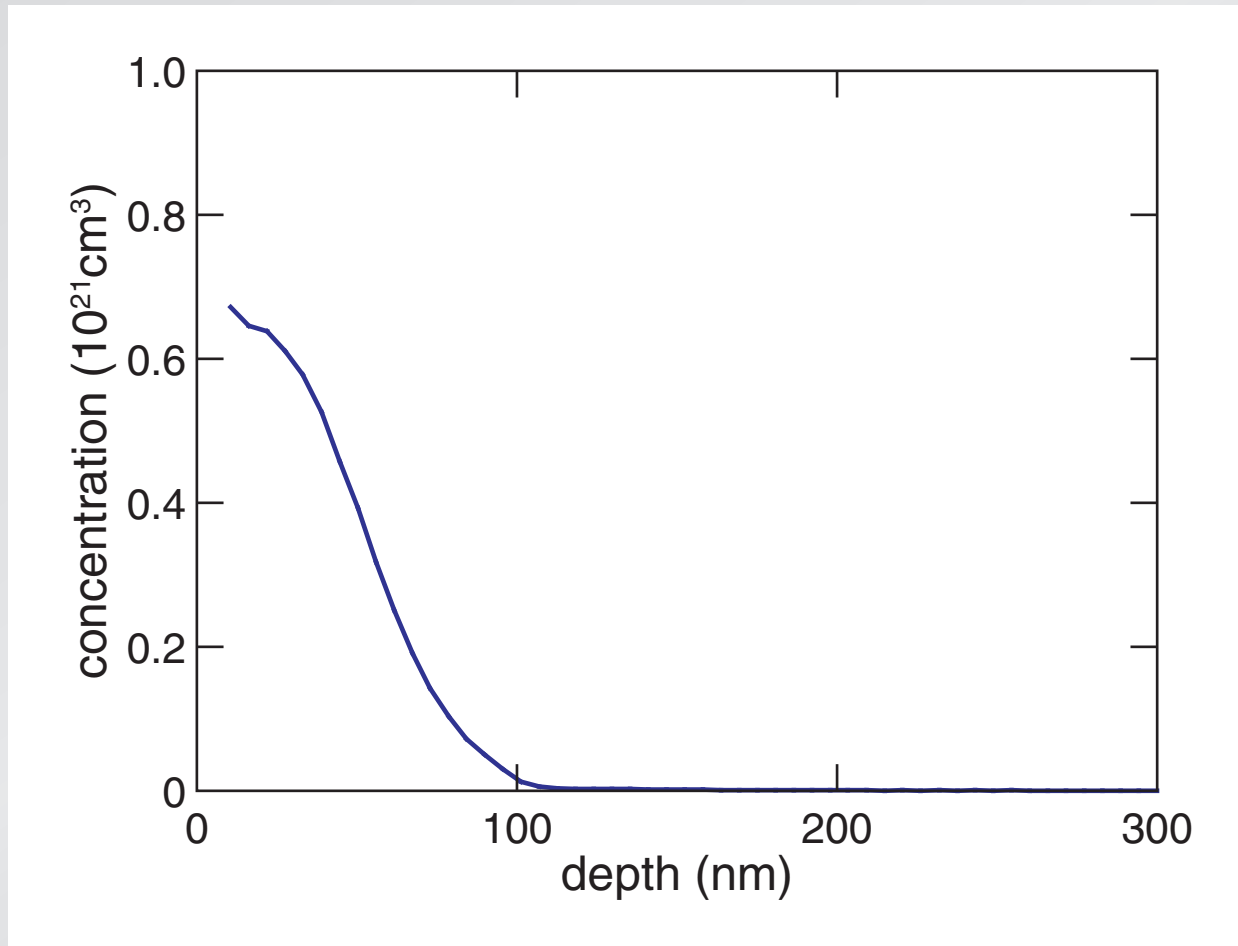
# Structure

decouple ablation from melting

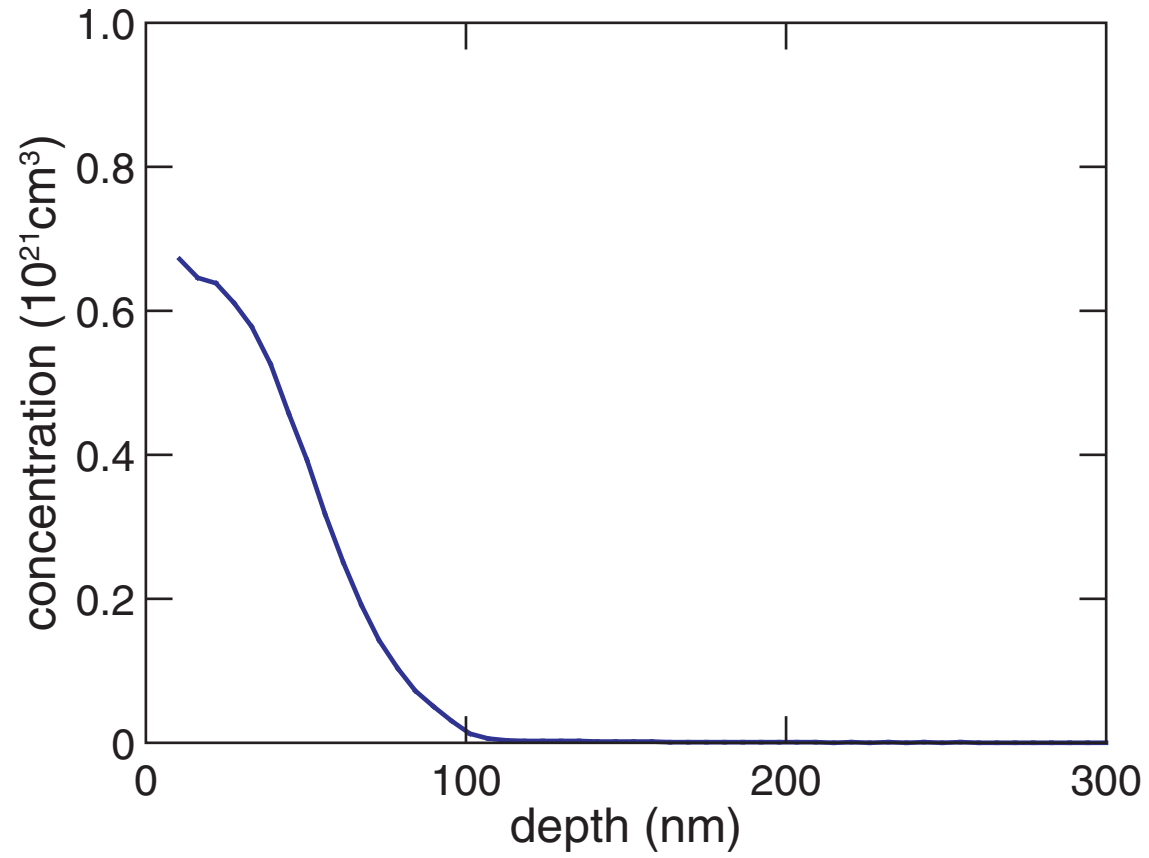
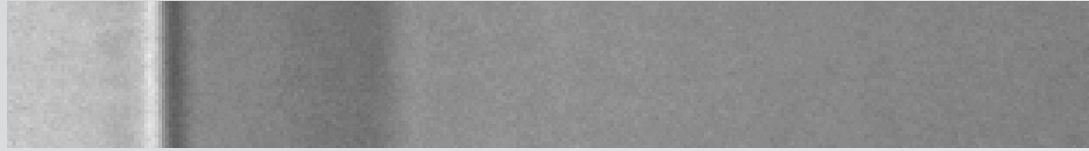


# Structure

## secondary ion mass spectrometry



# Structure





# Structure

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

**dopant in two different chemical states**

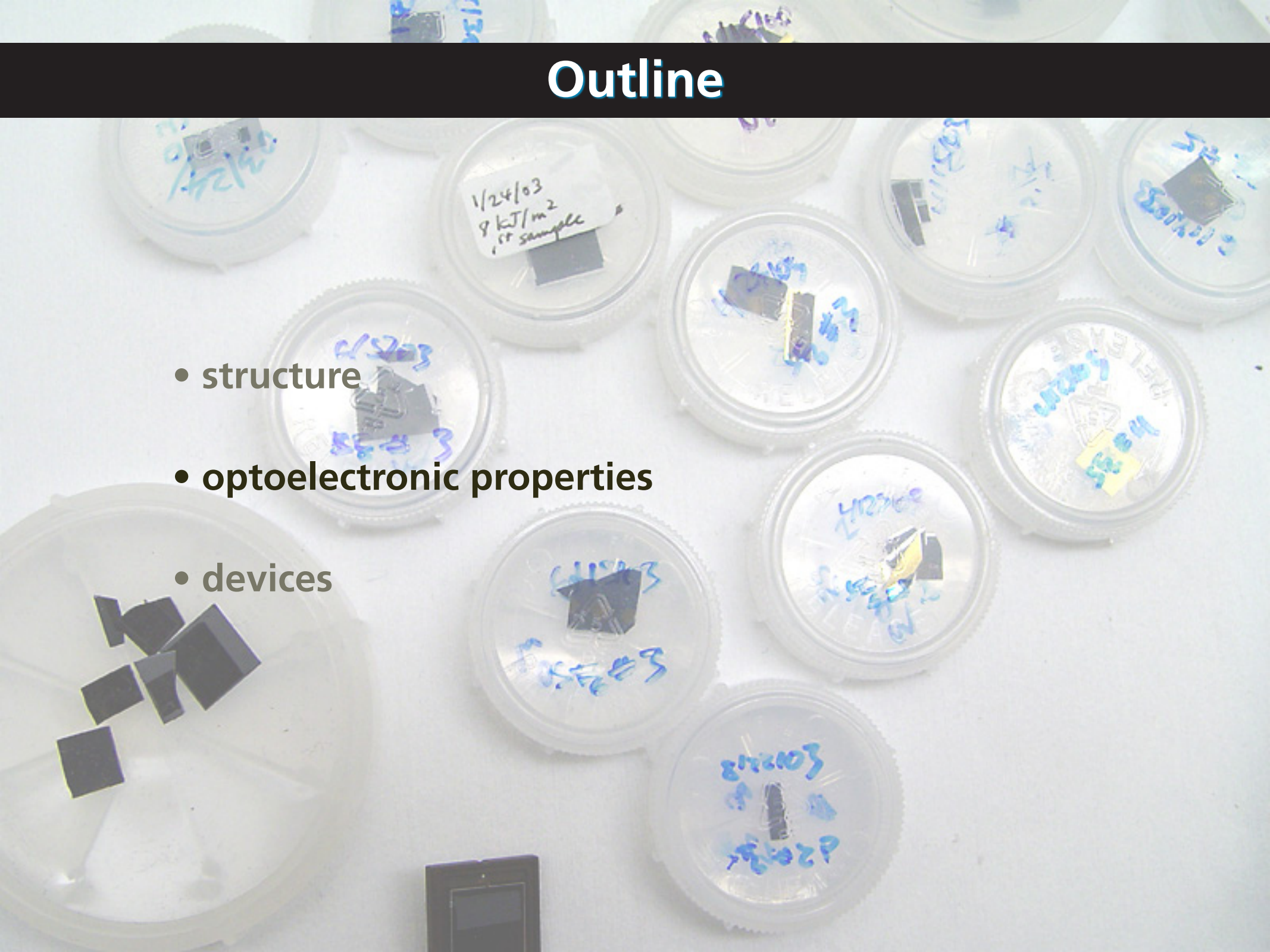
# Structure

## 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

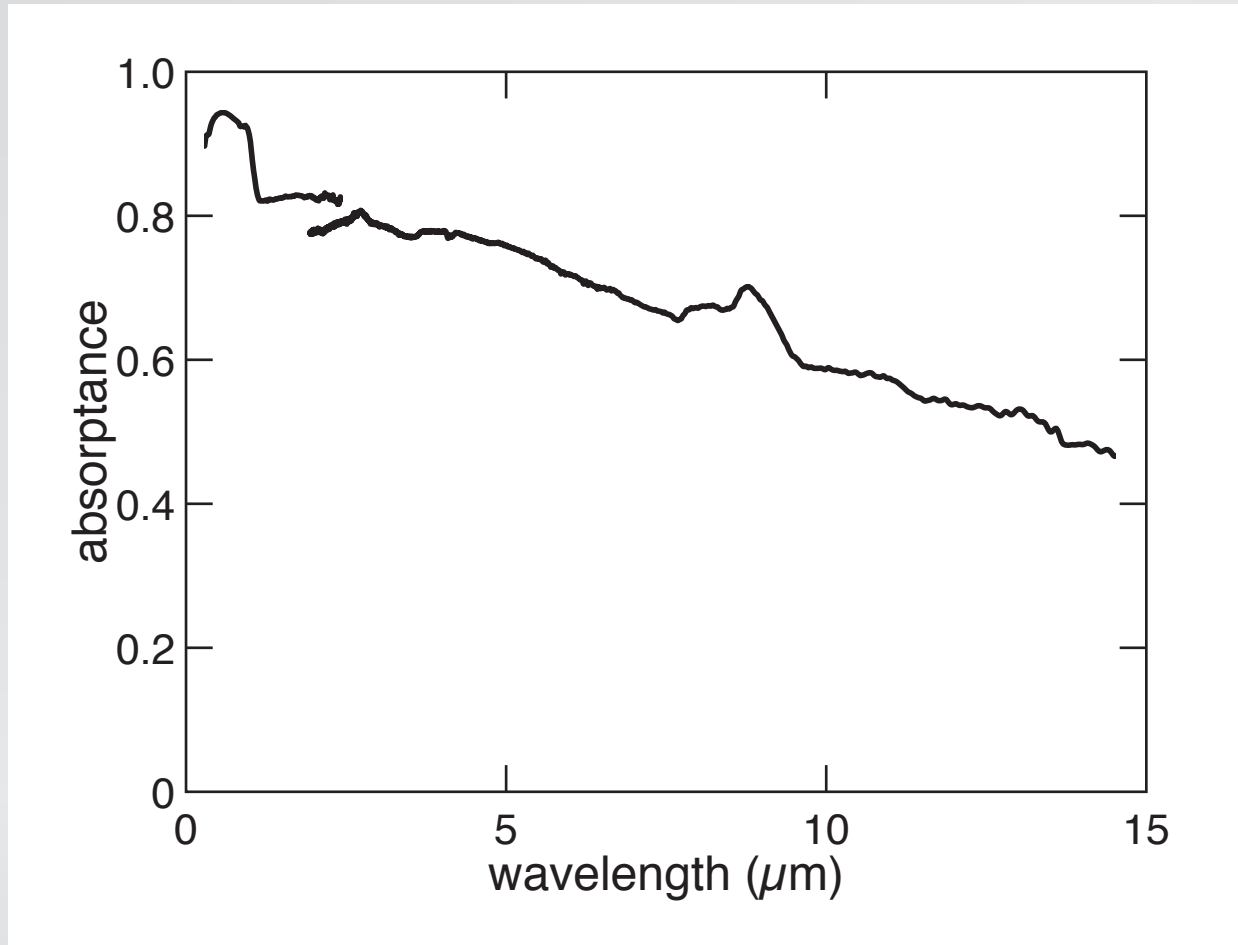
- structure
- optoelectronic properties
- devices





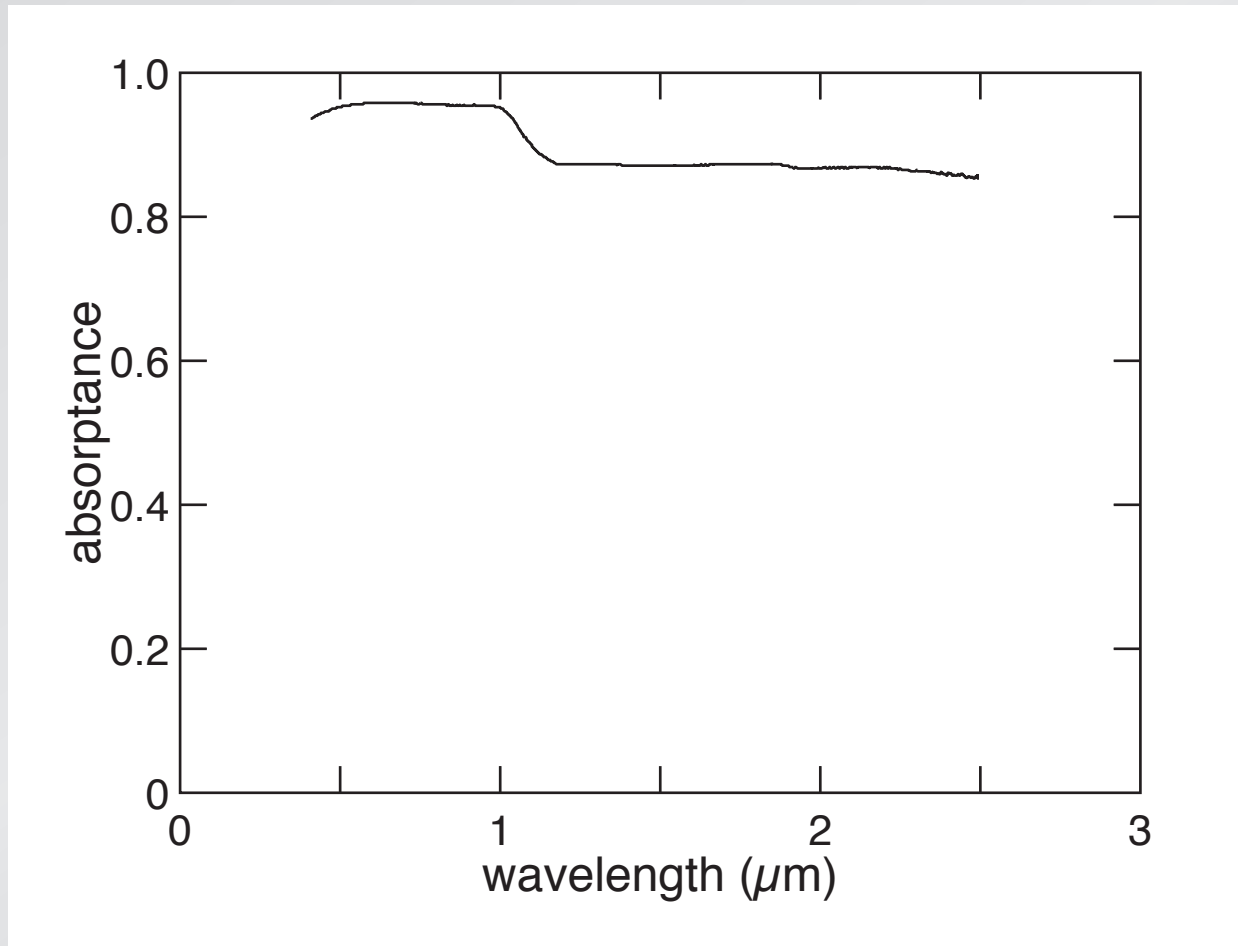
# Optoelectronic properties

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



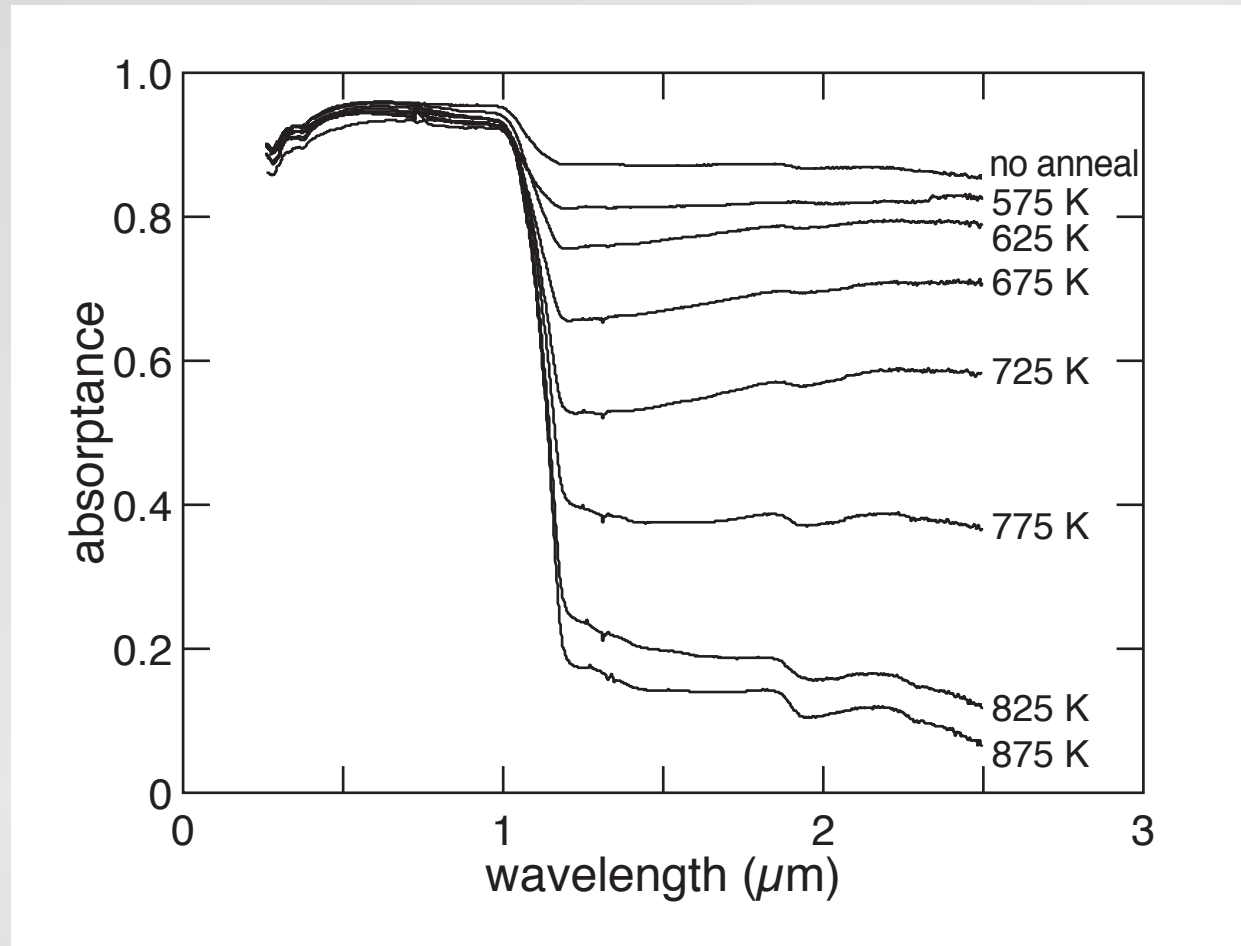
# Optoelectronic properties

effect of annealing on IR absorptance



# Optoelectronic properties

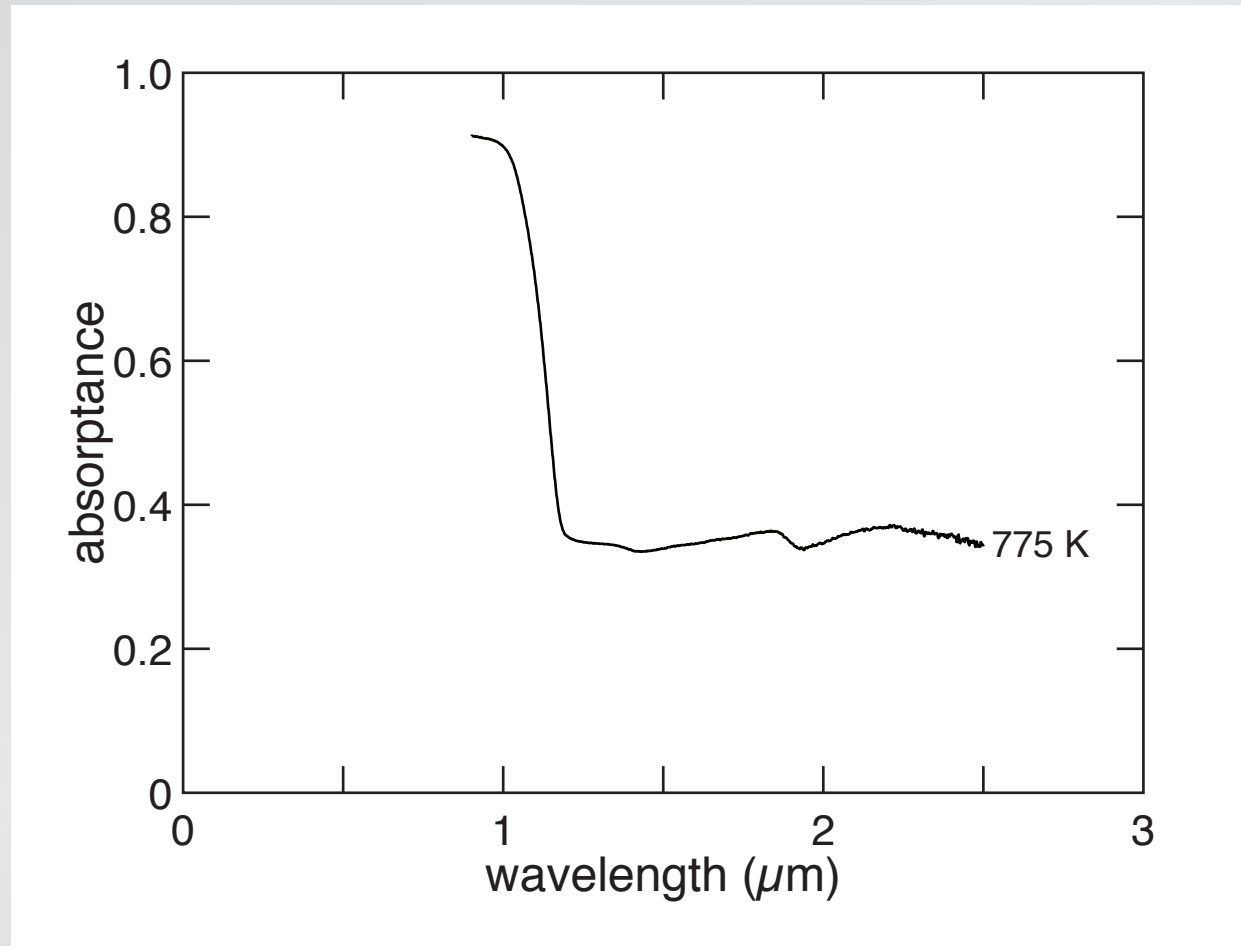
effect of annealing on IR absorptance





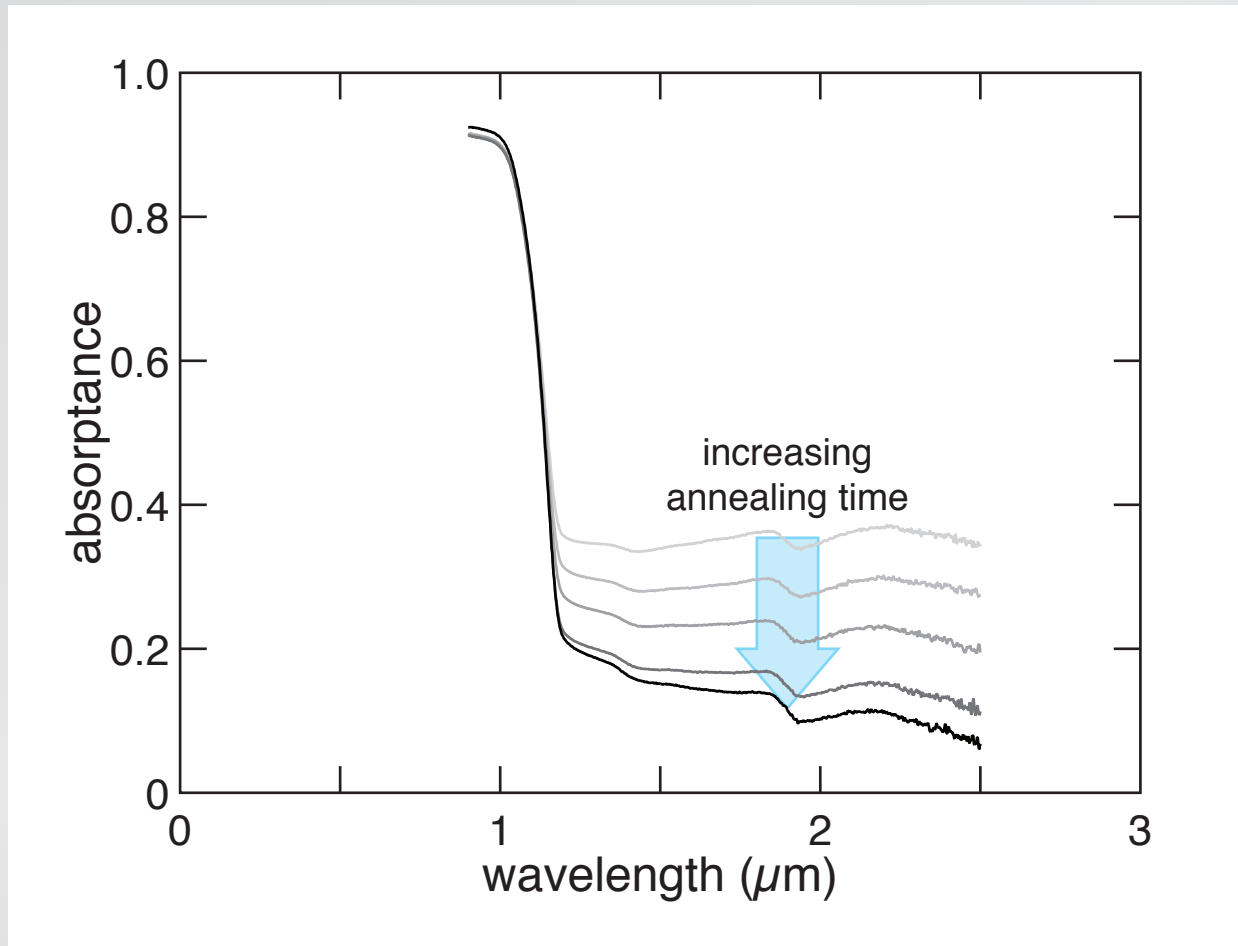
# Optoelectronic properties

vary annealing time



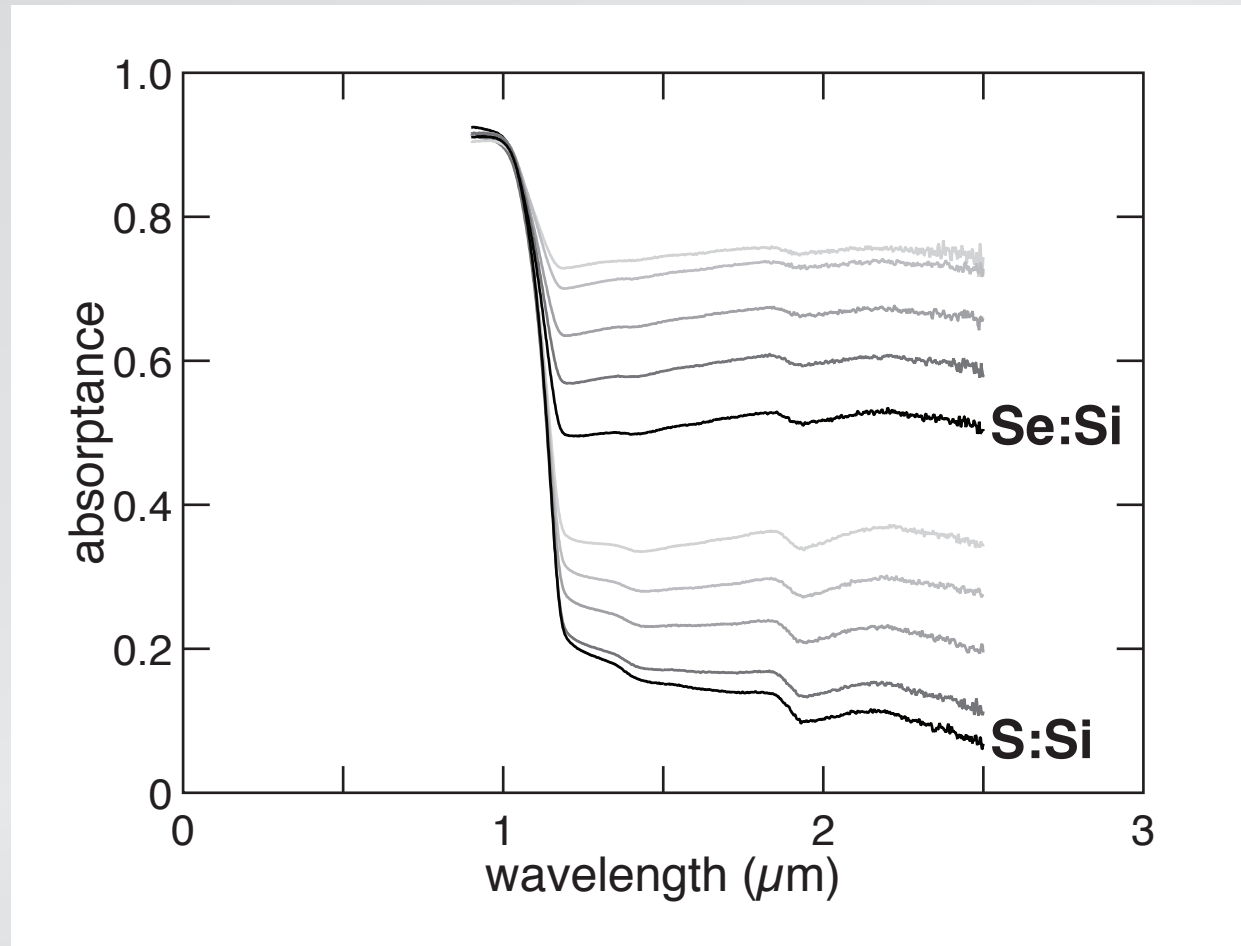
# Optoelectronic properties

longer annealing decreases IR absorptance



# Optoelectronic properties

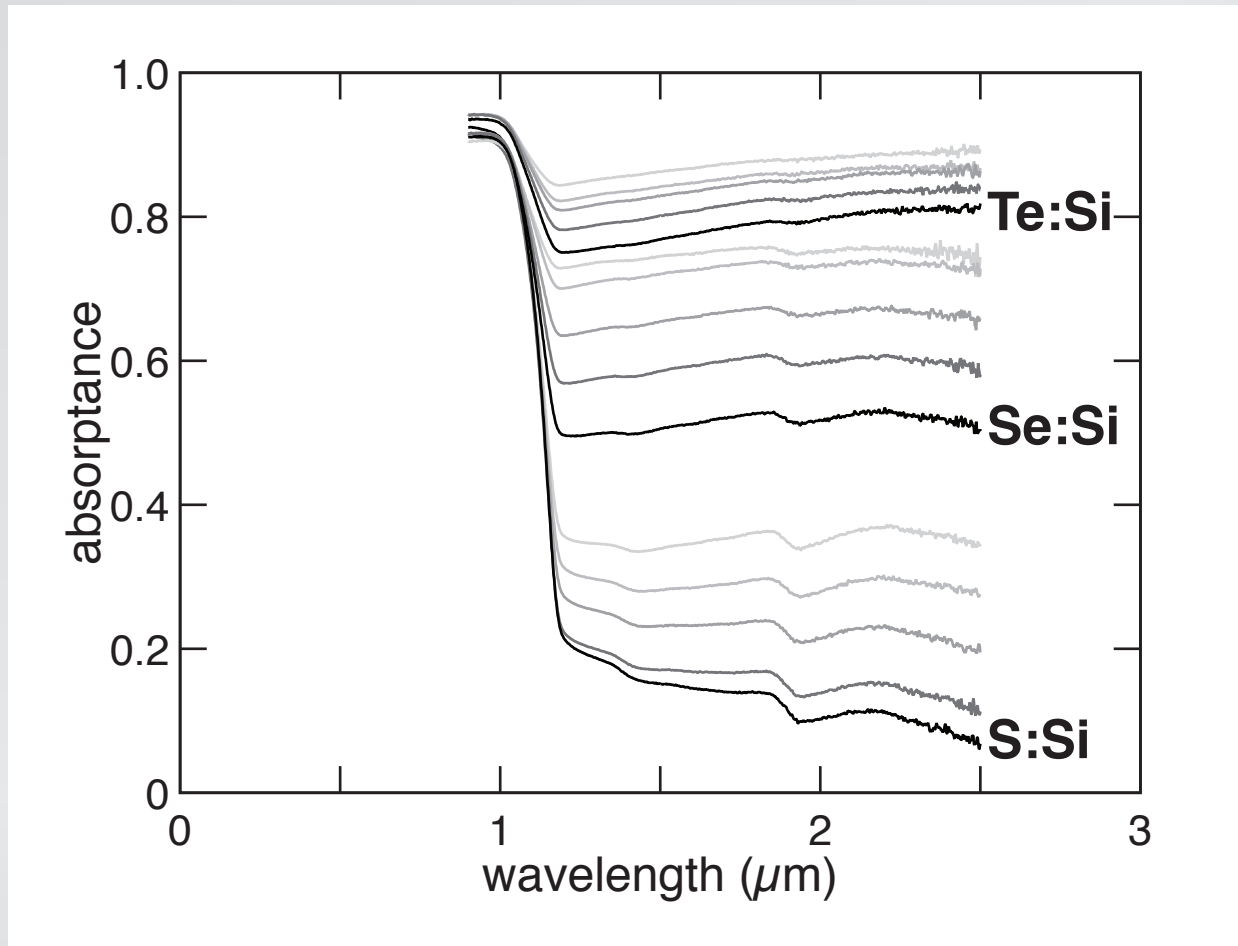
IR absorptance decreases less for Se-doped samples...





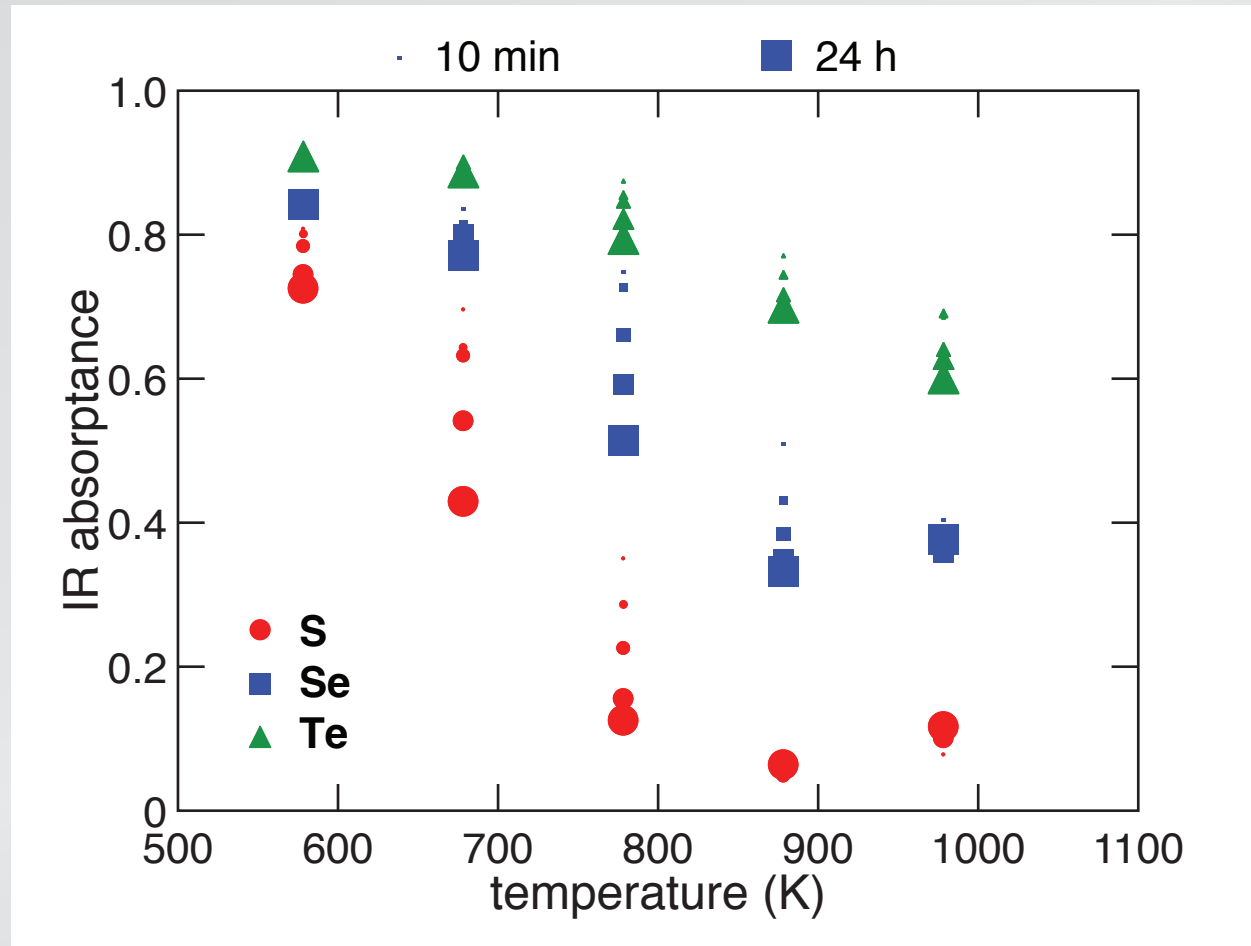
# Optoelectronic properties

and even less for Te-doped samples...



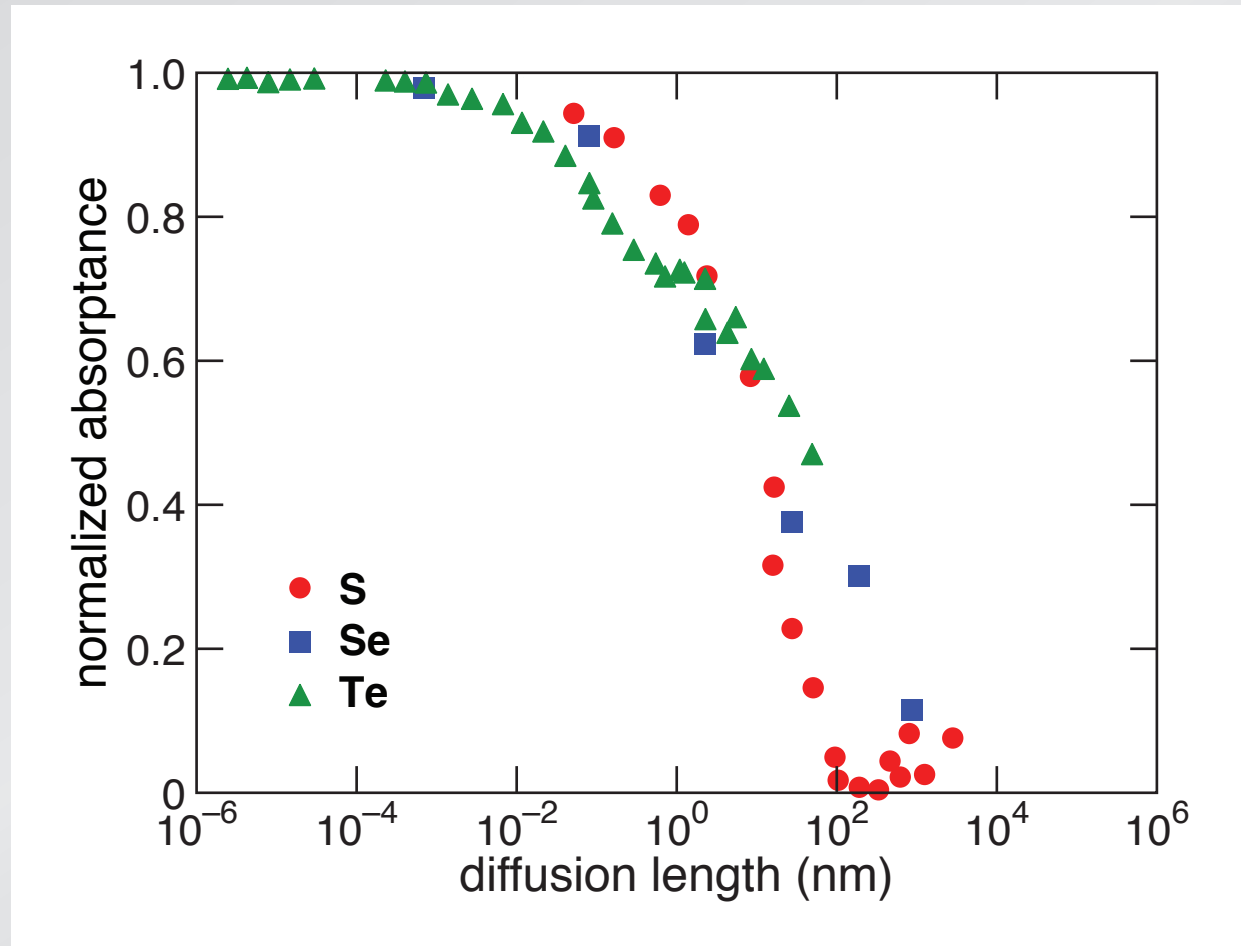
# Optoelectronic properties

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

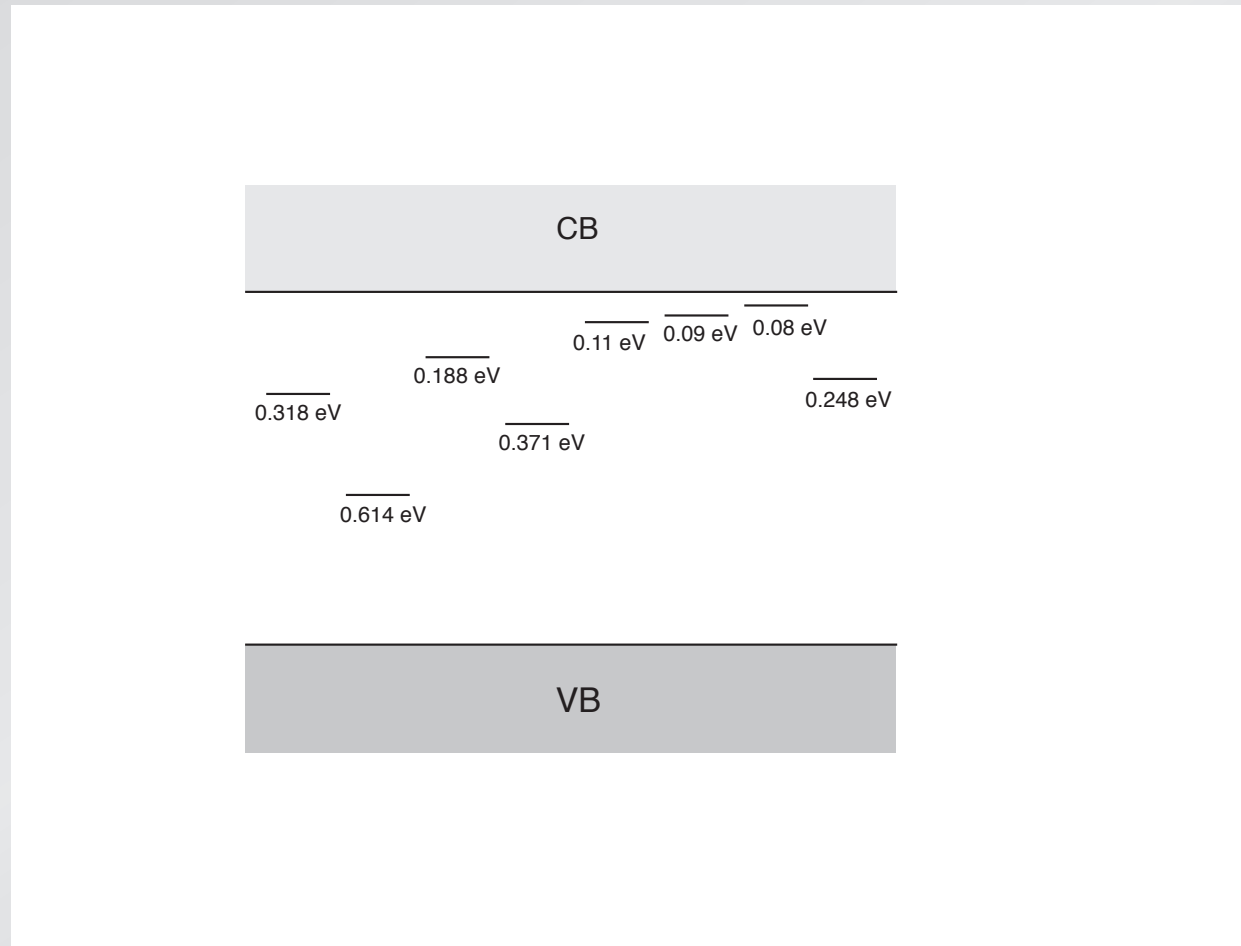


# Optoelectronic properties

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

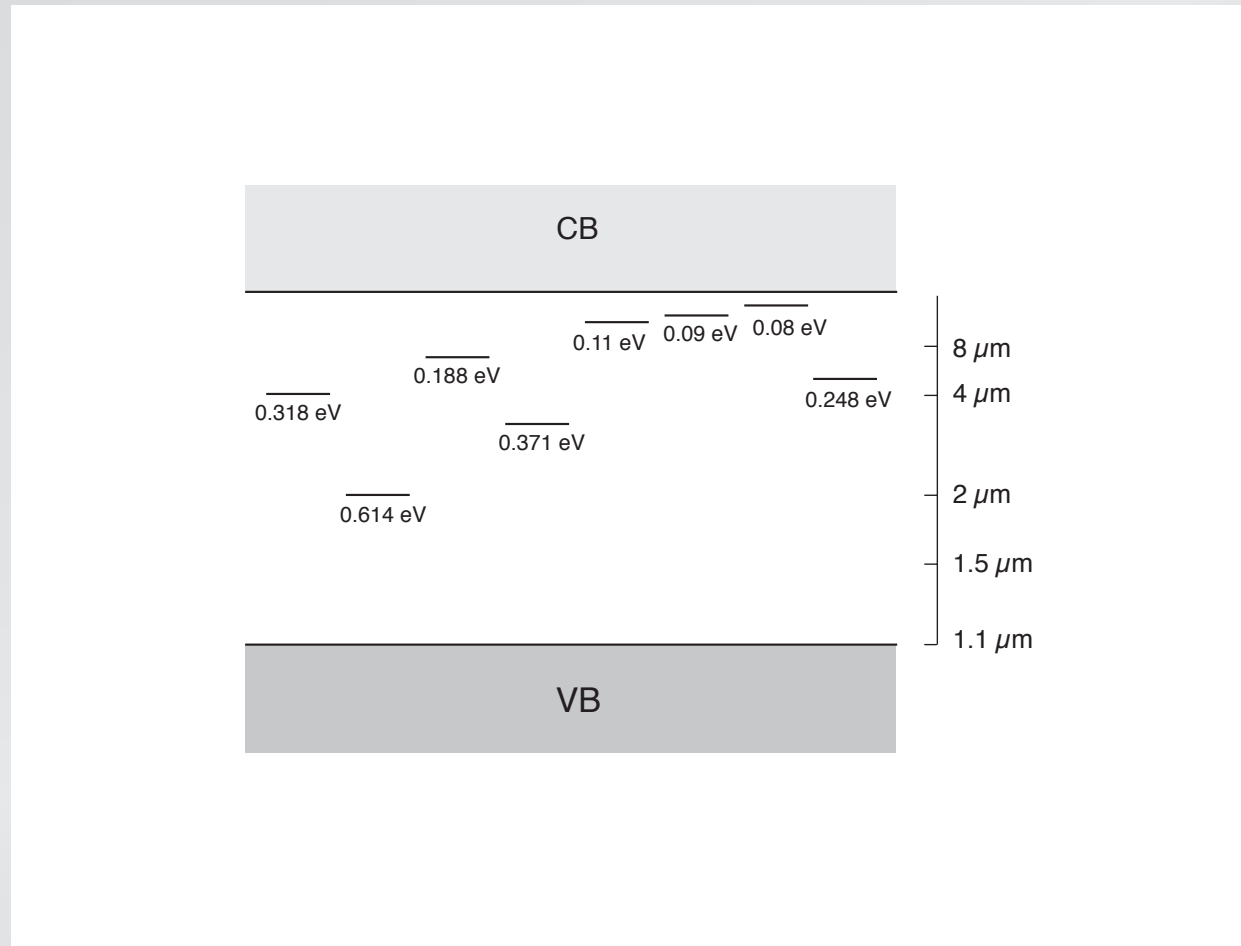
# Optoelectronic properties

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



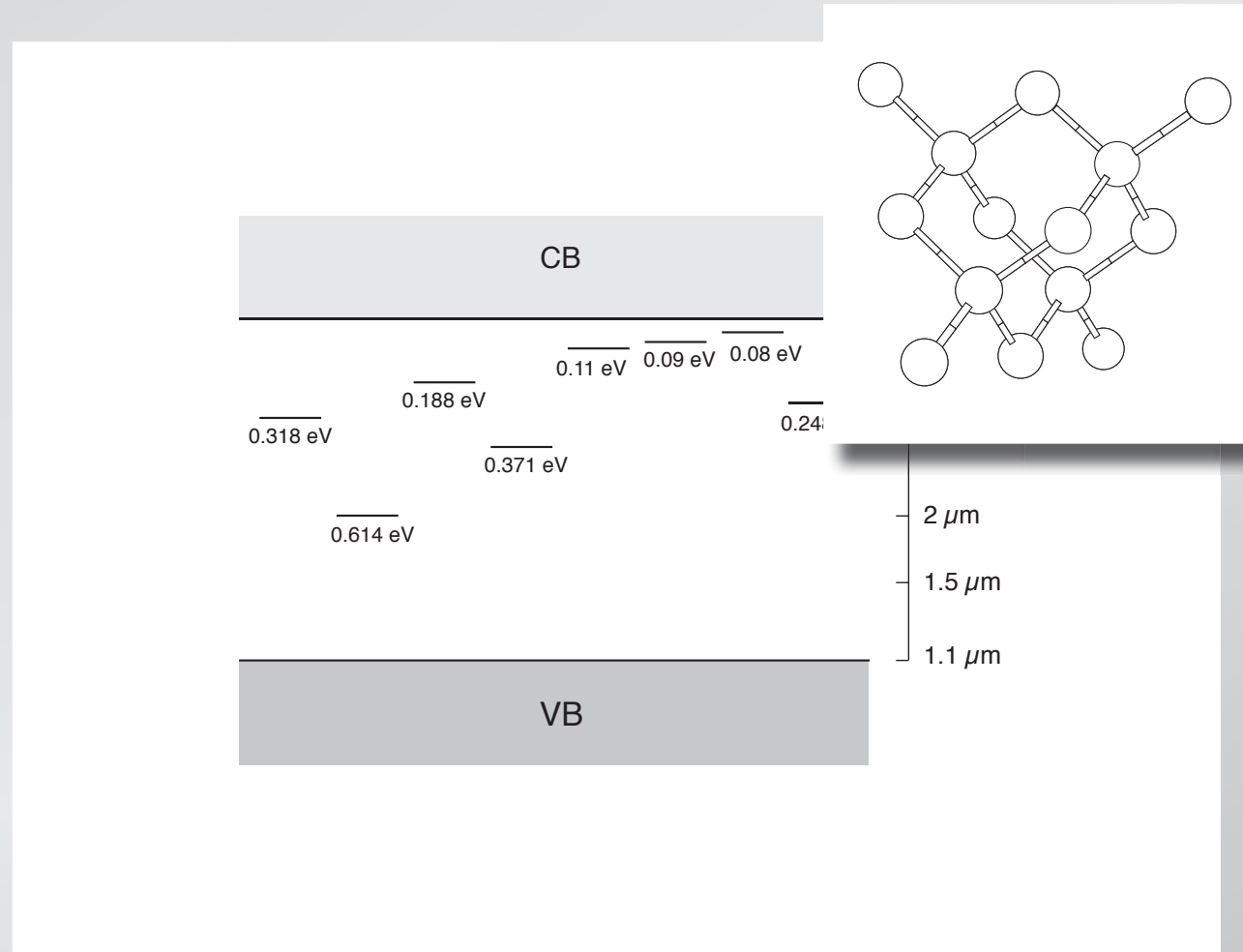
# Optoelectronic properties

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



# Optoelectronic properties

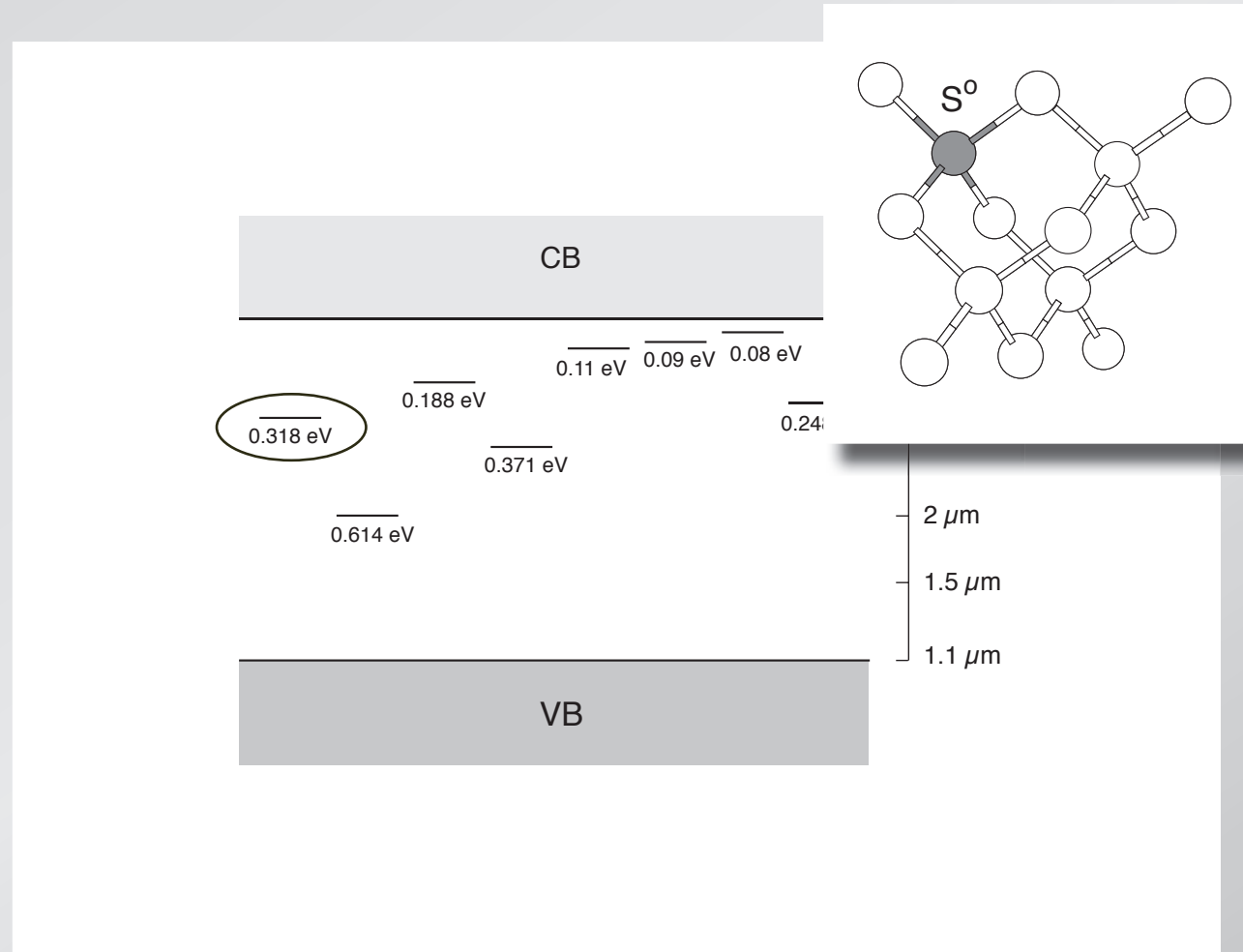
1 part in  $10^6$  sulfur introduces donor states in gap





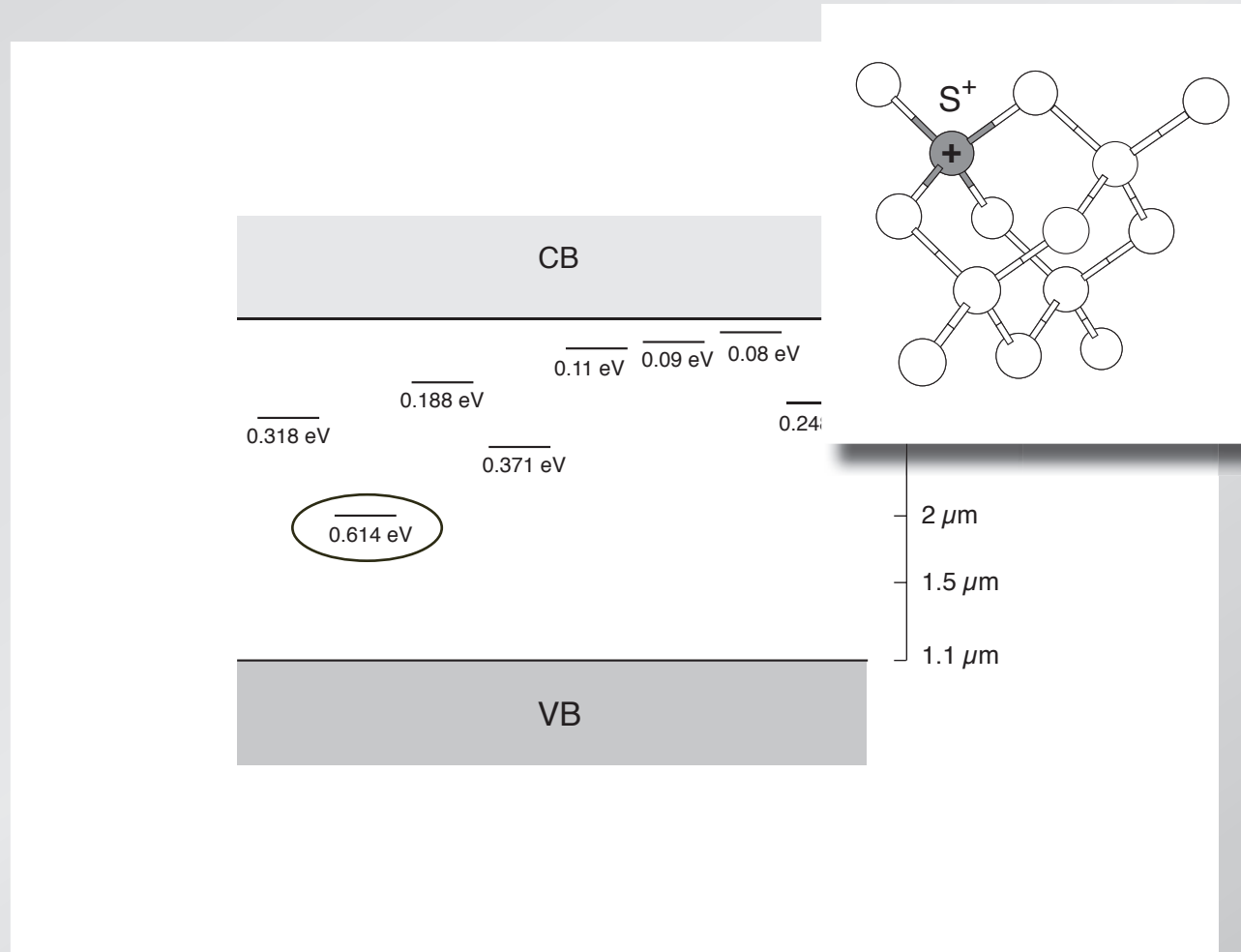
# Optoelectronic properties

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



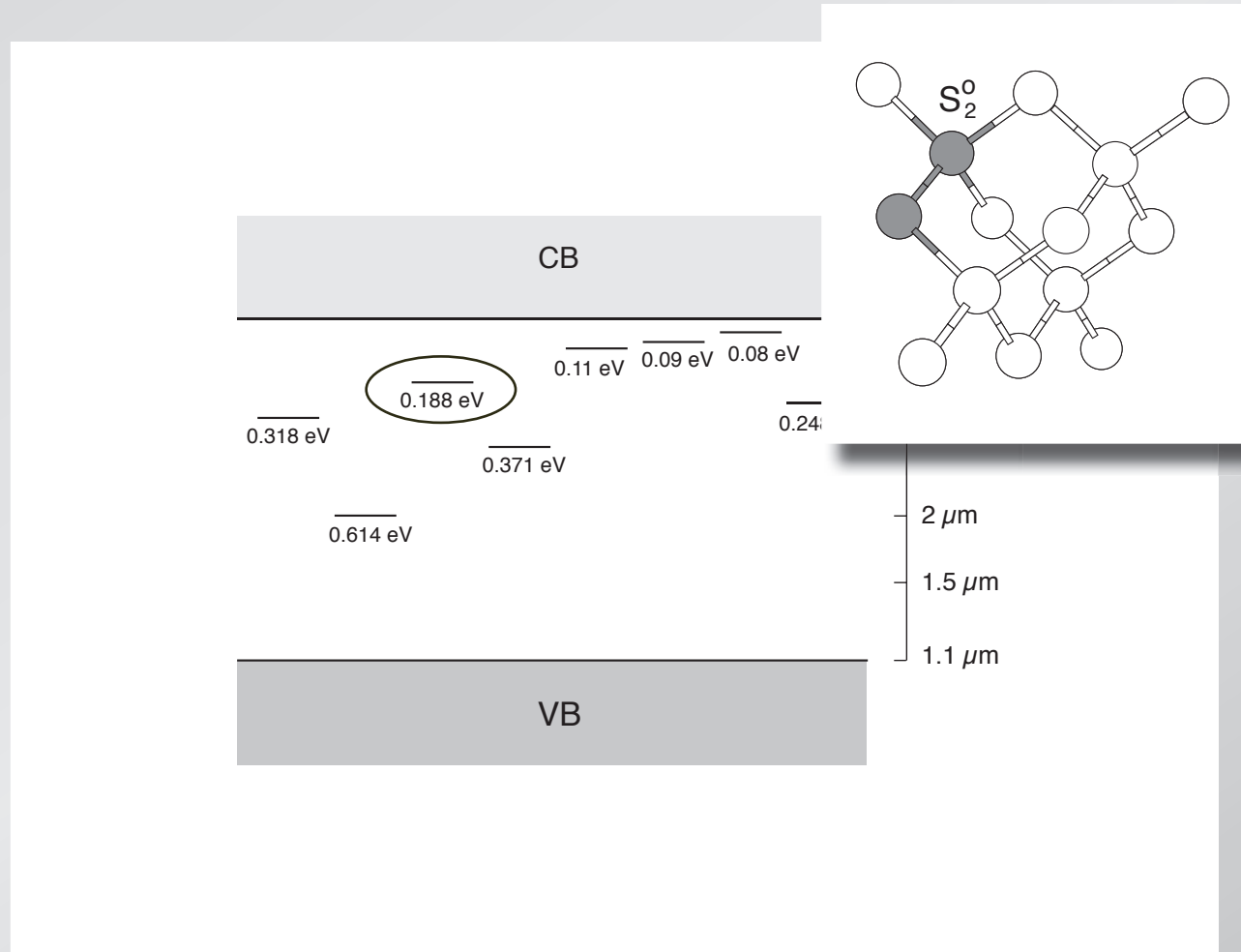
# Optoelectronic properties

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



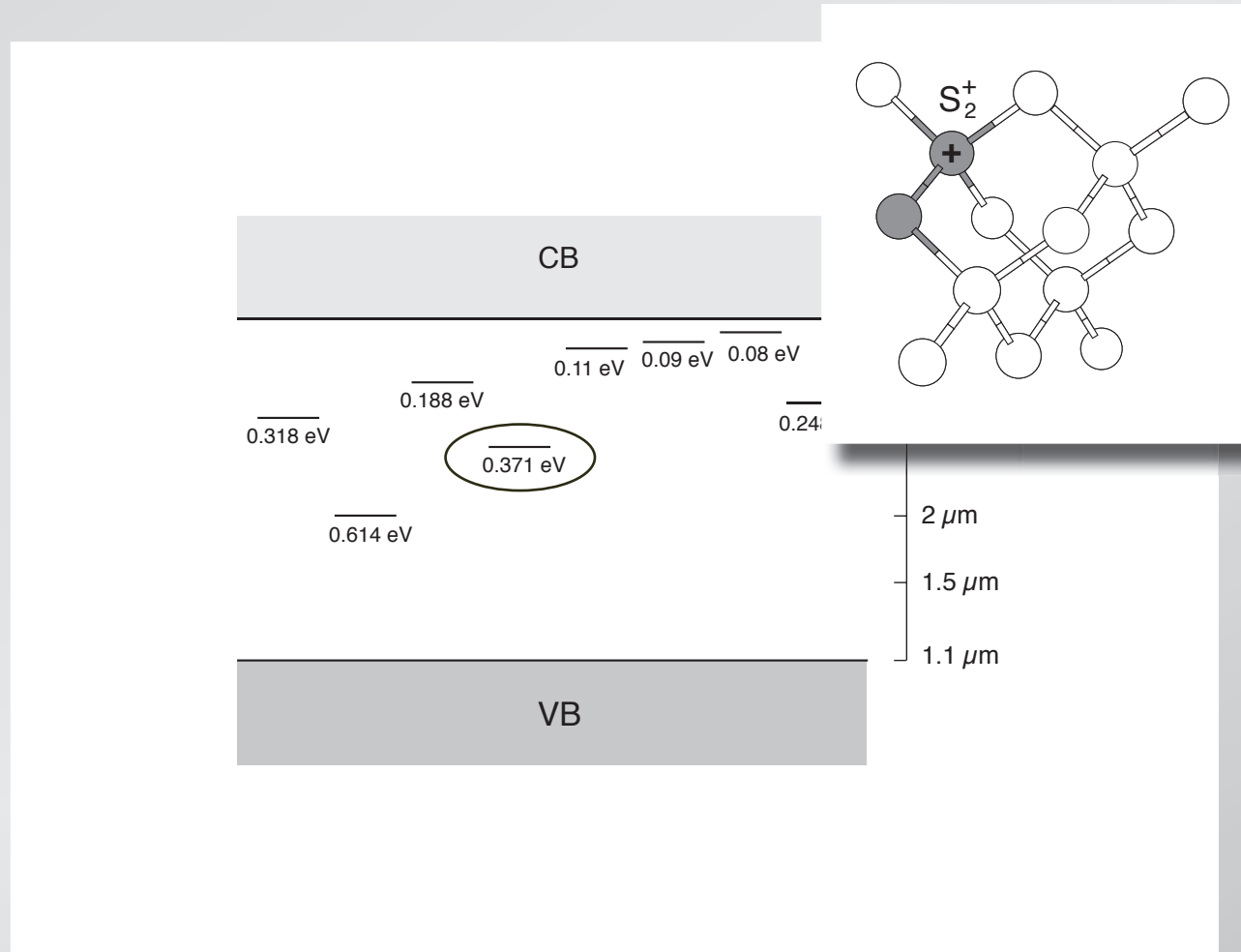
# Optoelectronic properties

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



# Optoelectronic properties

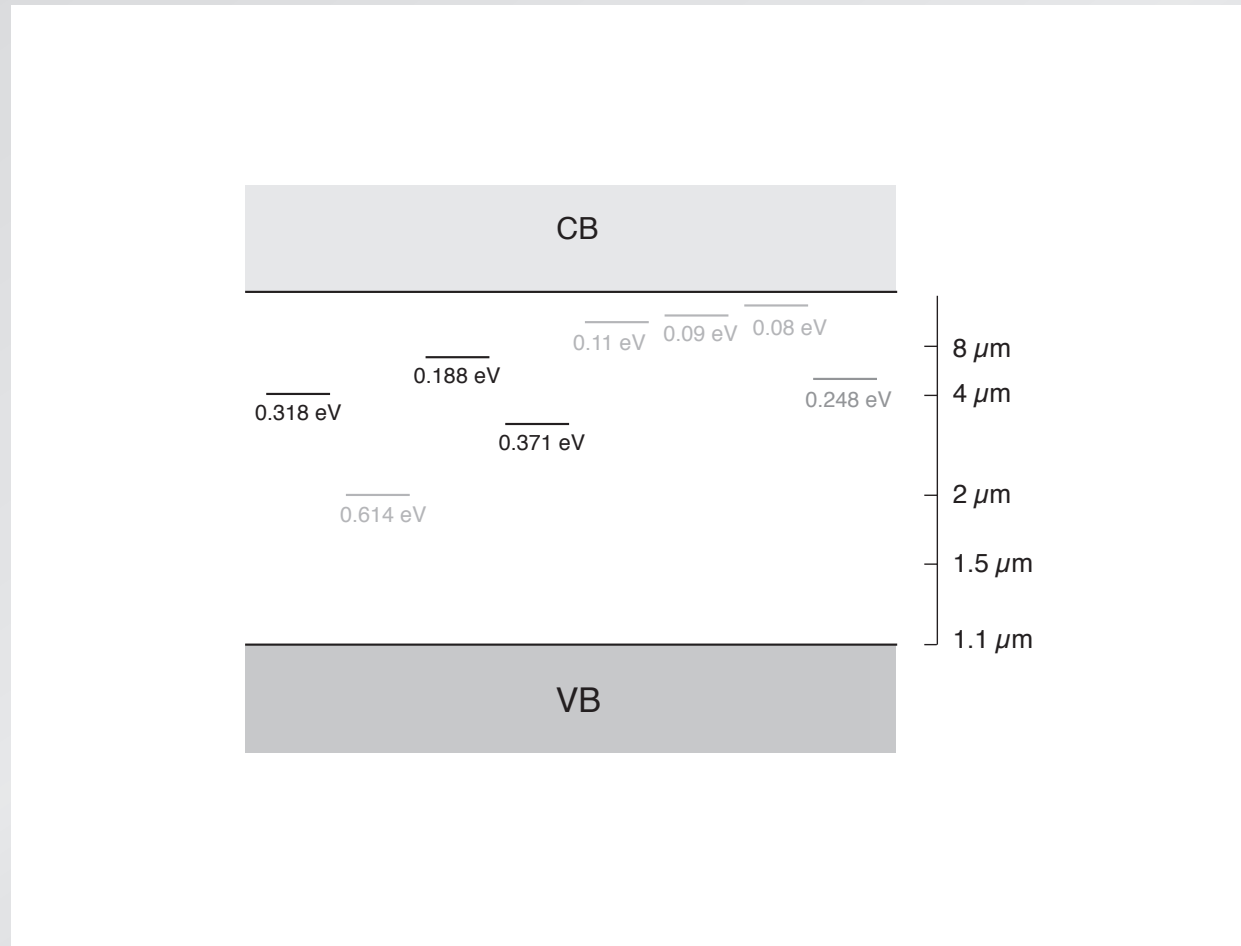
1 part in  $10^6$  sulfur introduces donor states in gap





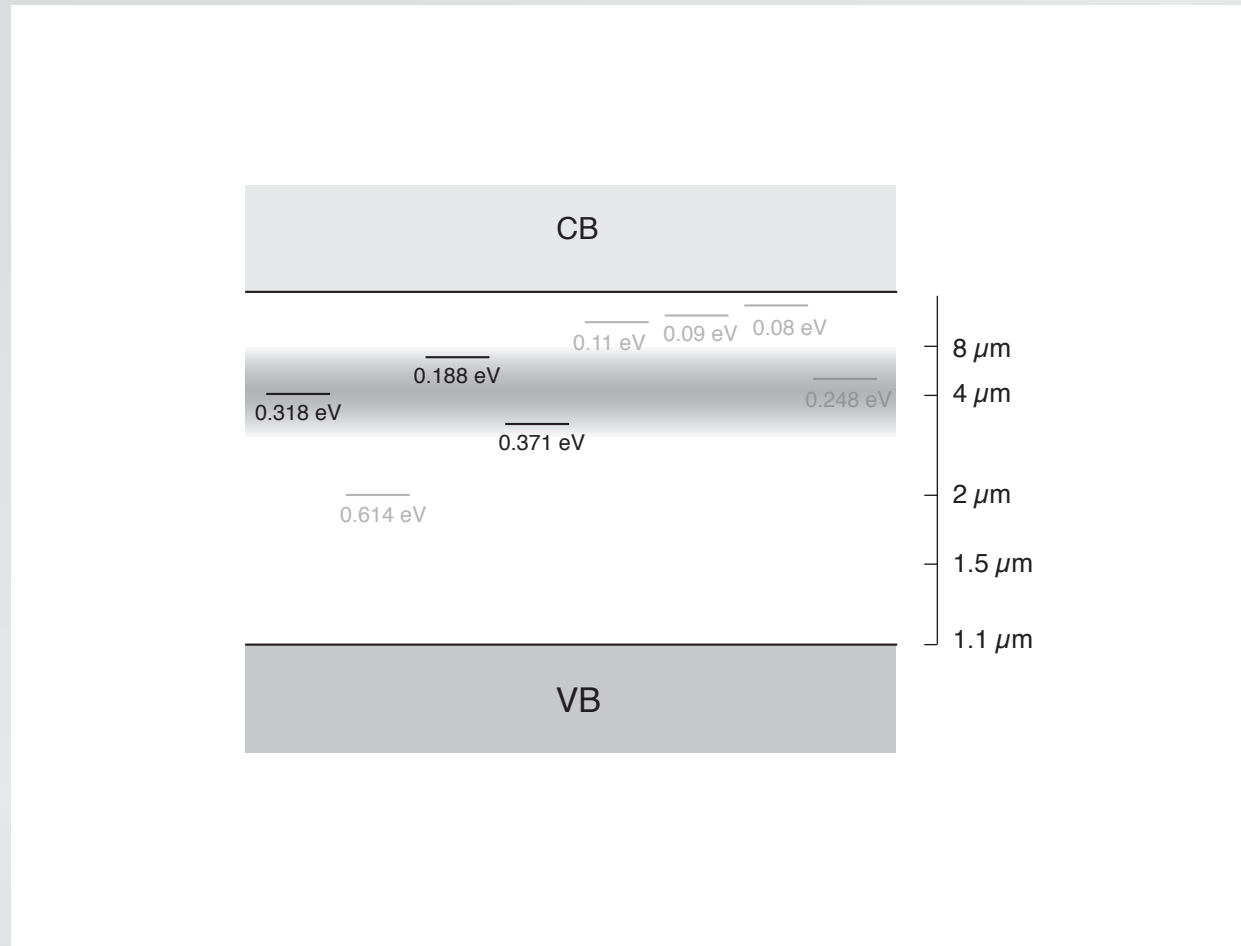
# Optoelectronic properties

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



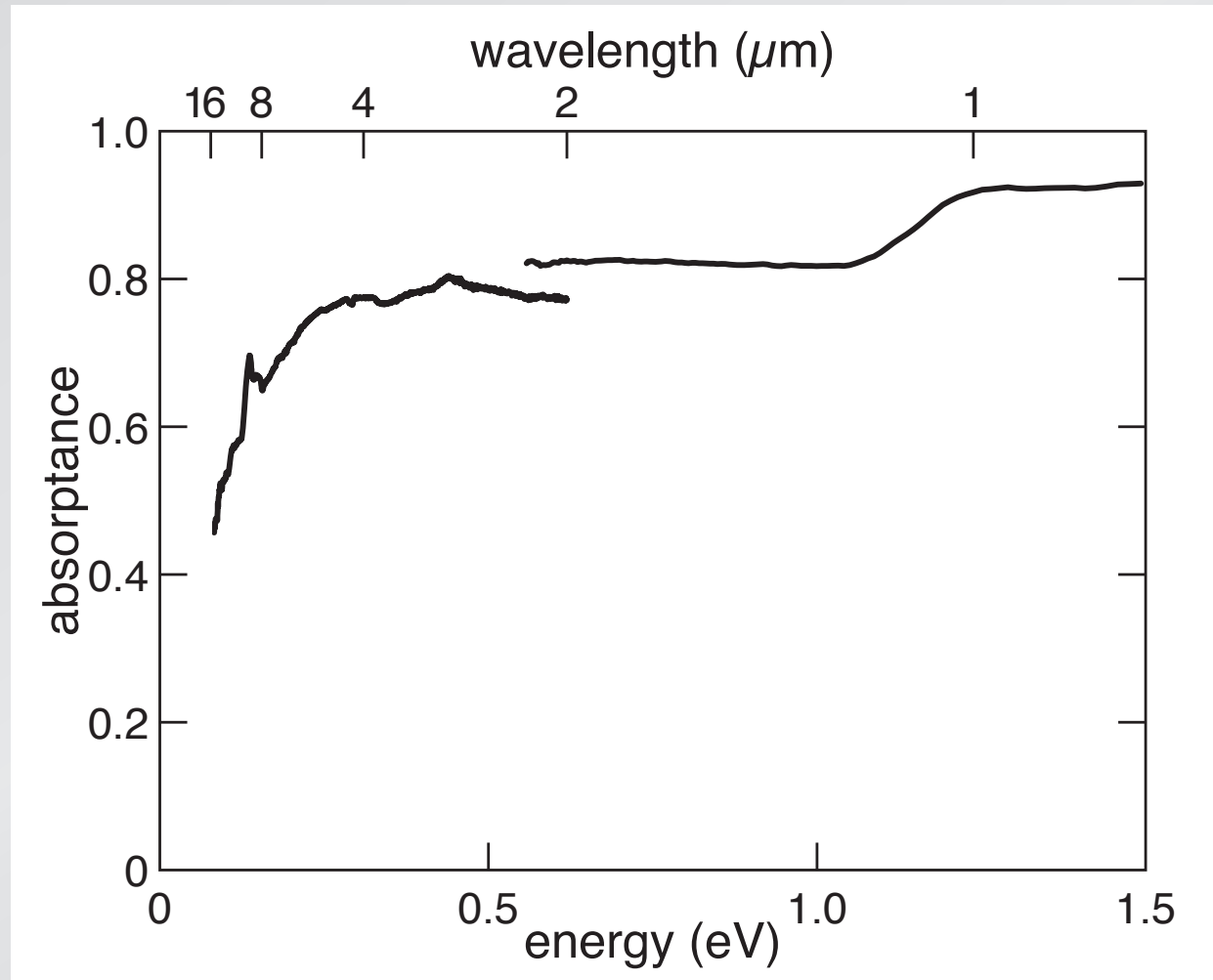
# Optoelectronic properties

at high concentration states broaden into band



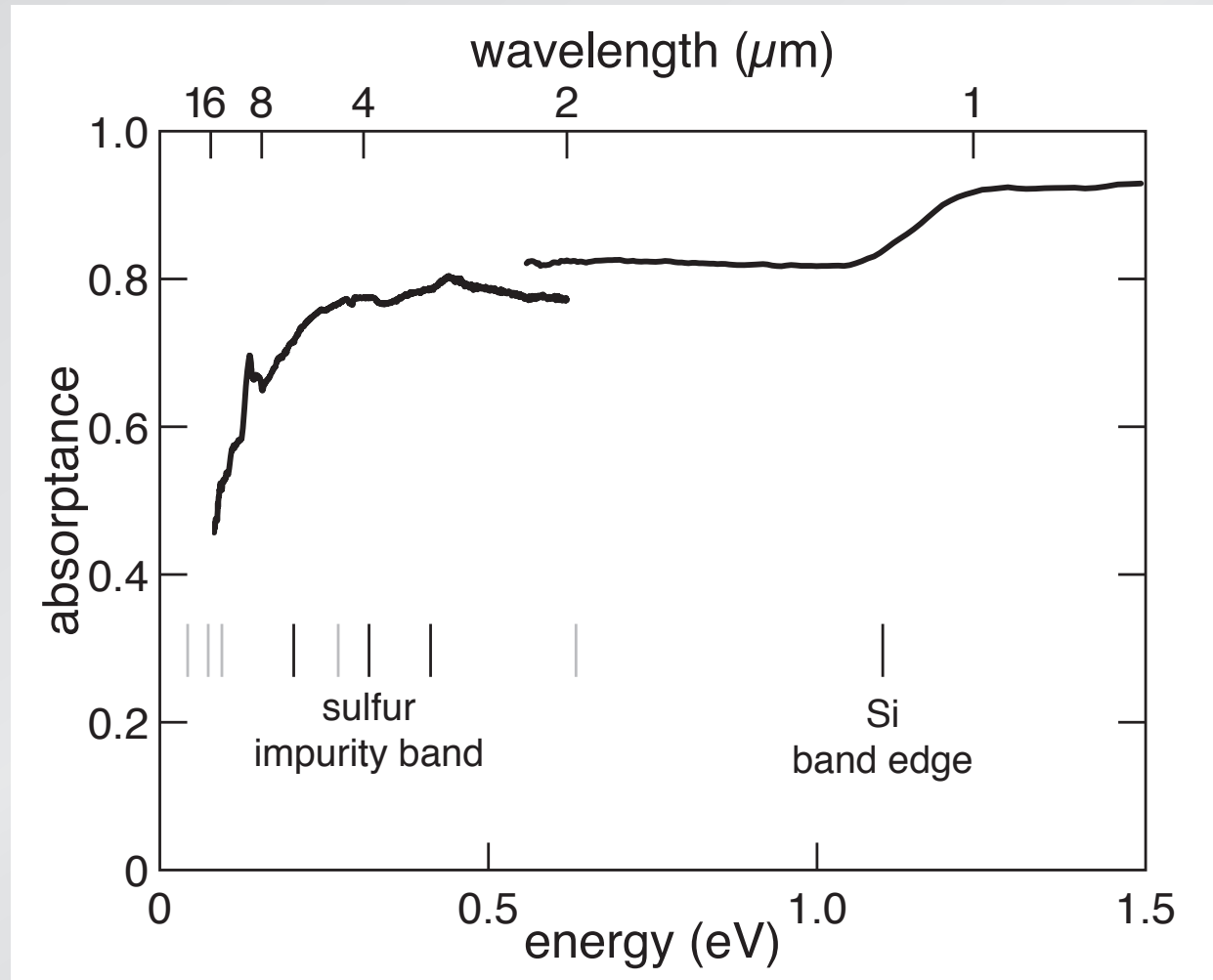
# Optoelectronic properties

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



# Optoelectronic properties

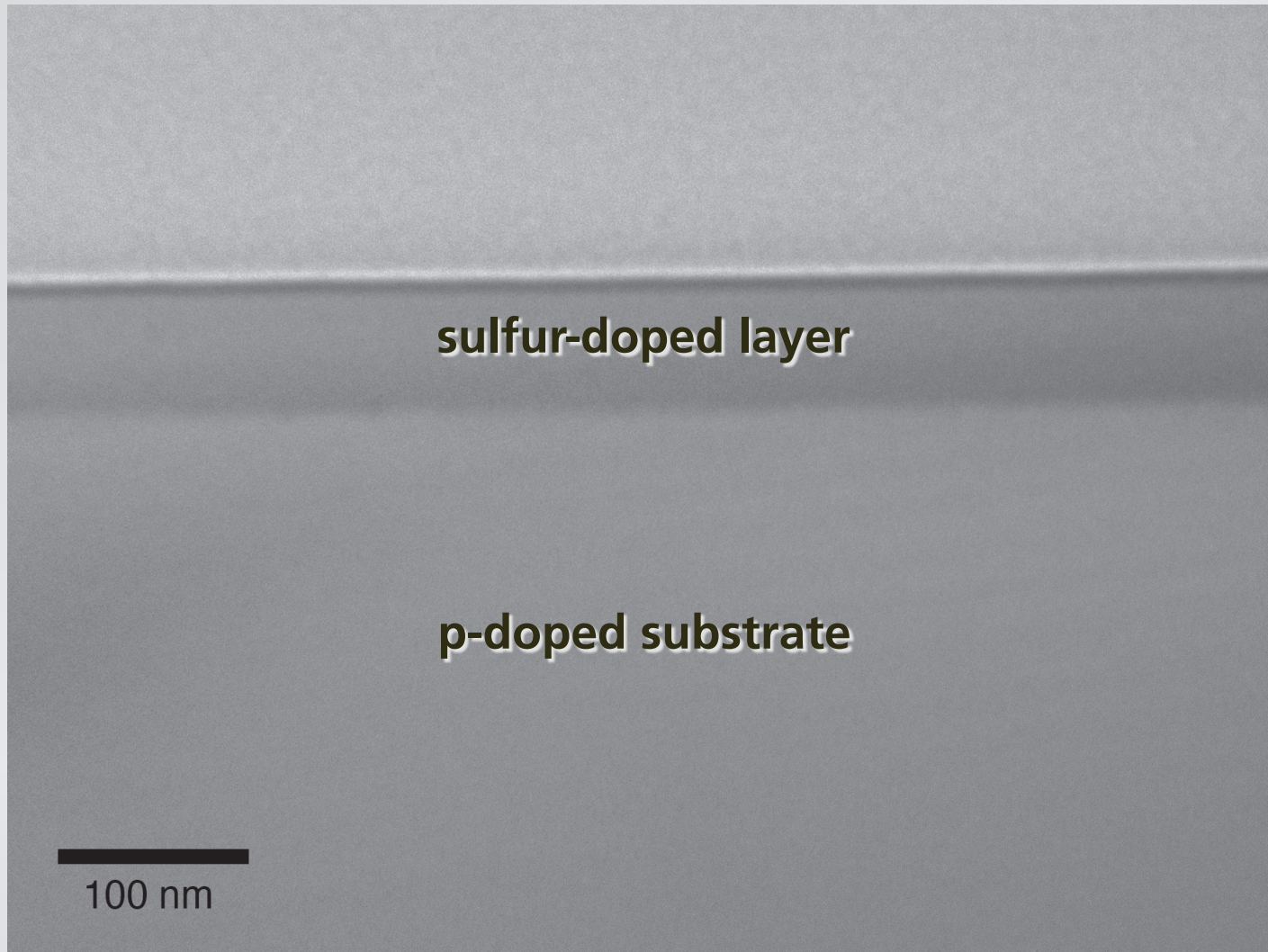
absorptance ( $1 - R_{int} - T_{int}$ )





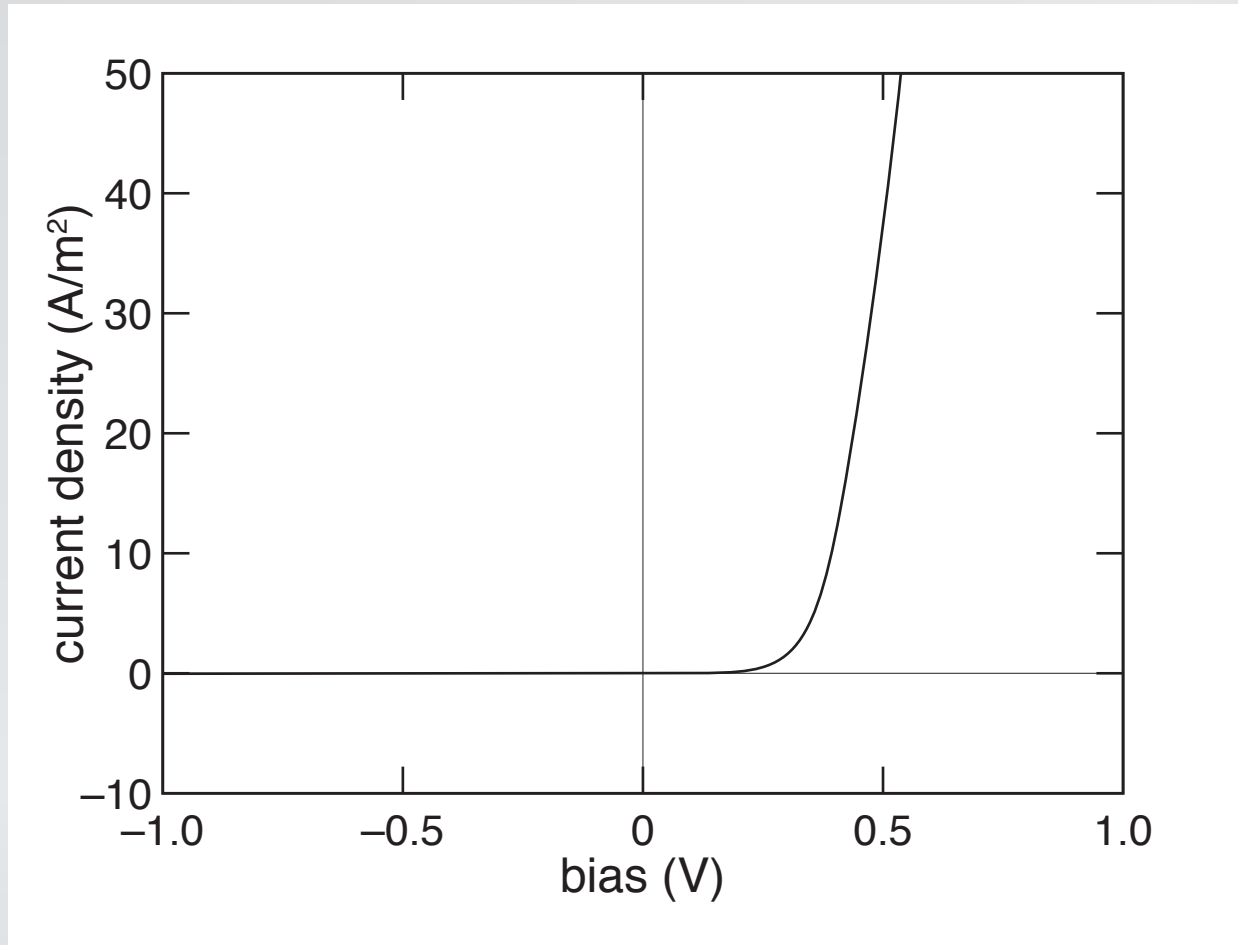
# Optoelectronic properties

should have shallow junction below surface



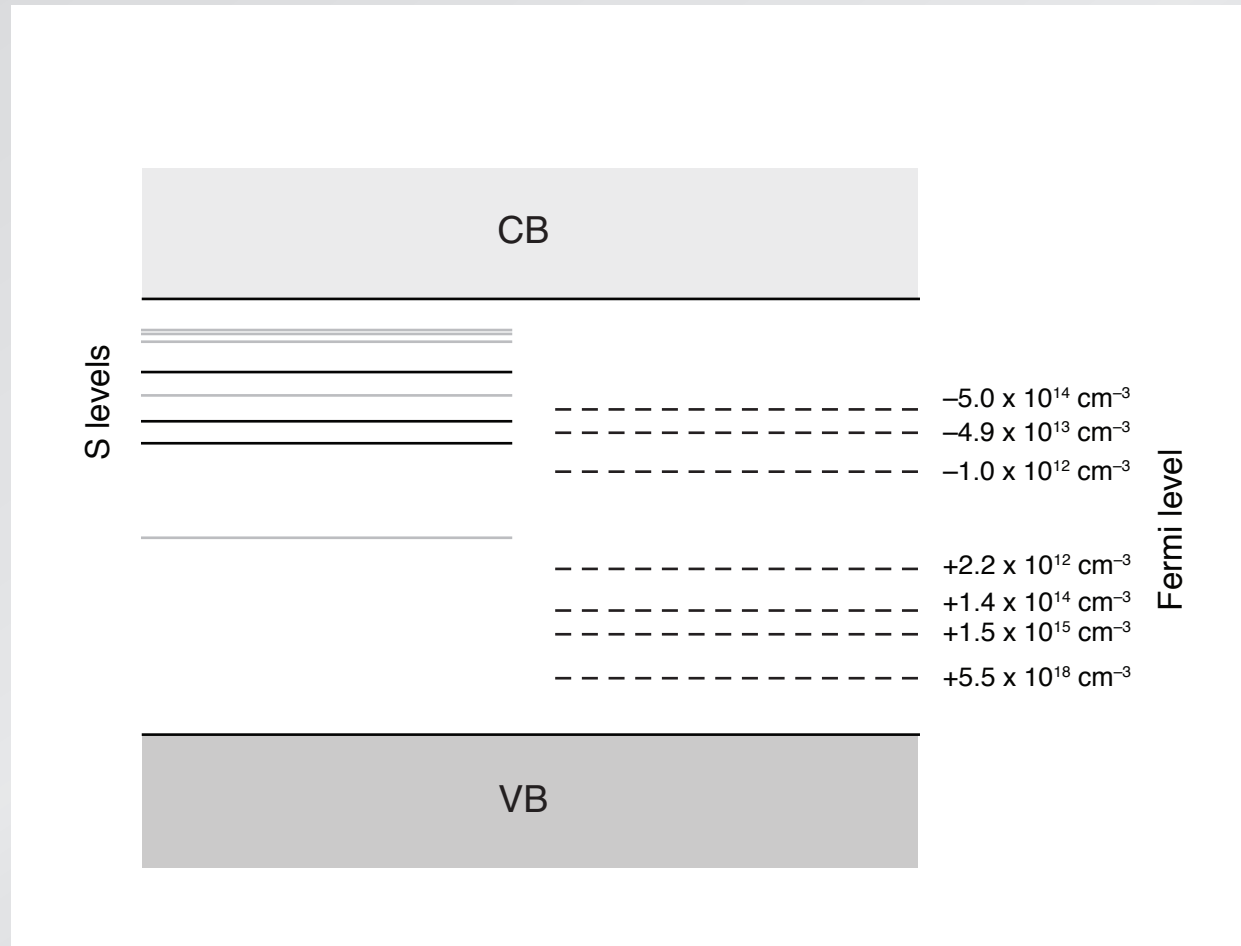
# Optoelectronic properties

excellent rectification (after annealing)



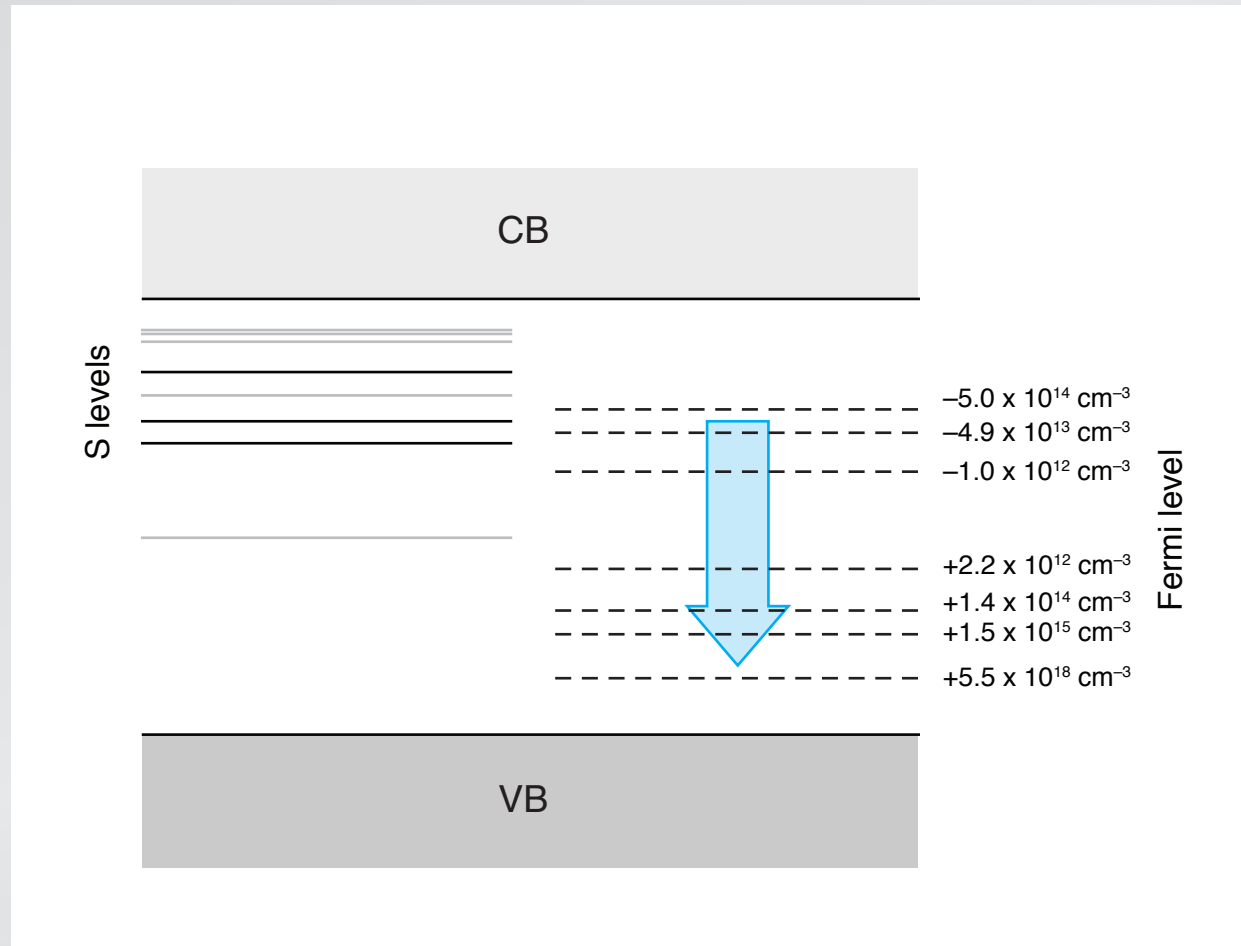
# Optoelectronic properties

probe impurity states by varying Fermi level in substrate



# Optoelectronic properties

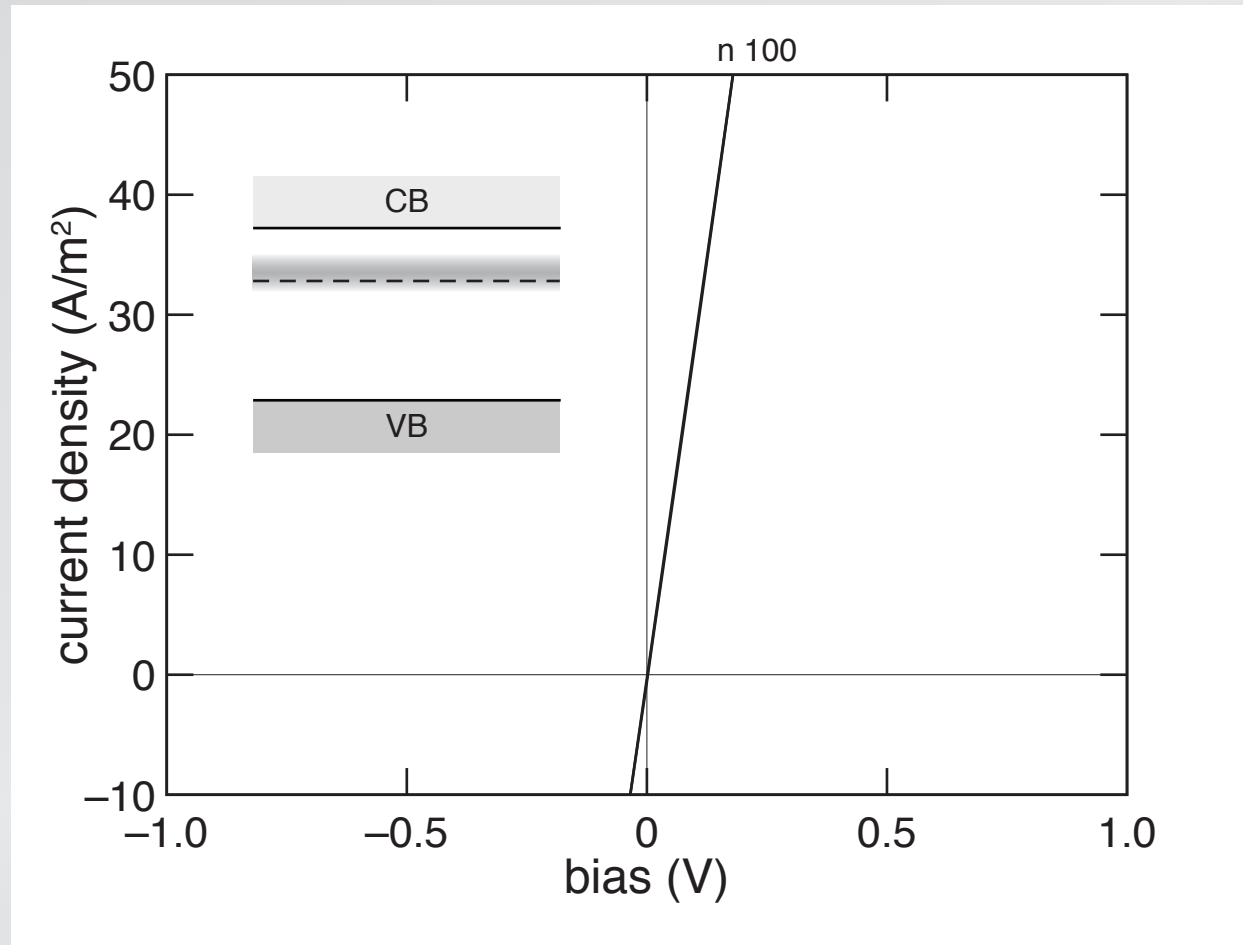
probe impurity states by varying Fermi level in substrate





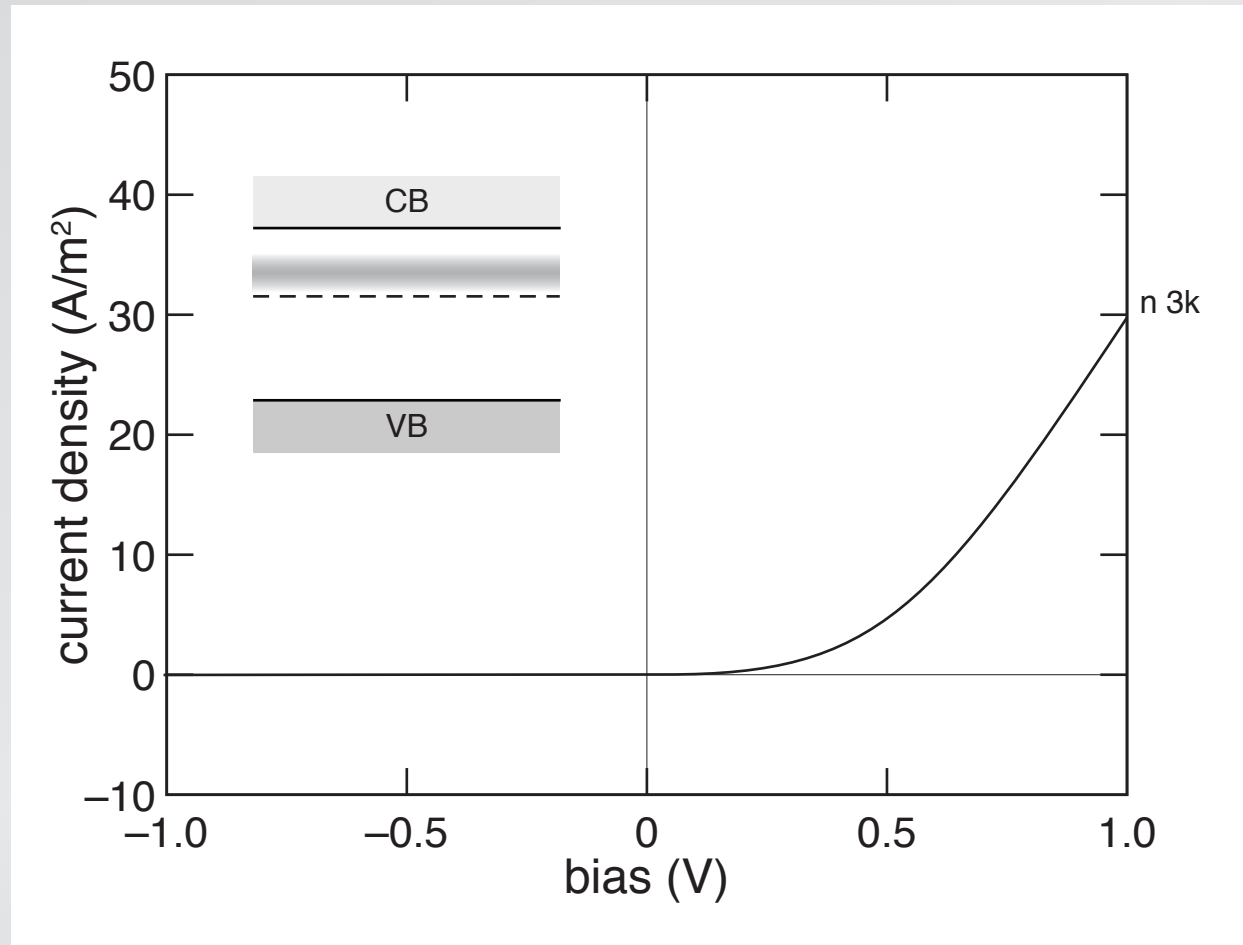
# Optoelectronic properties

vary substrate doping type and resistivity



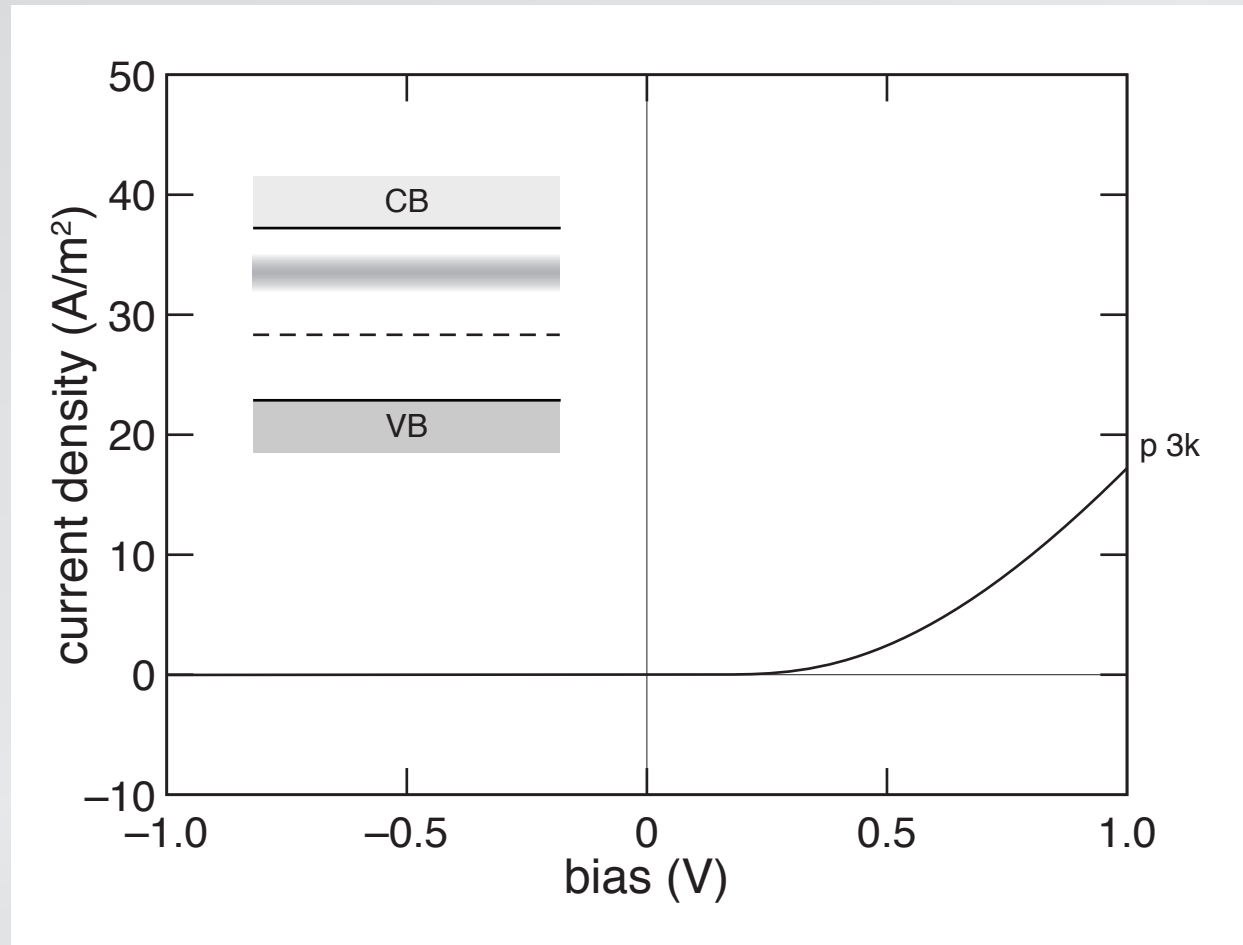
# Optoelectronic properties

vary substrate doping type and resistivity



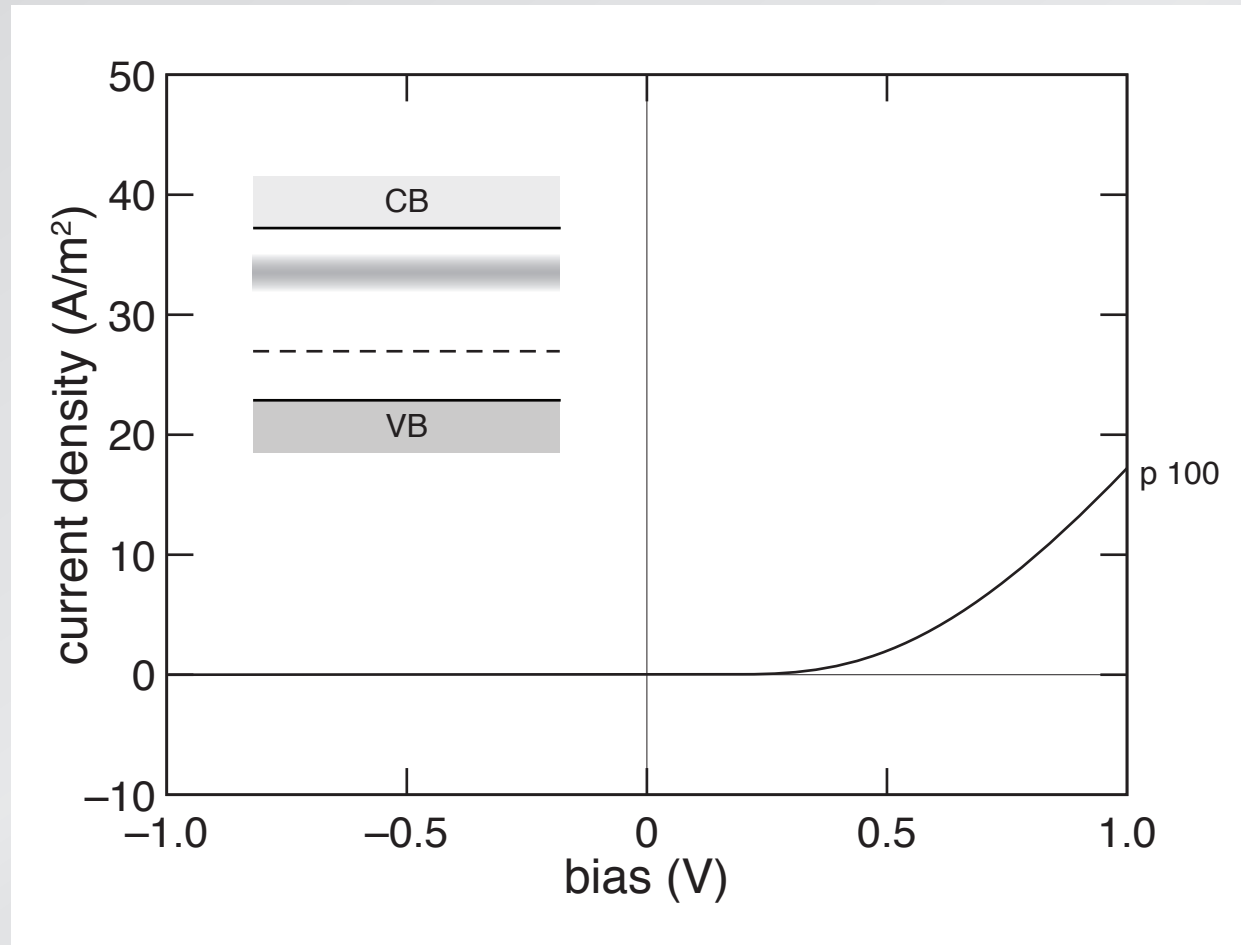
# Optoelectronic properties

vary substrate doping type and resistivity



# Optoelectronic properties

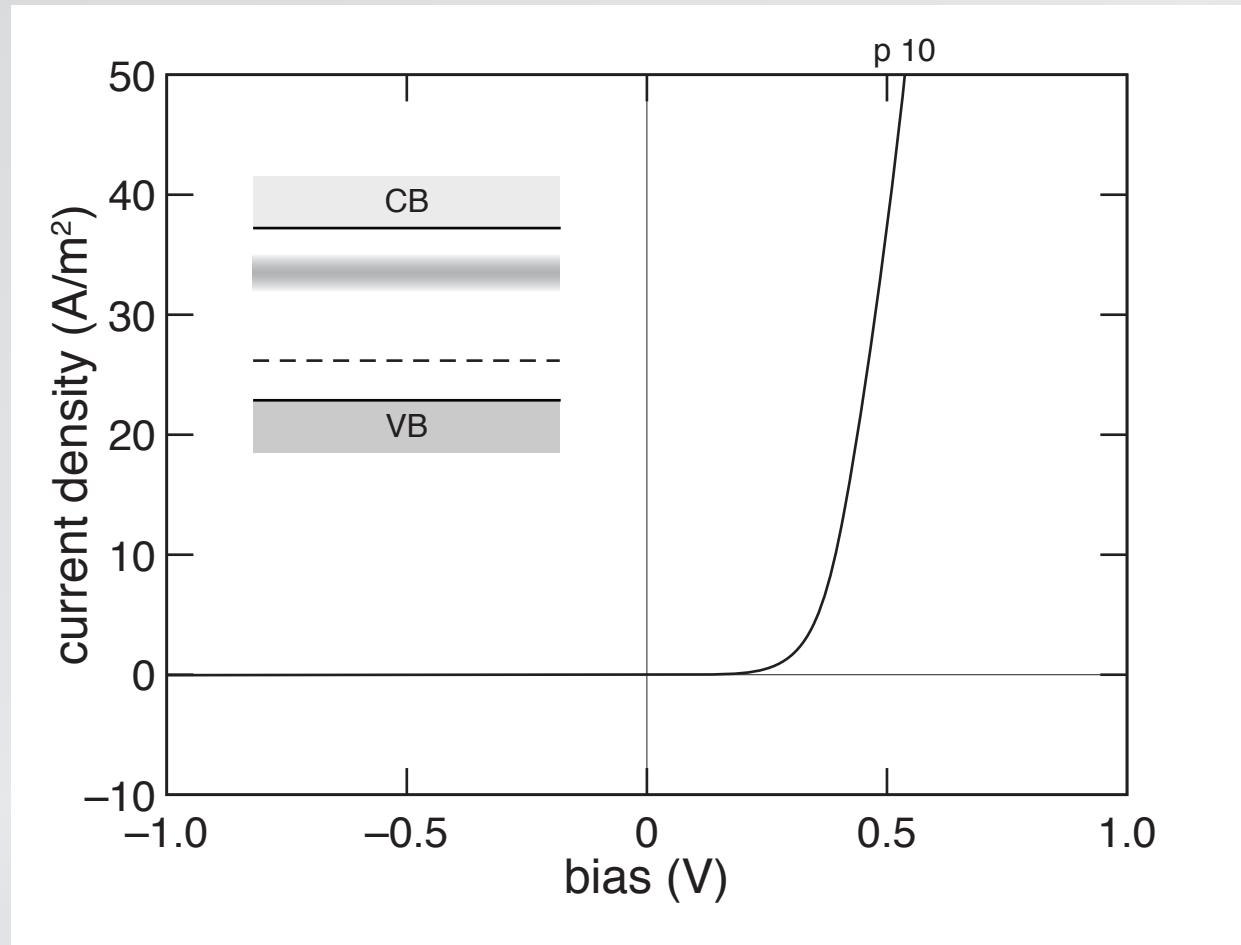
vary substrate doping type and resistivity





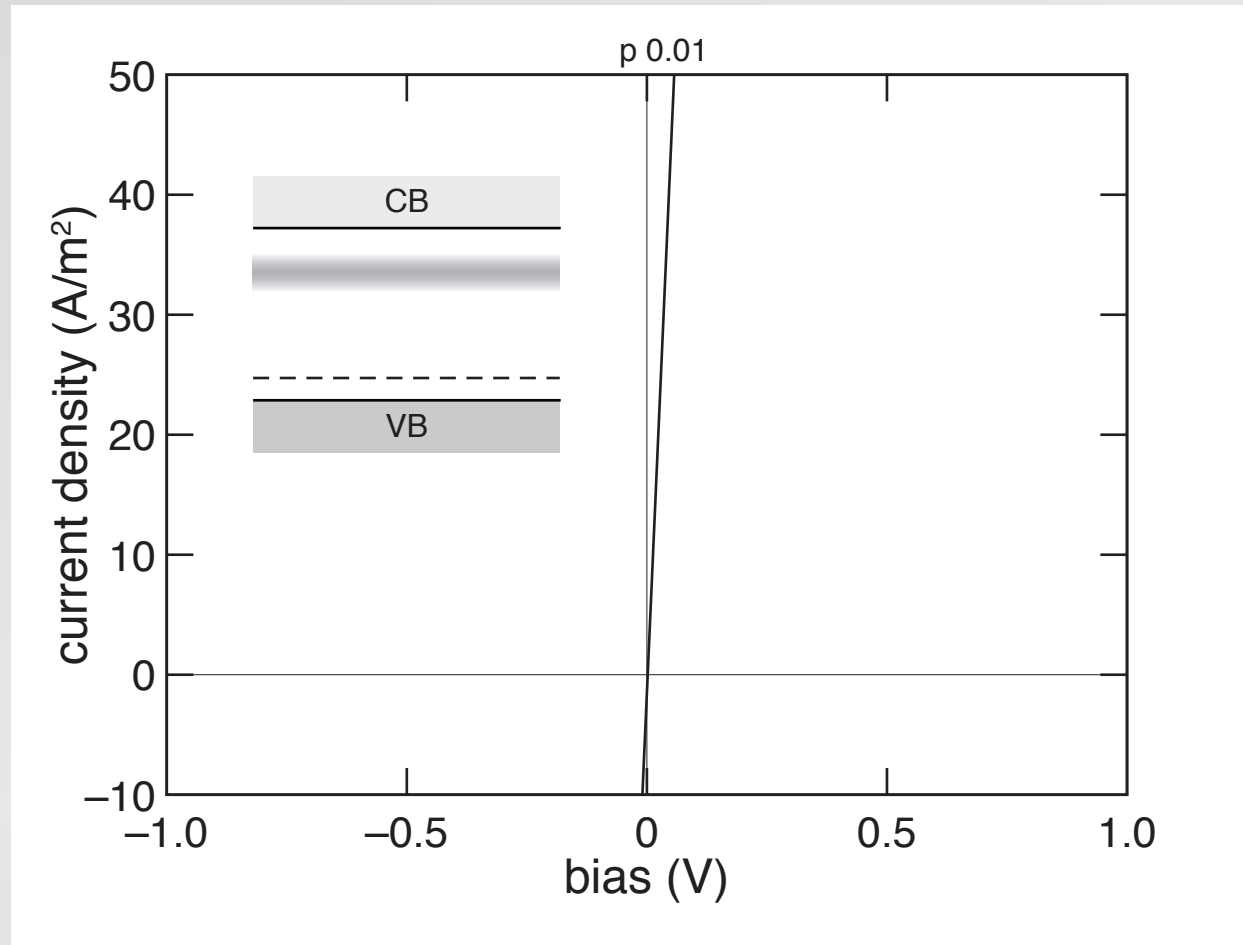
# Optoelectronic properties

vary substrate doping type and resistivity



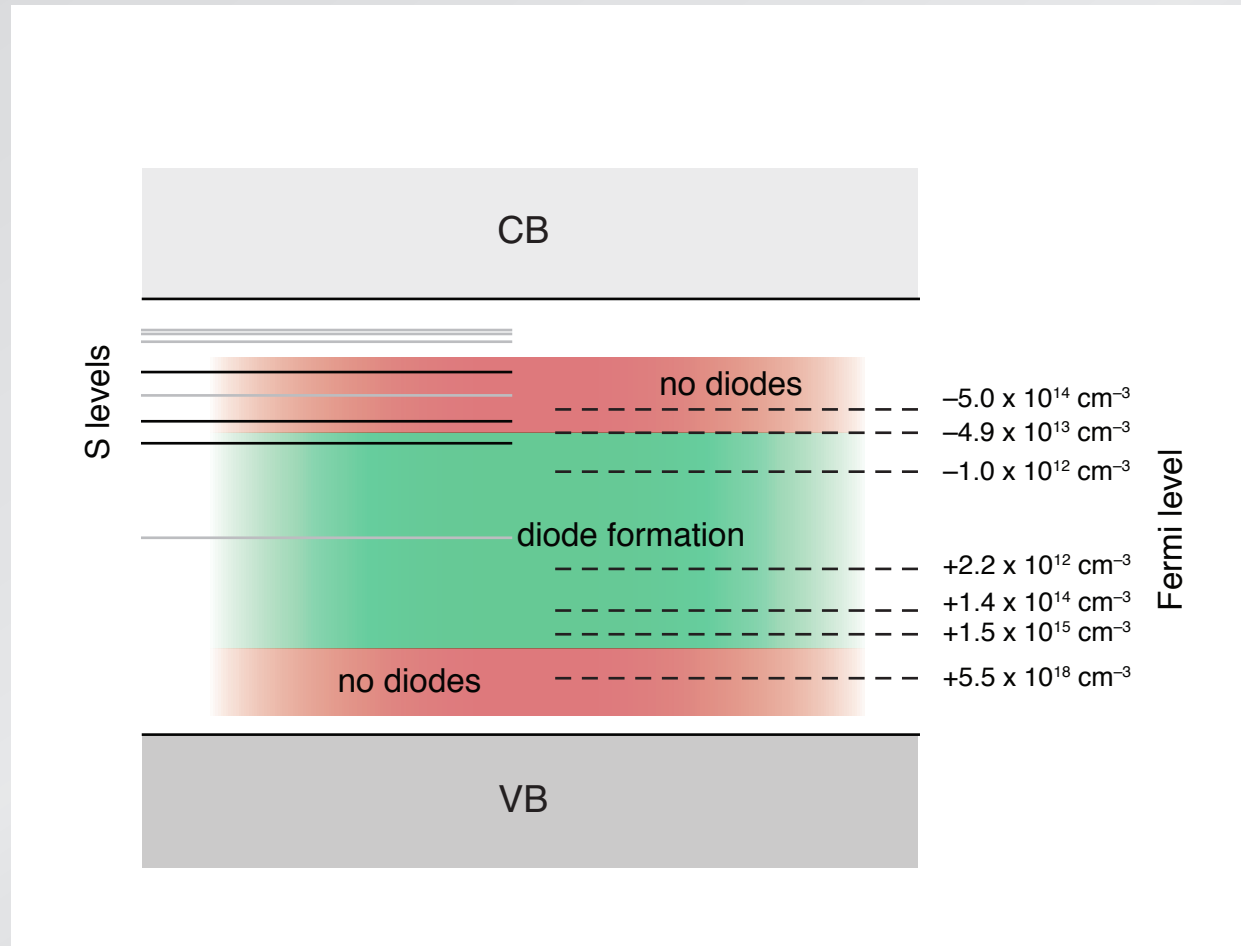
# Optoelectronic properties

vary substrate doping type and resistivity



# Optoelectronic properties

probe impurity states by varying Fermi level in substrate



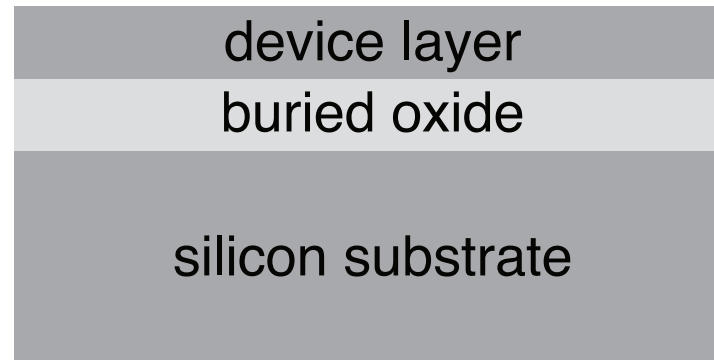
# Optoelectronic properties

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



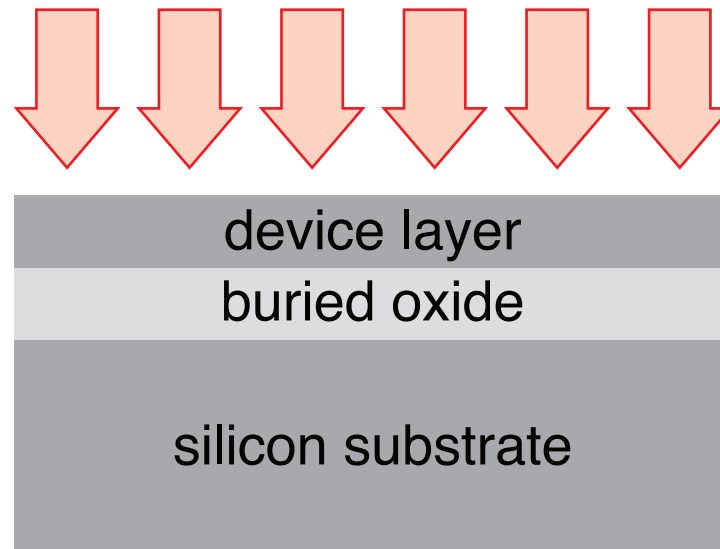
# Optoelectronic properties

isolate surface layer for Hall measurements



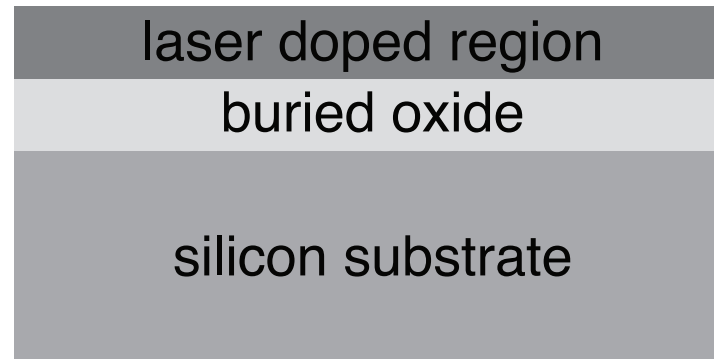
# Optoelectronic properties

isolate surface layer for Hall measurements



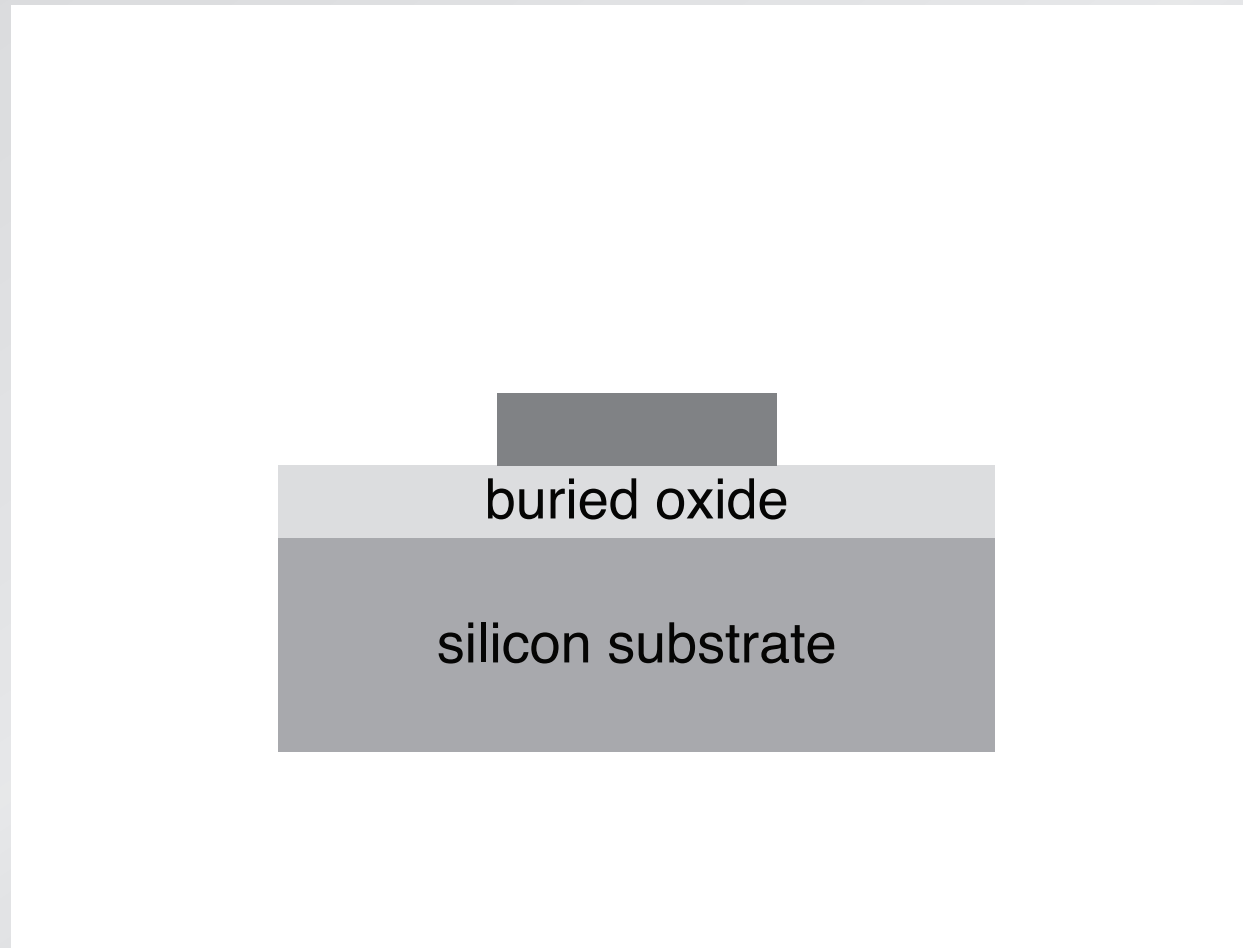
# Optoelectronic properties

isolate surface layer for Hall measurements



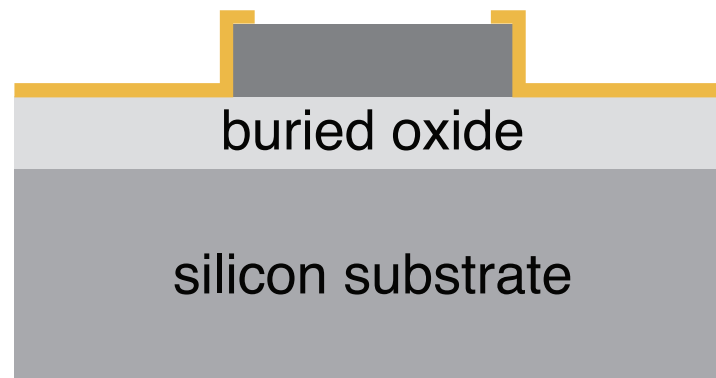
# Optoelectronic properties

isolate surface layer for Hall measurements



# Optoelectronic properties

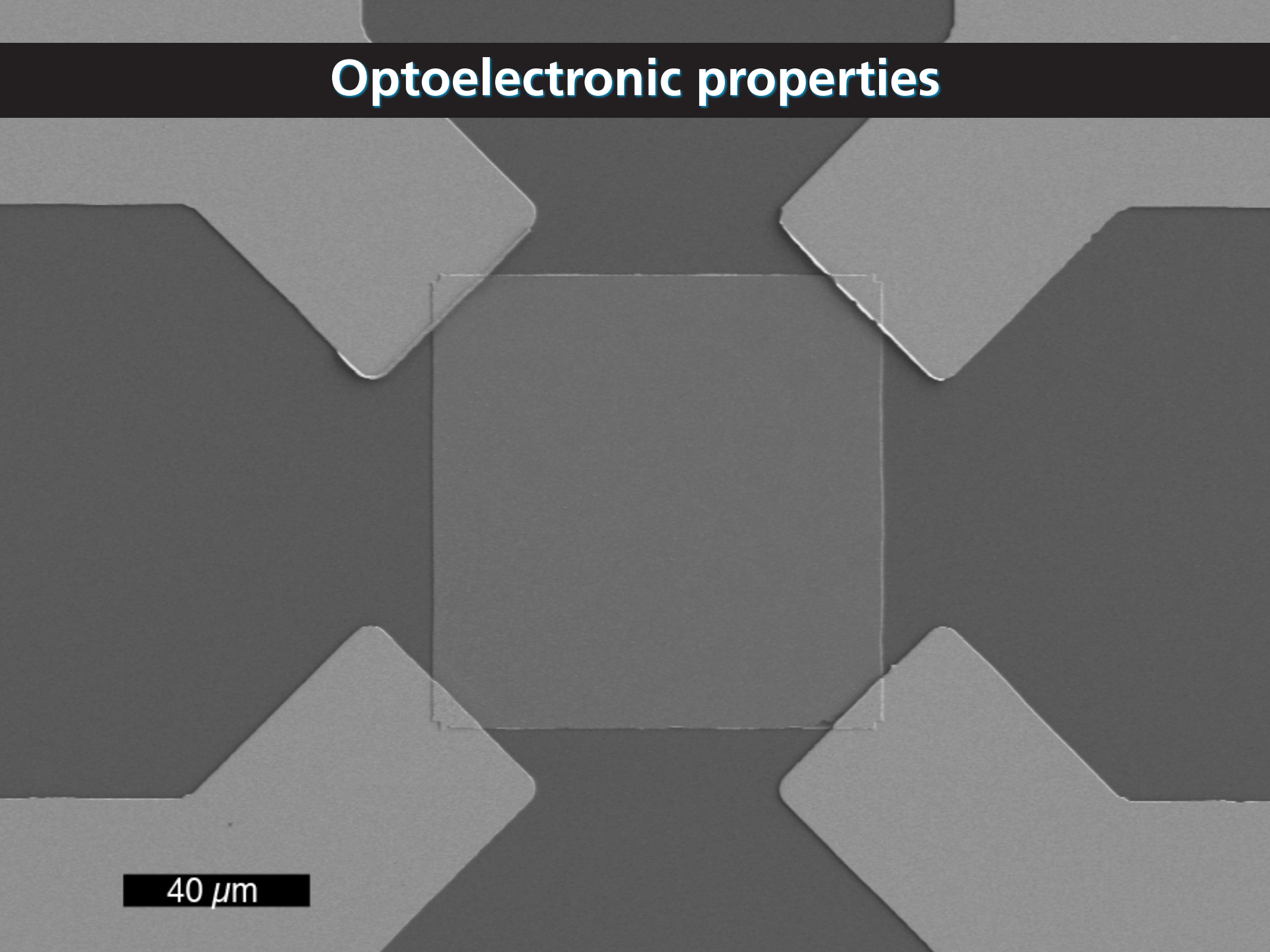
isolate surface layer for Hall measurements





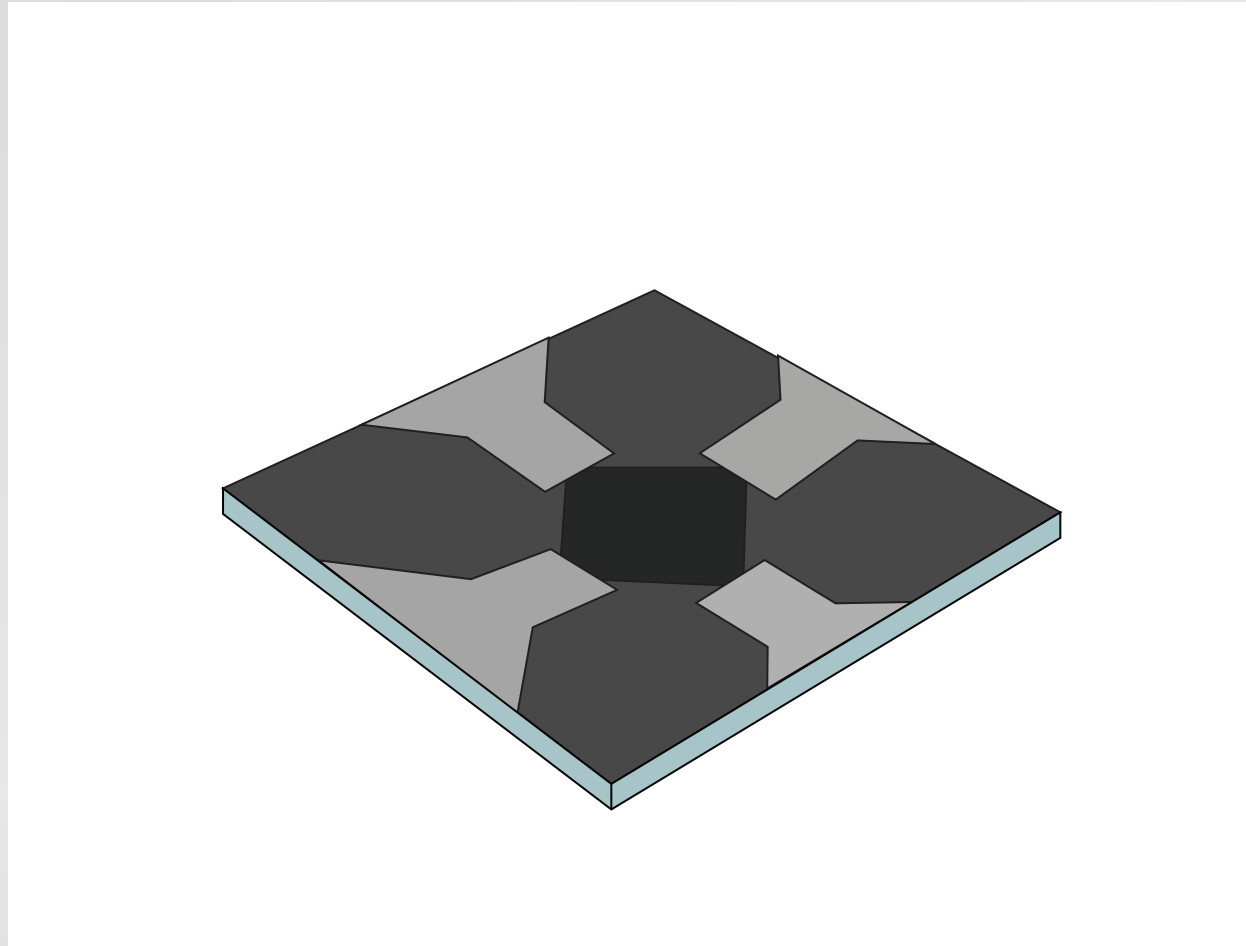
# Optoelectronic properties

40  $\mu\text{m}$

A grayscale micrograph showing a central square 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.

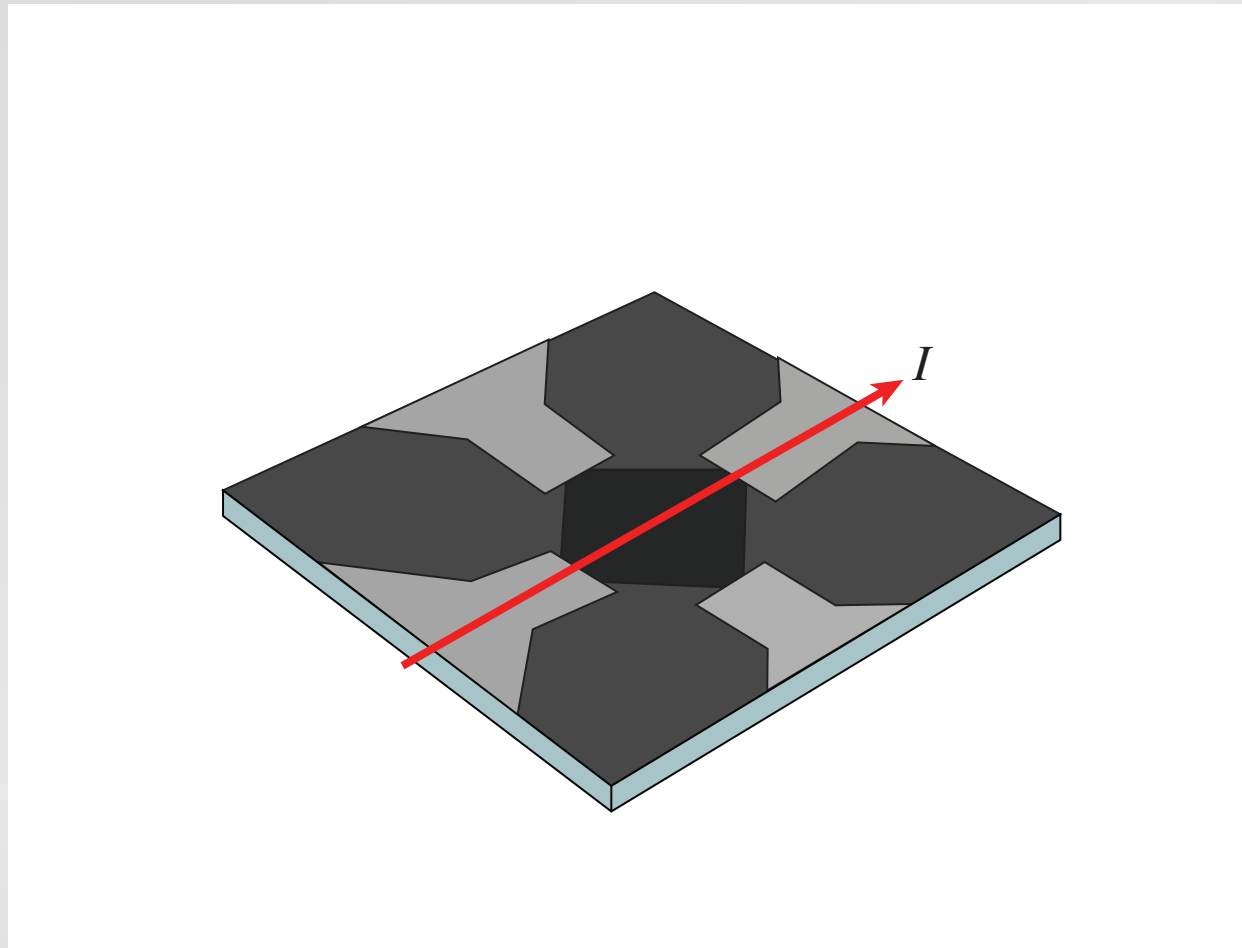
# Optoelectronic properties

## Hall measurements



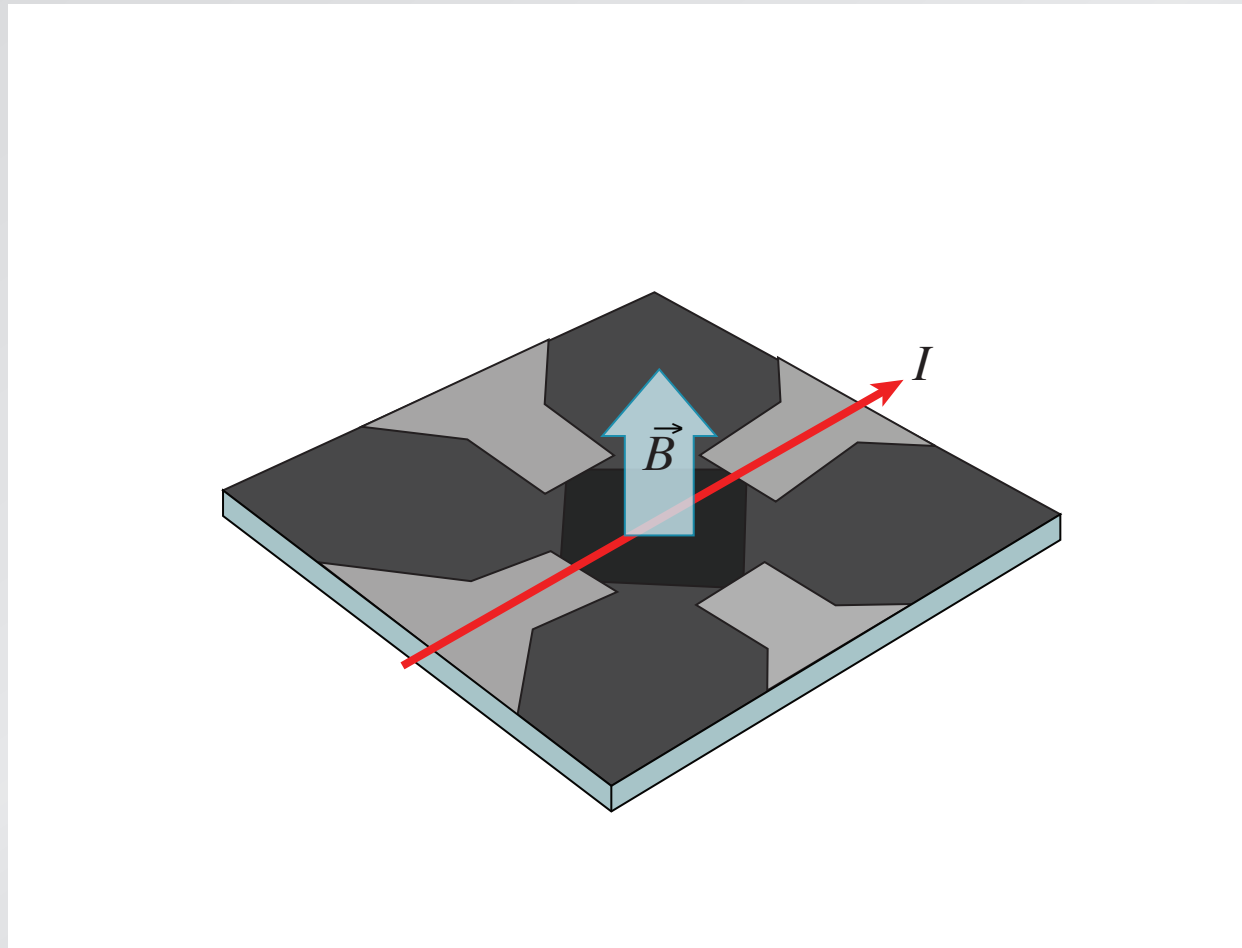
# Optoelectronic properties

## Hall measurements



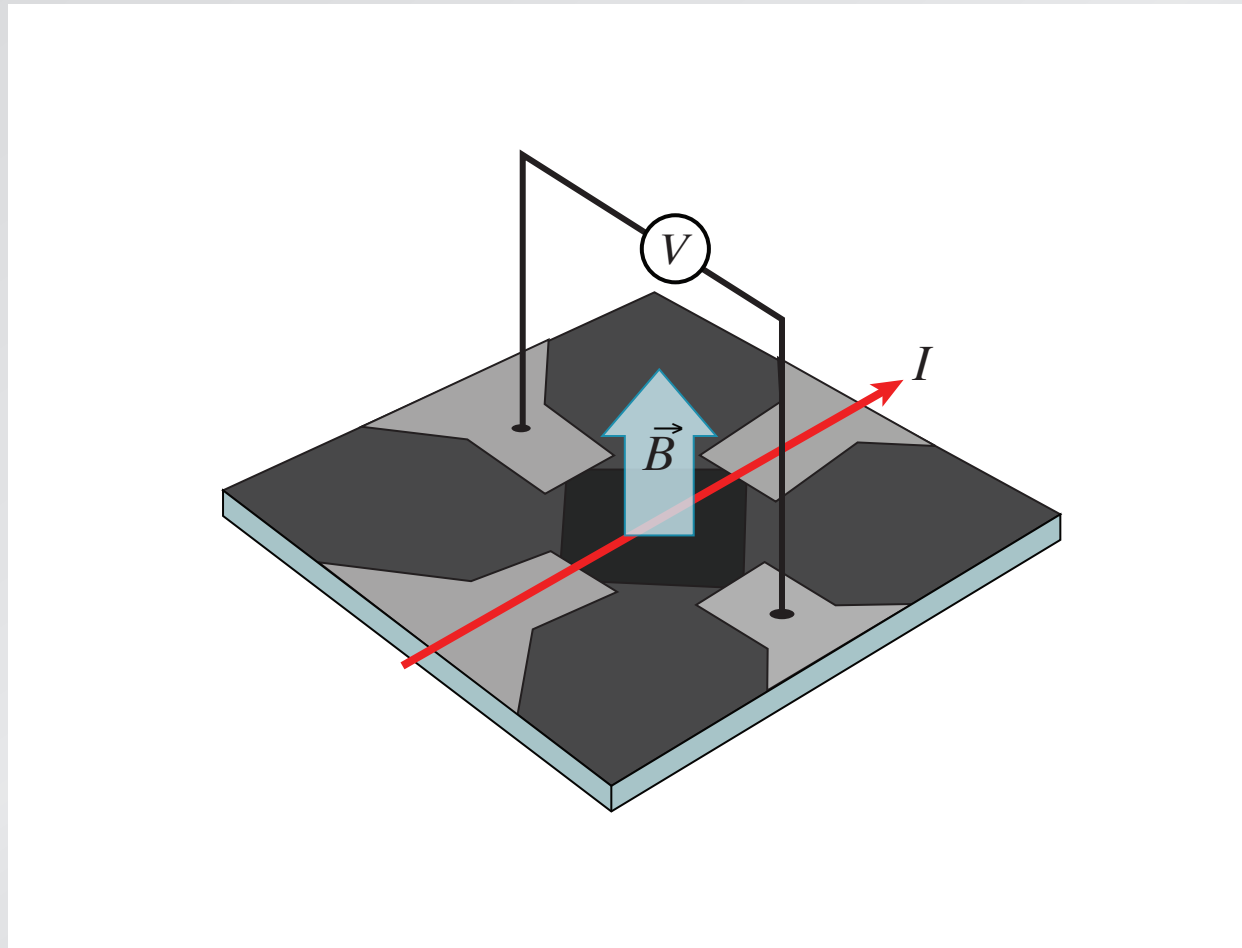
# Optoelectronic properties

## Hall measurements



# Optoelectronic properties

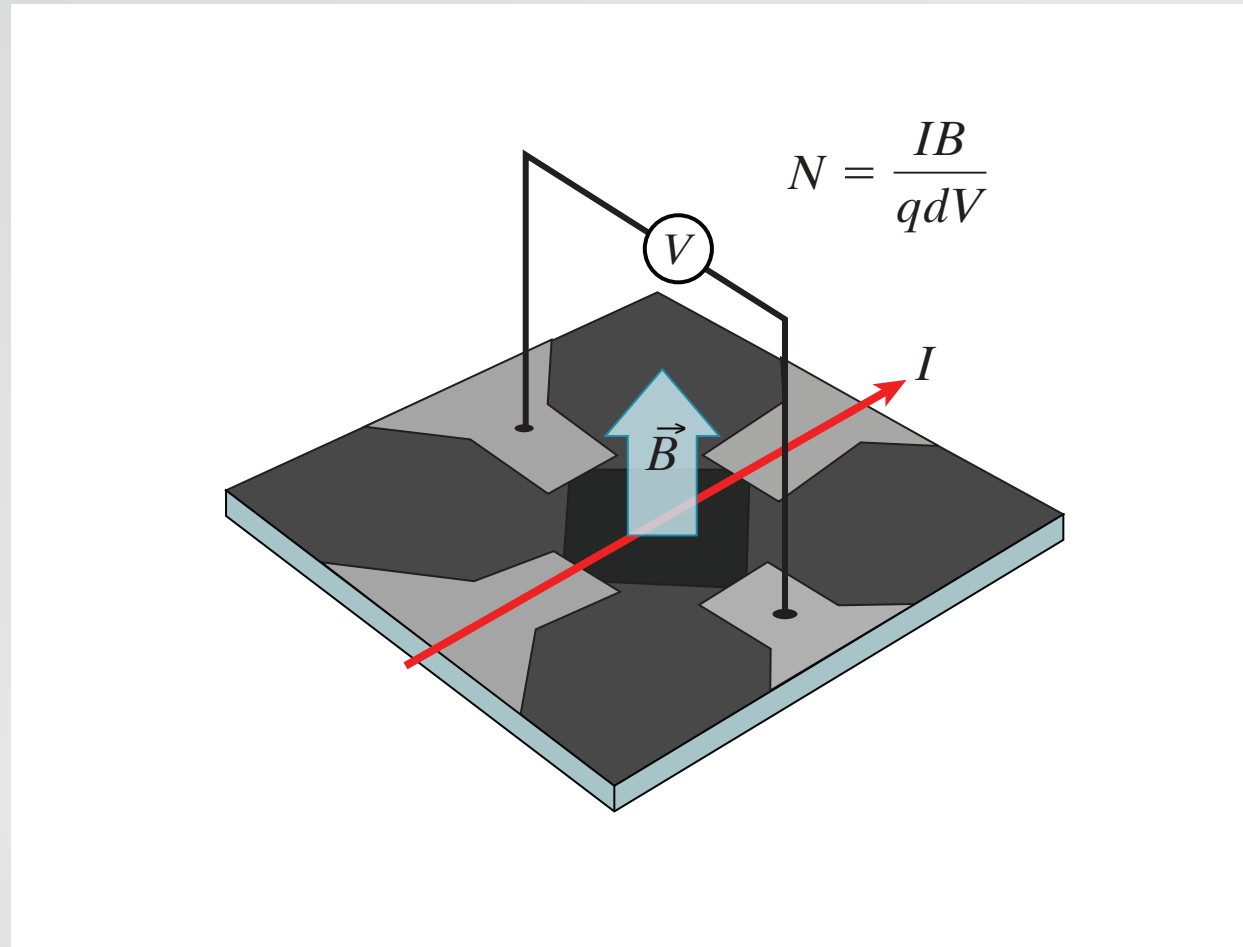
## Hall measurements





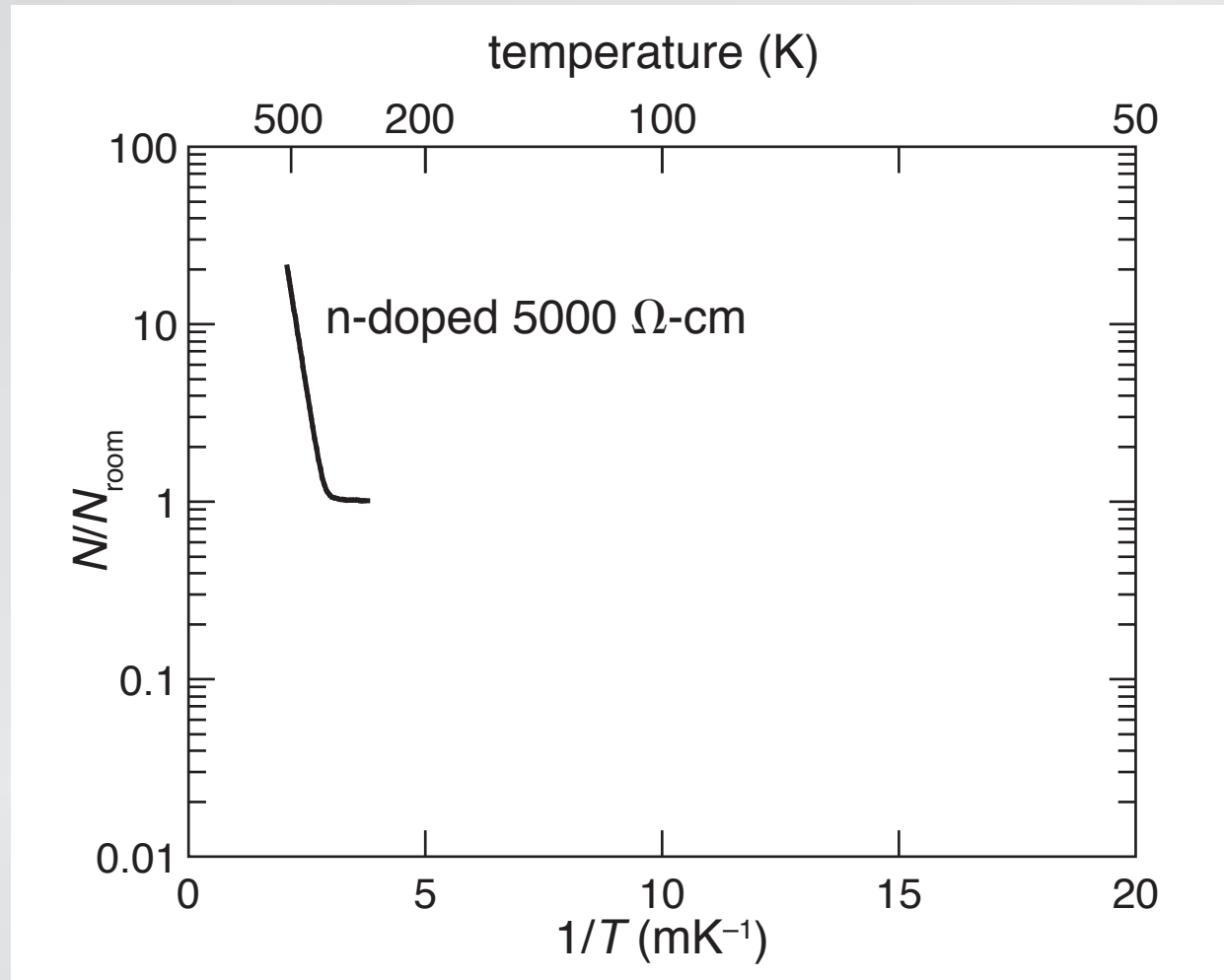
# Optoelectronic properties

## Hall measurements



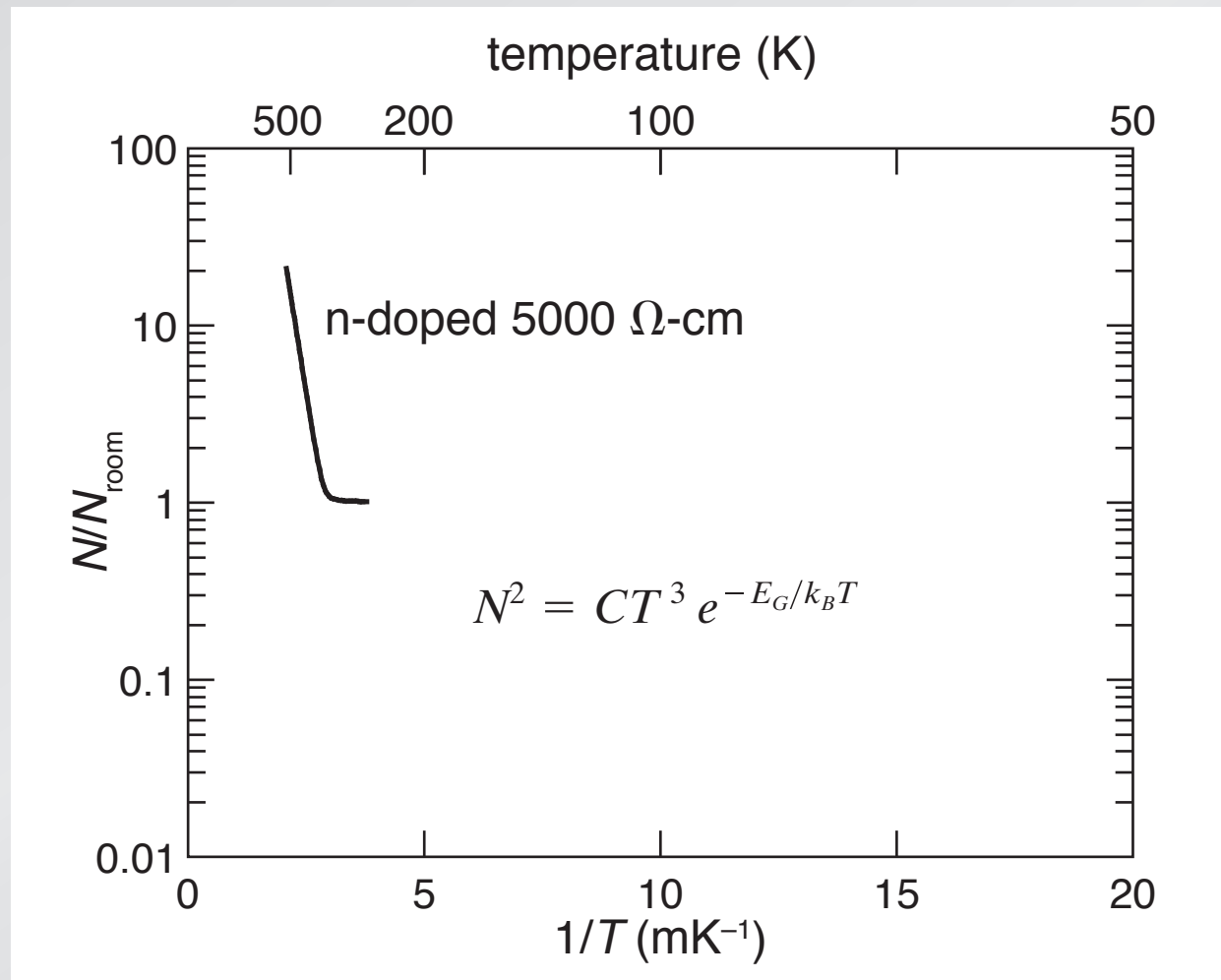
# Optoelectronic properties

## Hall measurements



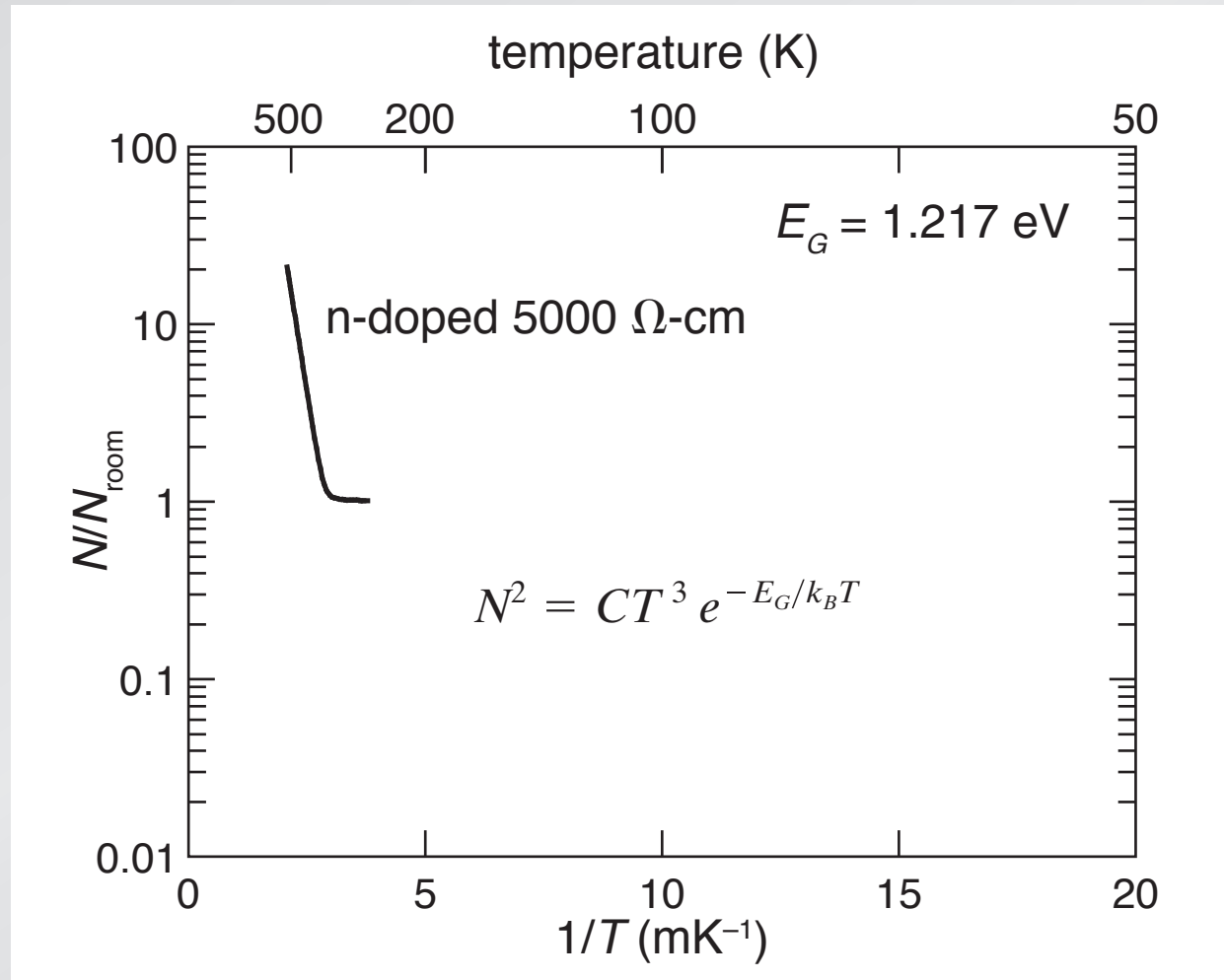
# Optoelectronic properties

## Hall measurements



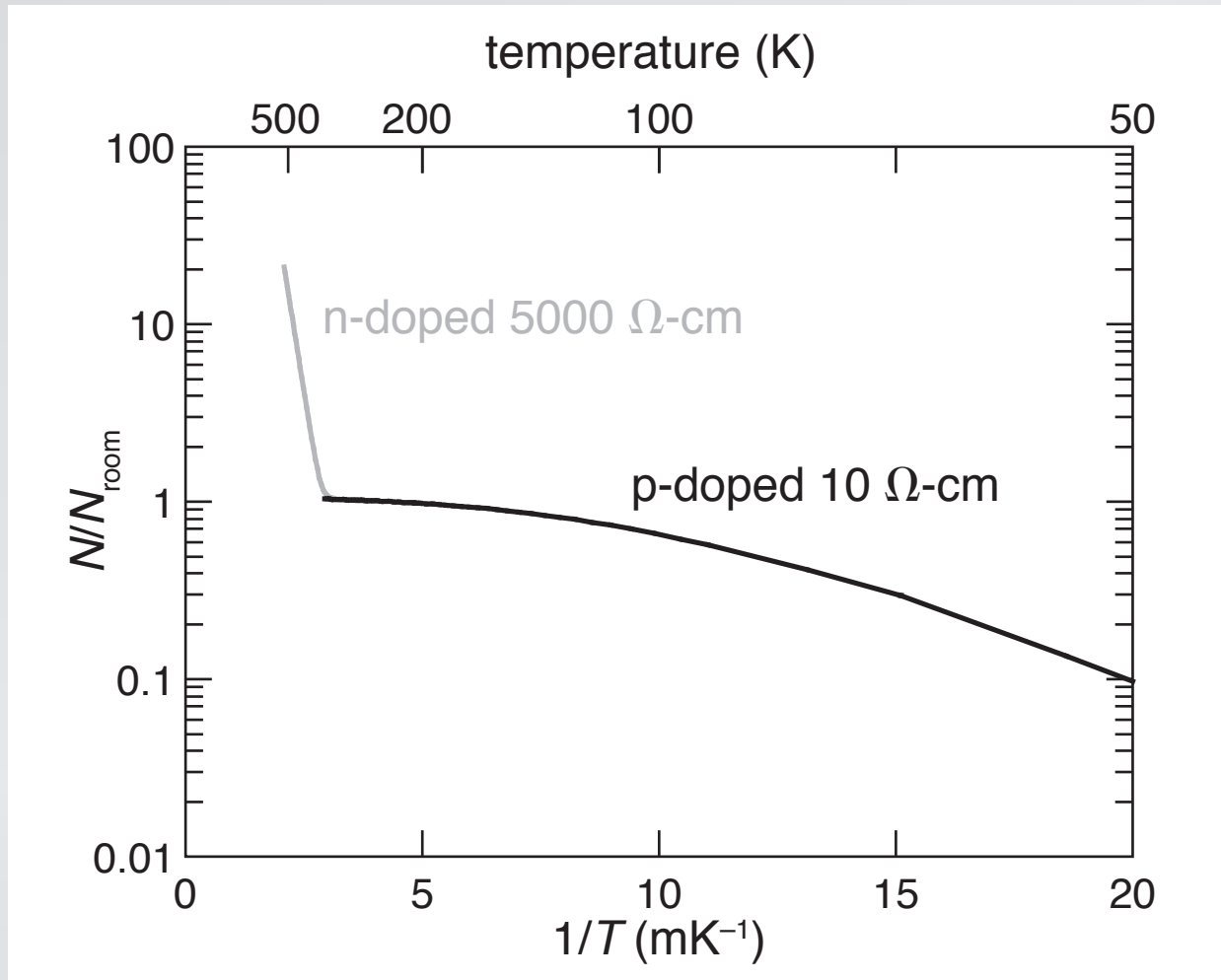
# Optoelectronic properties

## Hall measurements



# Optoelectronic properties

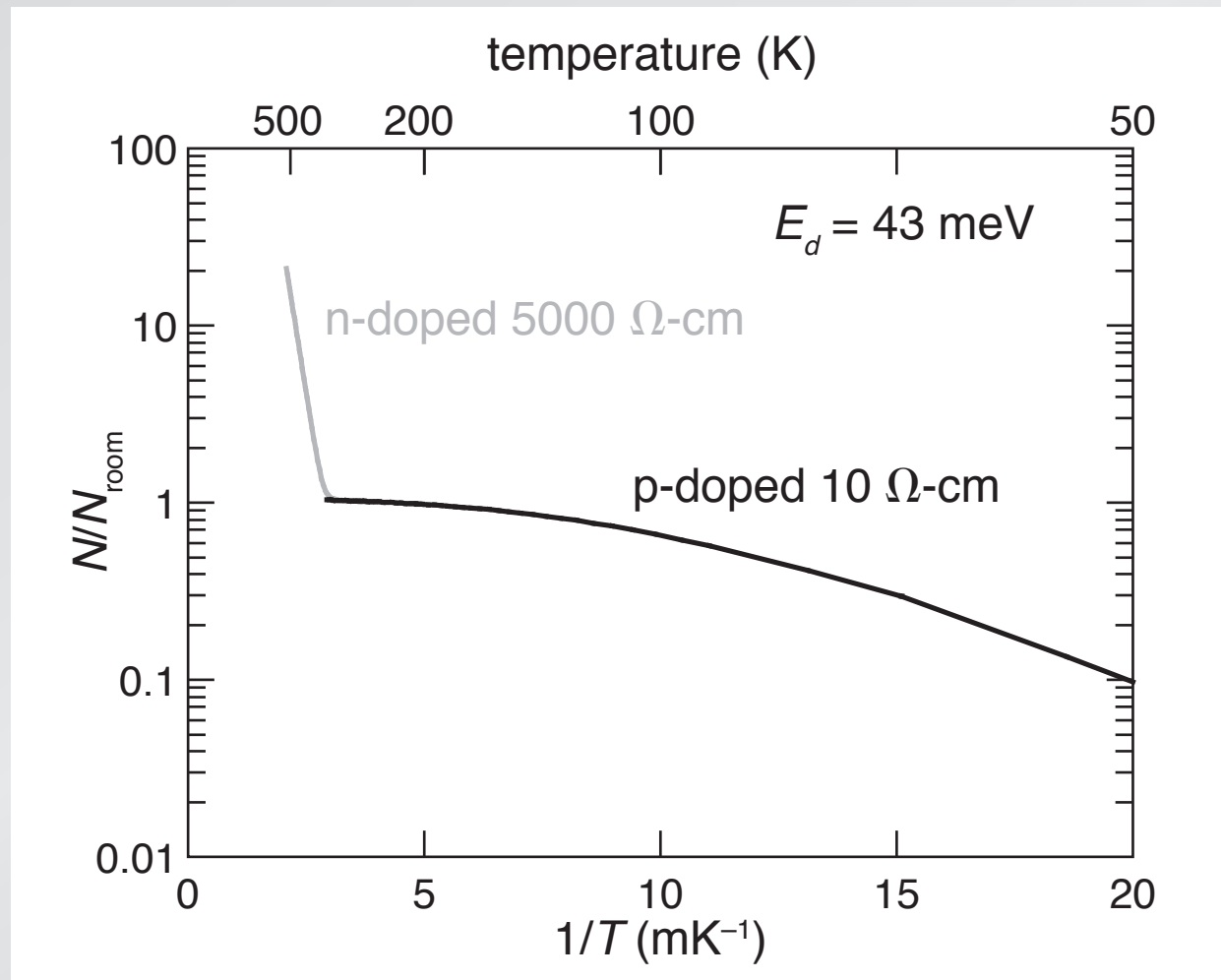
## Hall measurements





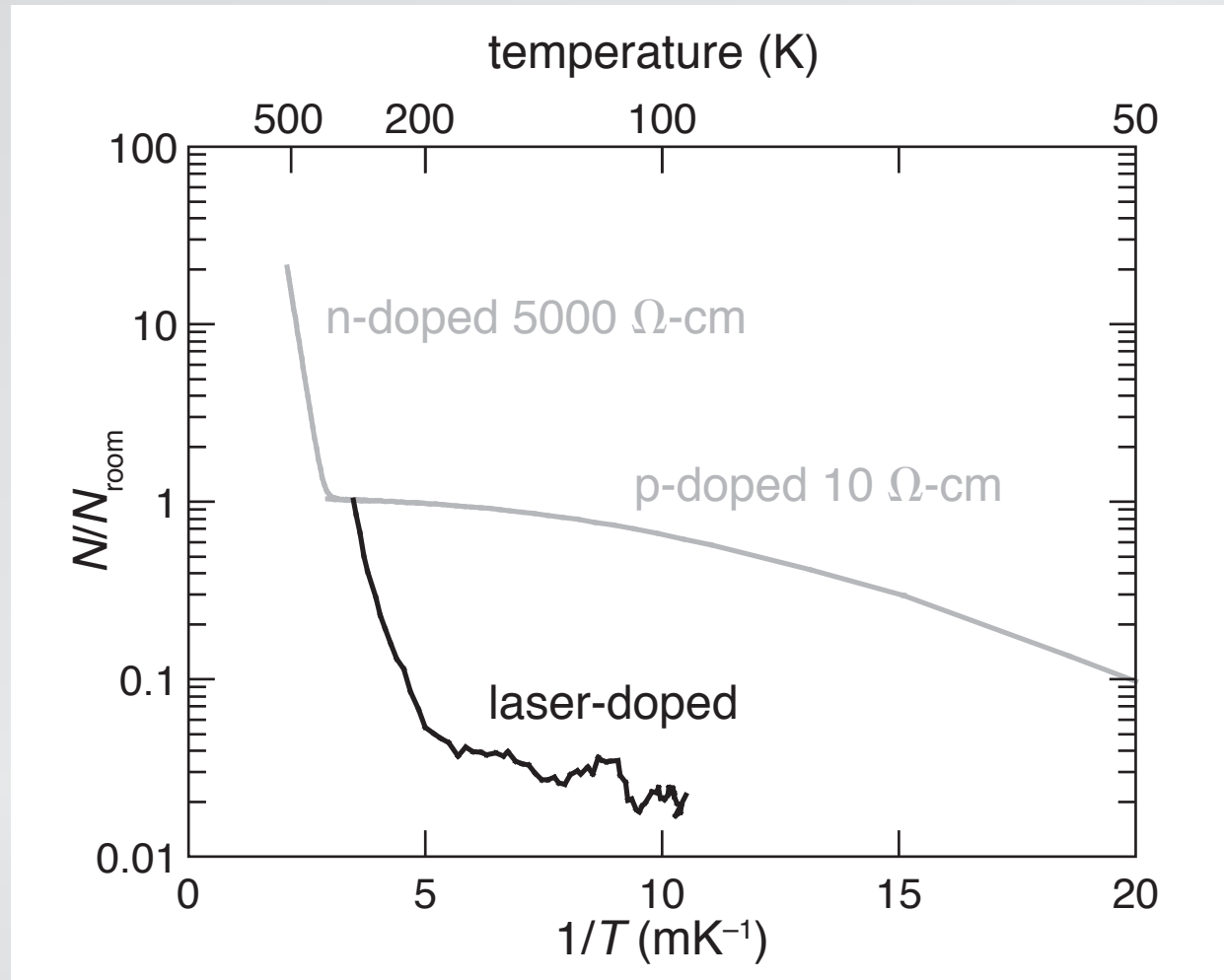
# Optoelectronic properties

## Hall measurements



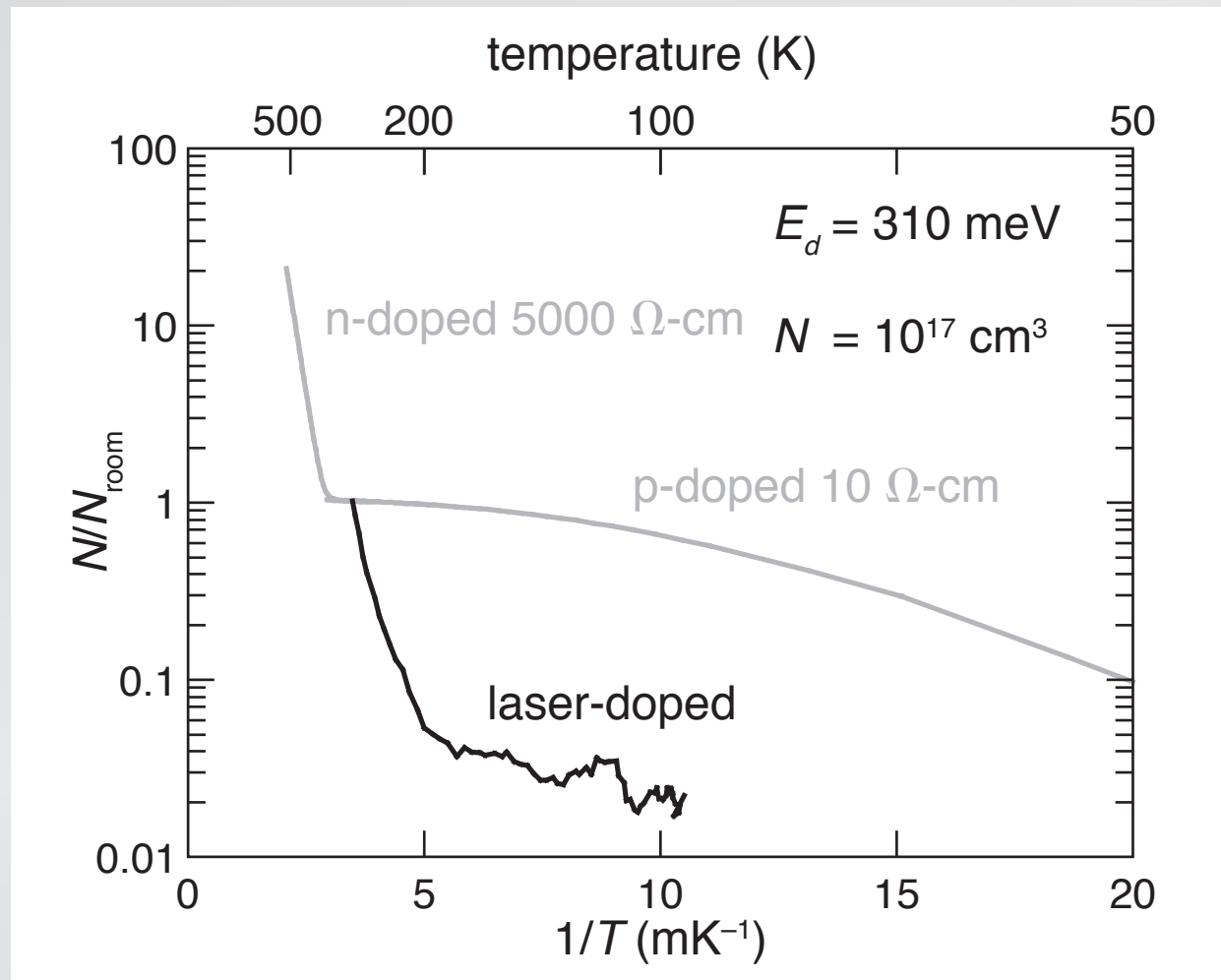
# Optoelectronic properties

## Hall measurements



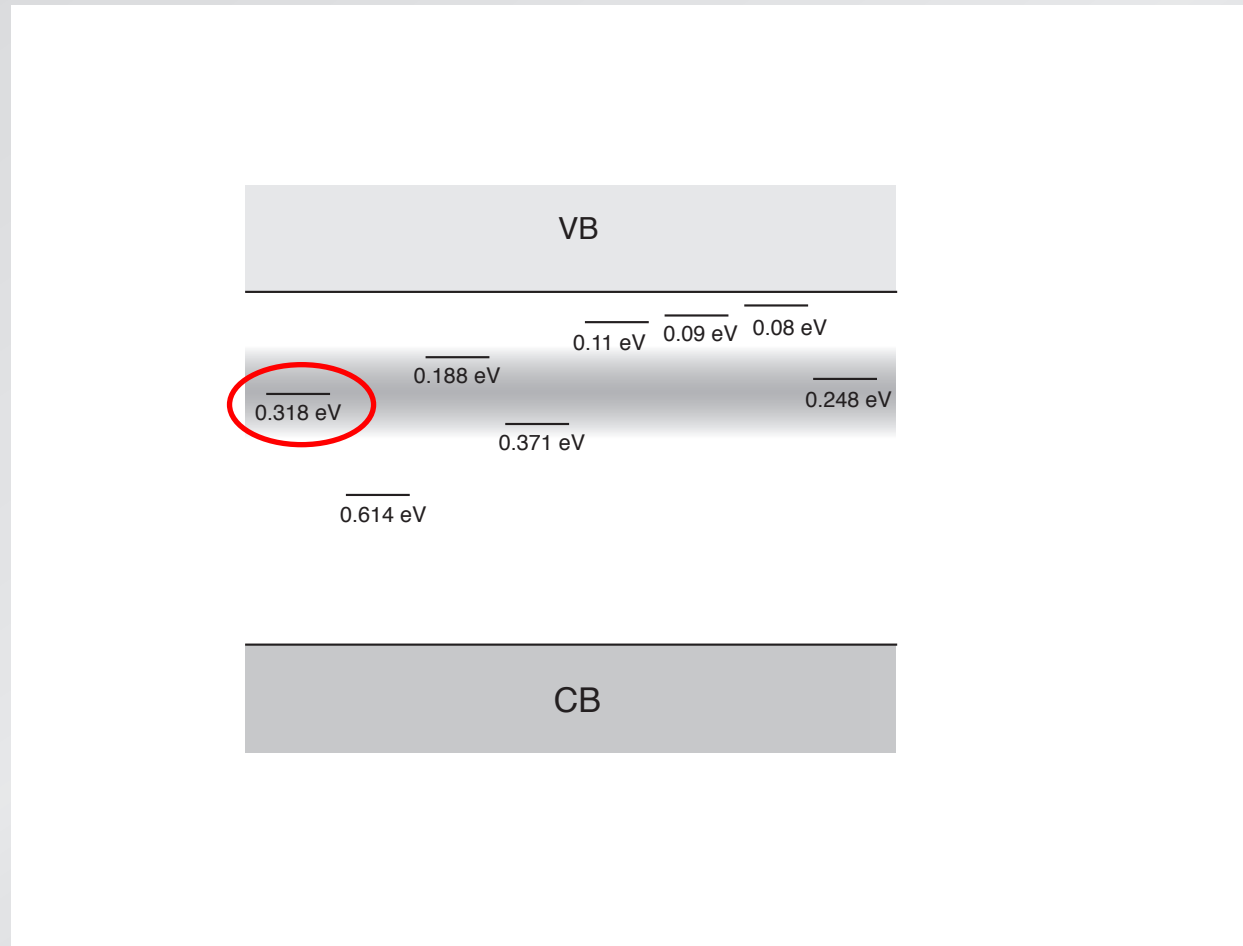
# Optoelectronic properties

## Hall measurements



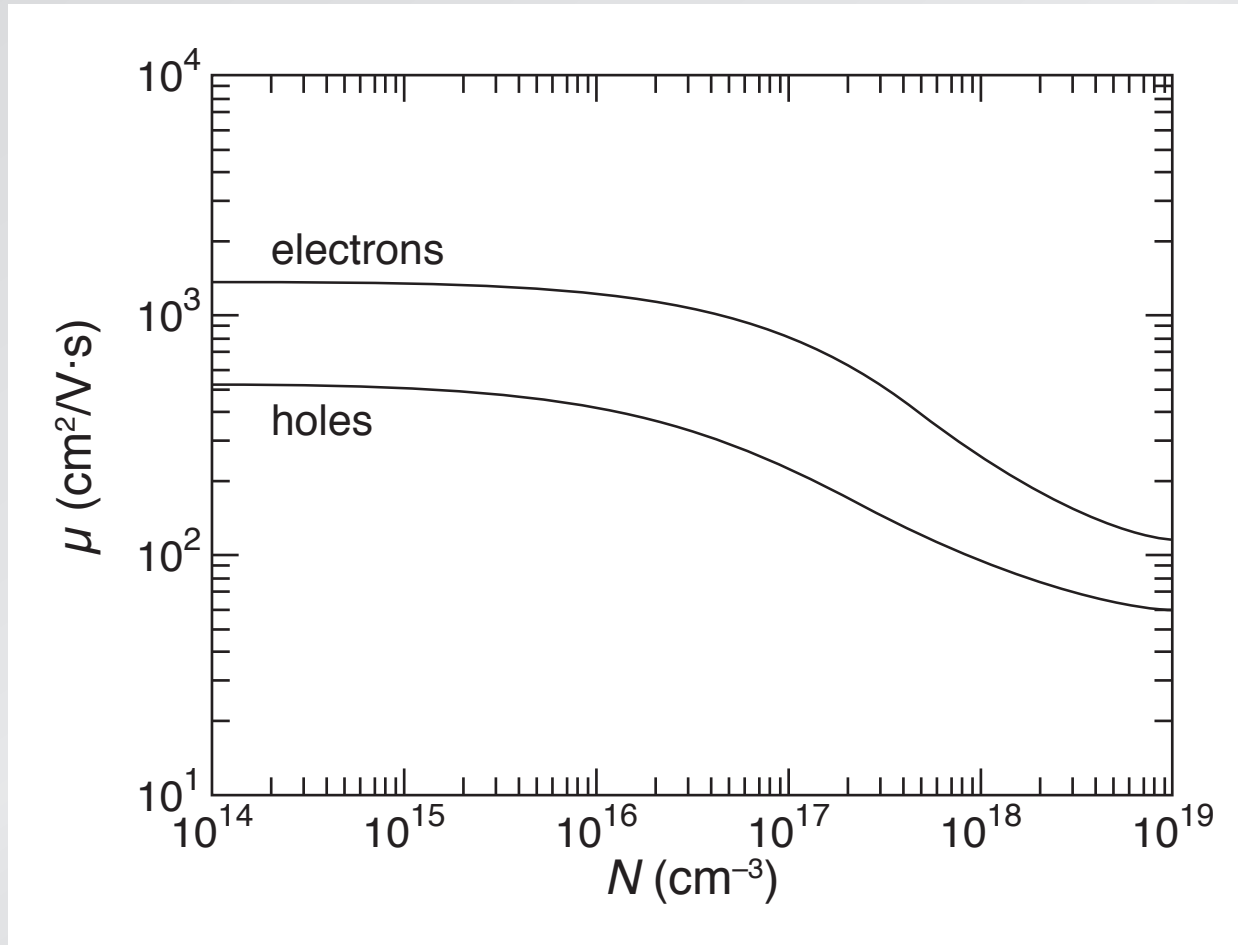
# Optoelectronic properties

impurity (donor) band centered at 310 meV



# Optoelectronic properties

## majority carrier mobility

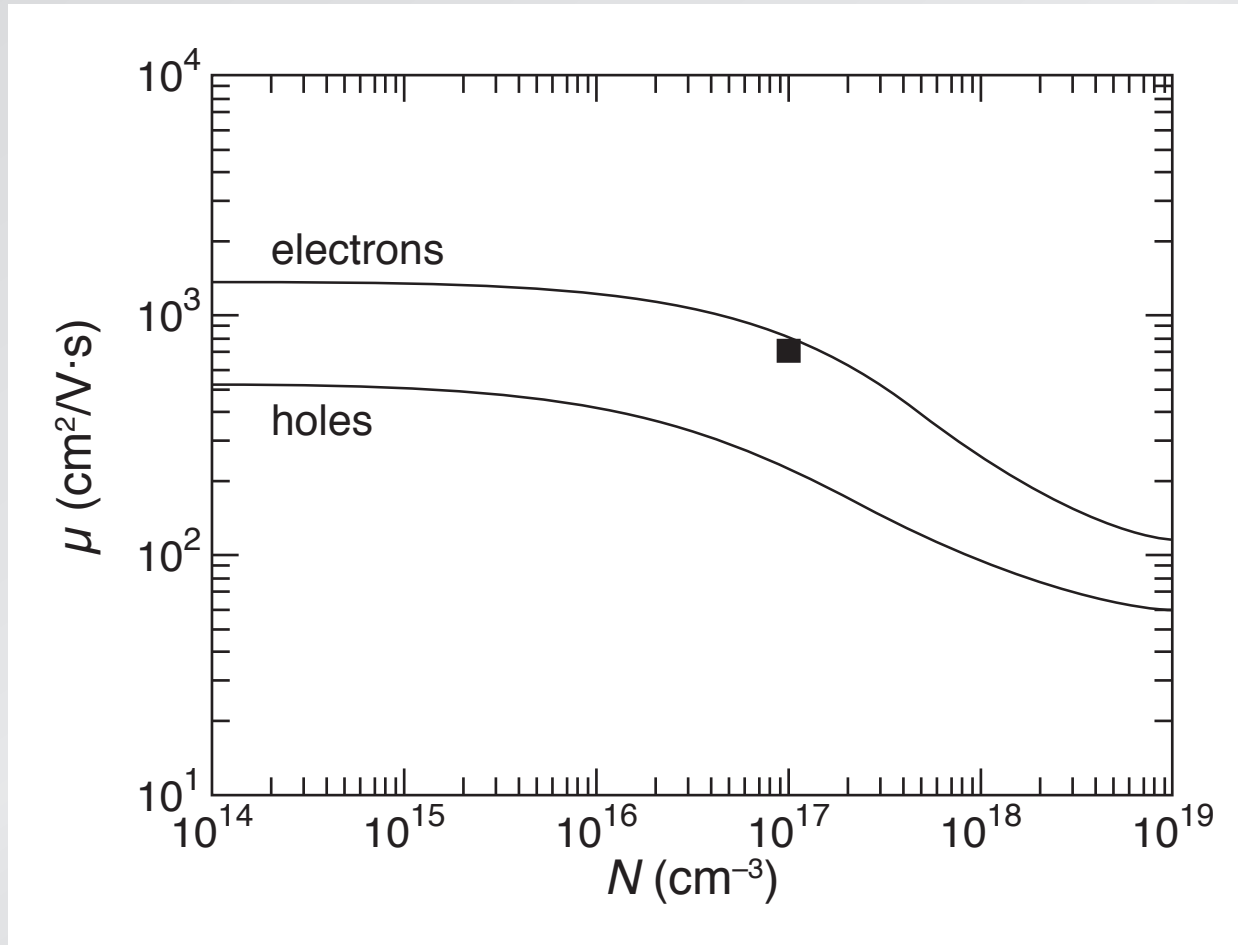


Caughey *et al.*, Proc. IEEE 55, 2192 (1967)



# Optoelectronic properties

## majority carrier mobility



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

# Optoelectronic properties

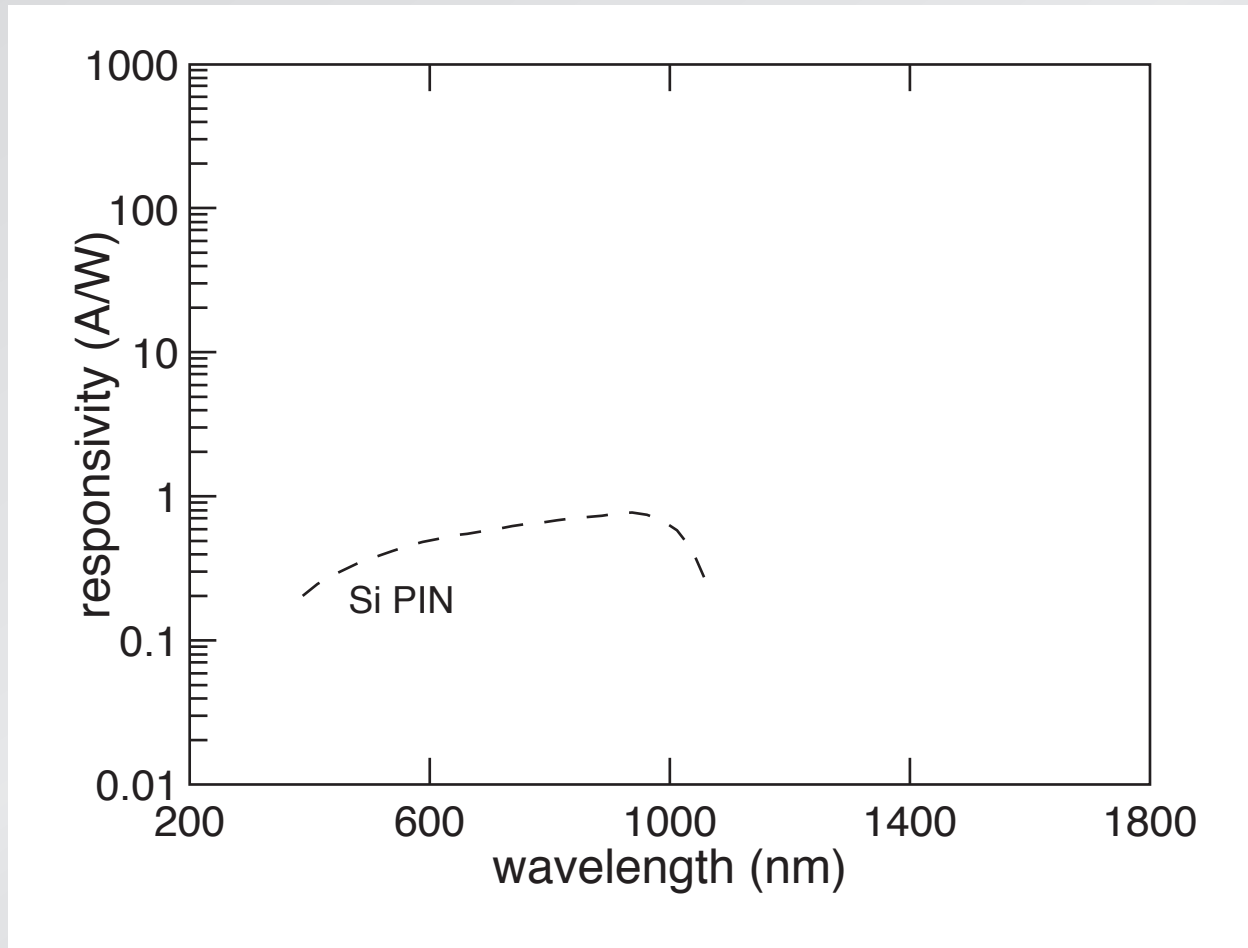
## Things to keep in mind

- 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



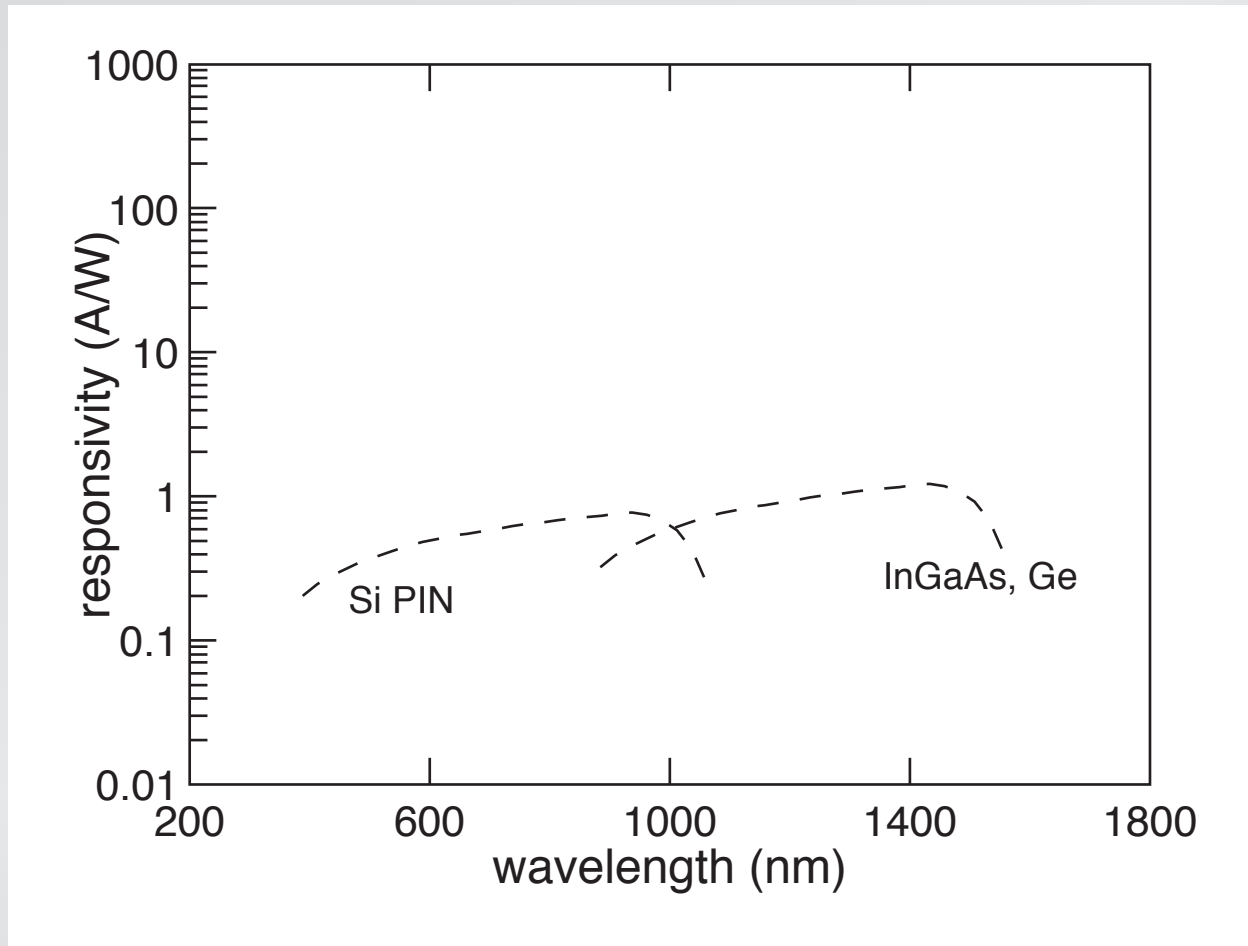
# Devices

## responsivity



# Devices

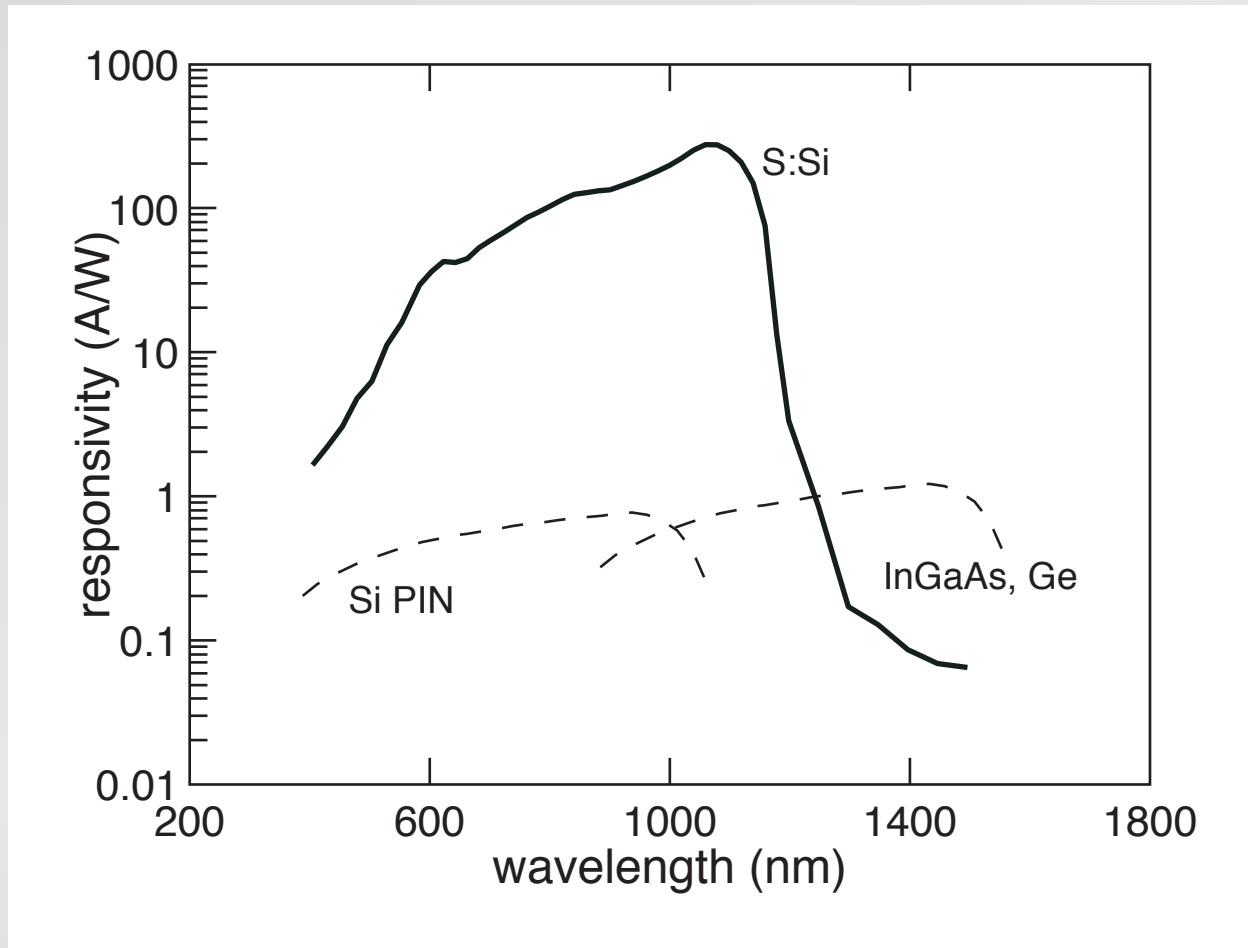
## responsivity





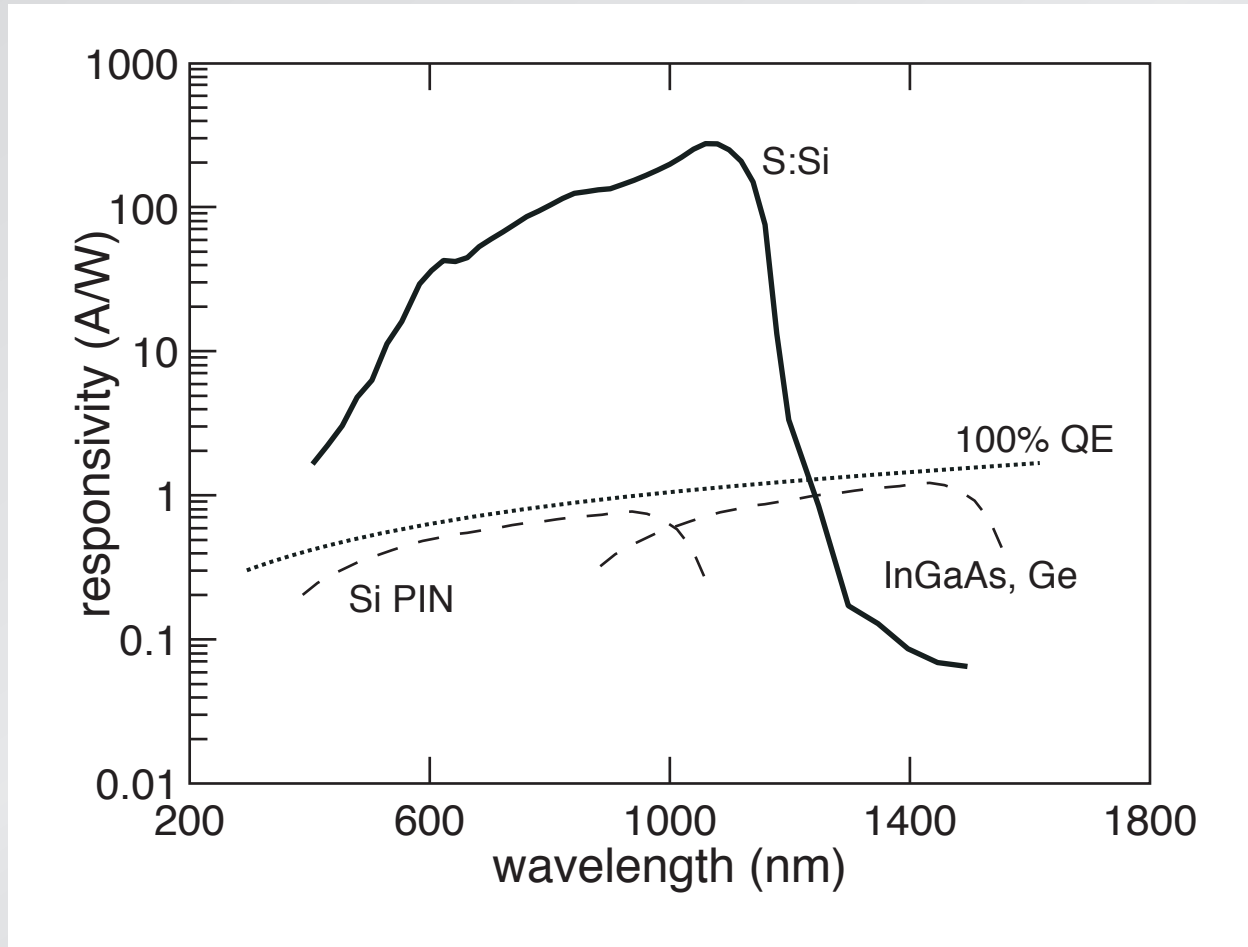
# Devices

## responsivity



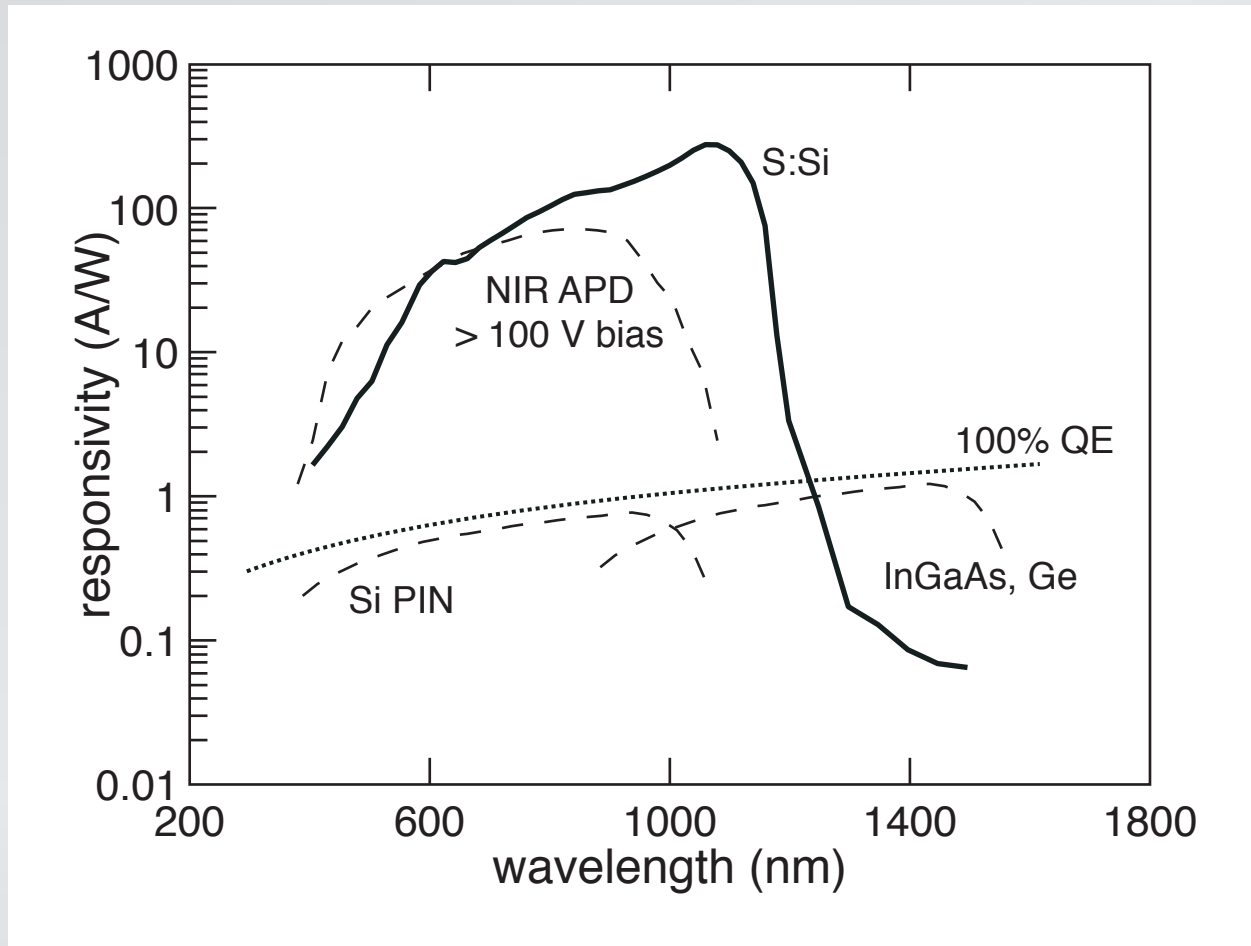
# Devices

## responsivity



# Devices

## responsivity

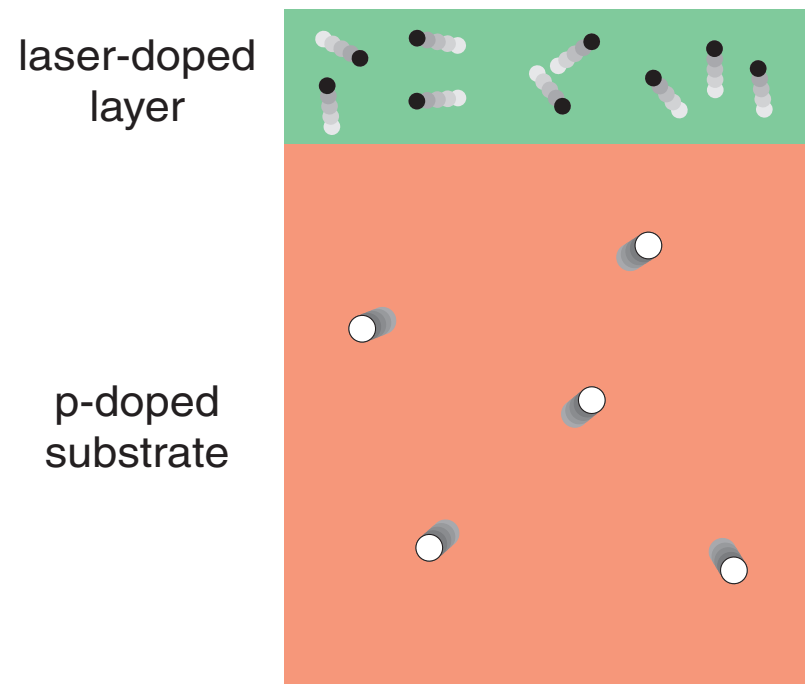


# Devices

**What causes gain?**

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

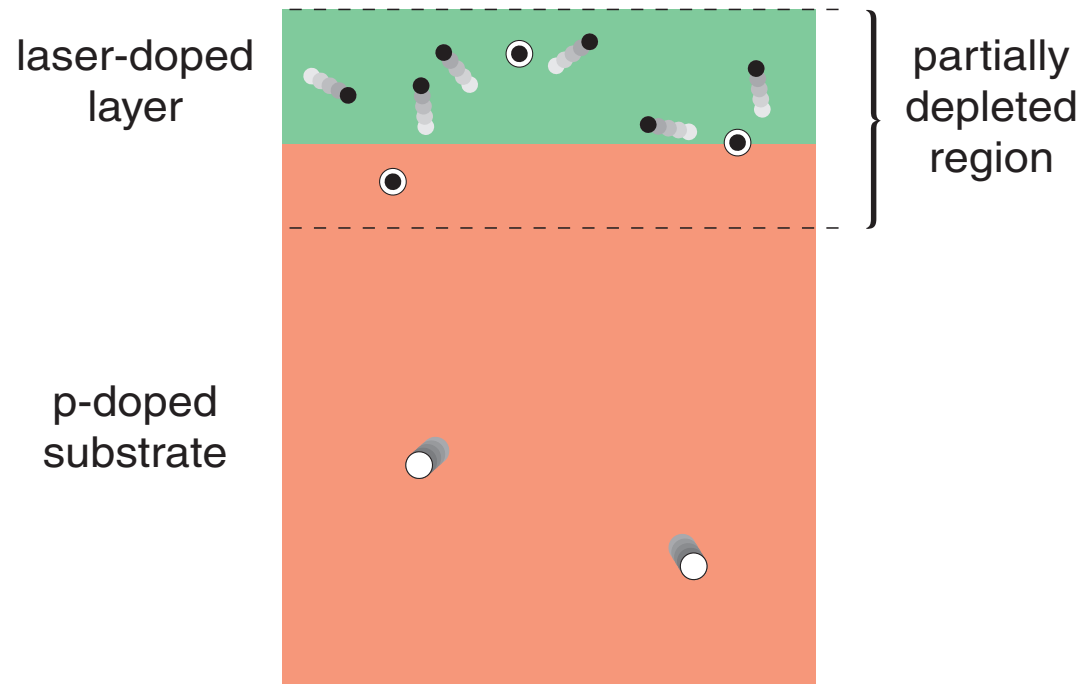
# Devices



**"pl junction"**

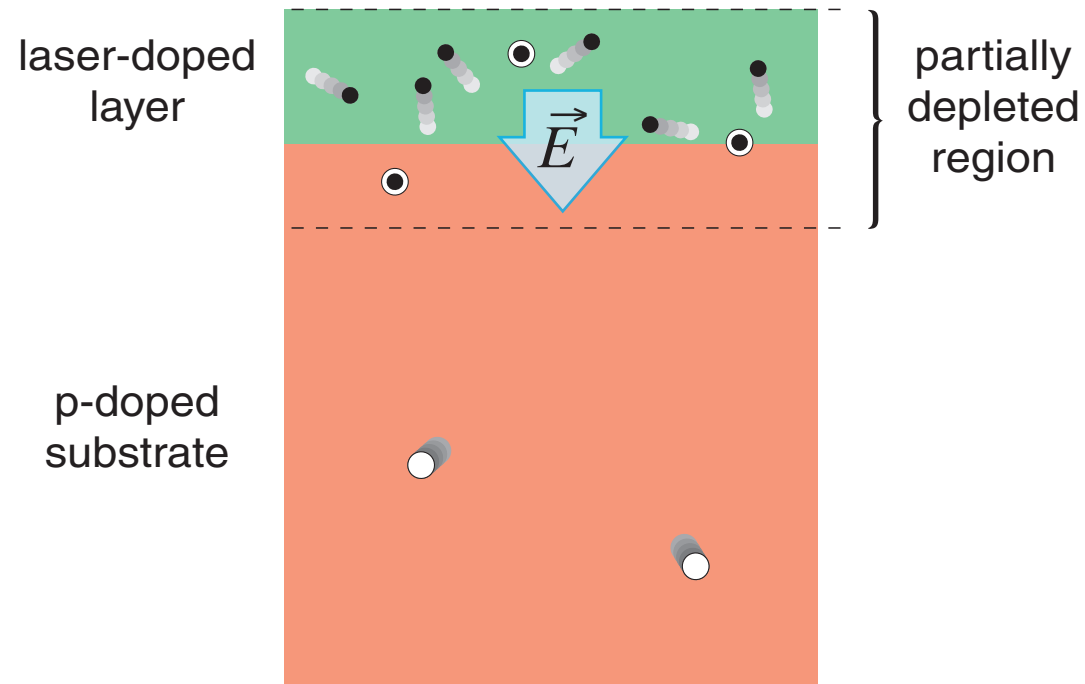


# Devices



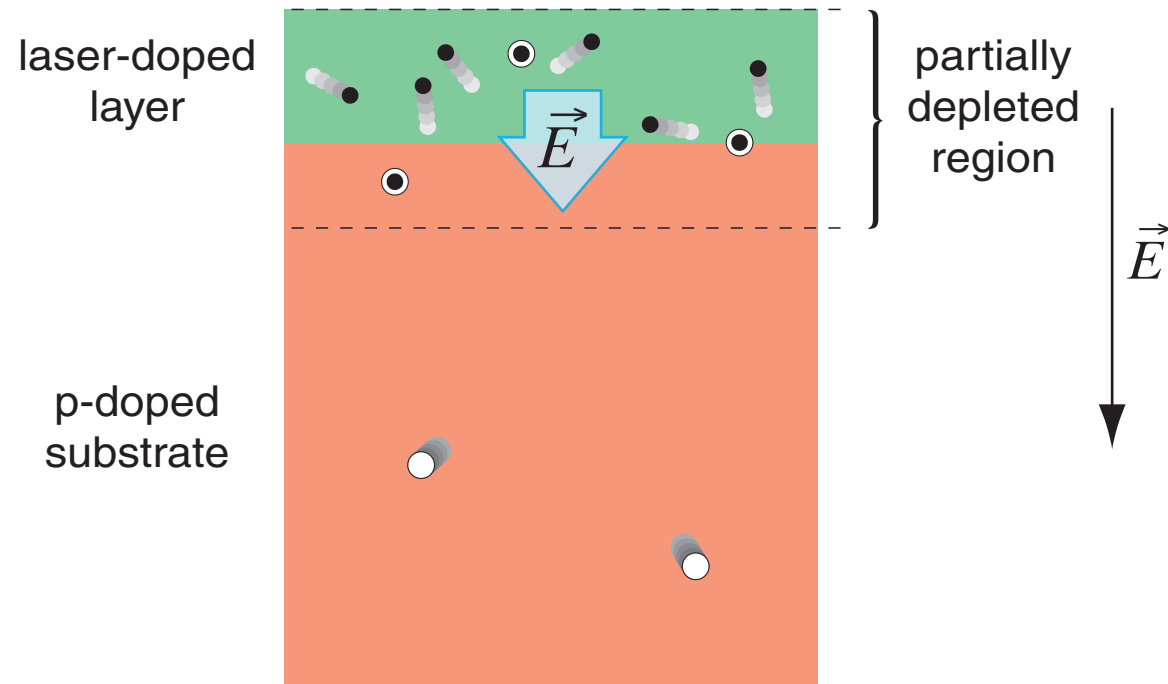
**formation of partially depleted region**

# Devices



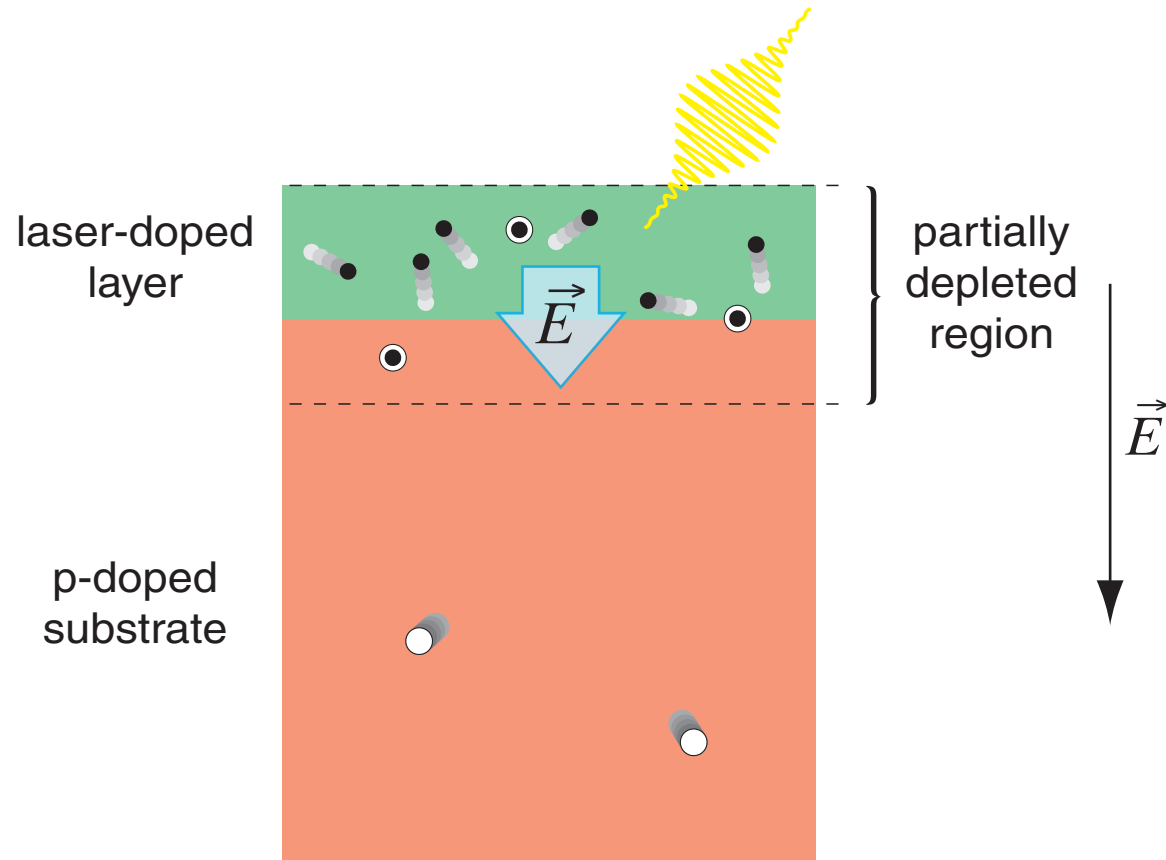
**formation of partially depleted region**

# Devices



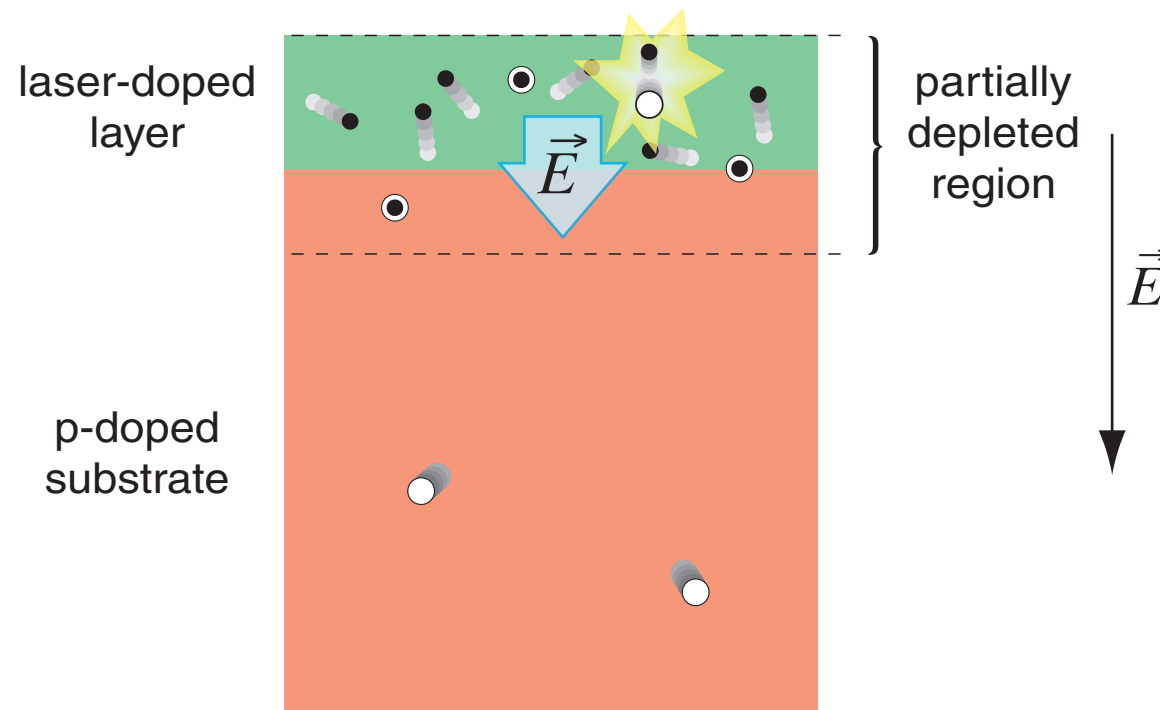
apply backward bias...

# Devices



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

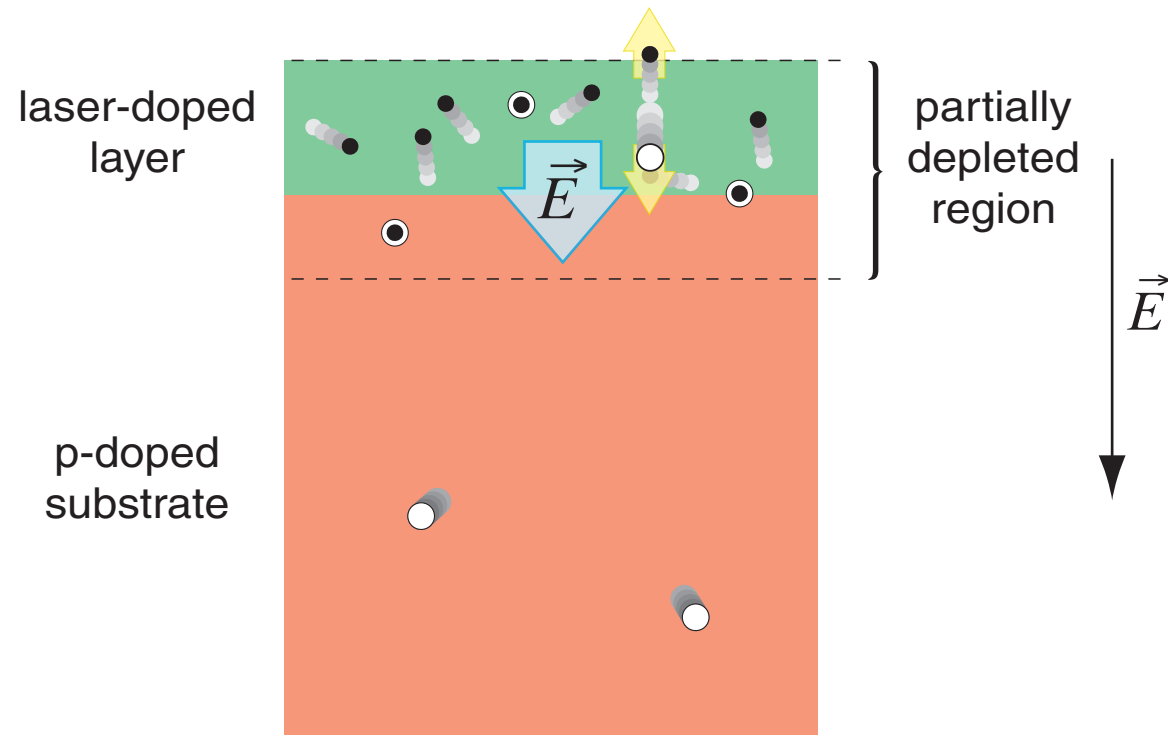
# Devices



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

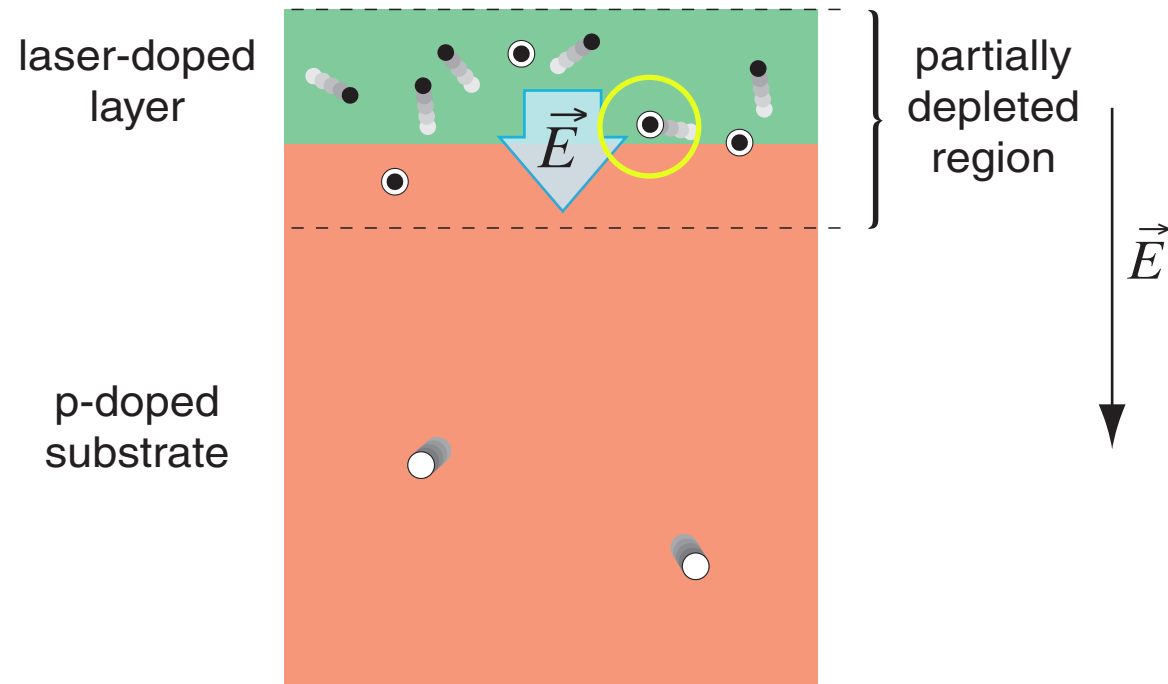


# Devices



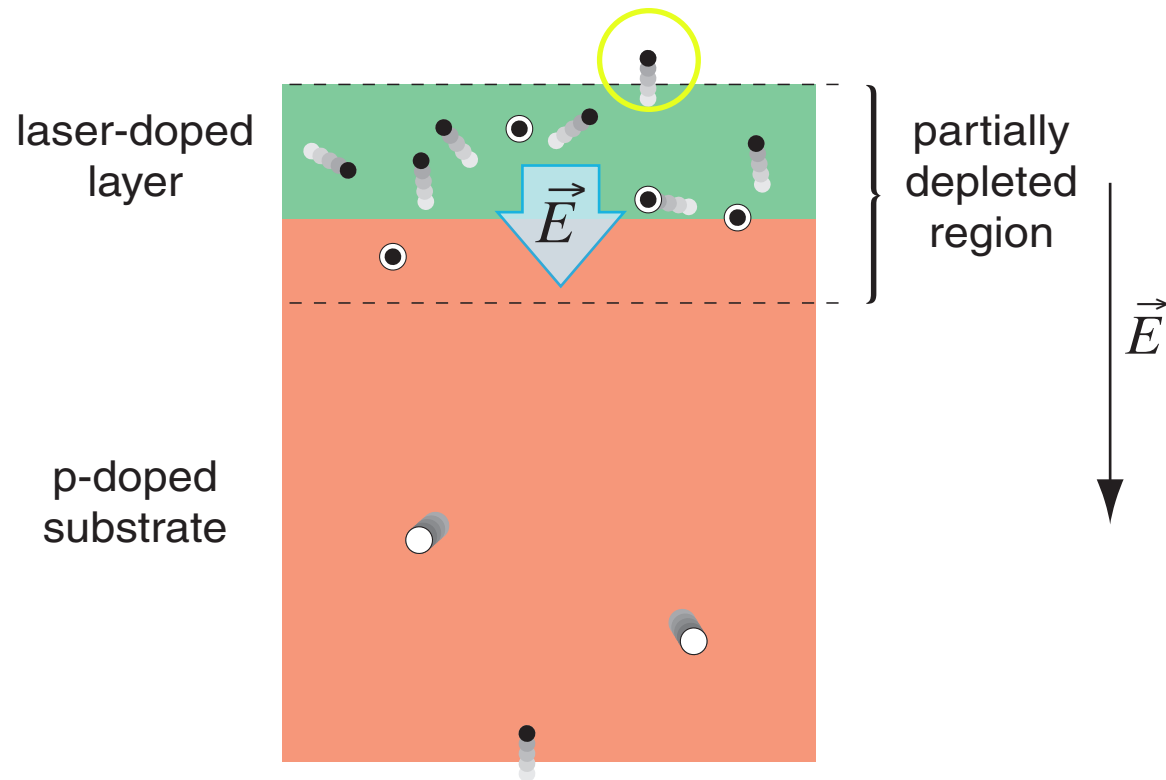
...carriers accelerate away from each other...

# Devices



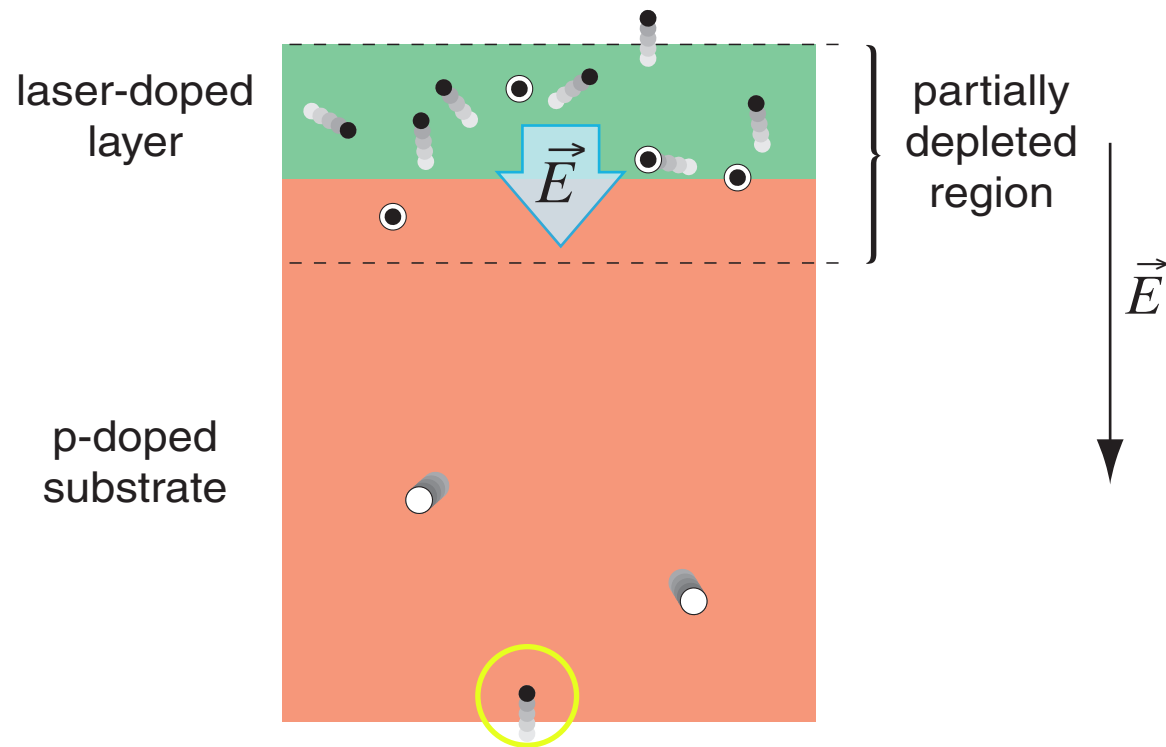
**...hole is trapped**

# 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, 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**

**NDSEG**

**National Science Foundation**

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

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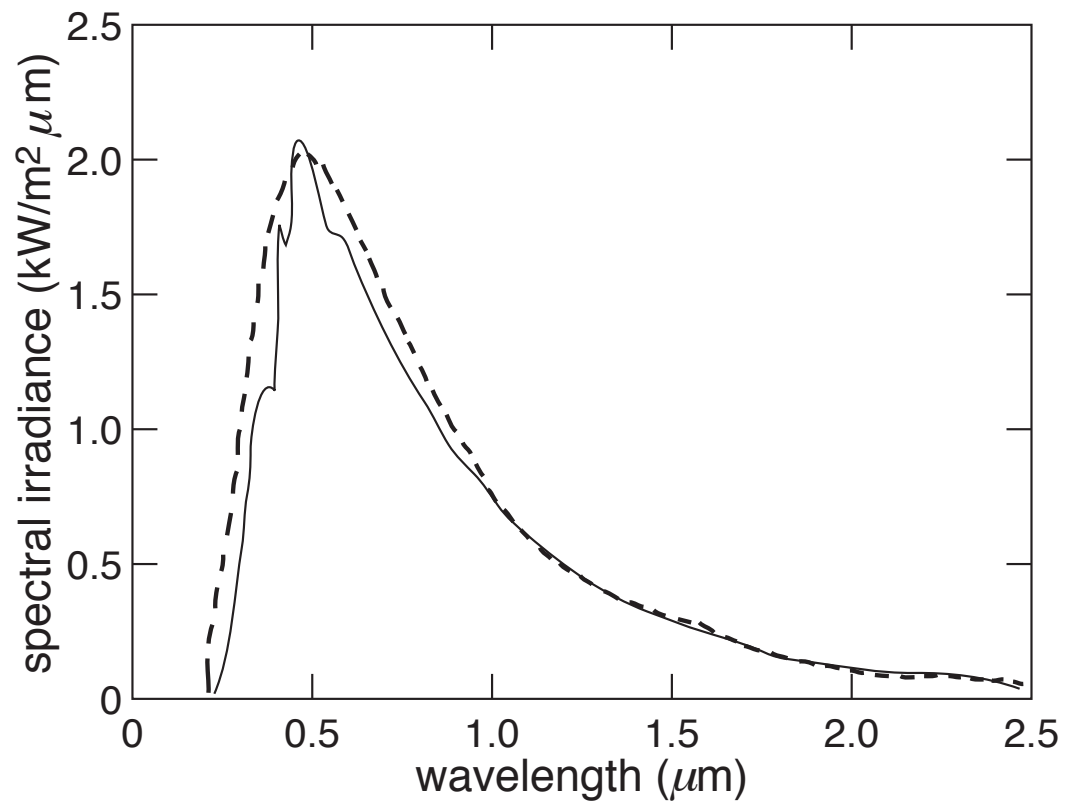
**Follow me!**



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# Devices

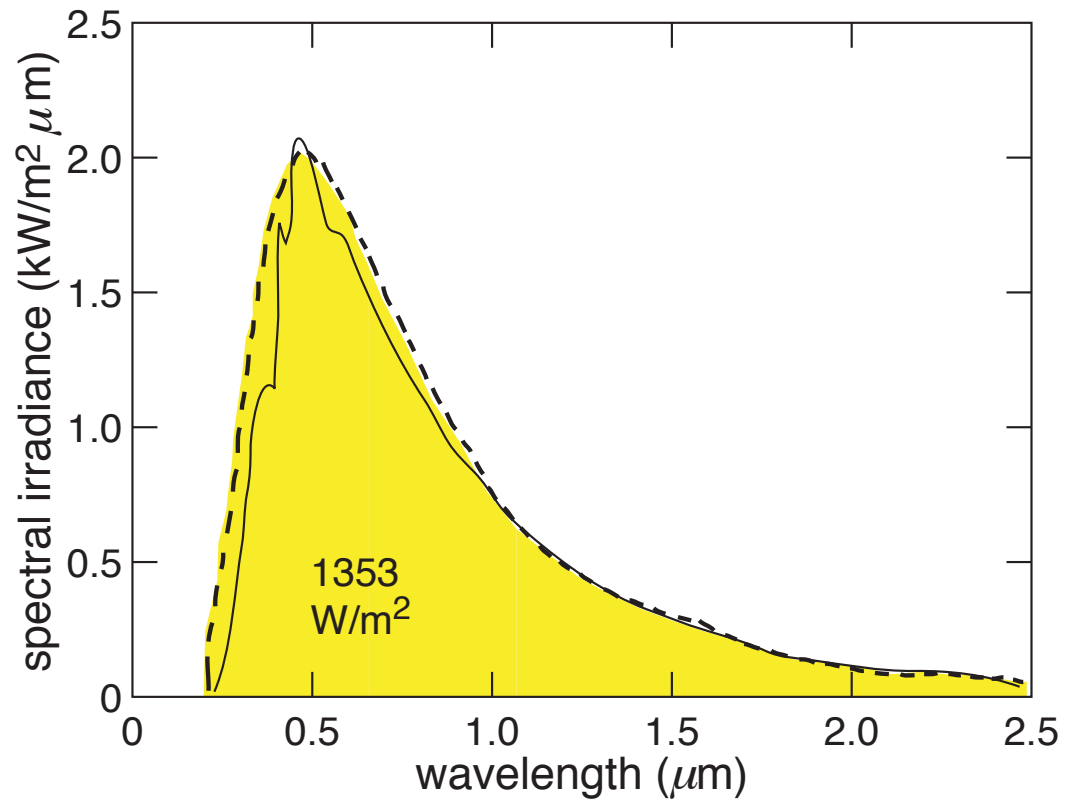
## solar spectrum





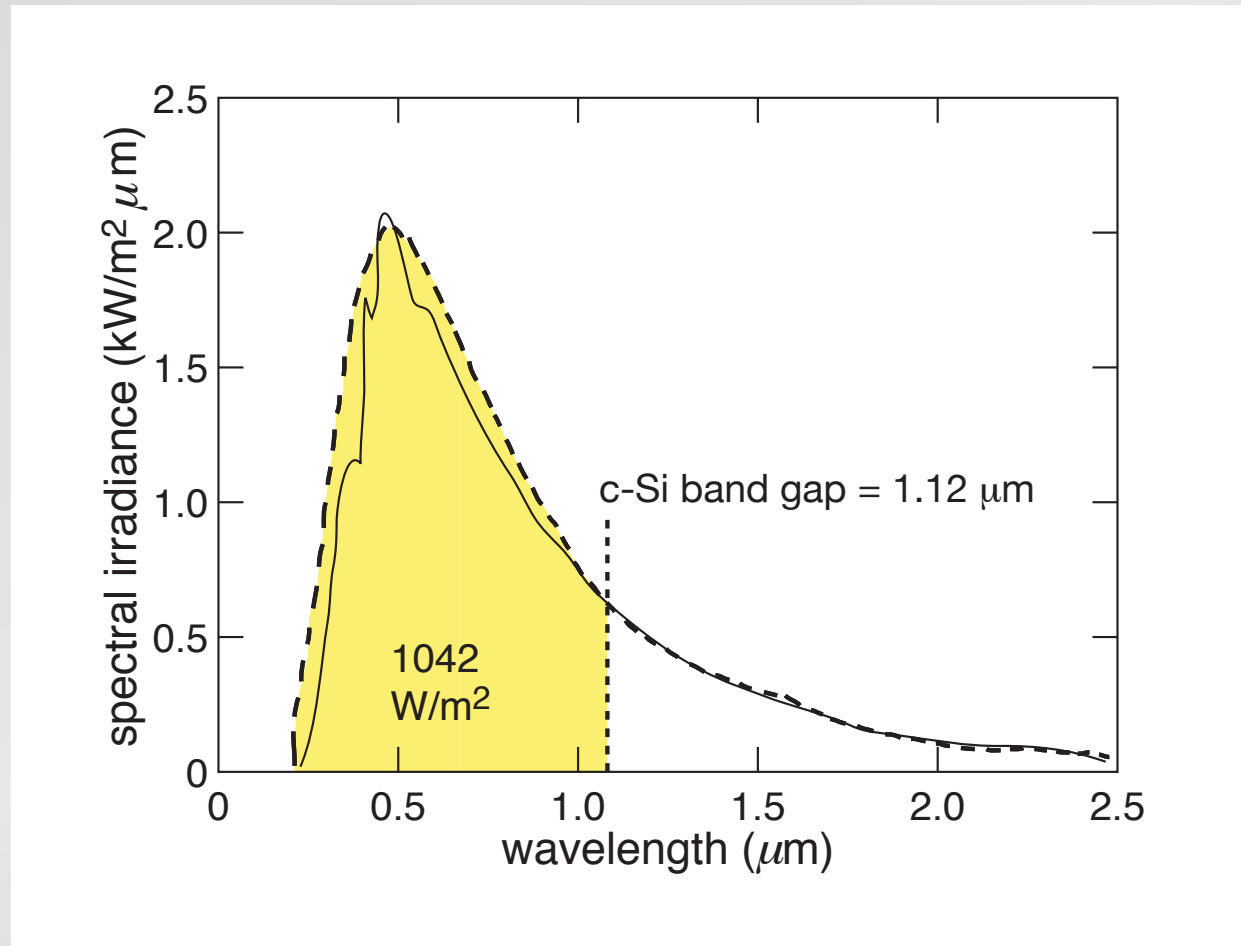
# Devices

## solar spectrum



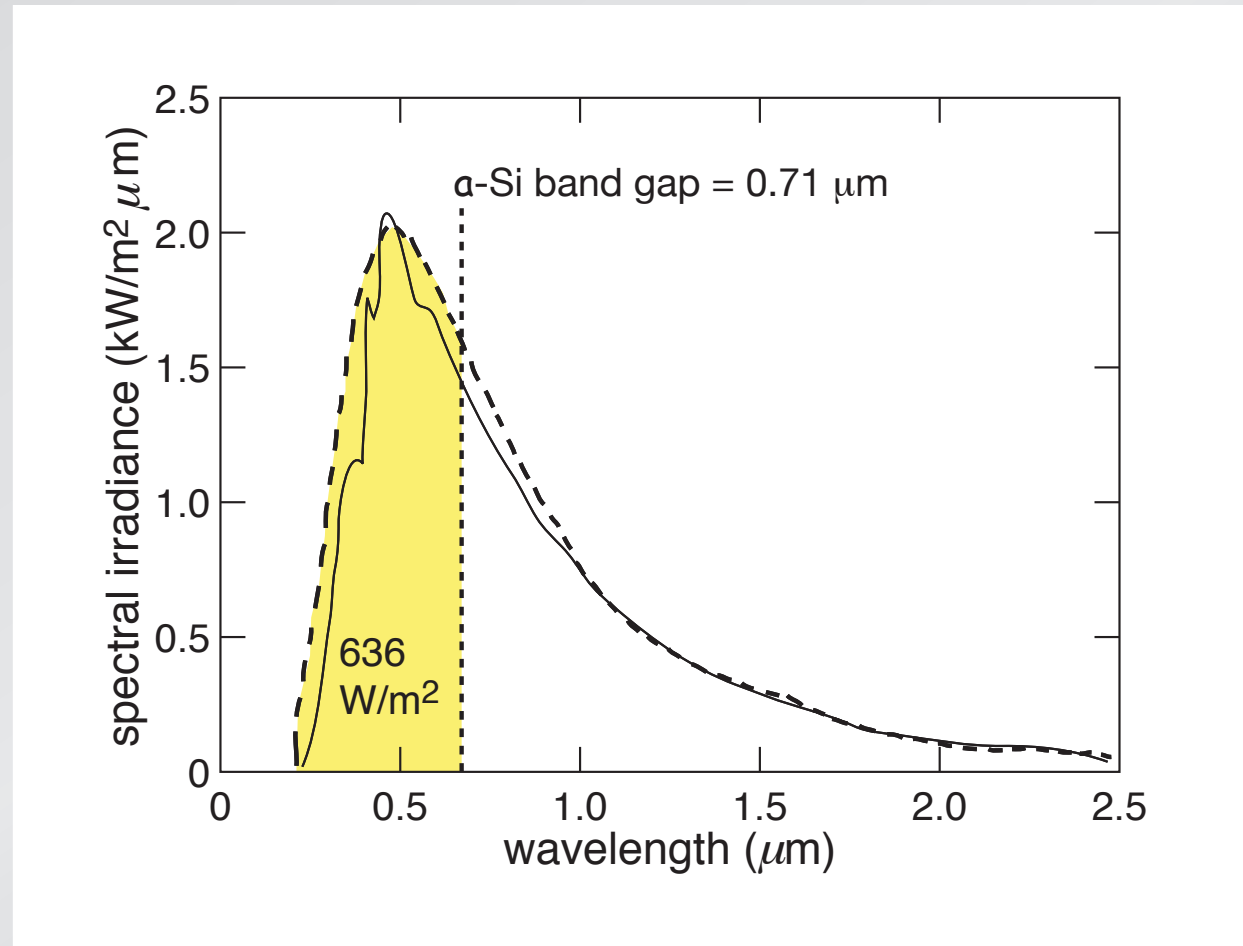
# Devices

crystalline silicon: transparent to 23% of solar radiation



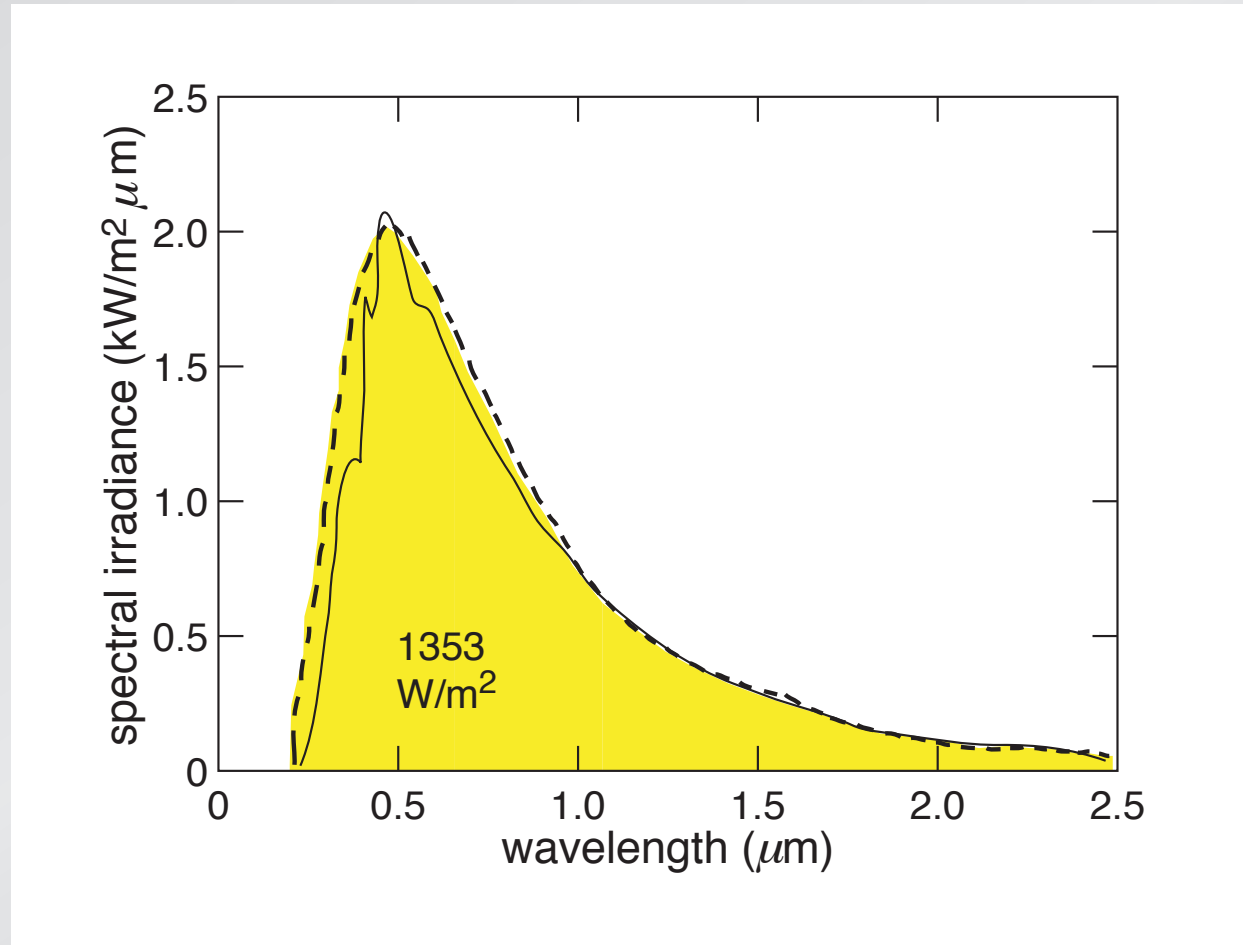
# Devices

amorphous silicon: transparent to 53% of solar radiation



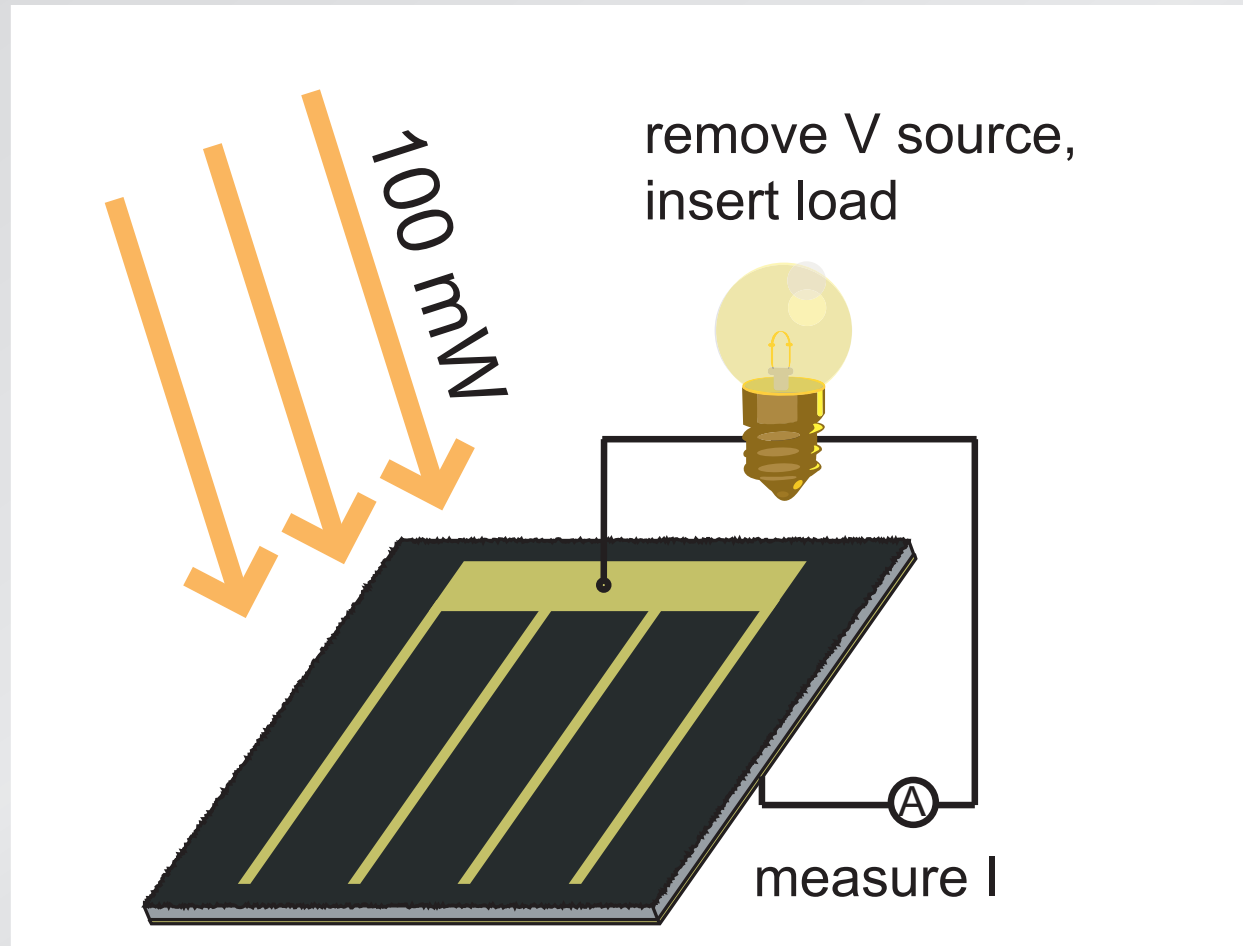
# Devices

black silicon: potential to recover transmitted energy



# Devices

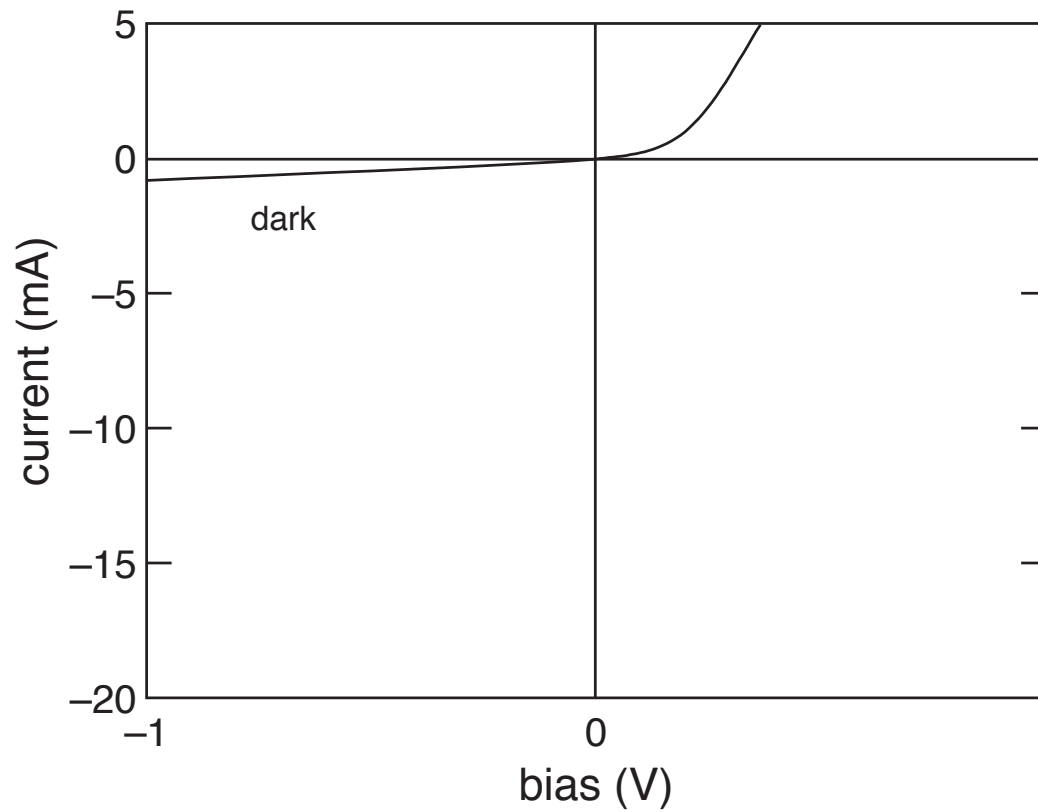
very preliminary photovoltaic cell





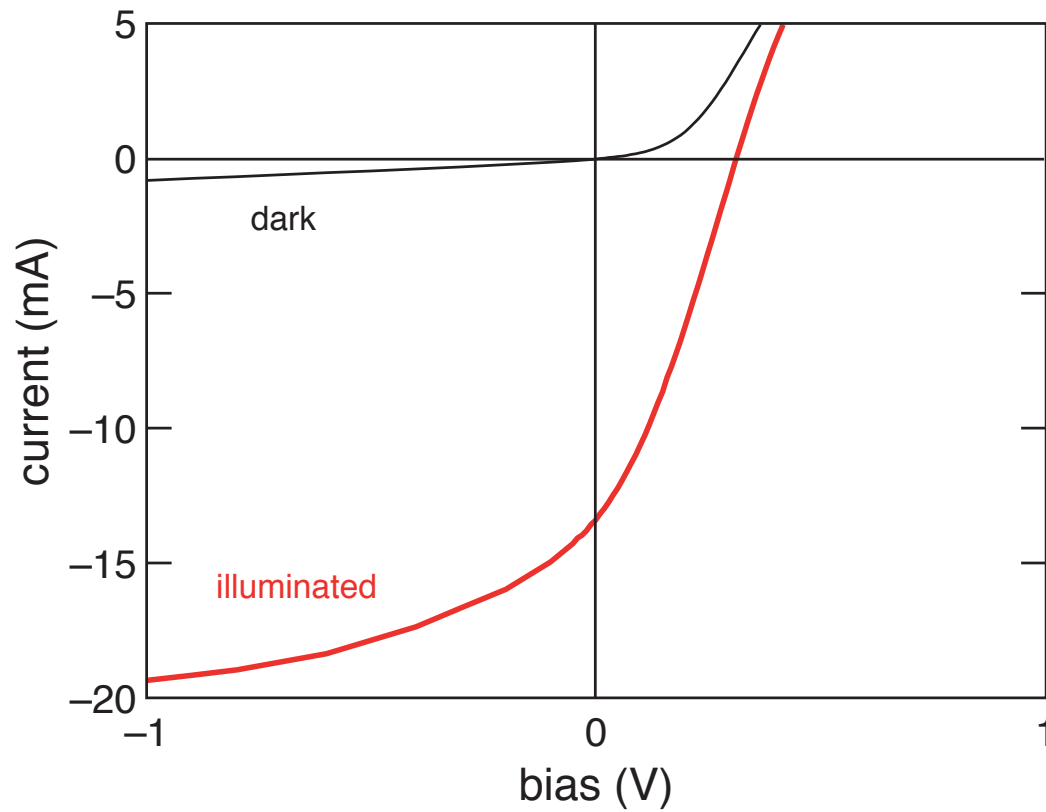
# Devices

very preliminary photovoltaic cell



# Devices

very preliminary photovoltaic cell



# Devices

1.5% efficiency, a good beginning

