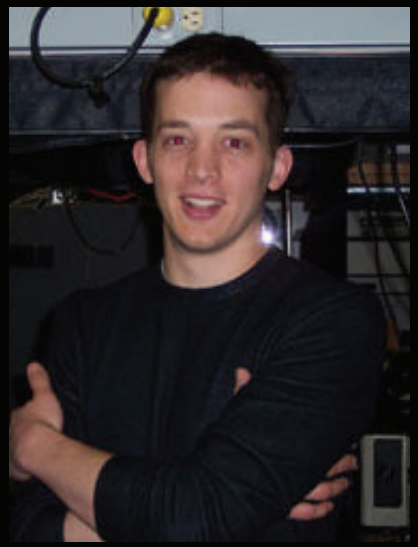
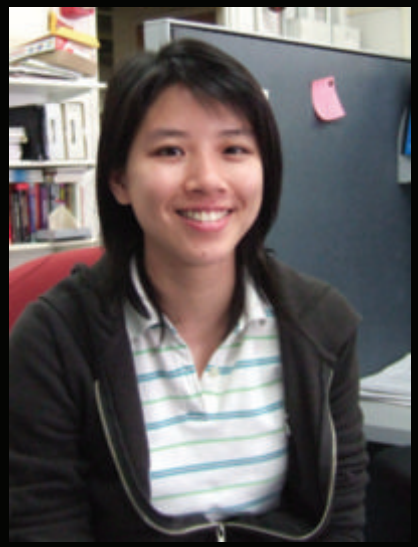
A brief history of black silicon

Black silicon symposium 2009
Albany, NY, 20 August 2009



Mark Winkler

Renee Sher



Yu-Ting Lin

Eric Mazur

and also....

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

Dr. John Chervinsky
Dr. Joshua Levinson

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

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

Prof. Augustinus Asenbaum (Vienna)

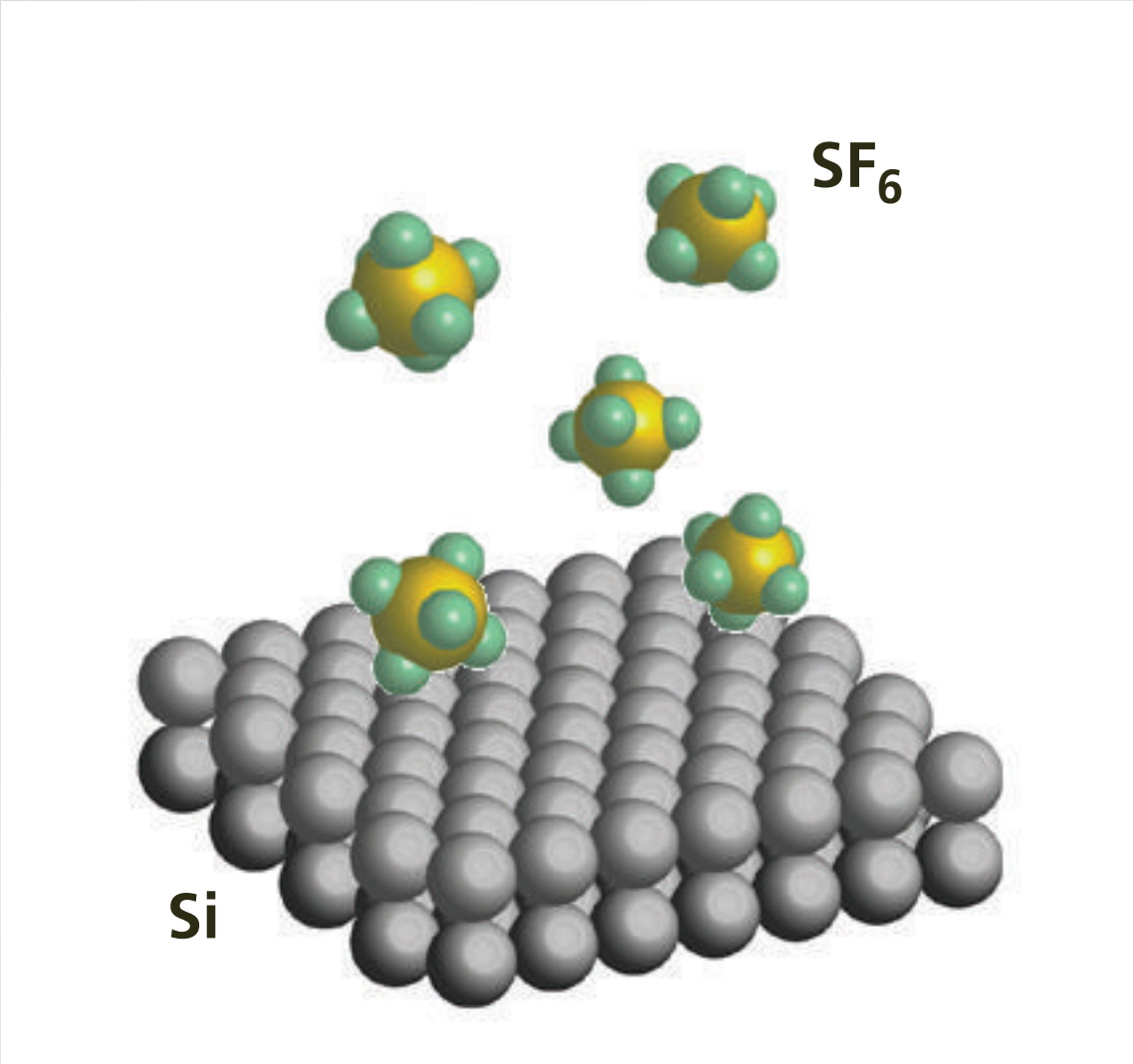
Dr. François Génin (LLNL)
Mark Wall (LLNL)

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

Dr. Pat Maloney (NVSED)

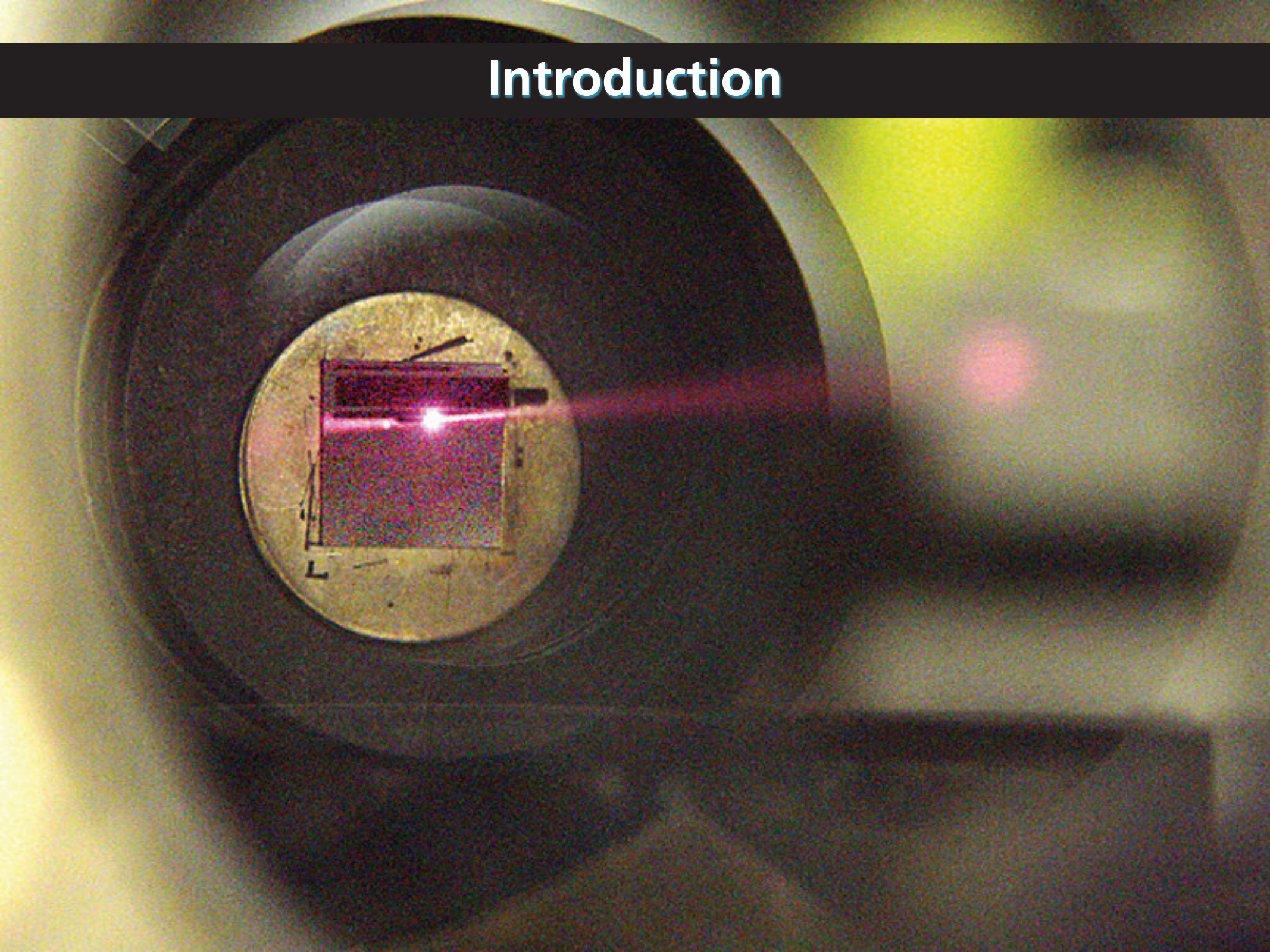
Dr. Jeffrey Warrander (ARDEC)

Introduction



irradiate with 100-fs 10 kJ/m^2 pulses

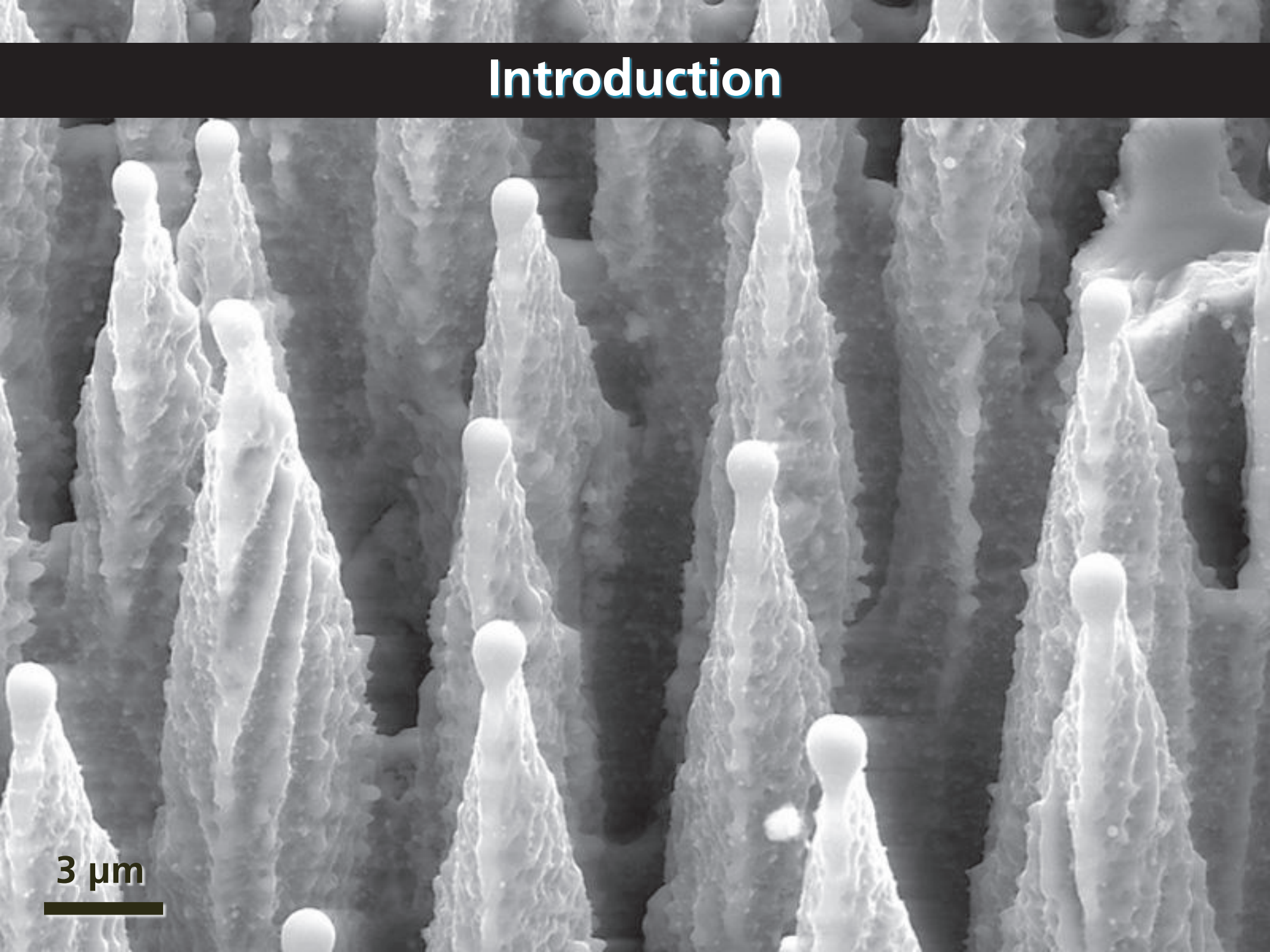
Introduction



Introduction

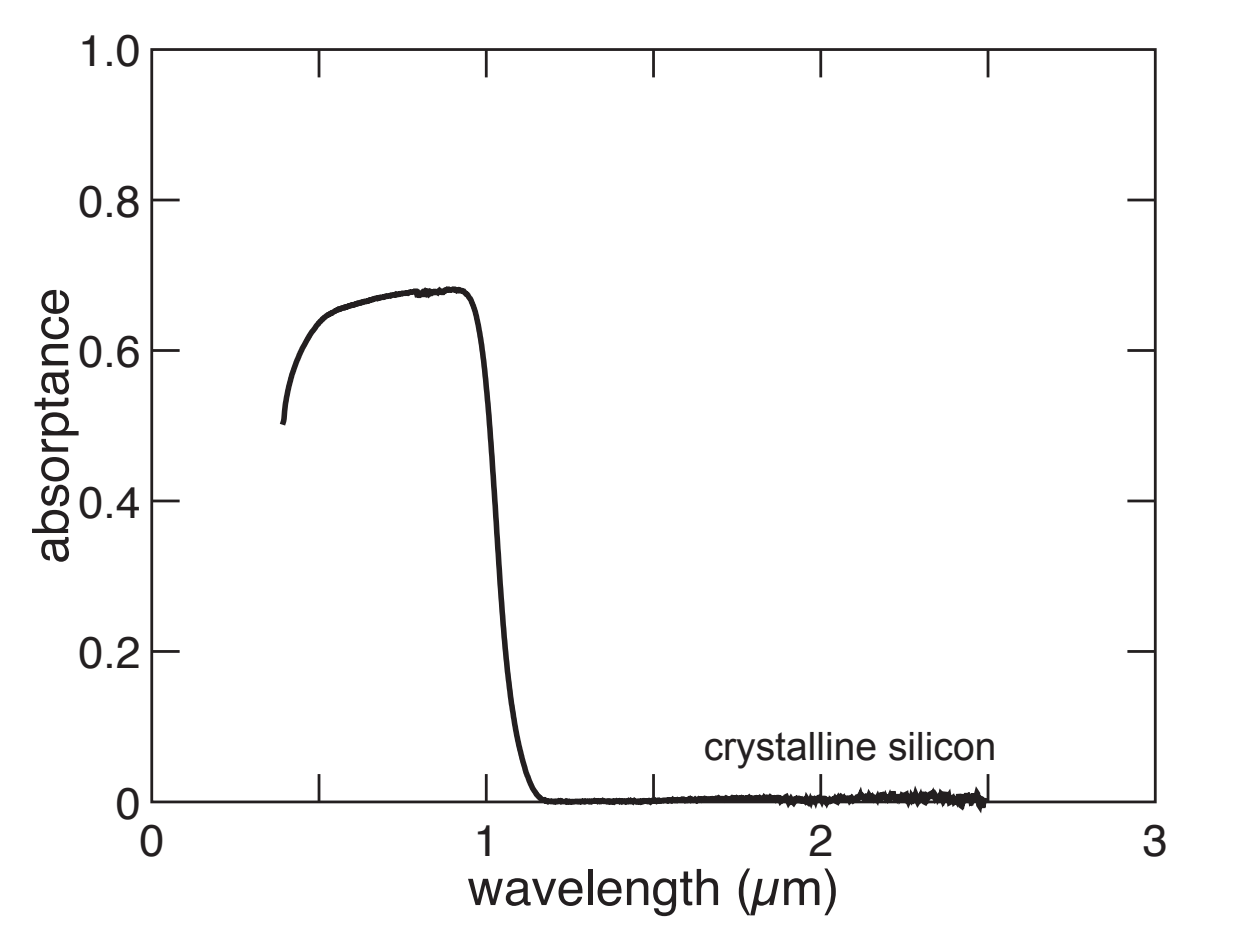
“black silicon”

Introduction



Introduction

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



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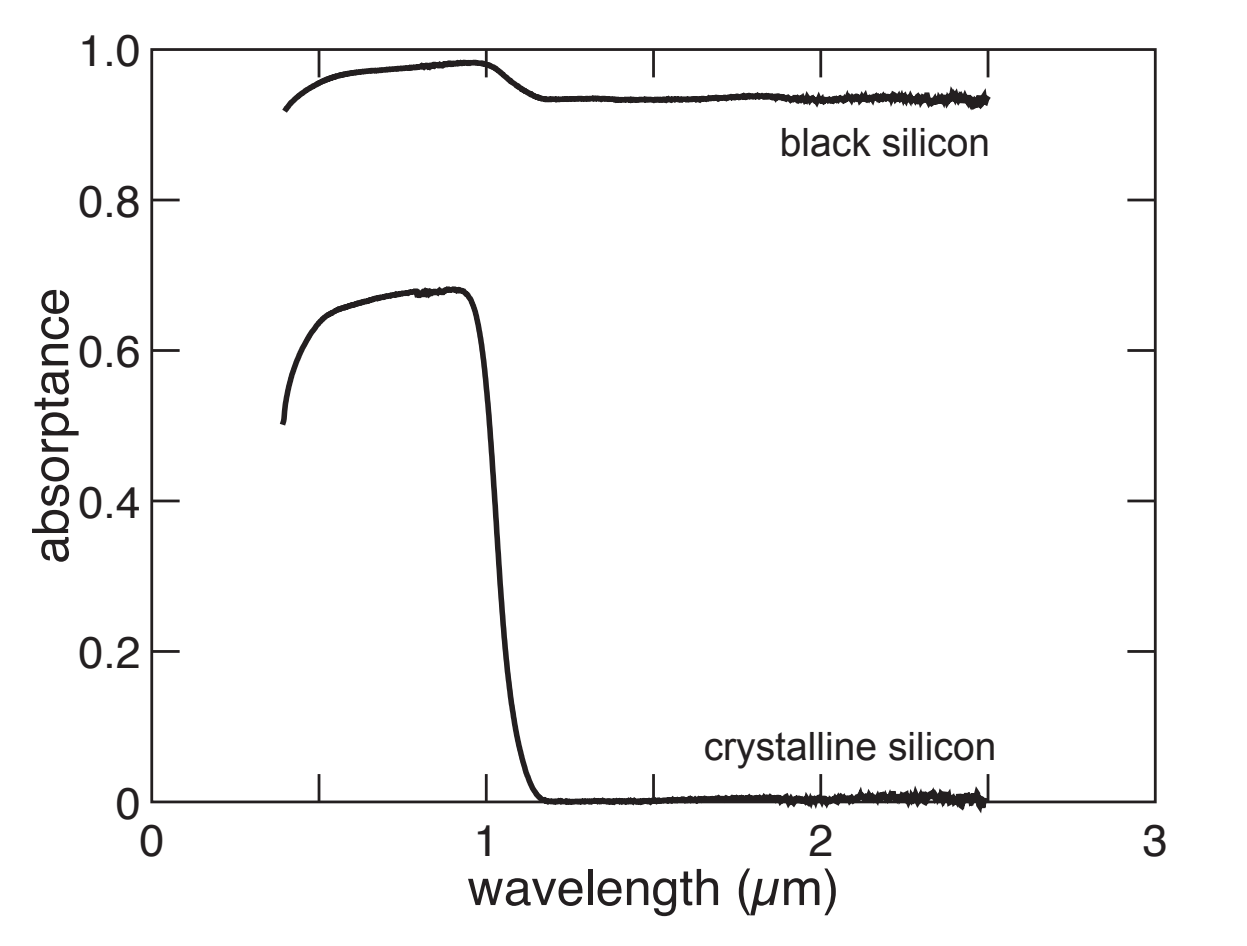

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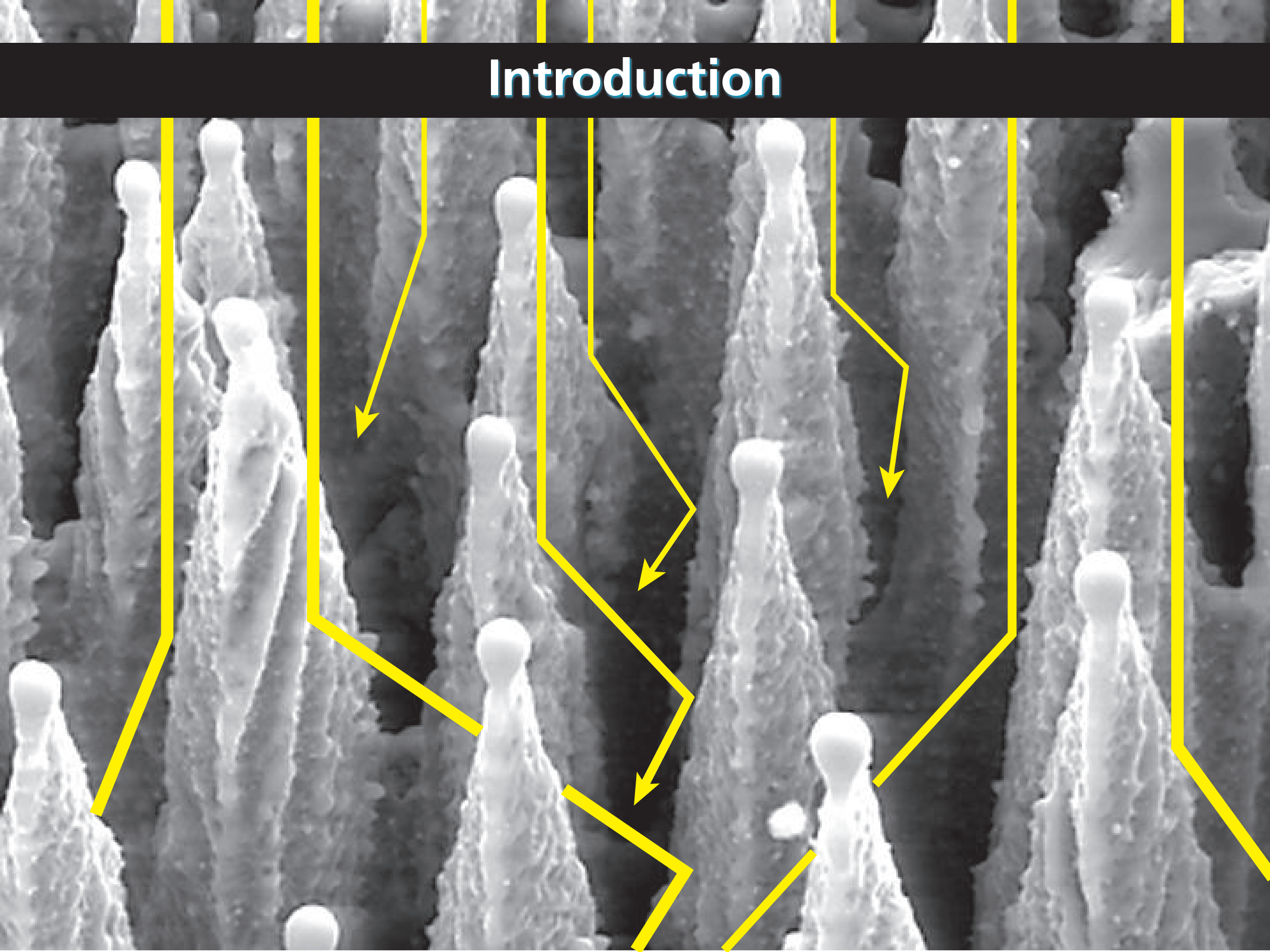

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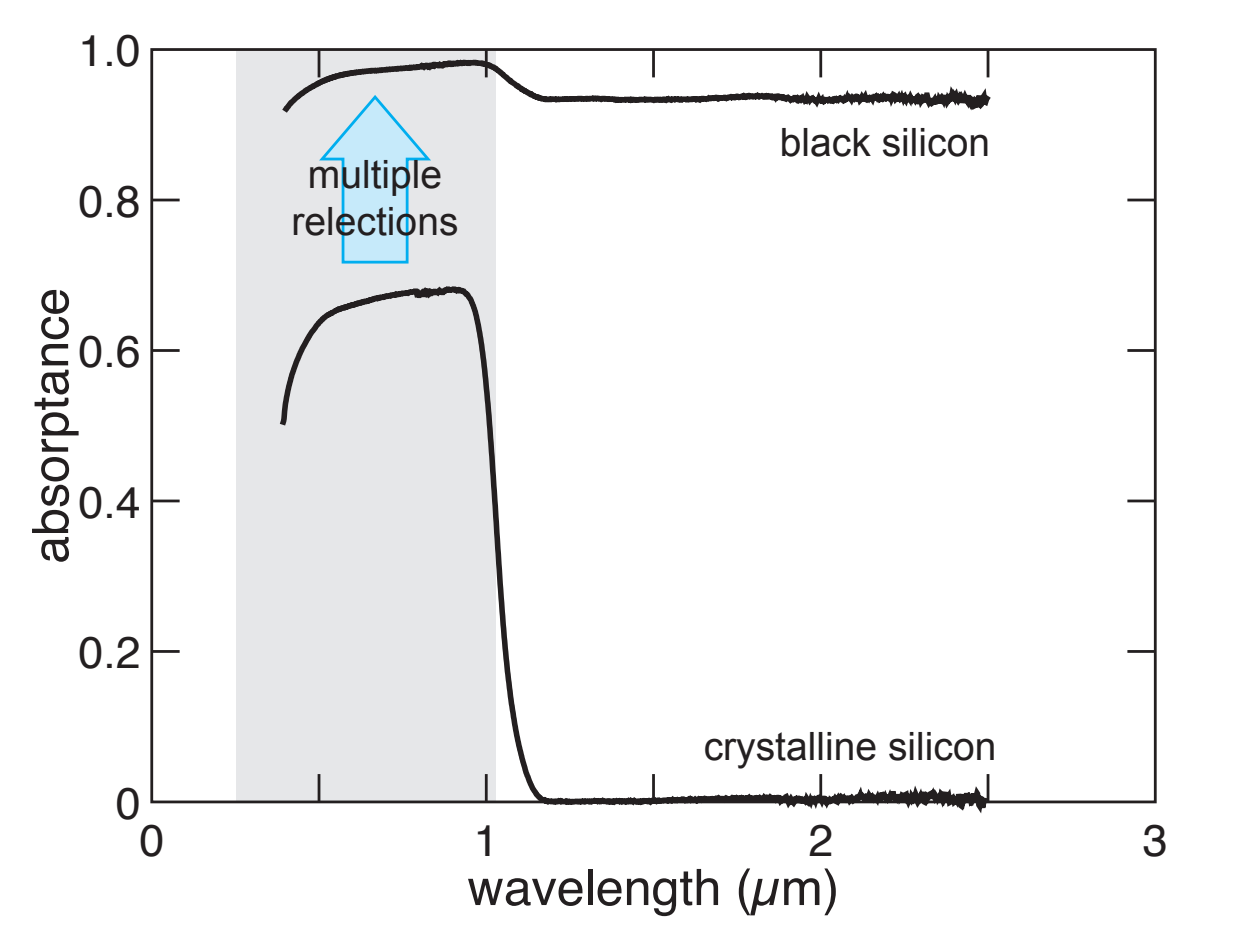


Introduction

silicon transparent in IR

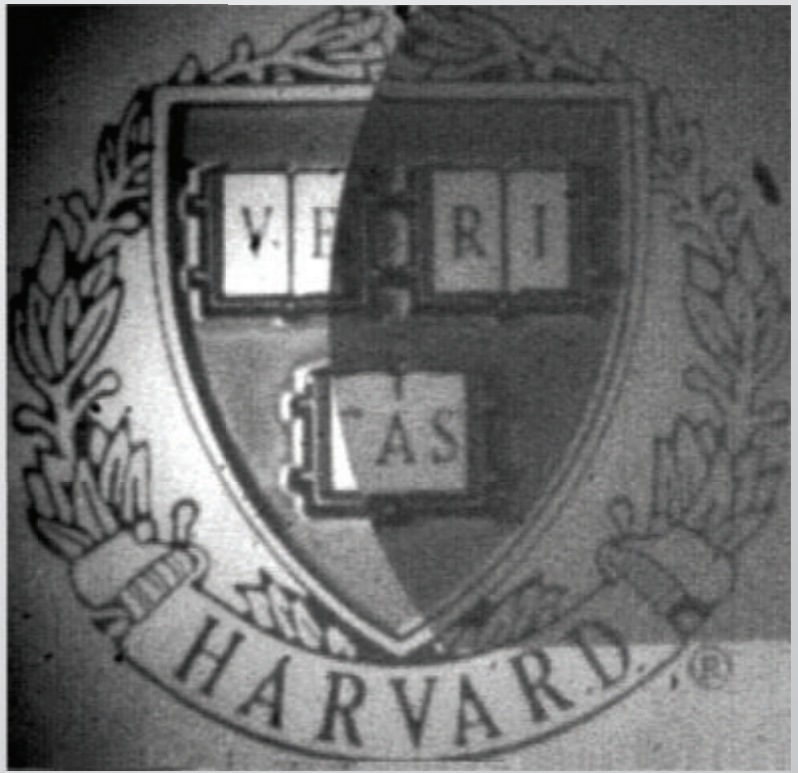
visible

Introduction

silicon transparent in IR

visible

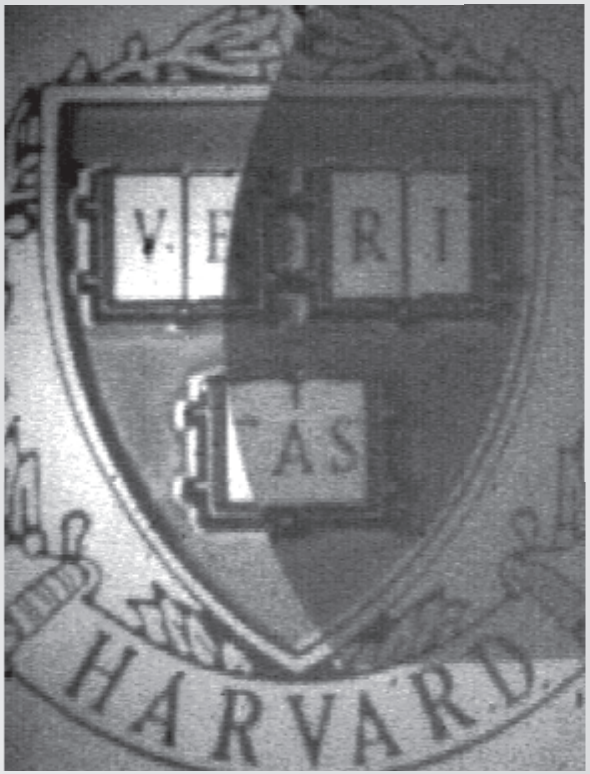
IR



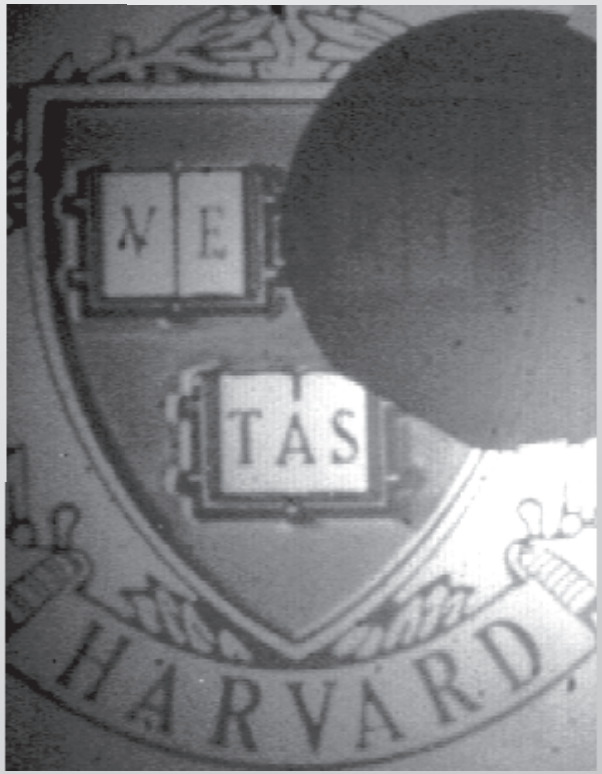
Introduction

roughening doesn't change IR transmission…

polished



unpolished



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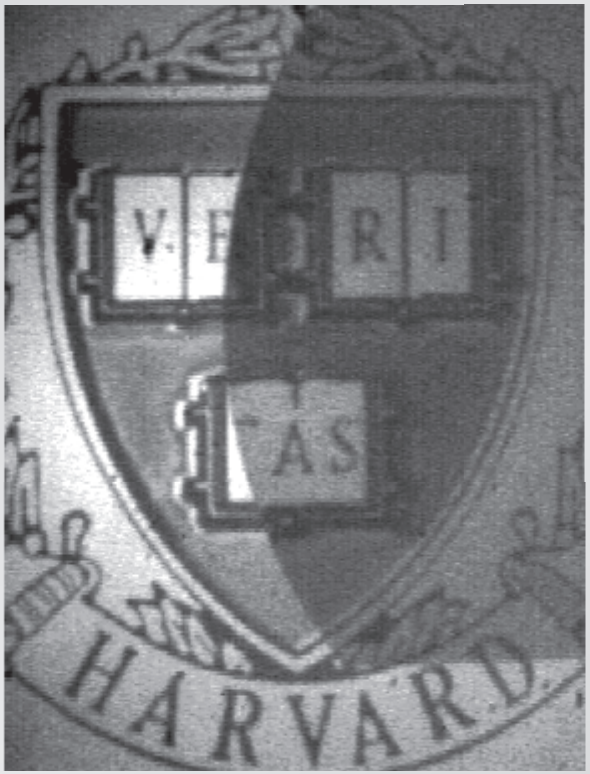

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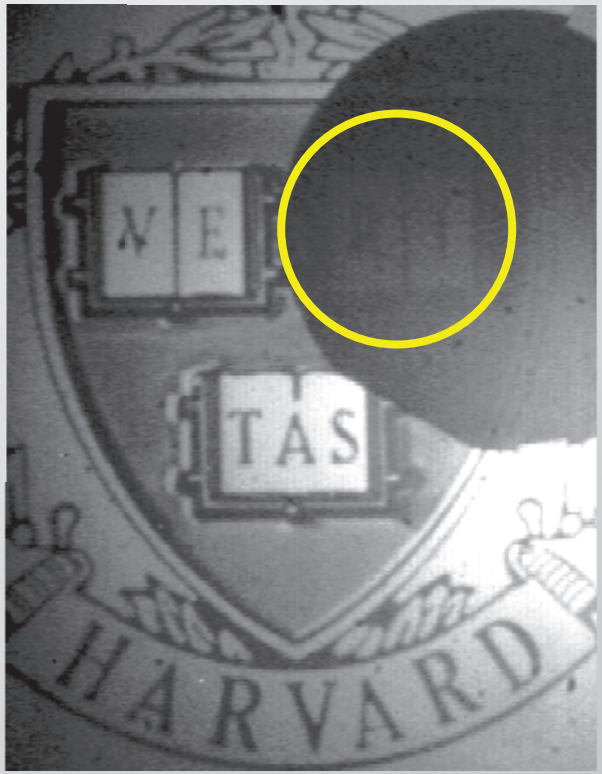
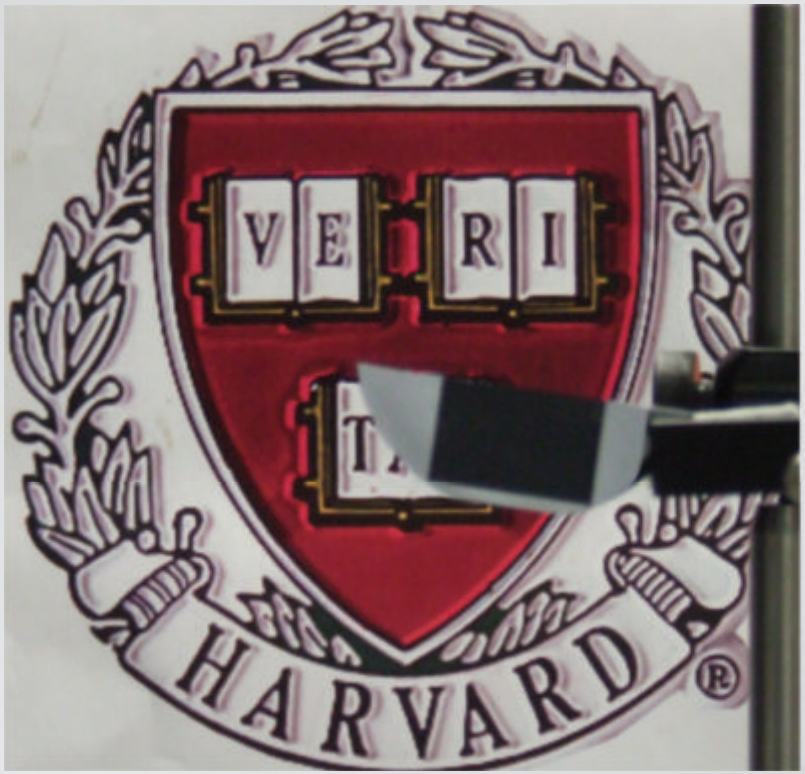


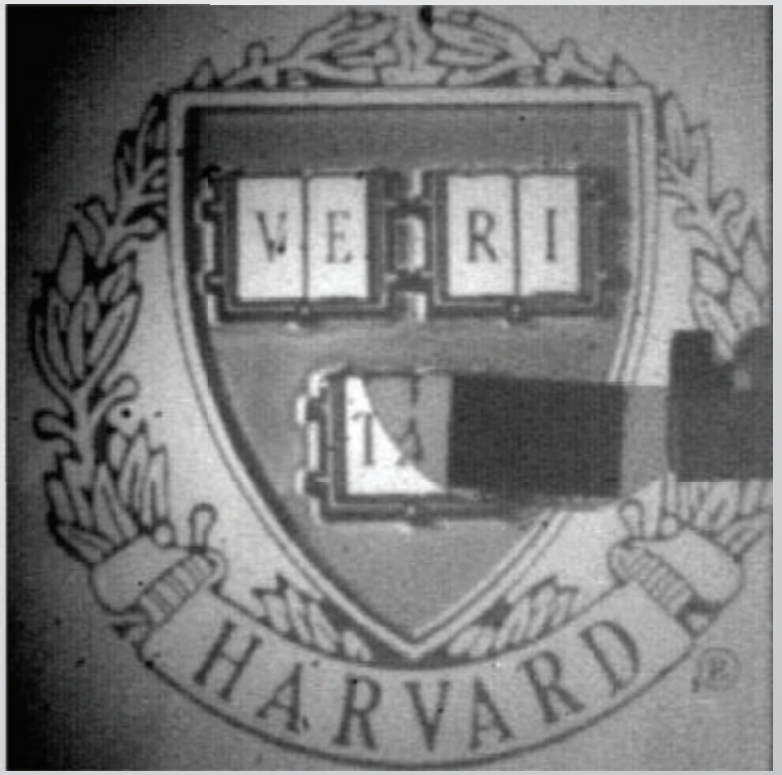
Introduction

…but black silicon blocks IR completely

visible



IR



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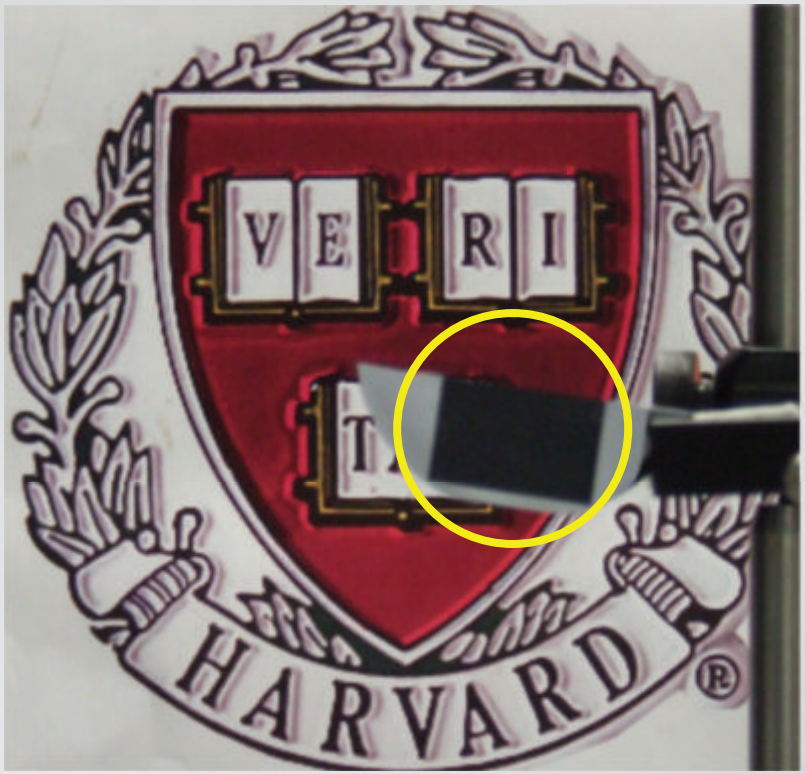
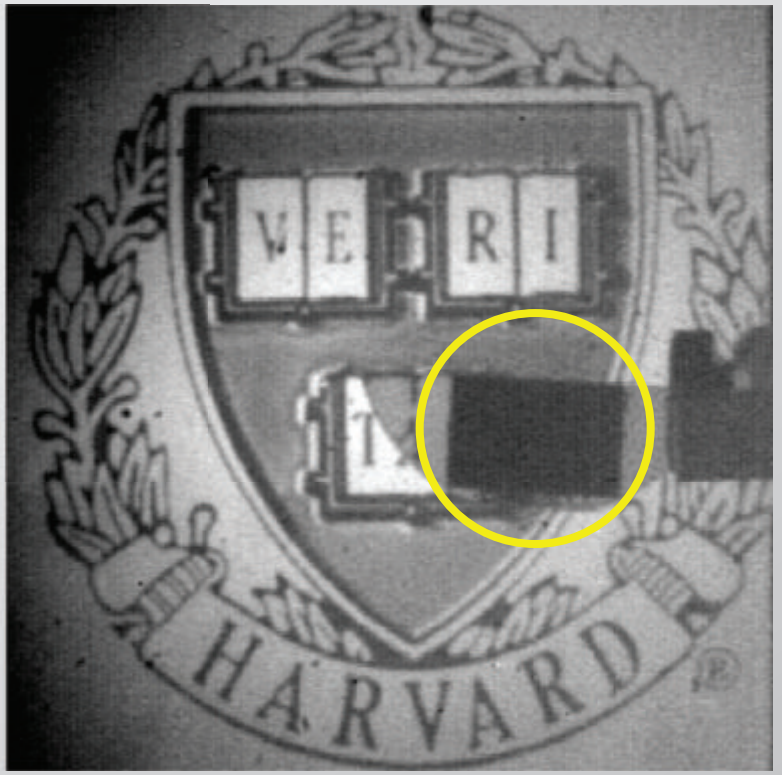


IR



Introduction

black silicon completely black in IR

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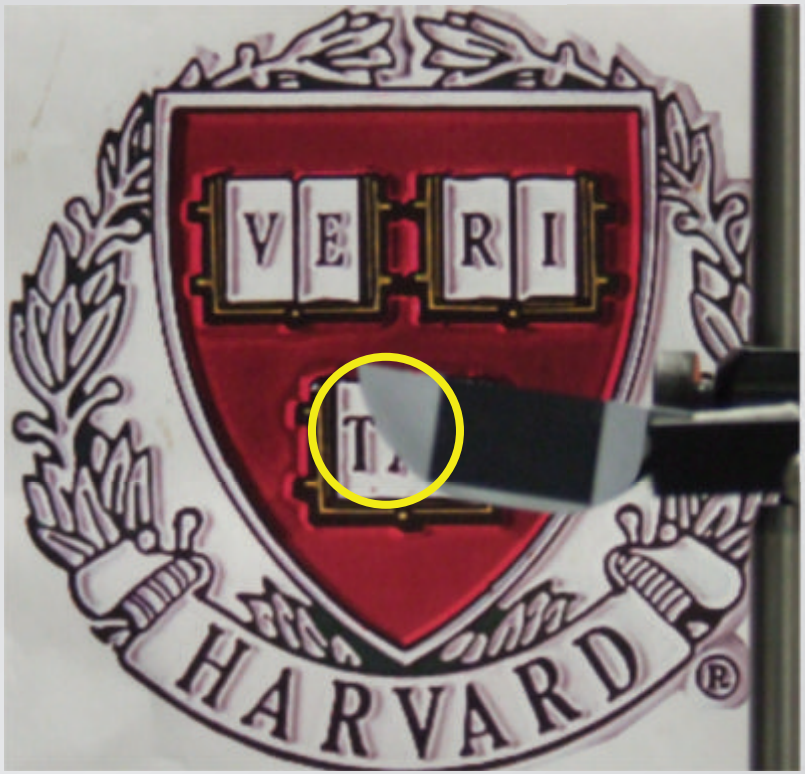
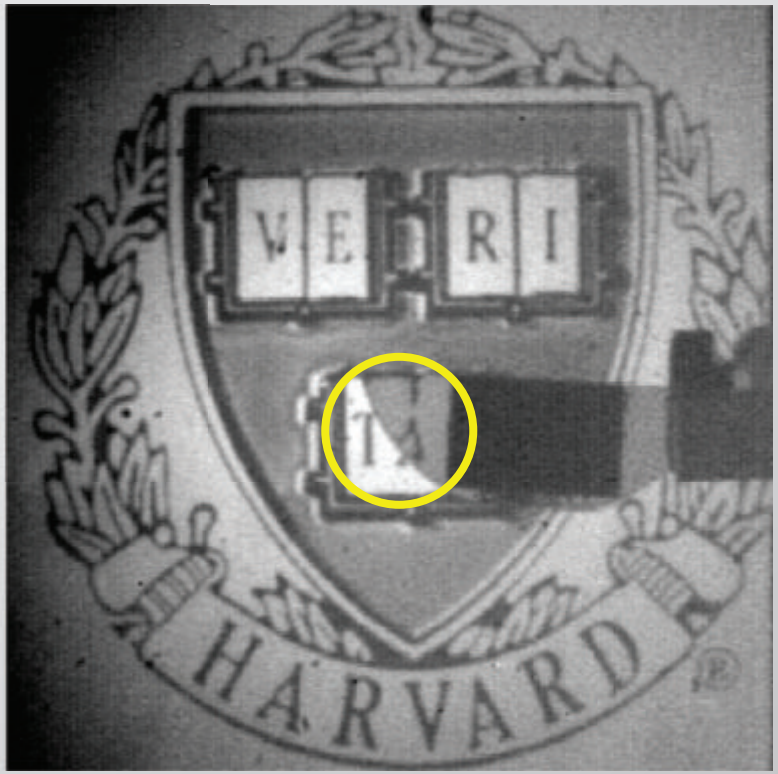


IR



Introduction

band structure changes: defects and/or impurities

Introduction

a decade of research

OPTICAL	ELECTRONIC	STRUCTURAL
UV-VIS-NIR	Hall measurements	SEM
FTIR	conductivity	TEM
photoluminescence	IV rectification	EDX
PTD spectroscopy	c-AFM	SAD
UPS		EXAFS
XPS		AFM
		SIMS
	responsivity	RBS
	photoconductivity	ion channeling

Introduction

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gap		
impurity band		
transitions		

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a decade of research

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gap	carrier concentration	
impurity band	mobilities	
transitions	junction properties	

Introduction

a decade of research

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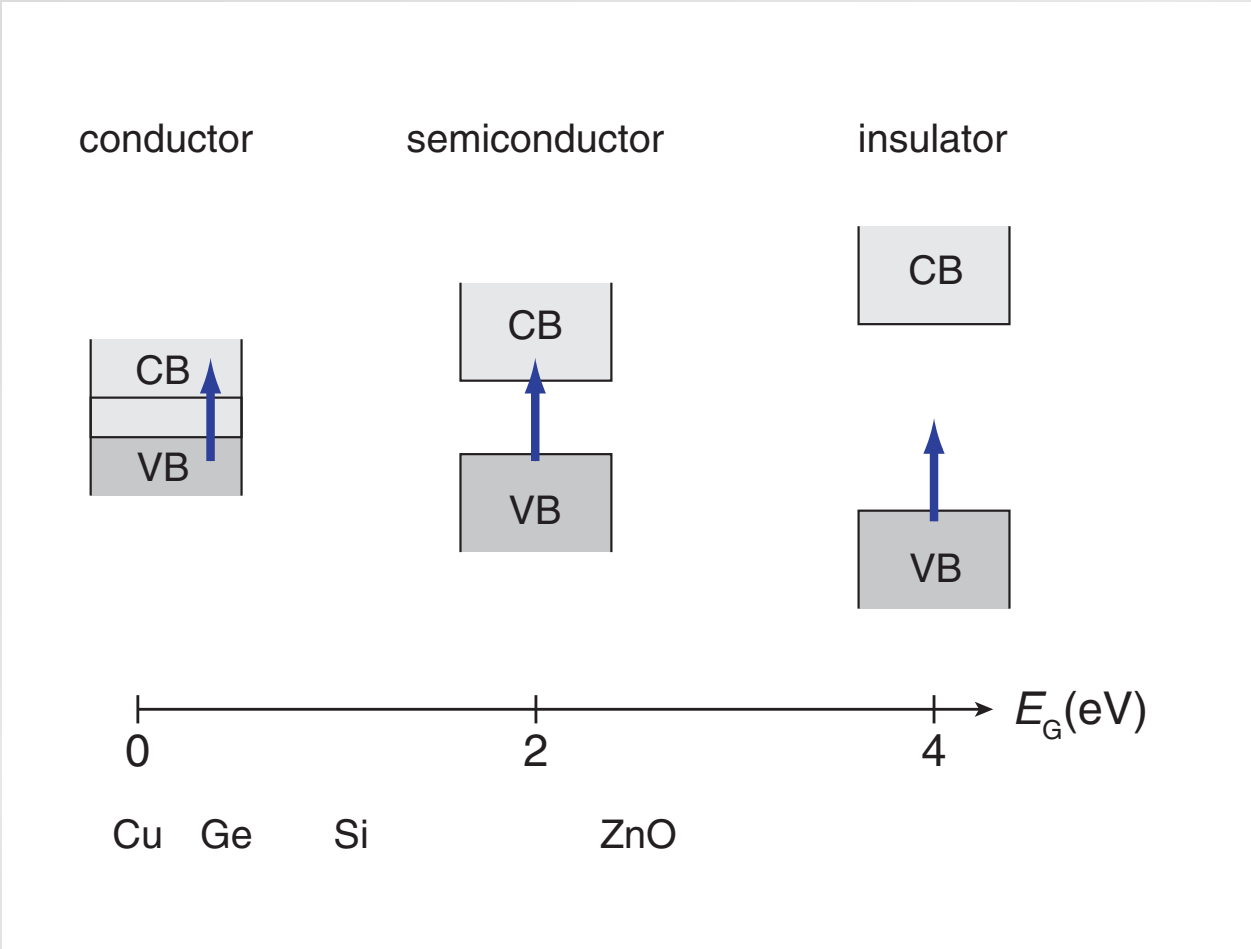
		SIMS
responsivity		RBS
photoconductivity		ion channeling
gap	carrier concentration	morphology
impurity band	mobilities	composition
transitions	junction properties	atomic structure

Introduction

new process & new class of material!



Introduction

substrate/dopant combinations

dopants:

N	O	F
P	S	Cl
	Se	
Sb	Te	

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dopants:

N	O	F
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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

black silicon “flavors”

reactive ion etching

fs/ns laser doping

ion implantation

Introduction

black silicon “flavors”

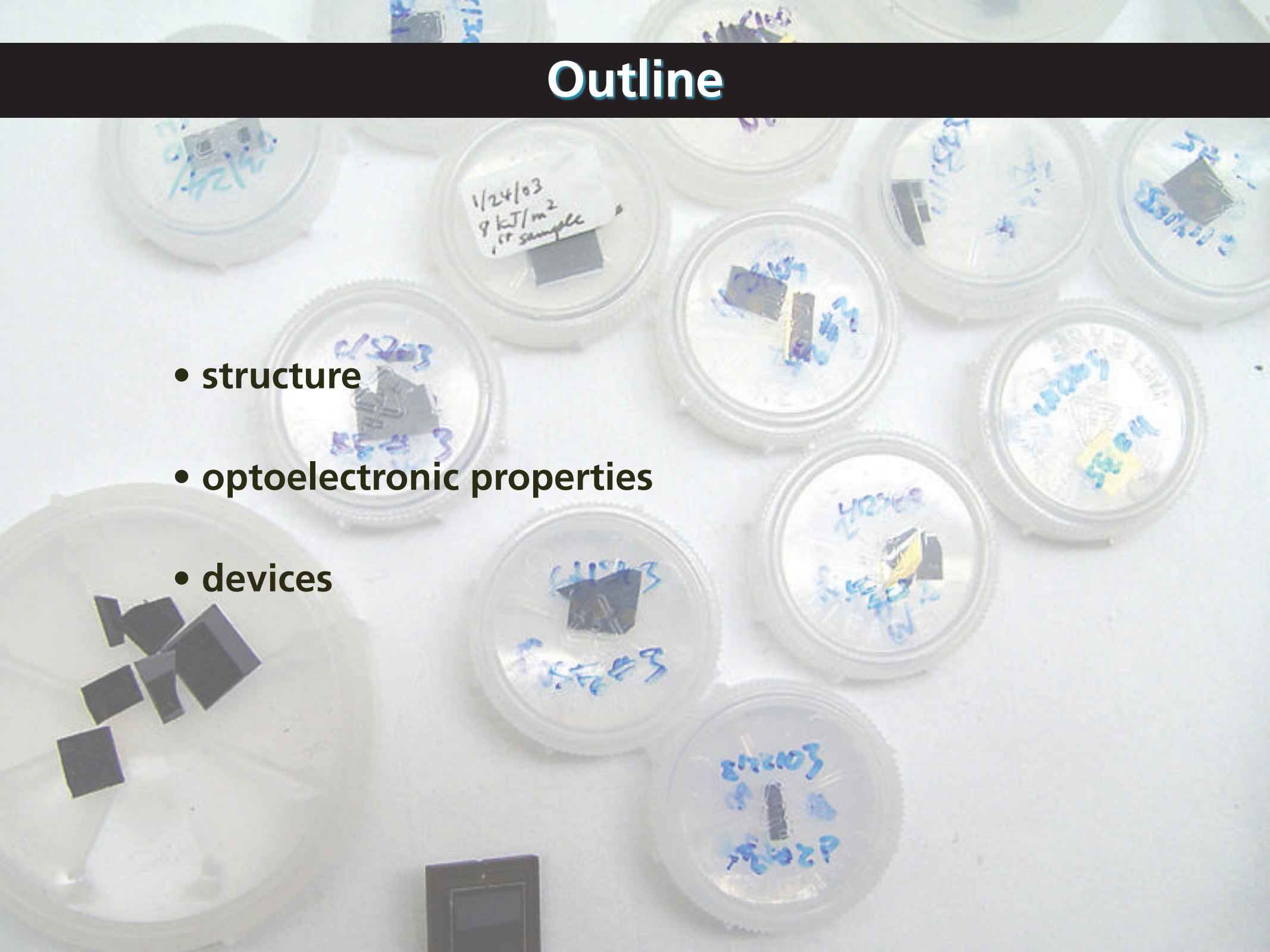
	surface structure	doping
reactive ion etching		
fs/ns laser doping		
ion implantation		

Introduction

black silicon “flavors”

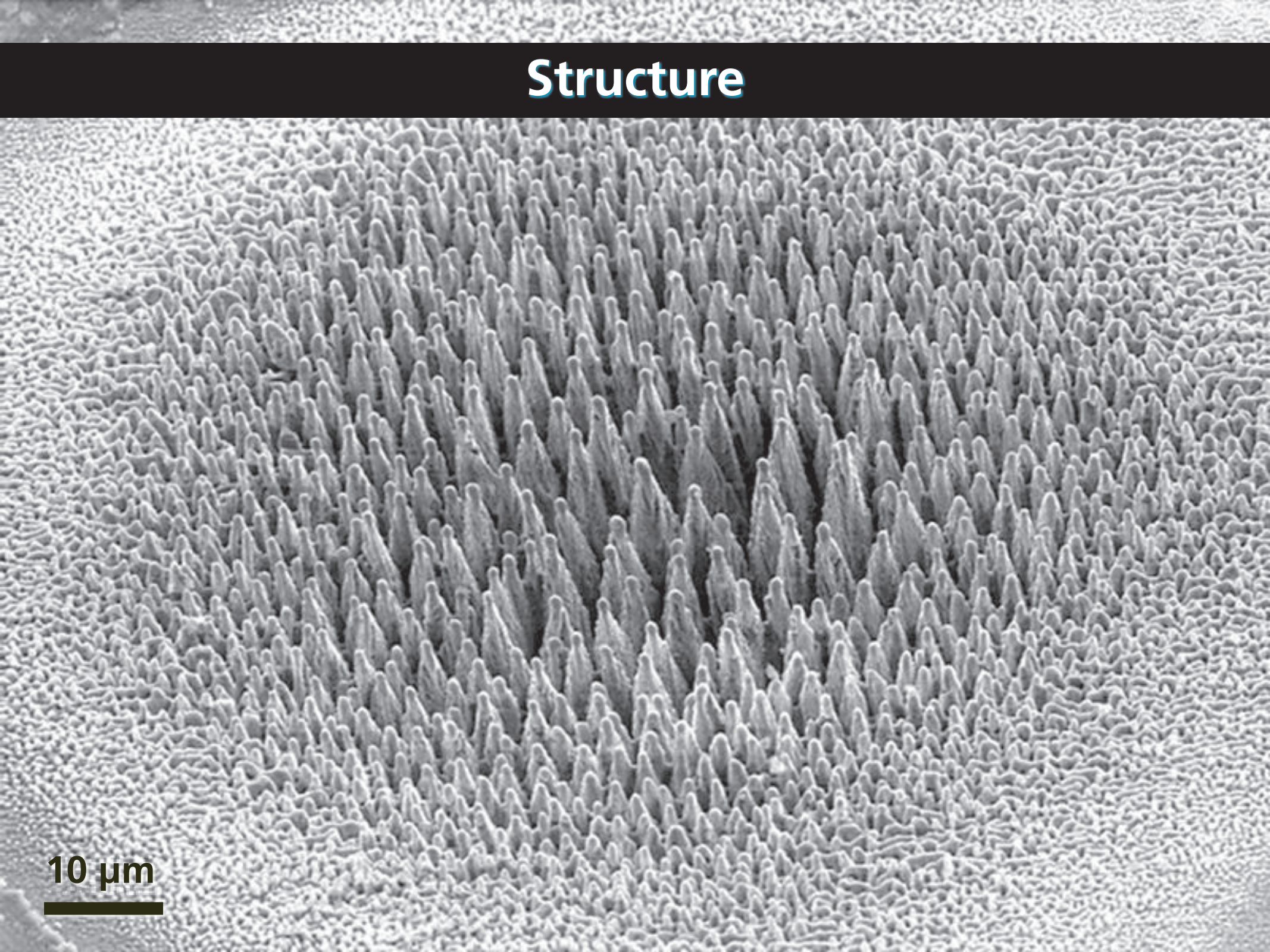
	surface structure	doping
reactive ion etching	✓	?
fs/ns laser doping	✓	✓
ion implantation	✗	✓

Outline

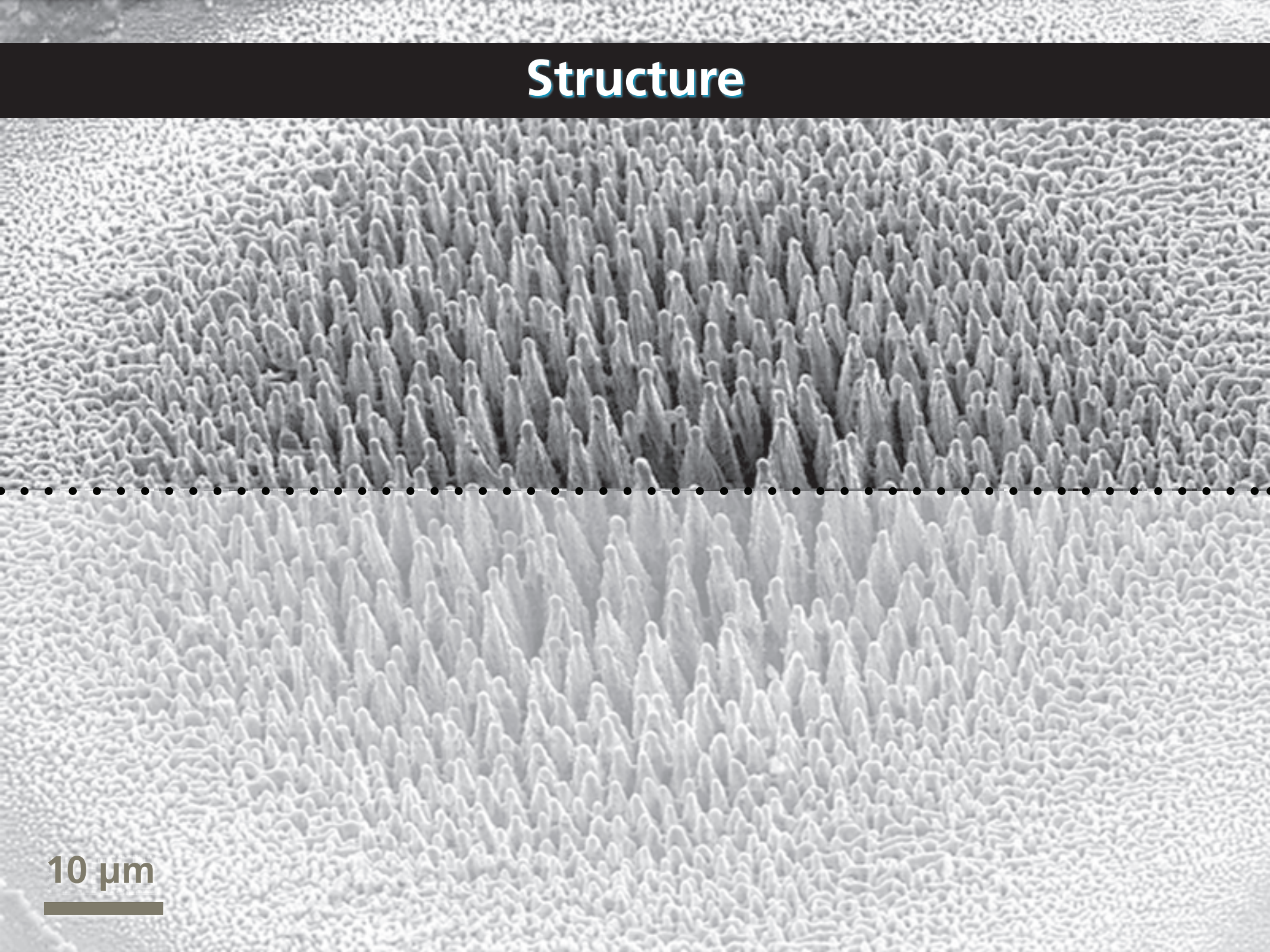


- structure
- optoelectronic properties
- devices

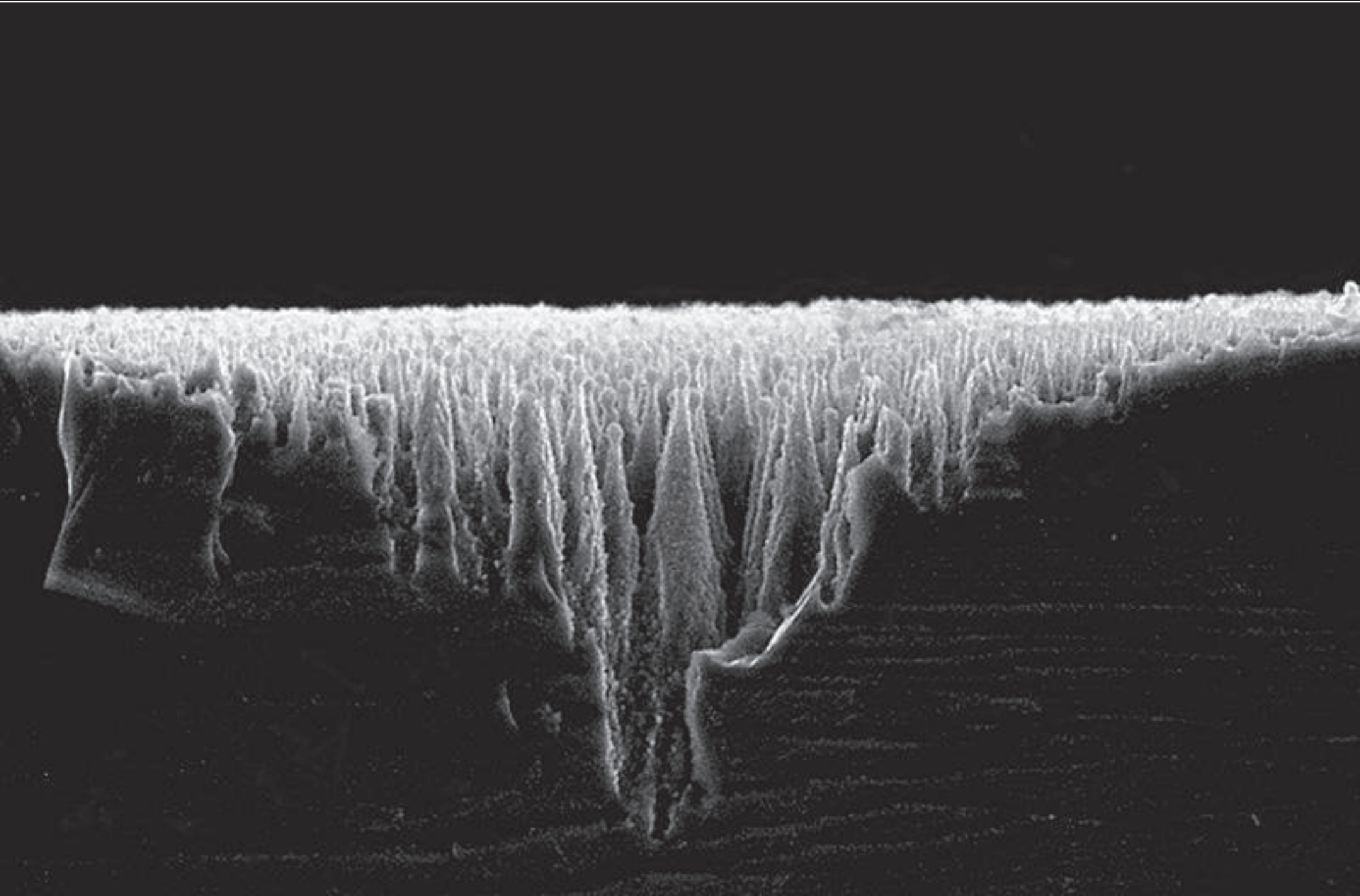
Structure



Structure



Structure



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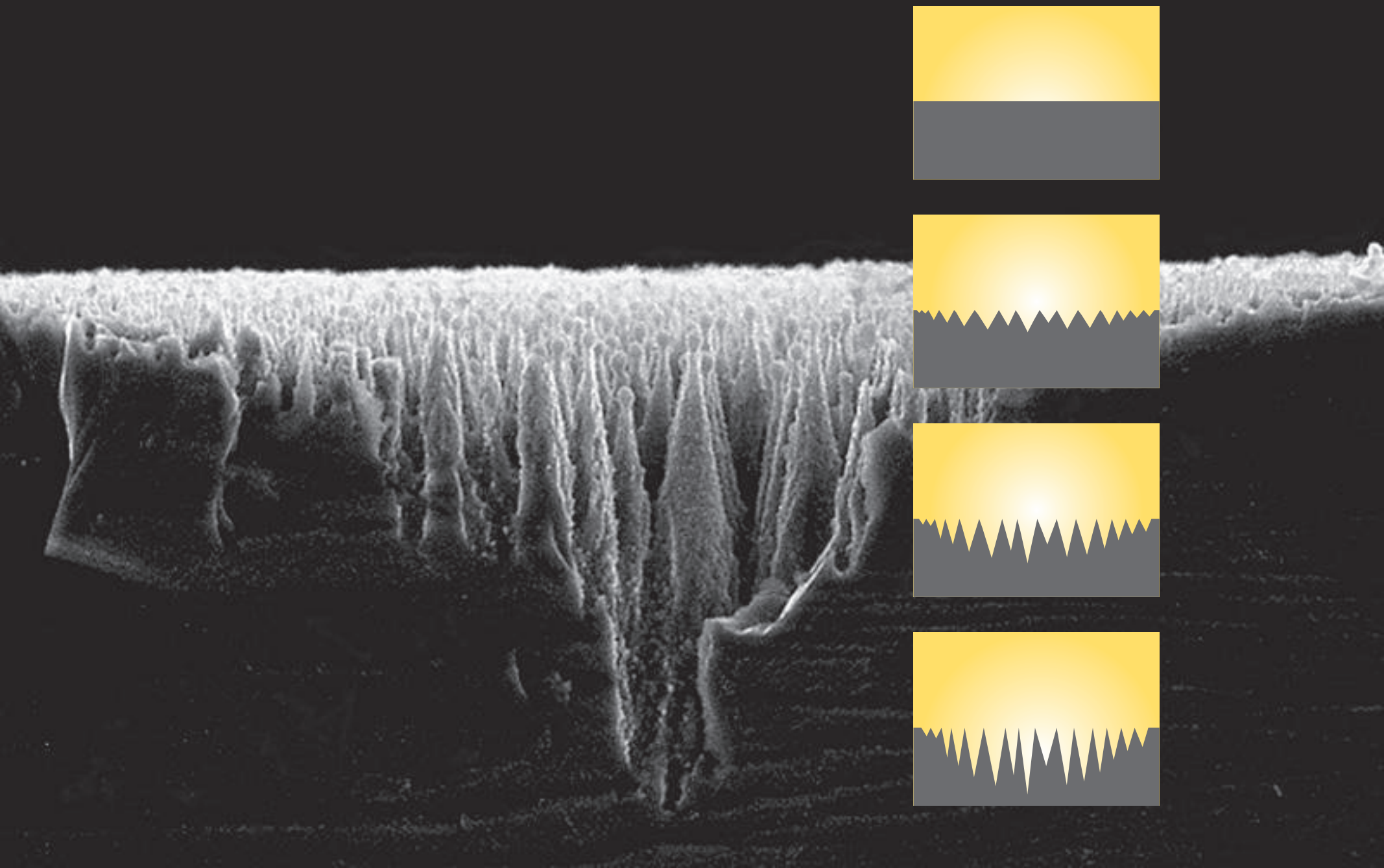

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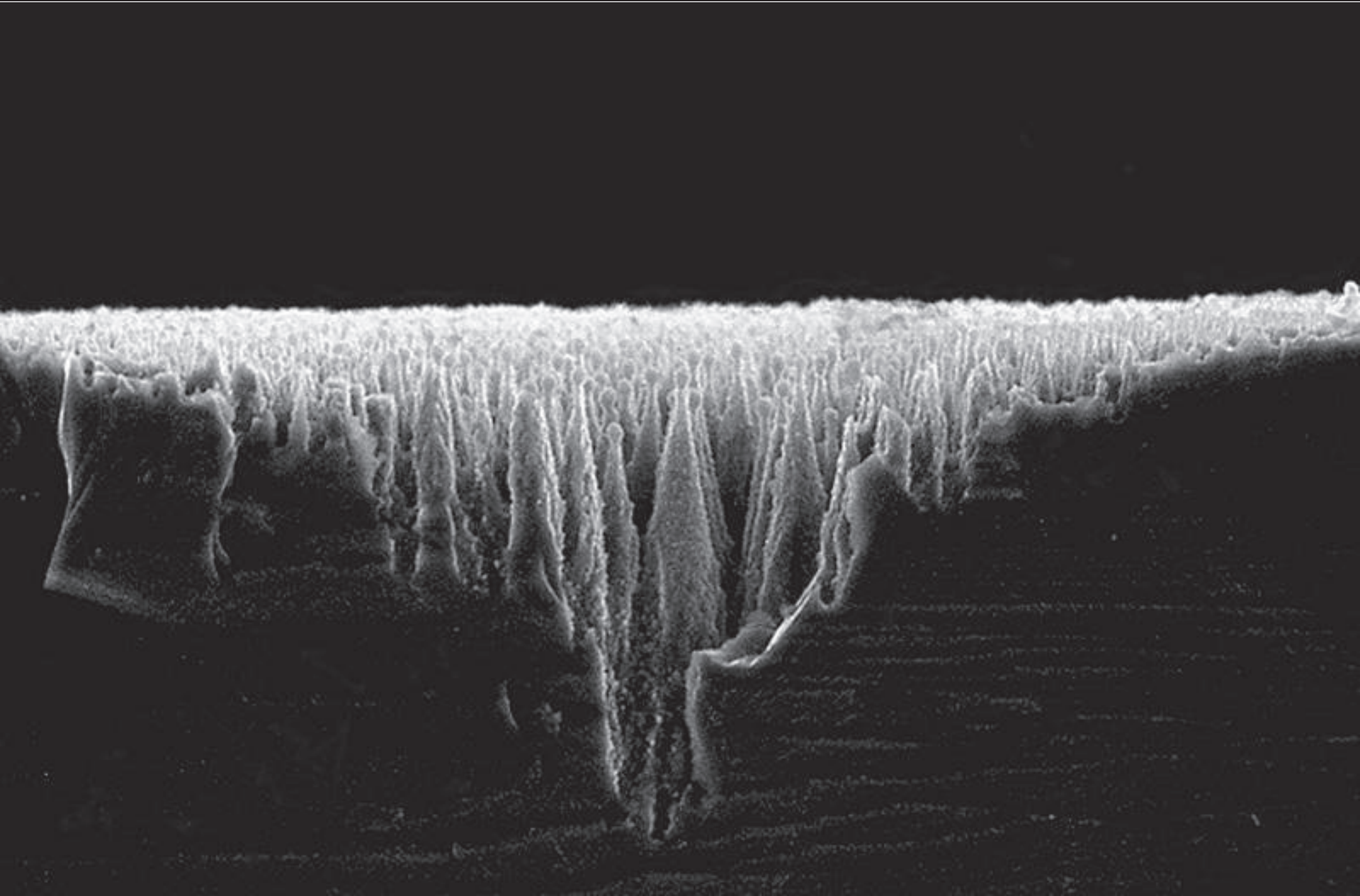

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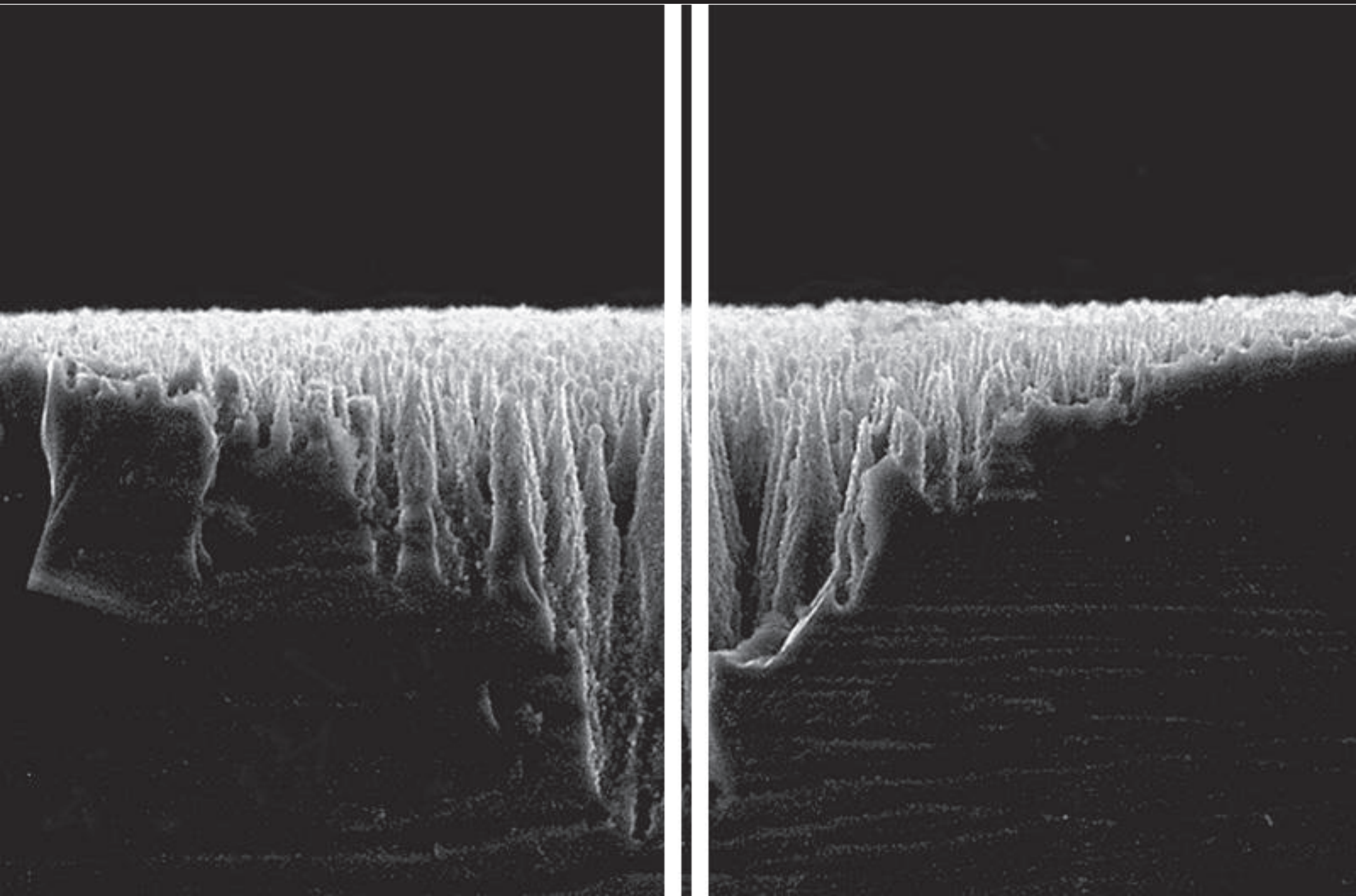
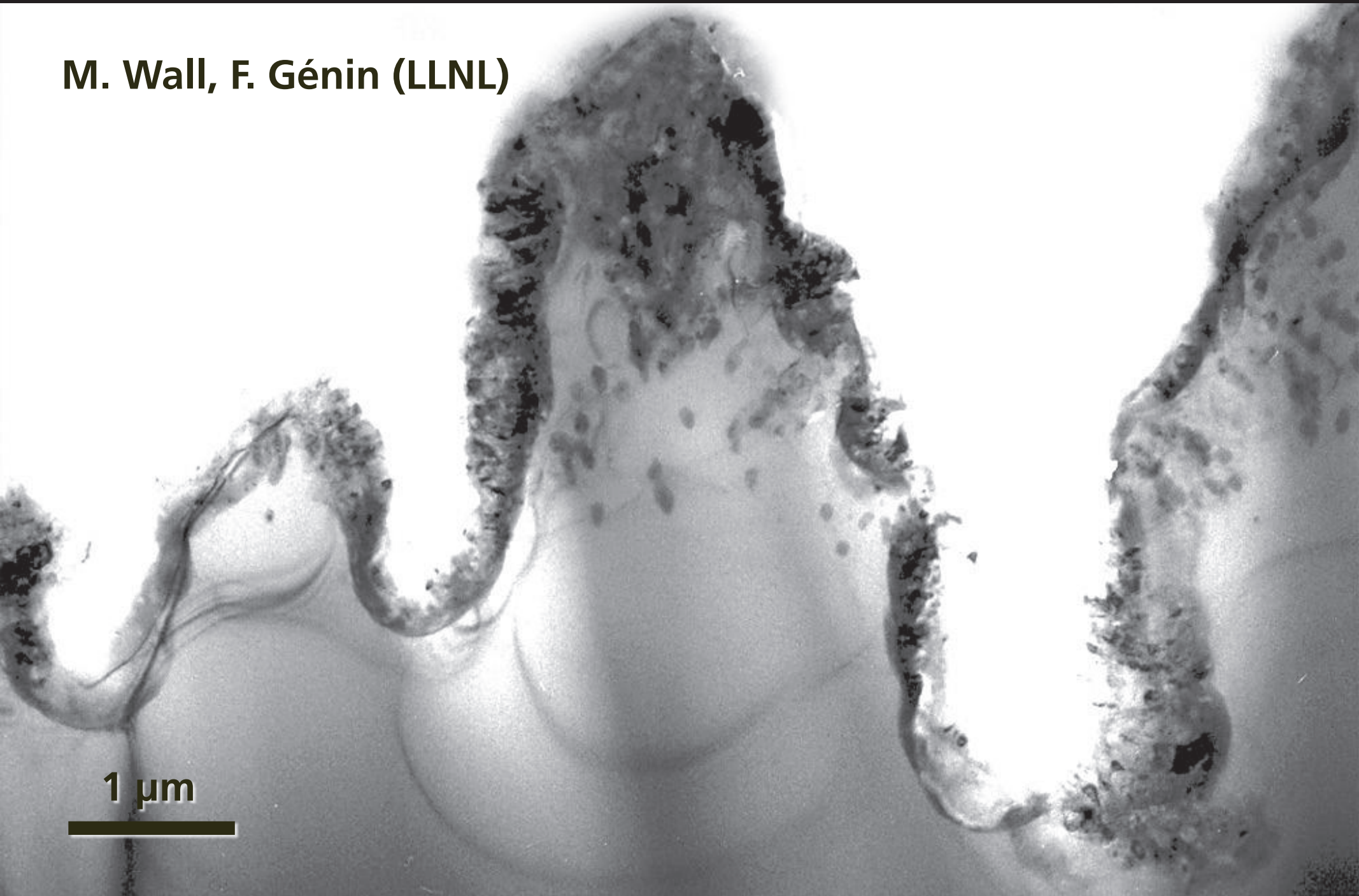


Structure

cross-sectional
Transmission Electron
Microscopy

Structure



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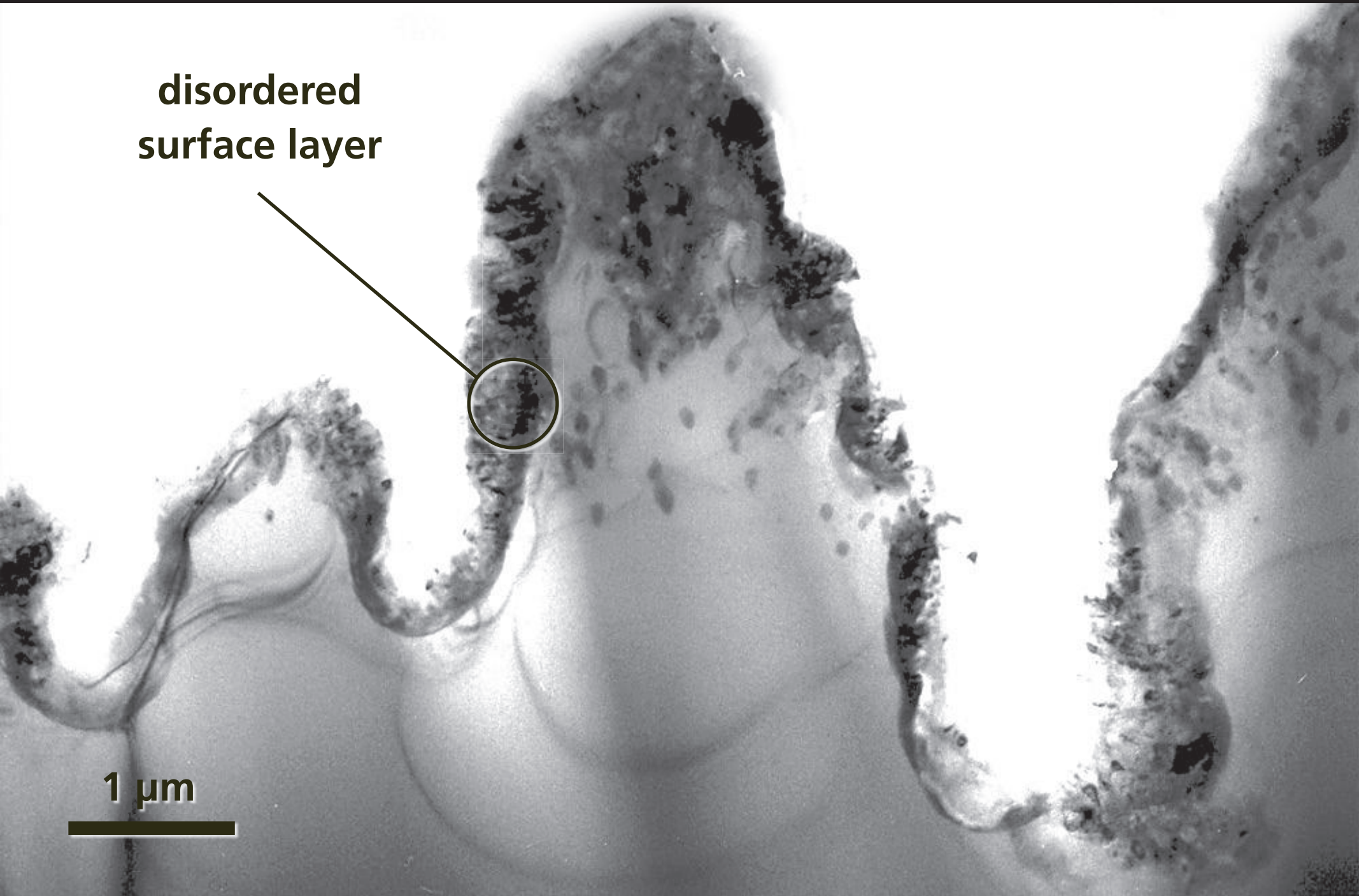

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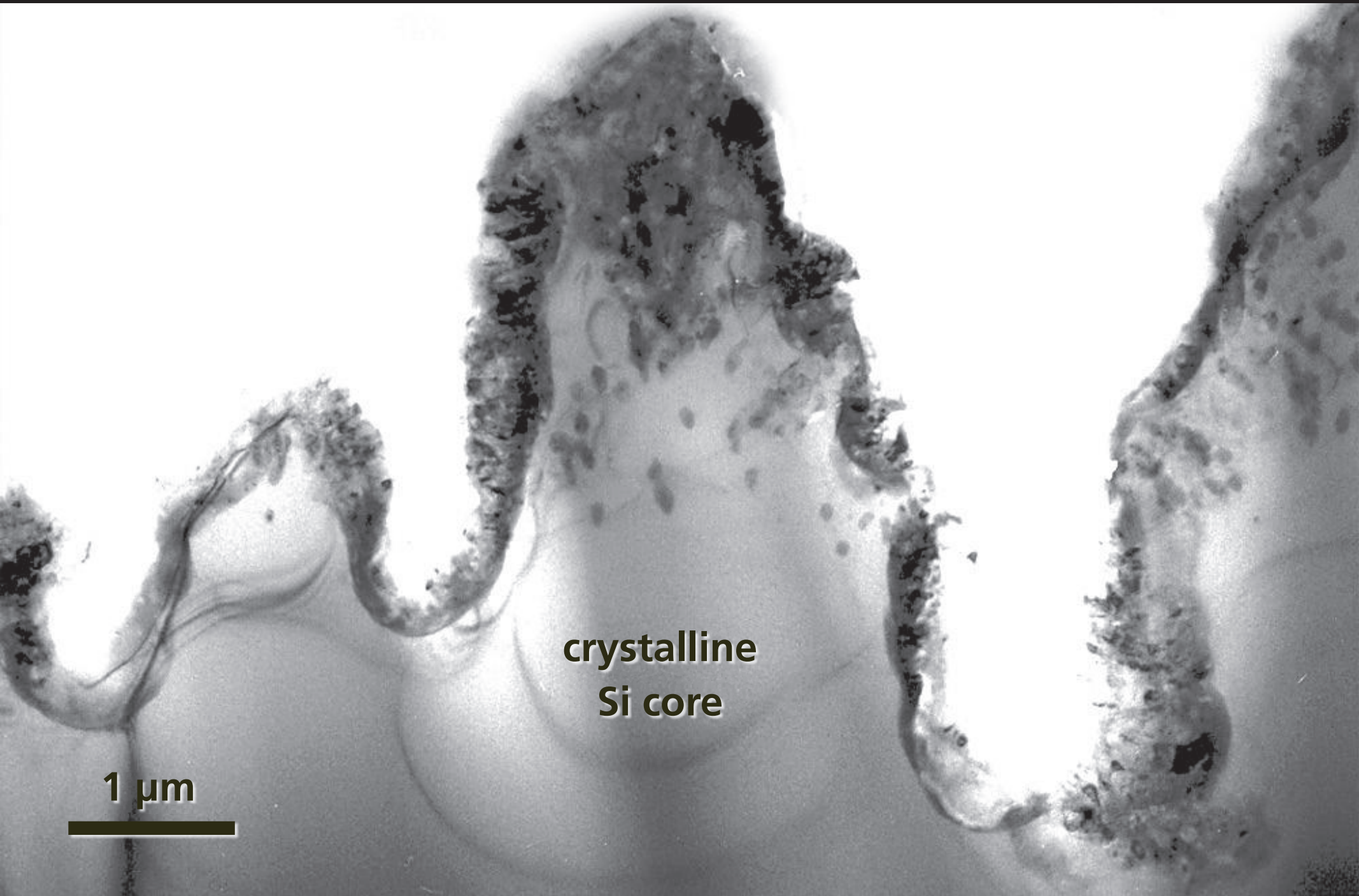

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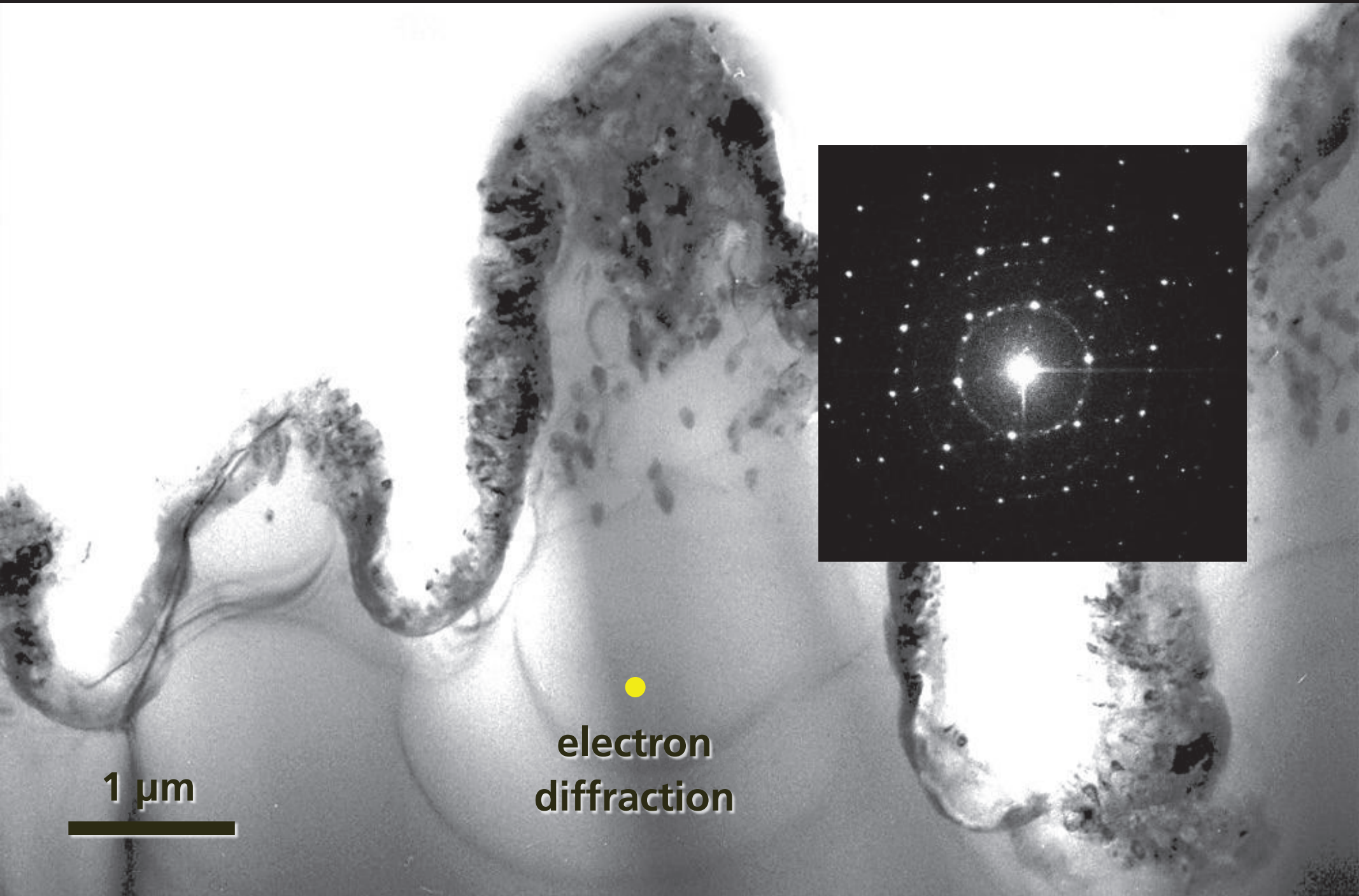

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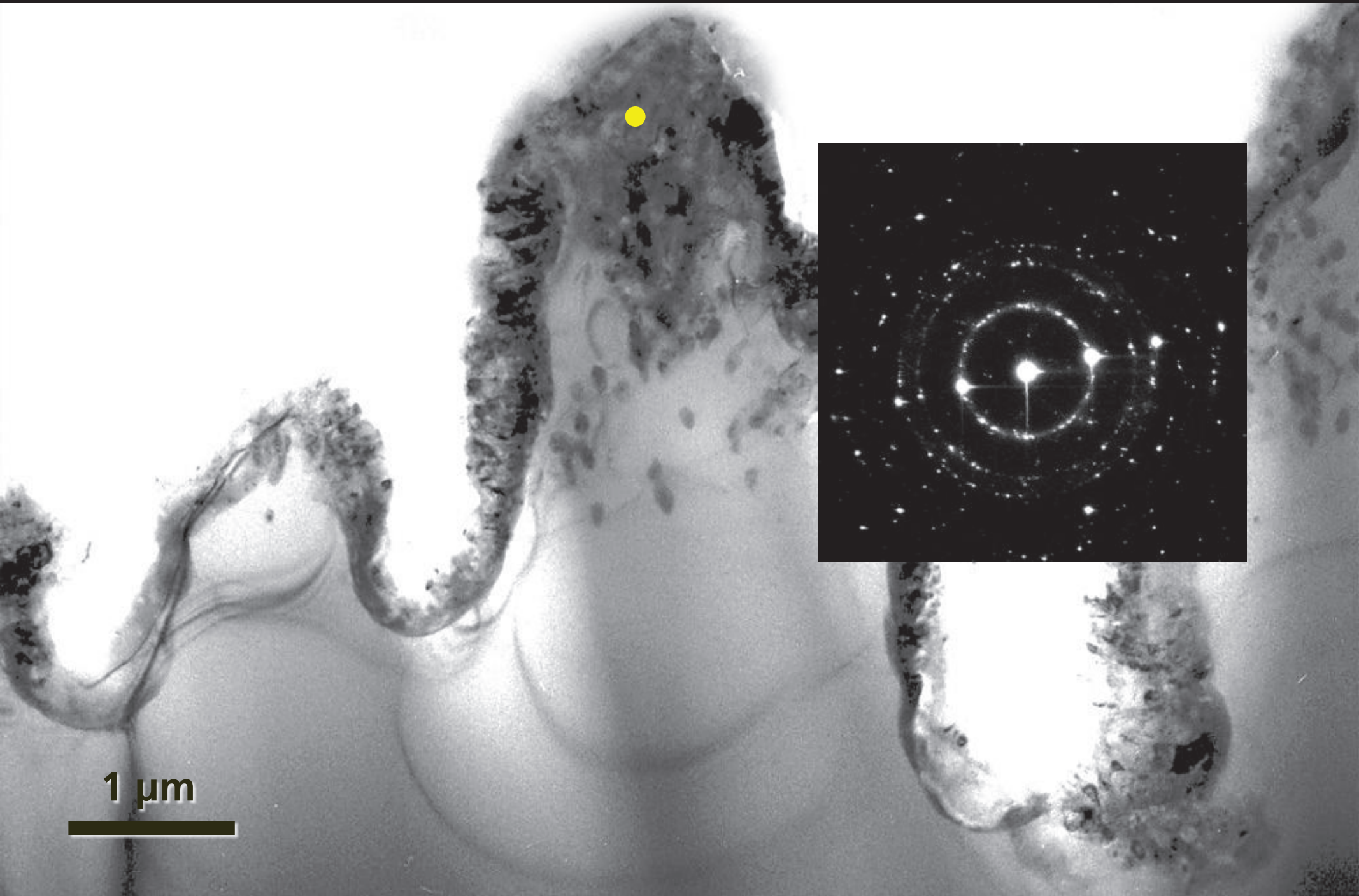

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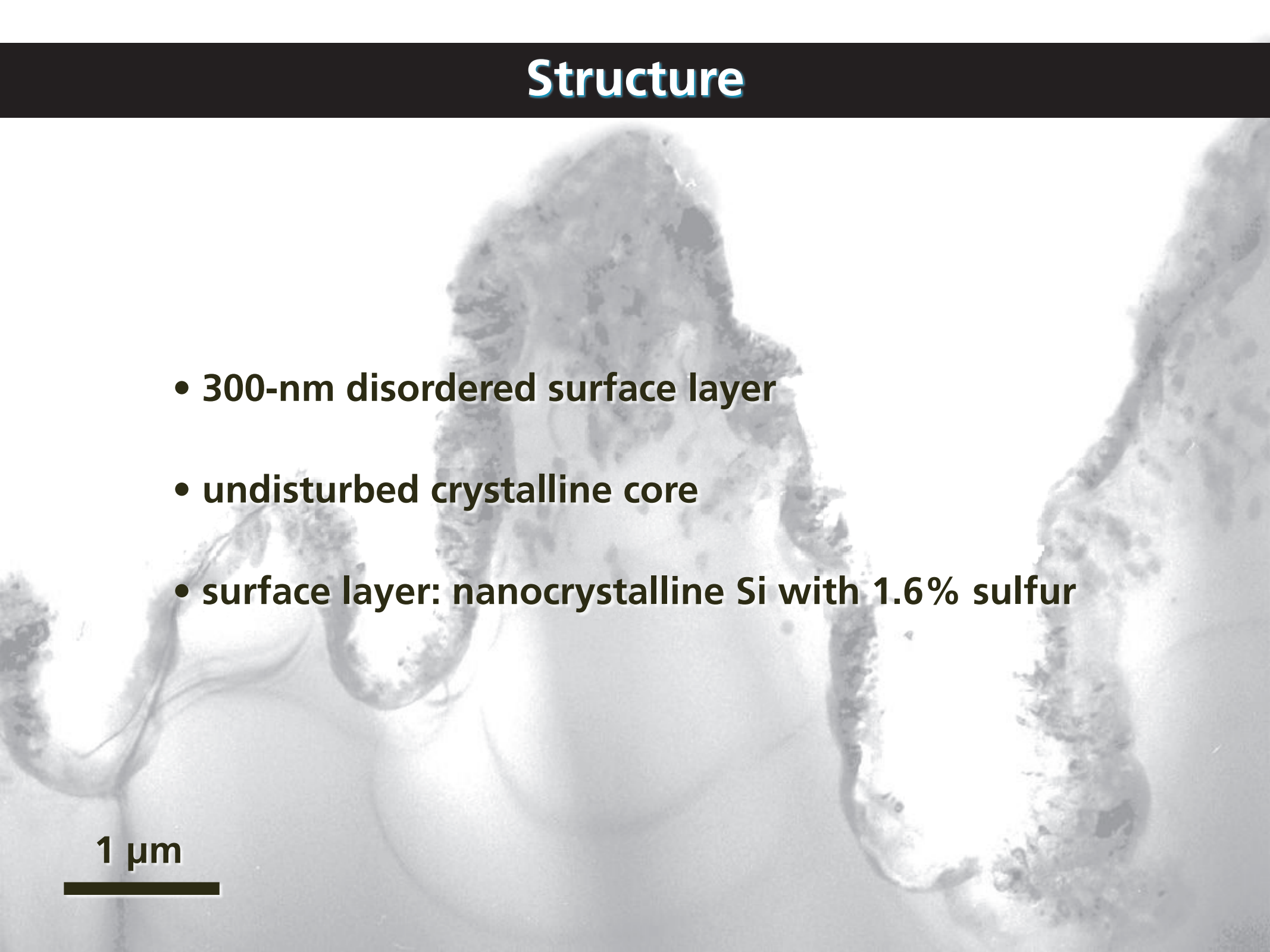


- 300-nm disordered surface layer
- undisturbed crystalline core
- surface layer: nanocrystalline Si with 1.6% sulfur

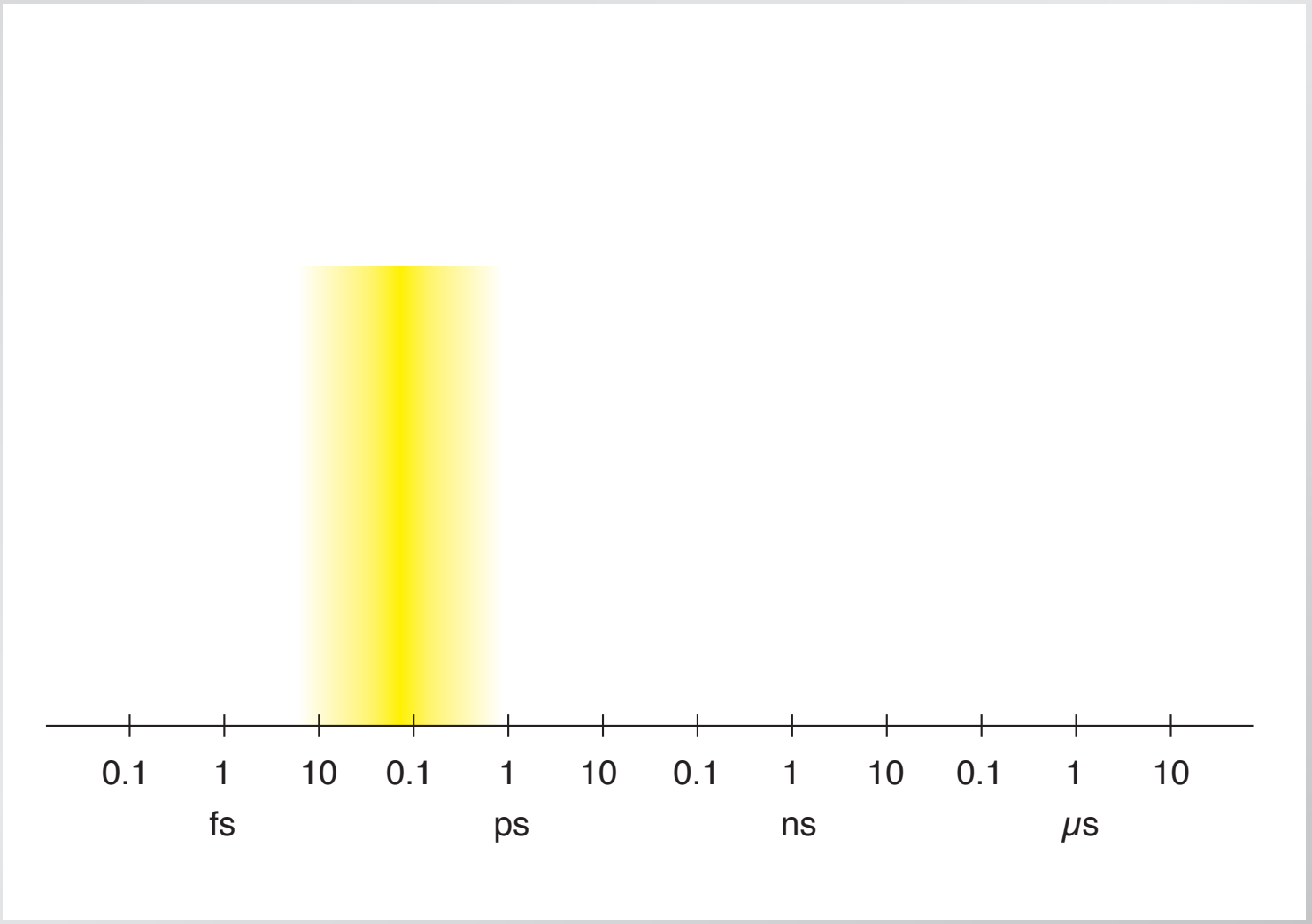
1 µm

Structure

two processes: melting and ablation

Structure

relevant time scales



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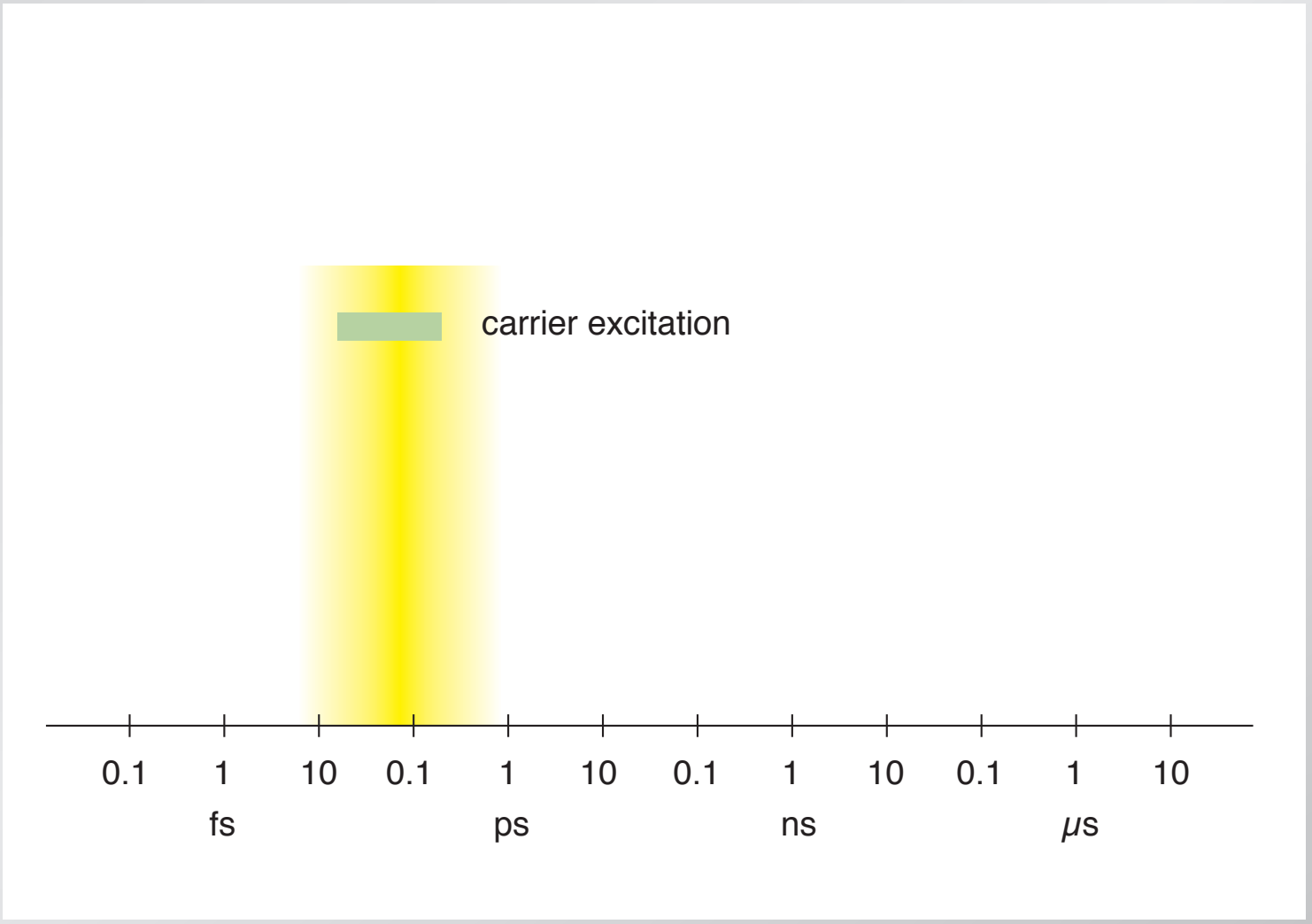

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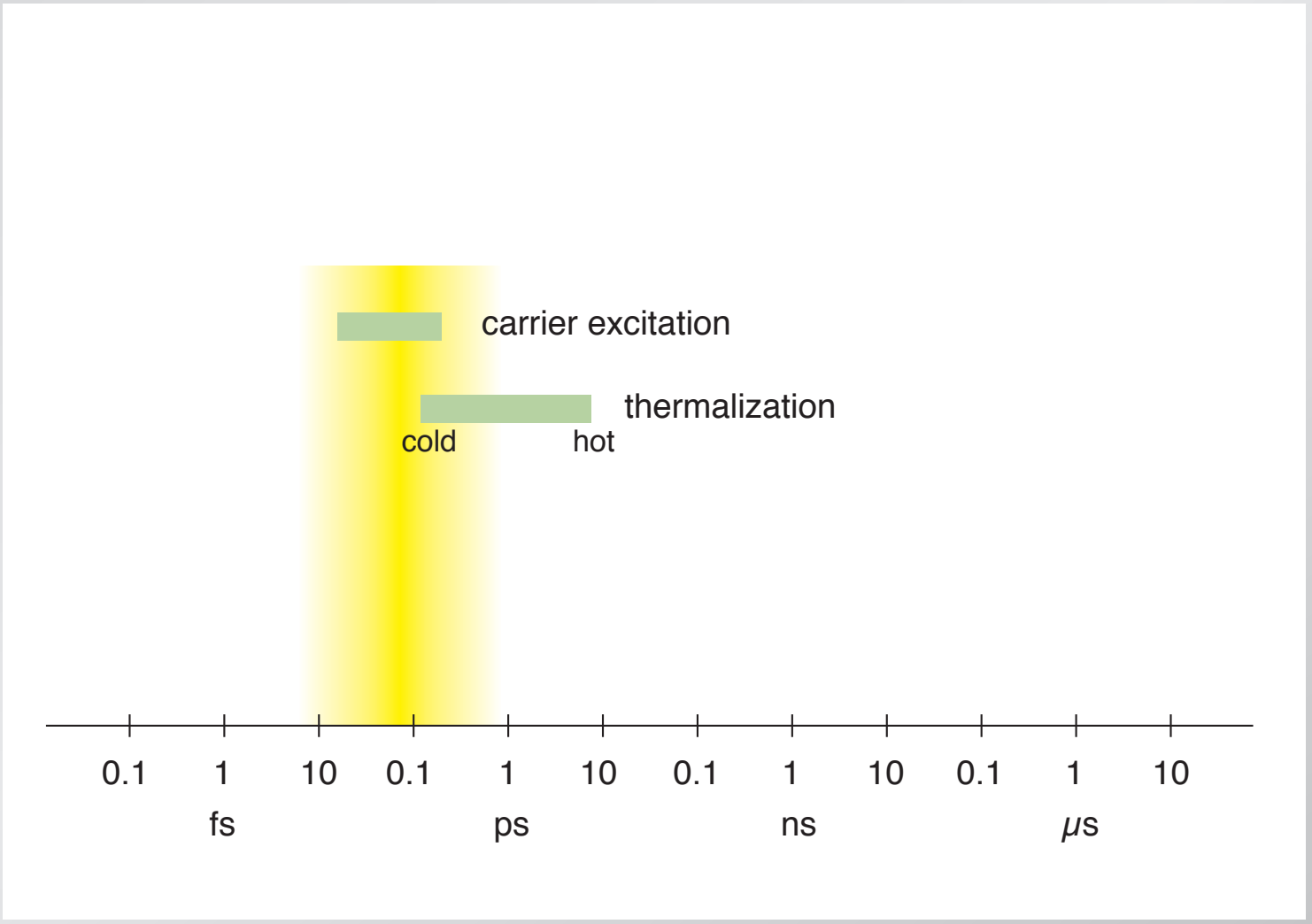

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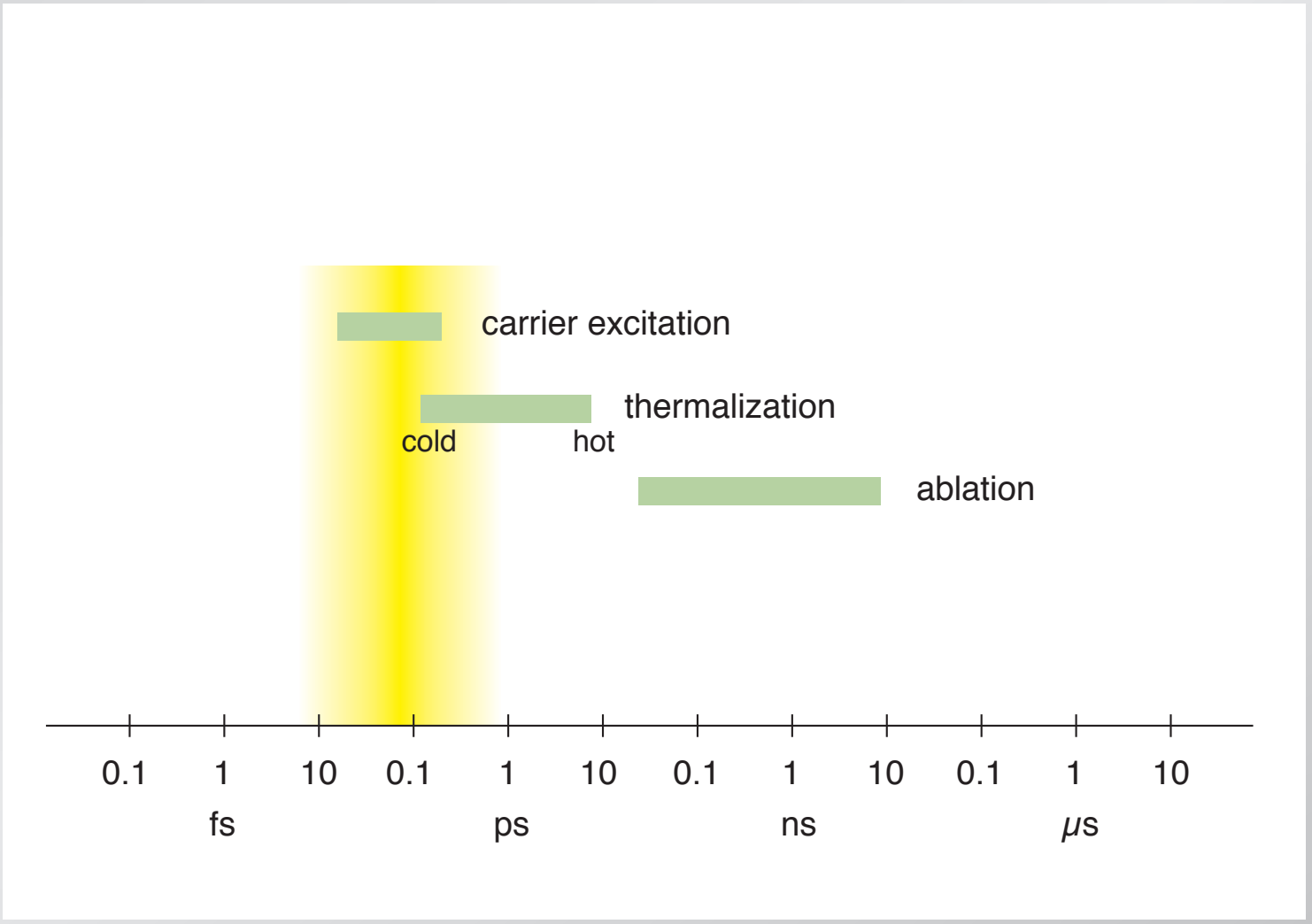

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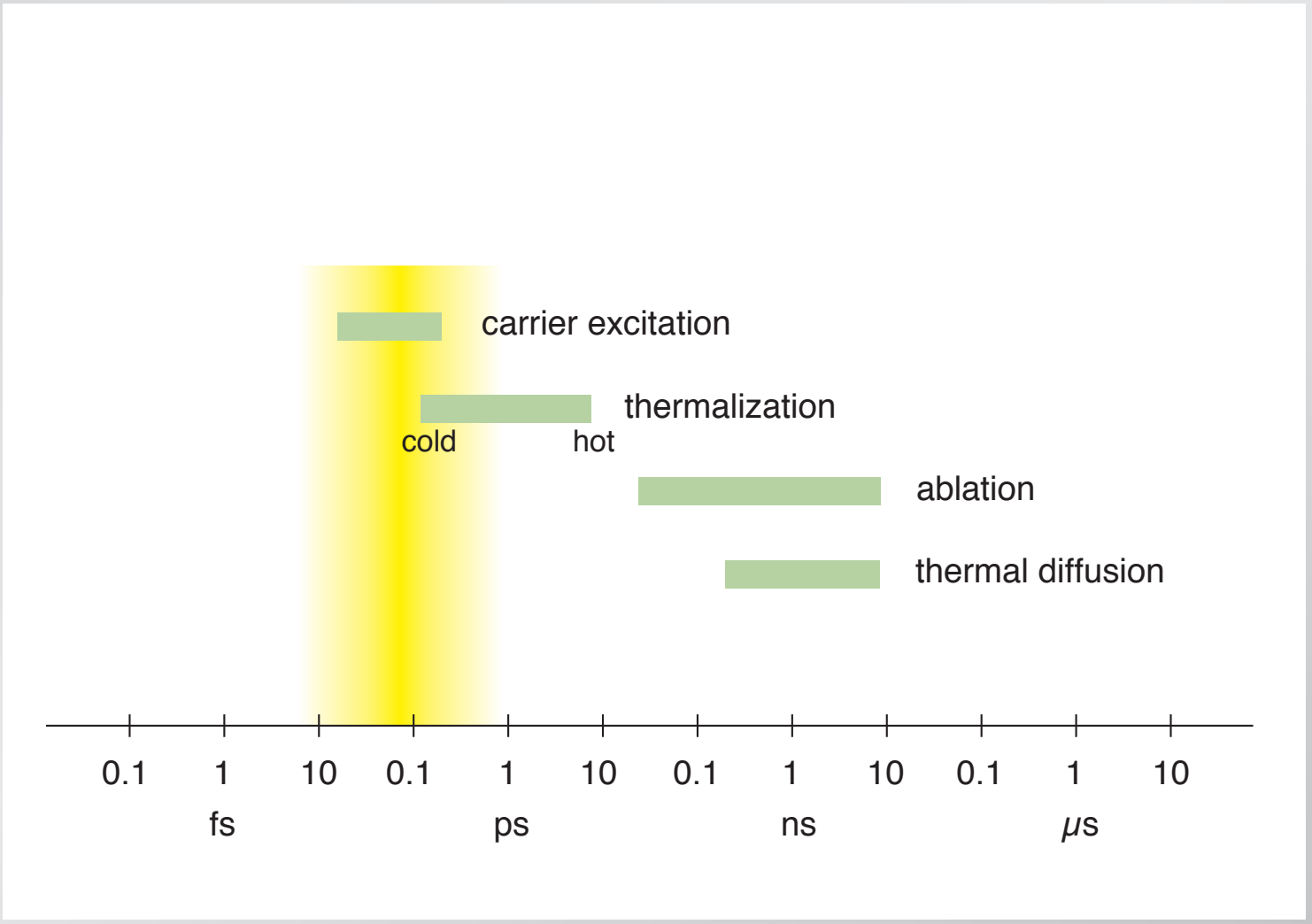

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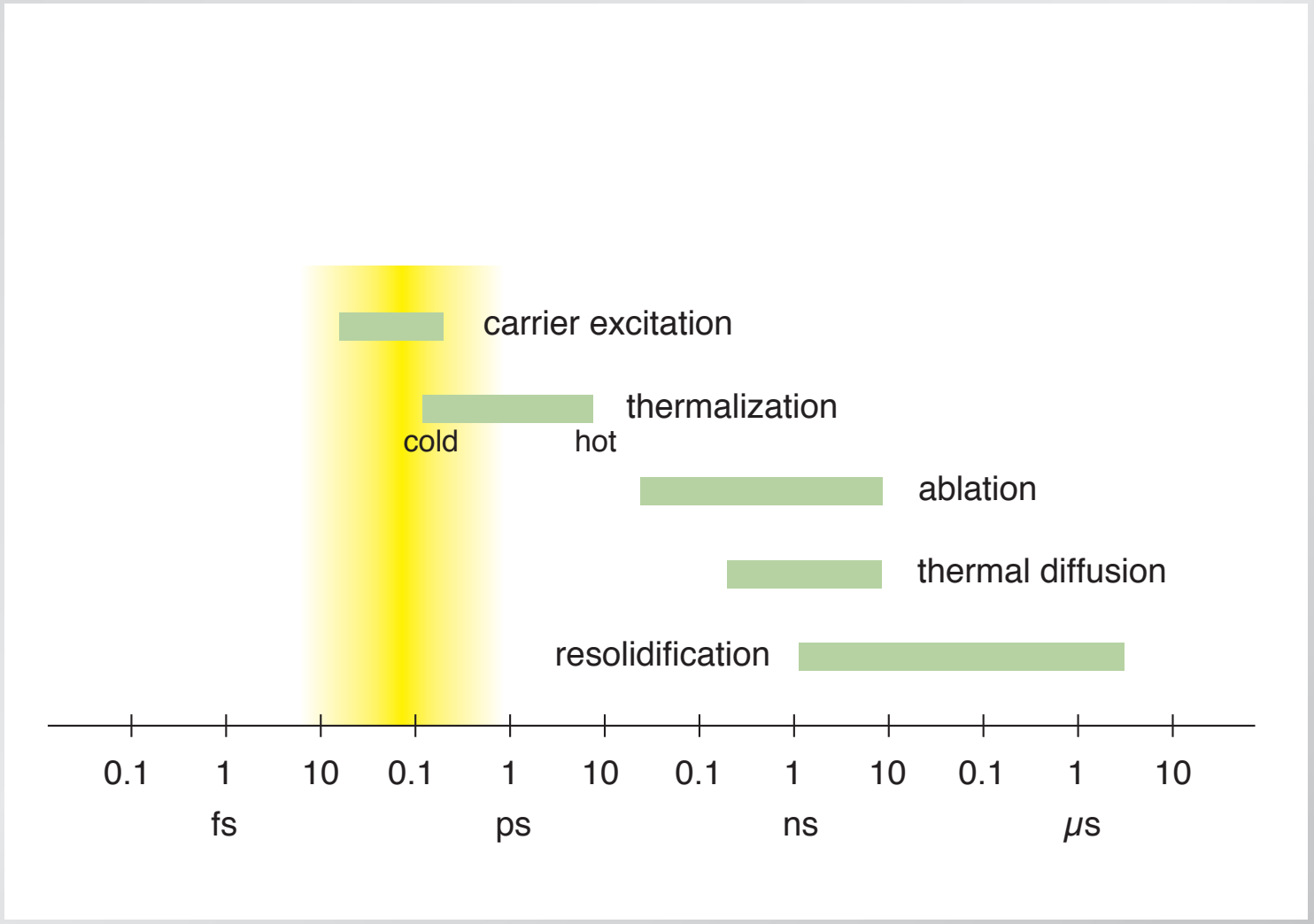

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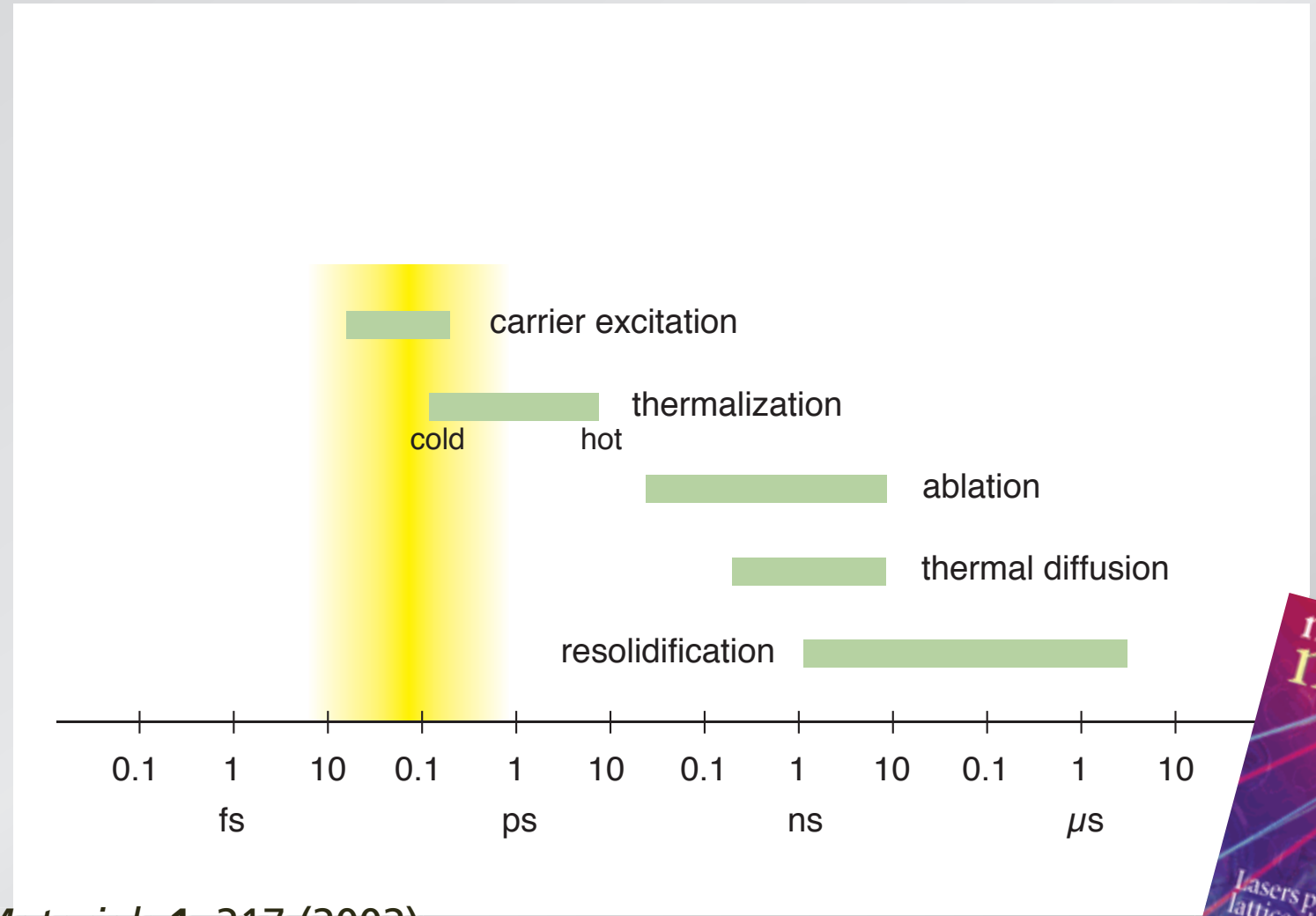

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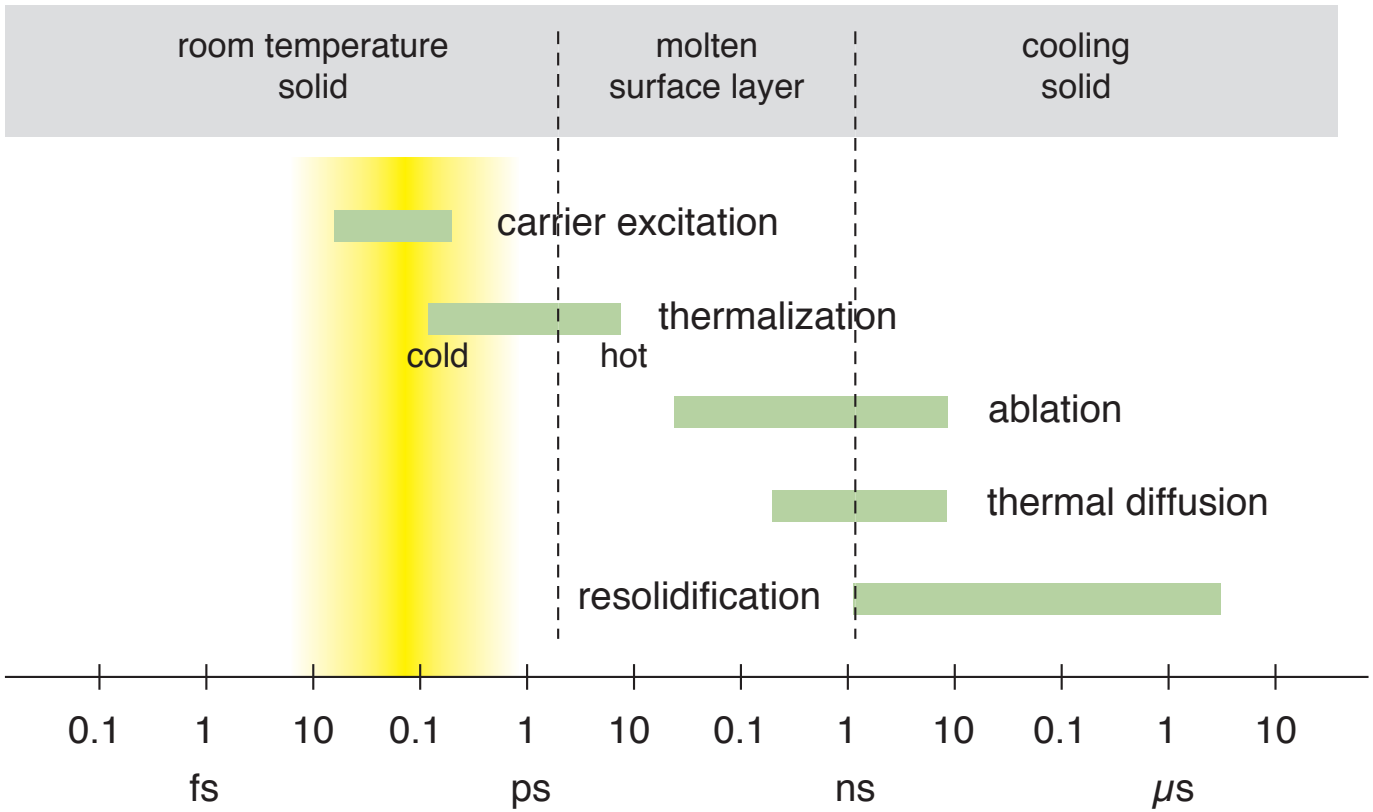
Structure

relevant time scales



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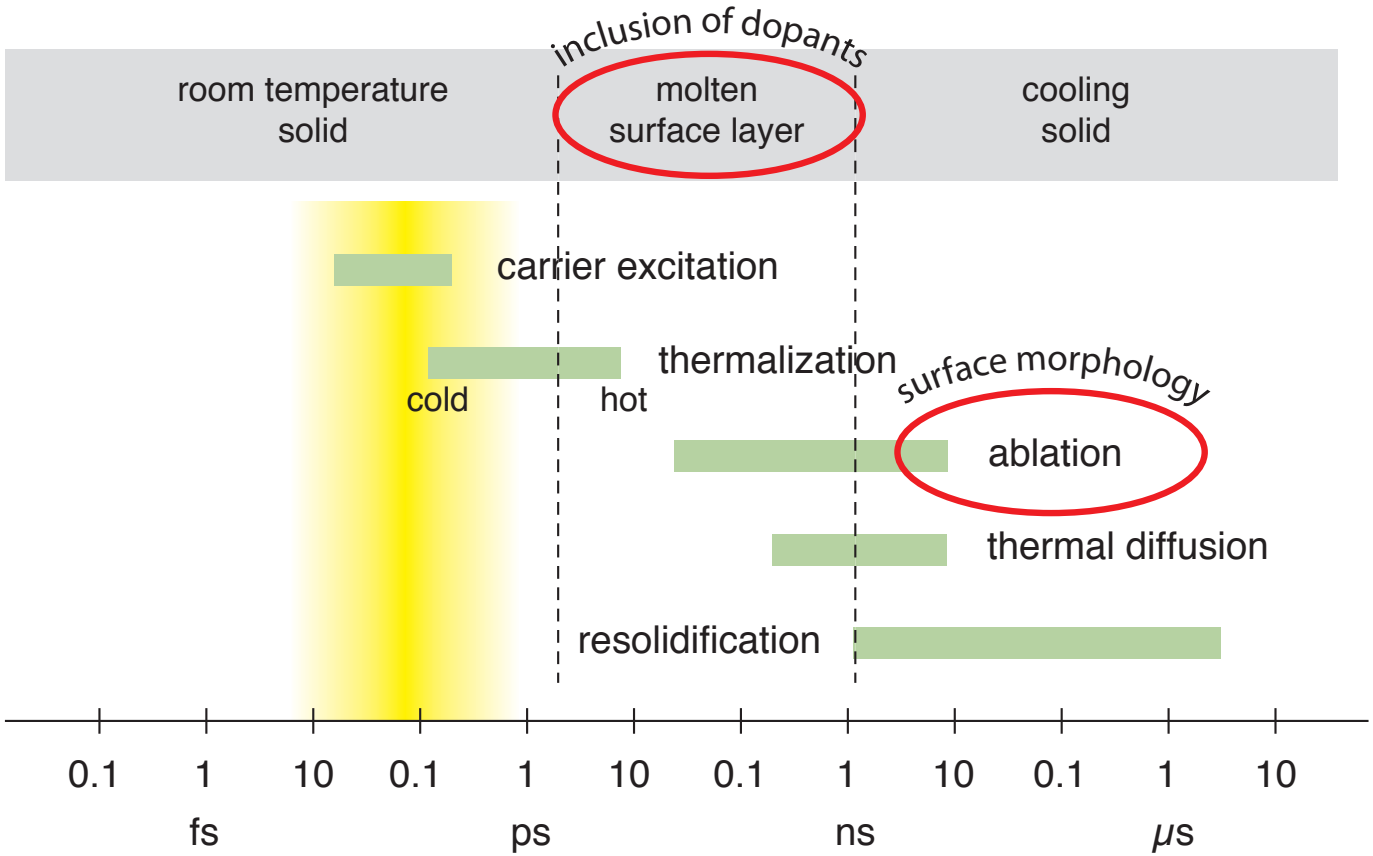


Structure

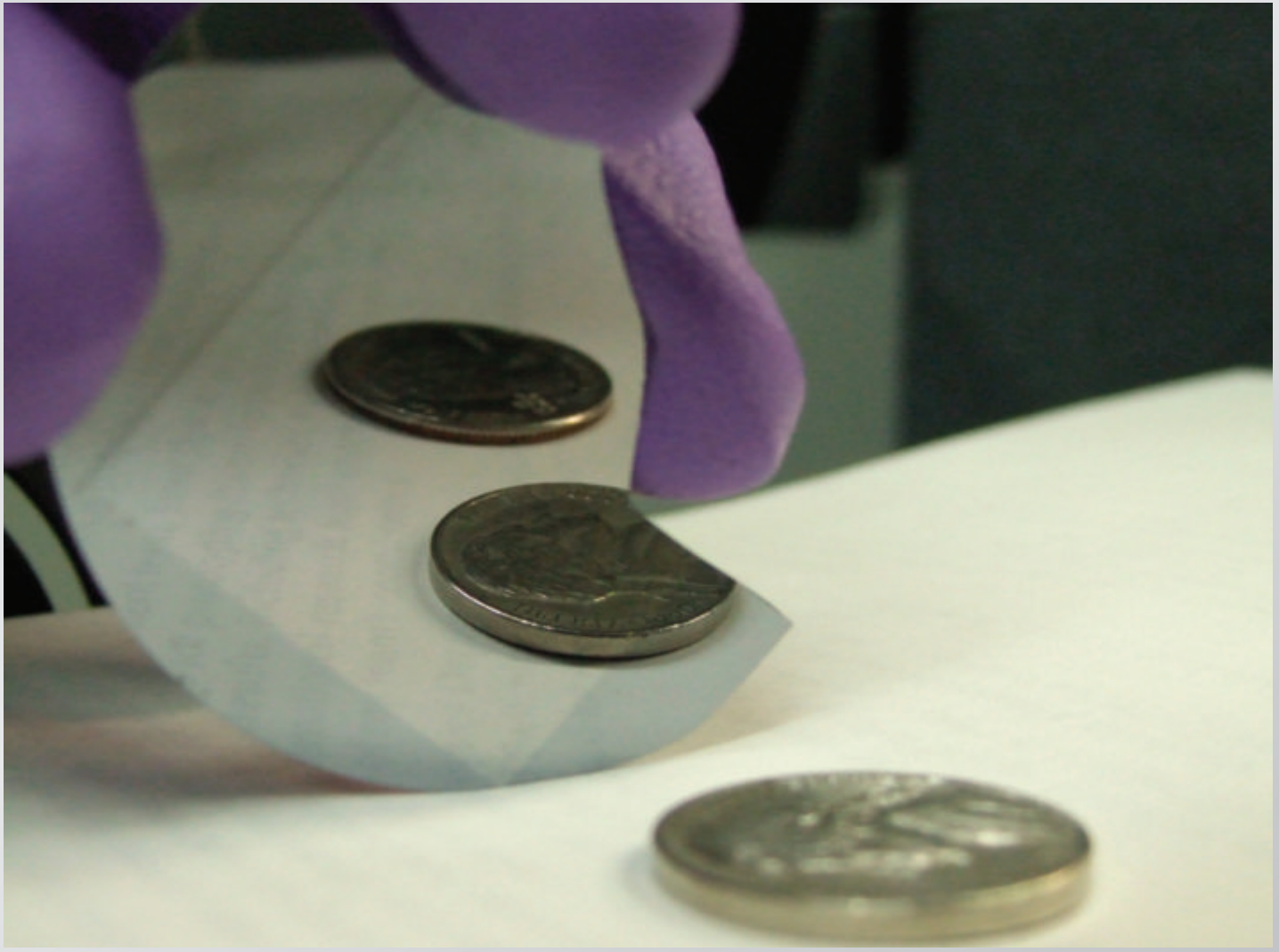
different thresholds:

melting: 1.5 kJ/m^2

ablation: 3.1 kJ/m^2

Structure

decouple ablation from melting



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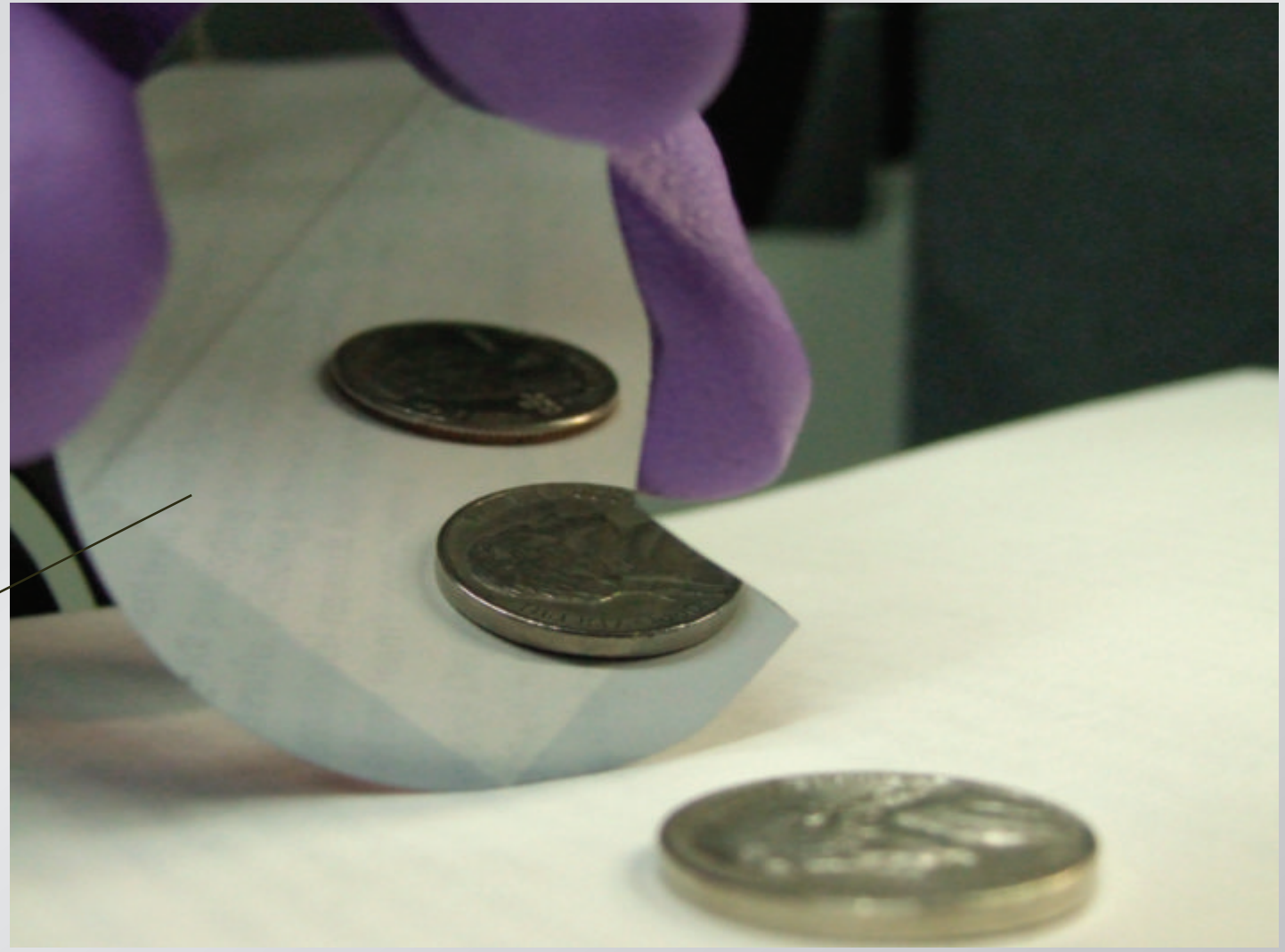

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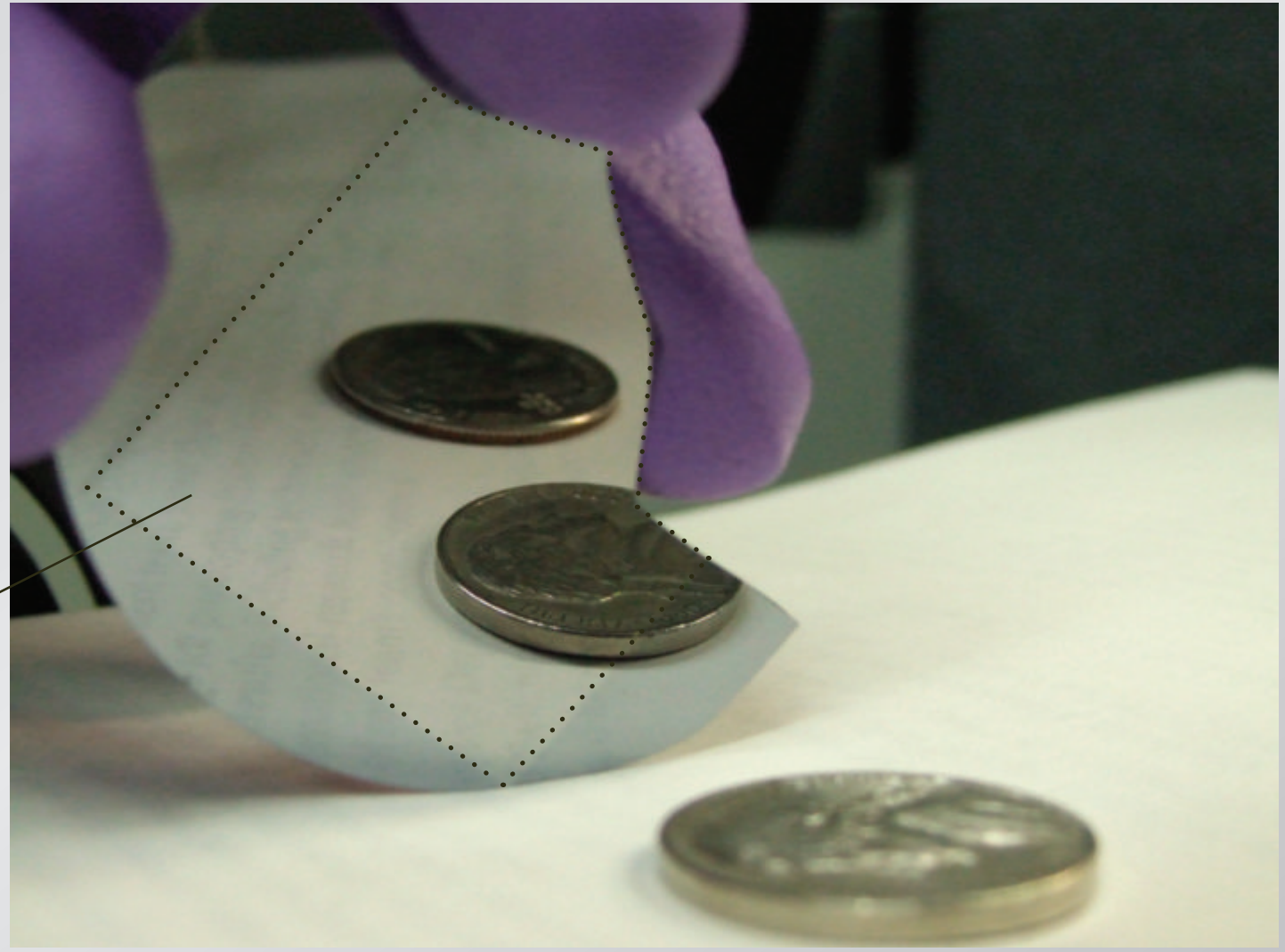

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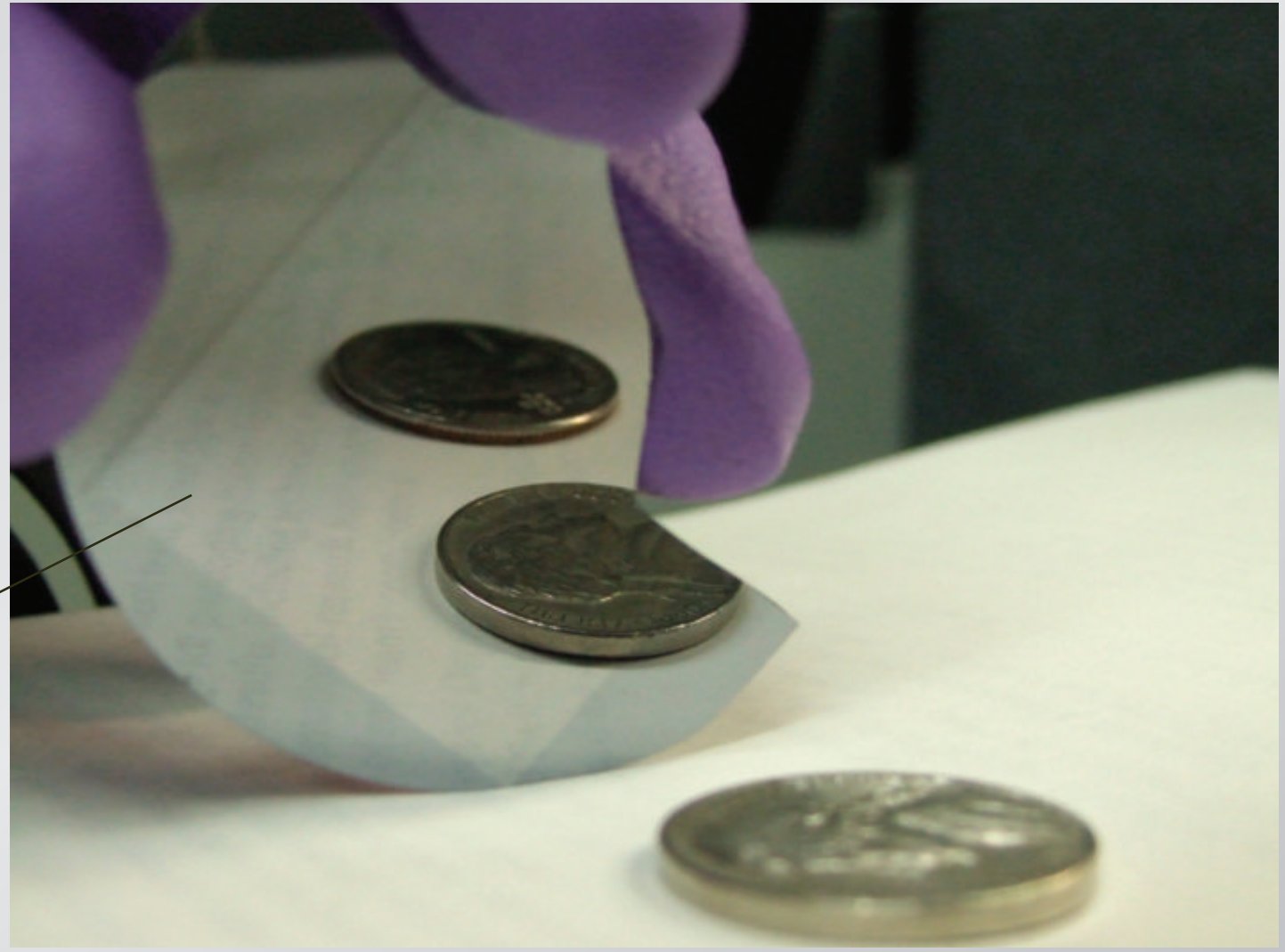

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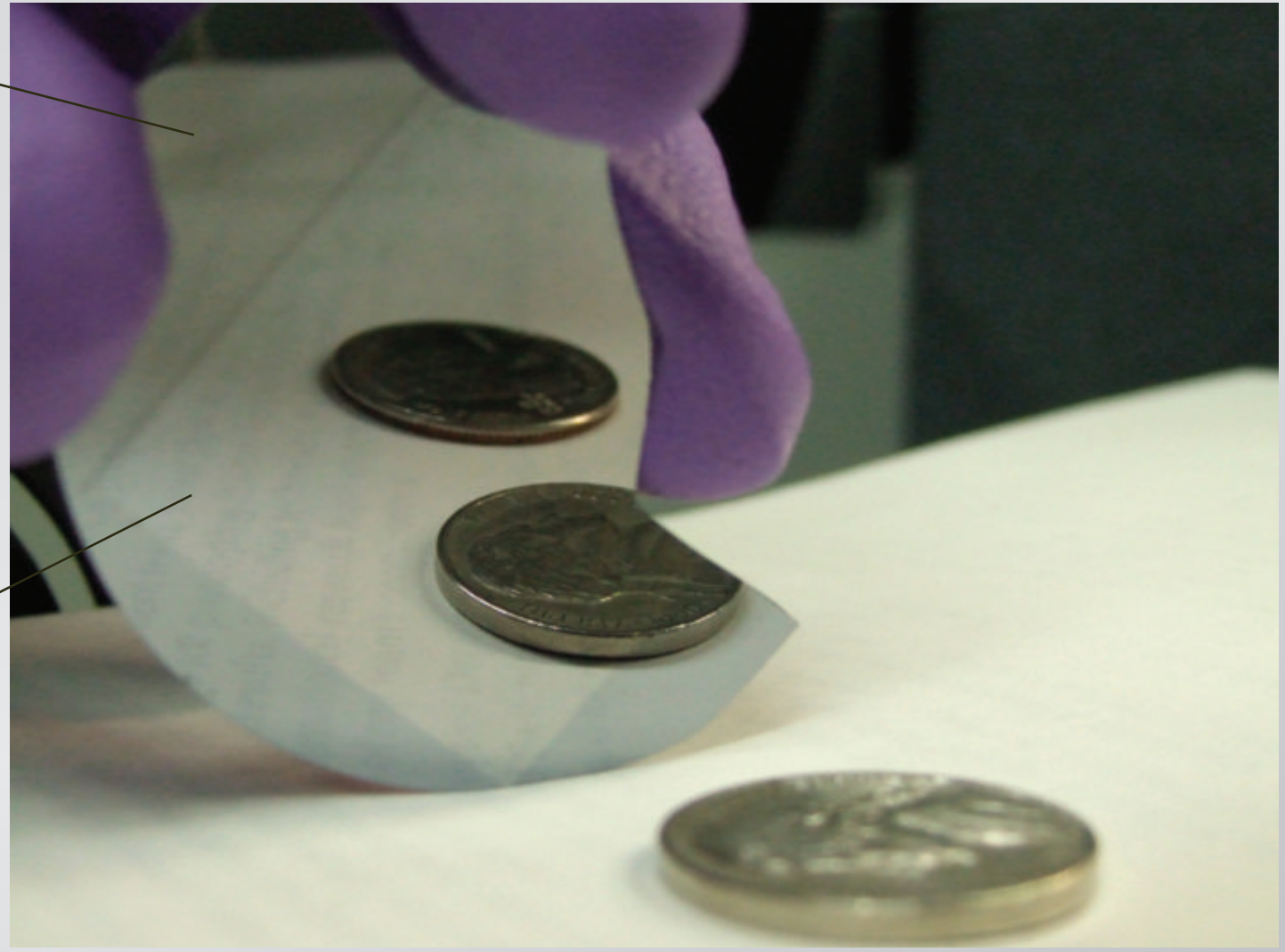

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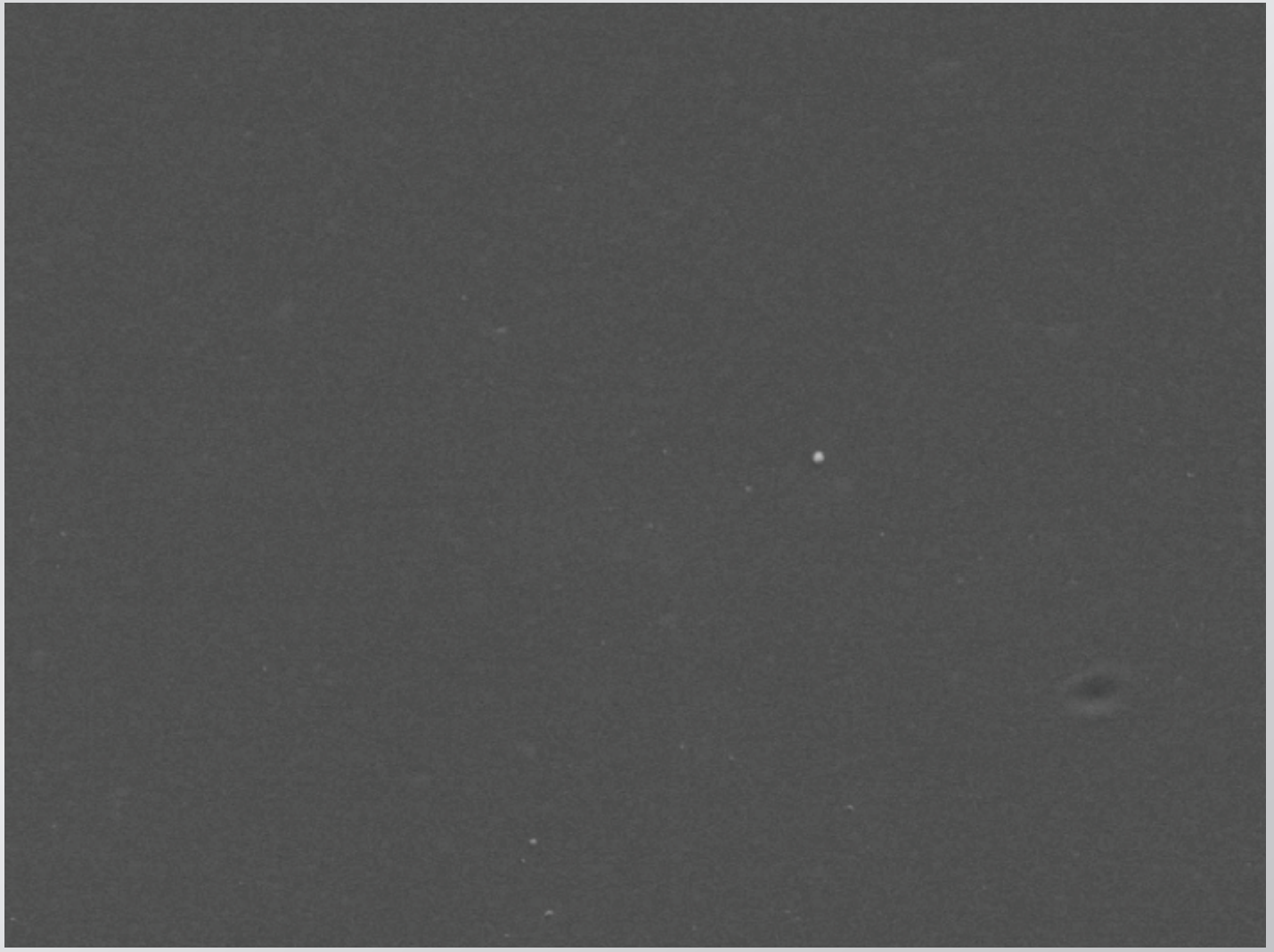
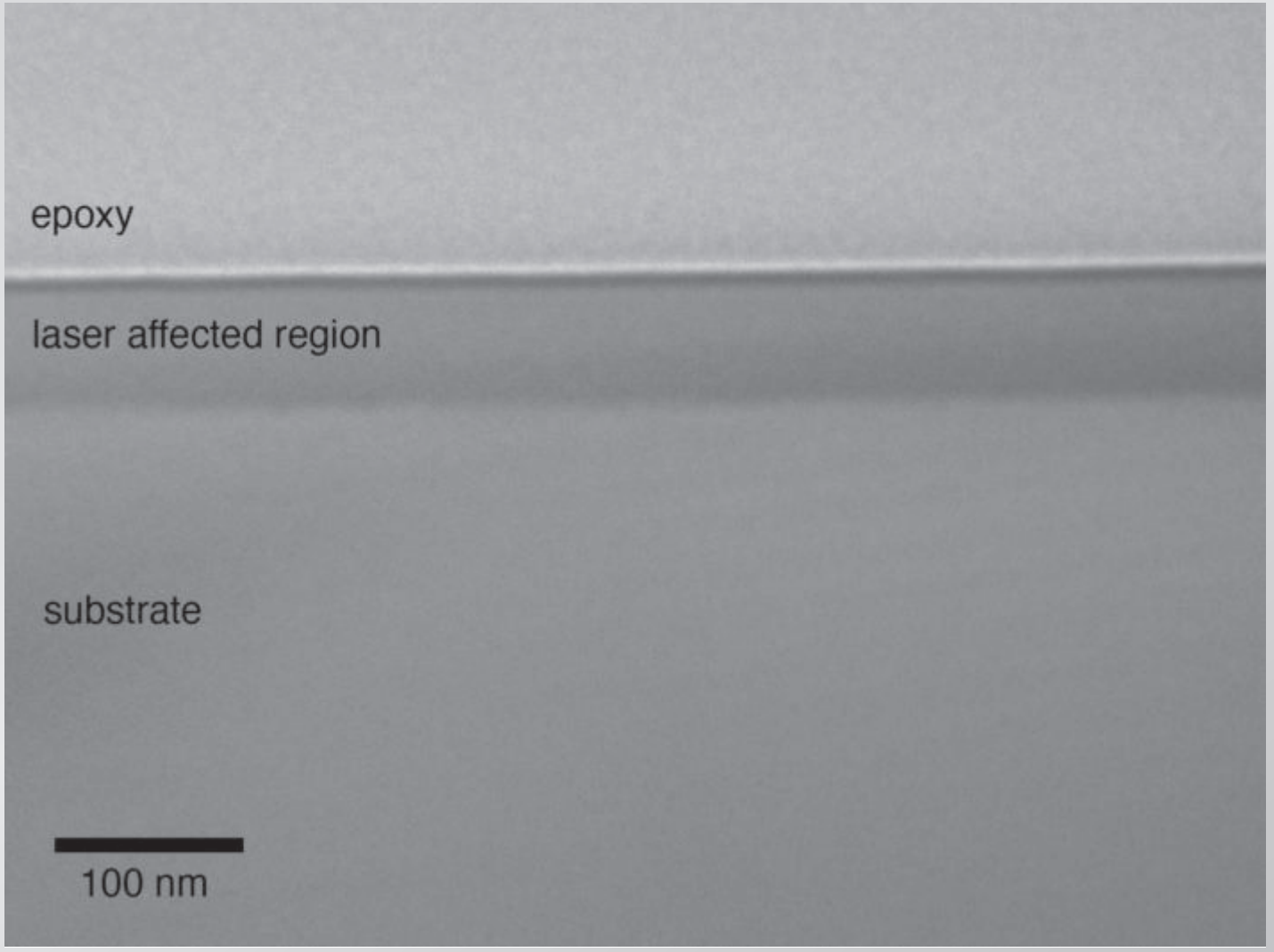


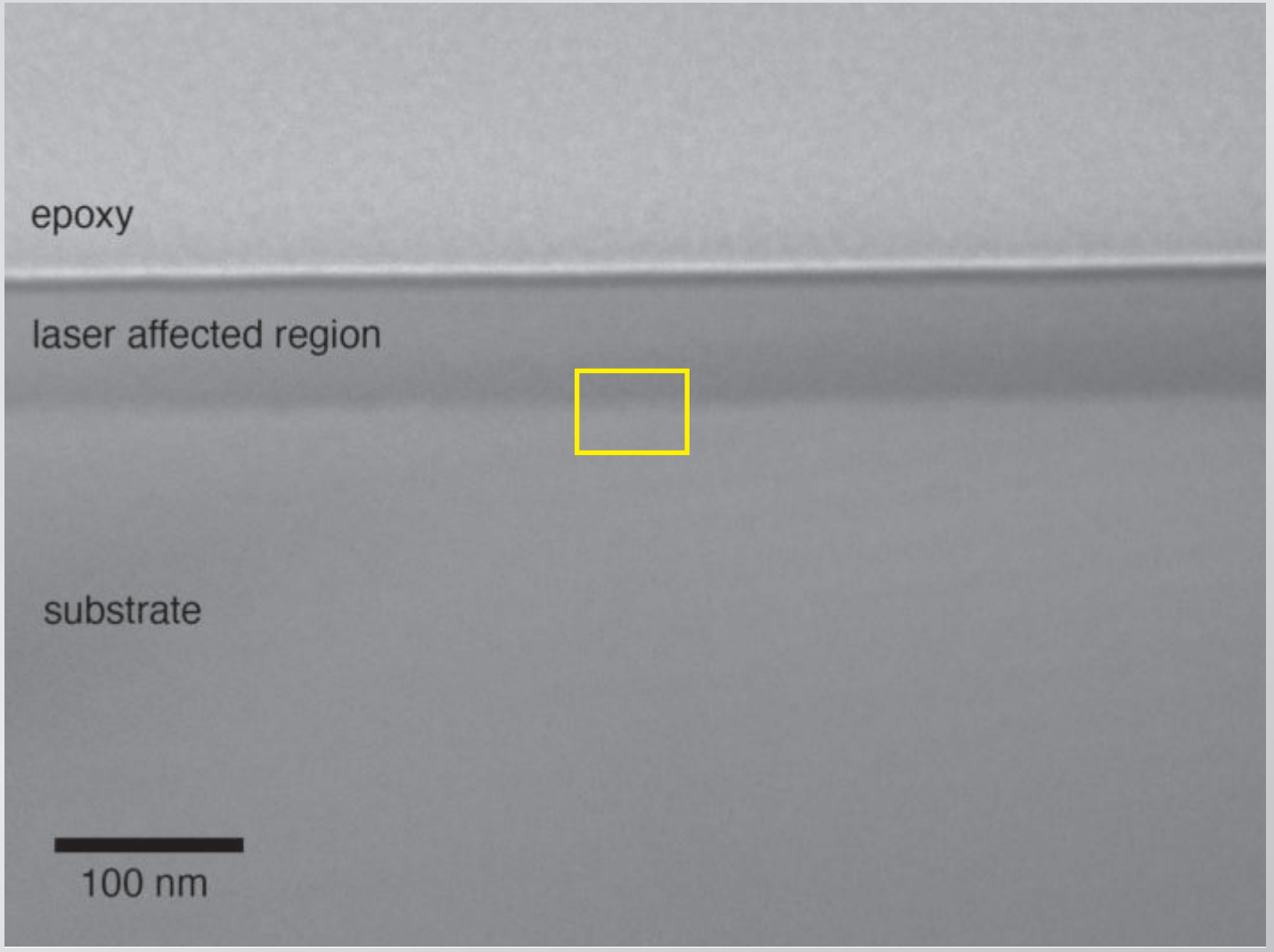
Structure

decouple ablation from melting



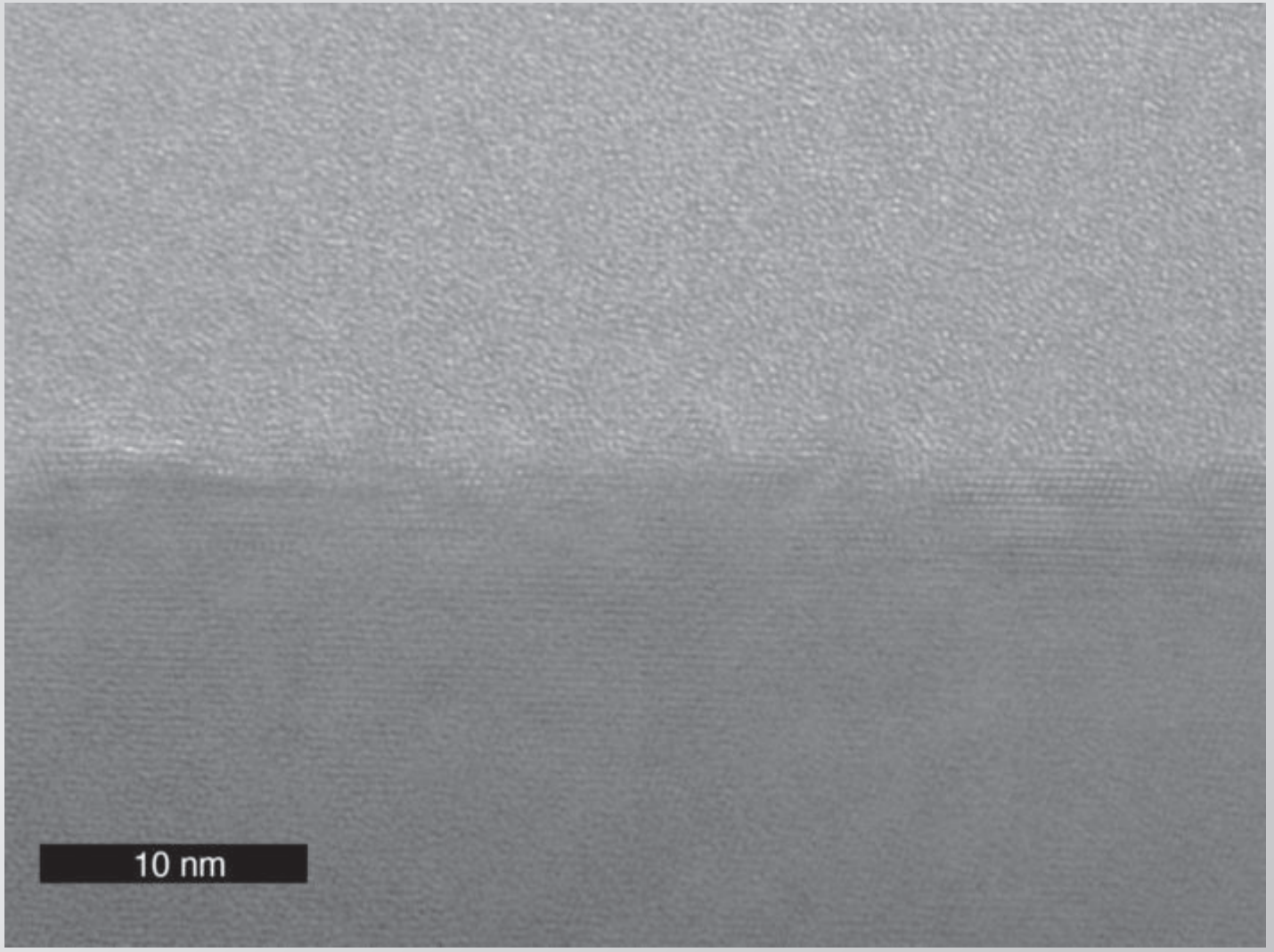
Structure

decouple ablation from melting



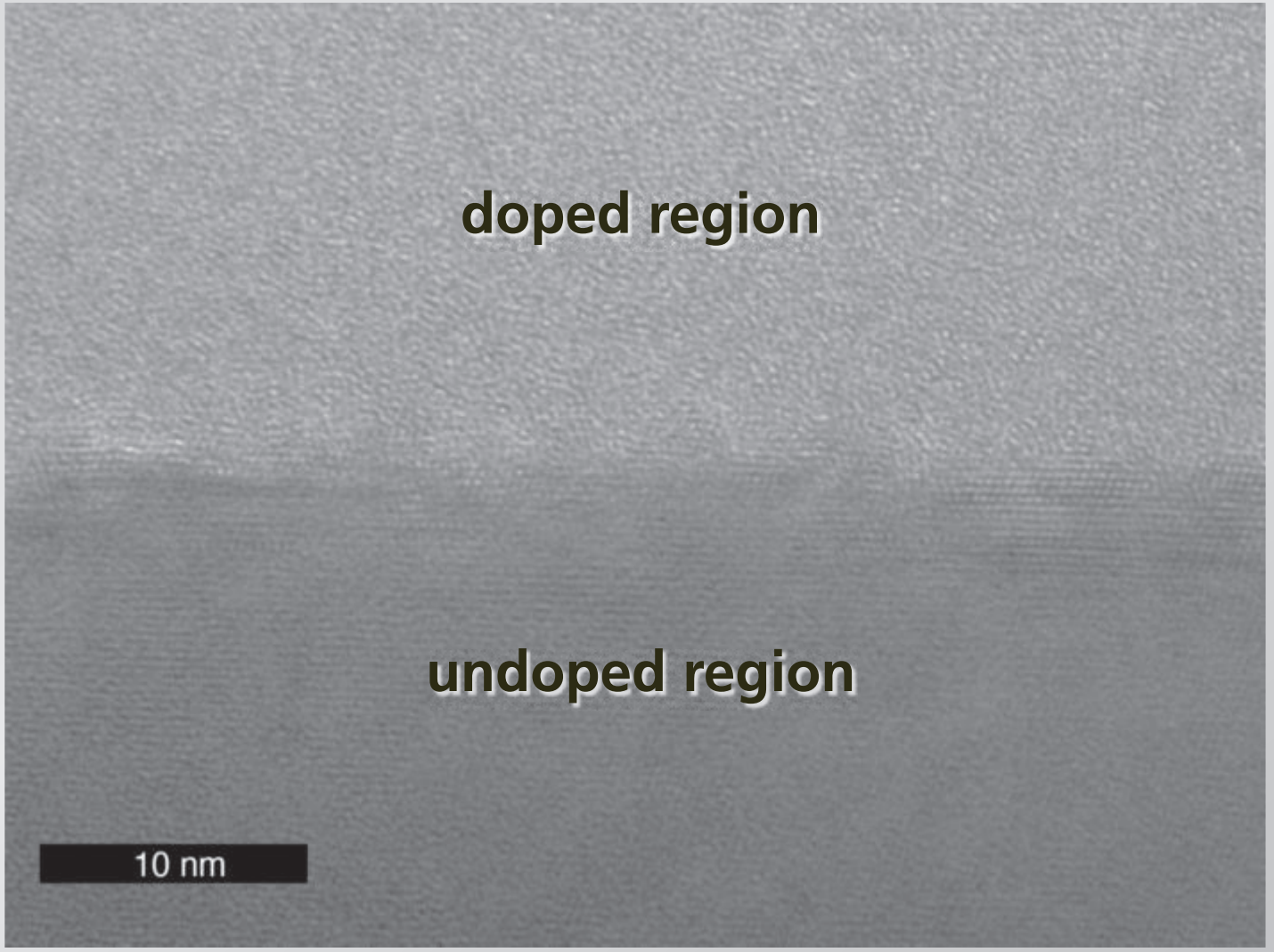
Structure

decouple ablation from melting



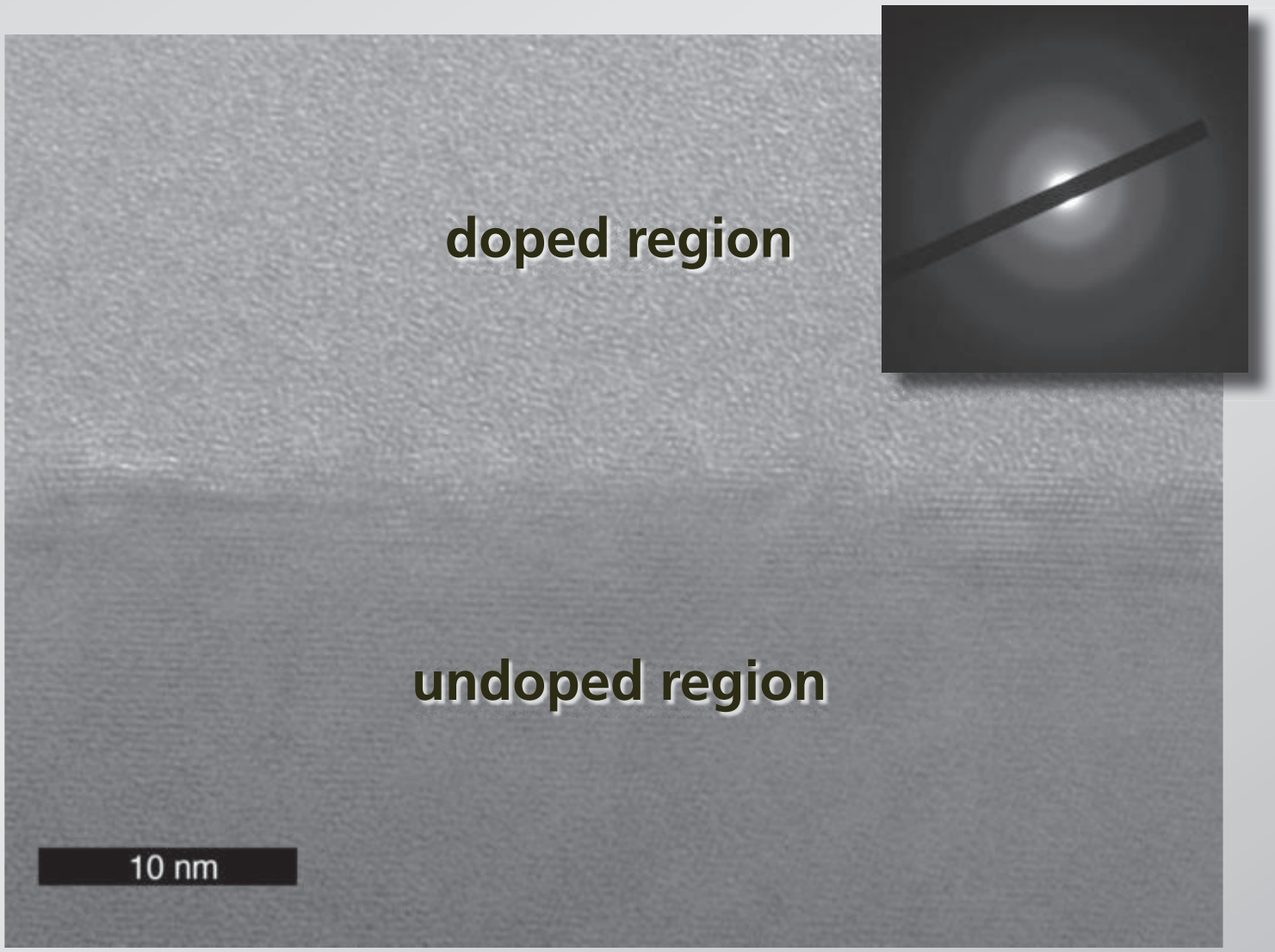
Structure

decouple ablation from melting



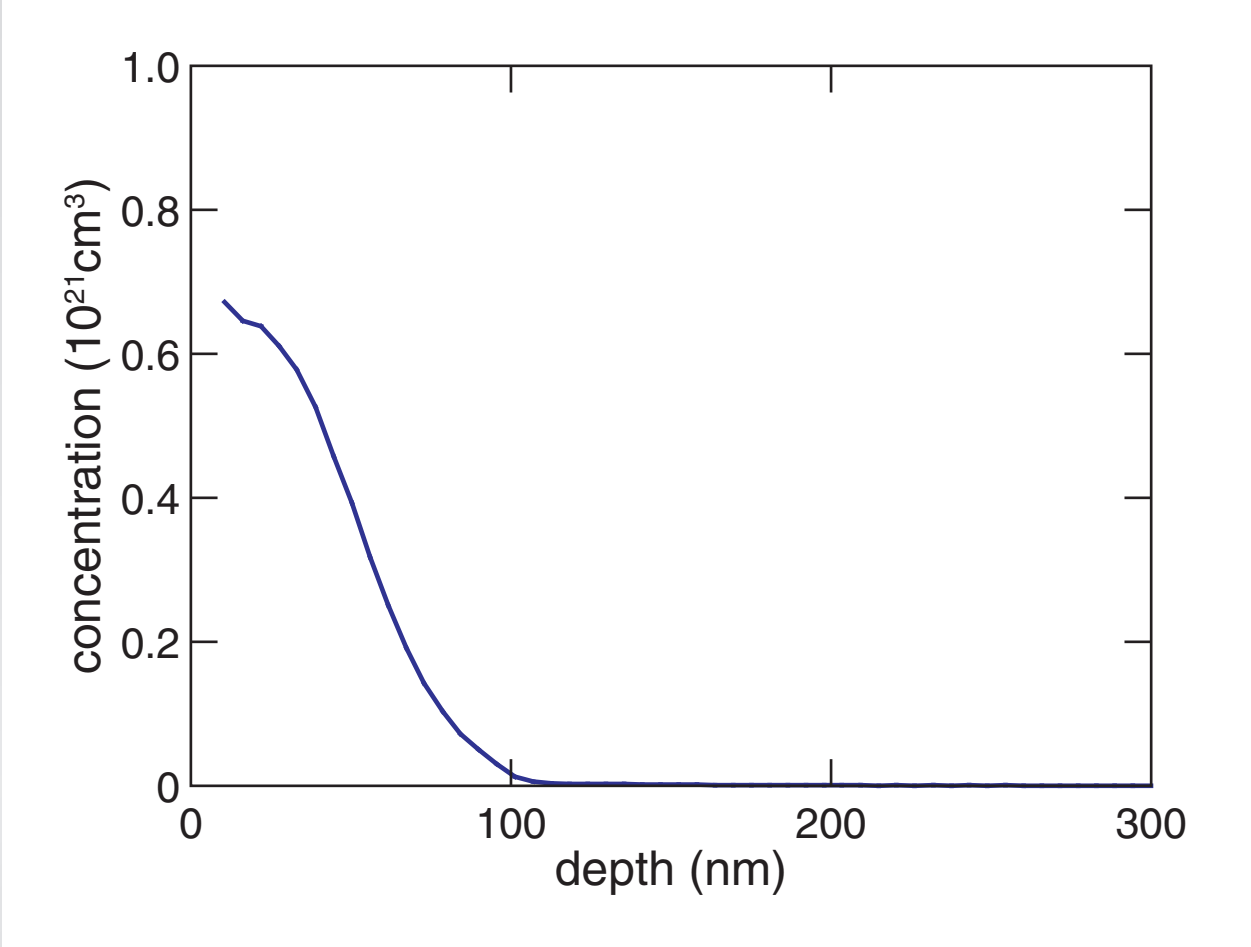
Structure

decouple ablation from melting

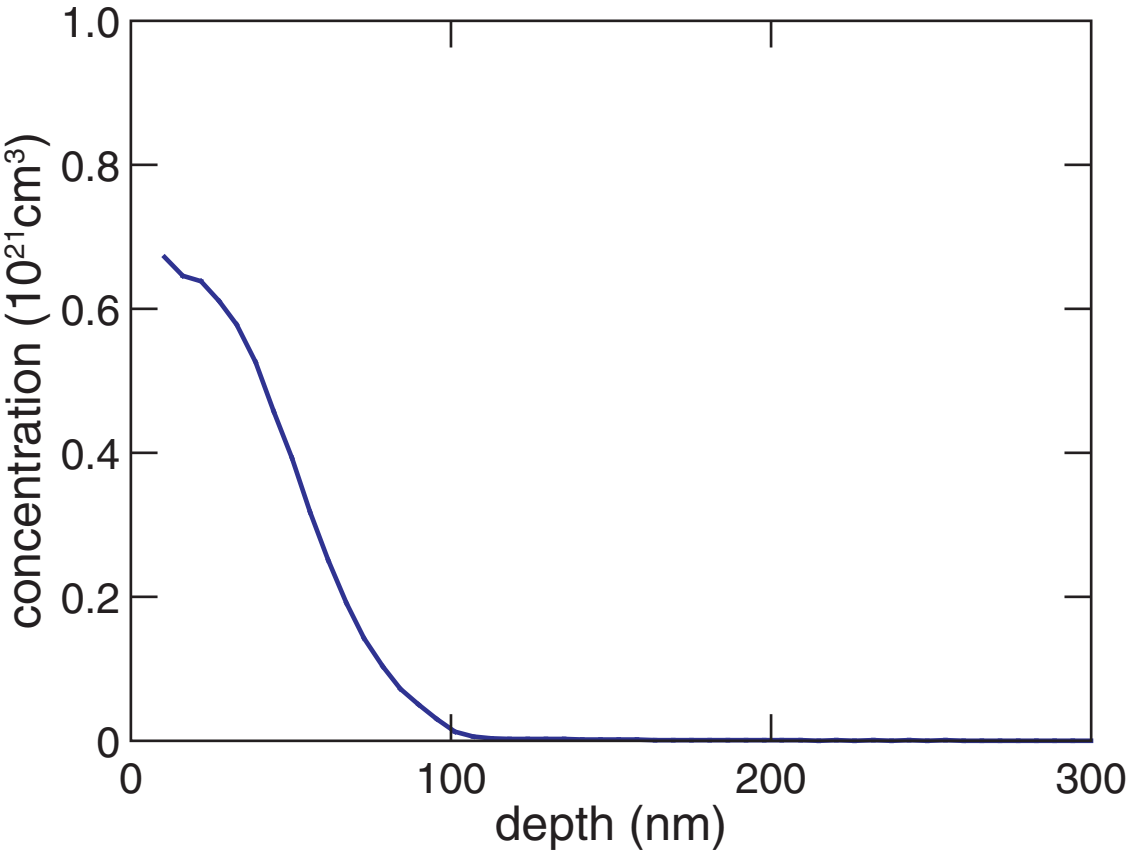


Structure

secondary ion mass spectrometry



Structure



Structure

extended x-ray absorption fine structure spectrum:

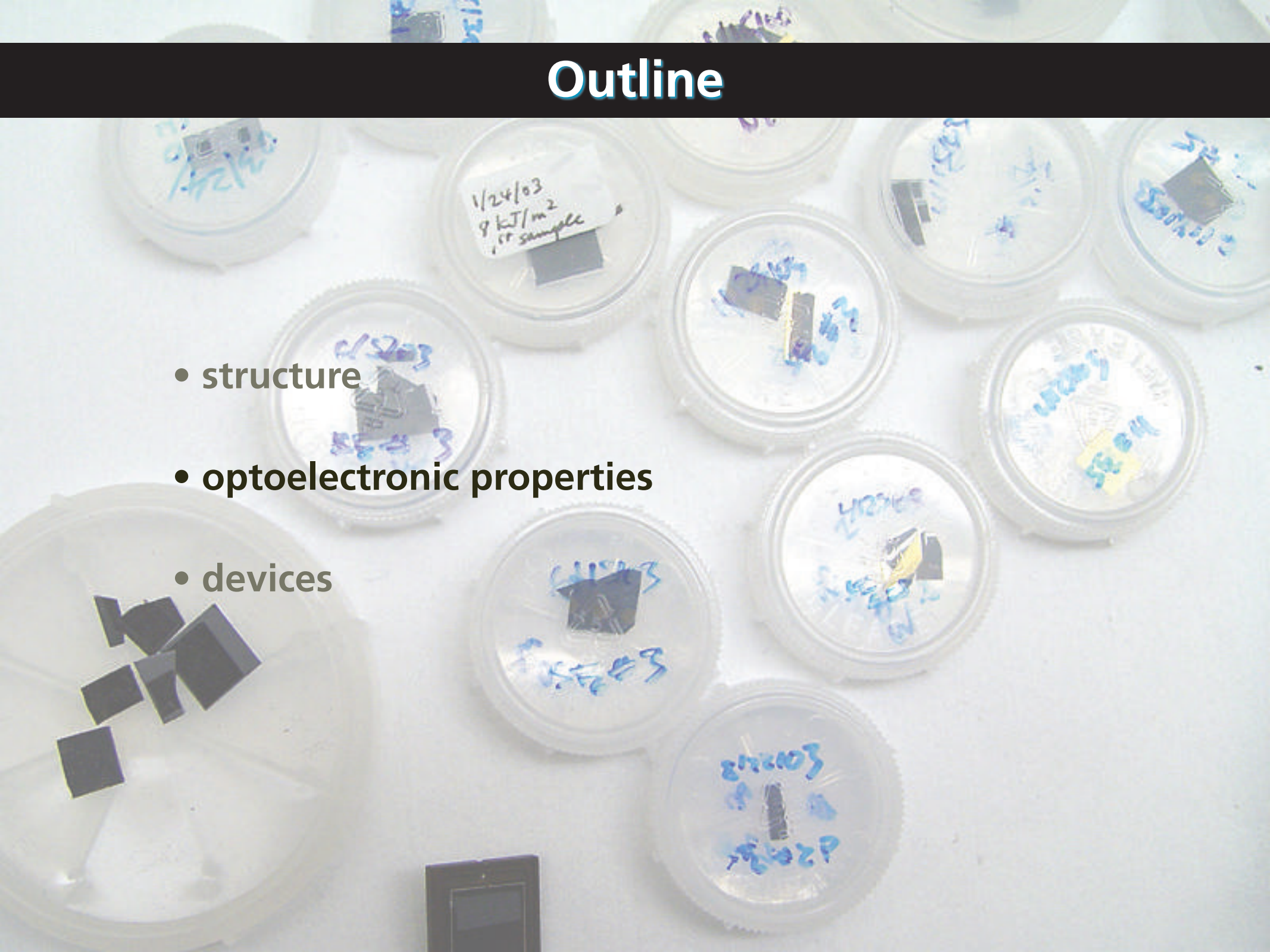
dopant in two different chemical states

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

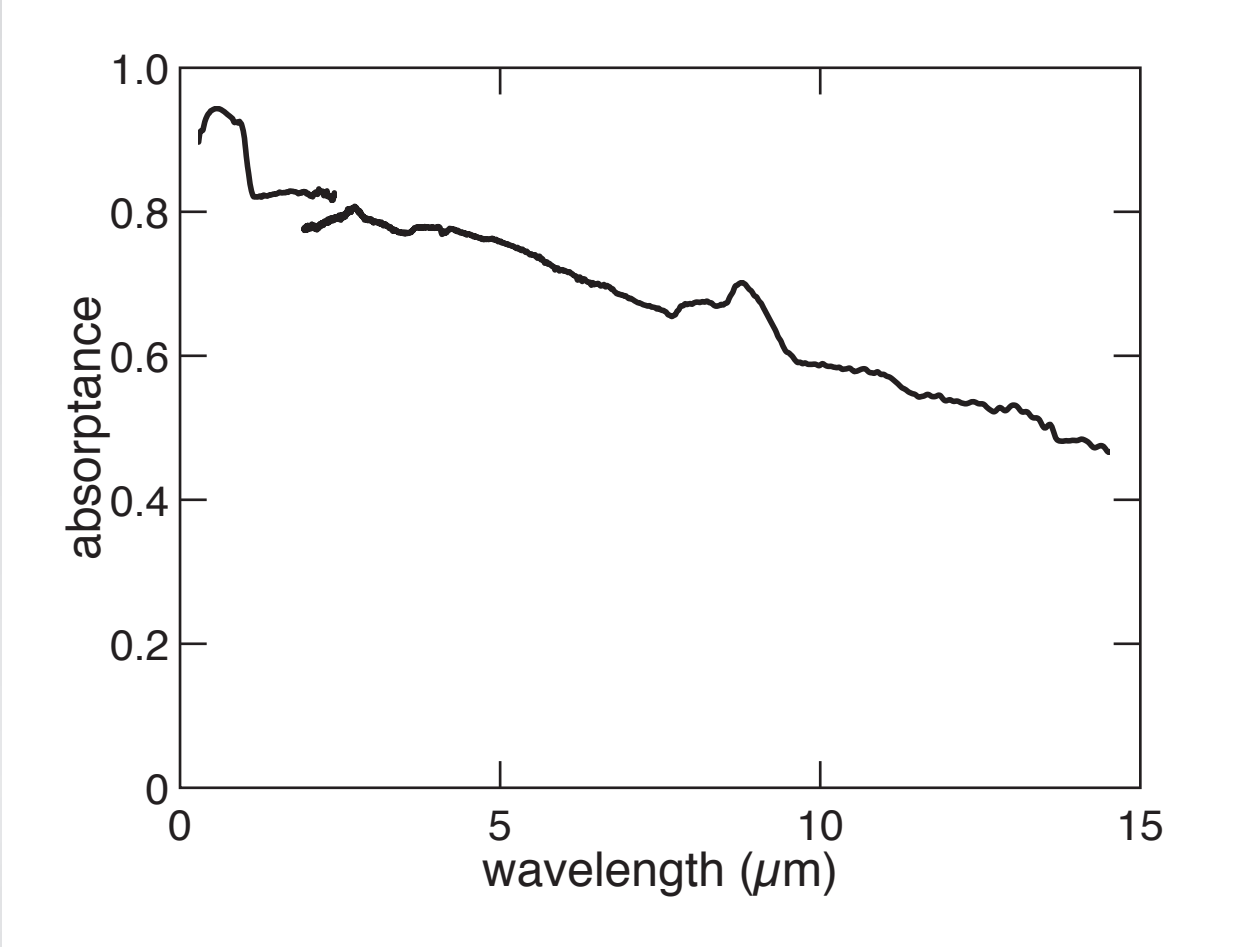
Outline



- structure
- **optoelectronic properties**
- devices

Optoelectronic properties

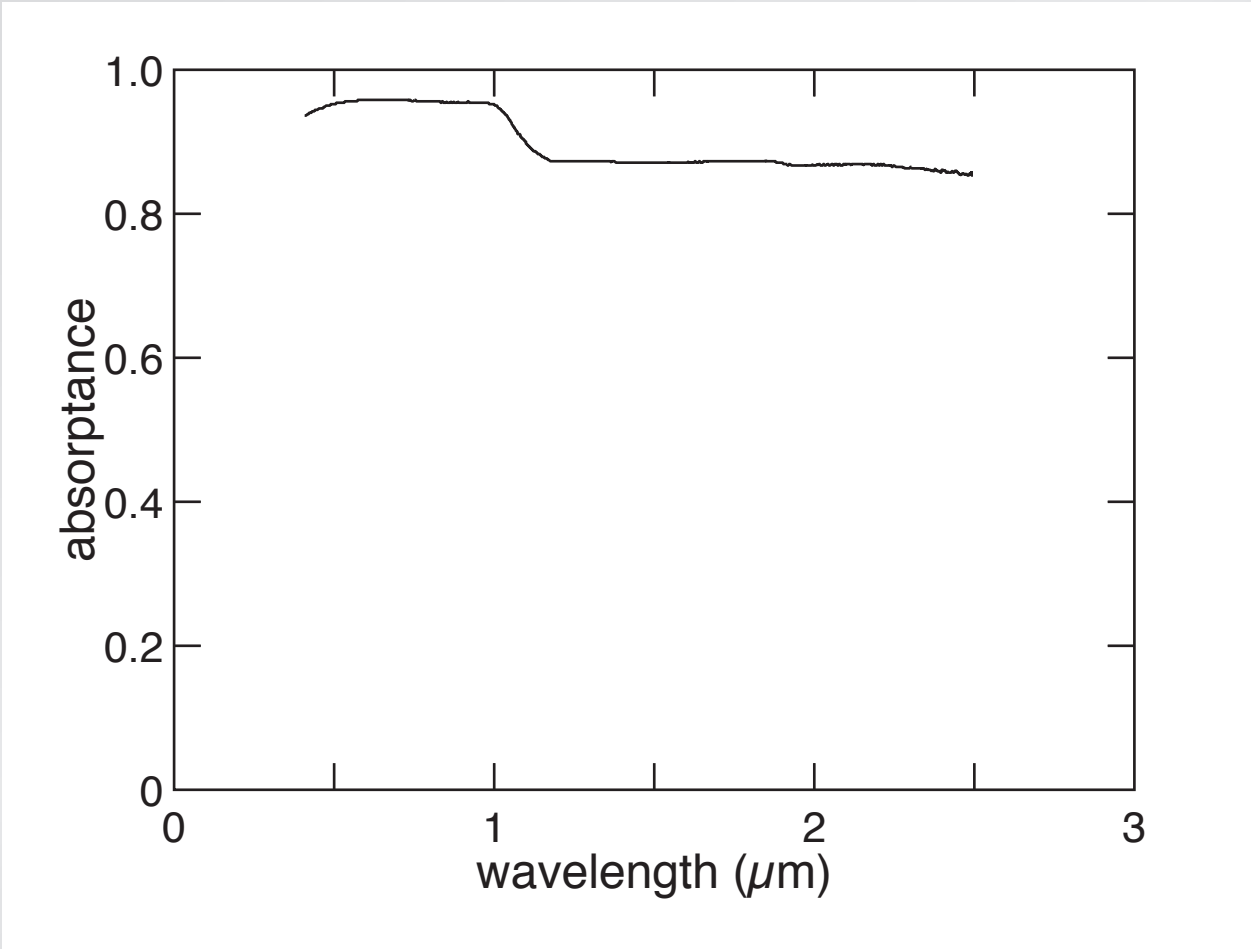
absorptance ($1 - R_{int} - T_{int}$)



Asenbaum, Vienna

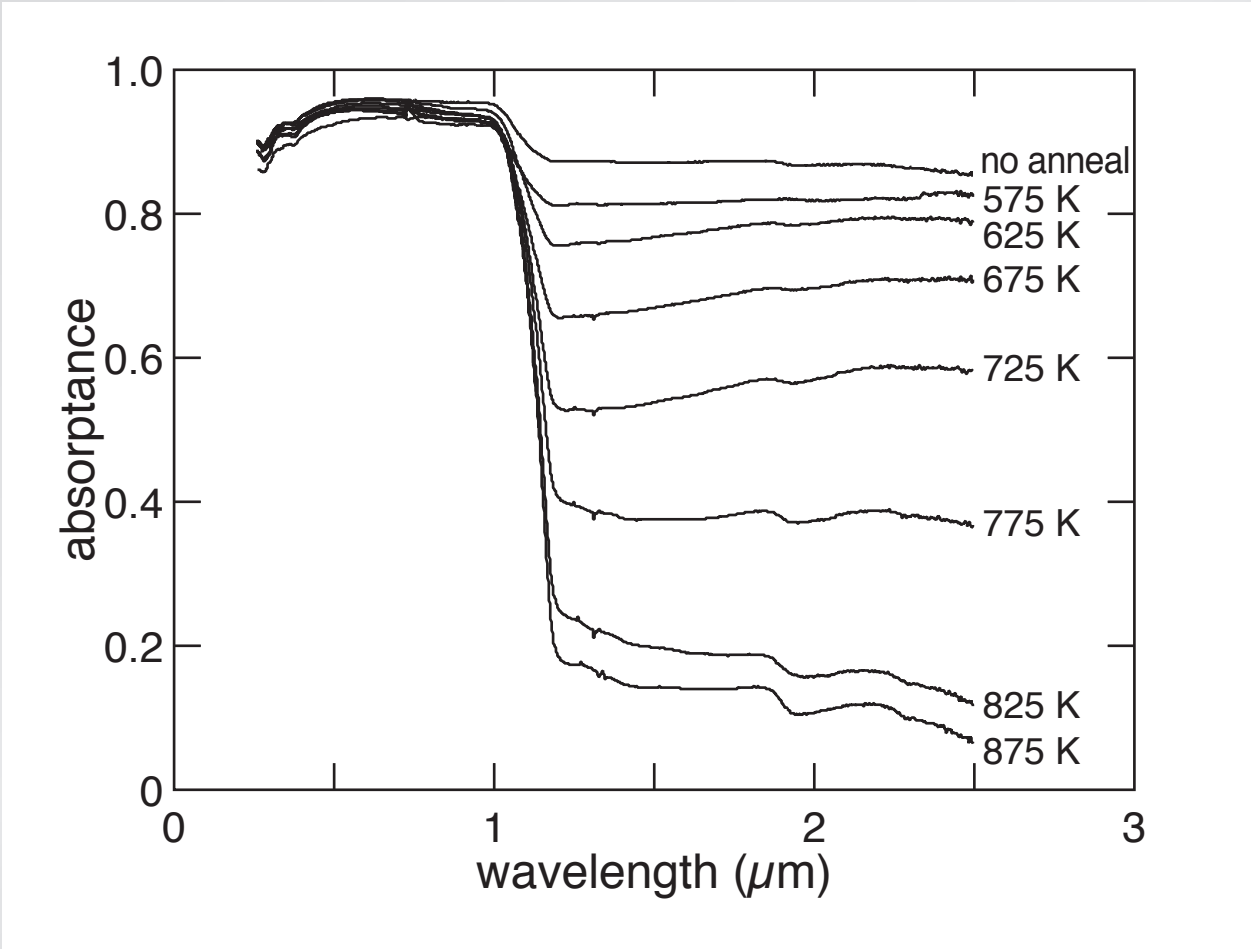
Optoelectronic properties

effect of annealing on IR absorptance



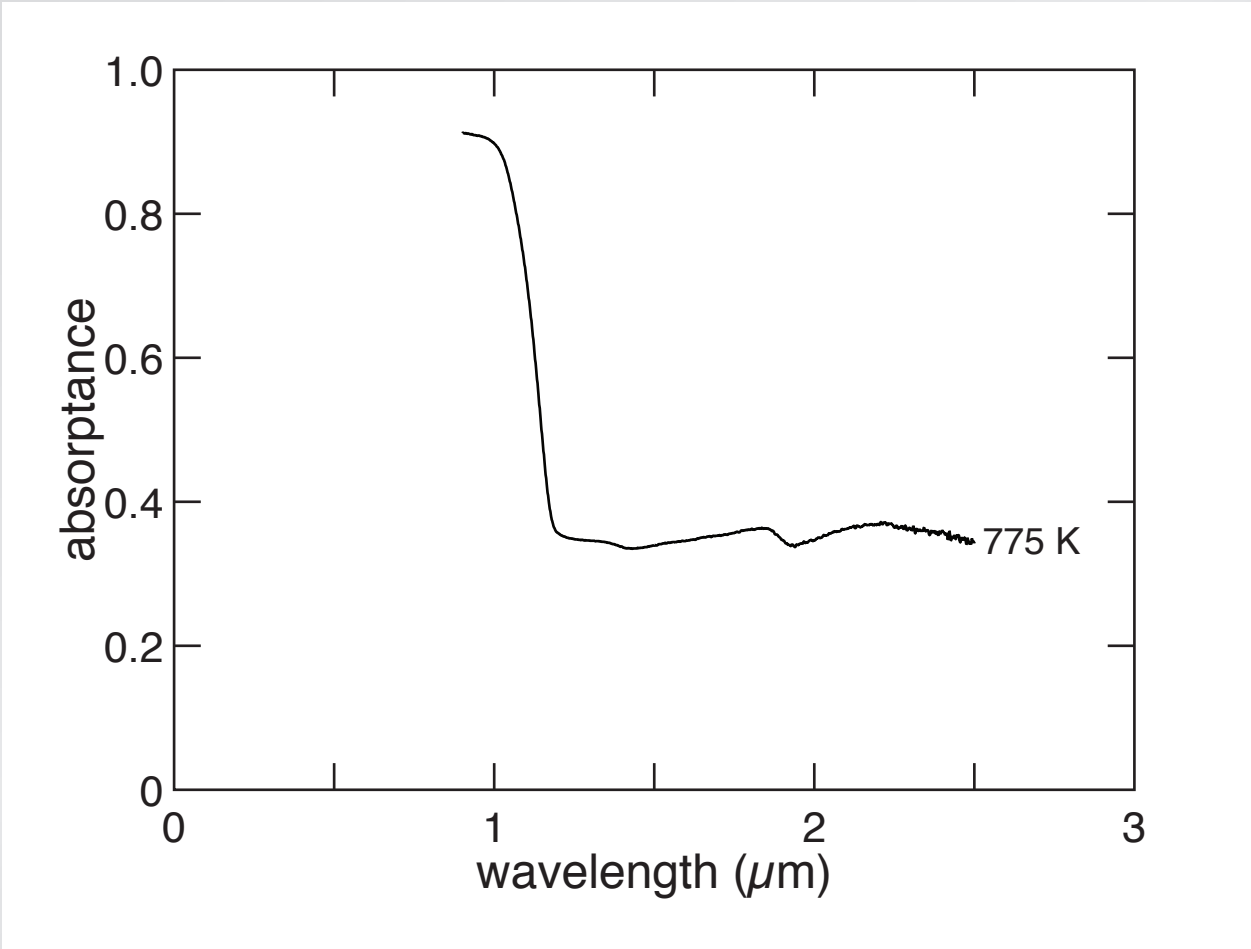
Optoelectronic properties

effect of annealing on IR absorptance



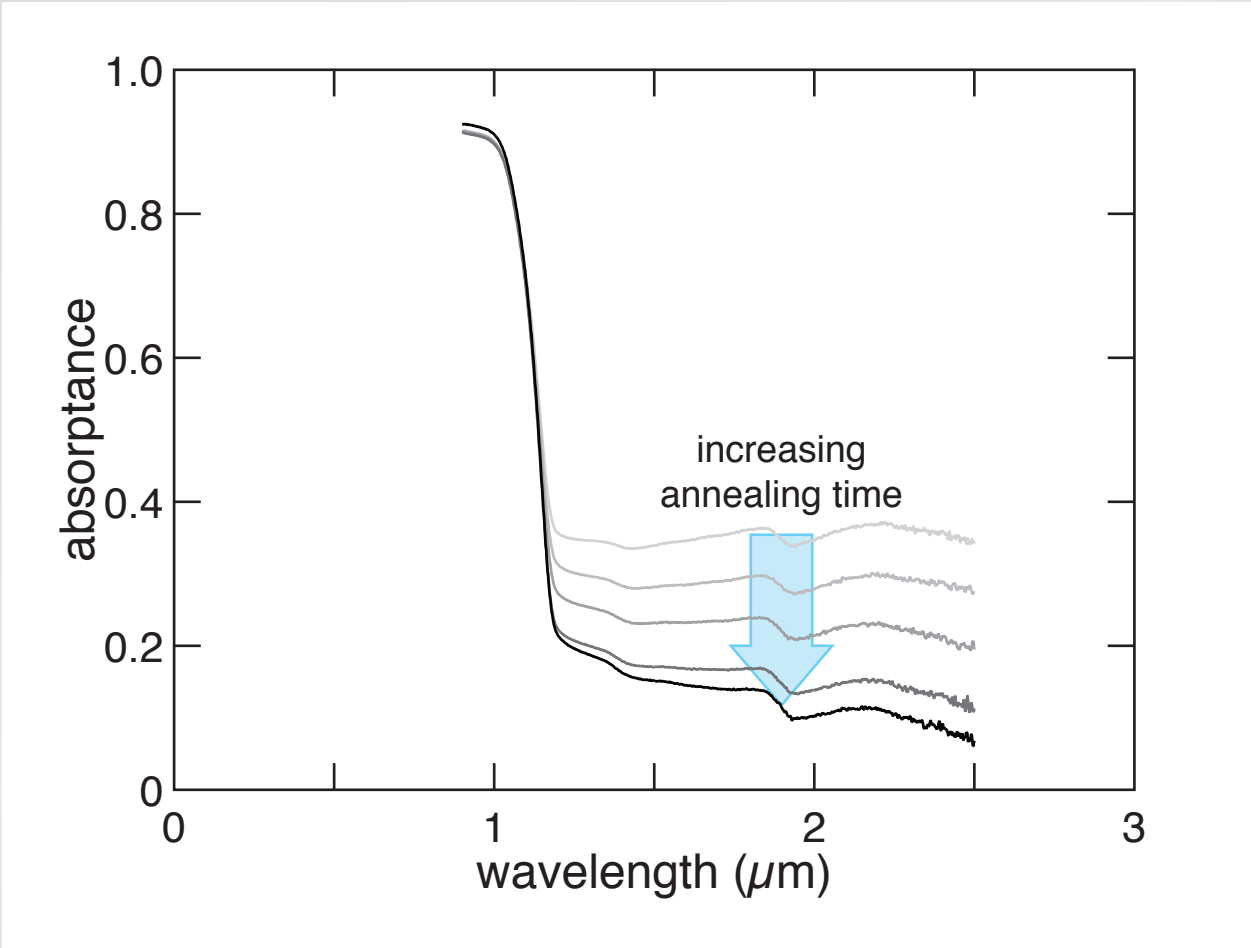
Optoelectronic properties

vary annealing time



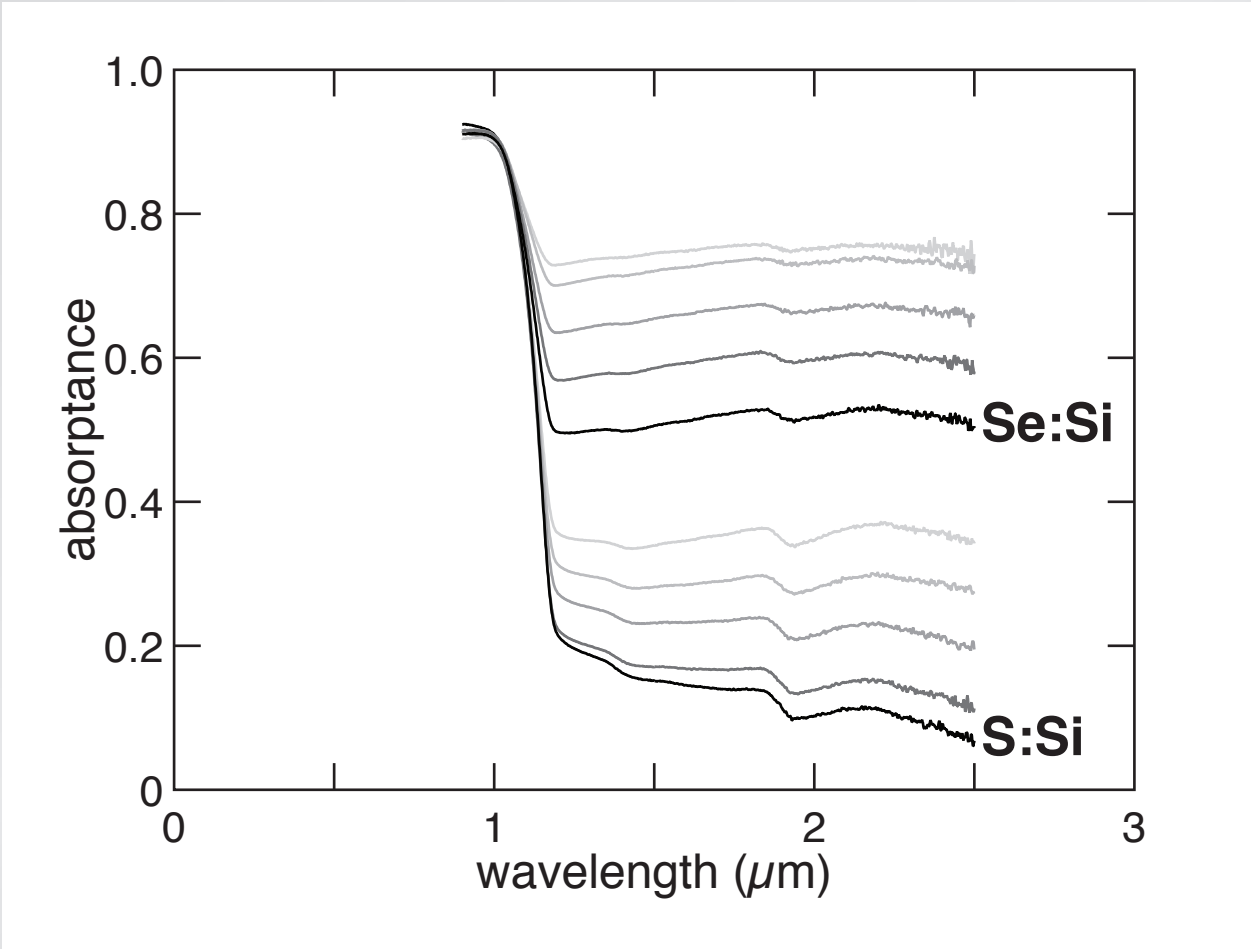
Optoelectronic properties

longer annealing decreases IR absorptance



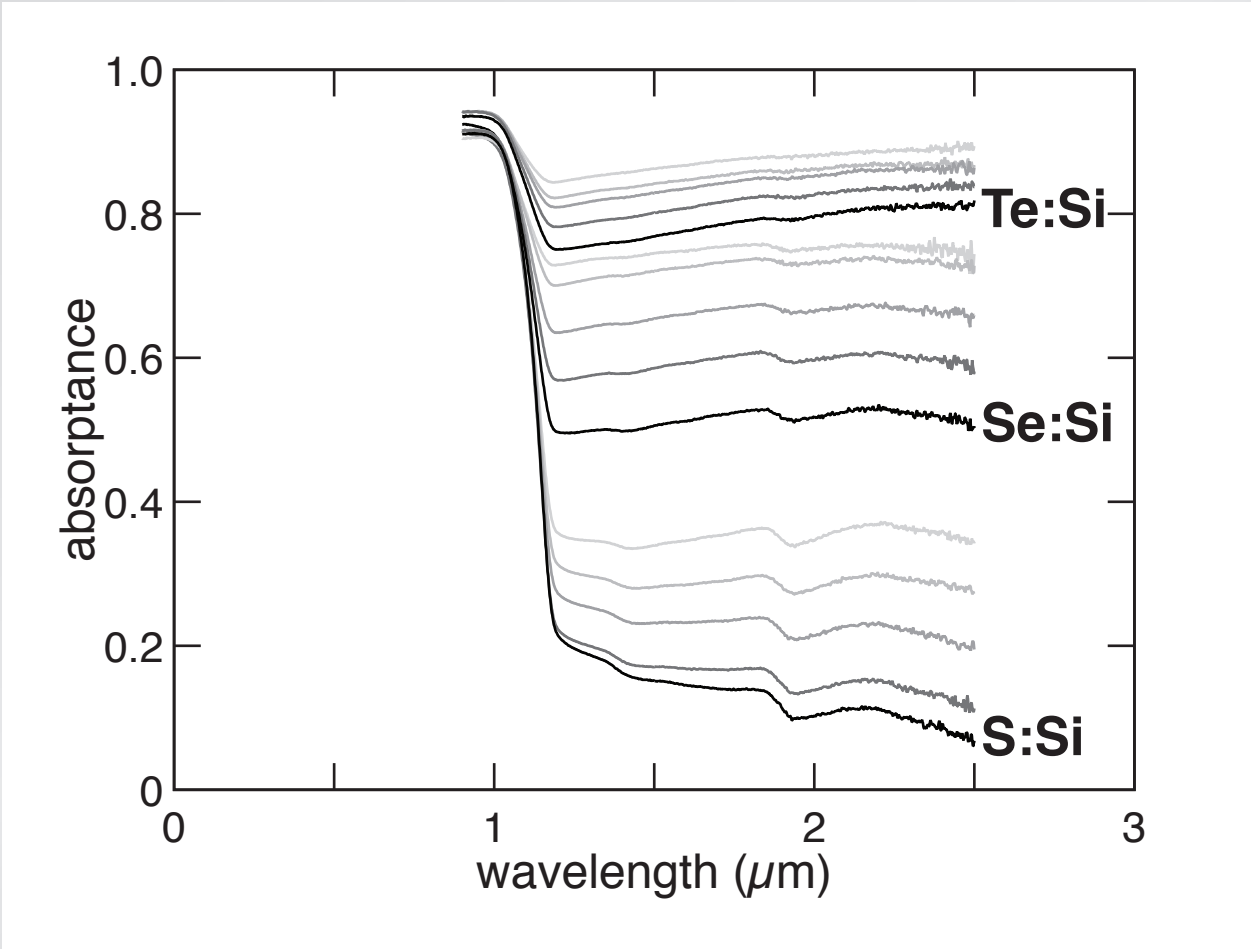
Optoelectronic properties

IR absorptance decreases less for Se-doped samples…



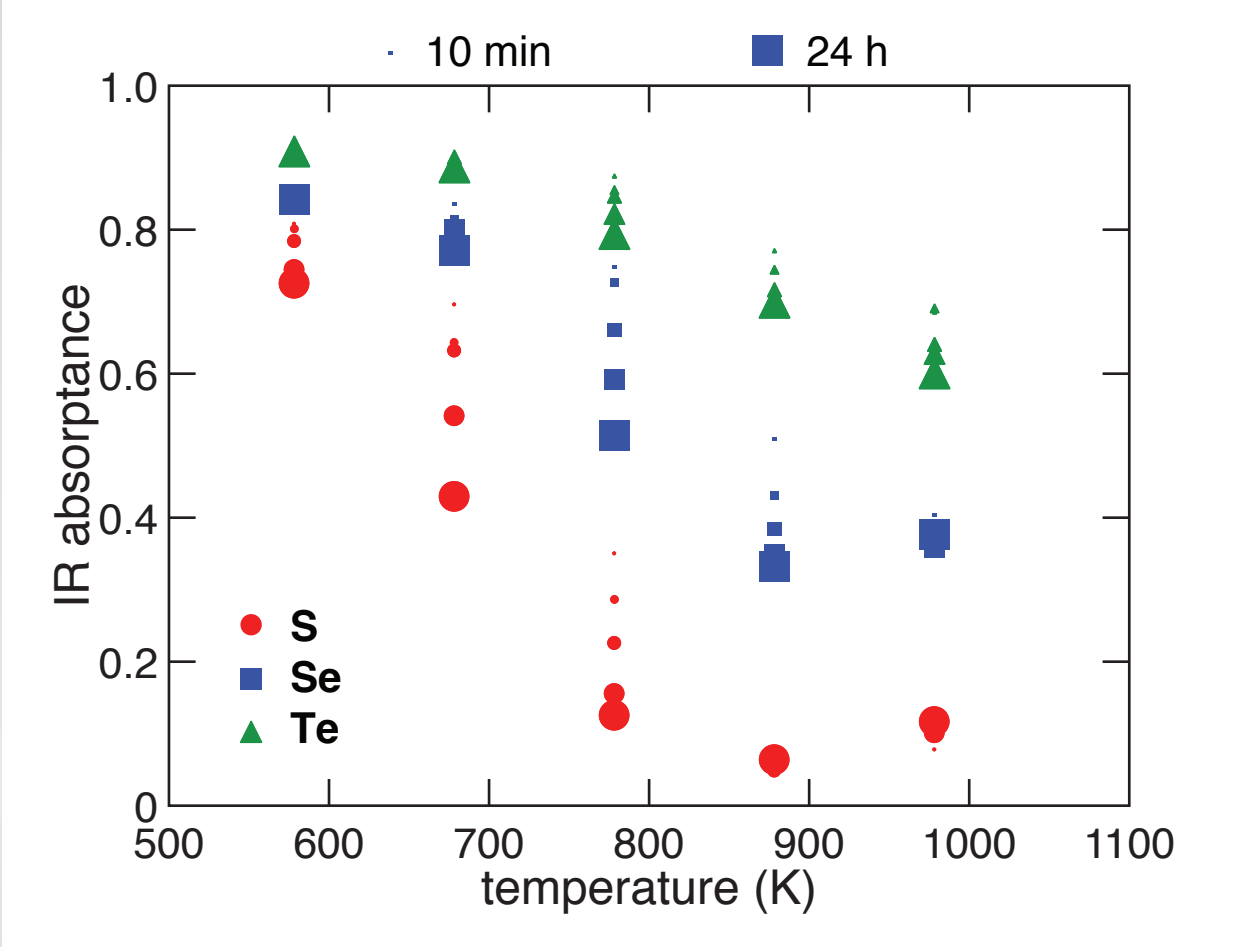
Optoelectronic properties

and even less for Te-doped samples…



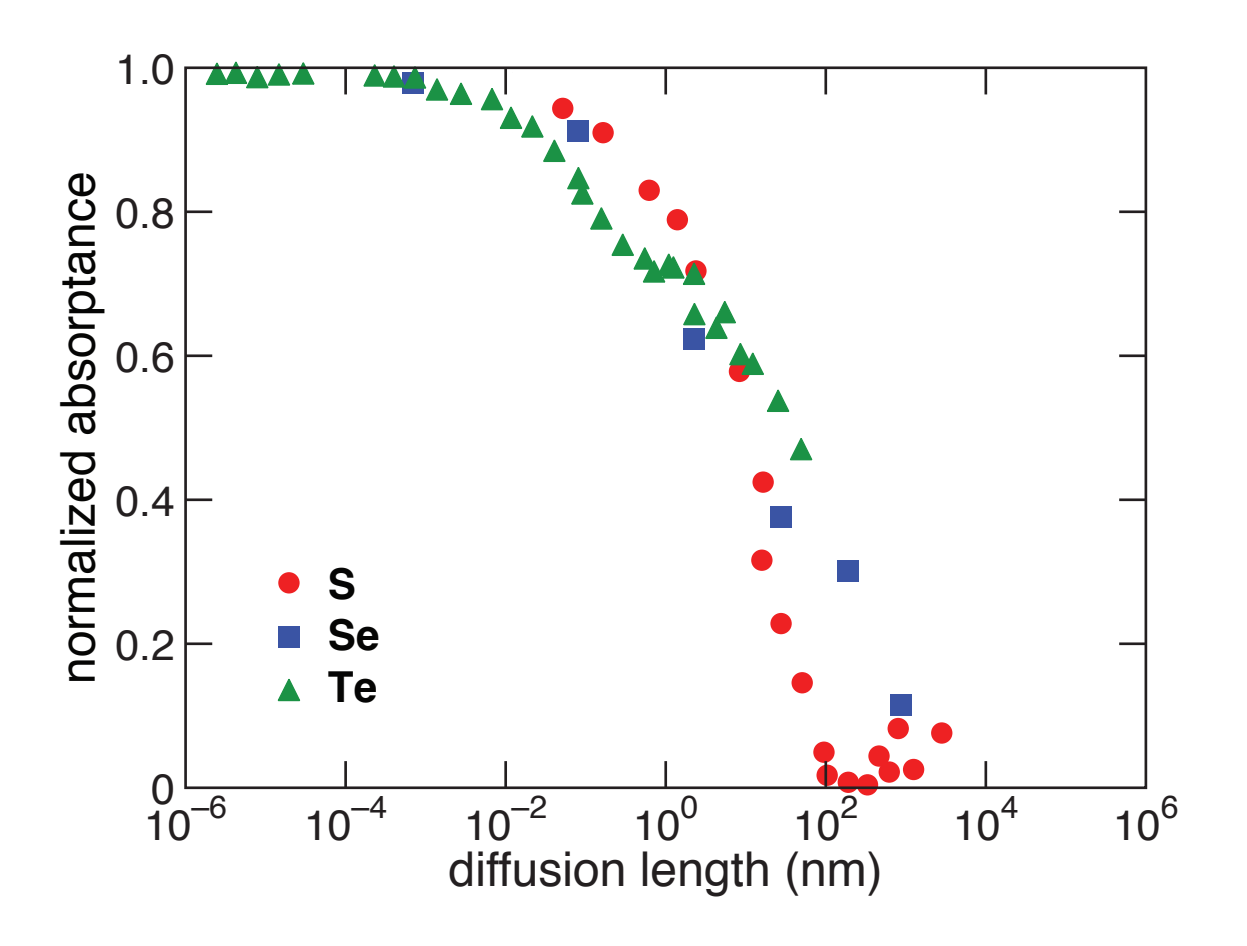
Optoelectronic properties

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



Optoelectronic properties

…but is unique function of diffusion length



Optoelectronic properties

annealing…

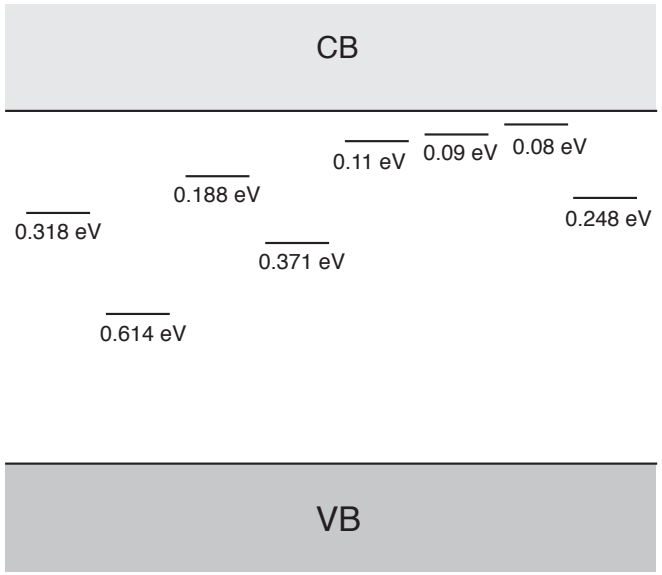
- decreases IR absorptance
- causes recoordination and diffusion of dopants
- IR absorptance reduced by 50% after 20 nm diffusion

Optoelectronic properties

what dopant states/bands cause IR absorption?

Optoelectronic properties

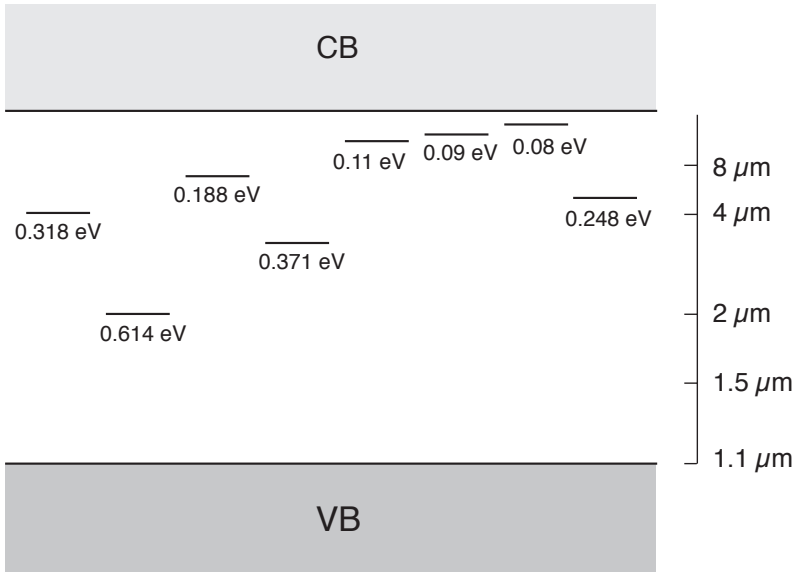
1 part in 10^6 sulfur introduces donor states in gap



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

Optoelectronic properties

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



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Optoelectronic properties

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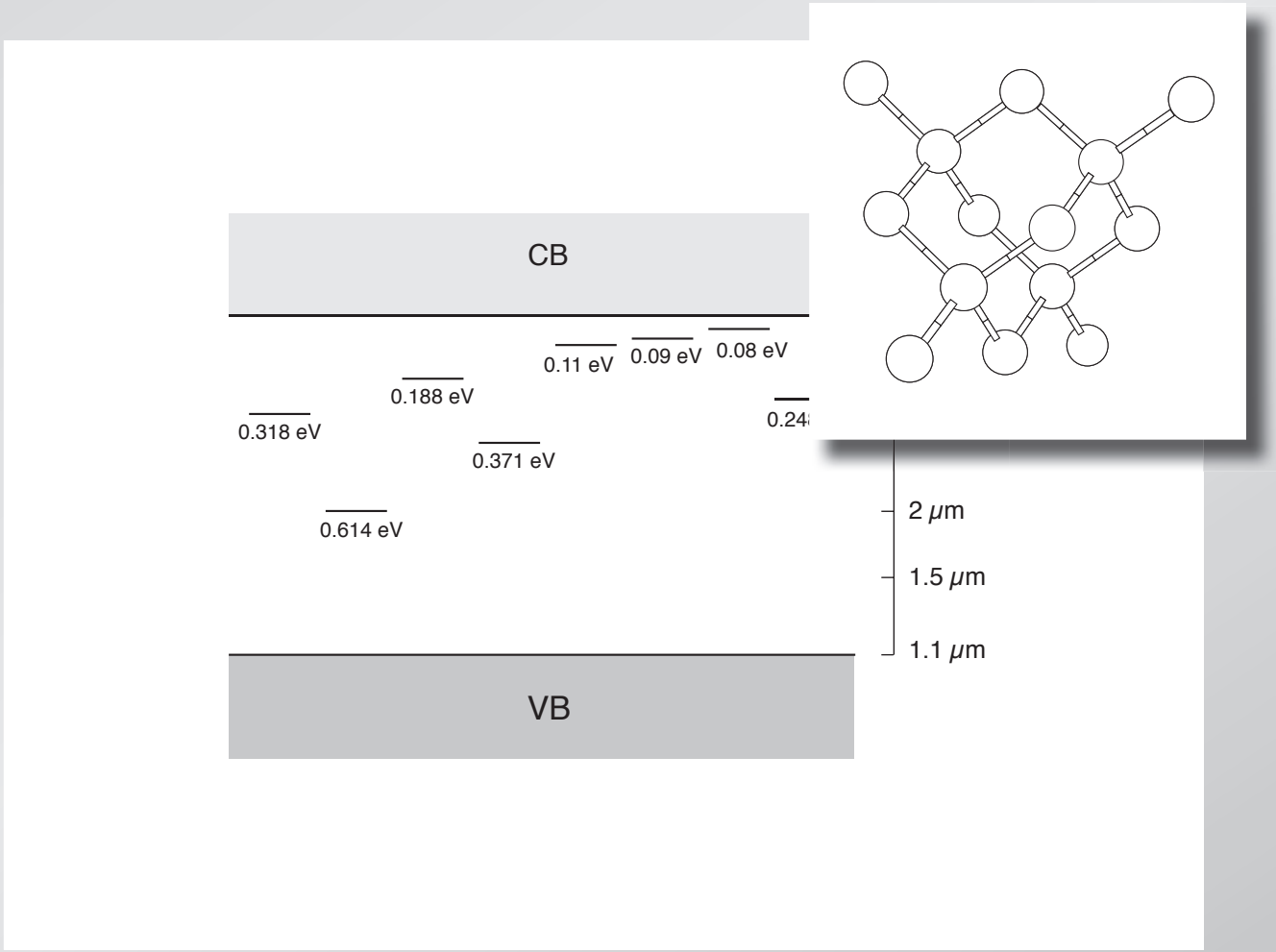

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Optoelectronic properties

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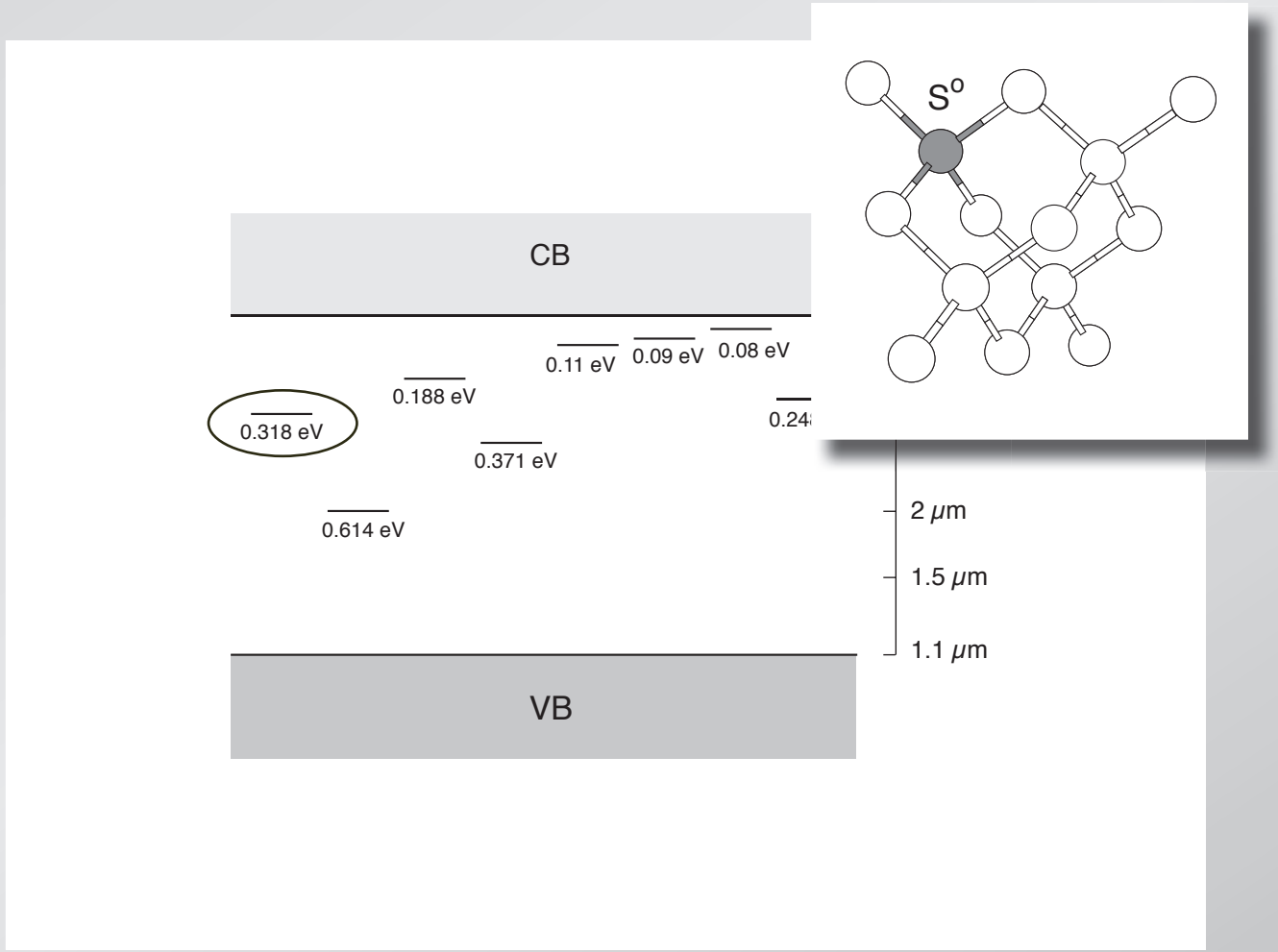

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Optoelectronic properties

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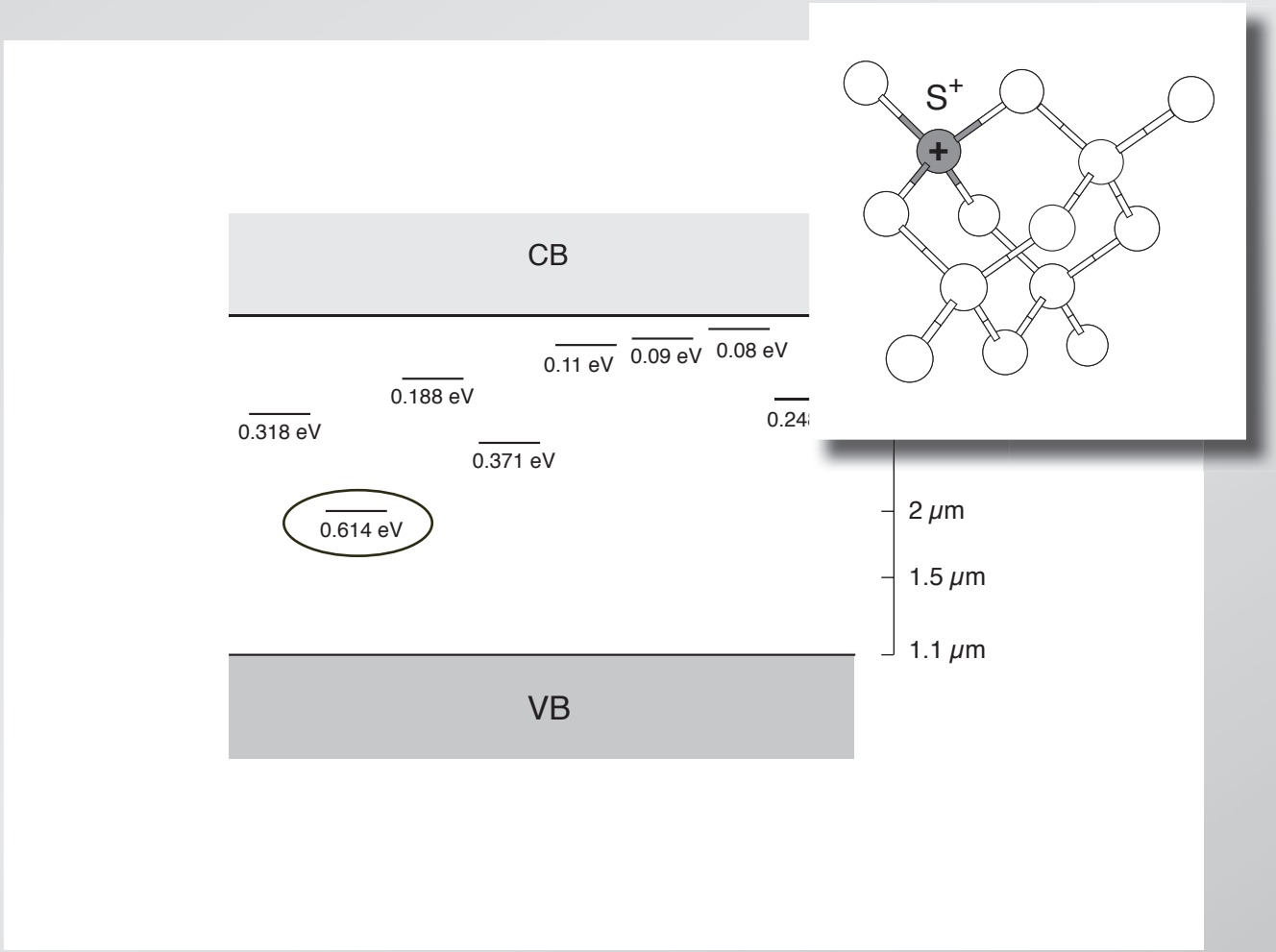

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Optoelectronic properties

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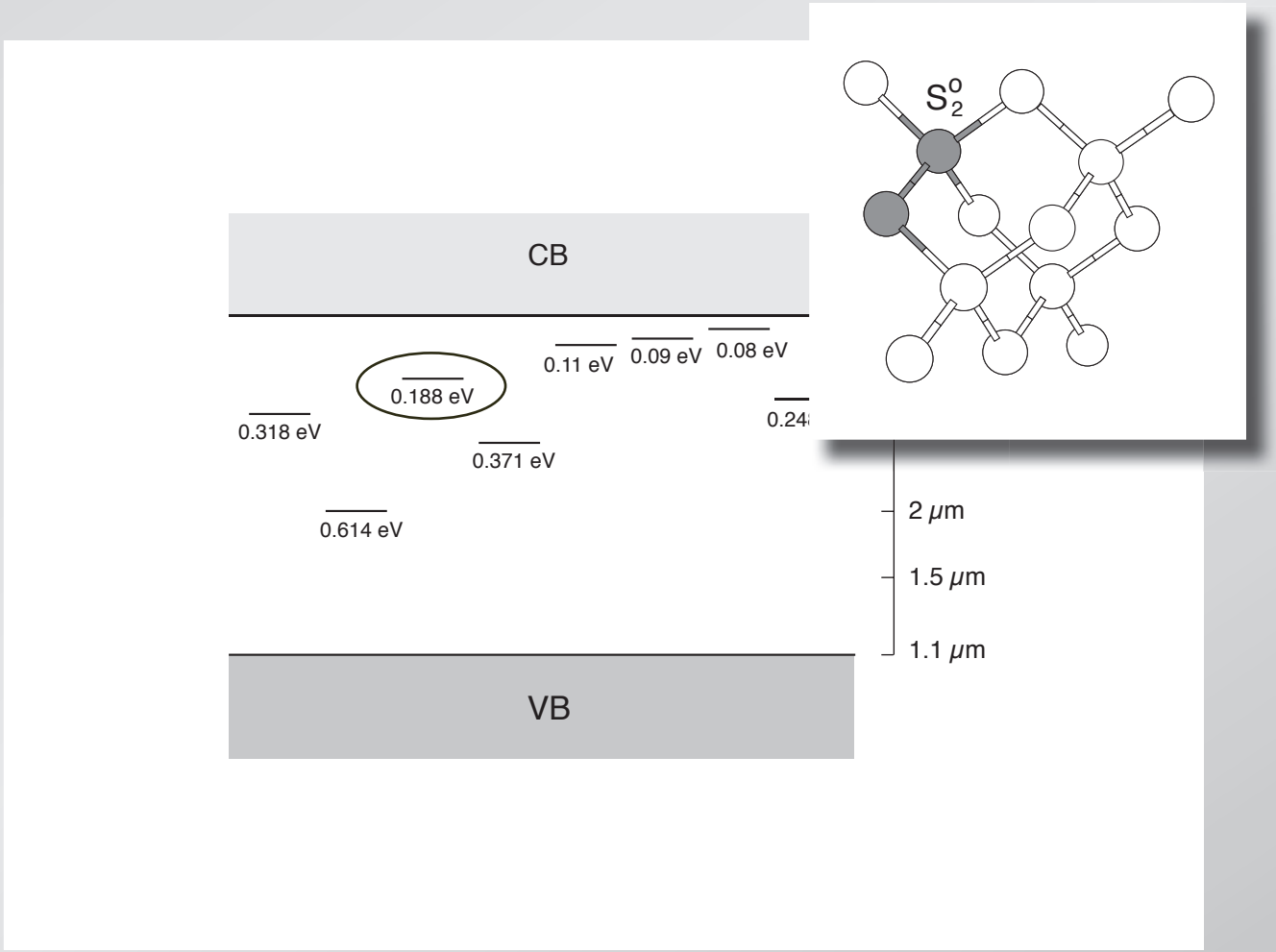

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Optoelectronic properties

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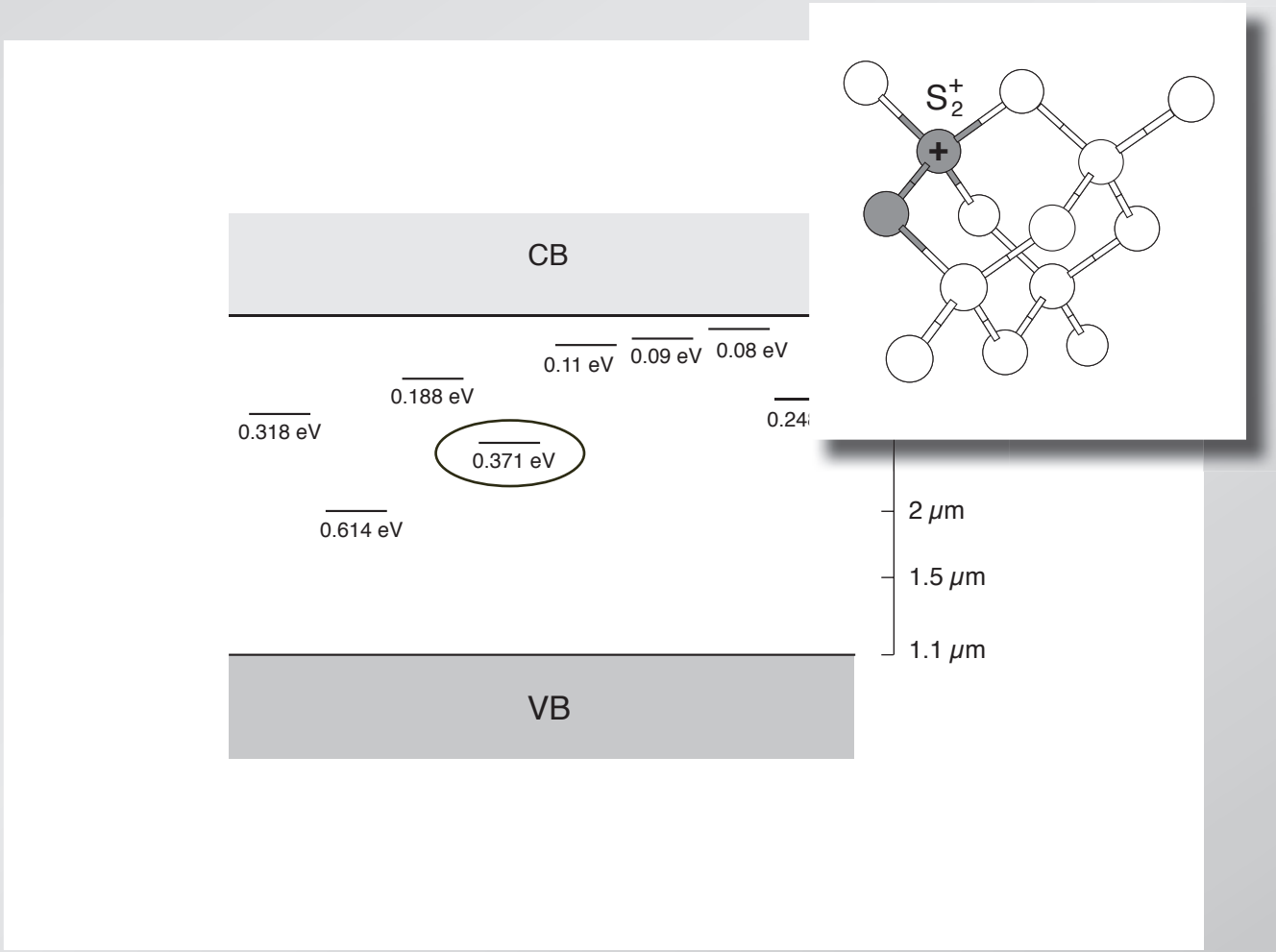

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Optoelectronic properties

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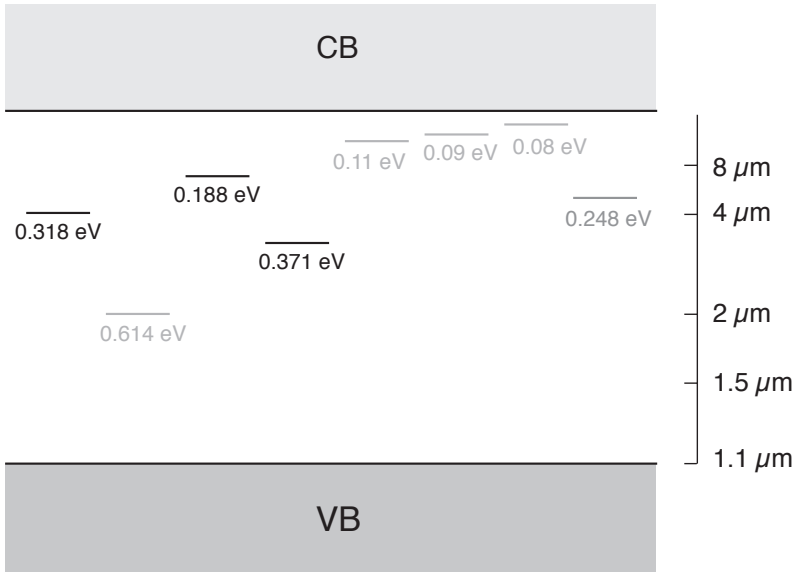
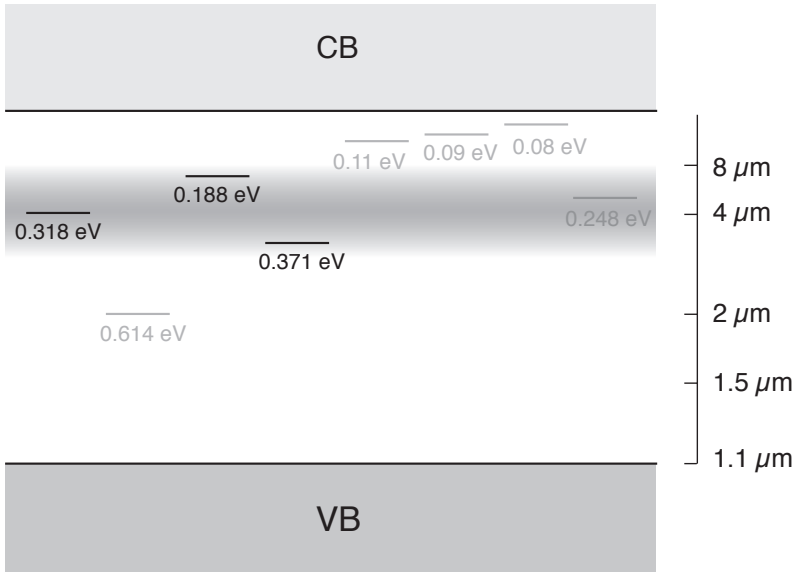


Janzén *et al.*, Phys. Rev. B 29, 1907 (1984)

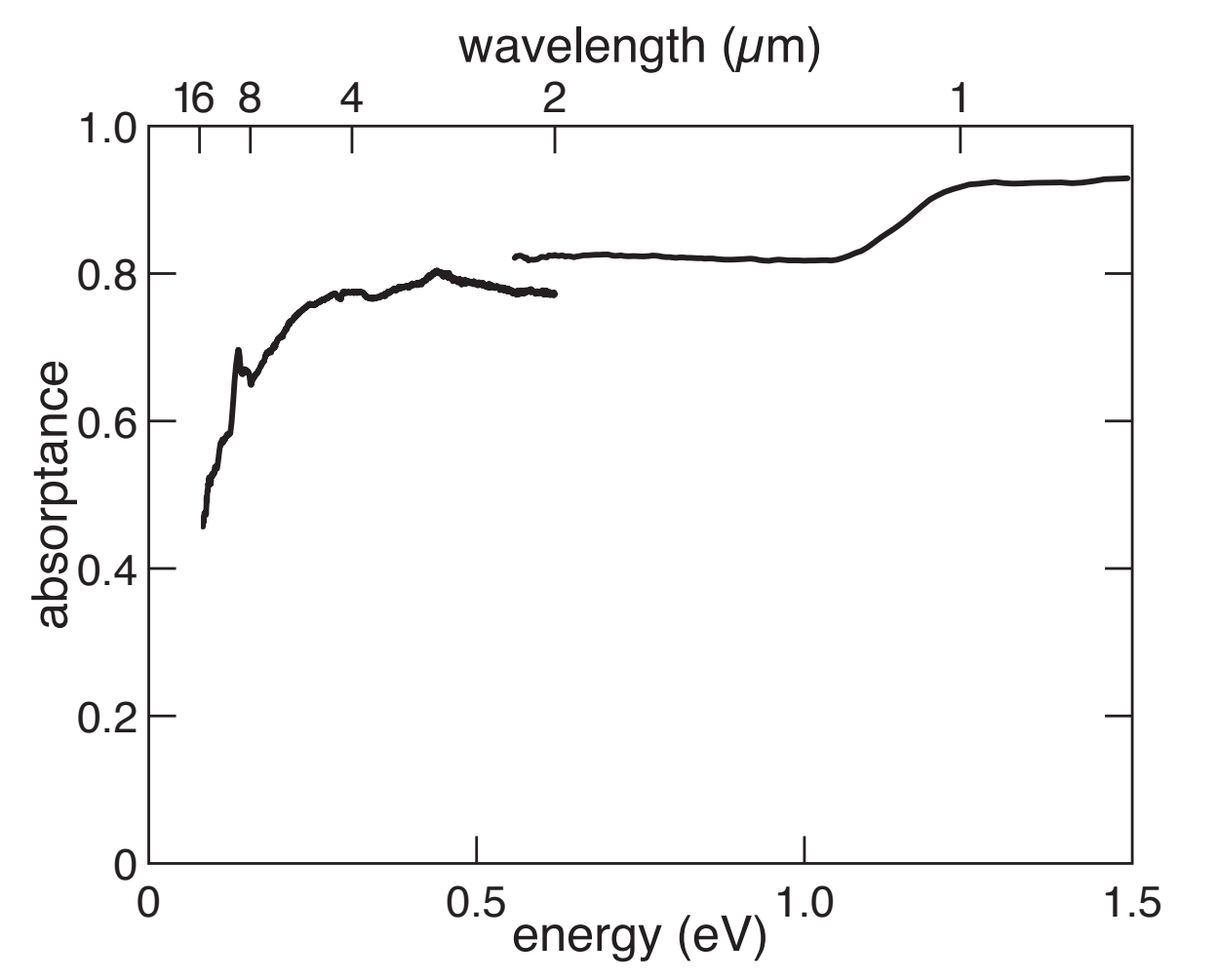
Optoelectronic properties

at high concentration states broaden into band



Optoelectronic properties

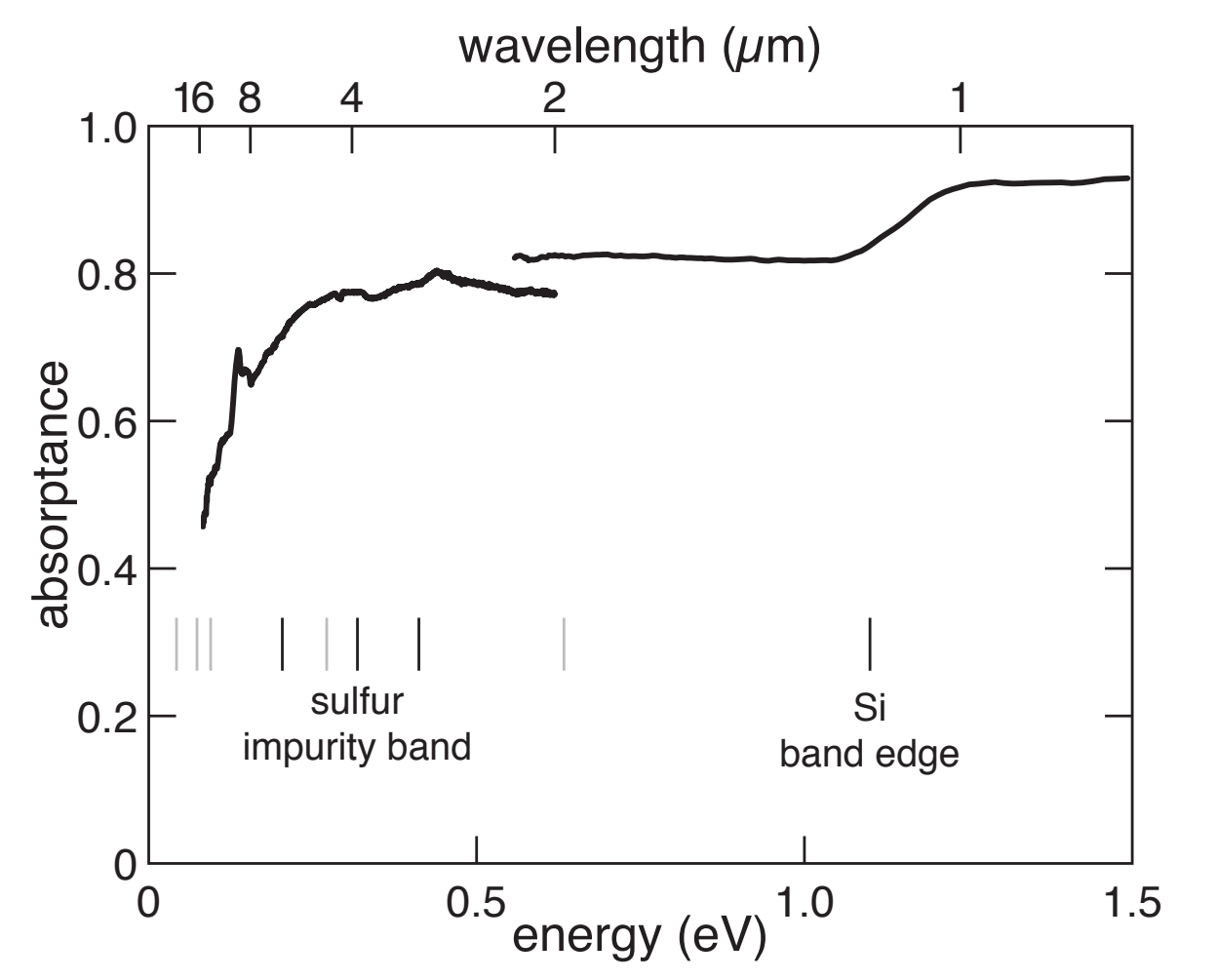
absorptance ($1 - R_{int} - T_{int}$)



Asenbaum, Vienna

Optoelectronic properties

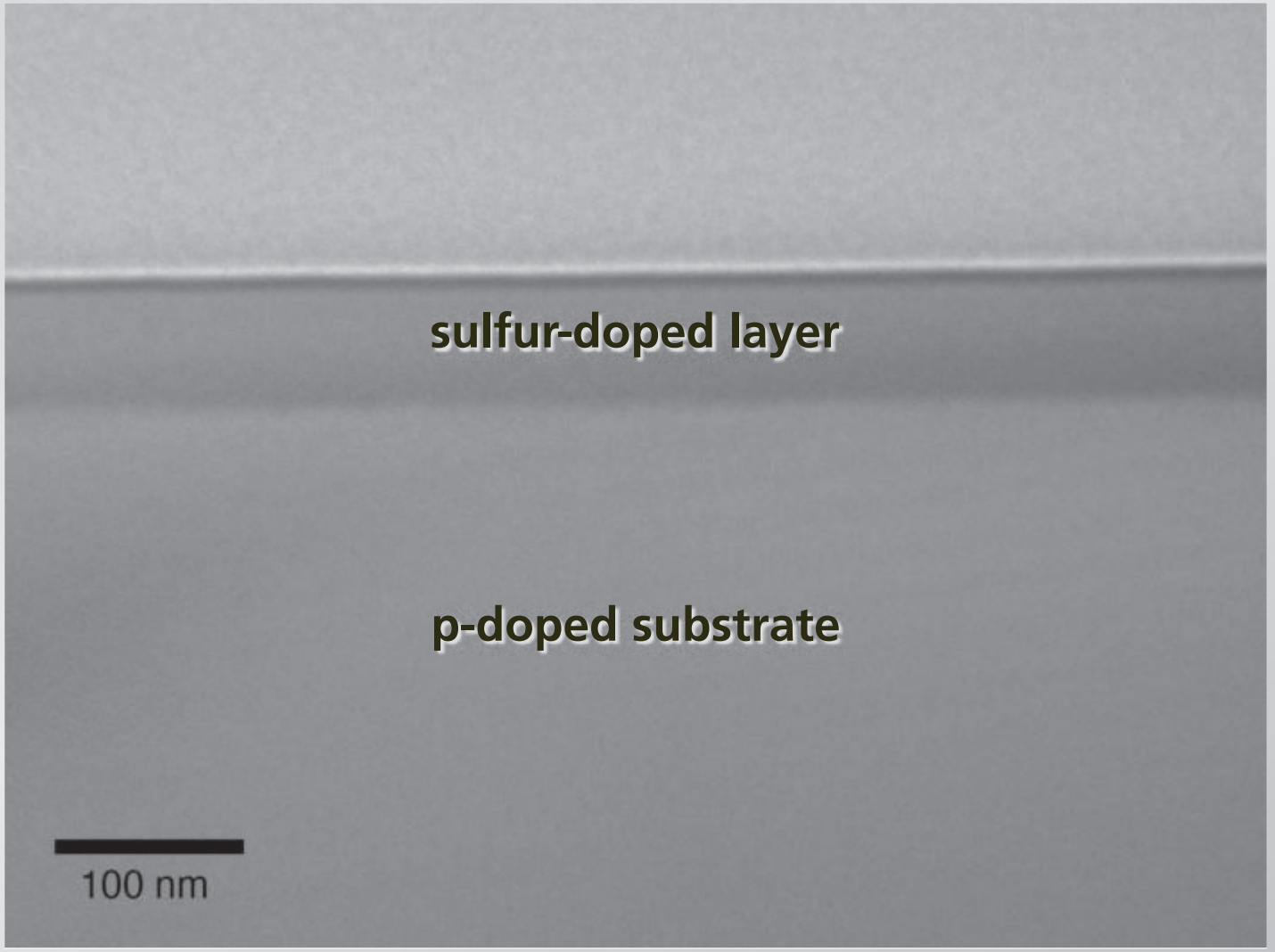
absorptance ($1 - R_{int} - T_{int}$)



Asenbaum, Vienna

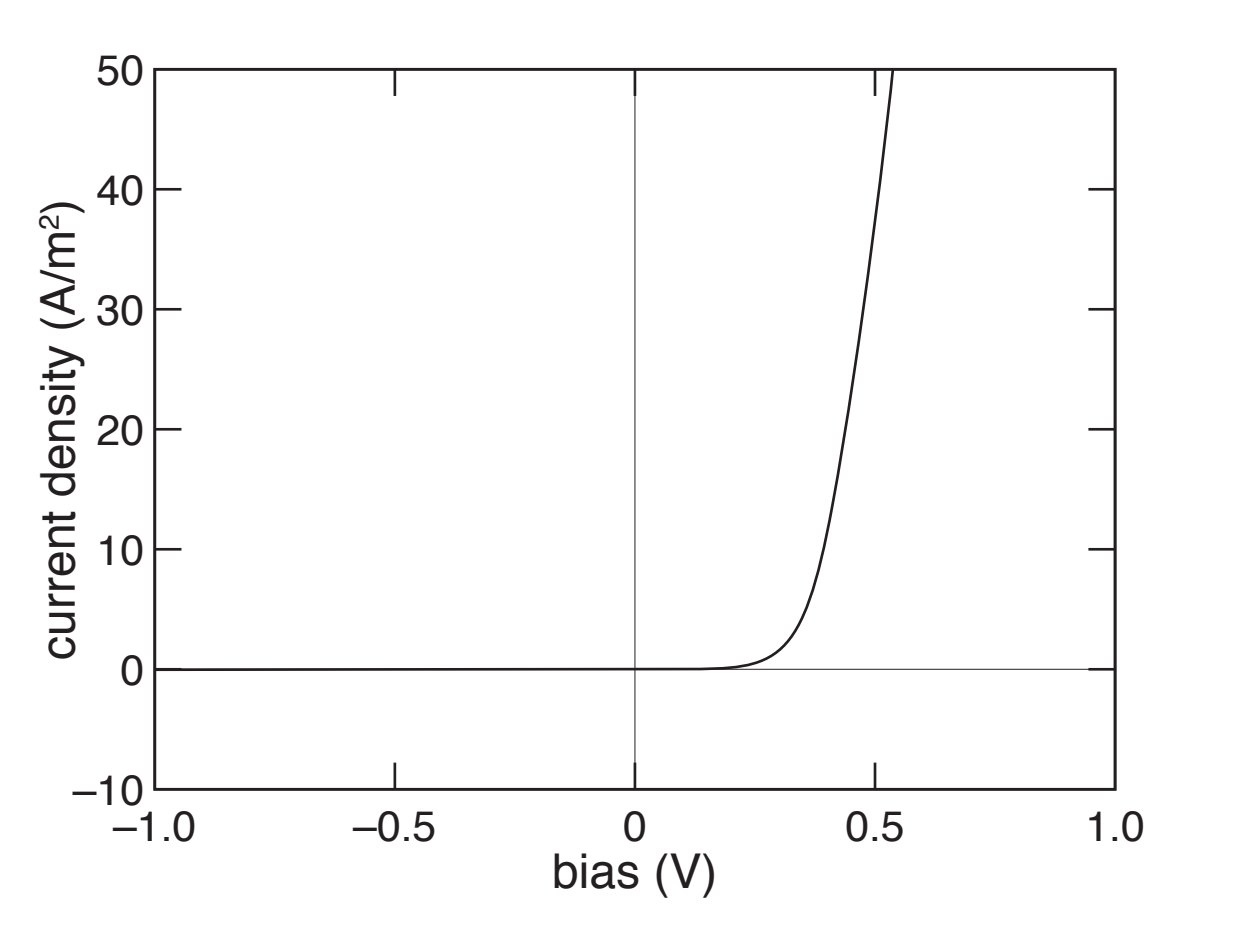
Optoelectronic properties

should have shallow junction below surface



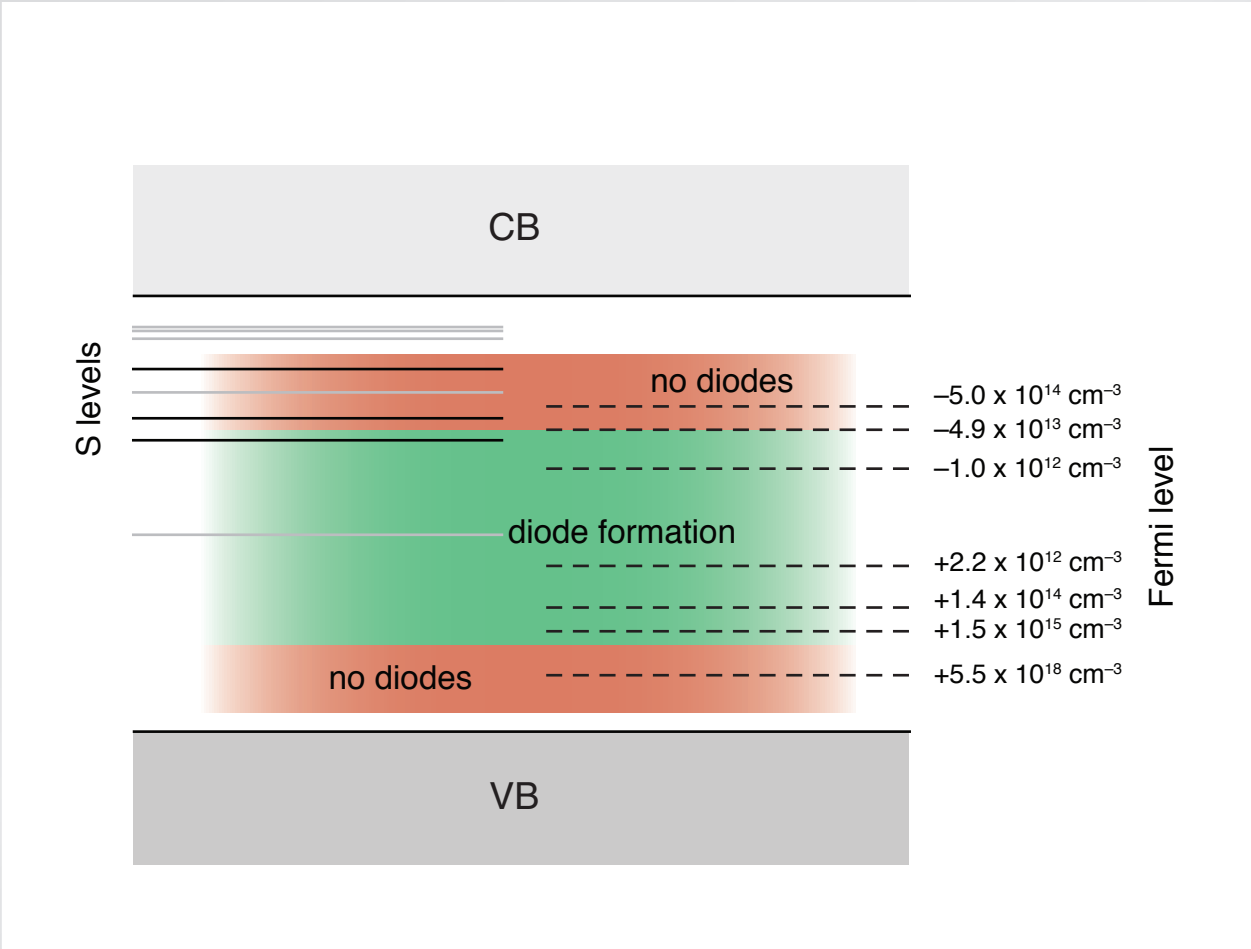
Optoelectronic properties

excellent rectification (after annealing)



Optoelectronic properties

probe impurity states by varying Fermi level in substrate



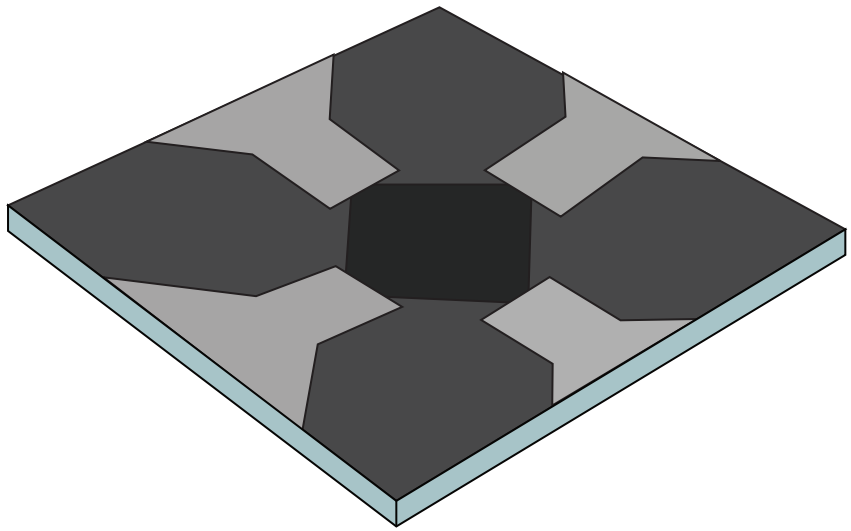
Optoelectronic properties

IV **behavior consistent with**

impurity band between 200 and 400 meV

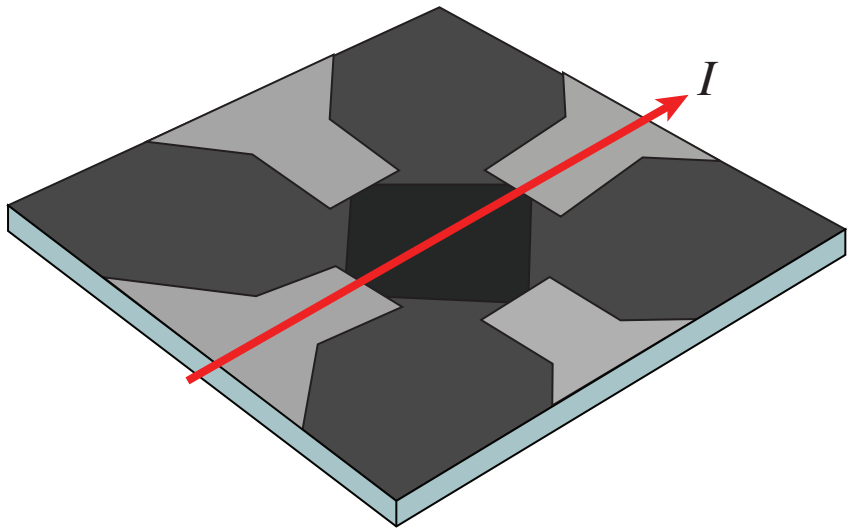
Optoelectronic properties

Hall measurements



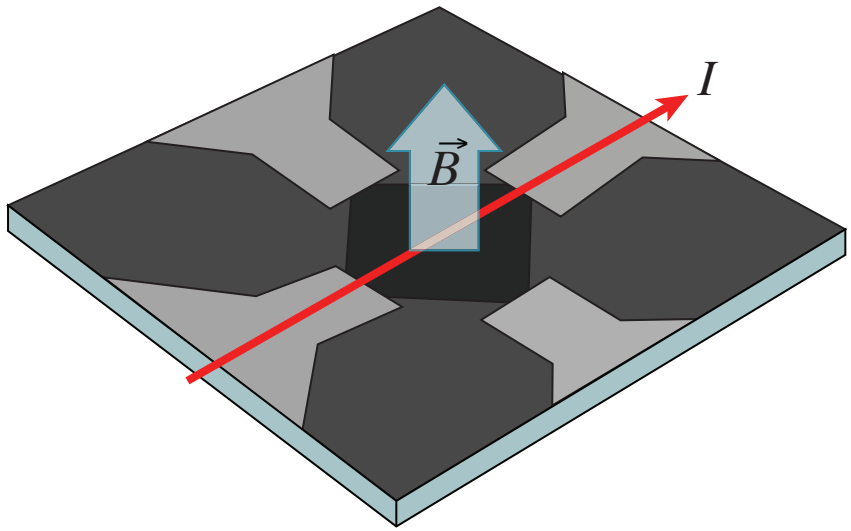
Optoelectronic properties

Hall measurements



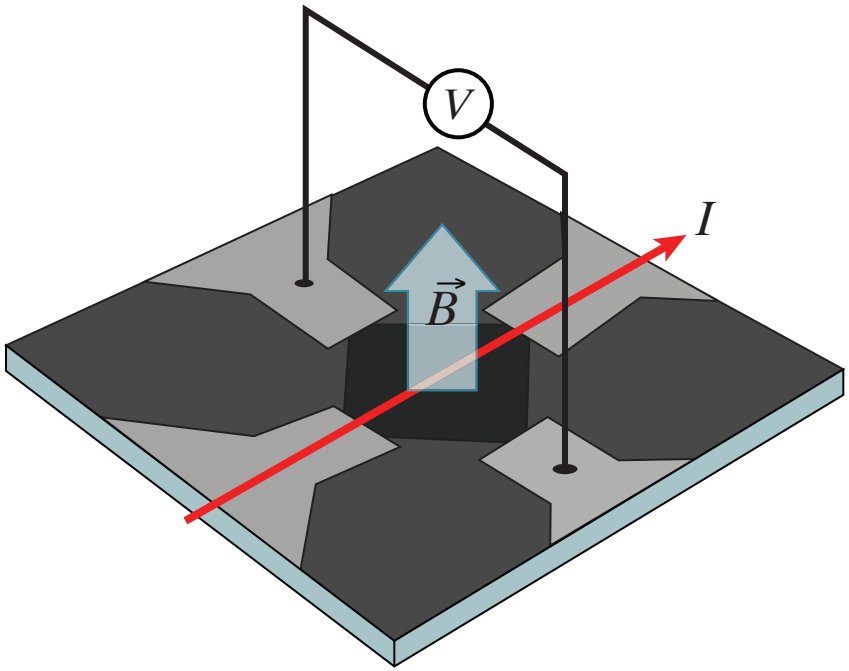
Optoelectronic properties

Hall measurements



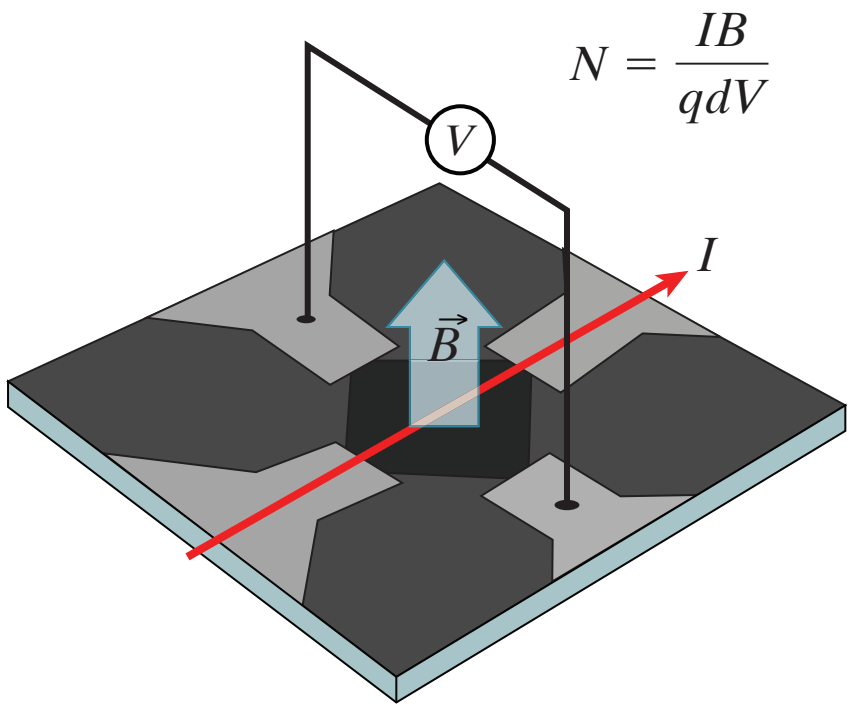
Optoelectronic properties

Hall measurements



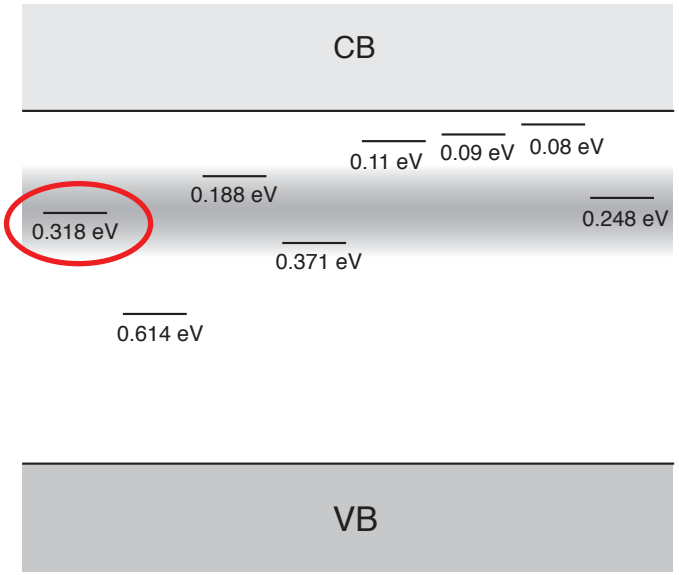
Optoelectronic properties

Hall measurements



Optoelectronic properties

impurity (donor) band centered at 310 meV

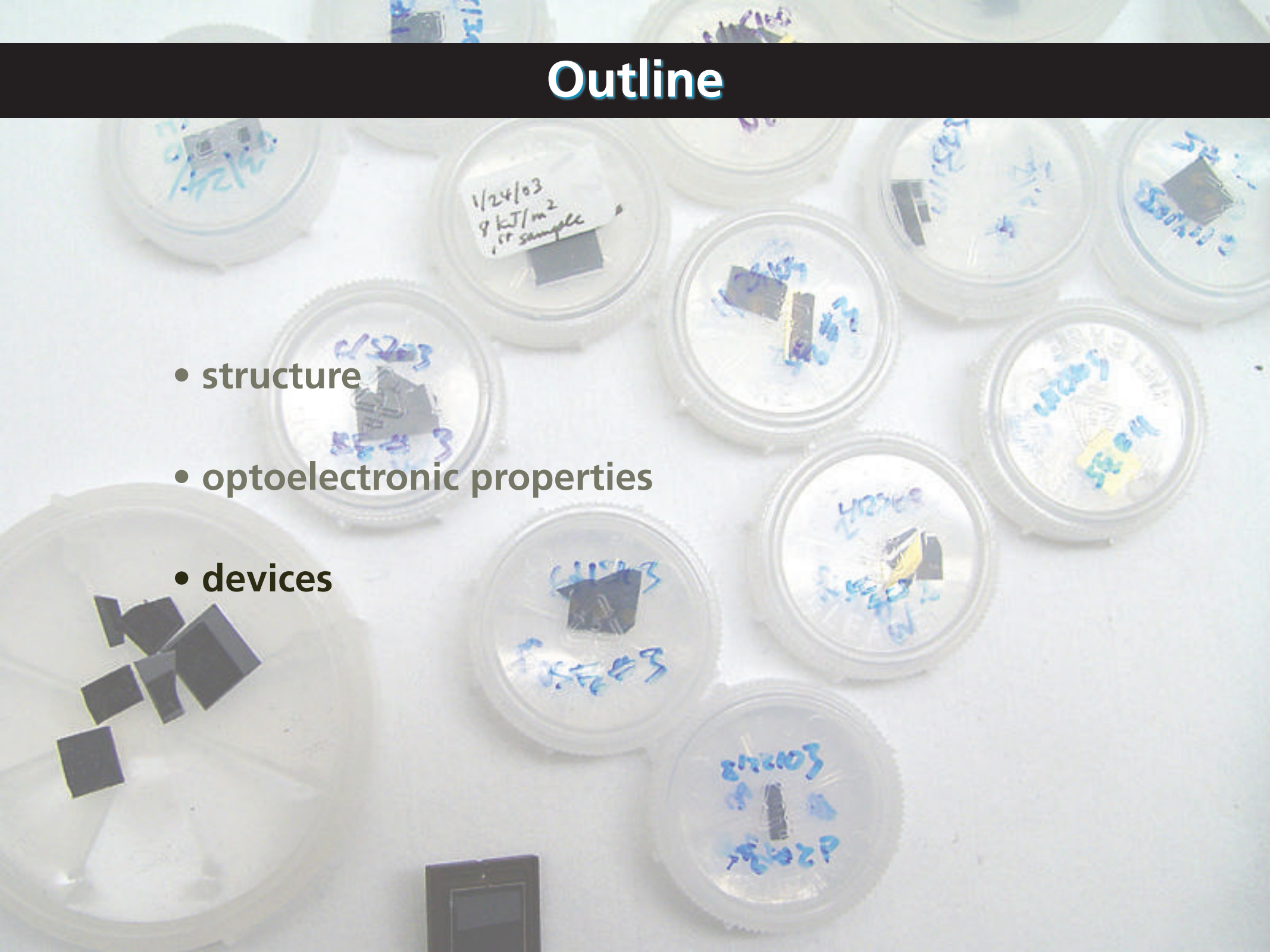


Optoelectronic properties

Things to keep in mind

- IR absorption rolls off around 8 μm
- 1 in 10^3 sulfur atoms are ionized donors at 300 K
- all data indicate these S donors are substitutional

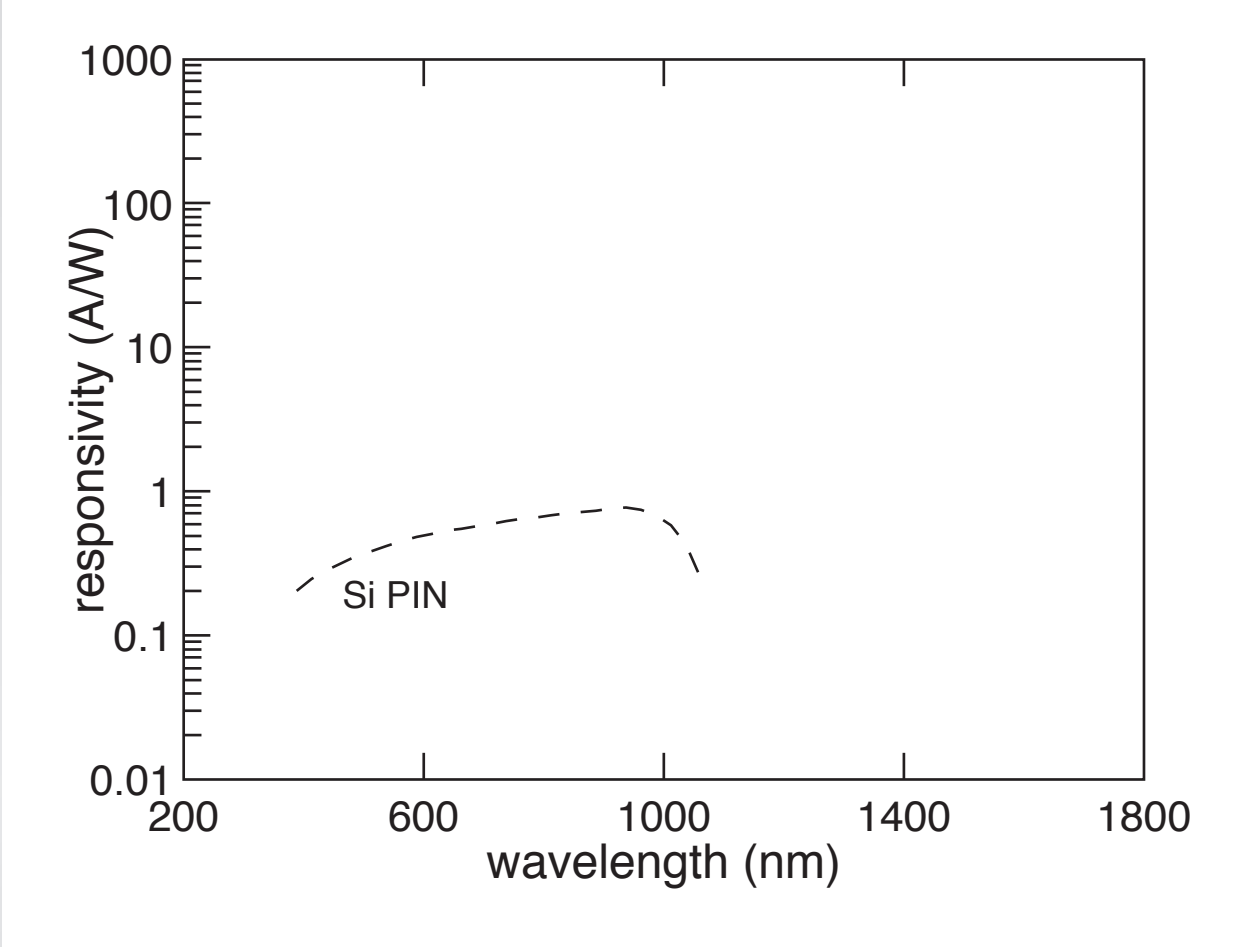
Outline



- structure
- optoelectronic properties
- devices

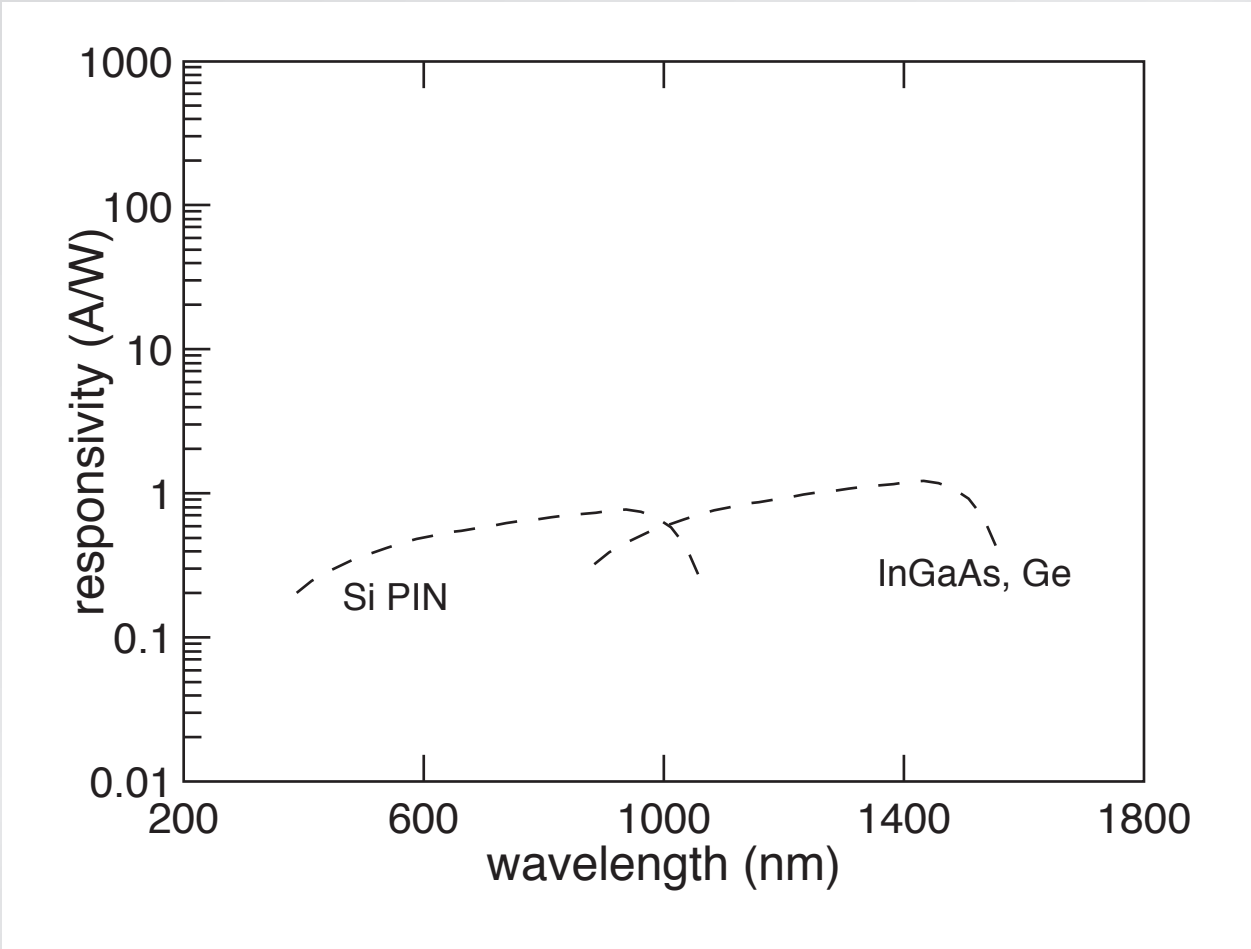
Devices

responsivity



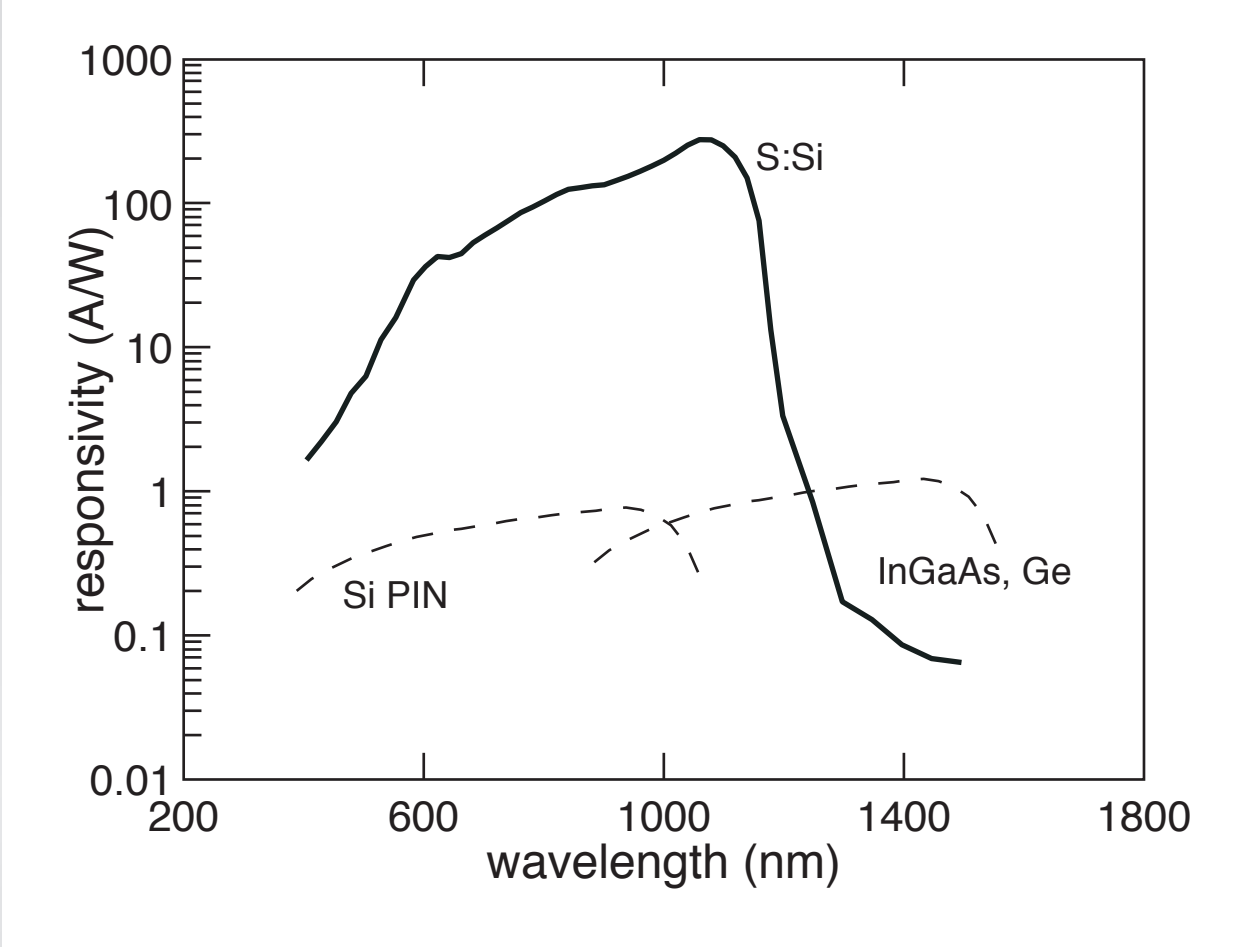
Devices

responsivity



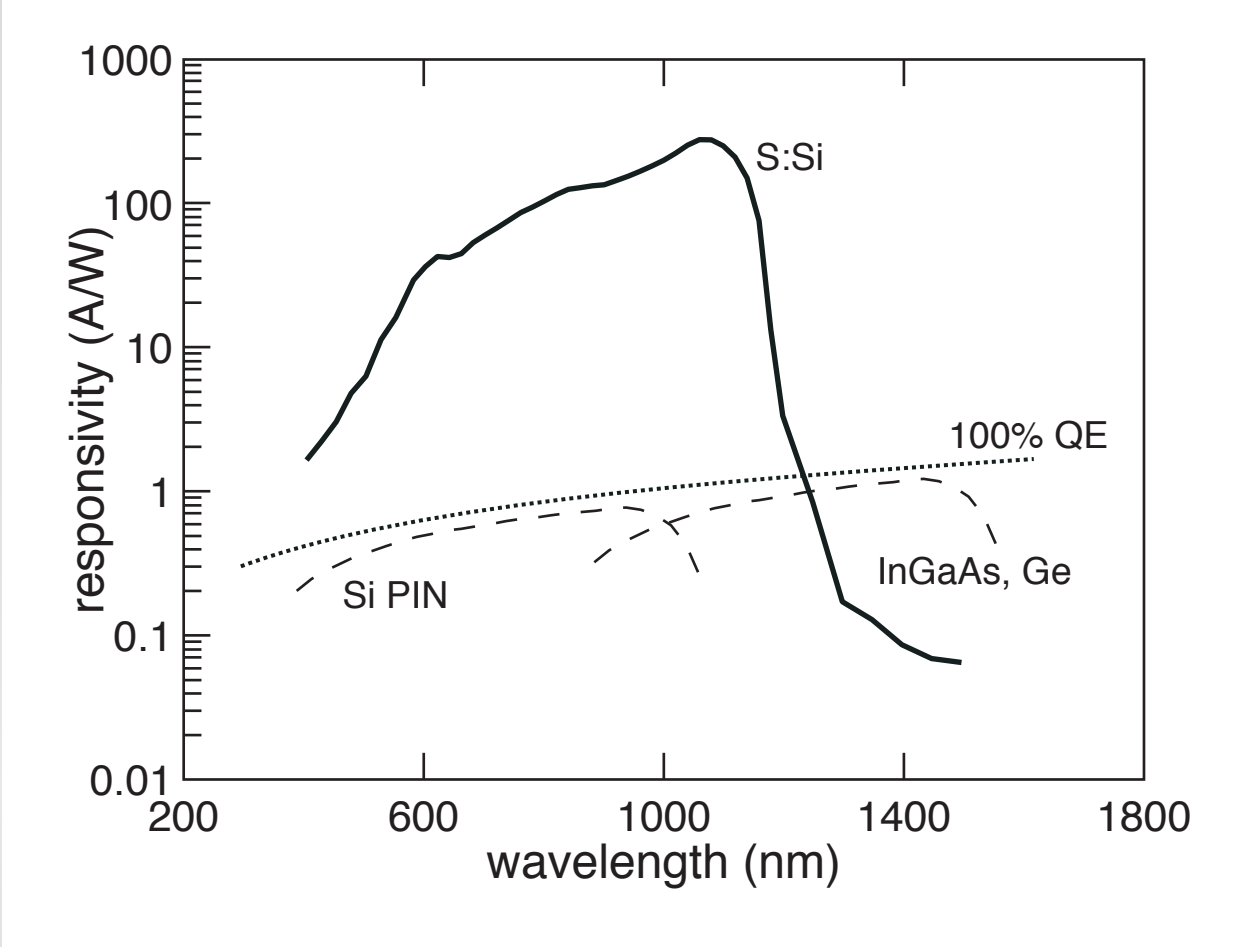
Devices

responsivity



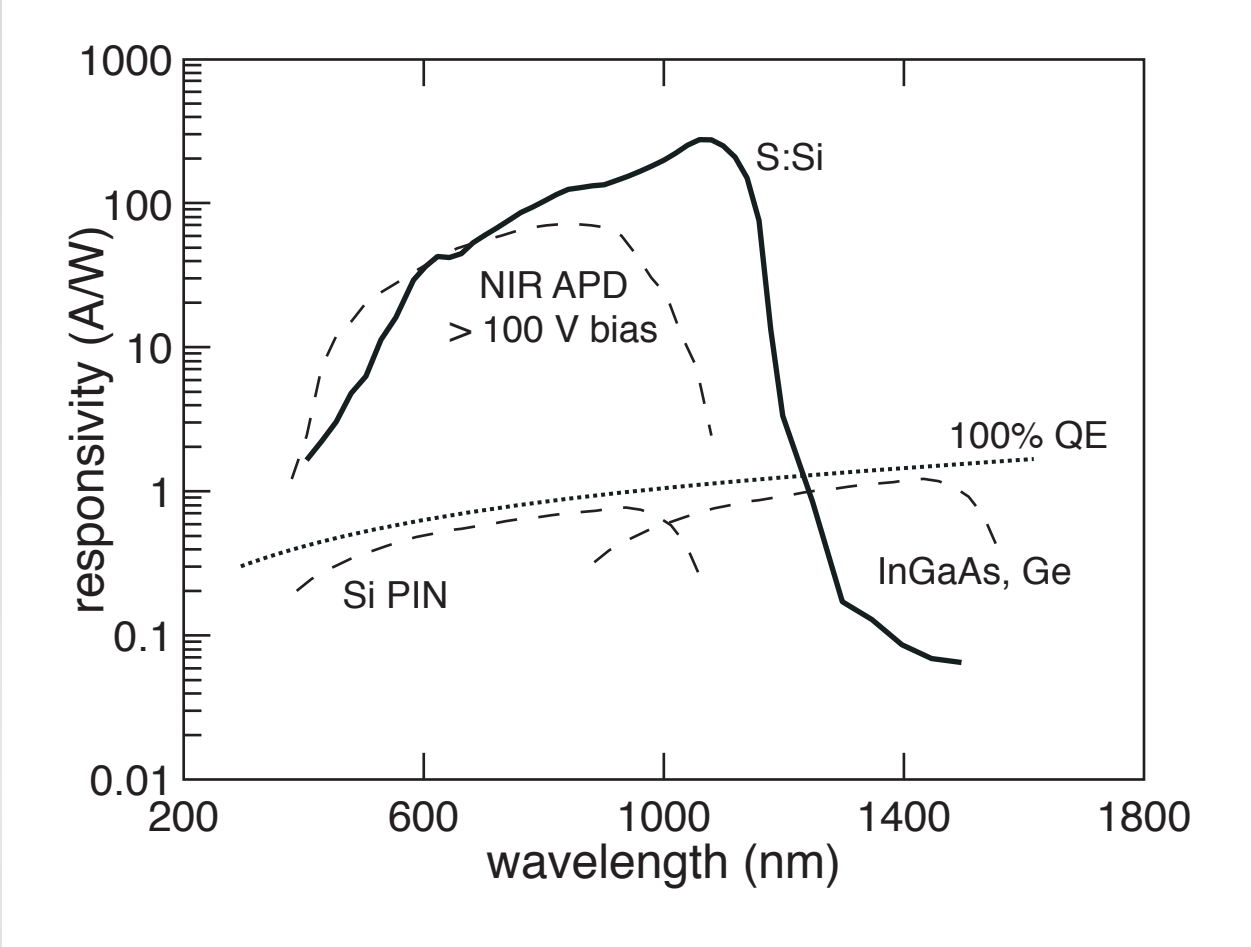
Devices

responsivity



Devices

responsivity

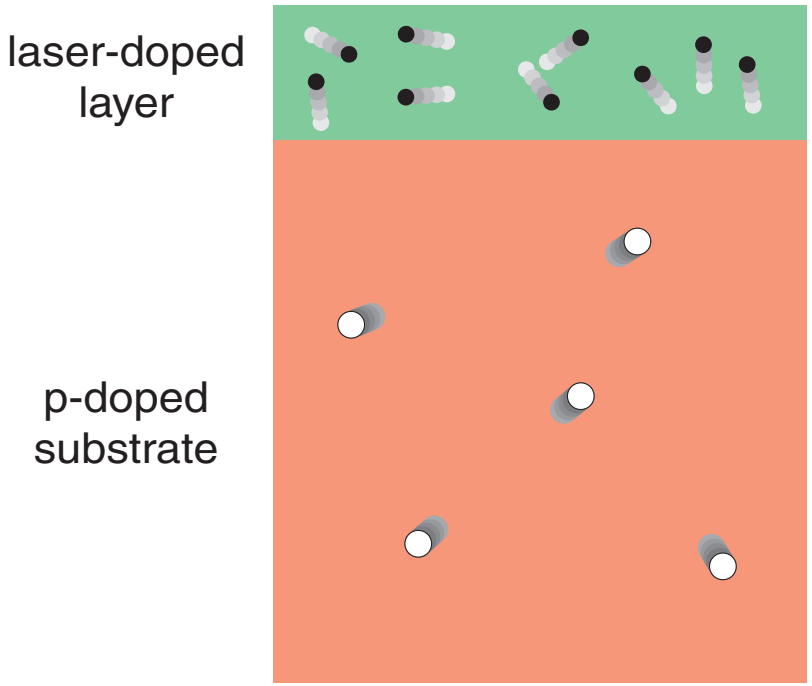


Devices

What causes gain?

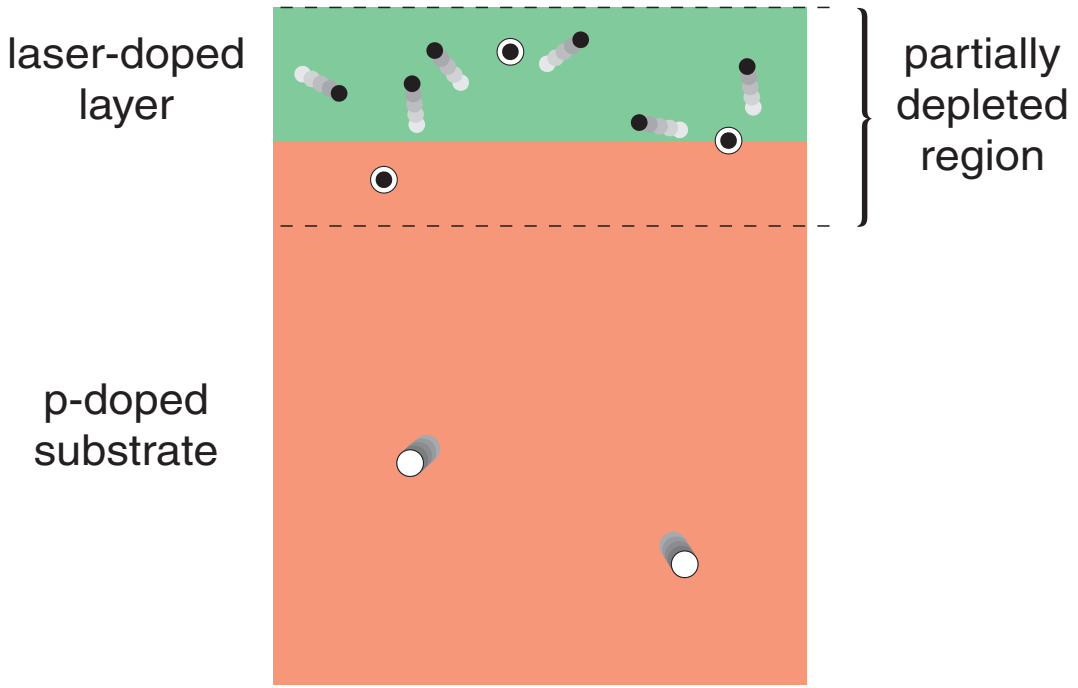
- impact excitation (avalanching)
- carrier lifetime >> transit time (photoconductive gain)
- some other mechanism

Devices



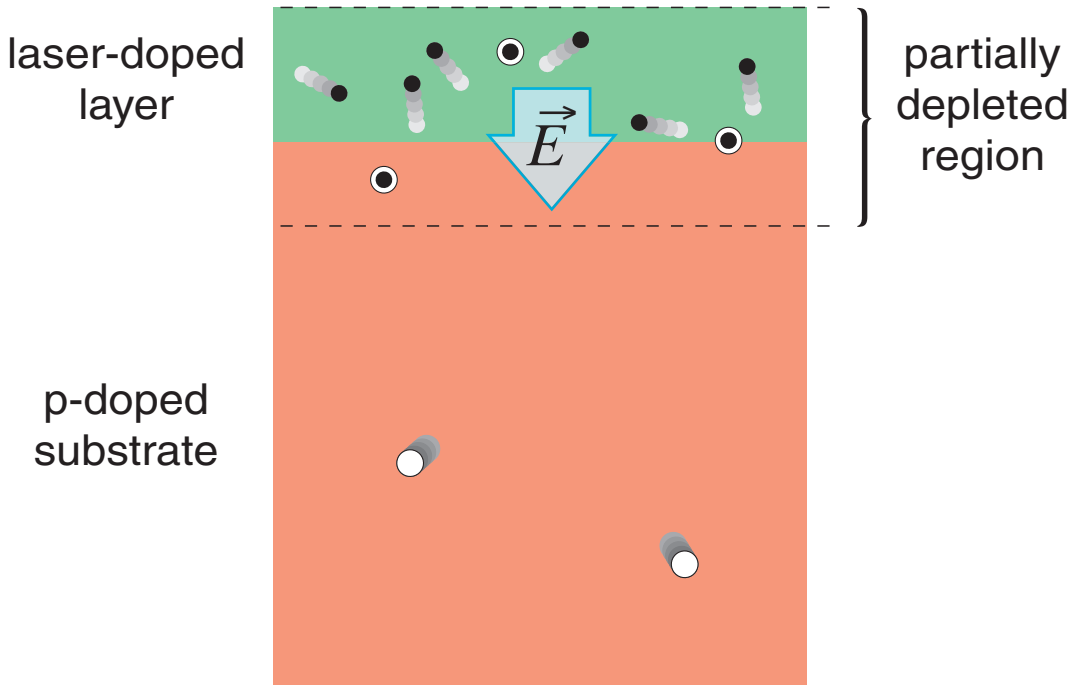
“pl junction”

Devices



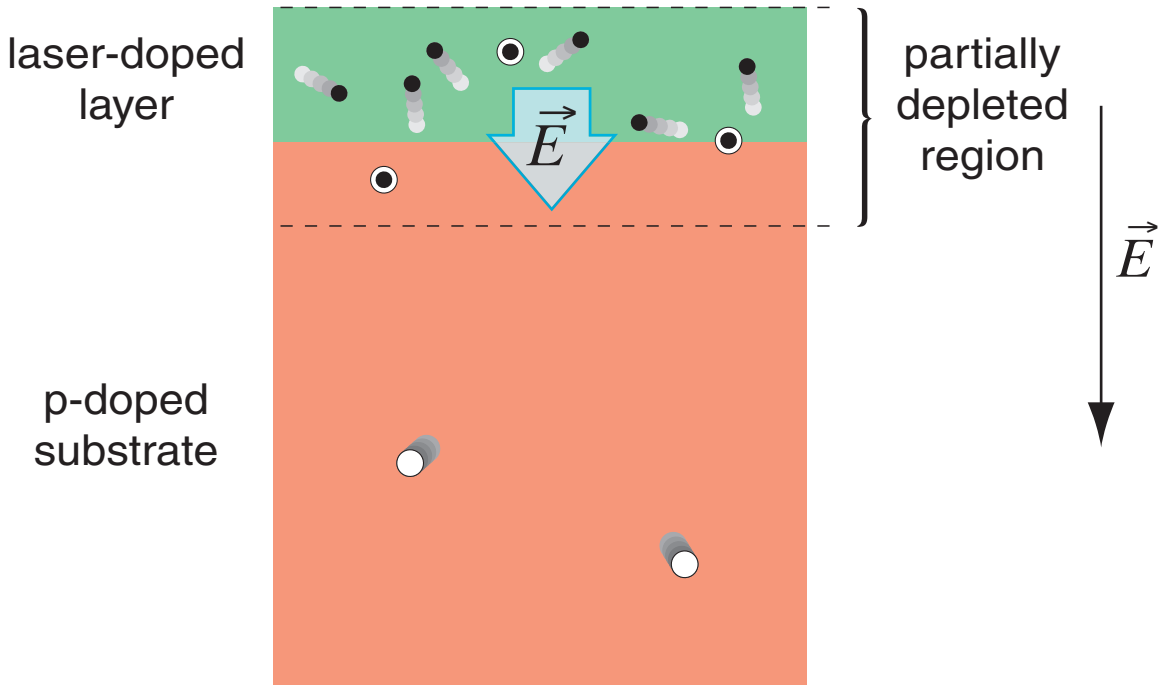
formation of partially depleted region

Devices



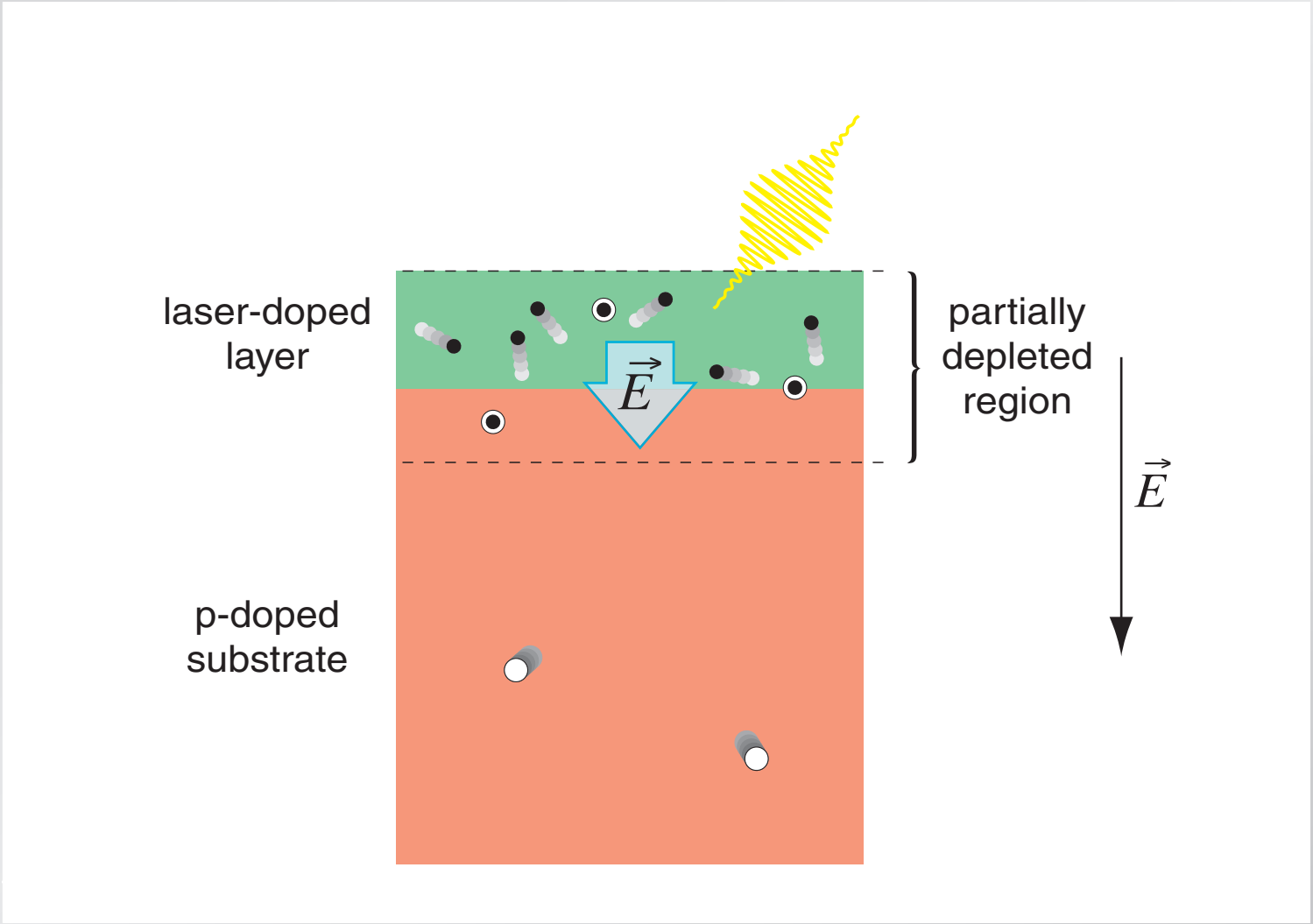
formation of partially depleted region

Devices



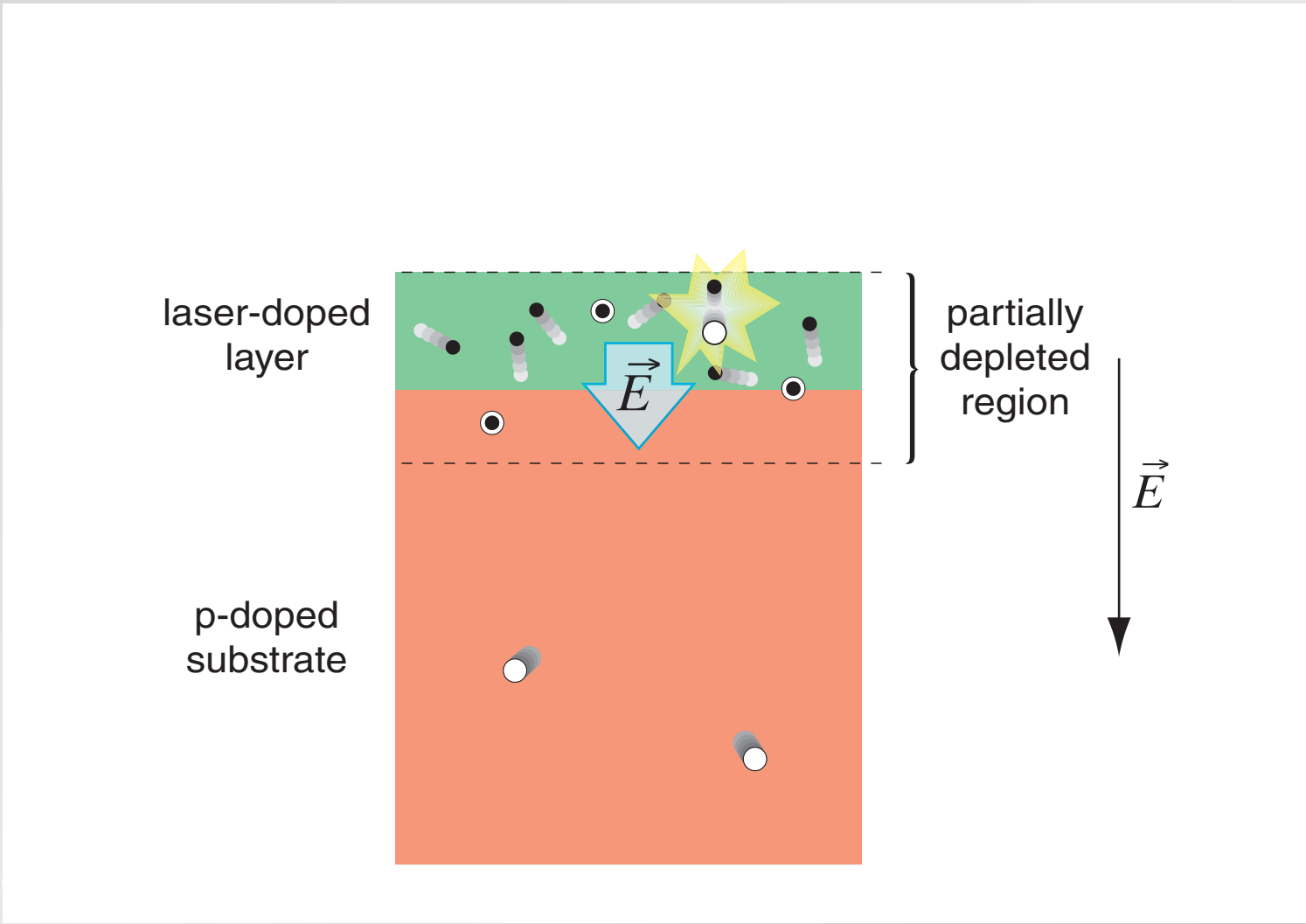
apply backward bias…

Devices



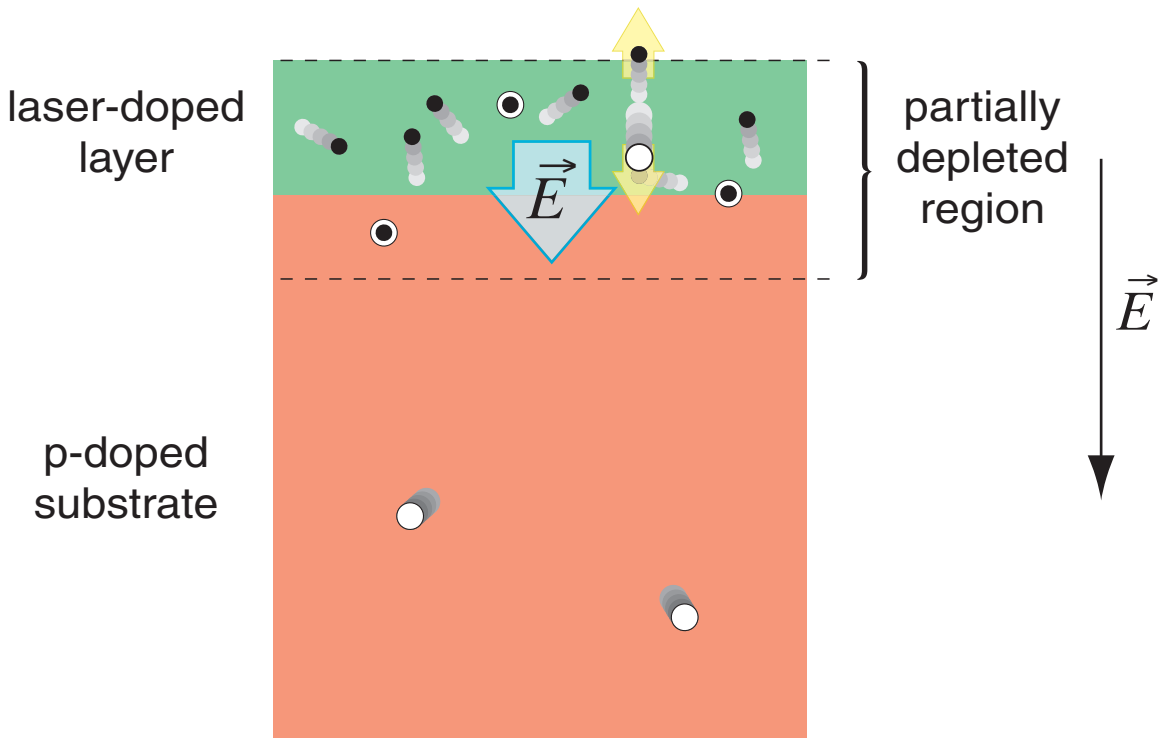
…incident photon generates electron-hole pair…

Devices



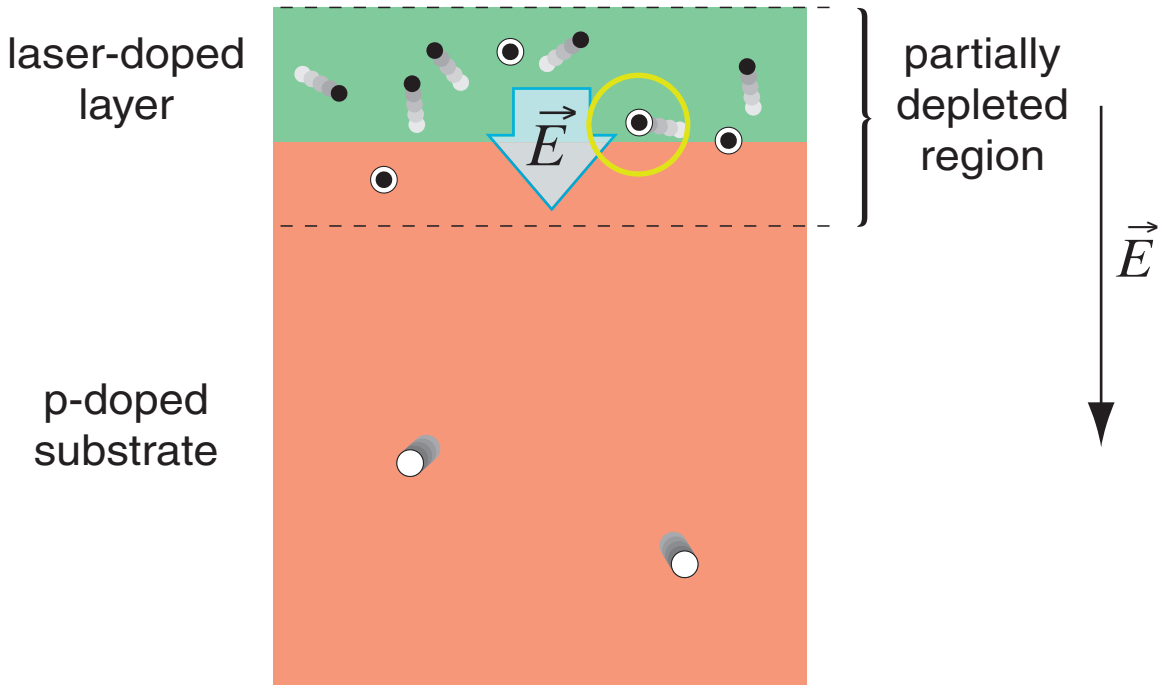
…incident photon generates electron-hole pair…

Devices



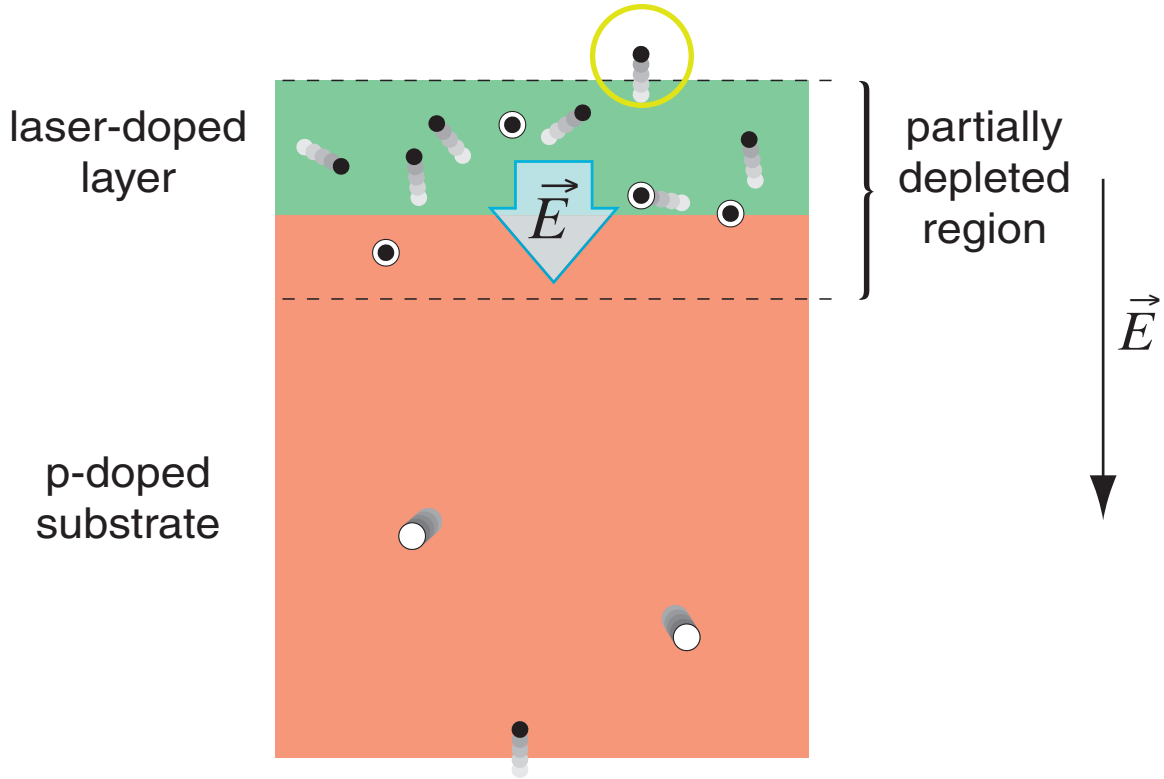
…carriers accelerate away from each other…

Devices



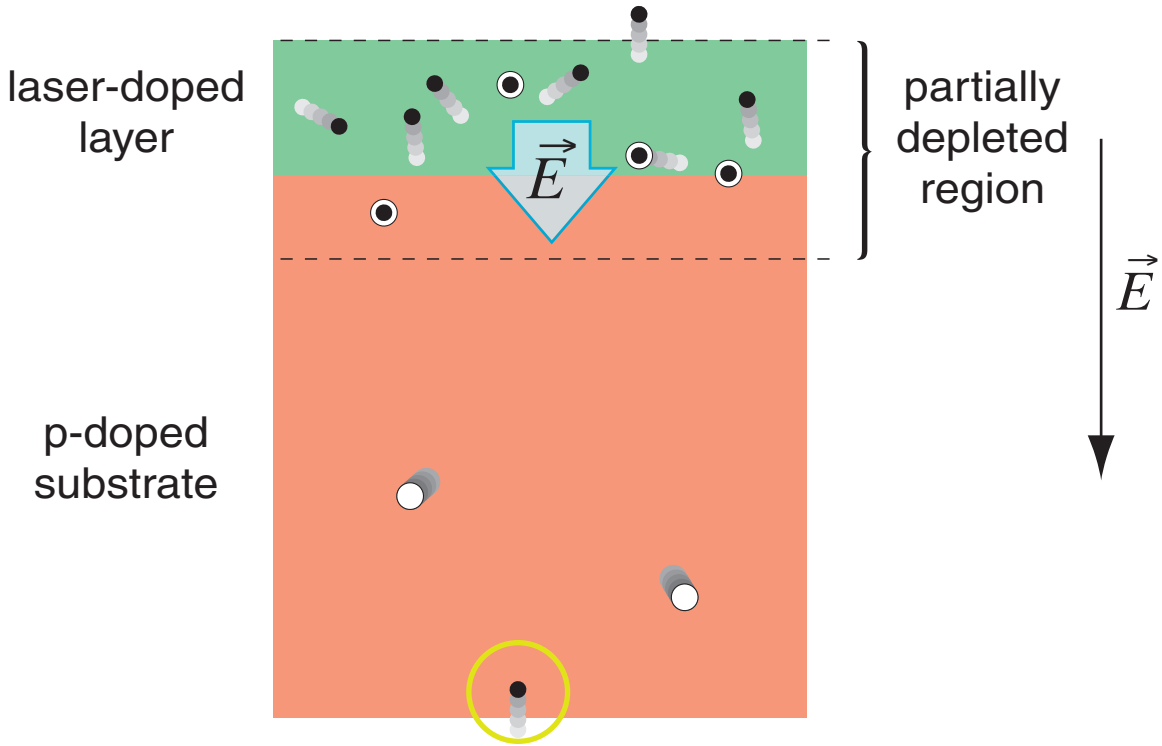
…hole is trapped

Devices



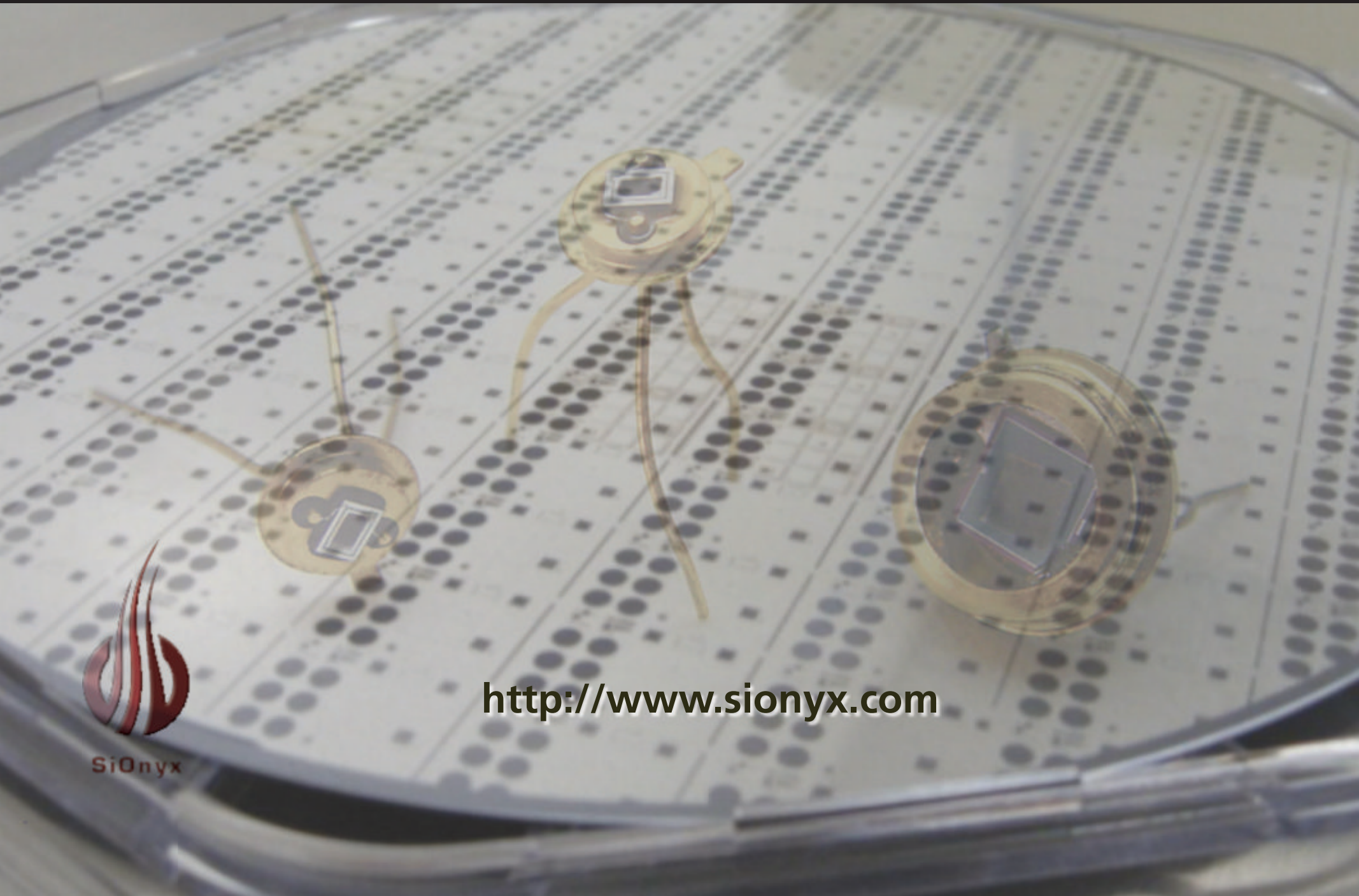
meanwhile electron exits sample…

Devices



…and source provides new electron

Devices



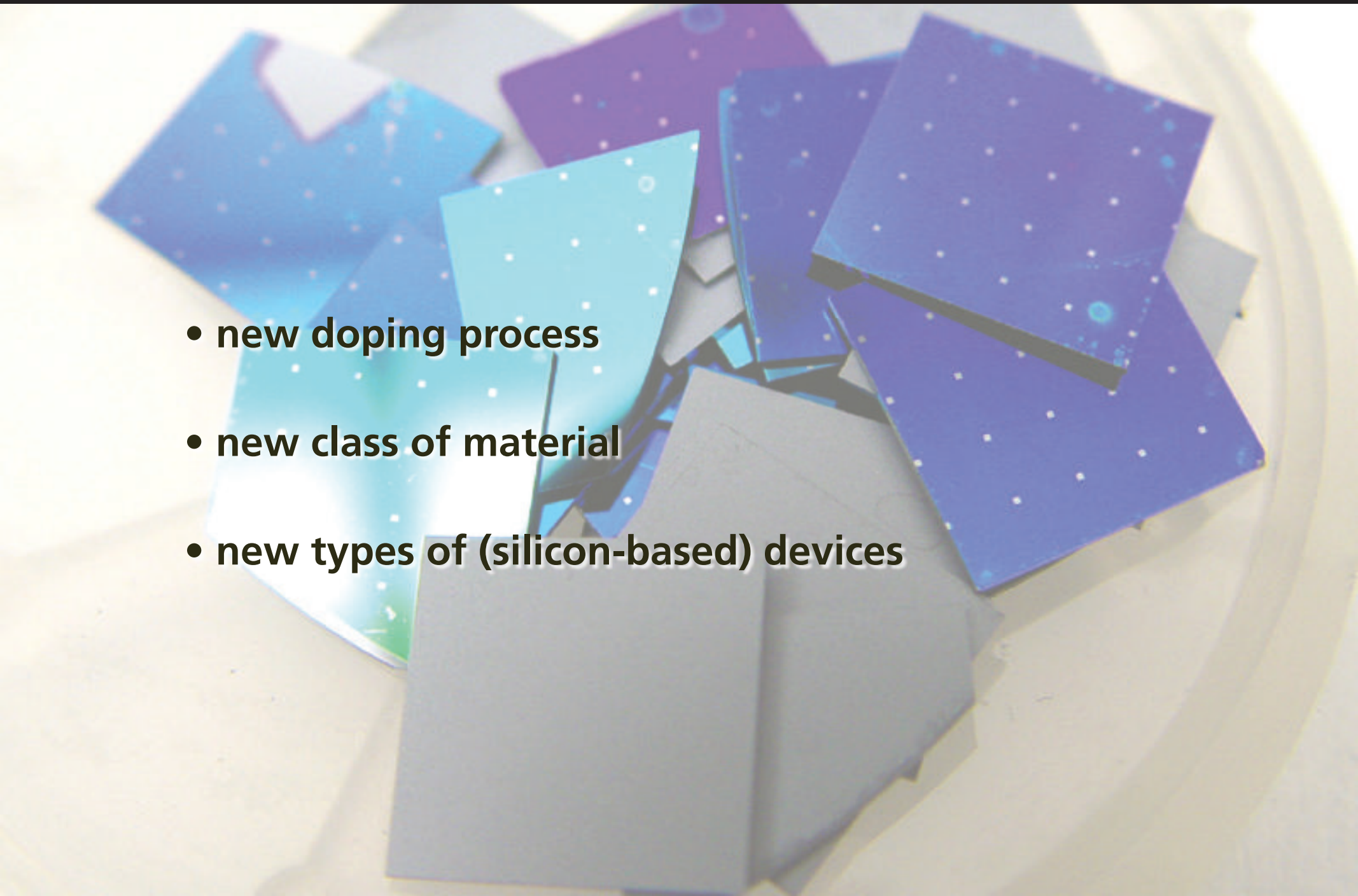
http://www.sionyx.com

Devices

Things to keep in mind

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

Conclusion

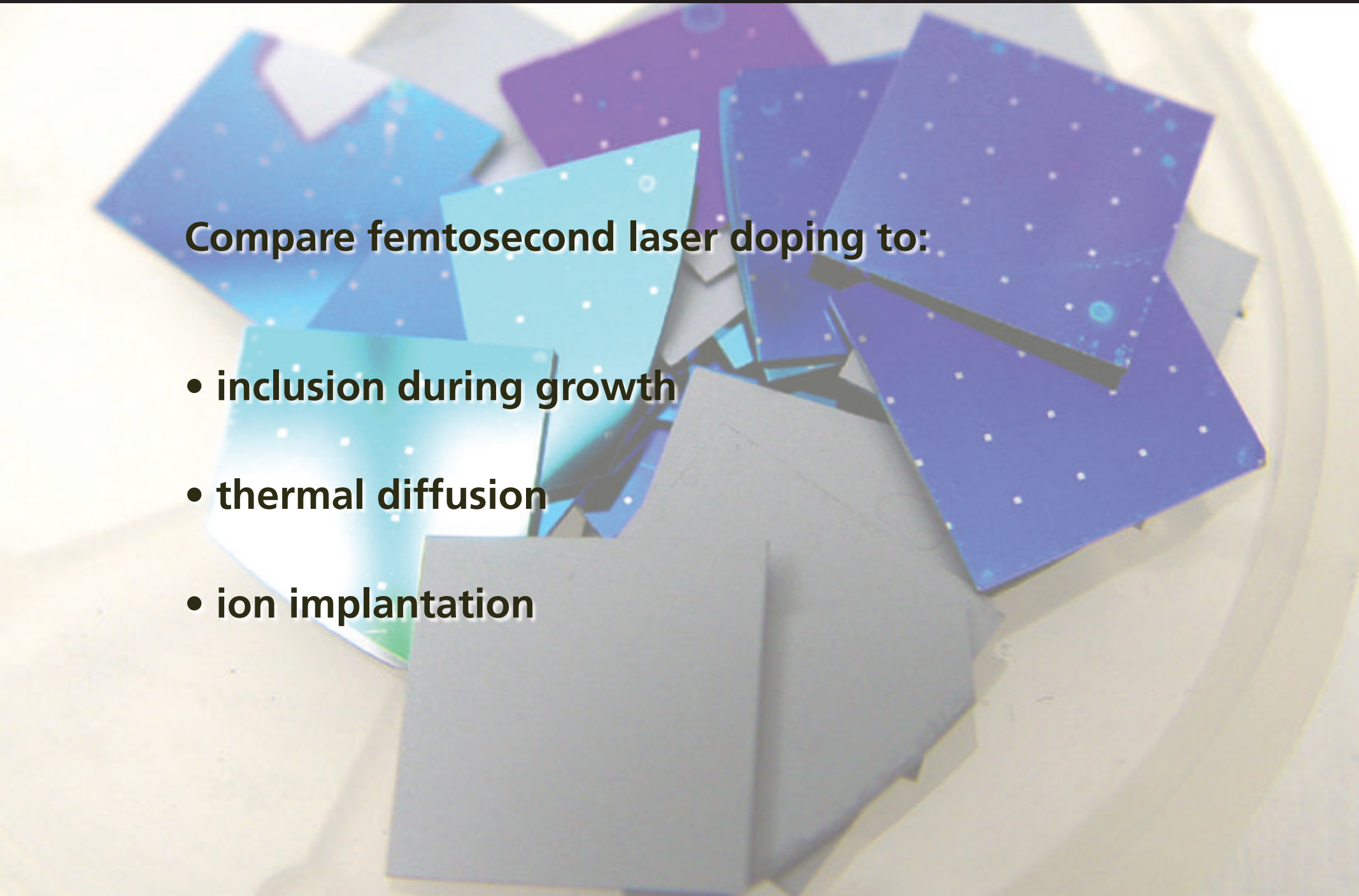


- new doping process
- new class of material
- new types of (silicon-based) devices

Conclusion

What is different about this process?

Conclusion



Compare femtosecond laser doping to:

- inclusion during growth
- thermal diffusion
- ion implantation

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for more information:

http://mazur-www.harvard.edu