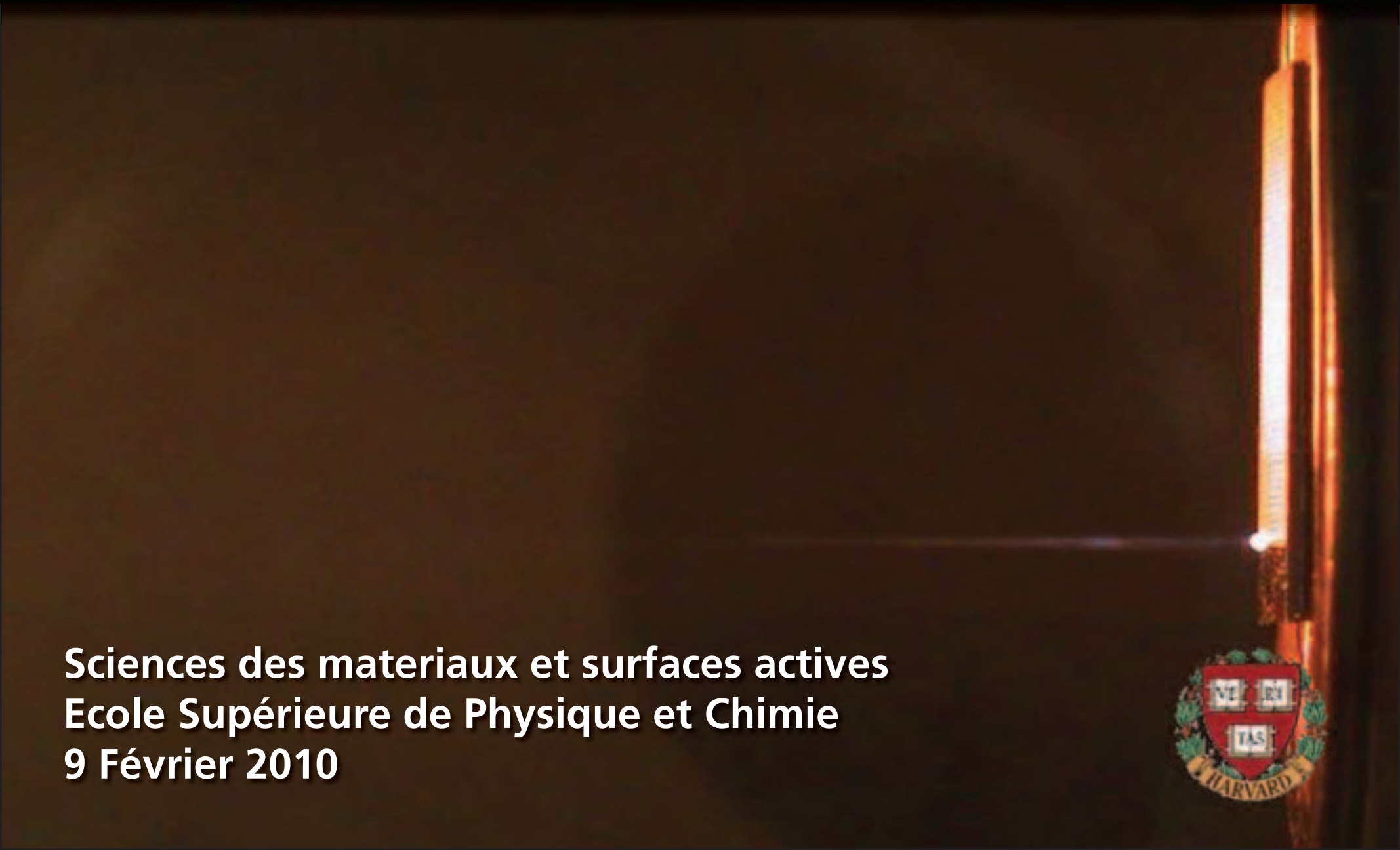
Femtosecond laser materials processing



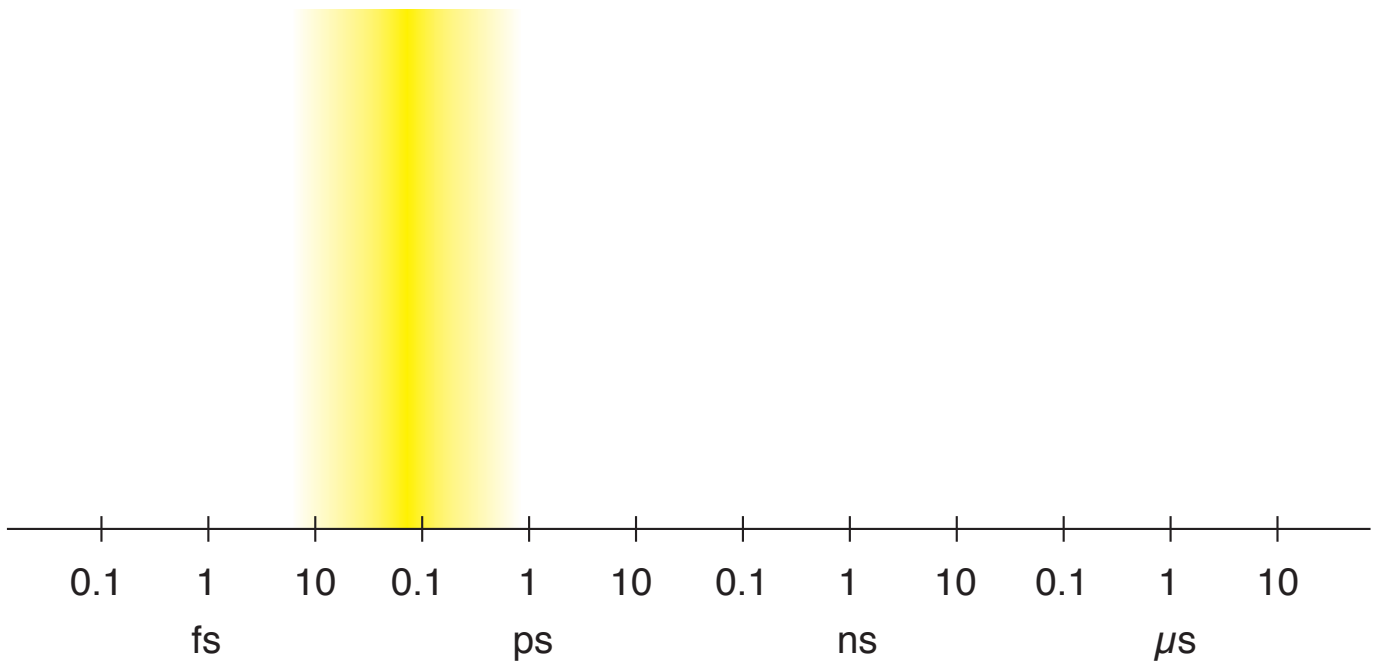
Sciences des materiaux et surfaces actives
Ecole Supérieure de Physique et Chimie
9 Février 2010

Introduction

why study materials with femtosecond pulses?

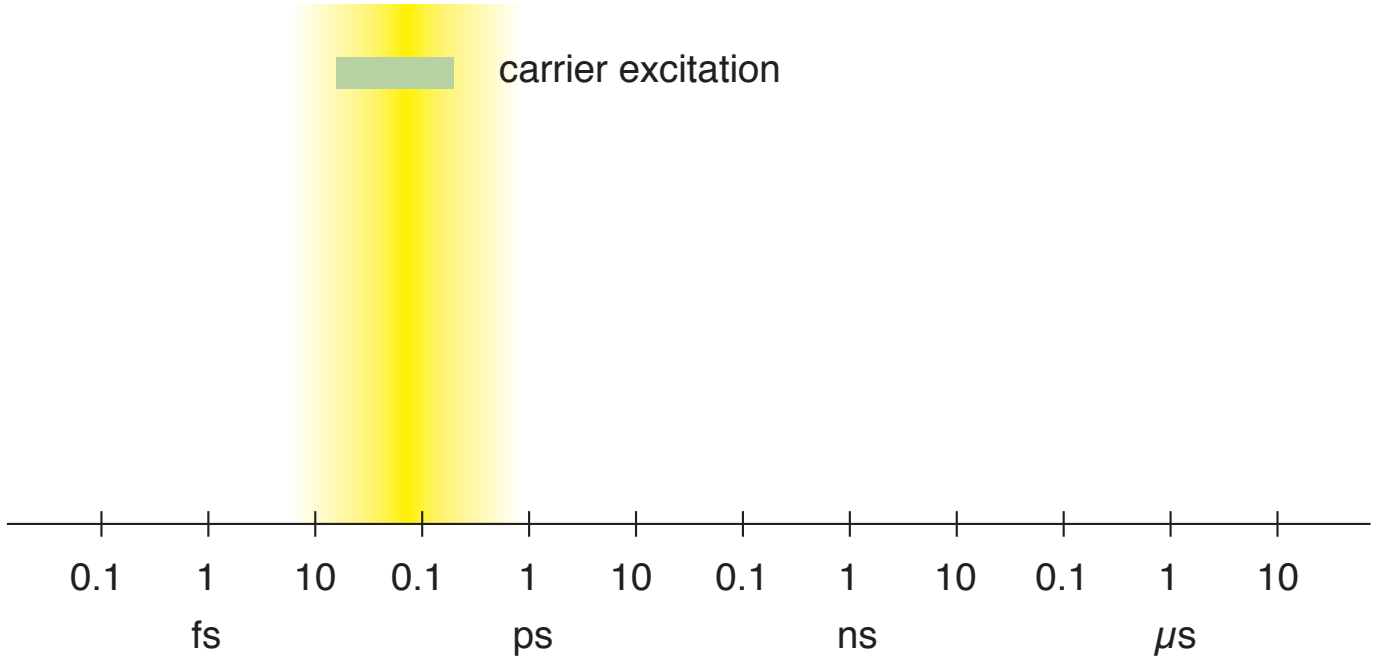
Introduction

relevant time scales



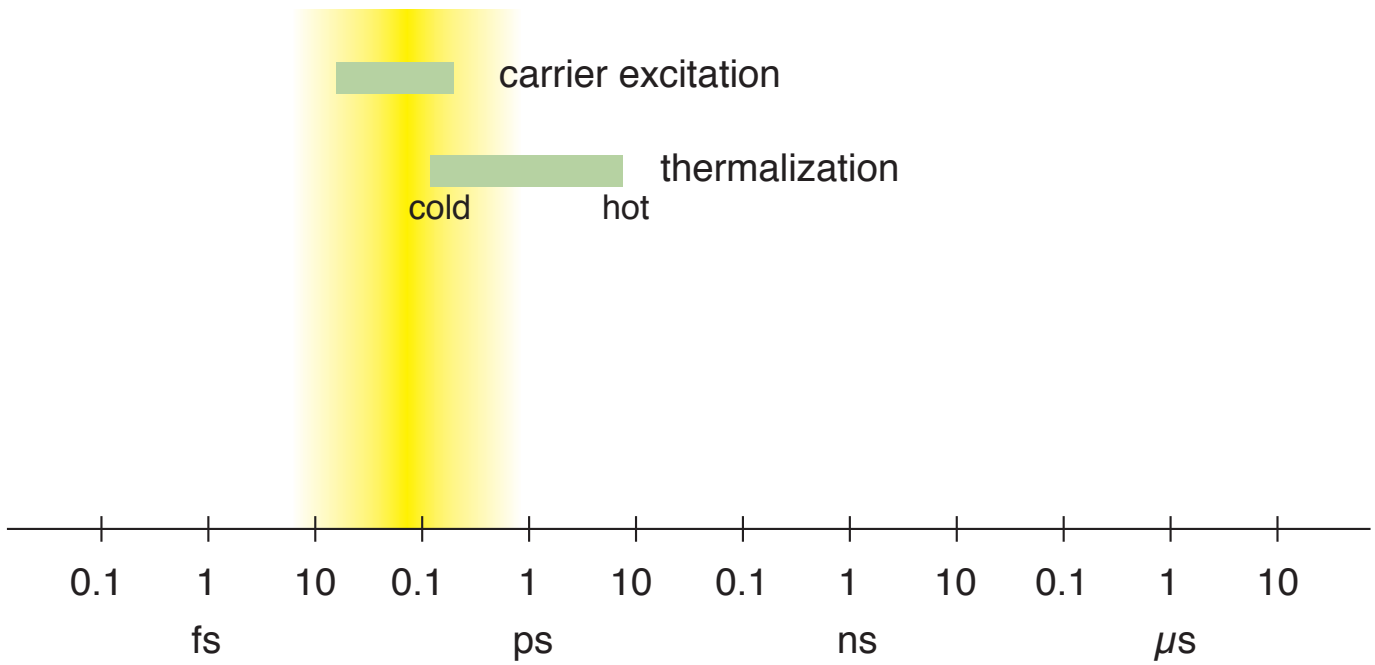
Introduction

relevant time scales



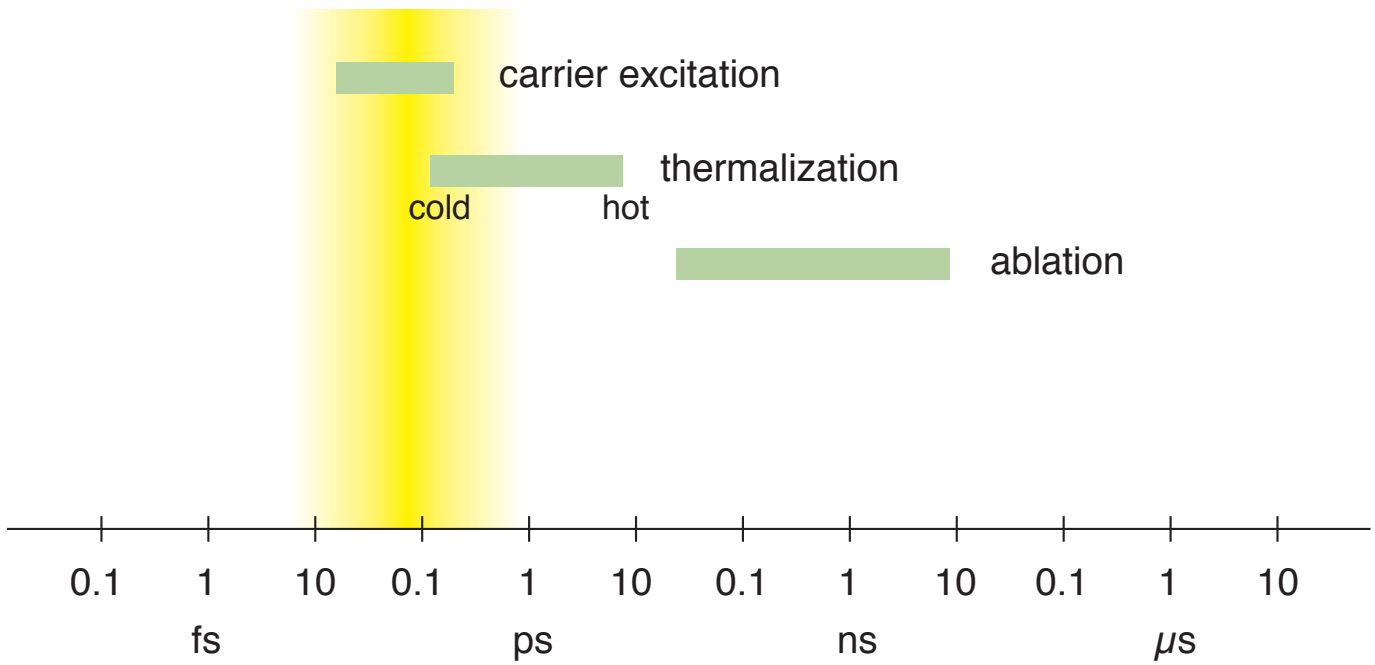
Introduction

relevant time scales



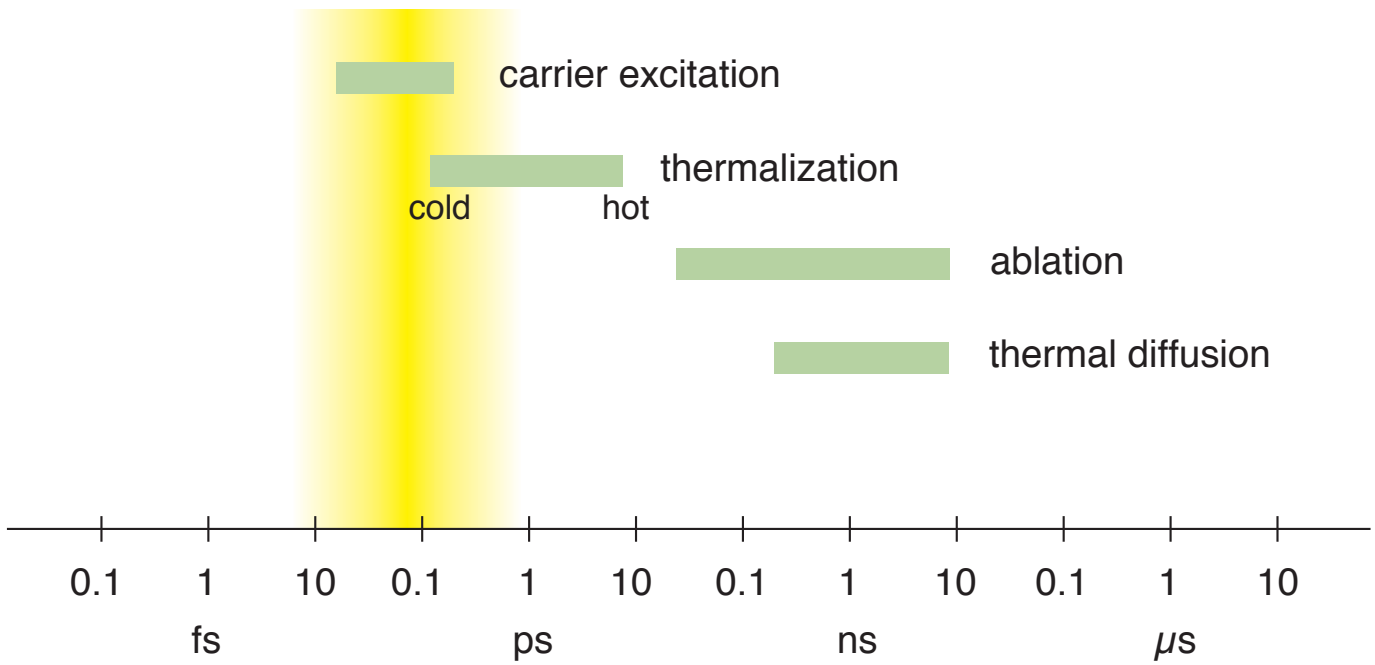
Introduction

relevant time scales



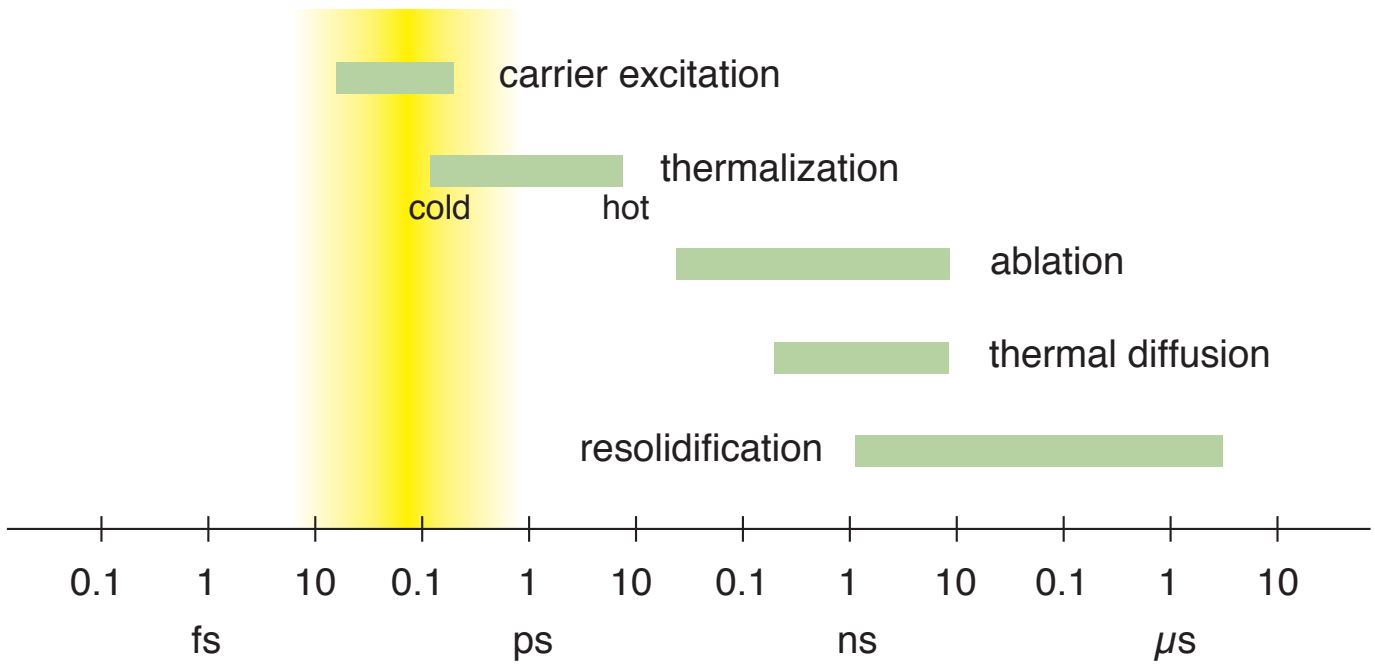
Introduction

relevant time scales



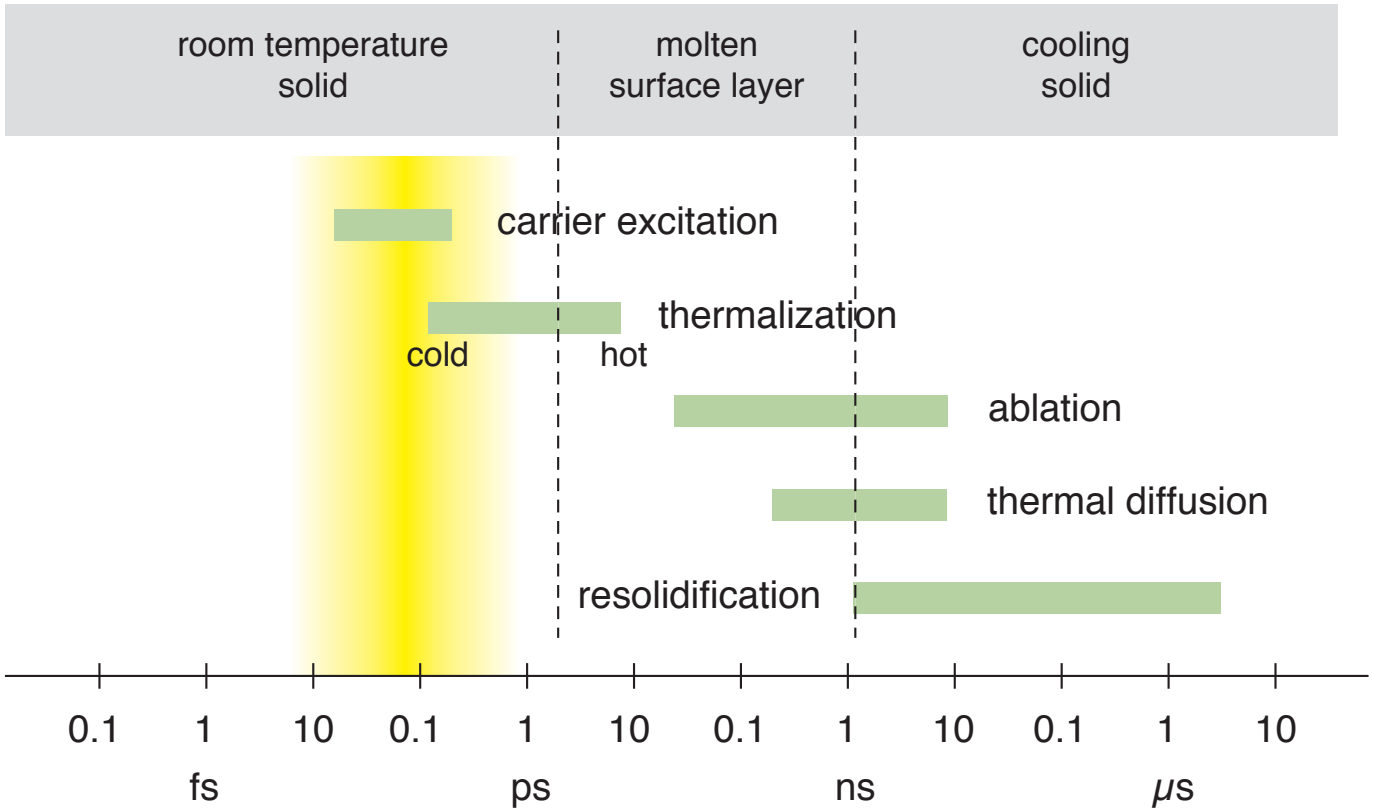
Introduction

relevant time scales



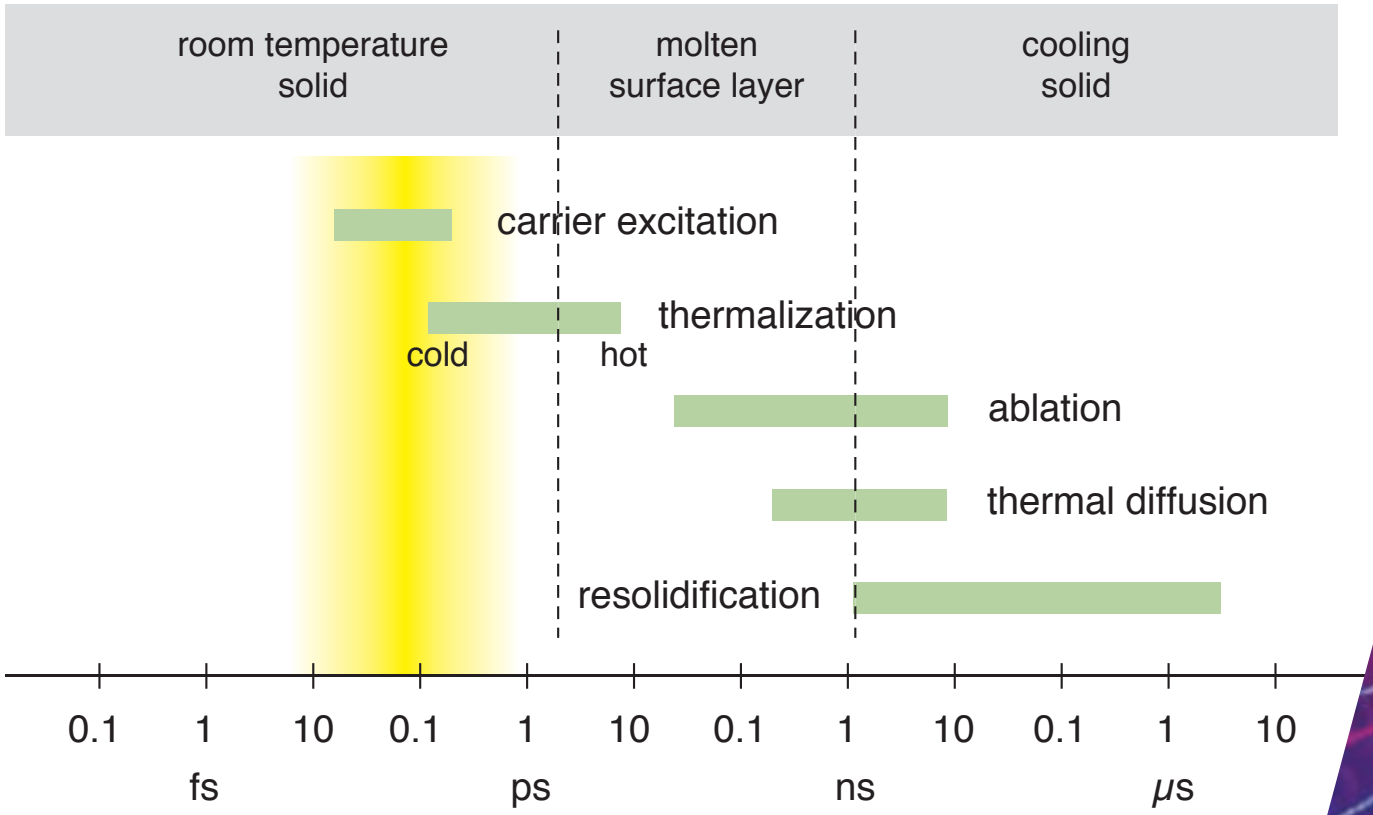
Introduction

relevant time scales



Introduction

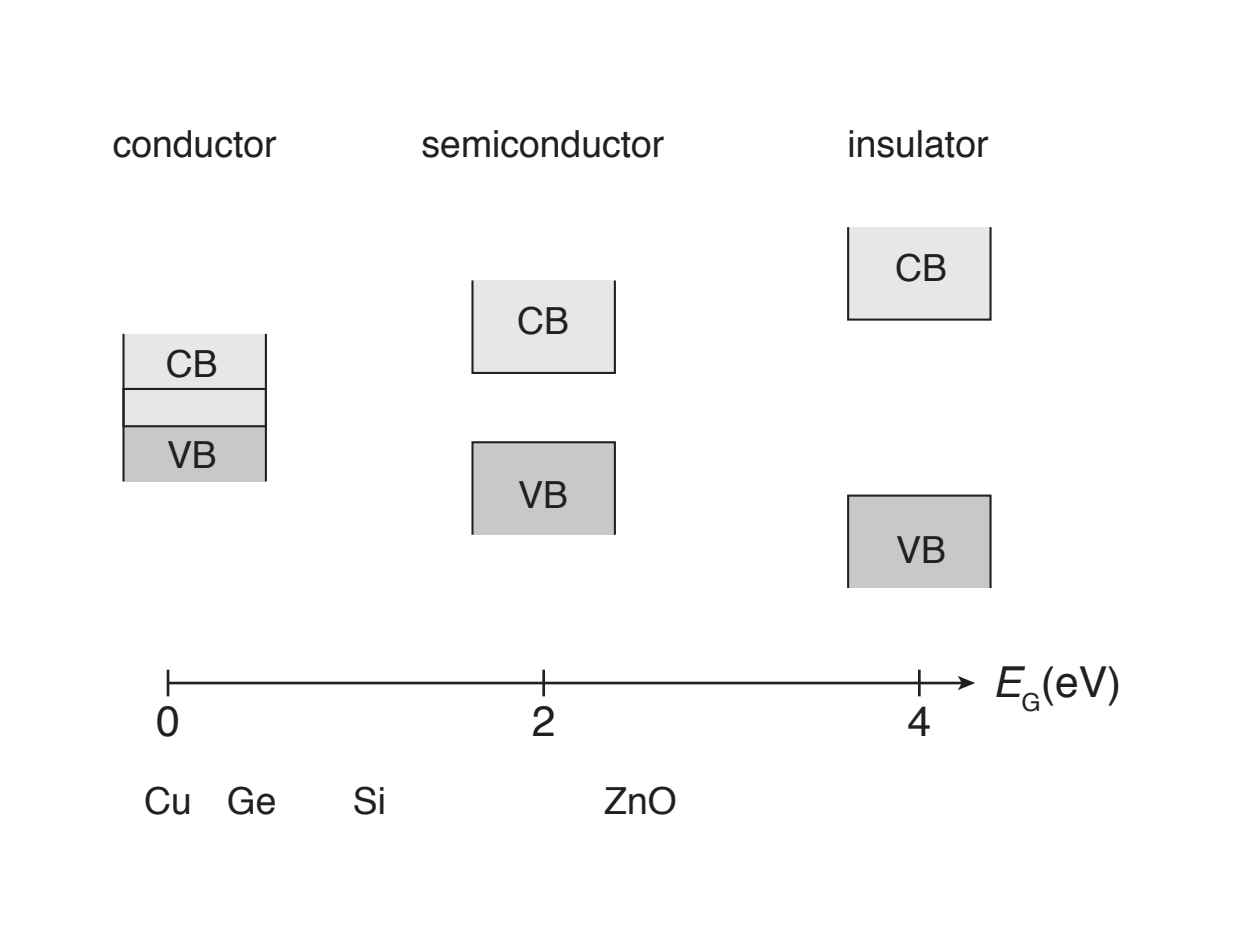
relevant time scales



Nature Materials **1**, 217 (2002)

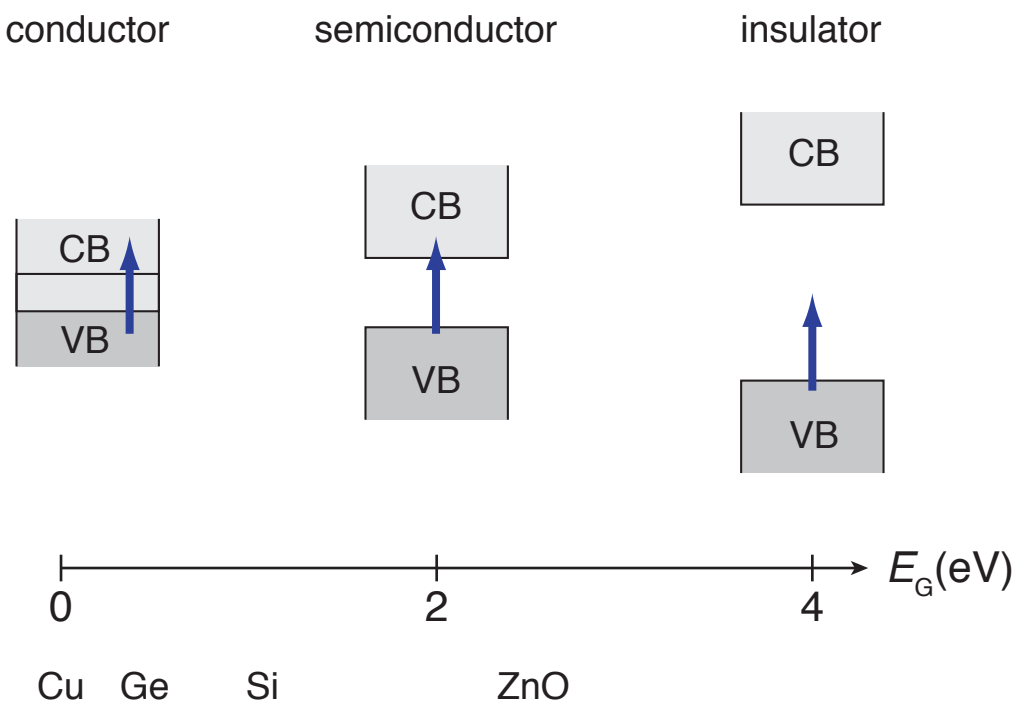
Introduction

gap determines interaction



Introduction

gap determines interaction

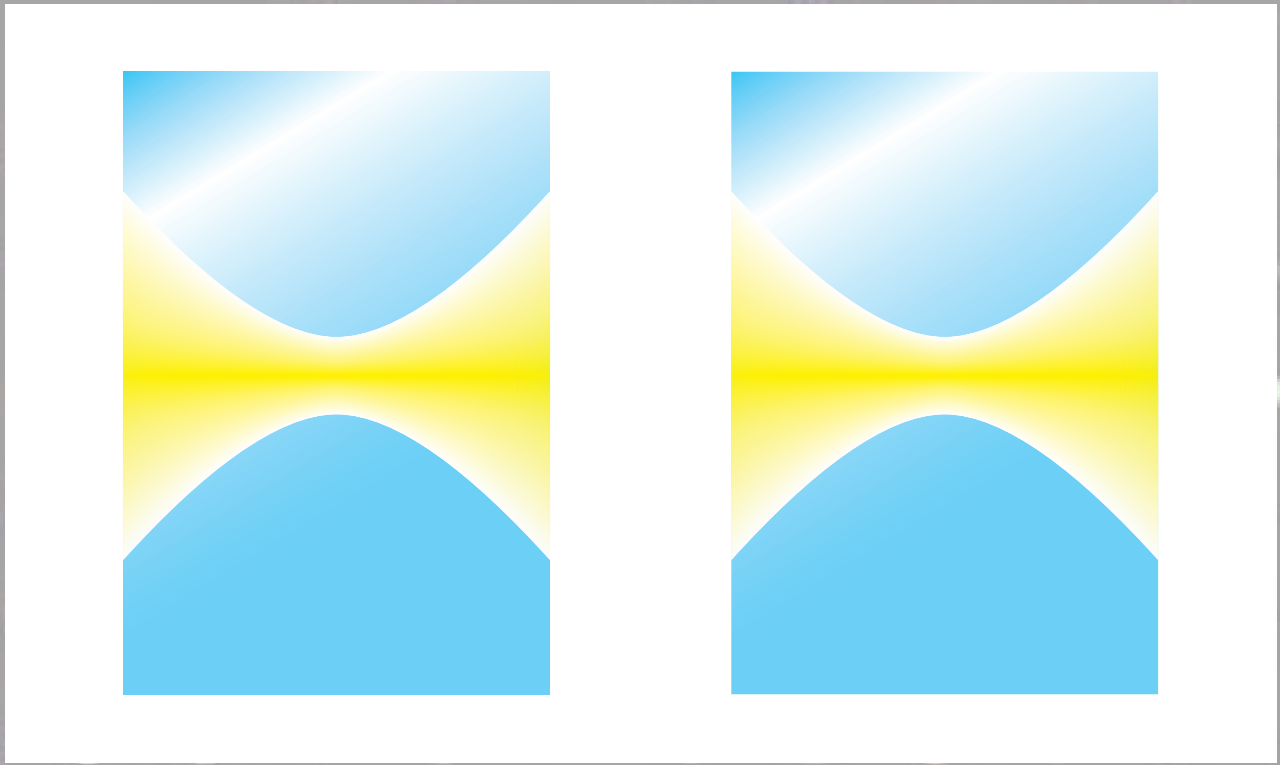


Introduction

photon energy < bandgap $\longrightarrow$ nonlinear interaction

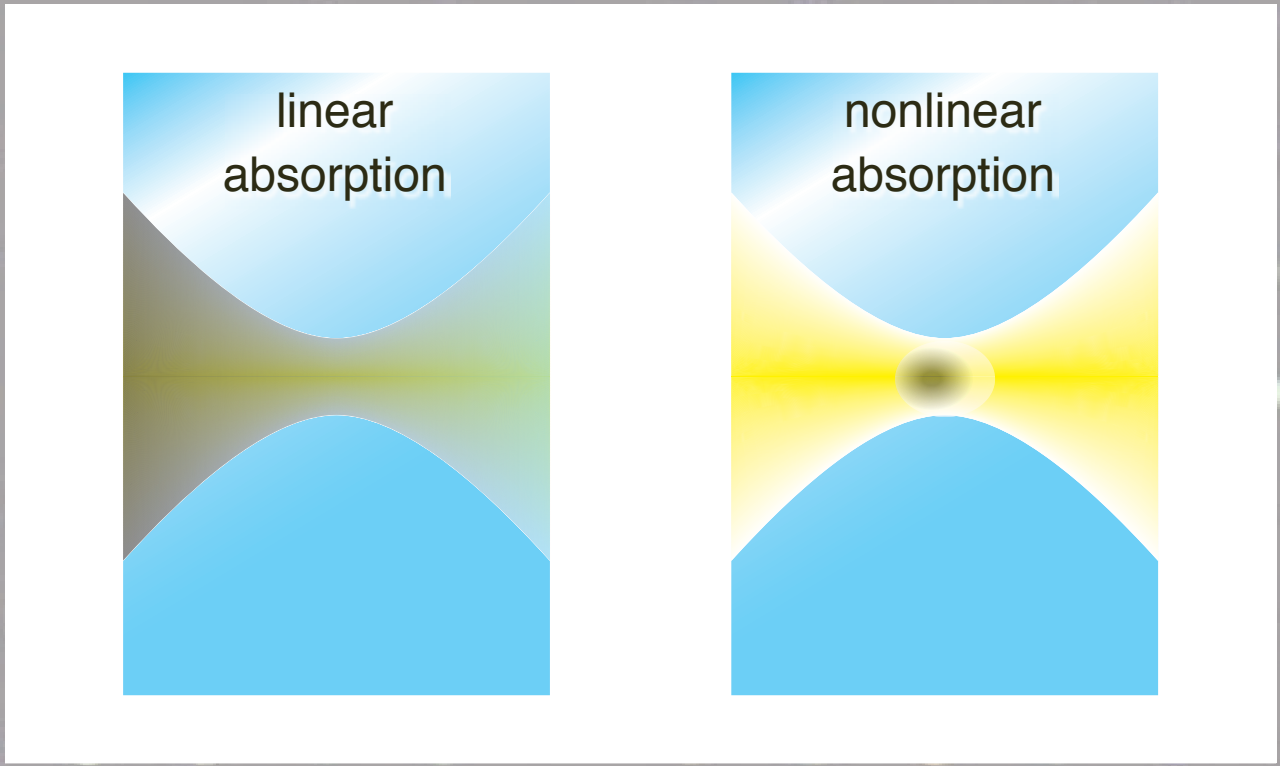
Introduction

nonlinear interaction provides bulk confinement



Introduction

nonlinear interaction provides bulk confinement



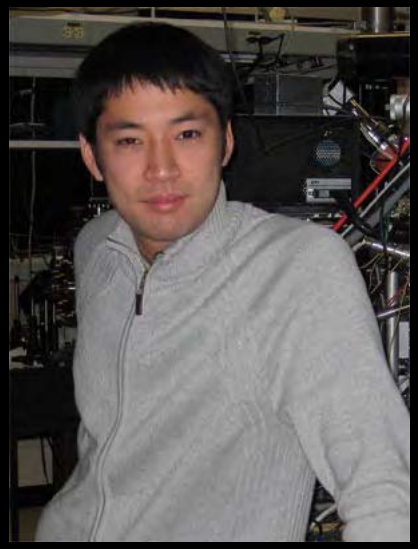
Part I: Femtosecond laser micromachining of transparent materials

Sciences des materiaux et surfaces actives
Ecole Supérieure de Physique et Chimie
9 Février 2010

Rafael Gattass

Loren Cerami

Tina Shih



Masanao Kamata

and also....

Iva Maxwell
San Chung
Eli Glezer
Chris Schaffer
Nozomi Nishimura
Jonathan Ashcom
Jeremy Hwang
Nan Shen
Dr. André Brodeur
Dr. Sanjoy Kumar
Dr. Limin Tong
Dr. Prissana Thamboon

Prof. Igor Khruschev (Aston University)
Prof. Denise Krol (UC Davis)
Dr. Yossi Chay (Sagitta, Inc.)
Dr. S.K. Sundaram (PNNL)
Prof. Minoru Obara (Keio University)
Prof. Don Ingber (Harvard Medical School)
Prof. Aravi Samuel (Harvard)

My message

fs micromachining: great technique for manipulating matter

Introduction

Introduction

216 J. Opt. Soc. Am. B/Vol. 13, No. 1/January 1996

Breakdown threshold and plasma formation in femtosecond laser–solid interaction

D. von der Linde and H. Schüler

Institut für Laser- und Plasmaphysik, Universität Essen, D-45117 Essen, Germany

Received March 6, 1995; revised manuscript received June 15, 1995

Combining femtosecond pump–probe techniques with optical microscopy, we have studied laser-induced optical breakdown in optically transparent solids with high temporal and spatial resolution. The threshold of plasma formation has been determined from measurements of the changes of the optical reflectivity associated with the developing plasma. It is shown that plasma generation occurs at the surface. We have observed a remarkable resistance to optical breakdown and material damage in the interaction of femtosecond laser pulses with bulk optical materials.

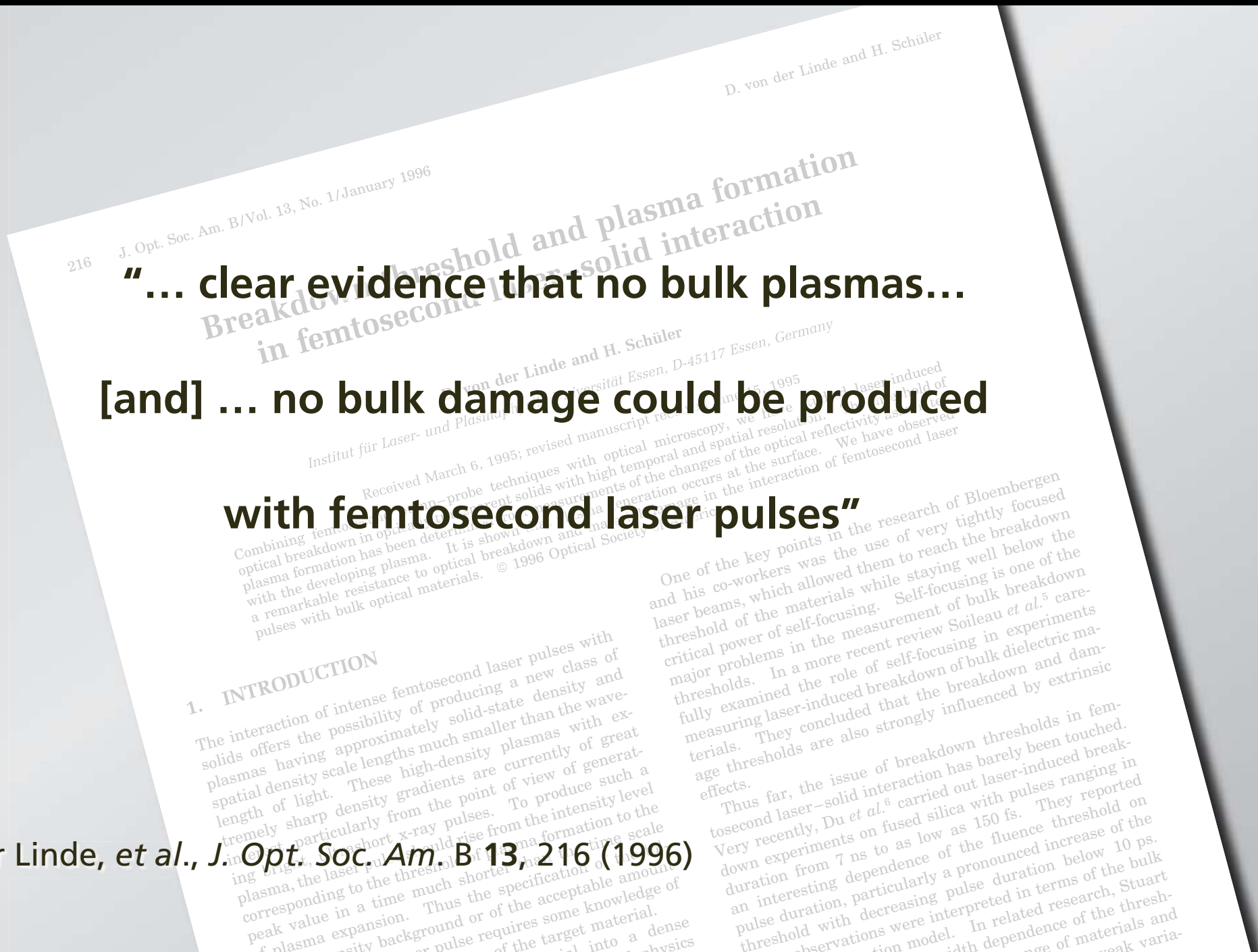
1. INTRODUCTION

The interaction of intense femtosecond laser pulses with solids offers the possibility of producing a new class of plasmas having approximately solid-state density and spatial density scale lengths much smaller than the wavelength of light. These high-density plasmas with extremely sharp density gradients are currently of great interest, particularly from the point of view of generating bright, ultrashort x-ray pulses. To produce such a plasma, the laser pulse should rise from the intensity level corresponding to the threshold of plasma formation to the peak value in a time much shorter than the time scale of plasma expansion. Thus the specification of the tolerable background or of the acceptable amount of pulse requires some knowledge of the target material. ensity into a dense physics

One of the key points in the research of Bloembergen and his co-workers was the use of very tightly focused laser beams, which allowed them to reach the breakdown threshold of the materials while staying well below the critical power of self-focusing. Self-focusing is one of the major problems in the measurement of bulk breakdown thresholds. In a more recent review Soileau *et al.*[5] carefully examined the role of self-focusing in experiments measuring laser-induced breakdown of bulk dielectric materials. They concluded that the breakdown and damage thresholds are also strongly influenced by extrinsic effects.

Thus far, the issue of breakdown thresholds in femtosecond laser–solid interaction has barely been touched. Very recently, Du *et al.*[6] carried out laser-induced breakdown experiments on fused silica with pulses ranging in duration from 7 ns to as low as 150 fs. They reported an interesting dependence of the fluence threshold on pulse duration, particularly a pronounced increase of the threshold with decreasing pulse duration below 10 ps. observations were interpreted in terms of the bulk tion model. In related research, Stuart idth dependence of the thresh- nge of materials and weak varia-

Introduction



"… clear evidence that no bulk plasmas…

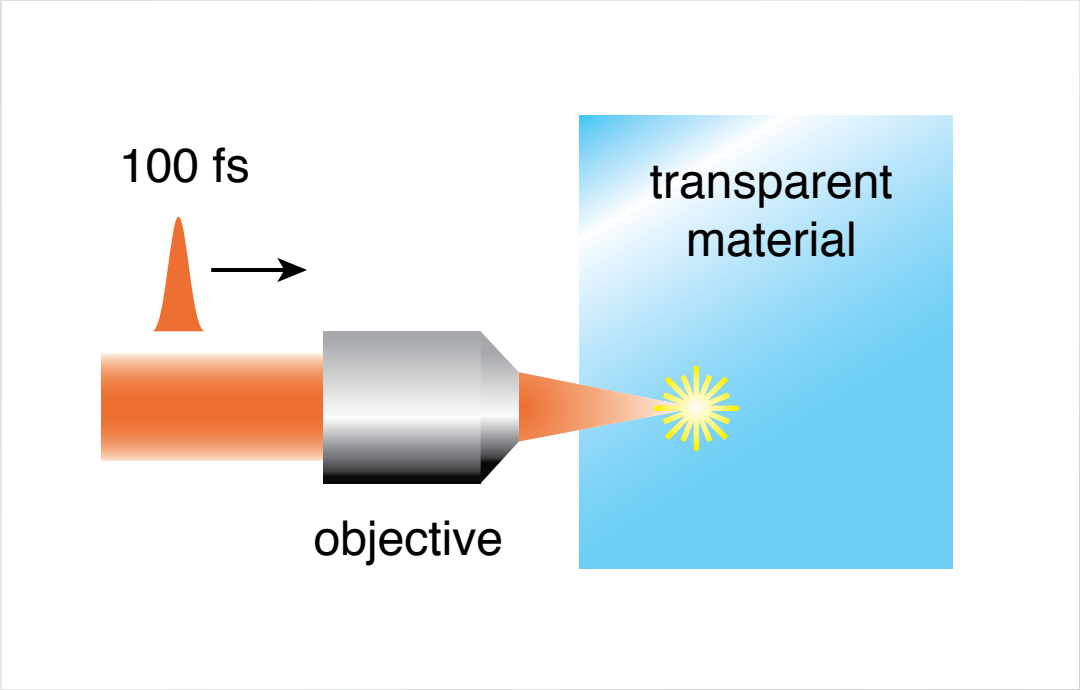
[and] … no bulk damage could be produced

with femtosecond laser pulses"

von der Linde, *et al.*, *J. Opt. Soc. Am.* B **13**, 216 (1996)

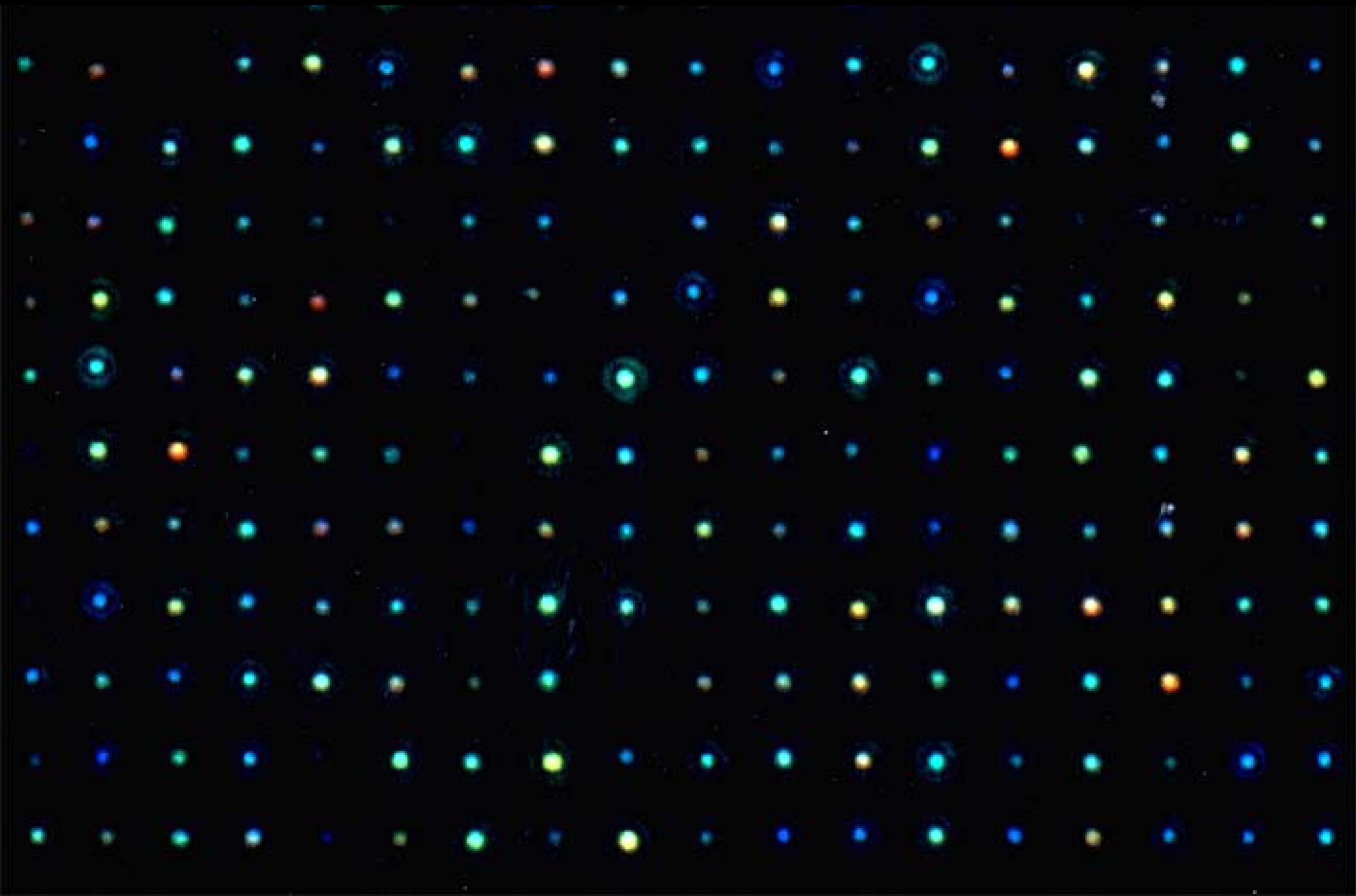
Introduction

focus laser beam inside material



Opt. Lett. **21**, 2023 (1996)

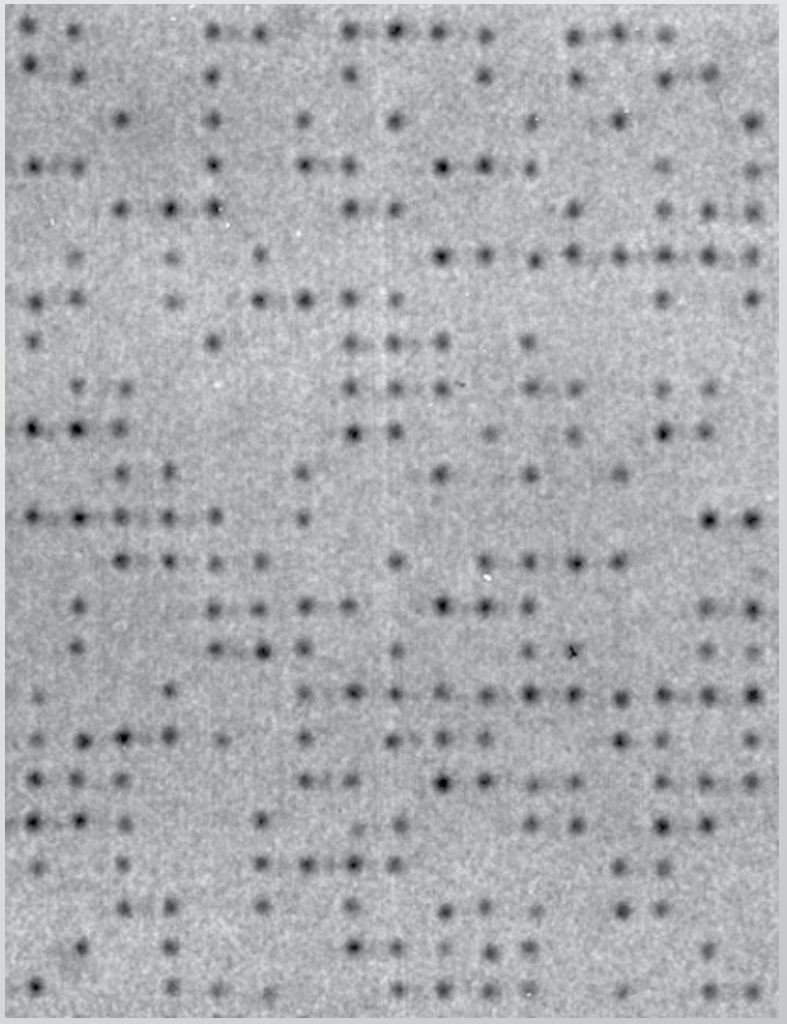
Introduction



Femtosecond micromachining

Some applications:

- data storage
- waveguides
- microfluidics

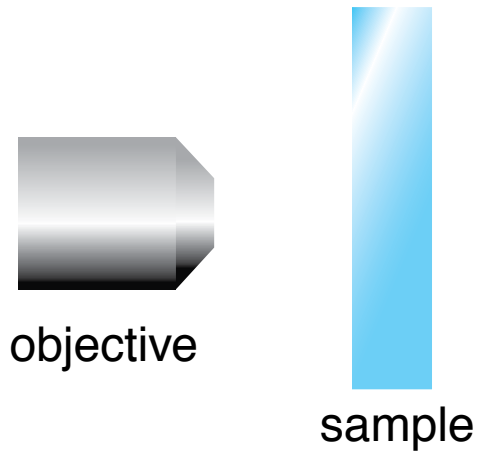


Outline

- femtosecond micromachining
- low-energy machining
- applications

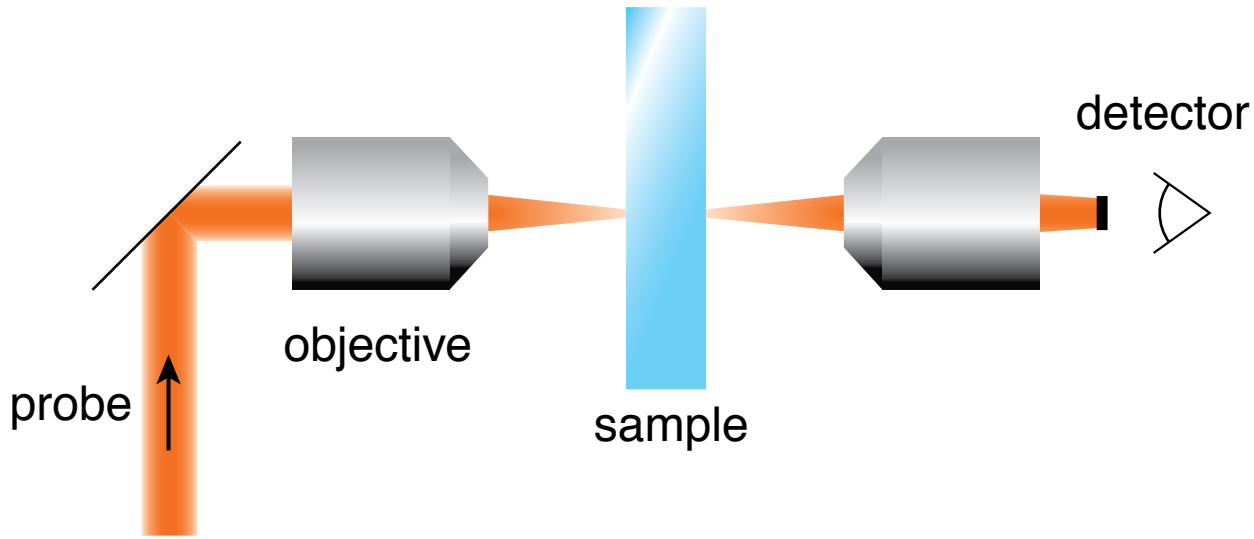
Femtosecond micromachining

Dark-field scattering



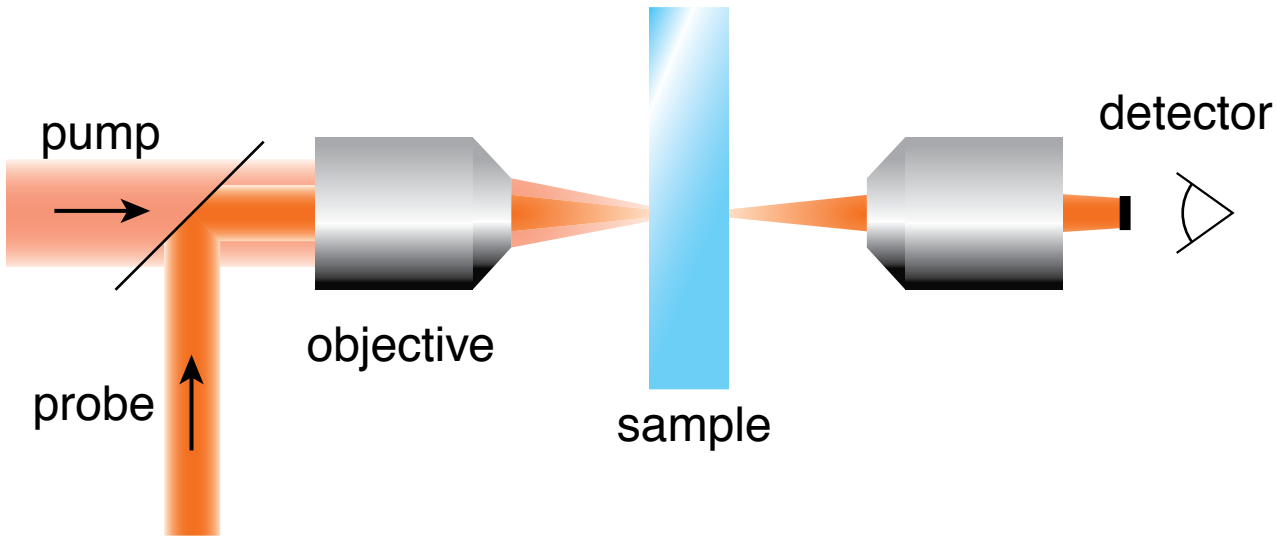
Femtosecond micromachining

block probe beam…



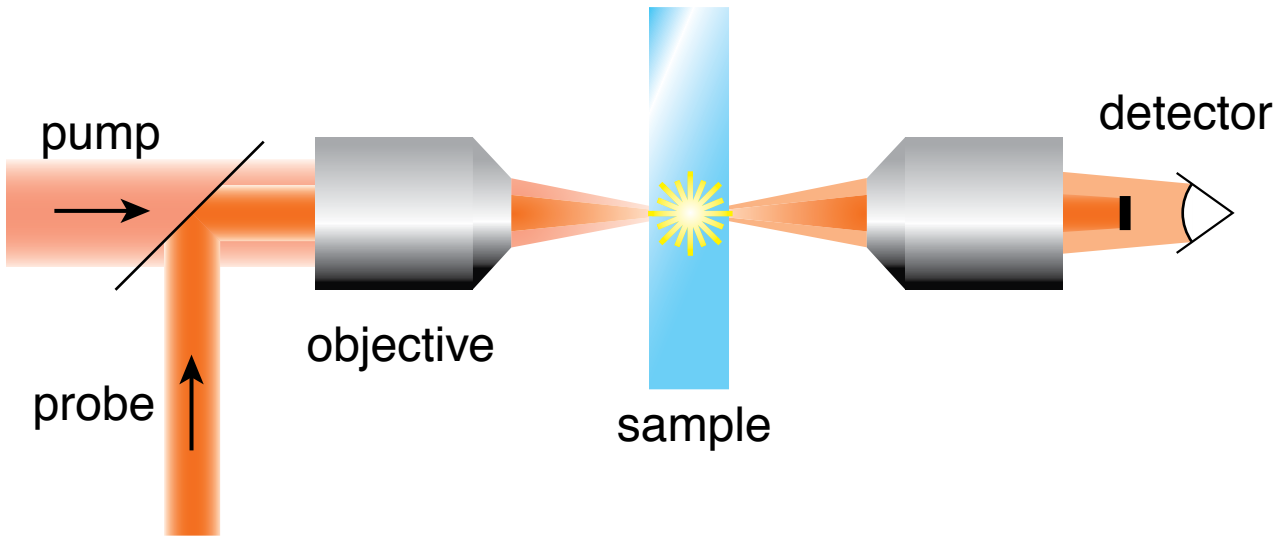
Femtosecond micromachining

… bring in pump beam…



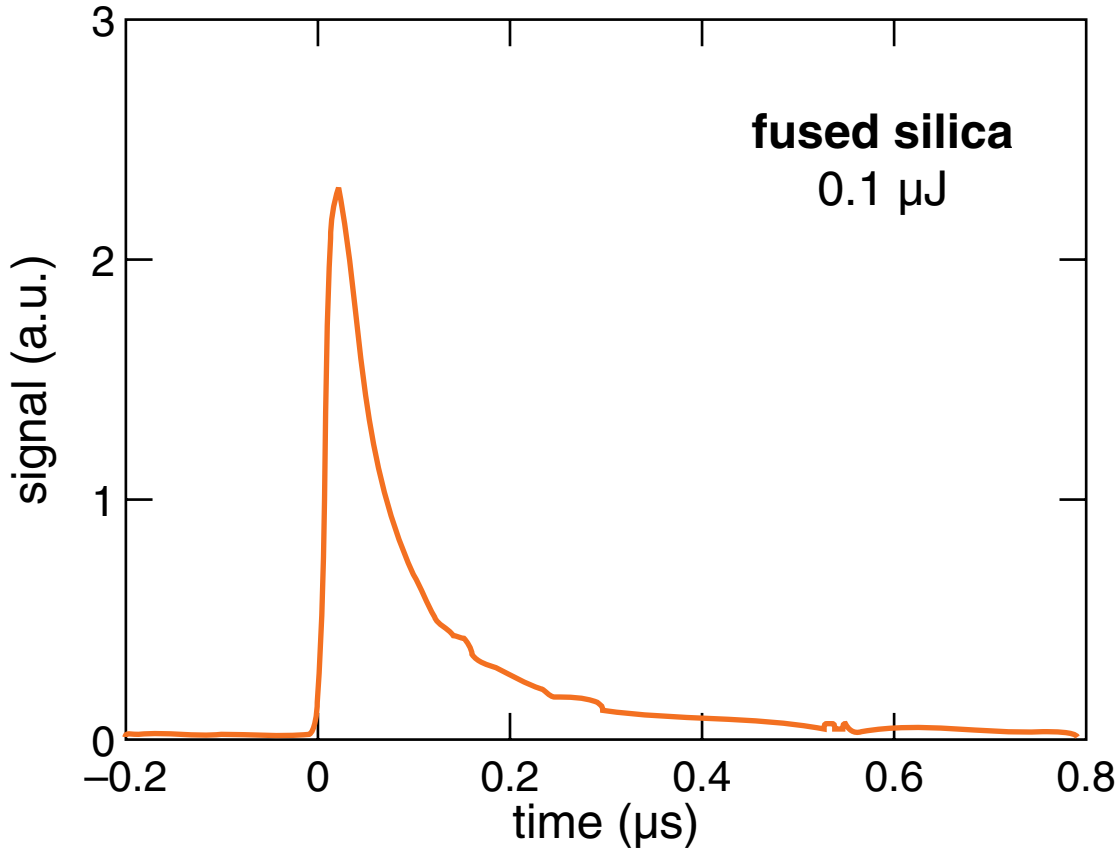
Femtosecond micromachining

… damage scatters probe beam



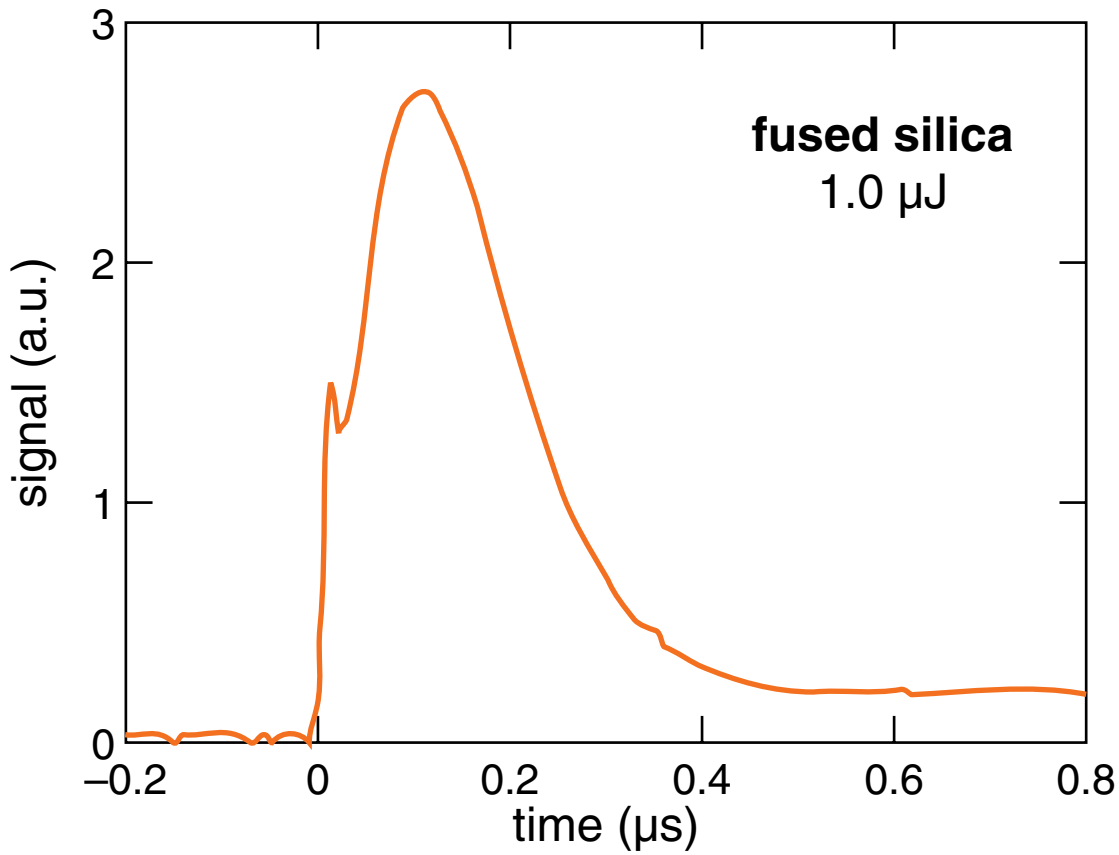
Femtosecond micromachining

scattered signal



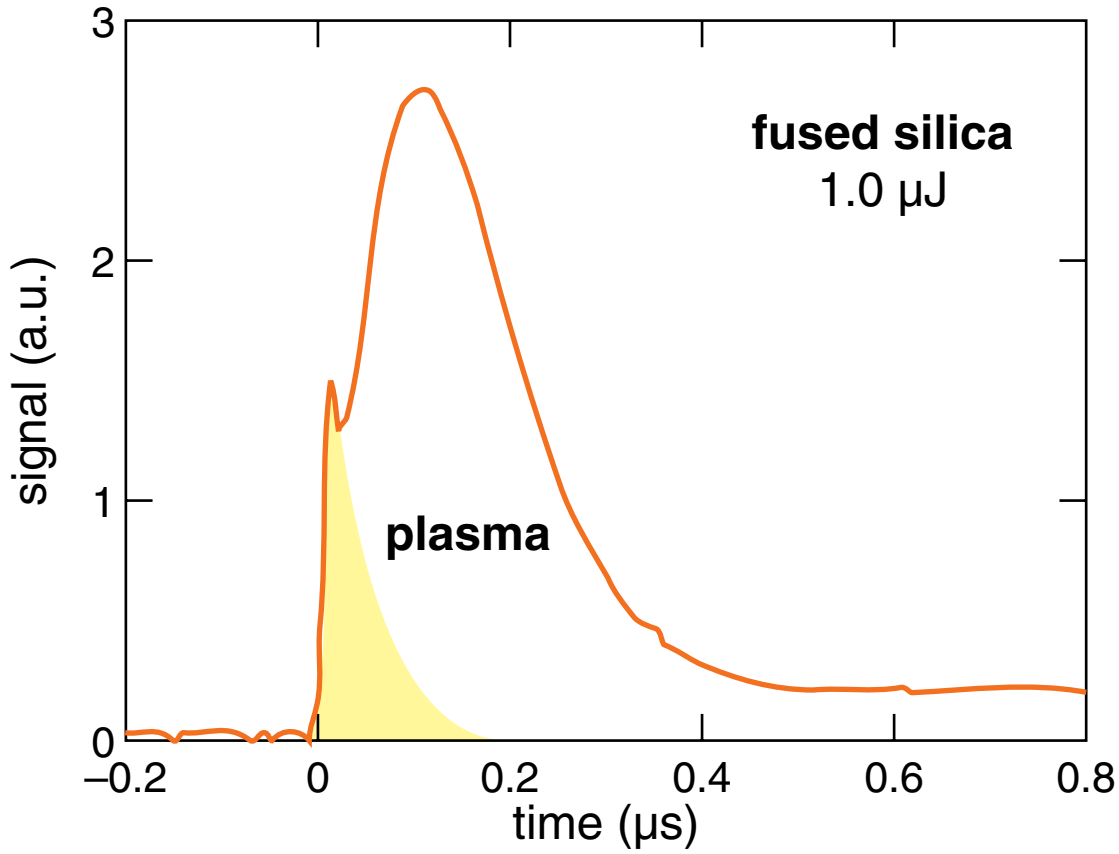
Femtosecond micromachining

scattered signal



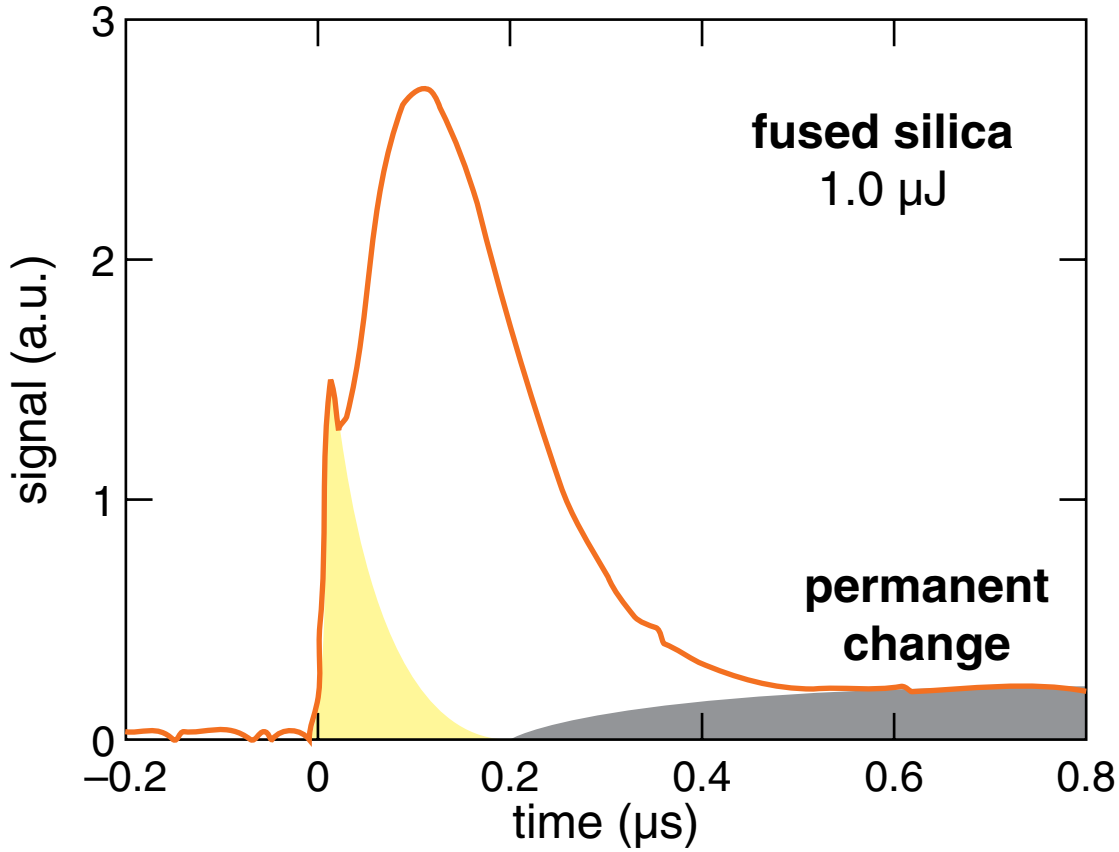
Femtosecond micromachining

scattered signal



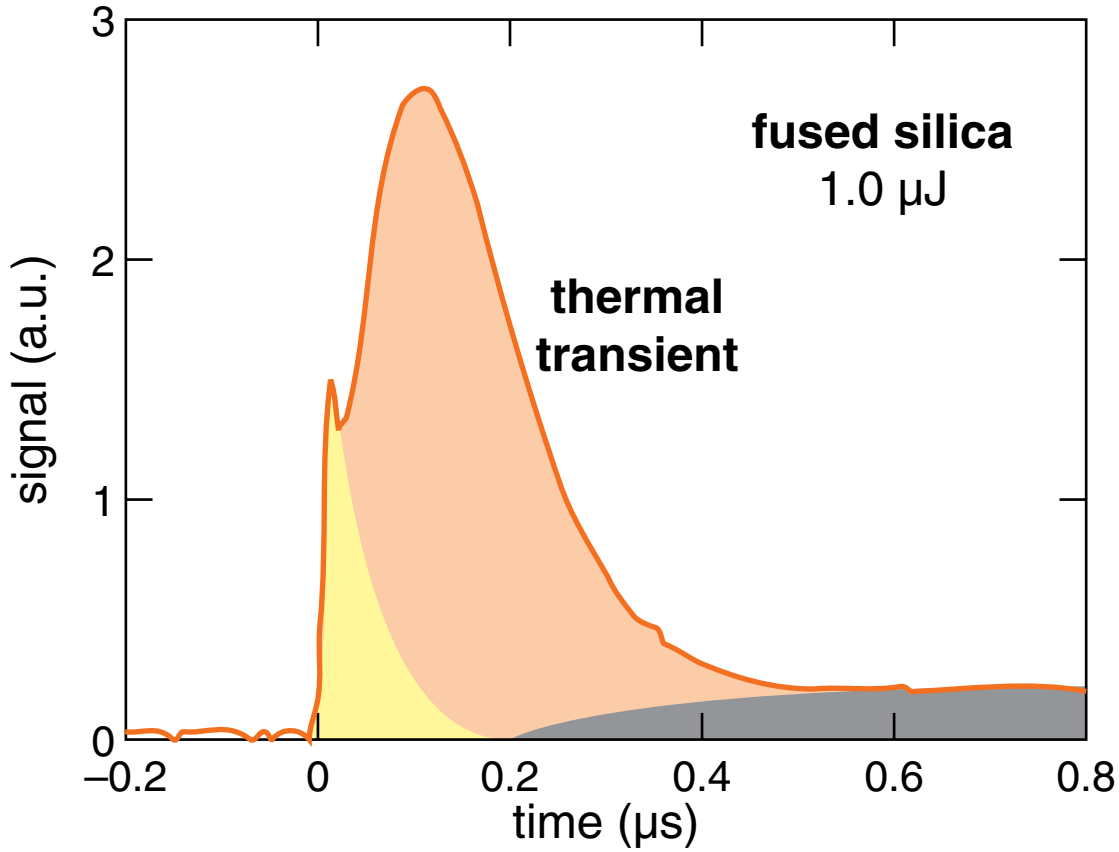
Femtosecond micromachining

scattered signal



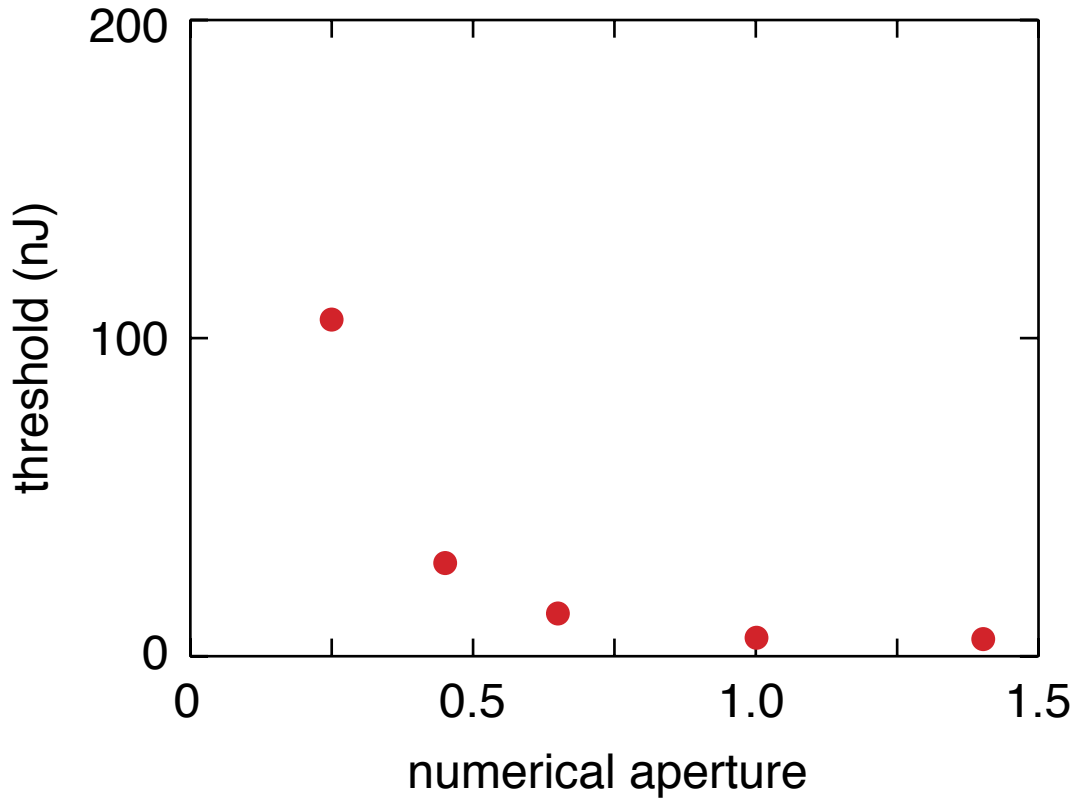
Femtosecond micromachining

scattered signal



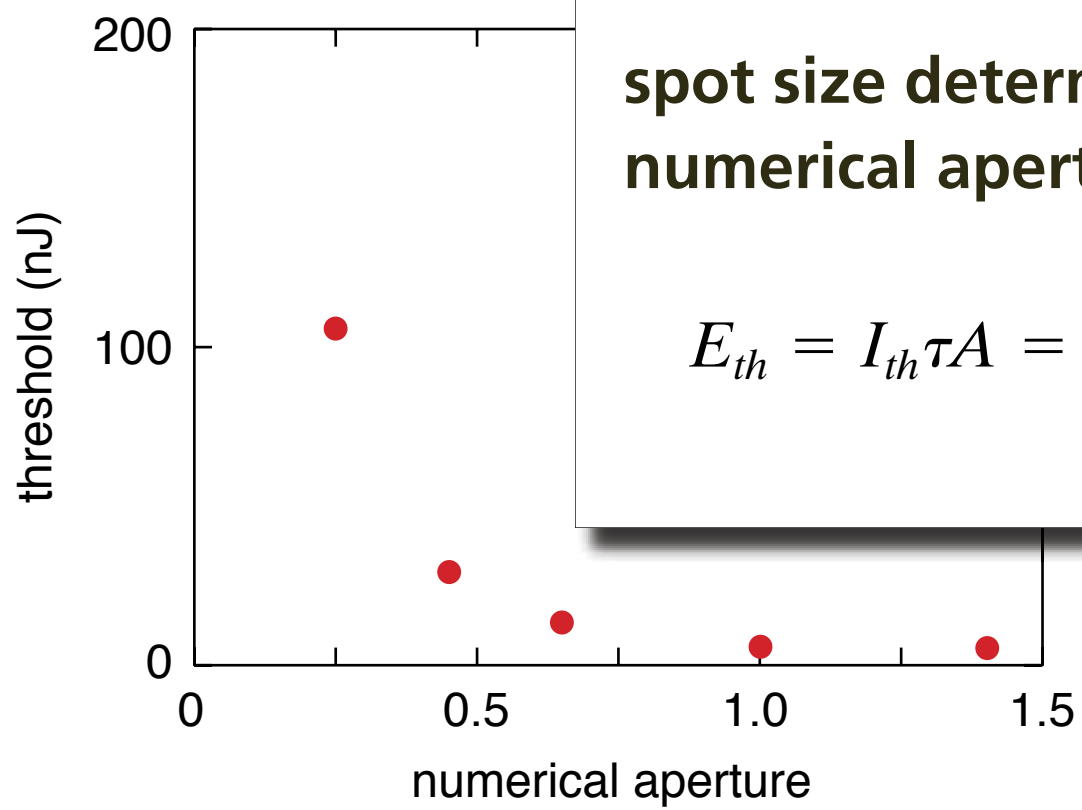
Femtosecond micromachining

vary numerical aperture



Femtosecond micromachining

vary numeric



intensity threshold:

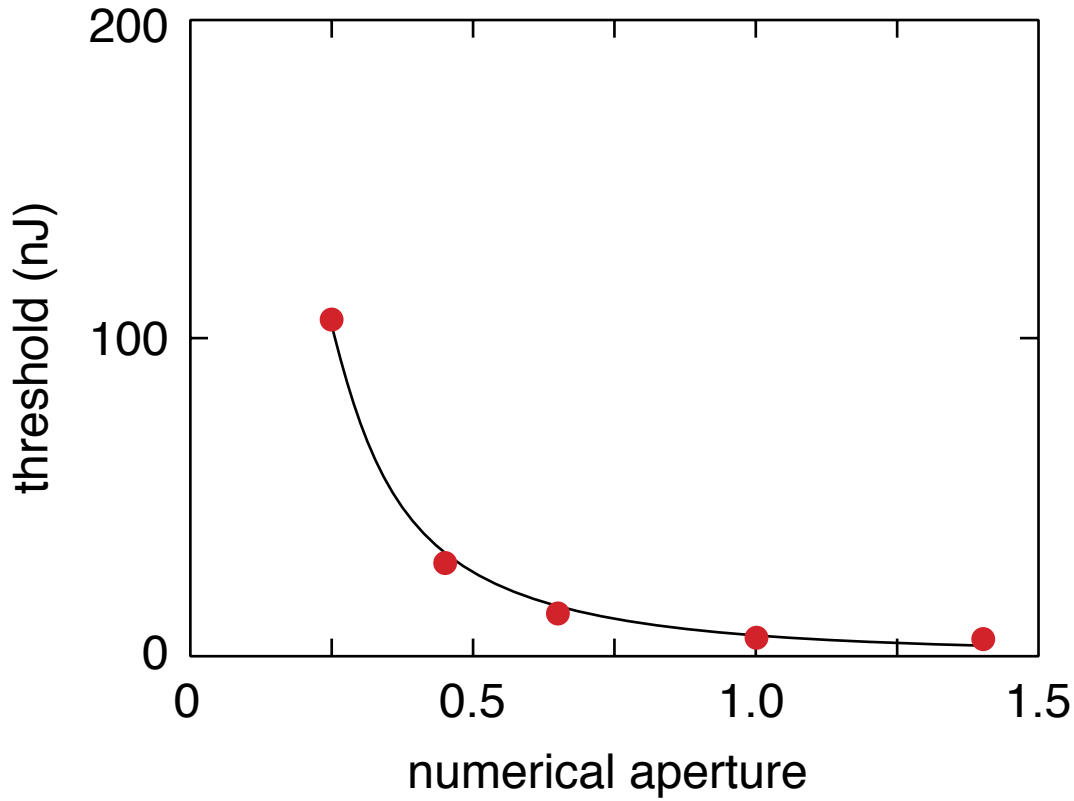
$$E_{th} = I_{th}\tau A$$

spot size determined by numerical aperture:

$$E_{th} = I_{th}\tau A = \frac{I_{th}\tau\lambda^2}{\pi(\mathrm{NA})^2}$$

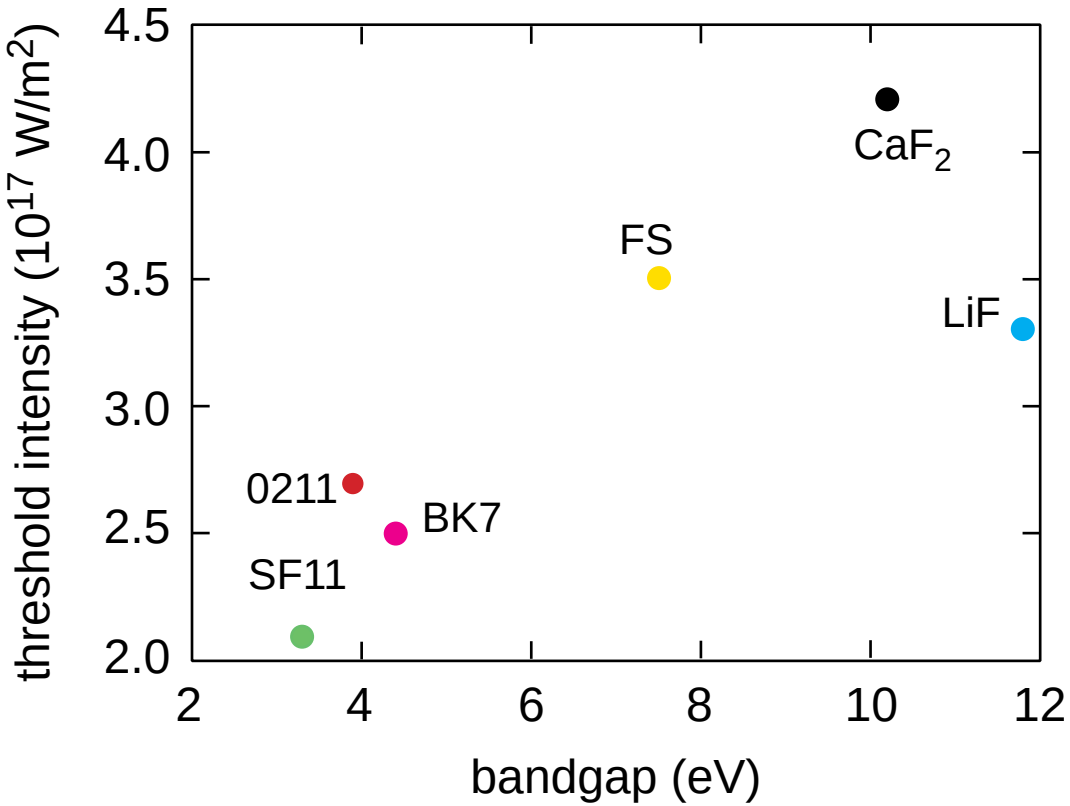
Femtosecond micromachining

fit gives threshold intensity: I_{th} = 2.5 x 10^{17} W/m^2



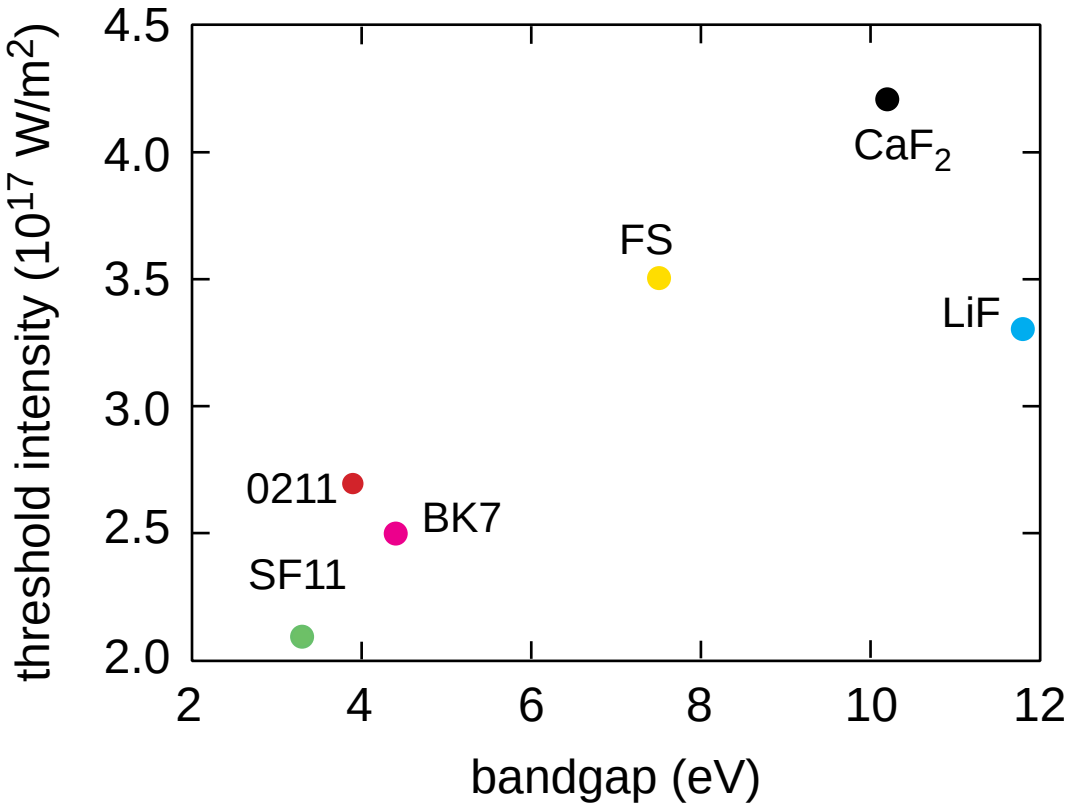
Femtosecond micromachining

vary material…



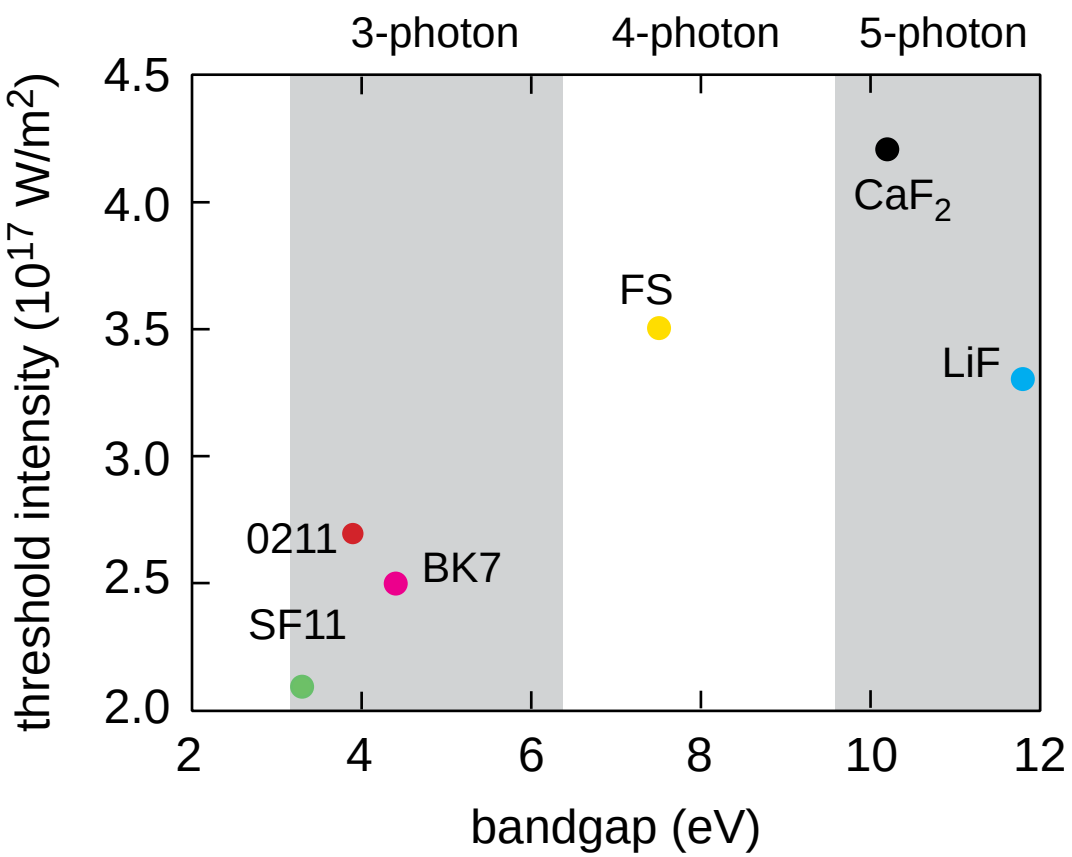
Femtosecond micromachining

…threshold varies with band gap (but not much!)



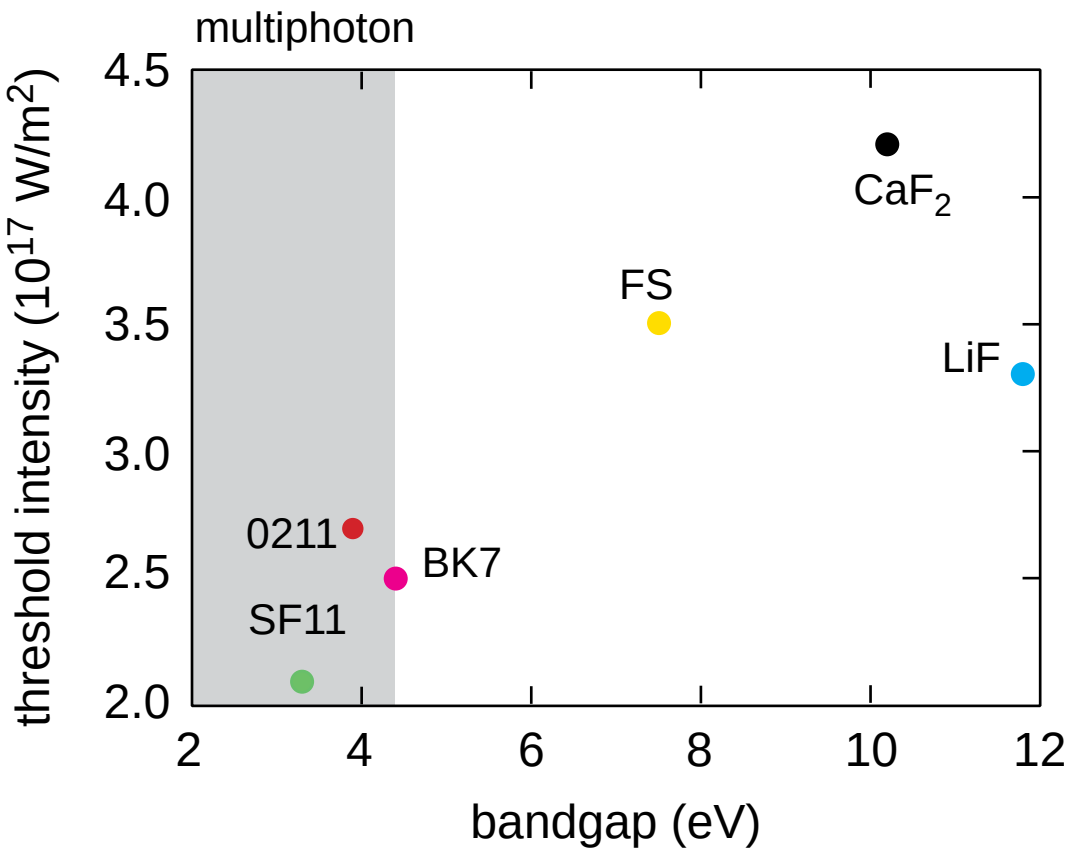
Femtosecond micromachining

would expect much more than a factor of 2



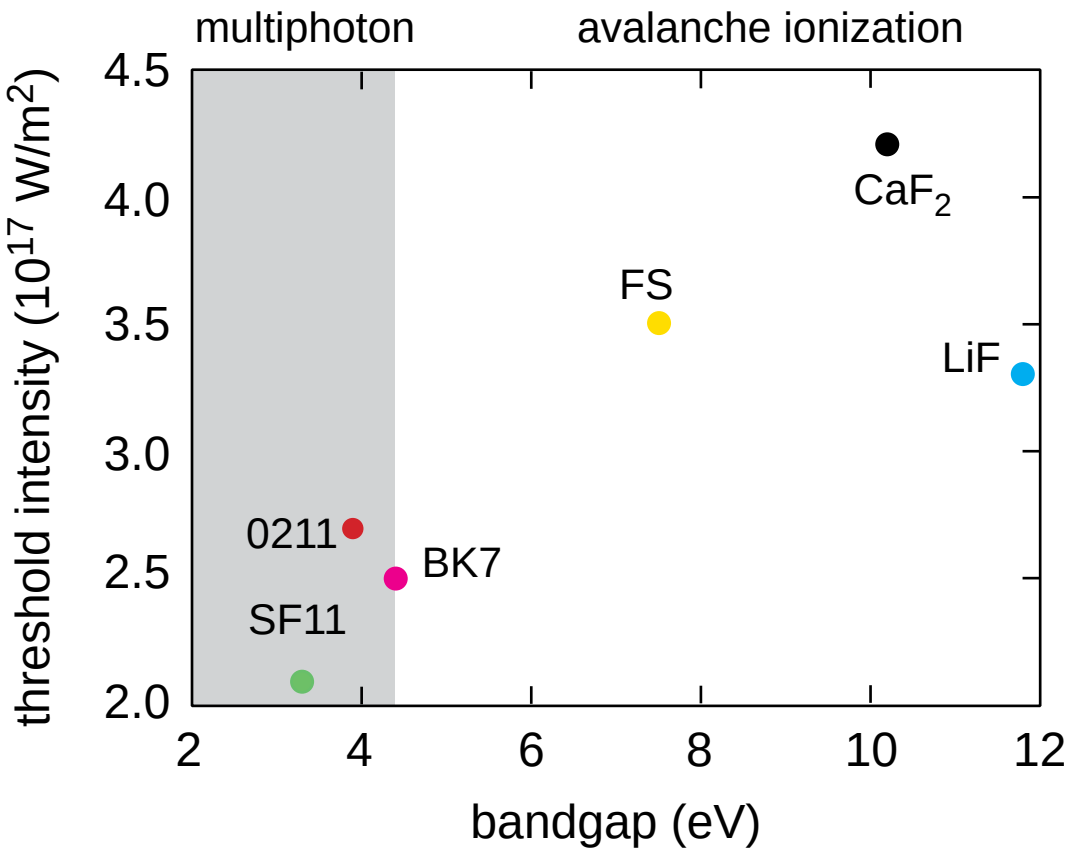
Femtosecond micromachining

critical density reached by multiphoton for low gap only



Femtosecond micromachining

avalanche ionization important at high gap



Femtosecond micromachining

what prevents damage at low NA?

Femtosecond micromachining

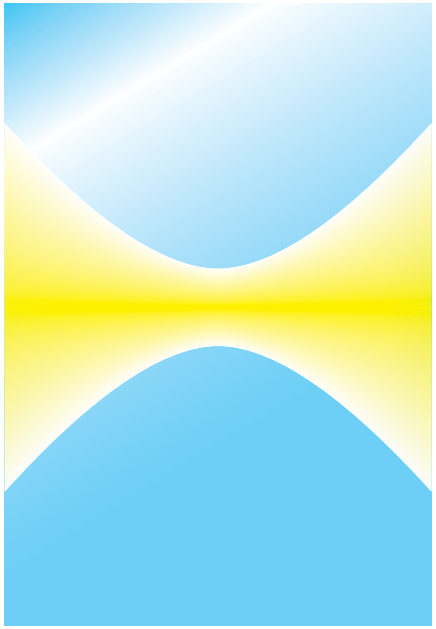
Competing nonlinear effects:

- multiphoton absorption
- supercontinuum generation
- self-focusing

Femtosecond micromachining

why the difference?

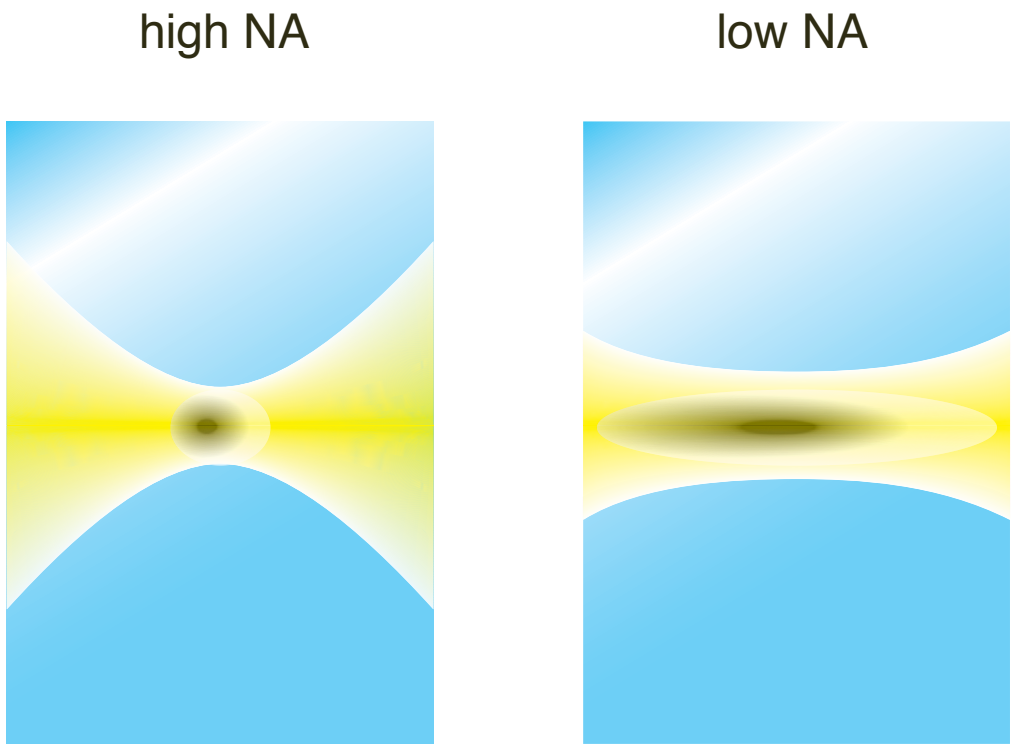
high NA



low NA

Femtosecond micromachining

very different confocal length/interaction length

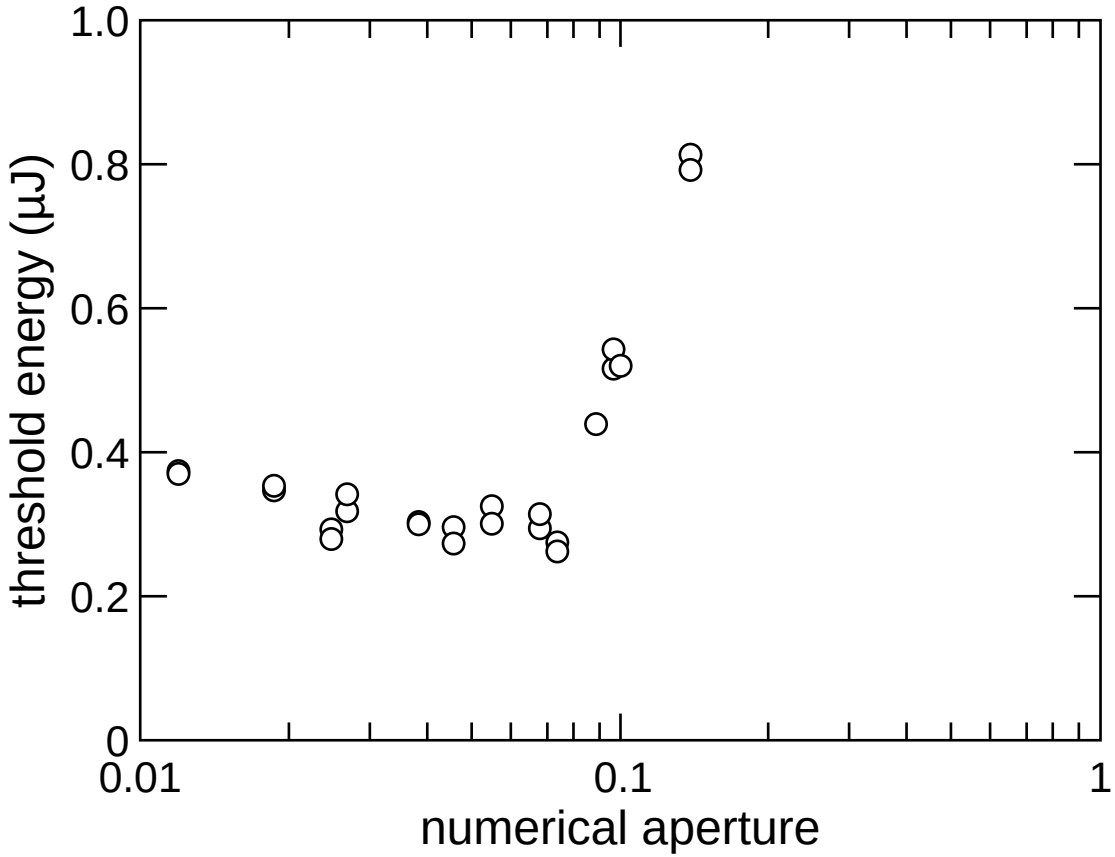


Femtosecond micromachining

high NA: interaction length too short for self-focusing

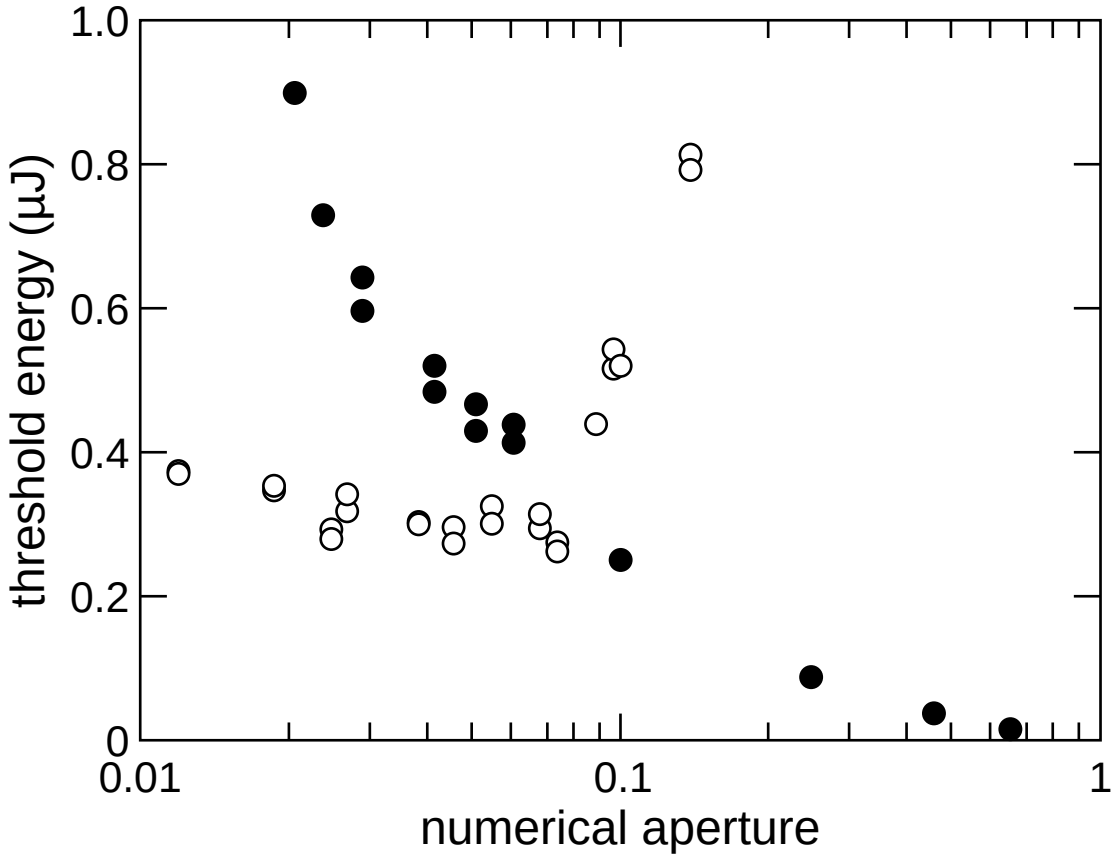
Femtosecond micromachining

threshold for supercontinuum generation



Femtosecond micromachining

threshold for damage



Femtosecond micromachining

Points to keep in mind:

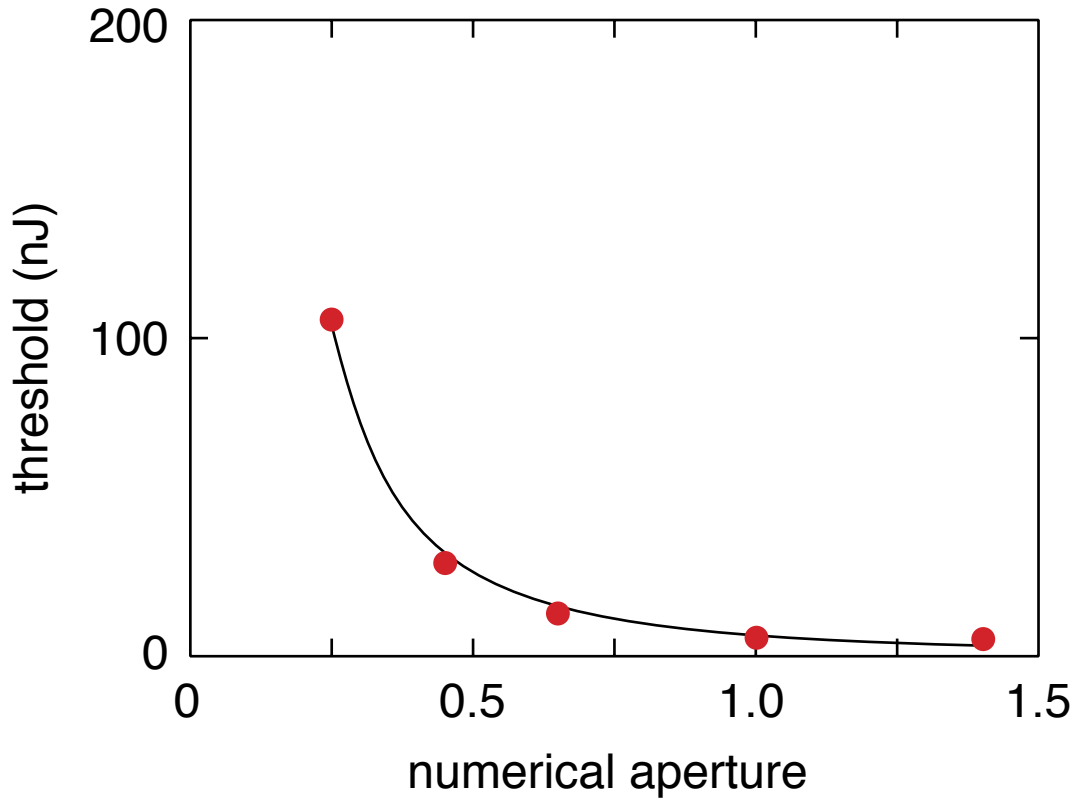
- threshold critically dependent on NA
- surprisingly little material dependence
- avalanche ionization important

Outline

- femtosecond micromachining
- **low-energy machining**
- applications

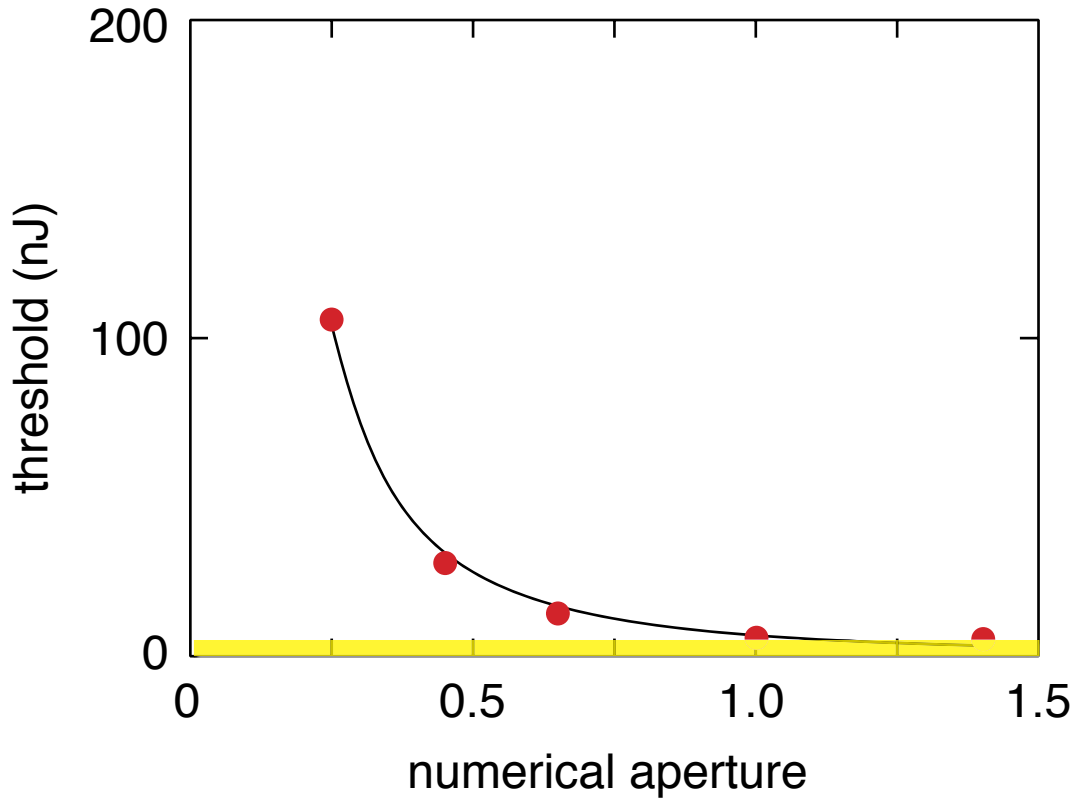
Low-energy machining

threshold decreases with increasing numerical aperture



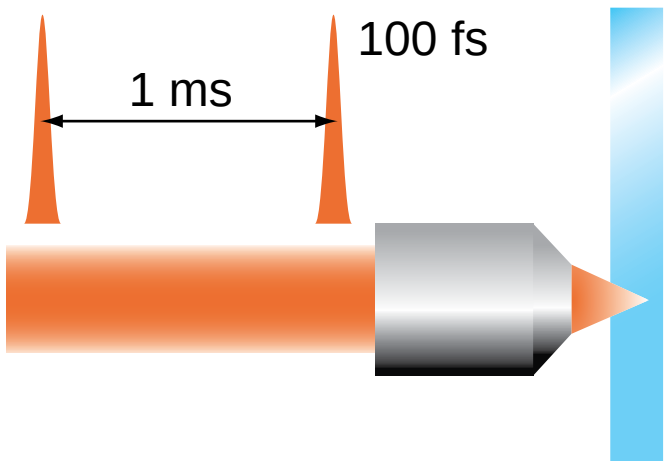
Low-energy machining

less than 10 nJ at high numerical aperture!



Low-energy machining

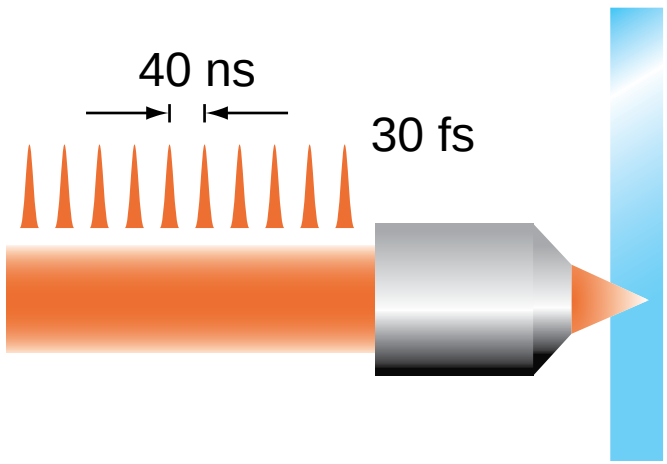
amplified laser: 1 kHz, 1 mJ



heat diffusion time: $\tau_{diff} \approx 1\ \mu s$

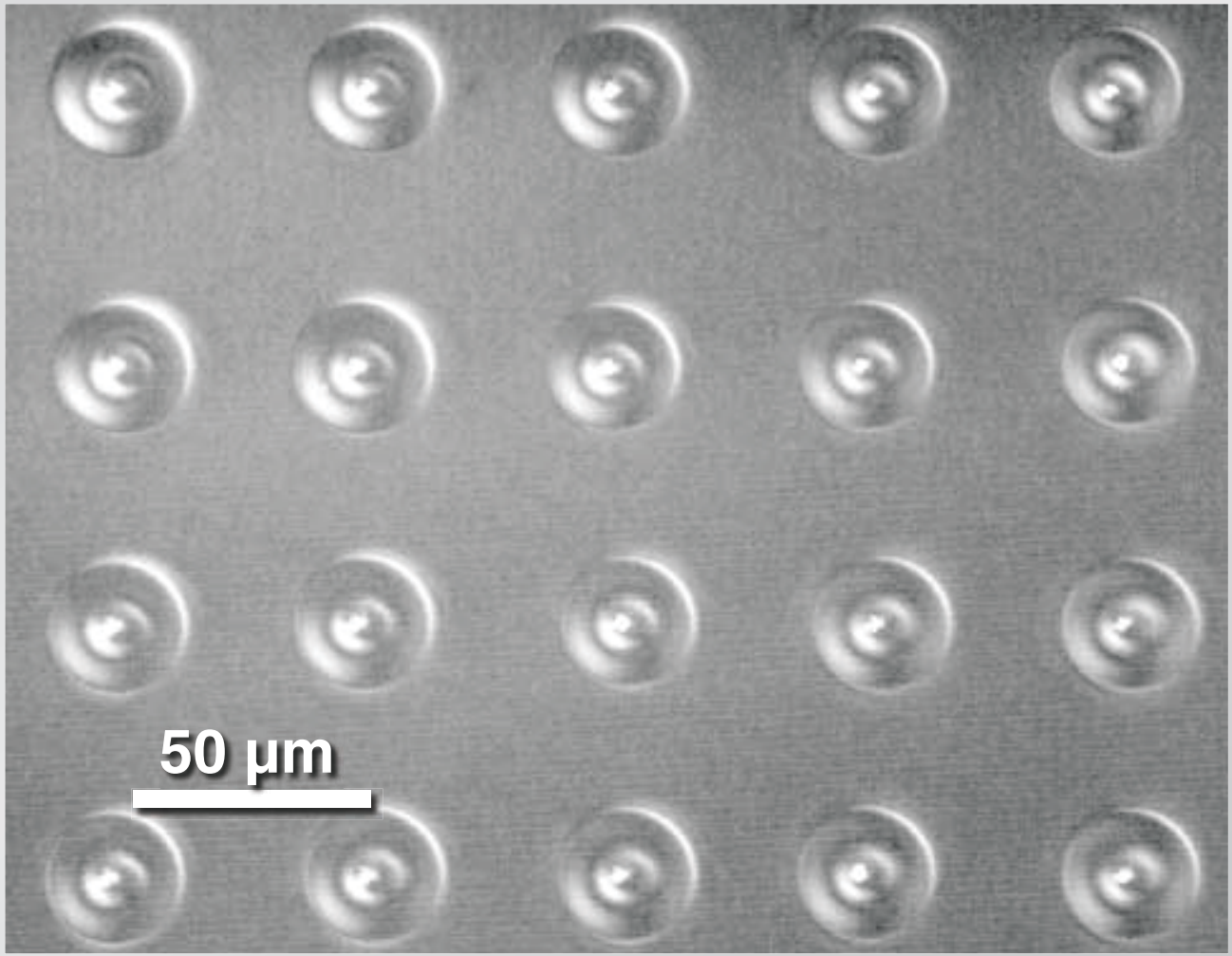
Low-energy machining

long cavity oscillator: 25 MHz, 25 nJ



heat diffusion time: $\tau_{diff} \approx 1\ \mu s$

Low-energy machining



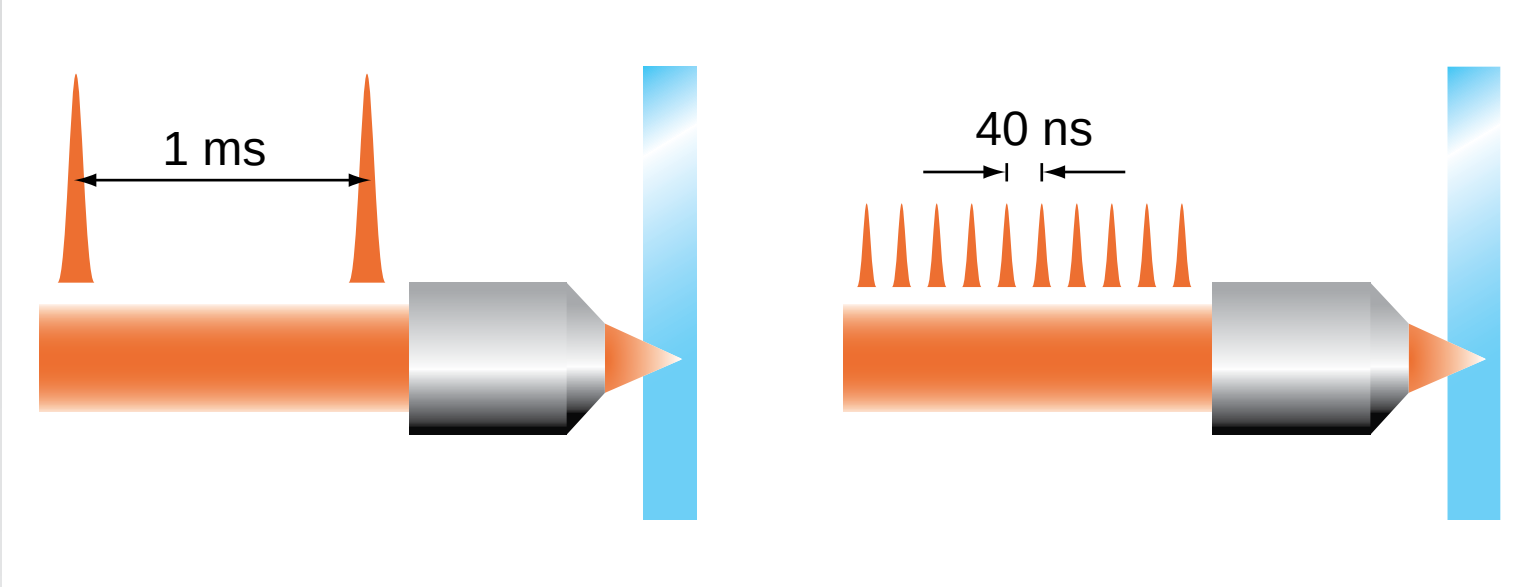
Low-energy machining

High repetition-rate micromachining:

- structural changes exceed focal volume
- spherical structures
- density change caused by melting

Low-energy machining

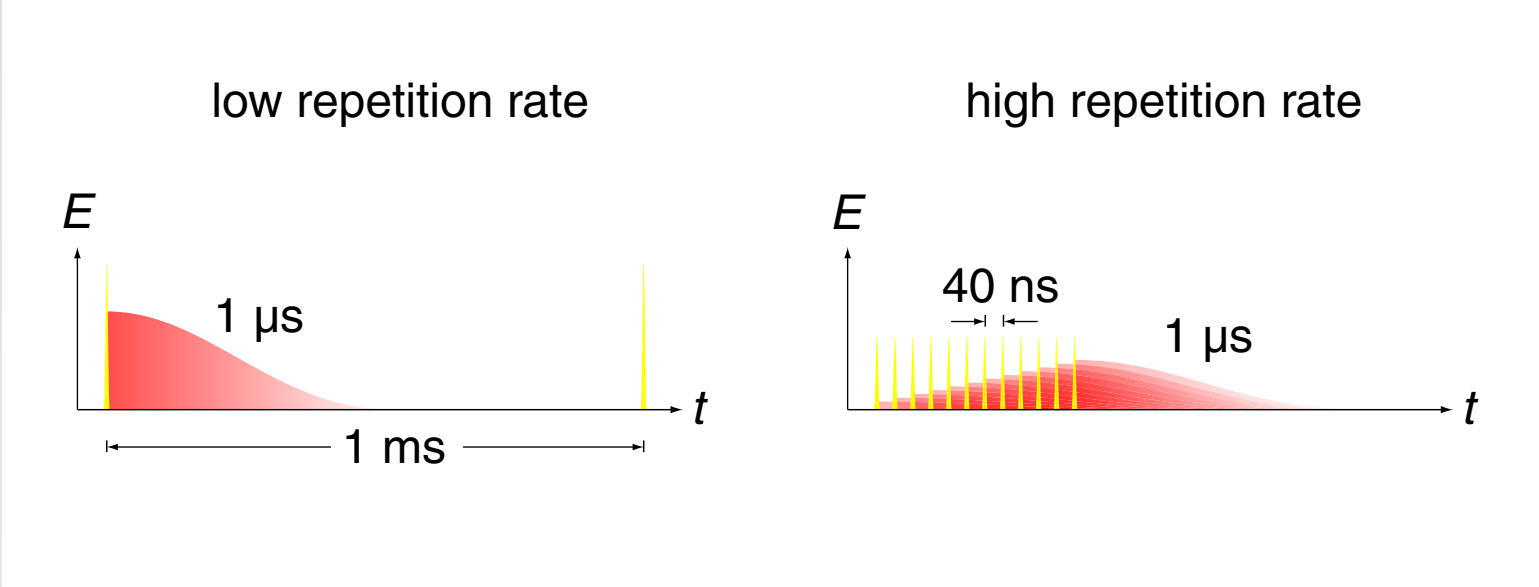
amplified laser **oscillator**



repetitive **cumulative**

Low-energy machining

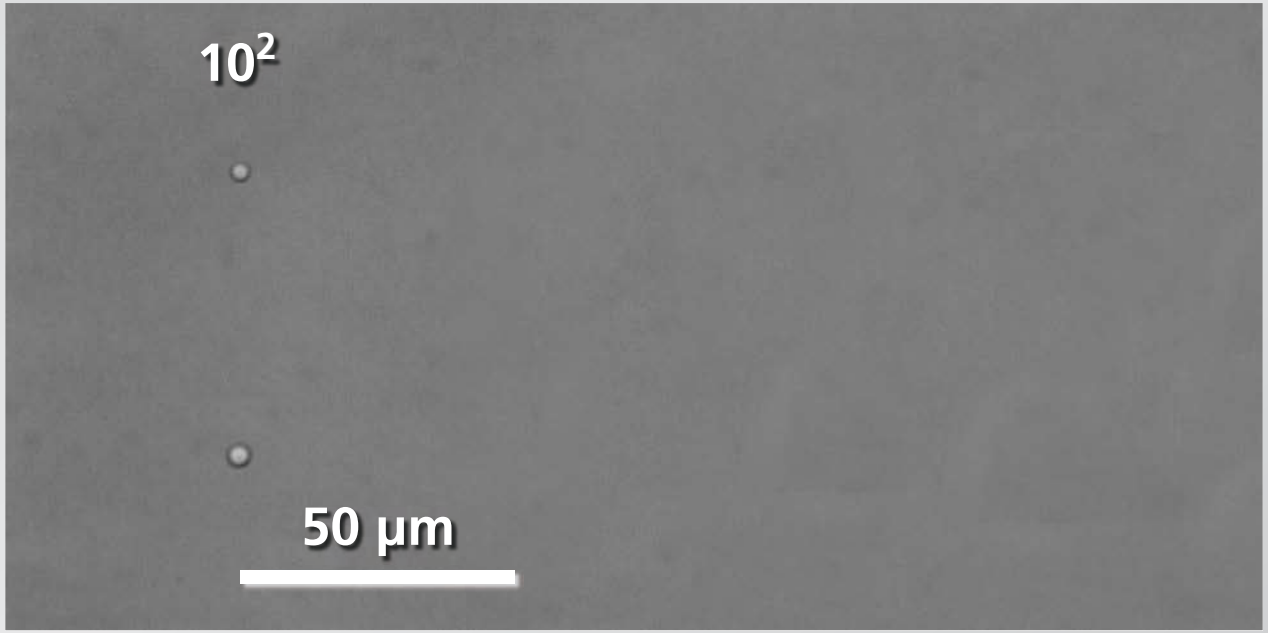
amplified laser **oscillator**



repetitive **cumulative**

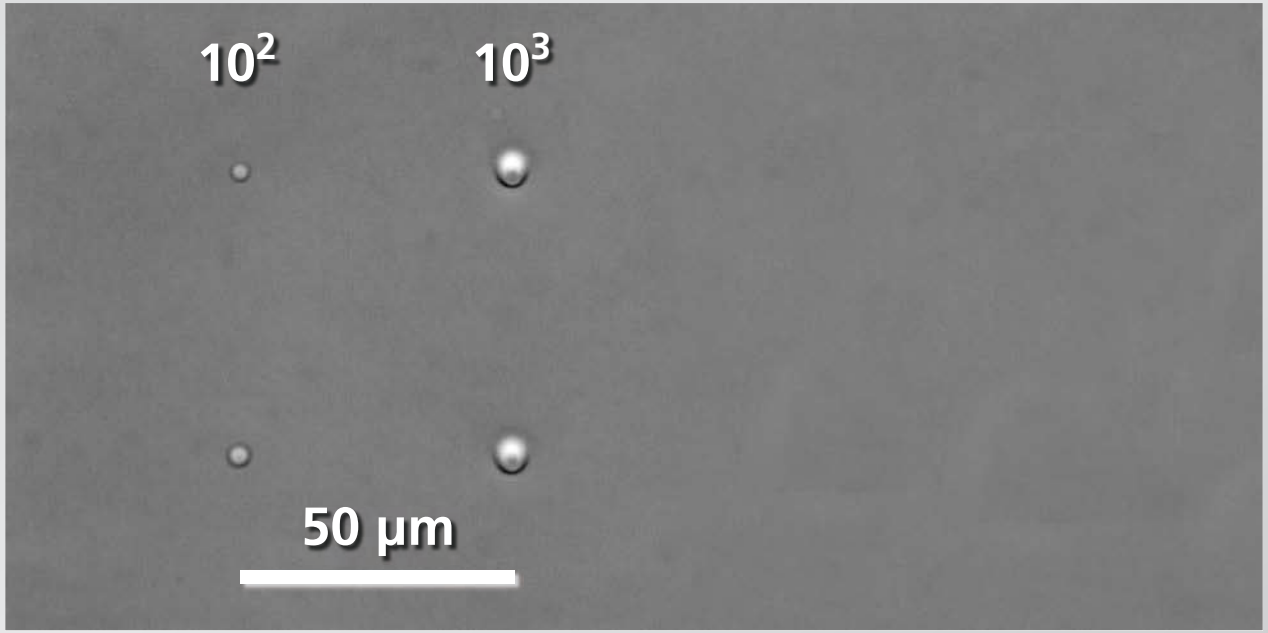
Low-energy machining

the longer the irradiation…



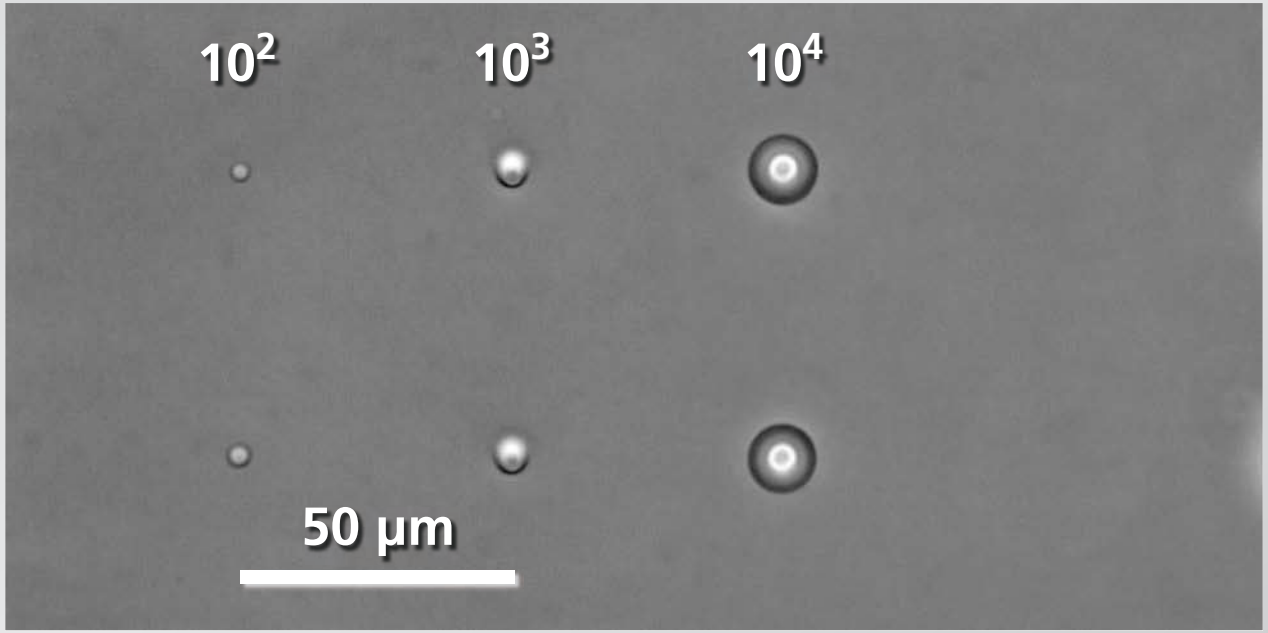
Low-energy machining

the longer the irradiation…



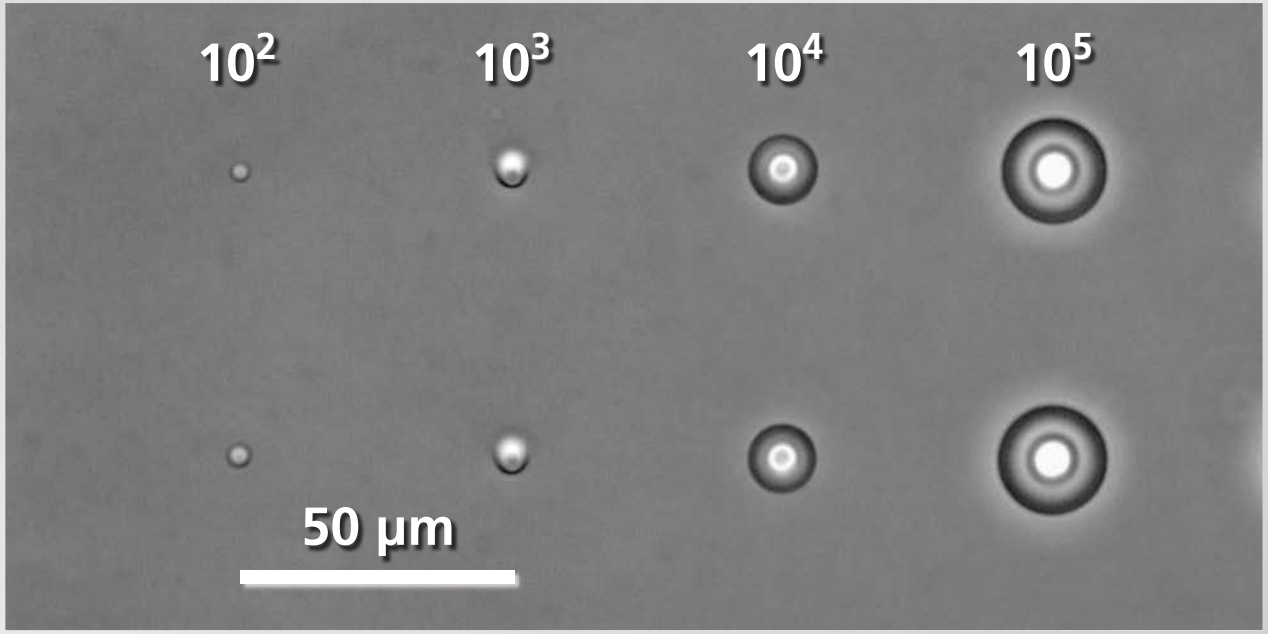
Low-energy machining

the longer the irradiation…



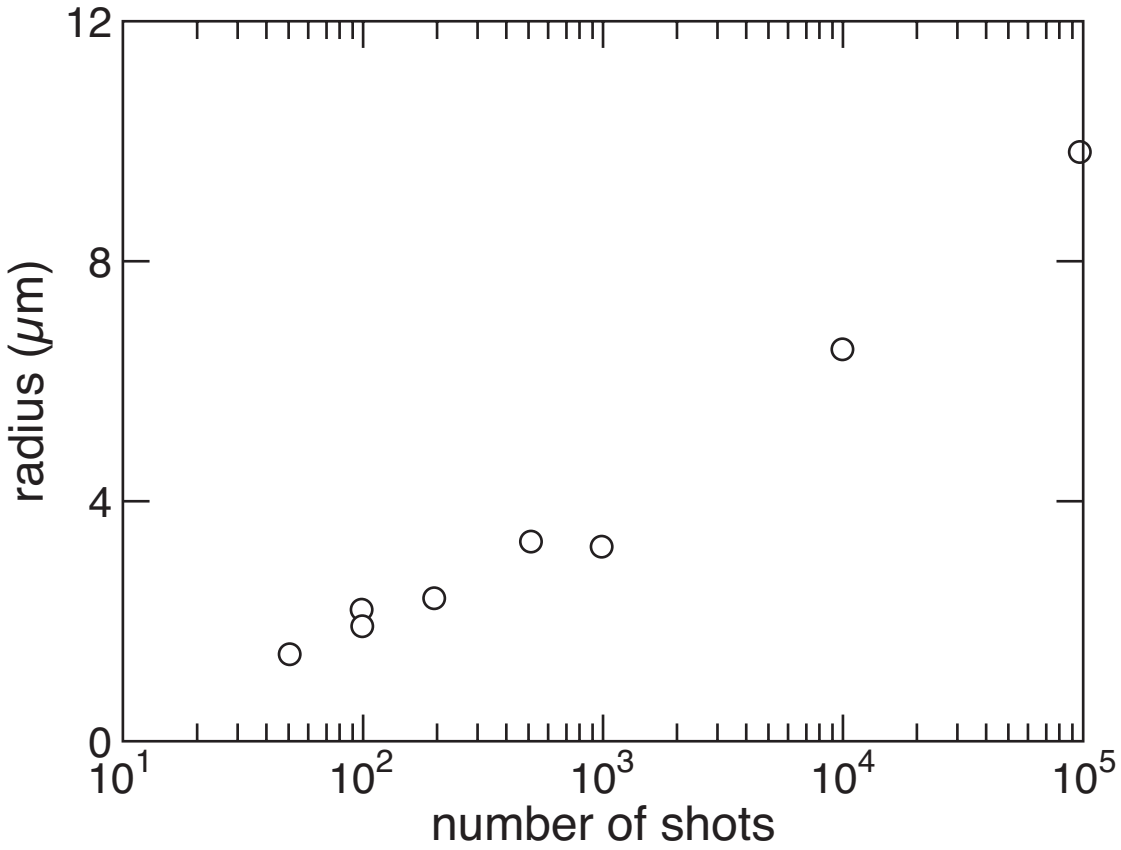
Low-energy machining

the longer the irradiation…



… the larger the radius

Low-energy machining



Low-energy machining

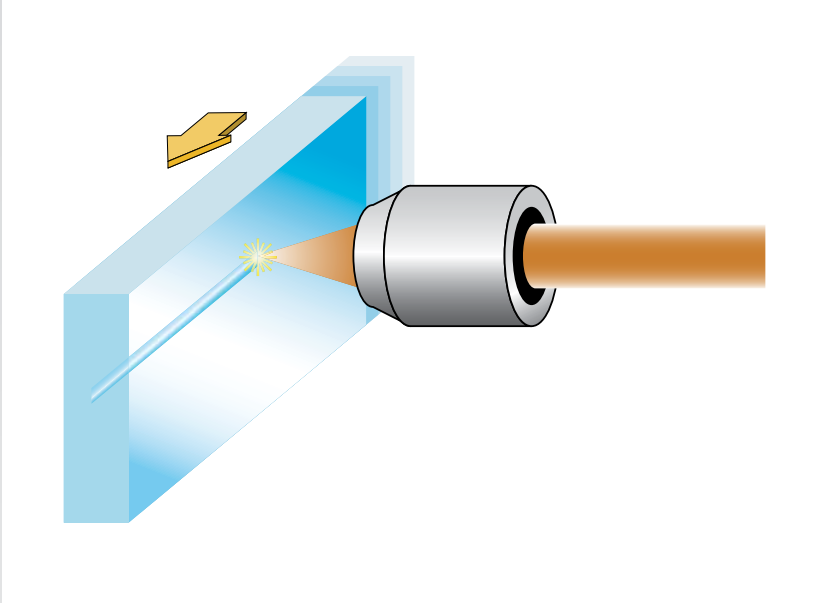
at high-rep rate: internal “point-source of heat”

Outline

- femtosecond micromachining
- low-energy machining
- applications

Low-energy machining

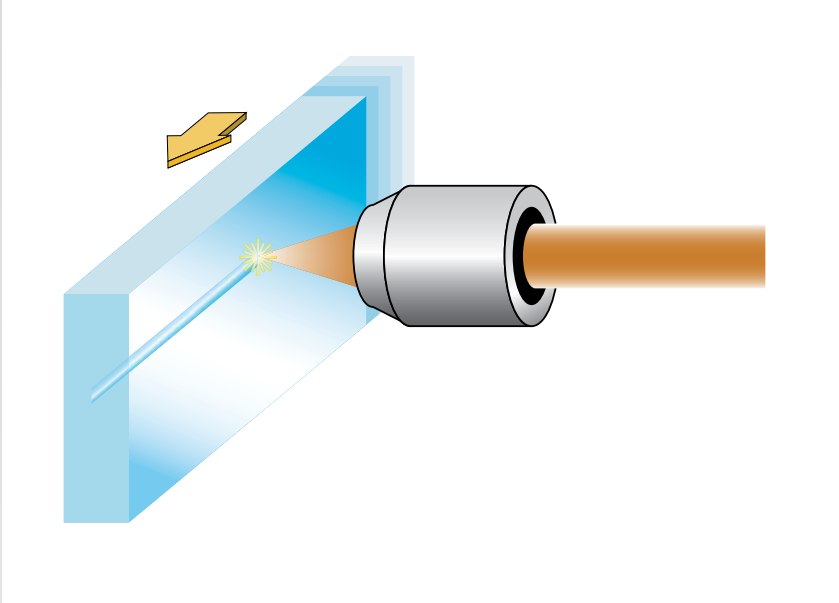
waveguide micromachining

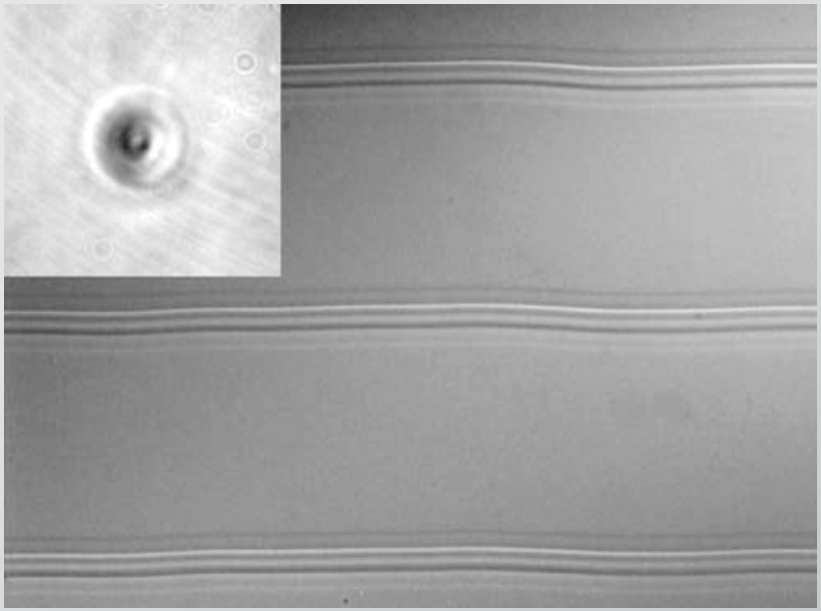


Opt. Lett. **26**, 93 (2001)

Low-energy machining

waveguide micromachining

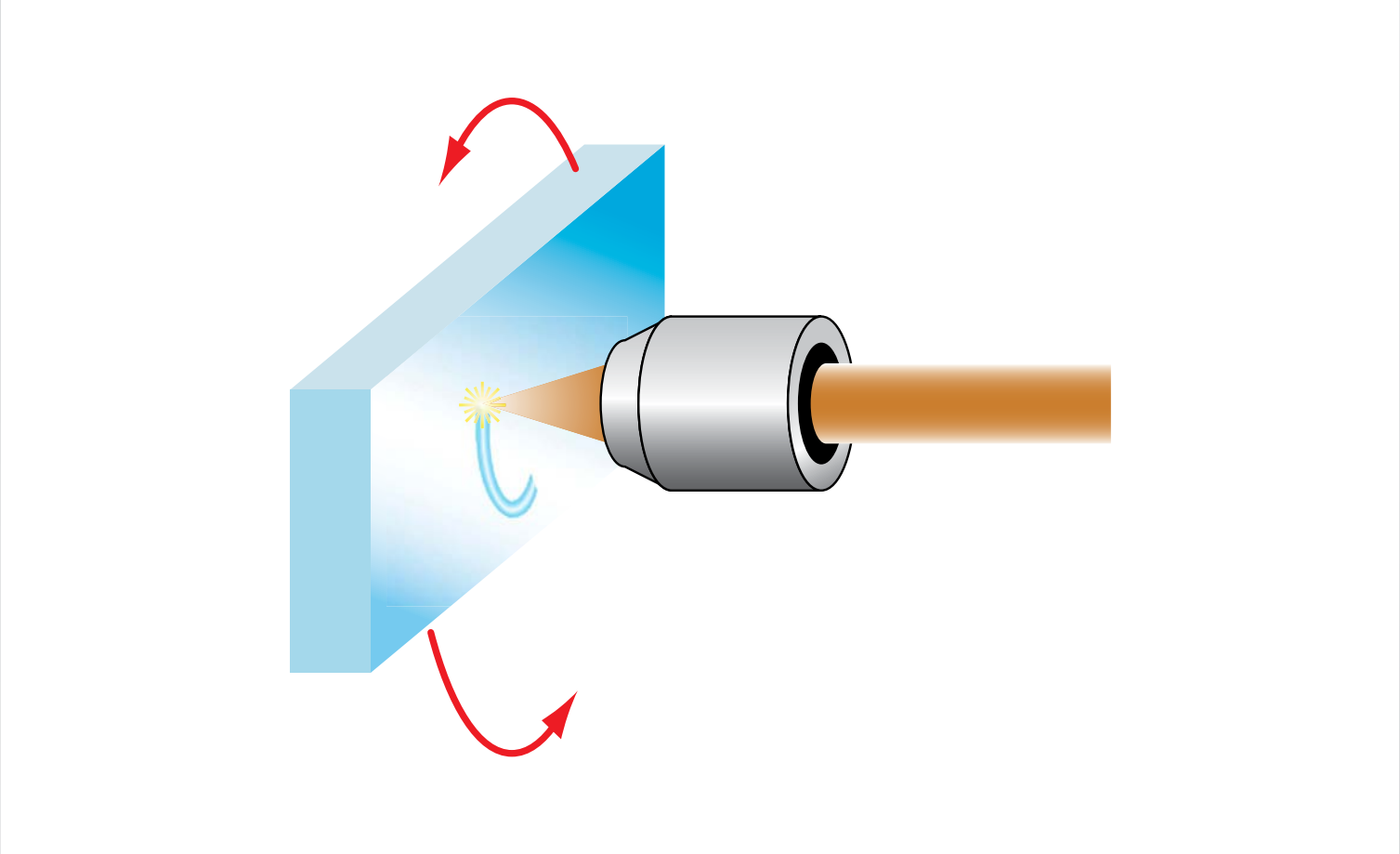




Opt. Lett. **26**, 93 (2001)

Applications

curved waveguides

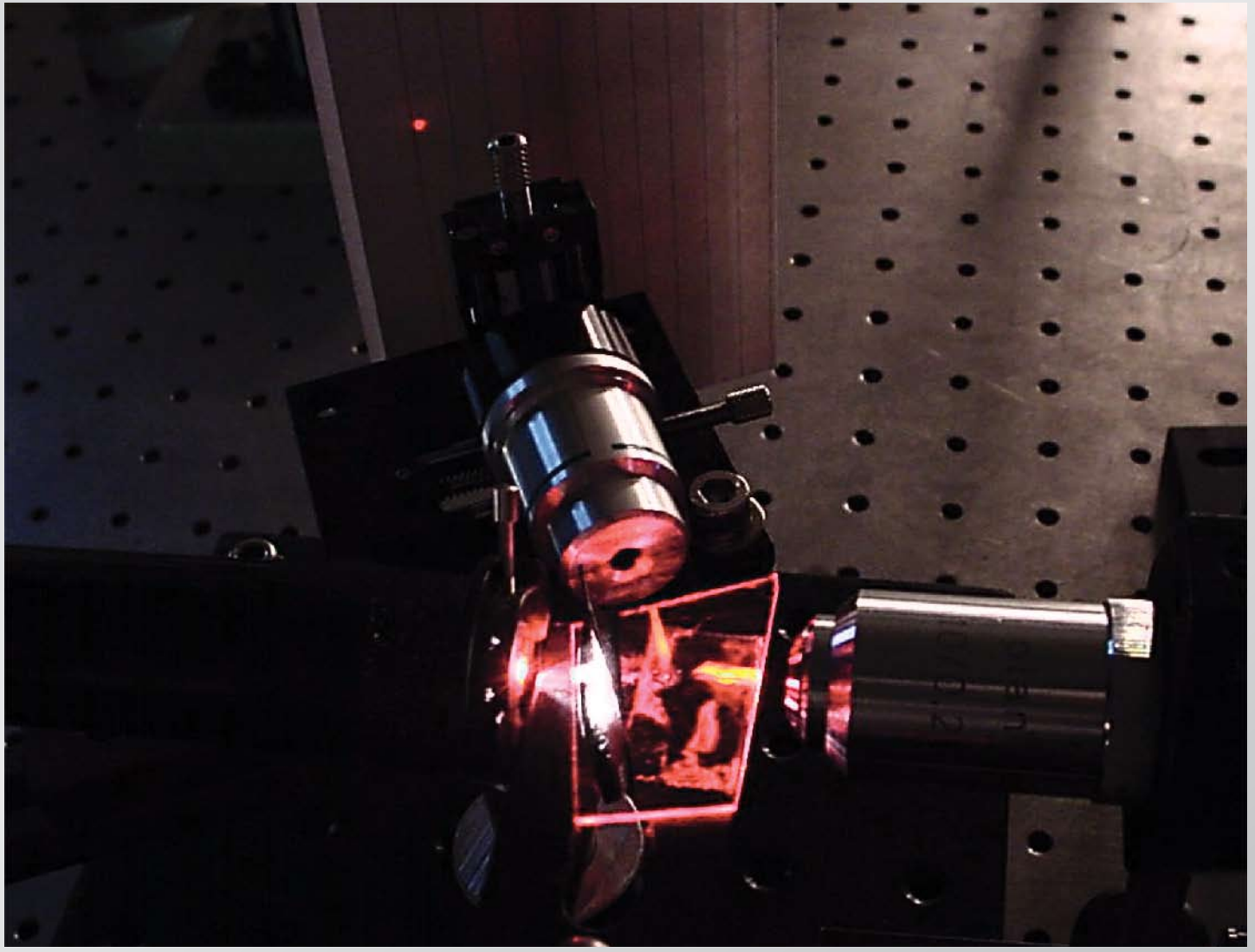


Applications

curved waveguides

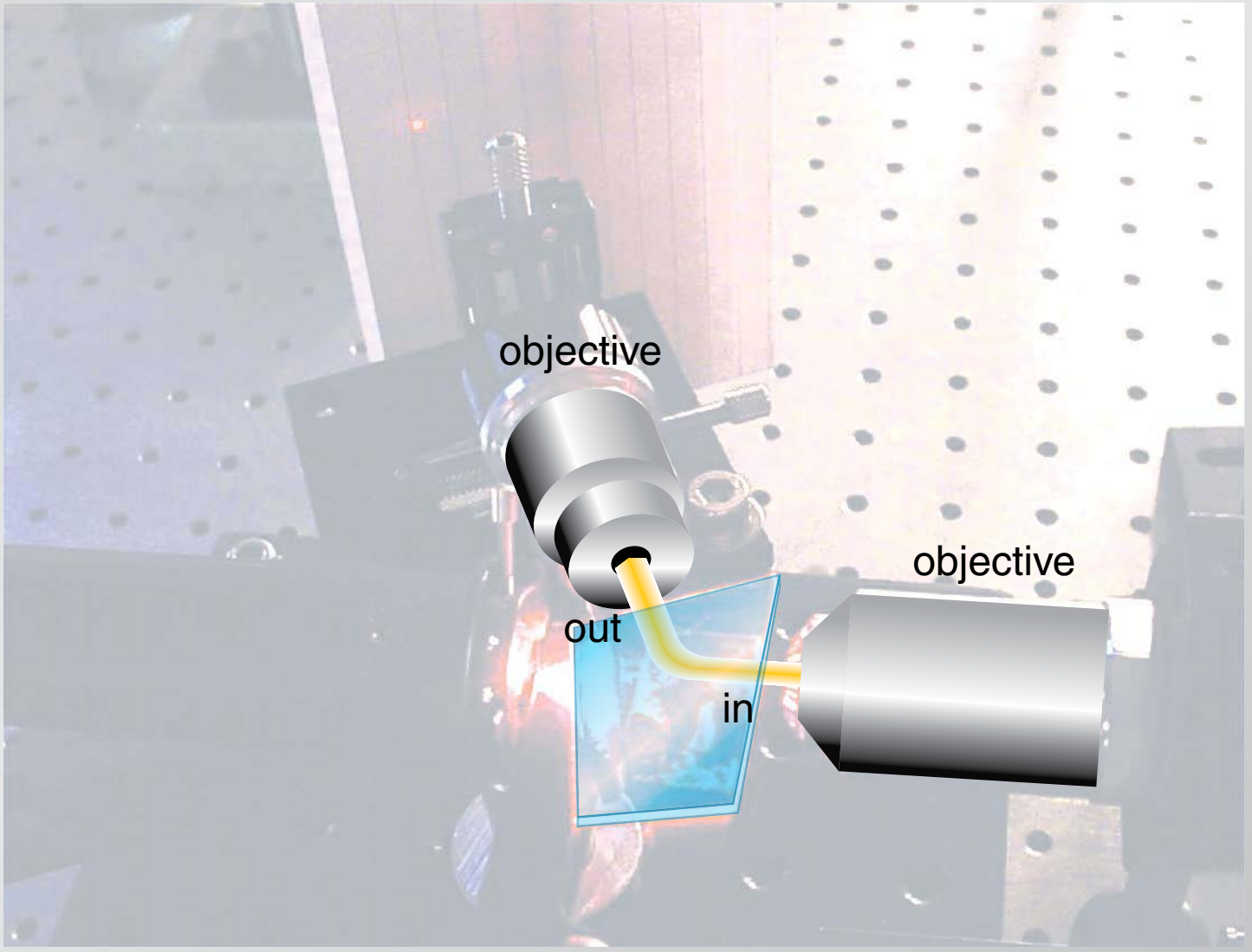
Applications

curved waveguides



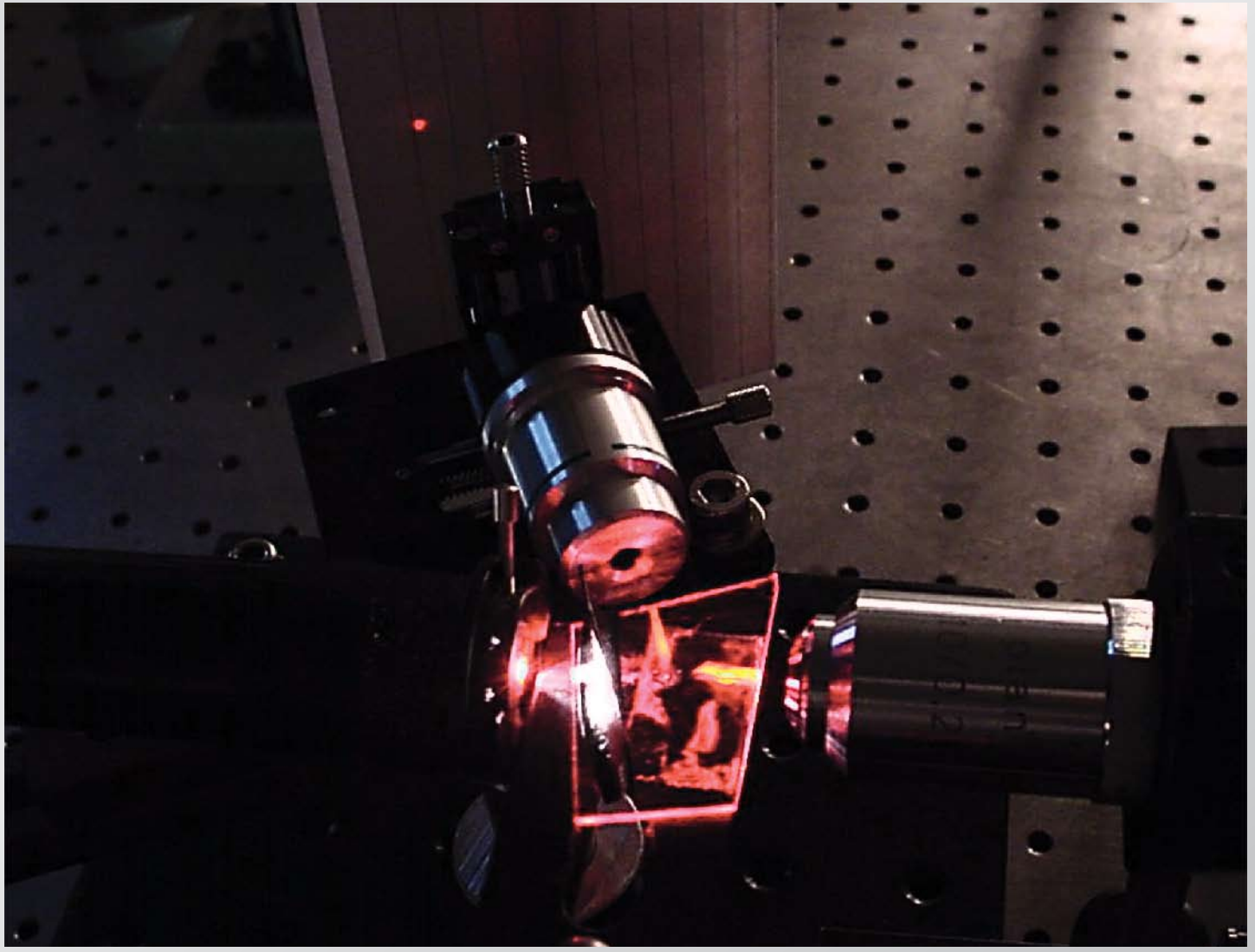
Applications

curved waveguides



Applications

curved waveguides



Applications

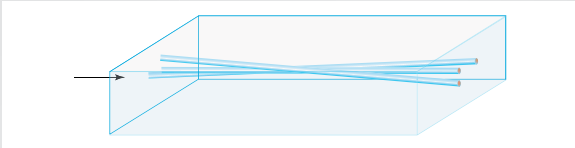
photonic fabrication techniques

	fs micromachining	other
loss (dB/cm)	< 3	0.1–3
bending radius	36 mm	30–40 mm
Δn	2×10^{-3}	10^{-4} – 0.5
3D integration	Y	N

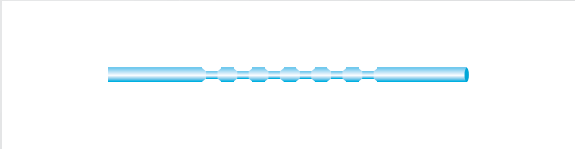
Applications

photonic devices

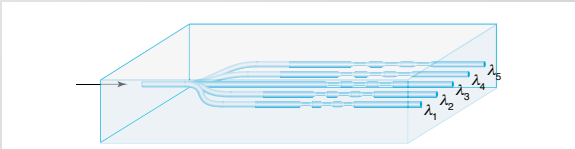
3D splitter



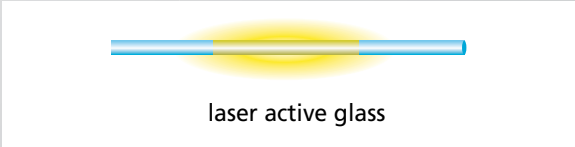
Bragg grating



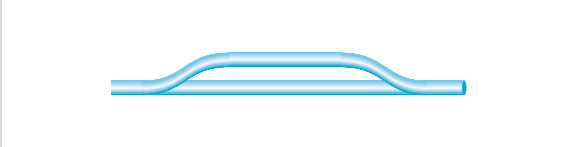
demultiplexer



amplifier

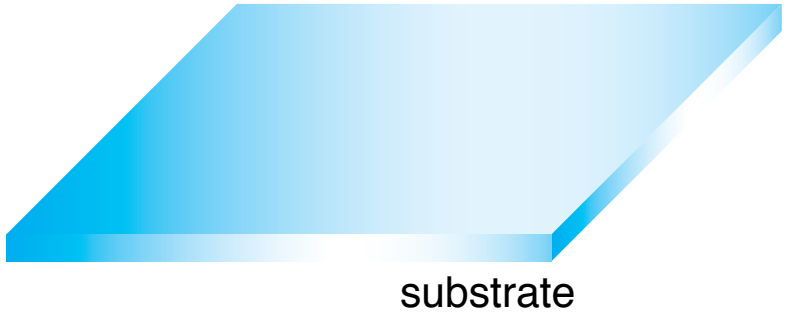


interferometer



Applications

all-optical sensor



Appl. Phys. Lett. **87**, 051106 (2005)

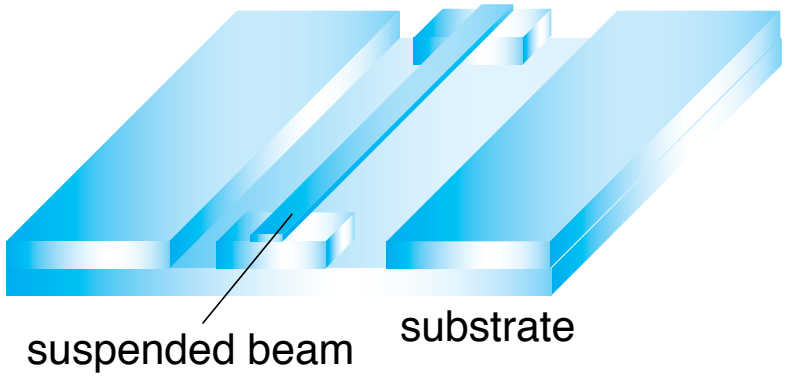
Applications

all-optical sensor

Appl. Phys. Lett. **87**, 051106 (2005)

Applications

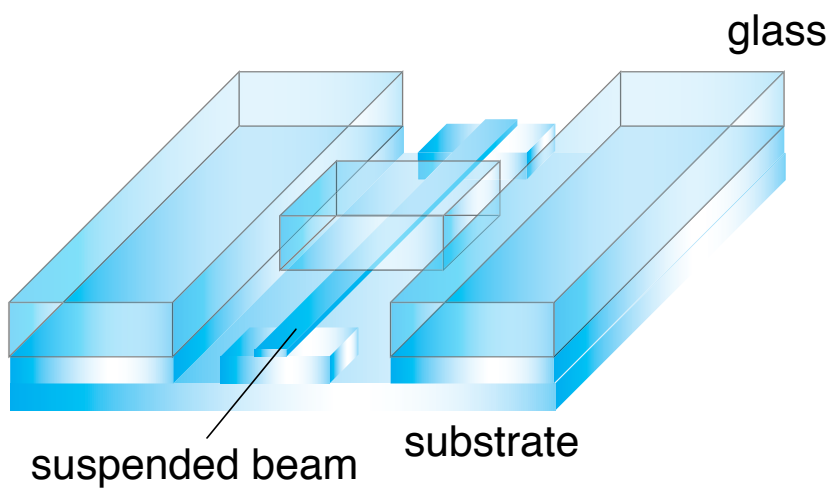
all-optical sensor



Appl. Phys. Lett. **87**, 051106 (2005)

Applications

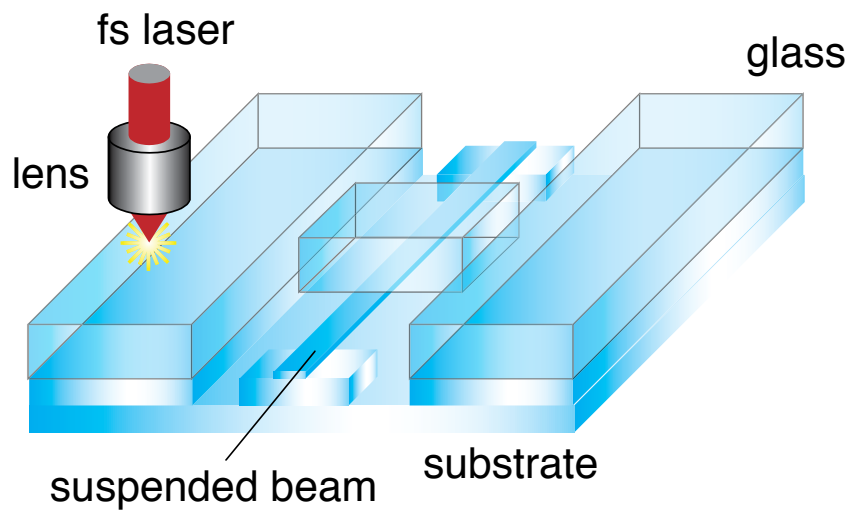
all-optical sensor



Appl. Phys. Lett. **87**, 051106 (2005)

Applications

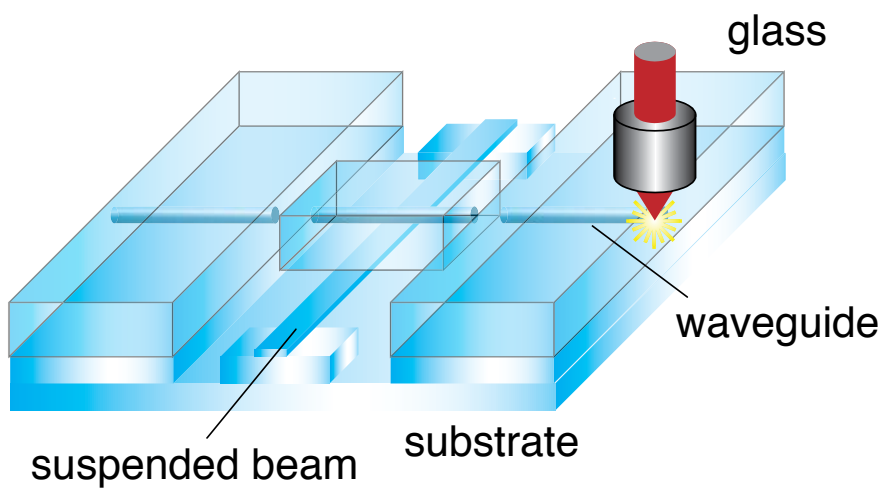
all-optical sensor



Appl. Phys. Lett. **87**, 051106 (2005)

Applications

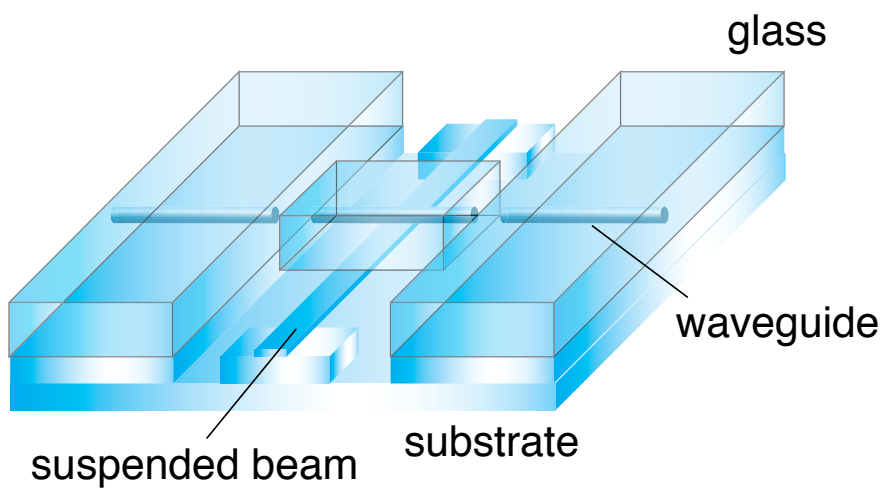
all-optical sensor



Appl. Phys. Lett. **87**, 051106 (2005)

Applications

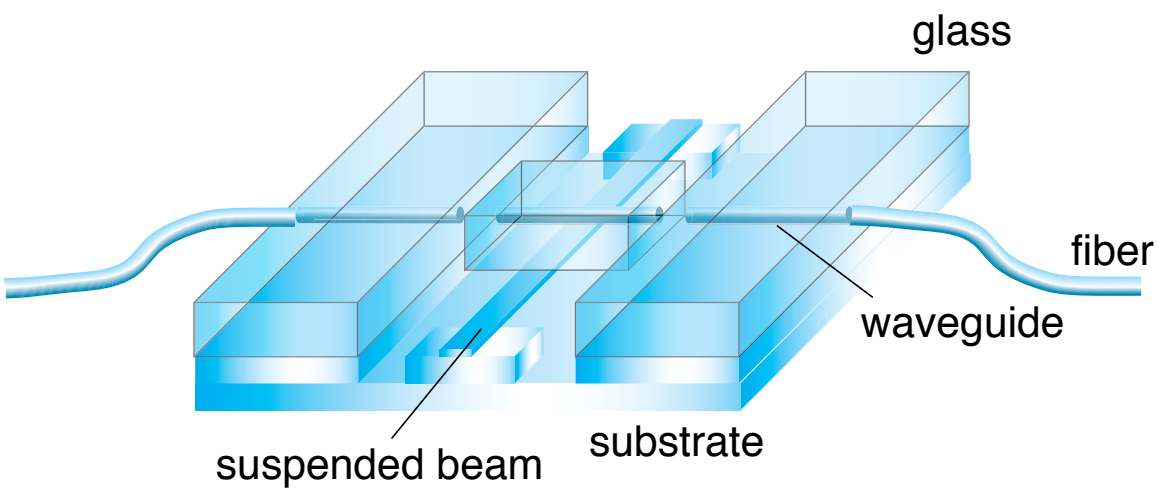
all-optical sensor



Appl. Phys. Lett. **87**, 051106 (2005)

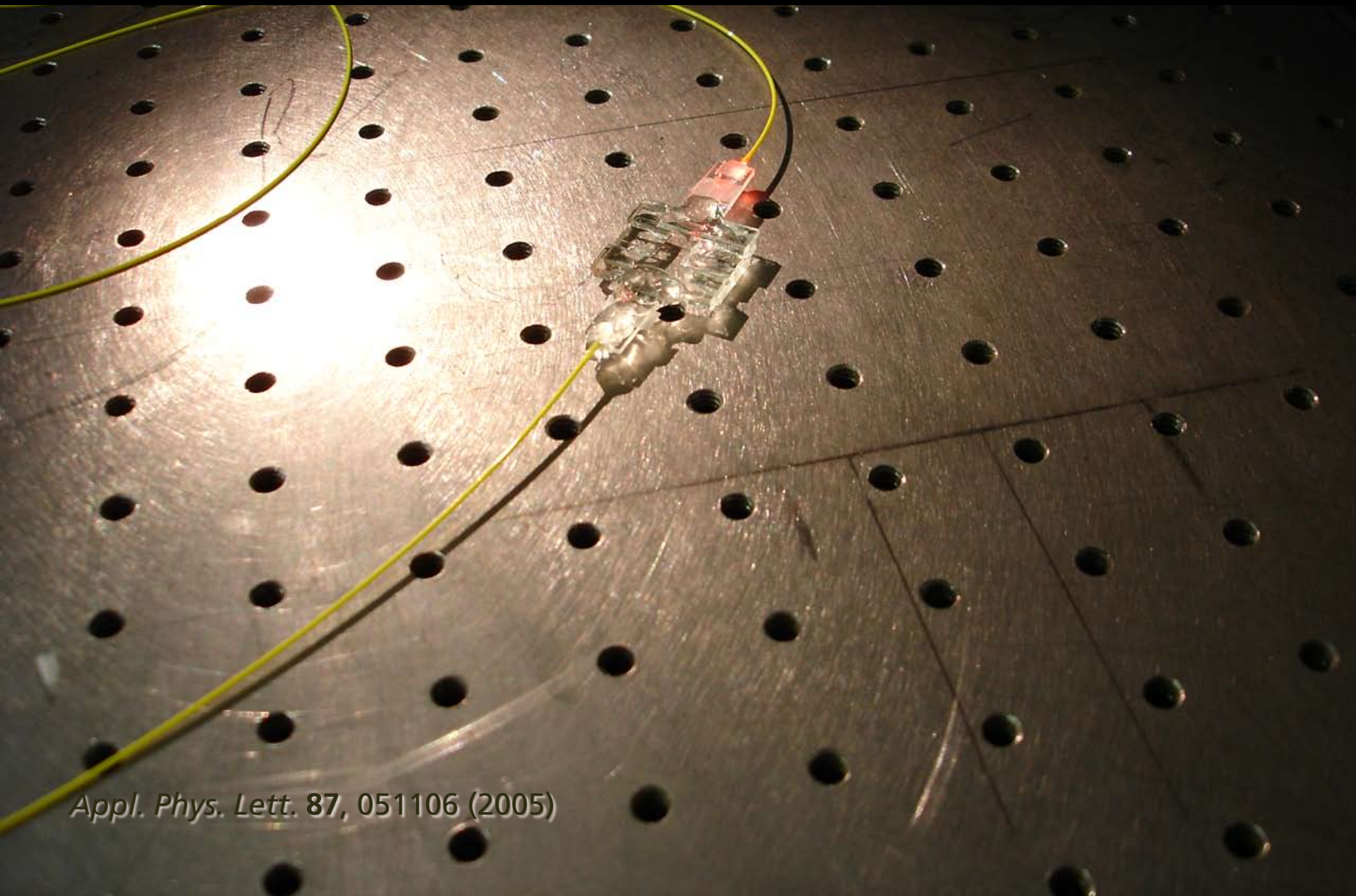
Applications

all-optical sensor



Appl. Phys. Lett. **87**, 051106 (2005)

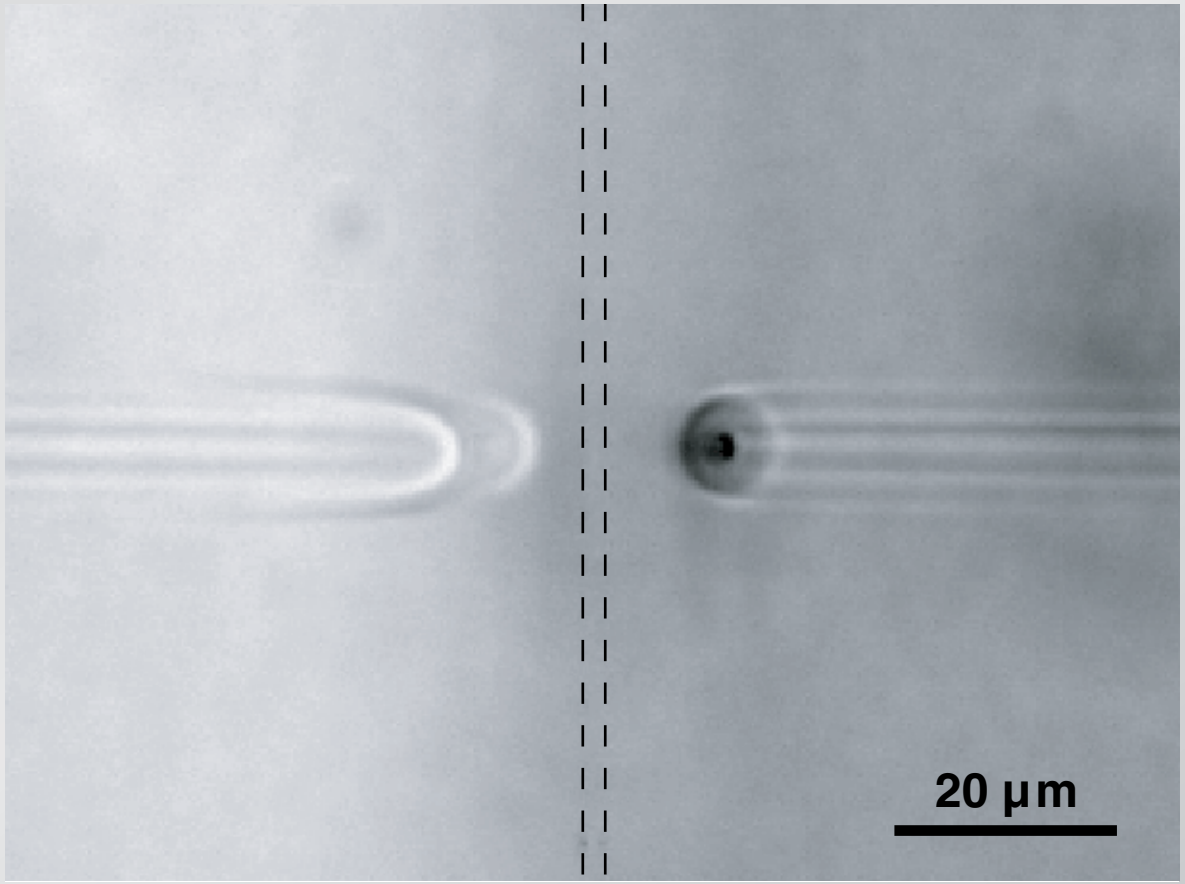
Applications



Appl. Phys. Lett. **87**, 051106 (2005)

Applications

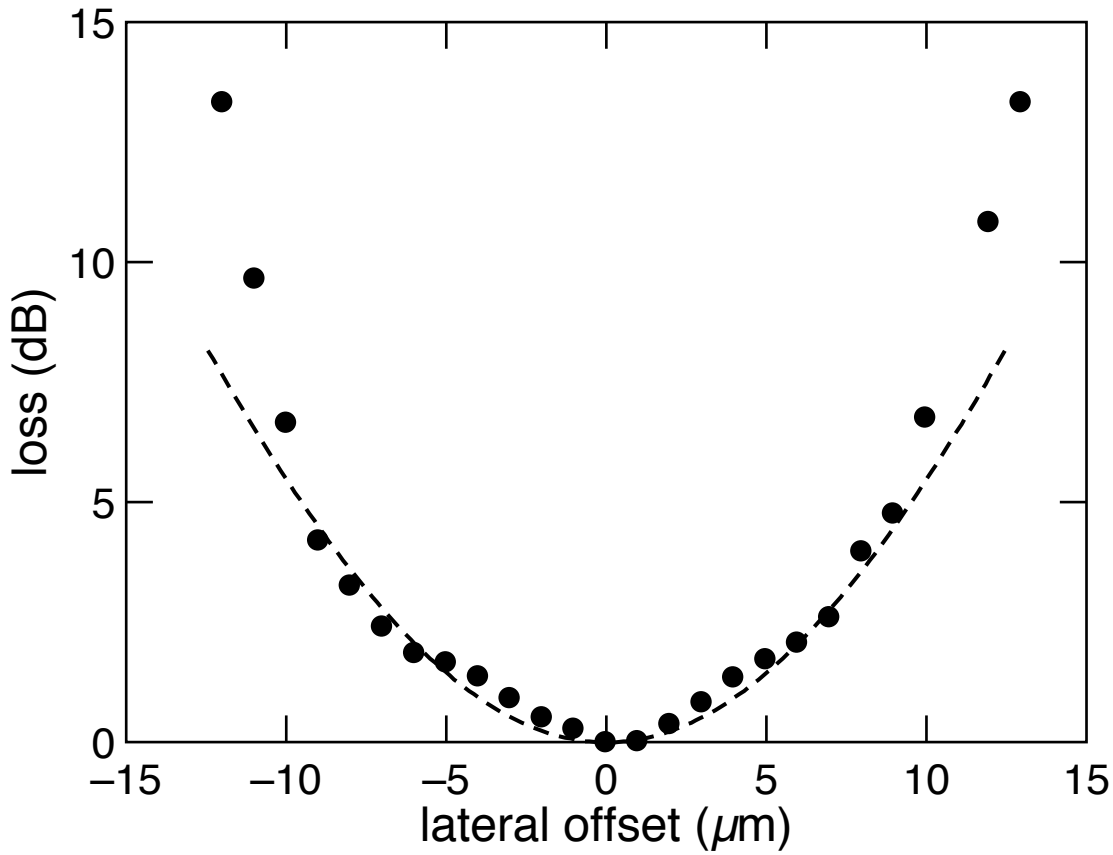
sensor gap



Appl. Phys. Lett. **87**, 051106 (2005)

Applications

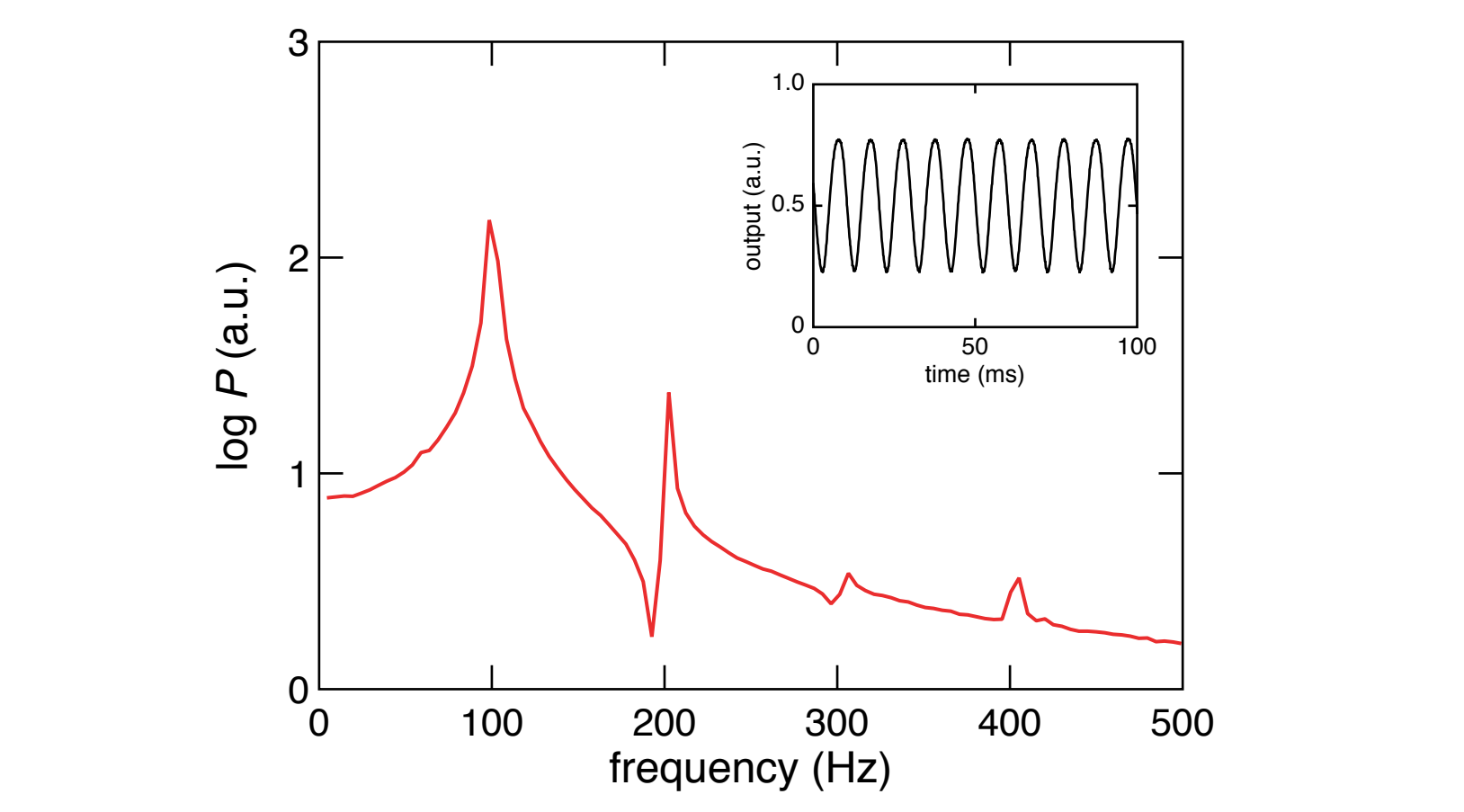
calibration



Appl. Phys. Lett. **87**, 051106 (2005)

Applications

sensor response to 100 Hz acoustic wave



Appl. Phys. Lett. **87**, 051106 (2005)

Applications

ideal tool for ablating (living) tissue

Applications

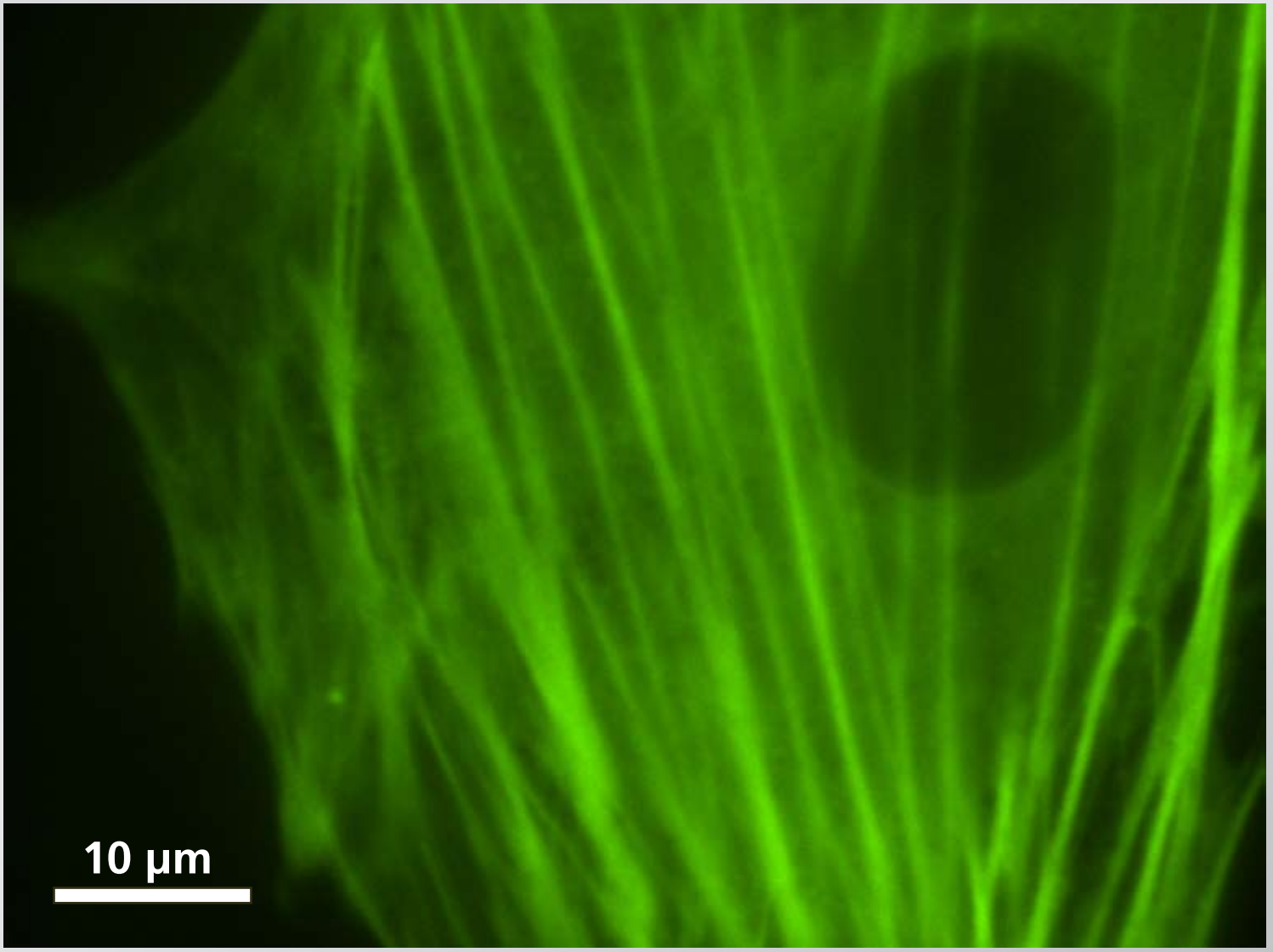
- standard biochemical tools: species selective
- fs laser “nanosurgery”: site specific

Applications

Q: can we probe the dynamics of the cytoskeleton?

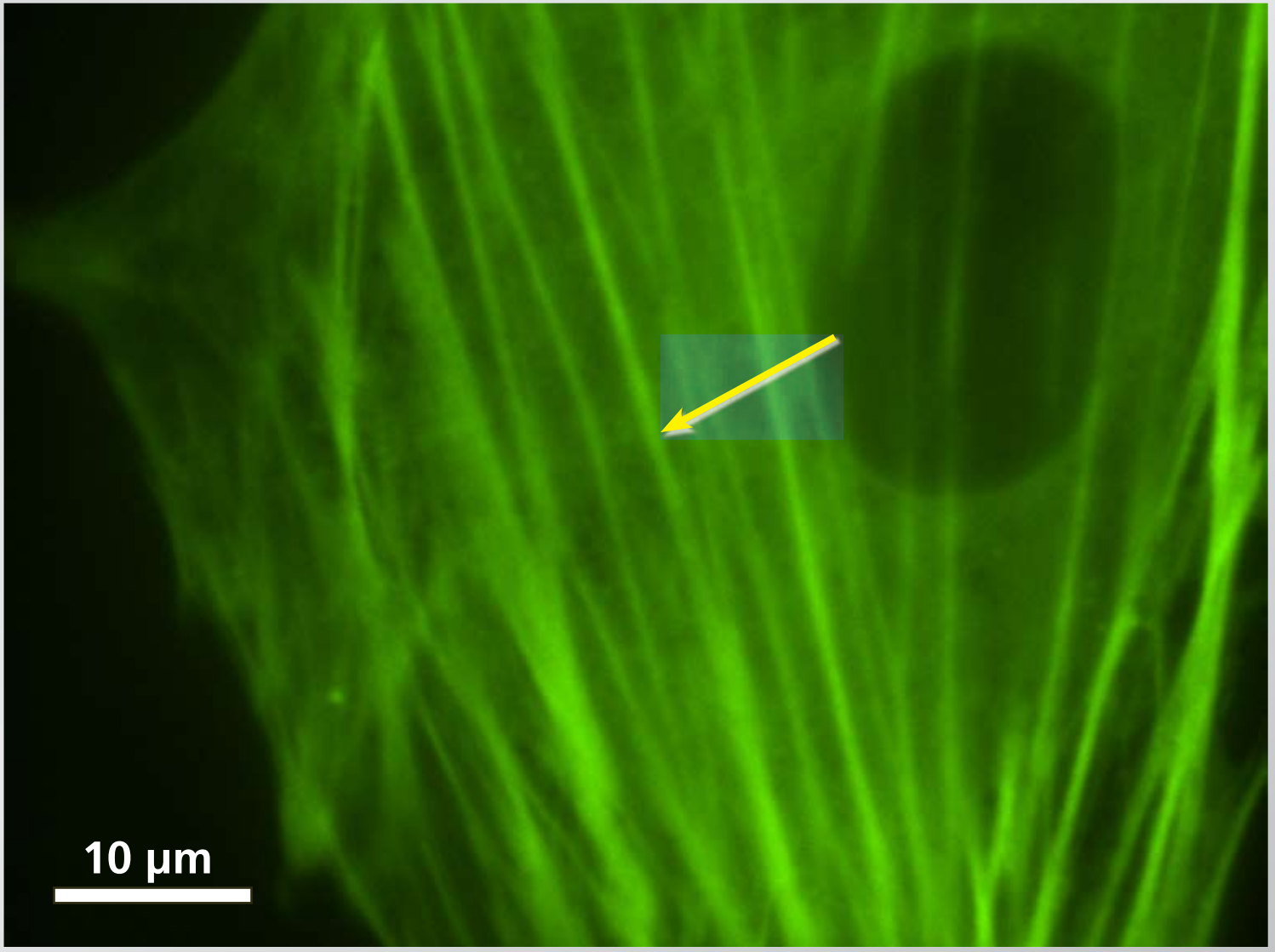
Applications

actin fiber network of a live cell



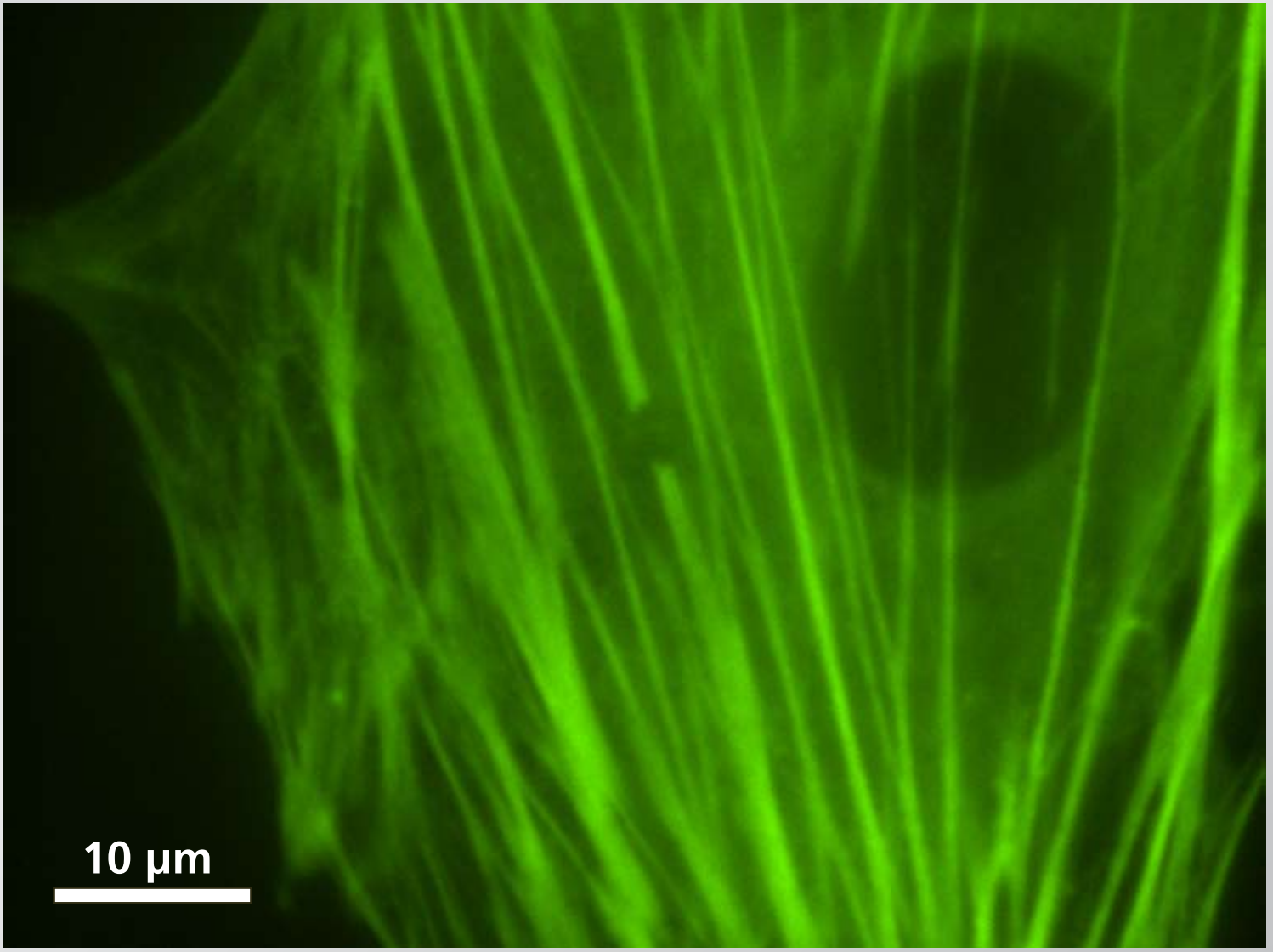
Applications

cut a single fiber bundle



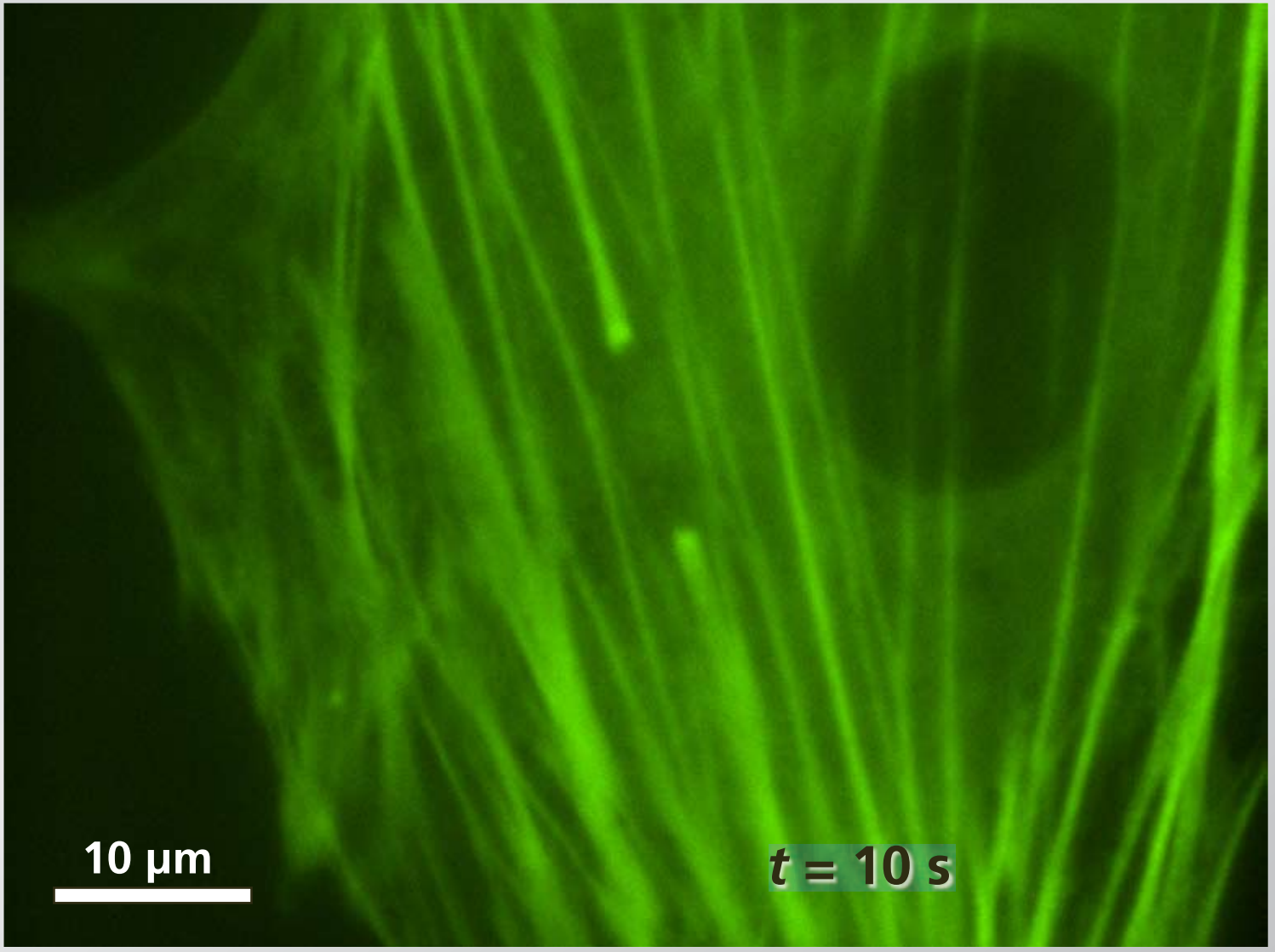
Applications

cut a single fiber bundle



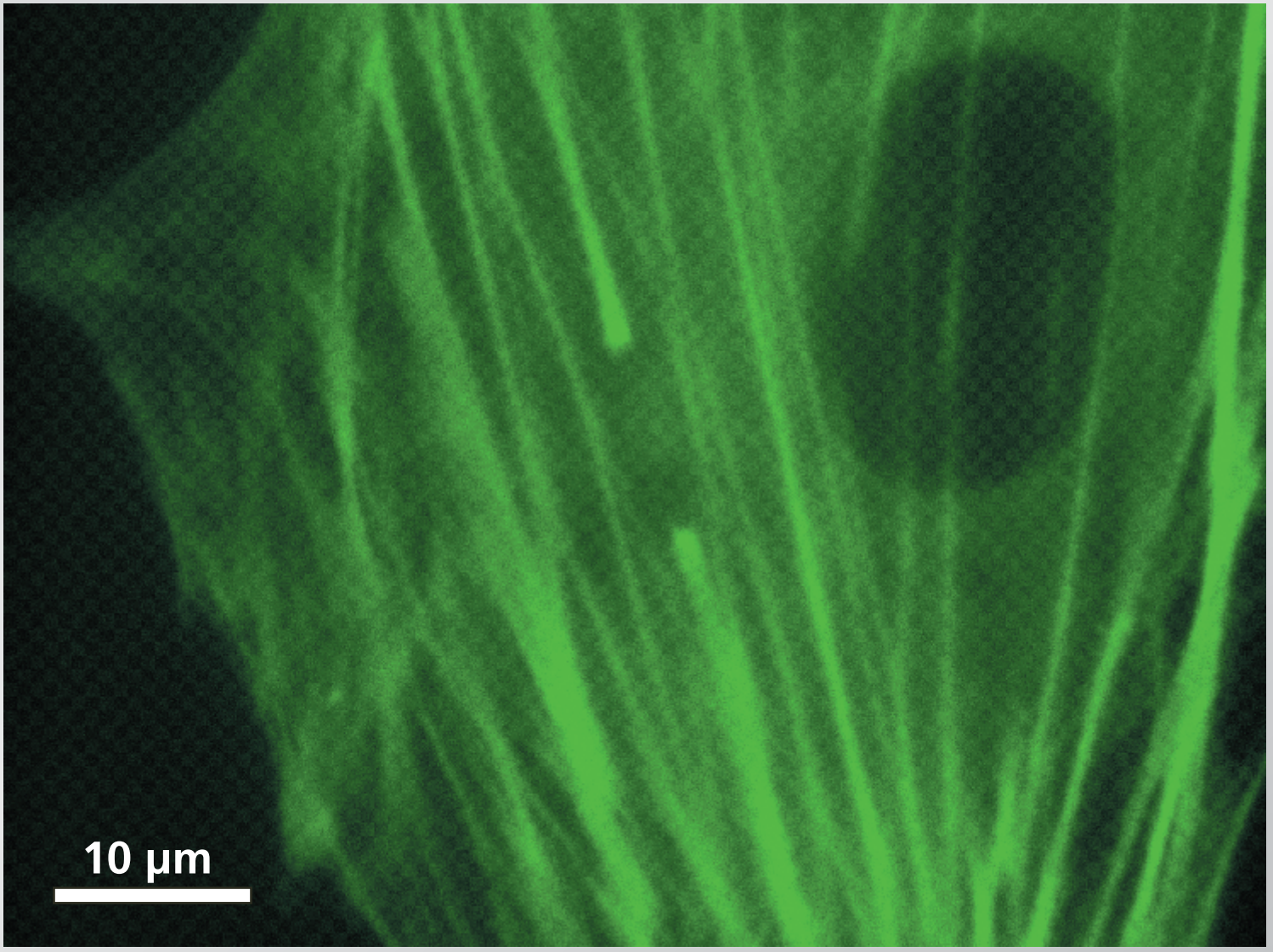
Applications

gap widens with time



Applications

dynamics provides information on *in vivo* mechanics



Applications

Q: can we probe the neurological origins of behavior?

Applications

Caenorhabditis Elegans

Juergen Berger & Ralph Sommer
Max-Planck Institute for Developmental Biology

Applications

Caenorhabditis Elegans

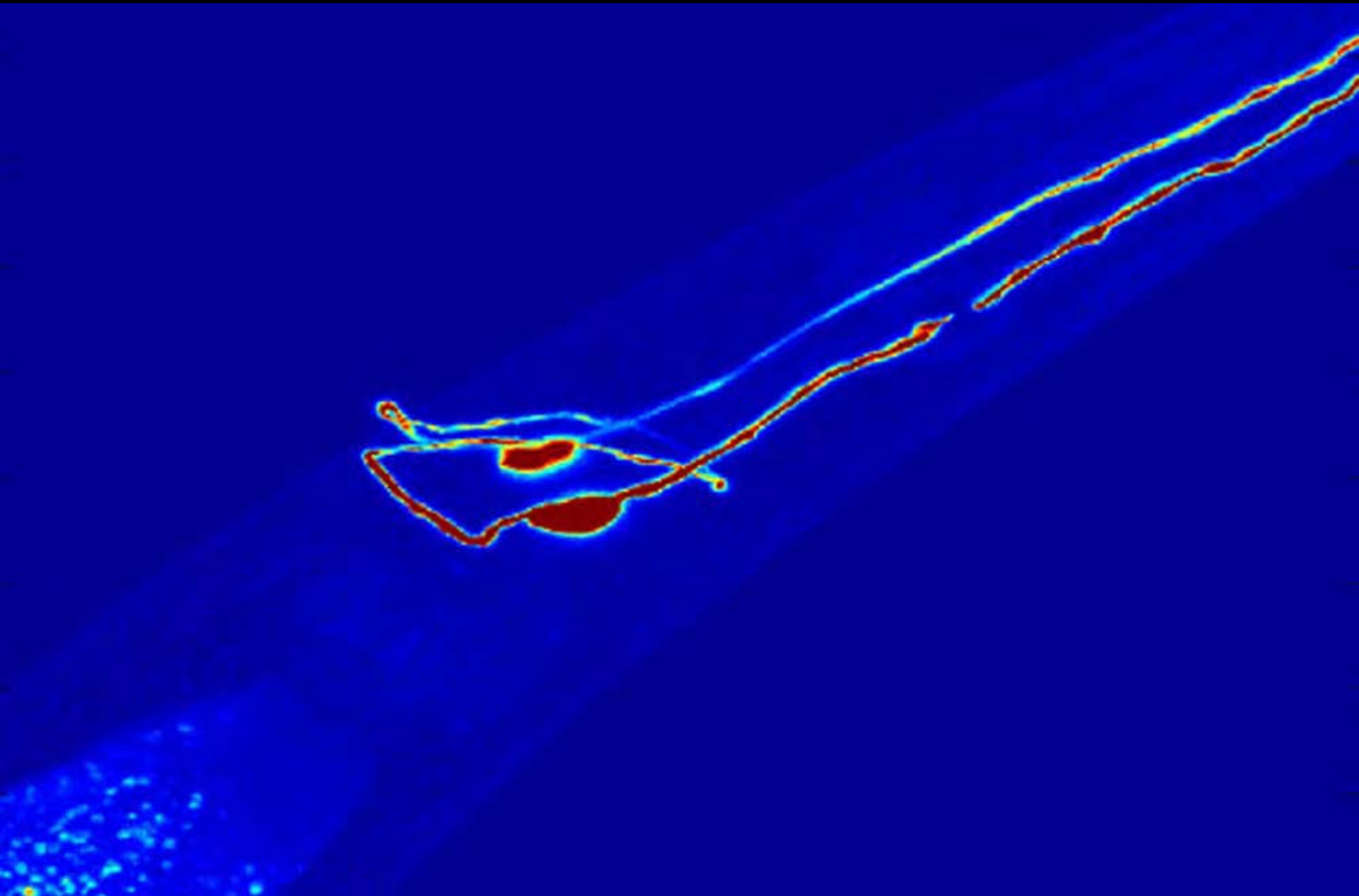
- simple model organism
- similarities to higher organisms
- genome fully sequenced
- easy to handle

Applications

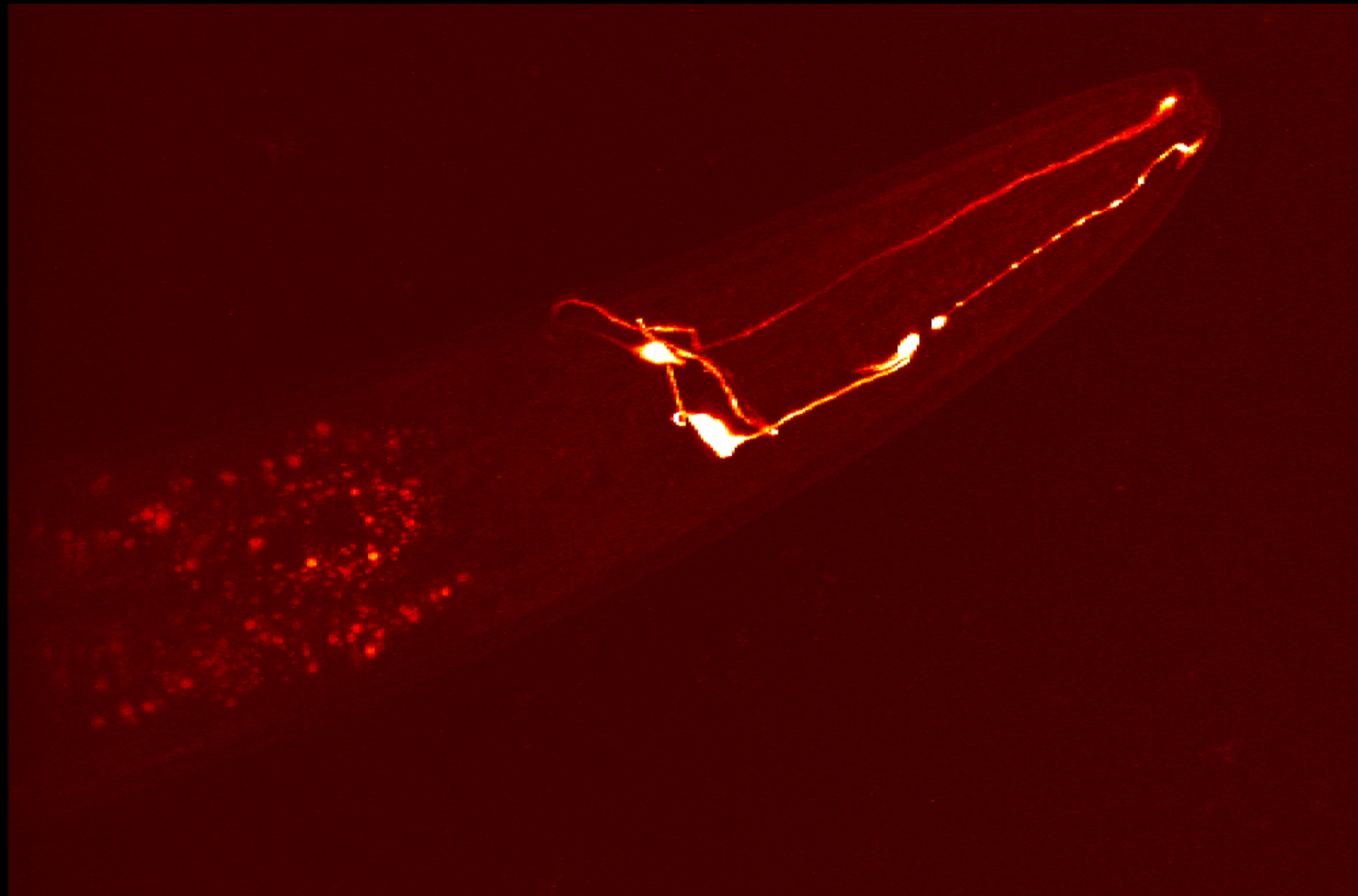
Caenorhabditis Elegans

- 80 μm x 1 mm
- about 1300 cells
- 302 neurons
- invariant wiring diagram
- neuronal system completely encodes behavior

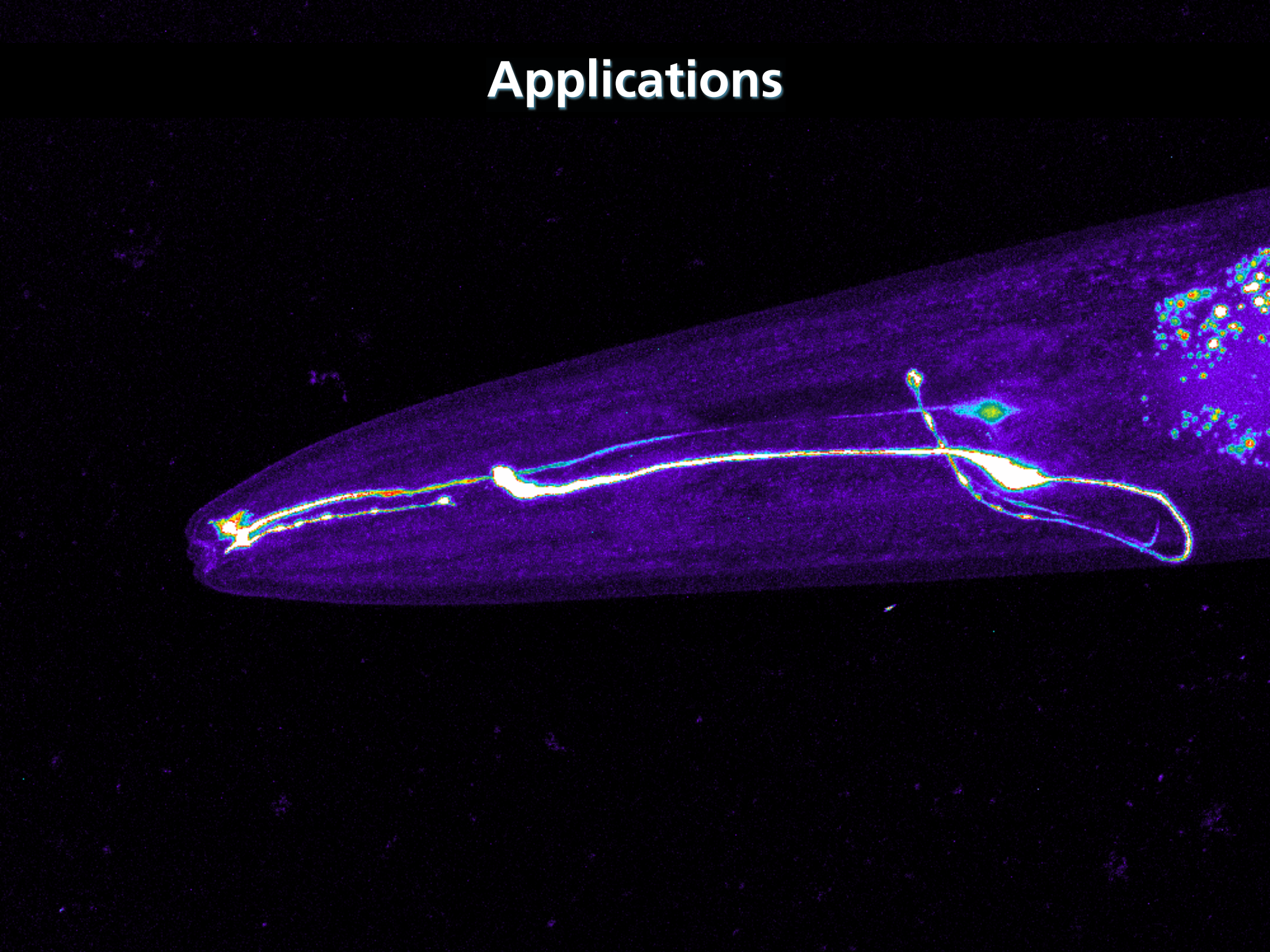
Applications



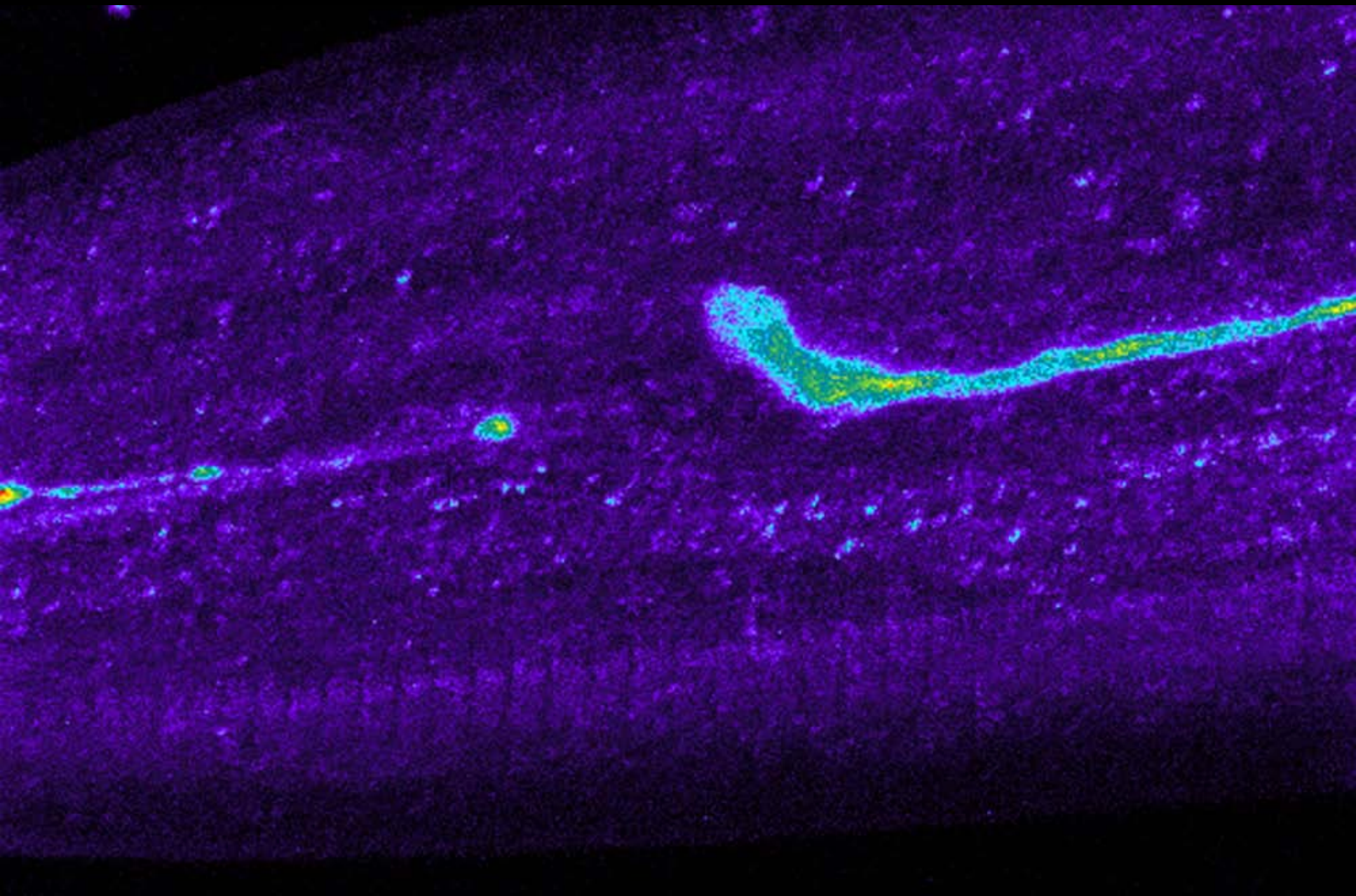
Applications



Applications

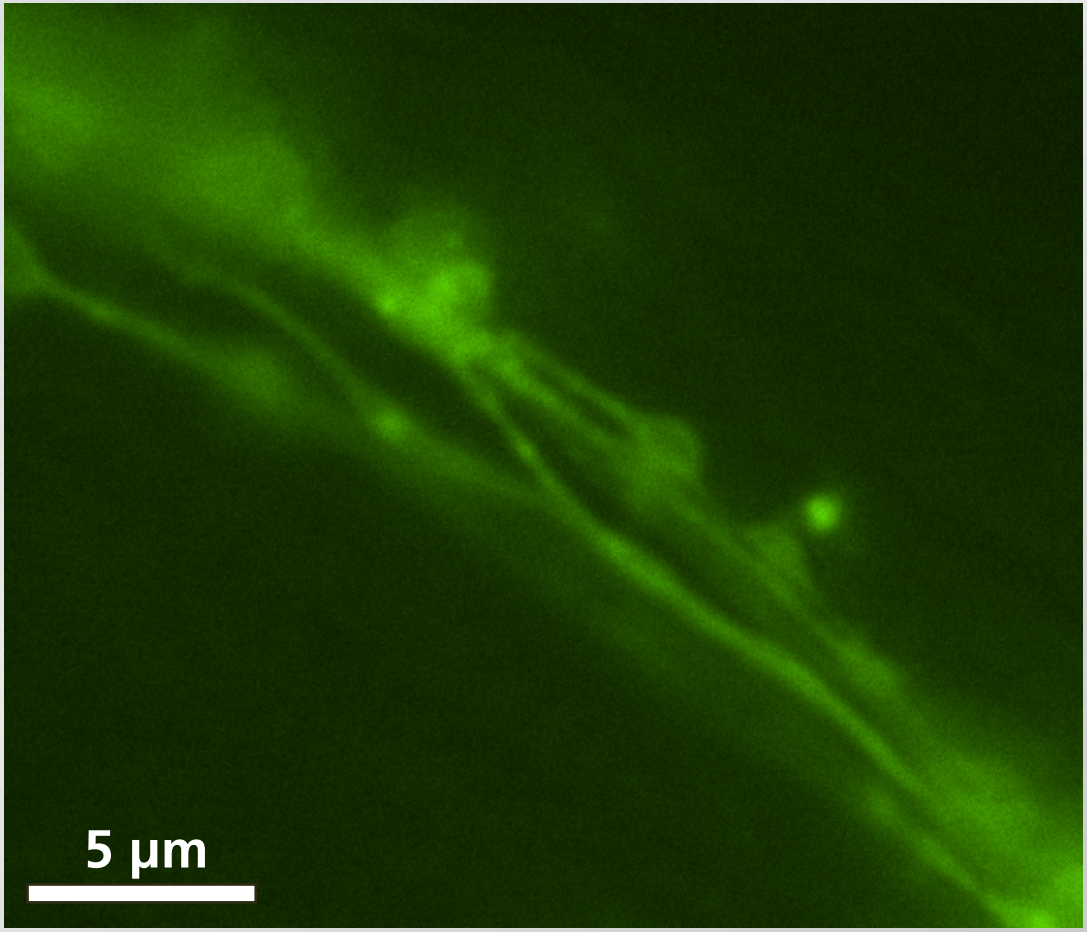


Applications



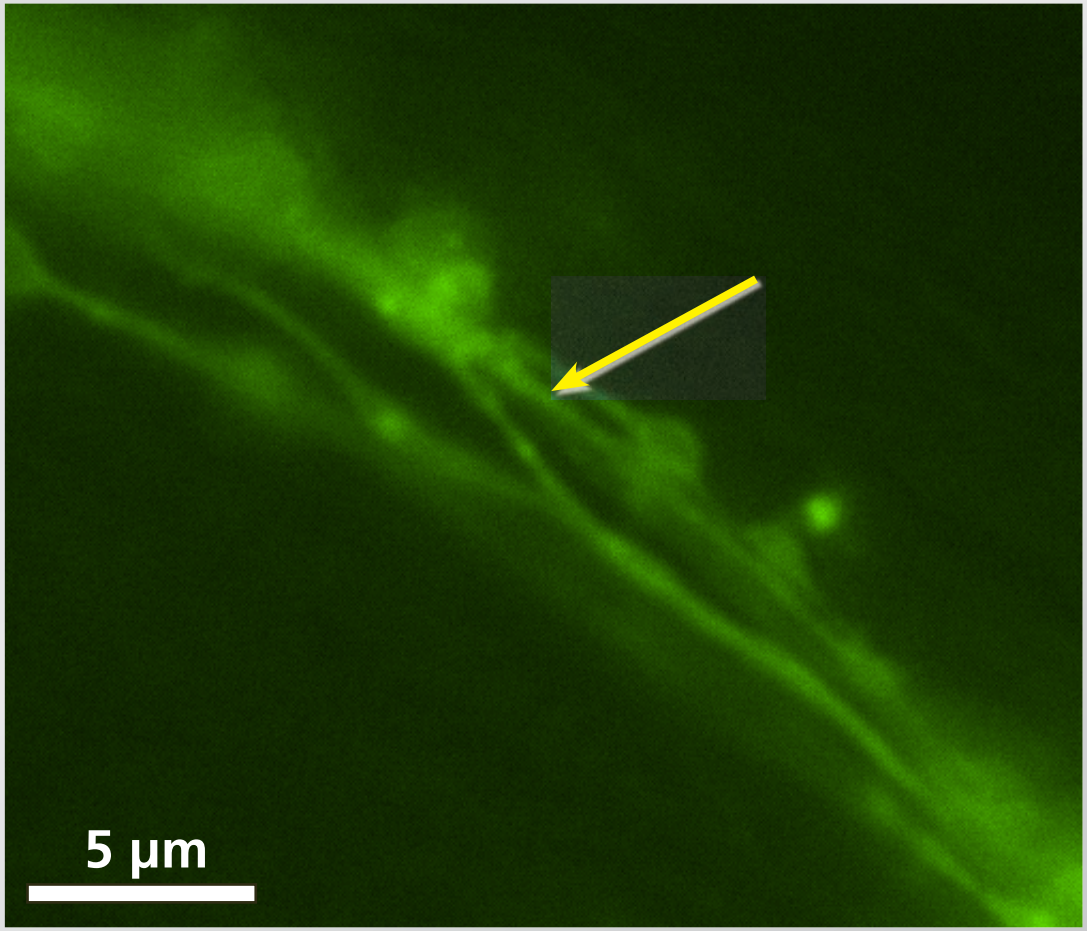
Applications

cut single dendrite in amphid bundle



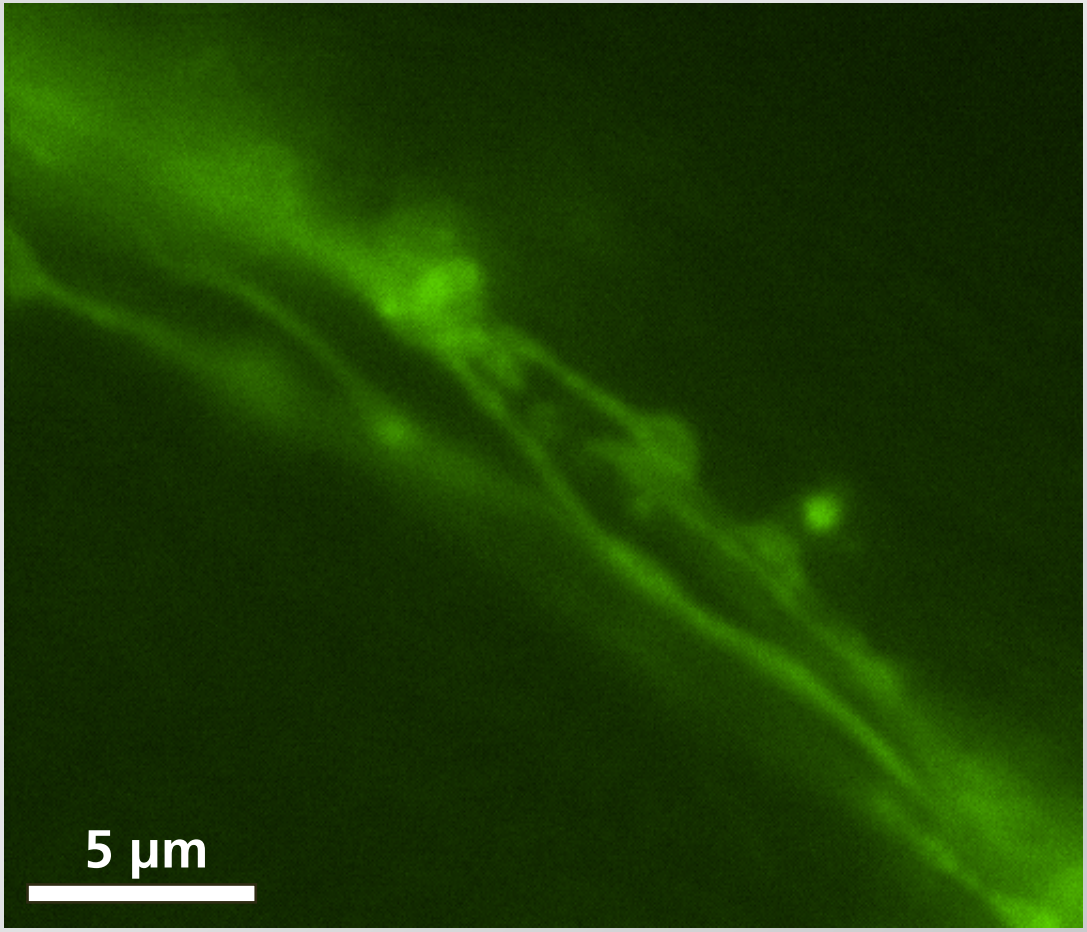
Applications

cut single dendrite in amphid bundle



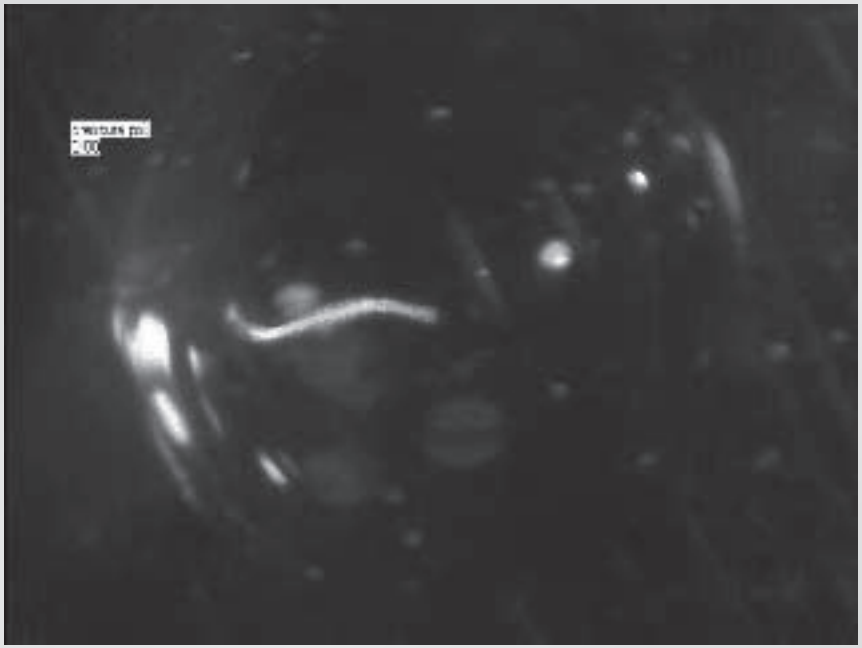
Applications

cut single dendrite in amphid bundle

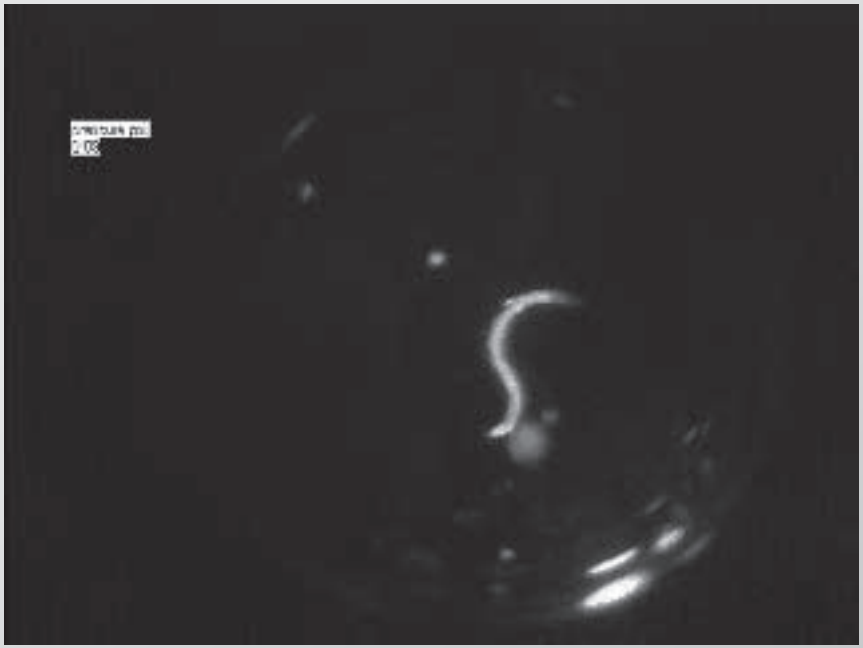


Applications

surgery results in quantifiable behavior changes



before



after

Summary

great tool for

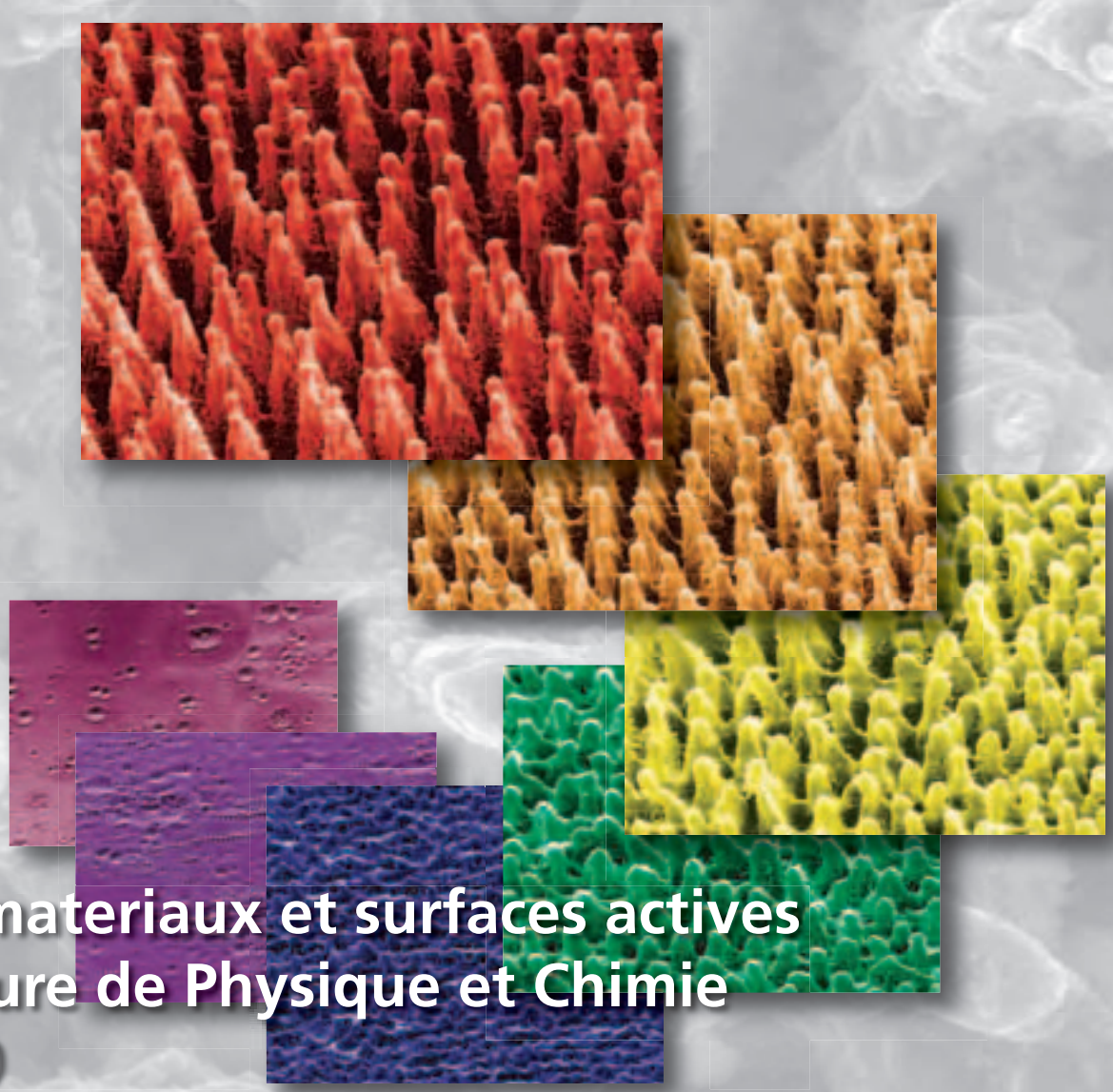
- “wiring light”
- micromanipulating the machinery of life

Summary

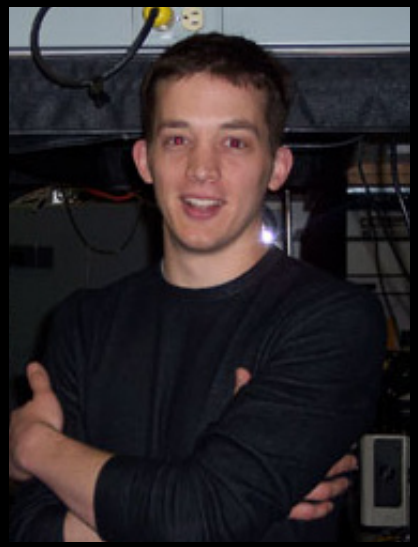
- important parameters: focusing, energy, repetition rate
- nearly material independent
- two regimes: low and high repetition rate
- high-repetition rate (thermal) machining fast, convenient


Funding:
Army Research Office
National Science Foundation
for a copy of this presentation:
http://mazur-www.harvard.edu
nature
photonics

Part II: Optical hyperdoping of materials with femtosecond laser pulses

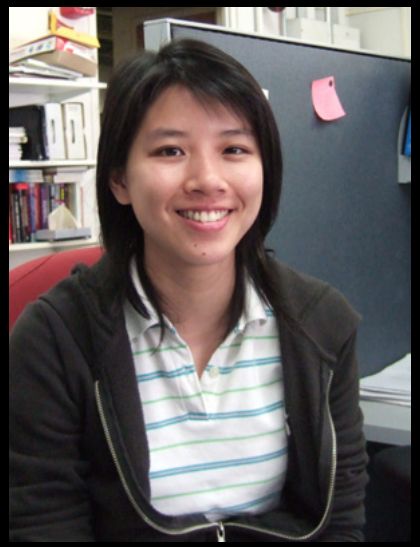


Sciences des materiaux et surfaces actives
Ecole Supérieure de Physique et Chimie
9 Février 2010



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)

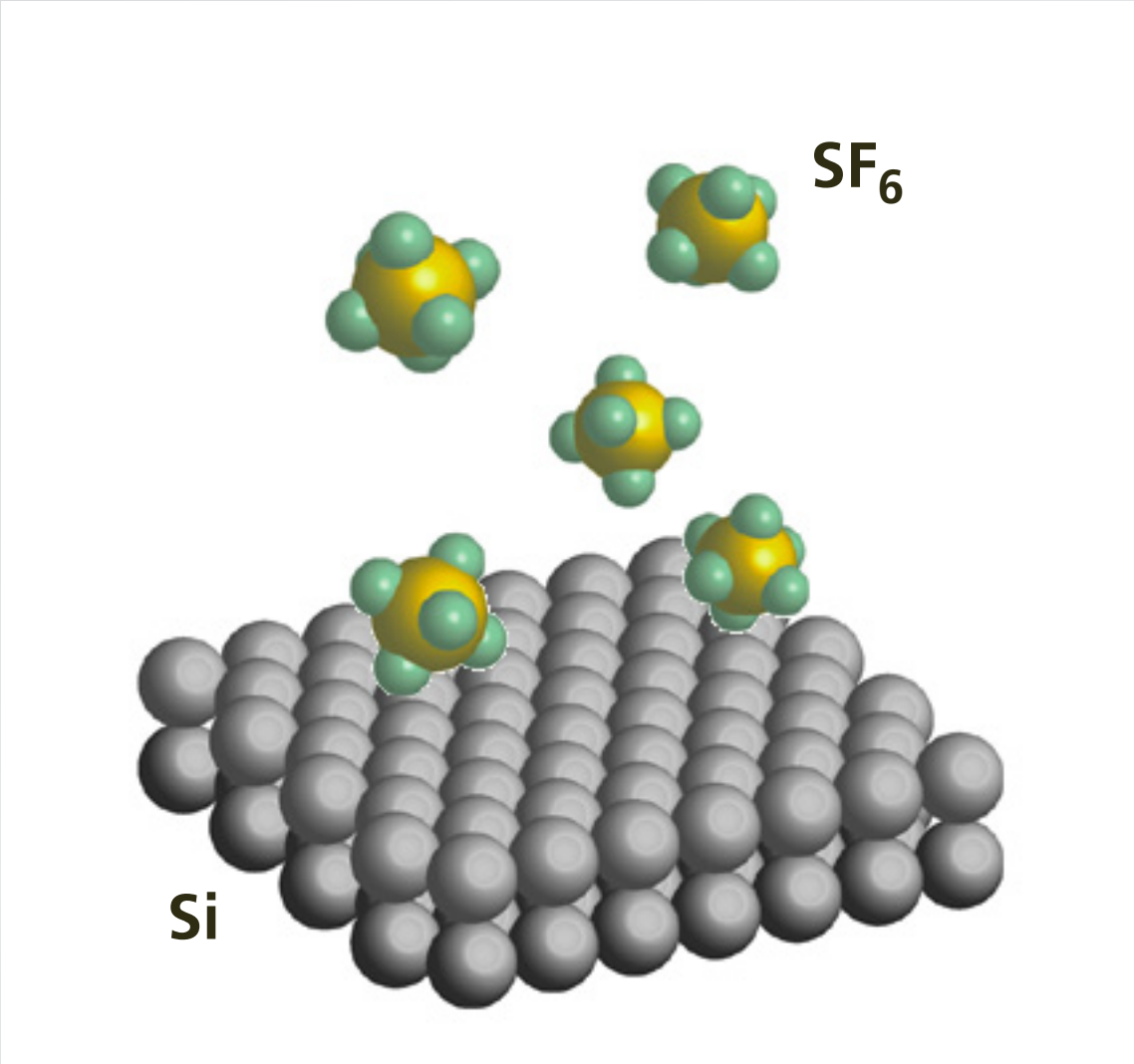
Dr. François Génin (LLNL)
Mark Wall (LLNL)

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

Dr. Pat Maloney (NVSED)

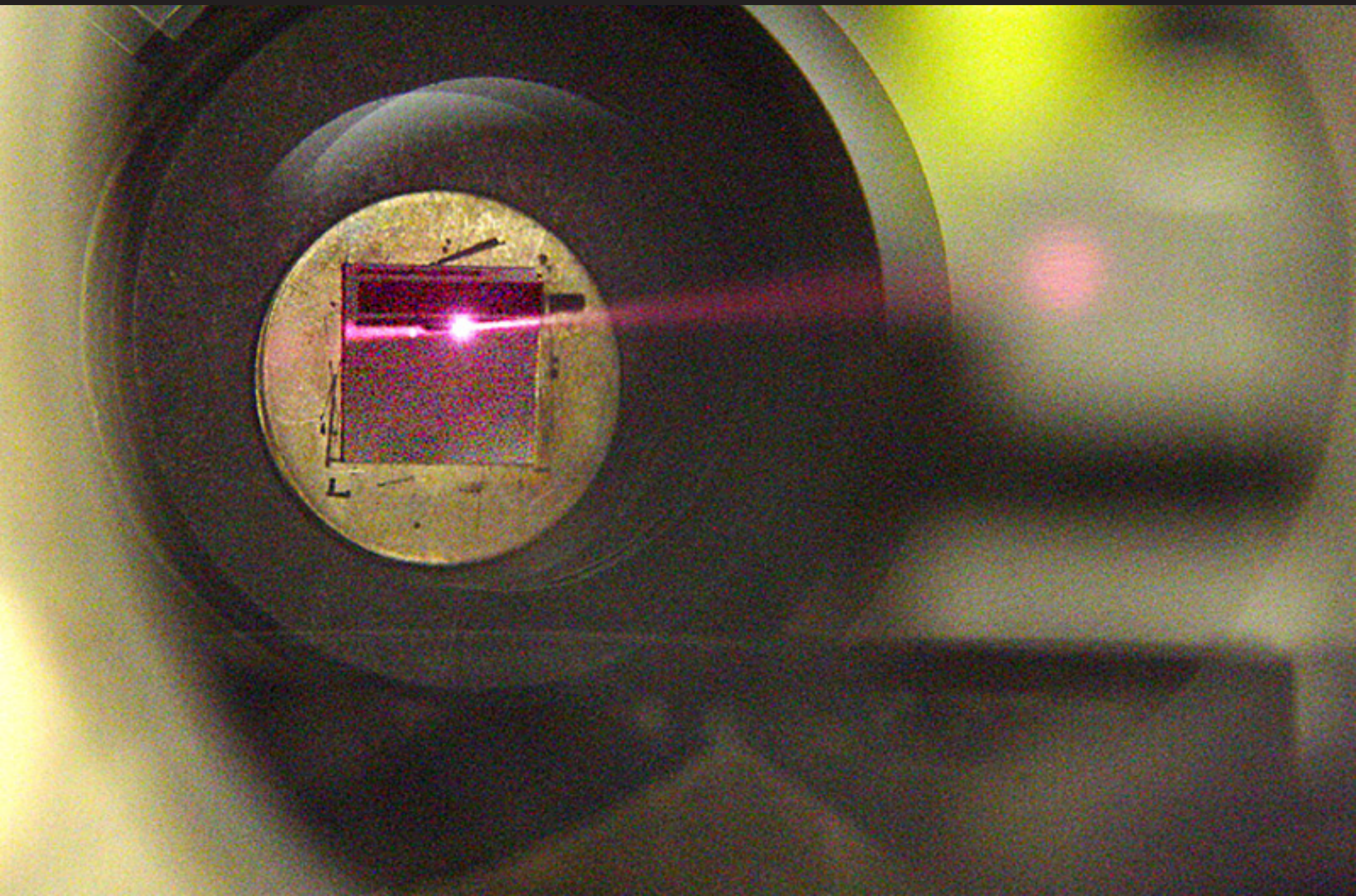
Dr. Jeffrey Warrander (ARDEC)

Introduction



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

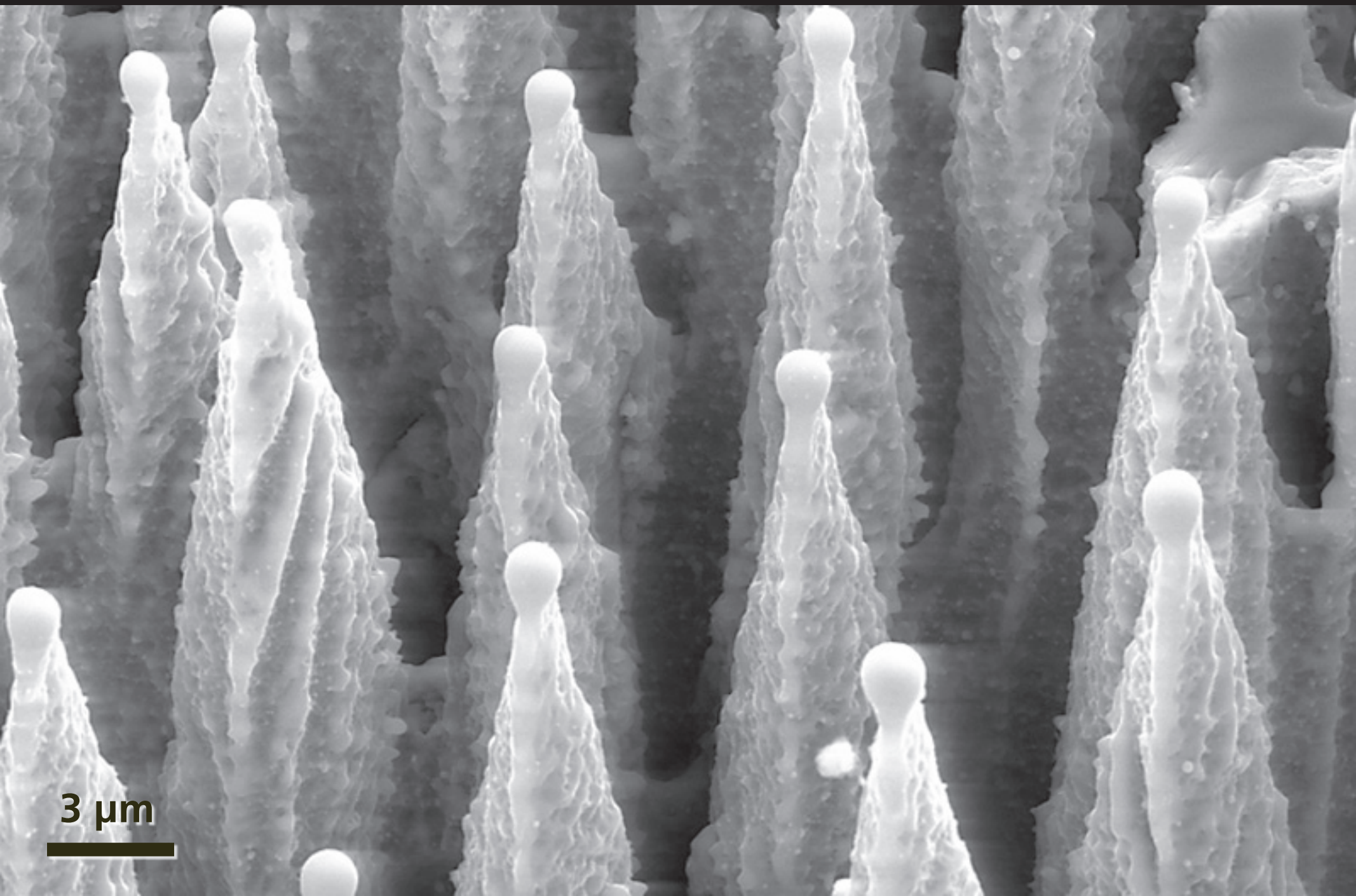
Introduction



Introduction

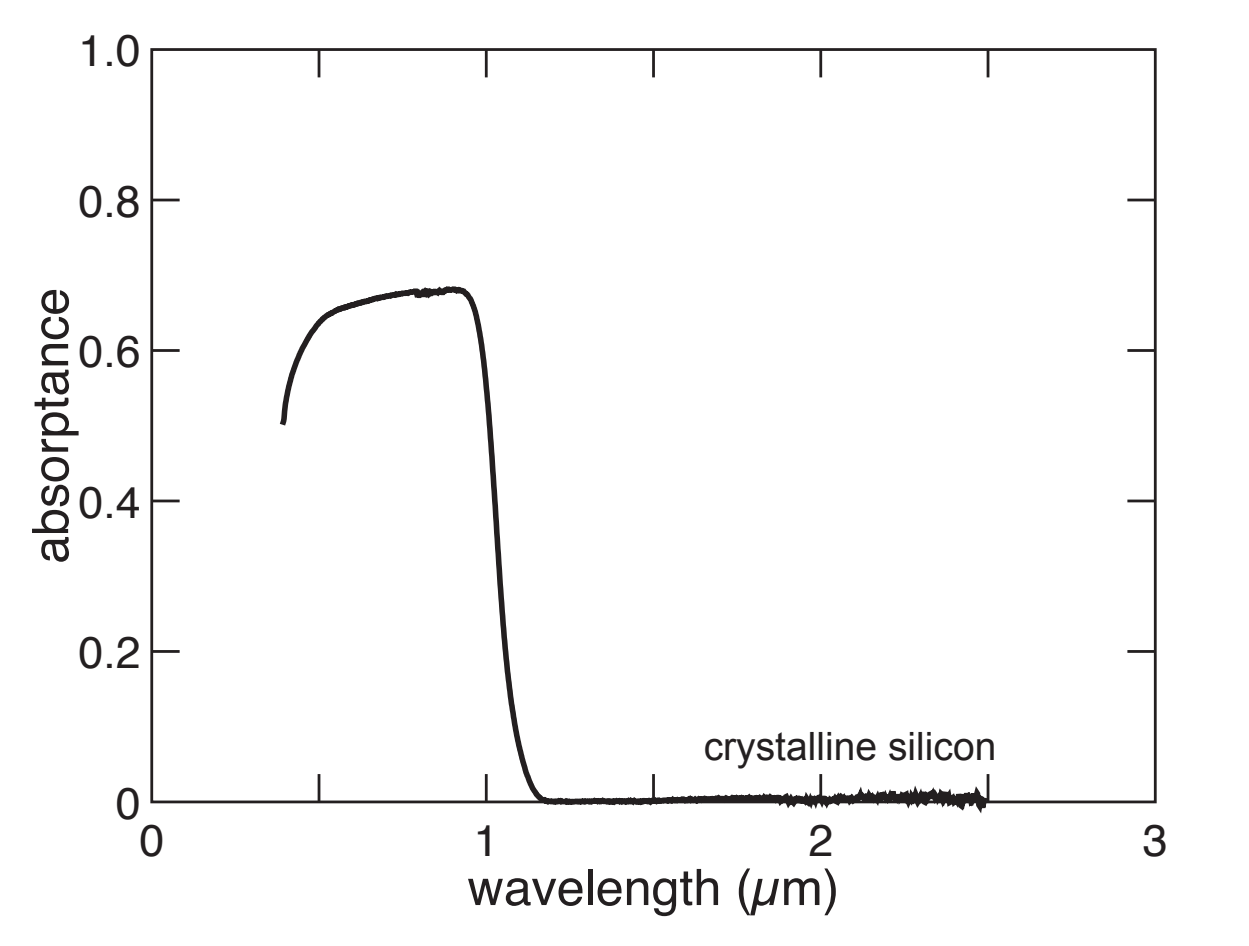
“black silicon”

Introduction



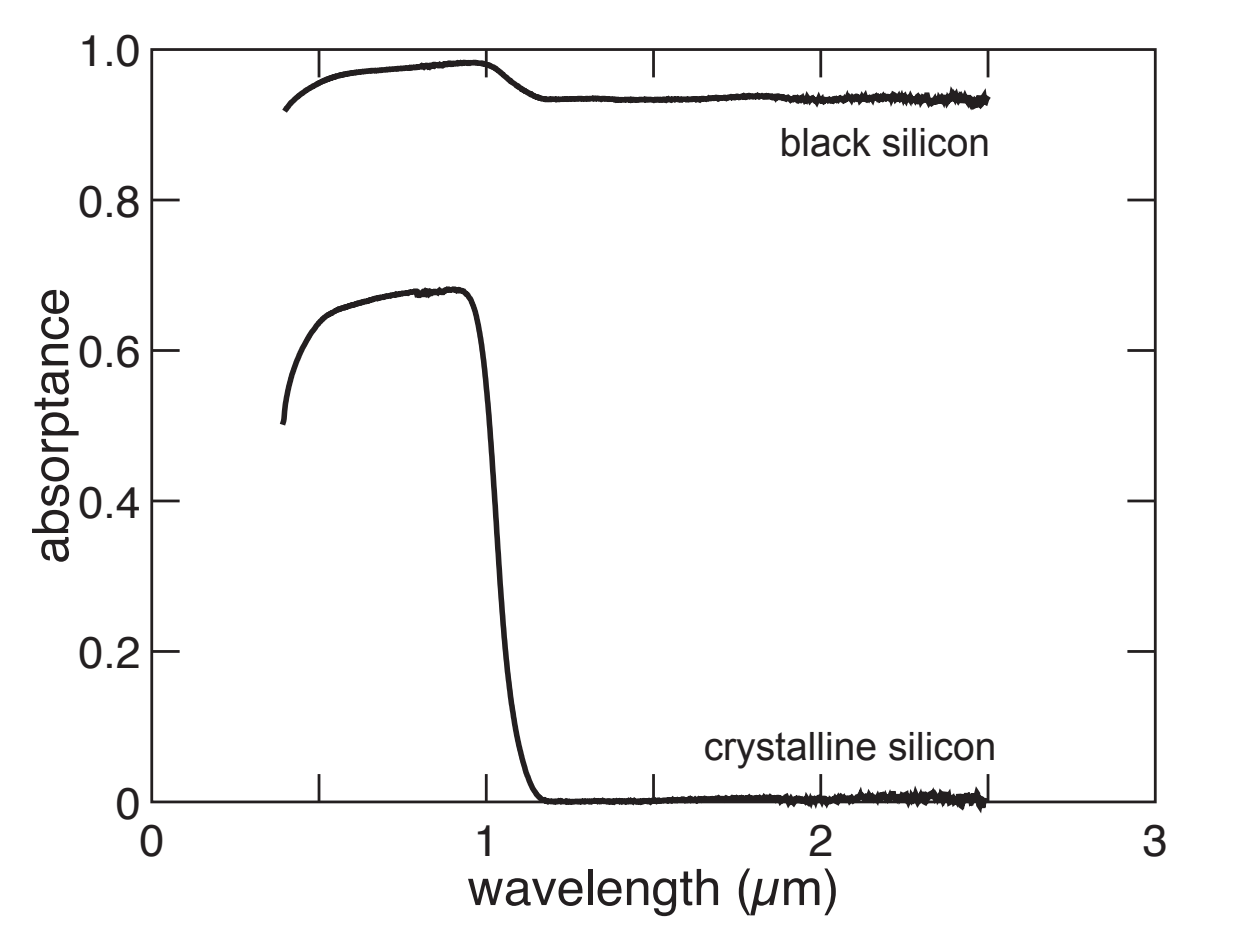
Introduction

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

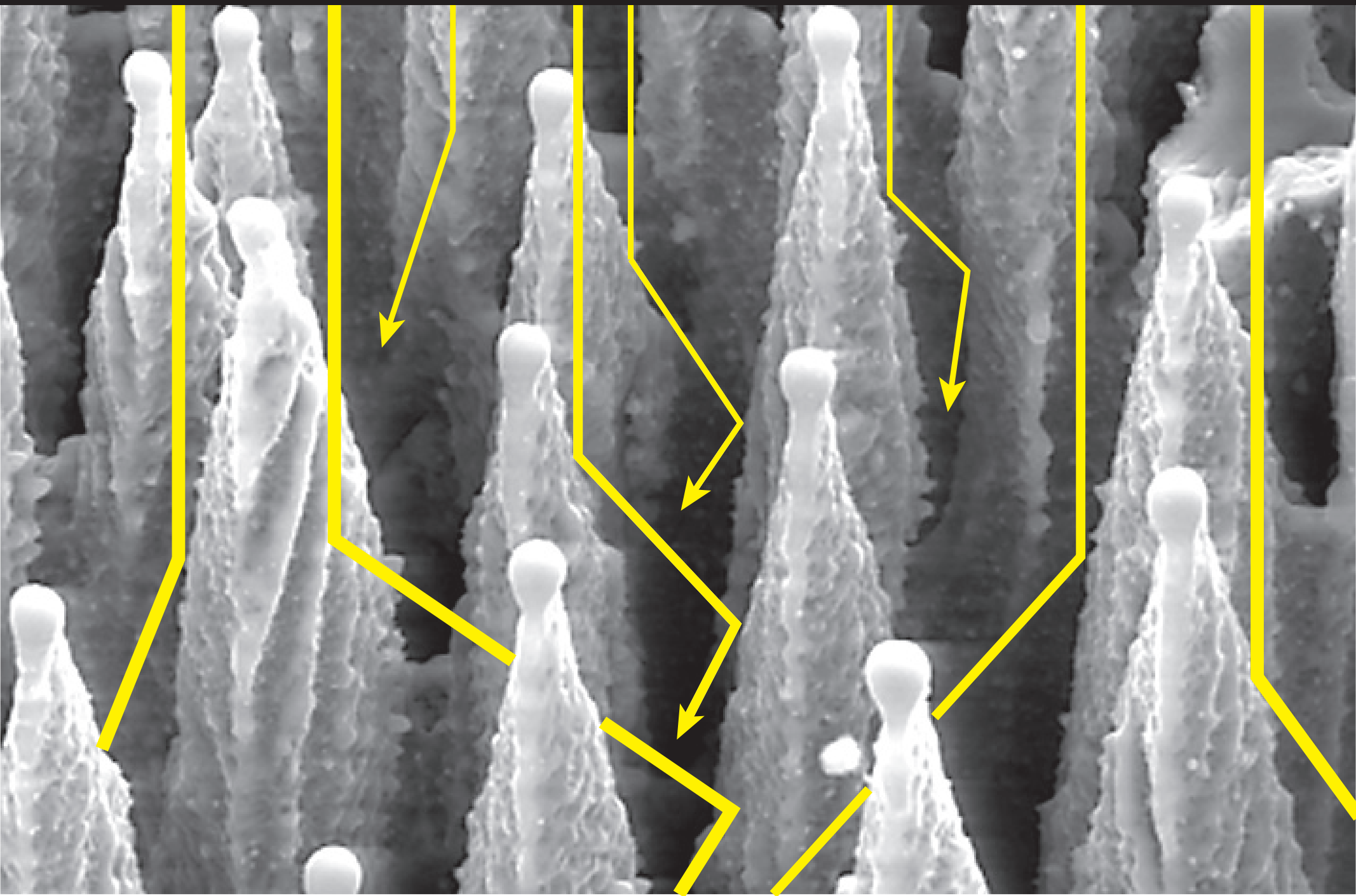


Introduction

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

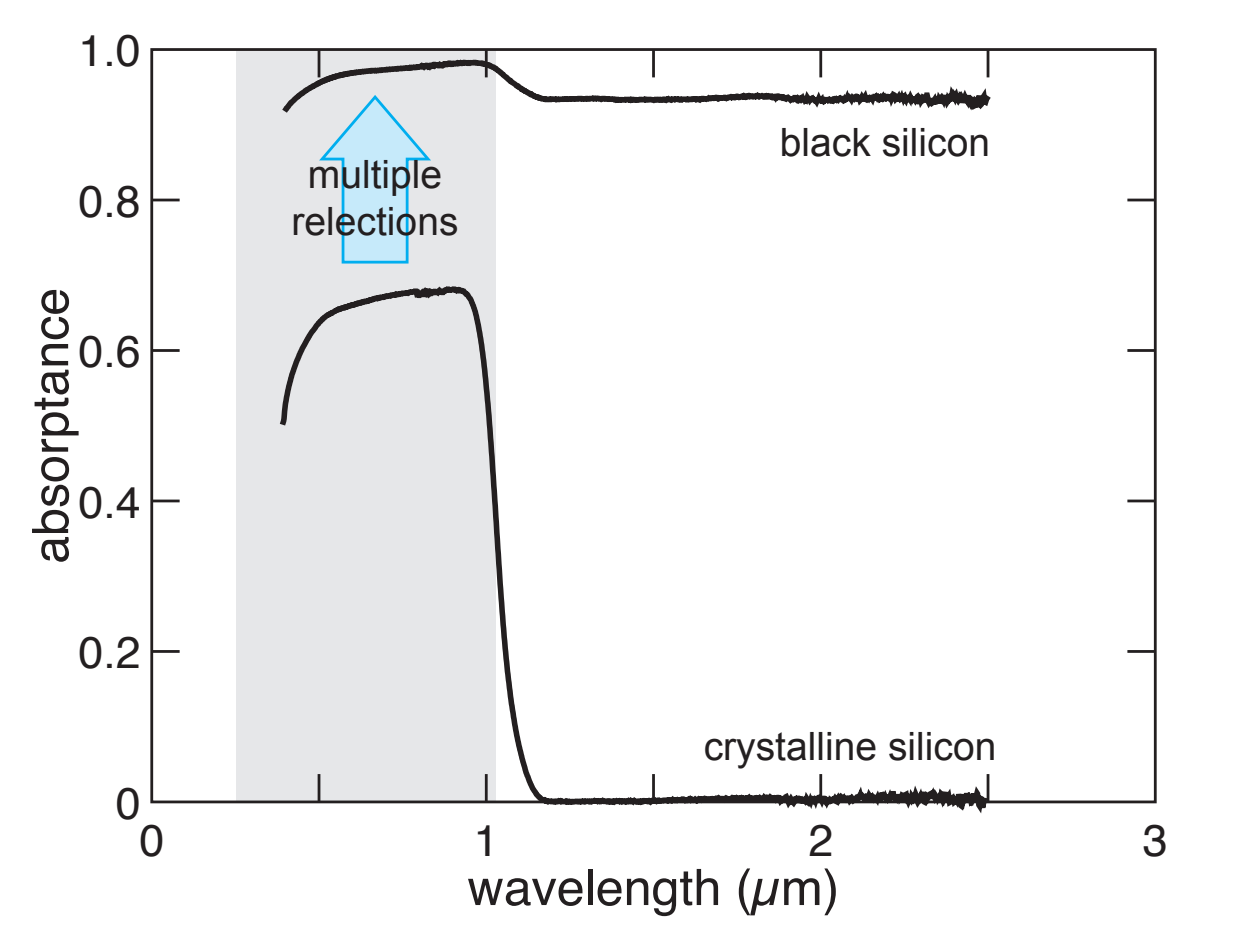


Introduction



Introduction

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



Introduction

silicon transparent in near IR

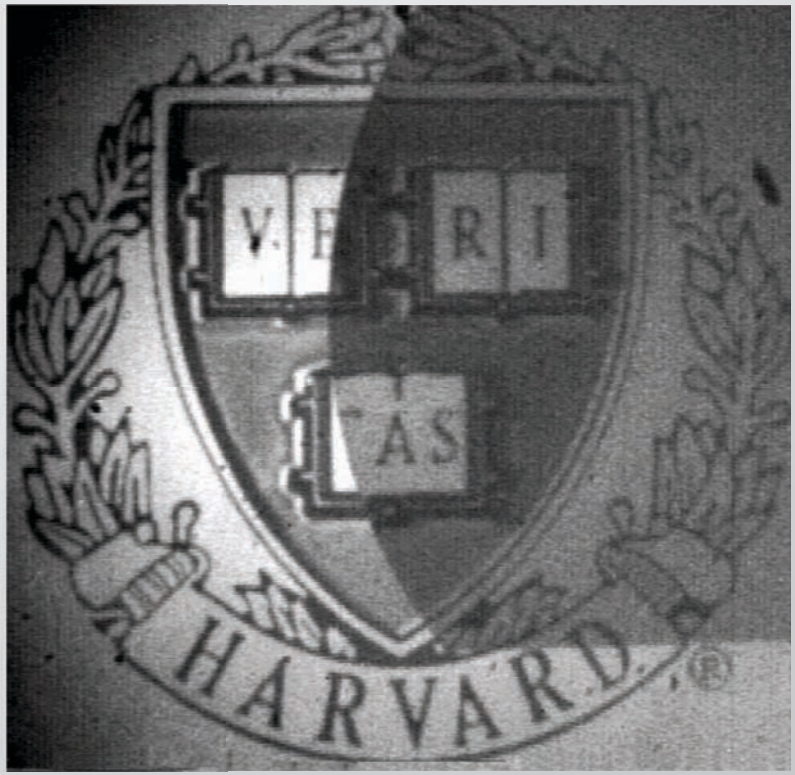
visible

Introduction

silicon transparent in near IR

visible

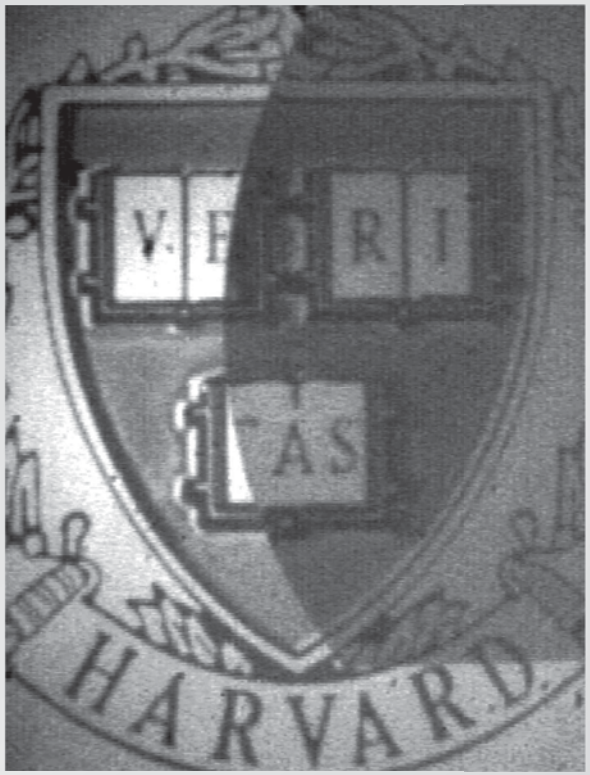
near IR



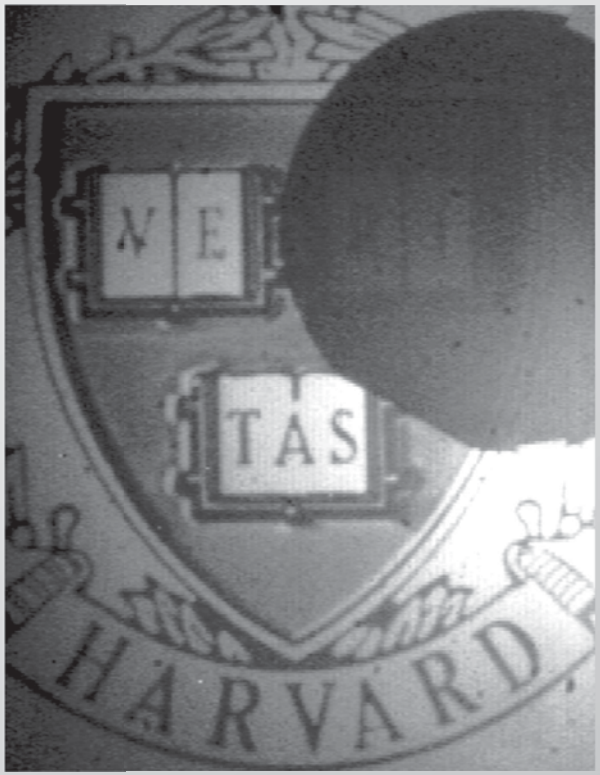
Introduction

roughening doesn't change IR transmission…

polished



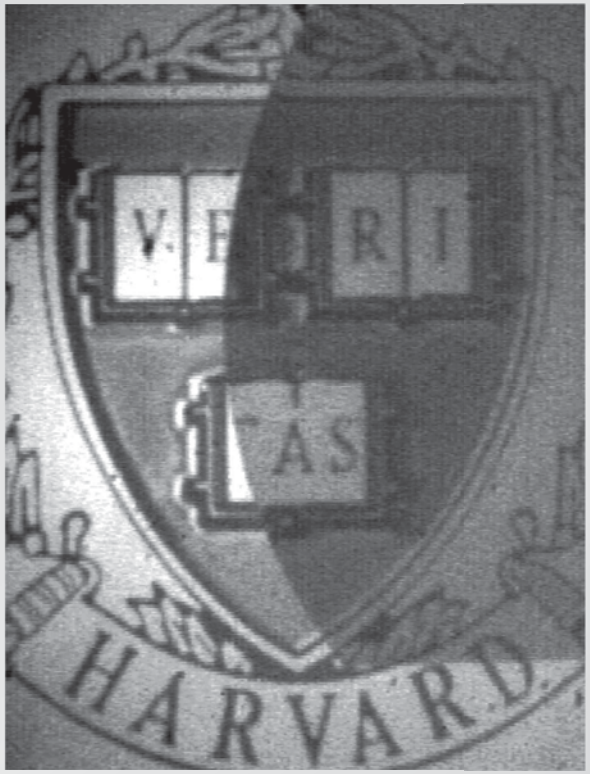
unpolished



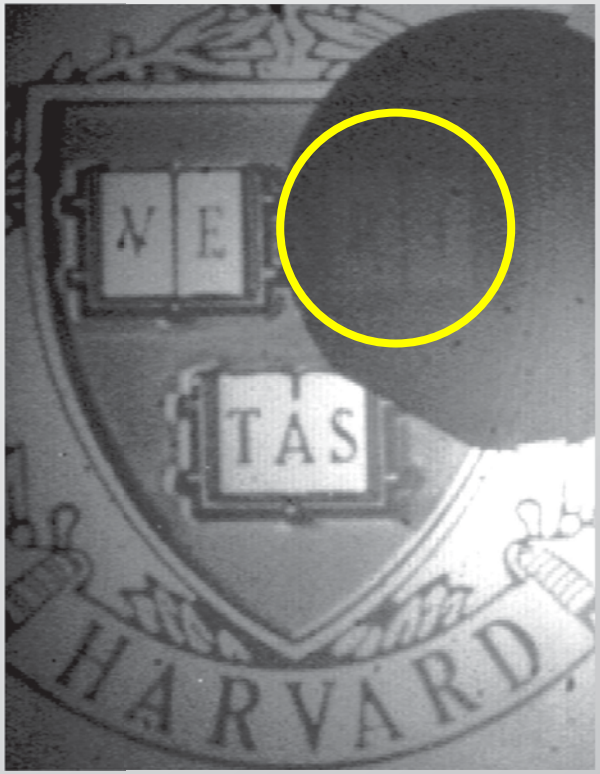
Introduction

roughening doesn't change IR transmission…

polished



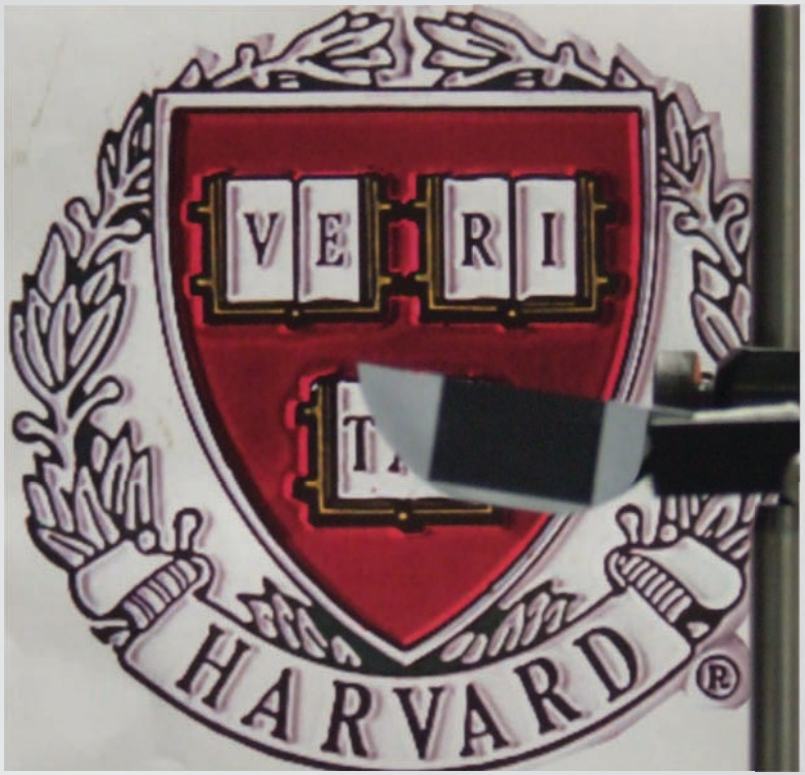
unpolished



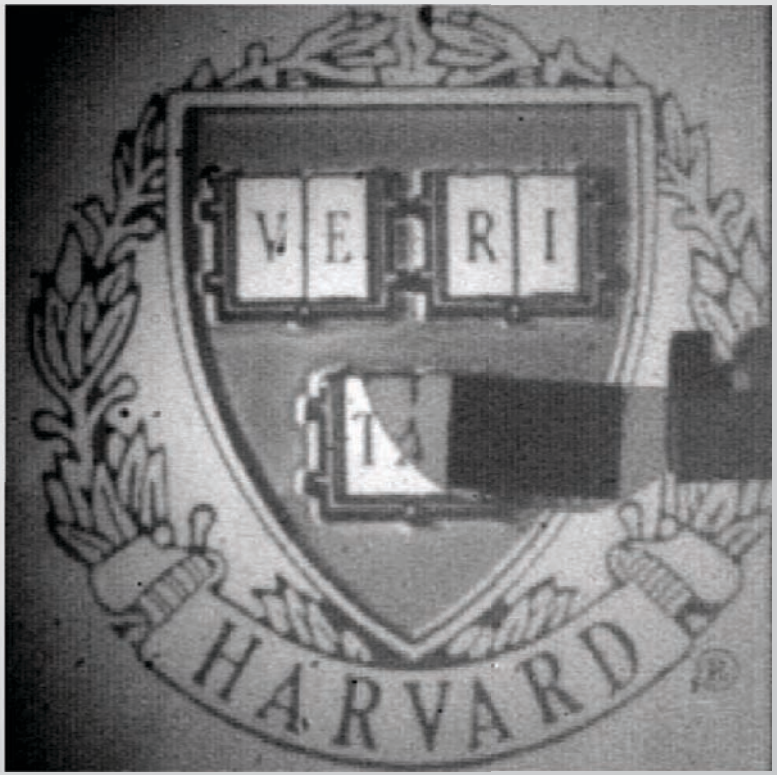
Introduction

…but black silicon blocks IR completely

visible



near IR



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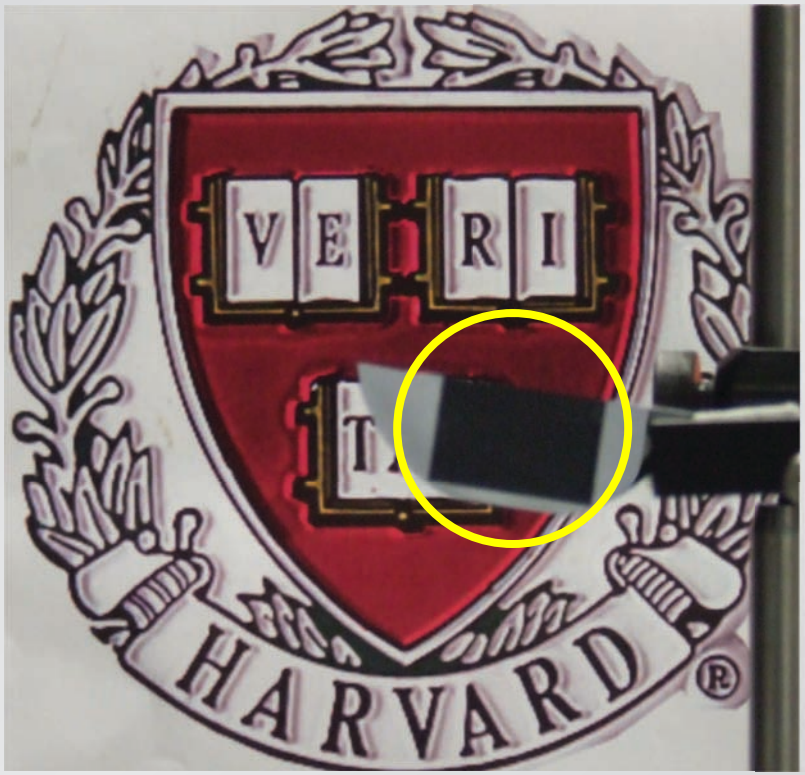
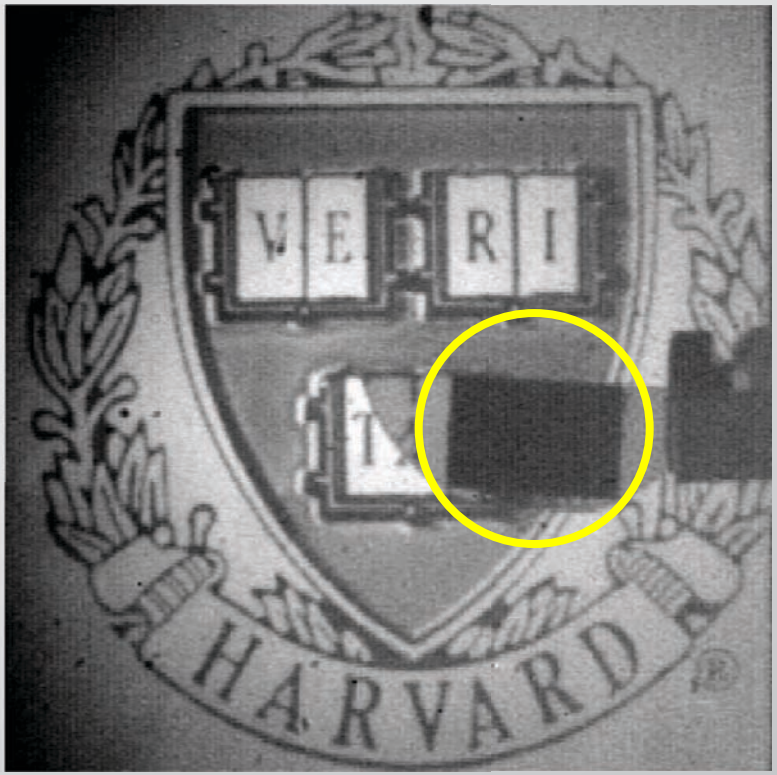


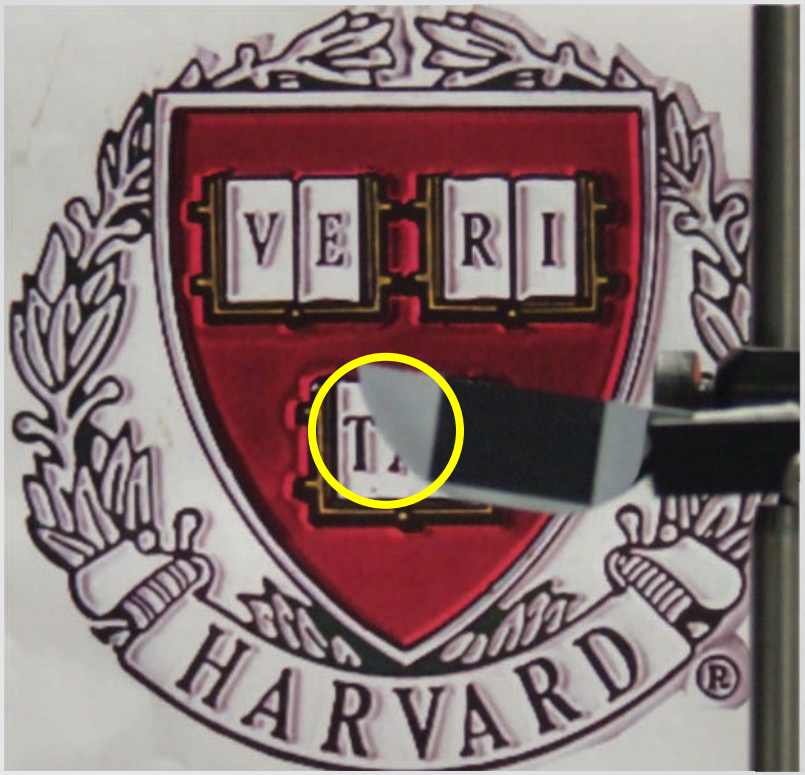
near IR



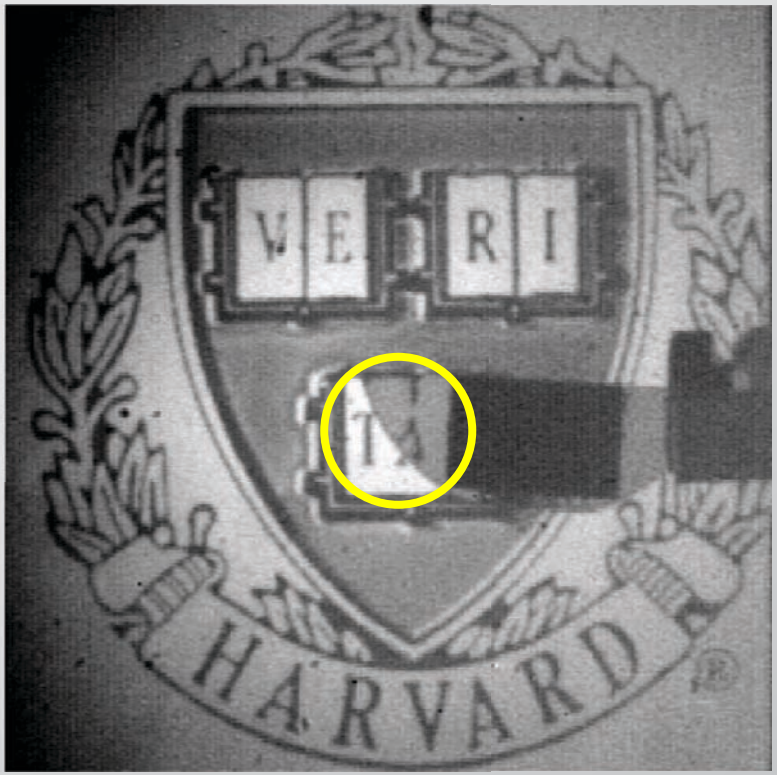
Introduction

black silicon completely black in IR

visible



near IR



Introduction

band structure changes: defects and/or impurities

Introduction

a decade of research

OPTICAL	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

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gap		
impurity band		
transitions		

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gap	carrier concentration	
impurity band	mobilities	
transitions	junction properties	

Introduction

a decade of research

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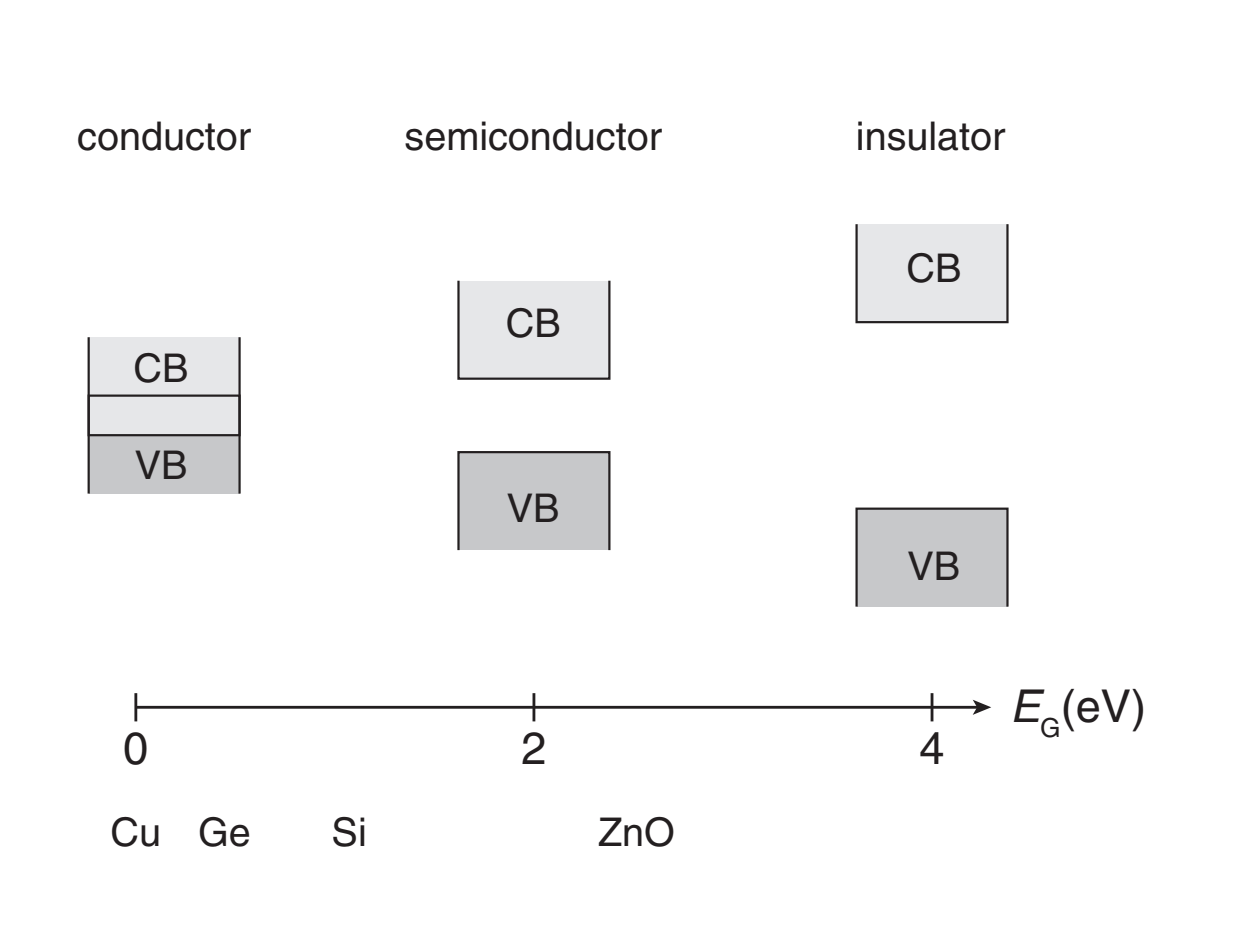
XPS		AFM
		SIMS
responsivity		RBS
photoconductivity		ion channeling
gap	carrier concentration	morphology
impurity band	mobilities	composition
transitions	junction properties	atomic structure

Introduction

new process & new class of material!



Introduction

substrate/dopant combinations

dopants:

N	O	F
P	S	Cl
	Se	
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substrates:

Si Ge ZnO InP GaAs

Ti Ag Al Cu Pd Rh Ta Pt

Introduction

focus on chalcogen-doped silicon

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Introduction

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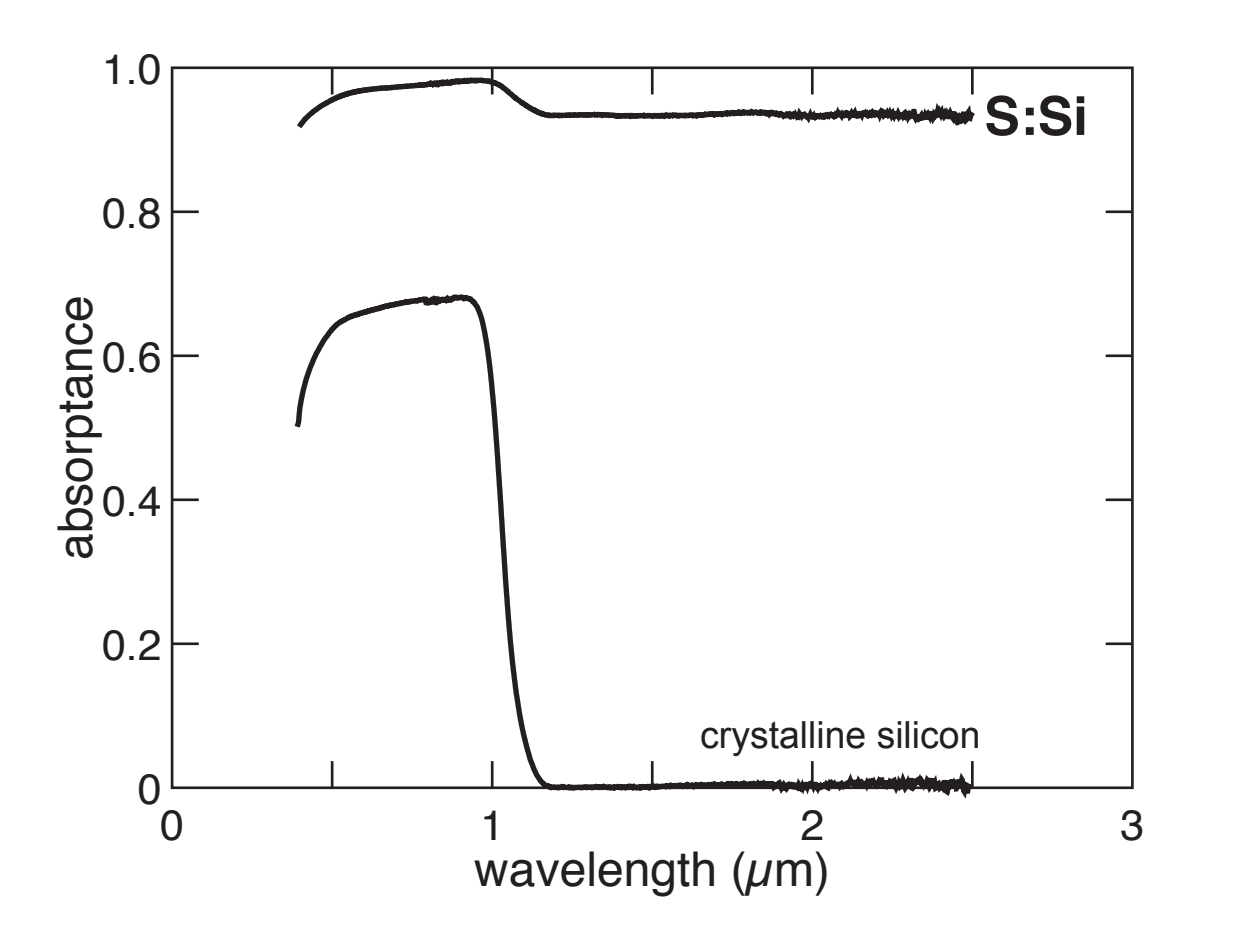
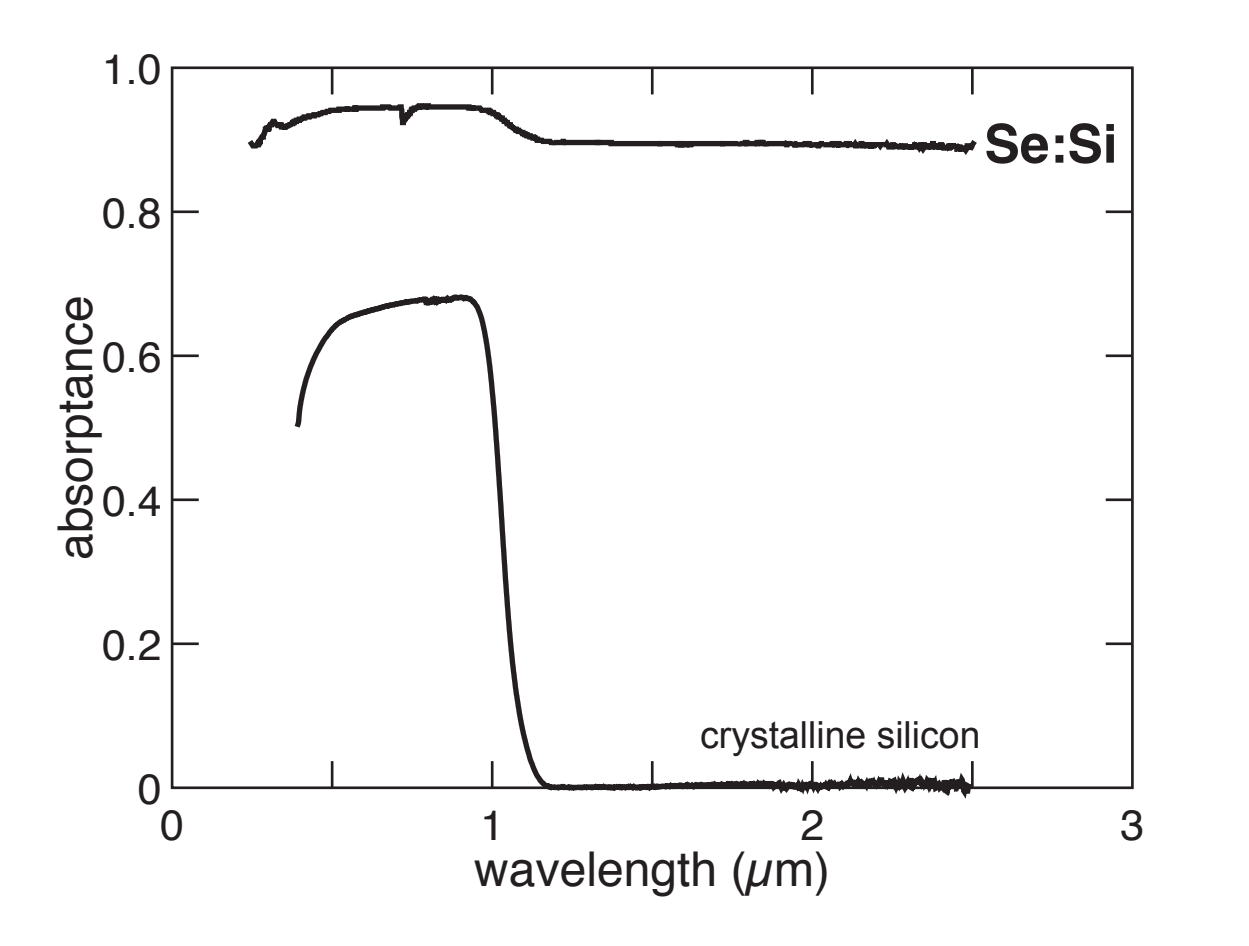


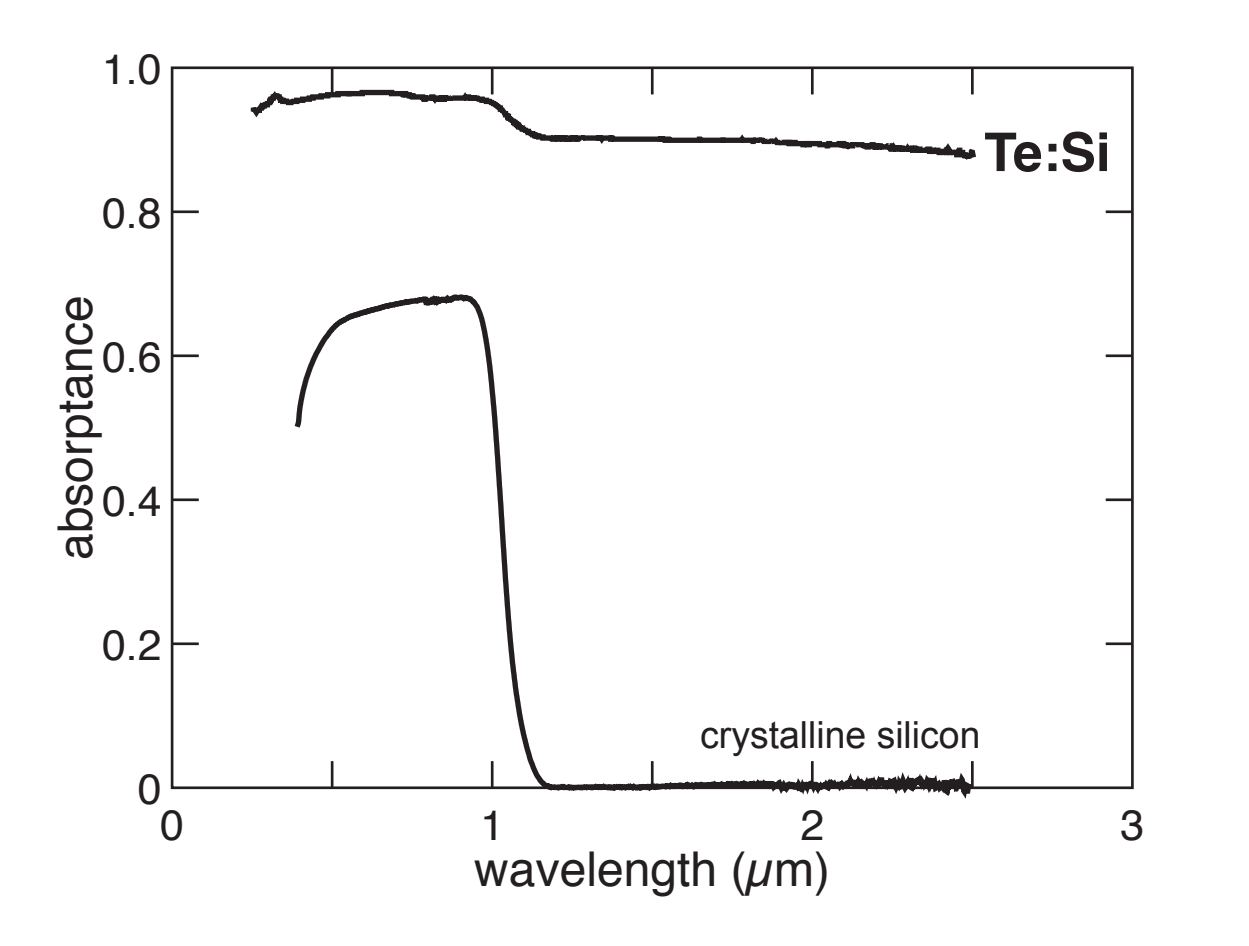
Introduction

focus on chalcogen-doped silicon



Introduction

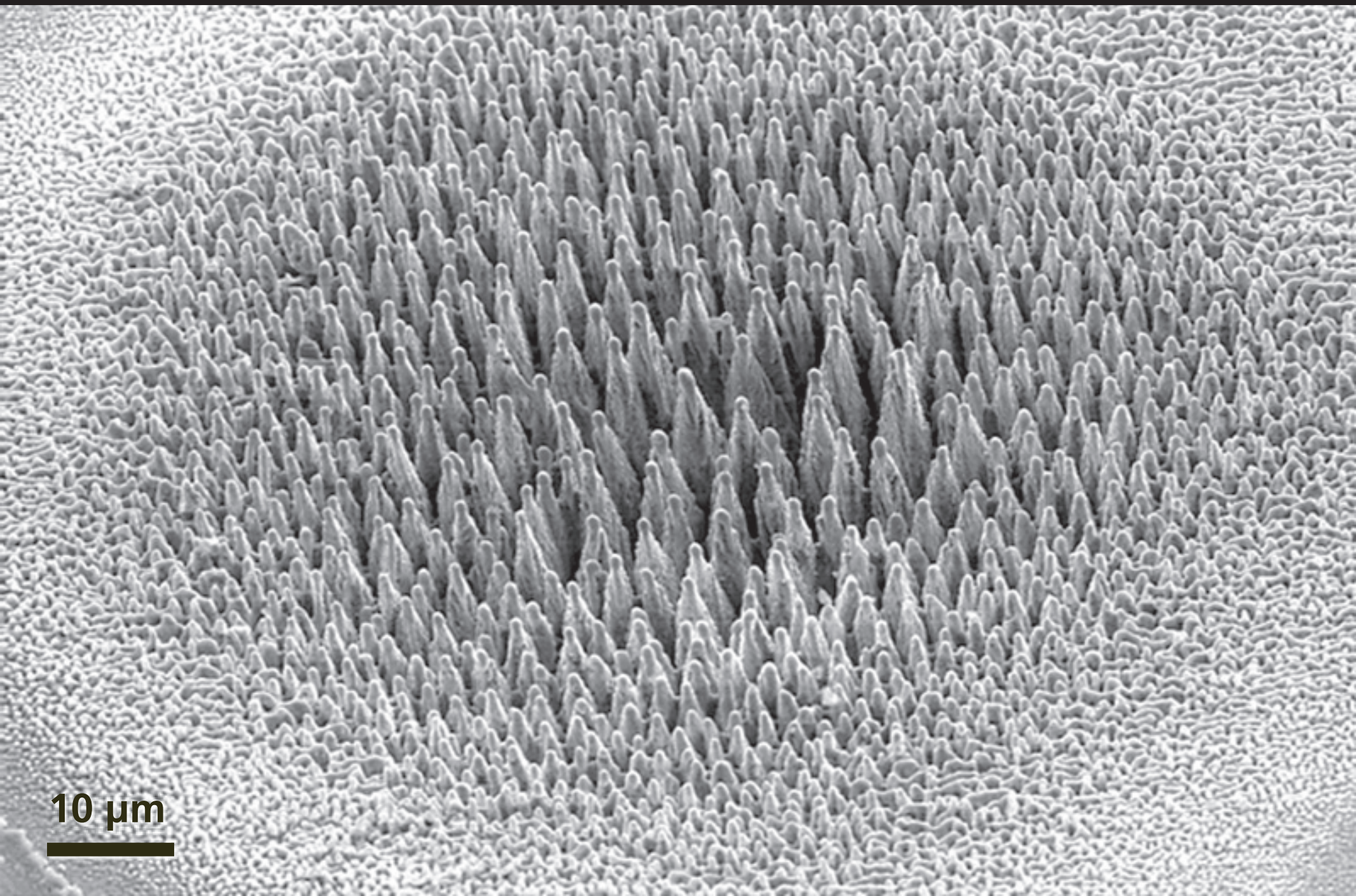
focus on chalcogen-doped silicon



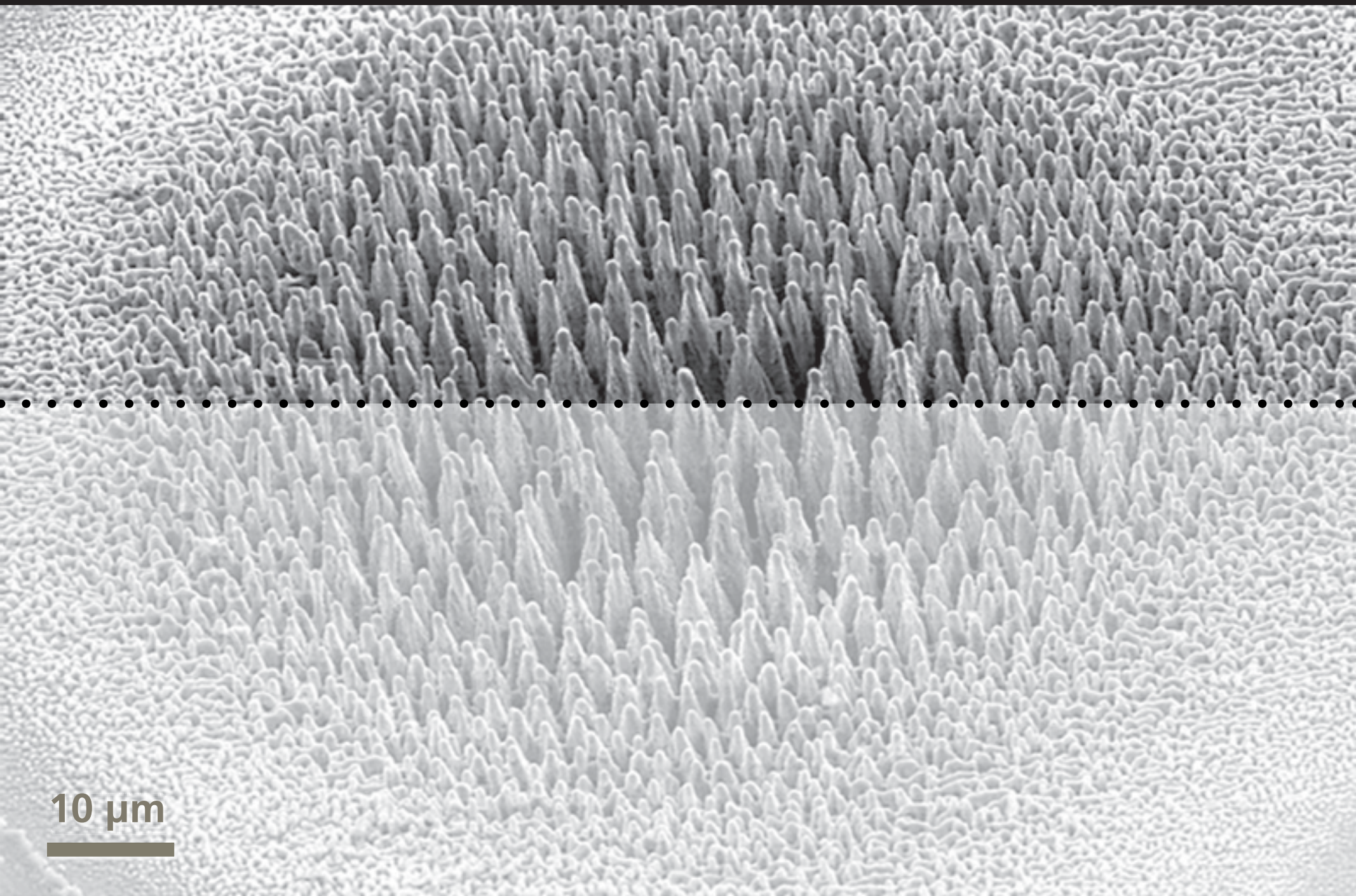
Outline

- structure
- optoelectronic properties
- devices

Structure



Structure



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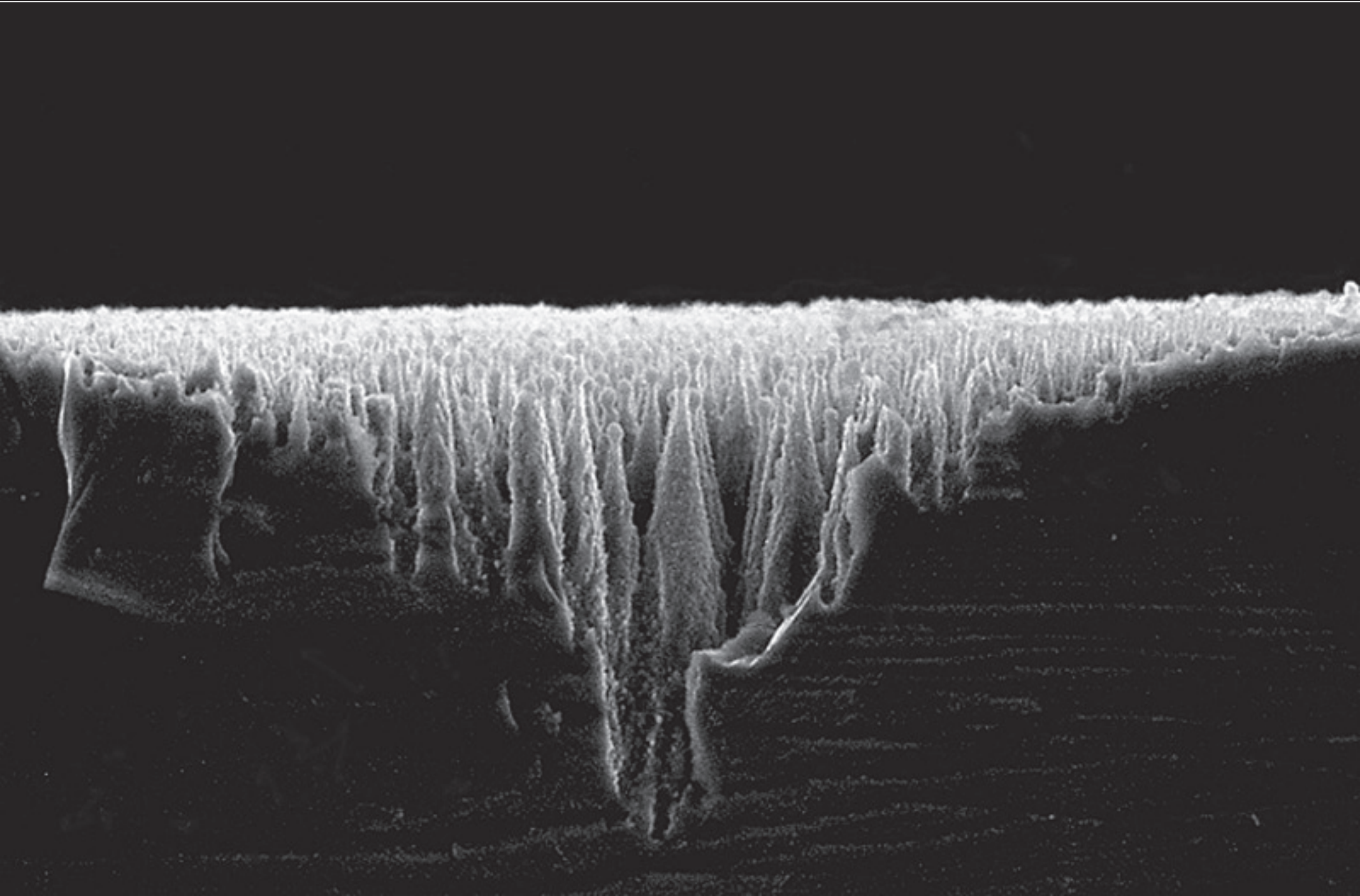

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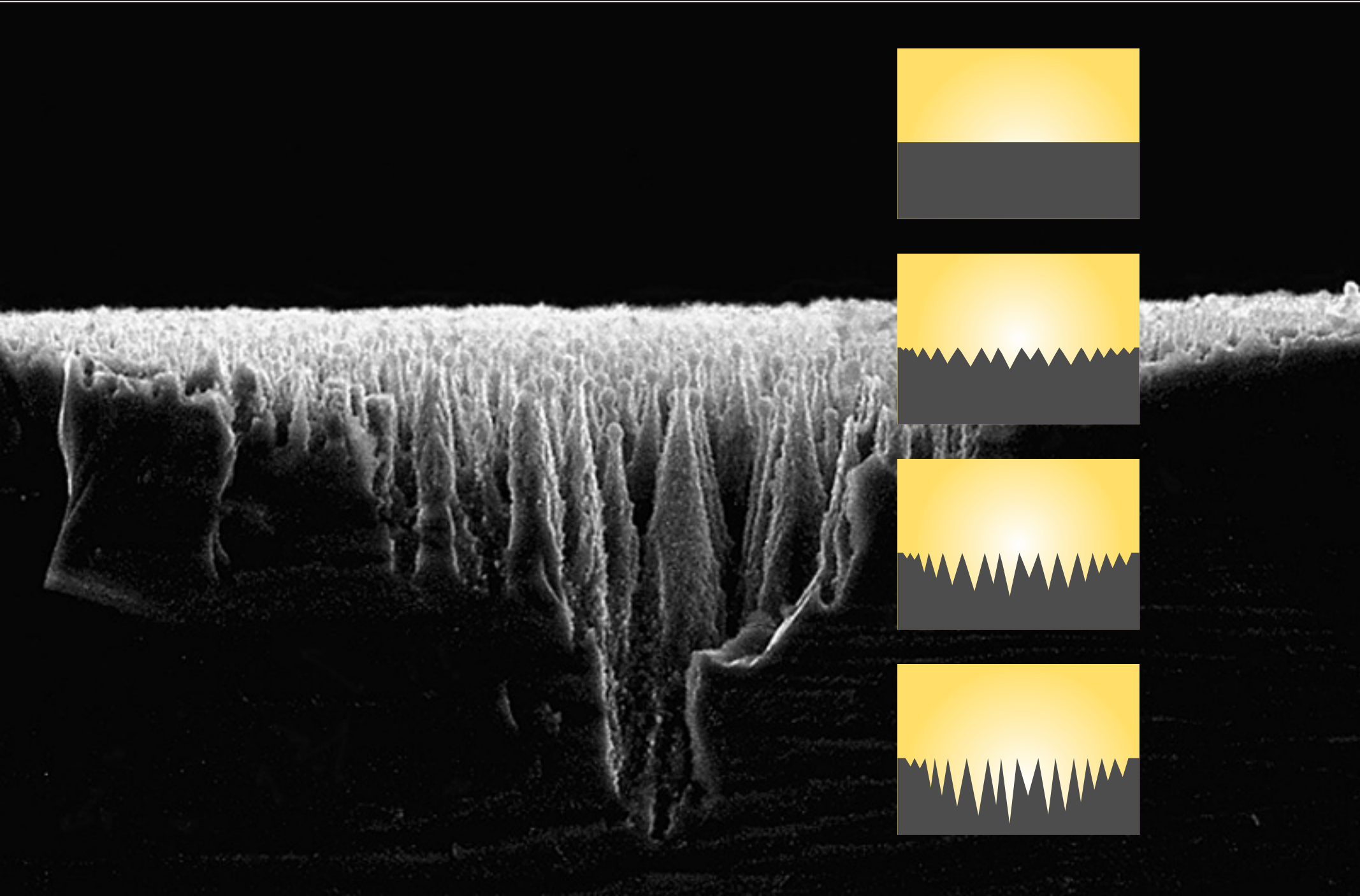

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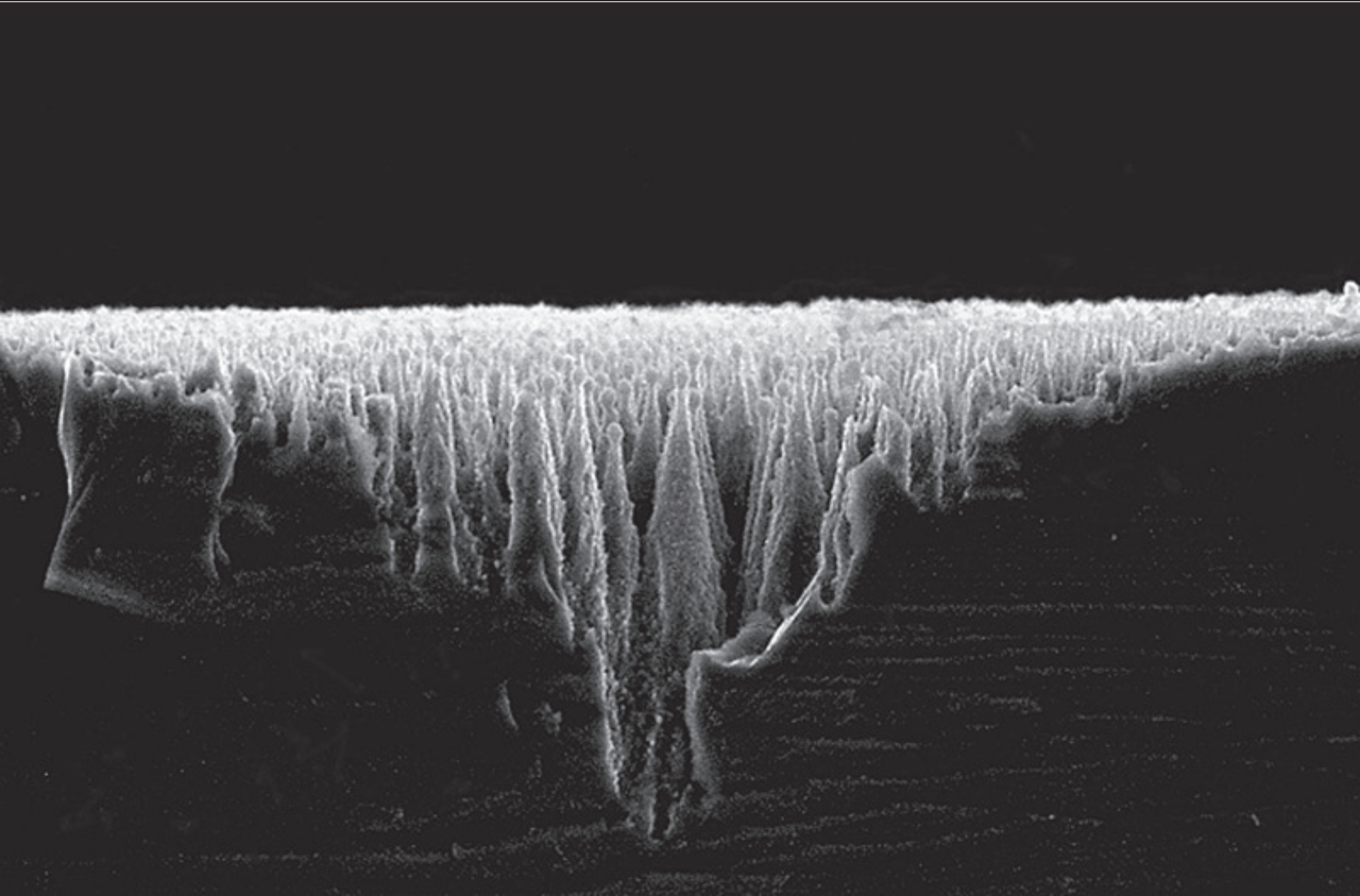
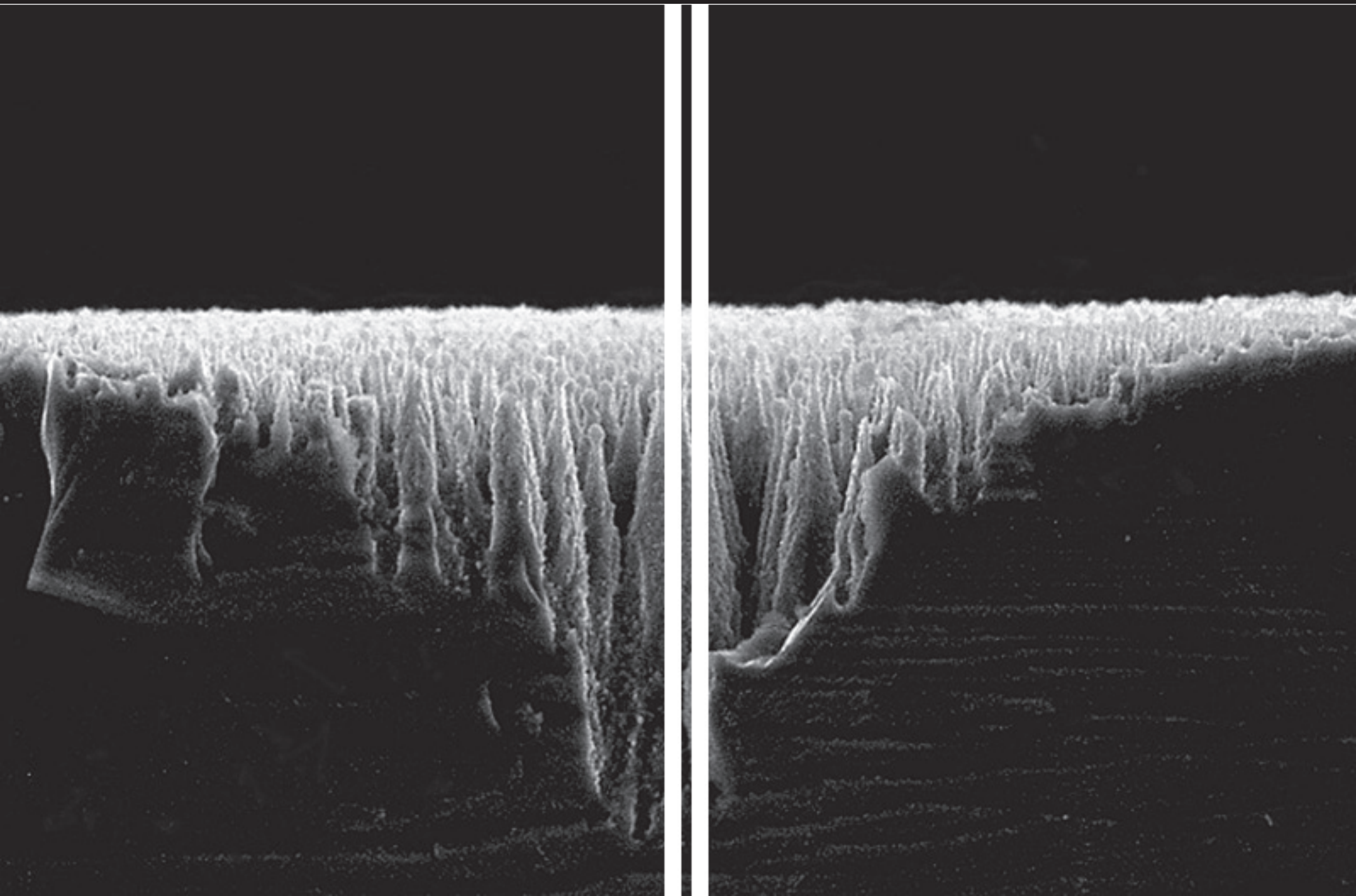
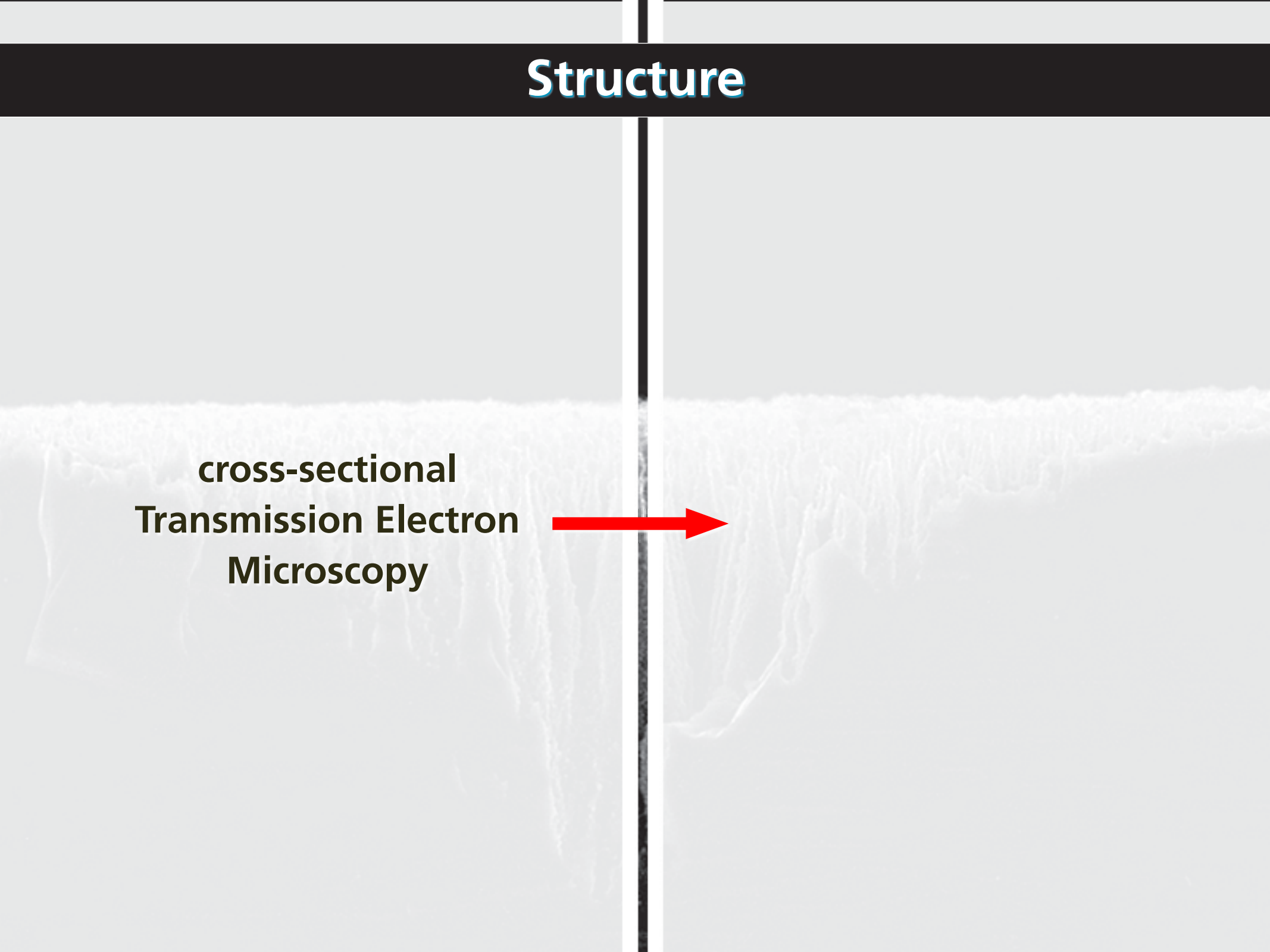


Structure



Structure

cross-sectional
Transmission Electron
Microscopy



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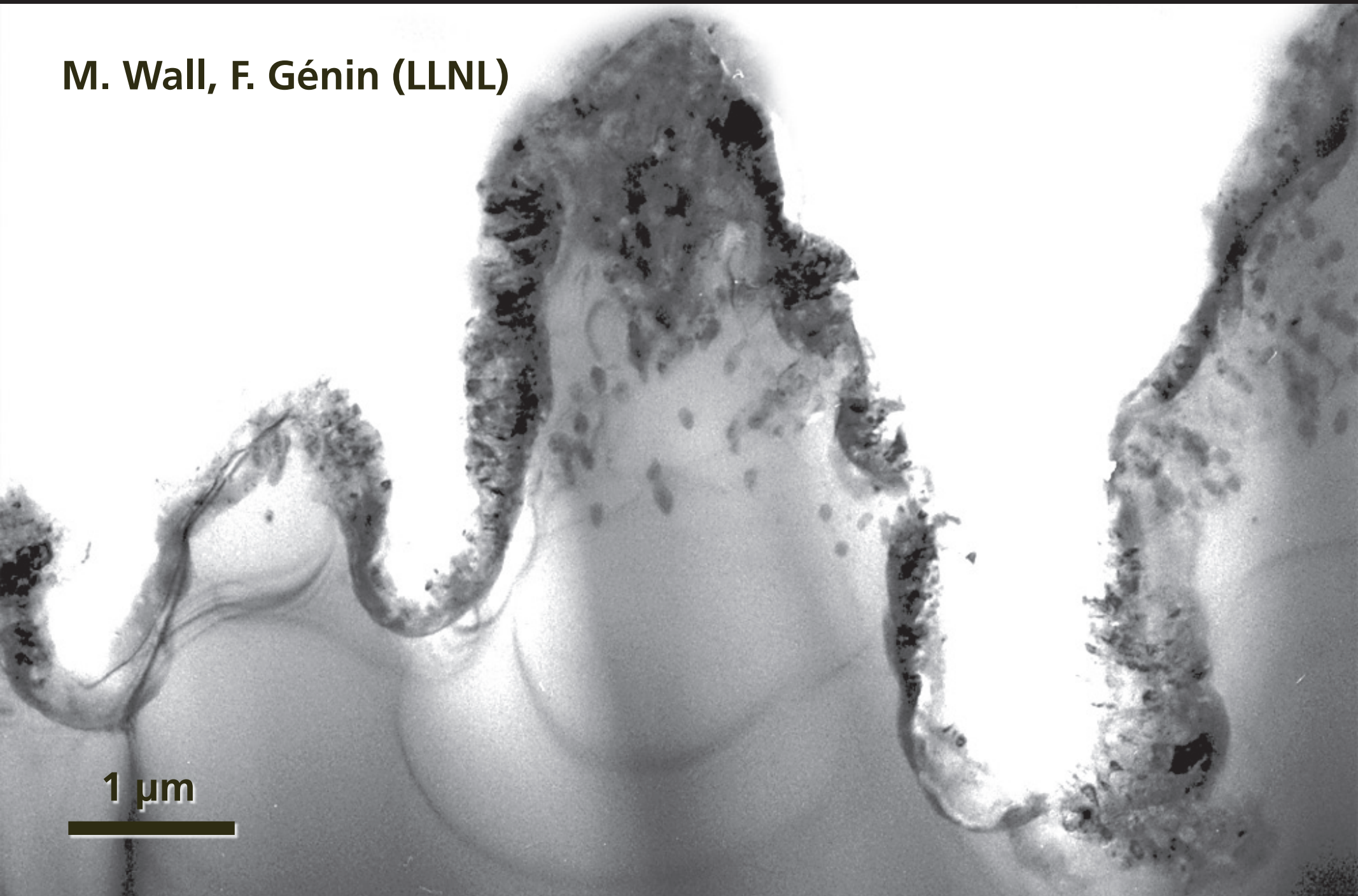

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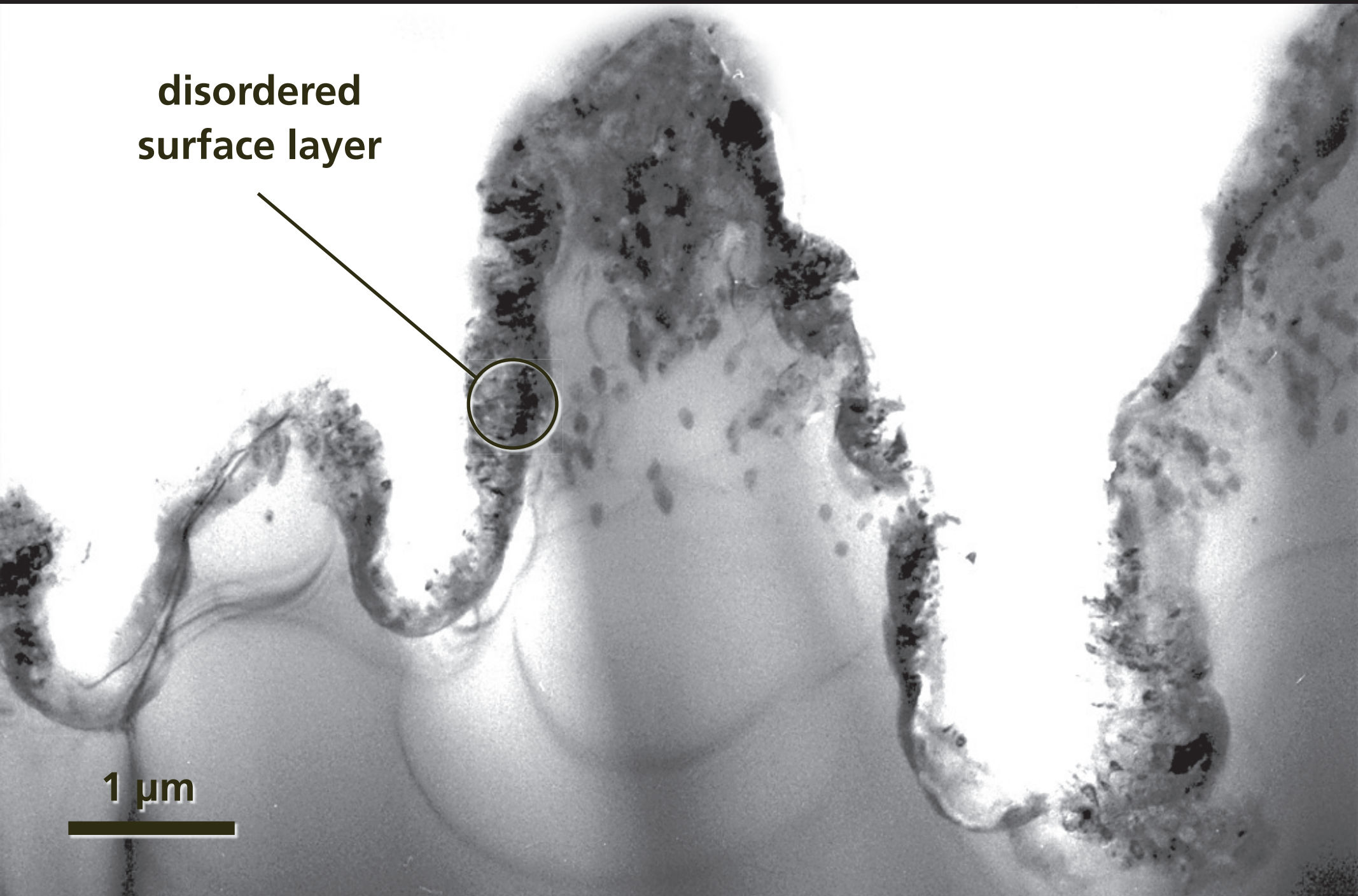

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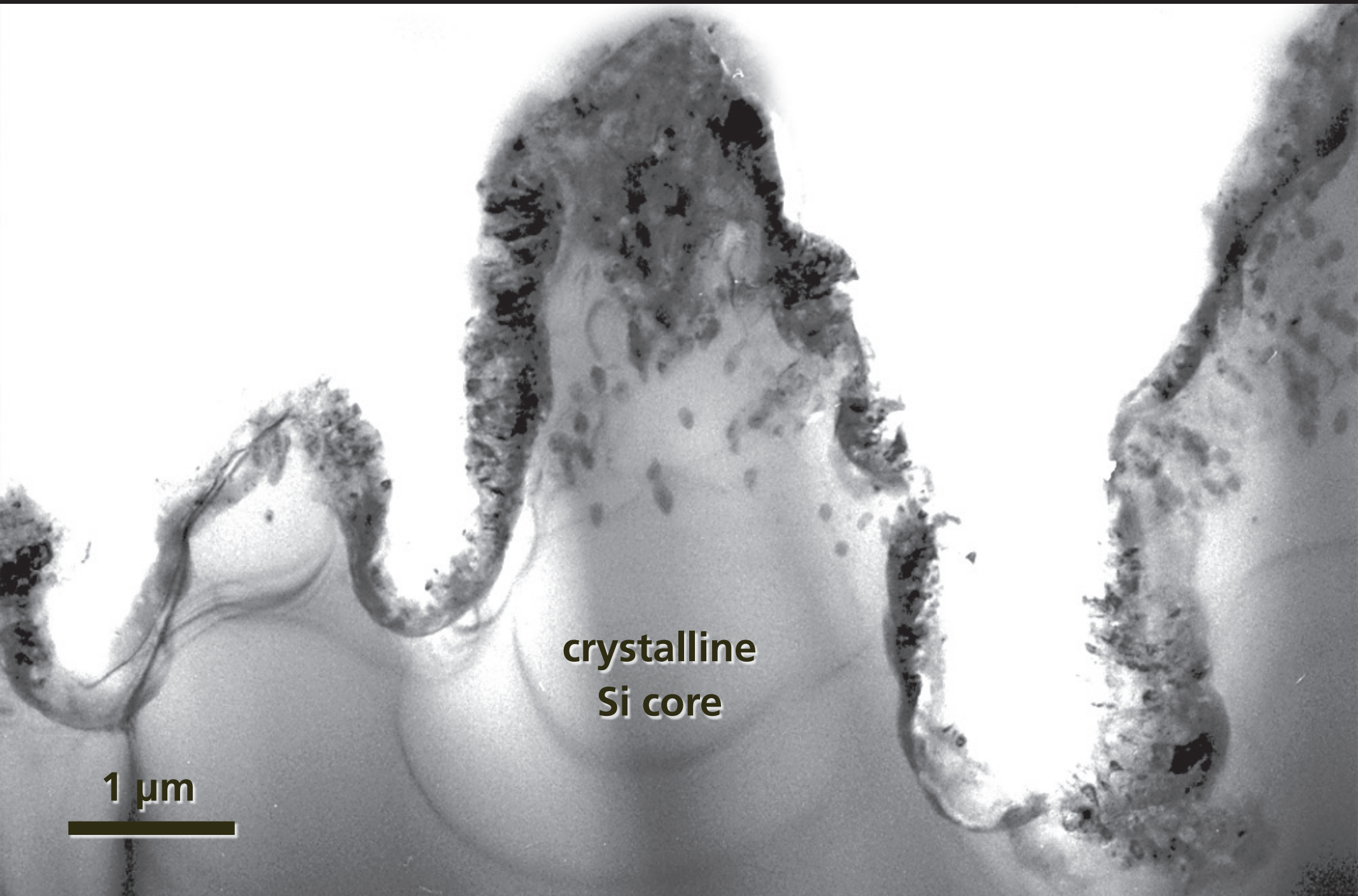

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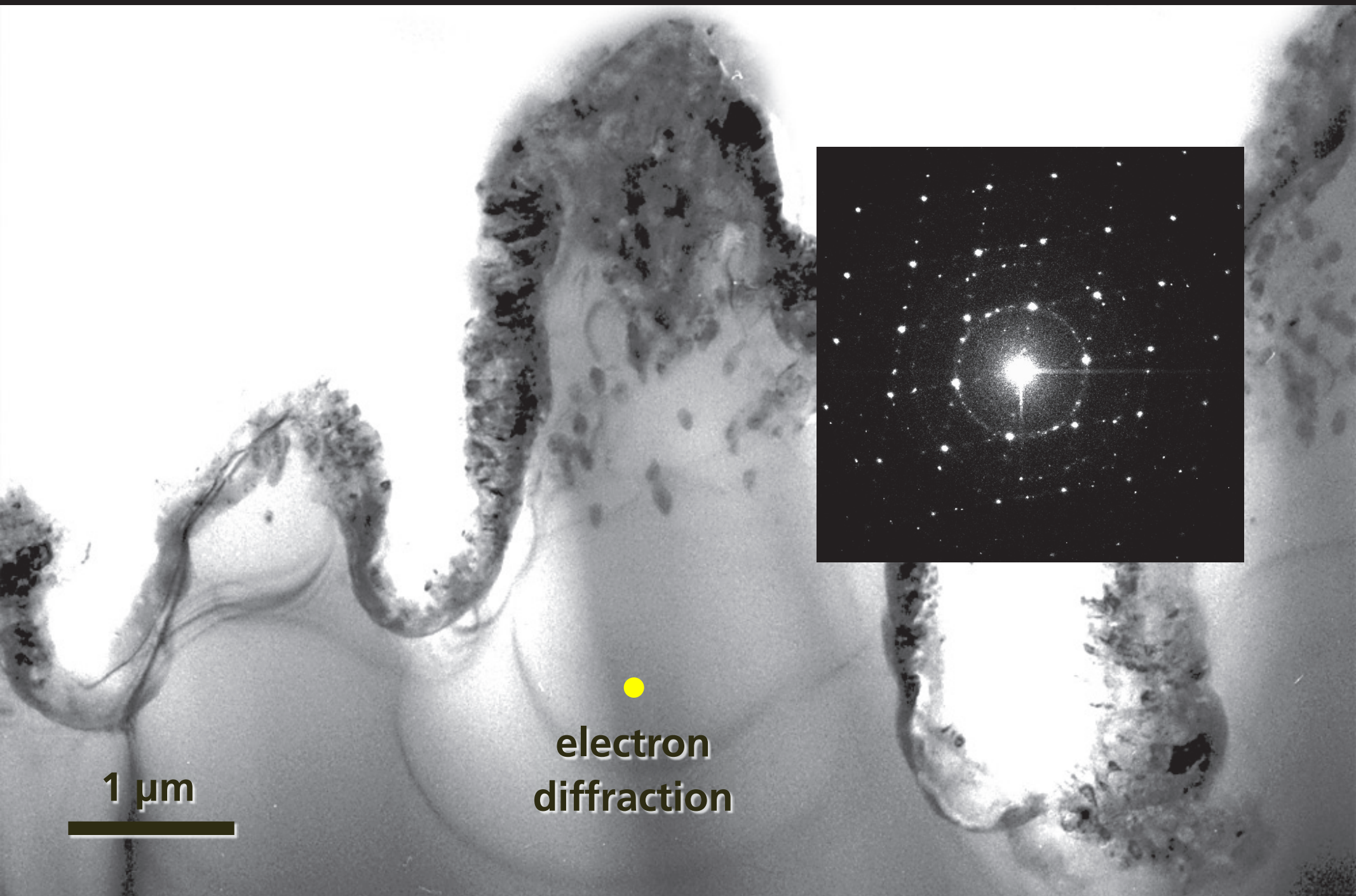

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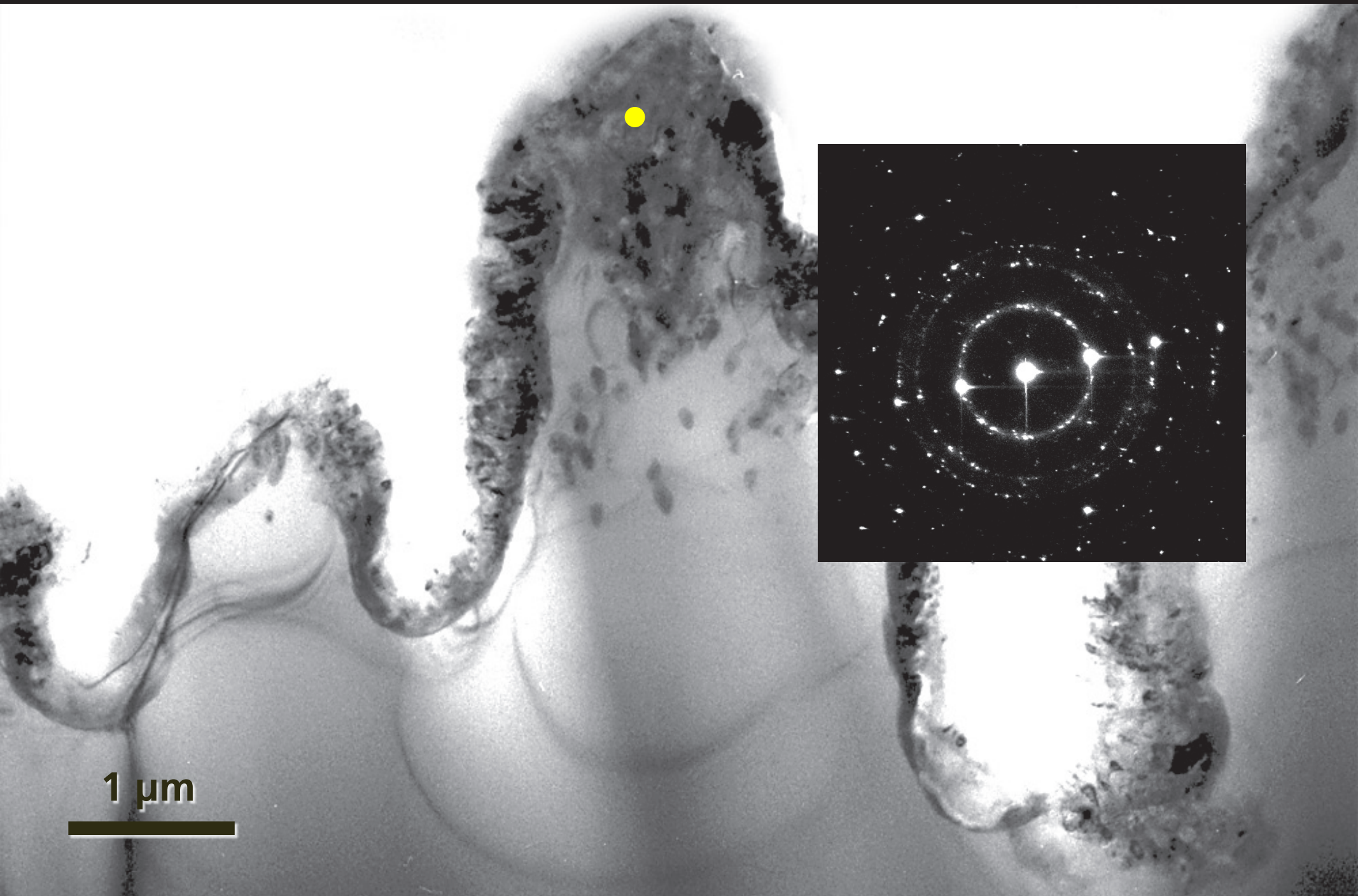

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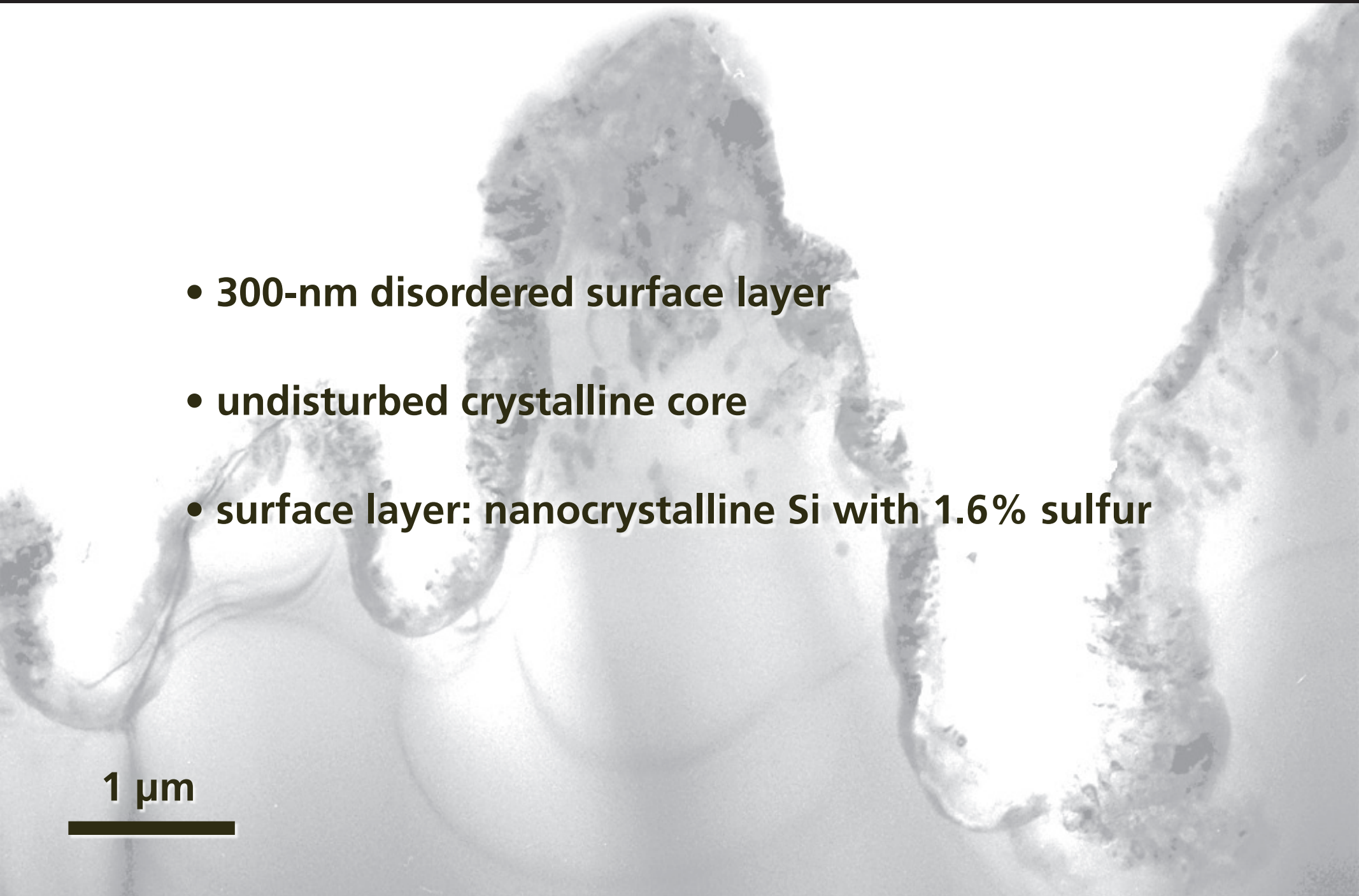


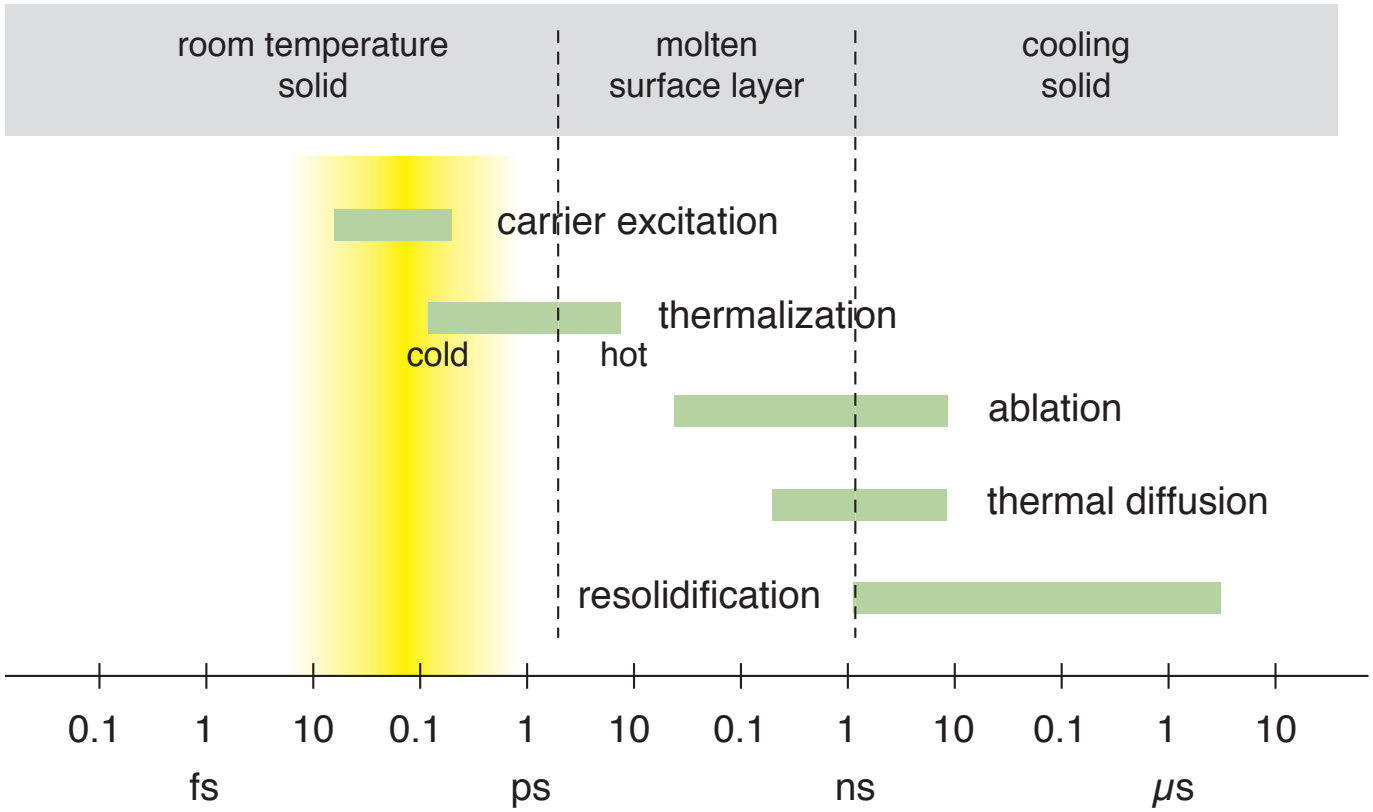
- 300-nm disordered surface layer
- undisturbed crystalline core
- surface layer: nanocrystalline Si with 1.6% sulfur

Structure

two processes: melting and ablation

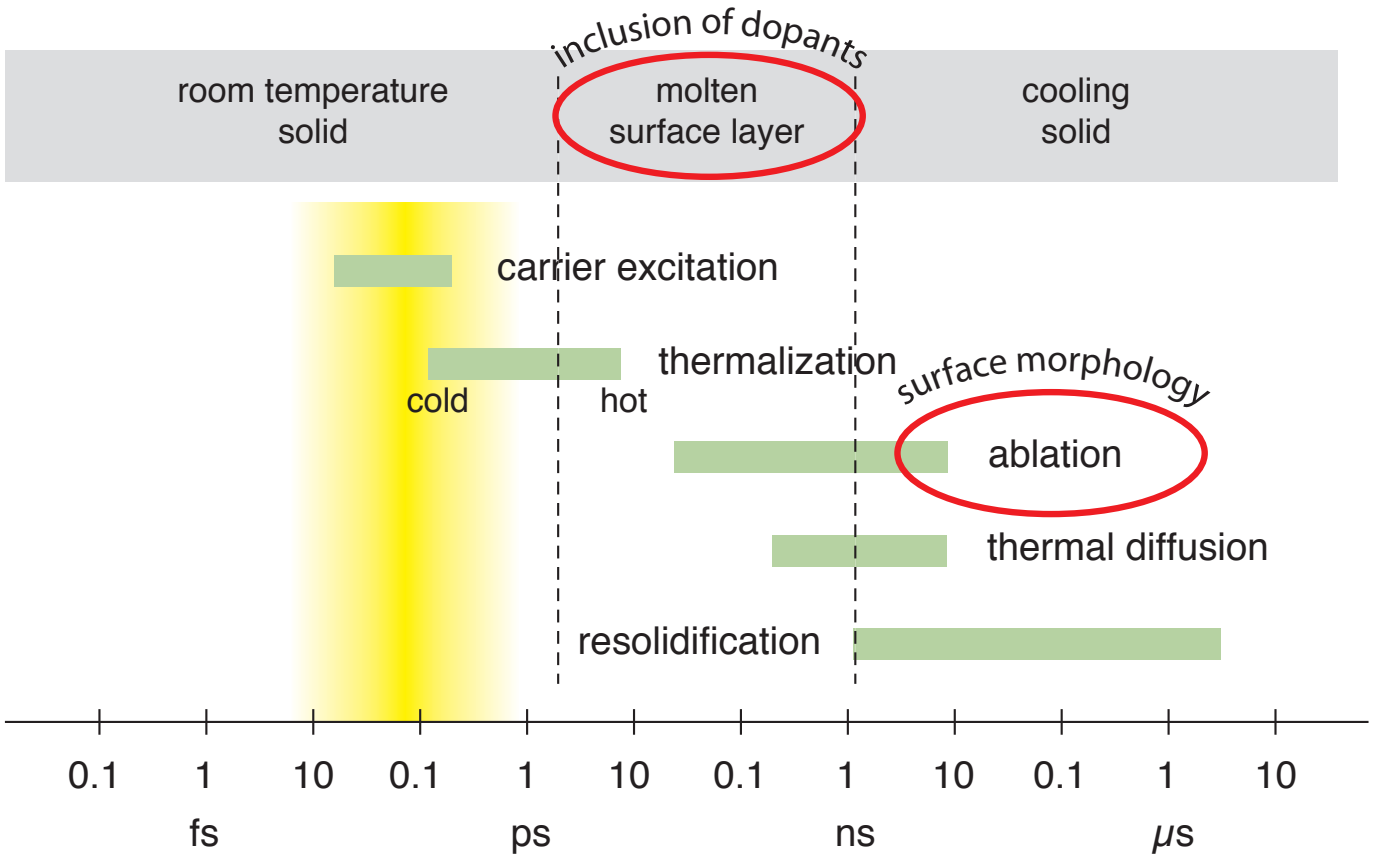
Structure

relevant time scales



Structure

relevant time scales



Structure

different thresholds:

melting: 1.5 kJ/m^2

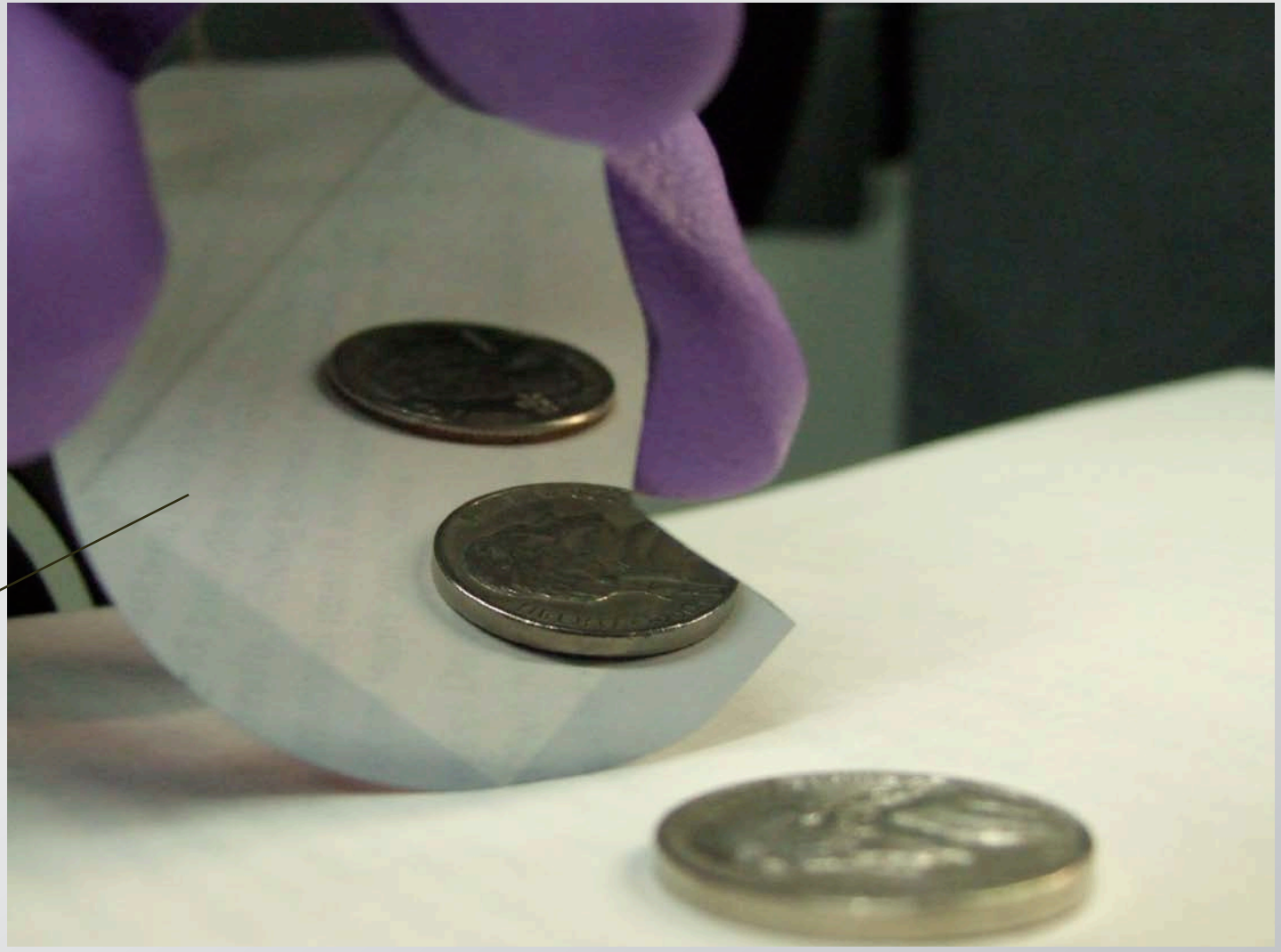
ablation: 3.1 kJ/m^2

Structure

decouple ablation from melting

Structure

decouple ablation from melting



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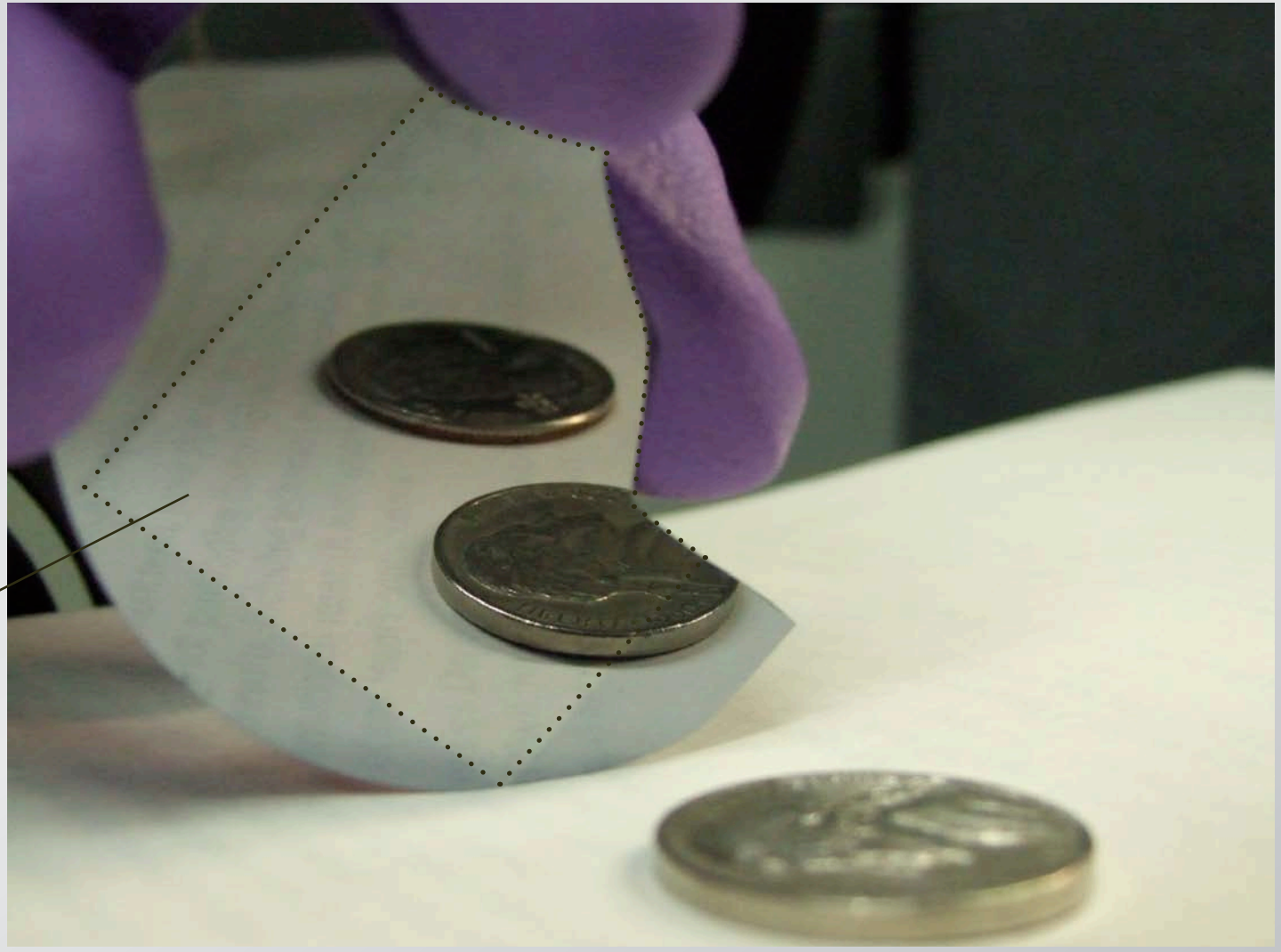

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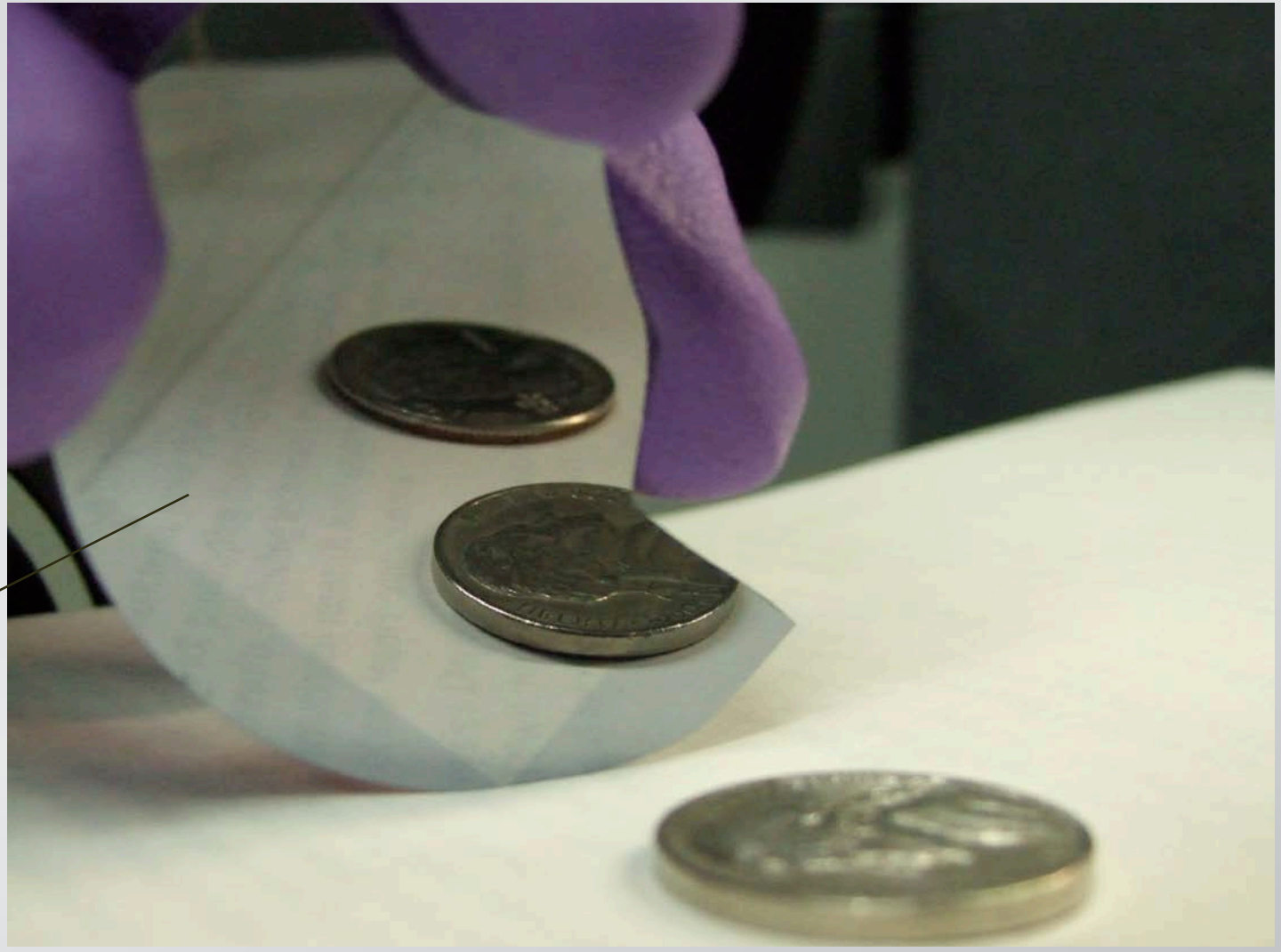

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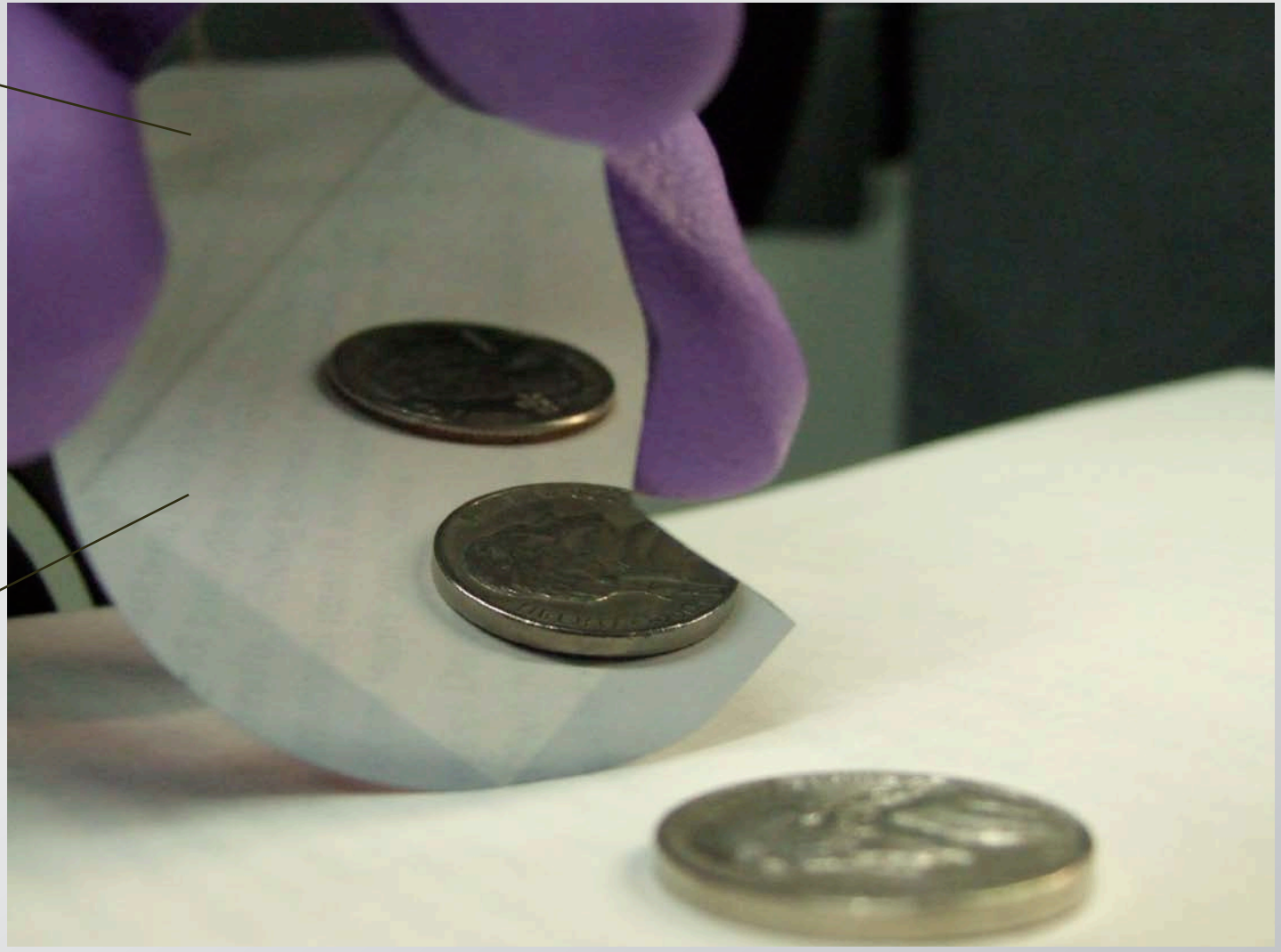
decouple ablation from melting



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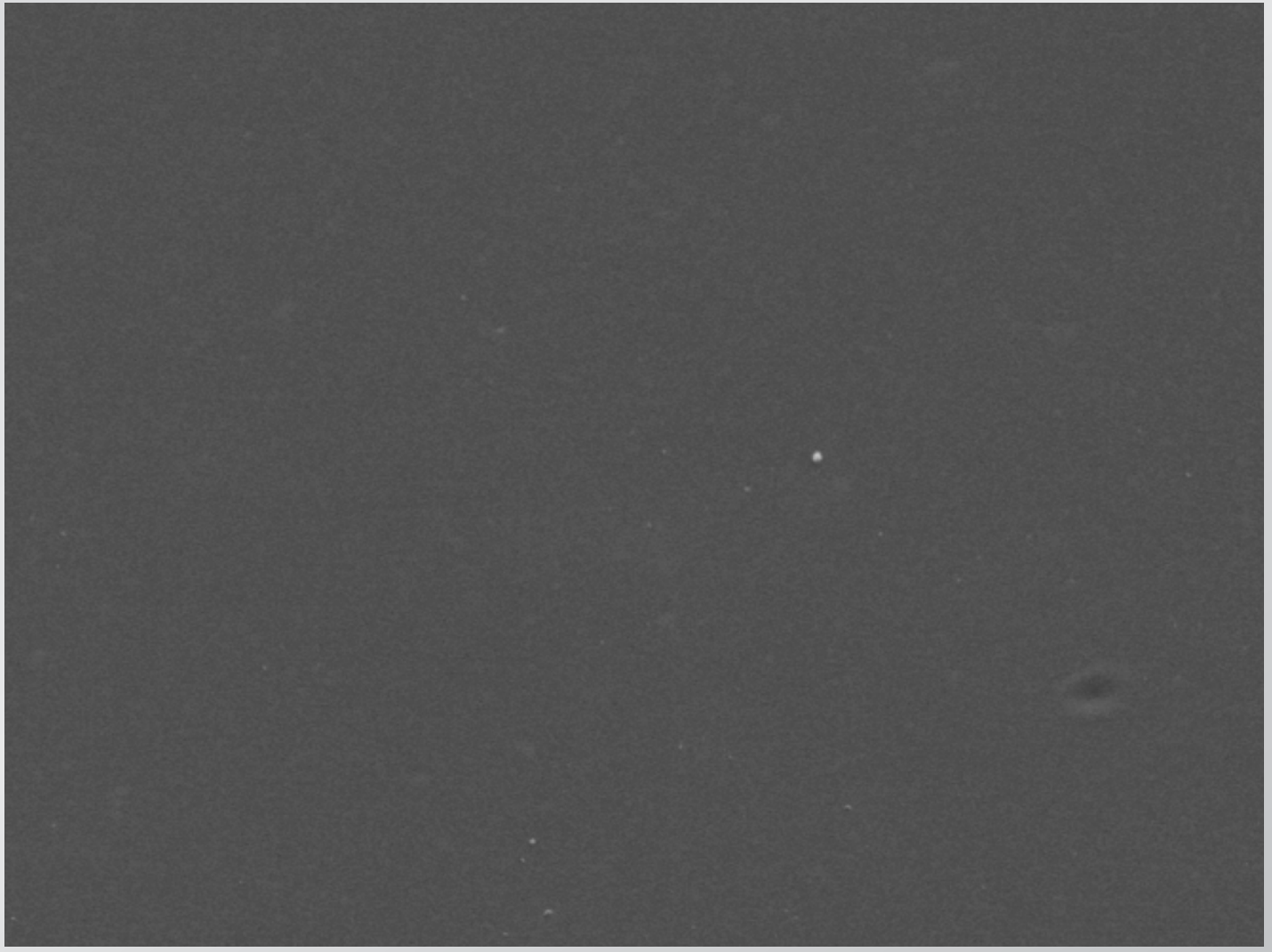

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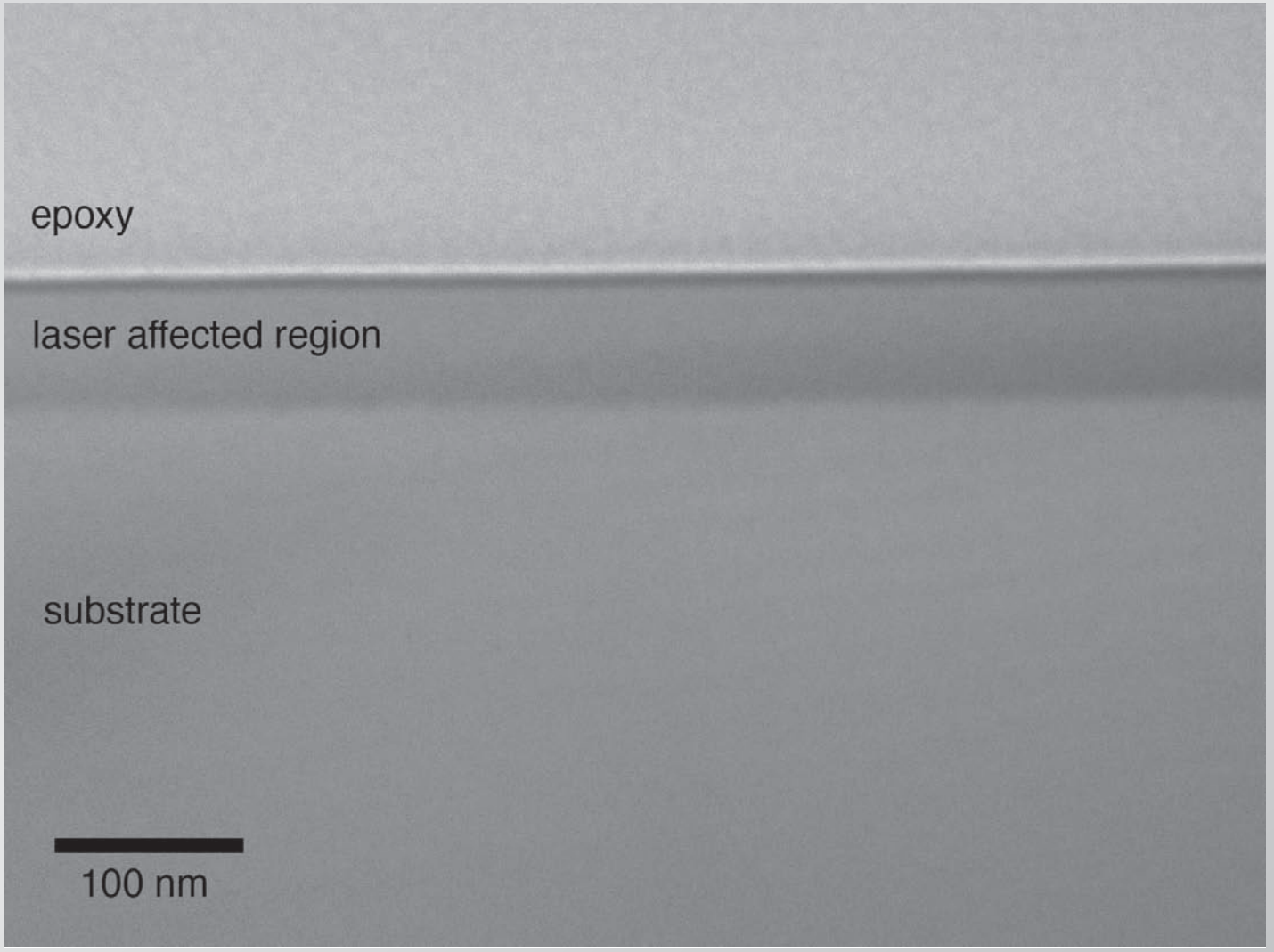

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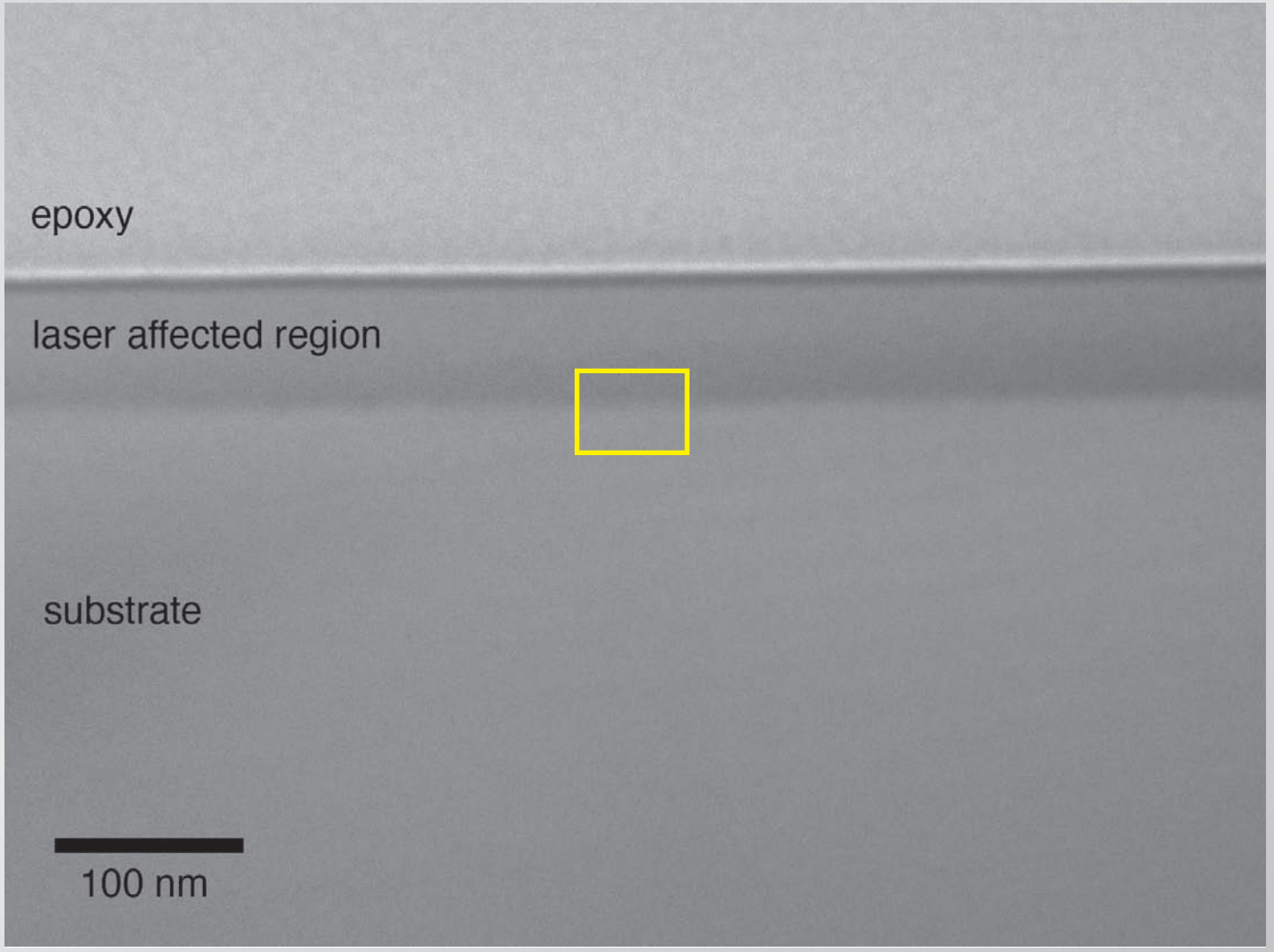
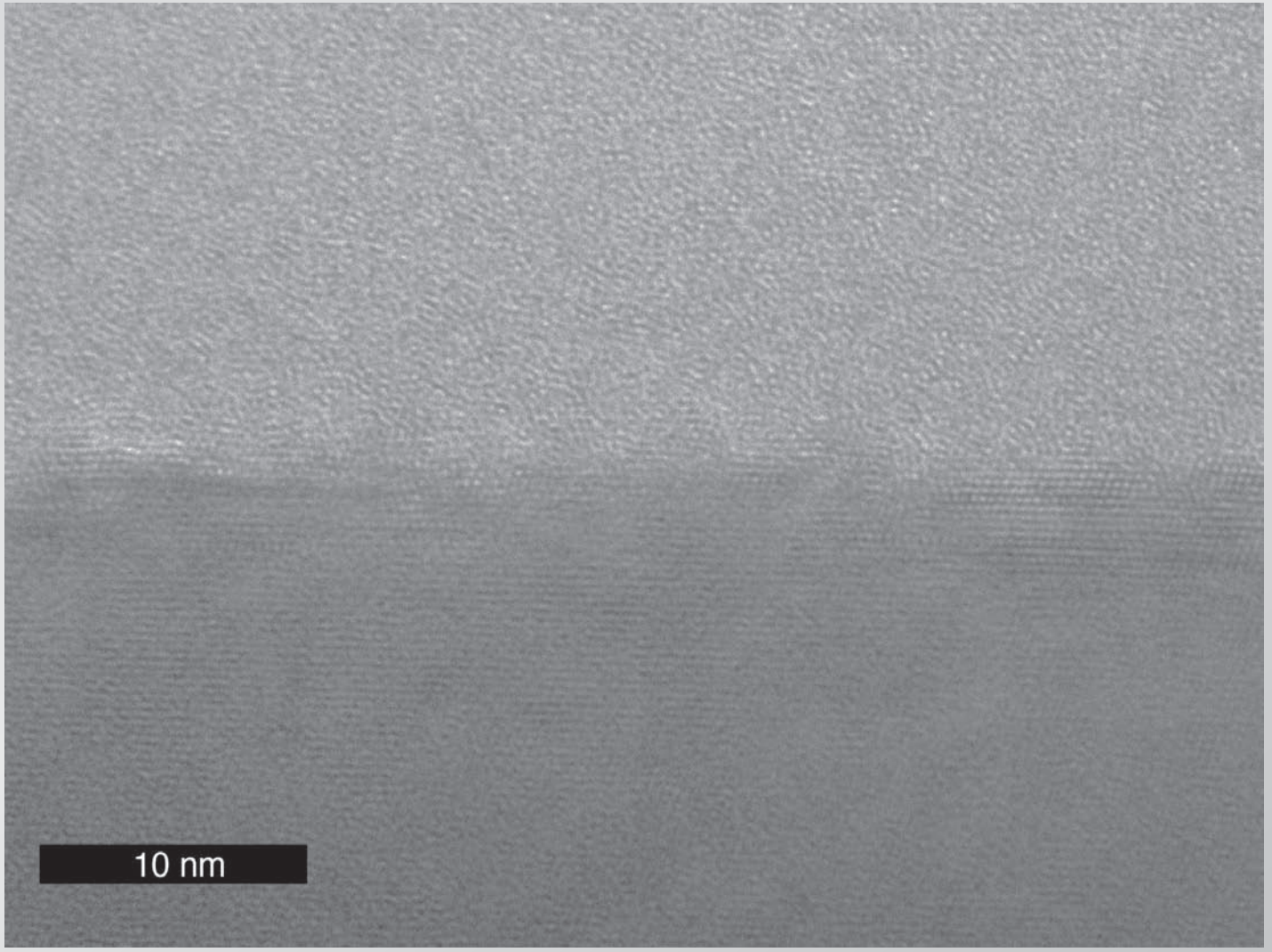
decouple ablation from melting



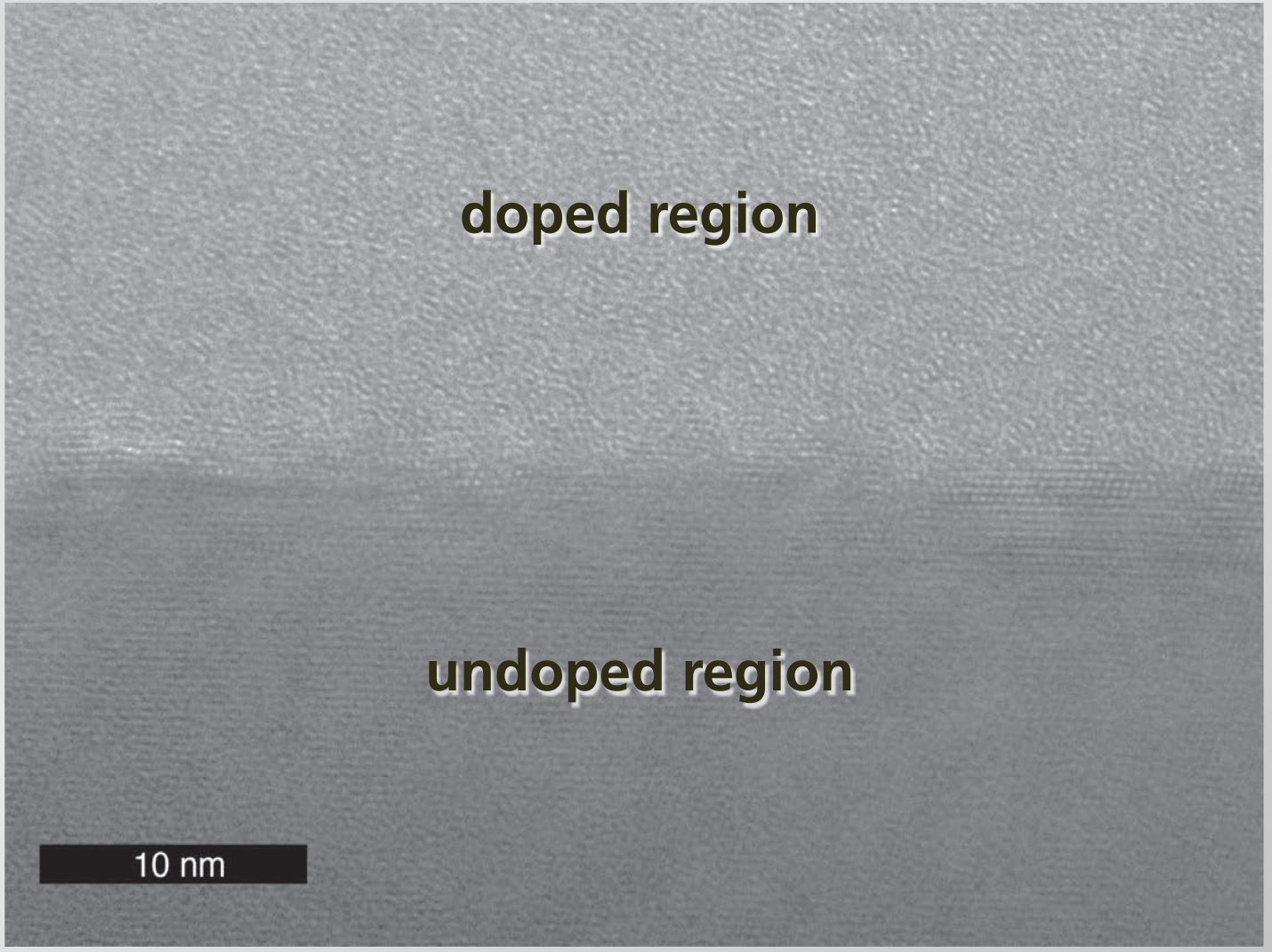
Structure

decouple ablation from melting



Structure

decouple ablation from melting



Structure

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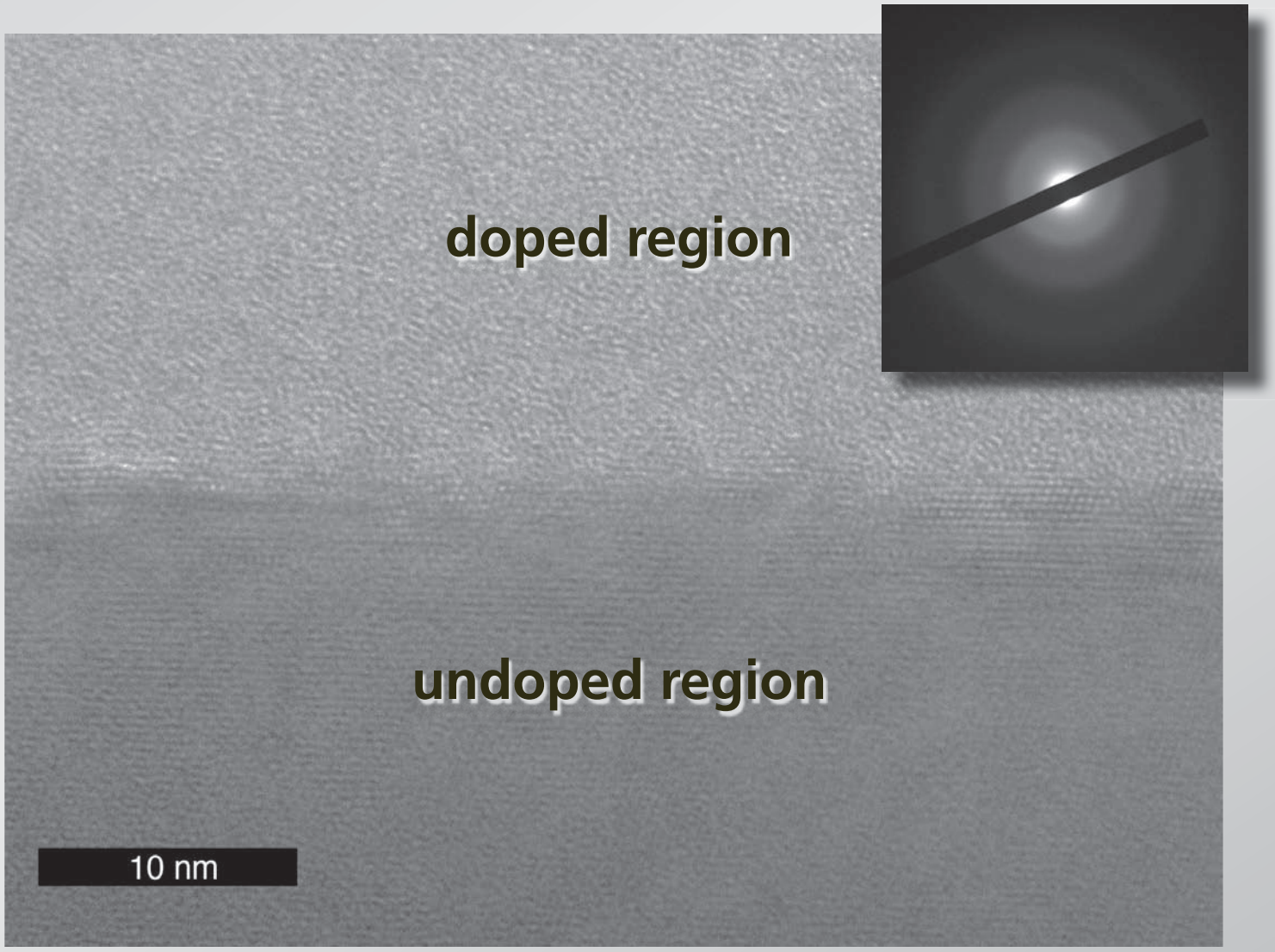
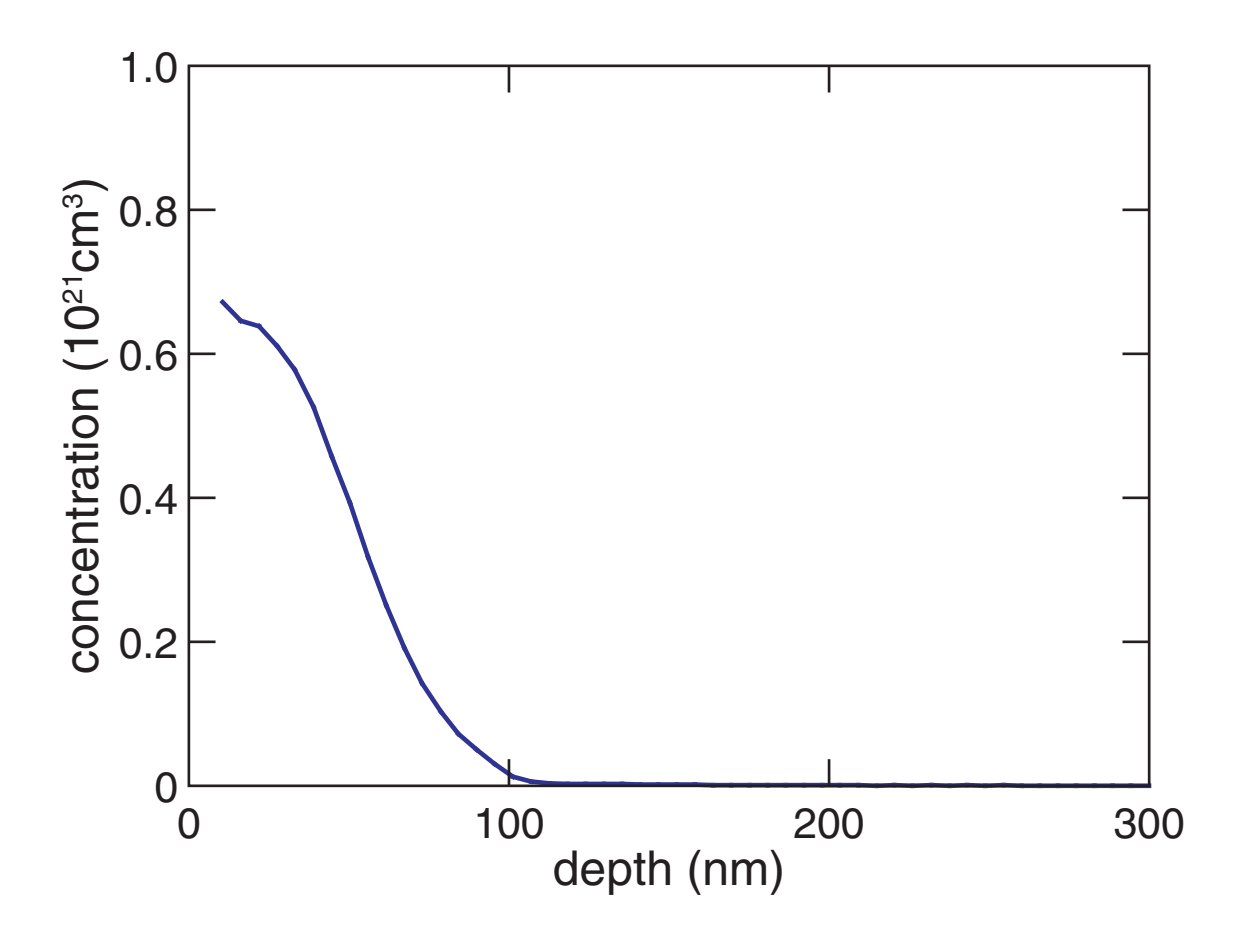
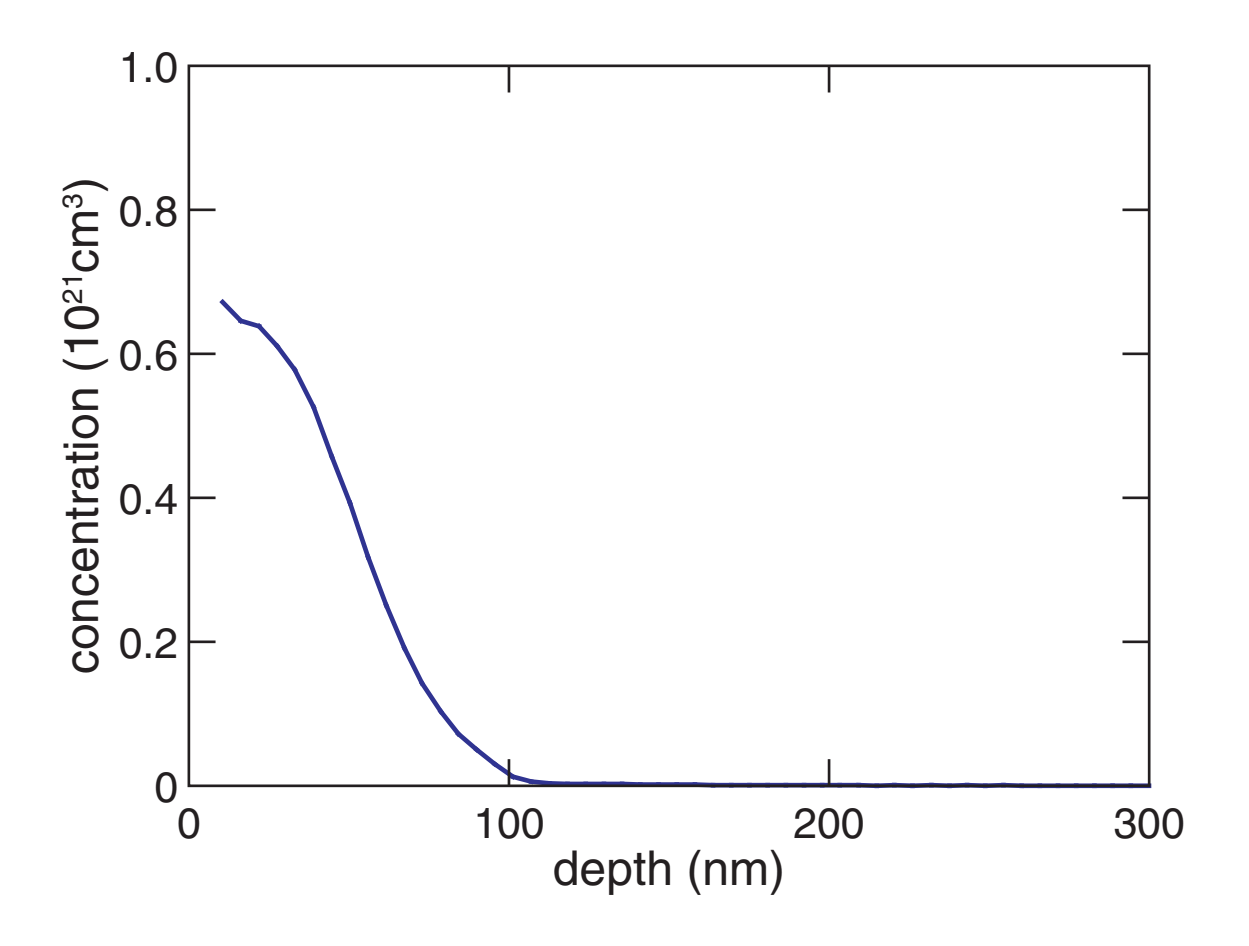


Structure

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

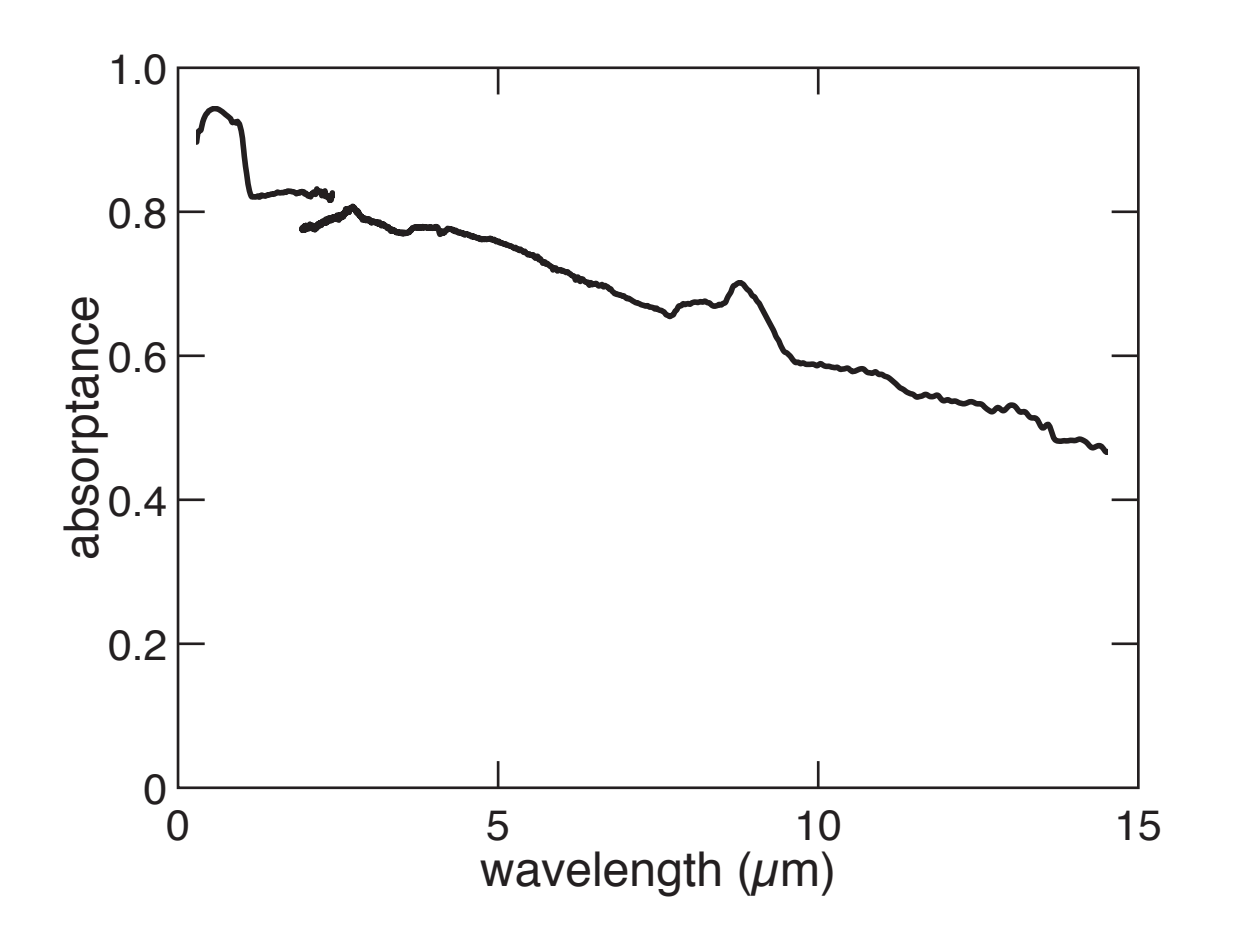
- rapid melting and resolidification causes doping
- ablation causes morphology changes
- about 1% impurity in 100-nm thick surface layer
- annealing changes impurity coordination

Outline

- structure
- **optoelectronic properties**
- devices

Optoelectronic properties

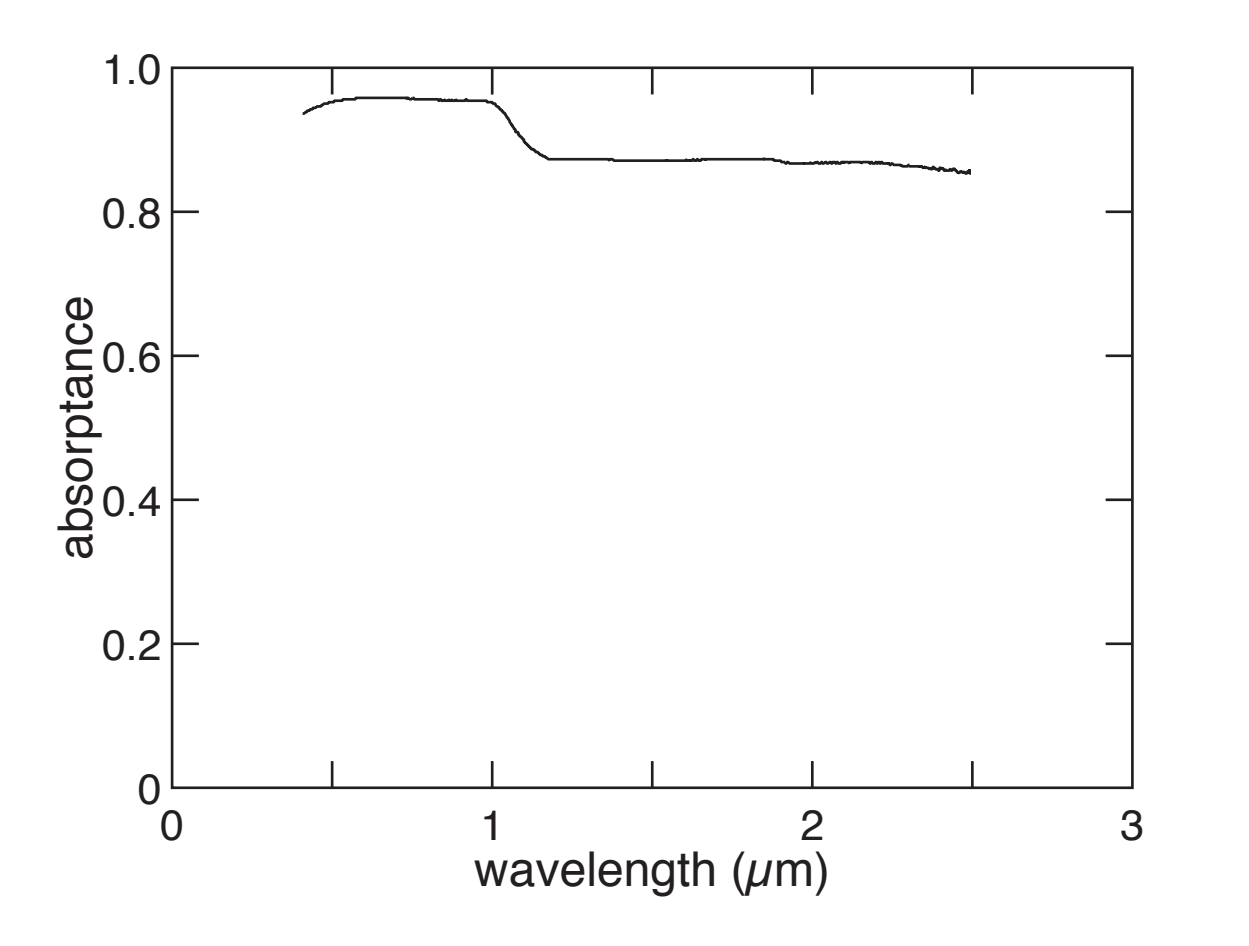
absorptance ($1 - R_{int} - T_{int}$)



Asenbaum, Vienna

Optoelectronic properties

effect of annealing on IR absorptance



Optoelectronic properties

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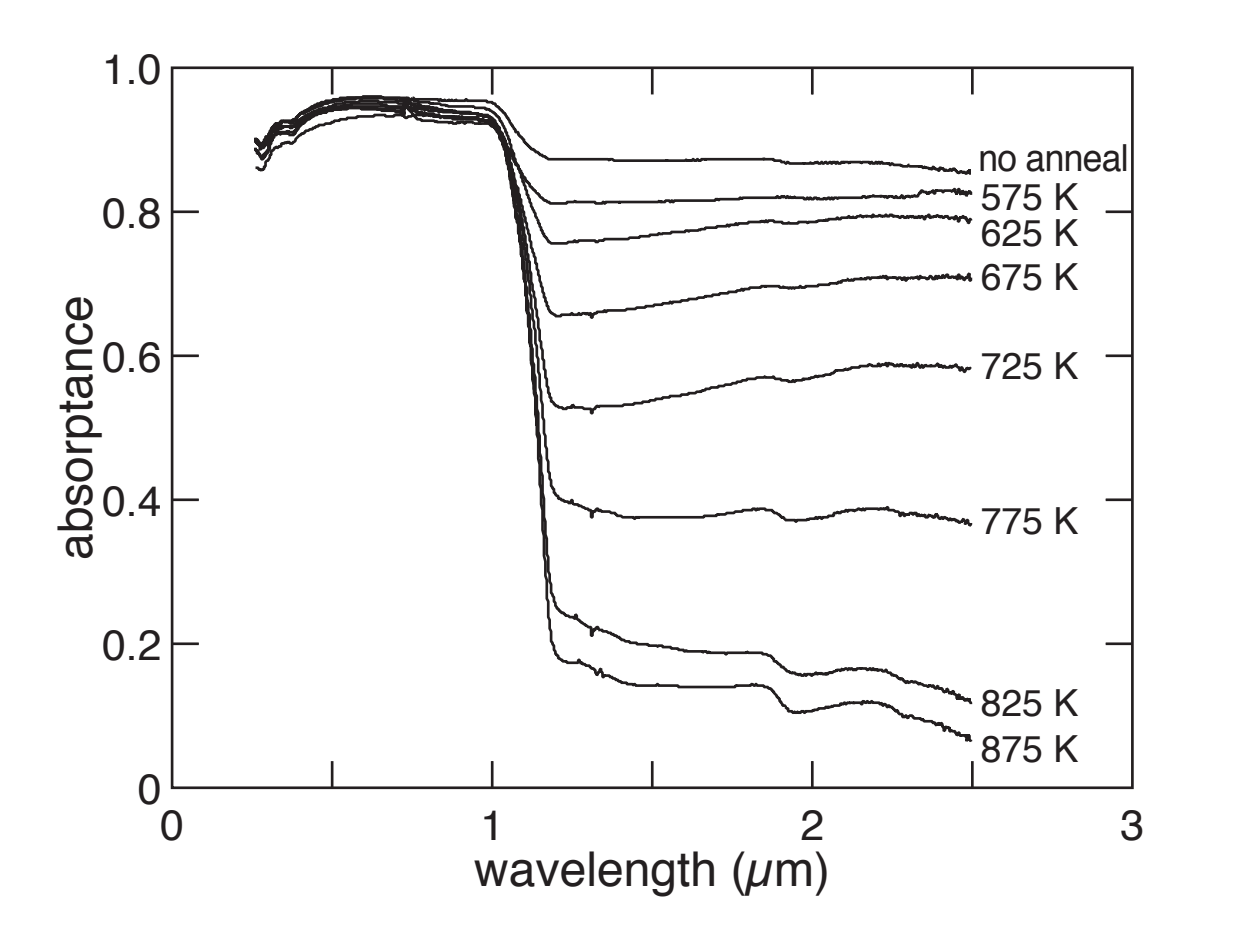
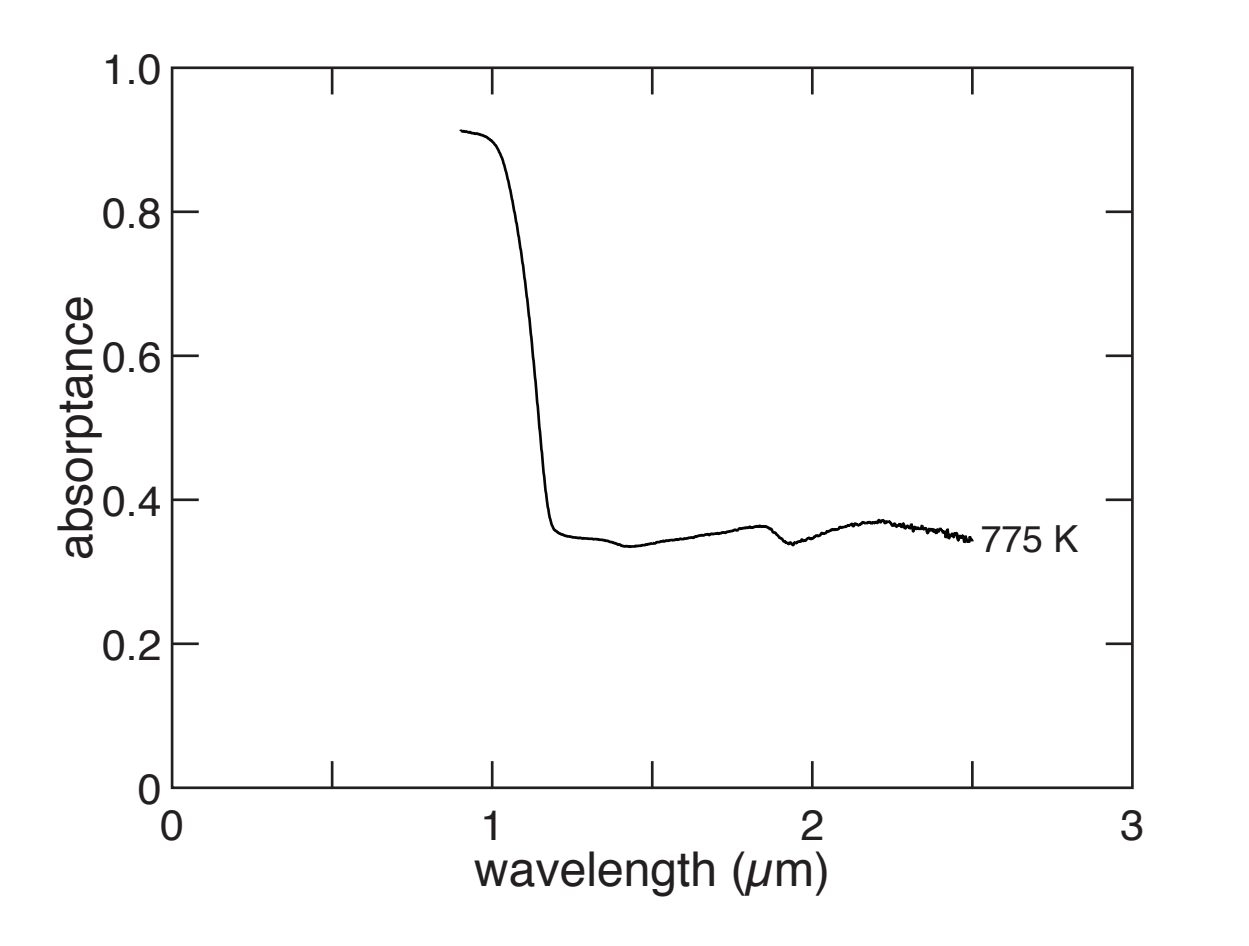


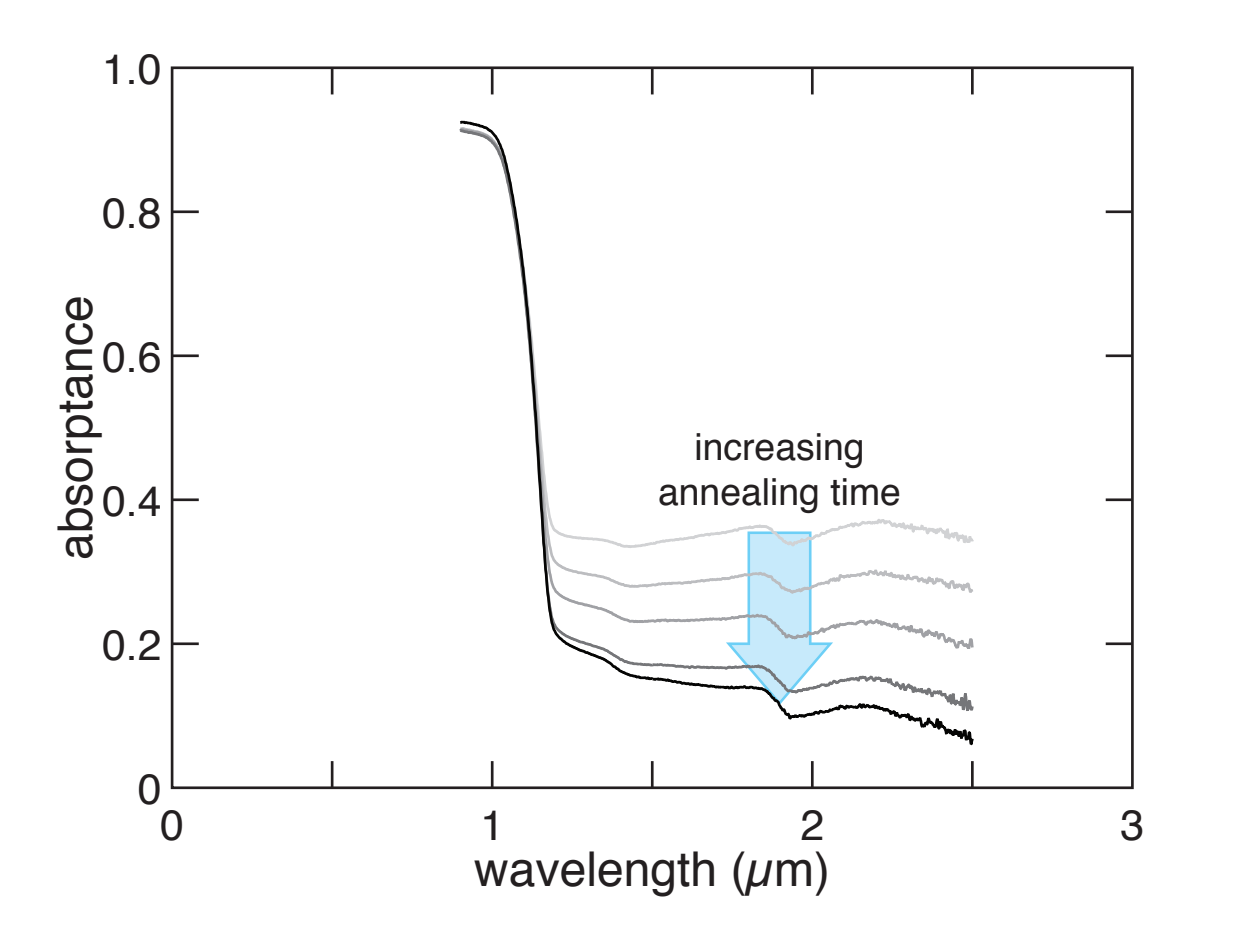
Optoelectronic properties

vary annealing time



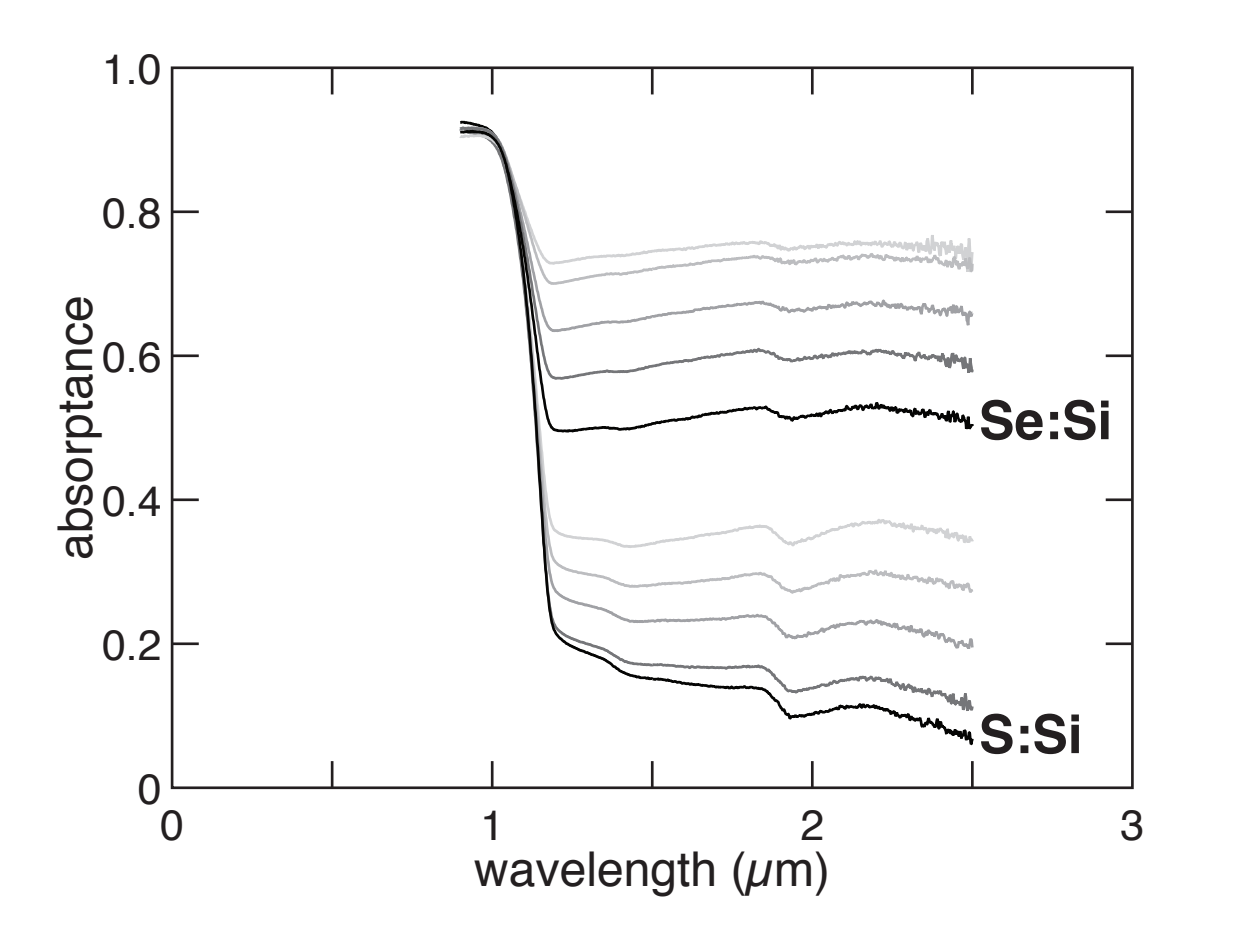
Optoelectronic properties

longer annealing decreases IR absorptance



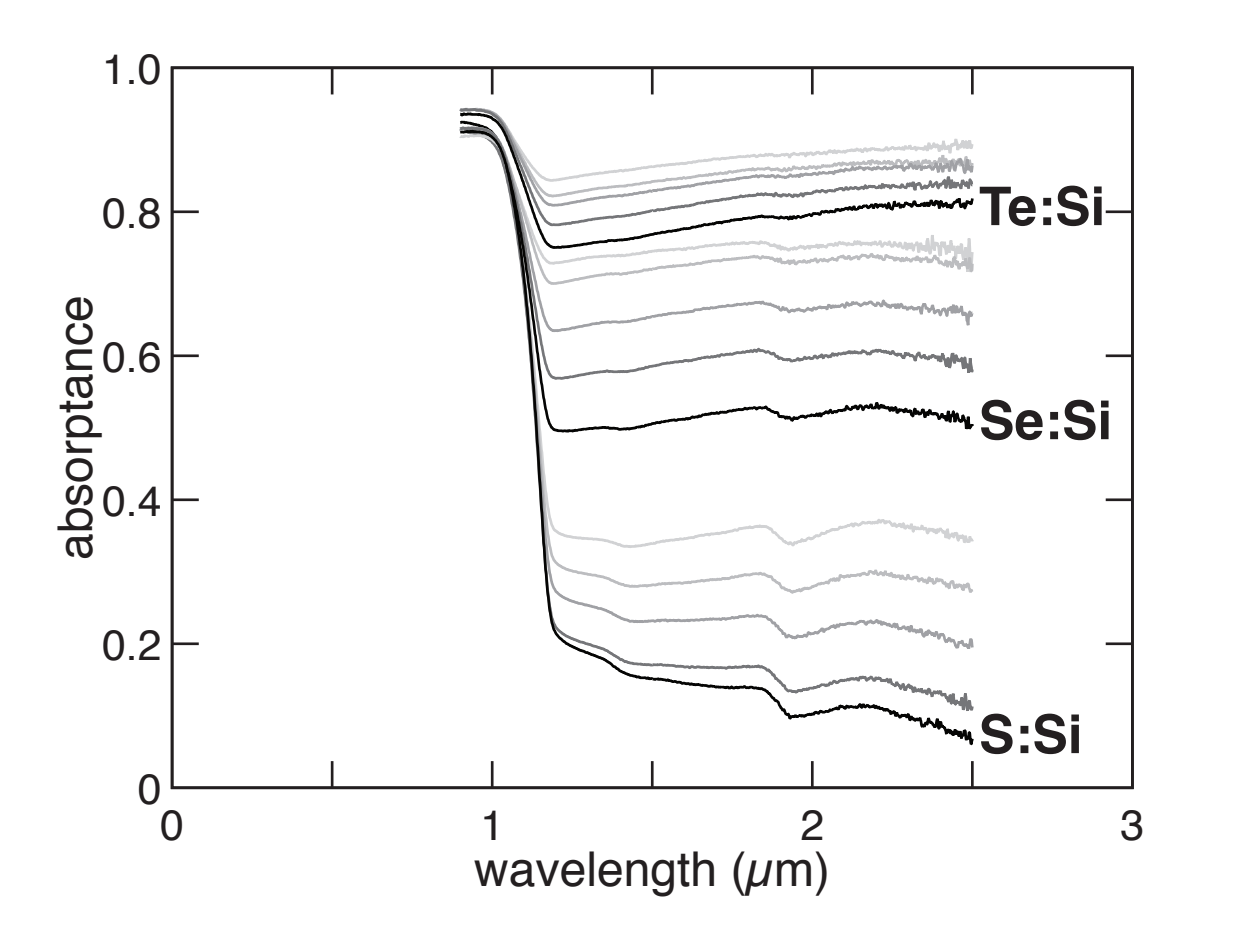
Optoelectronic properties

IR absorptance decreases less for Se-doped samples…



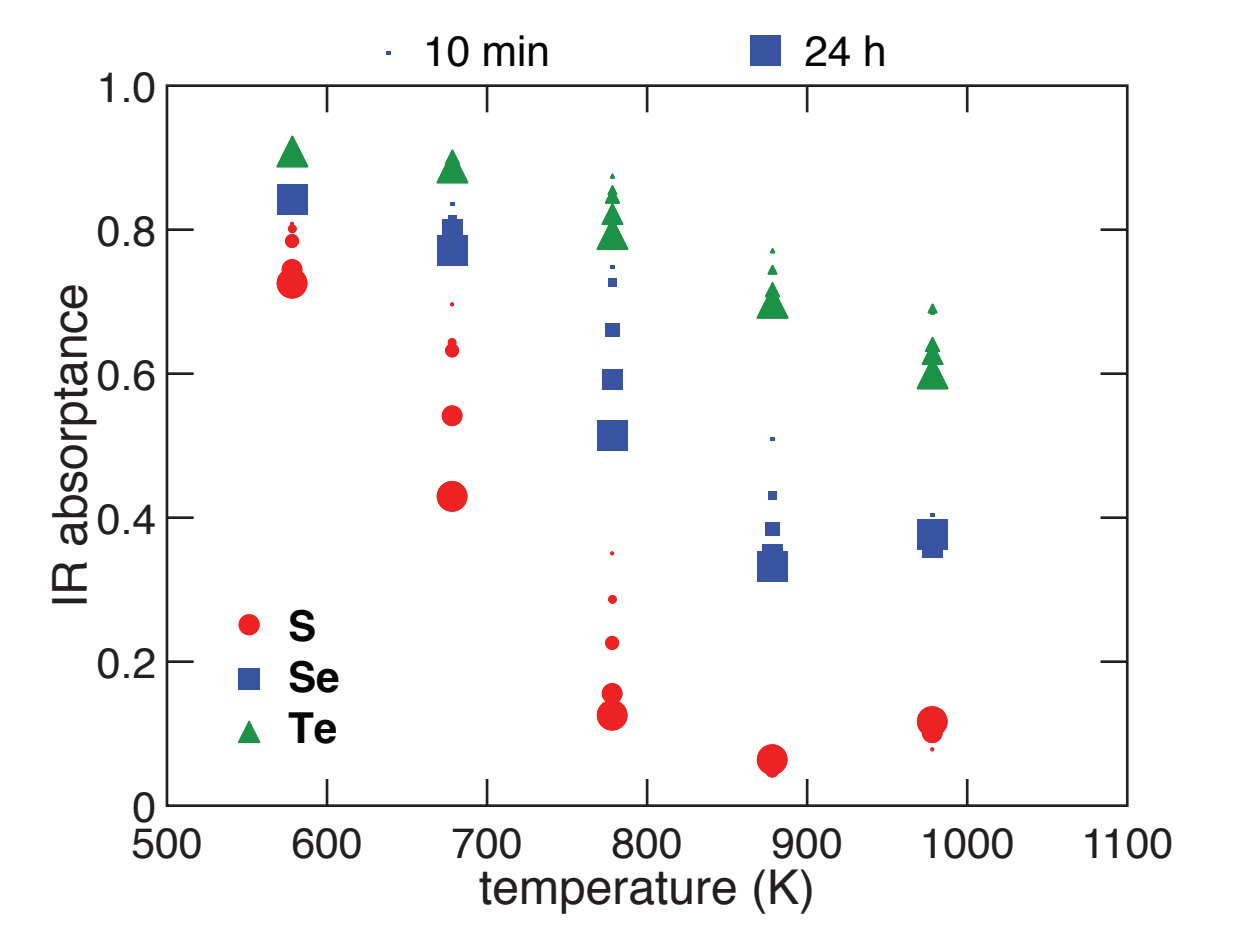
Optoelectronic properties

and even less for Te-doped samples…



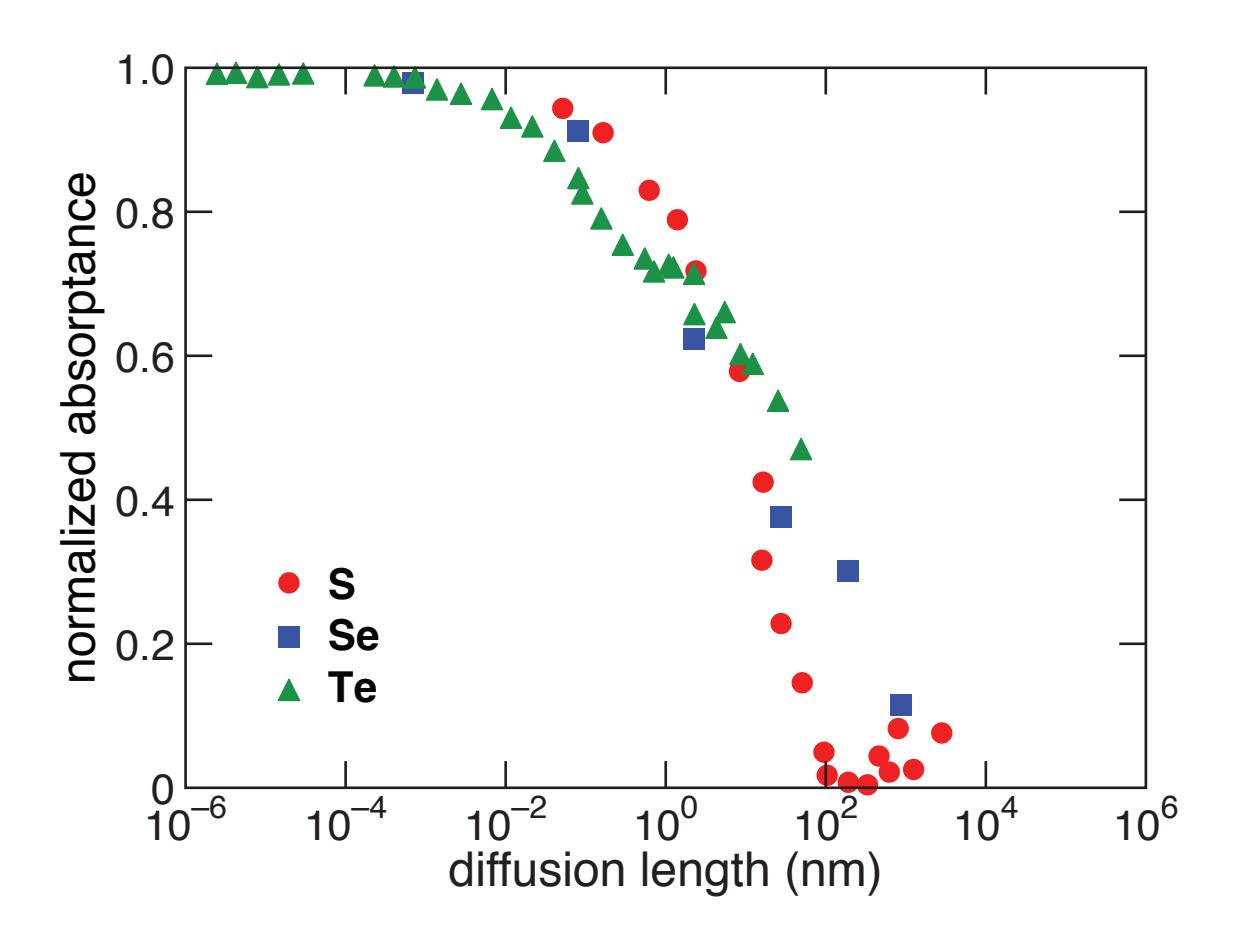
Optoelectronic properties

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



Optoelectronic properties

…but is unique function of diffusion length



Optoelectronic properties

annealing…

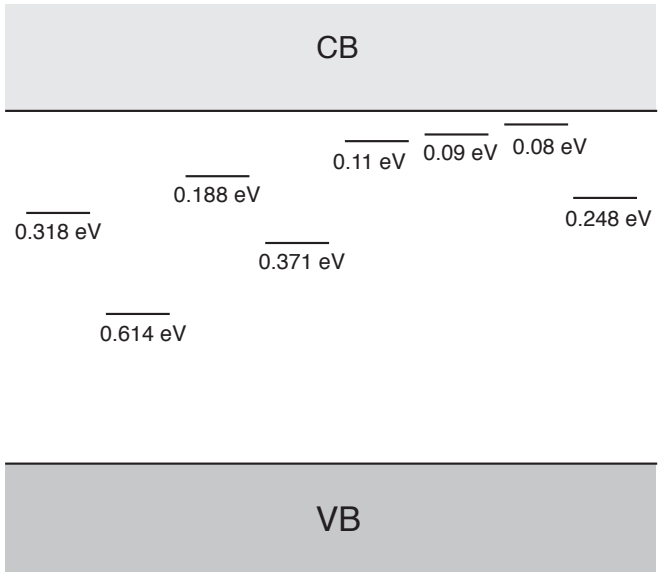
- decreases IR absorptance
- causes recoordination and diffusion of dopants
- IR absorptance reduced by 50% after 20 nm diffusion

Optoelectronic properties

what dopant states/bands cause IR absorption?

Optoelectronic properties

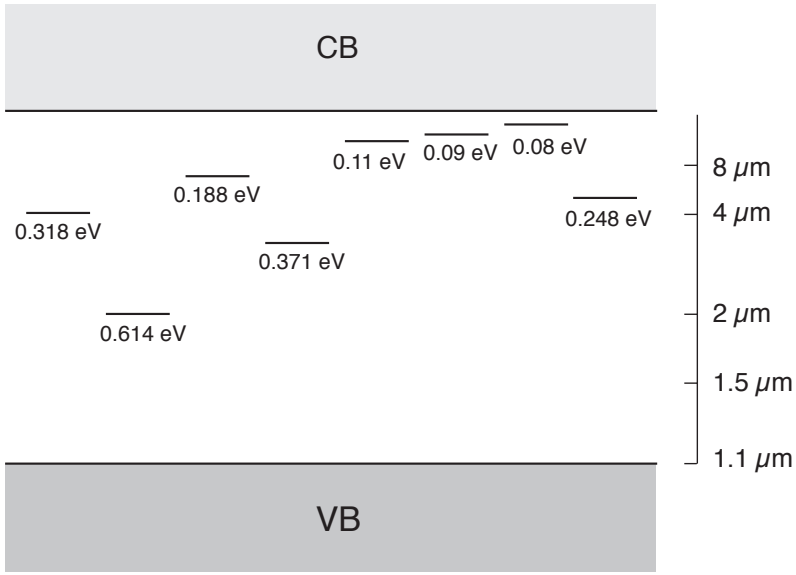
1 part in 10^6 sulfur introduces donor states in gap



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

Optoelectronic properties

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



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

Optoelectronic properties

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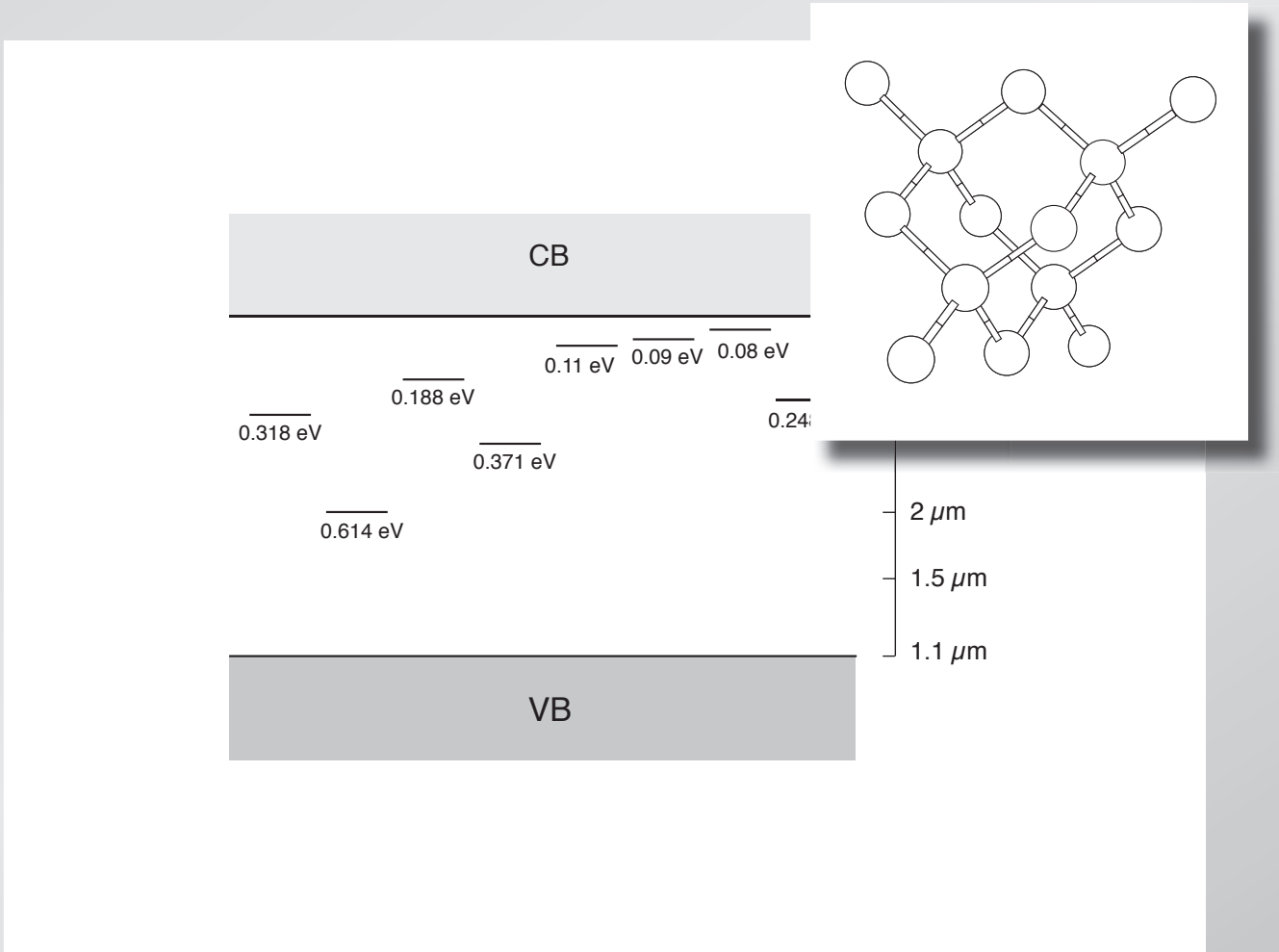

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Optoelectronic properties

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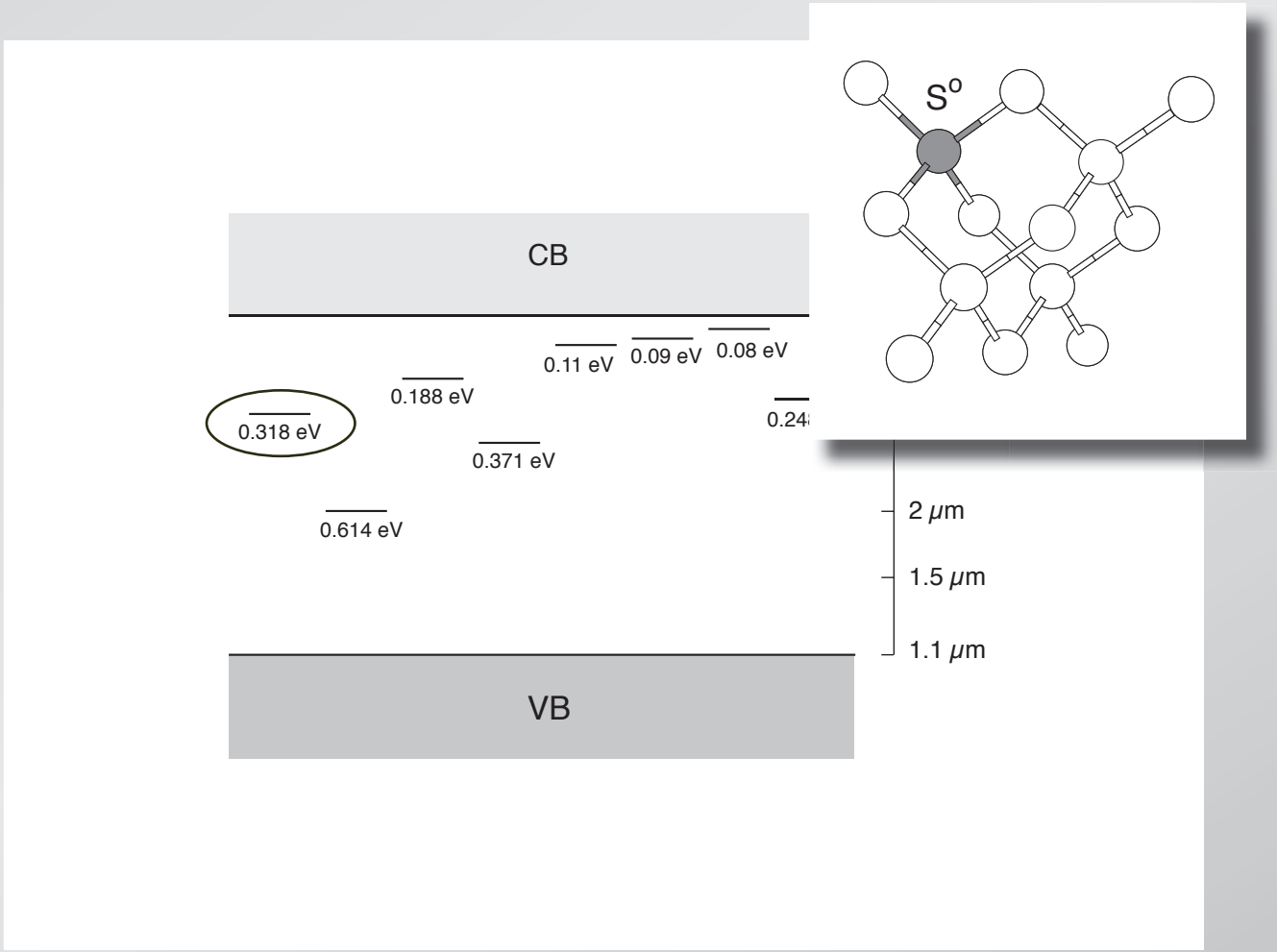

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Optoelectronic properties

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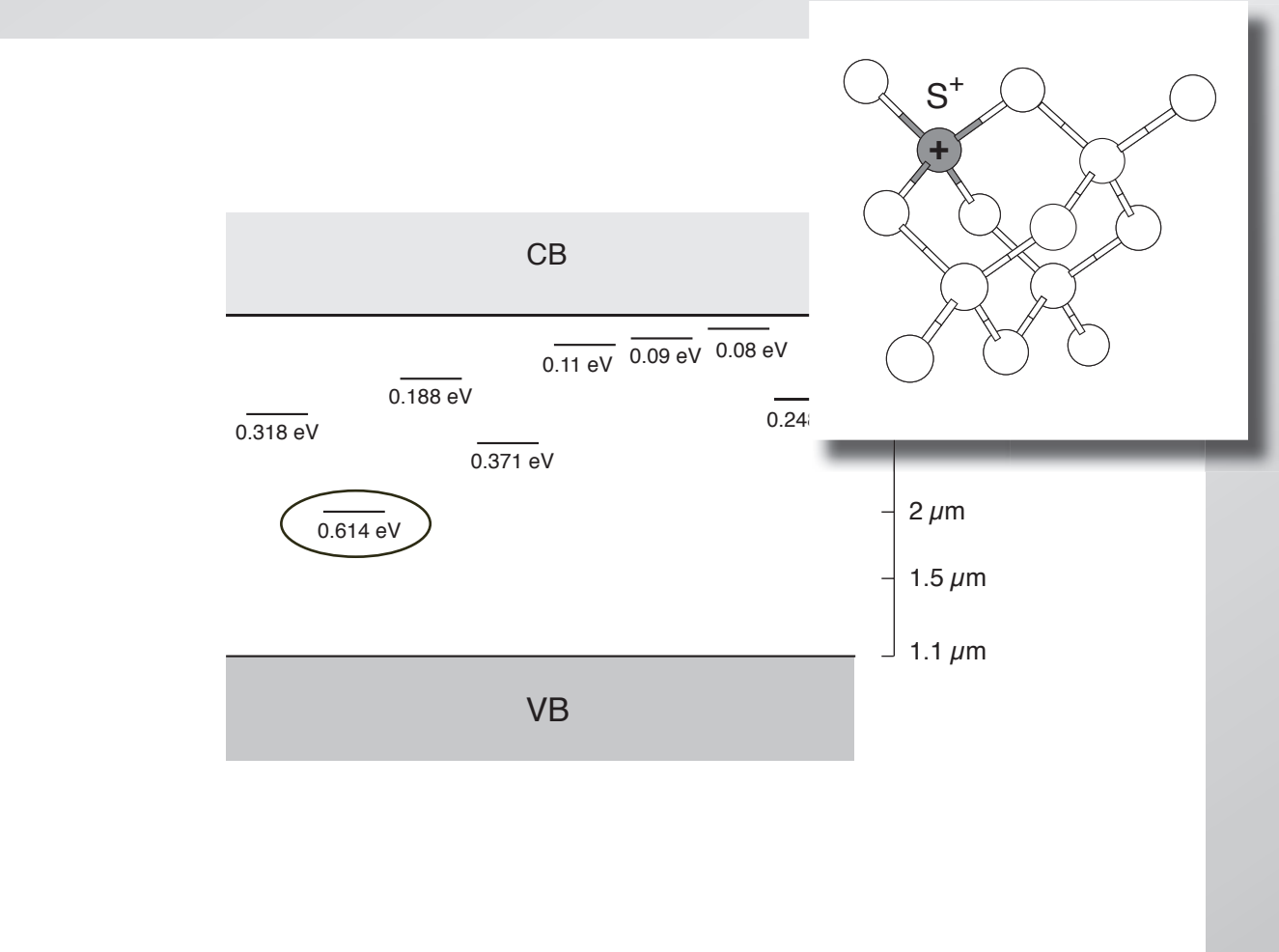

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Optoelectronic properties

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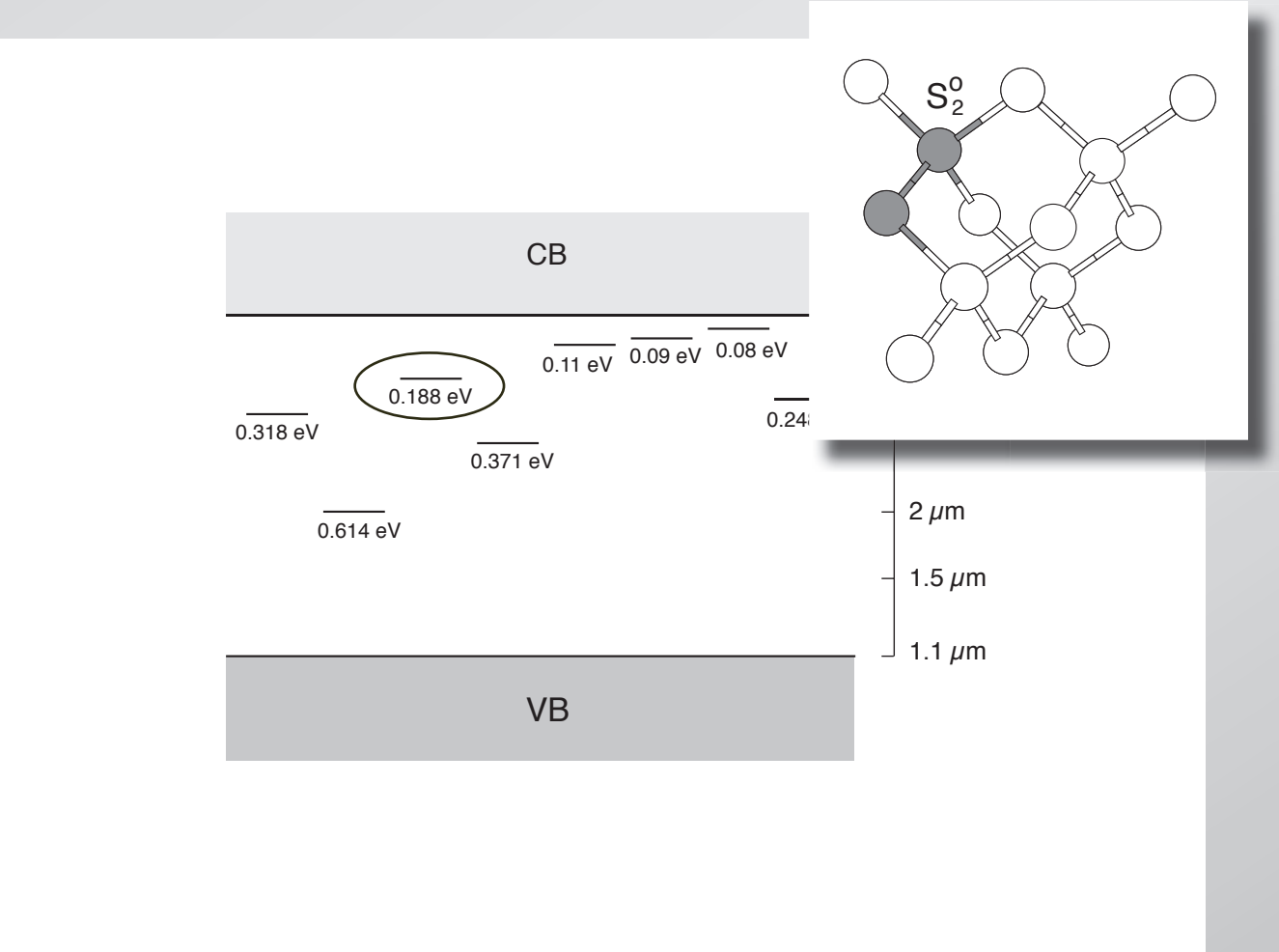

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Optoelectronic properties

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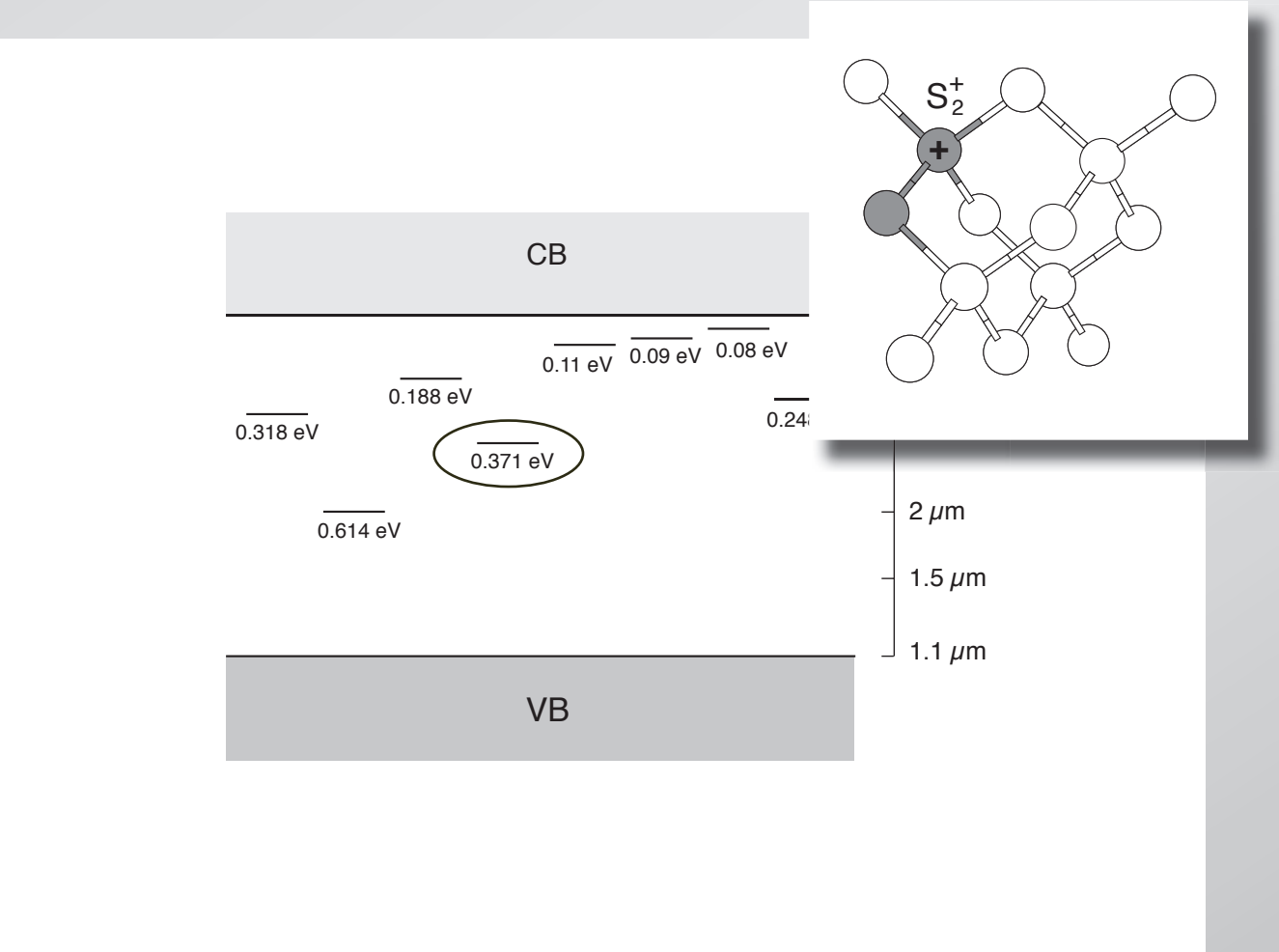


Janzén *et al.*, Phys. Rev. B 29, 1907 (1984)

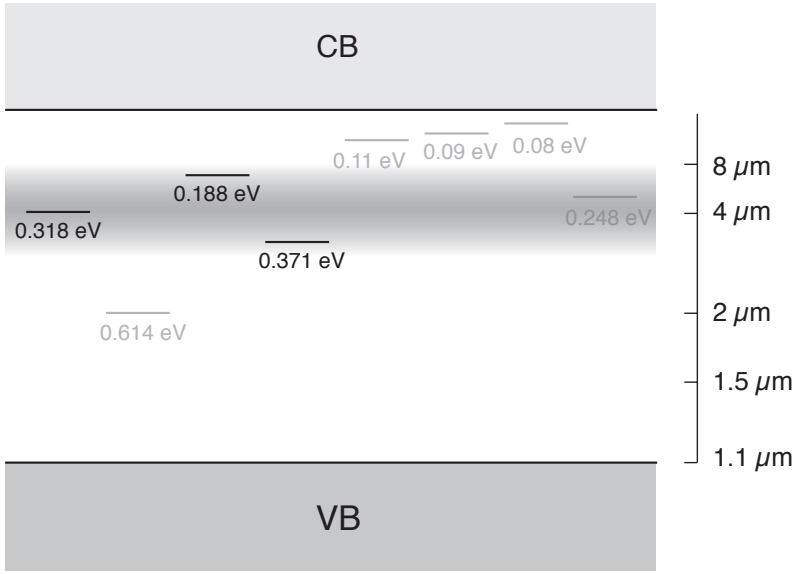
Optoelectronic properties

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

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

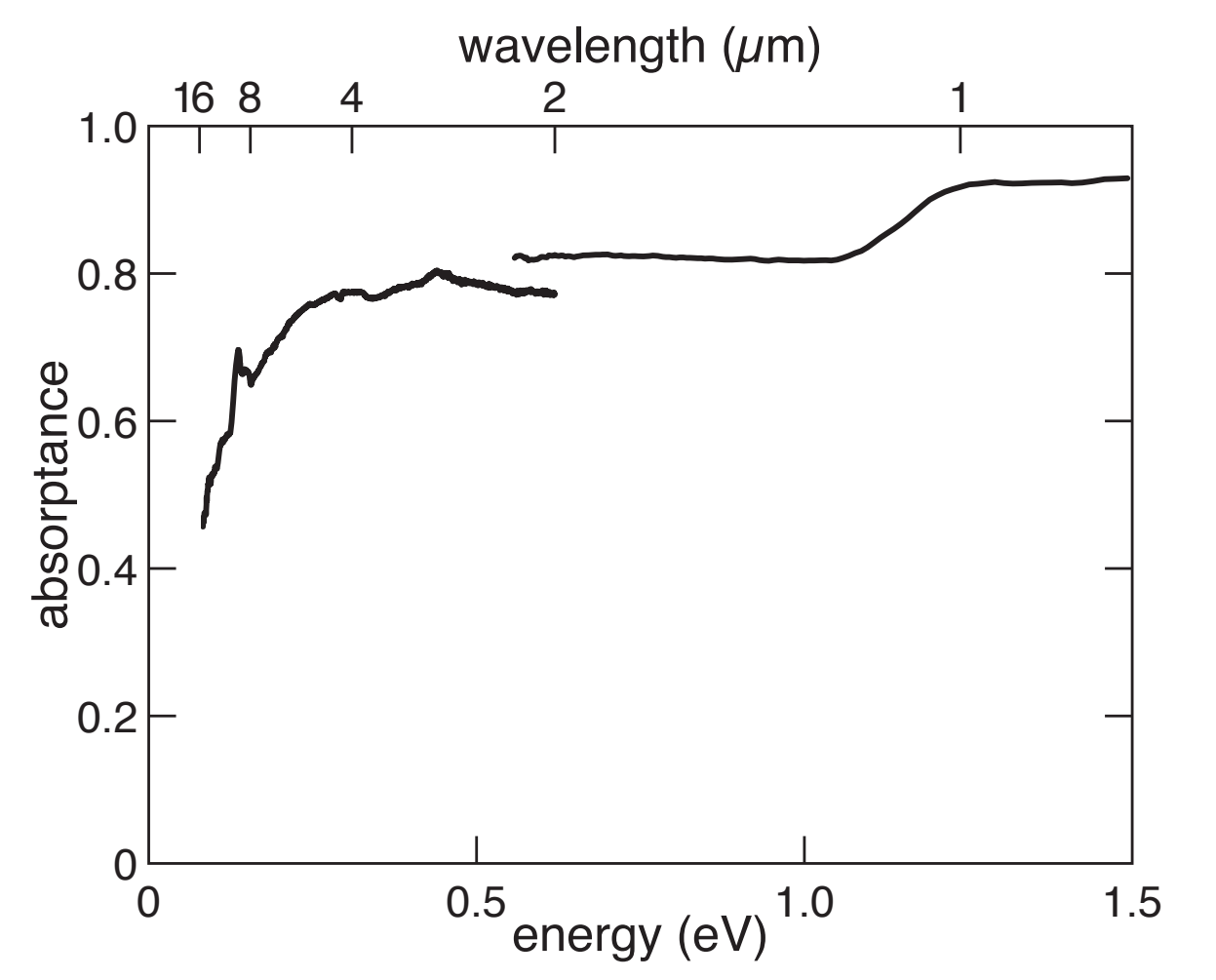
Optoelectronic properties

at high concentration states broaden into band



Optoelectronic properties

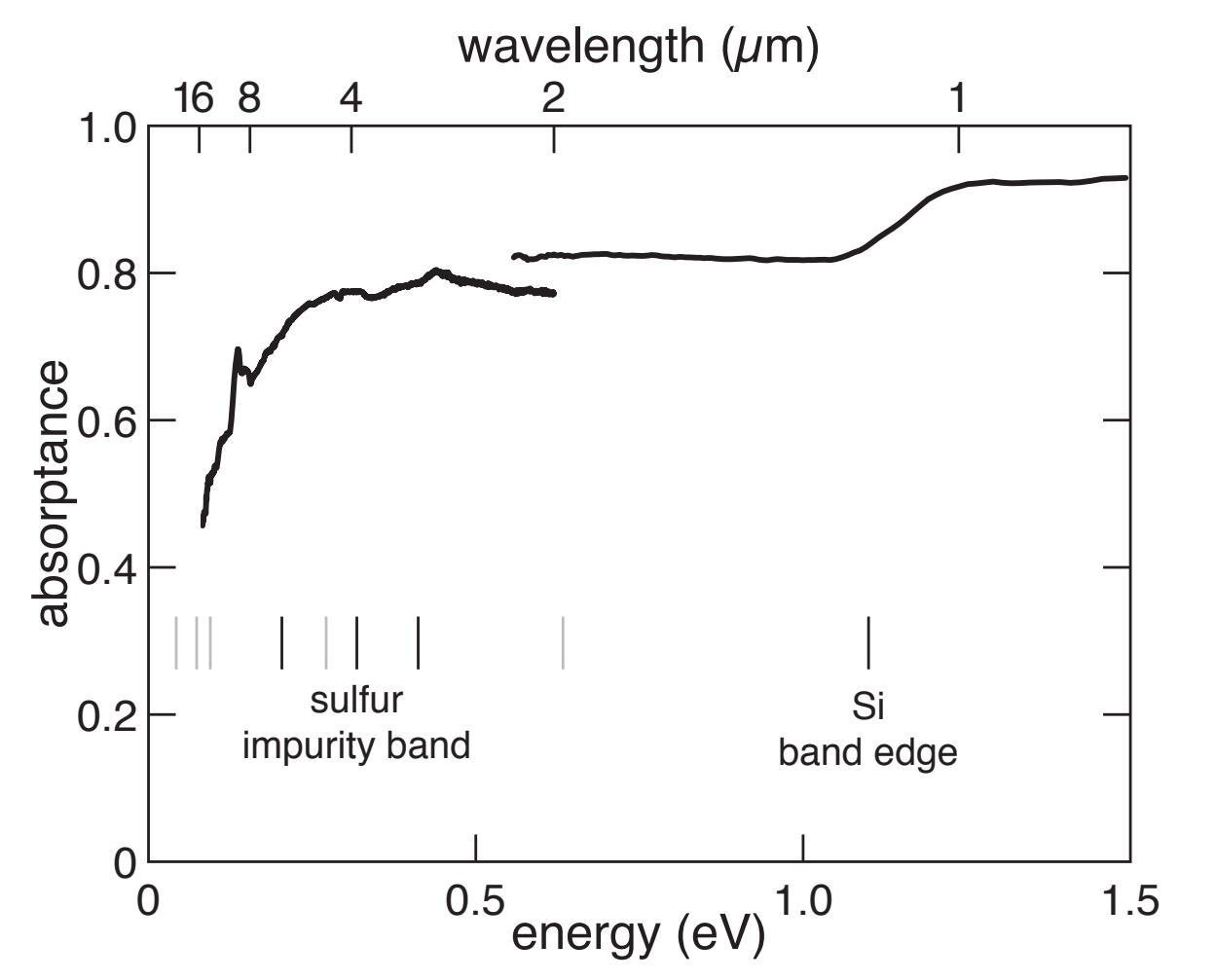
absorptance ($1 - R_{int} - T_{int}$)



Asenbaum, Vienna

Optoelectronic properties

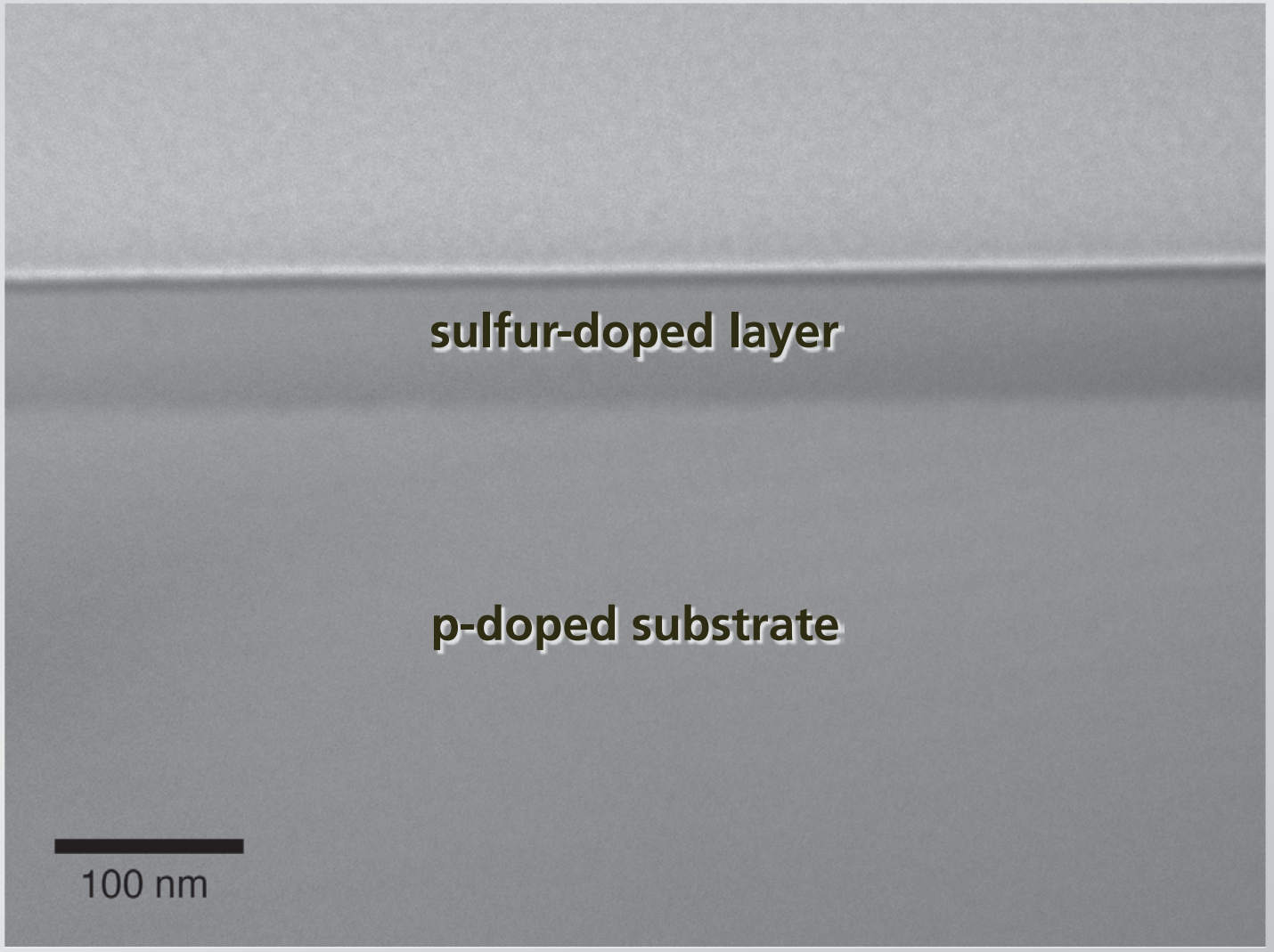
absorptance ($1 - R_{int} - T_{int}$)



Asenbaum, Vienna

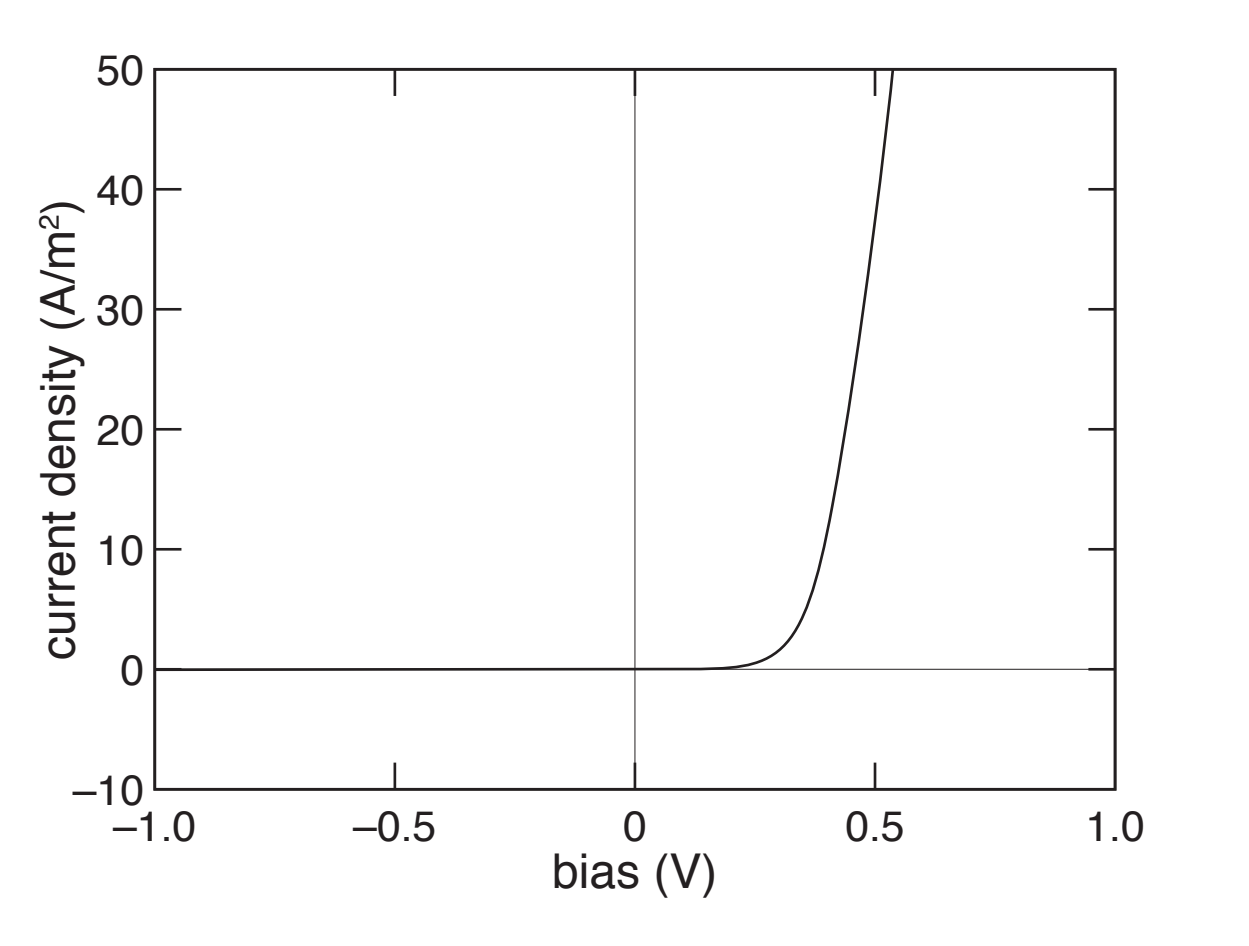
Optoelectronic properties

should have shallow junction below surface



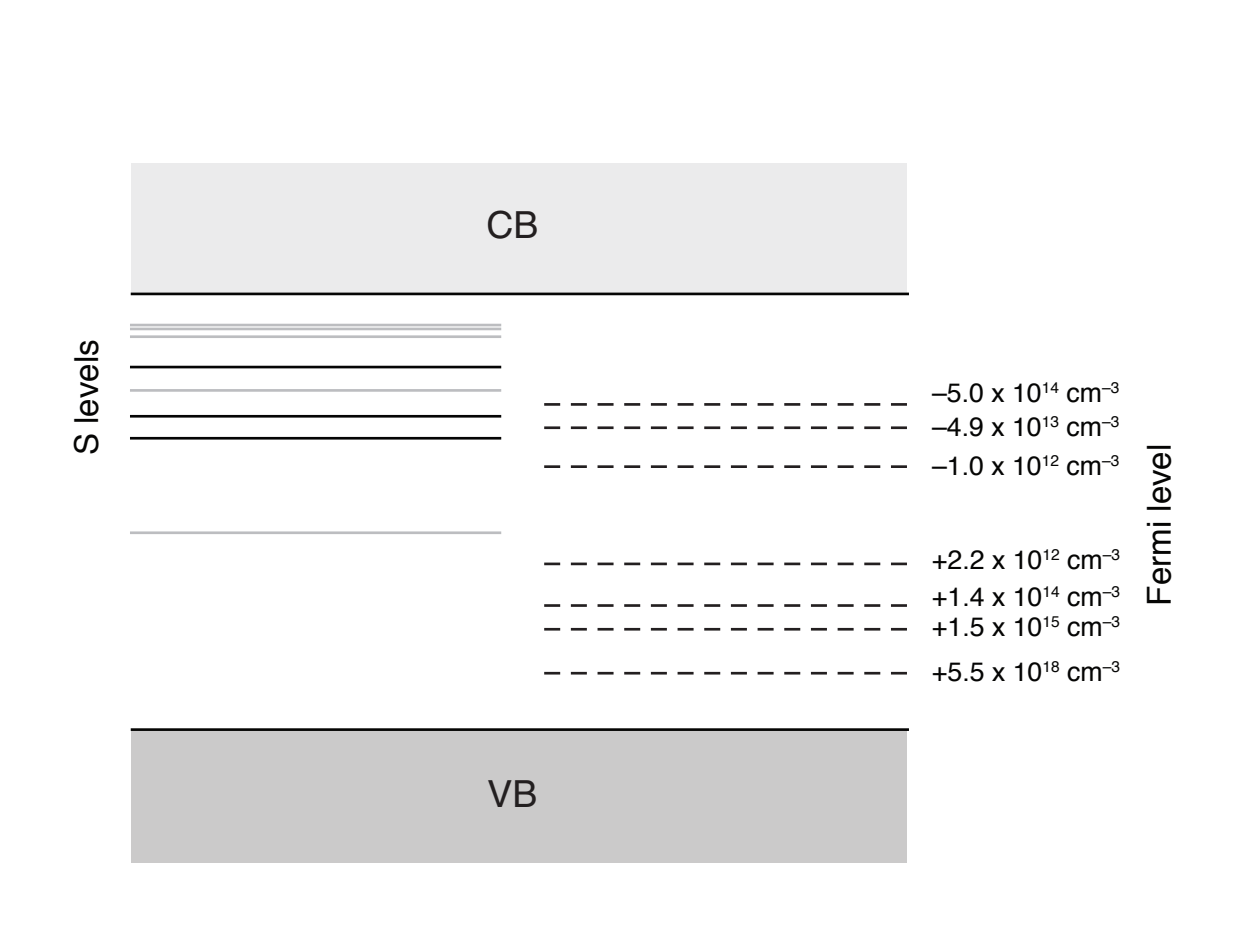
Optoelectronic properties

excellent rectification (after annealing)



Optoelectronic properties

probe impurity states by varying Fermi level in substrate



Optoelectronic properties

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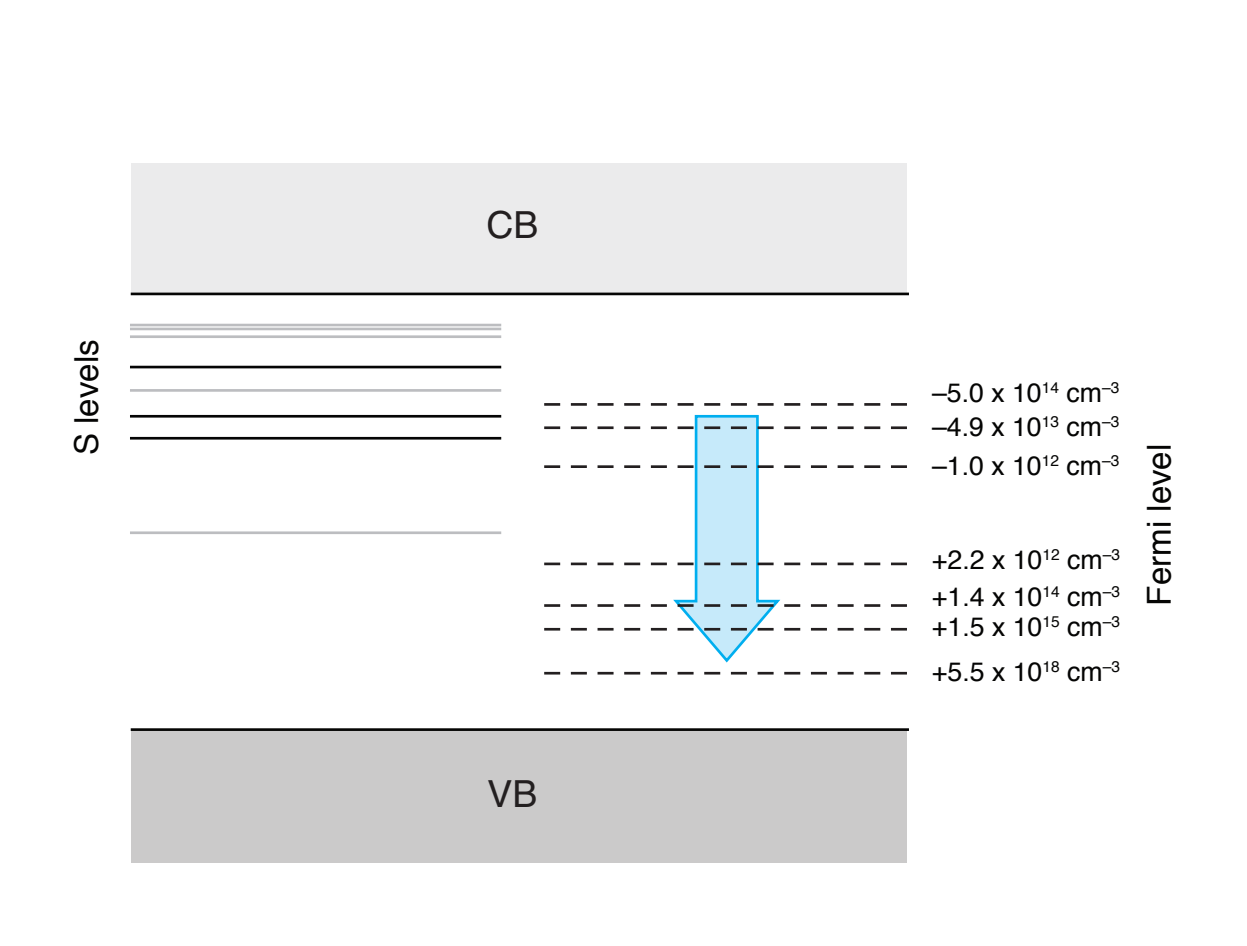
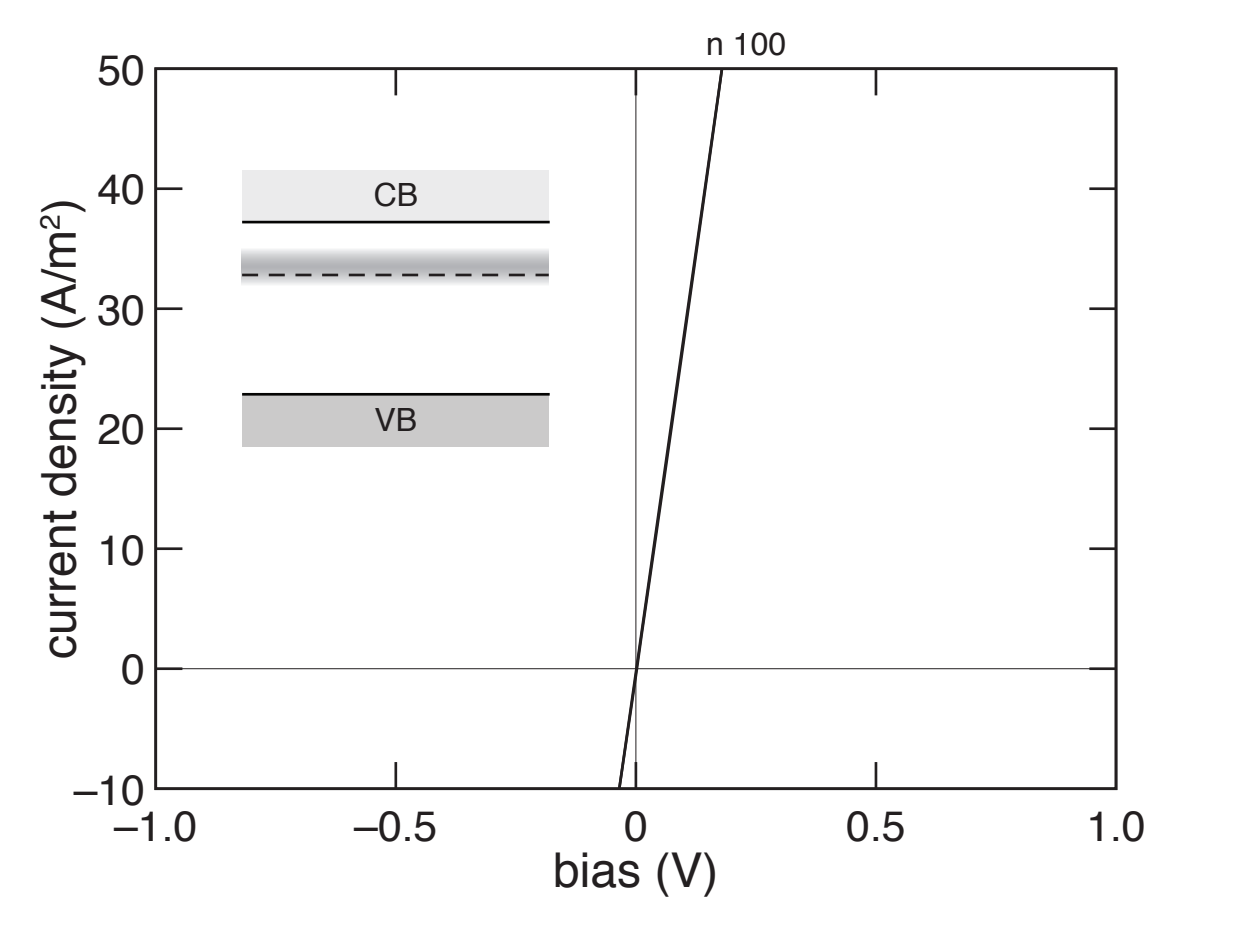


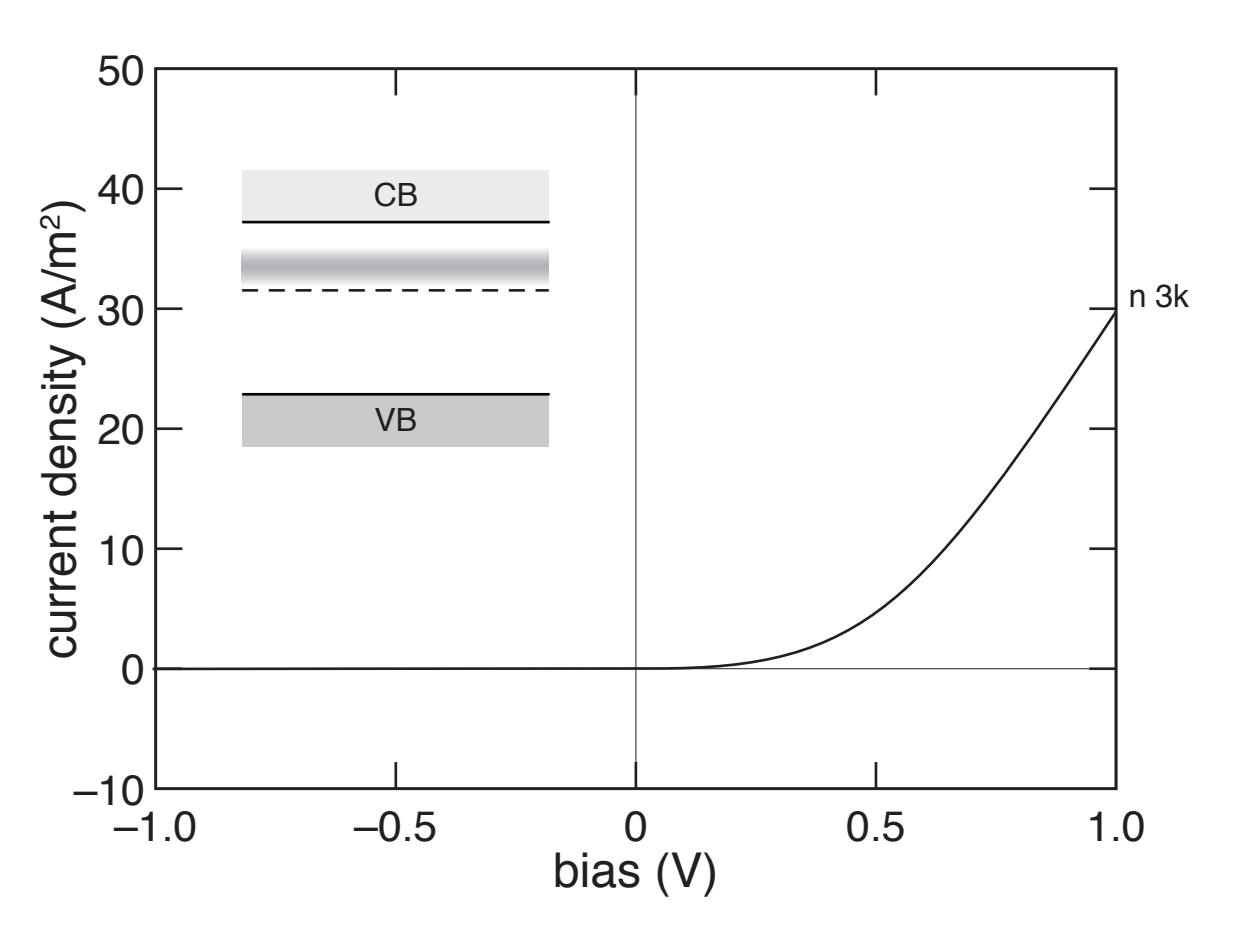
Optoelectronic properties

vary substrate doping type and resistivity



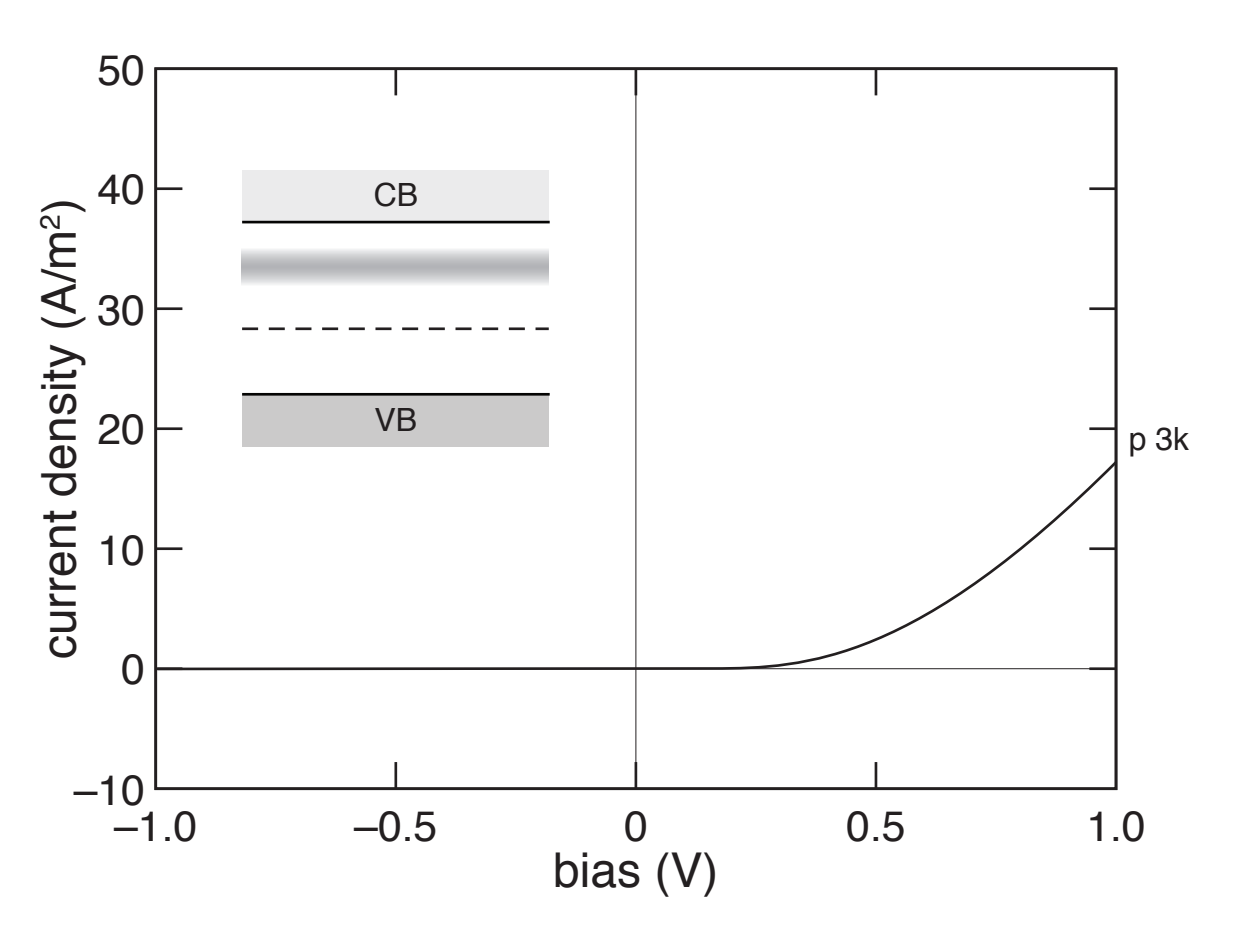
Optoelectronic properties

vary substrate doping type and resistivity



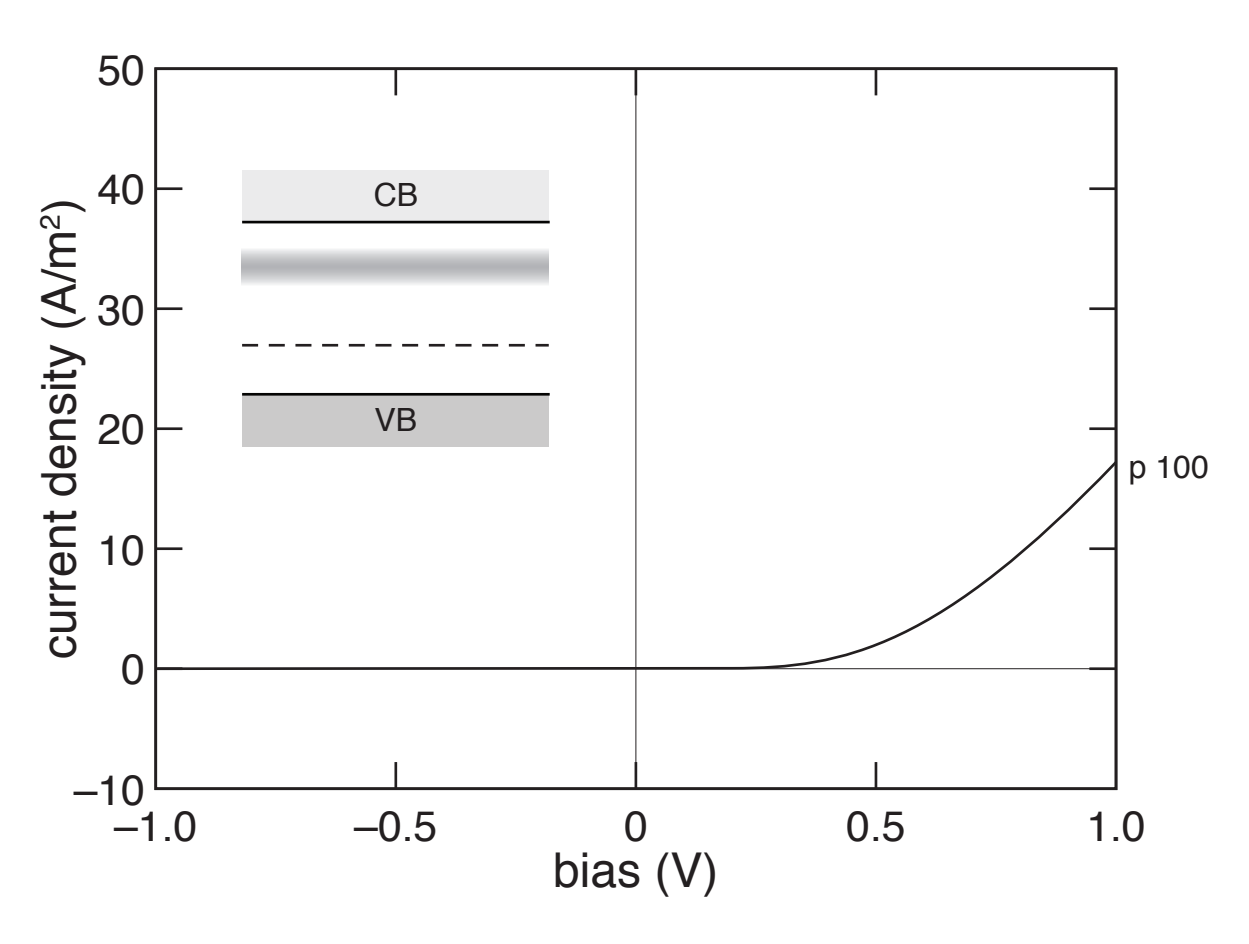
Optoelectronic properties

vary substrate doping type and resistivity



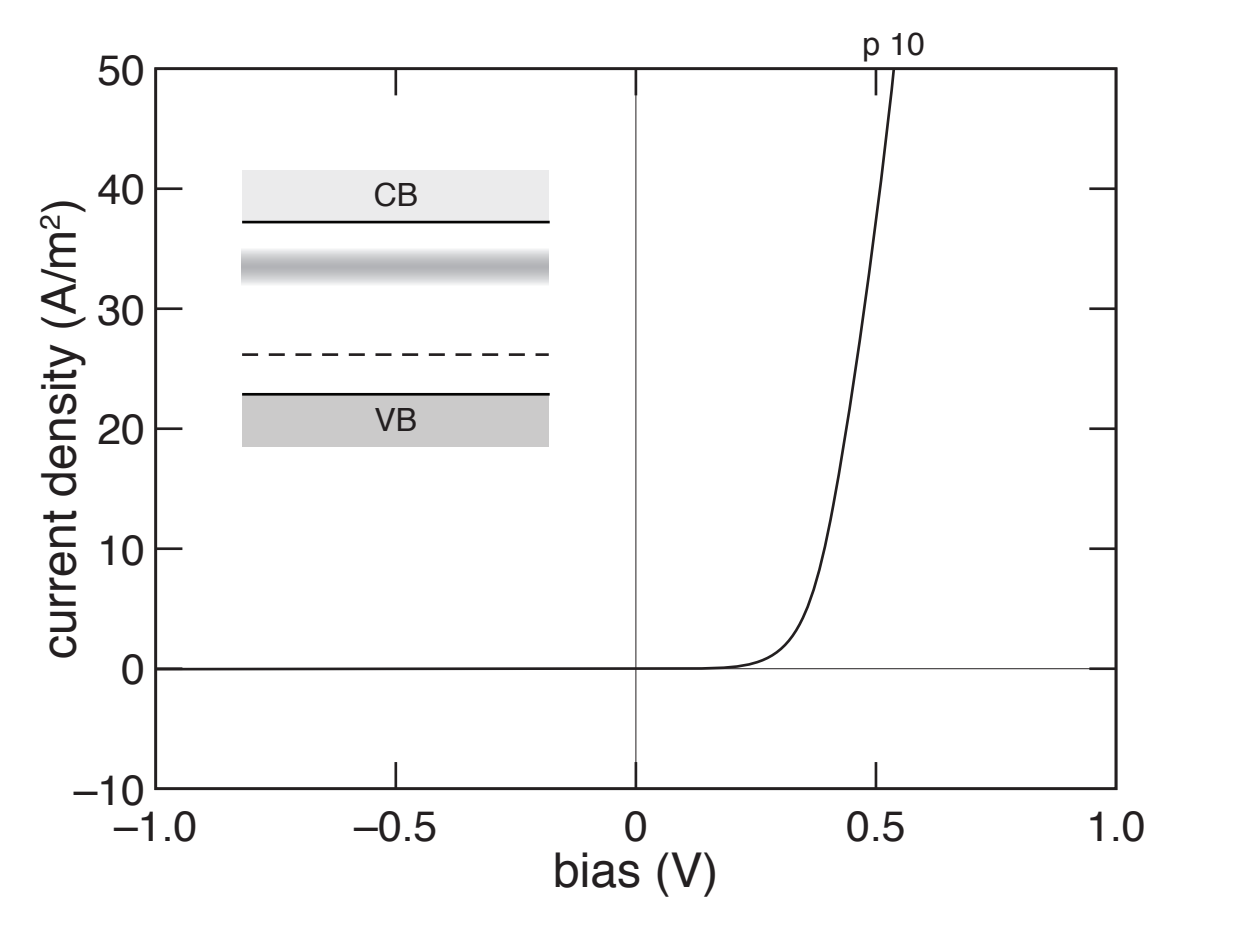
Optoelectronic properties

vary substrate doping type and resistivity



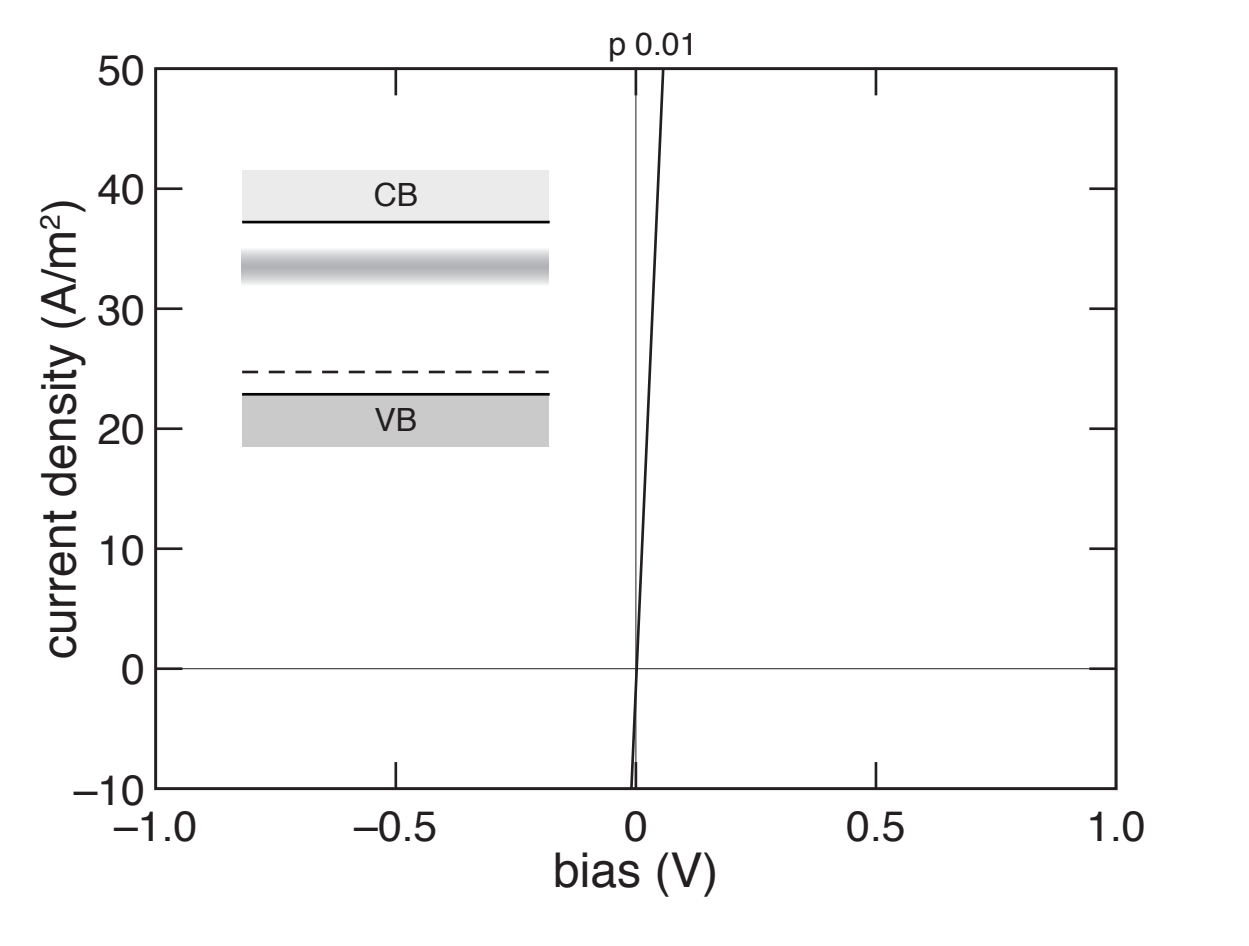
Optoelectronic properties

vary substrate doping type and resistivity



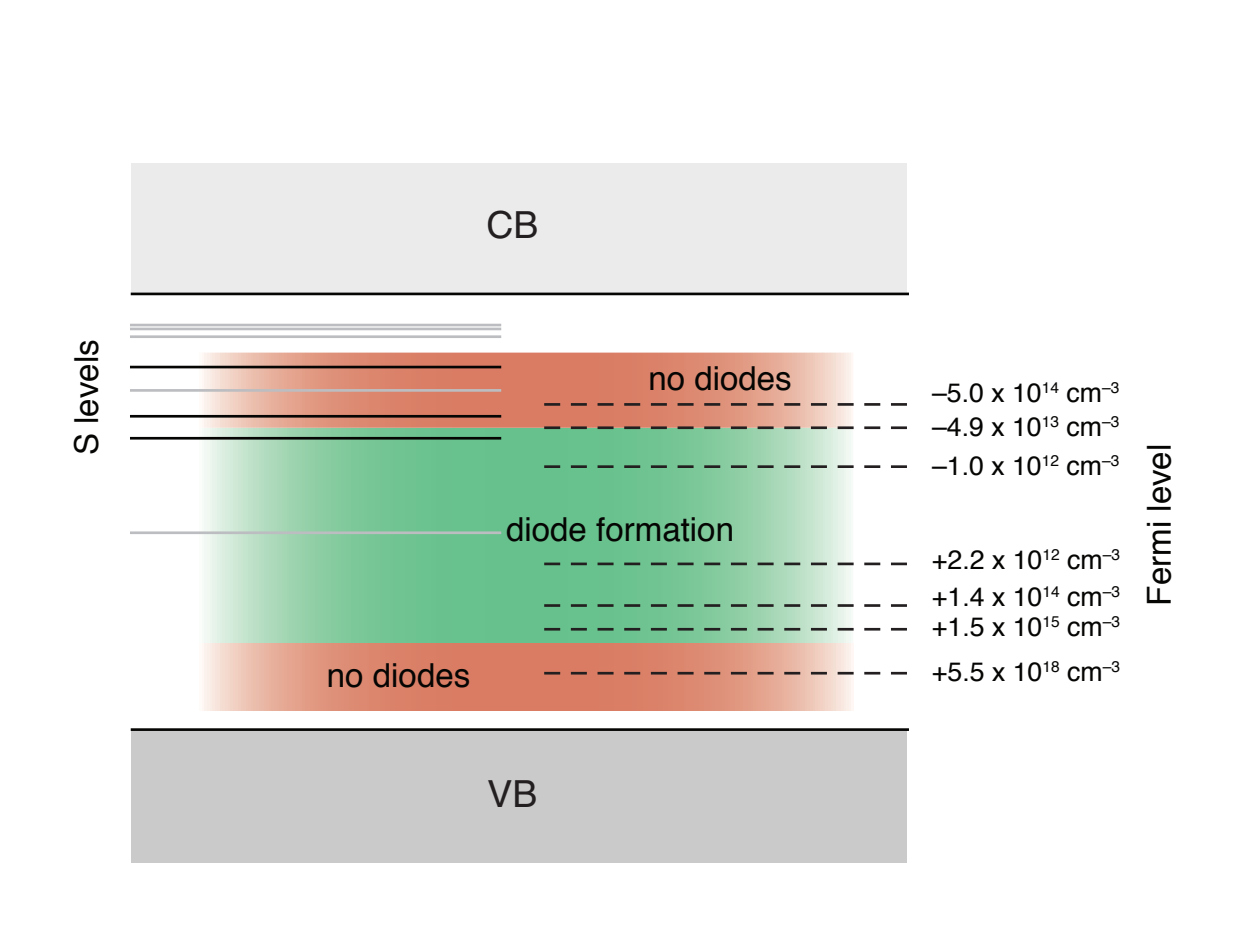
Optoelectronic properties

vary substrate doping type and resistivity



Optoelectronic properties

probe impurity states by varying Fermi level in substrate



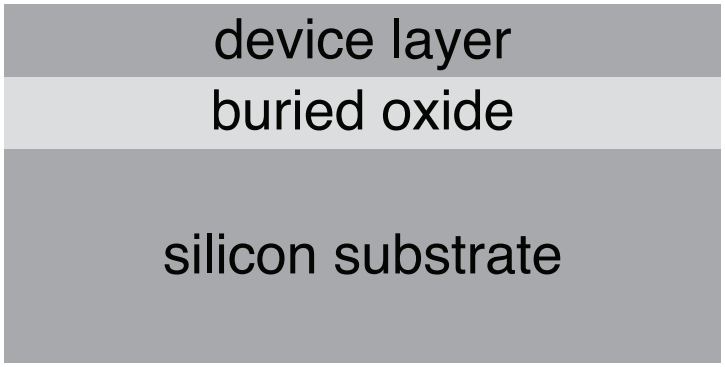
Optoelectronic properties

IV **behavior consistent with**

impurity band between 200 and 400 meV

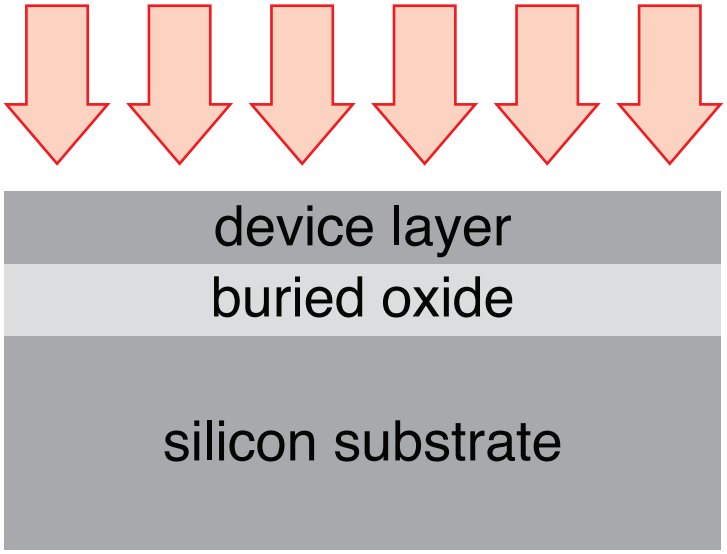
Optoelectronic properties

isolate surface layer for Hall measurements



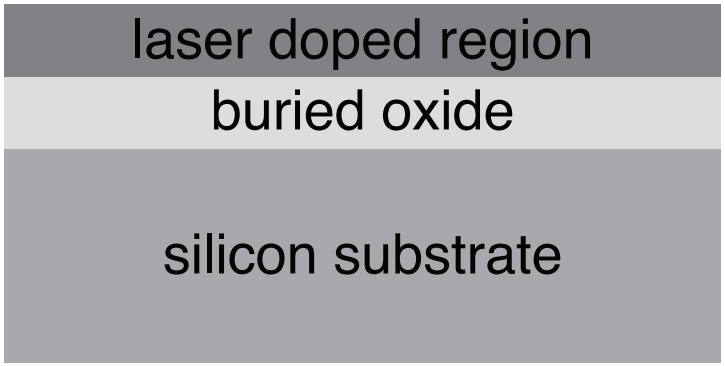
Optoelectronic properties

isolate surface layer for Hall measurements



Optoelectronic properties

isolate surface layer for Hall measurements



Optoelectronic properties

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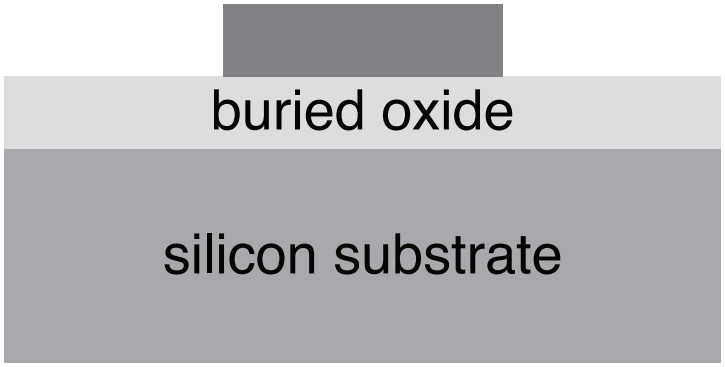

Optoelectronic properties

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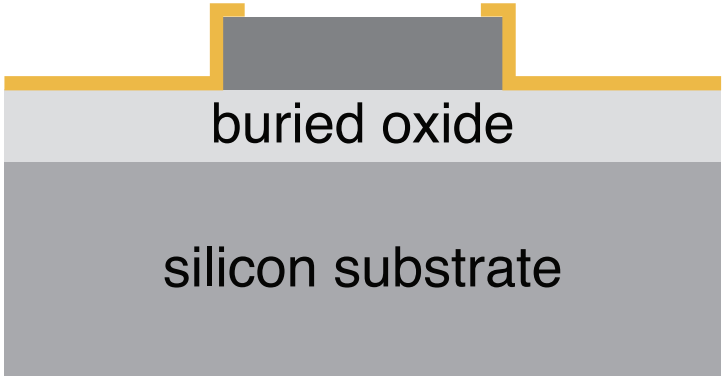
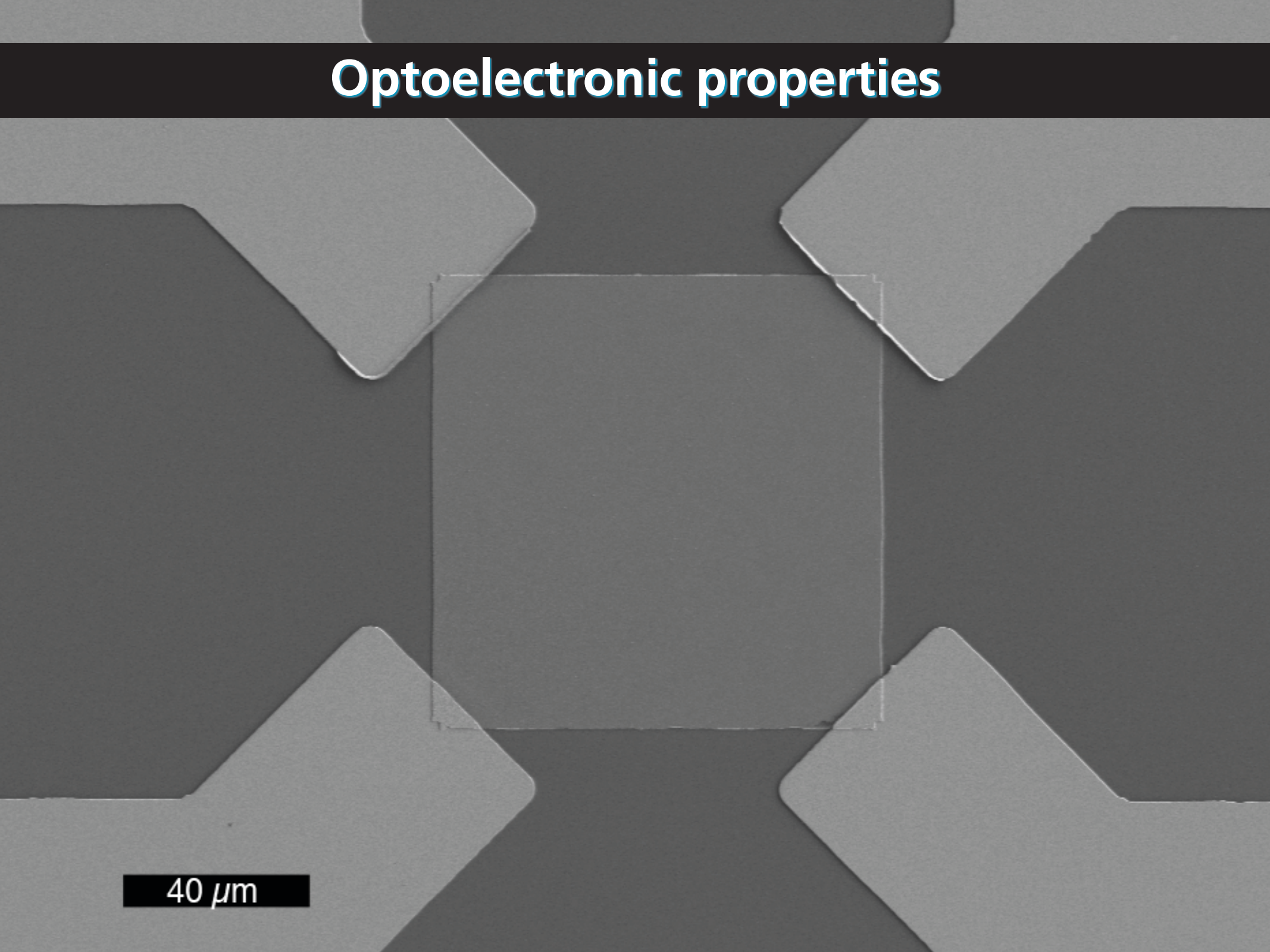
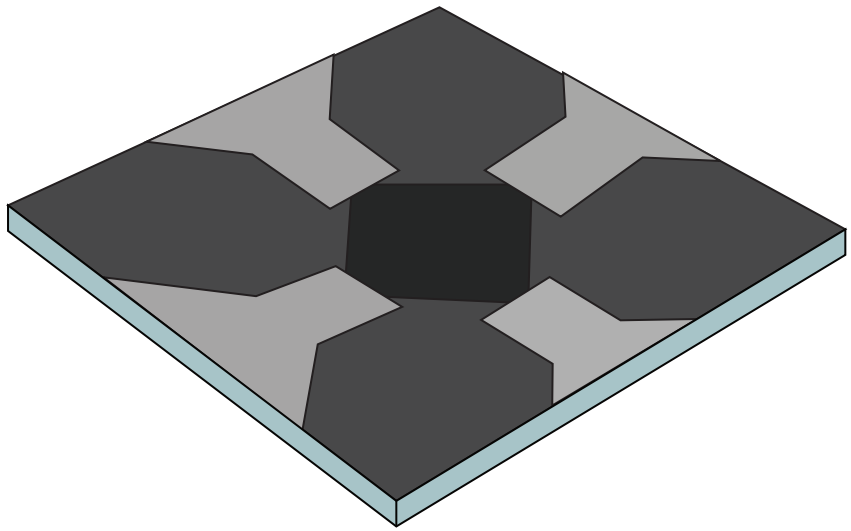


Optoelectronic properties



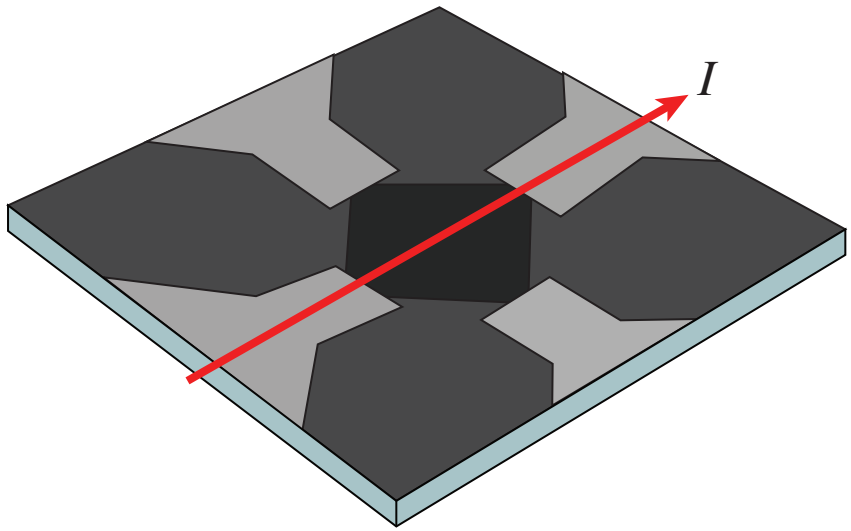
Optoelectronic properties

Hall measurements



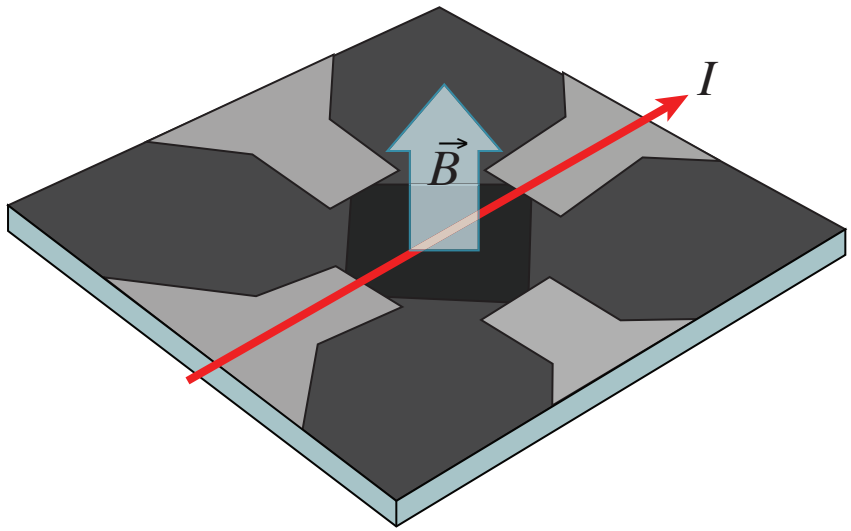
Optoelectronic properties

Hall measurements



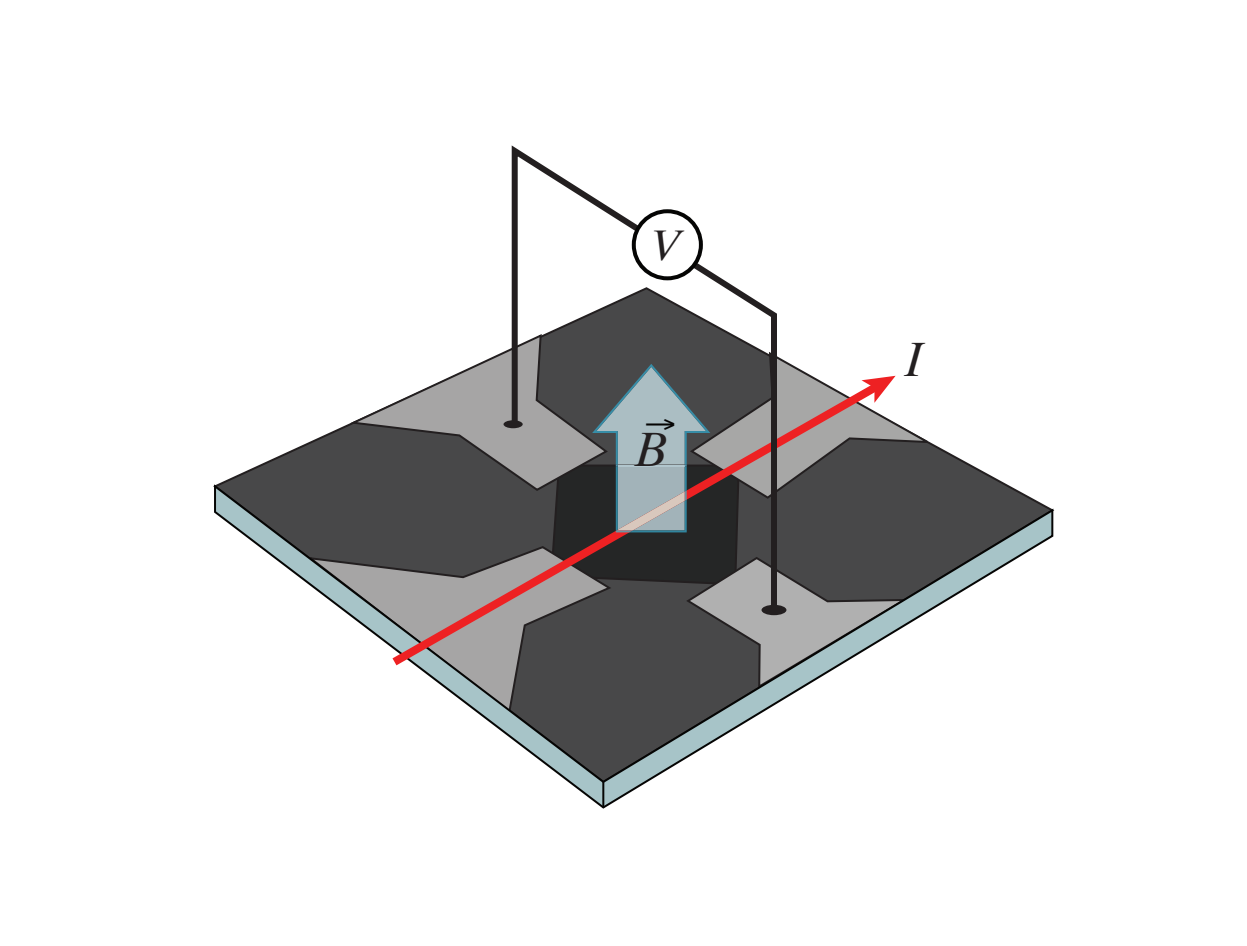
Optoelectronic properties

Hall measurements



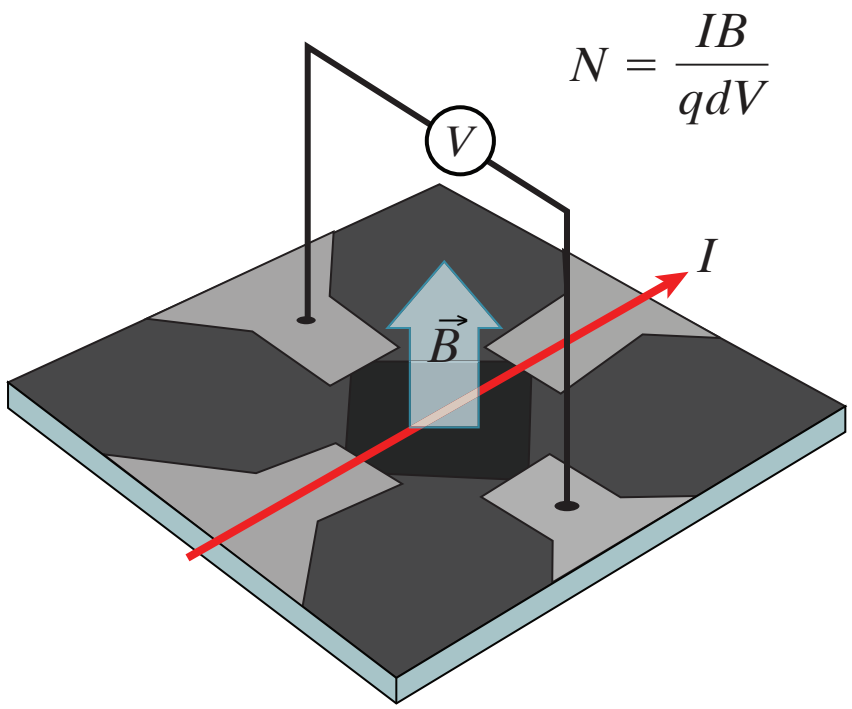
Optoelectronic properties

Hall measurements



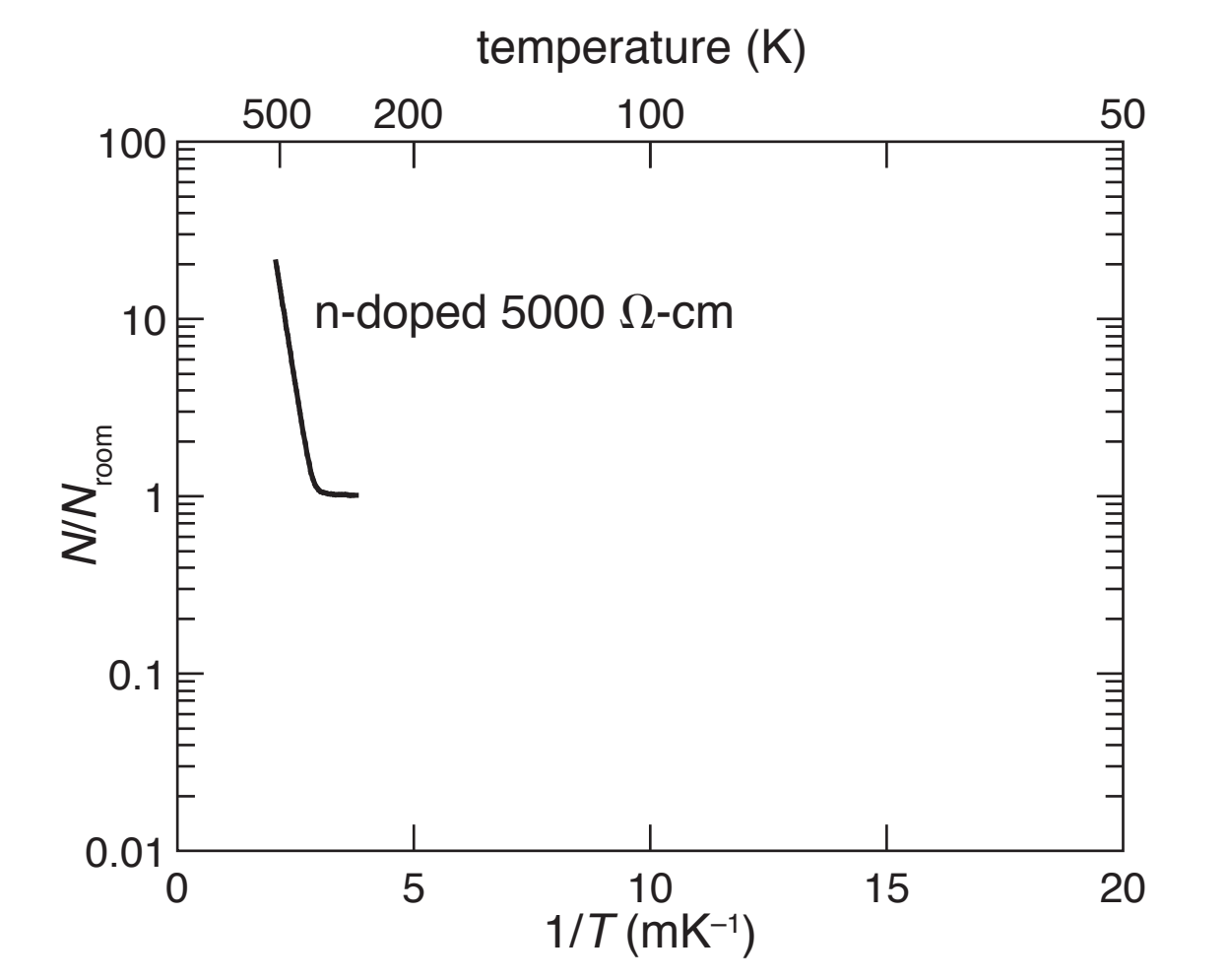
Optoelectronic properties

Hall measurements



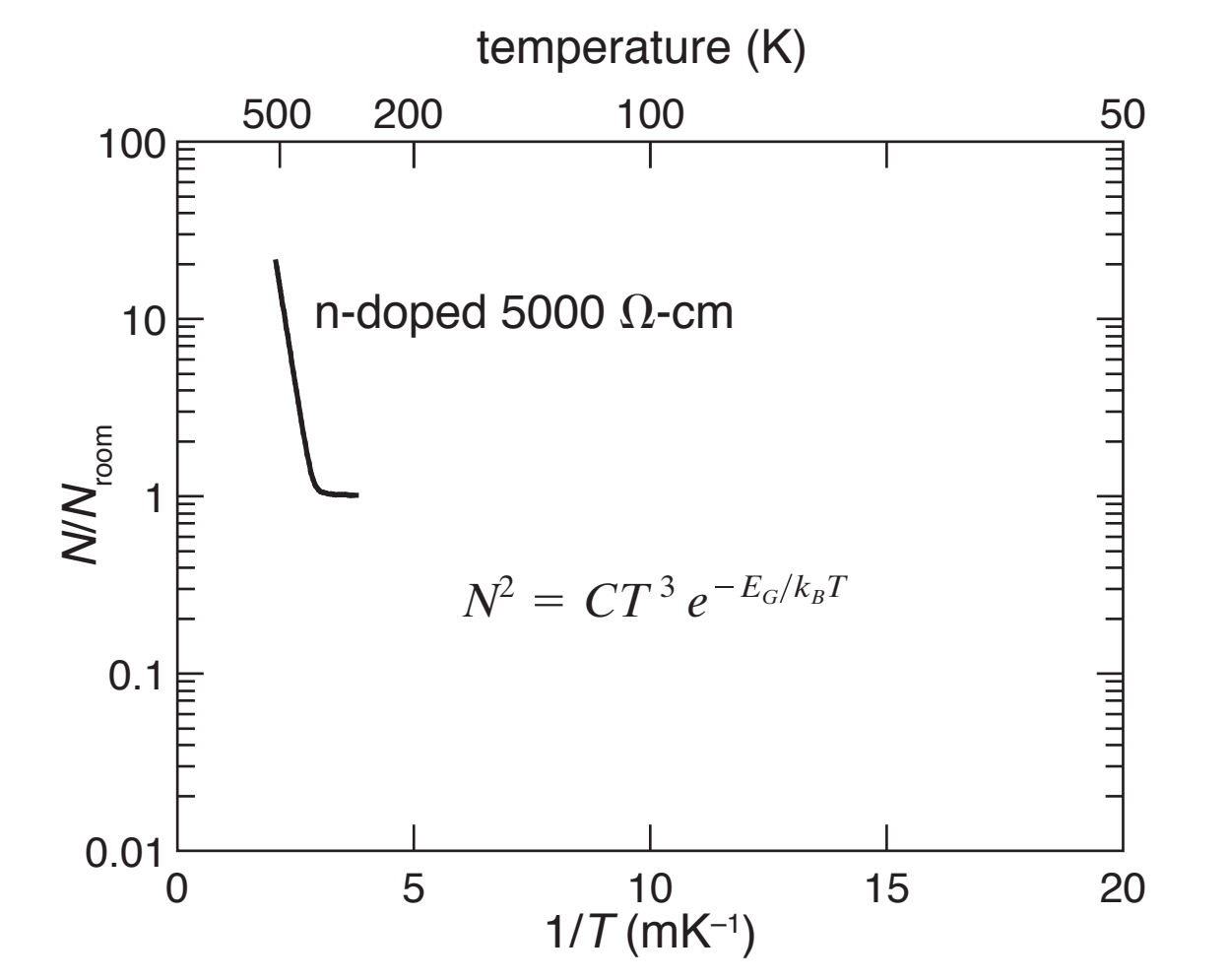
Optoelectronic properties

Hall measurements



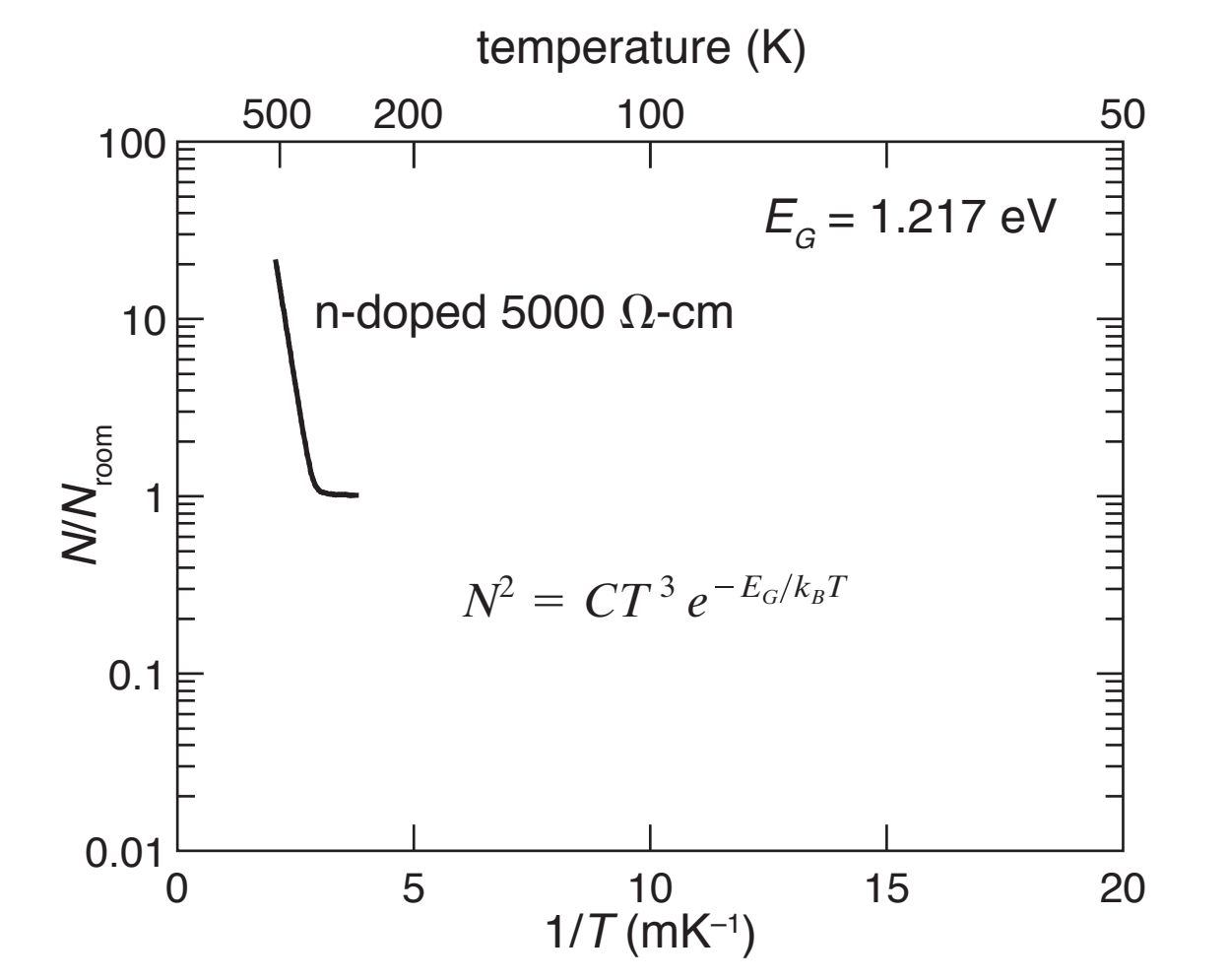
Optoelectronic properties

Hall measurements



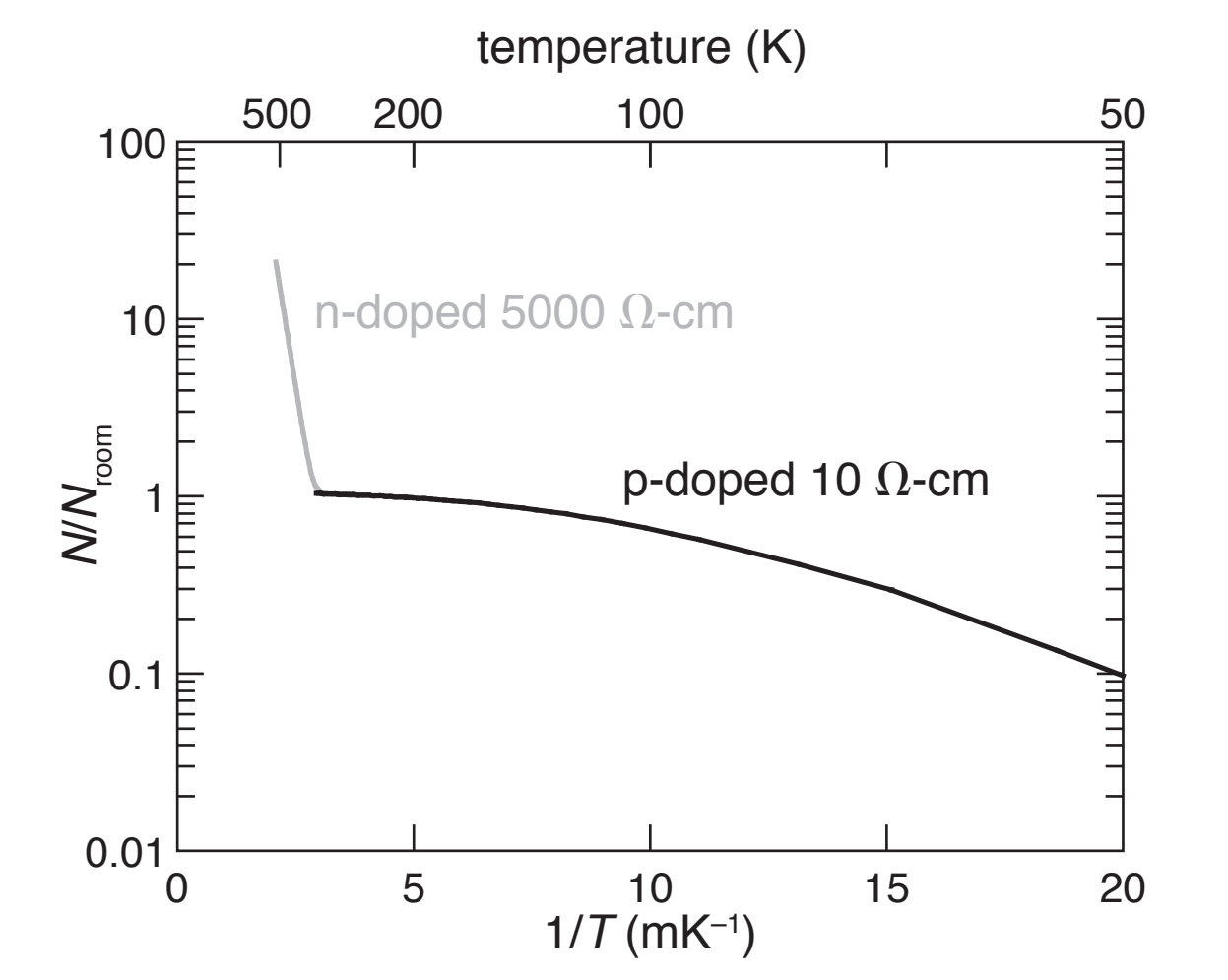
Optoelectronic properties

Hall measurements



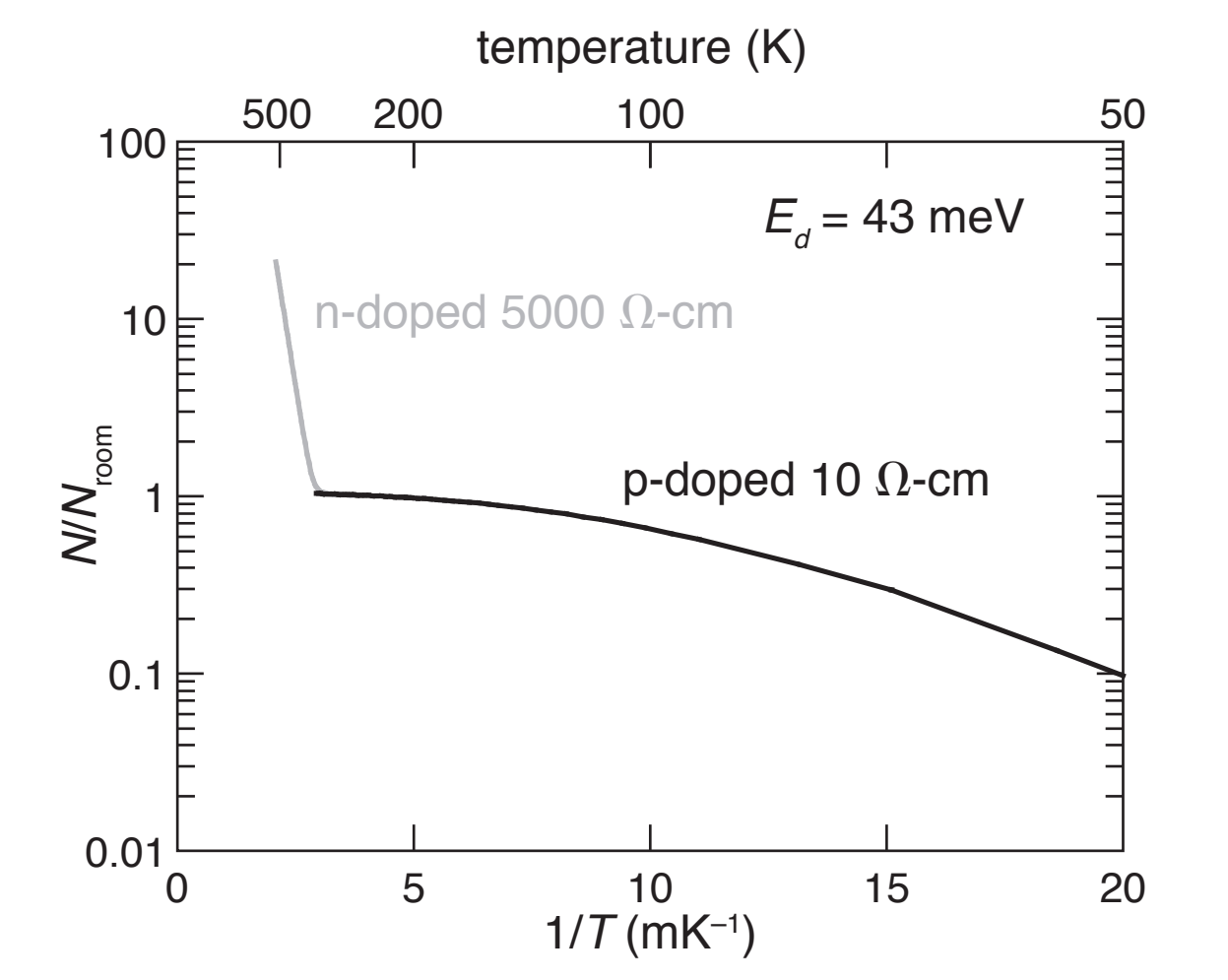
Optoelectronic properties

Hall measurements



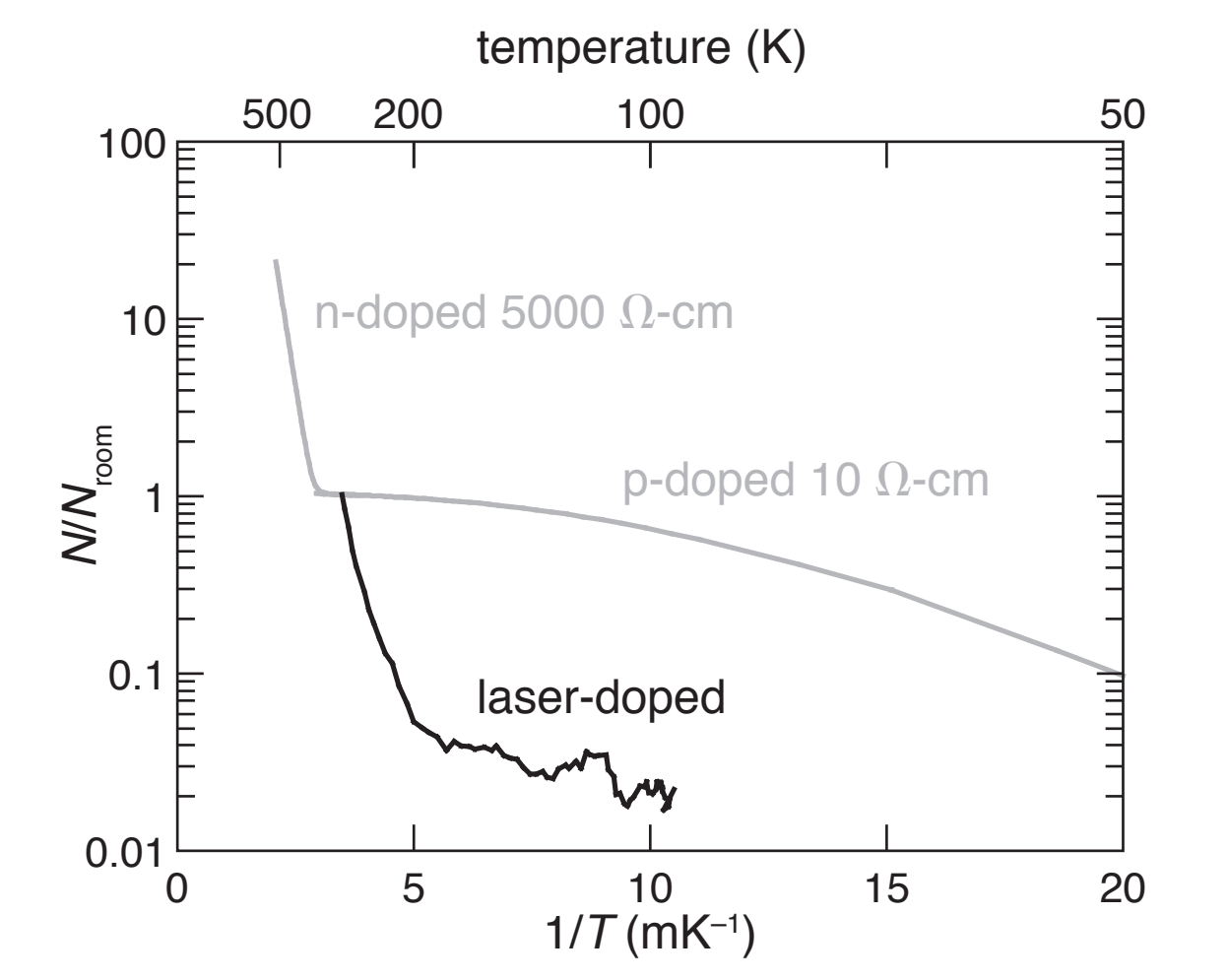
Optoelectronic properties

Hall measurements



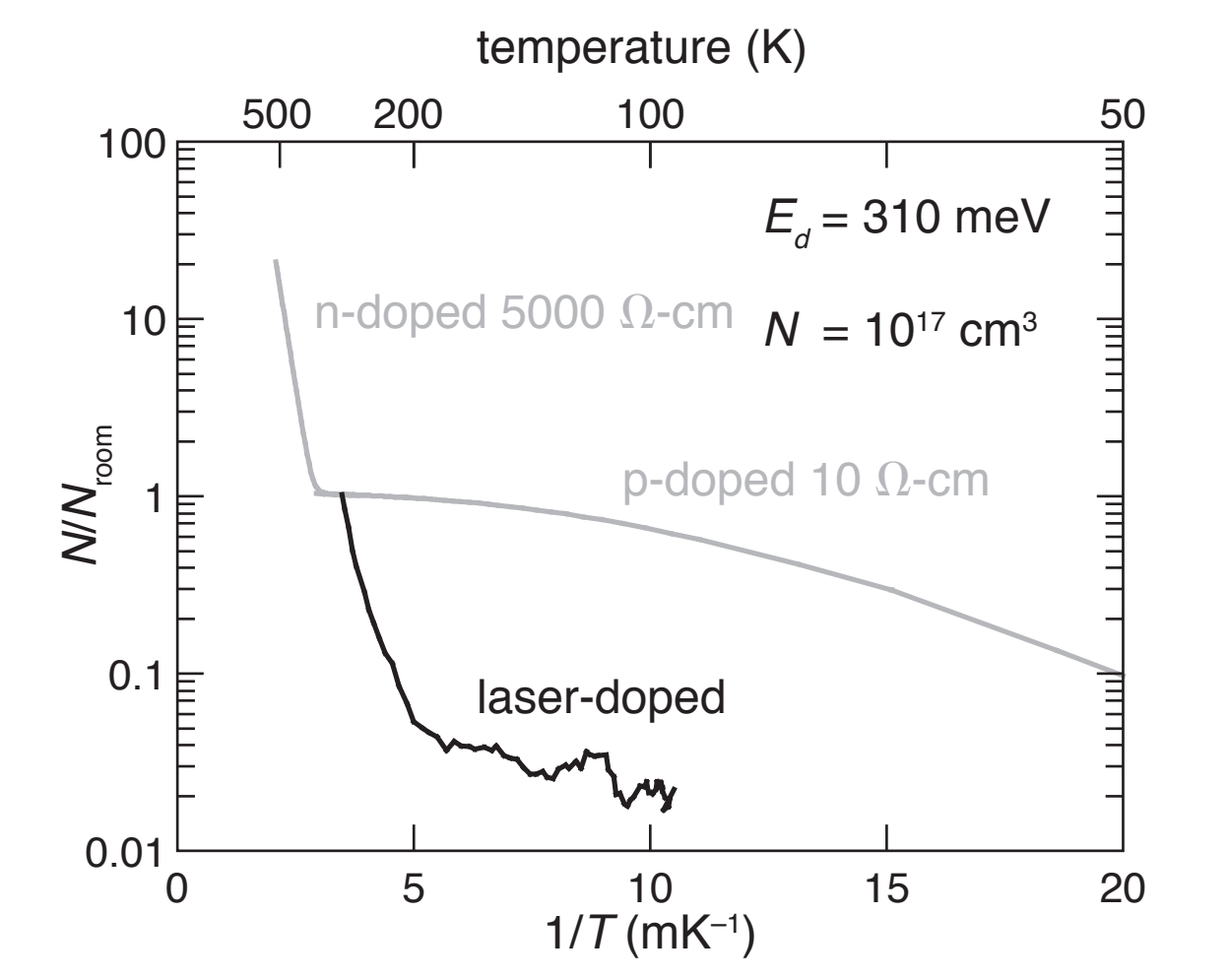
Optoelectronic properties

Hall measurements



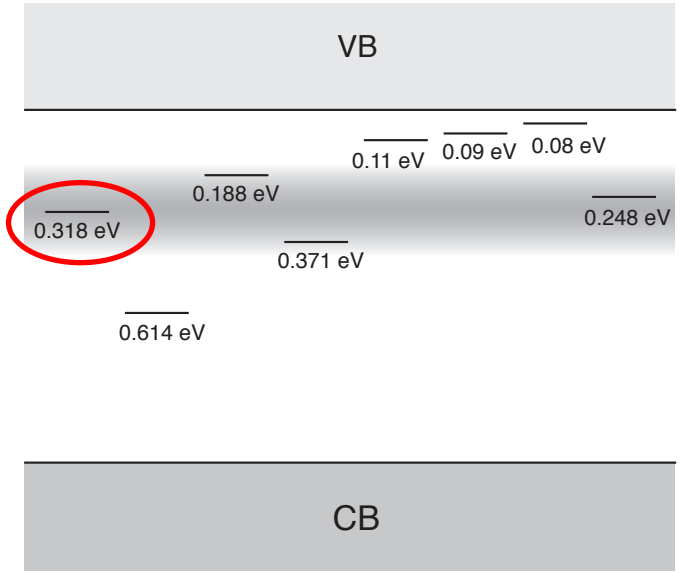
Optoelectronic properties

Hall measurements



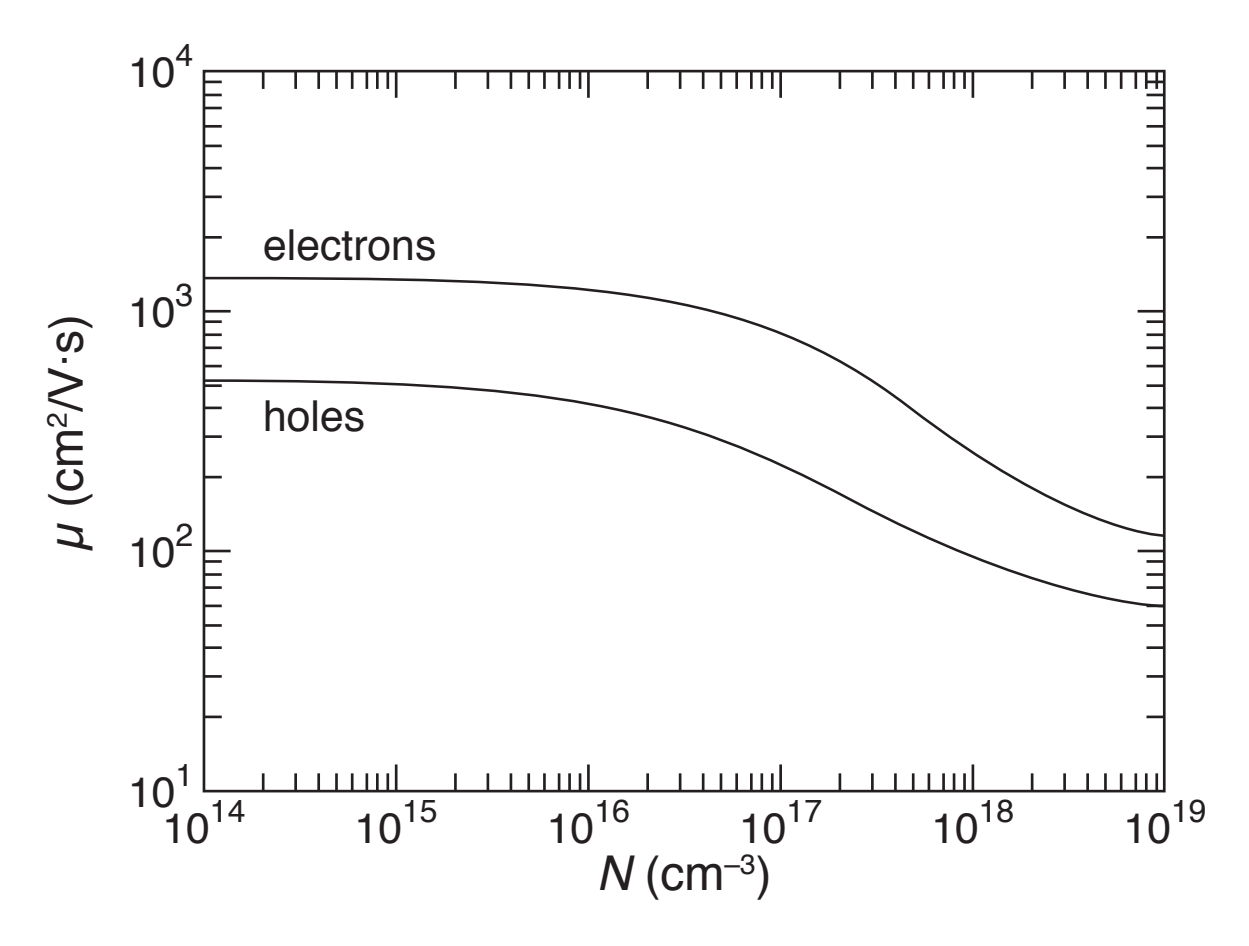
Optoelectronic properties

impurity (donor) band centered at 310 meV



Optoelectronic properties

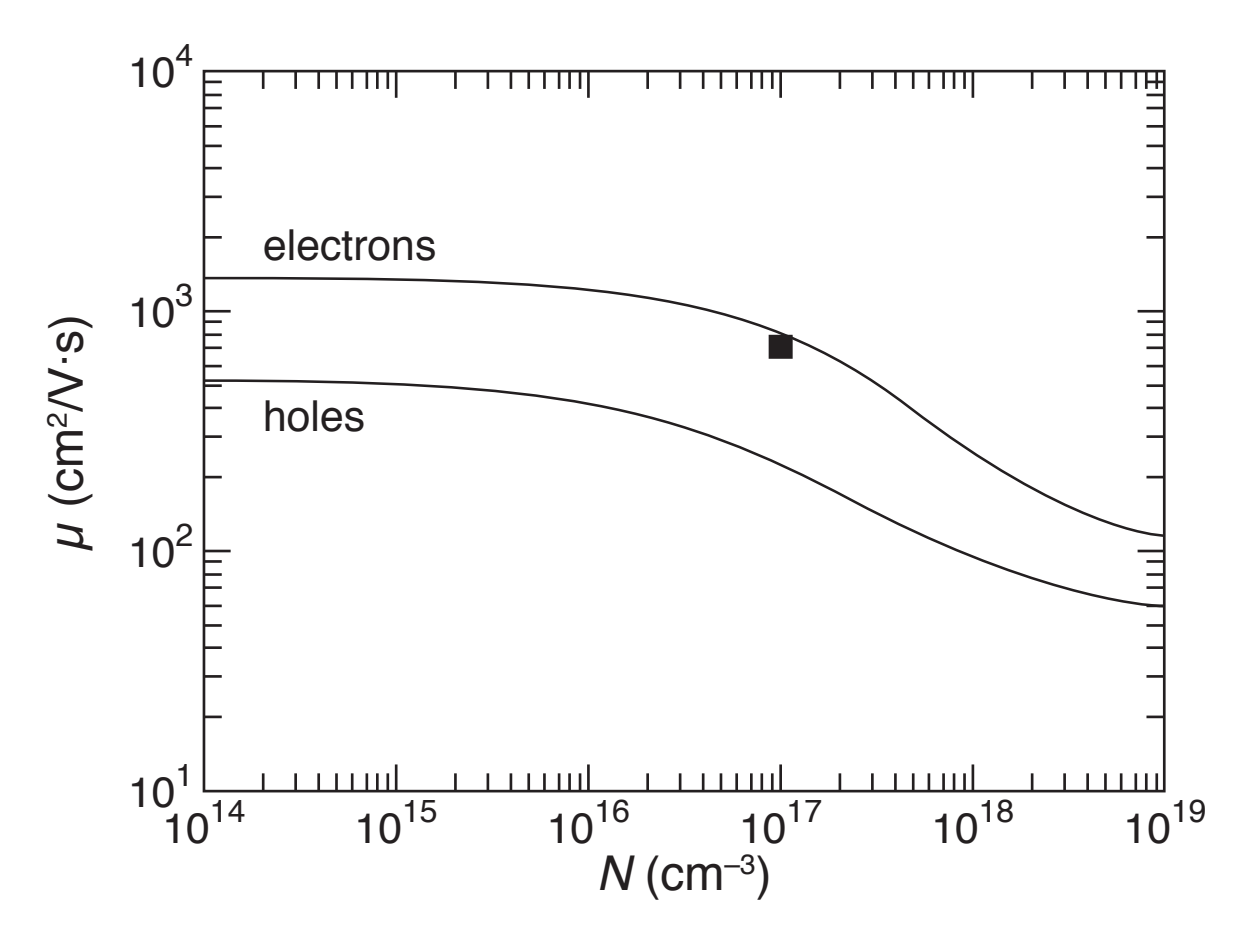
majority carrier mobility



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

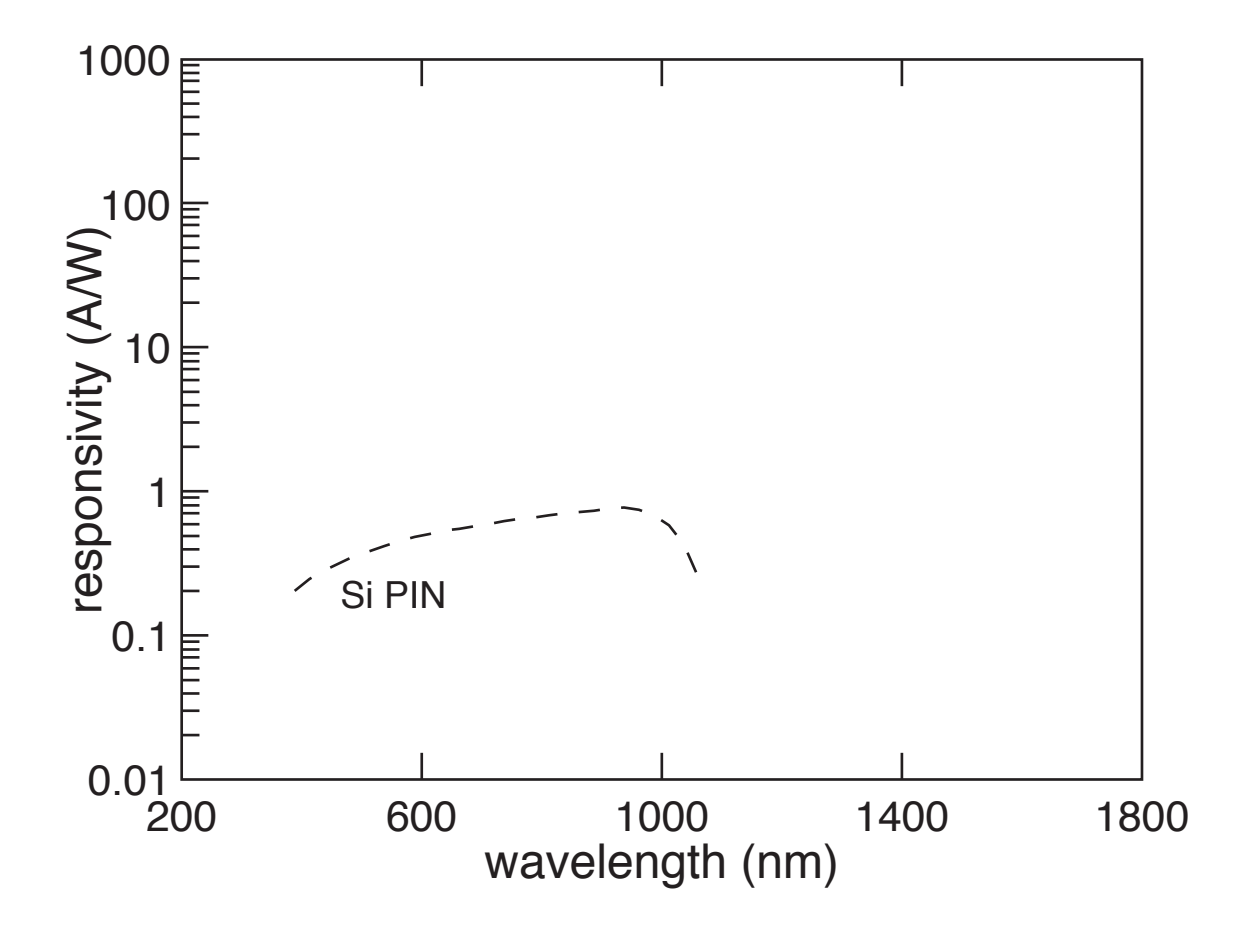
- IR absorption rolls off around 8 μm
- 1 in 10^3 sulfur atoms are ionized donors at 300 K
- all data indicate these S donors are substitutional

Outline

- structure
- optoelectronic properties
- devices

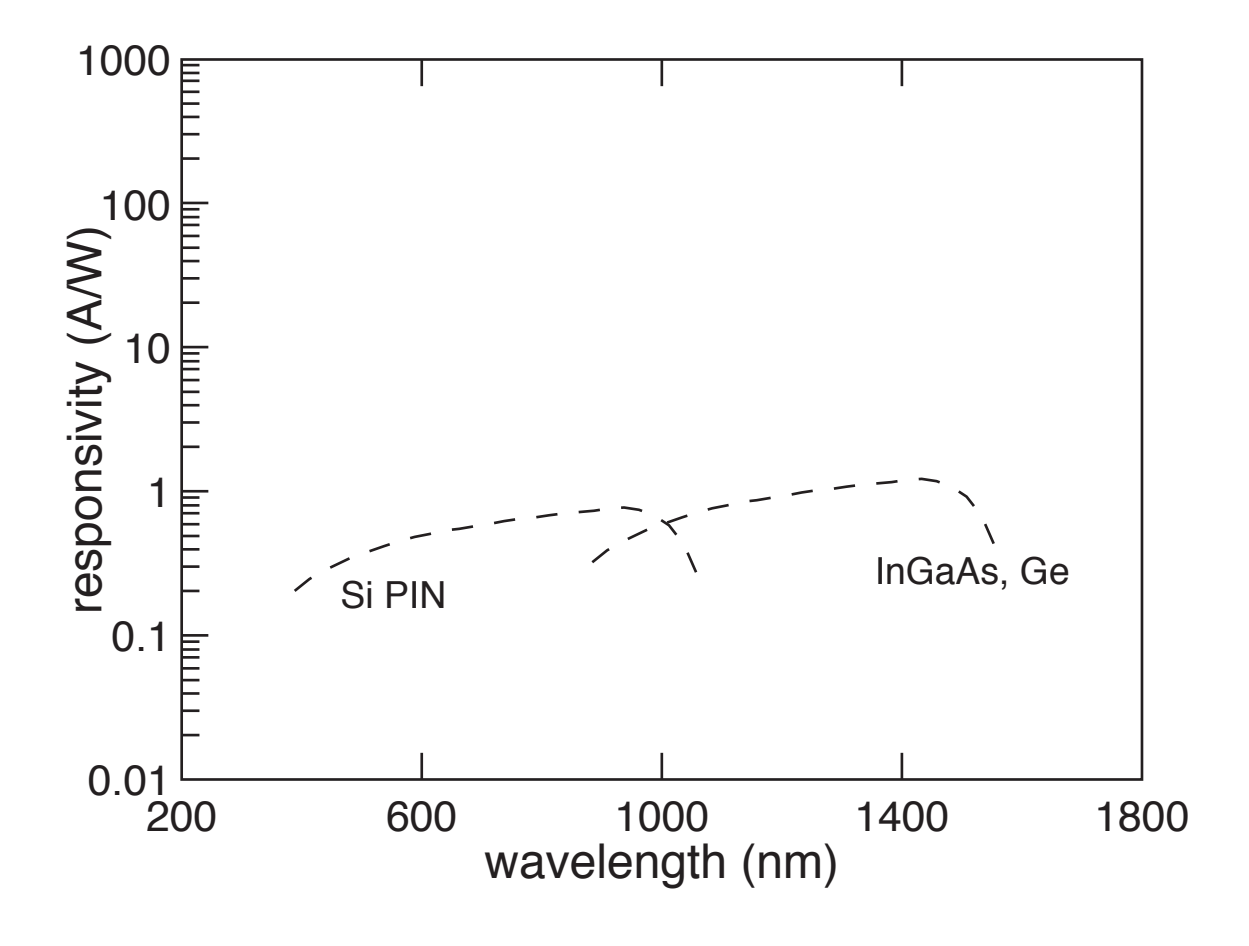
Devices

responsivity



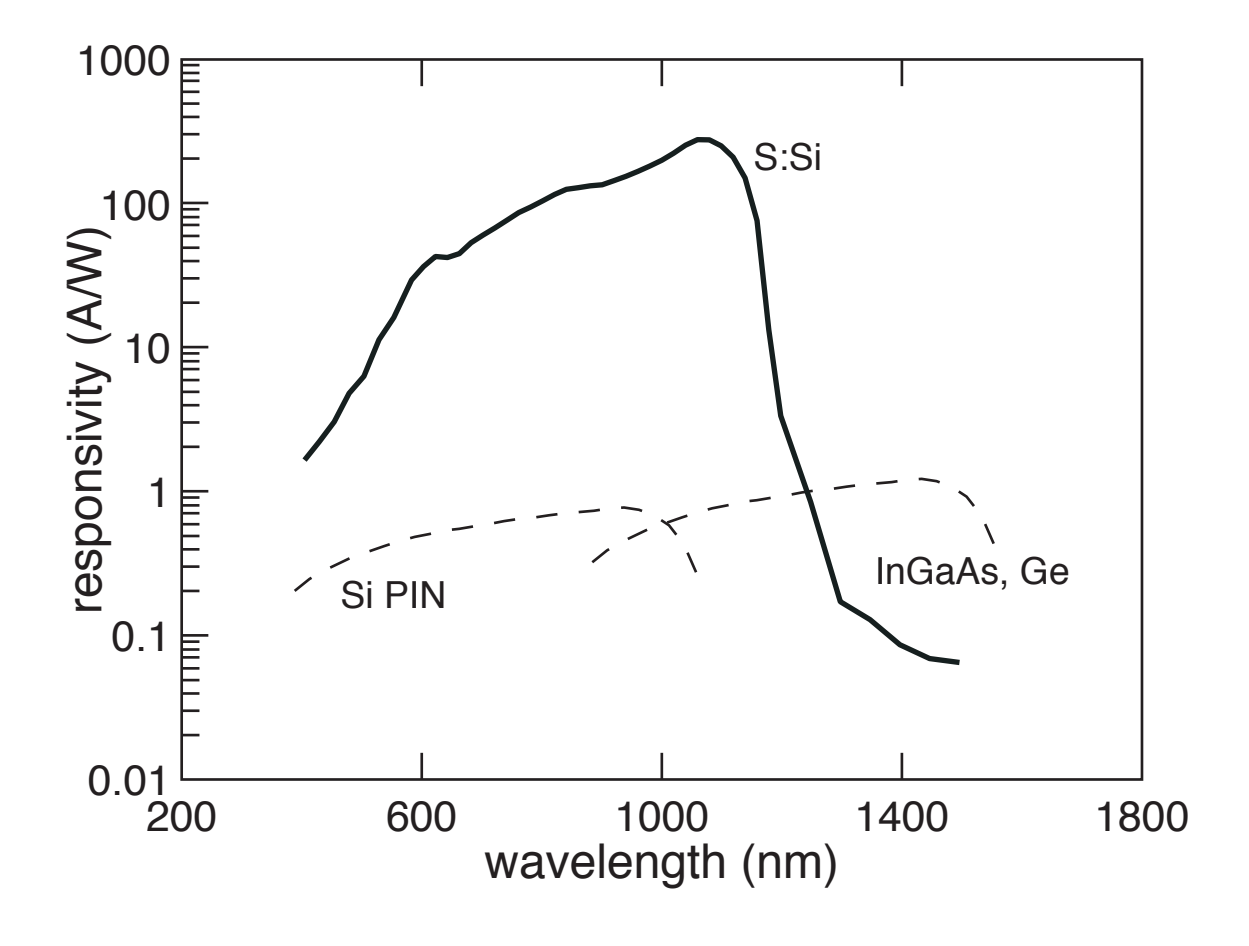
Devices

responsivity



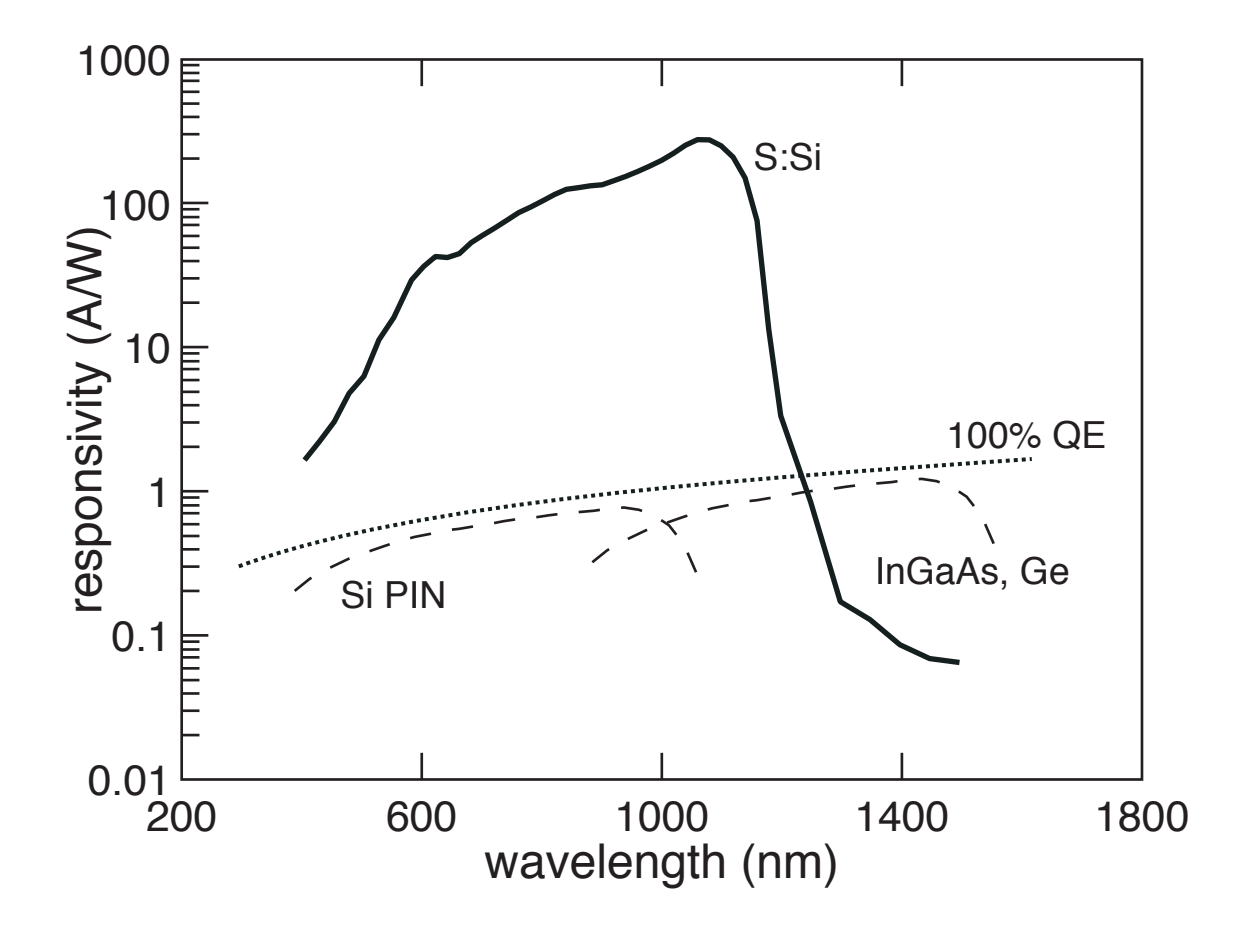
Devices

responsivity



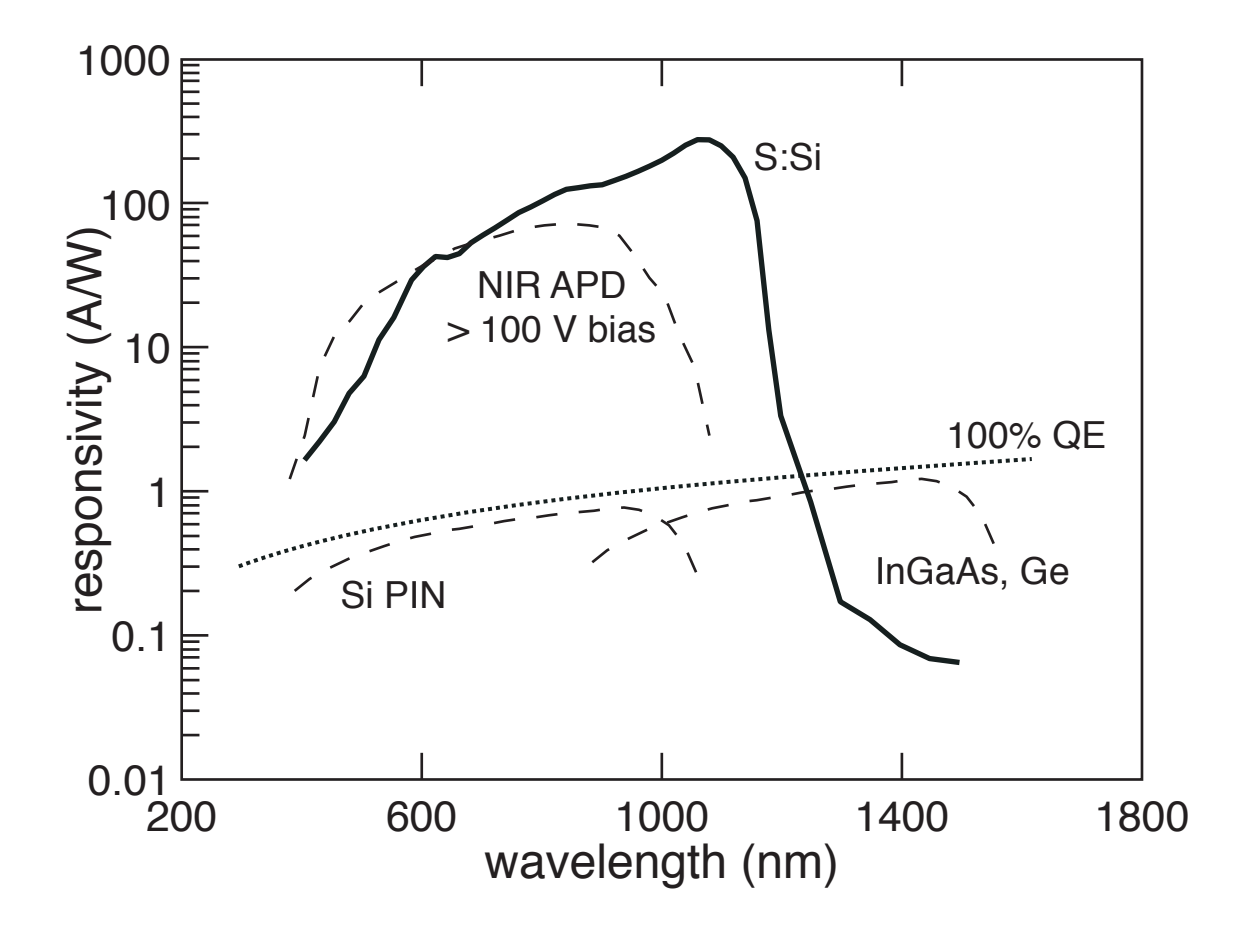
Devices

responsivity



Devices

responsivity

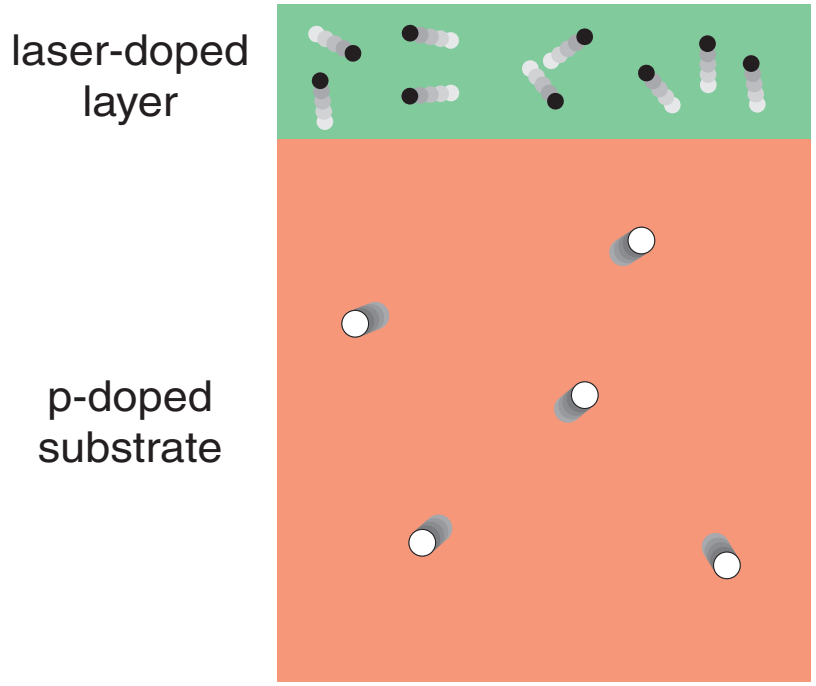


Devices

What causes gain?

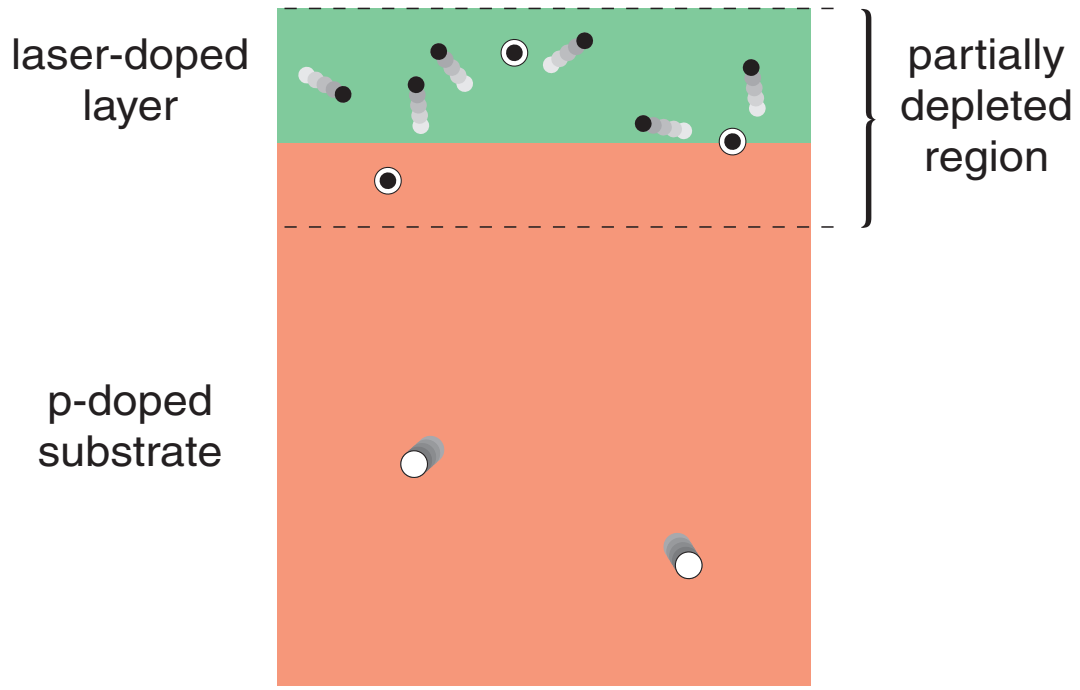
- impact excitation (avalanching)
- carrier lifetime >> transit time (photoconductive gain)
- some other mechanism

Devices



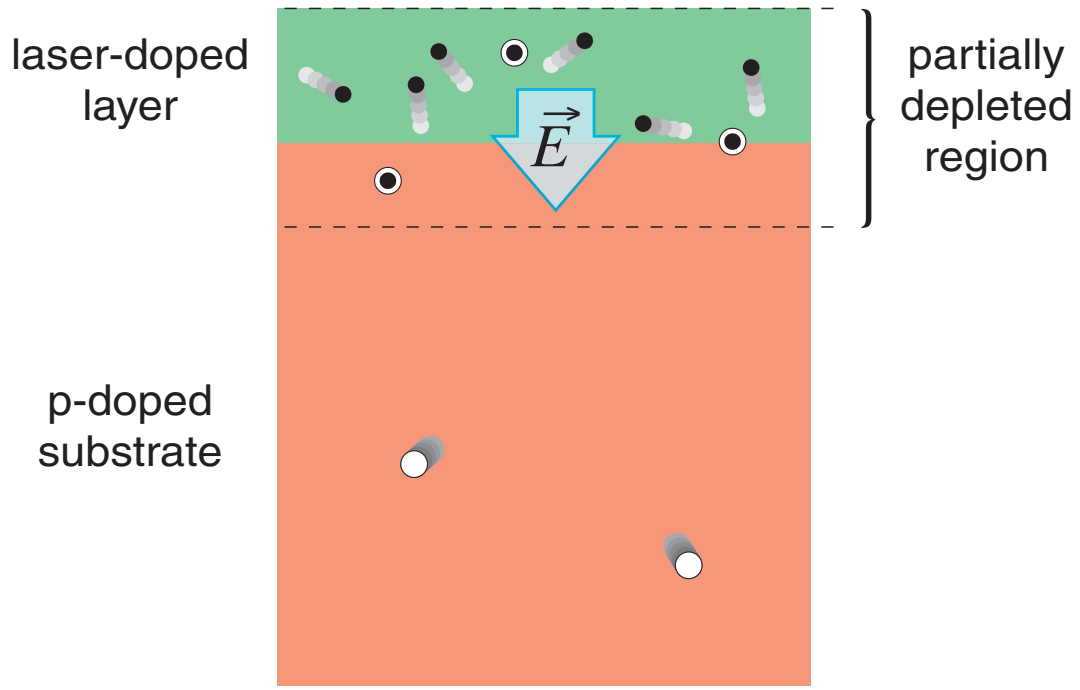
“pl junction”

Devices



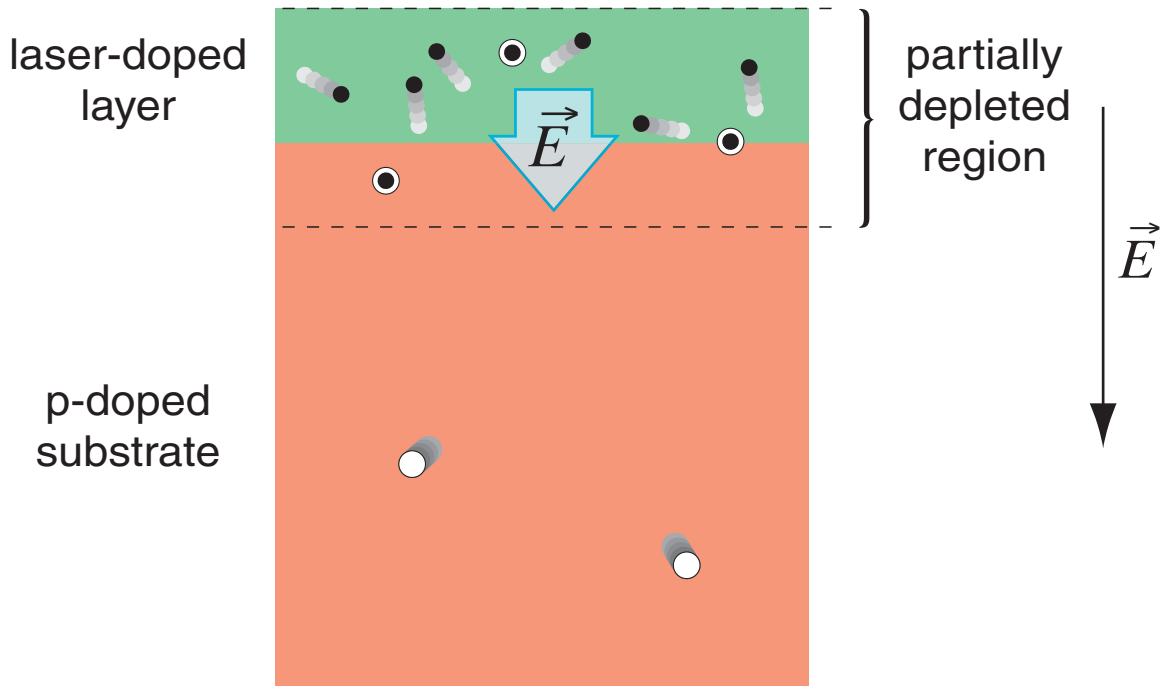
formation of partially depleted region

Devices



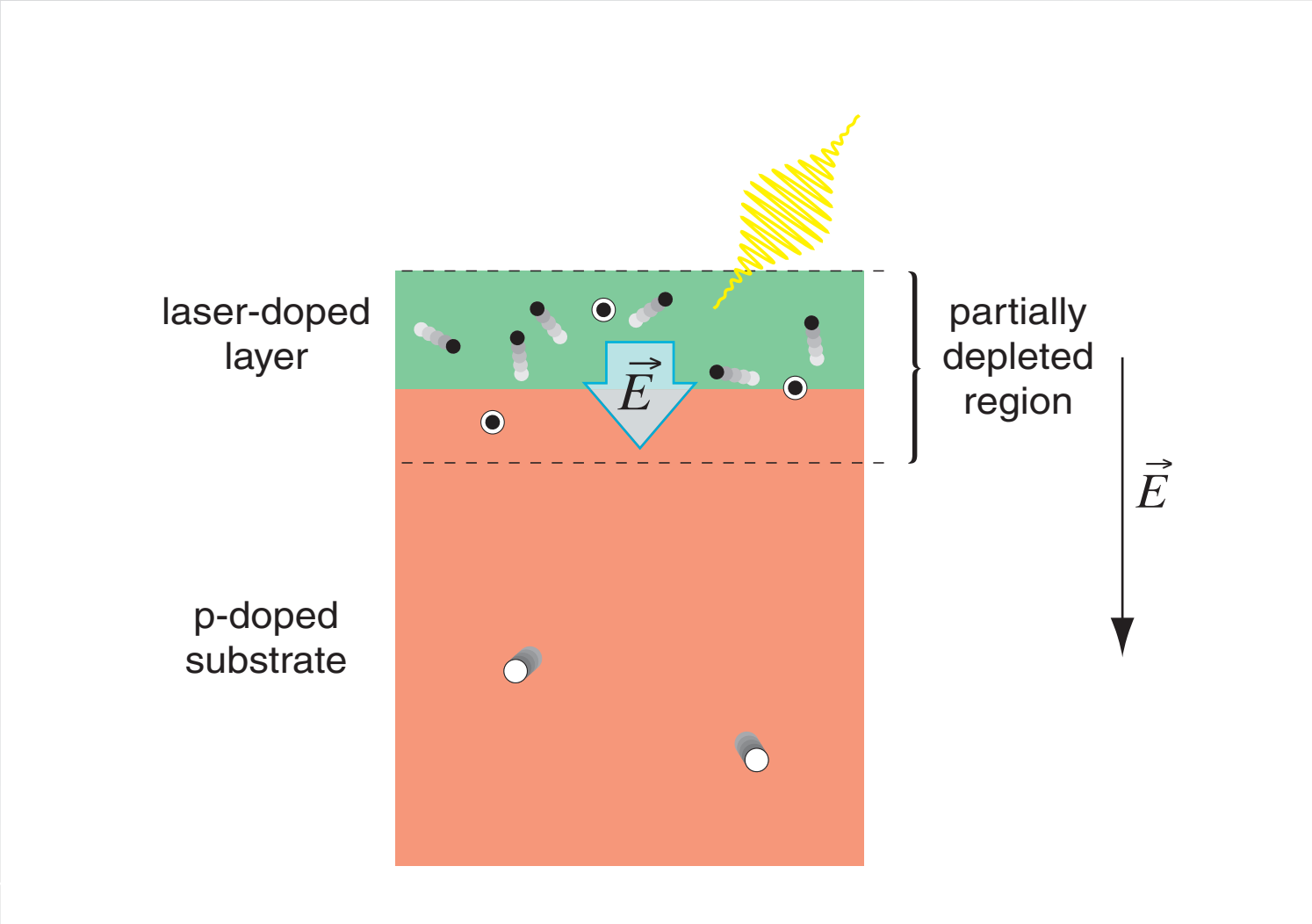
formation of partially depleted region

Devices



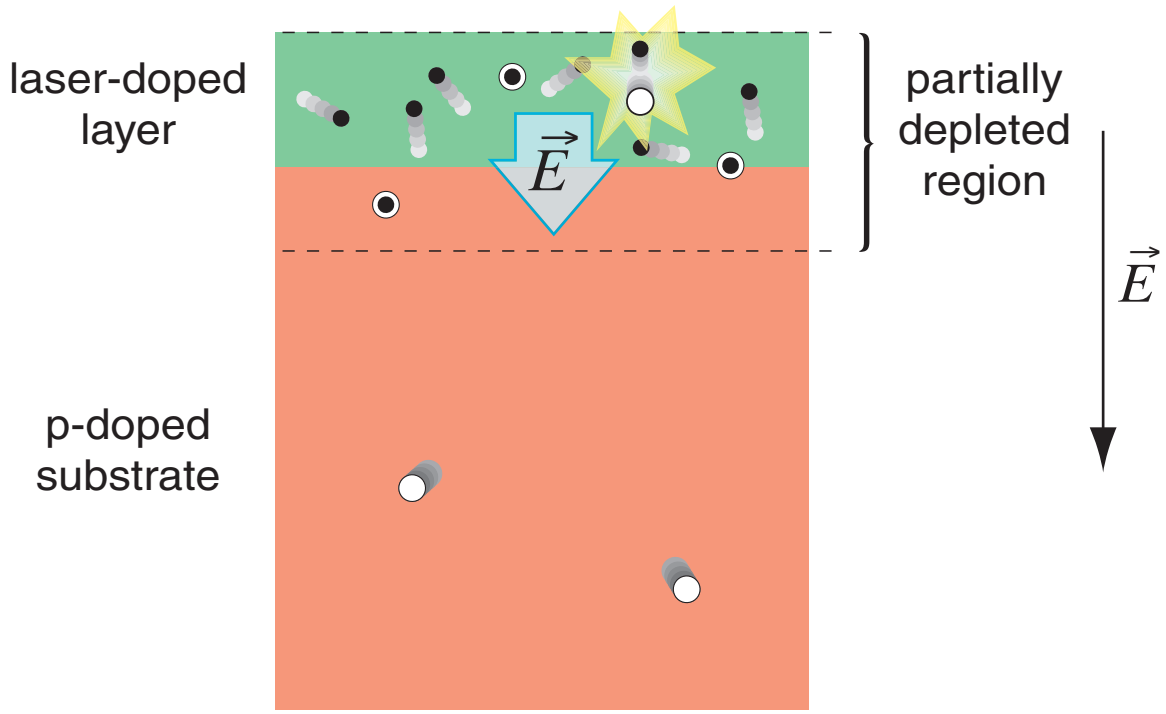
apply backward bias…

Devices



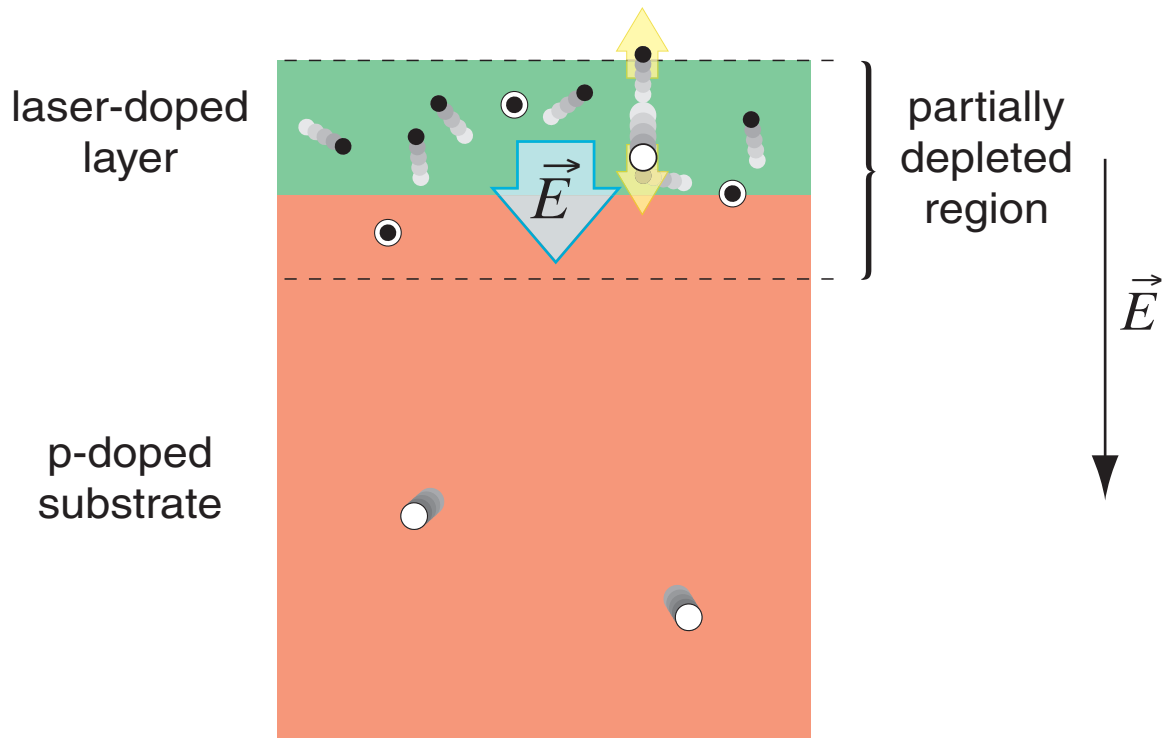
…incident photon generates electron-hole pair…

Devices



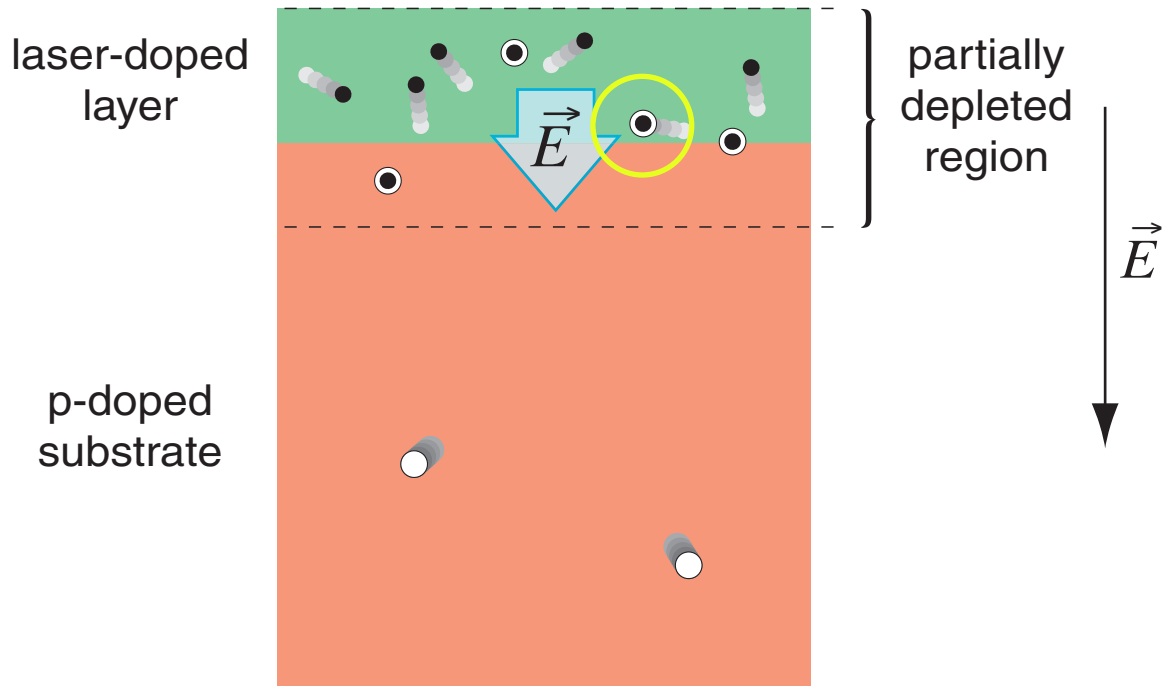
…incident photon generates electron-hole pair…

Devices



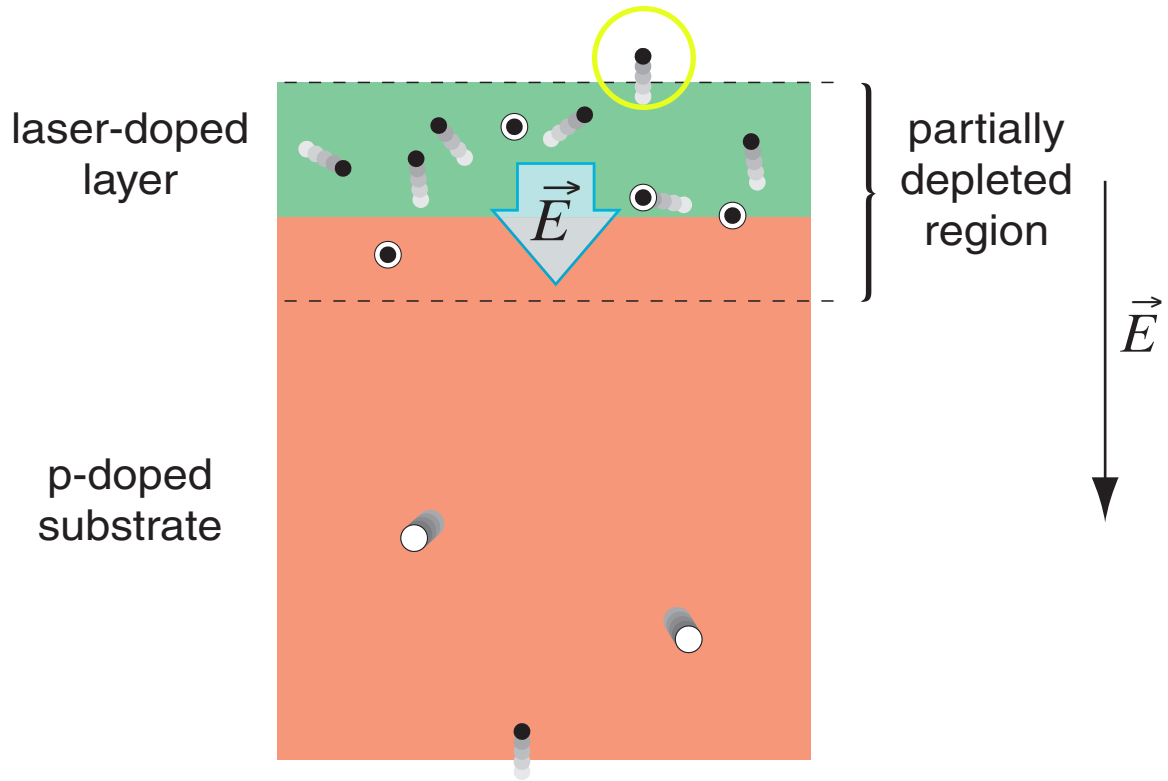
…carriers accelerate away from each other…

Devices



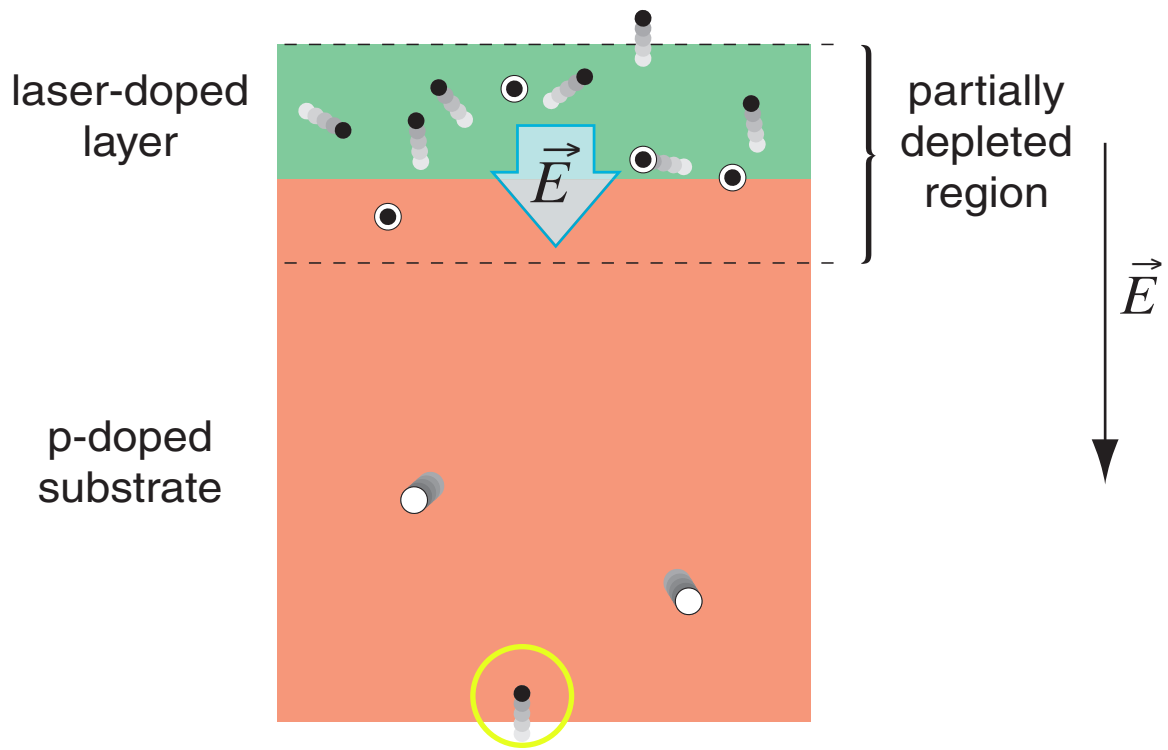
…hole is trapped

Devices



meanwhile electron exits sample…

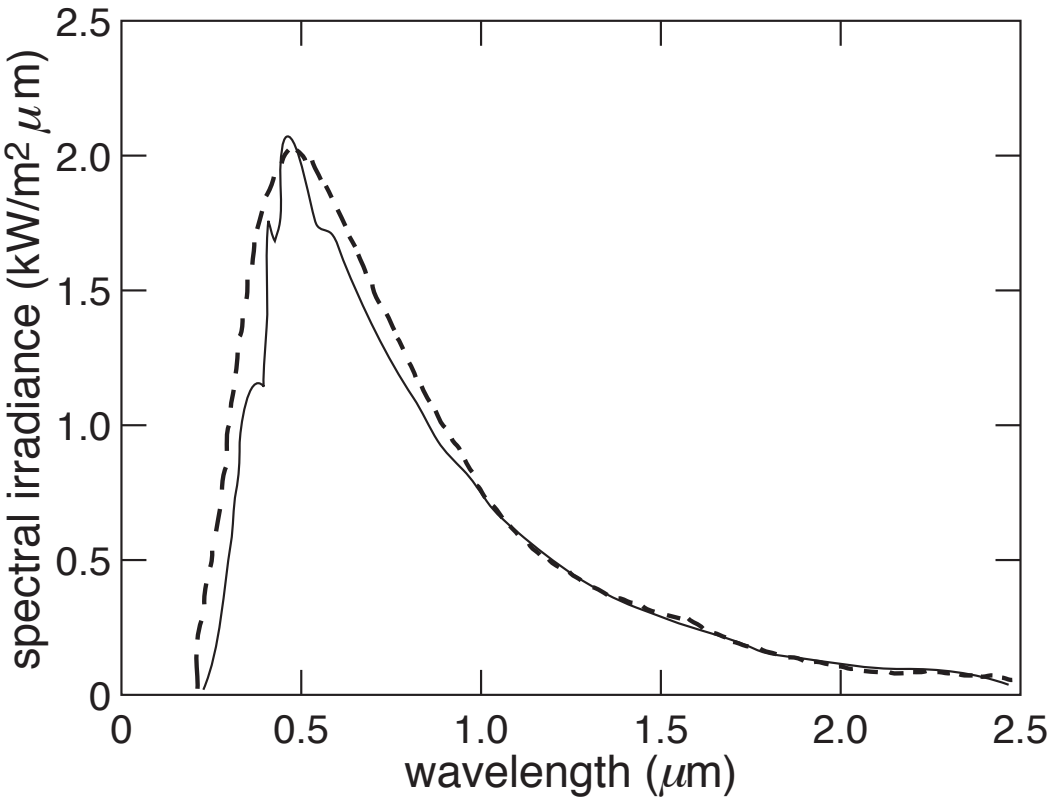
Devices



…and source provides new electron

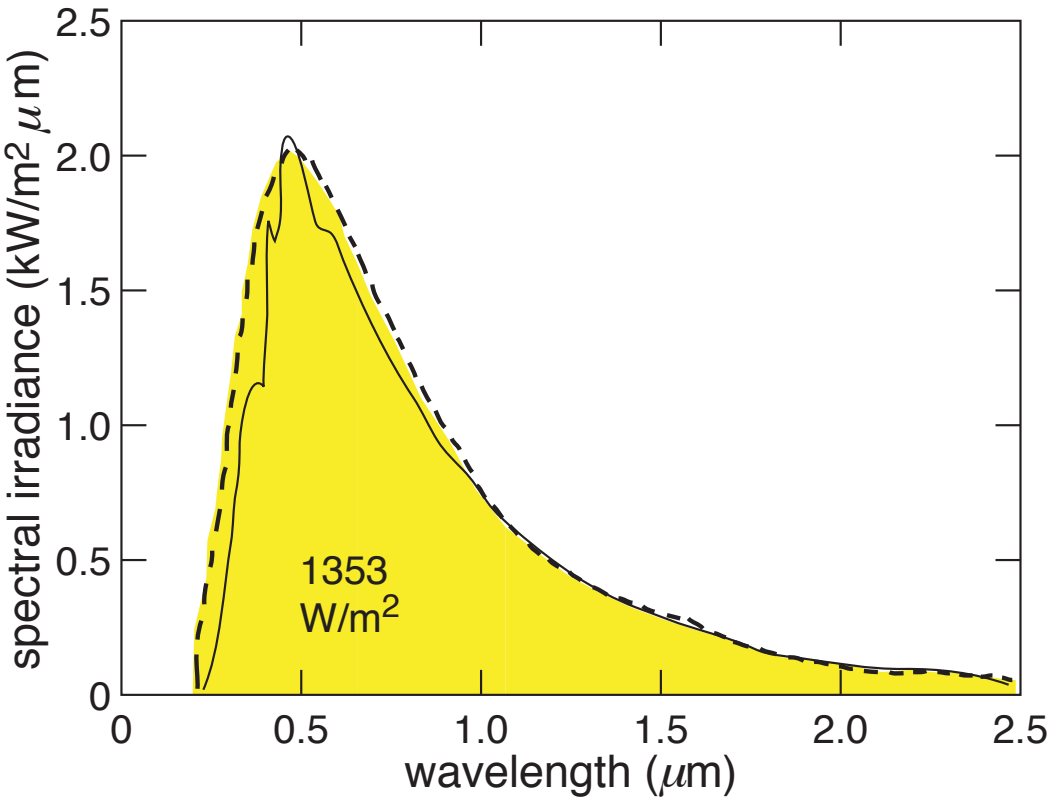
Devices

solar spectrum



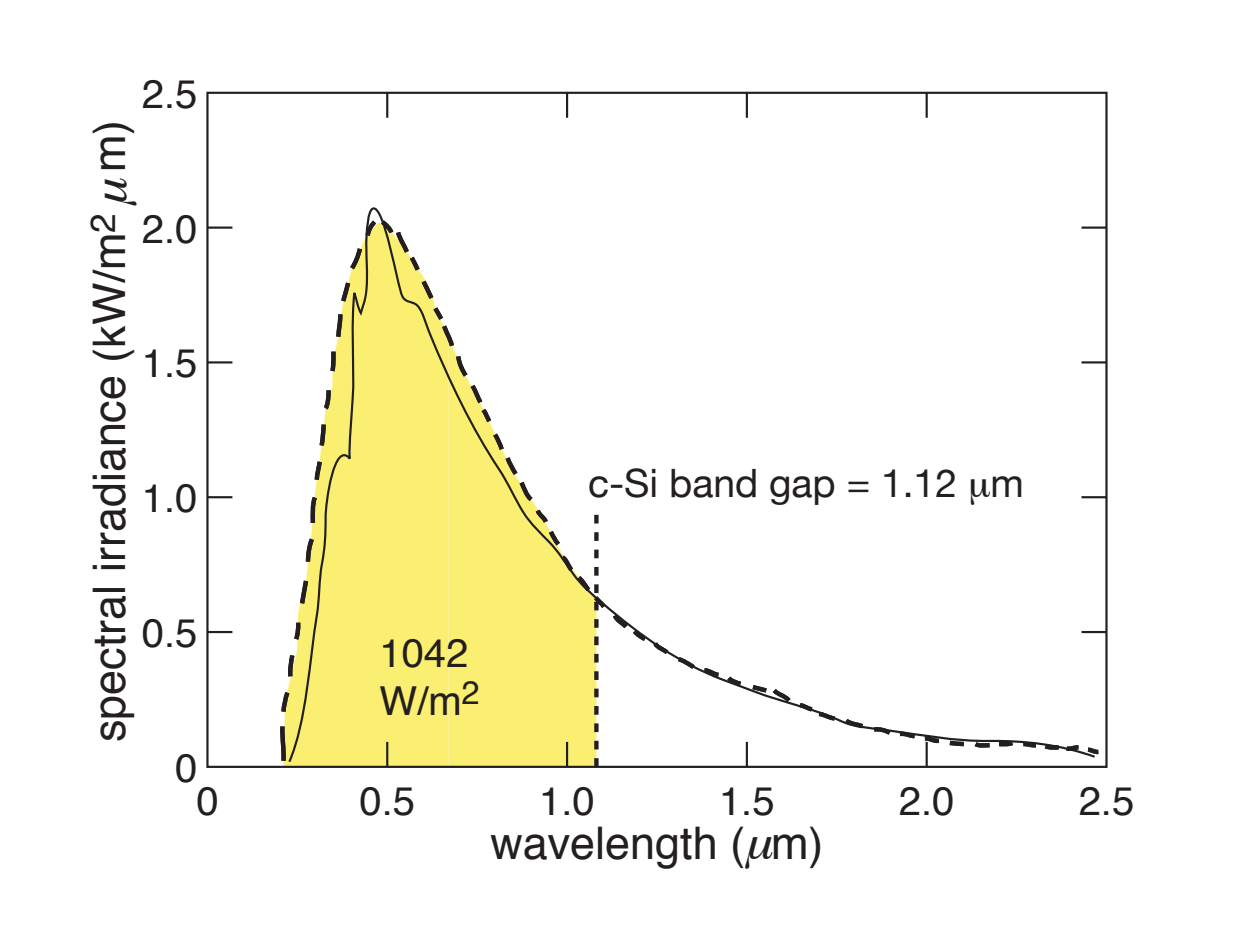
Devices

solar spectrum



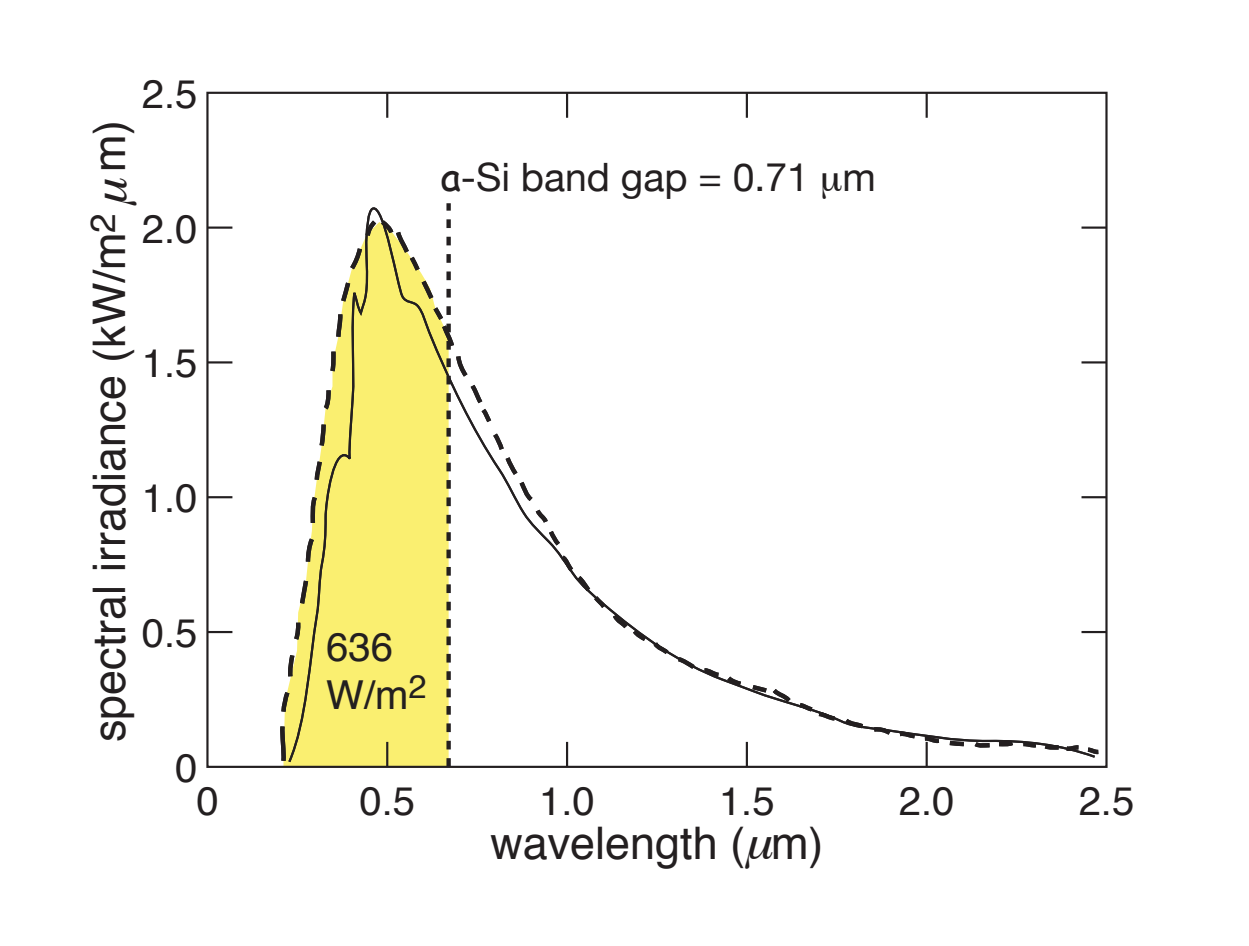
Devices

crystalline silicon: transparent to 23% of solar radiation



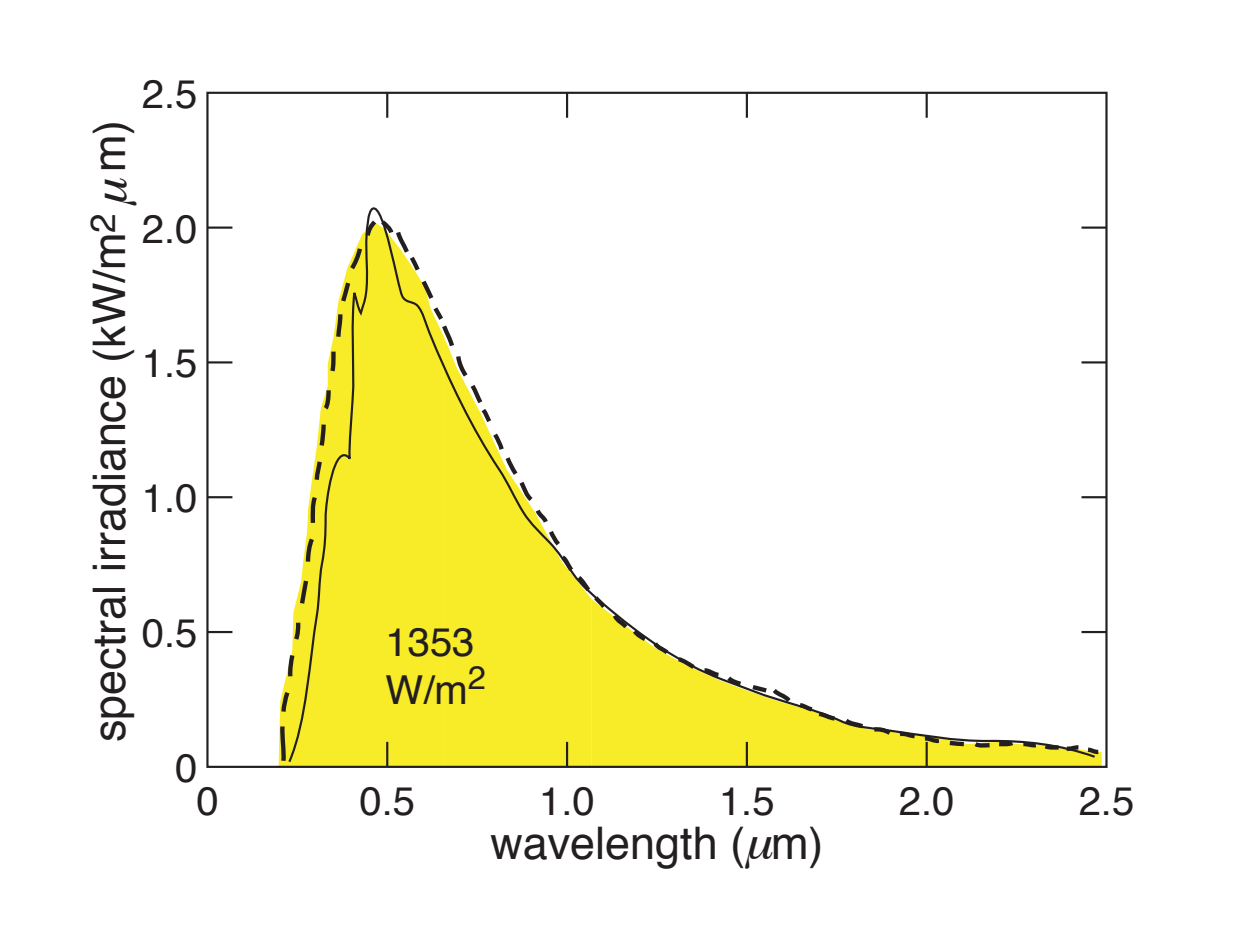
Devices

amorphous silicon: transparent to 53% of solar radiation



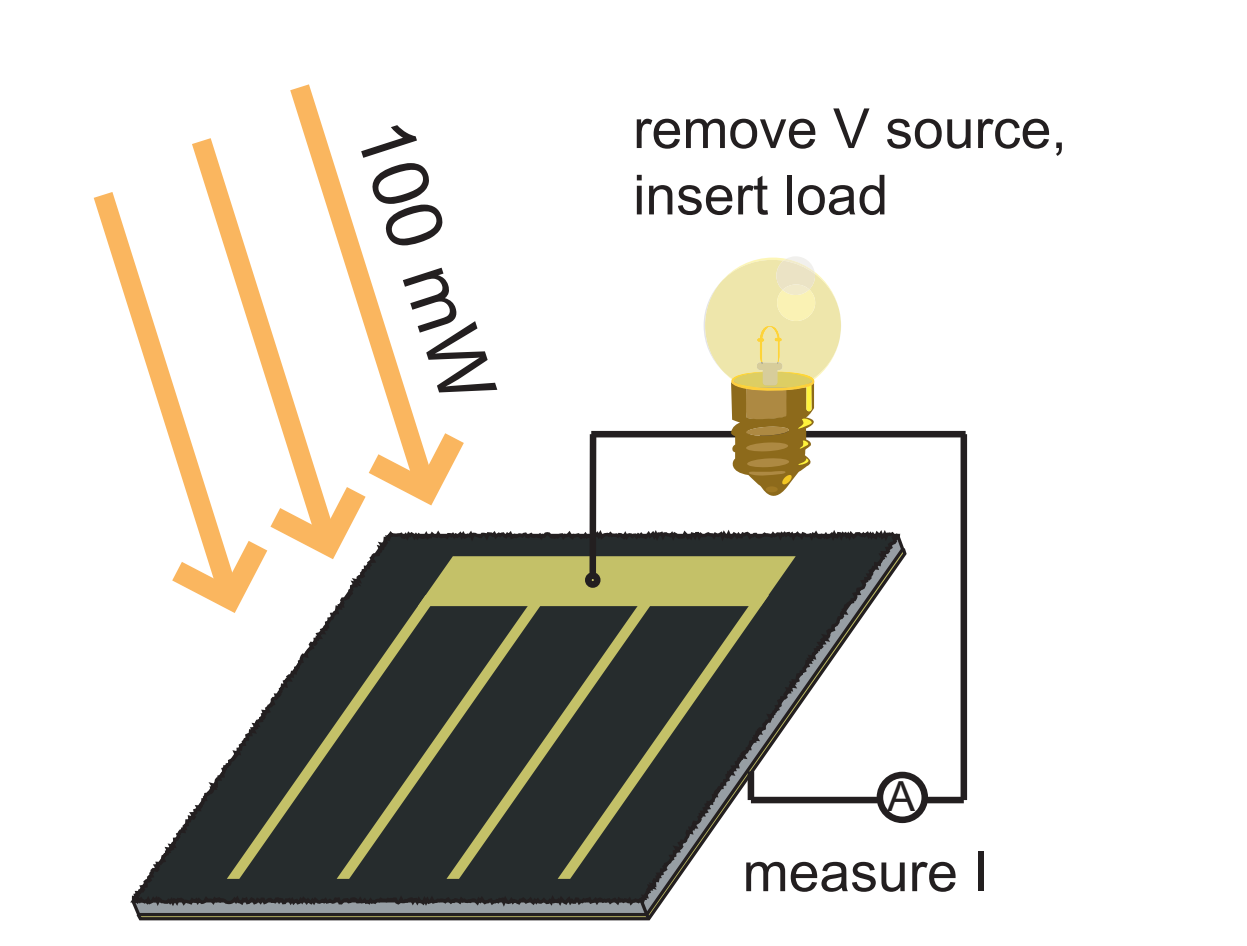
Devices

black silicon: potential to recover transmitted energy



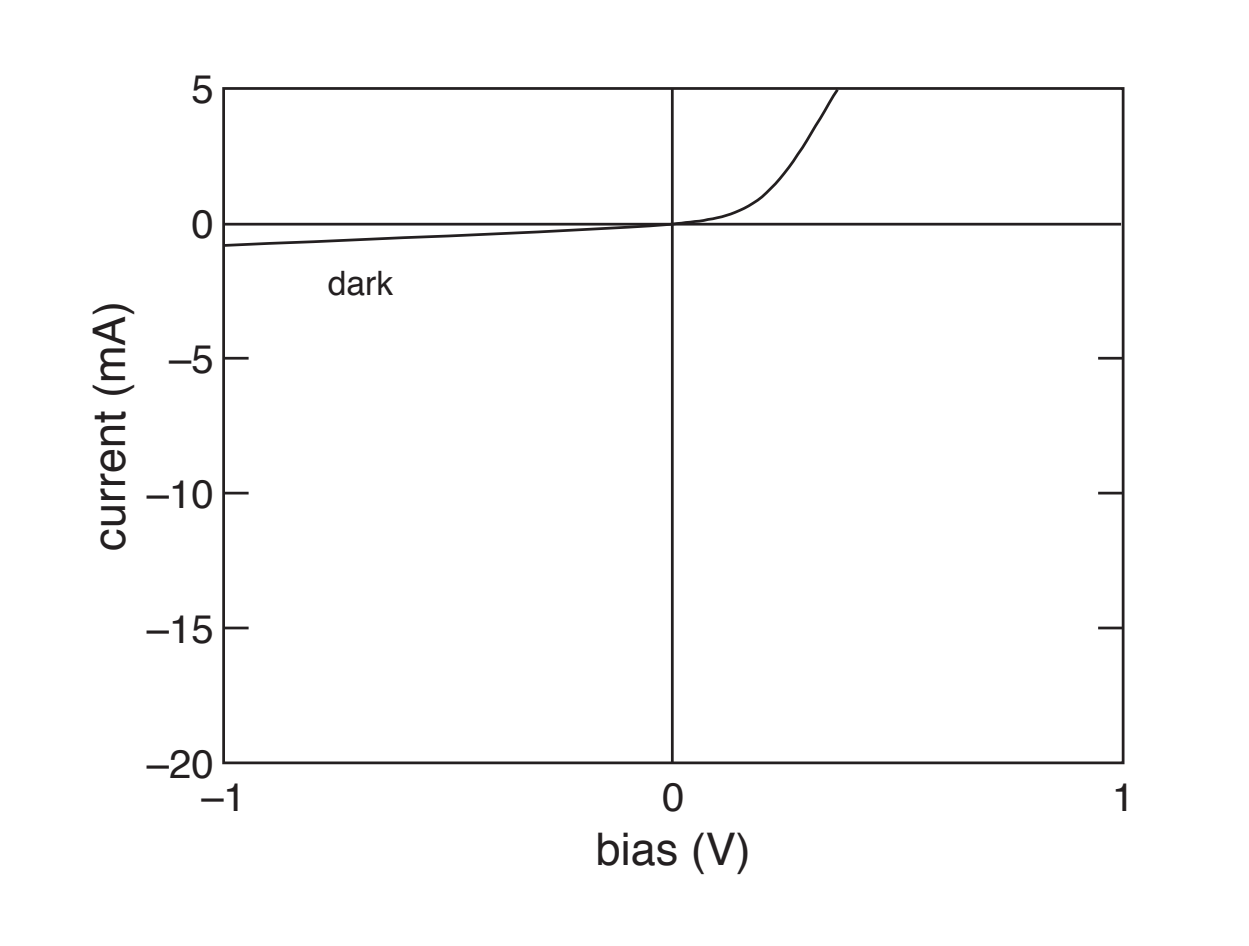
Devices

very preliminary photovoltaic cell



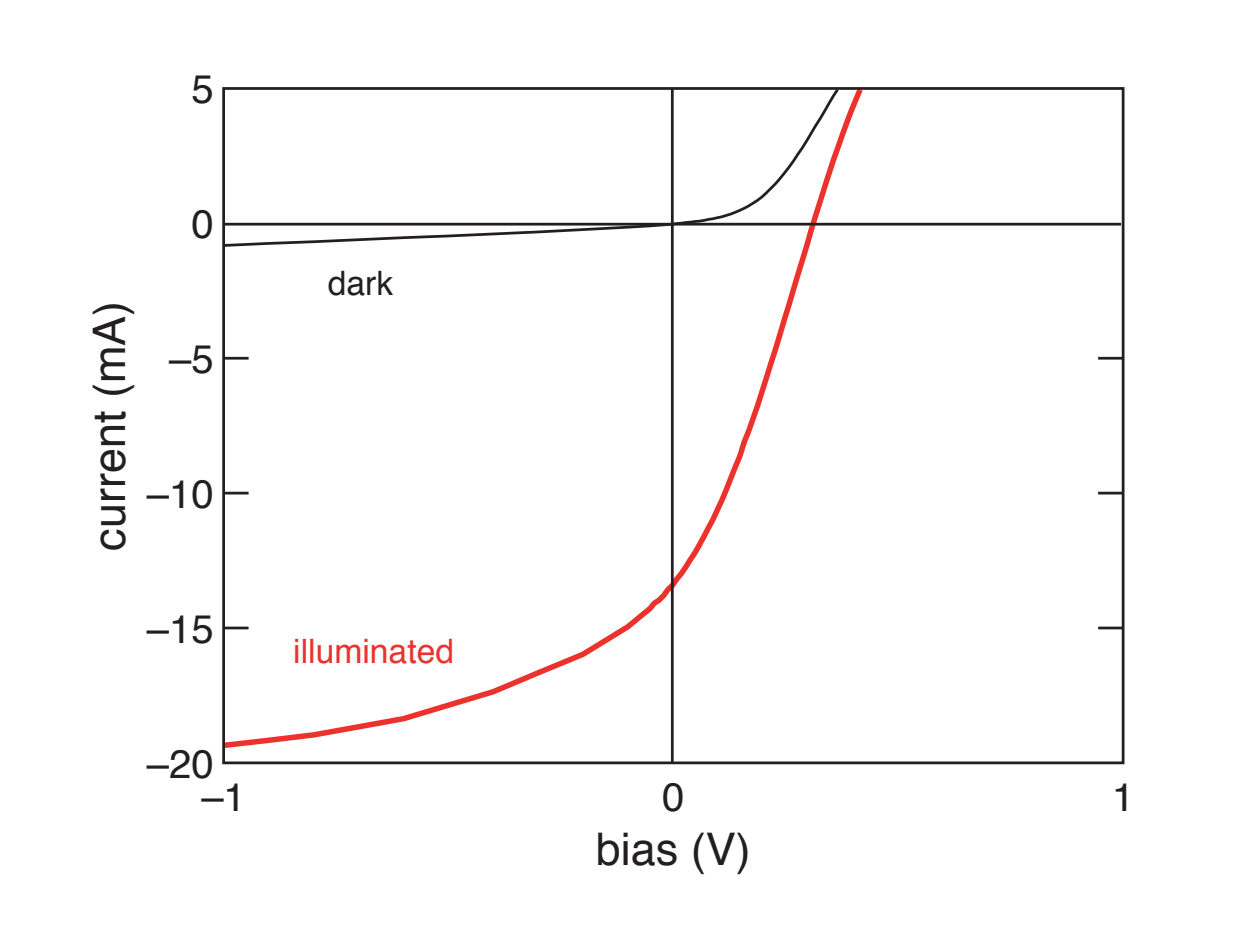
Devices

very preliminary photovoltaic cell



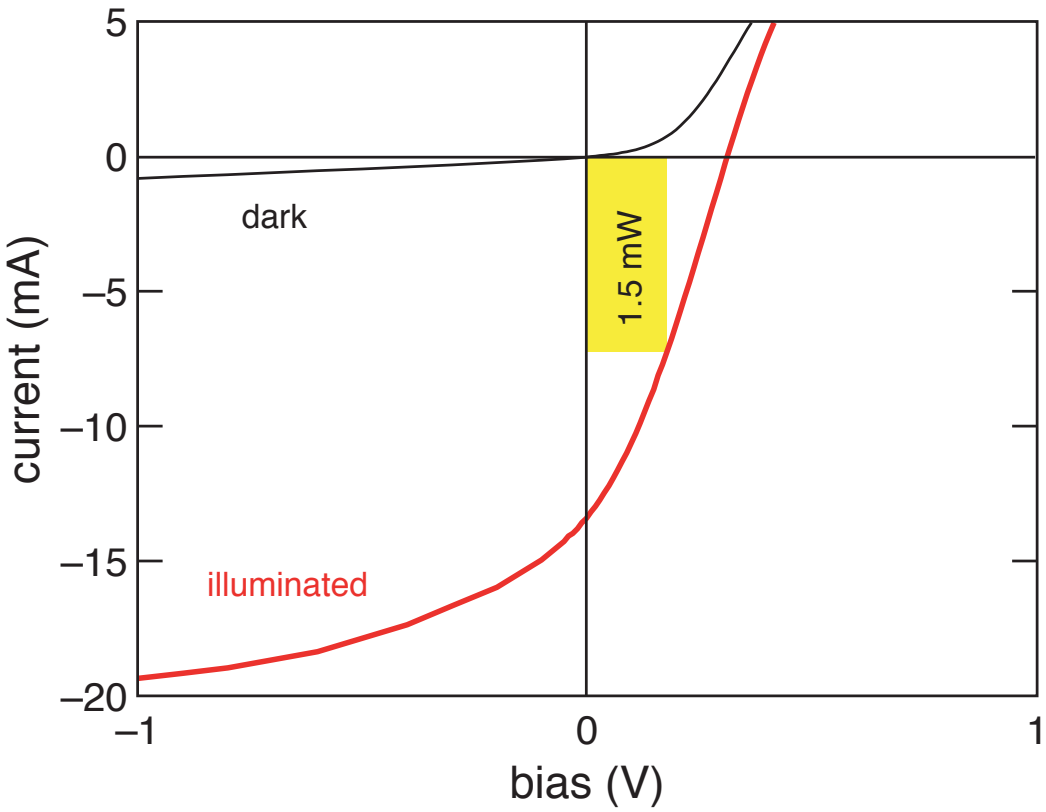
Devices

very preliminary photovoltaic cell



Devices

1.5% efficiency, a good beginning

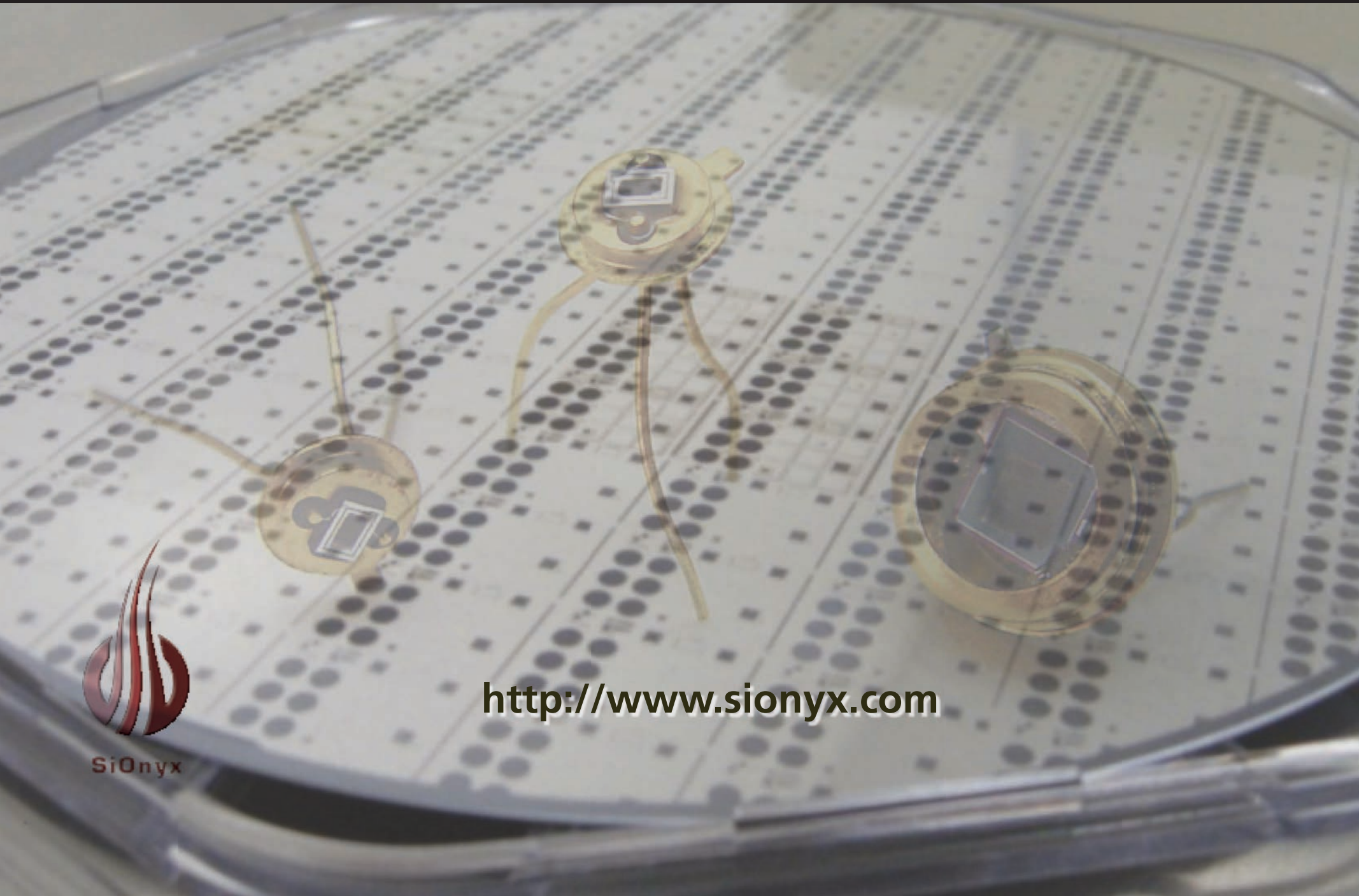


Devices

Things to keep in mind

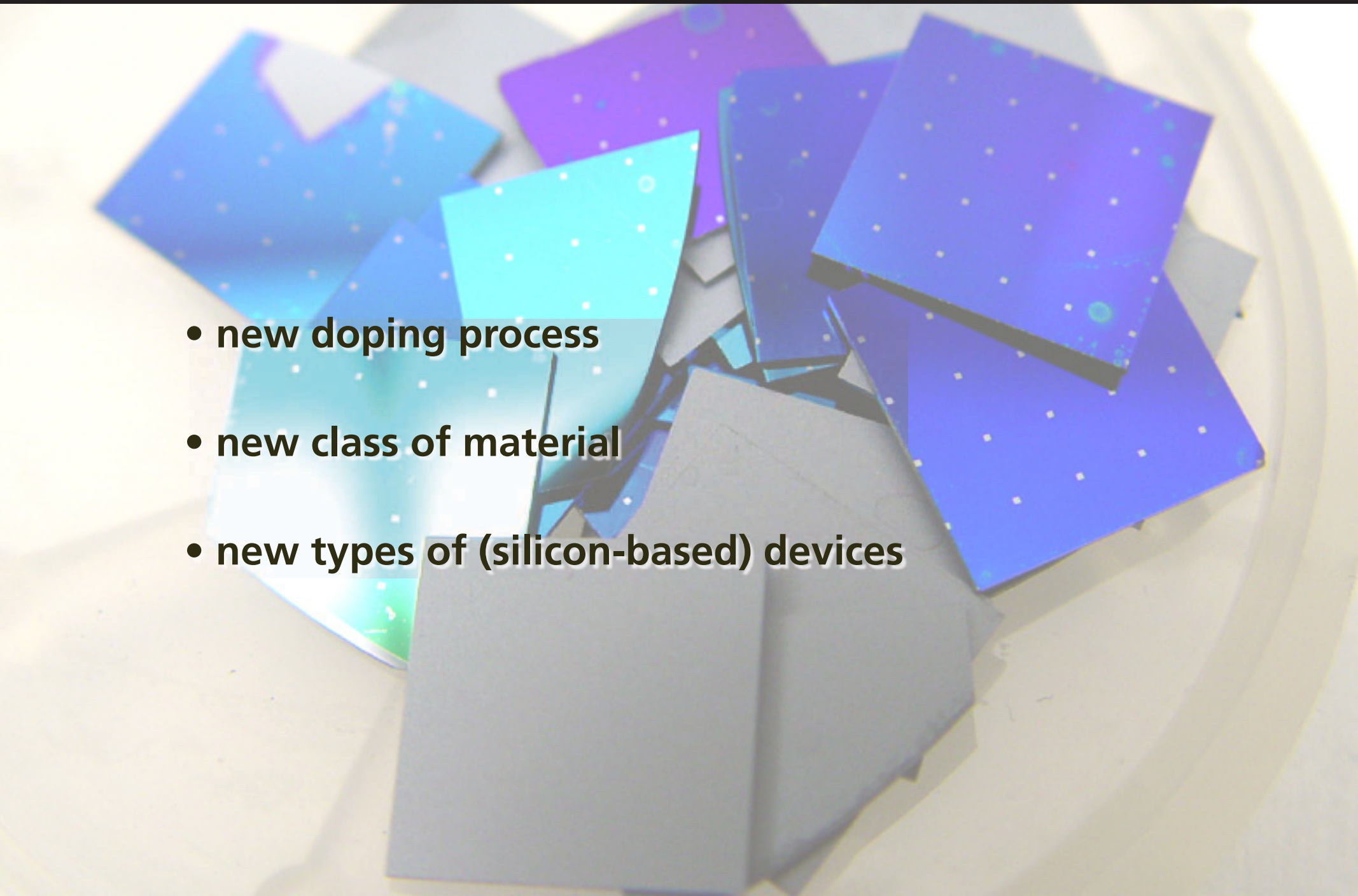
- can turn absorption into carrier generation
- very high responsivity in VIS and IR
- phenomenal photoconductive gain

Devices



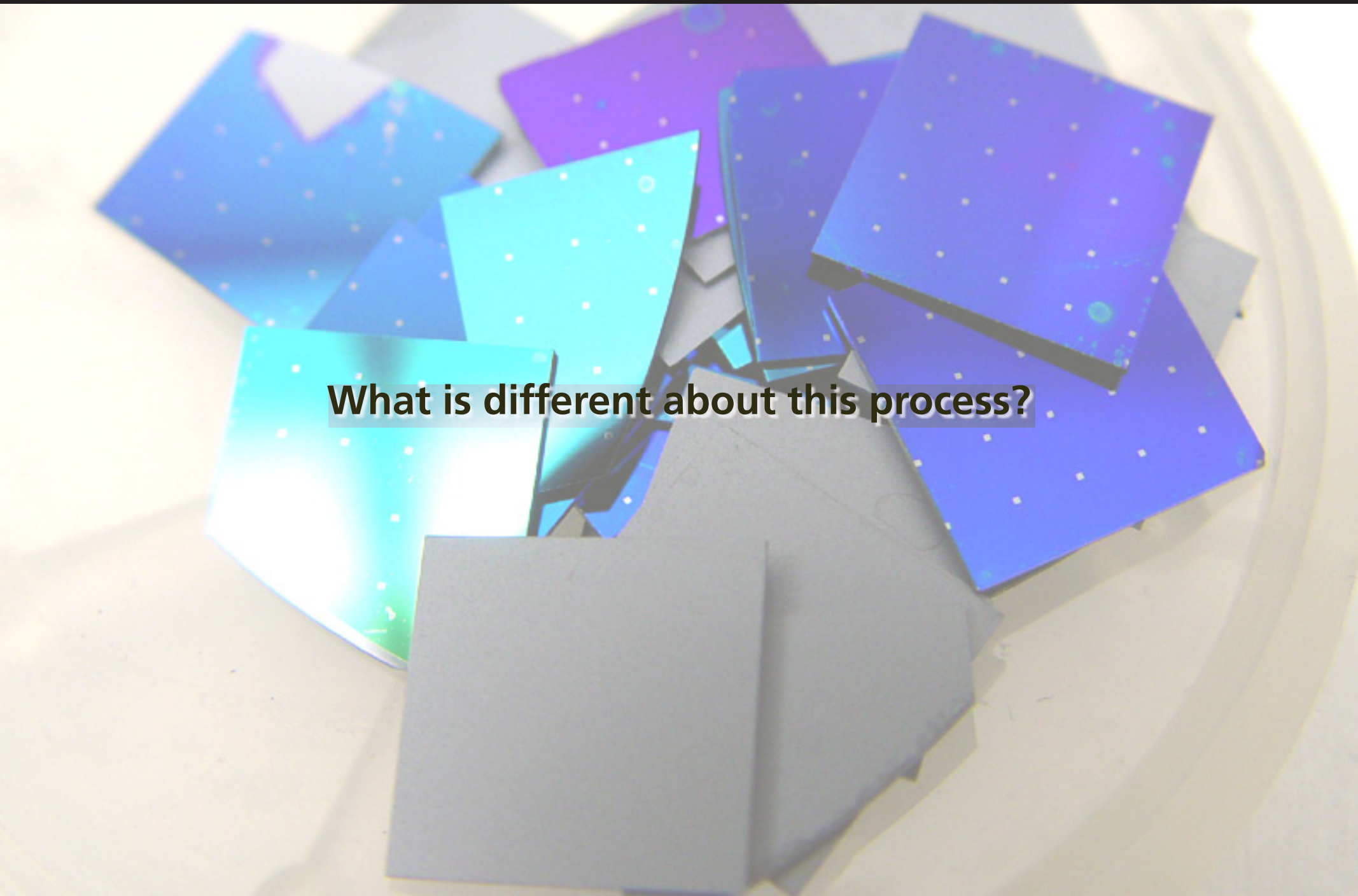
http://www.sionyx.com

Conclusion



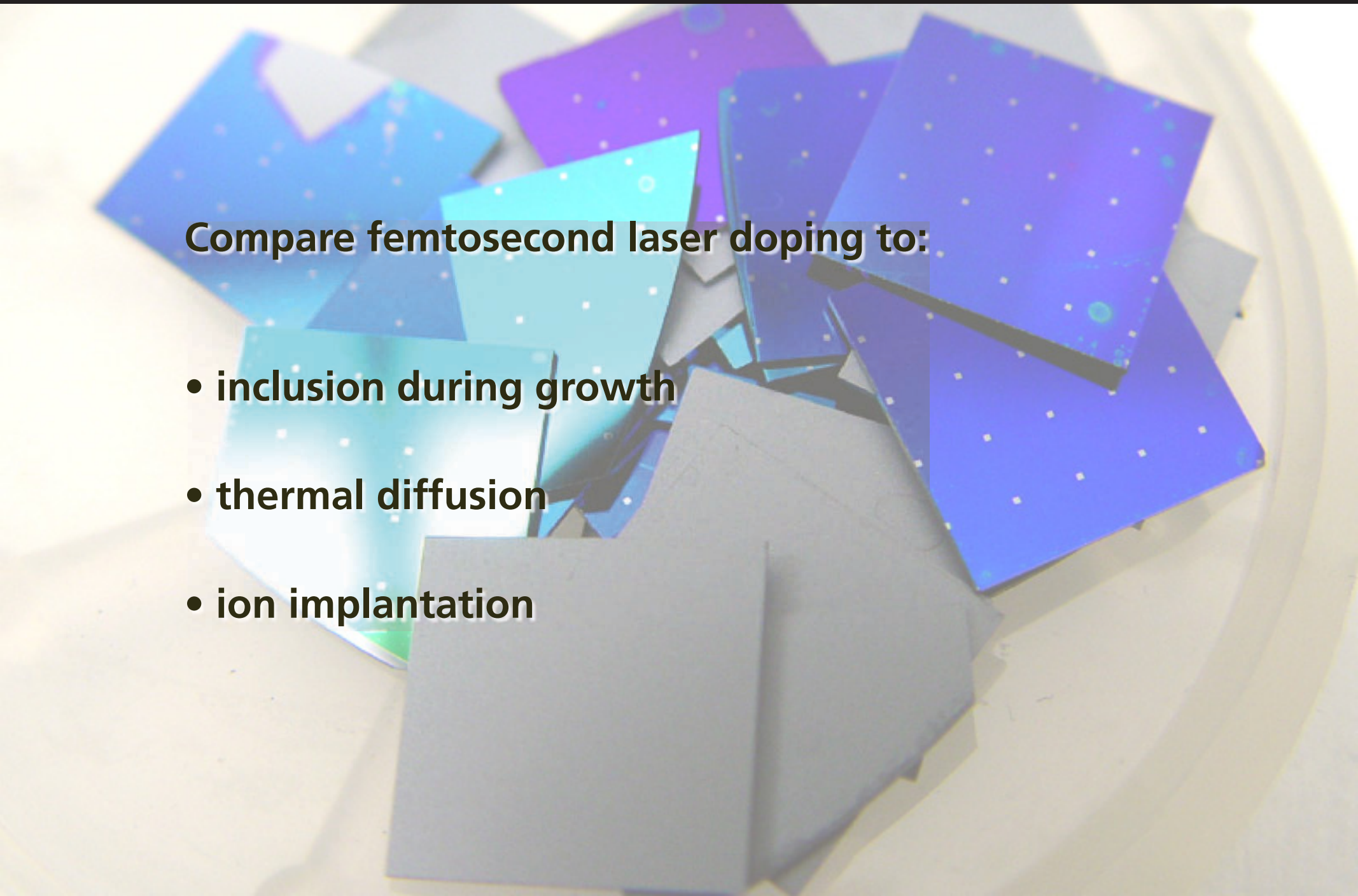
- new doping process
- new class of material
- new types of (silicon-based) devices

Conclusion



What is different about this process?

Conclusion



Compare femtosecond laser doping to:

- inclusion during growth
- thermal diffusion
- ion implantation

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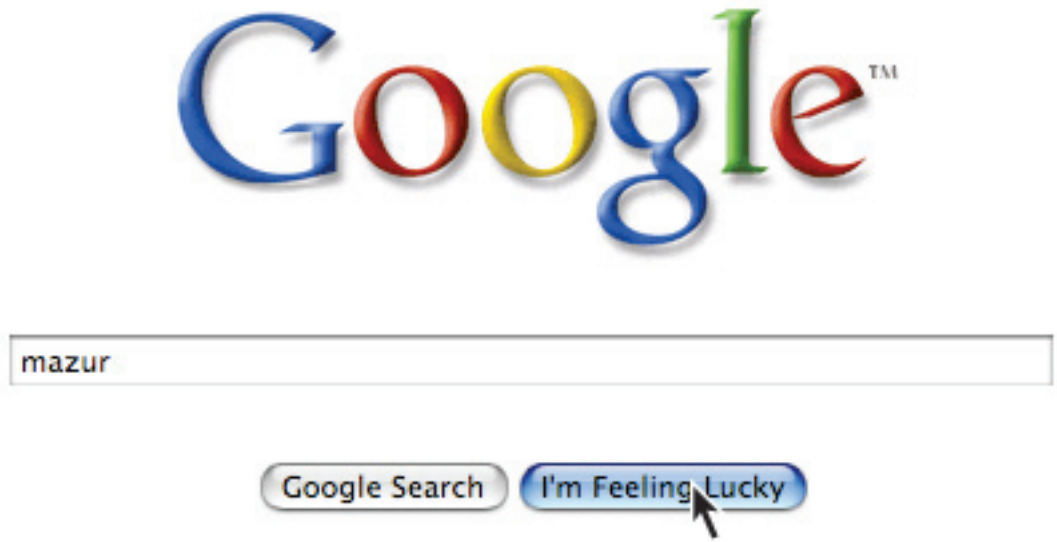
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