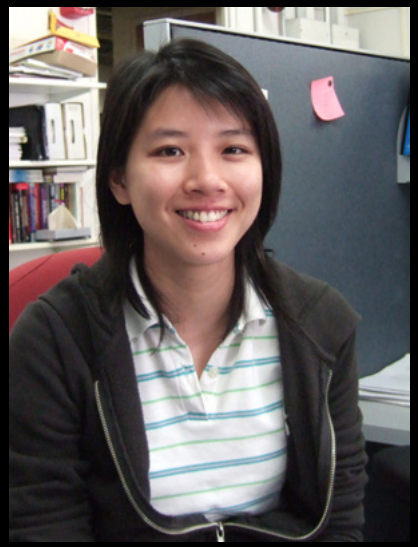
Towards increased efficiency in solar energy harvesting via intermediate states

Ben Franta

PACRIM 2013

Coronado, CA, 6 June 2013

Renee Sher



Yu-Ting Lin

Kasey Philips

Ben Franta

eric_mazur

and also....

Marc Winkler
Eric Diebold
Haifei Albert Zhang
Dr. Brian Tull
Dr. Jim Carey (SiOnyx)
Prof. Tsing-Hua Her (UNC Charlotte)
Dr. Shrenik Deliwala
Dr. Richard Finlay
Dr. Michael Sheehy
Dr. Claudia Wu
Dr. Rebecca Younkin
Prof. Catherine Crouch (Swarthmore)
Prof. Mengyan Shen (Lowell U)
Prof. Li Zhao (Fudan U)

Dr. Elizabeth Landis
Dr. John Chervinsky

Prof. Alan Aspuru-Guzik
Prof. Michael Aziz
Prof. Michael Brenner
Prof. Cynthia Friend
Prof. Howard Stone

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

Prof. Augustinus Asenbaum (Vienna)

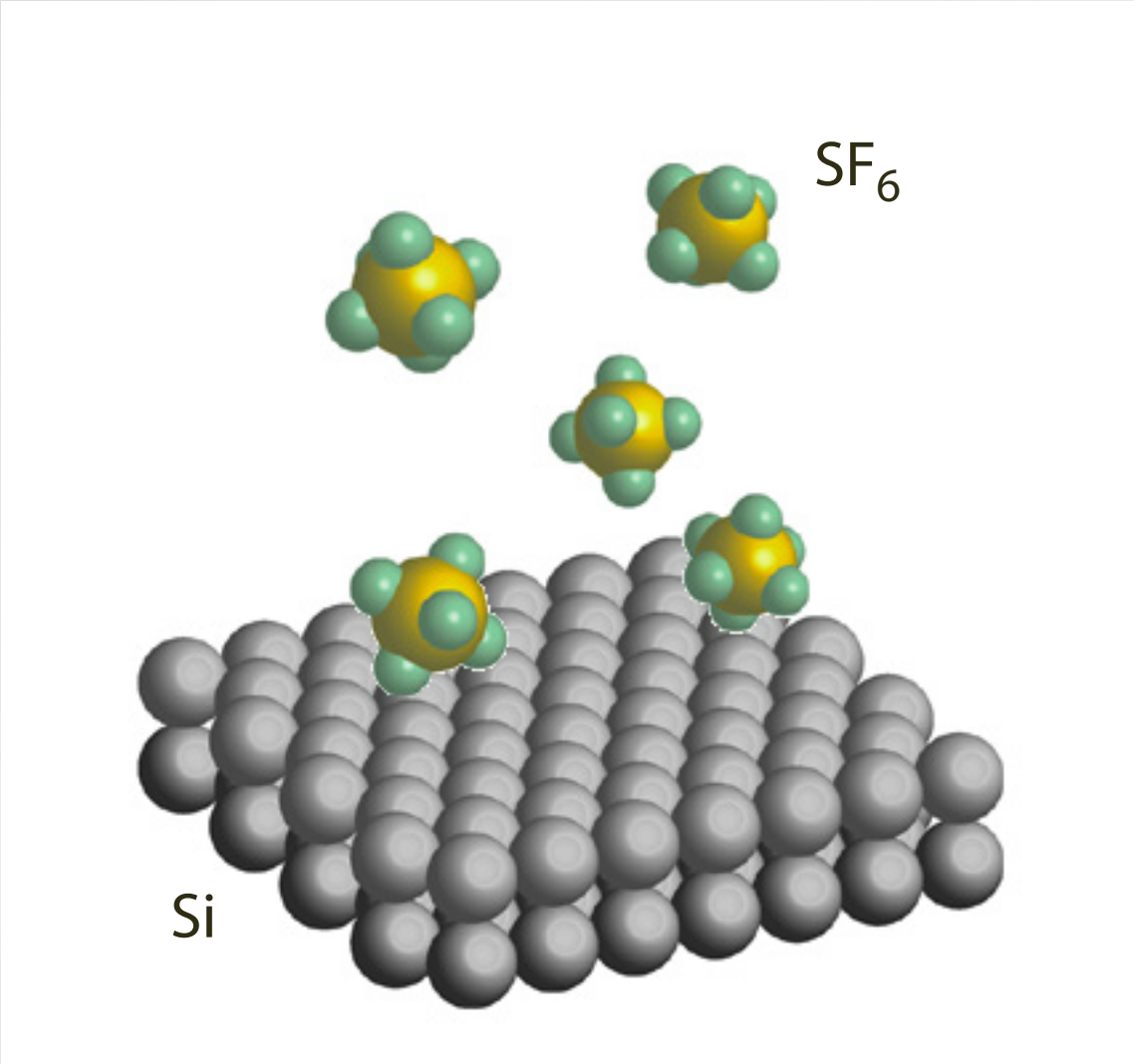
Dr. François Génin (LLNL)
Mark Wall (LLNL)

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

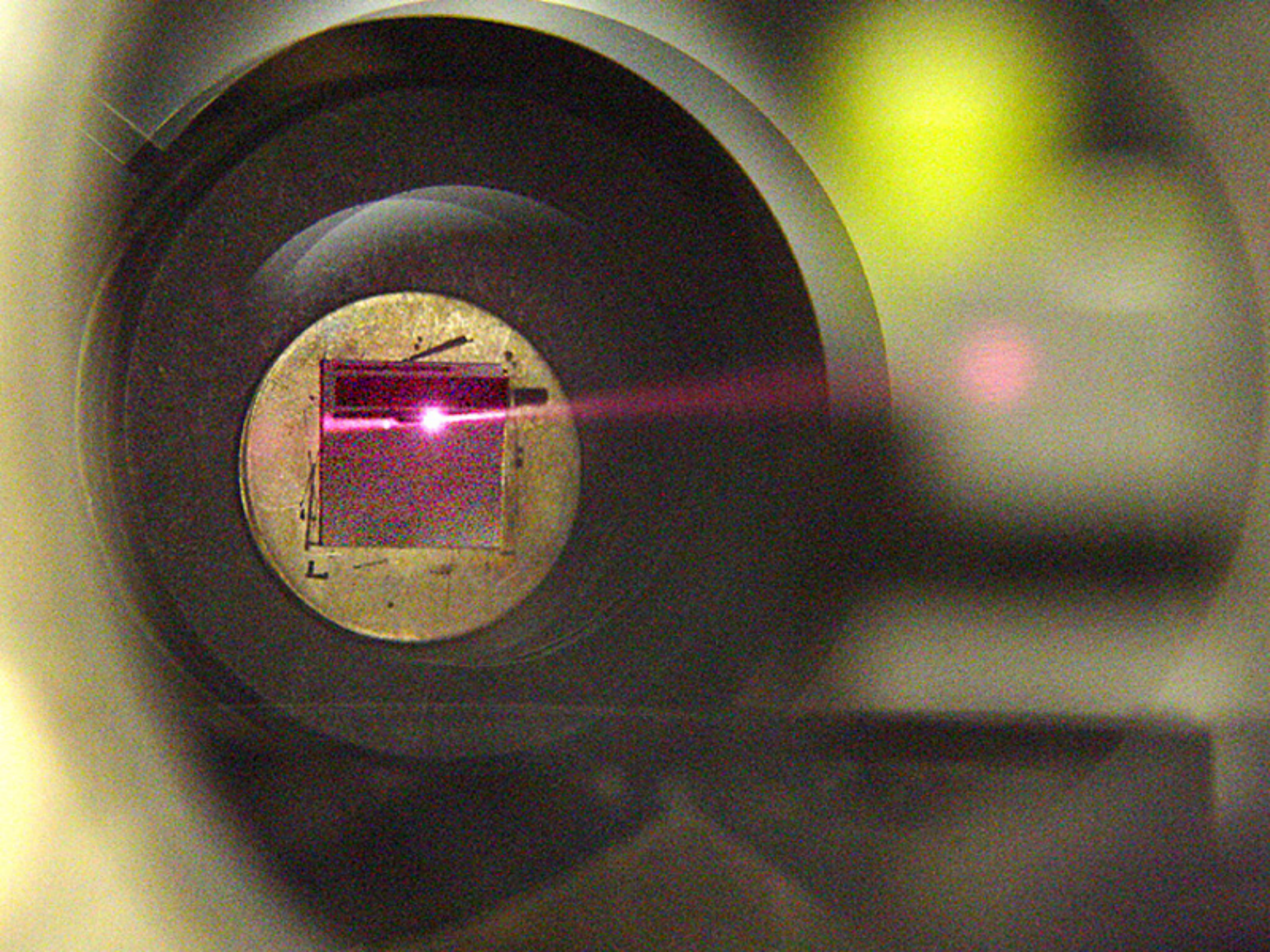
Dr. Pat Maloney (NVSED)

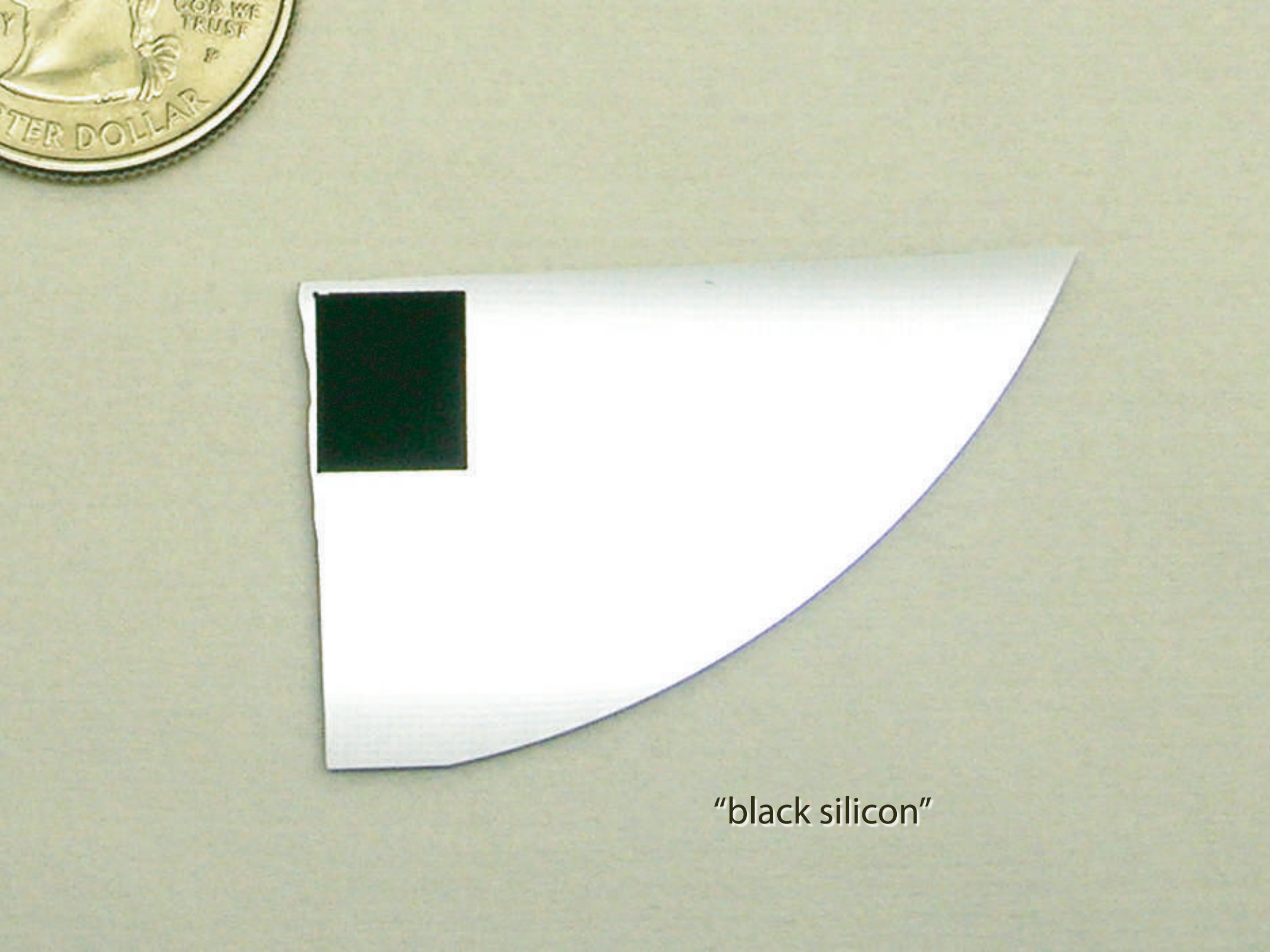
Dr. Jeffrey Warrander (ARDEC)

…and the people at SiOnyx

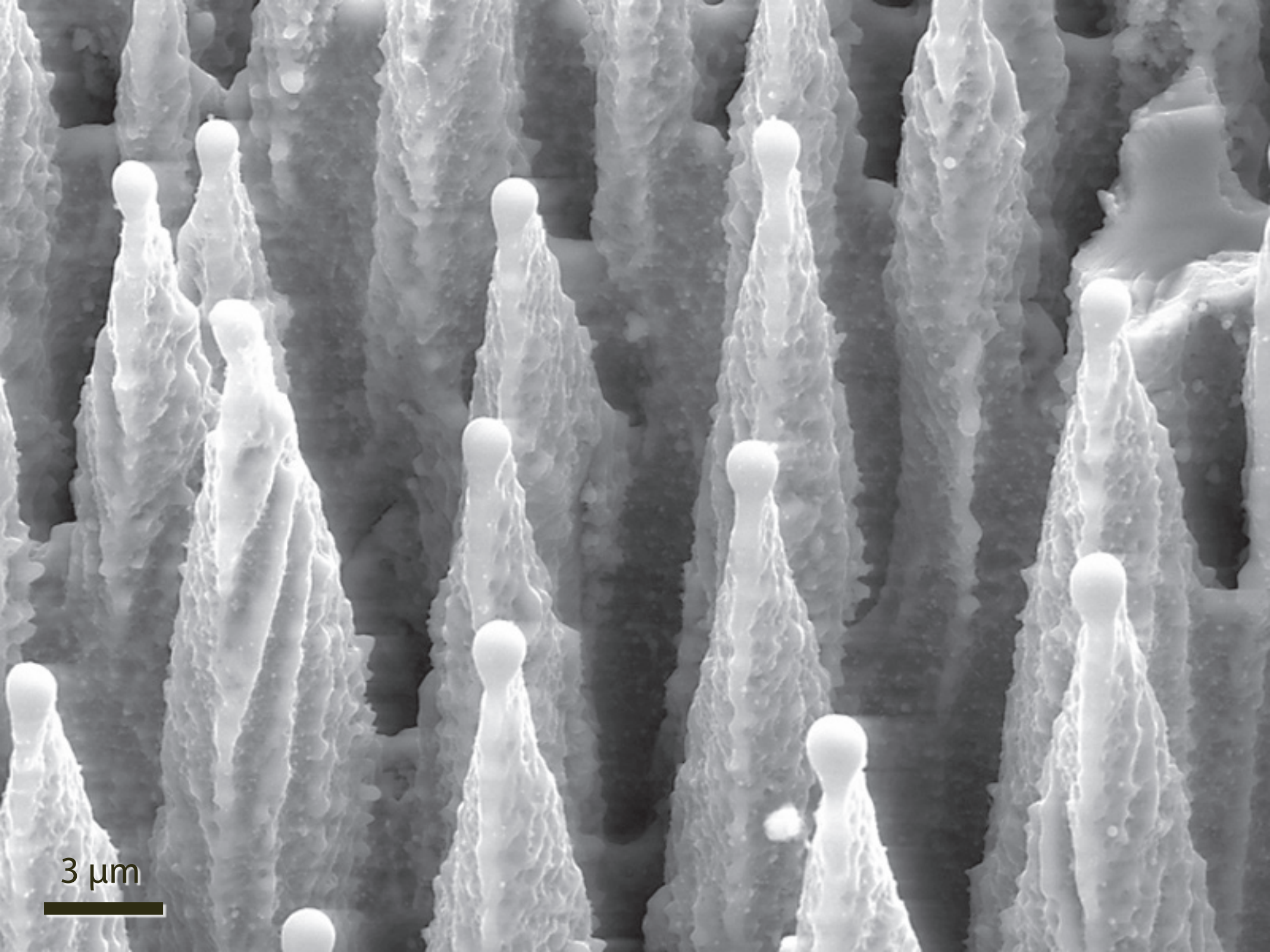


irradiate with 100-fs 10 kJ/m^2 pulses

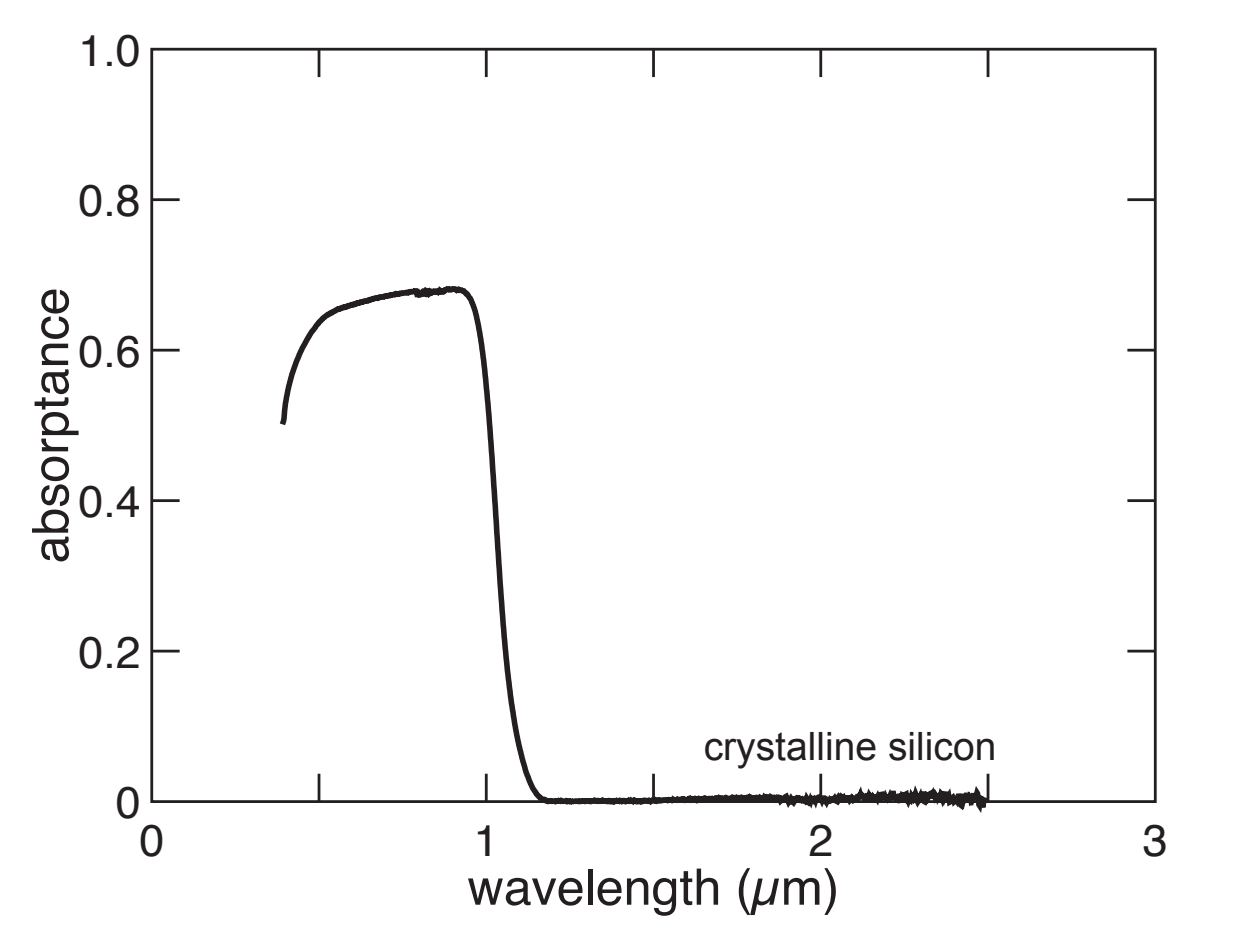




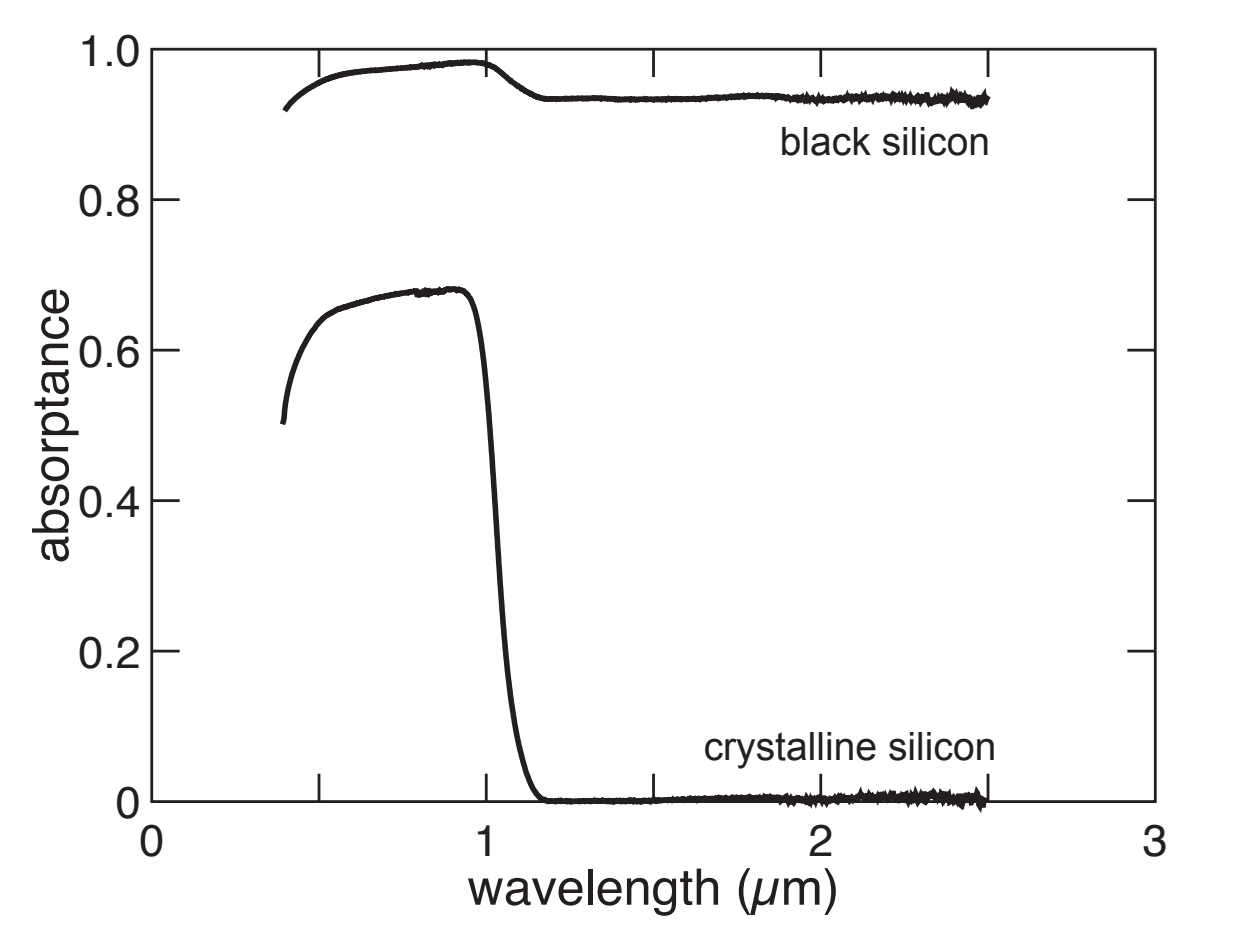
“black silicon”

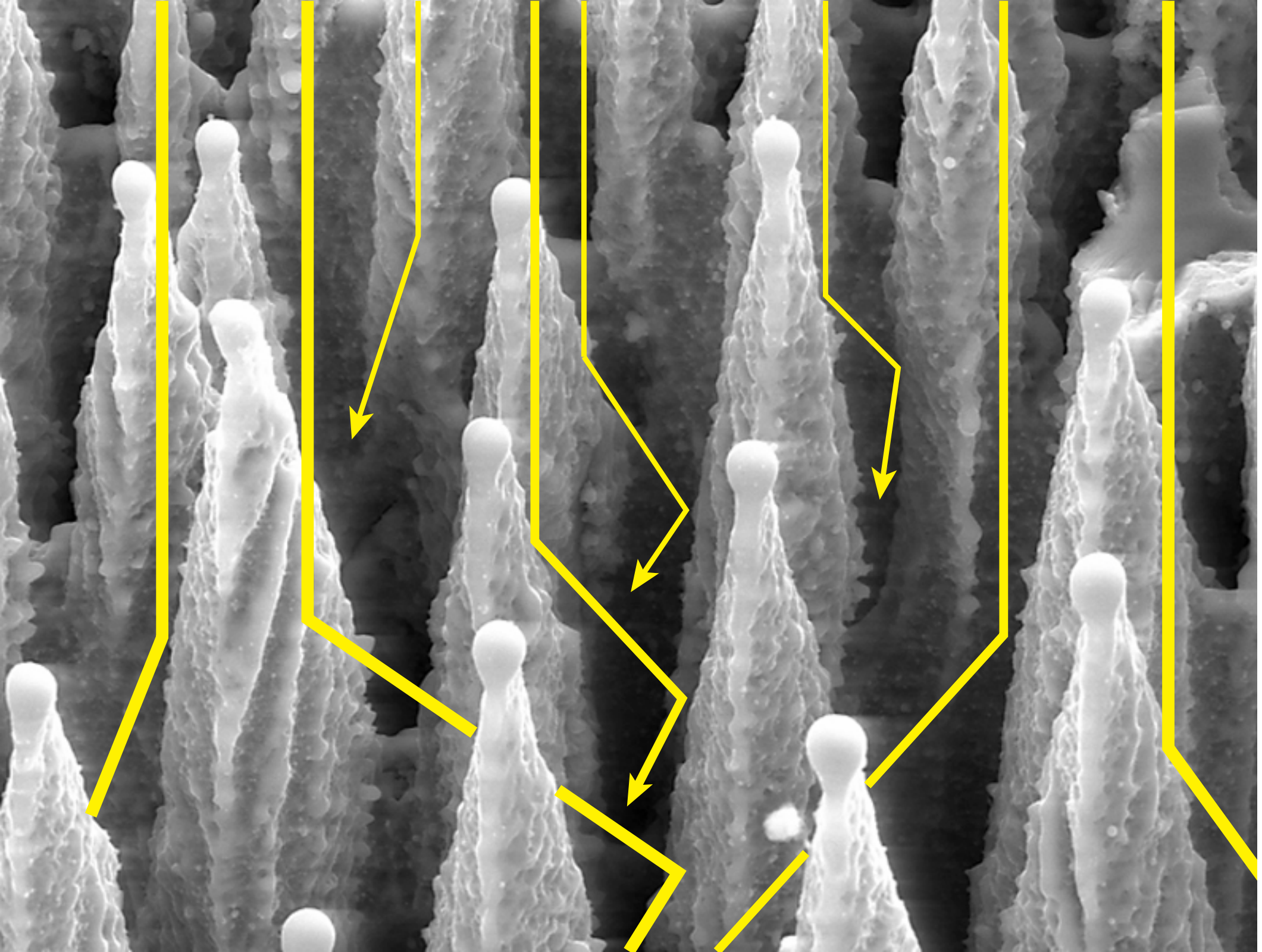

3 µm

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

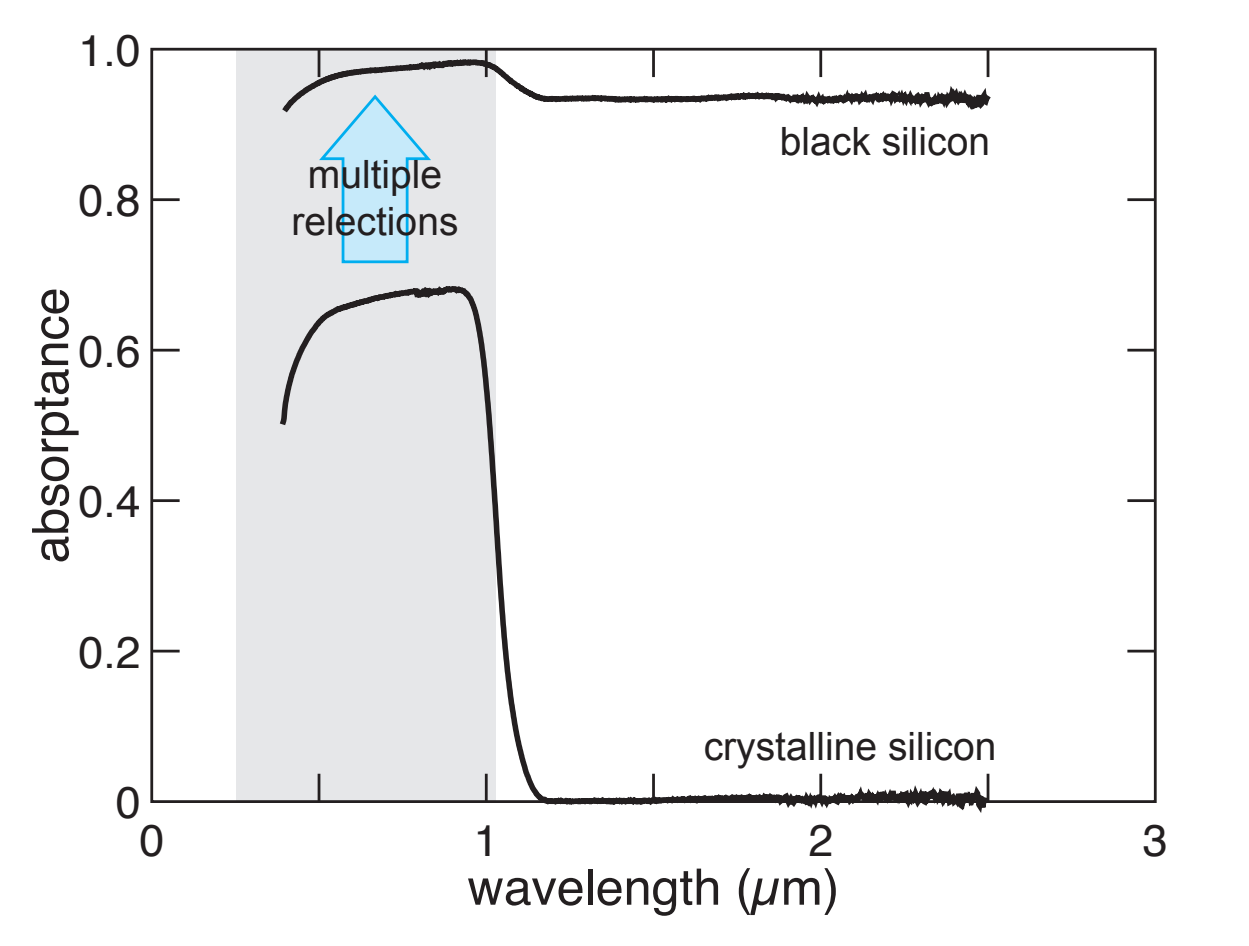


absorptance $(1 - R_{int} - T_{int})$

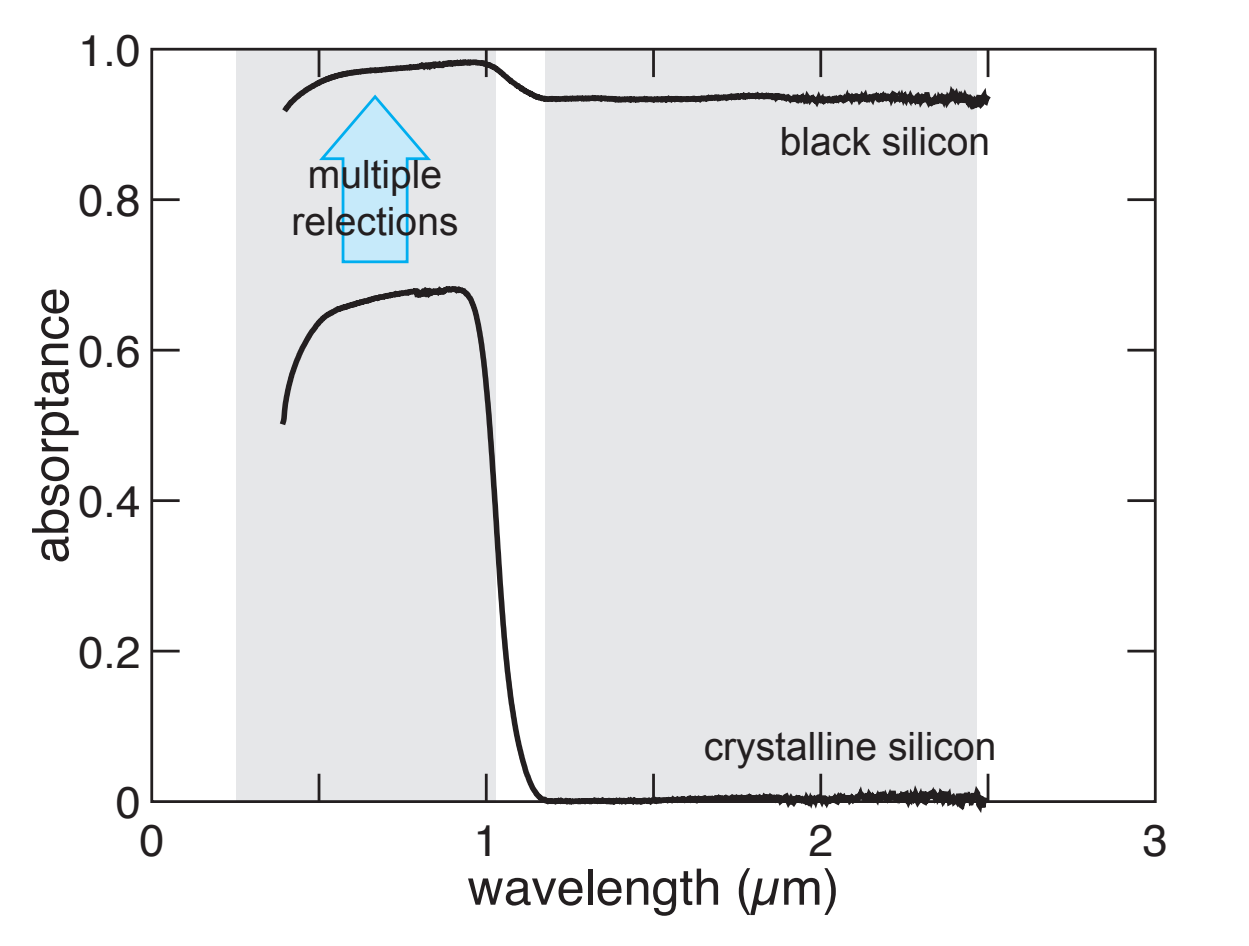




absorptance $(1 - R_{int} - T_{int})$



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



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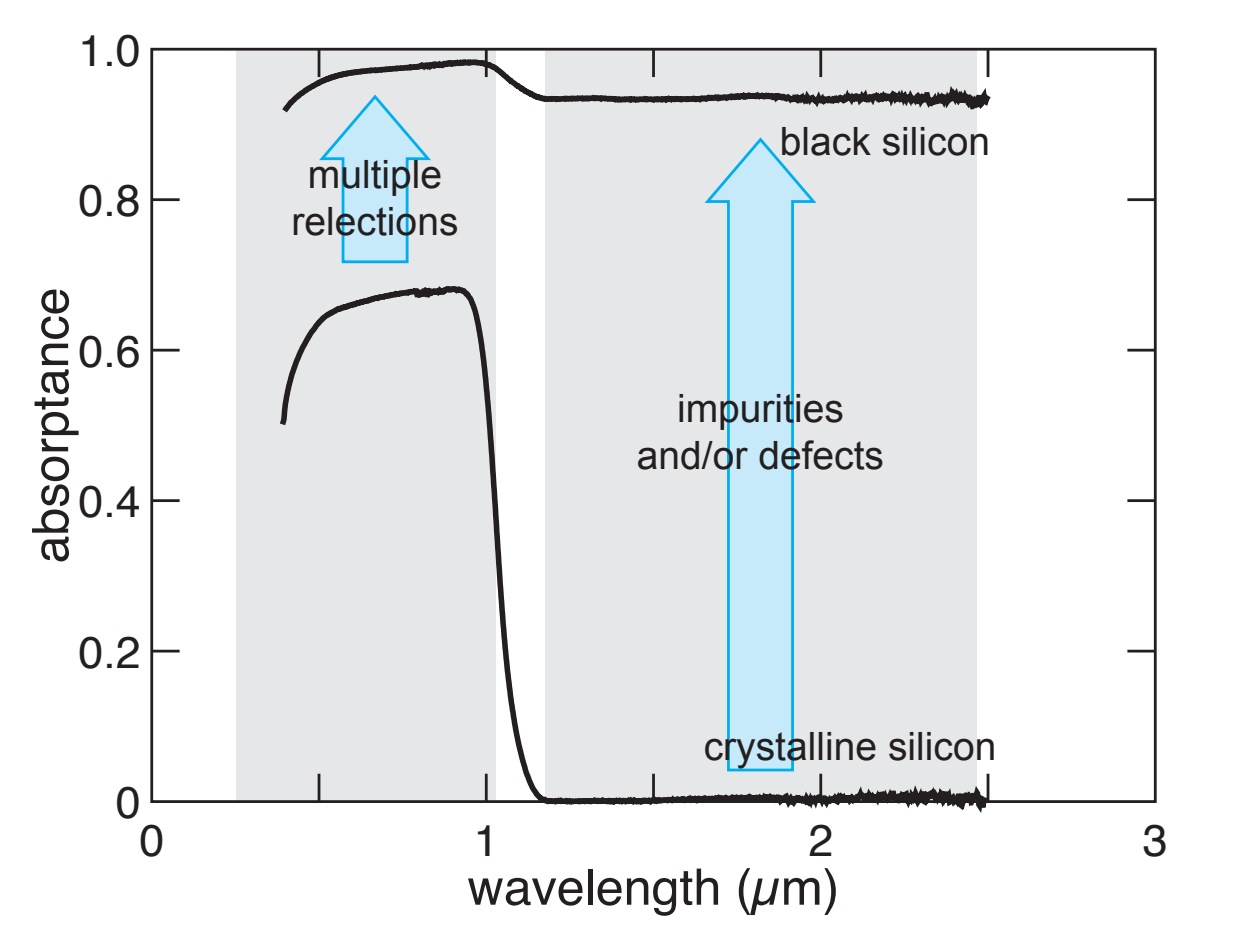

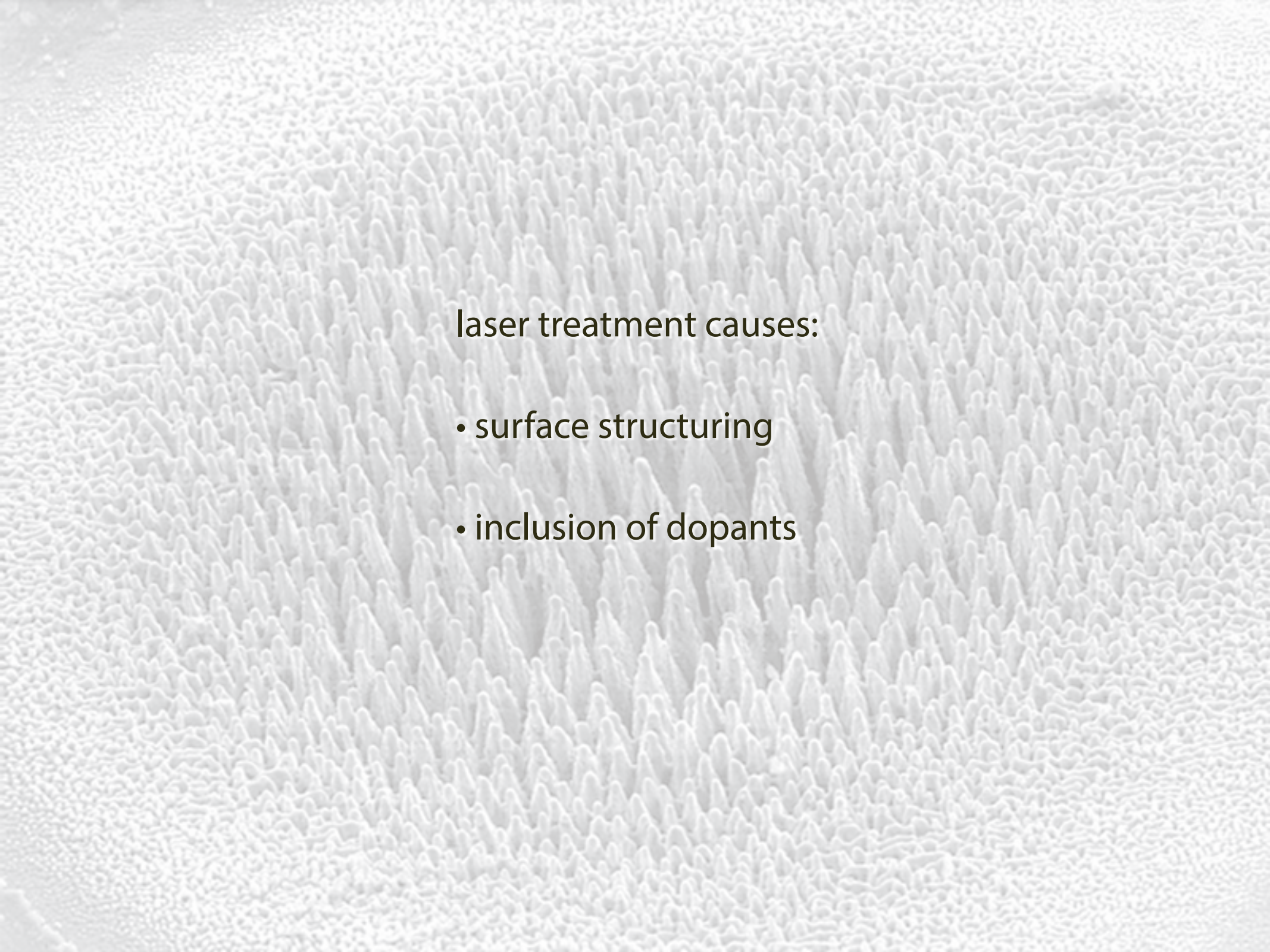

laser treatment causes:

- surface structuring
- inclusion of dopants

substrate/dopant combinations

dopants:

I																	VIII
H	II											III	IV	V	VI	VII	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe

substrates:

Si

substrate/dopant combinations

dopants:

I																	VIII
H	II											III	IV	V	VI	VII	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
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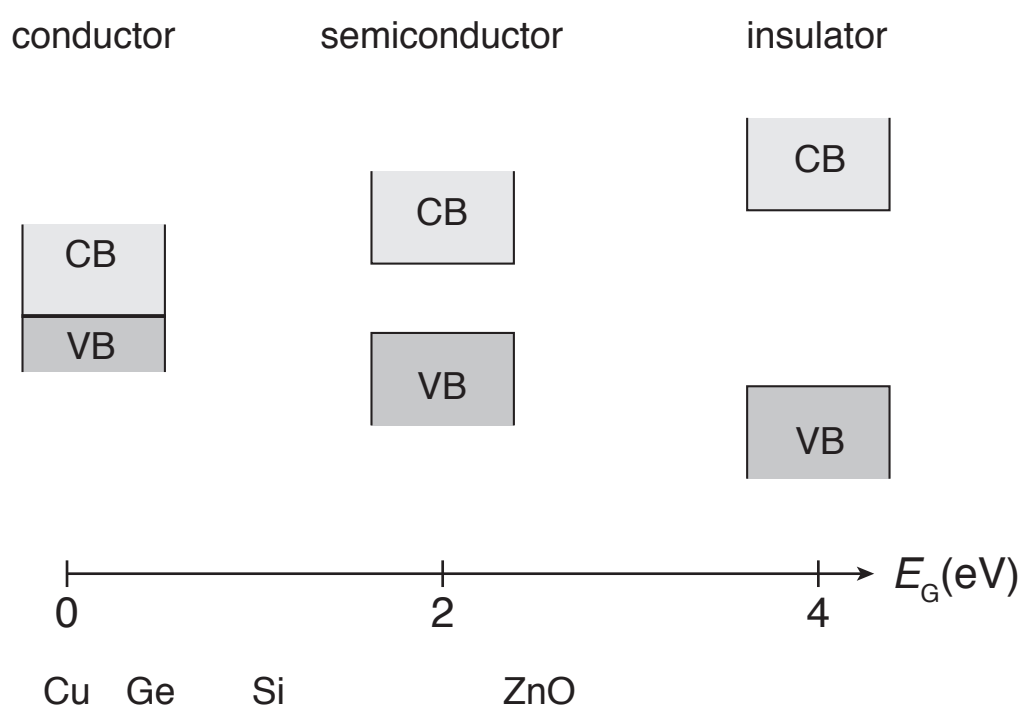
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe

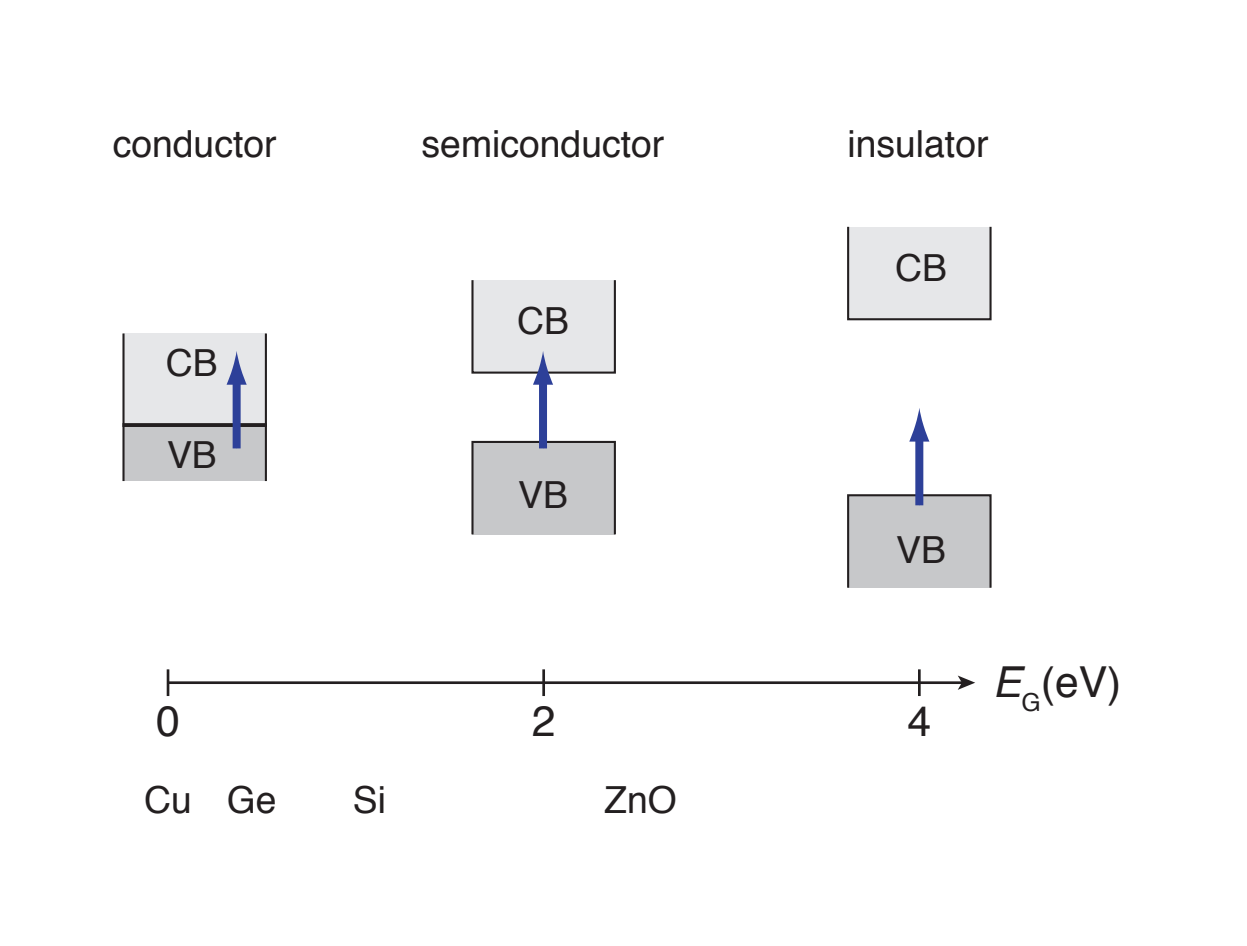
substrates:

Si Ge ZnO InP GaAs

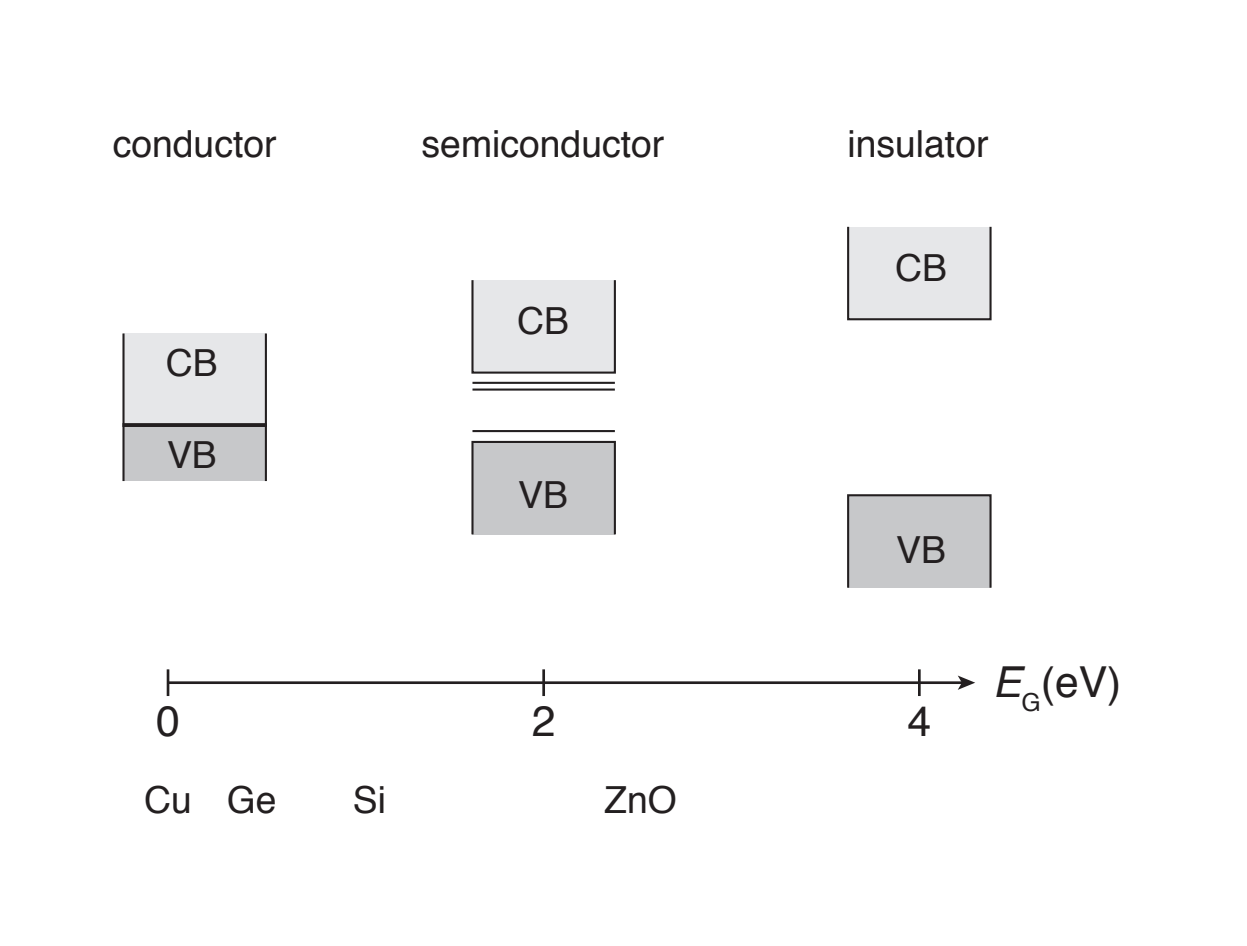
Ti Ag Al Cu Pd Rh Ta Pt TiO_2


conductor
semiconductor
insulator
CB
VB
CB
VB
CB
VB
0
2
4
E_G(eV)
Cu
Ge
Si
ZnO

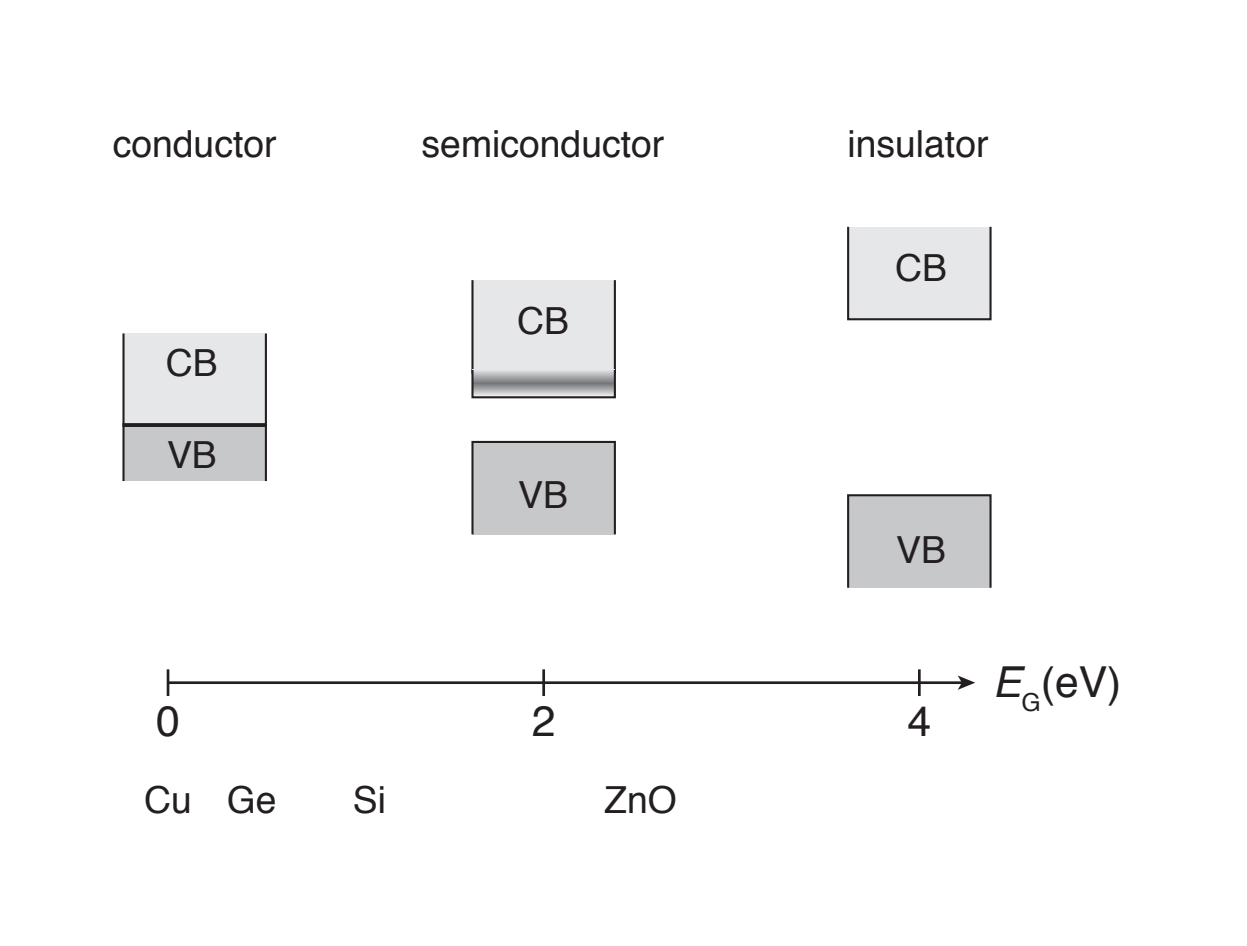
gap determines optical and electronic properties



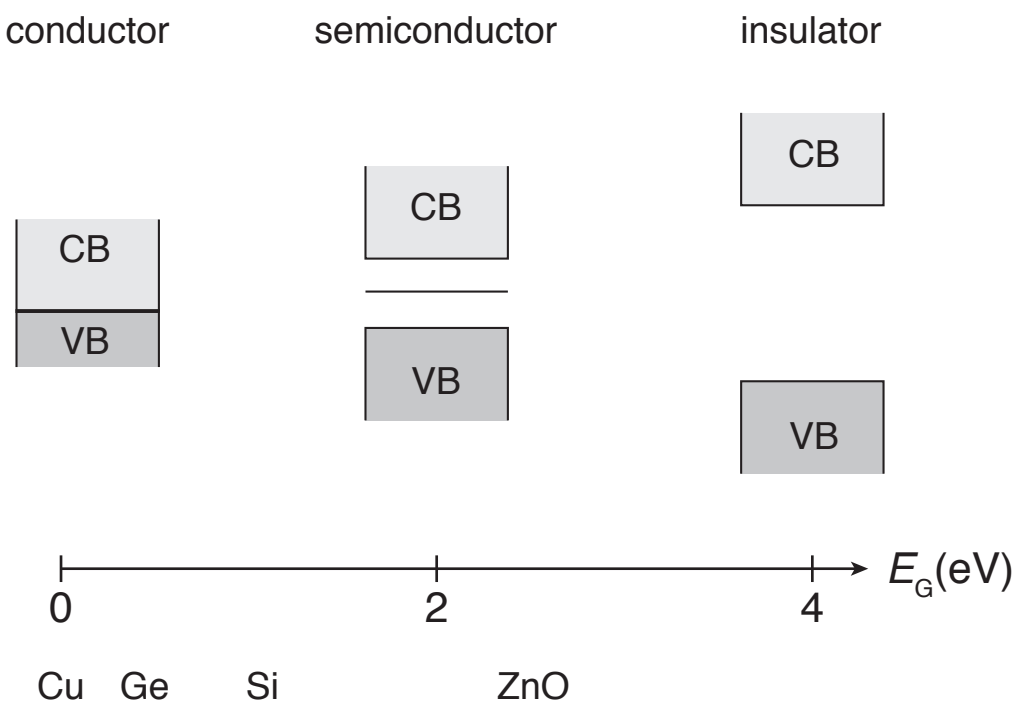
shallow-level dopants control electronic properties



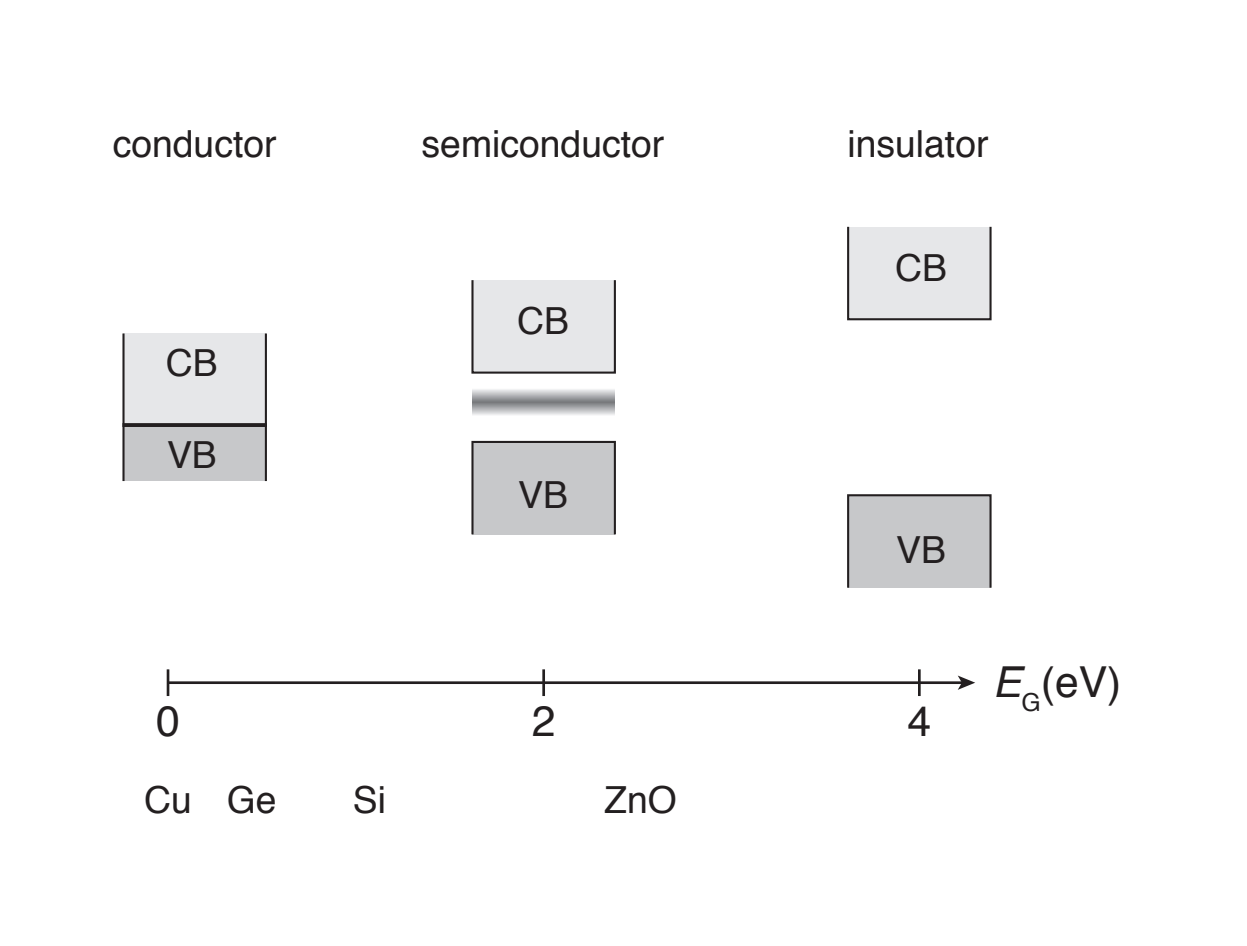
shallow-level dopants control electronic properties

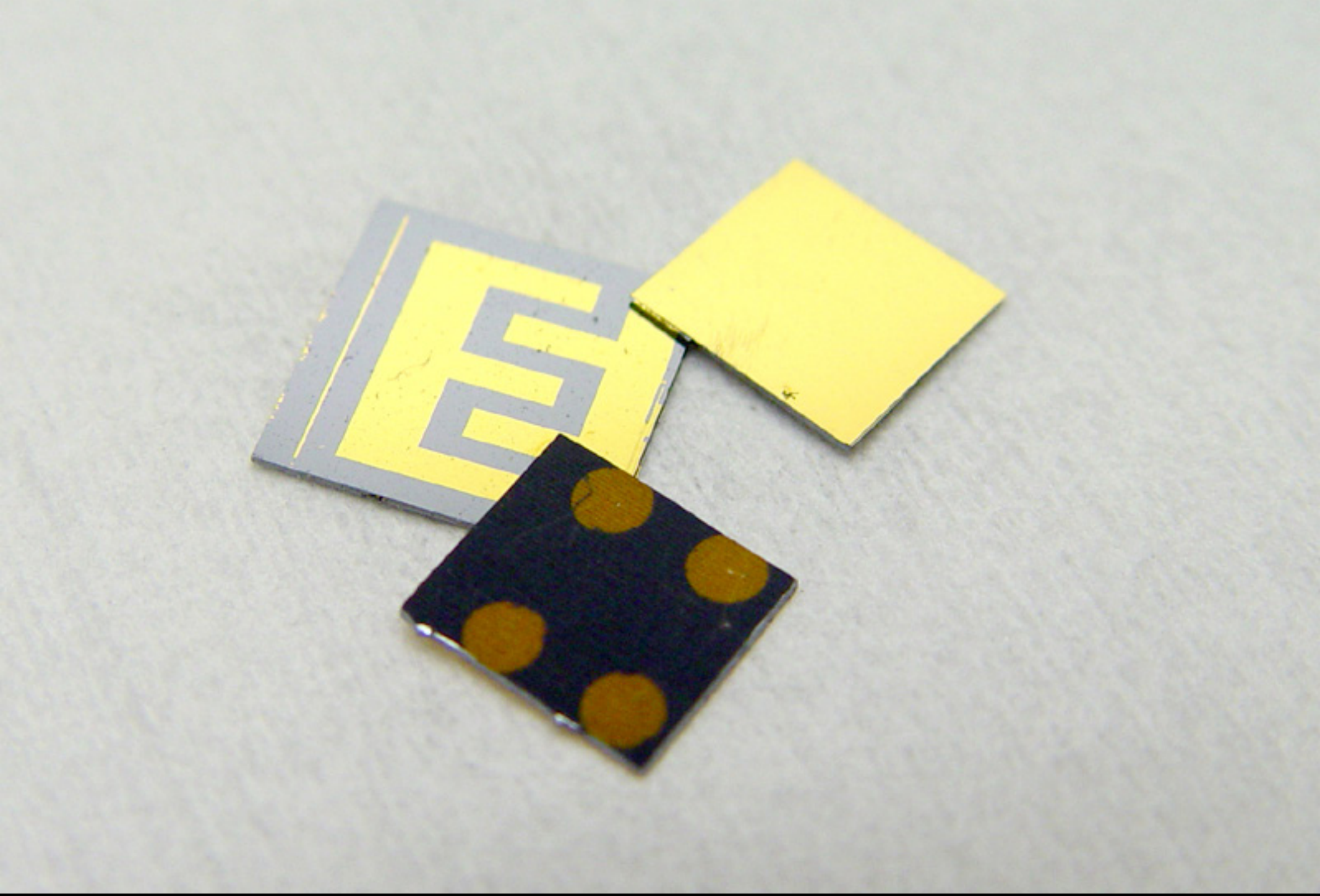


deep-level dopants typically avoided

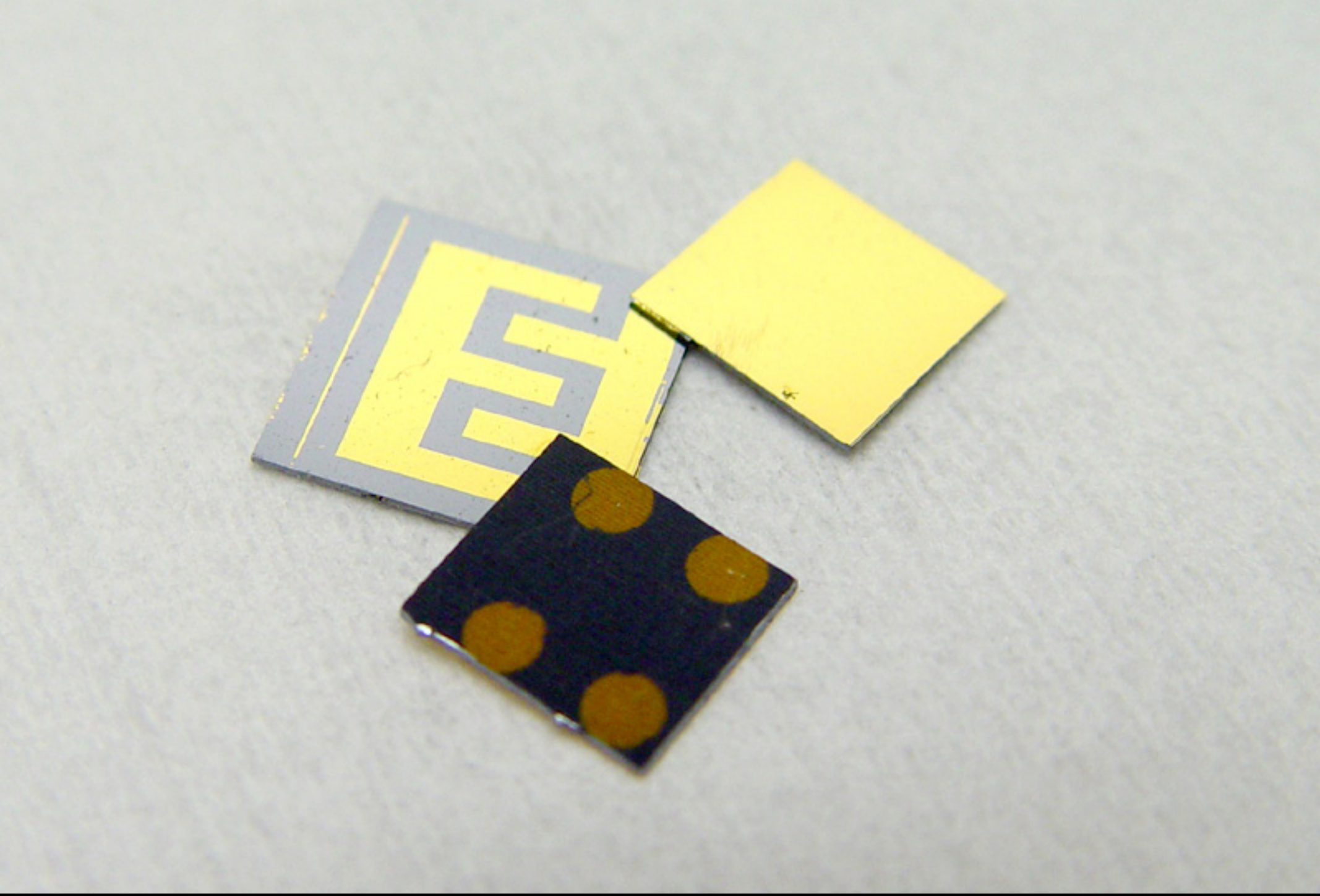


femtosecond laser-doping gives rise to intermediate band



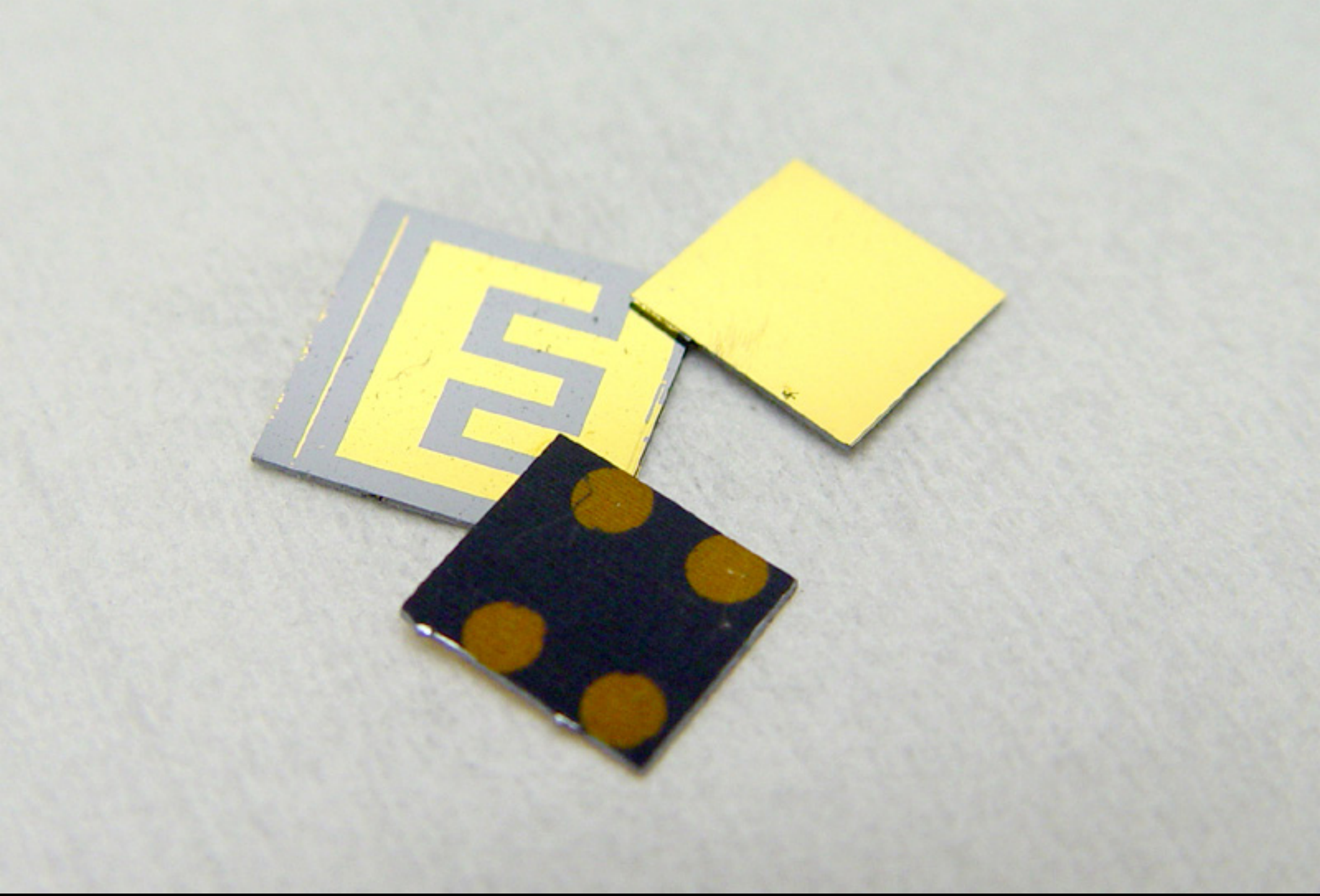


1 intermediate band



1 intermediate band

2 Si devices



1 intermediate band

2 Si devices

3 X:TiO_2

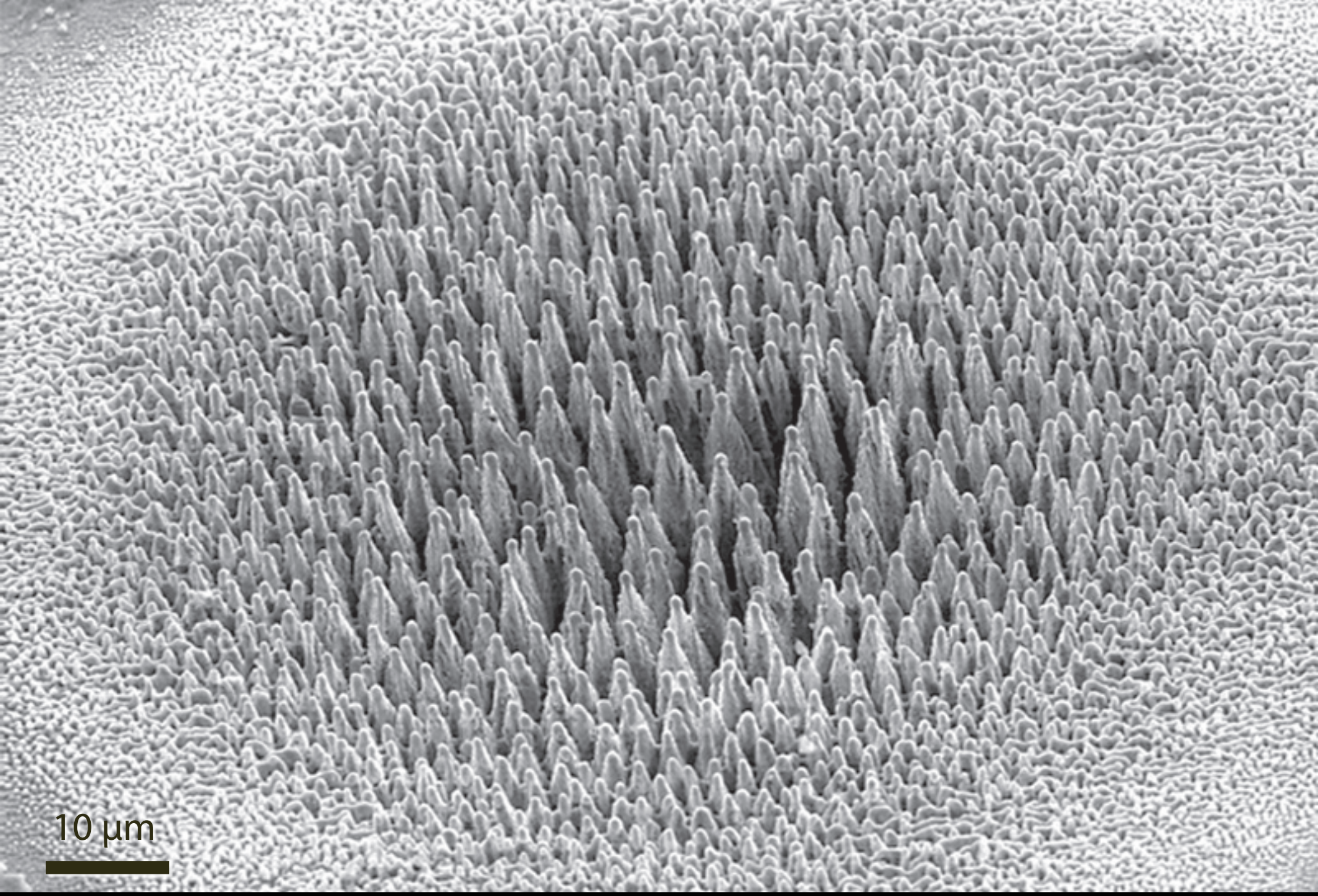
intermediate band formation in chalcogen-hyperdoped Si

dopants:

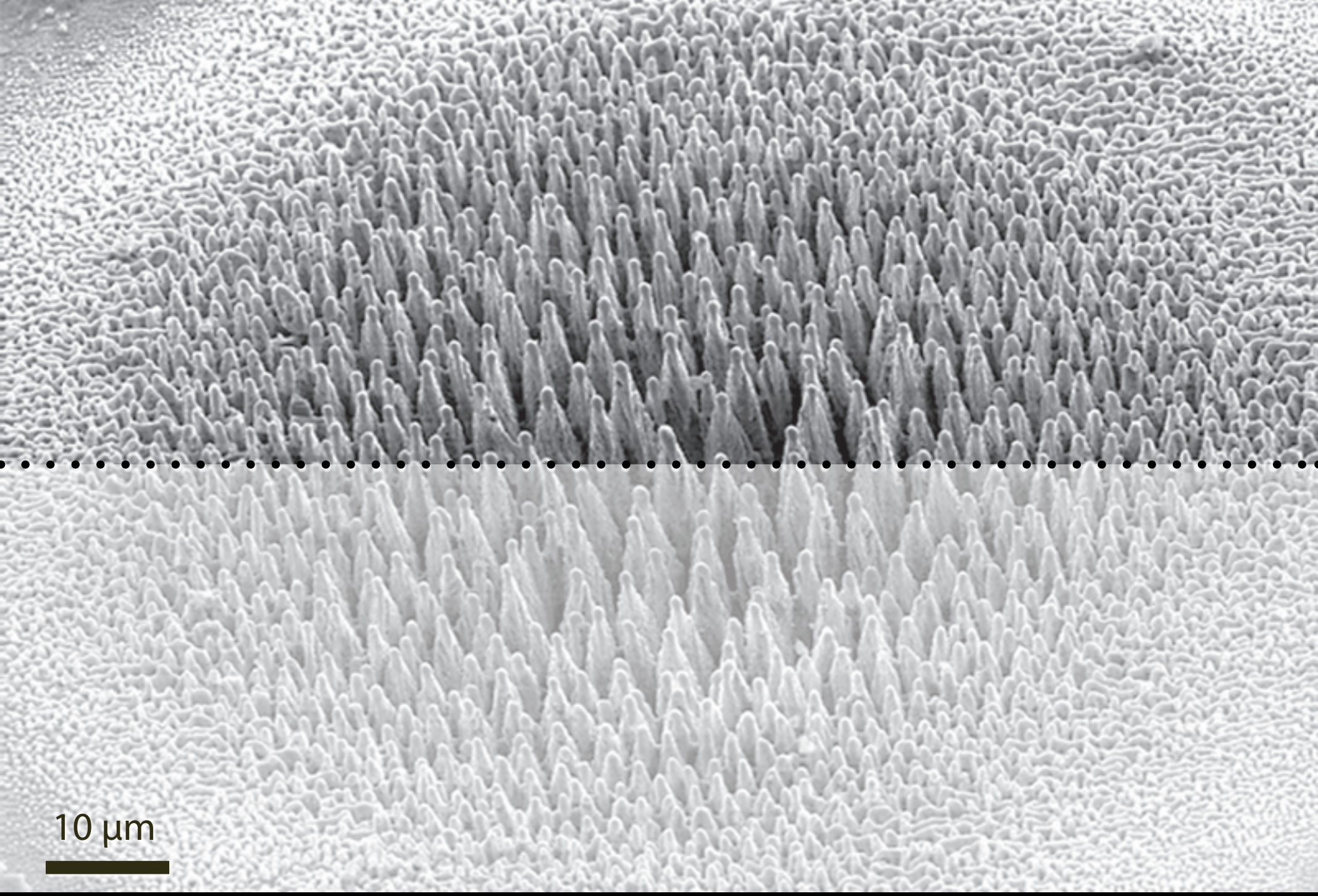
I																	VIII
H	II											III	IV	V	VI	VII	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe

substrates:

Si



1 intermediate band



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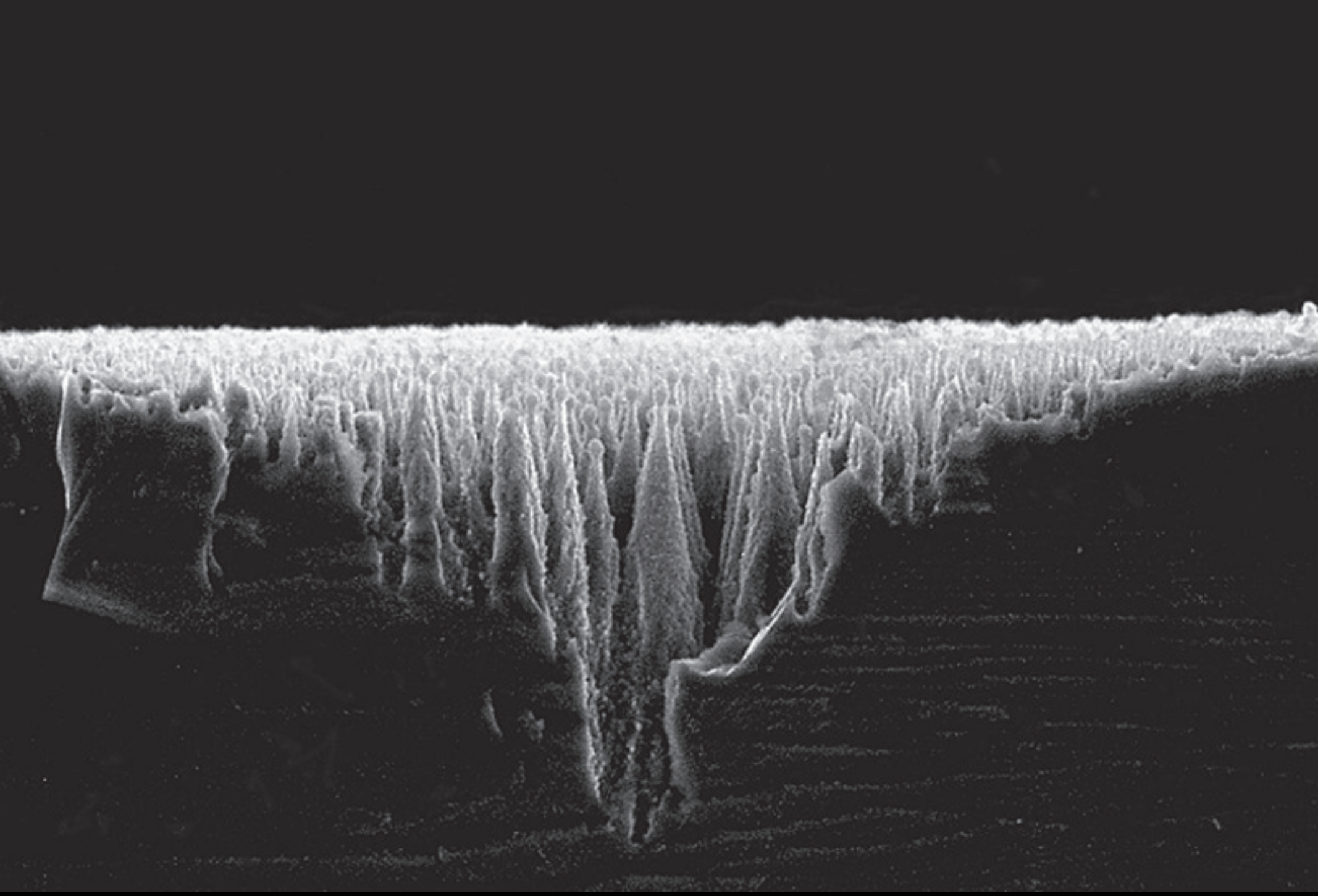

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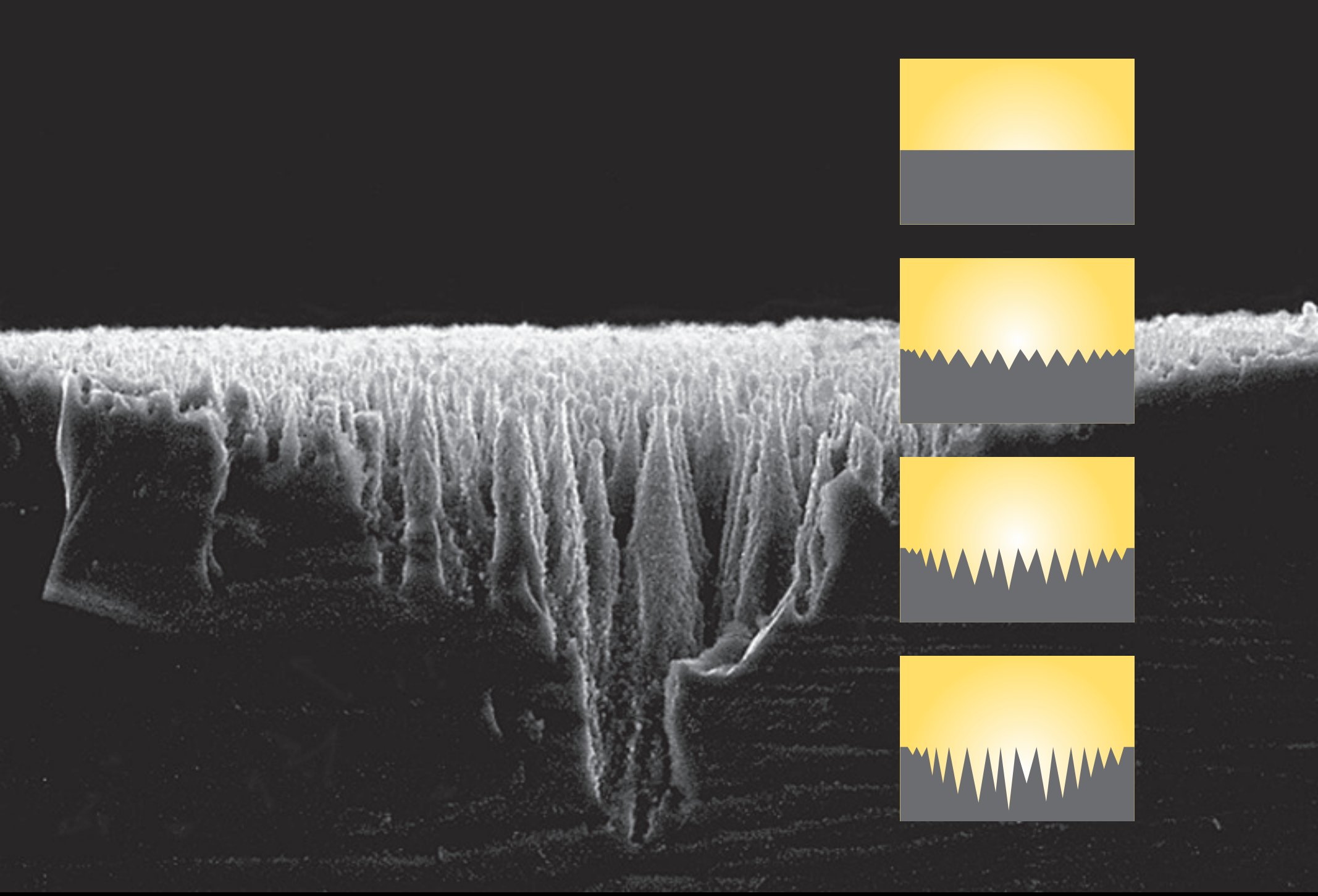

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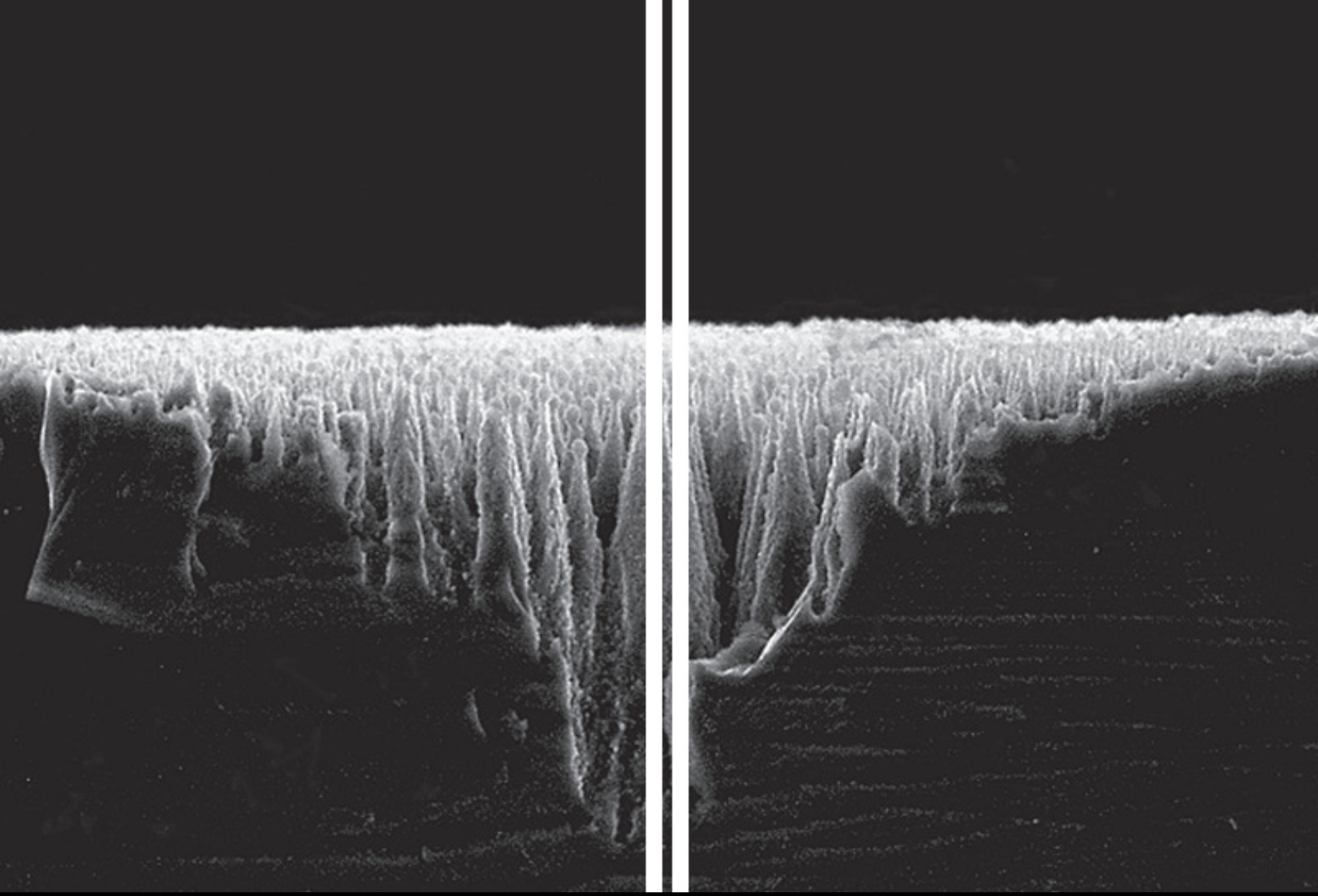

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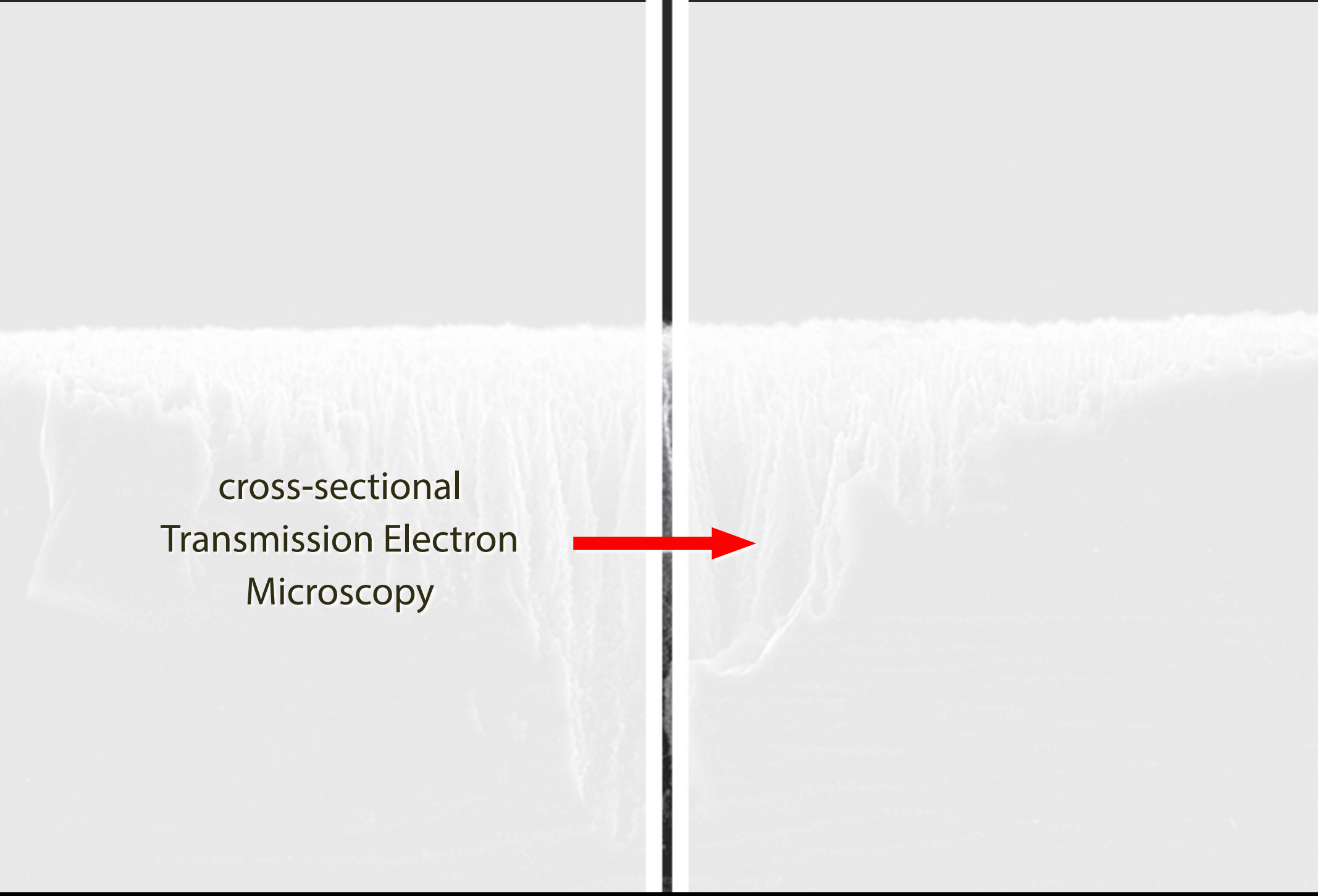

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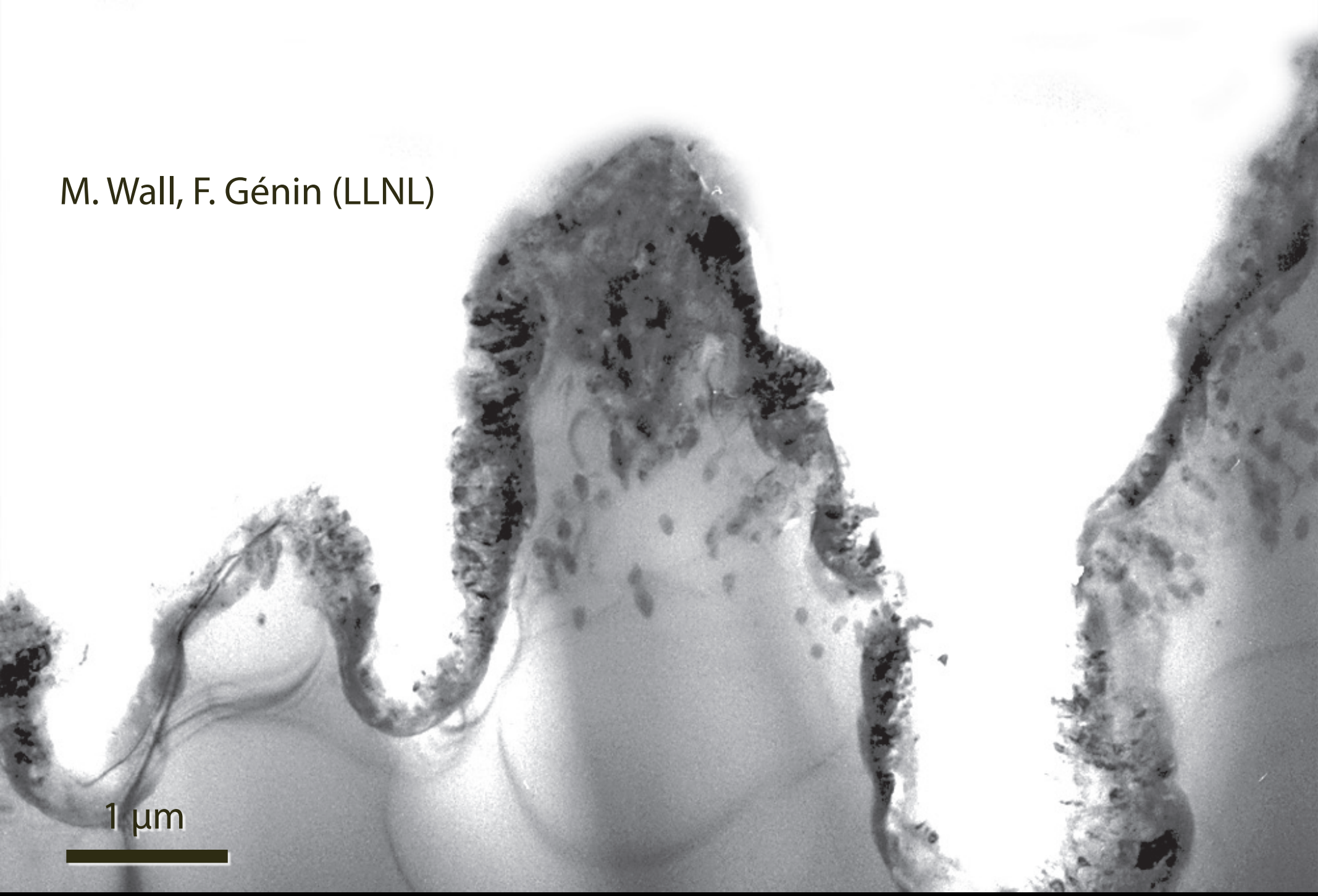
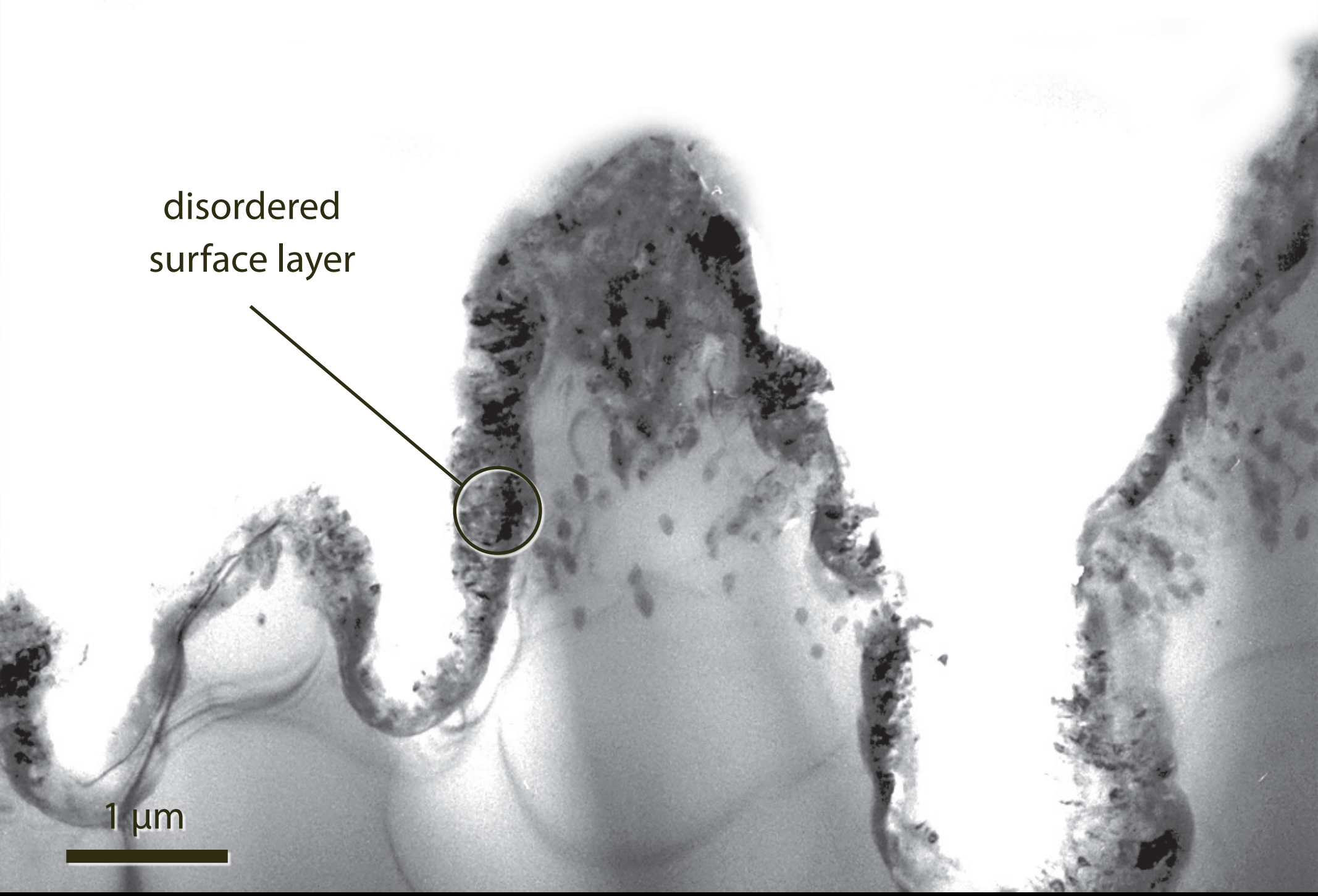


1 intermediate band



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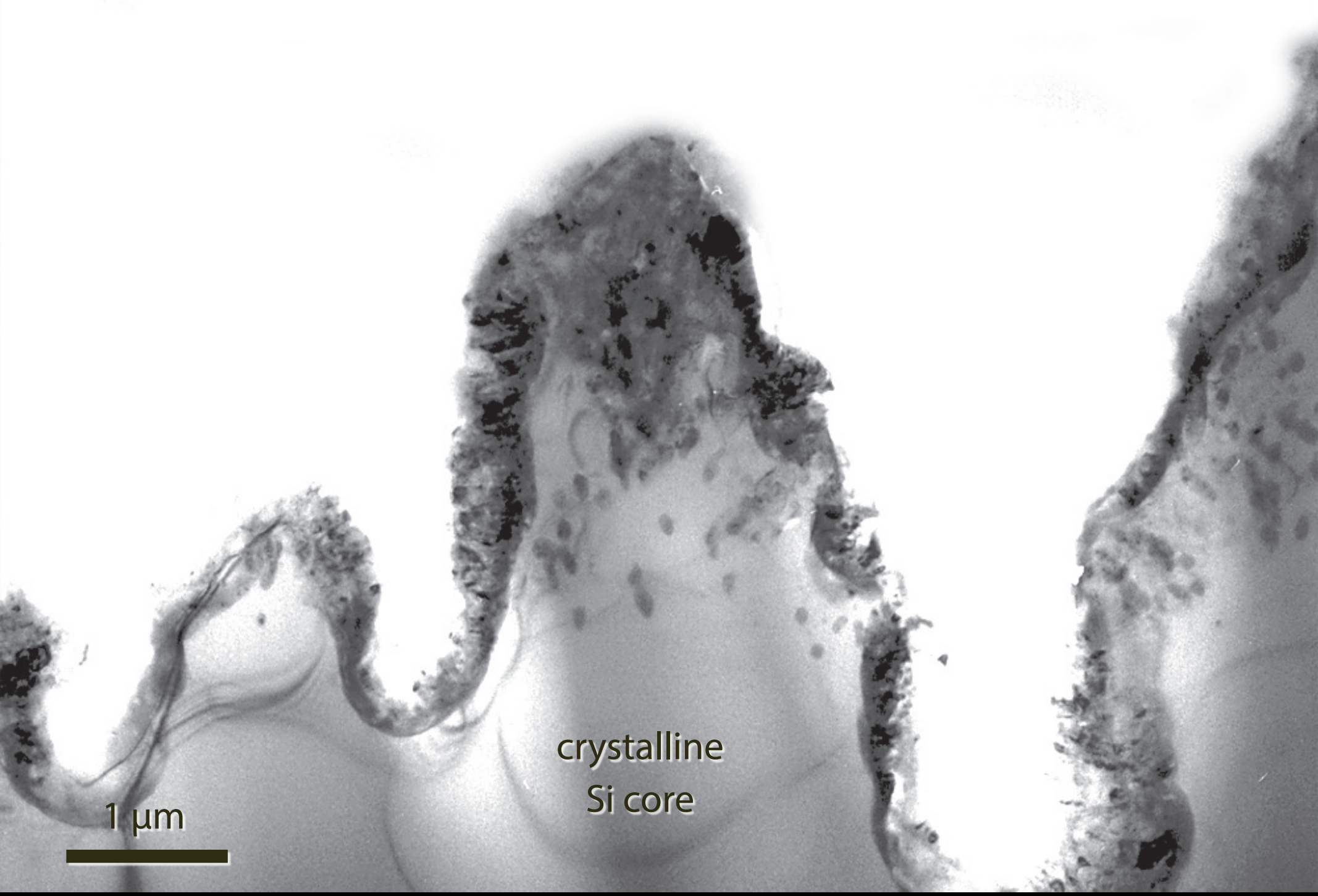

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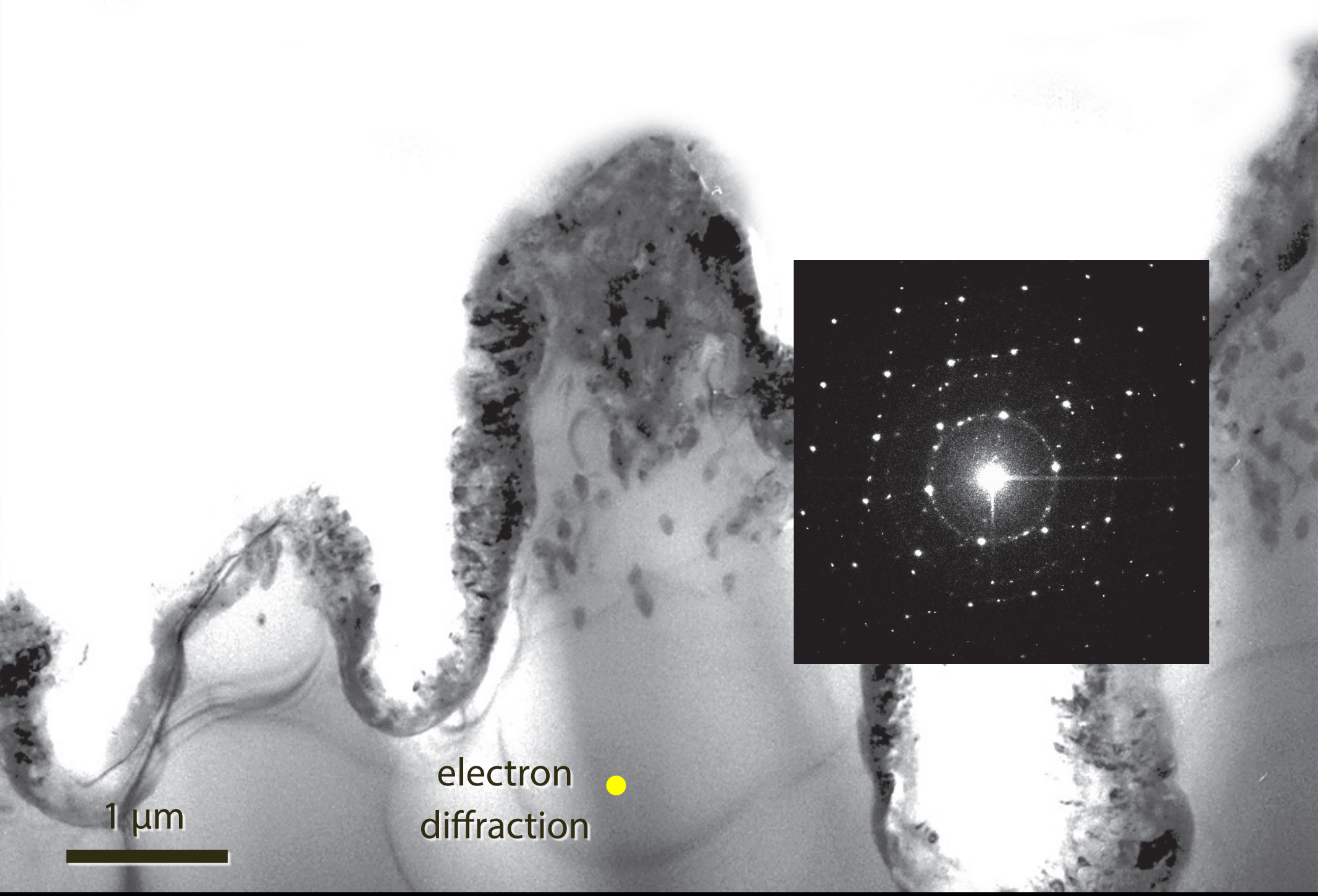

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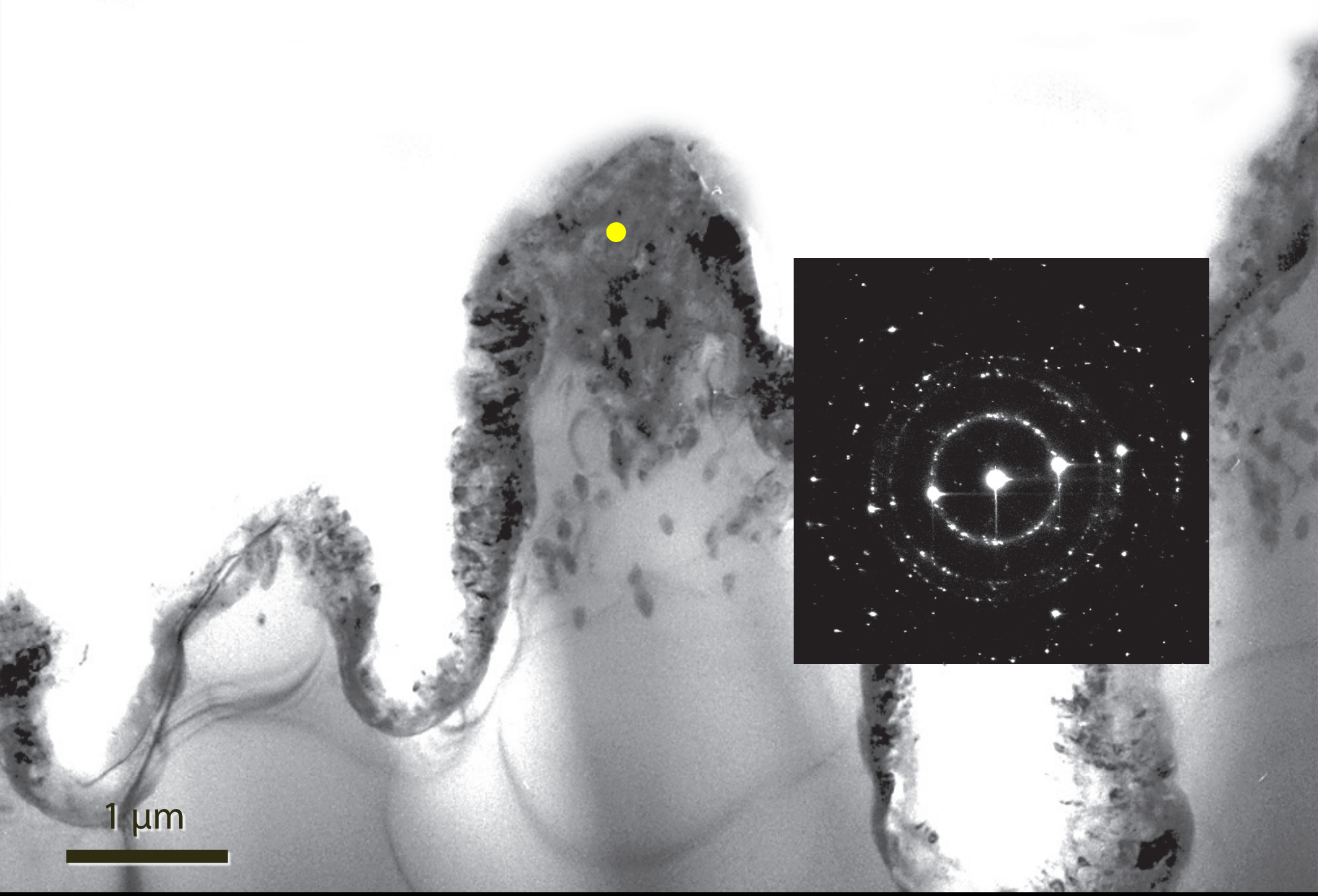

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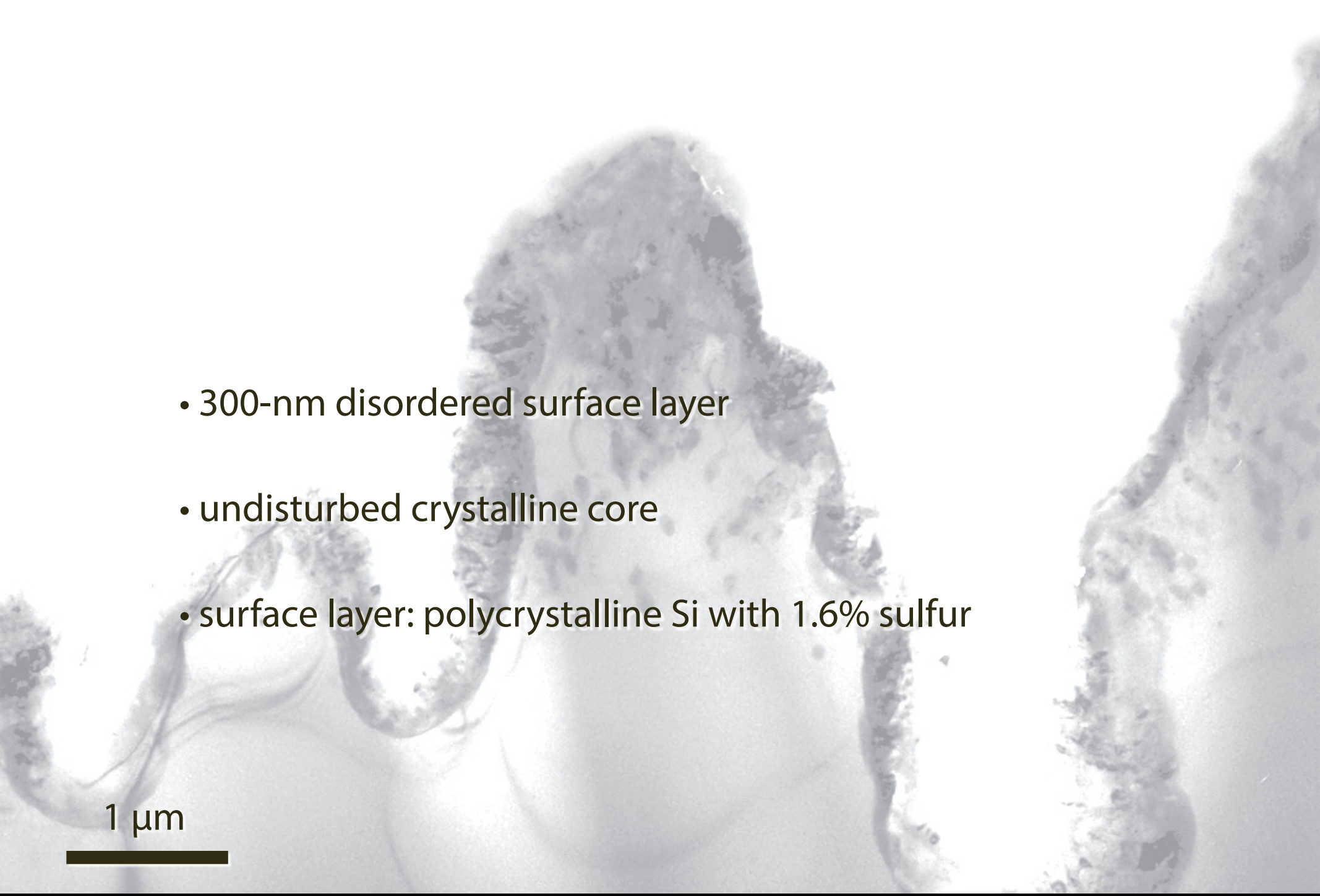
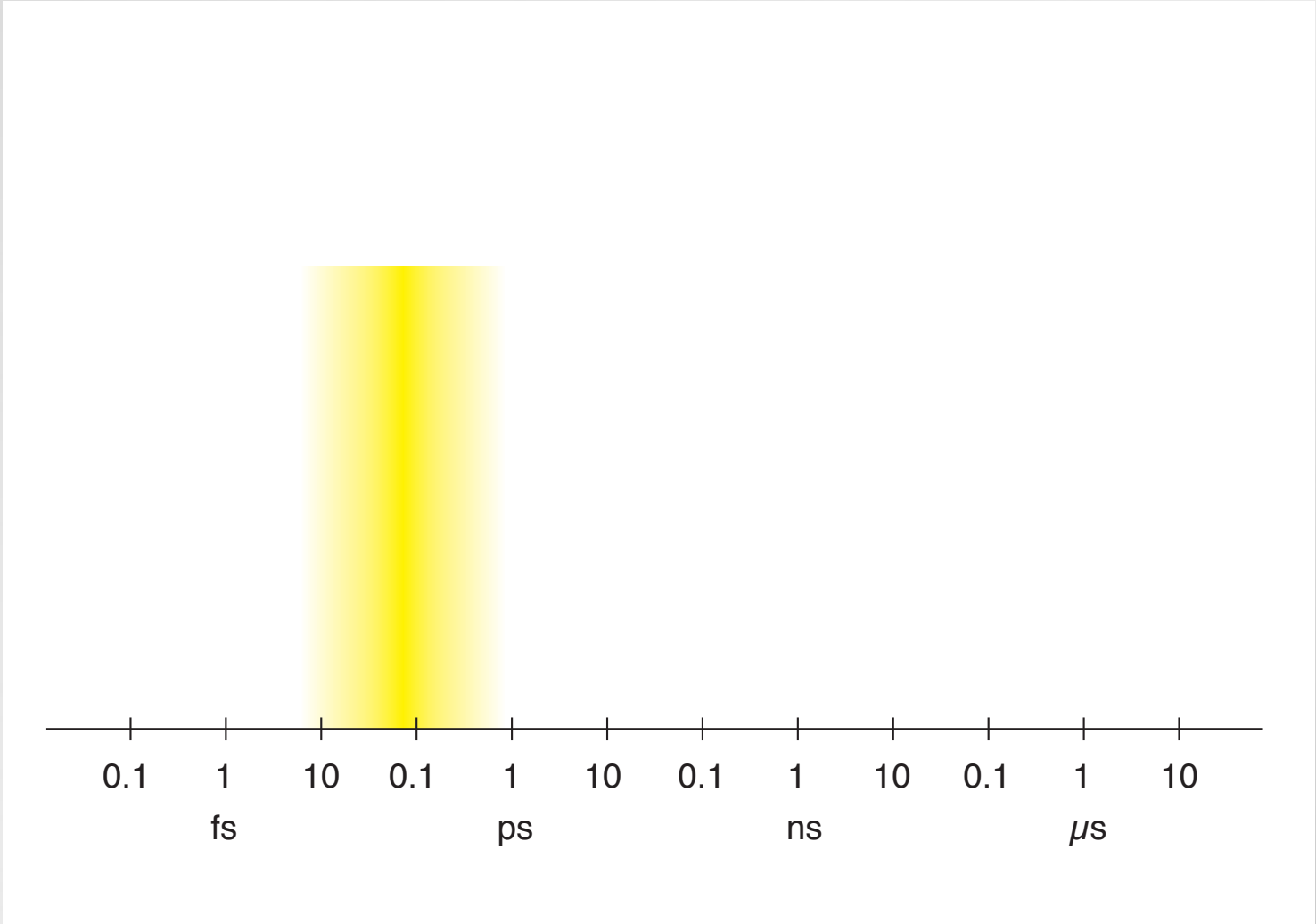


1 intermediate band

relevant time scales



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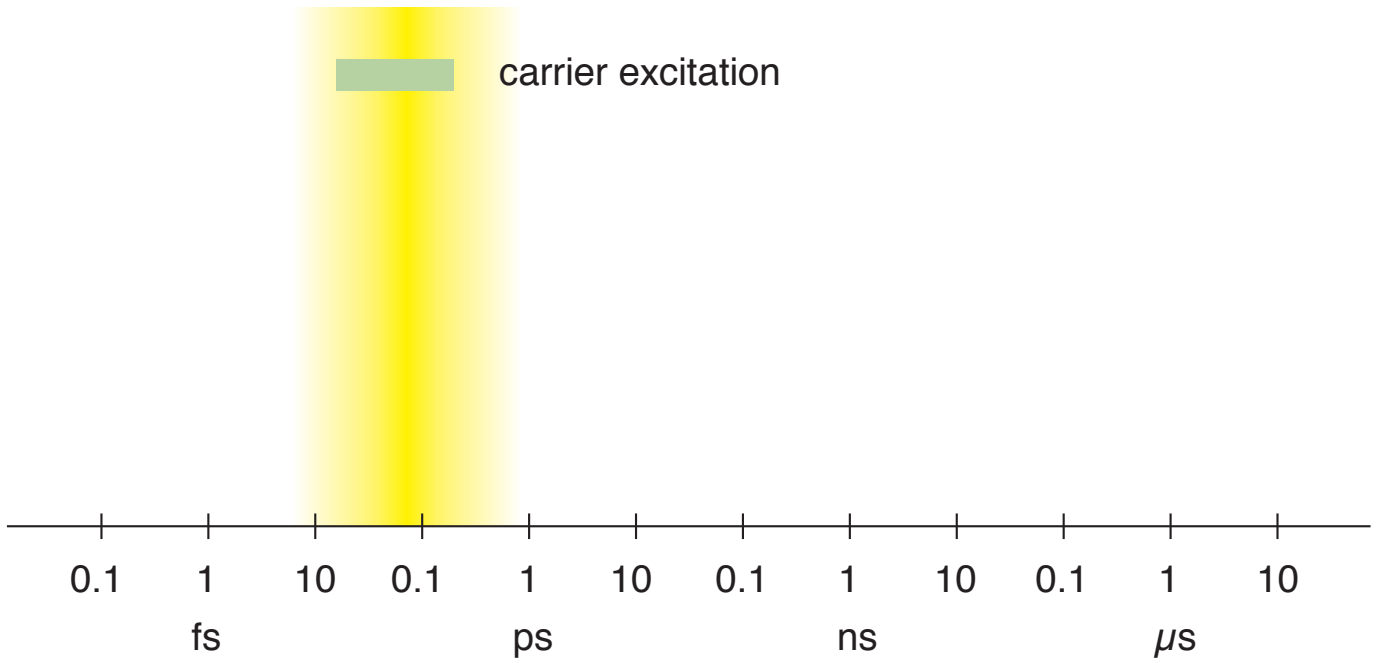
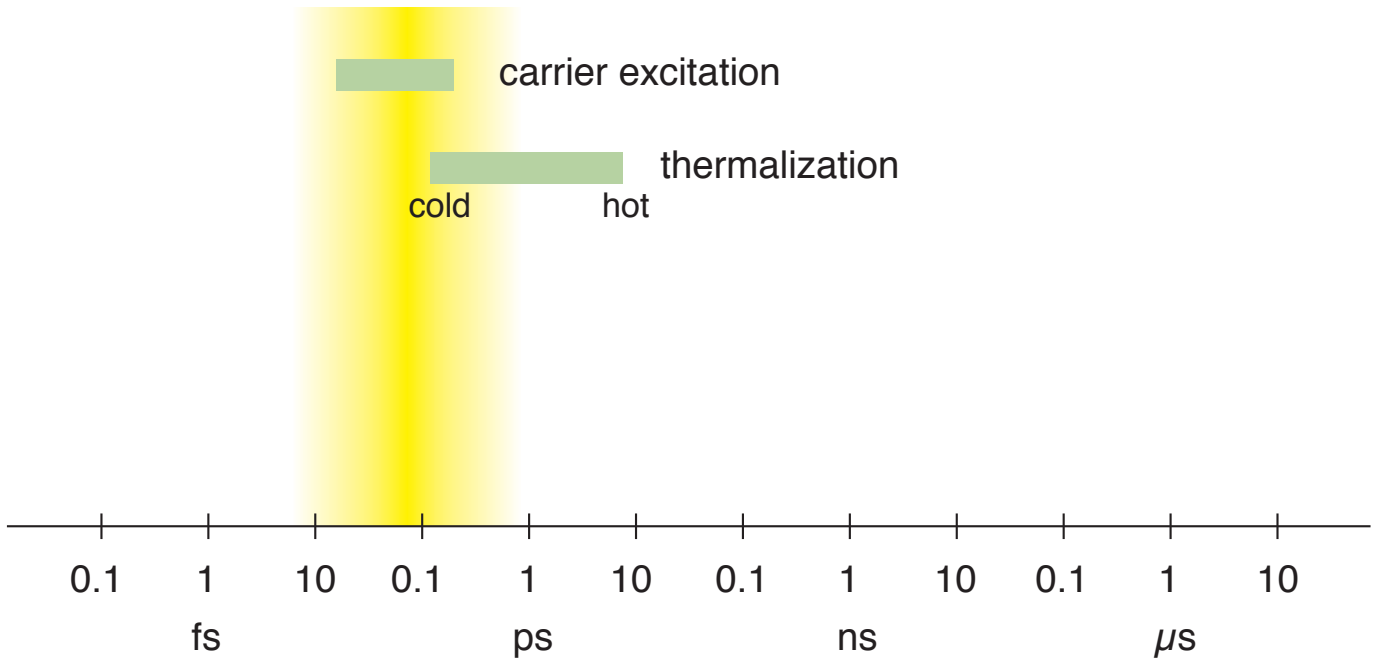
relevant time scales



relevant time scales



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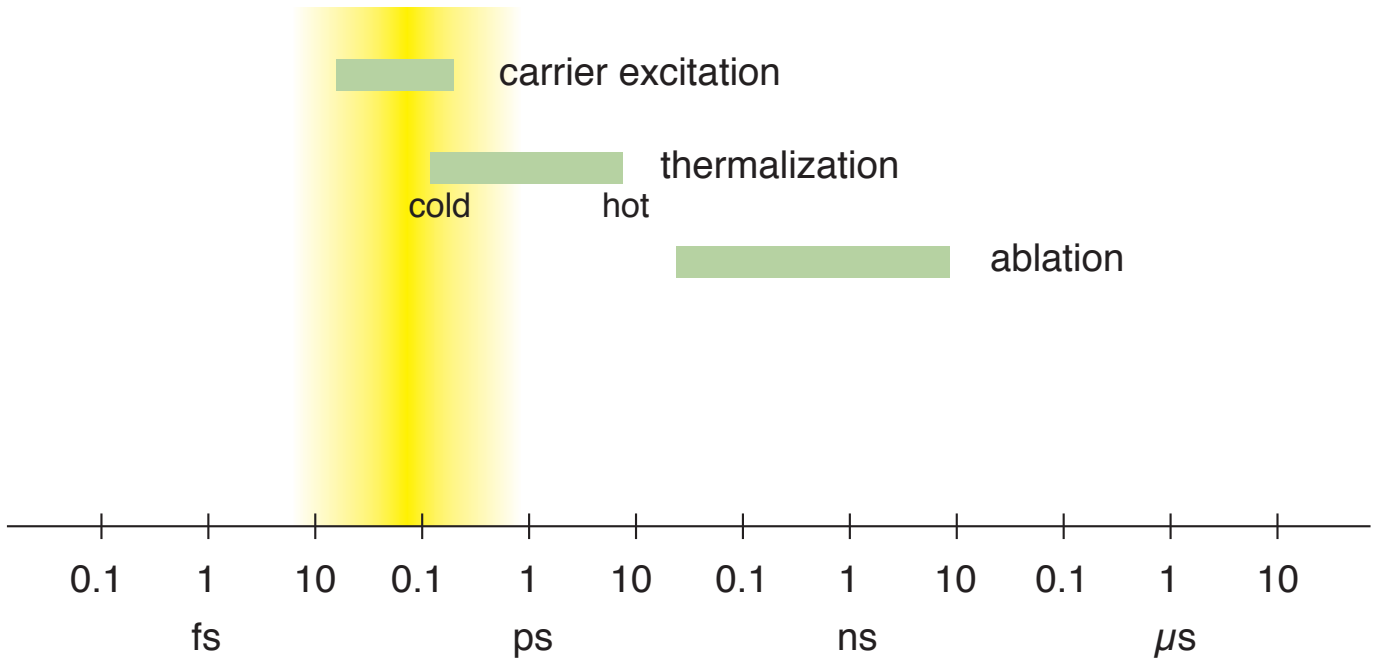

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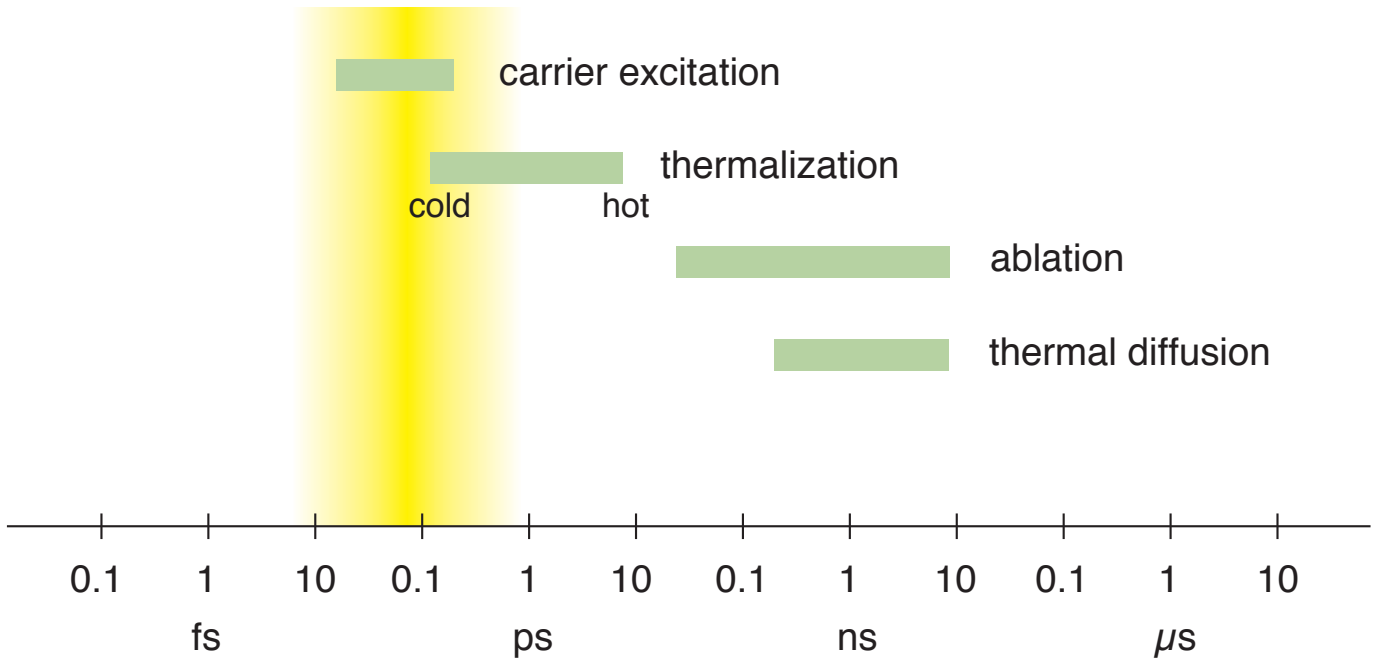

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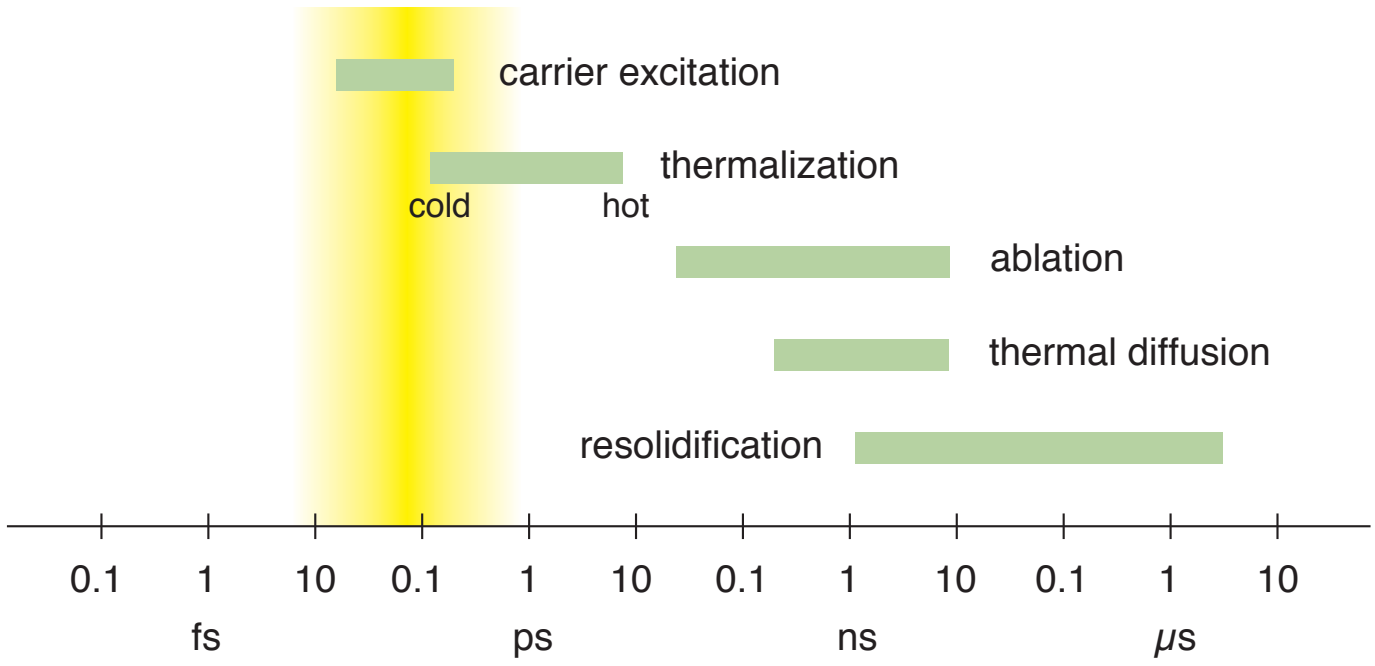
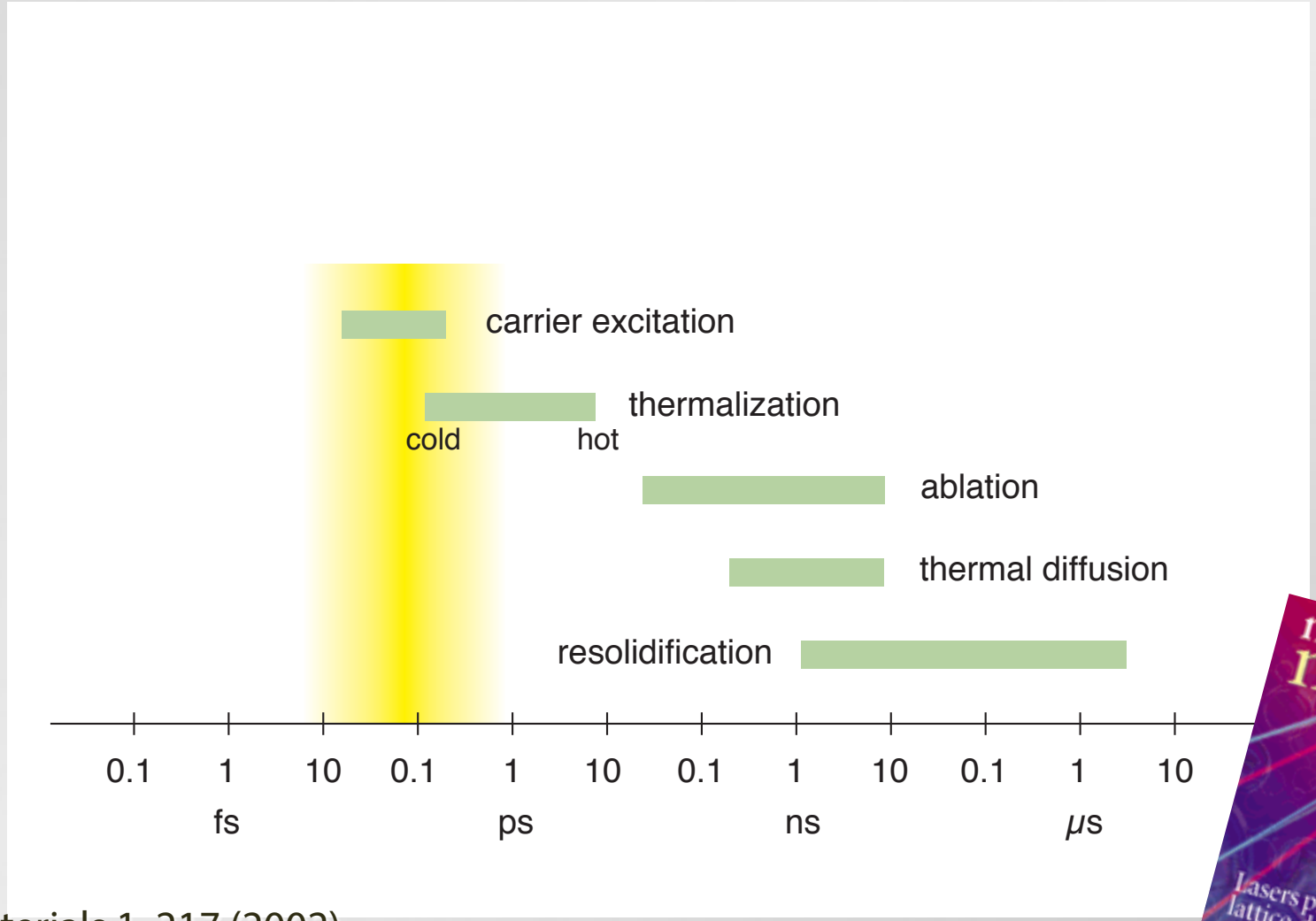
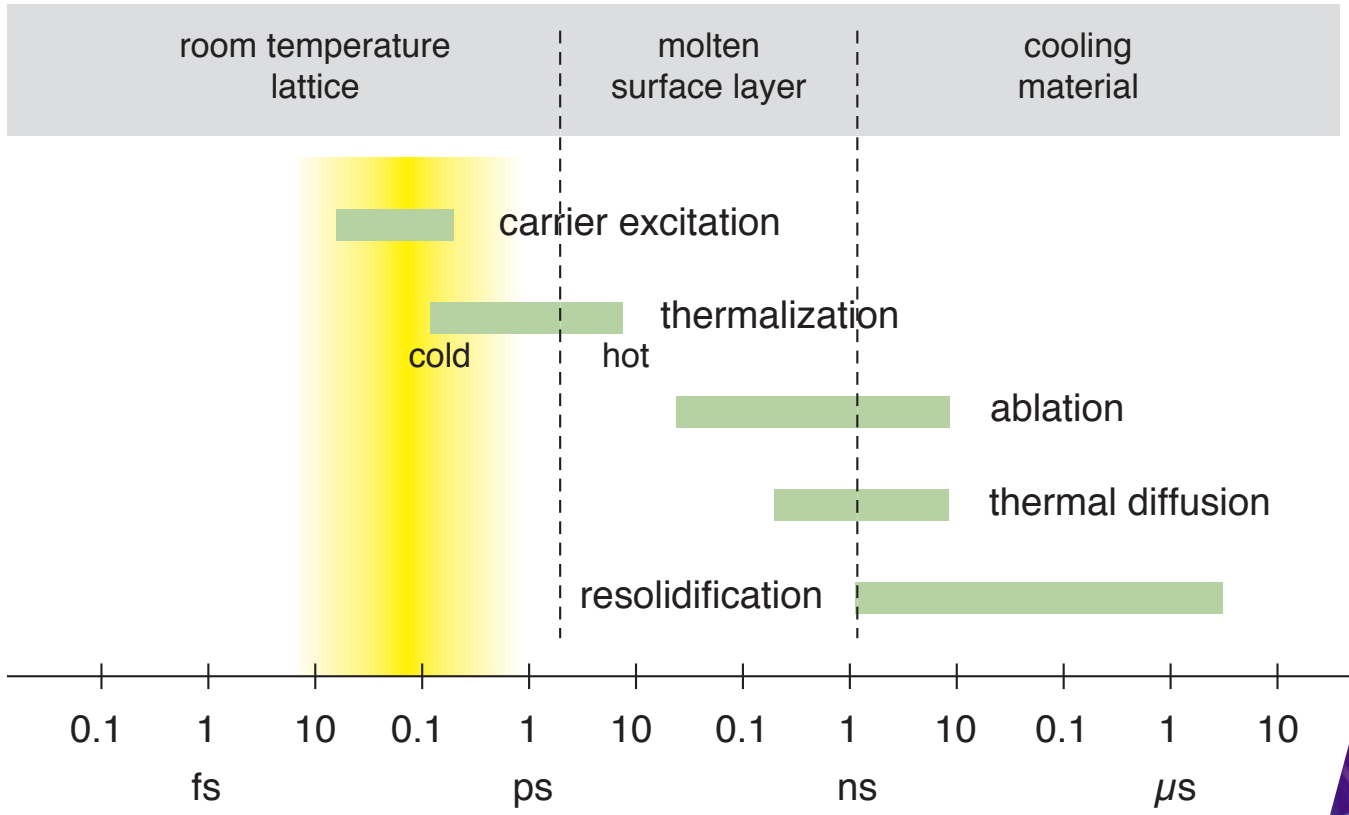


relevant time scales



Nature Materials 1, 217 (2002)

relevant time scales



Nature Materials 1, 217 (2002)

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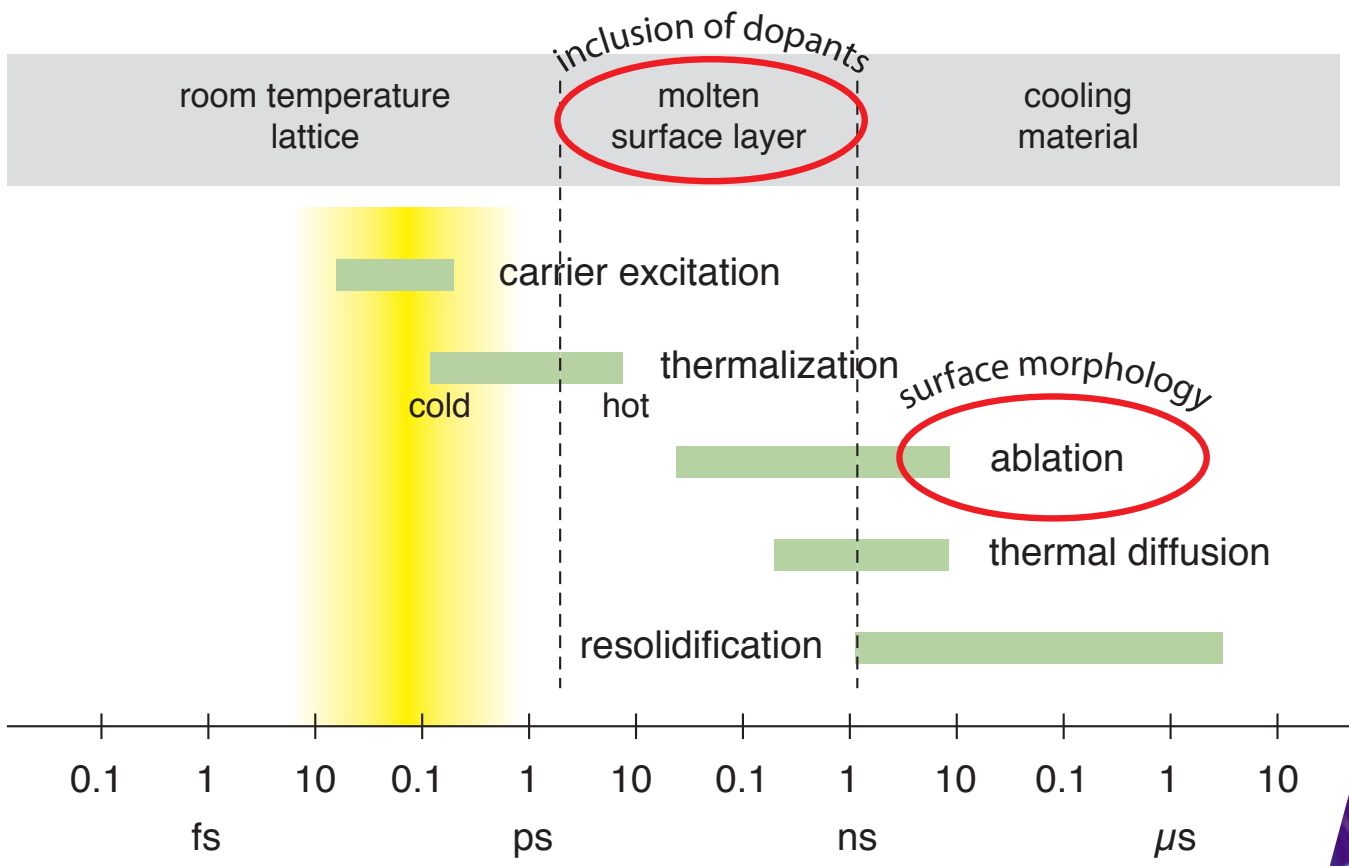
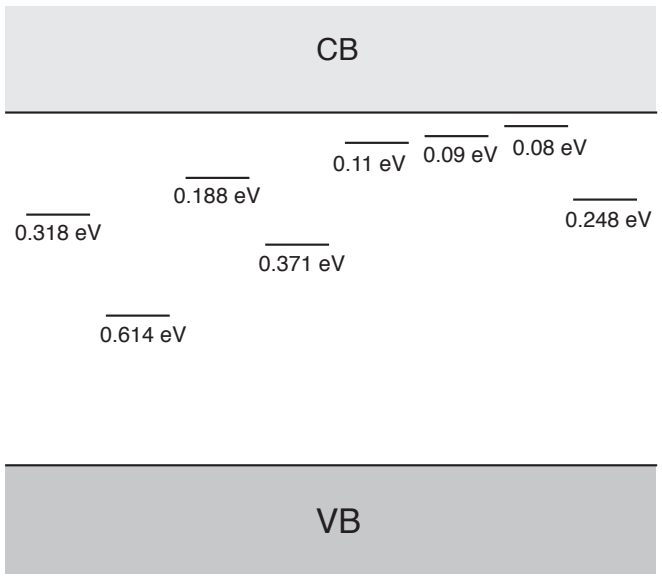


Nature Materials 1, 217 (2002)

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



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

1 intermediate band

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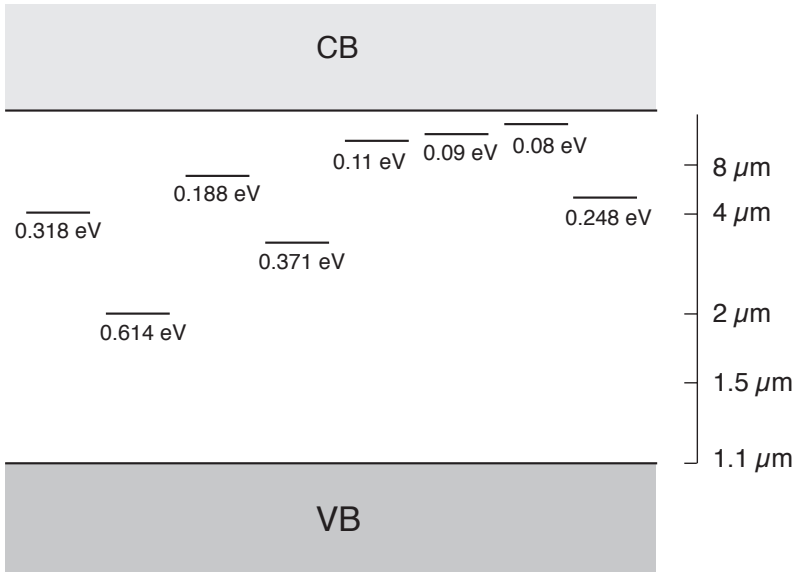

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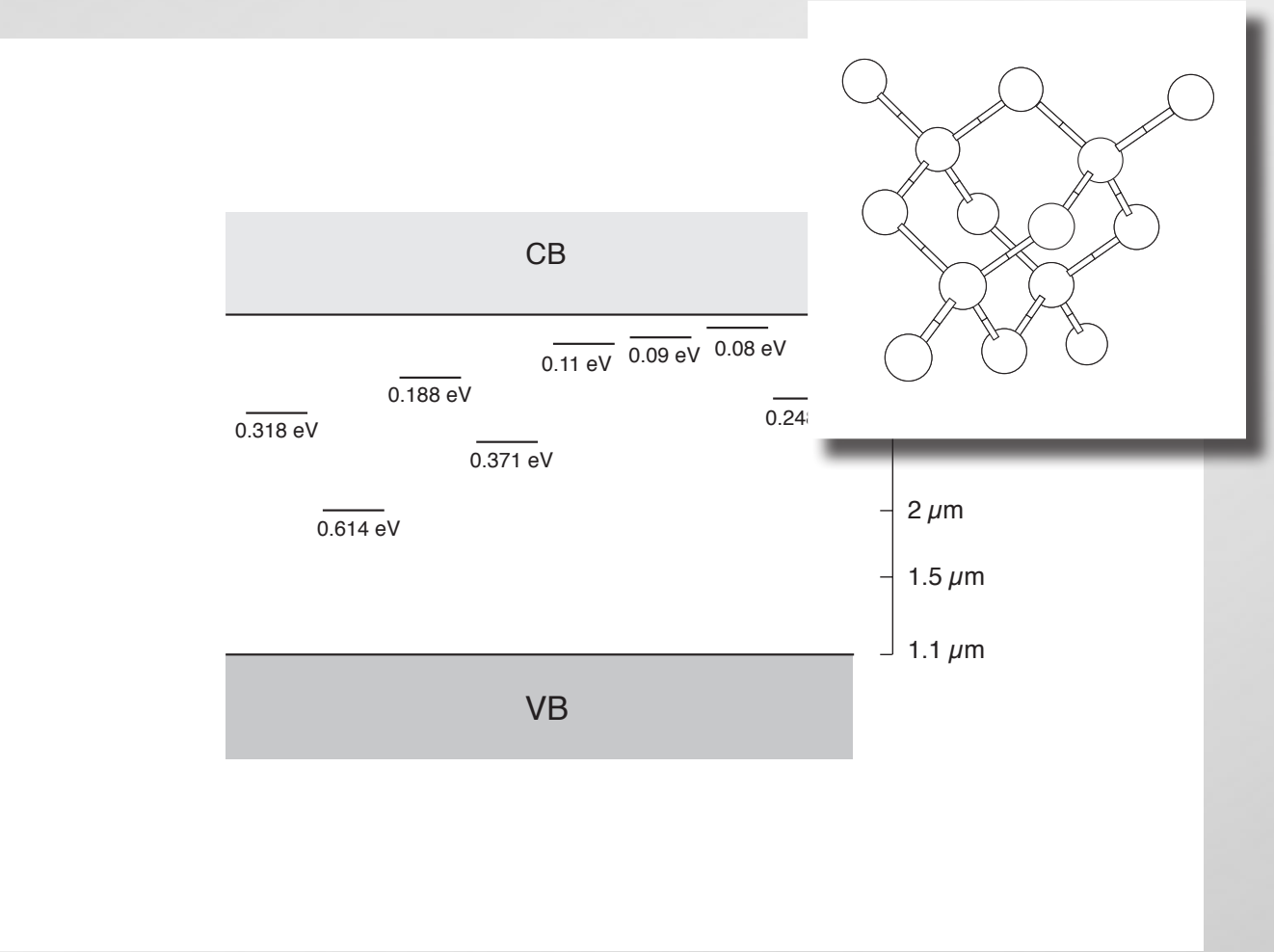

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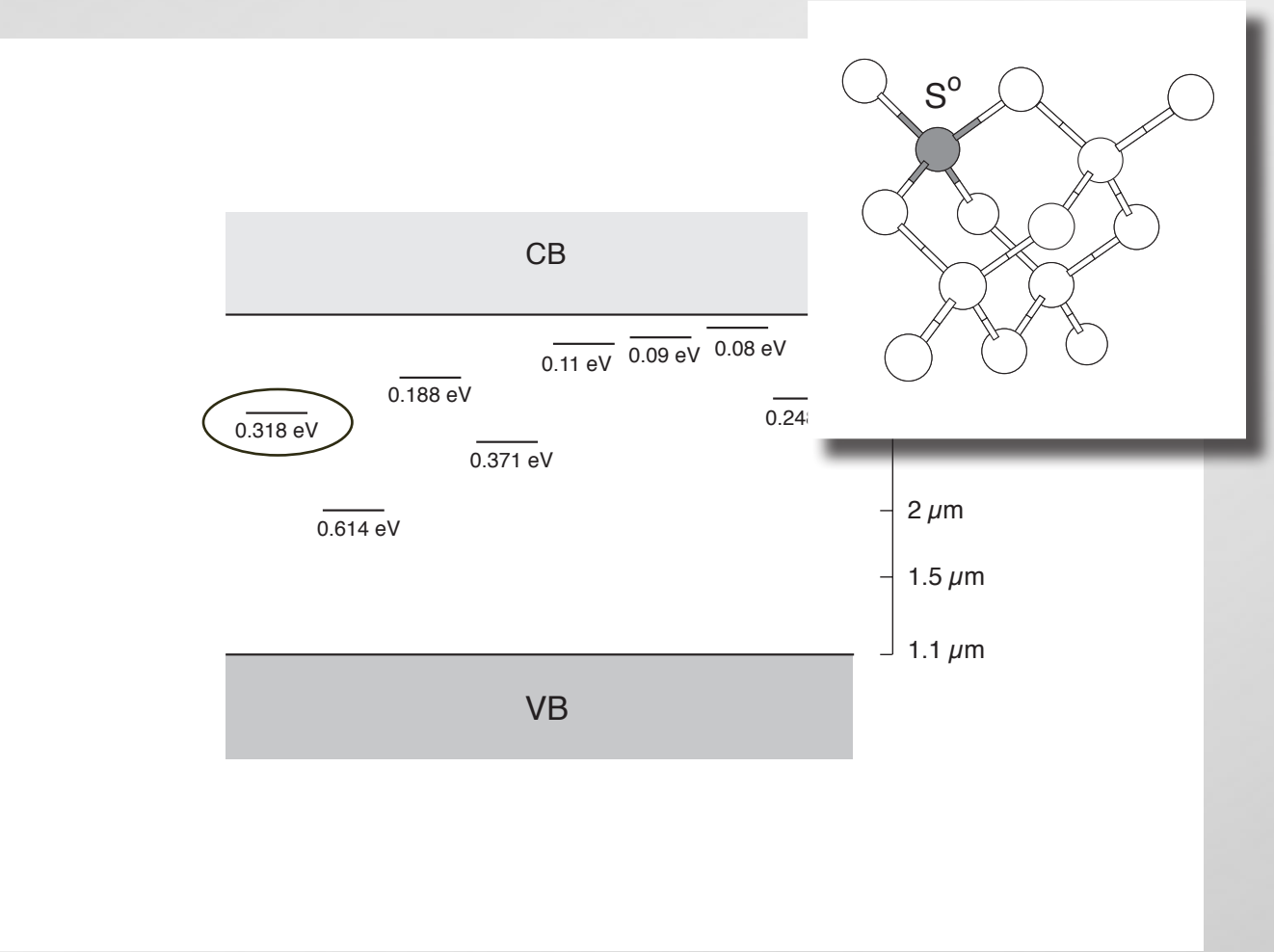

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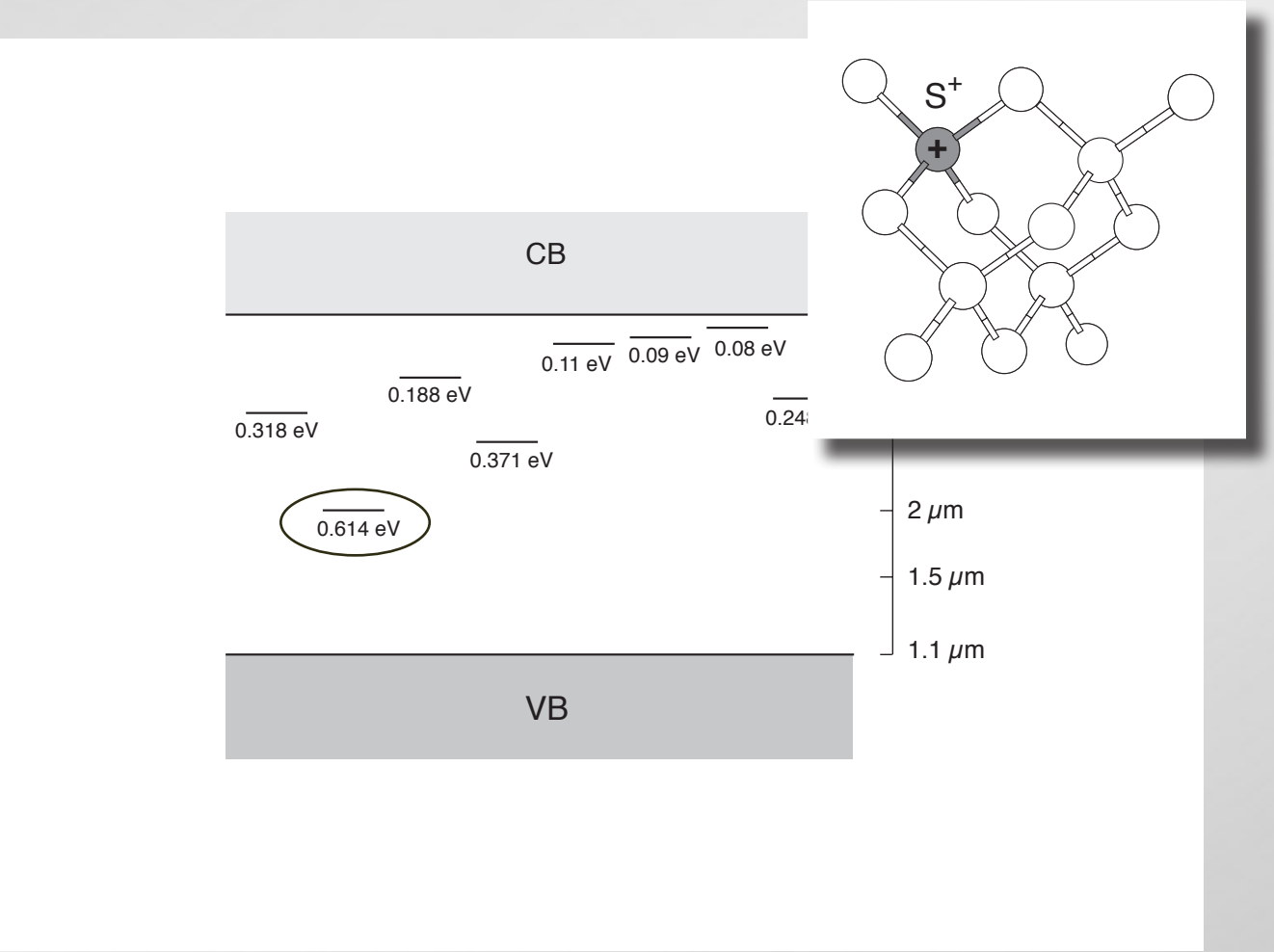

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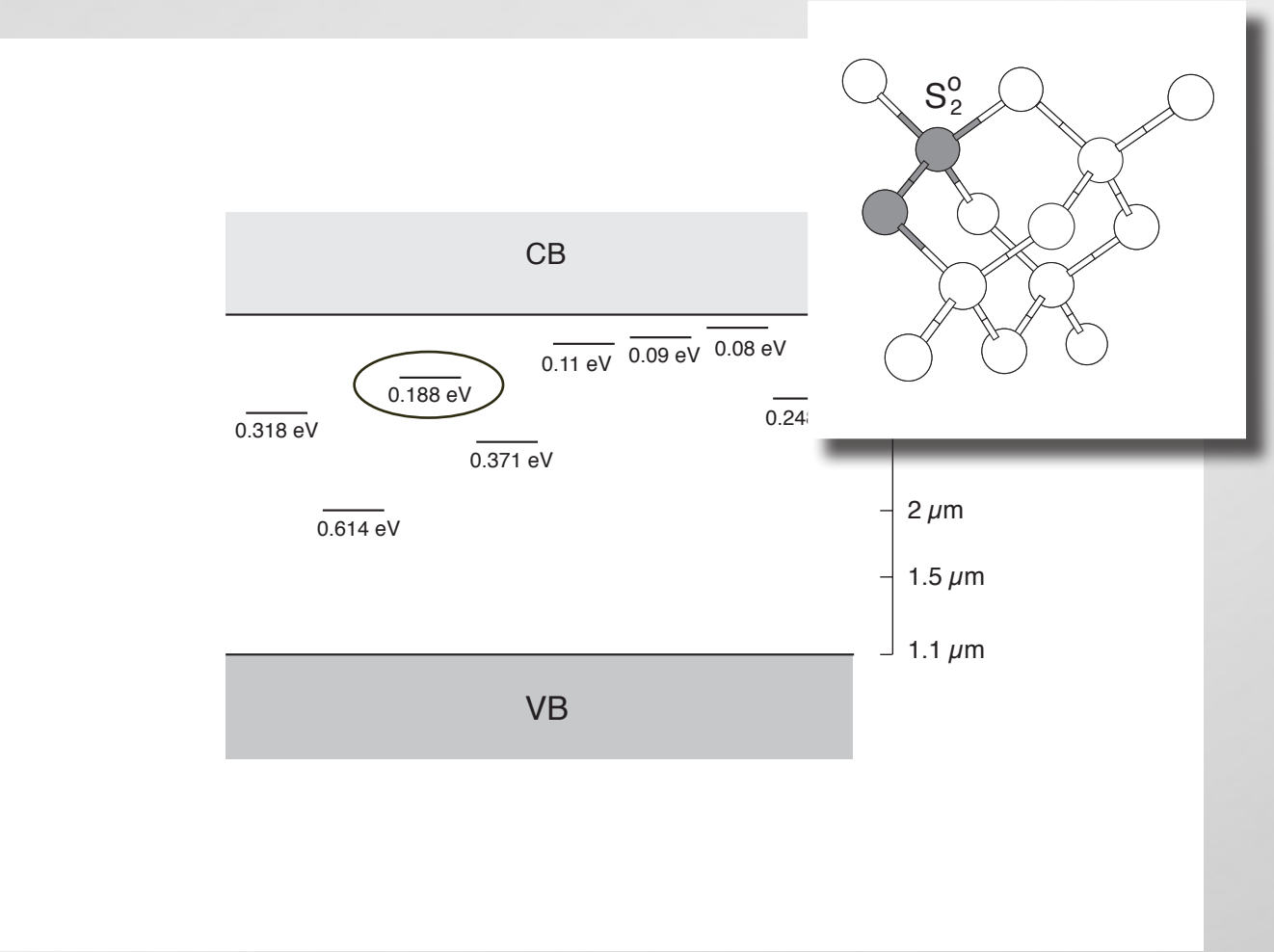

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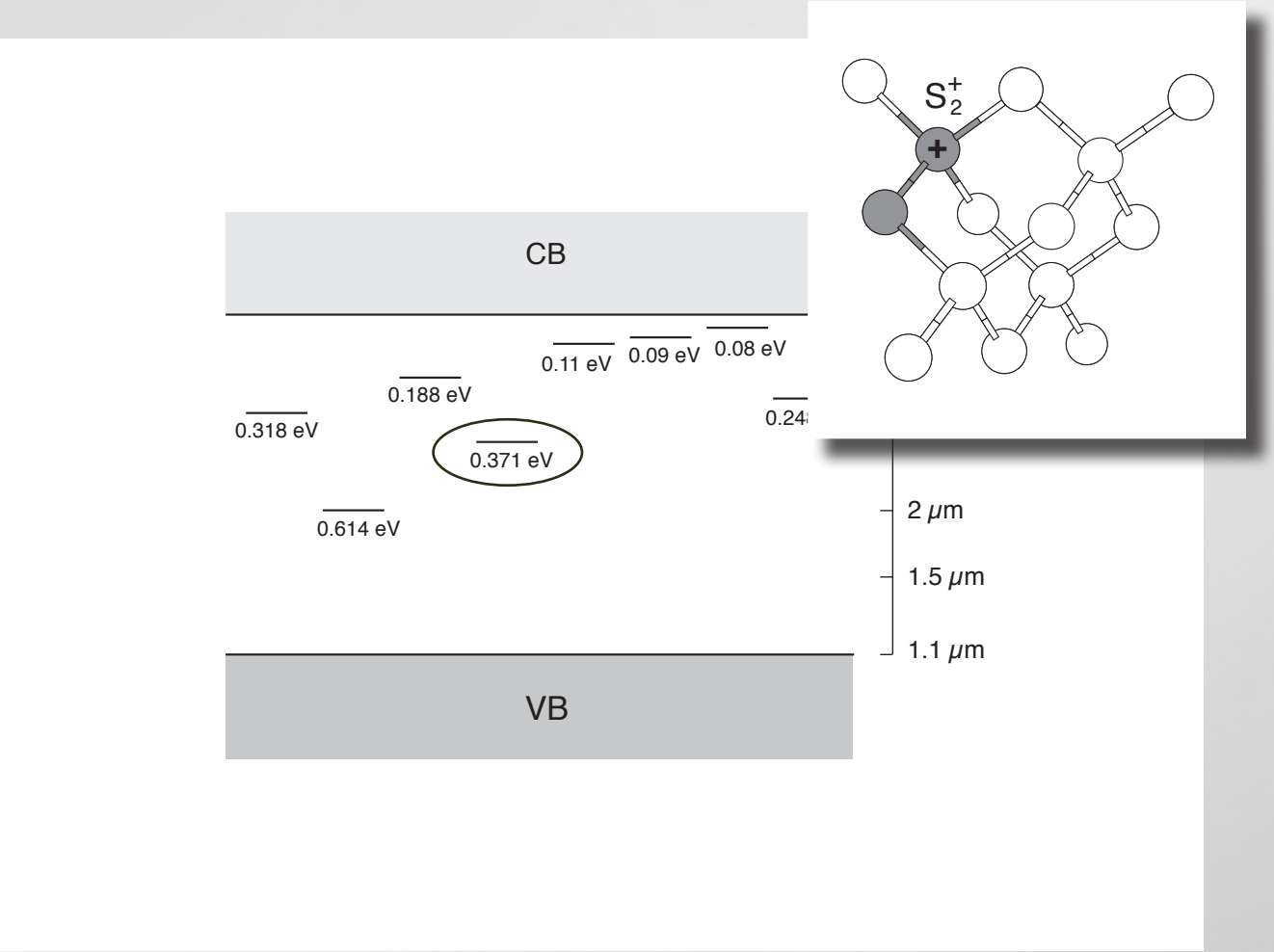

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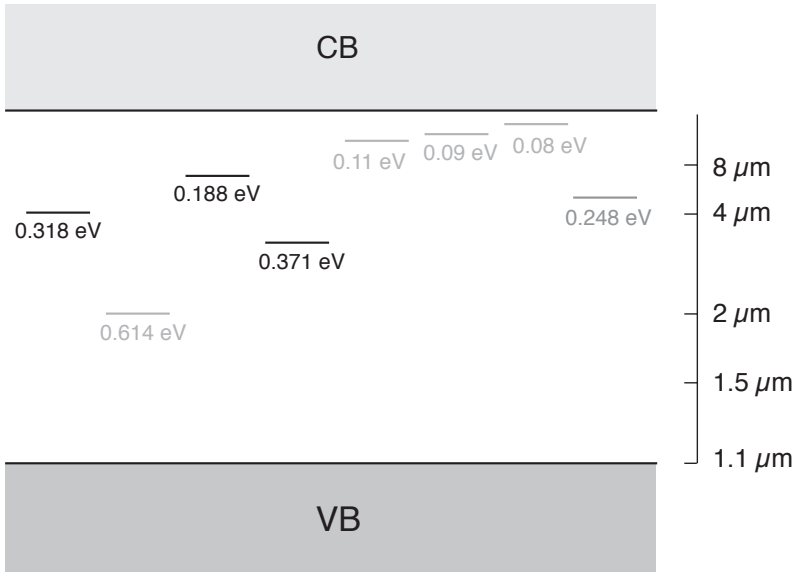
1 intermediate band

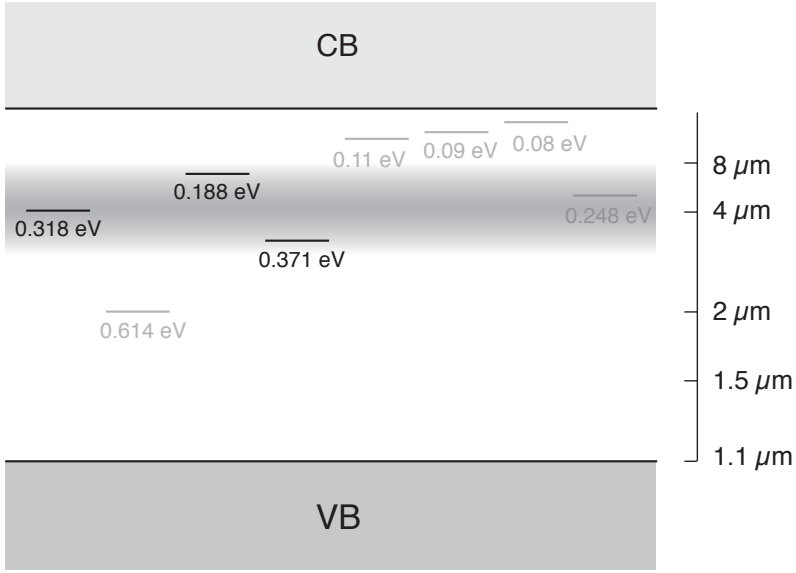
1 part in 10^6 sulfur introduces donor states in gap



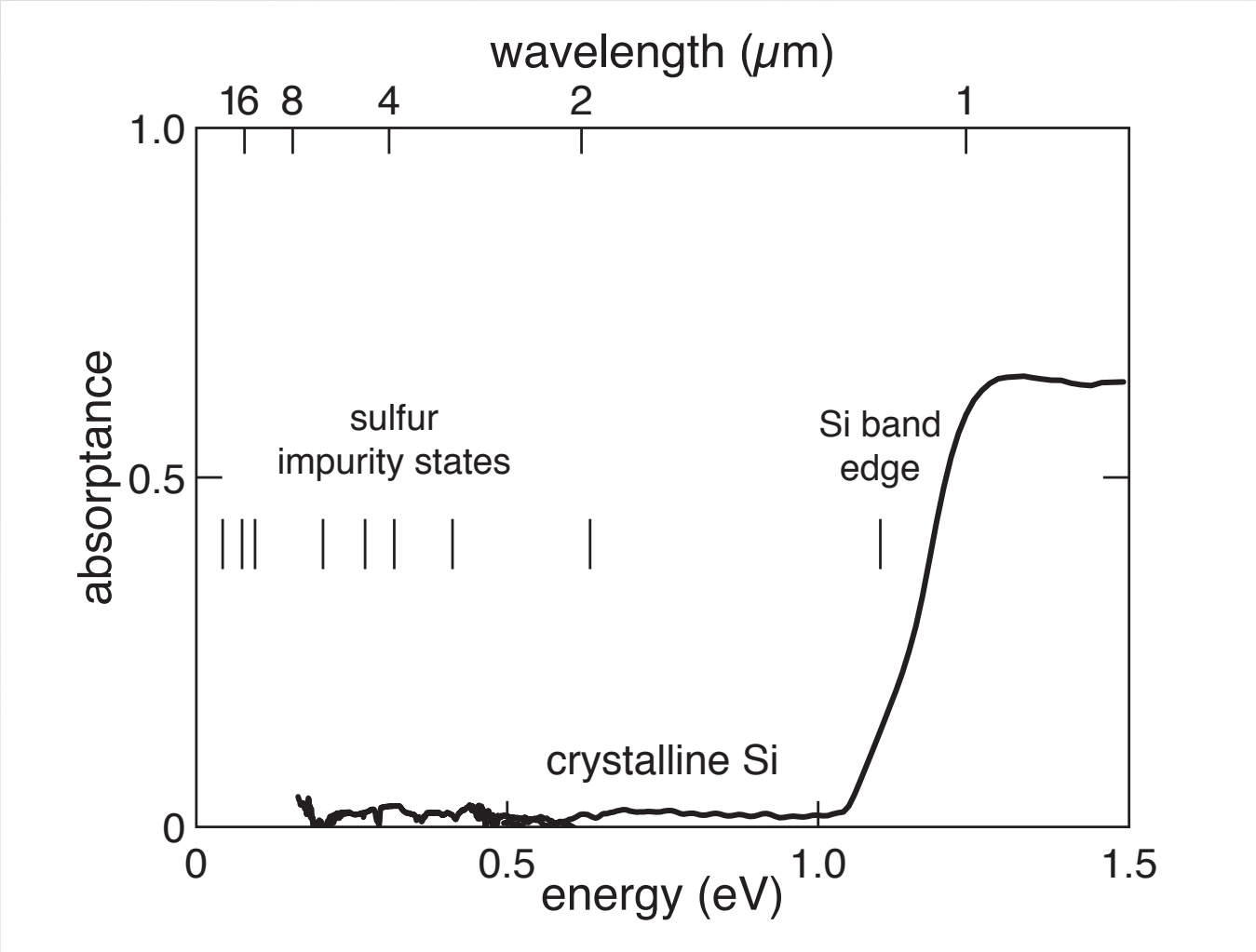
Janzén et al., Phys. Rev. B 29, 1907 (1984)

1 intermediate band

at high concentration states broaden into band

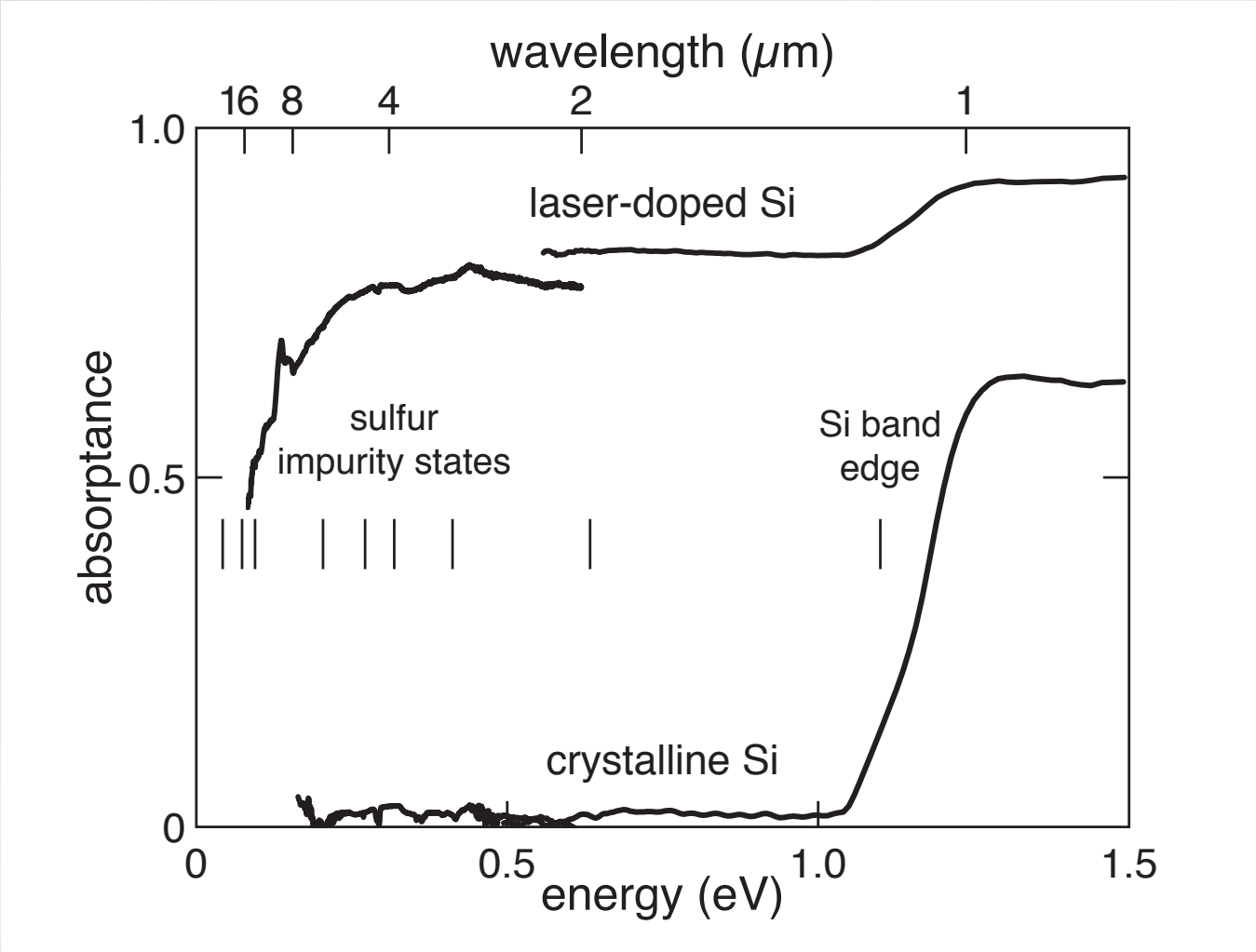


10^{-6} sulfur doping



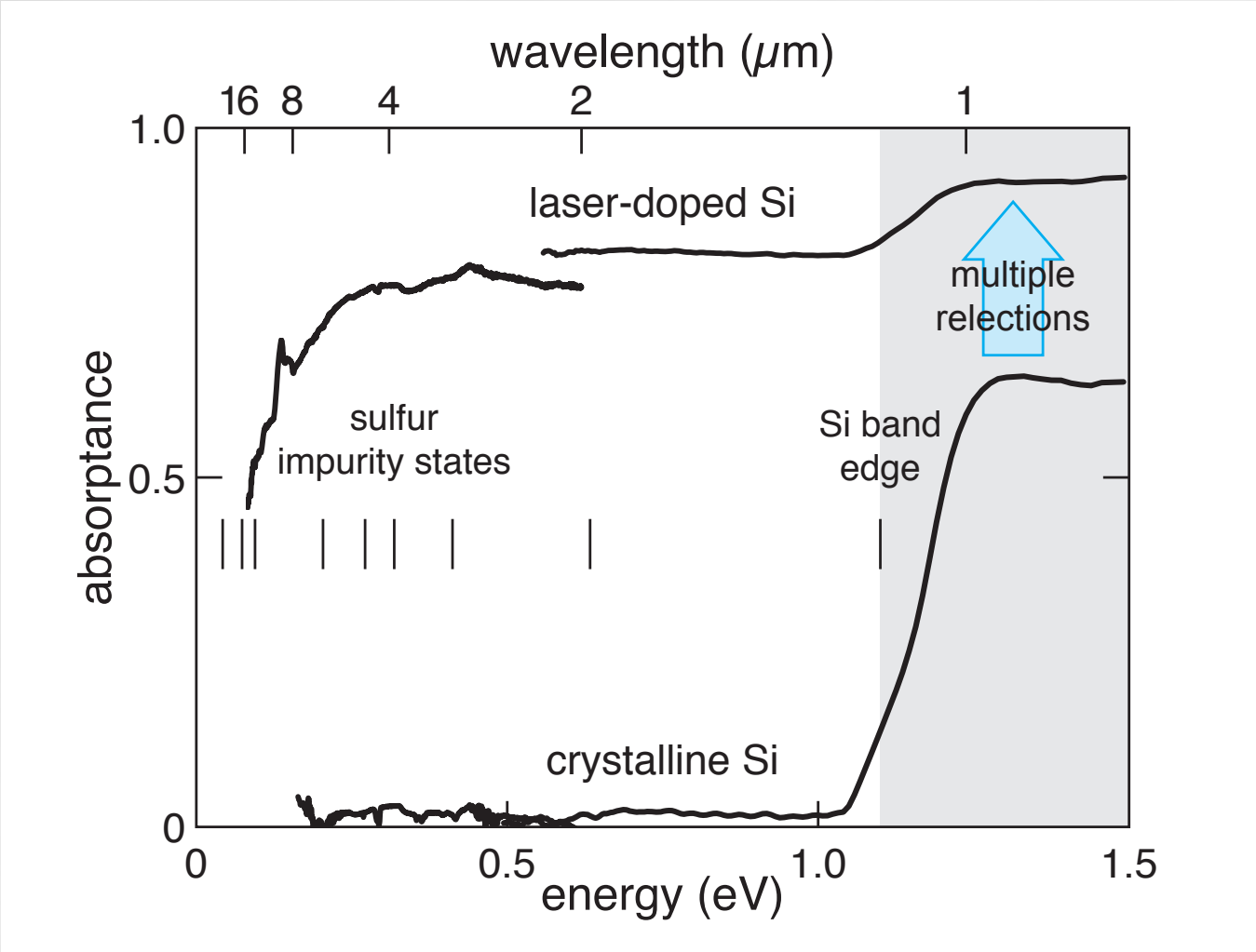
1 intermediate band

laser-doped S:Si



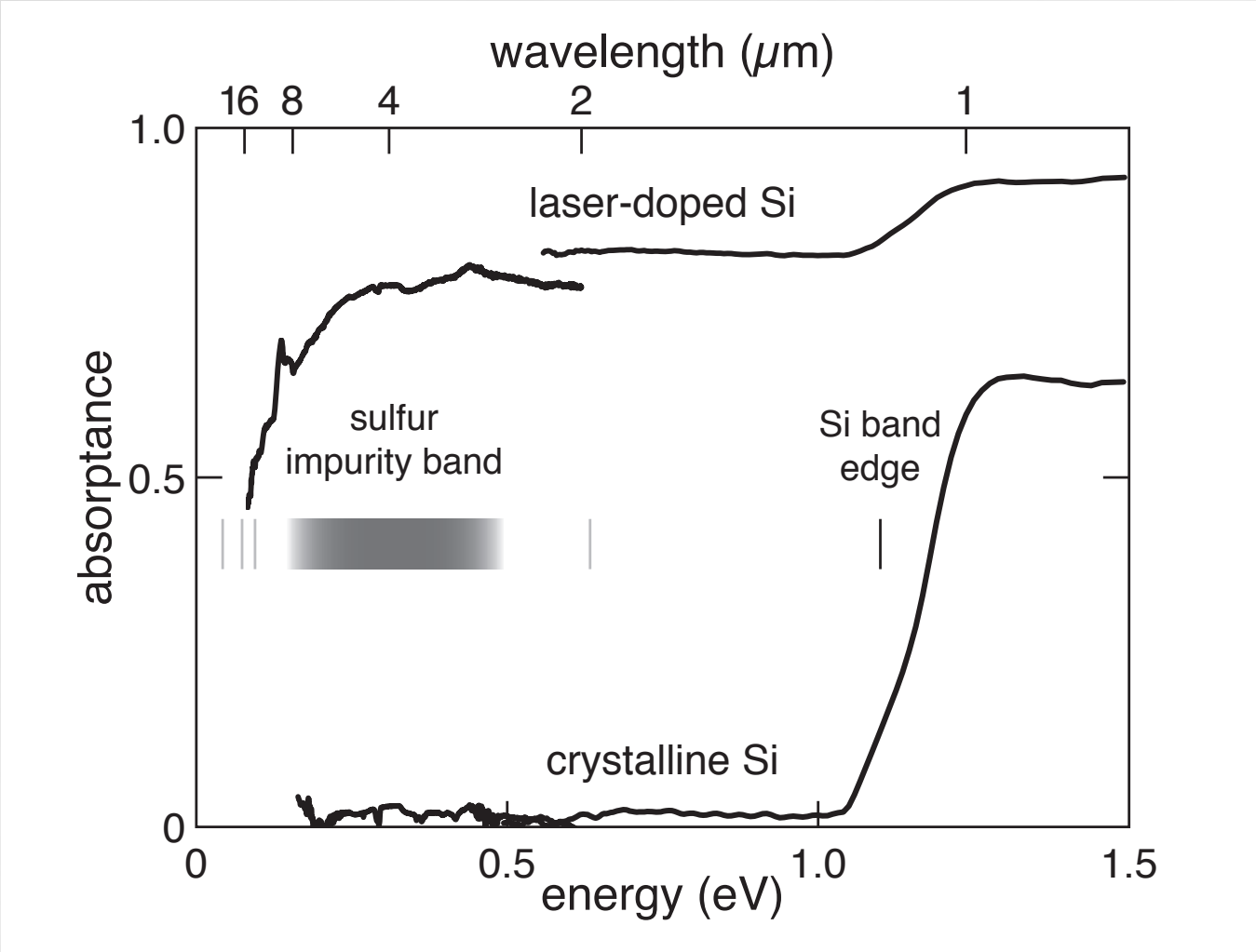
1 intermediate band

laser-doped S:Si



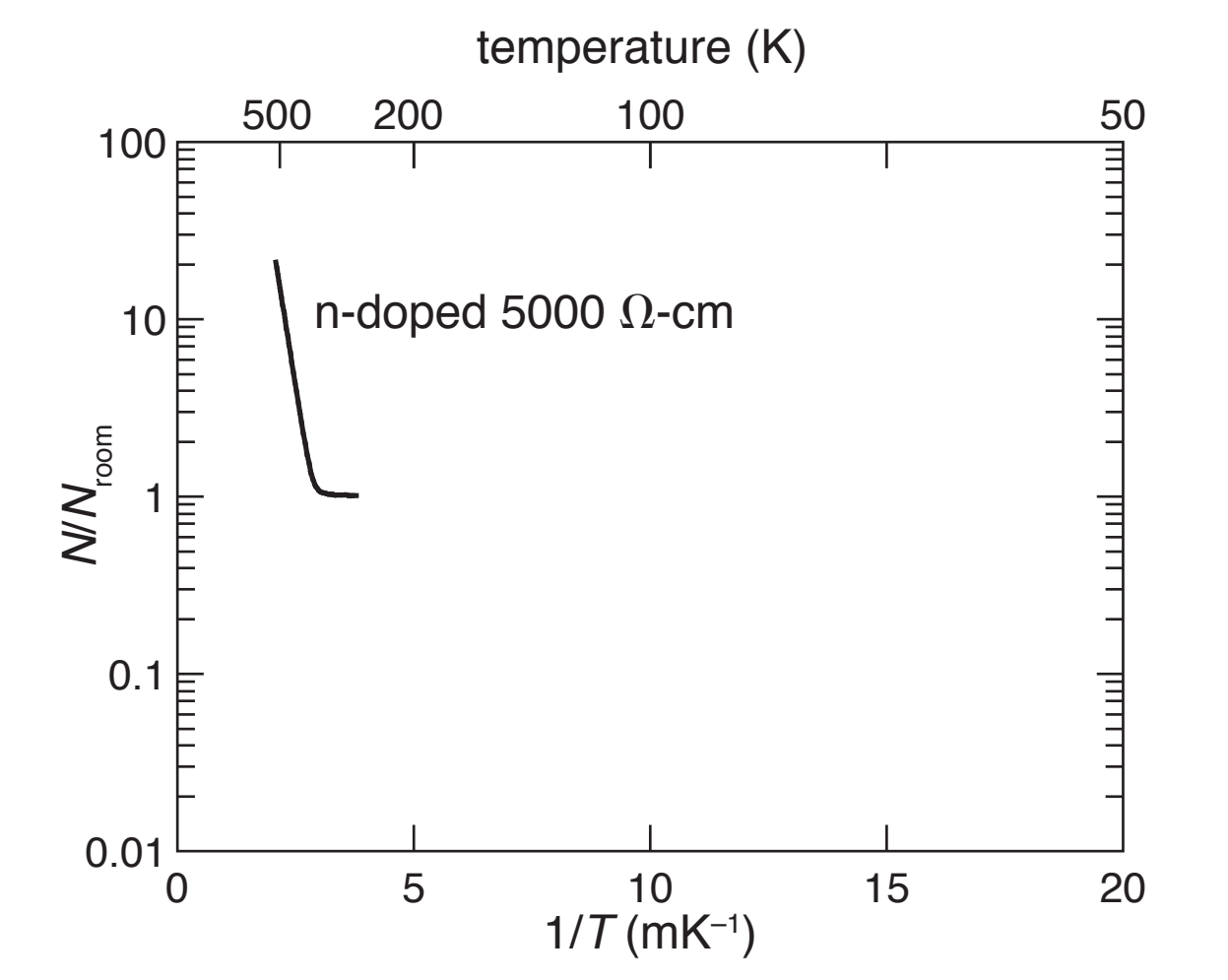
1 intermediate band

laser-doped S:Si

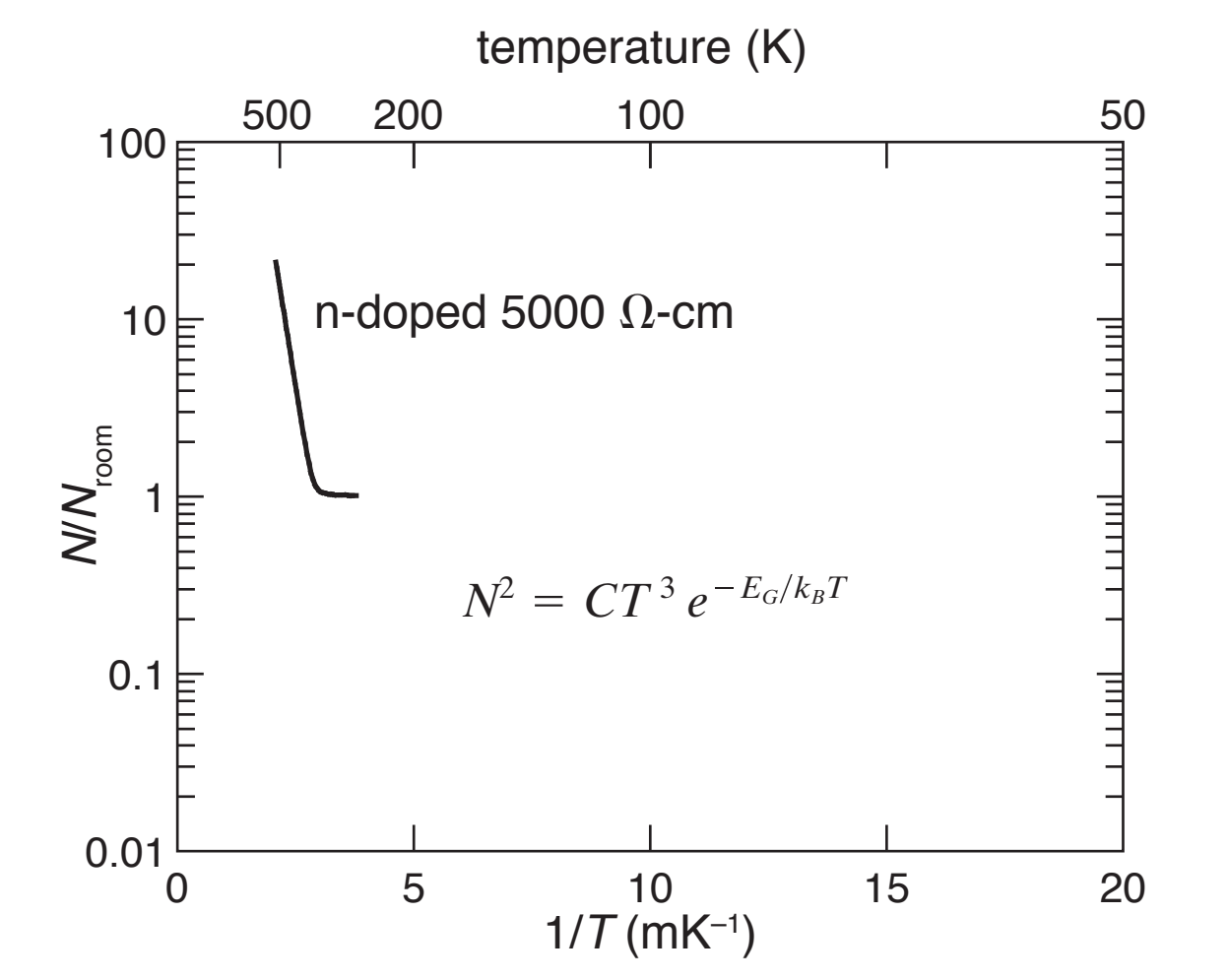


1 intermediate band

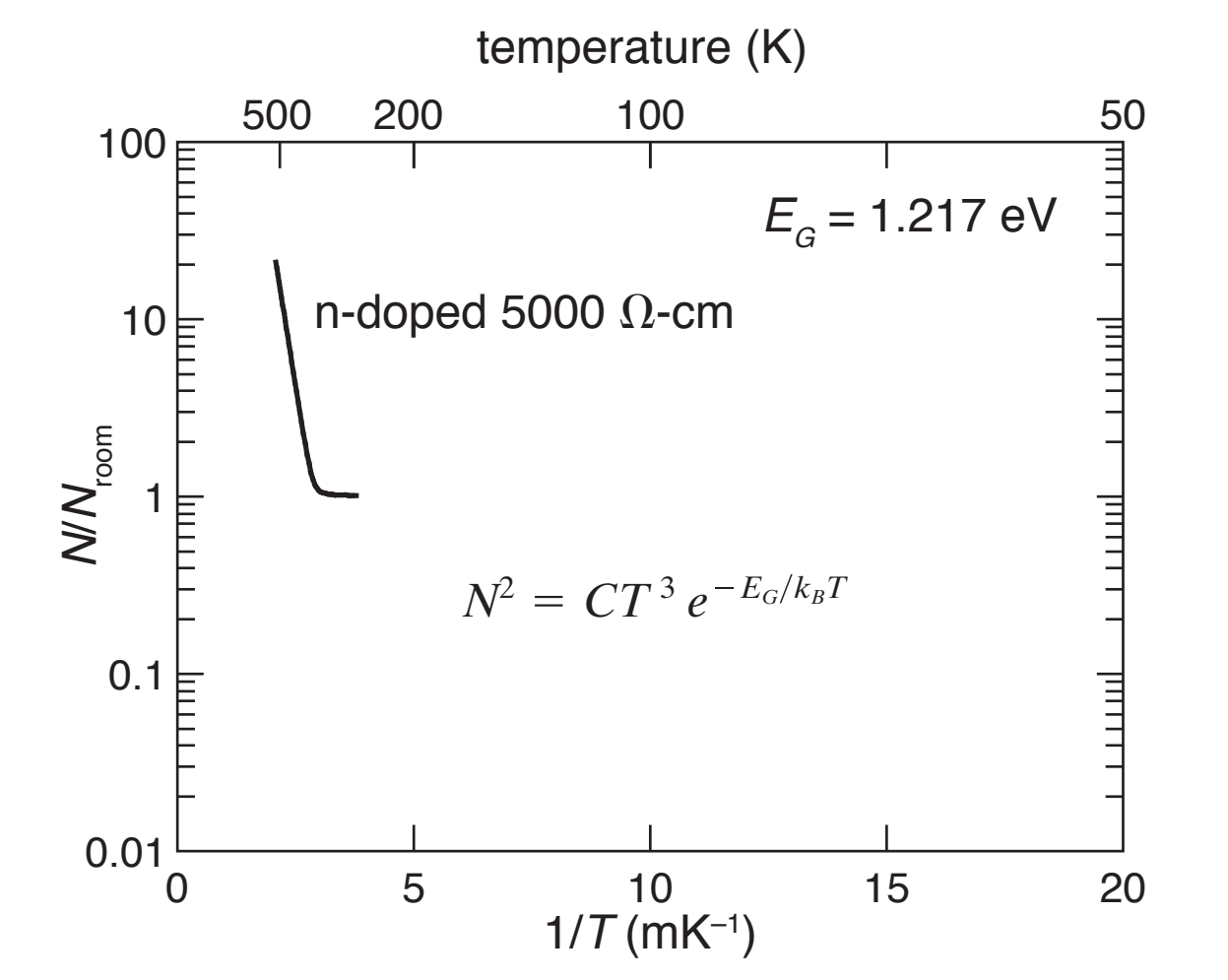
Hall measurements



Hall measurements

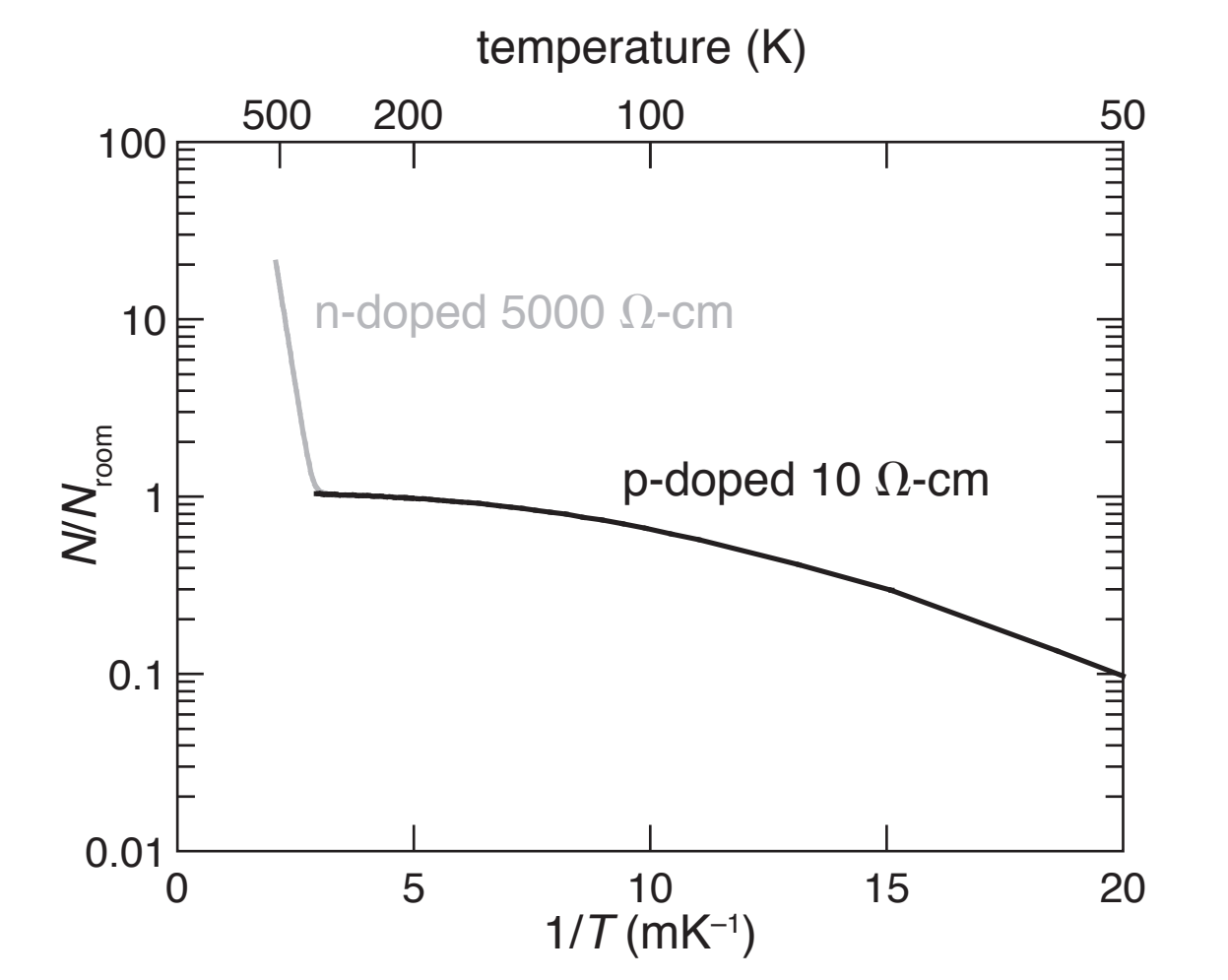


Hall measurements



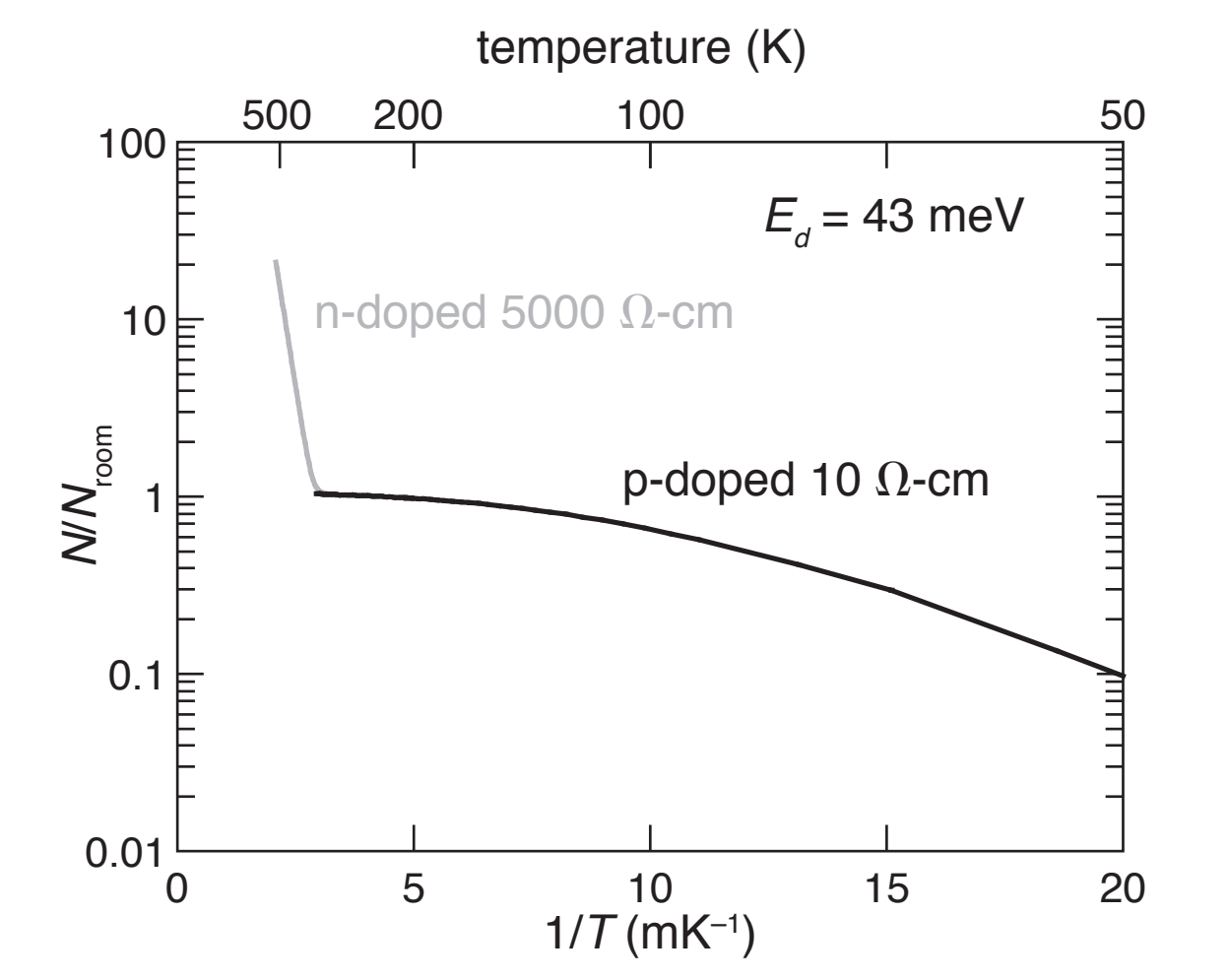
1 intermediate band

Hall measurements



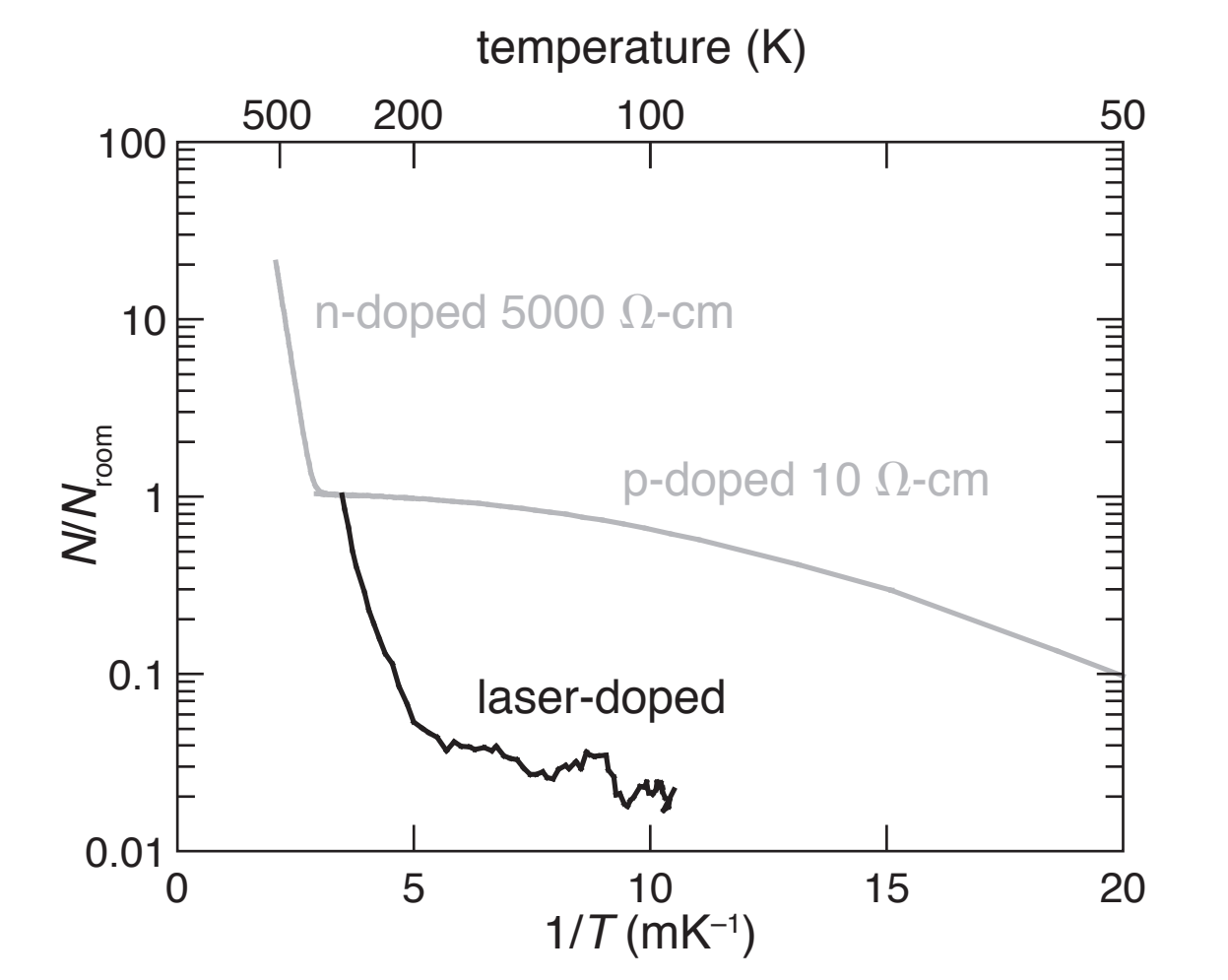
1 intermediate band

Hall measurements



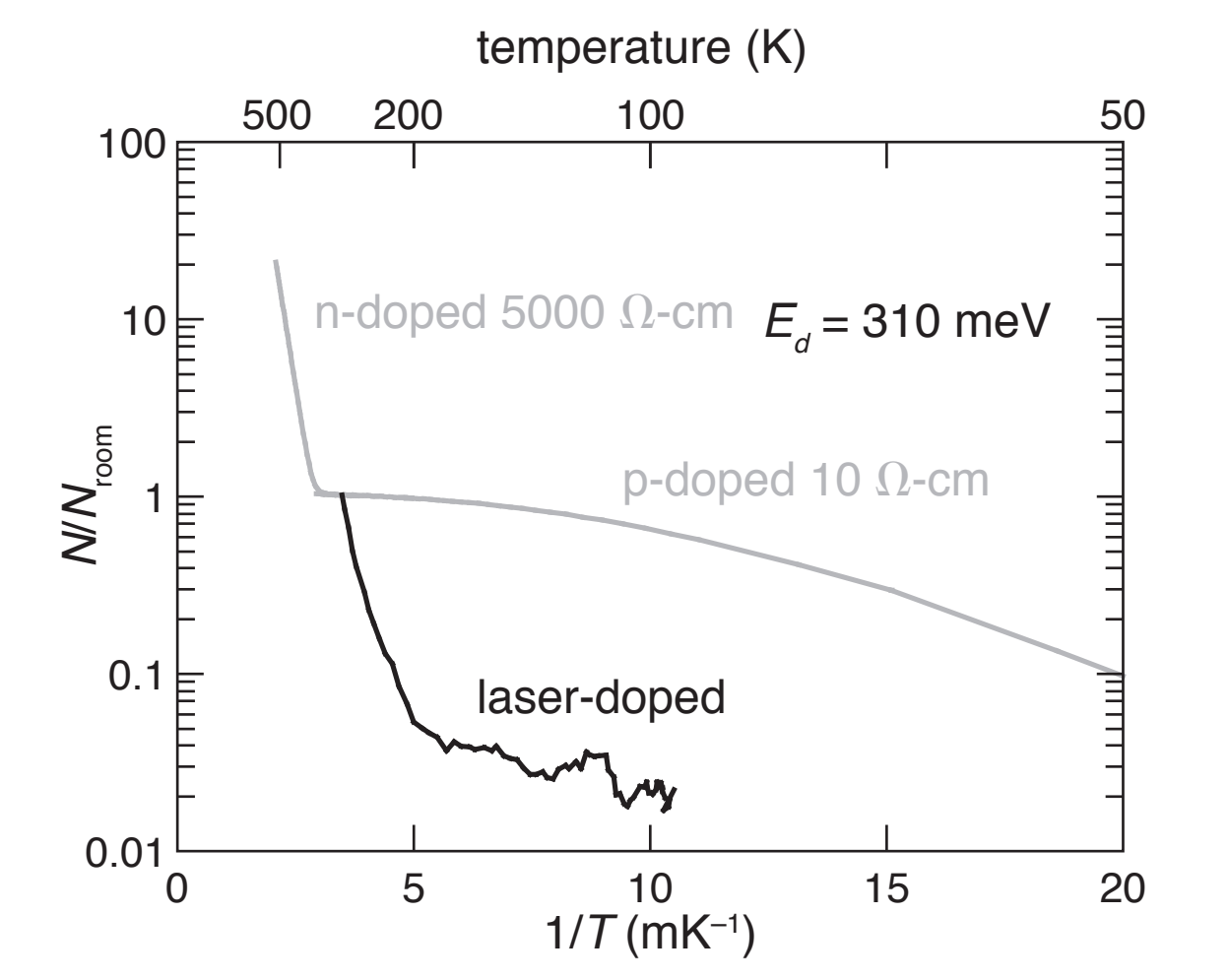
1 intermediate band

Hall measurements



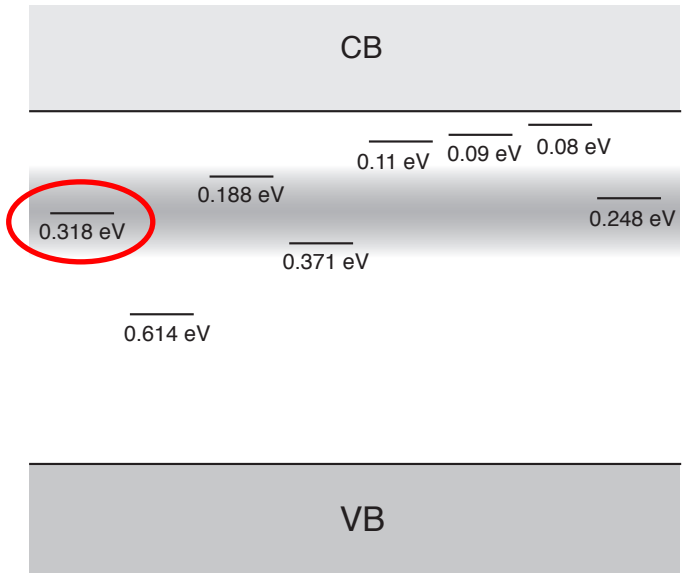
1 intermediate band

Hall measurements



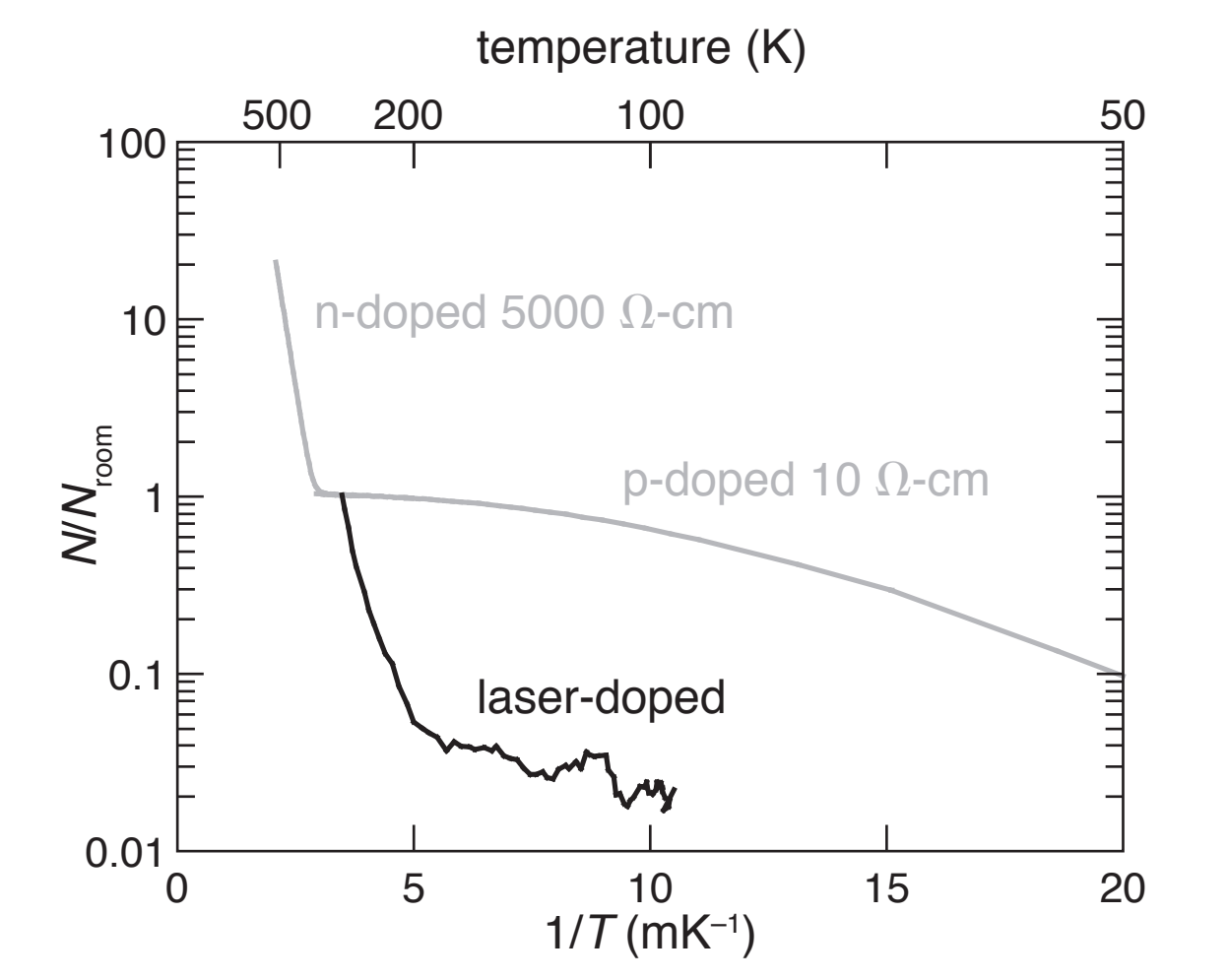
1 intermediate band

impurity (donor) band centered at 310 meV



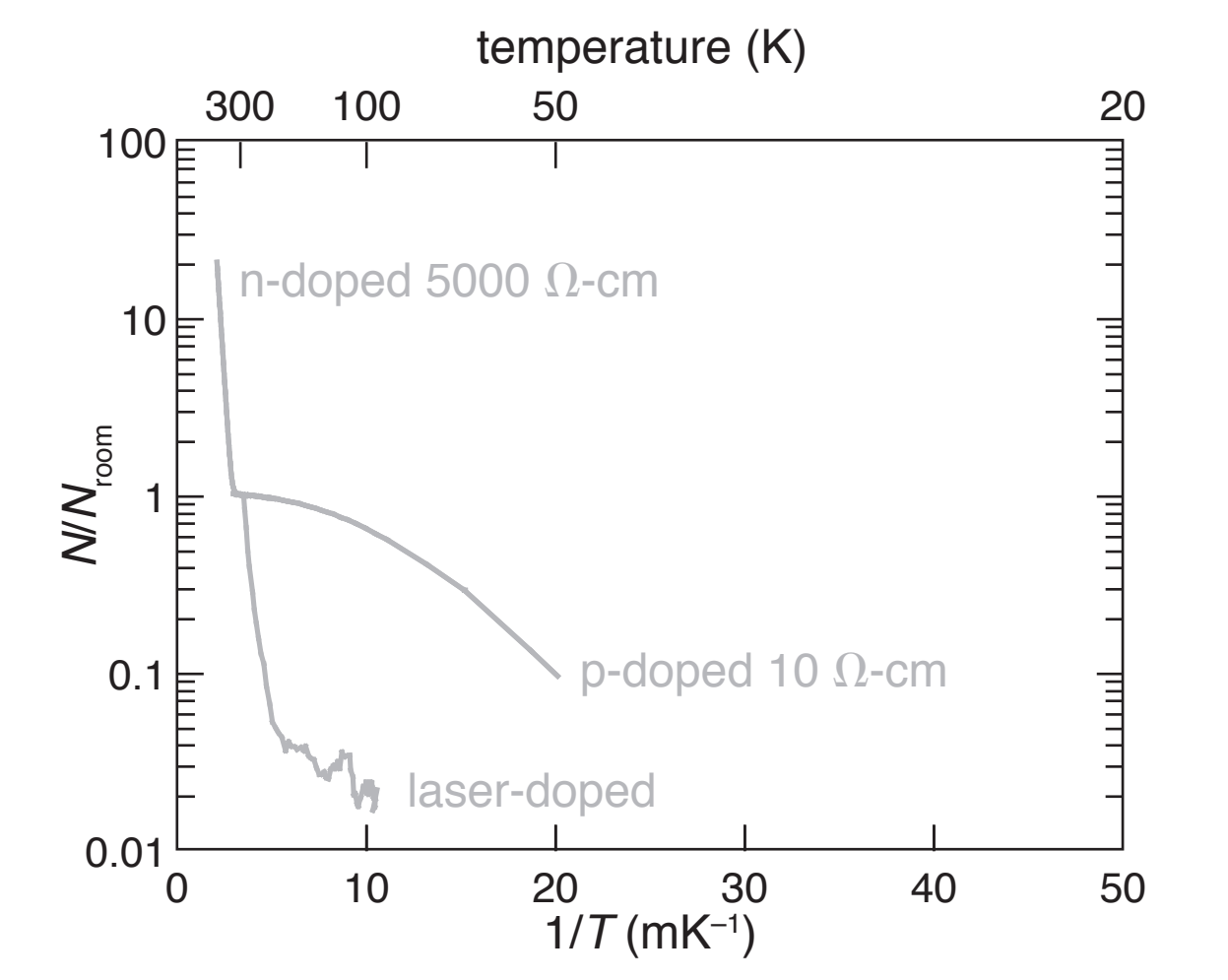
1 intermediate band

Hall measurements



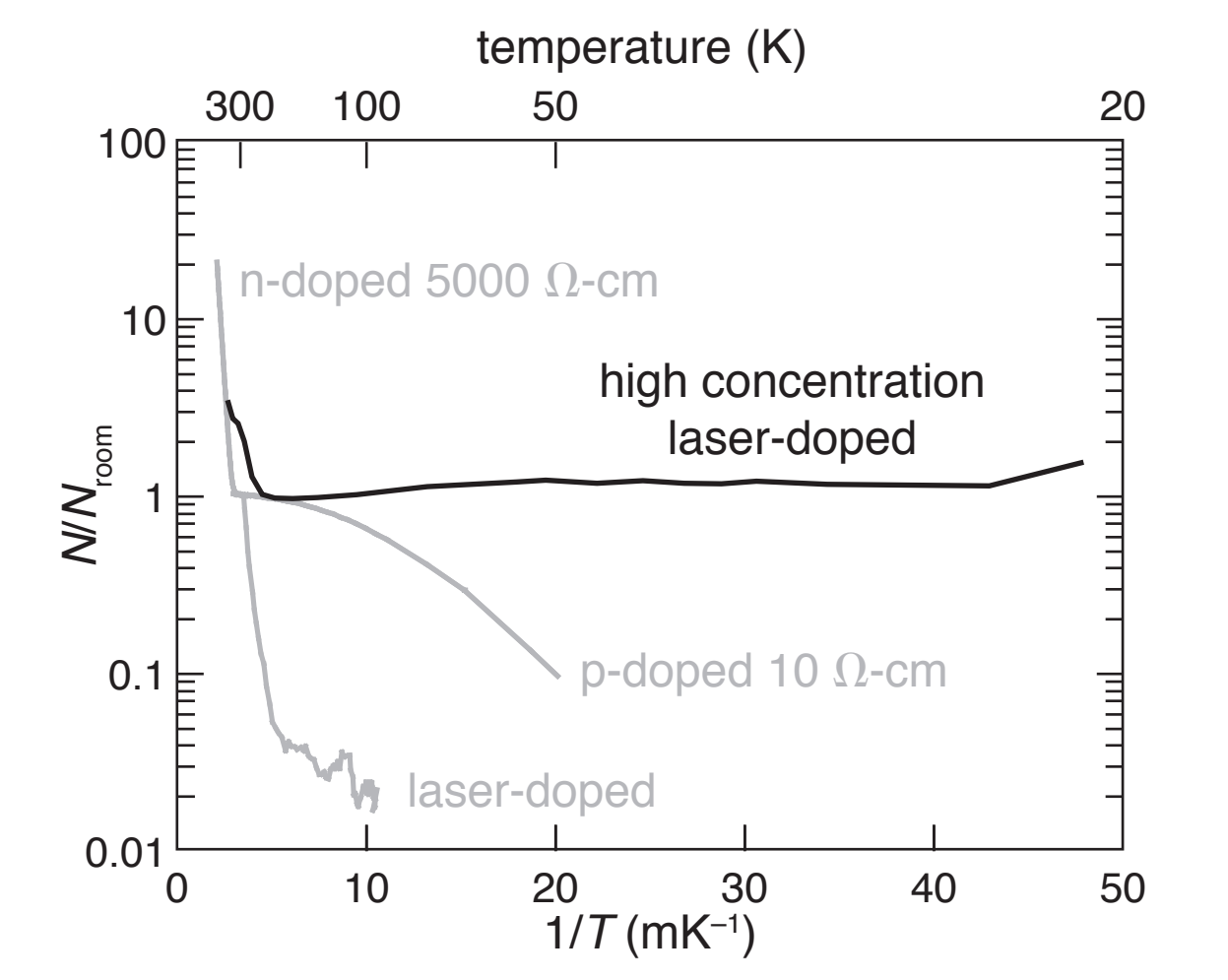
1 intermediate band

Hall measurements

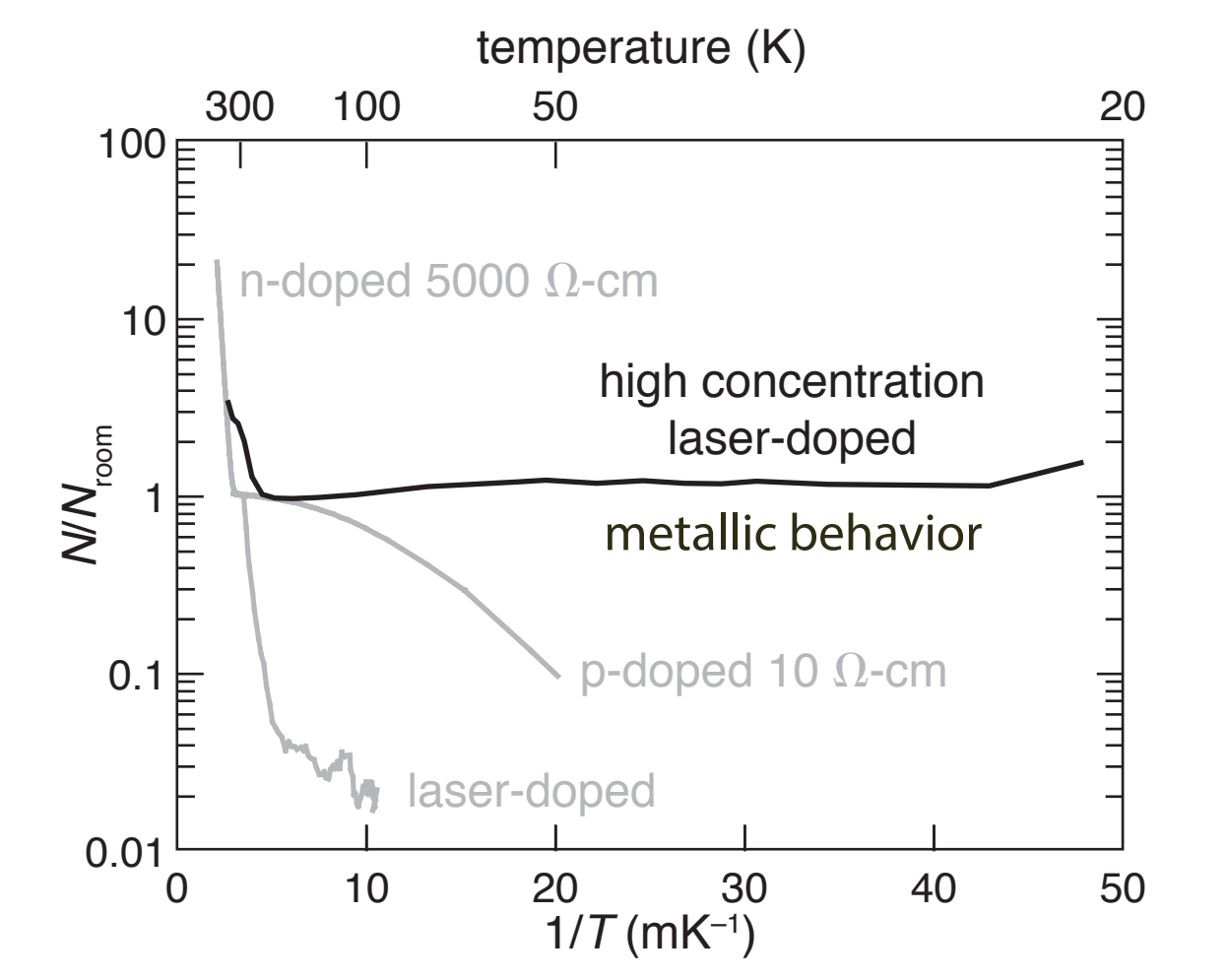


1 intermediate band

Hall measurements

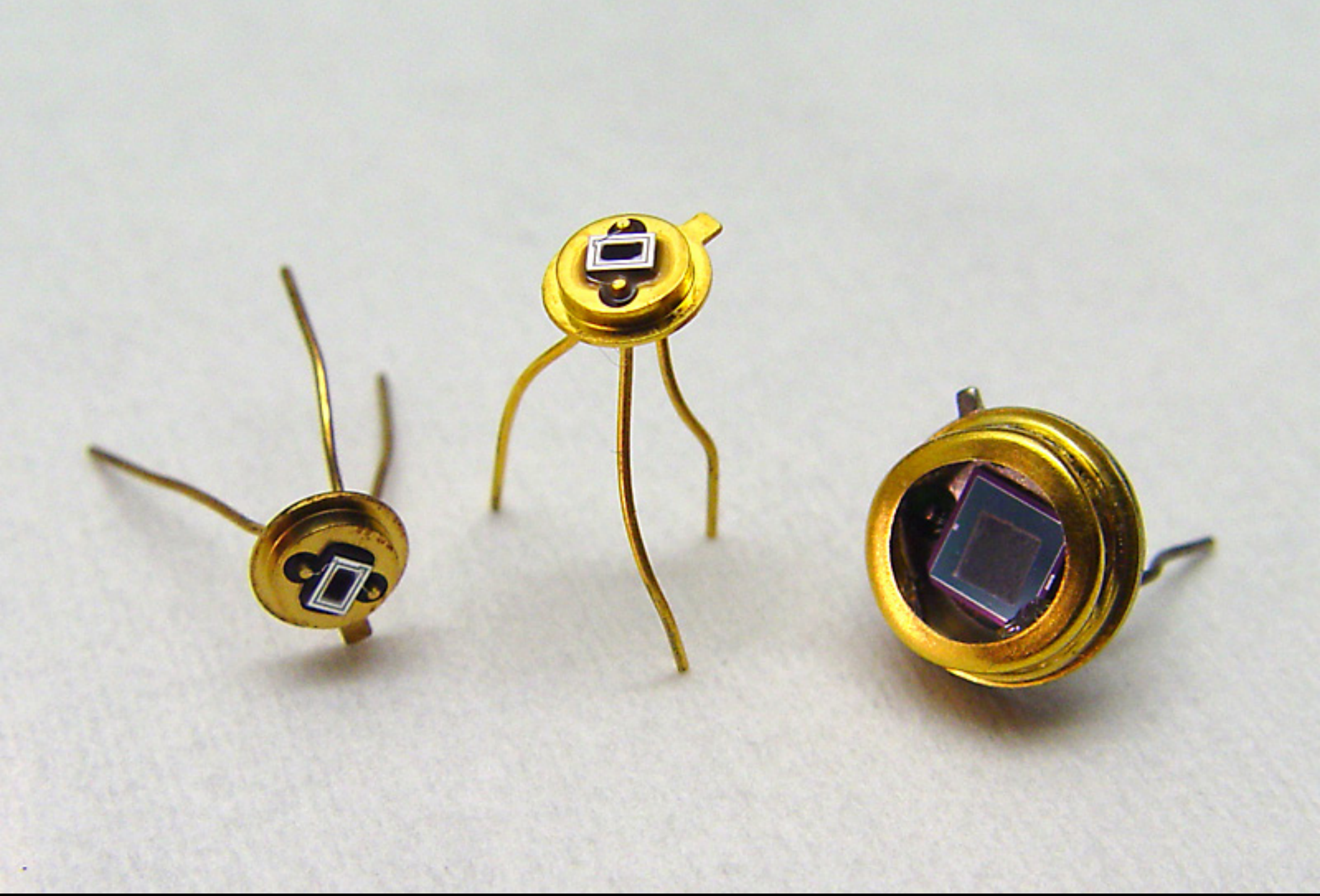


Hall measurements



Things to keep in mind

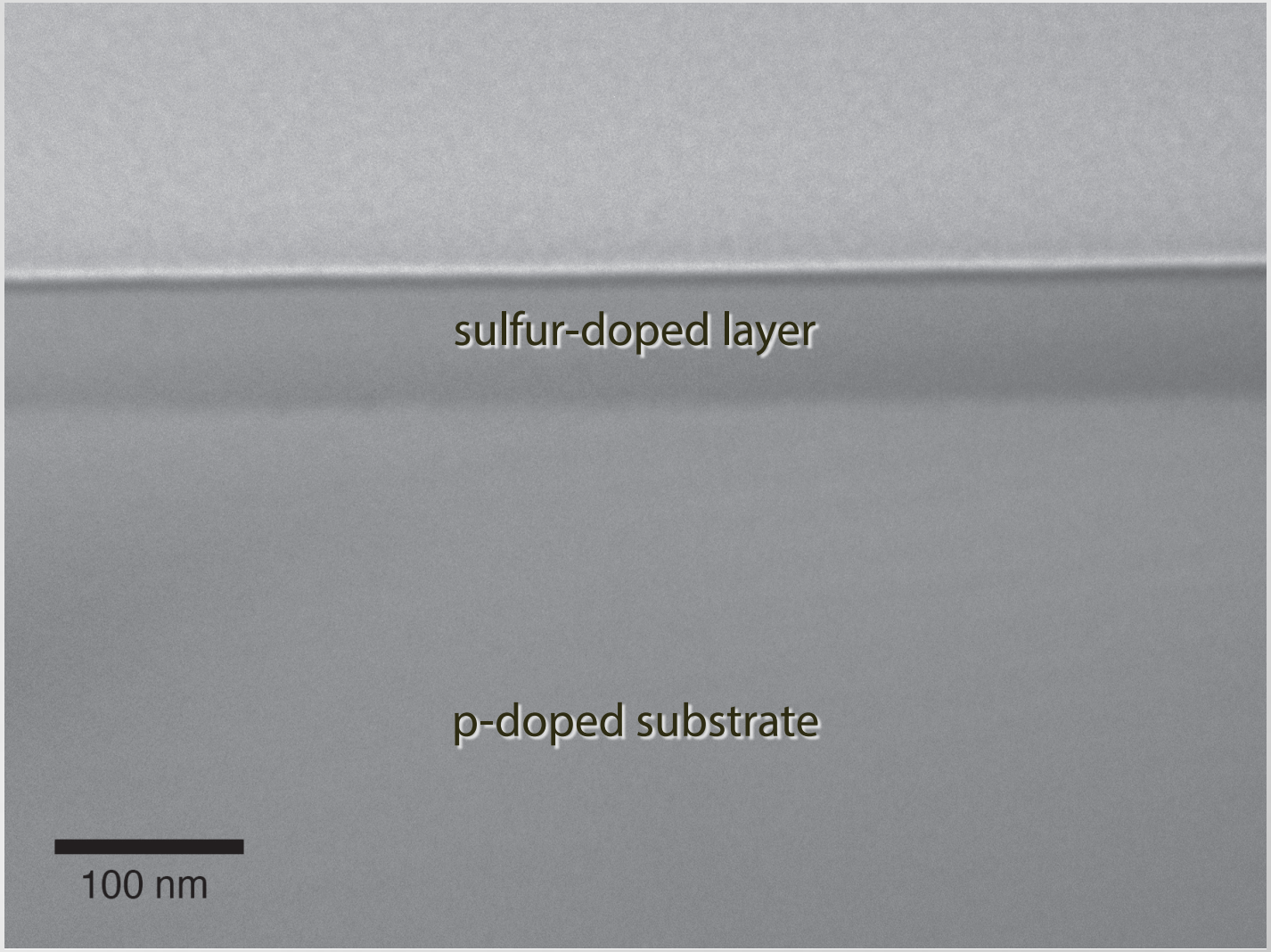
- IR absorption rolls off around 8 μm
- evidence of intermediate band formation
- intermediate band due to substitutional S donors
- intermediate band 0–300 meV below CB



1 intermediate band

2 Si devices

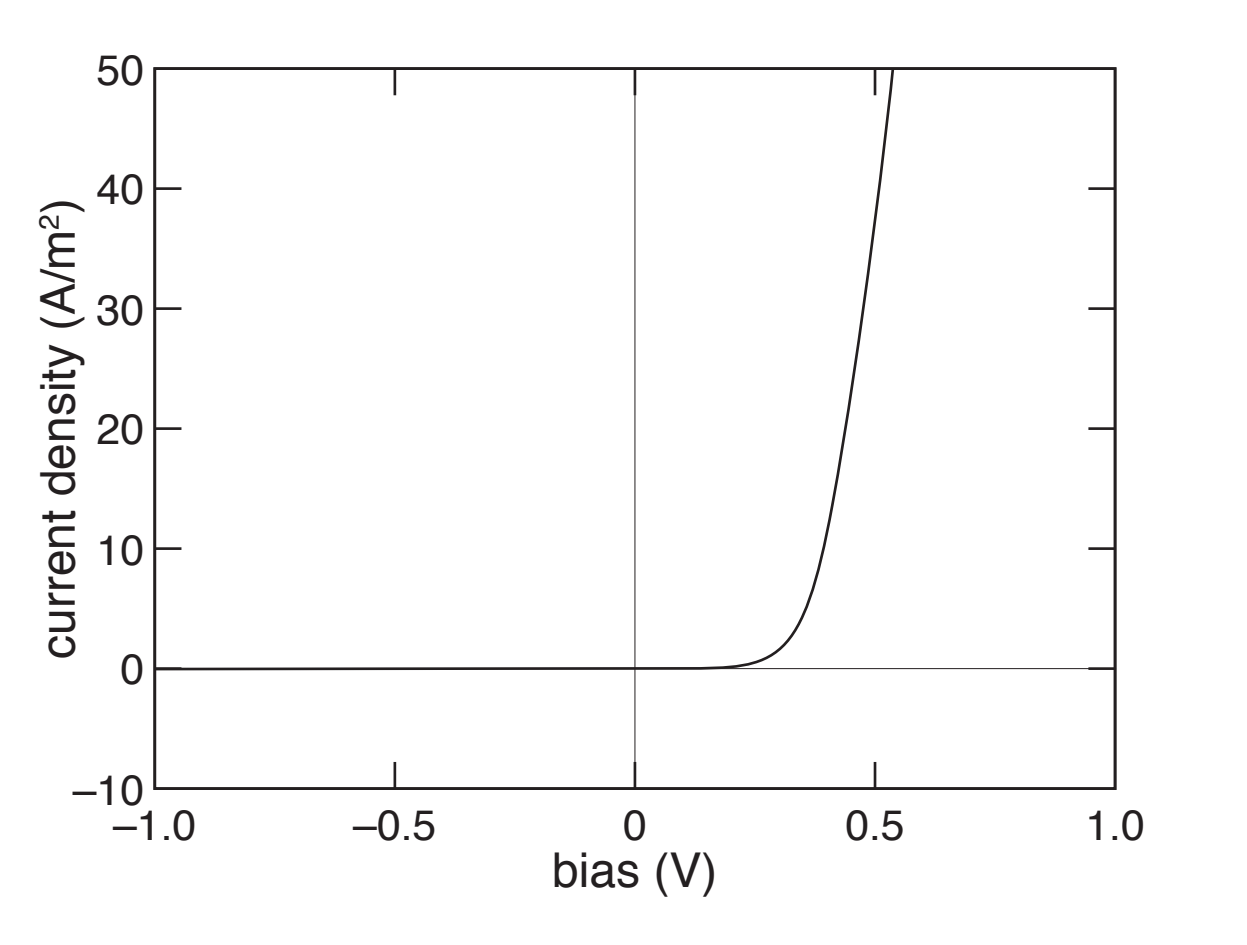
should have shallow junction below surface



1 intermediate band

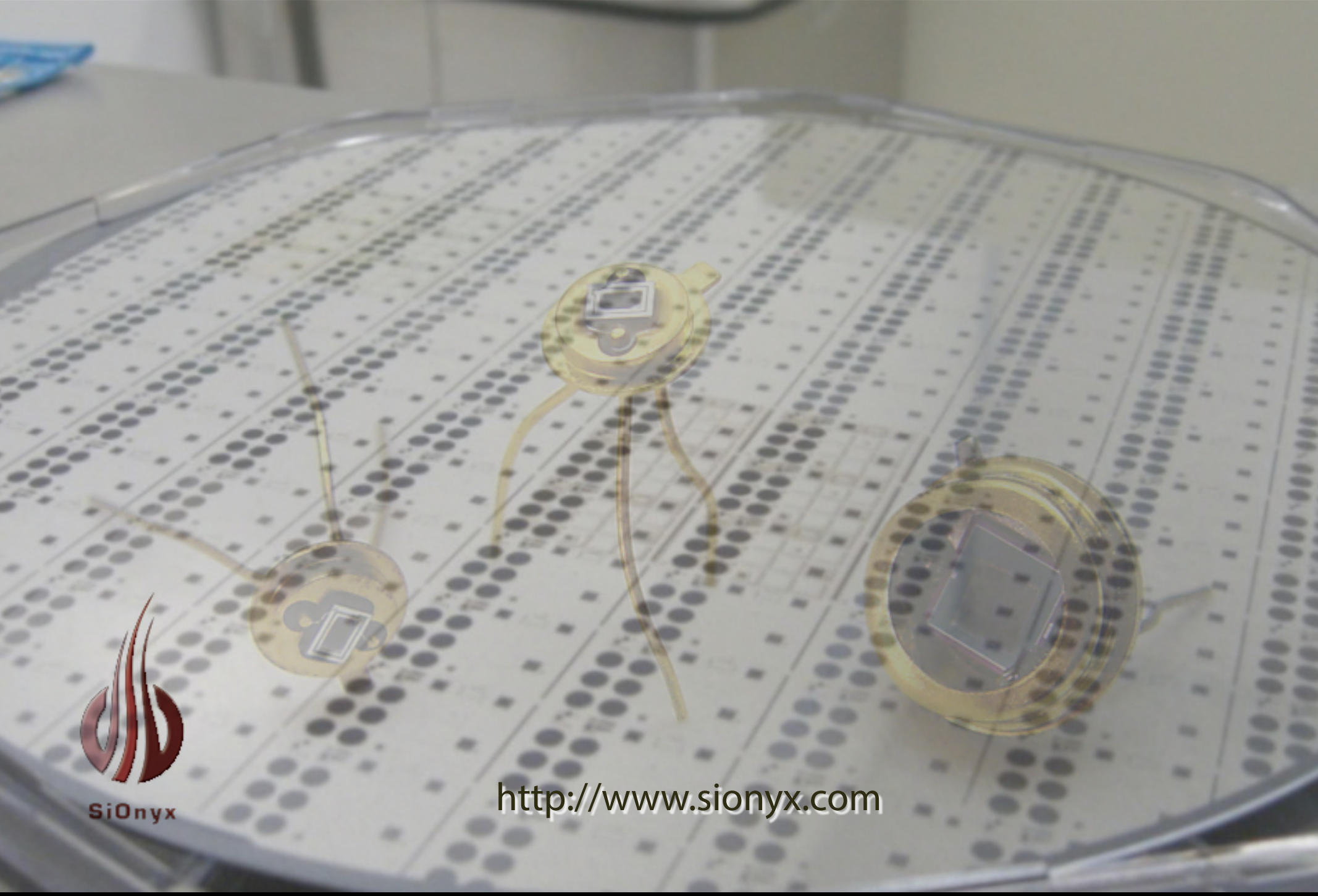
2 Si devices

excellent rectification (after annealing)



1 intermediate band

2 Si devices



1 intermediate band

2 Si devices

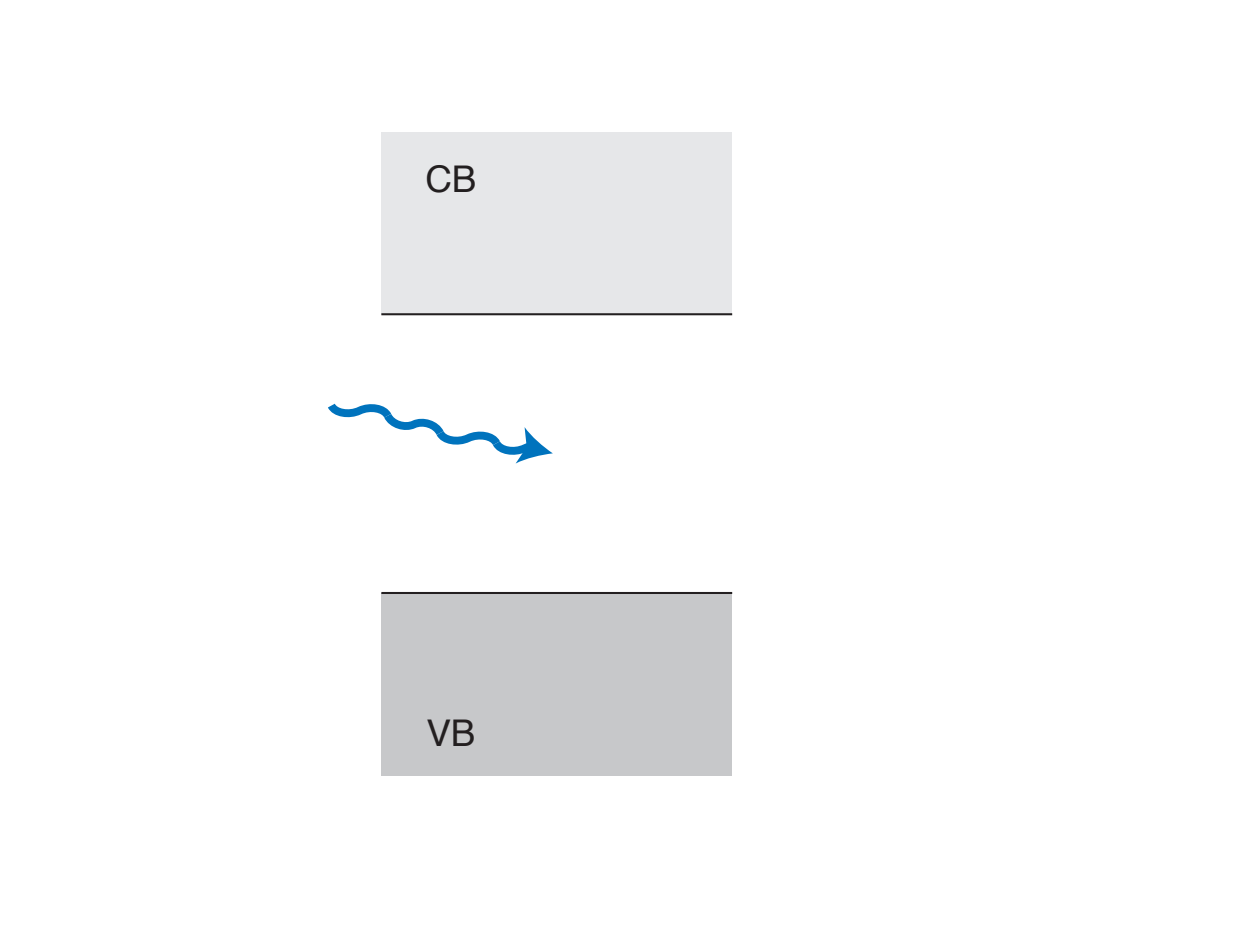
Potential benefits for photovoltaics

- surface structure
- absorption in submicrometer layer
- extended IR absorption
- intermediate band

1 intermediate band

2 Si devices

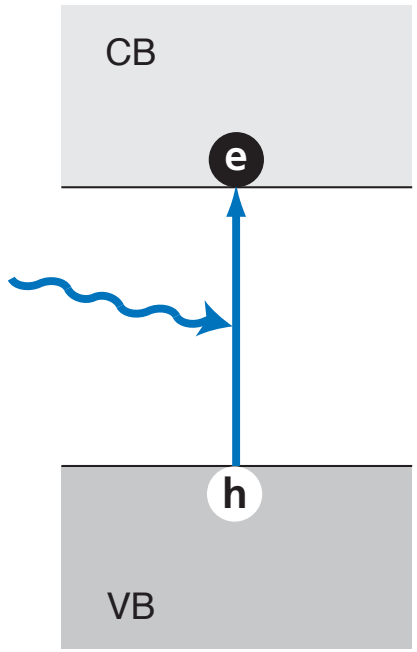
photon with gap energy



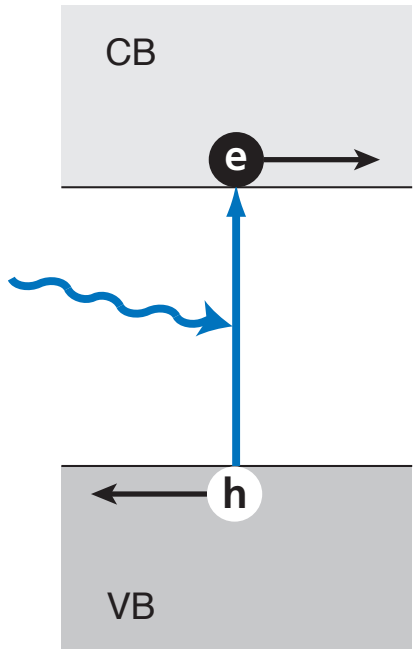
1 intermediate band

2 Si devices

photon creates electron-hole pair…



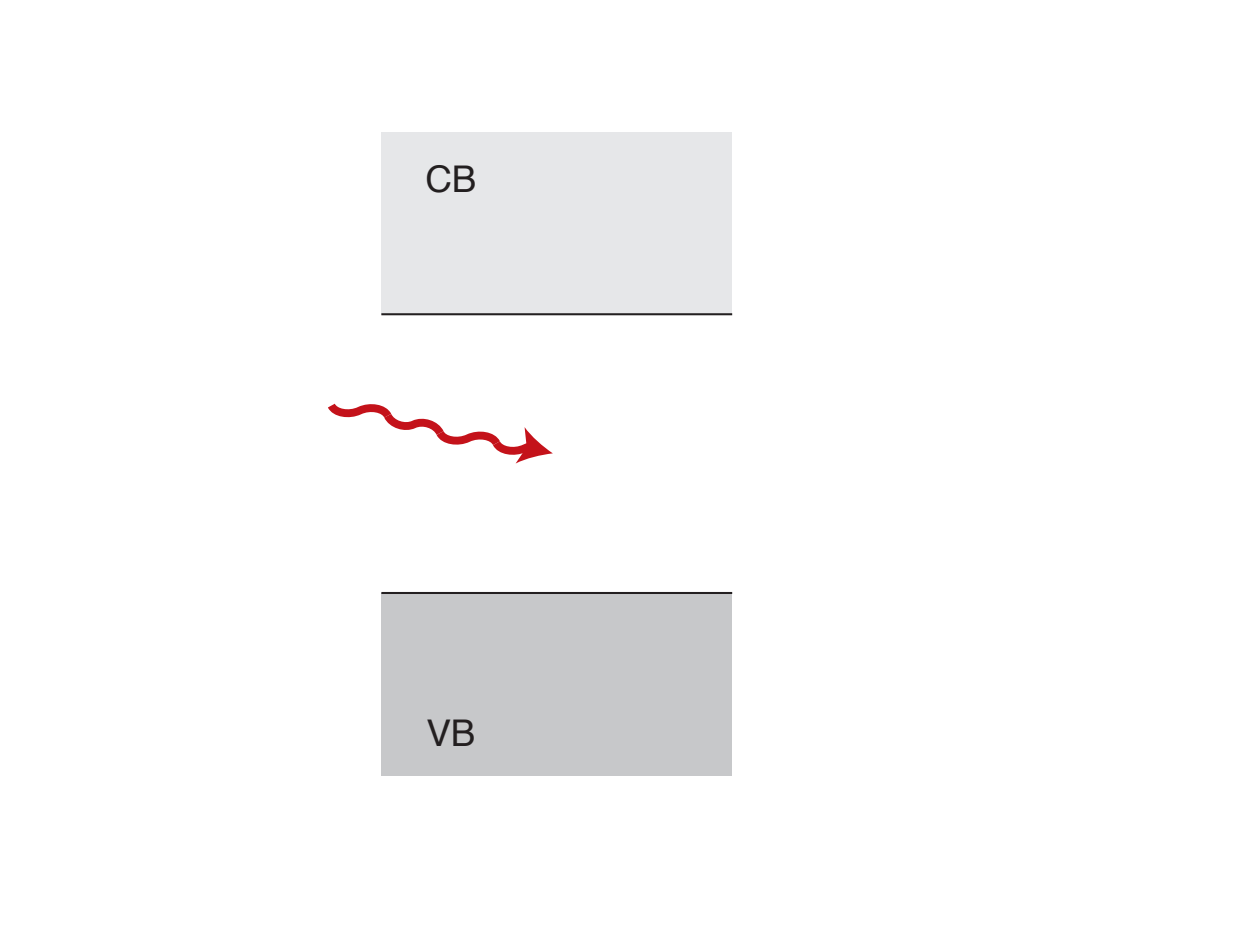
…whose energy can be extracted



1 intermediate band

2 Si devices

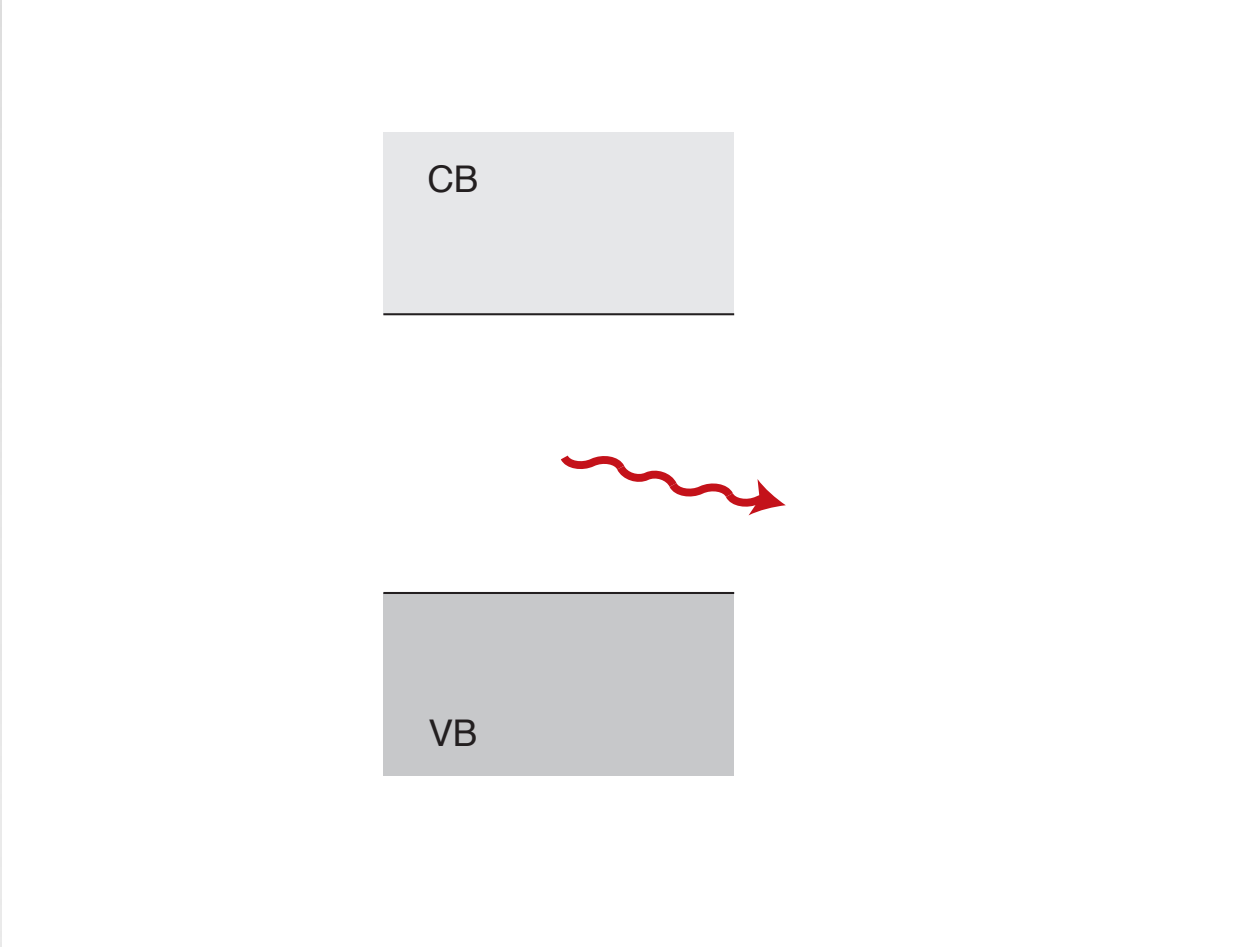
photons with energy smaller than gap…



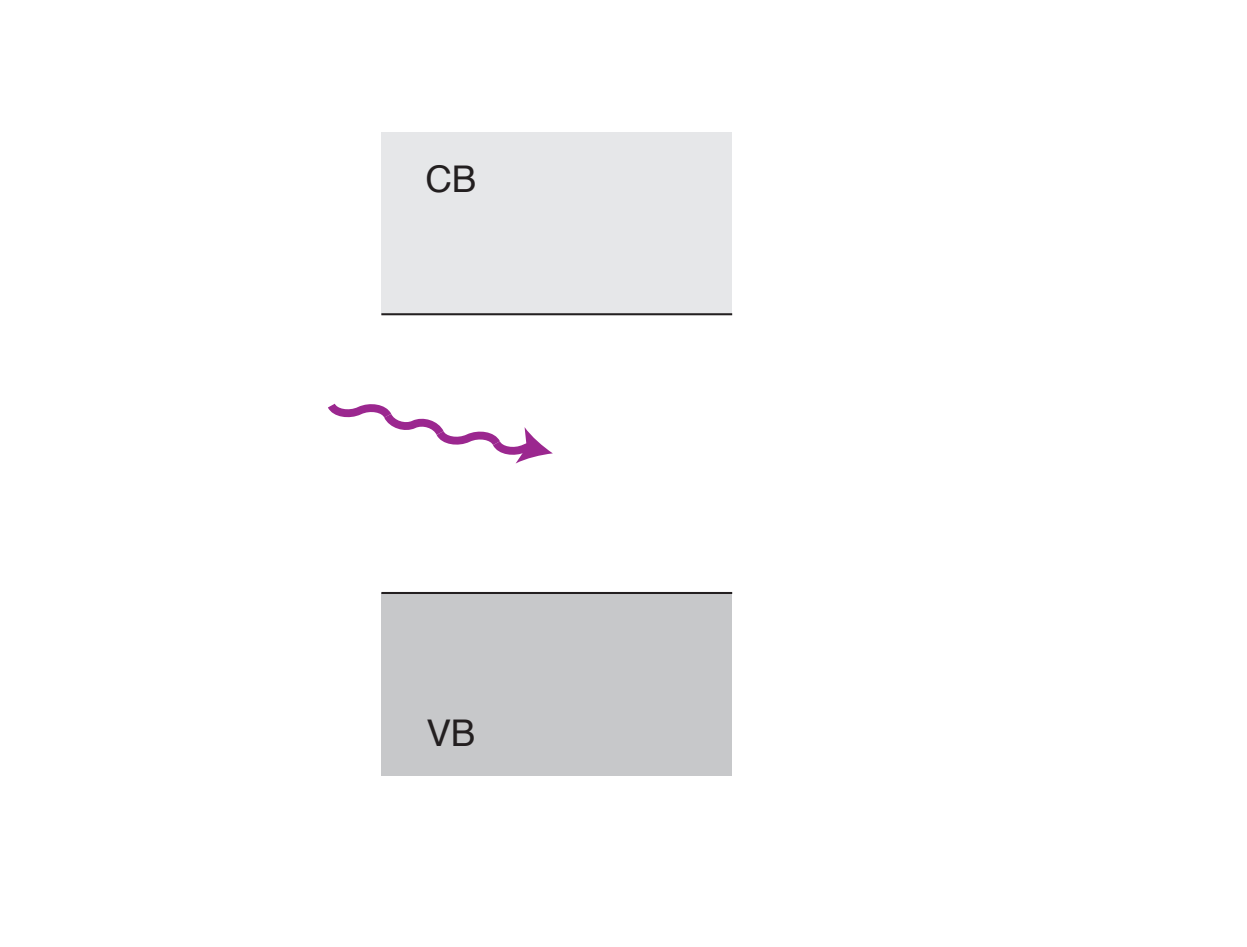
1 intermediate band

2 Si devices

…do not get absorbed



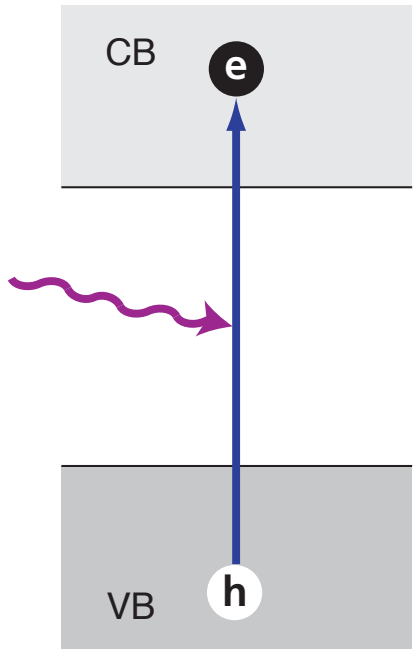
photons with energy larger than the gap…



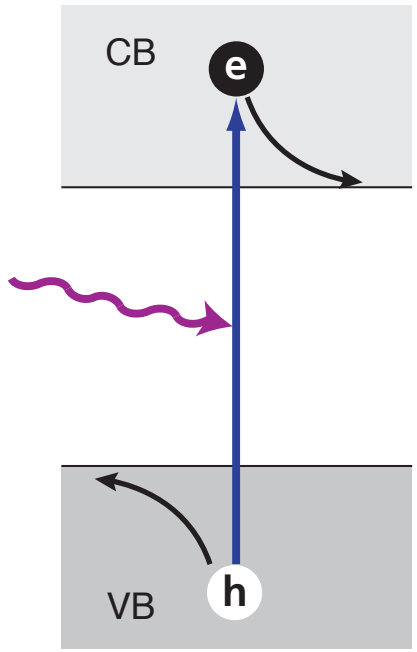
1 intermediate band

2 Si devices

…create electron-hole pairs with excess energy…



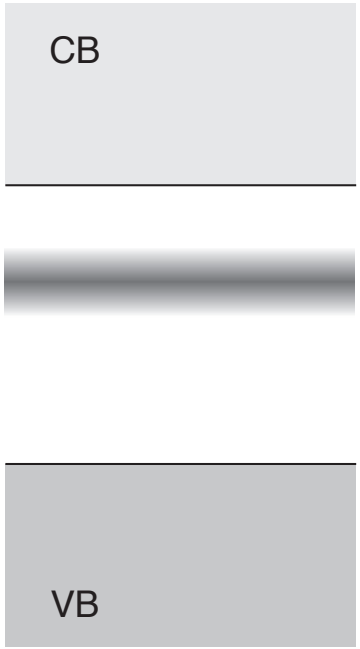
…which is lost rapidly



1 intermediate band

2 Si devices

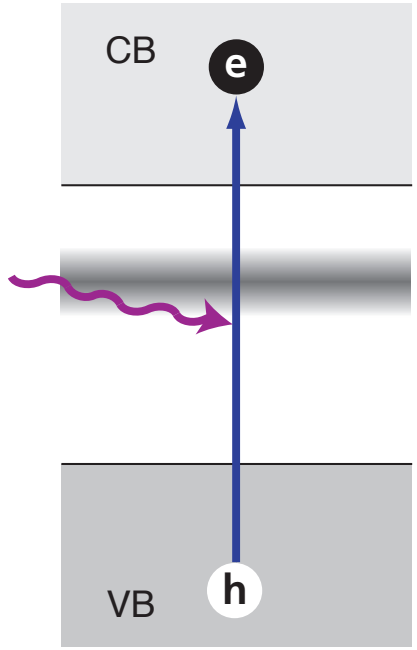
black silicon has an intermediate band



1 intermediate band

2 Si devices

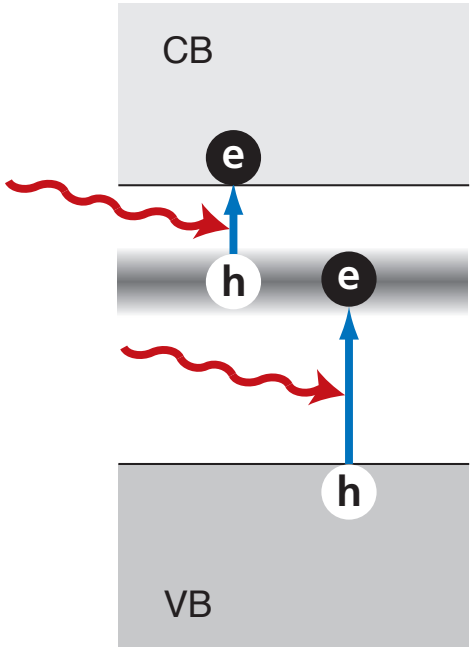
absorbs same photons as ordinary silicon…



1 intermediate band

2 Si devices

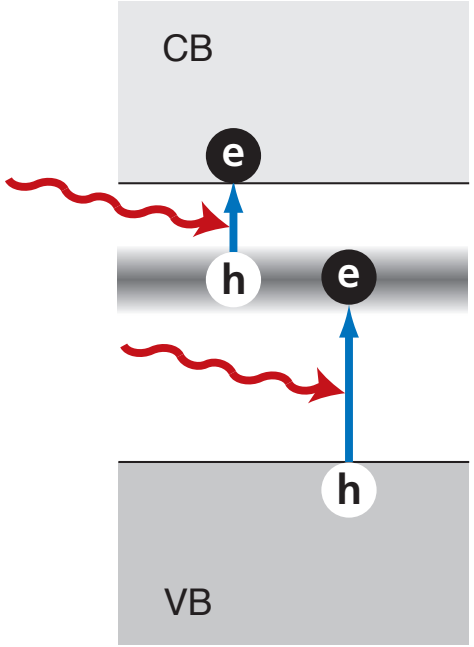
…but extends absorption to longer wavelengths



1 intermediate band

2 Si devices

could theoretically get efficiencies over 50%

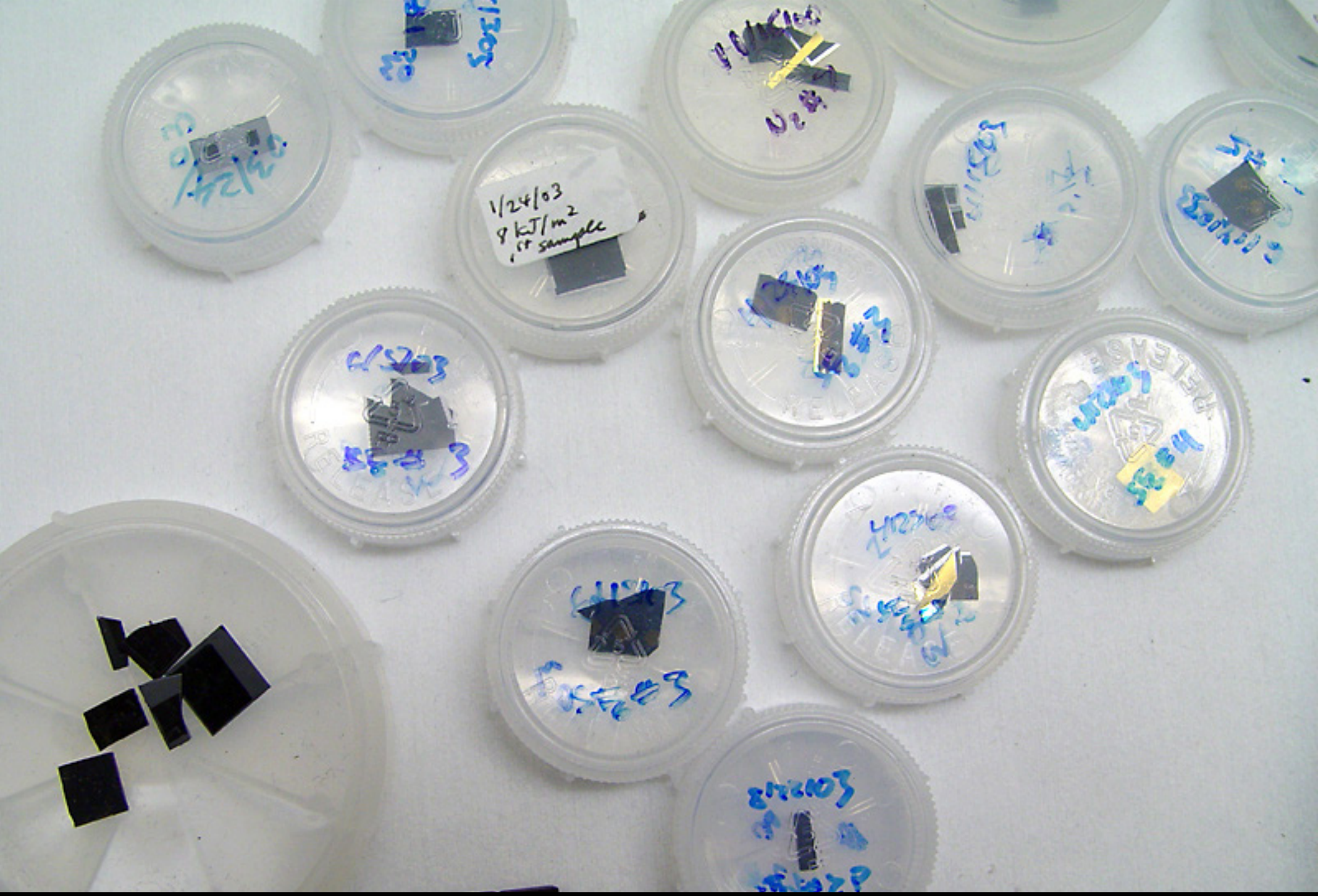


1 intermediate band

2 Si devices

Things to keep in mind

- can turn absorption into carrier generation (photodetectors)
- very high optical density
- intermediate band photovoltaic devices?

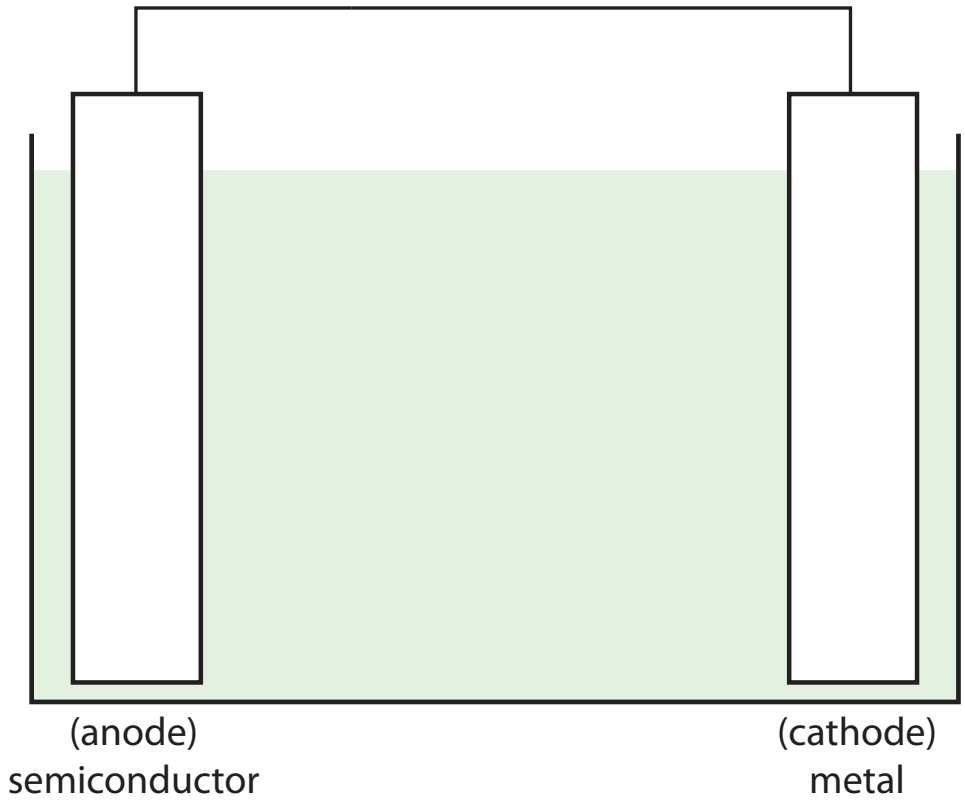


1 intermediate band

2 Si devices

3 X:TiO_2

water splitting



1 intermediate band

2 Si devices

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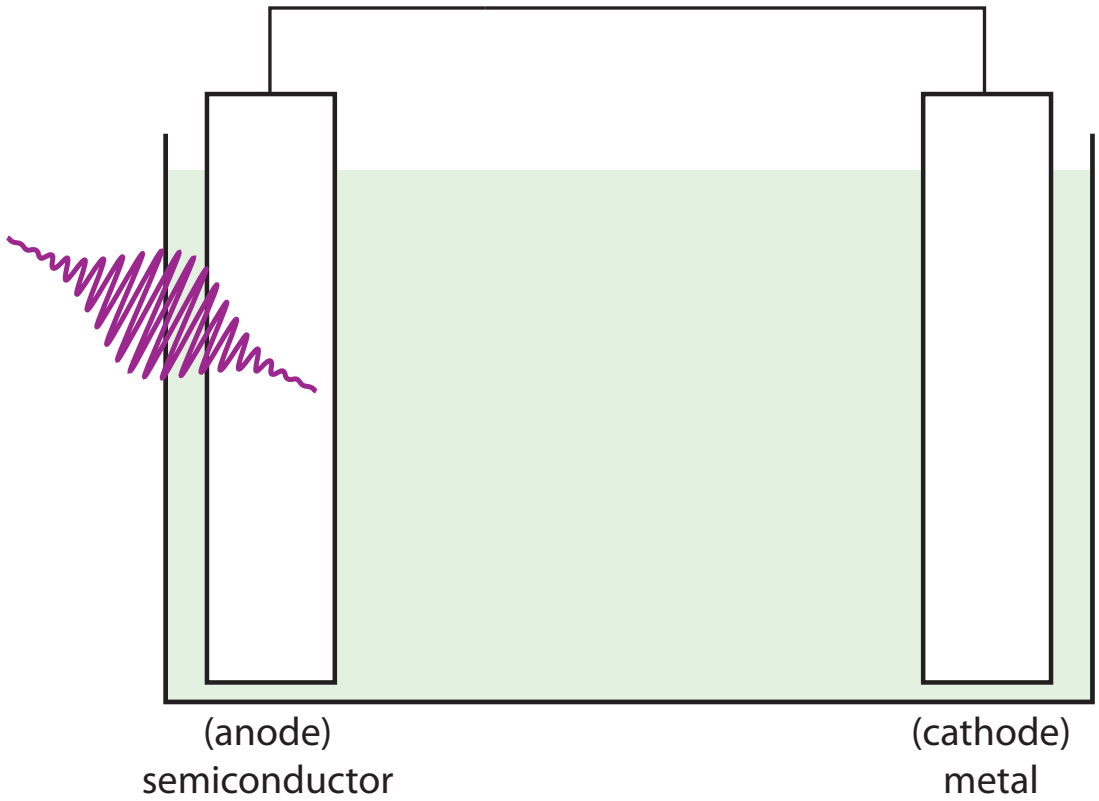
water splitting



1 intermediate band

2 Si devices

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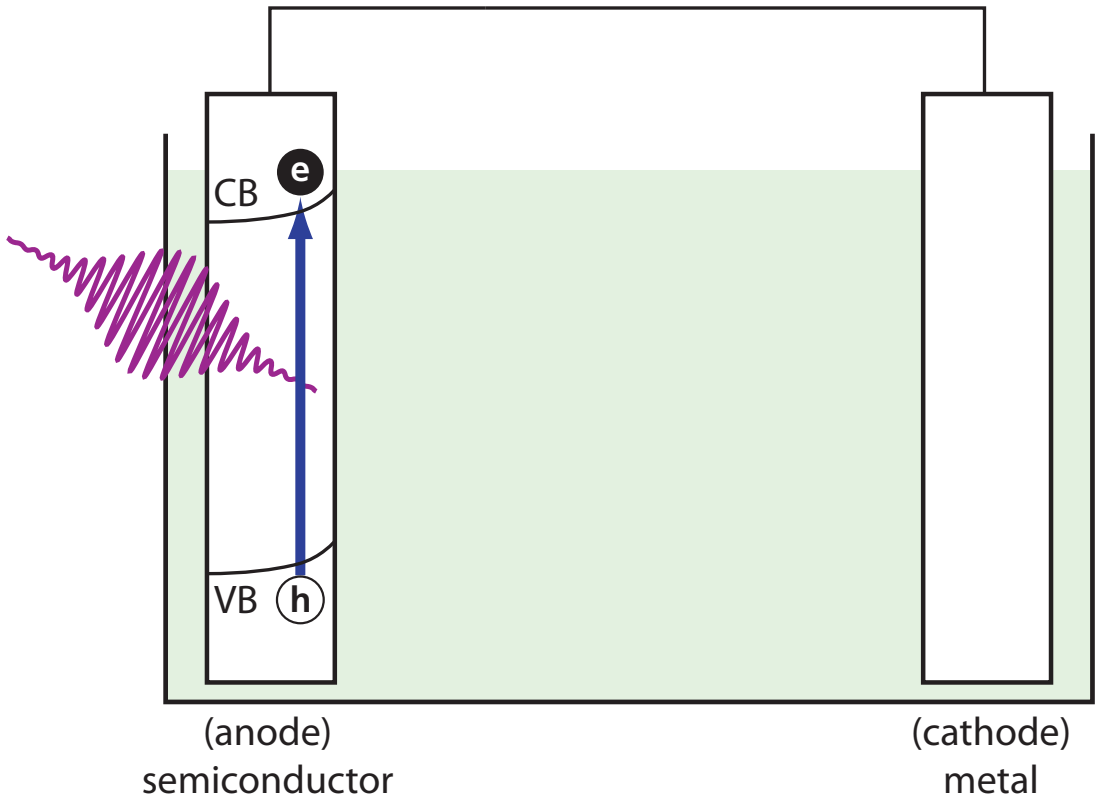
water splitting



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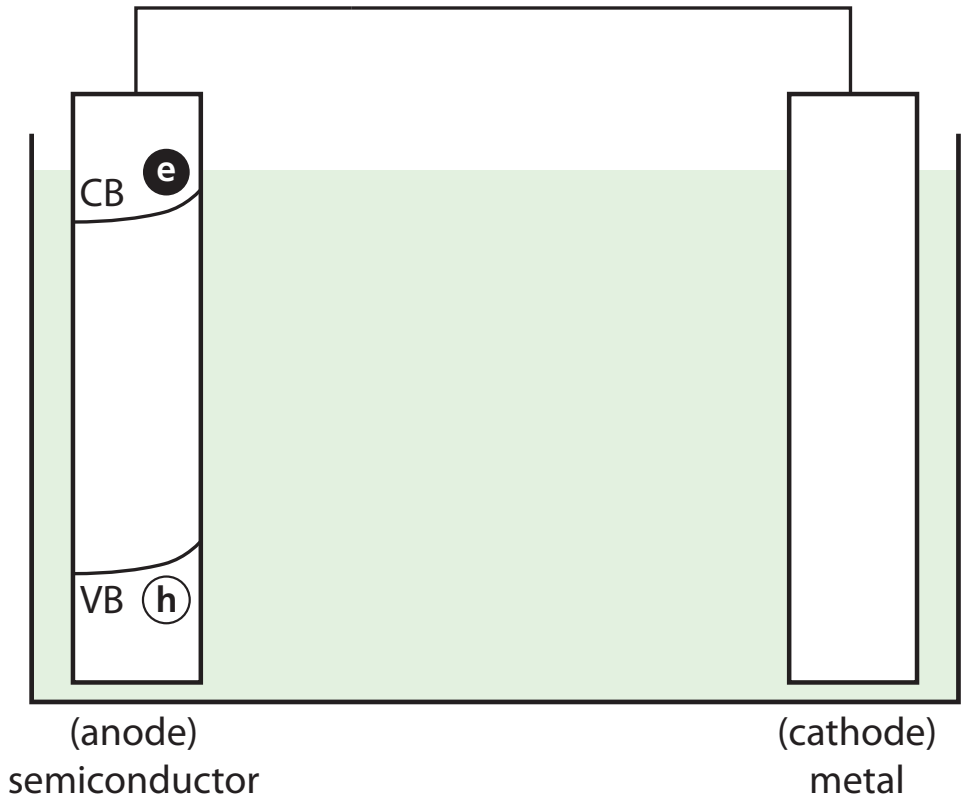

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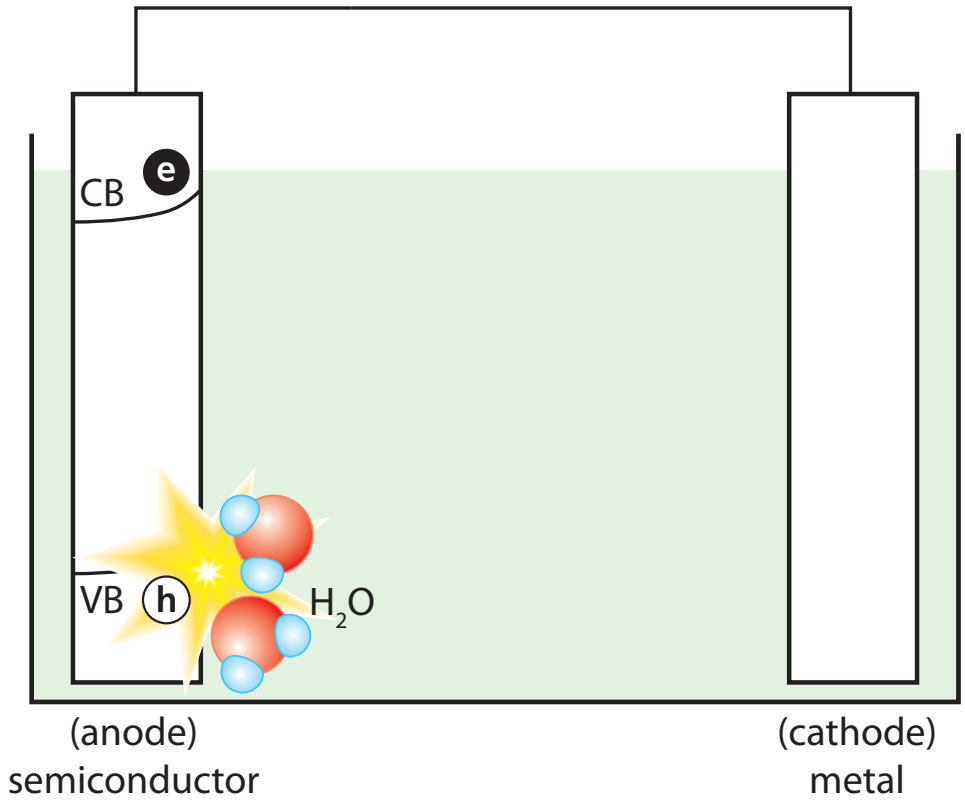
2 Si devices

3 X:TiO_2

water splitting

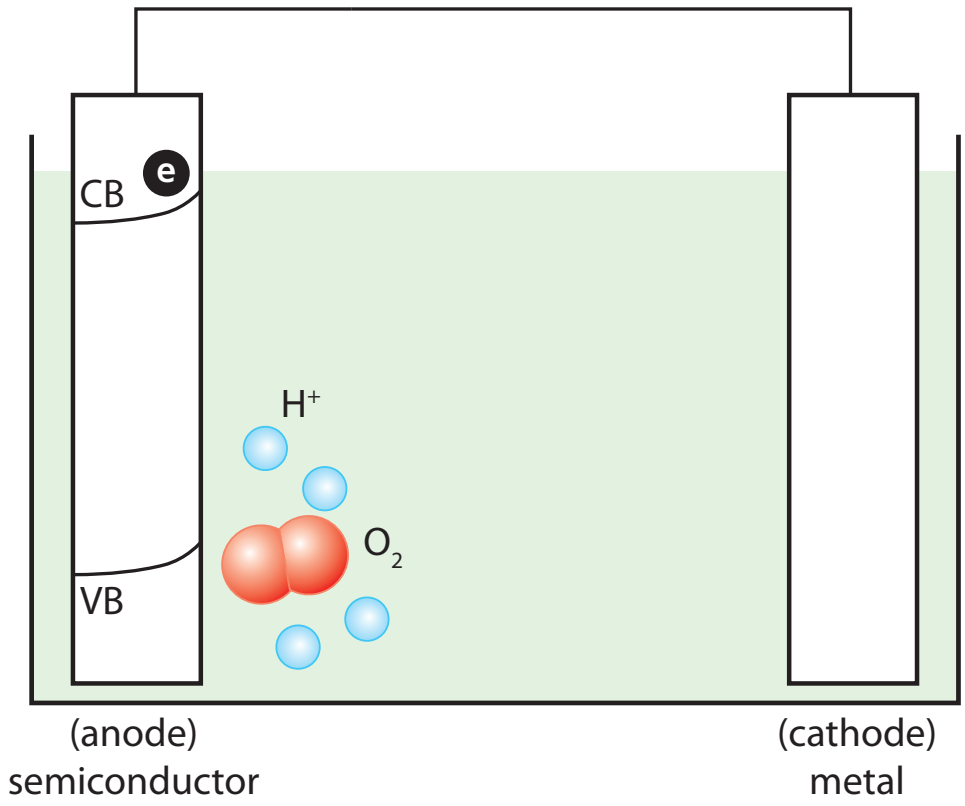


1 intermediate band

2 Si devices

3 $X:TiO_2$

water splitting

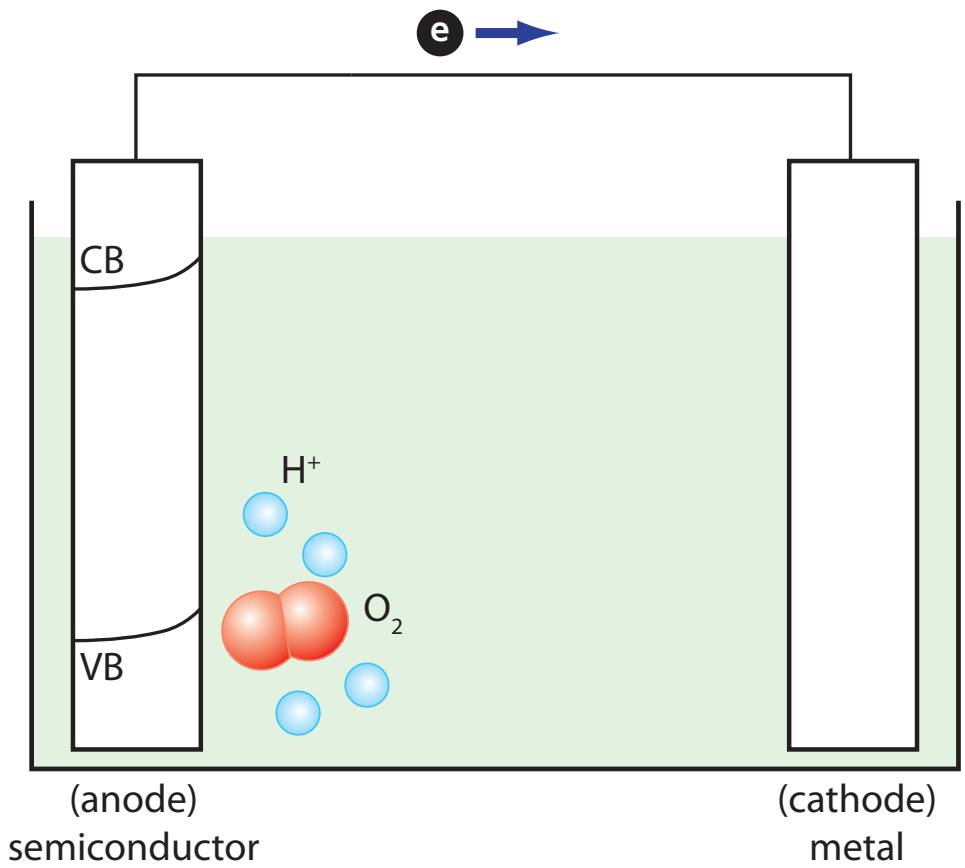


1 intermediate band

2 Si devices

3 X:TiO_2

water splitting



1 intermediate band

2 Si devices

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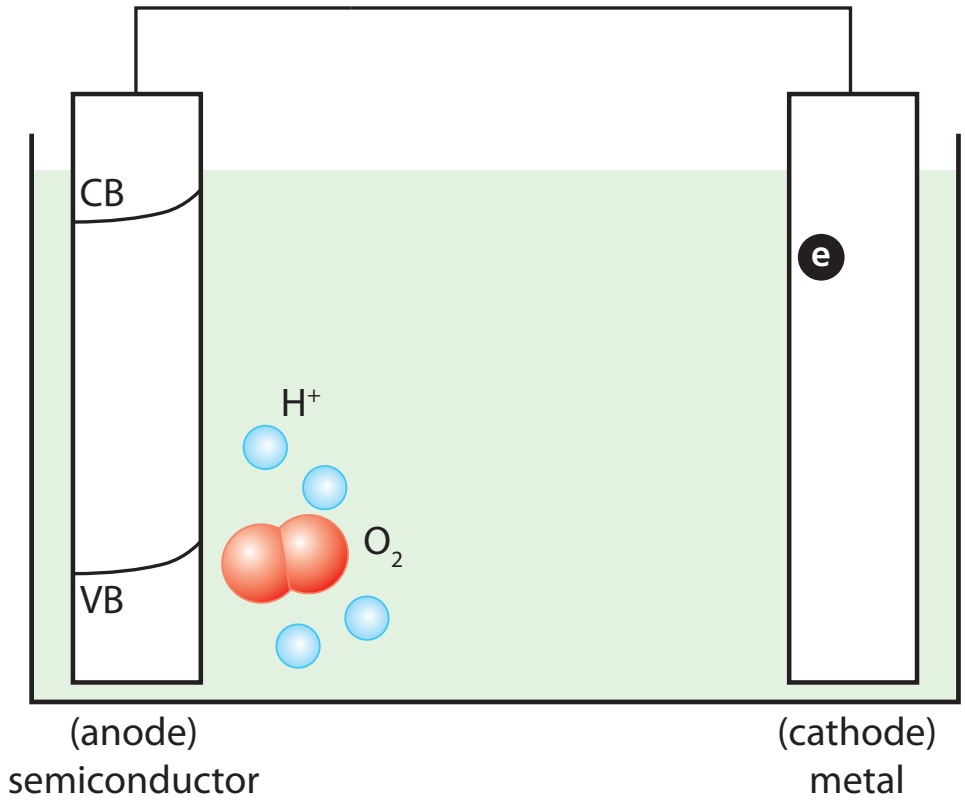
water splitting



1 intermediate band

2 Si devices

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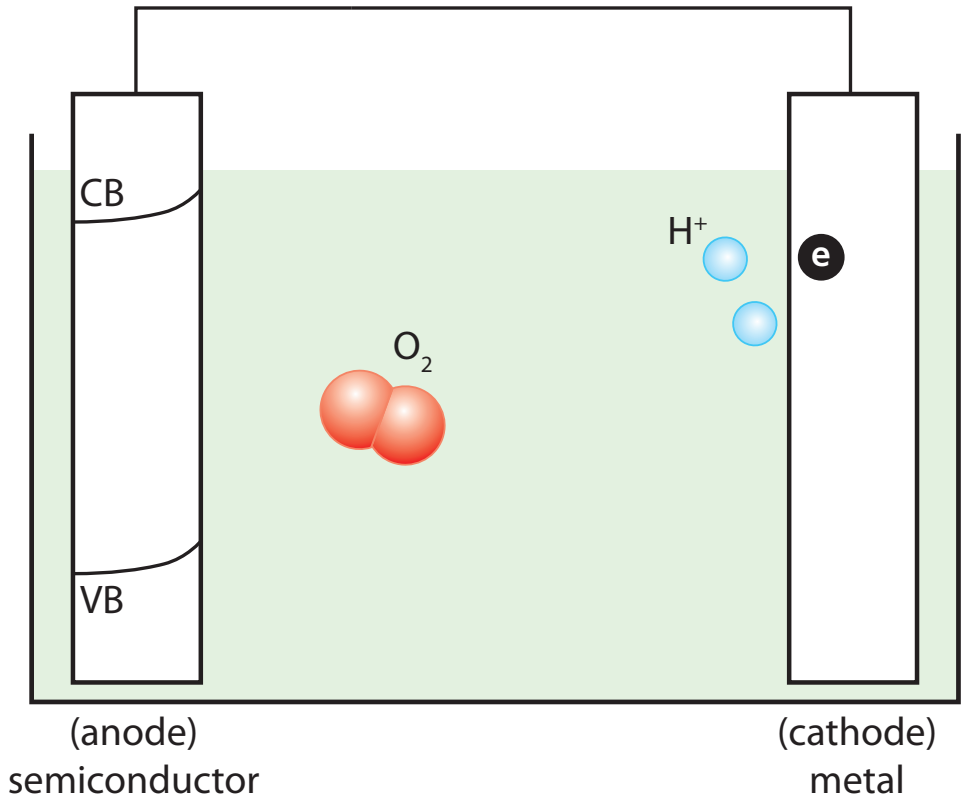
water splitting

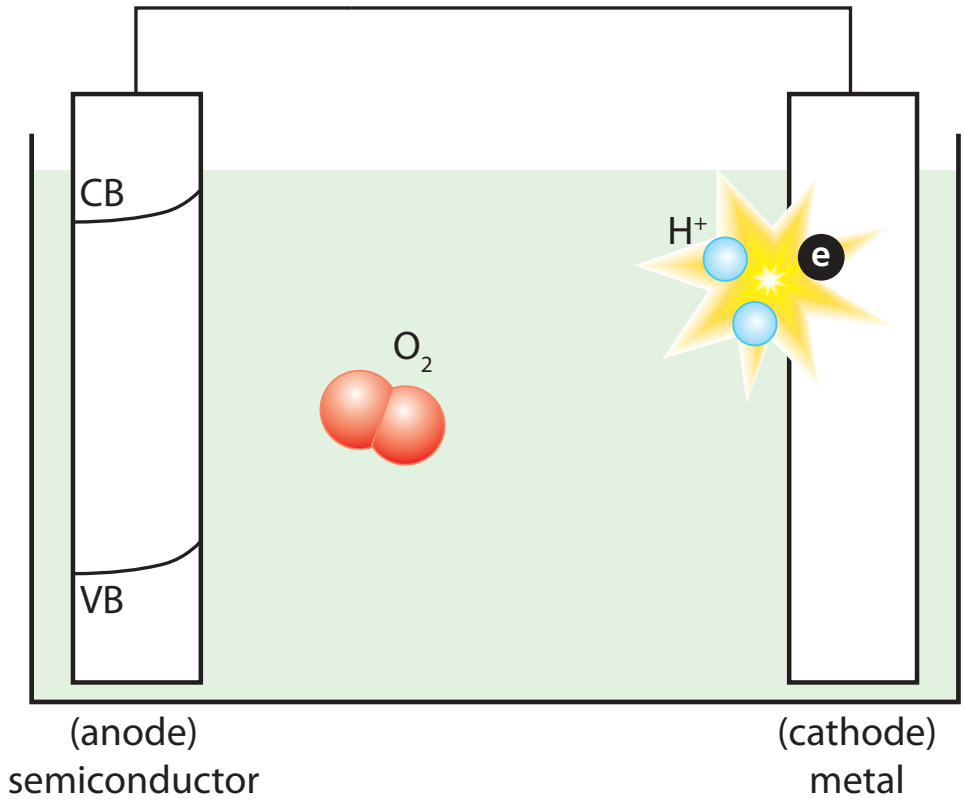


1 intermediate band

2 Si devices

3 $X:TiO_2$

water splitting

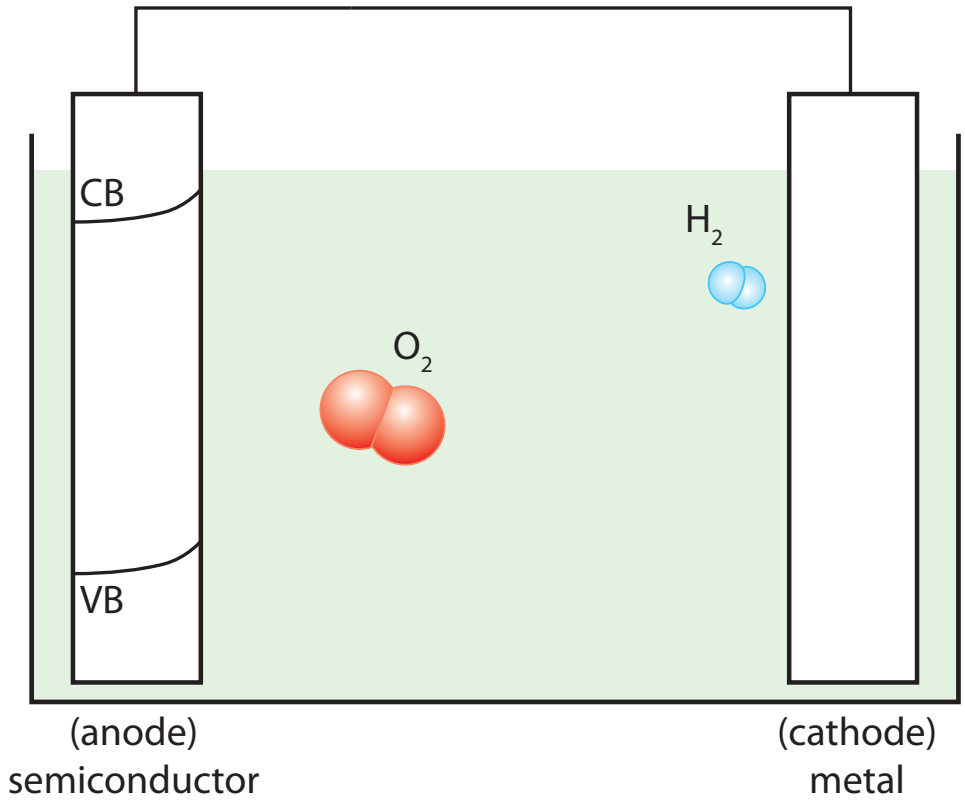


1 intermediate band

2 Si devices

3 $X:TiO_2$

water splitting

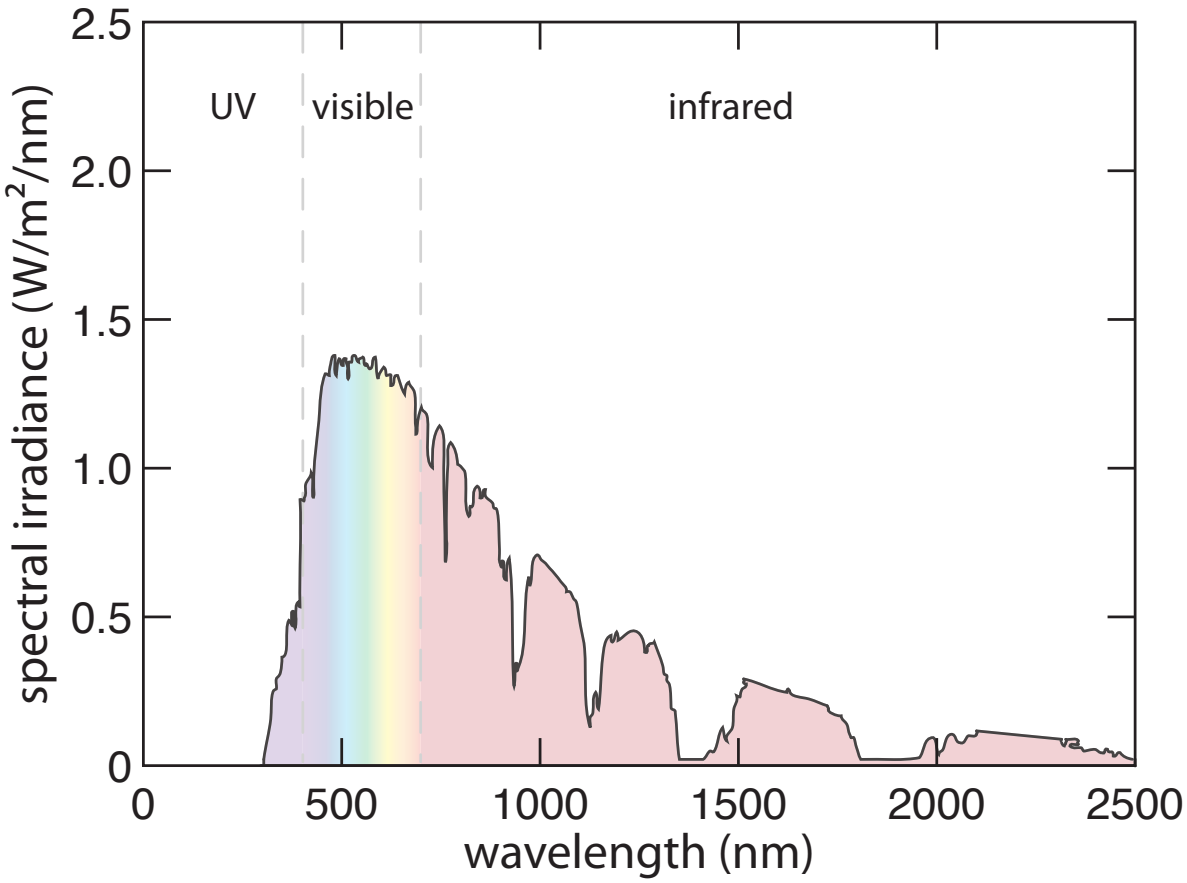


1 intermediate band

2 Si devices

3 $X:TiO_2$

solar radiation spectrum

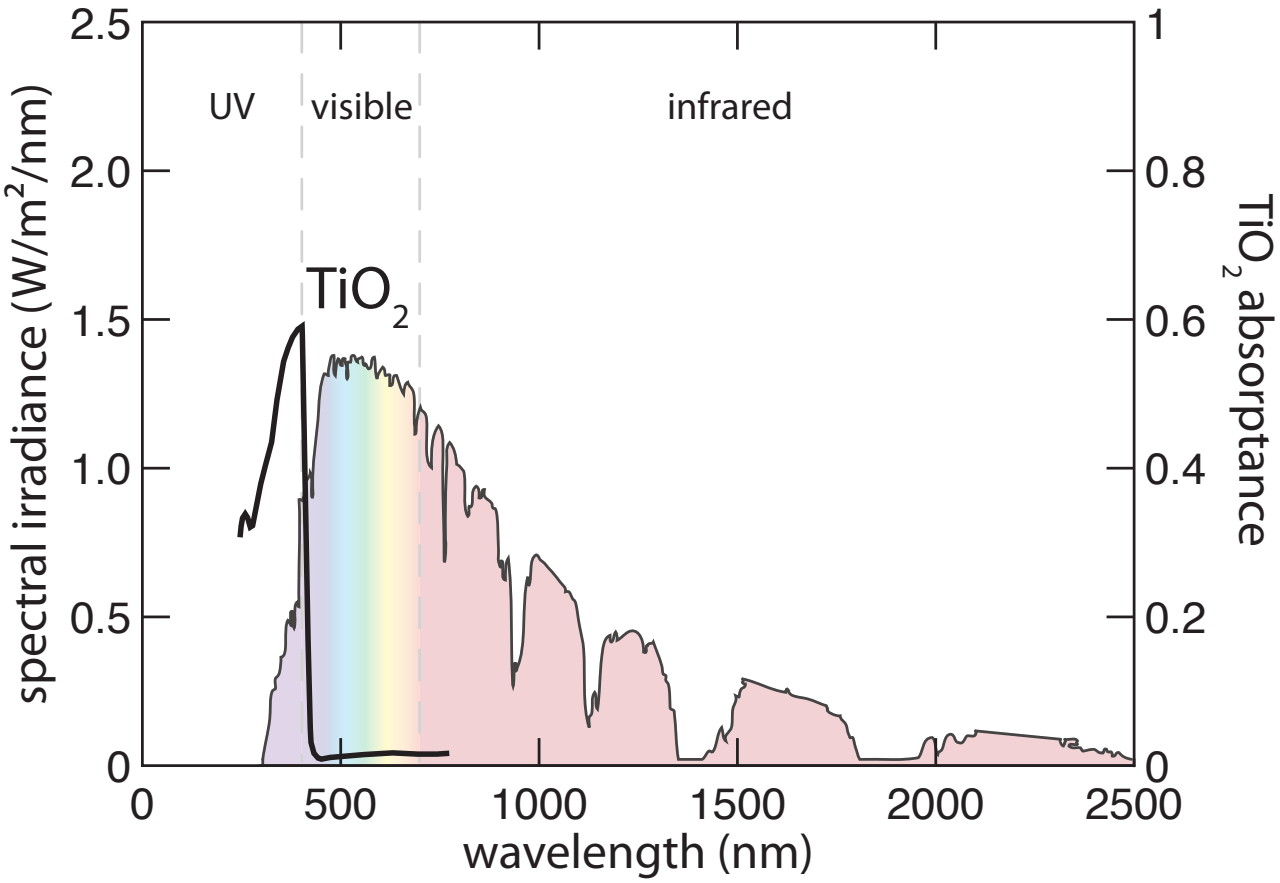


1 intermediate band

2 Si devices

3 X:TiO_2

solar radiation spectrum

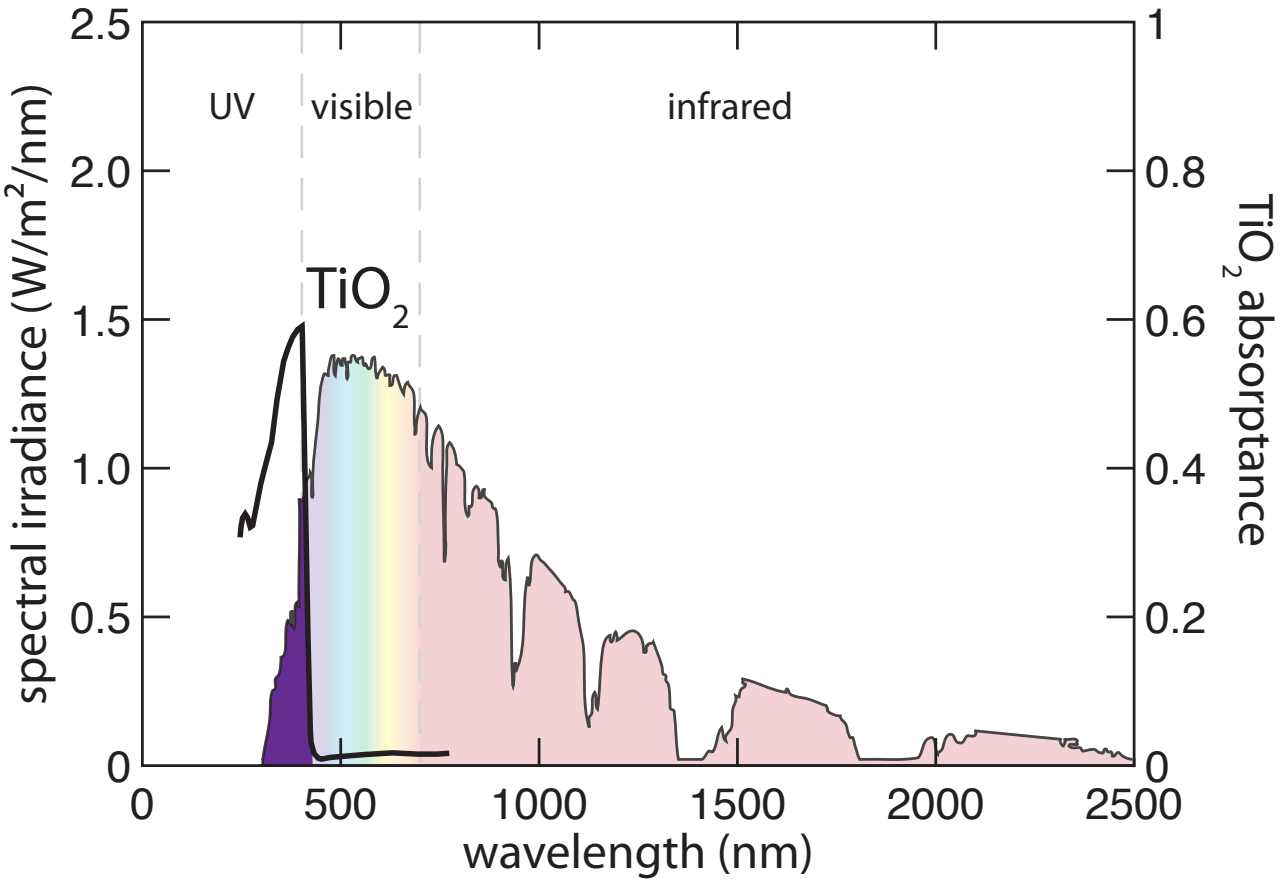


1 intermediate band

2 Si devices

3 X:TiO_2

solar radiation spectrum



1 intermediate band

2 Si devices

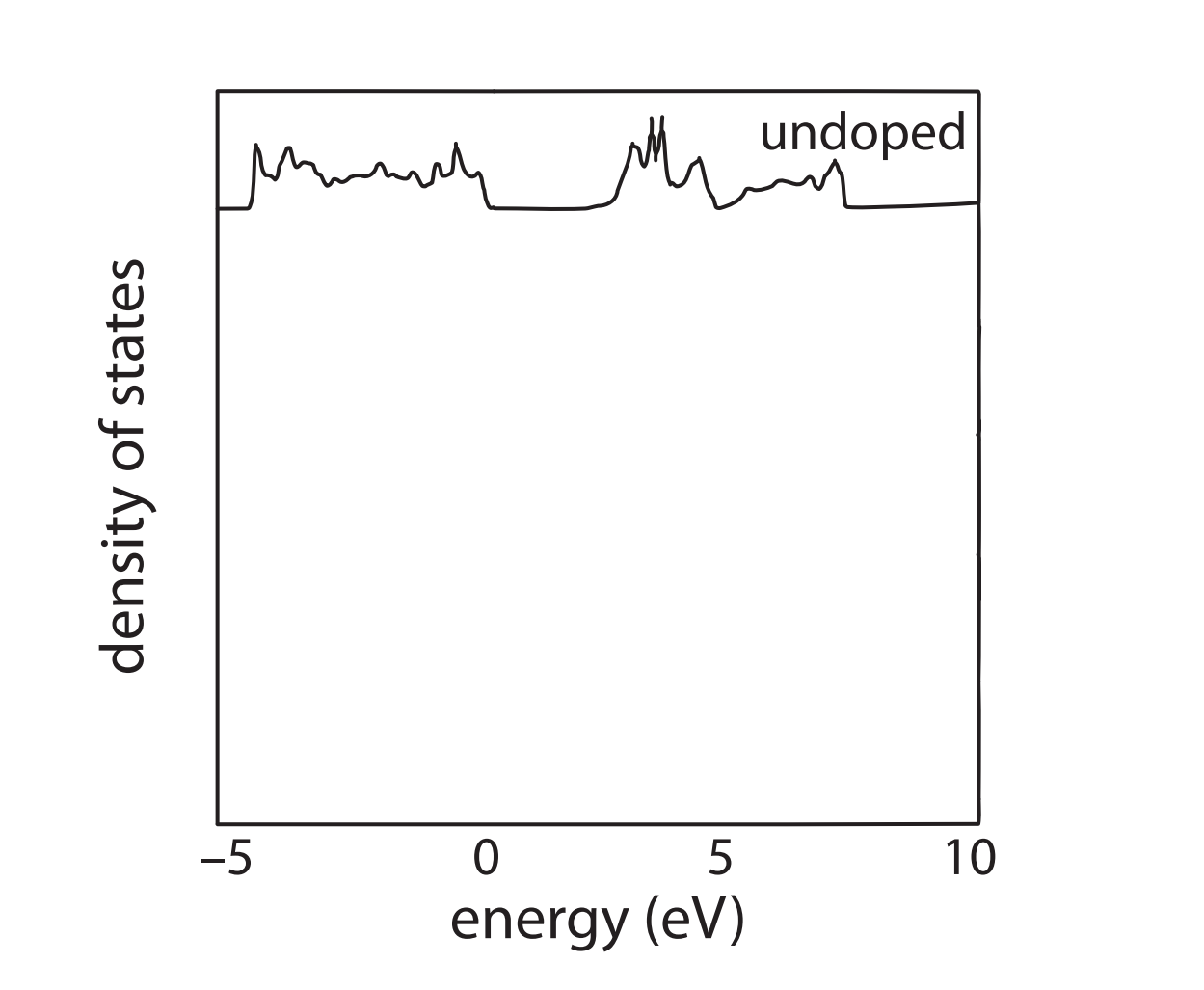
3 X:TiO_2

increase efficiency by:

- increasing surface area
- shifting band edge

1 intermediate band 2 Si devices 3 X:TiO_2

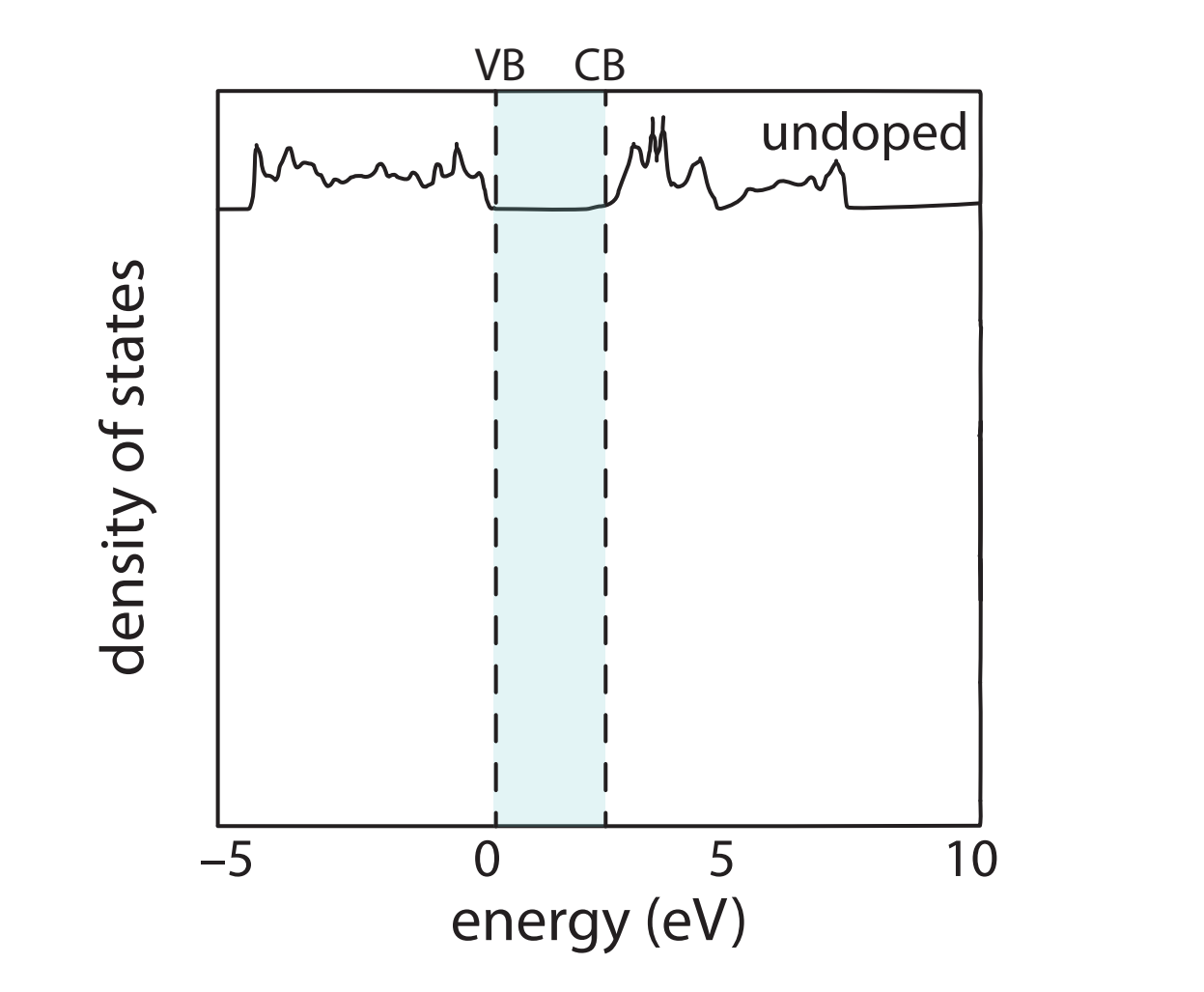
TiO_2 density of states



Asahi et al., Science (2001)

1 intermediate band 2 Si devices 3 X:TiO_2

need to create band(s) in gap



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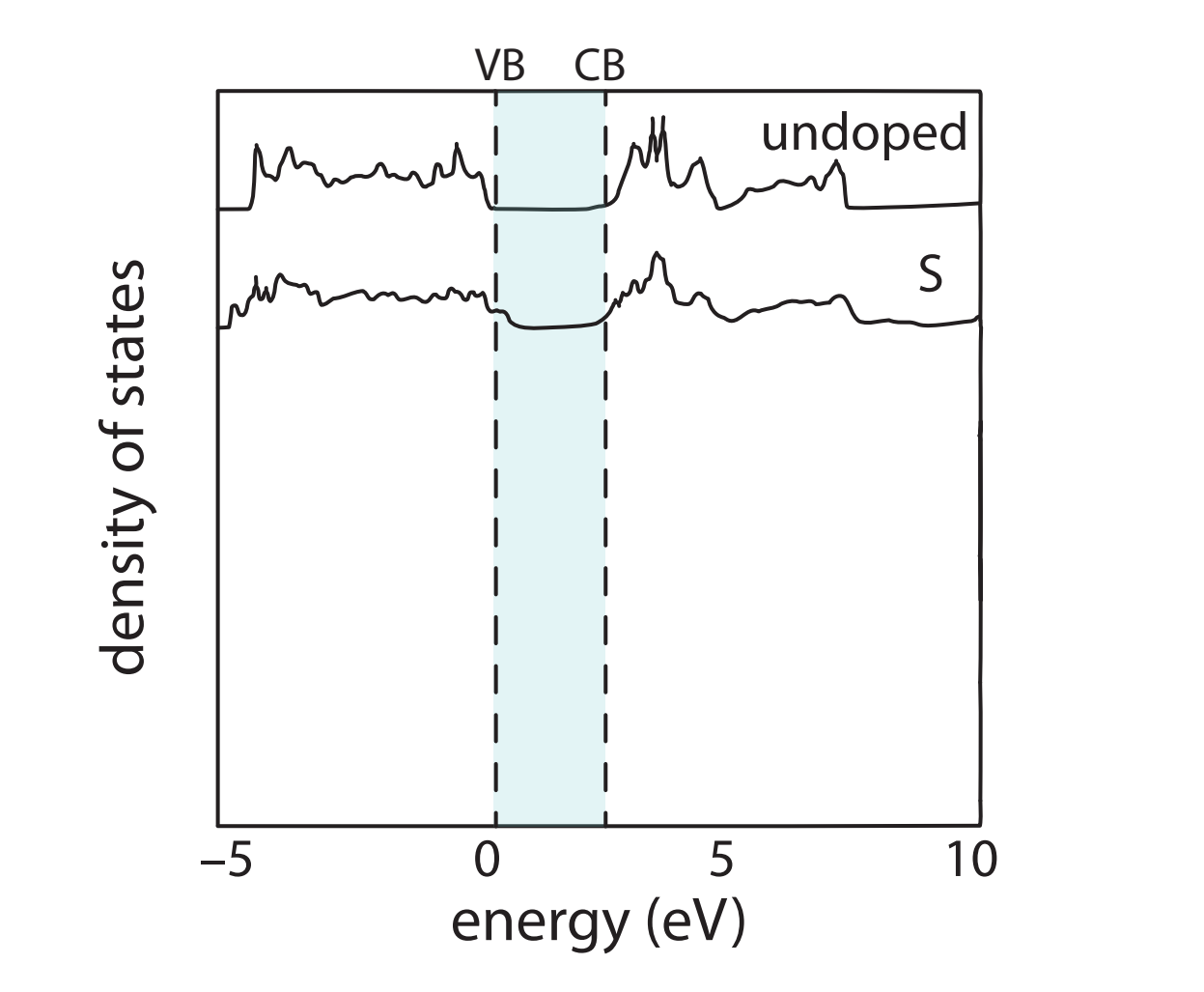

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1 intermediate band 2 Si devices 3 X:TiO_2

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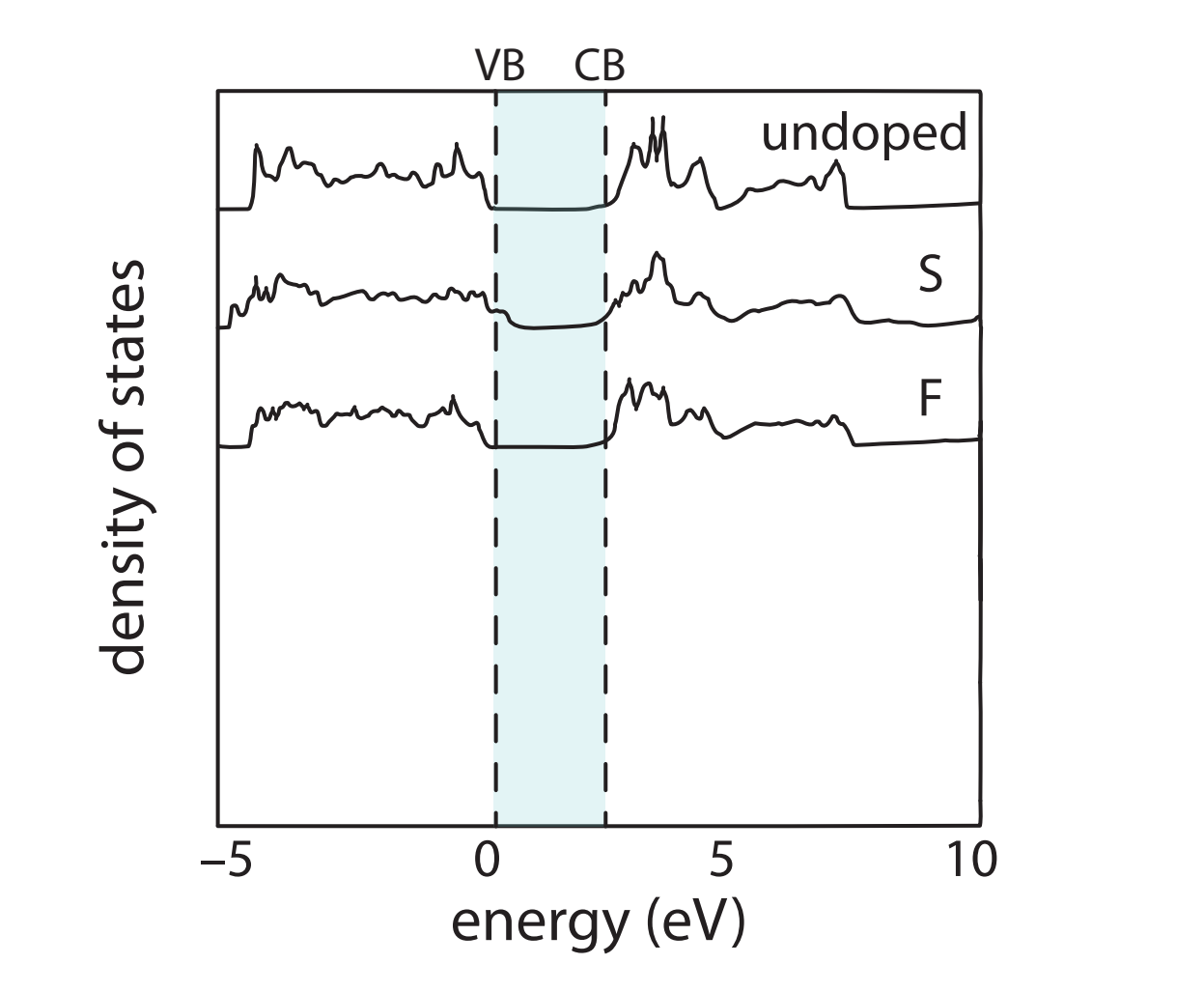

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1 intermediate band 2 Si devices 3 X:TiO_2

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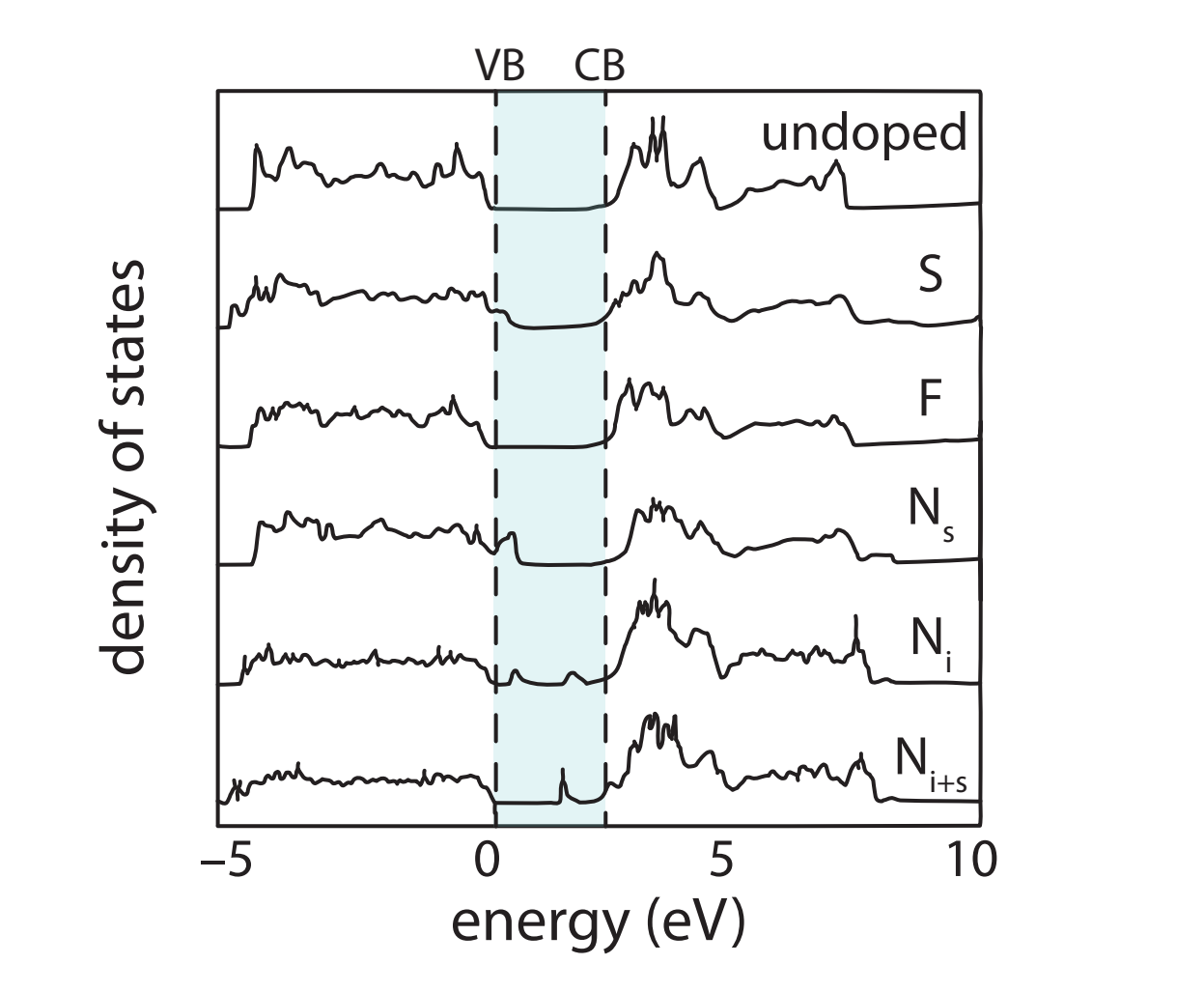
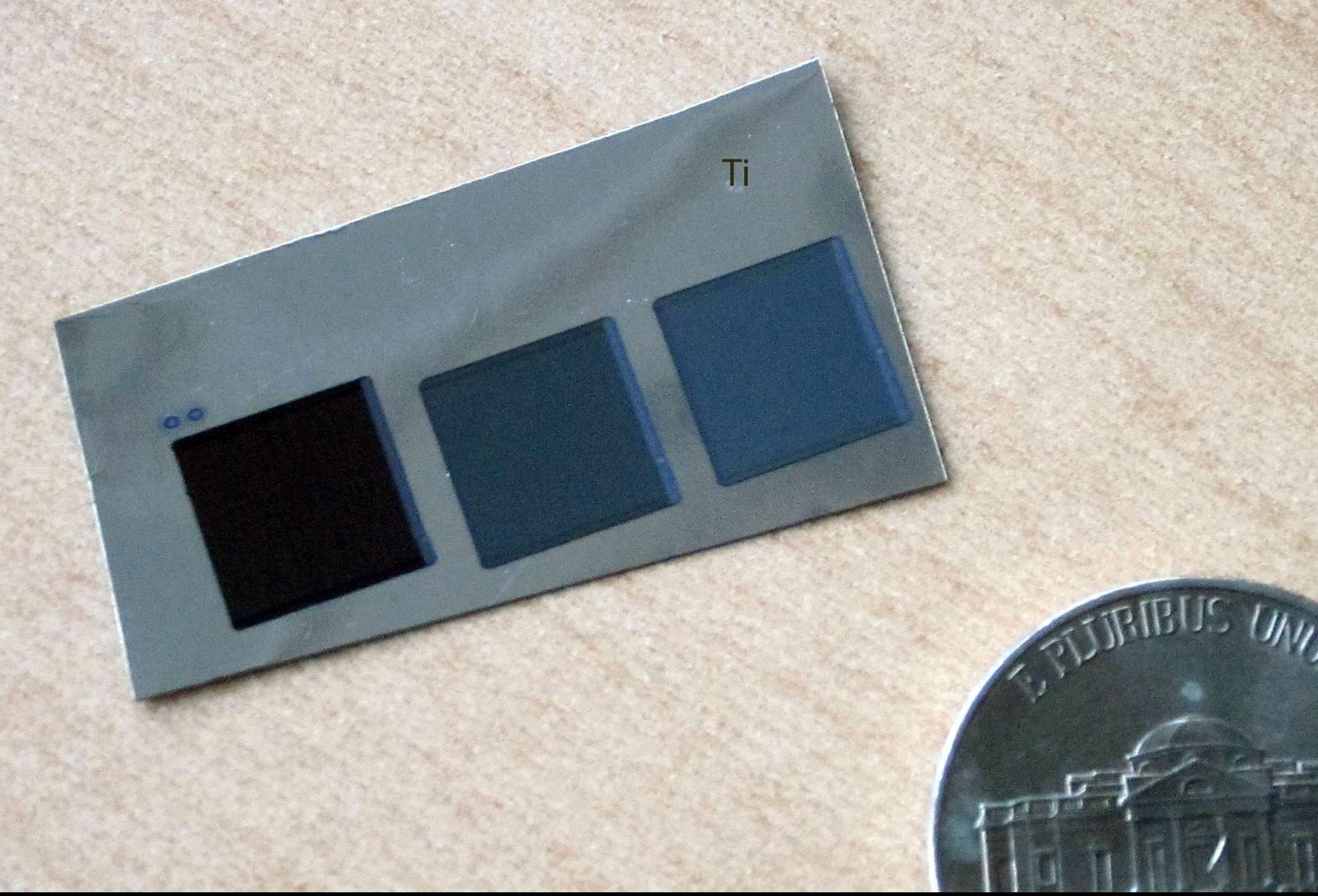


Asahi et al., Science (2001)

1 intermediate band 2 Si devices 3 $X:TiO_2$

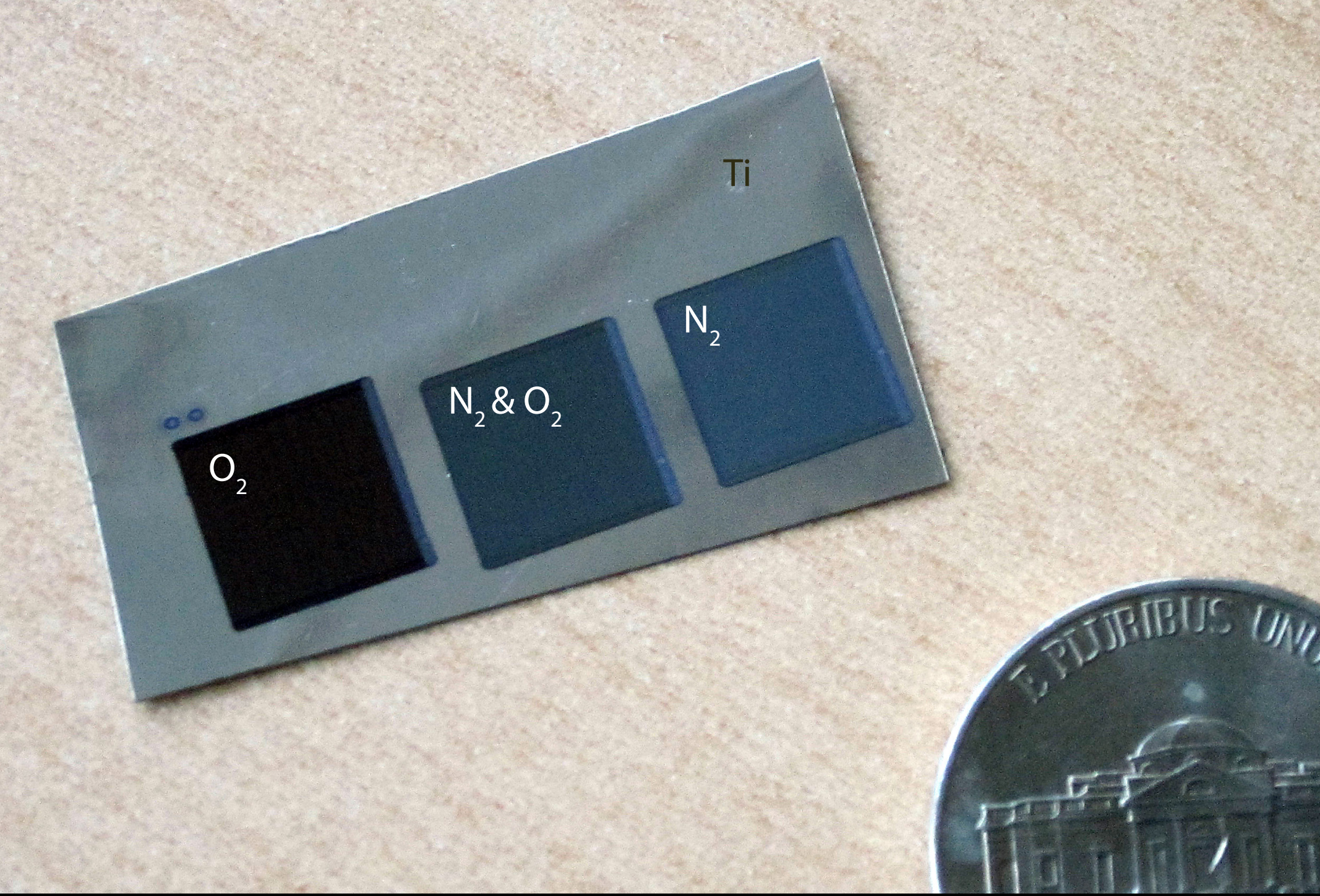
structuring TiO_2 in N_2 doesn't work



1 intermediate band

2 Si devices

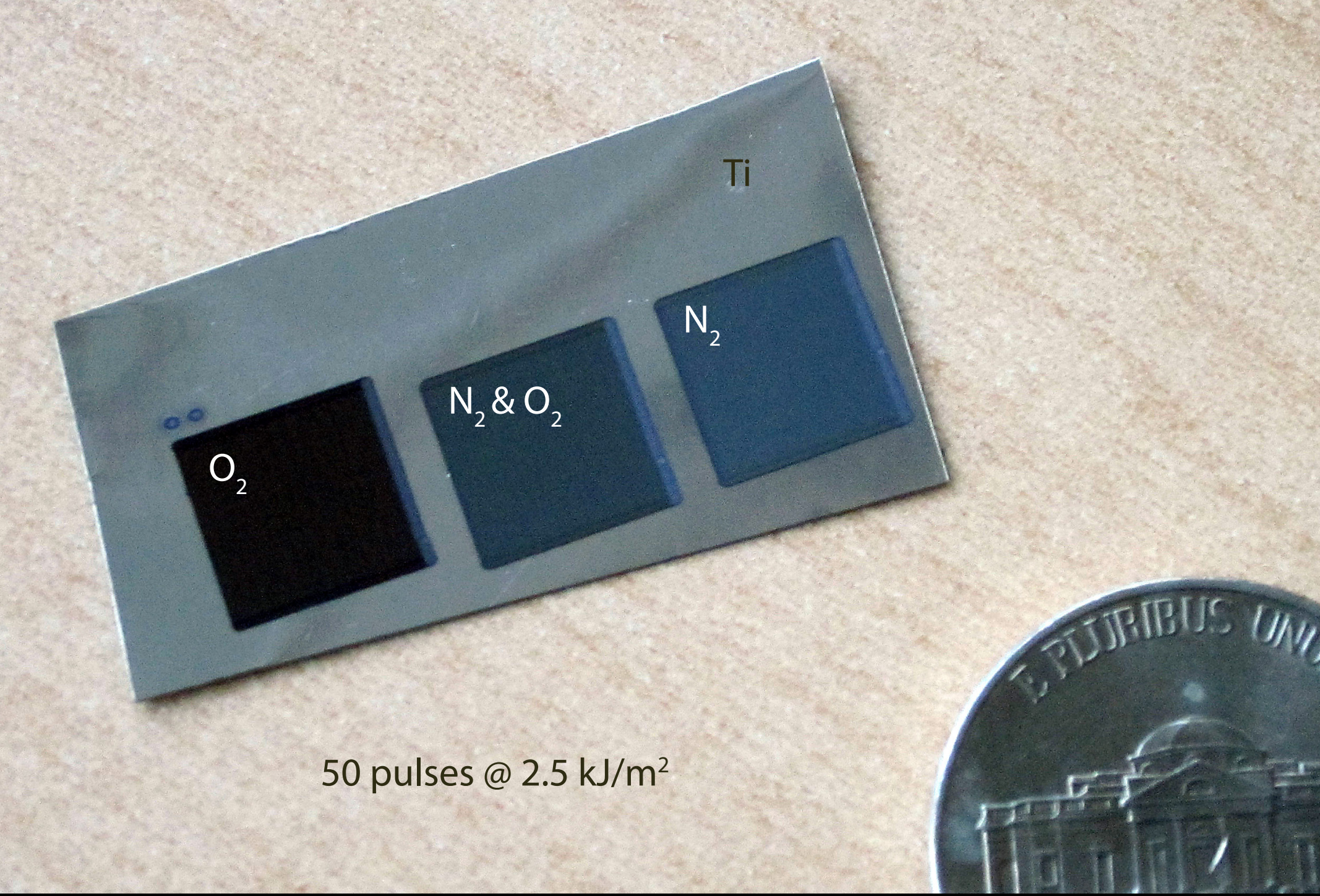
3 X:TiO_2



1 intermediate band

2 Si devices

3 X:TiO_2

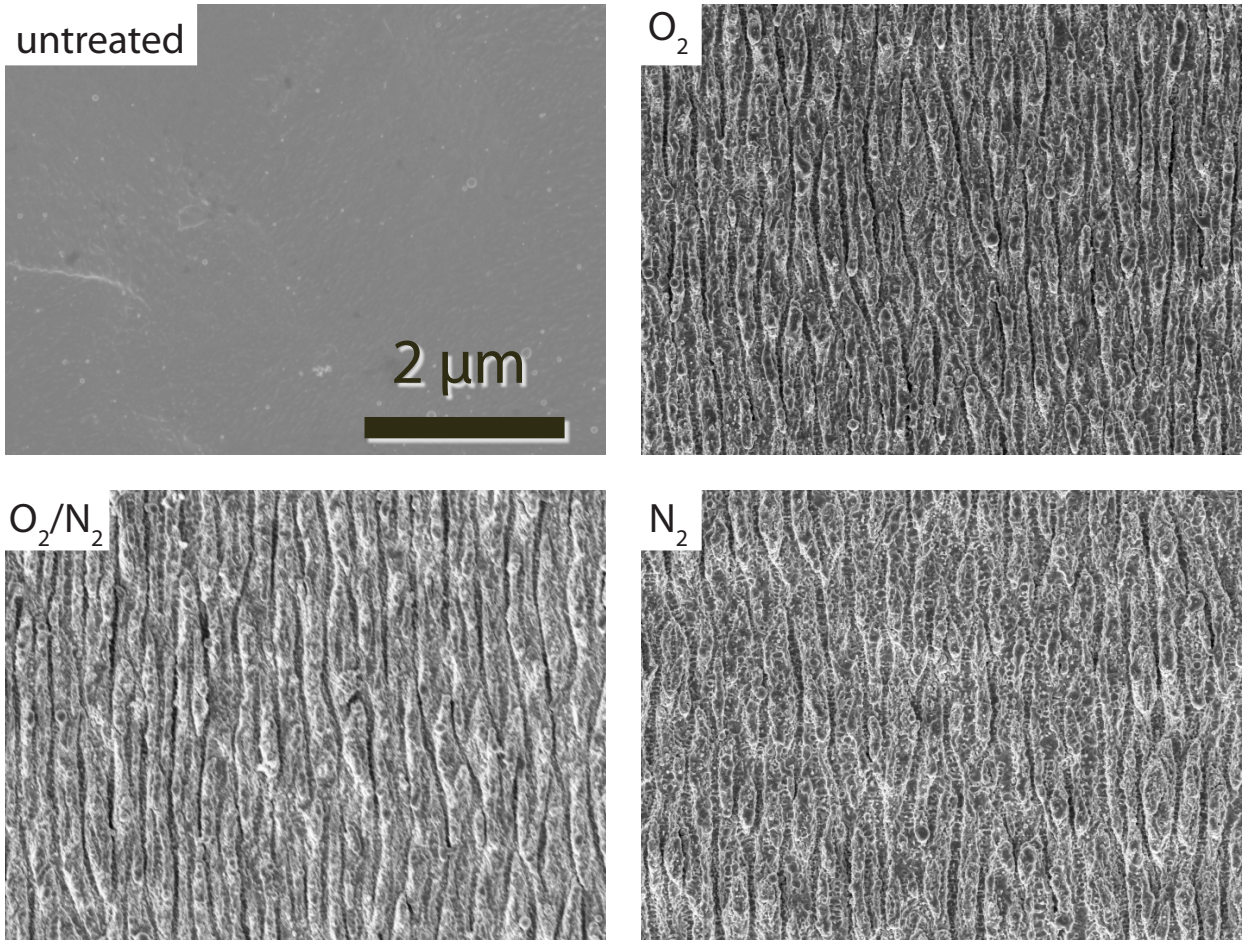


1 intermediate band

2 Si devices

3 X:TiO_2

50 pulses @ 2.5 kJ/m^2

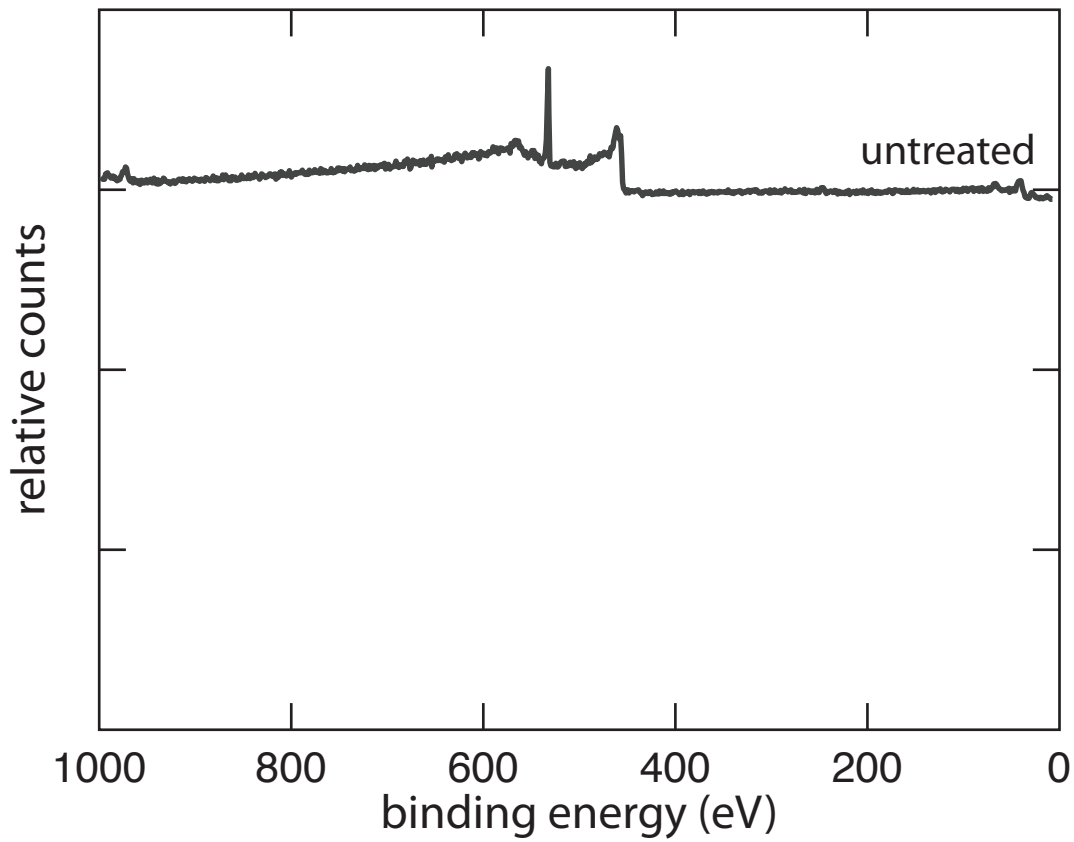


1 intermediate band

2 Si devices

3 X:TiO_2

X-ray photoelectron spectroscopy

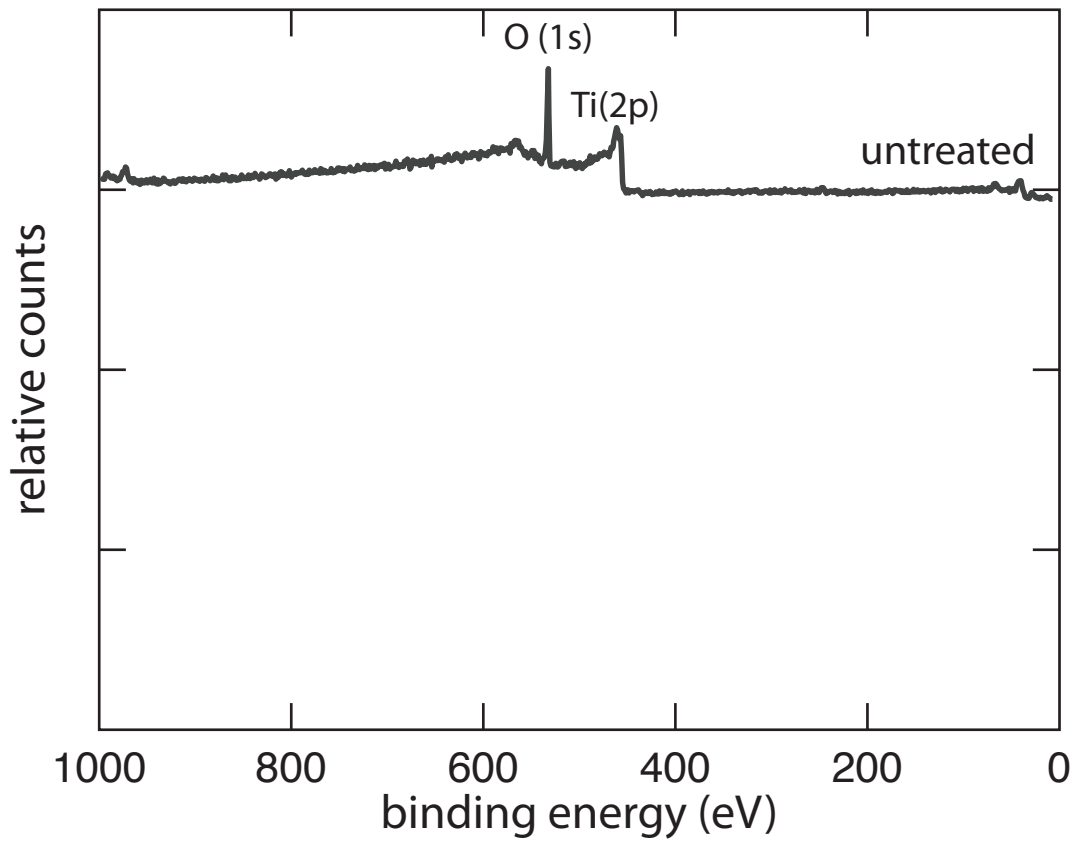


1 intermediate band

2 Si devices

3 X:TiO_2

X-ray photoelectron spectroscopy

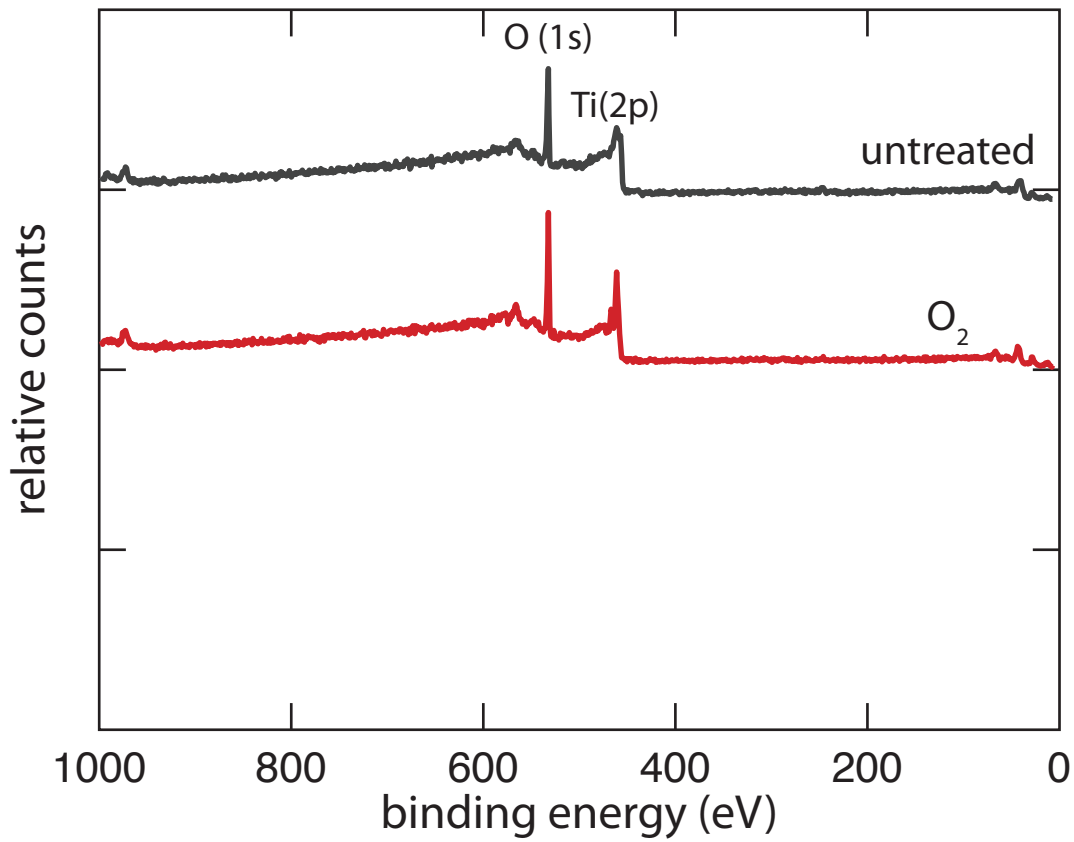


1 intermediate band

2 Si devices

3 X:TiO_2

X-ray photoelectron spectroscopy

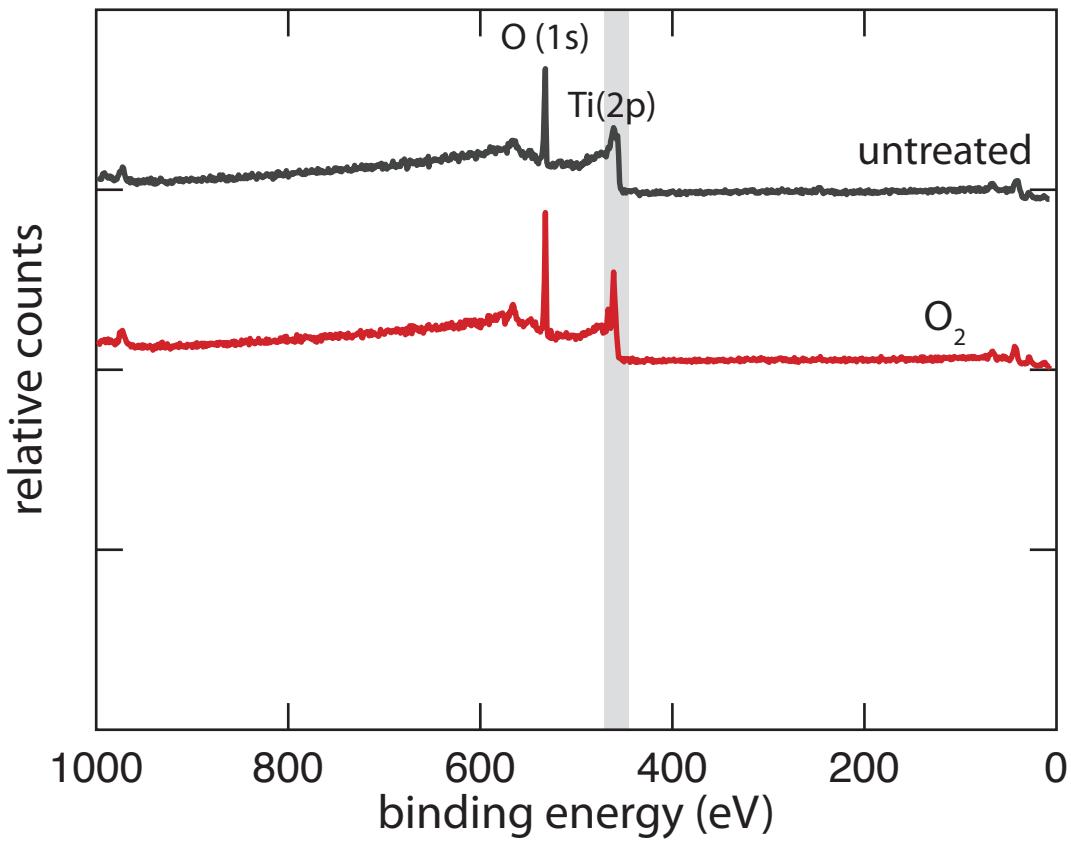


1 intermediate band

2 Si devices

3 X:TiO_2

X-ray photoelectron spectroscopy

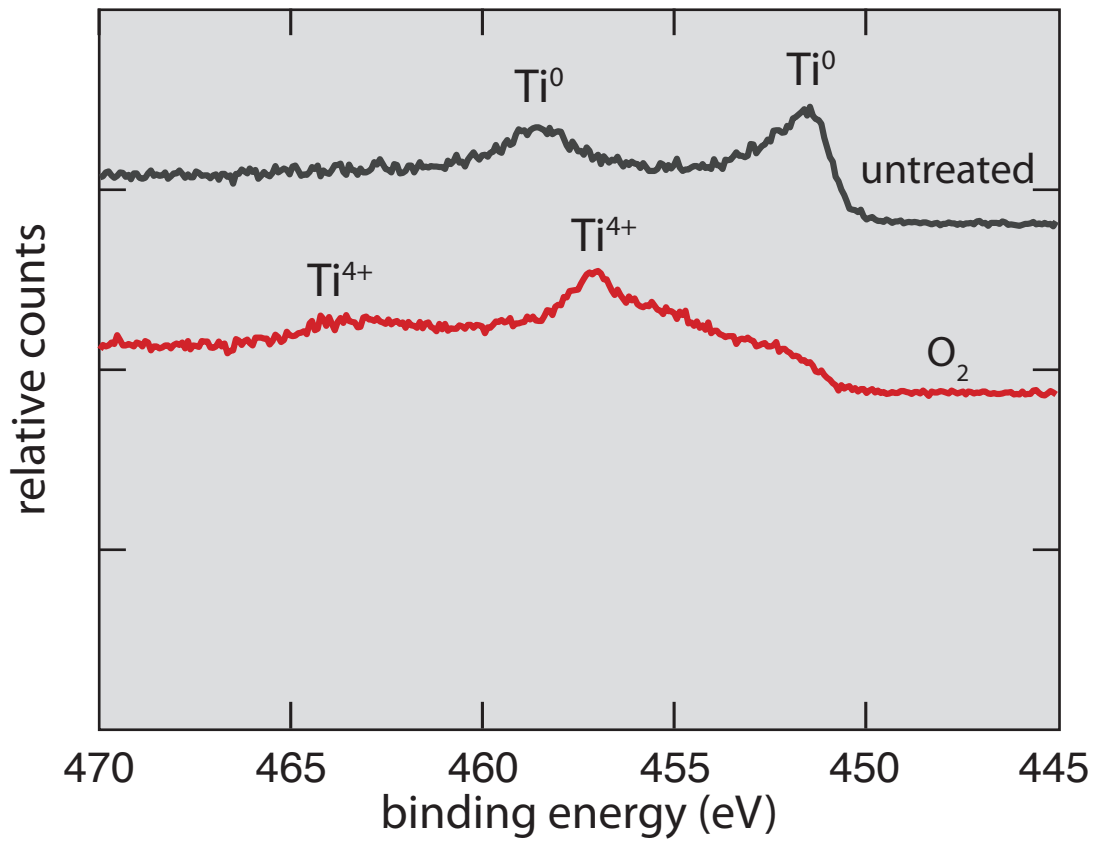


1 intermediate band

2 Si devices

3 X:TiO_2

oxygen is incorporated!

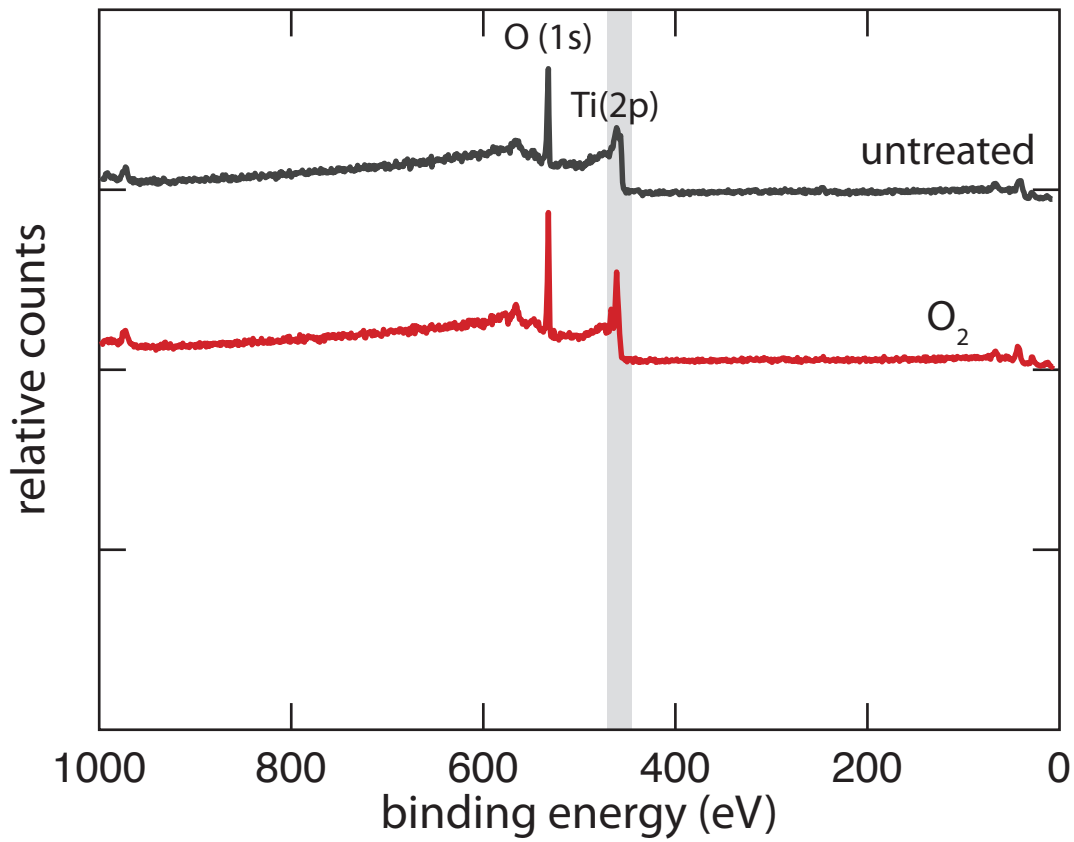


1 intermediate band

2 Si devices

3 X:TiO_2

oxygen is incorporated!

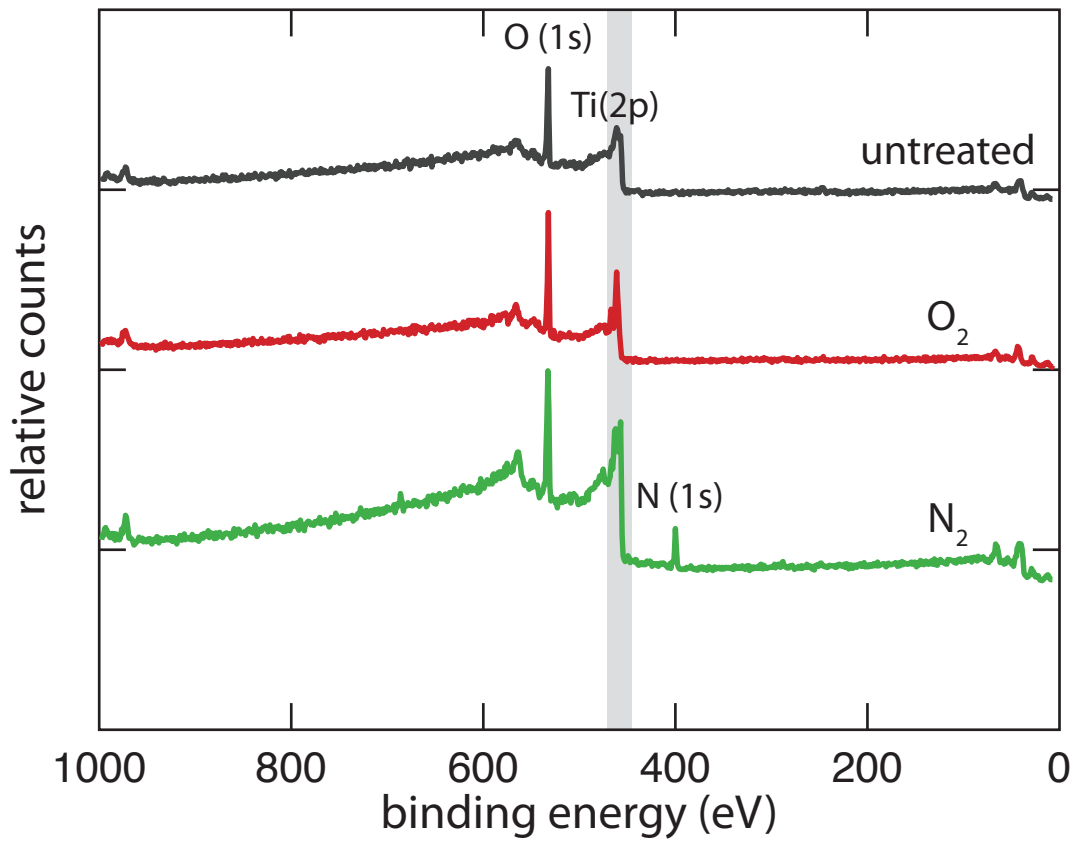


1 intermediate band

2 Si devices

3 $X:TiO_2$

nitrogen peak appears…

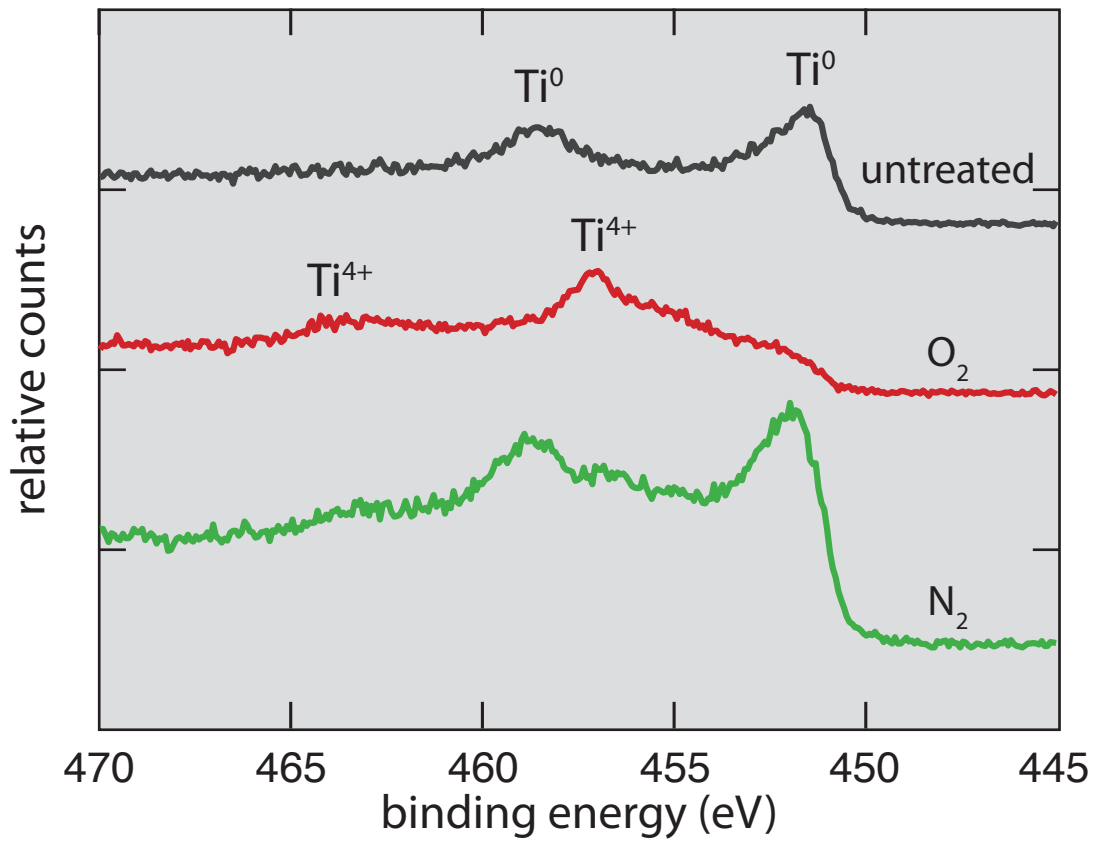


1 intermediate band

2 Si devices

3 $X:TiO_2$

… but nitrogen not chemically incorporated

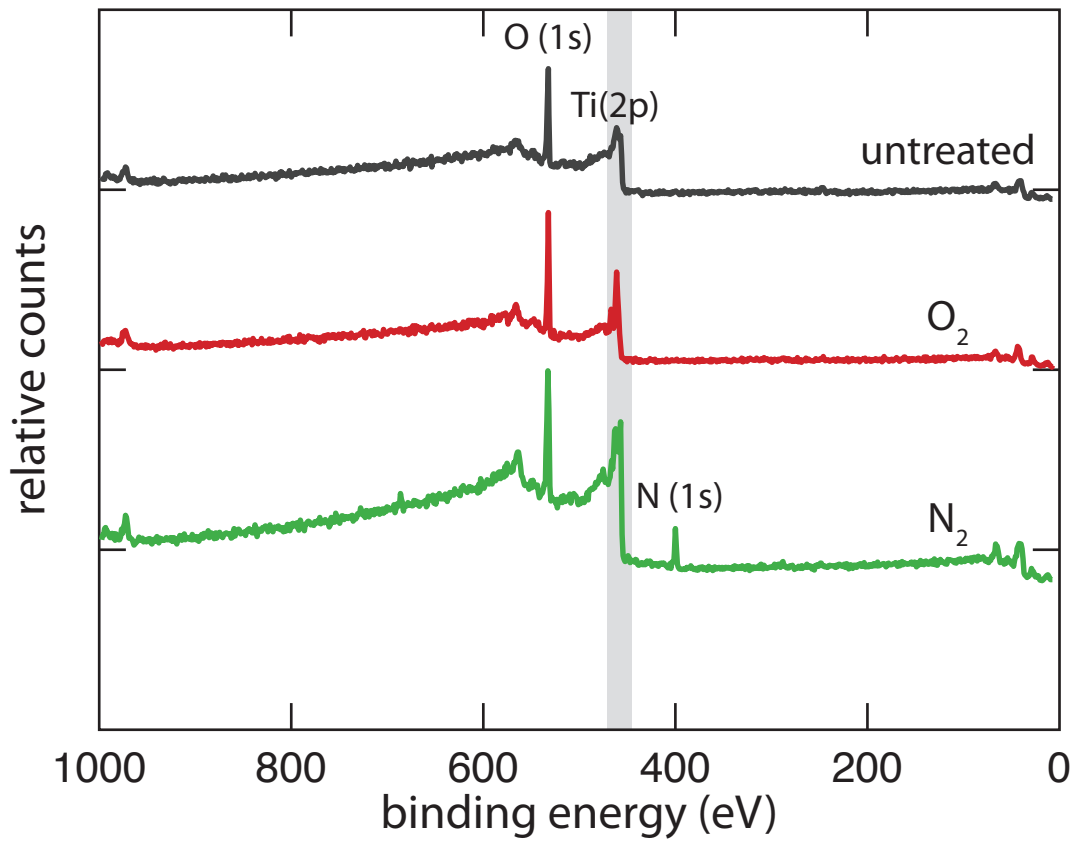


1 intermediate band

2 Si devices

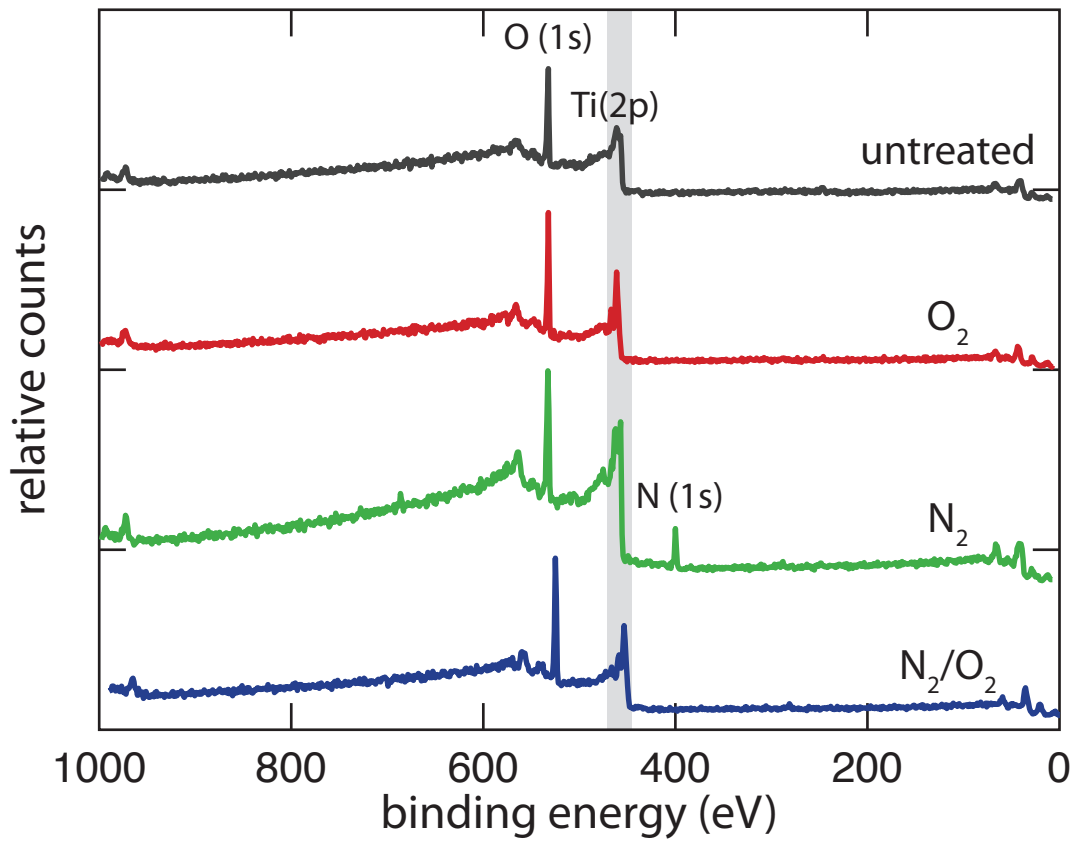
3 X:TiO_2

… but nitrogen not chemically incorporated



1 intermediate band 2 Si devices 3 $X:TiO_2$

with both nitrogen and oxygen…

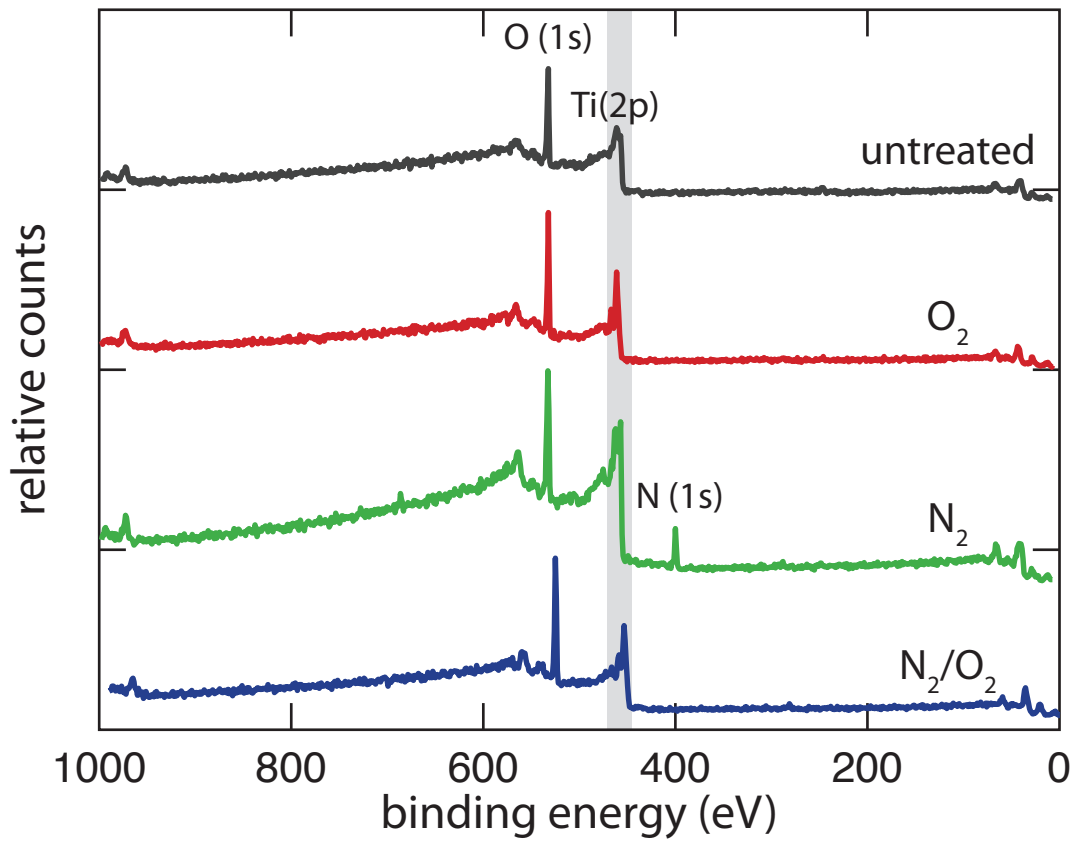


1 intermediate band

2 Si devices

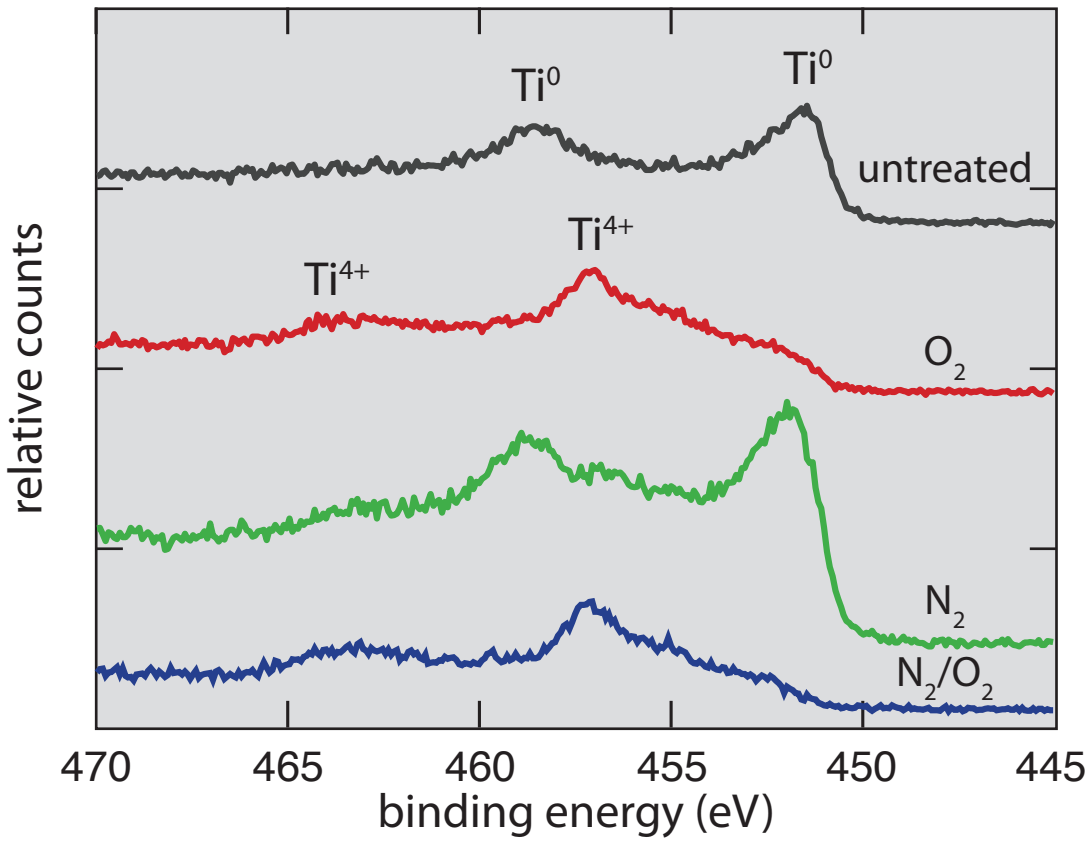
3 $X:TiO_2$

… just 1% of oxygen prevents nitrogen incorporation…



1 intermediate band 2 Si devices 3 $X:TiO_2$

… although oxygen is incorporated



1 intermediate band

2 Si devices

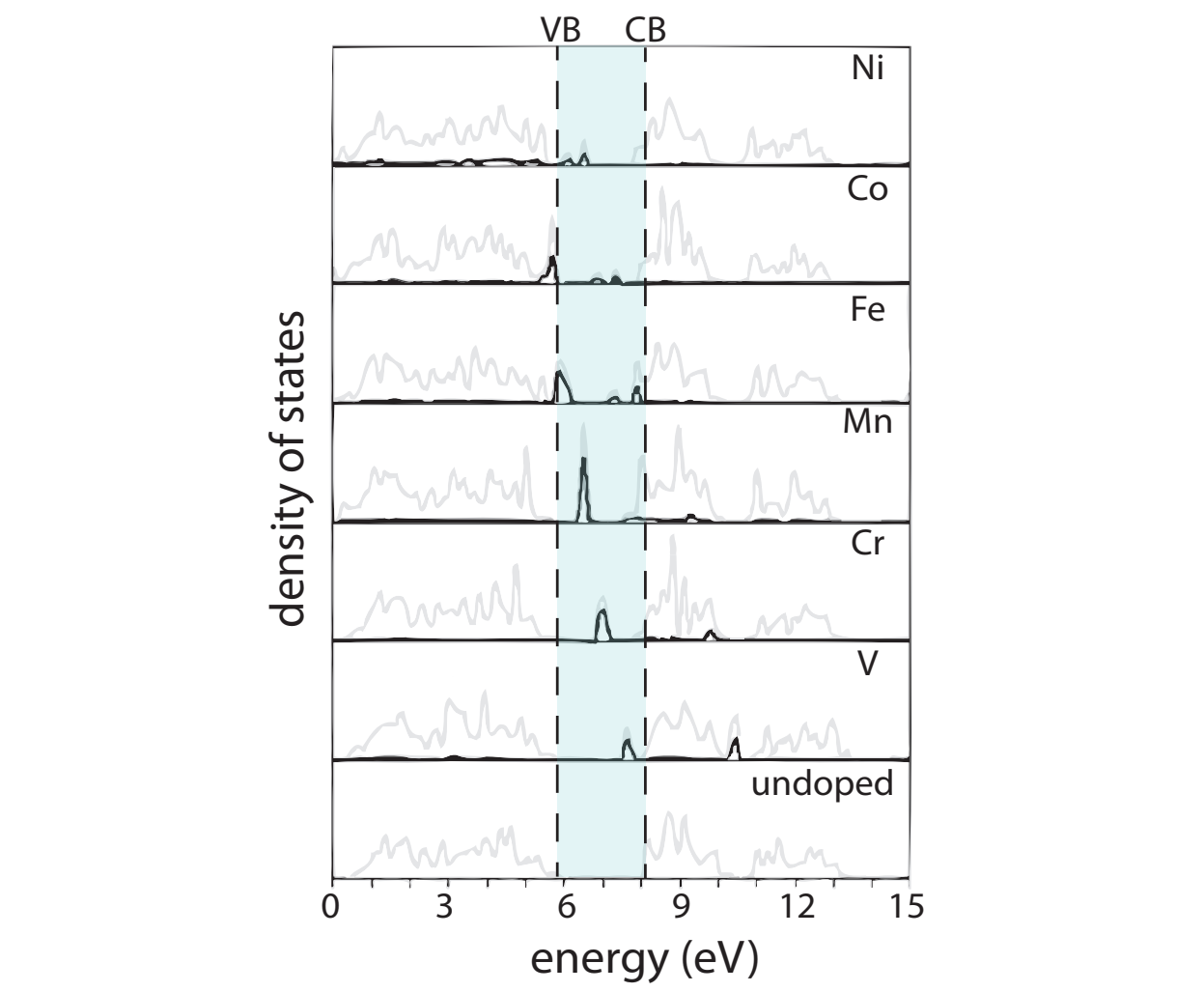
3 X:TiO_2

can get N_2 or O_2 incorporated, but not both

can get N_2 or O_2 incorporated, but not both

textured TiO_2/Ti: high biocompatibility

TiO_2 density of states: other dopants



1 intermediate band

2 Si devices

3 X:TiO_2

how about incorporating chromium with oxygen?

1 intermediate band

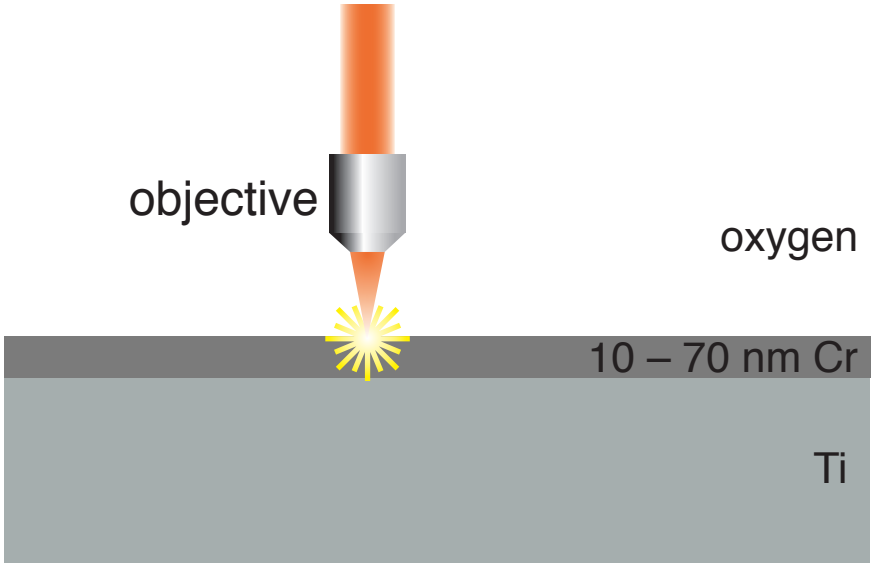
2 Si devices

3 X:TiO_2

evaporate 10 – 70 nm chromium on titanium…

…place in oxygen atmosphere…

…irradiate with laser…



1 intermediate band

2 Si devices

3 X:TiO_2

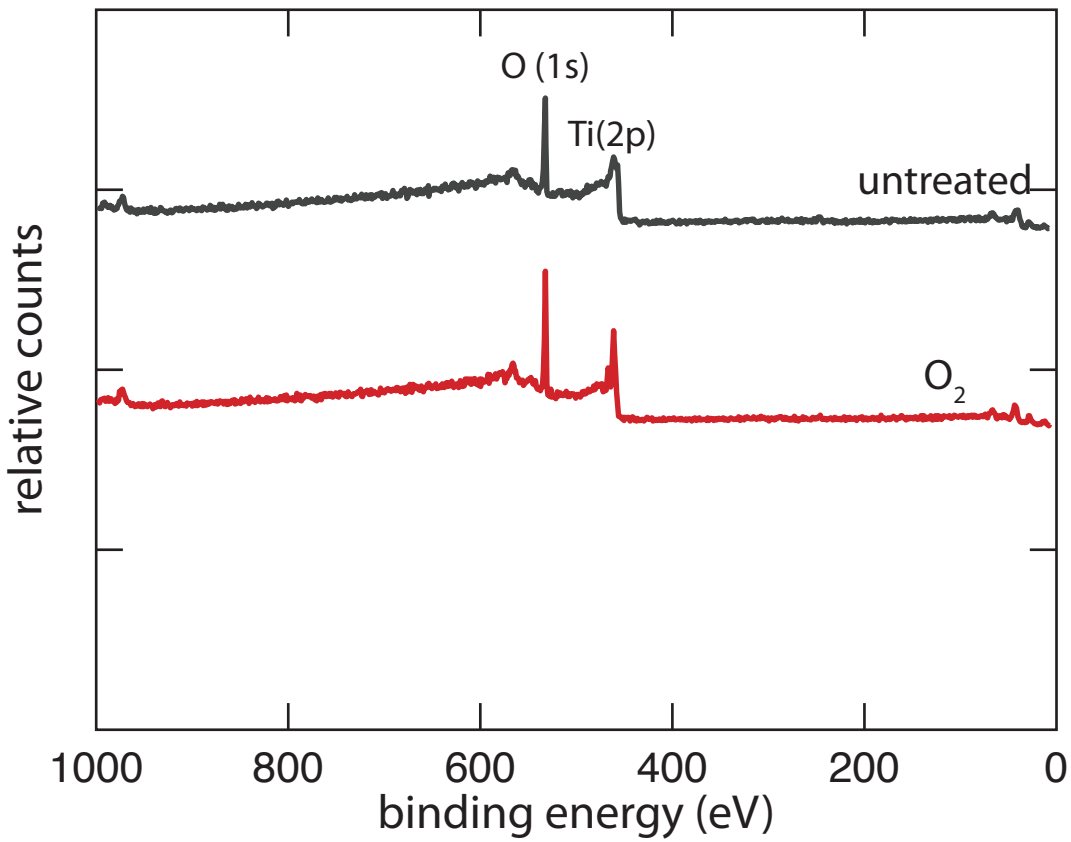
…and raster scan to structure

1 intermediate band

2 Si devices

3 X:TiO_2

X-ray photoelectron spectroscopy

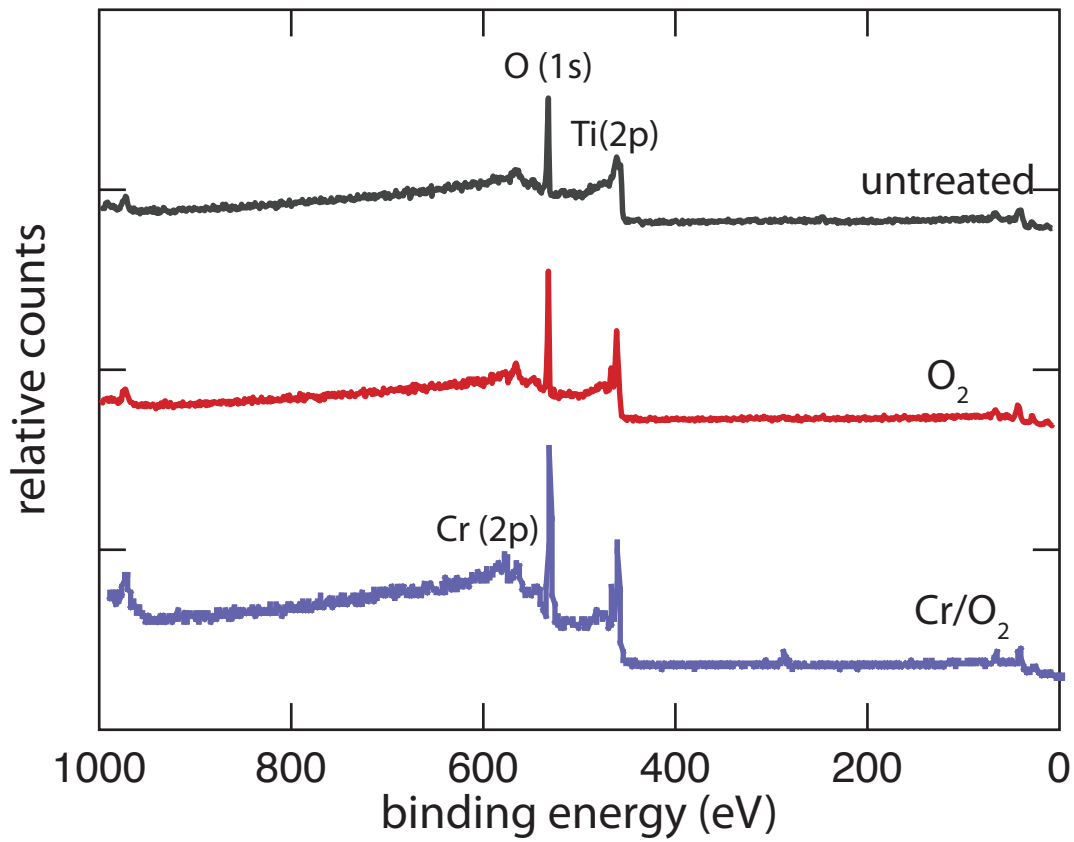


1 intermediate band

2 Si devices

3 X:TiO_2

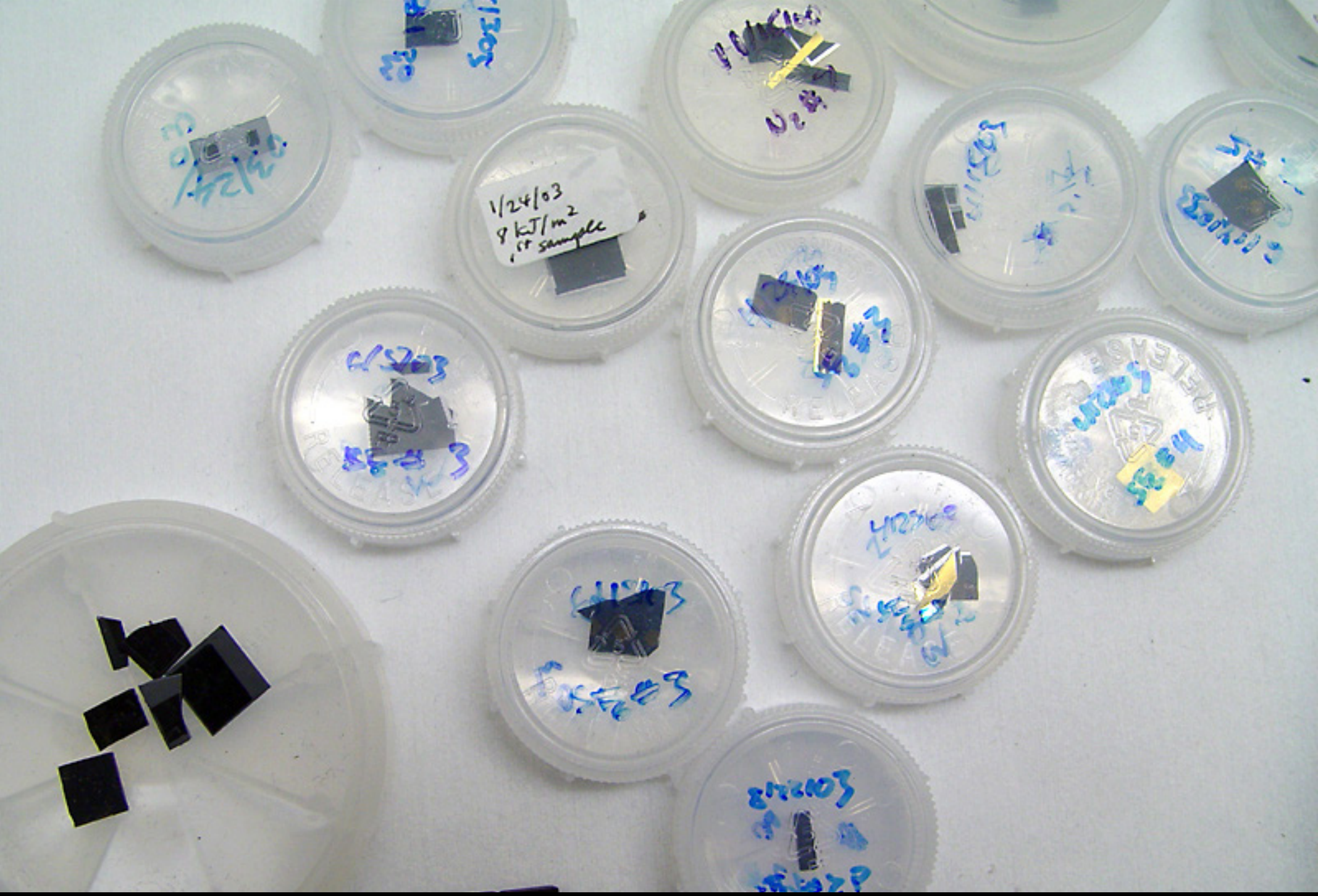
both chromium and oxygen incorporated!



1 intermediate band

2 Si devices

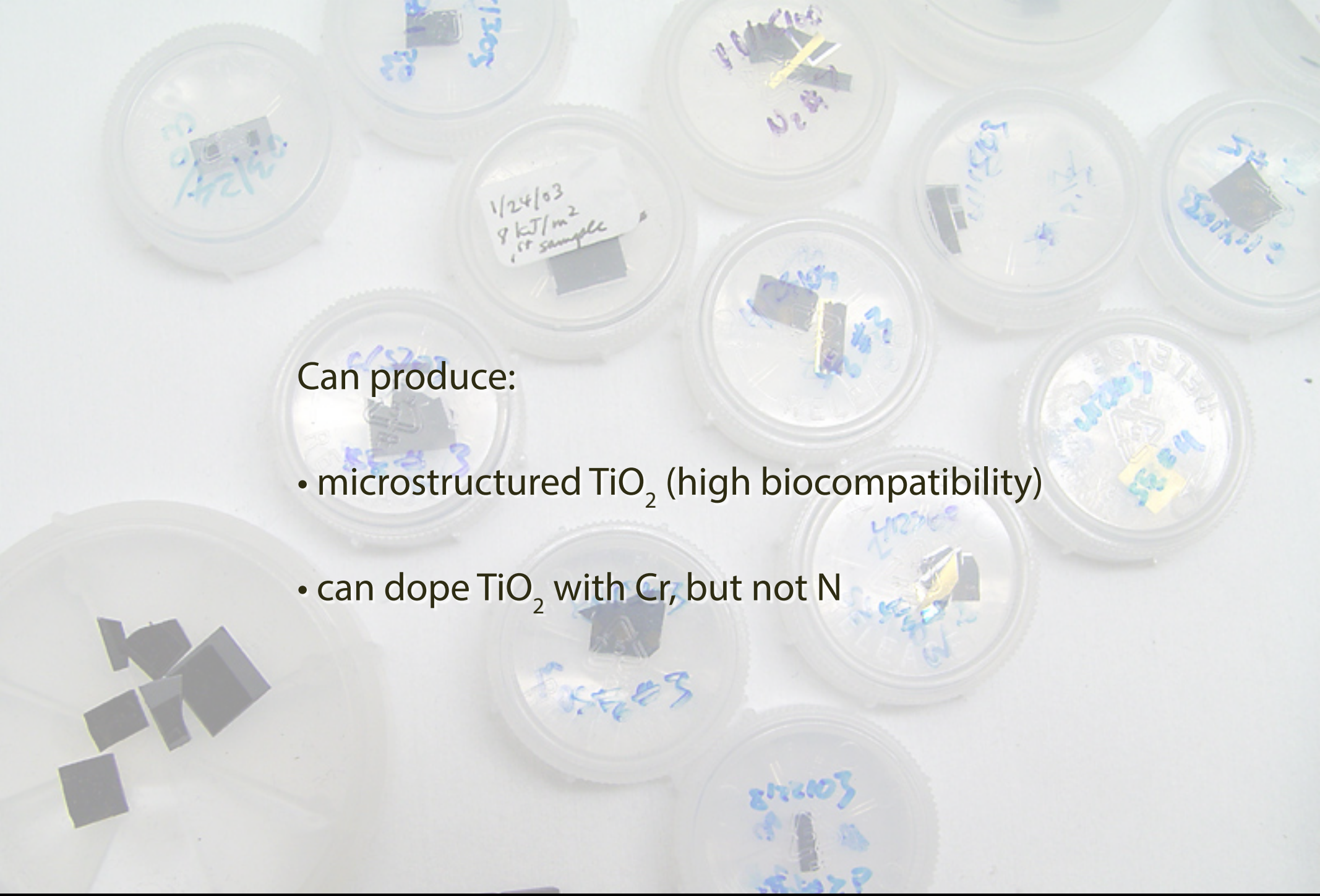
3 $X:TiO_2$



1 intermediate band

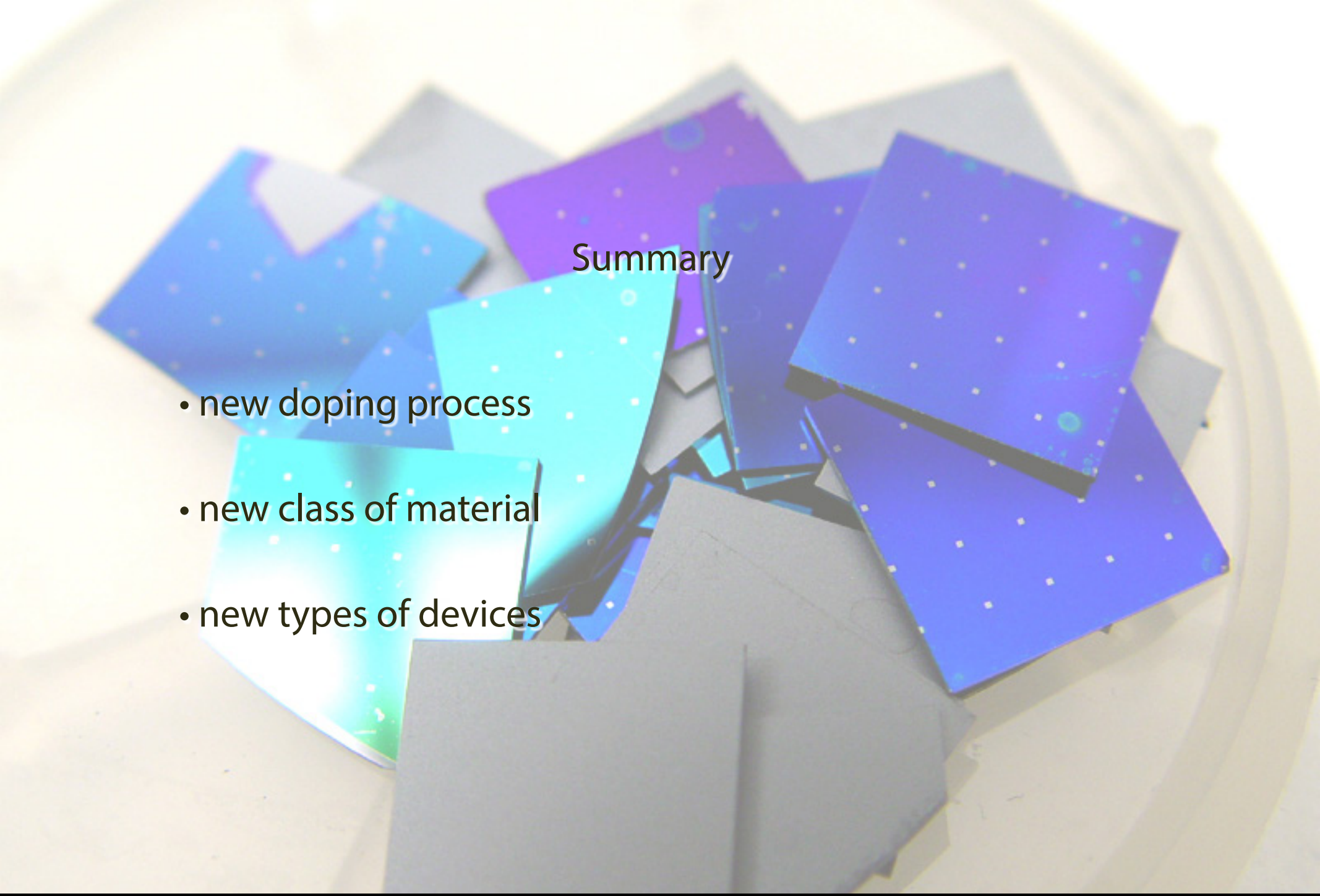
2 Si devices

3 X:TiO_2



Can produce:

- microstructured TiO_2 (high biocompatibility)
- can dope TiO_2 with Cr, but not N



Summary

- new doping process
- new class of material
- new types of devices

1 intermediate band

2 Si devices

3 X:TiO_2

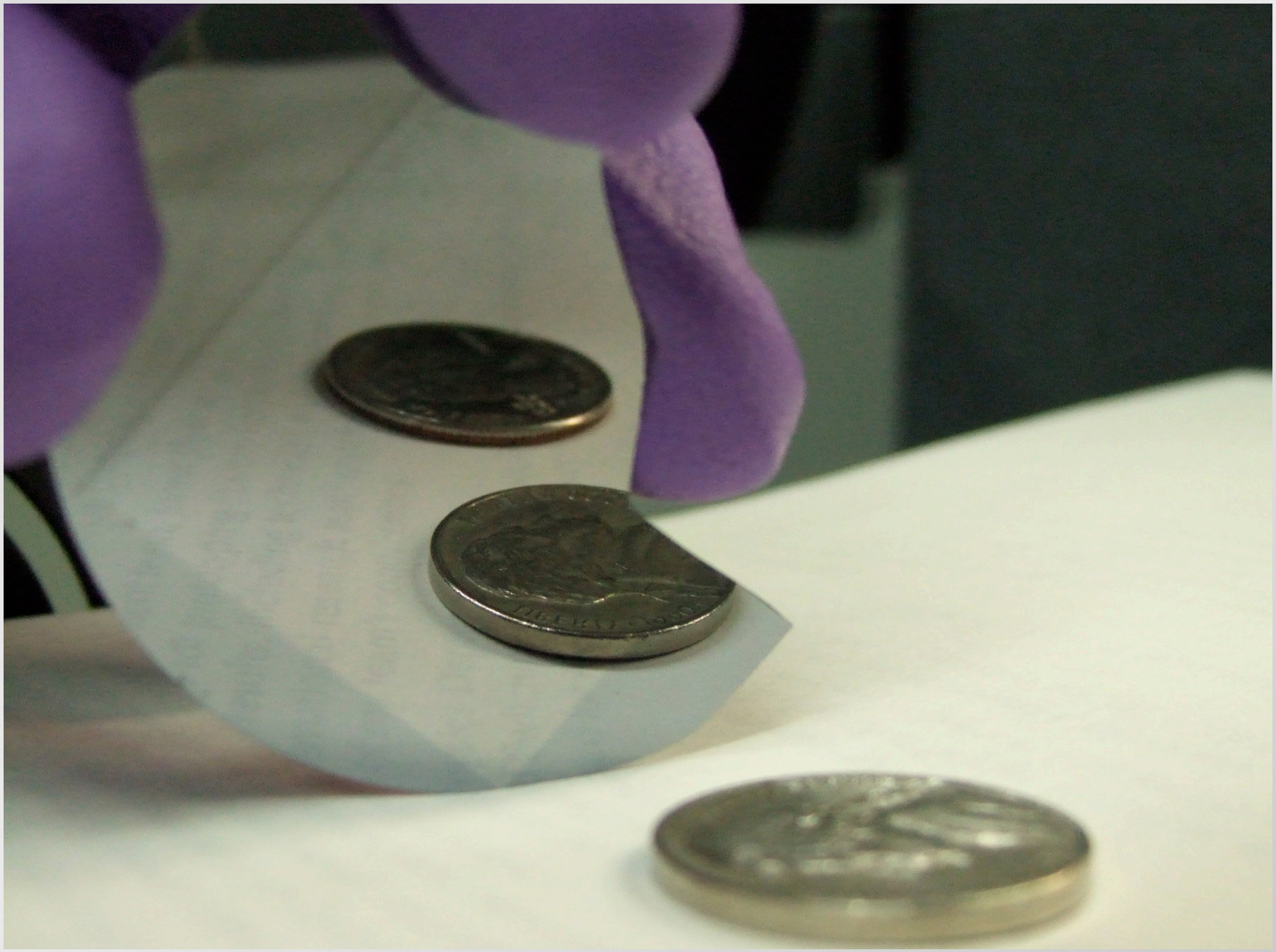
Funding:

Army Research Office
DARPA
Department of Energy
NDSEG
National Science Foundation

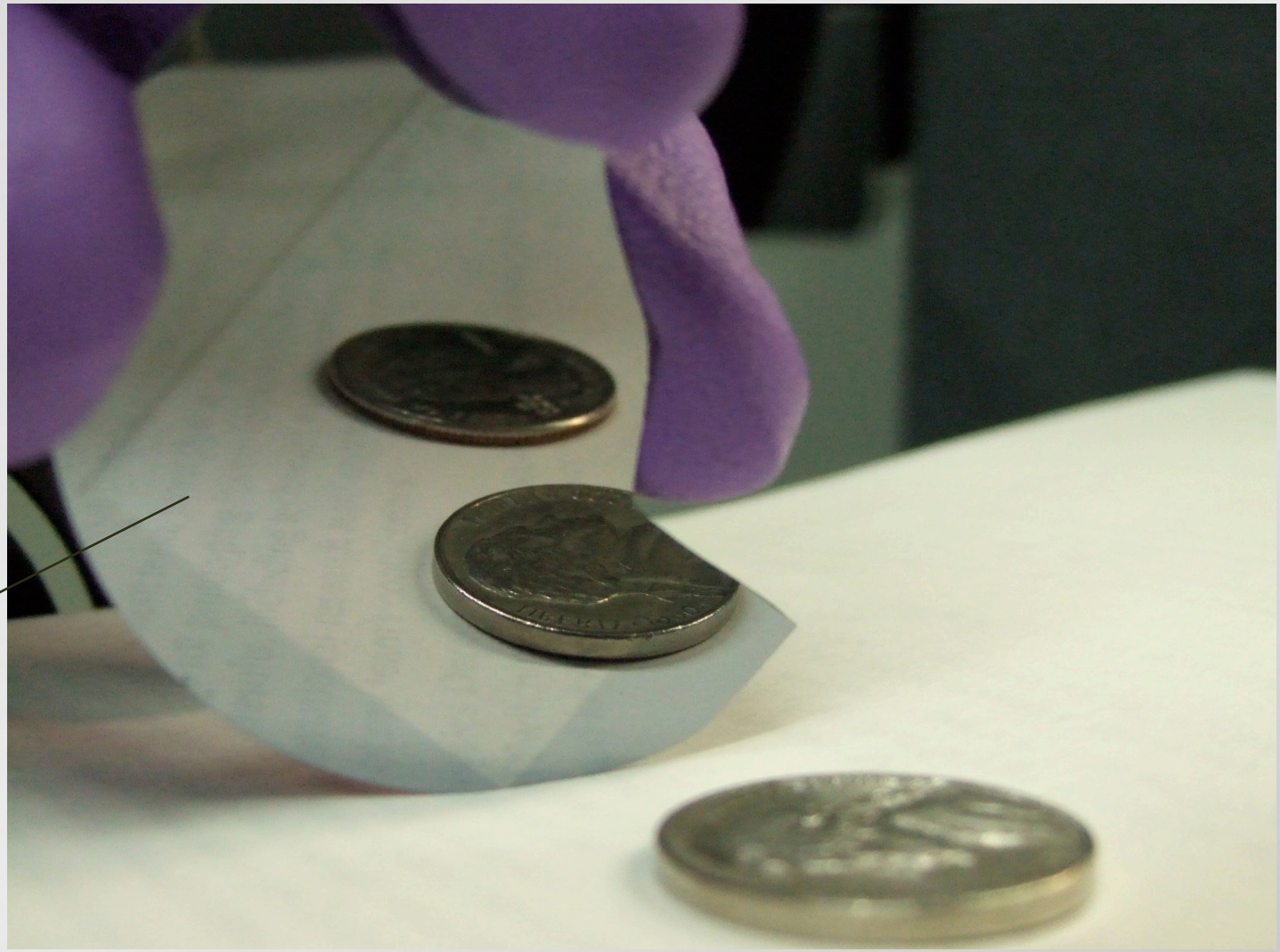
for more information and a copy of this presentation:

http://mazur.harvard.edu

decouple ablation from melting

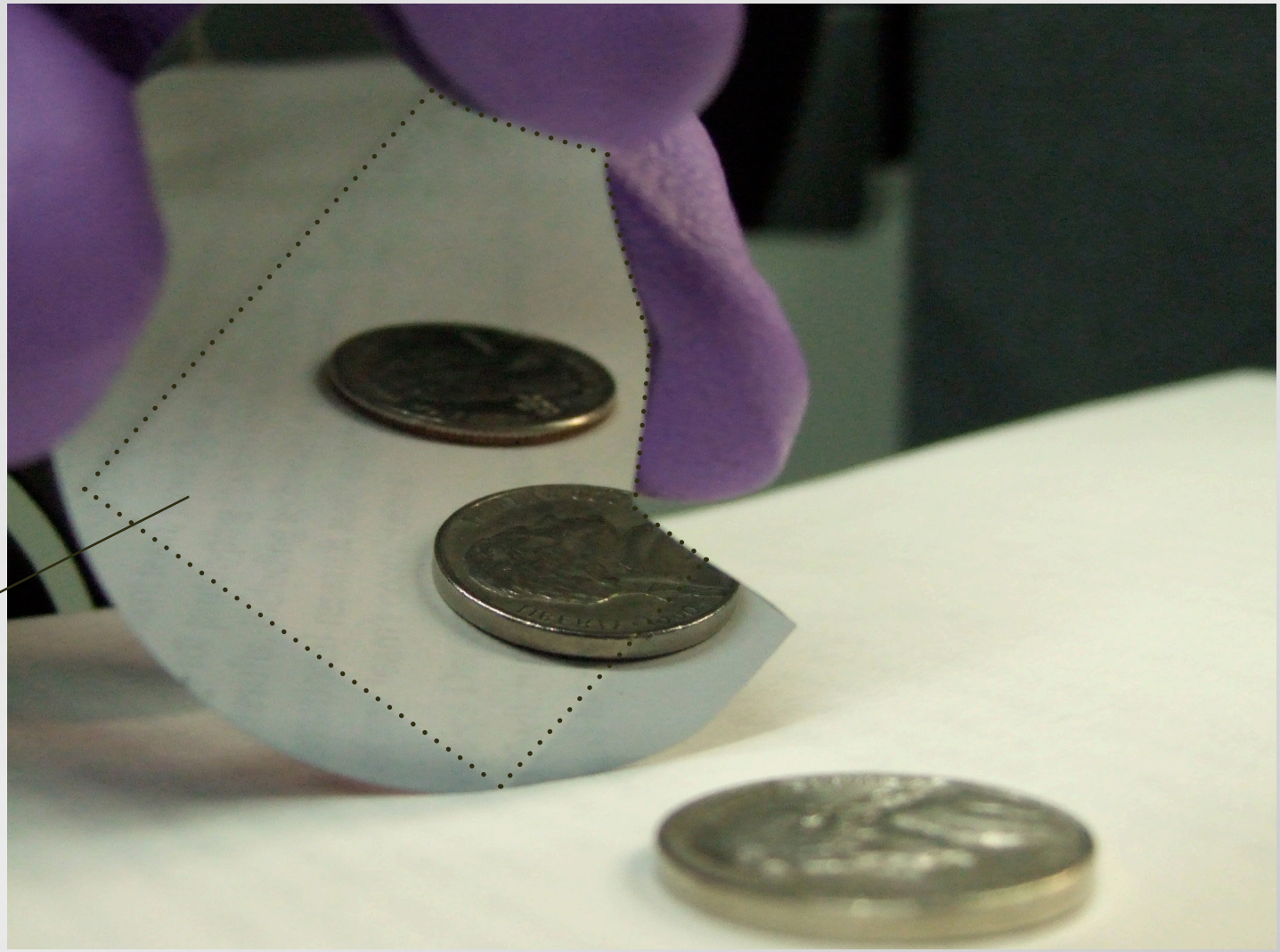


decouple ablation from melting



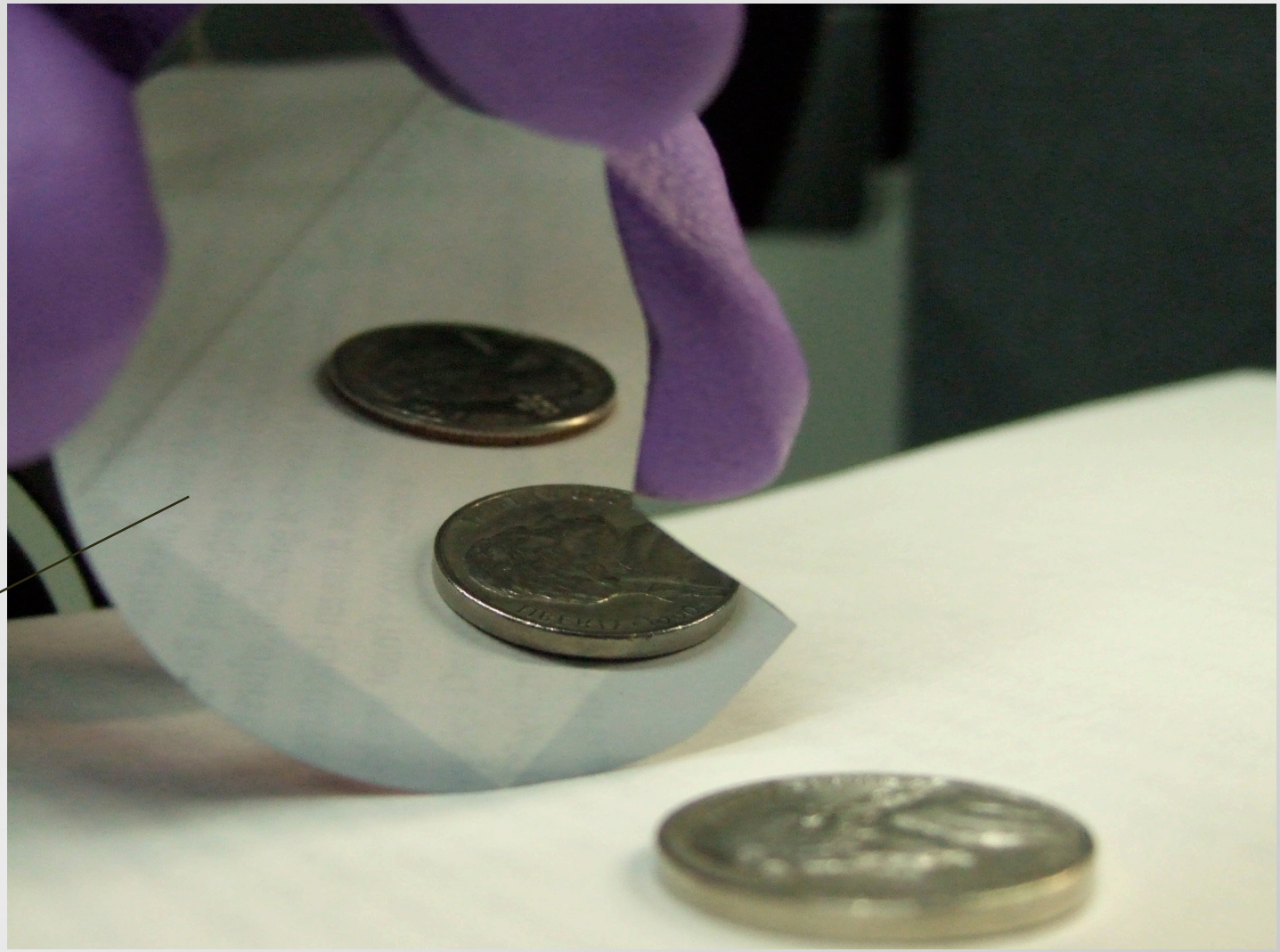
1 intermediate band

decouple ablation from melting



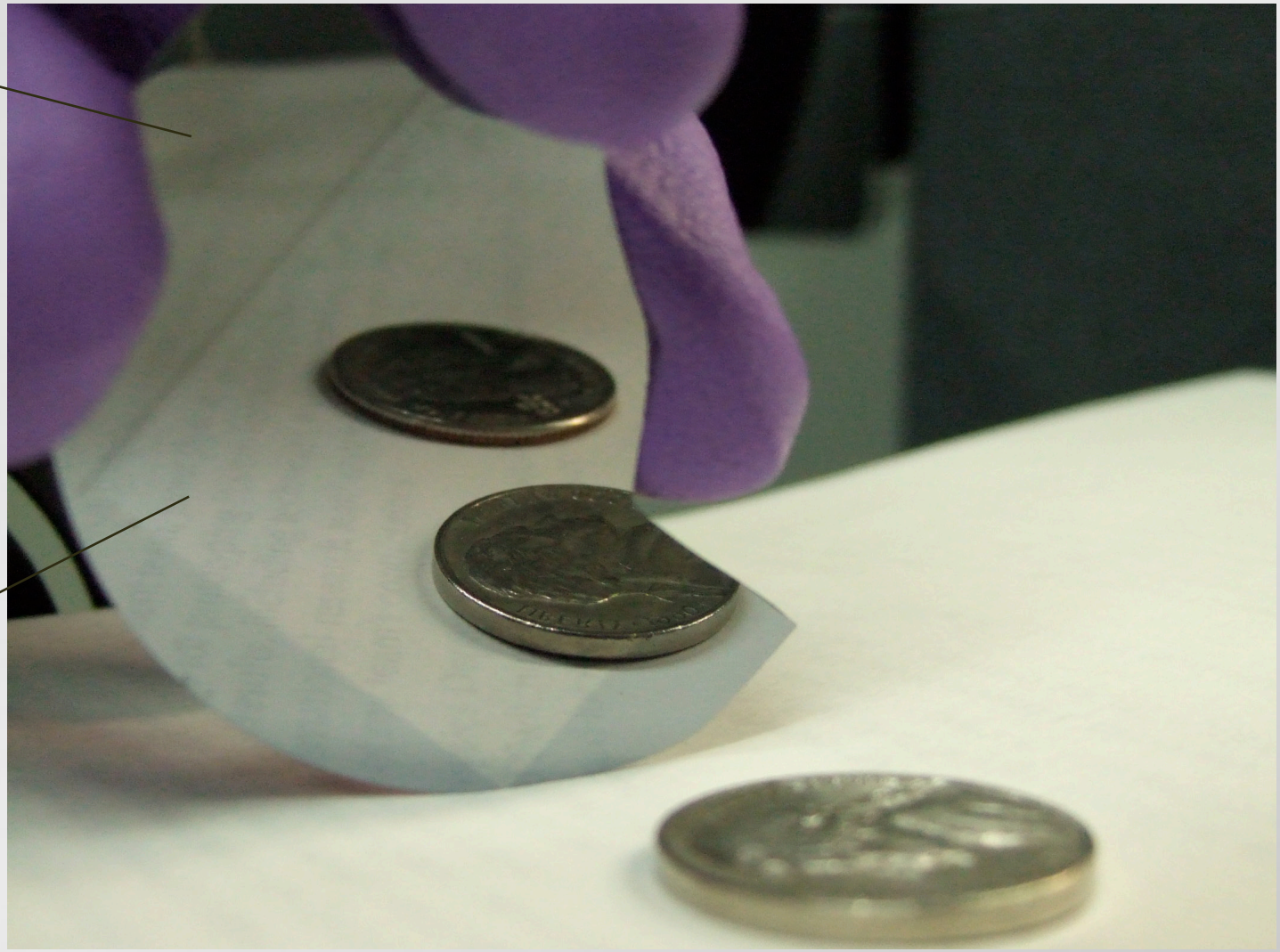
1 intermediate band

decouple ablation from melting



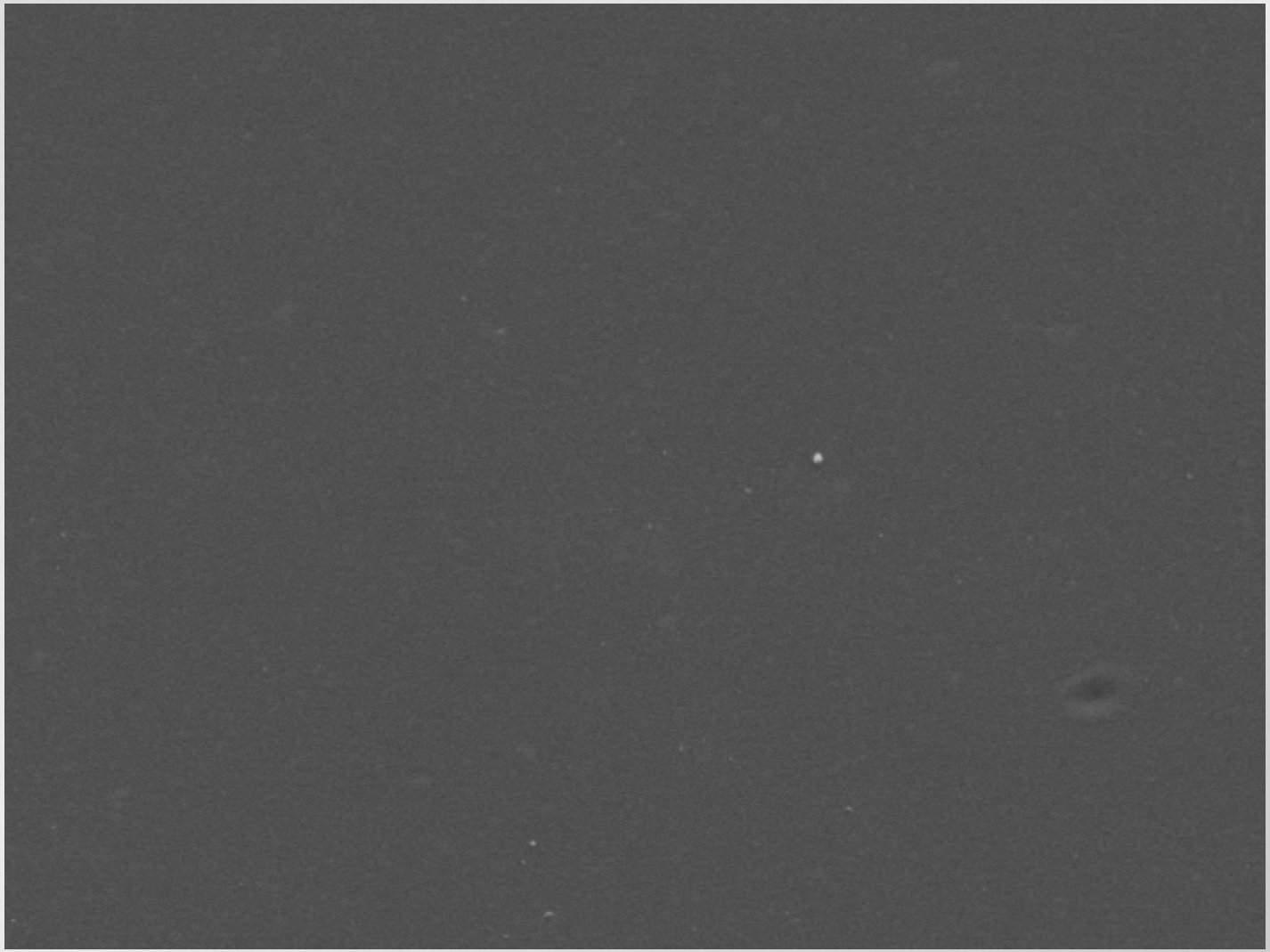
1 intermediate band

decouple ablation from melting



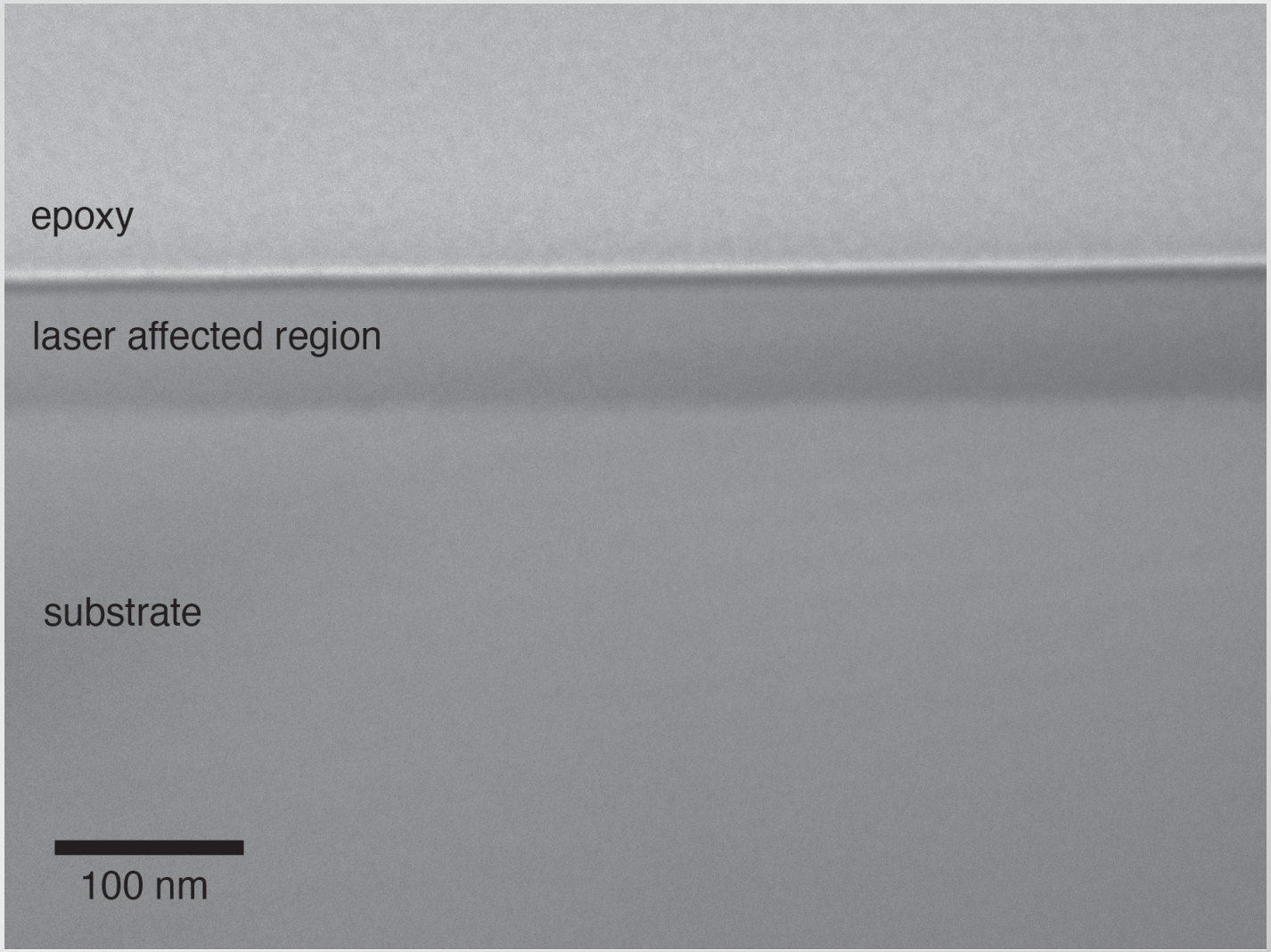
1 intermediate band

decouple ablation from melting

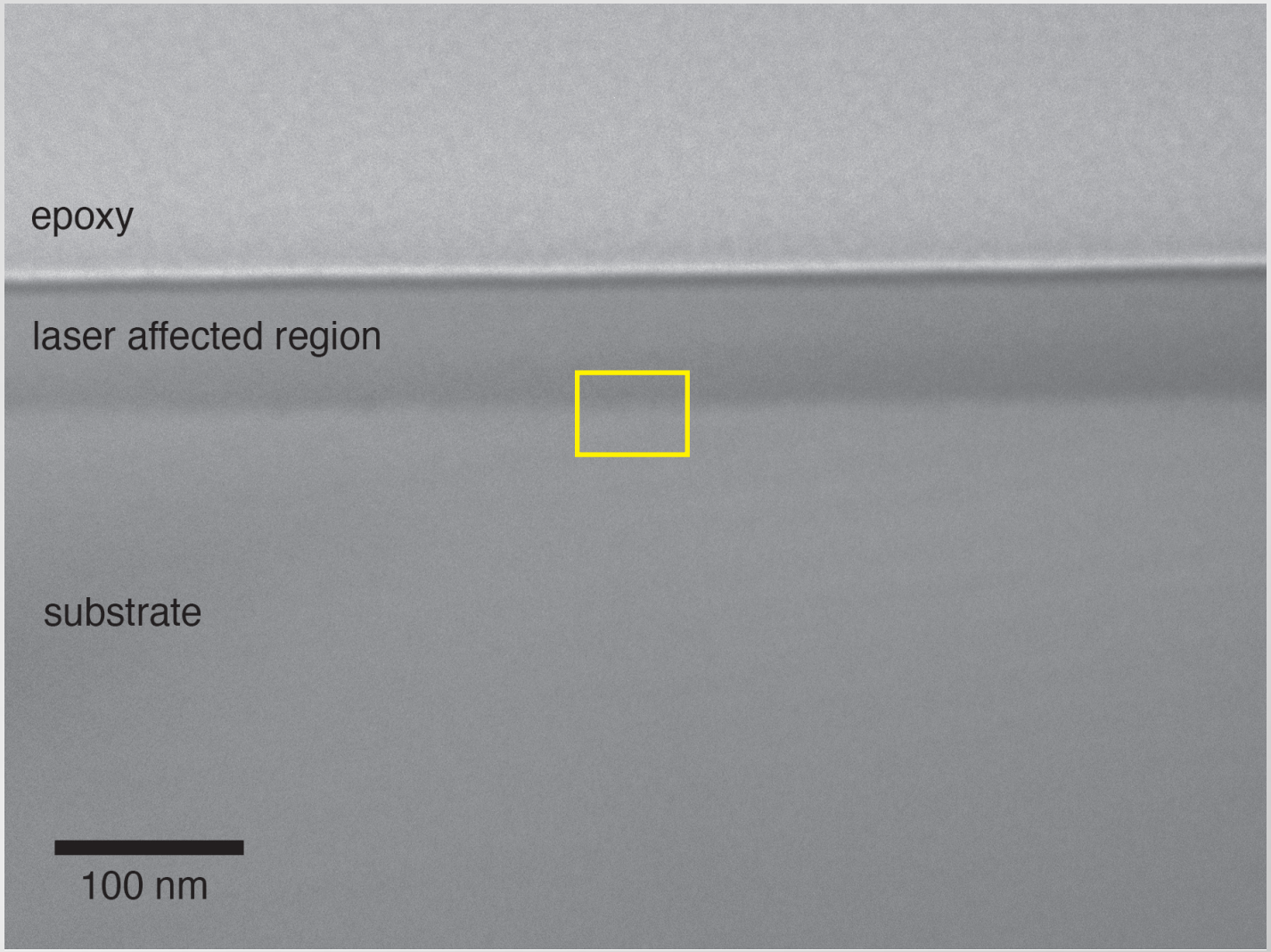


1 intermediate band

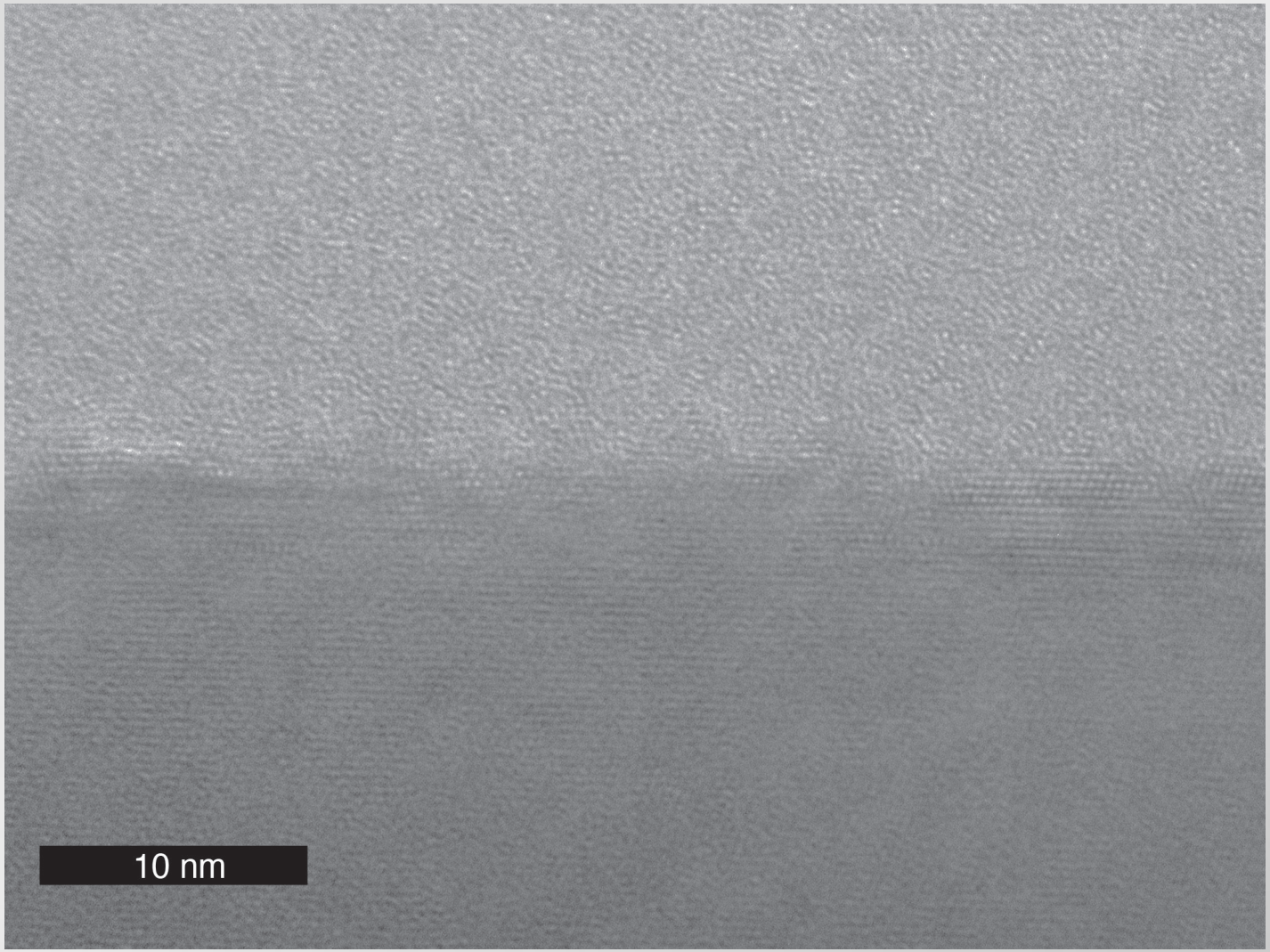
decouple ablation from melting



decouple ablation from melting

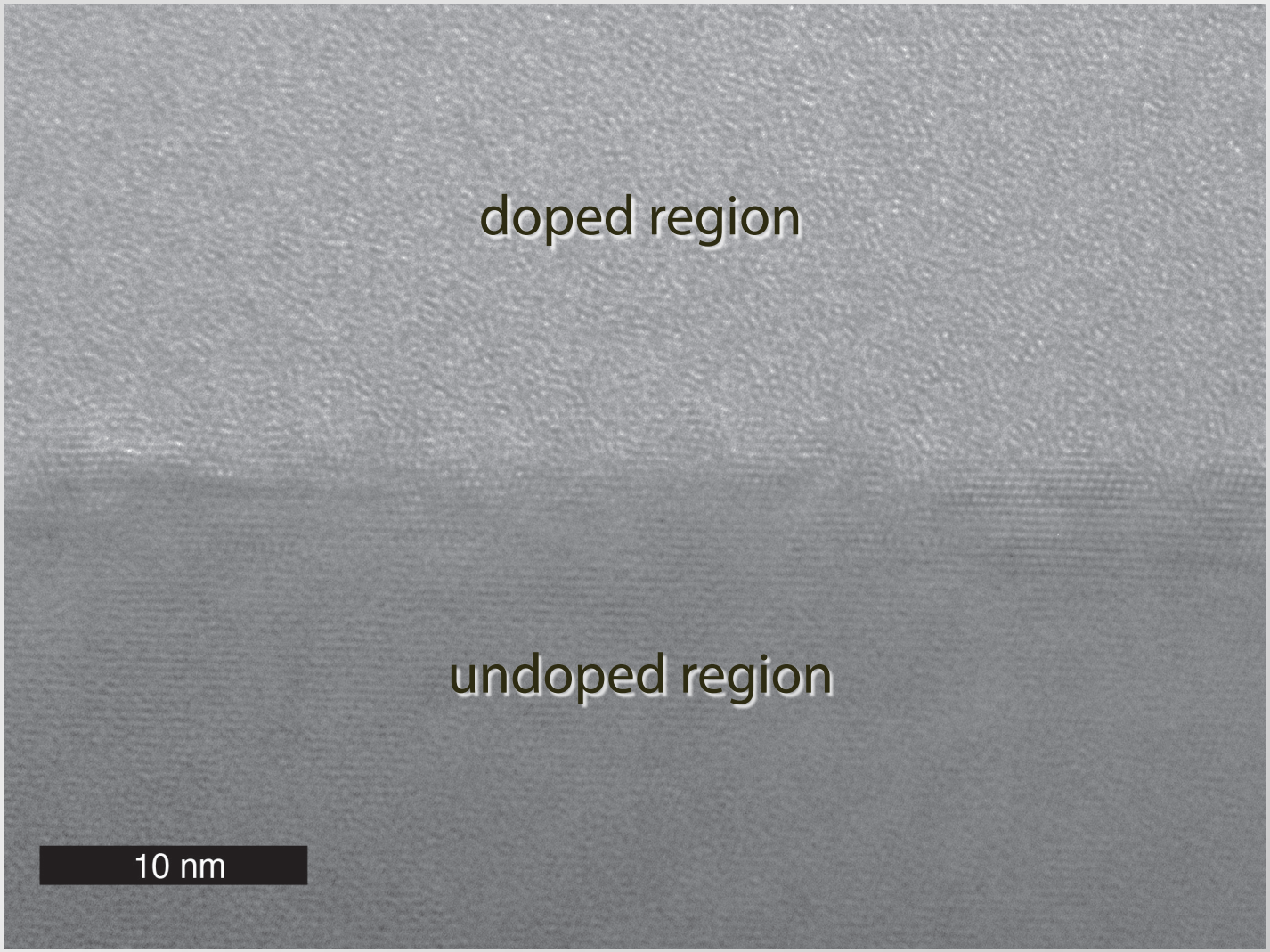


decouple ablation from melting

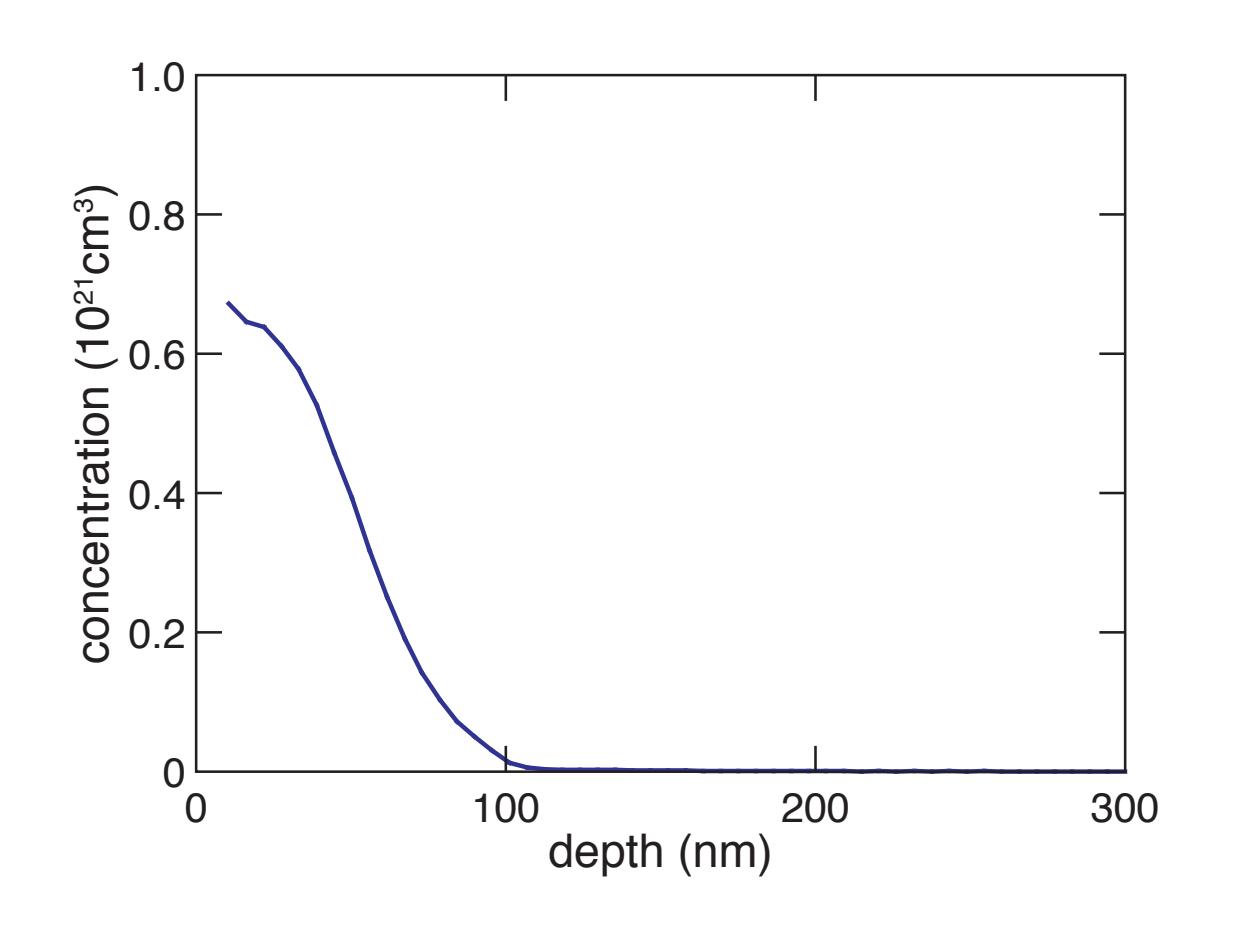


1 intermediate band

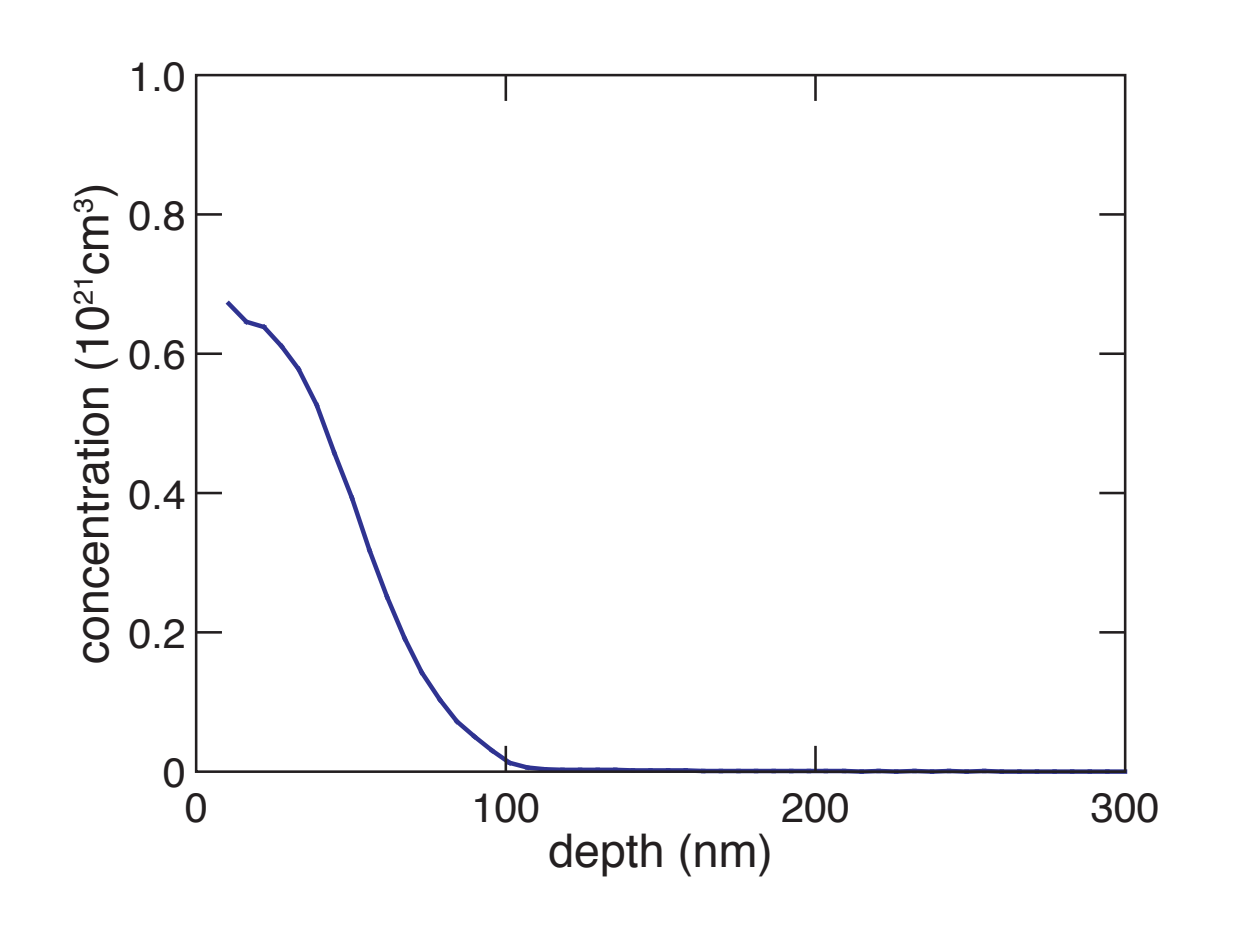
decouple ablation from melting



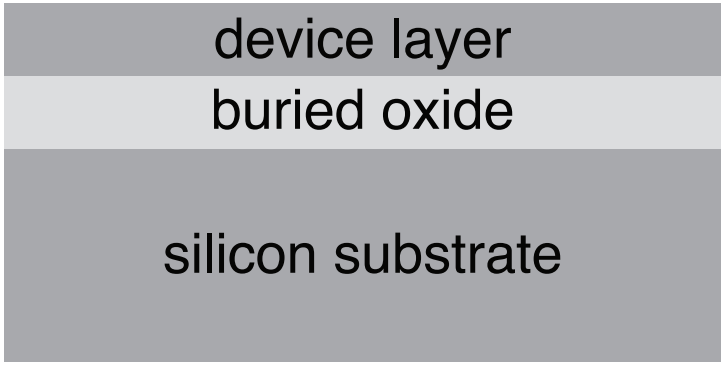
secondary ion mass spectrometry



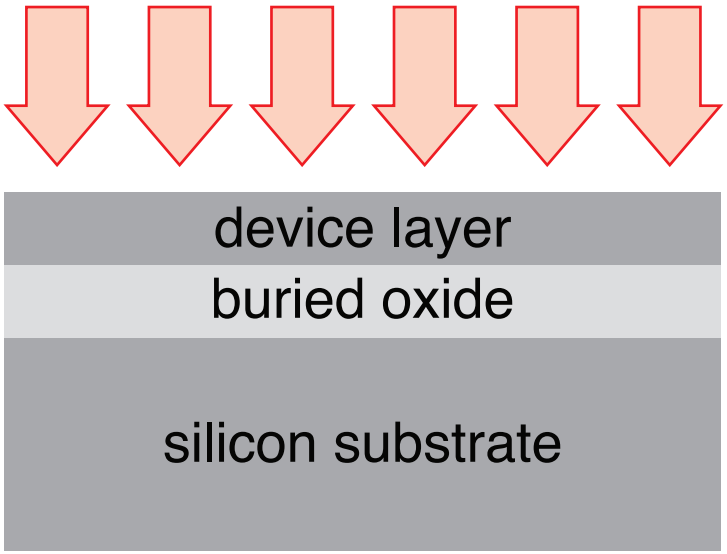
secondary ion mass spectrometry



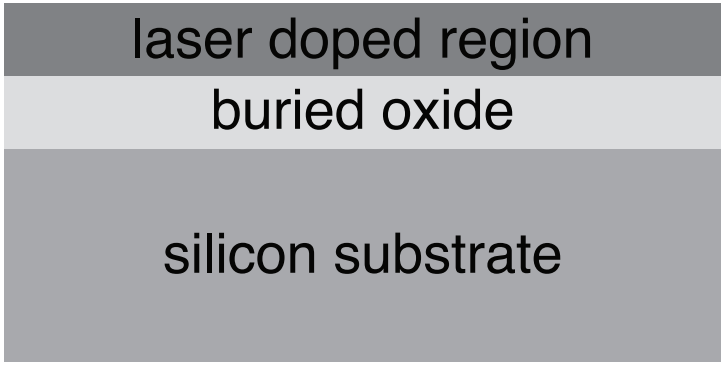
isolate surface layer for Hall measurements



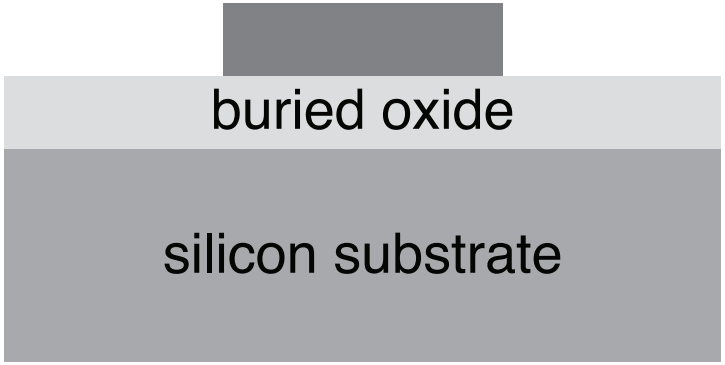
isolate surface layer for Hall measurements



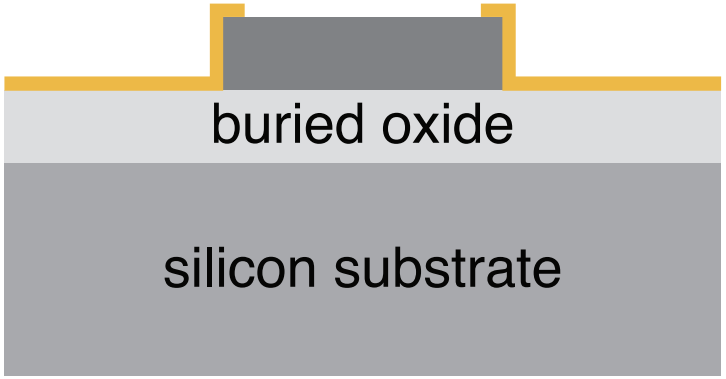
isolate surface layer for Hall measurements

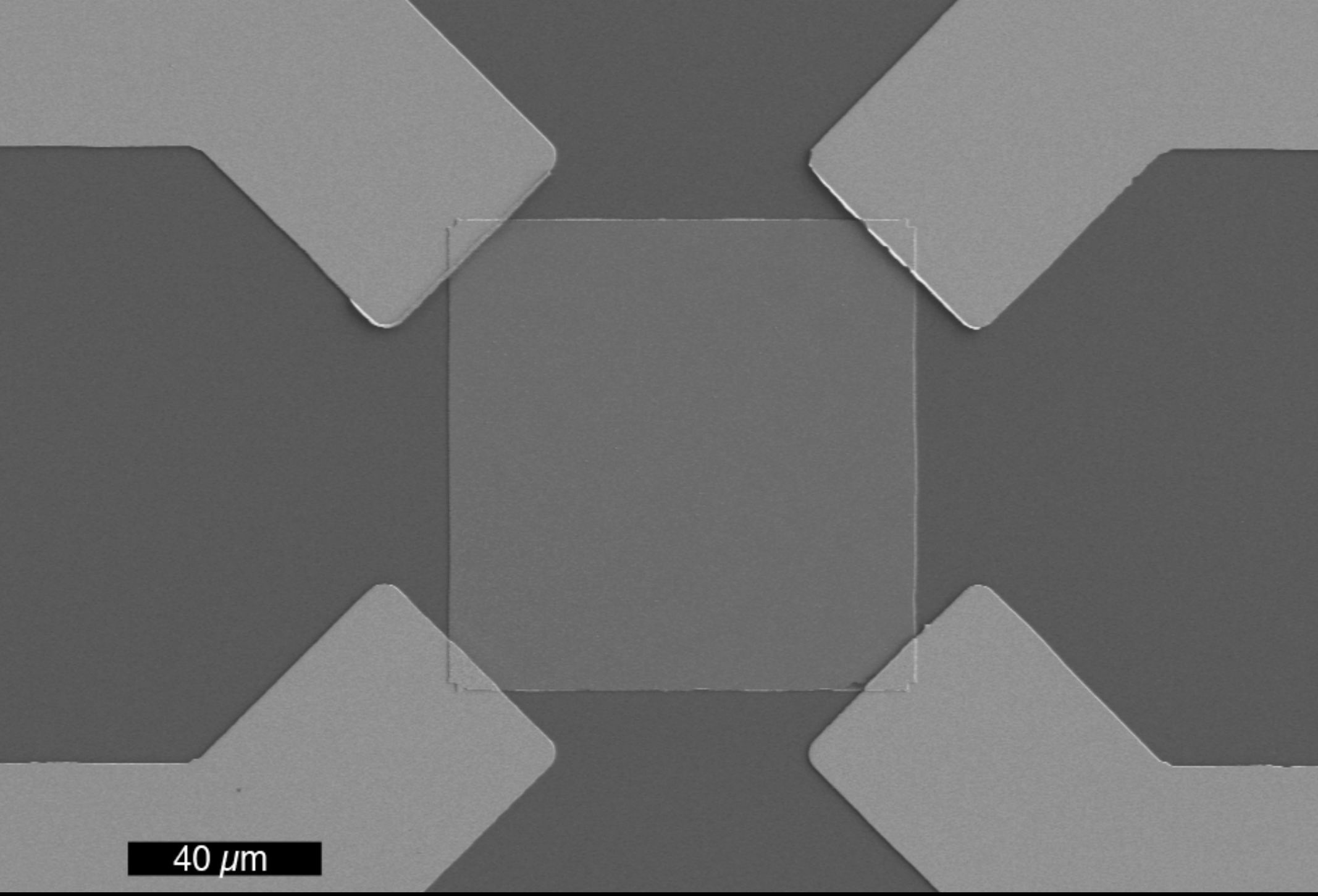


isolate surface layer for Hall measurements



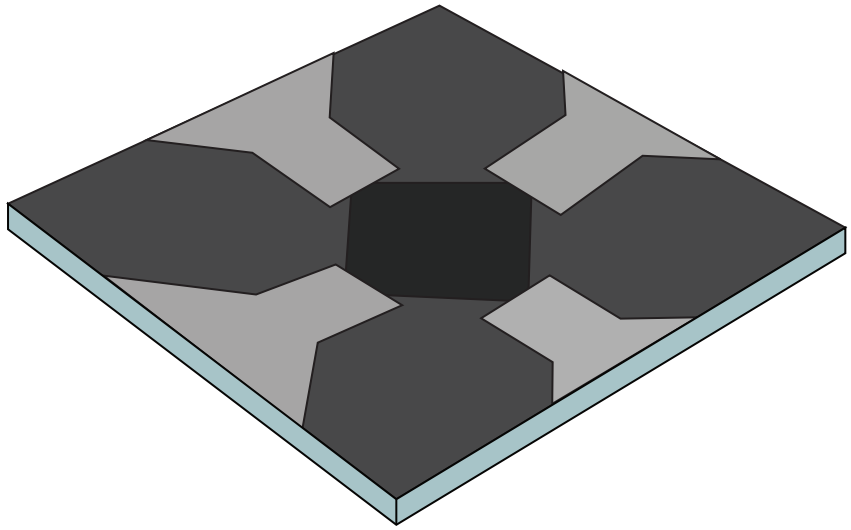
isolate surface layer for Hall measurements



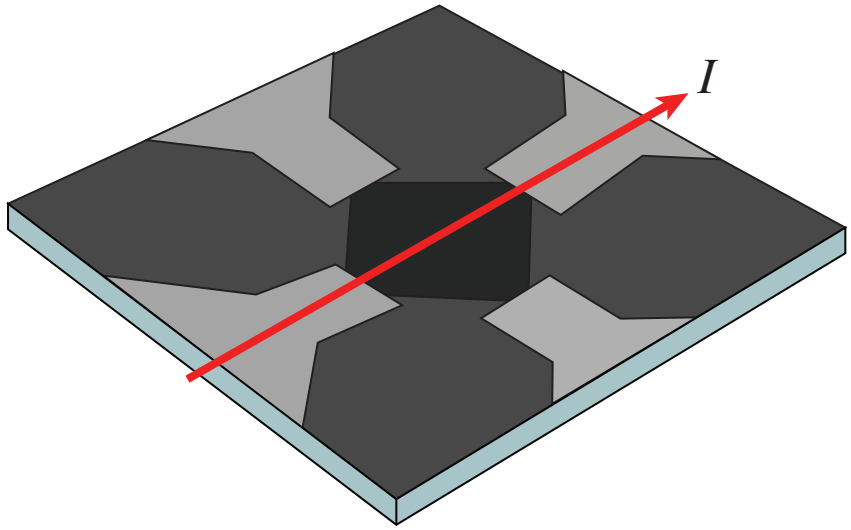


1 intermediate band

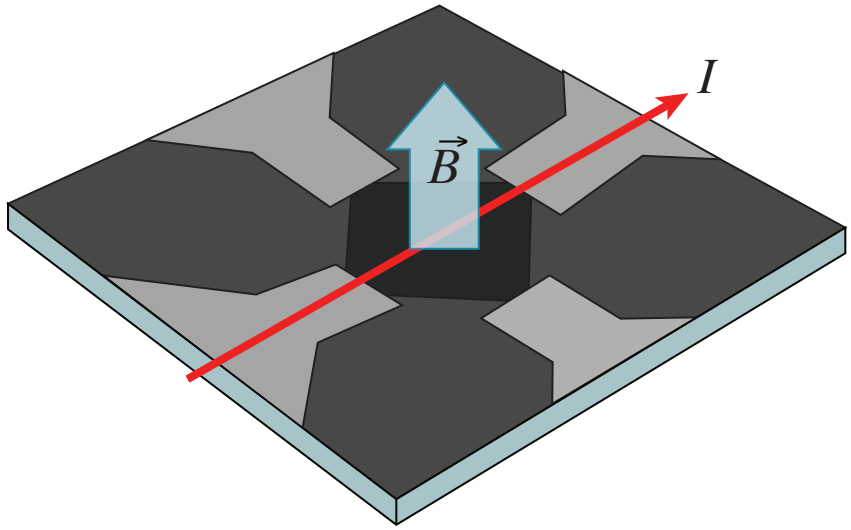
Hall measurements



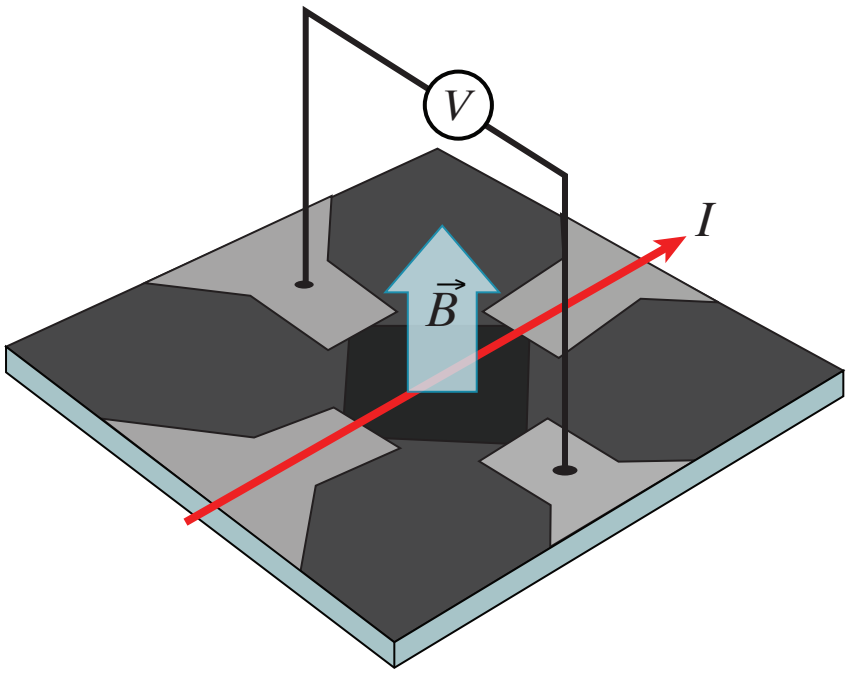
Hall measurements



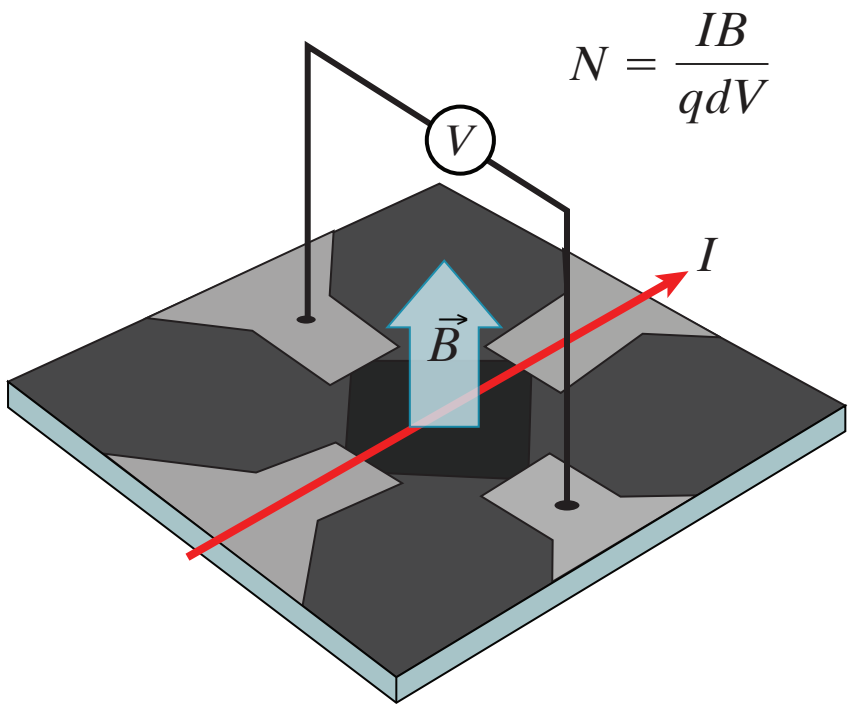
Hall measurements



Hall measurements

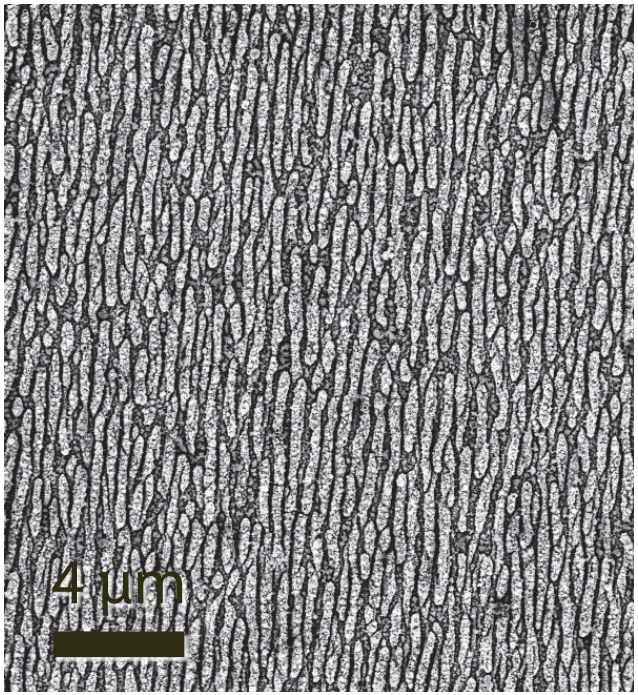


Hall measurements

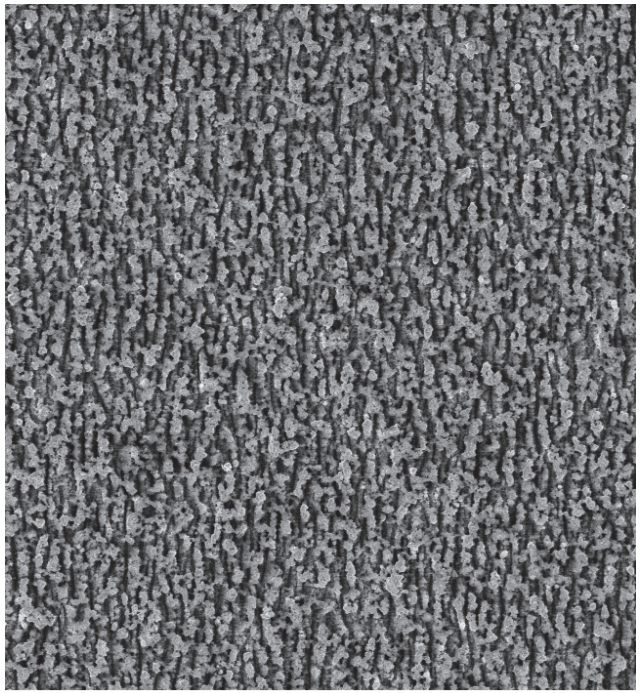


titanium/chromium in oxygen

titanium only



titanium/chromium



1 intermediate band

2 Si devices

3 X:TiO_2

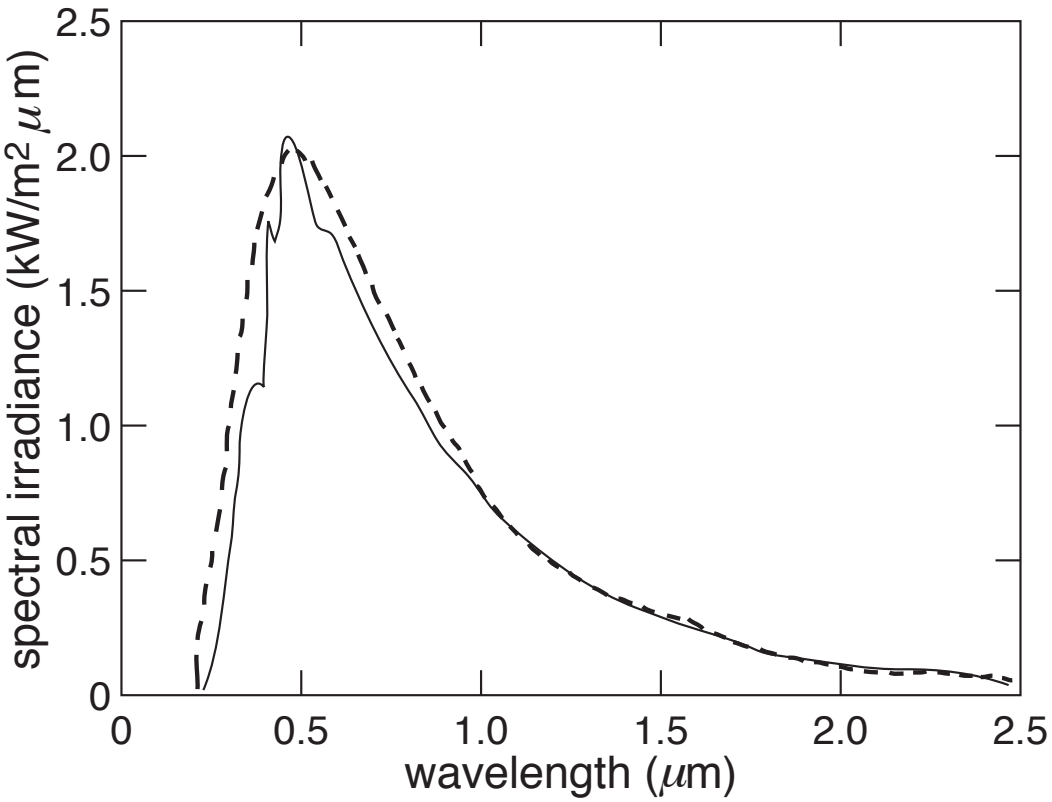
two processes: melting and ablation

different thresholds:

melting: 1.5 kJ/m^2

ablation: 3.1 kJ/m^2

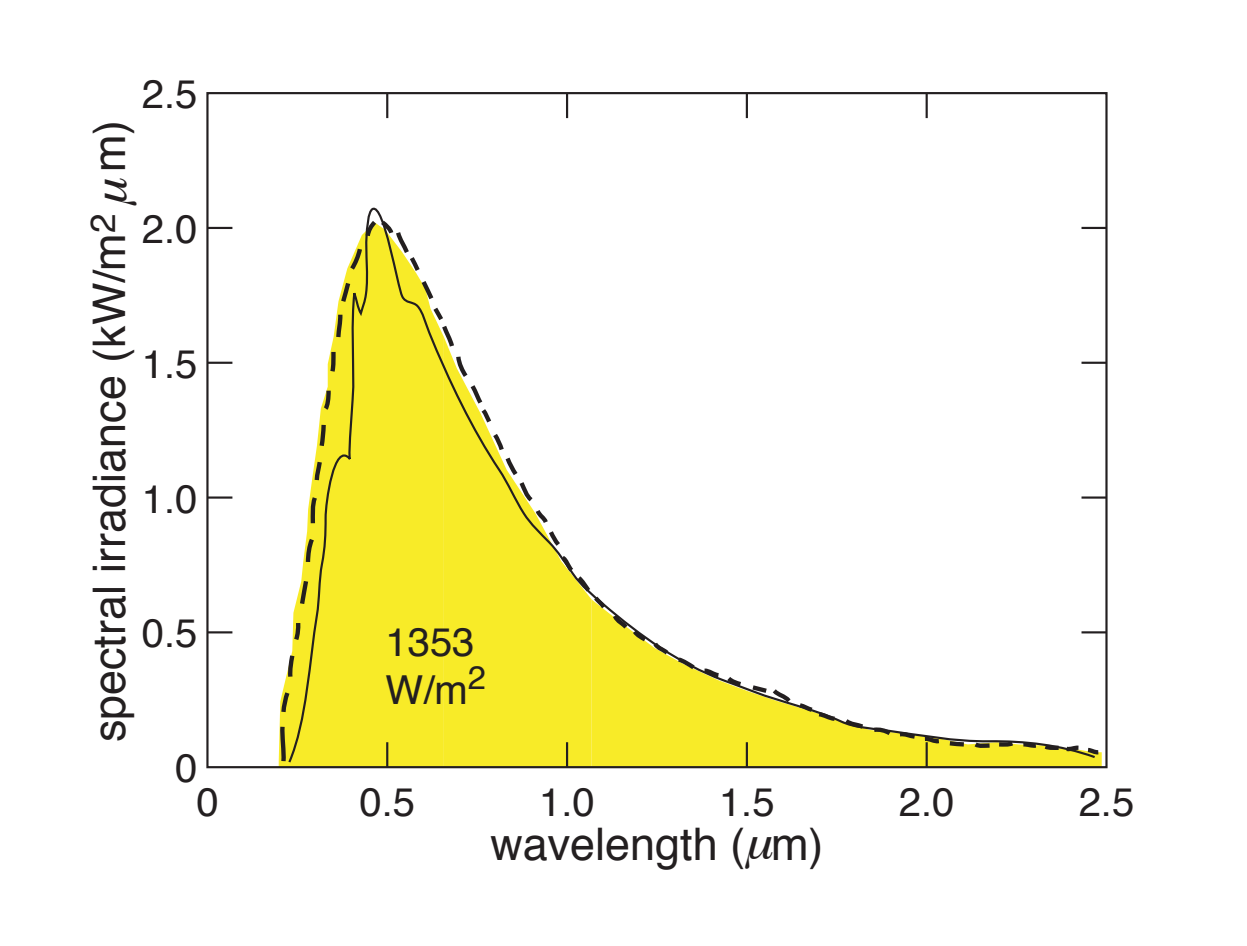
solar spectrum



1 intermediate band

2 Si devices

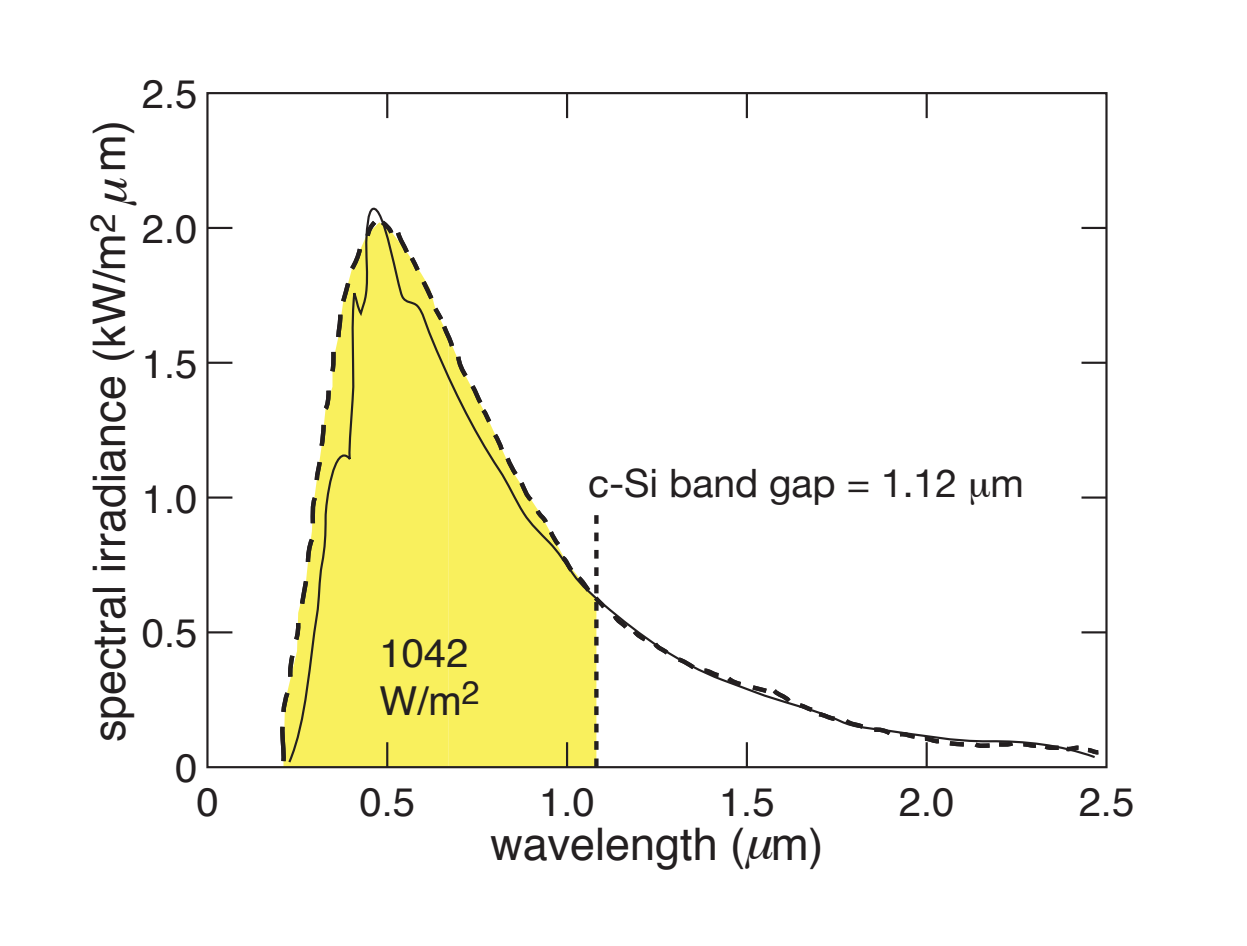
solar spectrum



1 intermediate band

2 Si devices

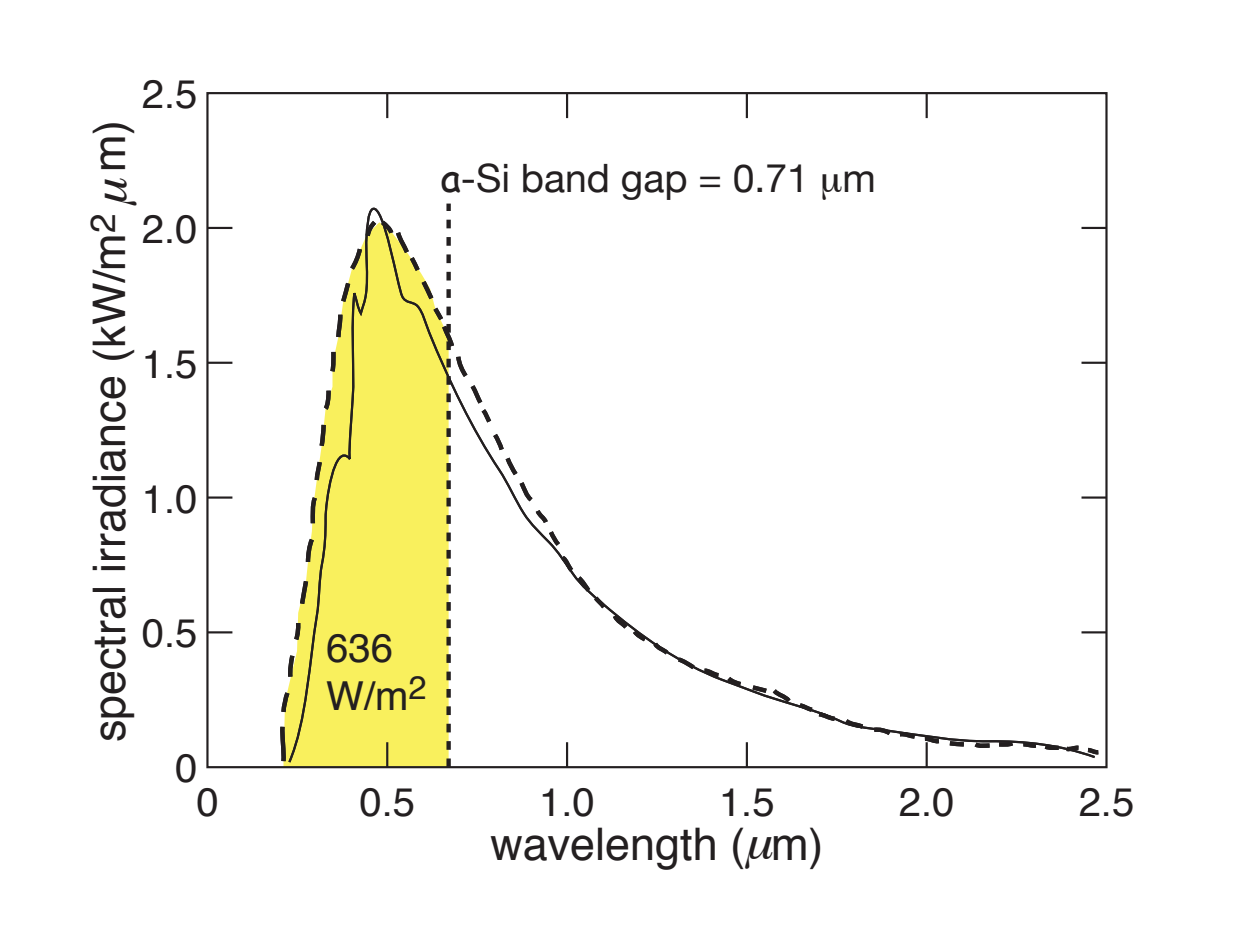
crystalline silicon: transparent to 23% of solar radiation



1 intermediate band

2 Si devices

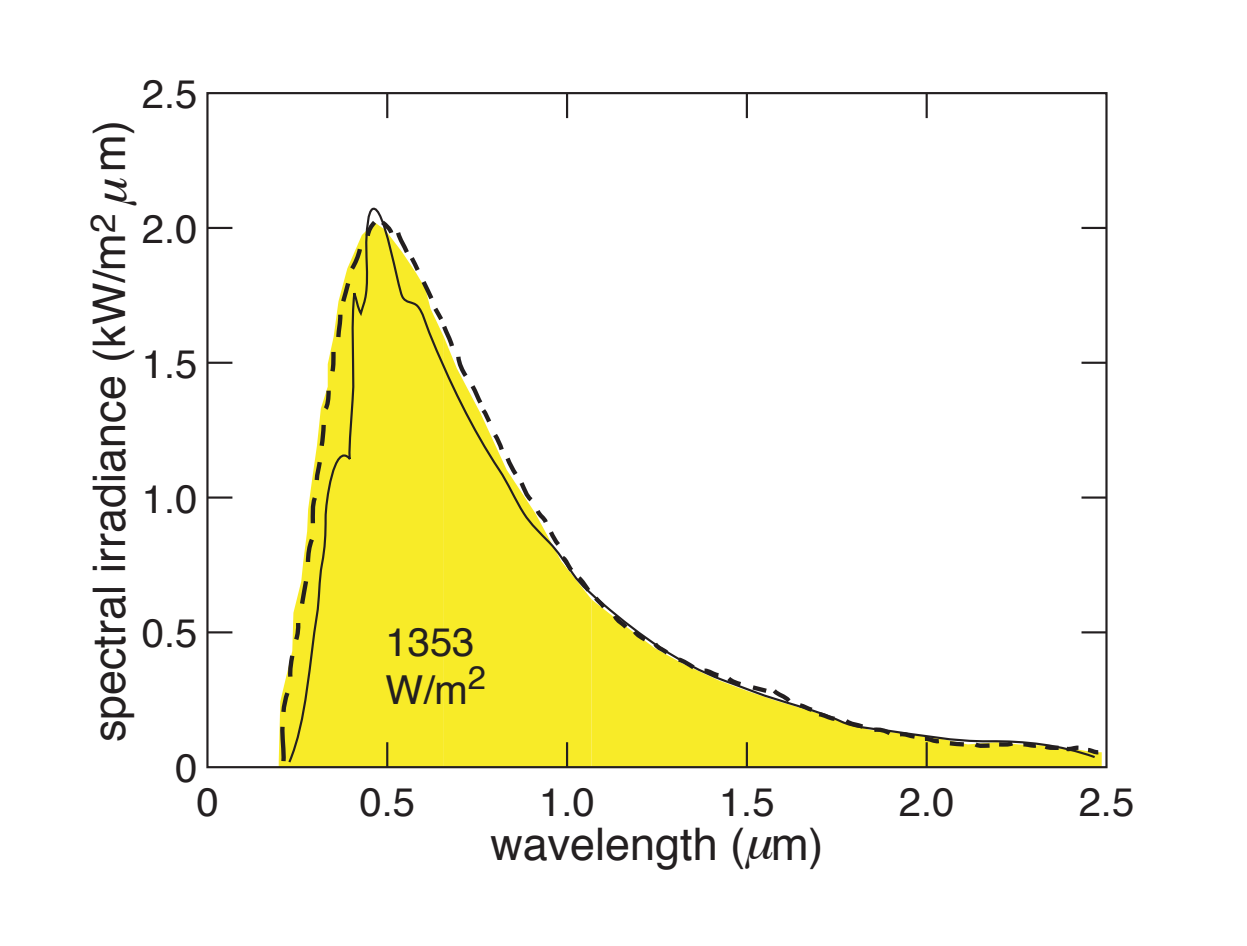
amorphous silicon: transparent to 53% of solar radiation



1 intermediate band

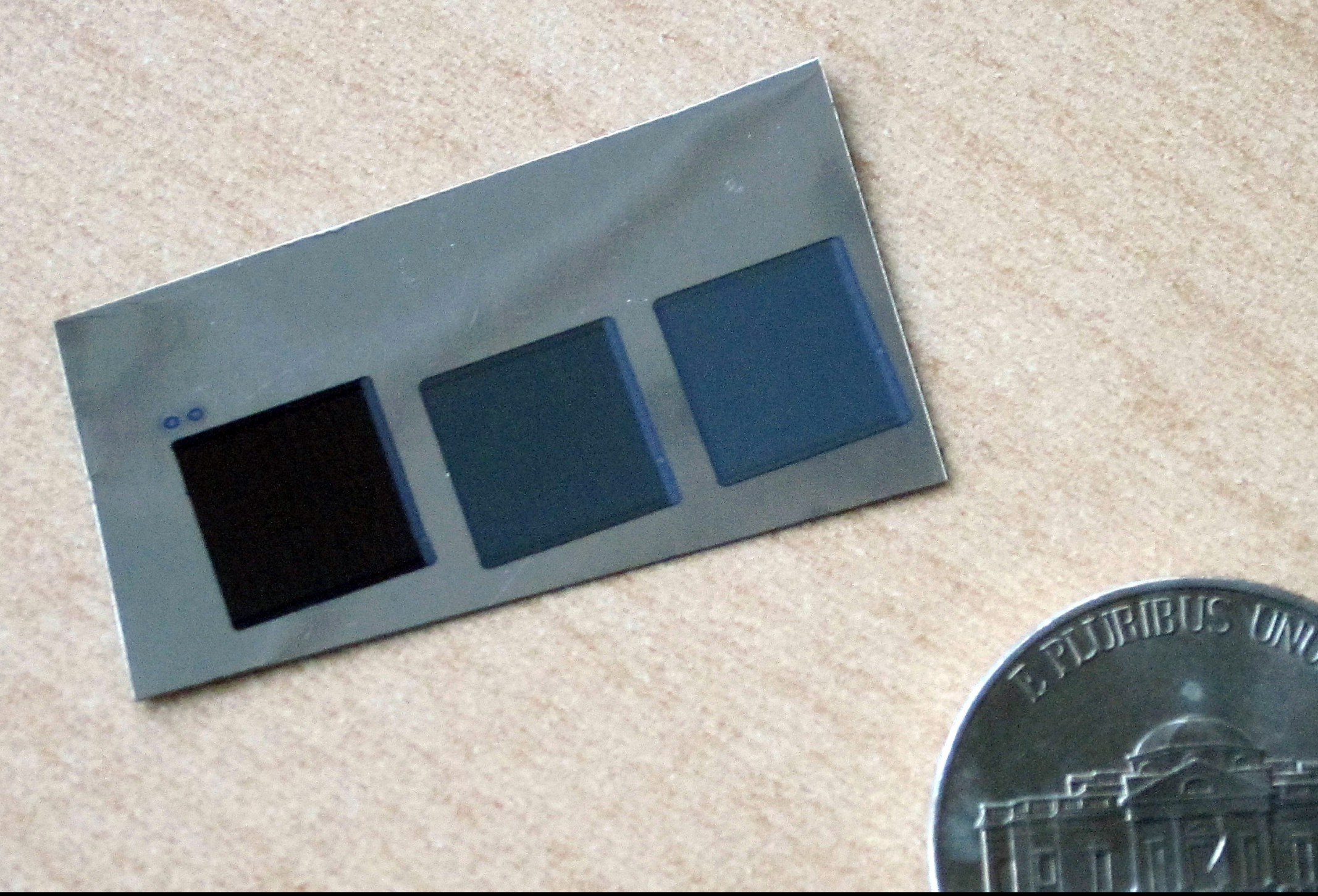
2 Si devices

black silicon: potential to recover transmitted energy



1 intermediate band

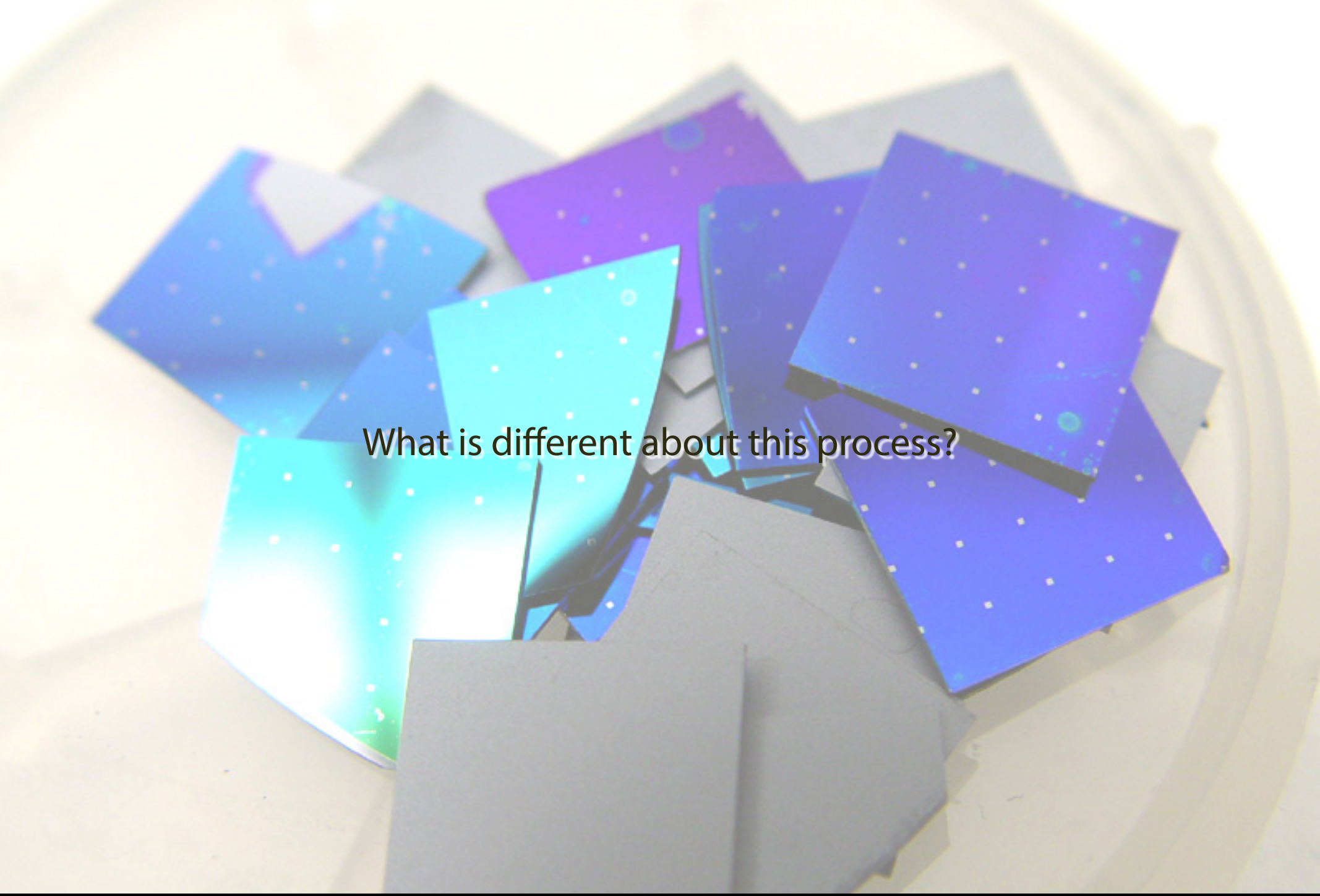
2 Si devices



1 intermediate band

2 Si devices

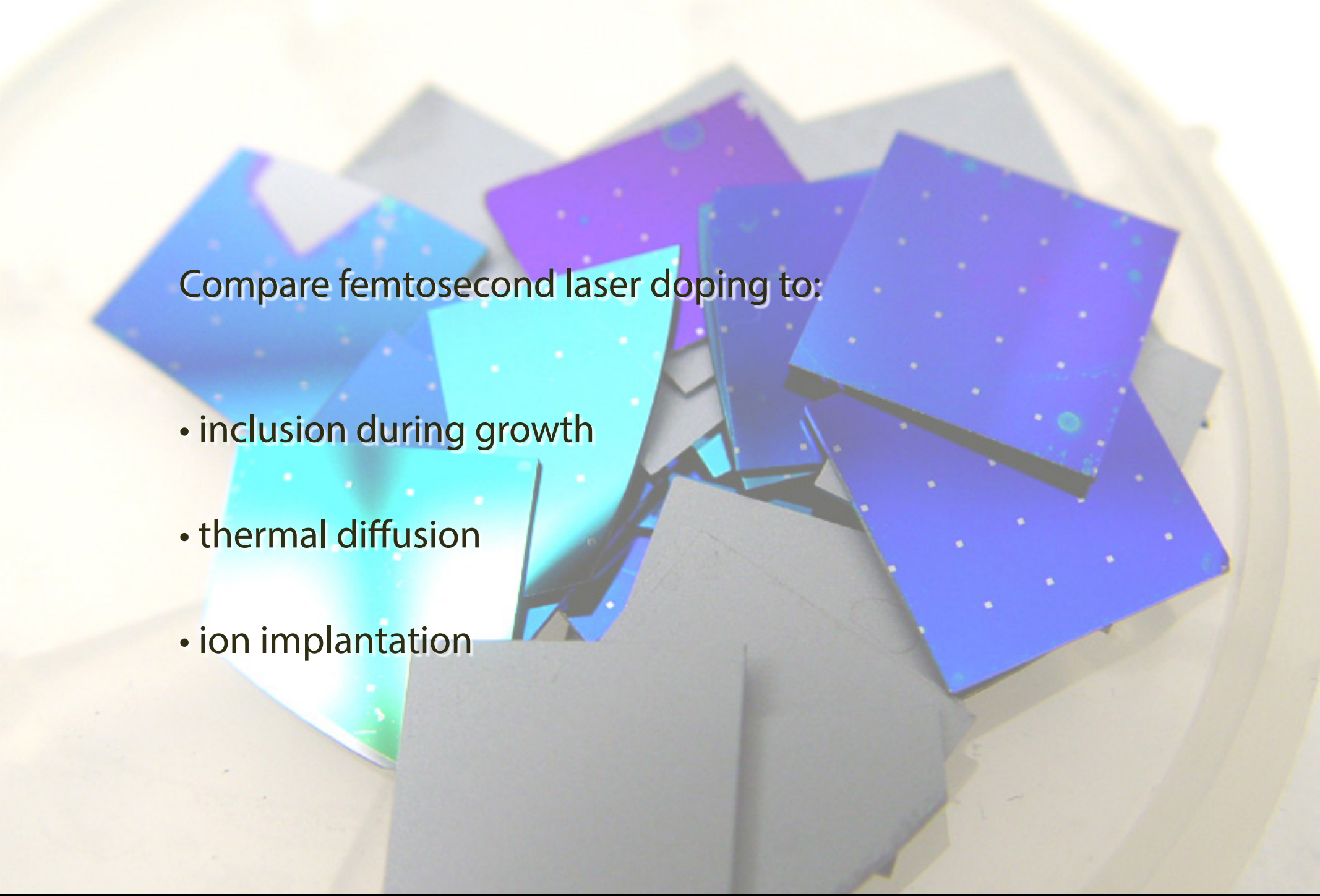
3 X:TiO_2



1 intermediate band

2 Si devices

3 X:TiO_2



Compare femtosecond laser doping to:

- inclusion during growth
- thermal diffusion
- ion implantation

1 intermediate band

2 Si devices

3 X:TiO_2