

# Applications of femtosecond lasers in materials processing



Data Storage Institute  
Singapore, 30 March 2012

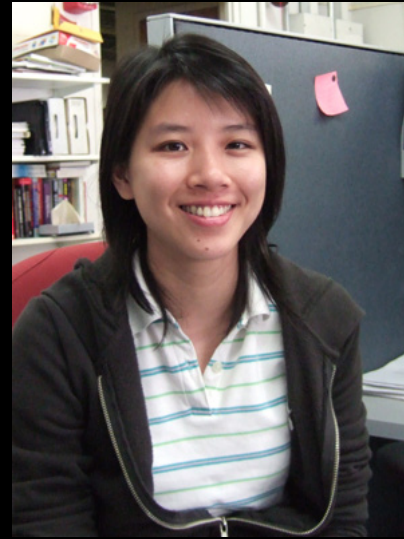




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**Nozomi Nishimura**  
**Jonathan Ashcom**  
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**Prof. Igor Khrushchev (Aston University)**  
**Prof. Denise Krol (UC Davis)**  
**Dr. Yossi Chay (Sagitta, Inc.)**  
**Dr. S.K. Sundaram (PNNL)**  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

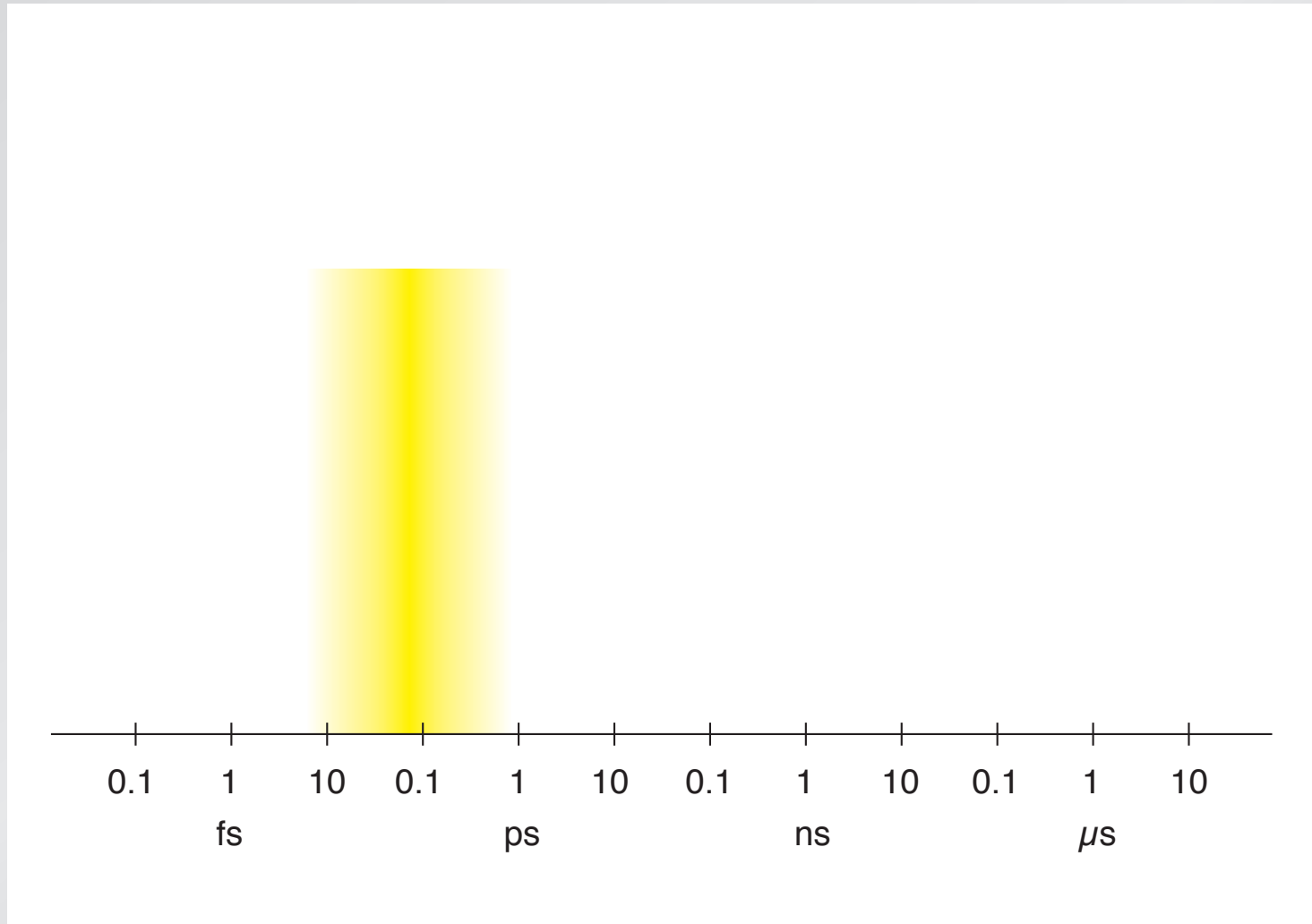
# Introduction

**why study materials with femtosecond pulses?**



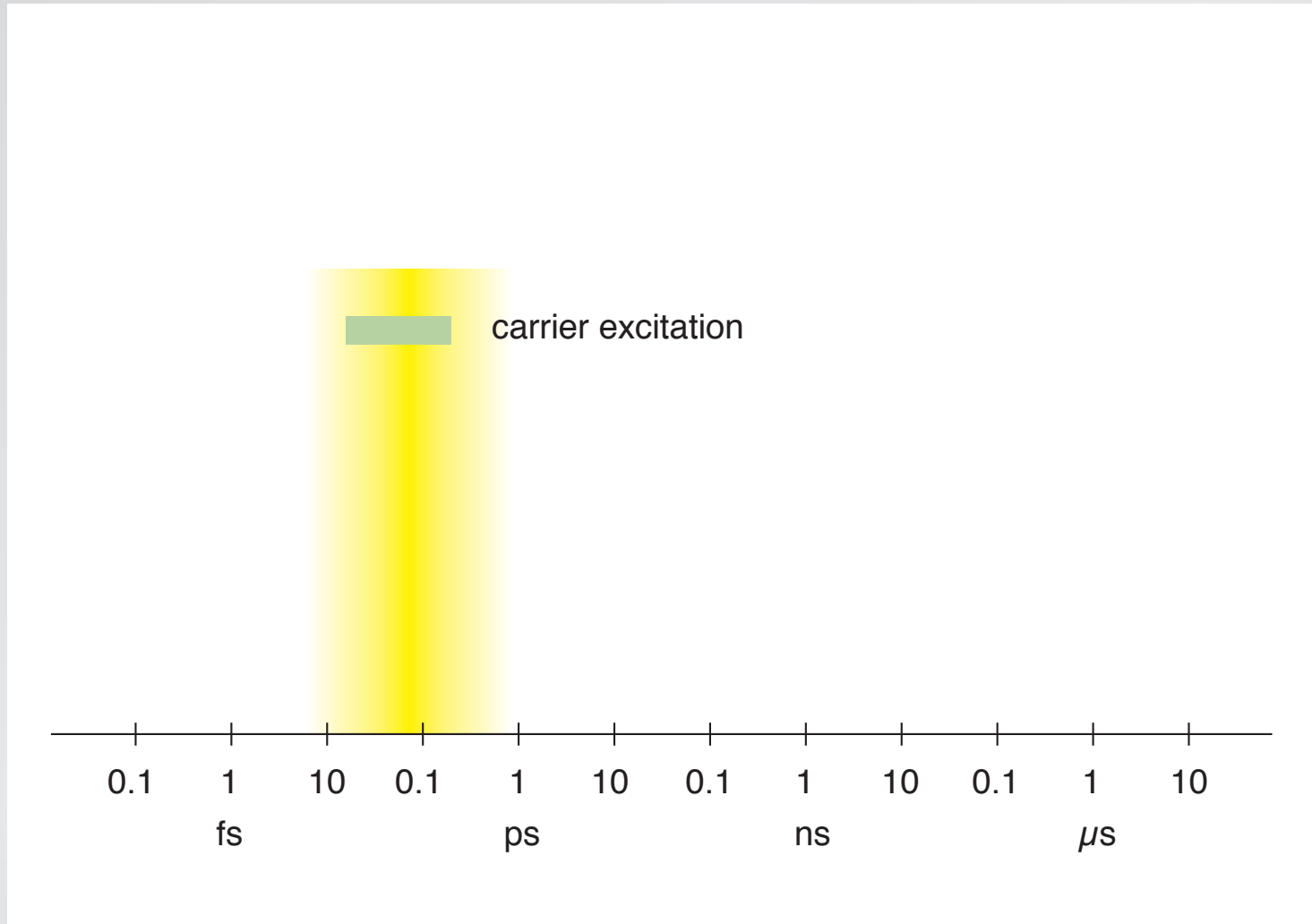
# Introduction

## relevant time scales



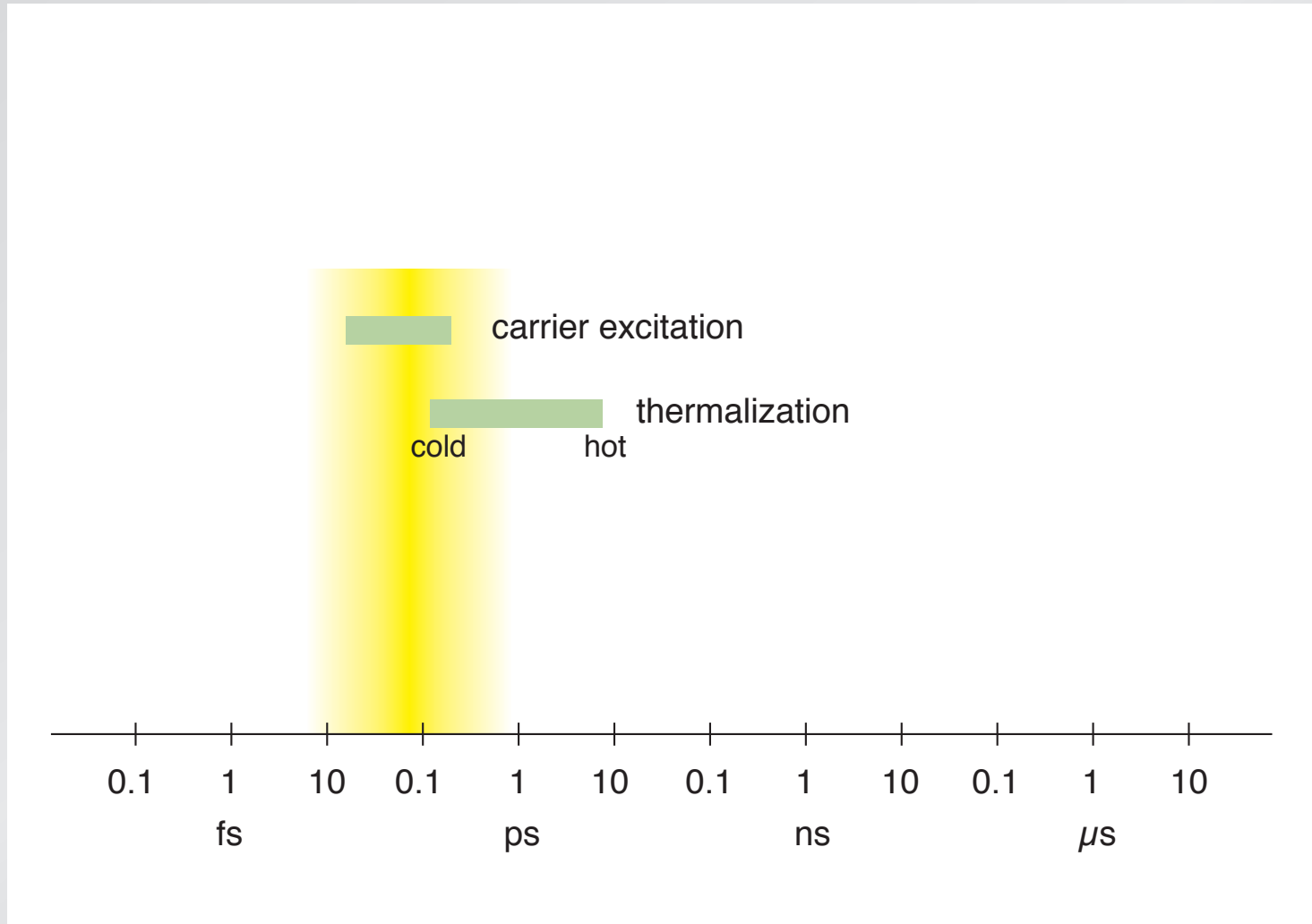
# Introduction

## relevant time scales



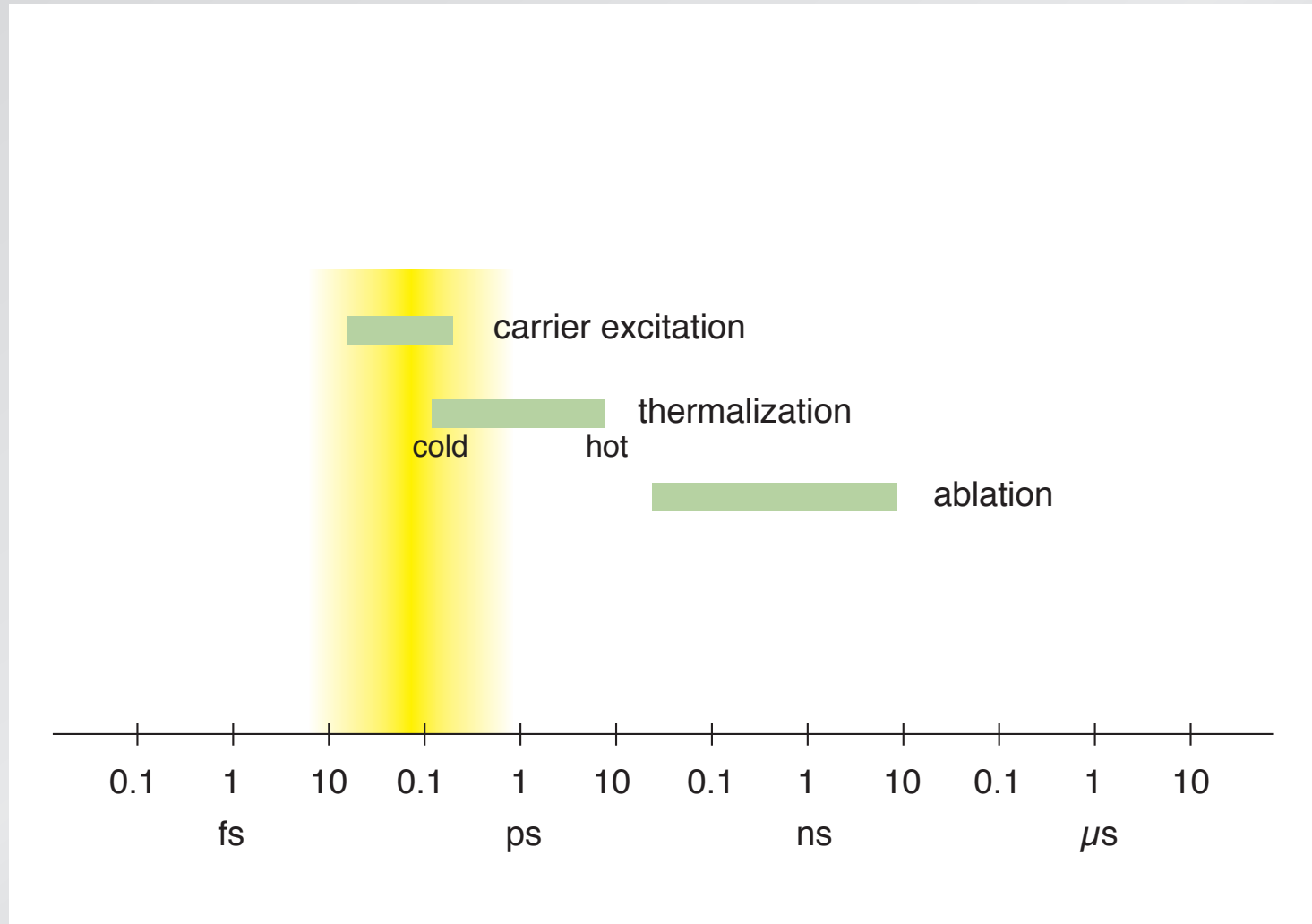
# Introduction

## relevant time scales



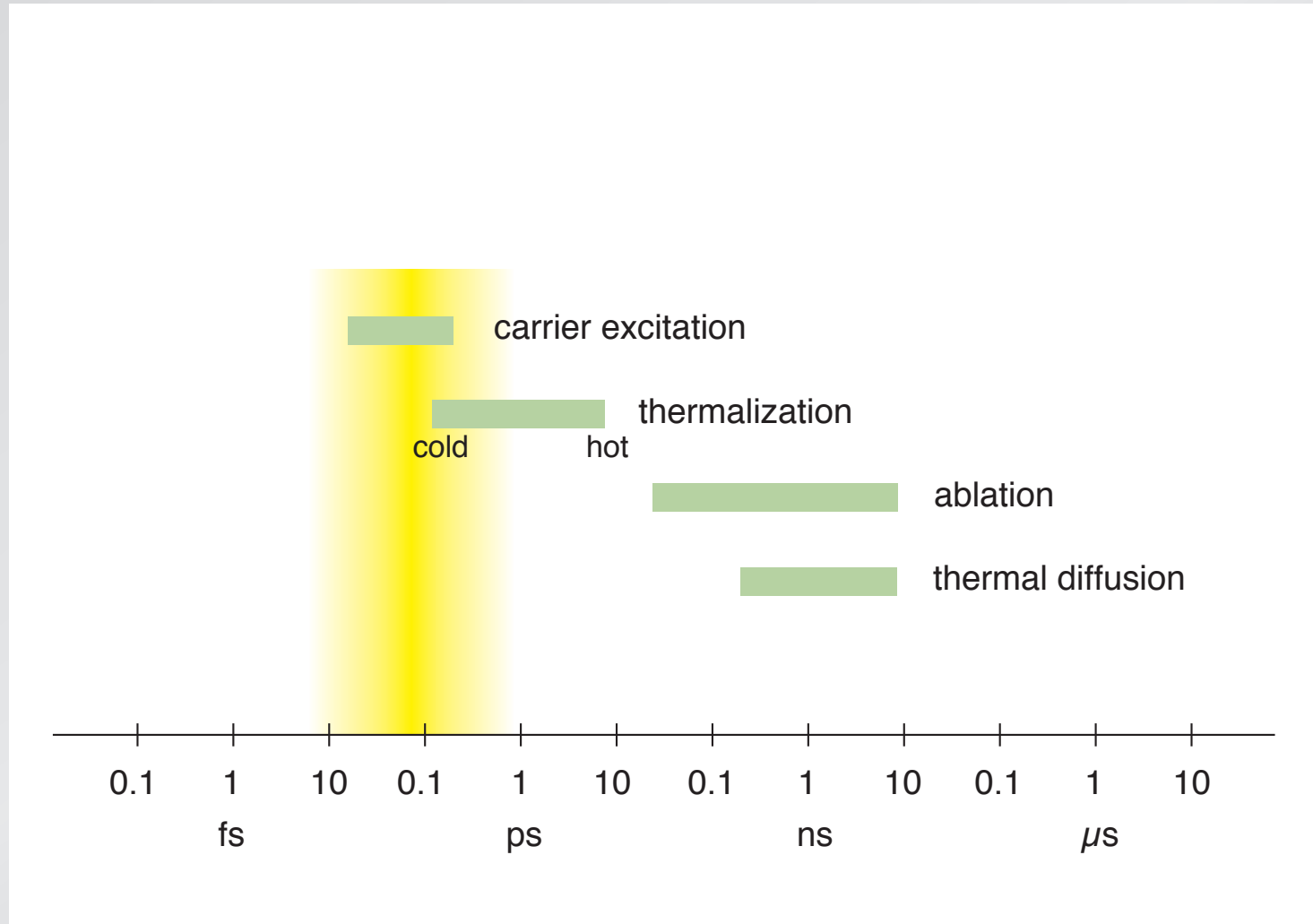
# Introduction

## relevant time scales



# Introduction

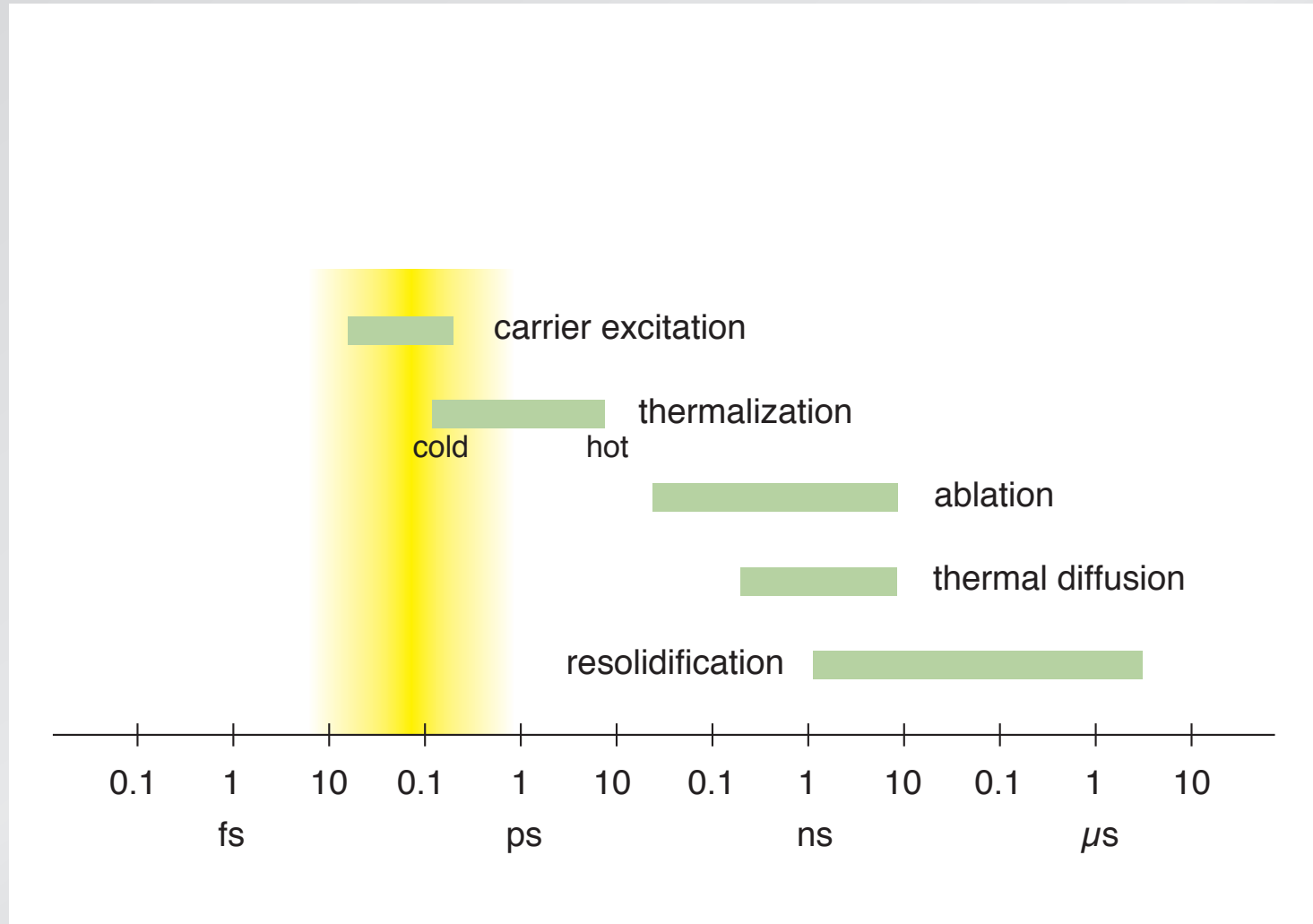
## relevant time scales





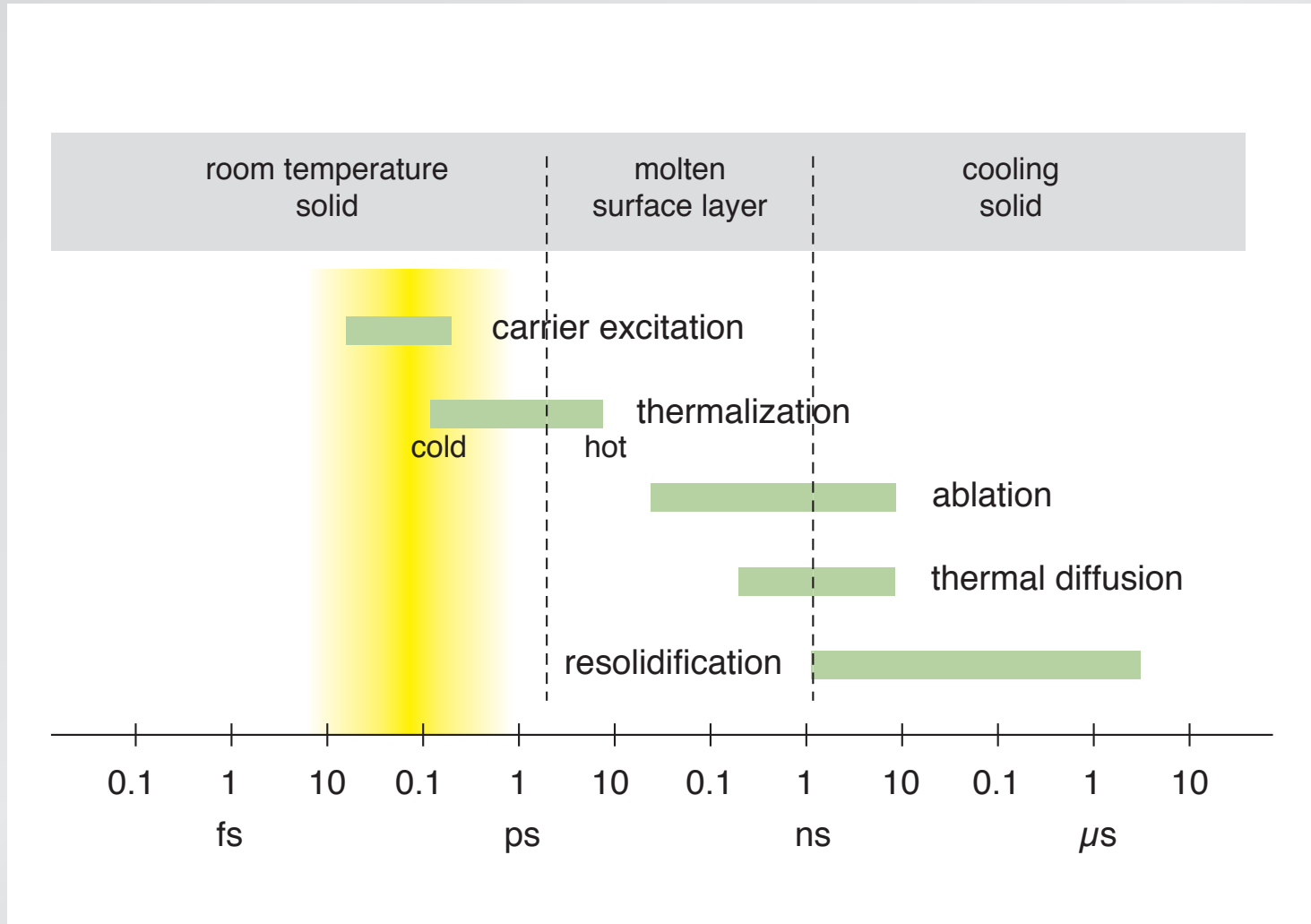
# Introduction

## relevant time scales



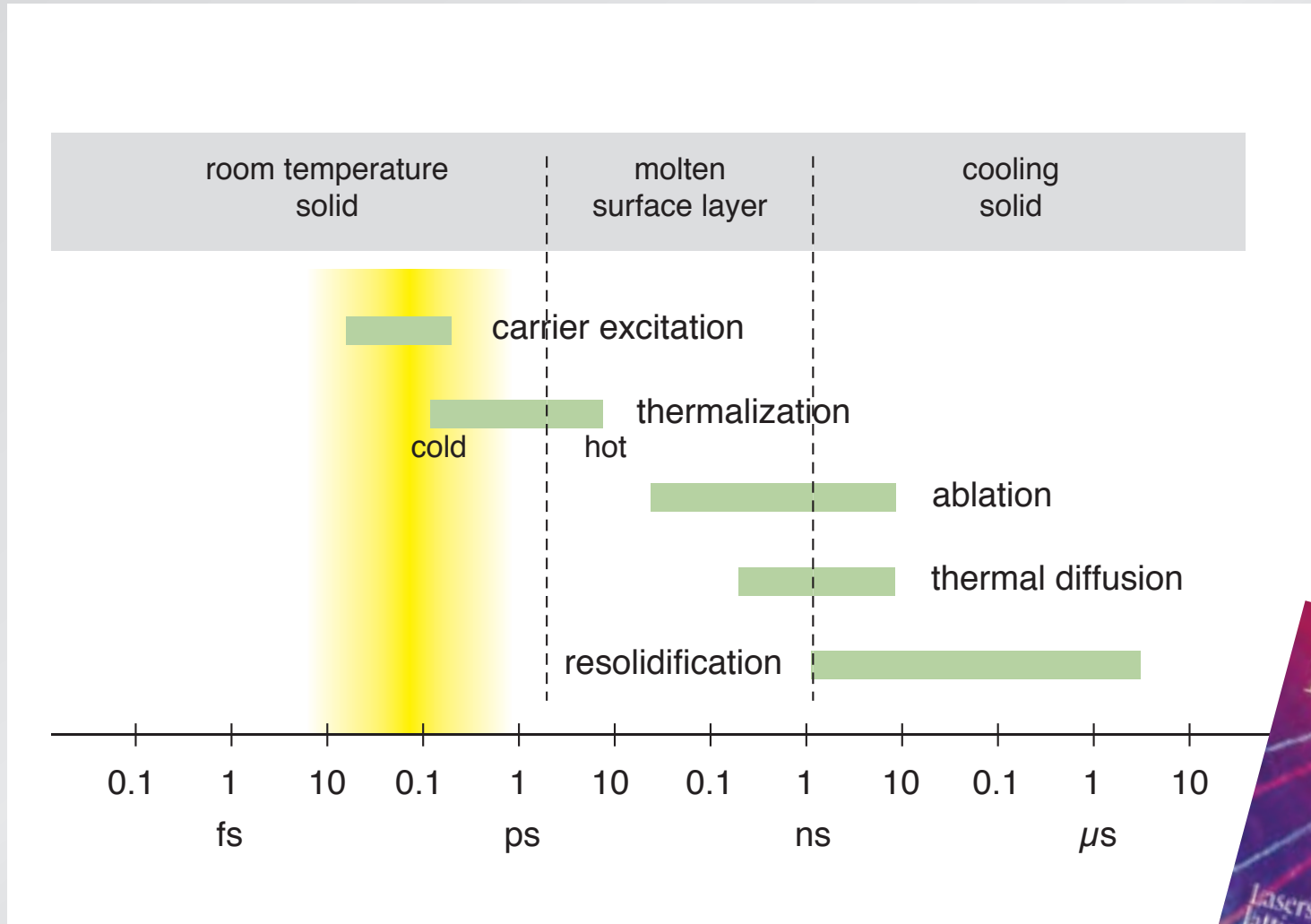
# Introduction

## relevant time scales

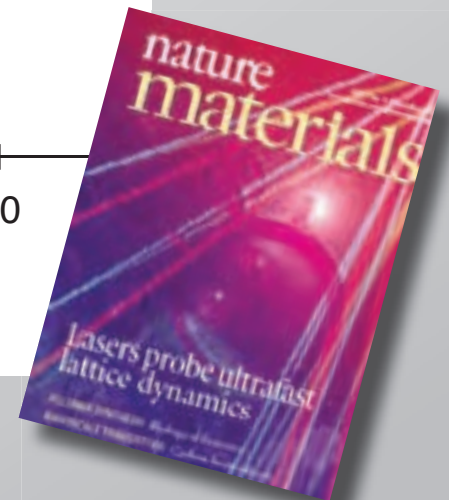


# Introduction

## relevant time scales

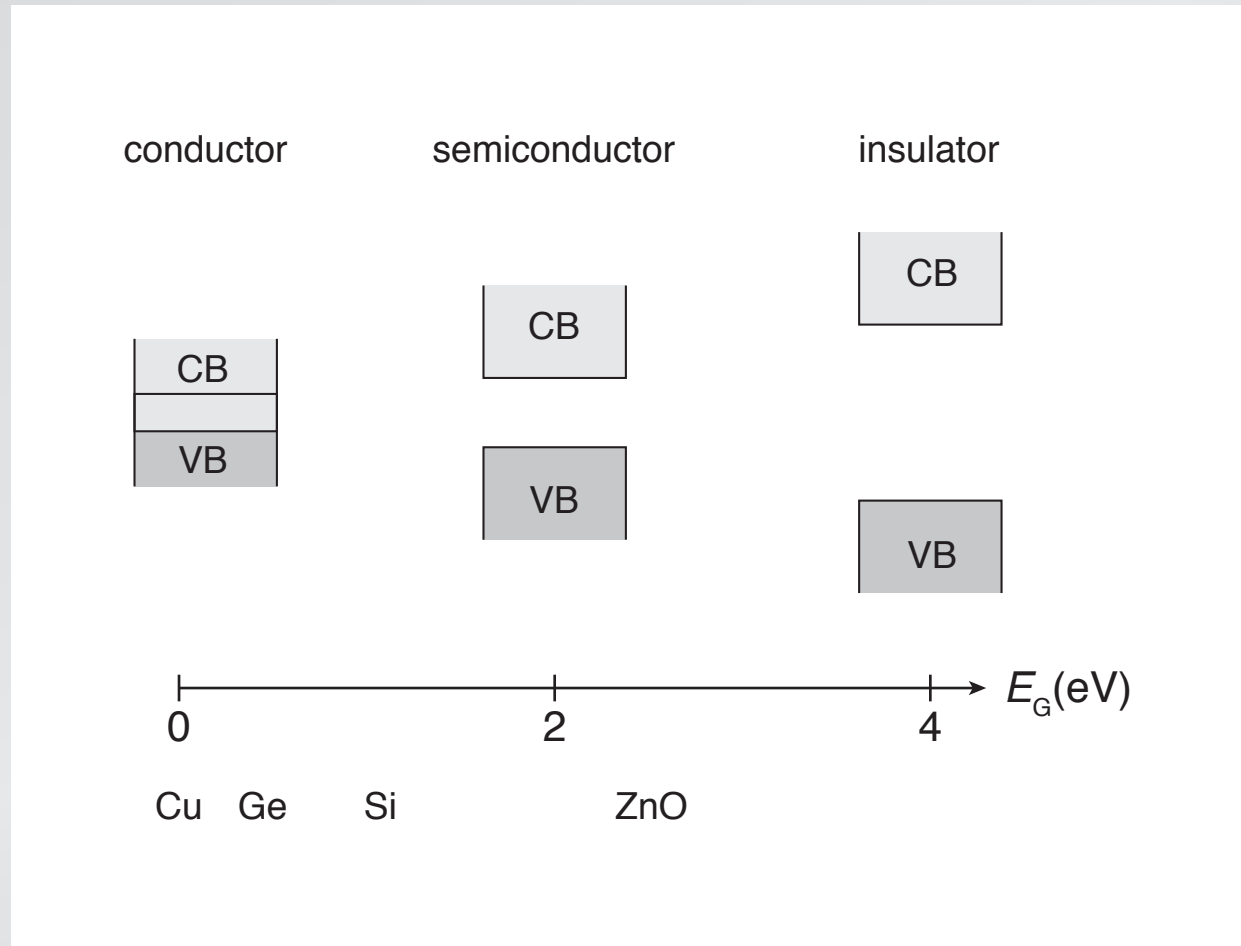


*Nature Materials* 1, 217 (2002)



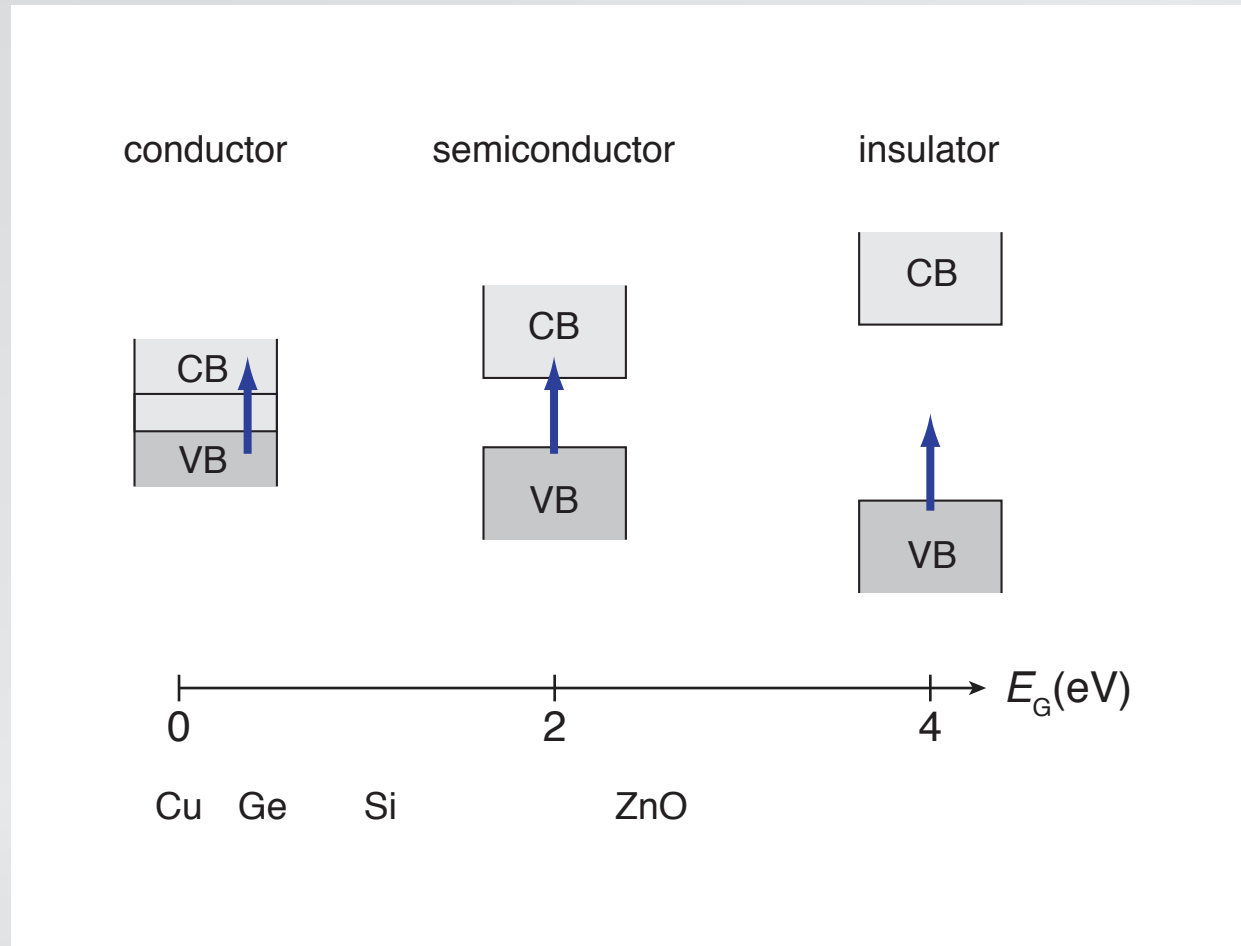
# Introduction

gap determines interaction



# Introduction

gap determines interaction



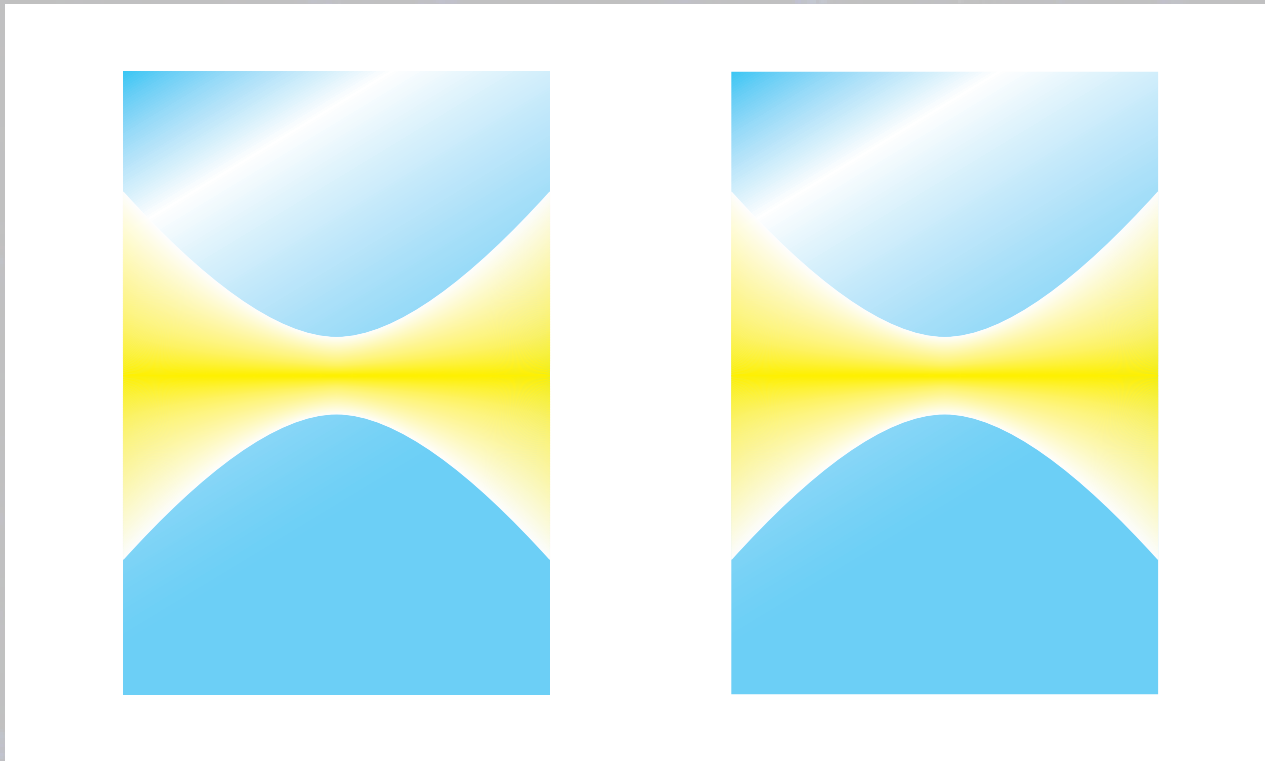


# Introduction

photon energy  $<$  bandgap  $\longrightarrow$  nonlinear interaction

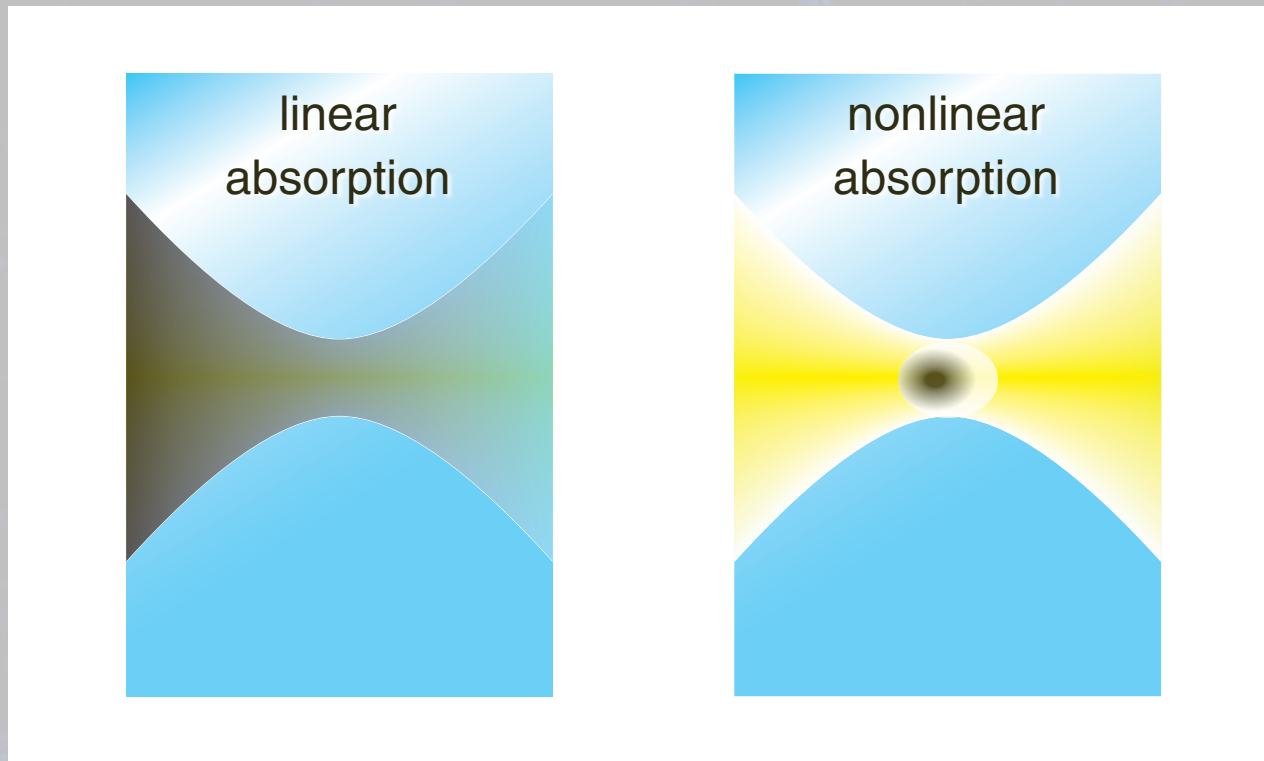
# Introduction

**nonlinear interaction provides bulk confinement**



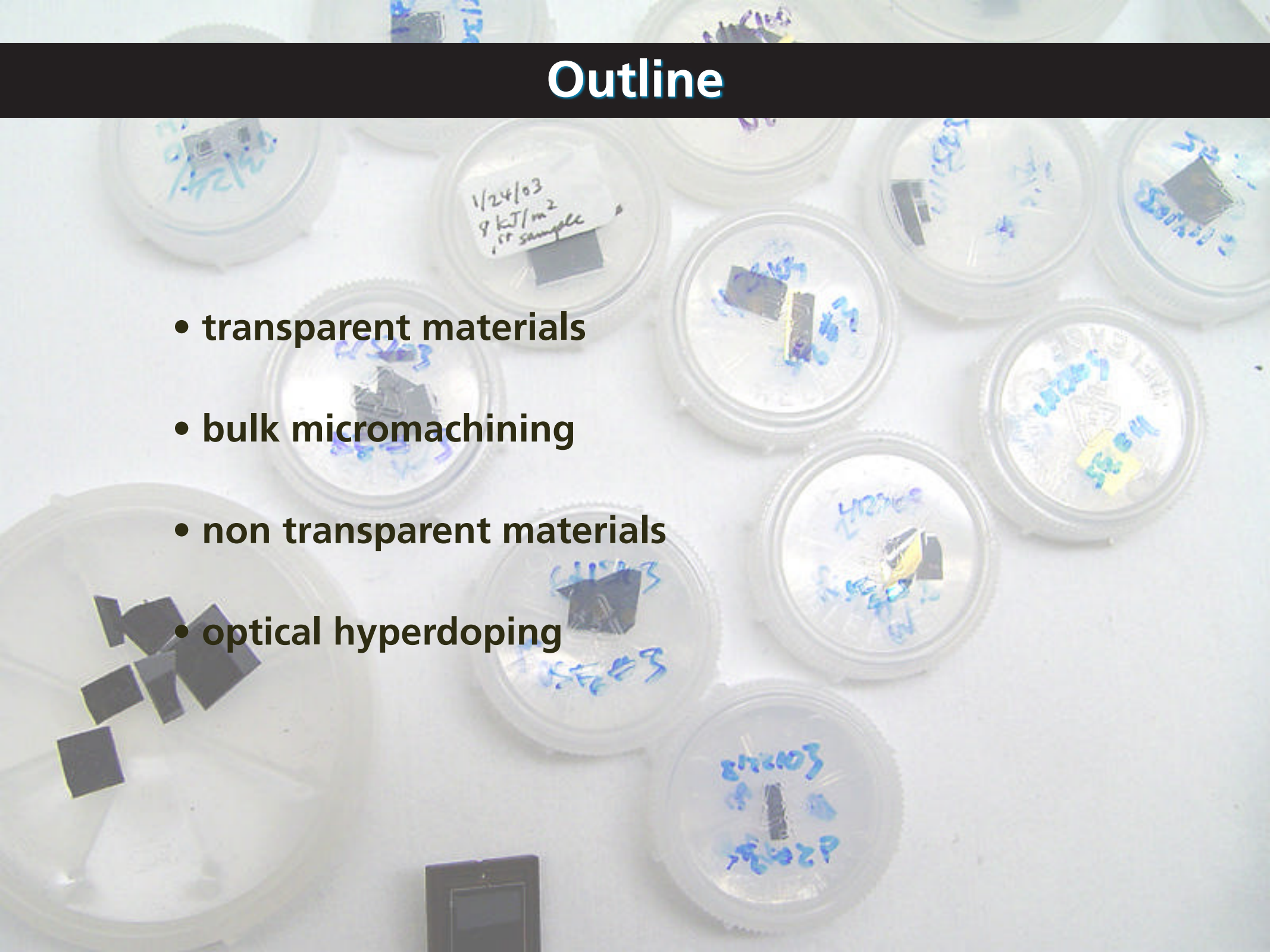
# Introduction

**nonlinear interaction provides bulk confinement**



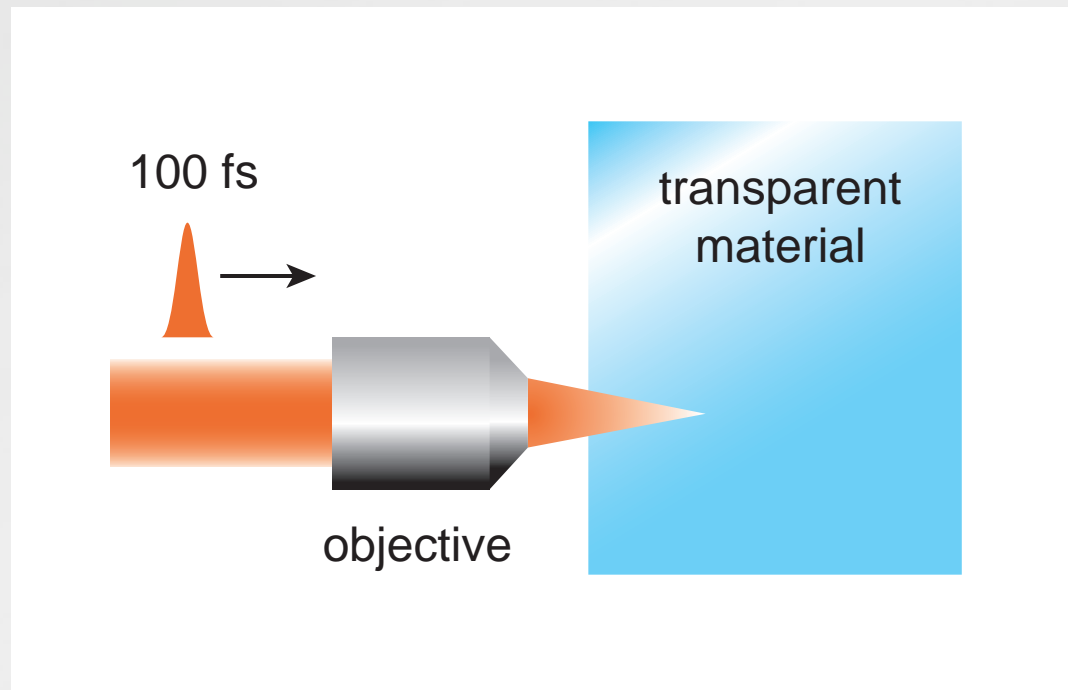
# Outline

- transparent materials
- bulk micromachining
- non transparent materials
- optical hyperdoping



# Transparent materials

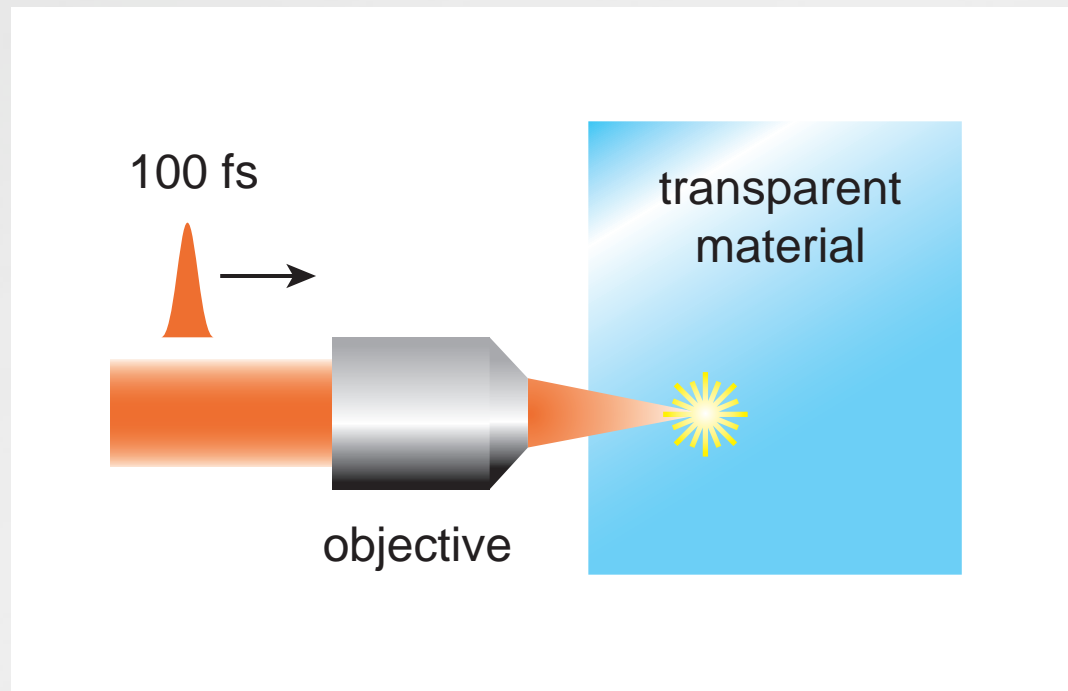
high intensity at focus...





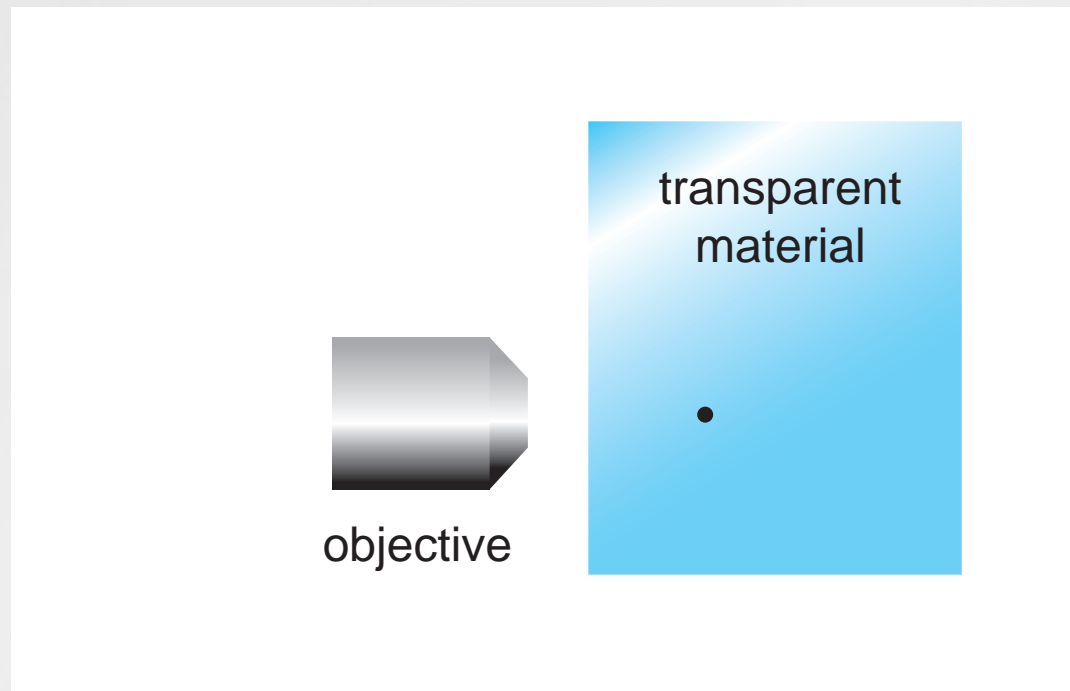
# Transparent materials

...causes nonlinear ionization...

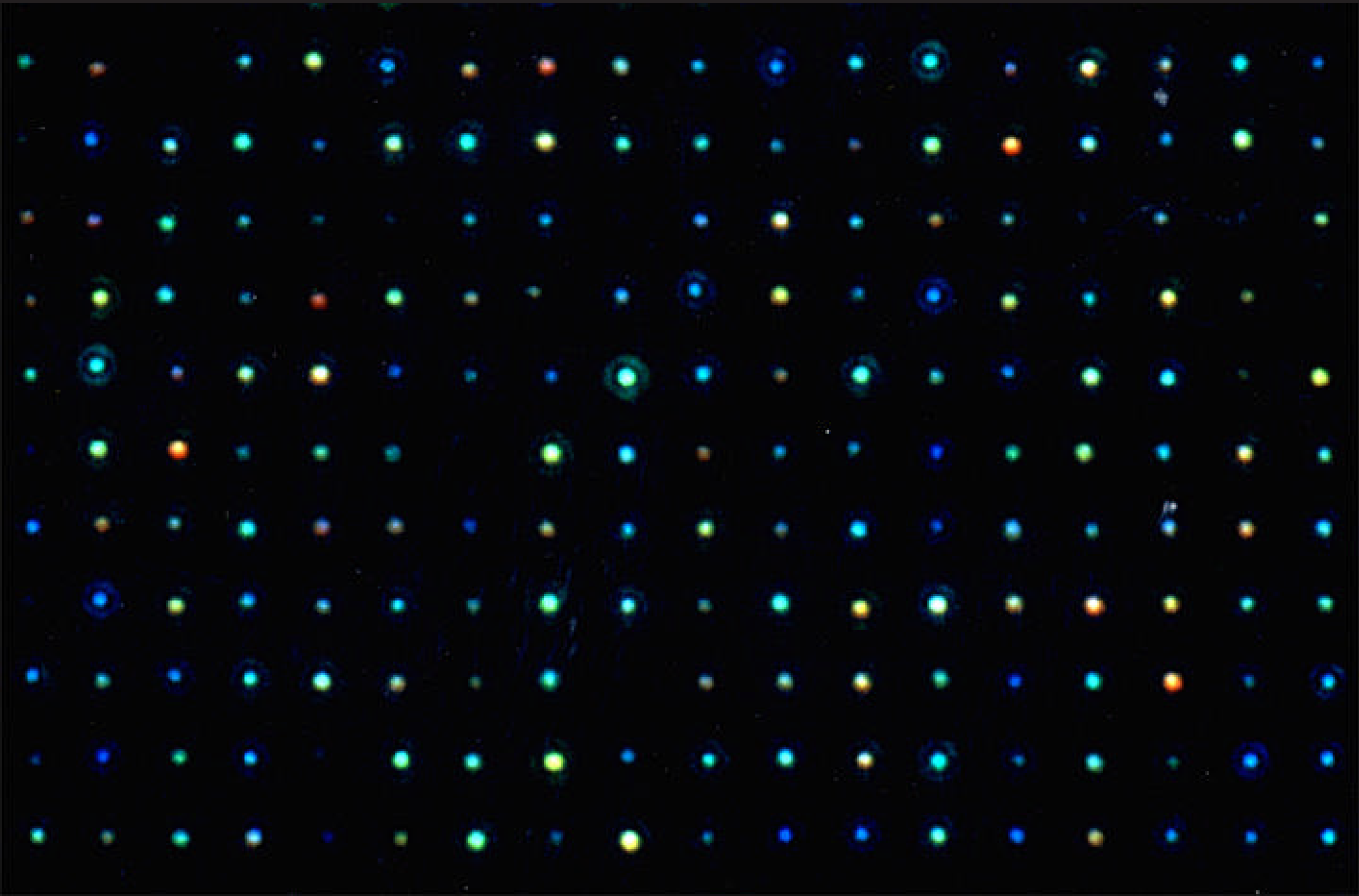


# Transparent materials

and 'microexplosion' causes microscopic damage...



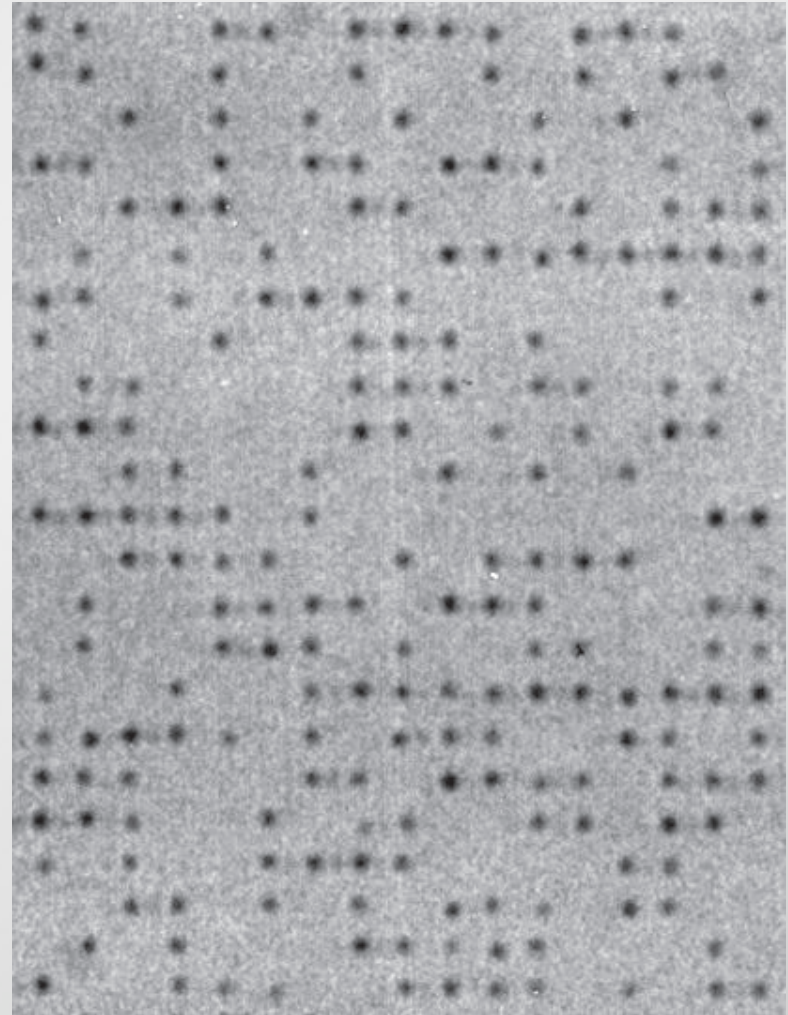
# Transparent materials



# Transparent materials

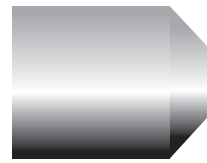
**Some applications:**

- **data storage**
- **waveguides**
- **microfluidics**



# Transparent materials

## Dark-field scattering



objective

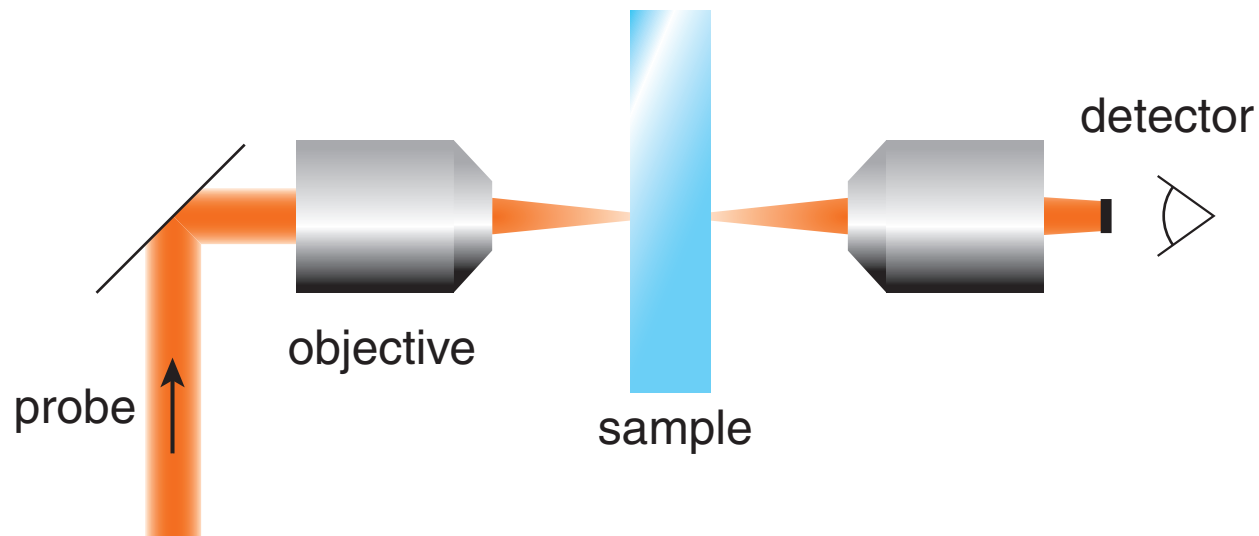


sample



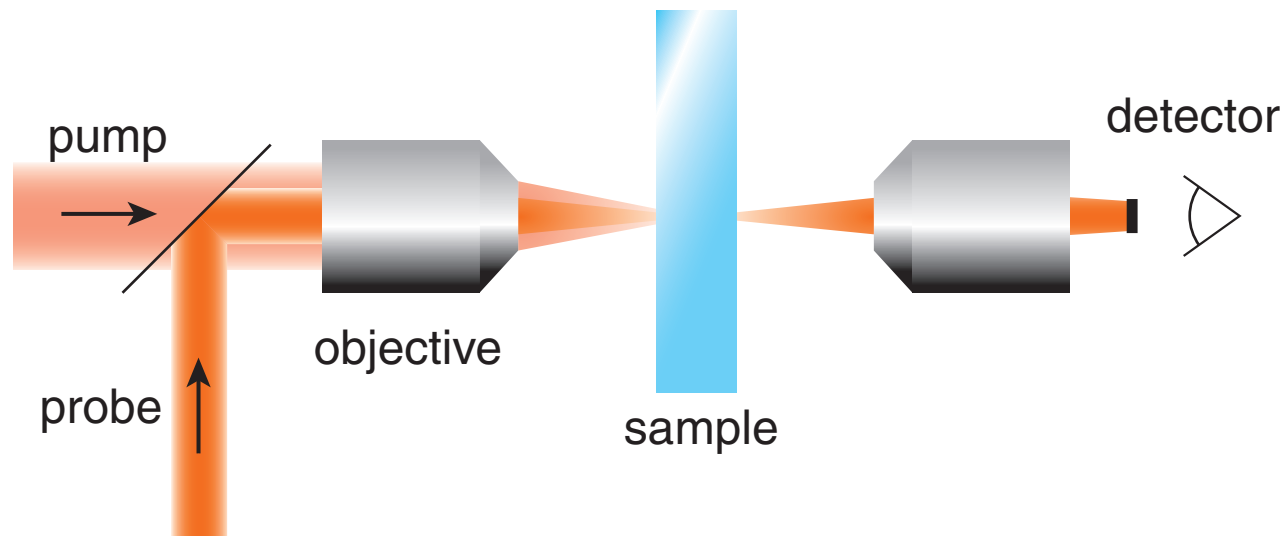
# Transparent materials

block probe beam...



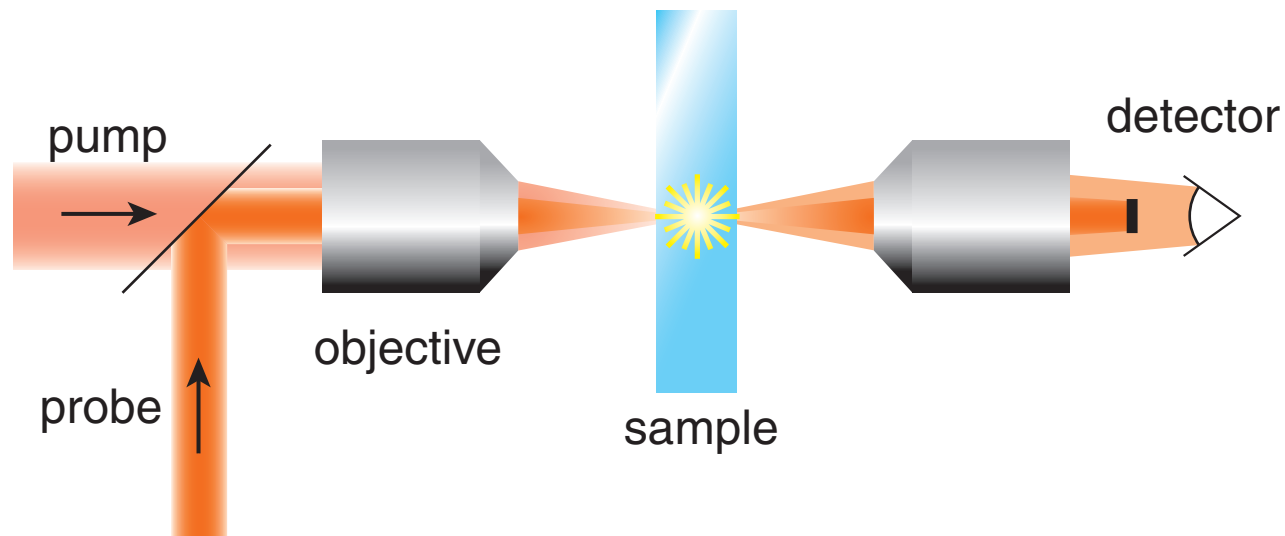
# Transparent materials

... bring in pump beam...



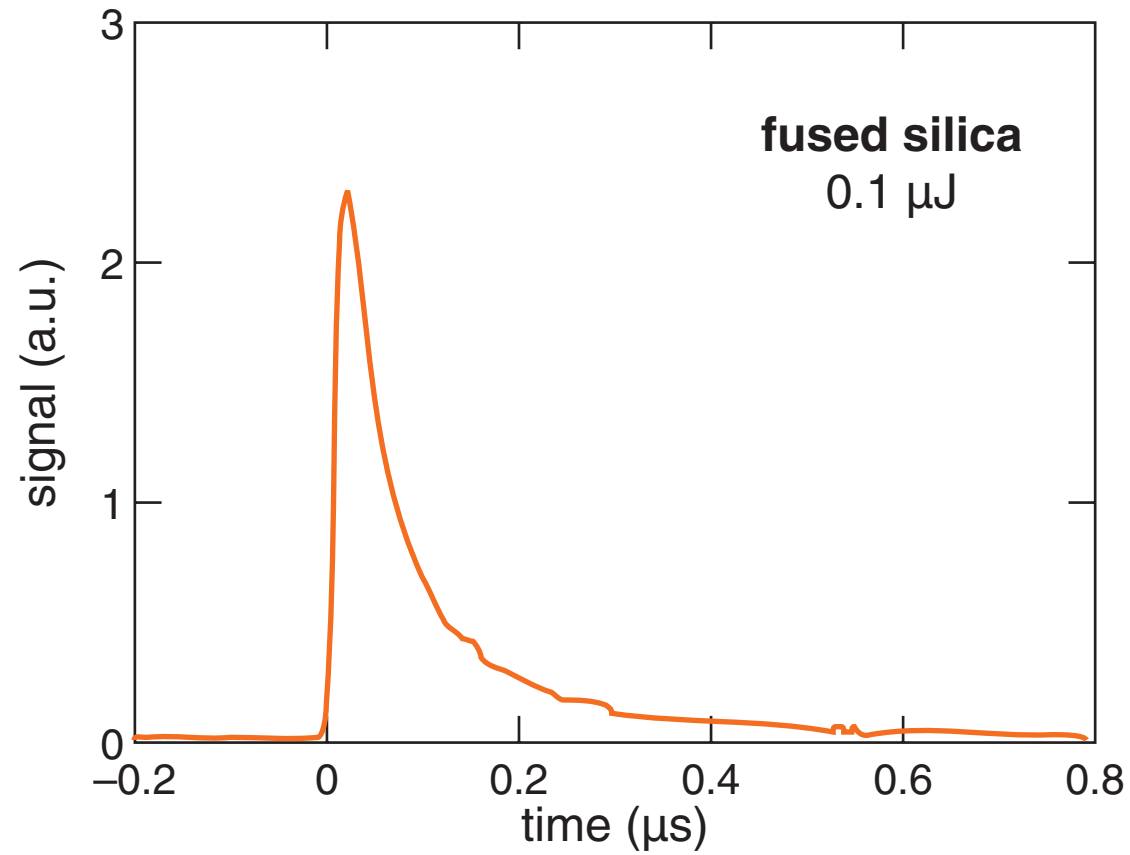
# Transparent materials

... damage scatters probe beam



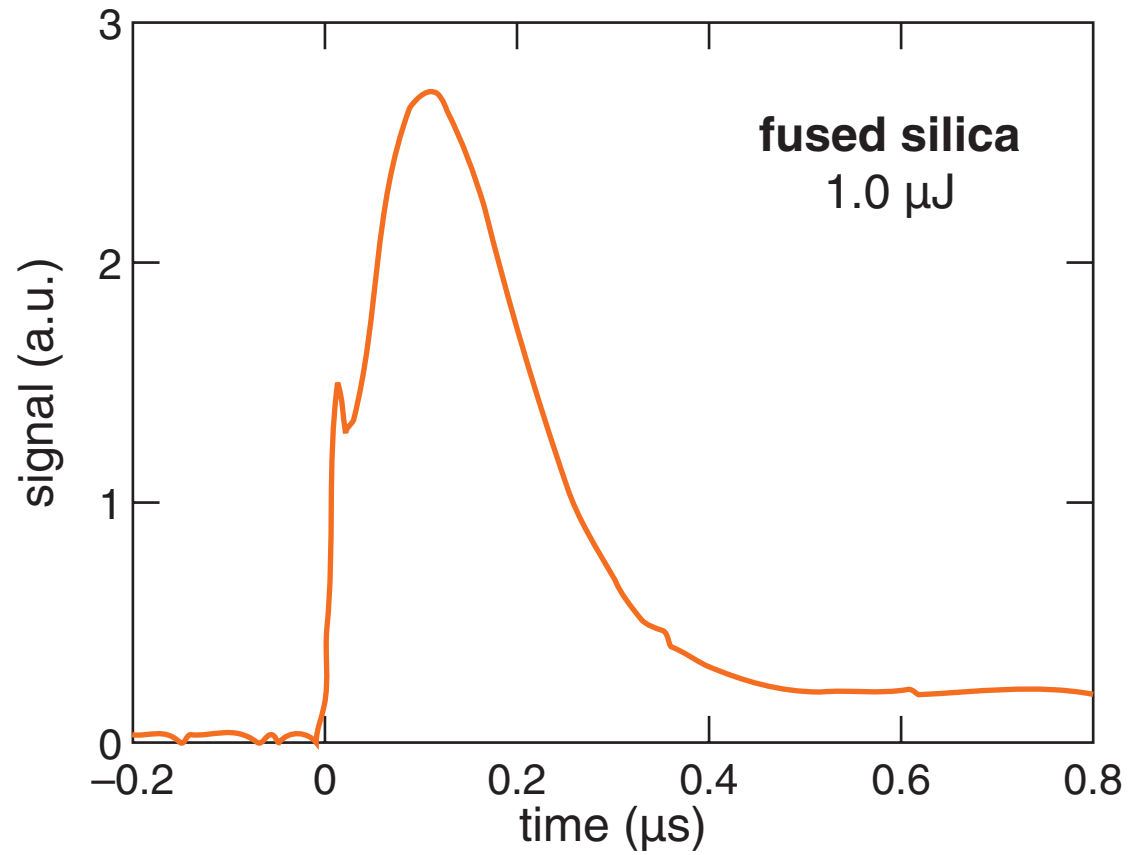
# Transparent materials

scattered signal



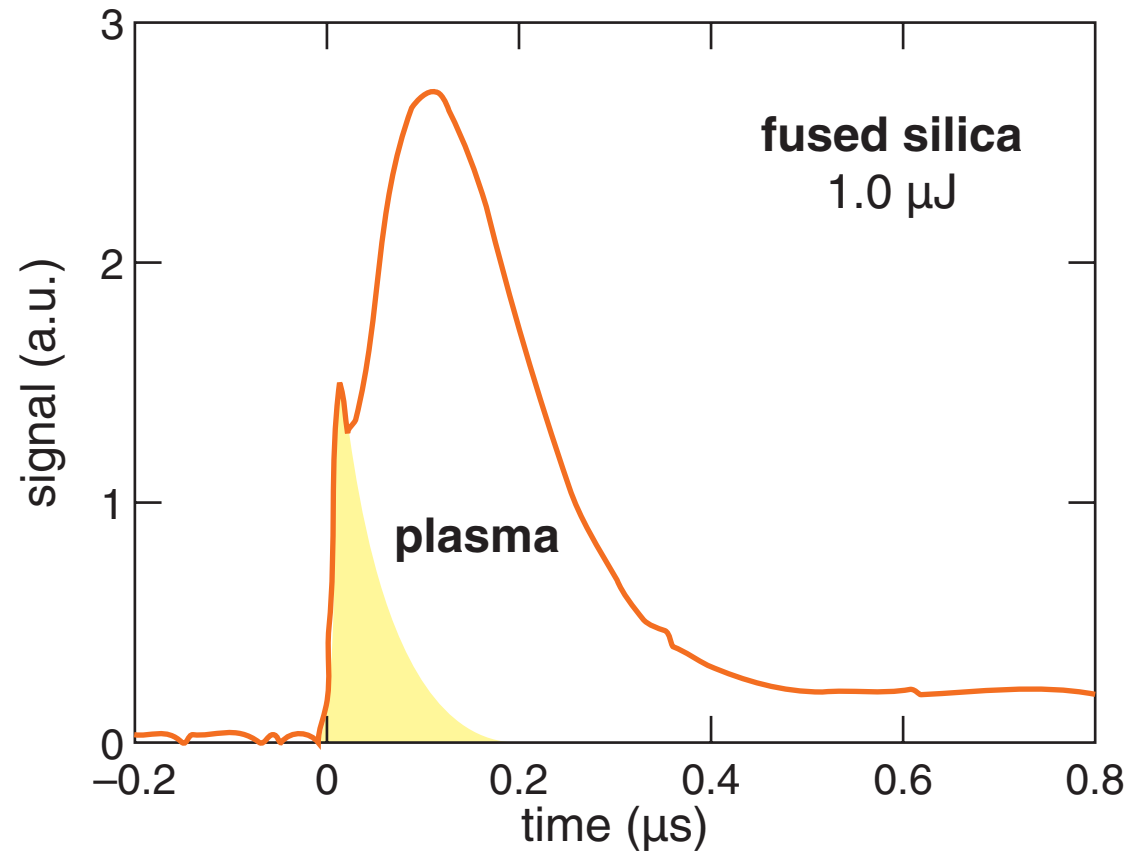
# Transparent materials

scattered signal



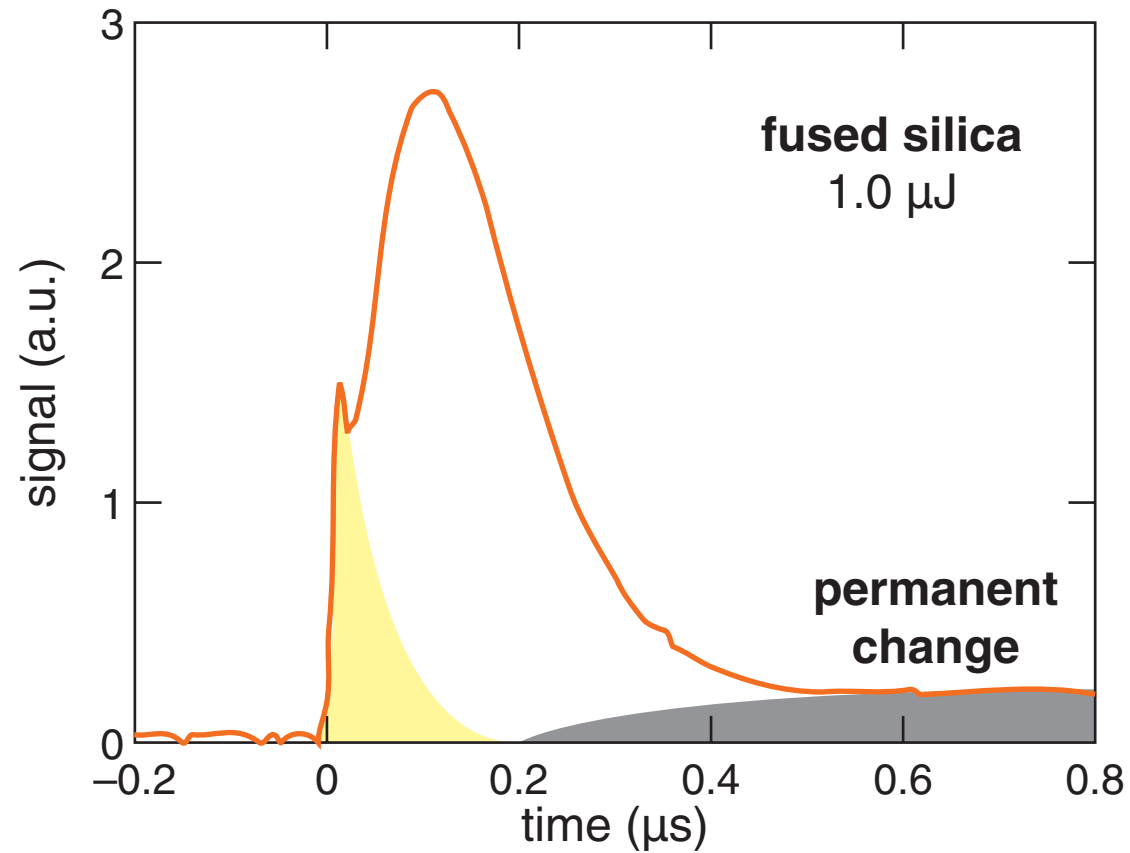
# Transparent materials

scattered signal



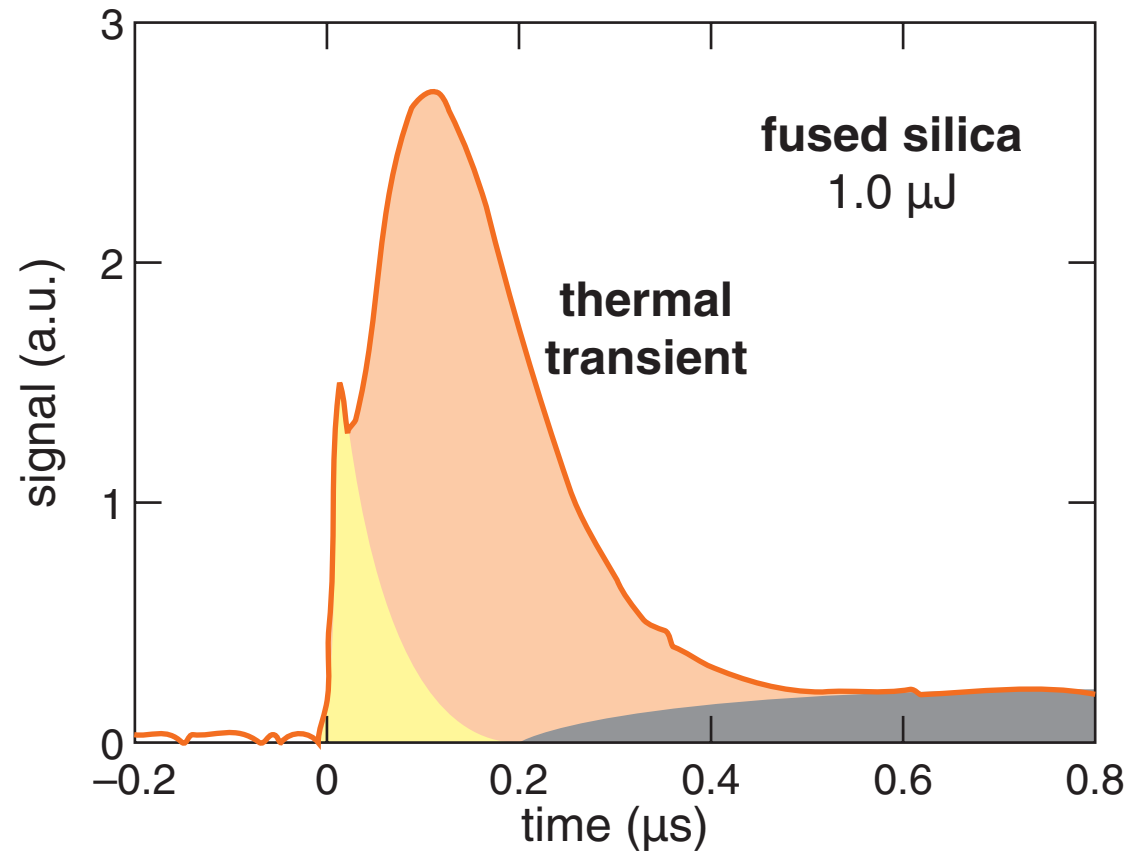
# Transparent materials

scattered signal



# Transparent materials

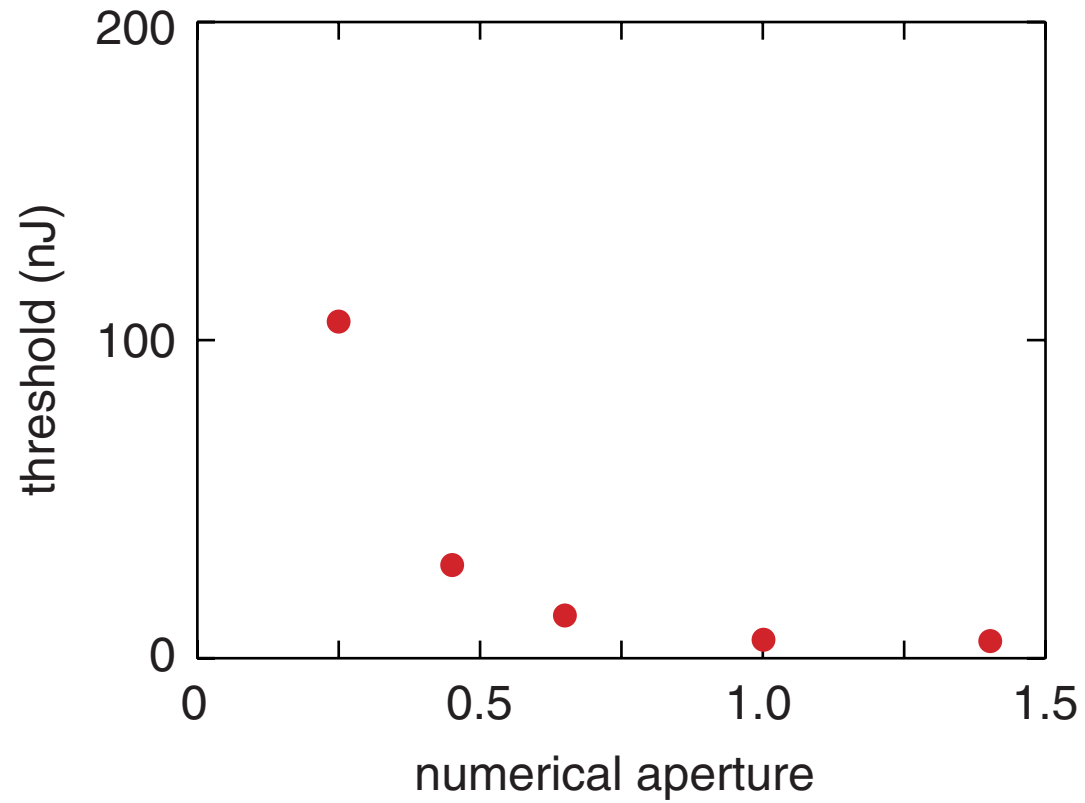
scattered signal





# Transparent materials

vary numerical aperture



# Transparent materials

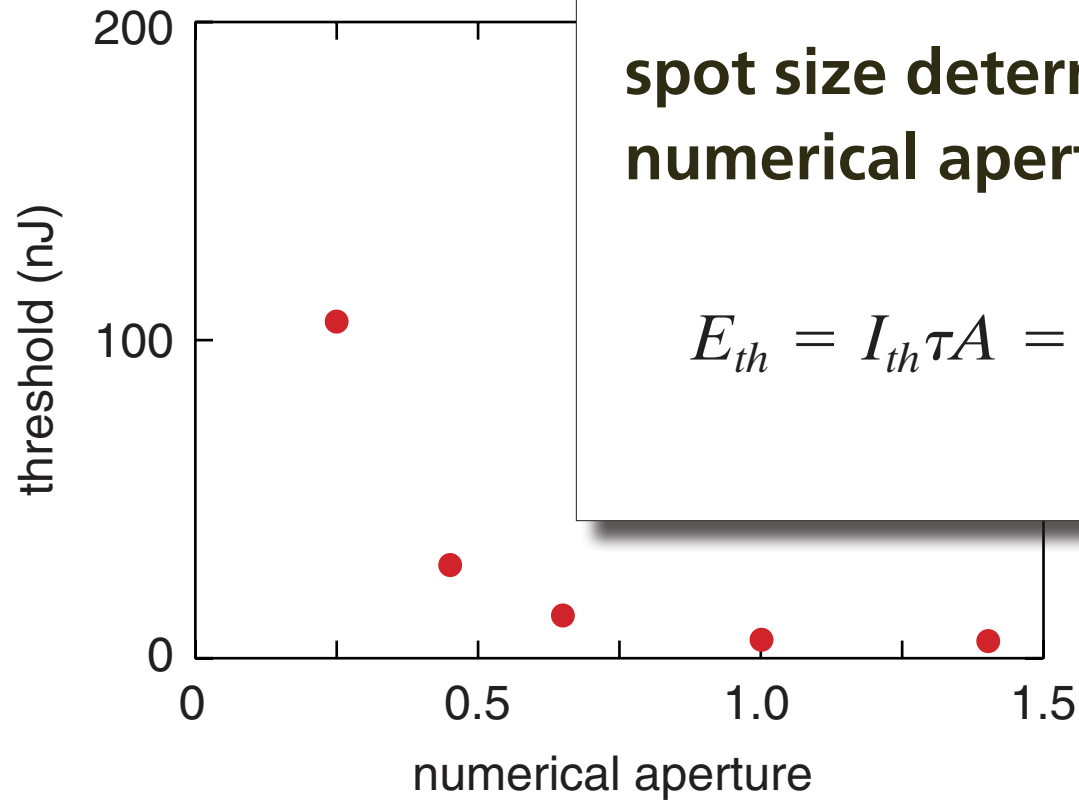
vary numeric

intensity threshold:

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

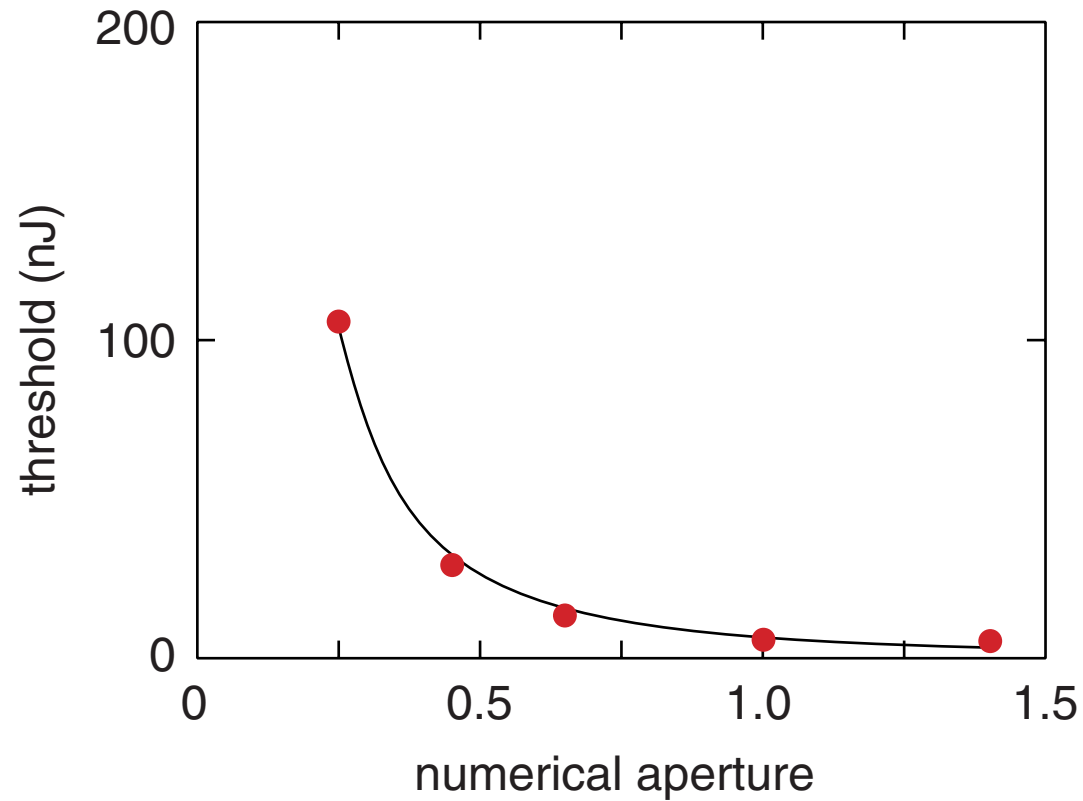
spot size determined by  
numerical aperture:

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



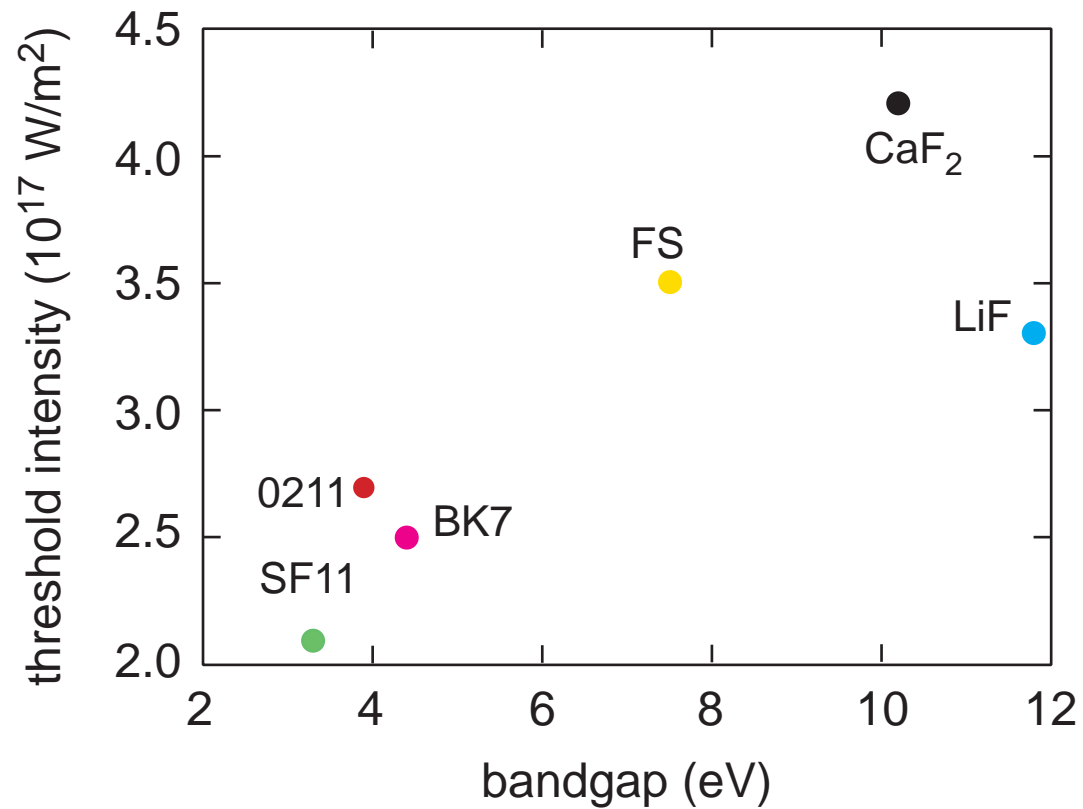
# Transparent materials

fit gives threshold intensity:  $I_{th} = 2.5 \times 10^{17} \text{ W/m}^2$



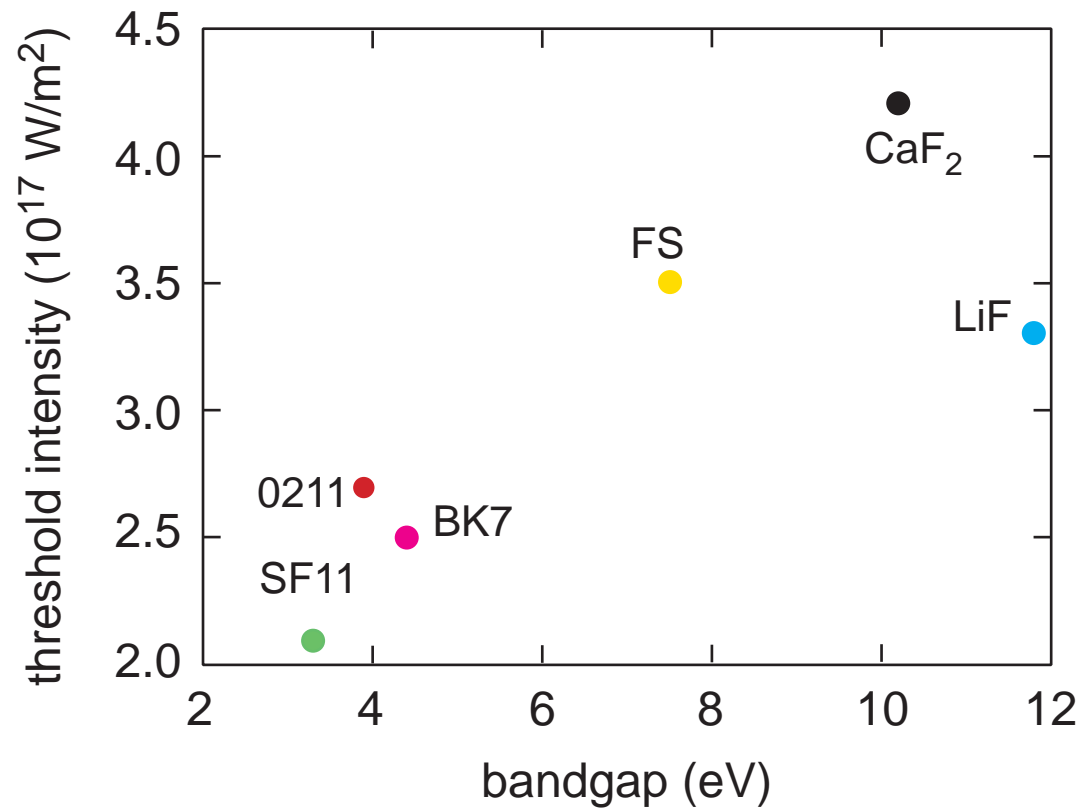
# Transparent materials

vary material...



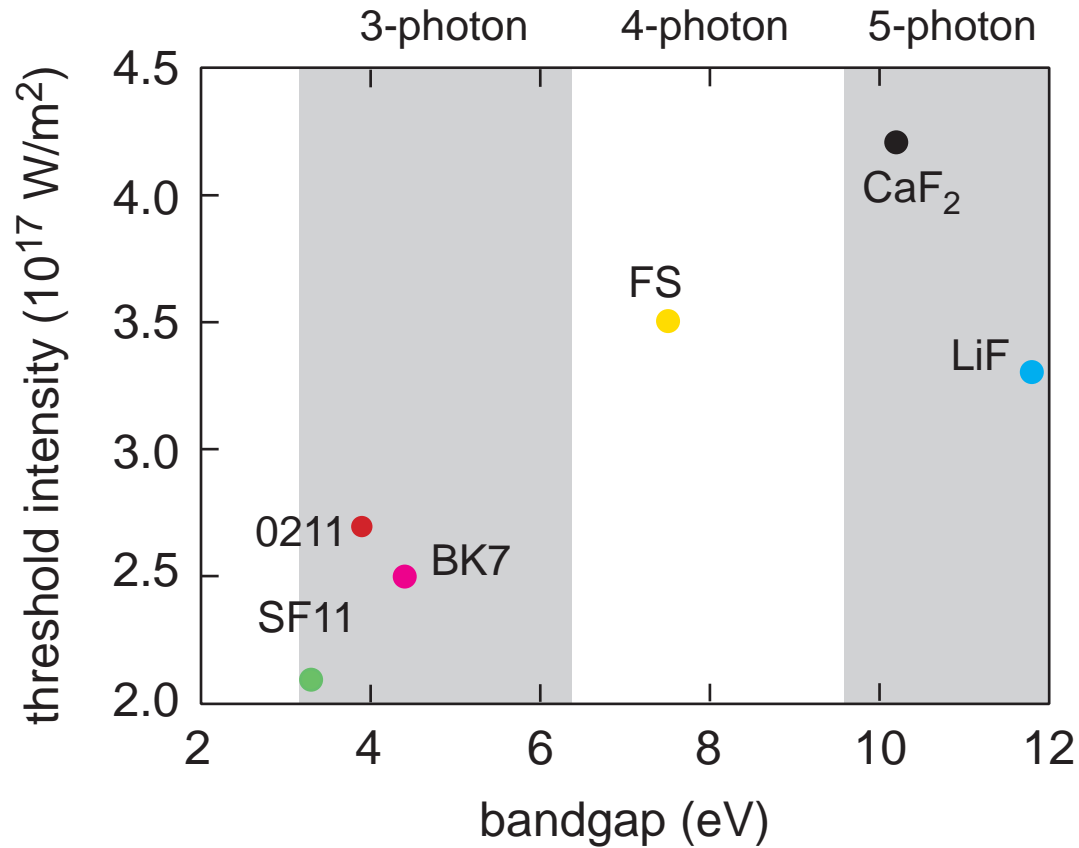
# Transparent materials

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



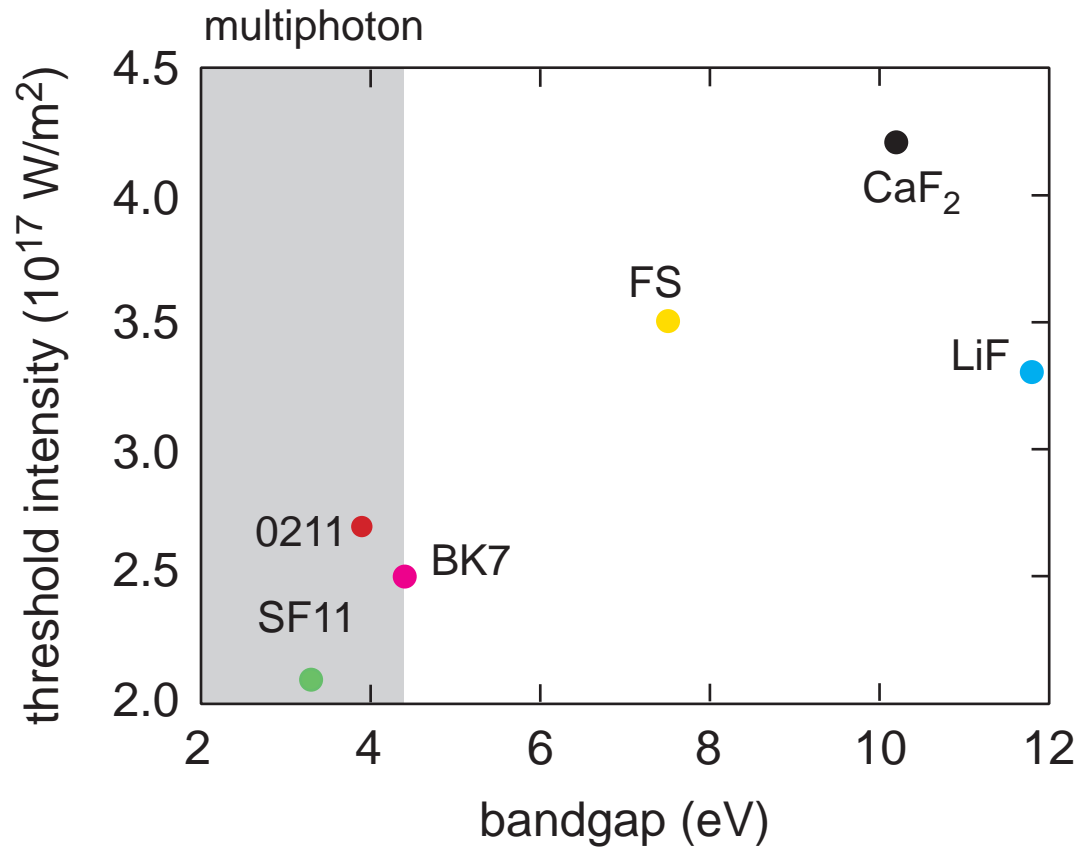
# Transparent materials

would expect much more than a factor of 2



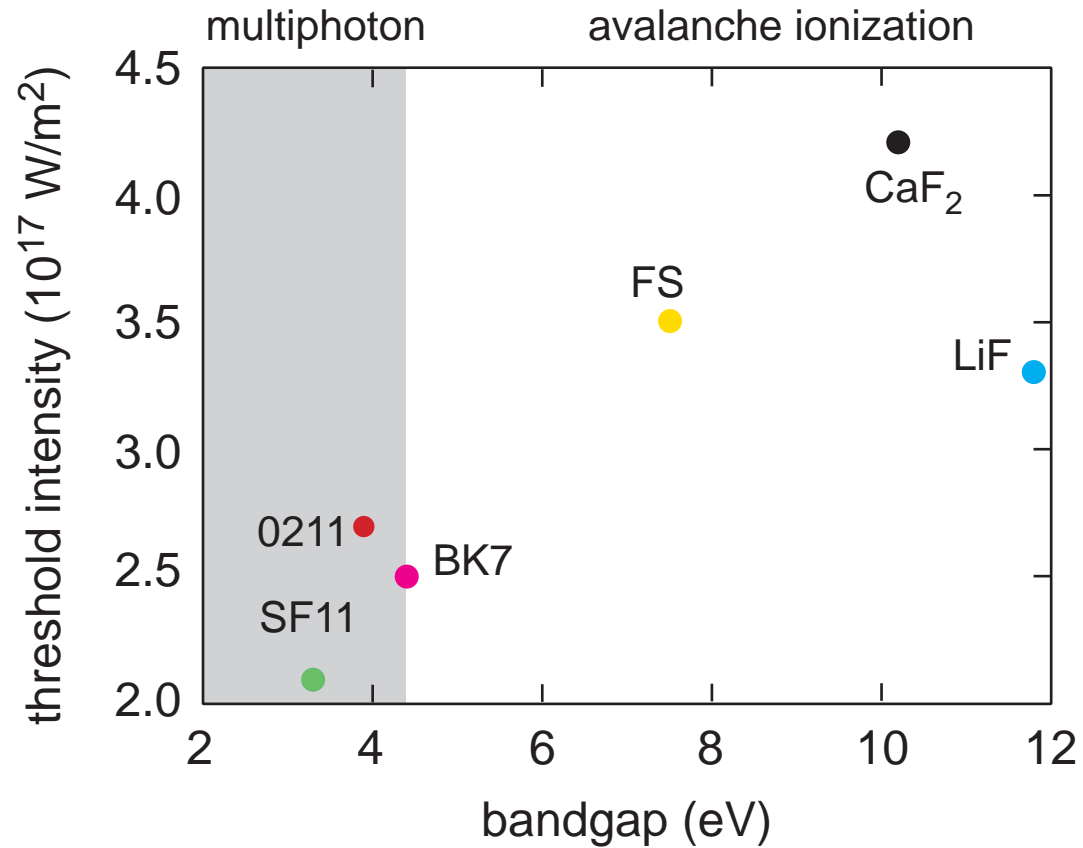
# Transparent materials

critical density reached by multiphoton for low gap only



# Transparent materials

avalanche ionization important at high gap





# Transparent materials

**what prevents damage at low NA?**

# Transparent materials

**Competing nonlinear effects:**

- **multiphoton absorption**
- **supercontinuum generation**
- **self-focusing**

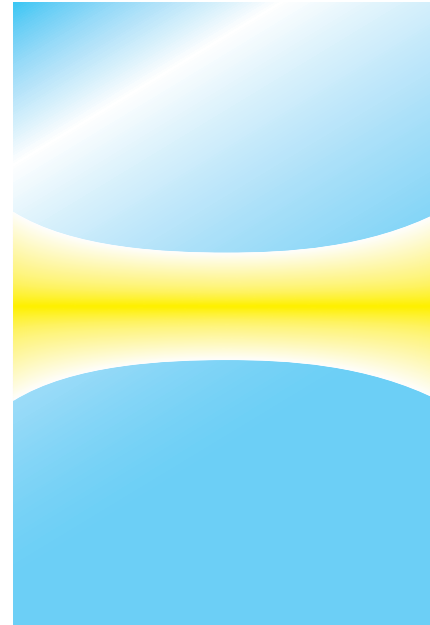
# Transparent materials

why the difference?

high NA



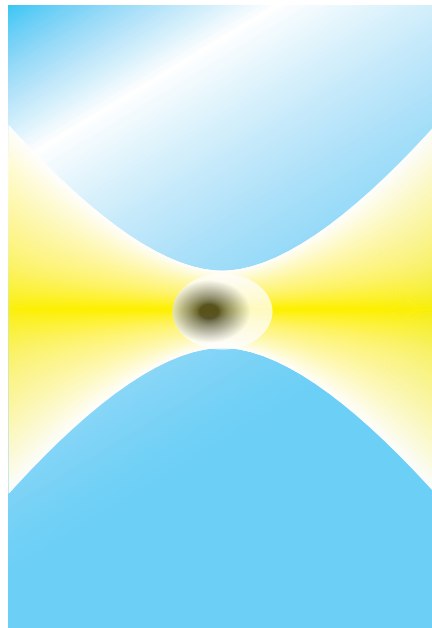
low NA



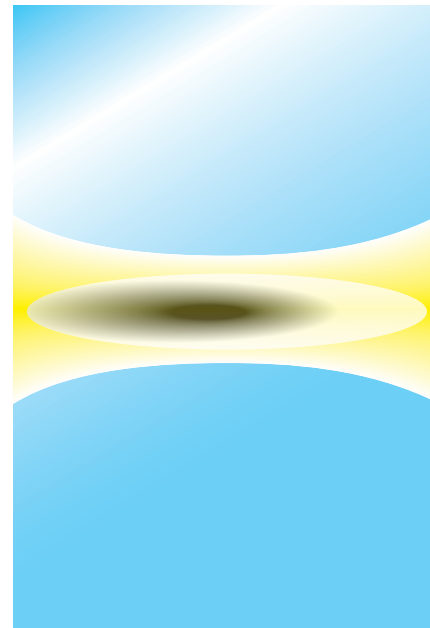
# Transparent materials

very different confocal length/interaction length

high NA



low NA

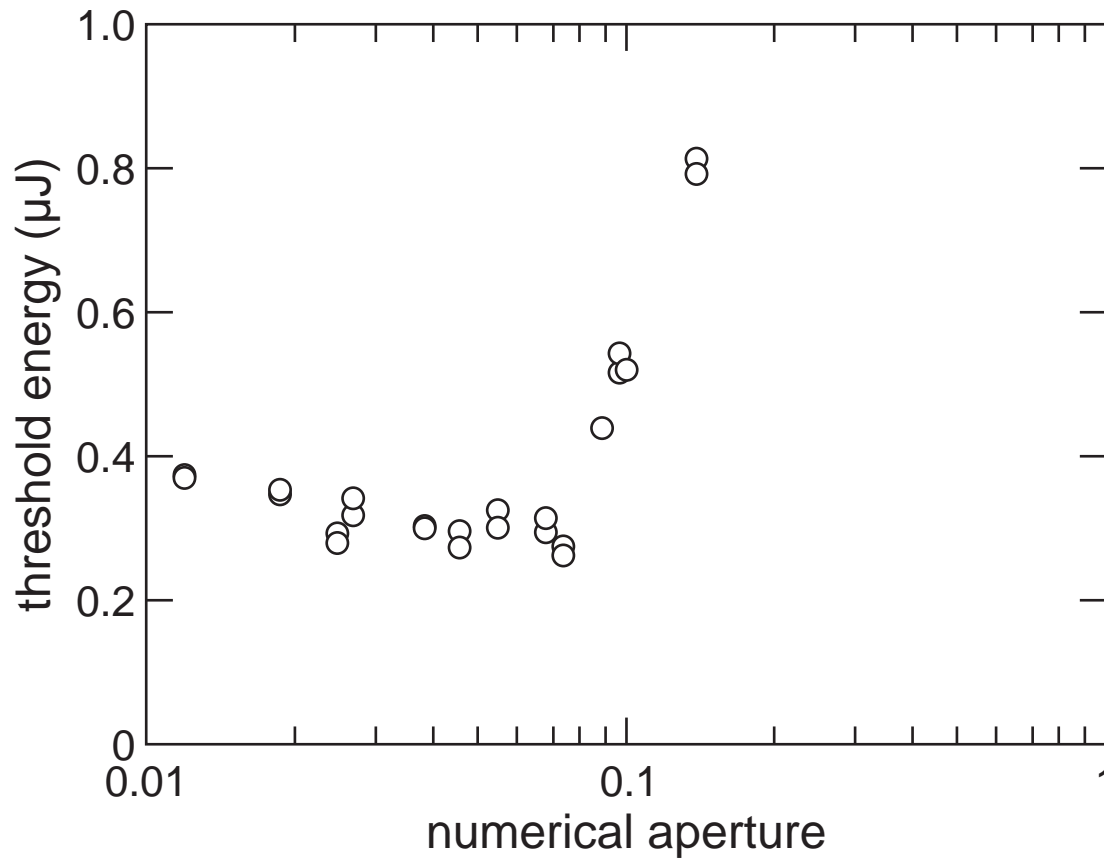


# Transparent materials

**high NA: interaction length too short for self-focusing**

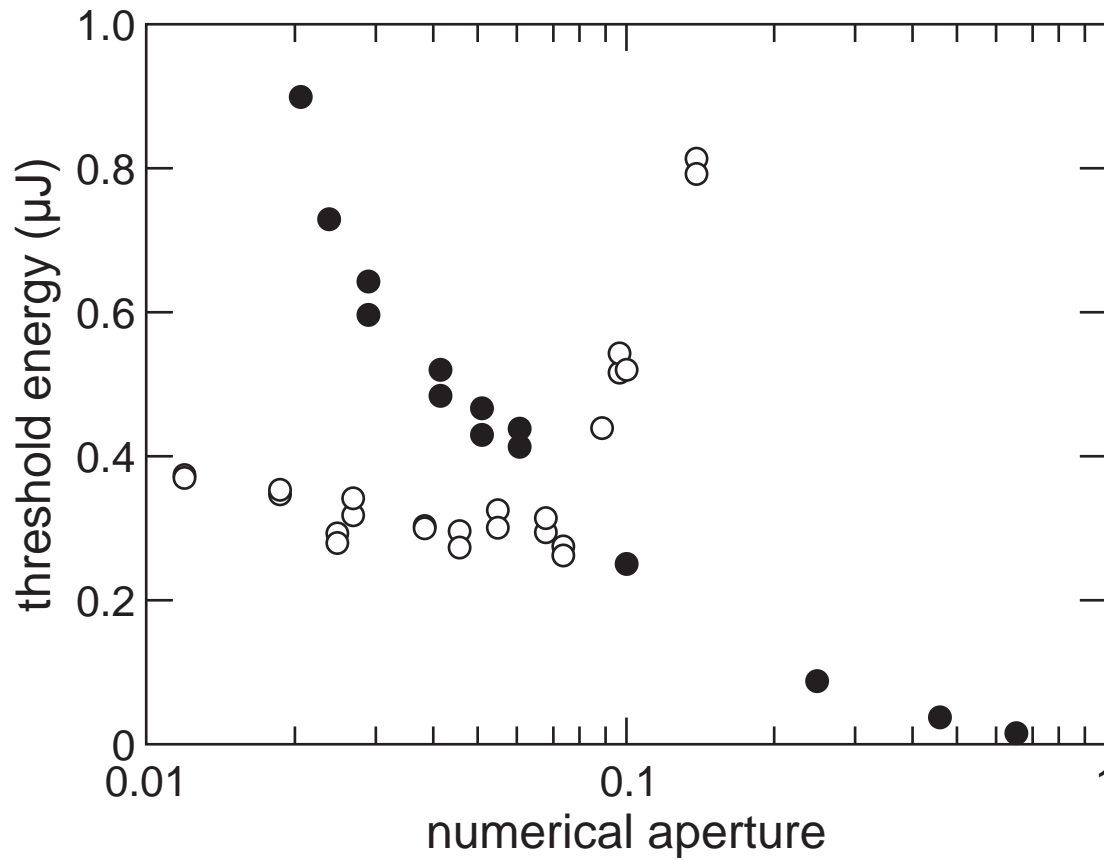
# Transparent materials

threshold for supercontinuum generation



# Transparent materials

threshold for damage



# Transparent materials

## Points to keep in mind:

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

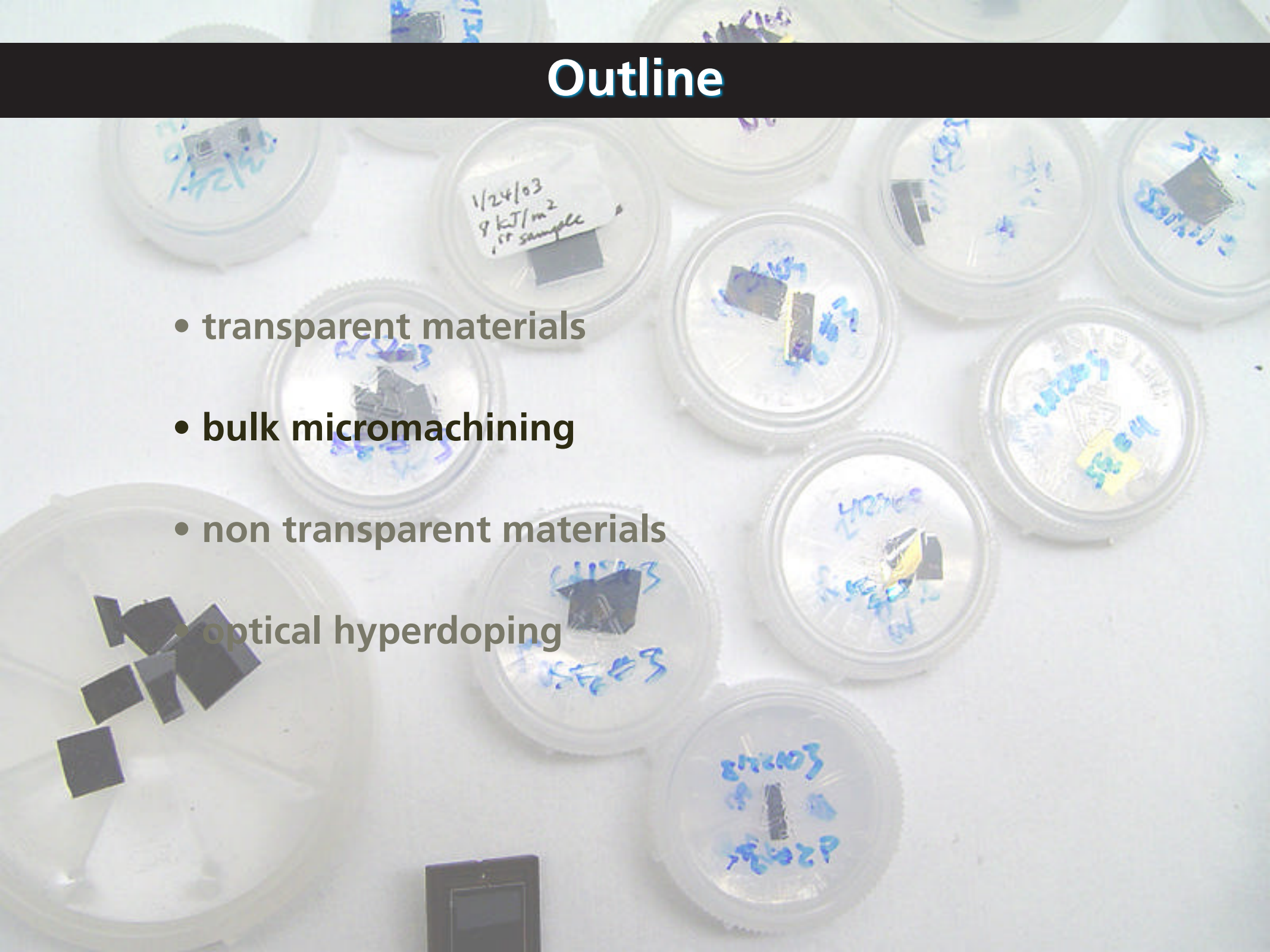
*Nature Photonics* 2, 219 (2008)





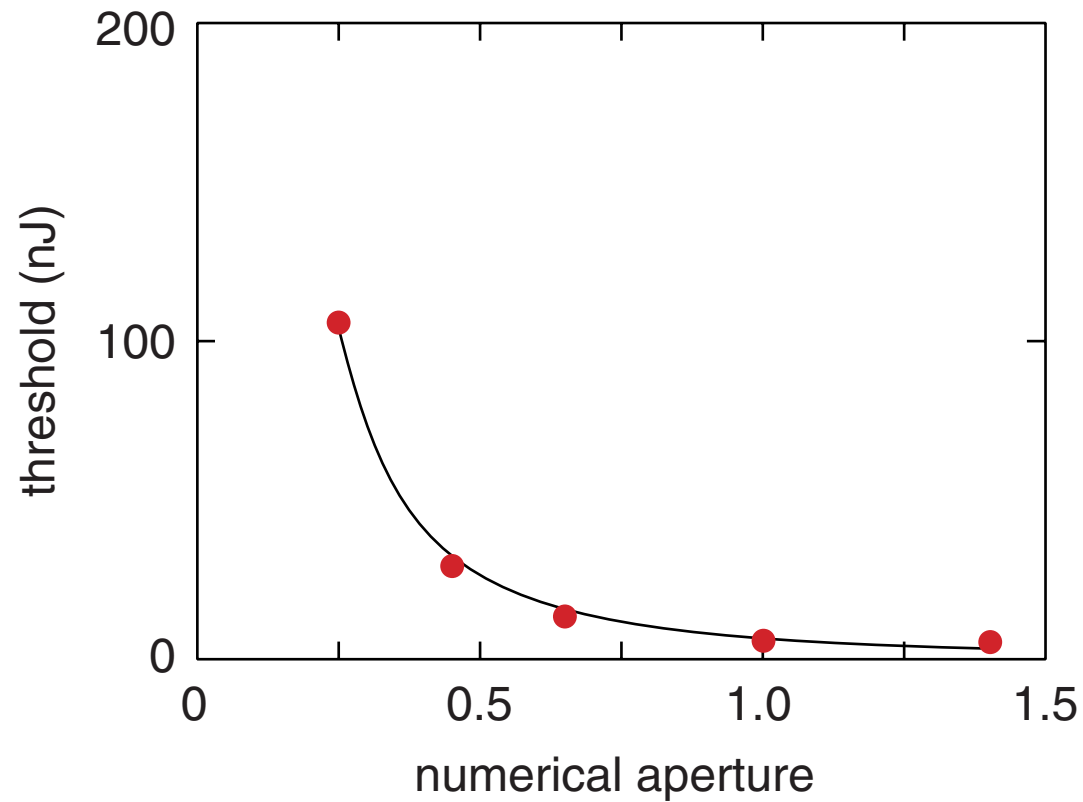
# Outline

- transparent materials
- bulk micromachining
- non transparent materials
- optical hyperdoping



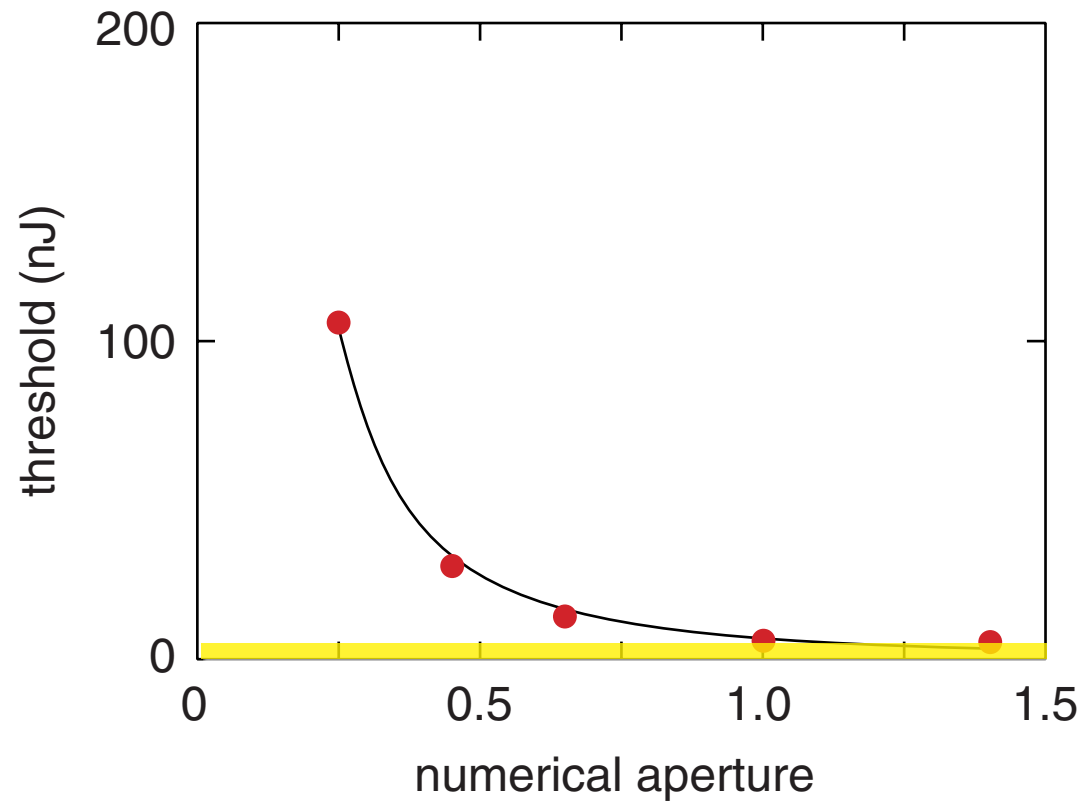
# Bulk micromachining

threshold decreases with increasing numerical aperture



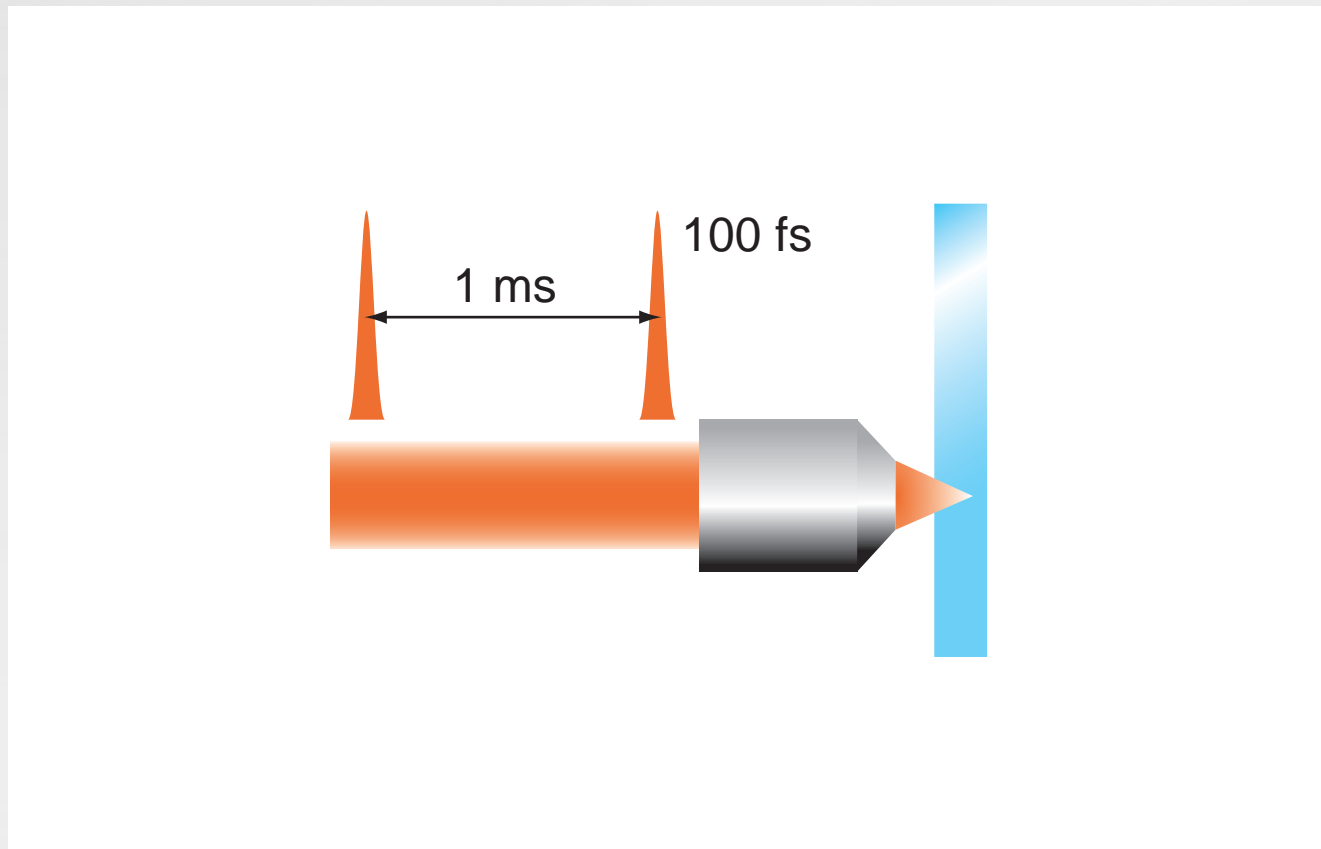
# Bulk micromachining

less than 10 nJ at high numerical aperture!



# Bulk micromachining

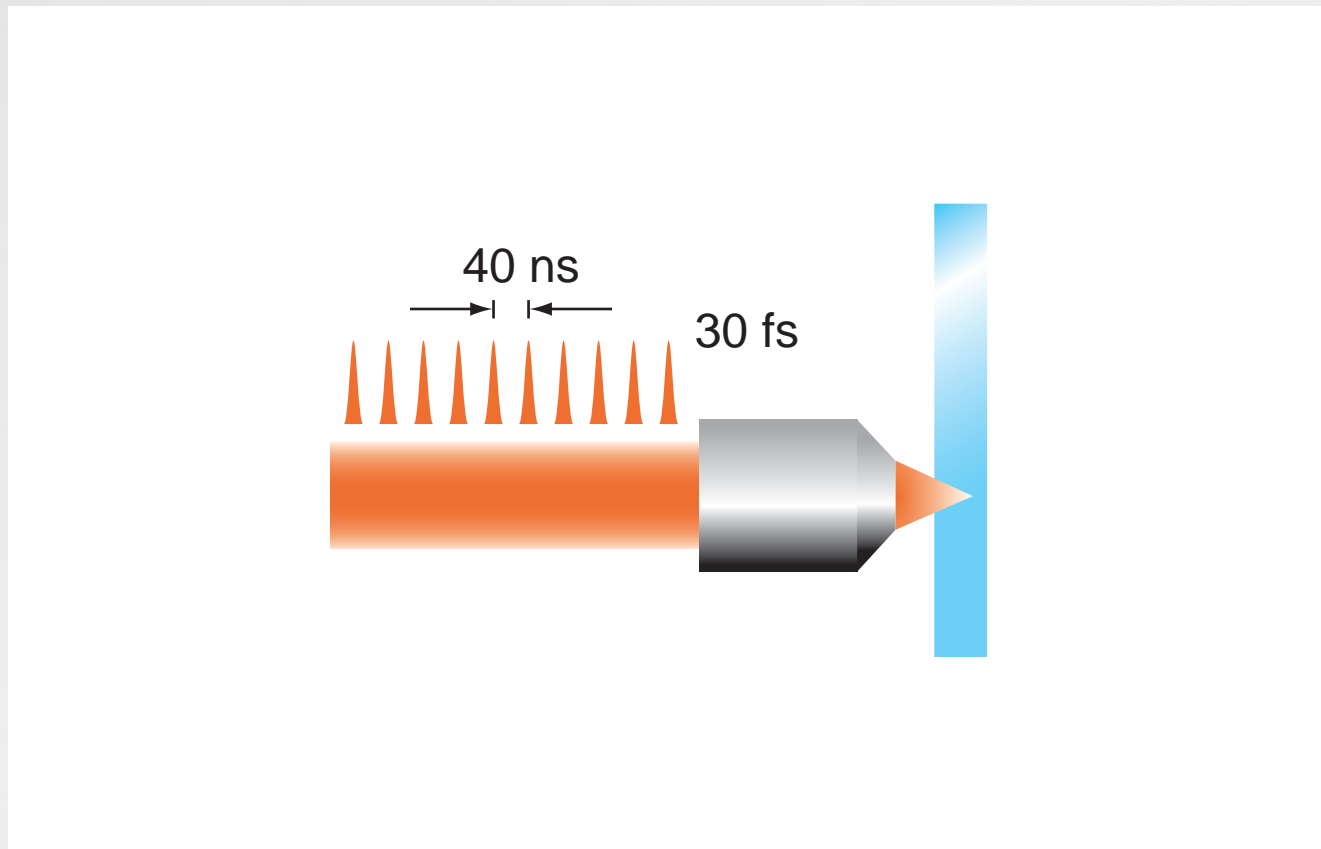
amplified laser: 1 kHz, 1 mJ



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

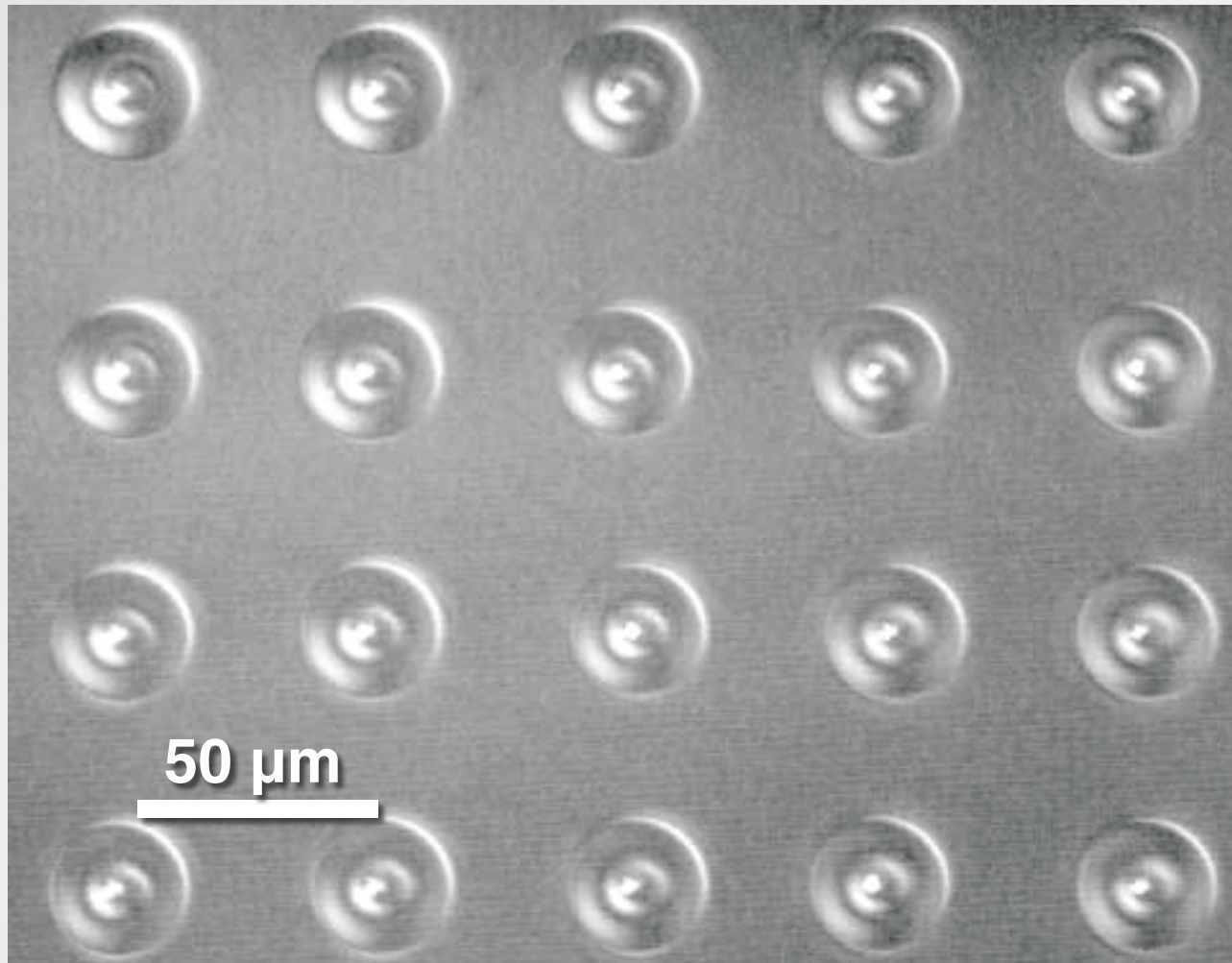
# Bulk micromachining

long cavity oscillator: 25 MHz, 25 nJ



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

# Bulk micromachining



# Bulk micromachining

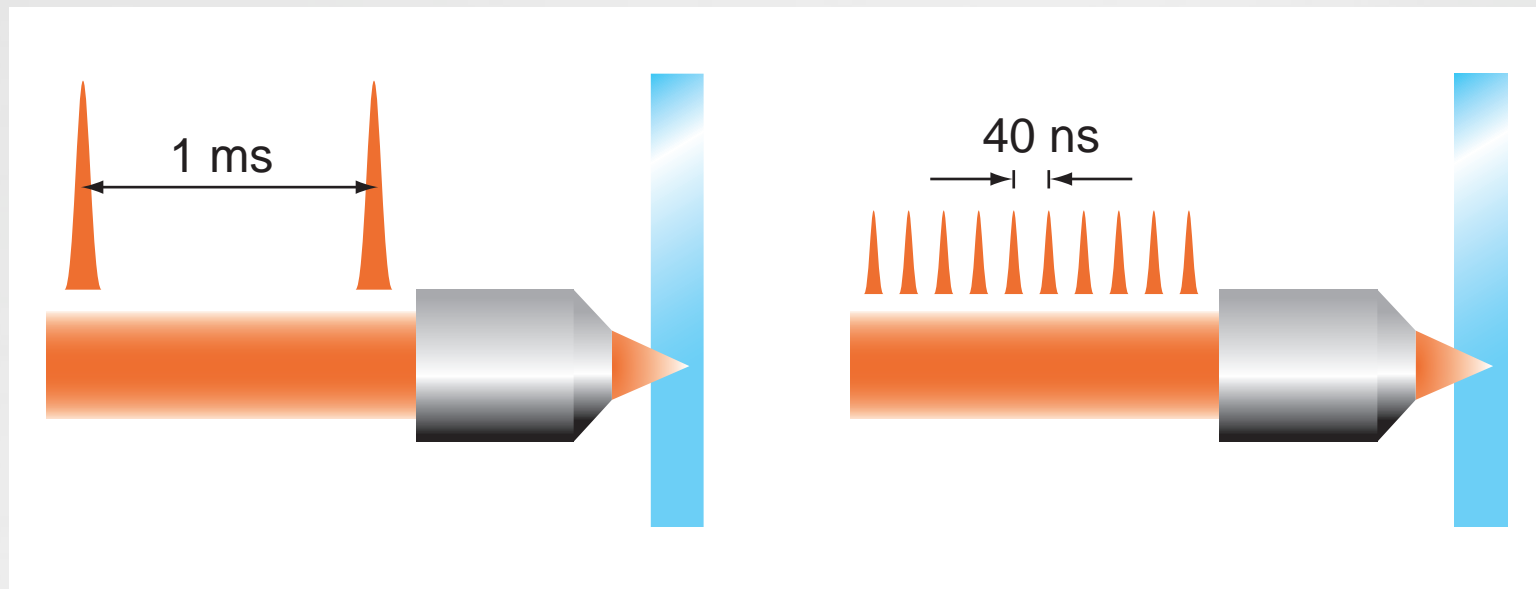
**High repetition-rate micromachining:**

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

# Bulk micromachining

amplified laser

oscillator



repetitive

cumulative

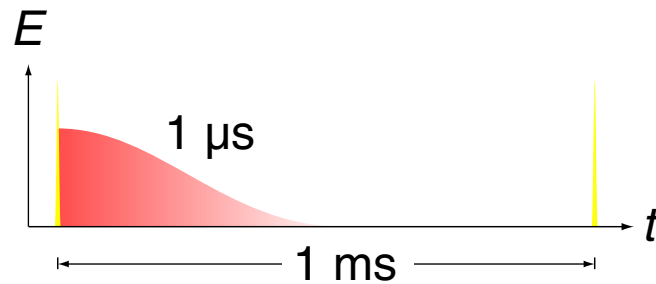


# Bulk micromachining

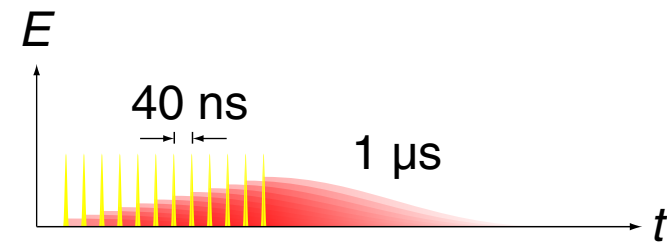
amplified laser

oscillator

low repetition rate



high repetition rate

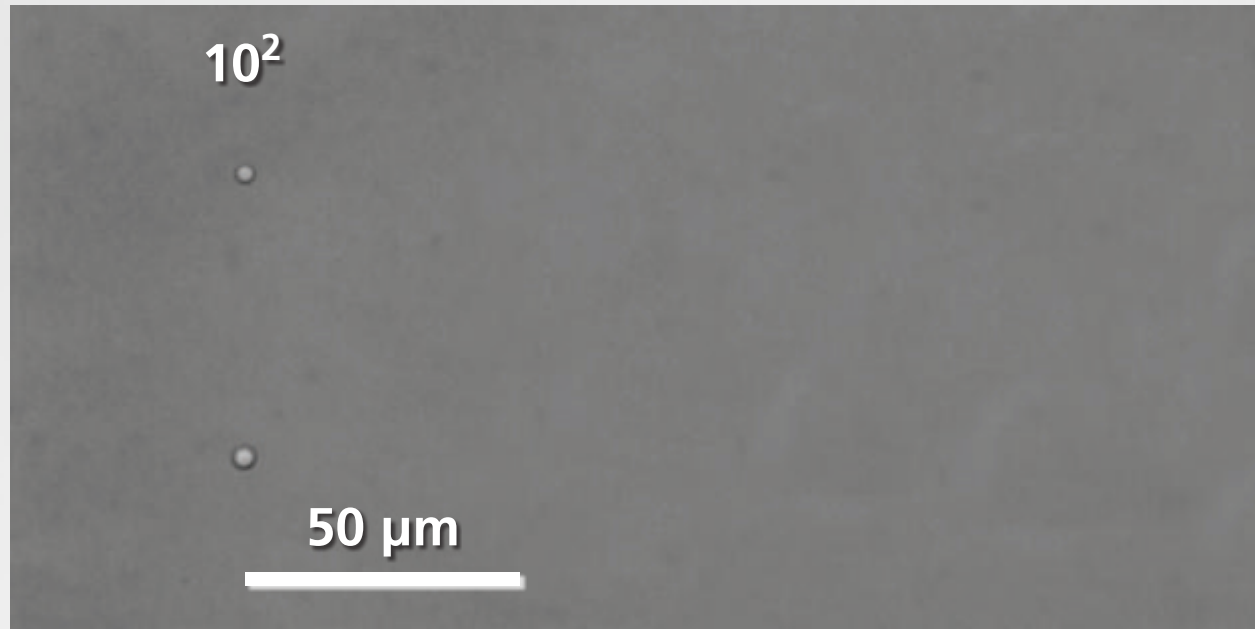


repetitive

cumulative

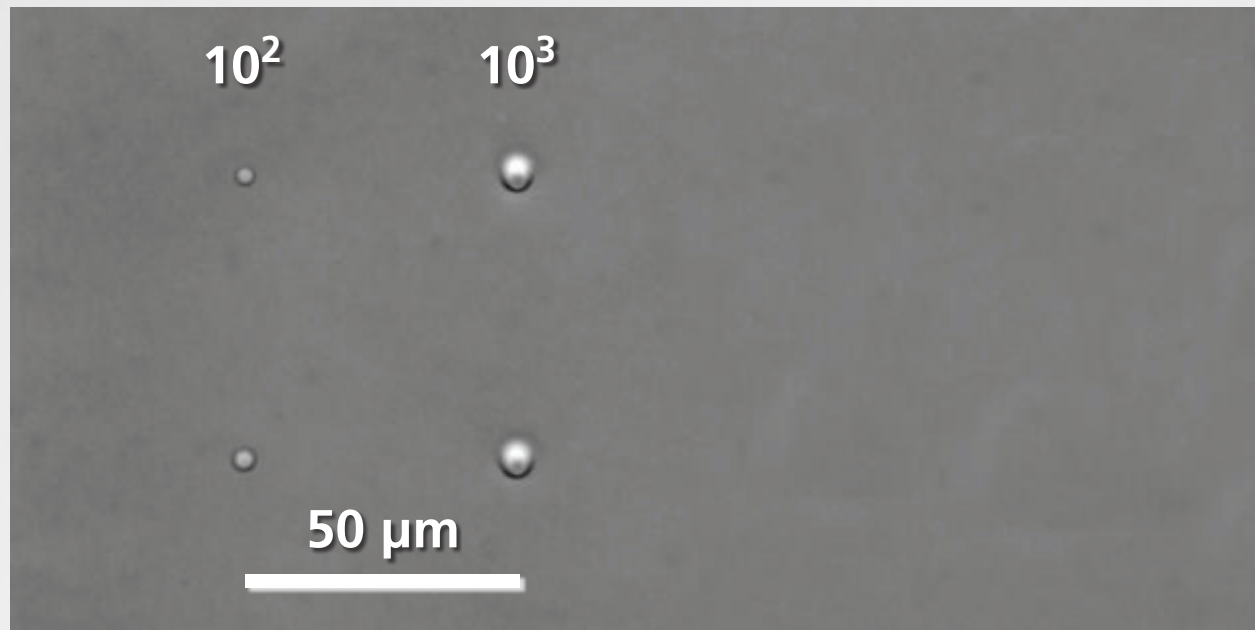
# Bulk micromachining

the longer the irradiation...



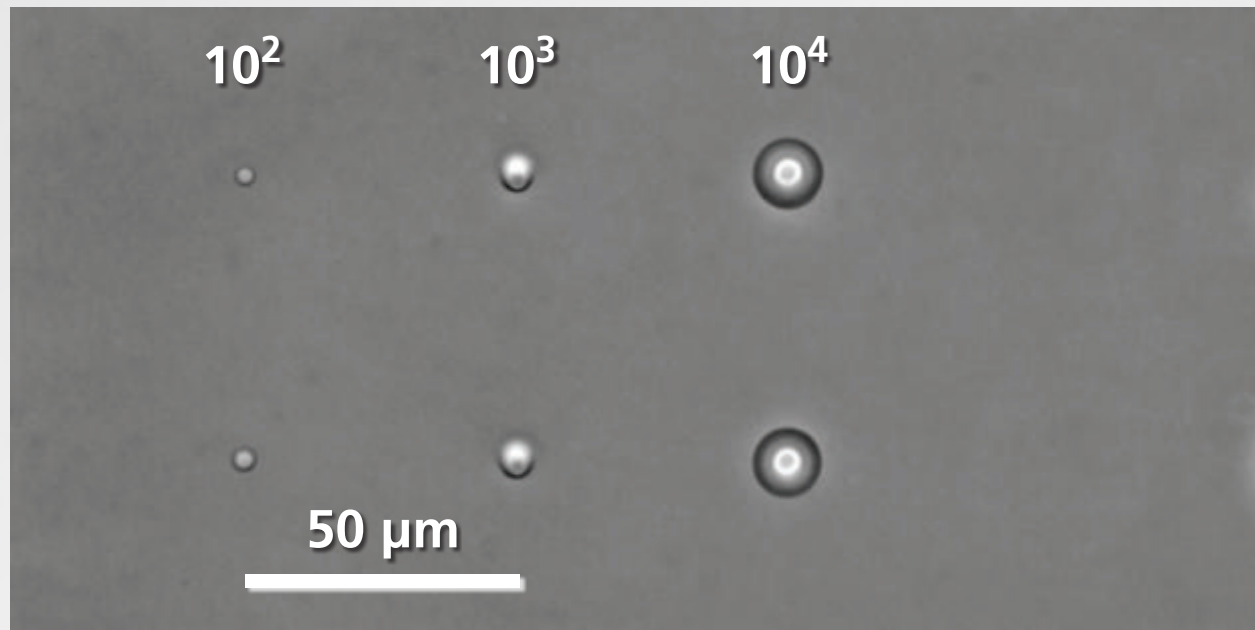
# Bulk micromachining

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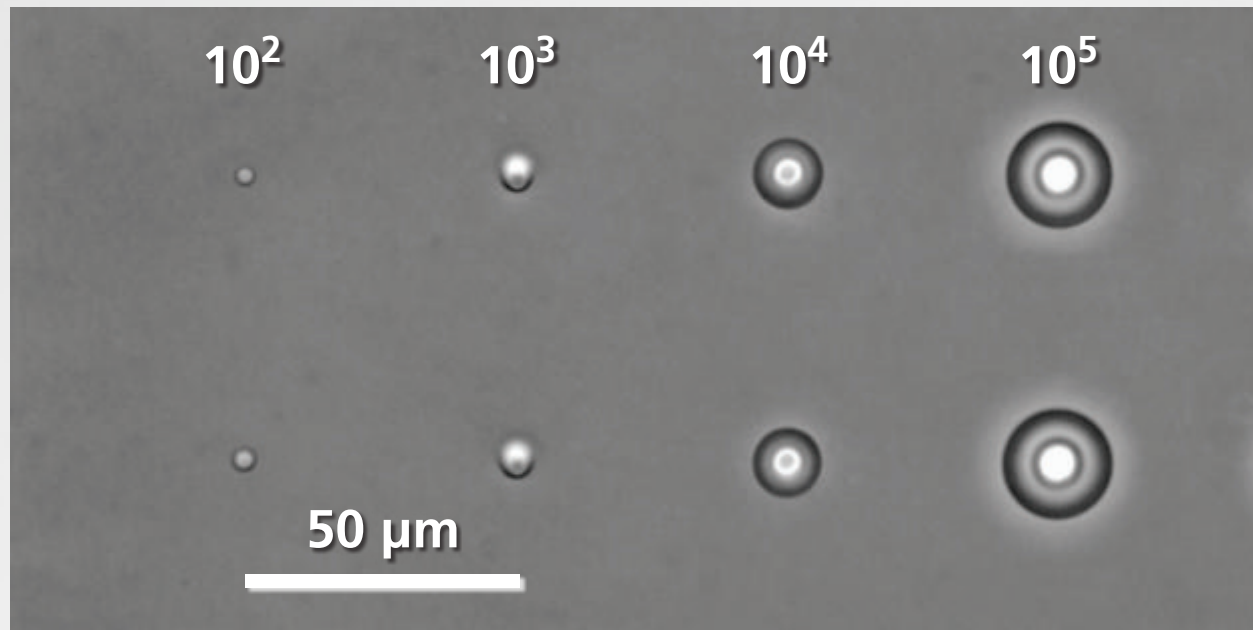
# Bulk micromachining

the longer the irradiation...



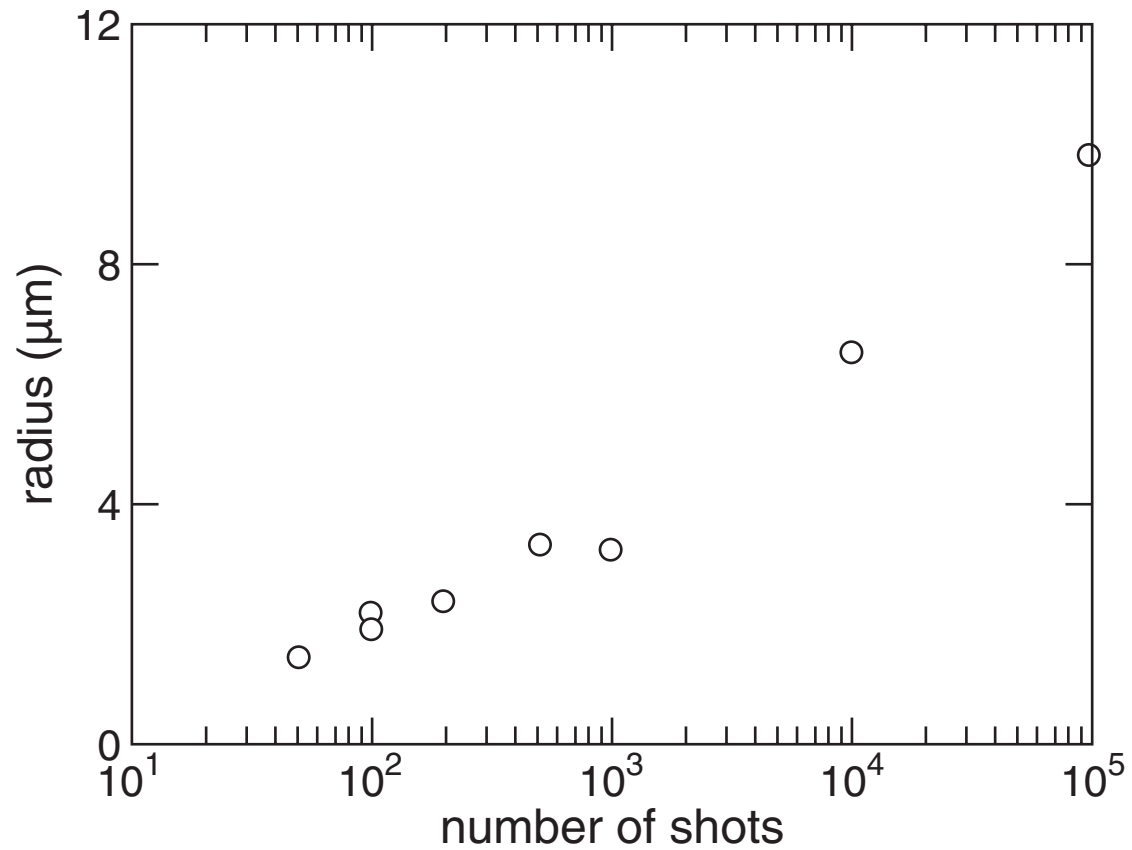
# Bulk micromachining

the longer the irradiation...



... the larger the radius

# Bulk micromachining

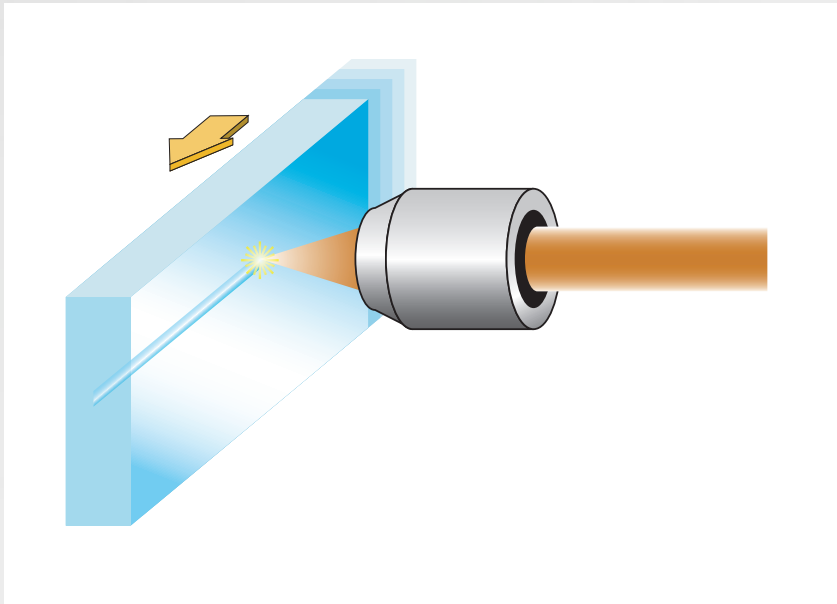


# Bulk micromachining

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

# Bulk micromachining

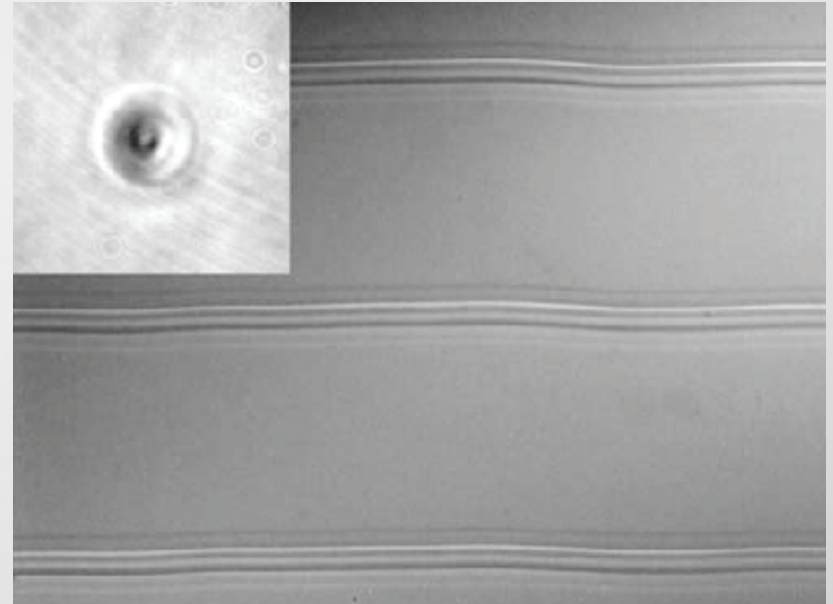
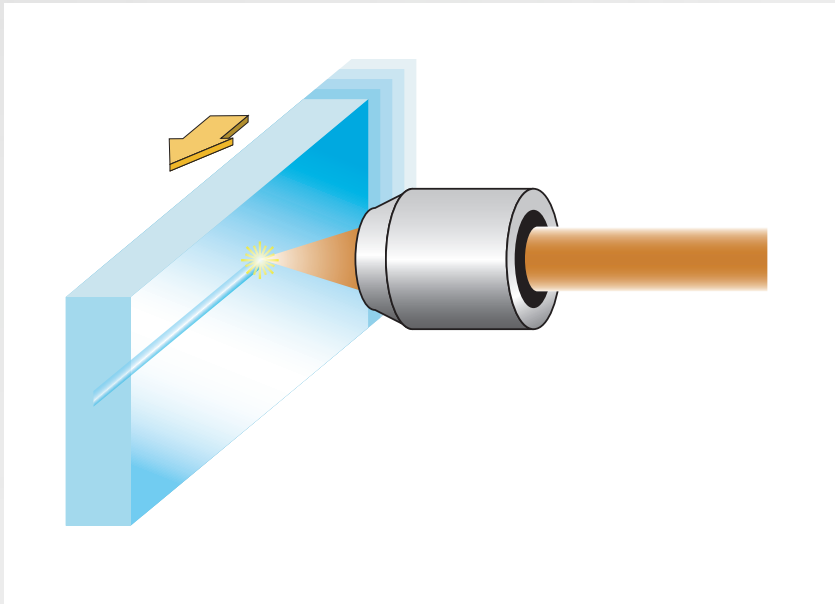
## waveguide micromachining





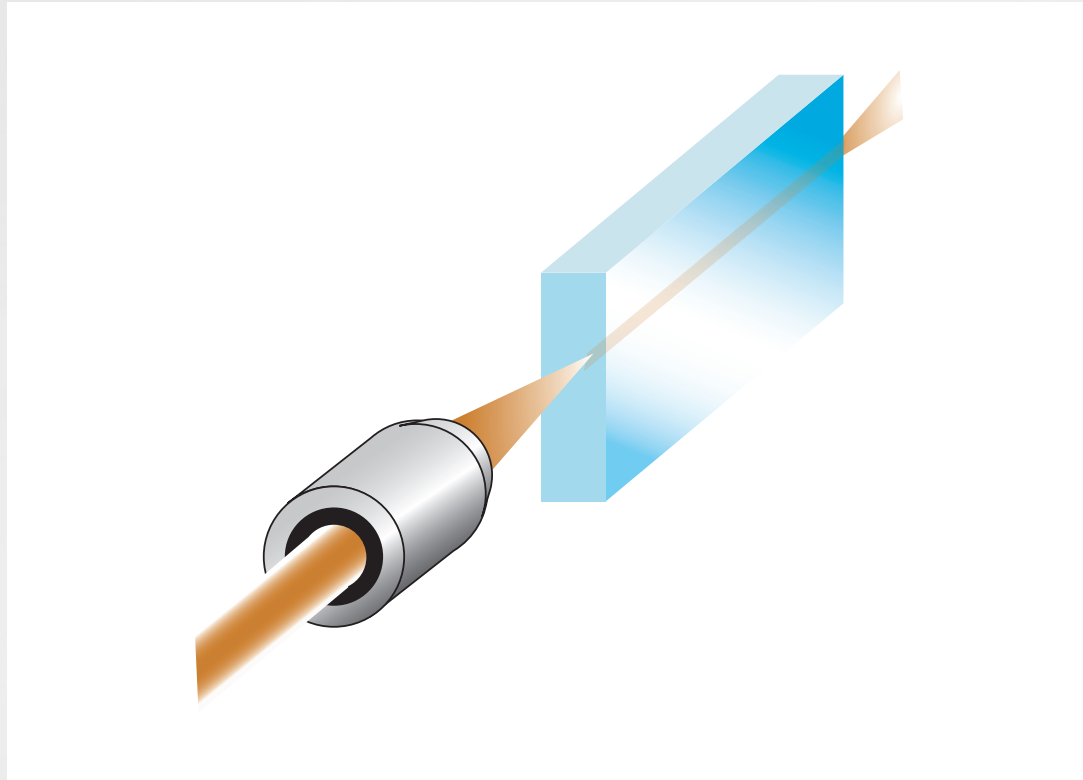
# Bulk micromachining

## waveguide micromachining



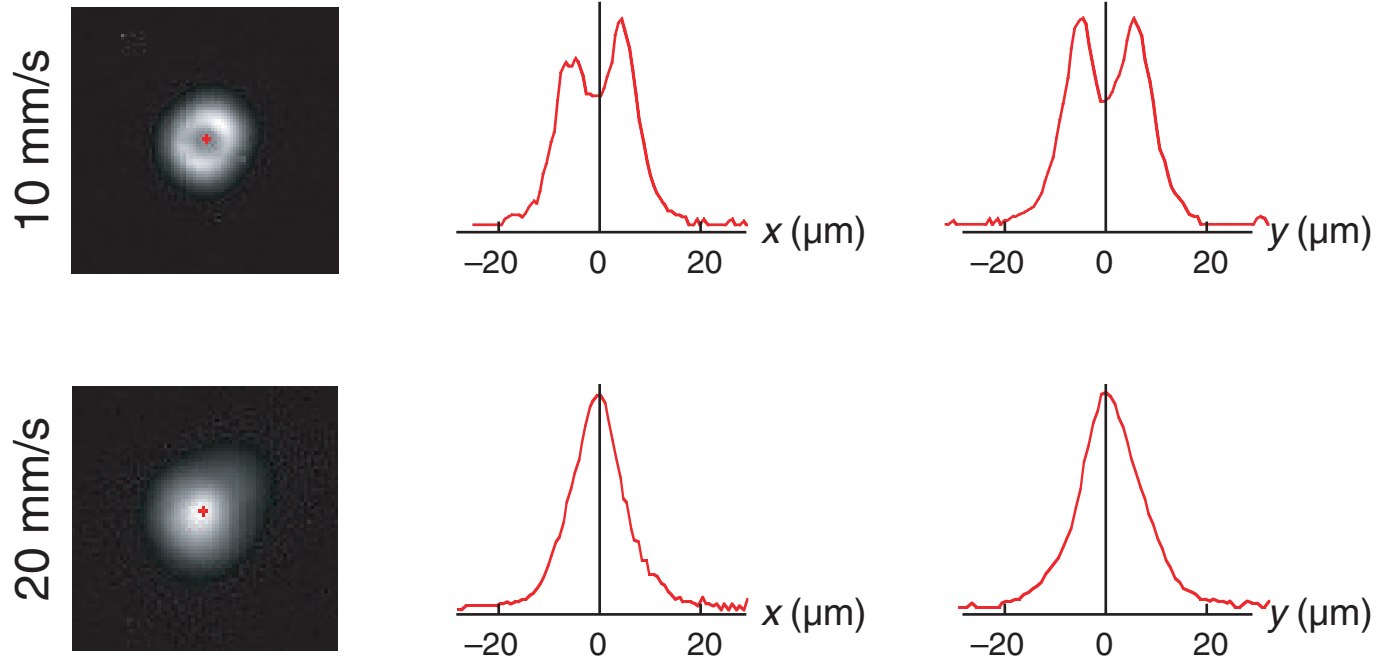
# Bulk micromachining

structures guide light



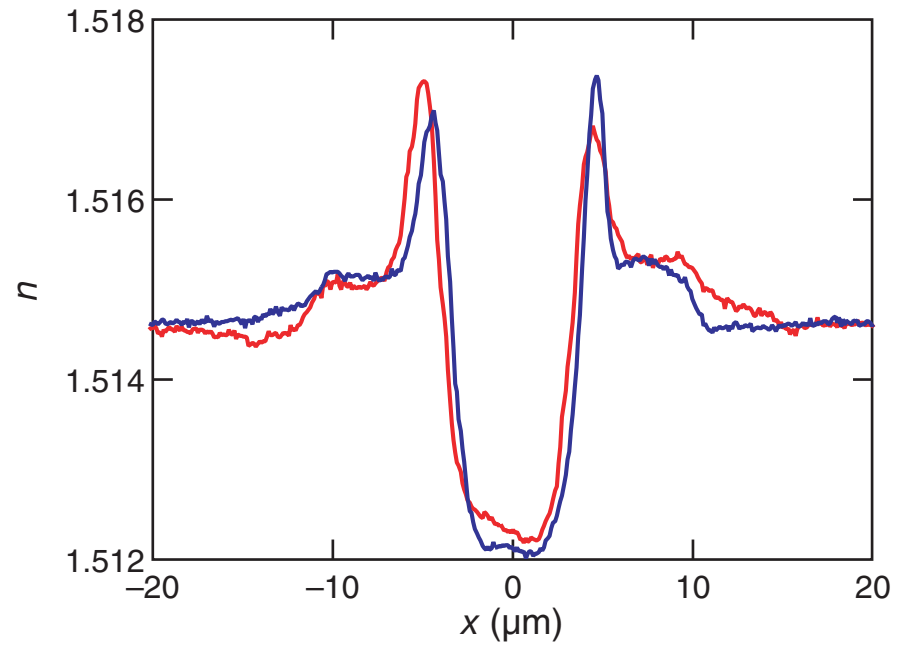
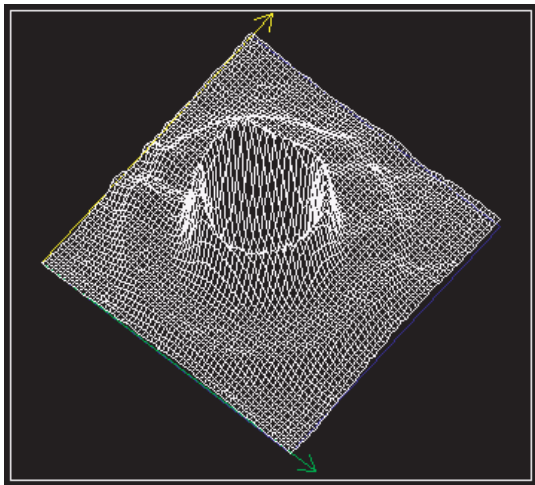
# Bulk micromachining

## near-field profiles



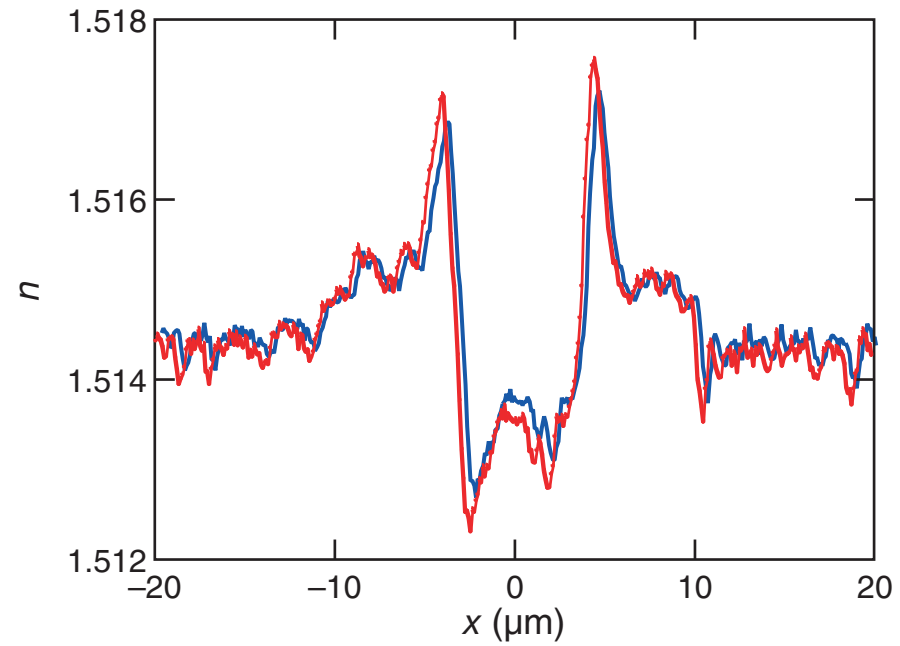
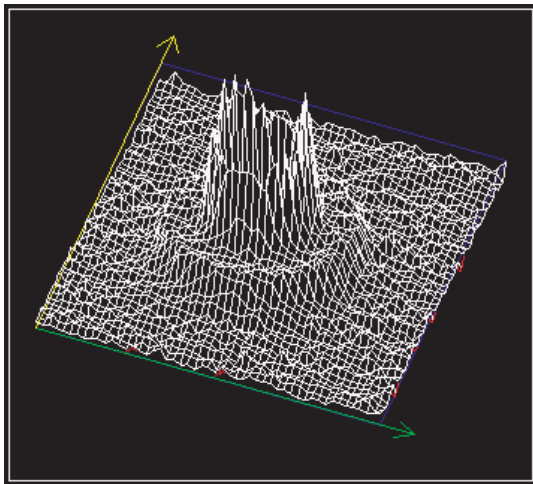
# Bulk micromachining

index profile at 2.5 mm/s



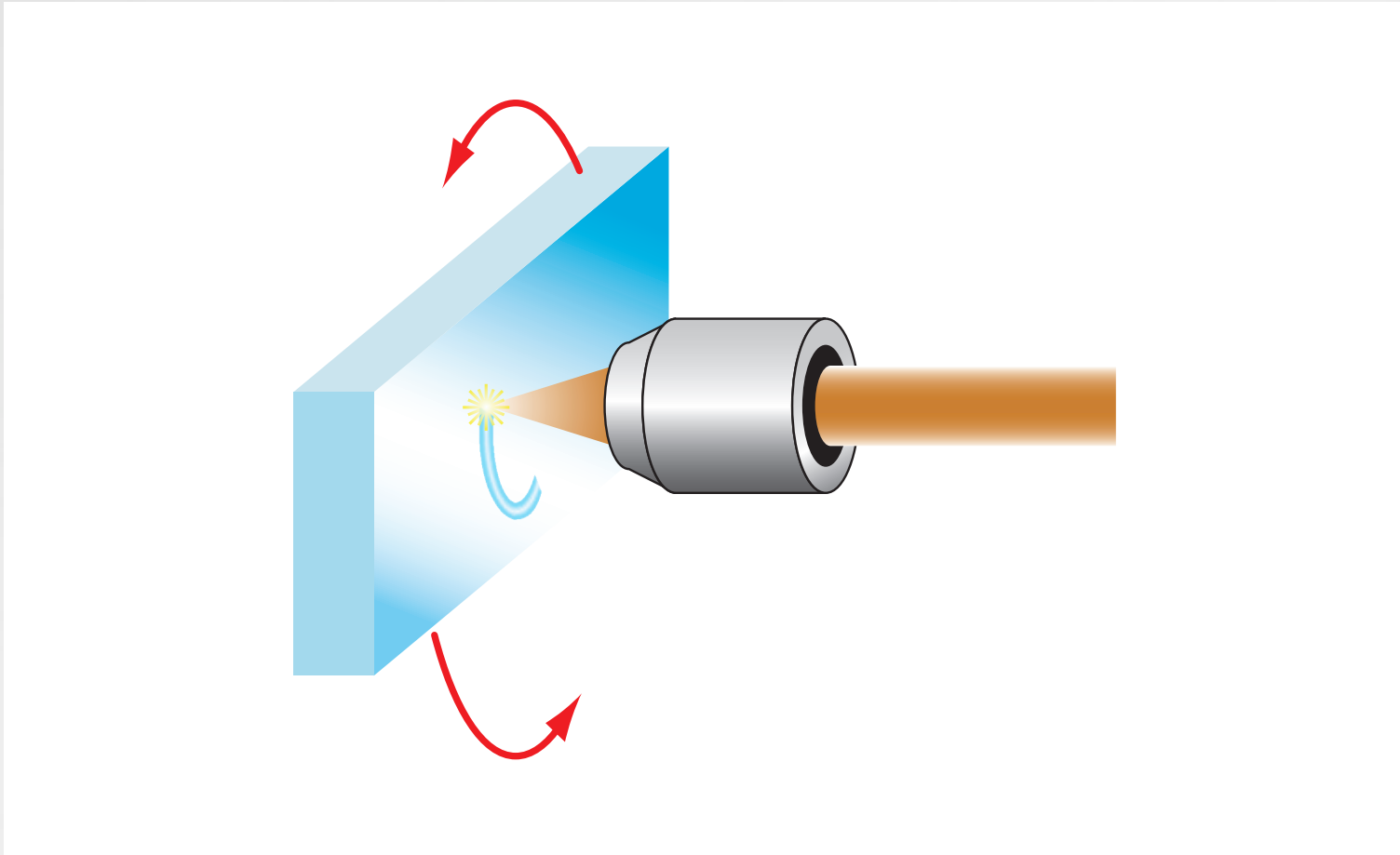
# Bulk micromachining

index profile at 10 mm/s



# Bulk micromachining

curved waveguides



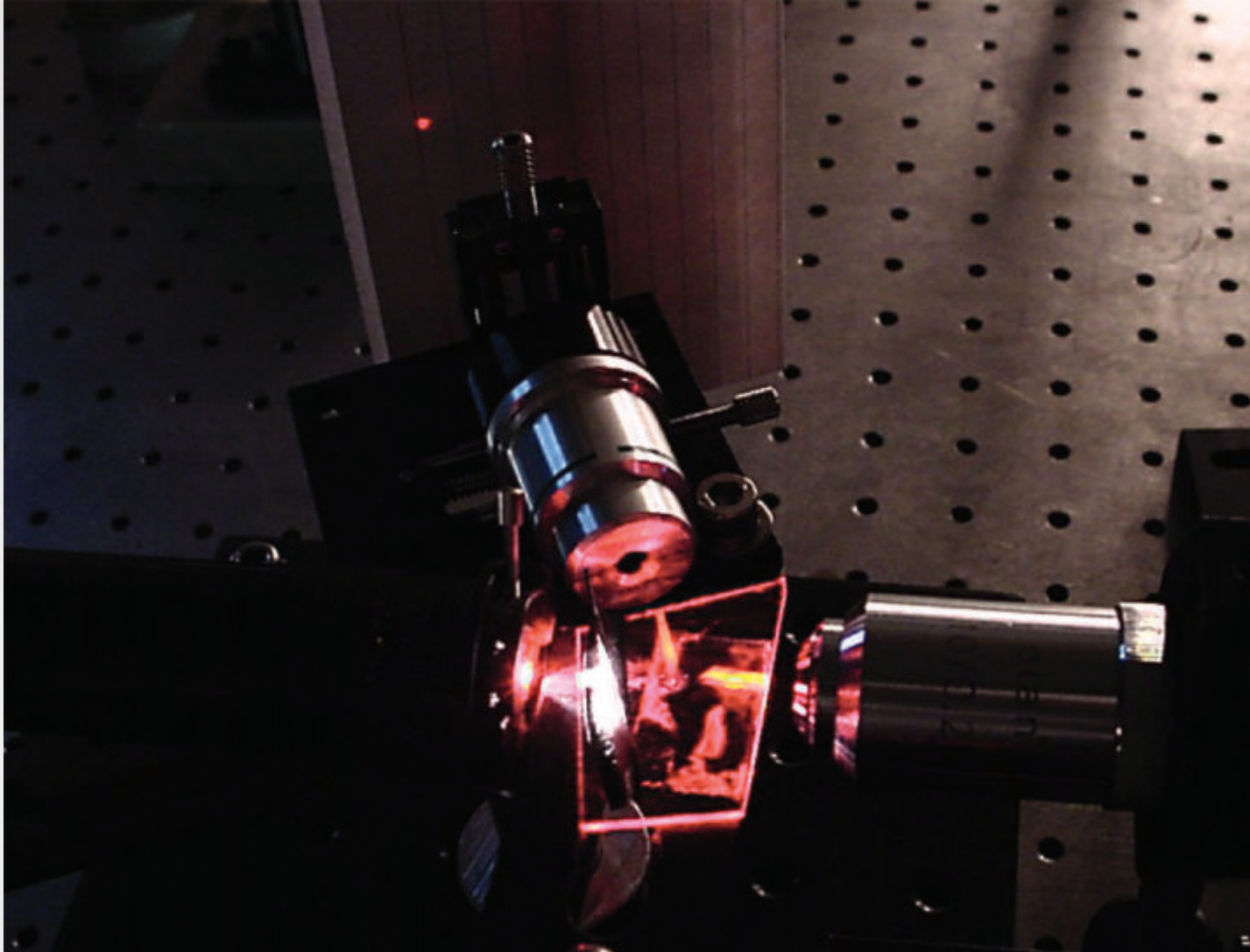
# Bulk micromachining

curved waveguides



# Bulk micromachining

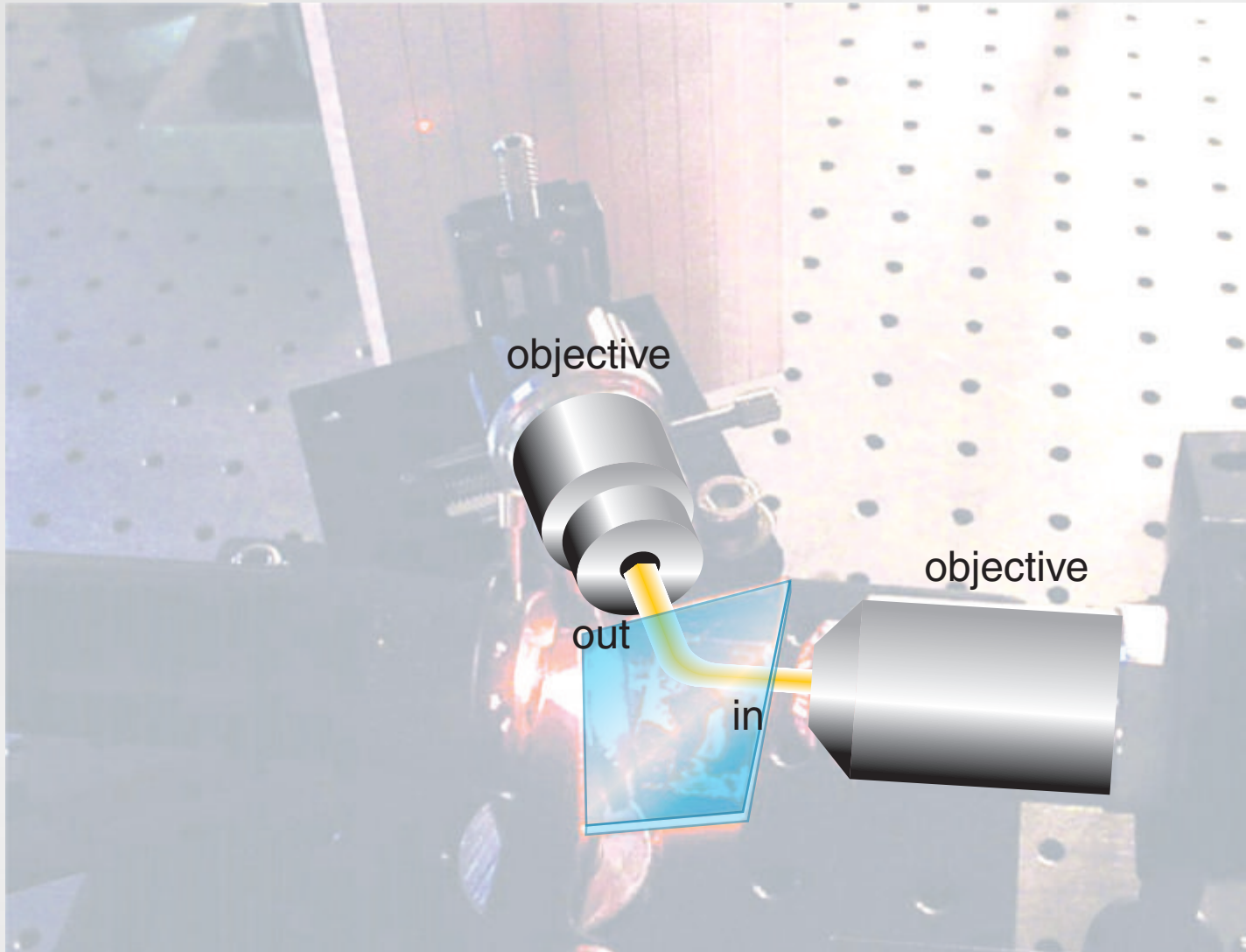
curved waveguides





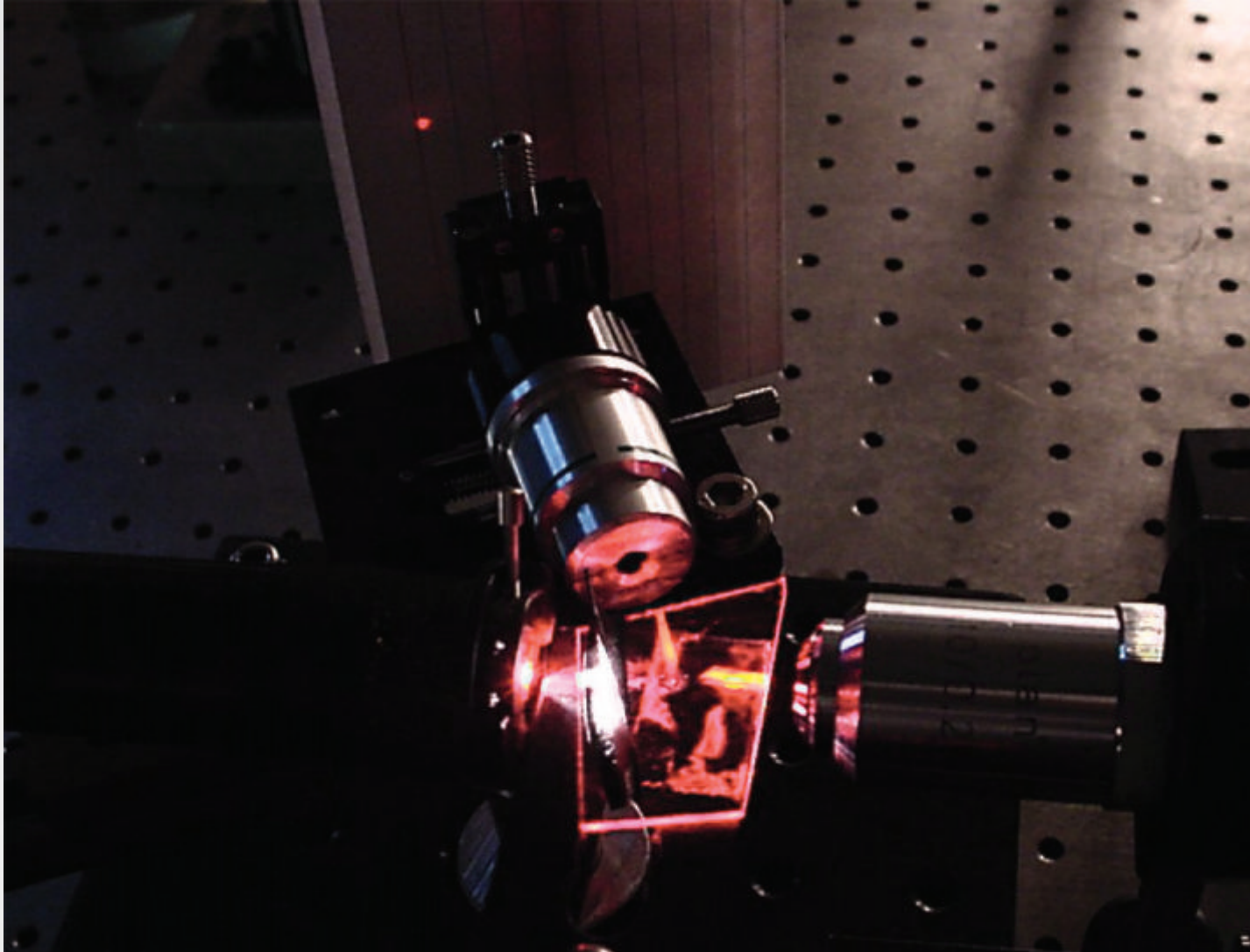
# Bulk micromachining

## curved waveguides



# Bulk micromachining

curved waveguides



# Bulk micromachining

## photonic fabrication techniques

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

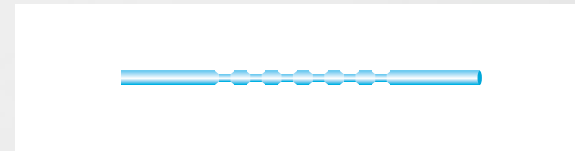
# Bulk micromachining

## photonic devices

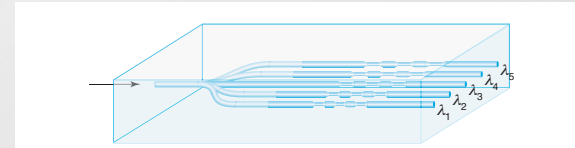
**3D splitter**



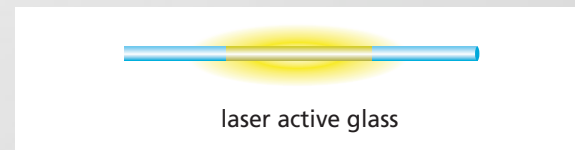
**Bragg grating**



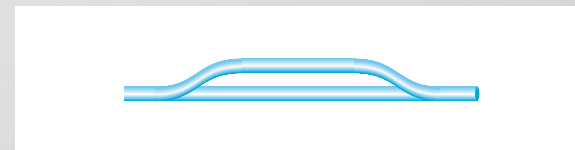
**demultiplexer**



**amplifier**



**interferometer**



# Bulk micromachining

all-optical sensor



substrate

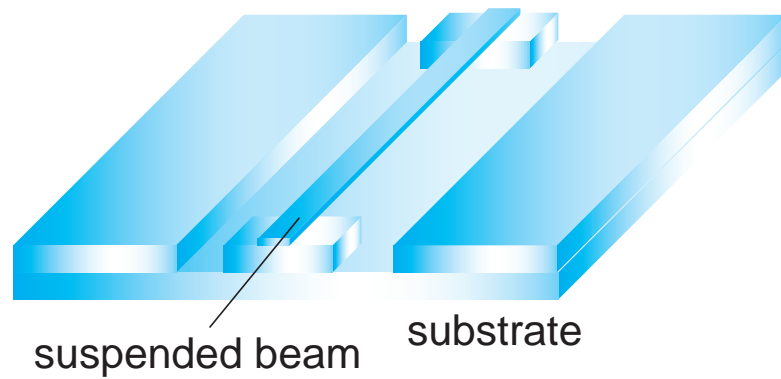
# Bulk micromachining

all-optical sensor



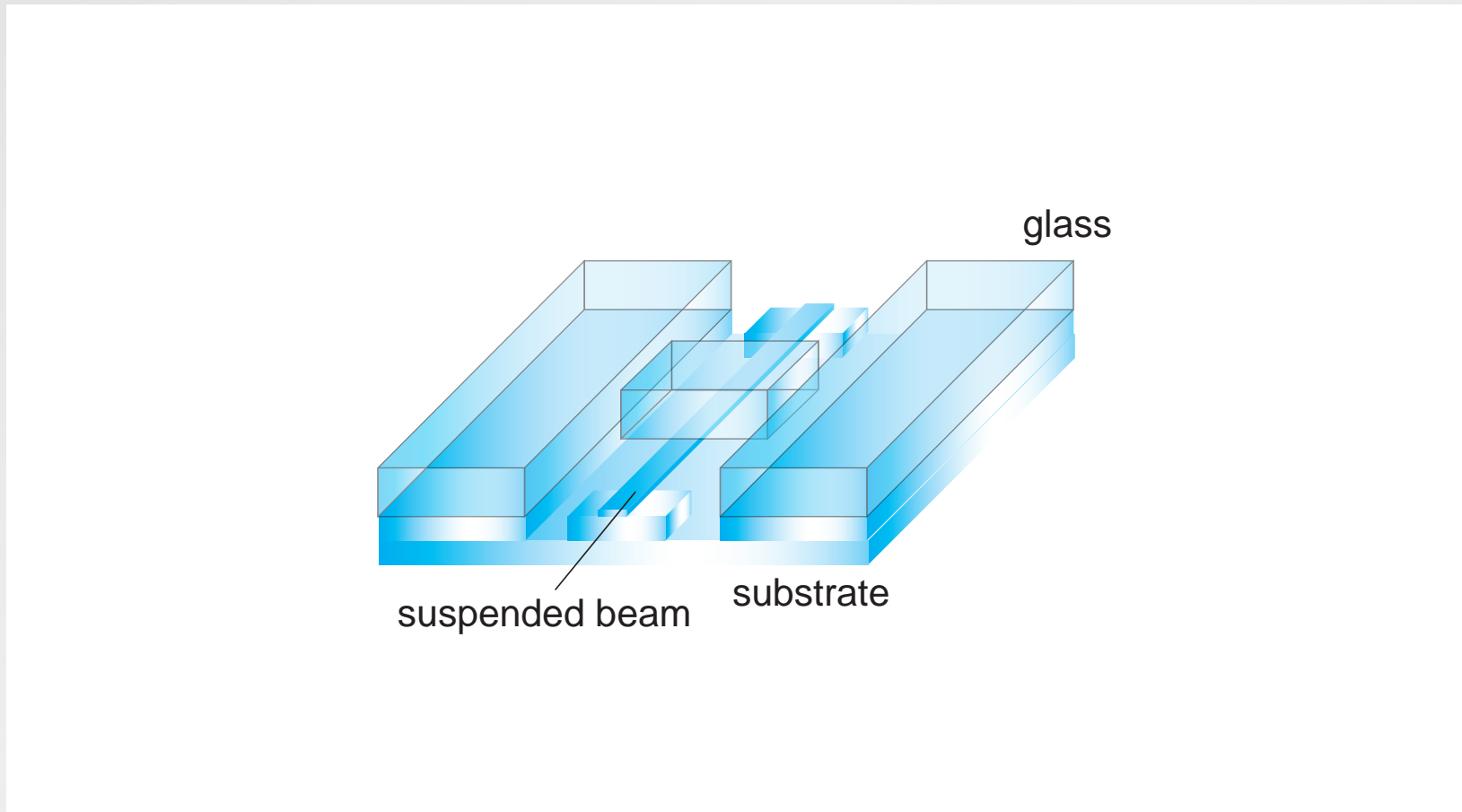
# Bulk micromachining

## all-optical sensor



# Bulk micromachining

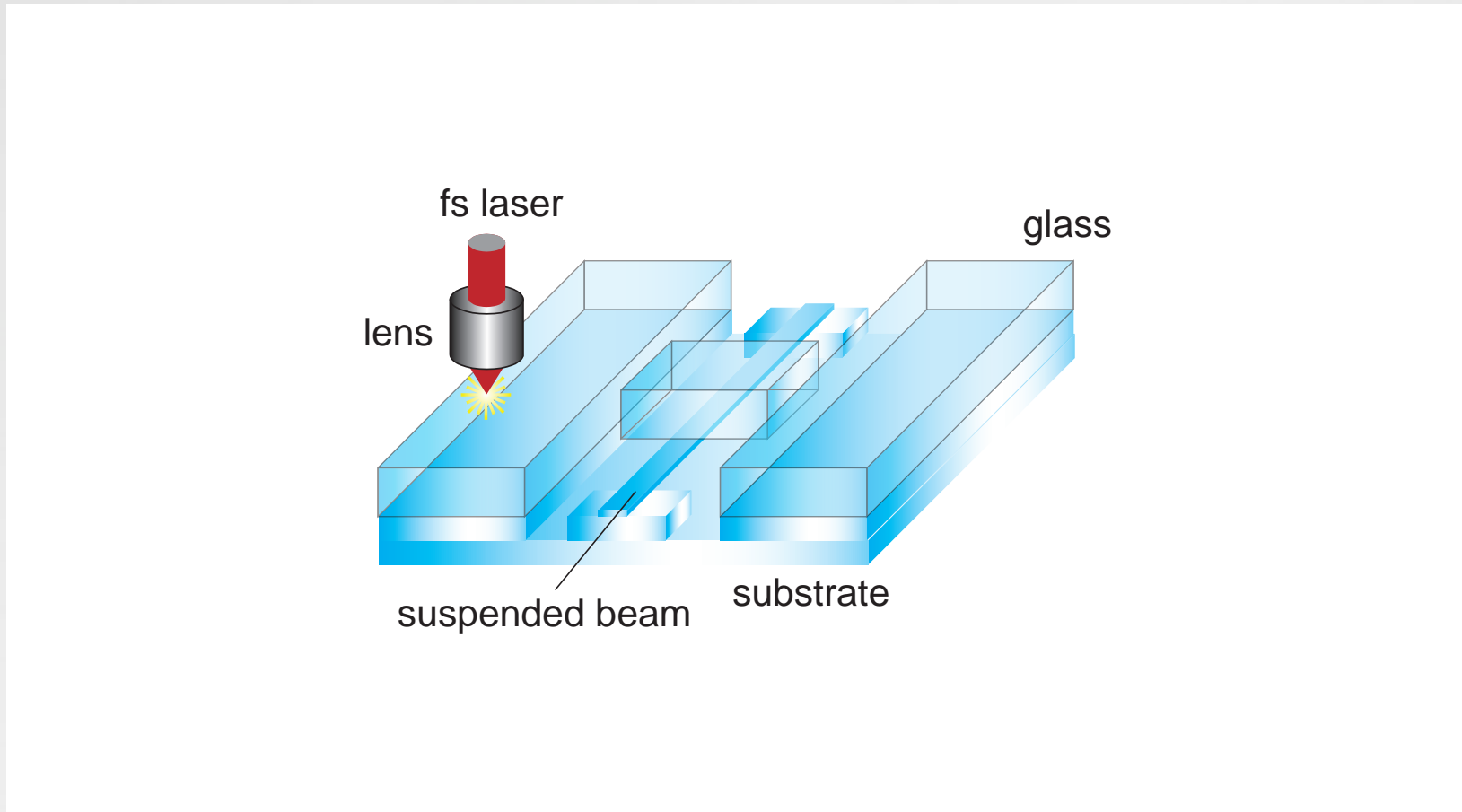
## all-optical sensor





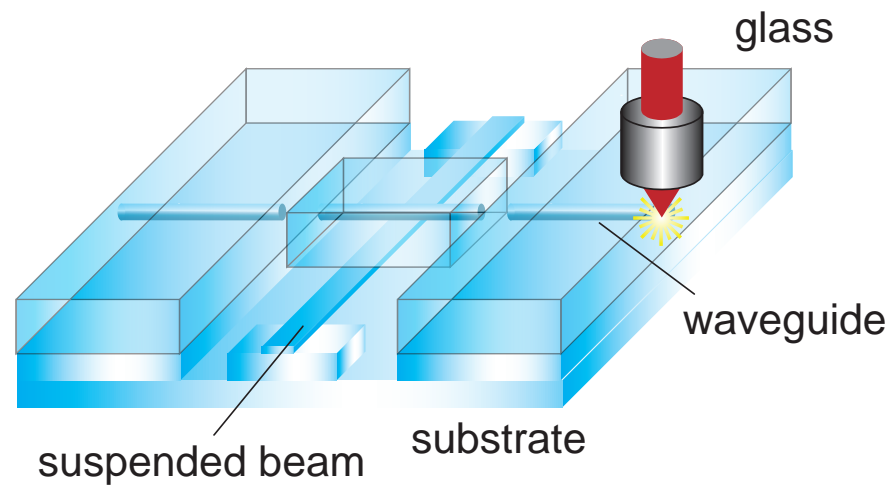
# Bulk micromachining

## all-optical sensor



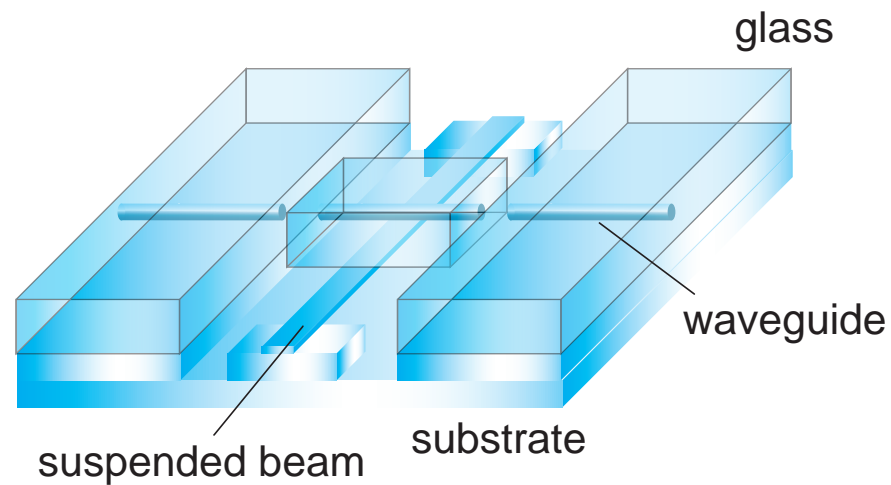
# Bulk micromachining

## all-optical sensor



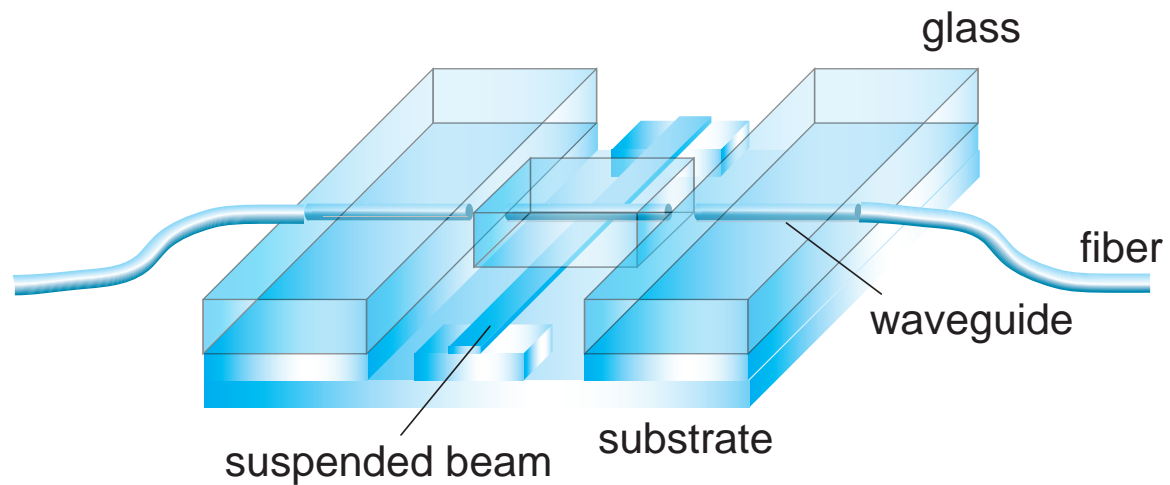
# Bulk micromachining

## all-optical sensor

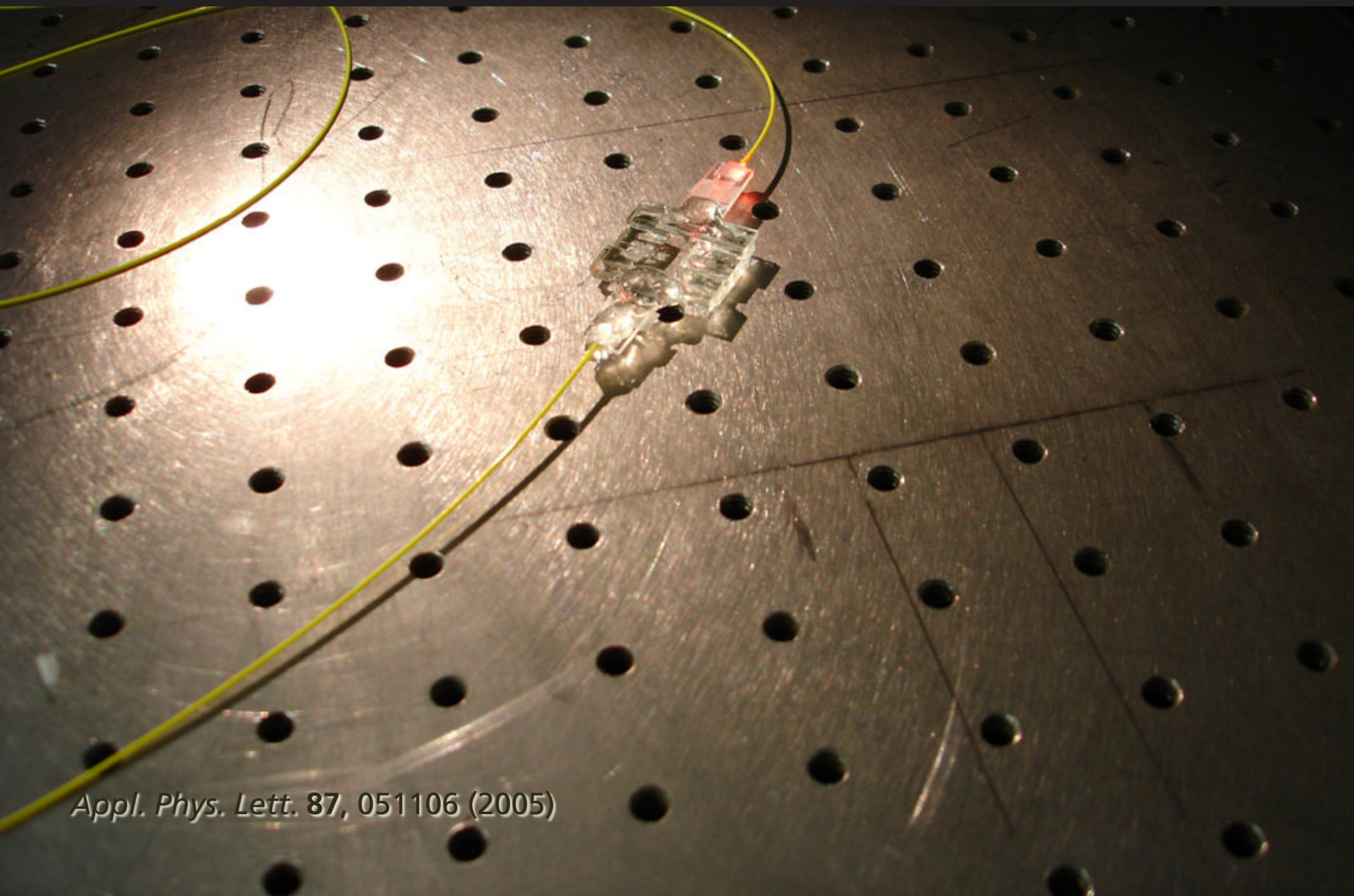


# Bulk micromachining

## all-optical sensor



# Bulk micromachining

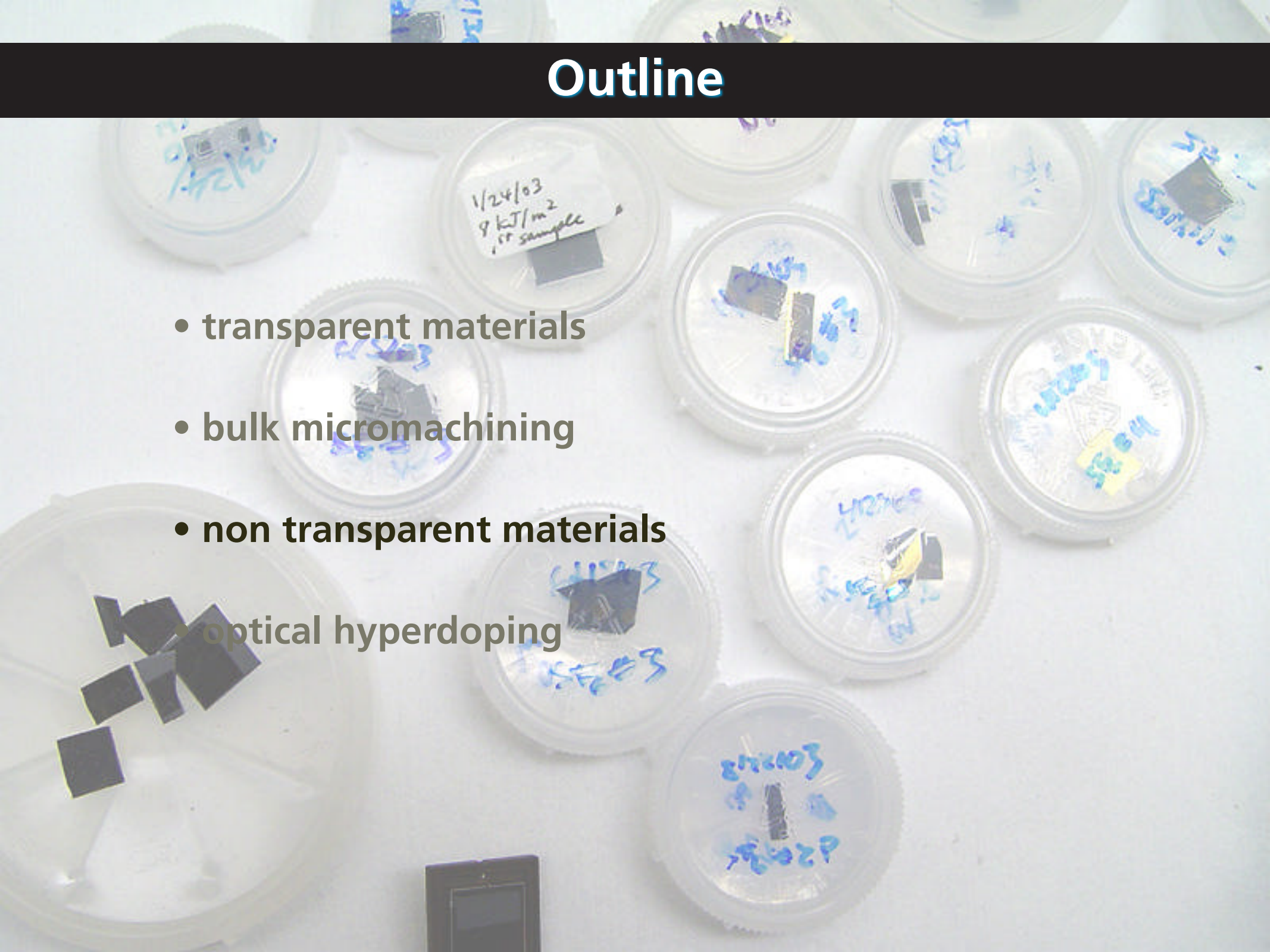


*Appl. Phys. Lett.* 87, 051106 (2005)

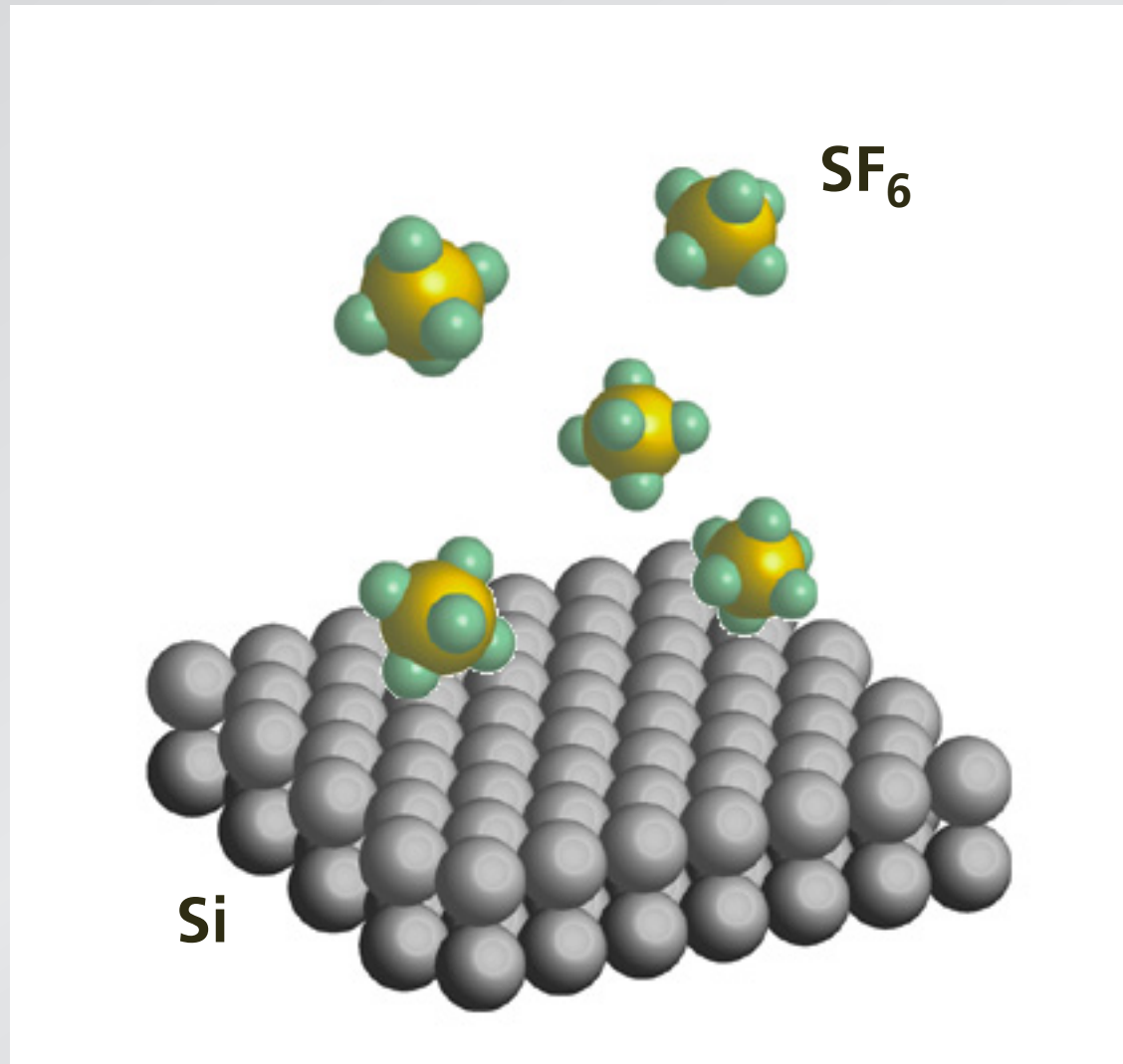


# Outline

- transparent materials
- bulk micromachining
- non transparent materials
- optical hyperdoping



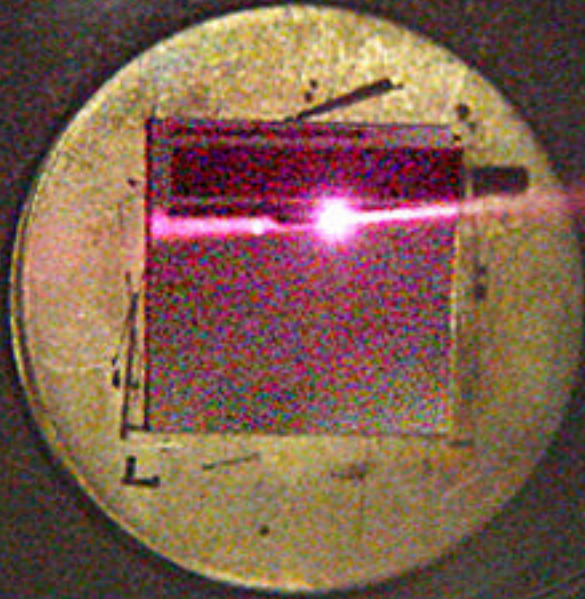
# Nontransparent materials



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



# Nontransparent materials



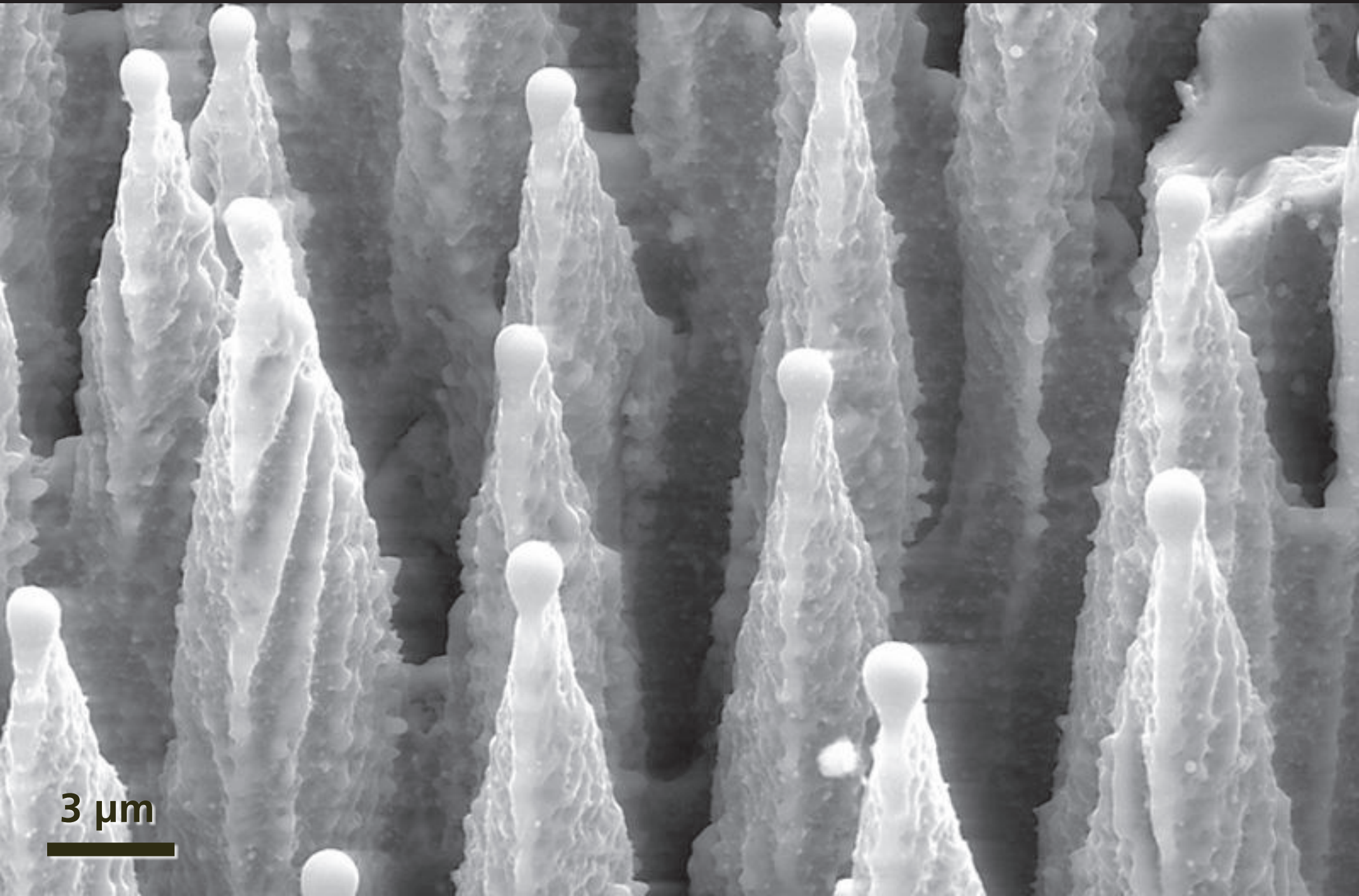


# Nontransparent materials



**"black silicon"**

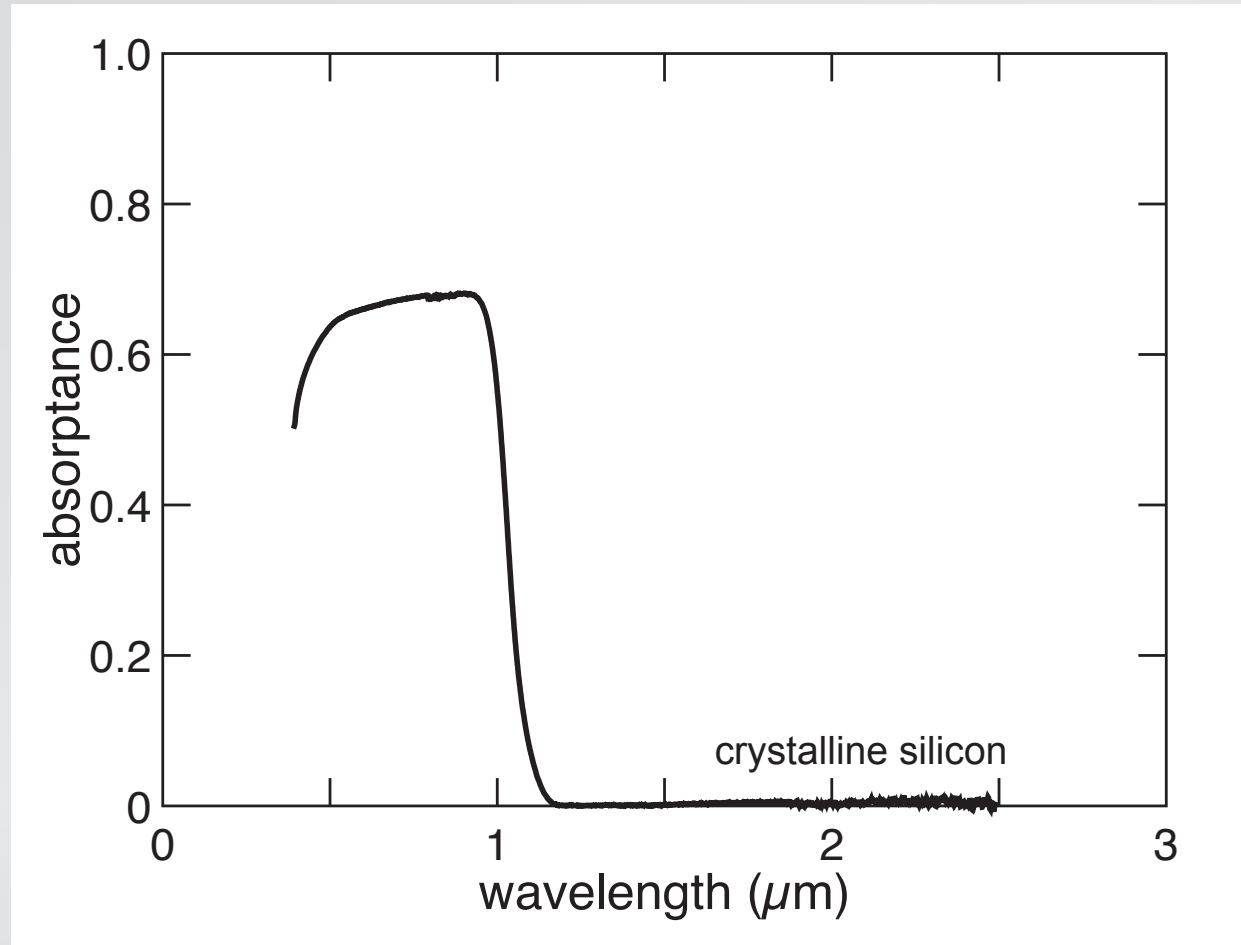
# Introduction



3  $\mu\text{m}$

# Introduction

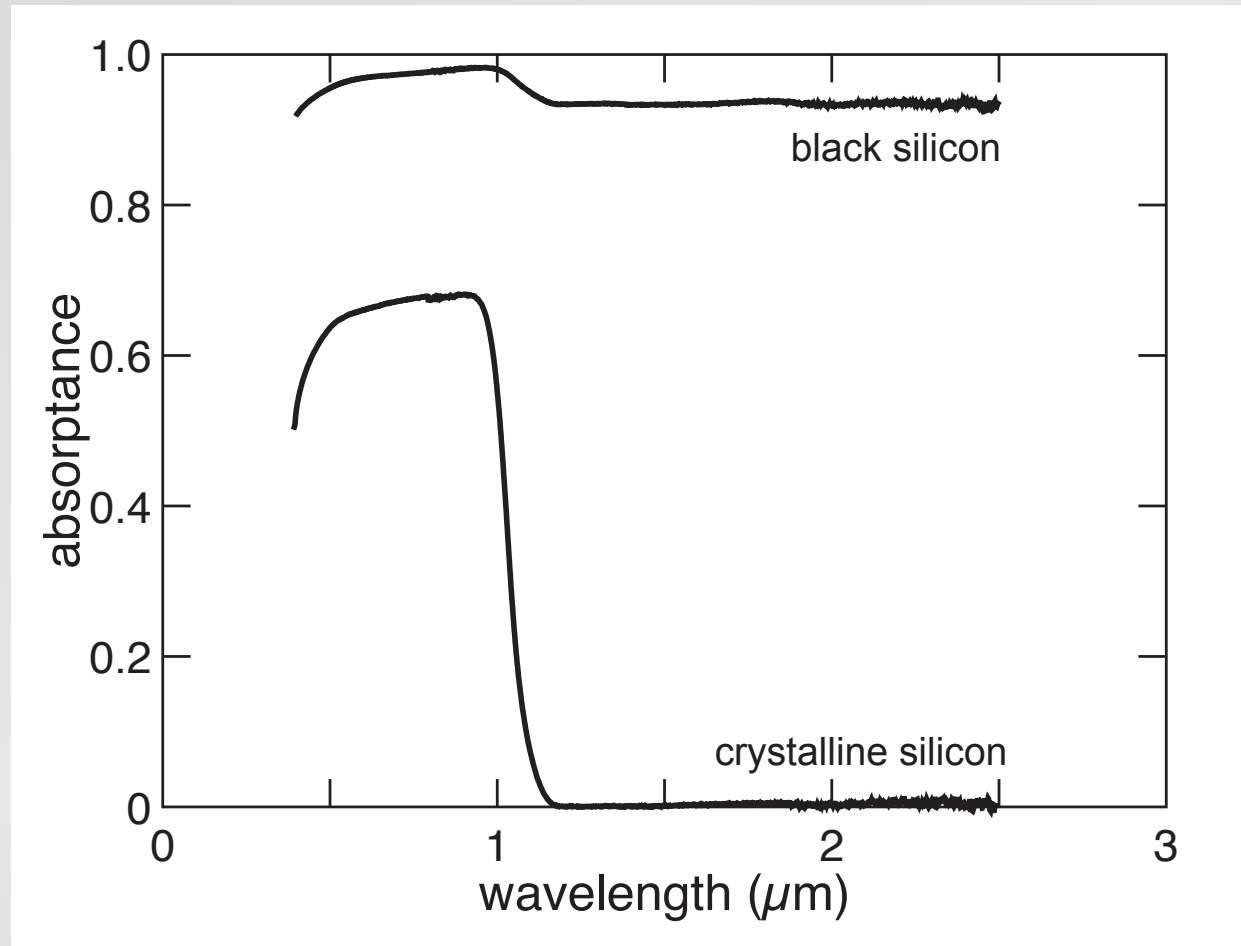
absorptance ( $1 - R_{int} - T_{int}$ )



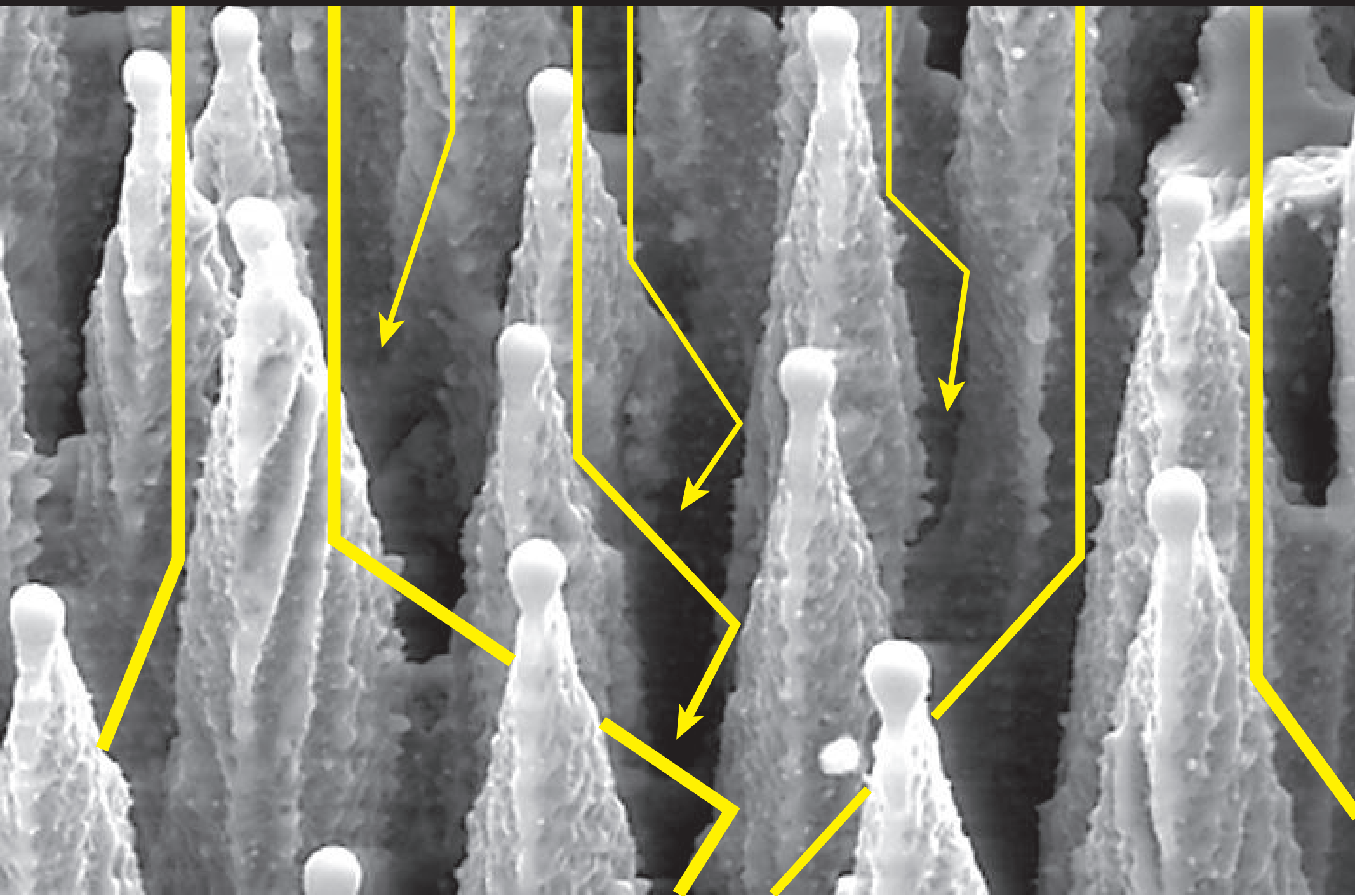


# Nontransparent materials

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

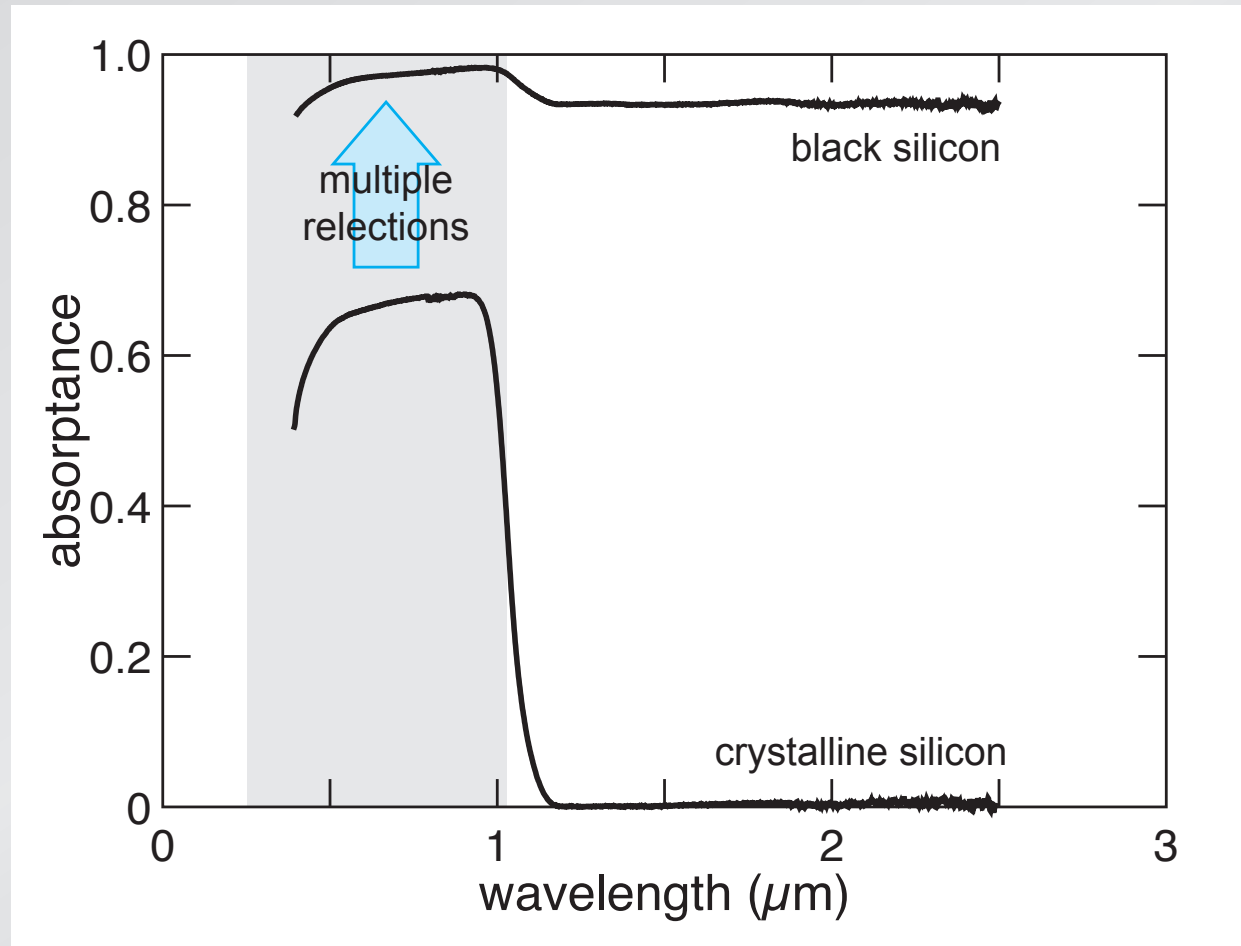


# Introduction



# Nontransparent materials

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



# Nontransparent materials

**band structure changes: defects and/or impurities**

# Nontransparent materials

## substrate/dopant combinations

dopants:

N	O	F
P	S	Cl
	Se	
Sb	Te	



# Nontransparent materials

## substrate/dopant combinations

**dopants:**

N	O	F
P	S	Cl
	Se	
Sb	Te	

**substrates:**

Si    Ge    ZnO    InP    GaAs

Ti    Ag    Al    Cu    Pd    Rh    Ta    Pt

# Nontransparent materials

focus on chalcogen-doped silicon

dopants:

N	O	F
P	S	Cl
	Se	
Sb	Te	

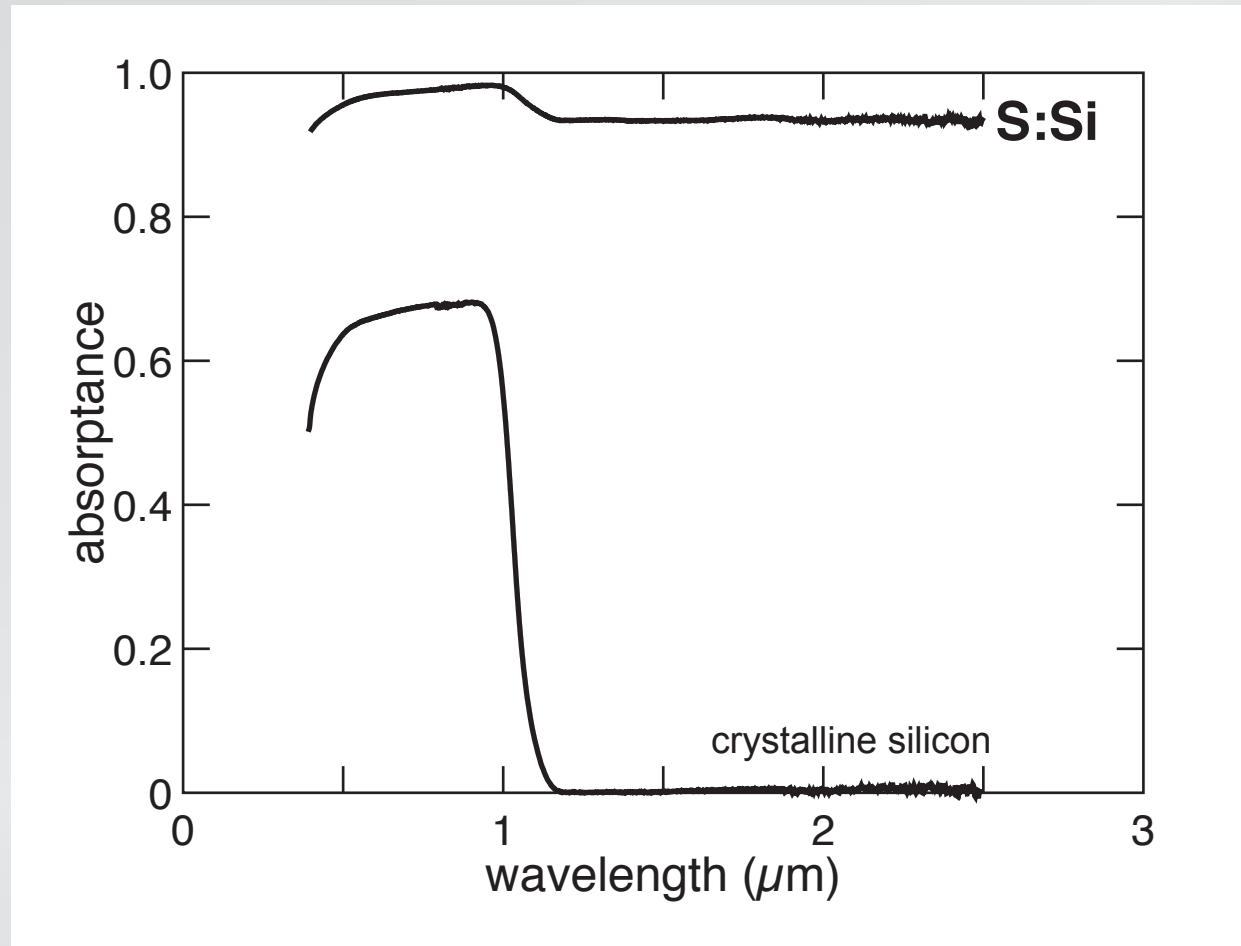
substrates:

Si Ge ZnO InP GaAs

Ti Ag Al Cu Pd Rh Ta Pt

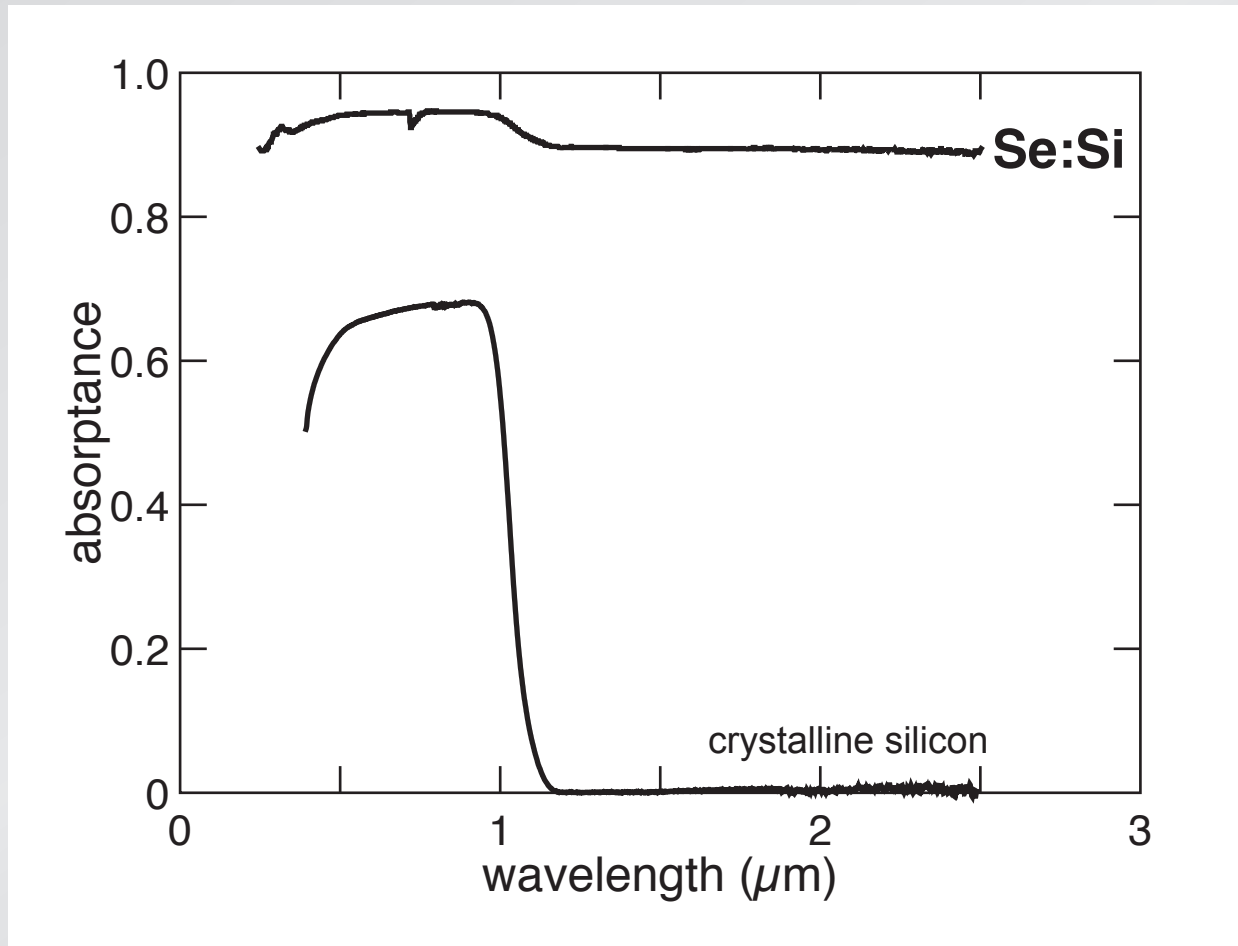
# Nontransparent materials

focus on chalcogen-doped silicon



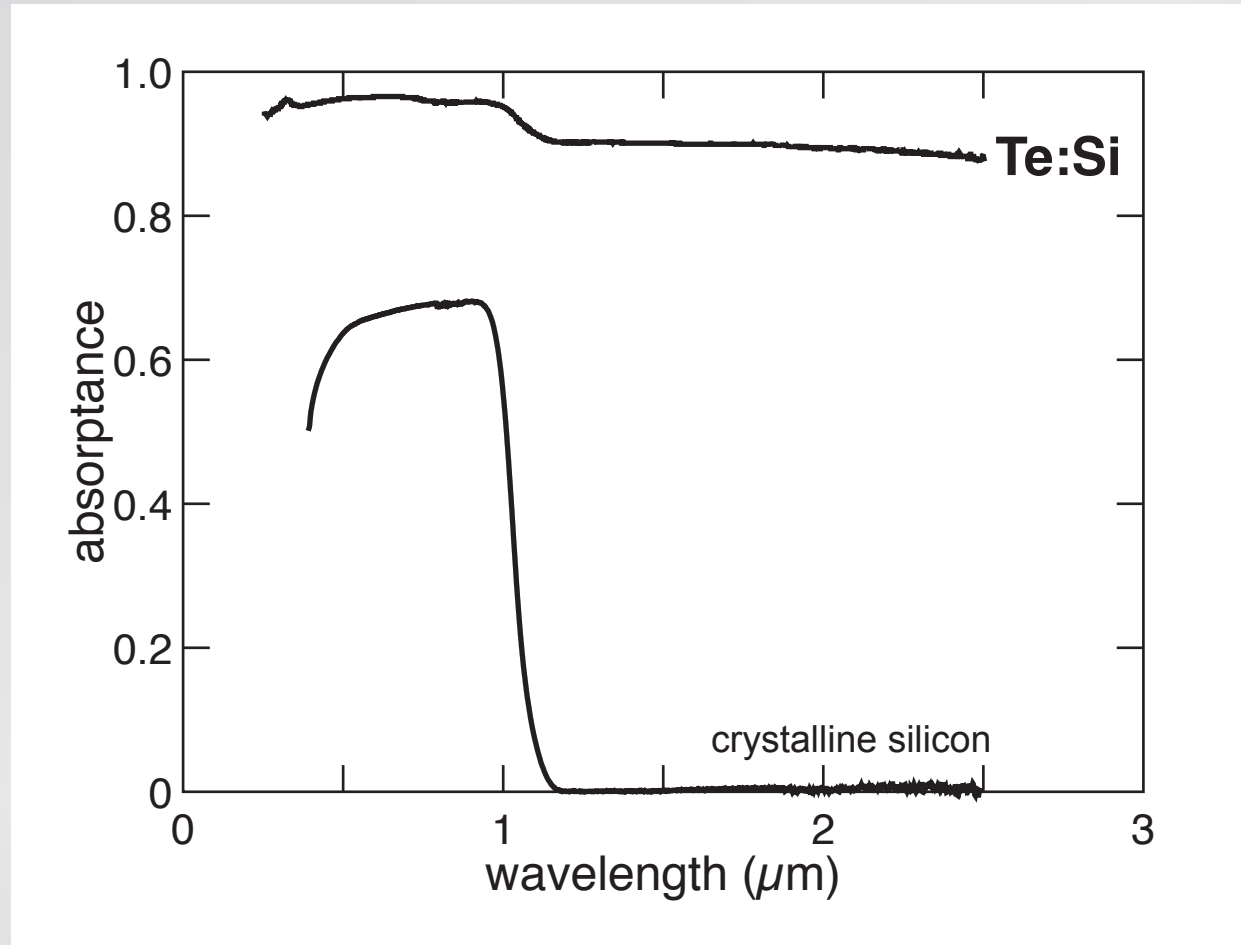
# Nontransparent materials

focus on chalcogen-doped silicon



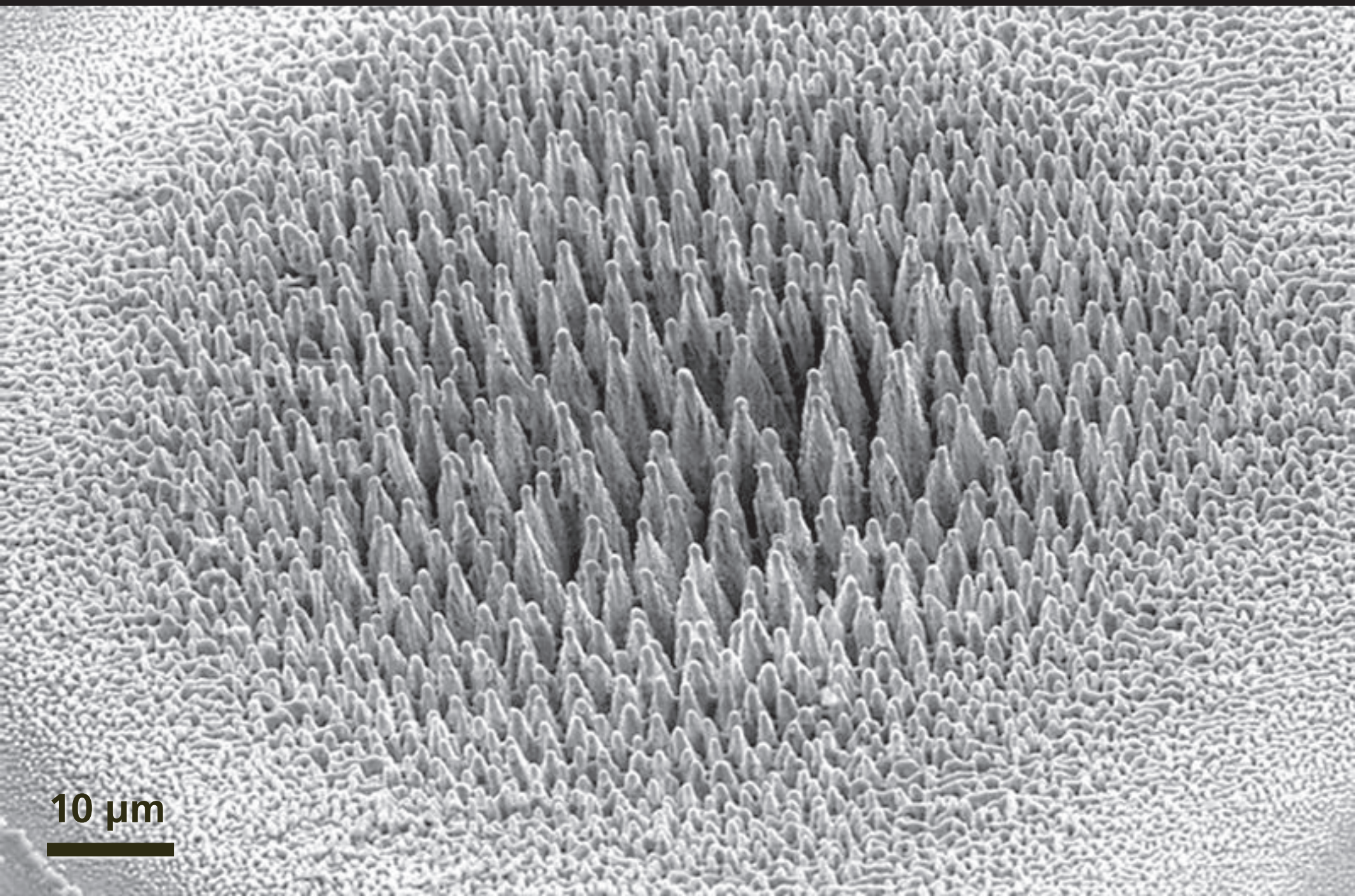
# Nontransparent materials

focus on chalcogen-doped silicon

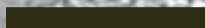




# Nontransparent materials

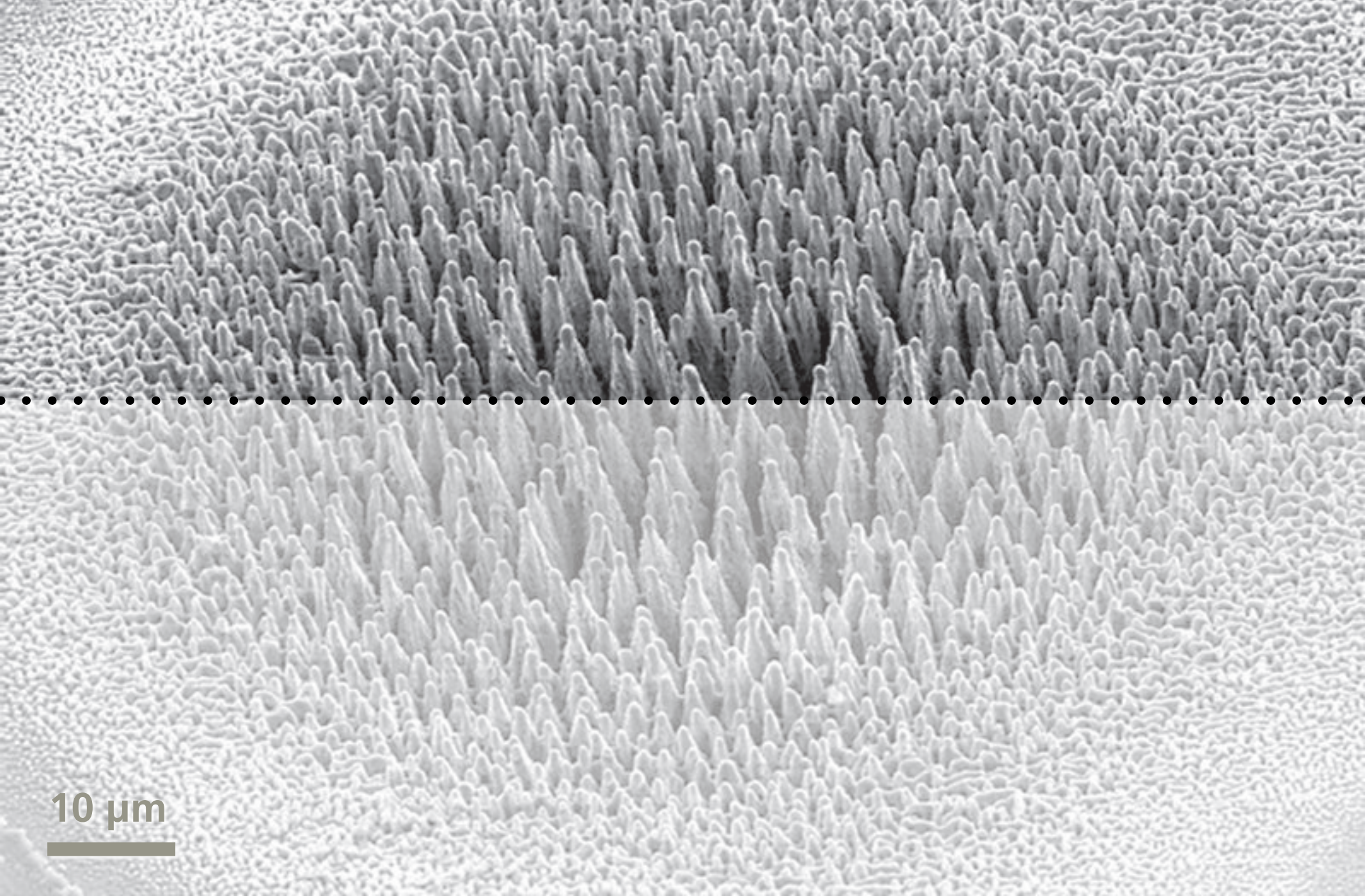


10  $\mu\text{m}$





# Nontransparent materials

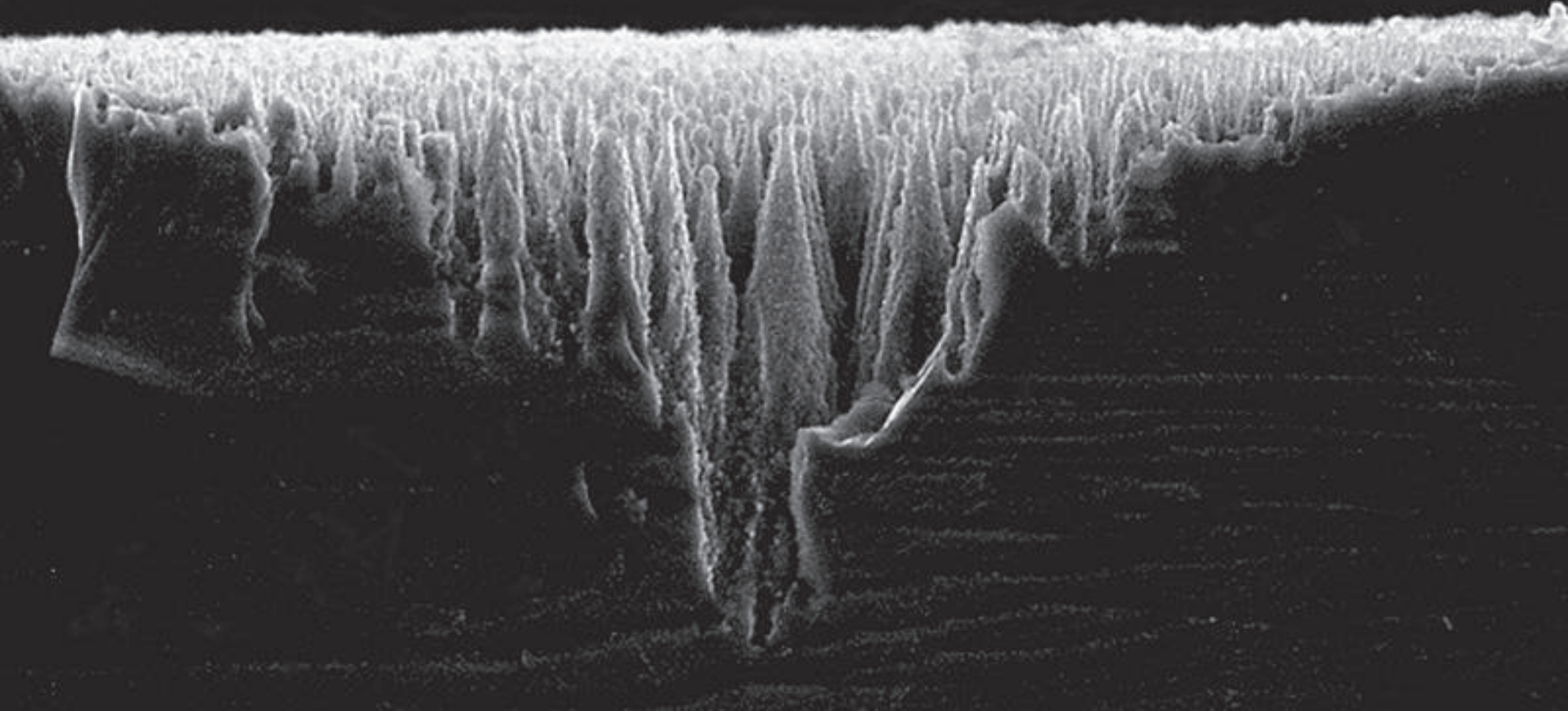


10 μm



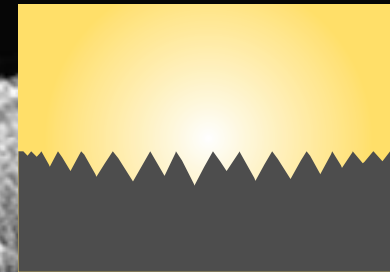
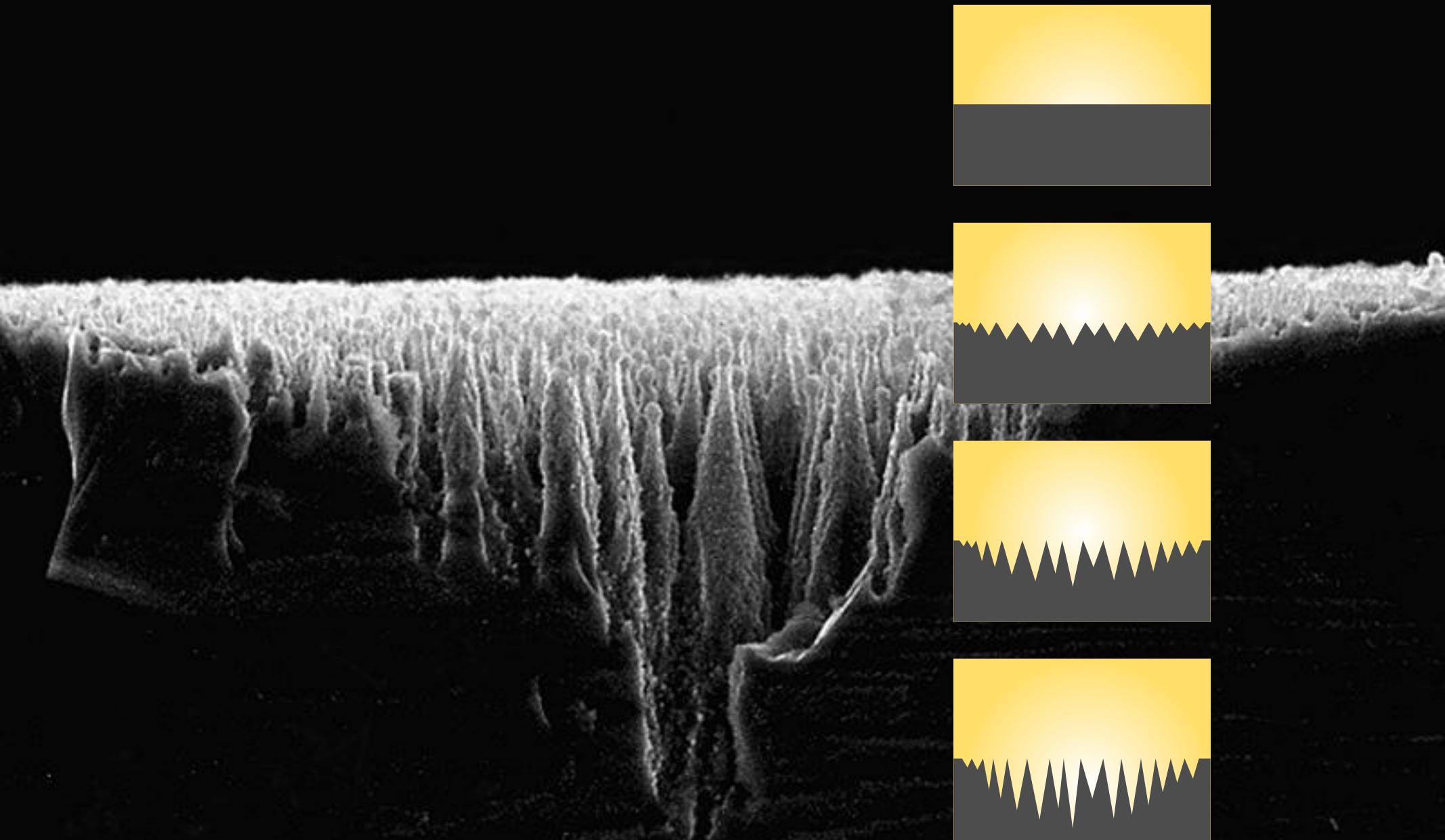


# Nontransparent materials

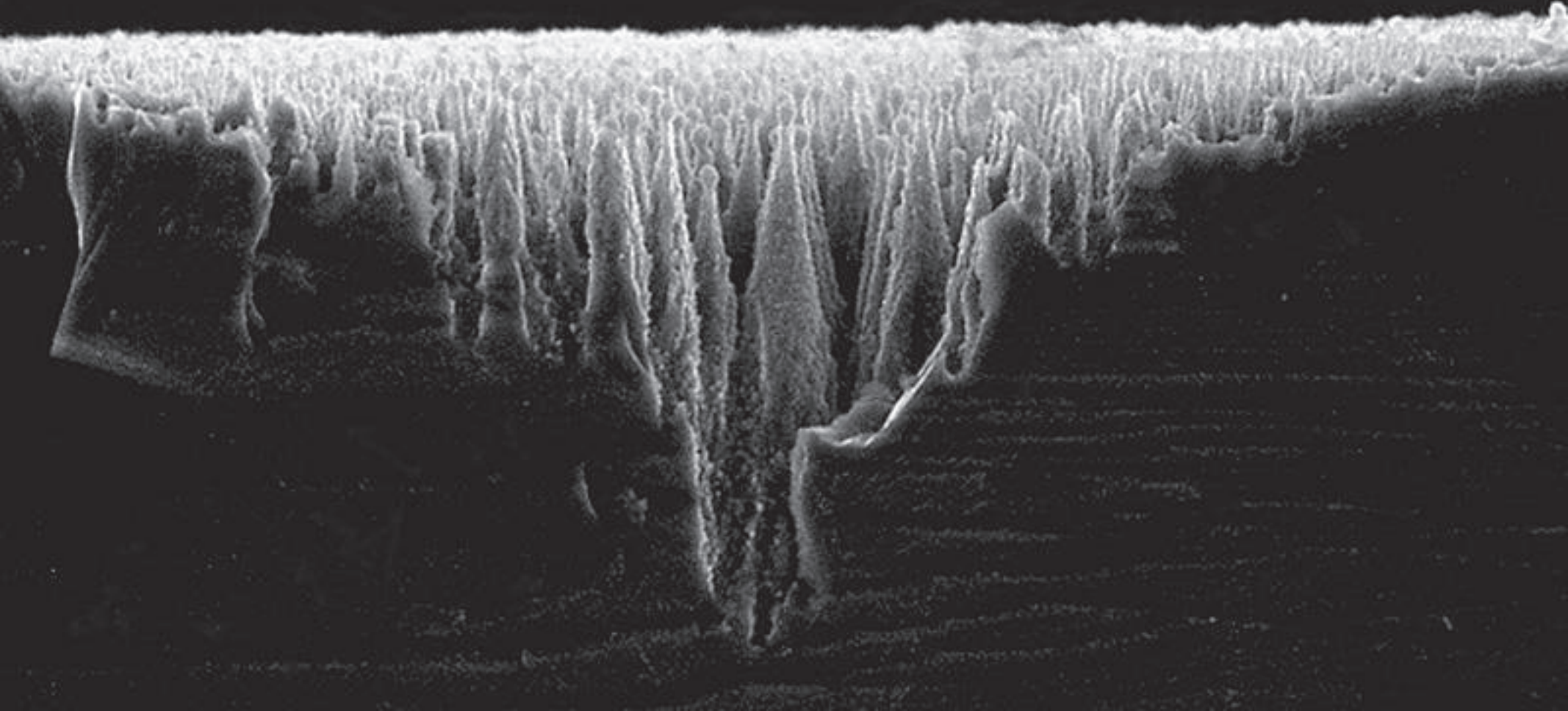




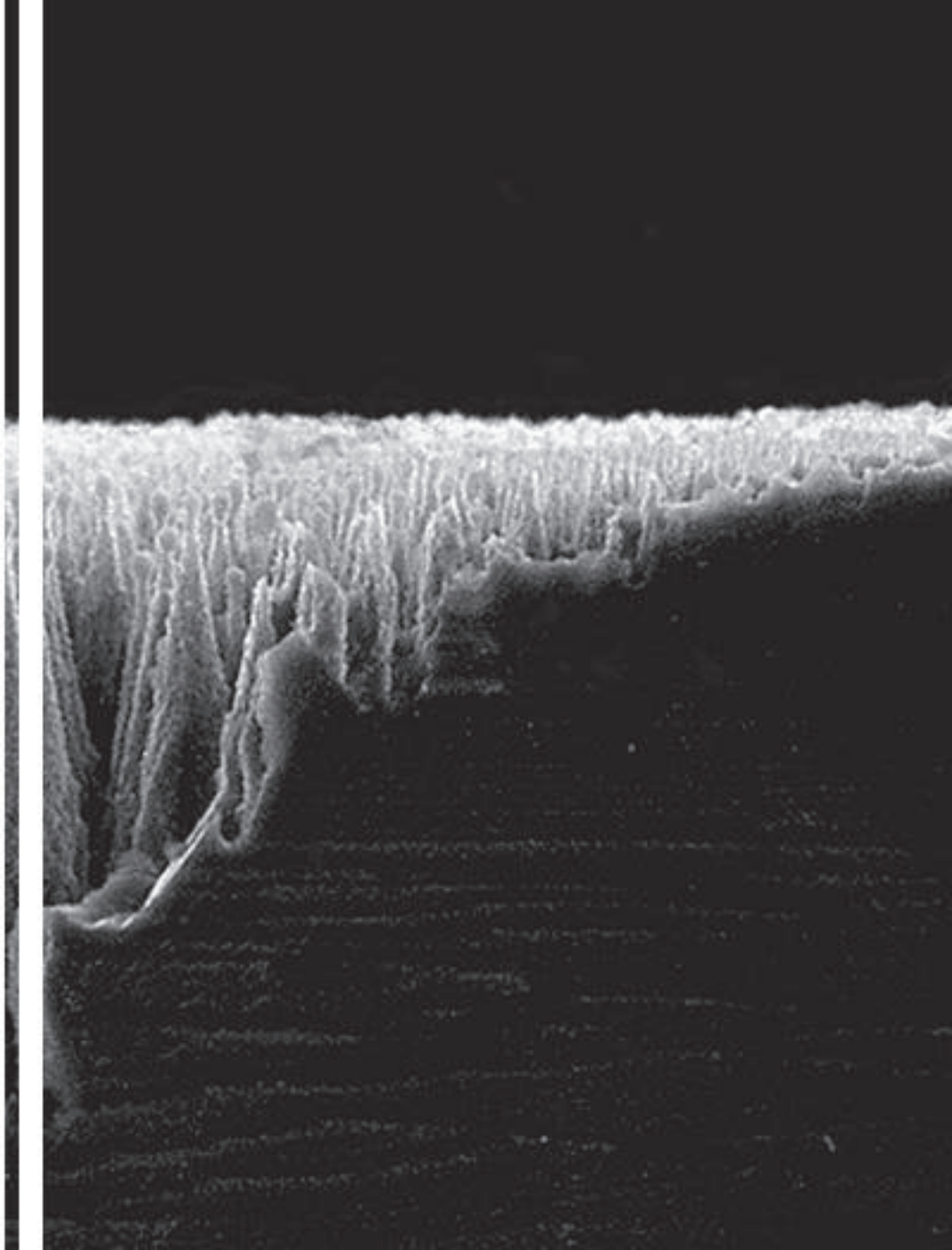
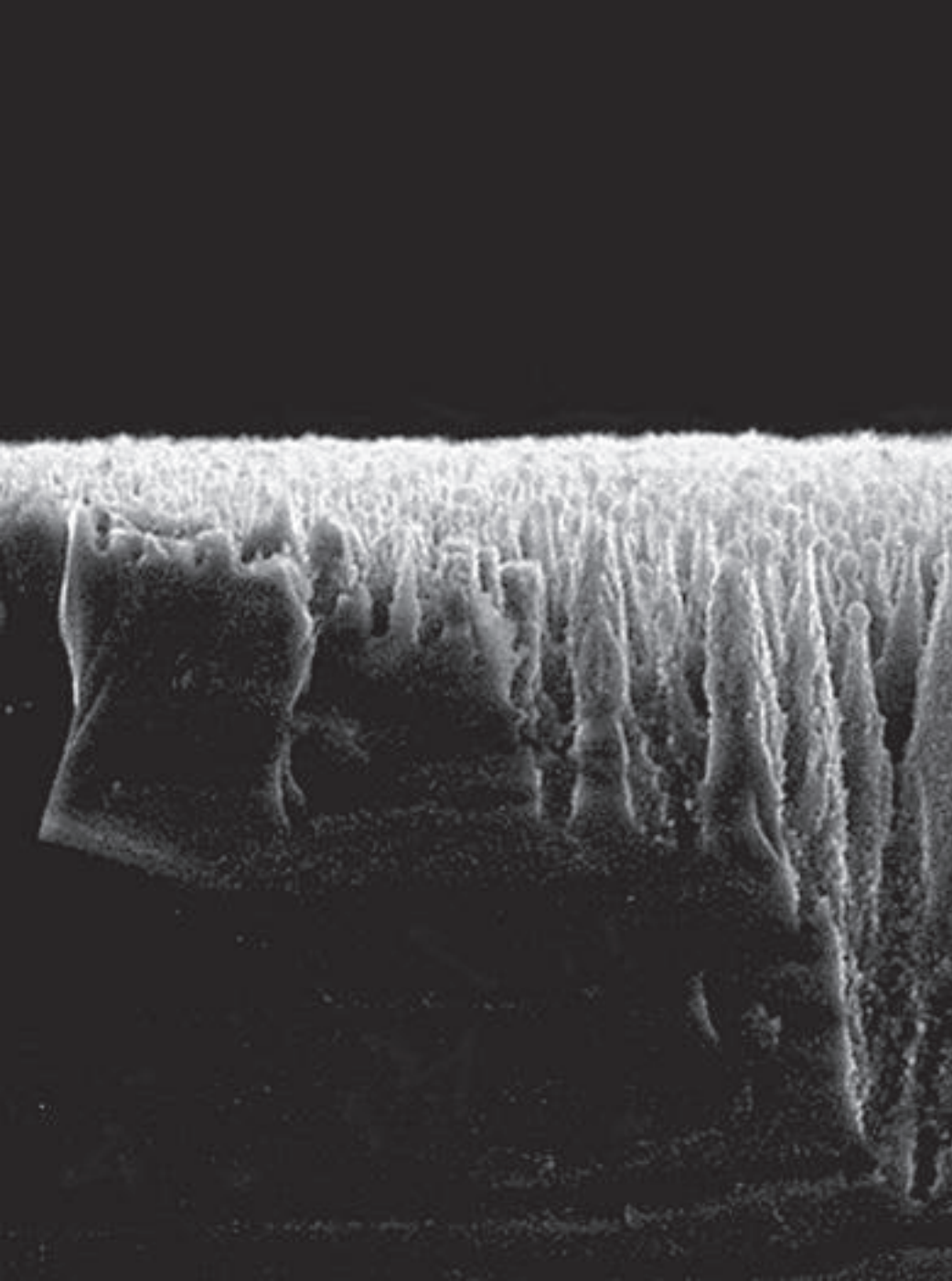
# Nontransparent materials



# Nontransparent materials



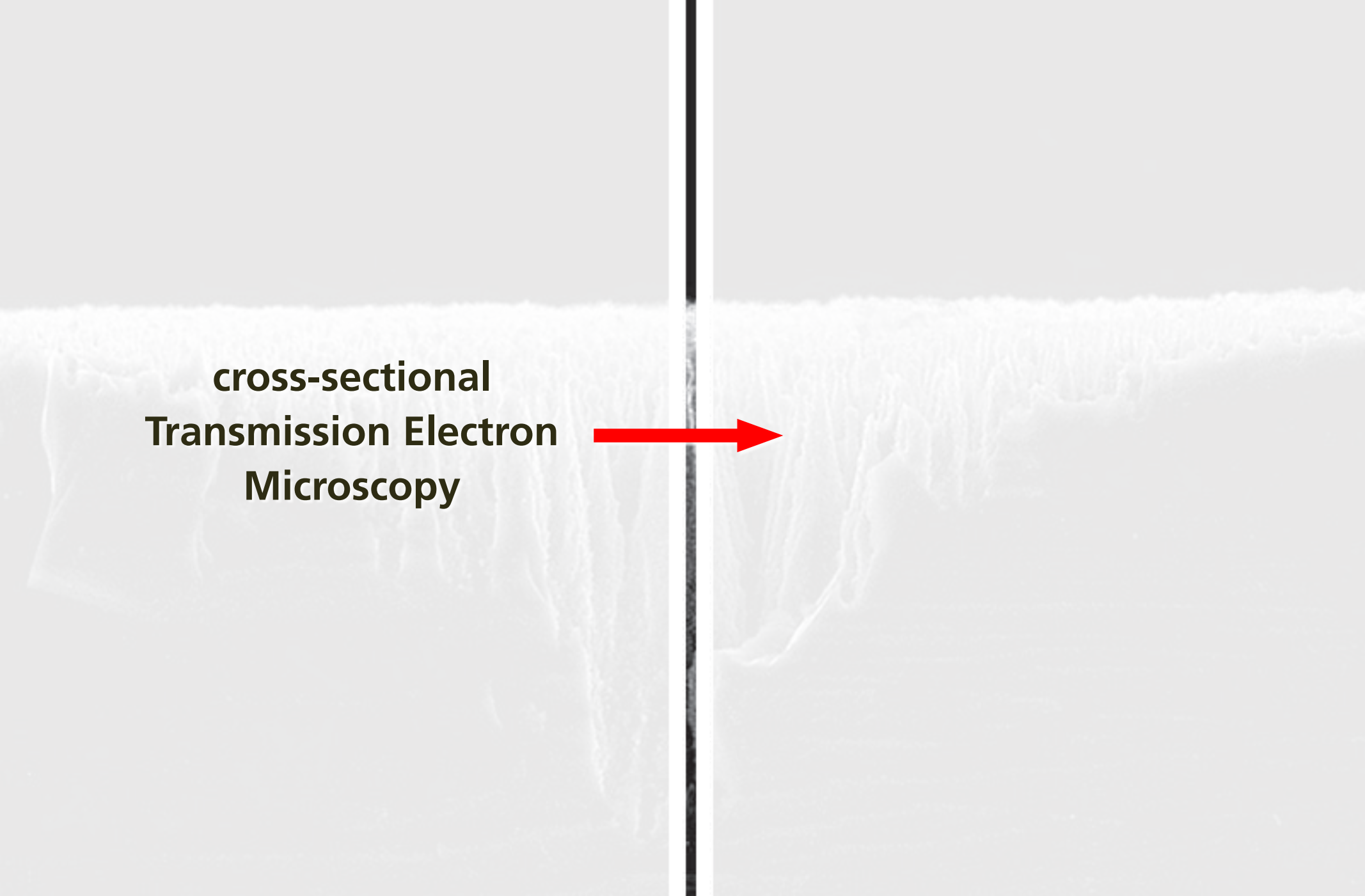
# Nontransparent materials





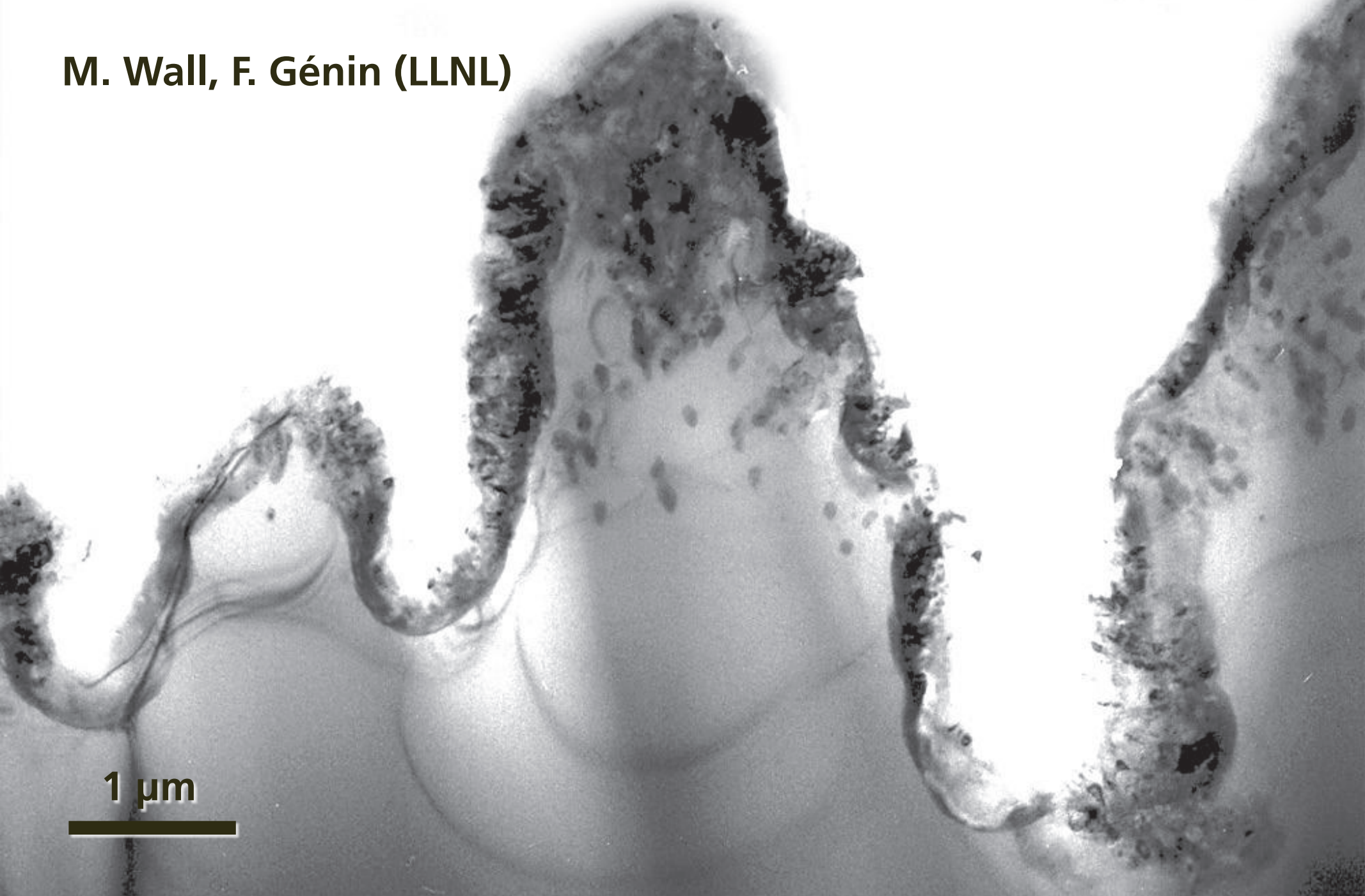
# Nontransparent materials

**cross-sectional  
Transmission Electron  
Microscopy**



# Nontransparent materials

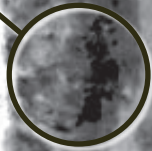
M. Wall, F. Génin (LLNL)



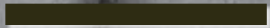


# Nontransparent materials

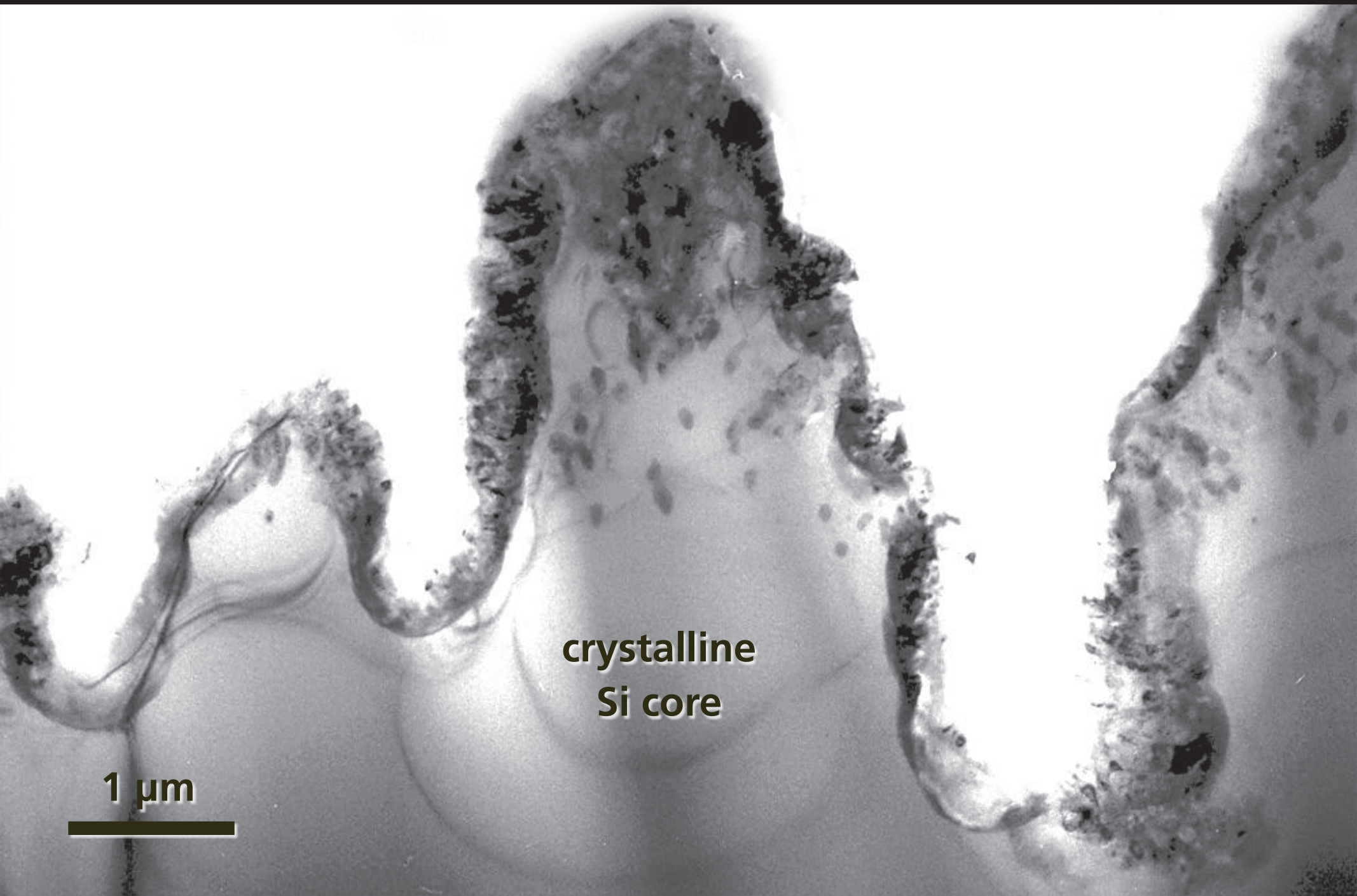
disordered  
surface layer



1  $\mu\text{m}$

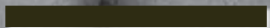


# Nontransparent materials



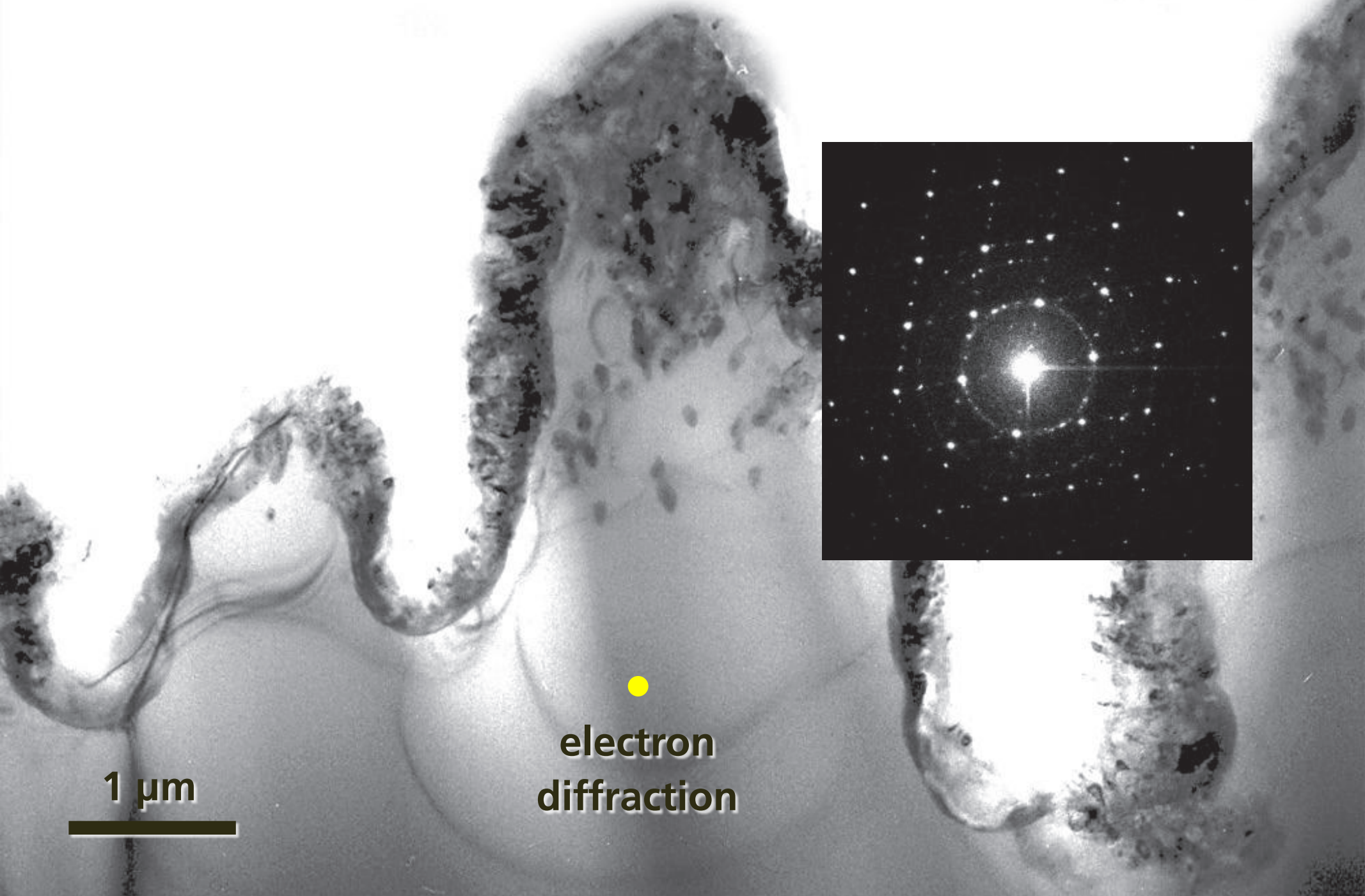
crystalline  
Si core

1  $\mu\text{m}$





# Nontransparent materials

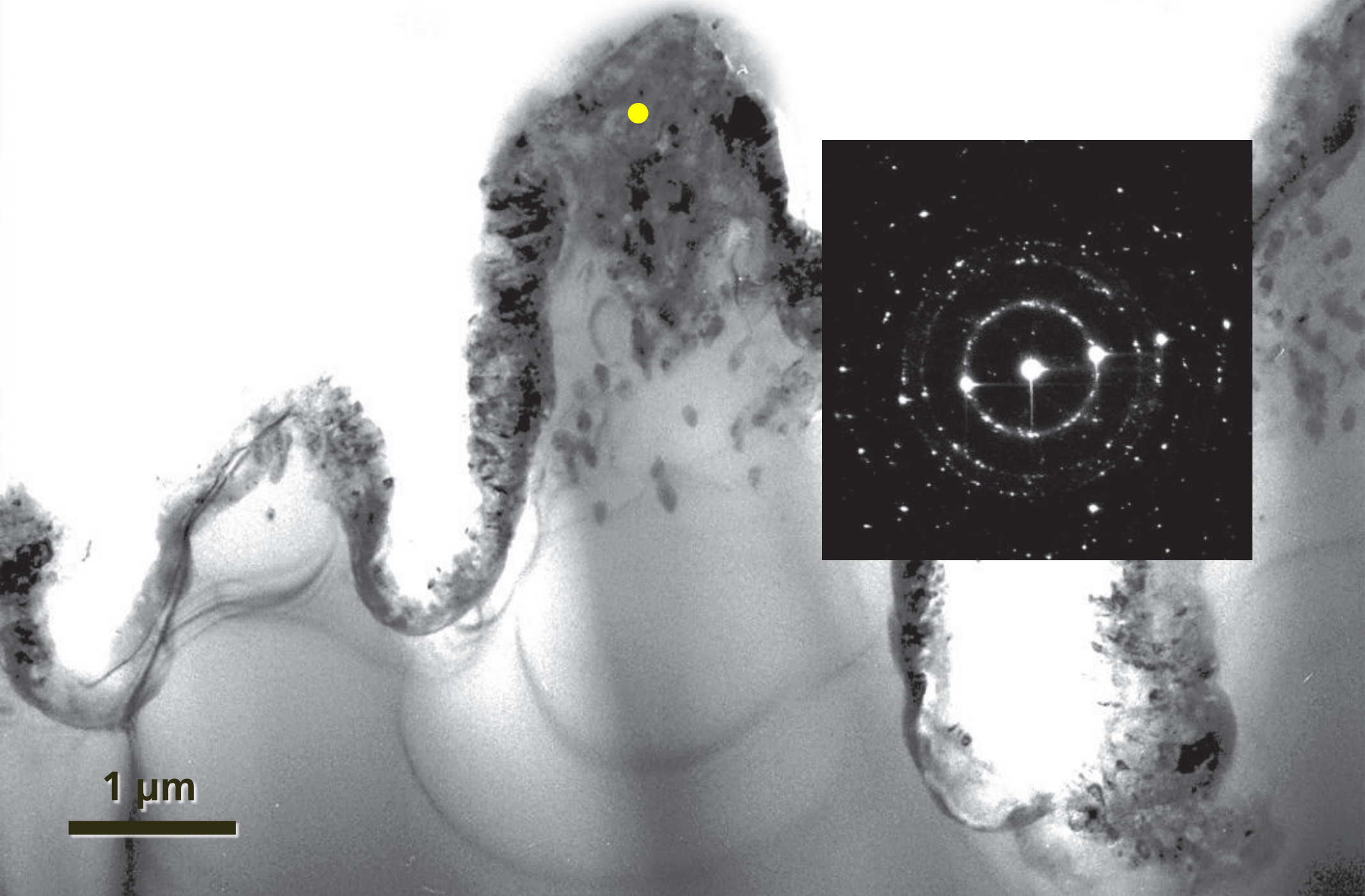


1 μm

●  
electron  
diffraction



# Nontransparent materials



# Nontransparent materials

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

1  $\mu\text{m}$

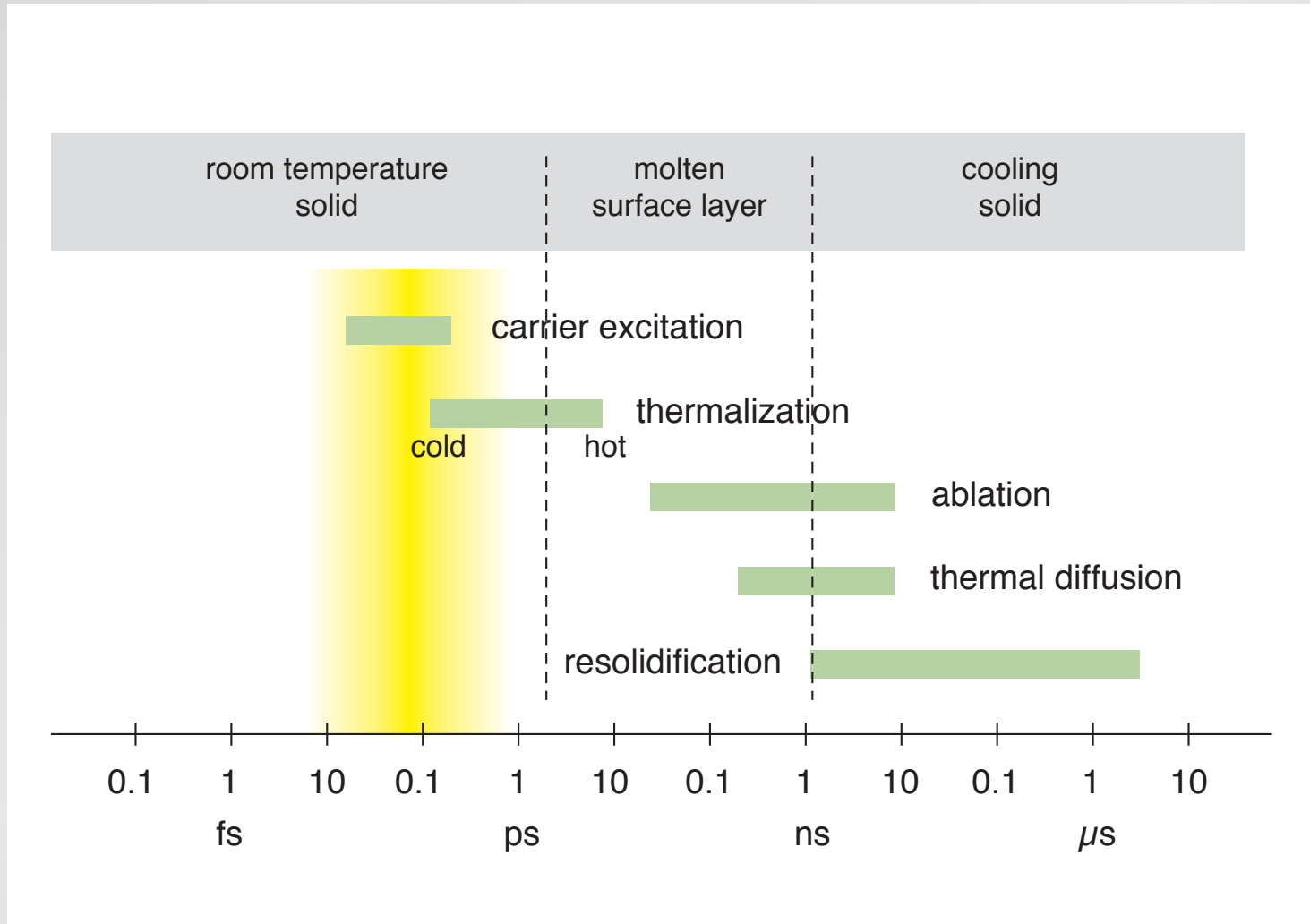
A grayscale micrograph showing a material with a disordered surface layer and a crystalline core. The surface layer is approximately 300 nm thick and contains nanocrystalline Si with 1.6% sulfur. The core is undisturbed and crystalline. A scale bar in the bottom left corner indicates 1 μm.

# Nontransparent materials

**two processes: melting and ablation**

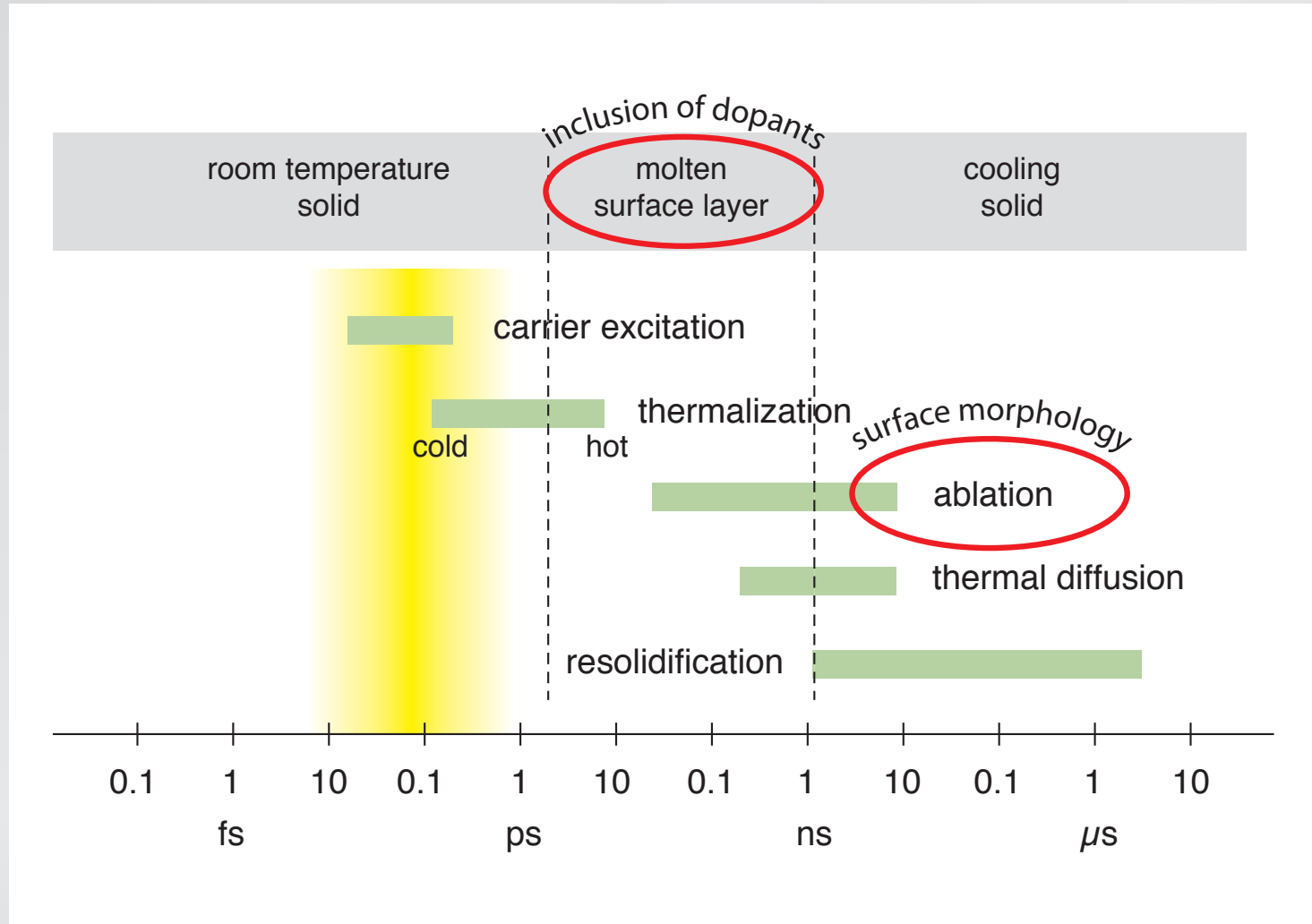
# Nontransparent materials

## relevant time scales



# Nontransparent materials

## relevant time scales



# Nontransparent materials

**different thresholds:**

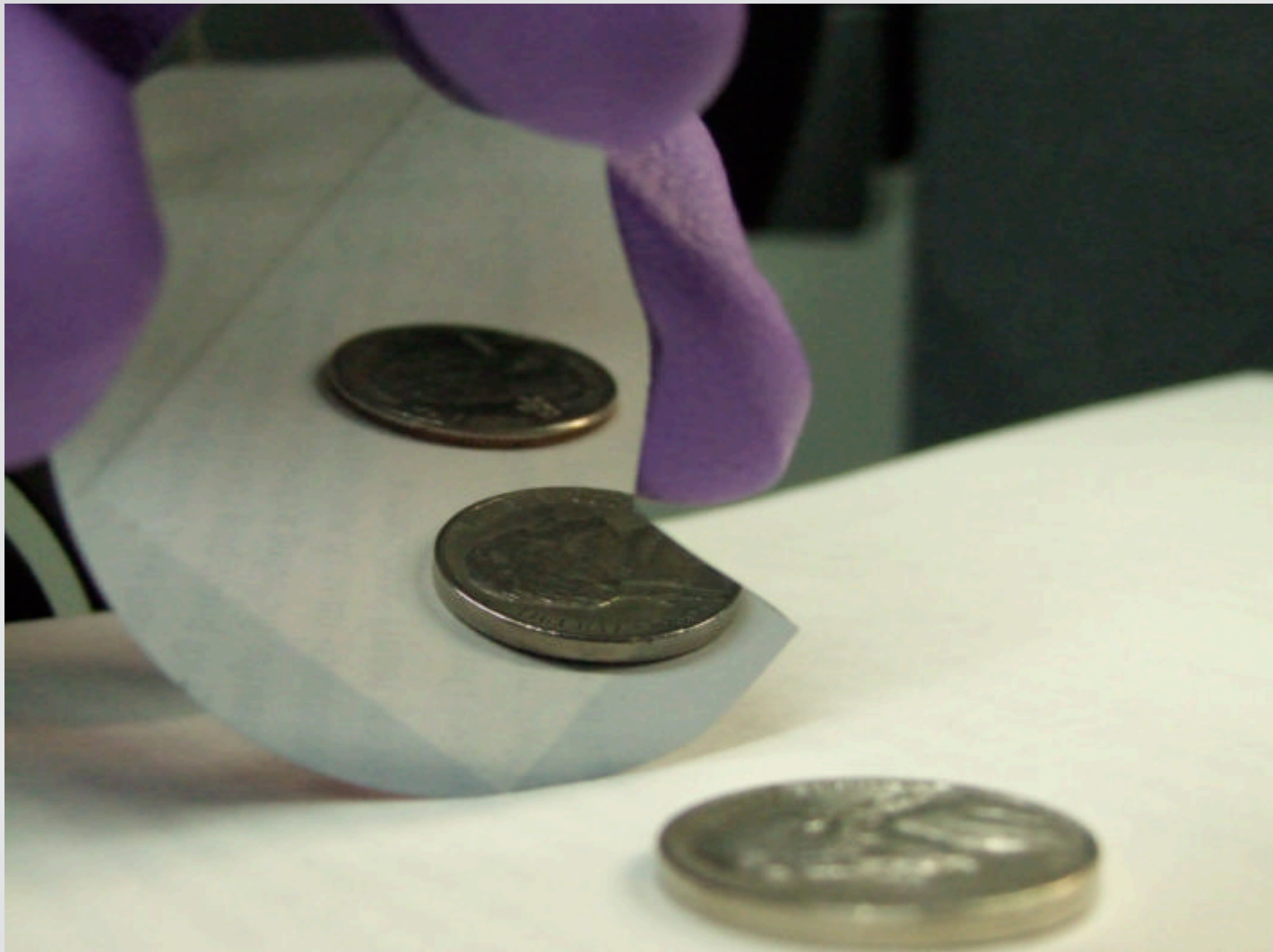
**melting: 1.5 kJ/m<sup>2</sup>**

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



# Nontransparent materials

decouple ablation from melting

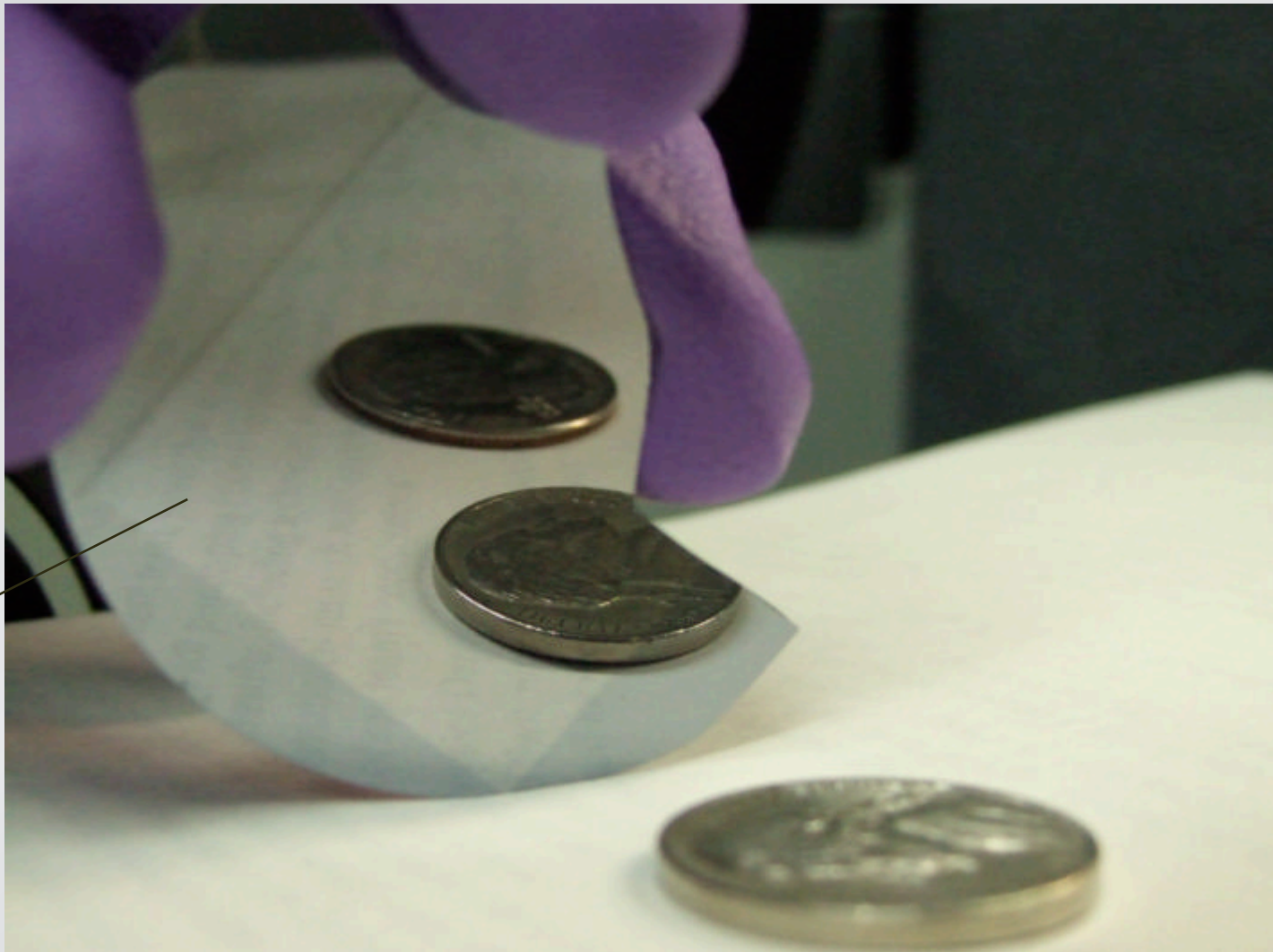




# Nontransparent materials

decouple ablation from melting

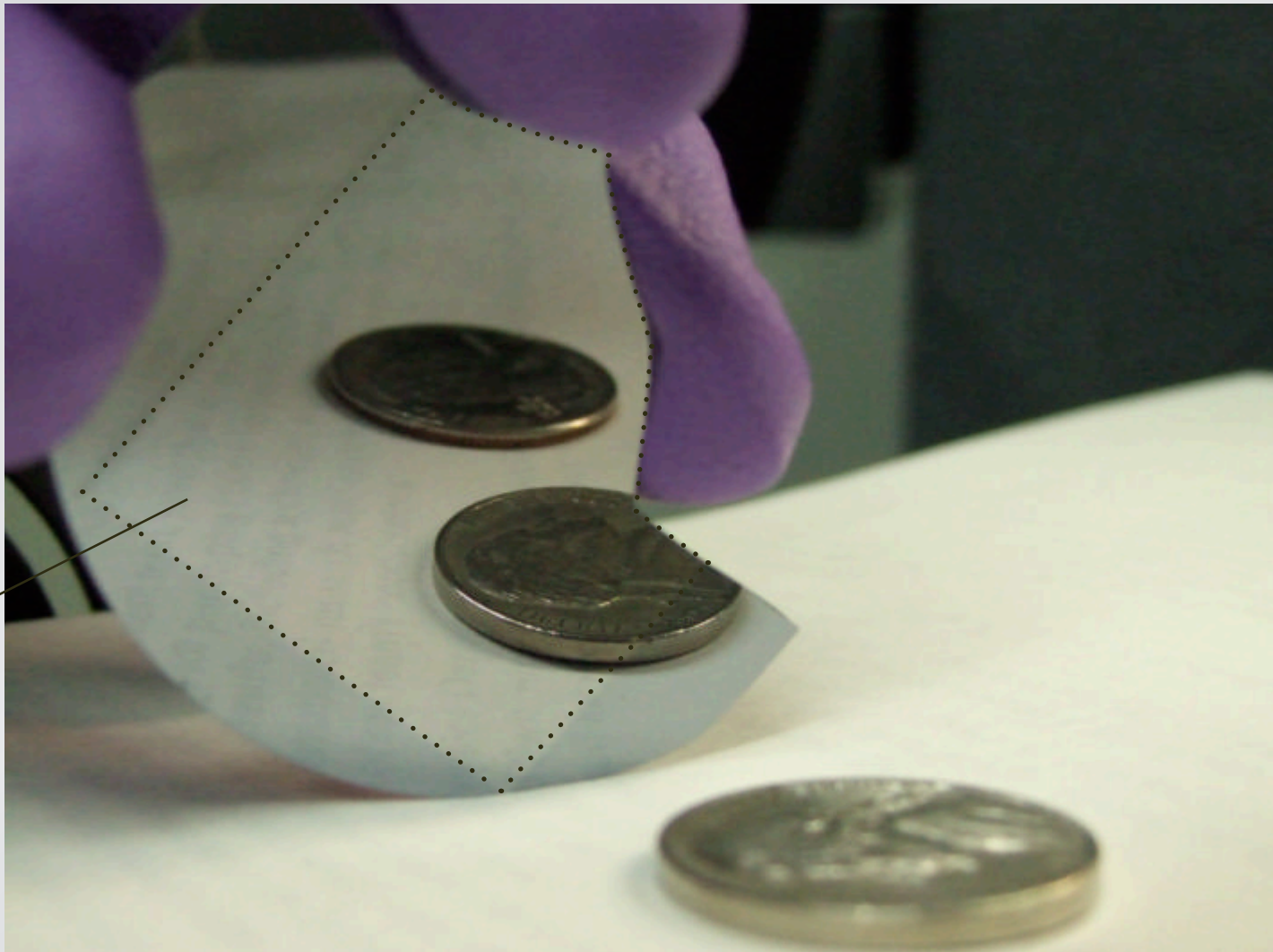
doped



# Nontransparent materials

decouple ablation from melting

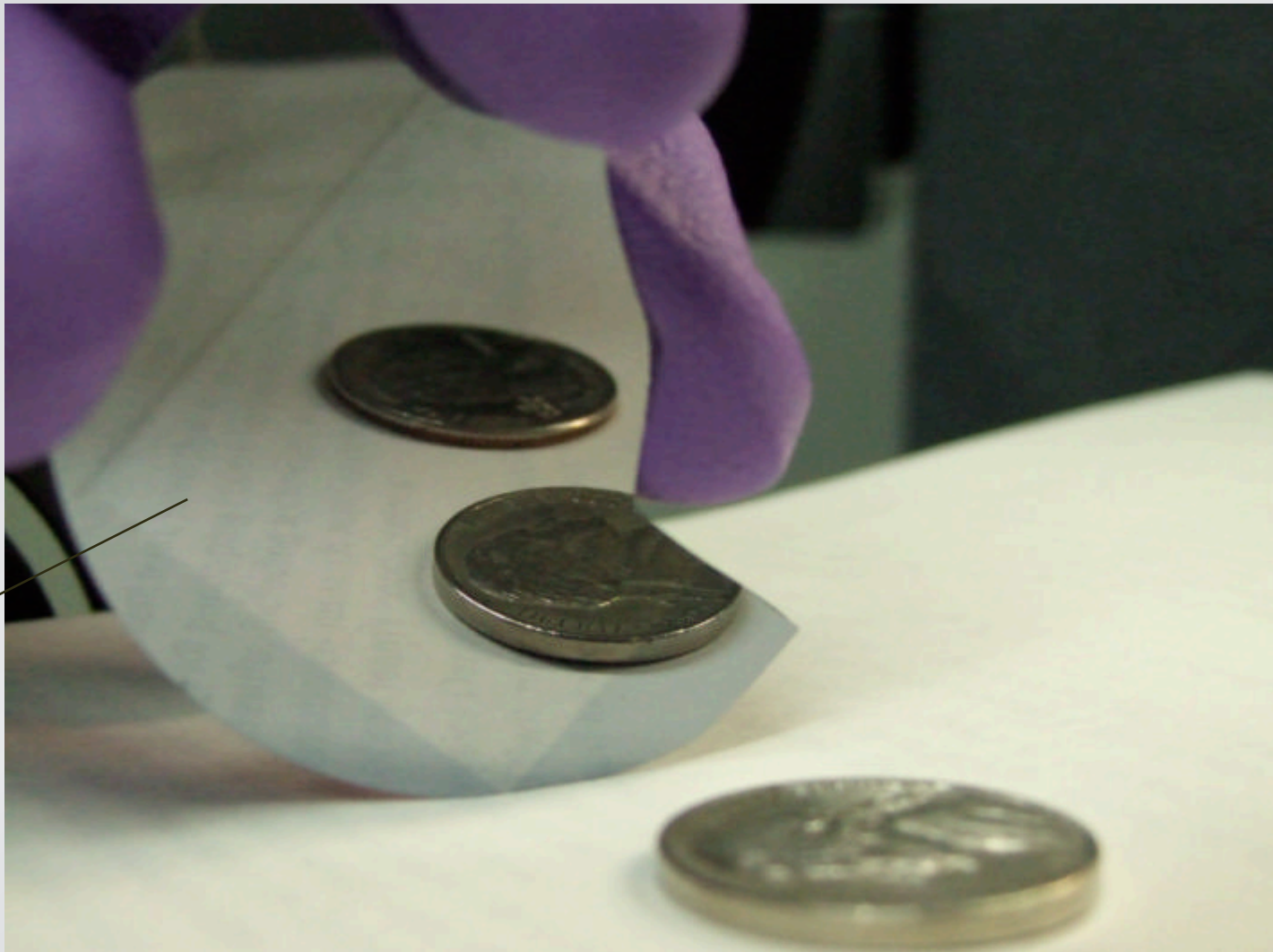
doped



# Nontransparent materials

decouple ablation from melting

doped



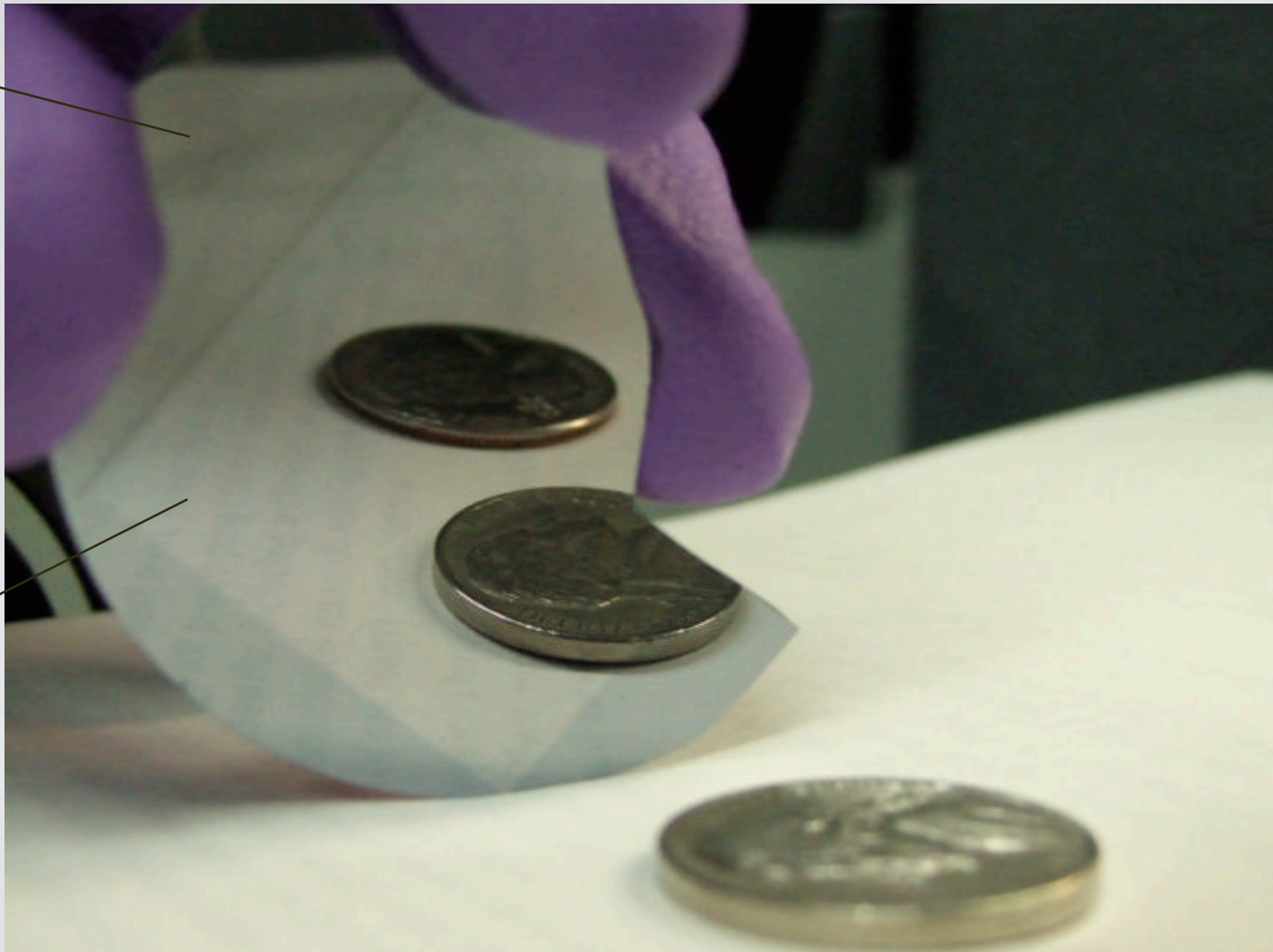


# Nontransparent materials

decouple ablation from melting

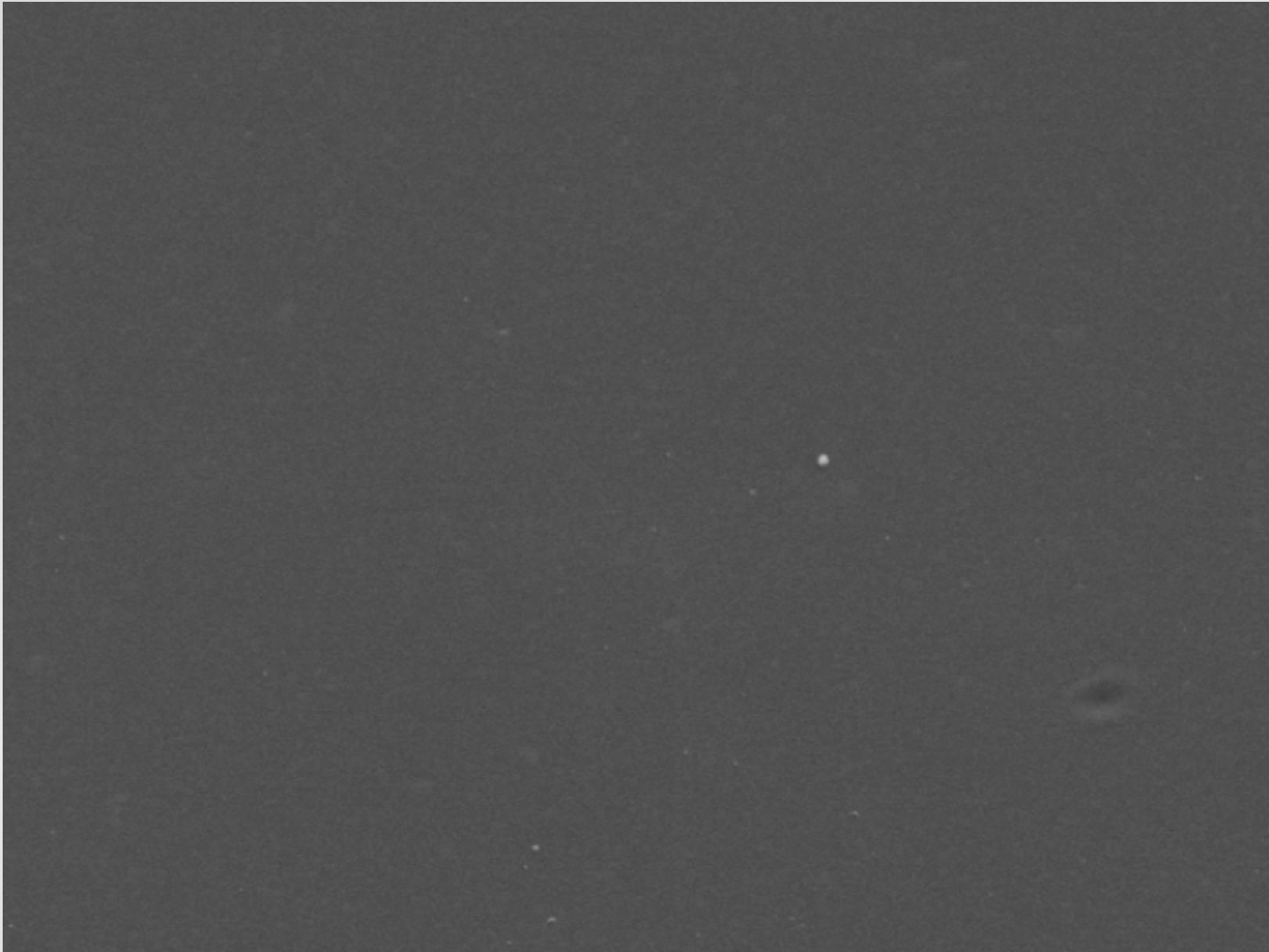
undoped

doped



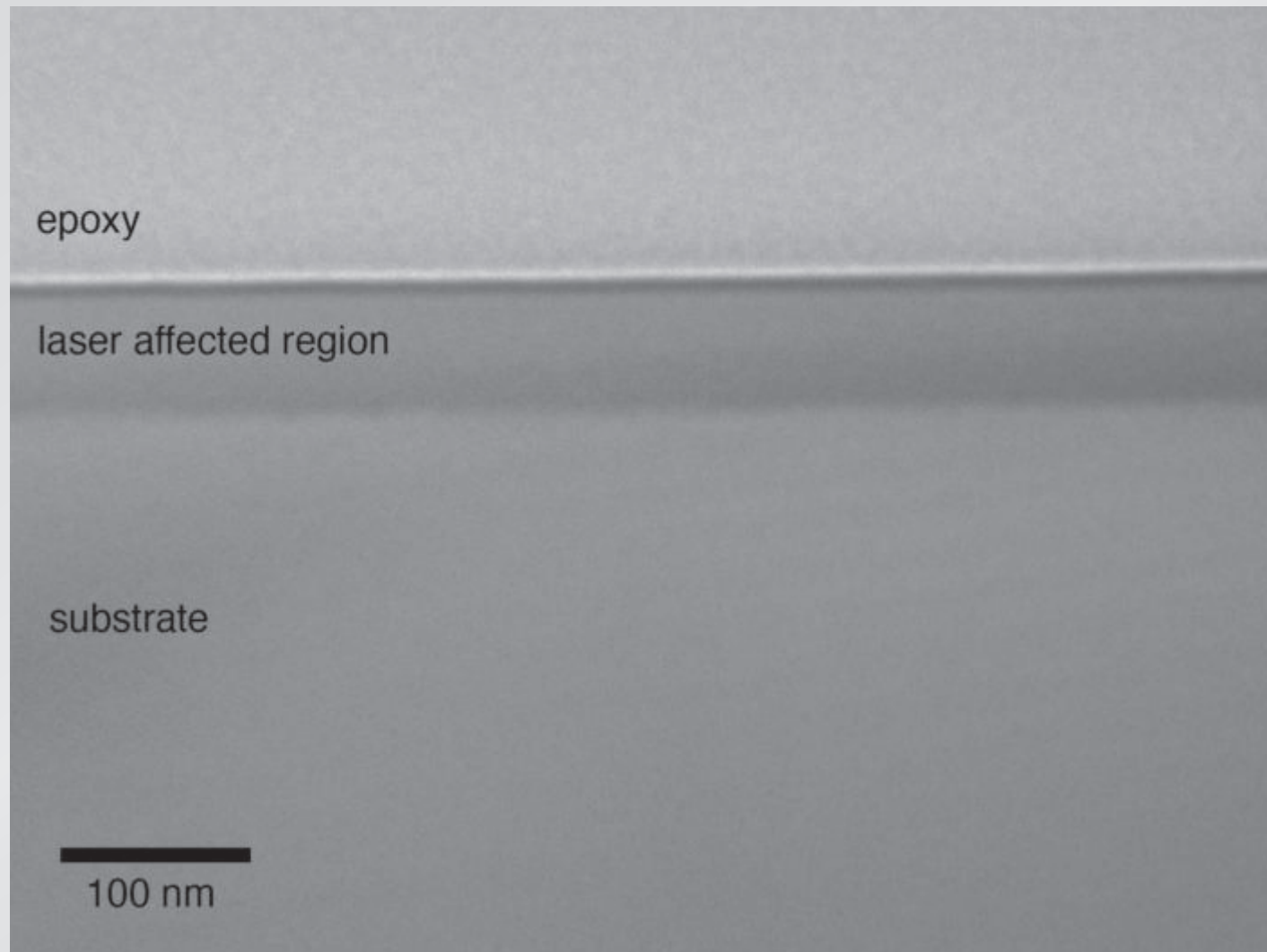
# Nontransparent materials

decouple ablation from melting



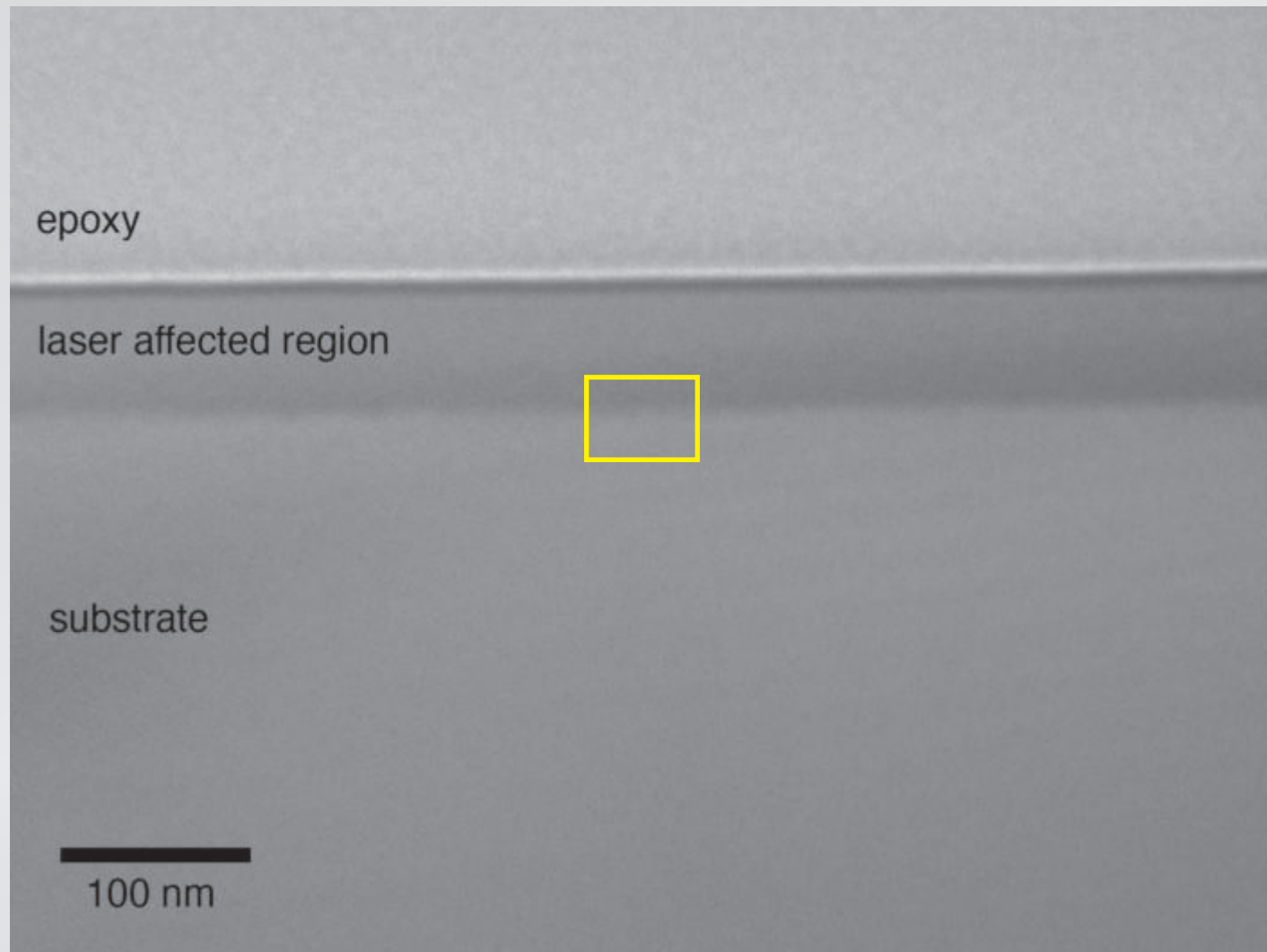
# Nontransparent materials

decouple ablation from melting



# Nontransparent materials

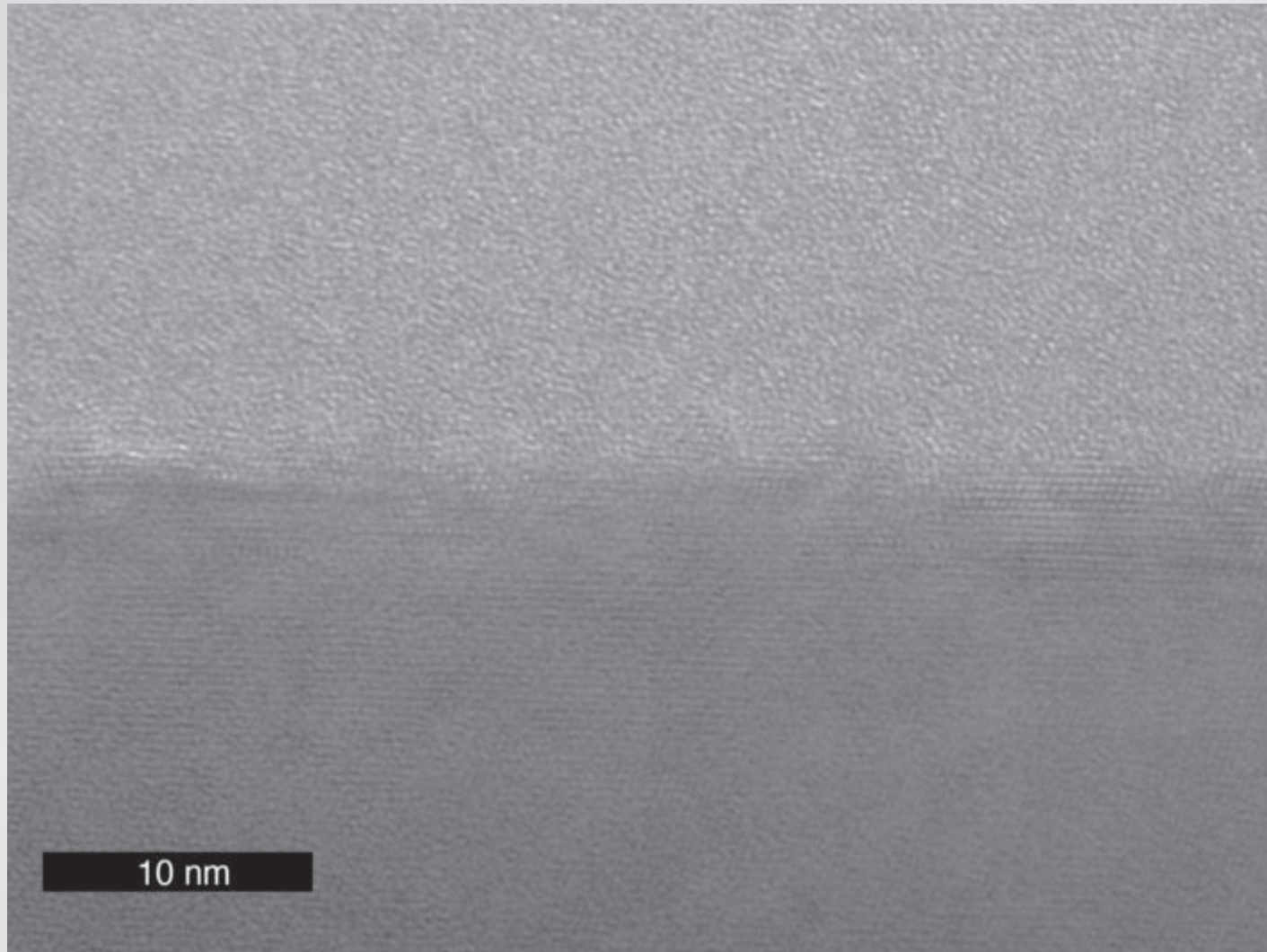
decouple ablation from melting





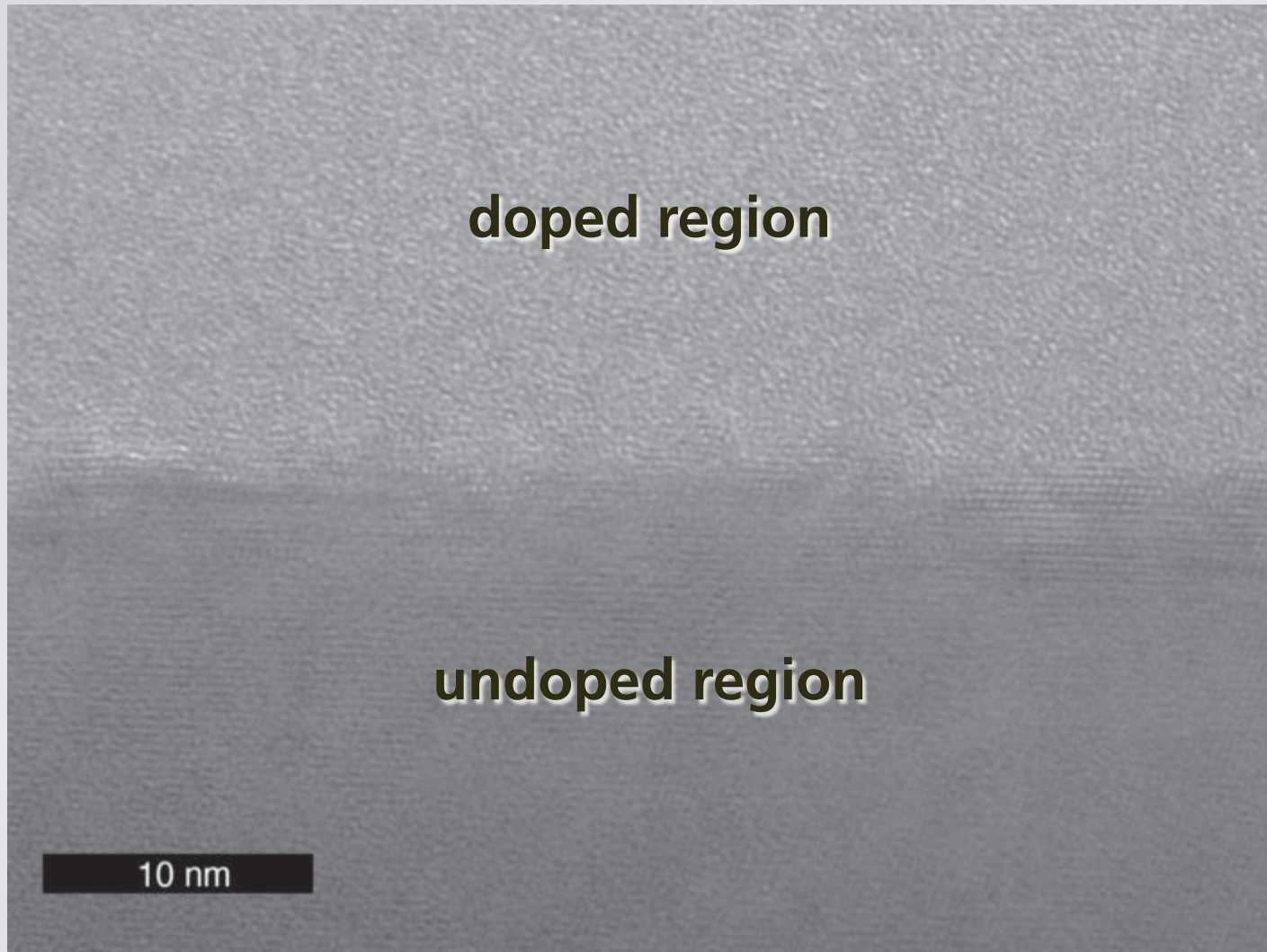
# Nontransparent materials

decouple ablation from melting



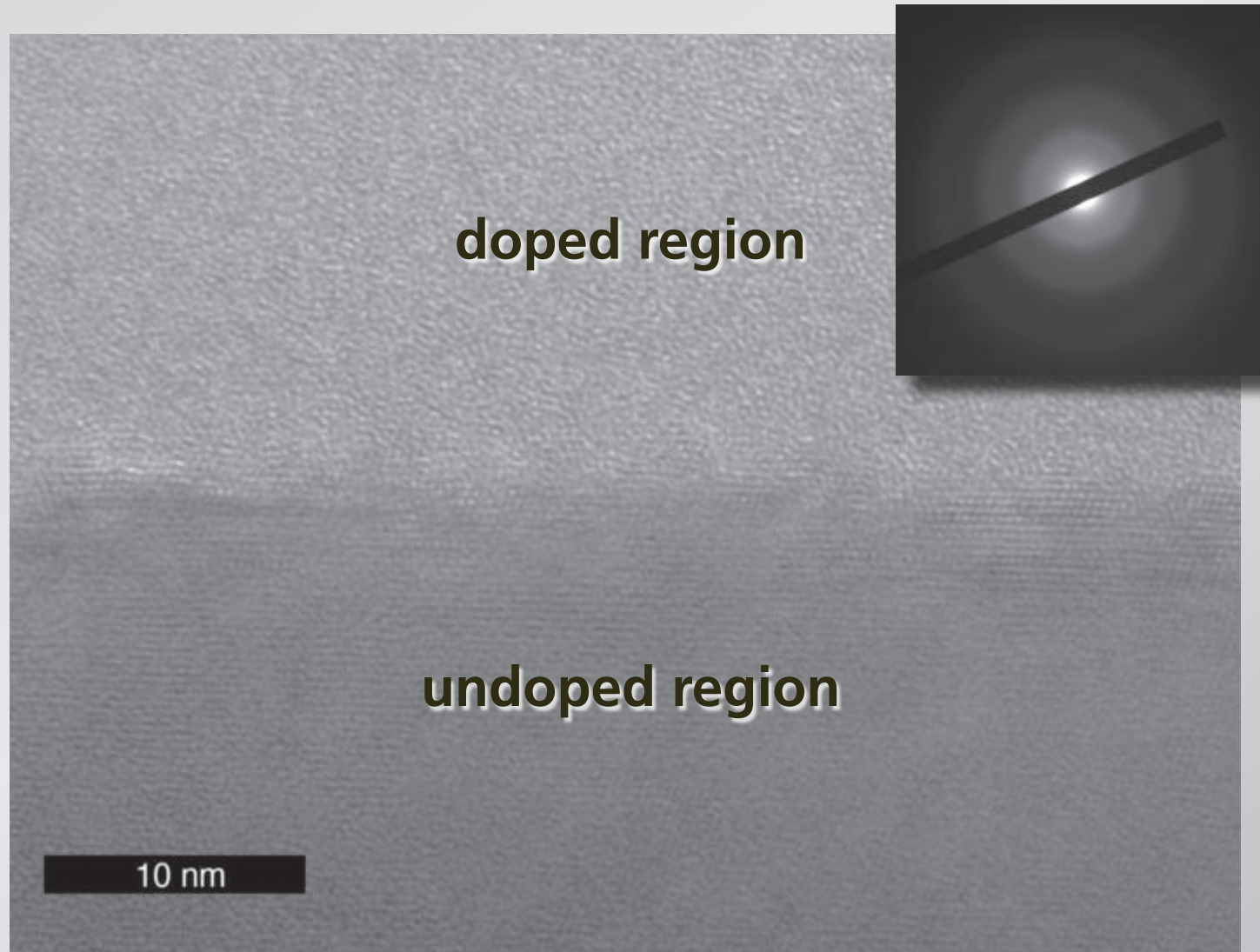
# Nontransparent materials

decouple ablation from melting



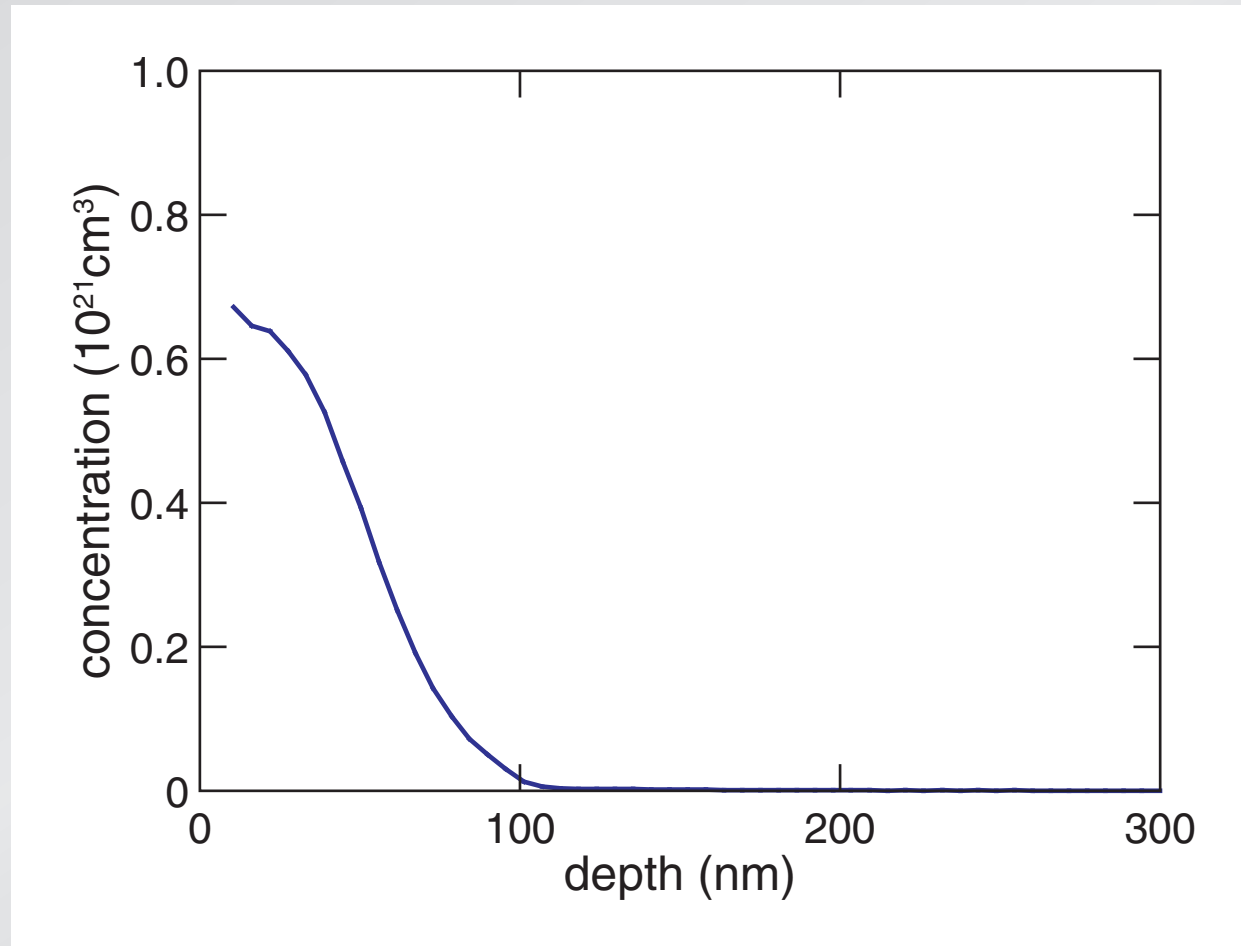
# Nontransparent materials

decouple ablation from melting

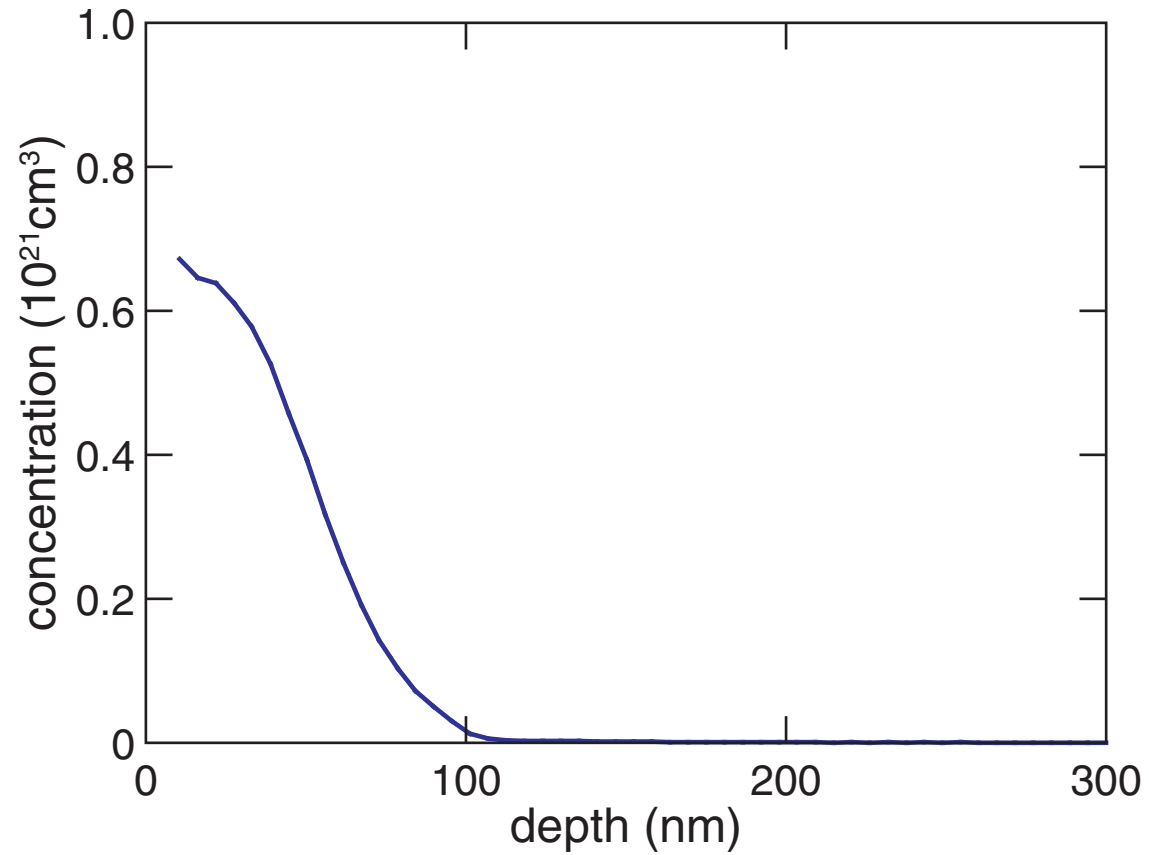


# Nontransparent materials

secondary ion mass spectrometry



# Nontransparent materials





# Nontransparent materials

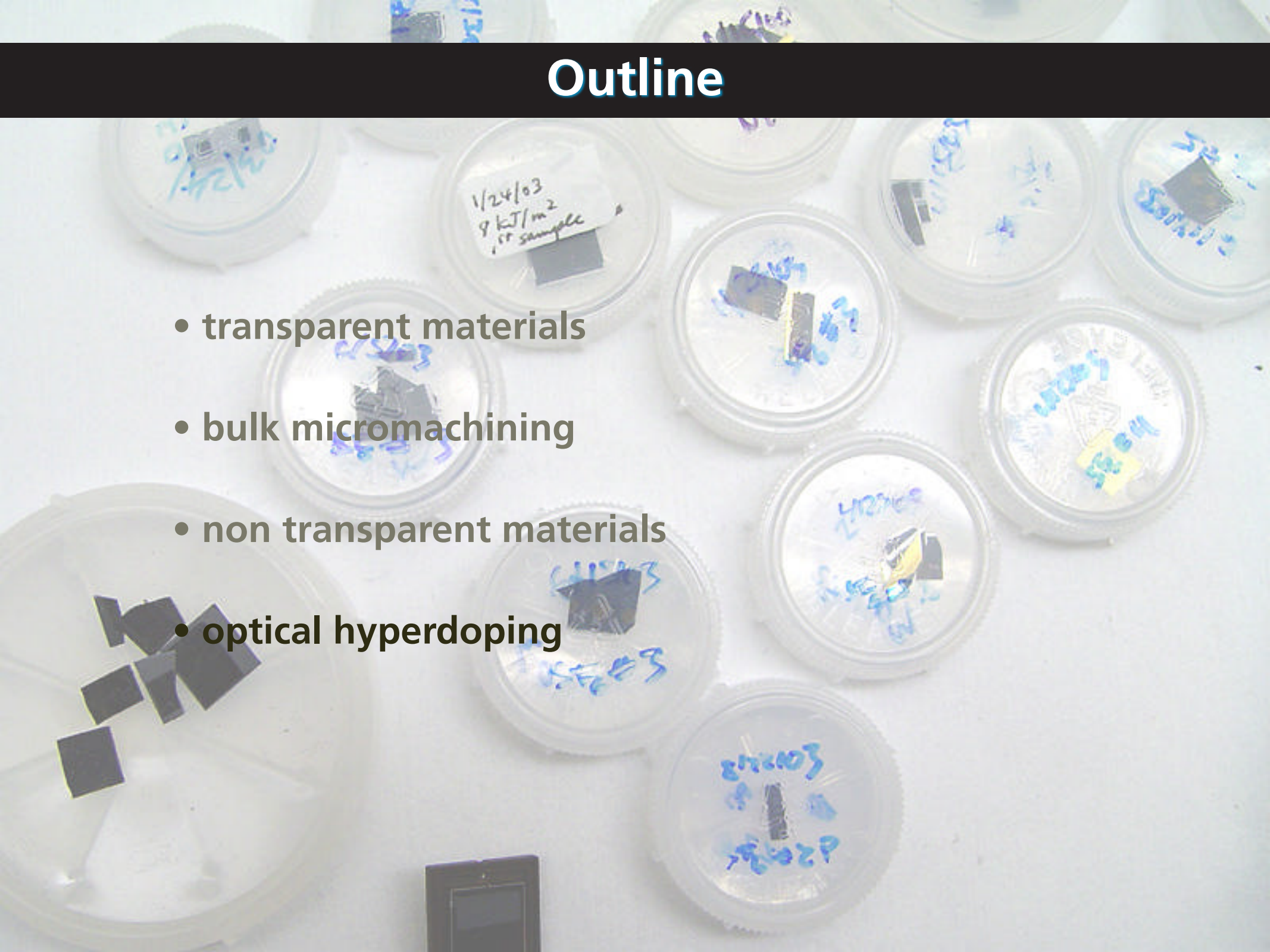
## Things to keep in mind

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



# Outline

- transparent materials
- bulk micromachining
- non transparent materials
- optical hyperdoping

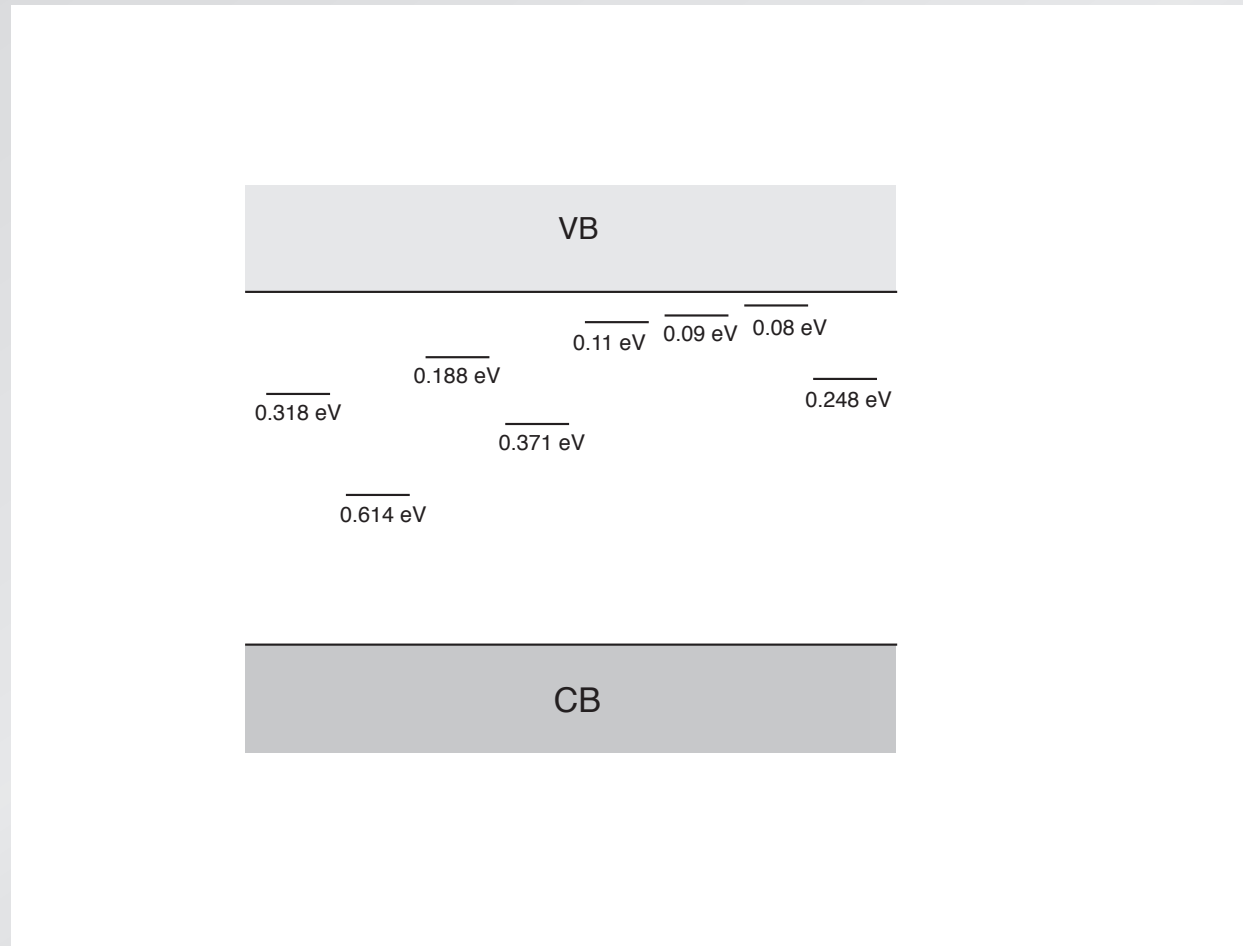


# Optical hyperdoping

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

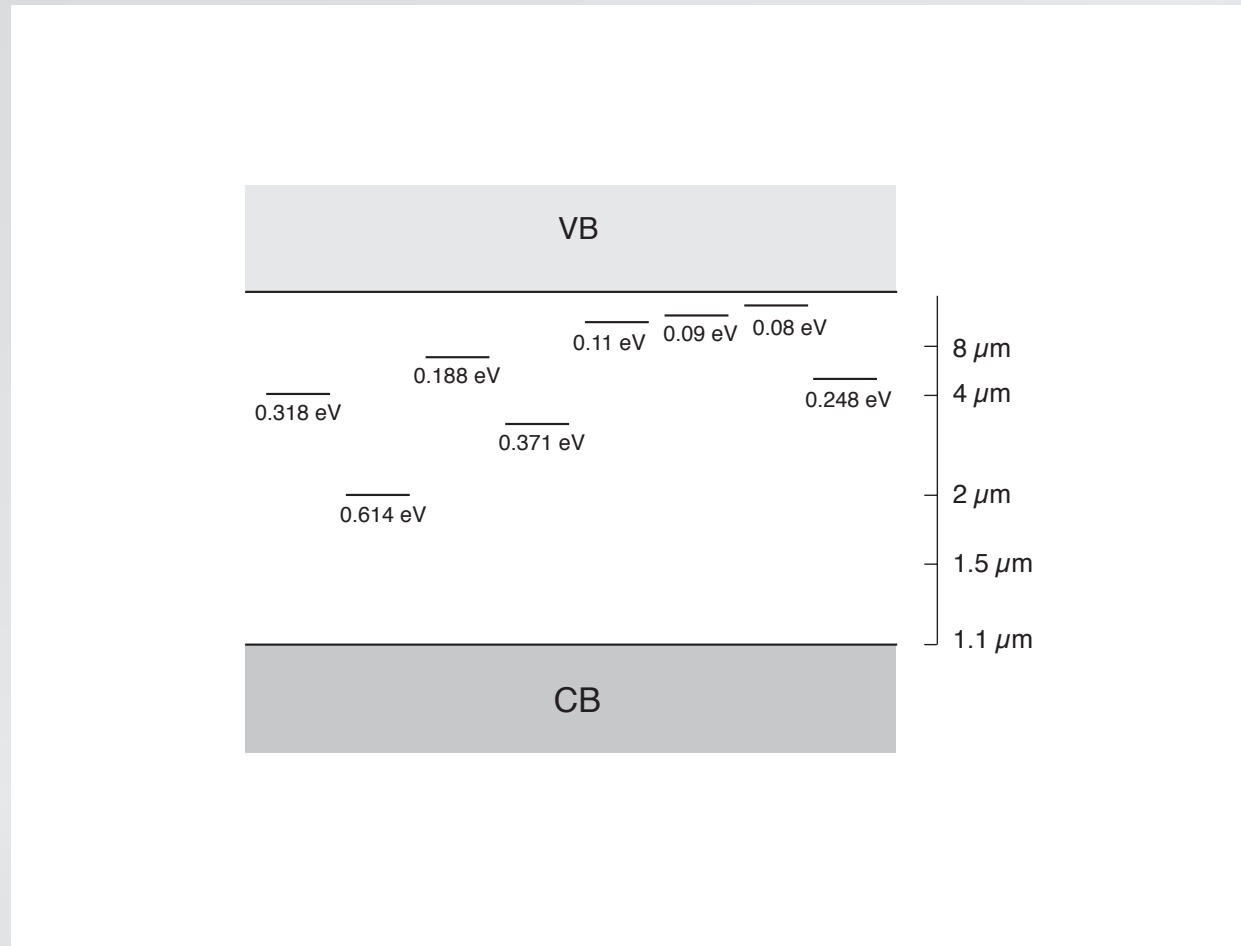
# Optical hyperdoping

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



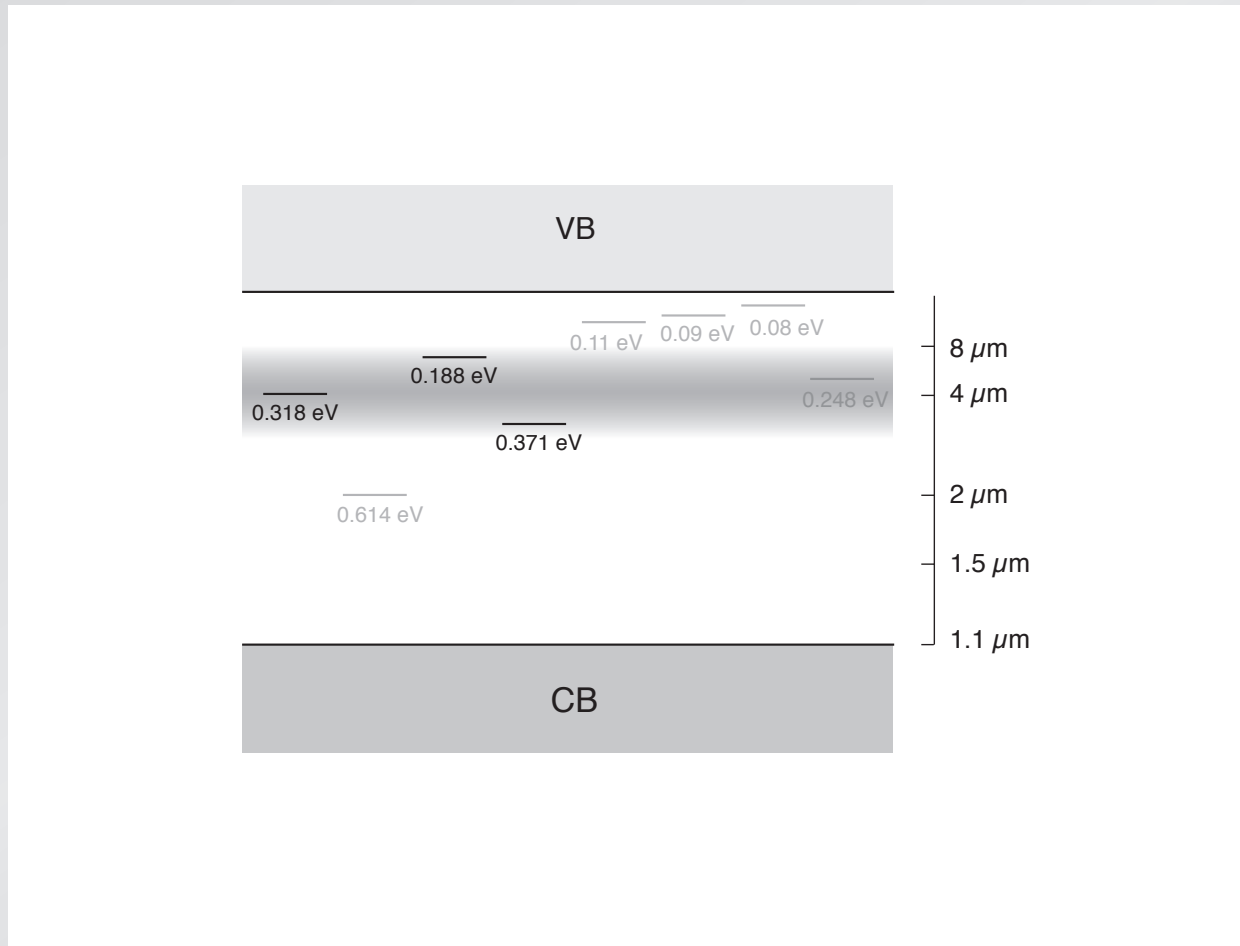
# Optical hyperdoping

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



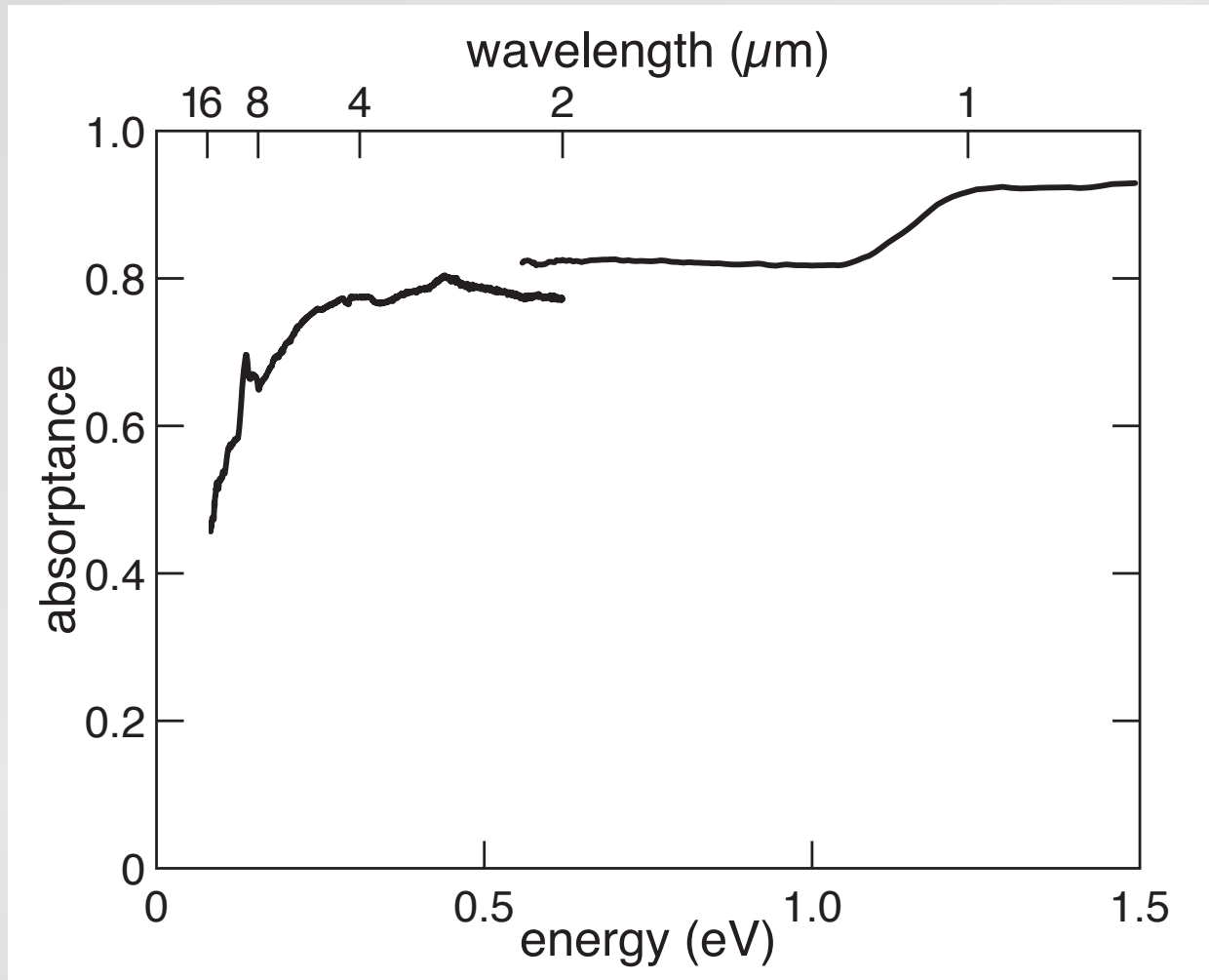
# Optical hyperdoping

at high concentration states broaden into band



# Optical hyperdoping

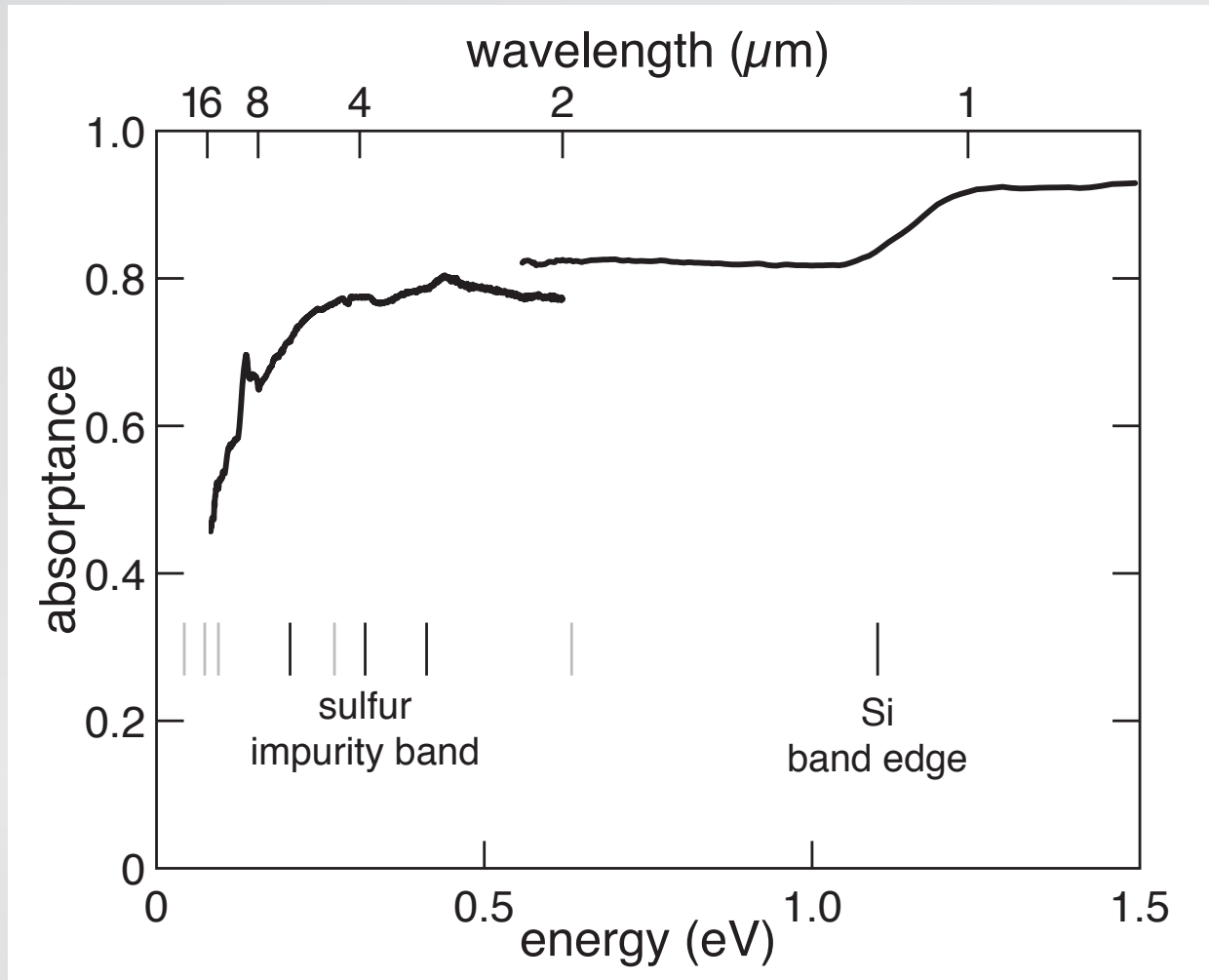
absorptance  $(1 - R_{int} - T_{int})$





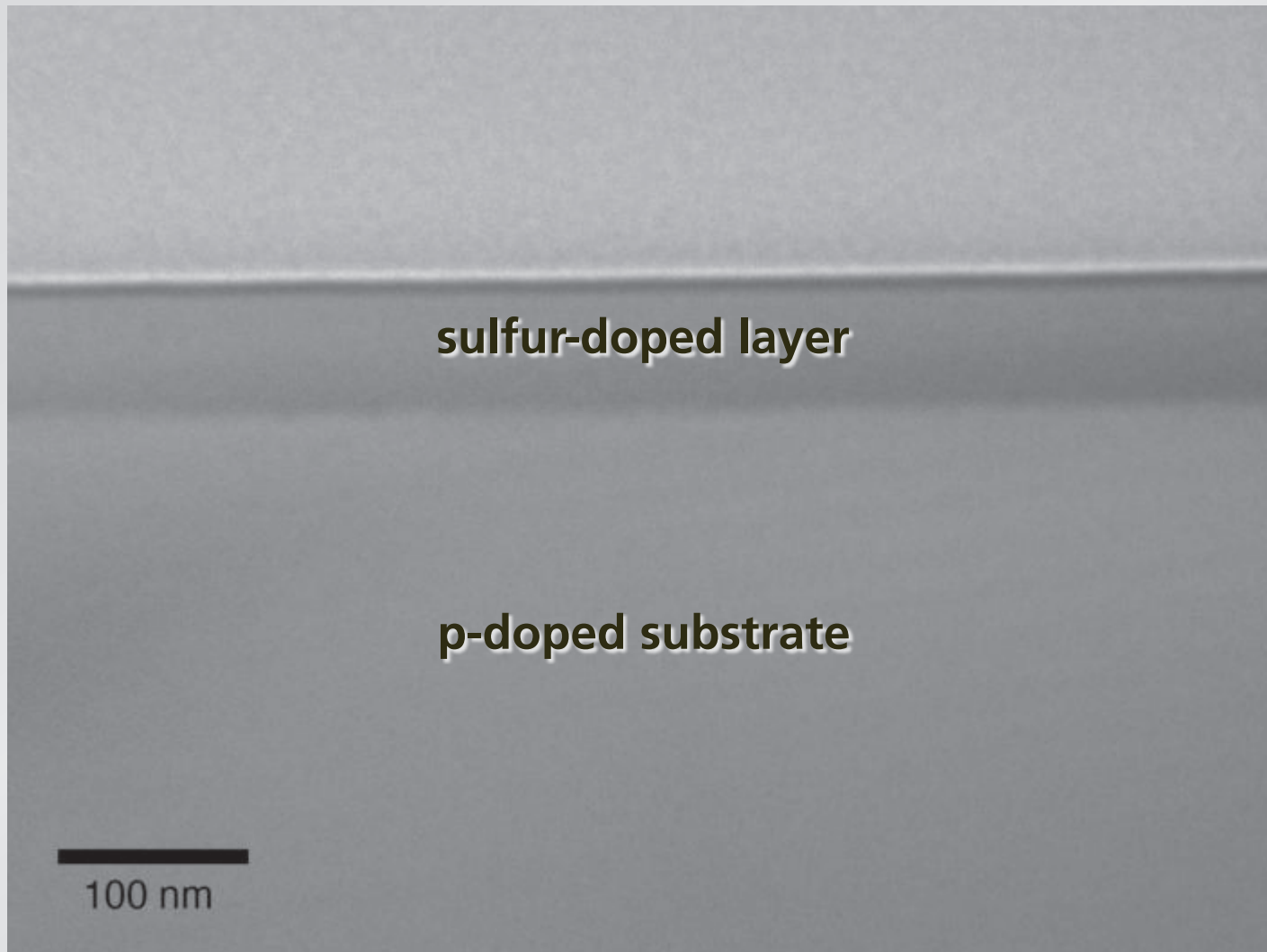
# Optical hyperdoping

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



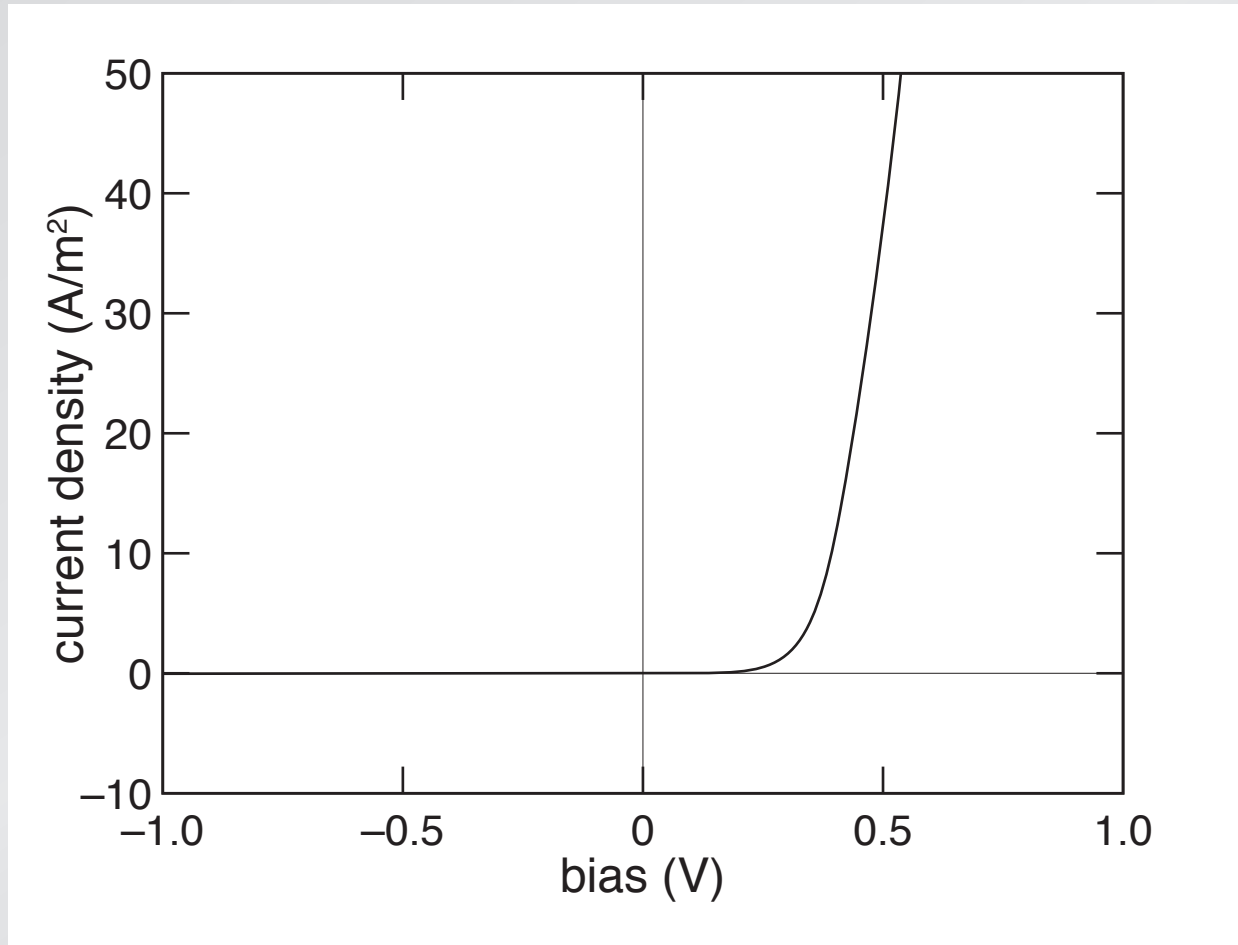
# Optical hyperdoping

should have shallow junction below surface



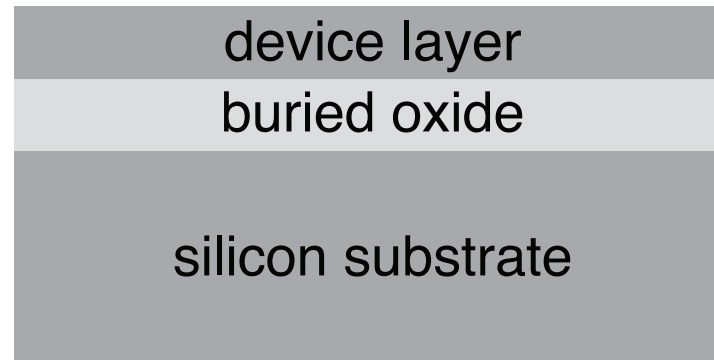
# Optical hyperdoping

excellent rectification (after annealing)



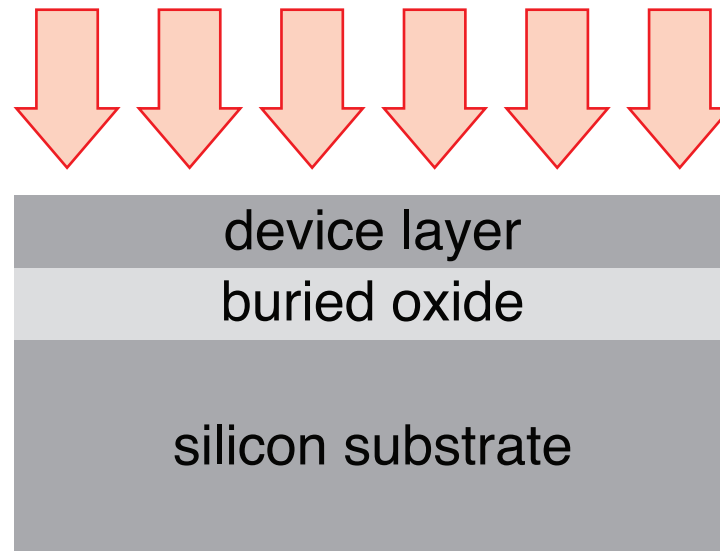
# Optical hyperdoping

isolate surface layer for Hall measurements



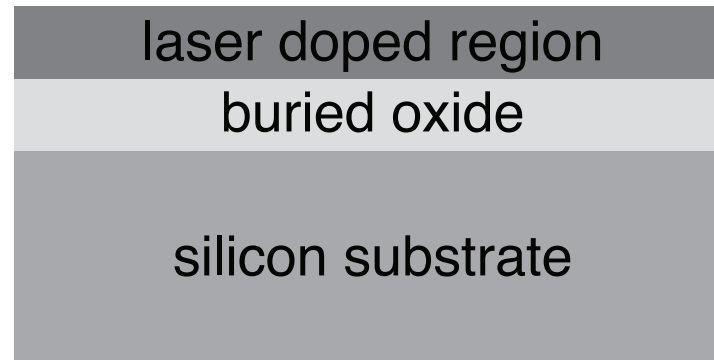
# Optical hyperdoping

isolate surface layer for Hall measurements



# Optical hyperdoping

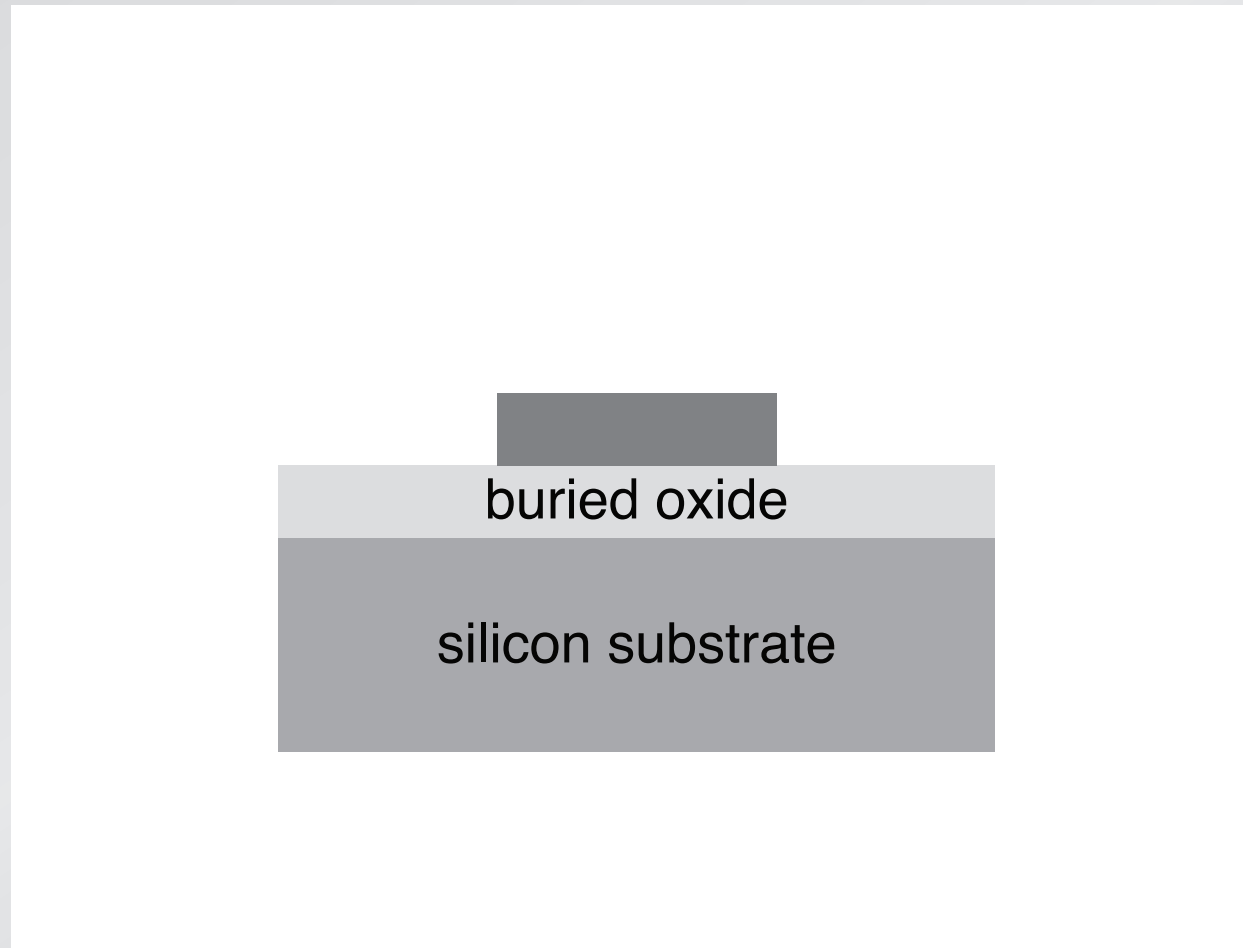
isolate surface layer for Hall measurements





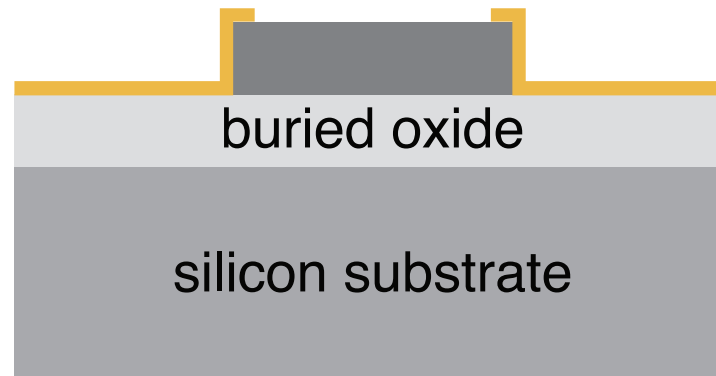
# Optical hyperdoping

isolate surface layer for Hall measurements



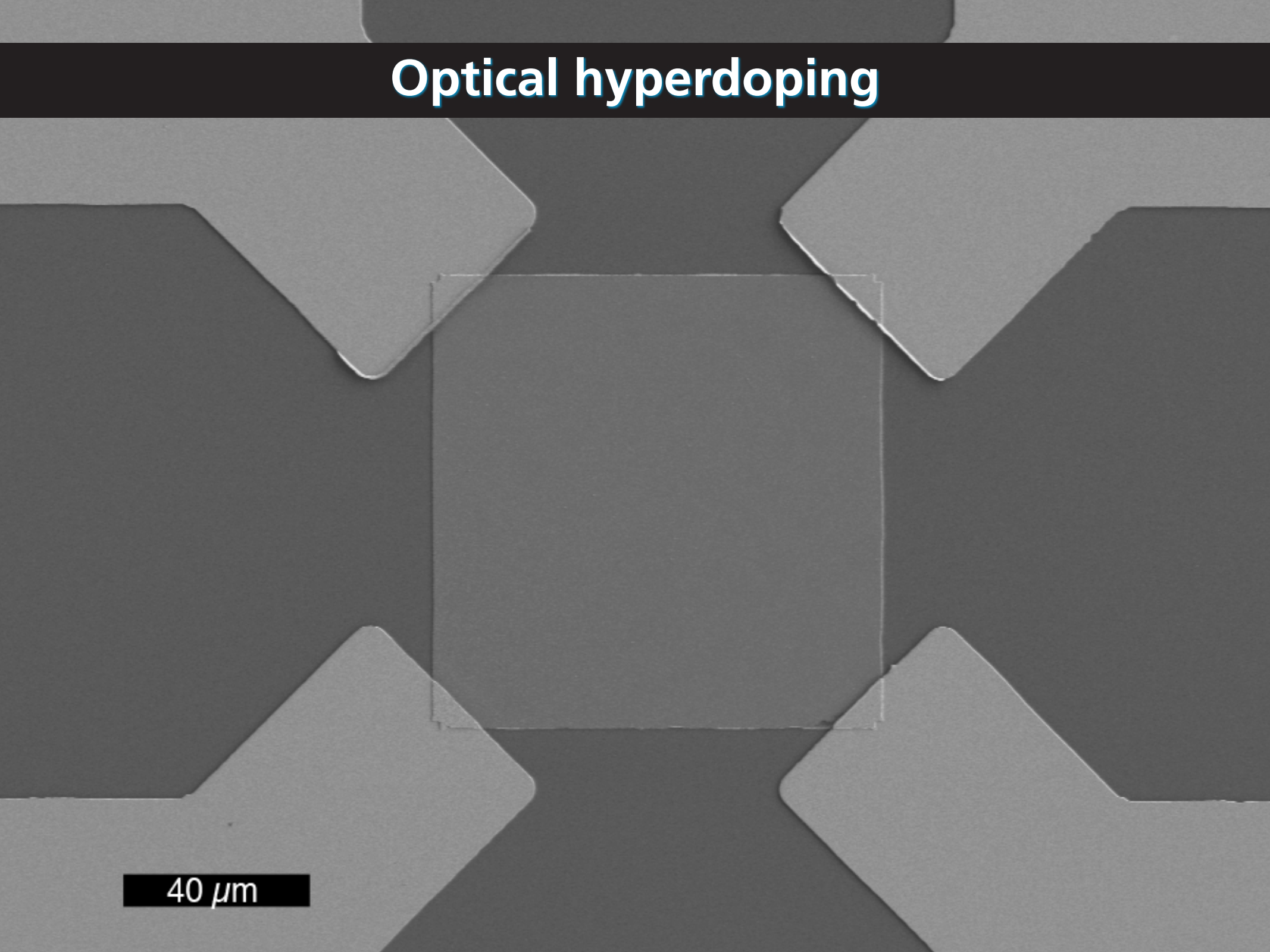
# Optical hyperdoping

isolate surface layer for Hall measurements



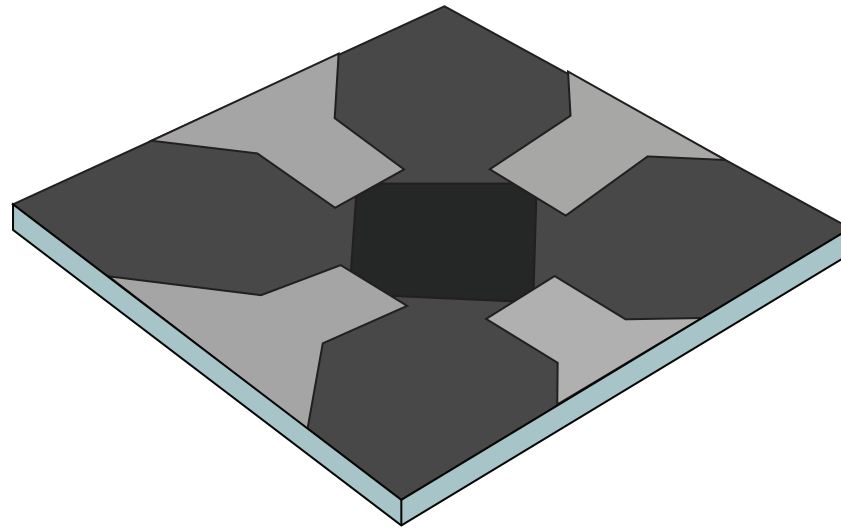
# Optical hyperdoping

40  $\mu\text{m}$

A grayscale micrograph showing a central square device on a substrate. The substrate has four trapezoidal pads, one in each corner, which appear to be part of a larger pattern. The central square is slightly darker than the surrounding substrate. A scale bar in the bottom left corner indicates a length of 40 micrometers.

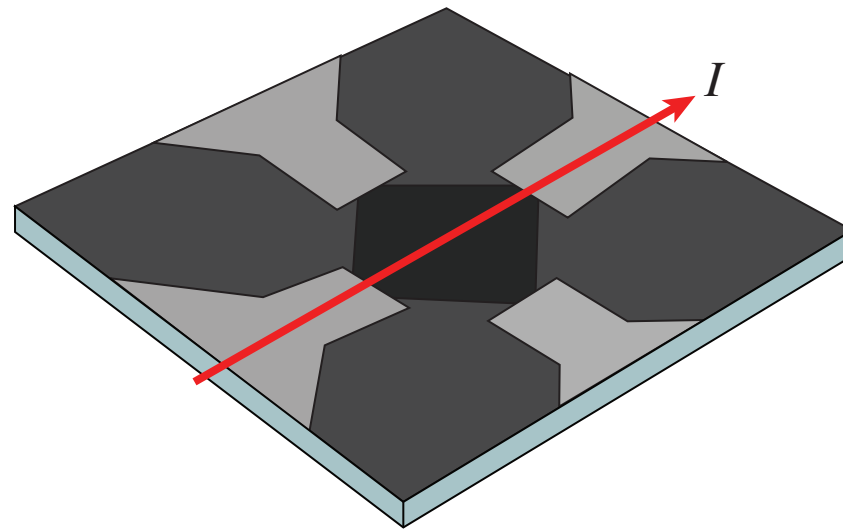
# Optical hyperdoping

## Hall measurements



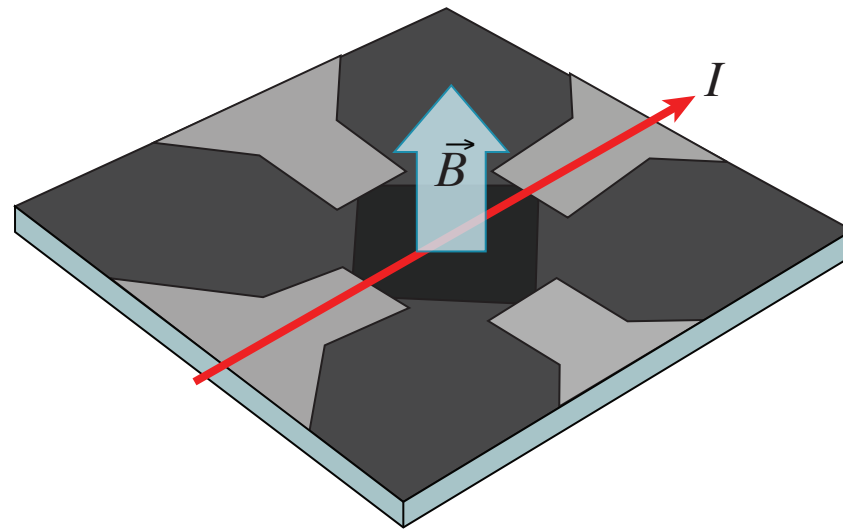
# Optical hyperdoping

## Hall measurements



# Optical hyperdoping

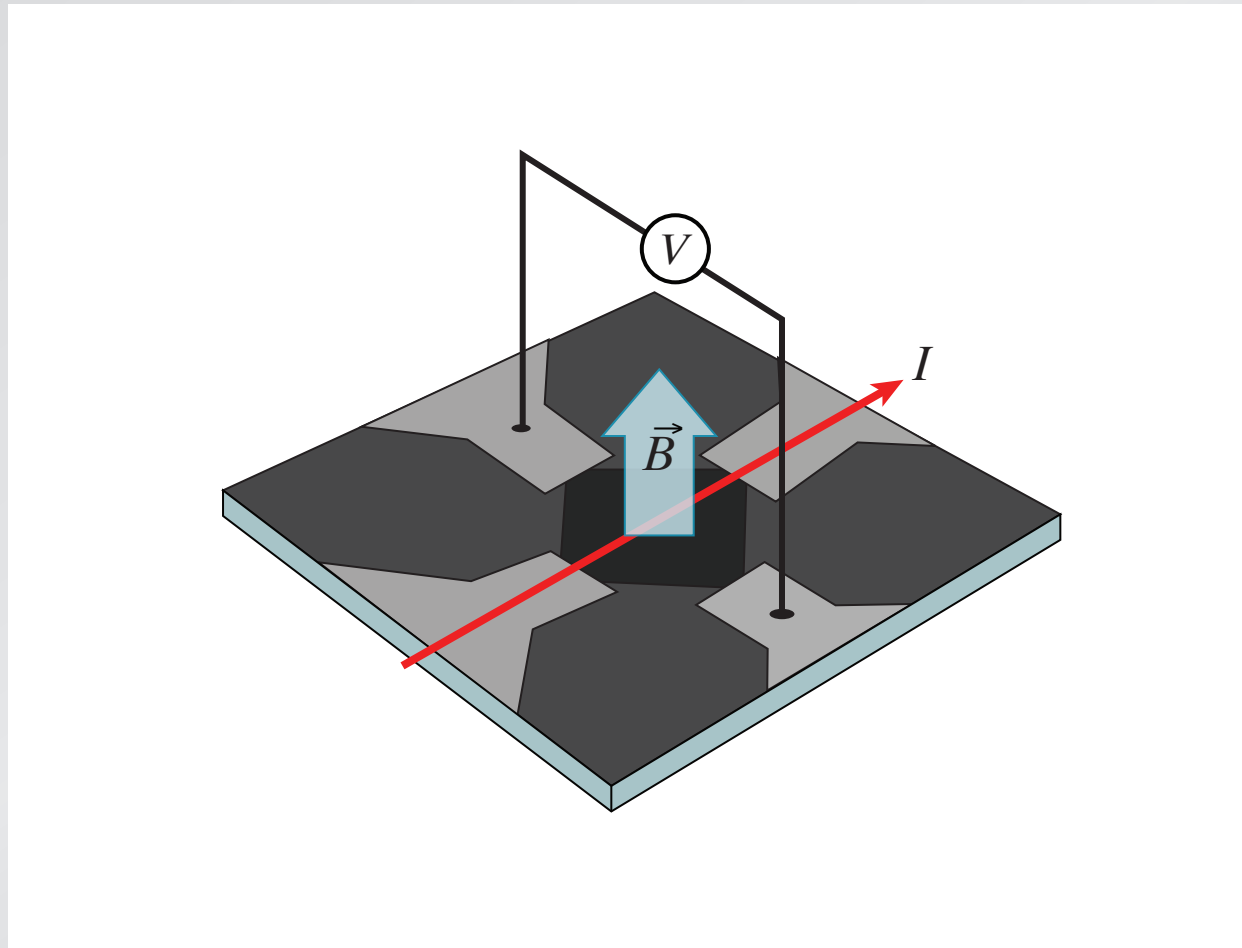
## Hall measurements





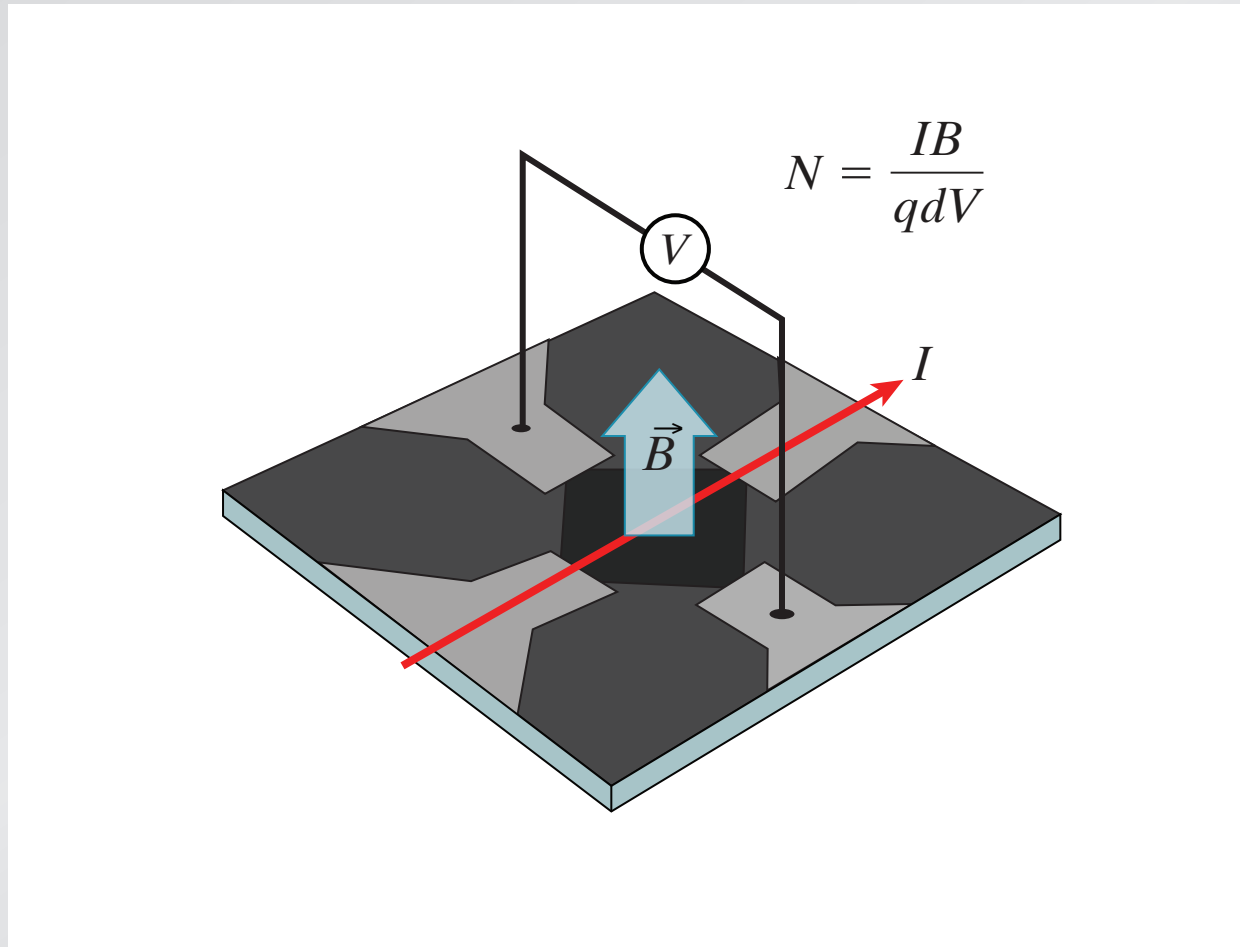
# Optical hyperdoping

## Hall measurements



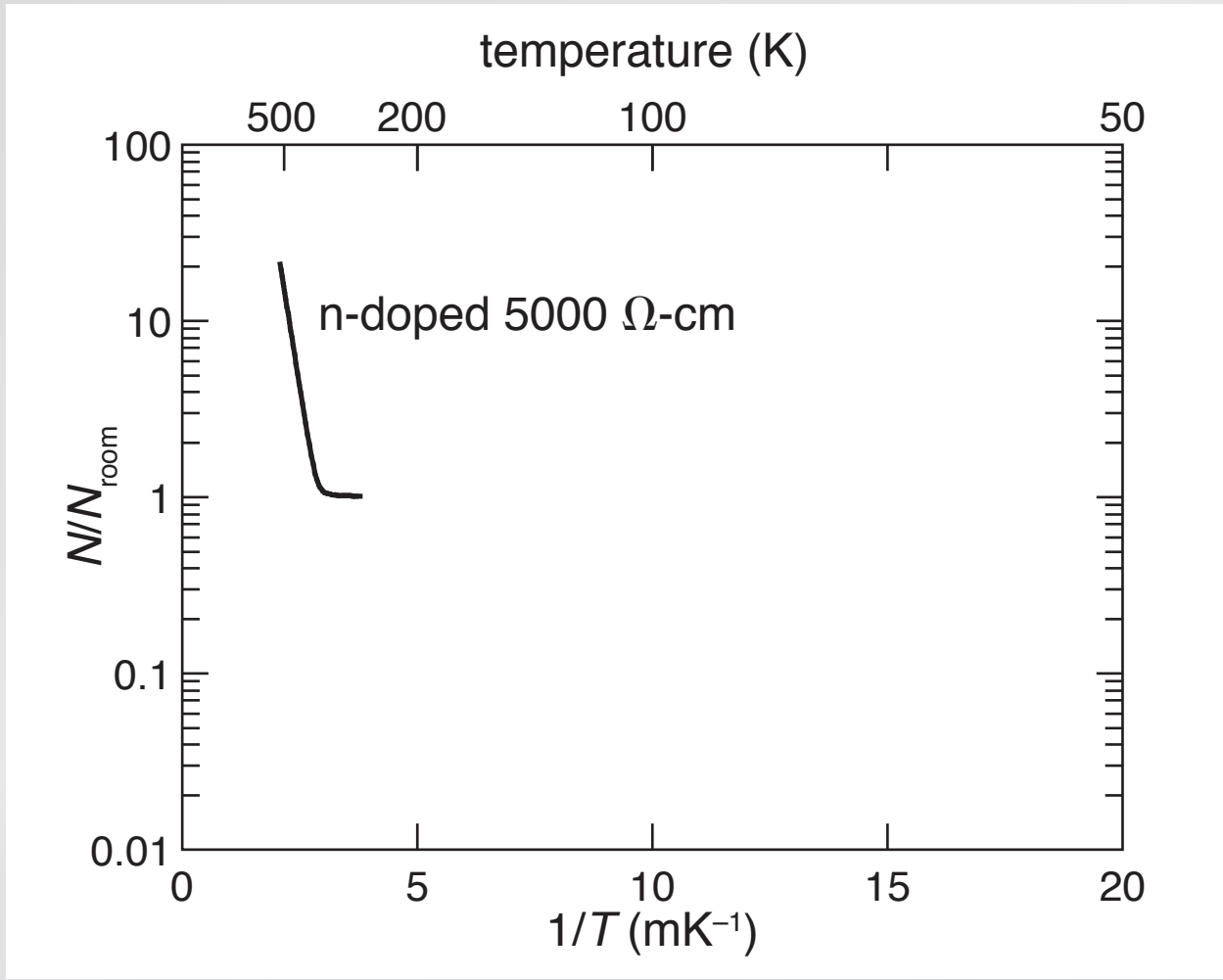
# Optical hyperdoping

## Hall measurements



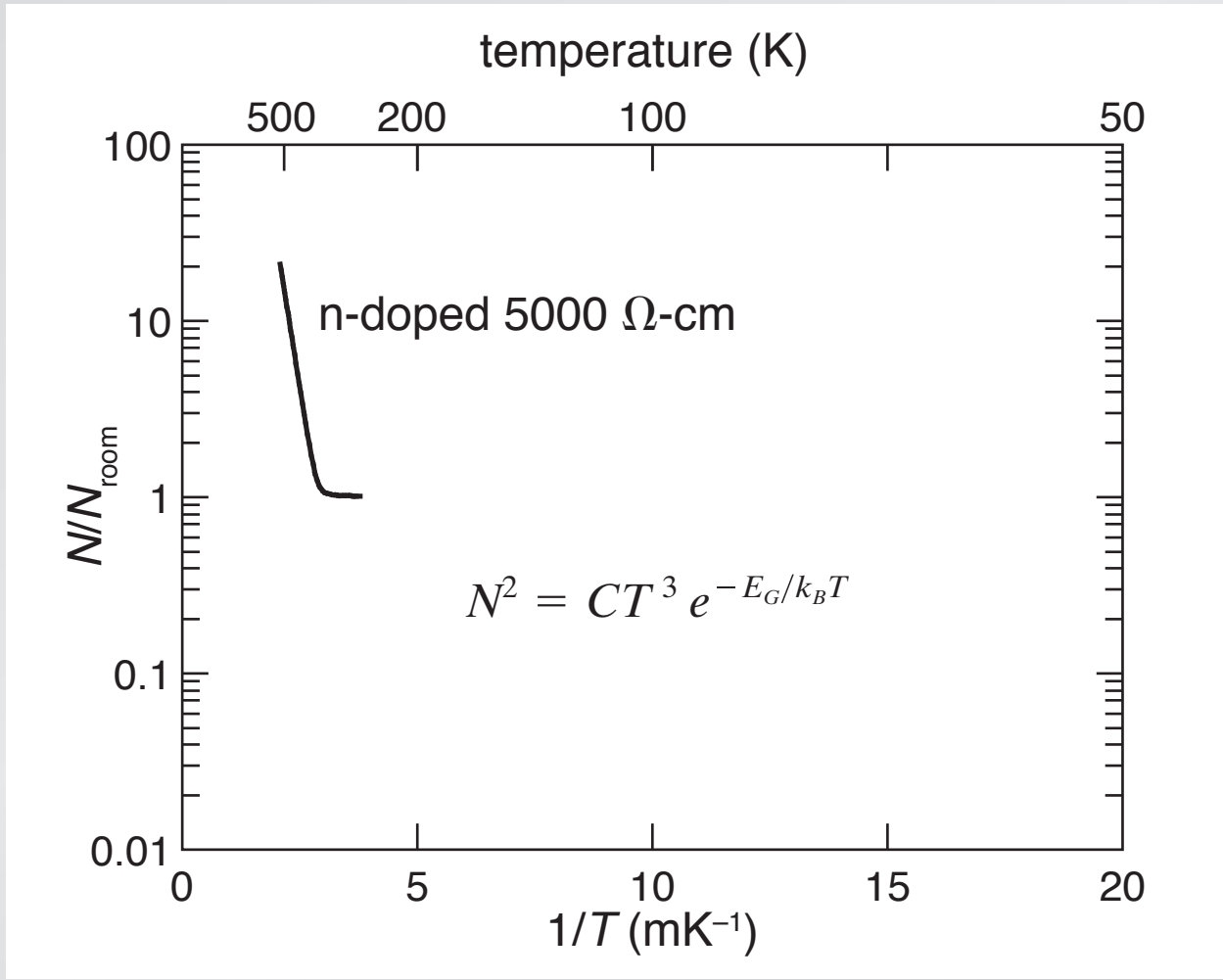
# Optical hyperdoping

## Hall measurements



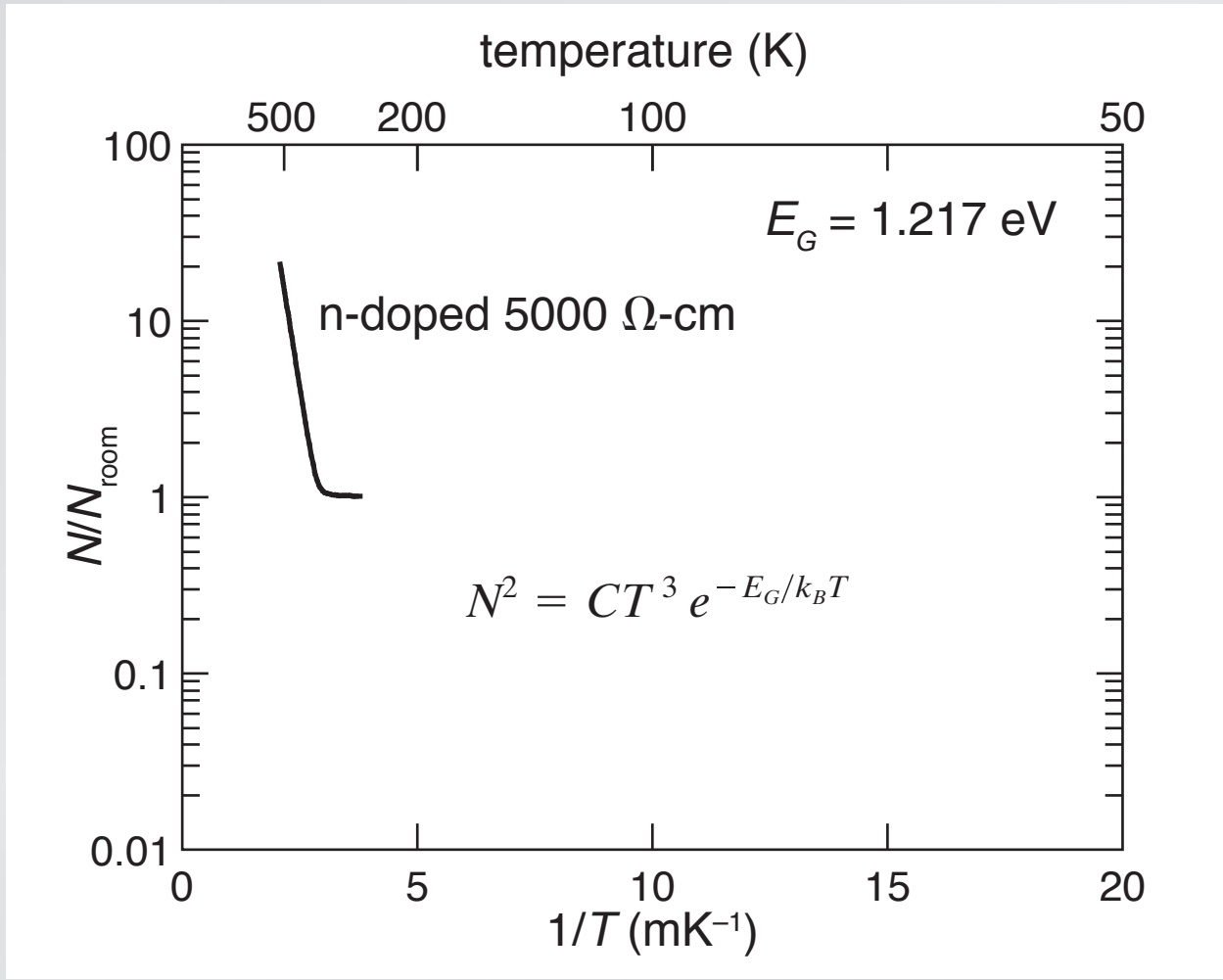
# Optical hyperdoping

## Hall measurements



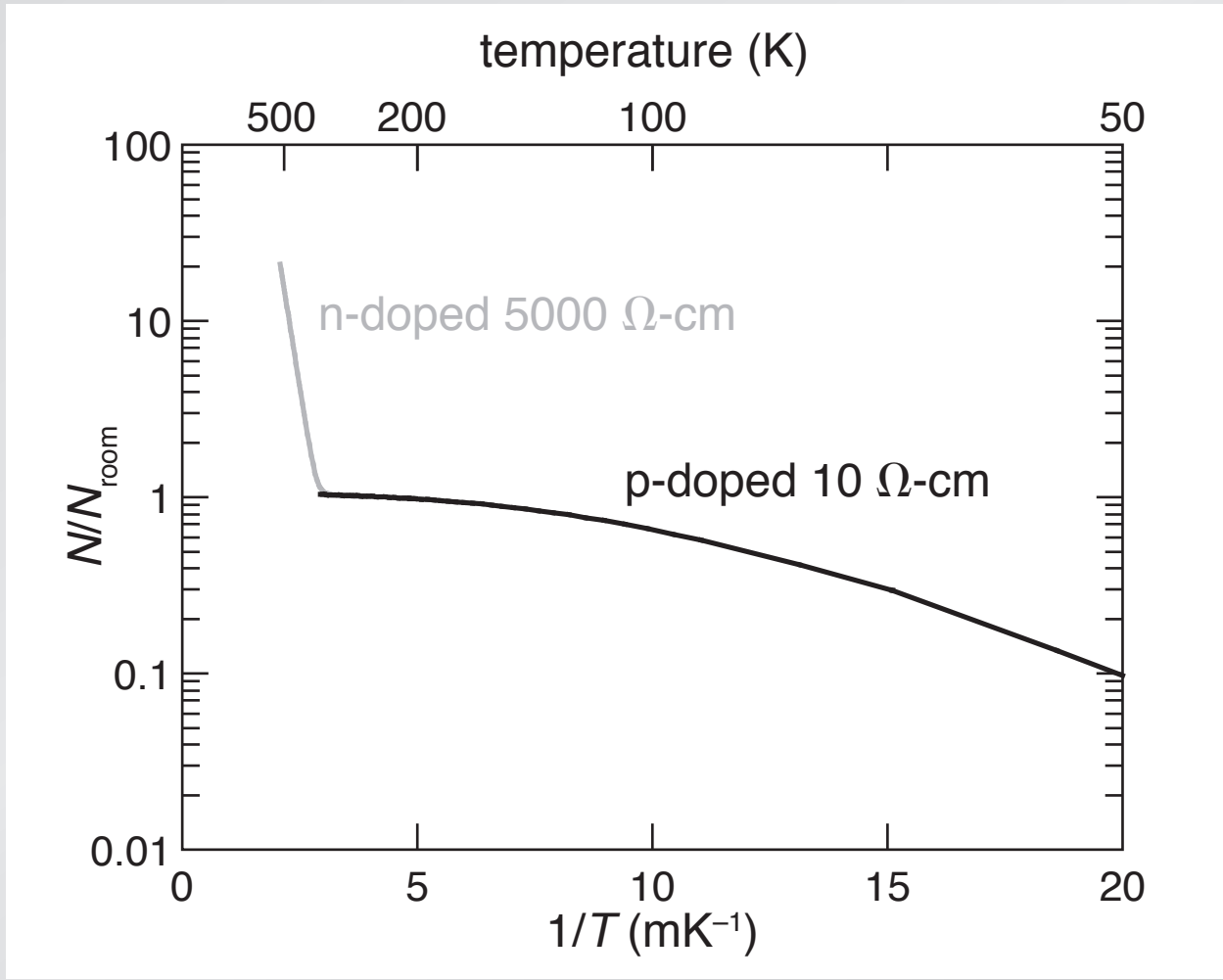
# Optical hyperdoping

## Hall measurements



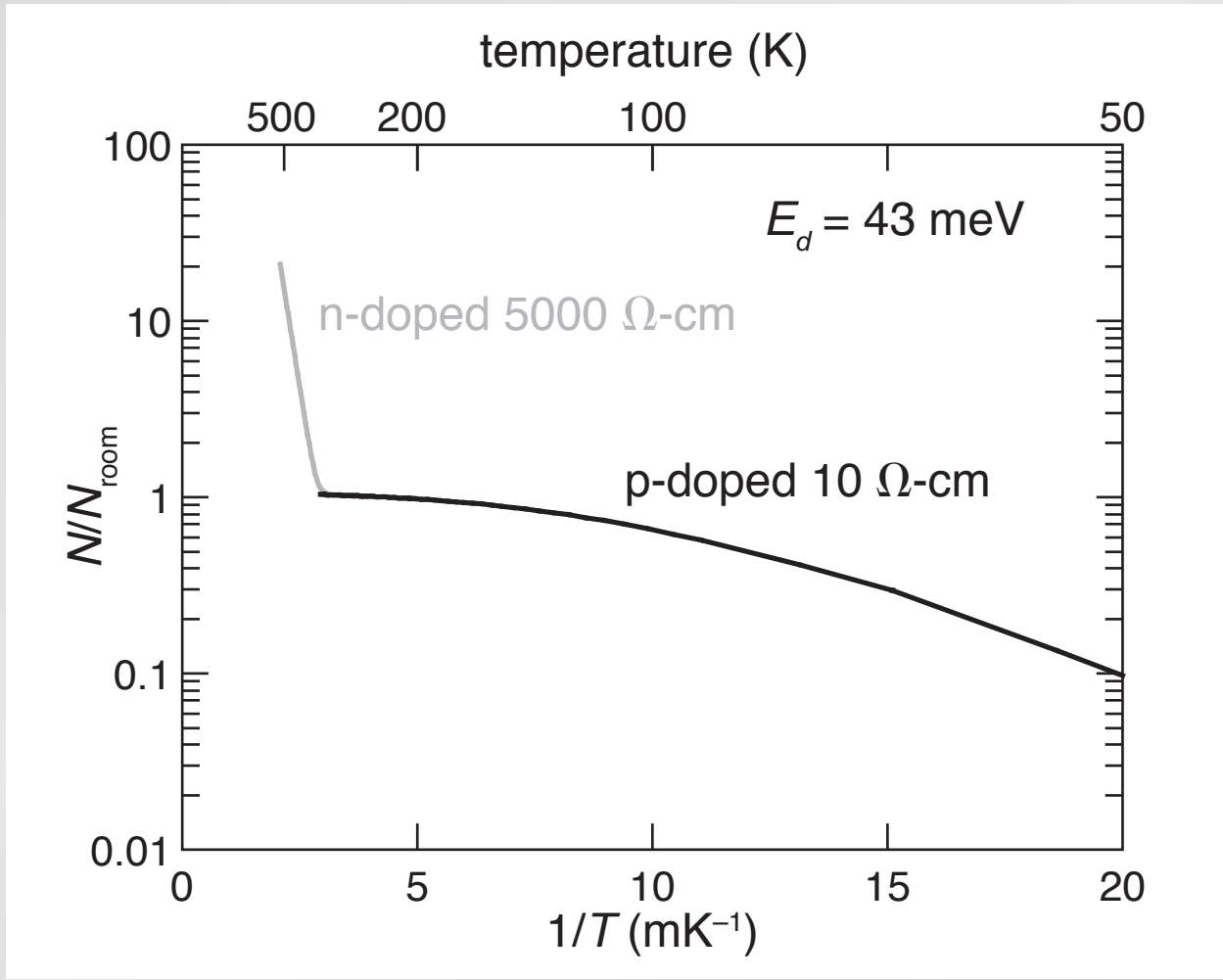
# Optical hyperdoping

## Hall measurements



# Optical hyperdoping

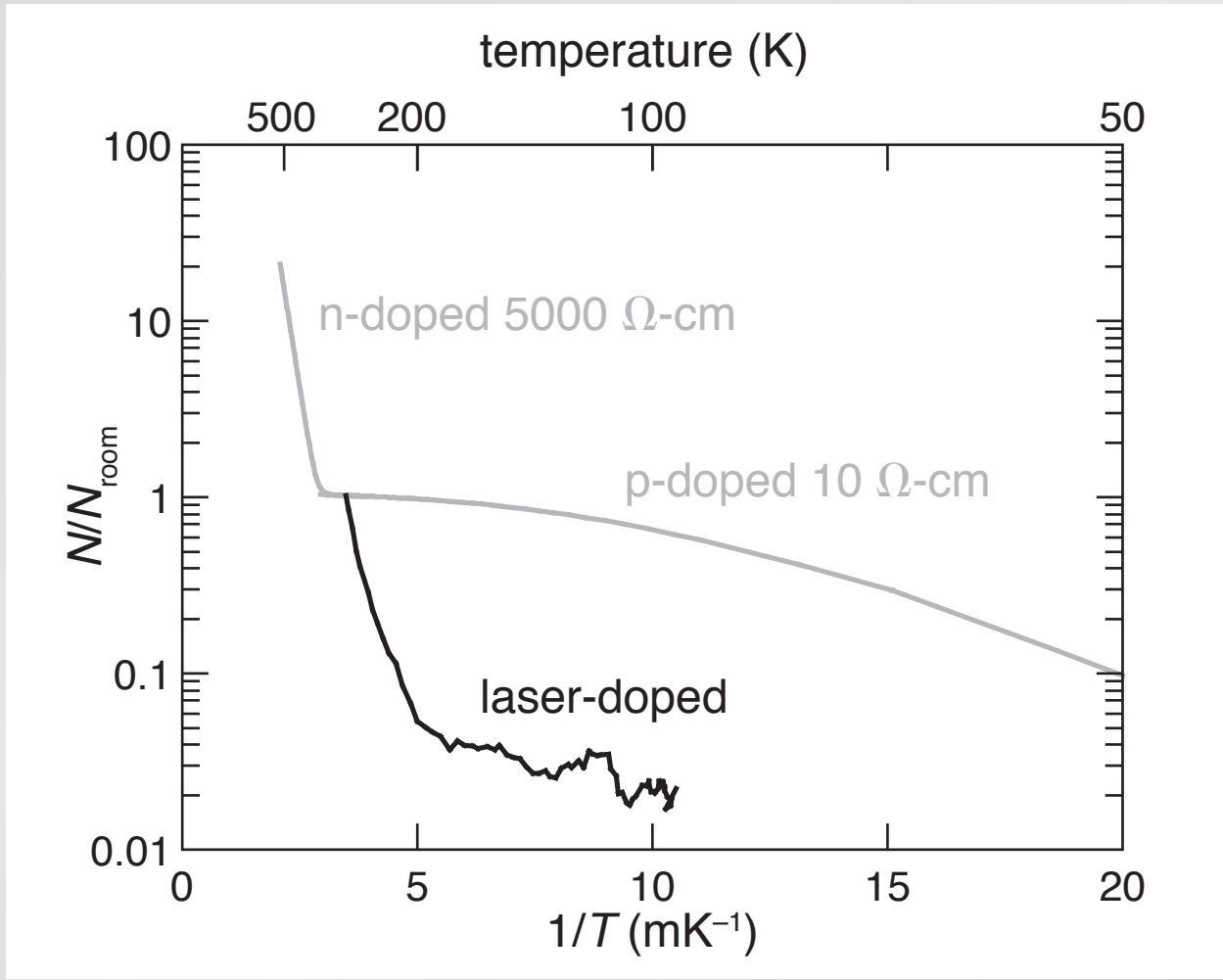
## Hall measurements





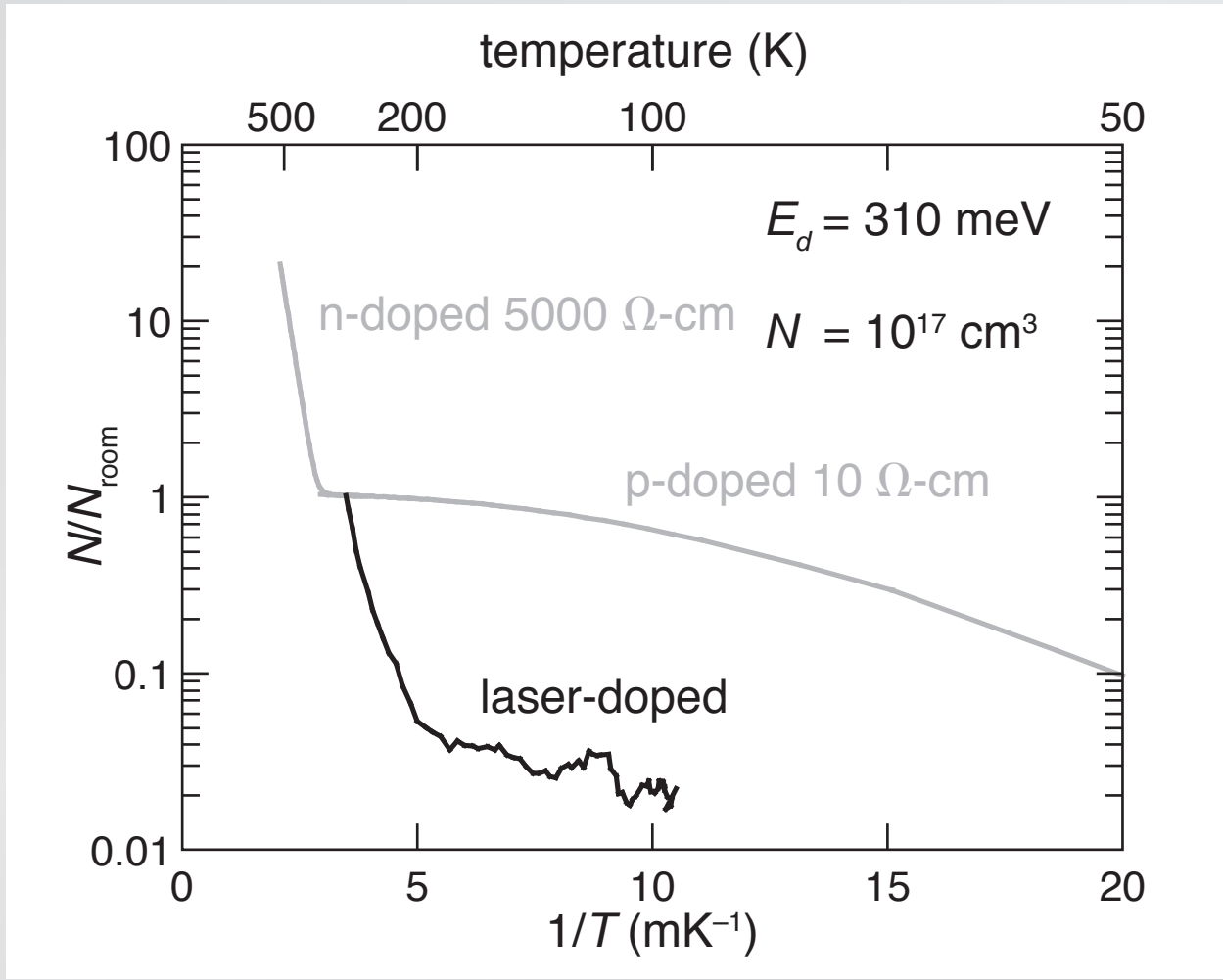
# Optical hyperdoping

## Hall measurements



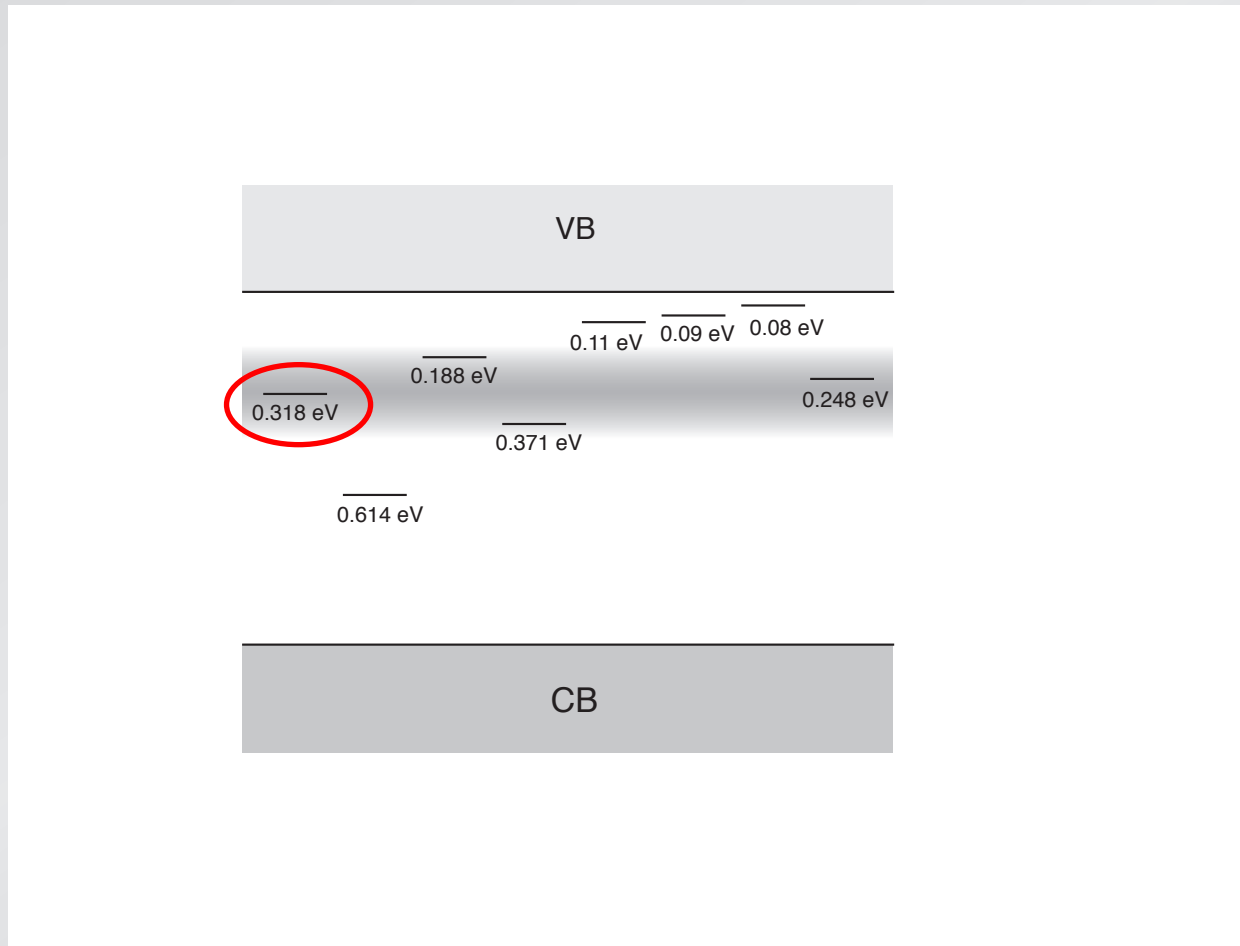
# Optical hyperdoping

## Hall measurements



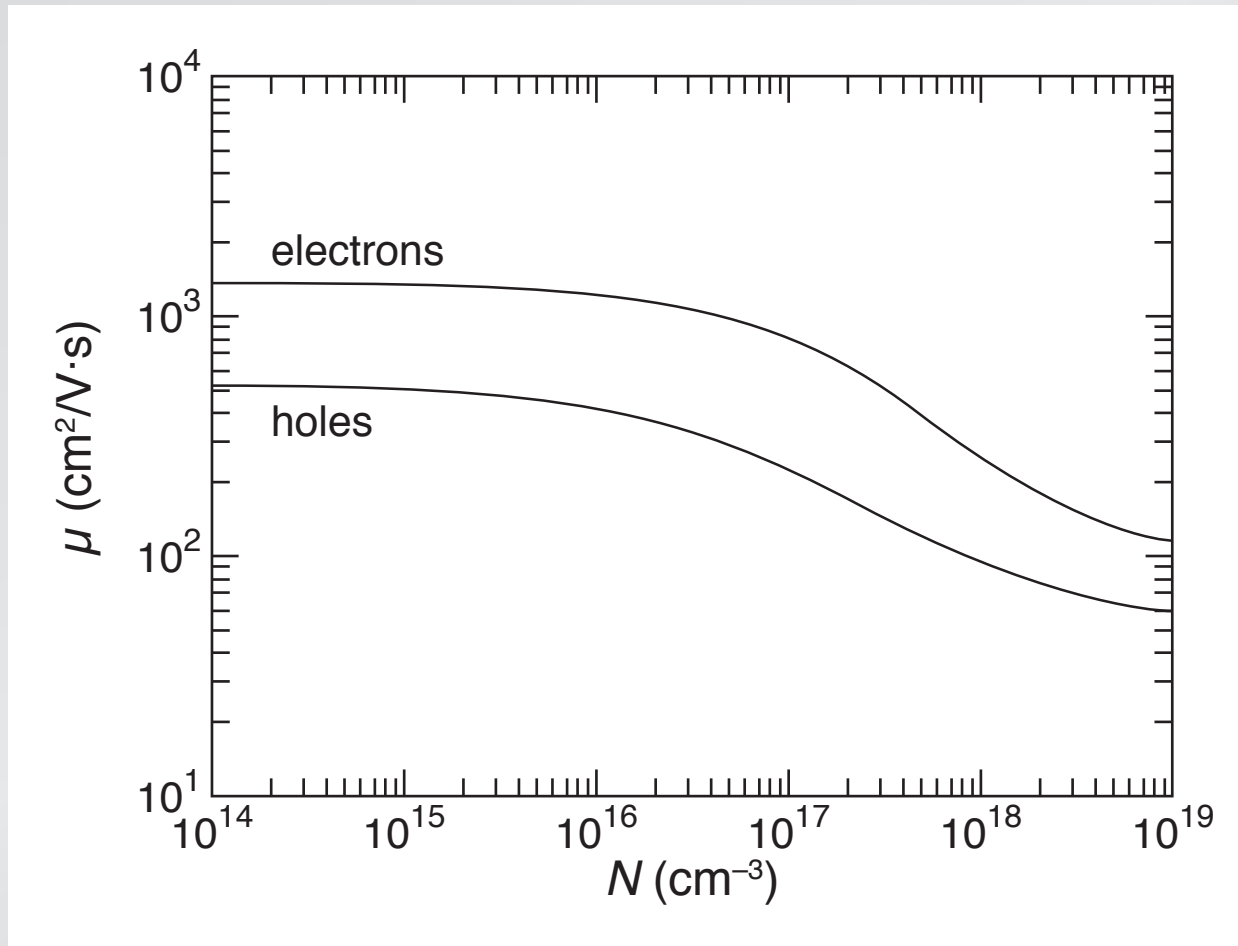
# Optical hyperdoping

impurity (donor) band centered at 310 meV



# Optical hyperdoping

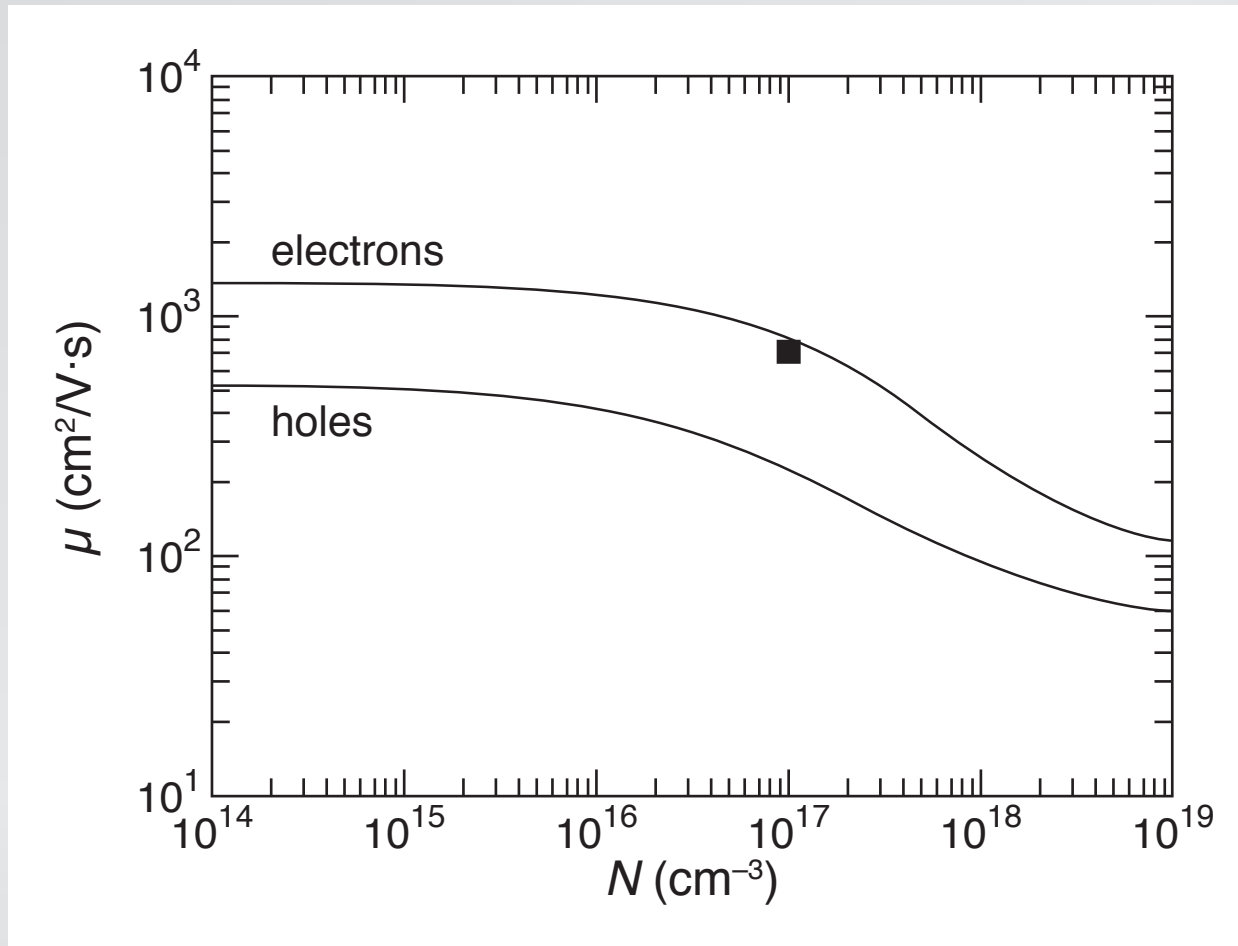
majority carrier mobility



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

# Optical hyperdoping

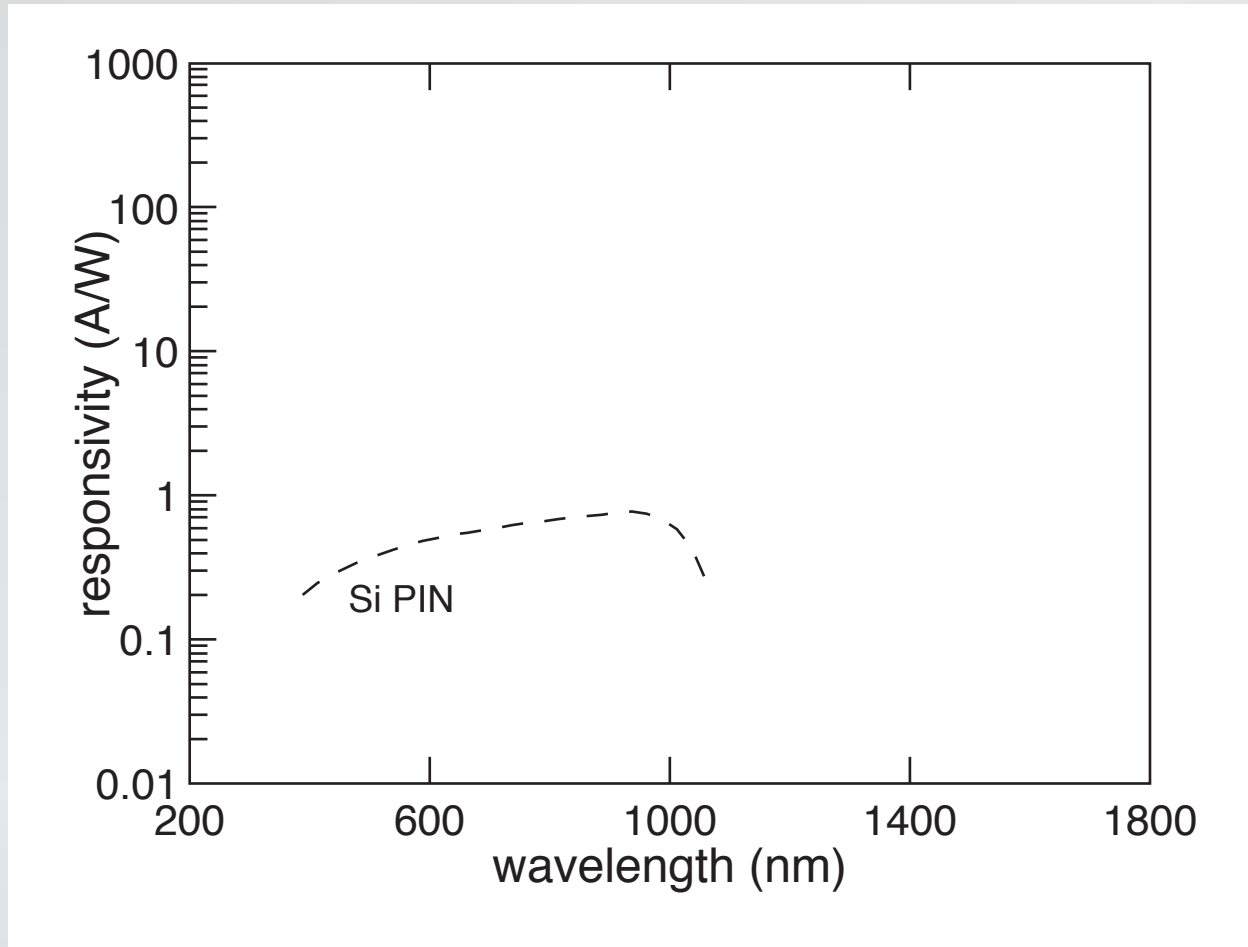
majority carrier mobility



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

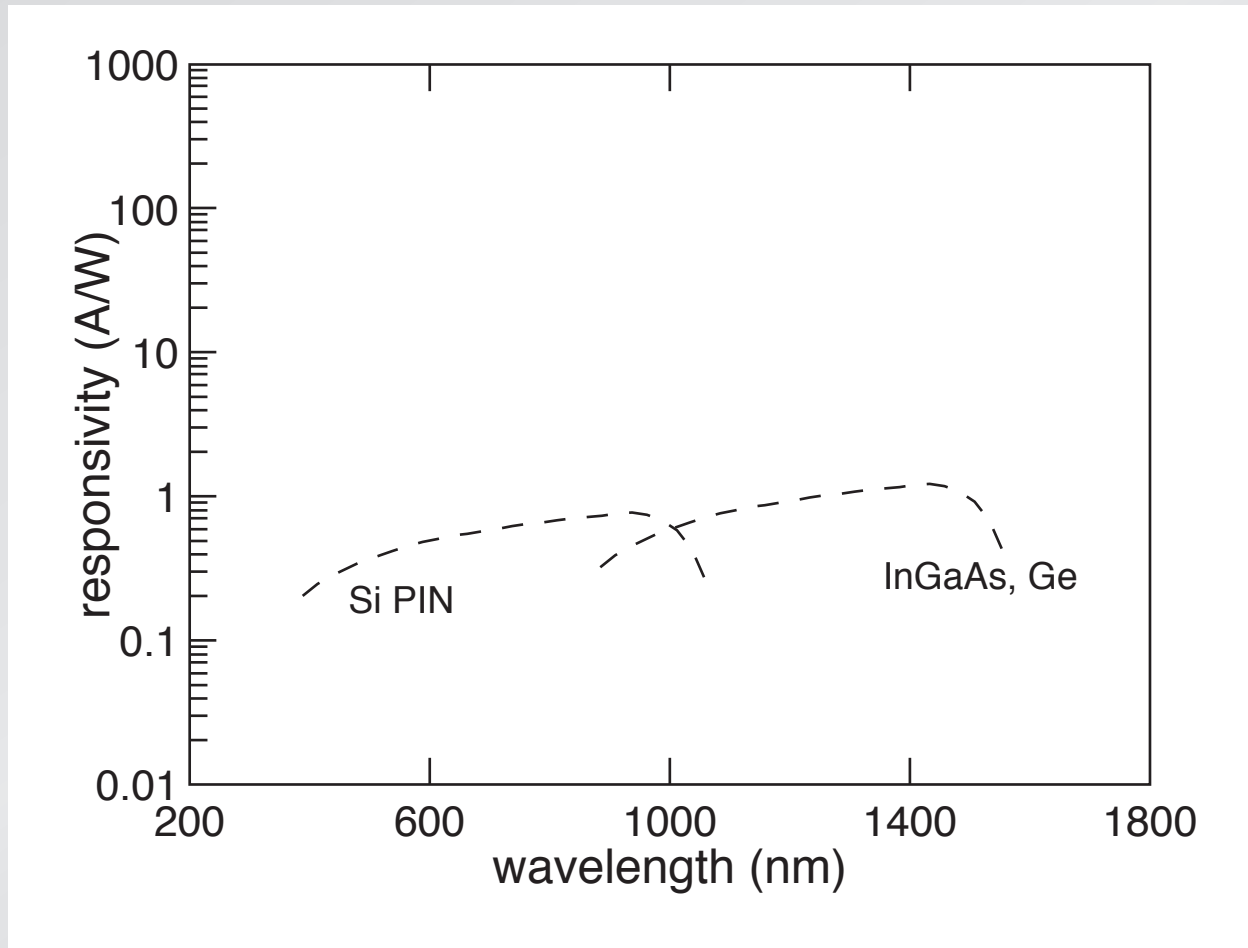
# Optical hyperdoping

responsivity



# Optical hyperdoping

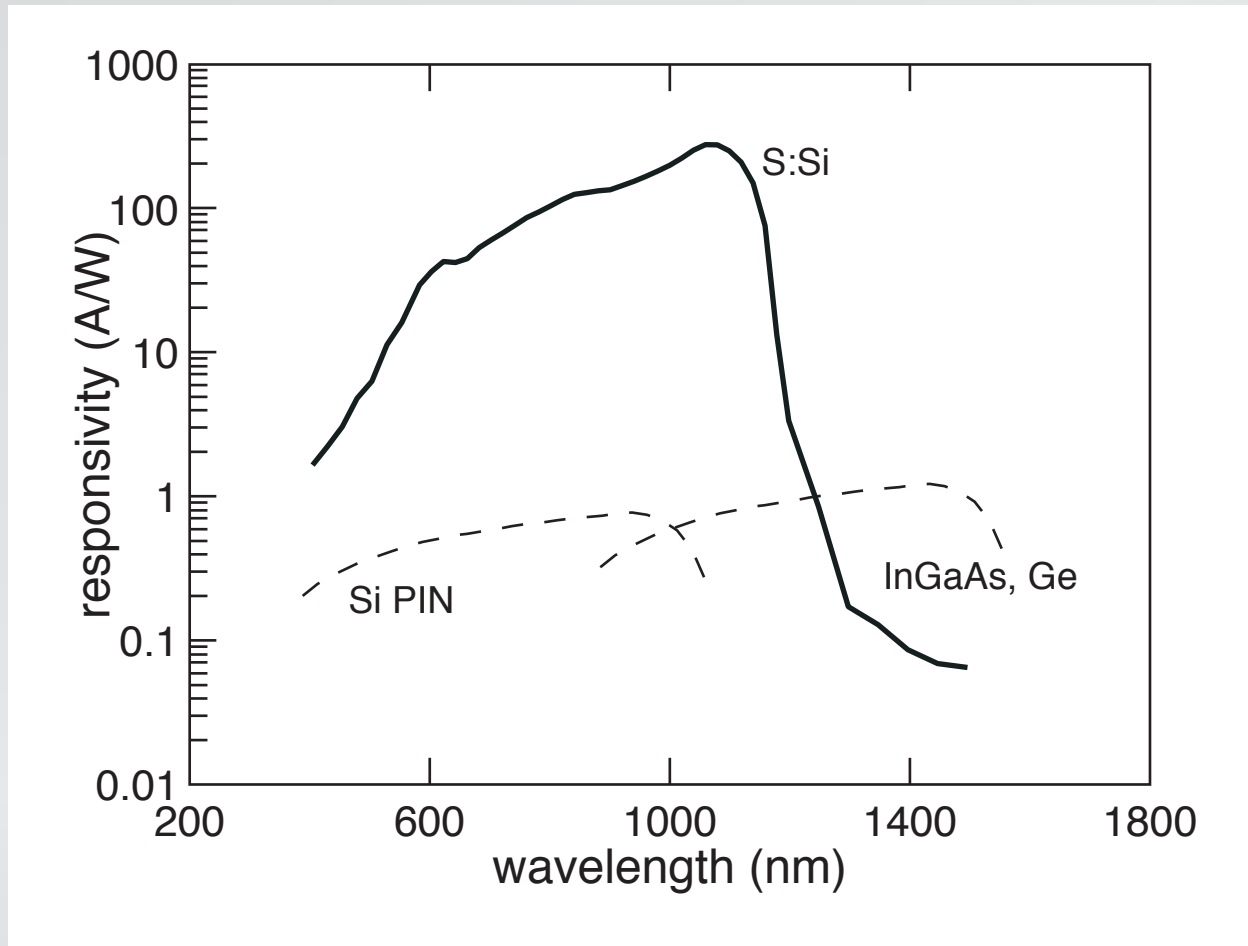
responsivity





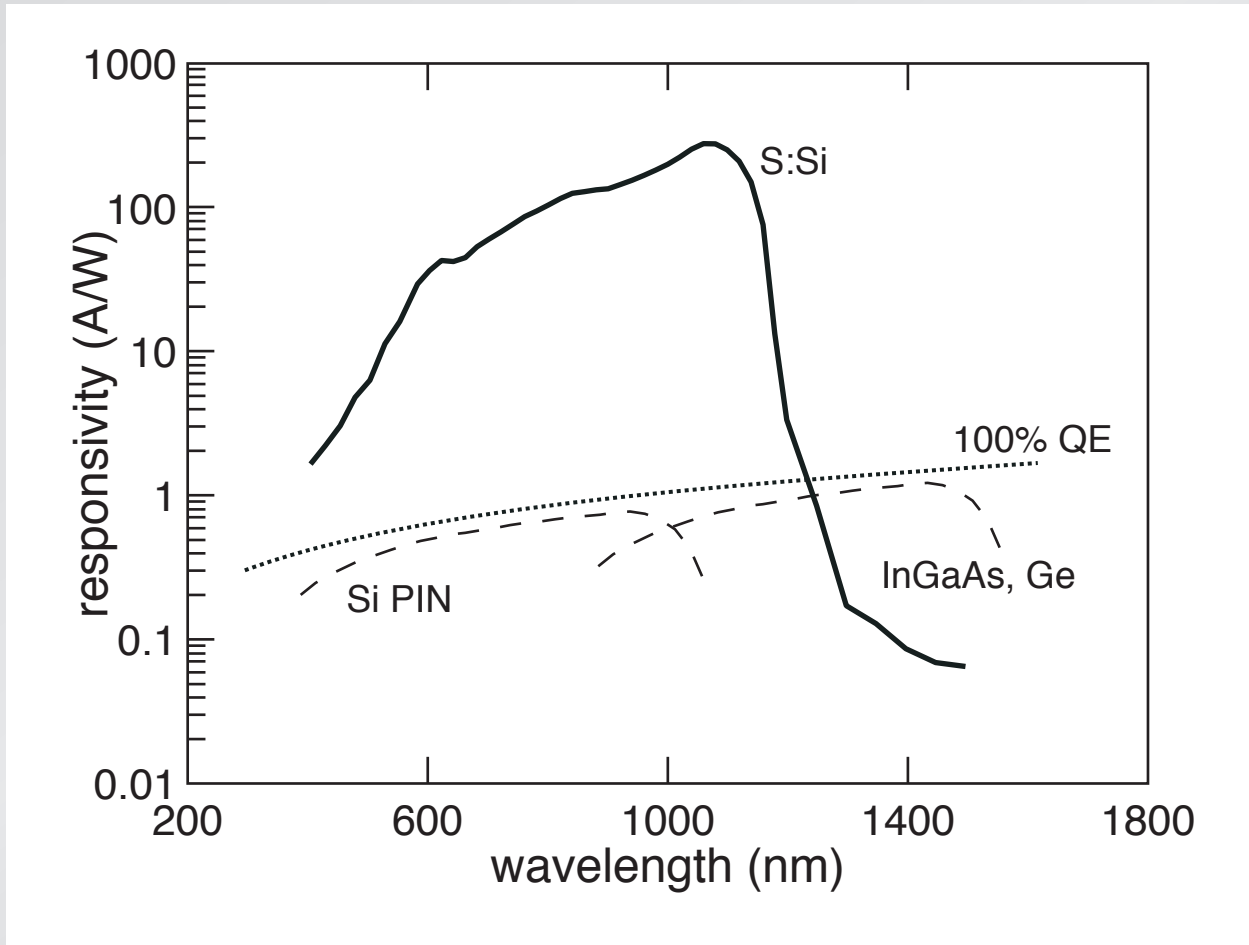
# Optical hyperdoping

responsivity



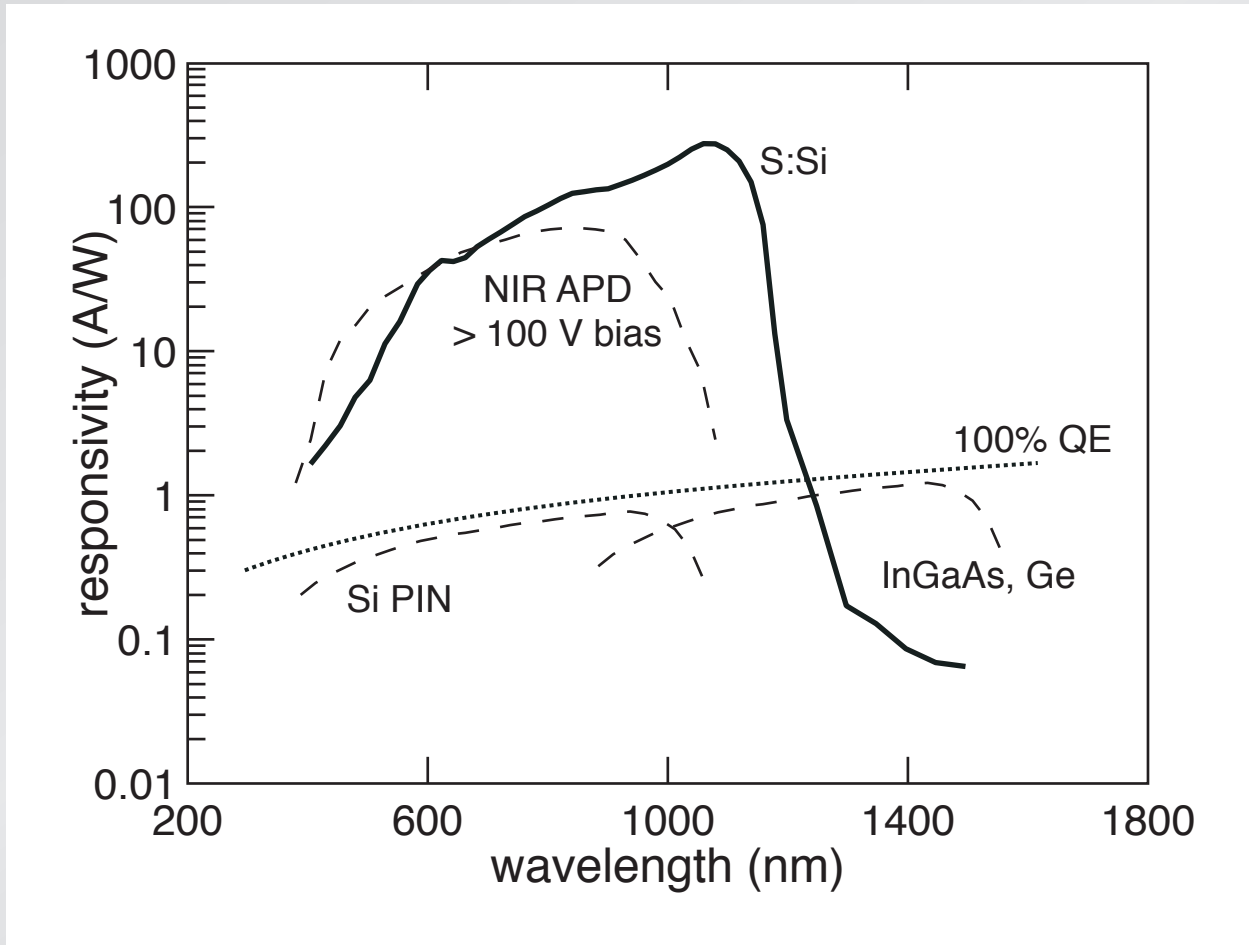
# Optical hyperdoping

responsivity



# Optical hyperdoping

responsivity

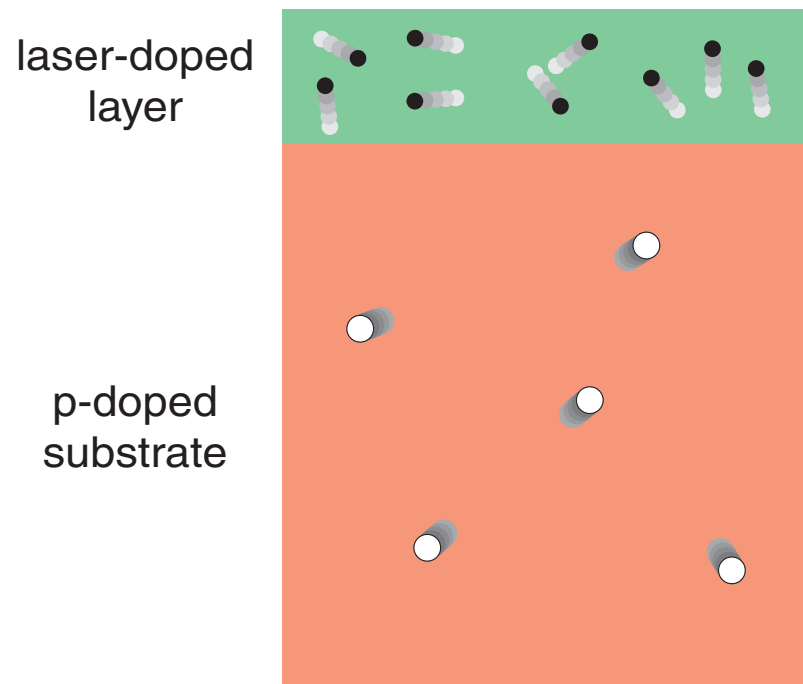


# Optical hyperdoping

What causes gain?

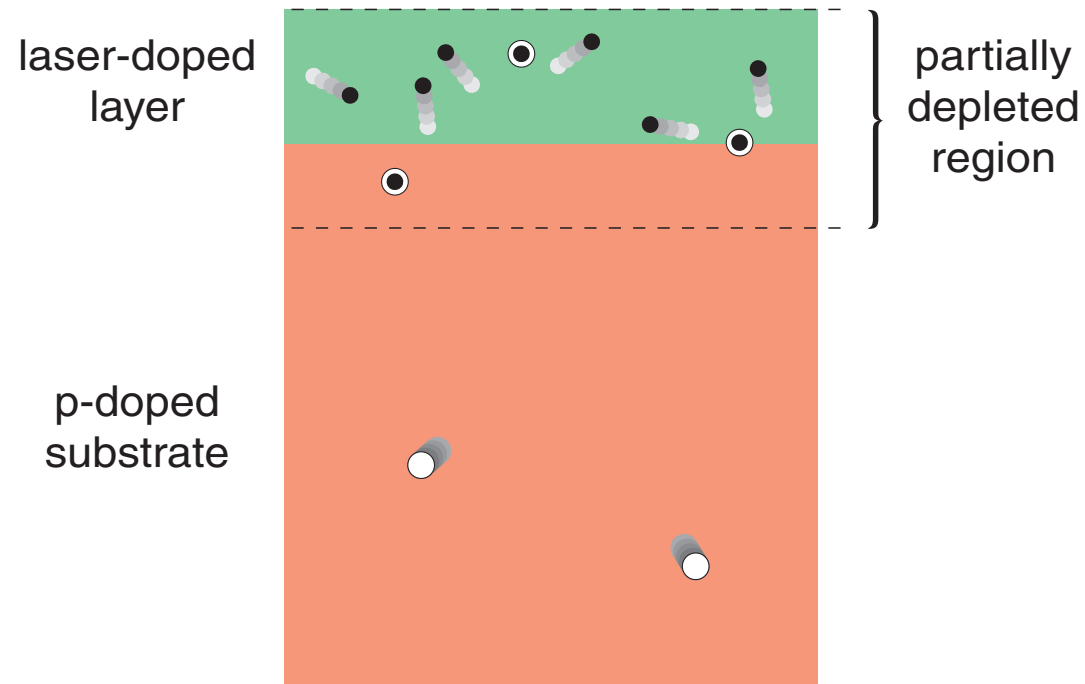
- impact excitation (avalanching)
- carrier lifetime  $\gg$  transit time (photoconductive gain)
- some other mechanism

# Optical hyperdoping



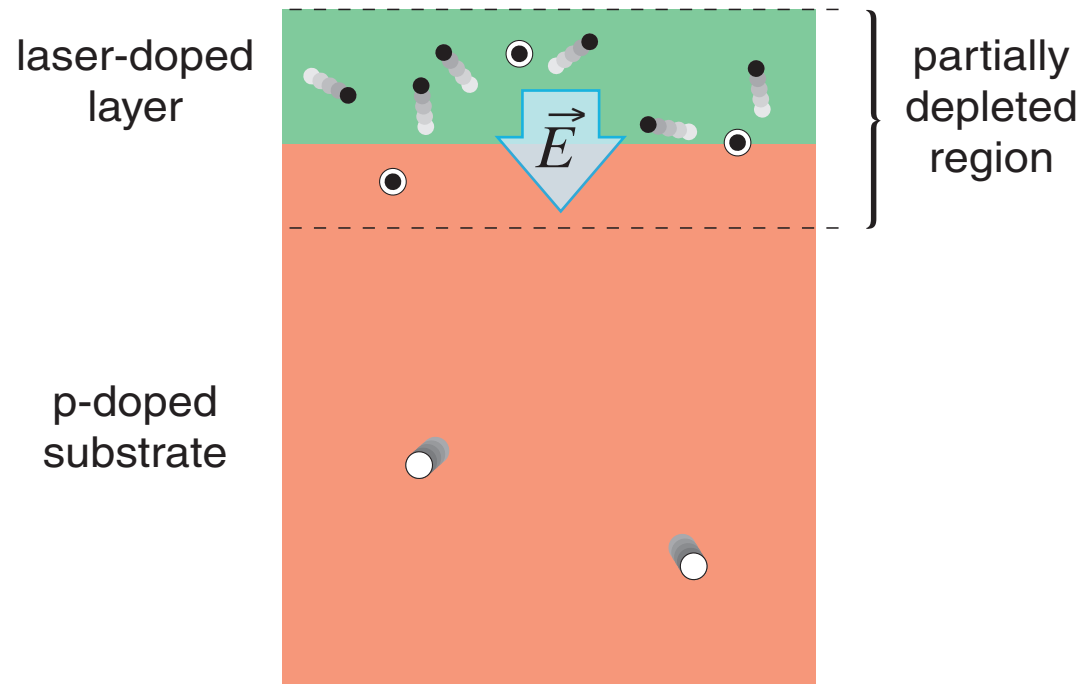
**"pn junction"**

# Optical hyperdoping



**formation of partially depleted region**

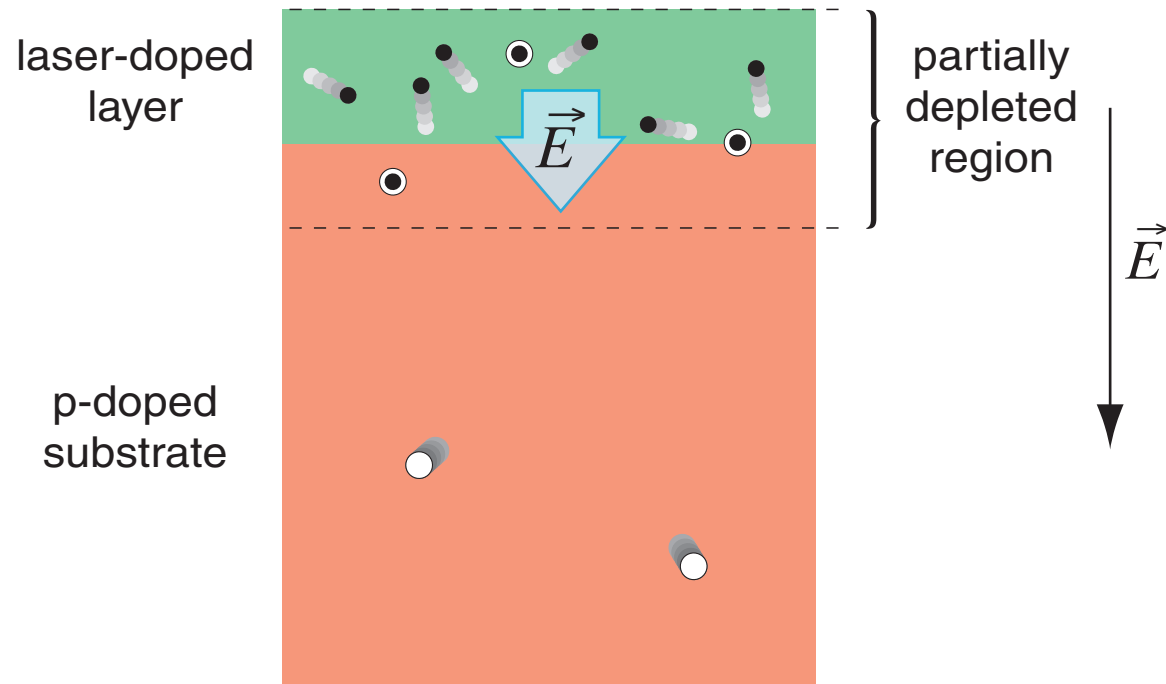
# Optical hyperdoping



**formation of partially depleted region**

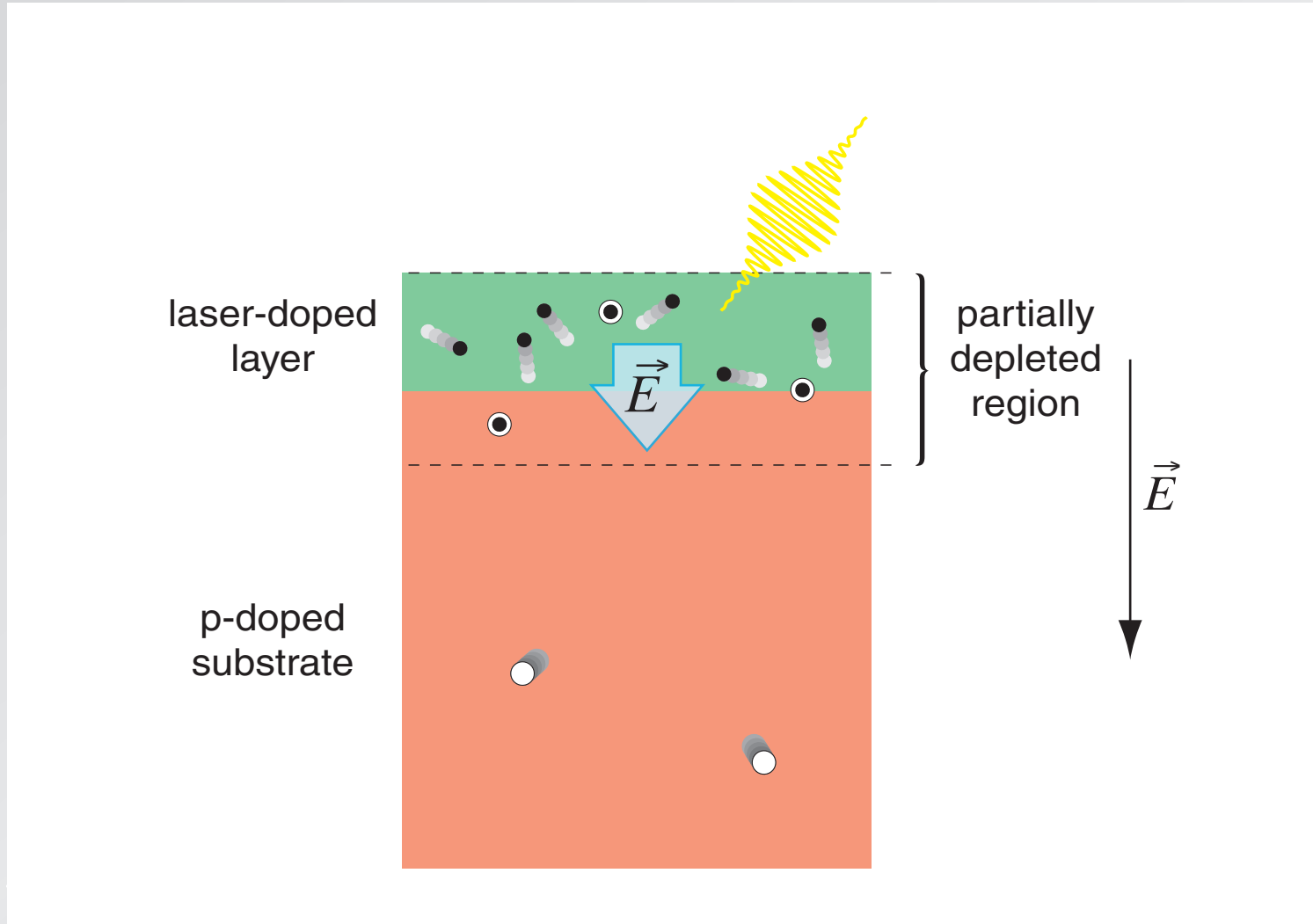


# Optical hyperdoping



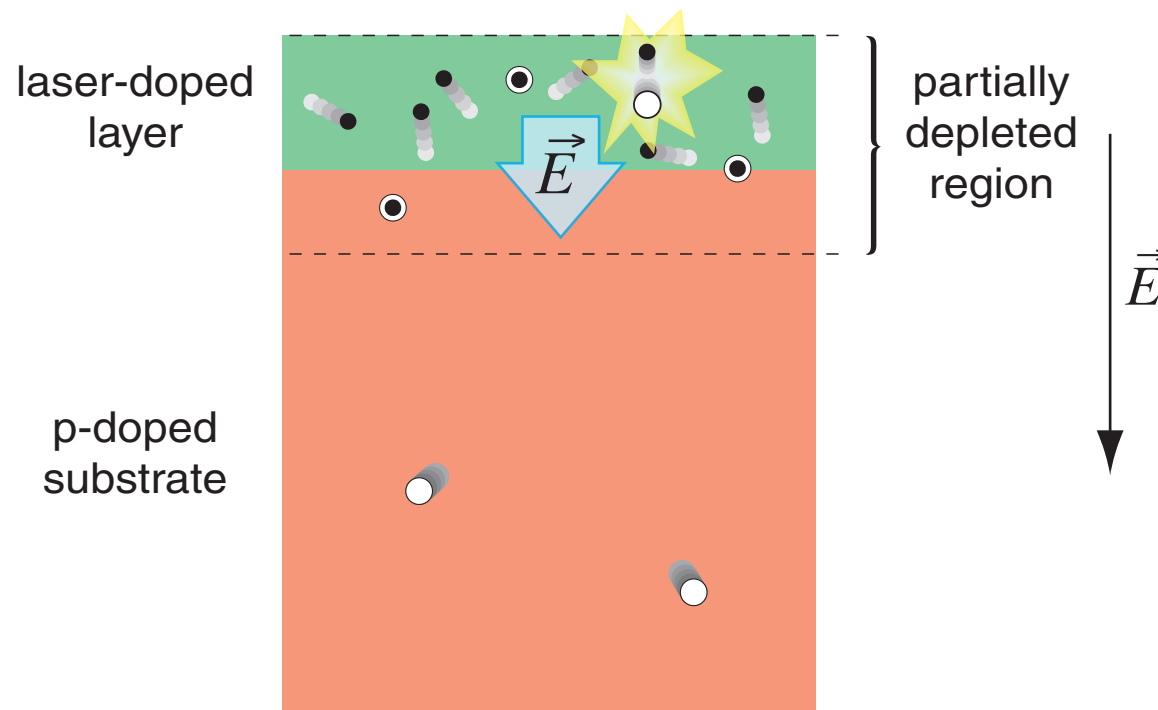
apply backward bias...

# Optical hyperdoping



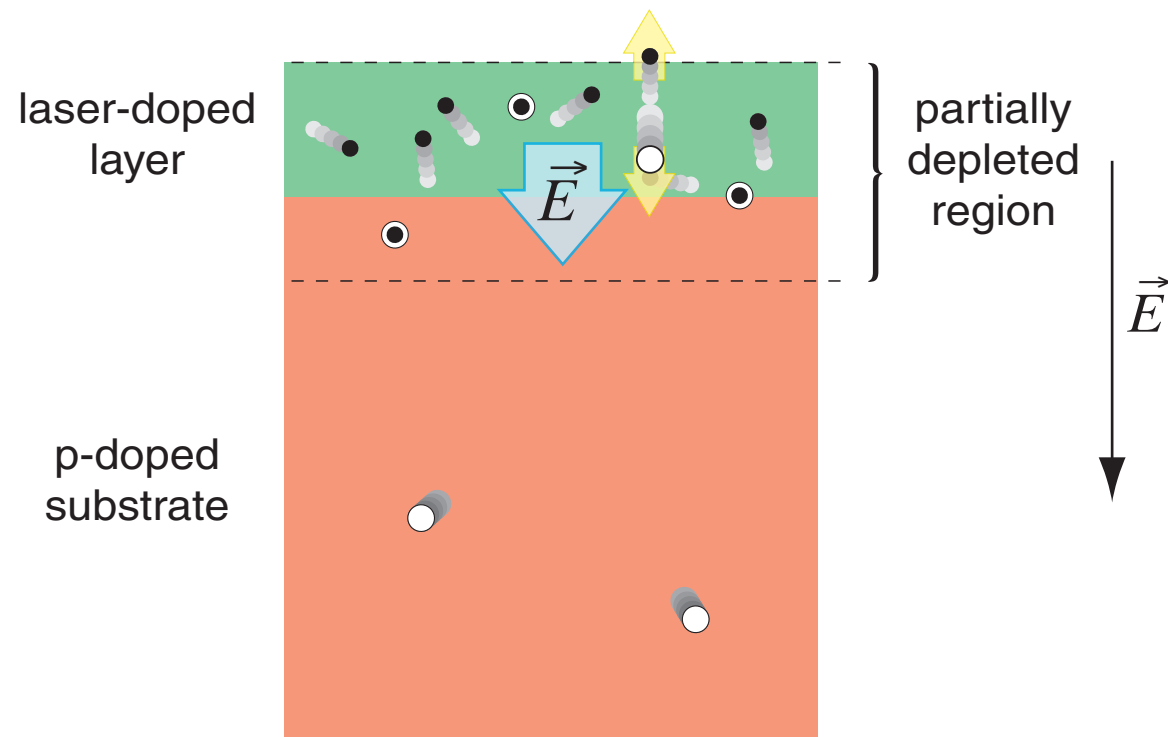
...incident photon generates electron-hole pair...

# Optical hyperdoping



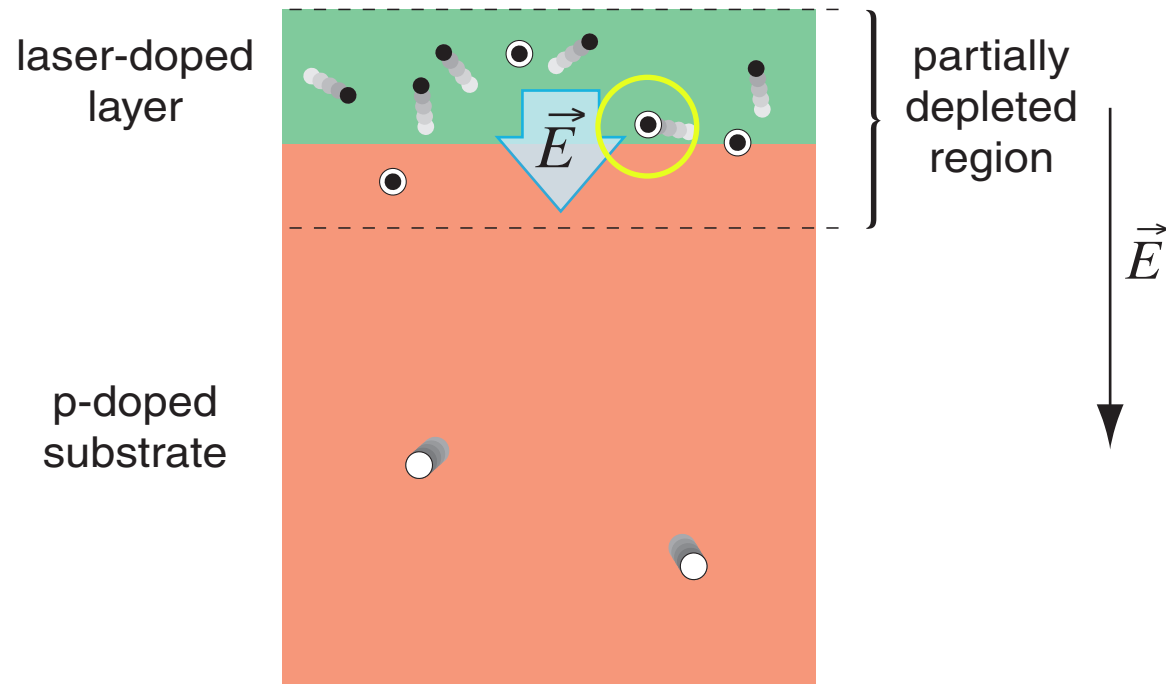
...incident photon generates electron-hole pair...

# Optical hyperdoping



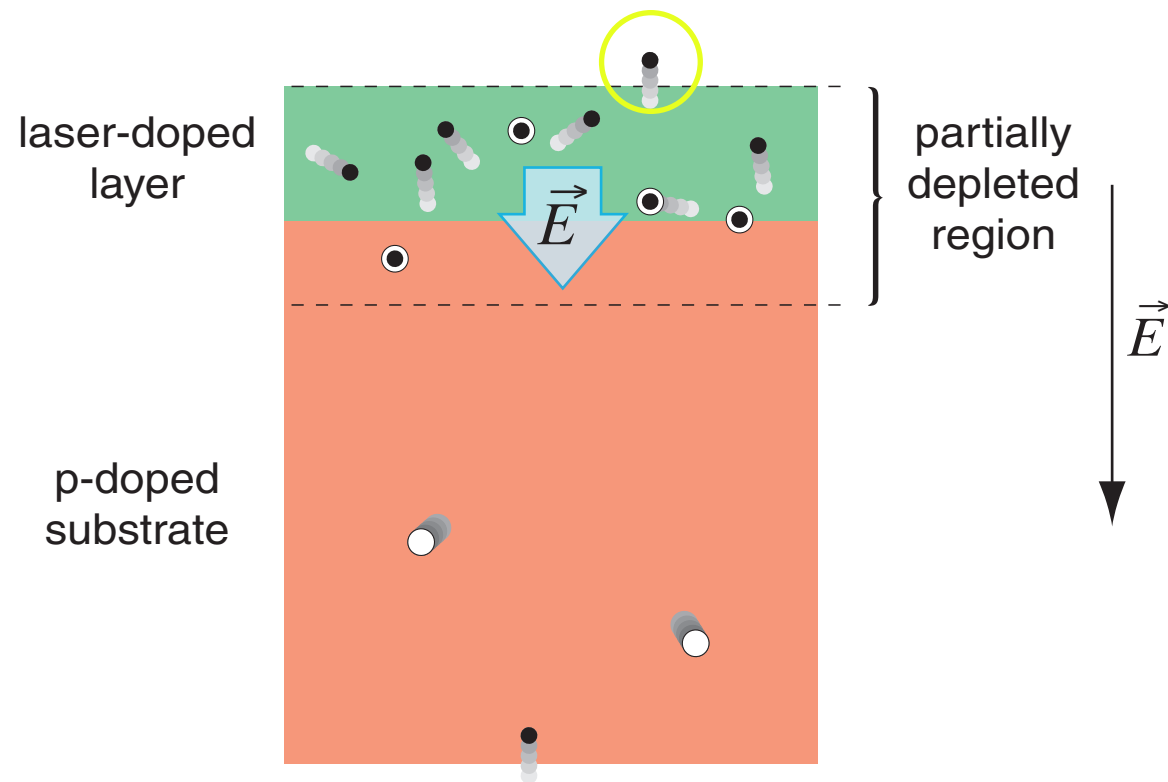
...carriers accelerate away from each other...

# Optical hyperdoping



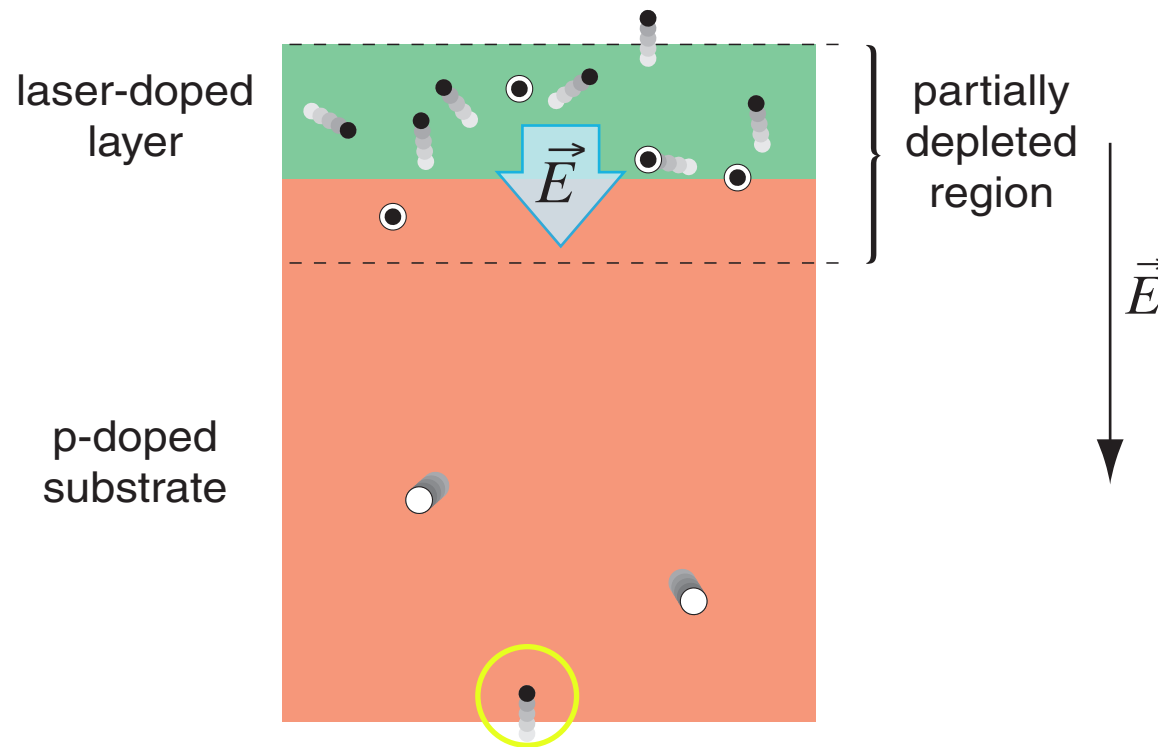
...hole is trapped

# Optical hyperdoping



meanwhile electron exits sample...

# Optical hyperdoping



...and source provides new electron



# Optical hyperdoping

## Things to keep in mind

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

# Optical hyperdoping



SiOnyx

<http://www.sionyx.com>

# Conclusion

**Materials processing with femtosecond lasers:**

- **new physics**
- **new processes**
- **new applications**



# Conclusion

**What is different about this doping process?**



# Conclusion

**Compare femtosecond laser doping to:**

- **inclusion during growth**
- **thermal diffusion**
- **ion implantation**







**Funding:**

**Army Research Office**

**DARPA**

**Department of Energy**

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