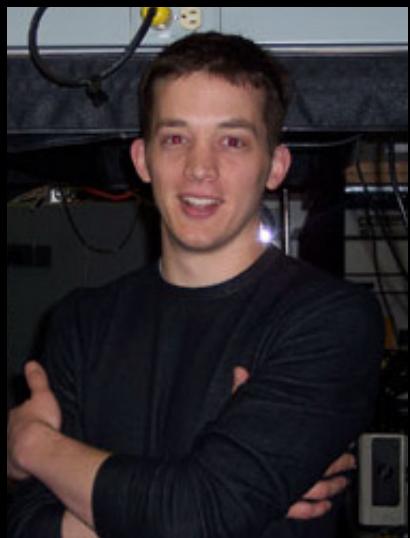




Black silicon

Konopinski Colloquium
Indiana University Bloomington
Bloomington, IN, 3 March 2010

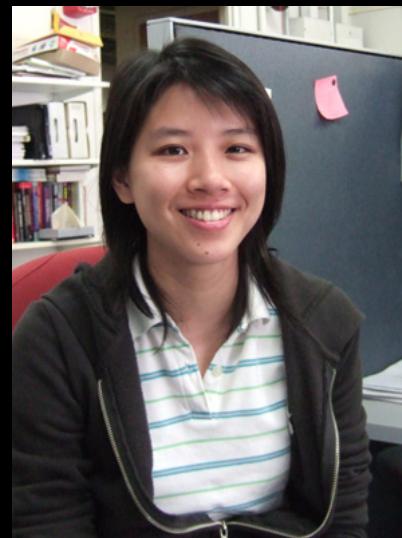




Mark Winkler



Renee Sher



Yu-Ting Lin



Eric Mazur

and also....

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

Dr. John Chervinsky
Dr. Joshua Levinson

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

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

Prof. Augustinus Asenbaum (Vienna)

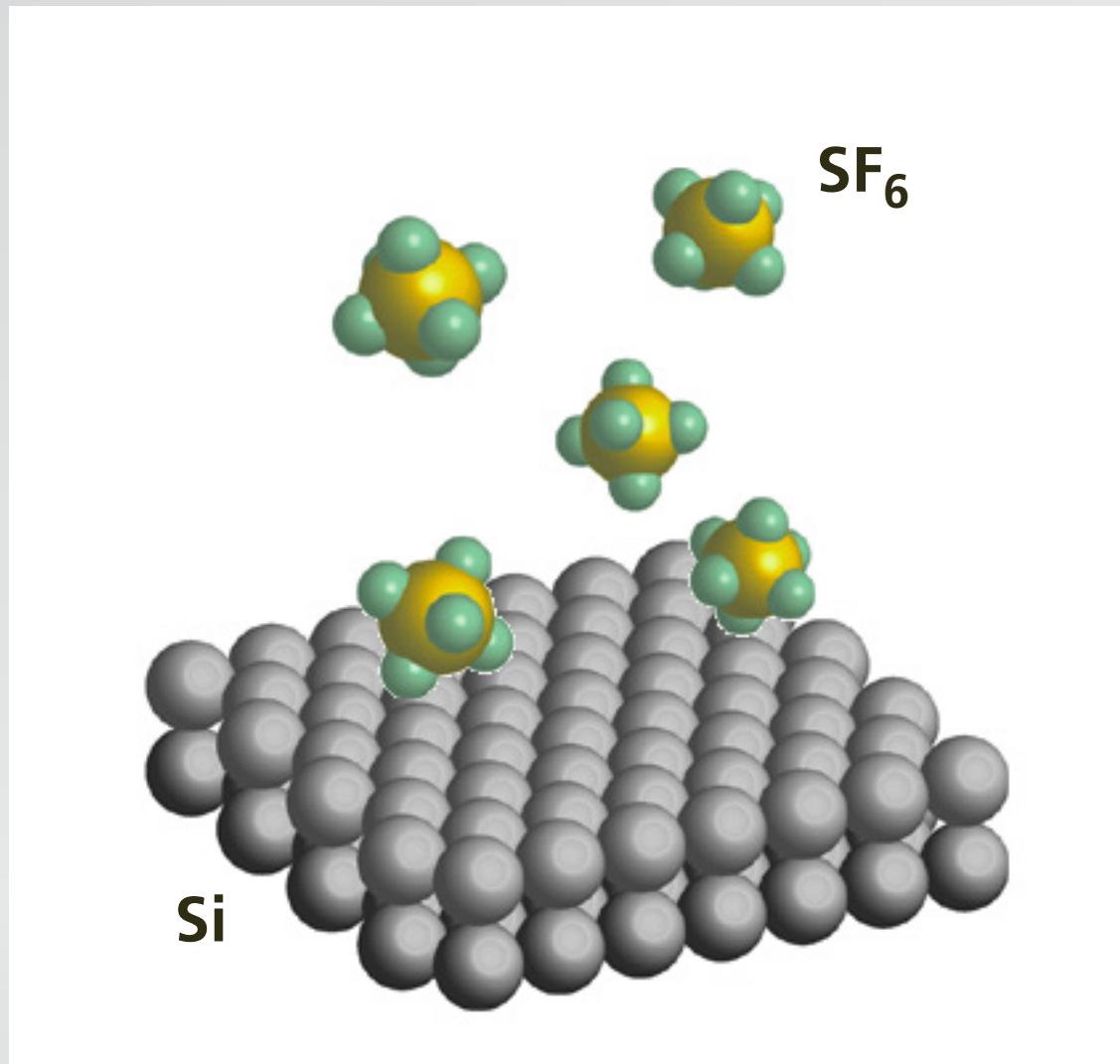
Dr. François Génin (LLNL)
Mark Wall (LLNL)

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

Dr. Pat Maloney (NVSED)

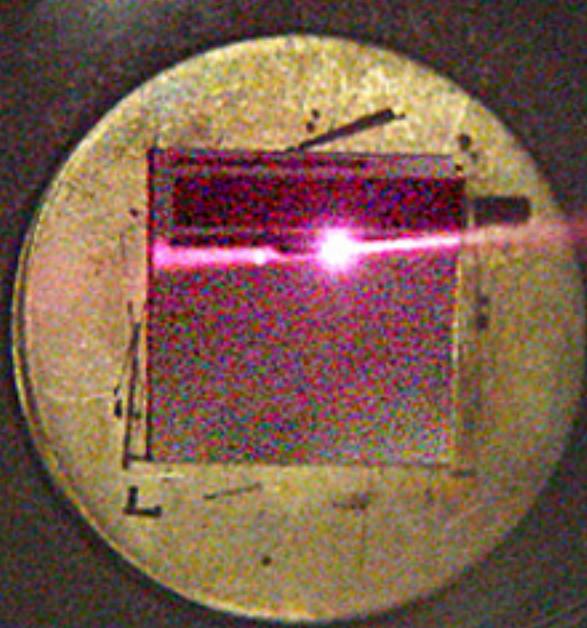
Dr. Jeffrey Warrander (ARDEC)

Introduction



irradiate with 100-fs 10 kJ/m² pulses

Introduction

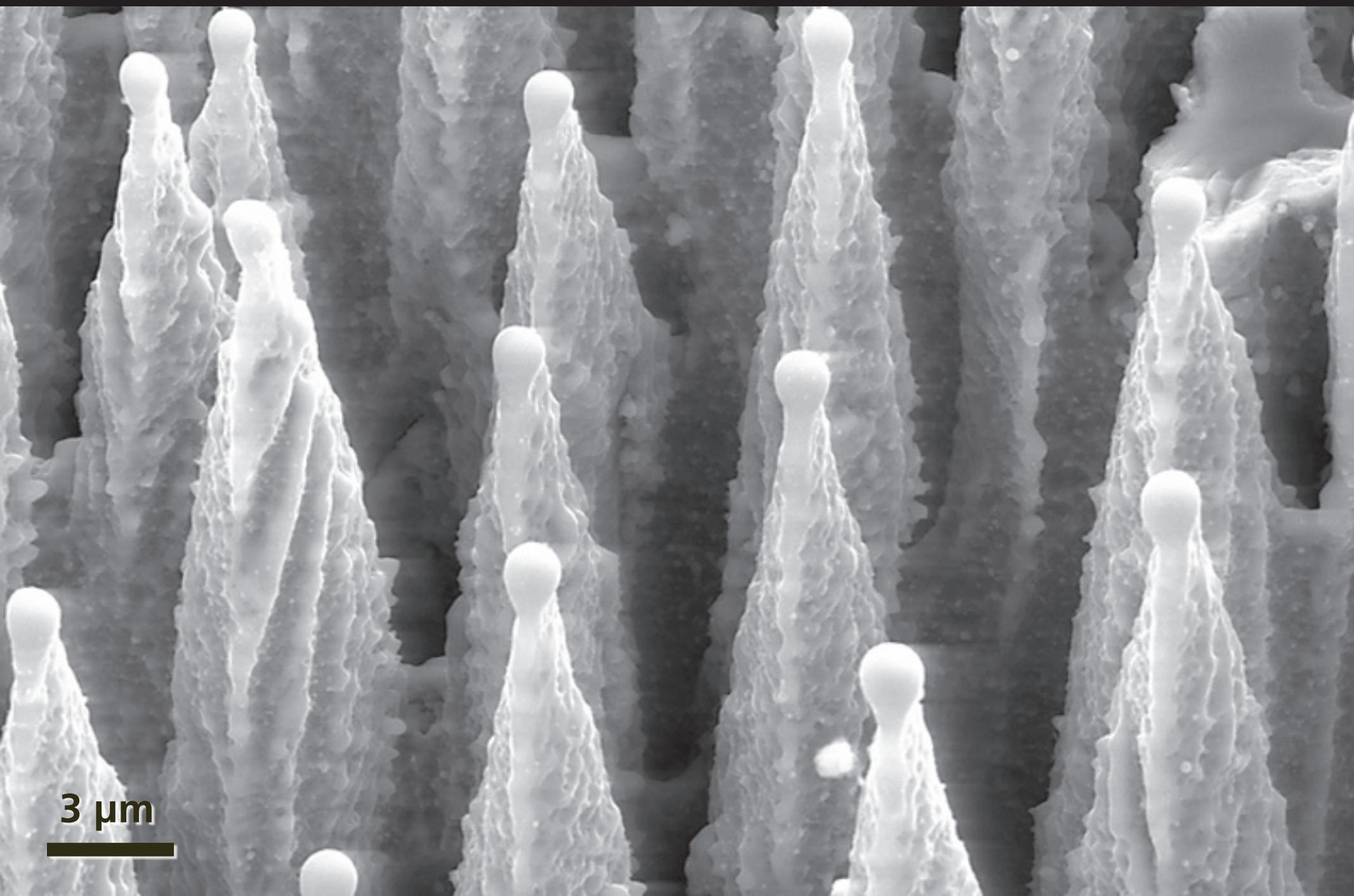


Introduction



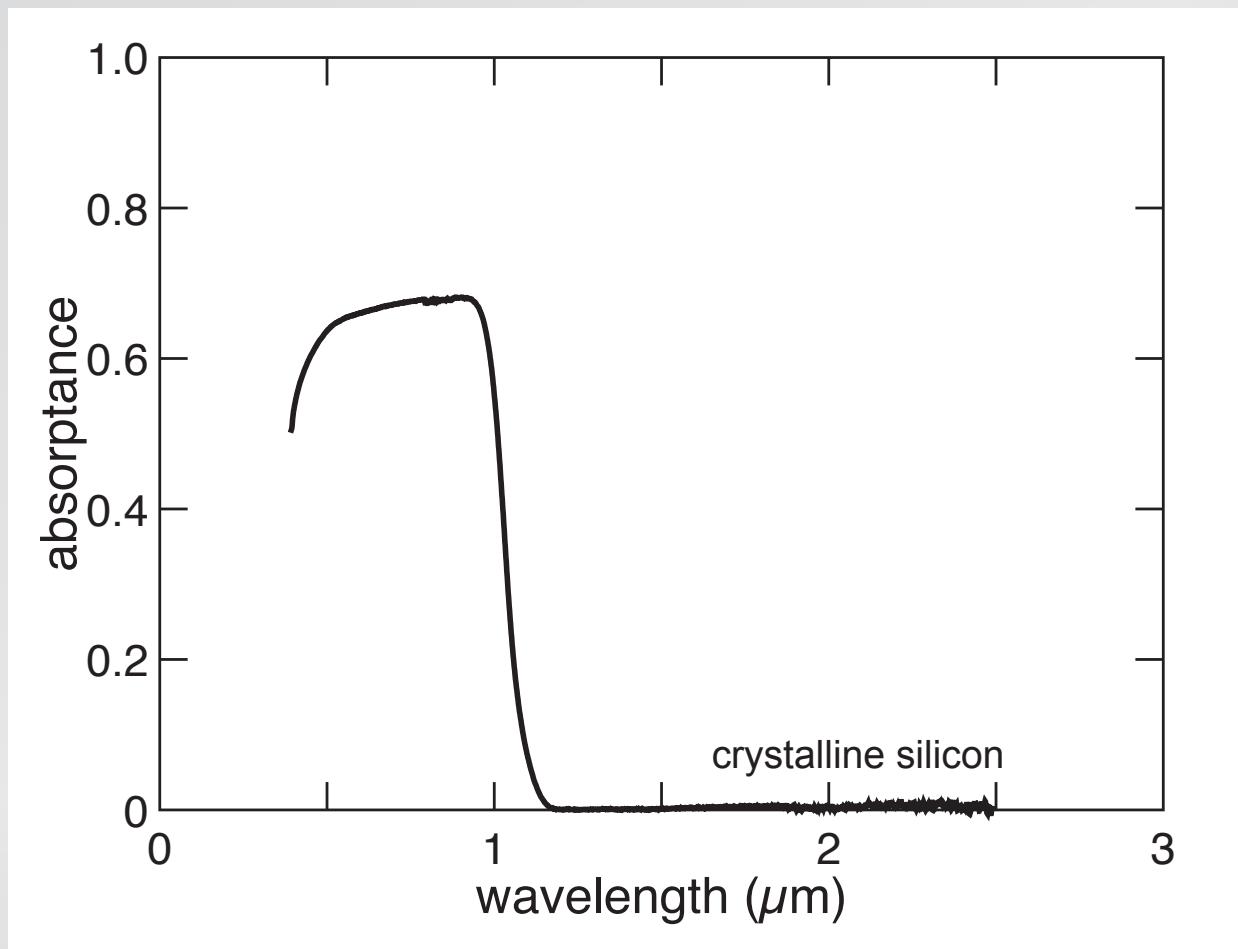
"black silicon"

Introduction



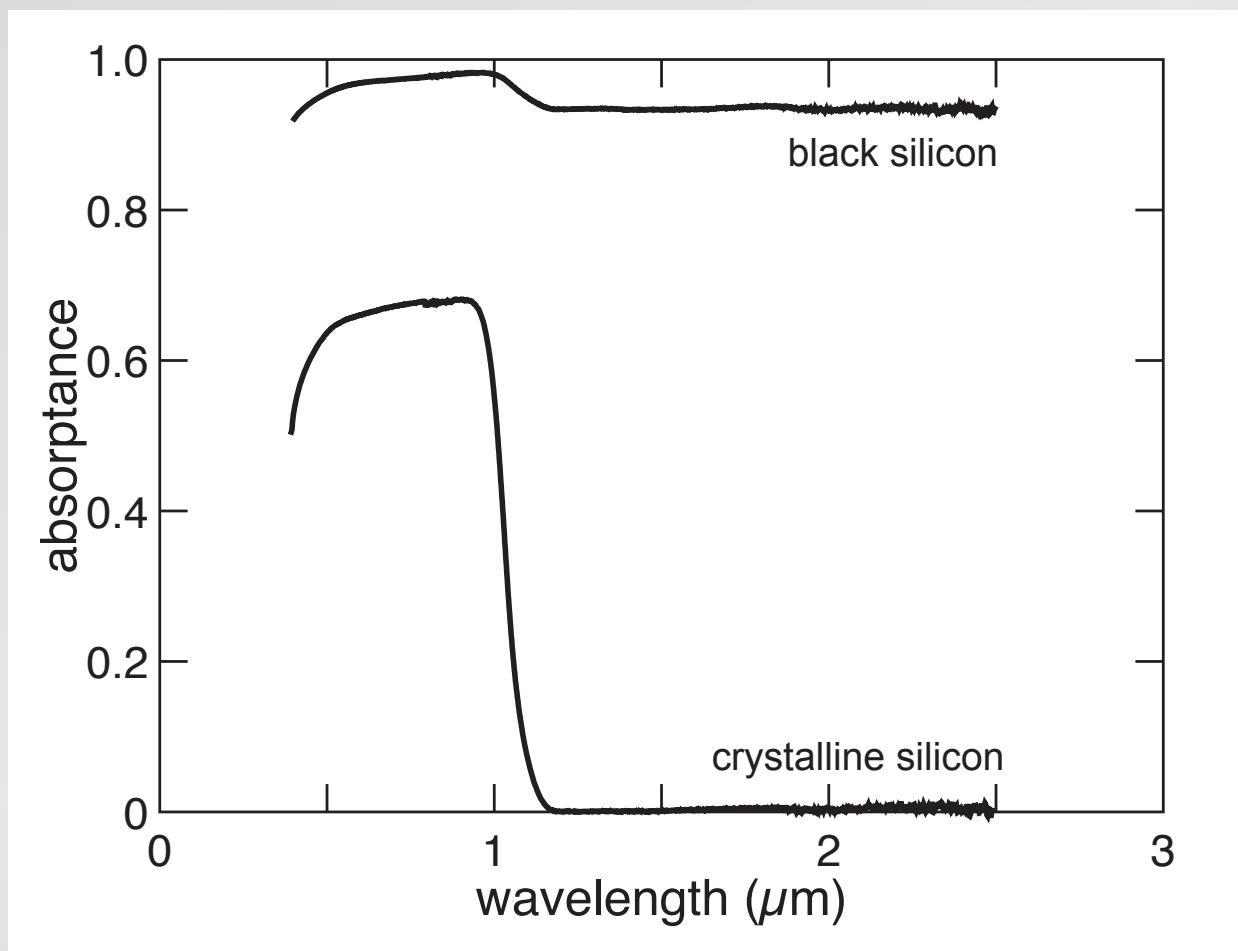
Introduction

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

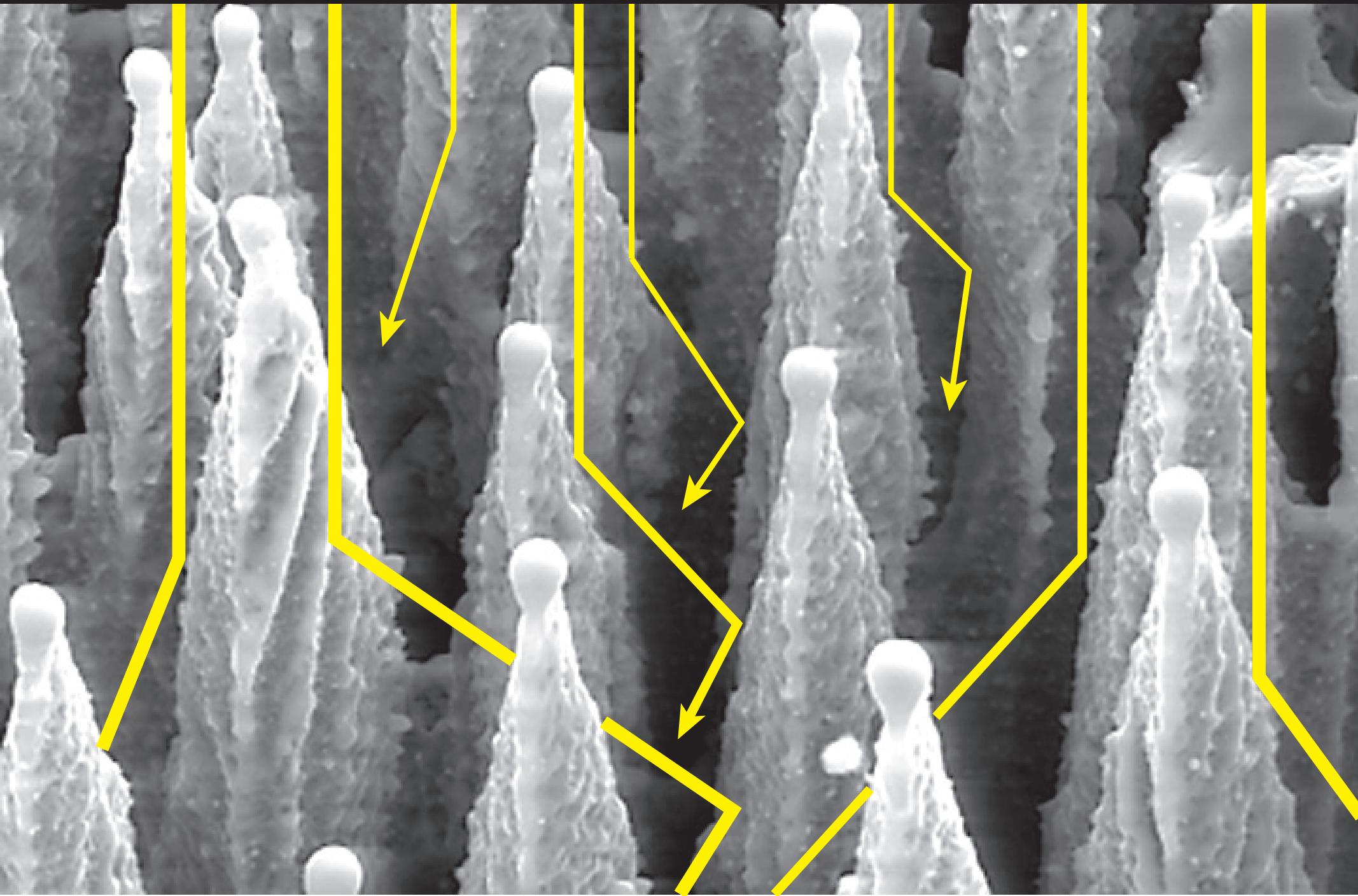


Introduction

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

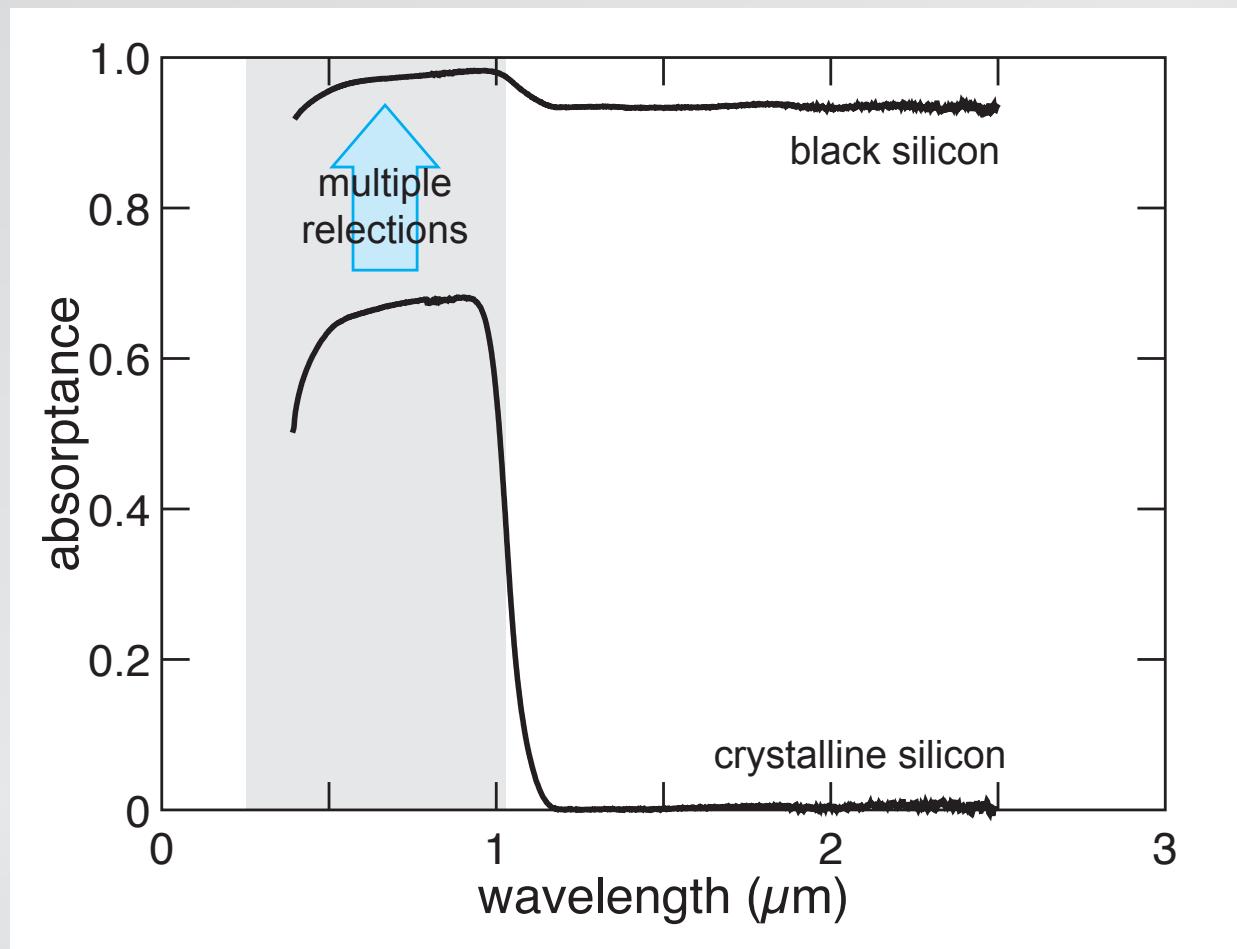


Introduction



Introduction

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



Introduction

silicon transparent in near IR

visible



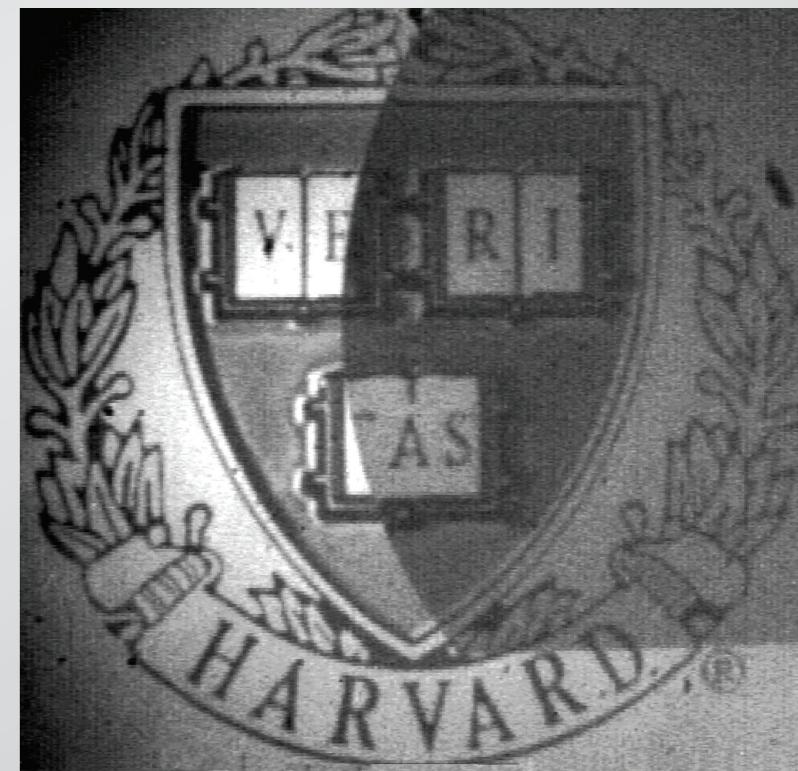
Introduction

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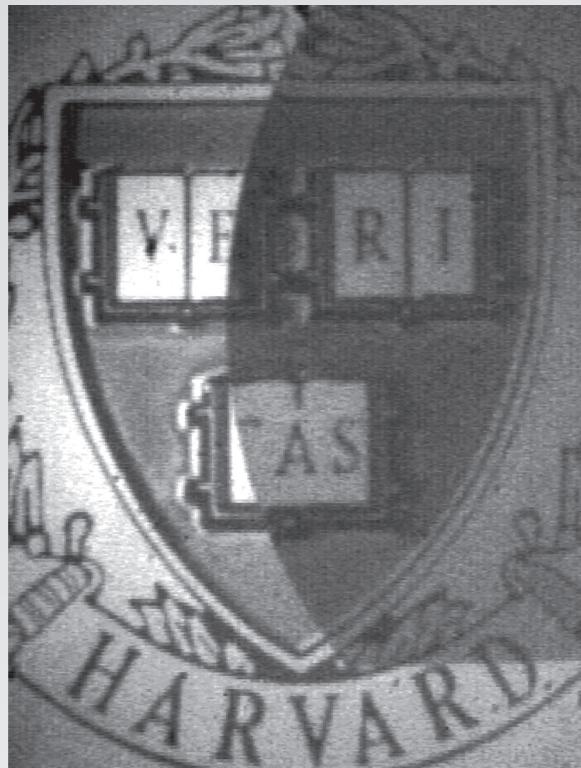
near IR



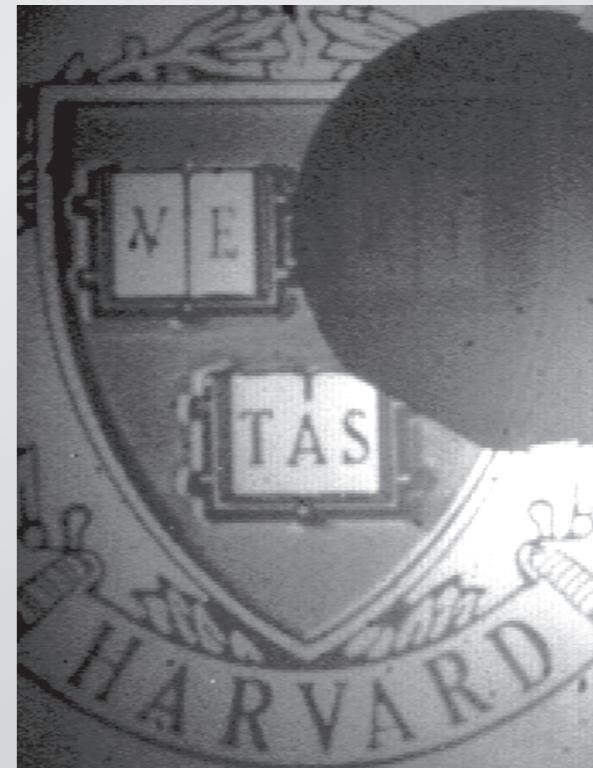
Introduction

roughening doesn't change IR transmission...

polished



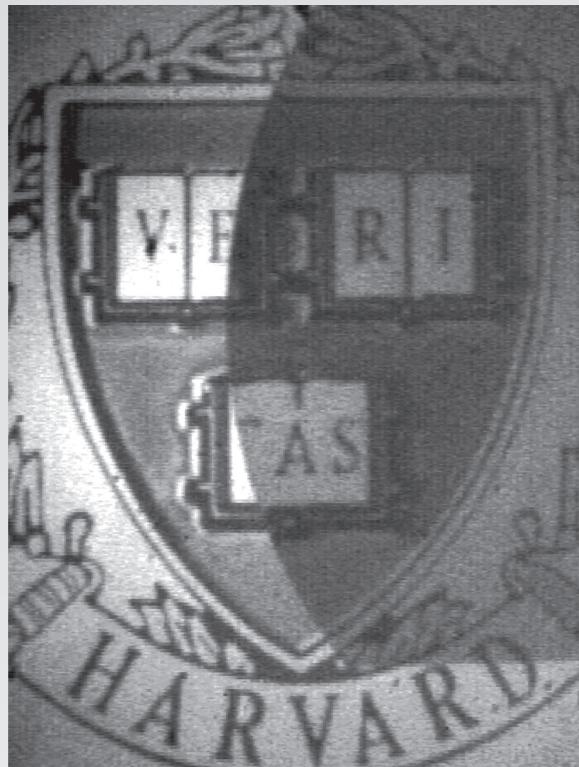
unpolished



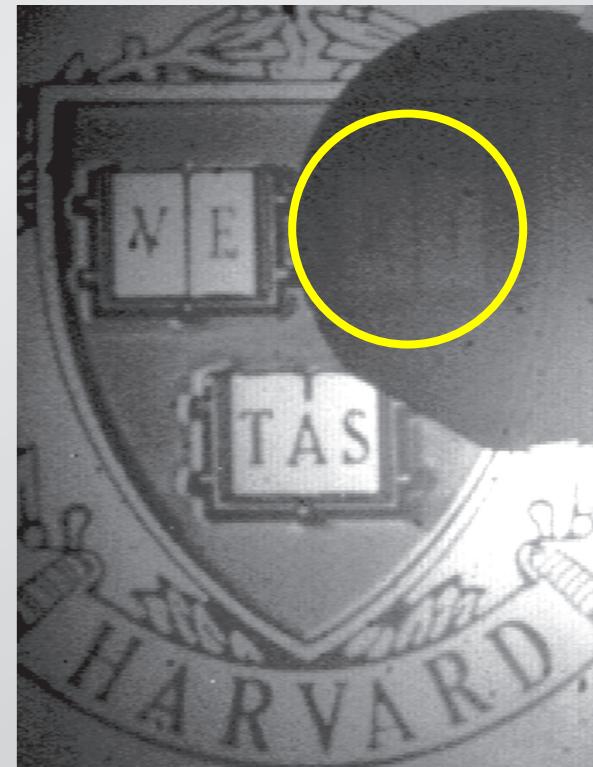
Introduction

roughening doesn't change IR transmission...

polished



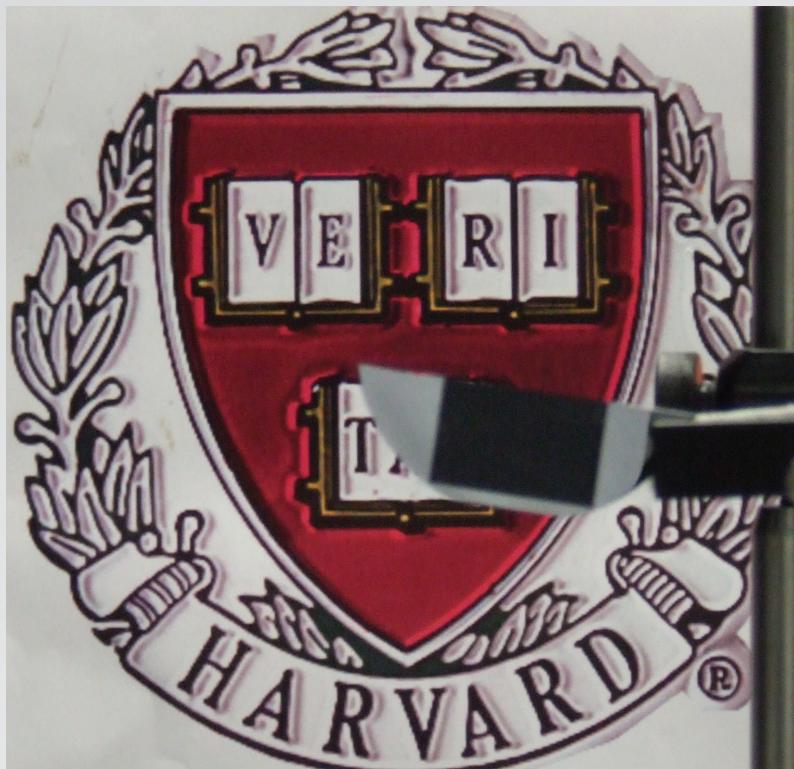
unpolished



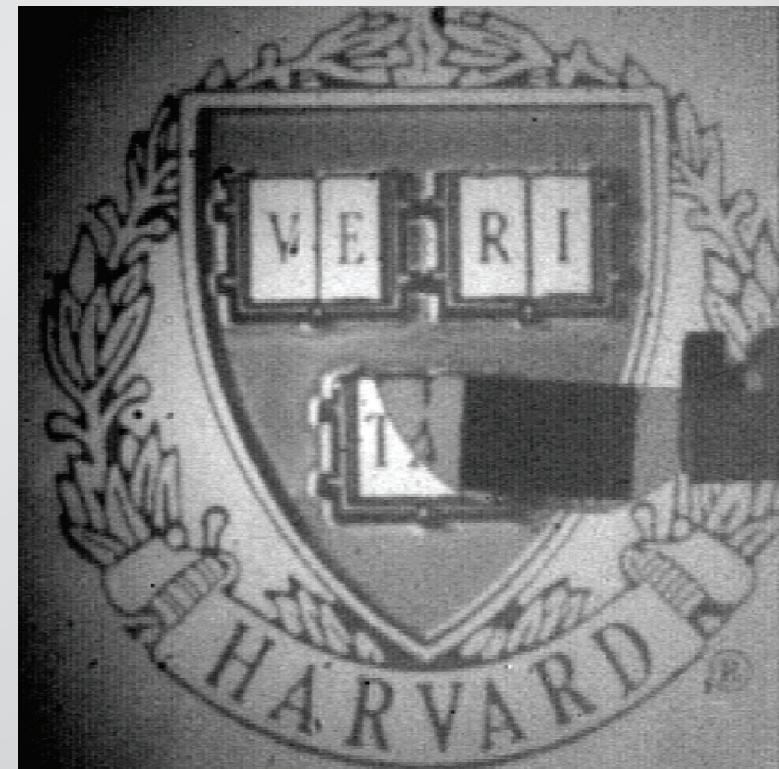
Introduction

...but black silicon blocks IR completely

visible



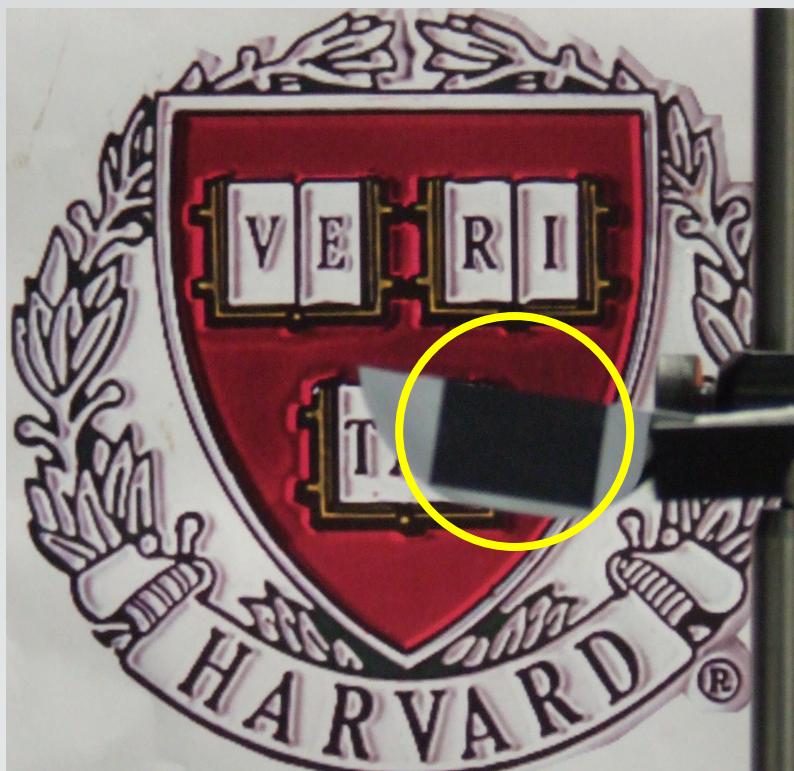
near IR



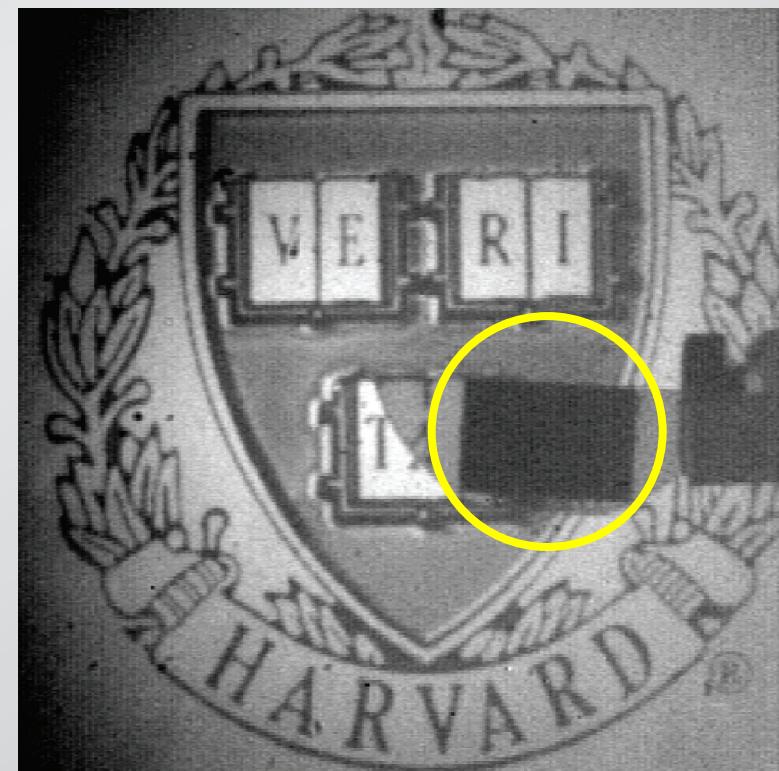
Introduction

...but black silicon blocks IR completely

visible



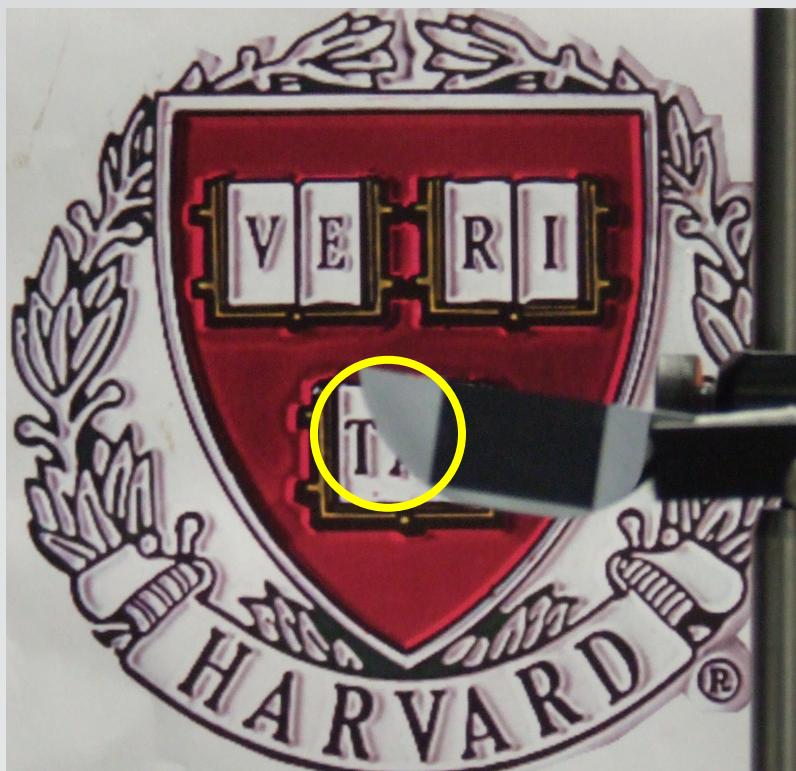
near IR



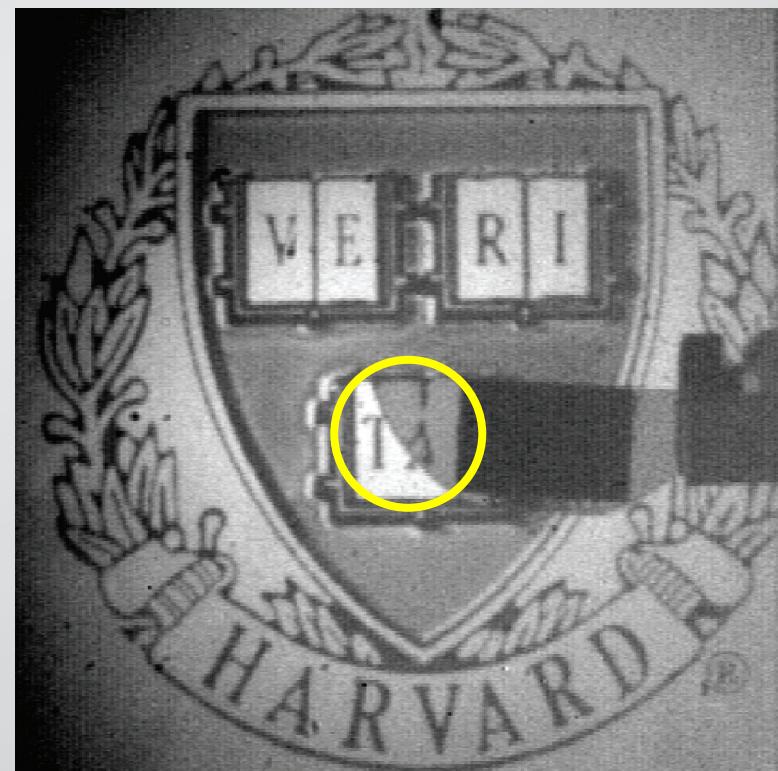
Introduction

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

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gap
impurity band
transitions

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Introduction

a decade of research

OPTICAL

UV-VIS-NIR
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UPS
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responsivity
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gap
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transitions

ELECTRONIC

Hall measurements
conductivity
IV rectification
c-AFM

carrier concentration
mobilities
junction properties

STRUCTURAL

SEM
TEM
EDX
SAD
EXAFS
AFM
SIMS
RBS
ion channeling

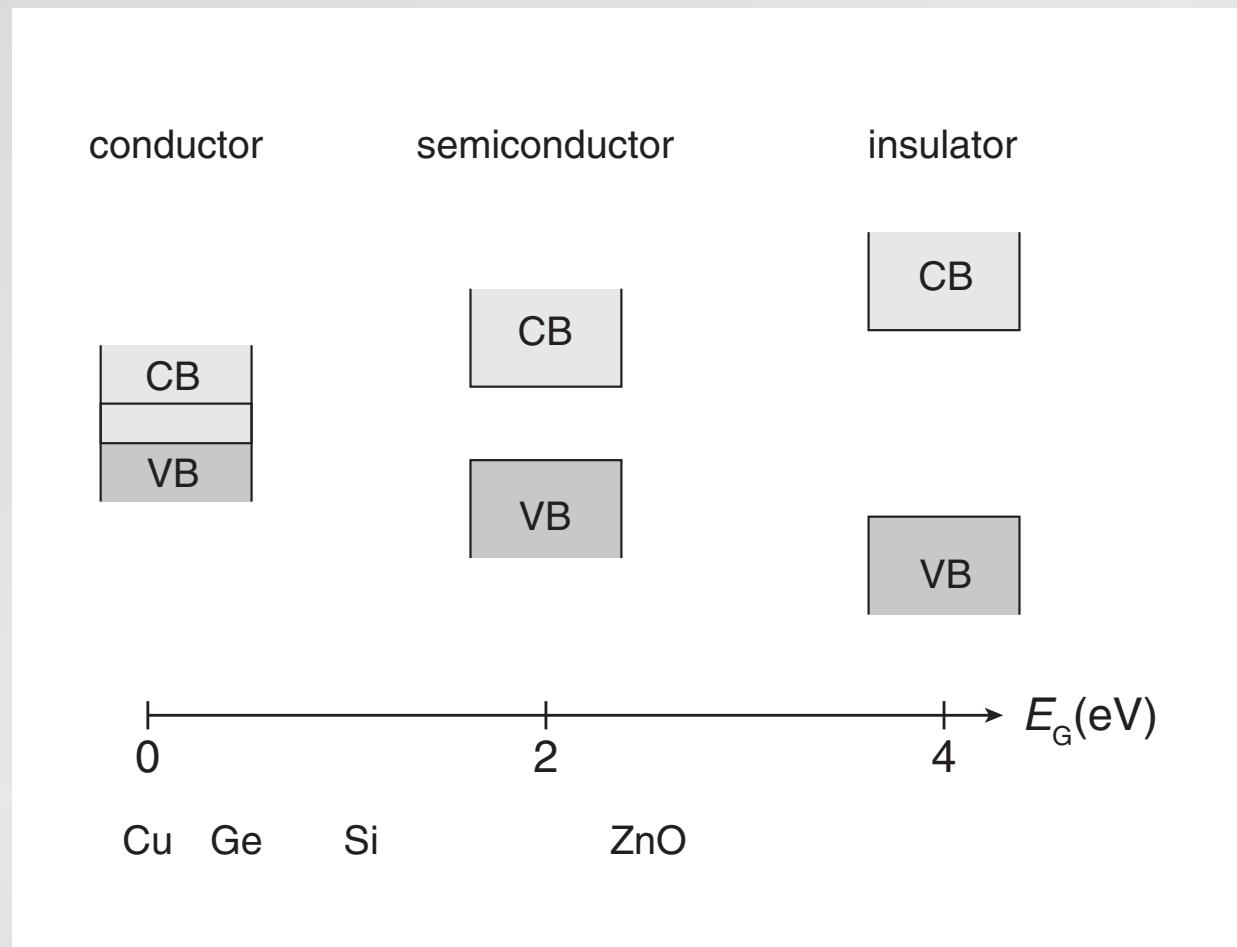
Introduction

a decade of research

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

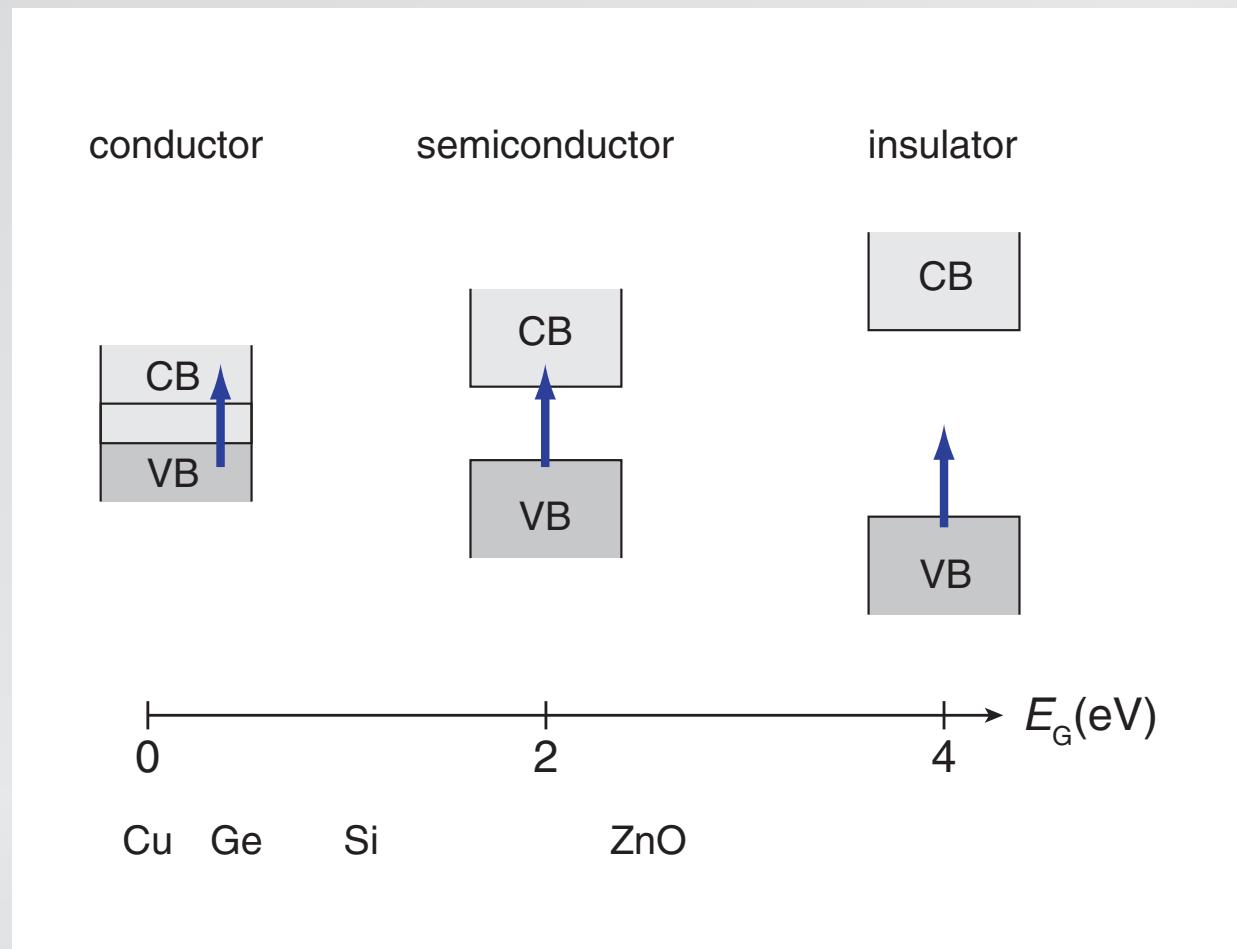
Introduction

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:

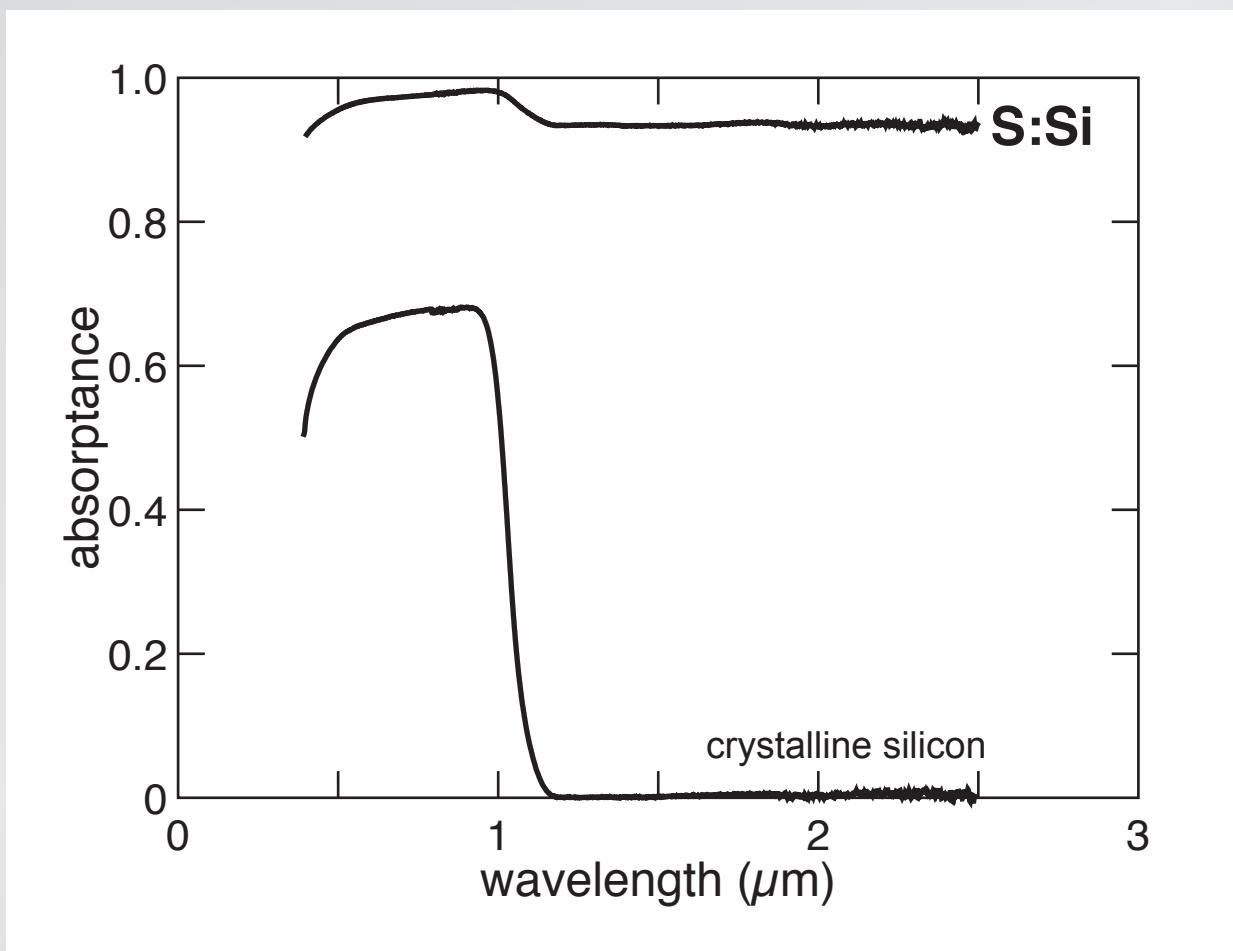
N	O	F
P	S	Cl
	Se	
Sb	Te	

substrates:

Si Ge ZnO InP GaAs
Ti Ag Al Cu Pd Rh Ta Pt

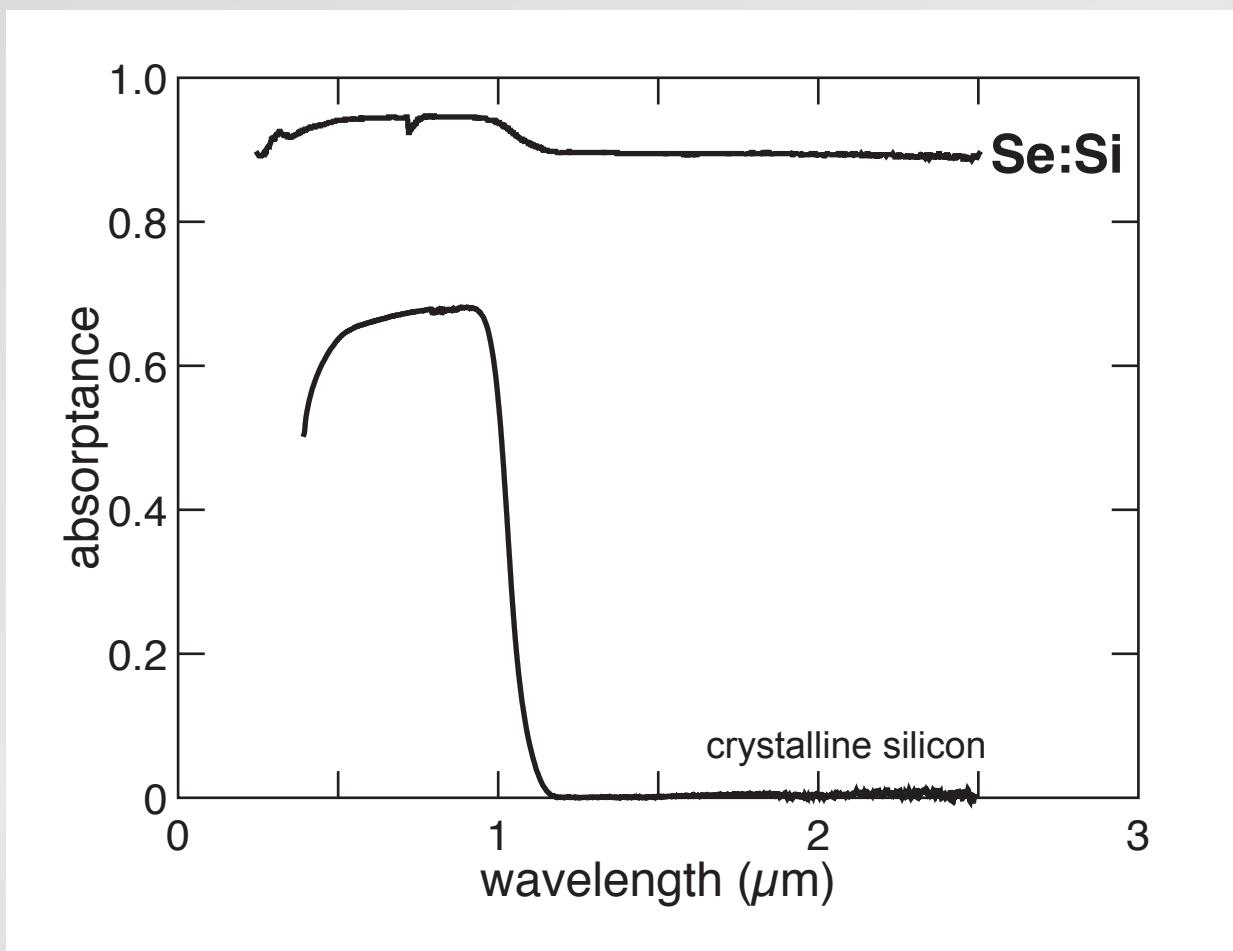
Introduction

focus on chalcogen-doped silicon



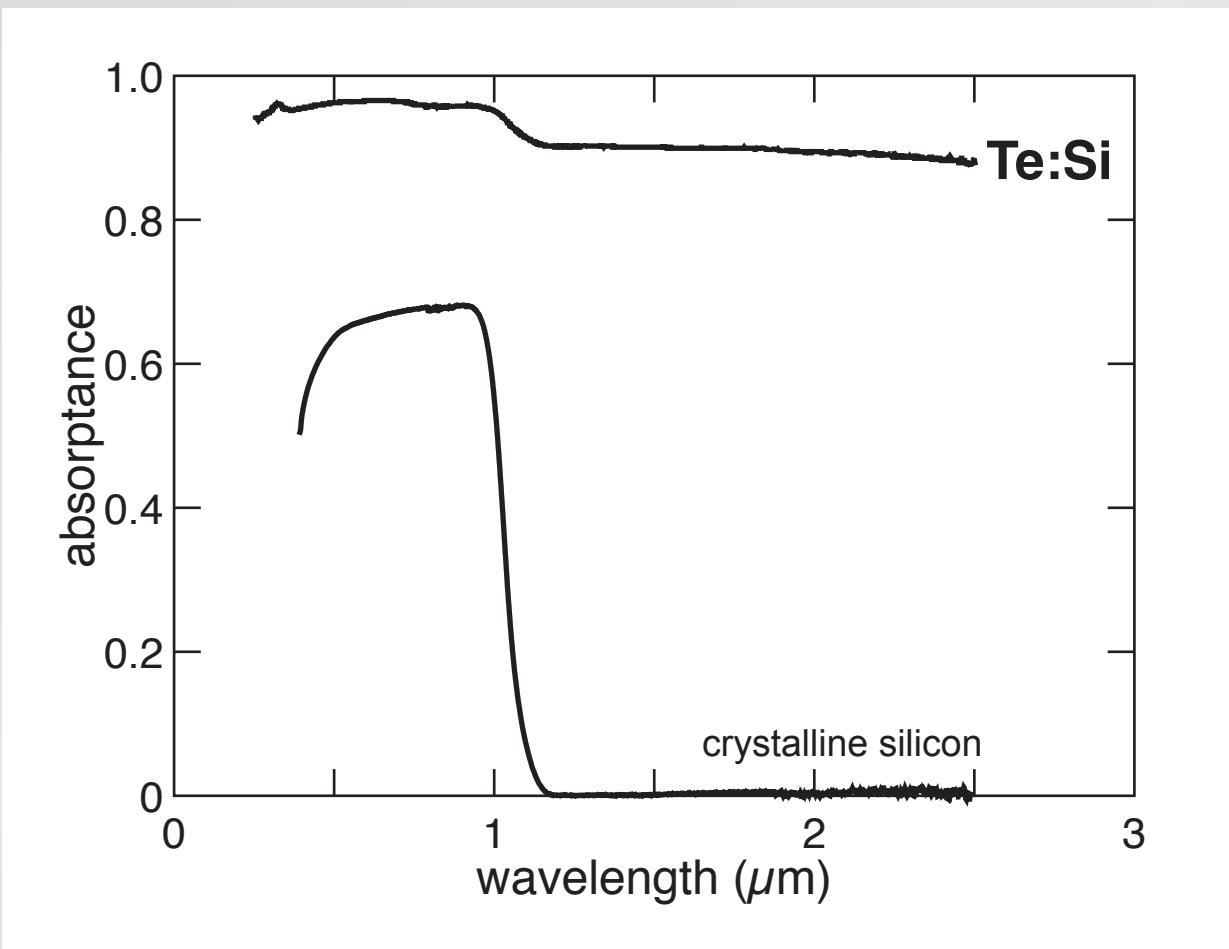
Introduction

focus on chalcogen-doped silicon



Introduction

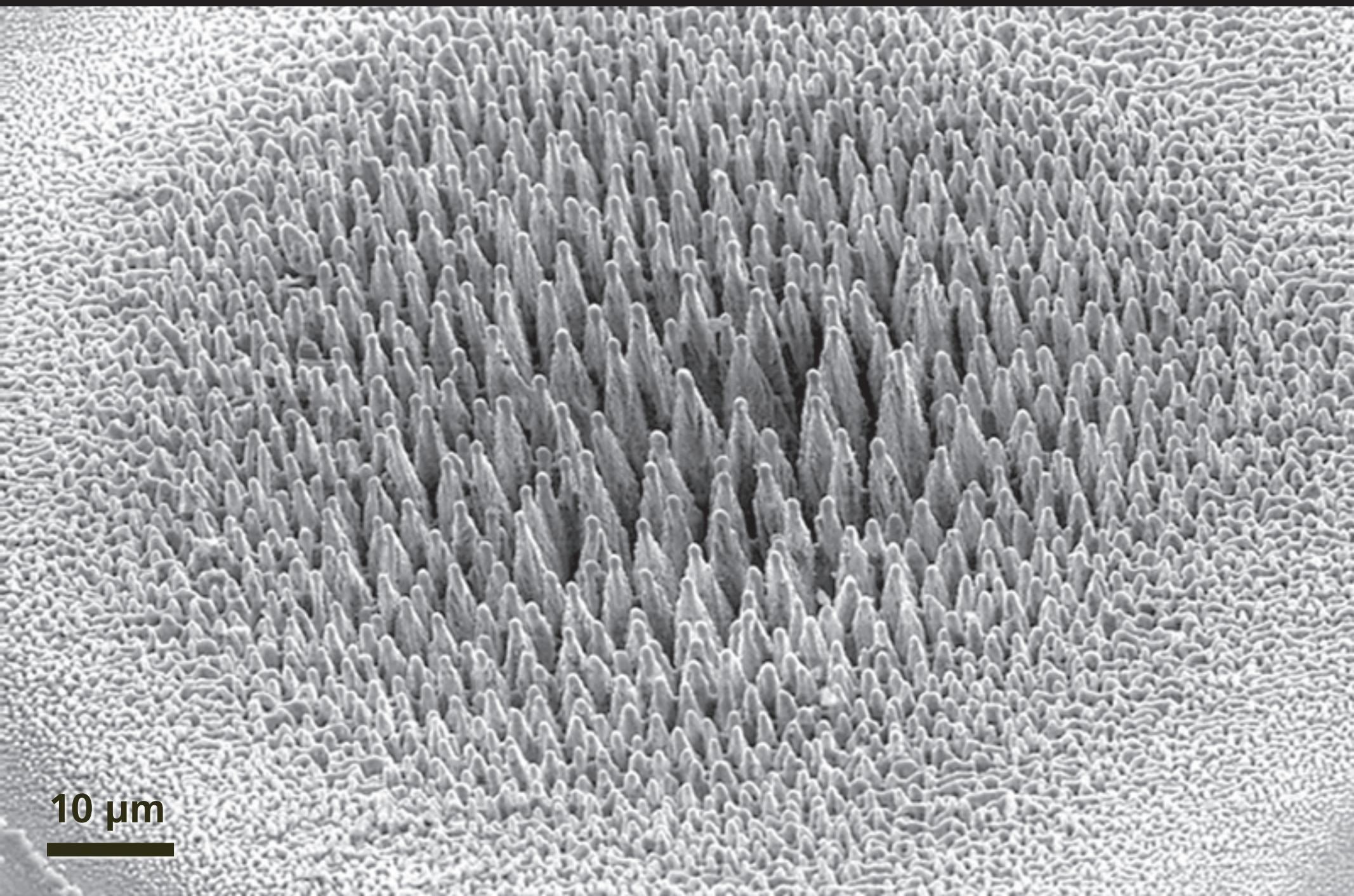
focus on chalcogen-doped silicon



Outline

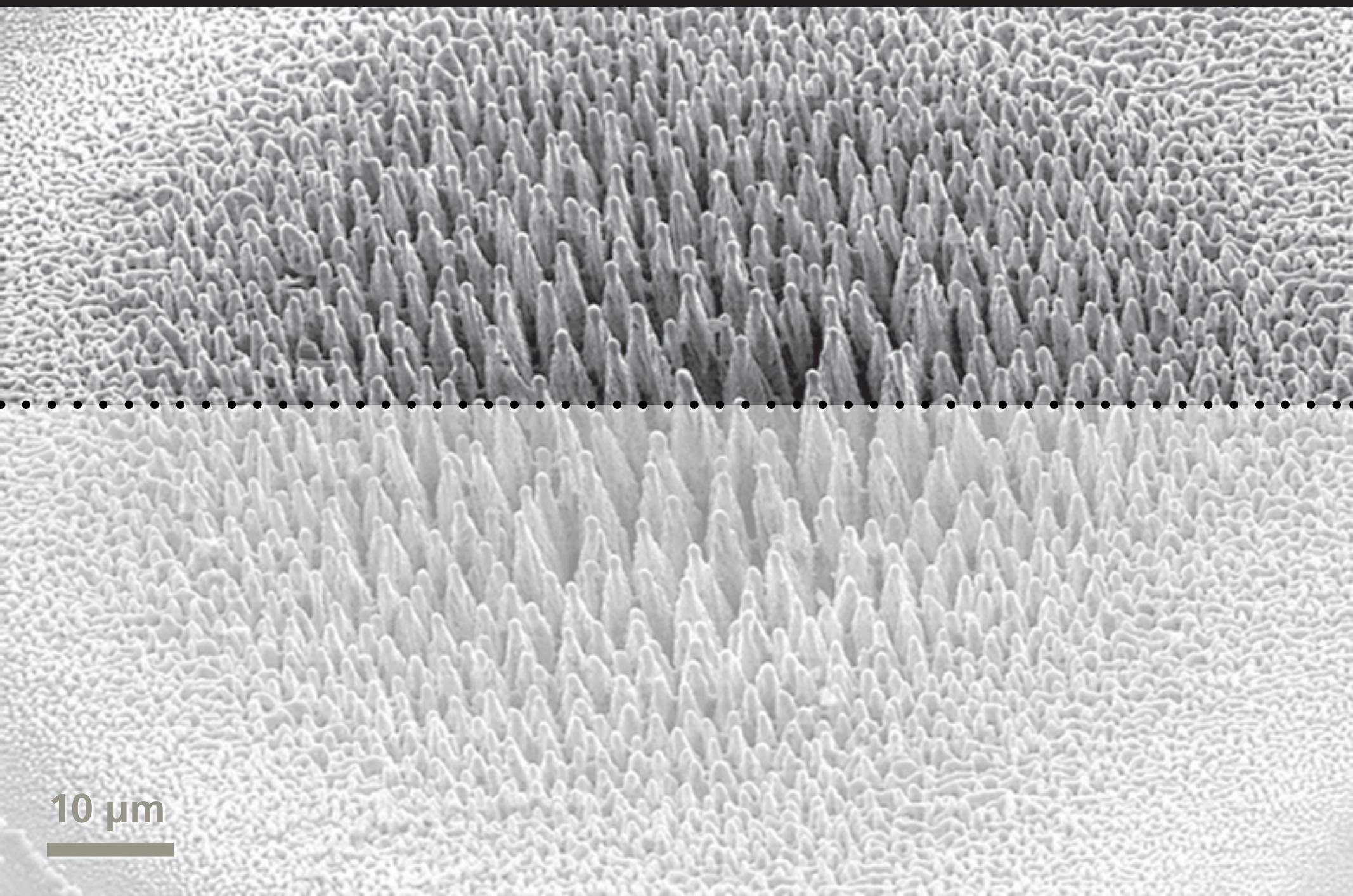
- structure
- optoelectronic properties
- devices

Structure



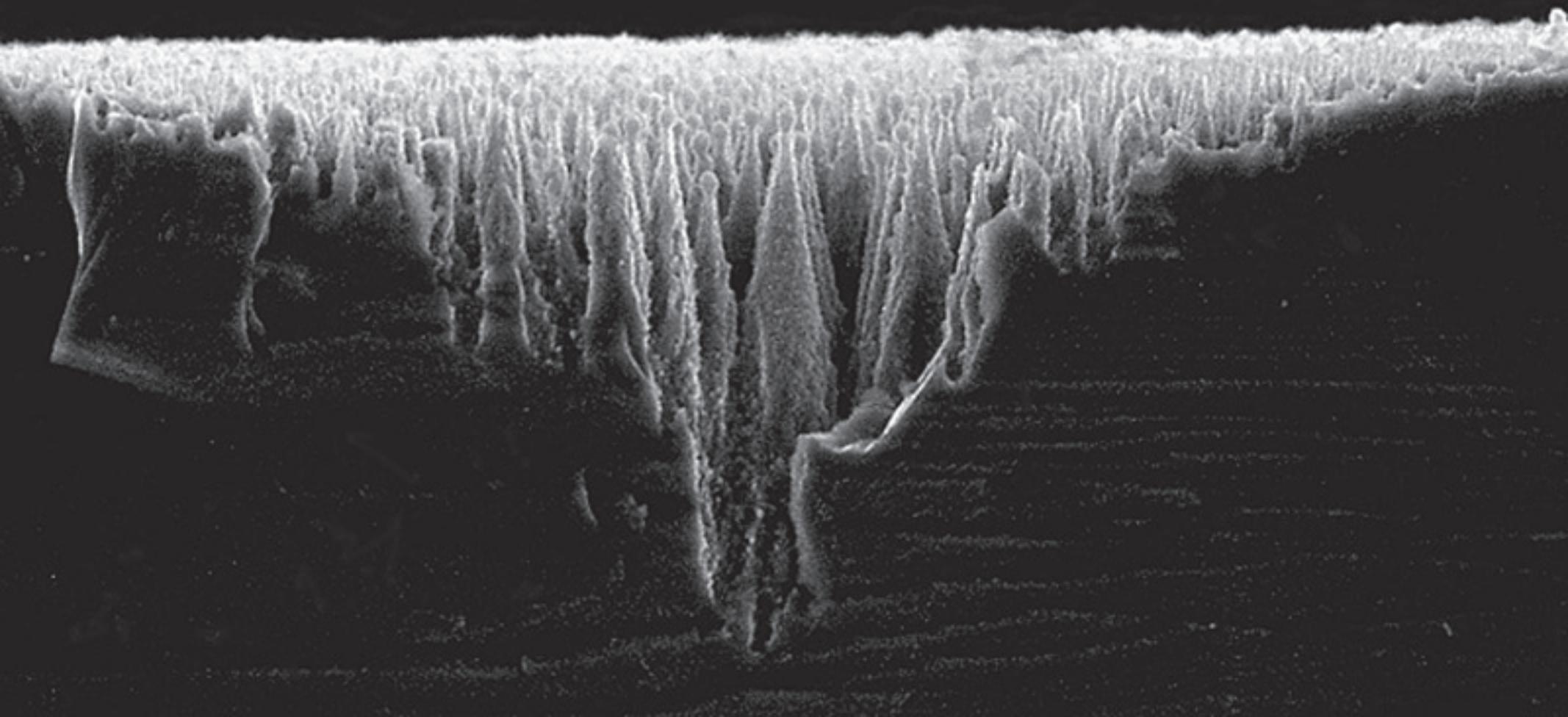
10 μm

Structure

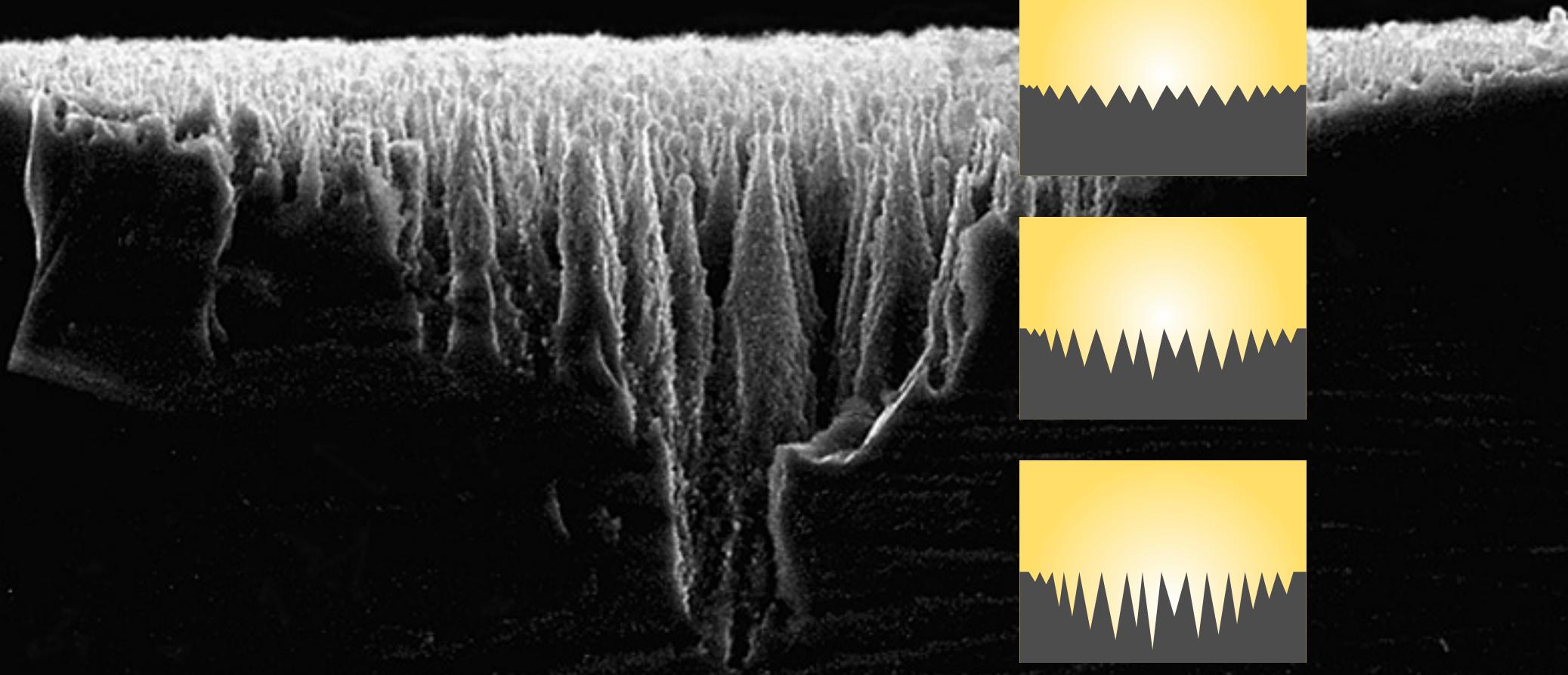
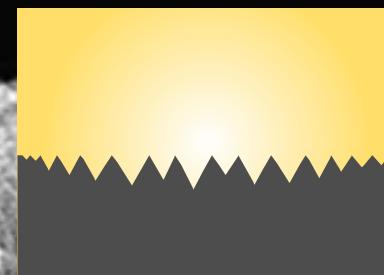


10 µm

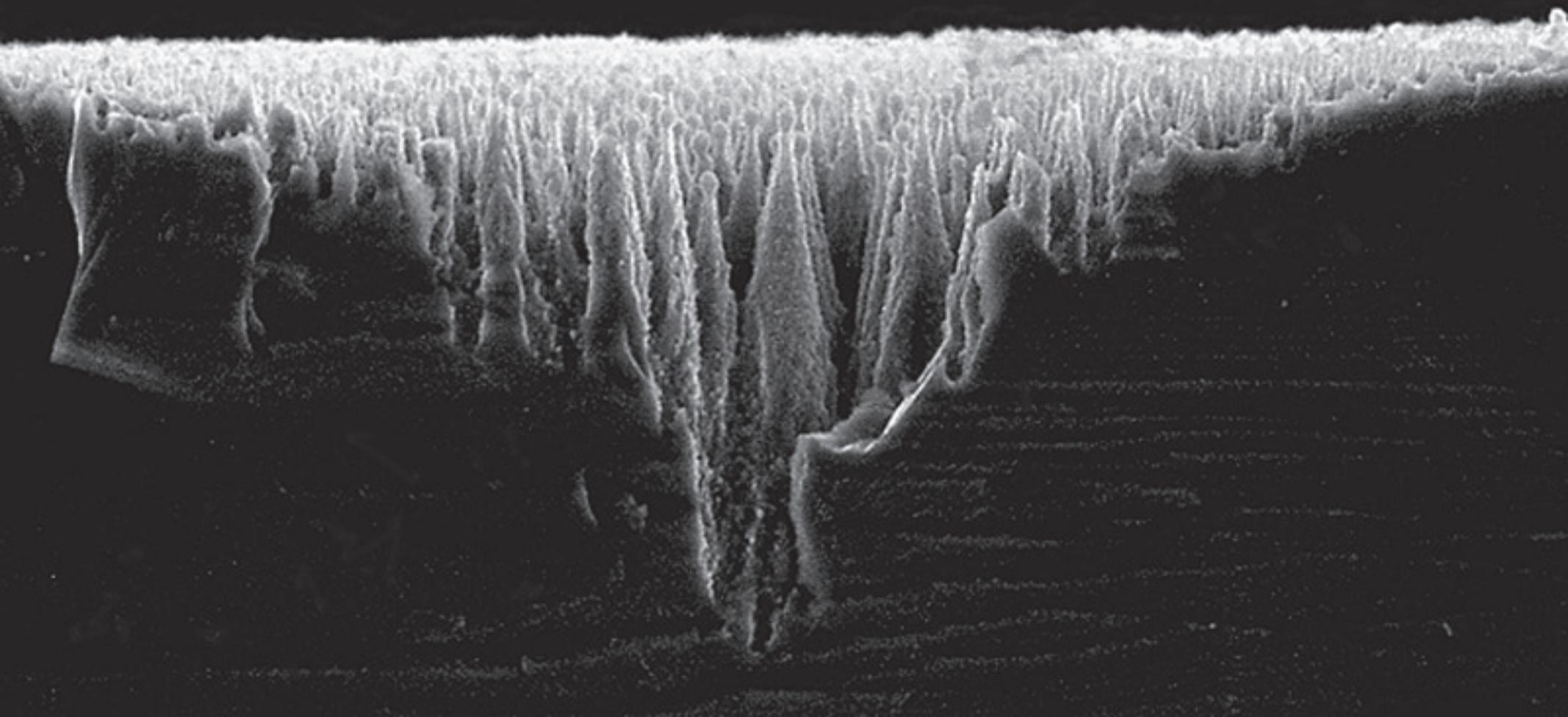
Structure



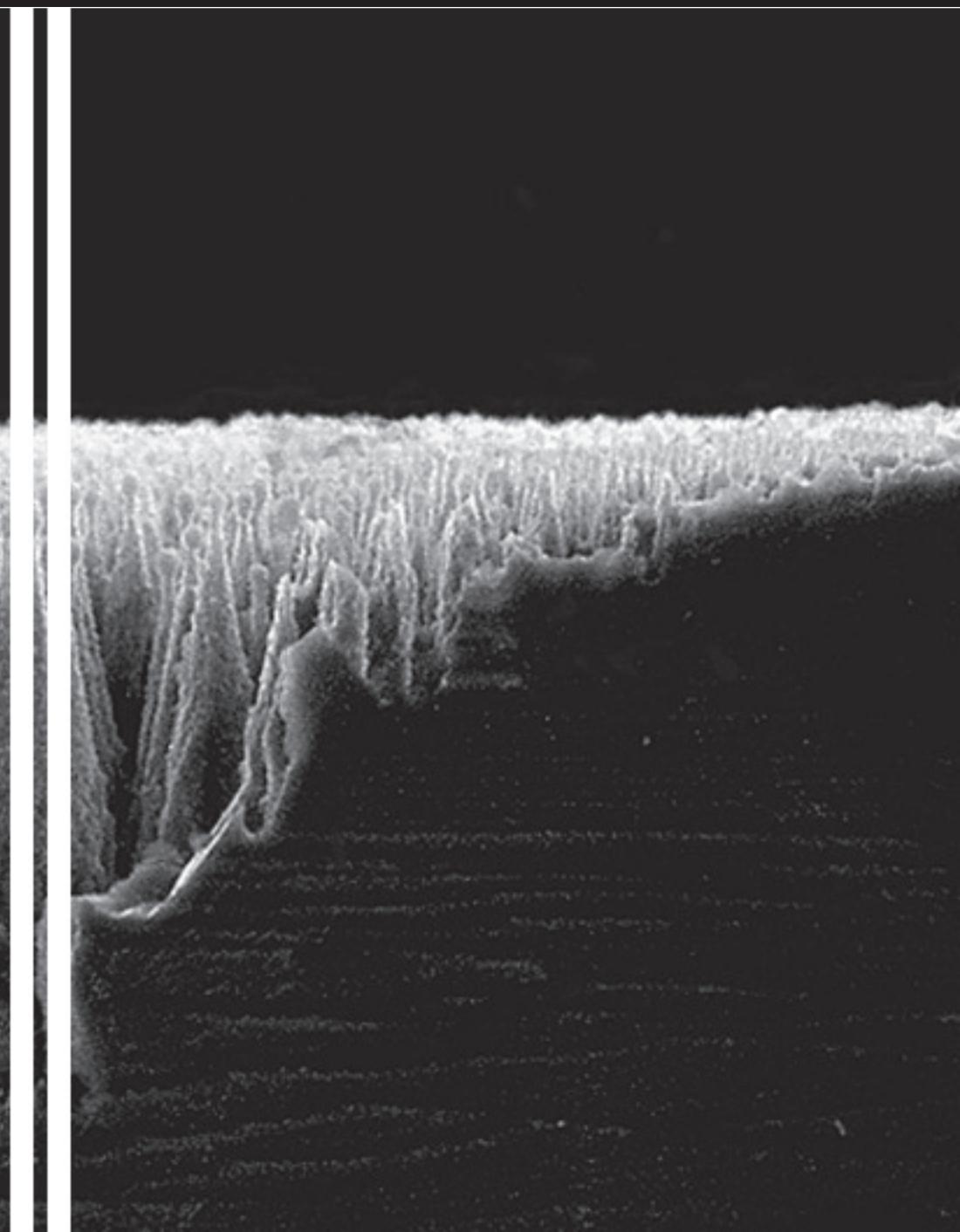
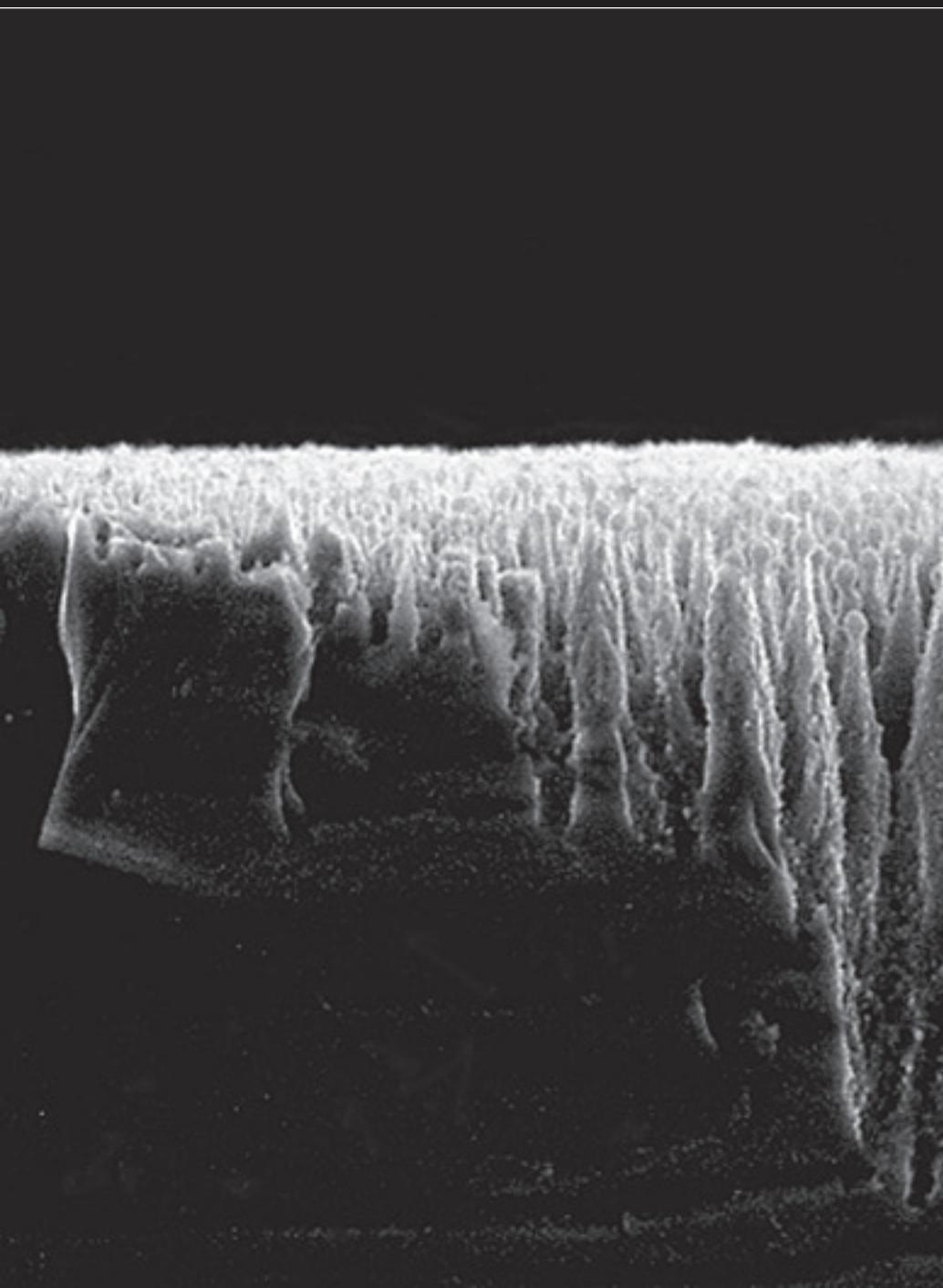
Structure



Structure



Structure



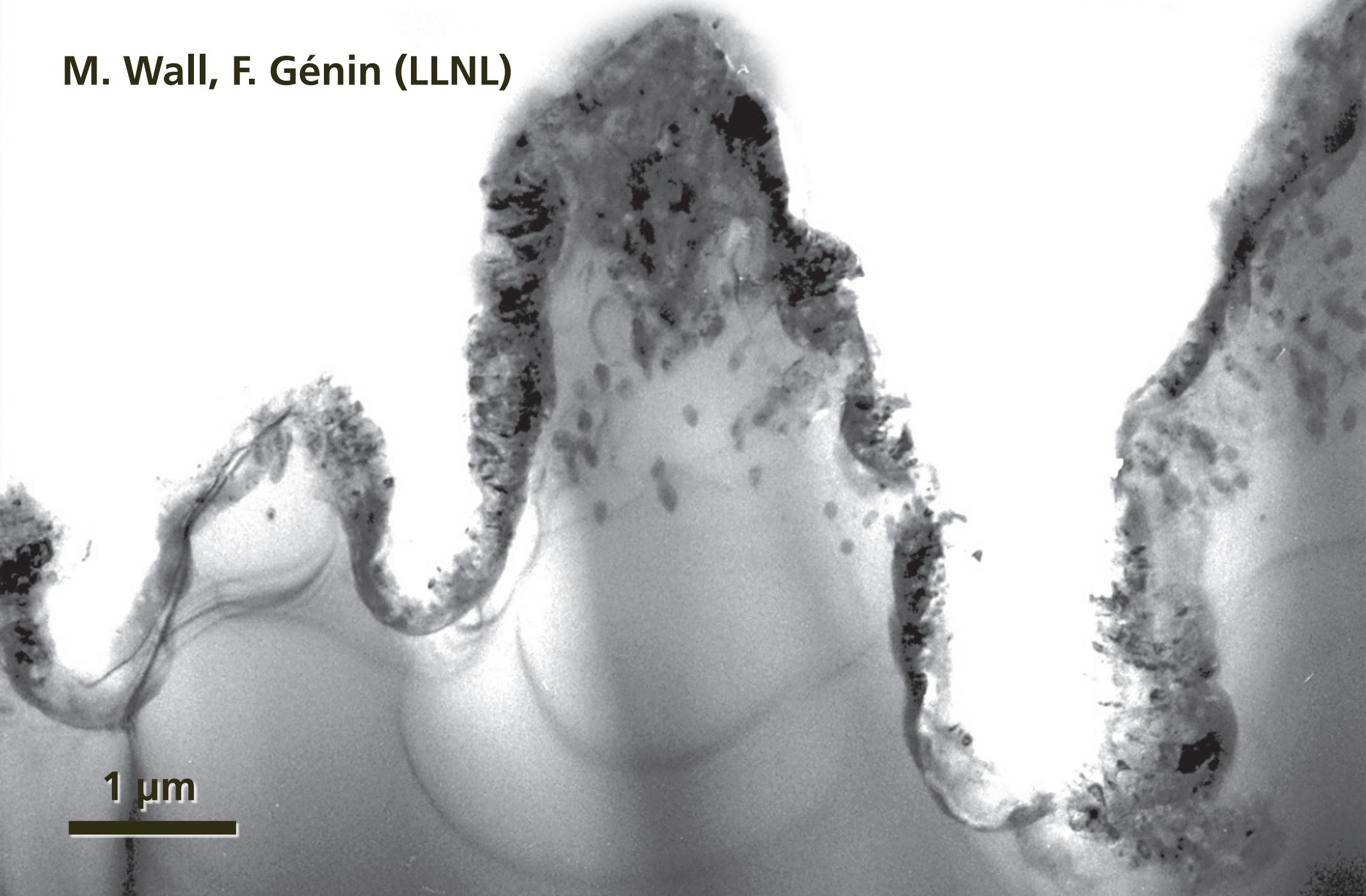
Structure

**cross-sectional
Transmission Electron
Microscopy**



Structure

M. Wall, F. Génin (LLNL)



1 μm

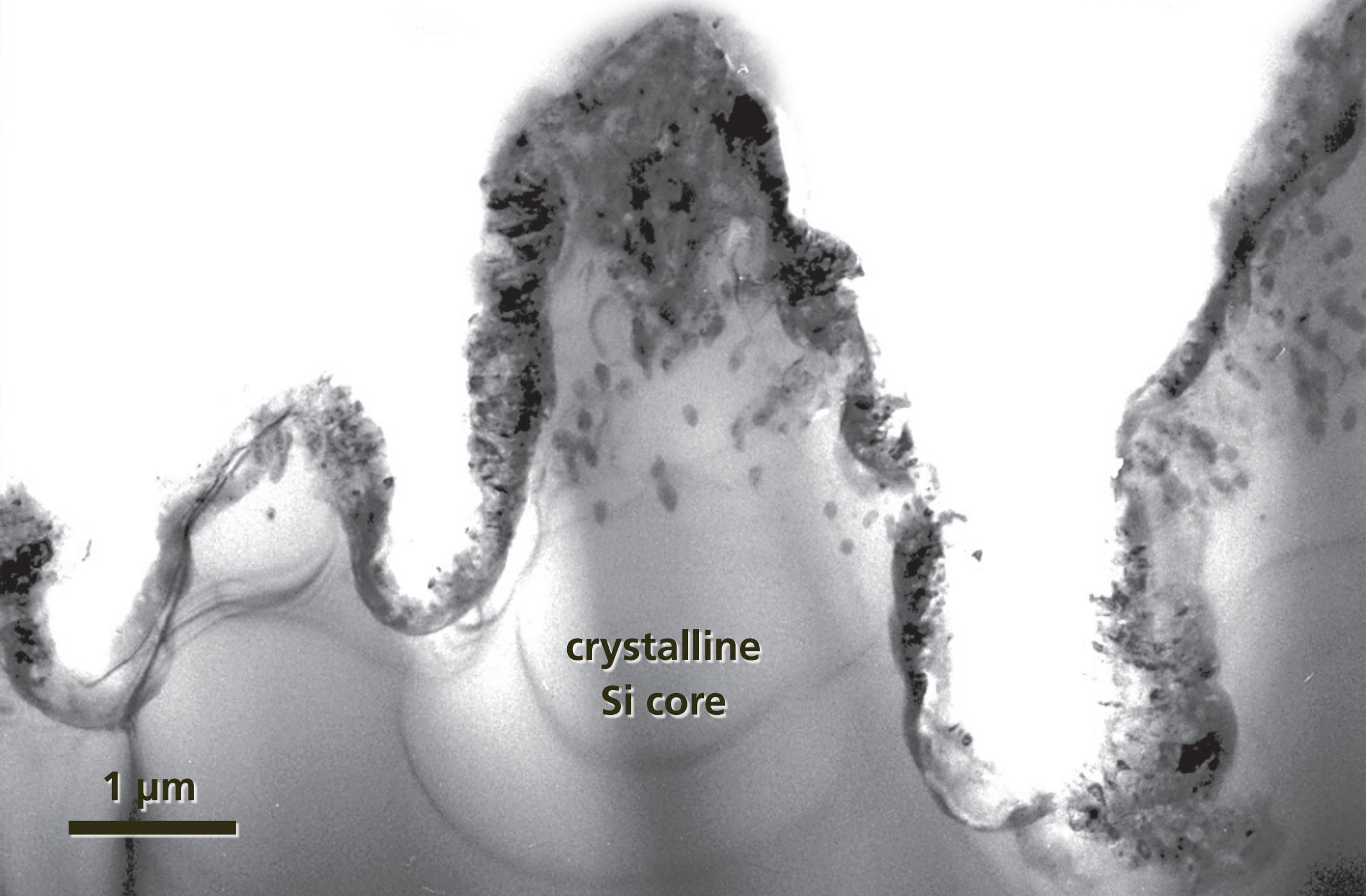
Structure

disordered
surface layer

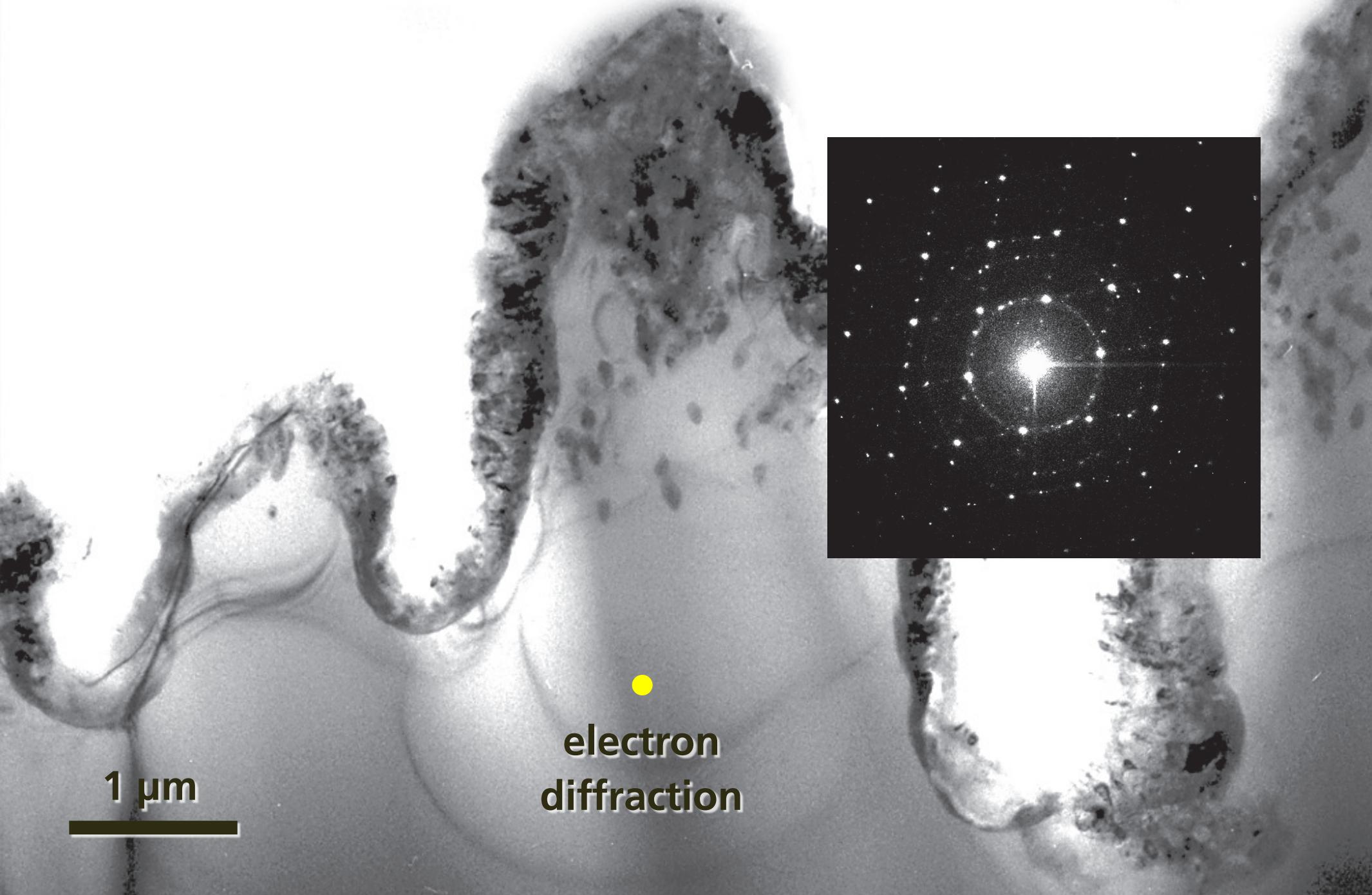


1 μm

Structure



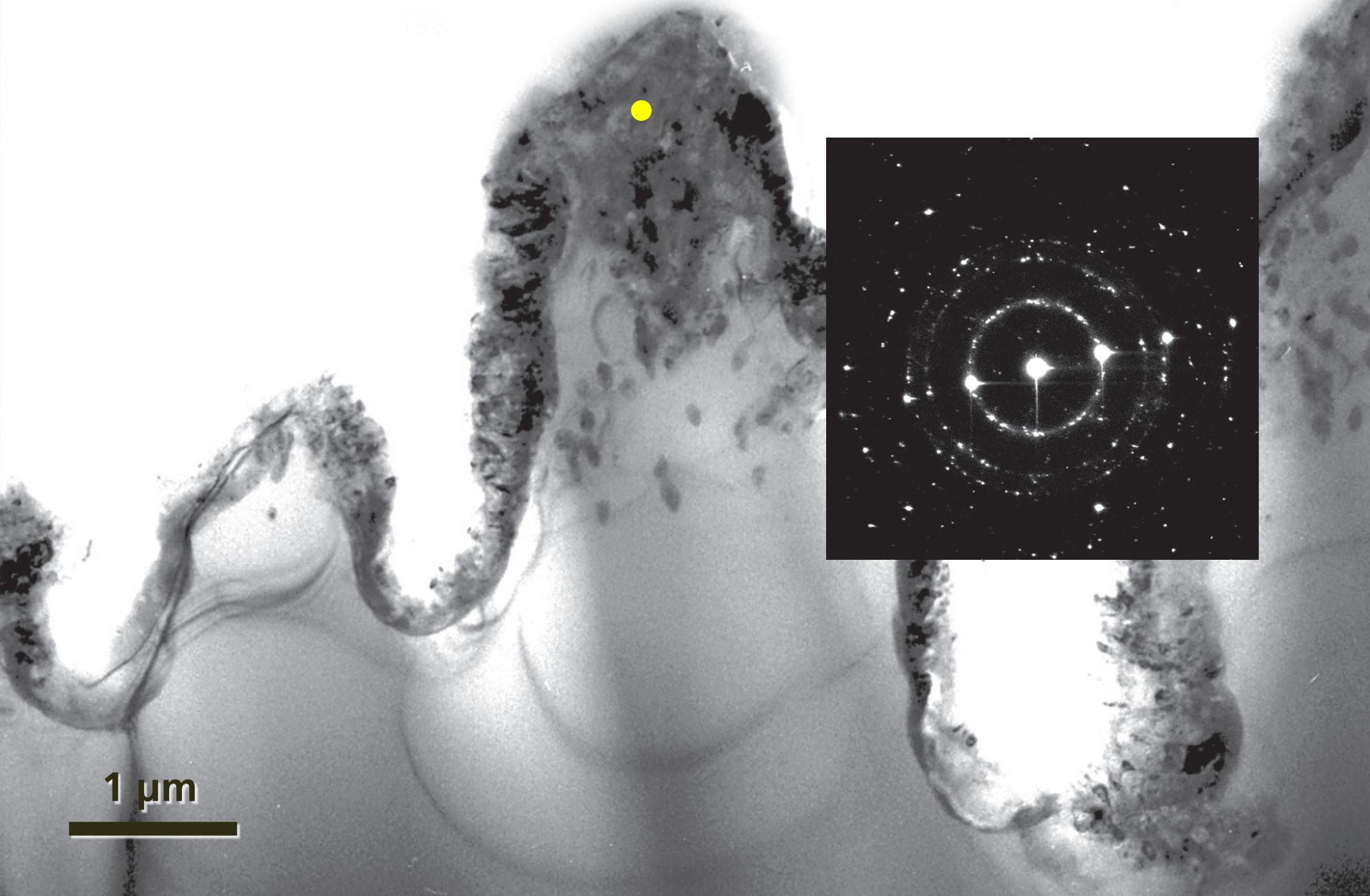
Structure



1 μm

electron
diffraction

Structure



Structure

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

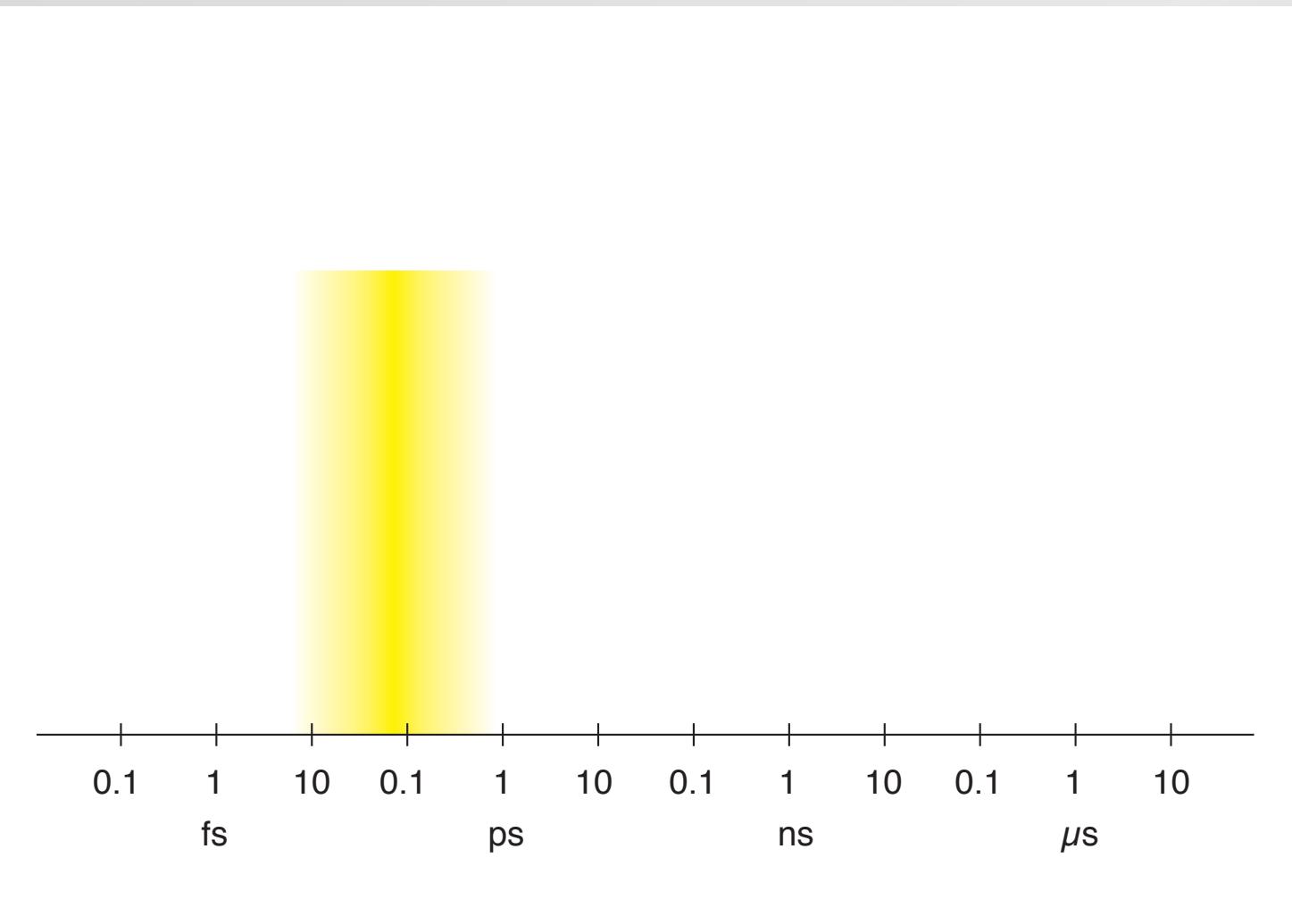
1 μm

Structure

two processes: melting and ablation

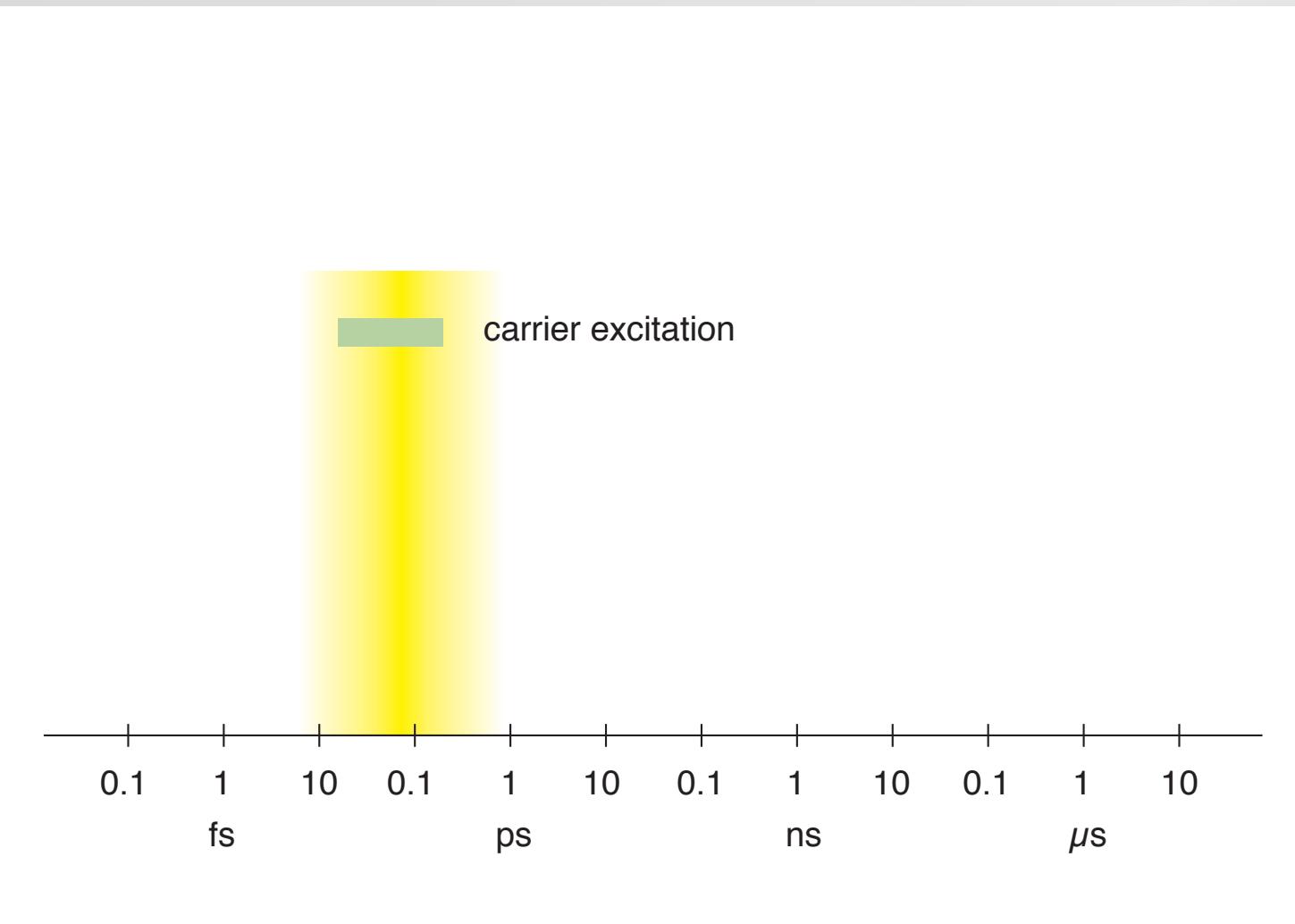
Structure

relevant time scales



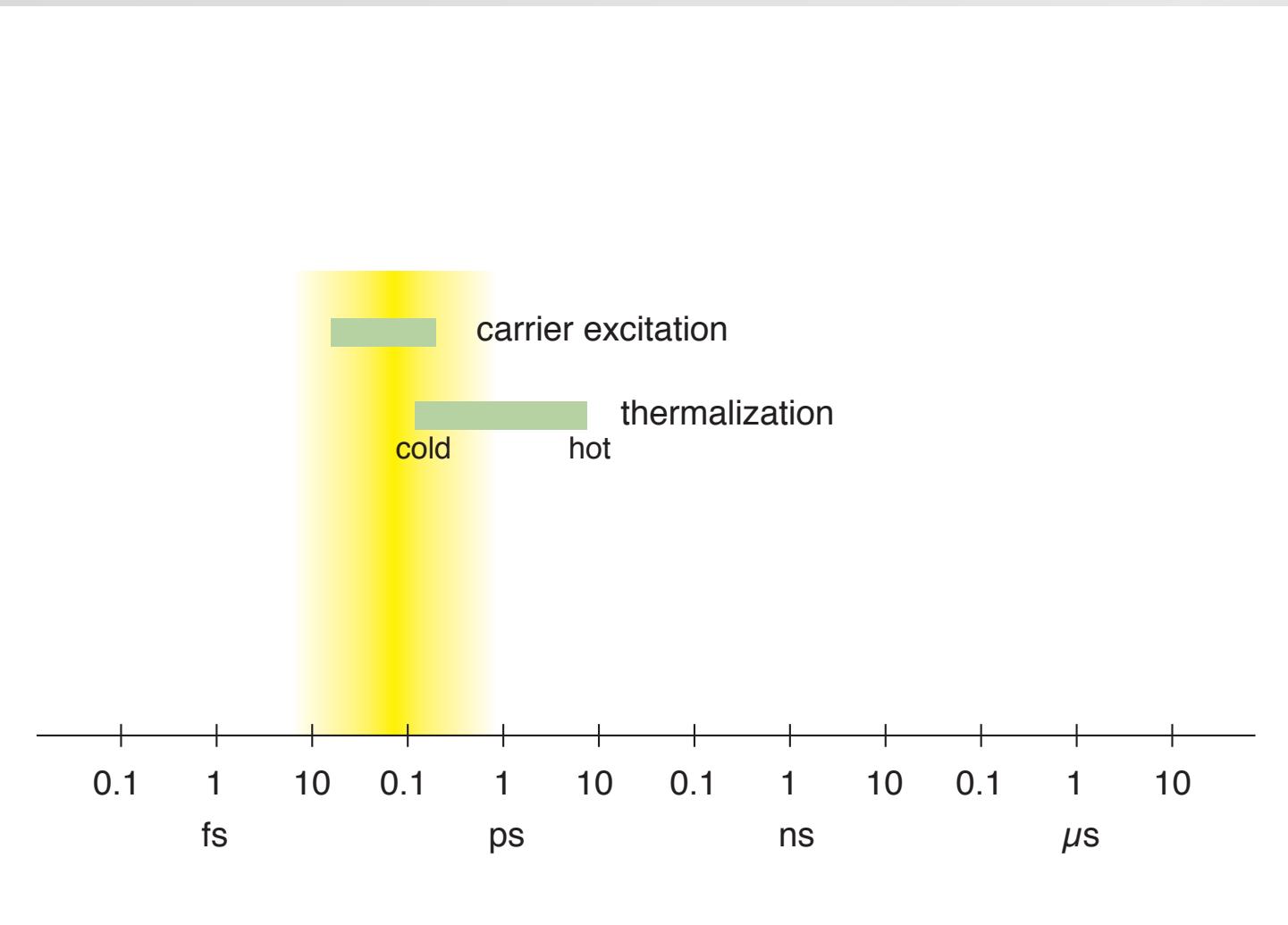
Structure

relevant time scales



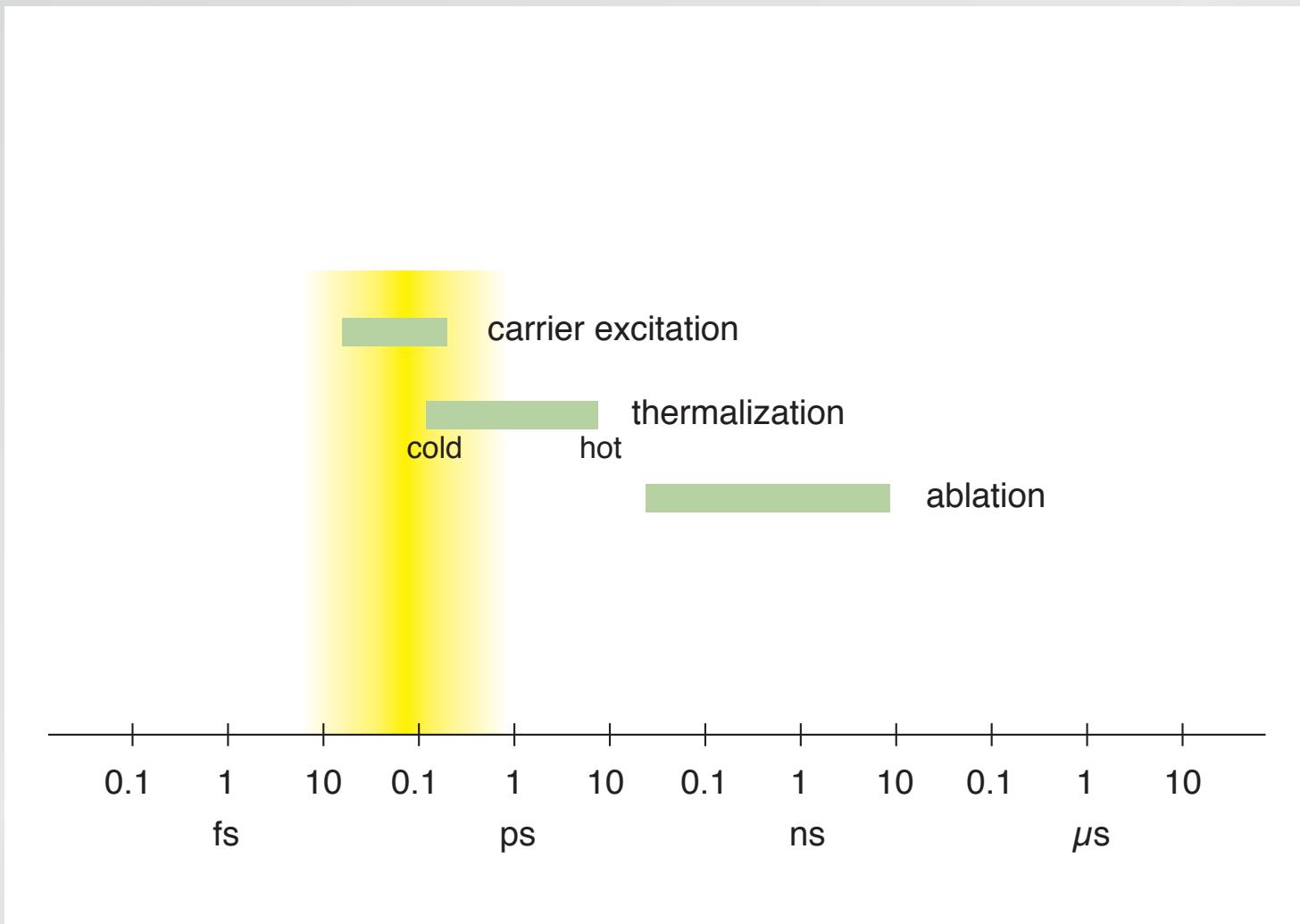
Structure

relevant time scales



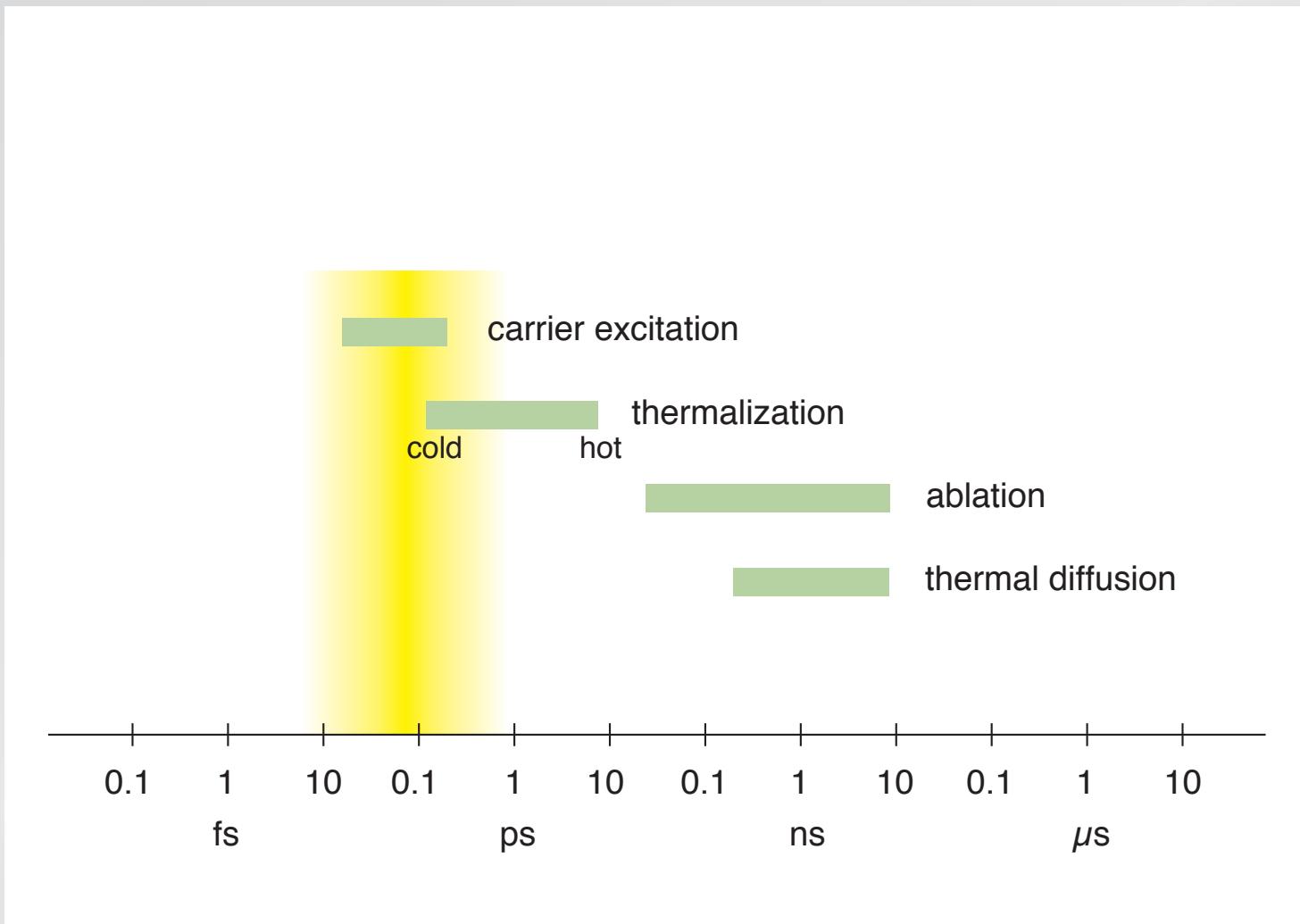
Structure

relevant time scales



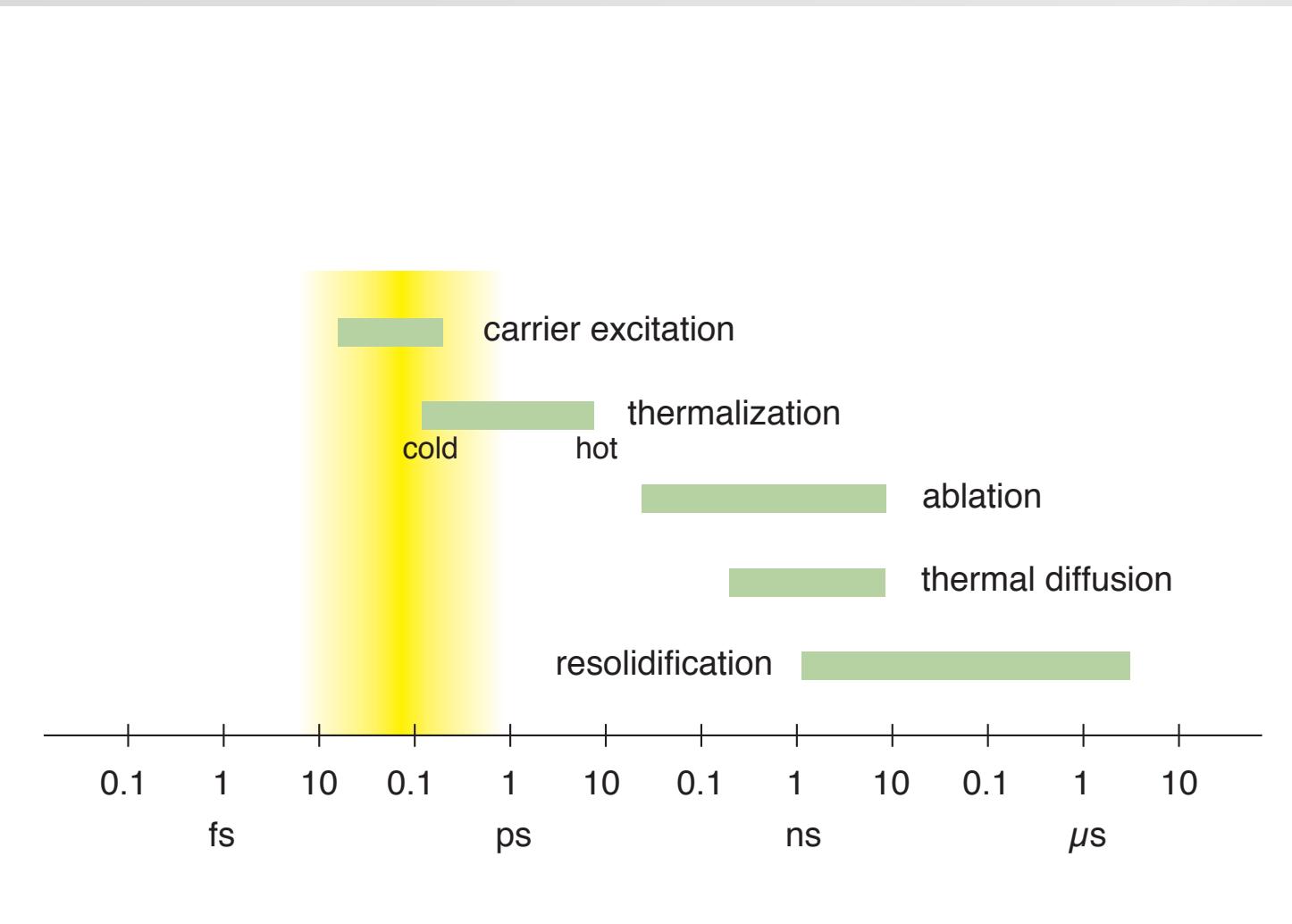
Structure

relevant time scales



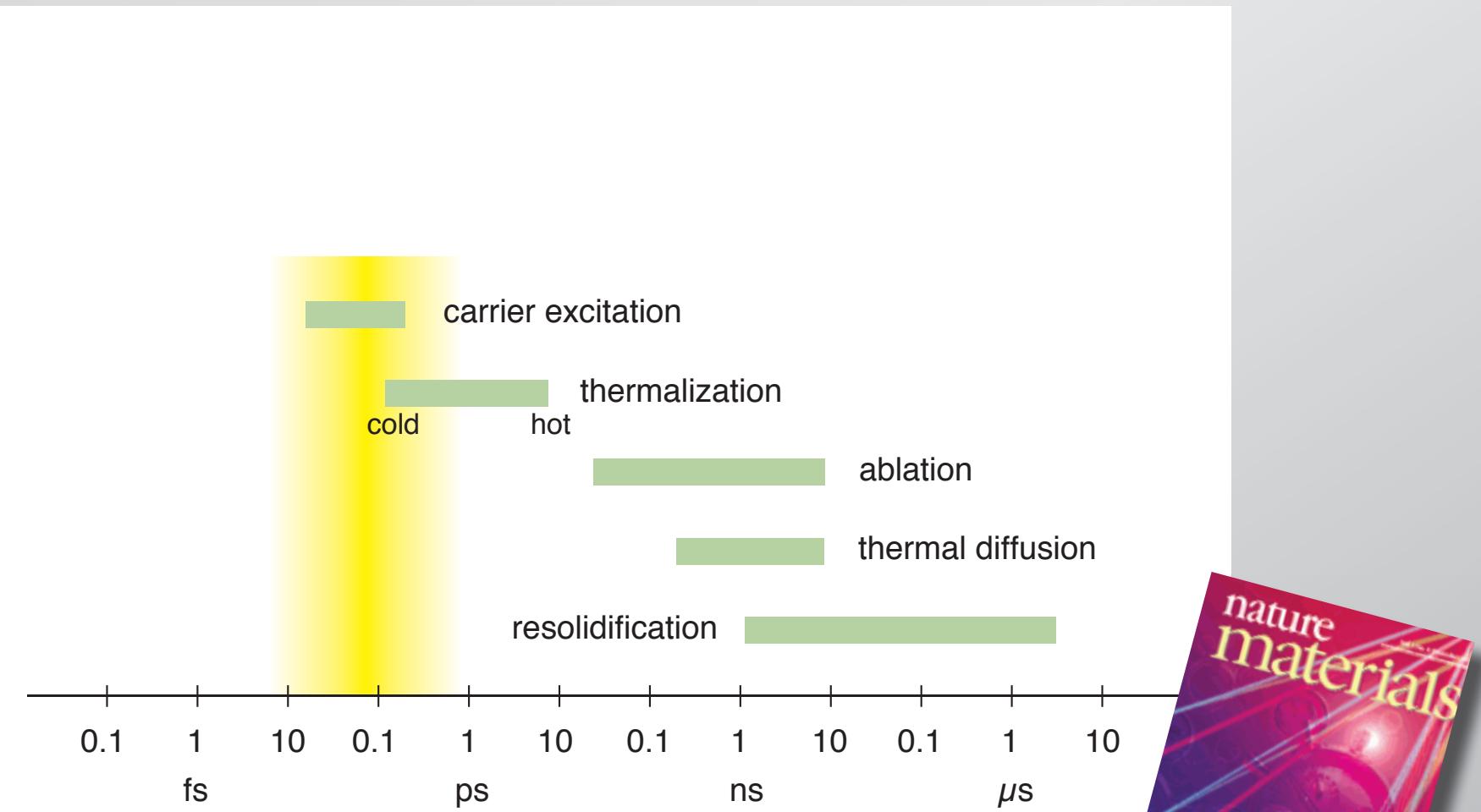
Structure

relevant time scales

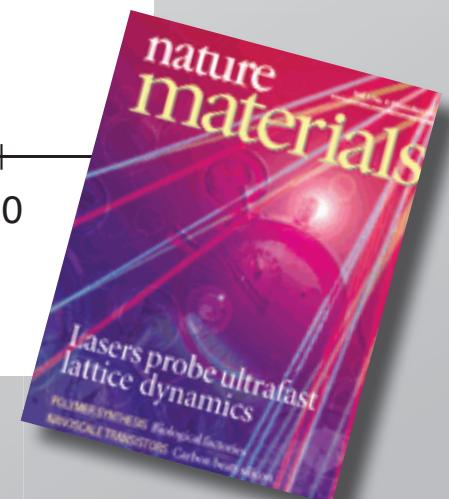


Structure

relevant time scales

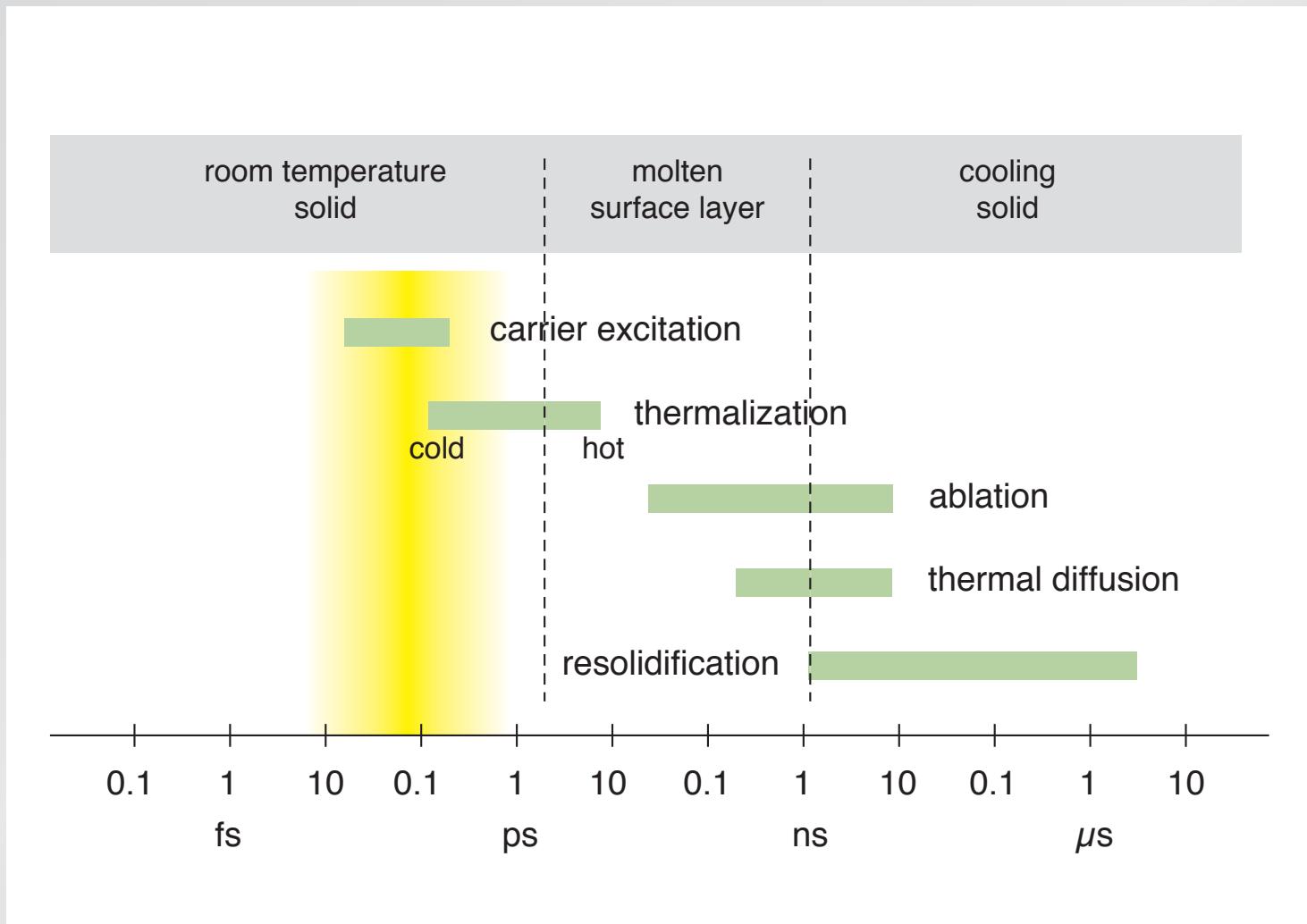


Nature Materials 1, 217 (2002)



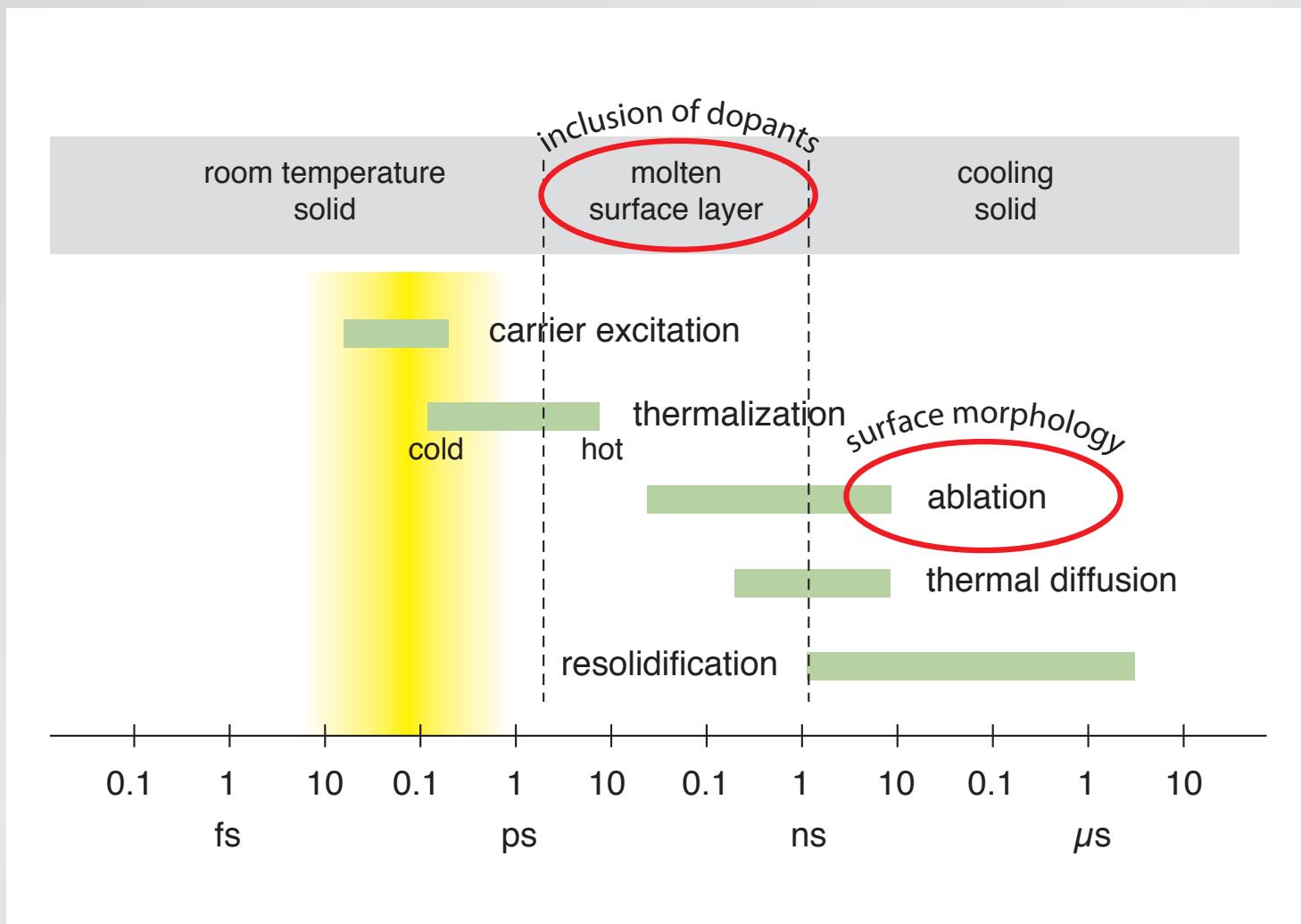
Structure

relevant time scales



Structure

relevant time scales



Structure

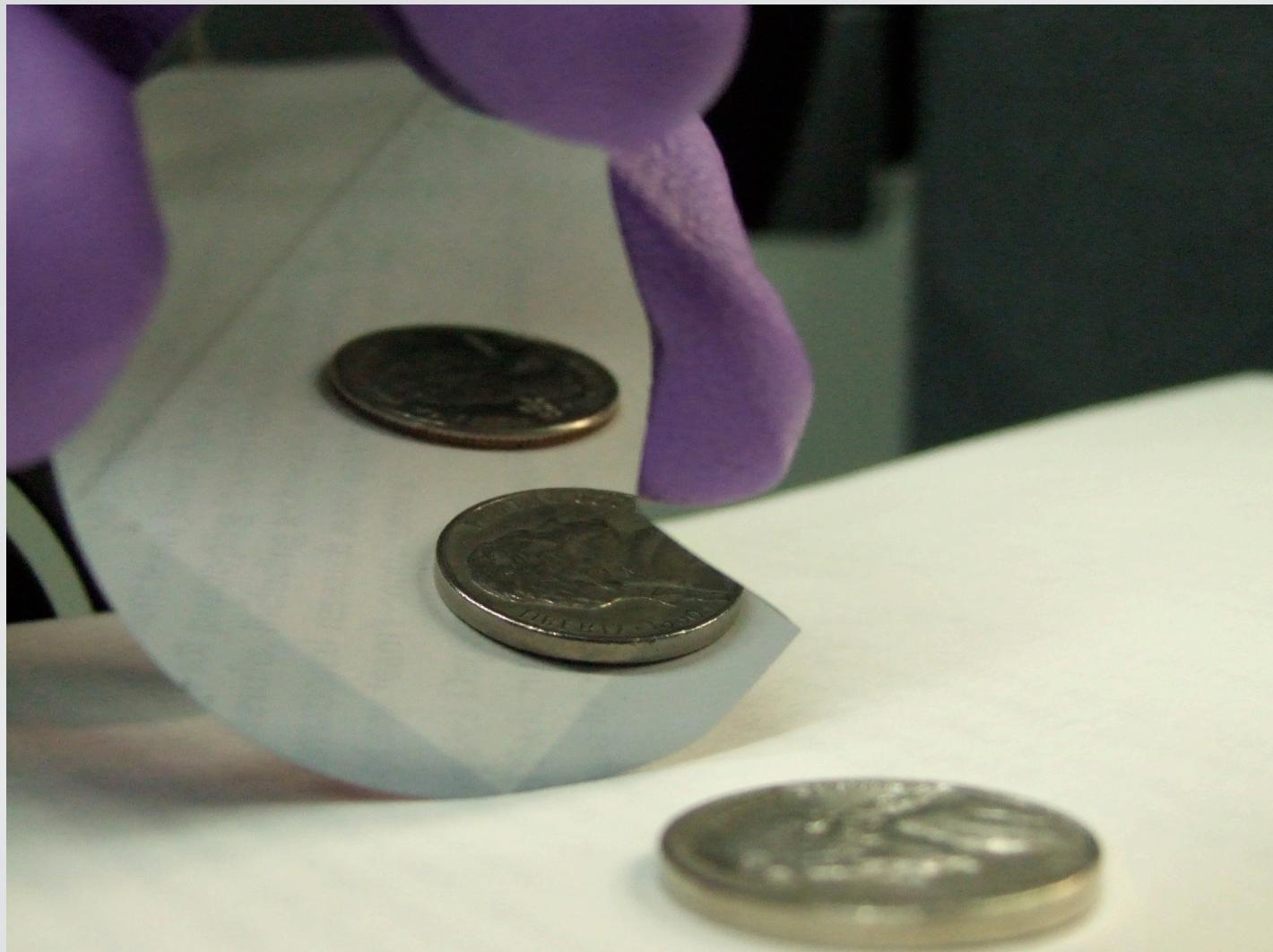
different thresholds:

melting: 1.5 kJ/m^2

ablation: 3.1 kJ/m^2

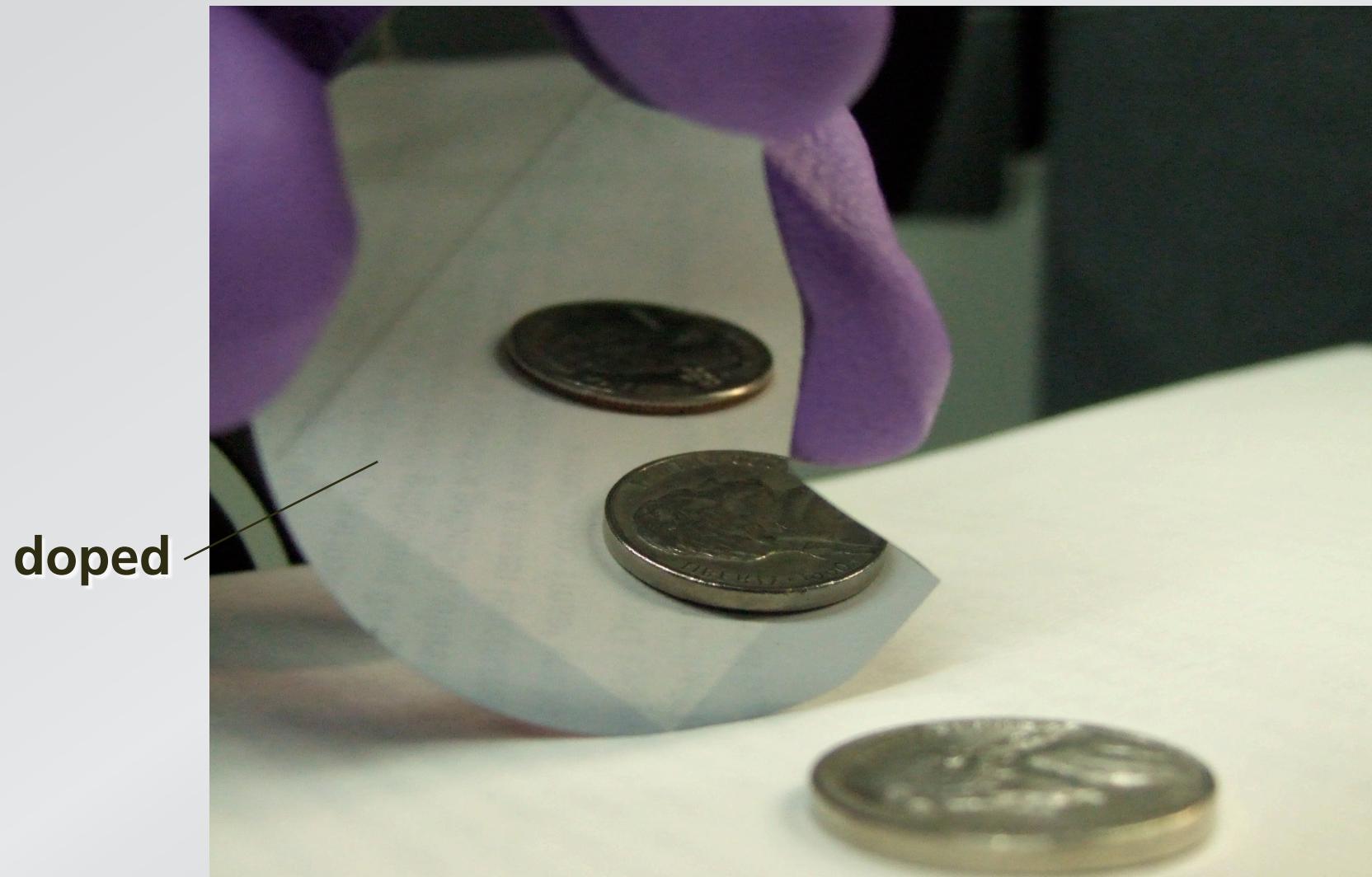
Structure

decouple ablation from melting



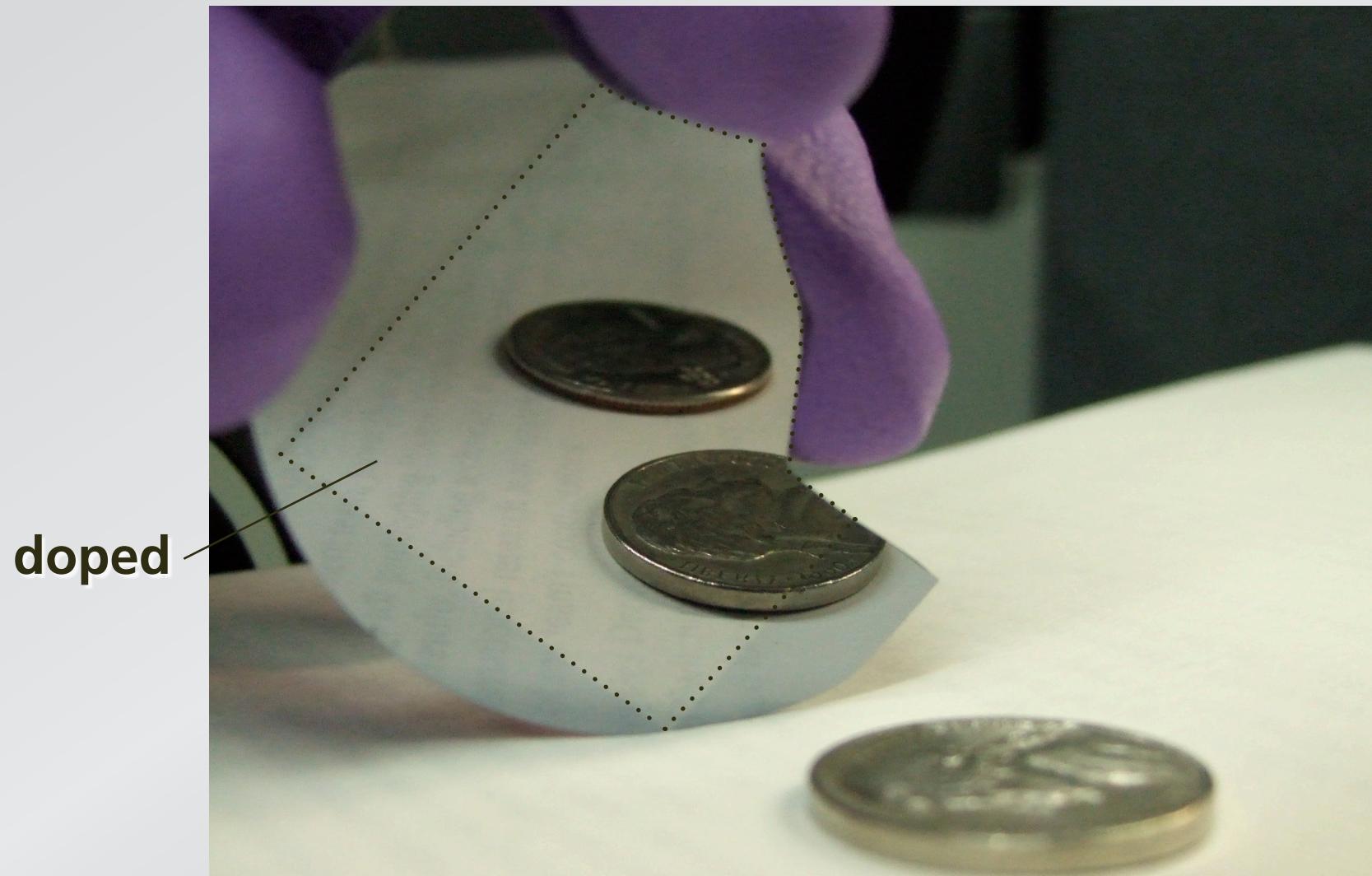
Structure

decouple ablation from melting



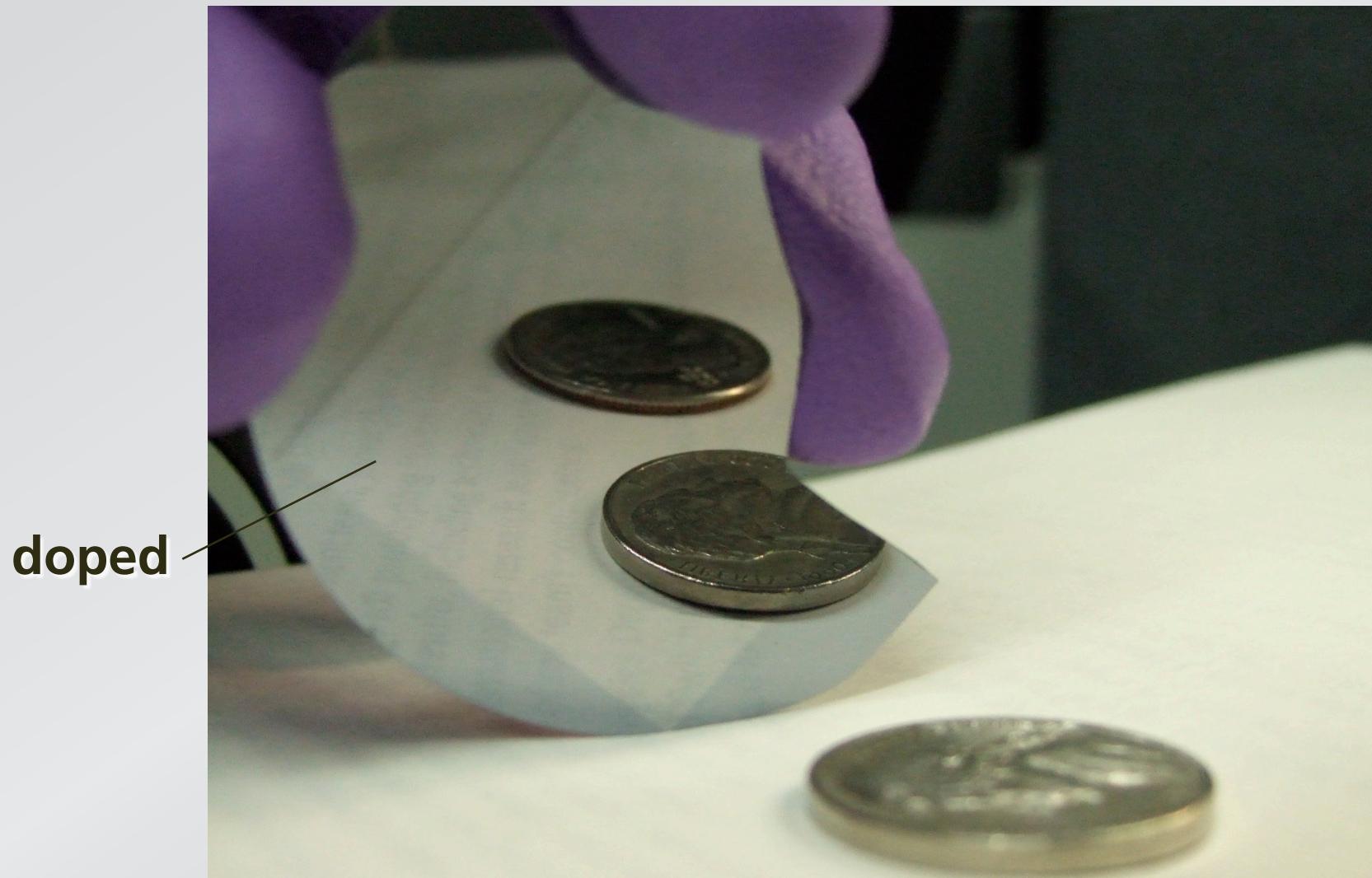
Structure

decouple ablation from melting



Structure

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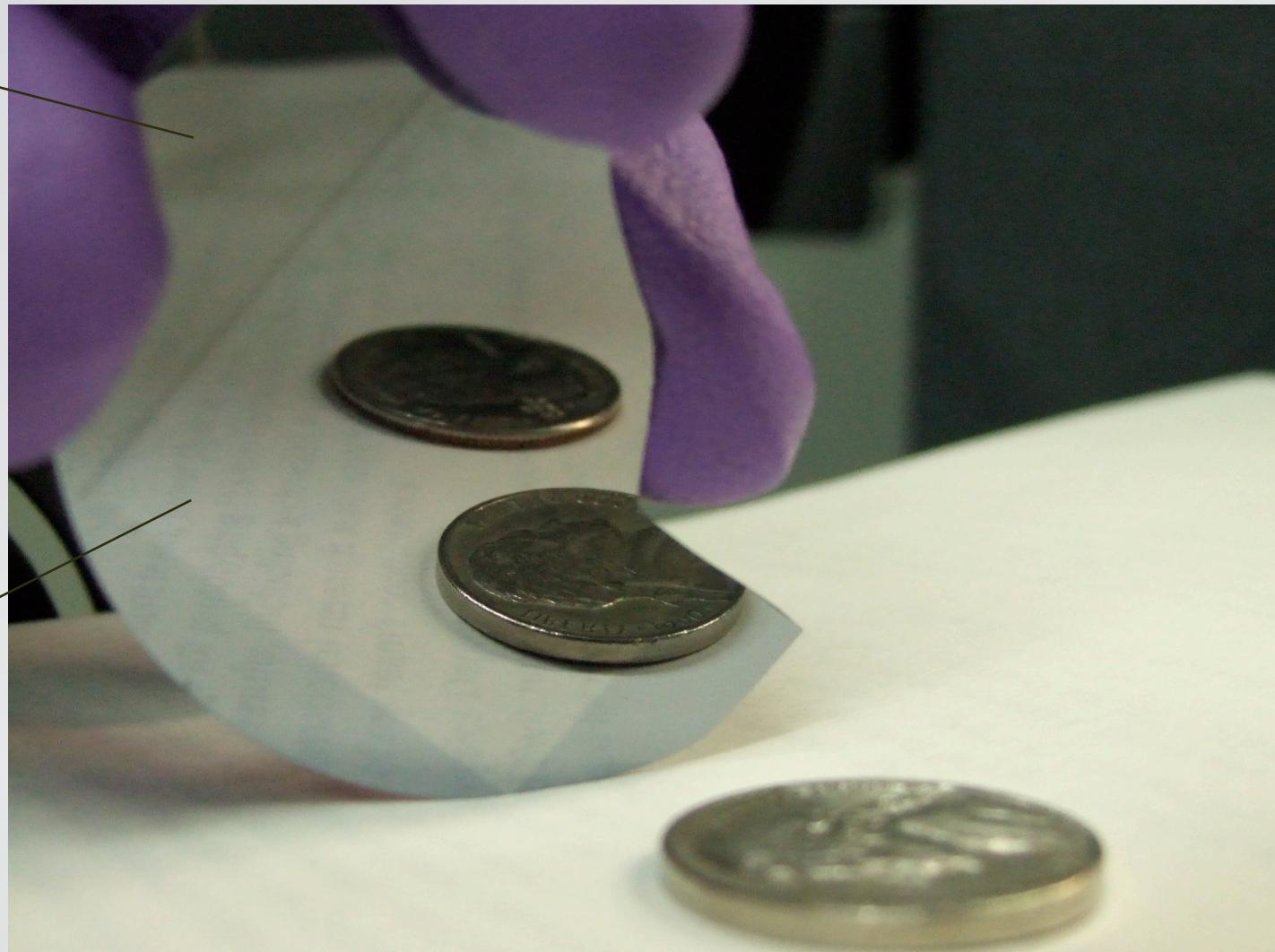


Structure

decouple ablation from melting

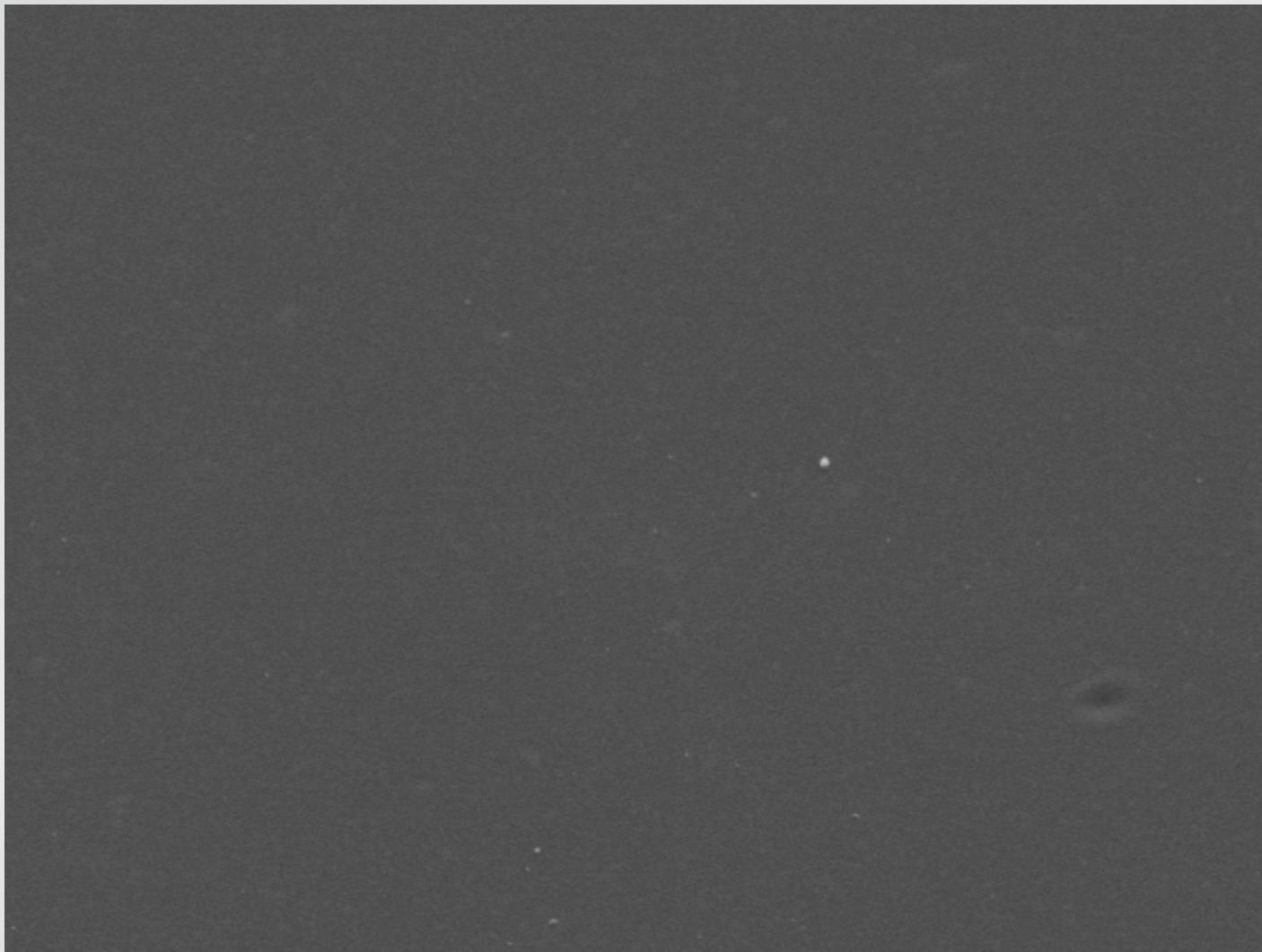
undoped

doped



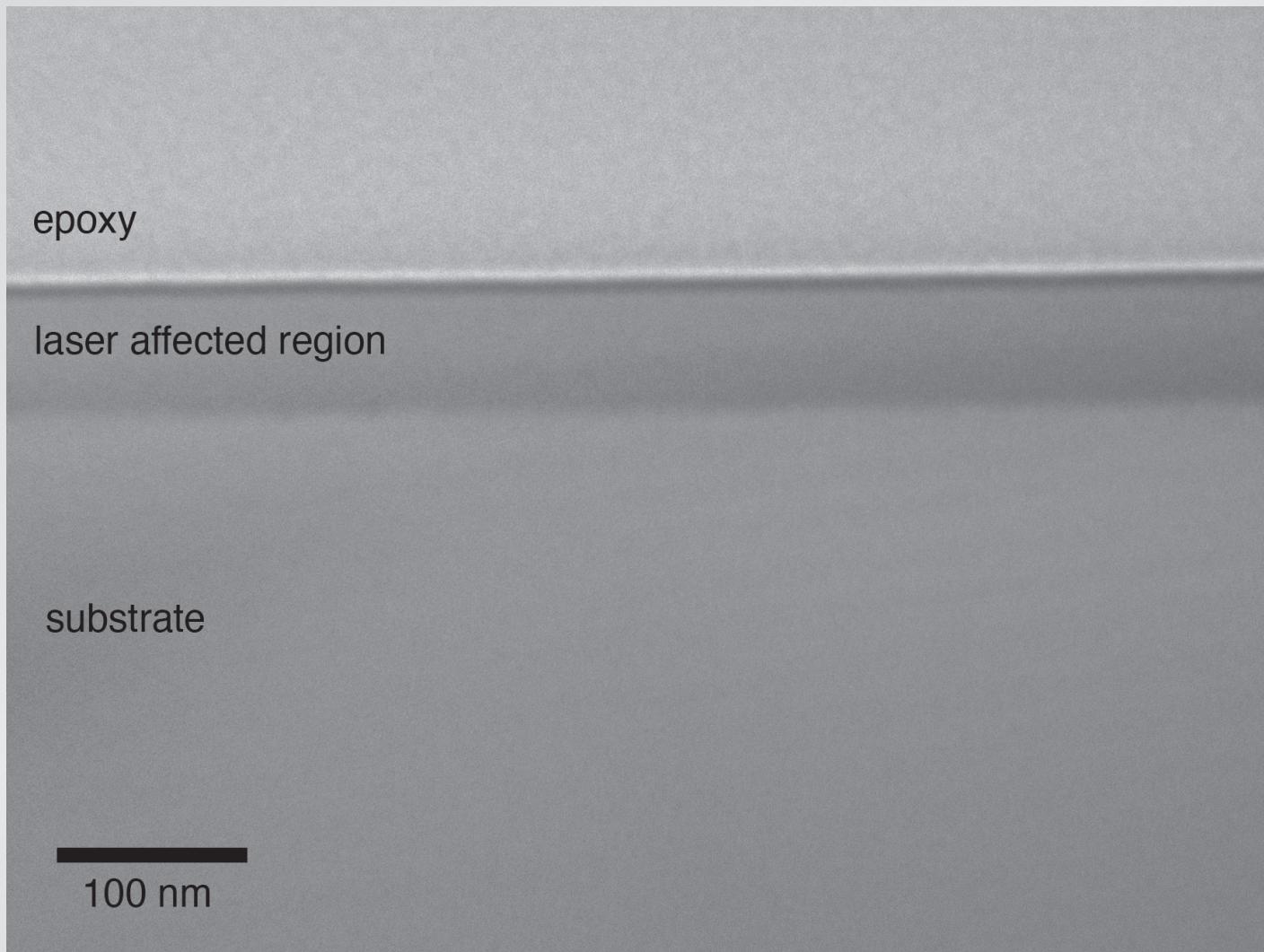
Structure

decouple ablation from melting



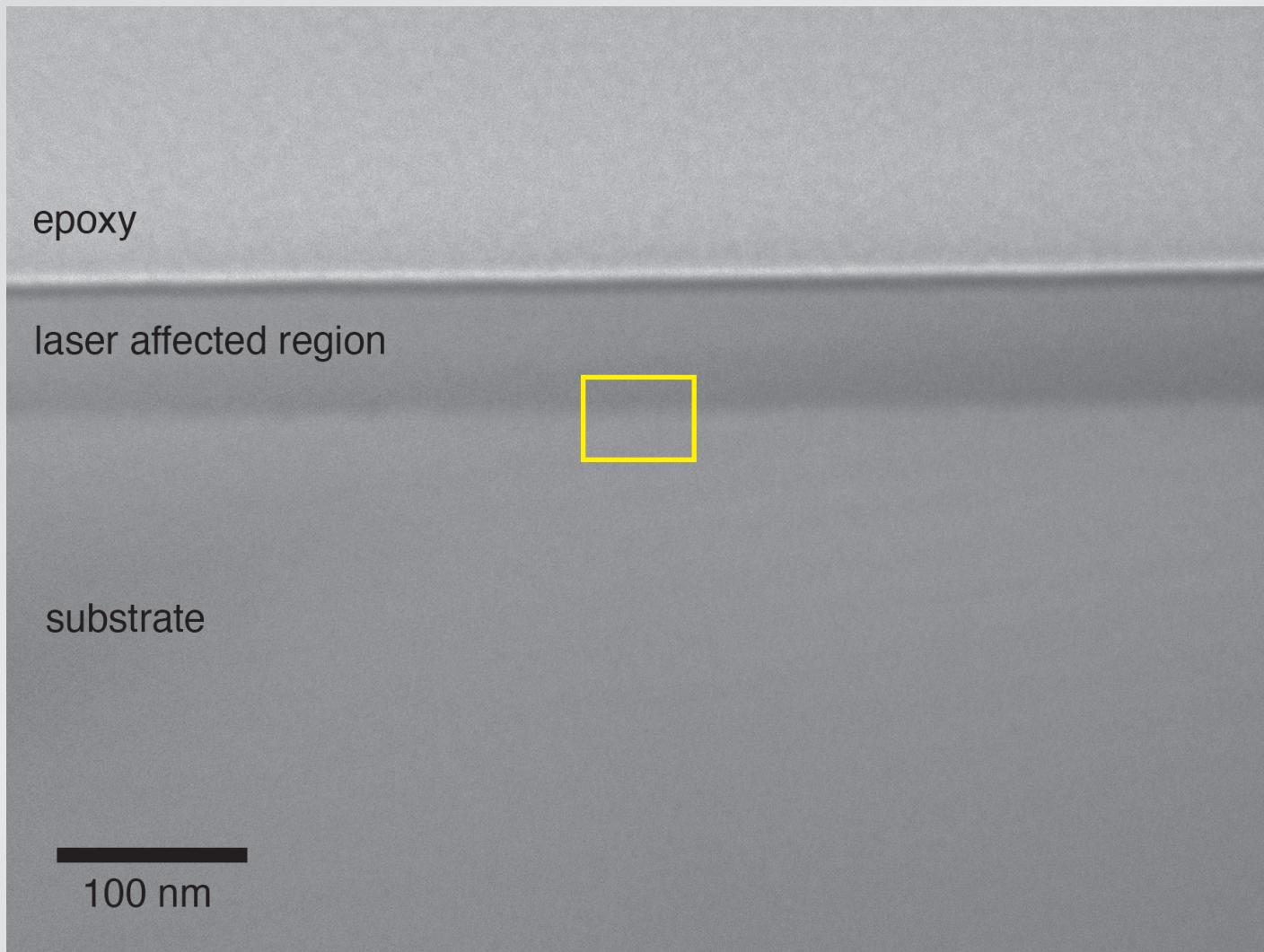
Structure

decouple ablation from melting



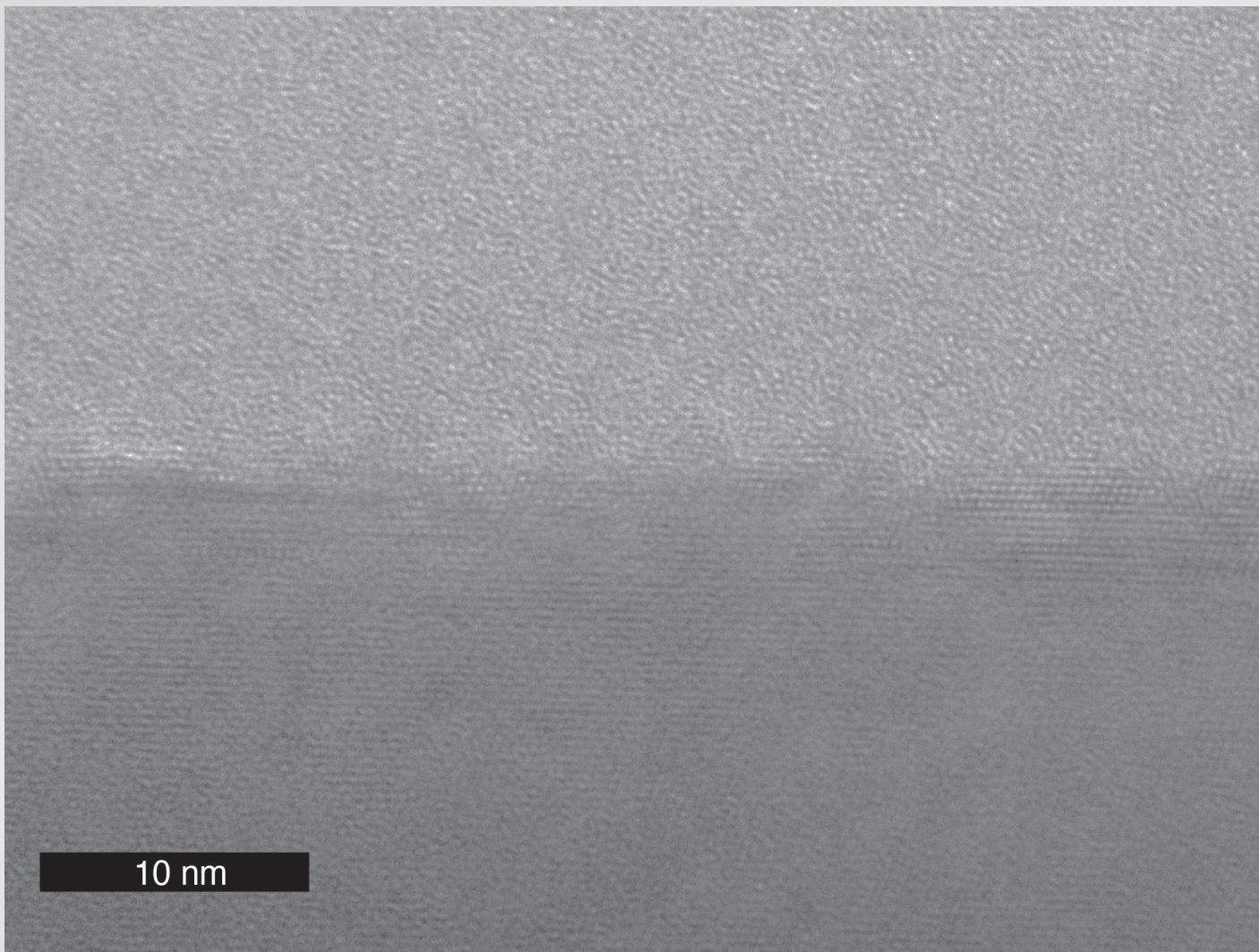
Structure

decouple ablation from melting



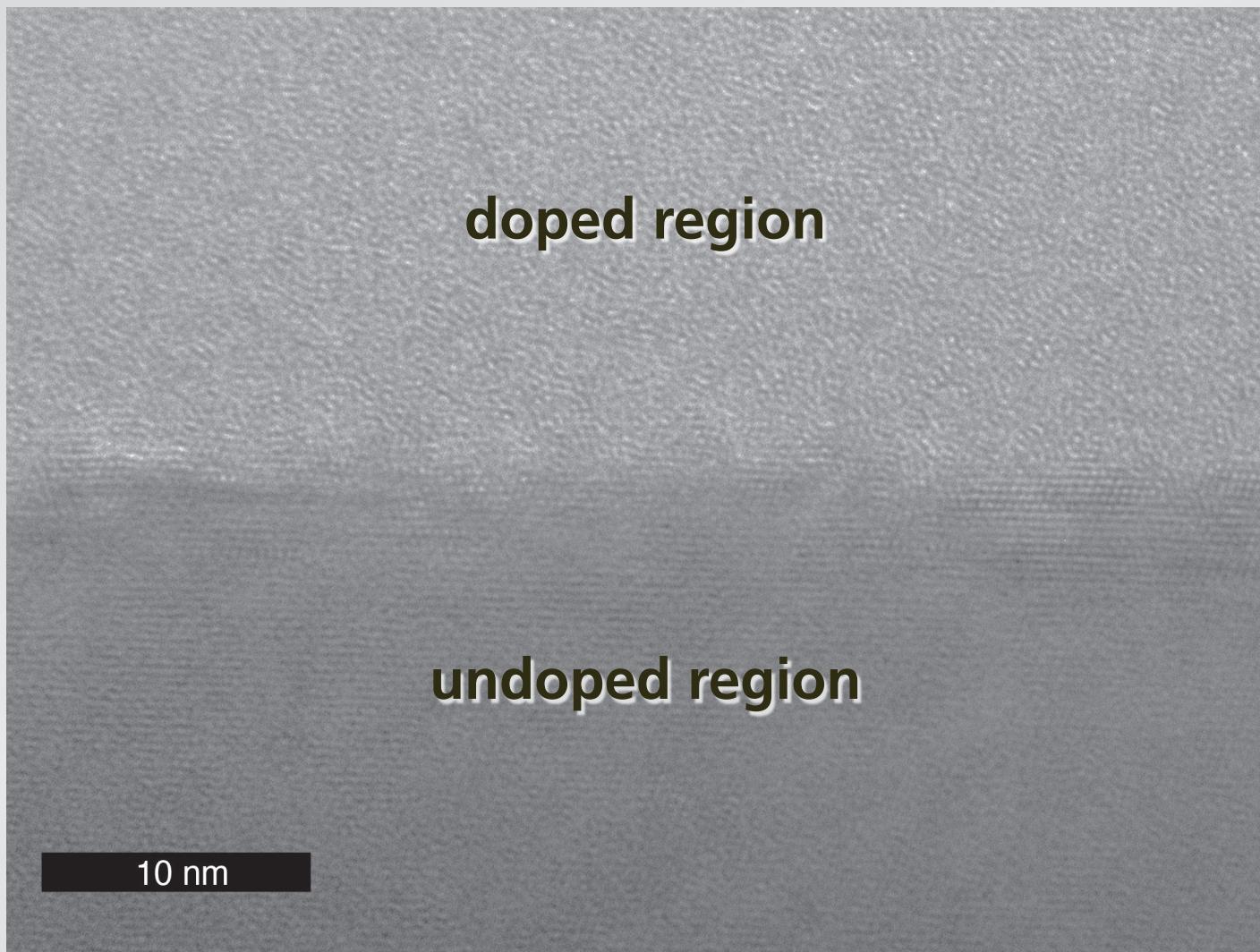
Structure

decouple ablation from melting



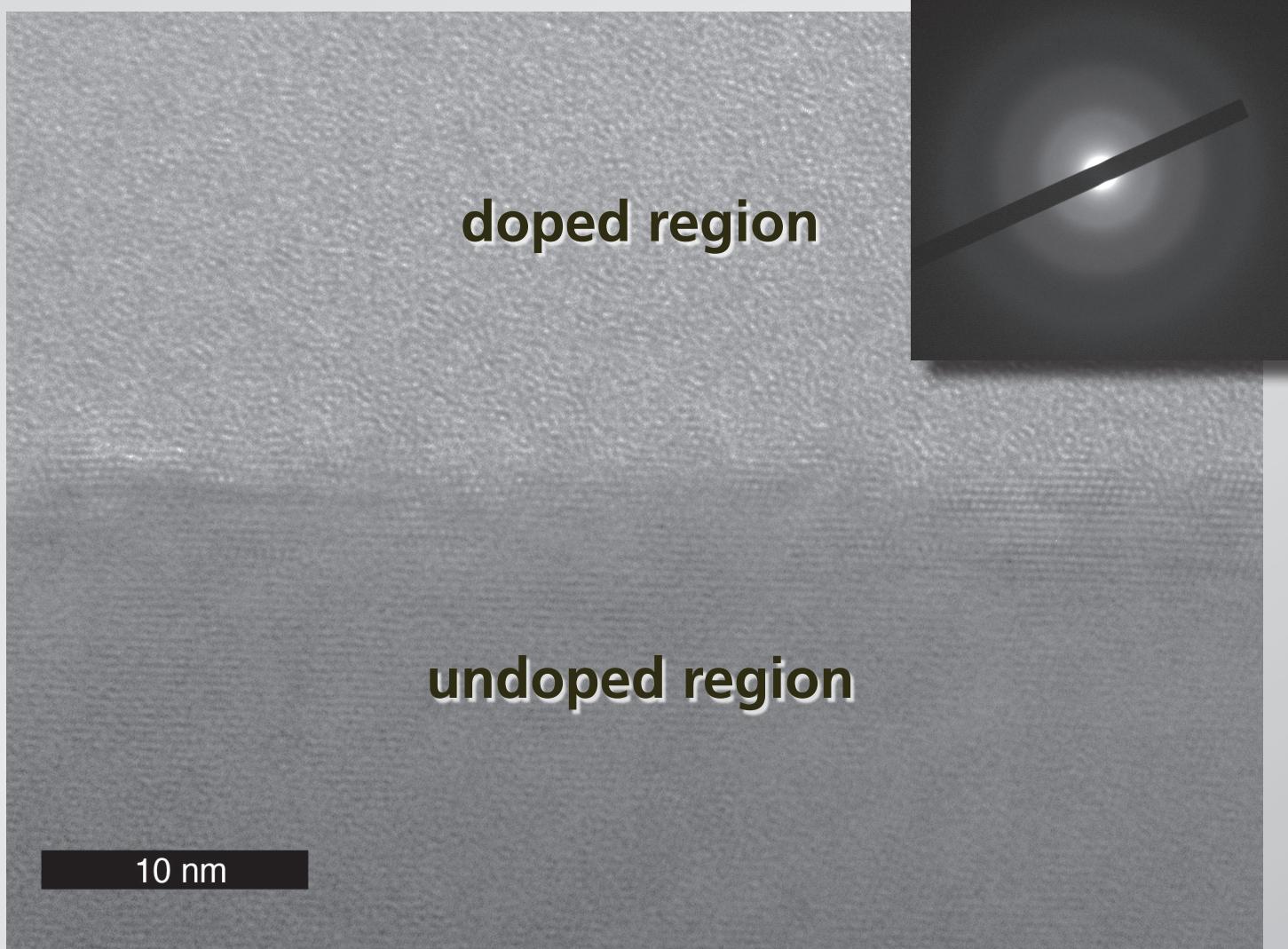
Structure

decouple ablation from melting



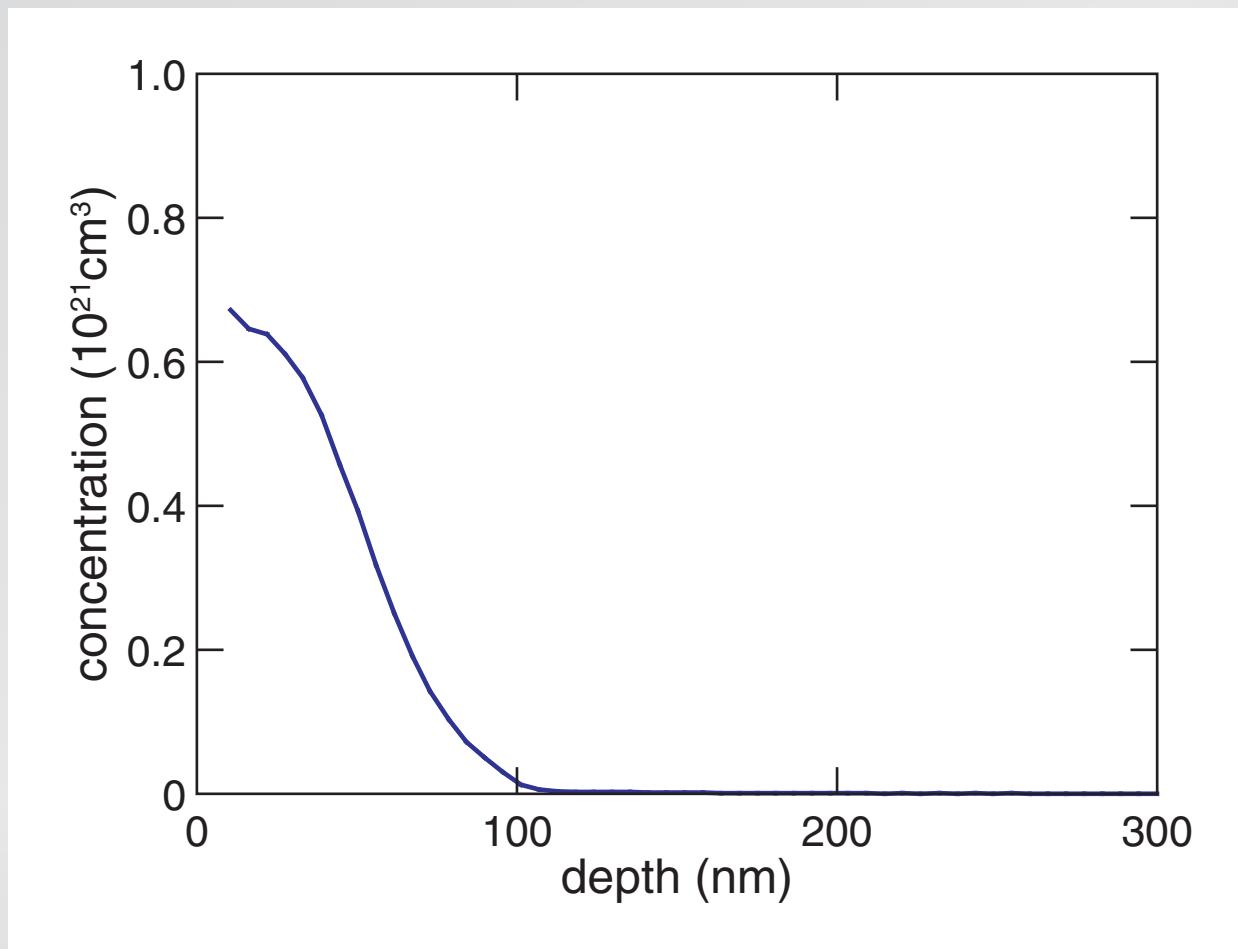
Structure

decouple ablation from melting

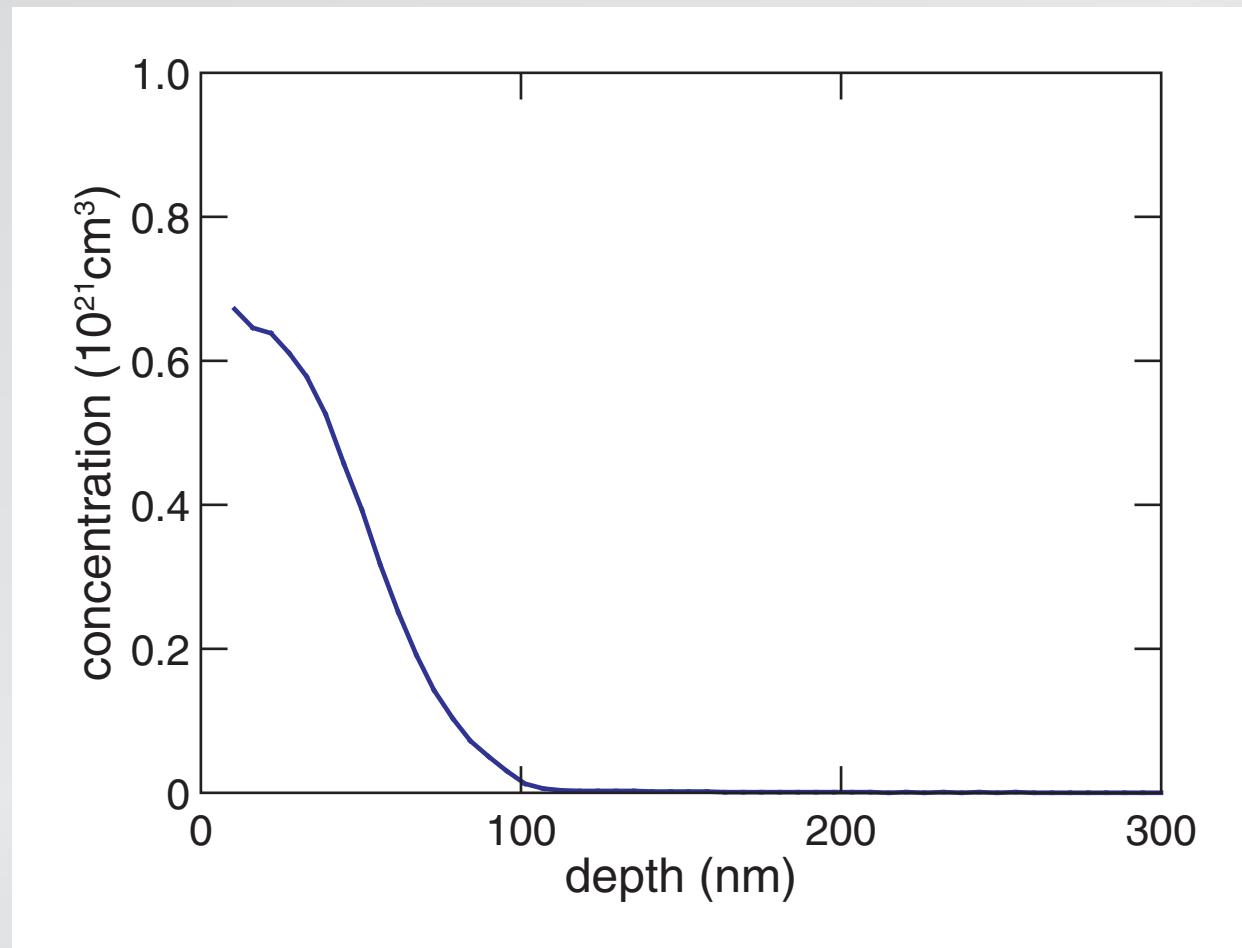


Structure

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

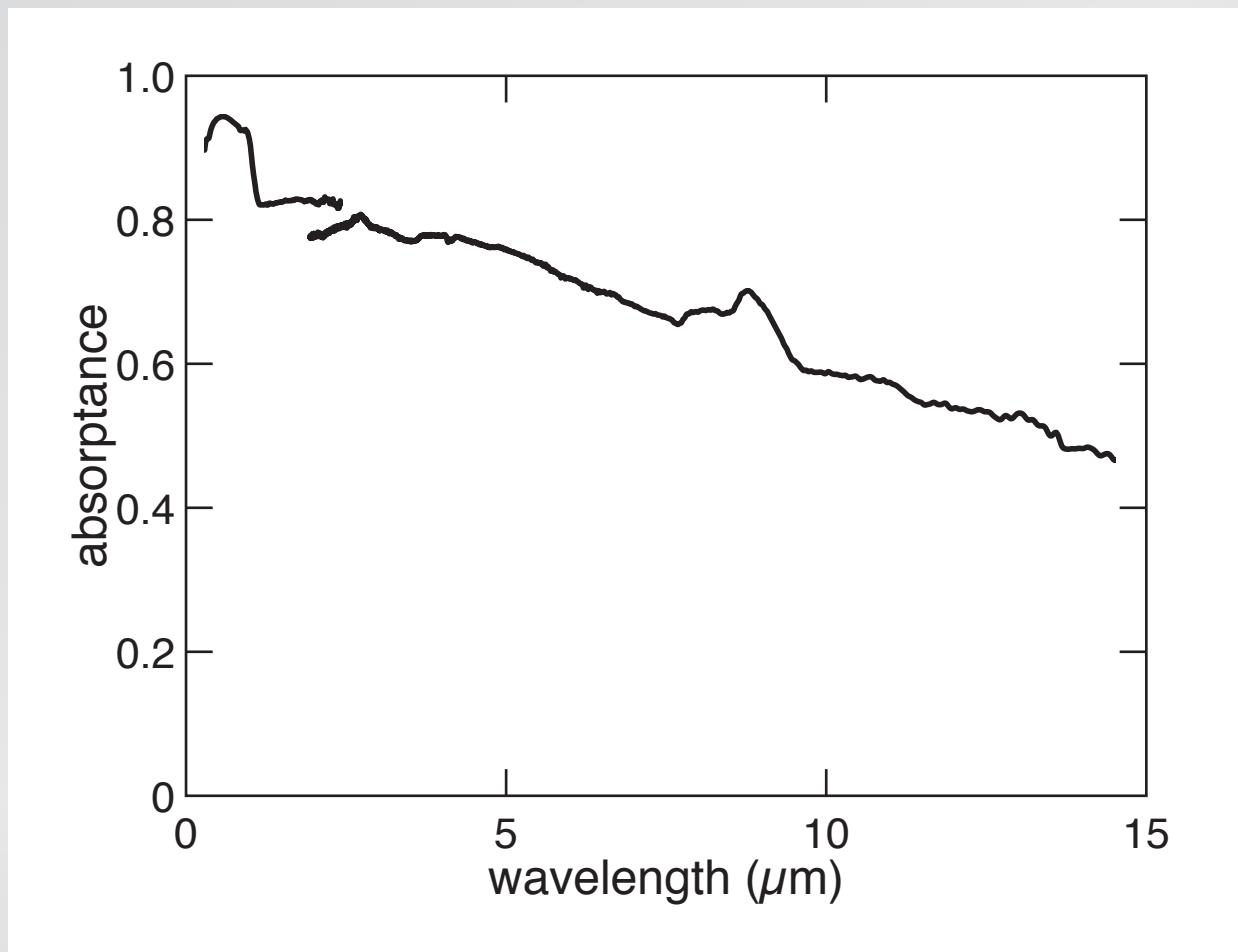
Outline

- structure
- optoelectronic properties

- devices

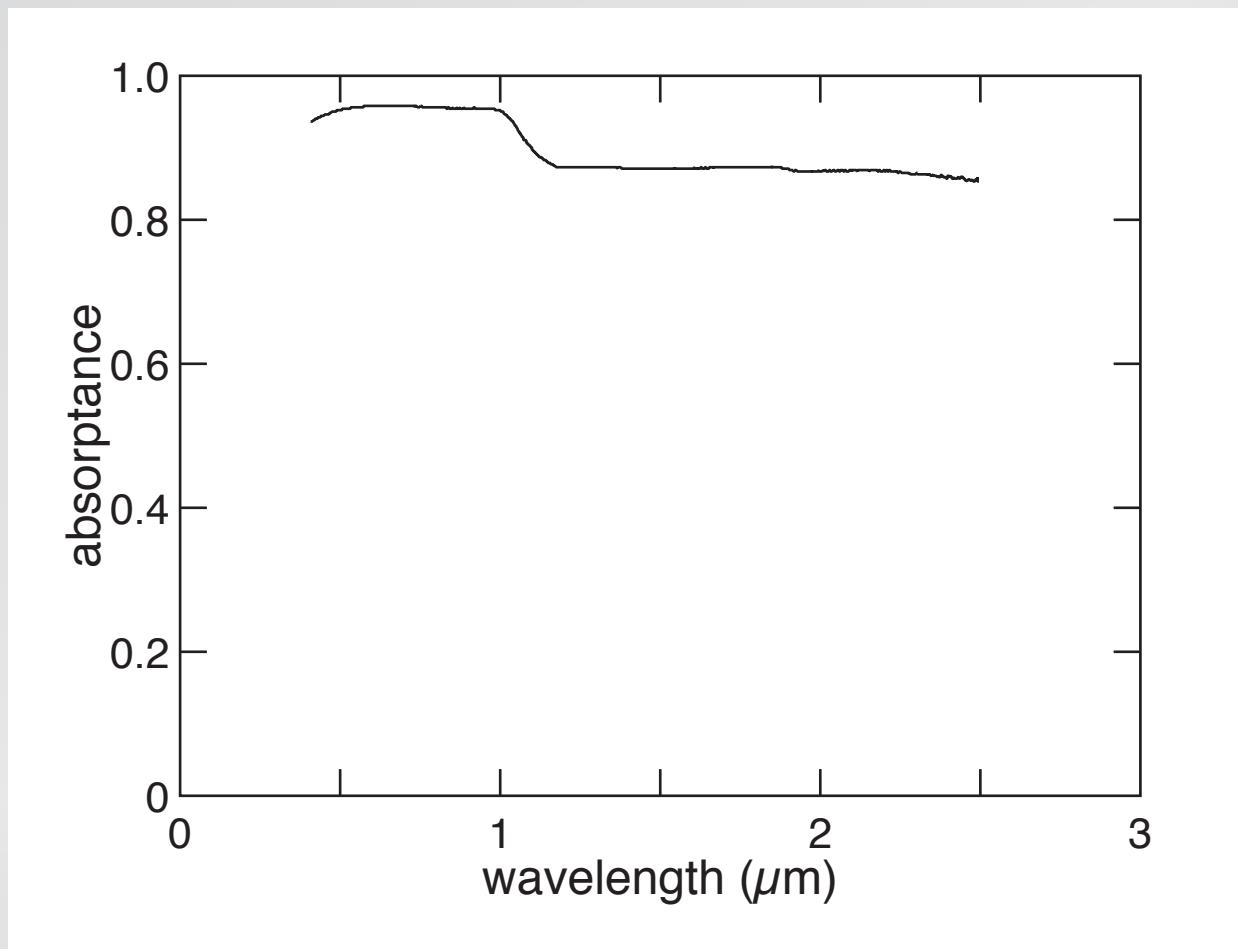
Optoelectronic properties

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



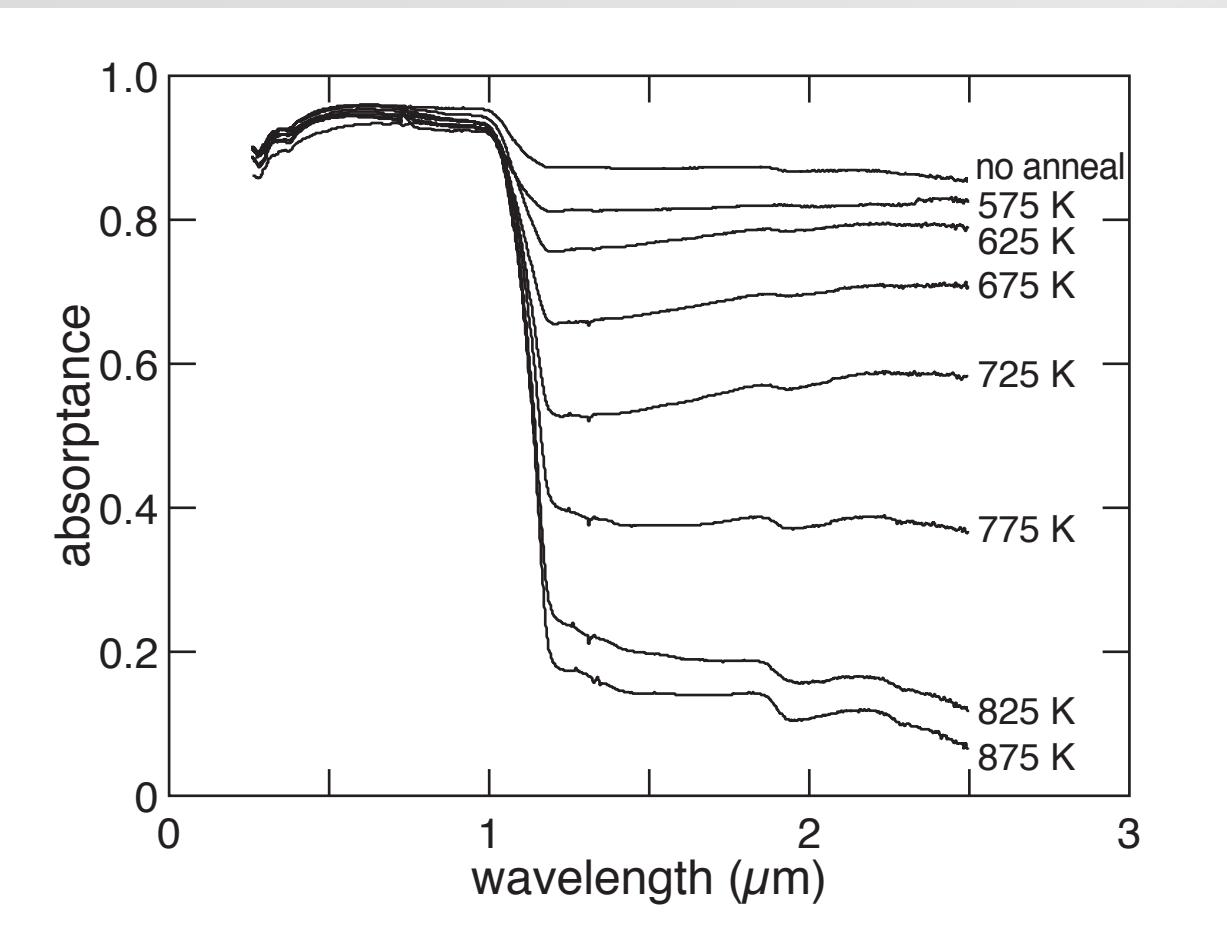
Optoelectronic properties

effect of annealing on IR absorptance



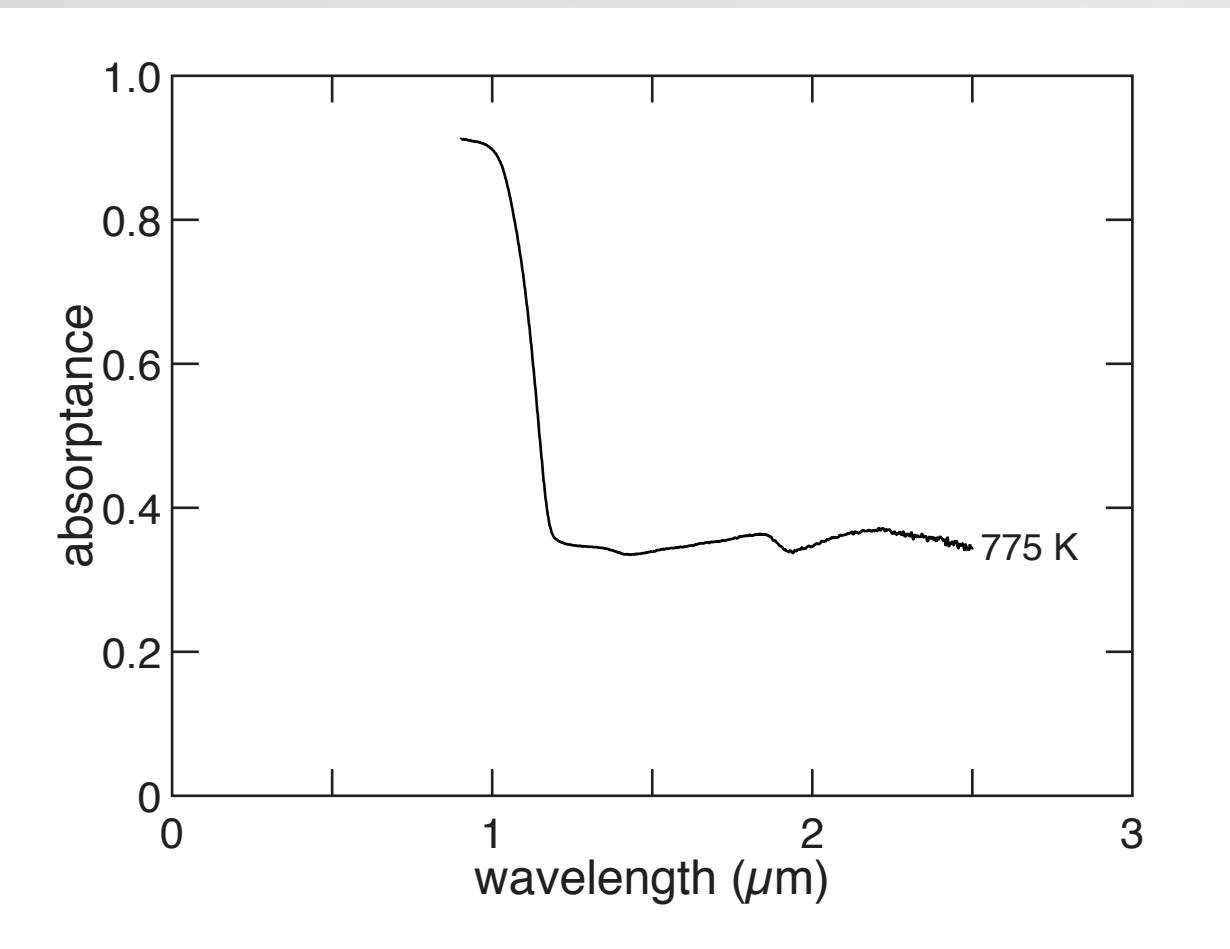
Optoelectronic properties

effect of annealing on IR absorptance



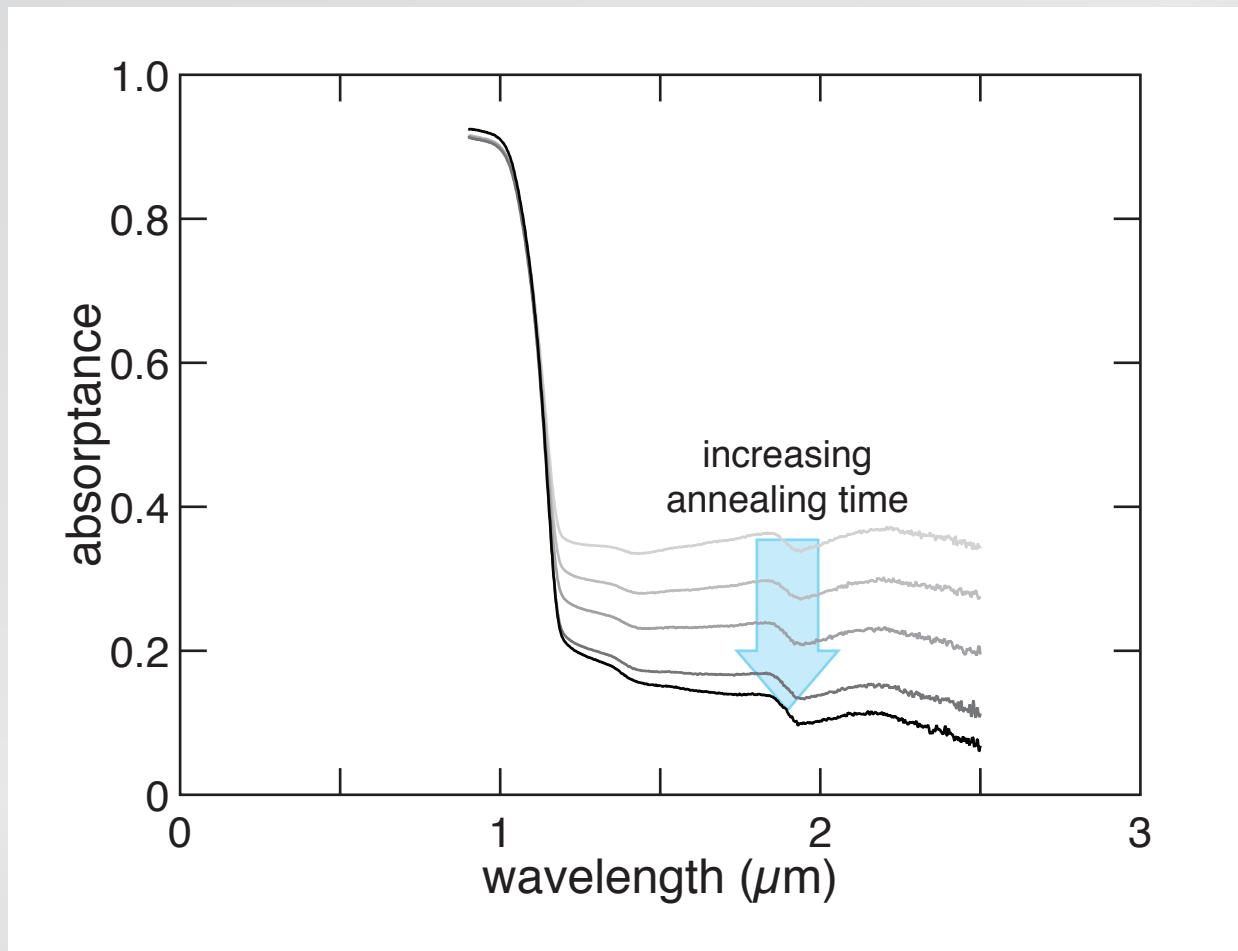
Optoelectronic properties

vary annealing time



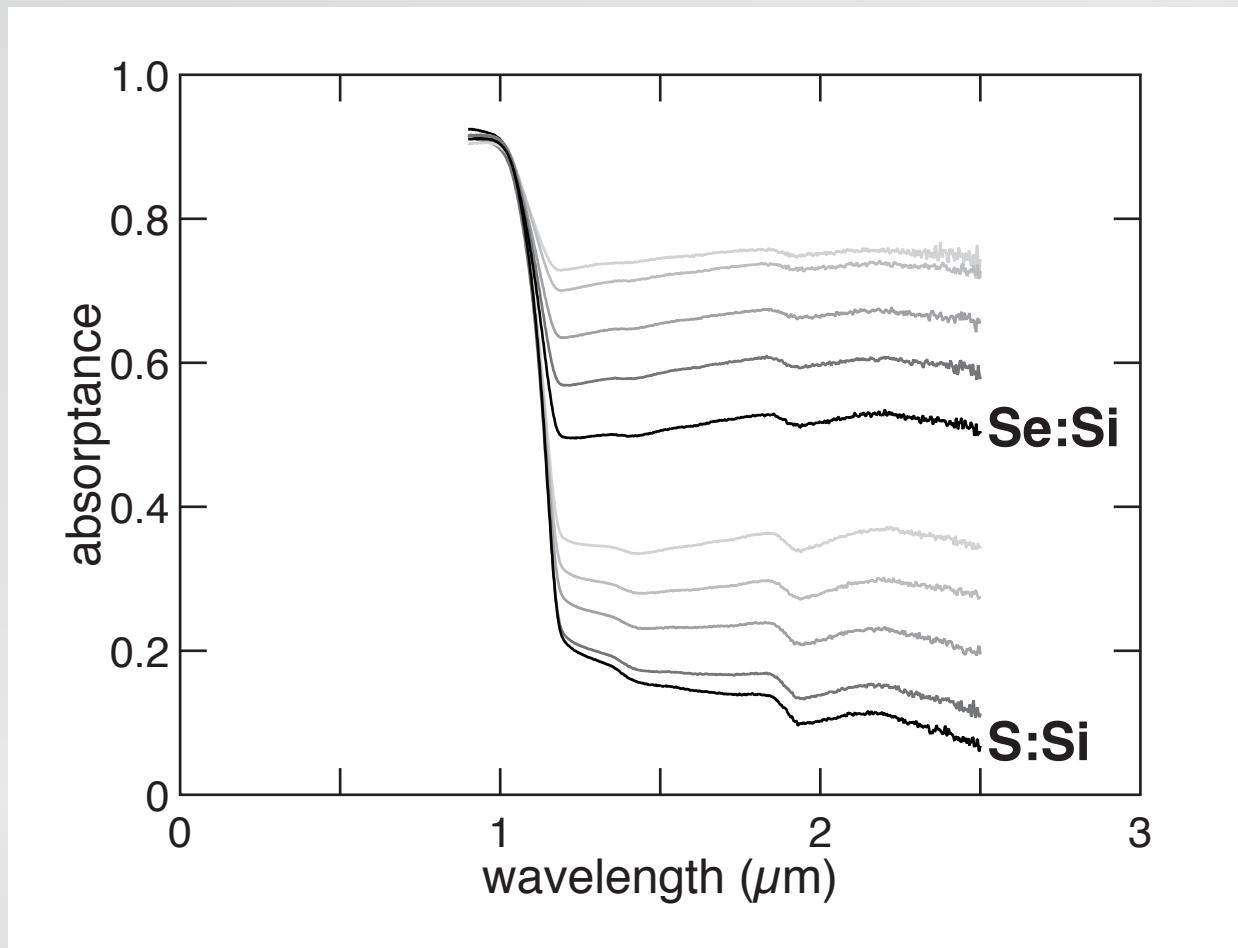
Optoelectronic properties

longer annealing decreases IR absorptance



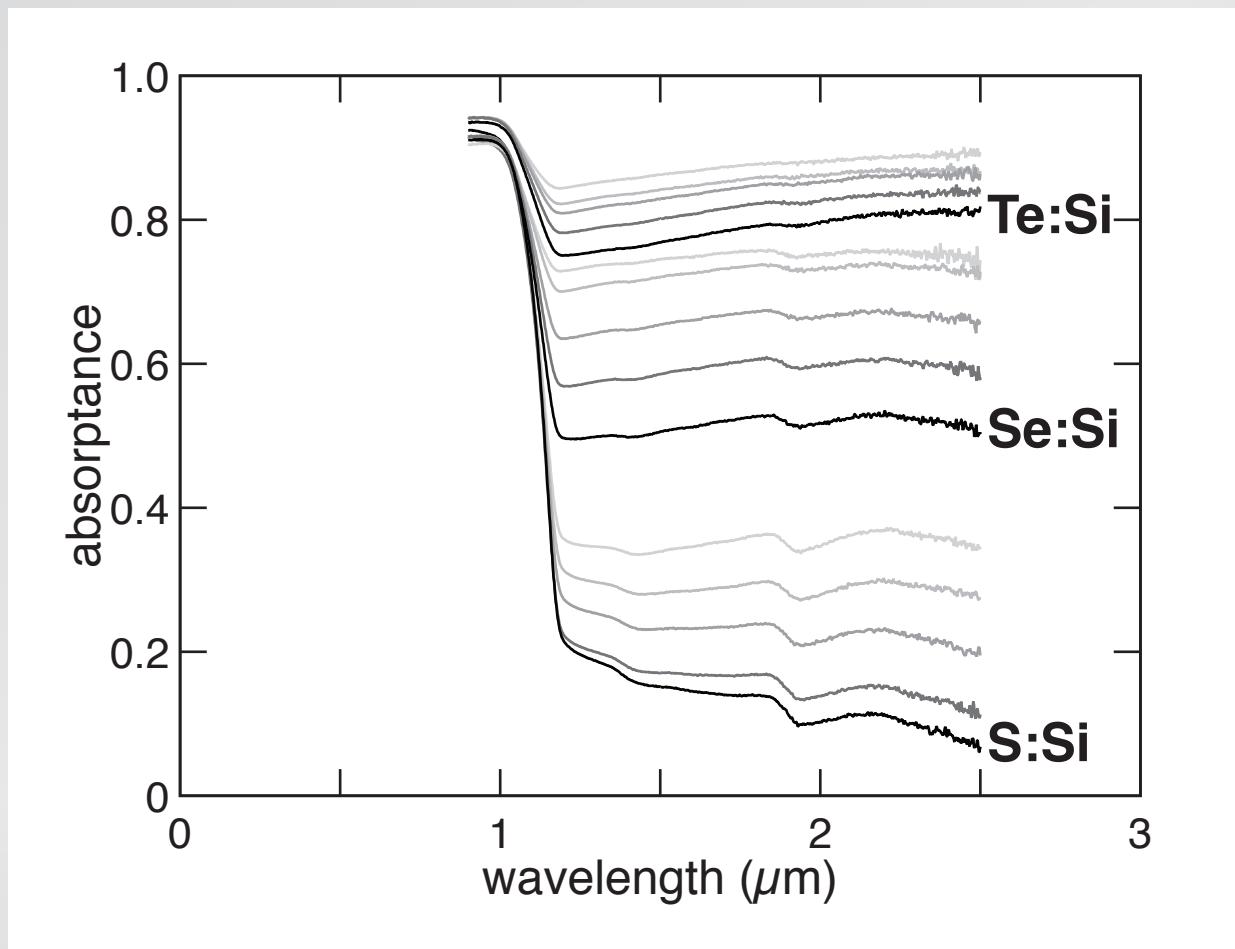
Optoelectronic properties

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



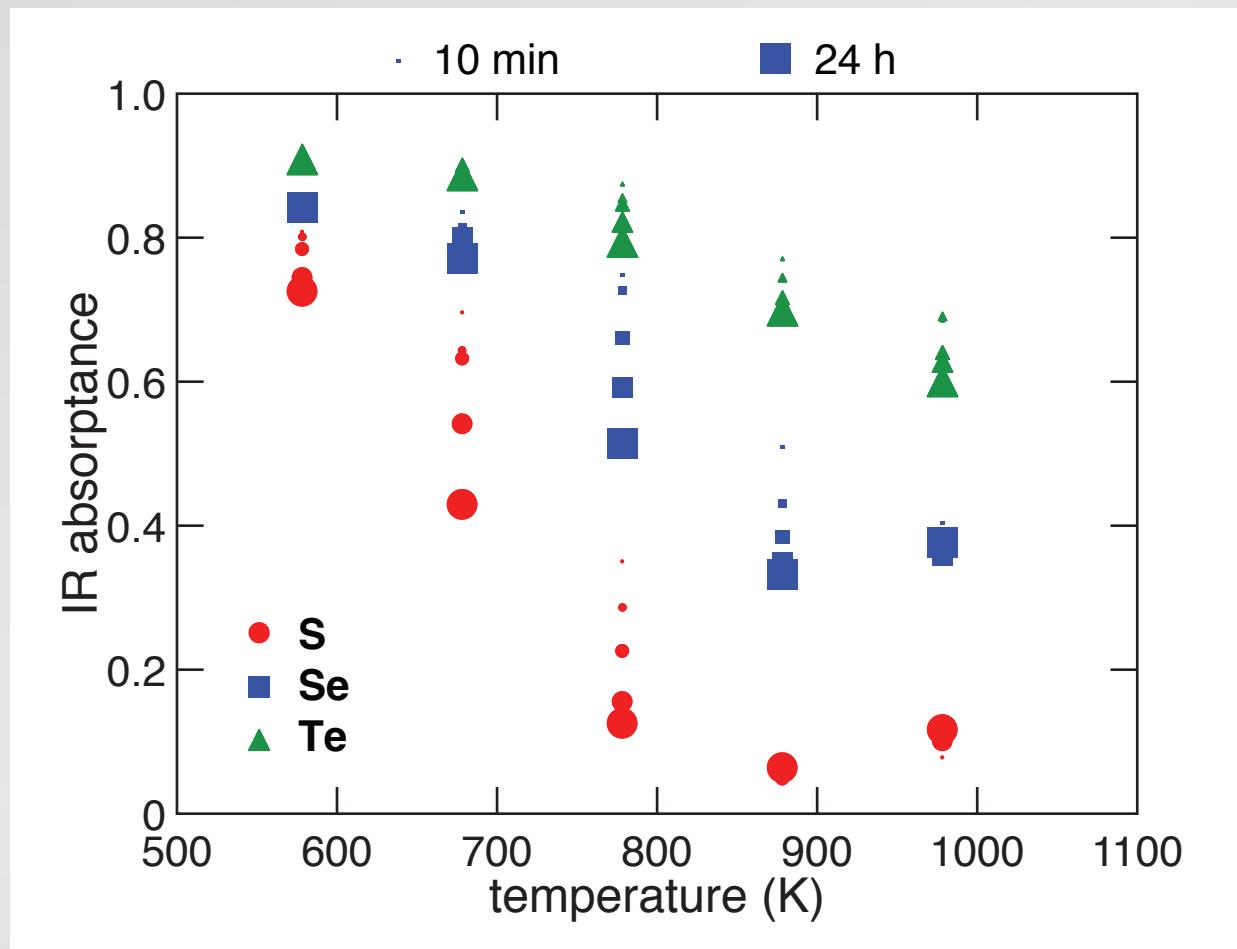
Optoelectronic properties

and even less for Te-doped samples...



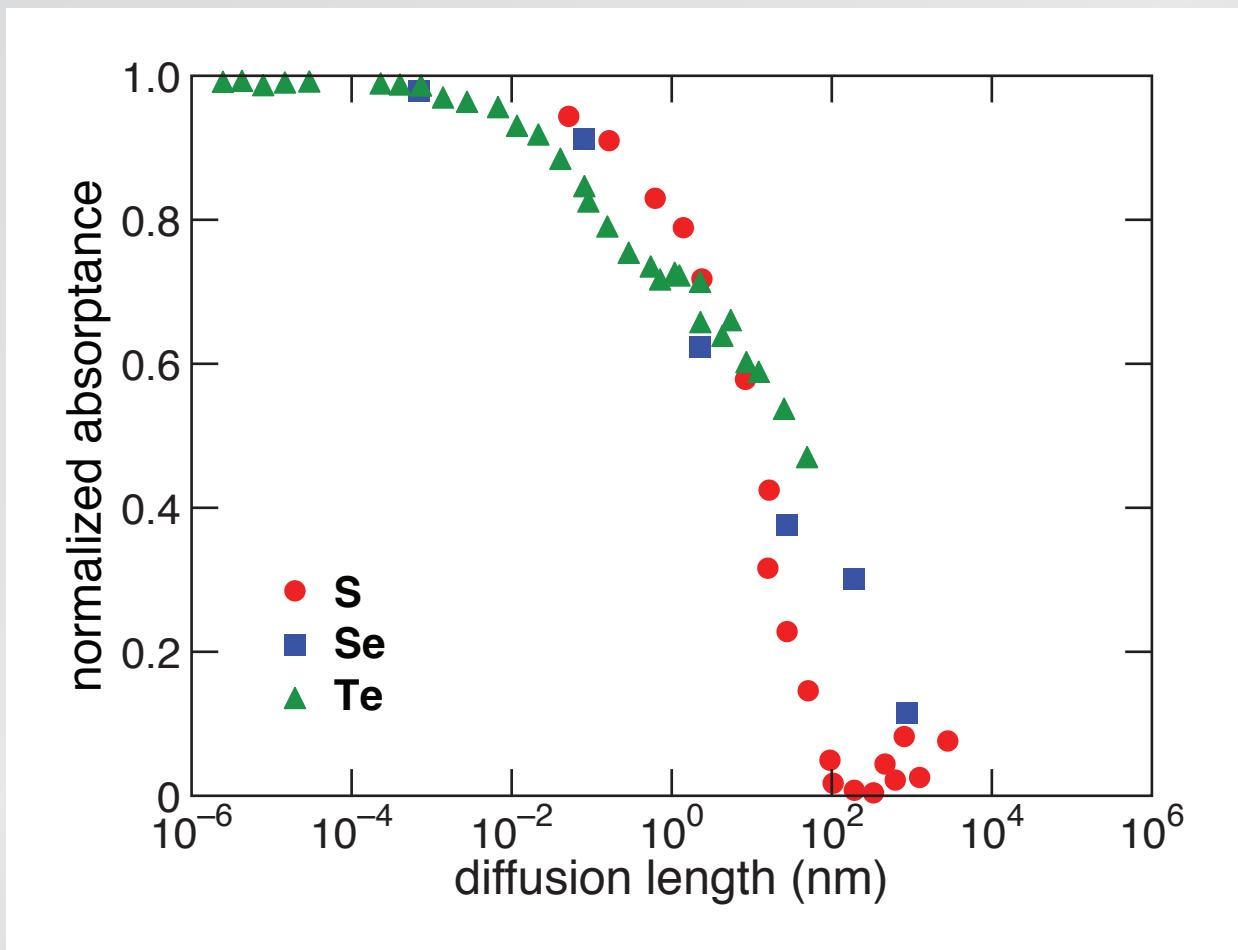
Optoelectronic properties

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



Optoelectronic properties

...but is unique function of diffusion length



Optoelectronic properties

annealing...

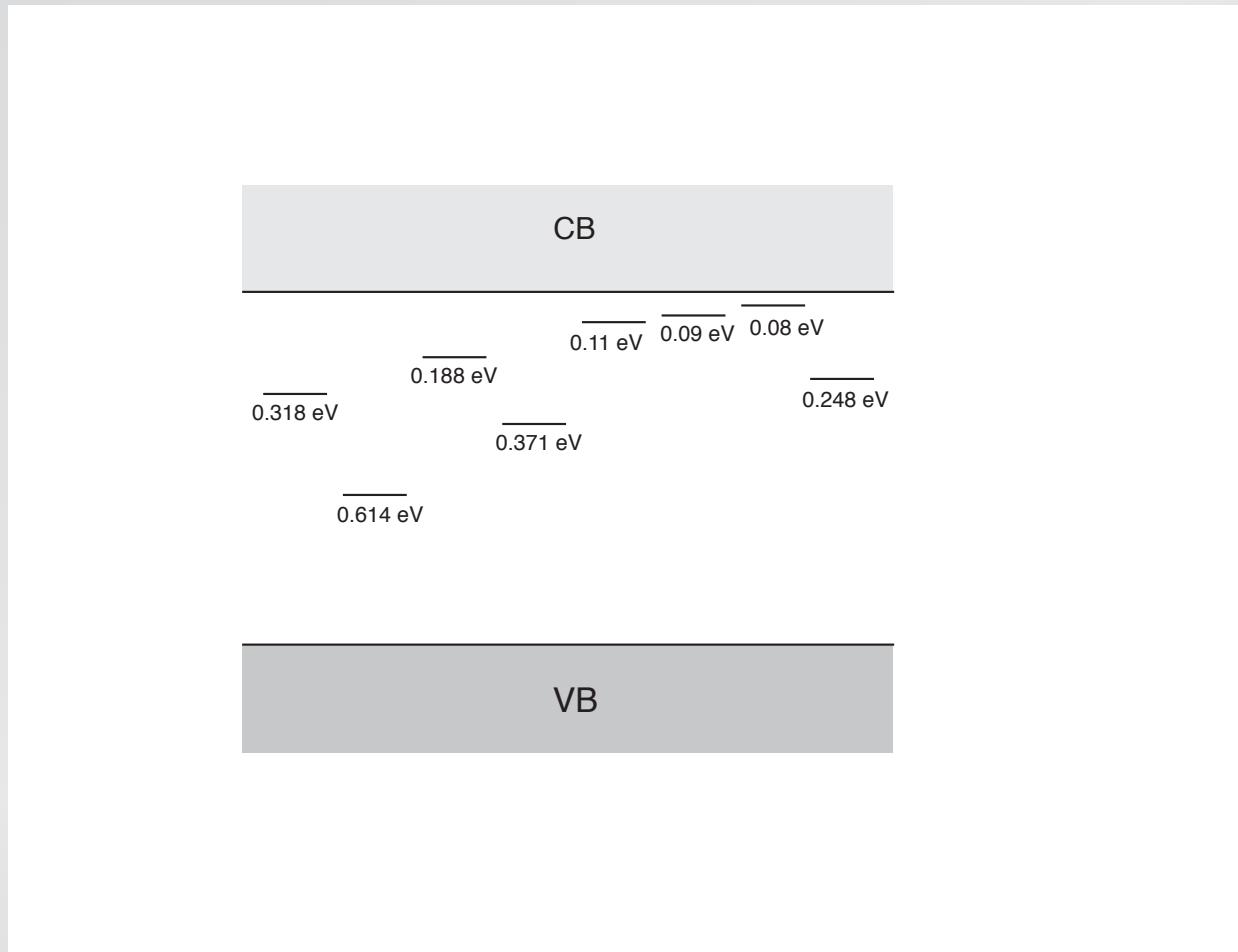
- decreases IR absorptance
- causes recoordination and diffusion of dopants
- IR absorptance reduced by 50% after 20 nm diffusion

Optoelectronic properties

what dopant states/bands cause IR absorption?

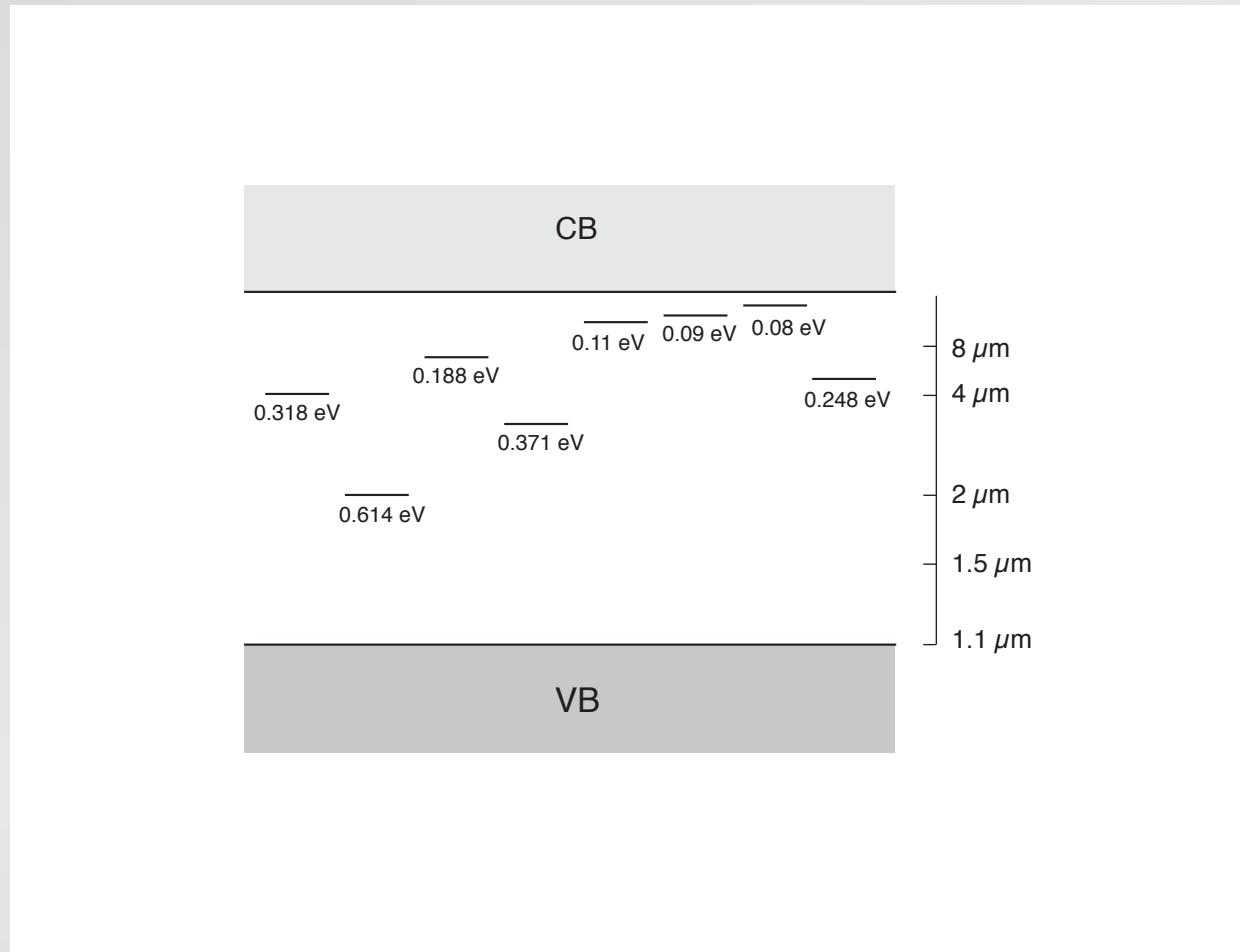
Optoelectronic properties

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



Optoelectronic properties

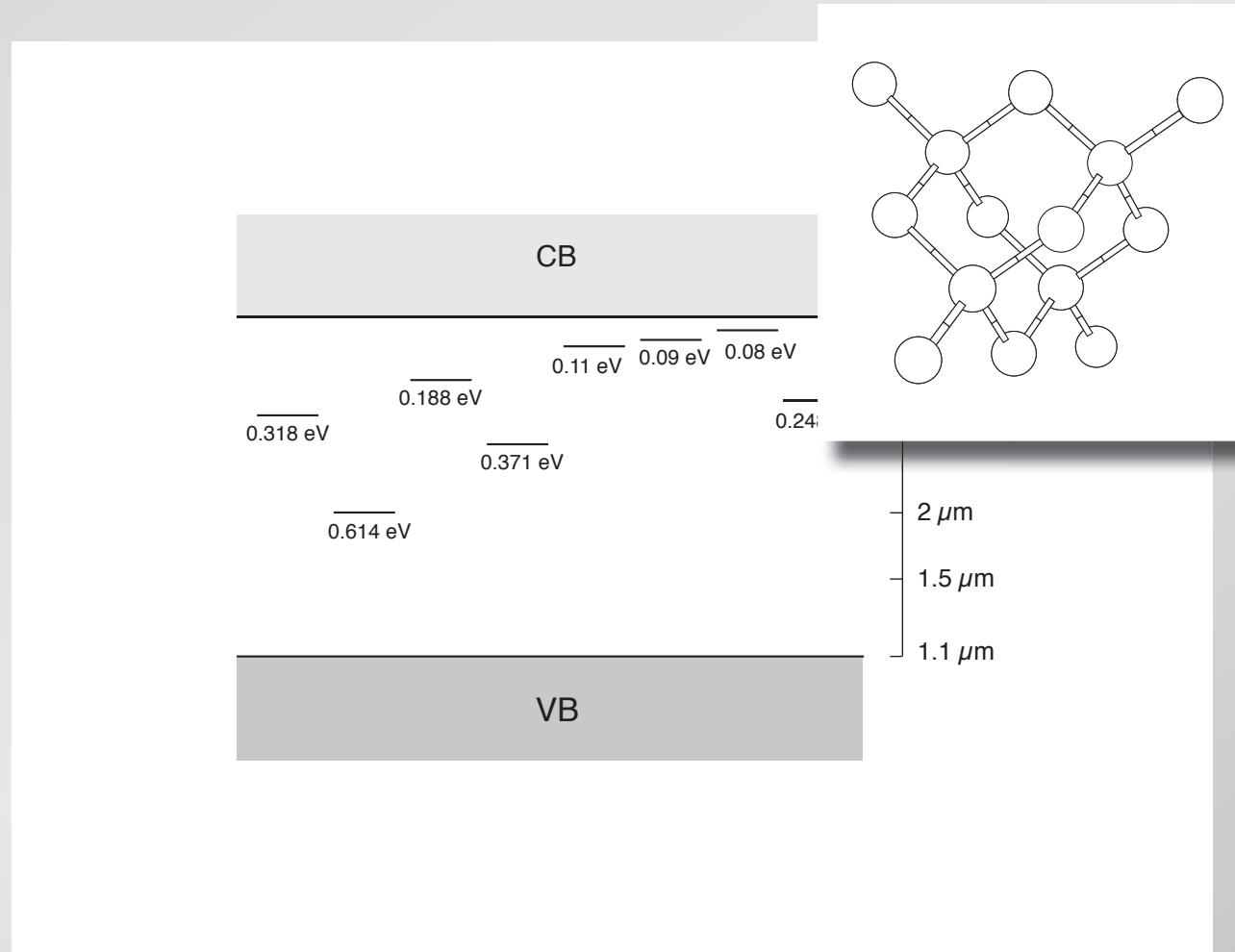
1 part in 10^6 sulfur introduces donor states in gap



Janzén et al., Phys. Rev. B 29, 1907 (1984)

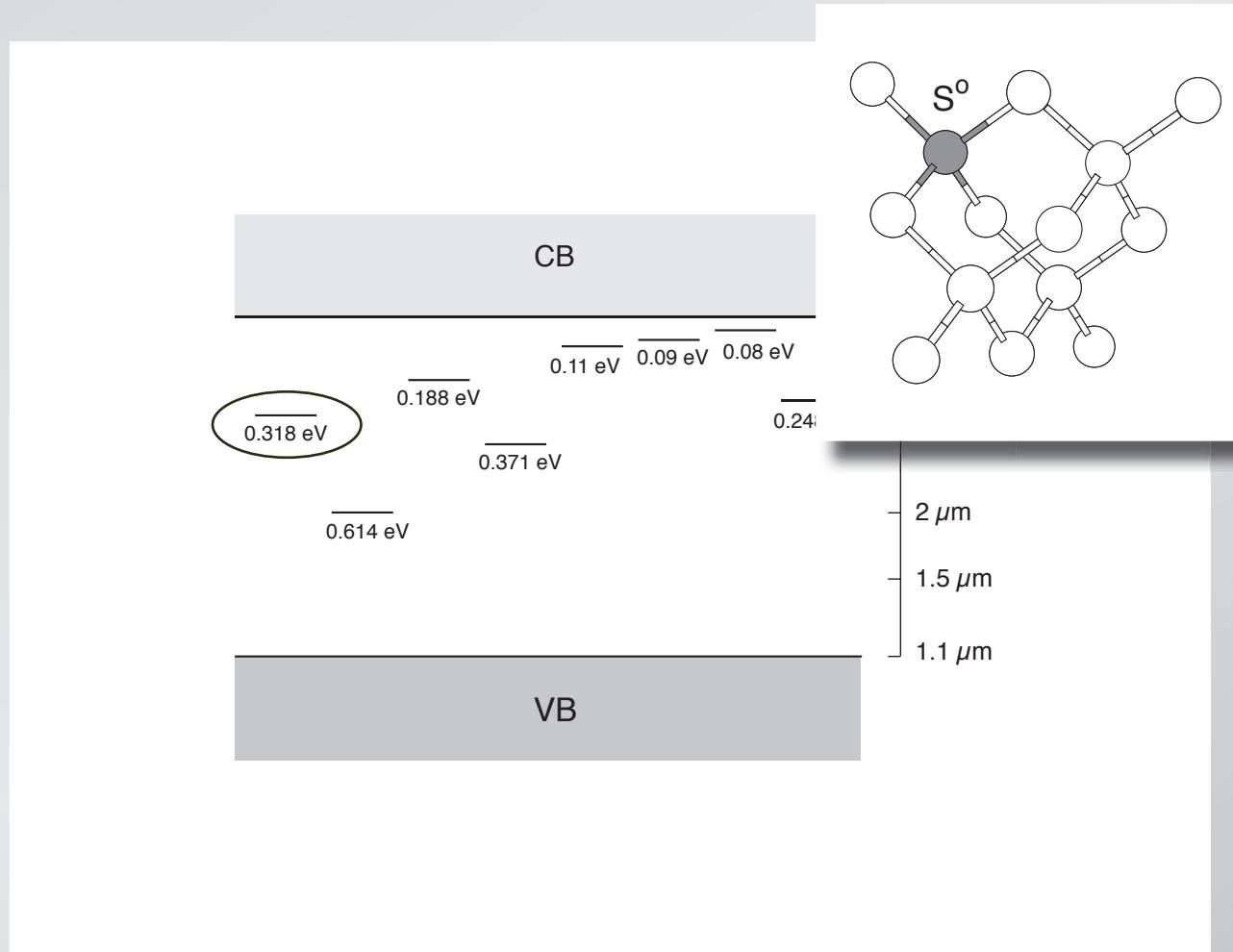
Optoelectronic properties

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



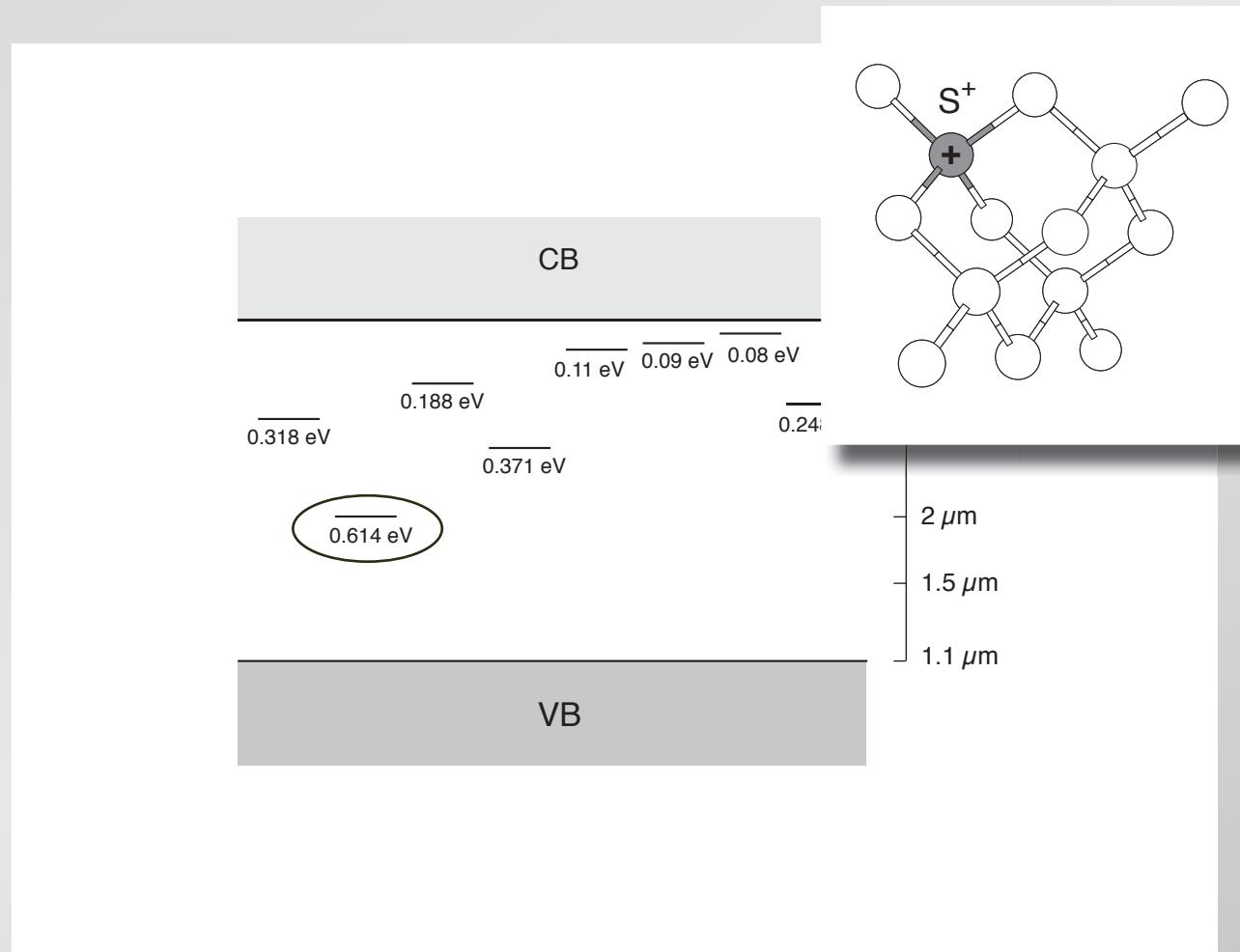
Optoelectronic properties

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



Optoelectronic properties

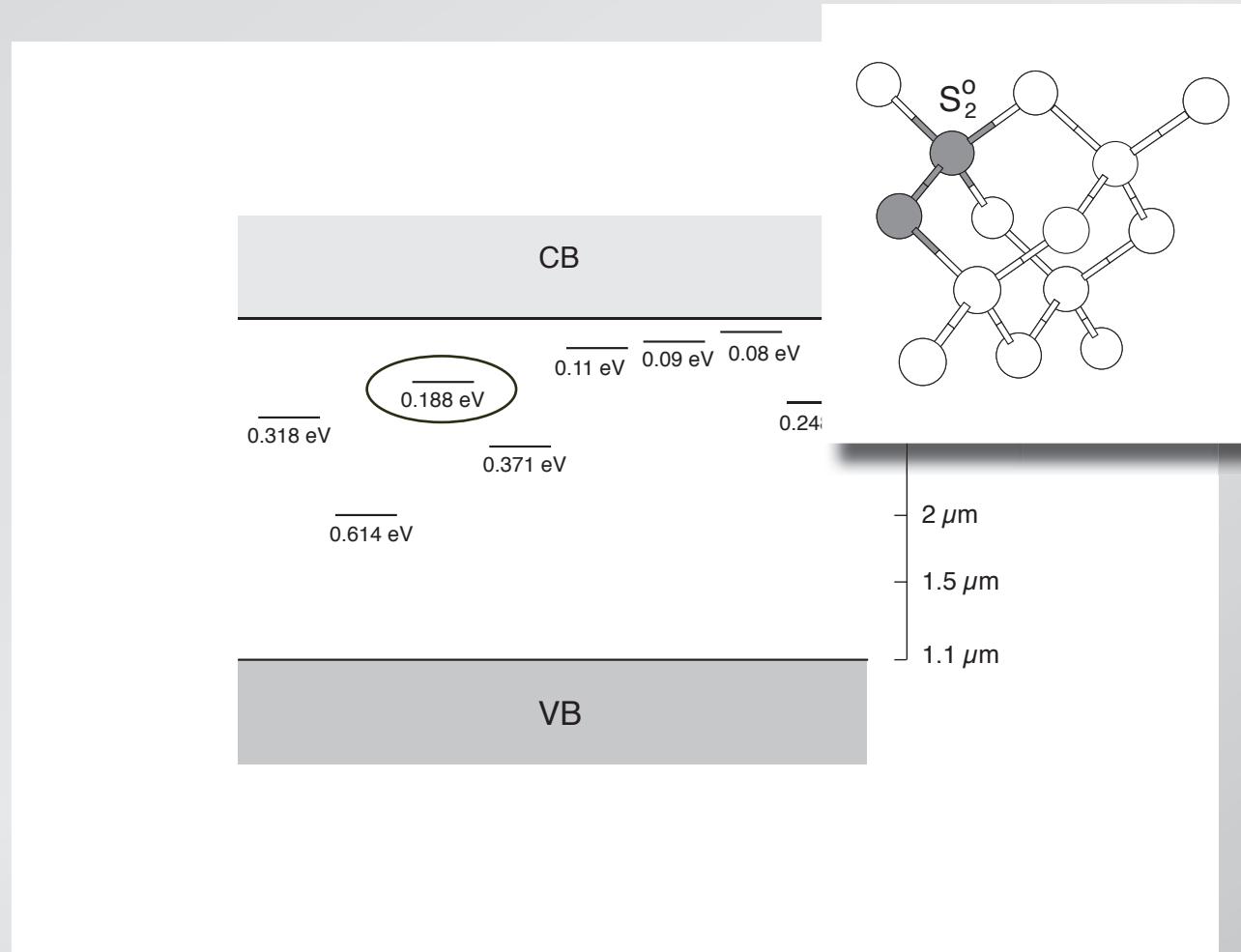
1 part in 10^6 sulfur introduces donor states in gap



Janzén et al., Phys. Rev. B 29, 1907 (1984)

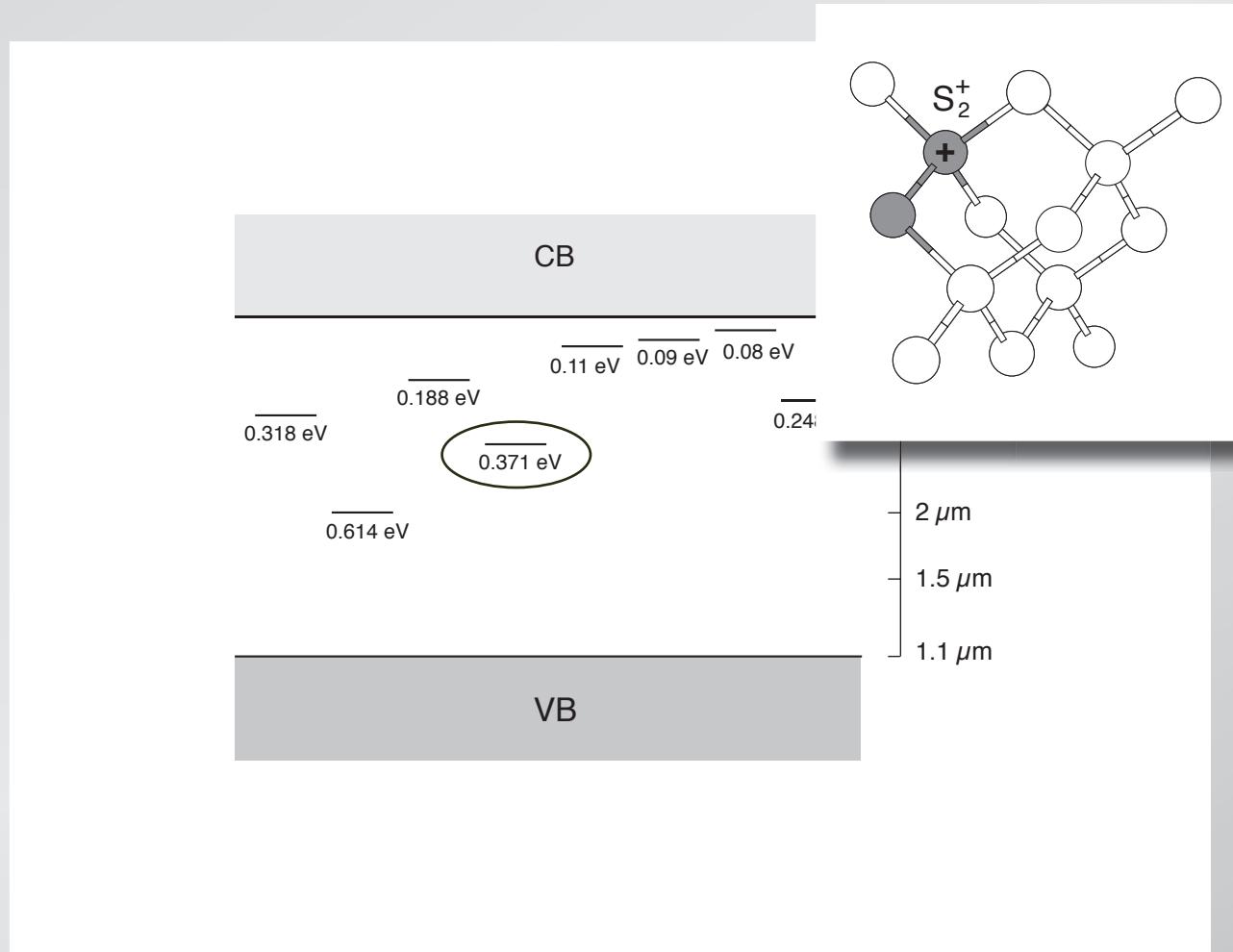
Optoelectronic properties

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



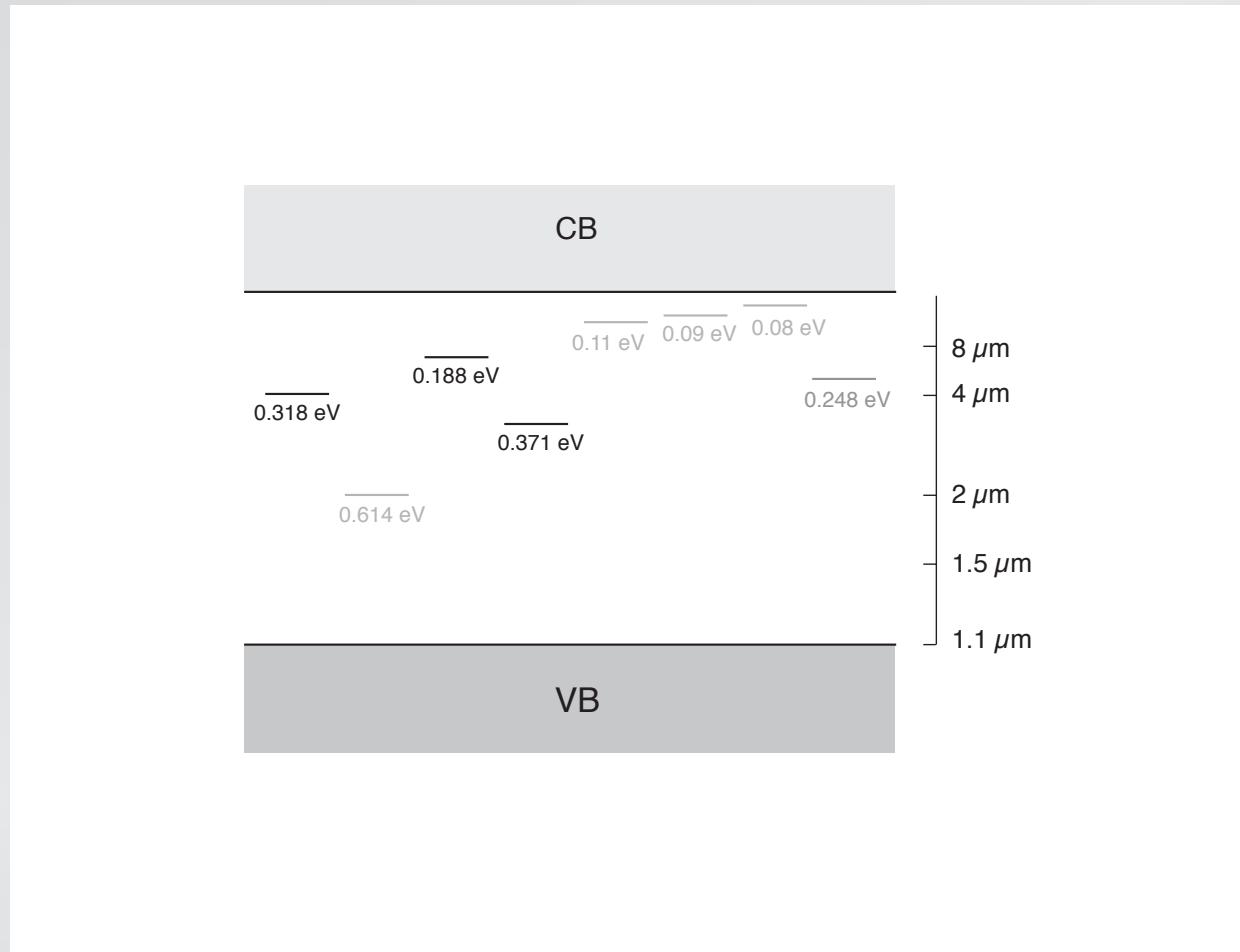
Optoelectronic properties

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



Optoelectronic properties

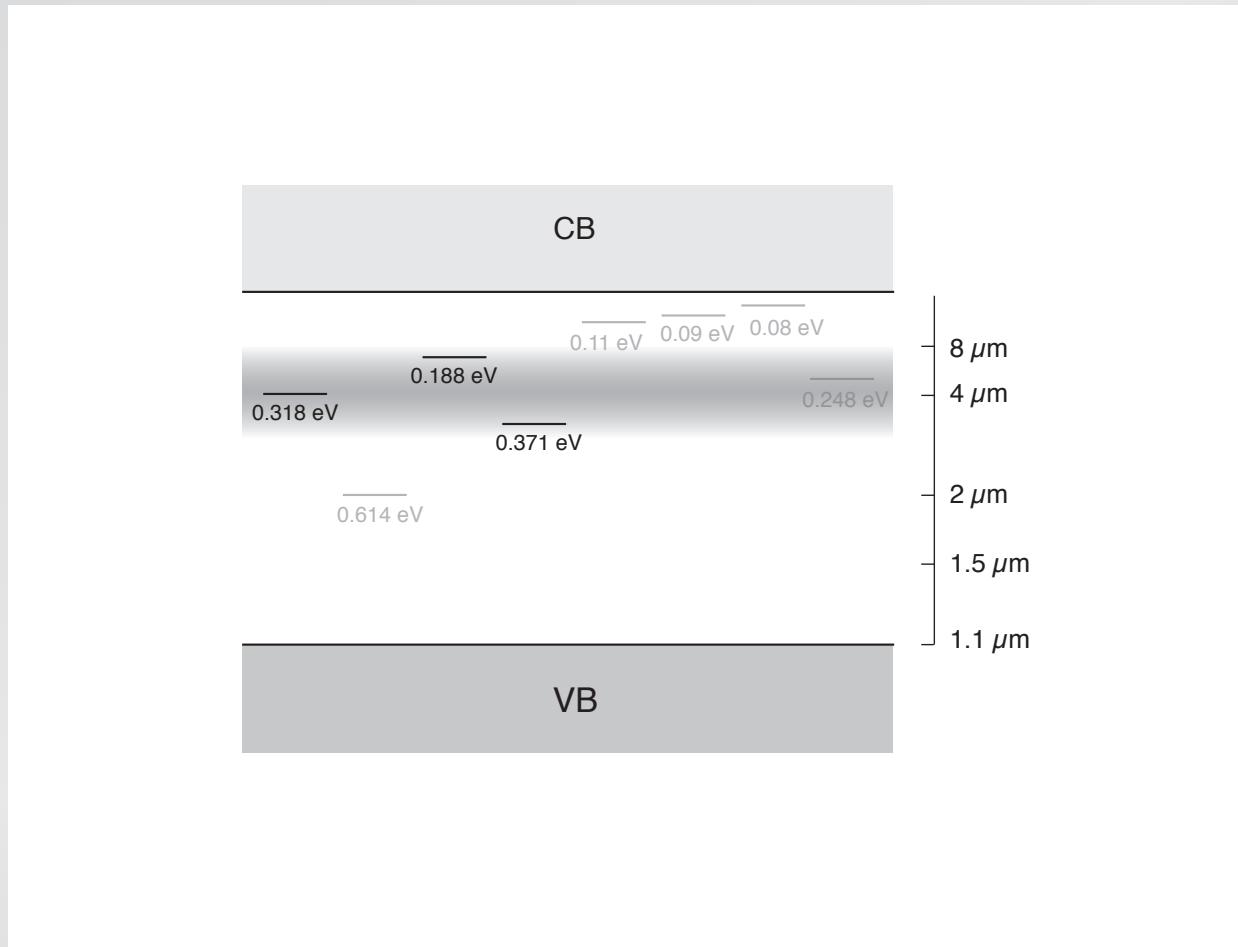
1 part in 10^6 sulfur introduces donor states in gap



Janzén et al., Phys. Rev. B 29, 1907 (1984)

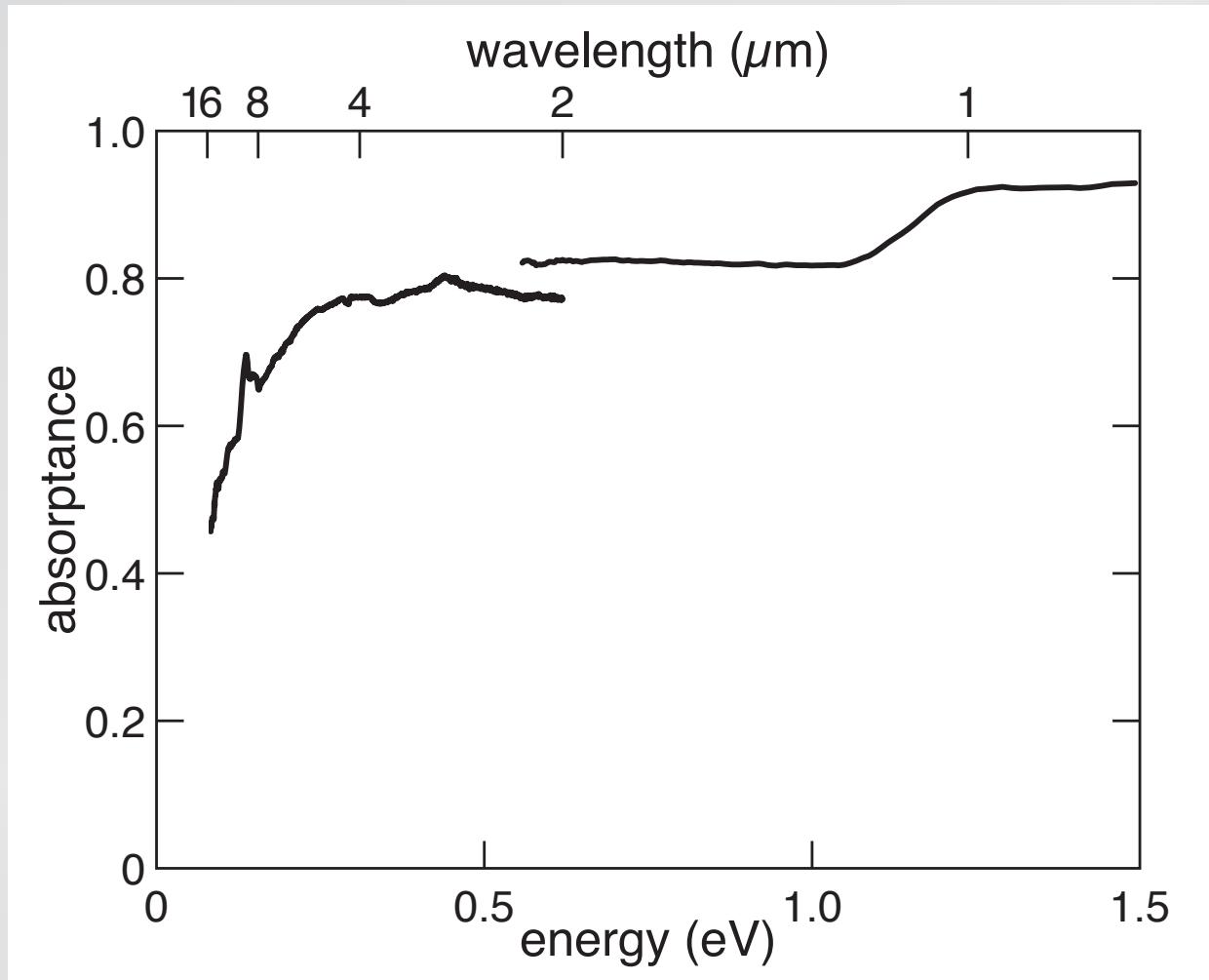
Optoelectronic properties

at high concentration states broaden into band



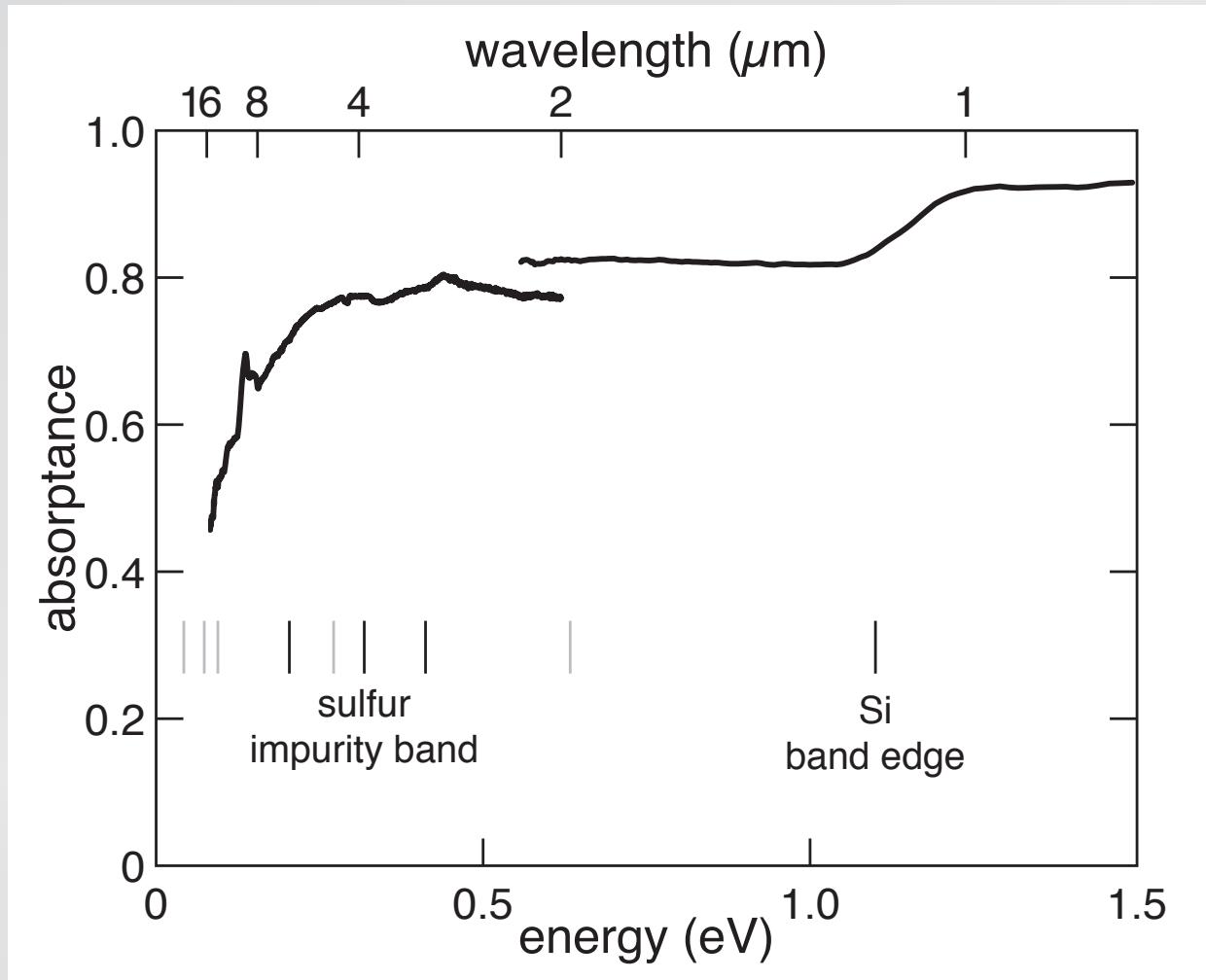
Optoelectronic properties

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



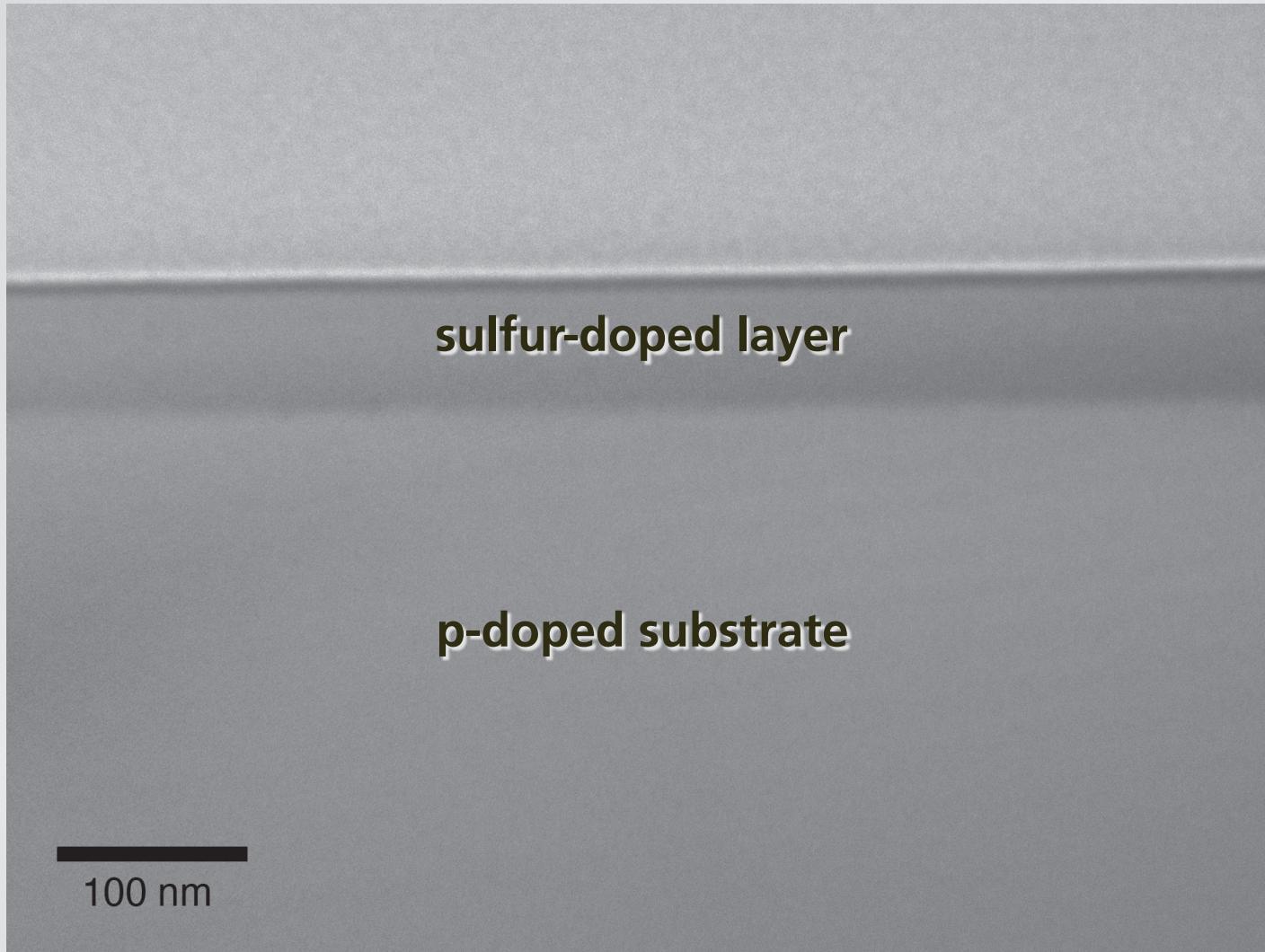
Optoelectronic properties

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



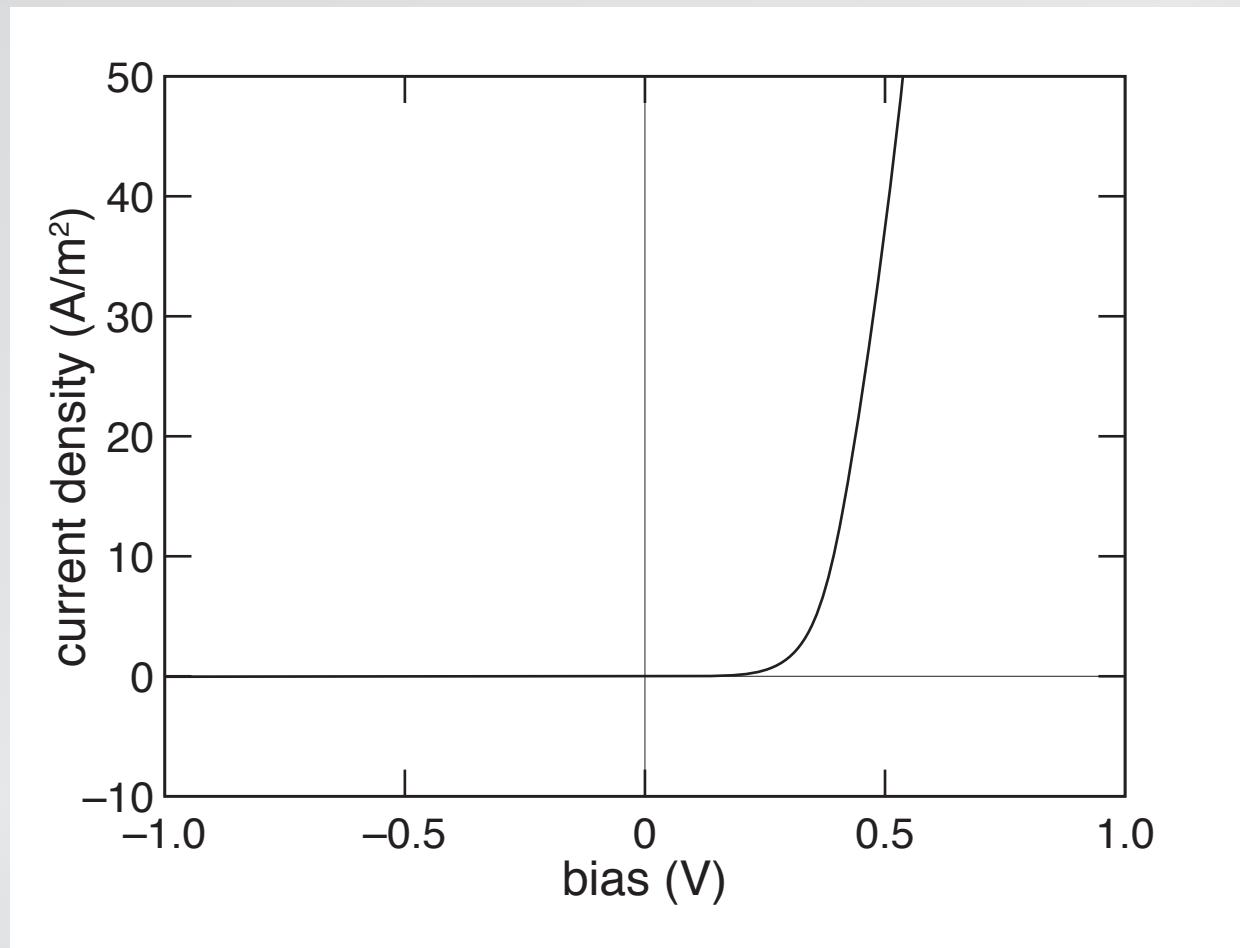
Optoelectronic properties

should have shallow junction below surface



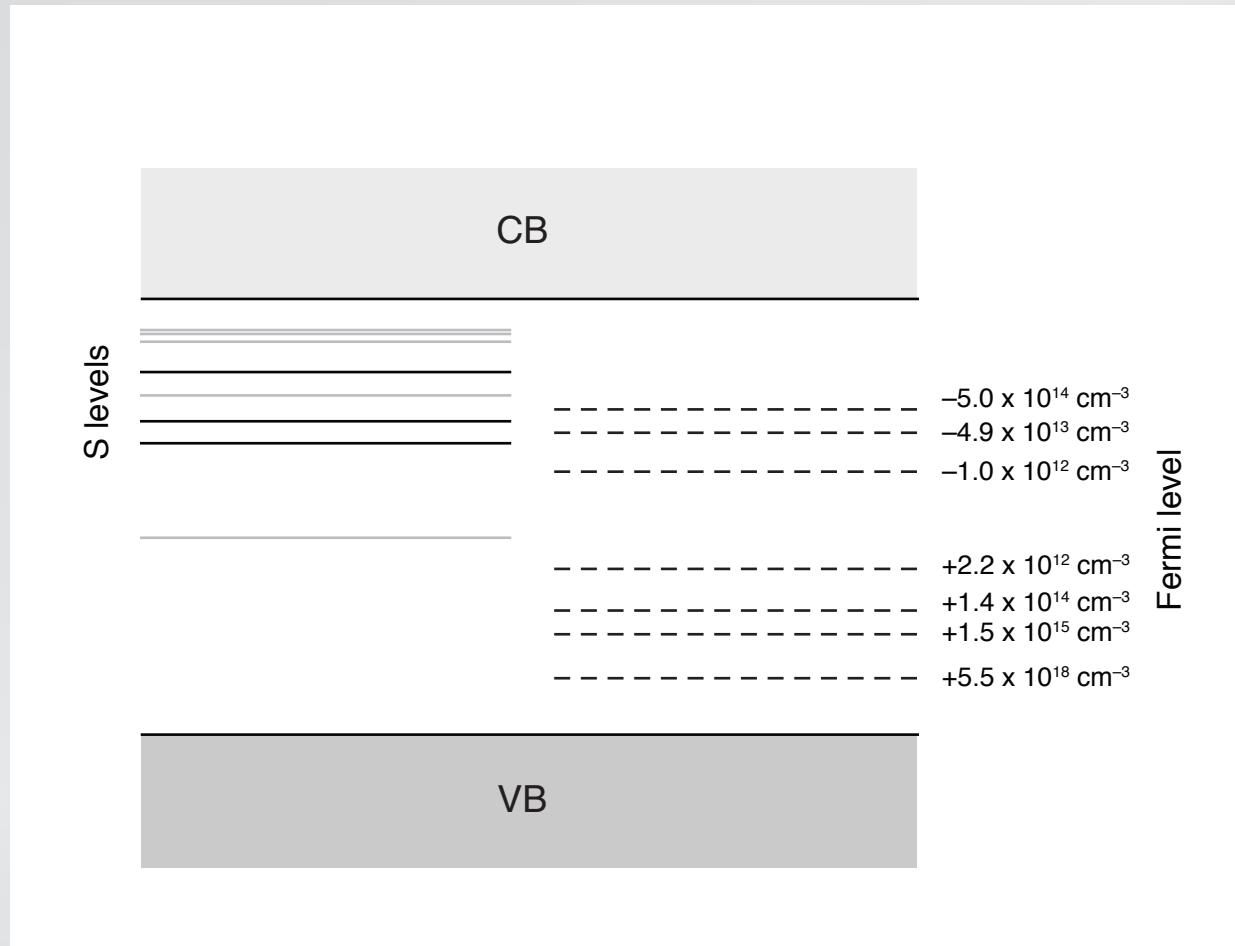
Optoelectronic properties

excellent rectification (after annealing)



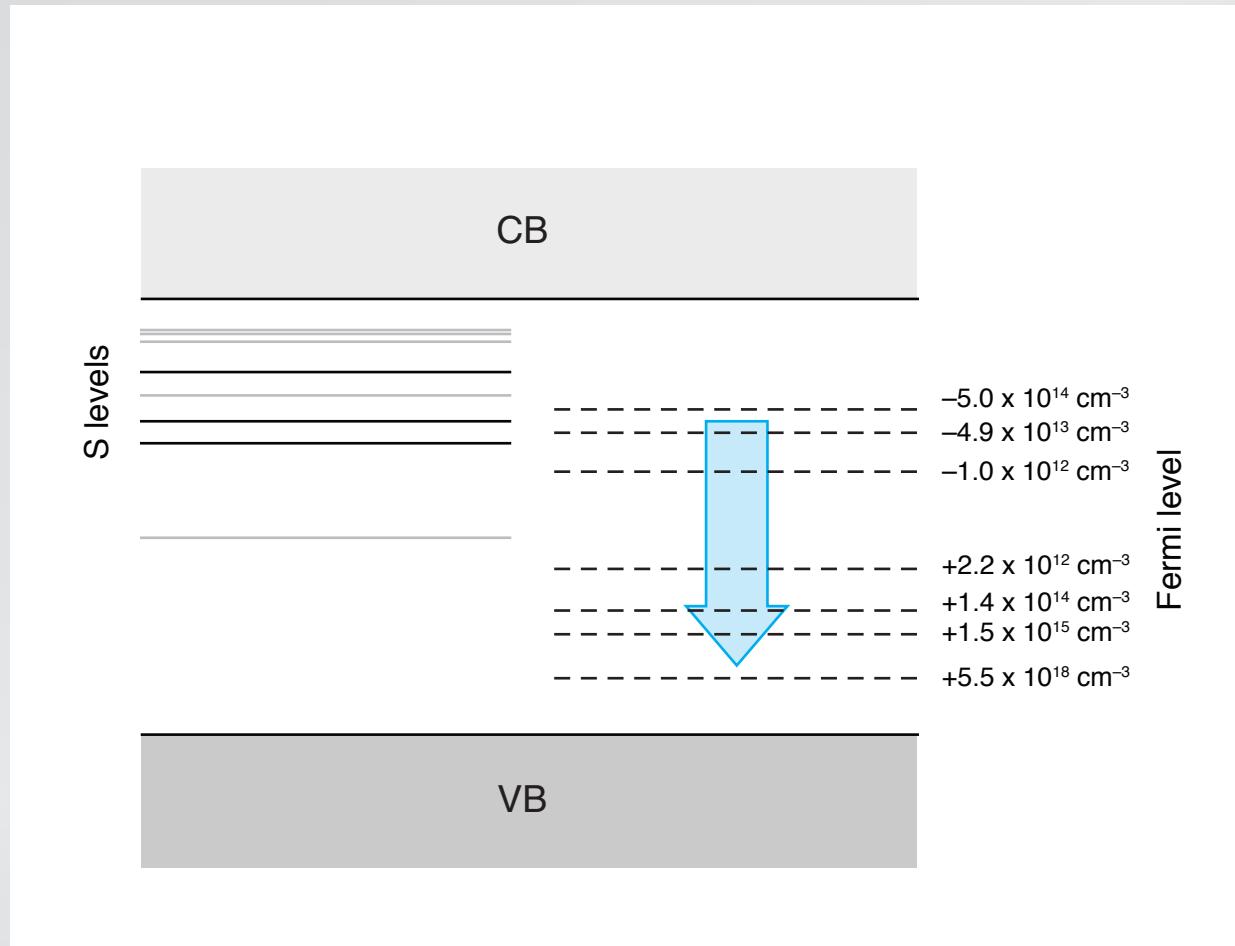
Optoelectronic properties

probe impurity states by varying Fermi level in substrate



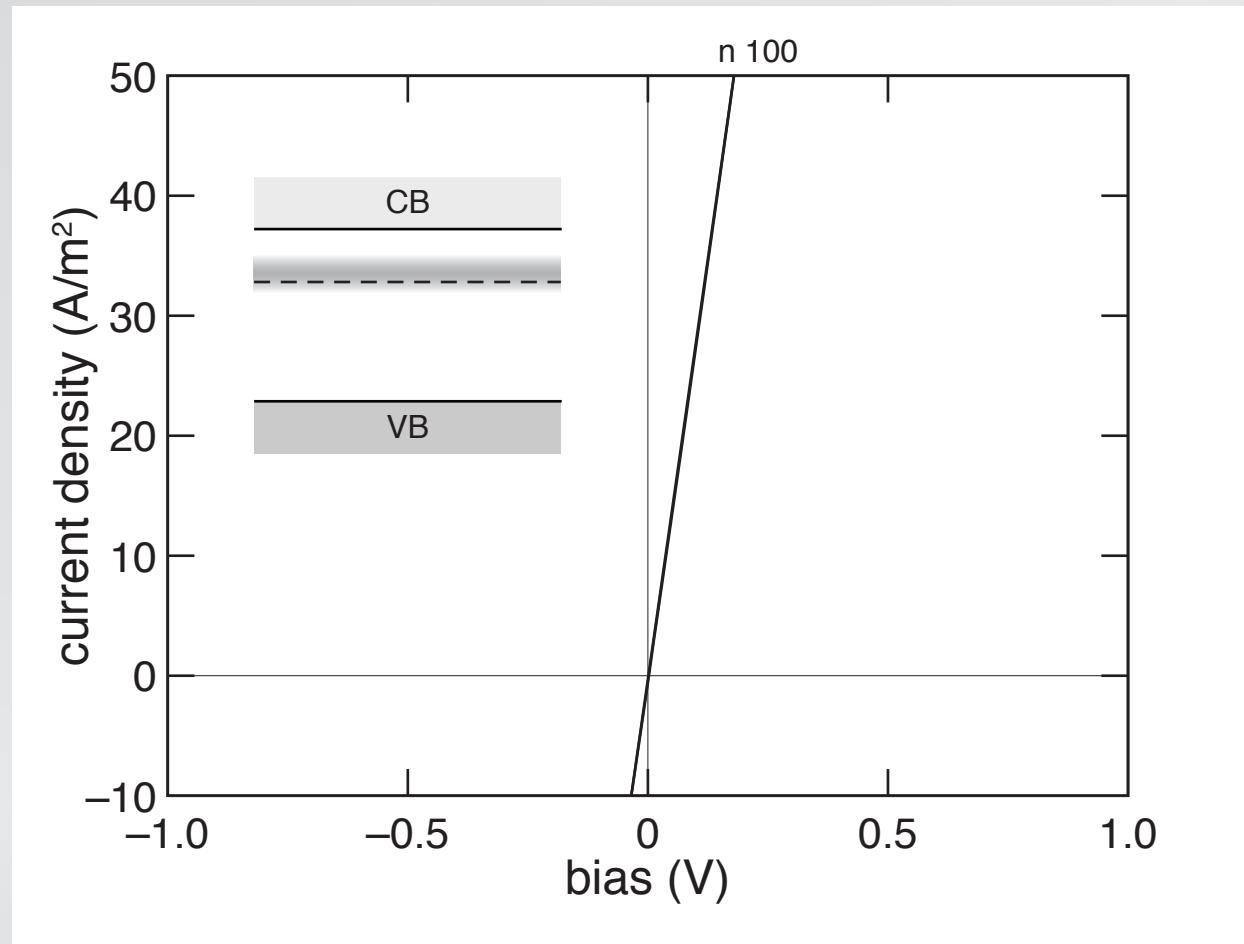
Optoelectronic properties

probe impurity states by varying Fermi level in substrate



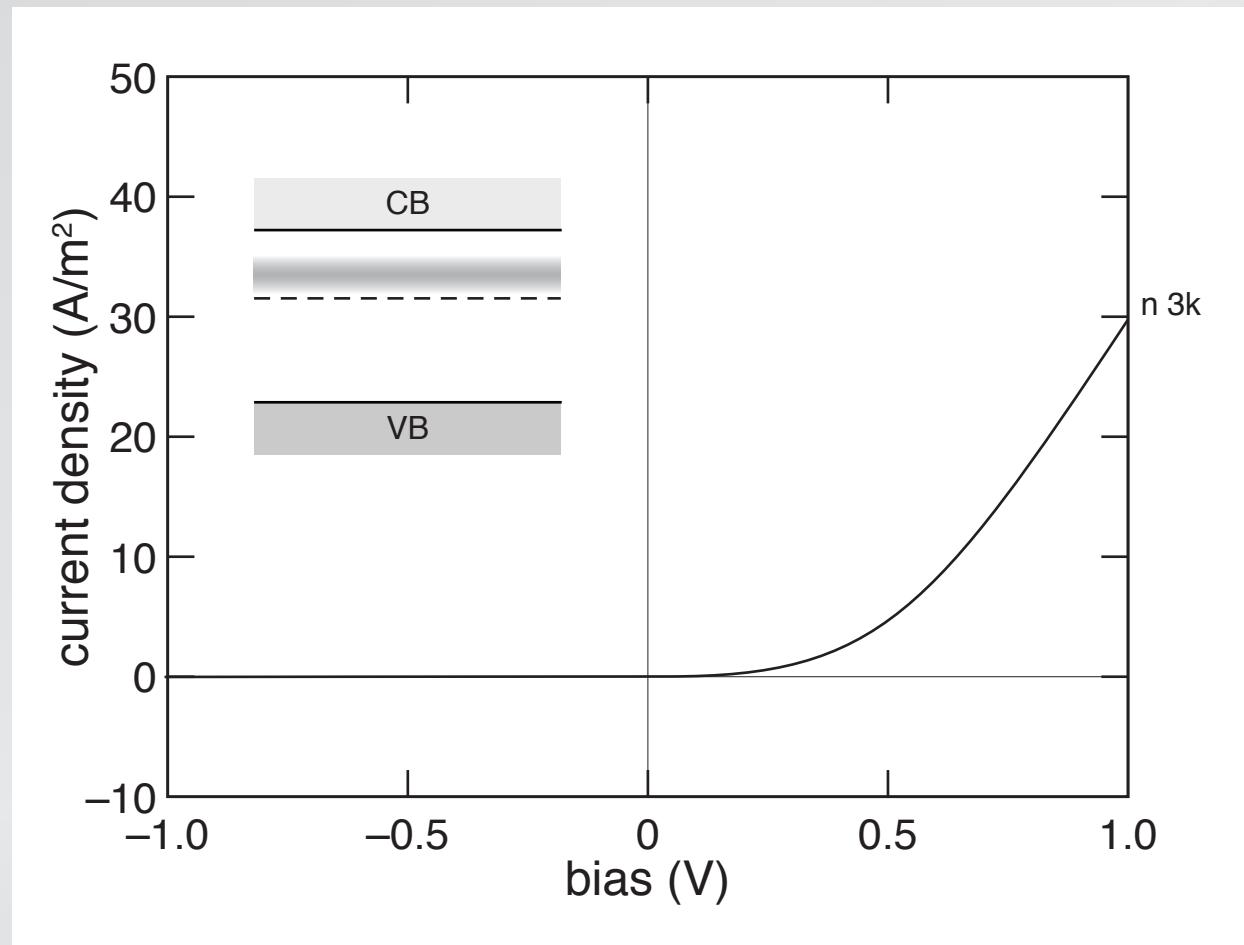
Optoelectronic properties

vary substrate doping type and resistivity



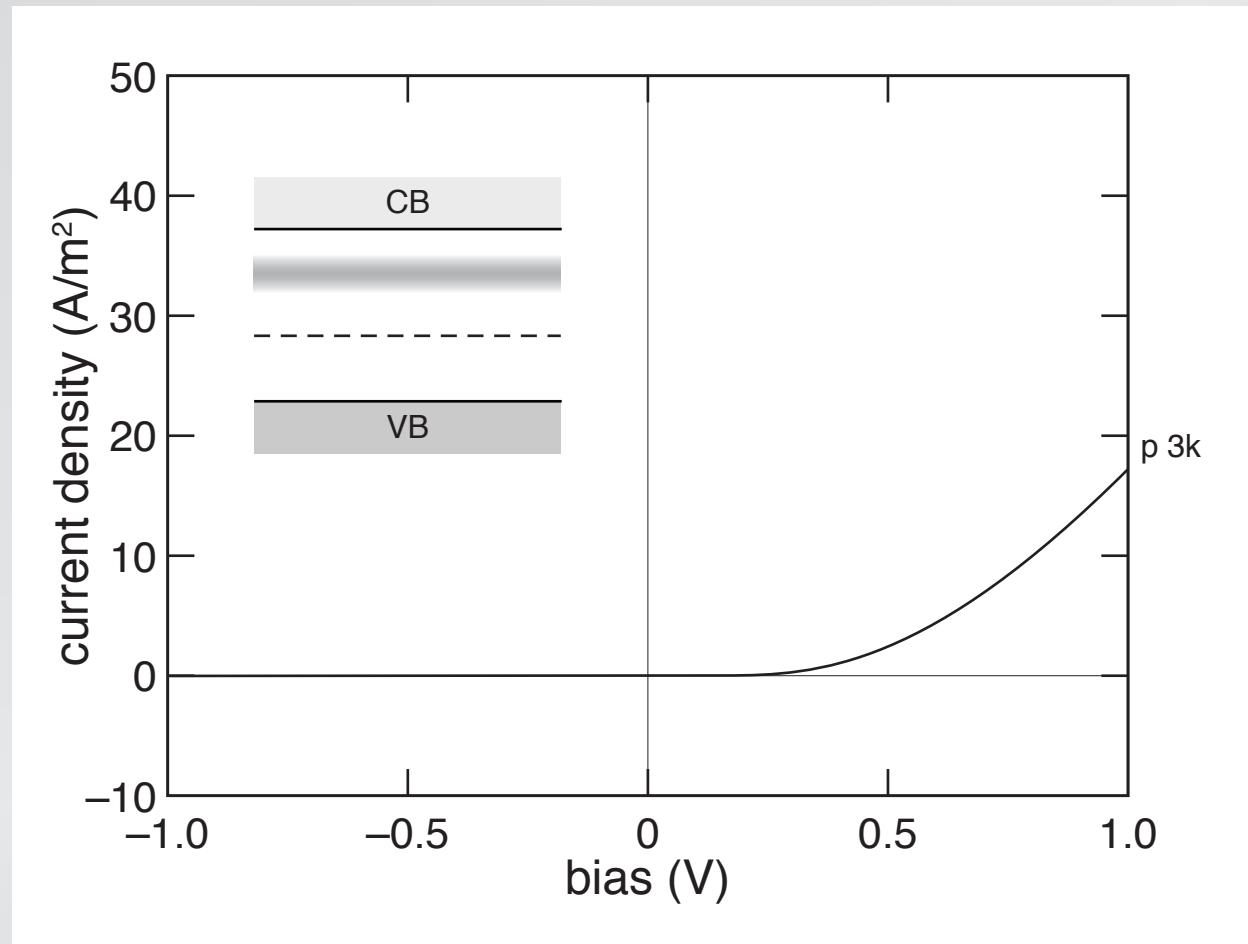
Optoelectronic properties

vary substrate doping type and resistivity



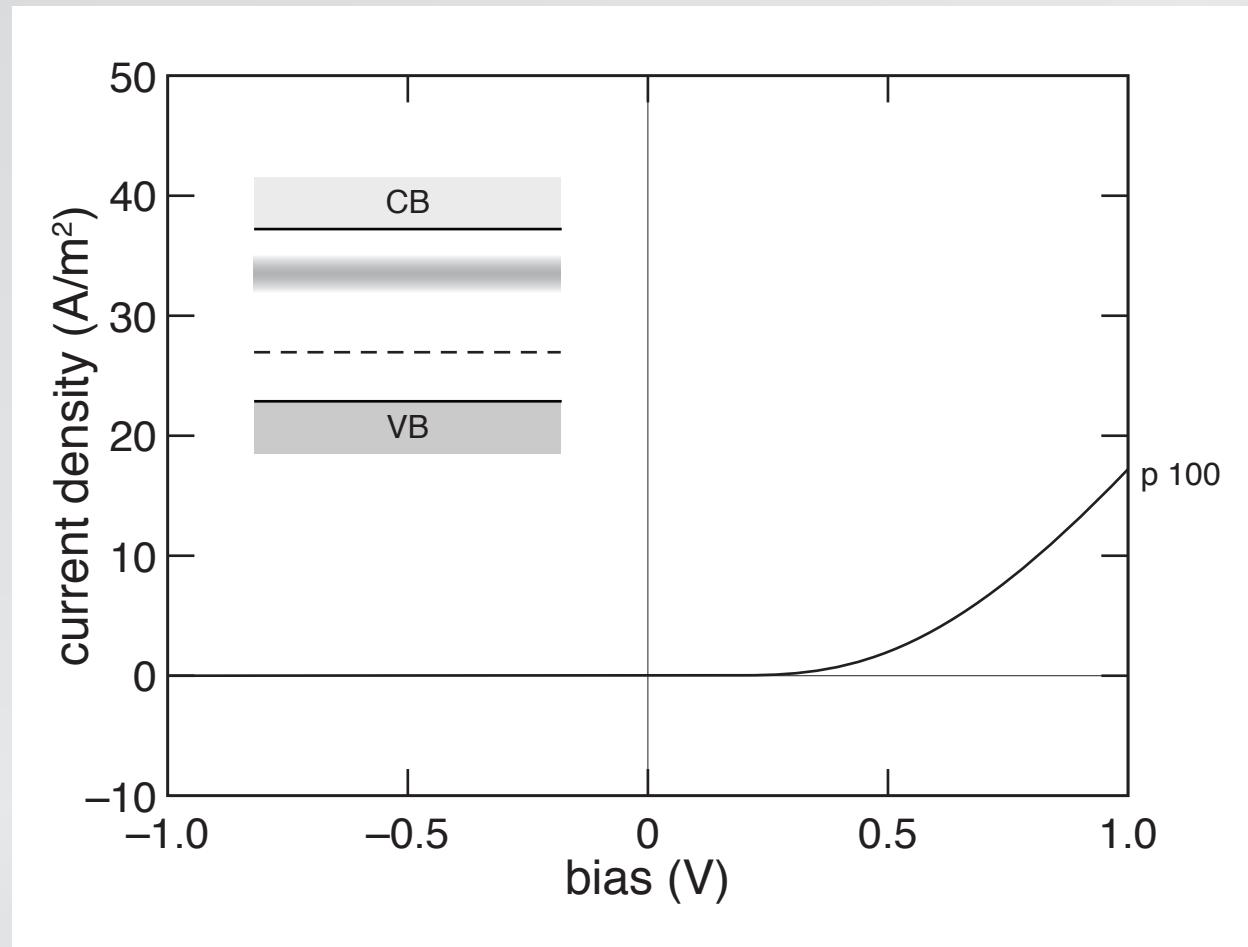
Optoelectronic properties

vary substrate doping type and resistivity



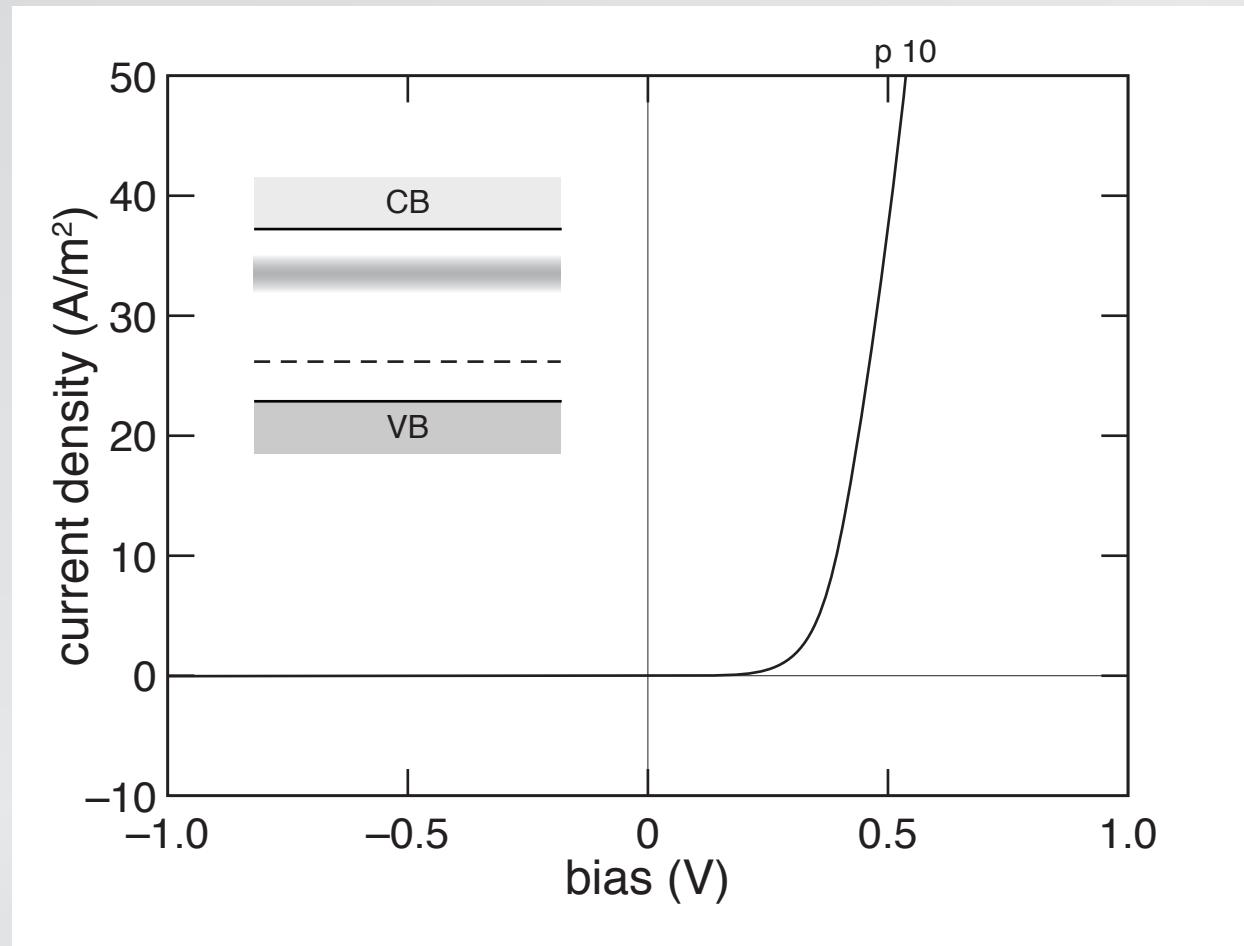
Optoelectronic properties

vary substrate doping type and resistivity



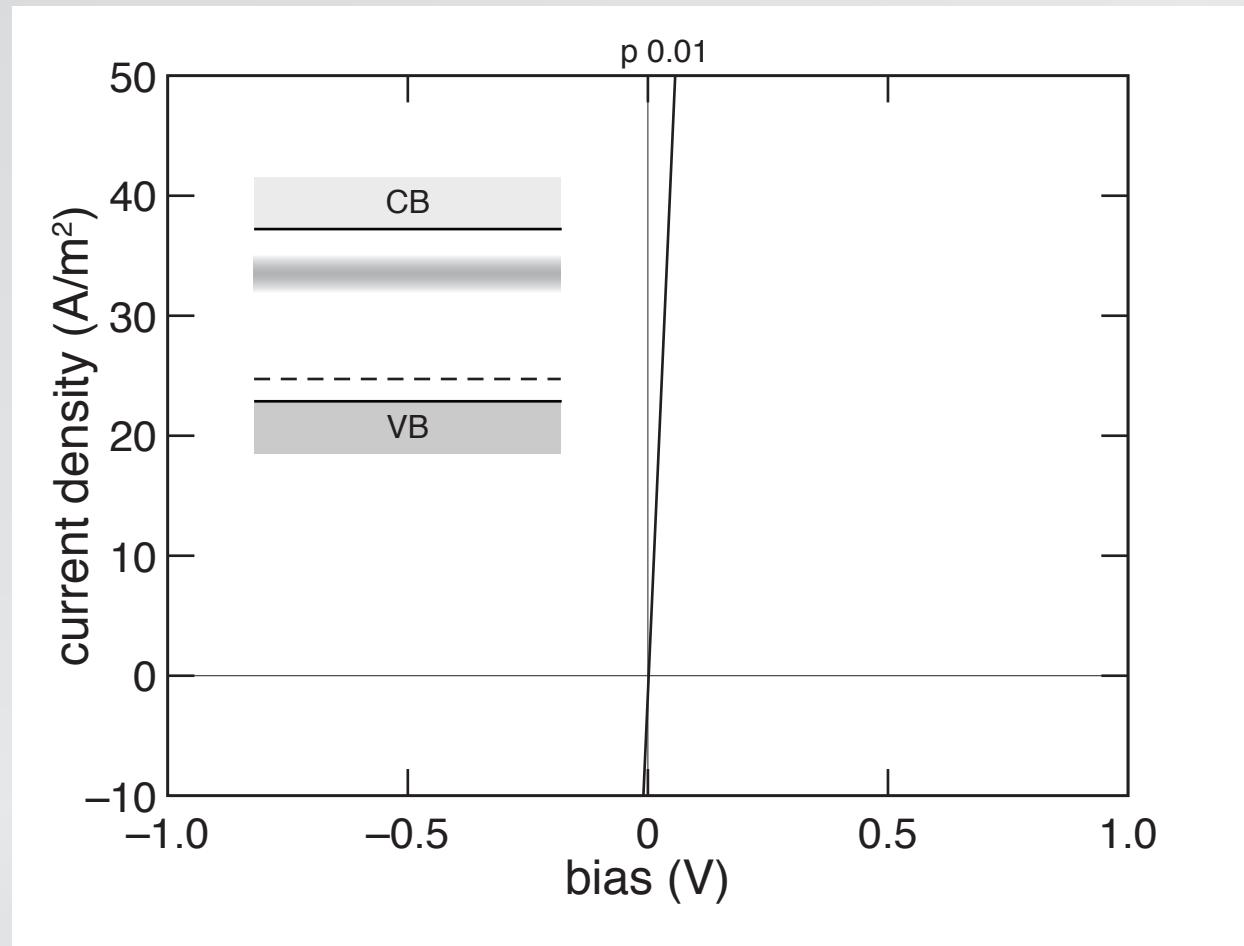
Optoelectronic properties

vary substrate doping type and resistivity



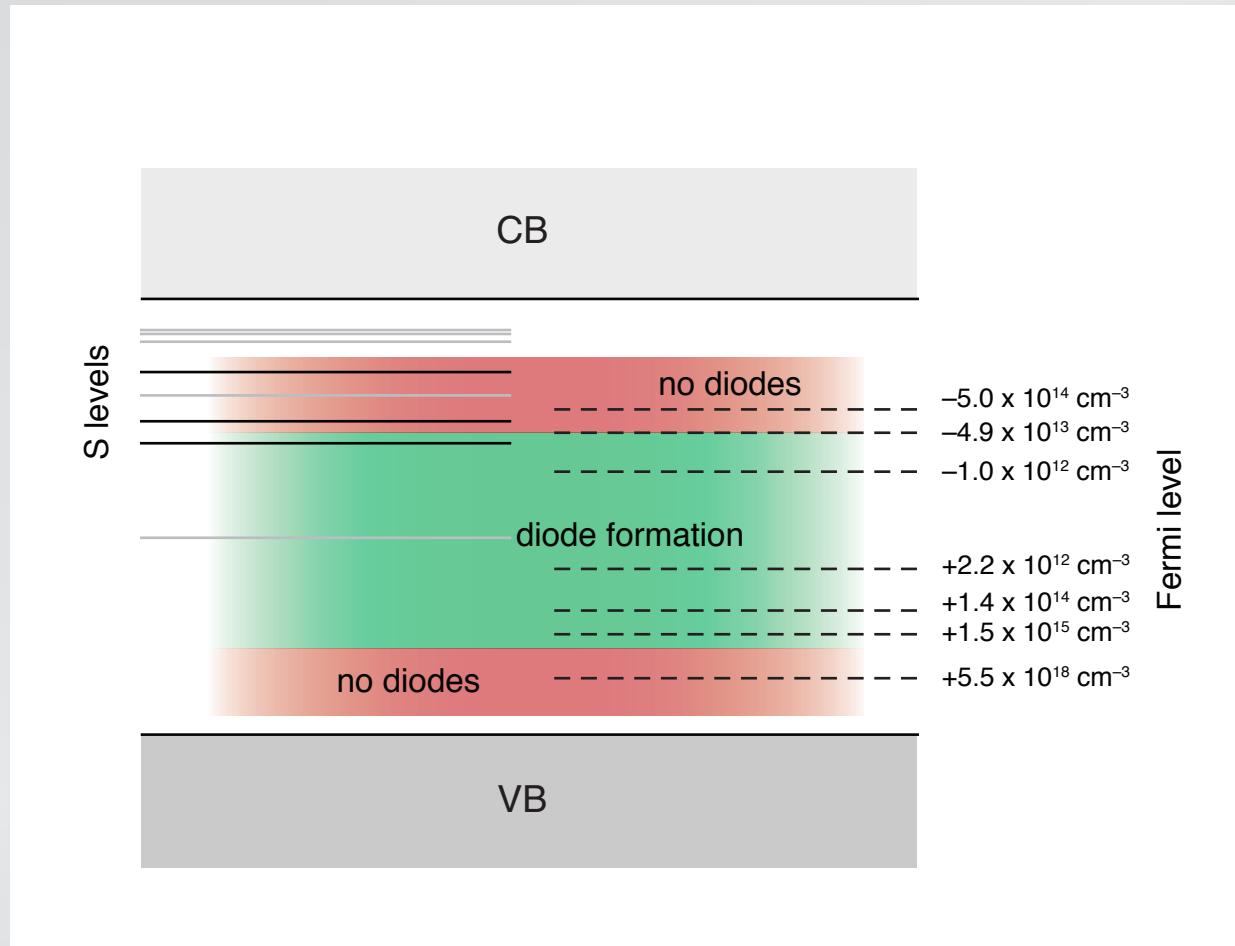
Optoelectronic properties

vary substrate doping type and resistivity



Optoelectronic properties

probe impurity states by varying Fermi level in substrate

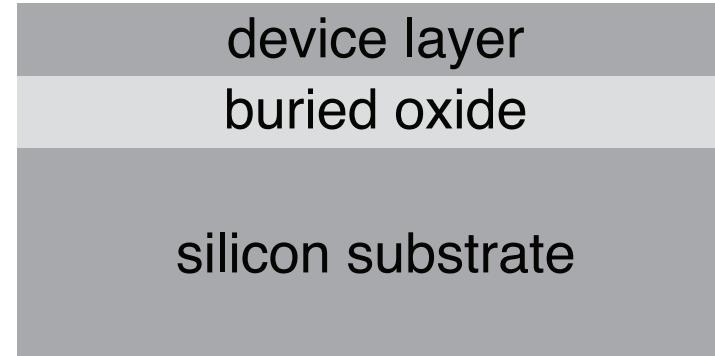


Optoelectronic properties

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

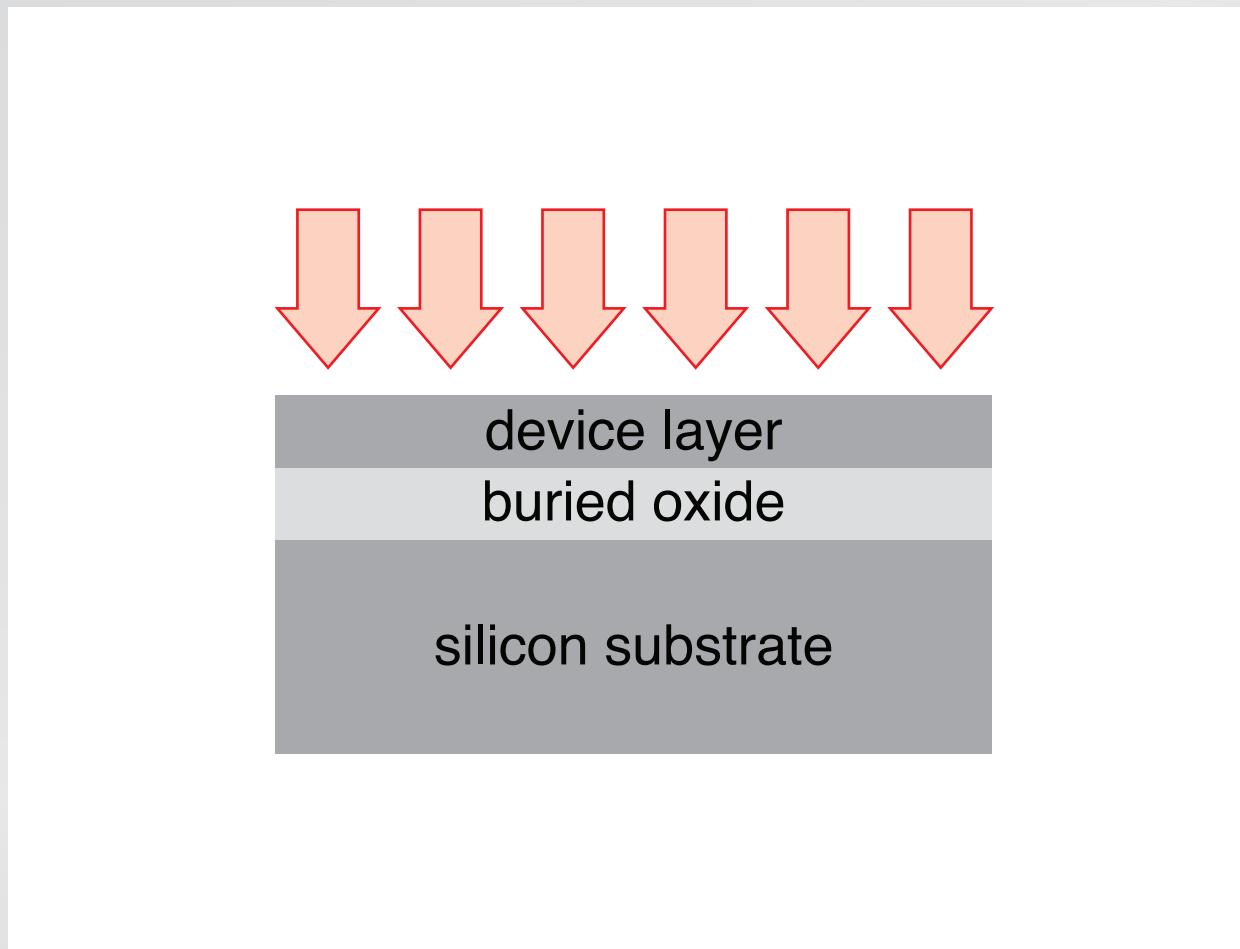
Optoelectronic properties

isolate surface layer for Hall measurements



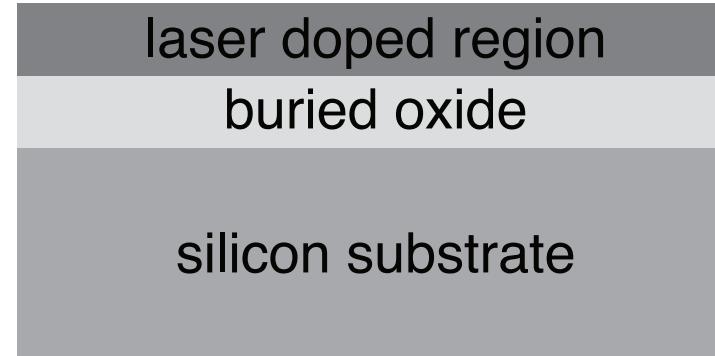
Optoelectronic properties

isolate surface layer for Hall measurements



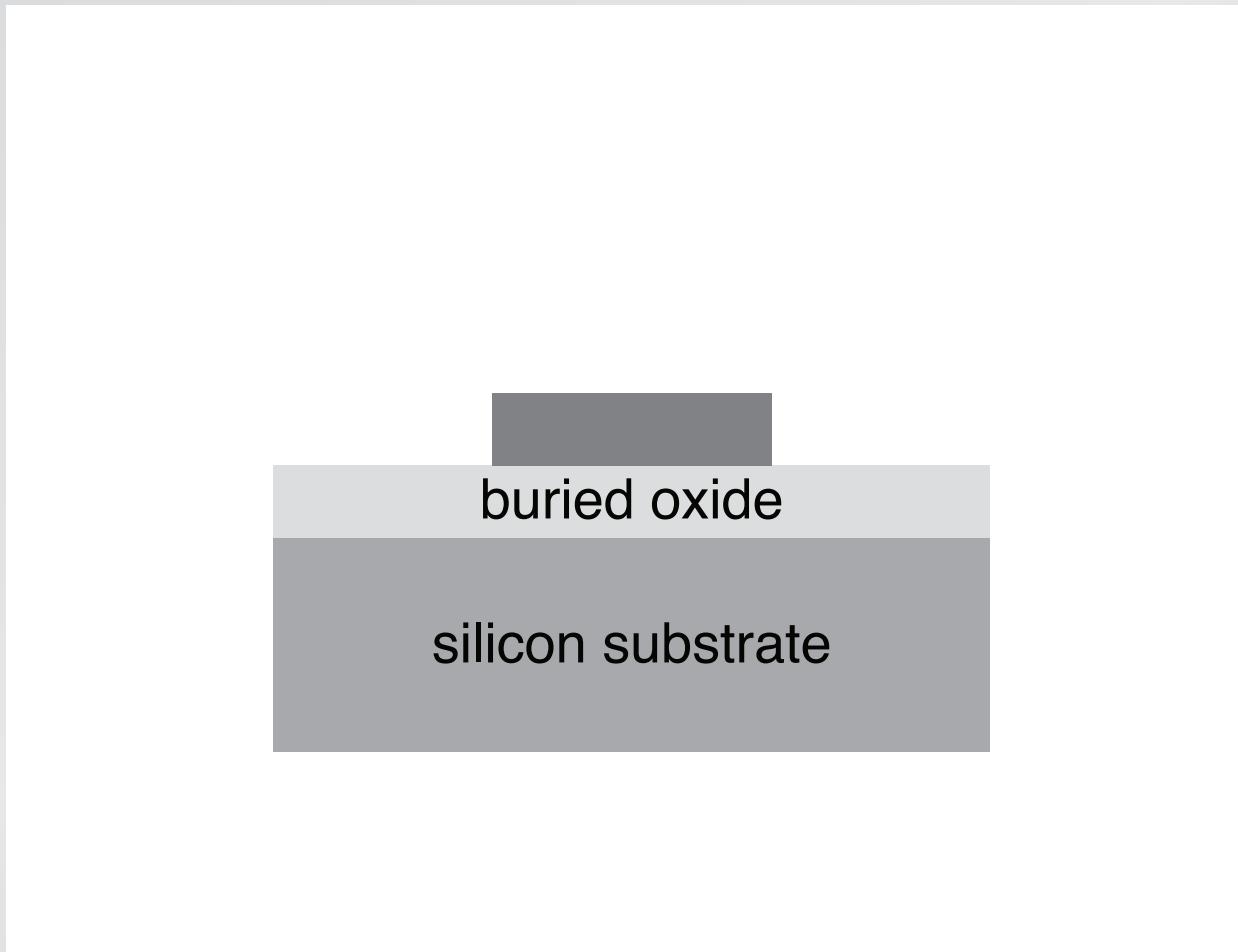
Optoelectronic properties

isolate surface layer for Hall measurements



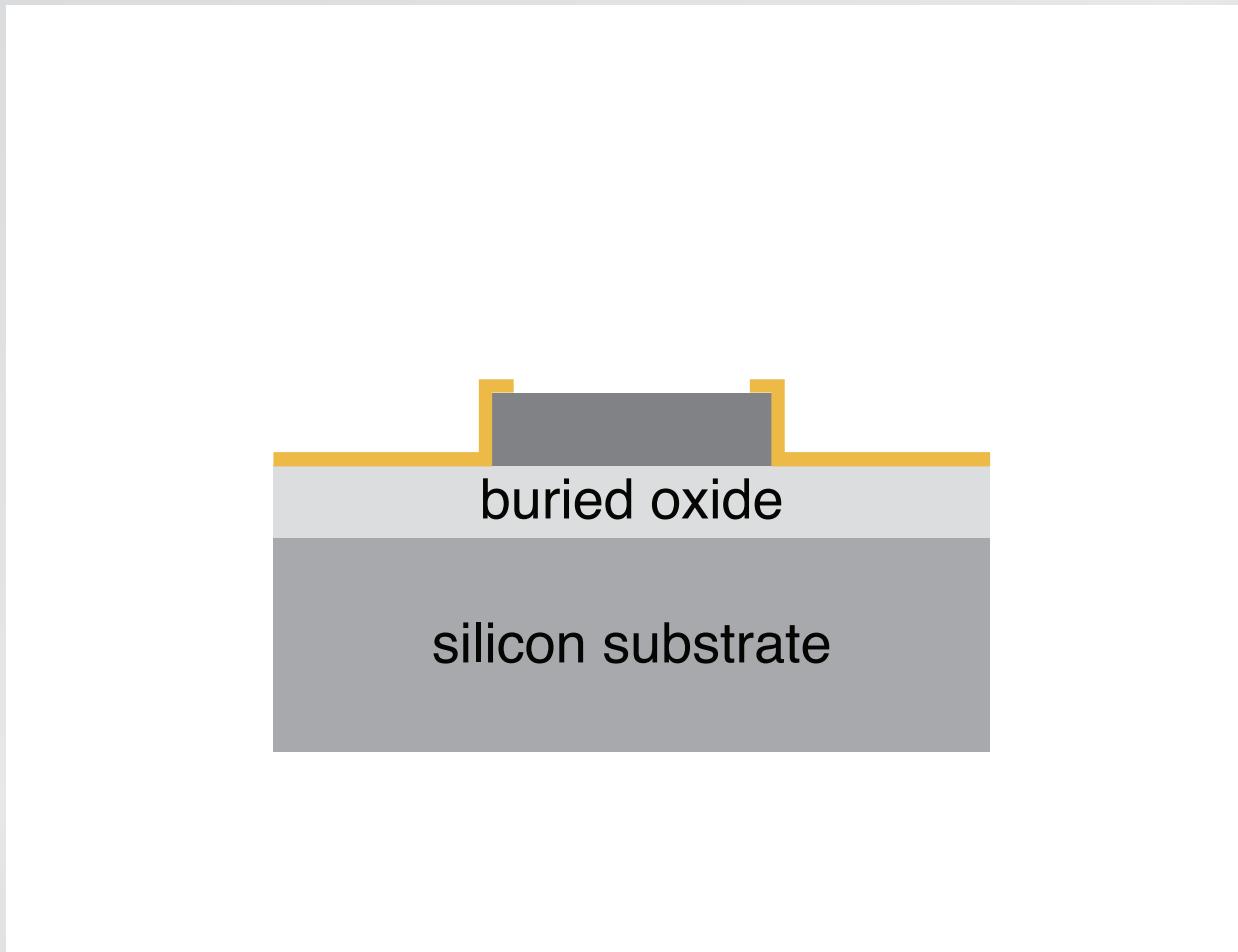
Optoelectronic properties

isolate surface layer for Hall measurements



Optoelectronic properties

isolate surface layer for Hall measurements

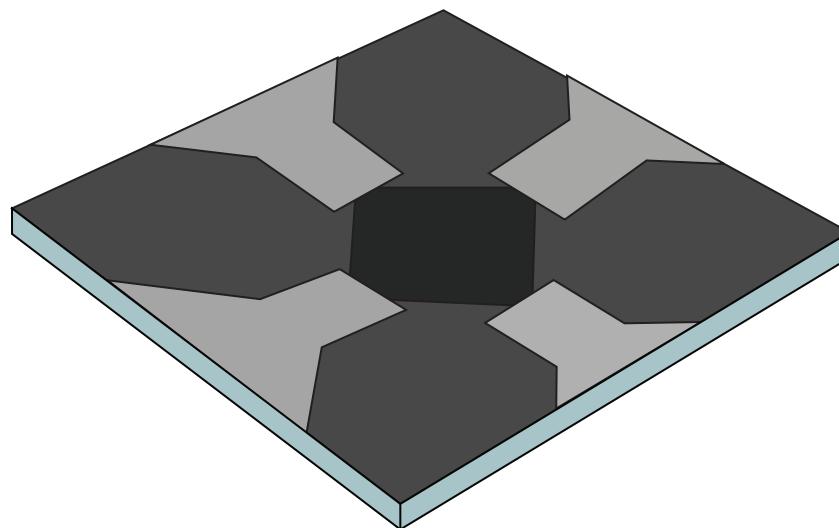


Optoelectronic properties

40 μm

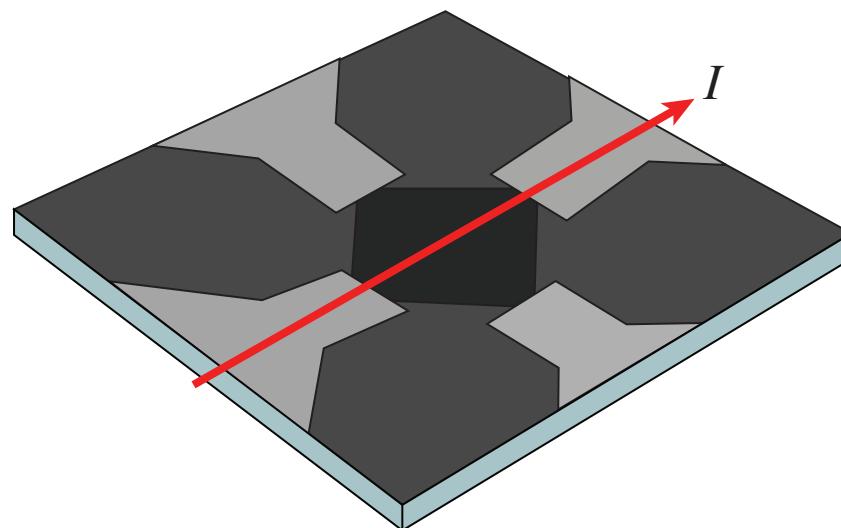
Optoelectronic properties

Hall measurements



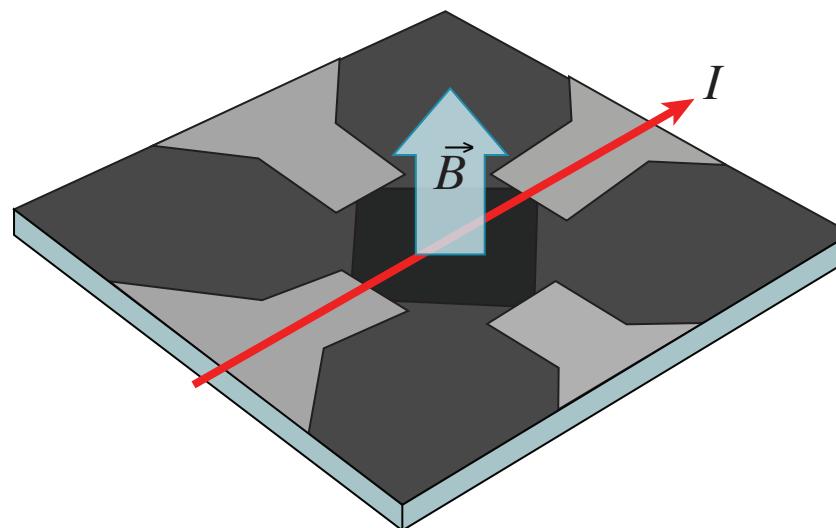
Optoelectronic properties

Hall measurements



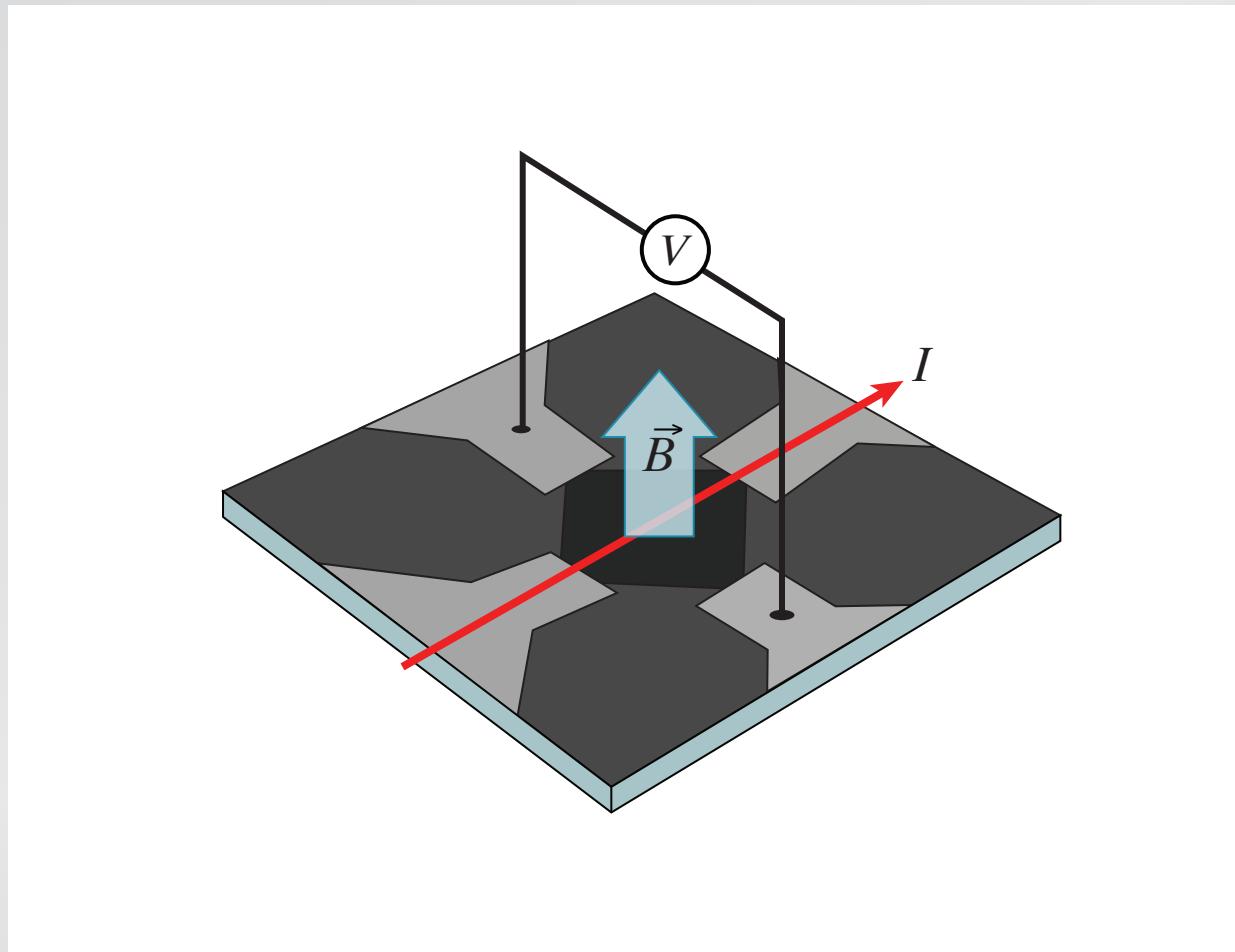
Optoelectronic properties

Hall measurements



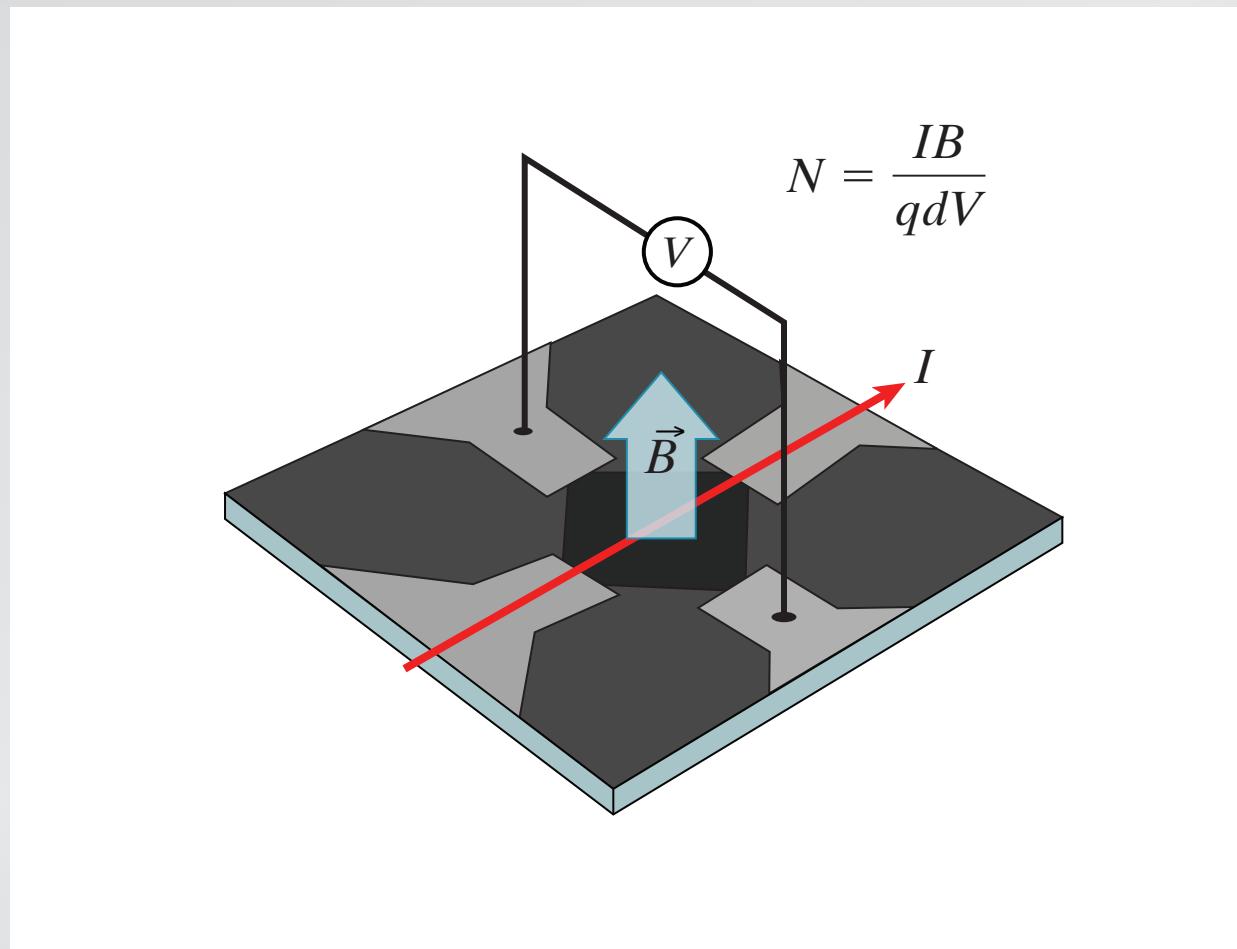
Optoelectronic properties

Hall measurements



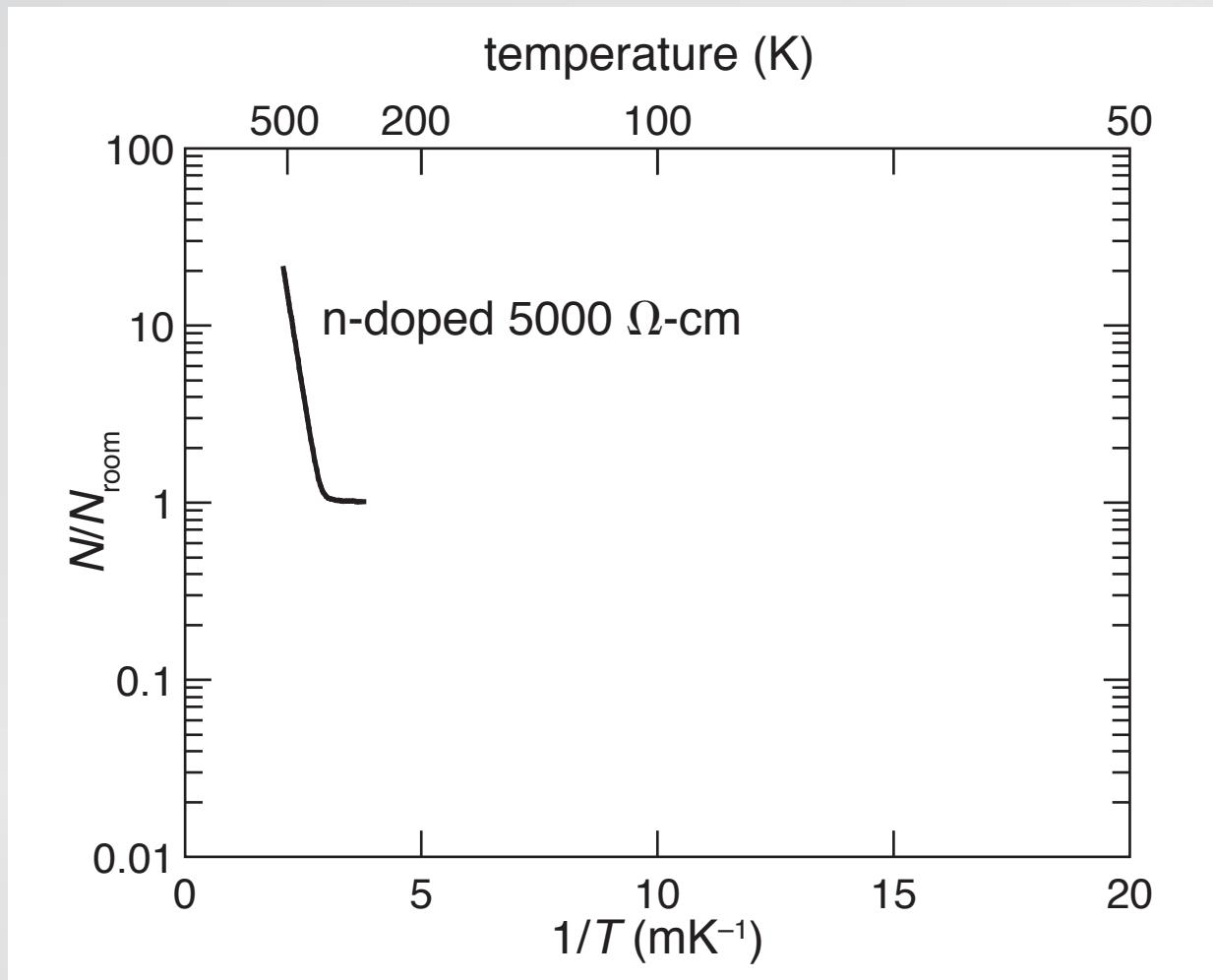
Optoelectronic properties

Hall measurements



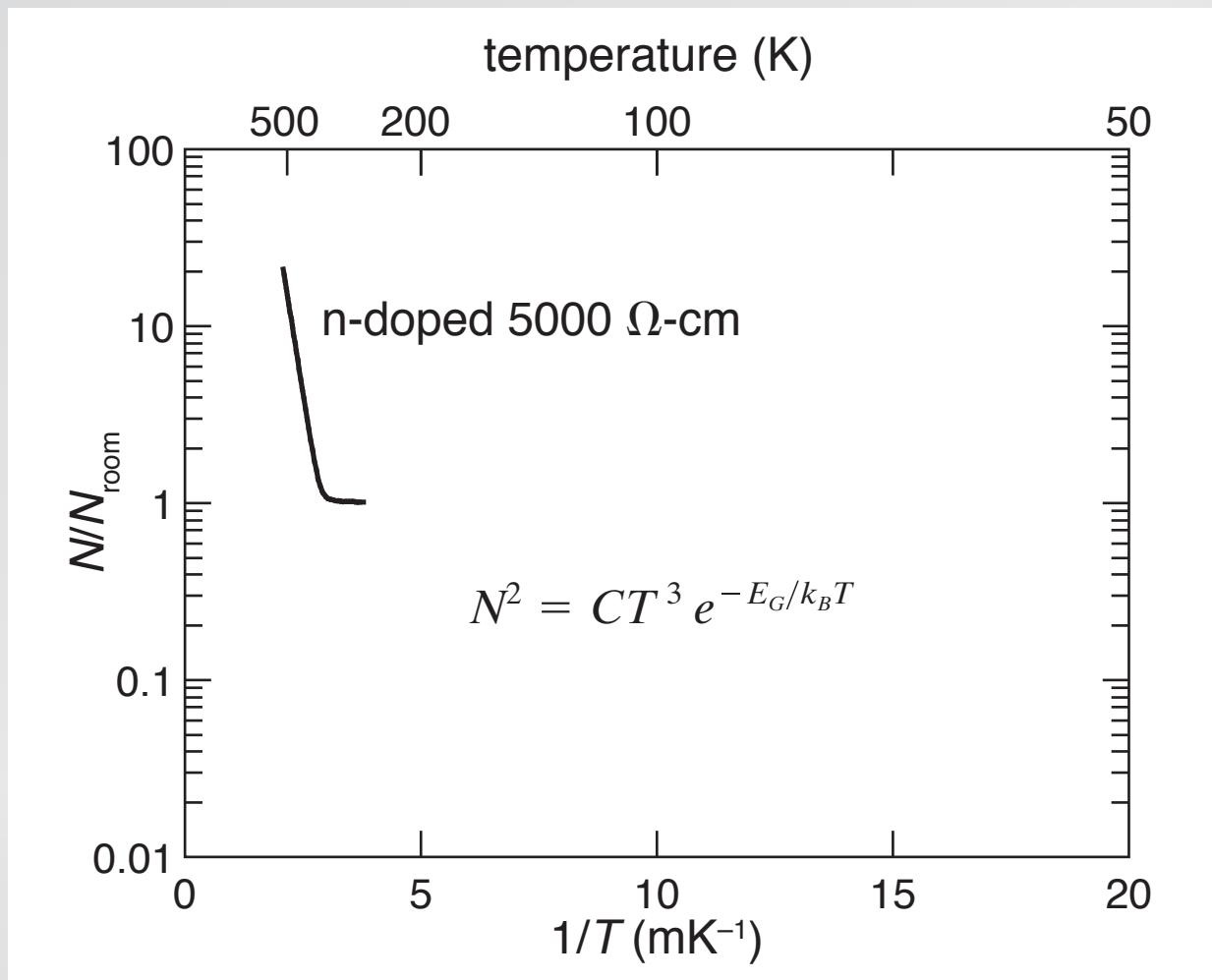
Optoelectronic properties

Hall measurements



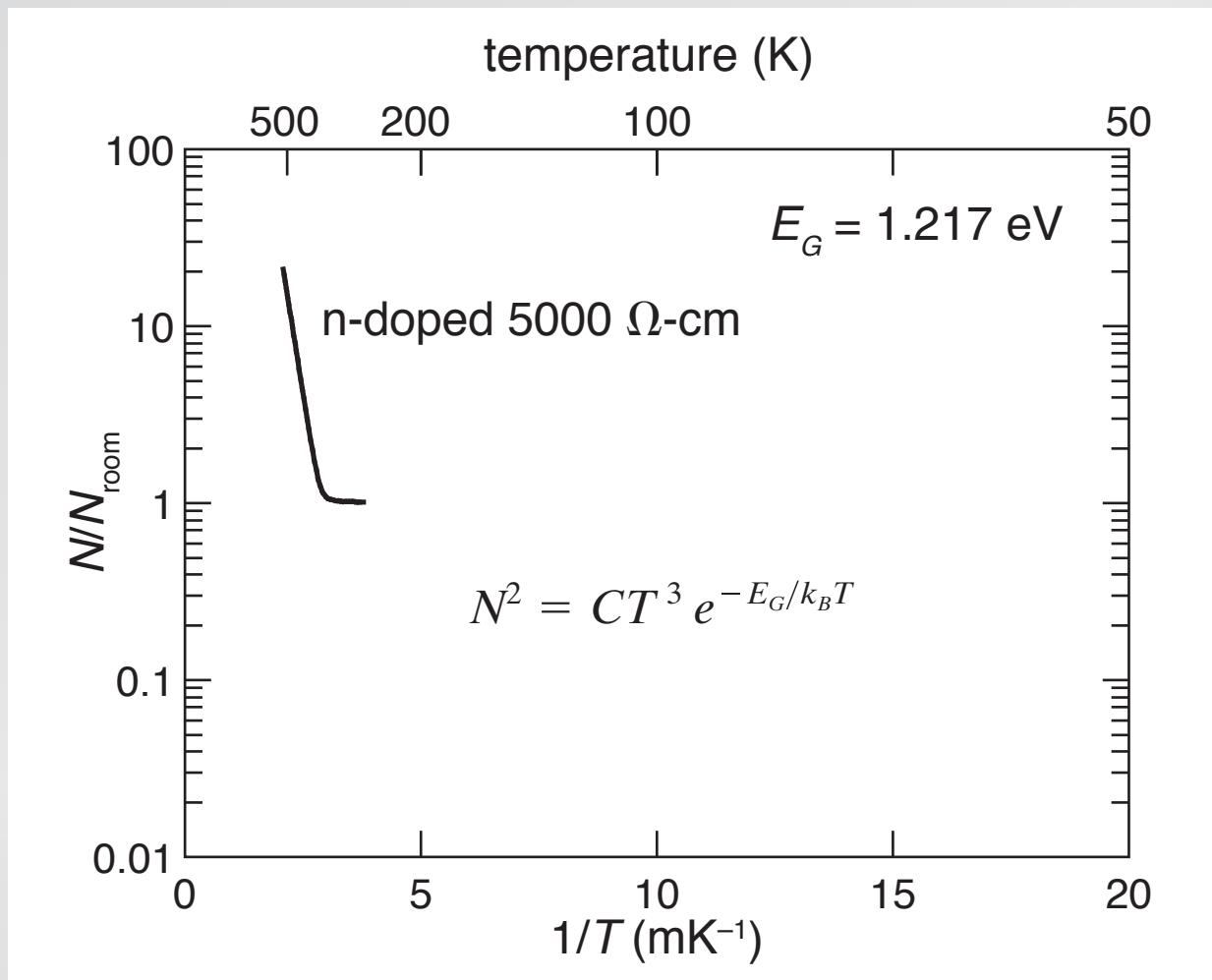
Optoelectronic properties

Hall measurements



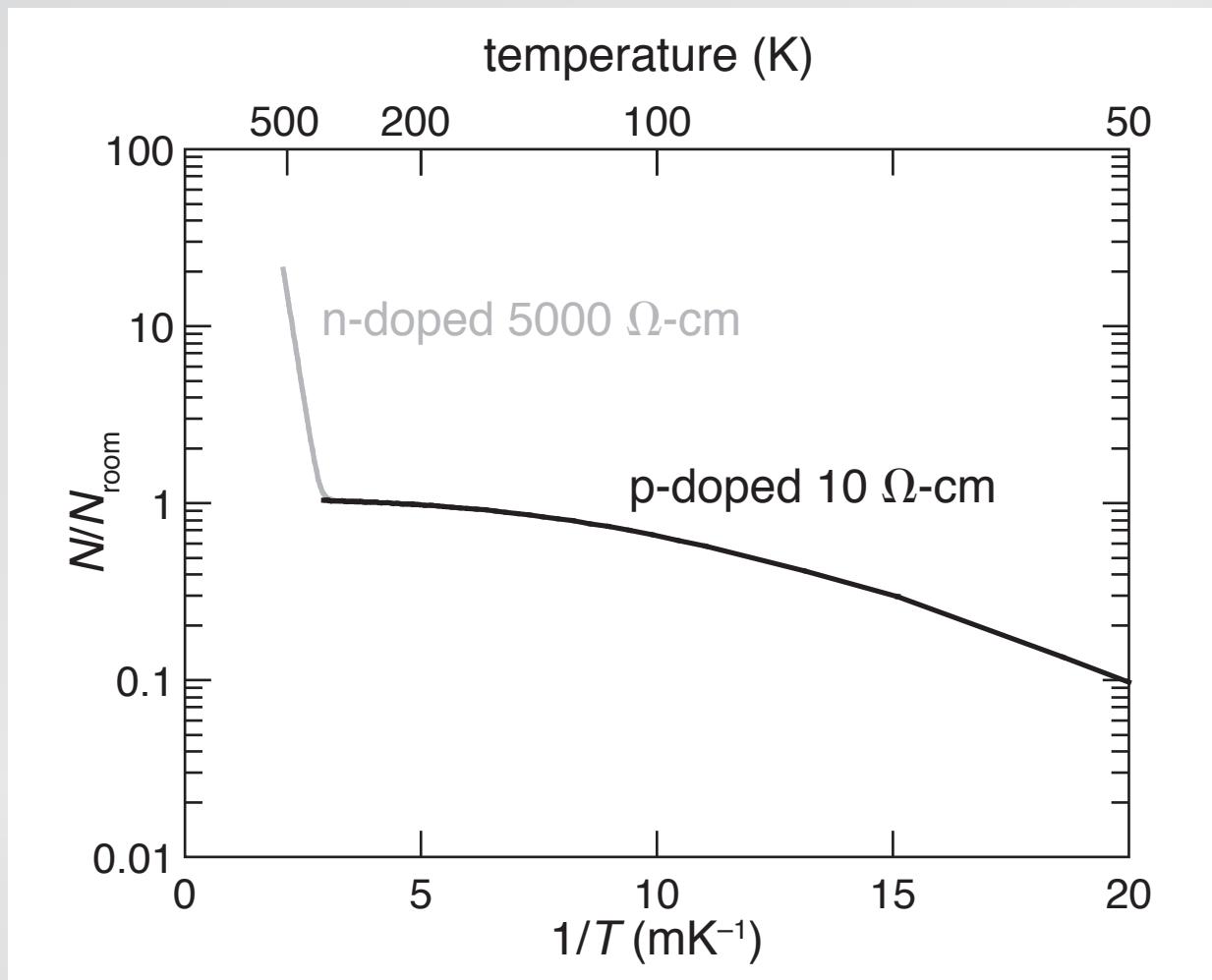
Optoelectronic properties

Hall measurements



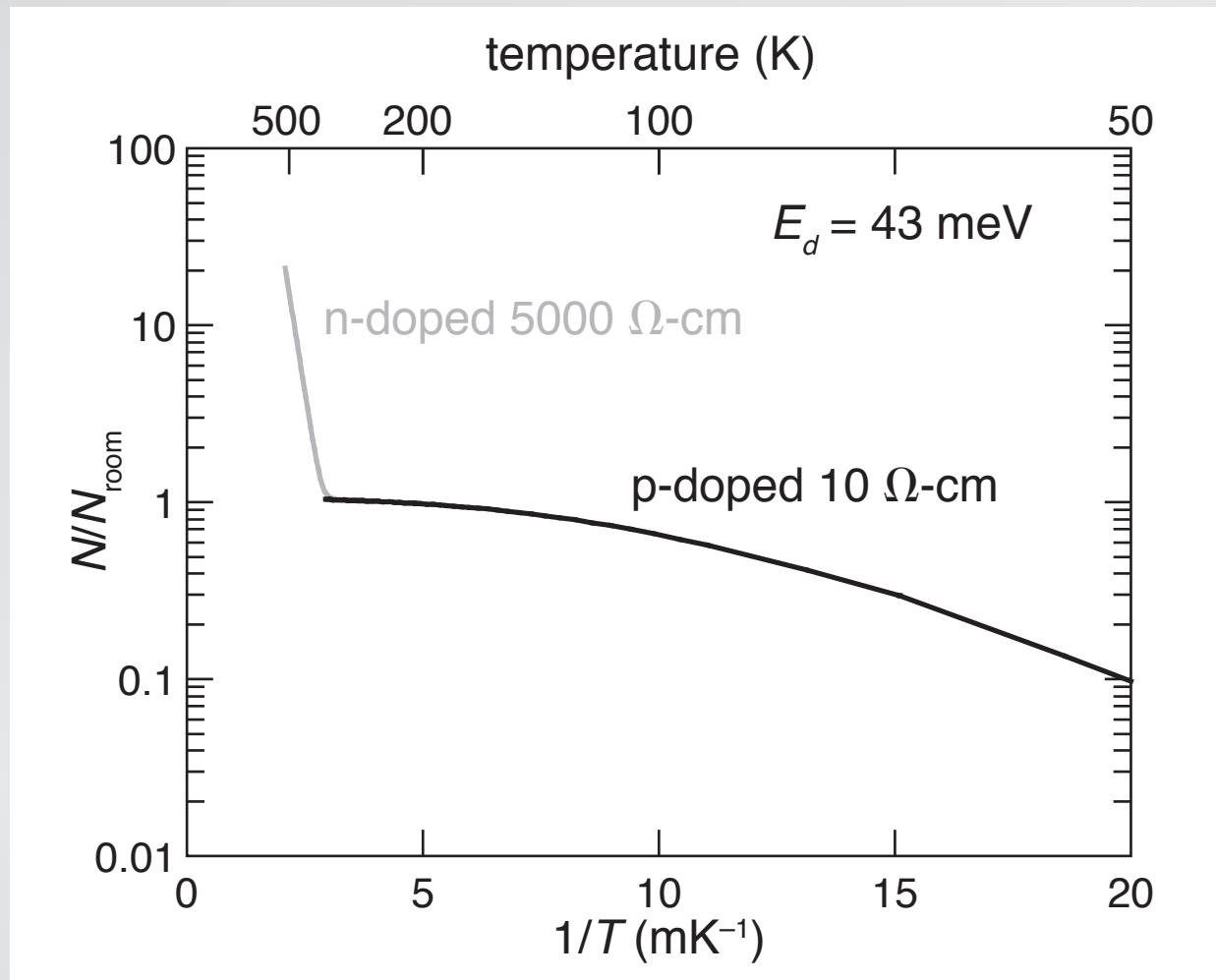
Optoelectronic properties

Hall measurements



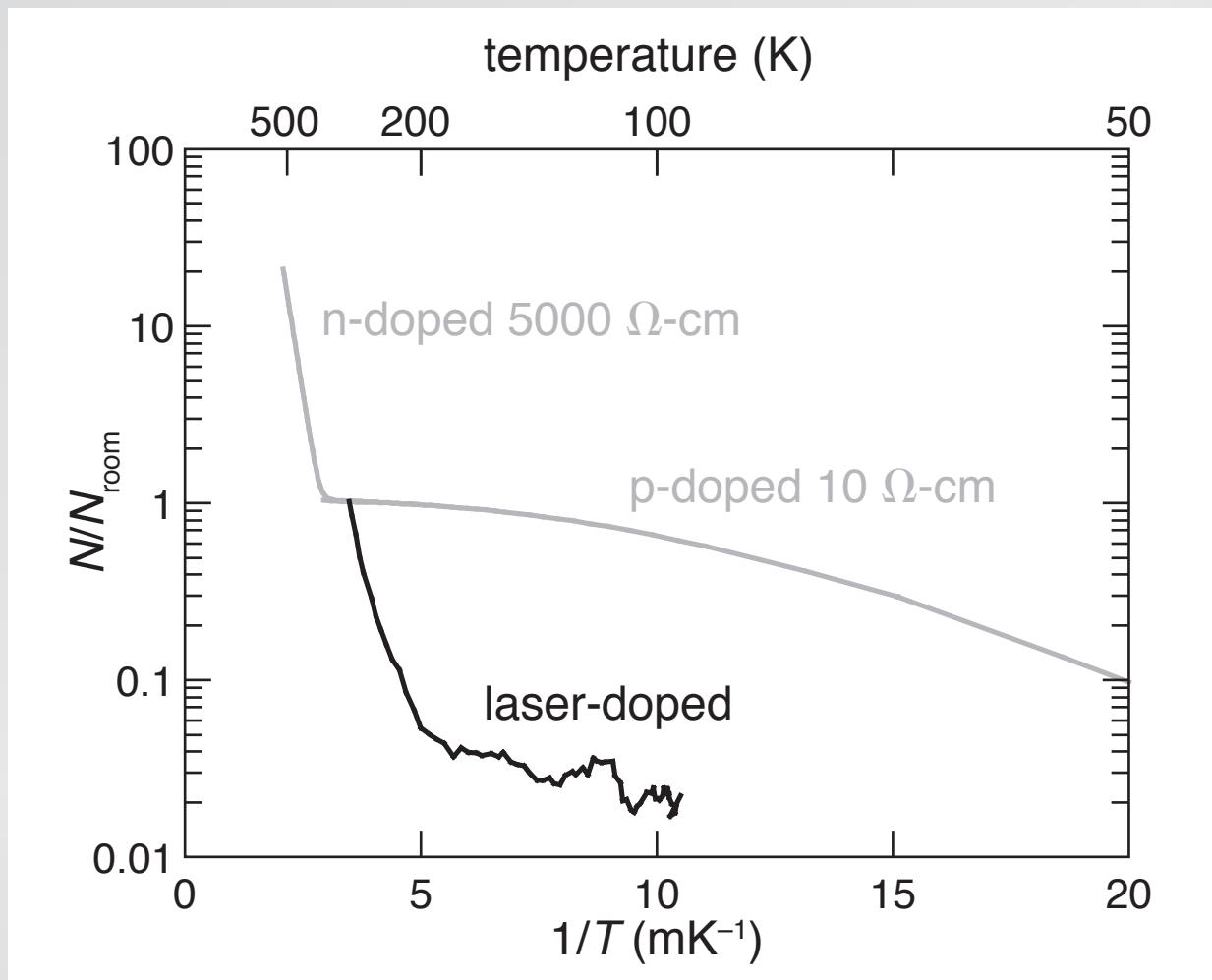
Optoelectronic properties

Hall measurements



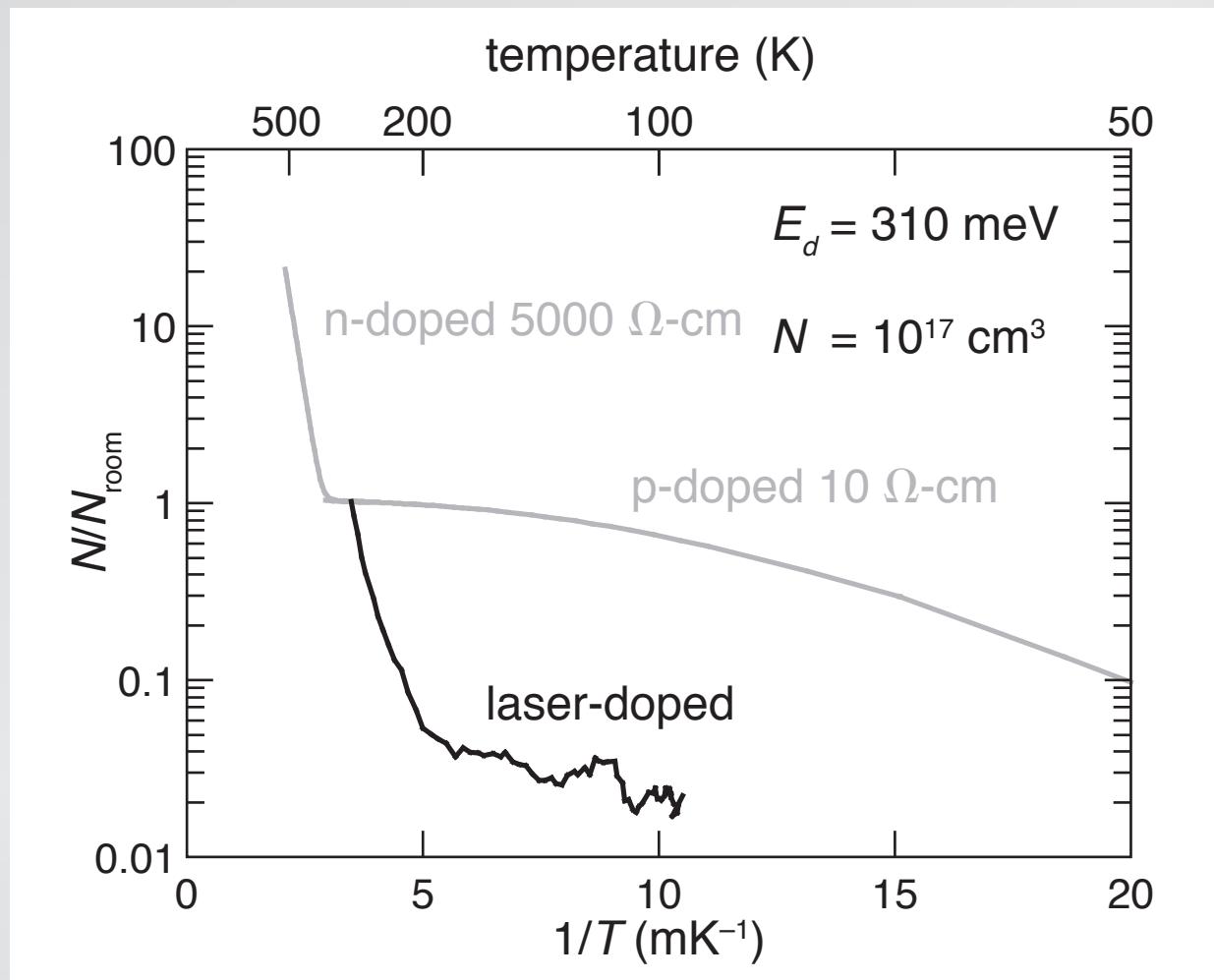
Optoelectronic properties

Hall measurements



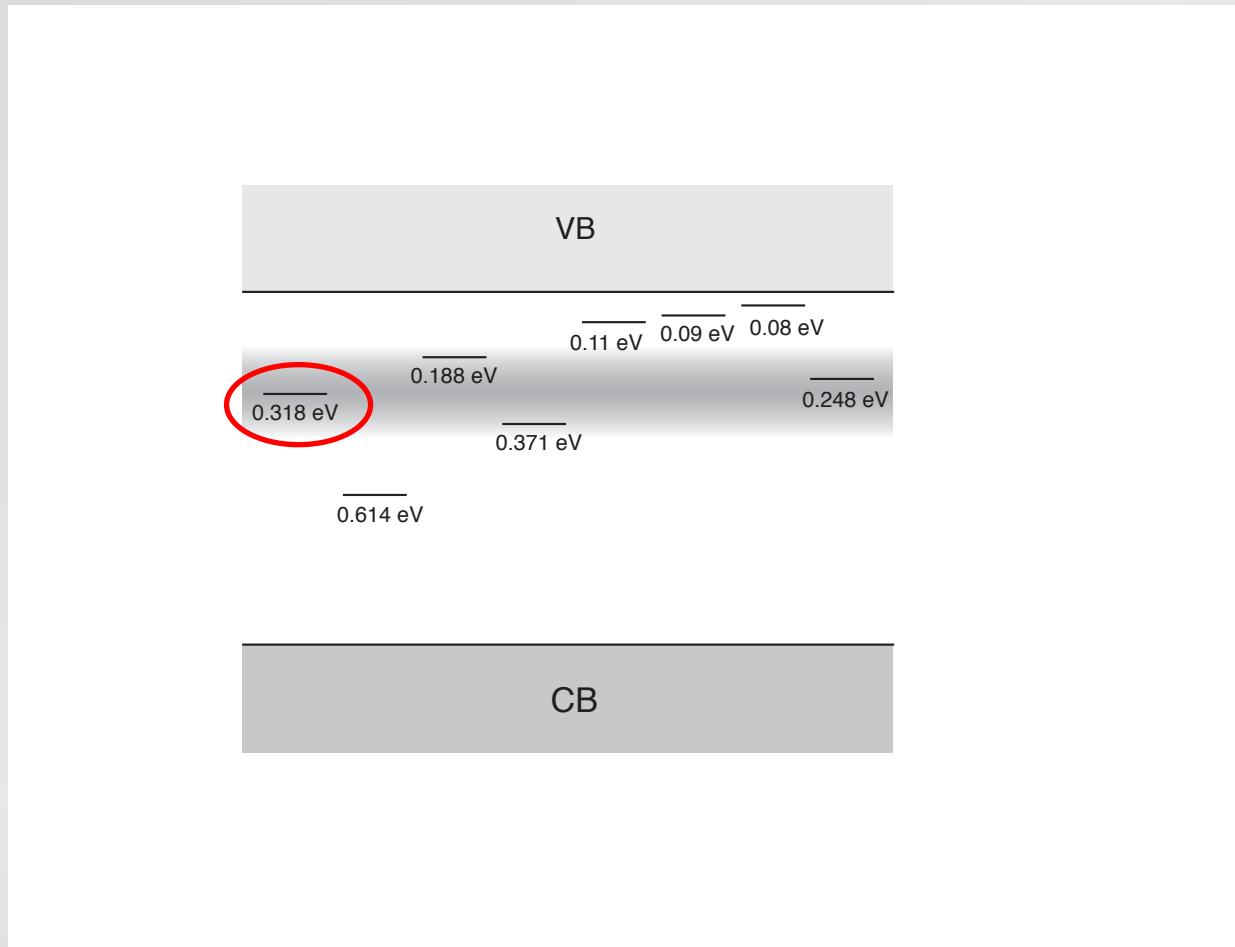
Optoelectronic properties

Hall measurements



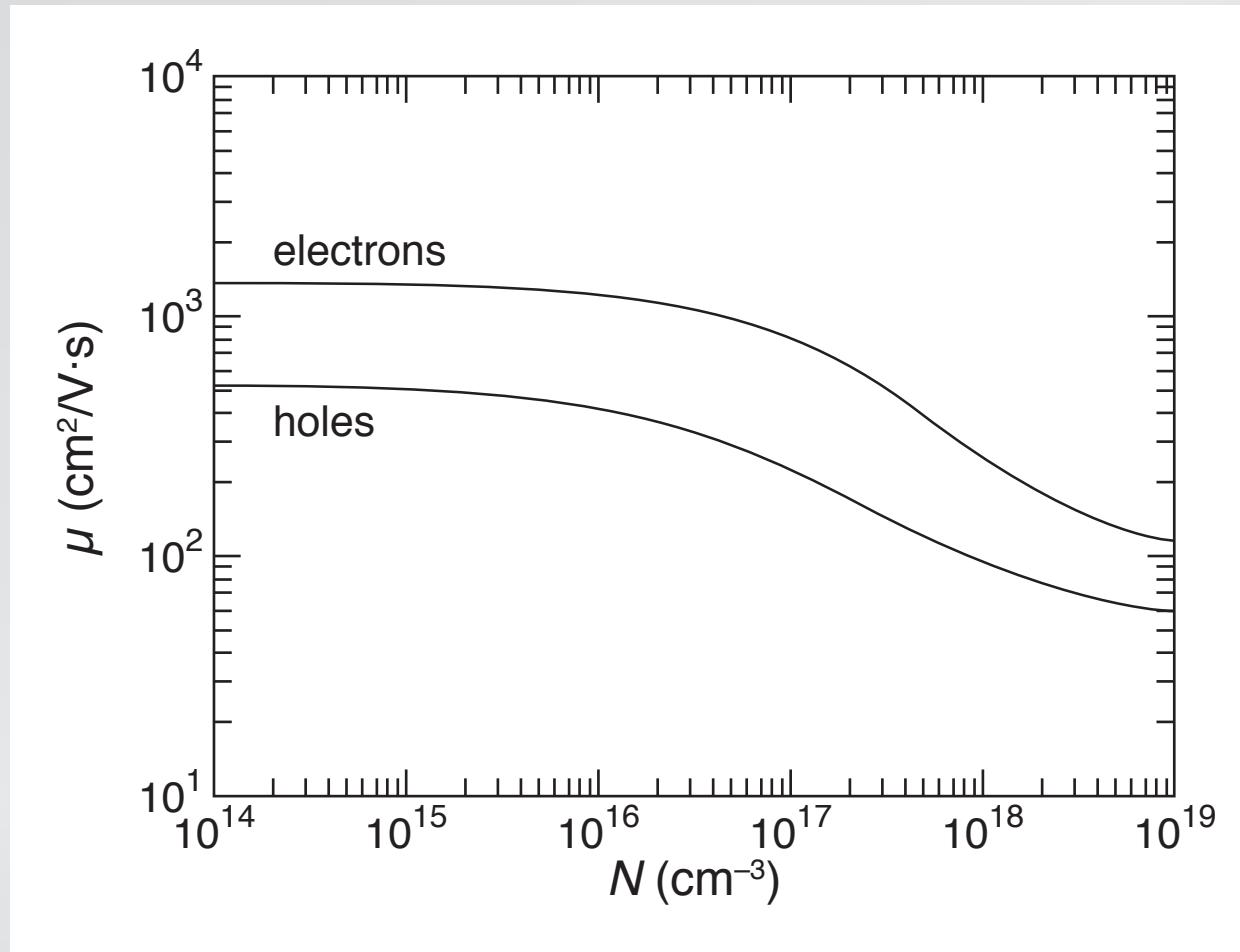
Optoelectronic properties

impurity (donor) band centered at 310 meV



Optoelectronic properties

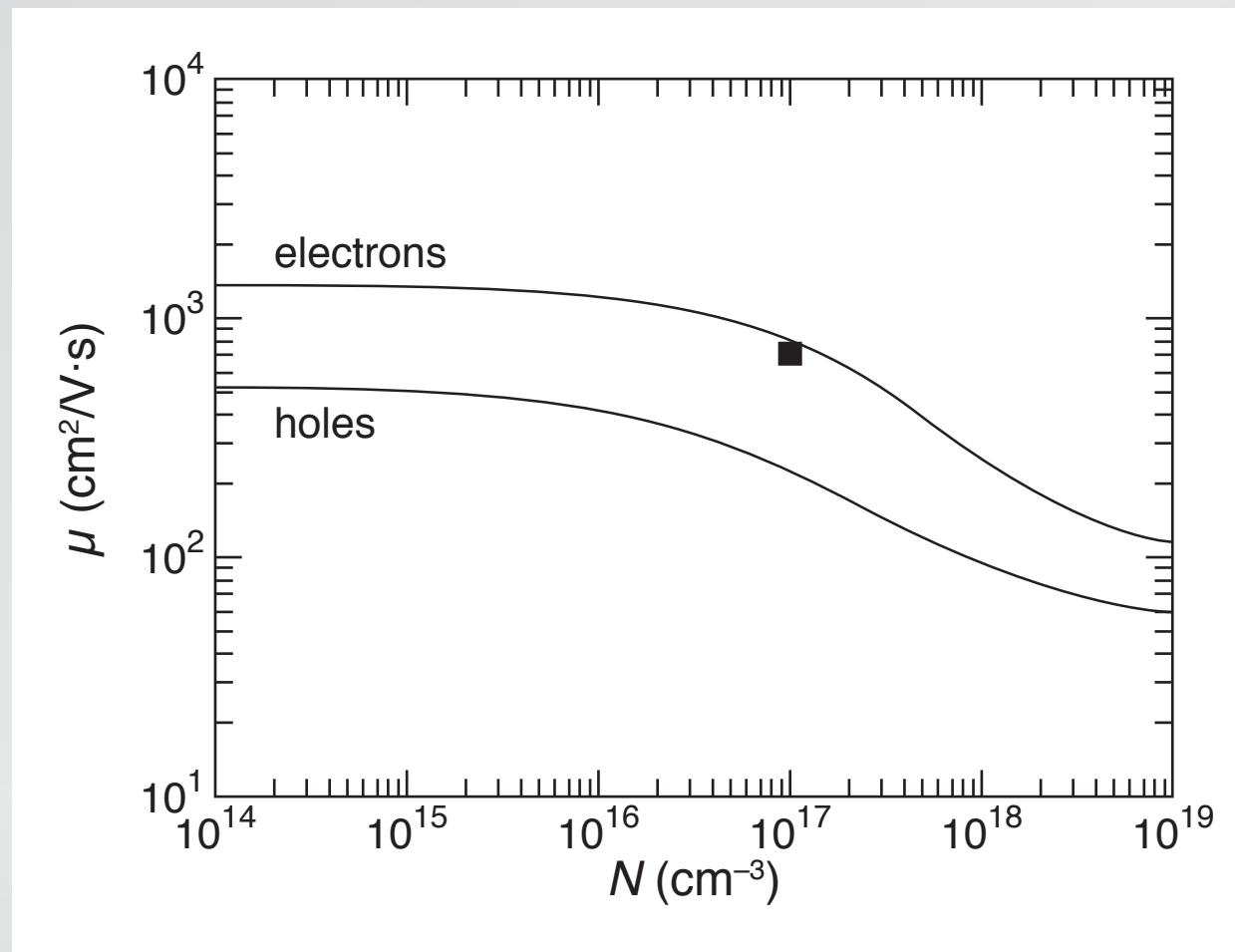
majority carrier mobility



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

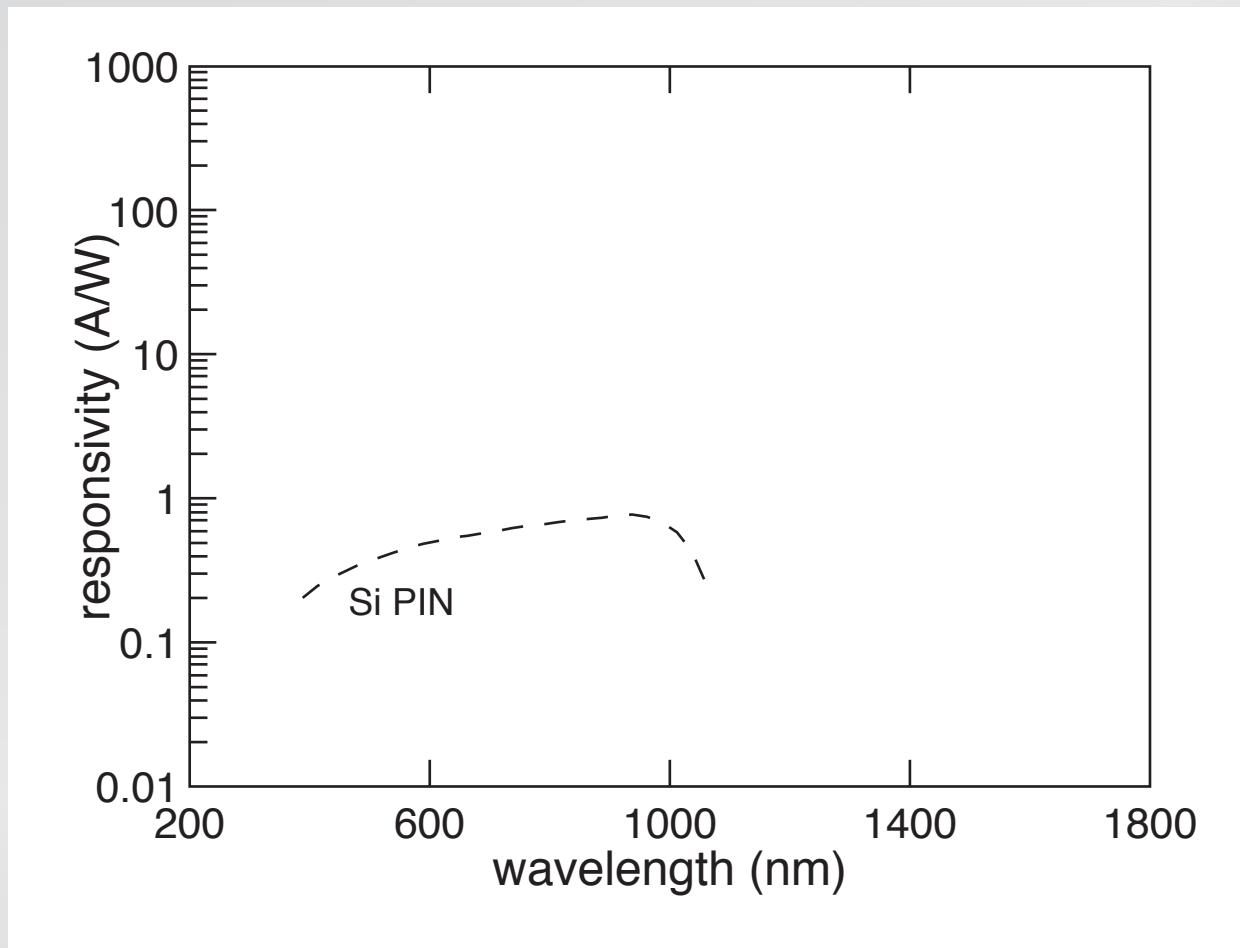
- IR absorption rolls off around $8 \mu\text{m}$
- 1 in 10^3 sulfur atoms are ionized donors at 300 K
- all data indicate these S donors are substitutional

Outline

- structure
- optoelectronic properties
- devices

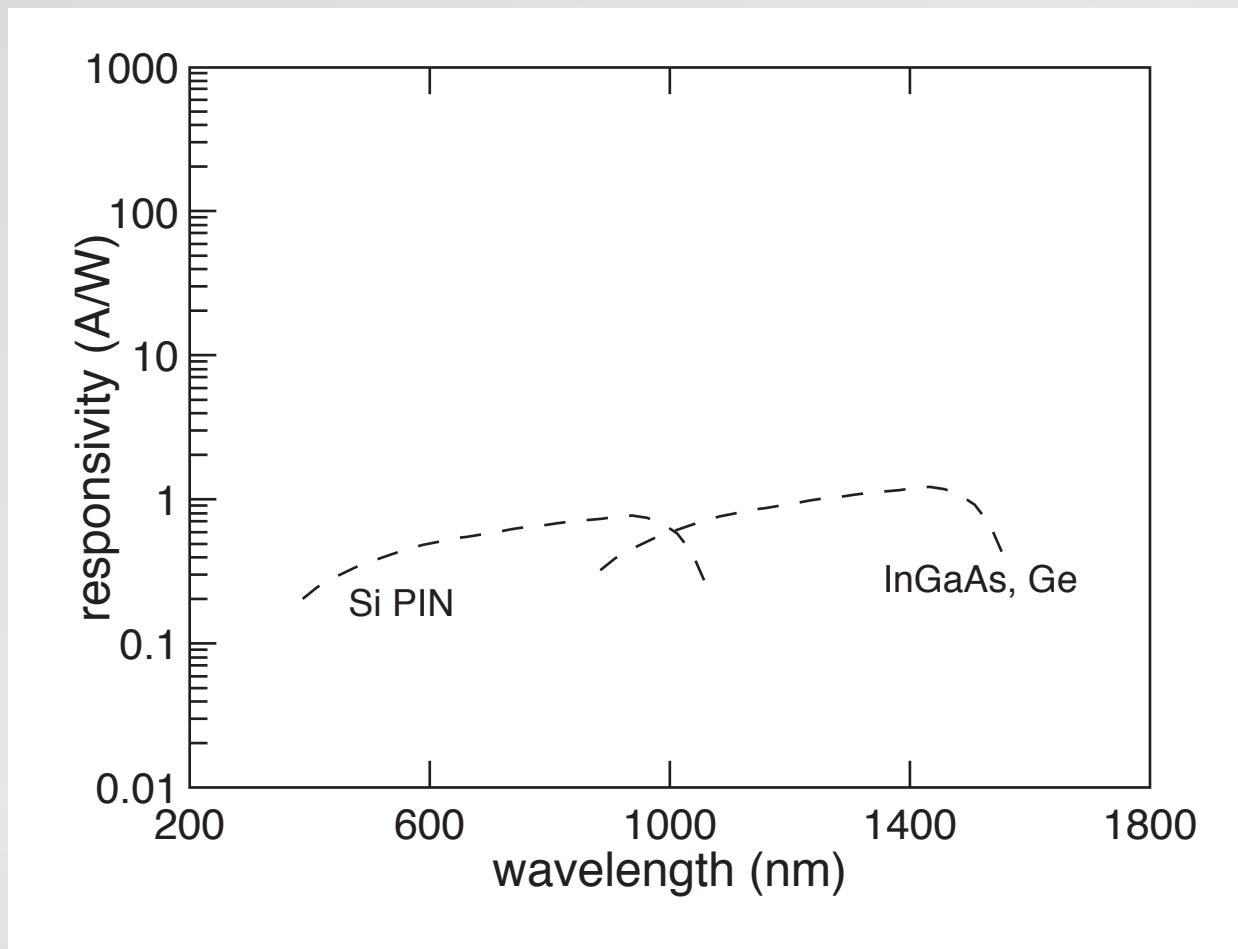
Devices

responsivity



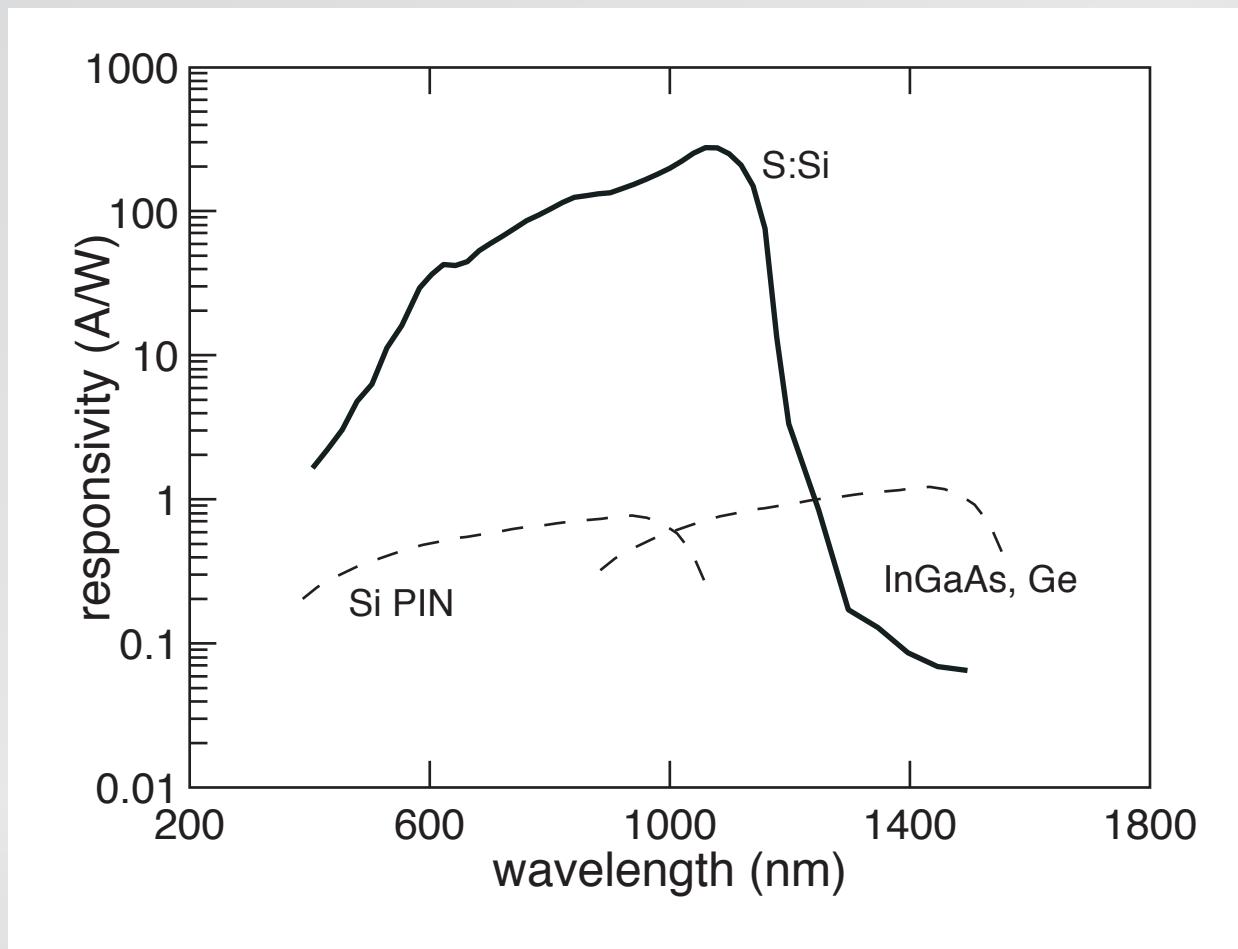
Devices

responsivity



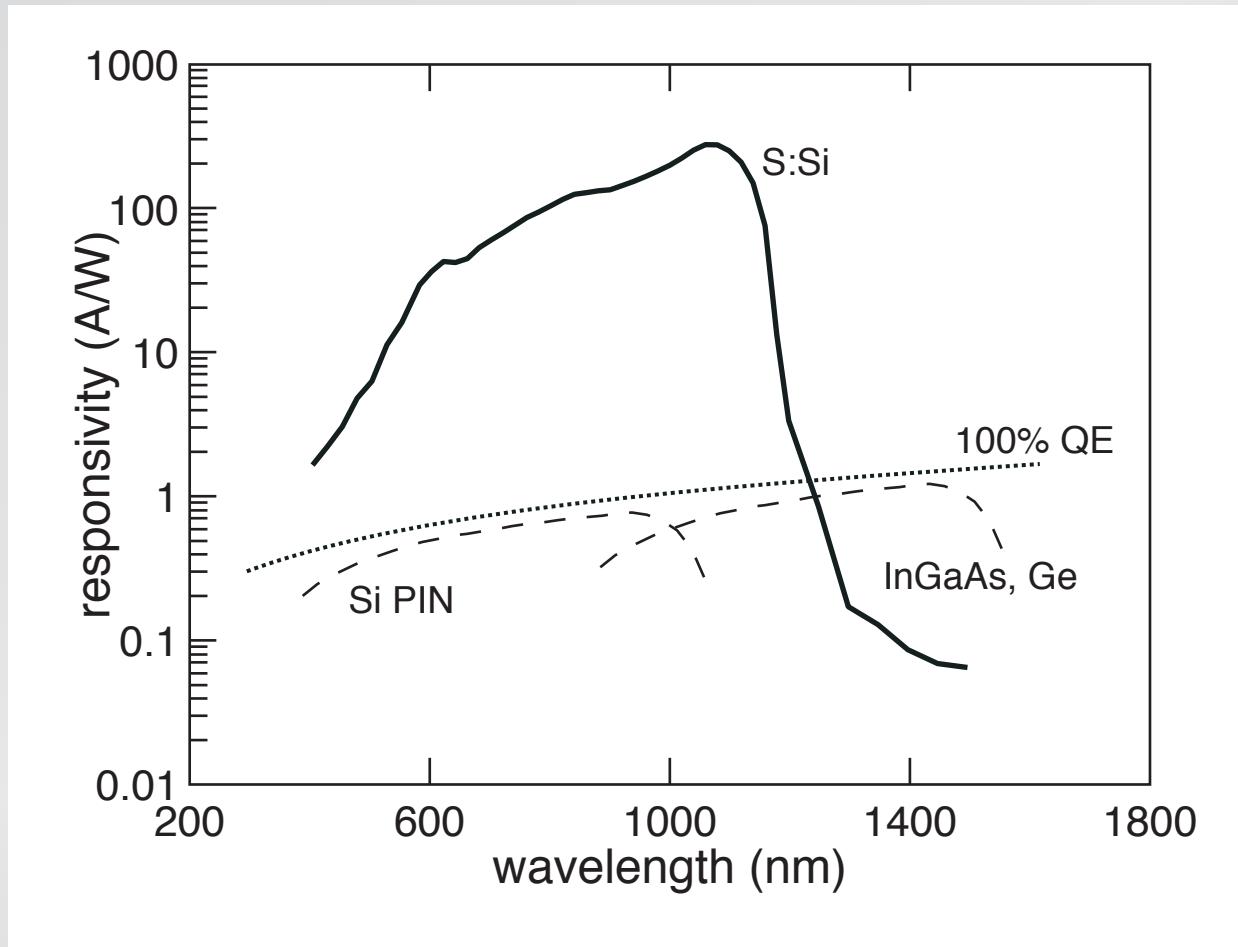
Devices

responsivity



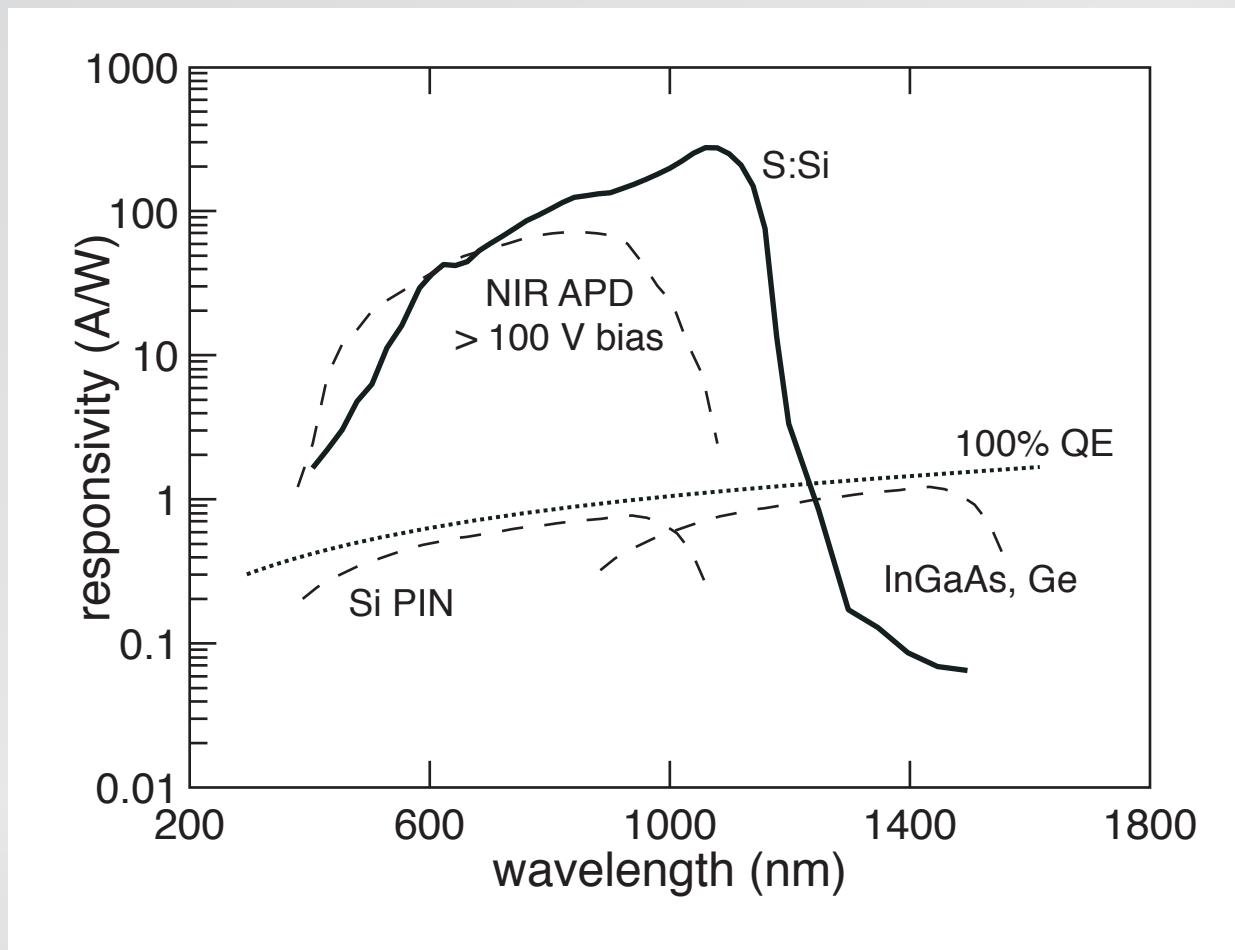
Devices

responsivity



Devices

responsivity

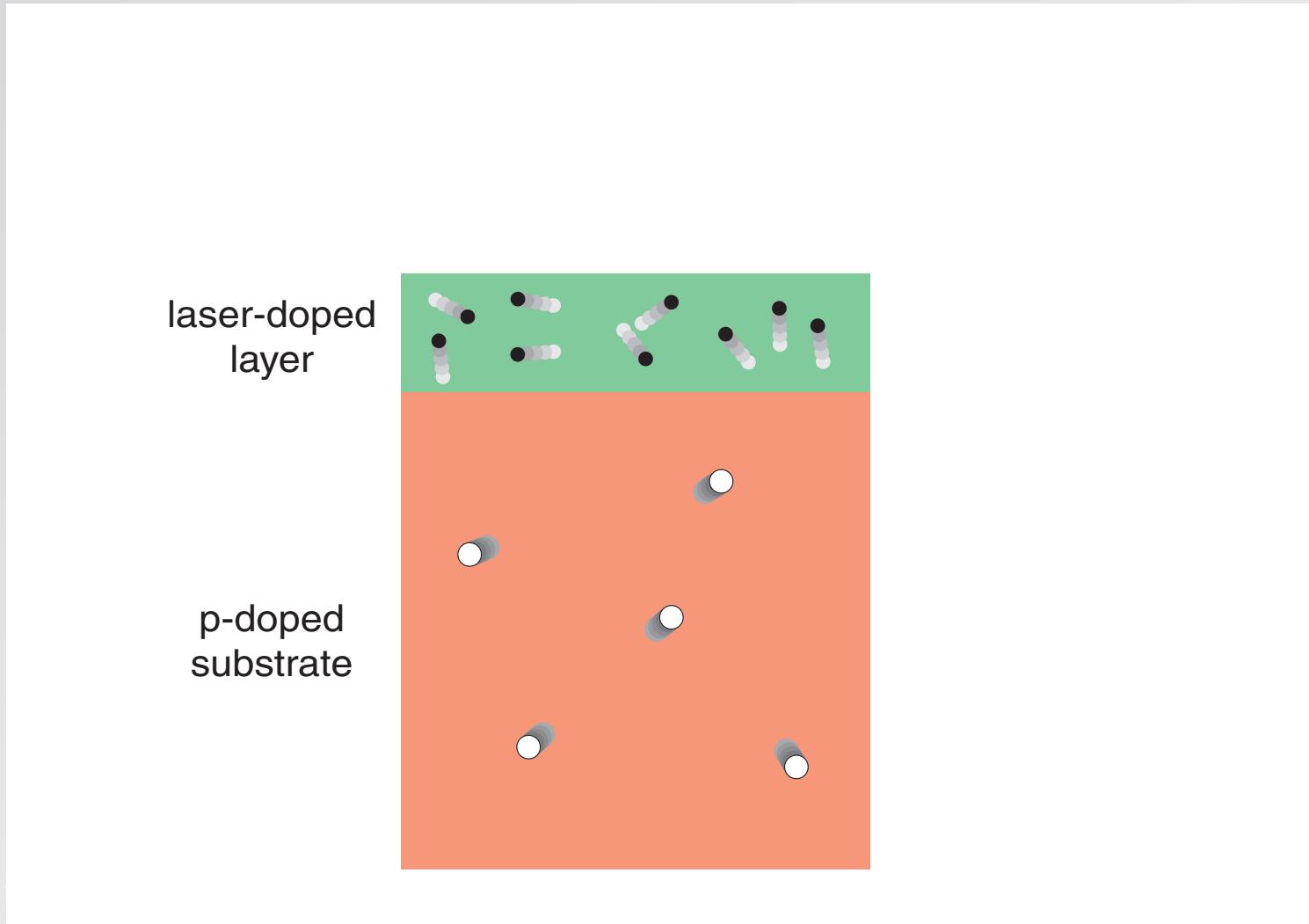


Devices

What causes gain?

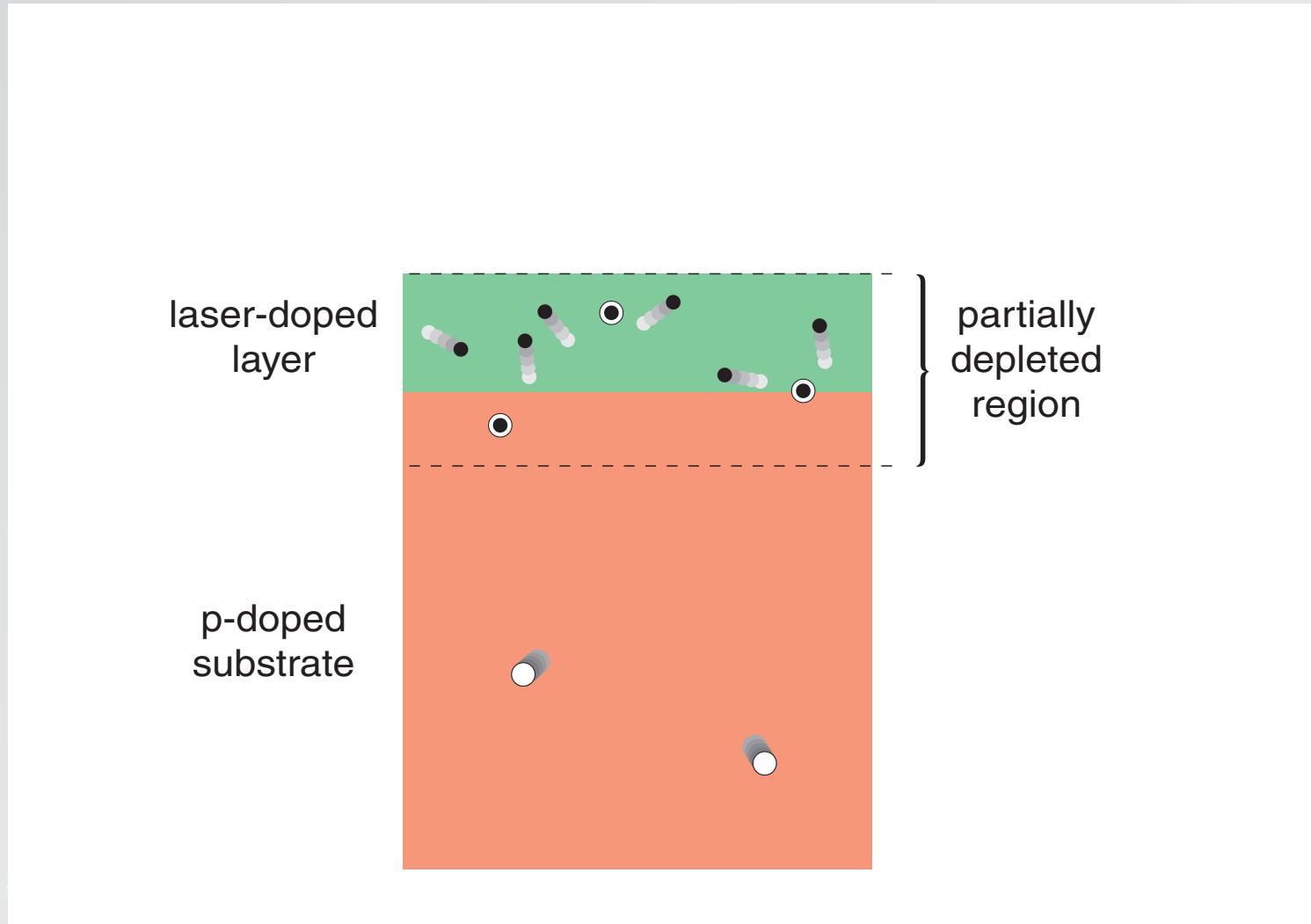
- impact excitation (avalanching)
- carrier lifetime >> transit time (photoconductive gain)
- some other mechanism

Devices



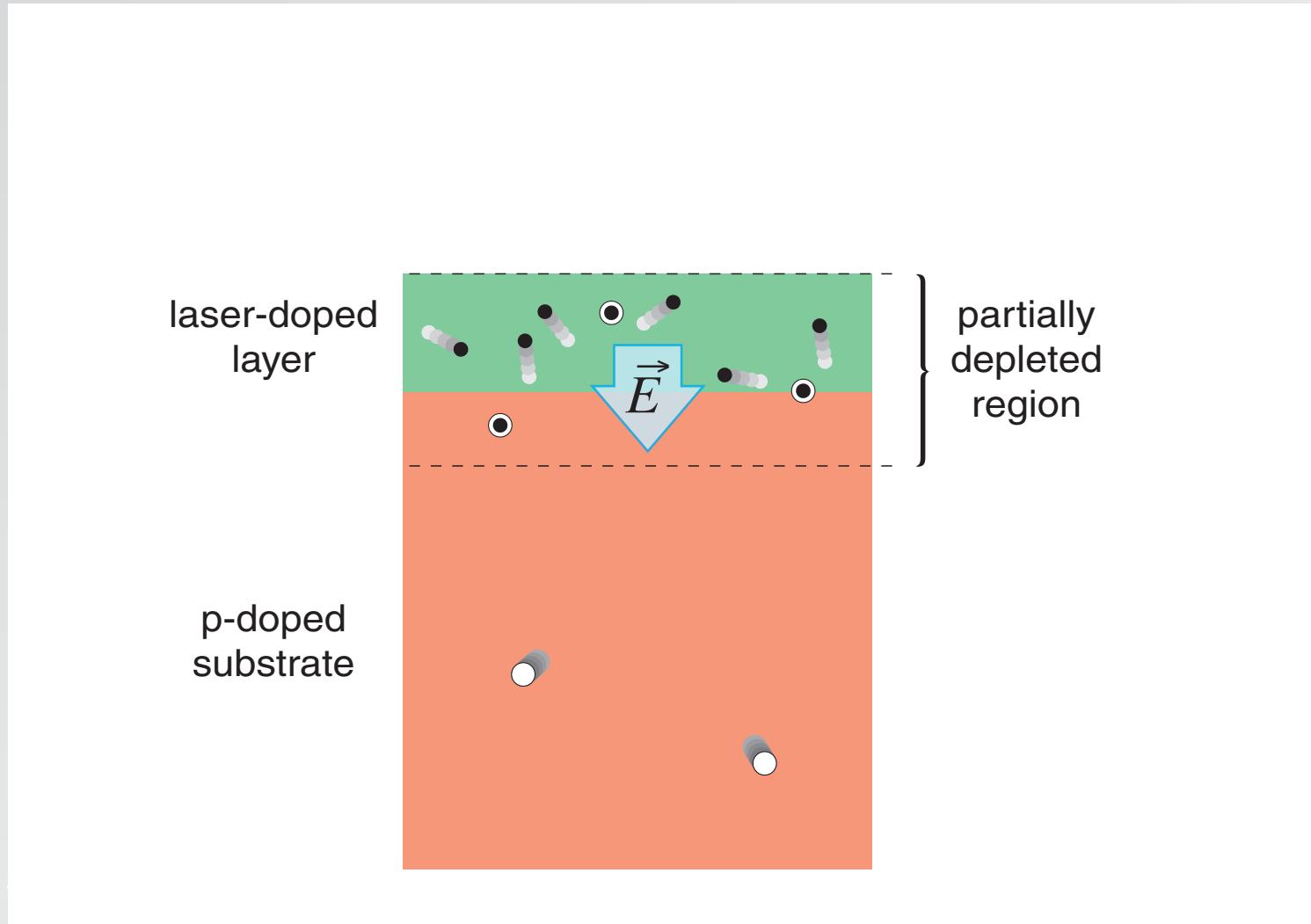
"p-n junction"

Devices



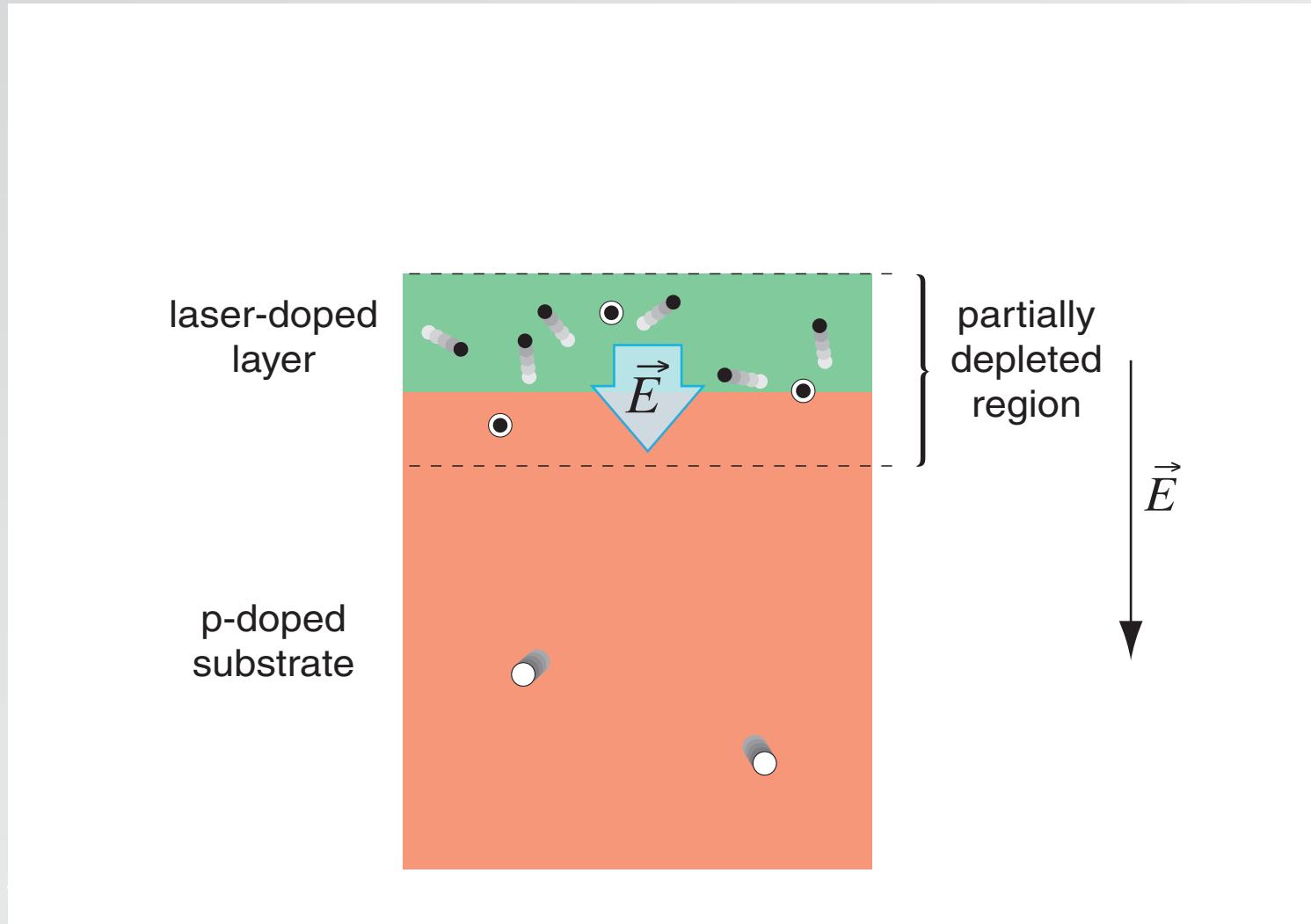
formation of partially depleted region

Devices



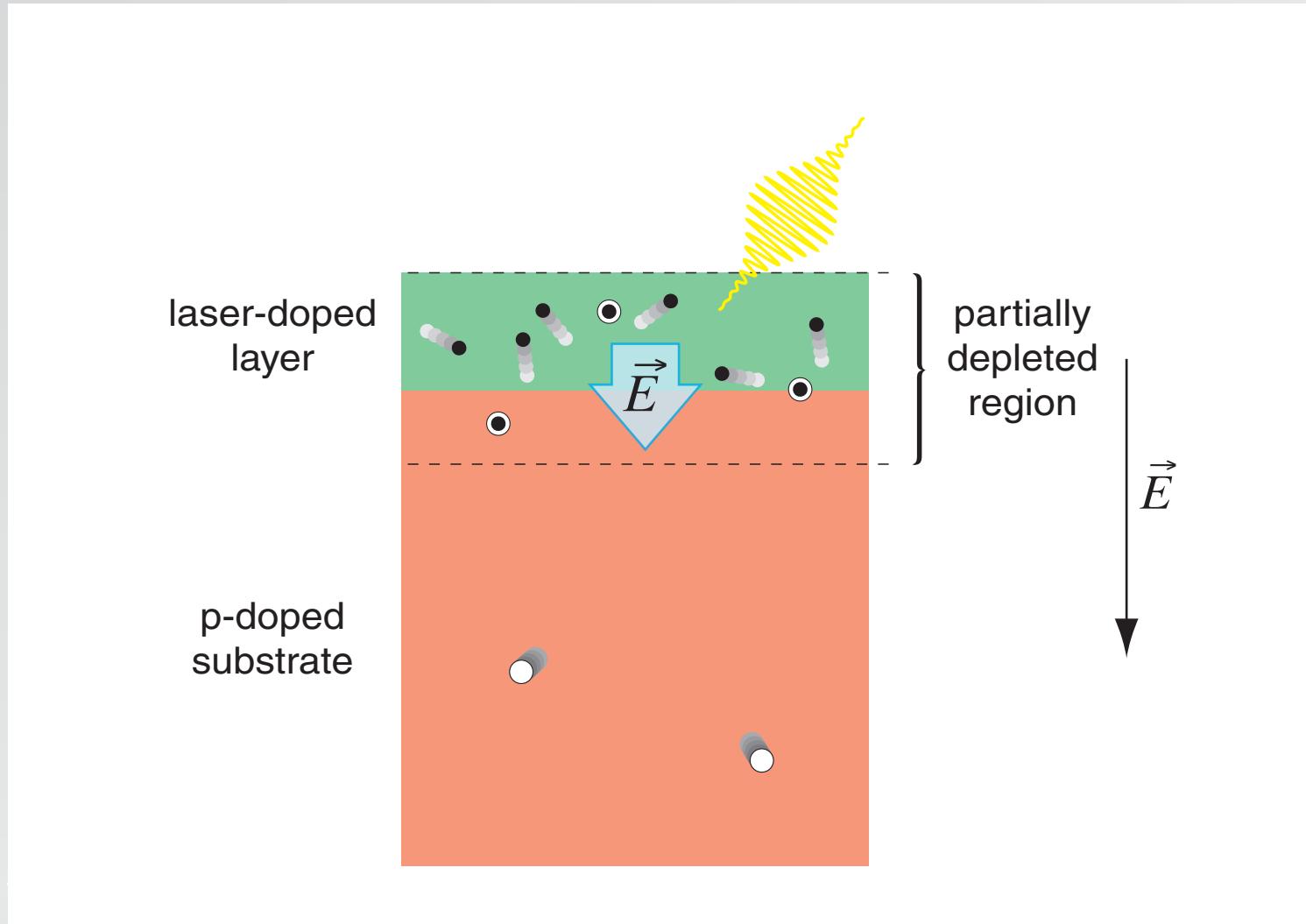
formation of partially depleted region

Devices



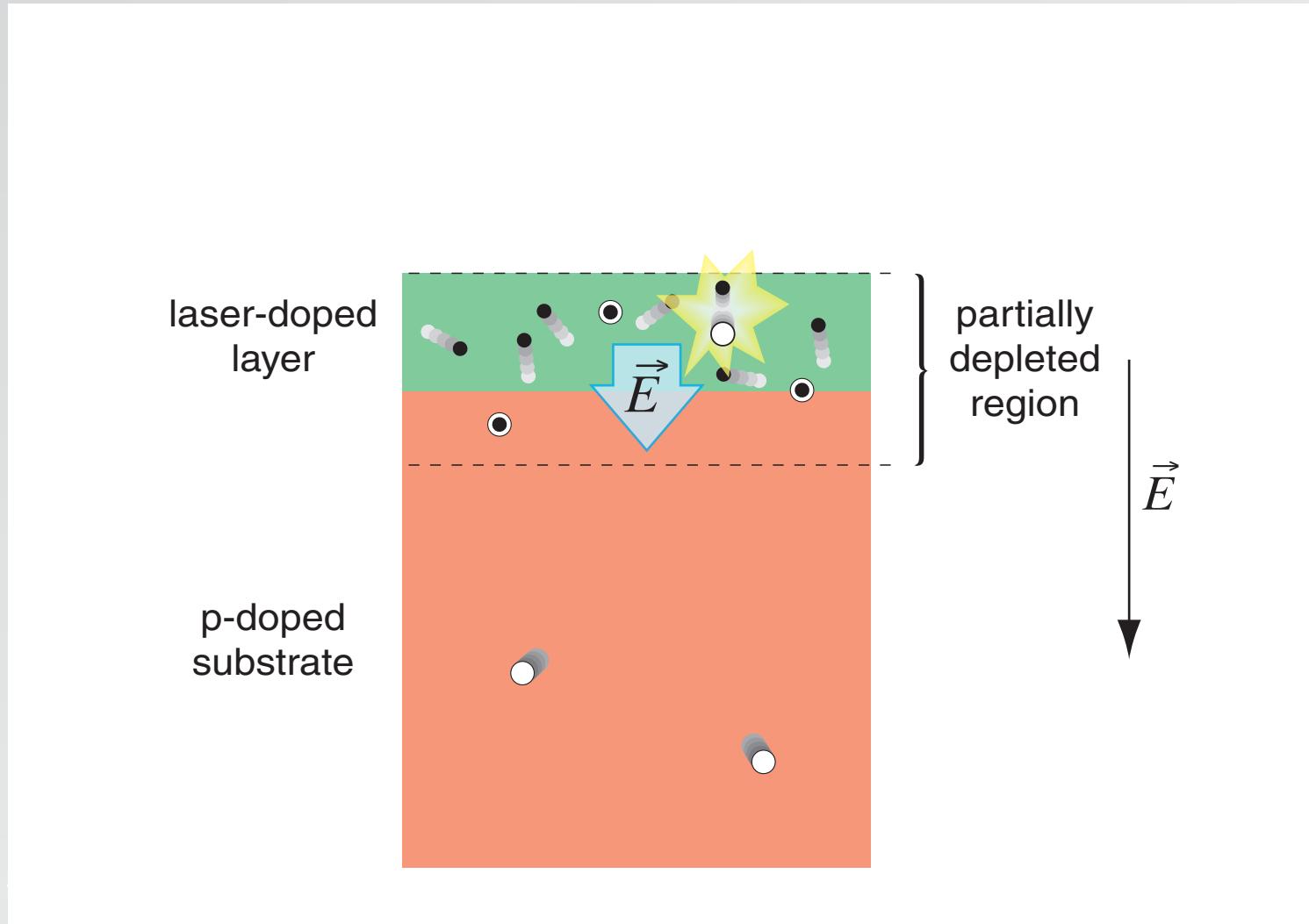
apply backward bias...

Devices



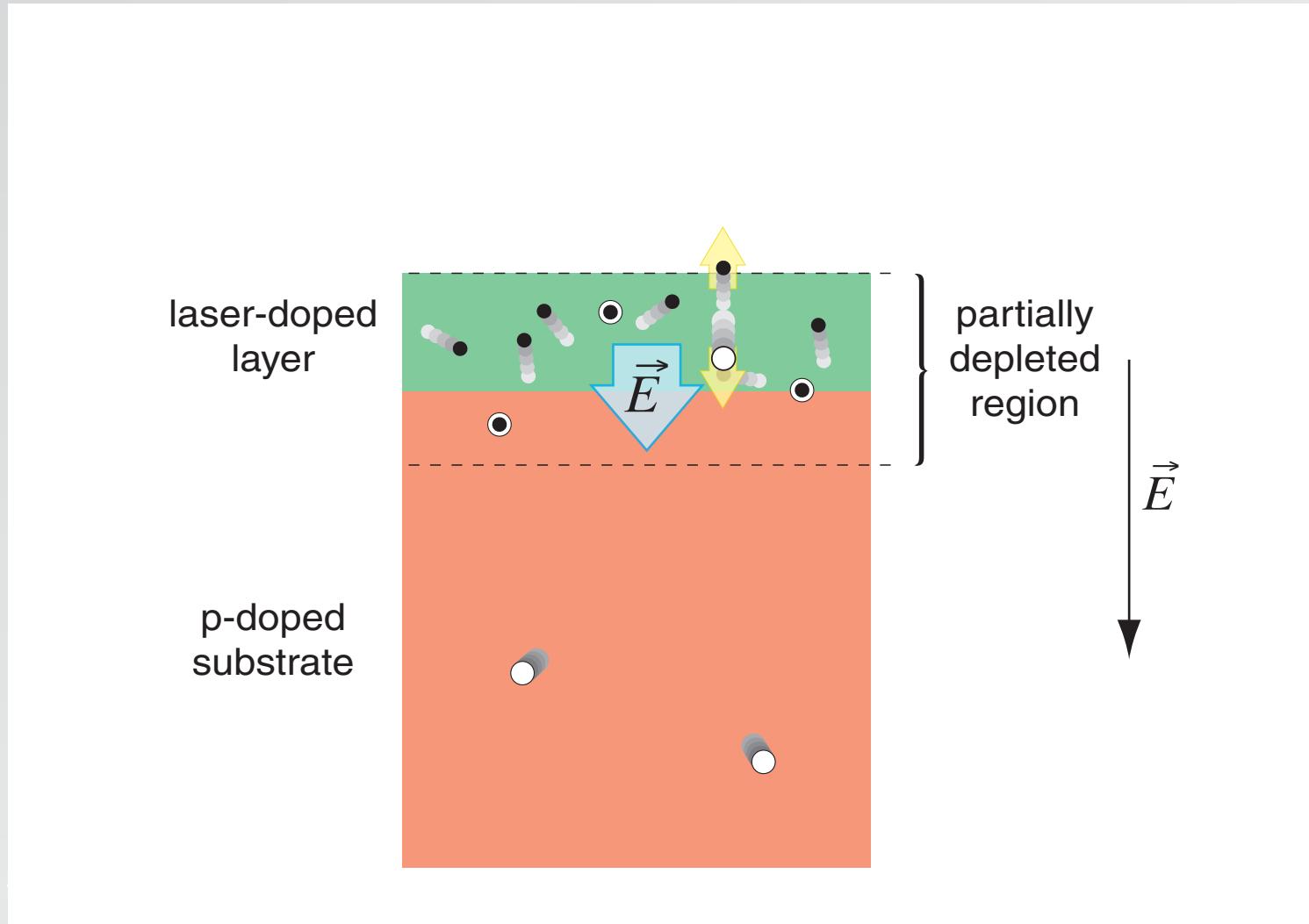
...incident photon generates electron-hole pair...

Devices



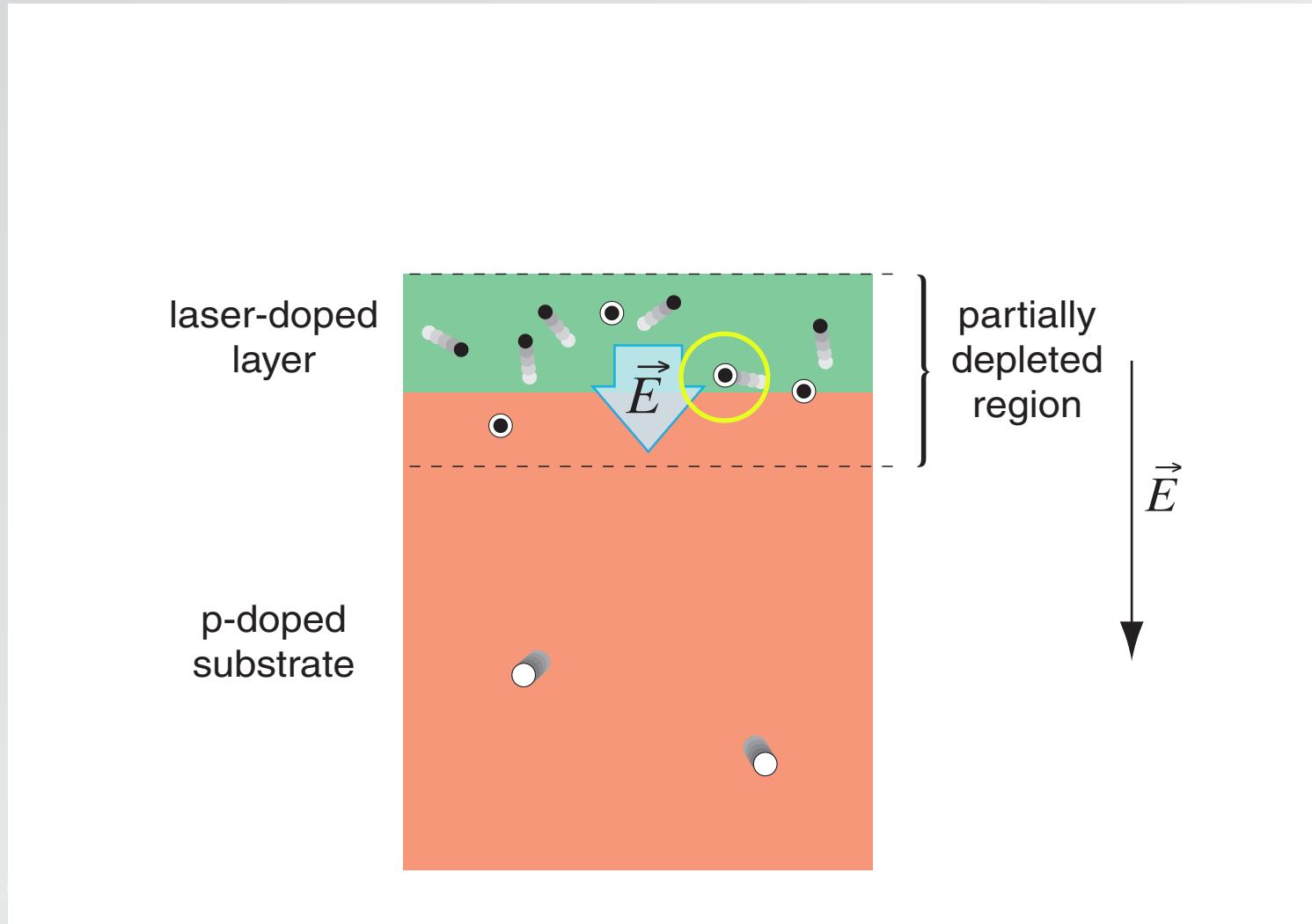
...incident photon generates electron-hole pair...

Devices



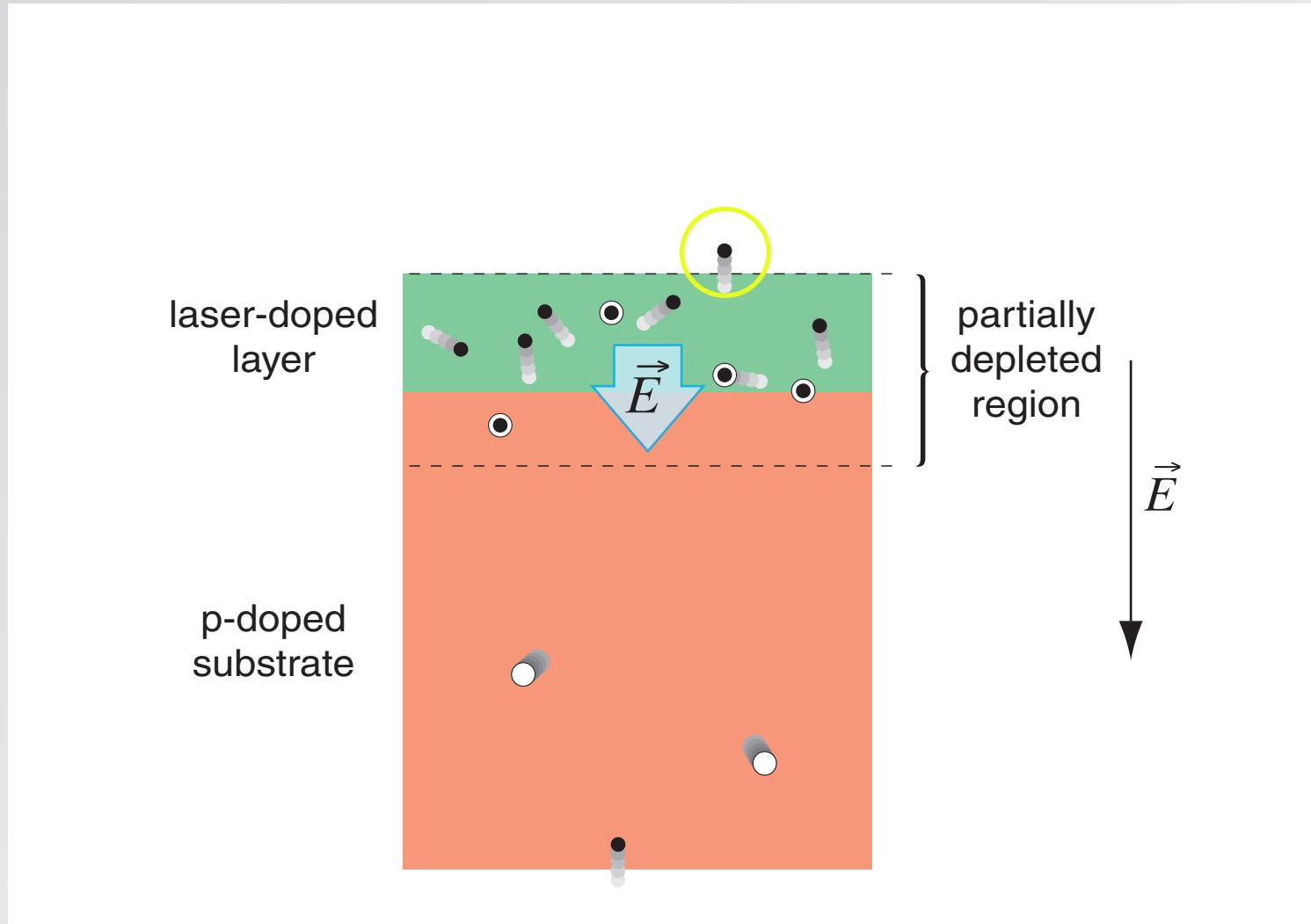
...carriers accelerate away from each other...

Devices



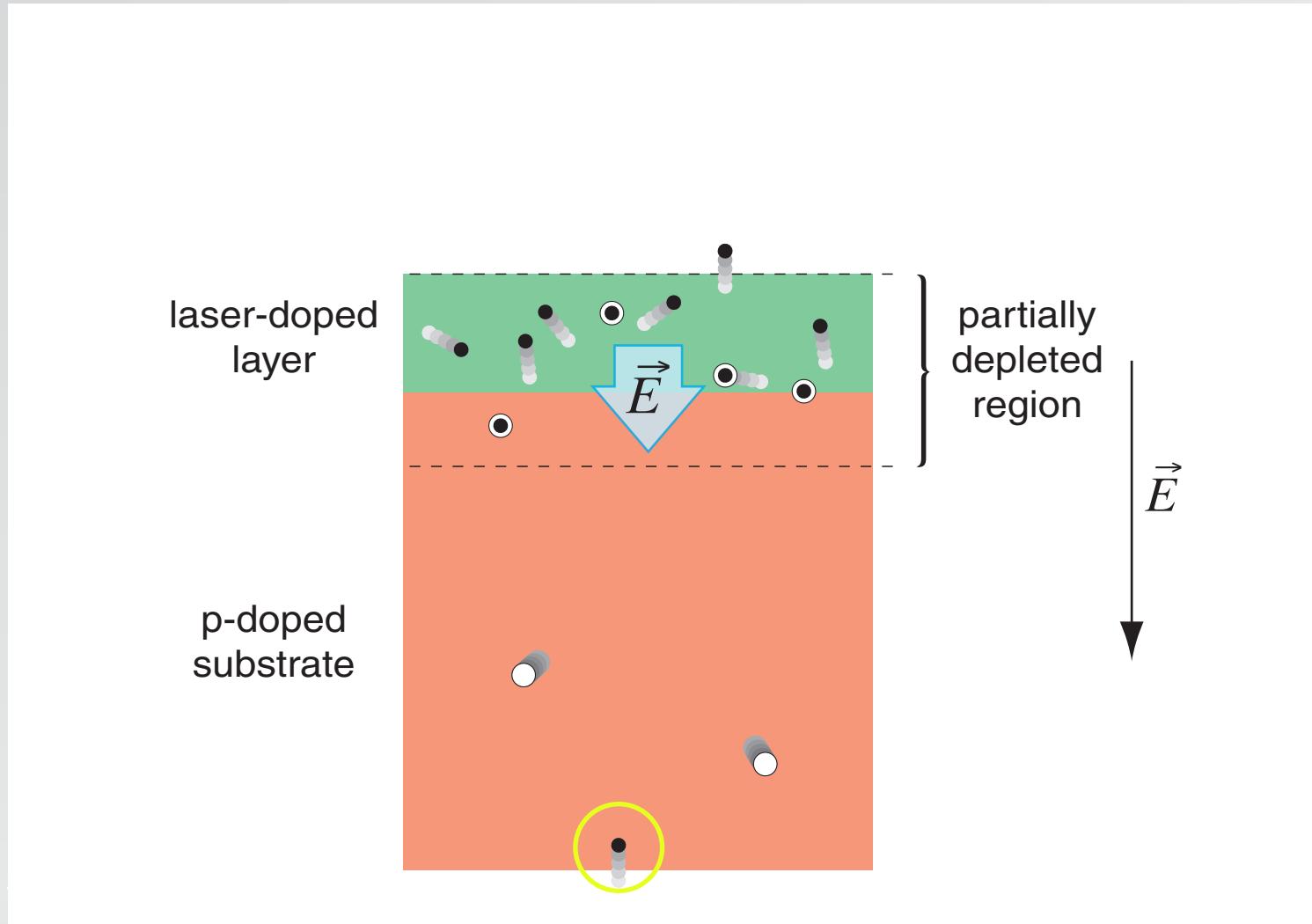
...hole is trapped

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



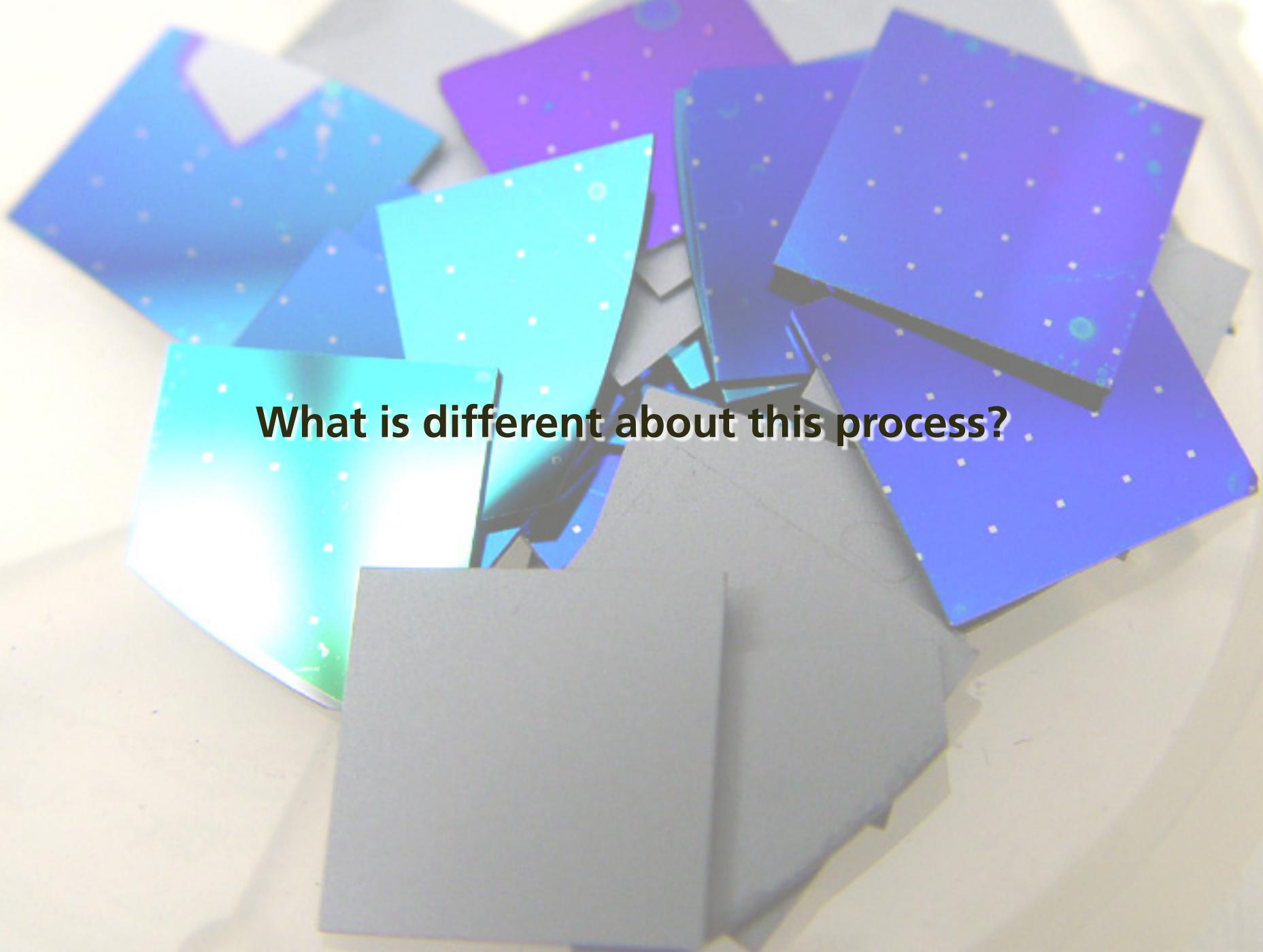
SiOnyx

<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?

Conclusion

Compare femtosecond laser doping to:

- inclusion during growth
- thermal diffusion
- ion implantation





Funding:

Army Research Office

DARPA

Department of Energy

NDSEG

National Science Foundation

for more information and a copy of this presentation:

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Two rounded rectangular buttons with black outlines. The left button contains the text "Google Search" and the right button contains "I'm Feeling Lucky".



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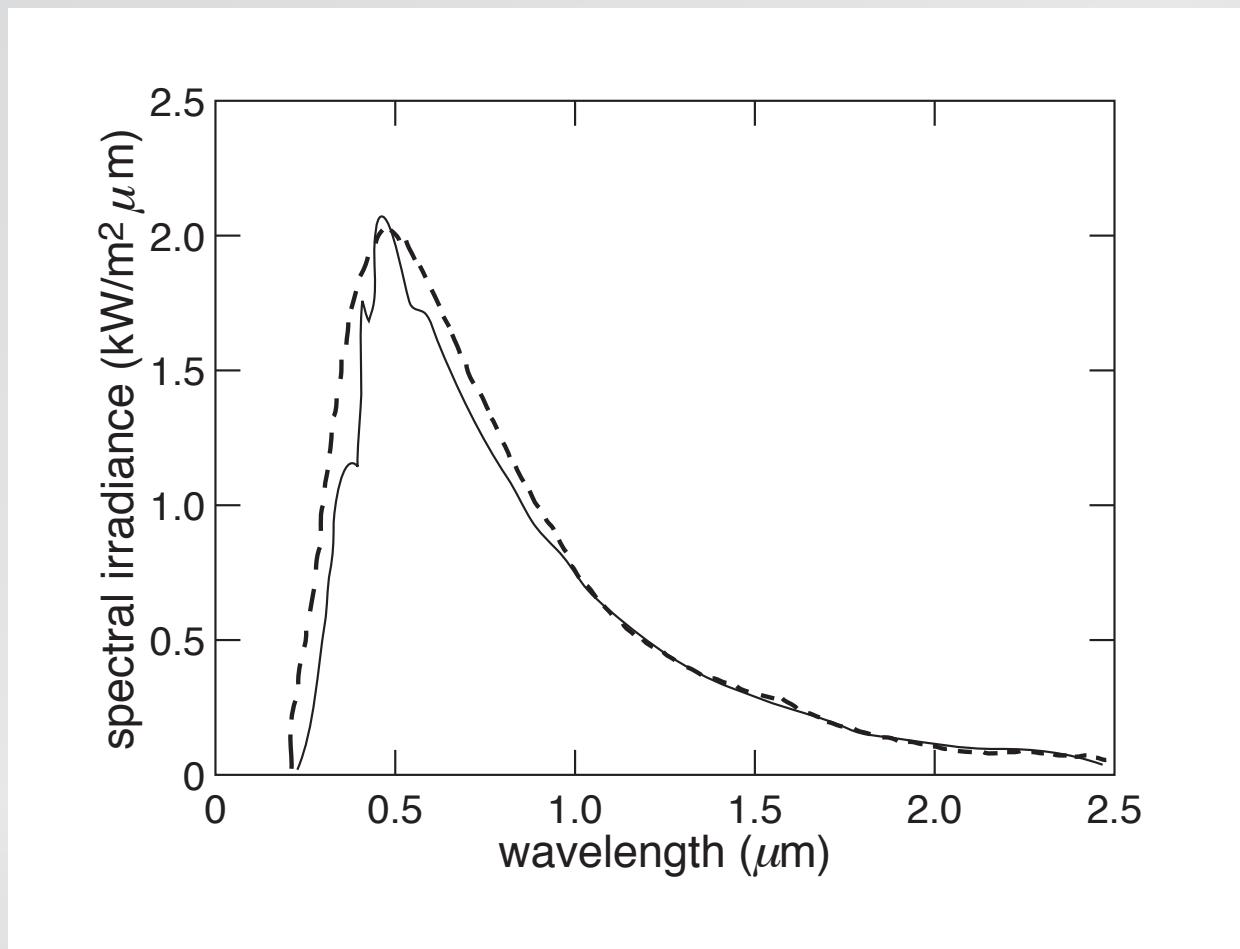
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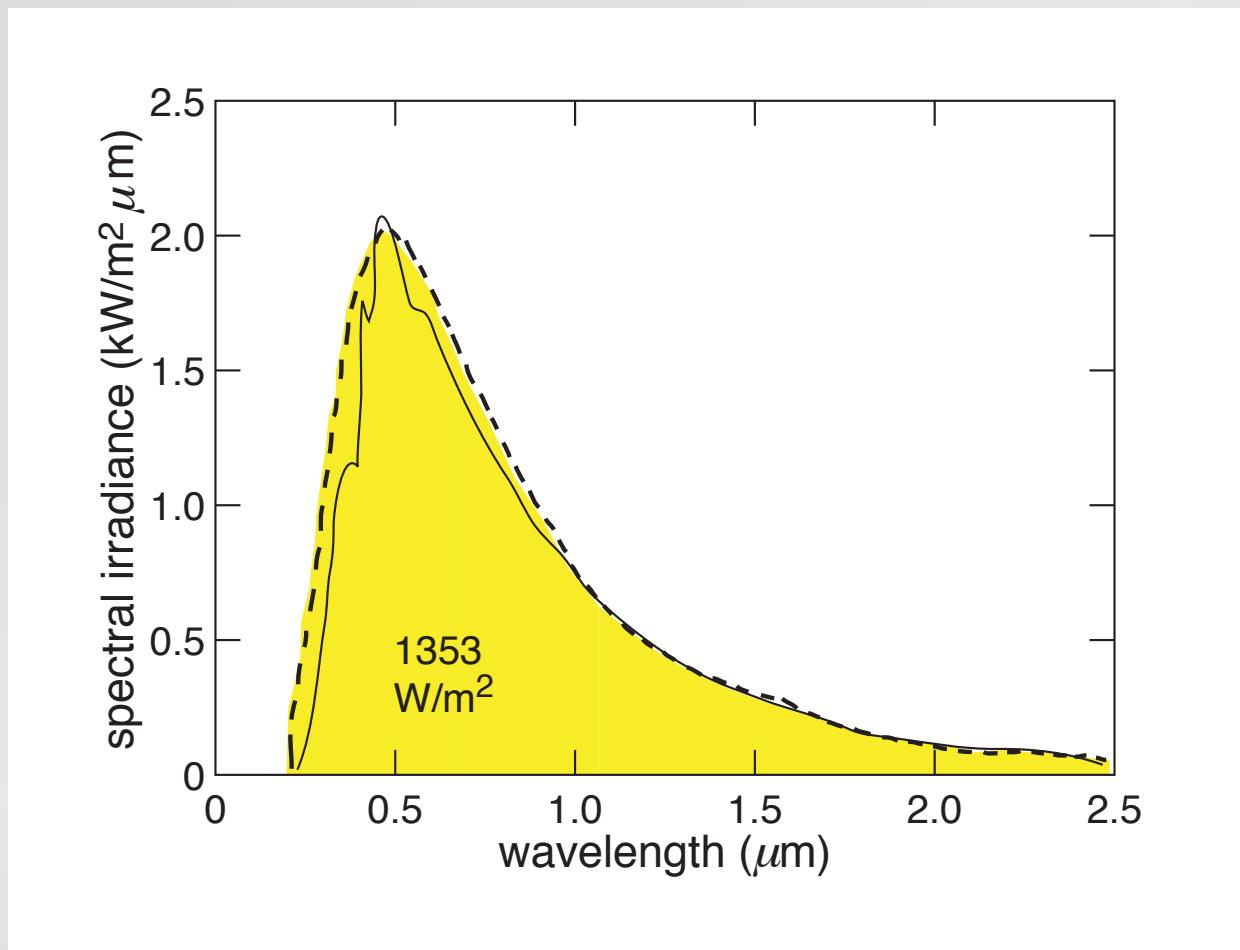
Devices

solar spectrum



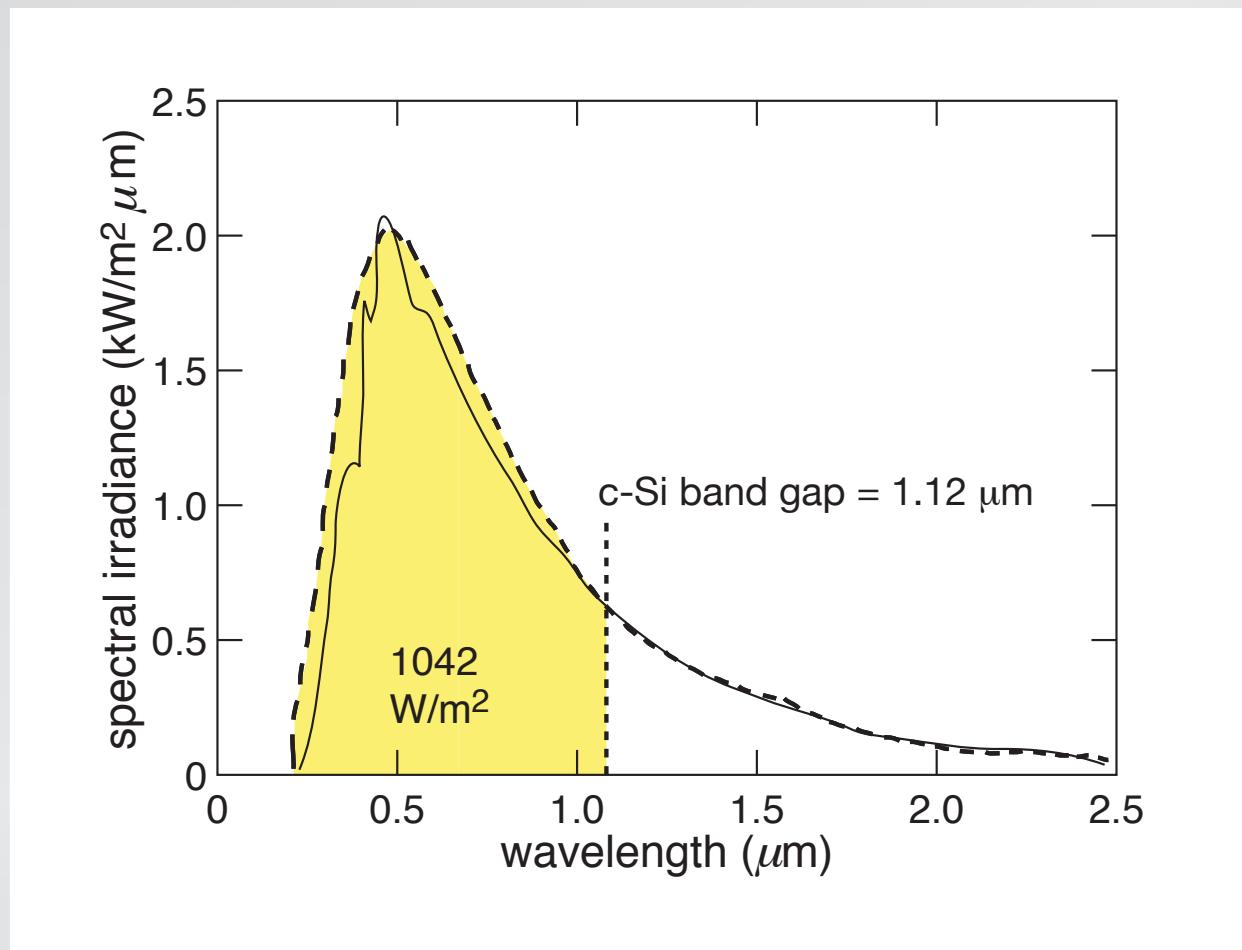
Devices

solar spectrum



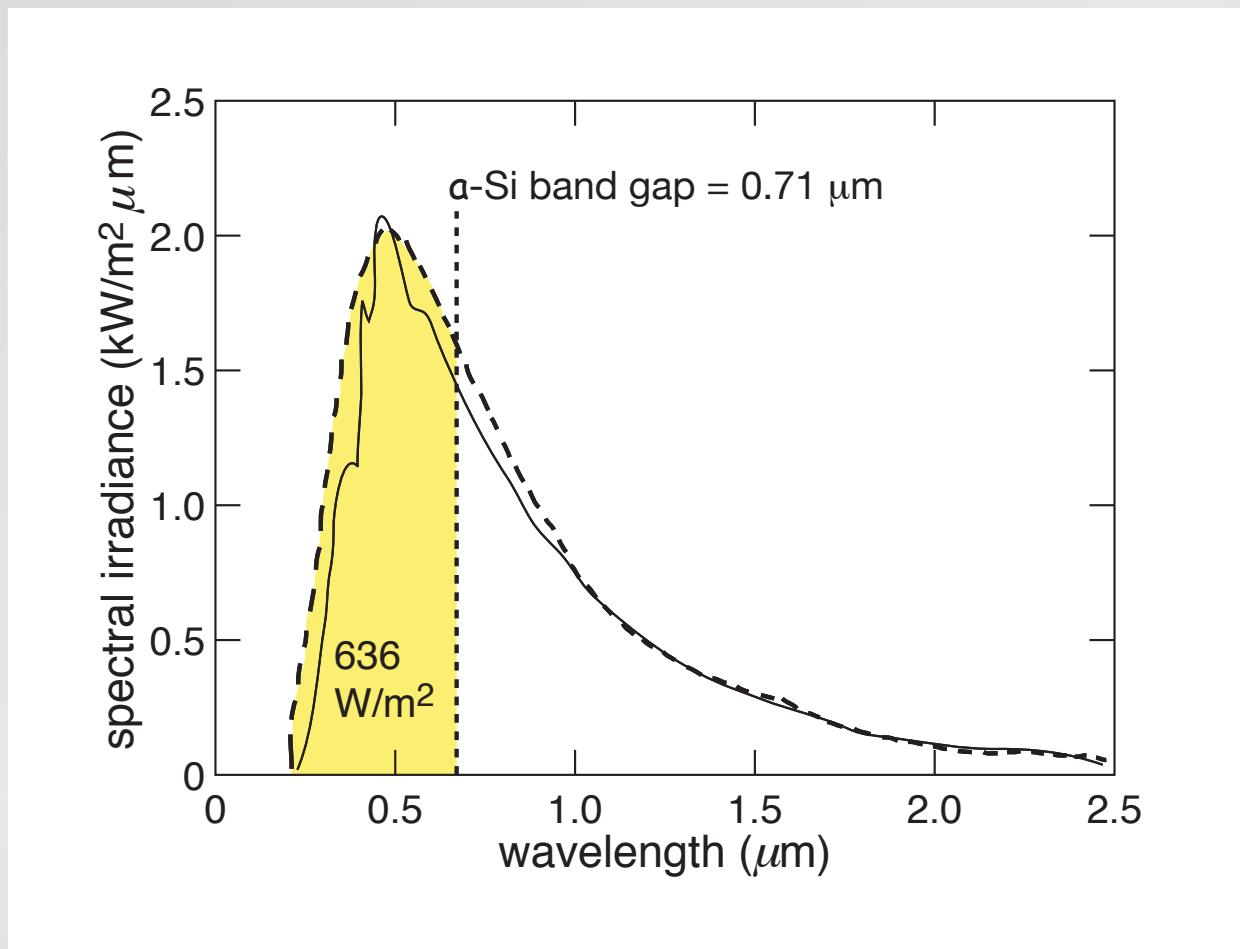
Devices

crystalline silicon: transparent to 23% of solar radiation



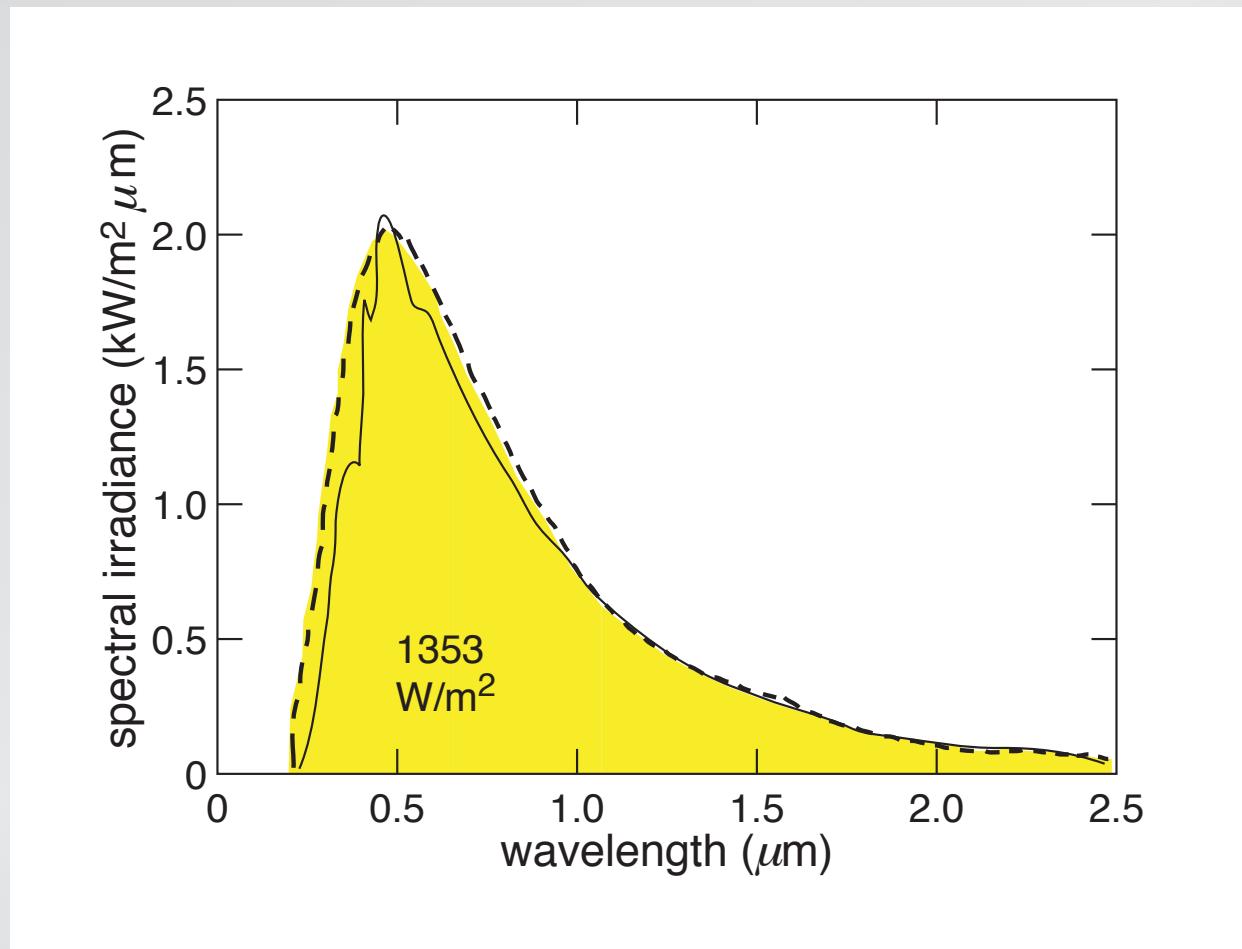
Devices

amorphous silicon: transparent to 53% of solar radiation



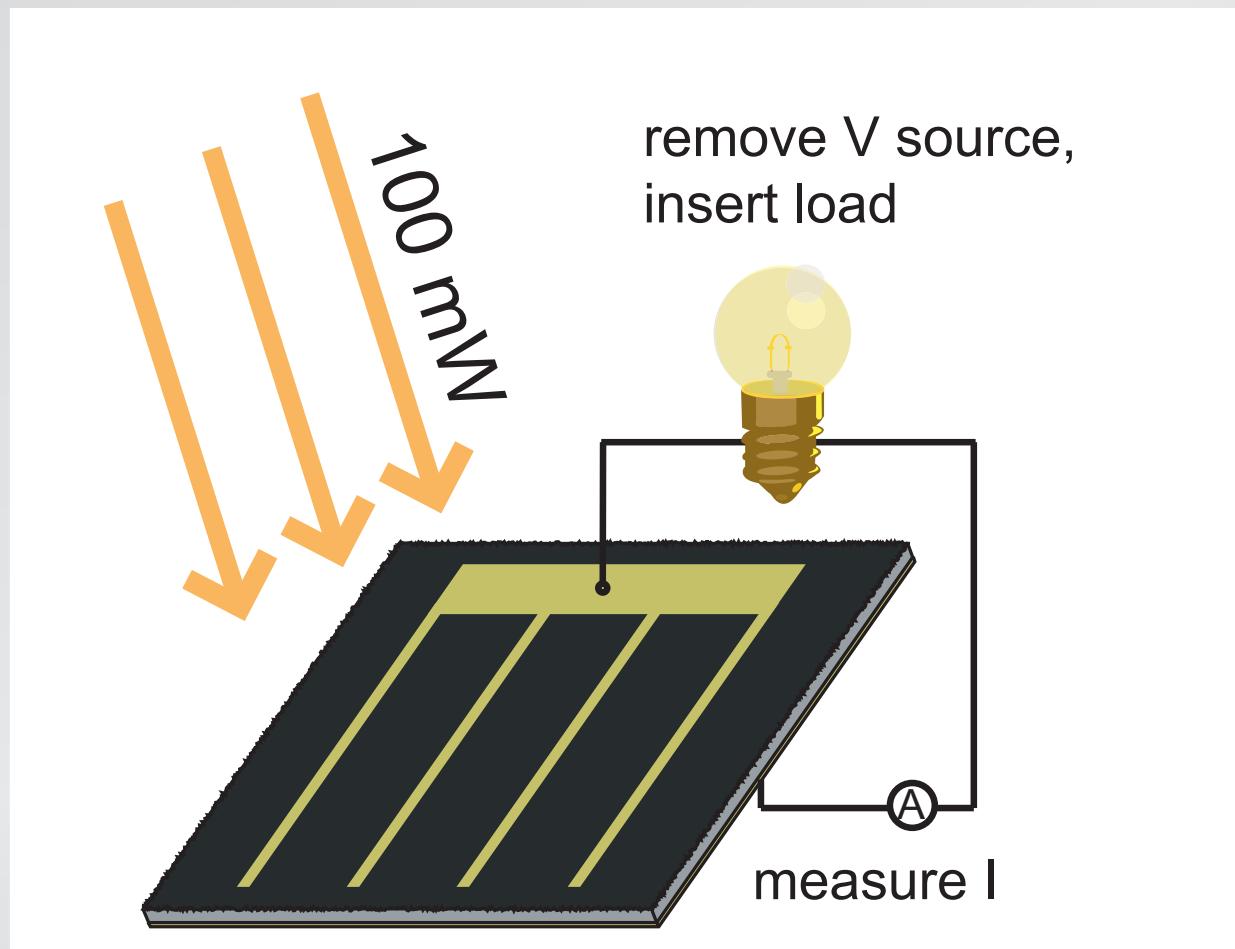
Devices

black silicon: potential to recover transmitted energy



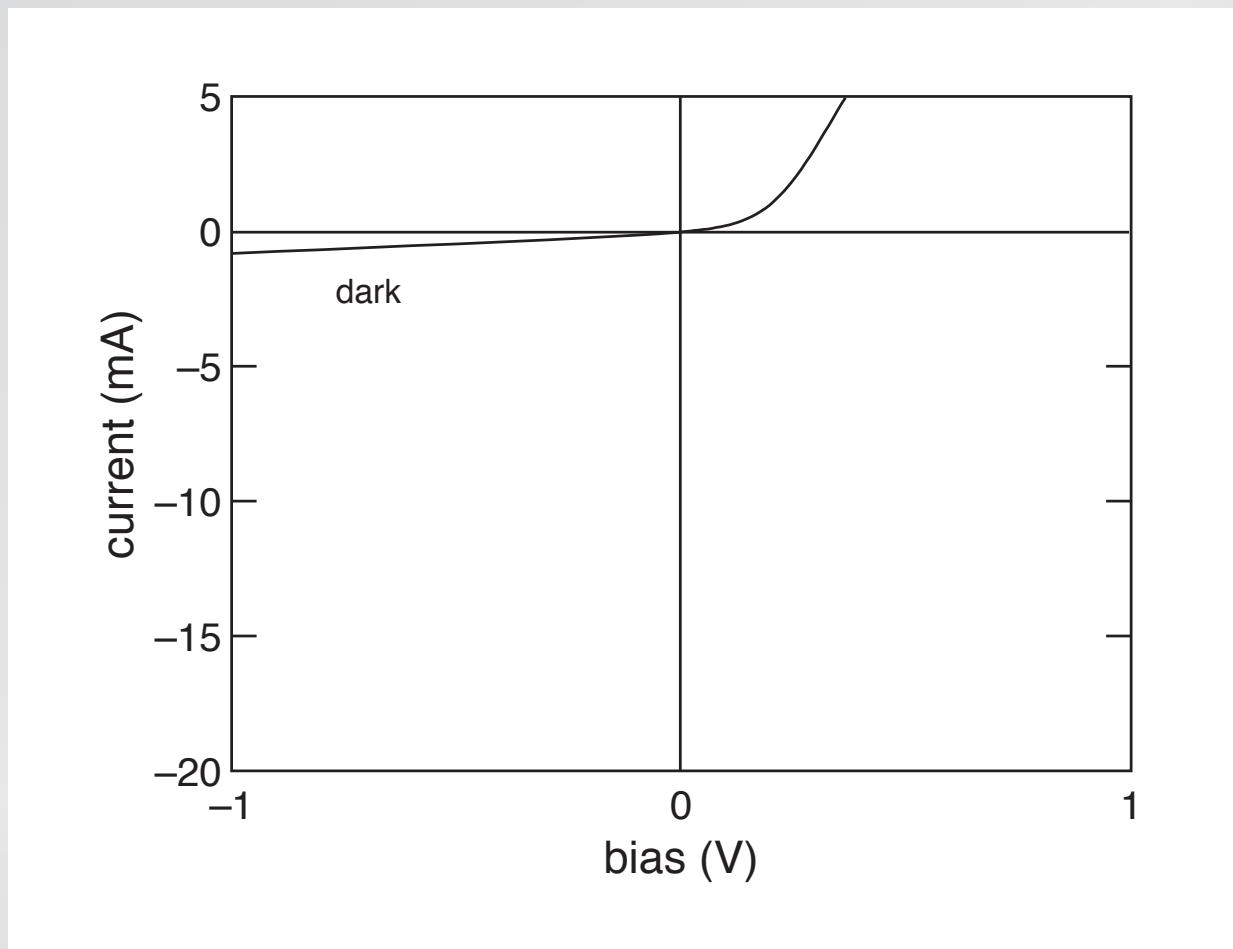
Devices

very preliminary photovoltaic cell



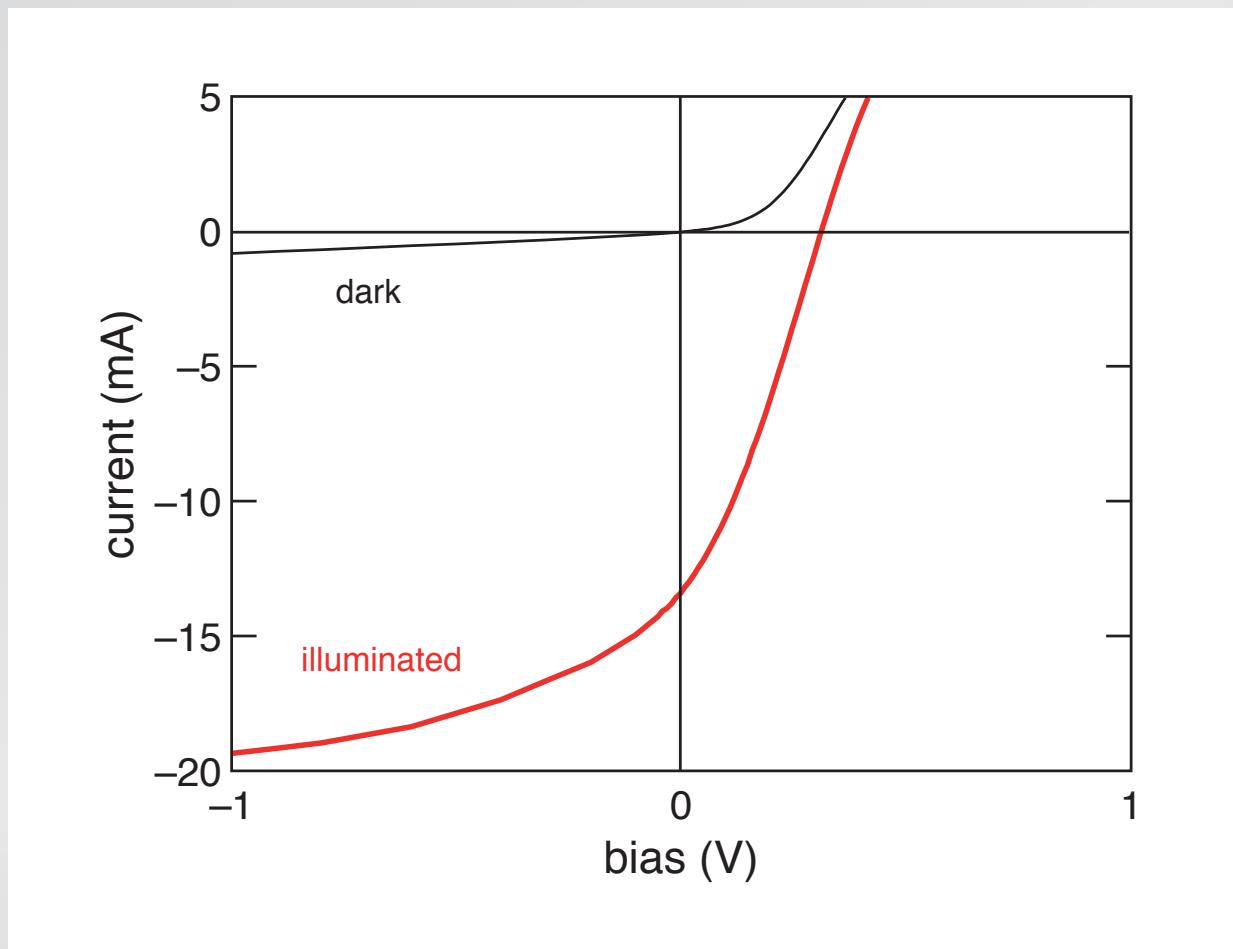
Devices

very preliminary photovoltaic cell



Devices

very preliminary photovoltaic cell



Devices

1.5% efficiency, a good beginning

