

Black silicon and the quest for intermediate band semiconductors

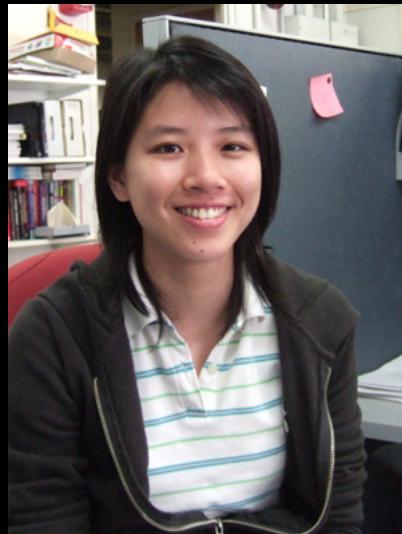


**Physics Seminar
Wright State University
Dayton, OH, 30 November 2012**





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)

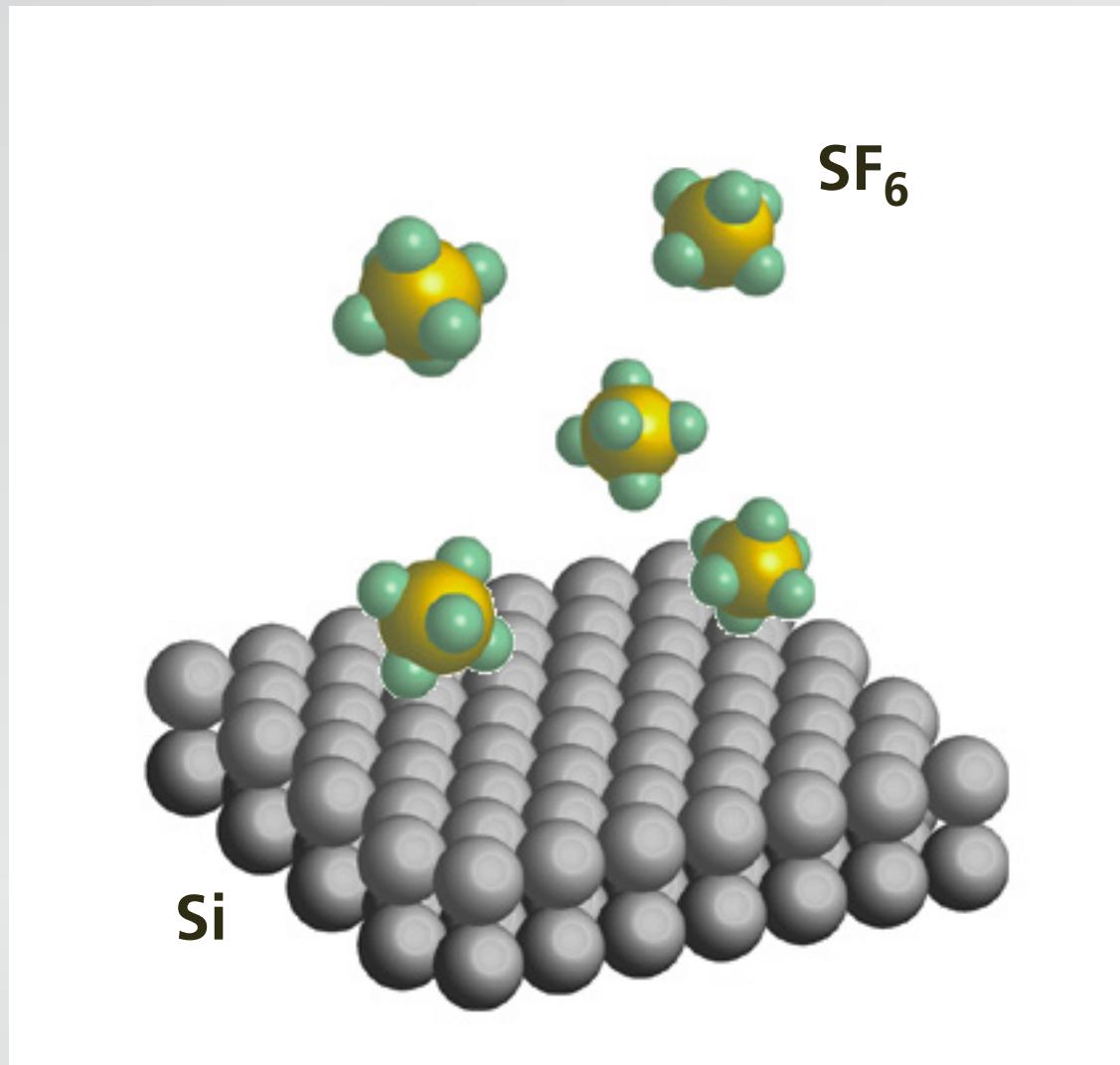
Dr. Arieh Karger (RMD)

Dr. Richard Meyers (RMD)

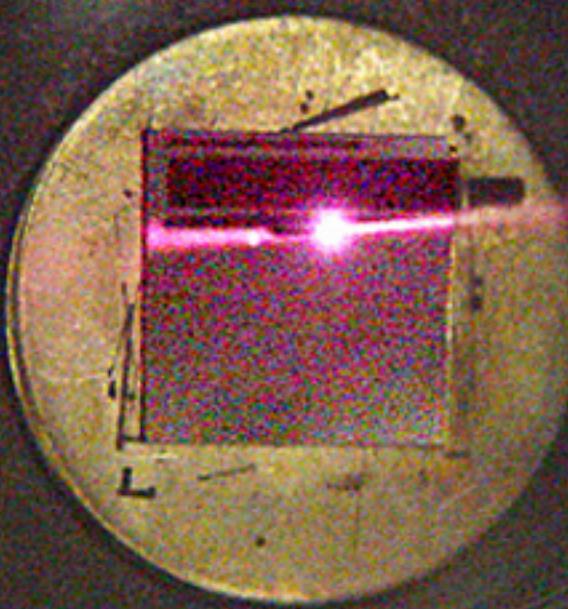
Dr. Pat Maloney (NVSED)

Dr. Jeffrey Warrander (ARDEC)

...and the people at SiOnyx

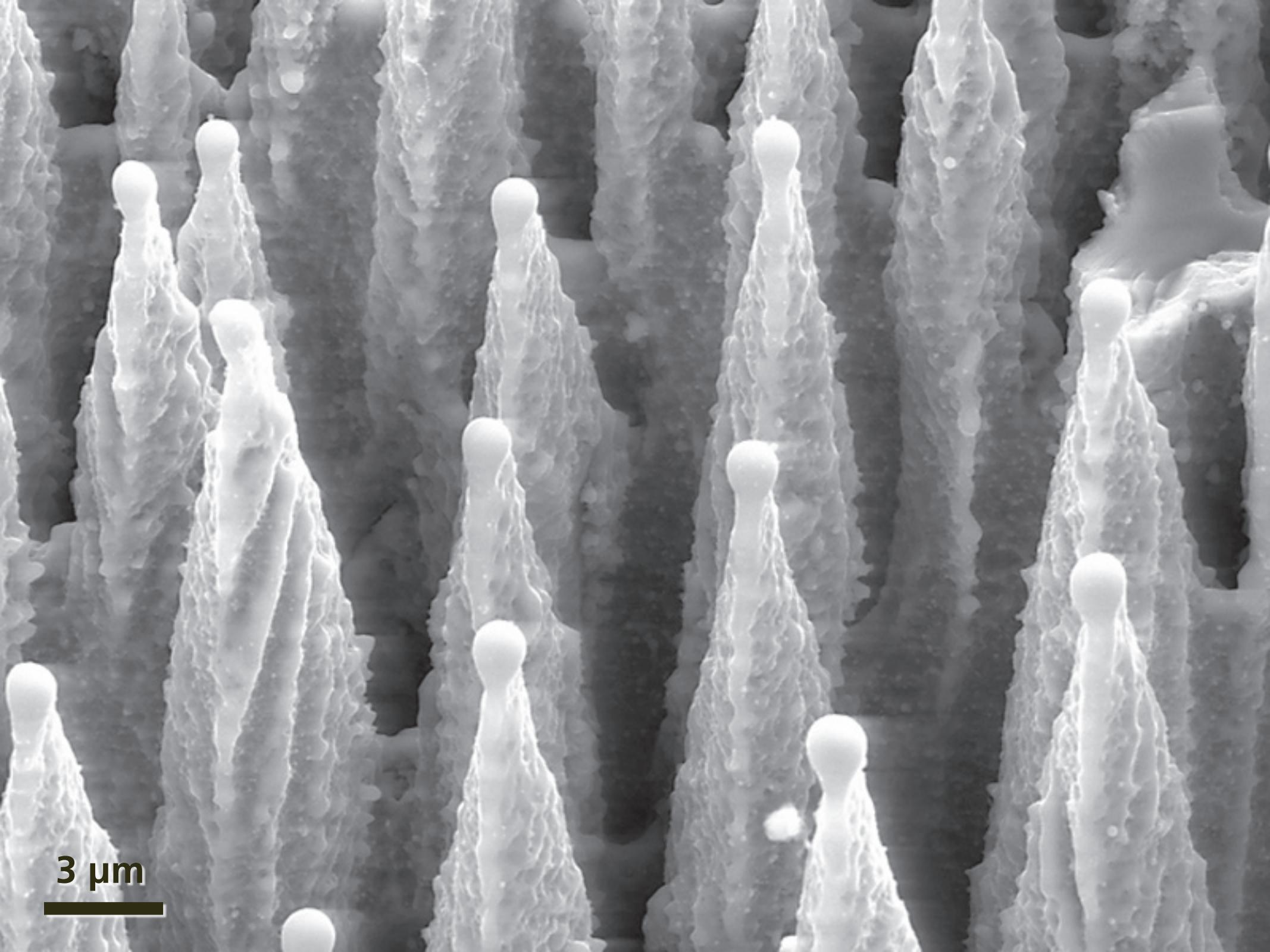


irradiate with 100-fs 10 kJ/m² pulses



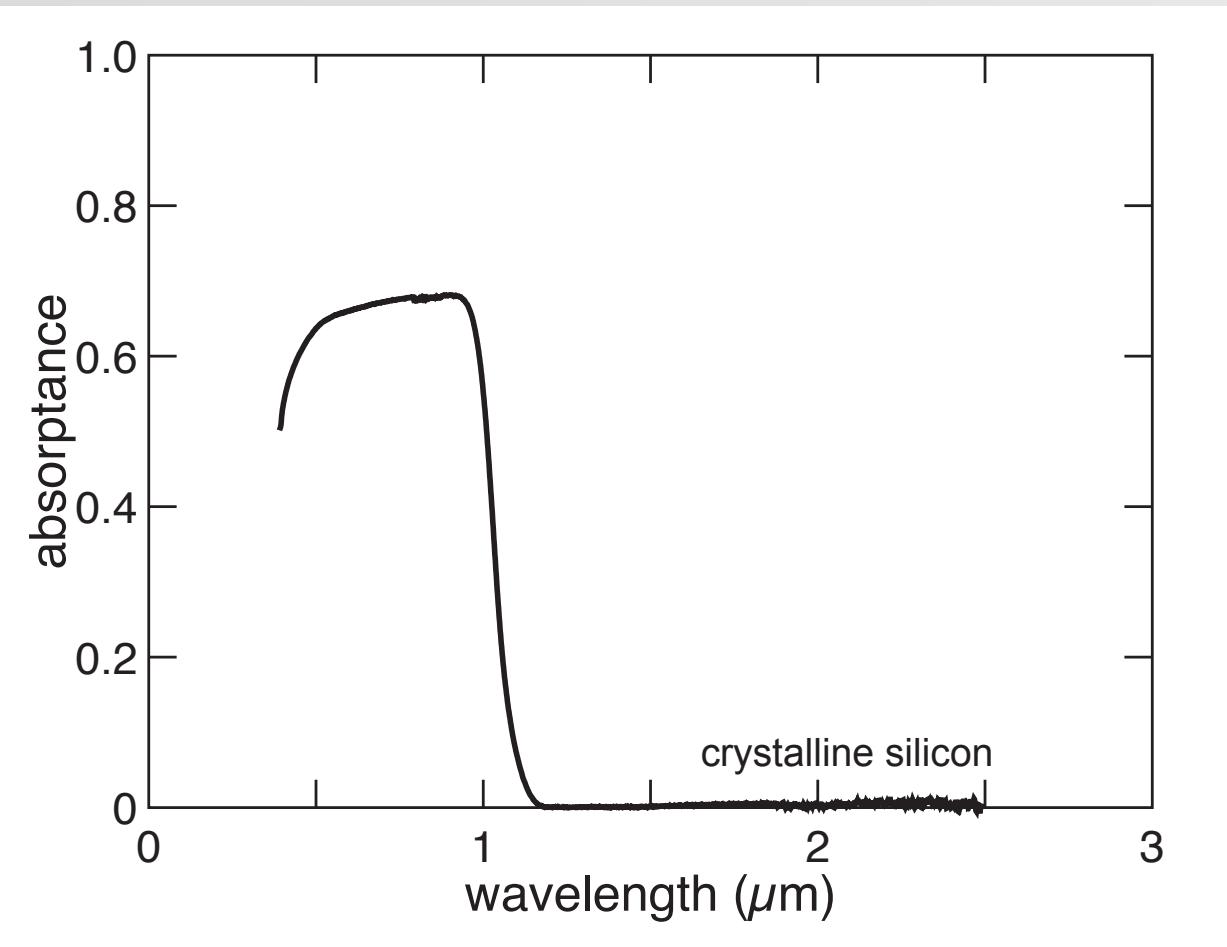


"black silicon"

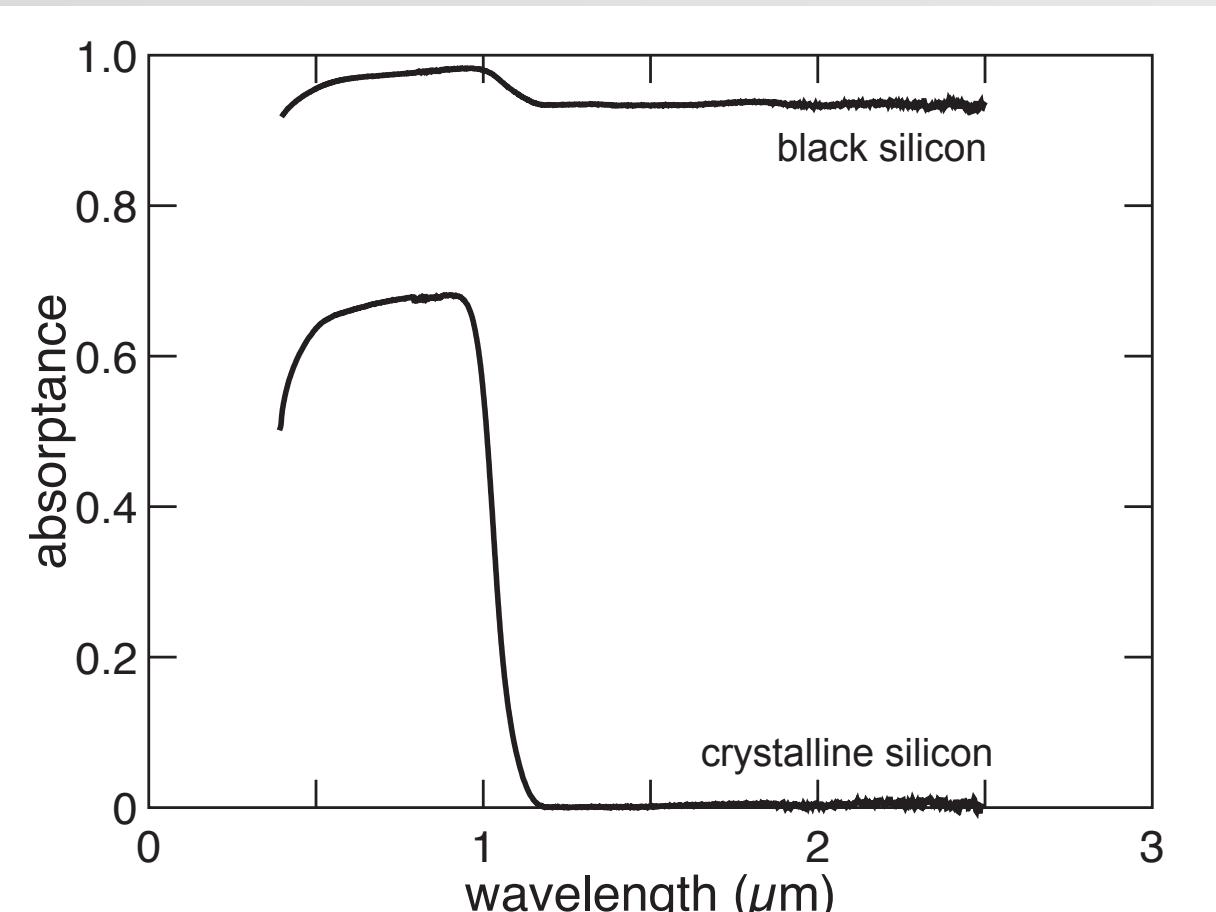


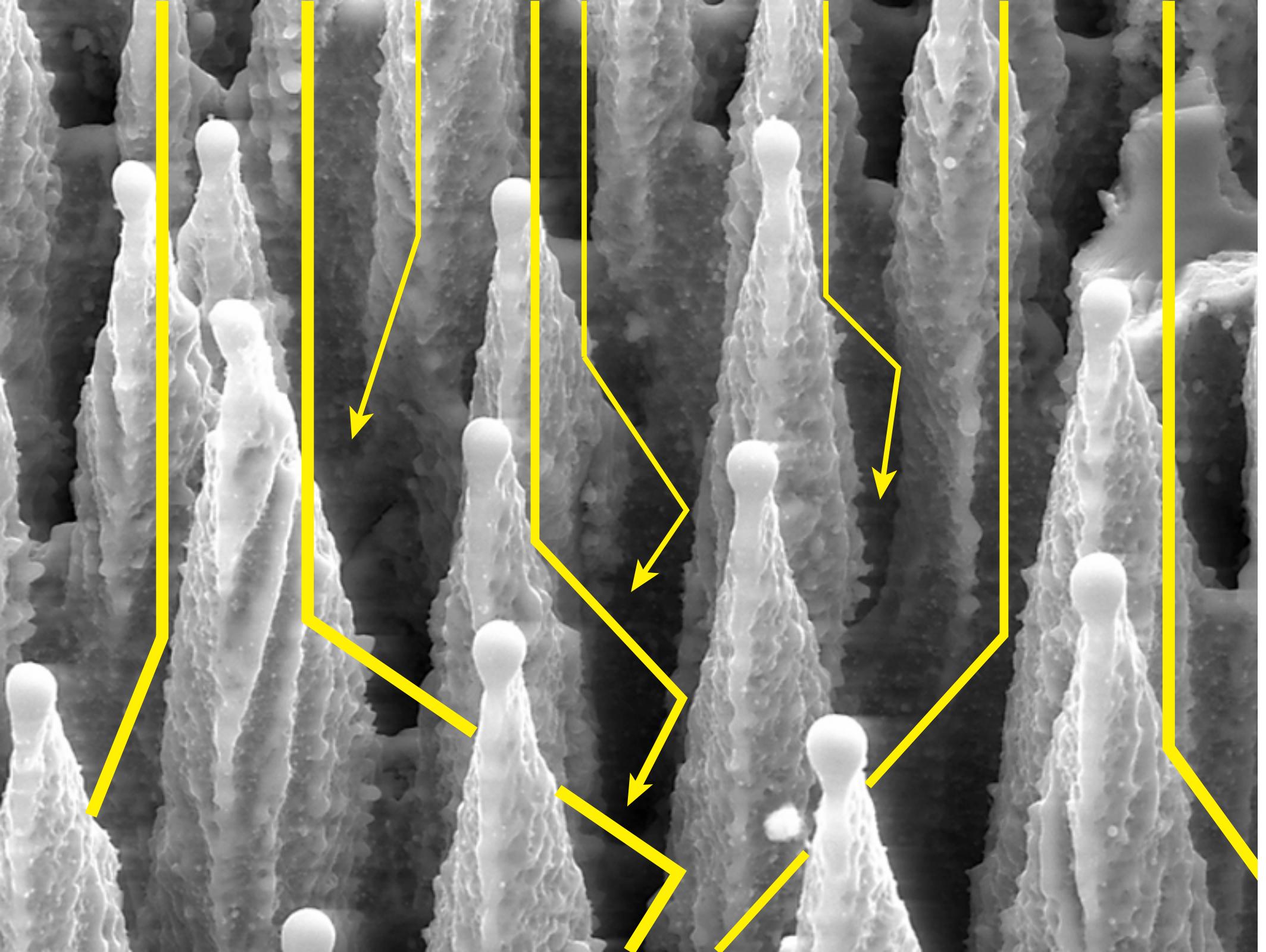
3 μm

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

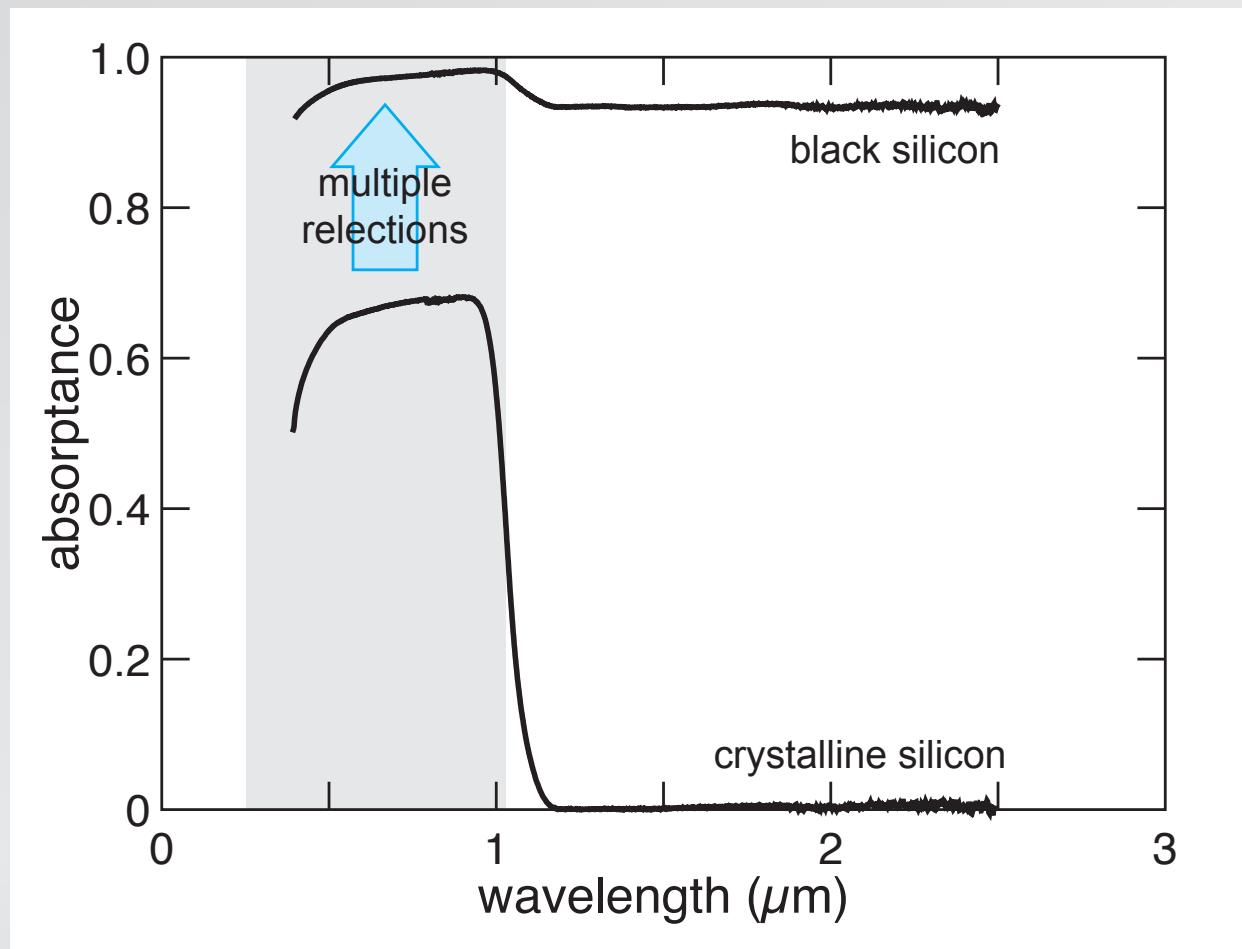


absorptance ($1 - R_{int} - T_{int}$)

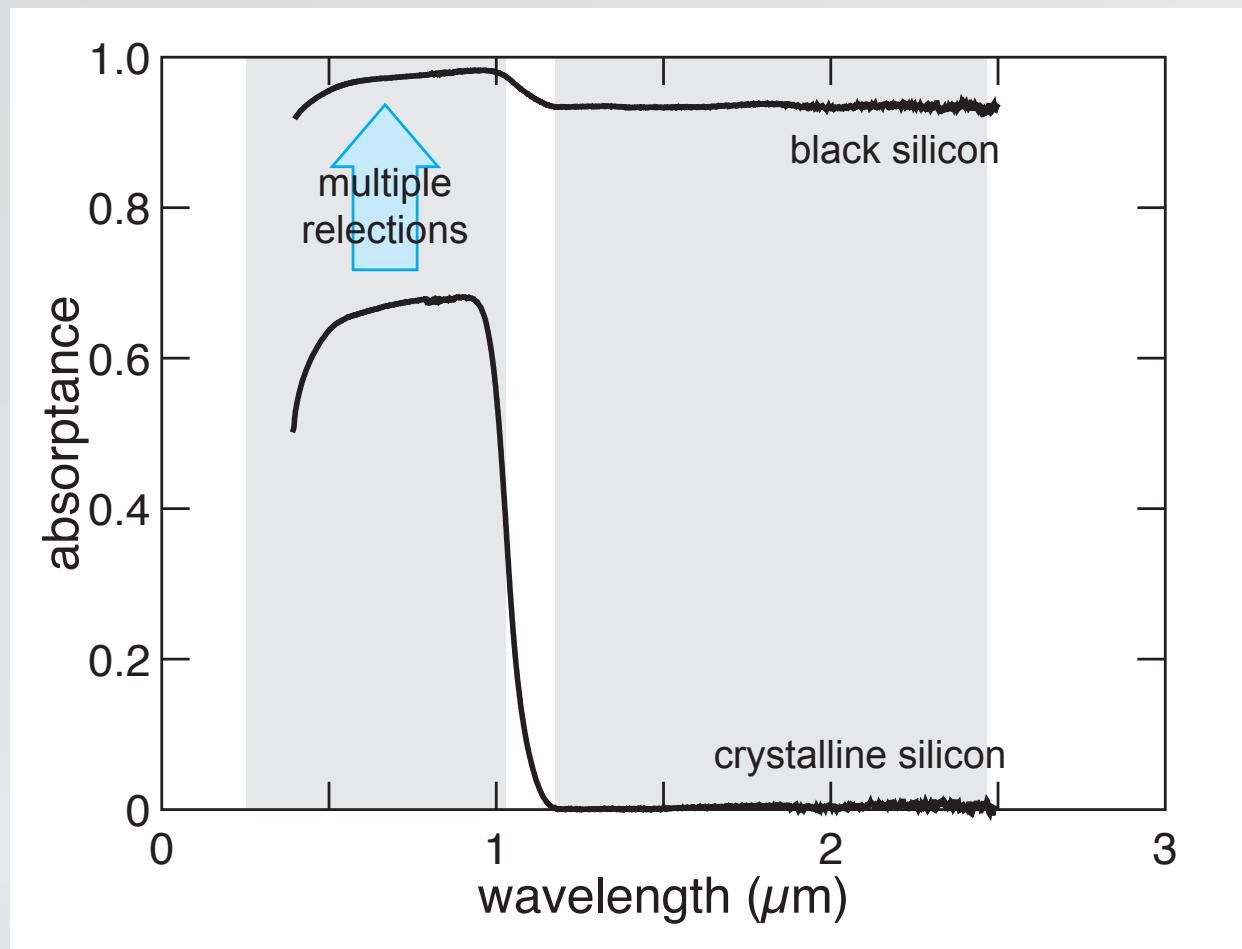




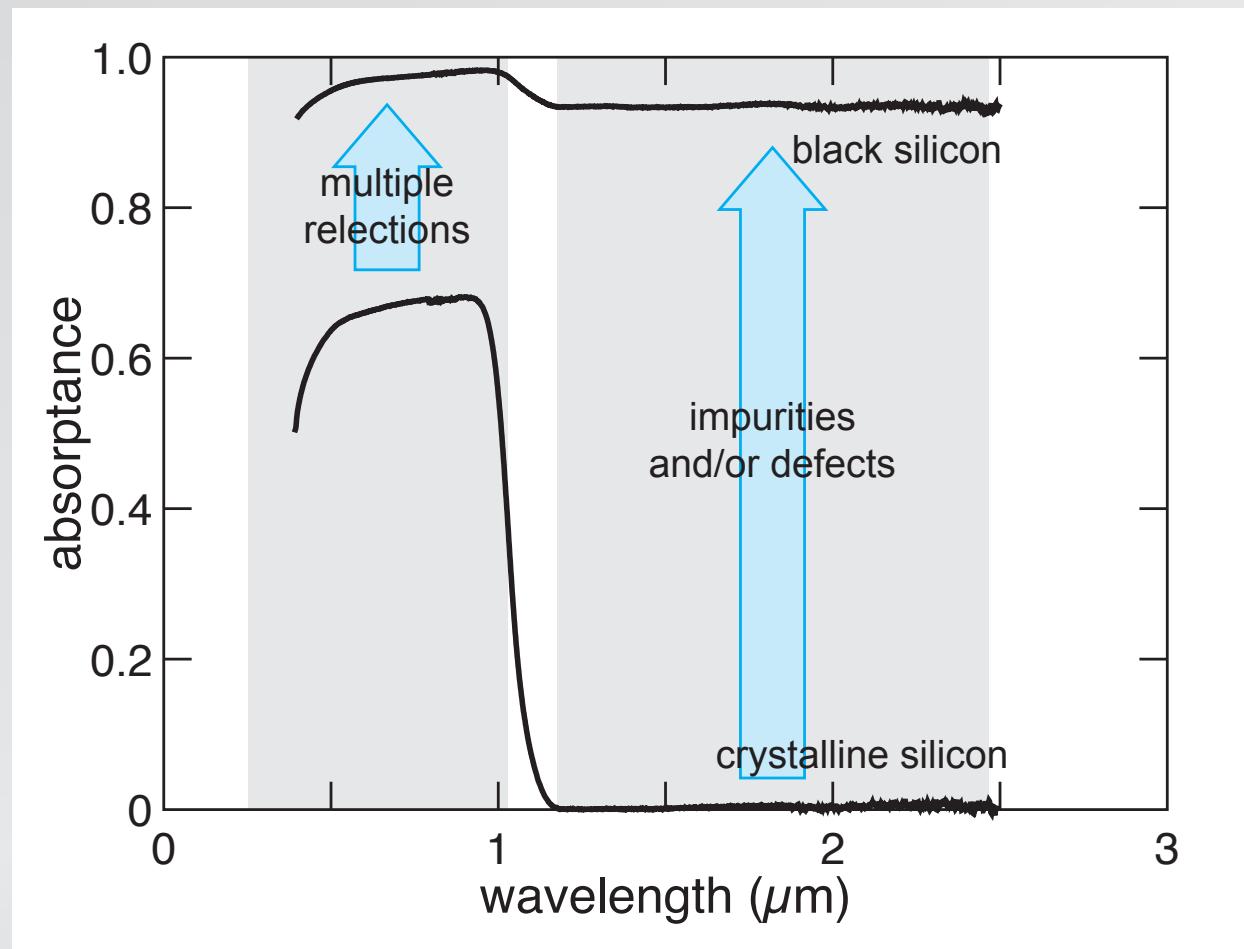
absorptance ($1 - R_{int} - T_{int}$)



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

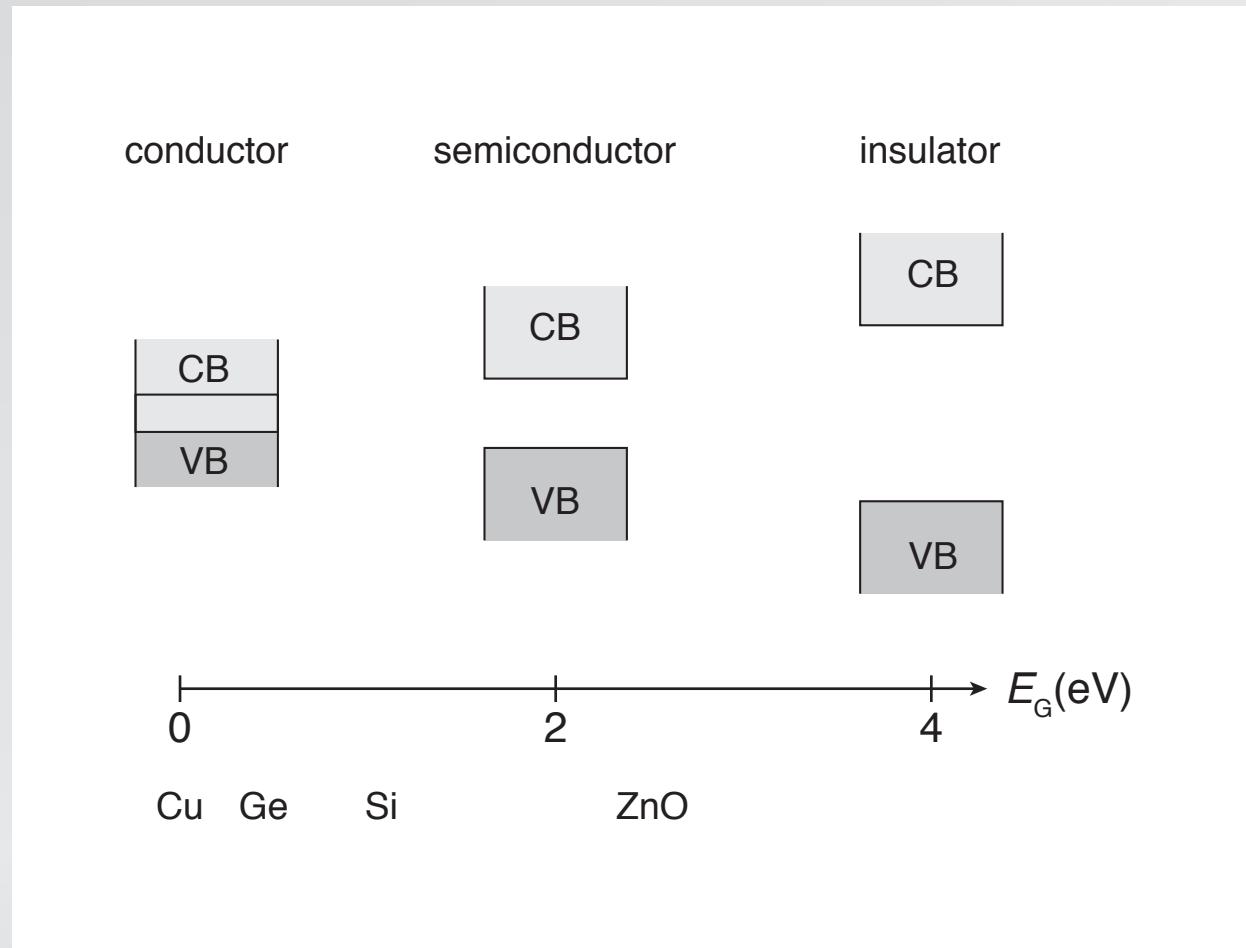


absorptance ($1 - R_{int} - T_{int}$)

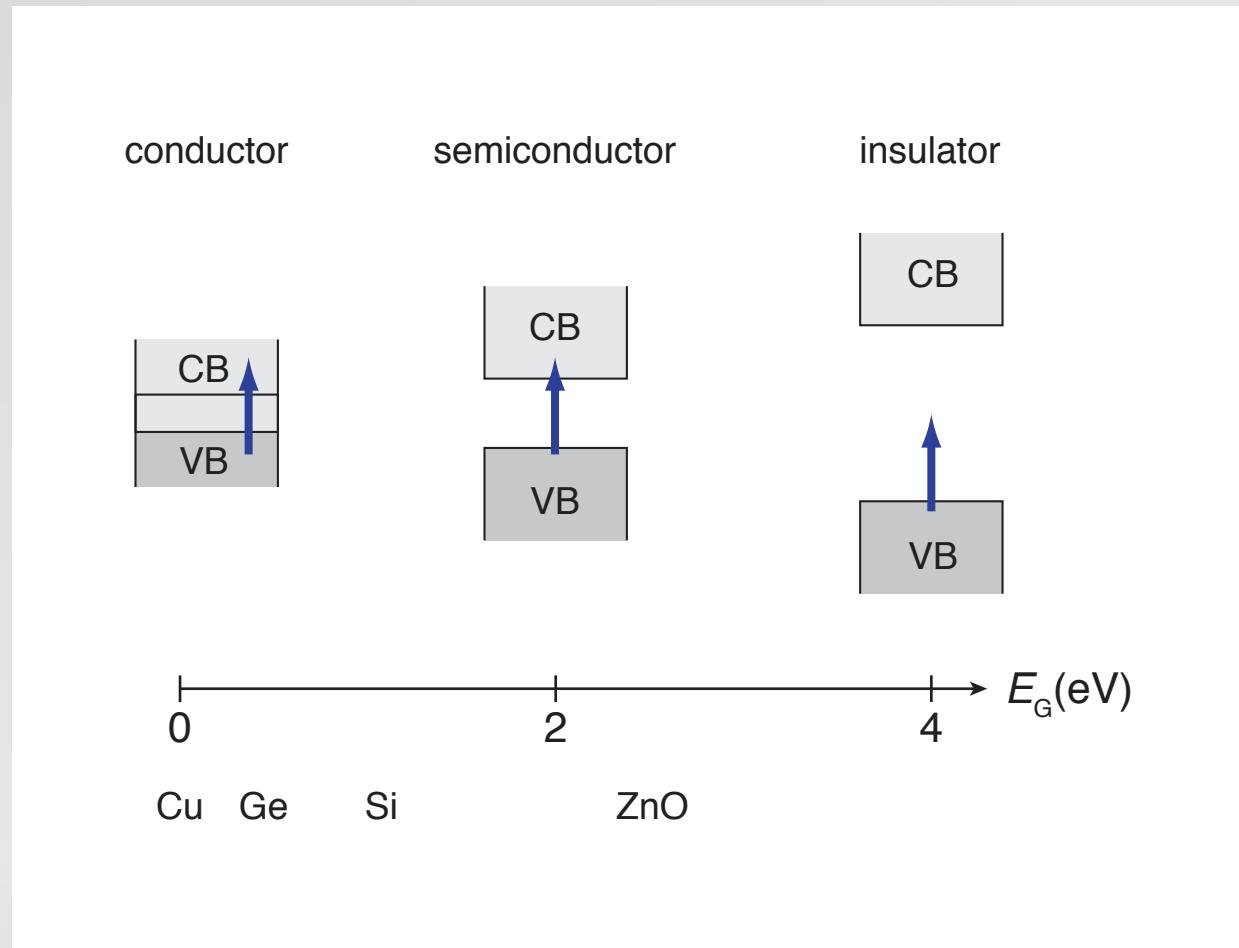


laser treatment causes:

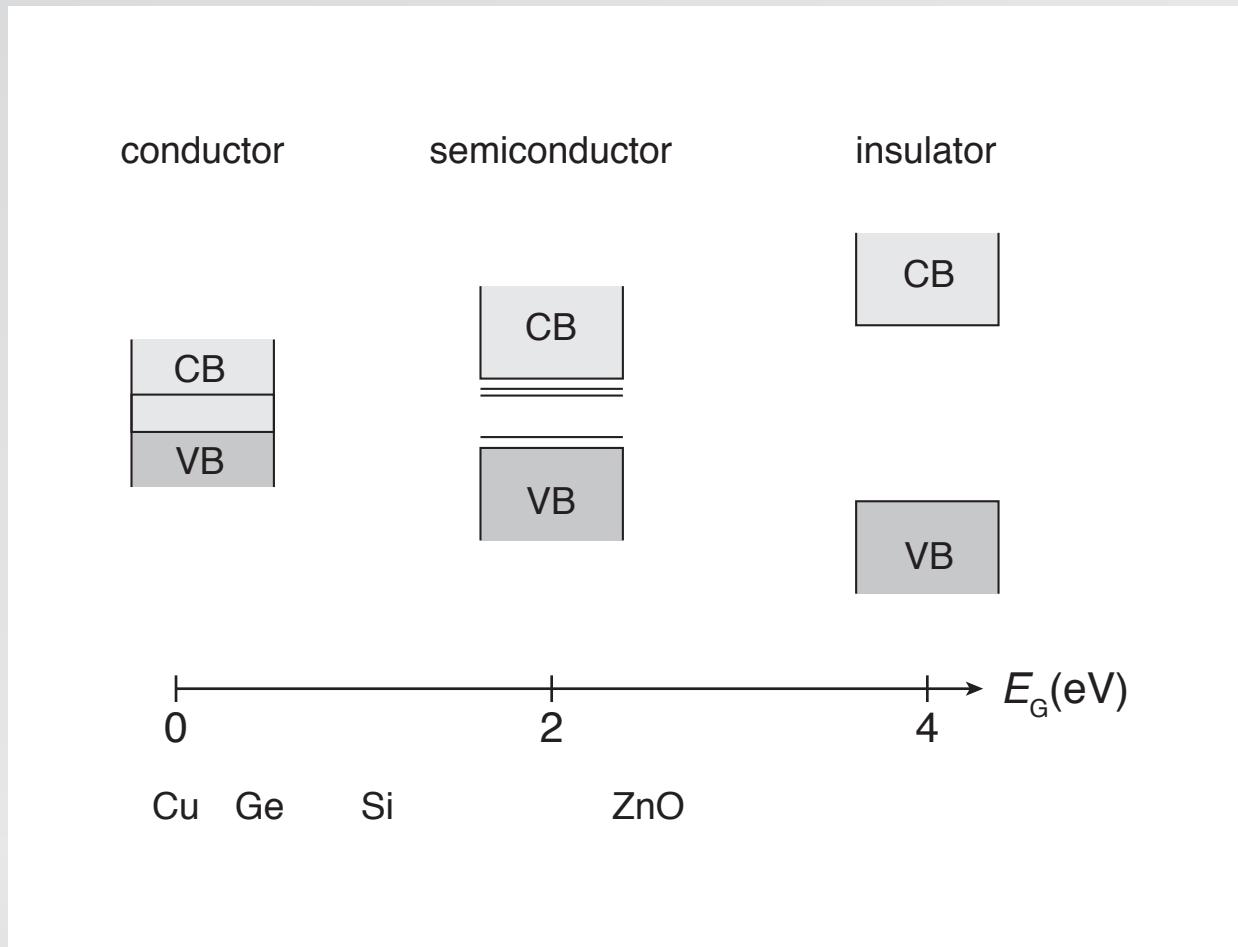
- **surface structuring**
- **inclusion of dopants**



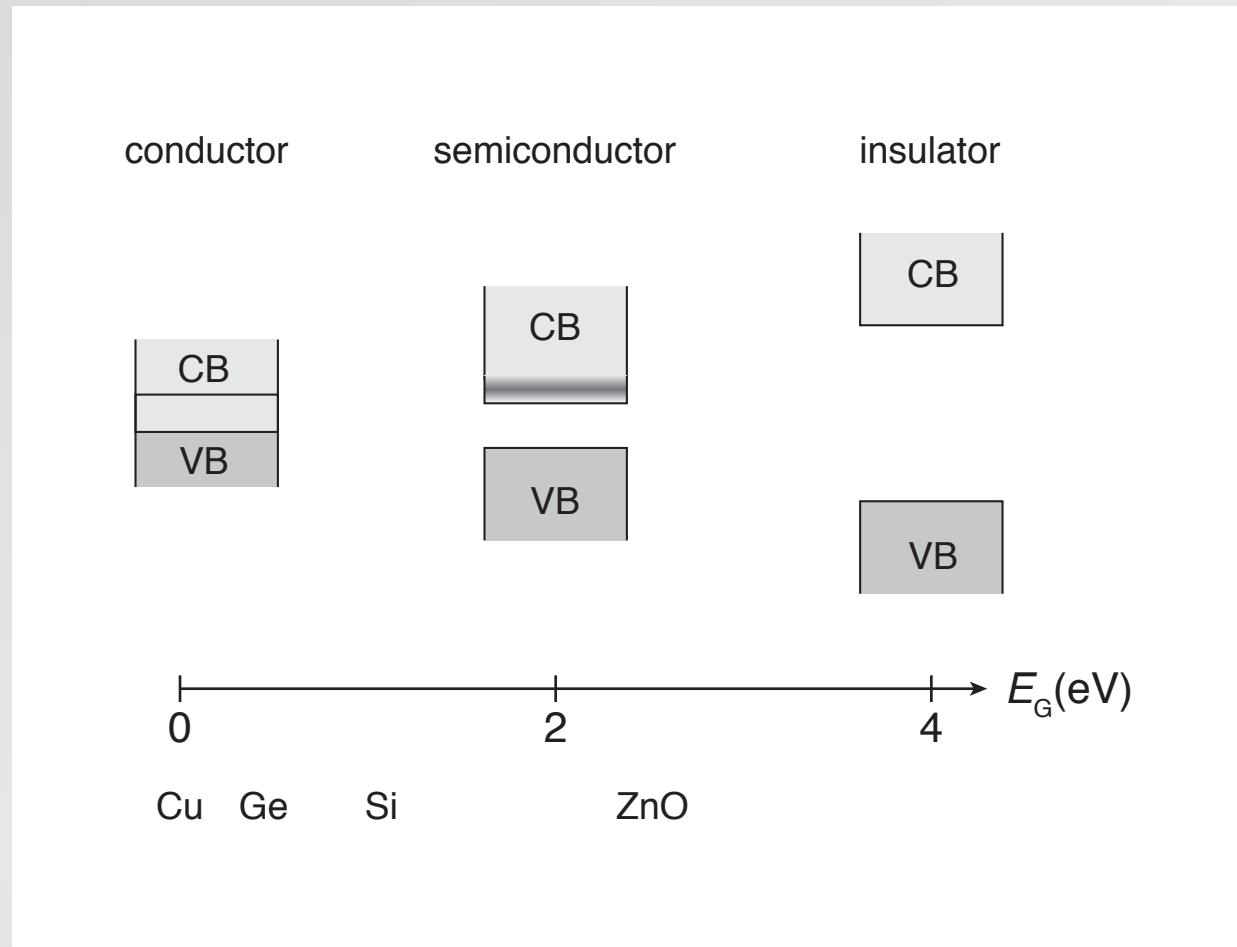
gap determines optical and electronic properties



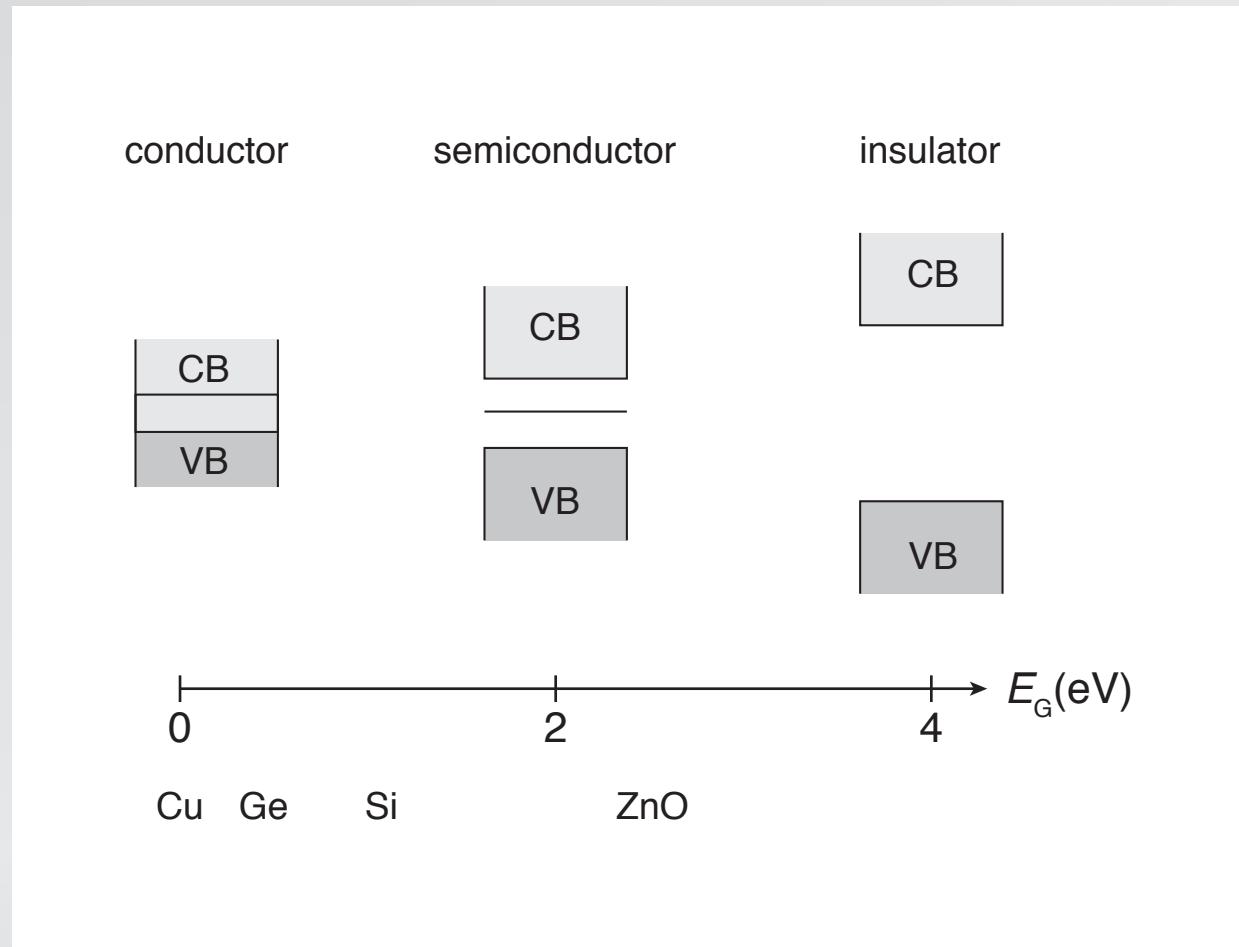
shallow-level dopants control electronic properties



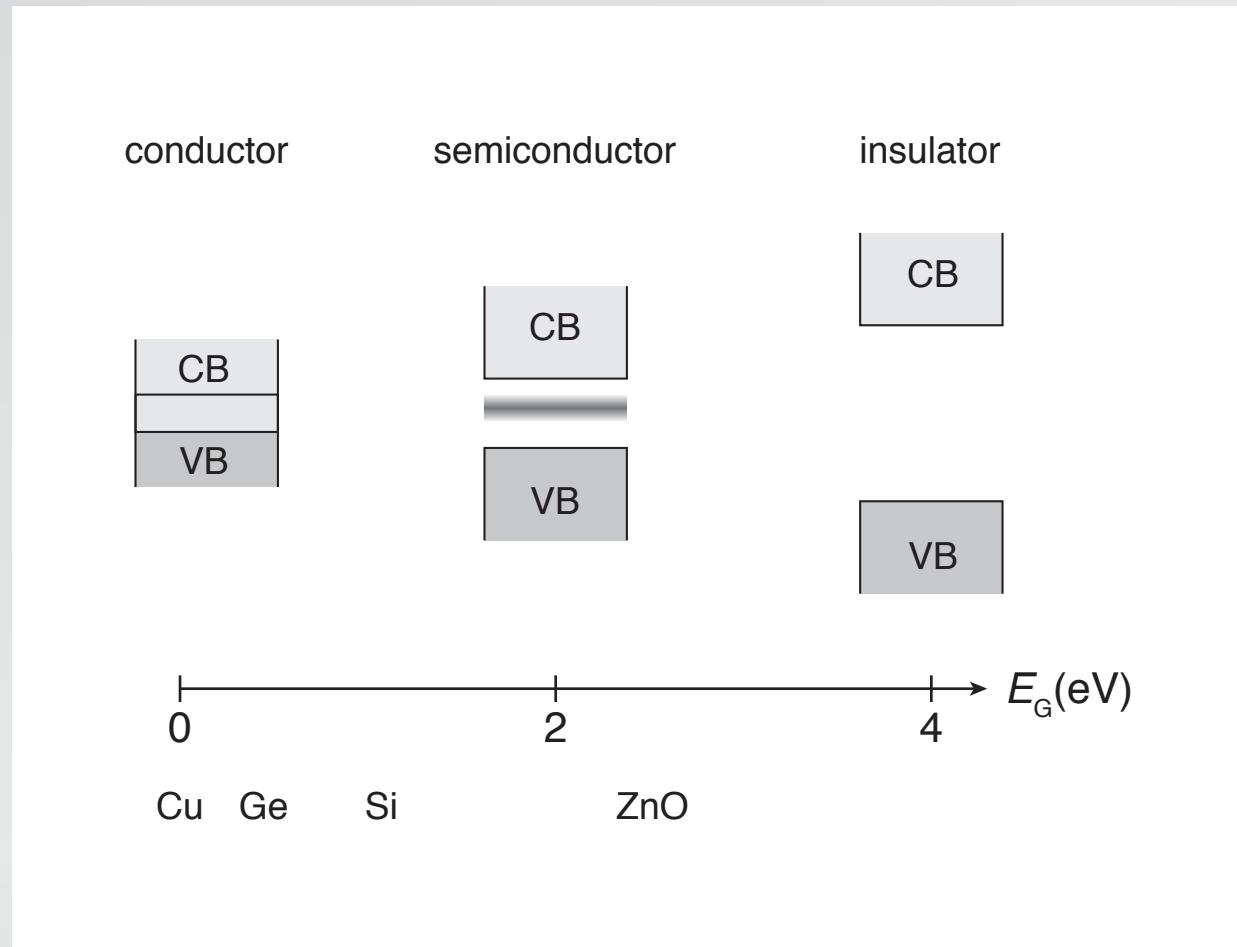
shallow-level dopants control electronic properties



deep-level dopants typically avoided



femtosecond laser-doping gives rise to intermediate band



substrate/dopant combinations

dopants:

I															VIII
H	II														
Li	Be														
Na	Mg														
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
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	II	III	IV	V	VI	VII	VIII										
H	Be	B	C	N	O	F	He										
Li	Mg	Al	Si	P	S	Cl	Ne										
Na		Ga	Ge	As	Se	Br	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

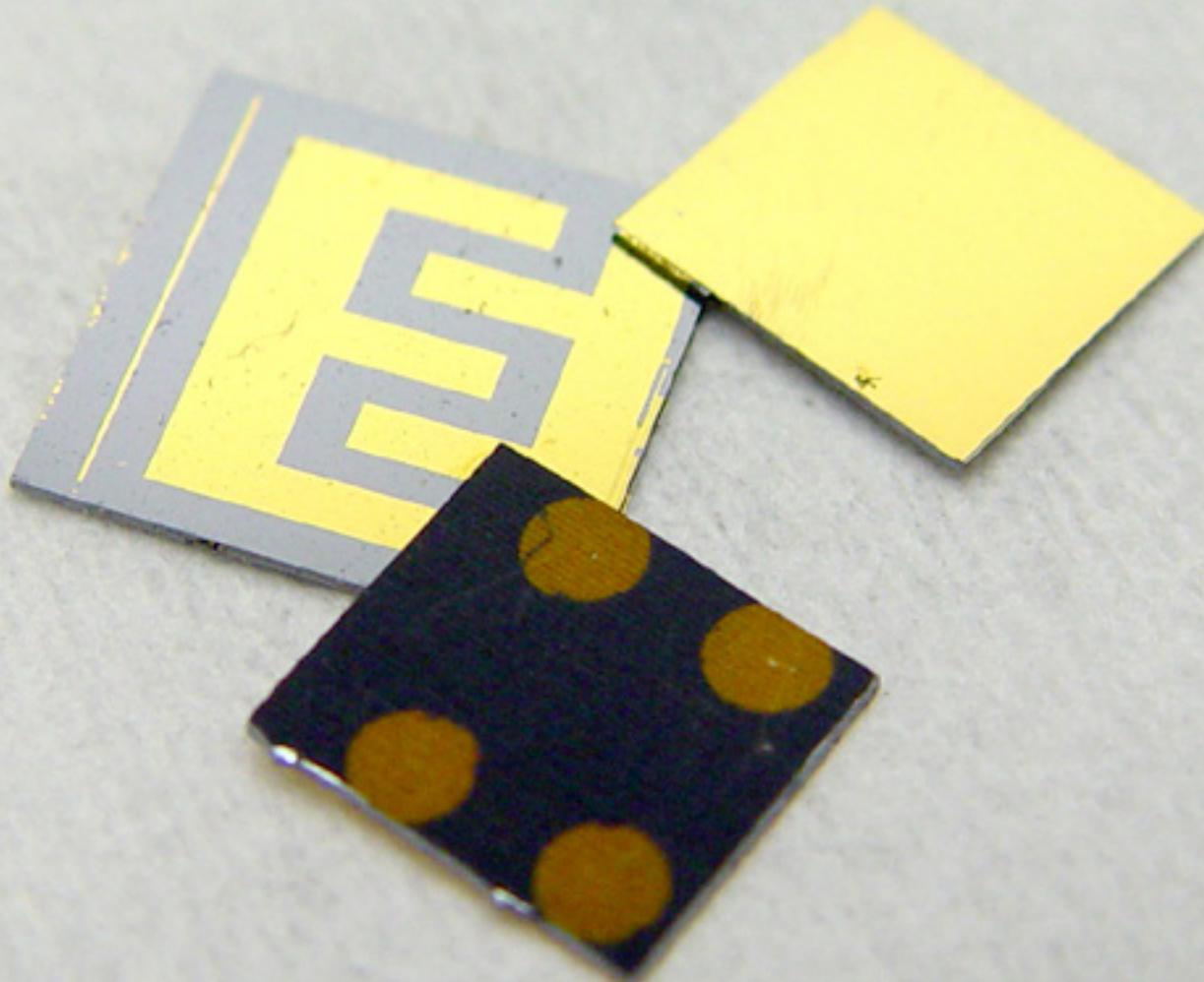
dopants:

I	II	III	IV	V	VI	VII	VIII										
H	Be	B	C	N	O	F	He										
Li	Mg	Al	Si	P	S	Cl	Ne										
Na		Ga	Ge	As	Se	Br	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

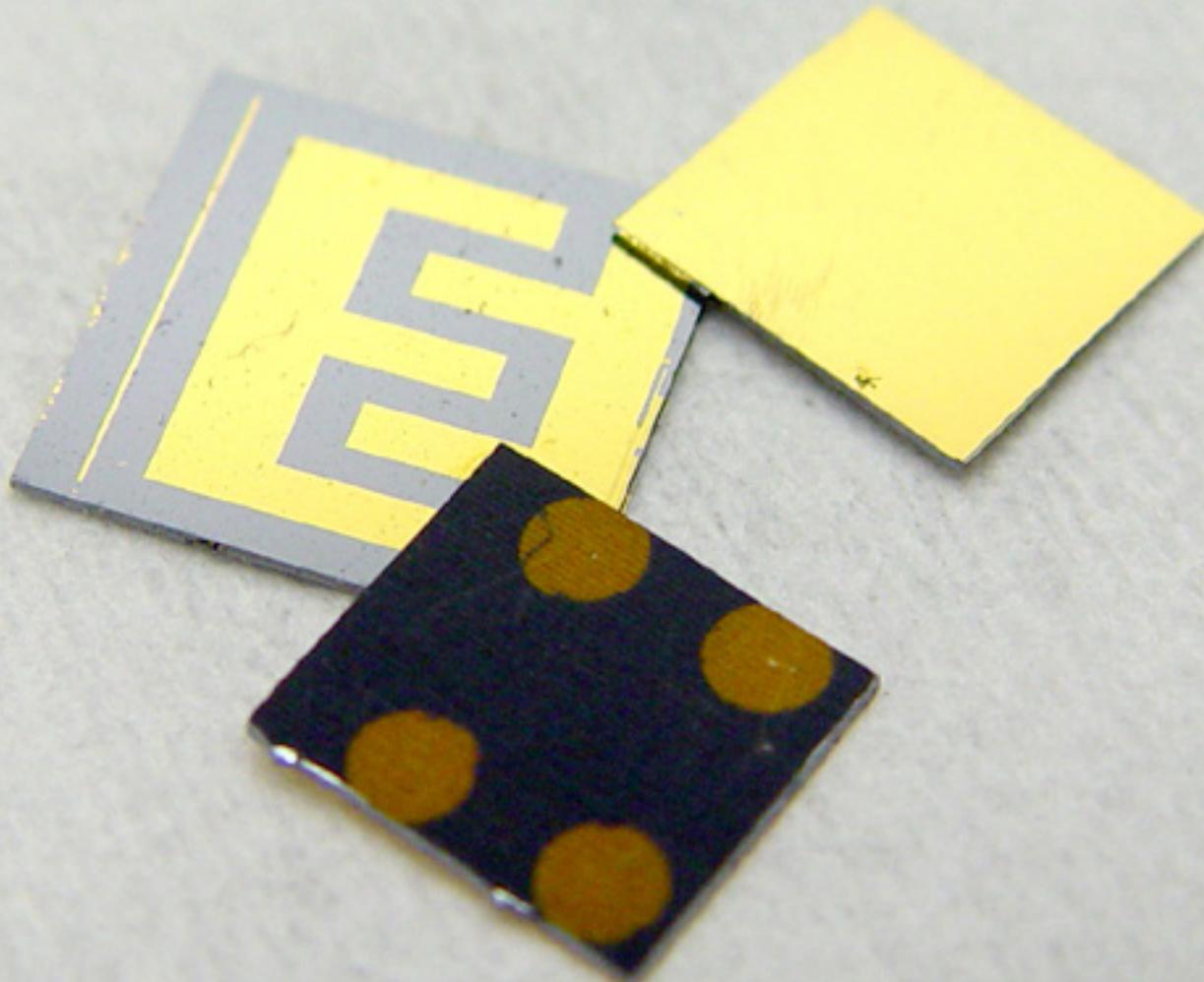
substrates:

Si Ge ZnO InP GaAs

Ti Ag Al Cu Pd Rh Ta Pt TiO₂

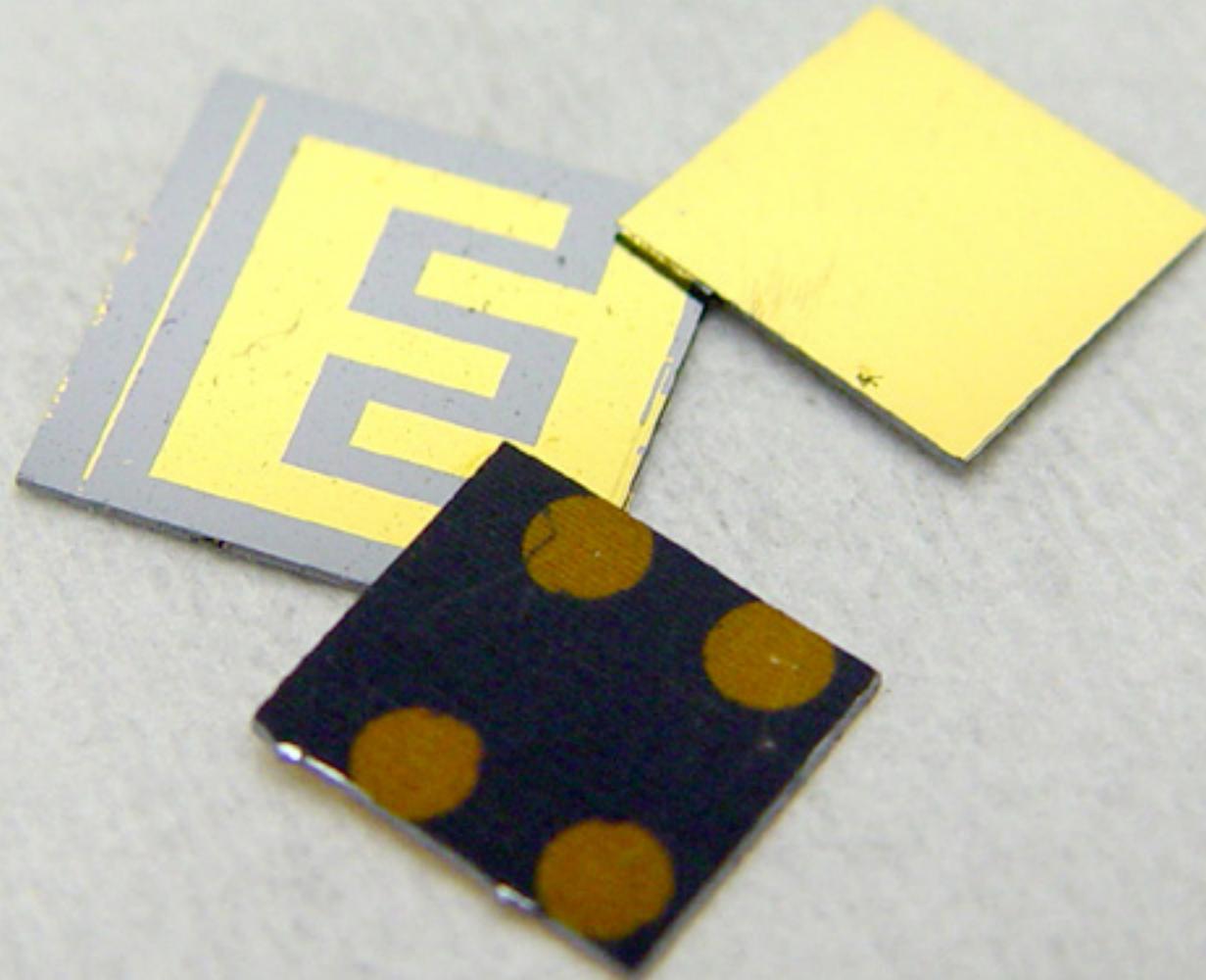


① intermediate band



1 intermediate band

2 Si devices



1 intermediate band

2 Si devices

3 X: TiO_2

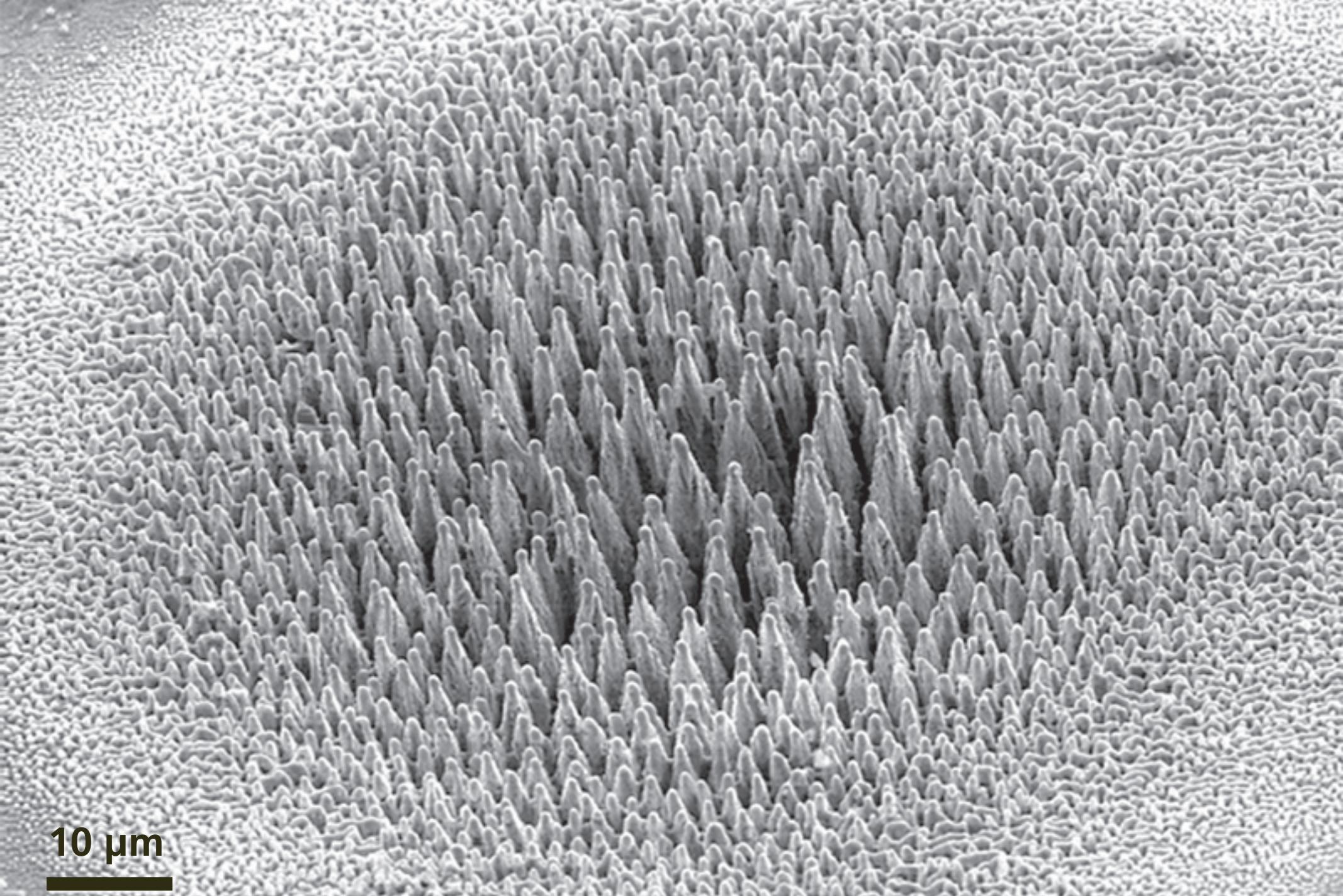
intermediate band formation in chalcogen-hyperdoped Si

dopants:

I															VIII
H															He
Li	Be														
Na	Mg														
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
															I
															Xe

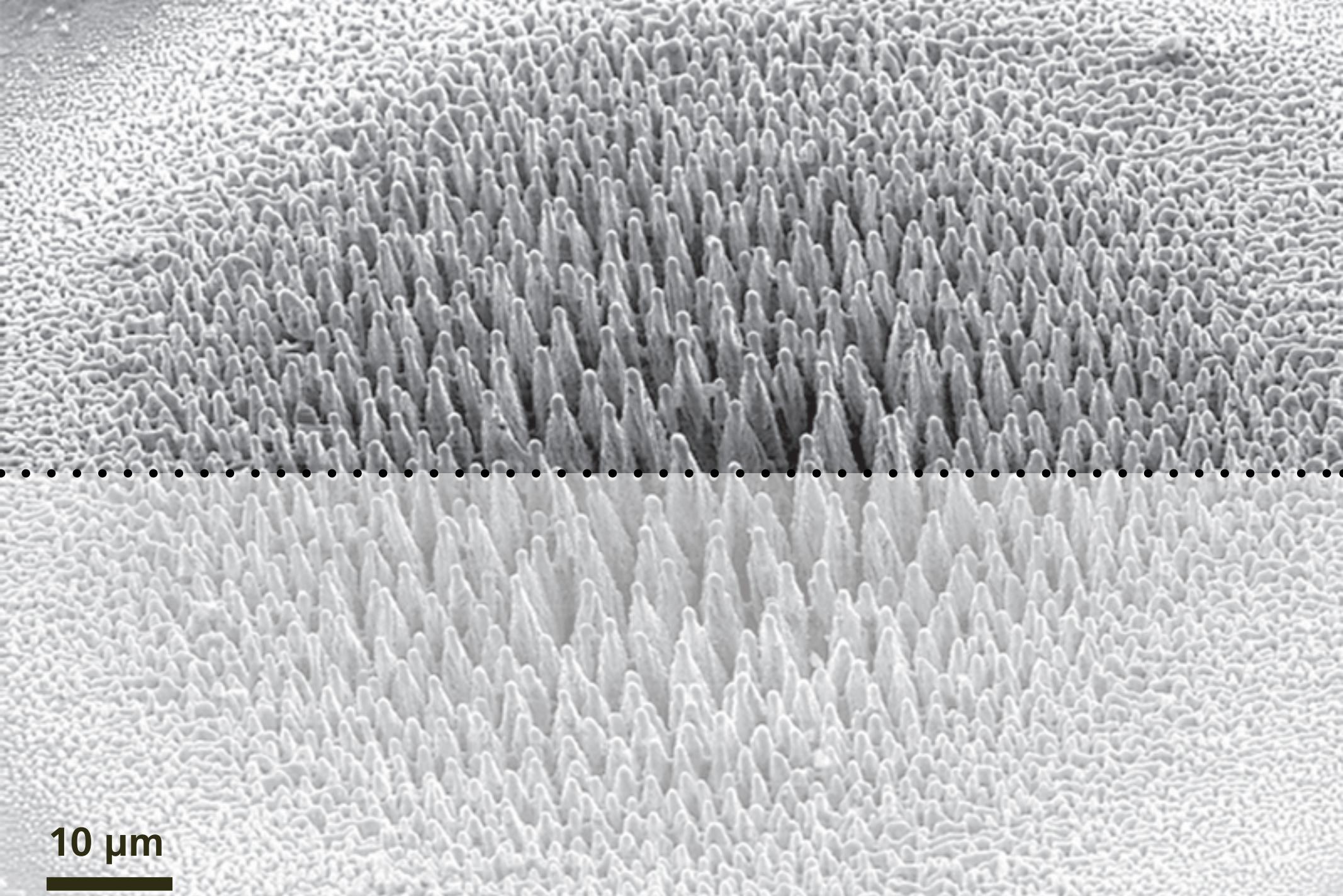
substrates:

Si



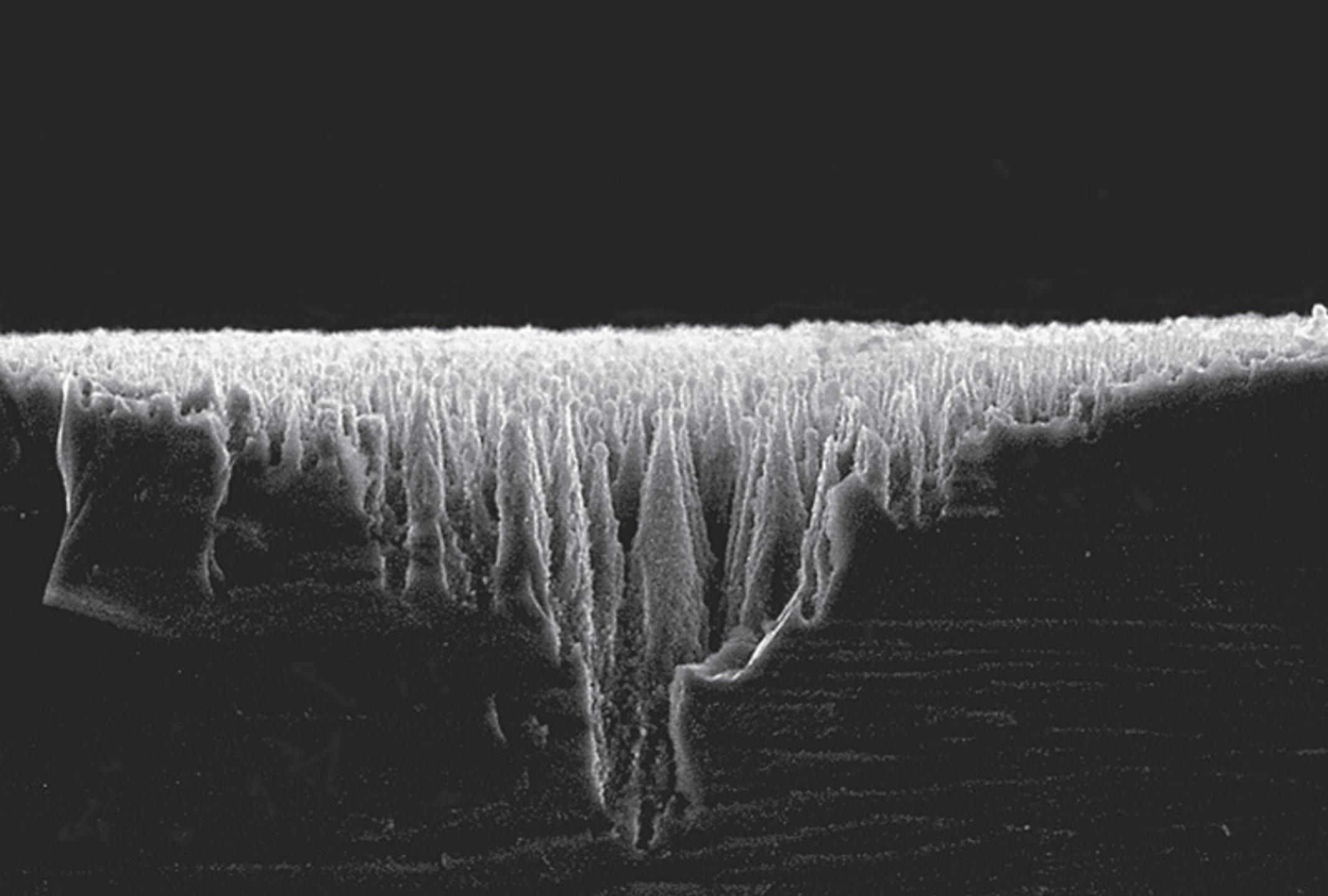
10 μm

① intermediate band

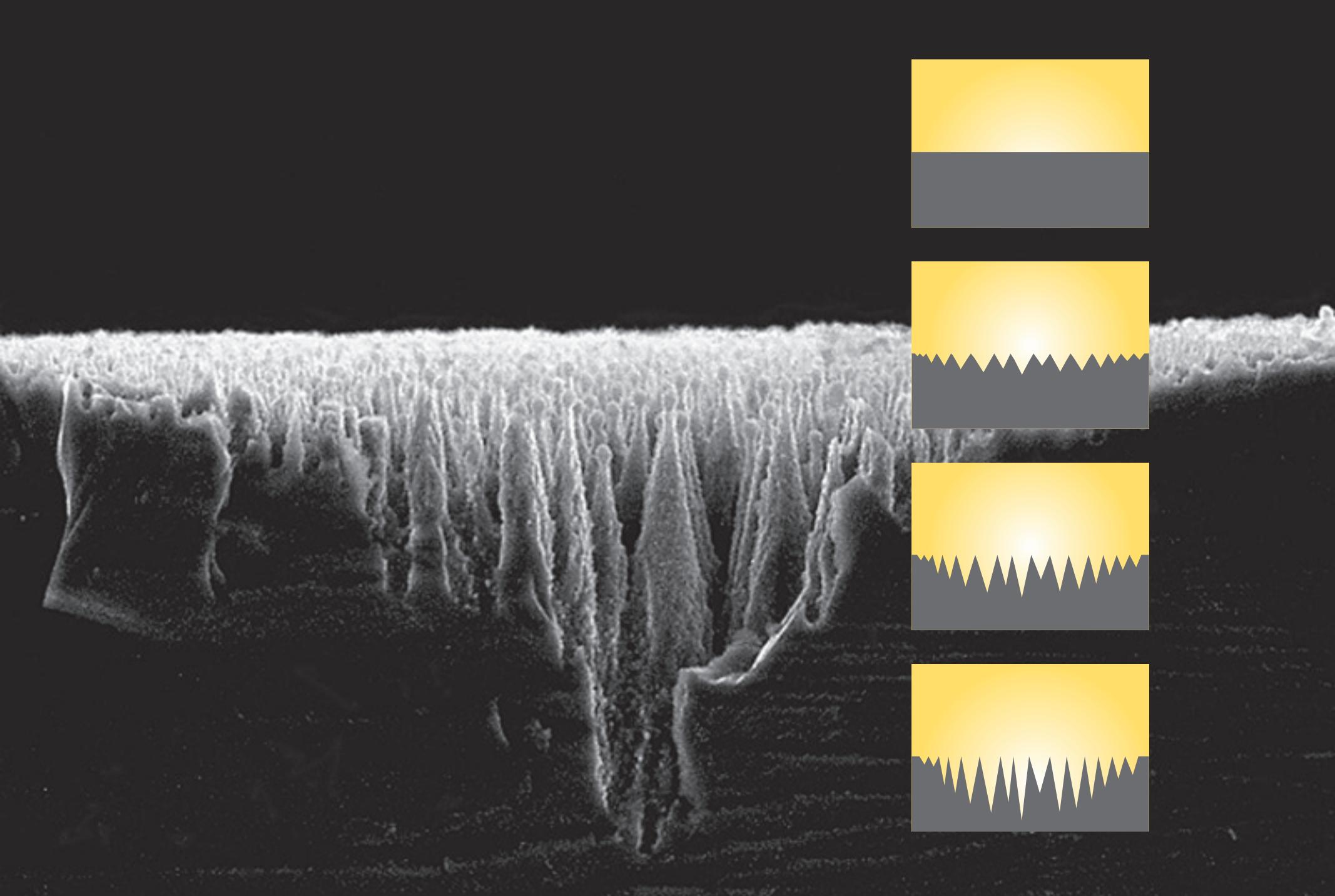


10 μm

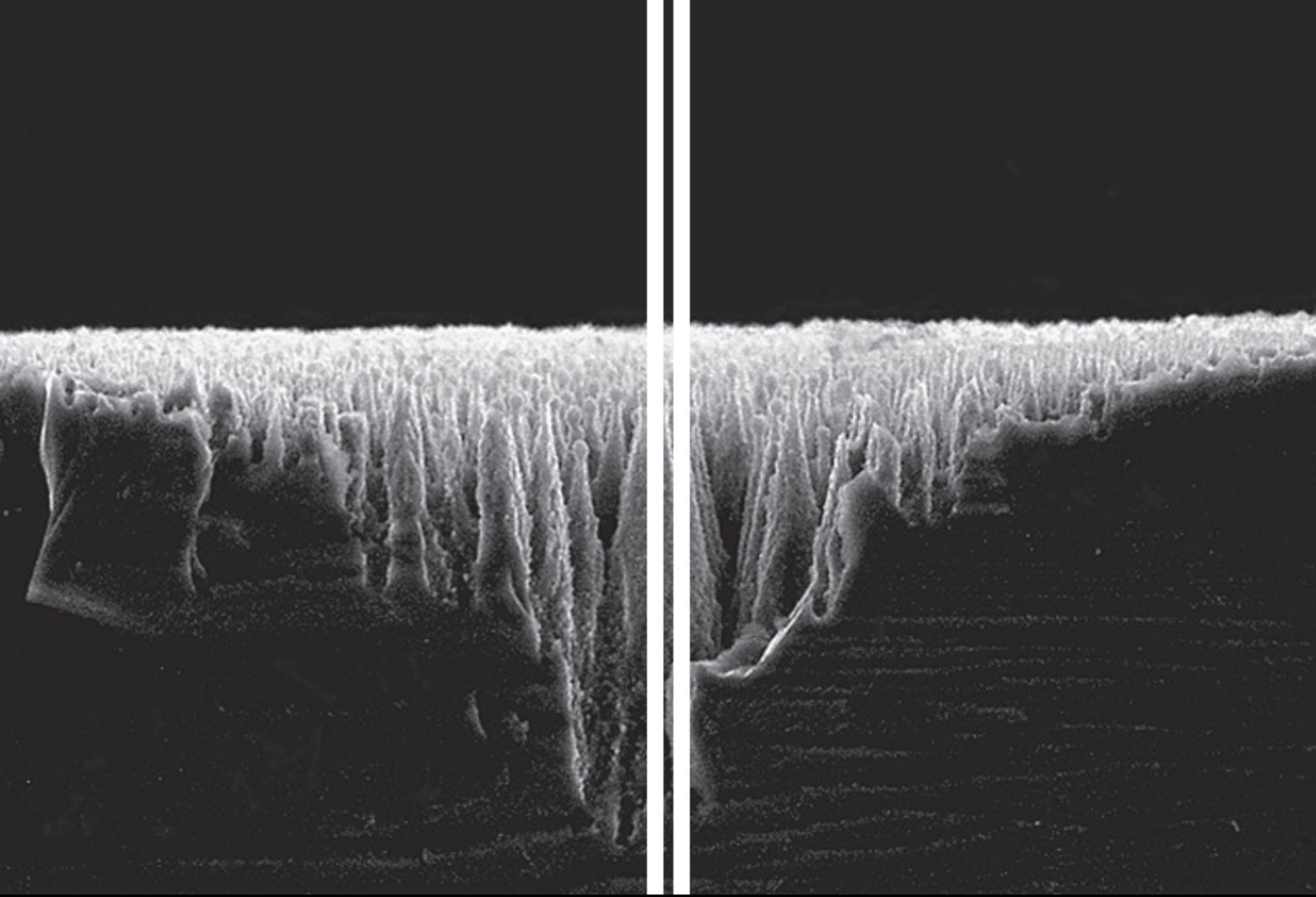
1 intermediate band



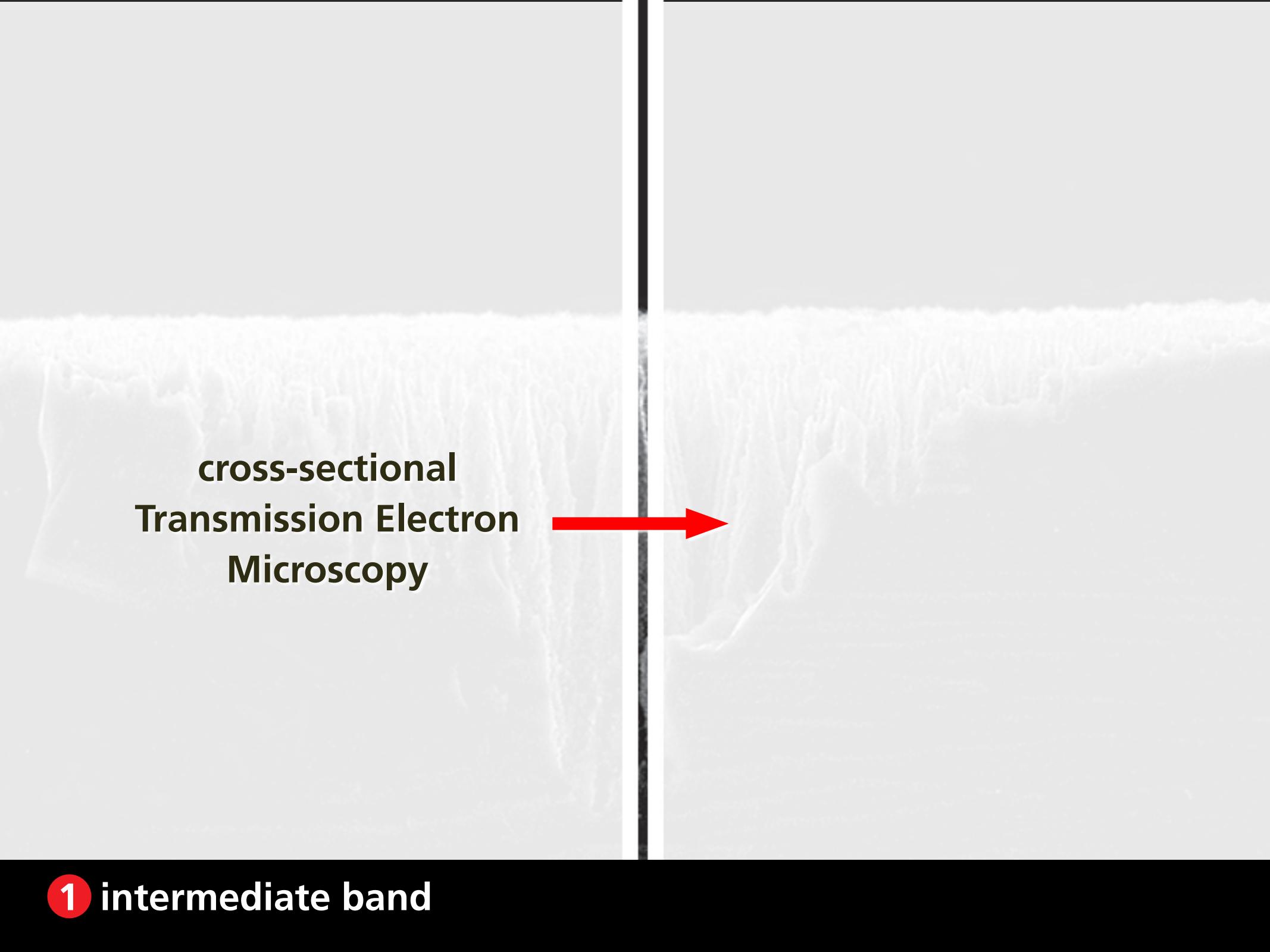
1 intermediate band



1 intermediate band



1 intermediate band

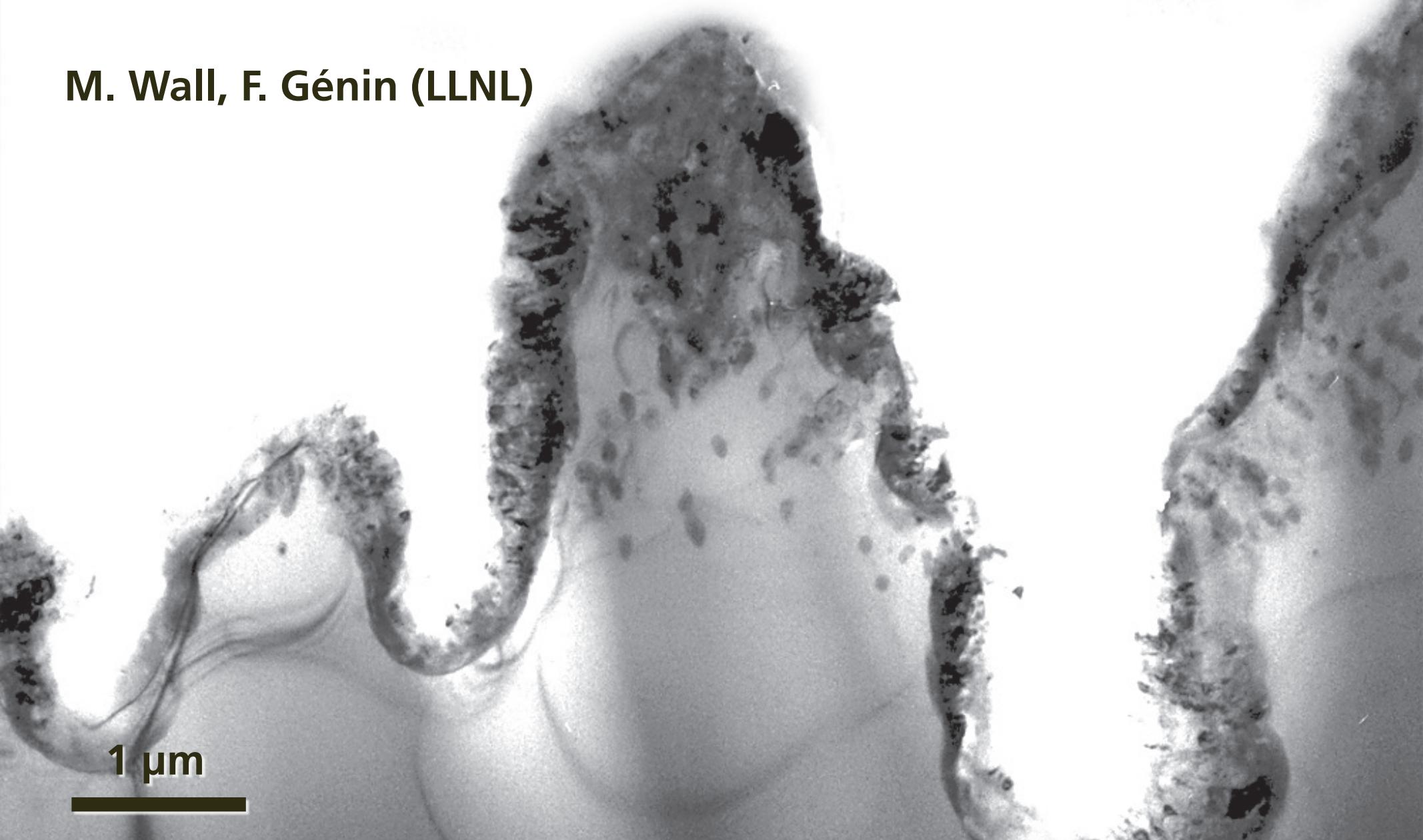


**cross-sectional
Transmission Electron
Microscopy**



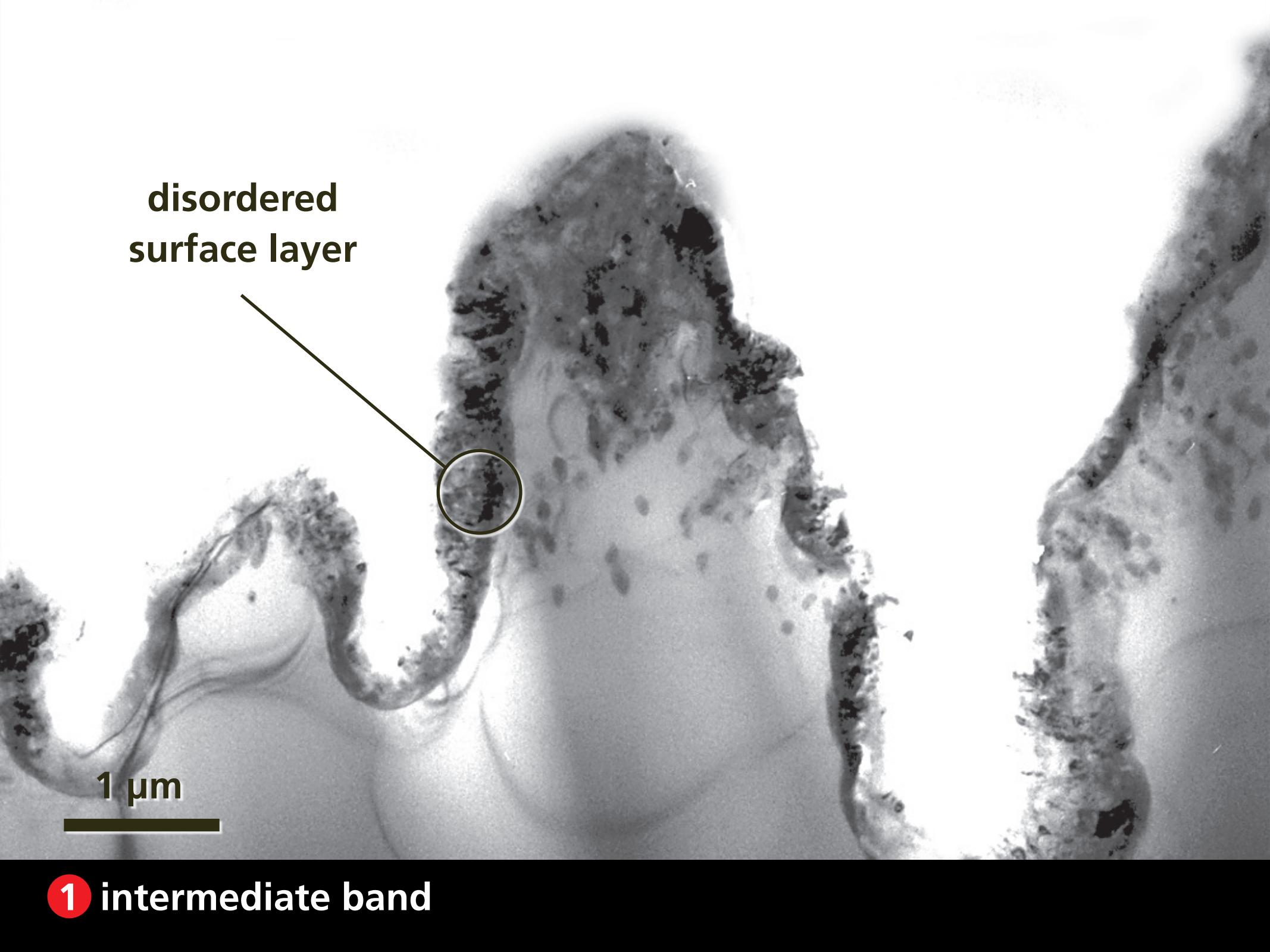
1 intermediate band

M. Wall, F. Génin (LLNL)



1 μm

1 intermediate band

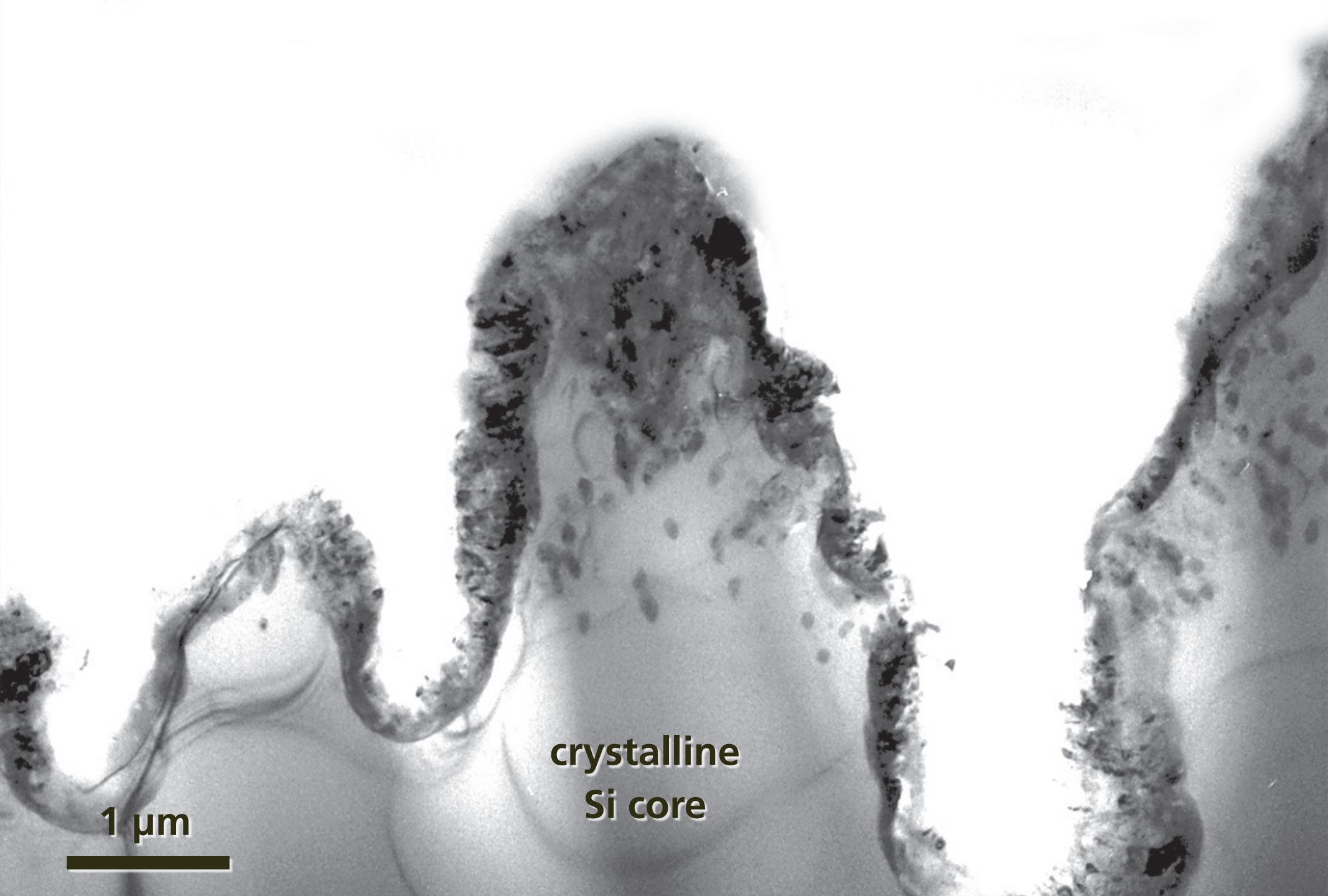


**disordered
surface layer**



1 μm

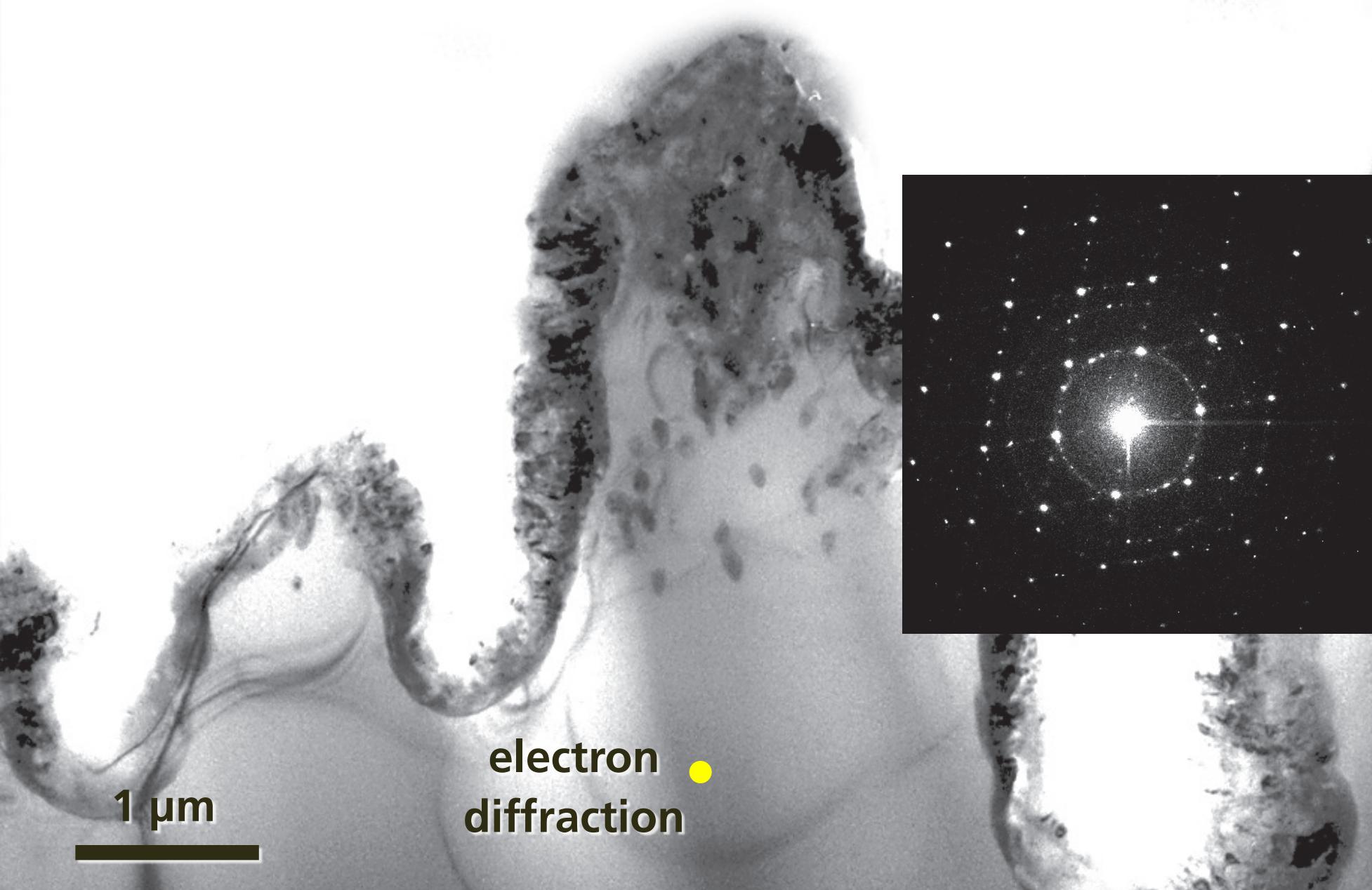
1 intermediate band



1 μm

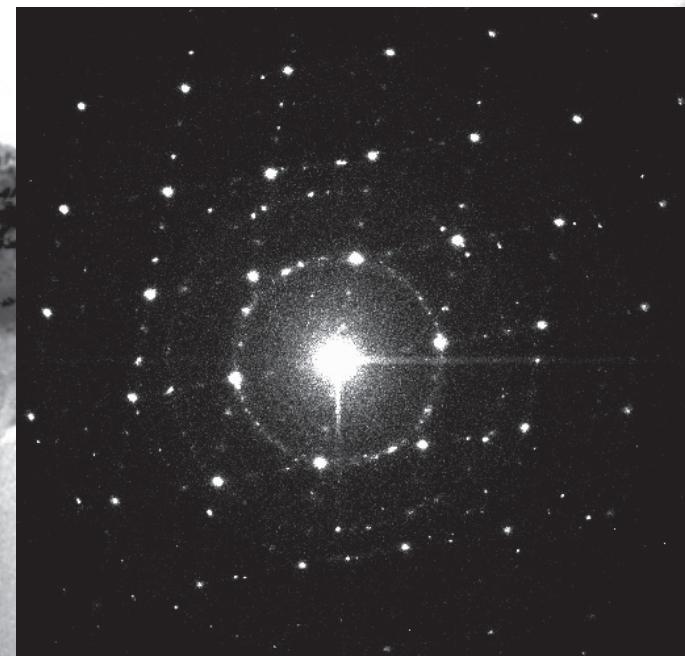
crystalline
Si core

1 intermediate band

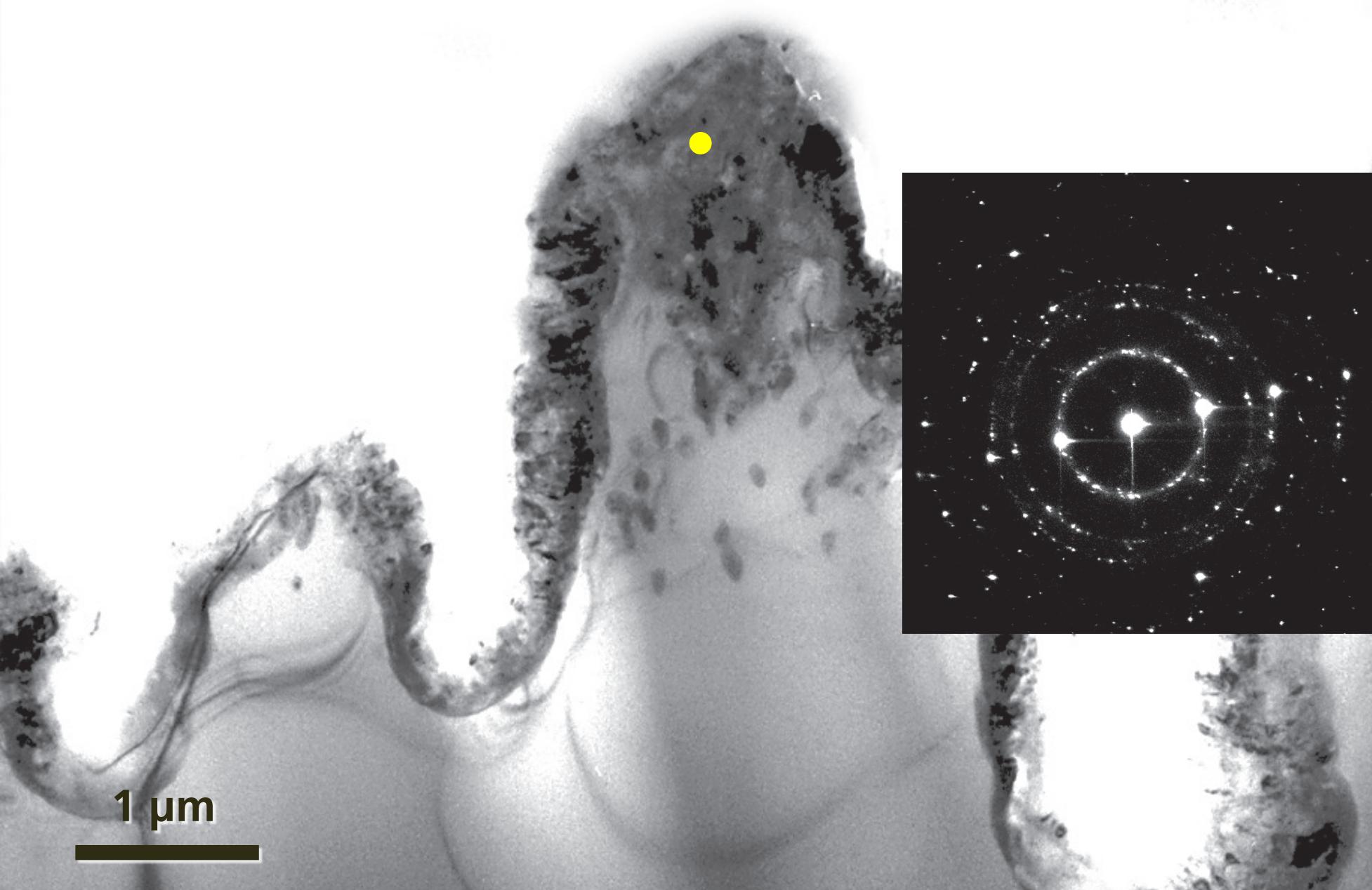


1 μm

electron
diffraction

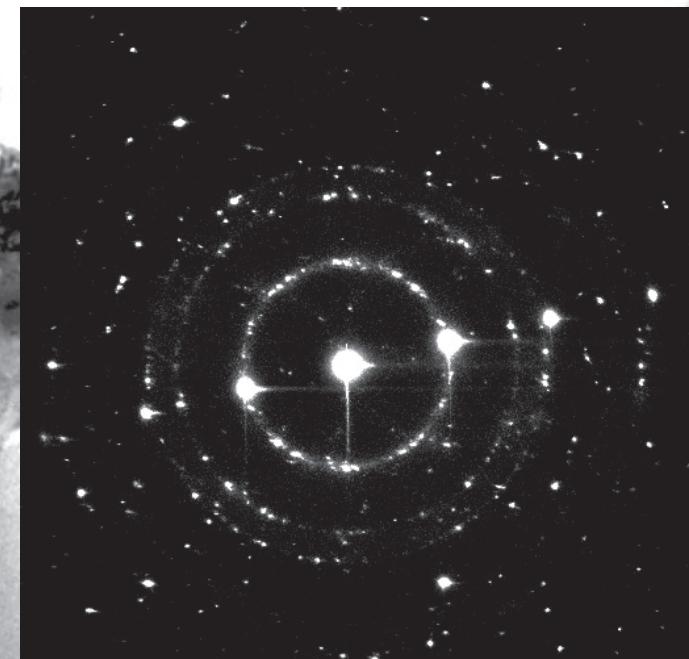


1 intermediate band



1 μm

1 intermediate band



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

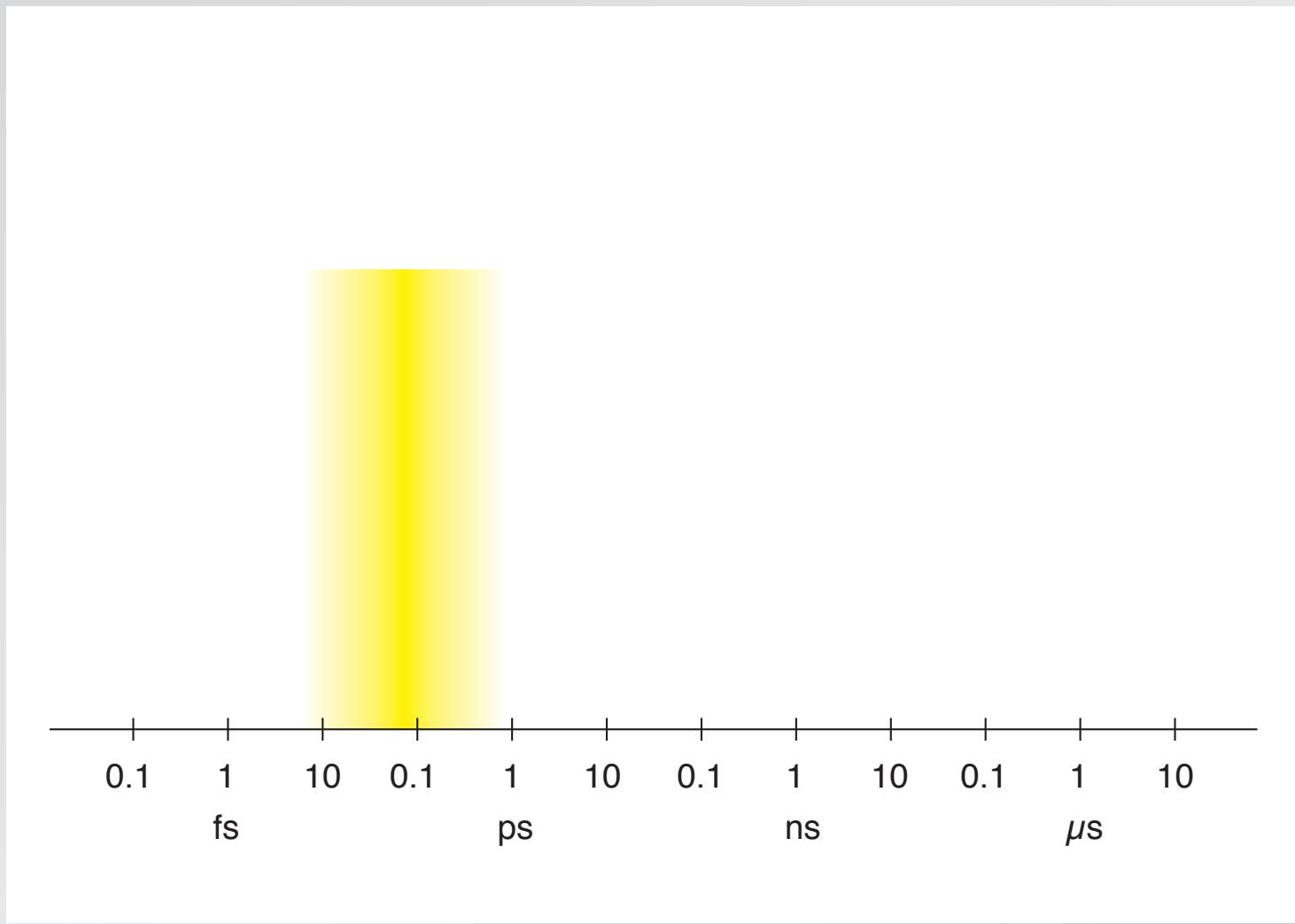
1 μm

1 intermediate band

two processes: melting and ablation

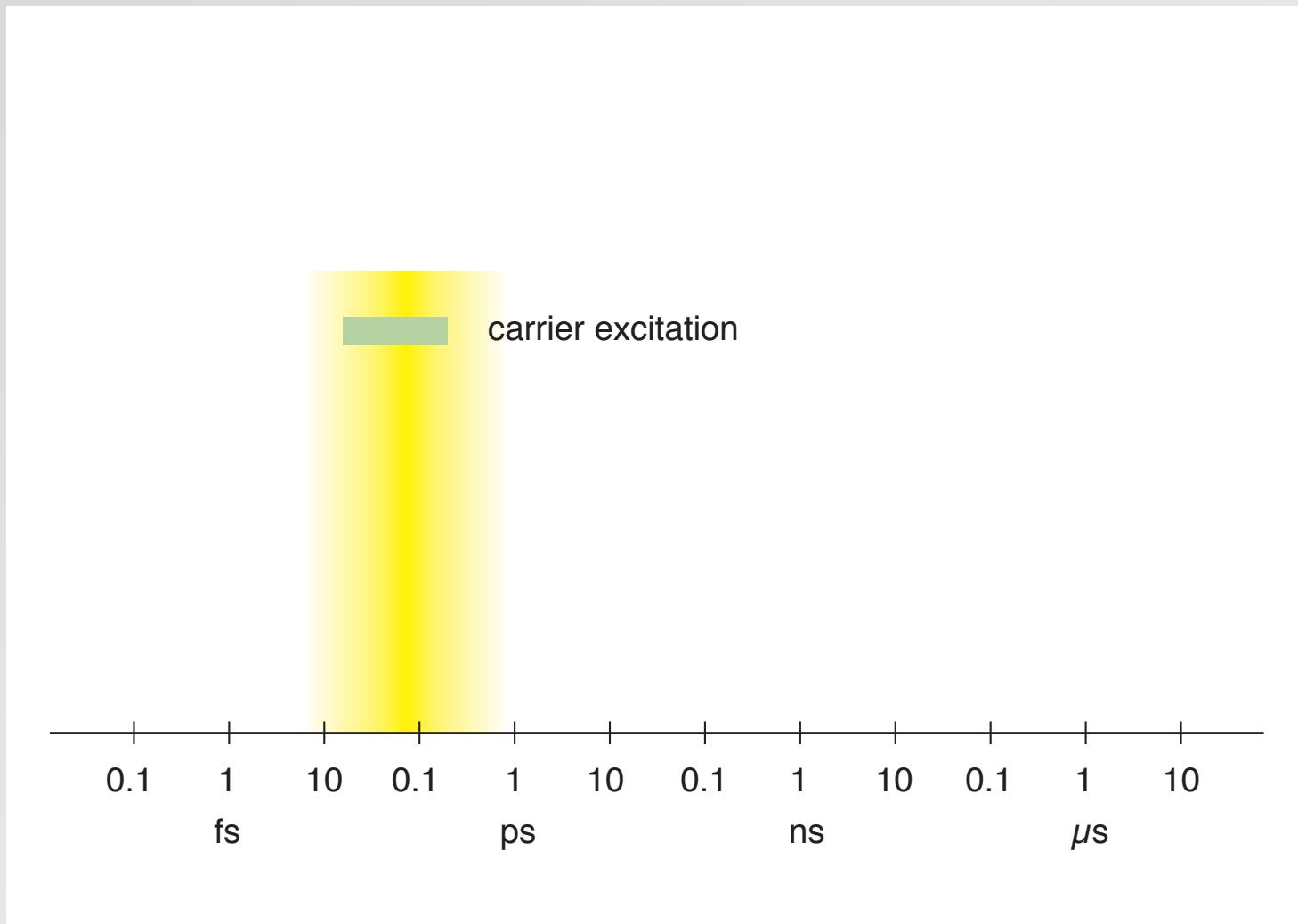
1 intermediate band

relevant time scales



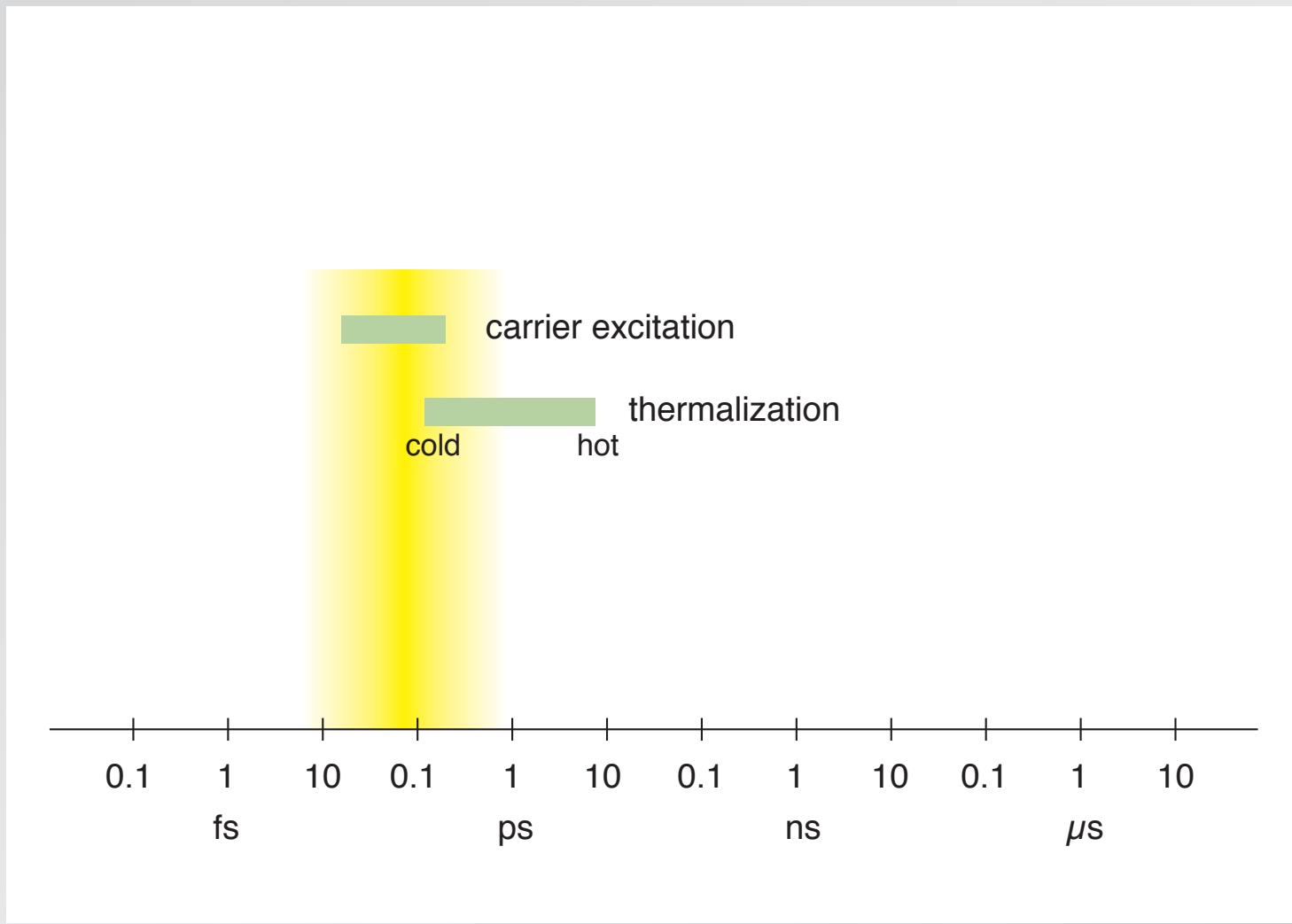
1 intermediate band

relevant time scales



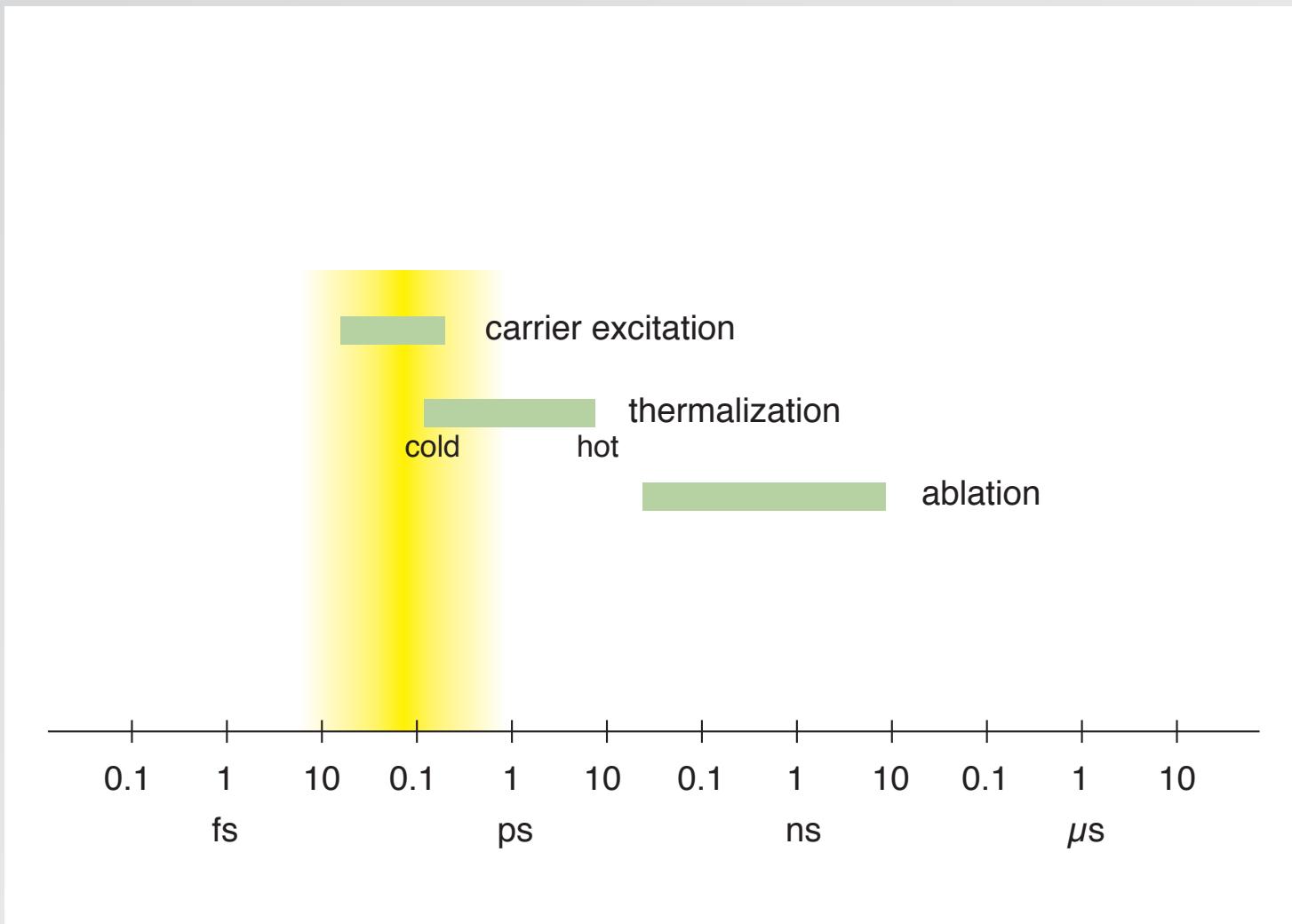
1 intermediate band

relevant time scales



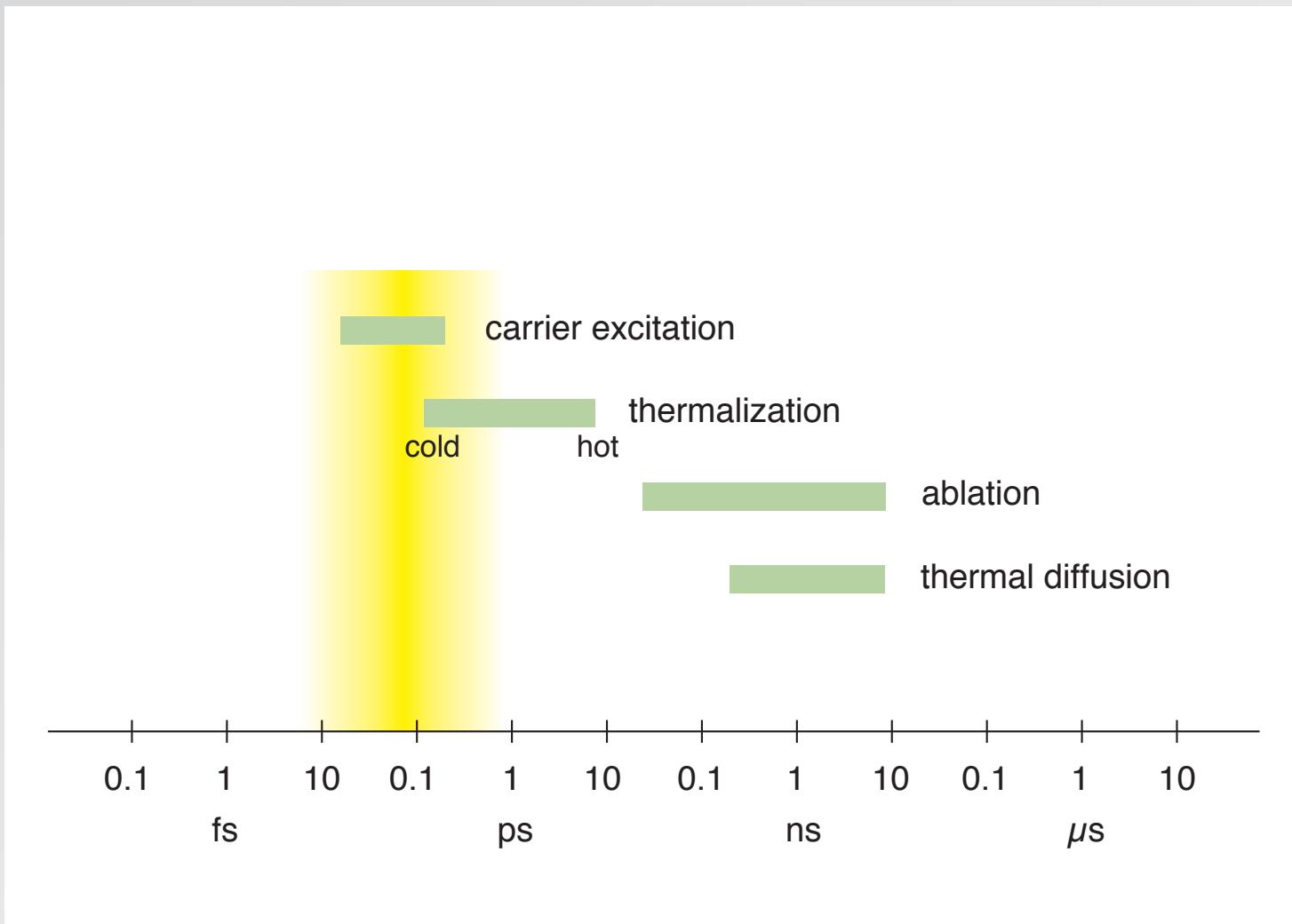
1 intermediate band

relevant time scales



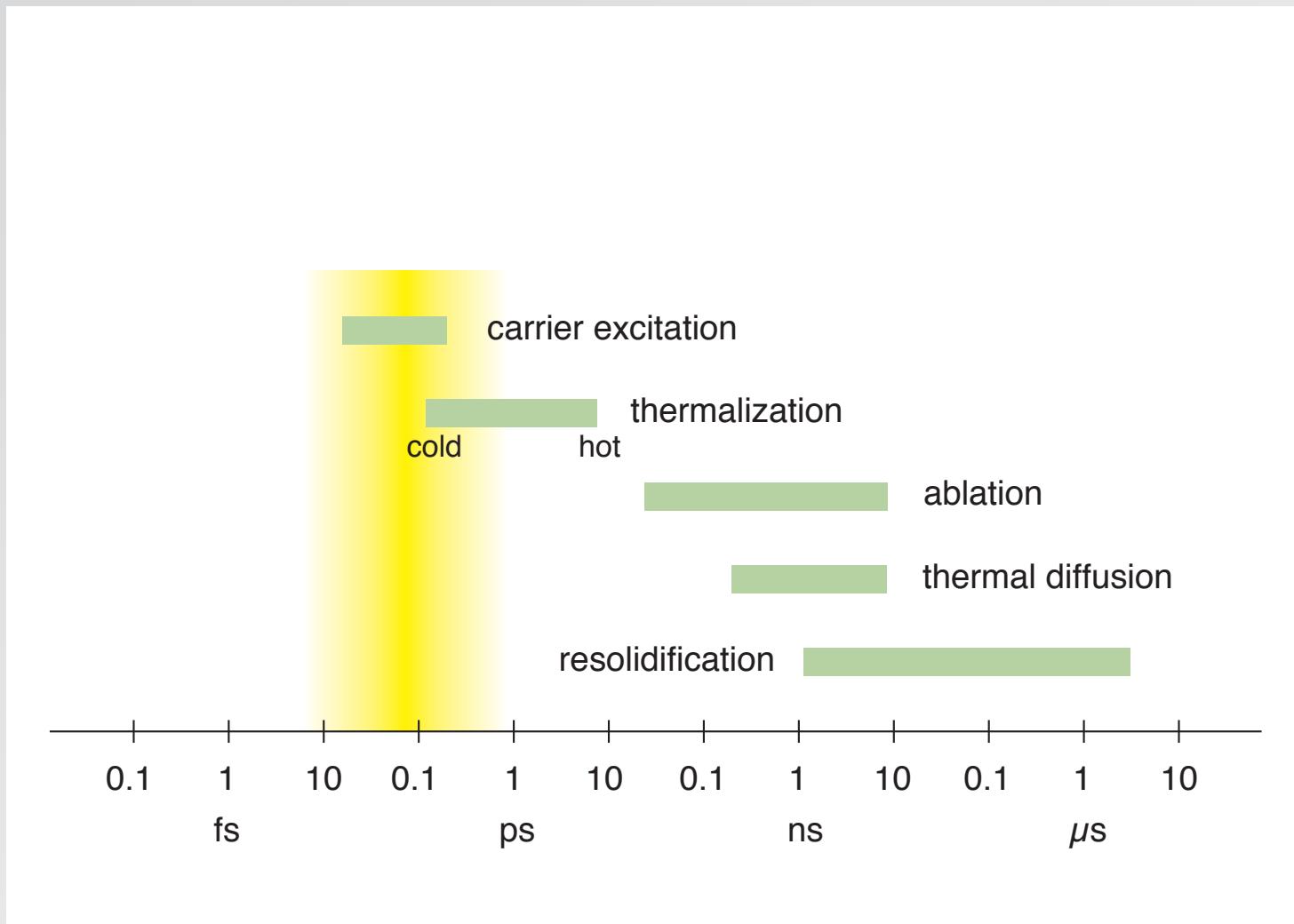
1 intermediate band

relevant time scales



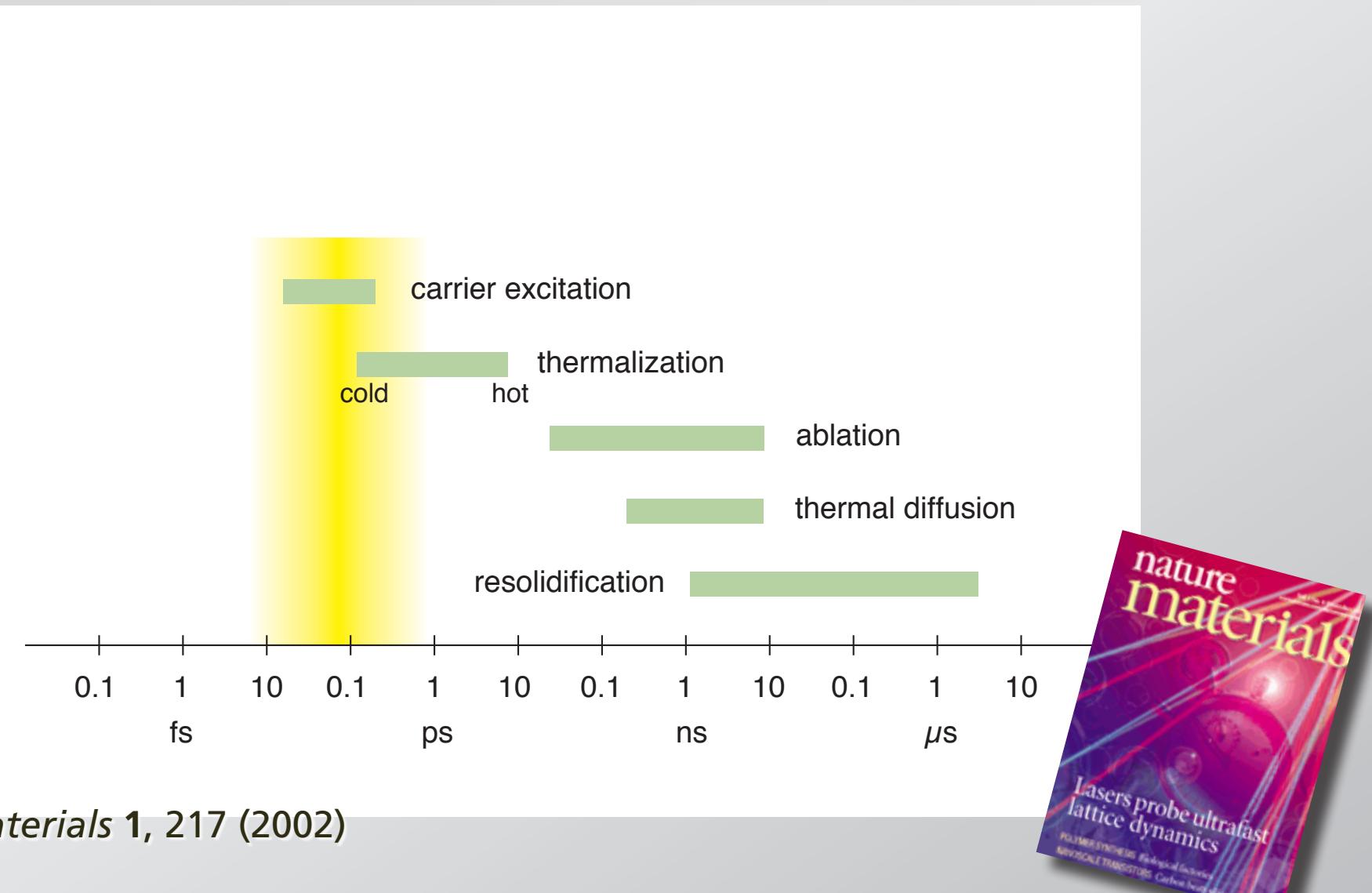
1 intermediate band

relevant time scales



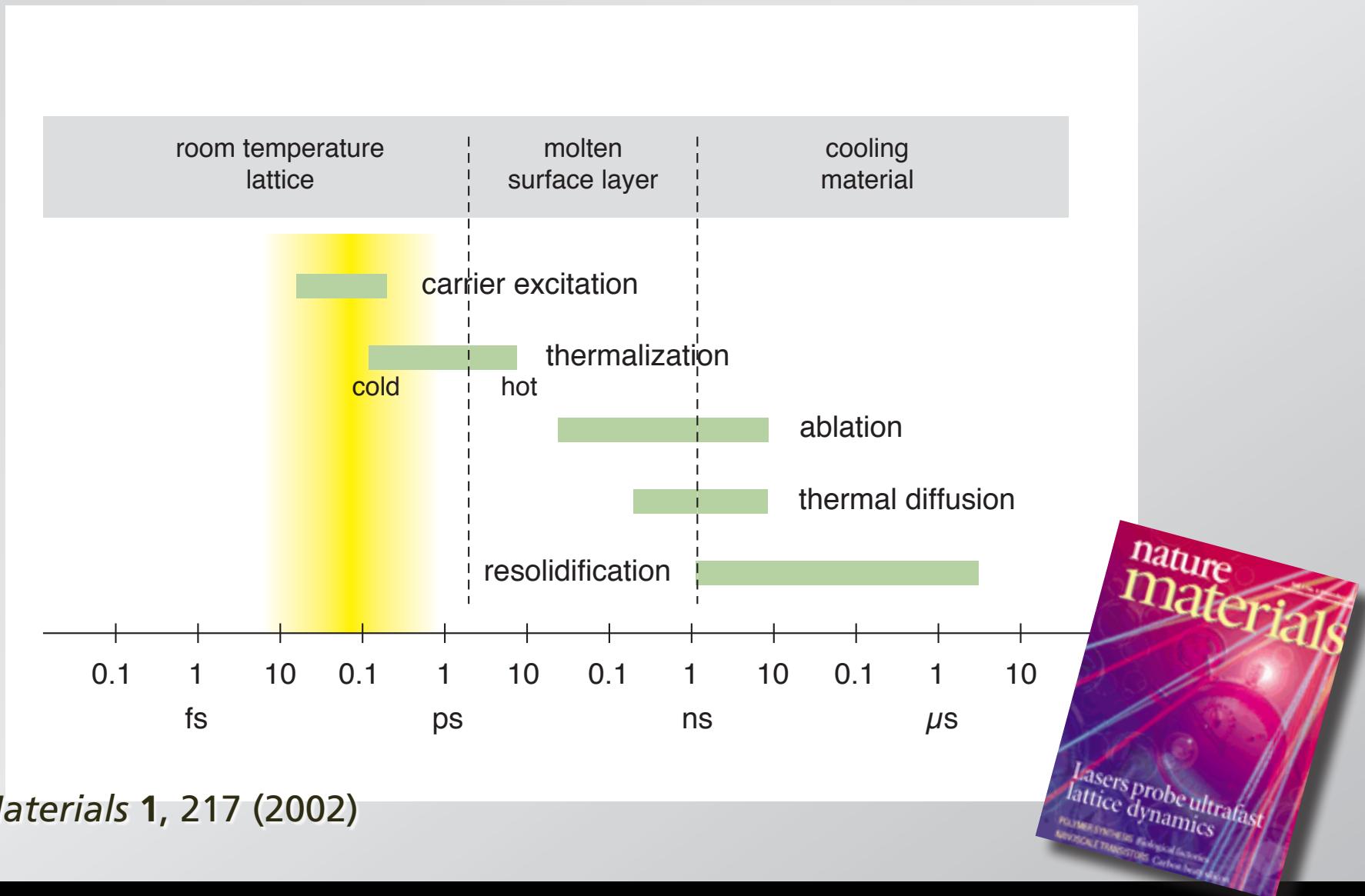
1 intermediate band

relevant time scales



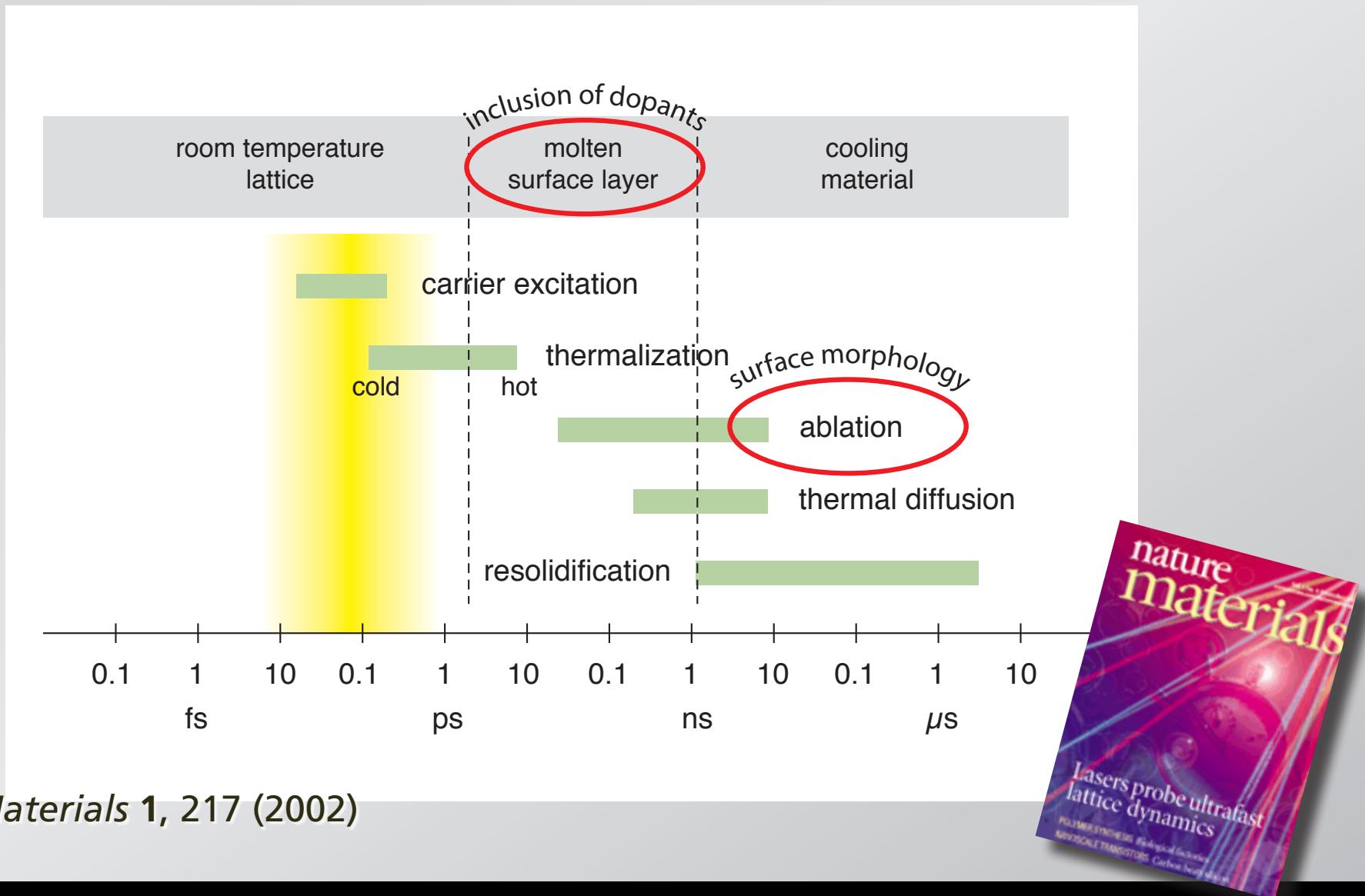
1 intermediate band

relevant time scales



1 intermediate band

relevant time scales



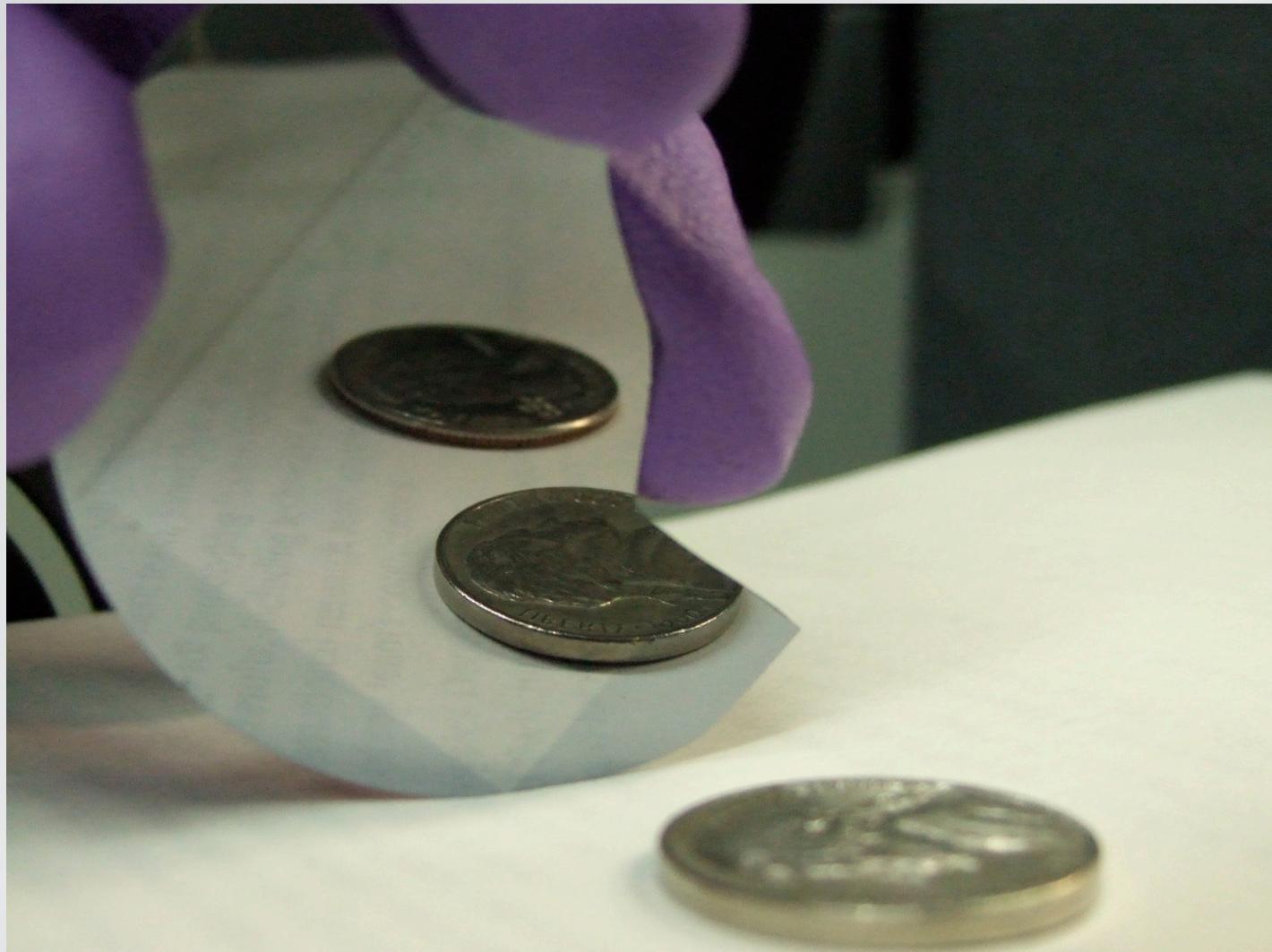
1 intermediate band

different thresholds:

melting: 1.5 kJ/m^2

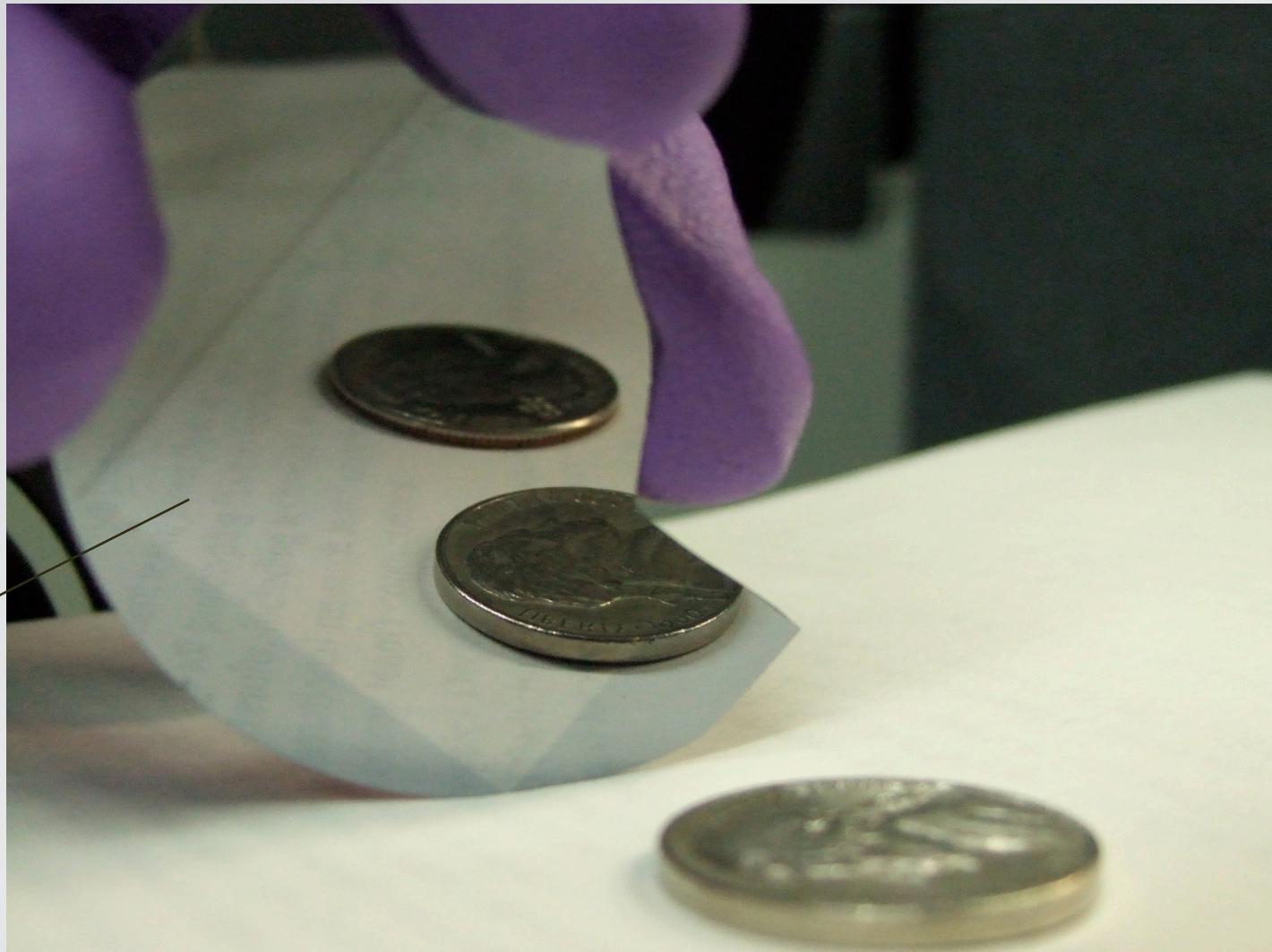
ablation: 3.1 kJ/m^2

decouple ablation from melting



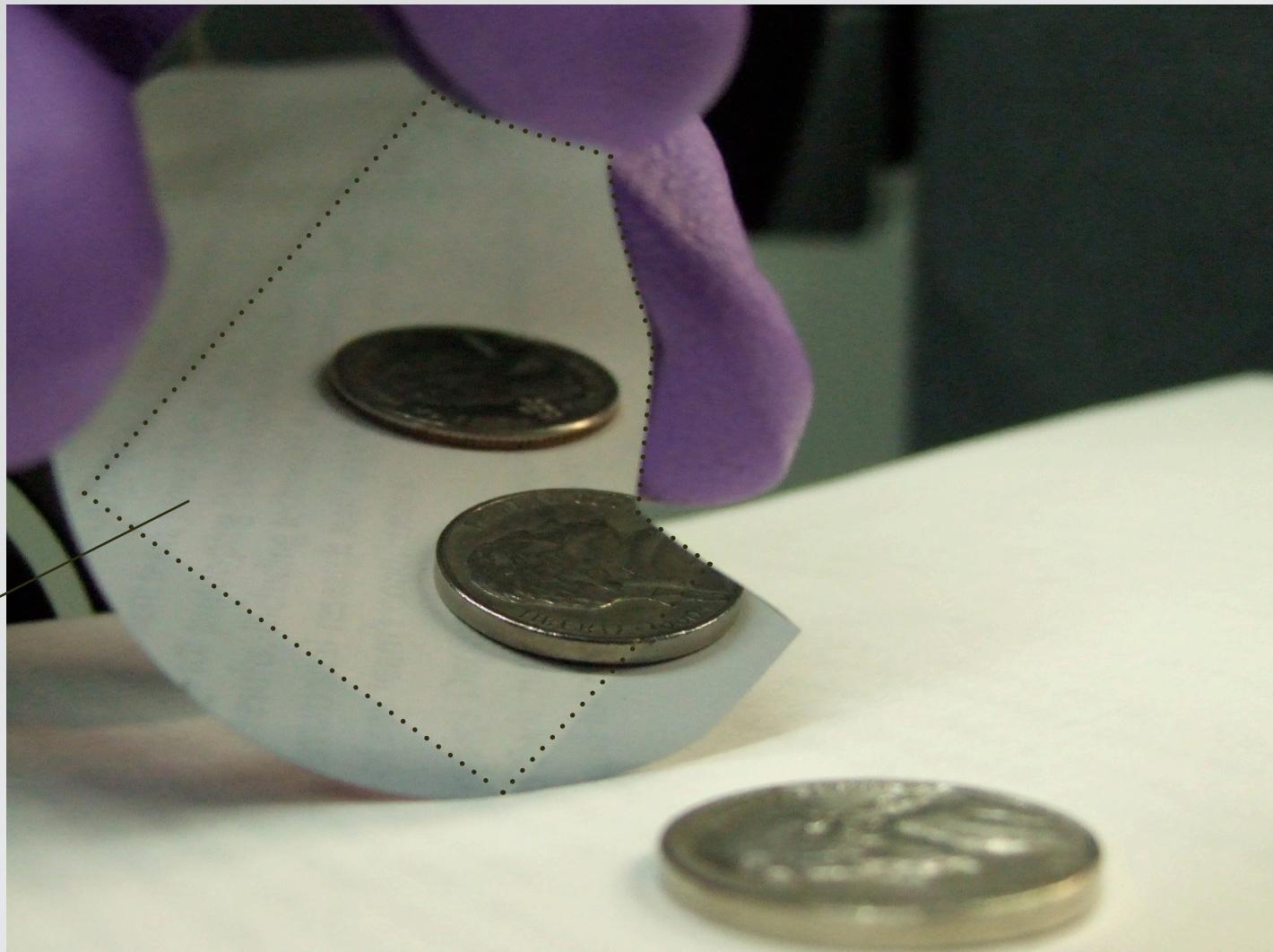
1 intermediate band

decouple ablation from melting



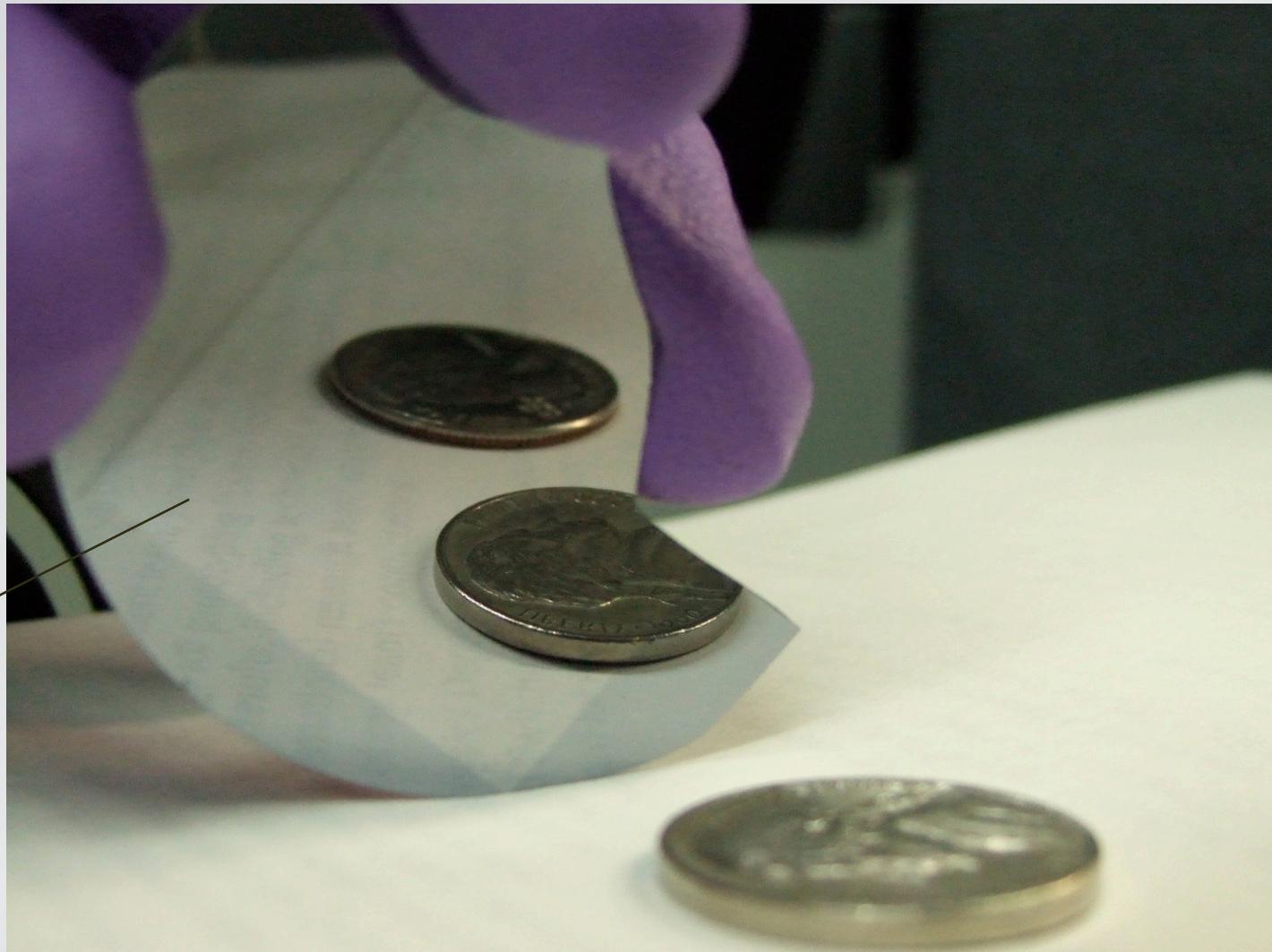
① intermediate band

decouple ablation from melting



1 intermediate band

decouple ablation from melting

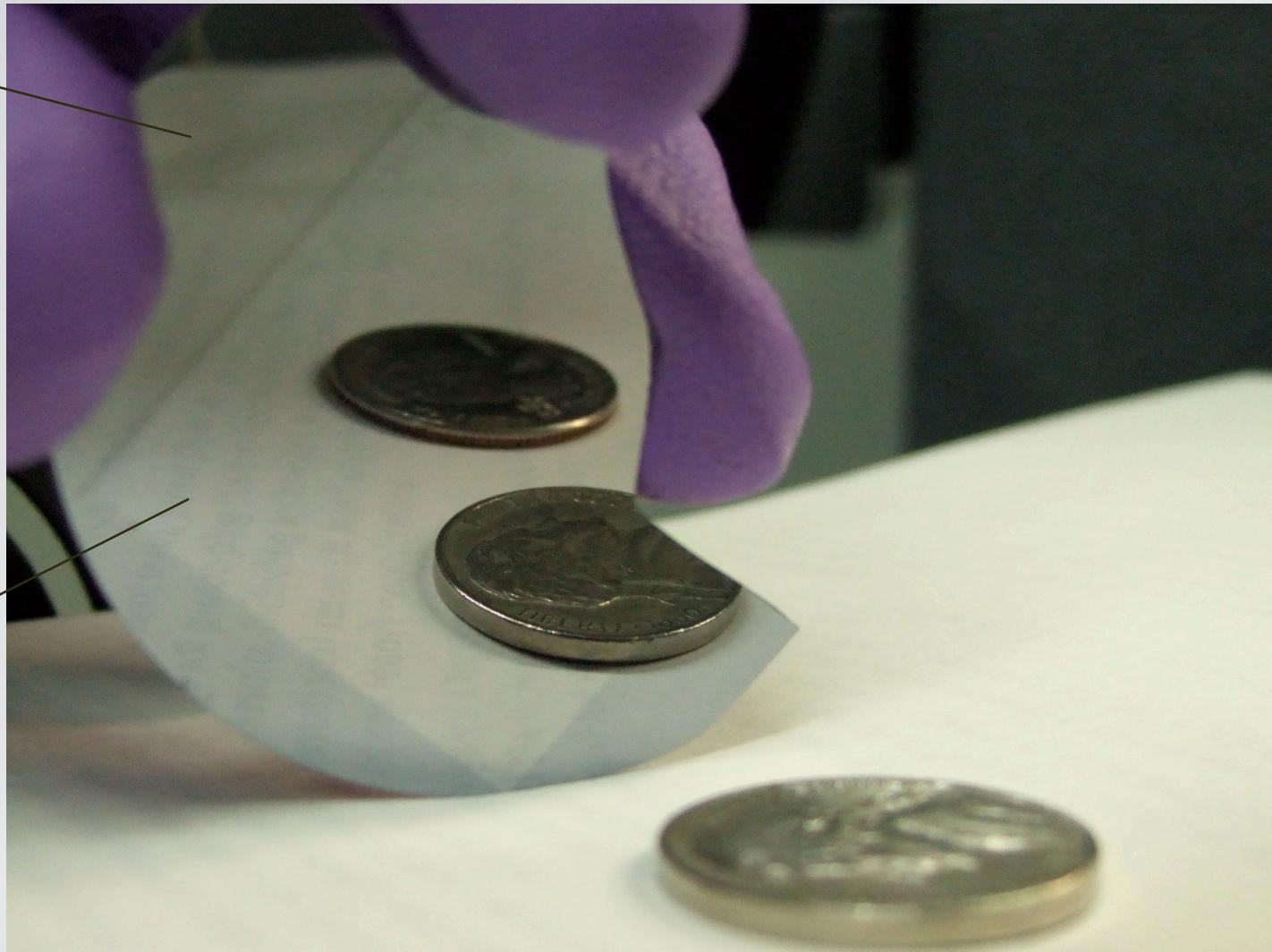


① intermediate band

decouple ablation from melting

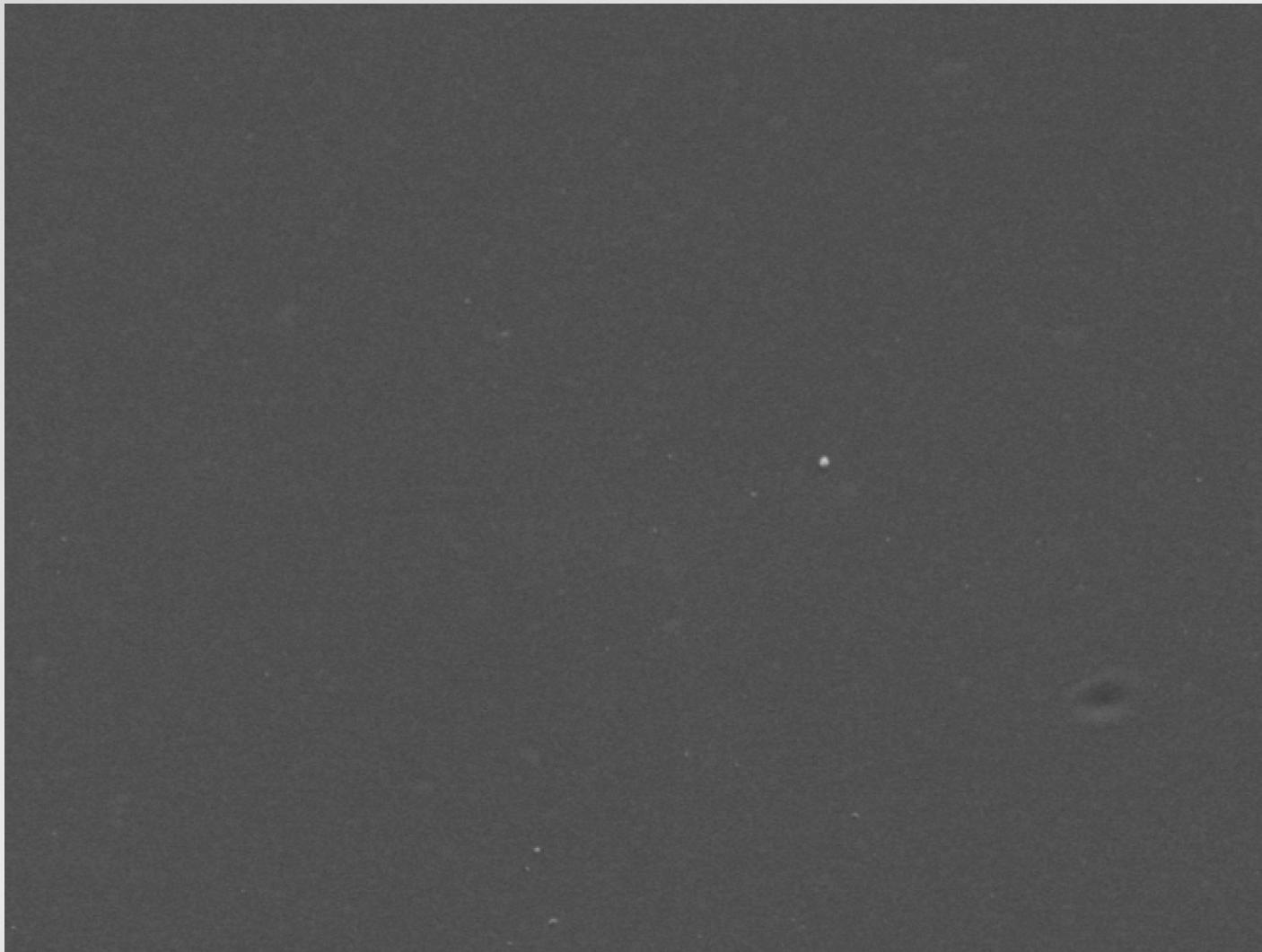
undoped

doped



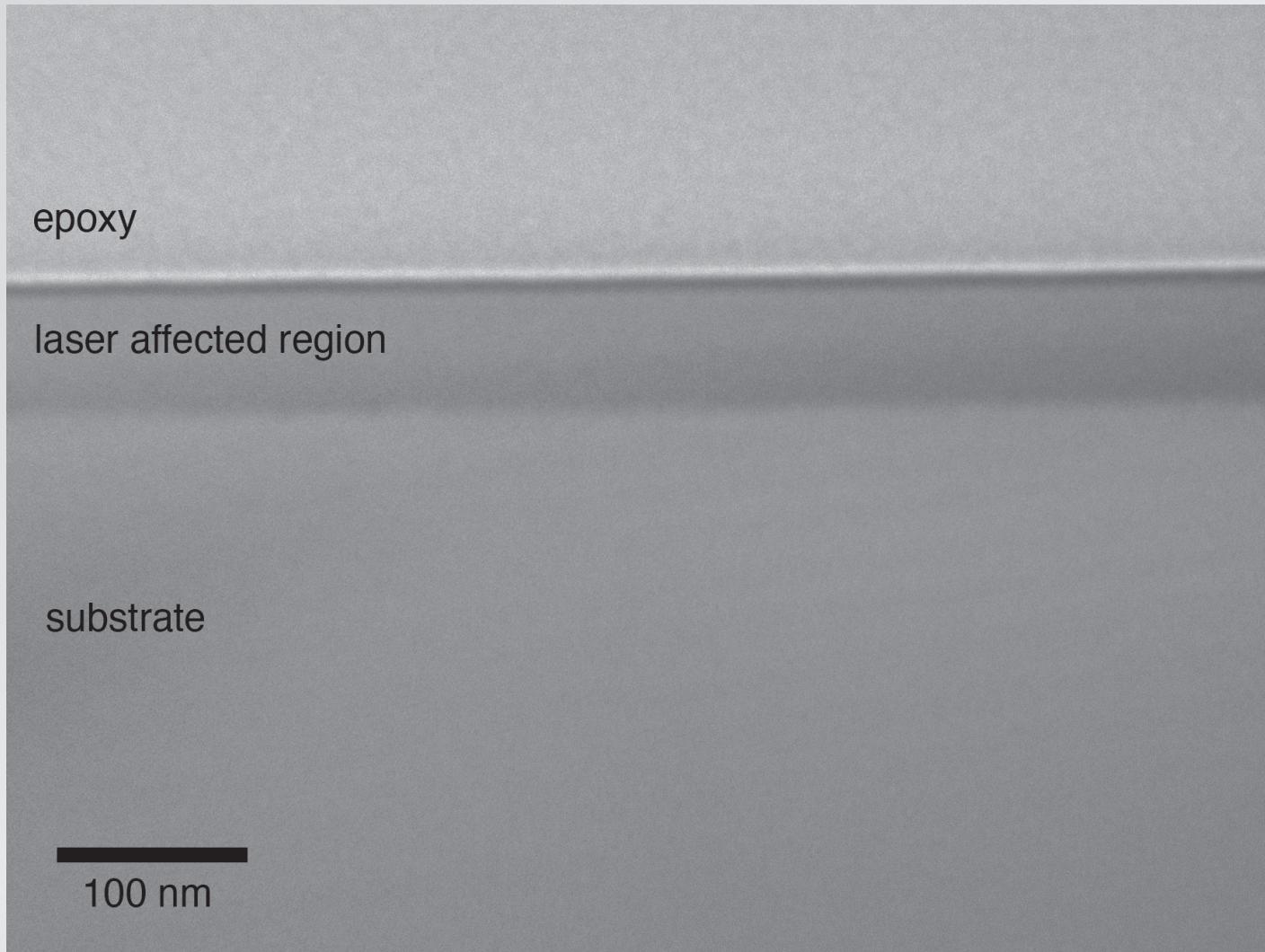
1 intermediate band

decouple ablation from melting



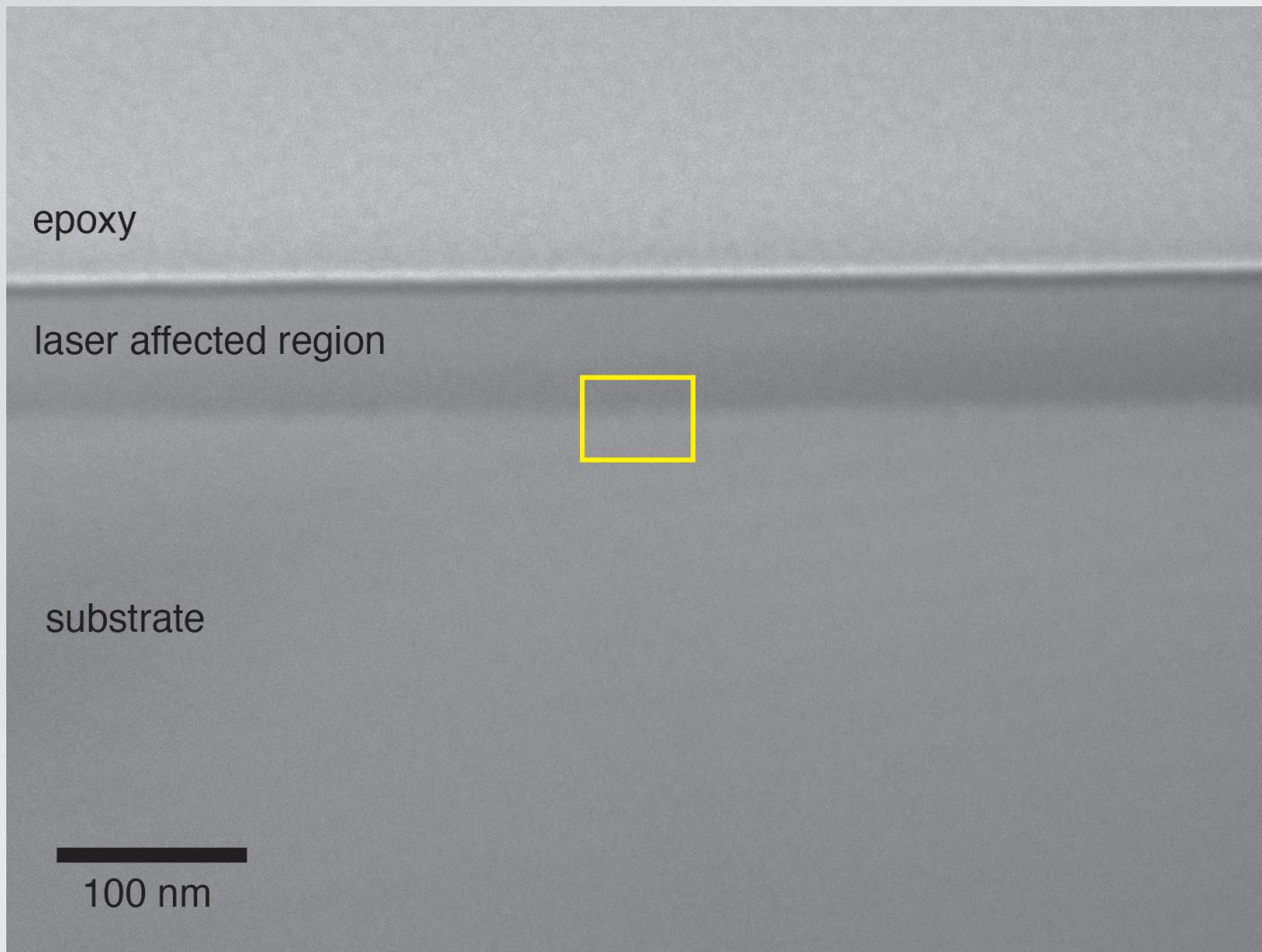
1 intermediate band

decouple ablation from melting



1 intermediate band

decouple ablation from melting



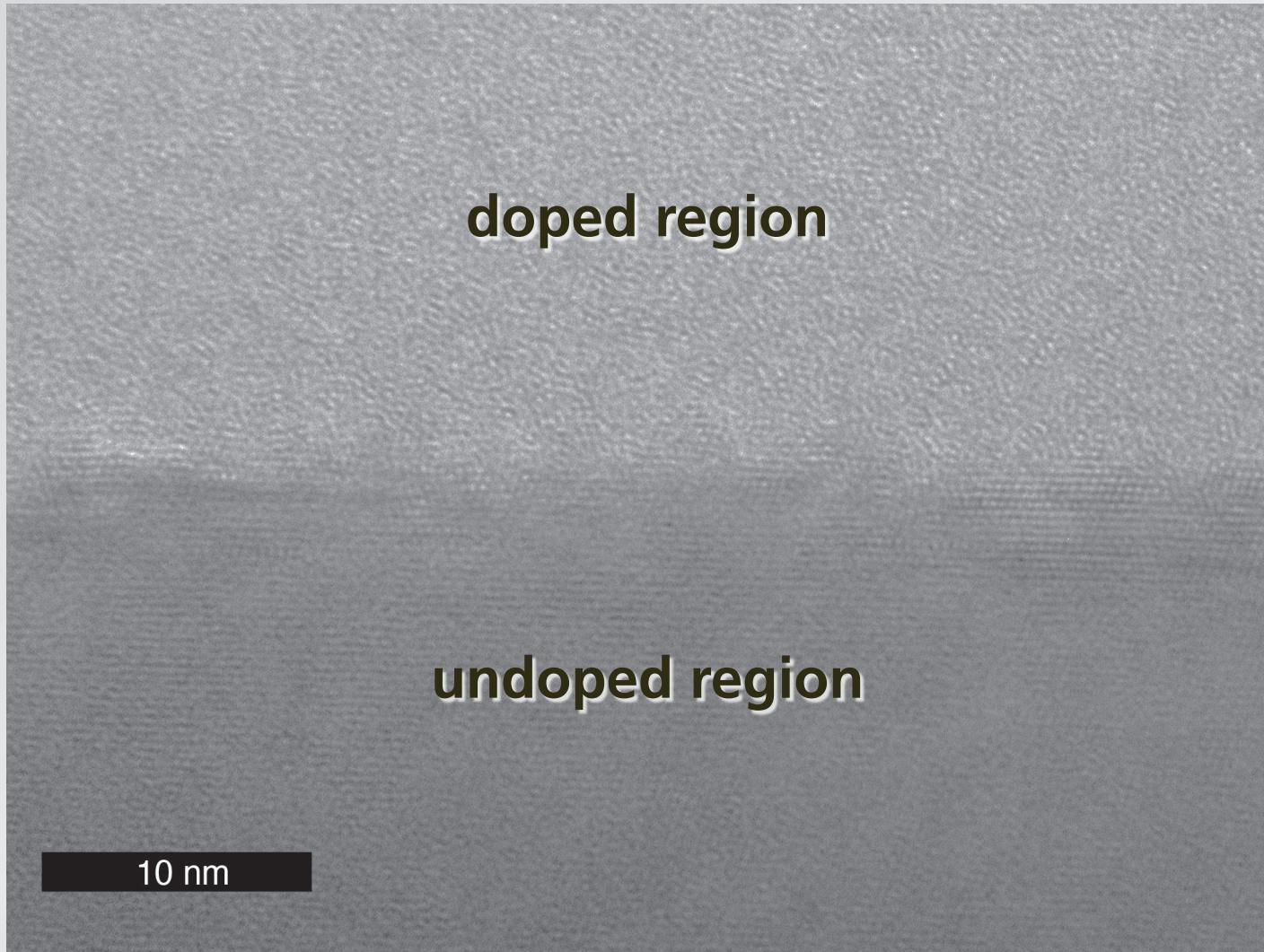
1 intermediate band

decouple ablation from melting



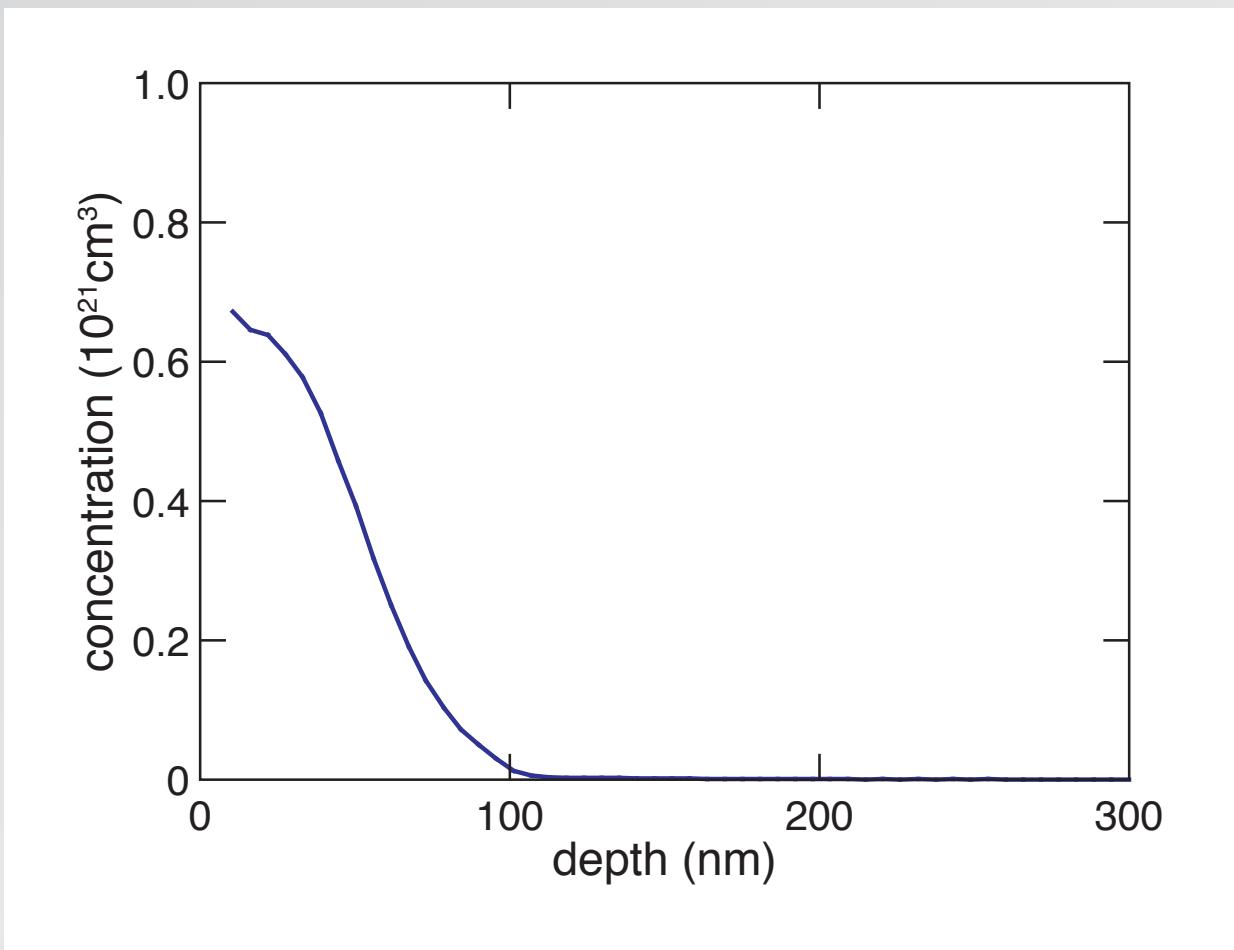
1 intermediate band

decouple ablation from melting



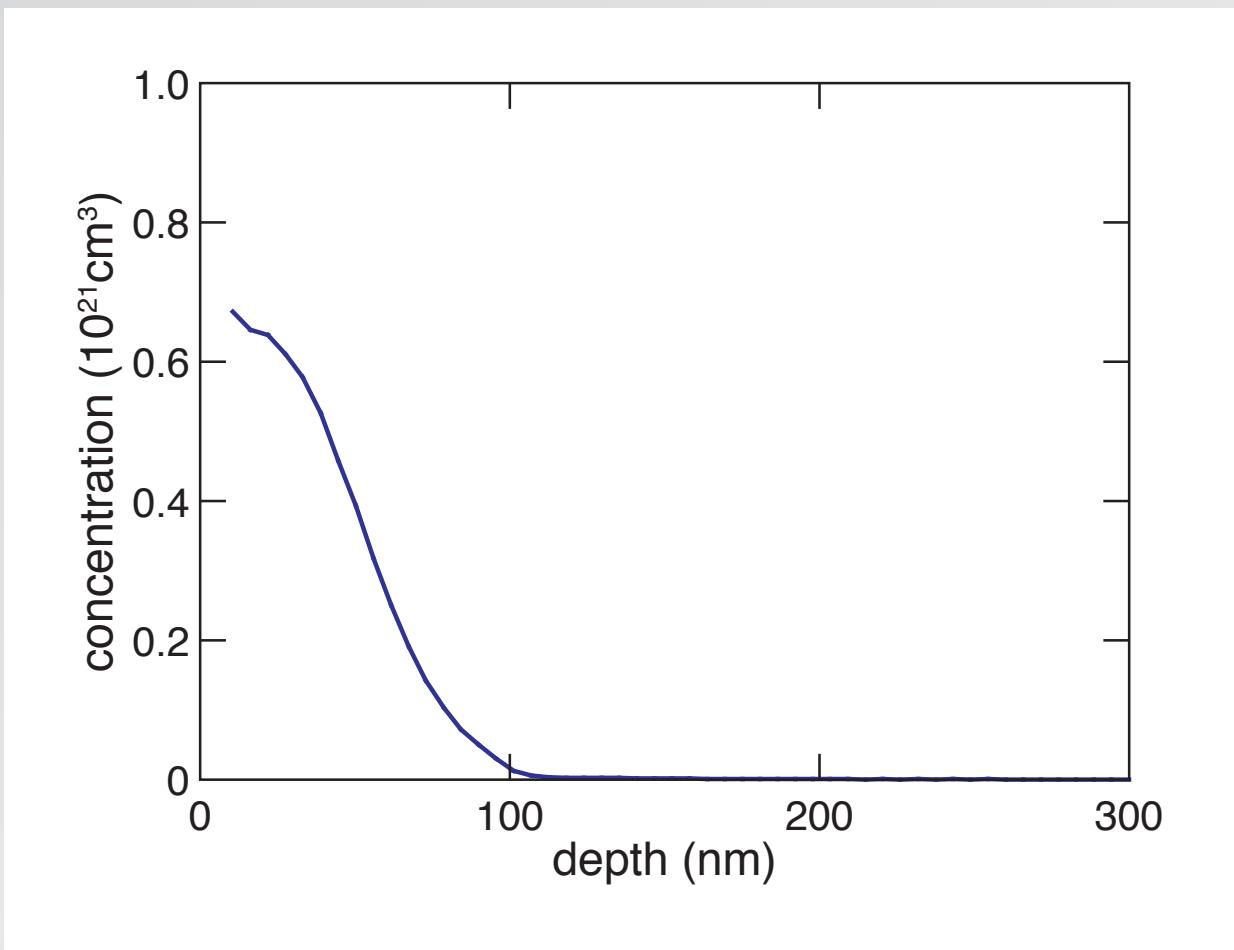
1 intermediate band

secondary ion mass spectrometry



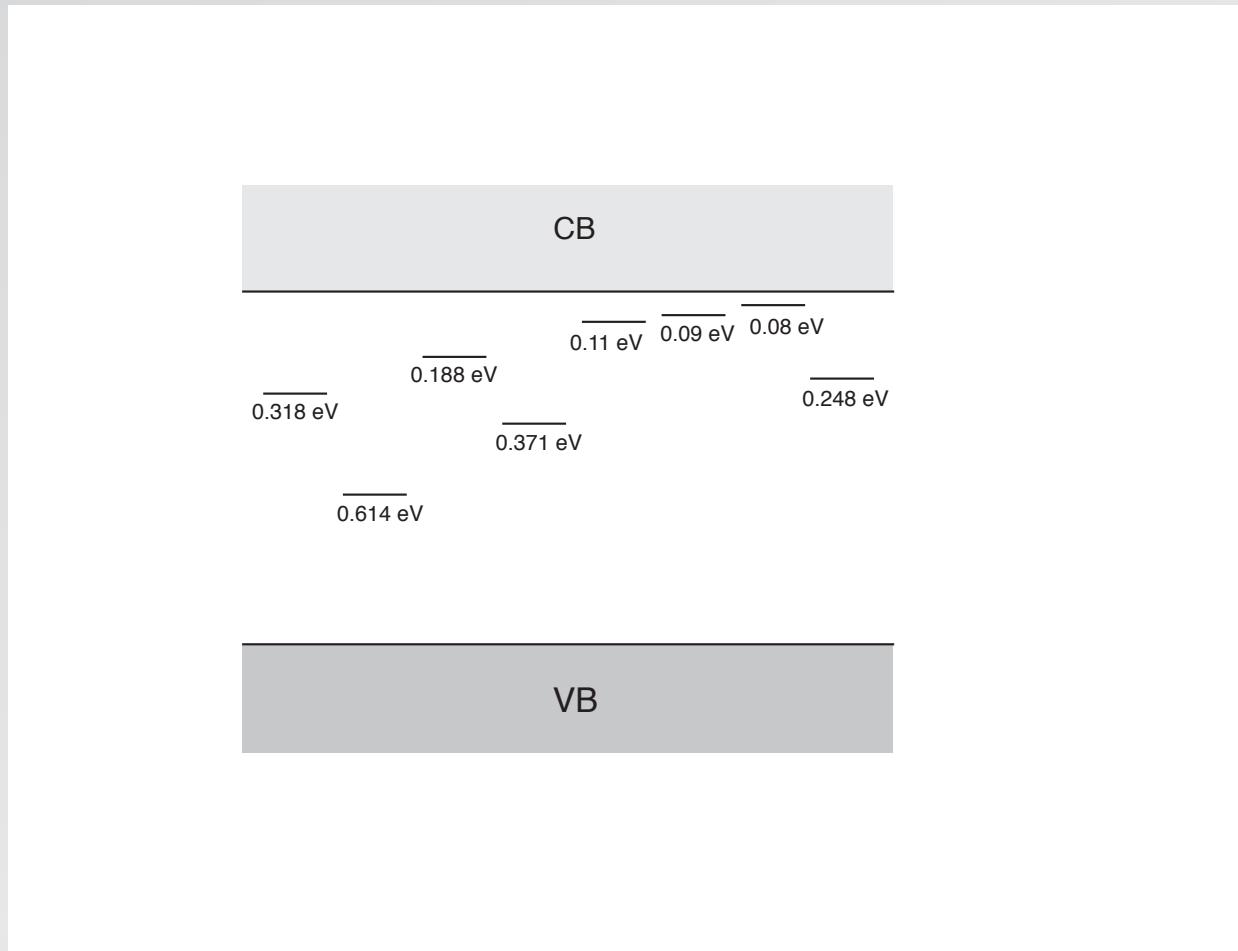
1 intermediate band

secondary ion mass spectrometry



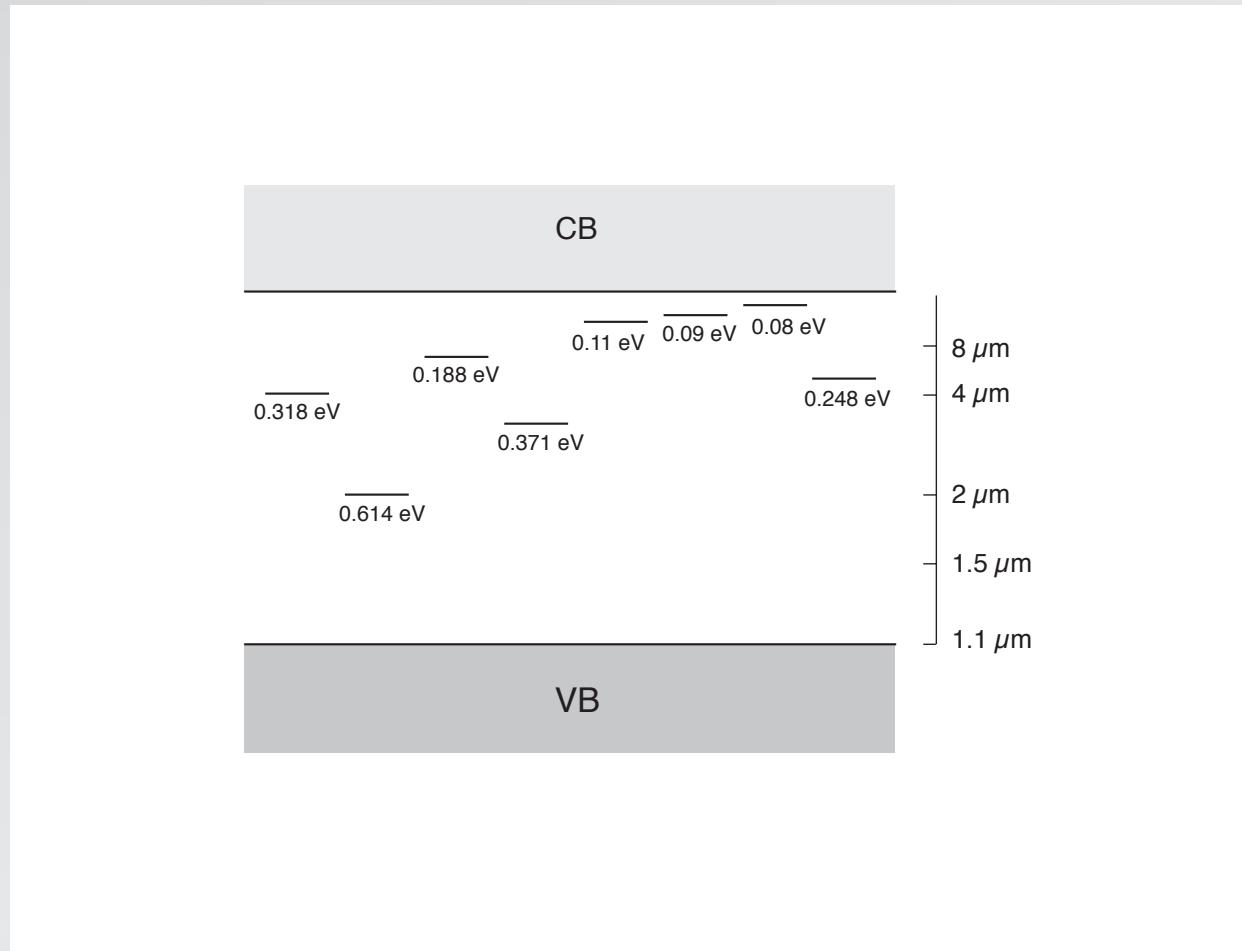
1 intermediate band

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



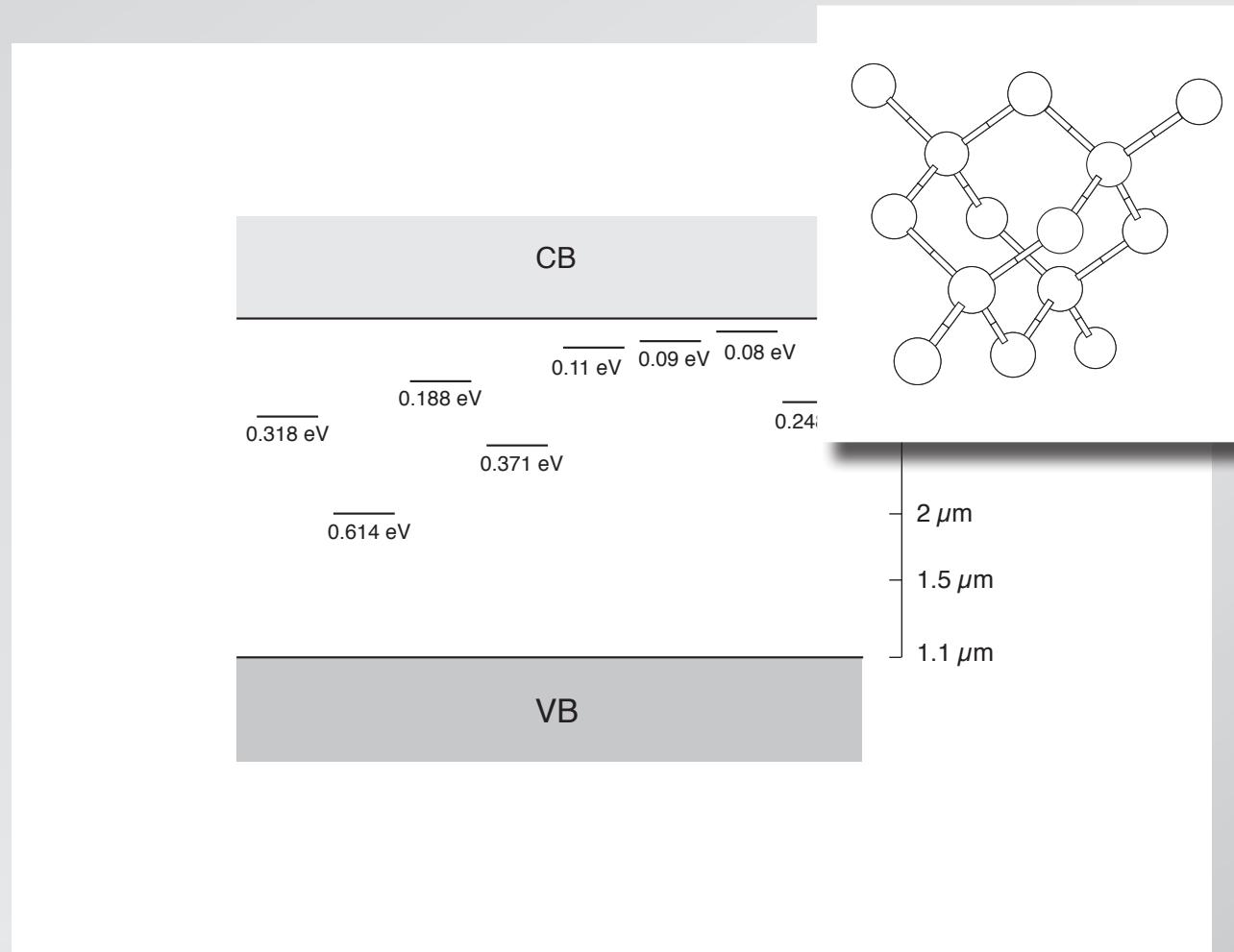
Janzén *et al.*, Phys. Rev. B 29, 1907 (1984)

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



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

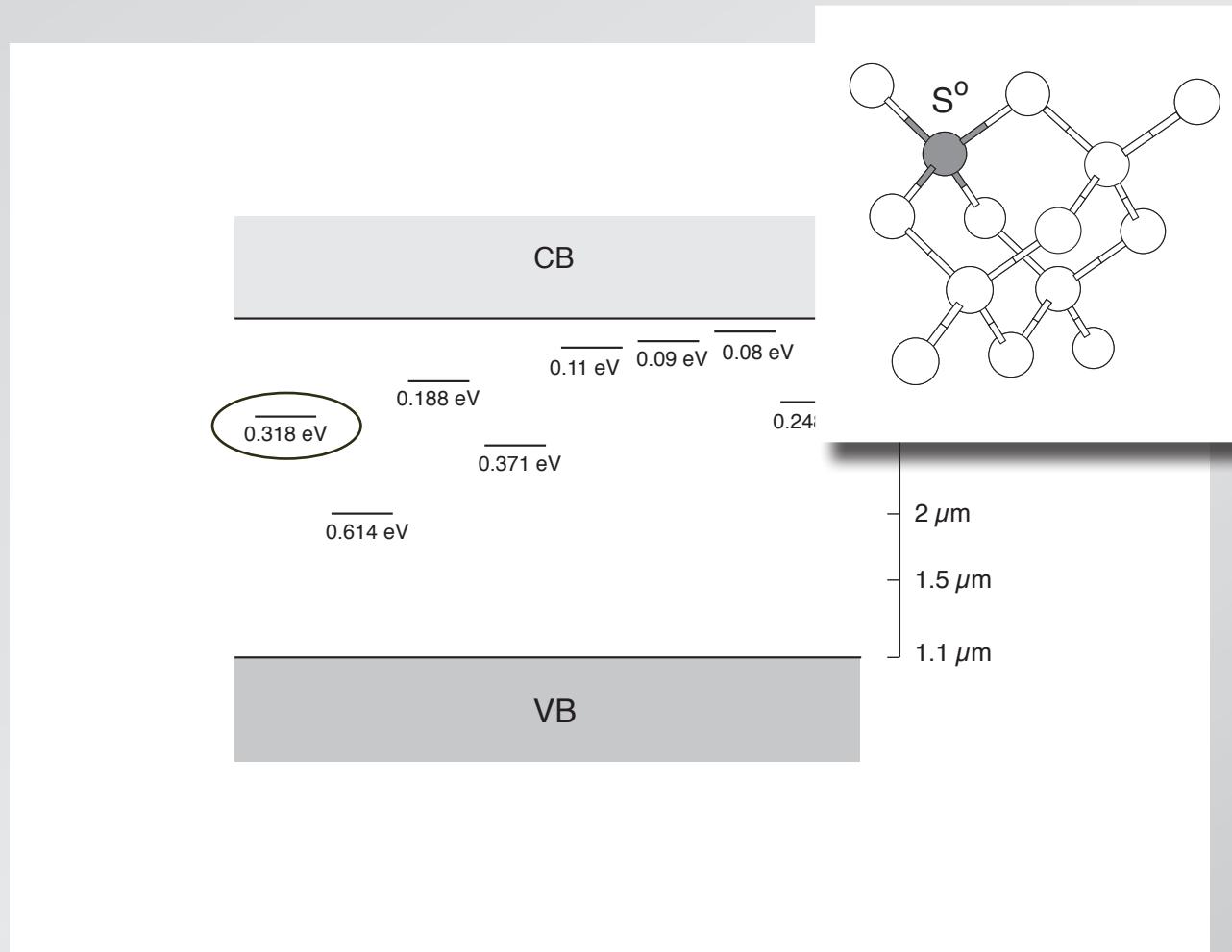
1 part in 10^6 sulfur introduces donor states in gap



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

1 intermediate band

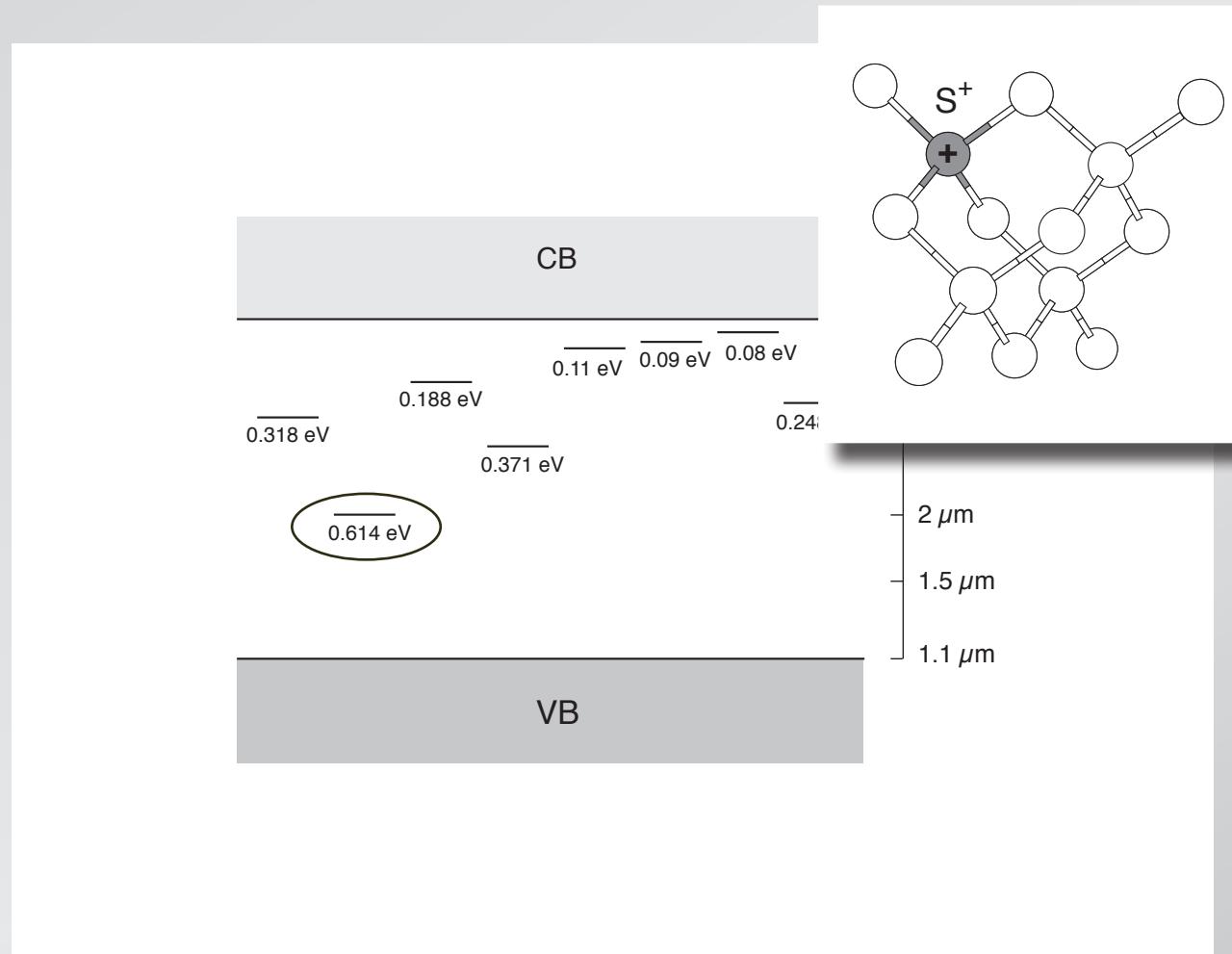
1 part in 10^6 sulfur introduces donor states in gap



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

1 intermediate band

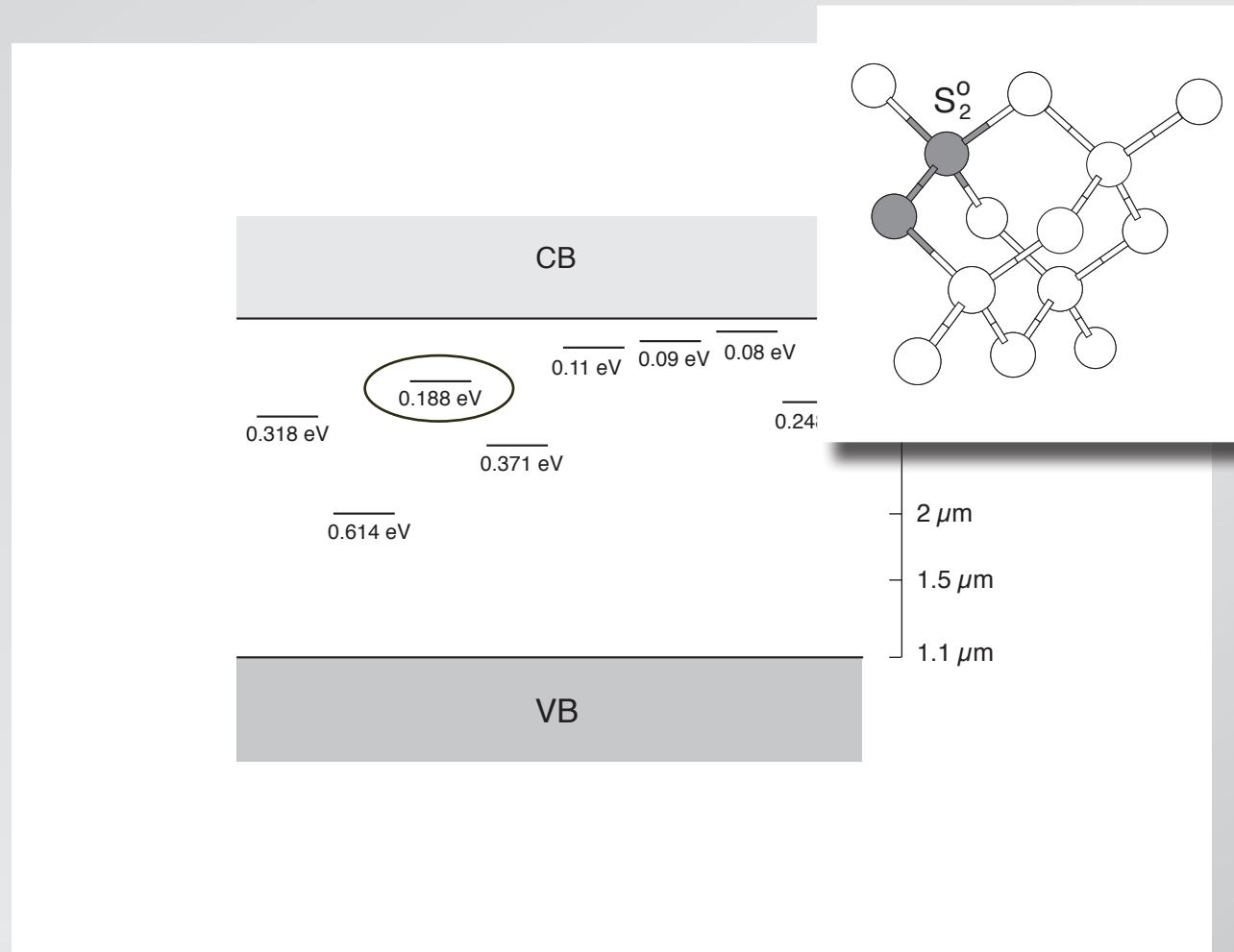
1 part in 10^6 sulfur introduces donor states in gap



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

1 intermediate band

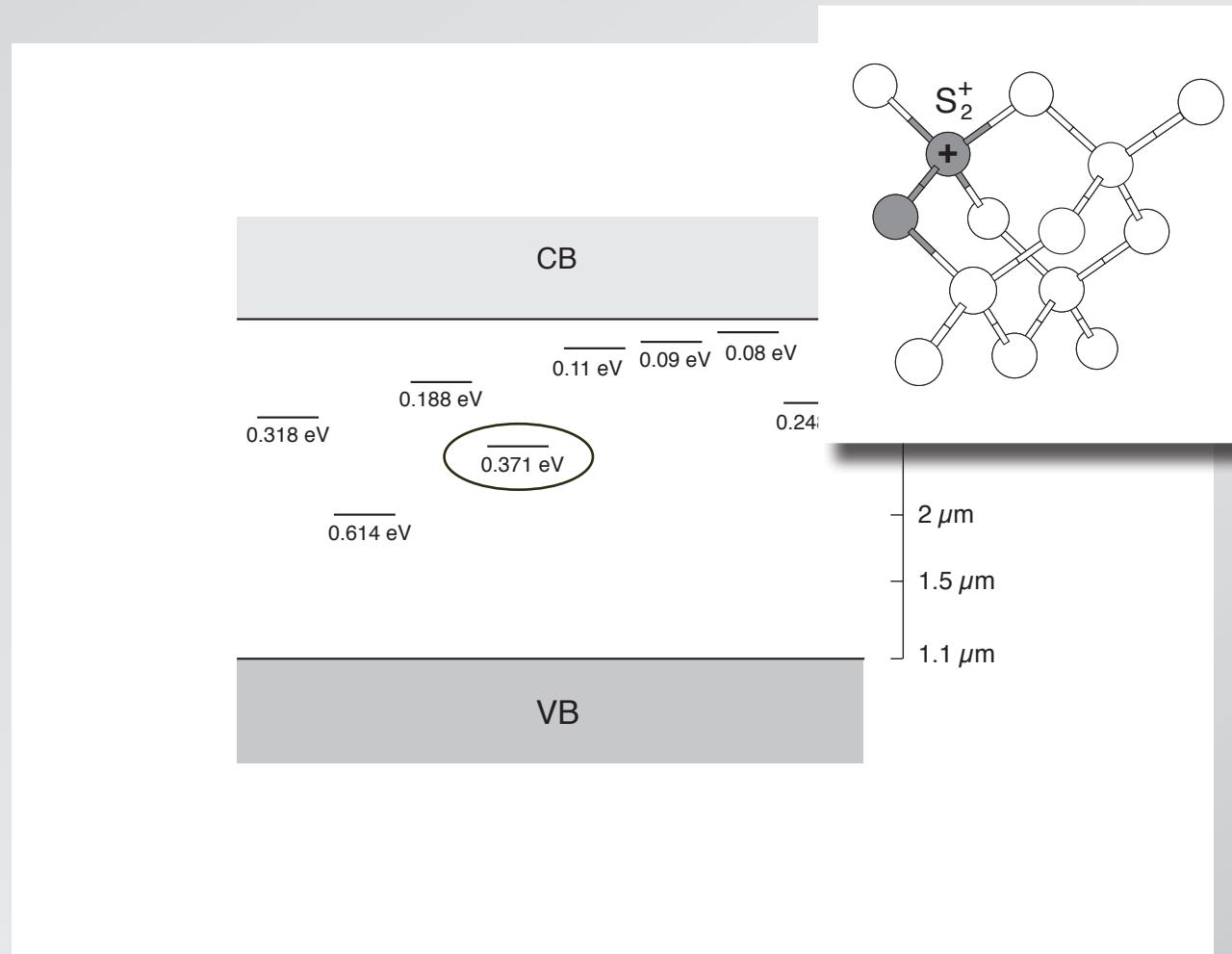
1 part in 10^6 sulfur introduces donor states in gap



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

1 intermediate band

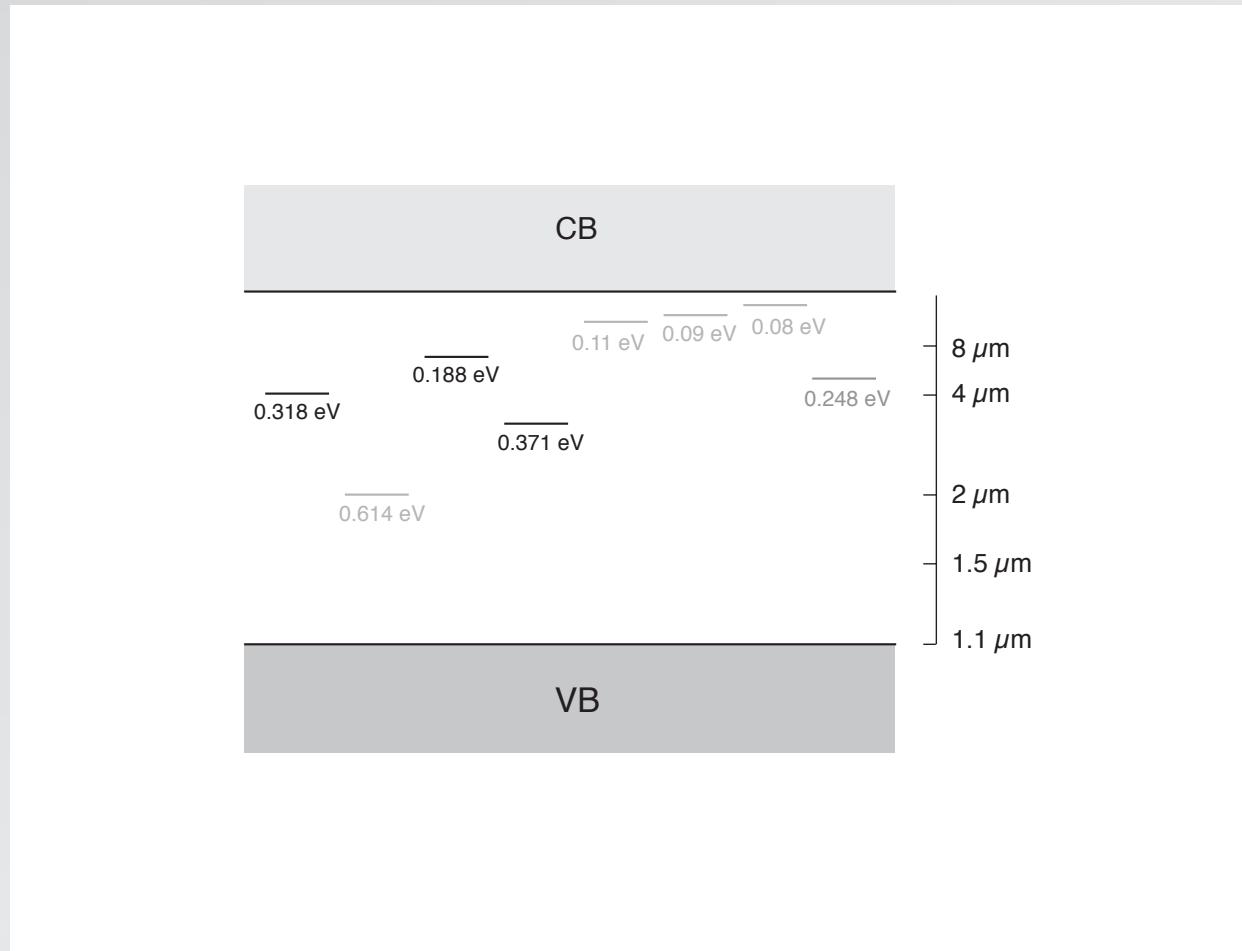
1 part in 10^6 sulfur introduces donor states in gap



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

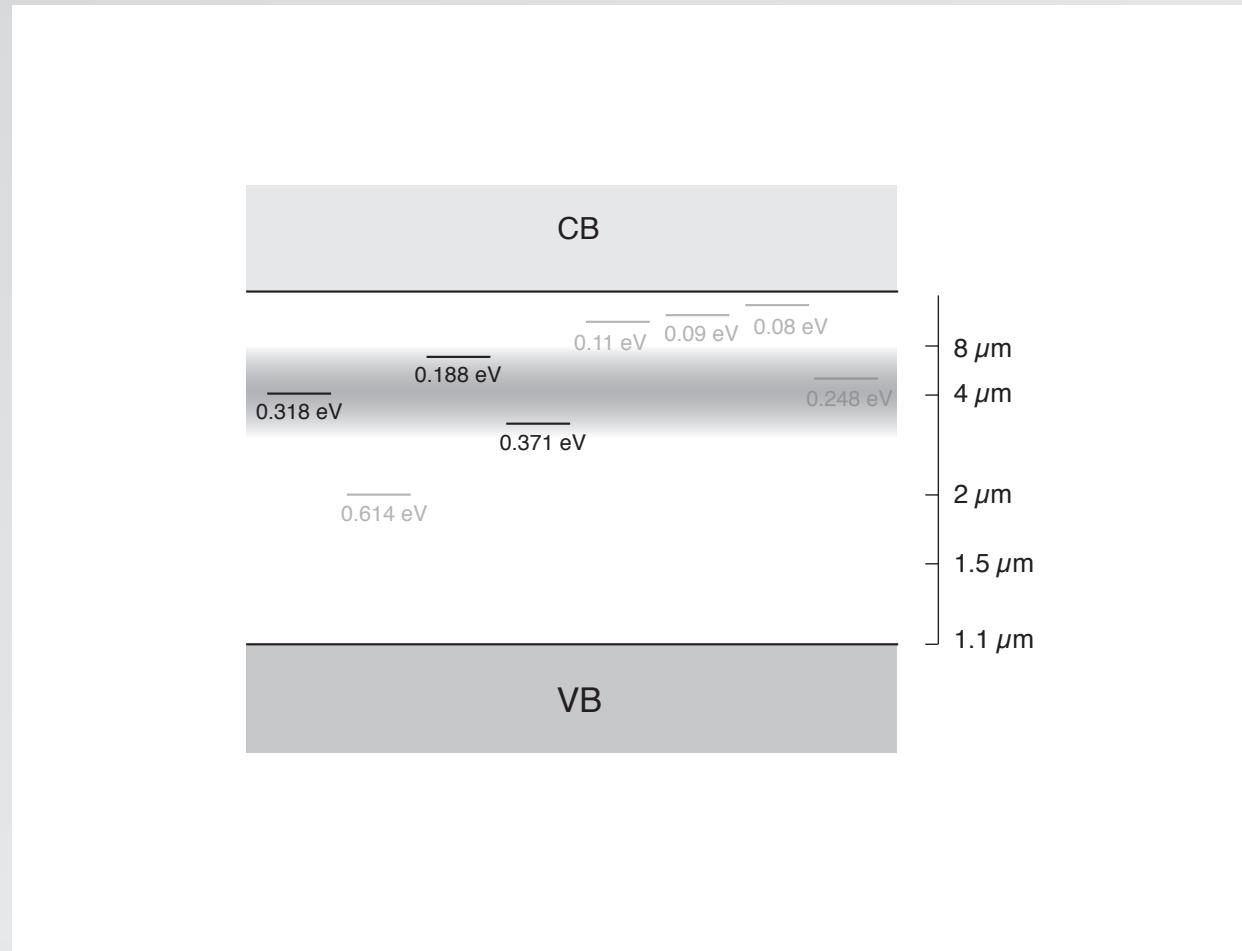
1 intermediate band

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



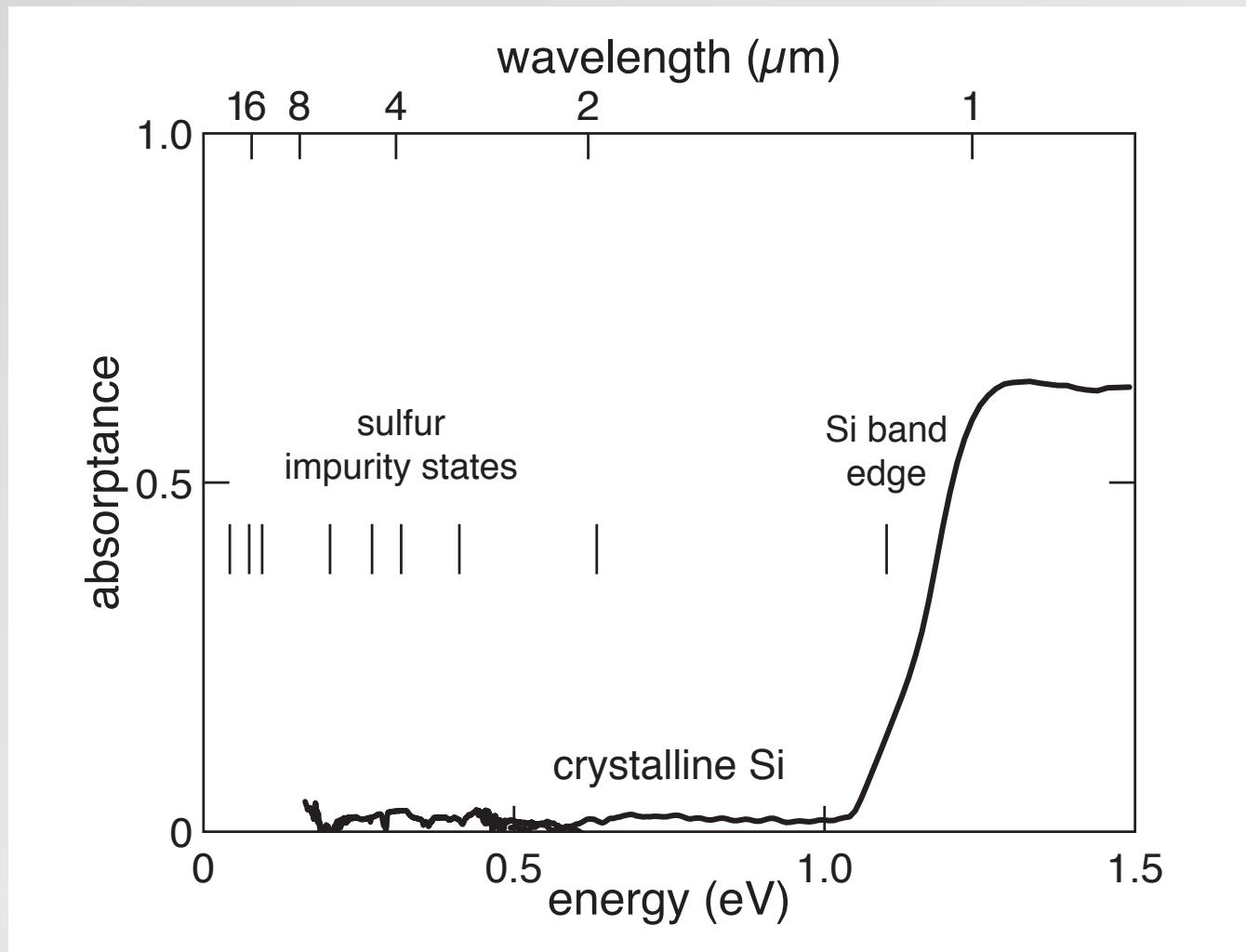
Janzén *et al.*, Phys. Rev. B 29, 1907 (1984)

at high concentration states broaden into band



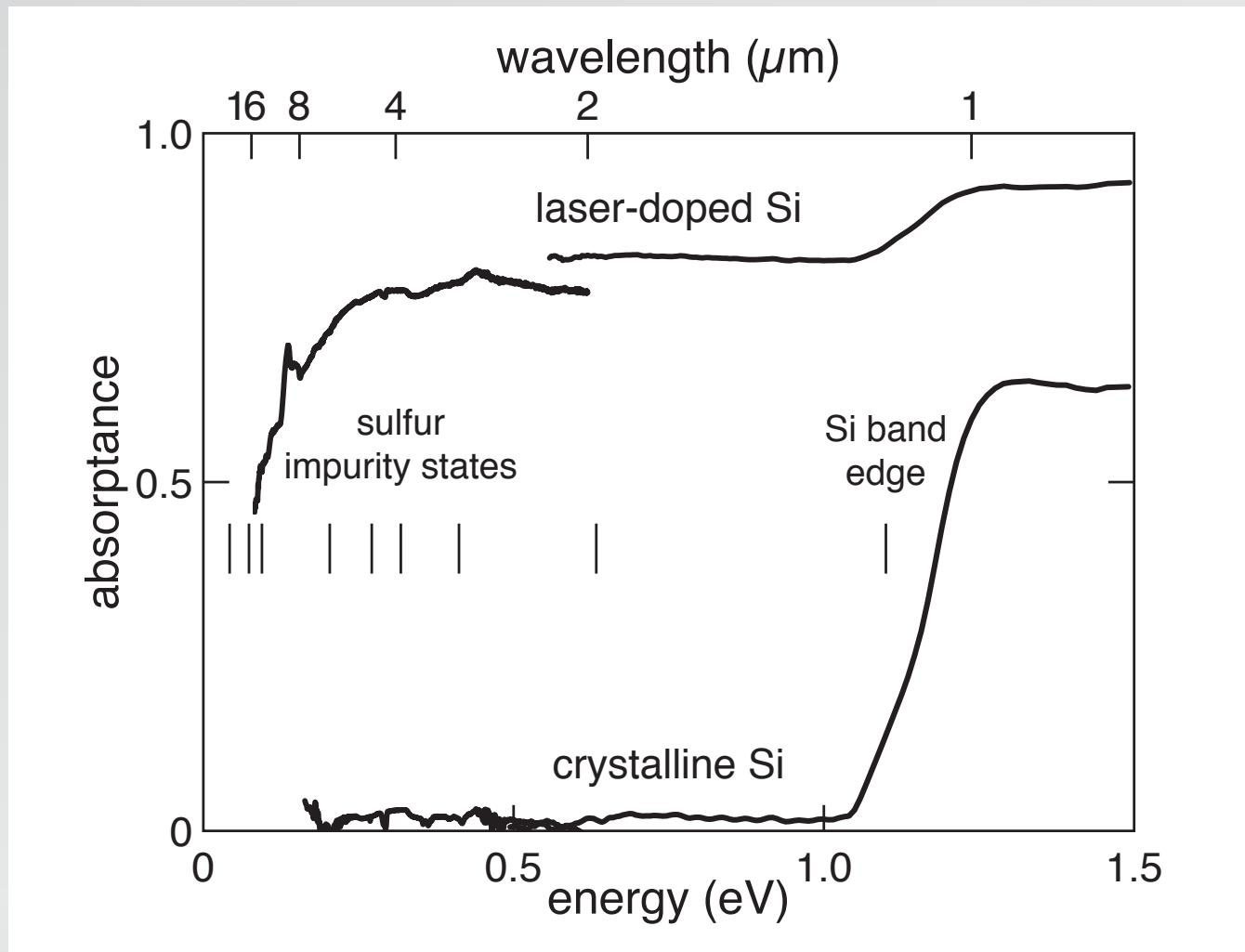
1 intermediate band

10^{-6} sulfur doping



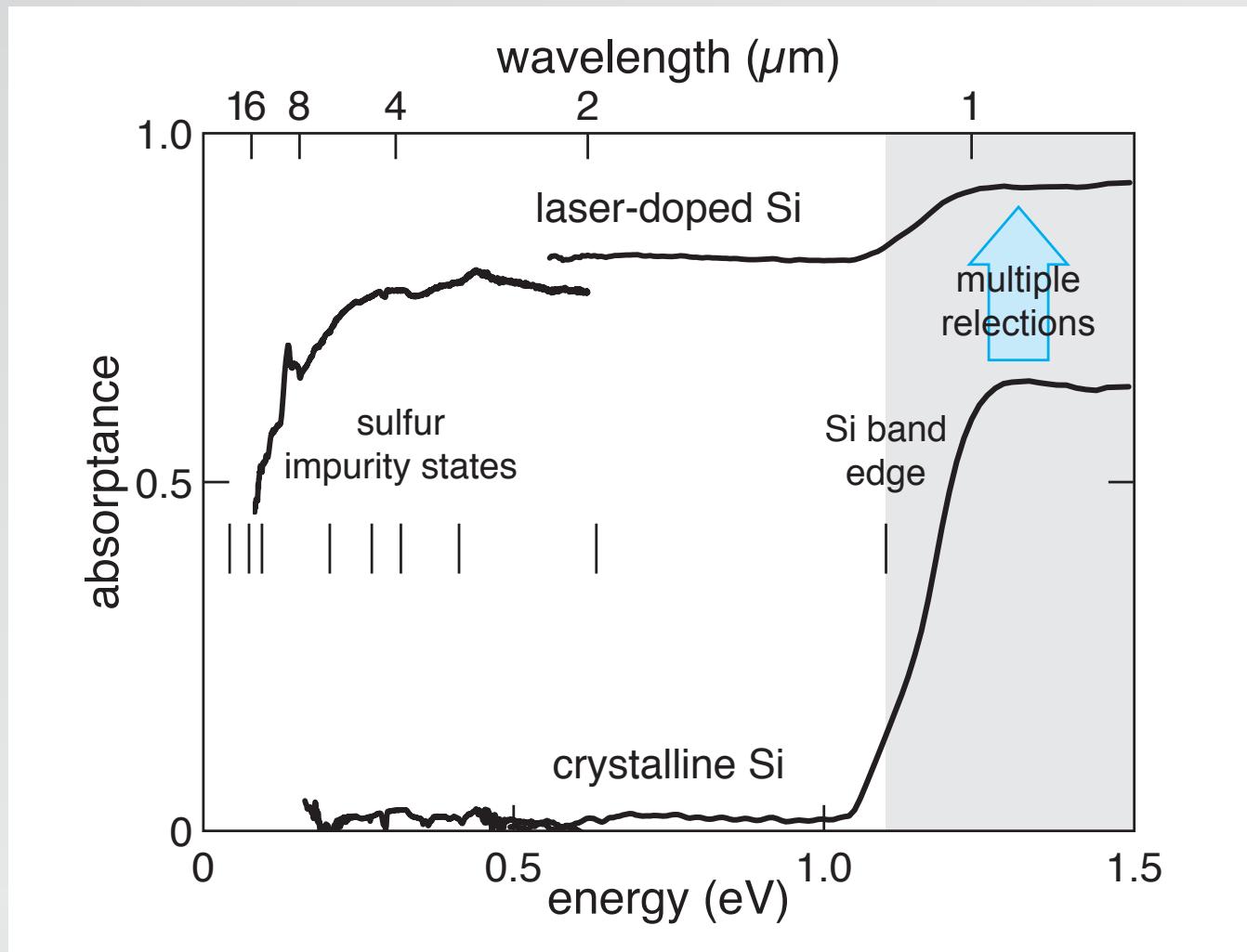
1 intermediate band

laser-doped S:Si



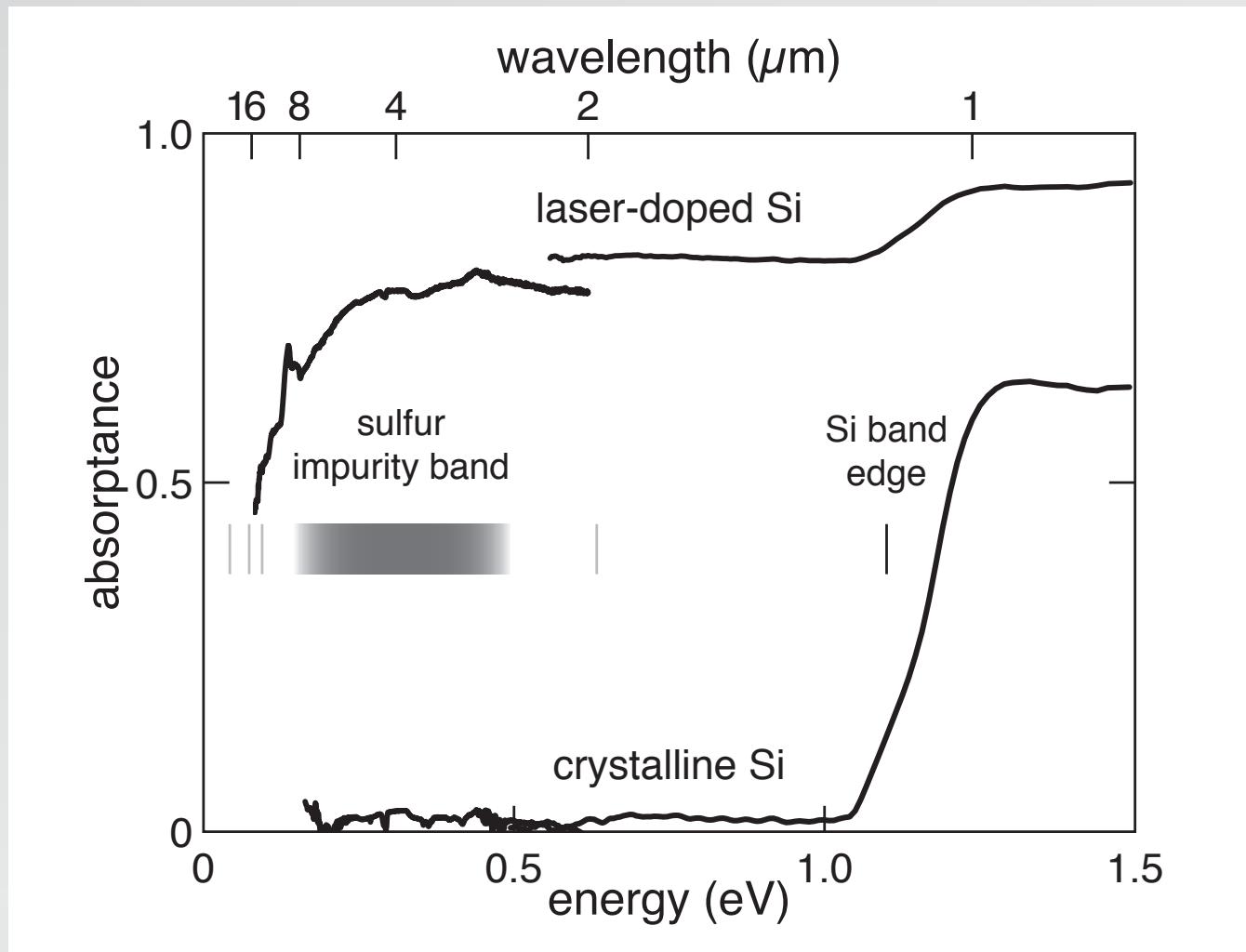
1 intermediate band

laser-doped S:Si



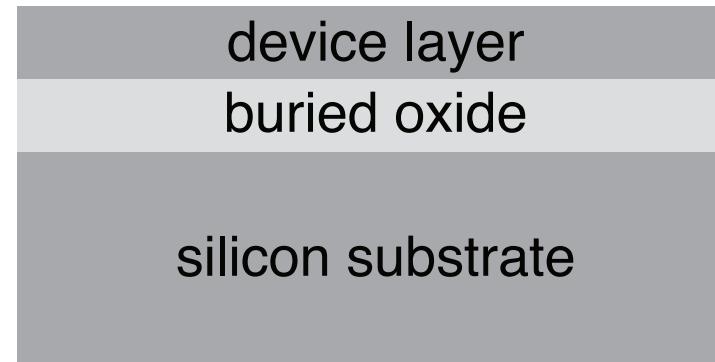
1 intermediate band

laser-doped S:Si



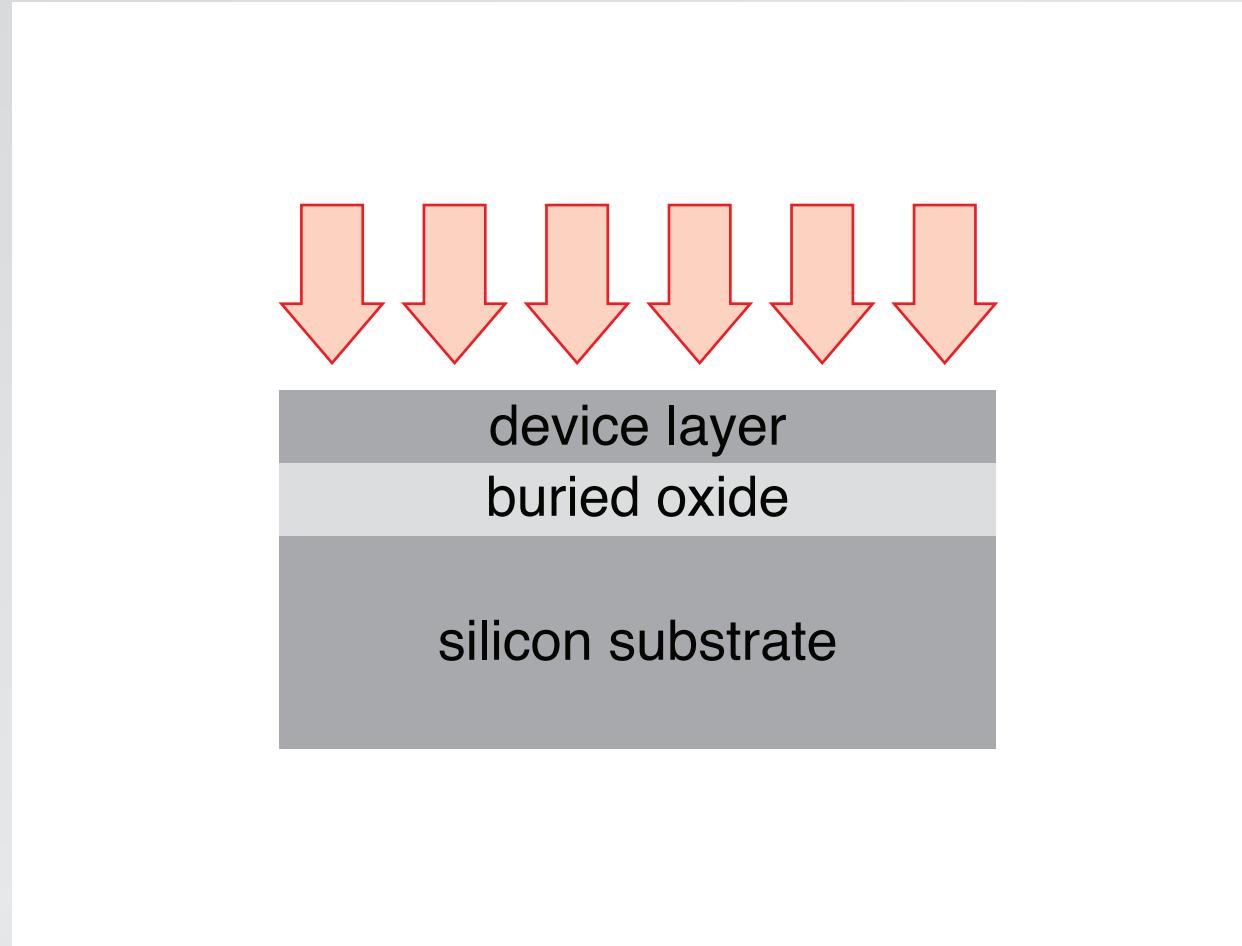
1 intermediate band

isolate surface layer for Hall measurements



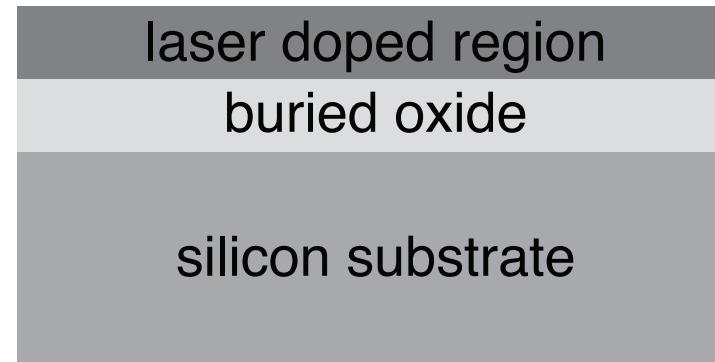
1 intermediate band

isolate surface layer for Hall measurements



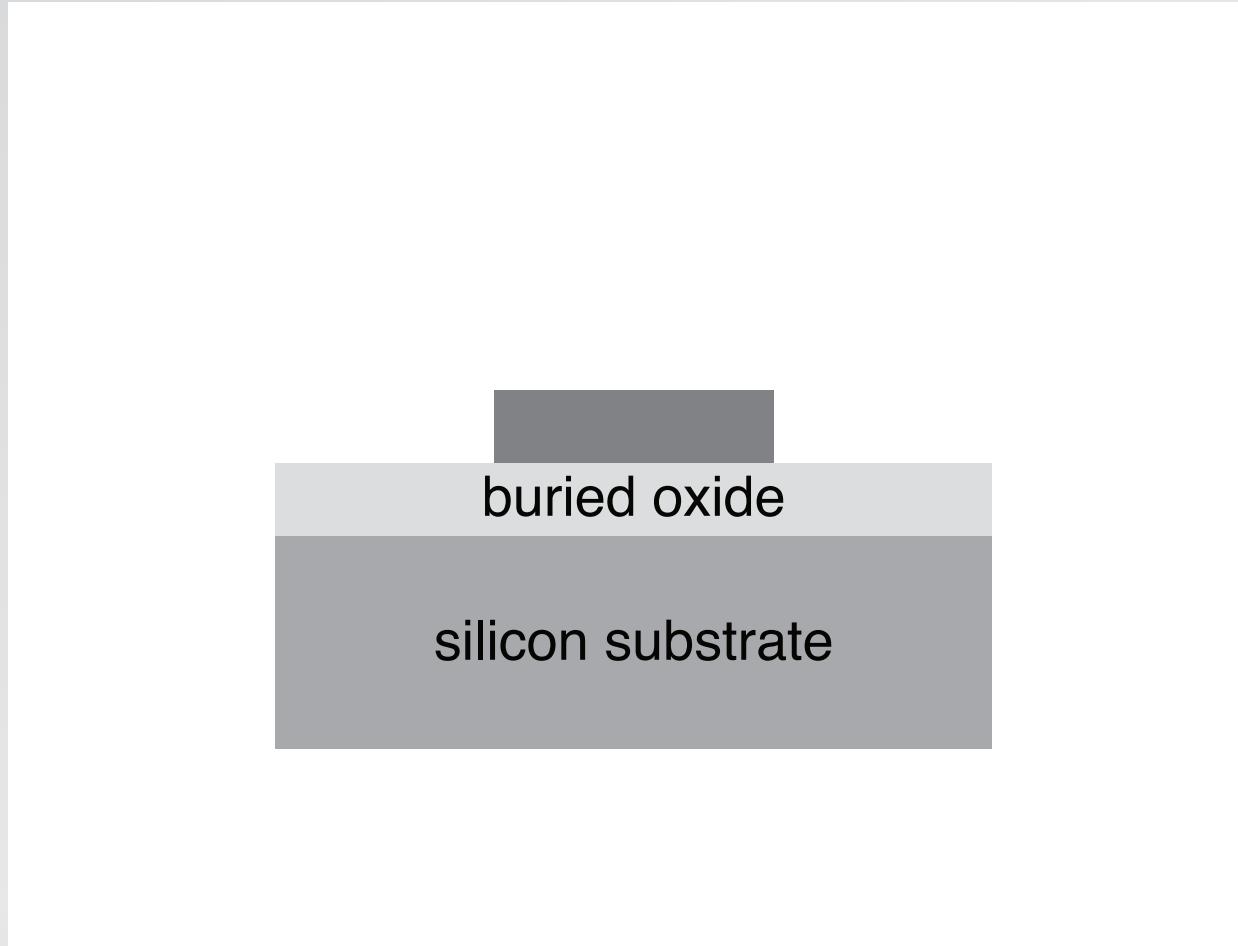
1 intermediate band

isolate surface layer for Hall measurements



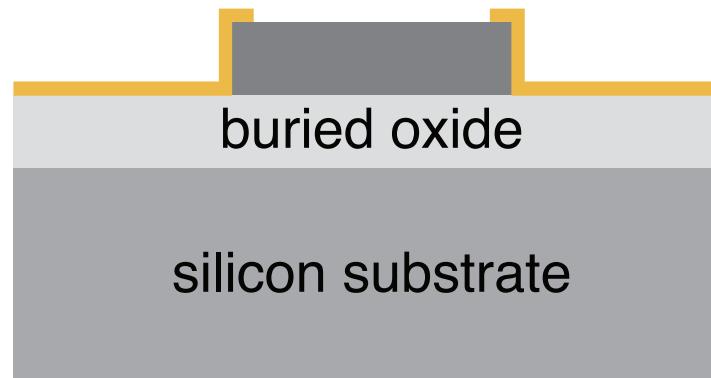
1 intermediate band

isolate surface layer for Hall measurements

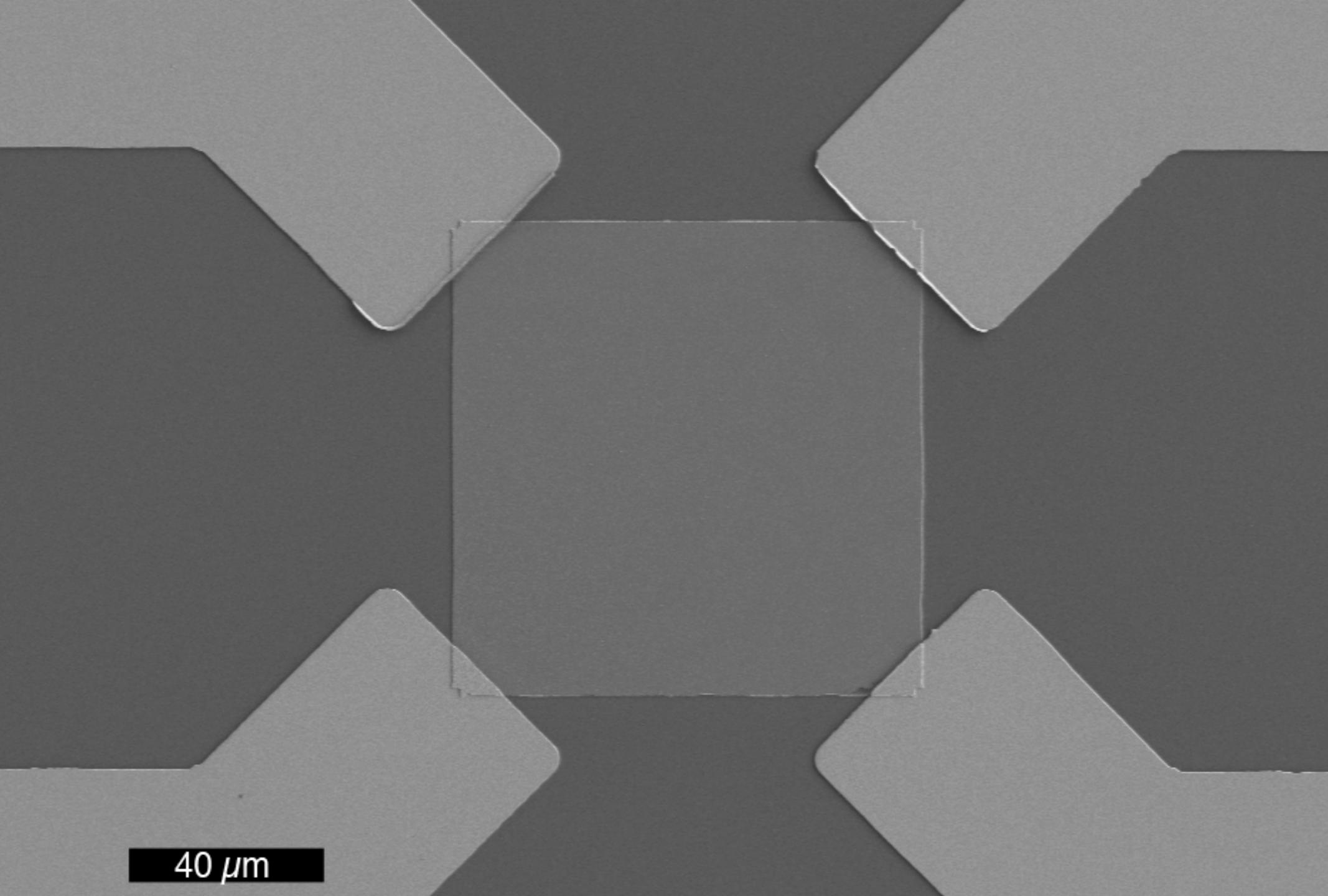


1 intermediate band

isolate surface layer for Hall measurements



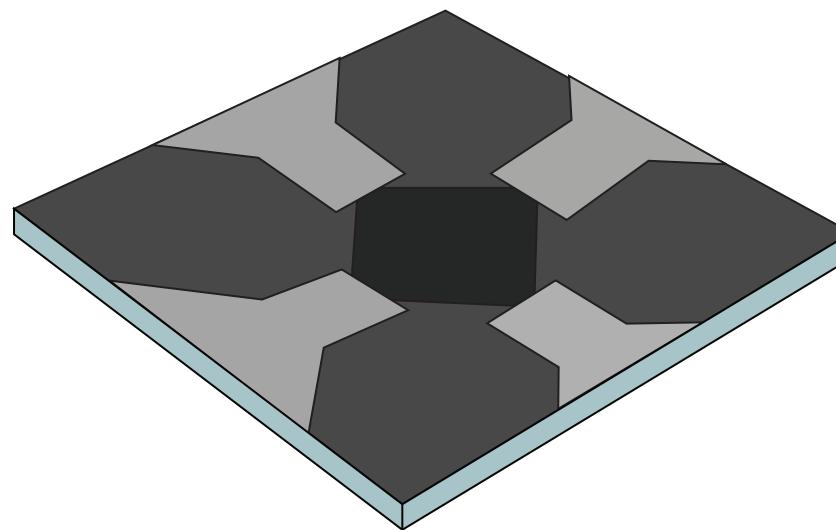
1 intermediate band



40 μm

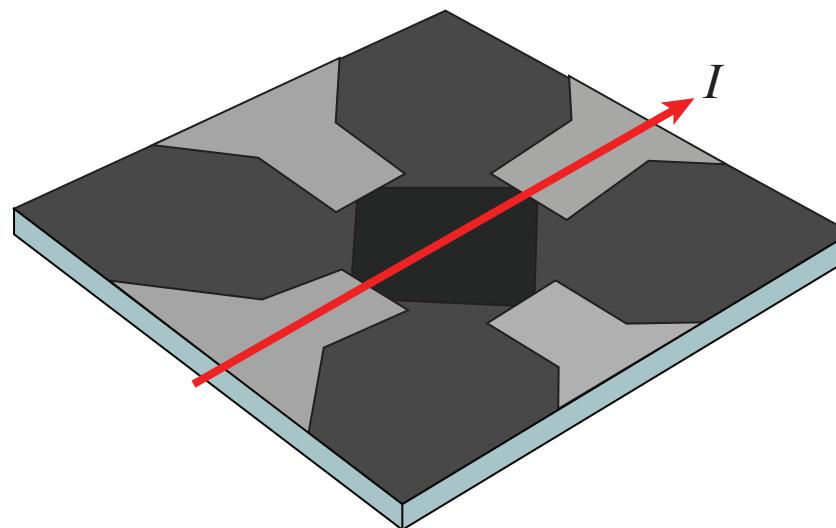
① intermediate band

Hall measurements



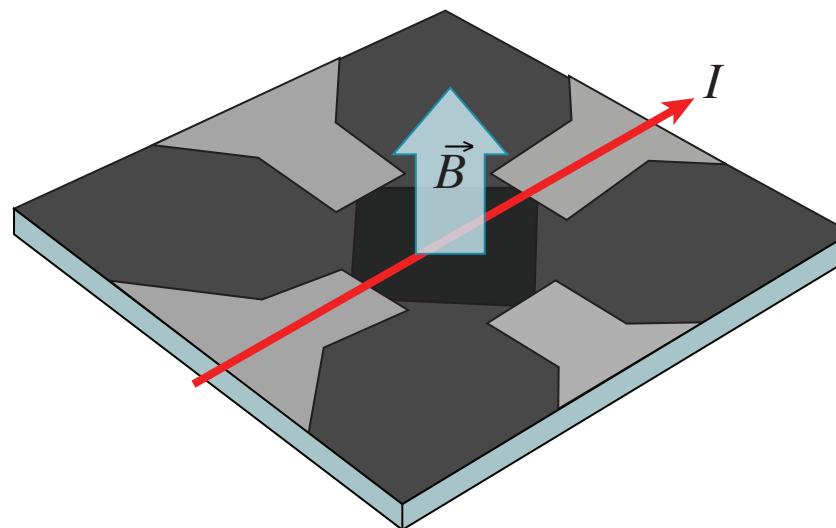
1 intermediate band

Hall measurements



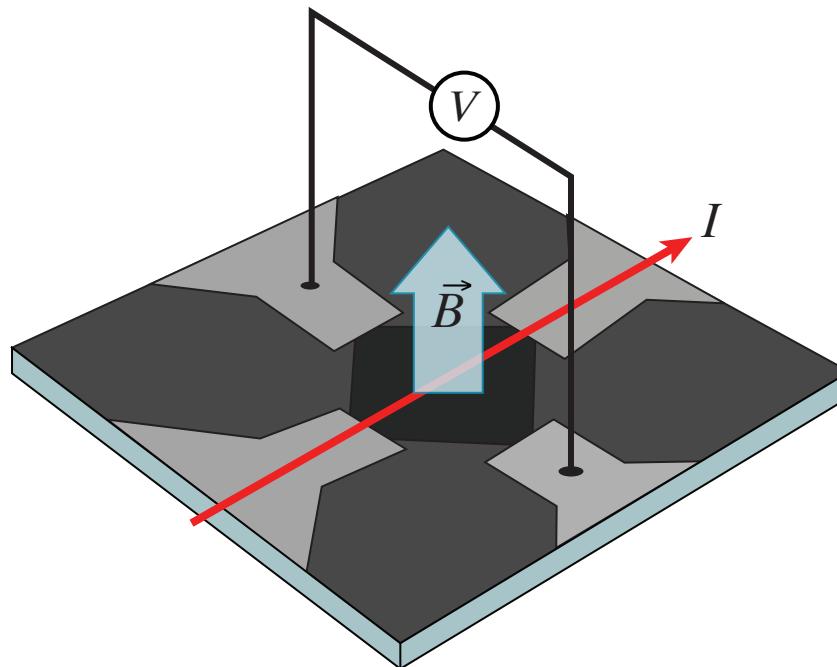
1 intermediate band

Hall measurements



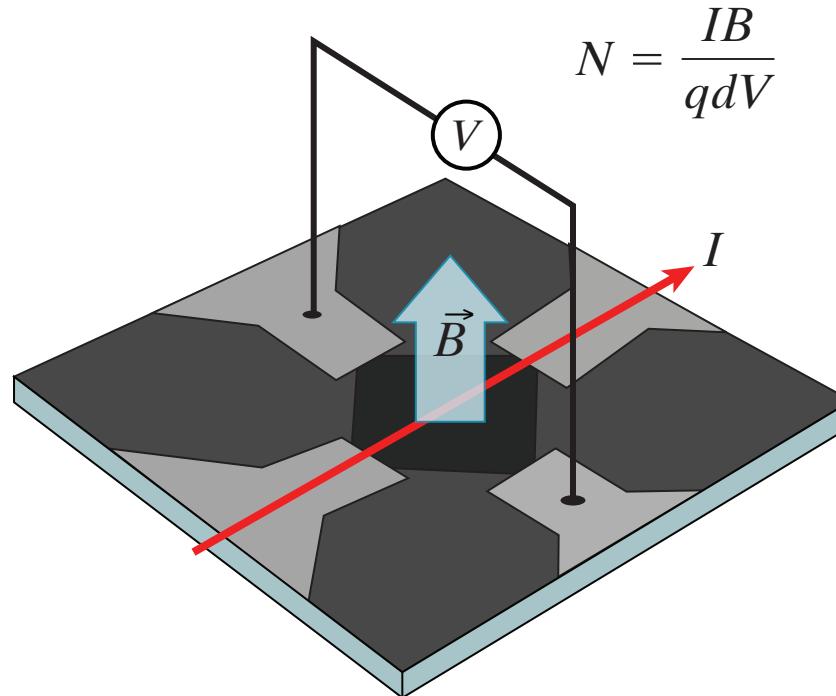
1 intermediate band

Hall measurements



1 intermediate band

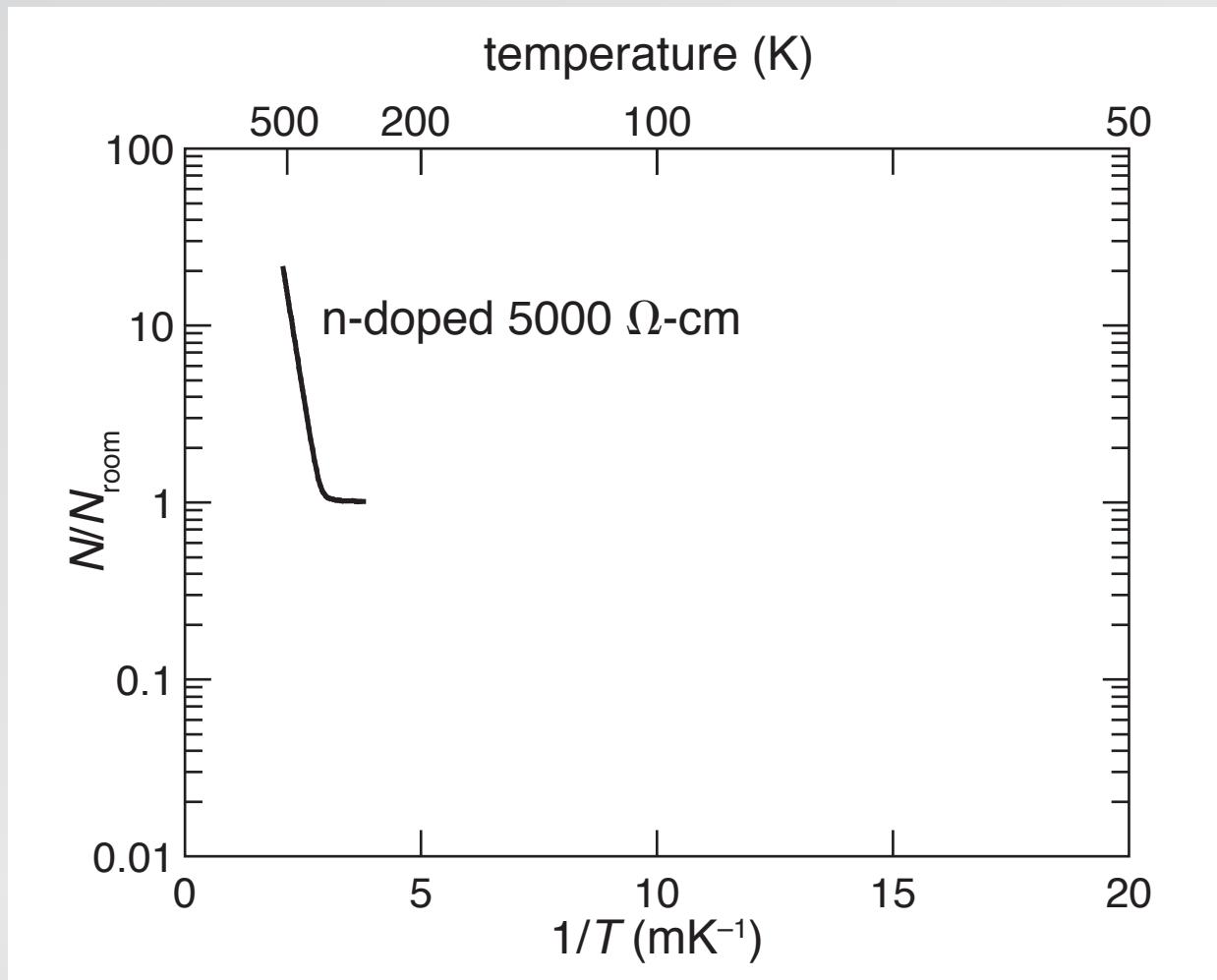
Hall measurements



$$N = \frac{IB}{qdV}$$

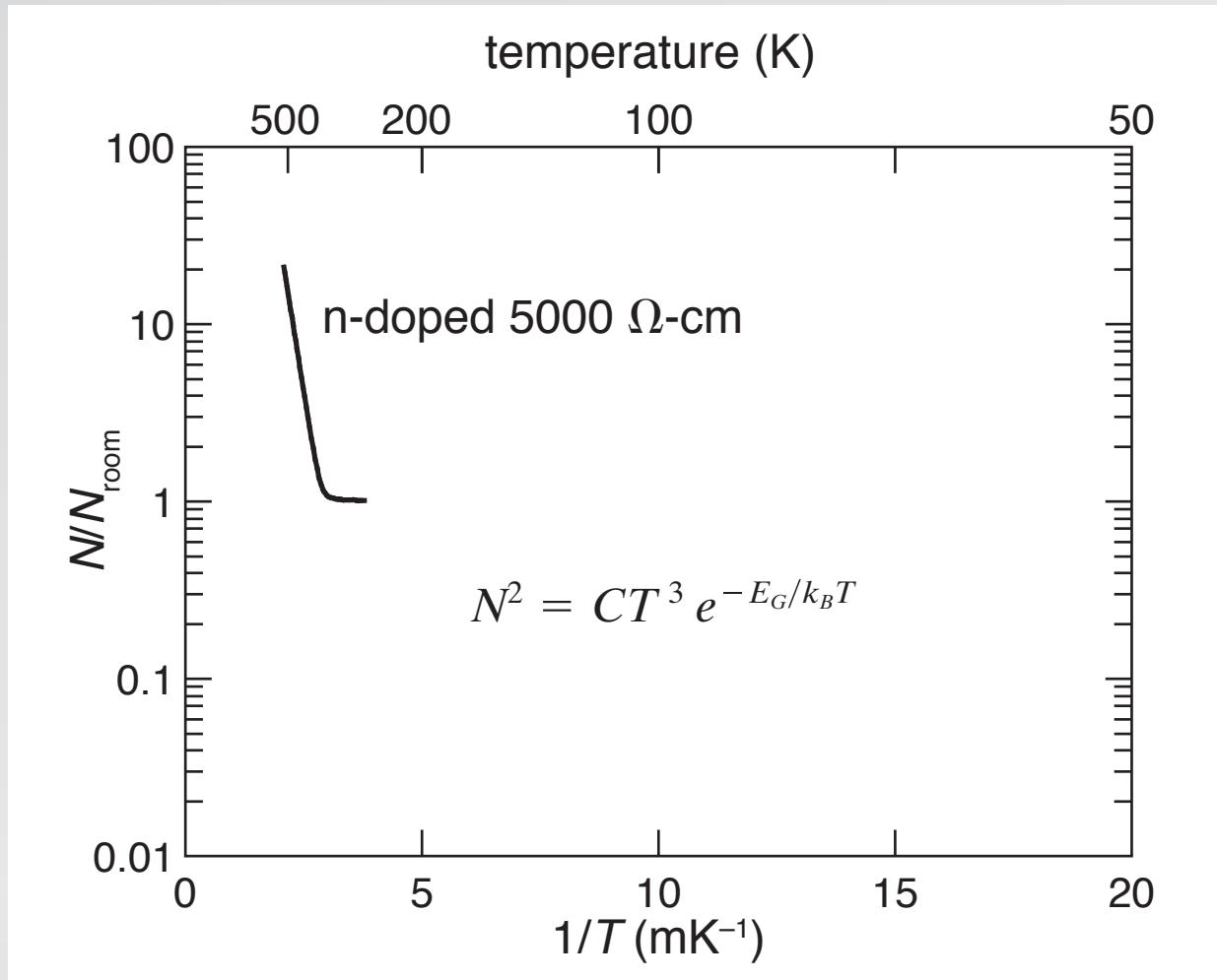
1 intermediate band

Hall measurements



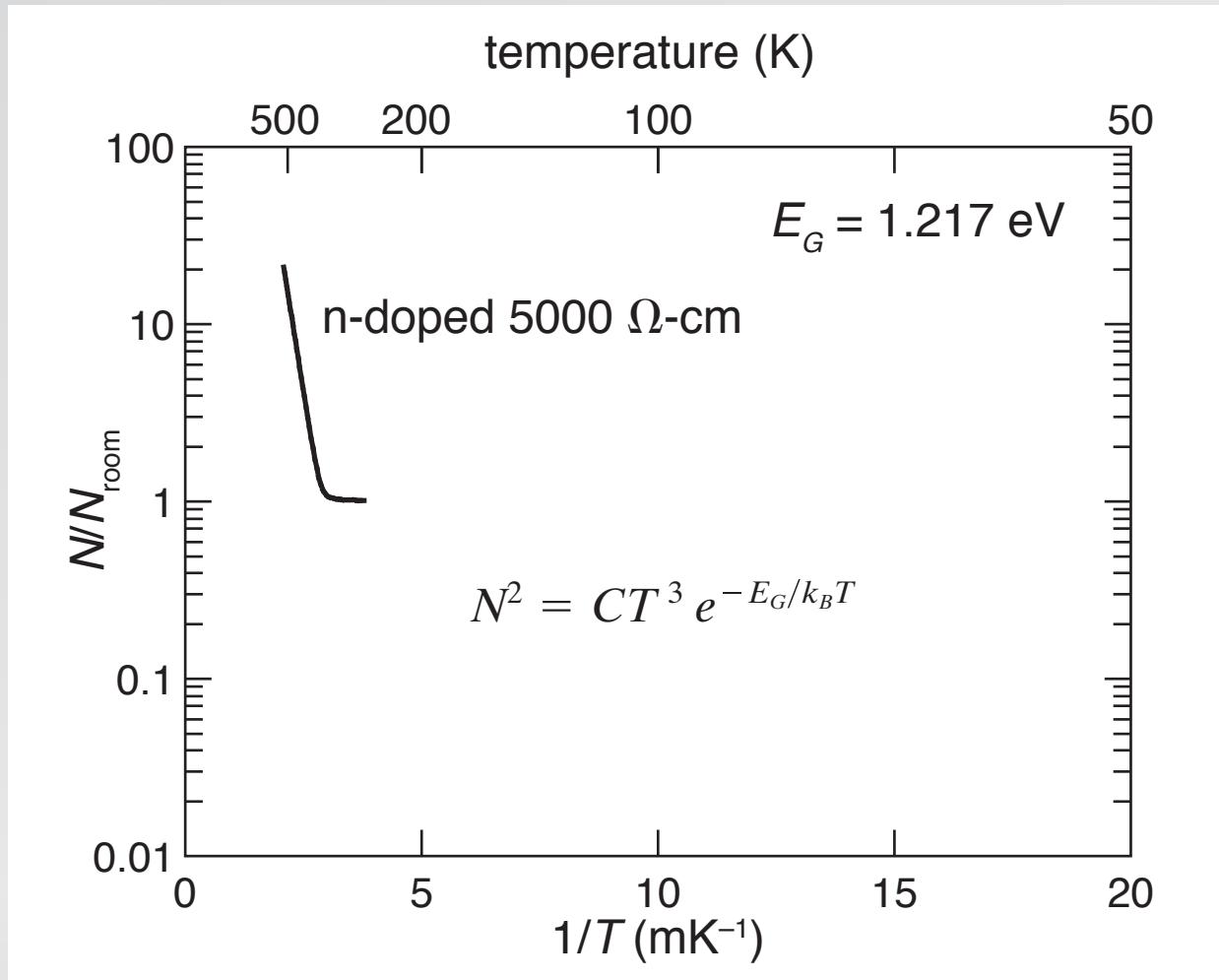
1 intermediate band

Hall measurements



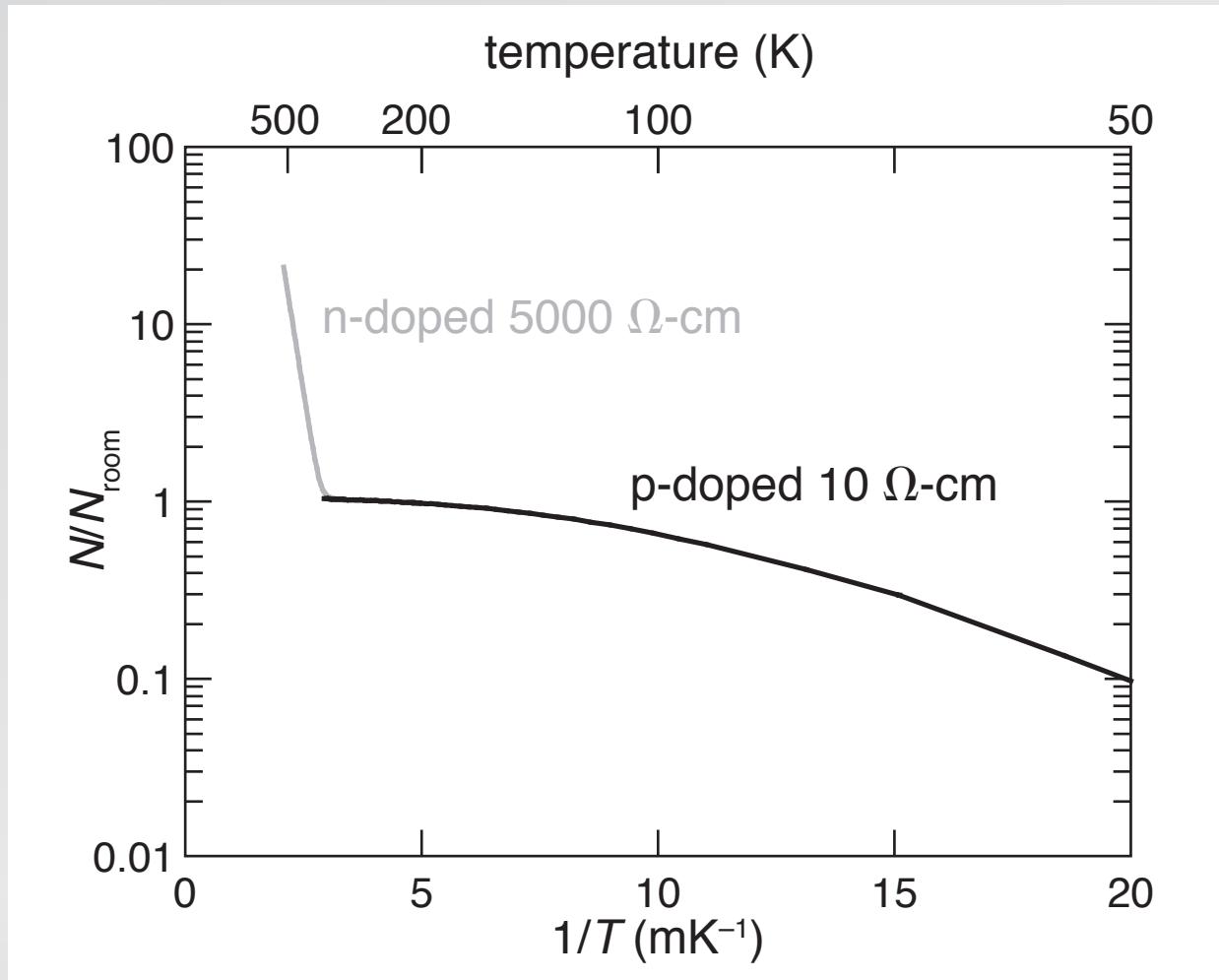
1 intermediate band

Hall measurements



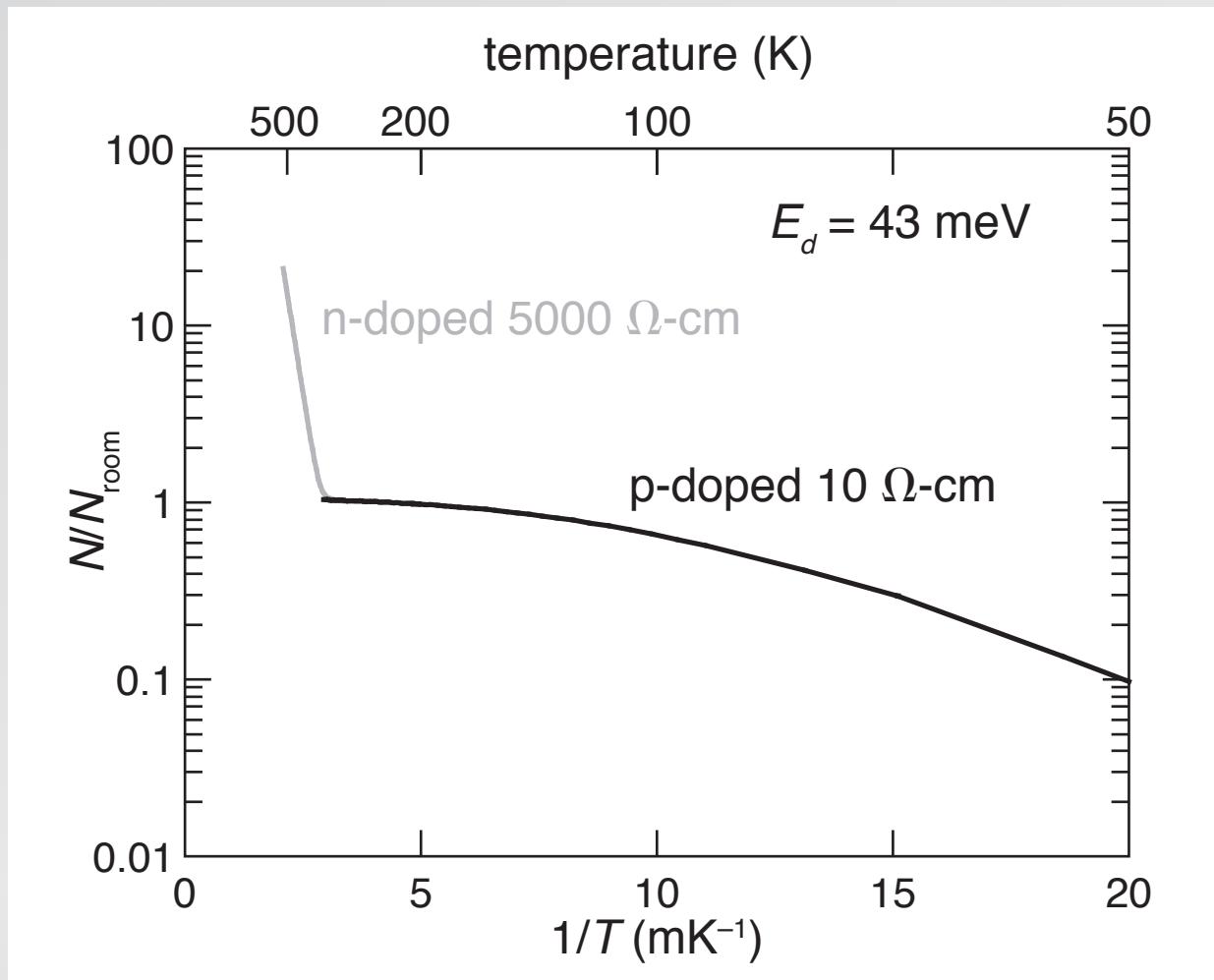
1 intermediate band

Hall measurements



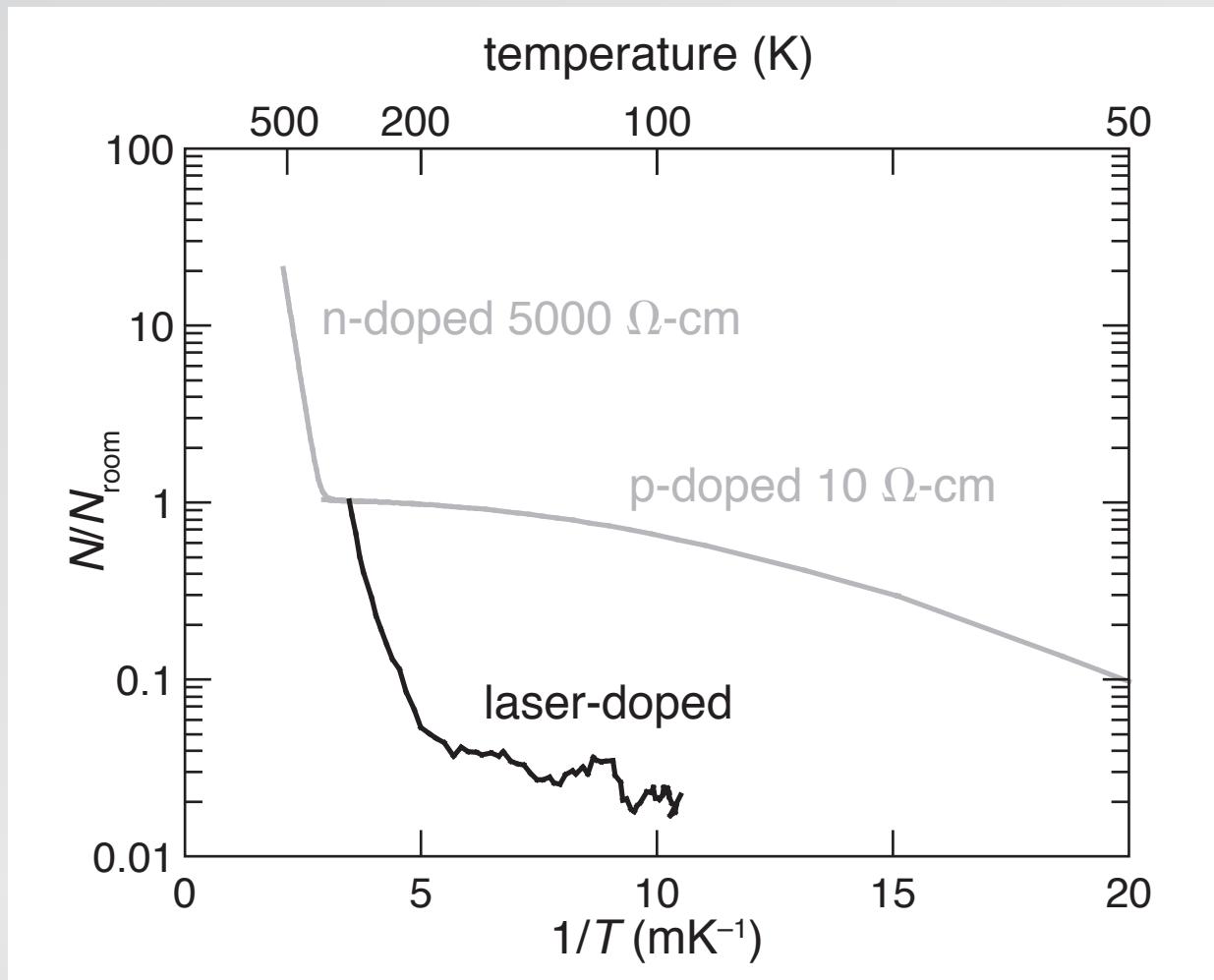
1 intermediate band

Hall measurements



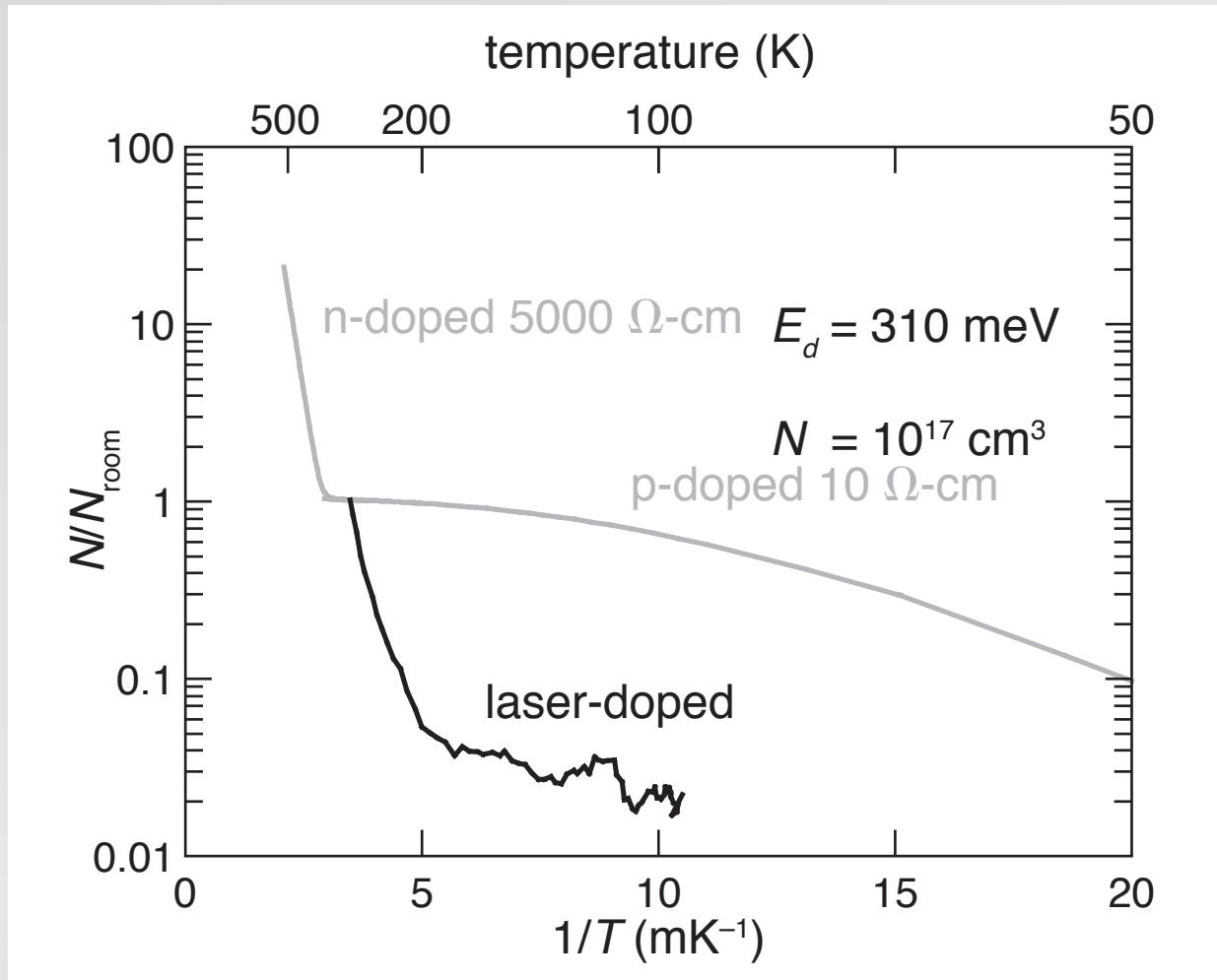
1 intermediate band

Hall measurements

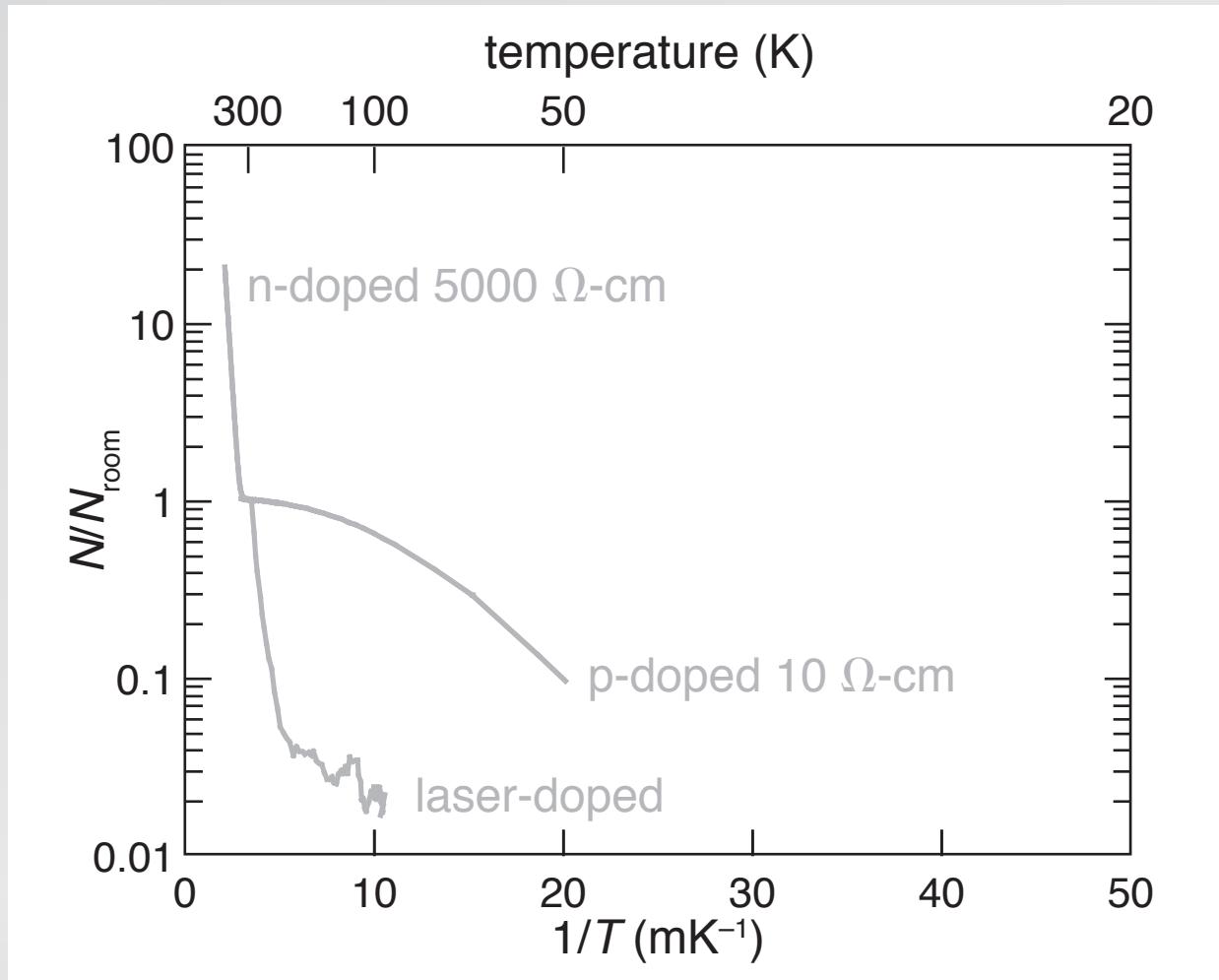


1 intermediate band

Hall measurements

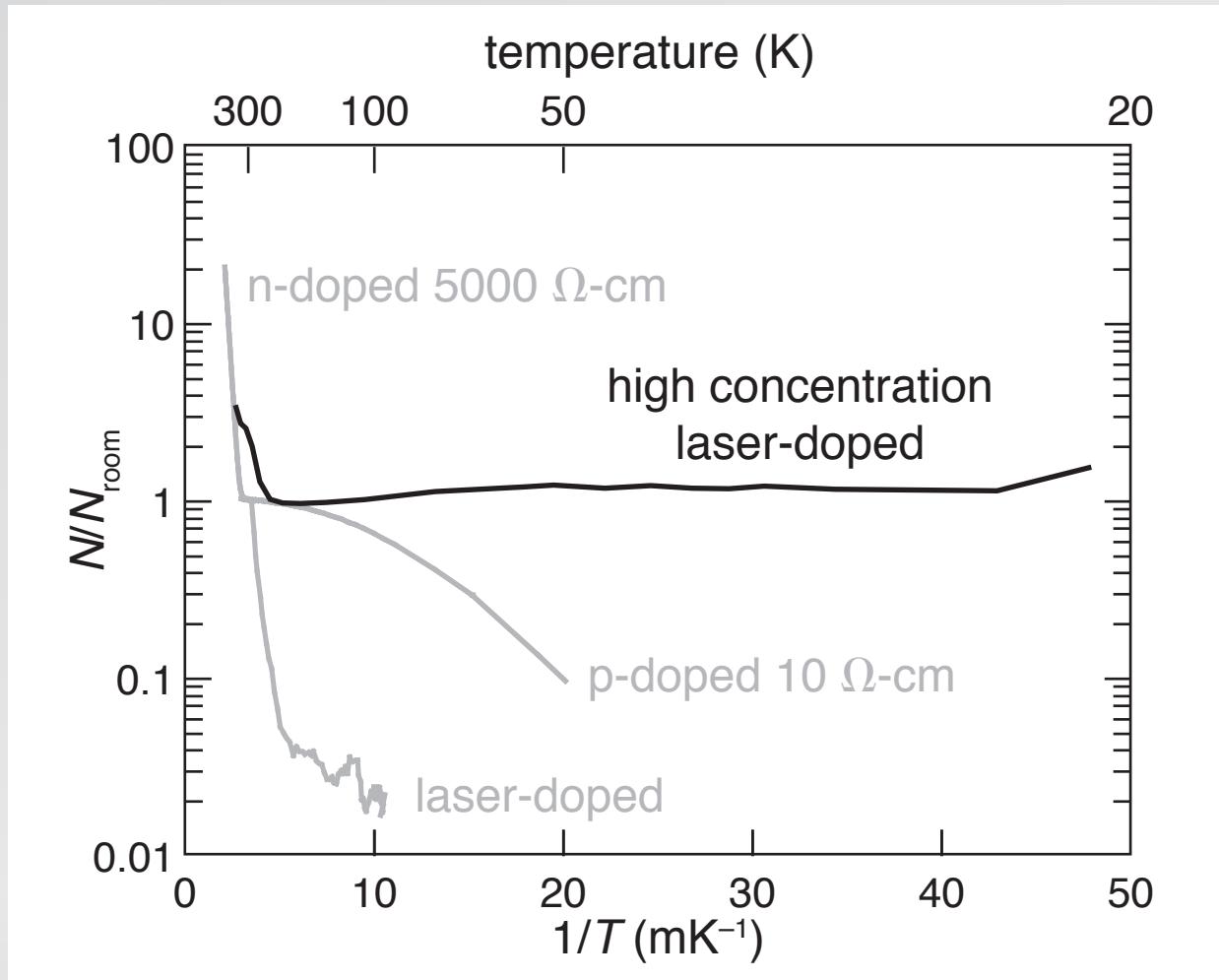


Hall measurements



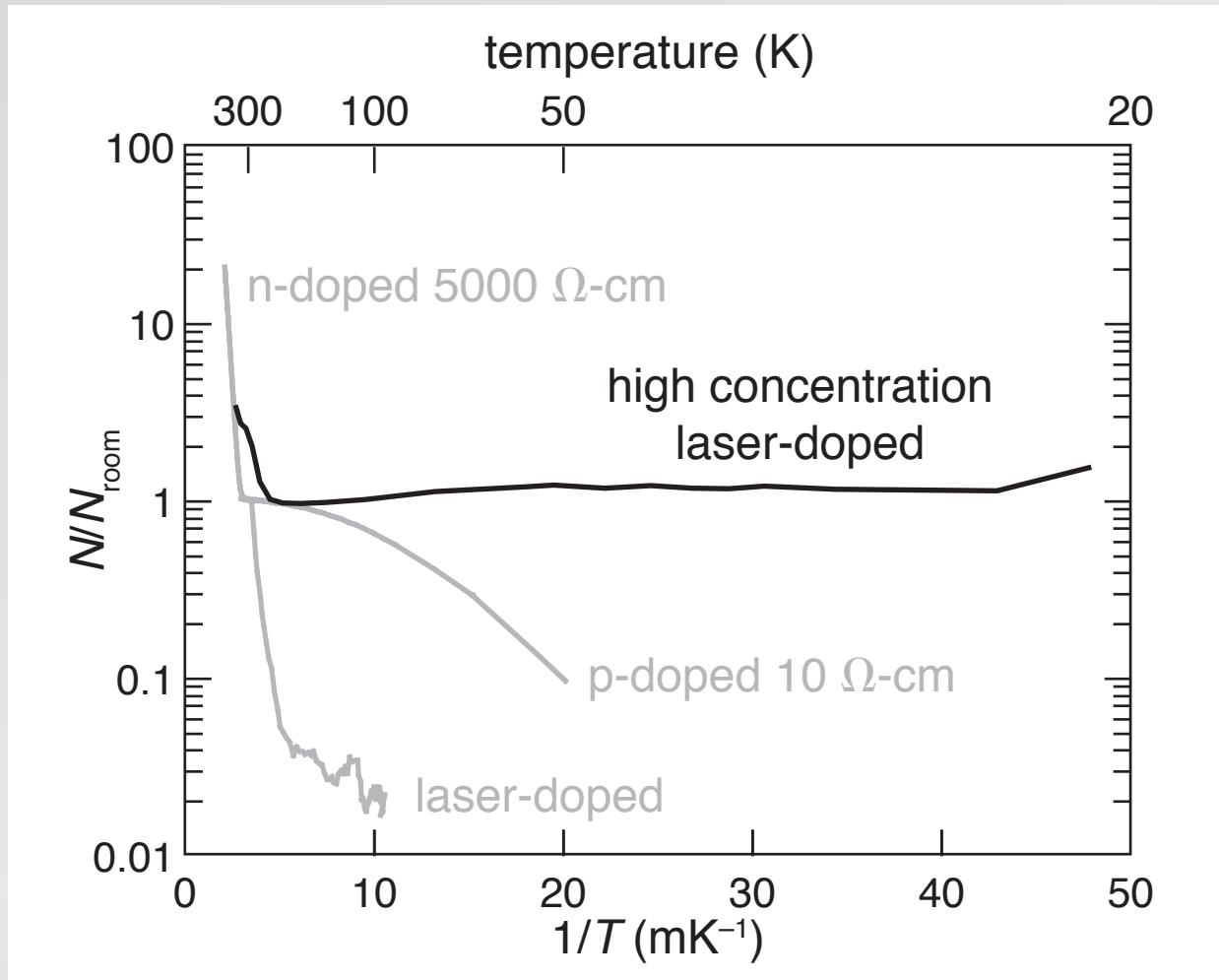
1 intermediate band

Hall measurements



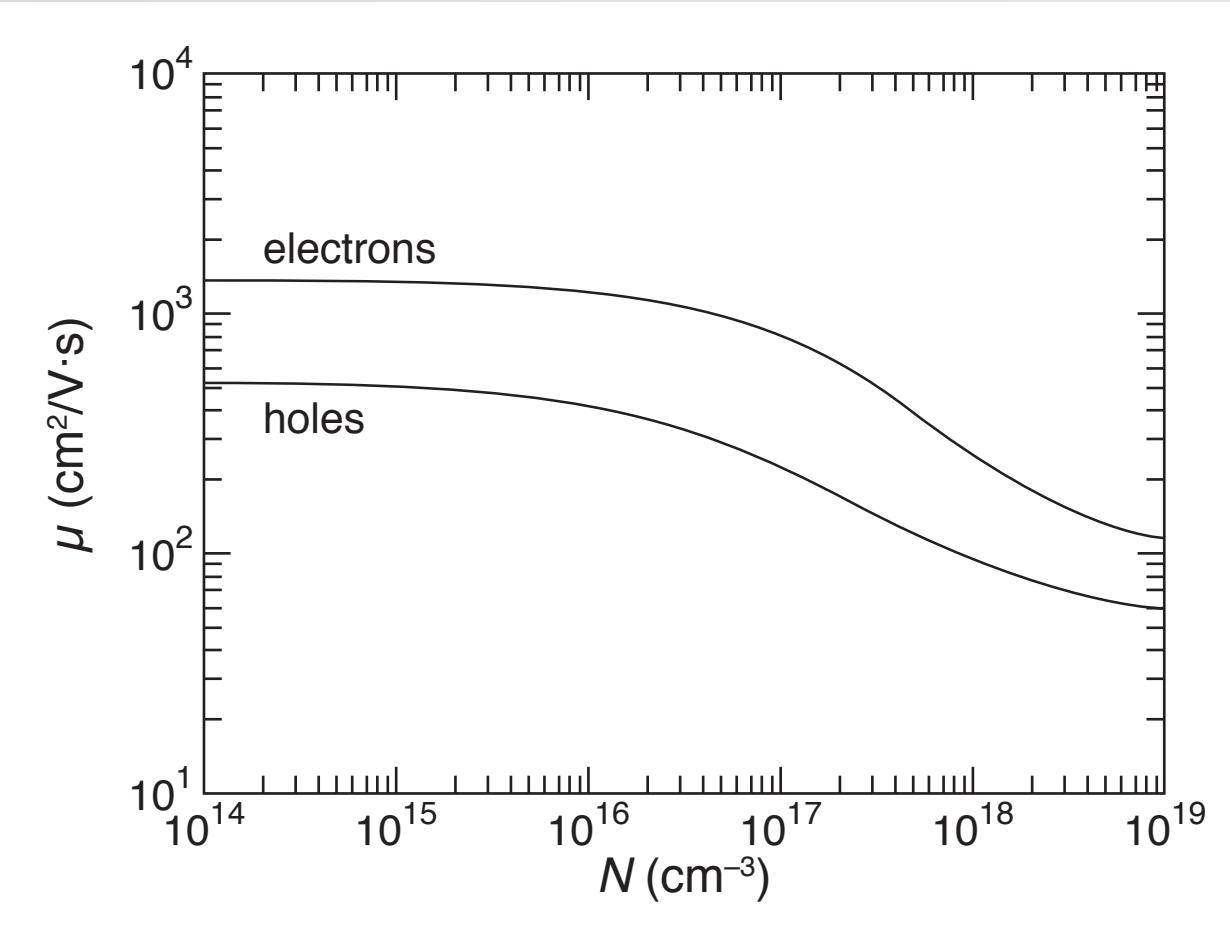
1 intermediate band

Hall measurements



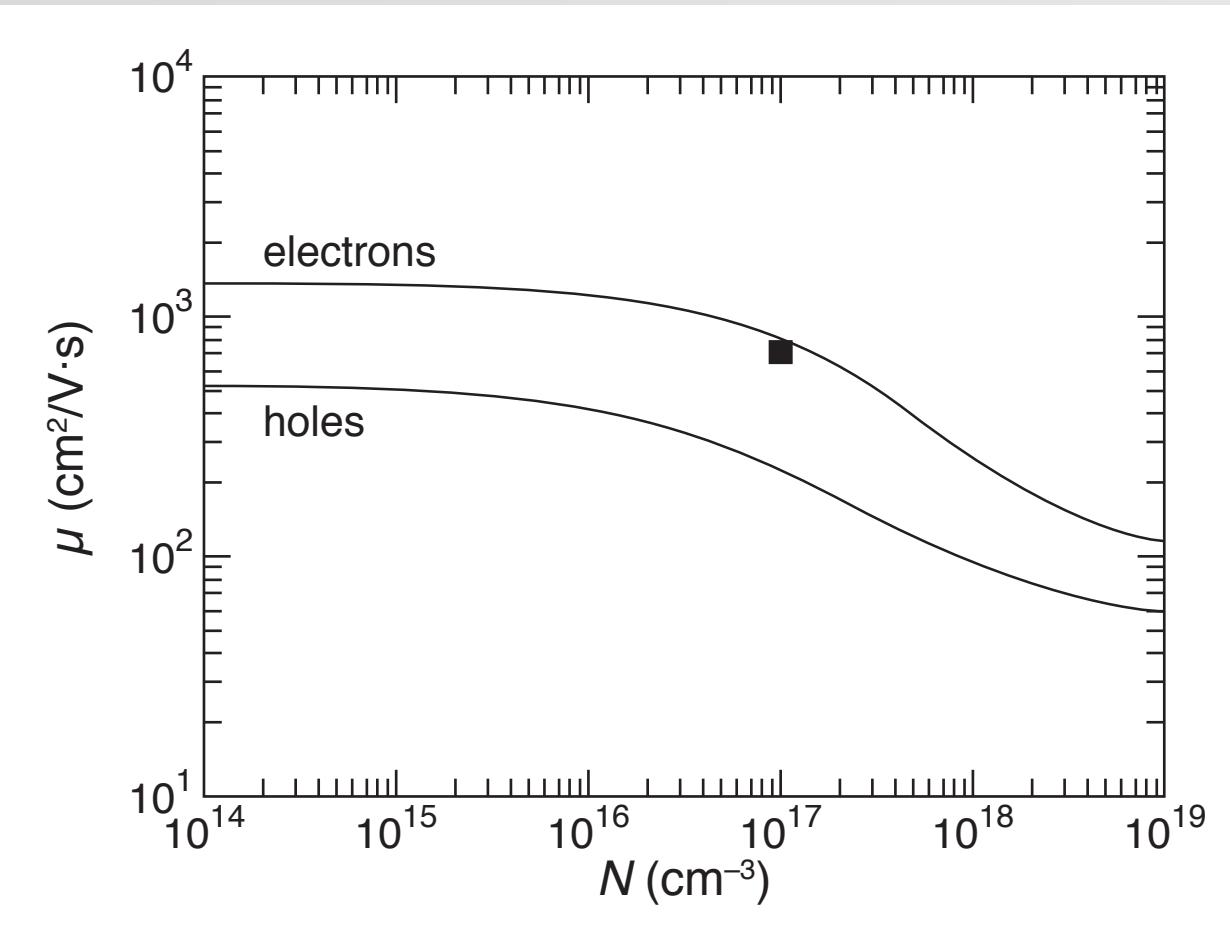
1 intermediate band

majority carrier mobility



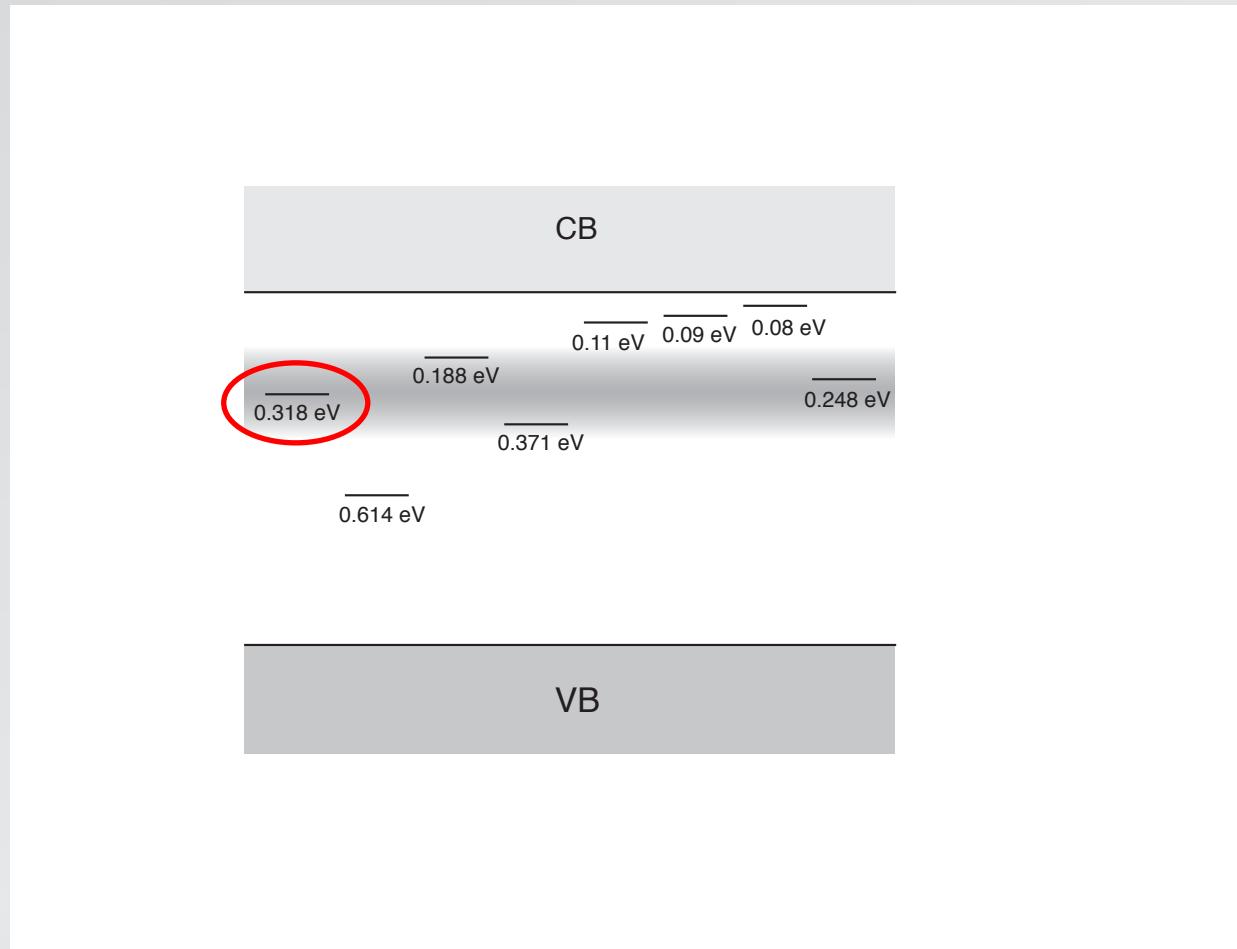
Caughey et al., Proc. IEEE 55, 2192 (1967)

majority carrier mobility



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

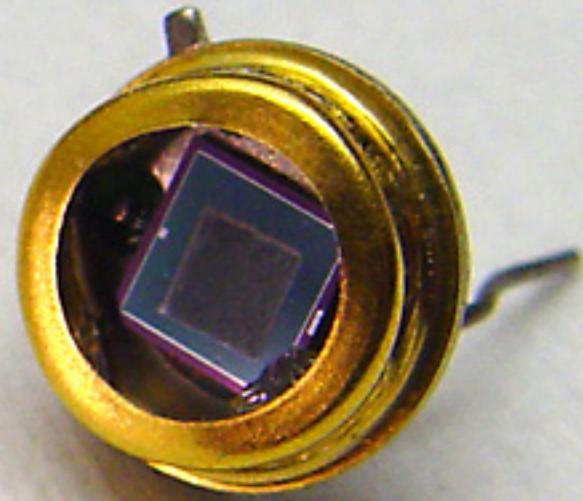
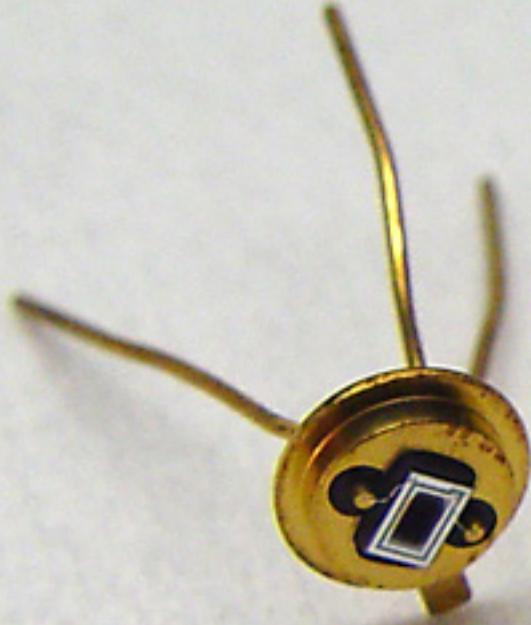
impurity (donor) band centered at 310 meV



1 intermediate band

Things to keep in mind

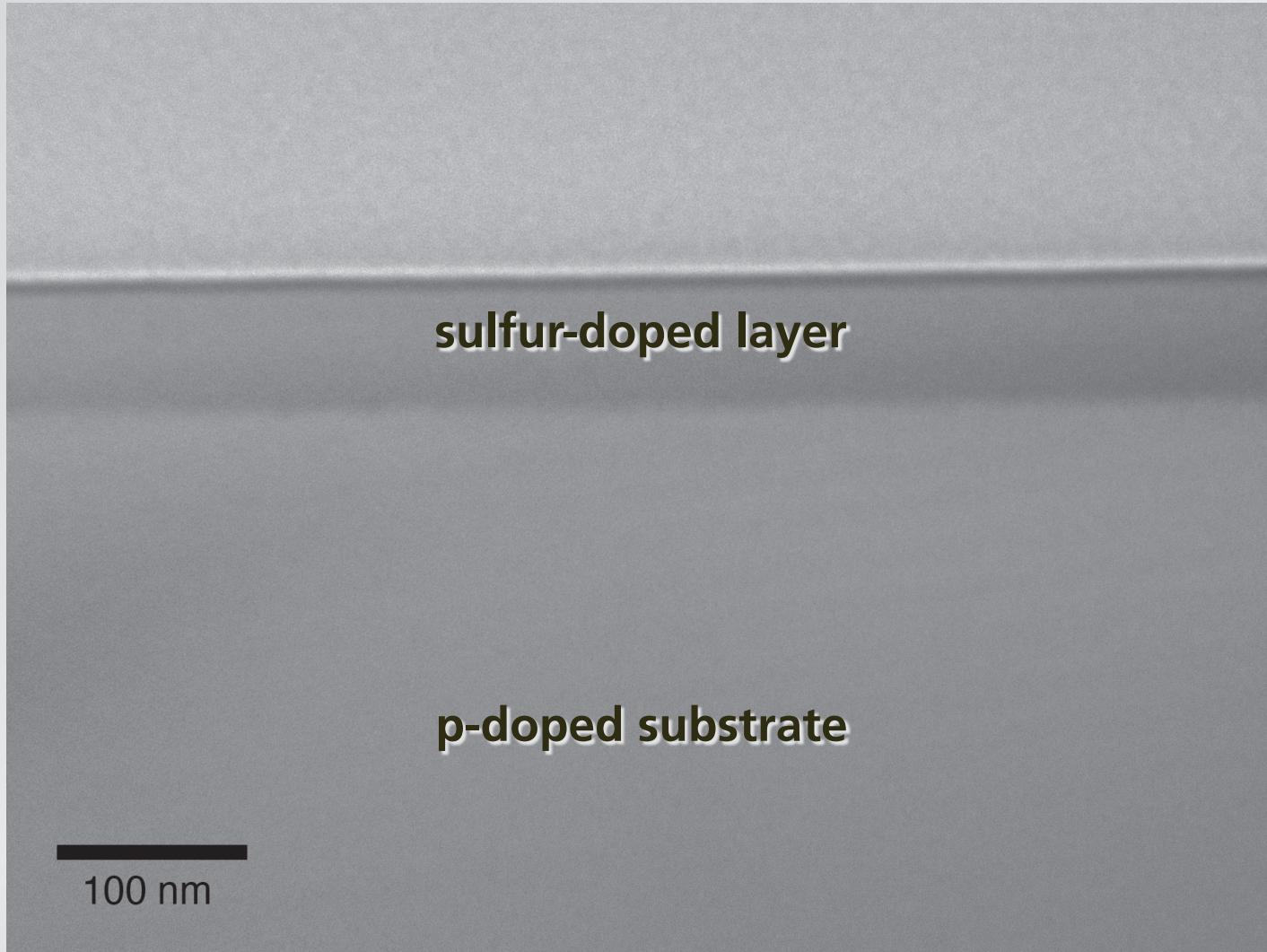
- IR absorption rolls off around 8 μm
- evidence of intermediate band formation
- intermediate band due to substitutional S donors
- intermediate band 0–300 meV below CB



1 intermediate band

2 Si devices

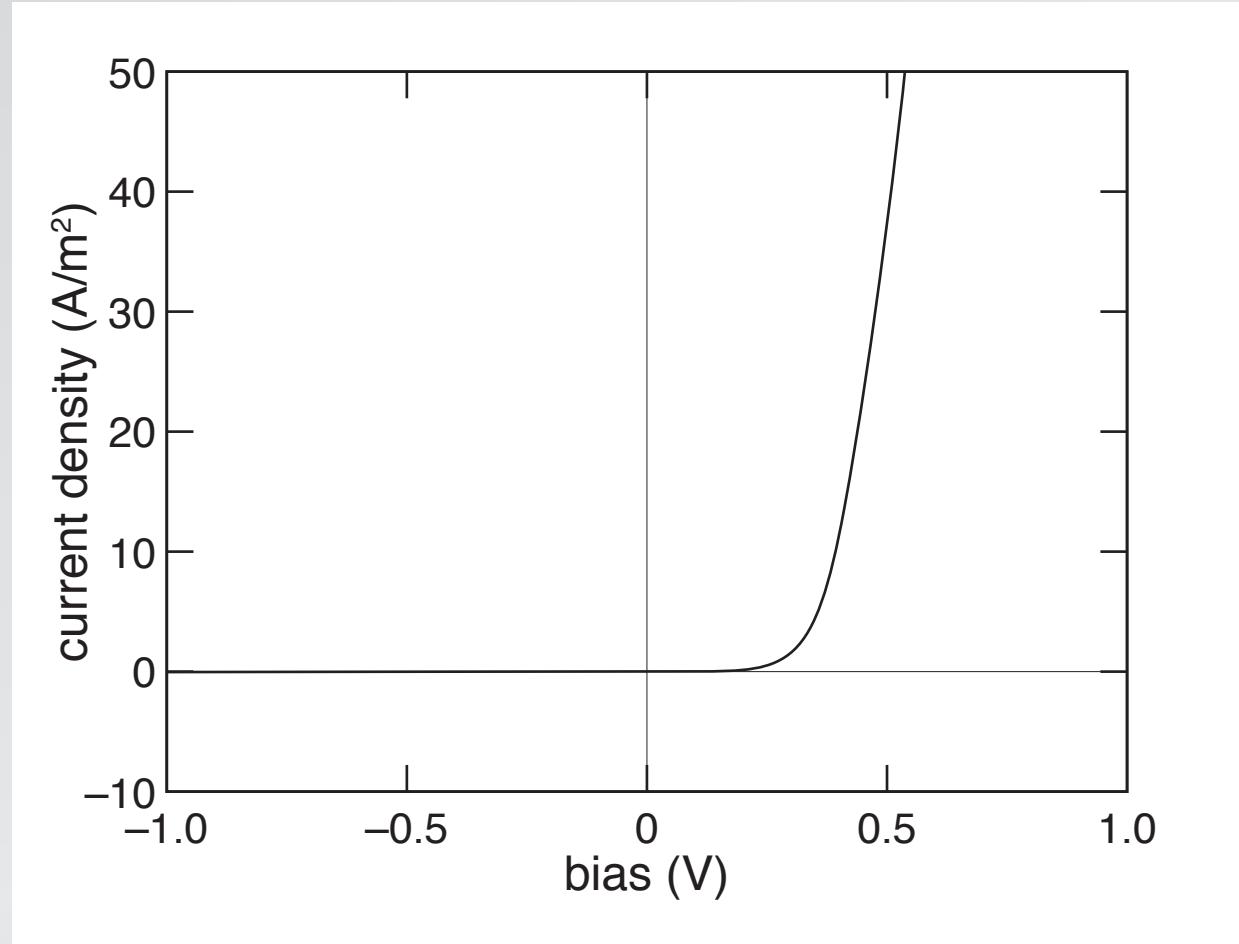
should have shallow junction below surface



1 intermediate band

2 Si devices

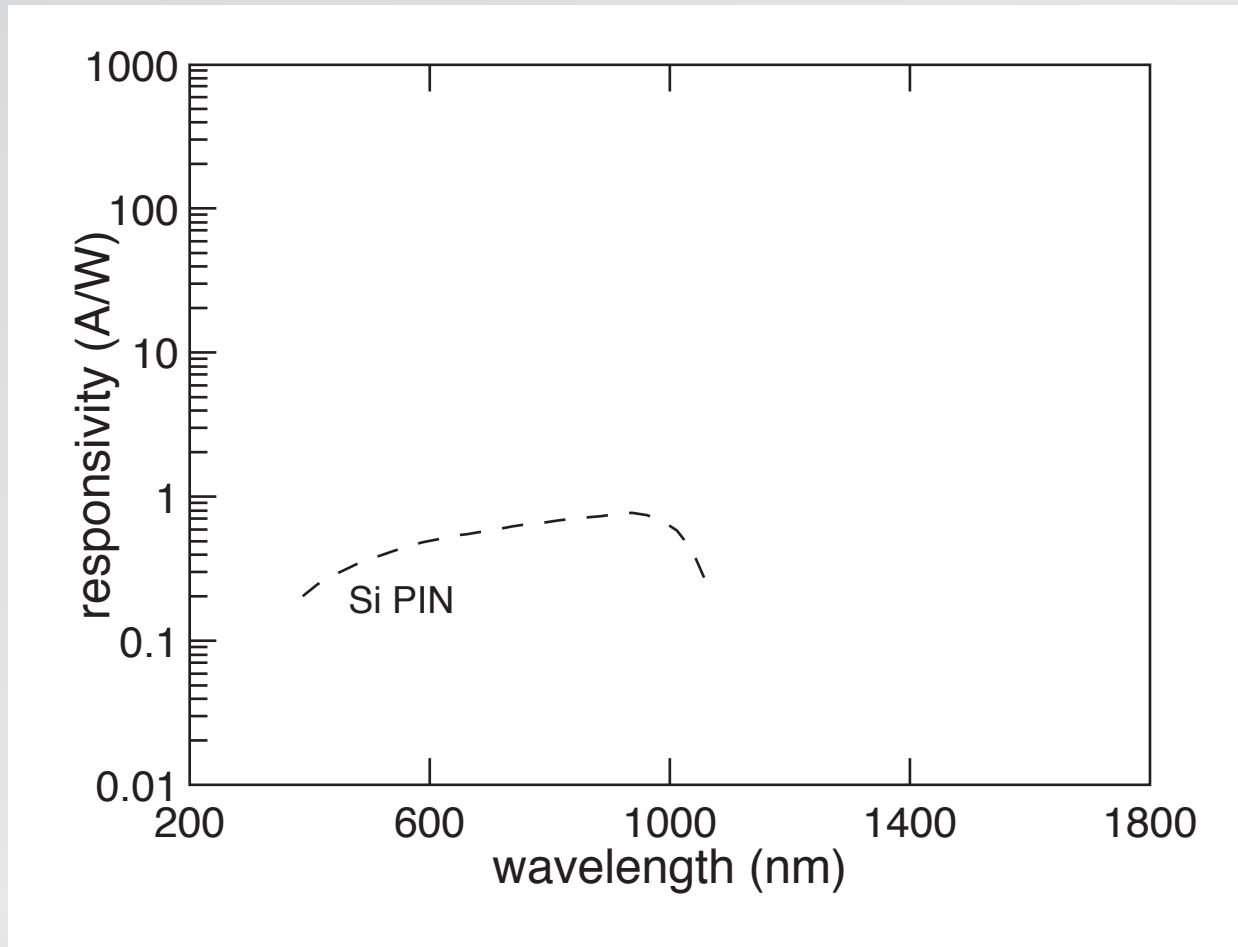
excellent rectification (after annealing)



1 intermediate band

2 Si devices

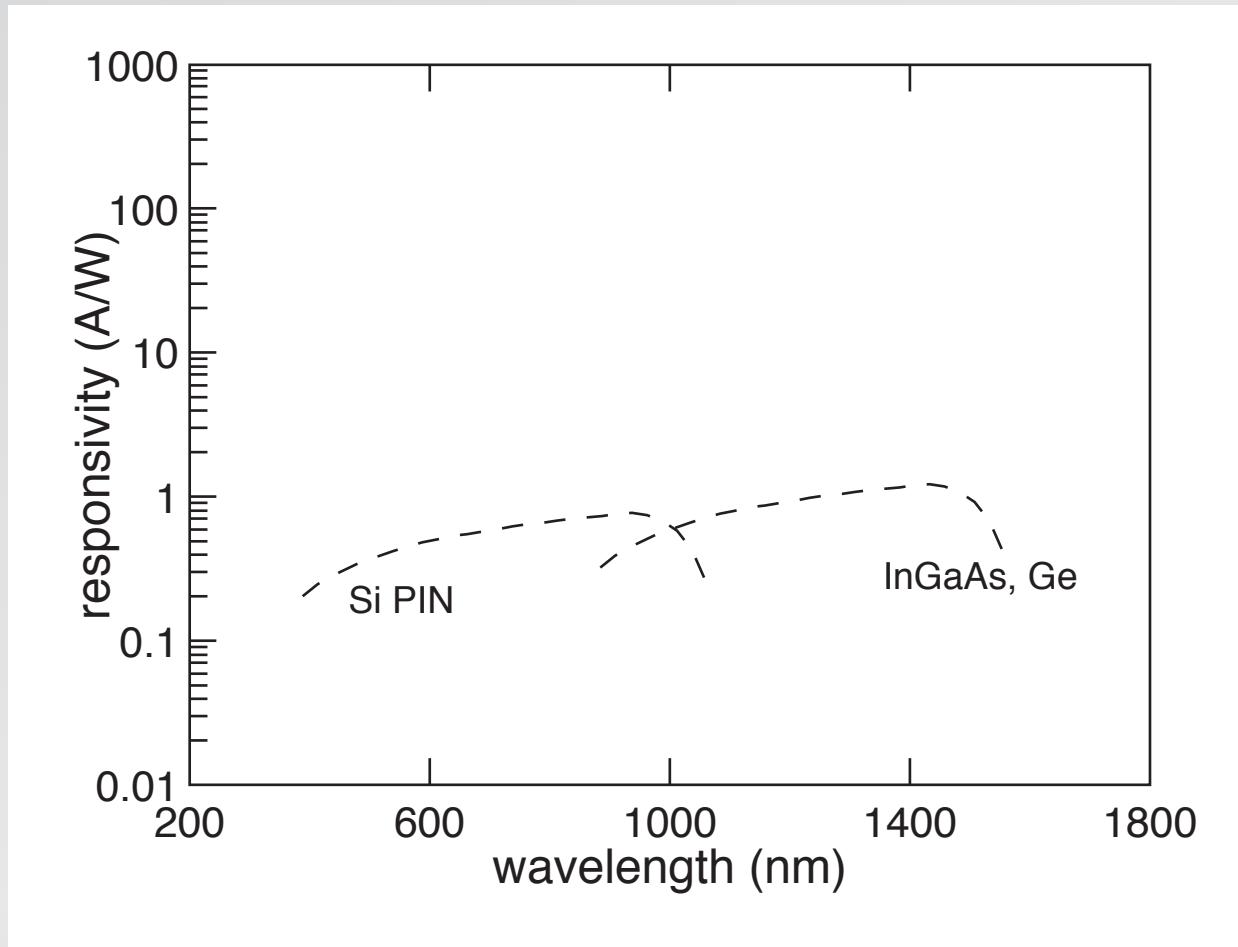
responsivity



1 intermediate band

2 Si devices

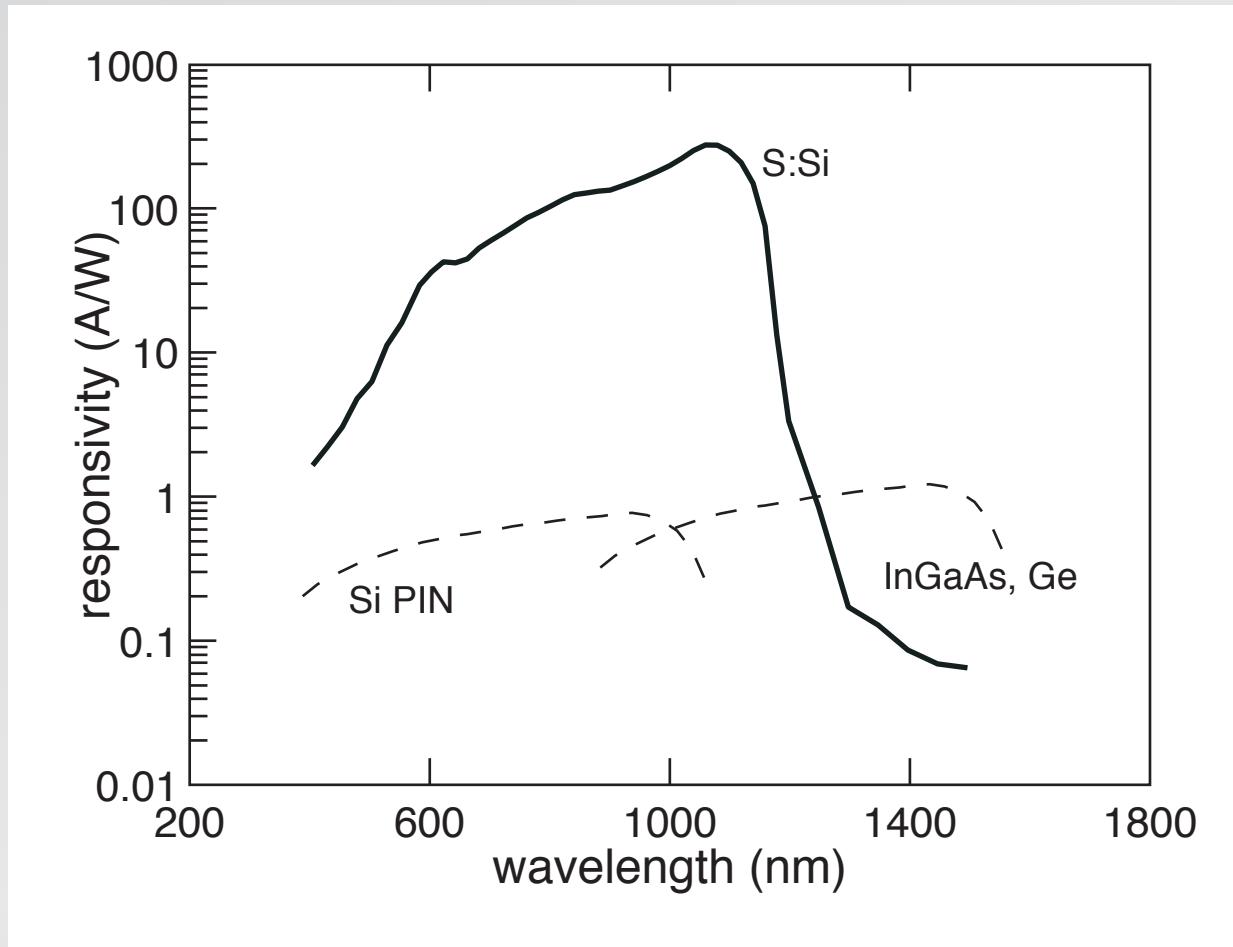
responsivity



1 intermediate band

2 Si devices

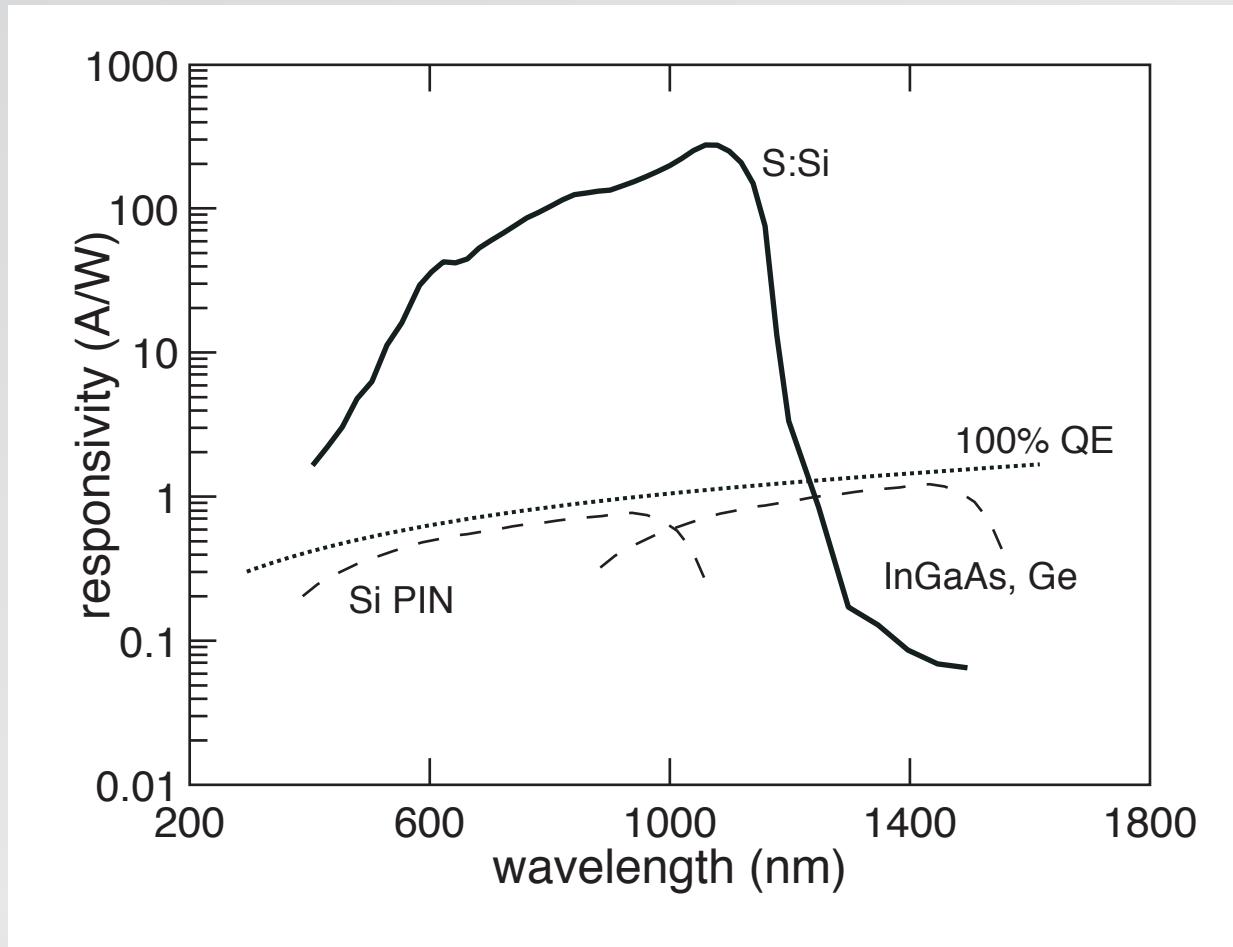
responsivity



1 intermediate band

2 Si devices

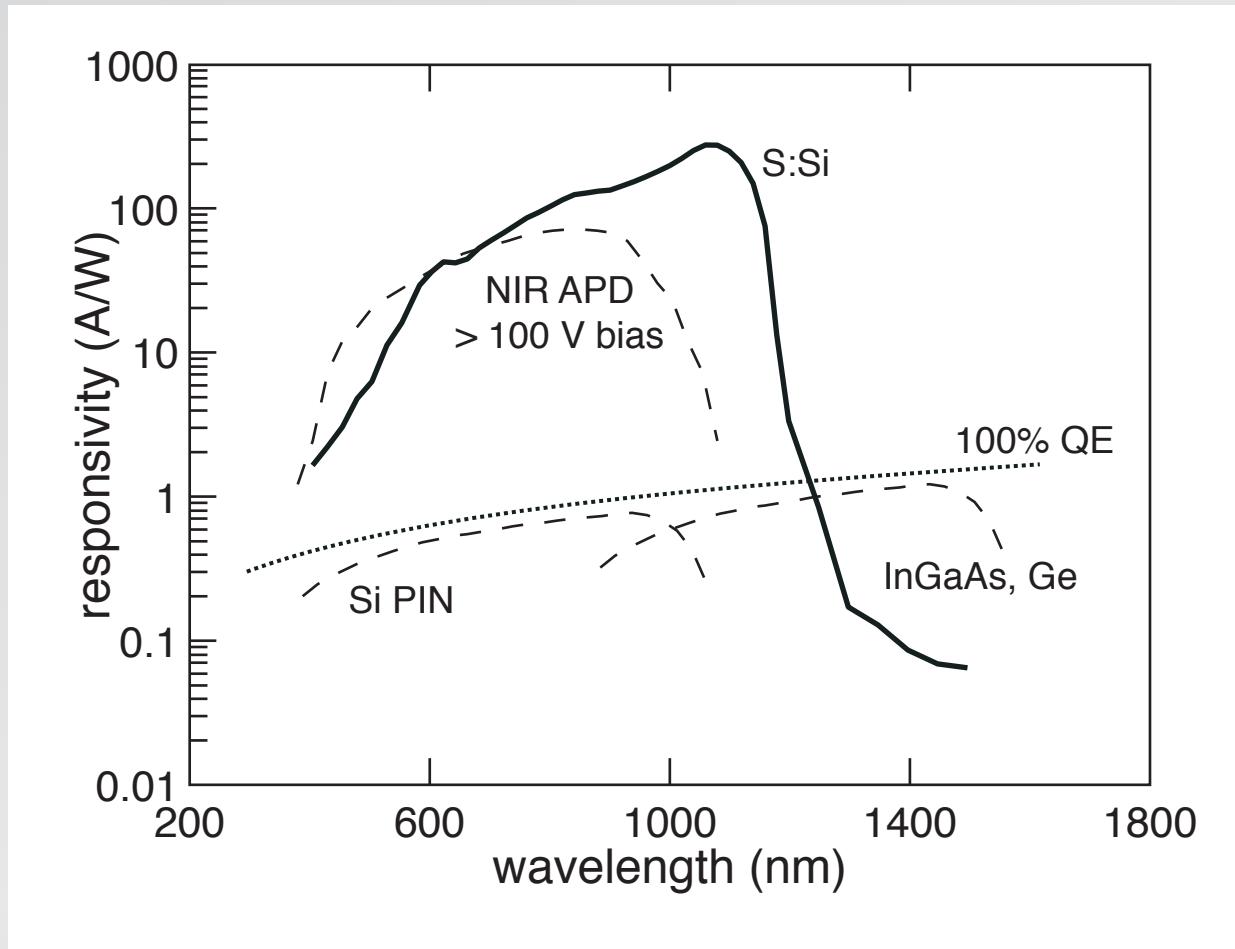
responsivity



1 intermediate band

2 Si devices

responsivity

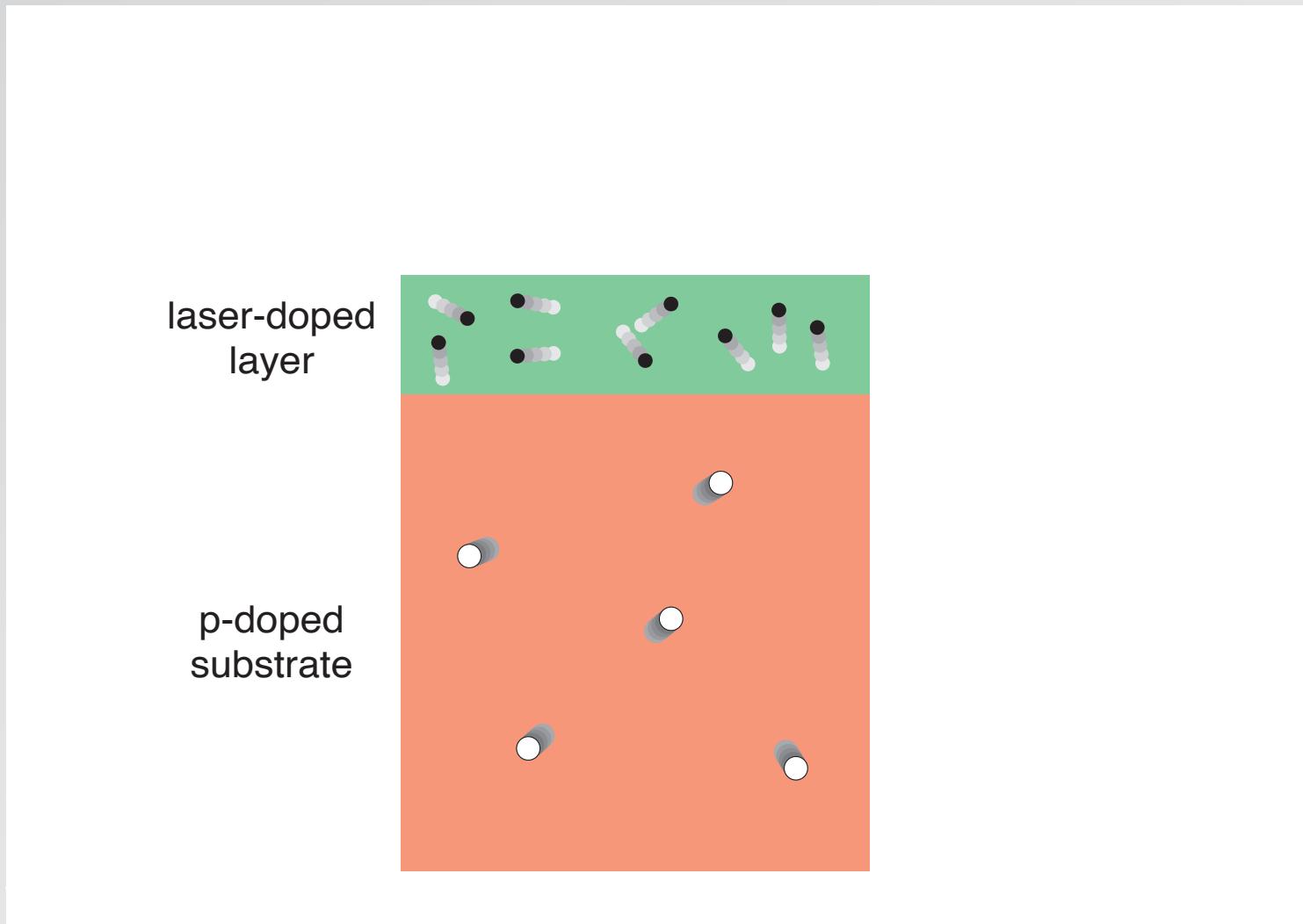


1 intermediate band

2 Si devices

What causes gain?

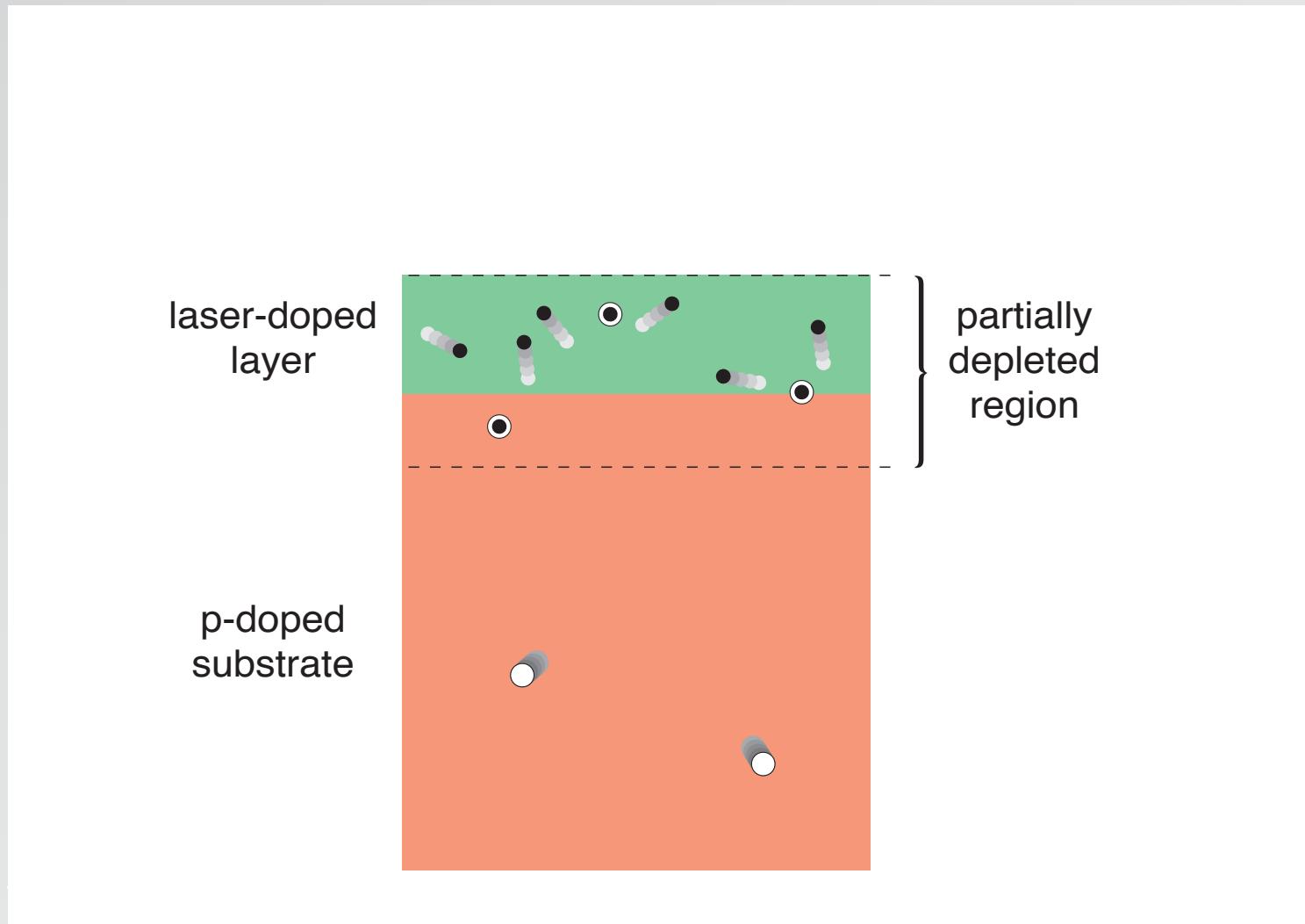
- impact excitation (avalanching)
- carrier lifetime >> transit time (photoconductive gain)
- some other mechanism



“pI junction”

1 intermediate band

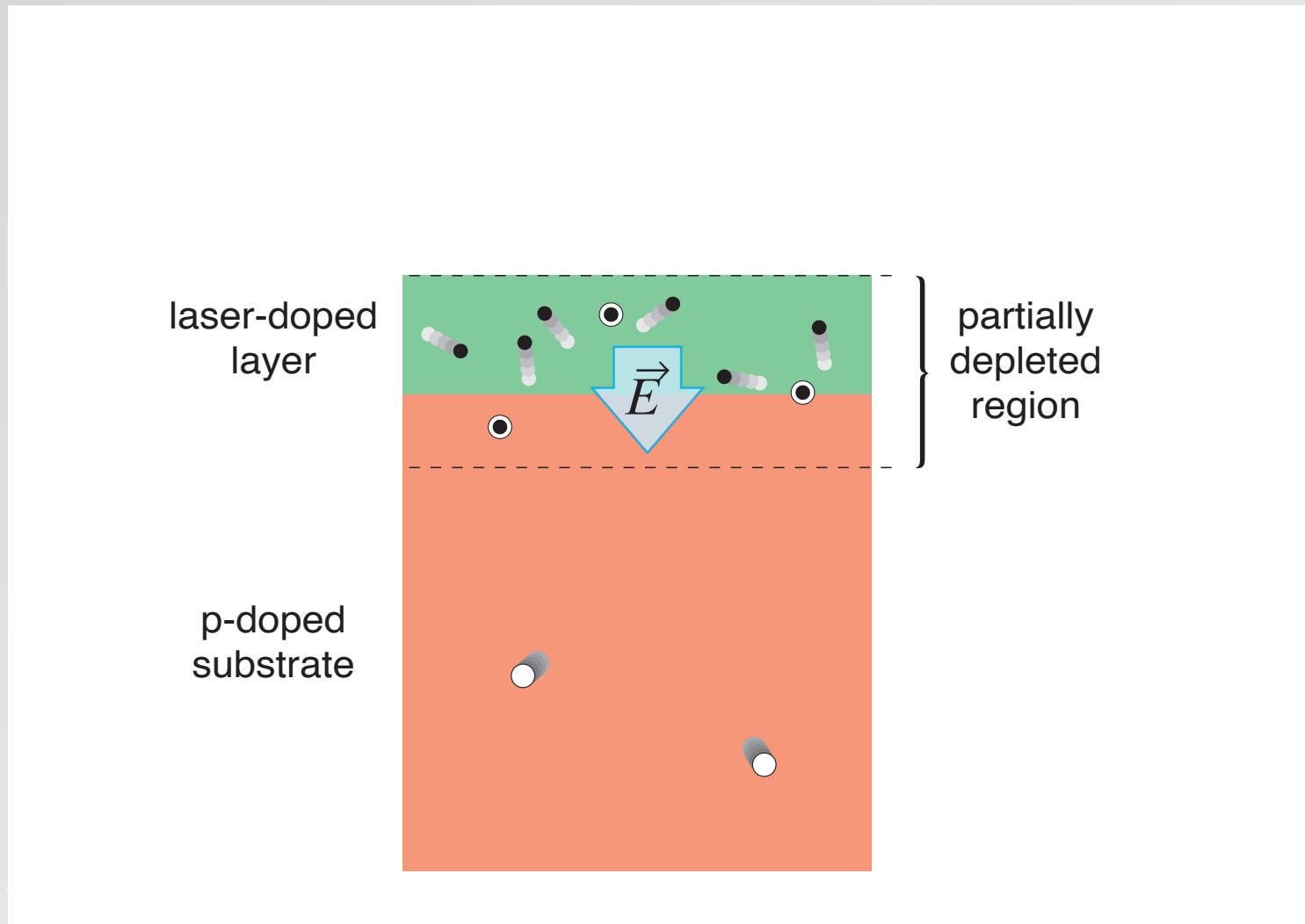
2 Si devices



formation of partially depleted region

1 intermediate band

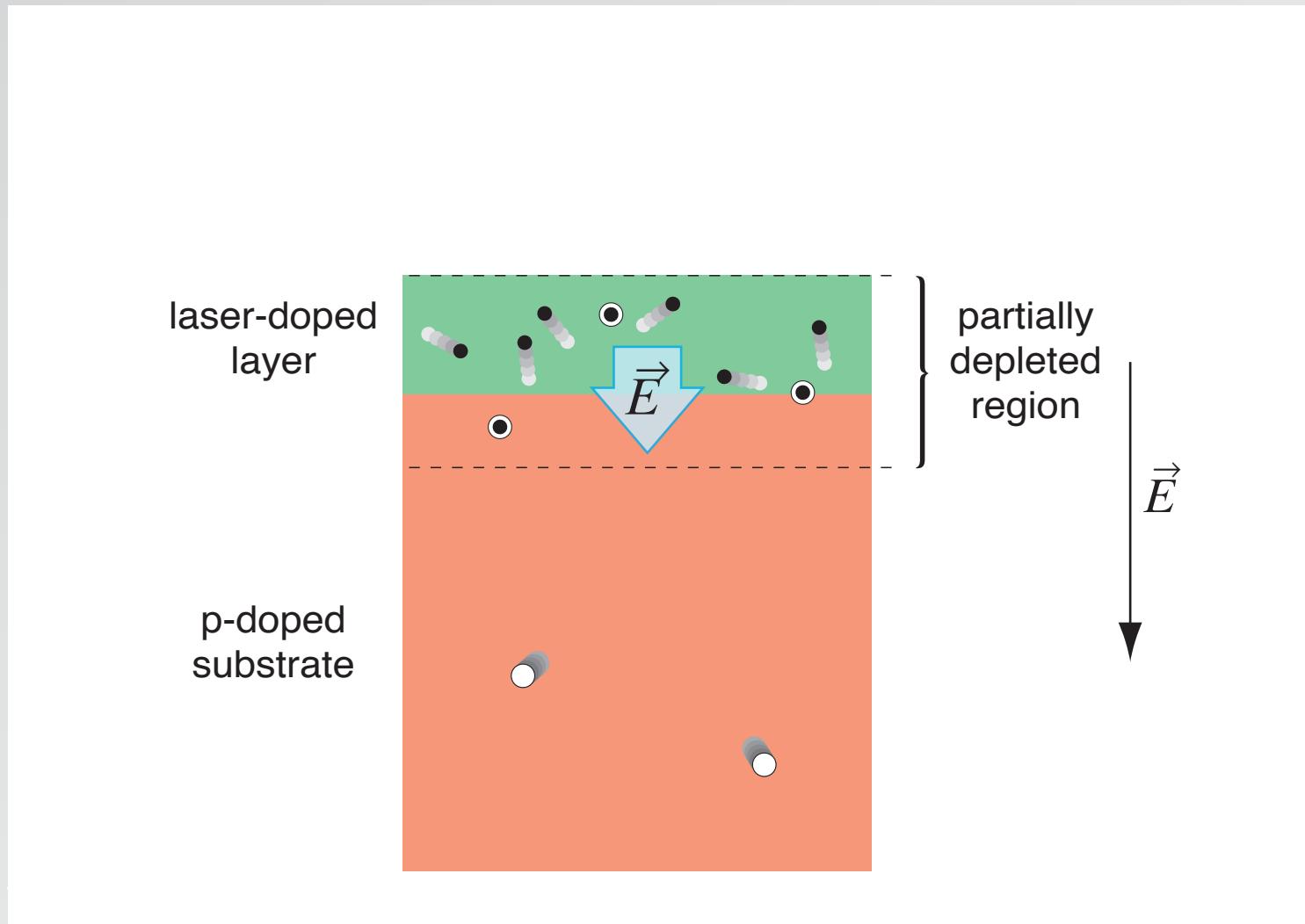
2 Si devices



formation of partially depleted region

1 intermediate band

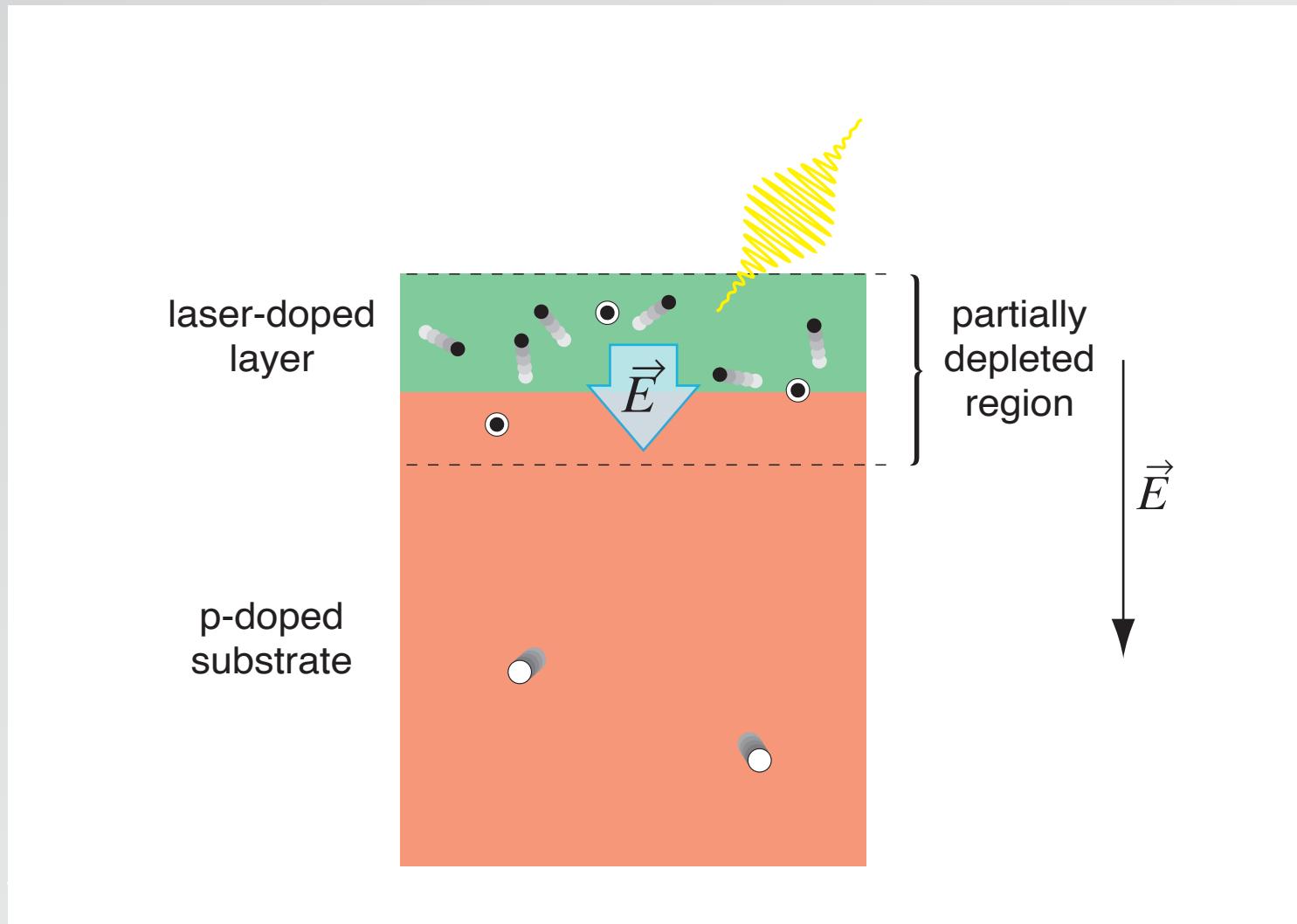
2 Si devices



apply backward bias...

1 intermediate band

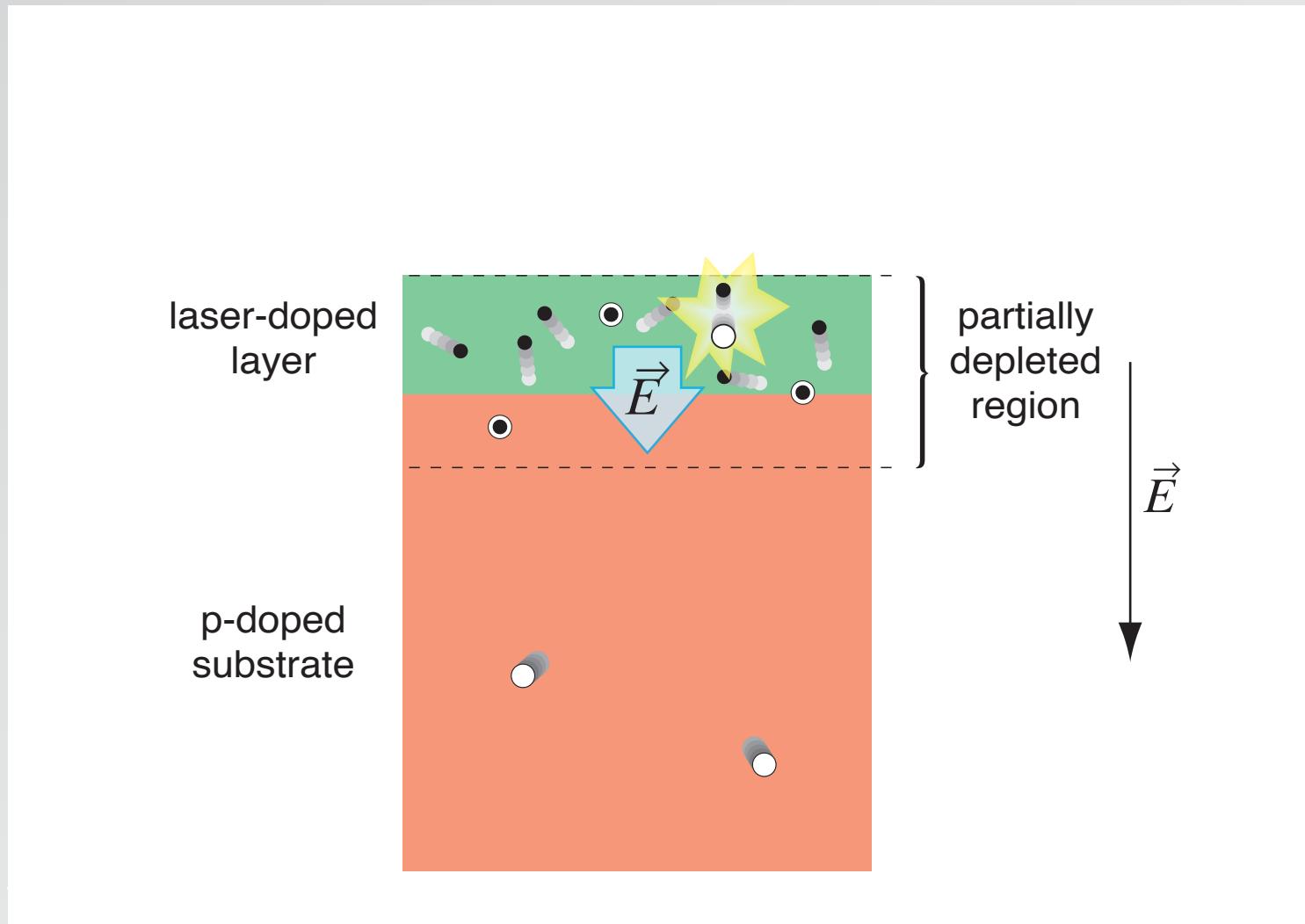
2 Si devices



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

1 intermediate band

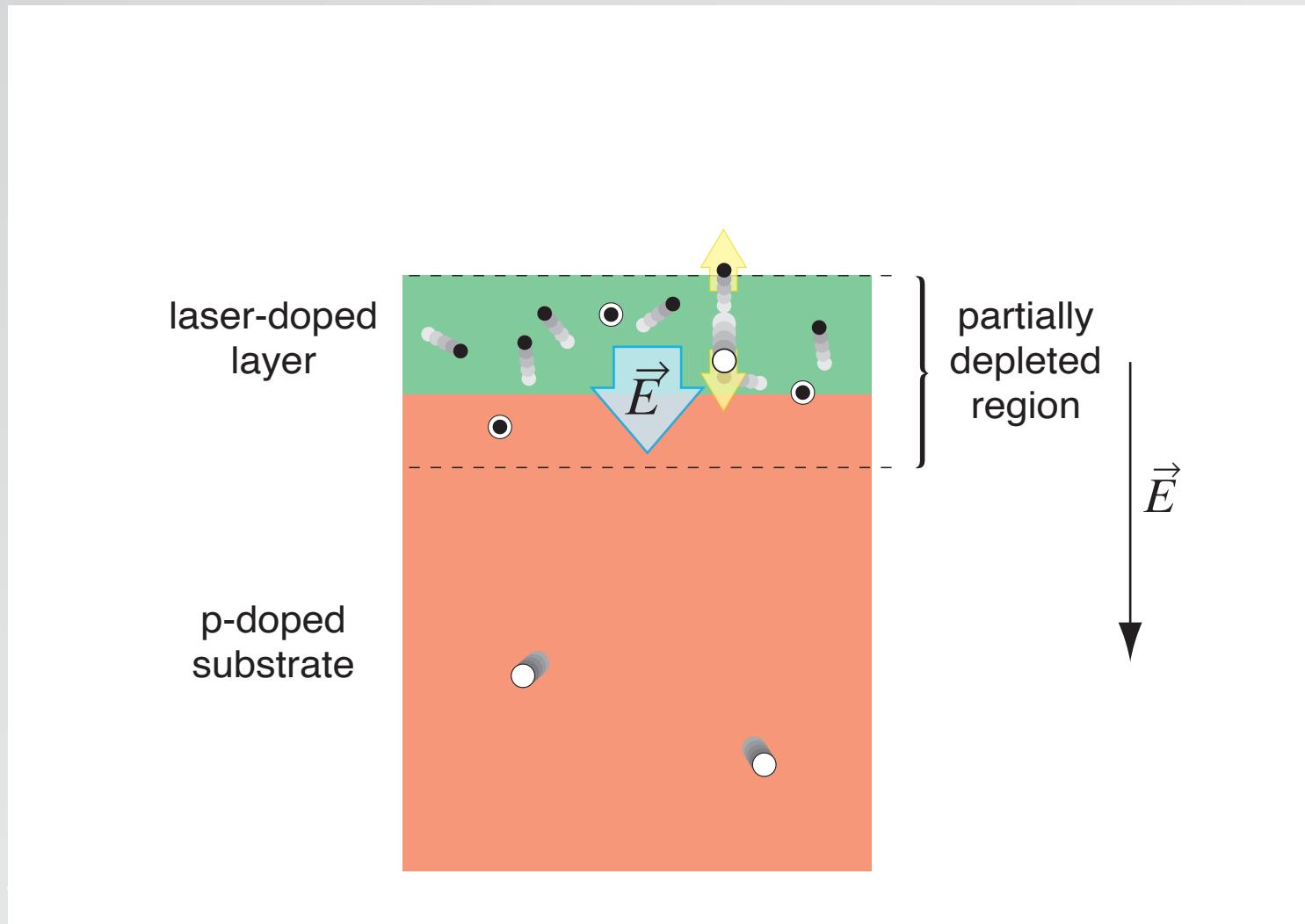
2 Si devices



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

1 intermediate band

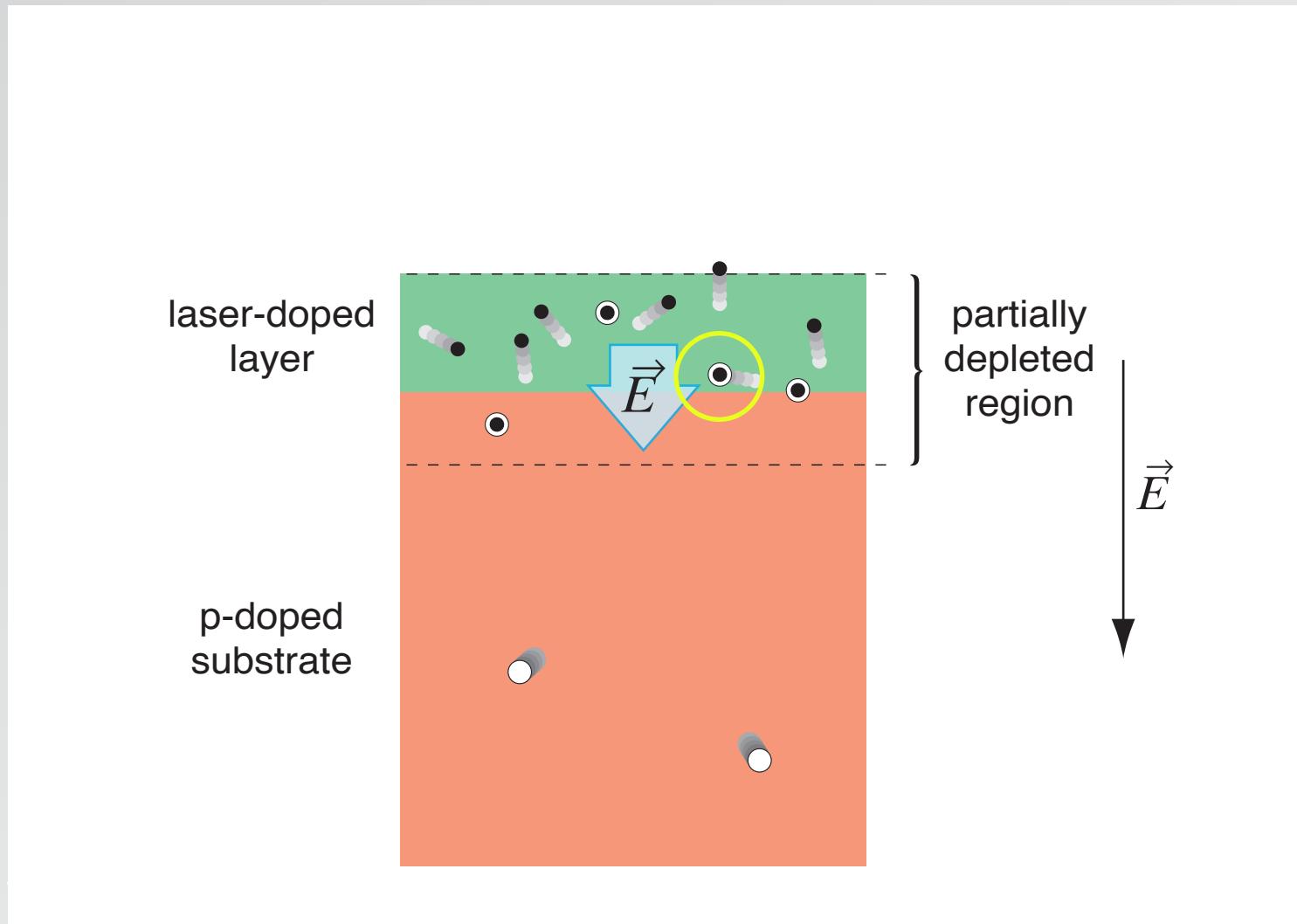
2 Si devices



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

1 intermediate band

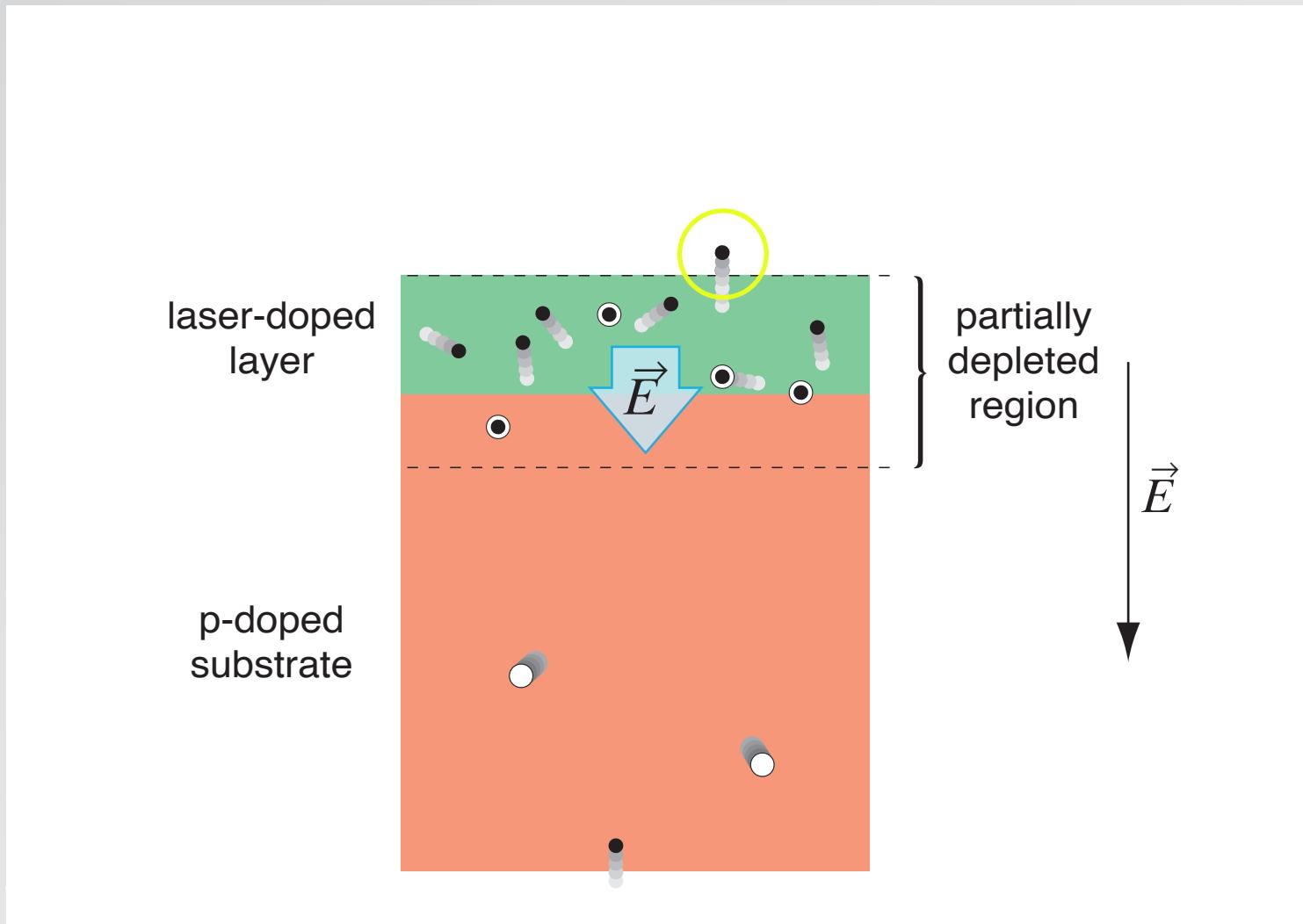
2 Si devices



...hole is trapped

1 intermediate band

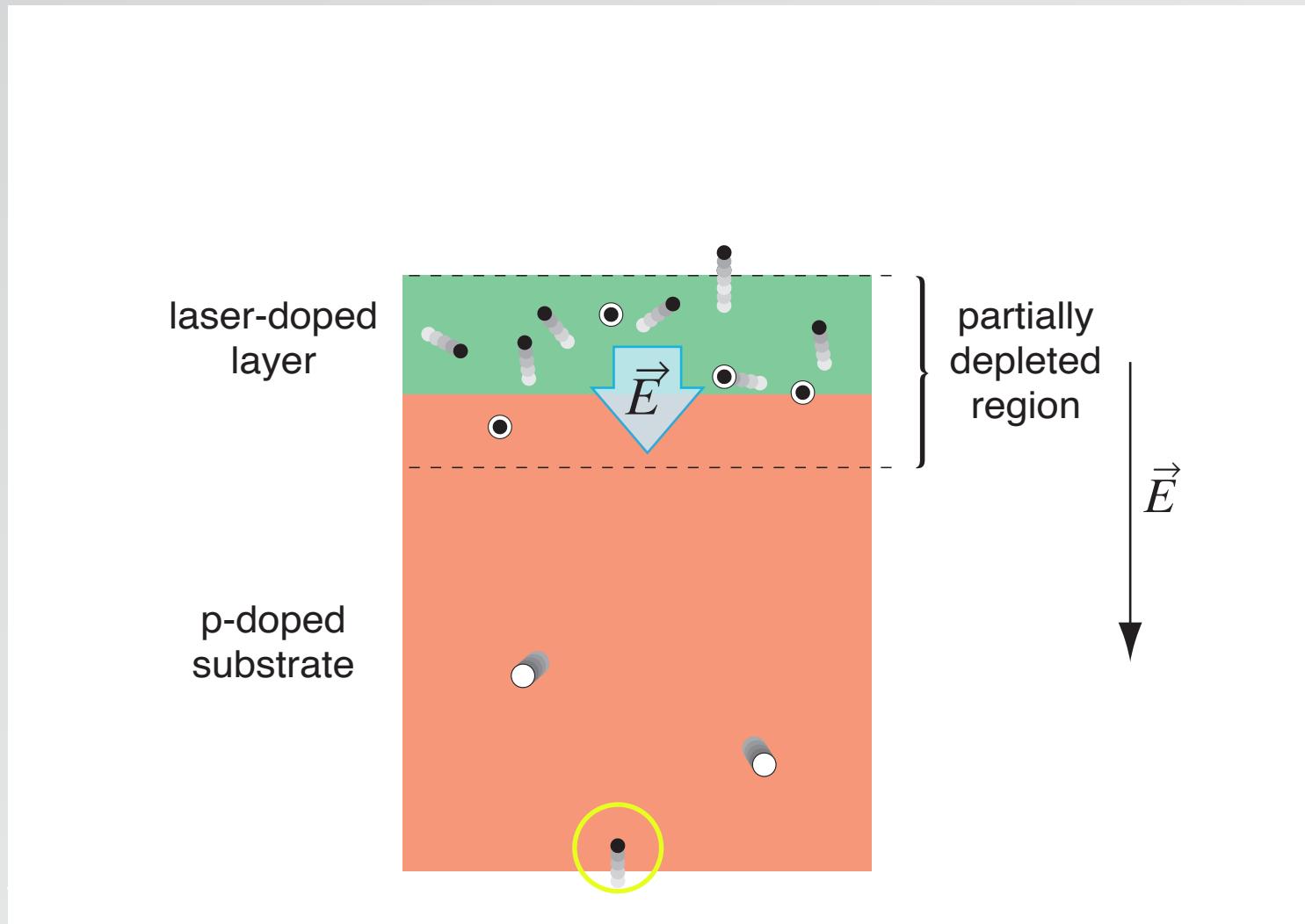
2 Si devices



meanwhile electron exits sample...

1 intermediate band

2 Si devices



...and source provides new electron

1 intermediate band

2 Si devices



<http://www.sionyx.com>

1 intermediate band

2 Si devices

Potential benefits for photovoltaics

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

1 intermediate band

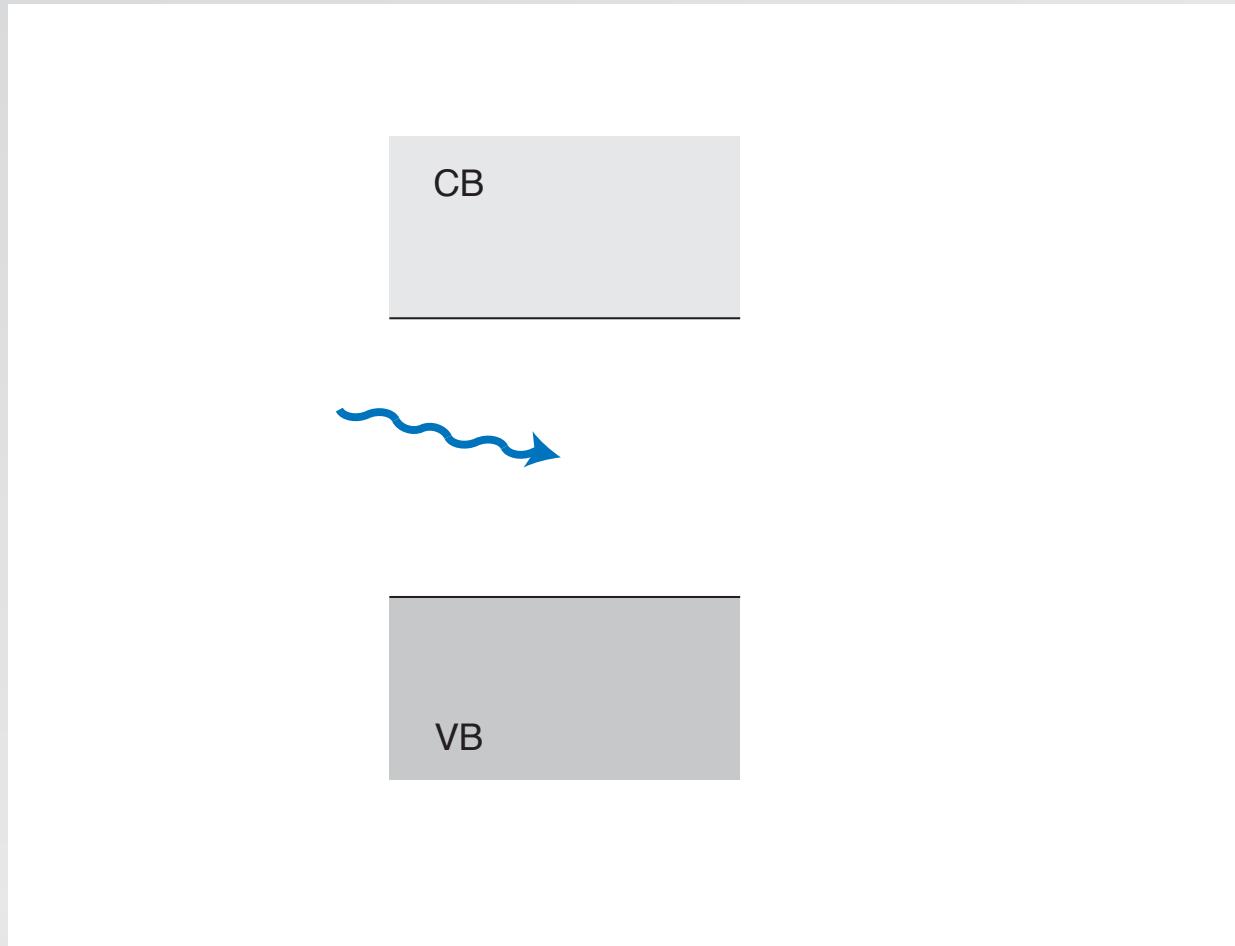
2 Si devices



1 intermediate band

2 Si devices

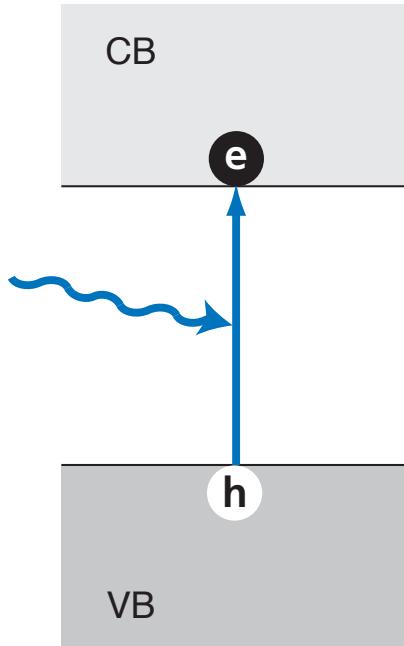
photon with gap energy



1 intermediate band

2 Si devices

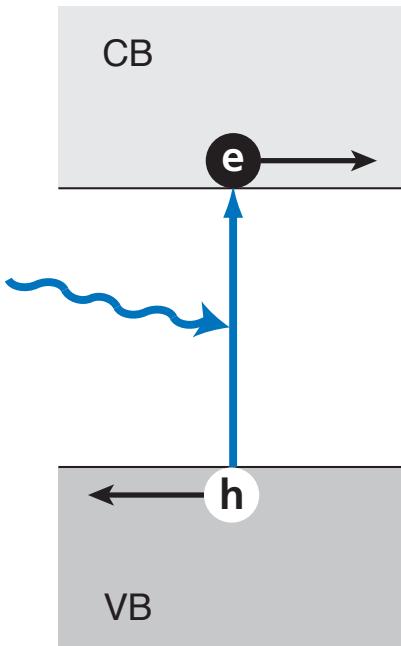
photon creates electron-hole pair...



1 intermediate band

2 Si devices

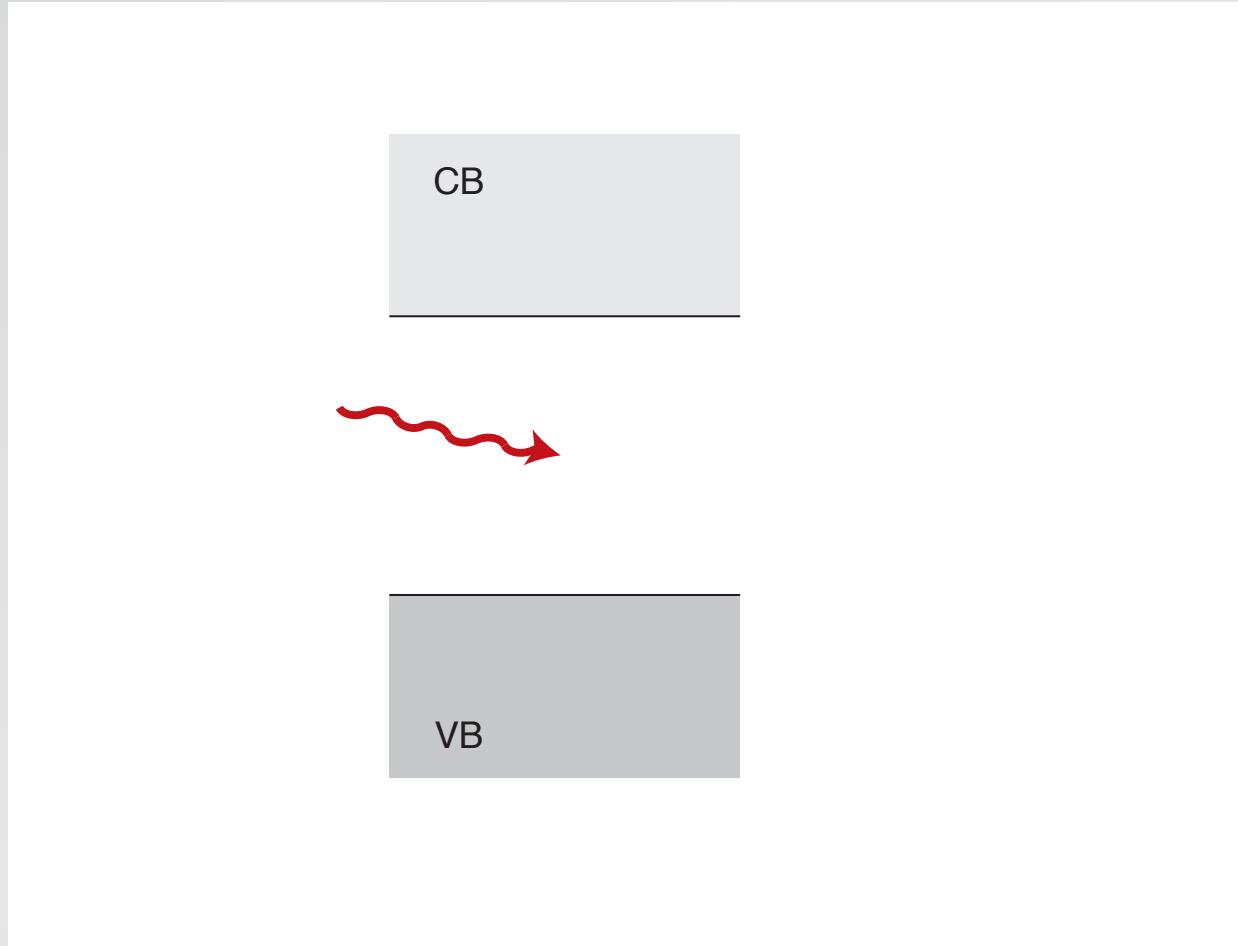
...whose energy can be extracted



1 intermediate band

2 Si devices

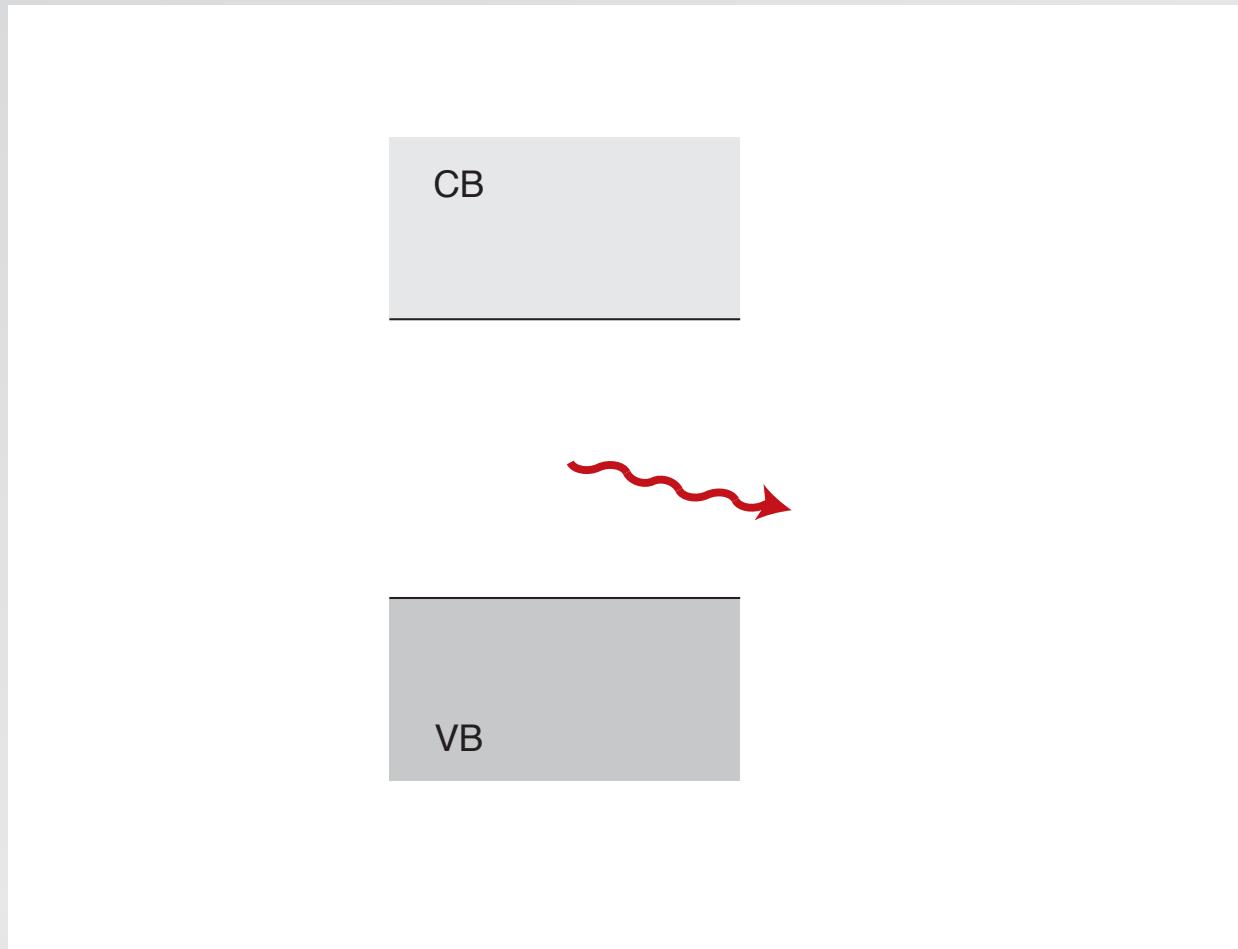
photons with energy smaller than gap...



1 intermediate band

2 Si devices

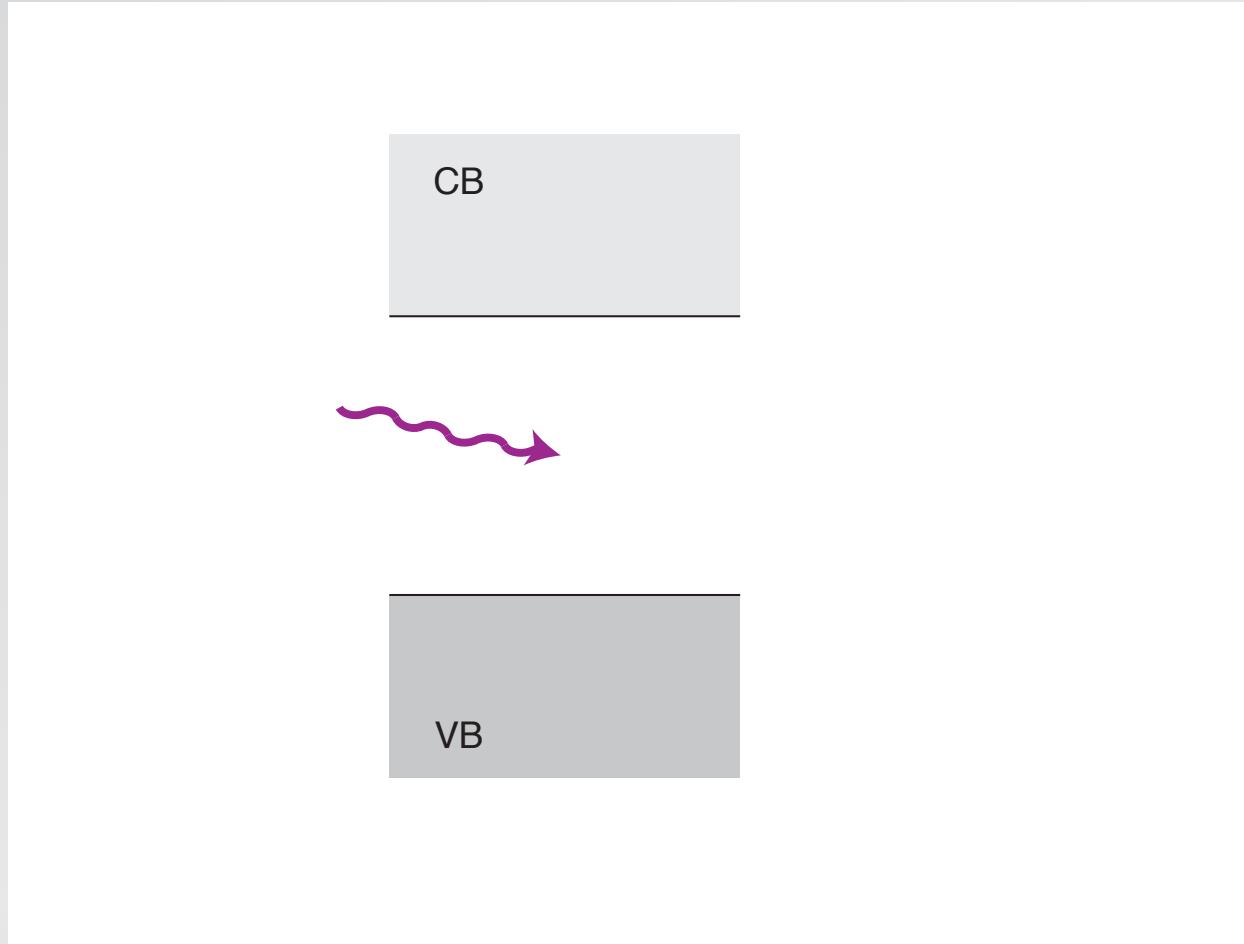
...do not get absorbed



1 intermediate band

2 Si devices

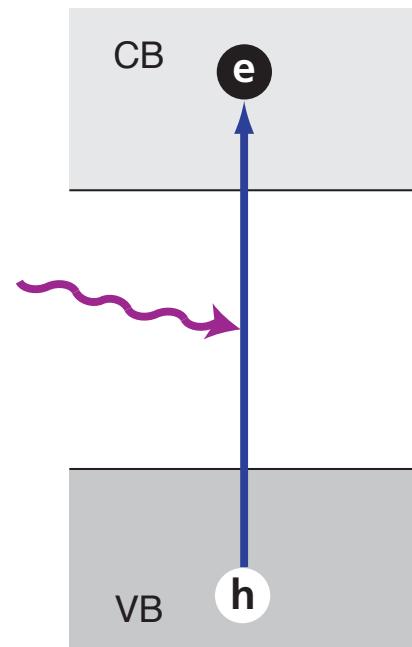
photons with energy larger than the gap...



1 intermediate band

2 Si devices

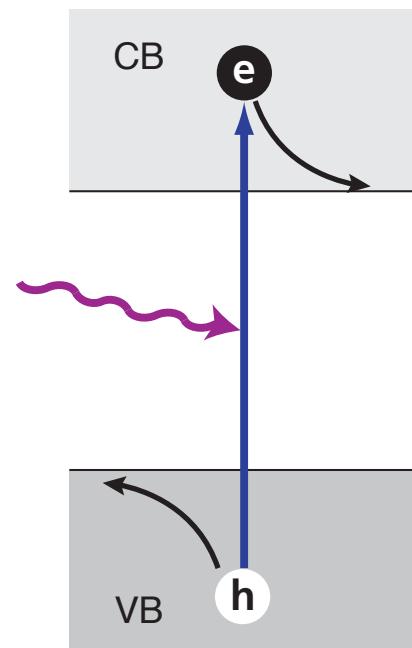
...create electron-hole pairs with excess energy...



1 intermediate band

2 Si devices

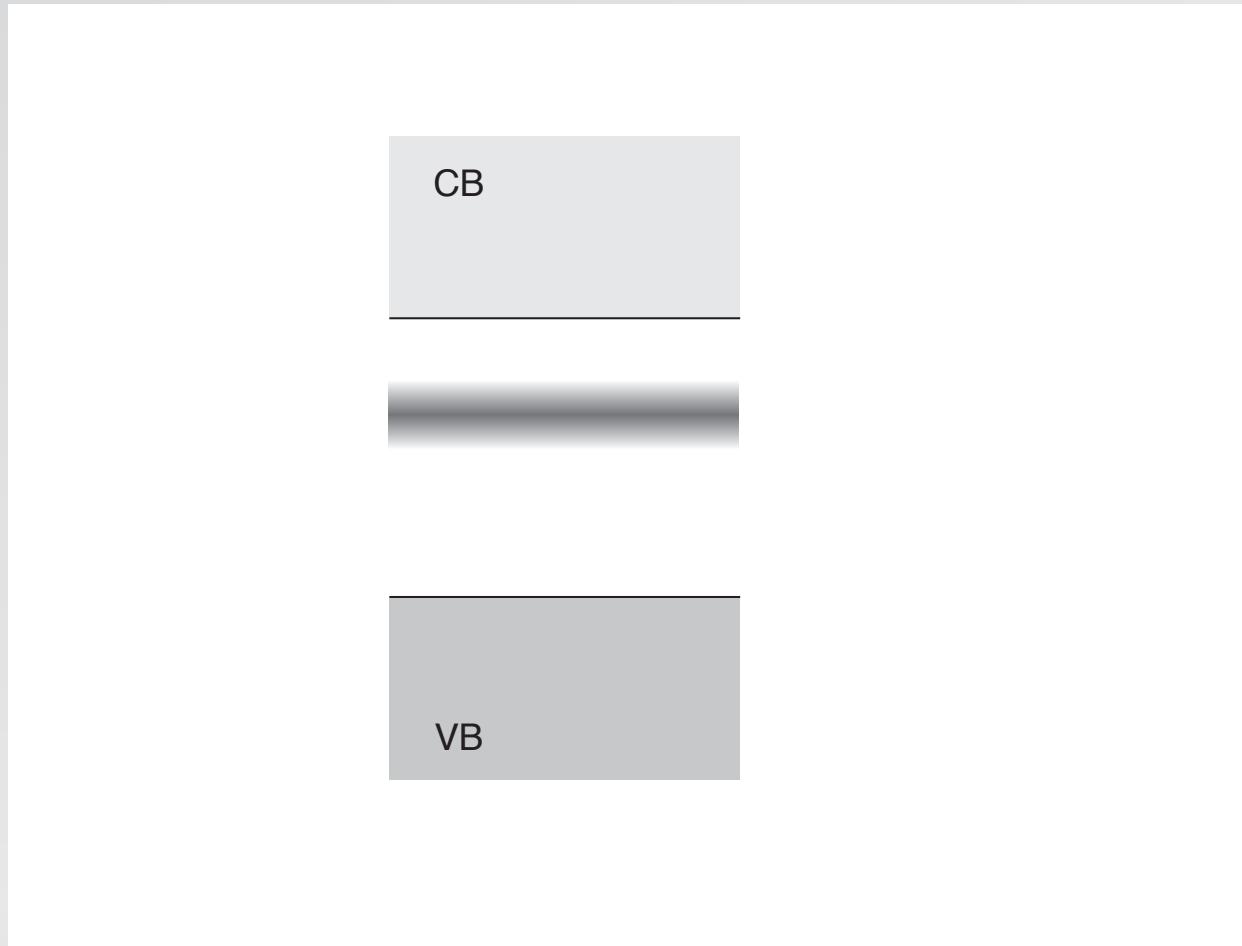
...which is lost rapidly



1 intermediate band

2 Si devices

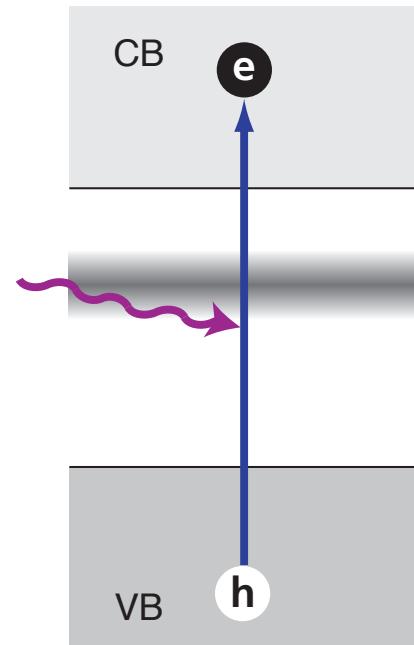
black silicon has an intermediate band



1 intermediate band

2 Si devices

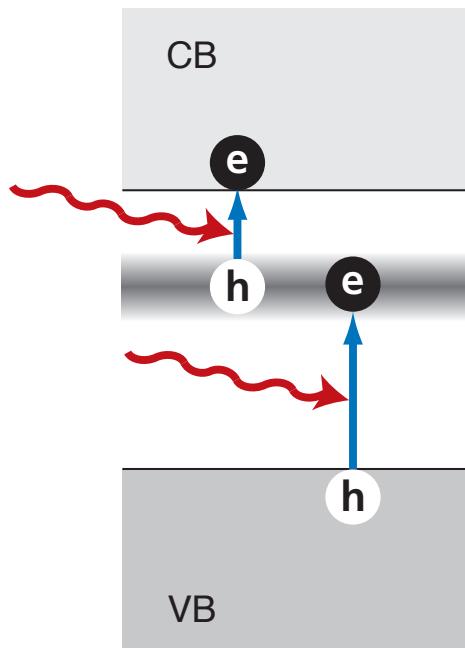
absorbs same photons as ordinary silicon...



1 intermediate band

2 Si devices

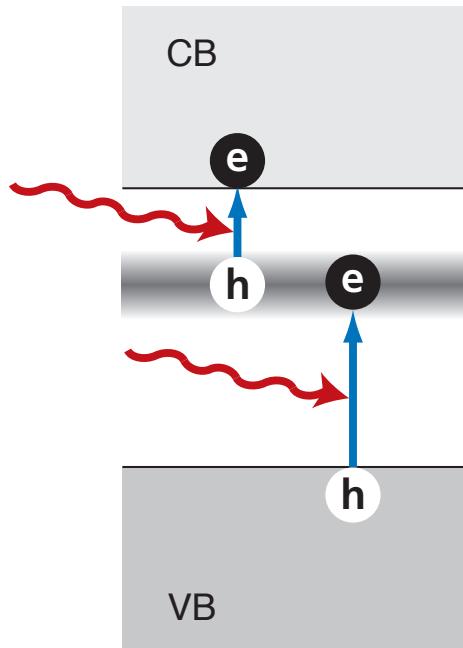
...but extends absorption to longer wavelengths



1 intermediate band

2 Si devices

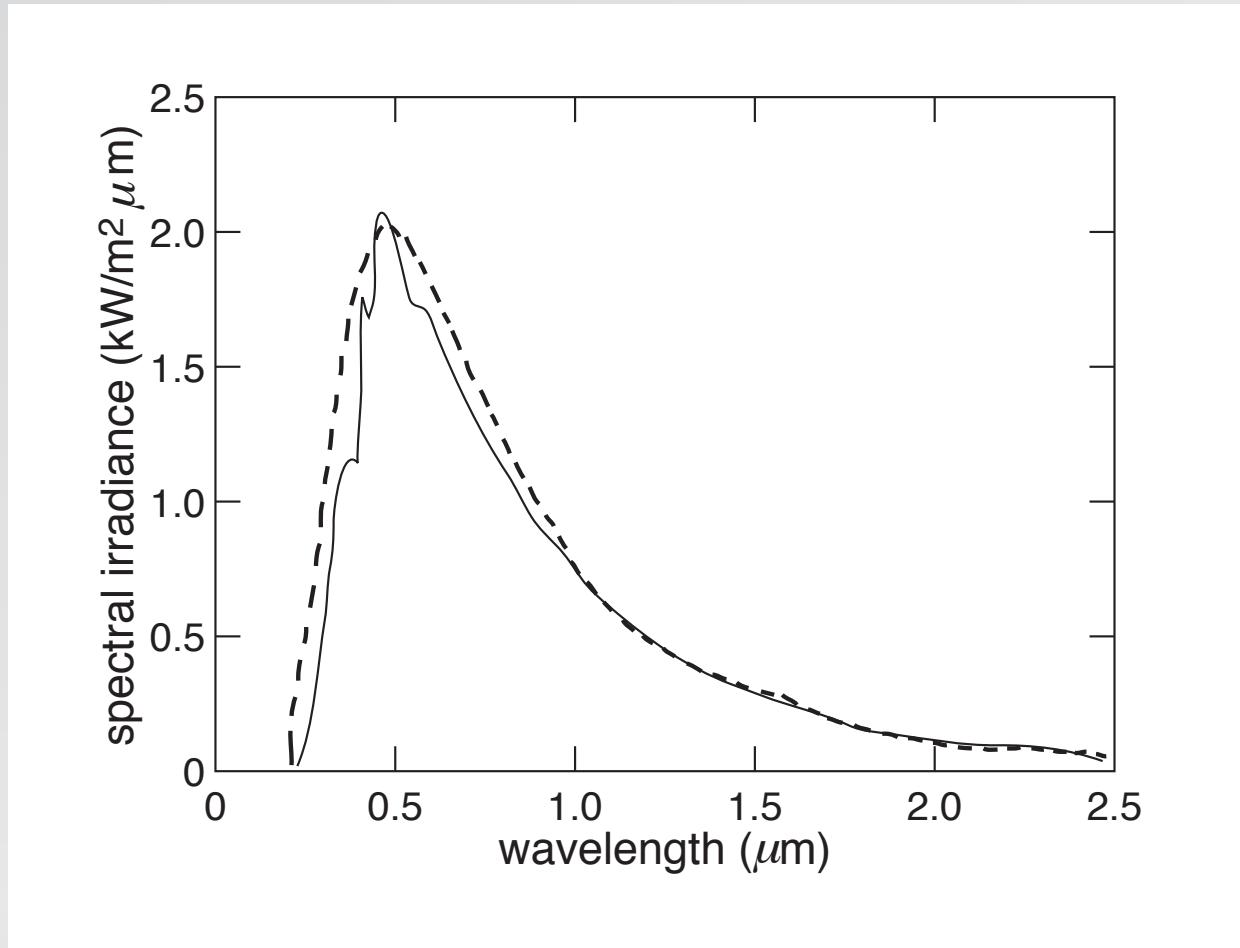
could theoretically get efficiencies over 50%



1 intermediate band

2 Si devices

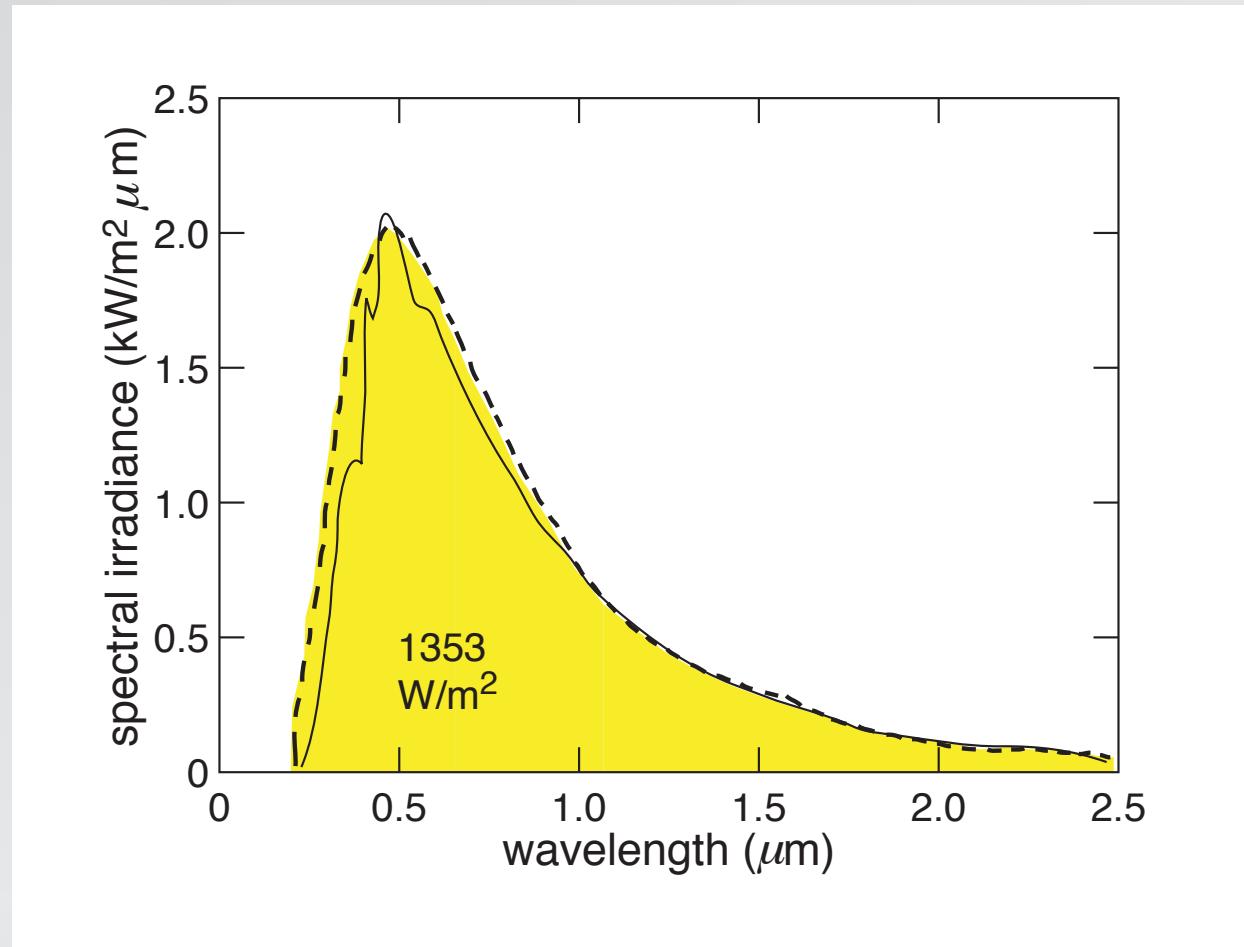
solar spectrum



1 intermediate band

2 Si devices

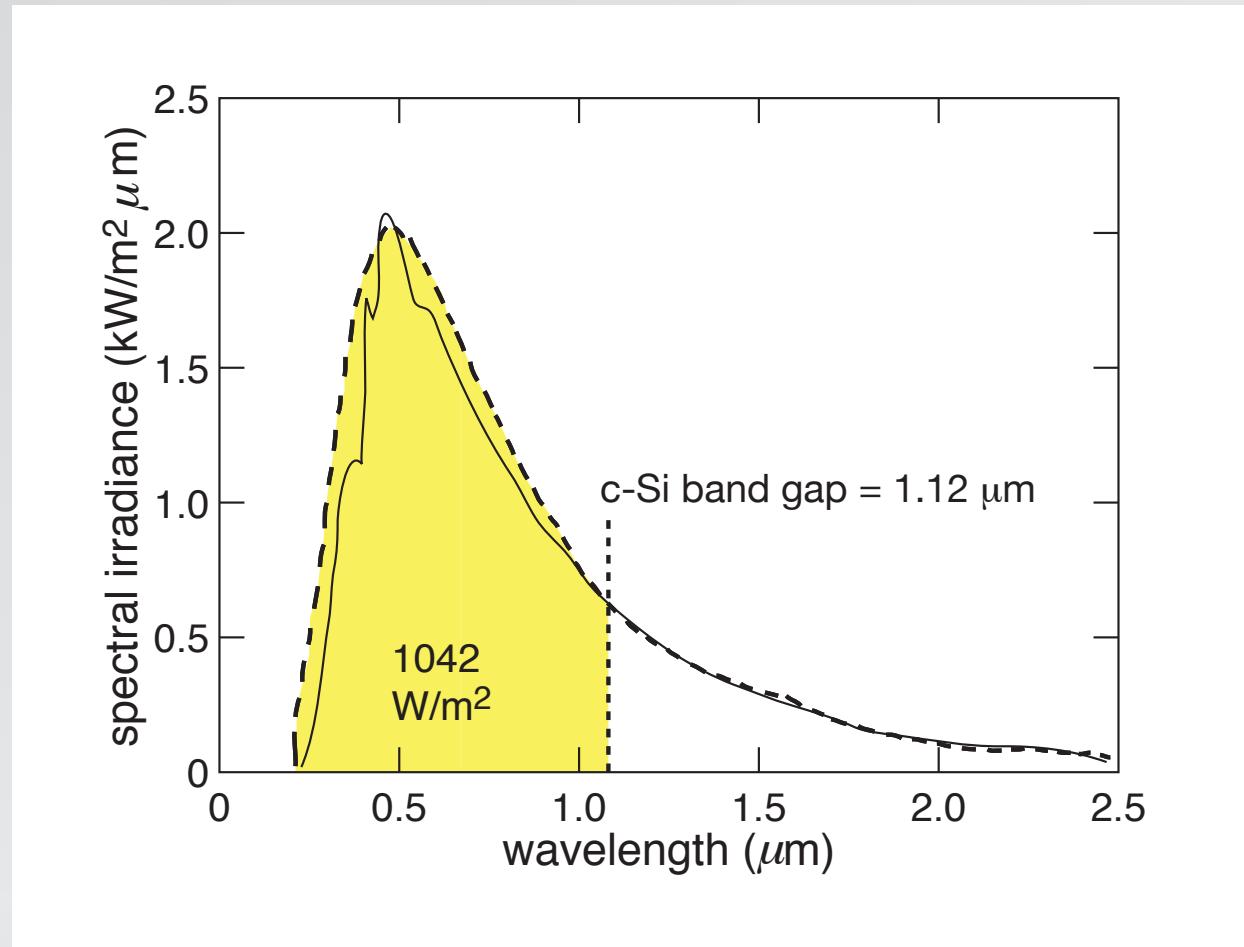
solar spectrum



1 intermediate band

2 Si devices

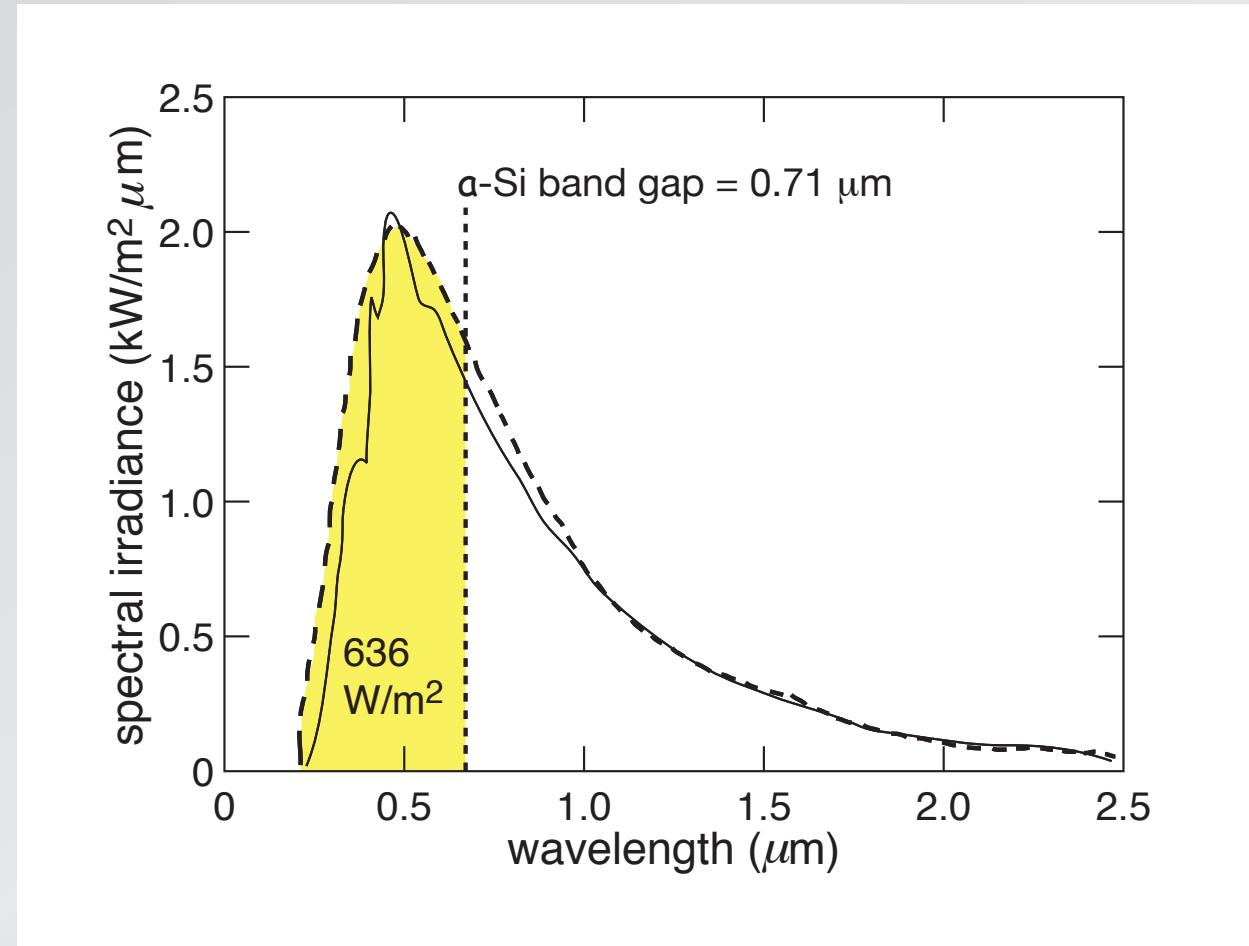
crystalline silicon: transparent to 23% of solar radiation



1 intermediate band

2 Si devices

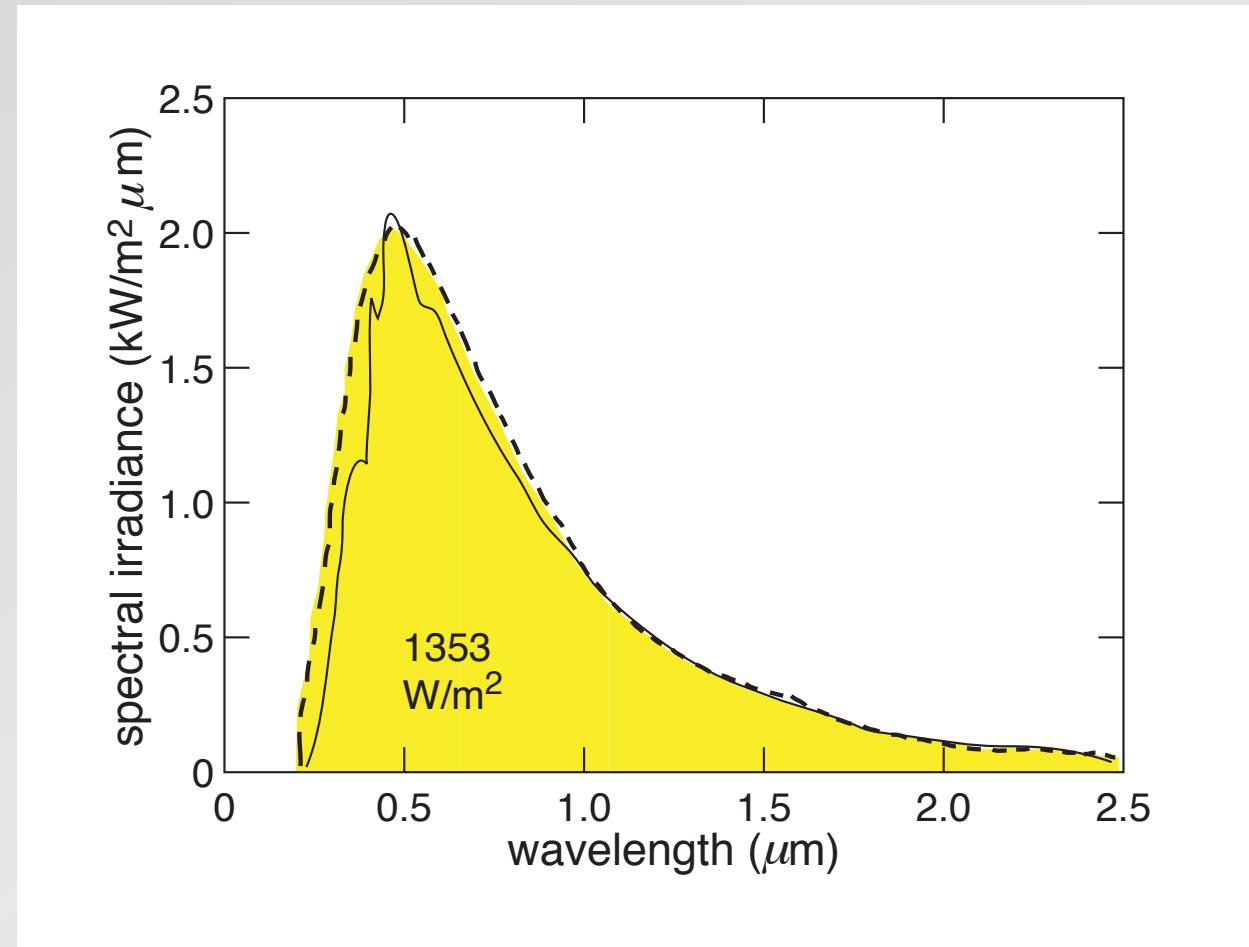
amorphous silicon: transparent to 53% of solar radiation



1 intermediate band

2 Si devices

black silicon: potential to recover transmitted energy



1 intermediate band

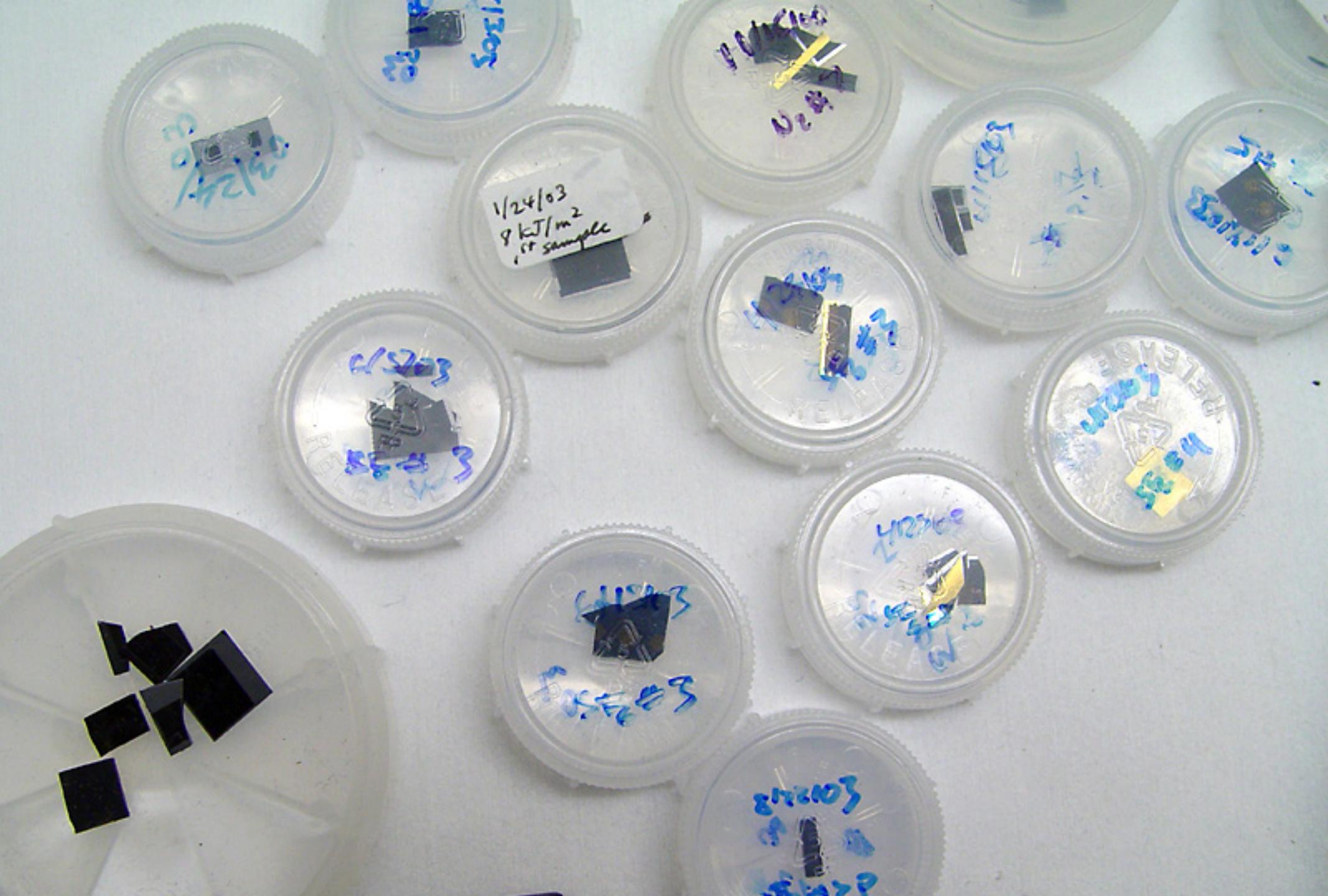
2 Si devices

Things to keep in mind

- can turn absorption into carrier generation
- very high responsivity in VIS and IR
- intermediate band photovoltaic devices?

Things to keep in mind

- can turn absorption into carrier generation
- very high responsivity in VIS and IR
- intermediate band photovoltaic devices?

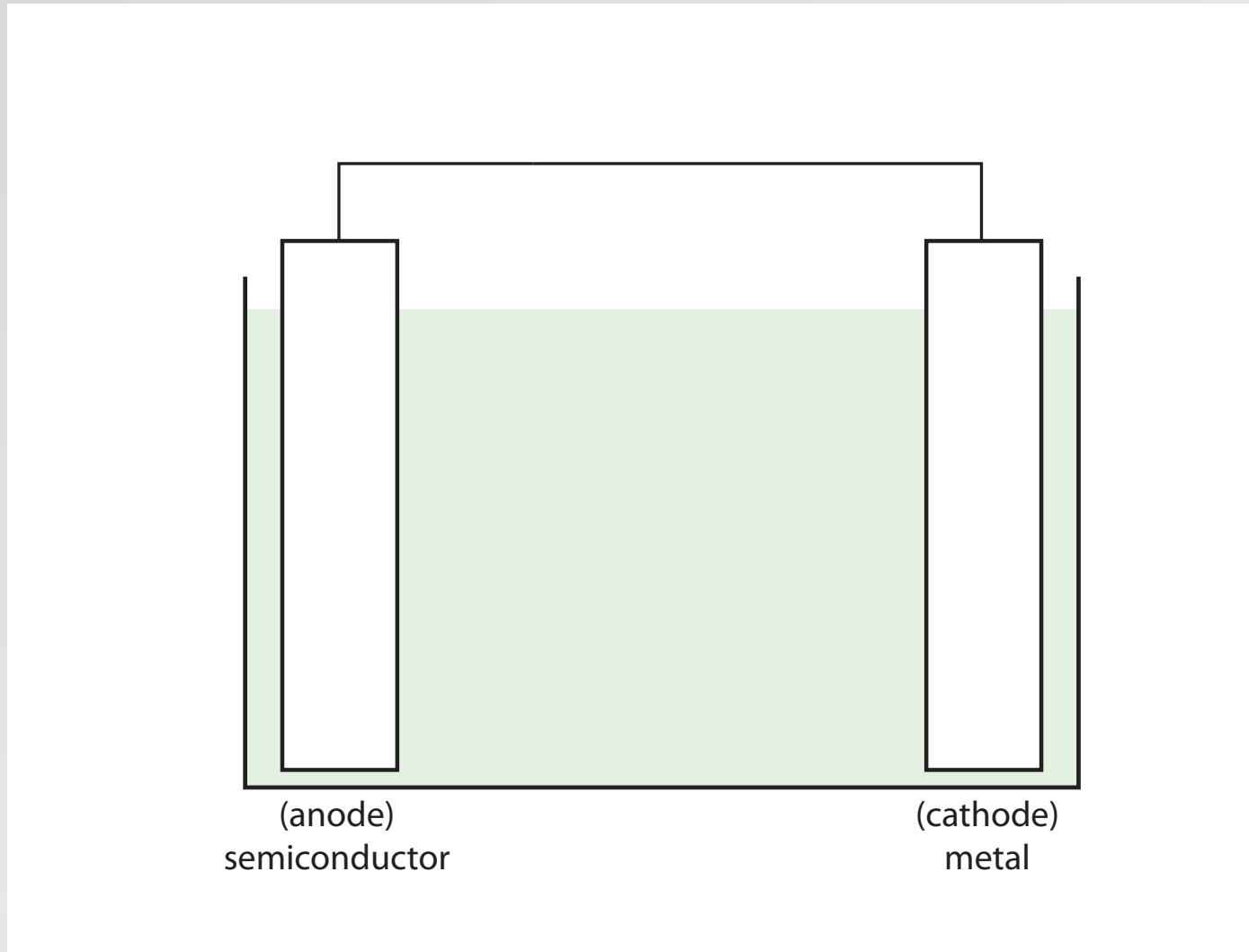


1 intermediate band

2 Si devices

3 X:TiO₂

water splitting

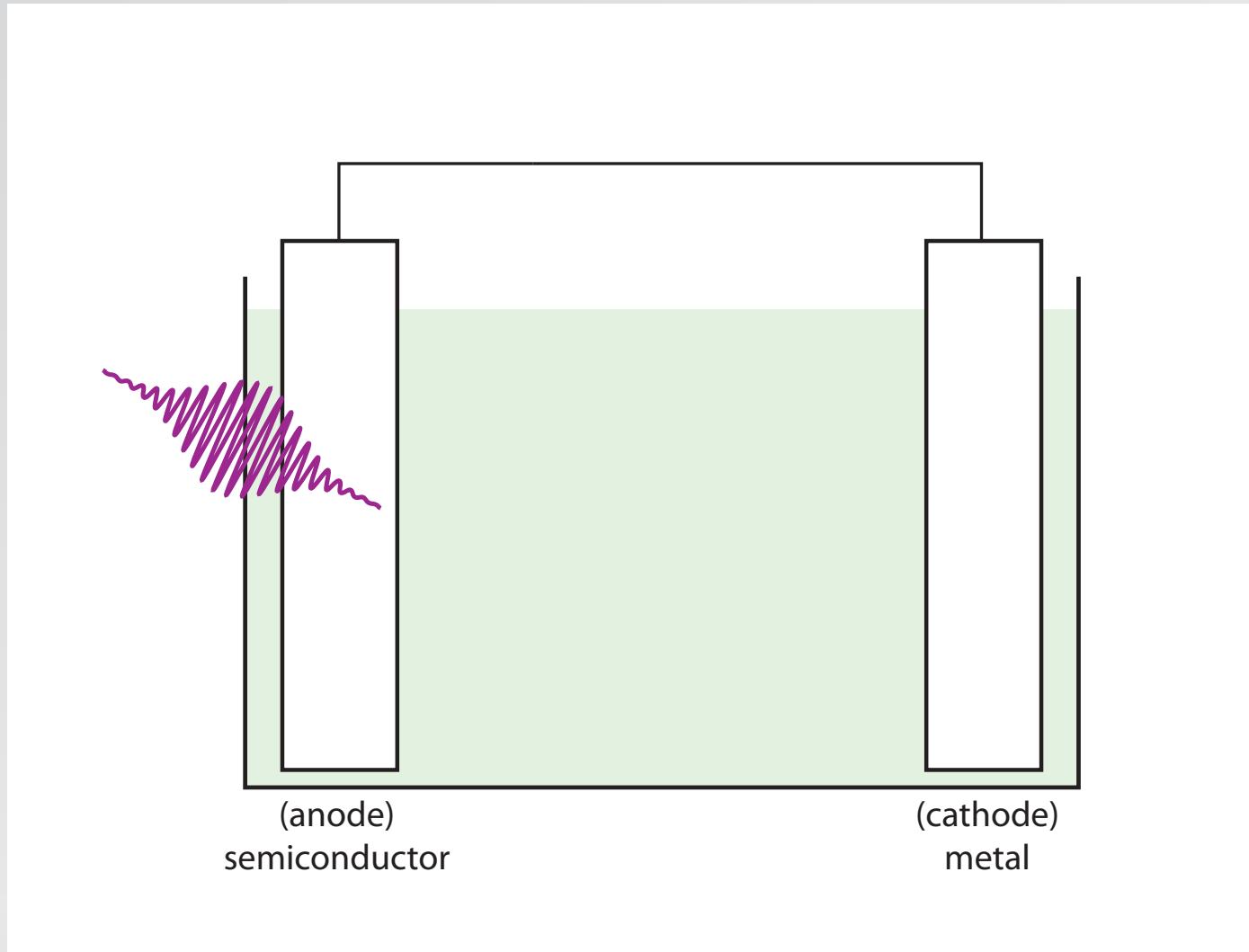


1 intermediate band

2 Si devices

3 X:TiO₂

water splitting

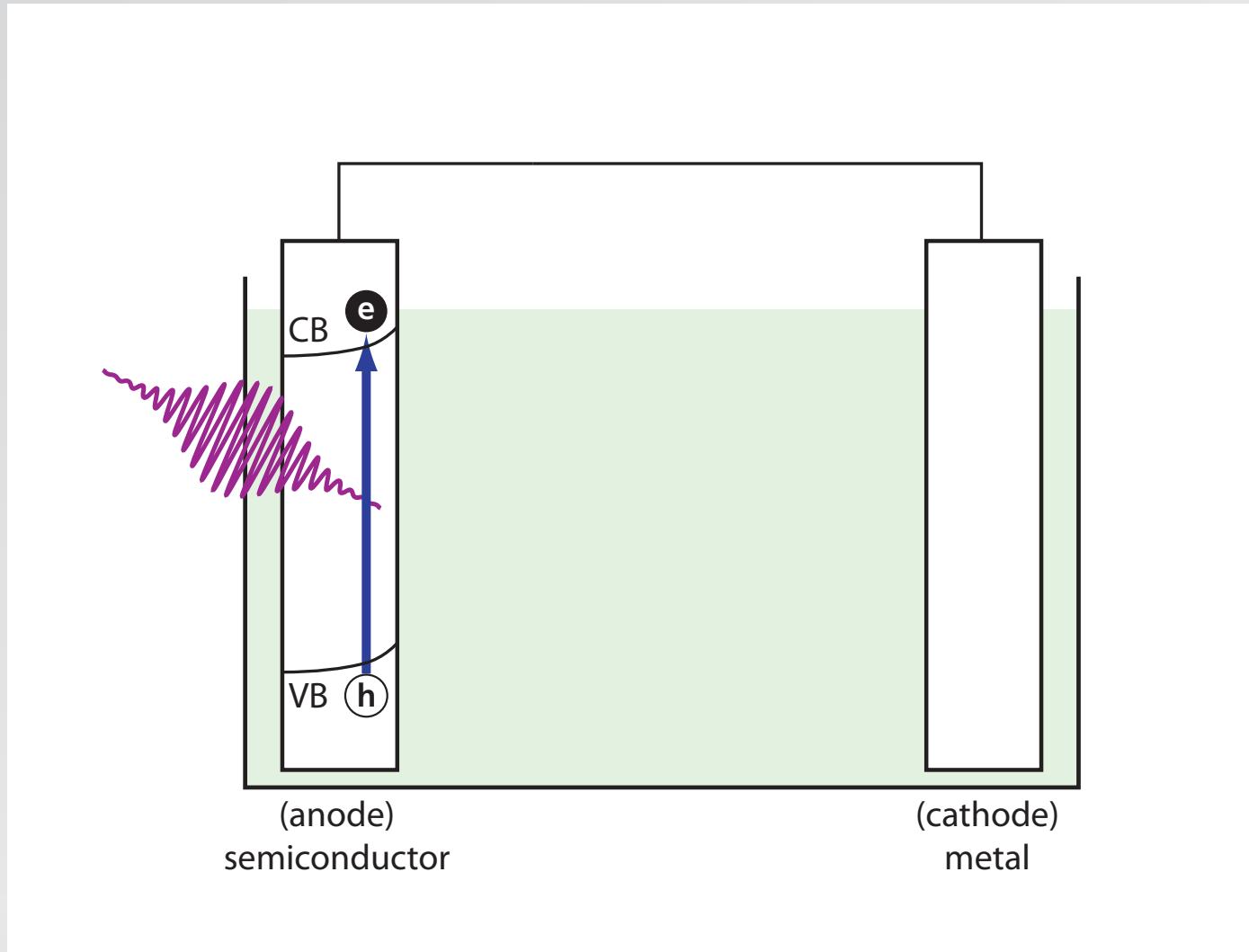


1 intermediate band

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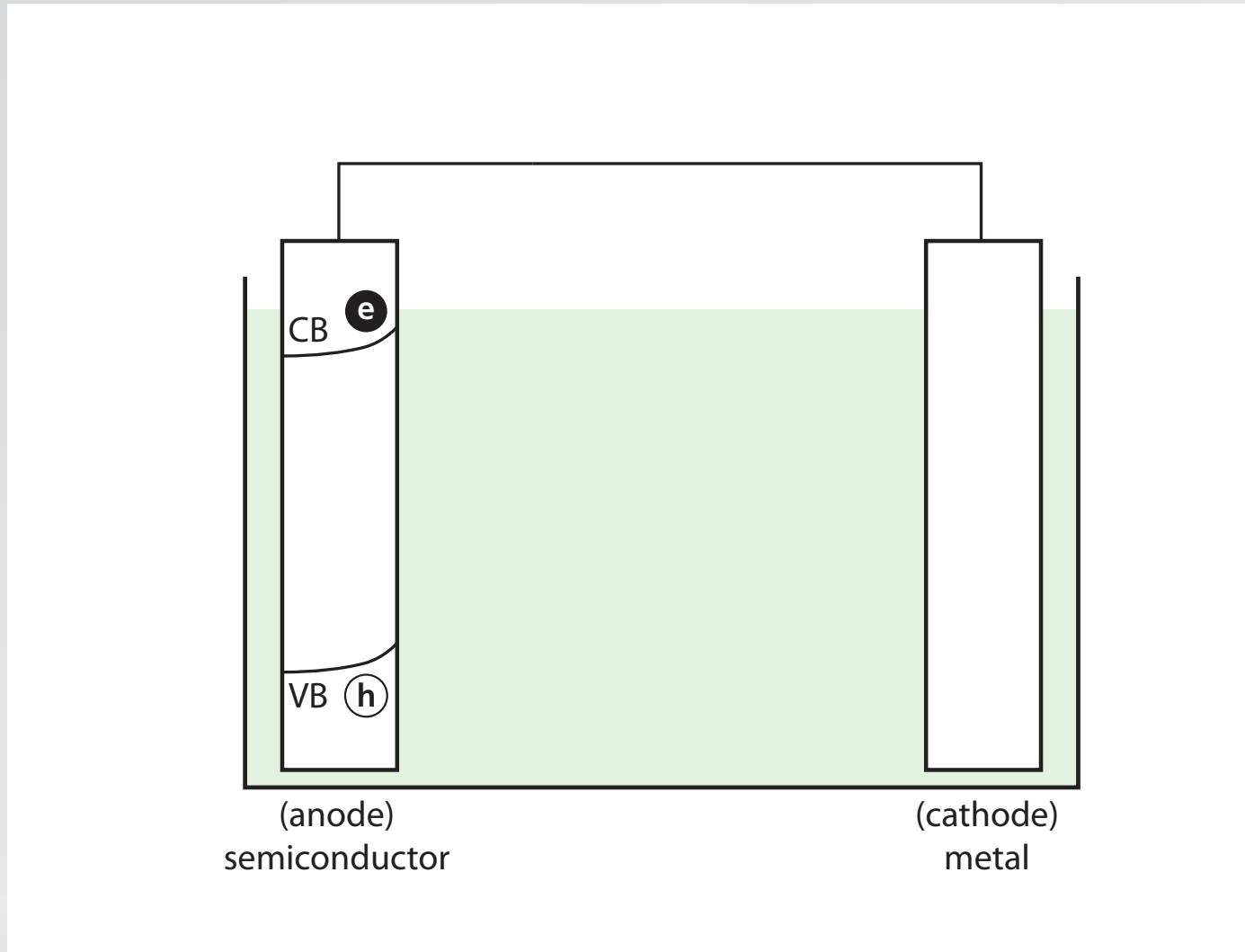


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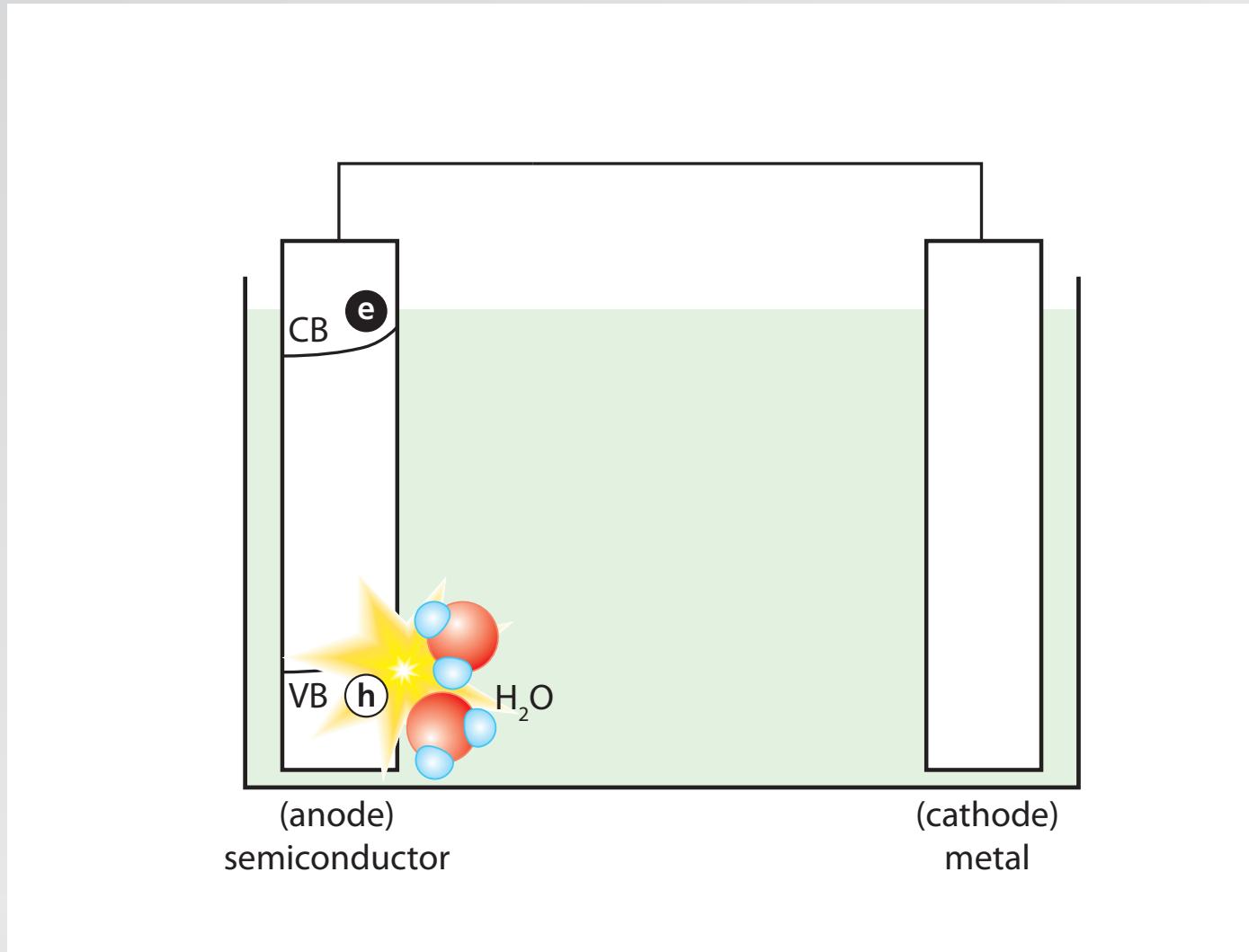


1 intermediate band

2 Si devices

3 X:TiO₂

water splitting

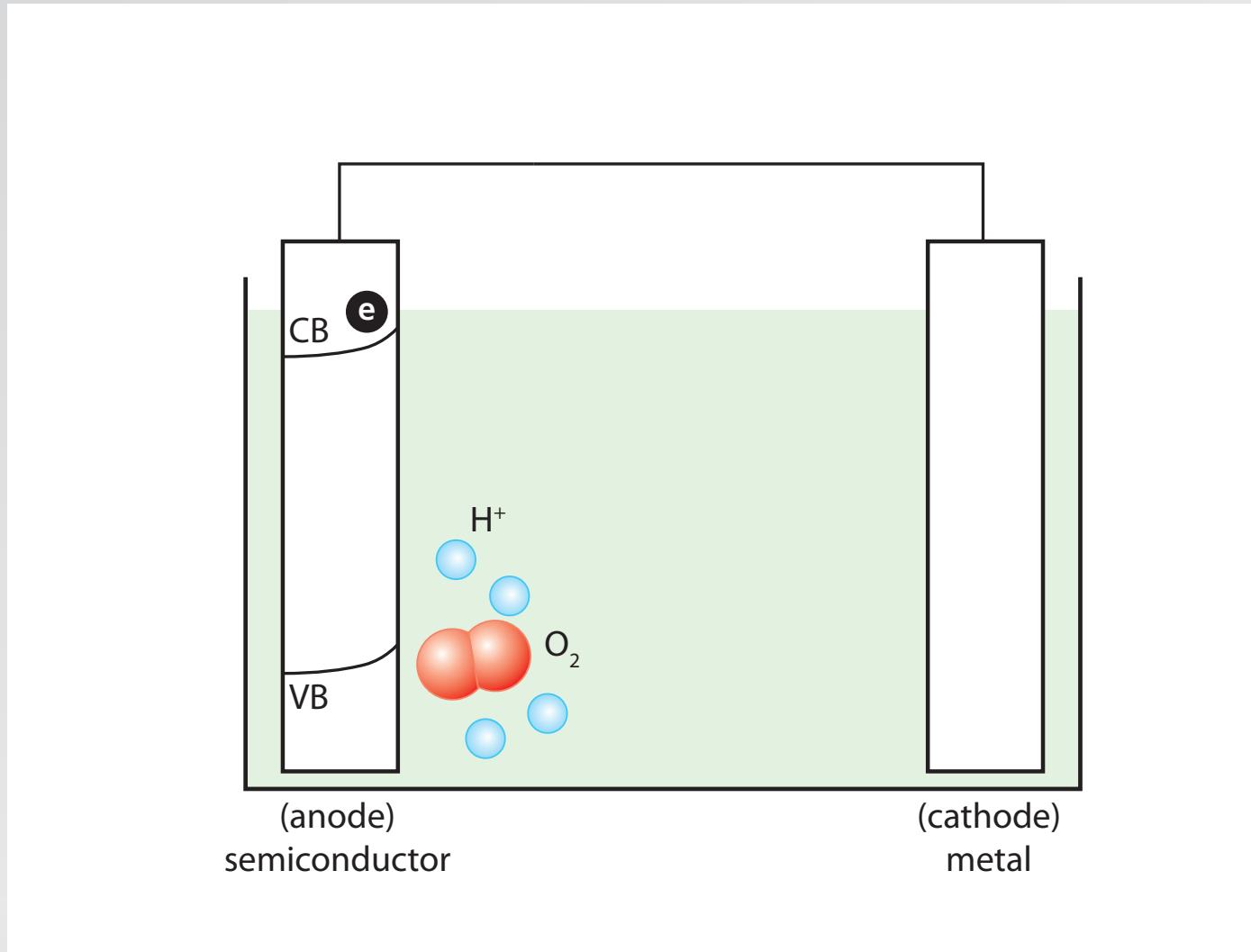


1 intermediate band

2 Si devices

3 X: TiO_2

water splitting

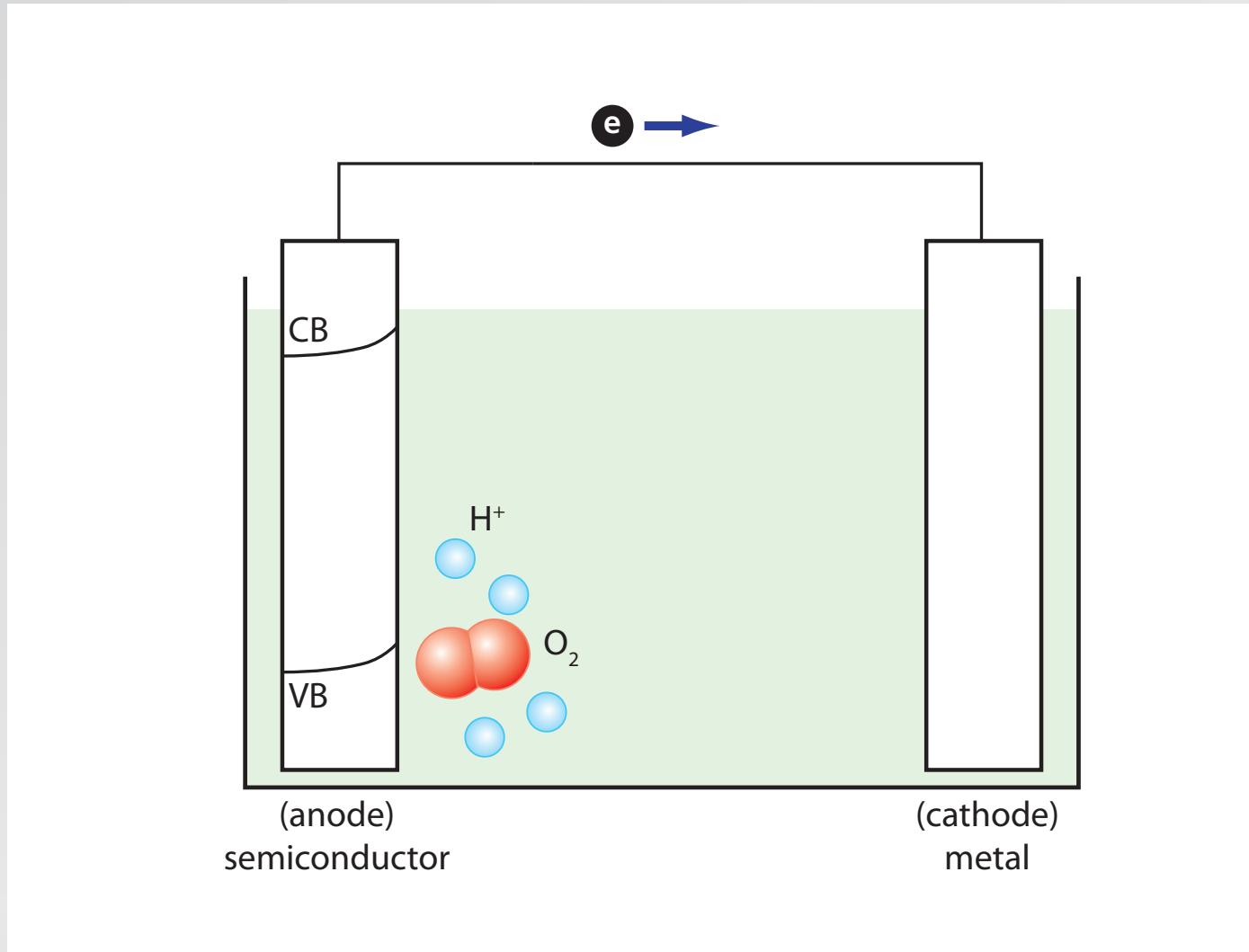


1 intermediate band

2 Si devices

3 X: TiO_2

water splitting

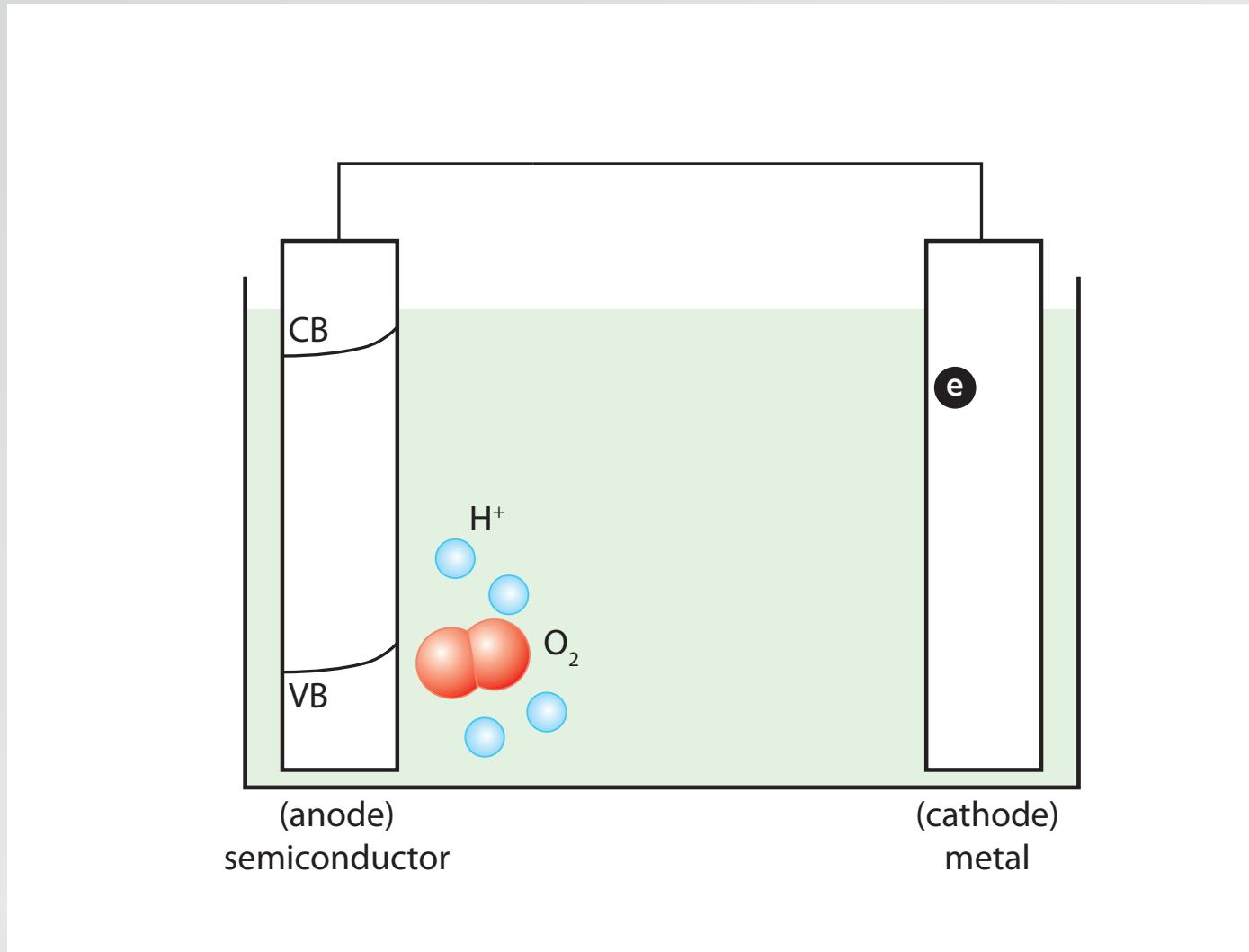


1 intermediate band

2 Si devices

3 X:TiO₂

water splitting

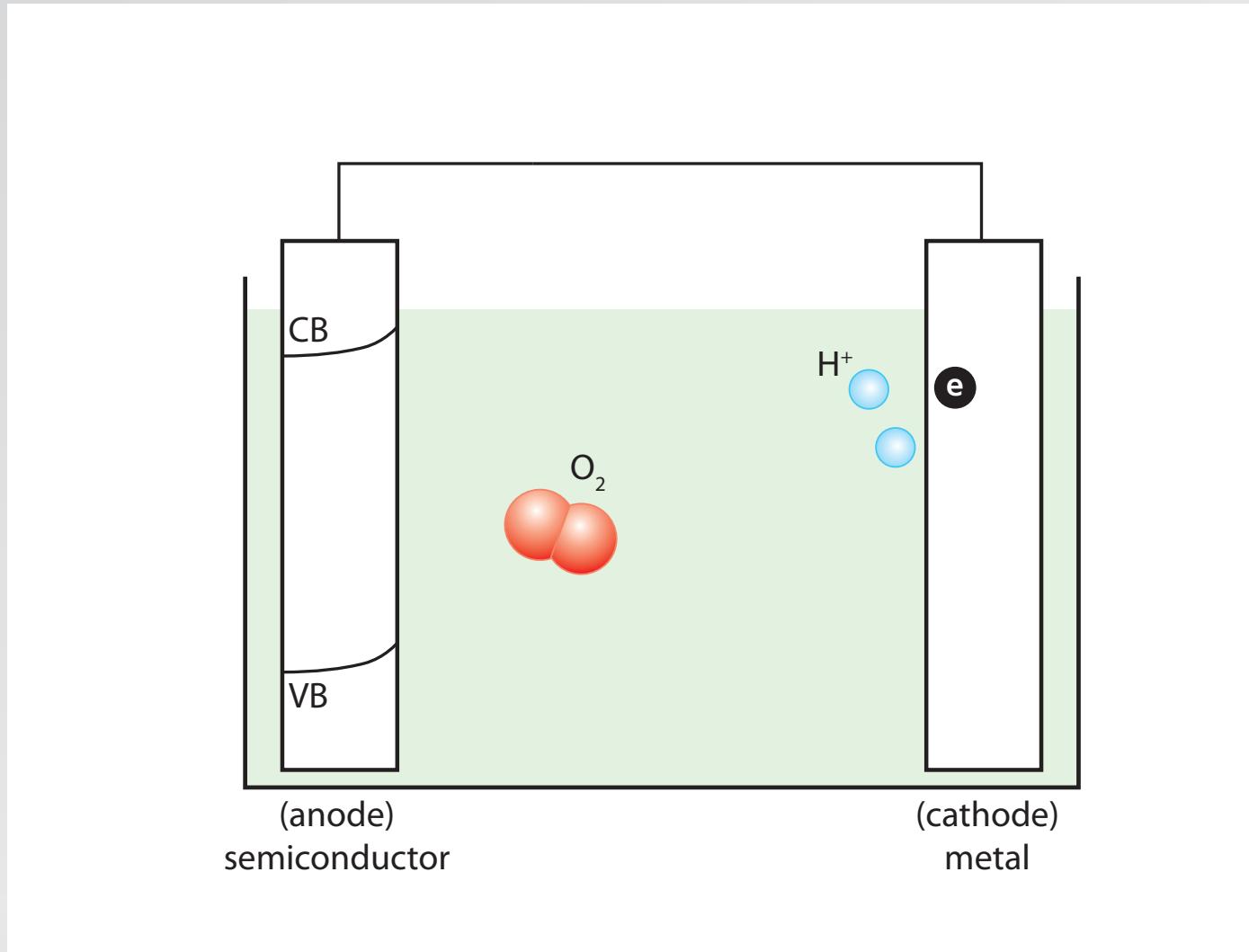


1 intermediate band

2 Si devices

3 X:TiO₂

water splitting

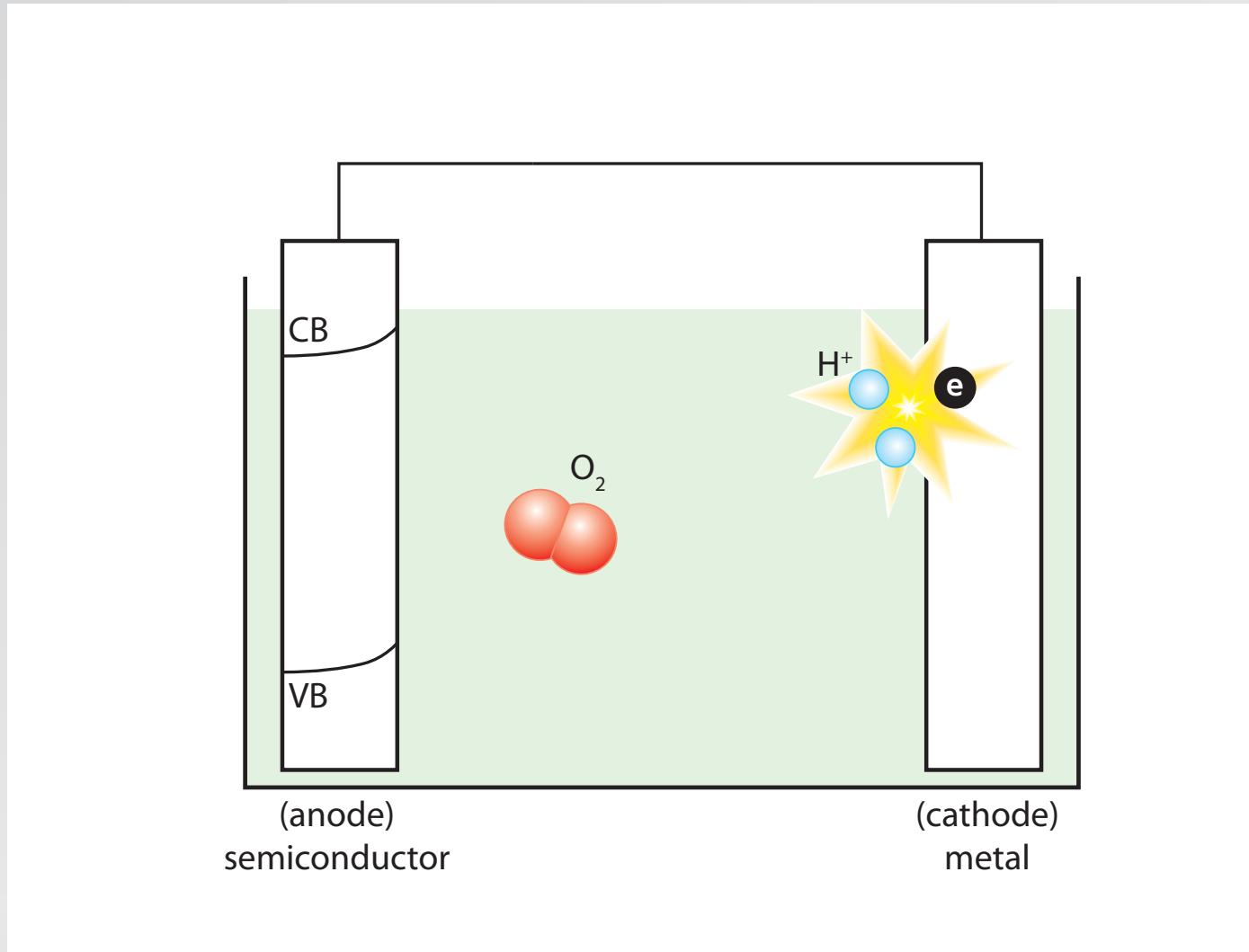


1 intermediate band

2 Si devices

3 X: TiO_2

water splitting

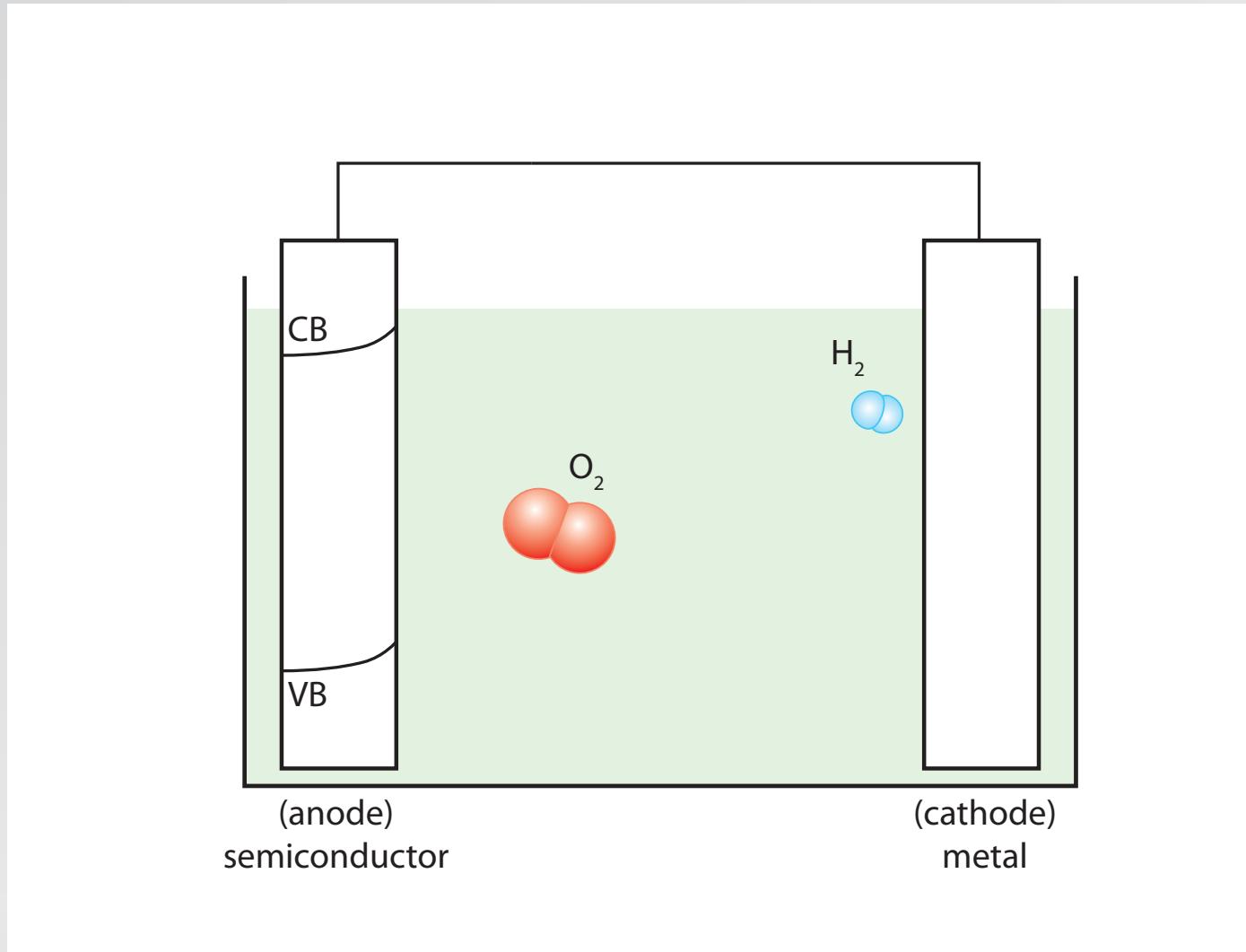


1 intermediate band

2 Si devices

3 X: TiO_2

water splitting

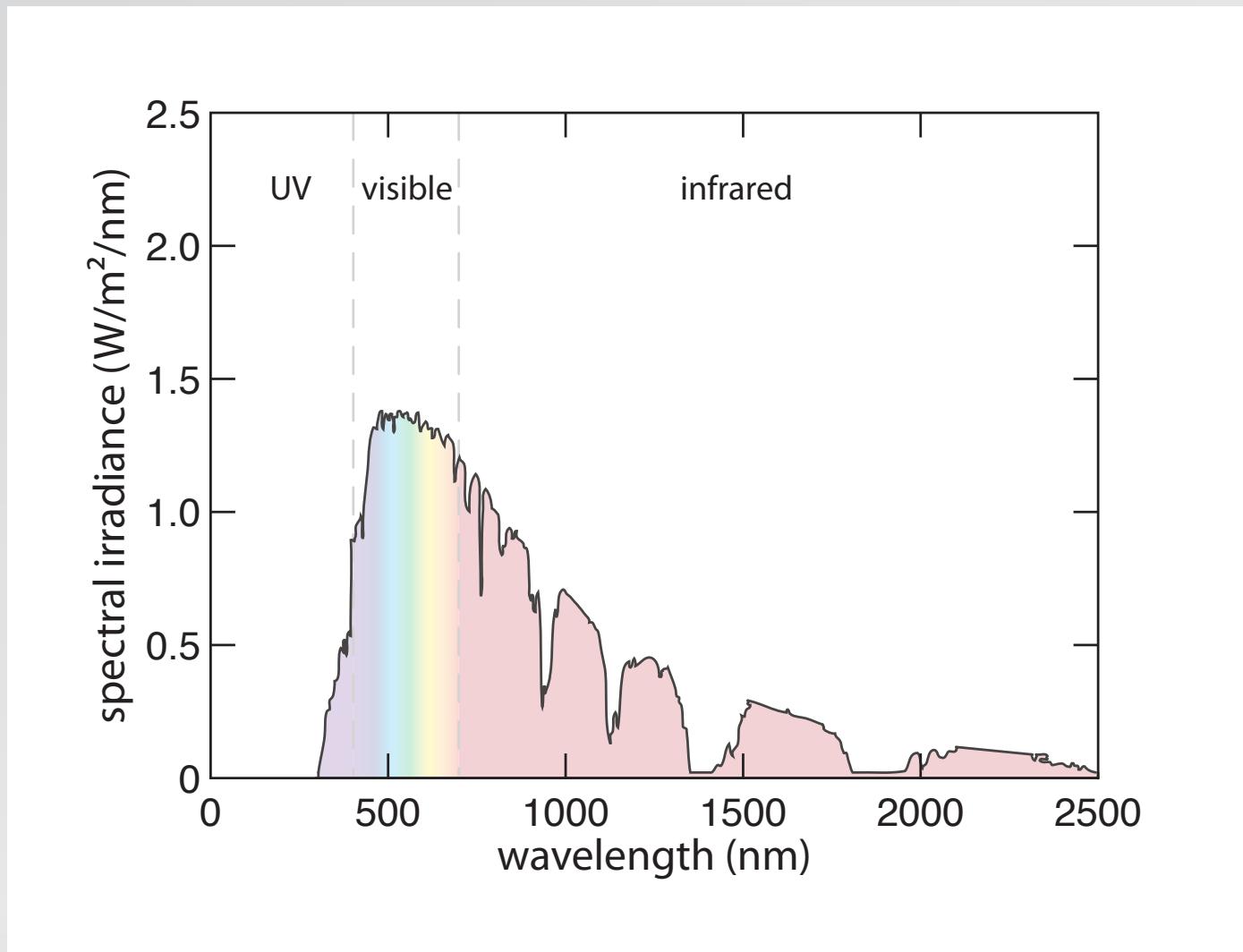


1 intermediate band

2 Si devices

3 X: TiO_2

solar radiation spectrum

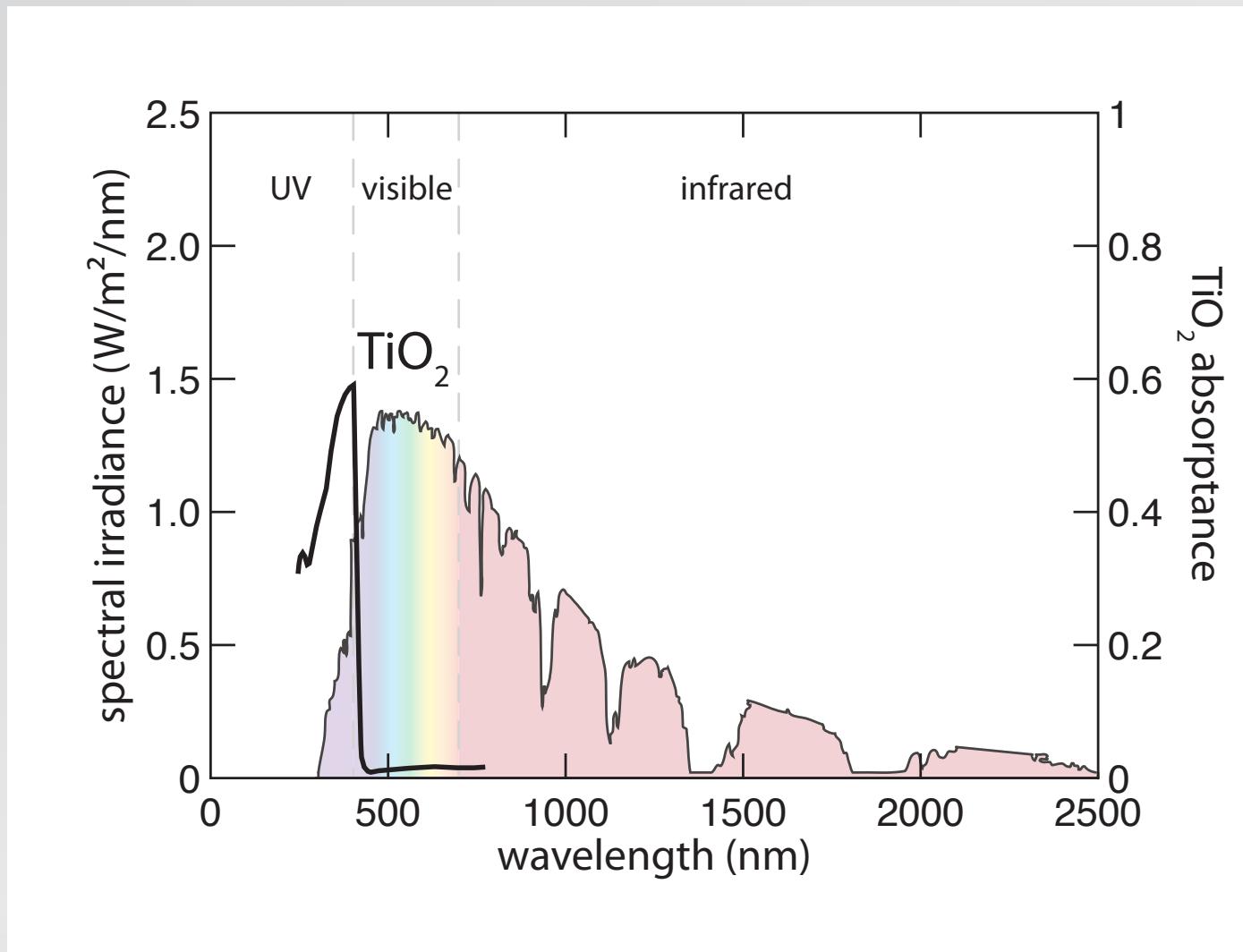


1 intermediate band

2 Si devices

3 X: TiO_2

solar radiation spectrum

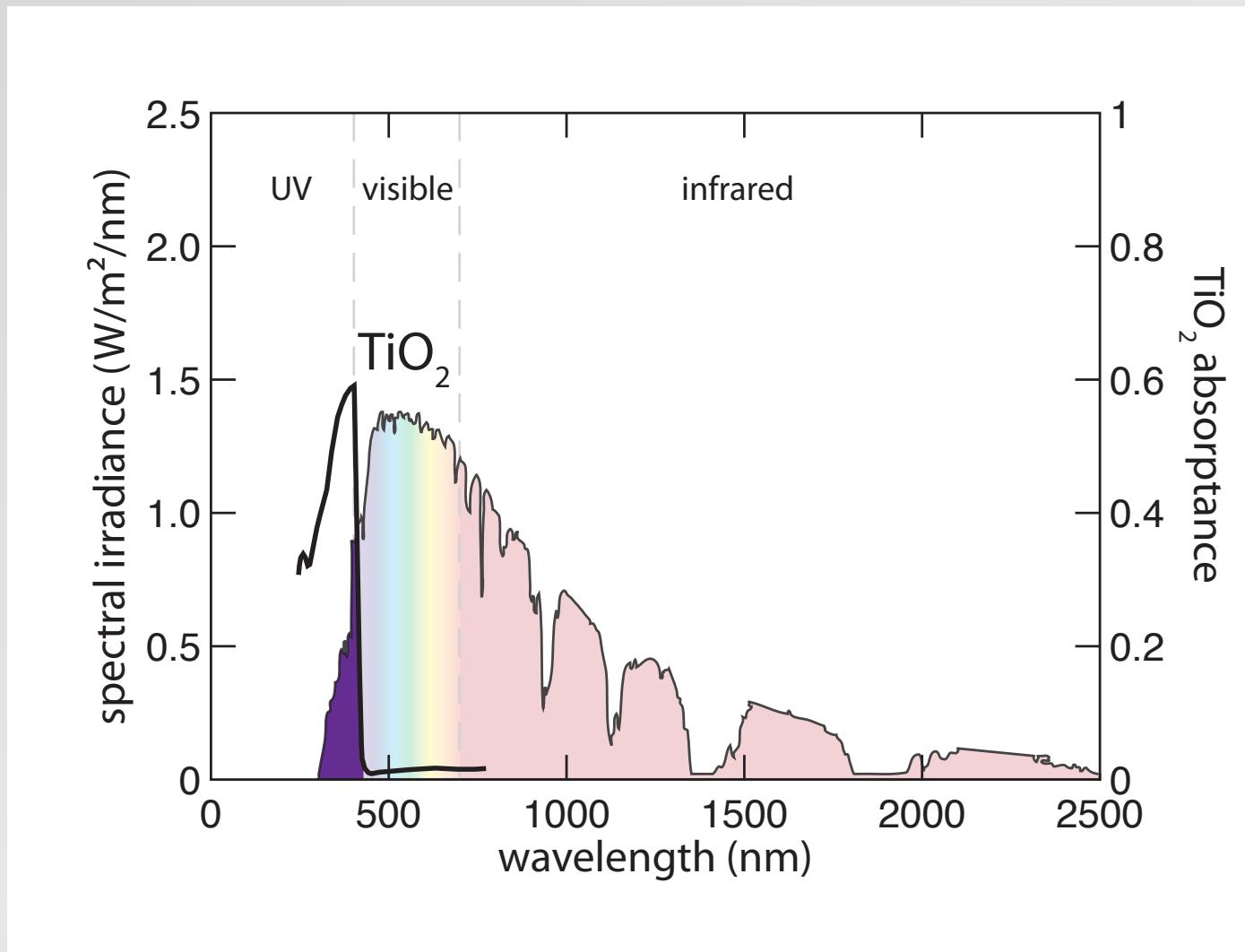


1 intermediate band

2 Si devices

3 X: TiO_2

solar radiation spectrum



1 intermediate band

2 Si devices

3 X: TiO_2



increase efficiency by:

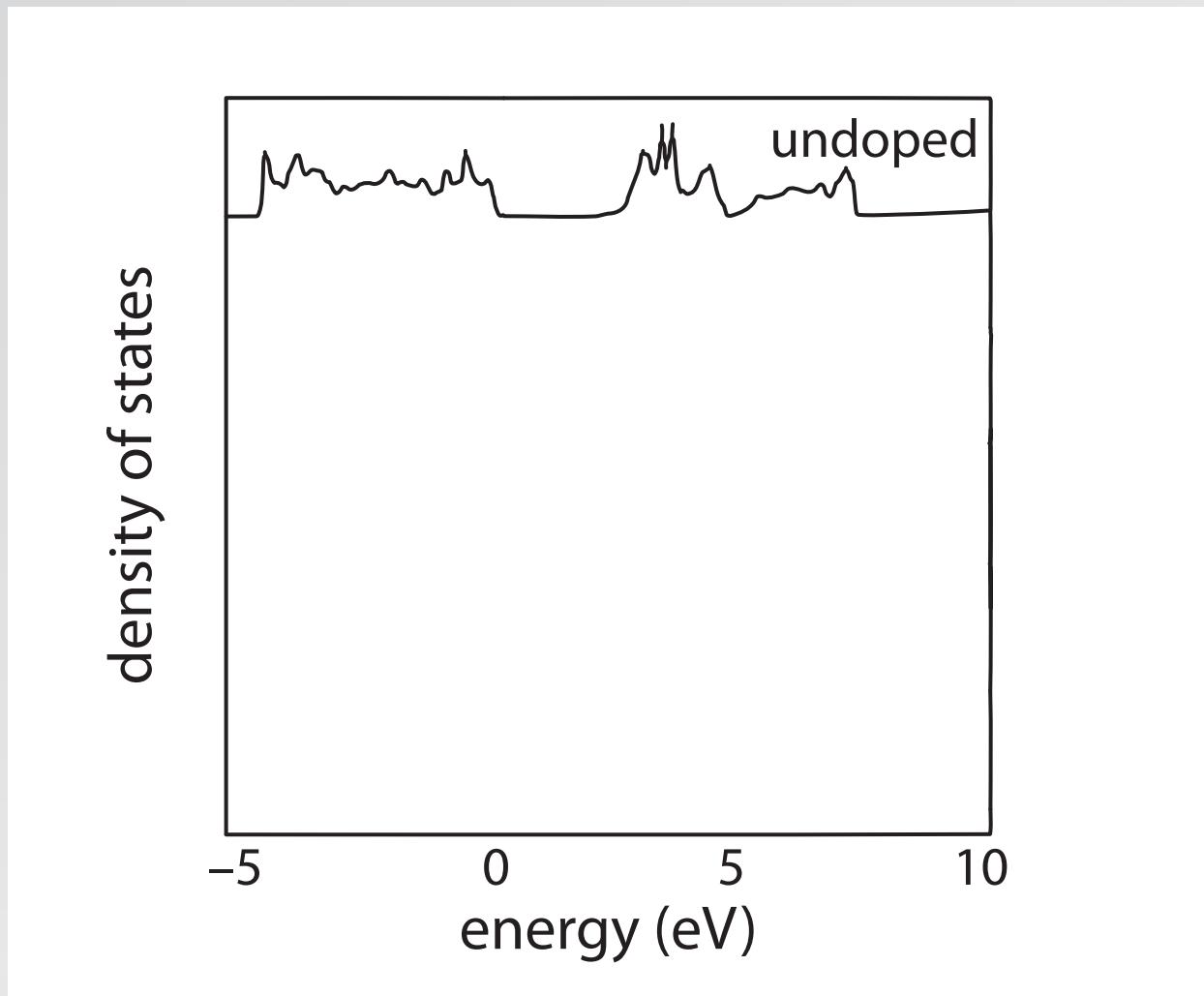
- increasing surface area
- shifting band edge

1 intermediate band

2 Si devices

3 X: TiO_2

TiO₂ density of states



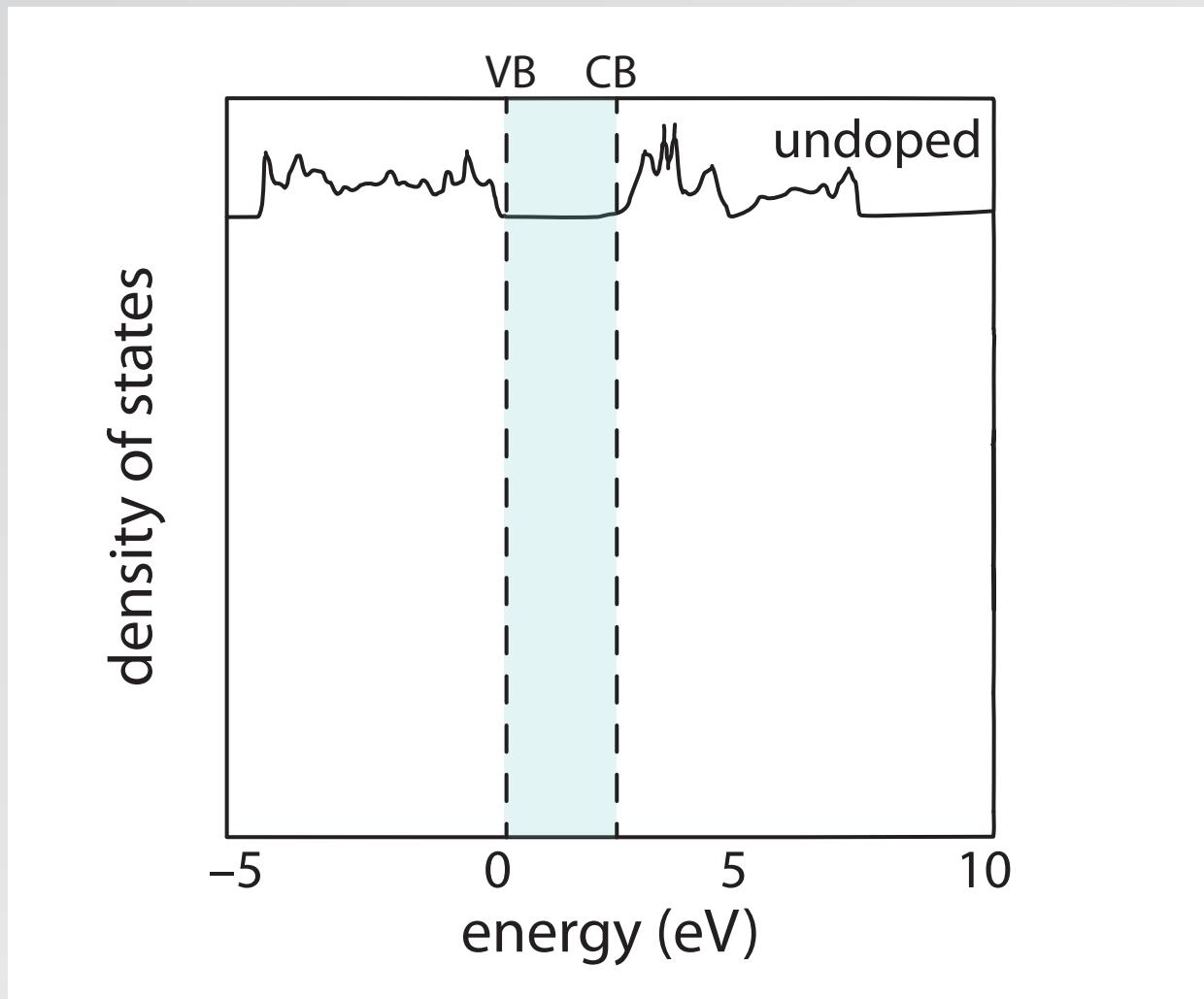
Asahi *et al.*, Science (2003)

1 intermediate band

2 Si devices

3 X:TiO₂

need to create band(s) in gap



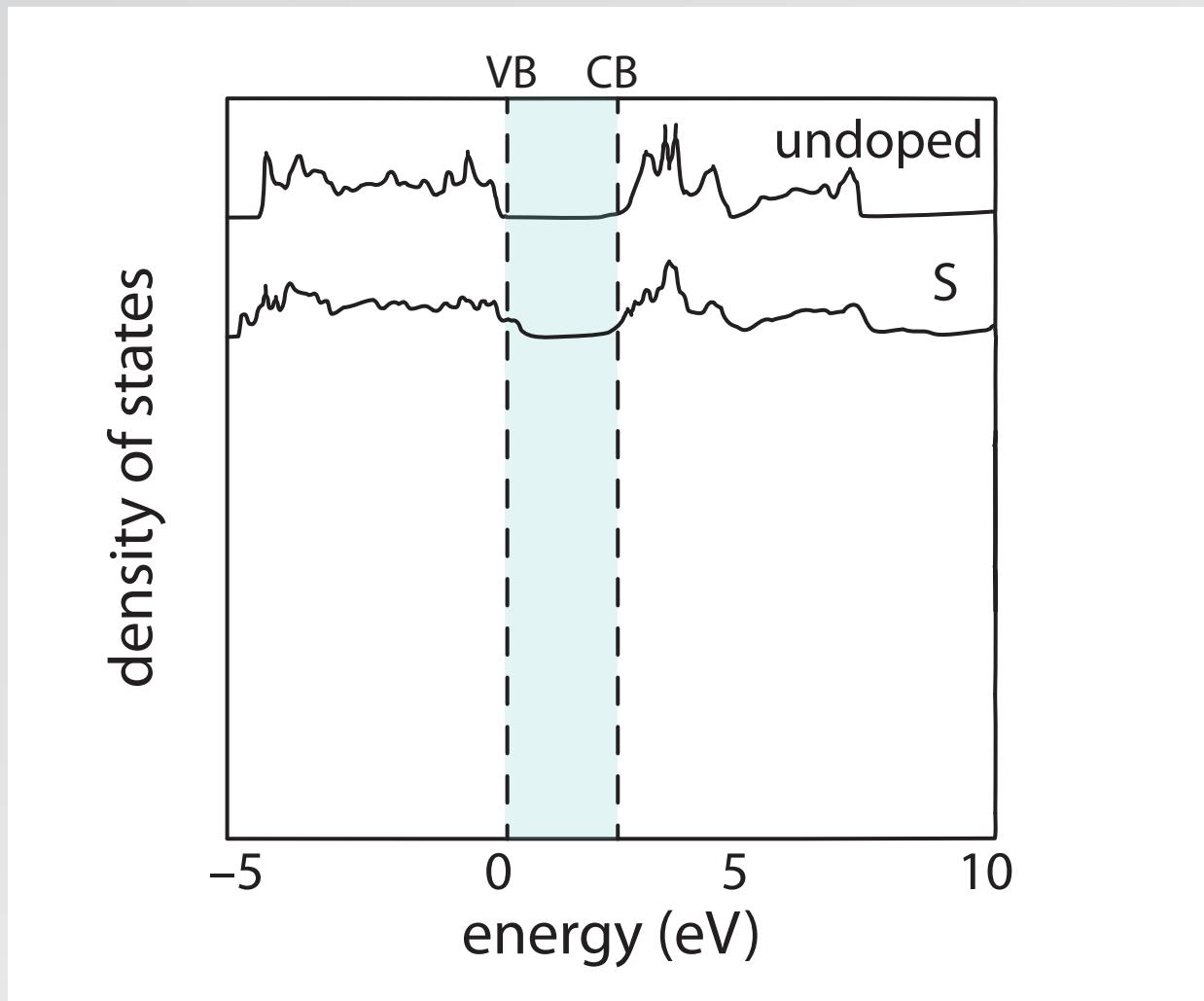
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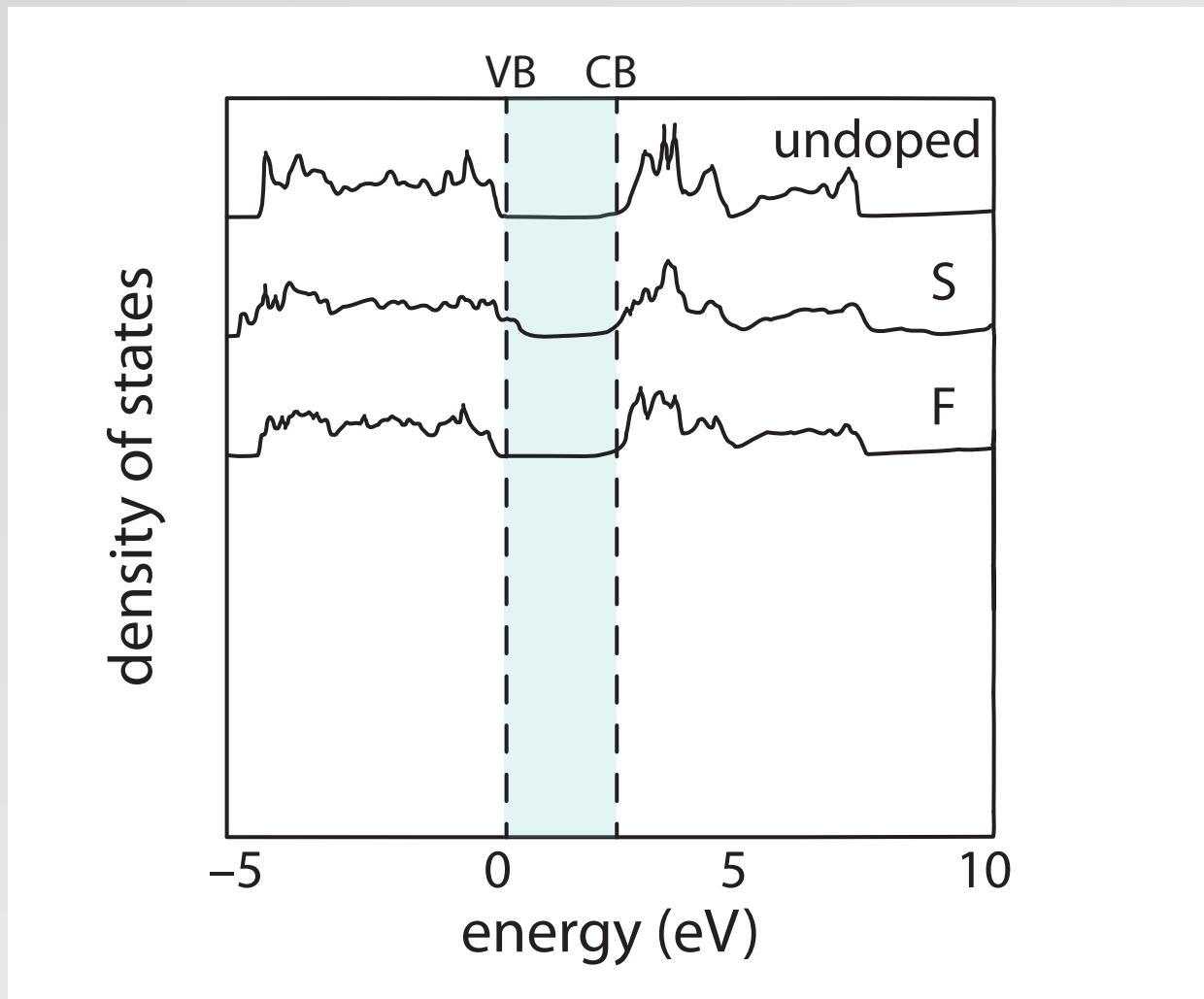
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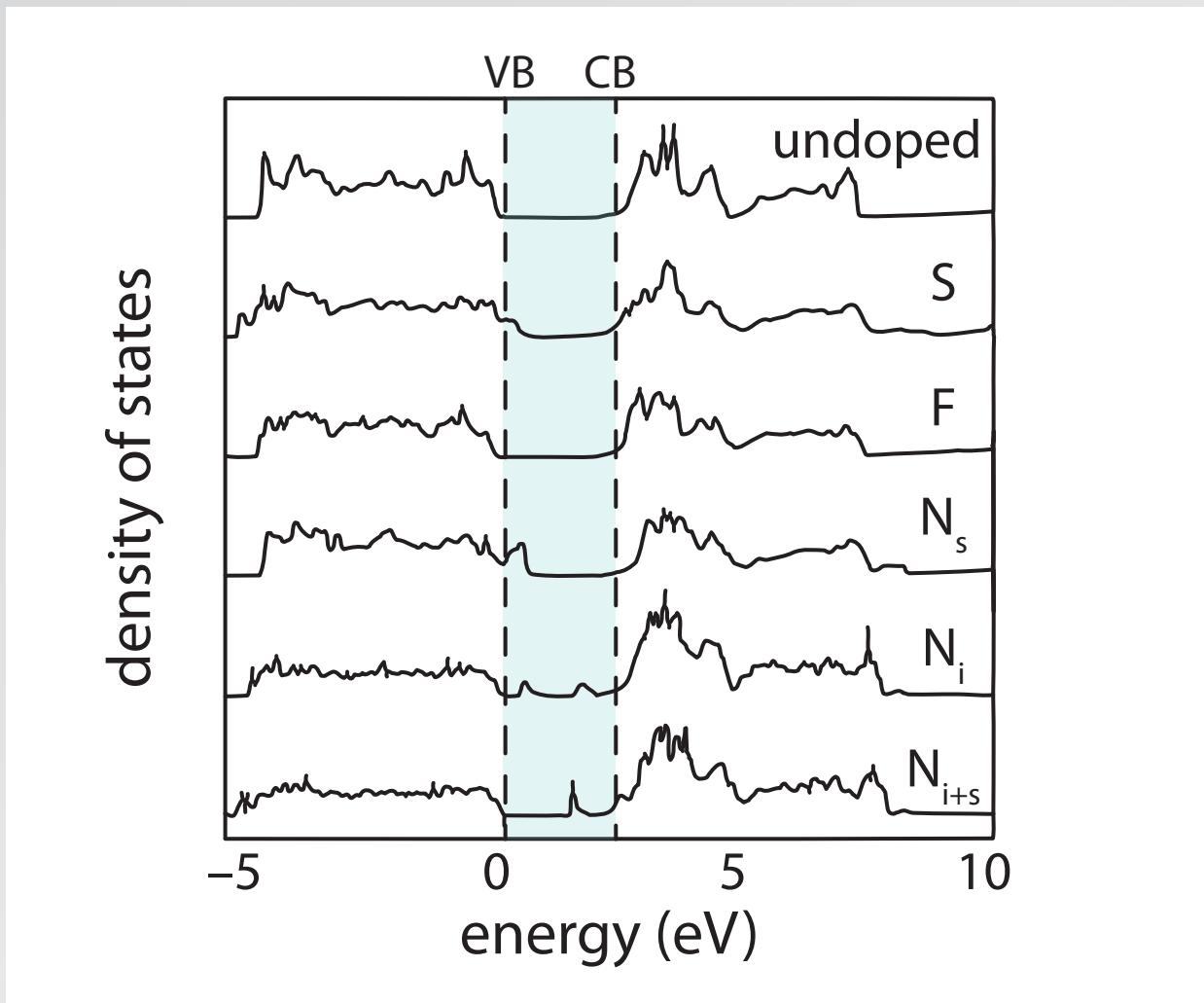
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1 intermediate band

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1 intermediate band

2 Si devices

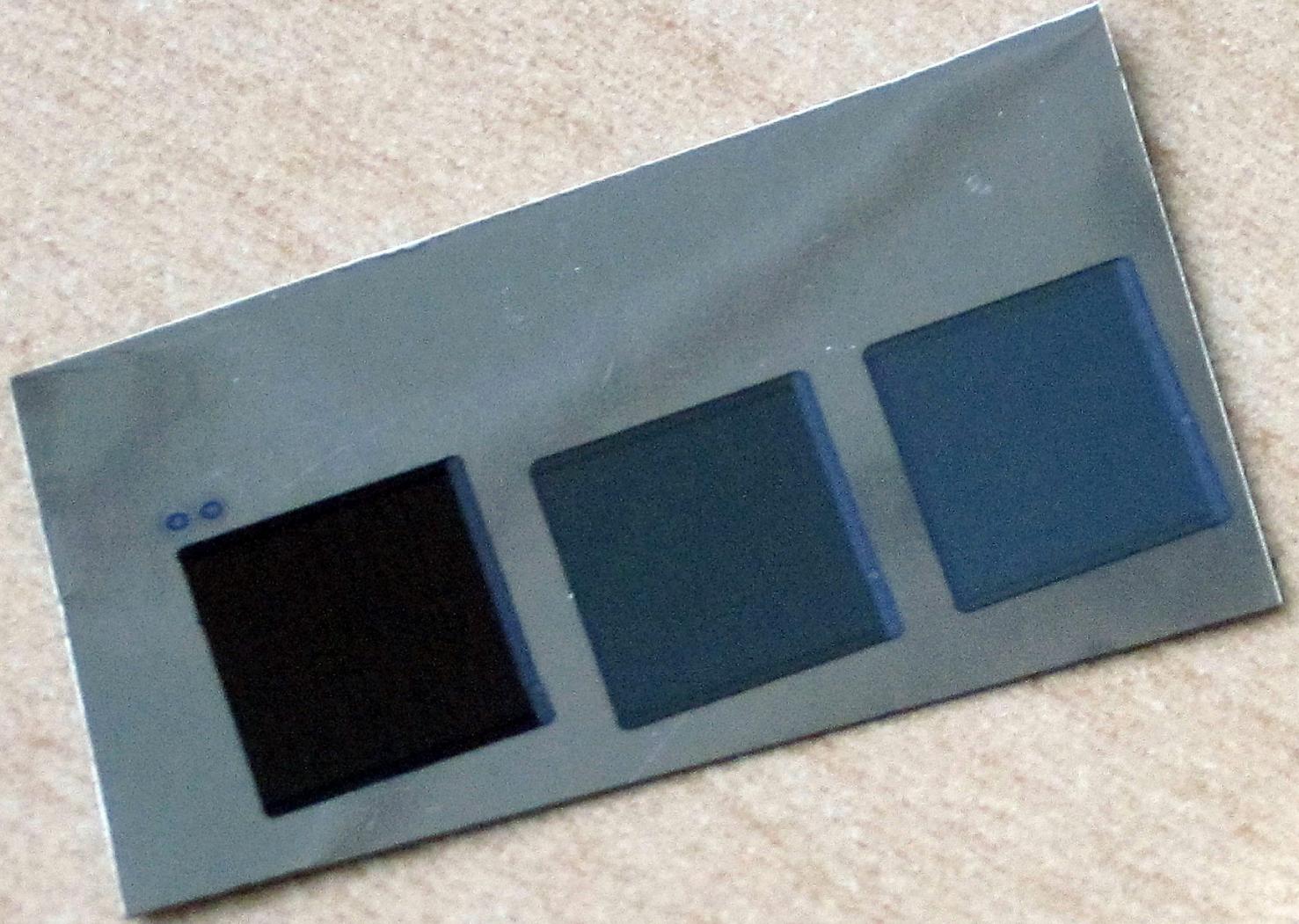
3 X:TiO₂

structuring TiO_2 in N_2 doesn't work

1 intermediate band

2 Si devices

3 X: TiO_2

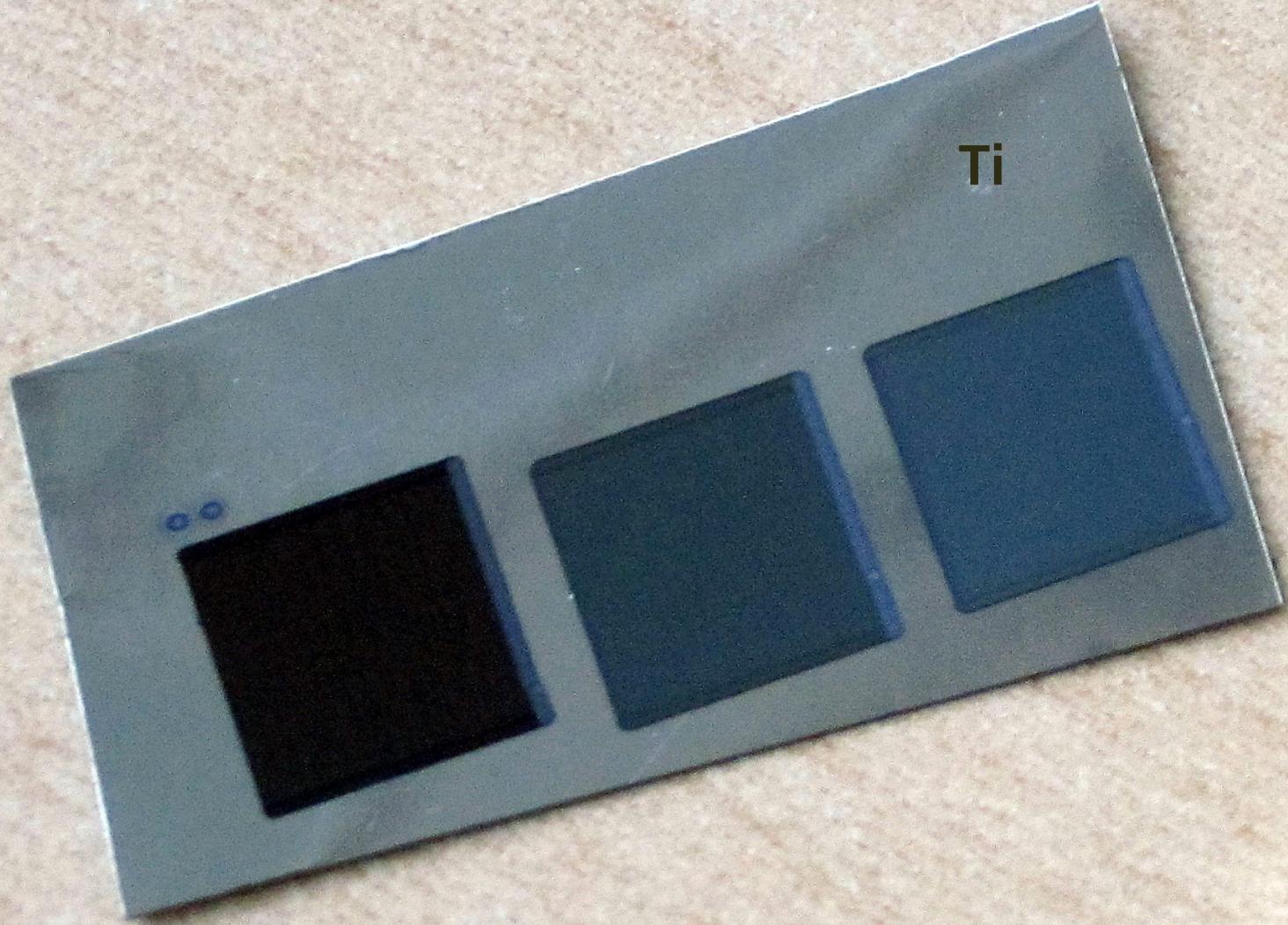


1 intermediate band

2 Si devices

3 X:TiO₂



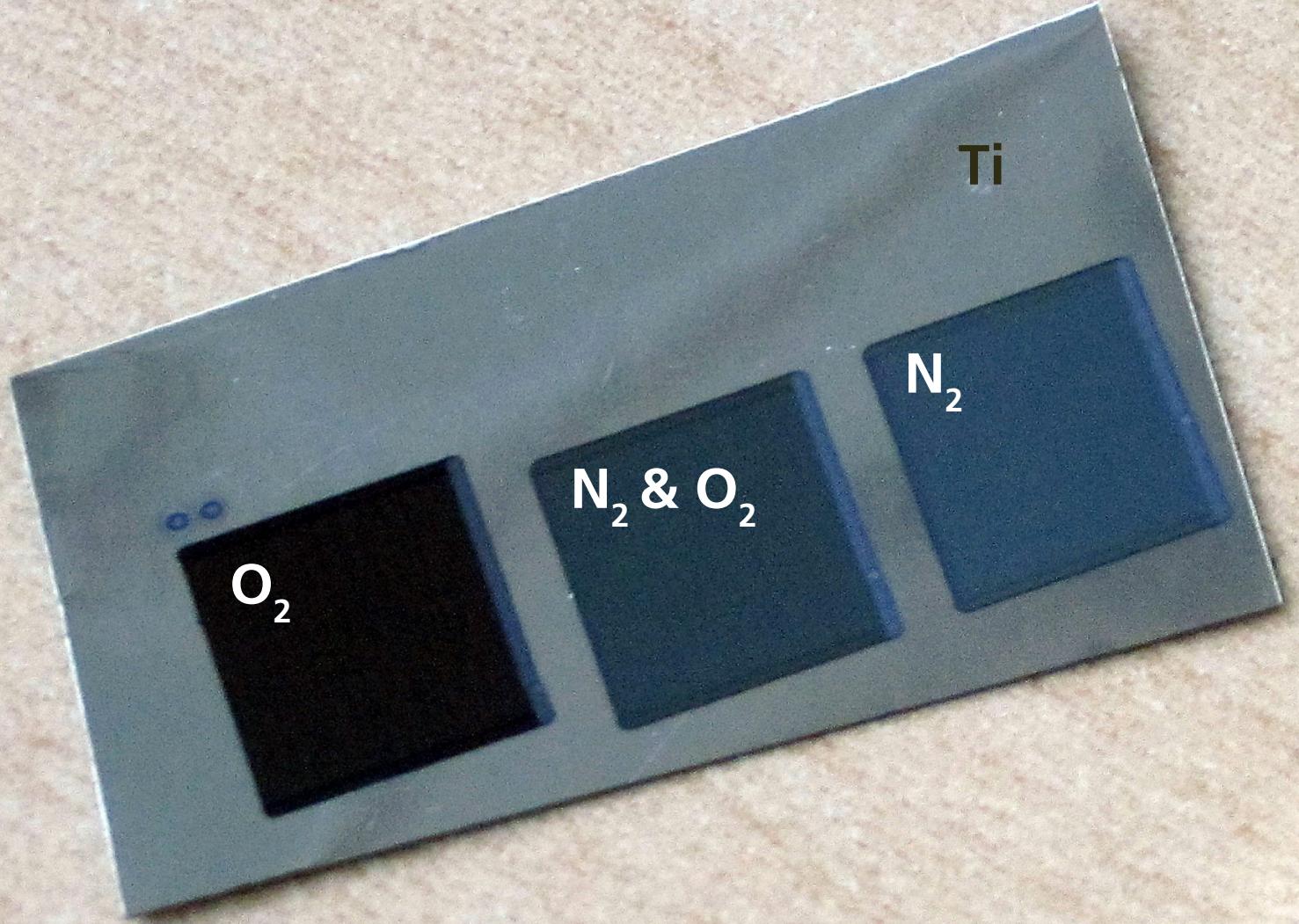


1 intermediate band

2 Si devices

3 X: TiO_2



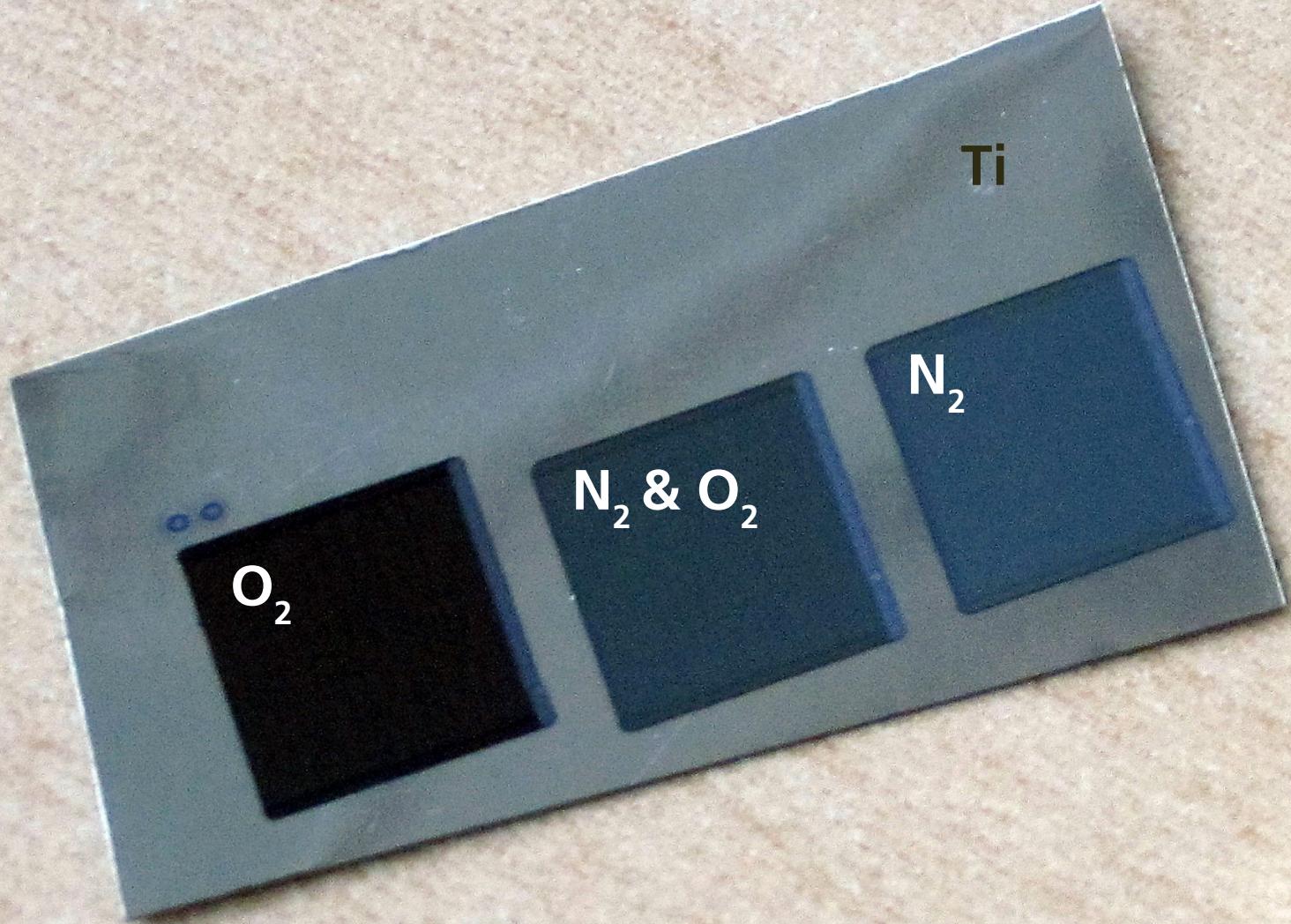


1 intermediate band

2 Si devices

3 X:TiO₂





50 pulses @ 2.5 kJ/m²

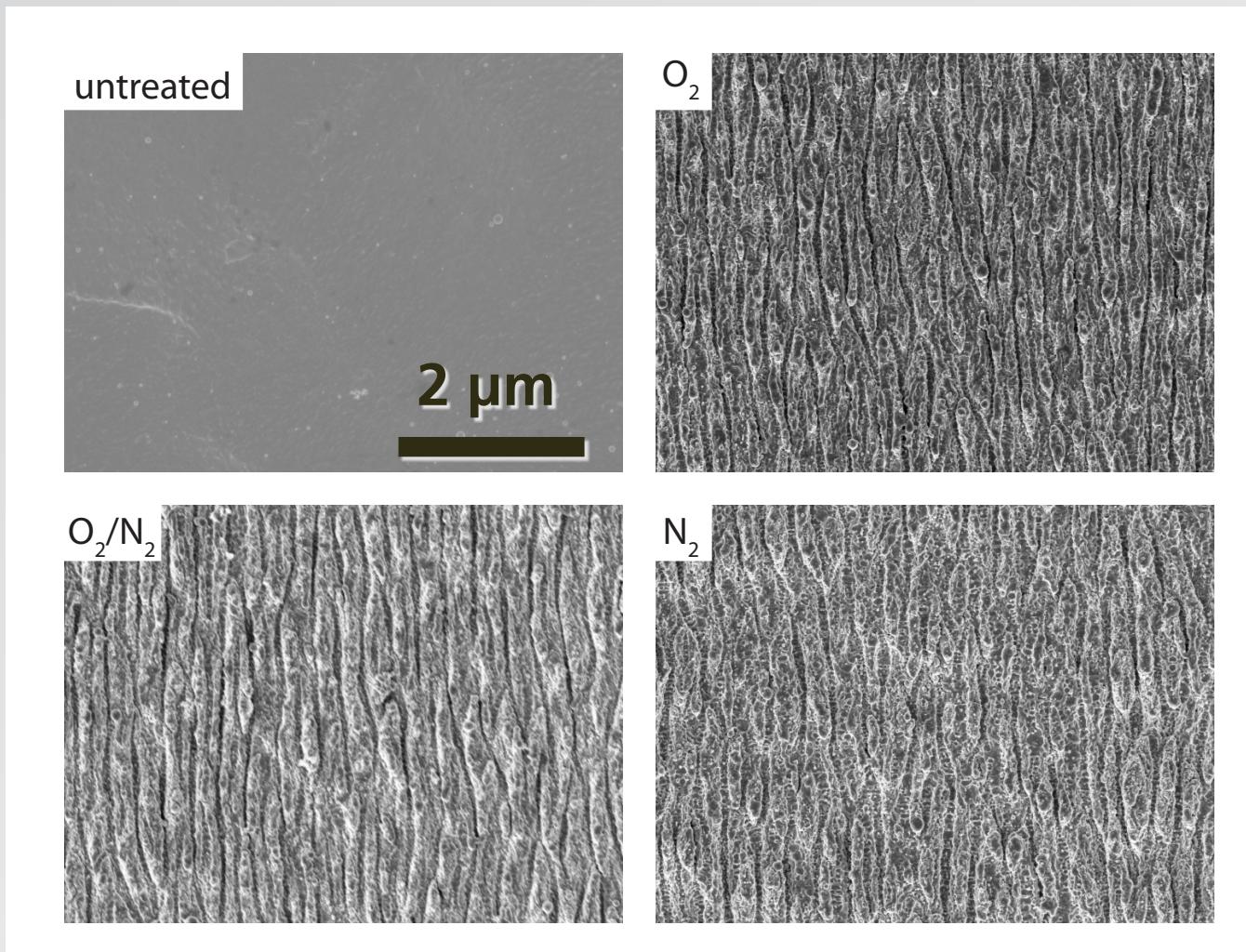
1 intermediate band

2 Si devices

3 X:TiO₂



50 pulses @ 2.5 kJ/m²

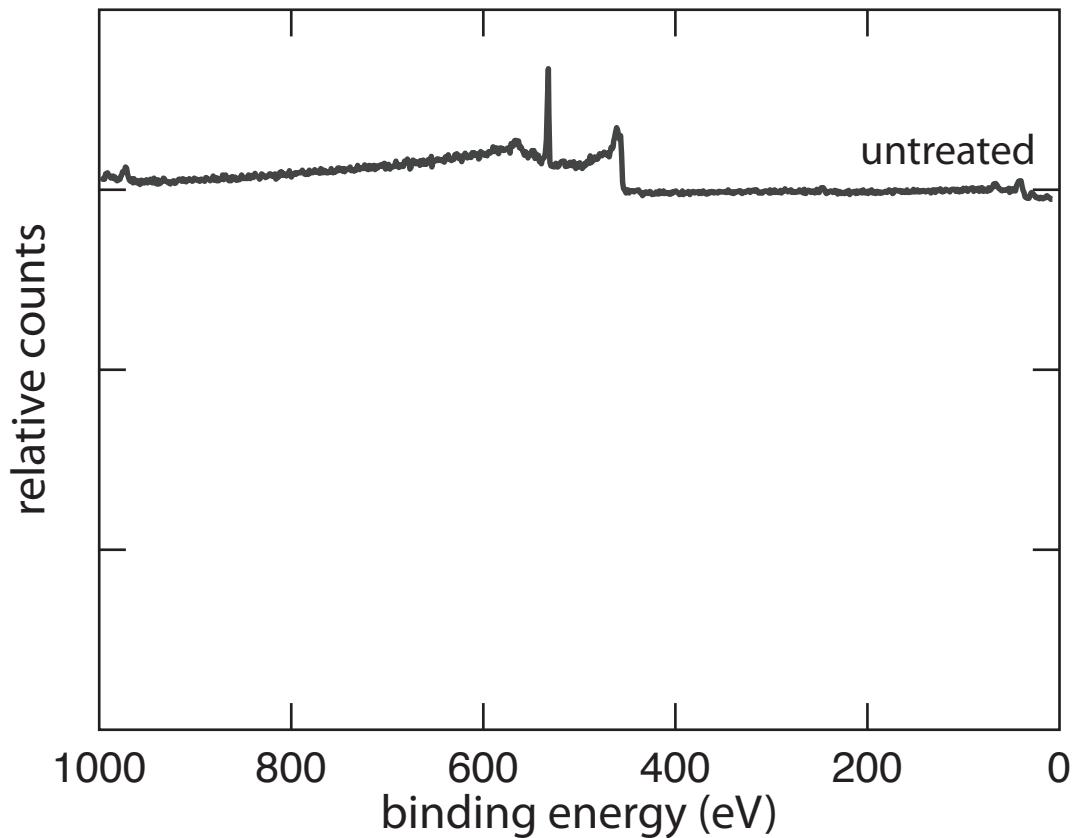


1 intermediate band

2 Si devices

3 X:TiO₂

X-ray photoelectron spectroscopy

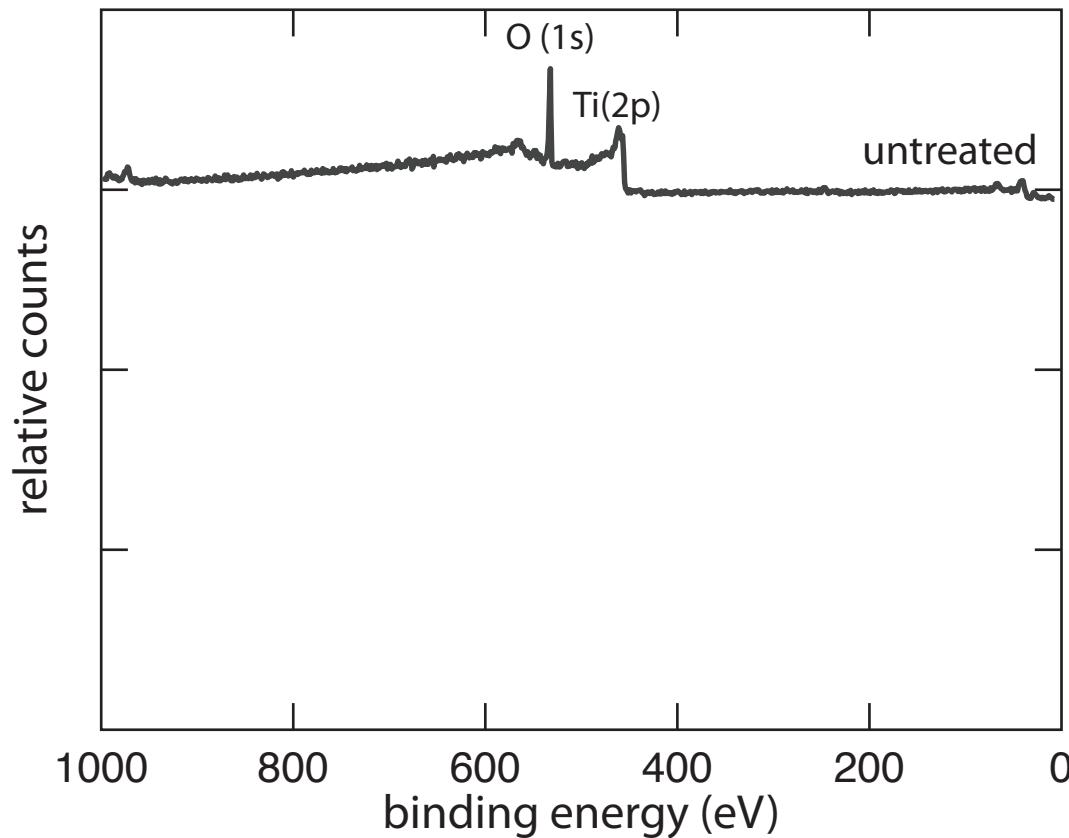


1 intermediate band

2 Si devices

3 X:TiO₂

X-ray photoelectron spectroscopy

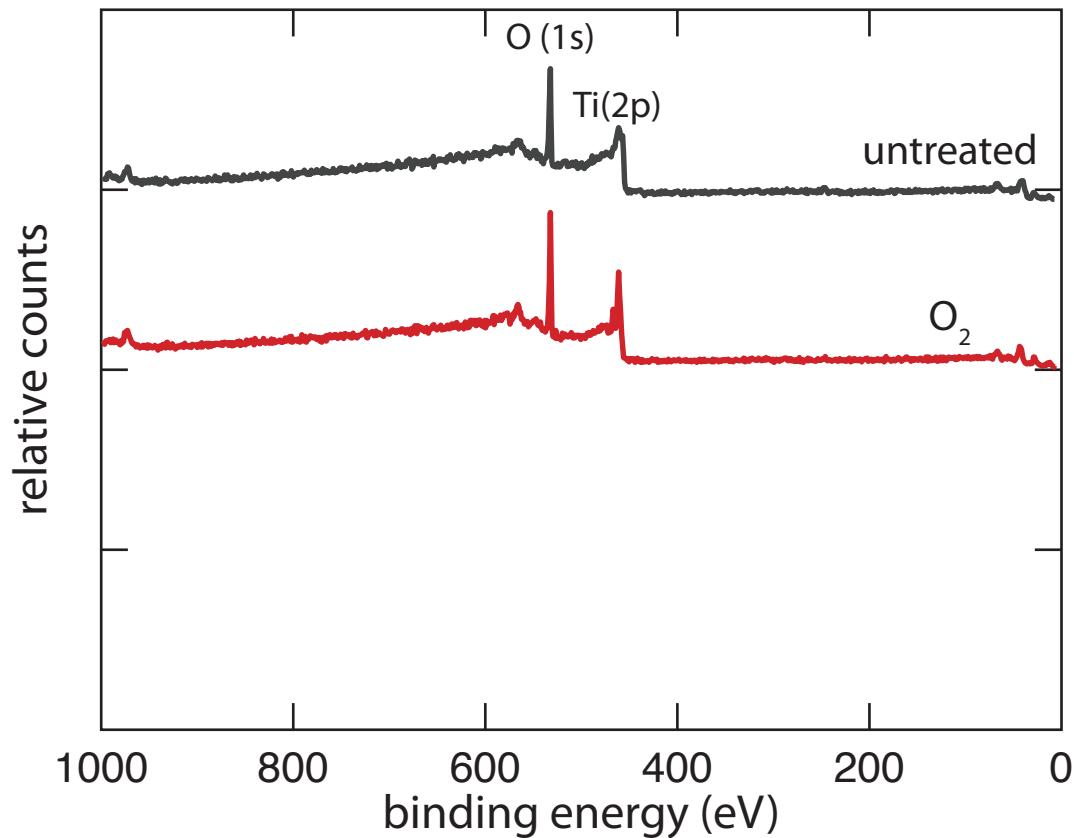


1 intermediate band

2 Si devices

3 X:TiO₂

X-ray photoelectron spectroscopy

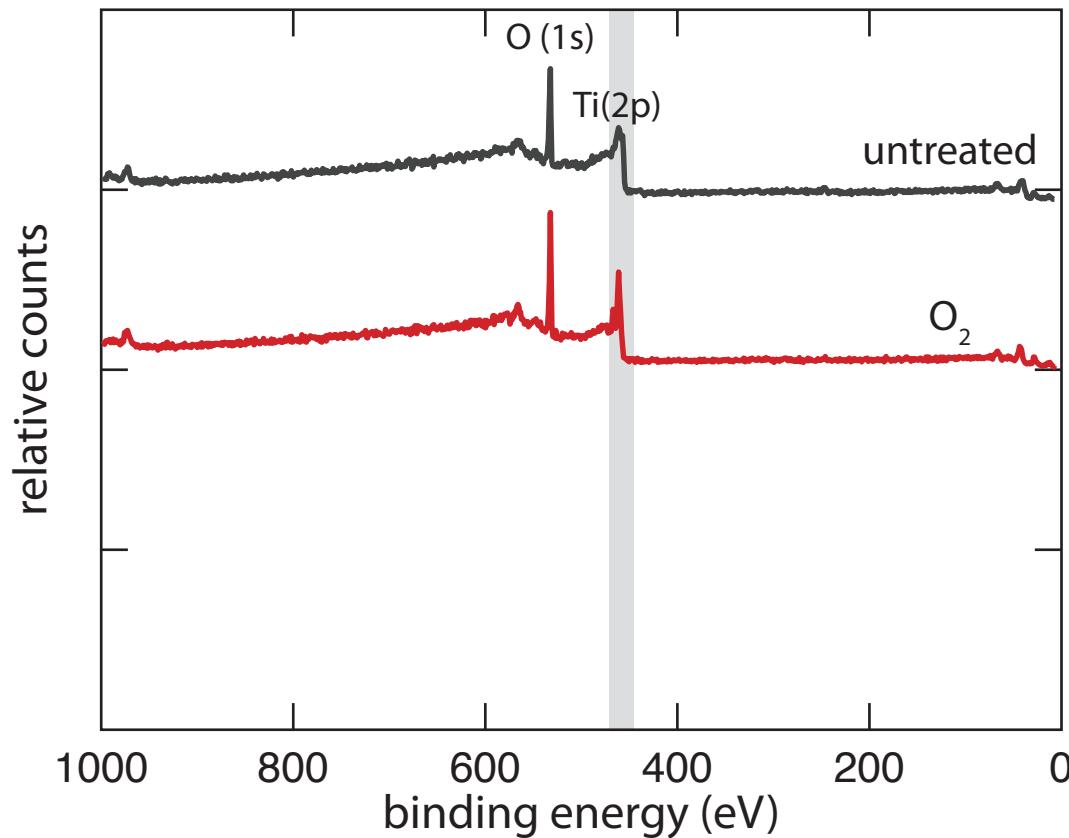


1 intermediate band

2 Si devices

3 X:TiO₂

X-ray photoelectron spectroscopy

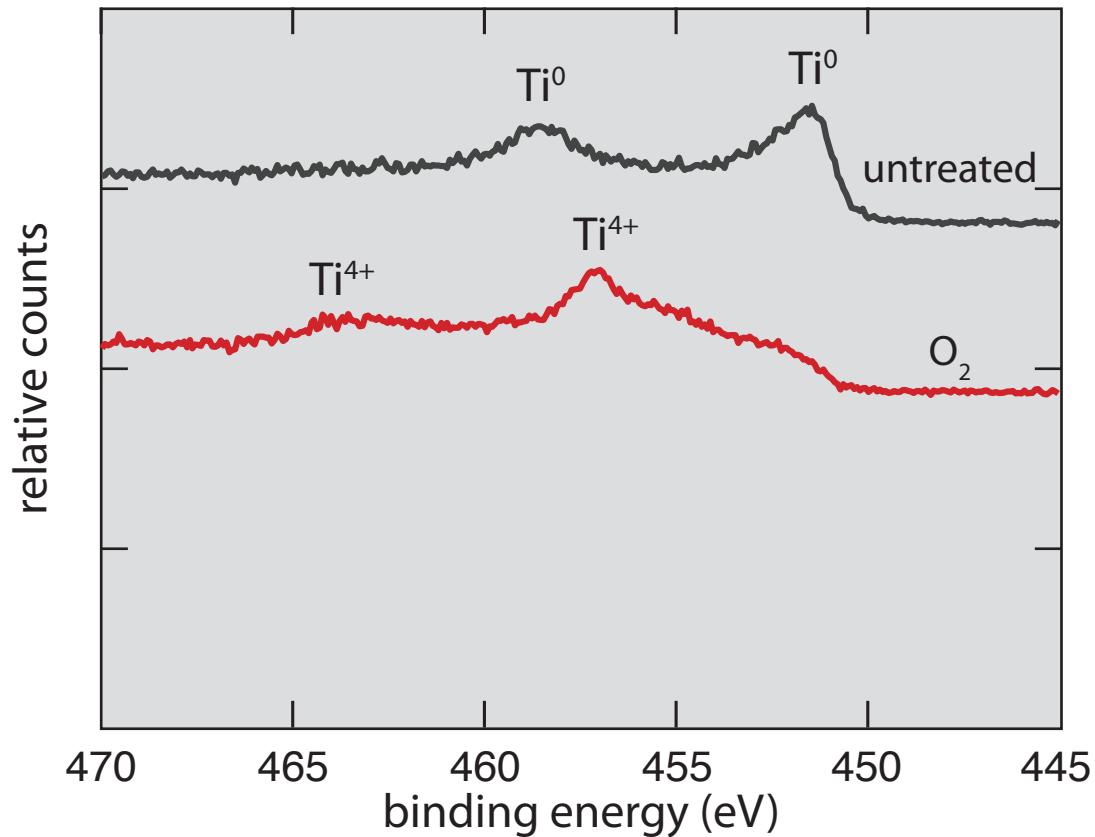


1 intermediate band

2 Si devices

3 X:TiO₂

oxygen is incorporated!

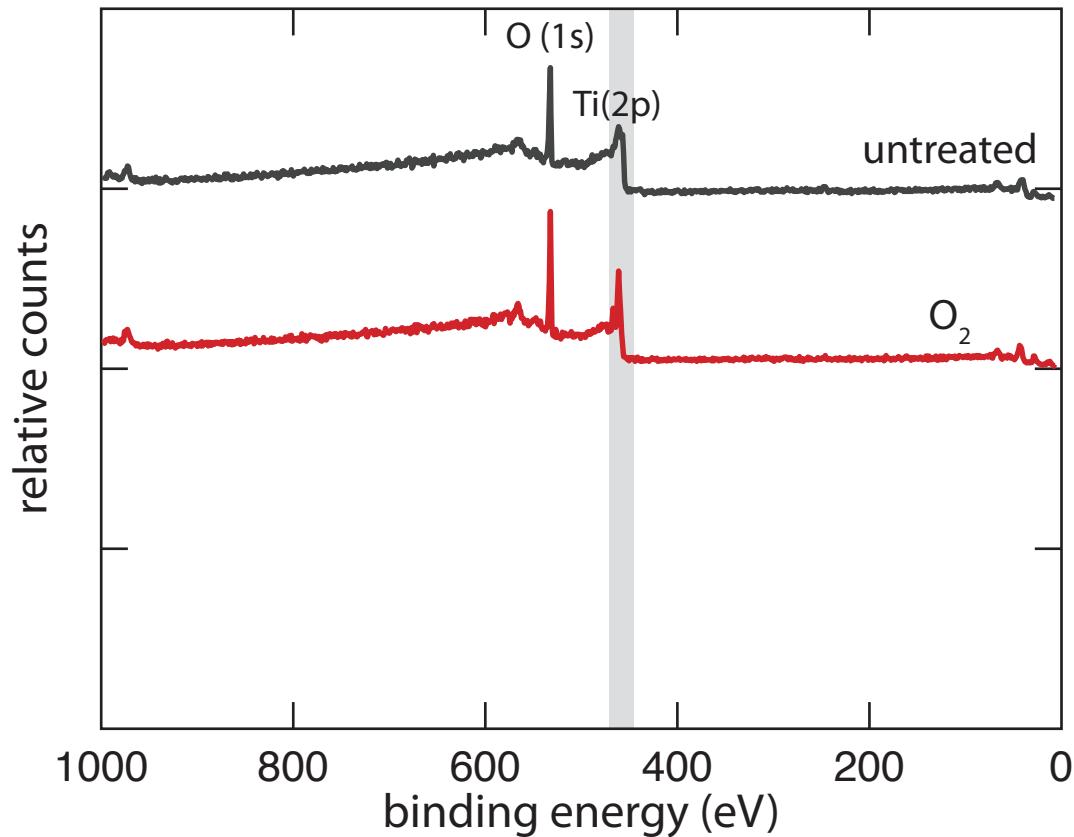


1 intermediate band

2 Si devices

3 X: TiO_2

oxygen is incorporated!

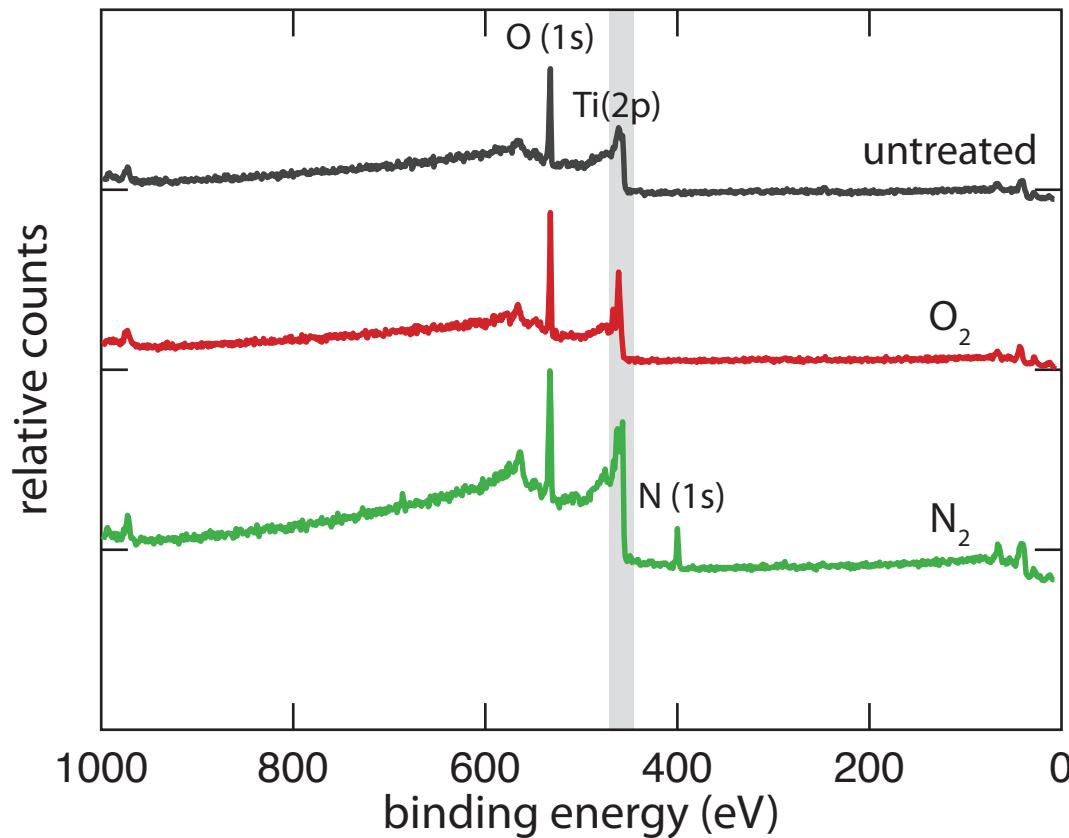


1 intermediate band

2 Si devices

3 X:TiO₂

nitrogen peak appears...

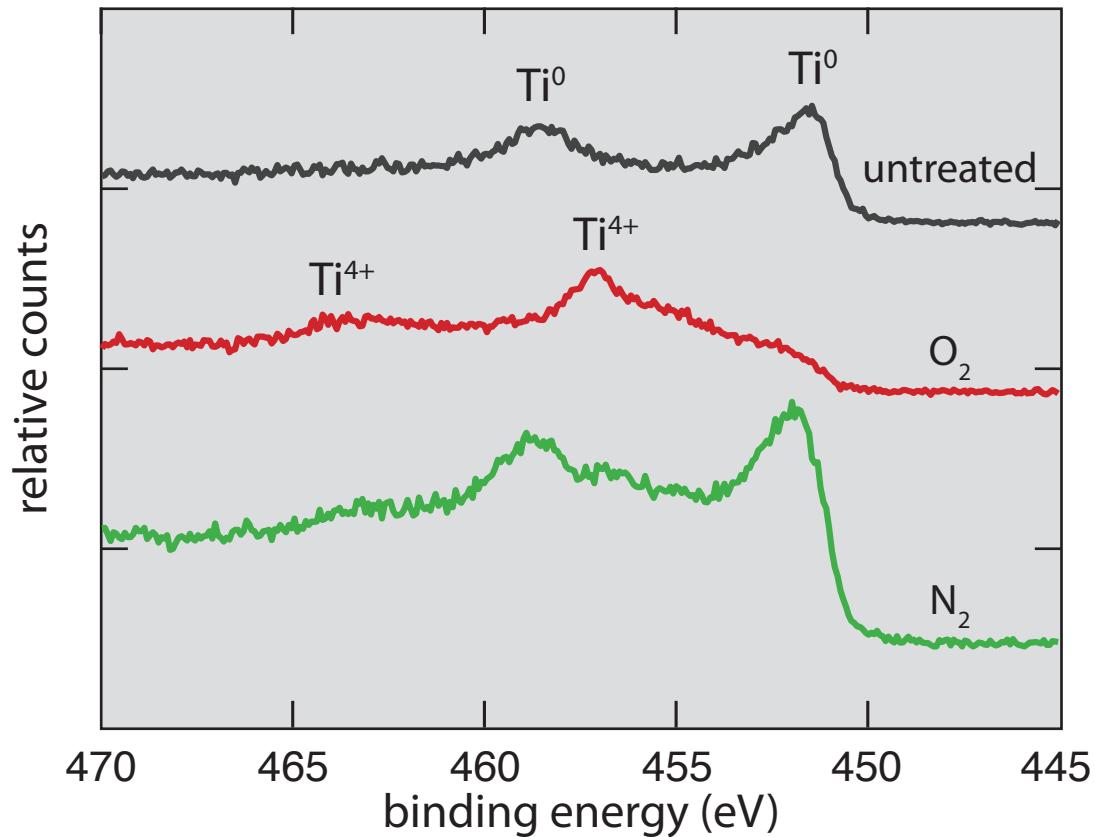


1 intermediate band

2 Si devices

3 X: TiO_2

... but nitrogen not chemically incorporated

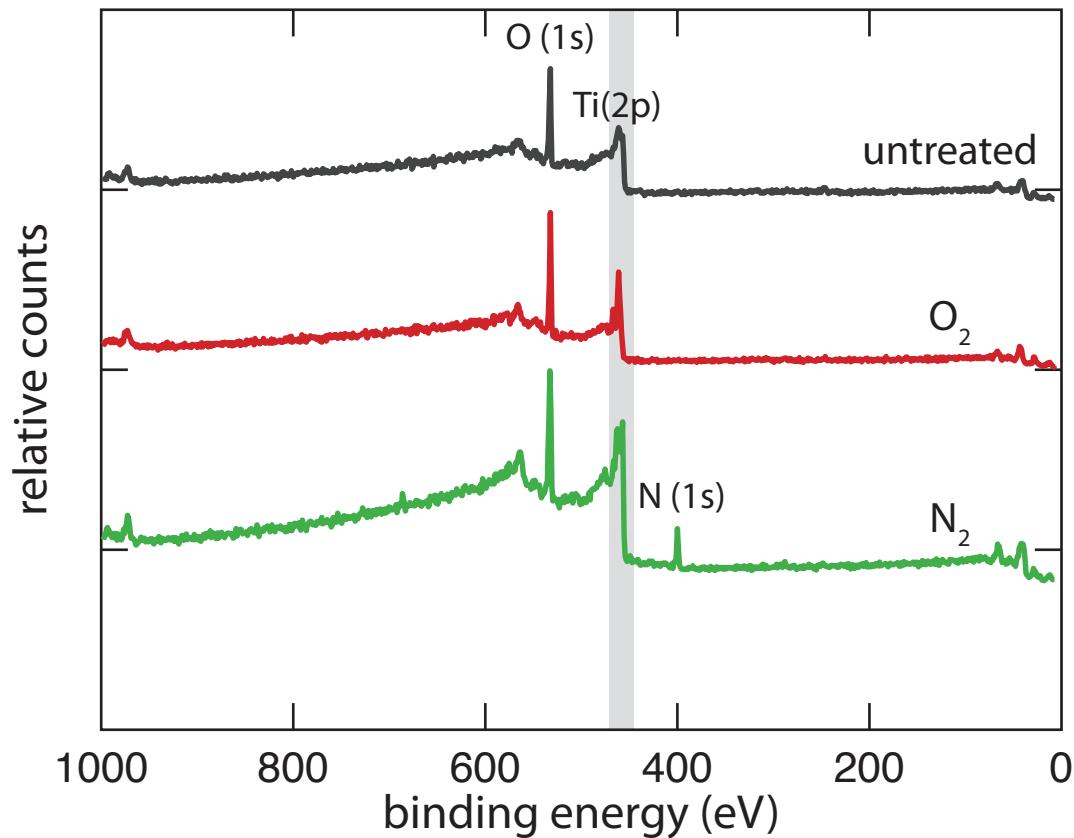


1 intermediate band

2 Si devices

3 X:TiO₂

... but nitrogen not chemically incorporated

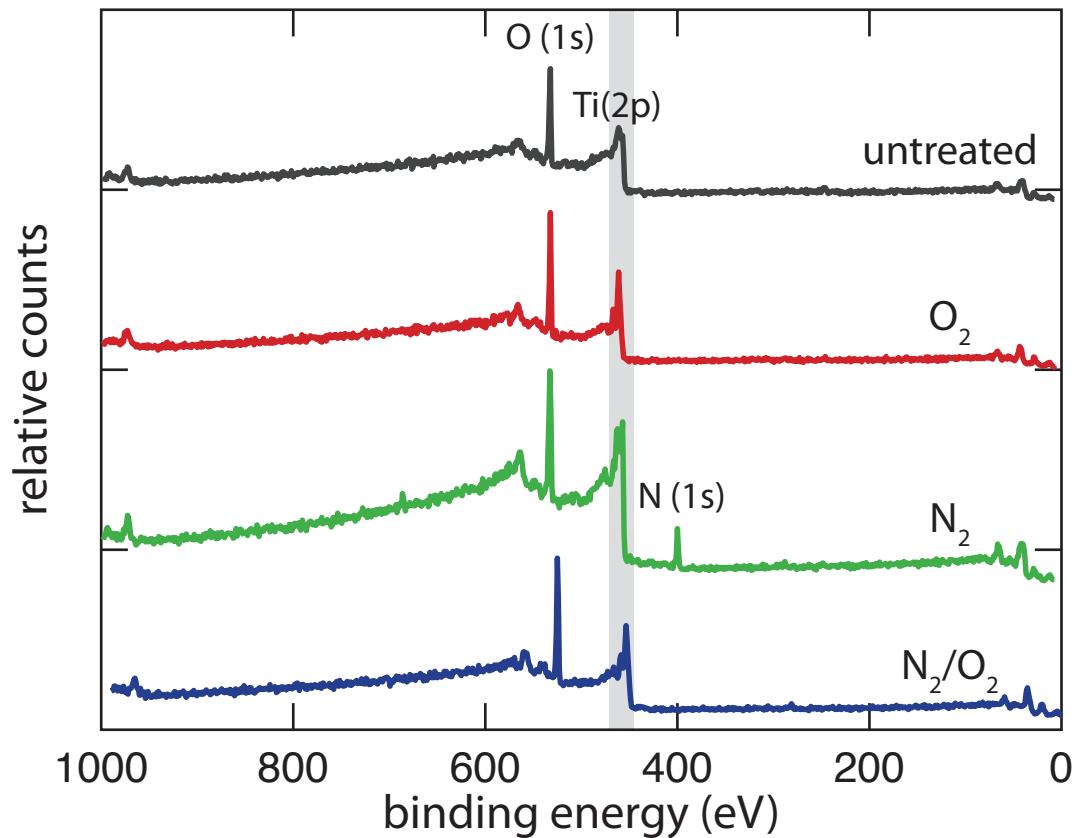


1 intermediate band

2 Si devices

3 X:TiO₂

with both nitrogen and oxygen...

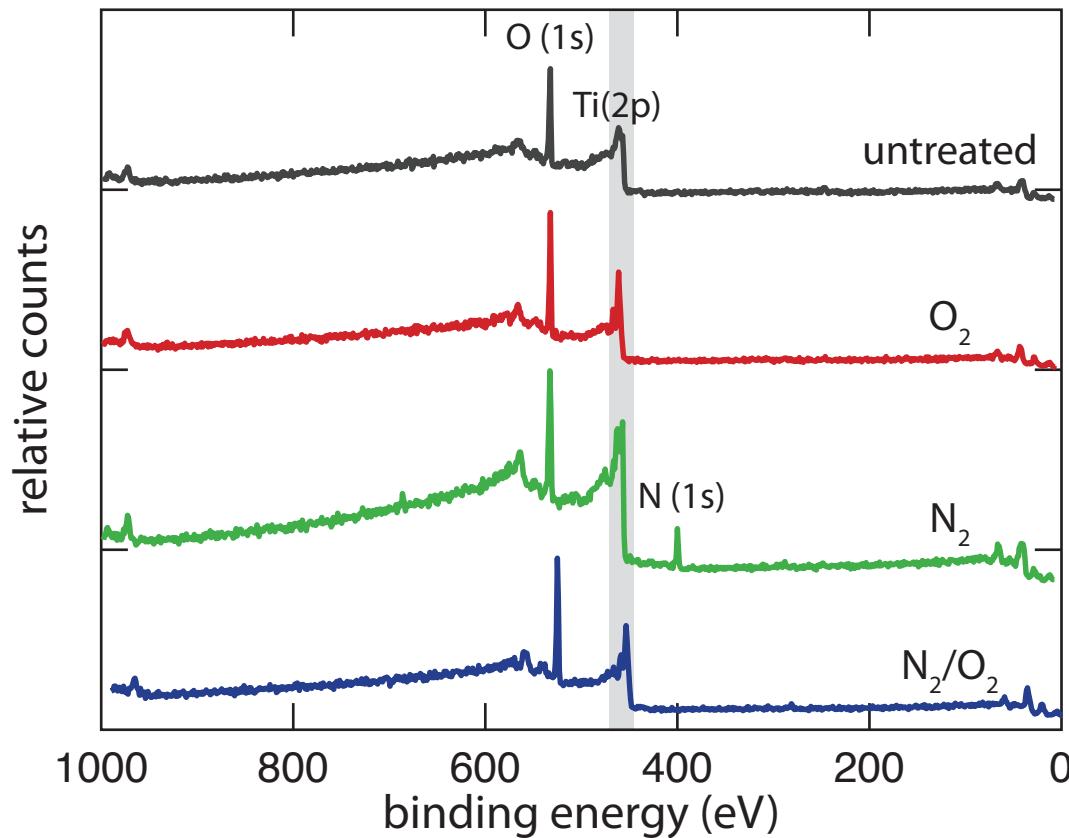


1 intermediate band

2 Si devices

3 X:TiO₂

... just 1% of oxygen prevents nitrogen incorporation...

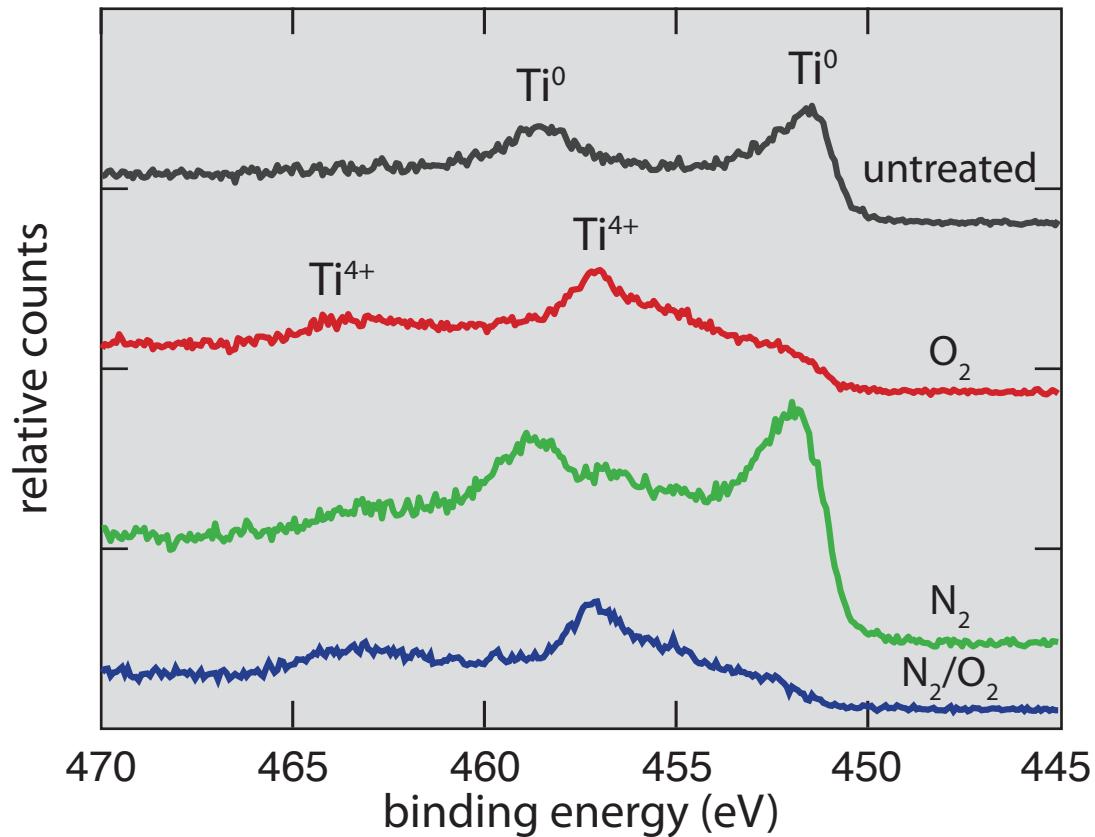


1 intermediate band

2 Si devices

3 X:TiO₂

... 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

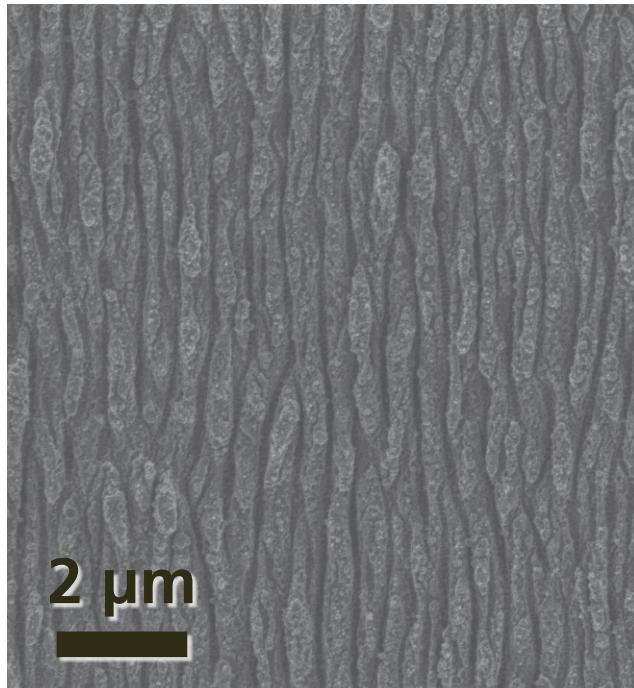
1 intermediate band

2 Si devices

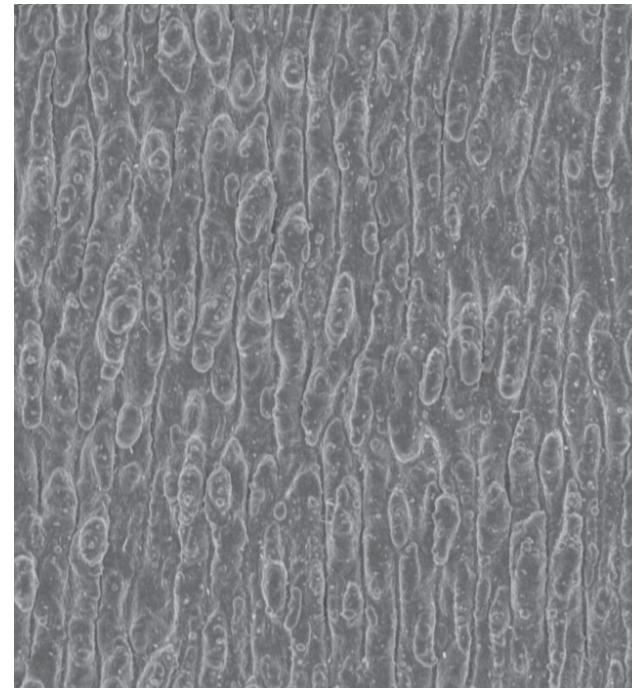
3 X: TiO_2

anneal N:Ti sample in O₂ (1h @ 900 K)

before annealing



after annealing

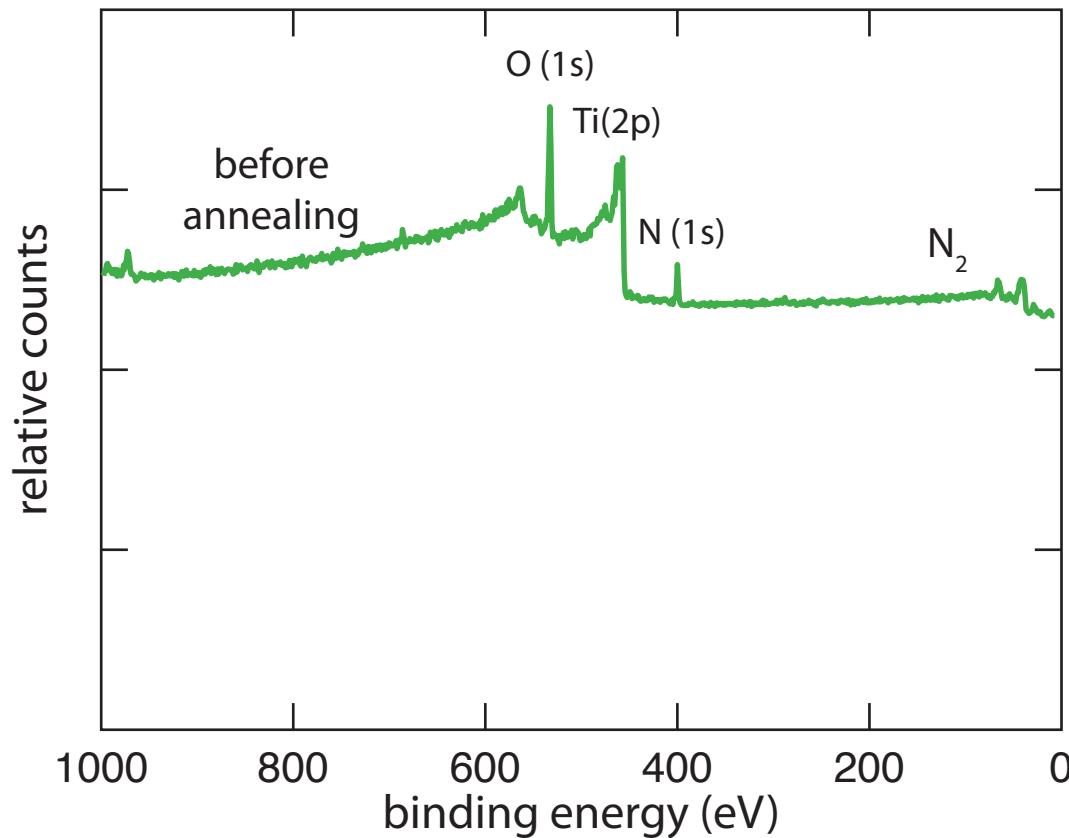


1 intermediate band

2 Si devices

3 X:TiO₂

anneal N:Ti sample in O₂ (1h @ 900 K)

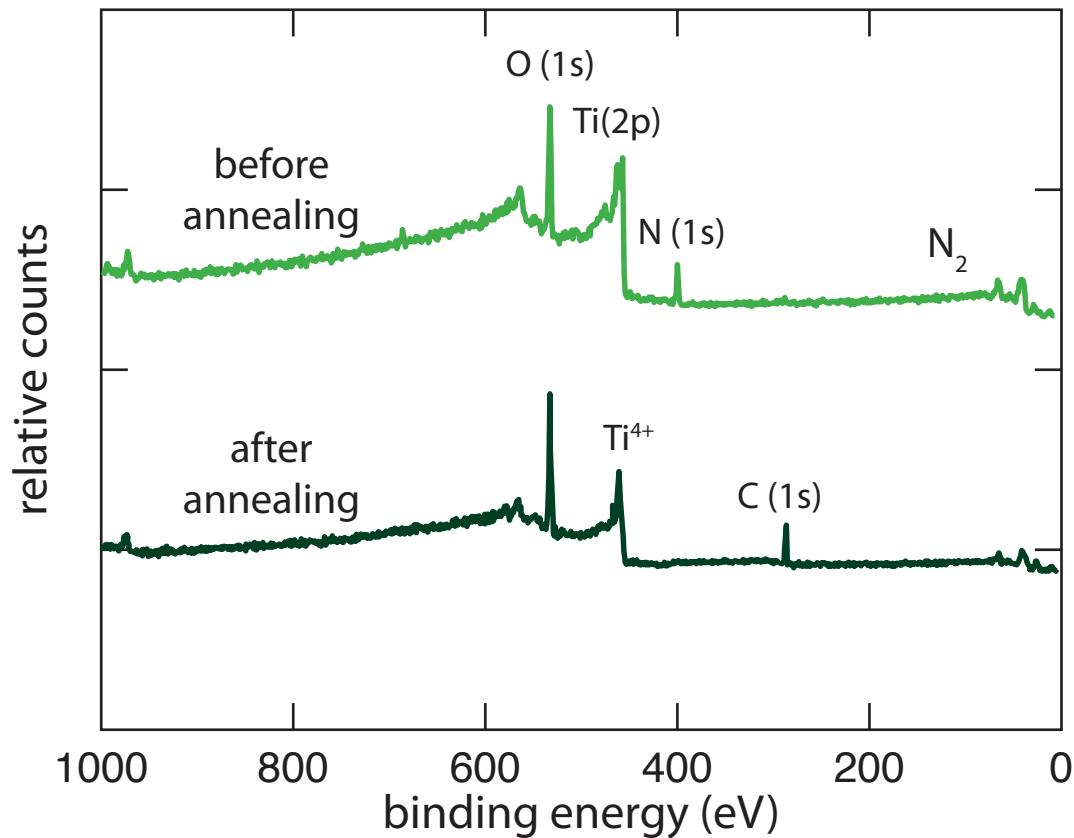


1 intermediate band

2 Si devices

3 X:TiO₂

...nitrogen anneals out...

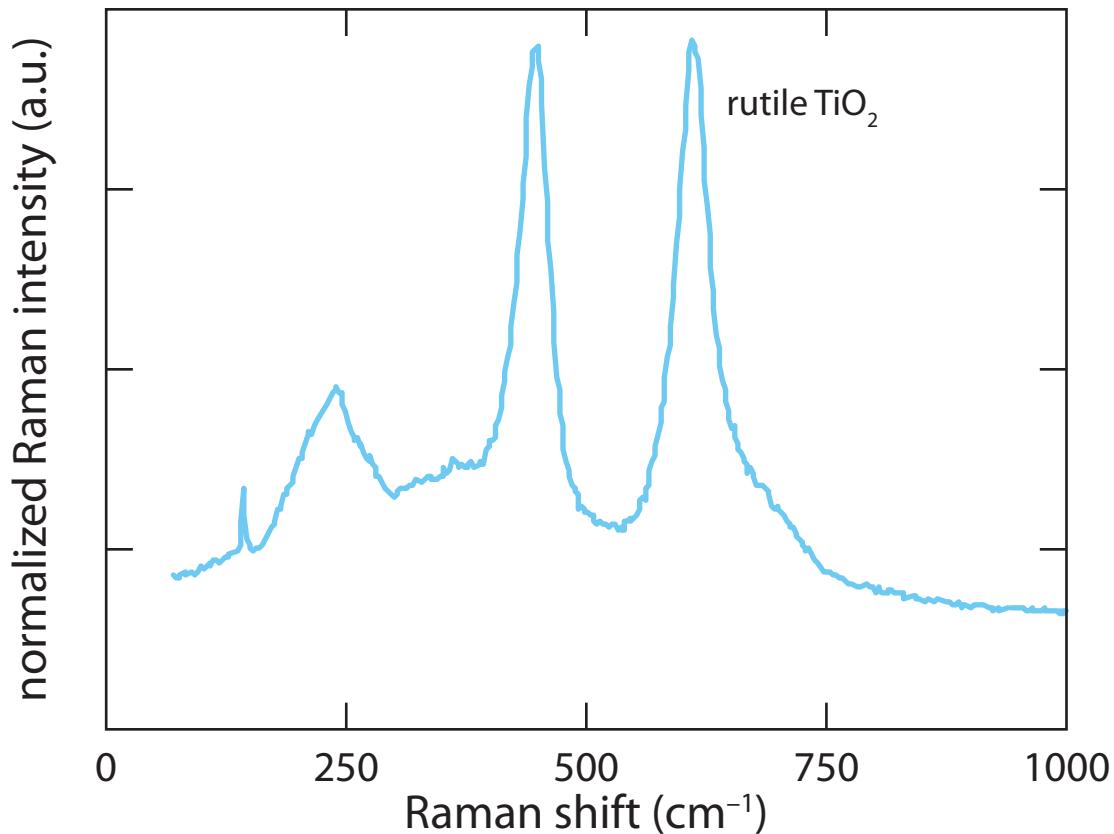


1 intermediate band

2 Si devices

3 X:TiO₂

...but Raman spectrum shows TiO_2 is formed

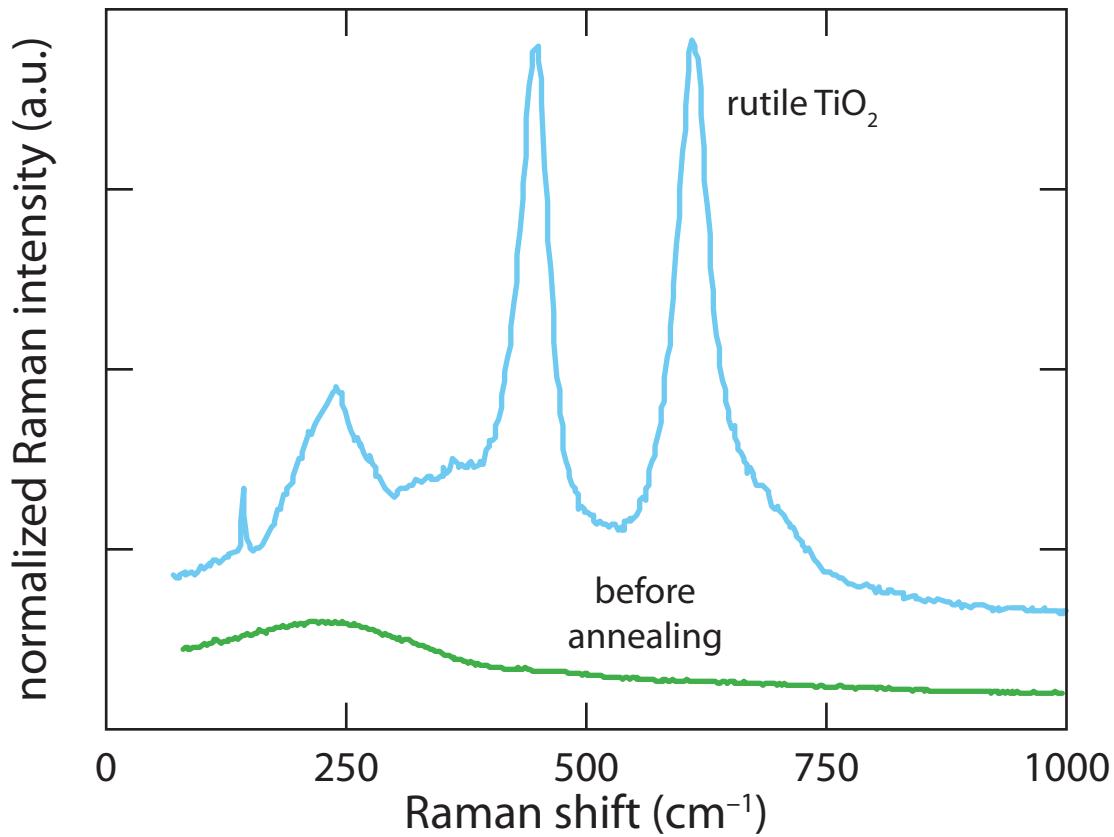


1 intermediate band

2 Si devices

3 X: TiO_2

...but Raman spectrum shows TiO_2 is formed

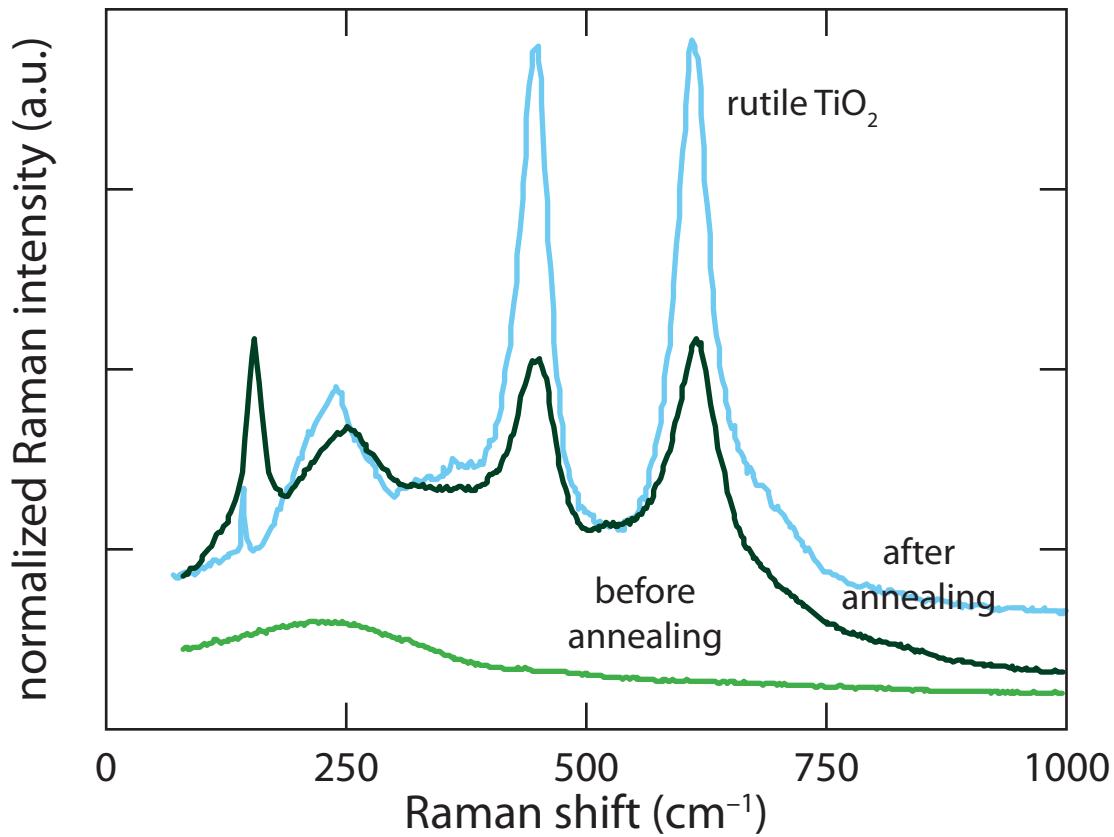


1 intermediate band

2 Si devices

3 X: TiO_2

...but Raman spectrum shows TiO_2 is formed

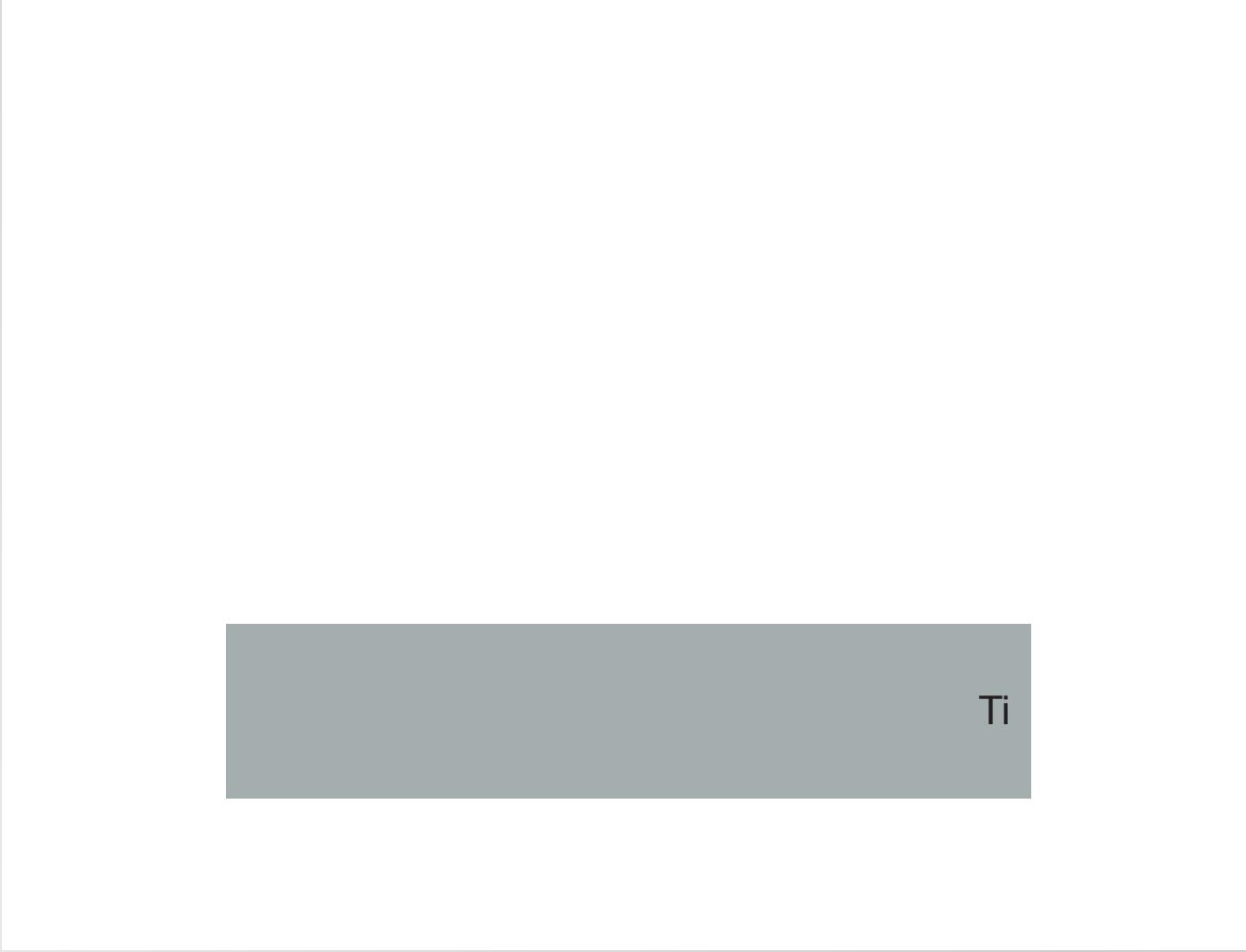


1 intermediate band

2 Si devices

3 X: TiO_2

how about incorporating chromium with oxygen?



Ti

1 intermediate band

2 Si devices

3 X: TiO_2

evaporate 10 – 70 nm chromium on titanium...

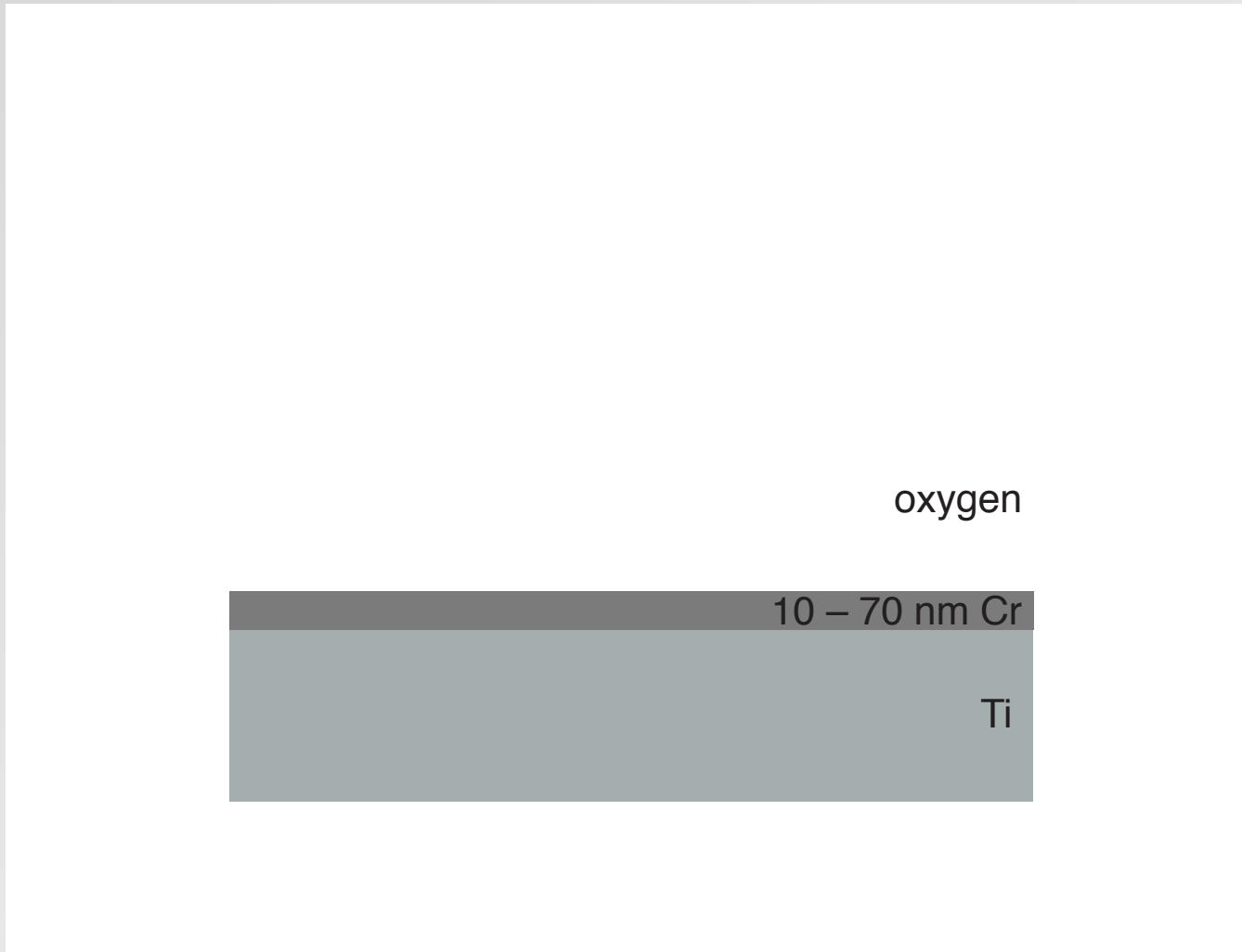


1 intermediate band

2 Si devices

3 X:TiO₂

...place in oxygen atmosphere...

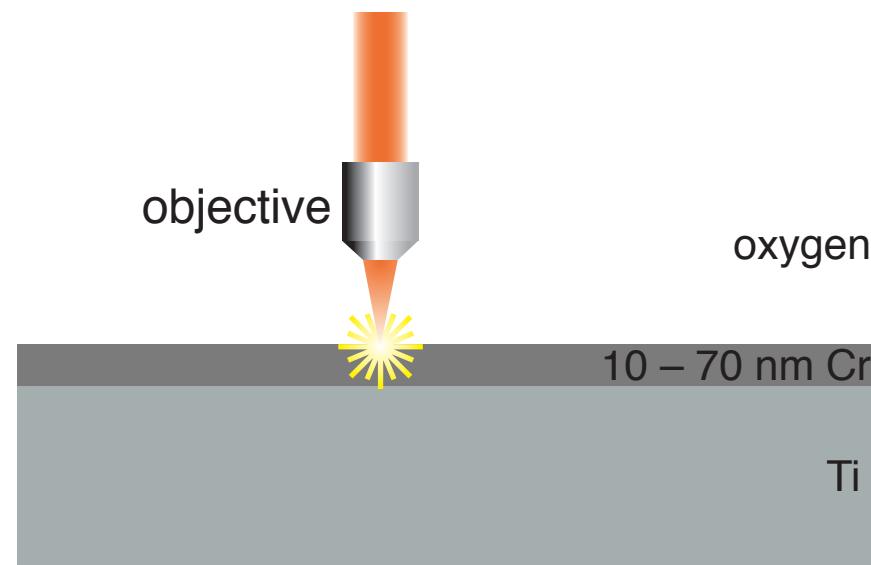


1 intermediate band

2 Si devices

3 X:TiO₂

...irradiate with laser...



1 intermediate band

2 Si devices

3 X:TiO₂

...and raster scan to structure



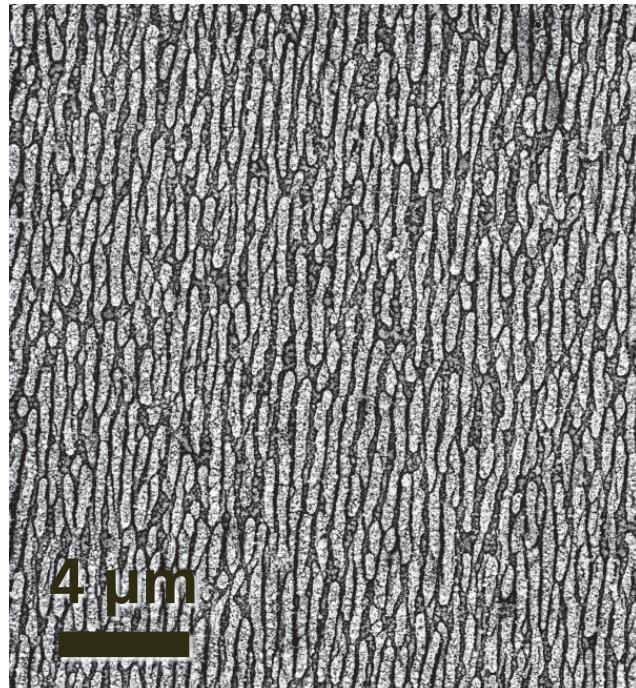
1 intermediate band

2 Si devices

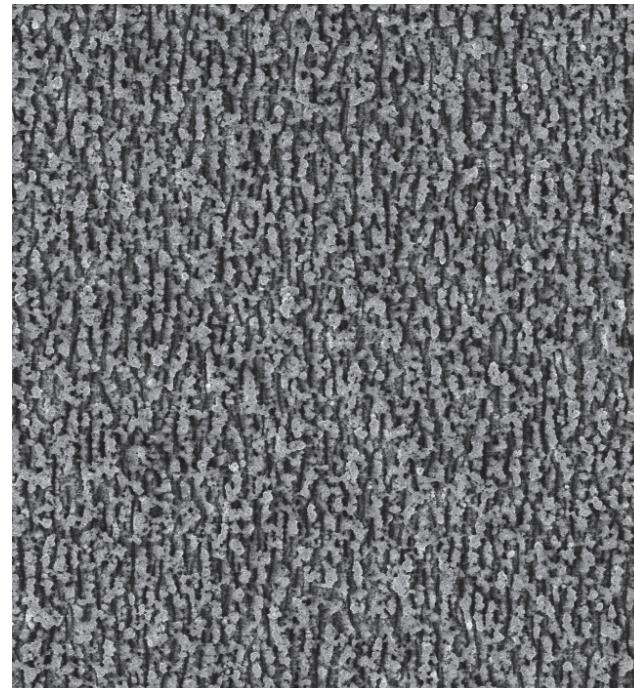
3 X:TiO₂

titanium/chromium in oxygen

titanium only



titanium/chromium

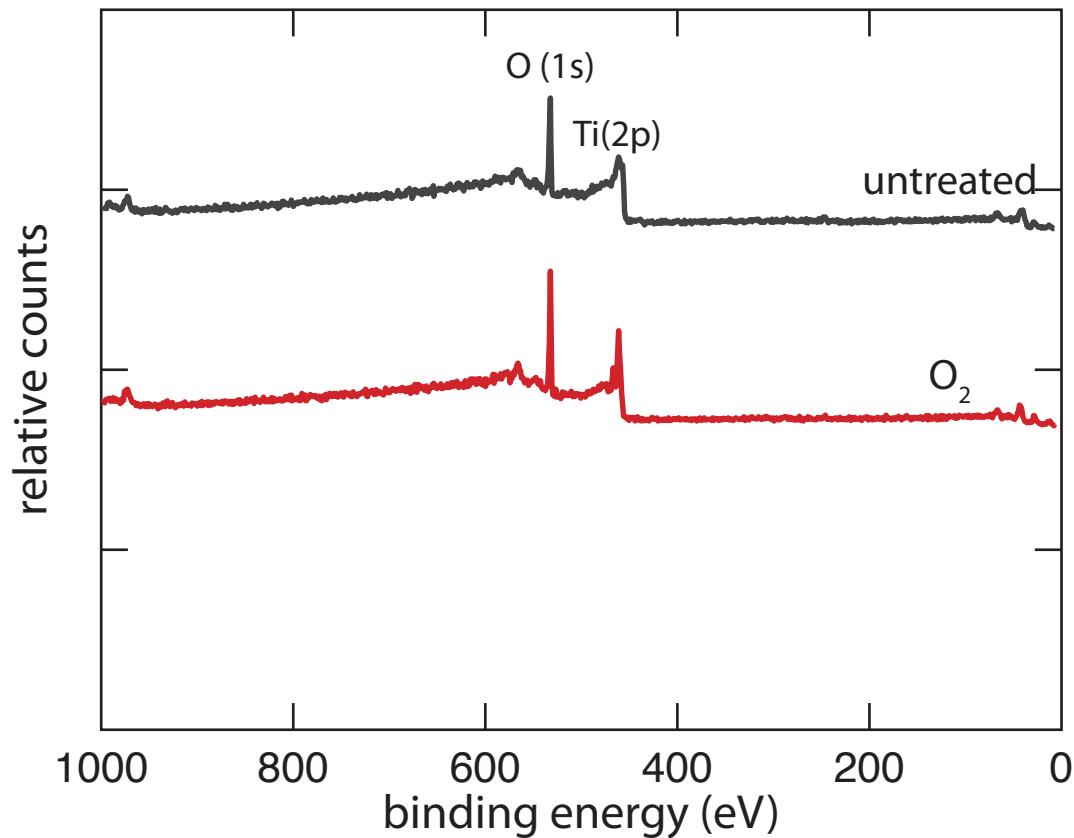


1 intermediate band

2 Si devices

3 X:TiO₂

X-ray photoelectron spectroscopy

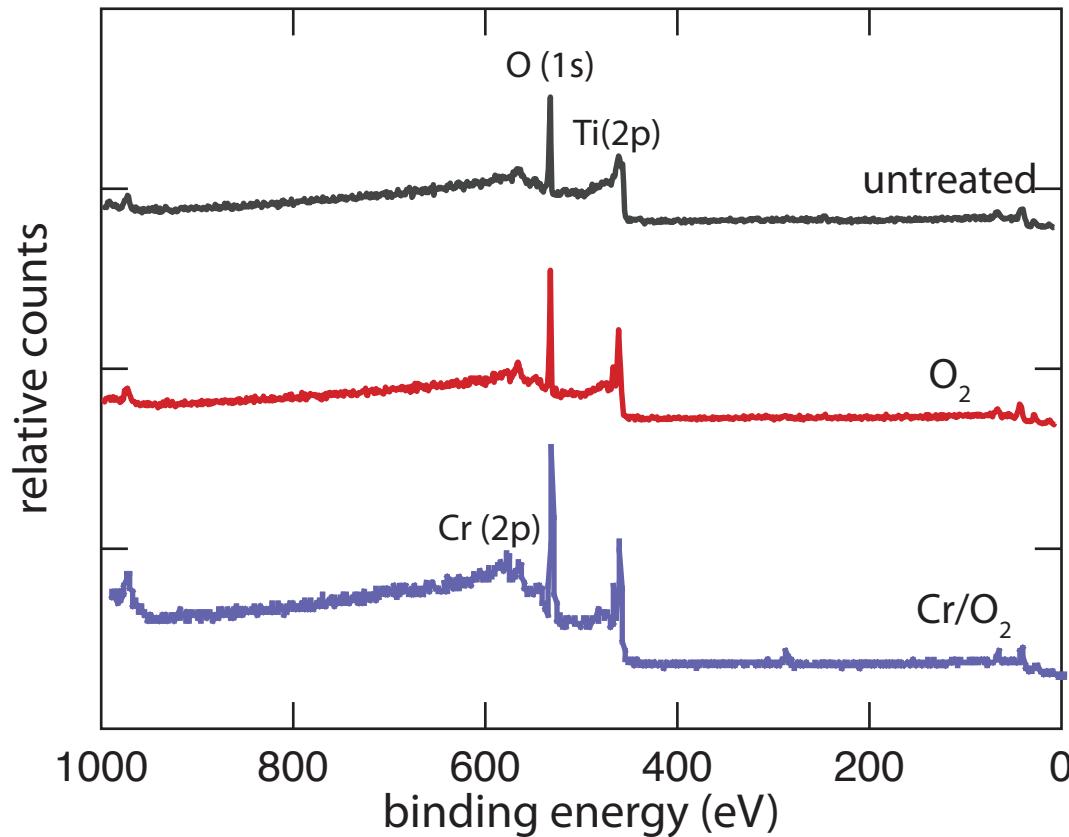


1 intermediate band

2 Si devices

3 X:TiO₂

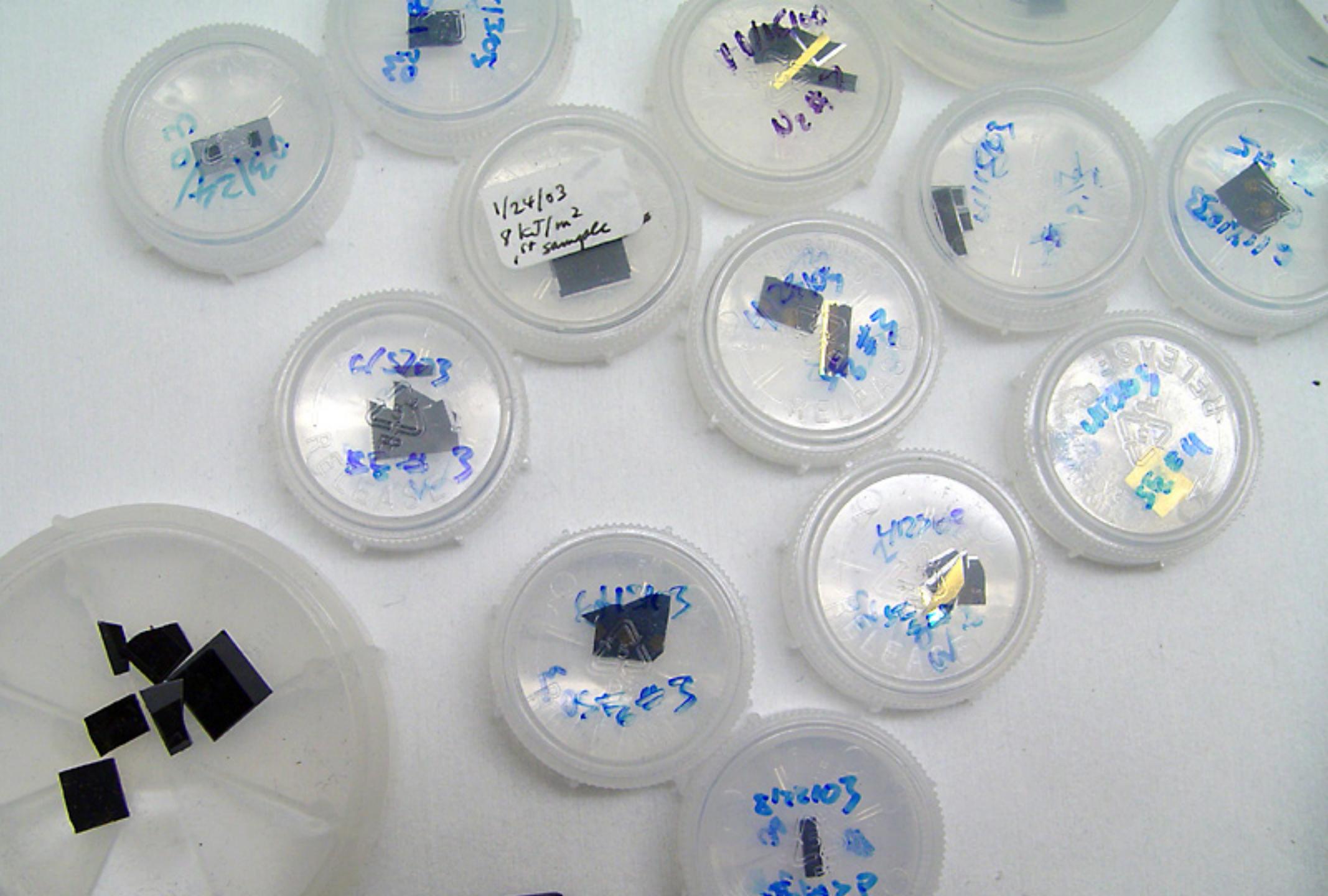
both chromium and oxygen incorporated!



1 intermediate band

2 Si devices

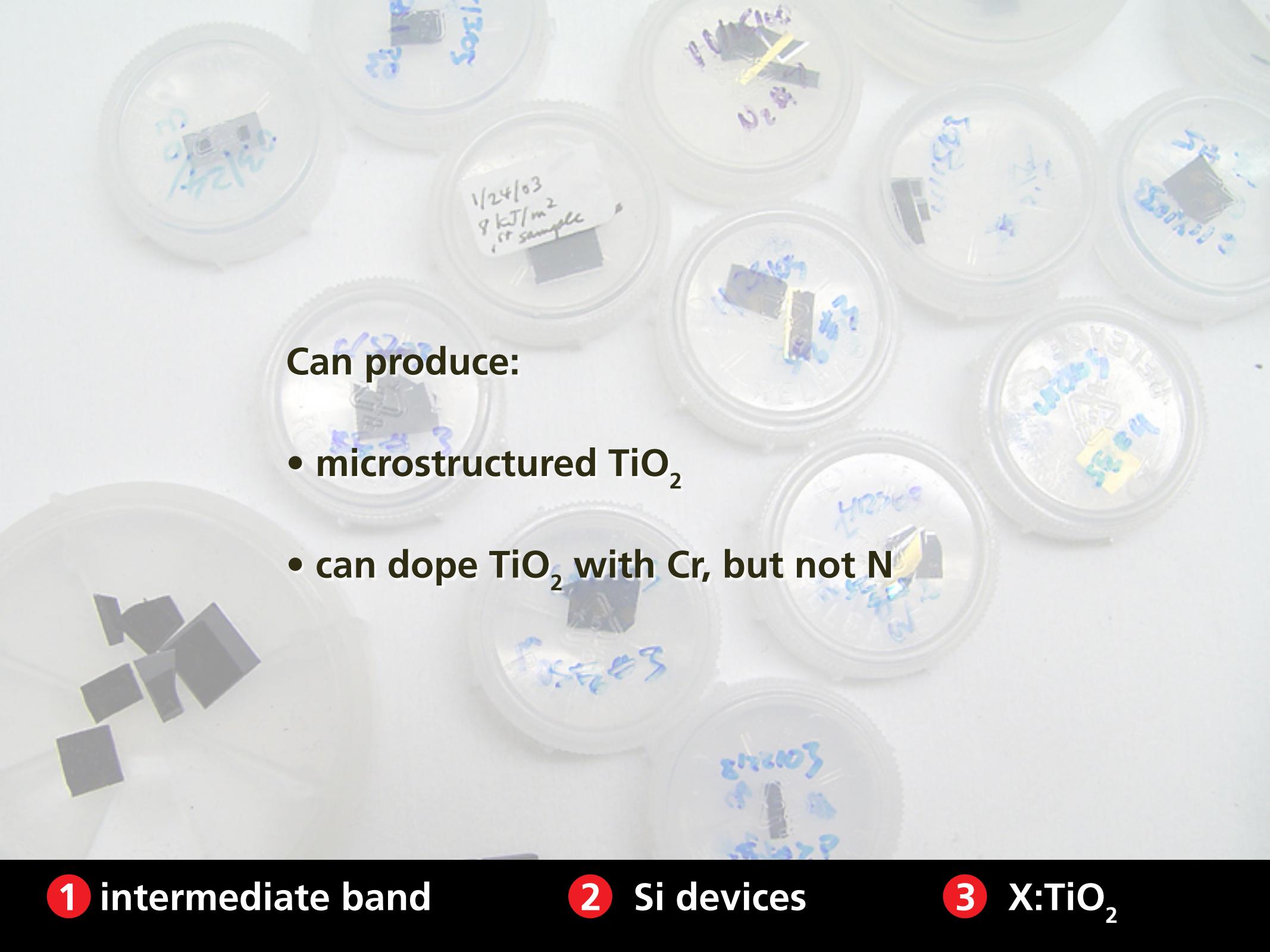
3 X:TiO₂



1 intermediate band

2 Si devices

3 X:TiO₂



Can produce:

- microstructured TiO_2
- can dope TiO_2 with Cr, but not N

1 intermediate band

2 Si devices

3 X: TiO_2



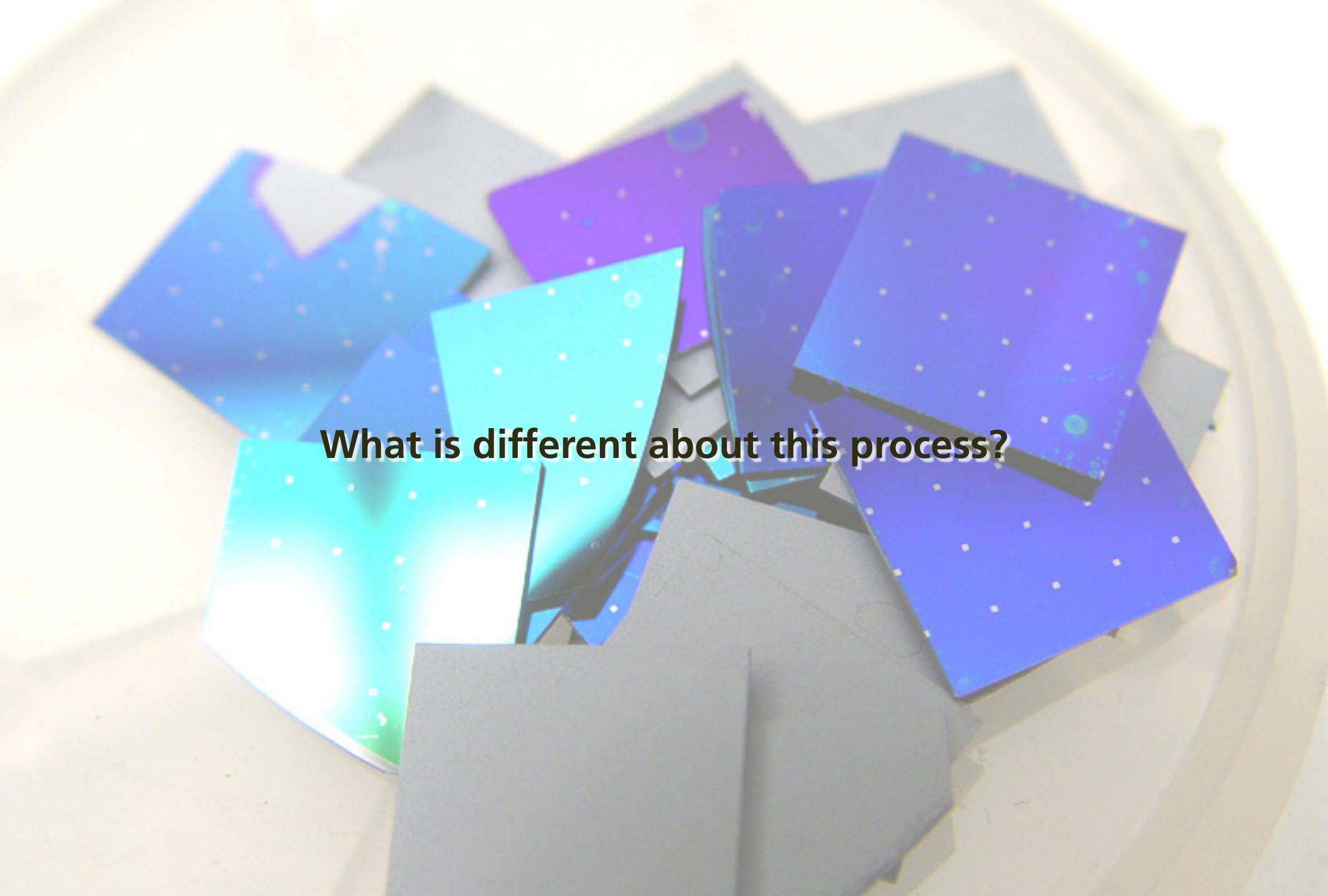
Summary

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

1 intermediate band

2 Si devices

3 X:TiO₂

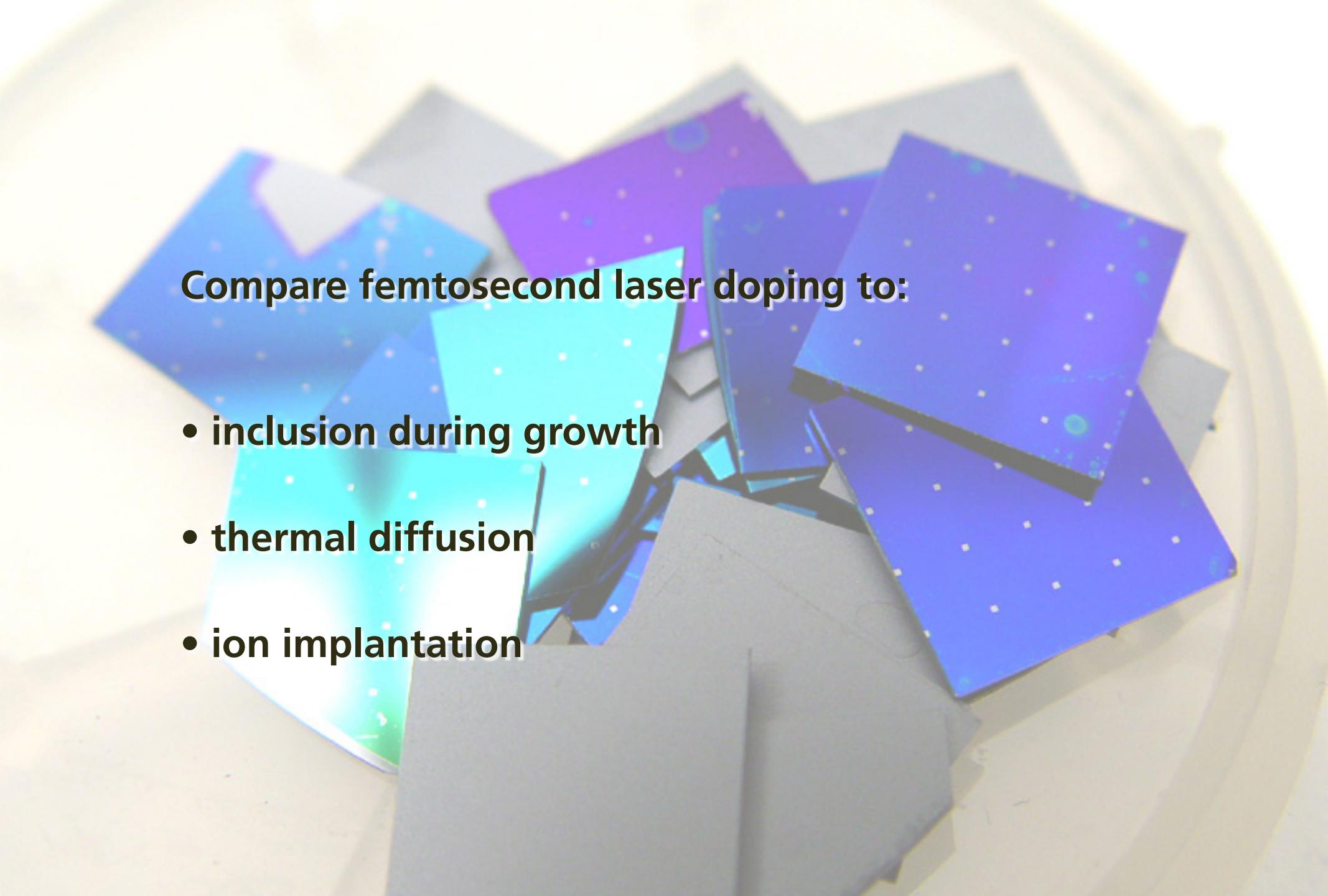


What is different about this process?

1 intermediate band

2 Si devices

3 X:TiO₂



Compare femtosecond laser doping to:

- inclusion during growth
- thermal diffusion
- ion implantation

1 intermediate band

2 Si devices

3 X:TiO₂





Funding:

Army Research Office

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NDSEG

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