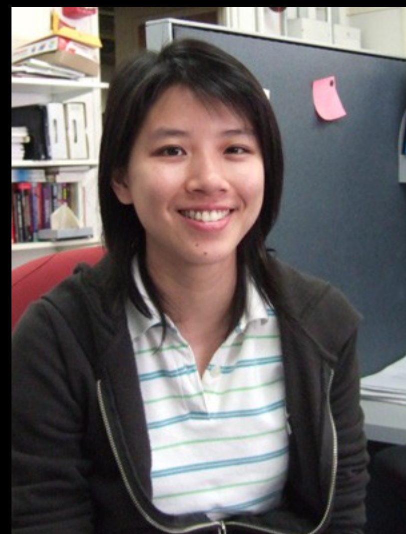
Fabricating nanostructured TiO_2 by femtosecond laser irradiating titanium

PIERS 2012
Kuala Lumpur, Malaysia, 28 March 2012


Renee Sher


Yu-Ting Lin


Kasey Phillips


Ben Franta

eric_mazur

and also....

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

Dr. Elizabeth Landis
Dr. John Chervinsky
Dr. Joshua Levinson

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

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

Prof. Augustinus Asenbaum (Vienna)

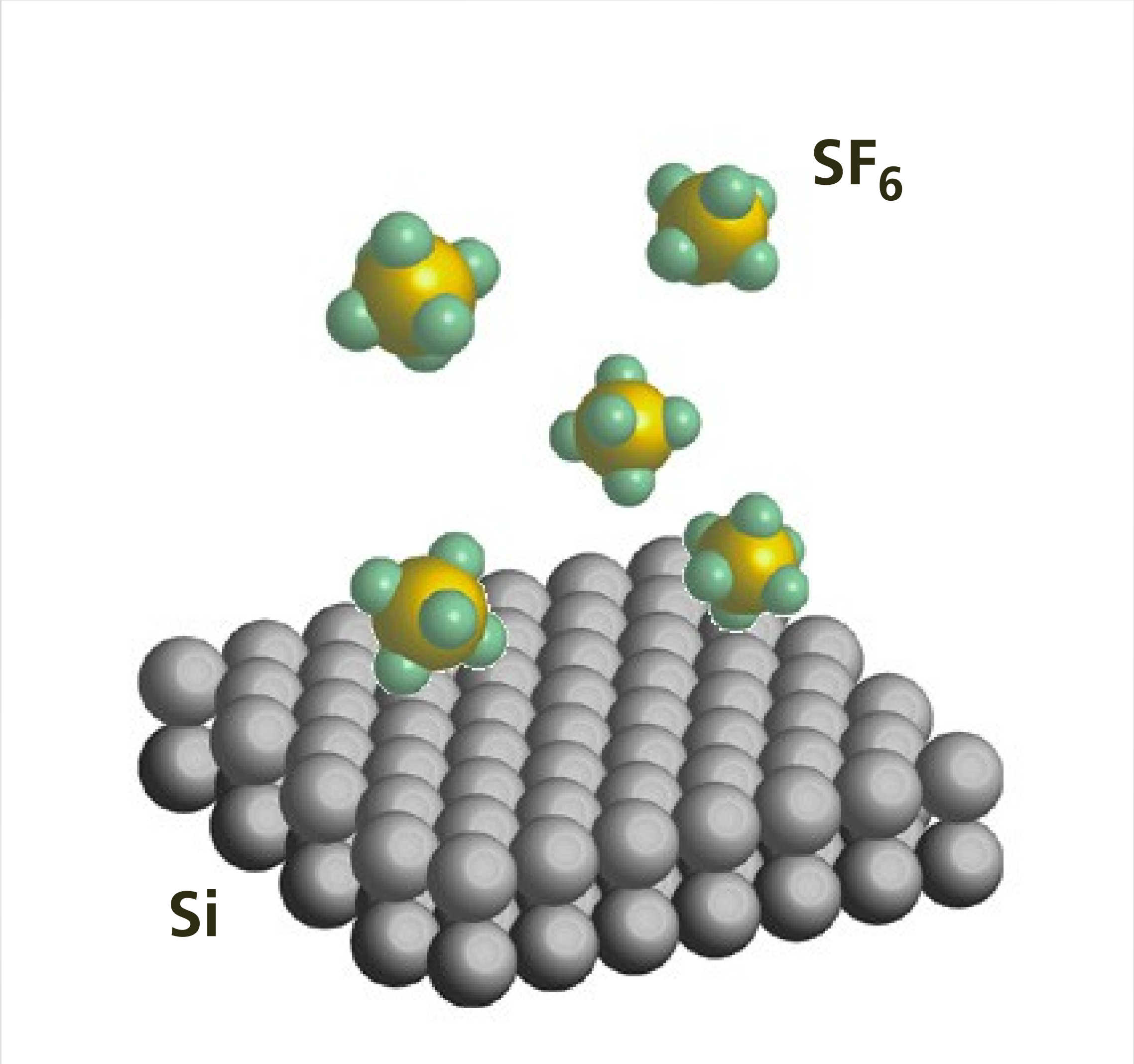
Dr. François Génin (LLNL)
Mark Wall (LLNL)

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

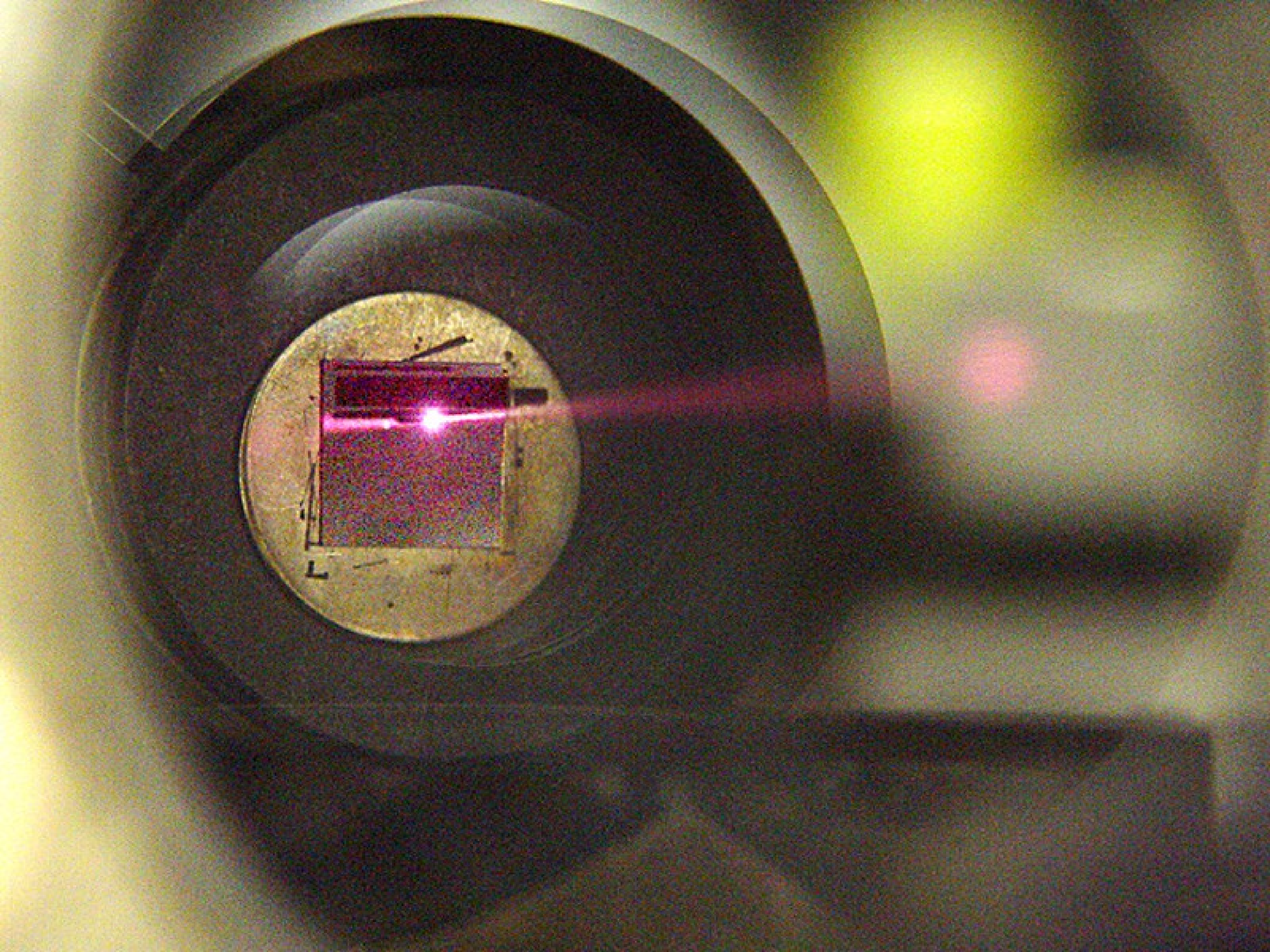
Dr. Pat Maloney (NVSED)

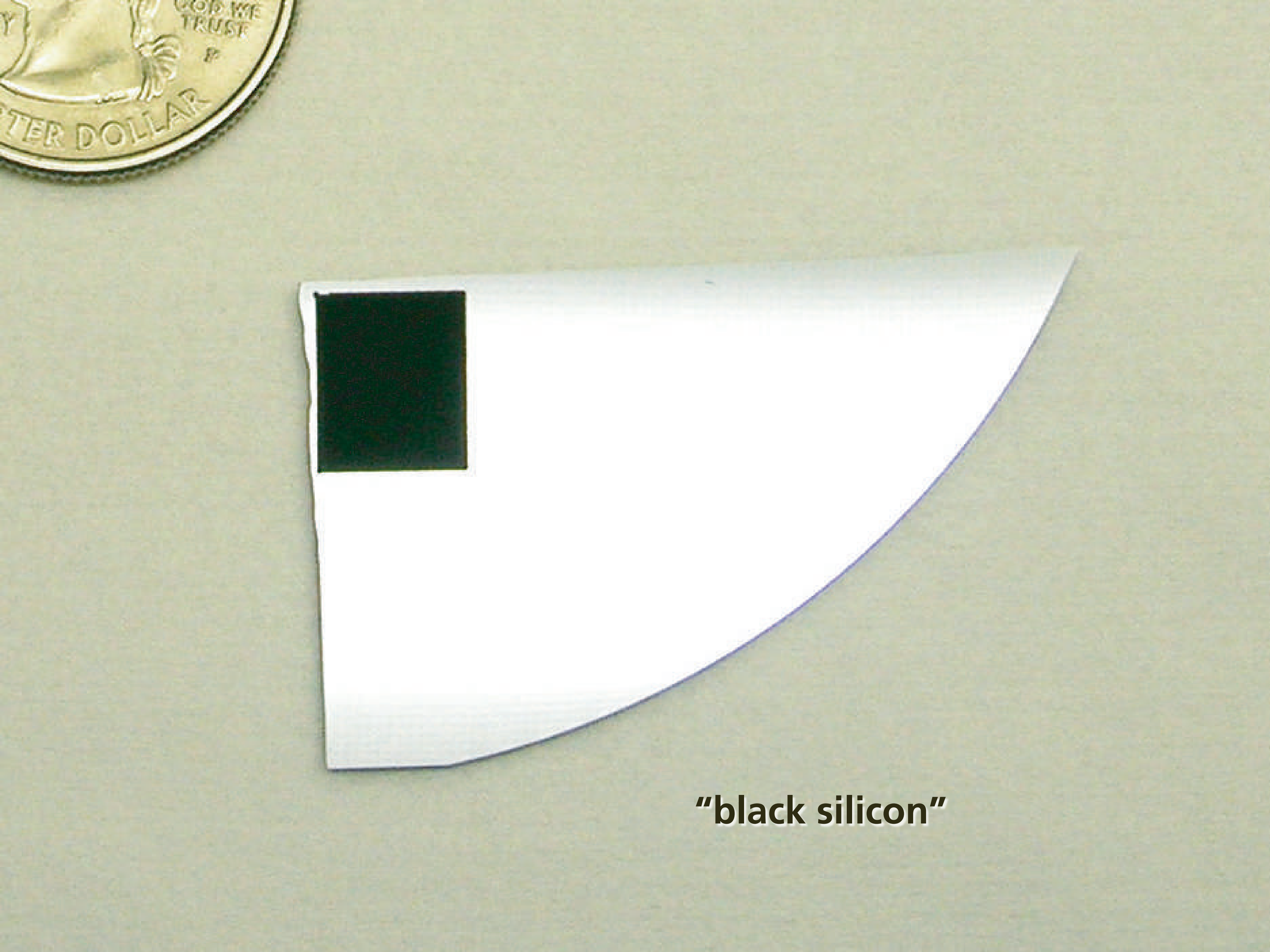
Dr. Jeffrey Warrander (ARDEC)

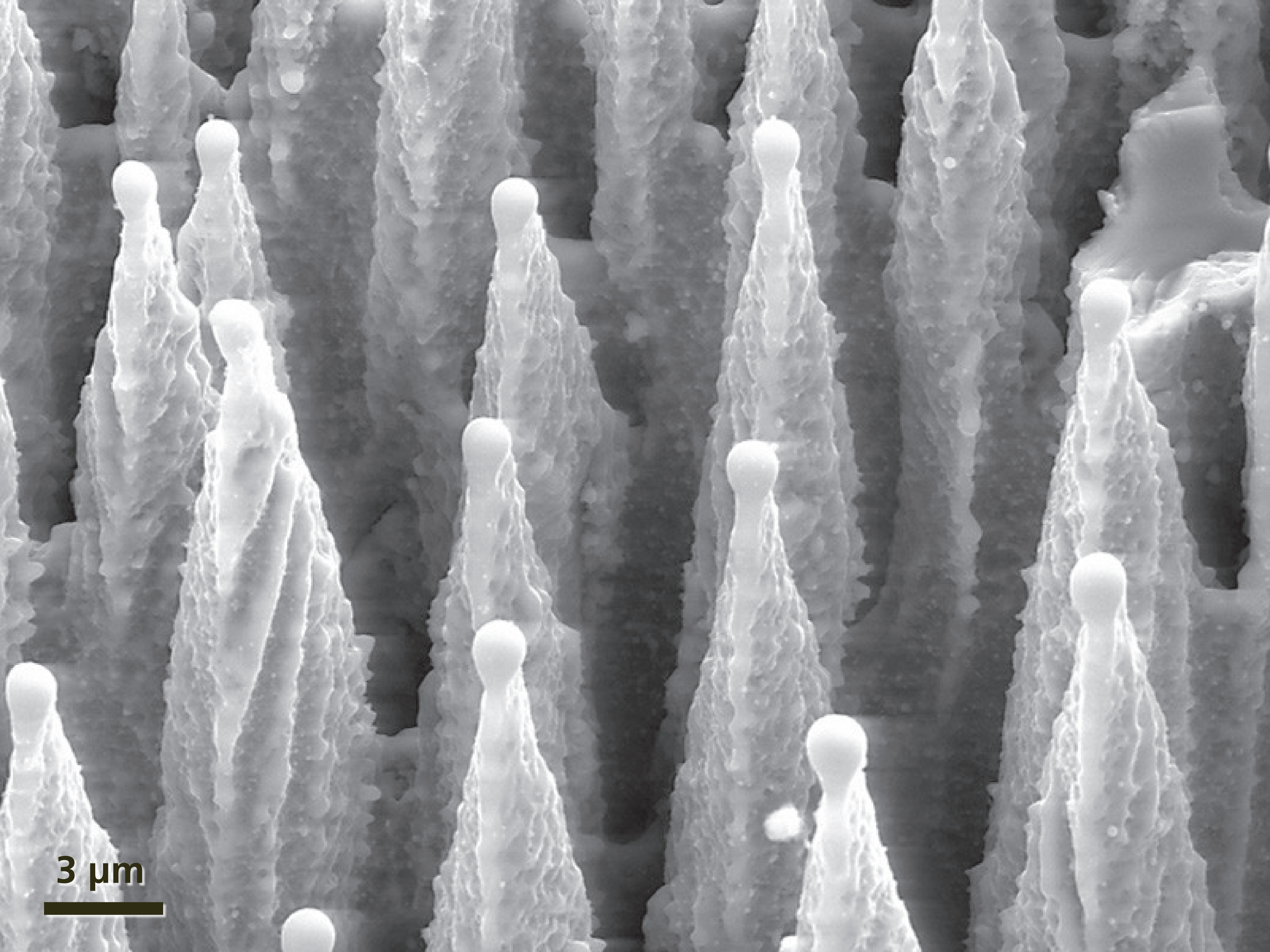
...and the people at SiOnyx



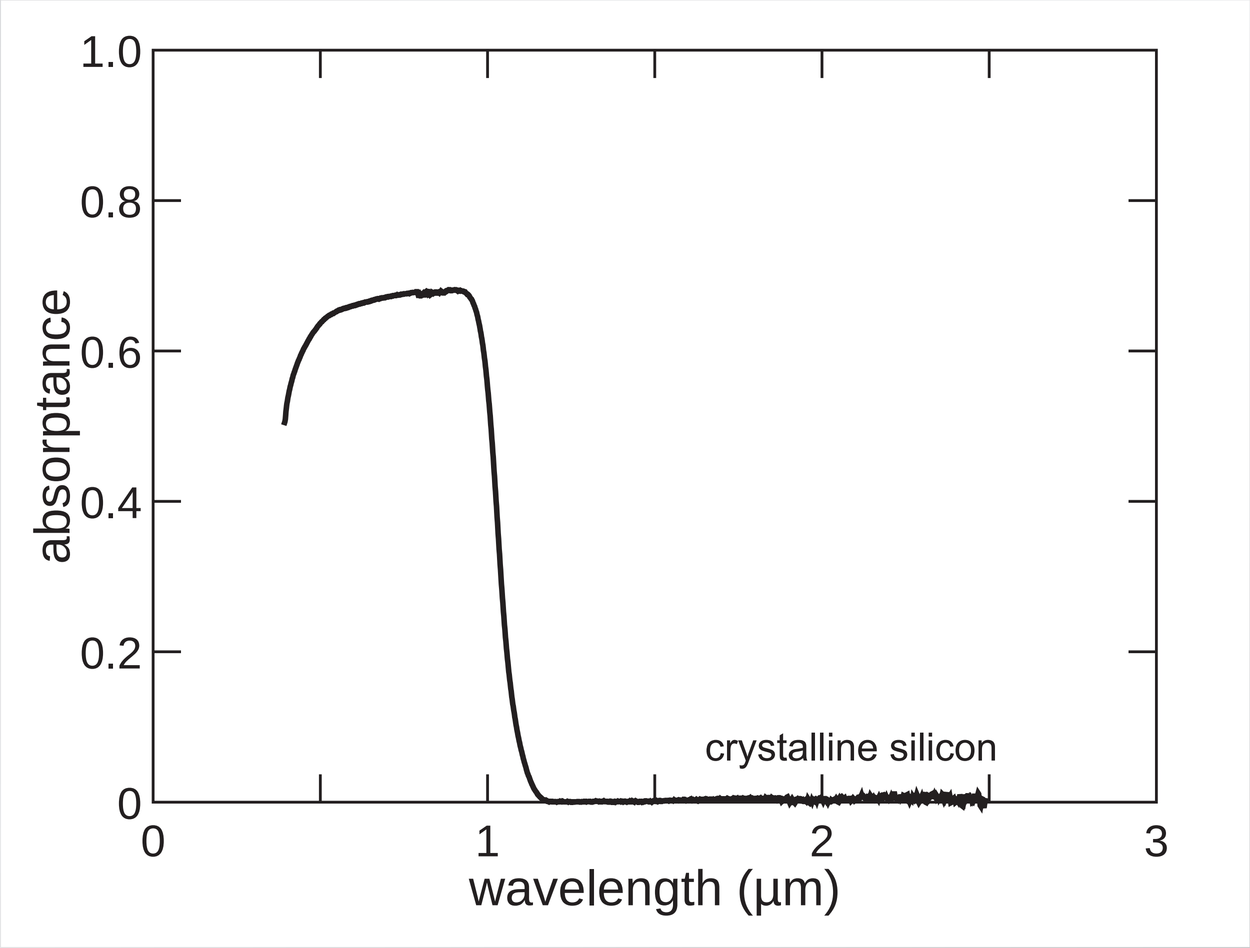
irradiate with 100-fs 10 kJ/m^2 pulses



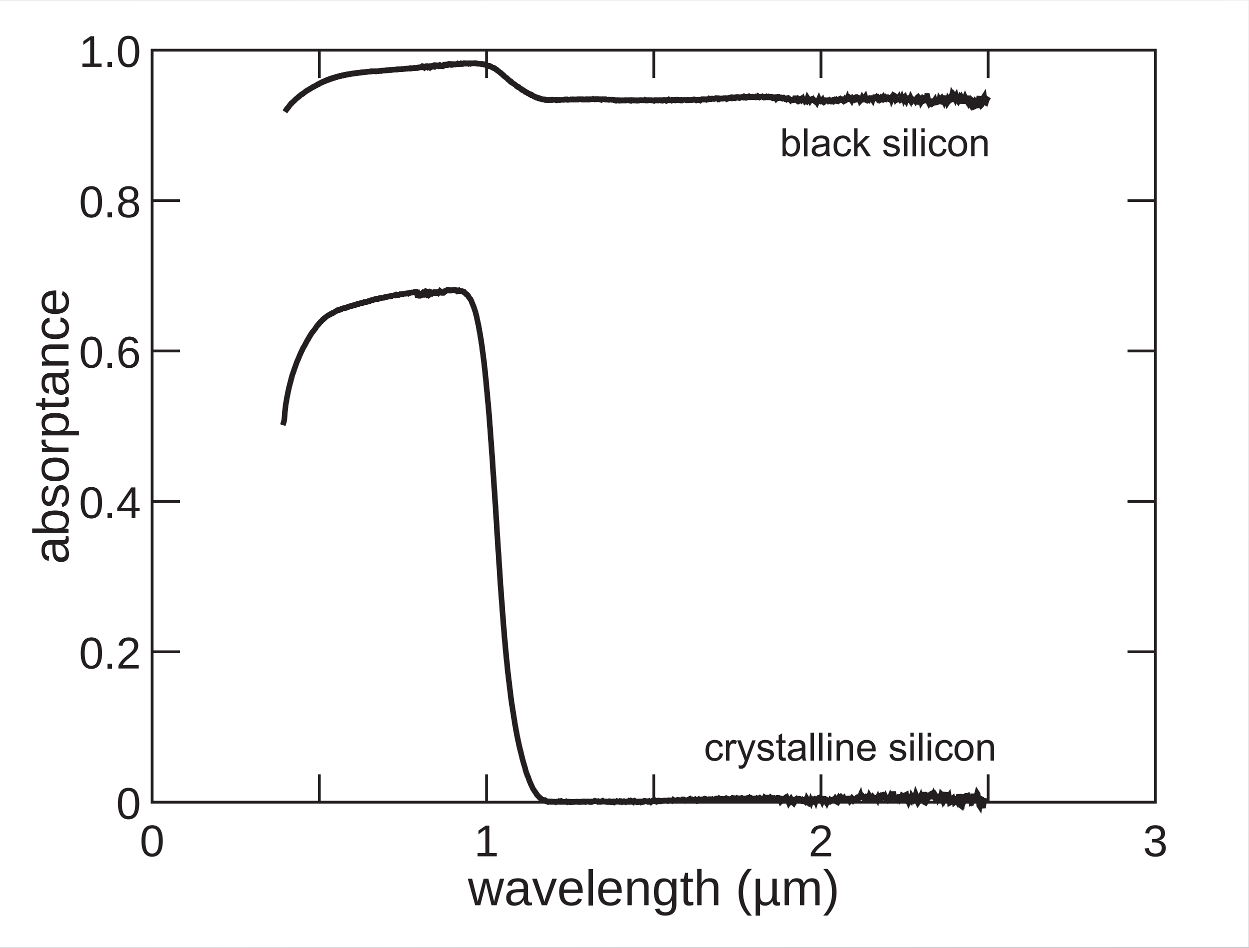

“black silicon”

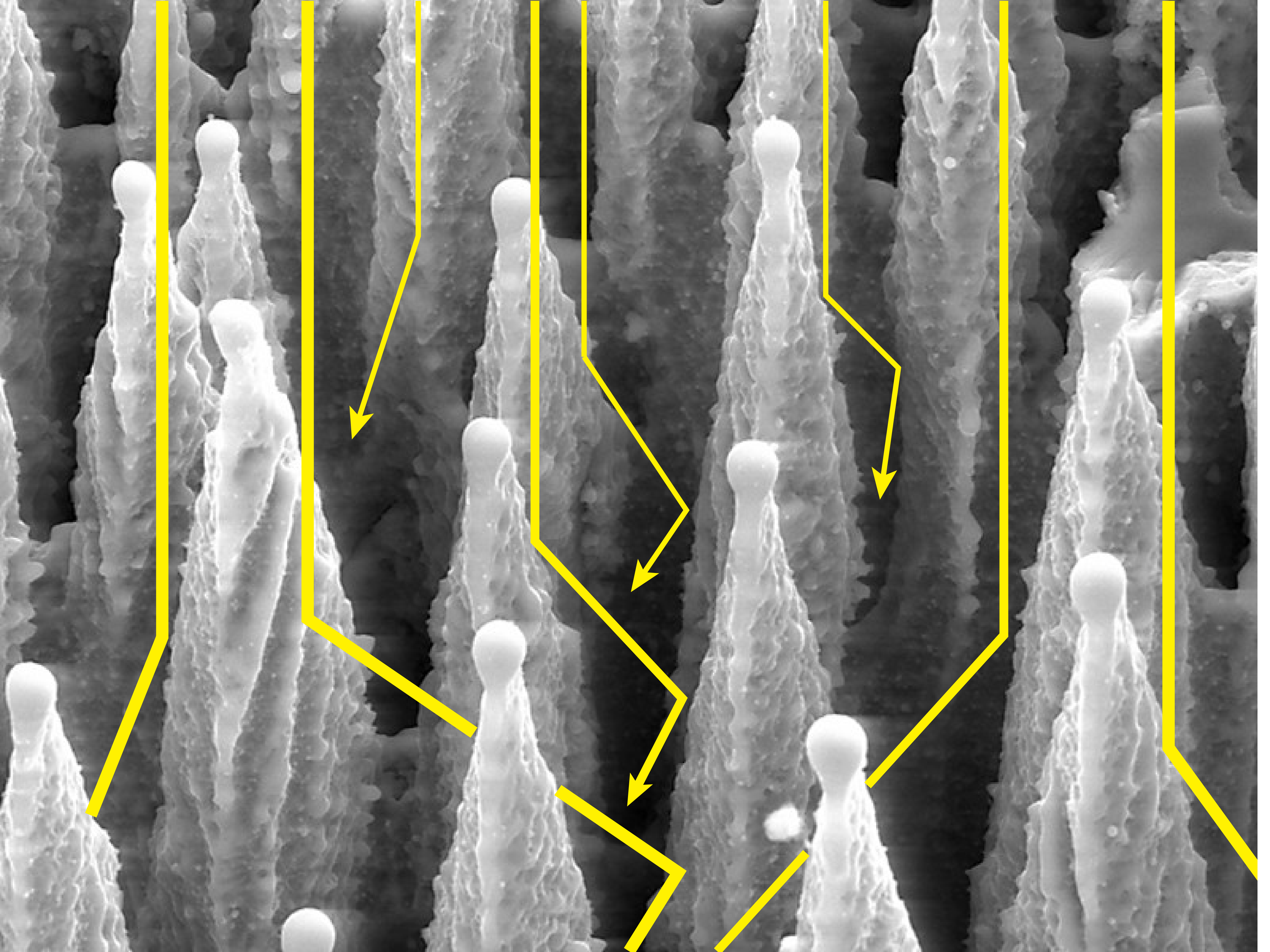

3 µm

absorptance (1 – R_{int} – T_{int})

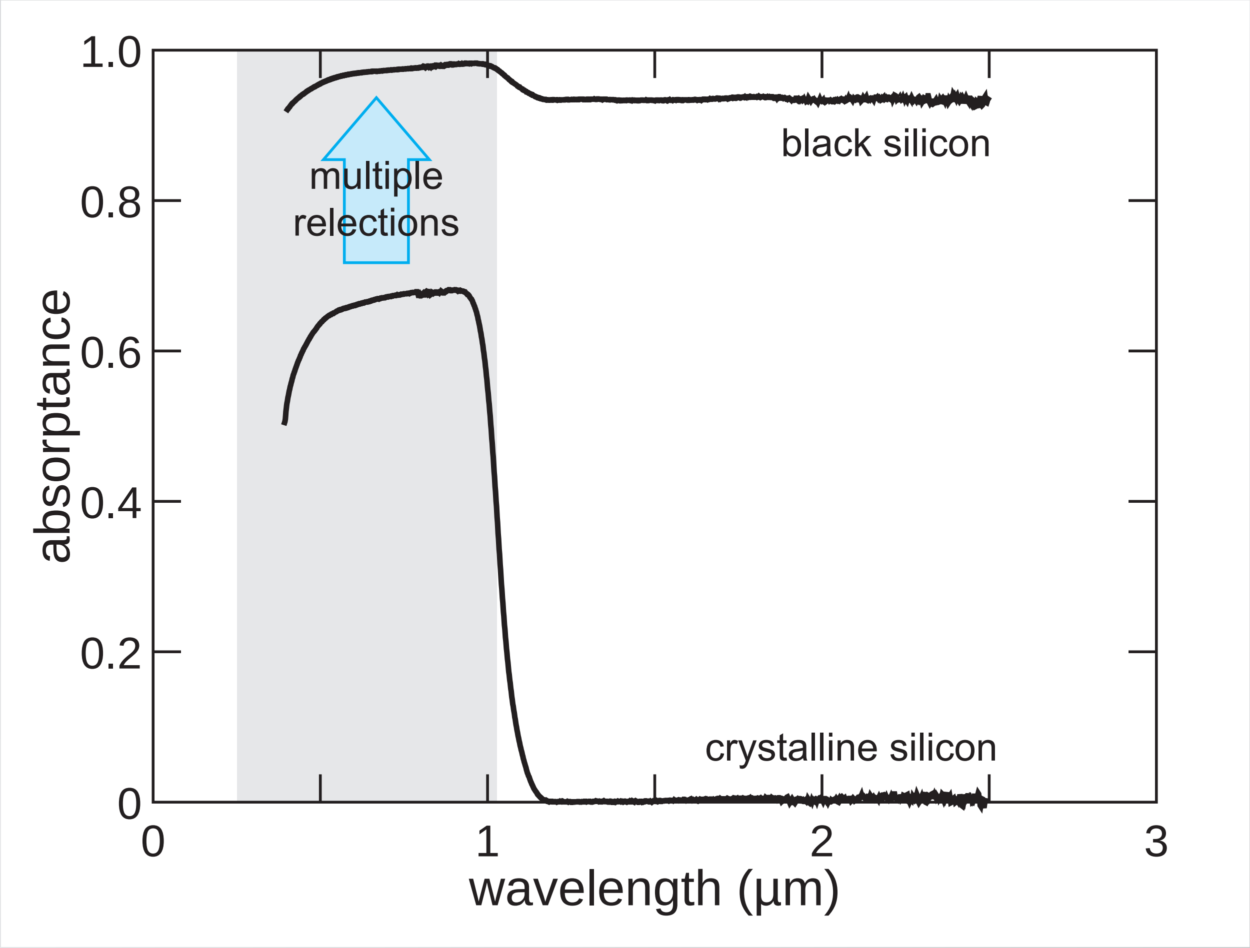


absorptance (1 – R_{int} – T_{int})

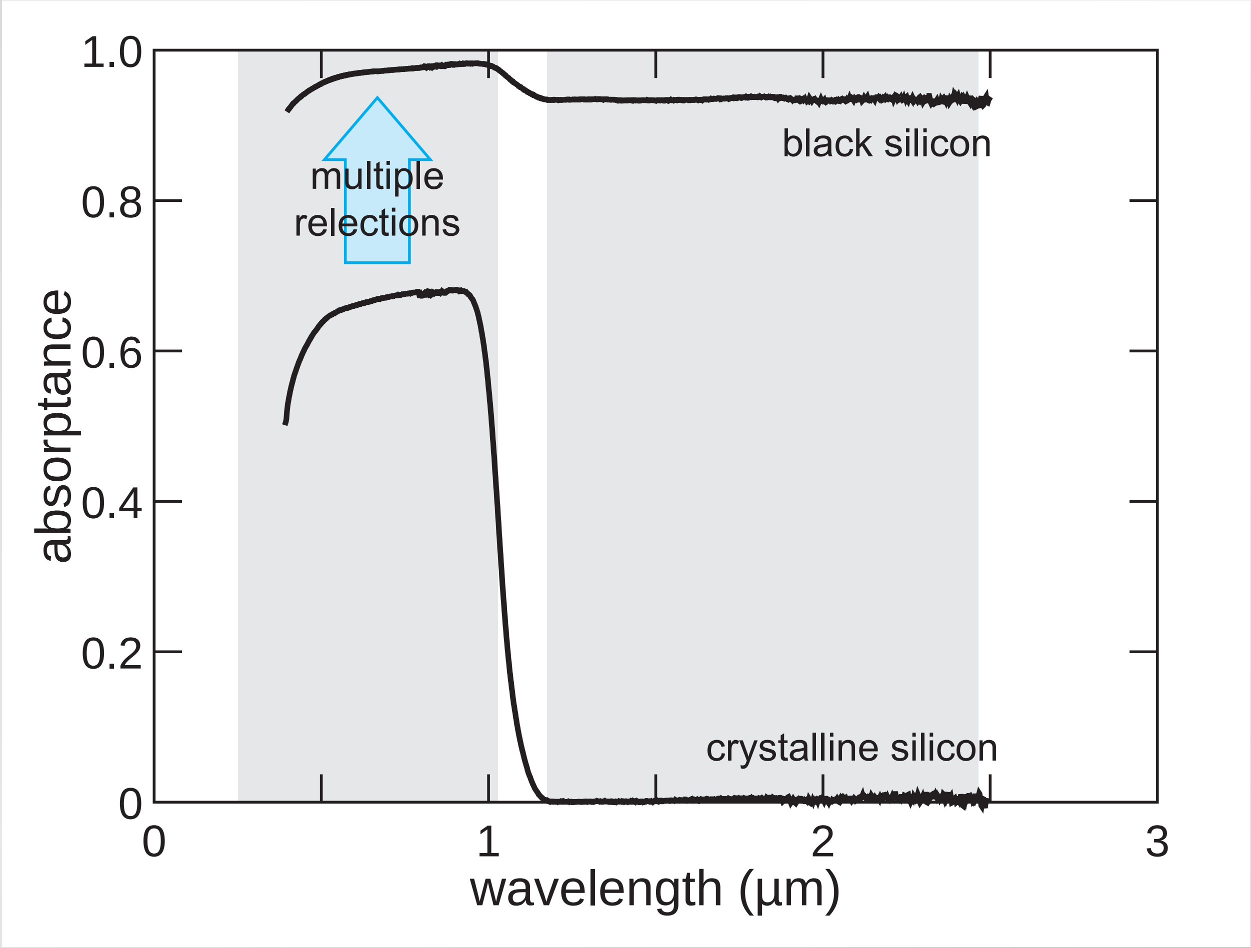




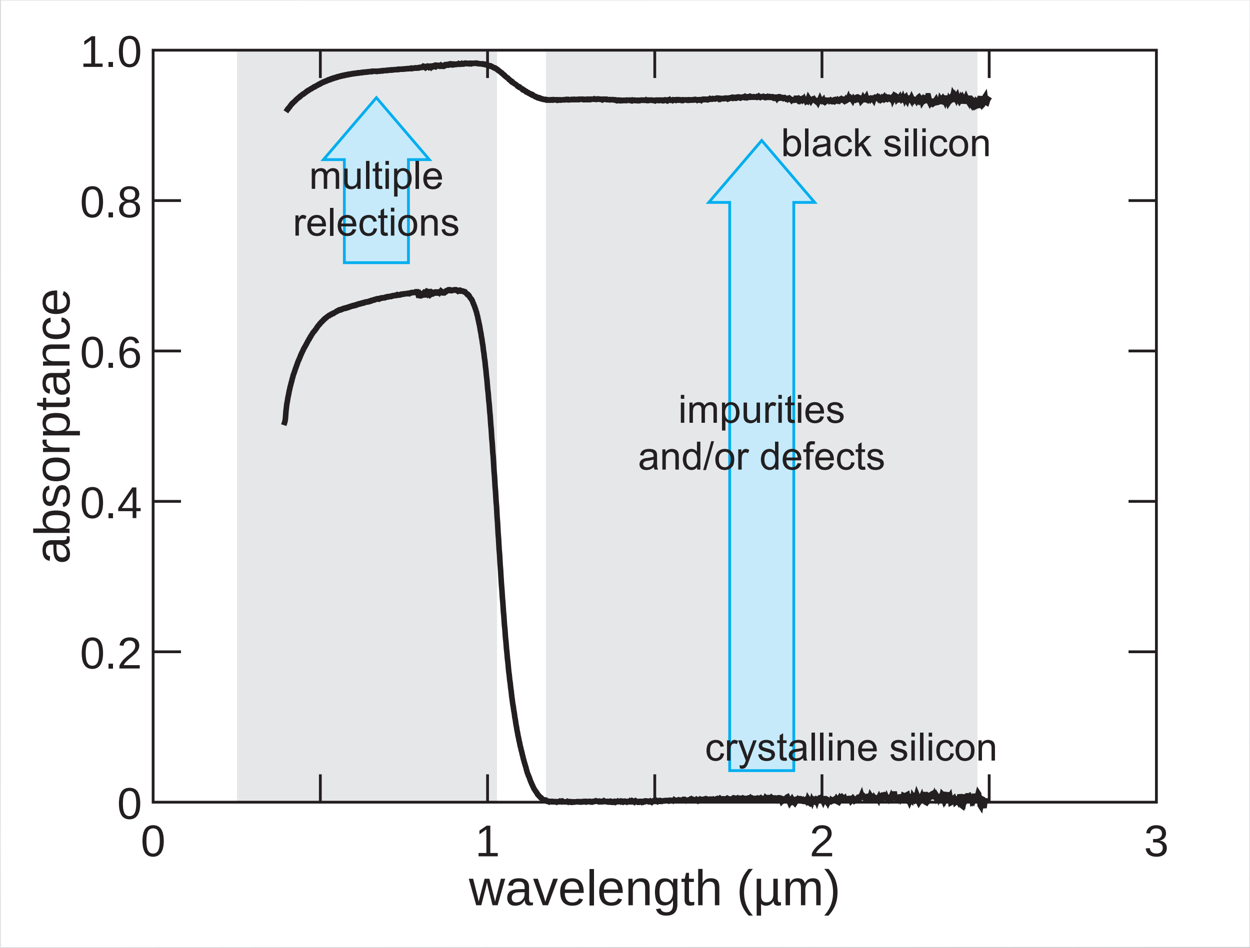
absorptance $(1 - R_{int} - T_{int})$

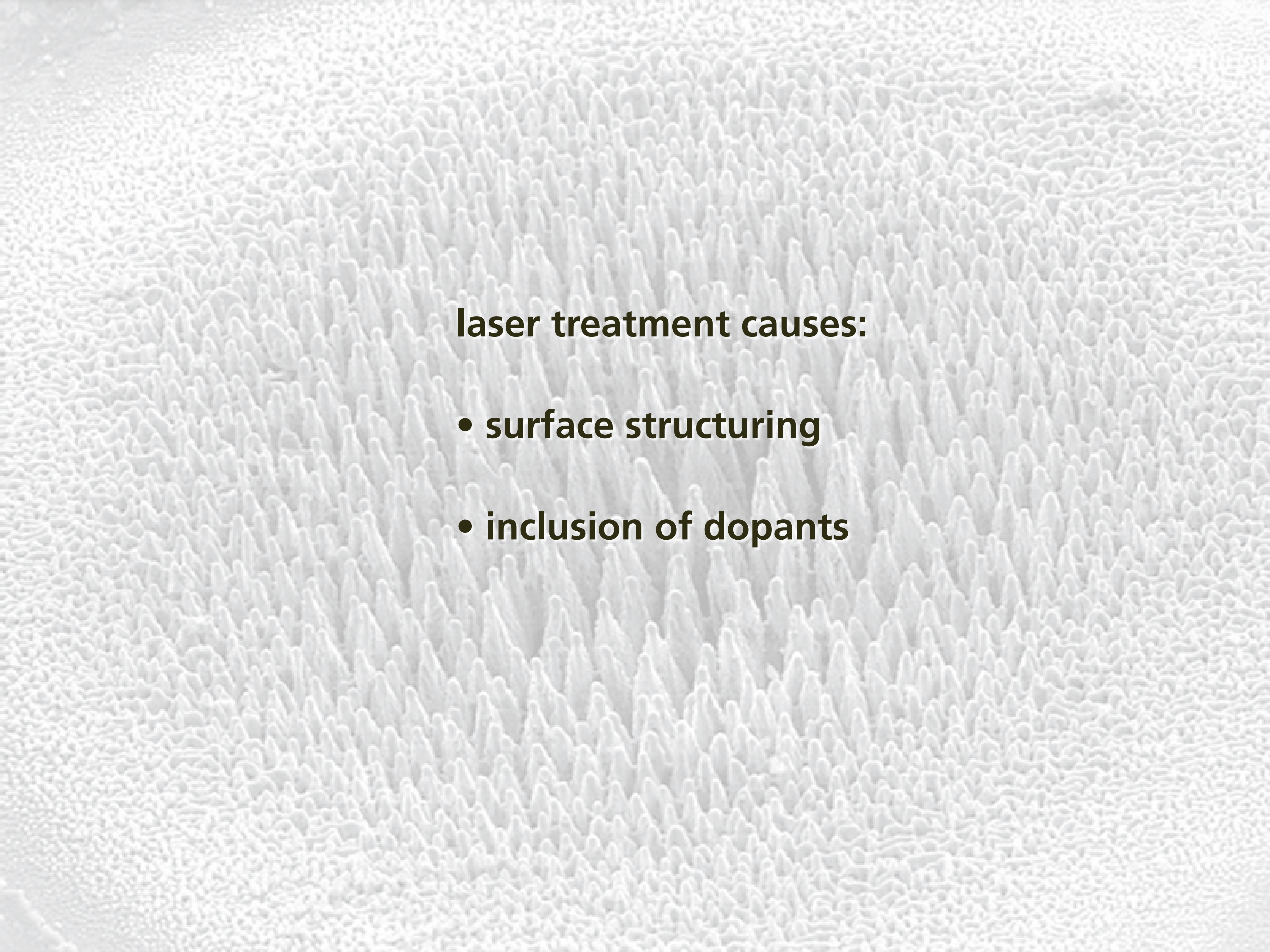


absorptance (1 – R_{int} – T_{int})



absorptance (1 – R_{int} – T_{int})




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	II											III	IV	V	VI	VII	VIII
H																	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
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
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 TiO_2

substrate/dopant combinations

dopants:

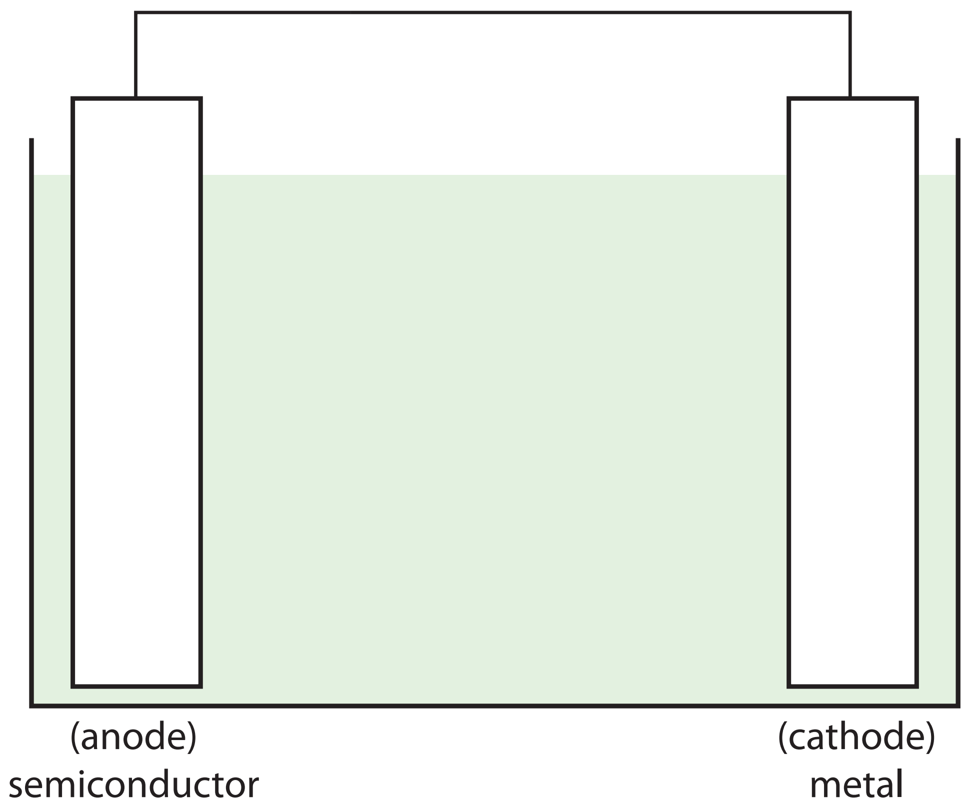
I																	VIII
H	II											III	IV	V	VI	VII	He
Li	Be											B	C	**N**	**O**	**F**	Ne
Na	Mg											Al	Si	**P**	**S**	**Cl**	Ar
K	Ca	Sc	Ti	V	**Cr**	**Mn**	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	**Se**	Br	Kr
Rb	Sr	Y	Zr	Nb	**Mo**	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	**Sb**	**Te**	I	Xe

substrates:

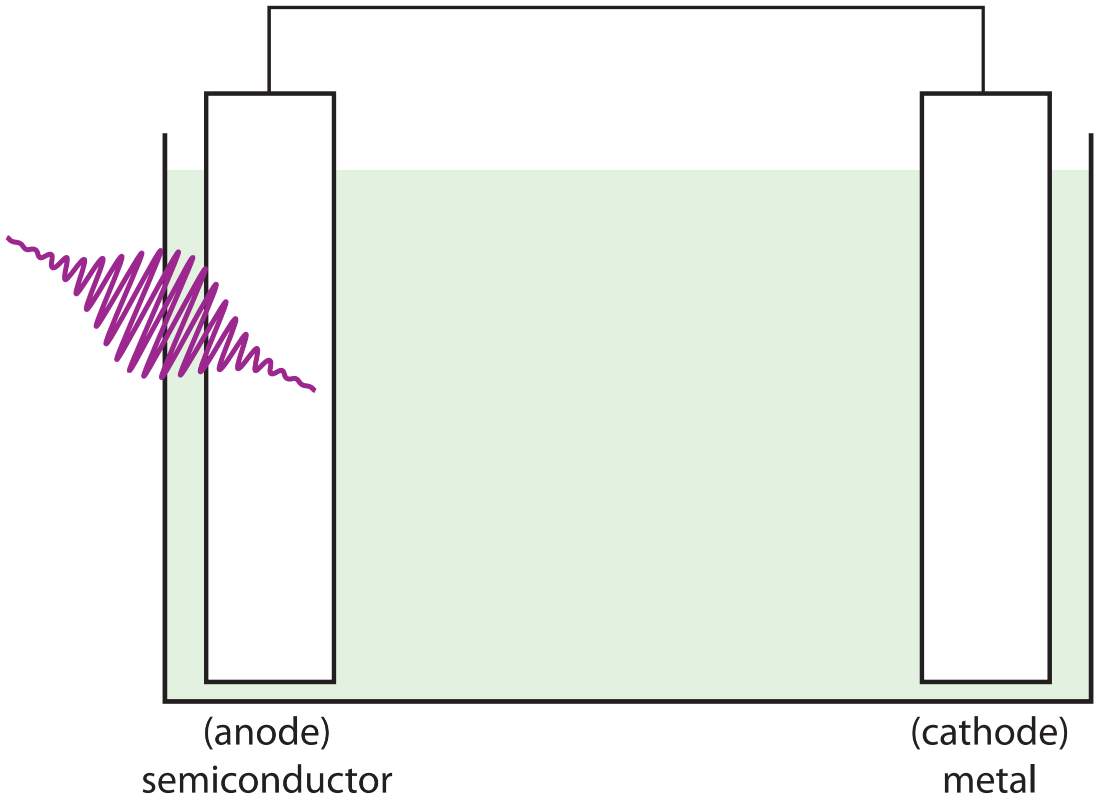
Si Ge ZnO InP GaAs

Ti Ag Al Cu Pd Rh Ta Pt **TiO_2**

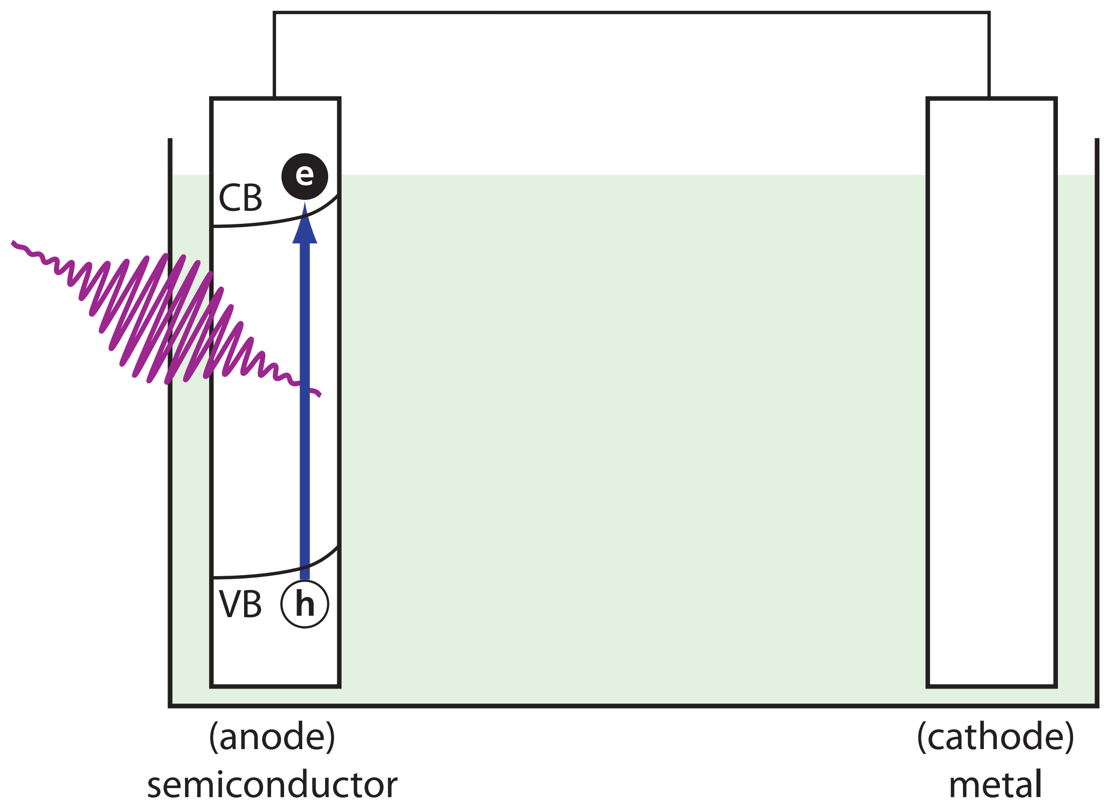
water splitting



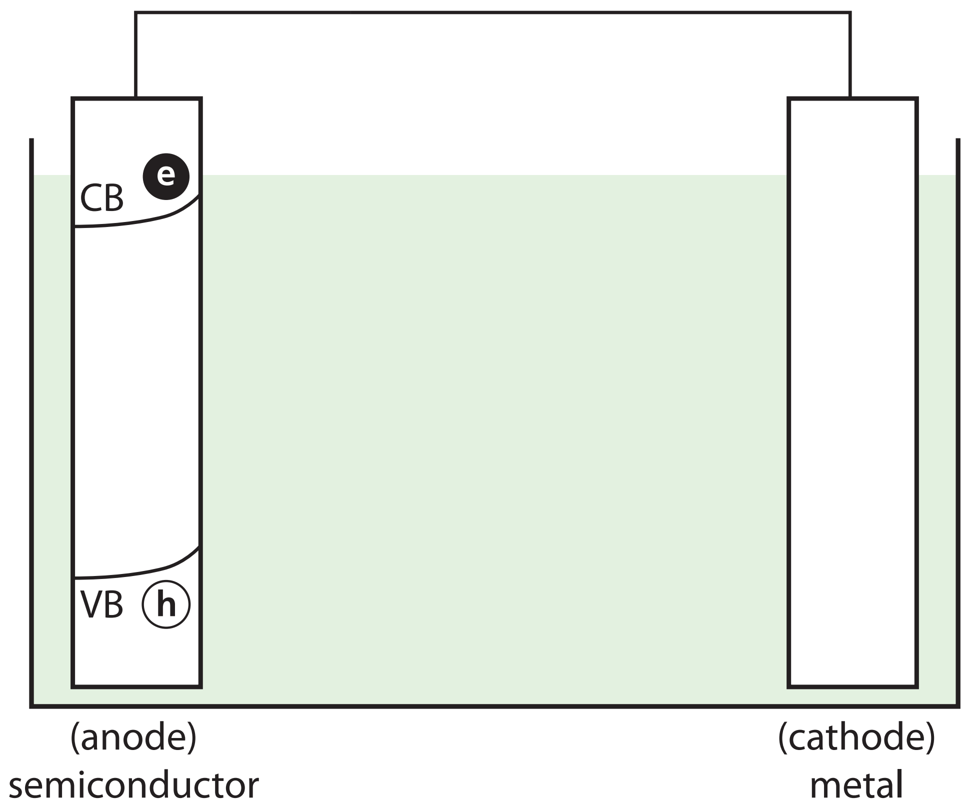
water splitting



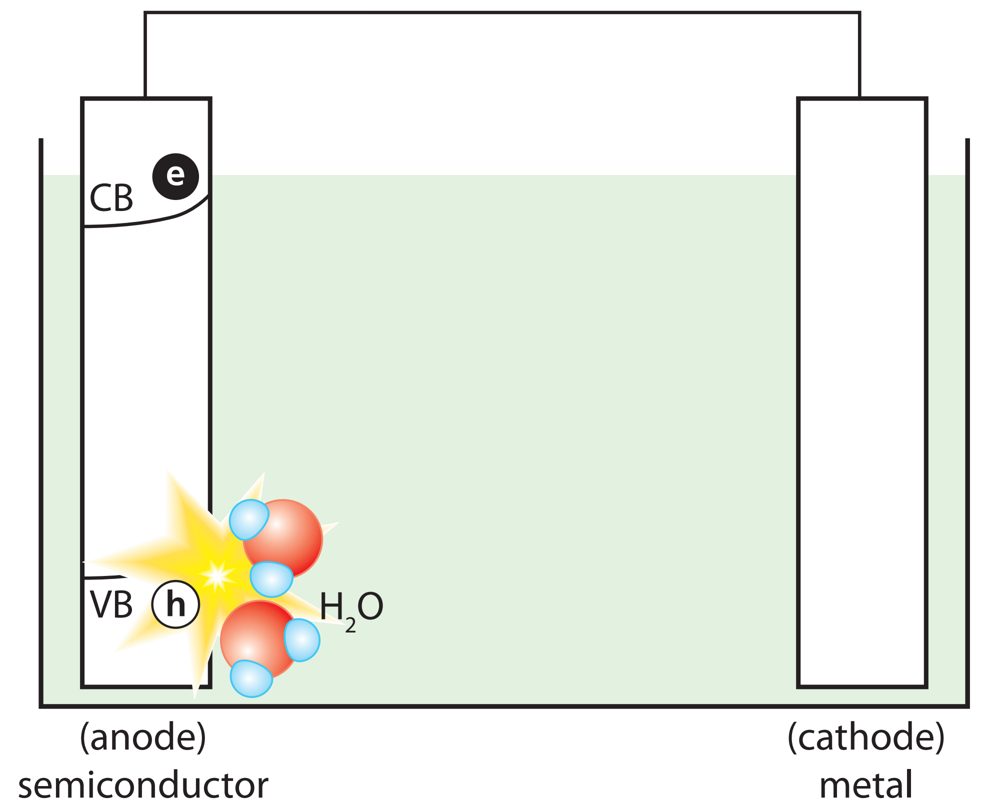
water splitting



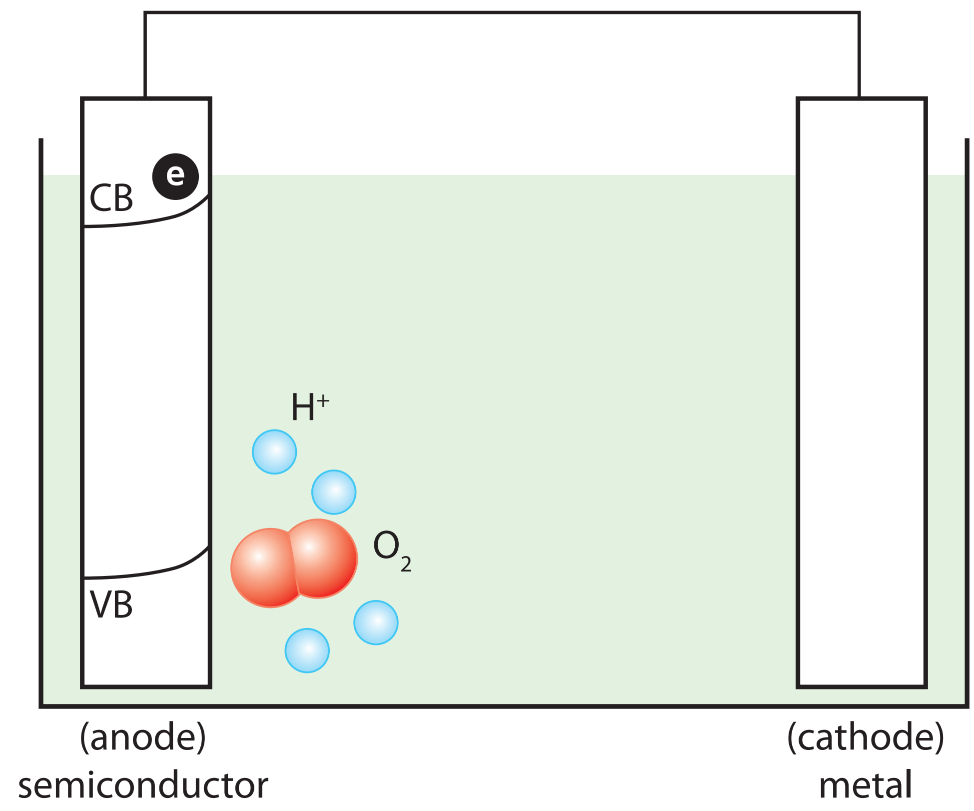
water splitting



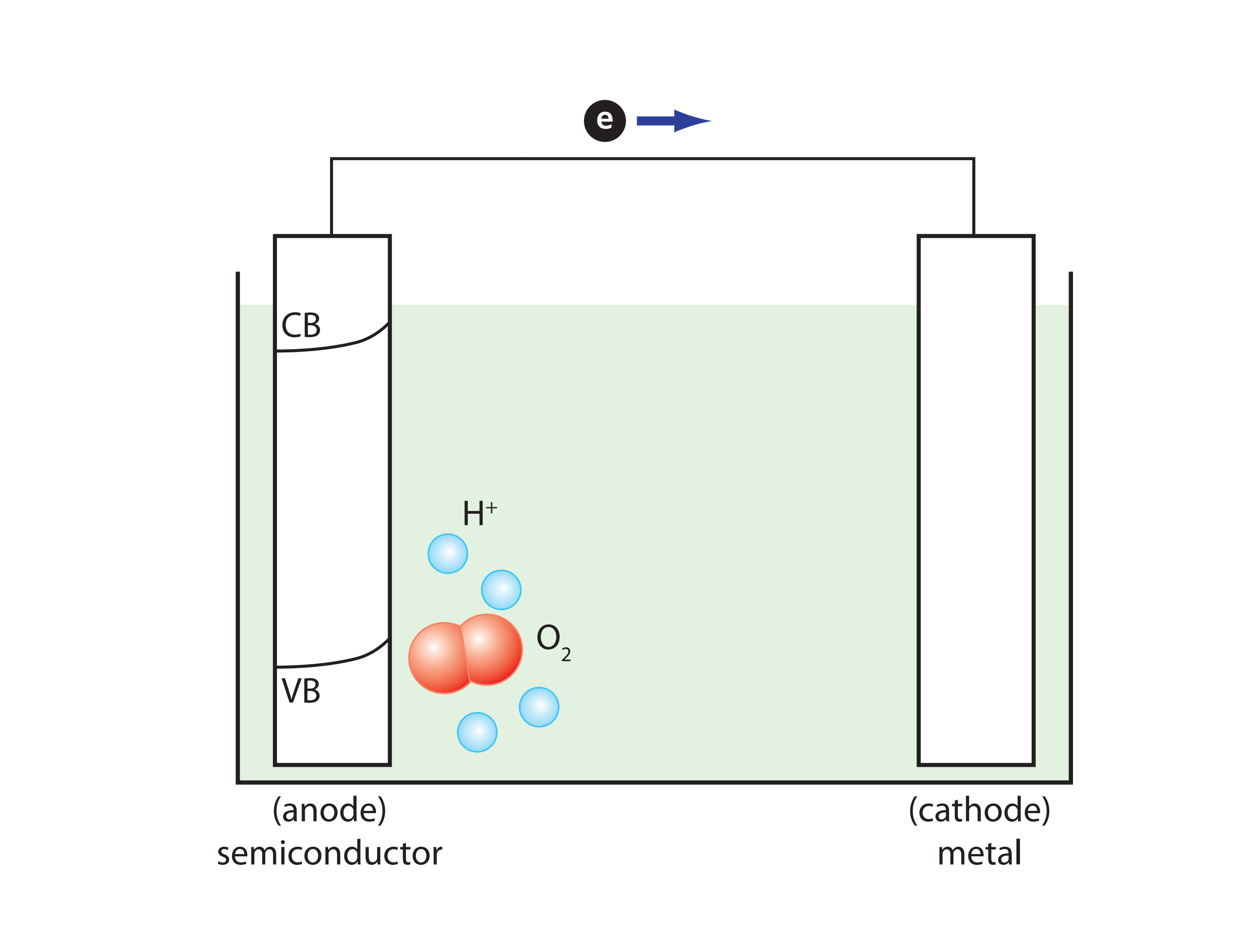
water splitting



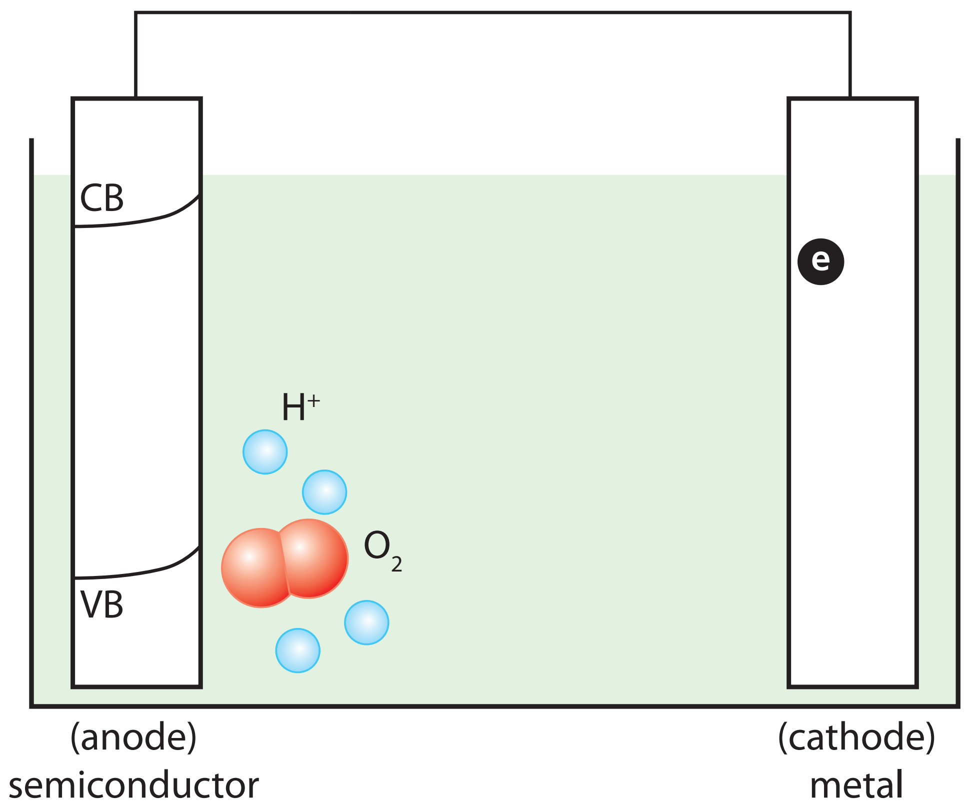
water splitting



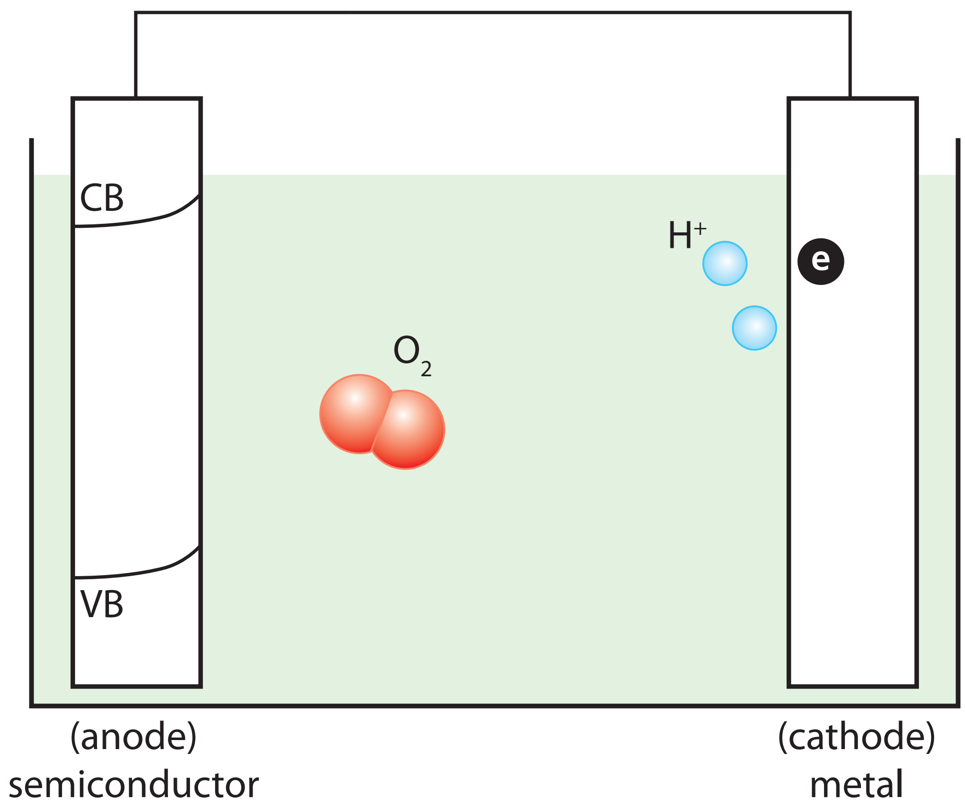
water splitting



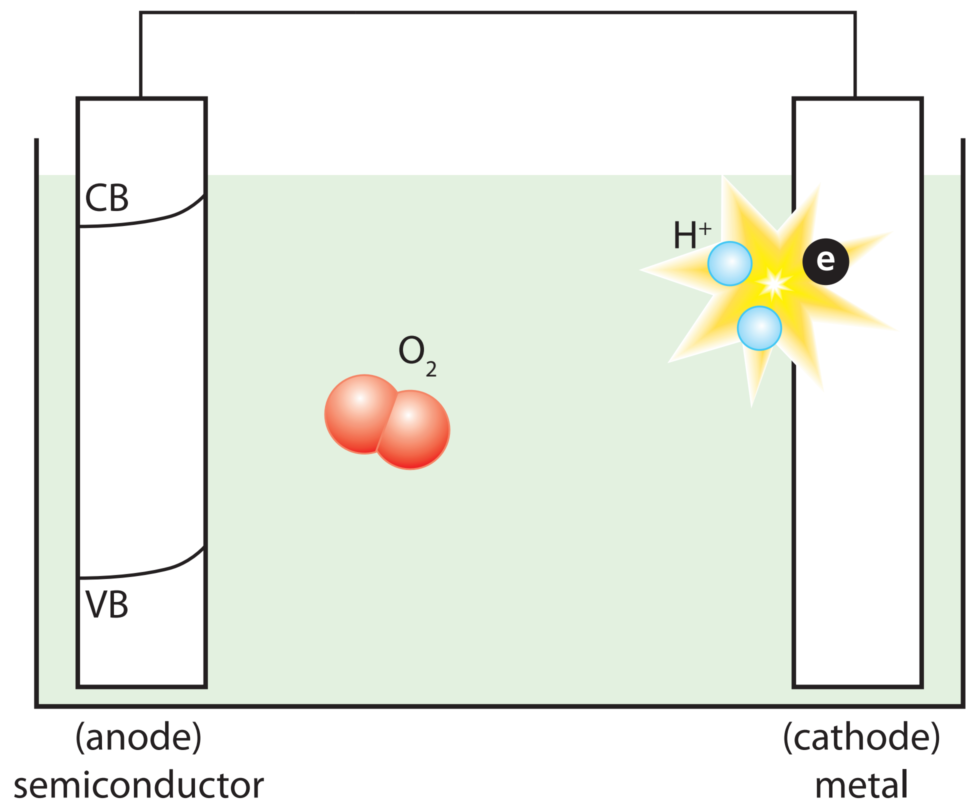
water splitting



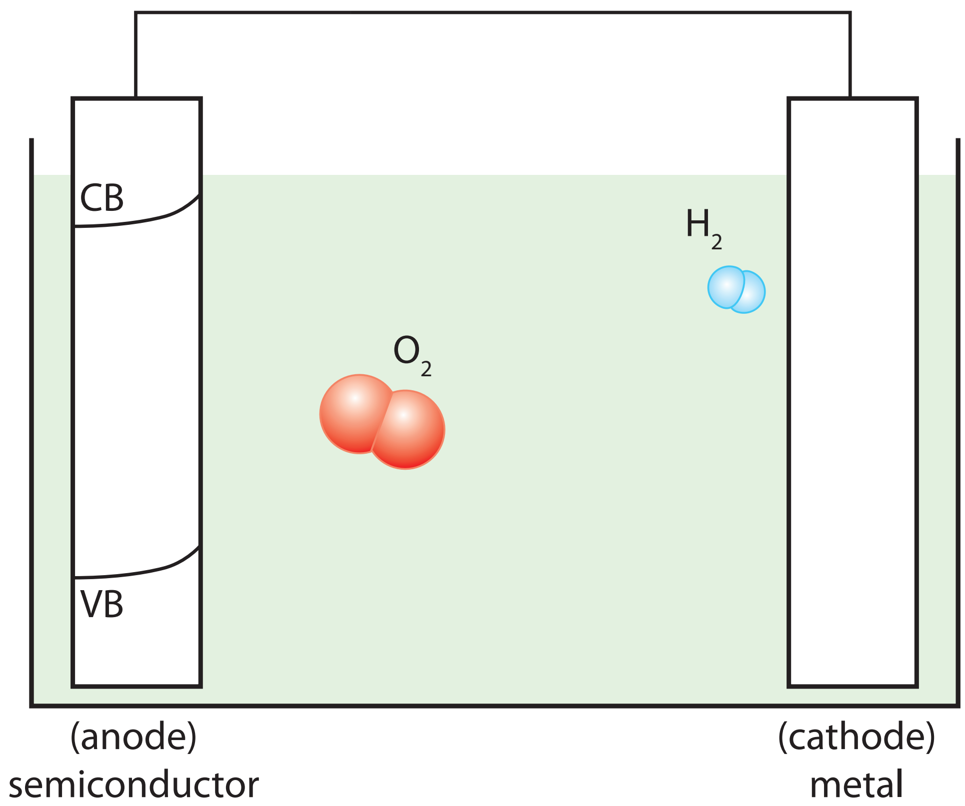
water splitting



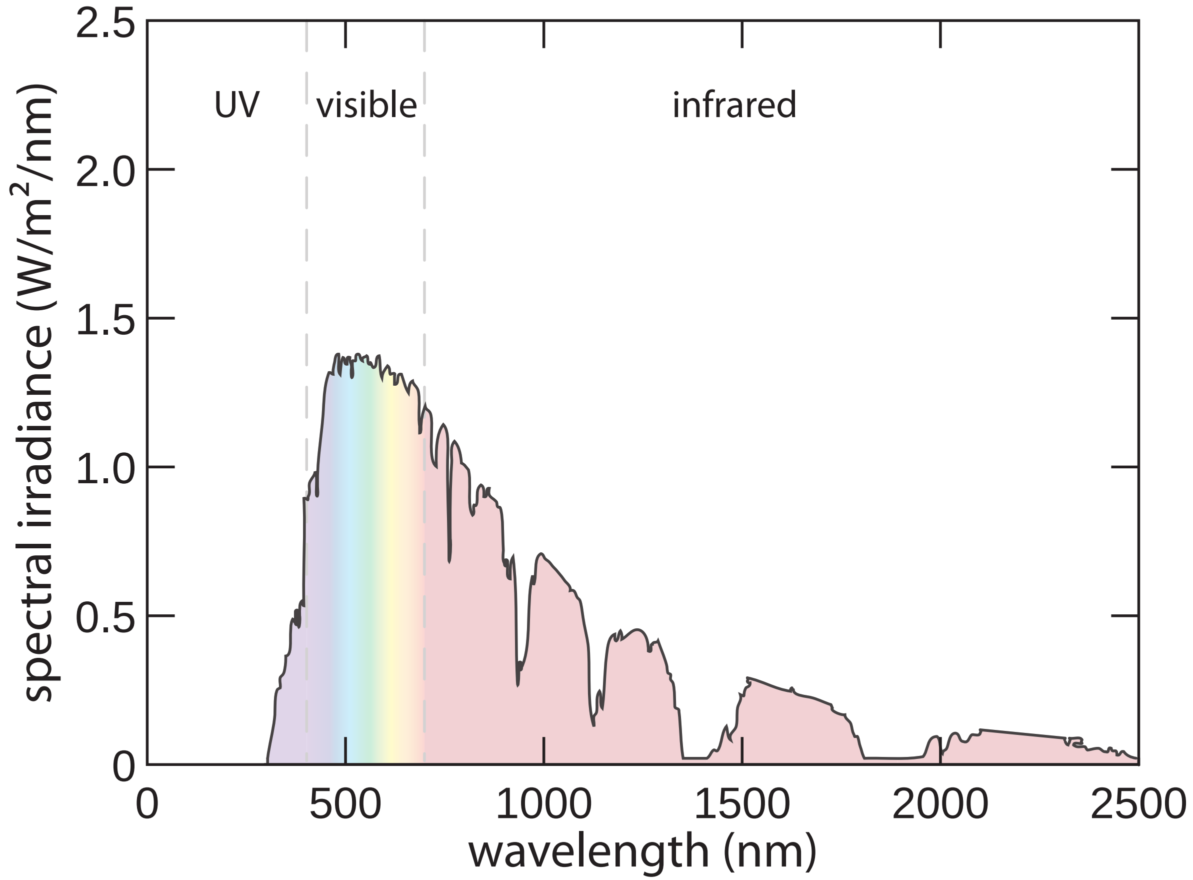
water splitting



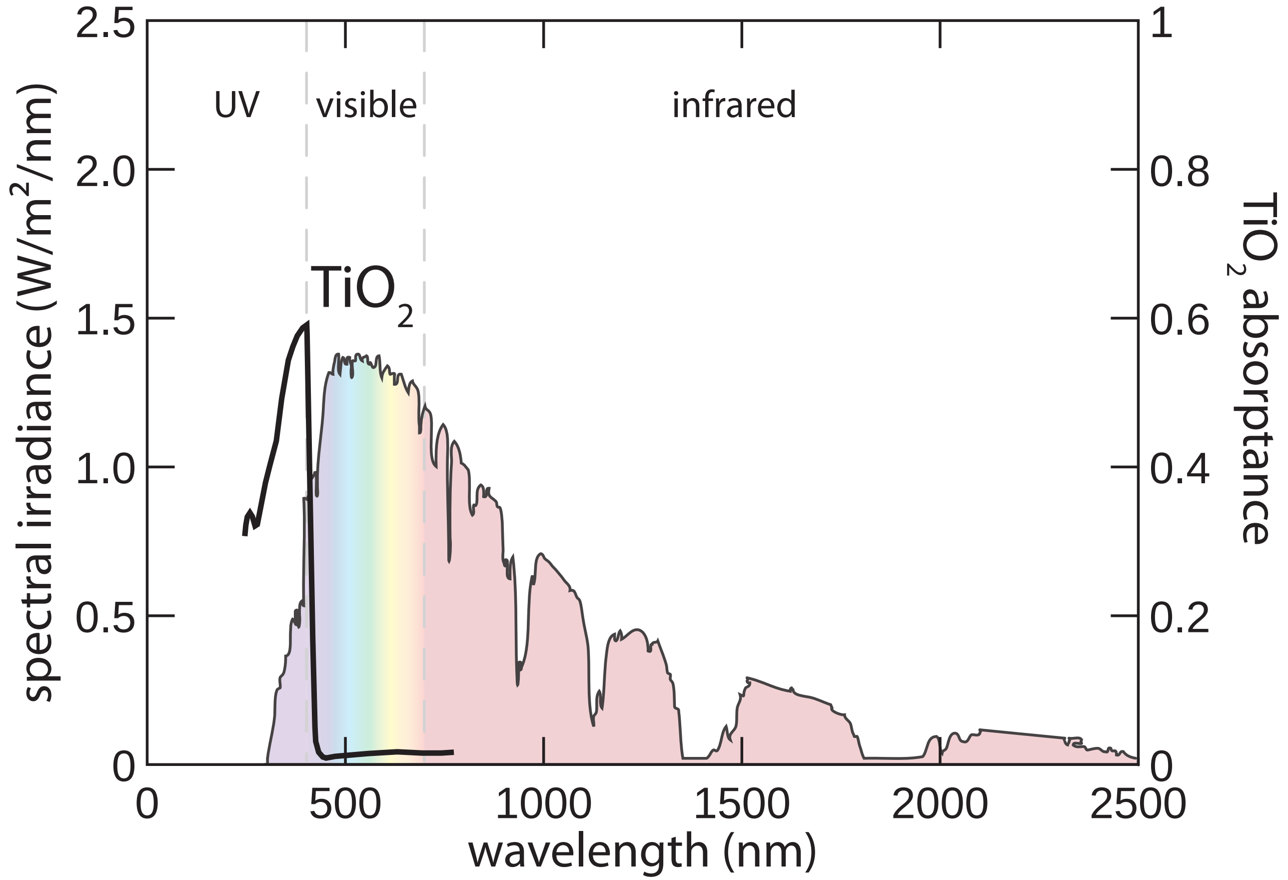
water splitting



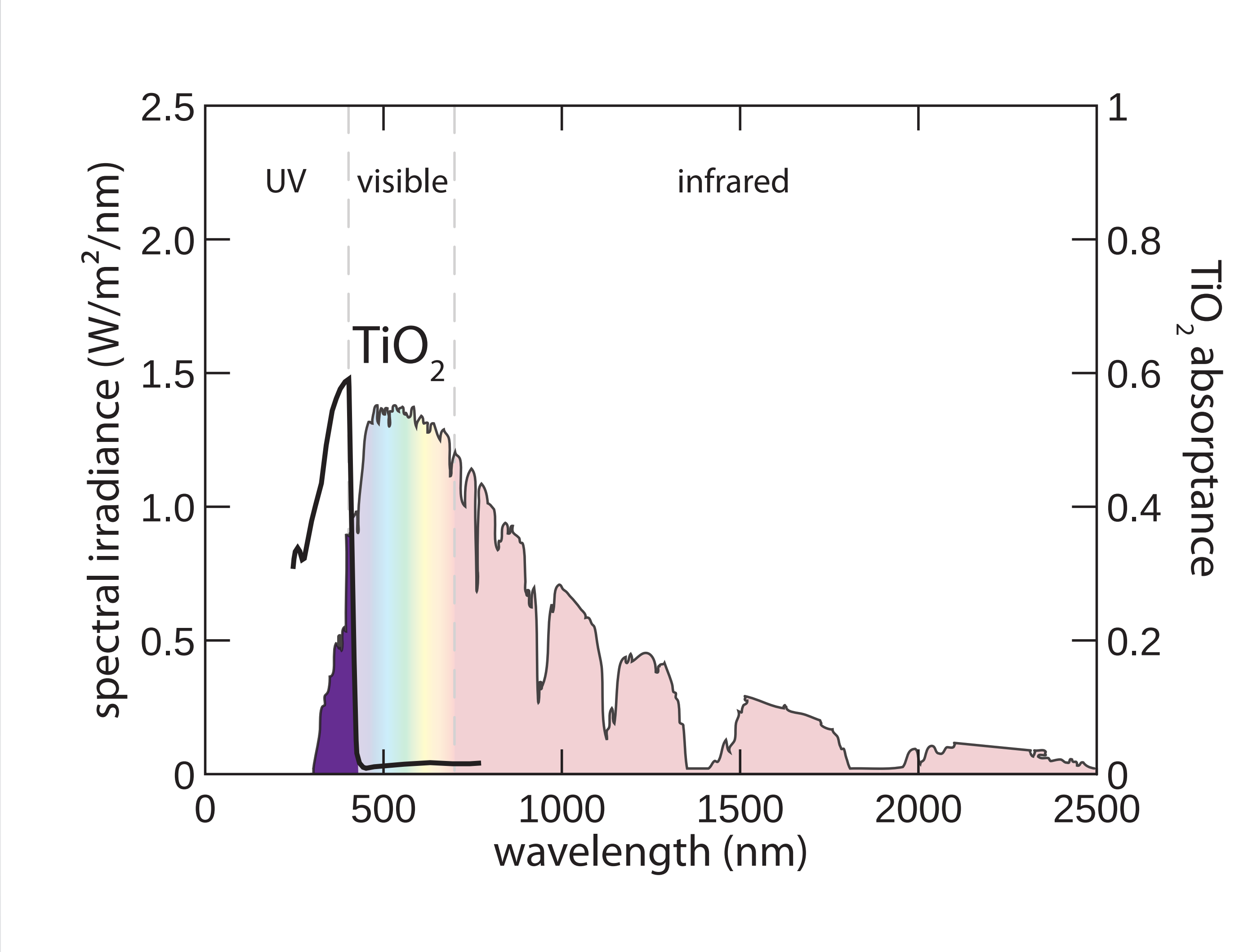
solar radiation spectrum



solar radiation spectrum

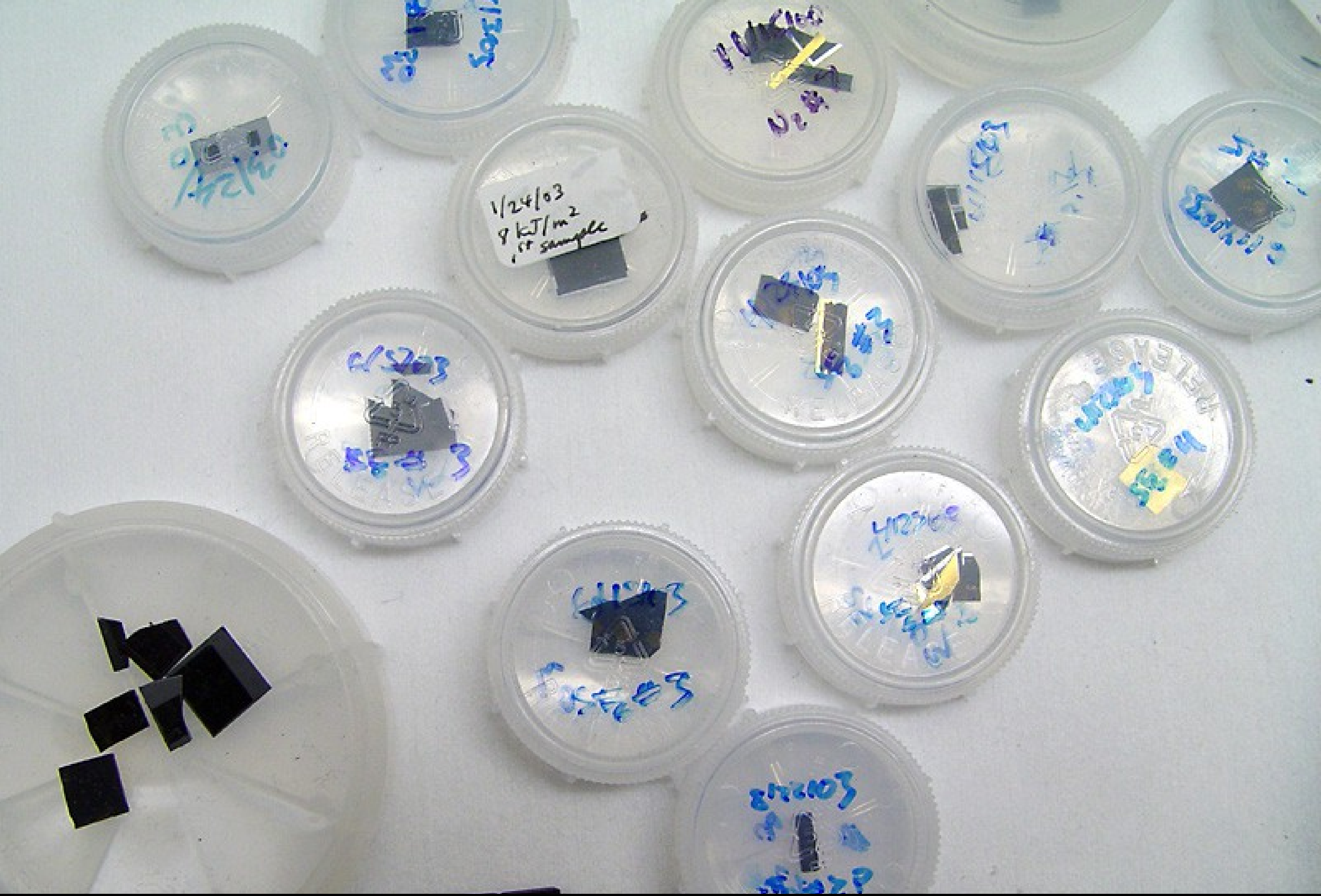


solar radiation spectrum

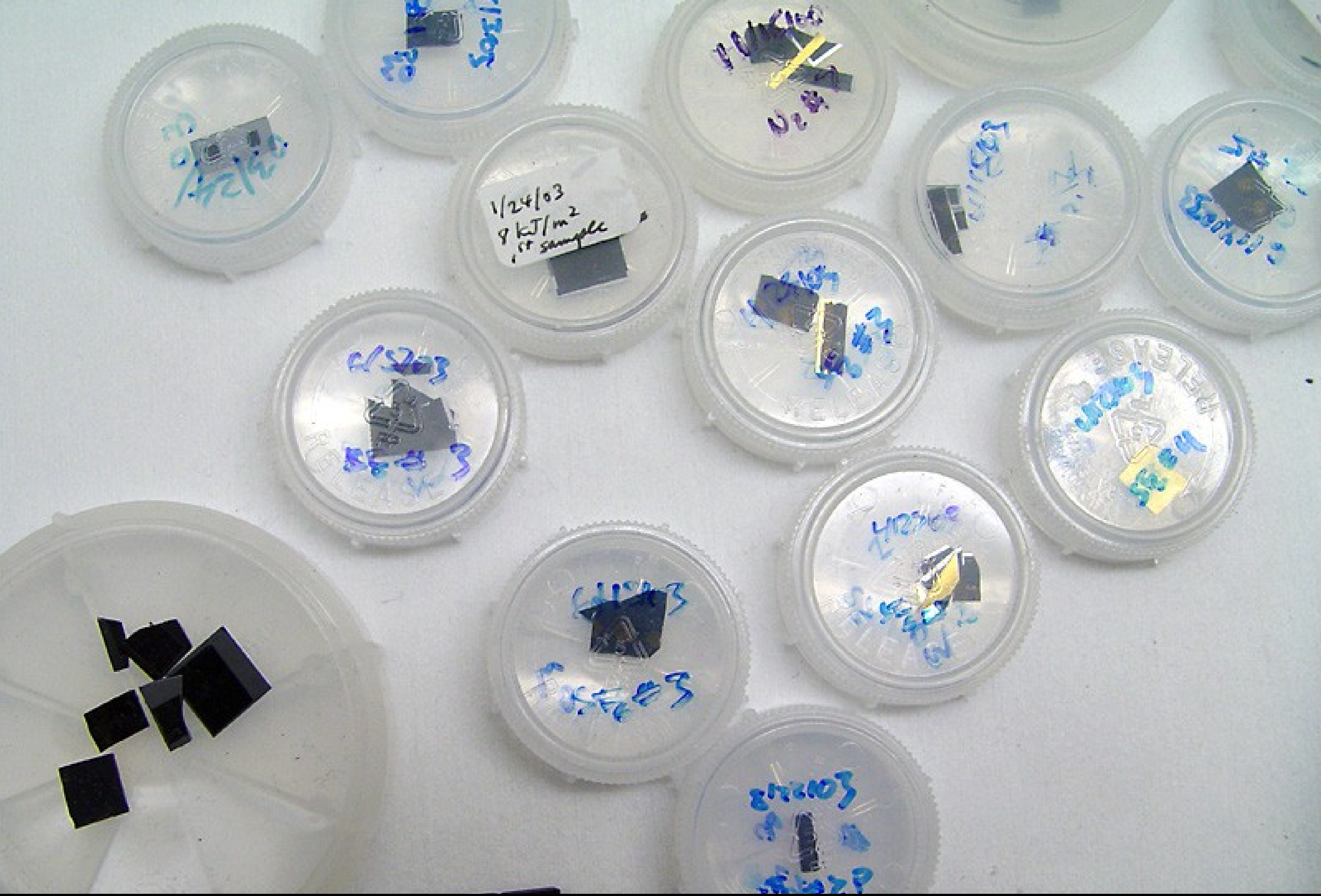


increase efficiency by:

- **increasing surface area**
- **shifting band edge**

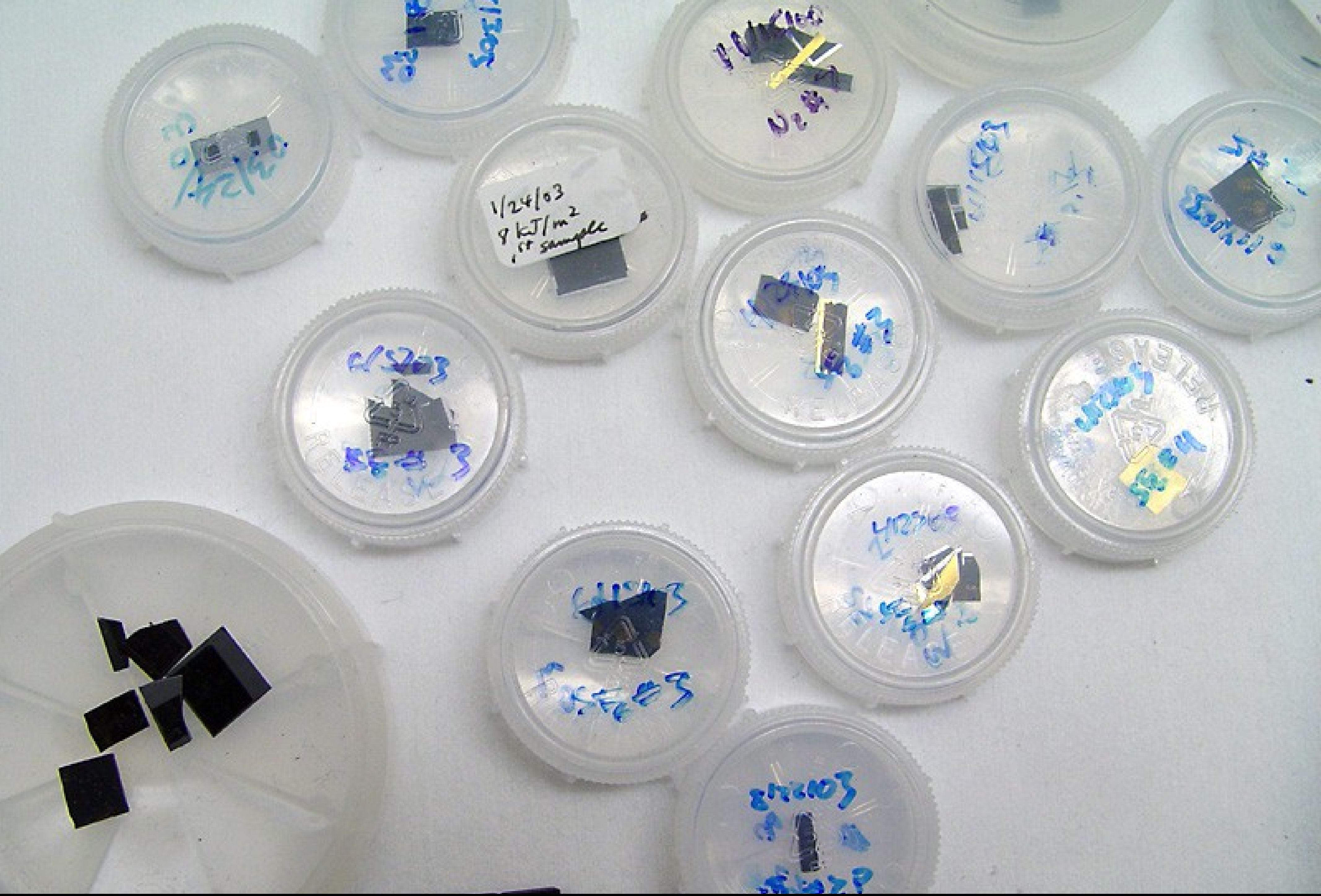


1 texturing

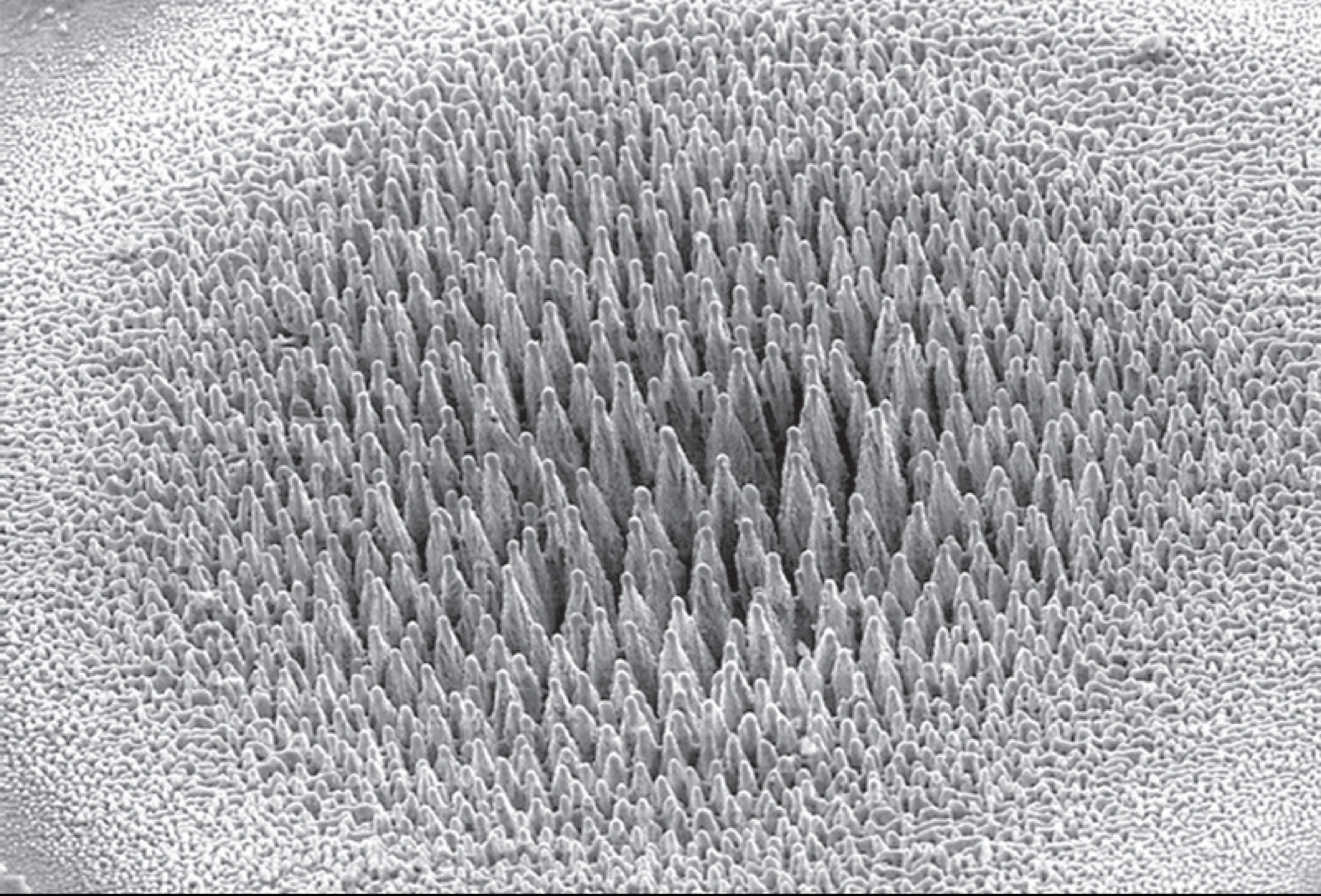


1 texturing

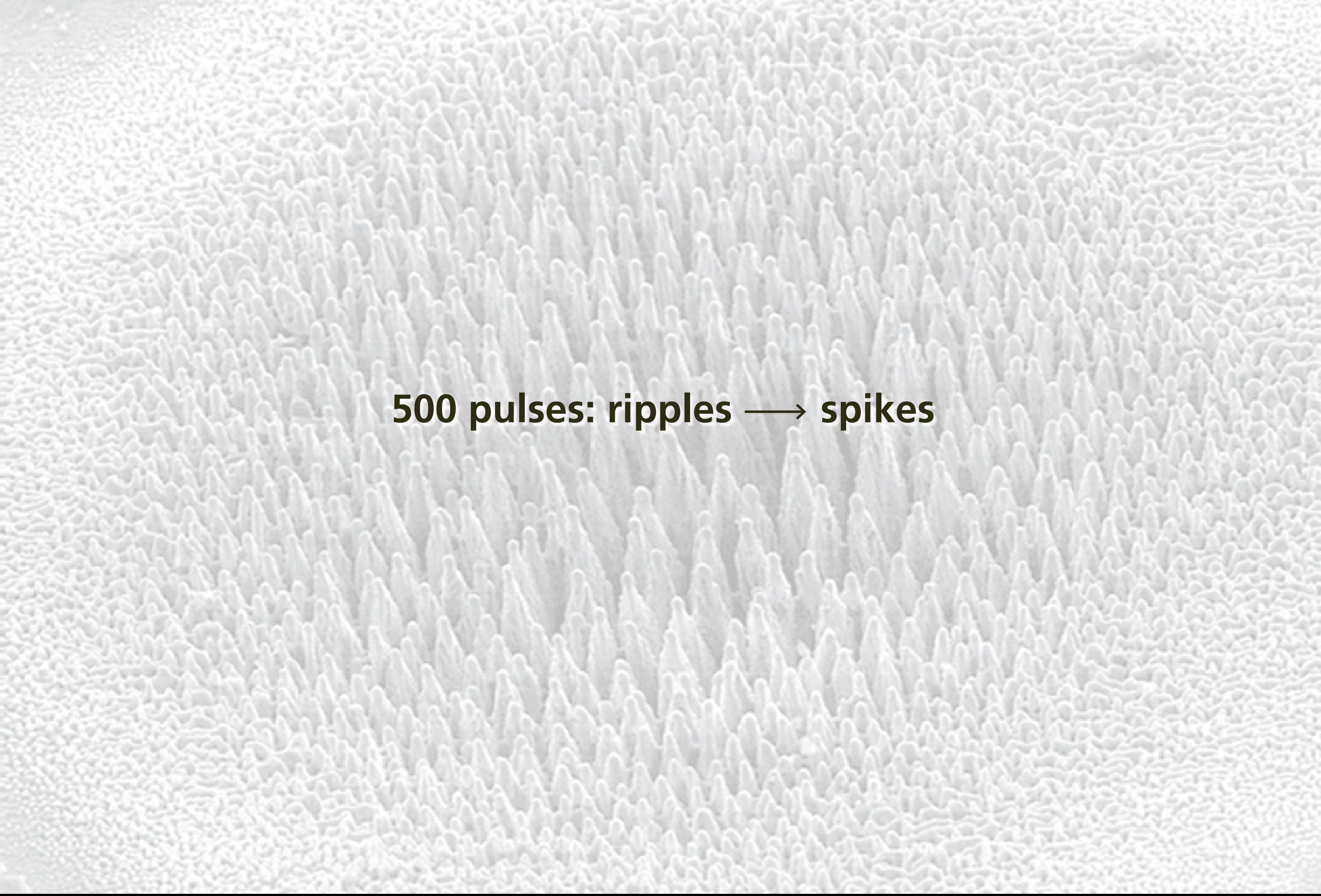
2 doping



1 texturing 2 doping 3 X:TiO_2

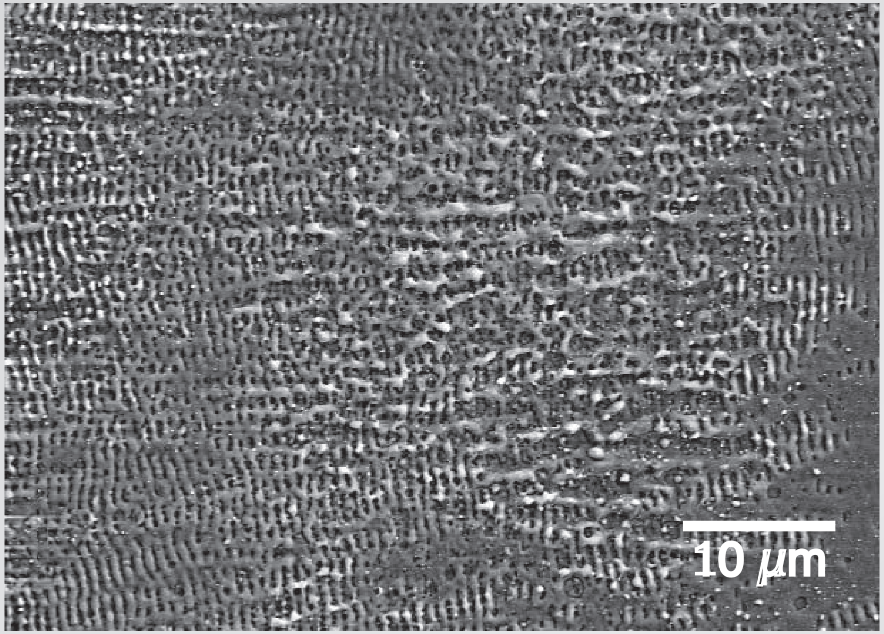


1 texturing



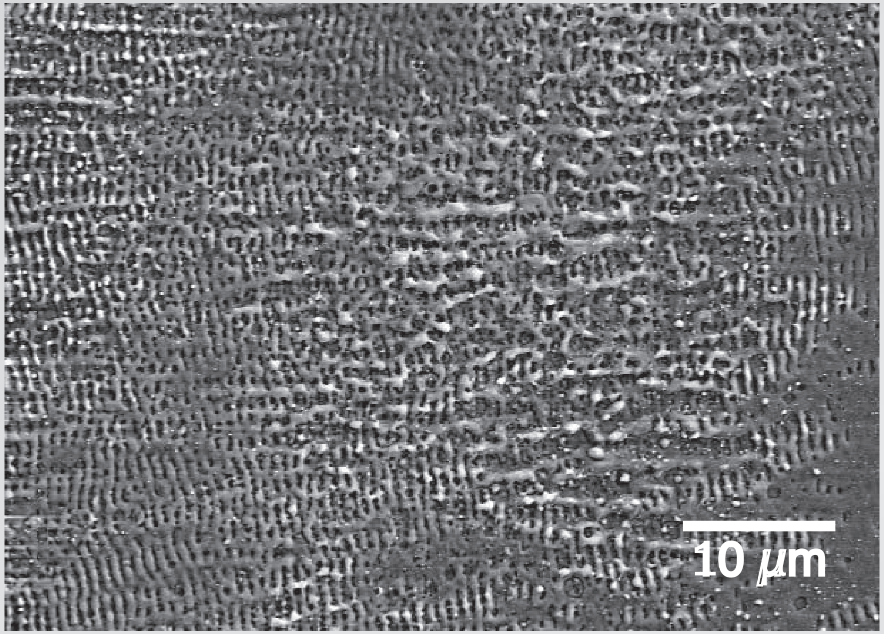
1 texturing

2 pulses



1 texturing

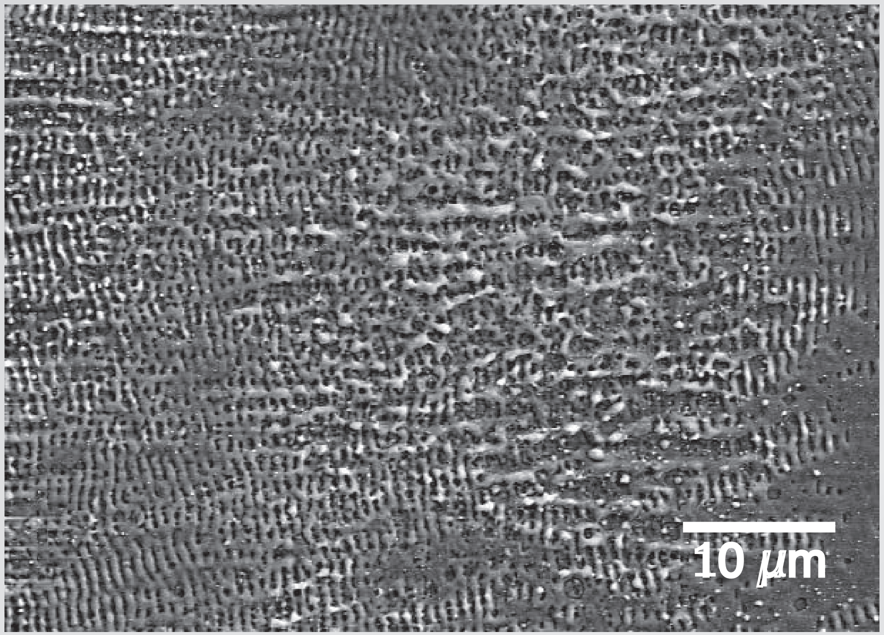
2 pulses

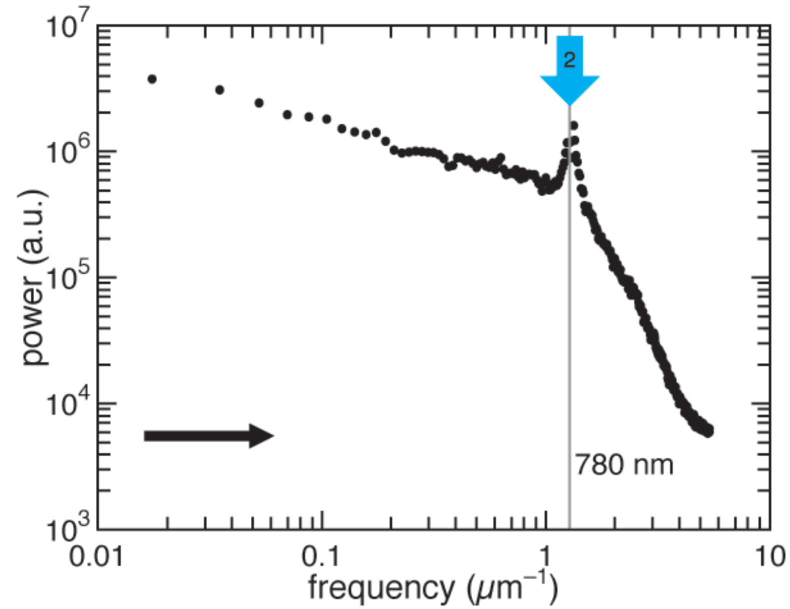


polarization →

1 texturing

2 pulses

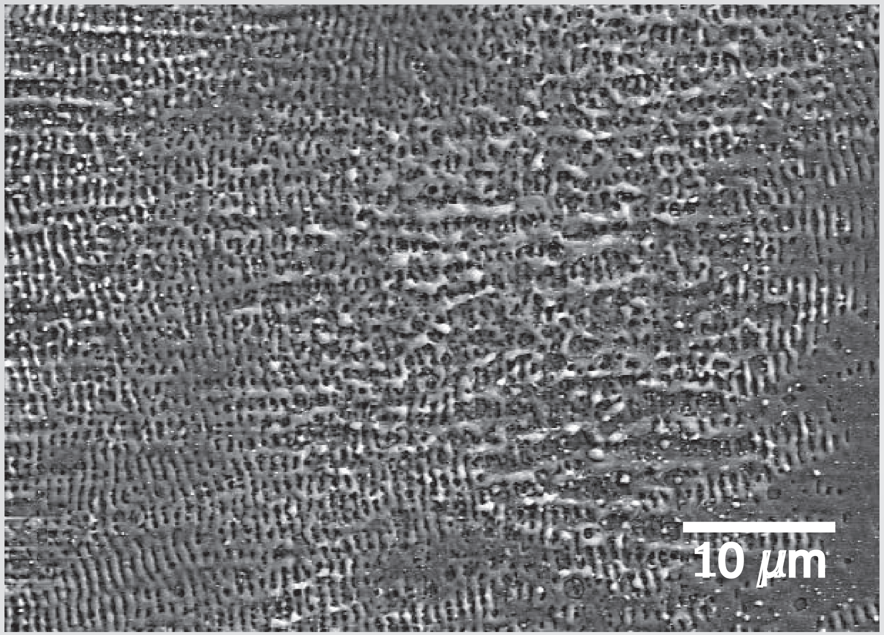




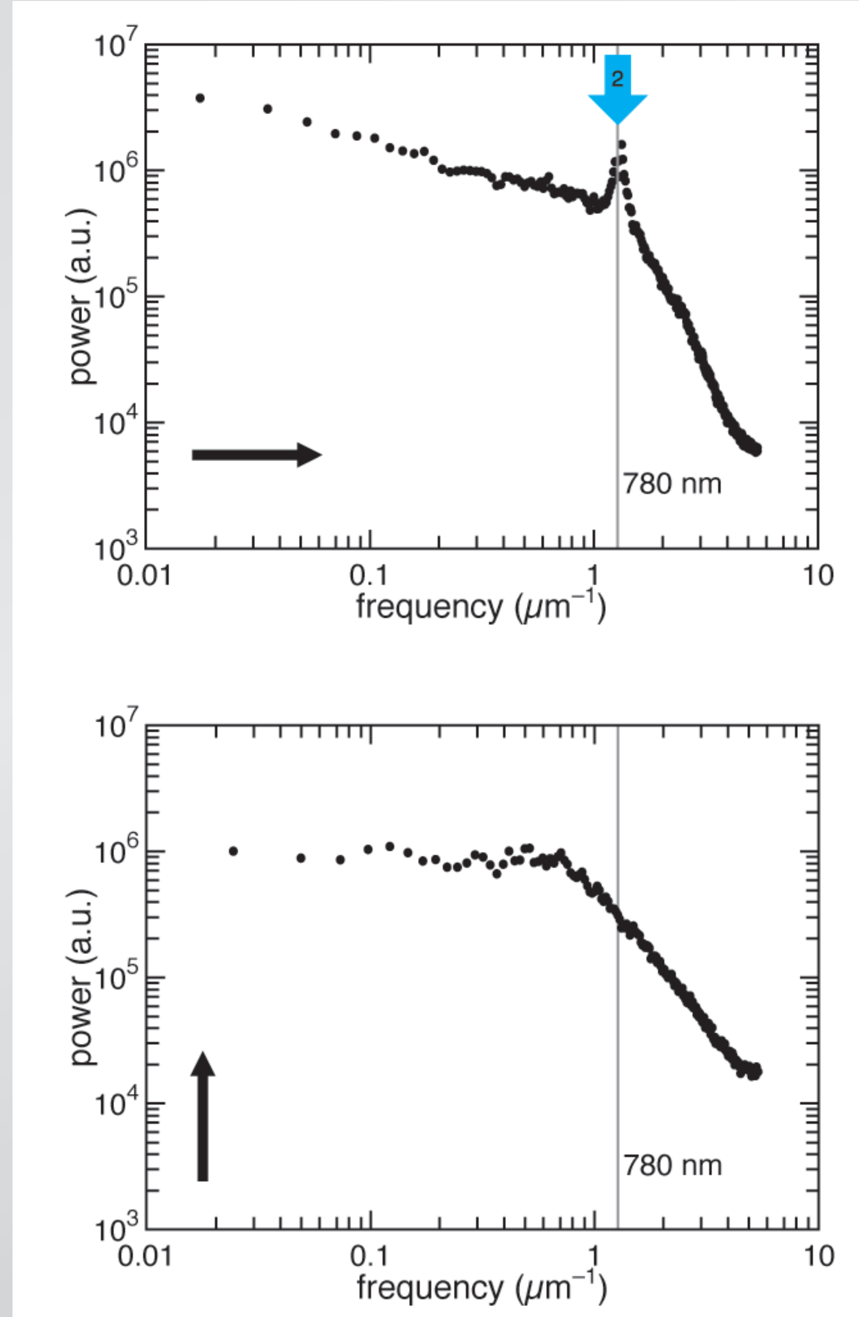
polarization

1 texturing

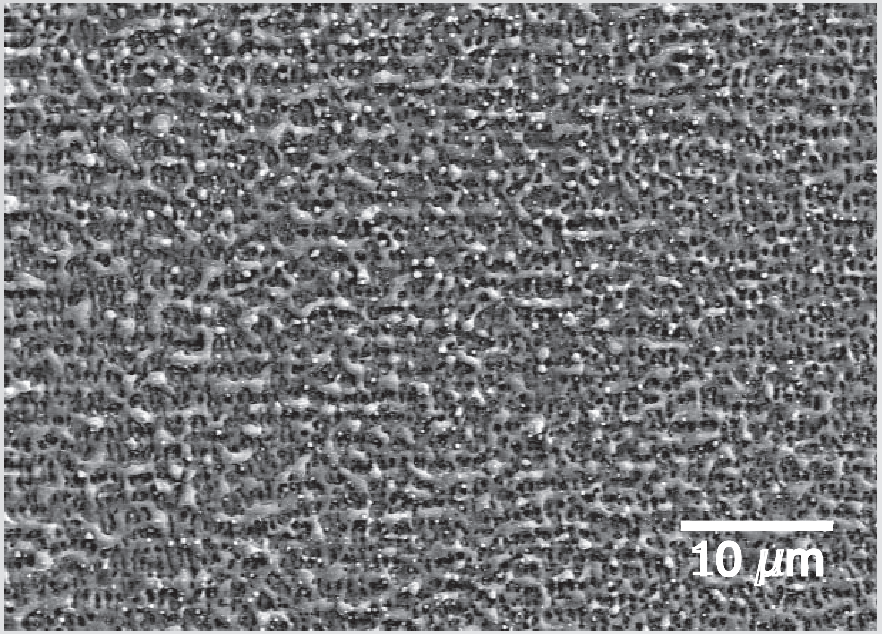
2 pulses

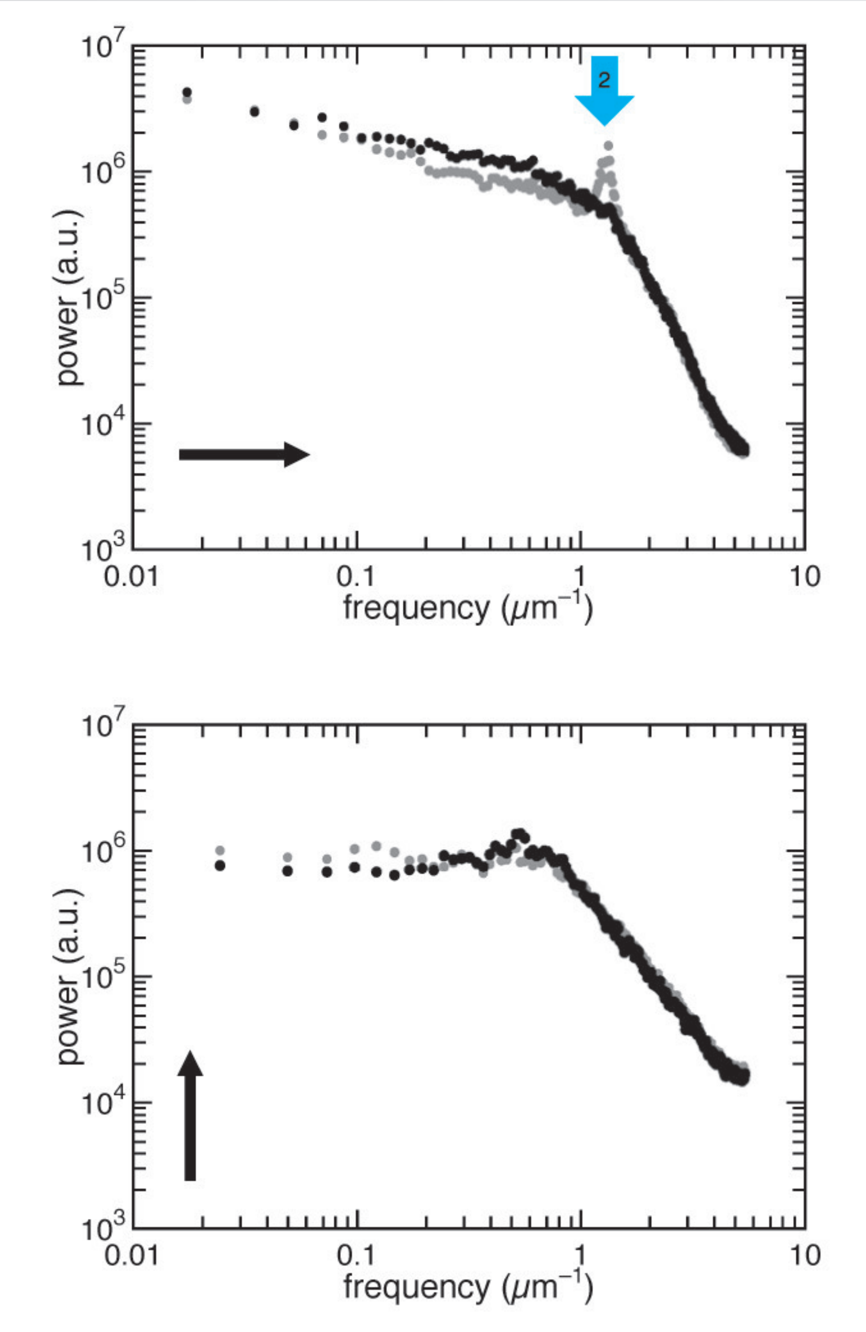


polarization

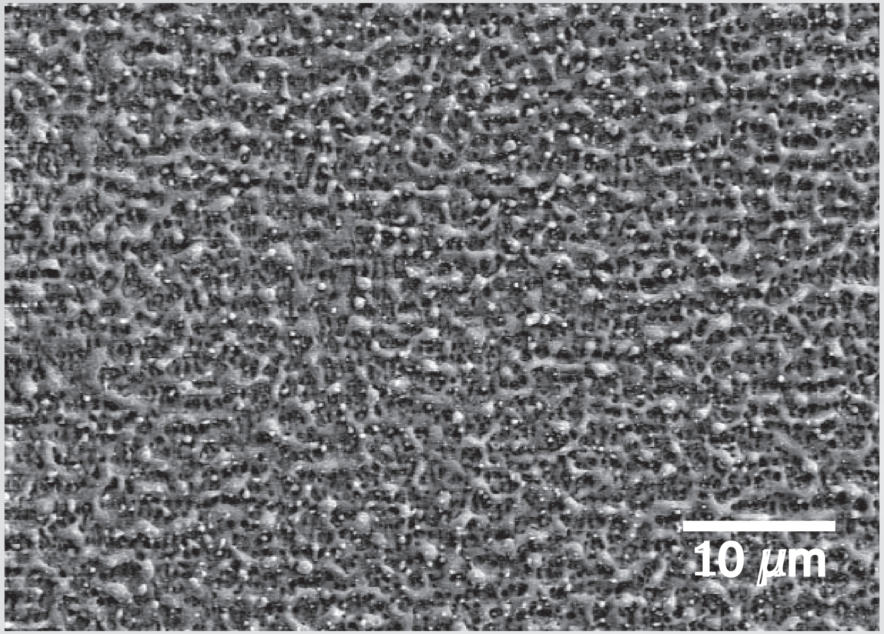


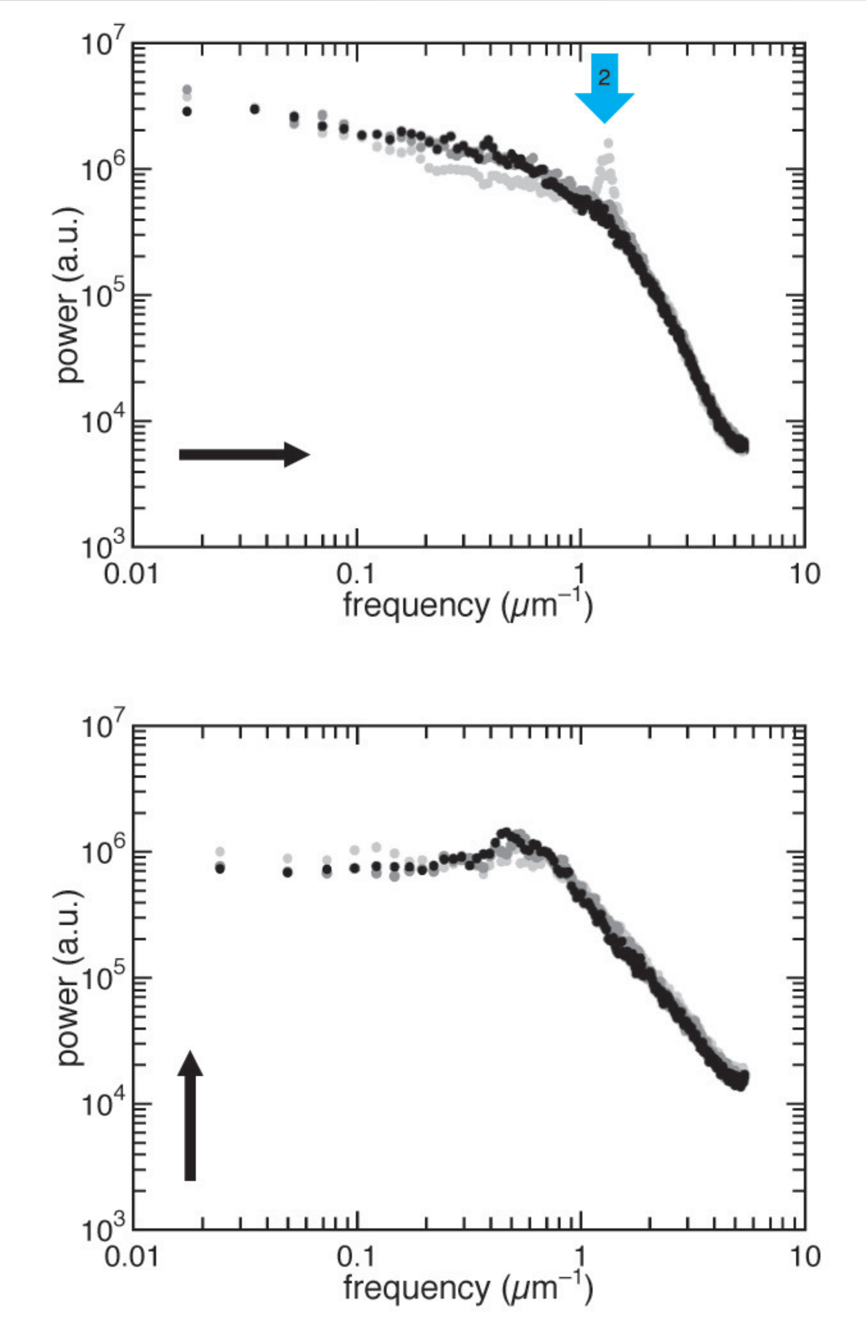
3 pulses





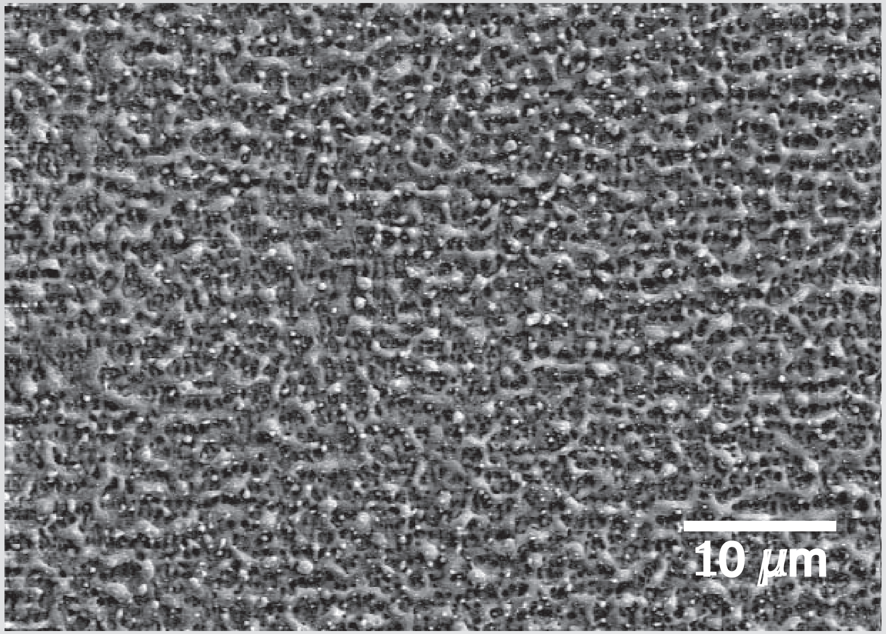
4 pulses

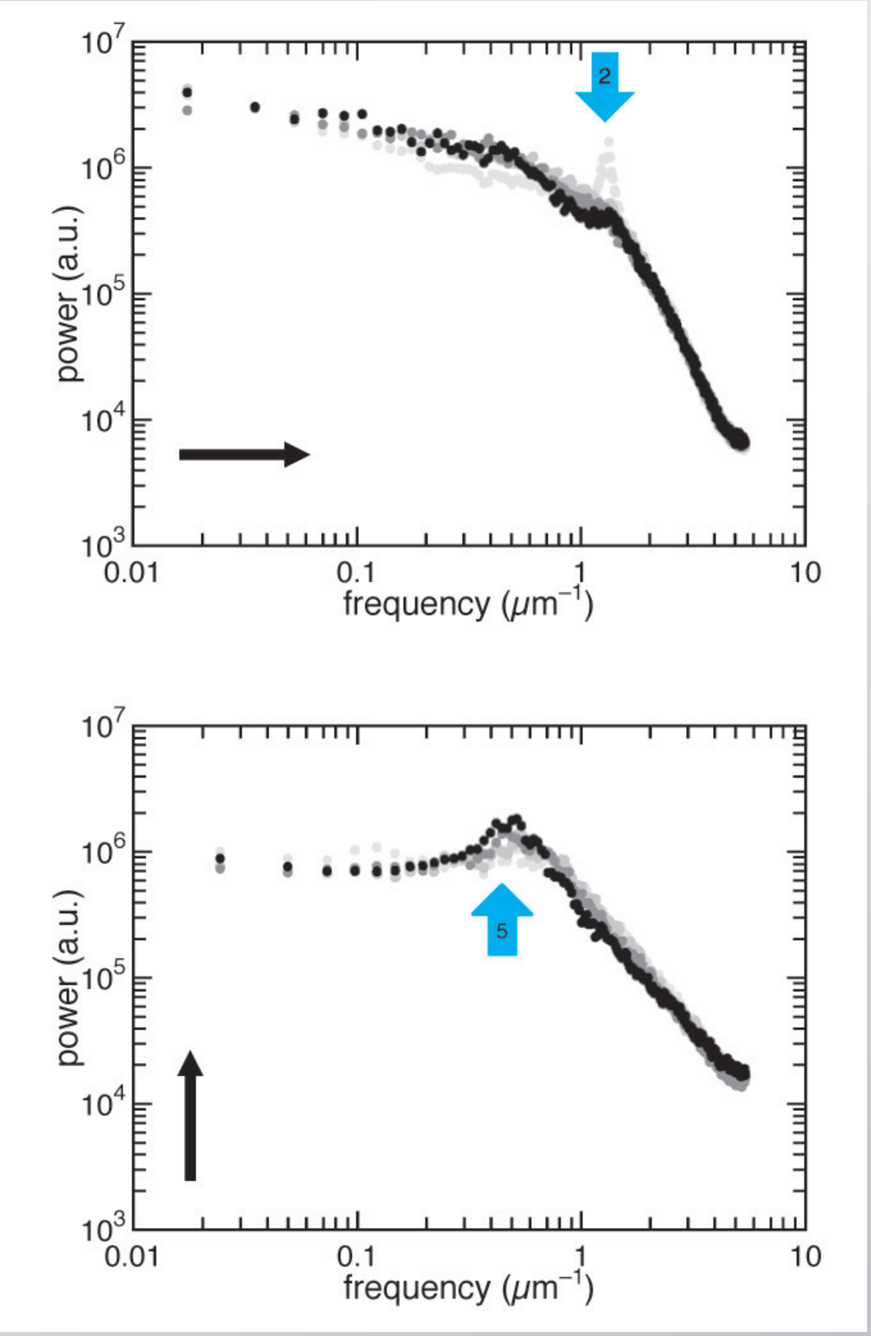




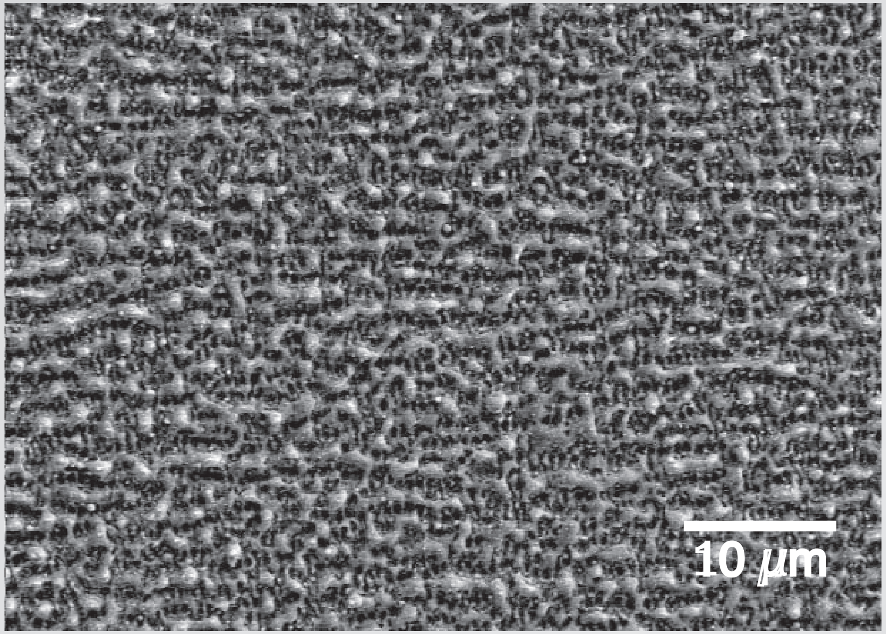
1 **texturing**

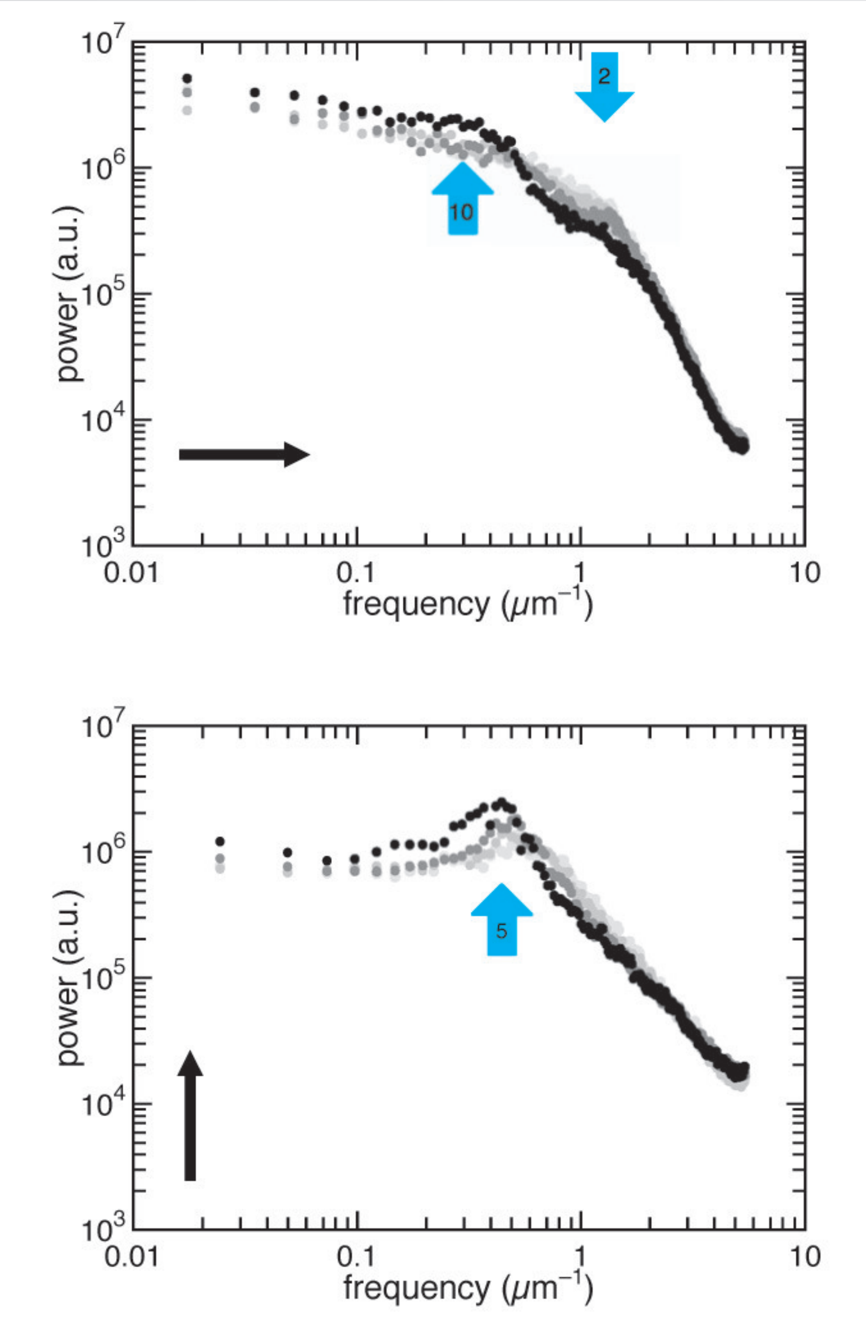
5 pulses



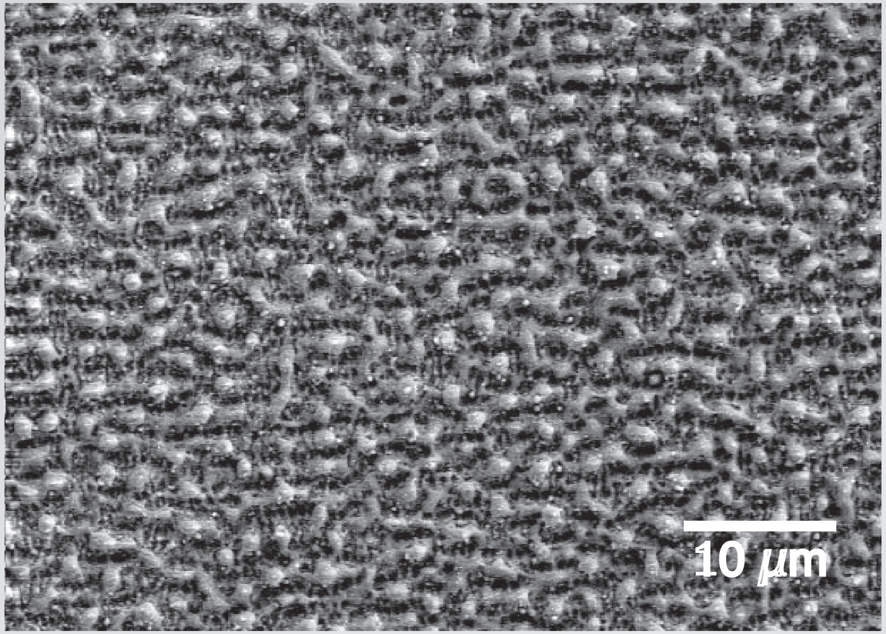


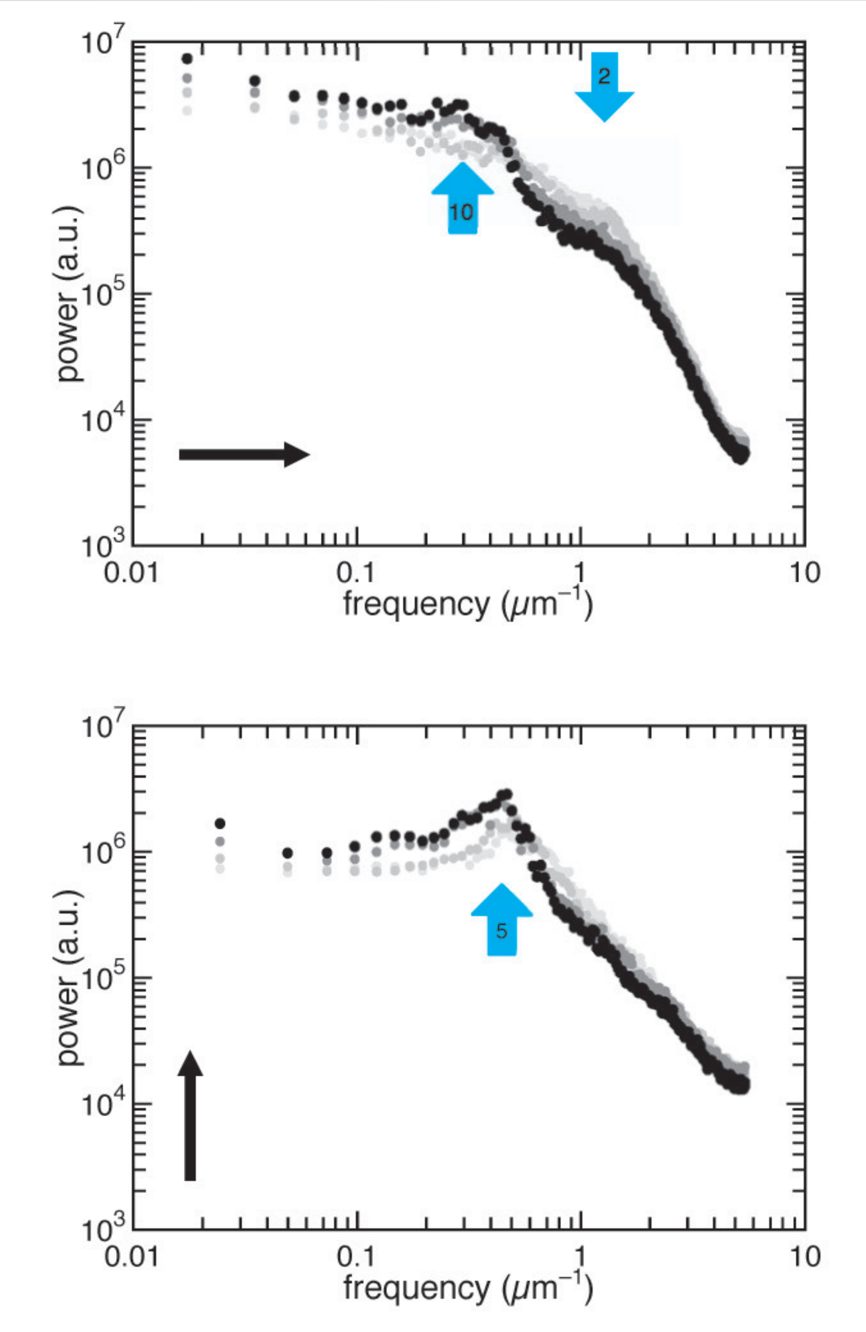
10 pulses



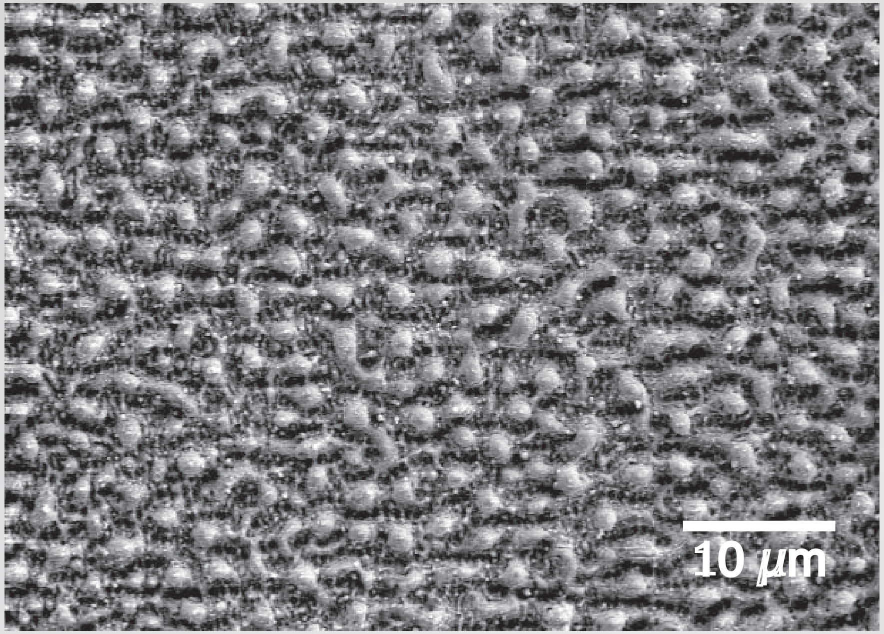


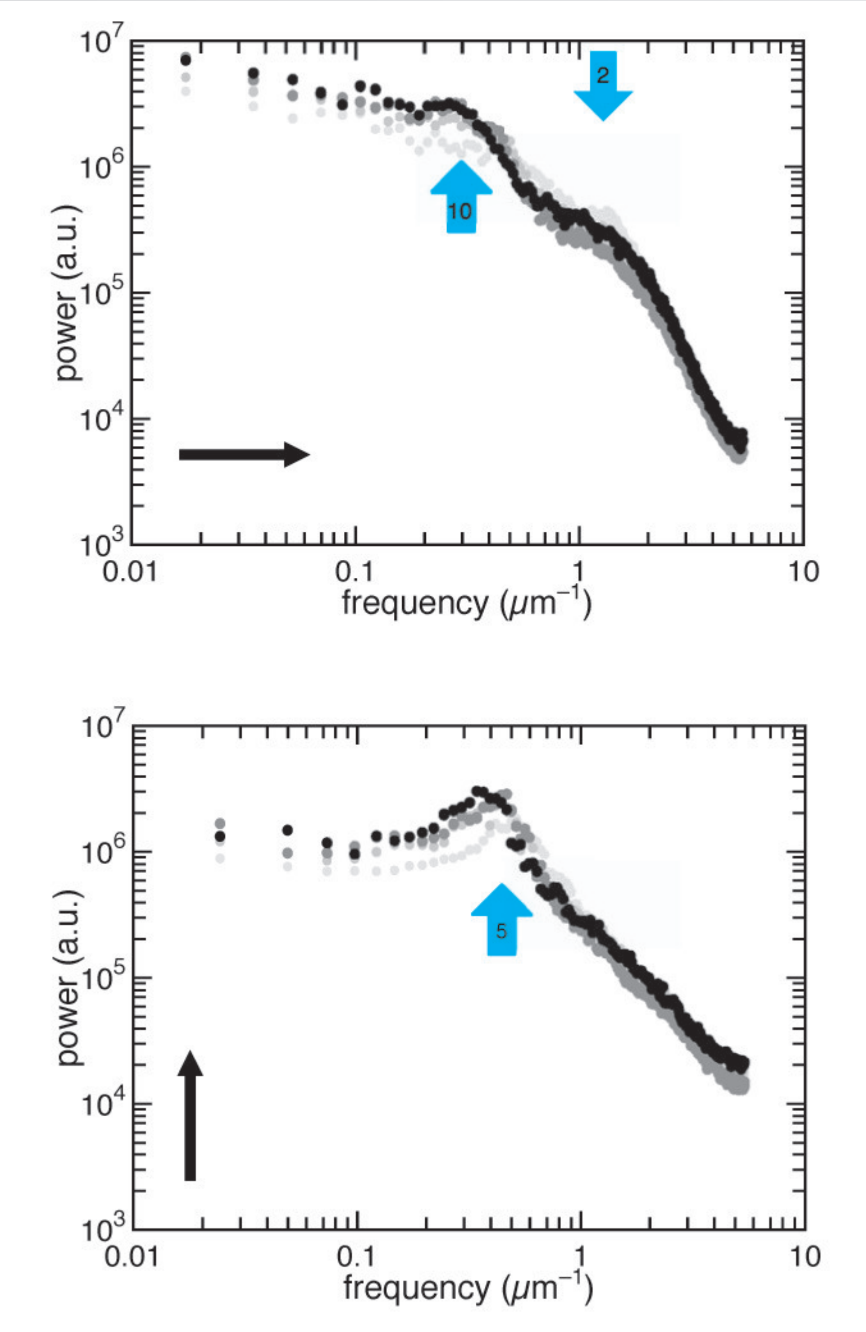
15 pulses





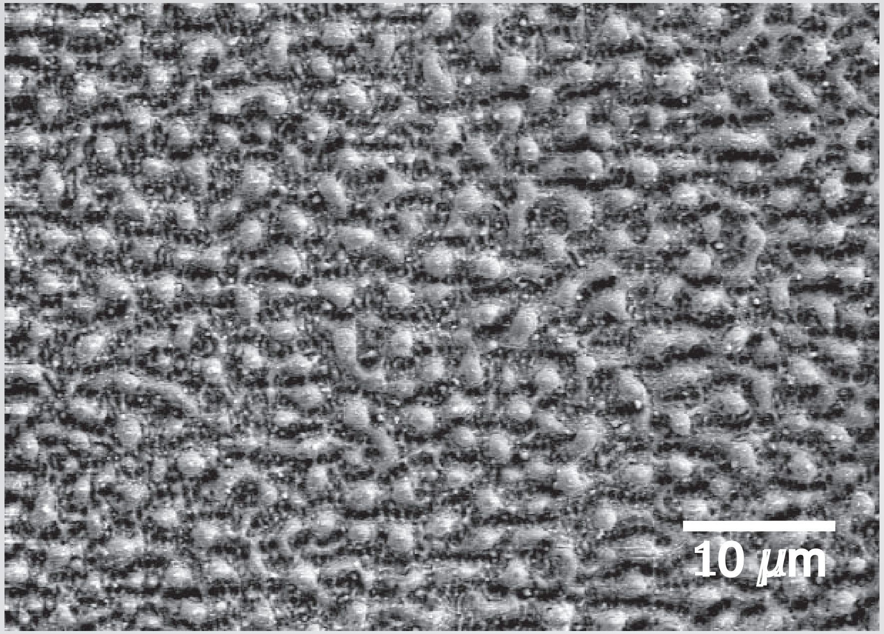
20 pulses

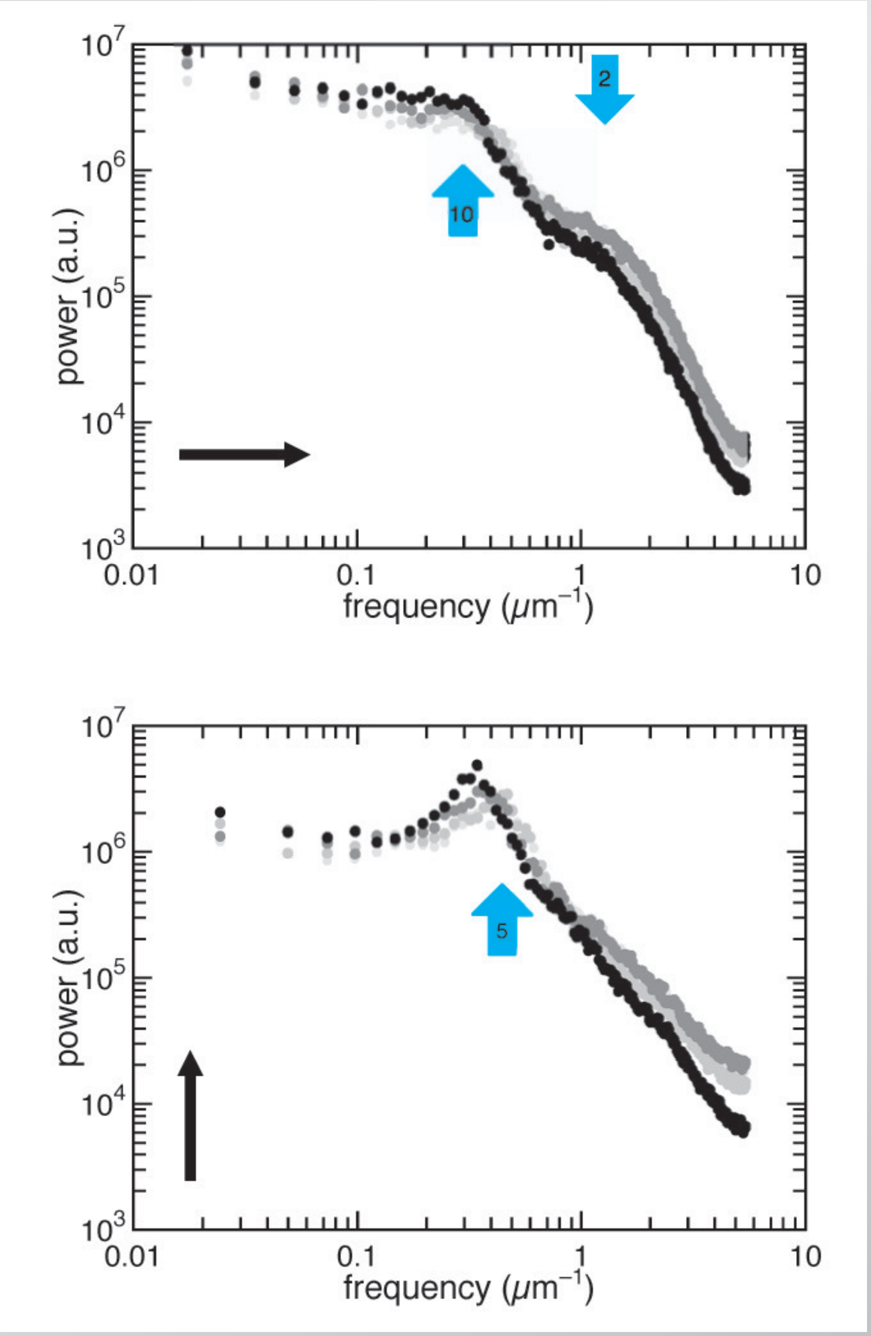




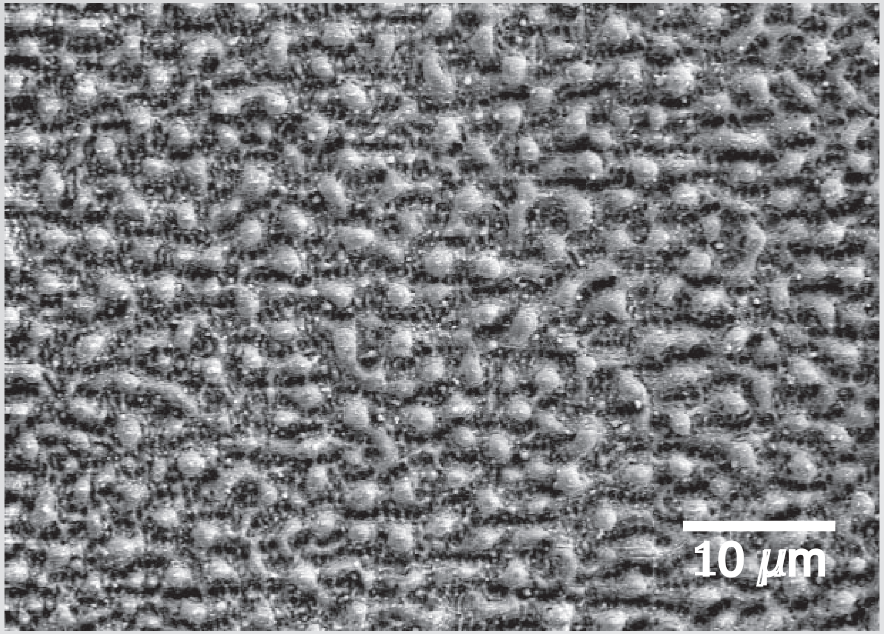
1 texturing

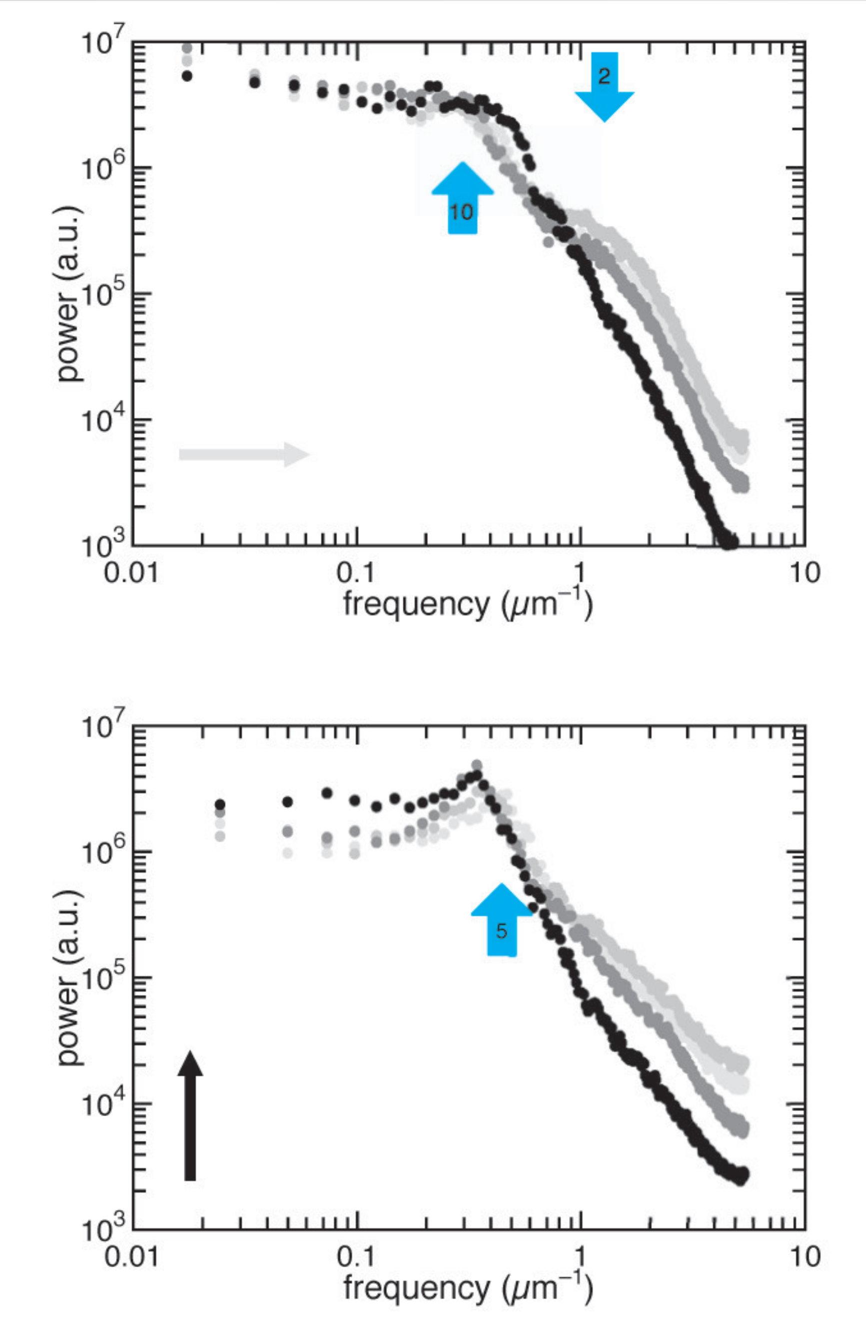
50 pulses





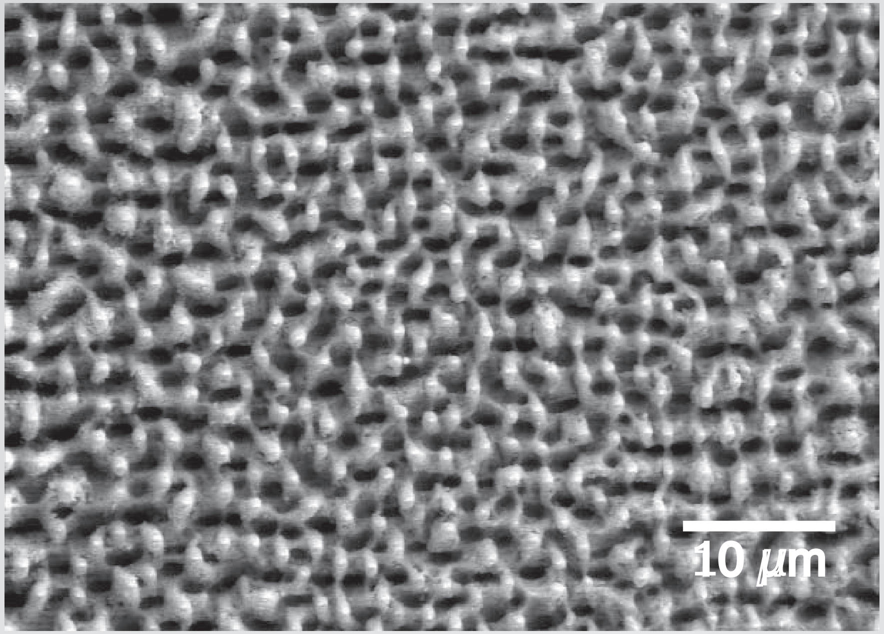
200 pulses

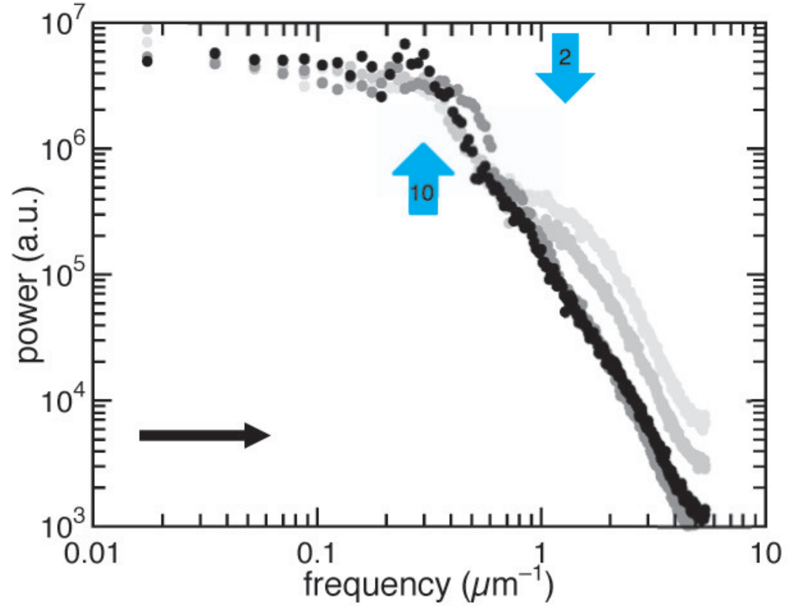


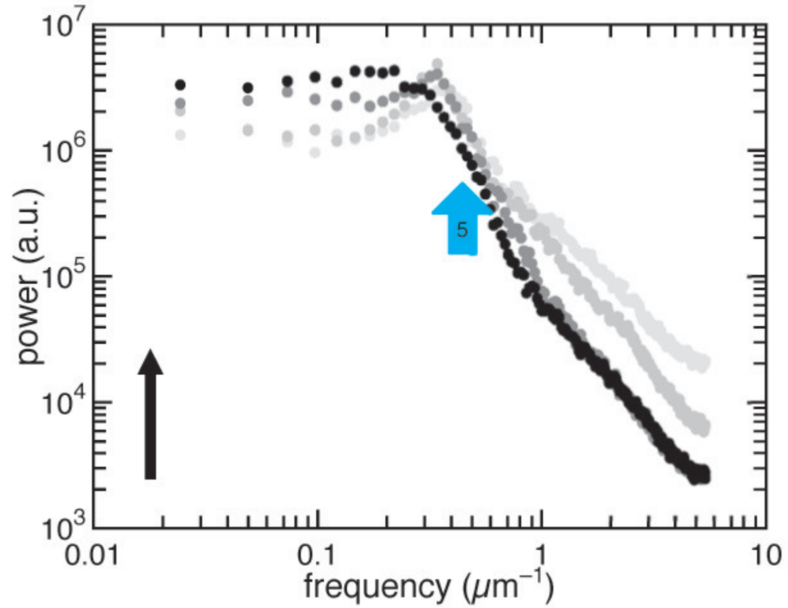


1 texturing

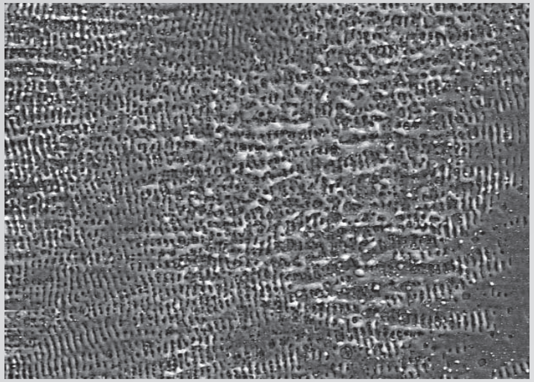
500 pulses





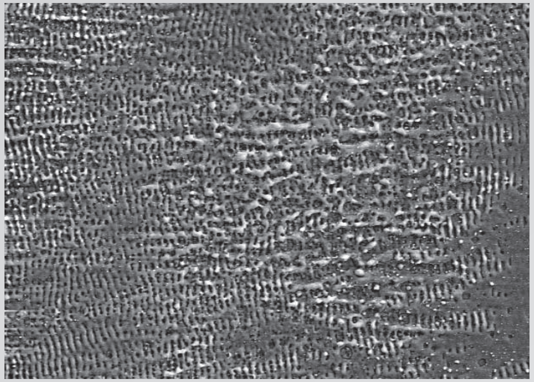


1 texturing



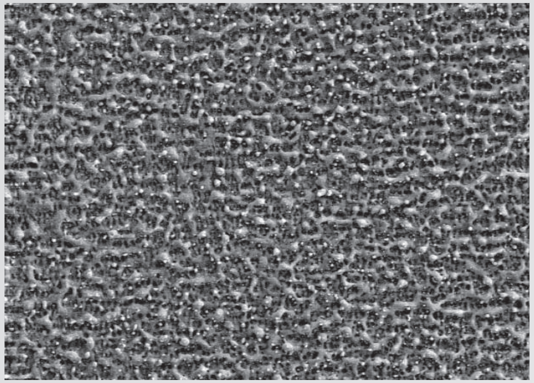
N = 2

interference ripples
(perpendicular to polarization)



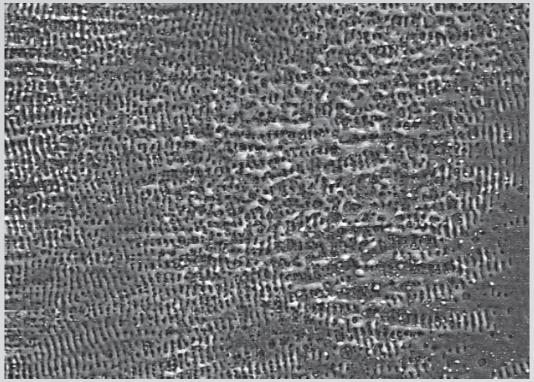
$N = 2$

interference ripples
(perpendicular to polarization)



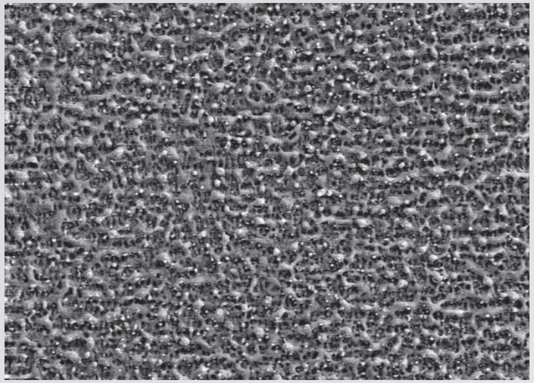
$N = 5$

coarsened ridges
(perpendicular to ripples)



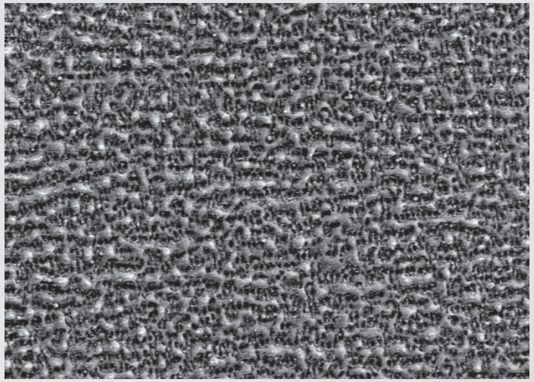
N = 2

interference ripples (perpendicular to polarization)



N = 5

coarsened ridges (perpendicular to ripples)



N = 10

beads sharpening into spikes (isotropic)

1 texturing

2 distinct length scales:

- ripples
- ridges/spikes

2 distinct length scales:

- ripples (laser wavelength)
- ridges/spikes

2 distinct length scales:

- ripples (laser wavelength)
- ridges/spikes (longest capillary wave)

melt depth d and melt duration τ limit capillary wavelength

$$\lambda = \left[\frac{\sigma d}{\rho} \right]^{\frac{1}{4}} \sqrt{2\pi\tau}$$

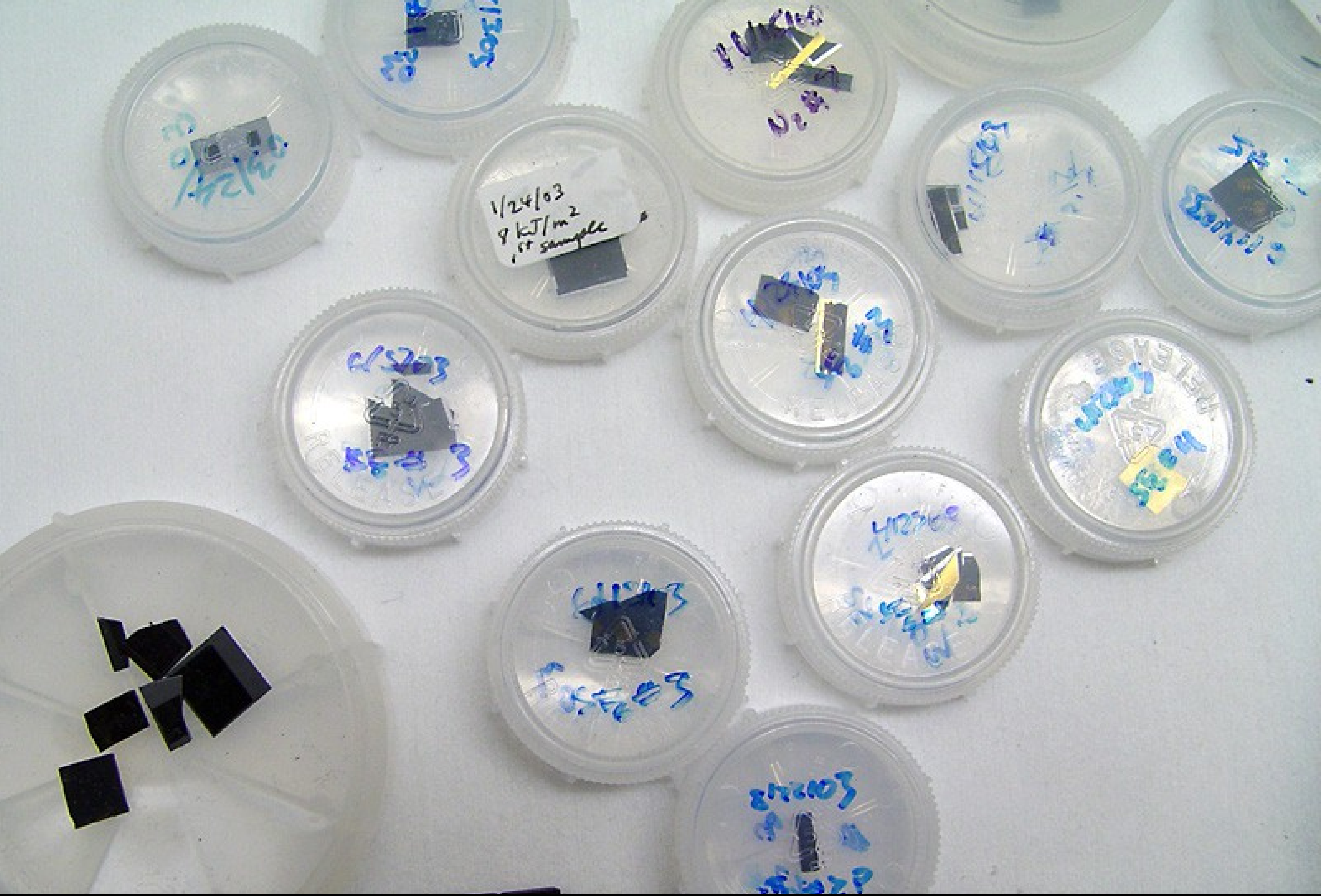
melt depth d and melt duration τ limit capillary wavelength

$$\lambda = \left[\frac{\sigma d}{\rho} \right]^{\frac{1}{4}} \sqrt{2\pi\tau}$$

- longest wavelenth ≈ spike separation (5 µm) melt depth d and melt duration τ limit capillary wavelength

$$\lambda = \left[\frac{\sigma d}{\rho} \right]^{\frac{1}{4}} \sqrt{2\pi\tau}$$

- longest wavelenth ≈ spike separation (5 µm)
- spike spacing & capillary wavelength increase with fluence



1 texturing

2 doping

two processes: melting and ablation

1 texturing

2 doping

different thresholds:

melting: 1.5 kJ/m^2

ablation: 3.1 kJ/m^2

1 texturing

2 doping

decouple ablation from melting

1 texturing   2 doping

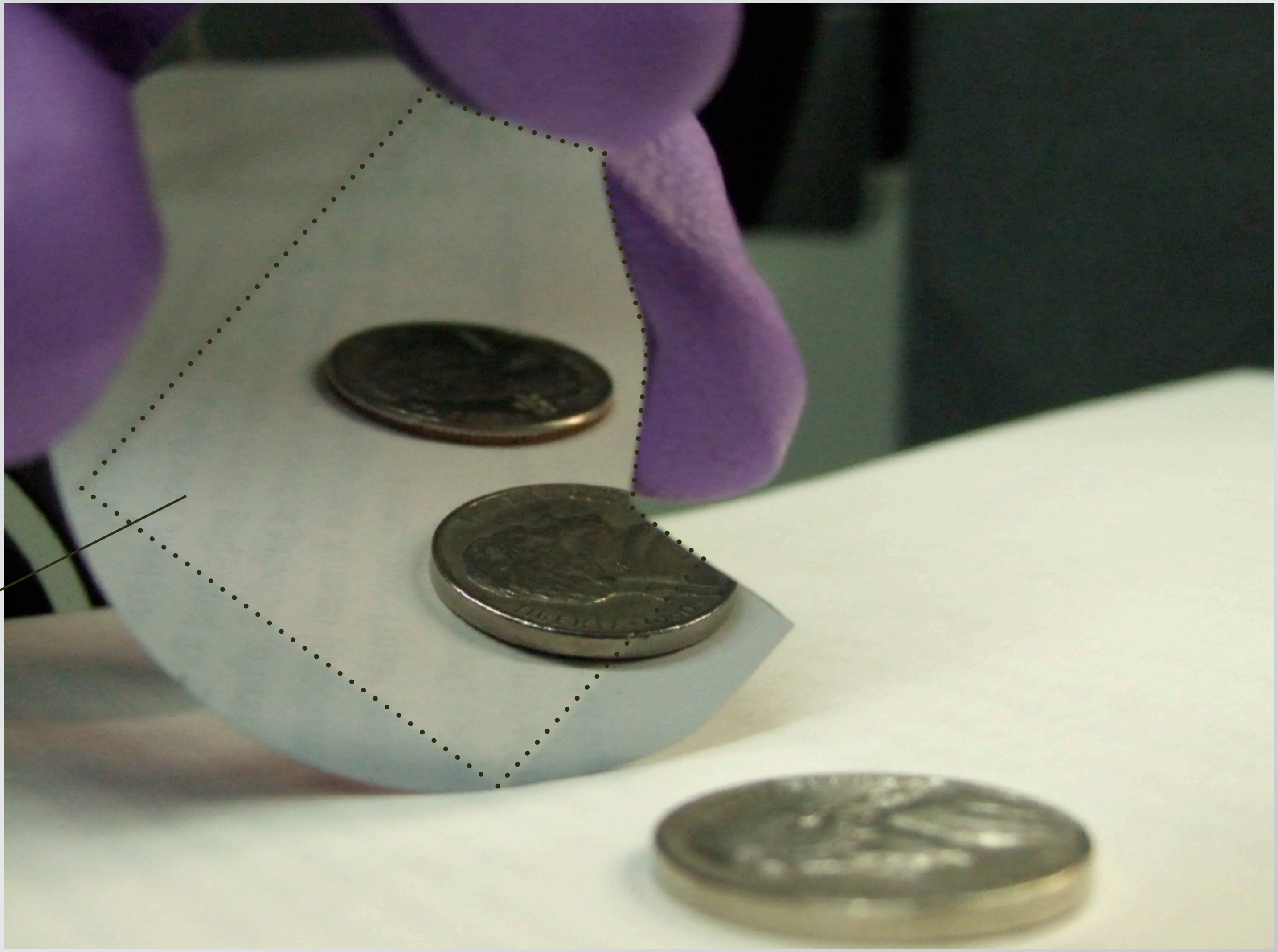
decouple ablation from melting

doped

1 texturing

2 doping

decouple ablation from melting



doped

1 texturing 2 doping

decouple ablation from melting

doped

1 texturing 2 doping

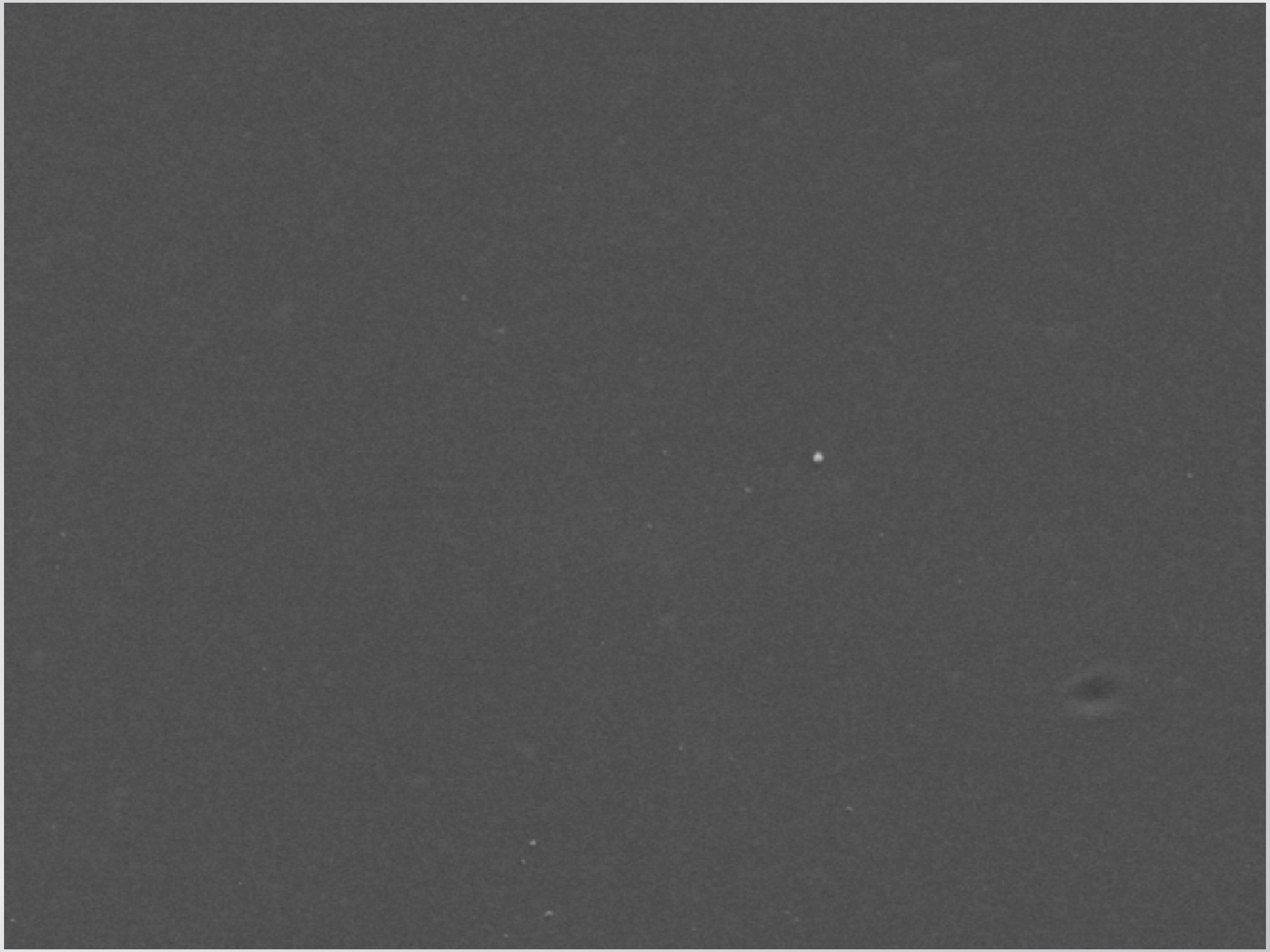
decouple ablation from melting

undoped

doped

1 texturing **2** doping

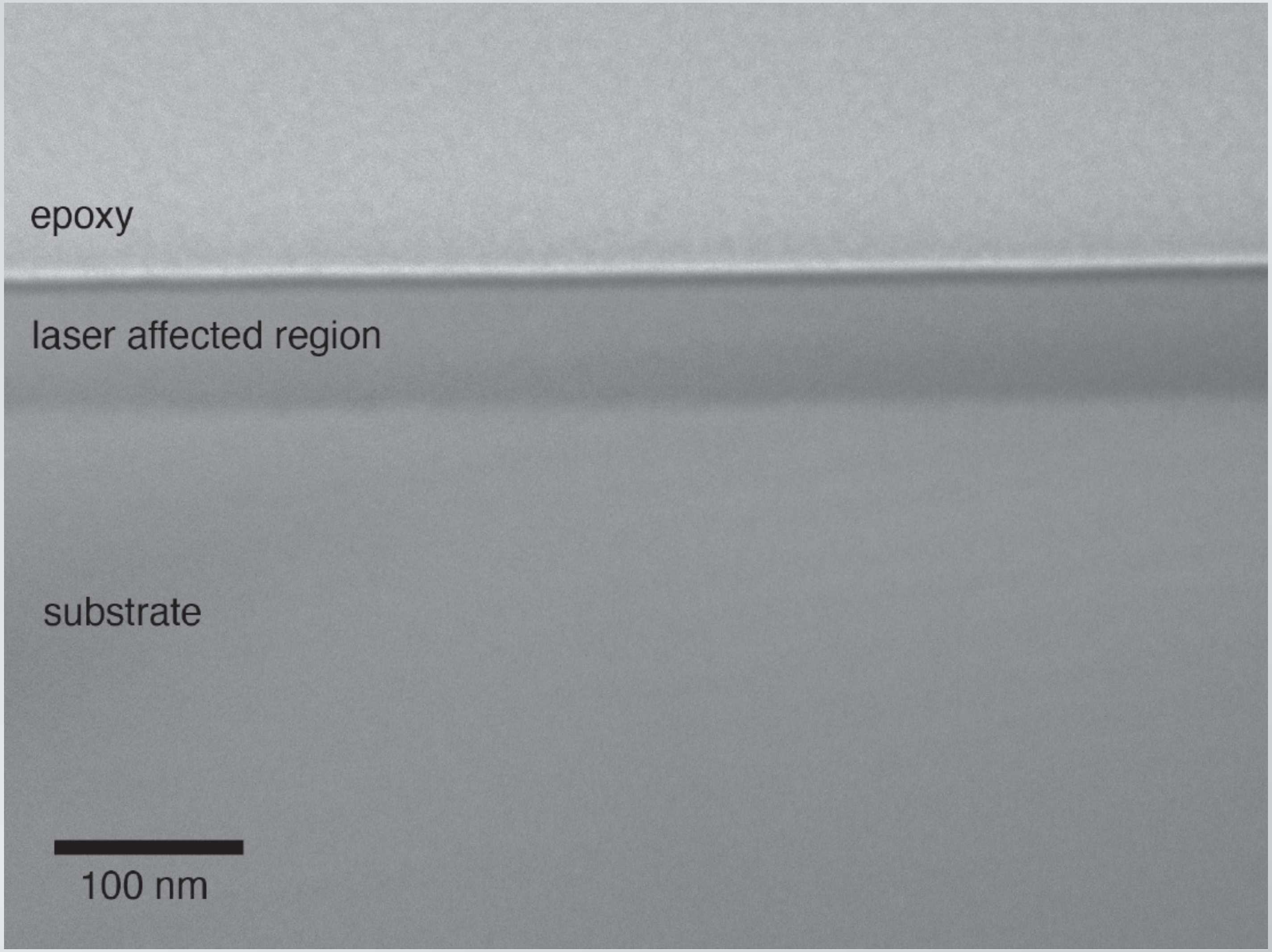
decouple ablation from melting



1 texturing

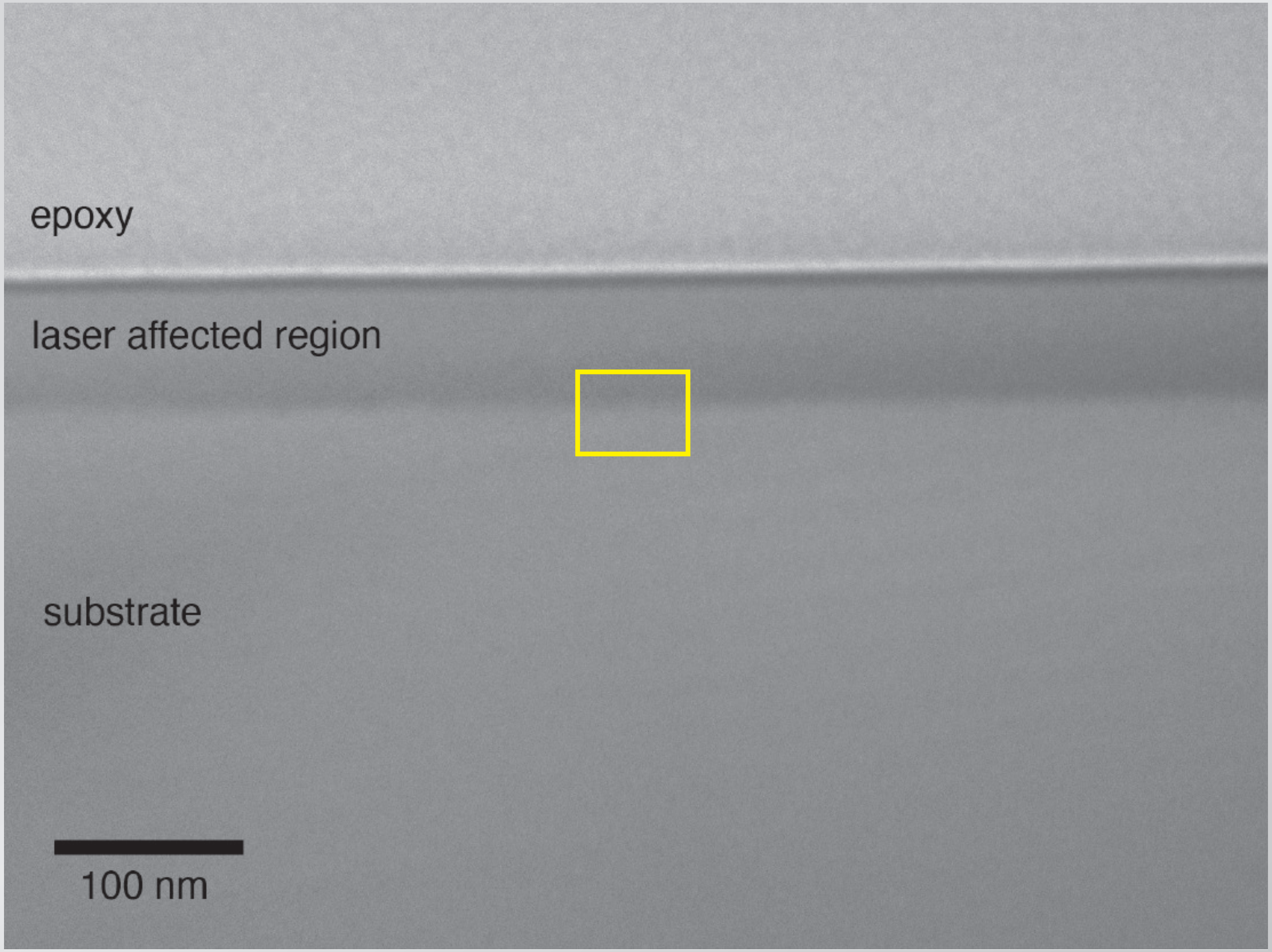
2 doping

decouple ablation from melting



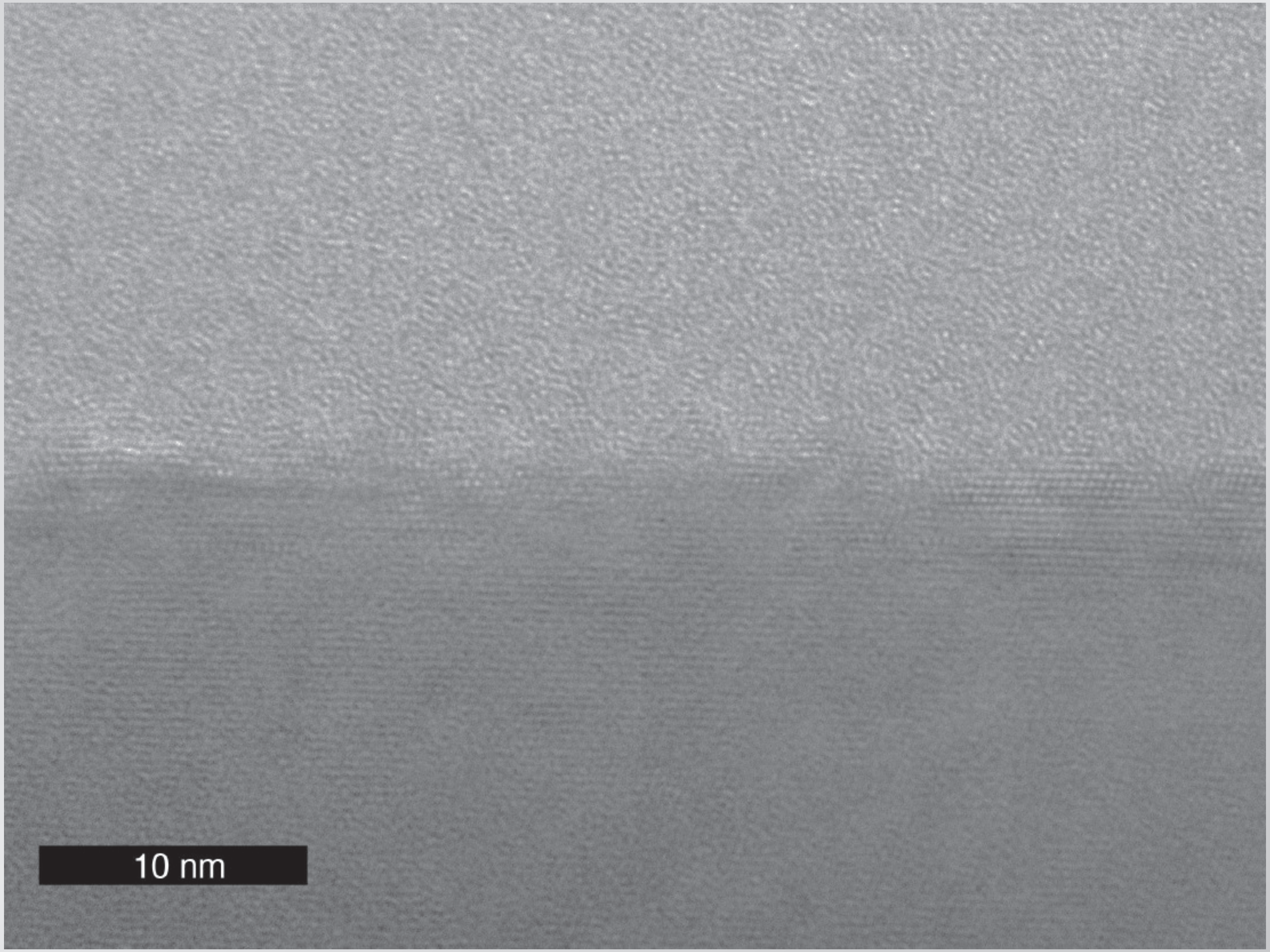
1 **texturing** **2** **doping**

decouple ablation from melting



1 texturing **2 doping**

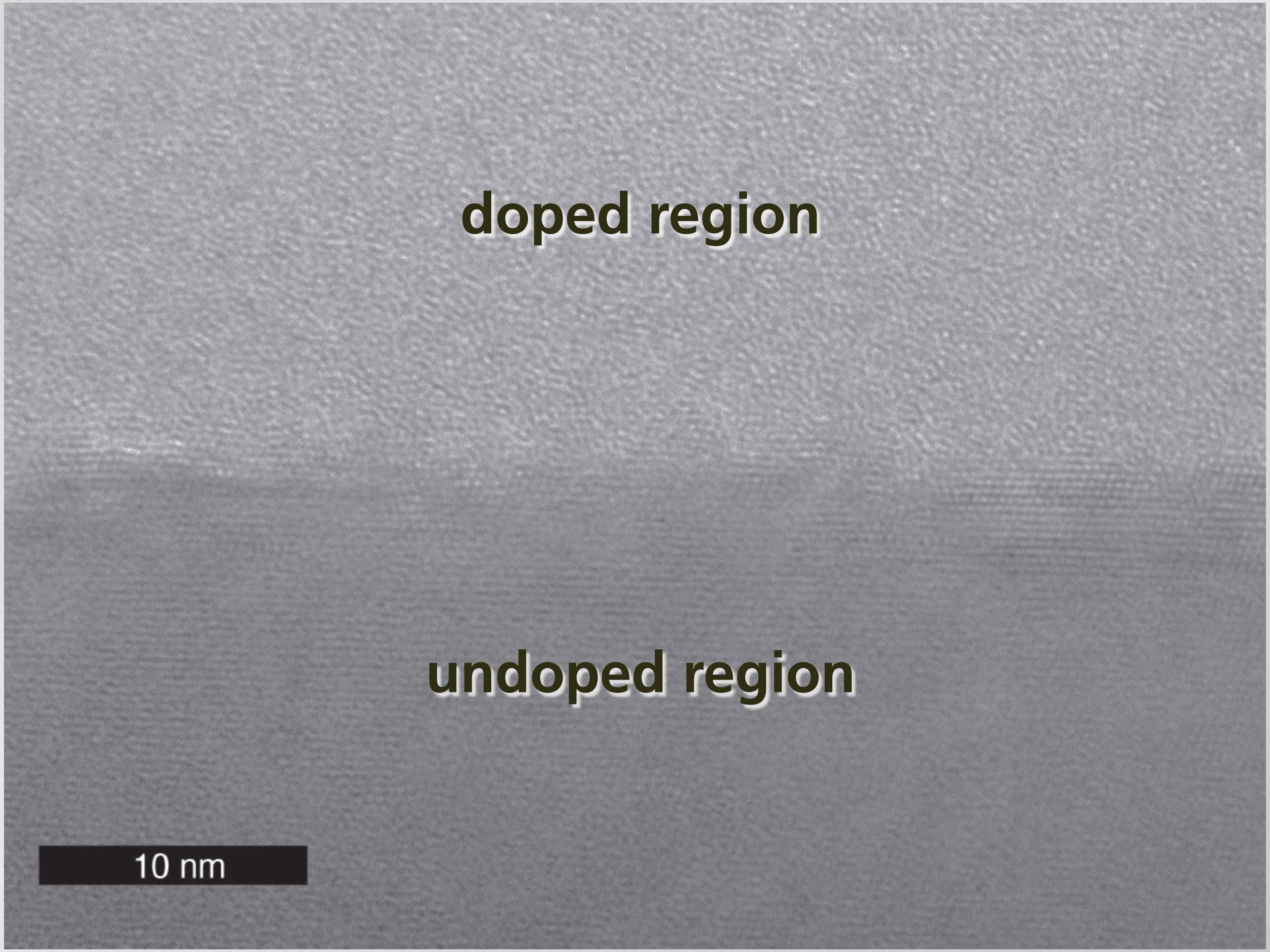
decouple ablation from melting



1 texturing

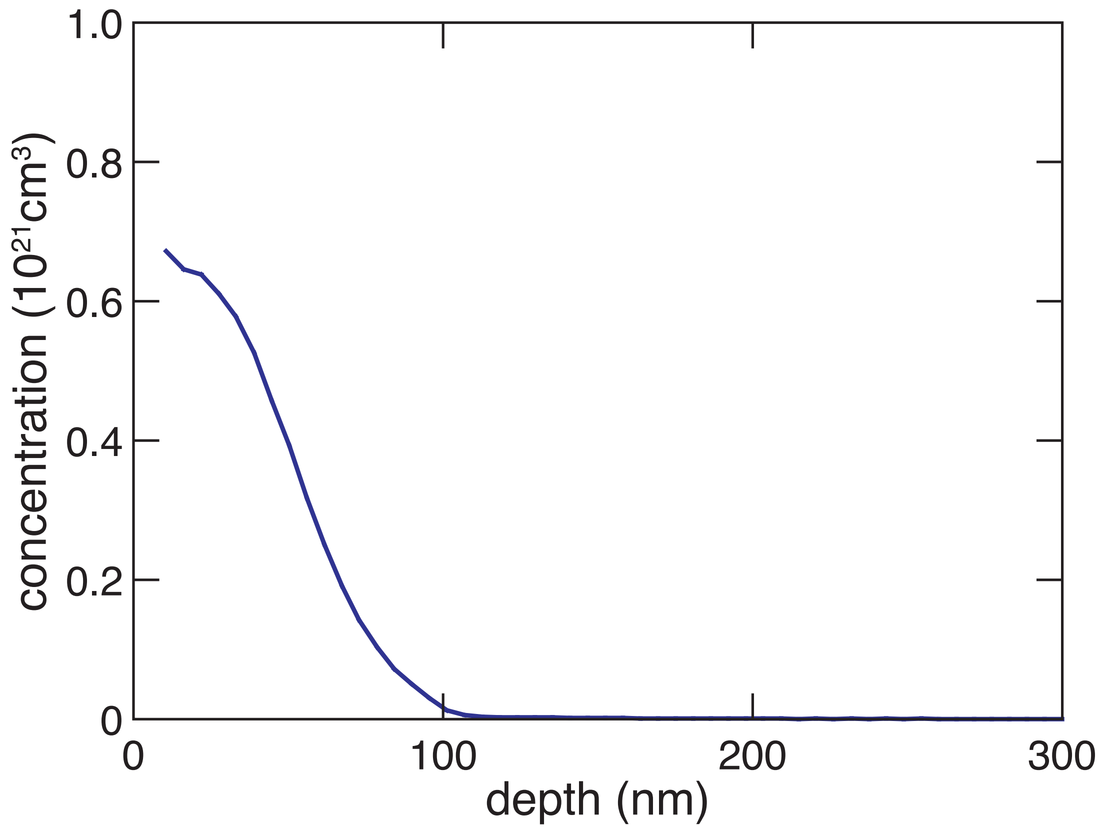
2 doping

decouple ablation from melting



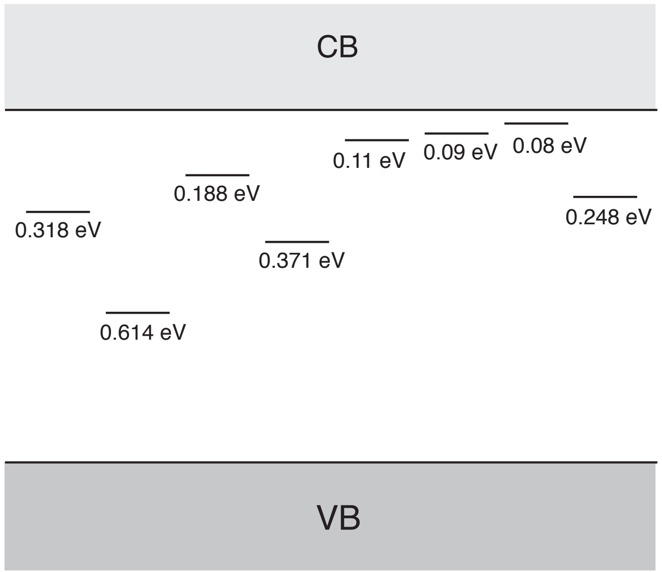
1 texturing 2 doping

secondary ion mass spectrometry



1 texturing **2 doping**

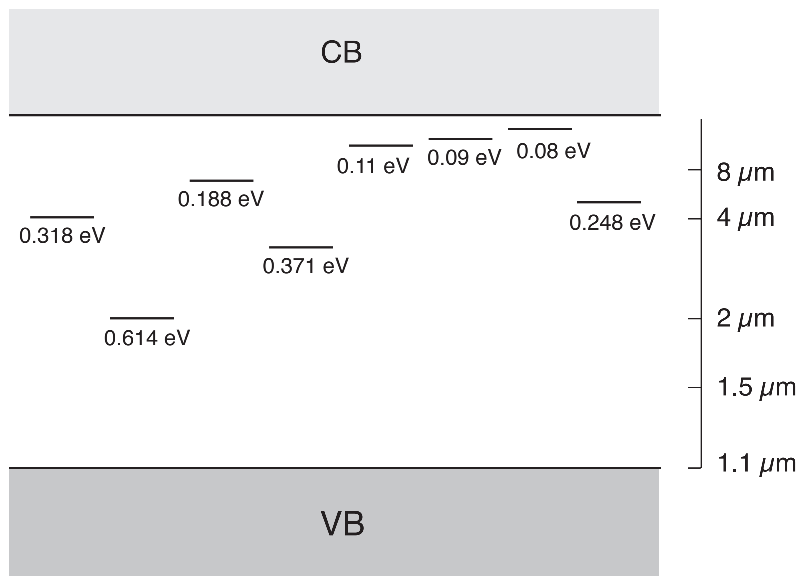
1 part in 10^6 sulfur introduces donor states in gap



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

1 texturing **2** doping

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

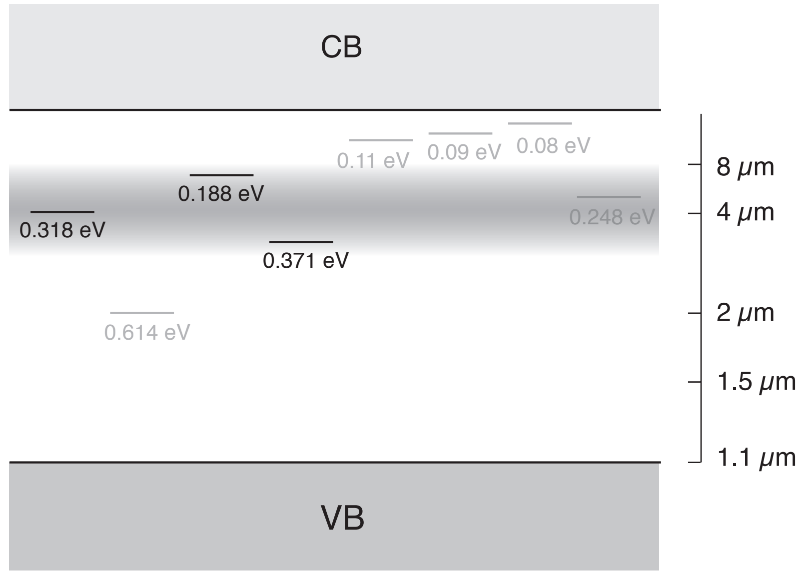


Janzén *et al.*, Phys. Rev. B 29, 1907 (1984)

1 texturing

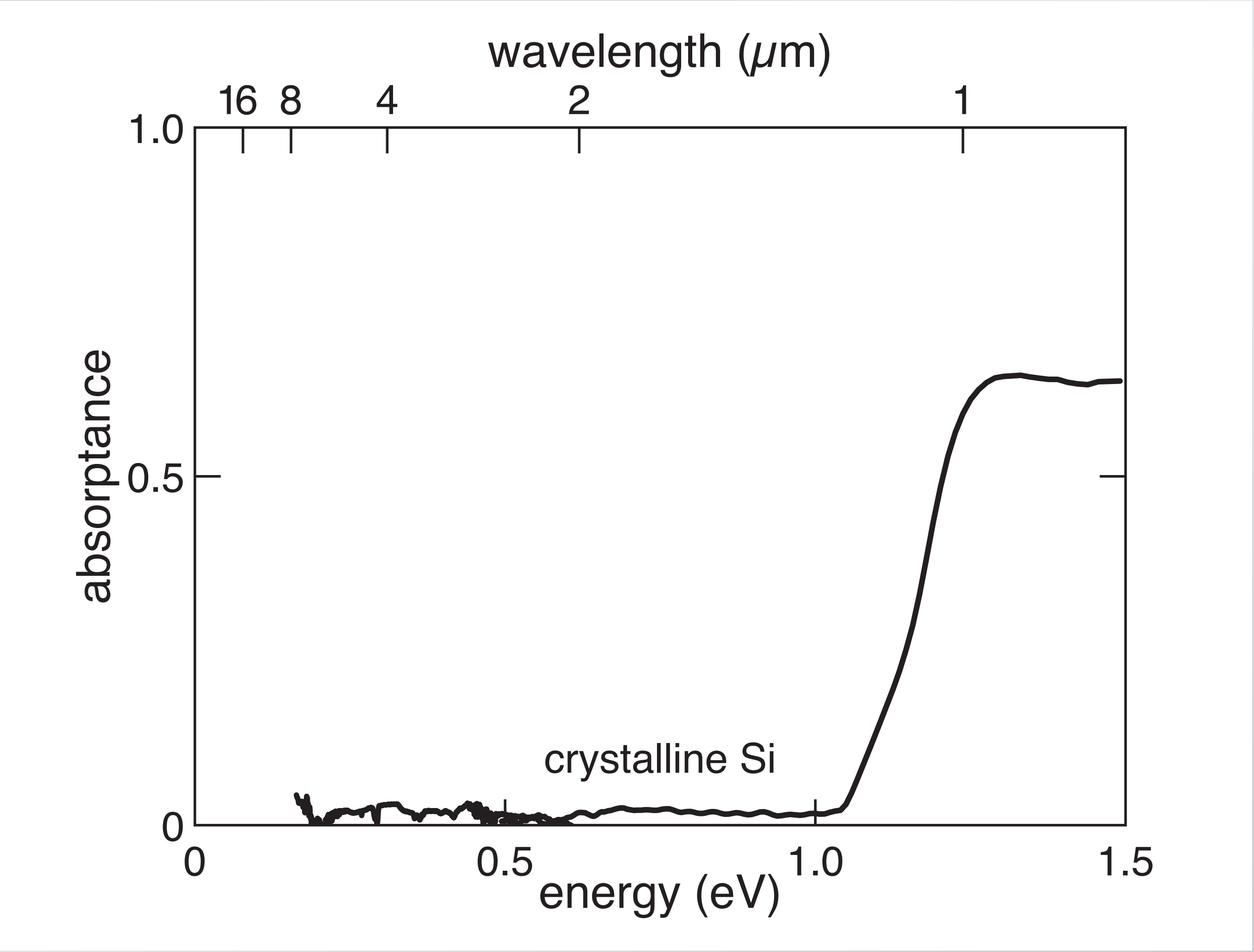
2 doping

at high concentration states broaden into band



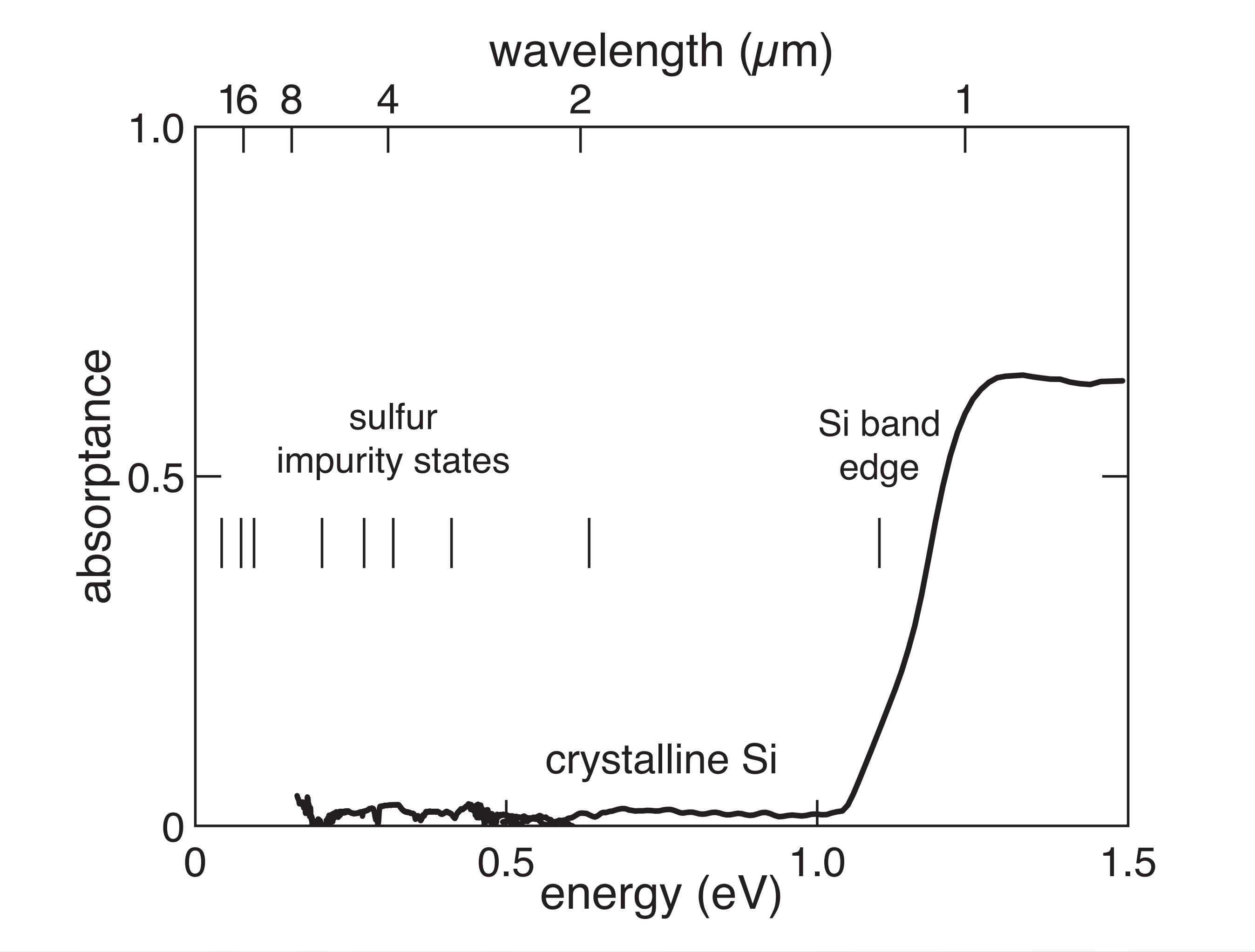
1 texturing **2 doping**

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



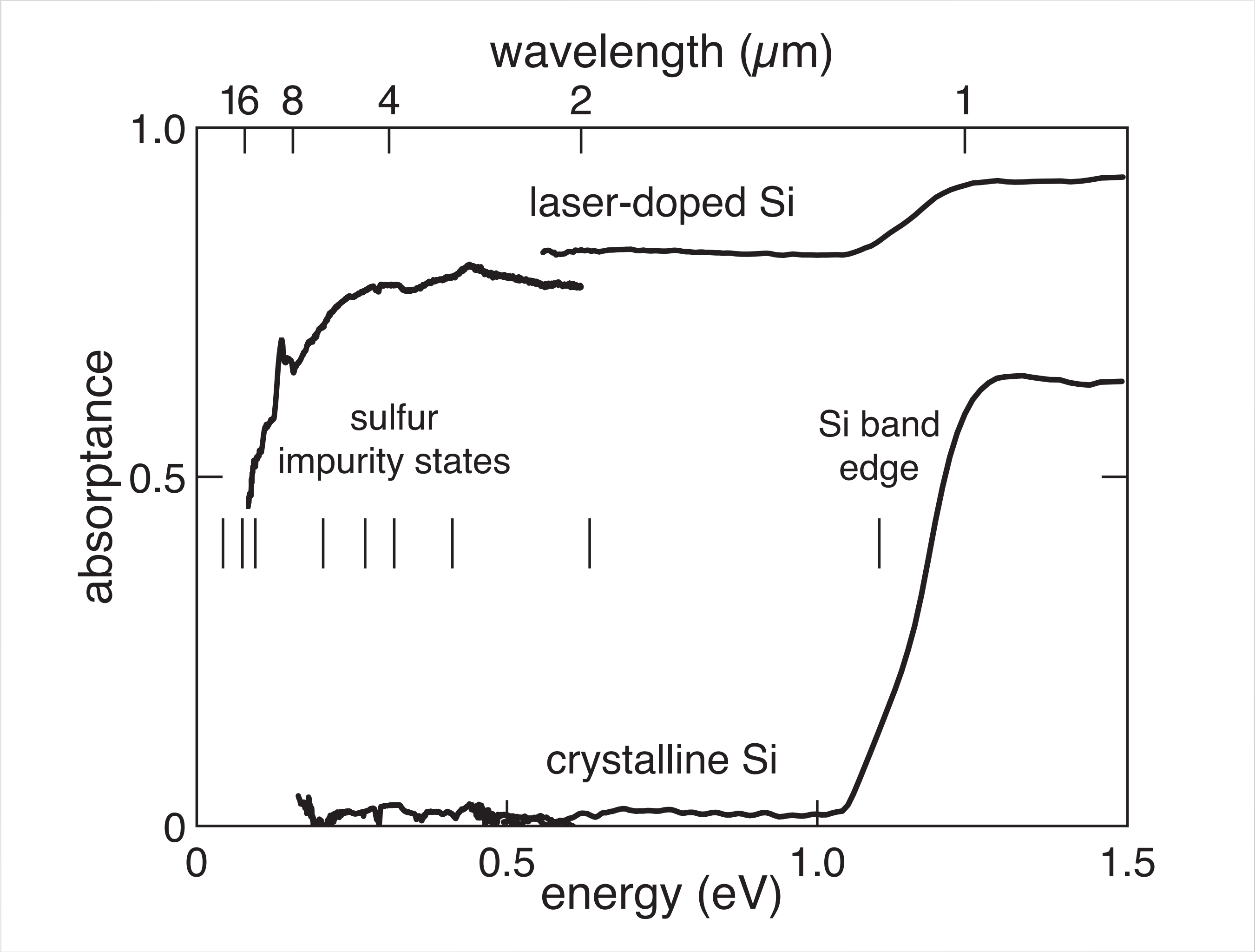
1 texturing **2 doping**

10^{-6} sulfur doping



1 texturing 2 doping

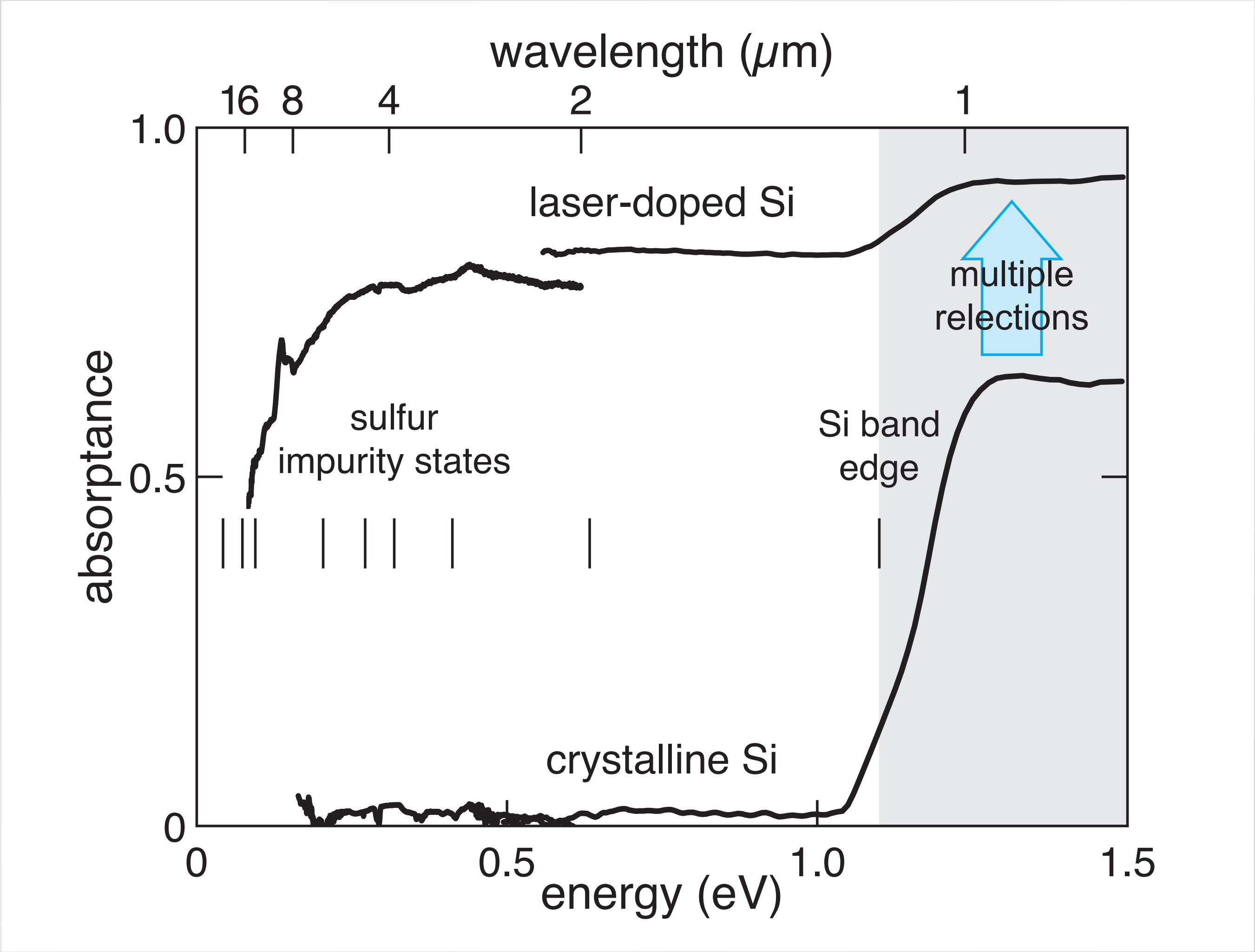
laser-doped S:Si



1 texturing

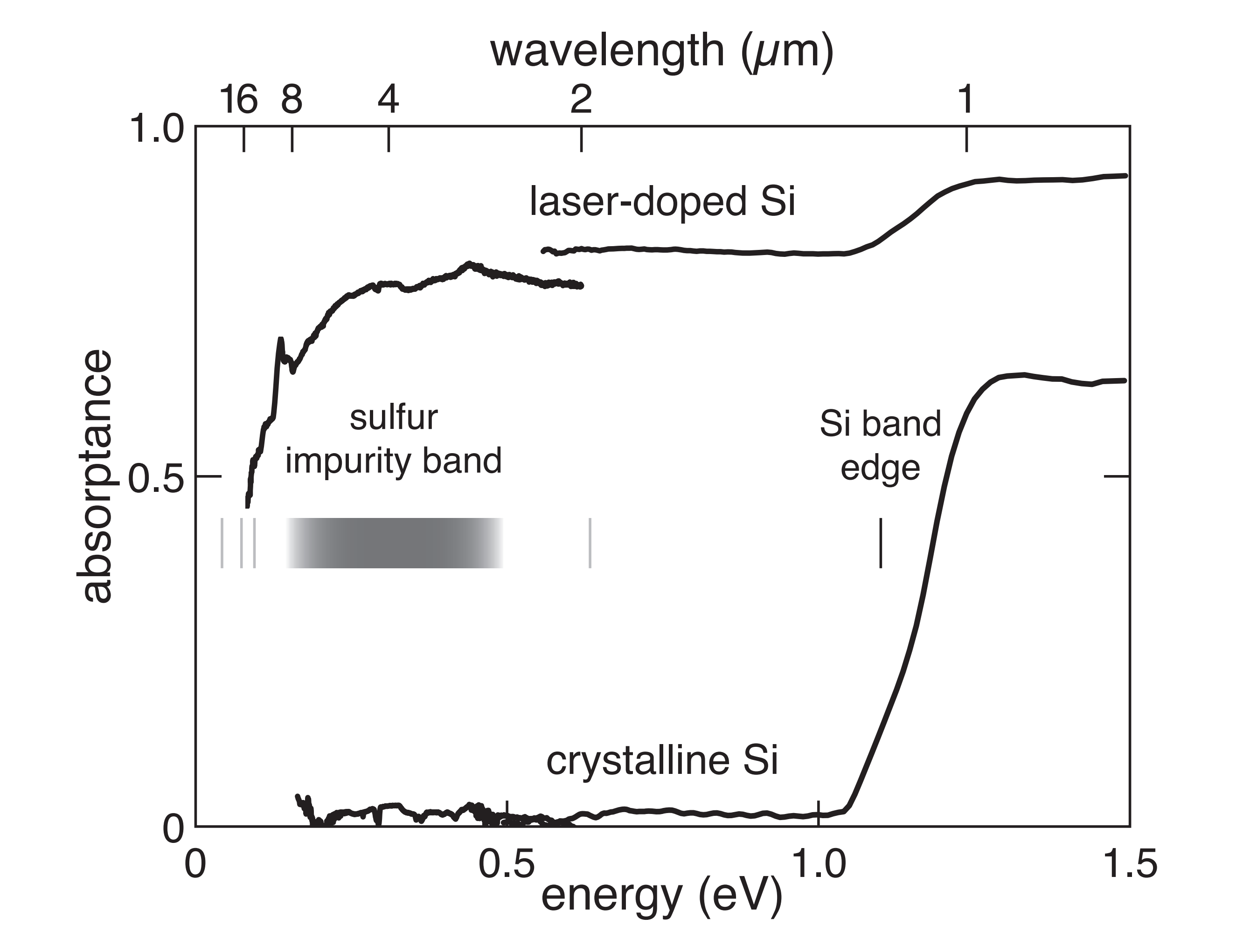
2 doping

laser-doped S:Si



1 texturing **2** doping

laser-doped S:Si

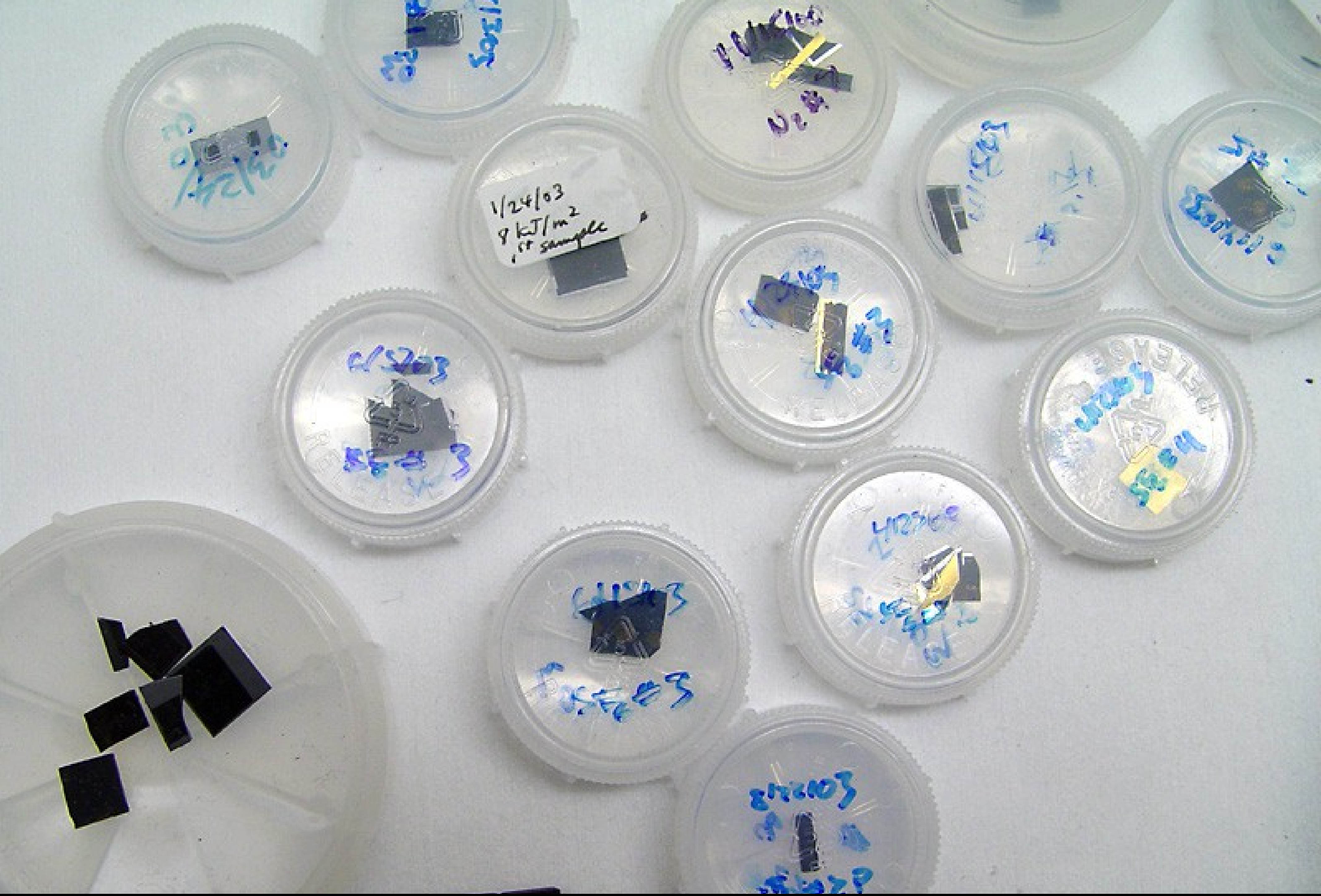


1 texturing **2 doping**

doping creates intermediate band

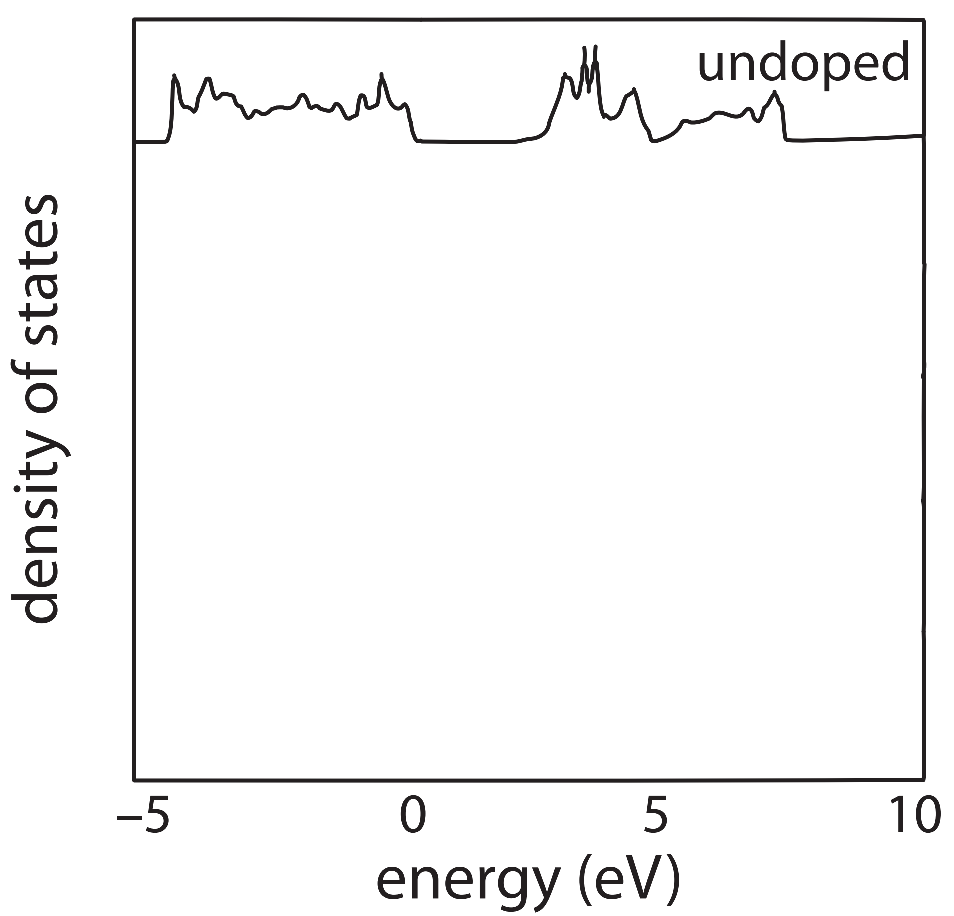
1 texturing

2 doping



1 texturing 2 doping 3 X:TiO_2

TiO_2 density of states



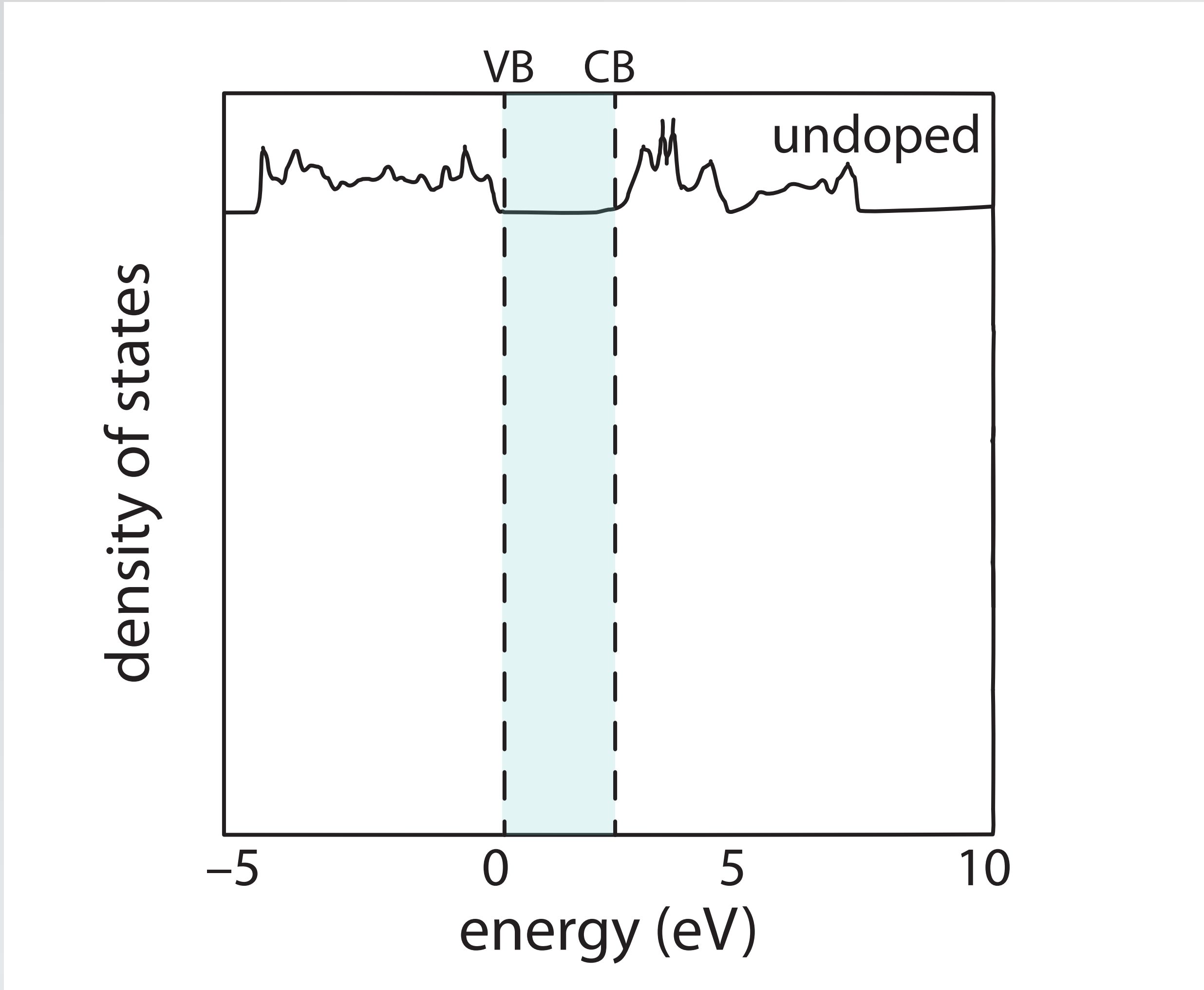
Asahi *et al.*, Science (2003)

1 texturing

2 doping

3 X:TiO_2

need to create band(s) in gap



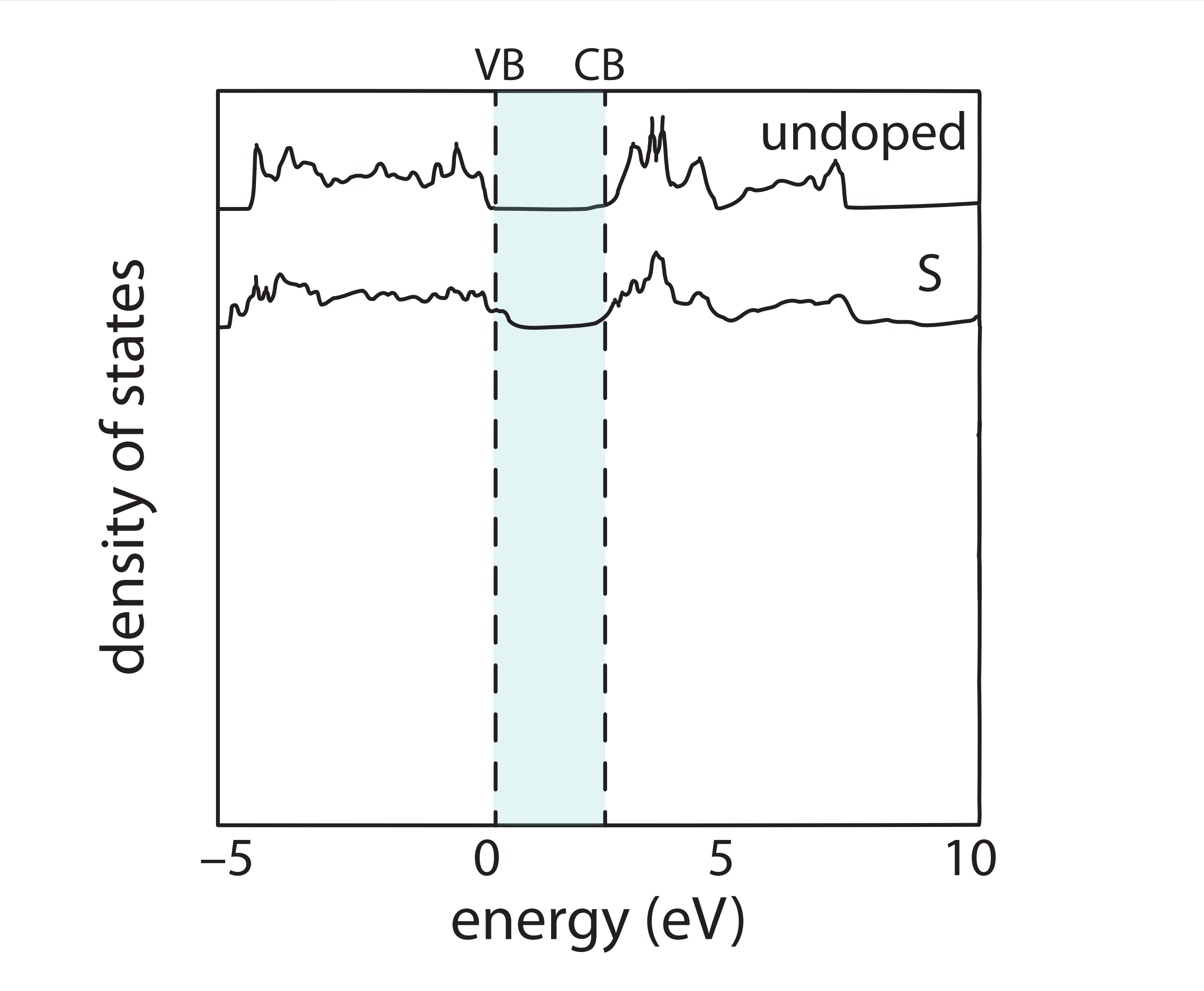
Asahi *et al.*, Science (2003)

1 texturing

2 doping

3 X:TiO_2

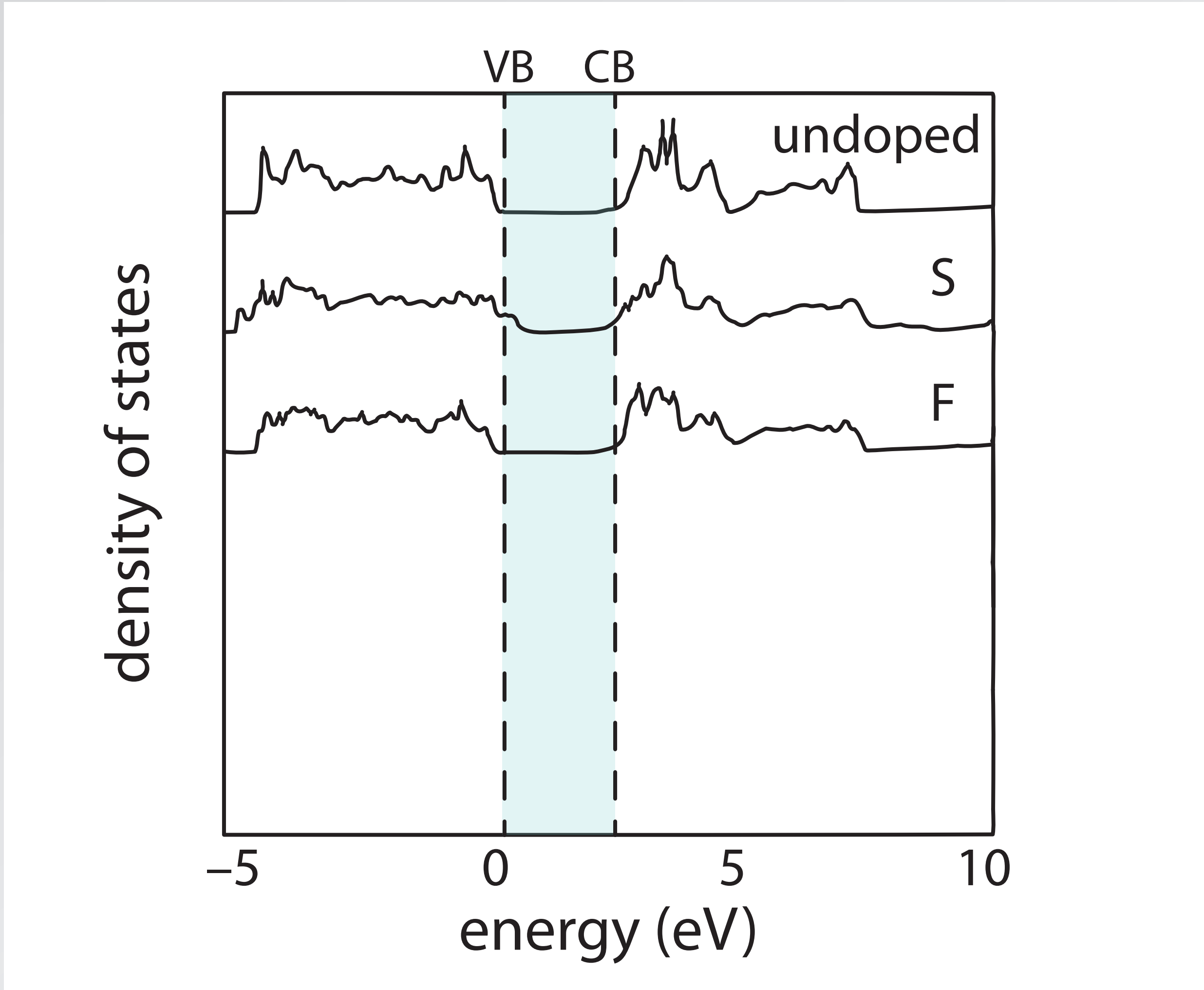
need to create band(s) in gap



Asahi *et al.*, Science (2003)

1 texturing 2 doping 3 X:TiO_2

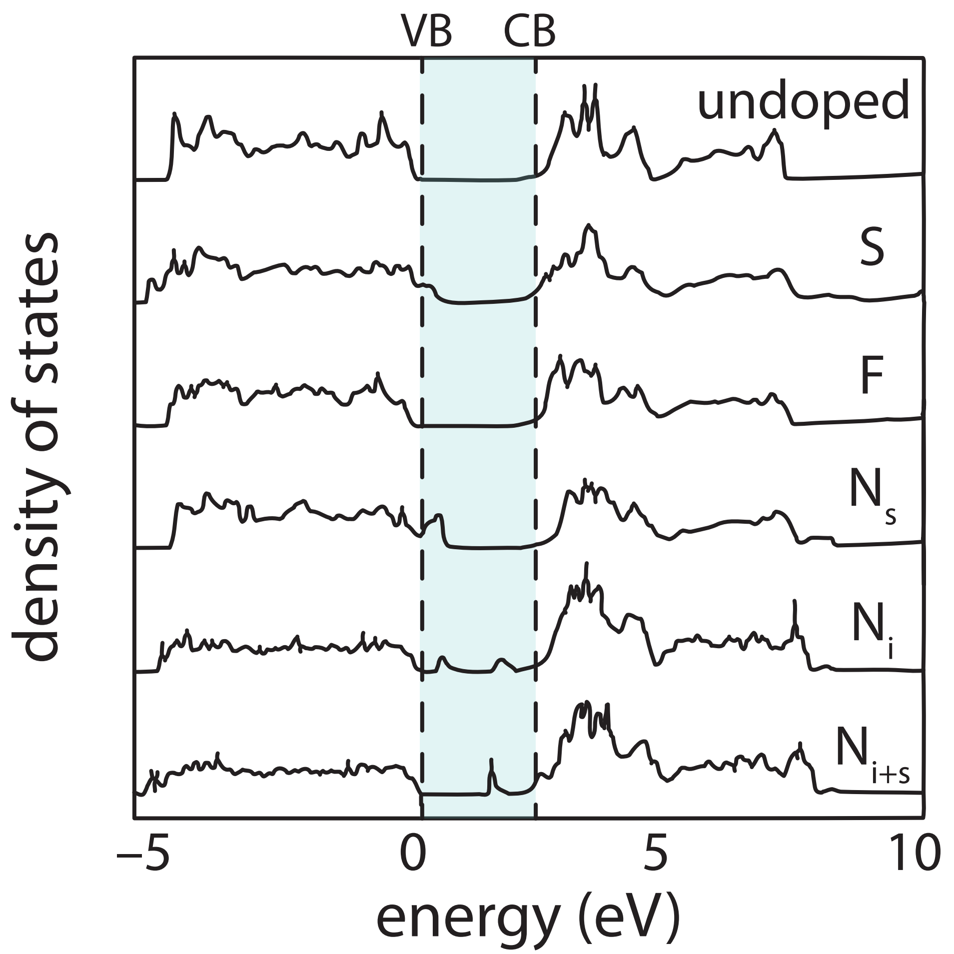
need to create band(s) in gap



Asahi *et al.*, Science (2003)

1 texturing 2 doping 3 X:TiO_2

need to create band(s) in gap



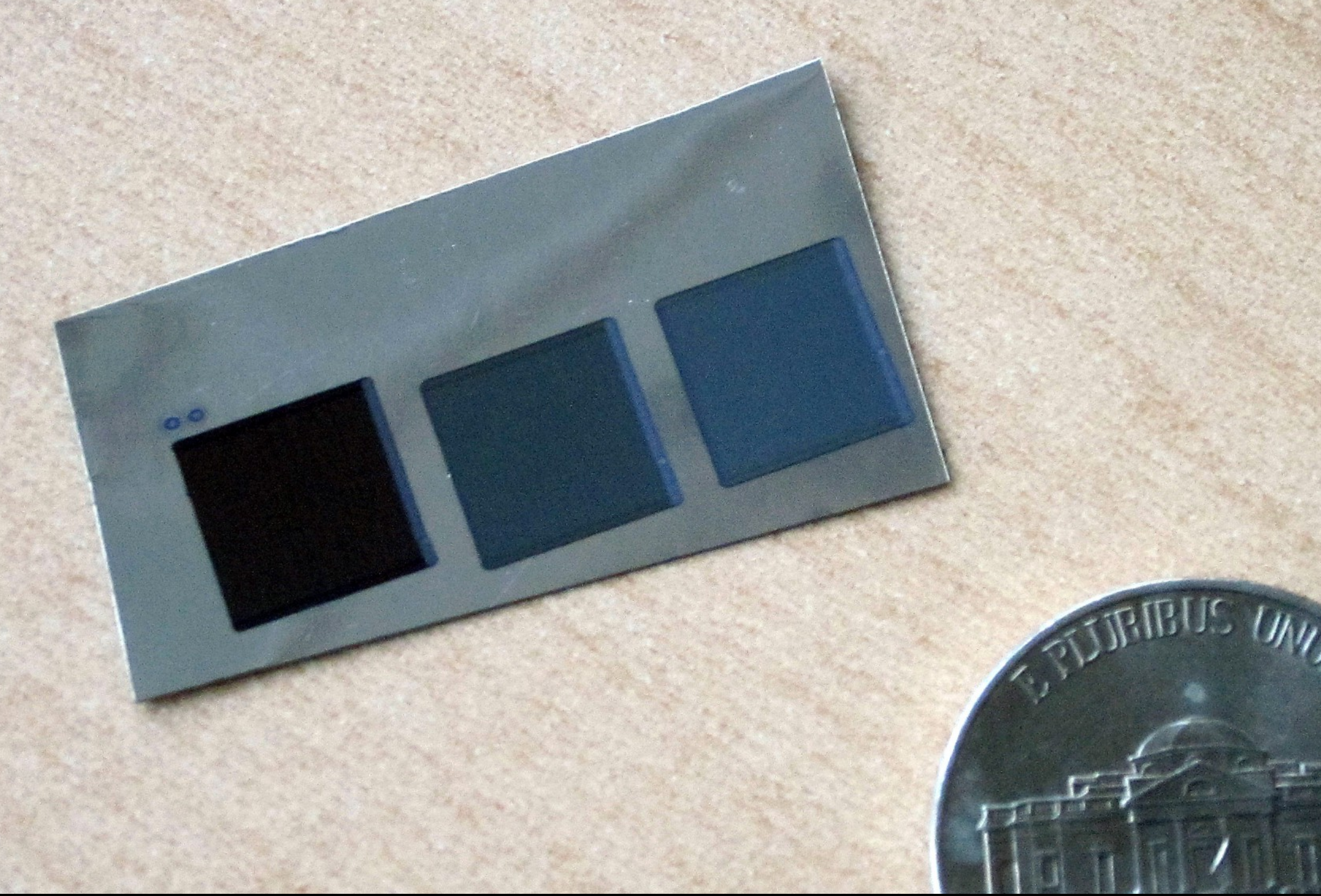
Asahi *et al.*, Science (2003)

1 texturing

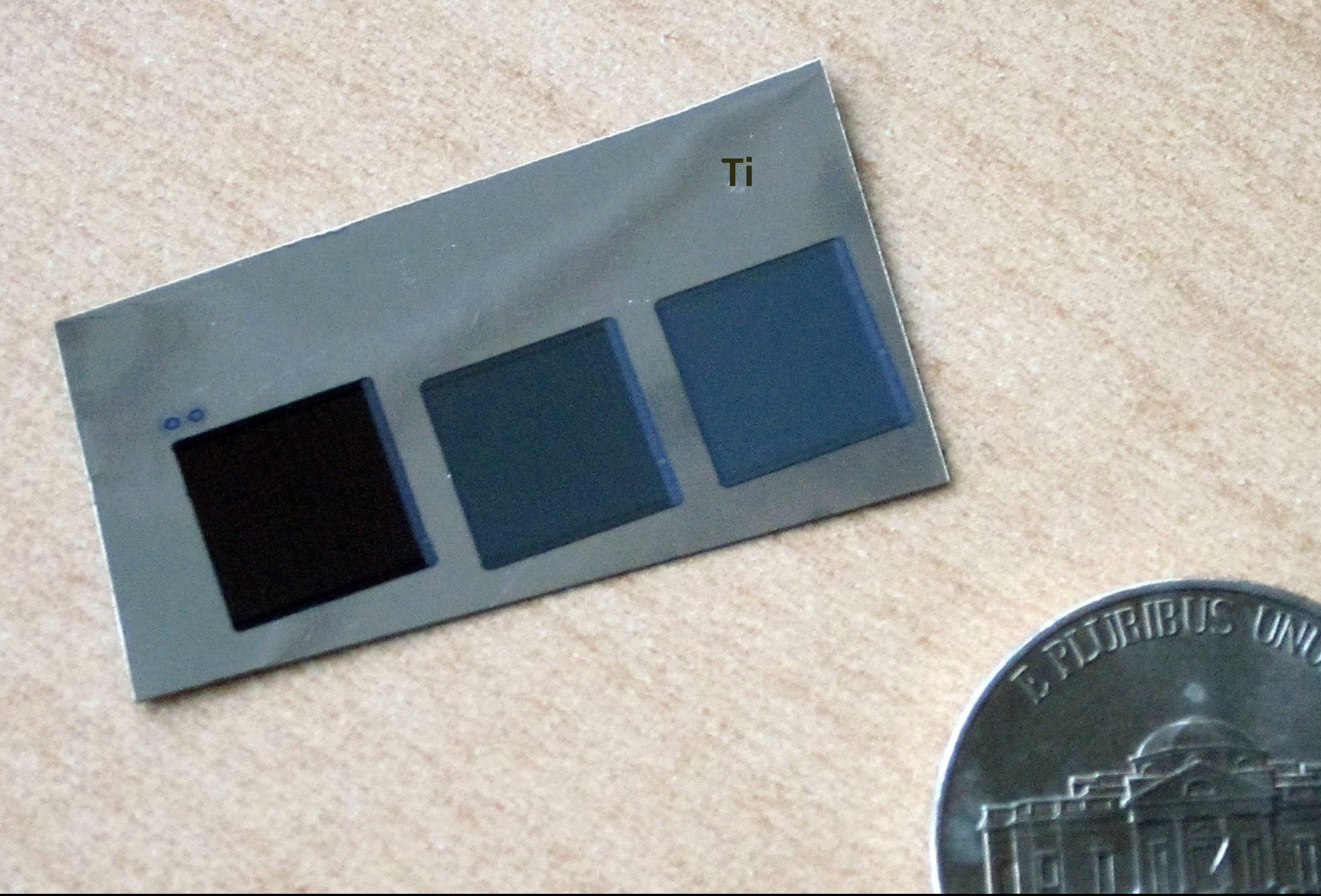
2 doping

3 X:TiO_2

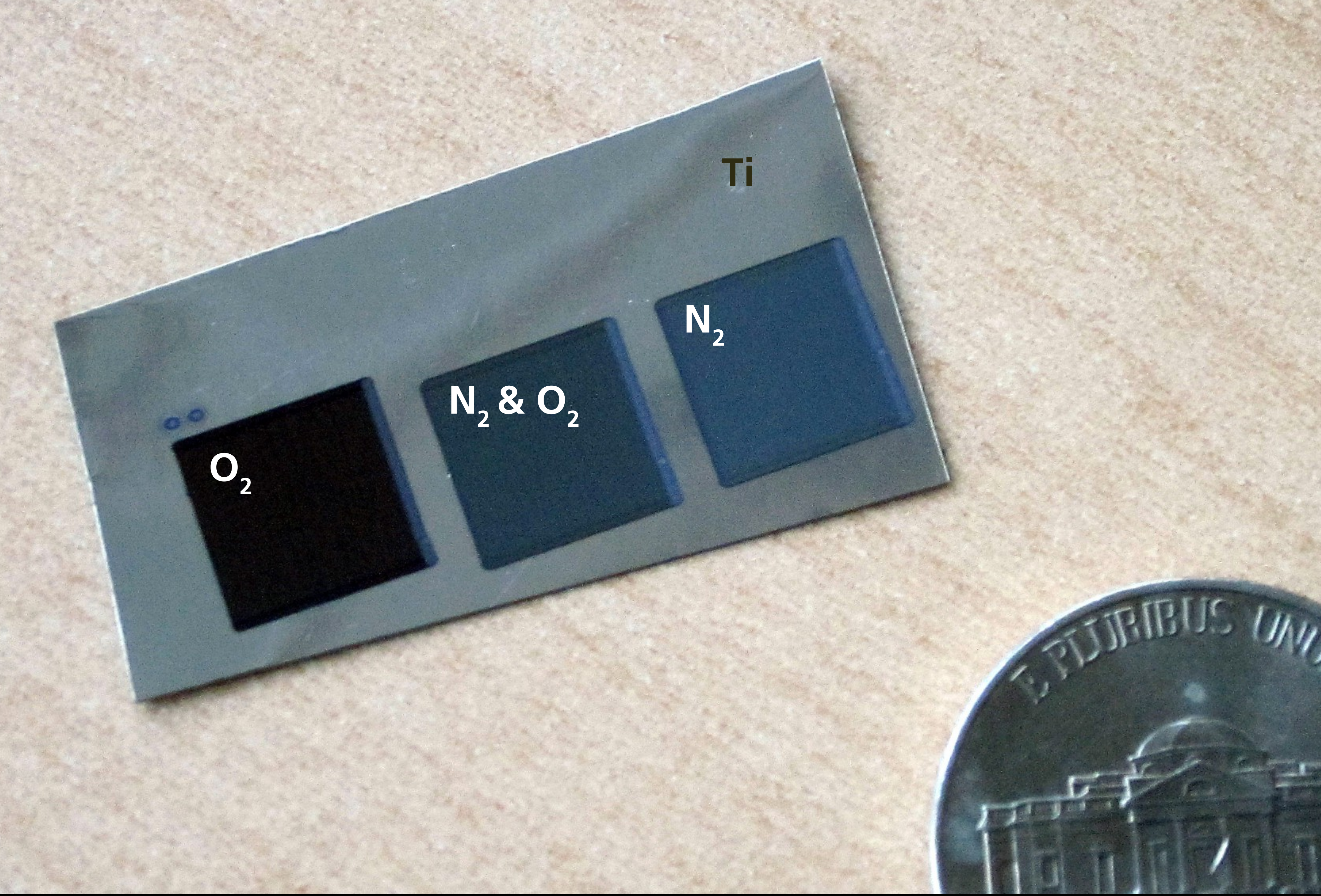
structuring TiO_2 in N_2 doesn't work



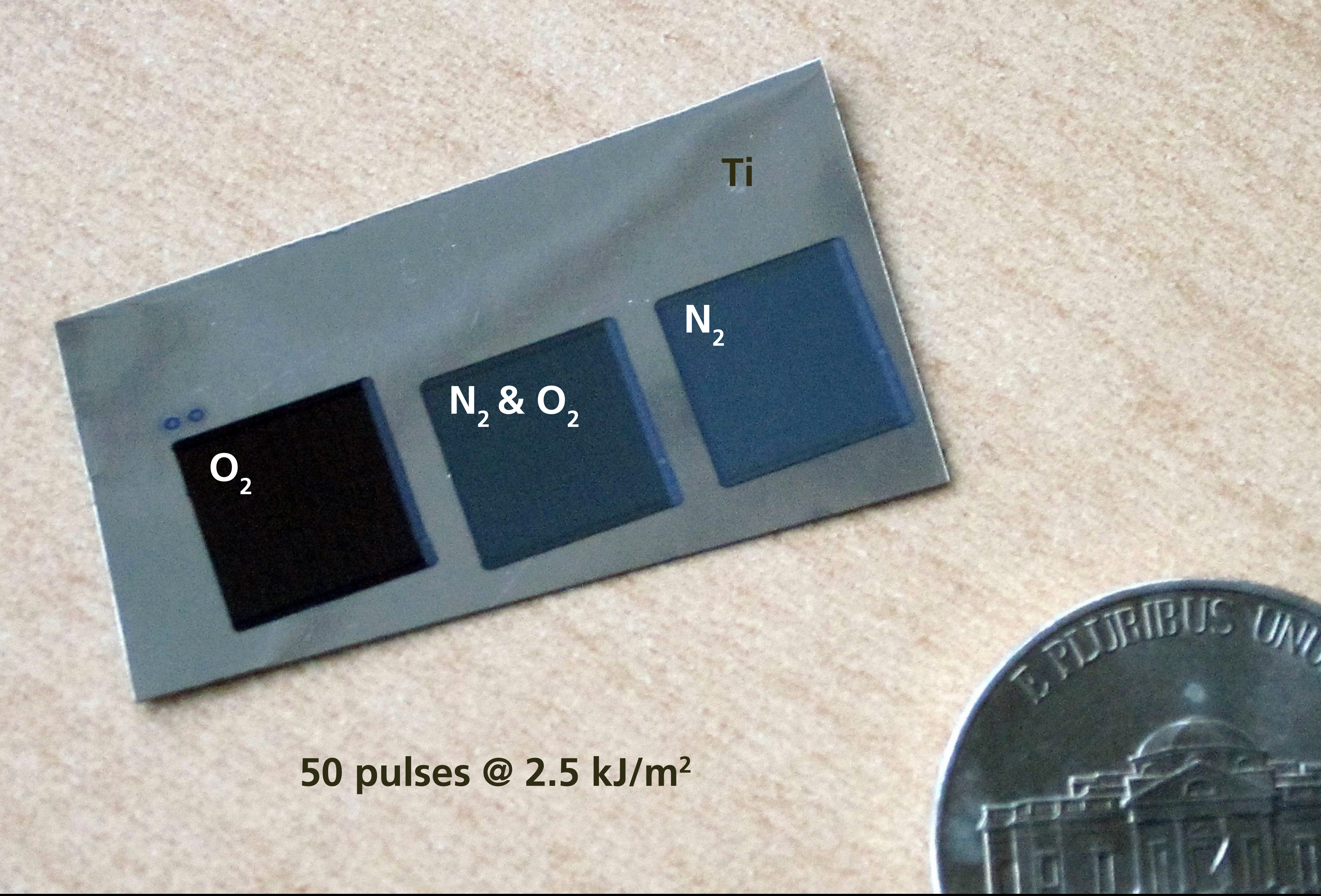
1 texturing **2** doping **3** X:TiO_2



1 texturing **2** doping **3** X:TiO_2

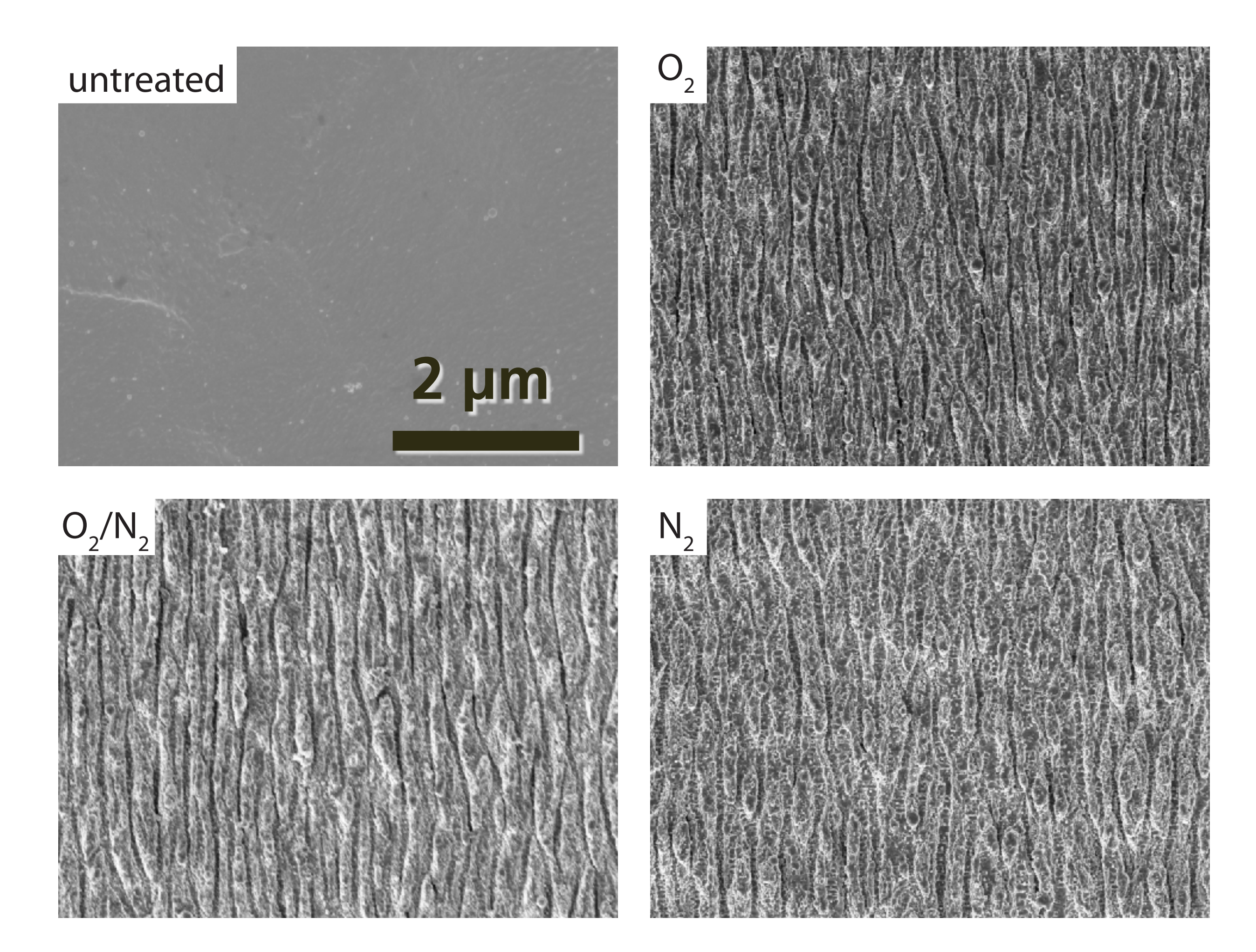


1 texturing 2 doping 3 $X:TiO_2$



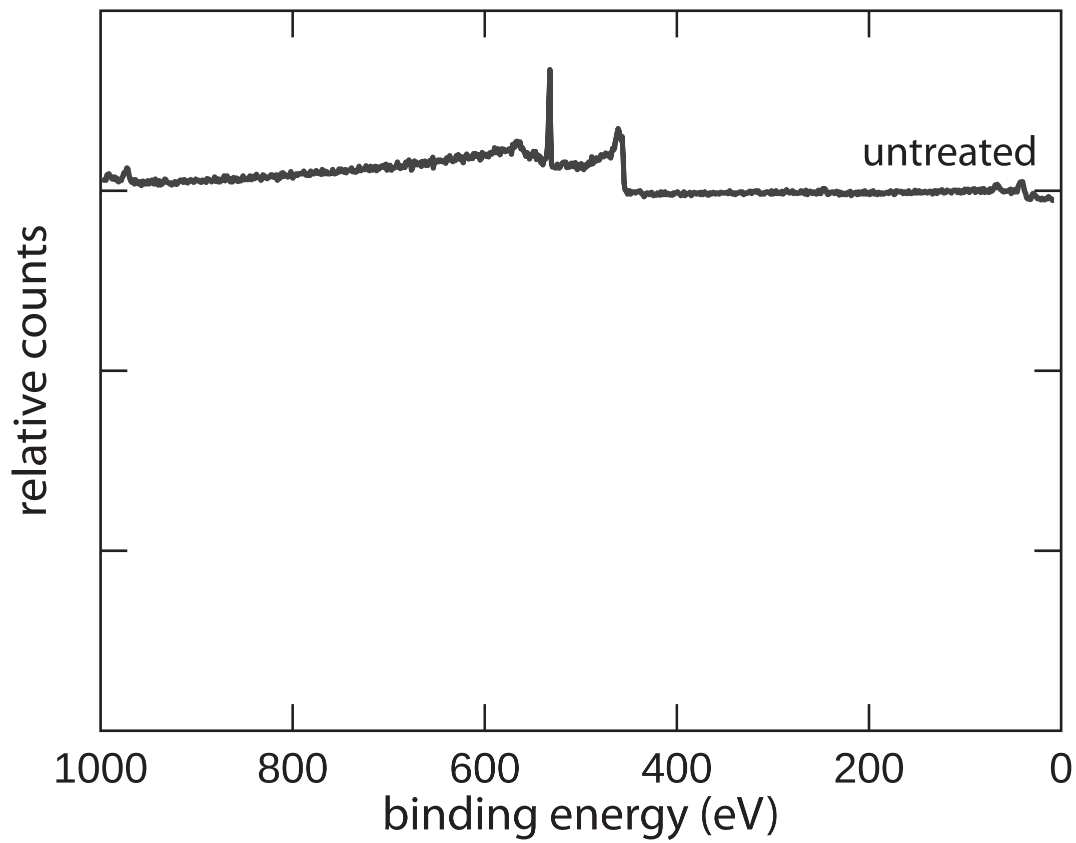
1 texturing 2 doping 3 X:TiO_2

50 pulses @ 2.5 kJ/m²



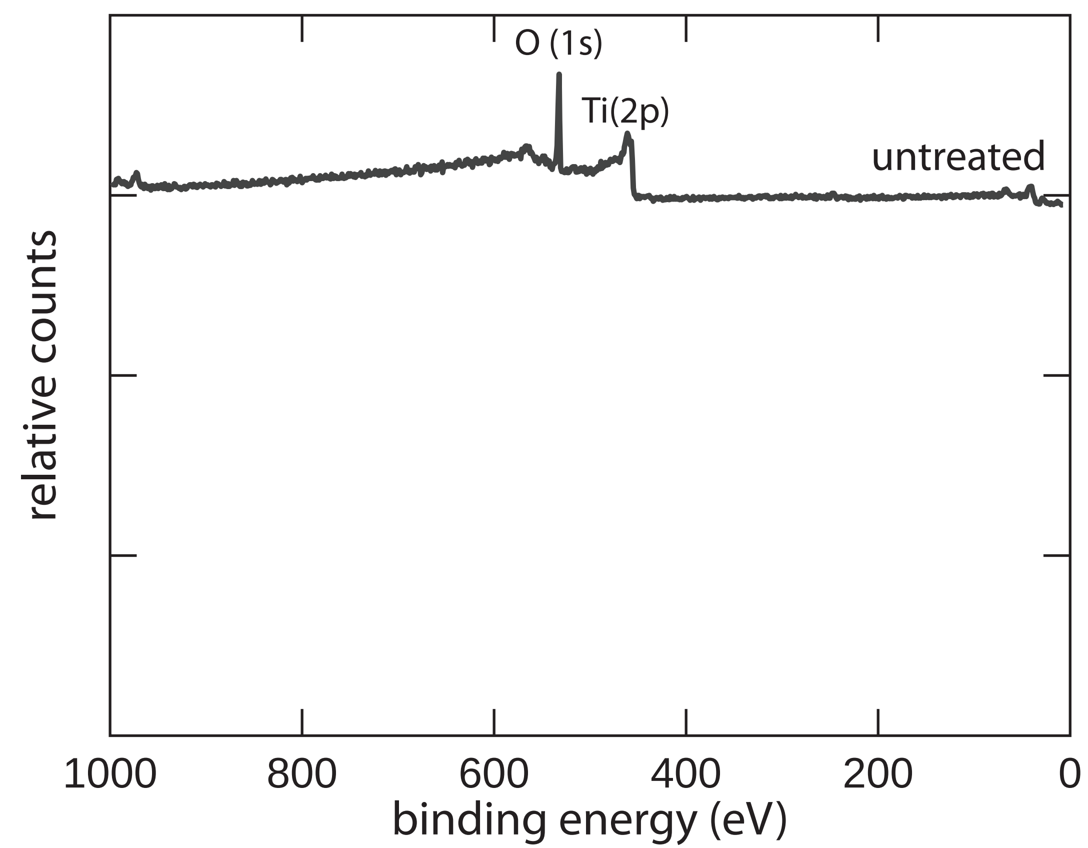
1 texturing **2** doping **3** X:TiO_2

X-ray photoelectron spectroscopy



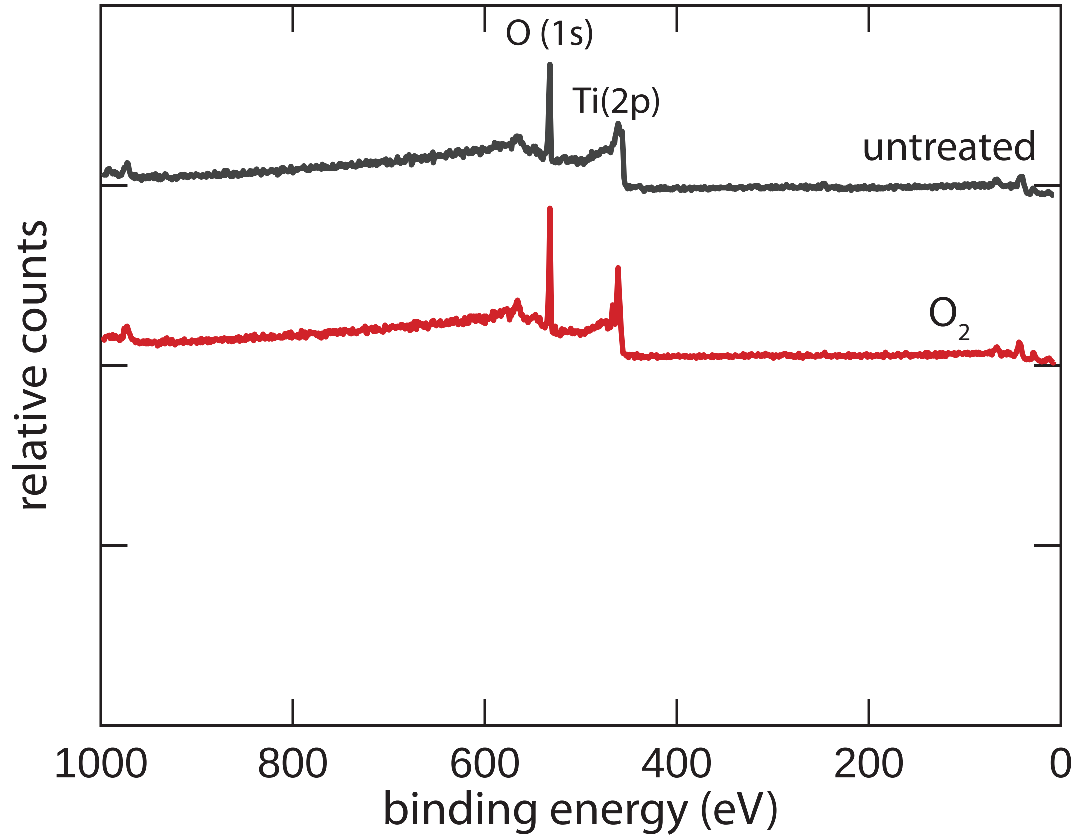
1 texturing   2 doping   3 X:TiO_2

X-ray photoelectron spectroscopy



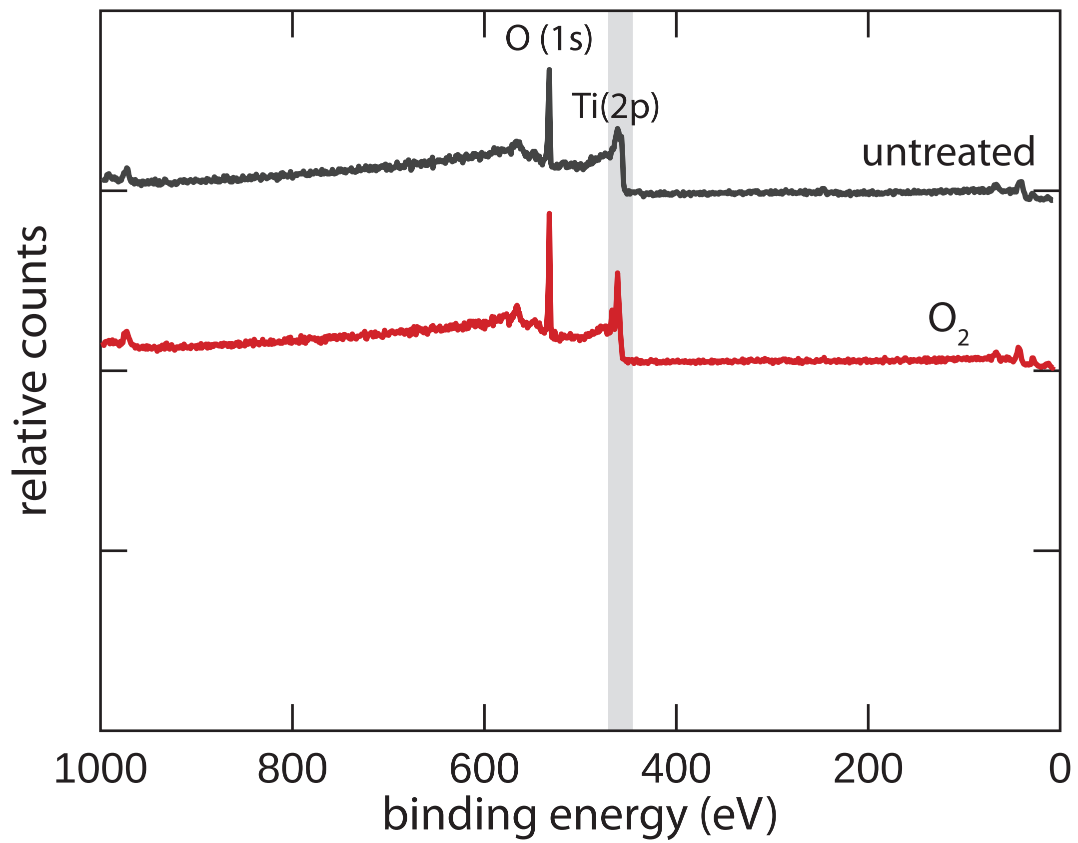
1 texturing 2 doping 3 $X:TiO_2$

X-ray photoelectron spectroscopy



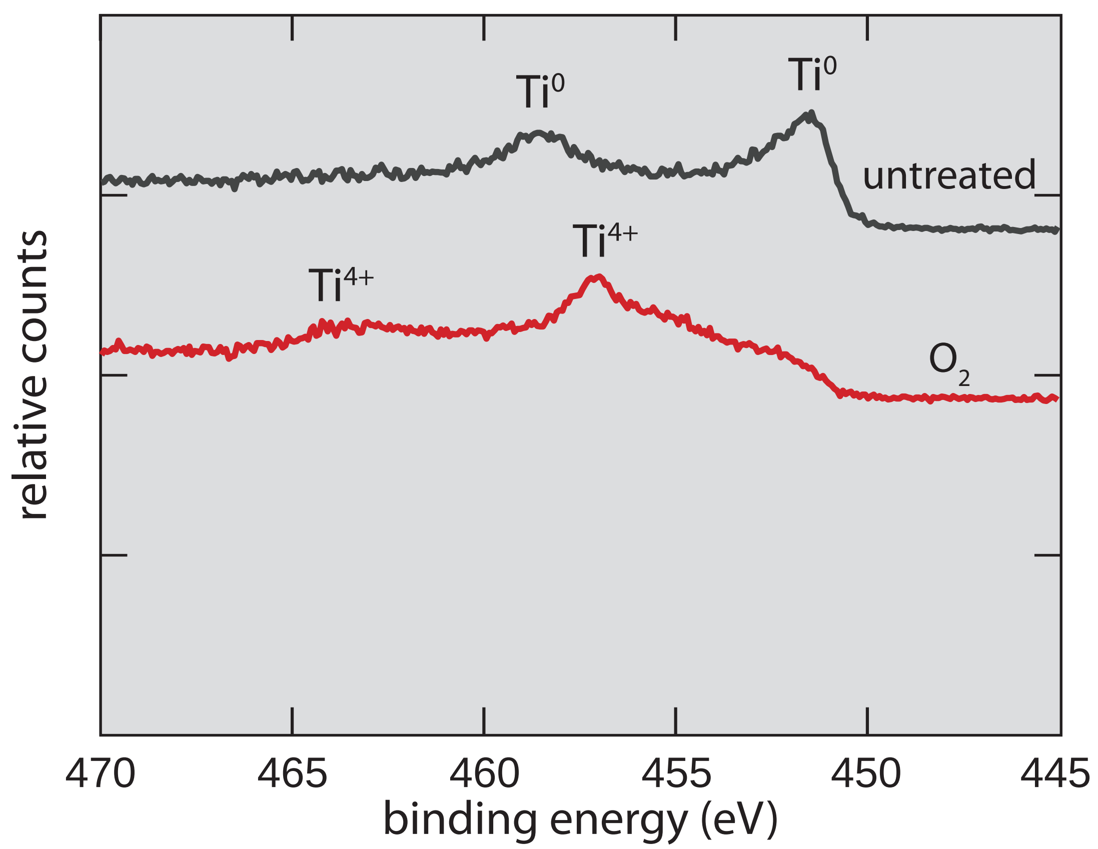
1 texturing **2** doping **3** $X:TiO_2$

X-ray photoelectron spectroscopy



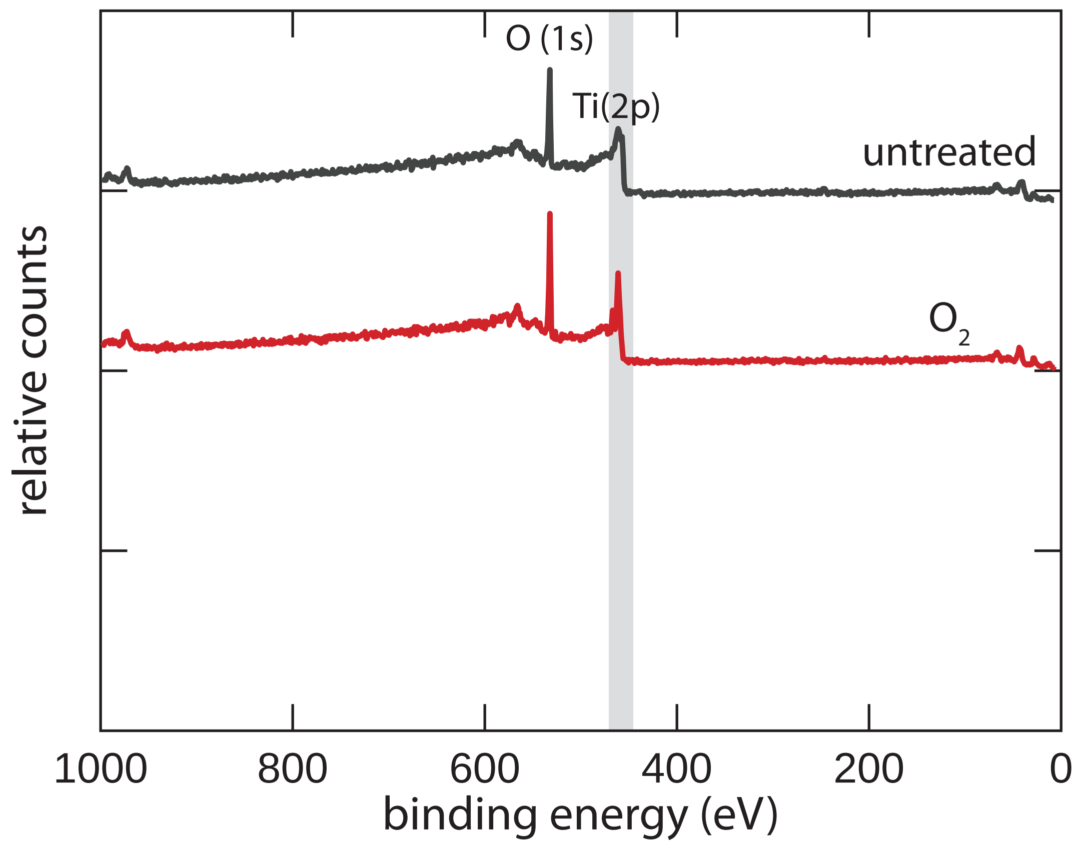
1 texturing 2 doping 3 X:TiO_2

oxygen is incorporated!



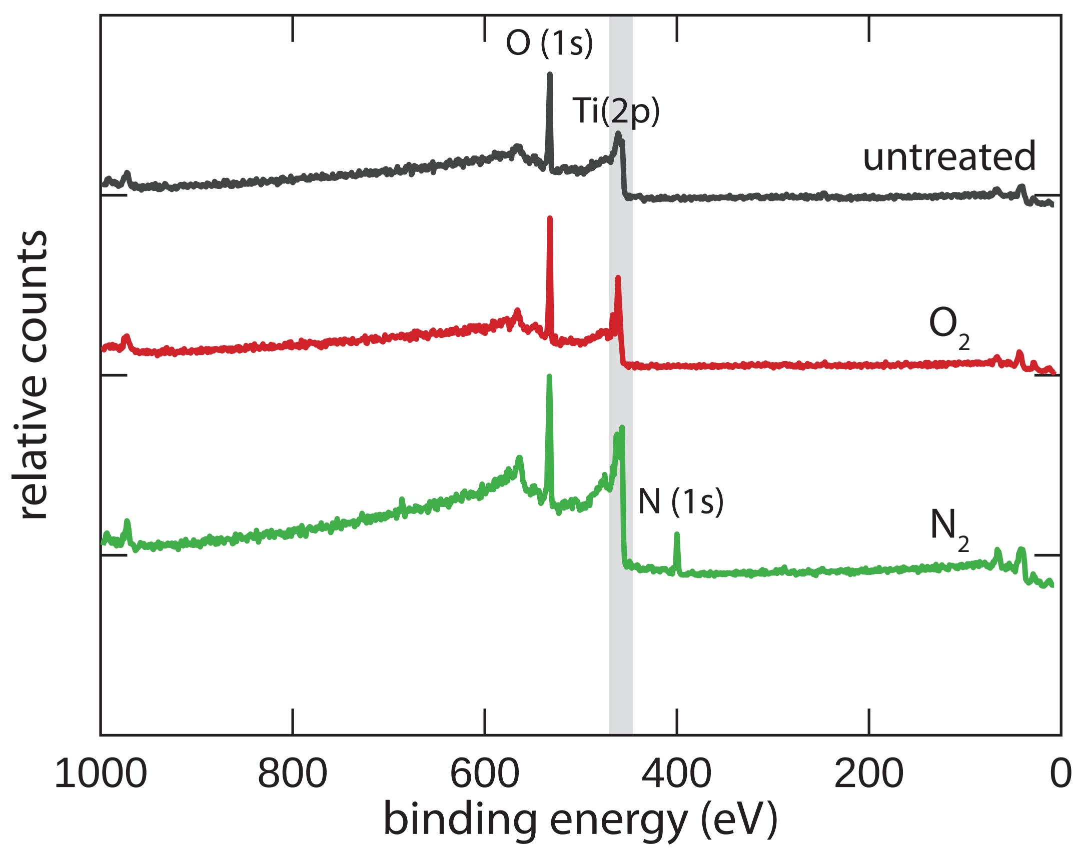
1 texturing **2 doping** **3 X:TiO_2**

oxygen is incorporated!



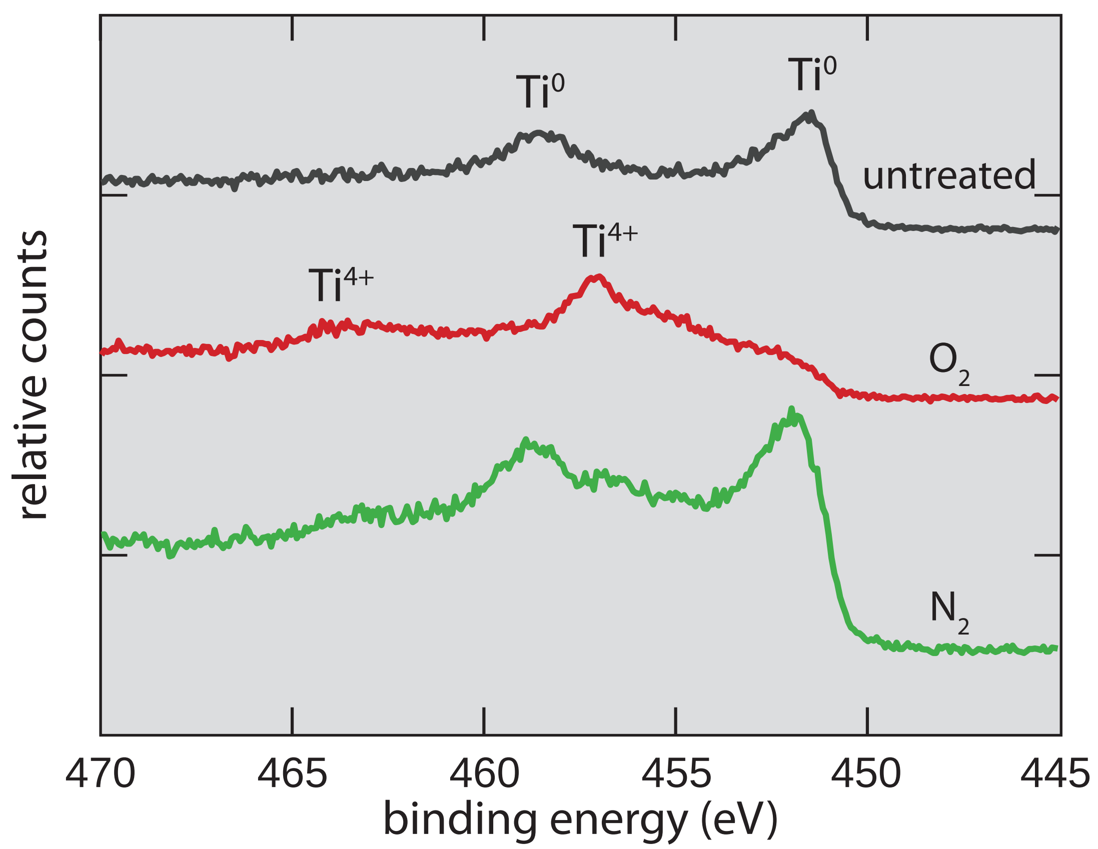
1 texturing 2 doping 3 X:TiO_2

nitrogen peak appears…

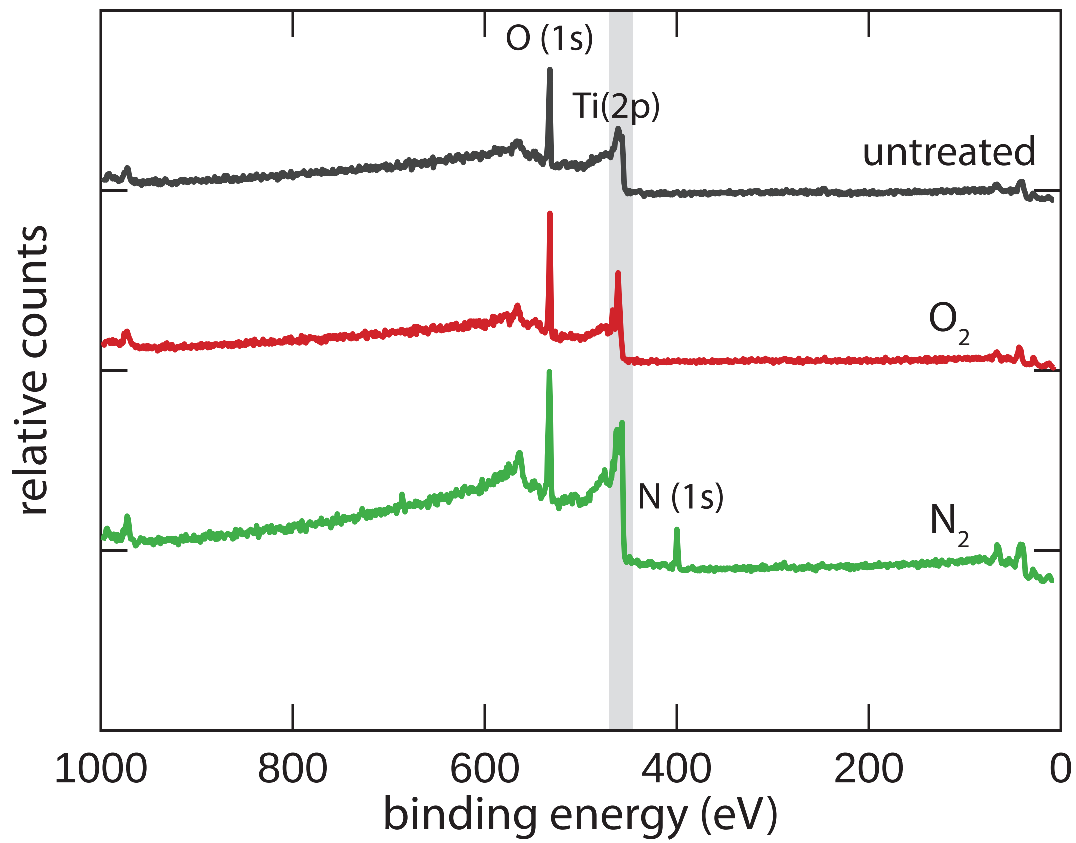


1 texturing 2 doping 3 $X:TiO_2$

… but nitrogen not chemically incorporated

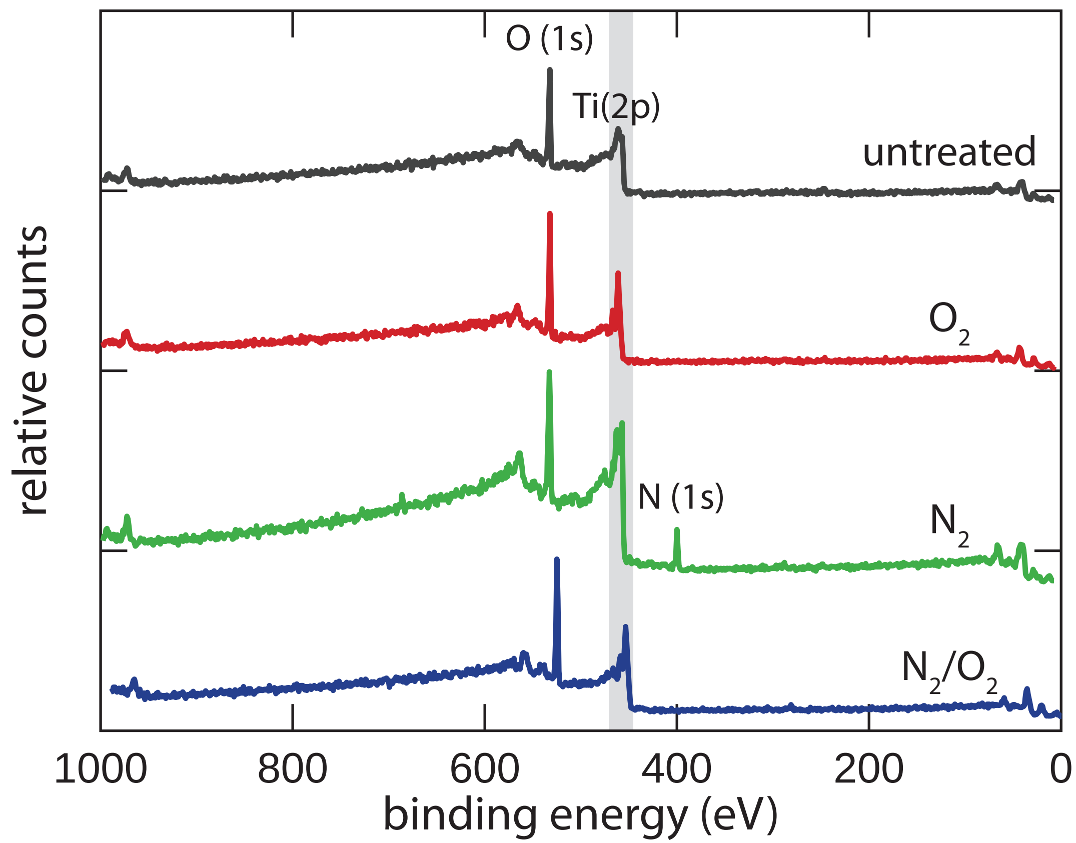


… but nitrogen not chemically incorporated



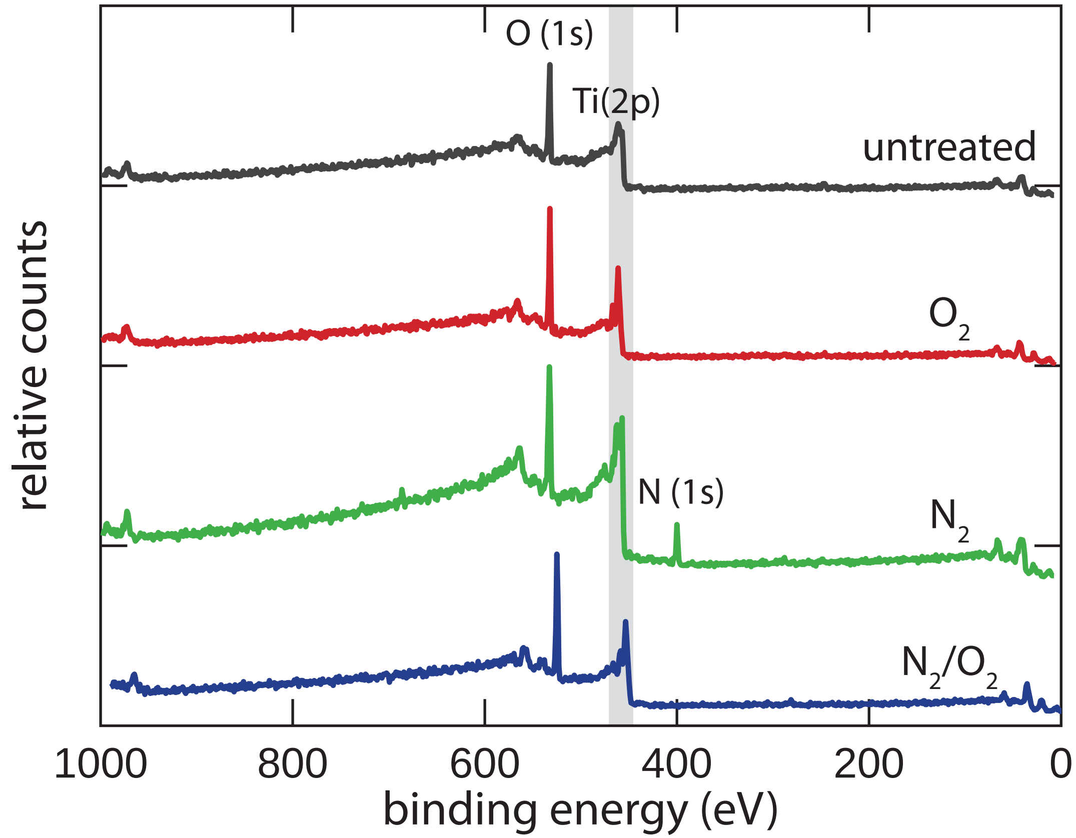
1 texturing 2 doping 3 X:TiO_2

with both nitrogen and oxygen…



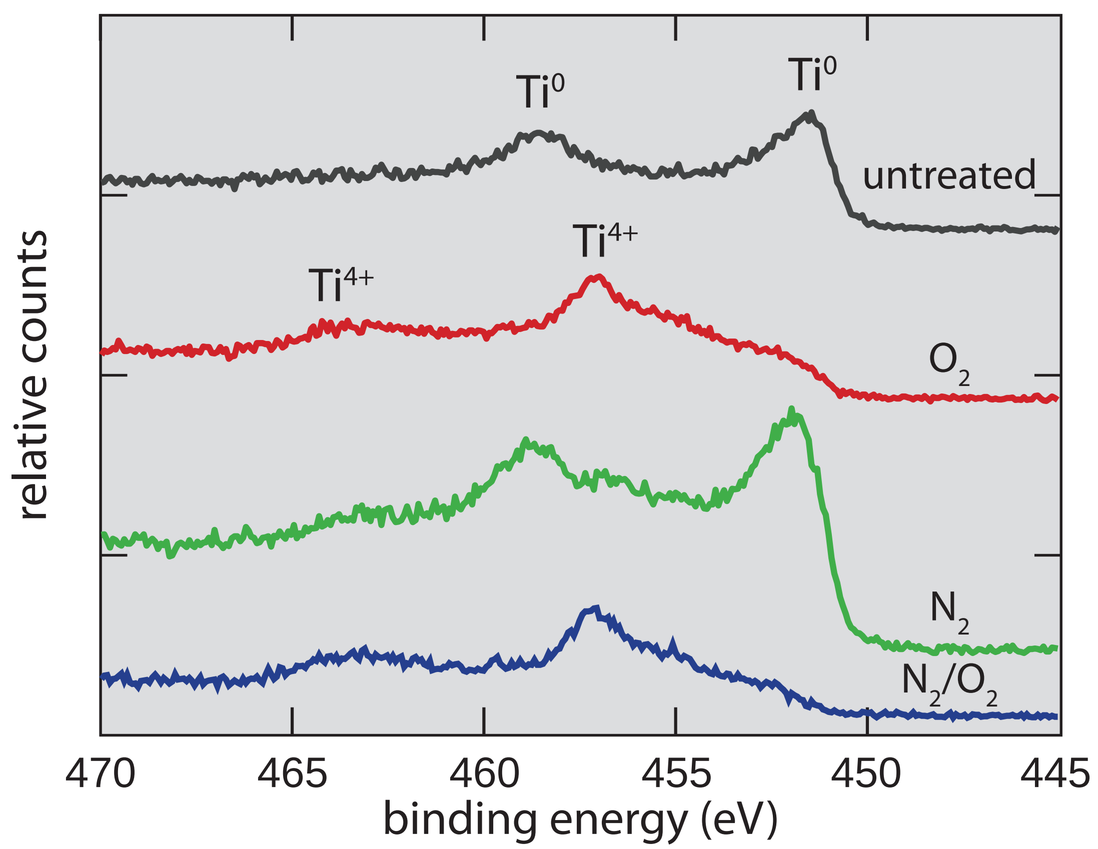
1 texturing 2 doping 3 X:TiO_2

… just 1% of oxygen prevents nitrogen incorporation…



1 texturing   2 doping   3 X:TiO_2

… although oxygen is incorporated

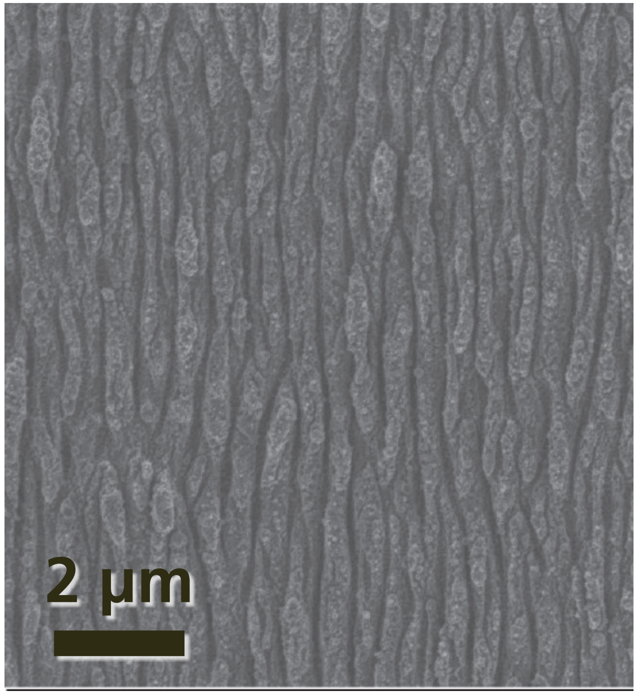


1 texturing 2 doping 3 X:TiO_2

can get N_2 or O_2 incorporated, but not both

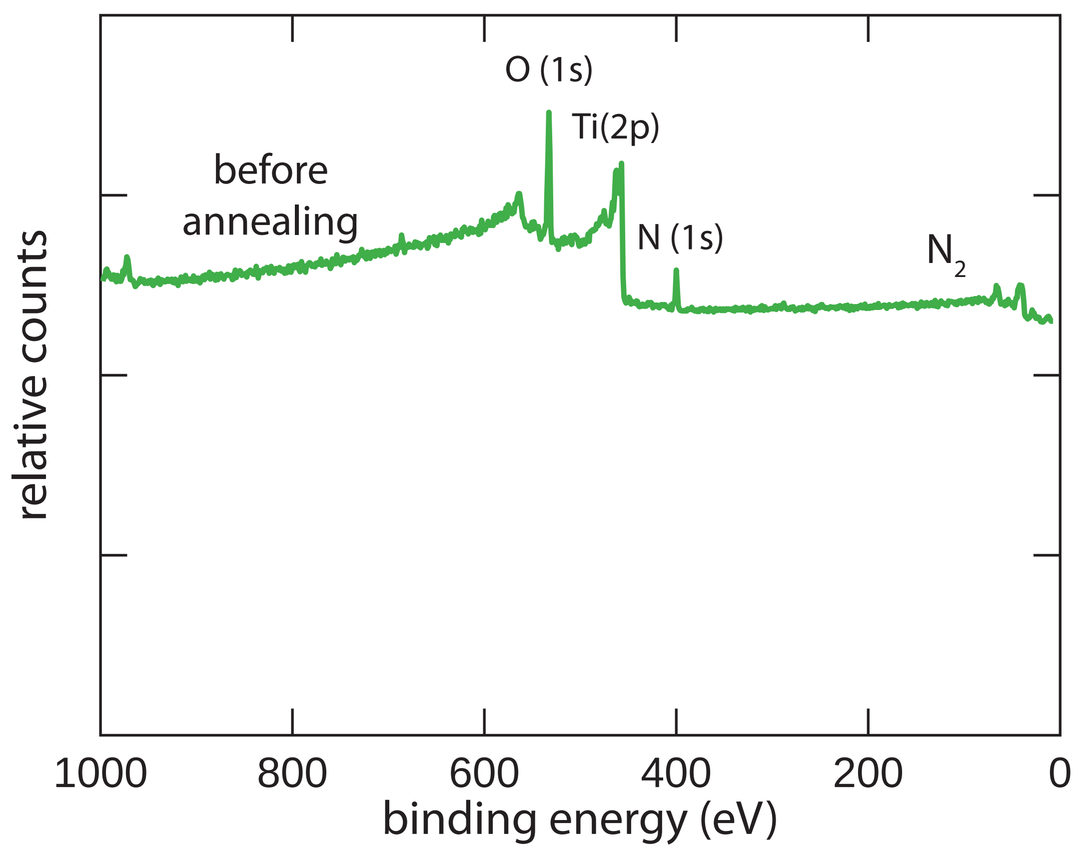
anneal N:Ti sample in O_2 (1h @ 900 K)

before annealing



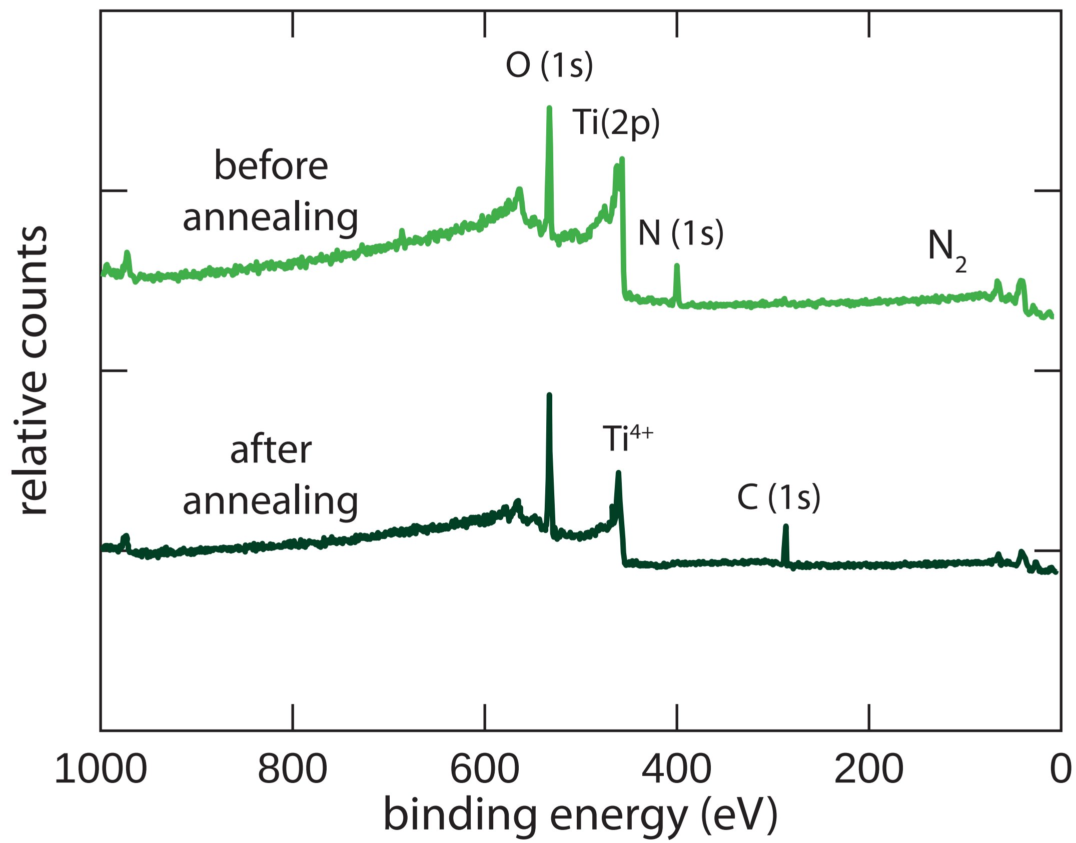
after annealing

anneal N:Ti sample in O_2 (1h @ 900 K)



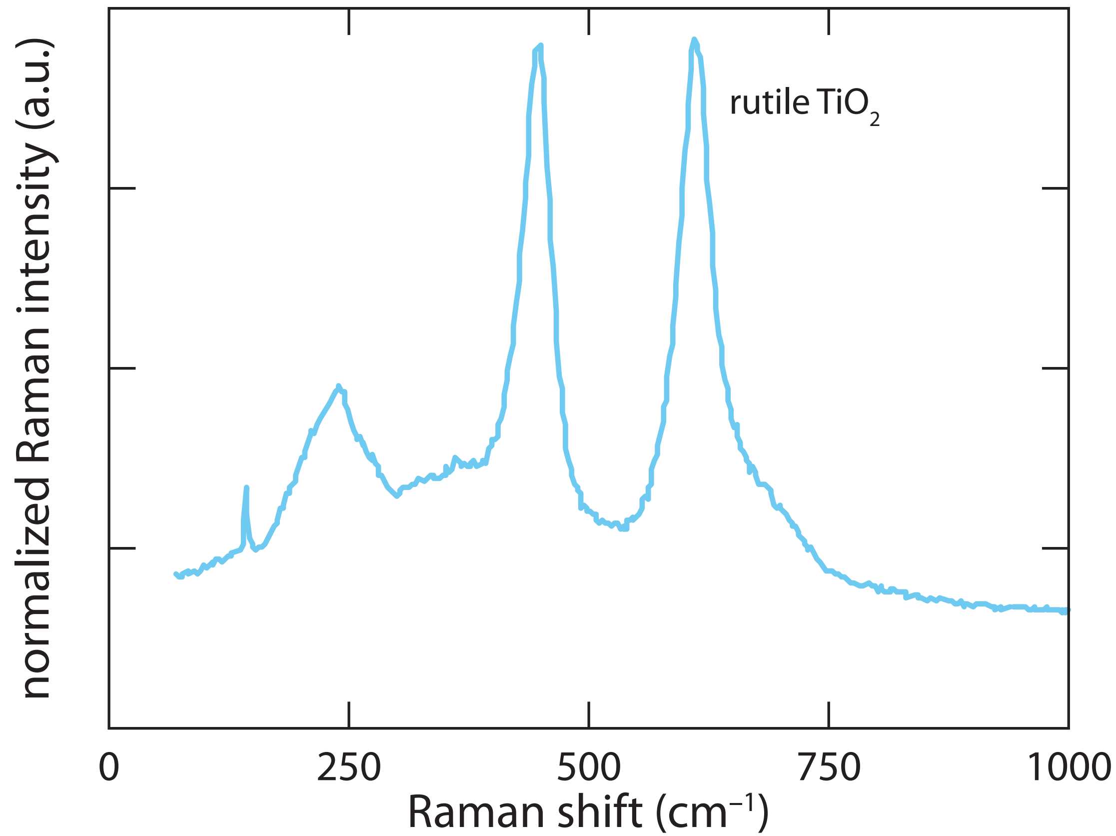
1 texturing 2 doping 3 X:TiO_2

…nitrogen anneals out…



1 texturing 2 doping 3 X:TiO_2

…but Raman spectrum shows TiO_2 is formed

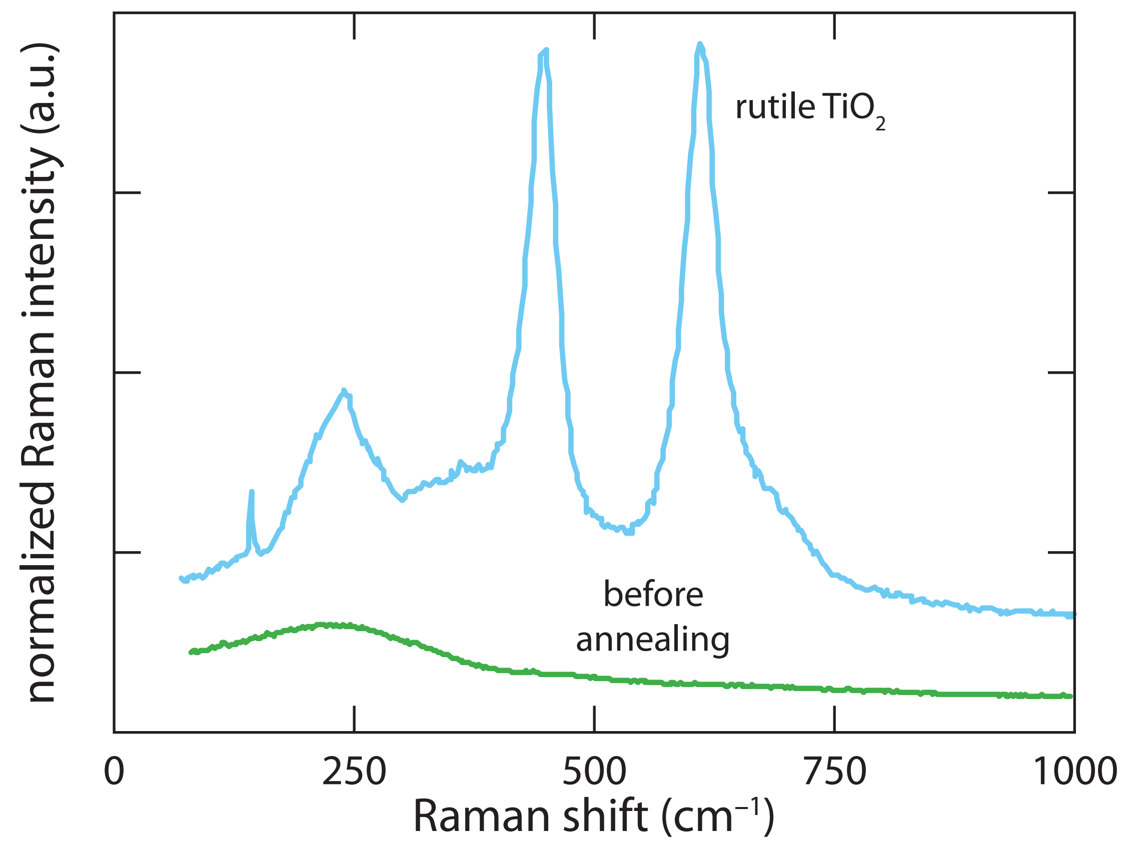


1 texturing

2 doping

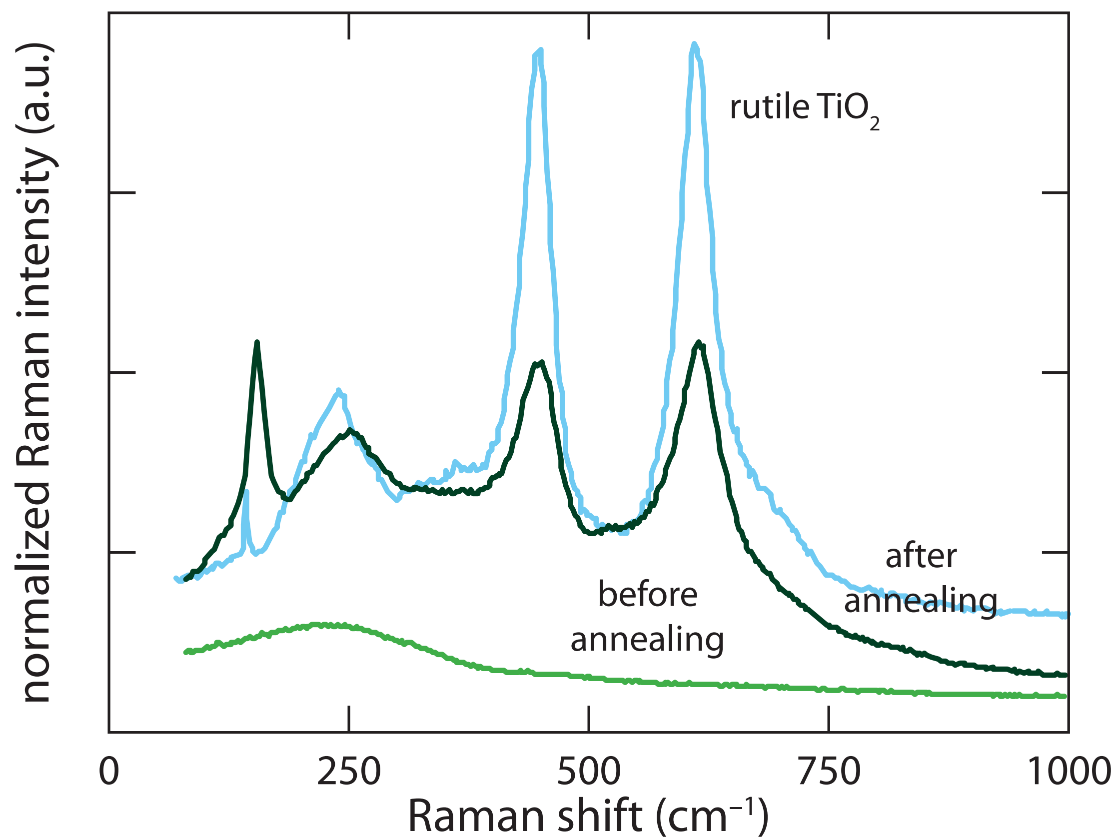
3 $X:TiO_2$

…but Raman spectrum shows TiO_2 is formed



1 texturing 2 doping 3 X:TiO_2

…but Raman spectrum shows TiO_2 is formed



1 texturing   2 doping   3 X:TiO_2

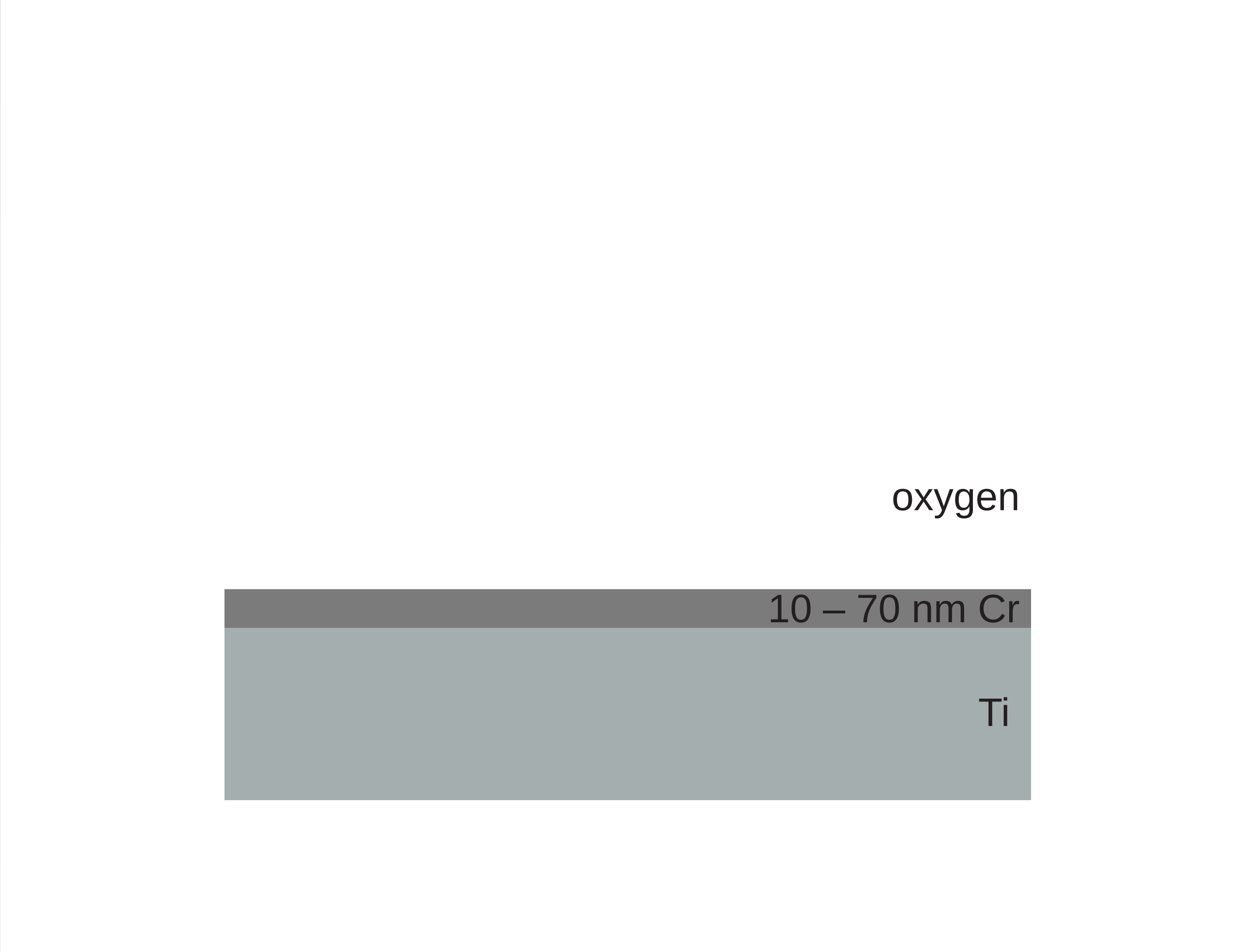
how about incorporating chromium with oxygen?

1 texturing 2 doping 3 X:TiO_2

evaporate 10 – 70 nm chromium on titanium…

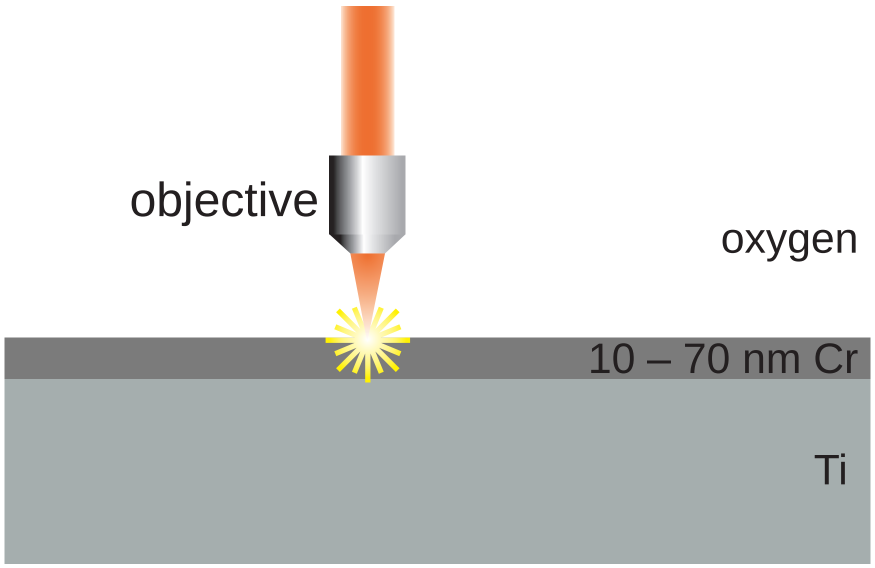
❶ texturing ❷ doping ❸ X:TiO_2

…place in oxygen atmosphere…



1 texturing
2 doping
3 X:TiO_2

...irradiate with laser...



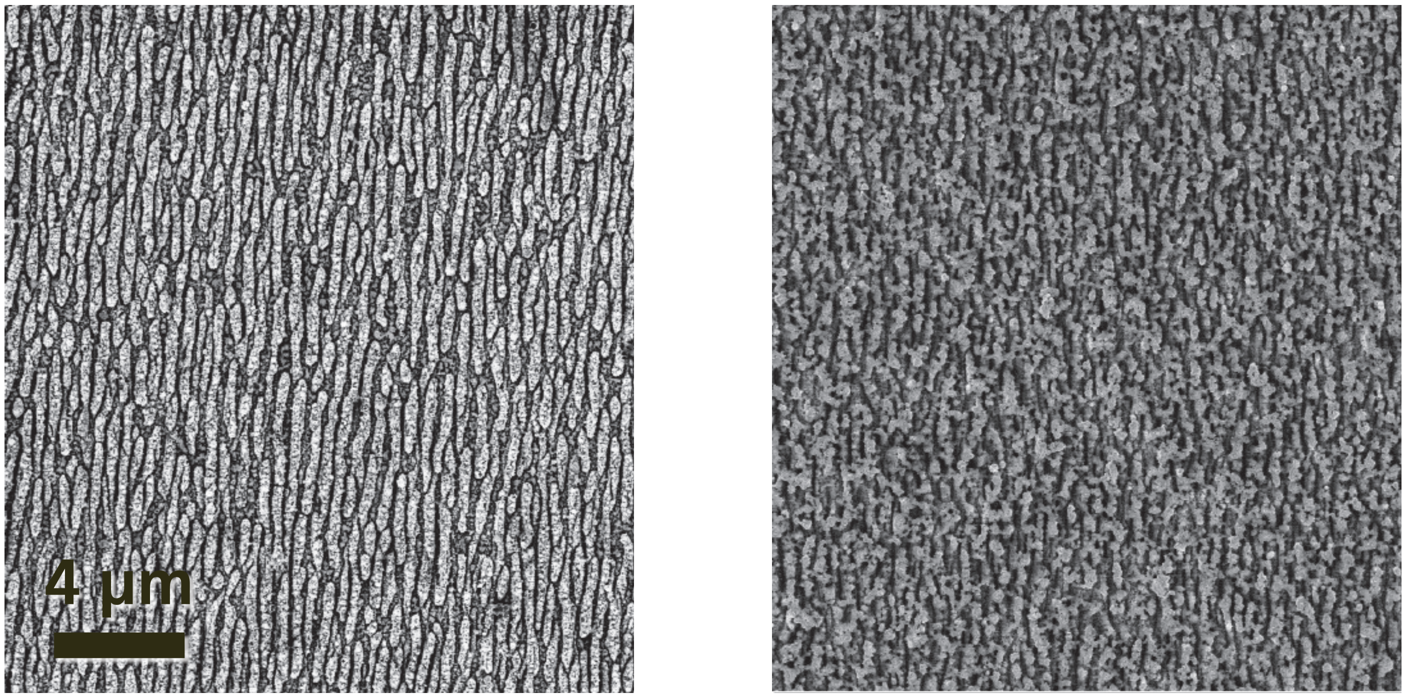
1 texturing **2** doping **3** X:TiO_2

…and raster scan to structure

1 texturing 2 doping 3 X:TiO_2

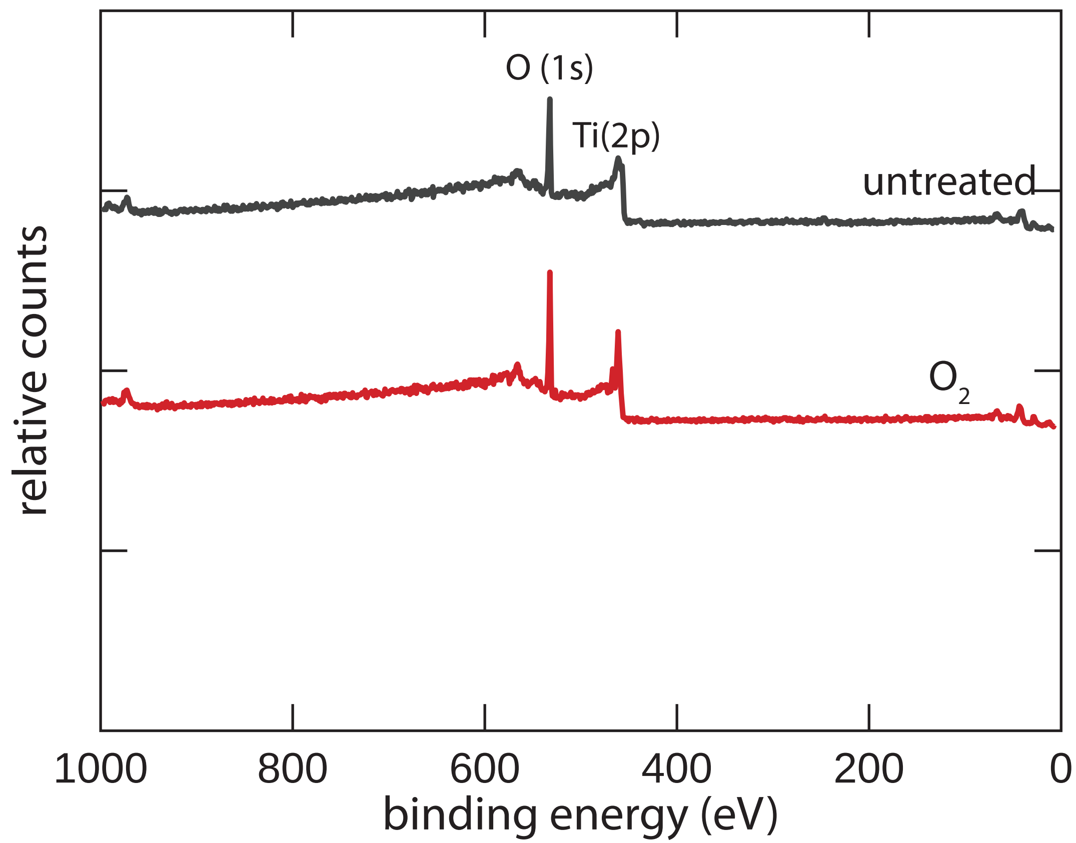
titanium/chromium in oxygen

titanium only | **titanium/chromium**



1 texturing 2 doping 3 X:TiO_2

X-ray photoelectron spectroscopy

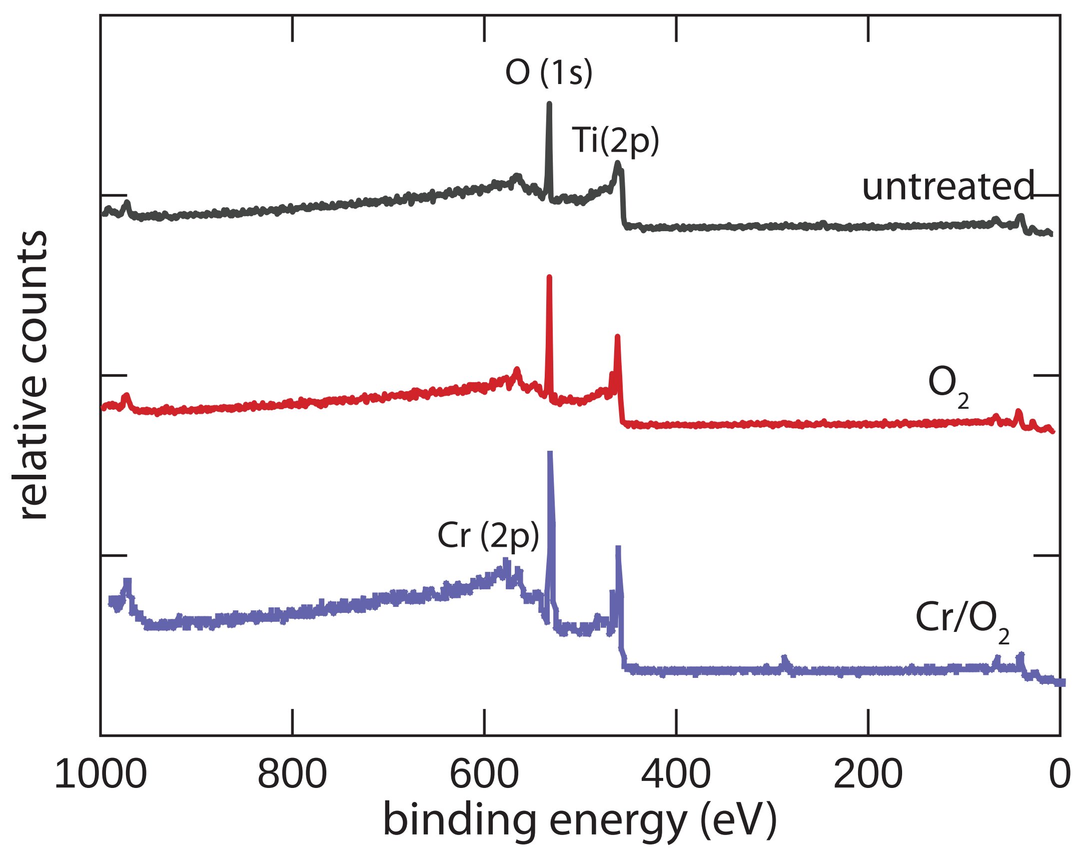


1 texturing

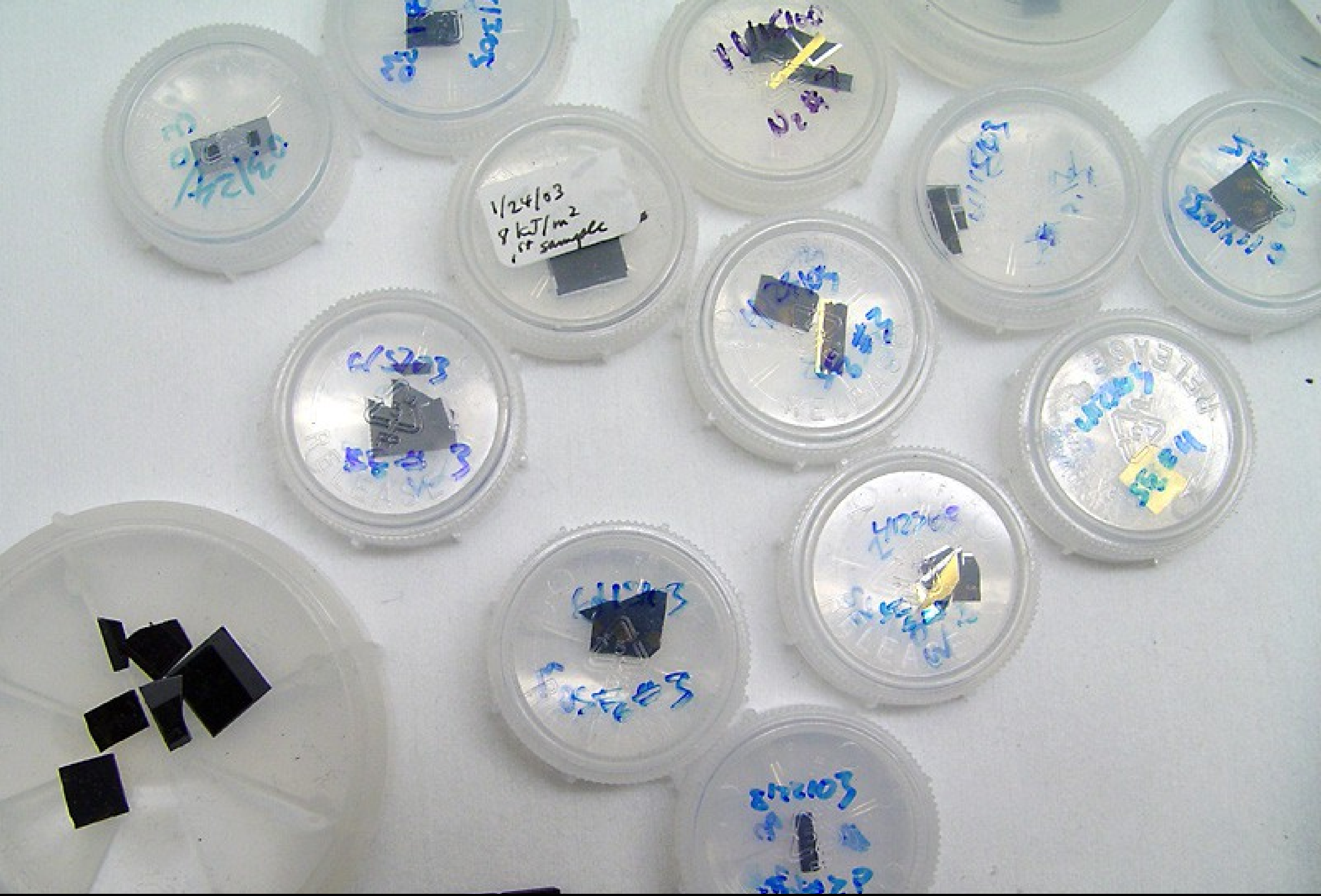
2 doping

3 X:TiO_2

both chromium and oxygen incorporated!



1 texturing 2 doping 3 X:TiO_2



1 texturing 2 doping 3 X:TiO_2

Summary

Can produce:

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

Funding:

Army Research Office
DARPA
Department of Energy
NDSEG
National Science Foundation

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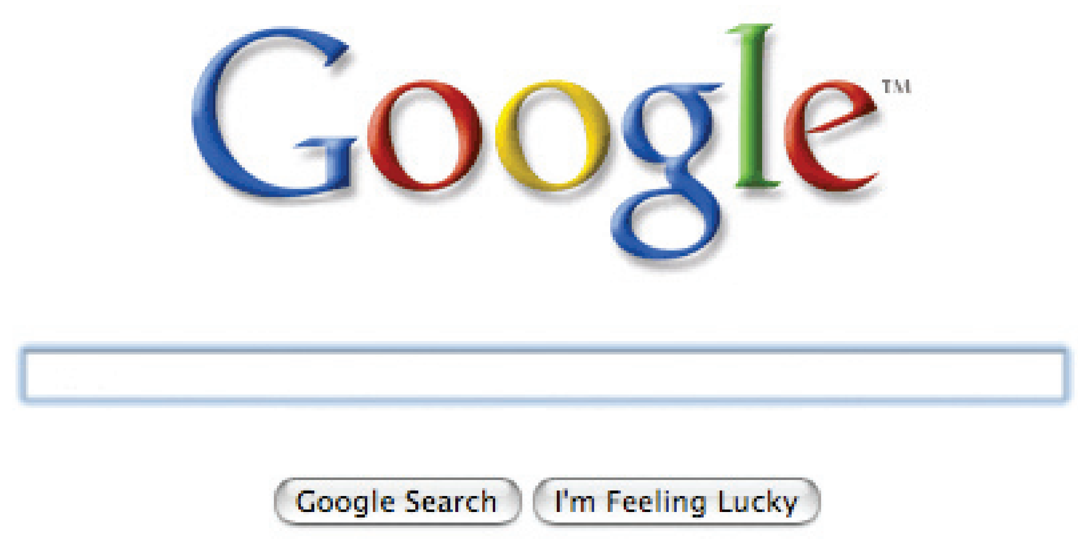
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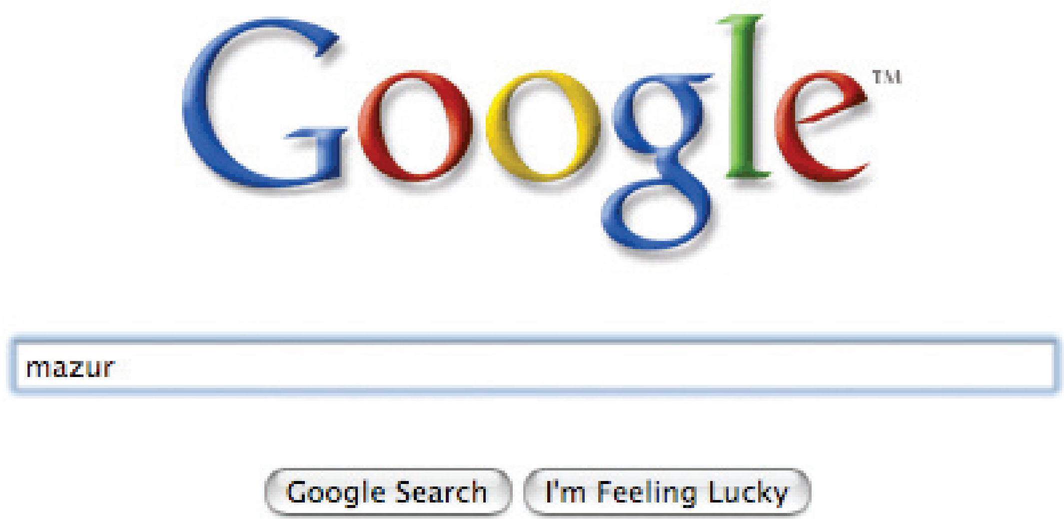
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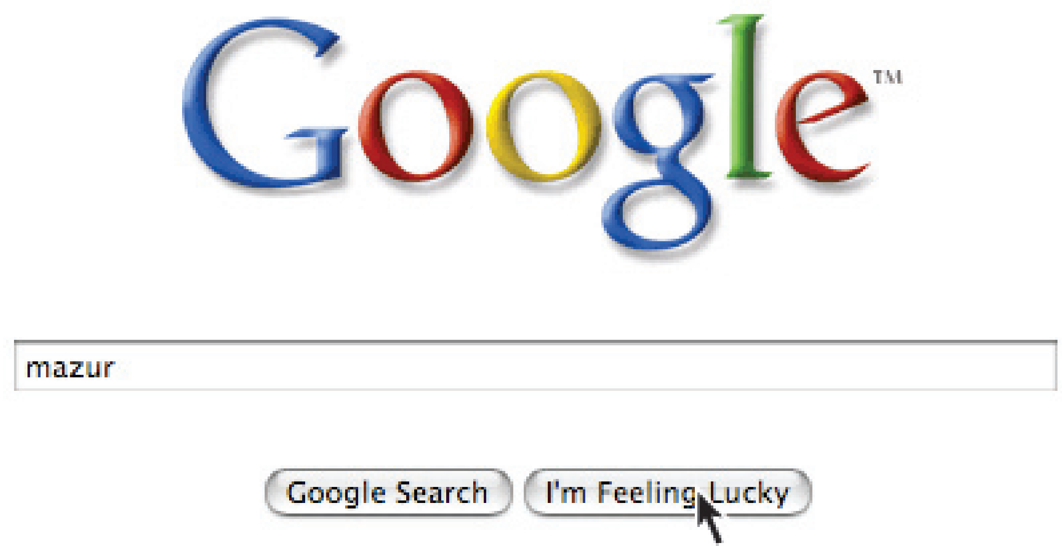
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mazur
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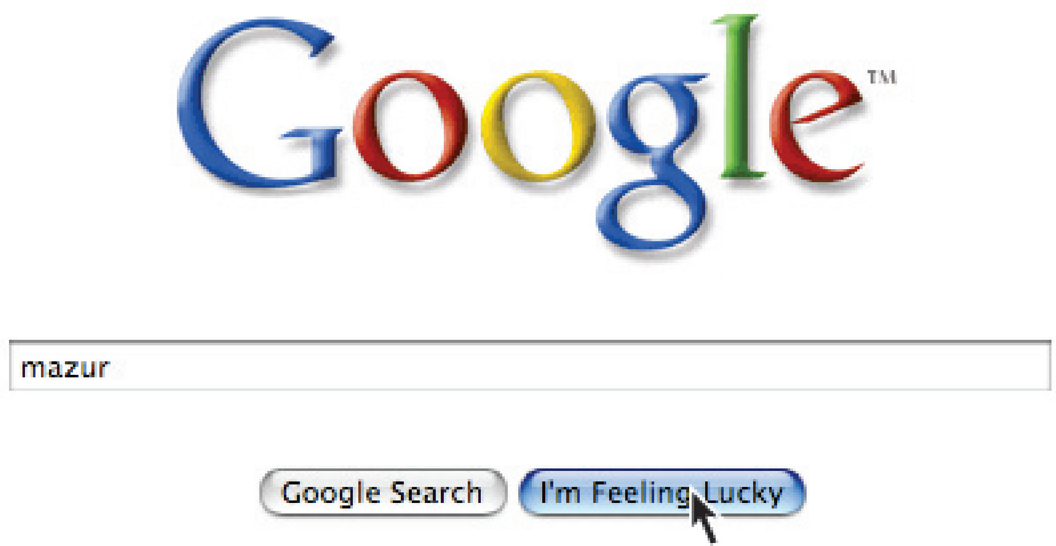
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