Femtosecond laser texturing and doping of semiconductors and metals for solar harvesting

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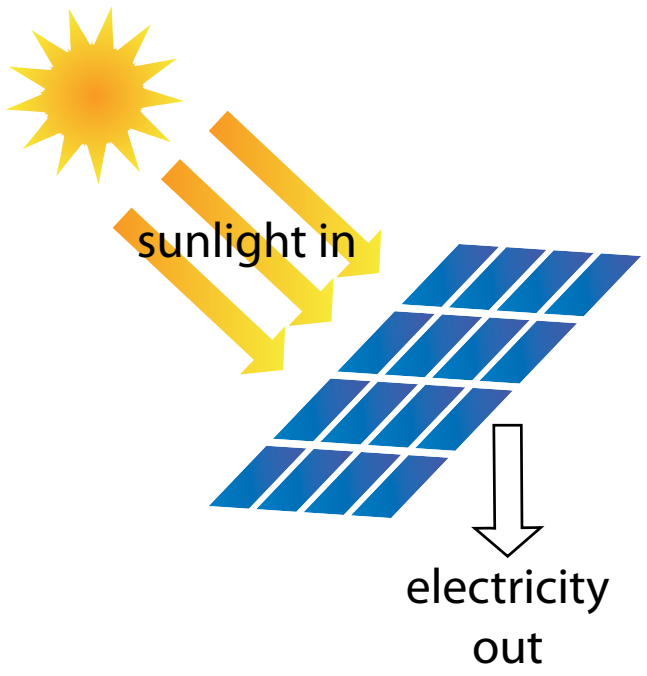
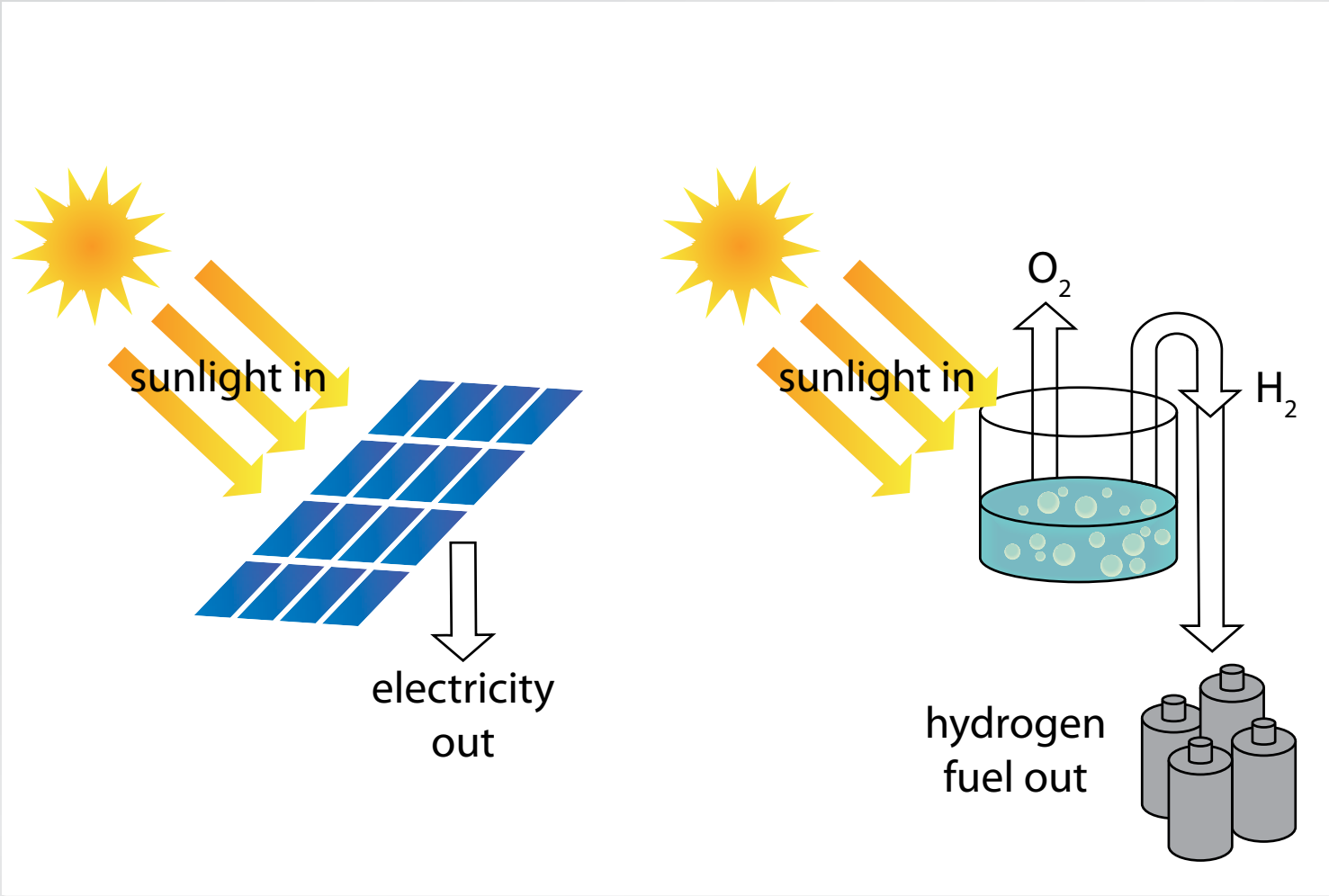
Yu-Ting Lin, Meng-Ju Sher & Eric Mazur
Harvard University
SPIE Optics + Photonics, San Diego, CA

MAZUR GROUP

solar harvesting

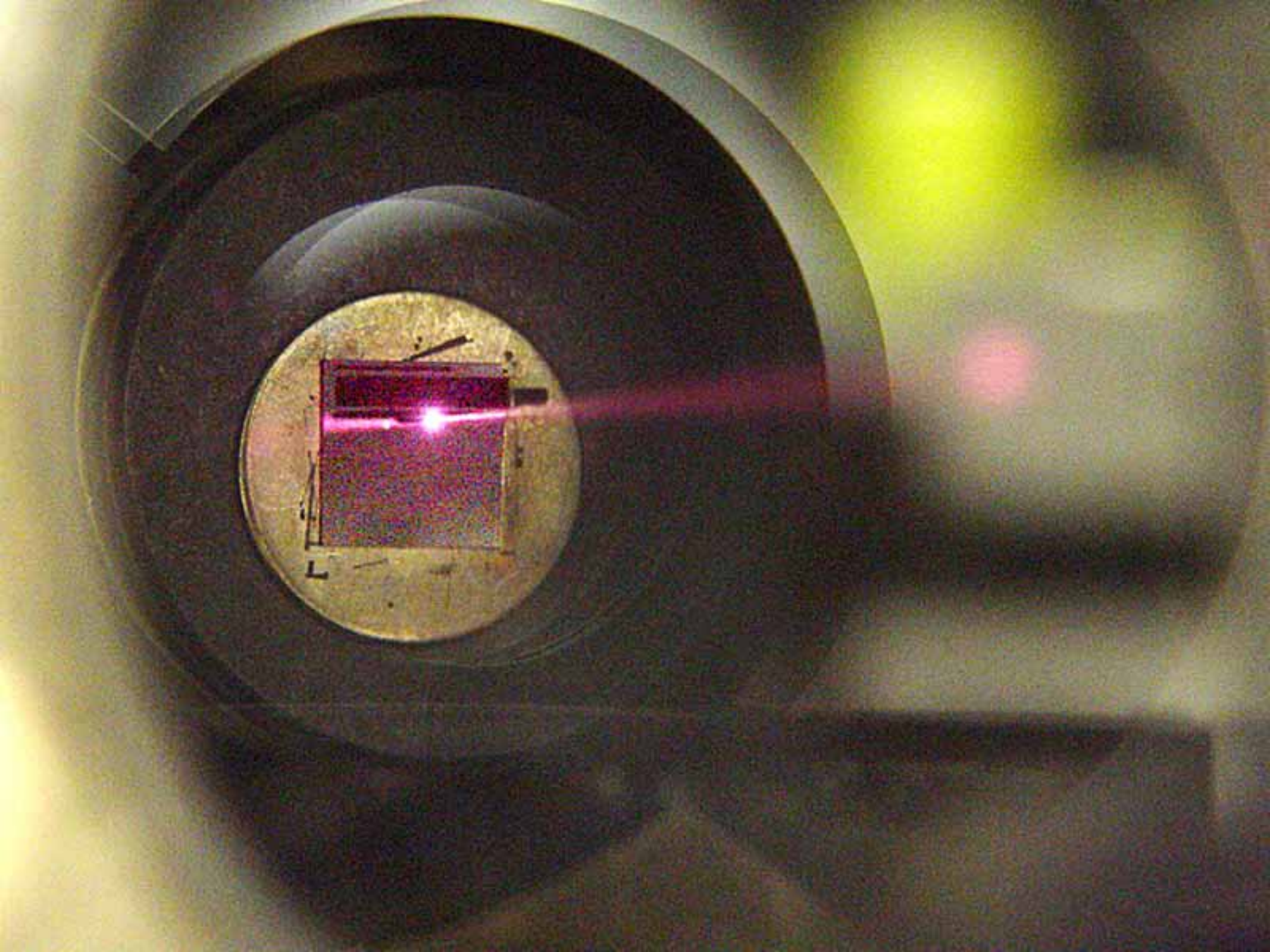


solar harvesting



Our goal:

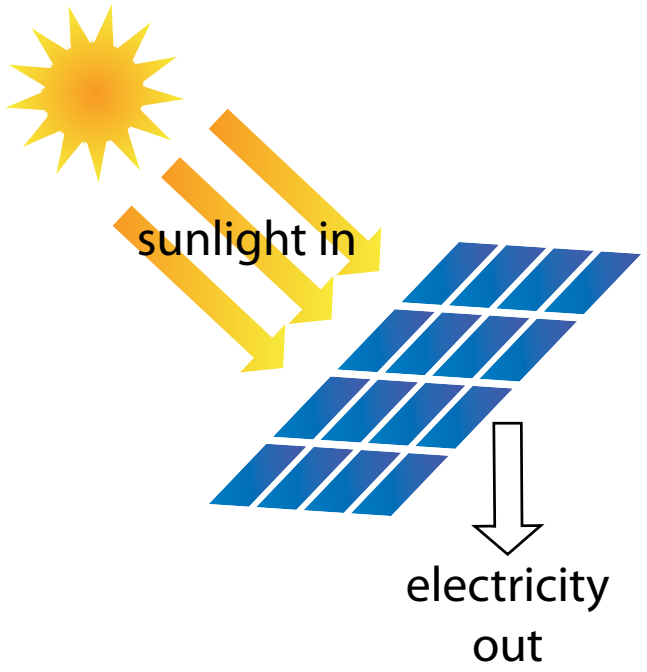
Create new materials
to capture light more effectively.



femtosecond laser processing causes:

- surface texturing
- inclusion of dopants

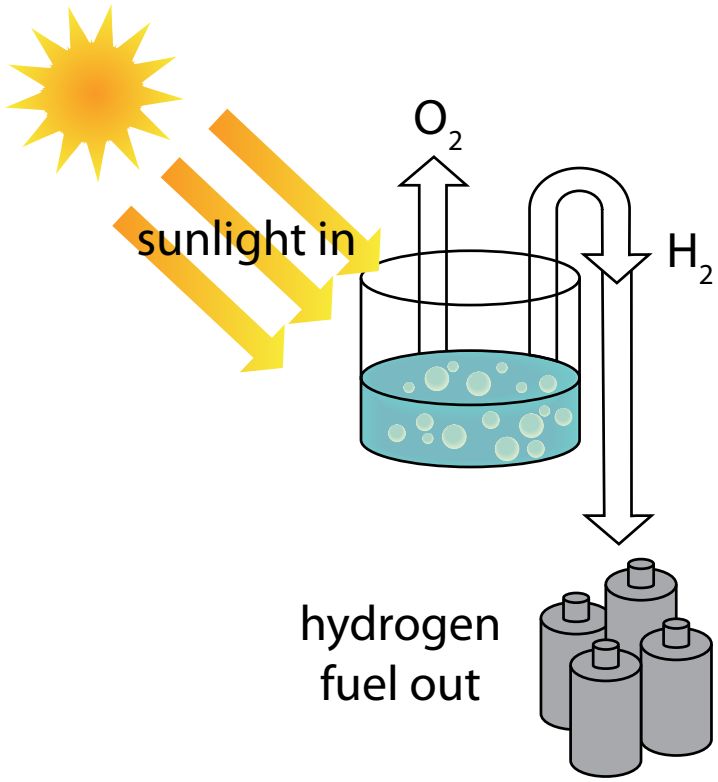
improving silicon photovoltaics

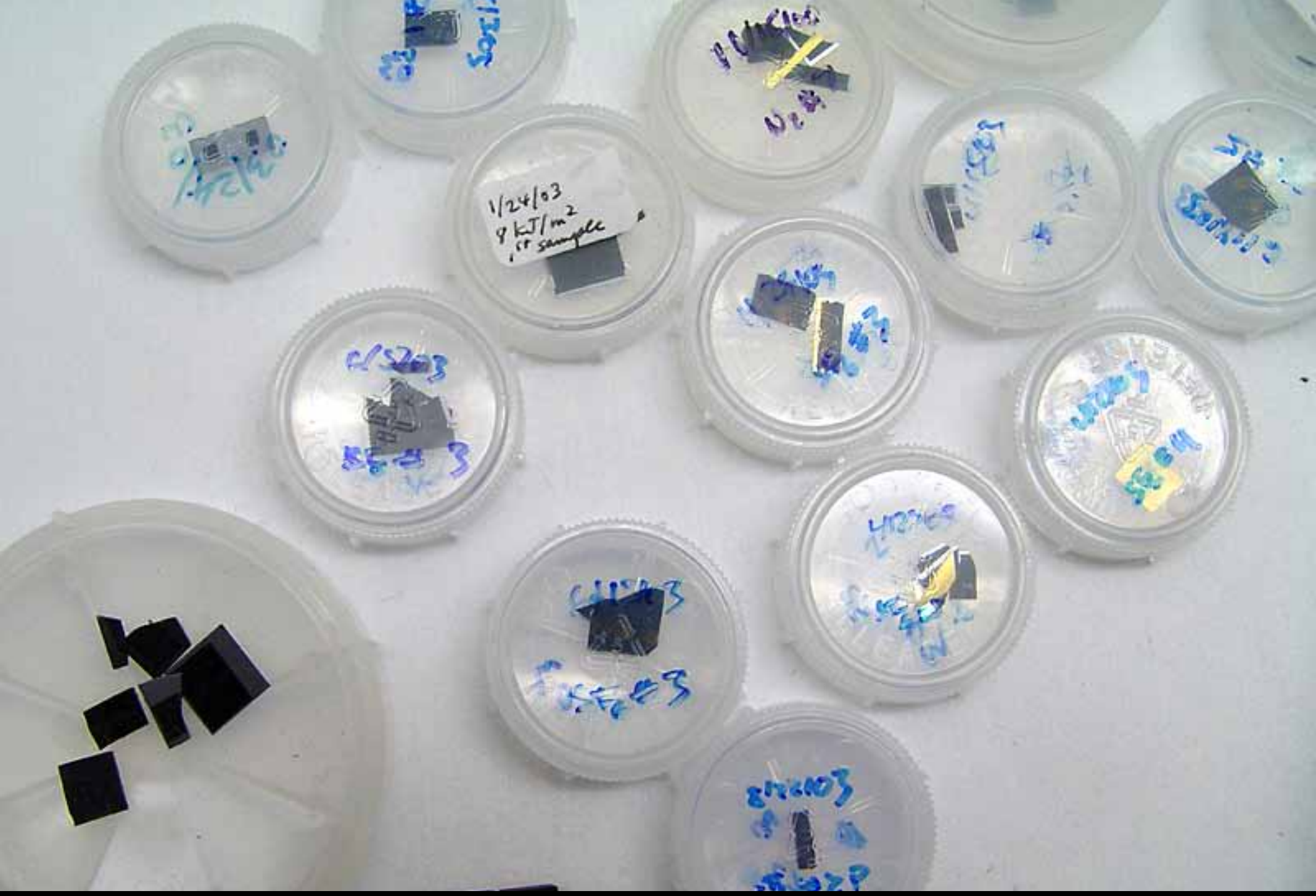


1 Si texturing

2 Si doping

improving watersplitting





1 Si texturing

Ultrafast laser irradiation
creates surface textures
with anti-reflective
and light-trapping properties.

Ultrafast laser irradiation
creates surface textures
with anti-reflective
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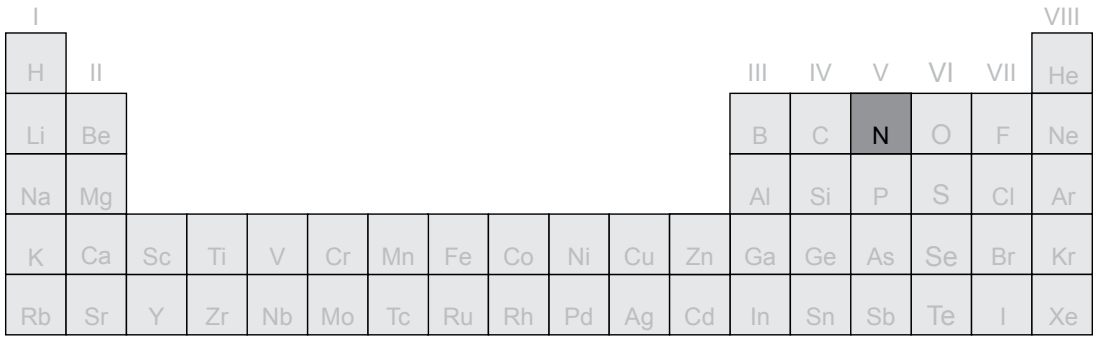
These properties are easily tunable.

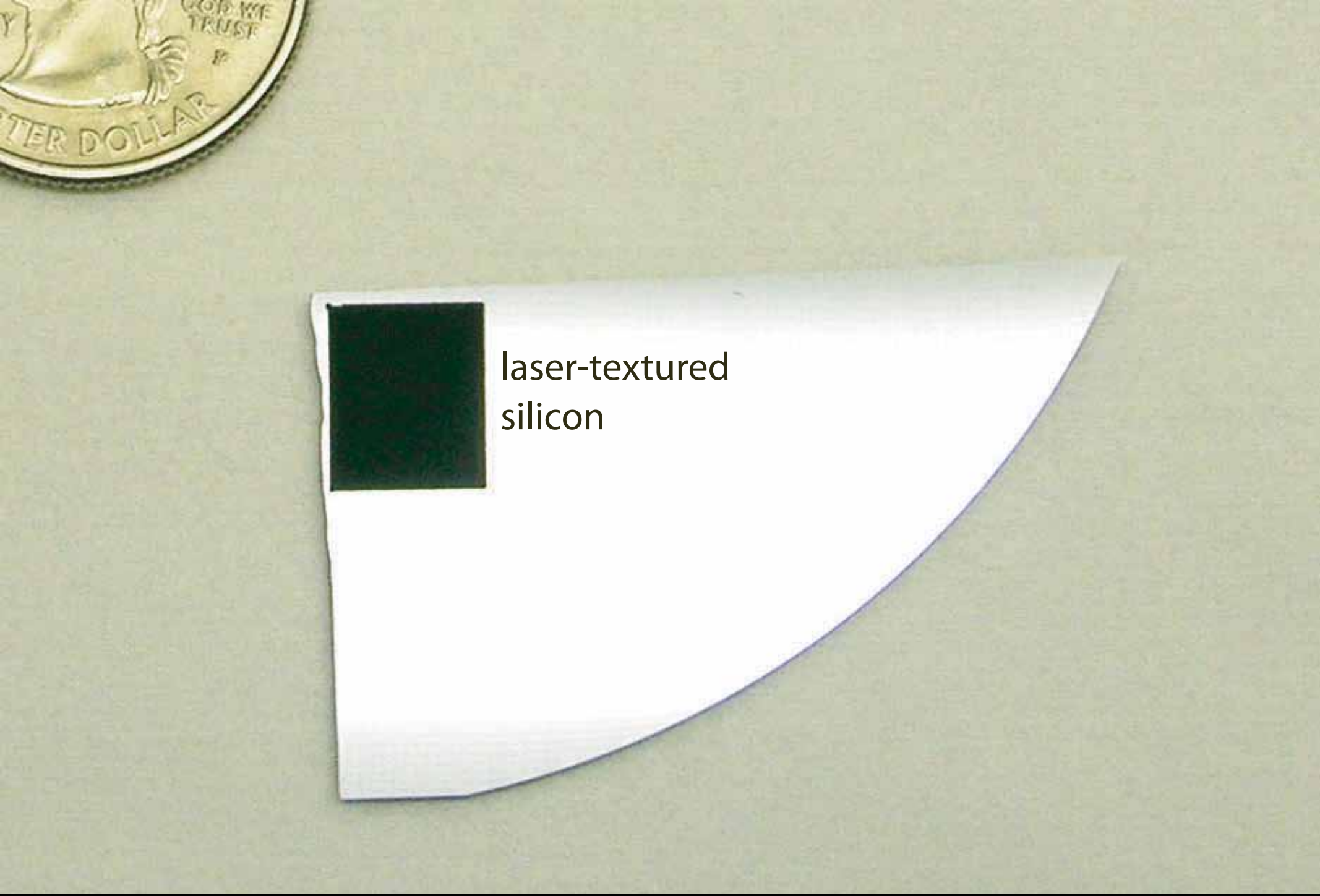
irradiation in N_2 environment

Dopants:



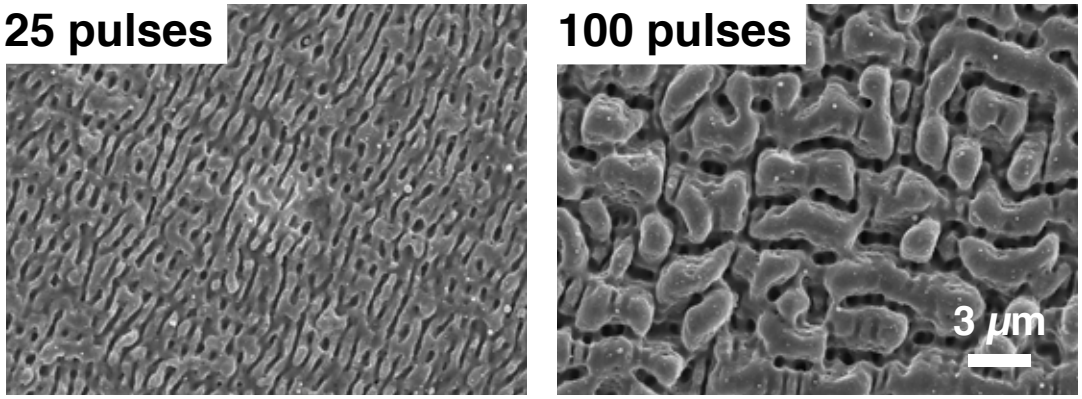
Substrates:

Si



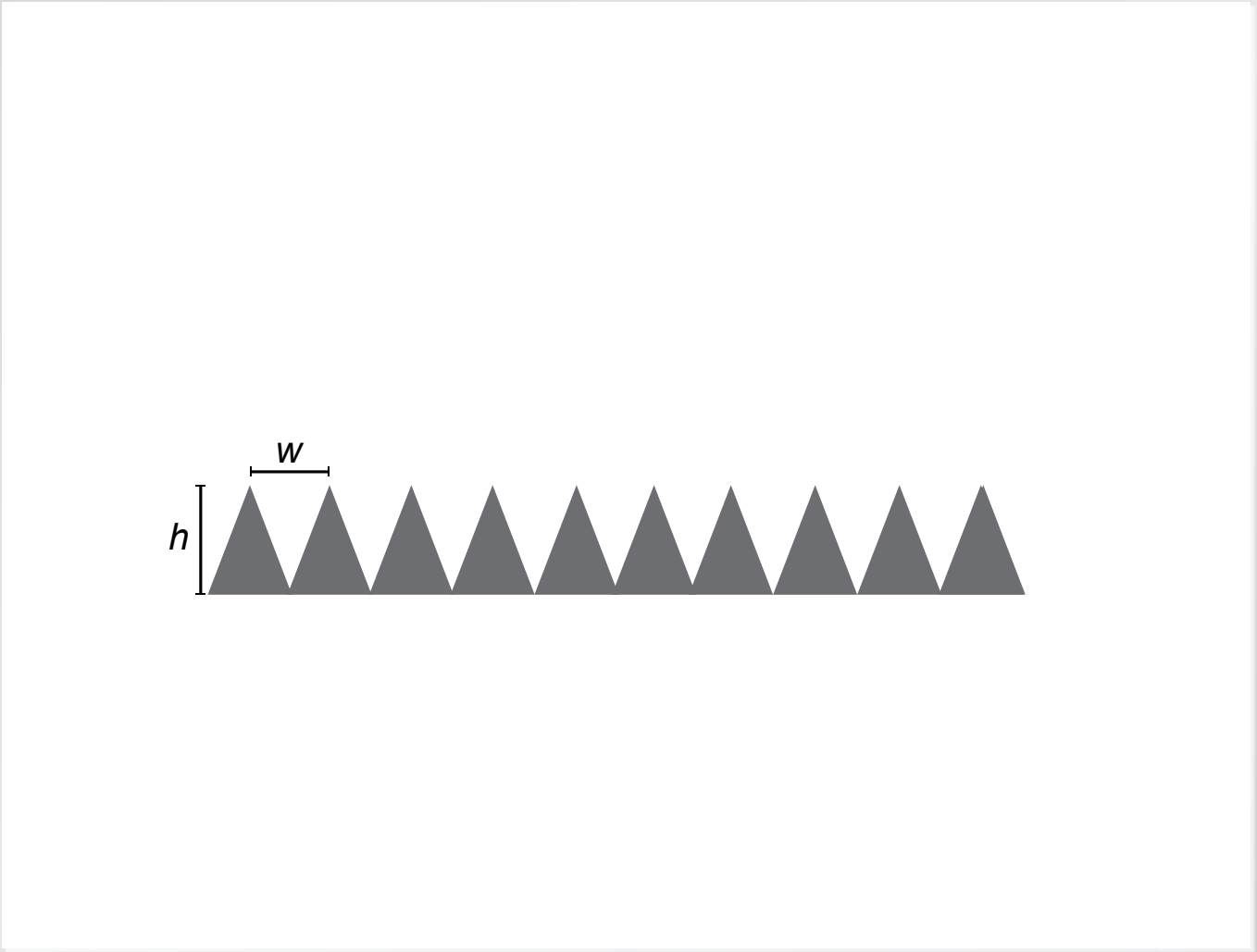
1 Si texturing

additional pulses lead to larger textures



Silicon wafers, 3 kJ/m^2 in N_2

effect of texture depends on size of texture



Sher et al. (in preparation)

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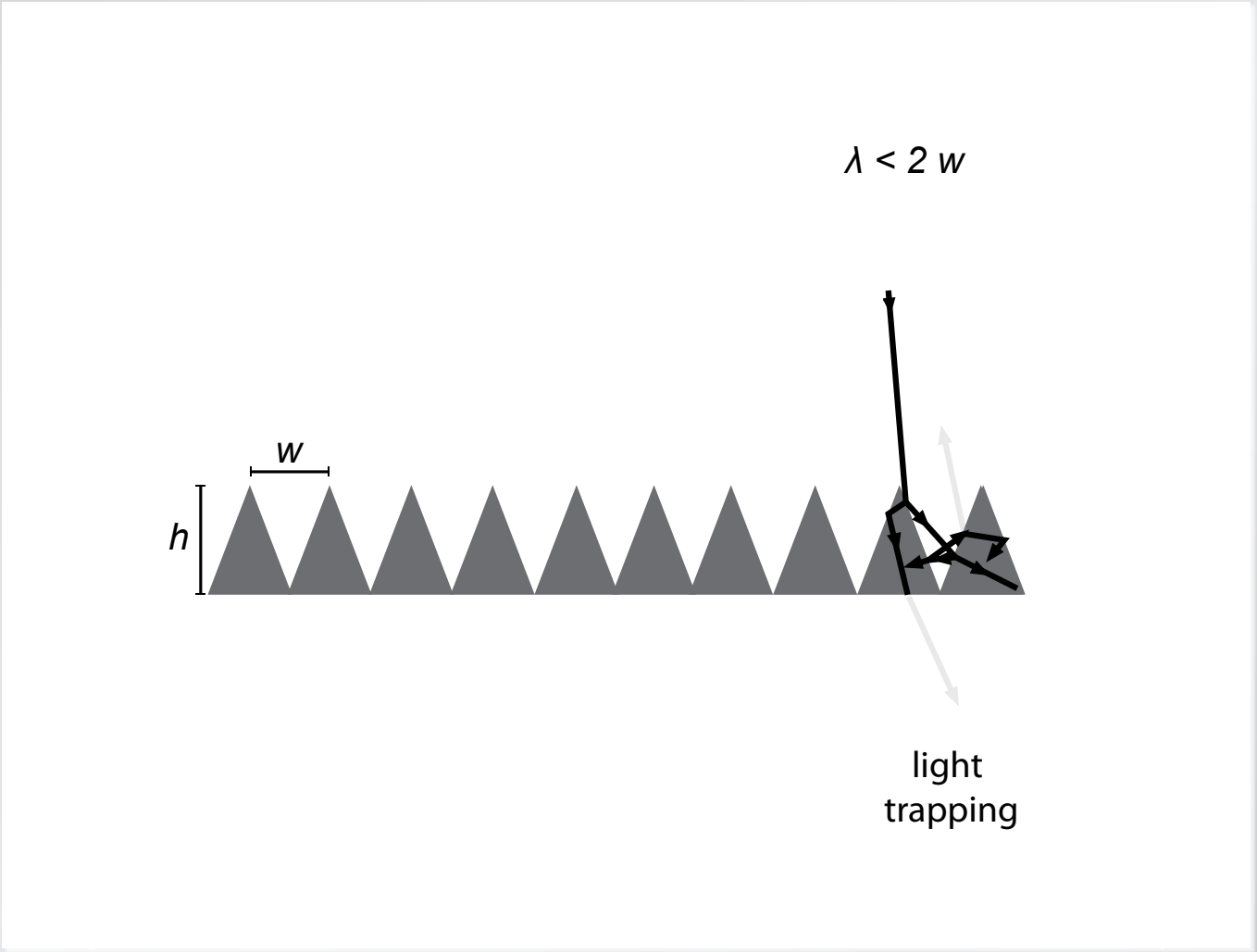

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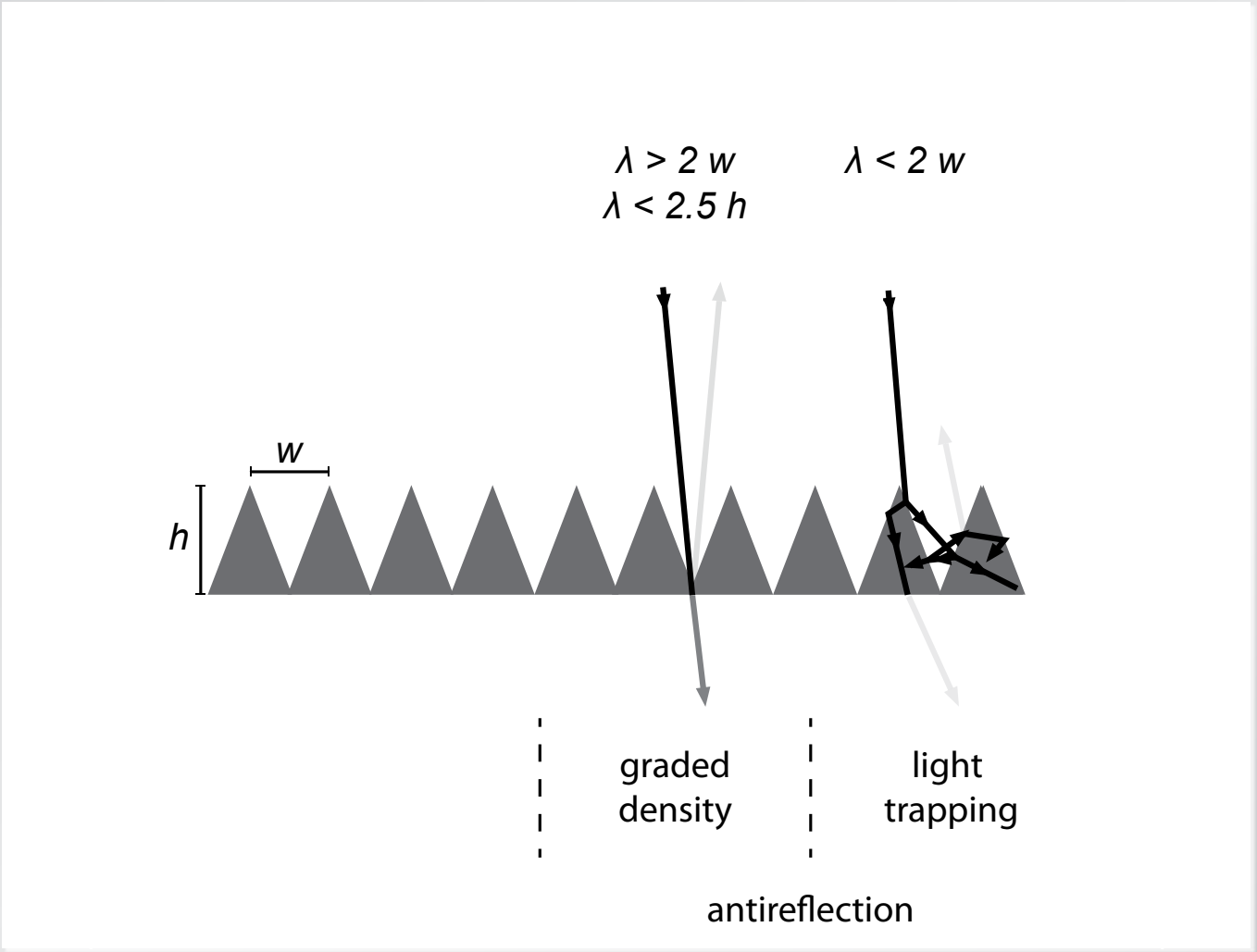

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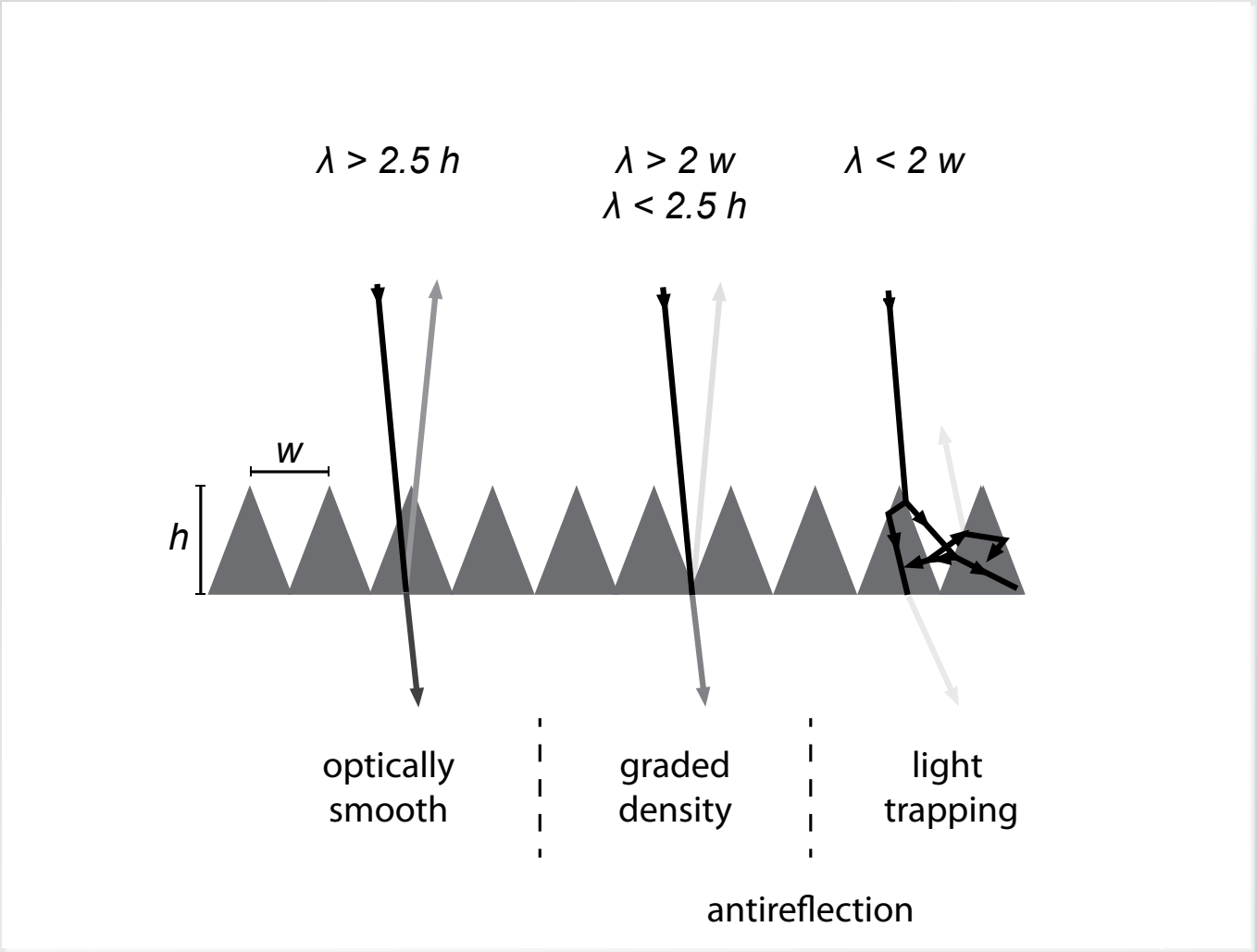

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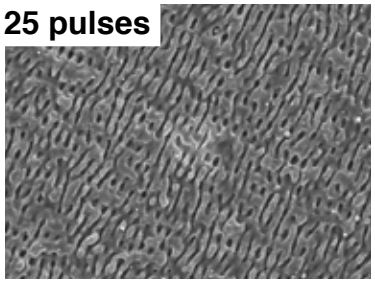
effect of texture depends on size of texture

25 pulses



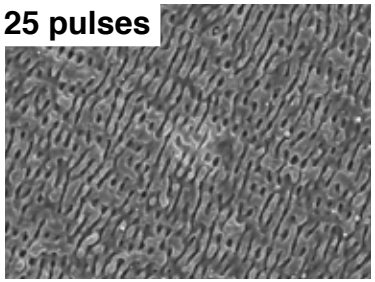
texture size: 600 nm

anti-reflection: $\lambda < 1500$ nm

light-trapping: $\lambda < 1200$ nm up to near-IR

effect of texture depends on size of texture

25 pulses

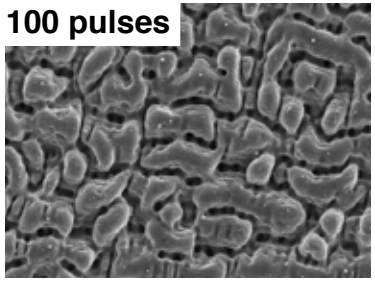


texture size: 600 nm

anti-reflection: $\lambda < 1500$ nm

light-trapping: $\lambda < 1200$ nm — up to near-IR

100 pulses

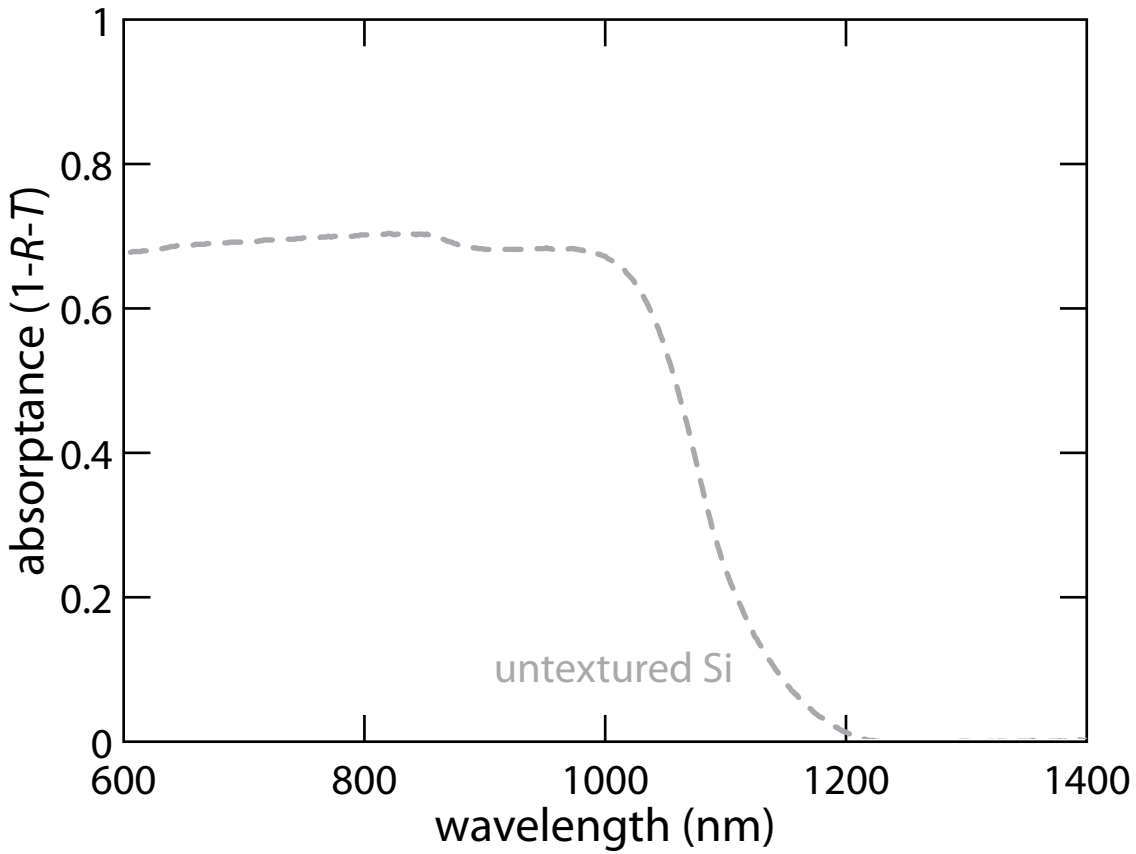


texture size: 3 um

anti-reflection: $\lambda < 7.5$ um

light-trapping: $\lambda < 6$ um — up to mid-IR

surface texturing gives enhanced absorptance



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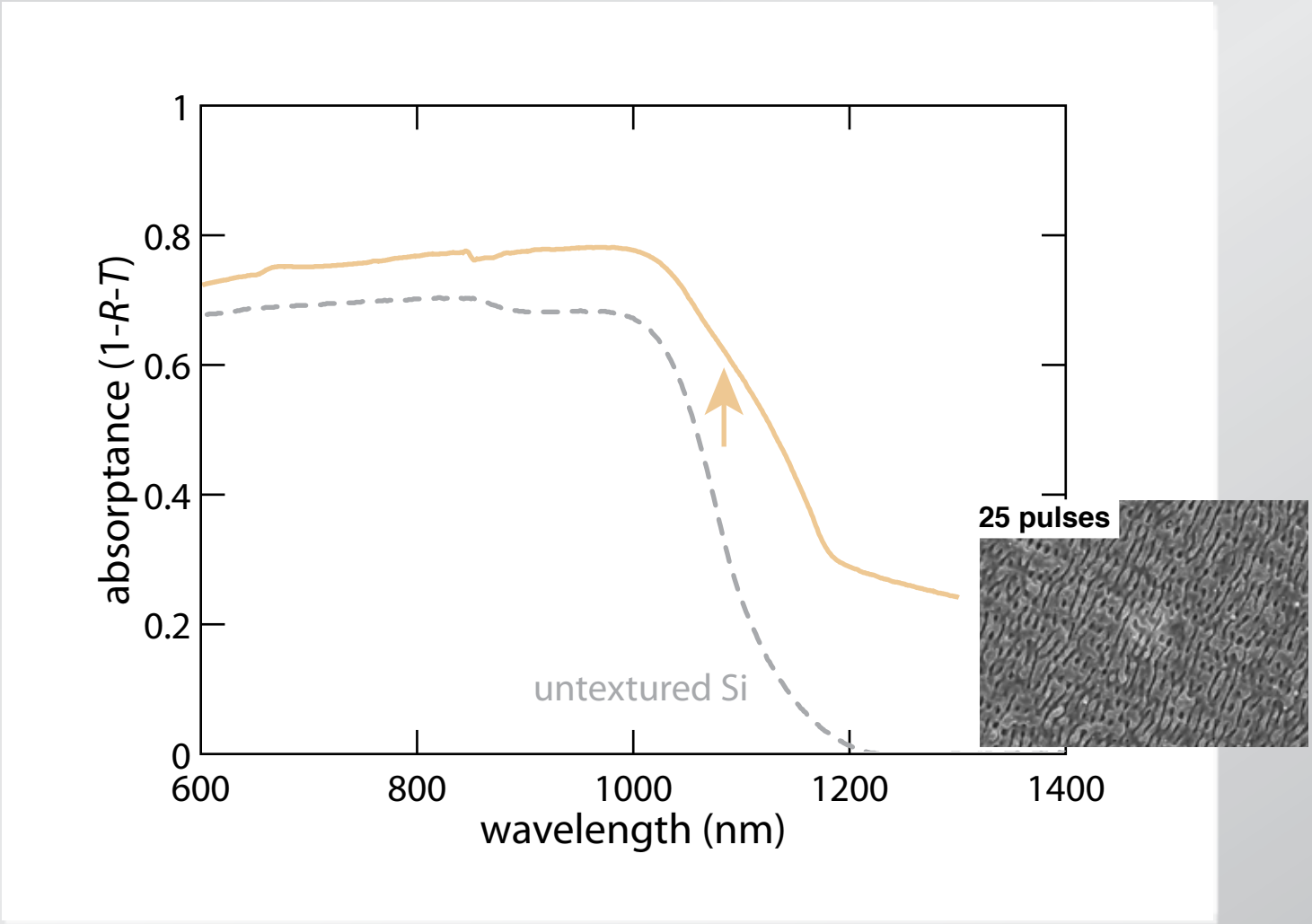

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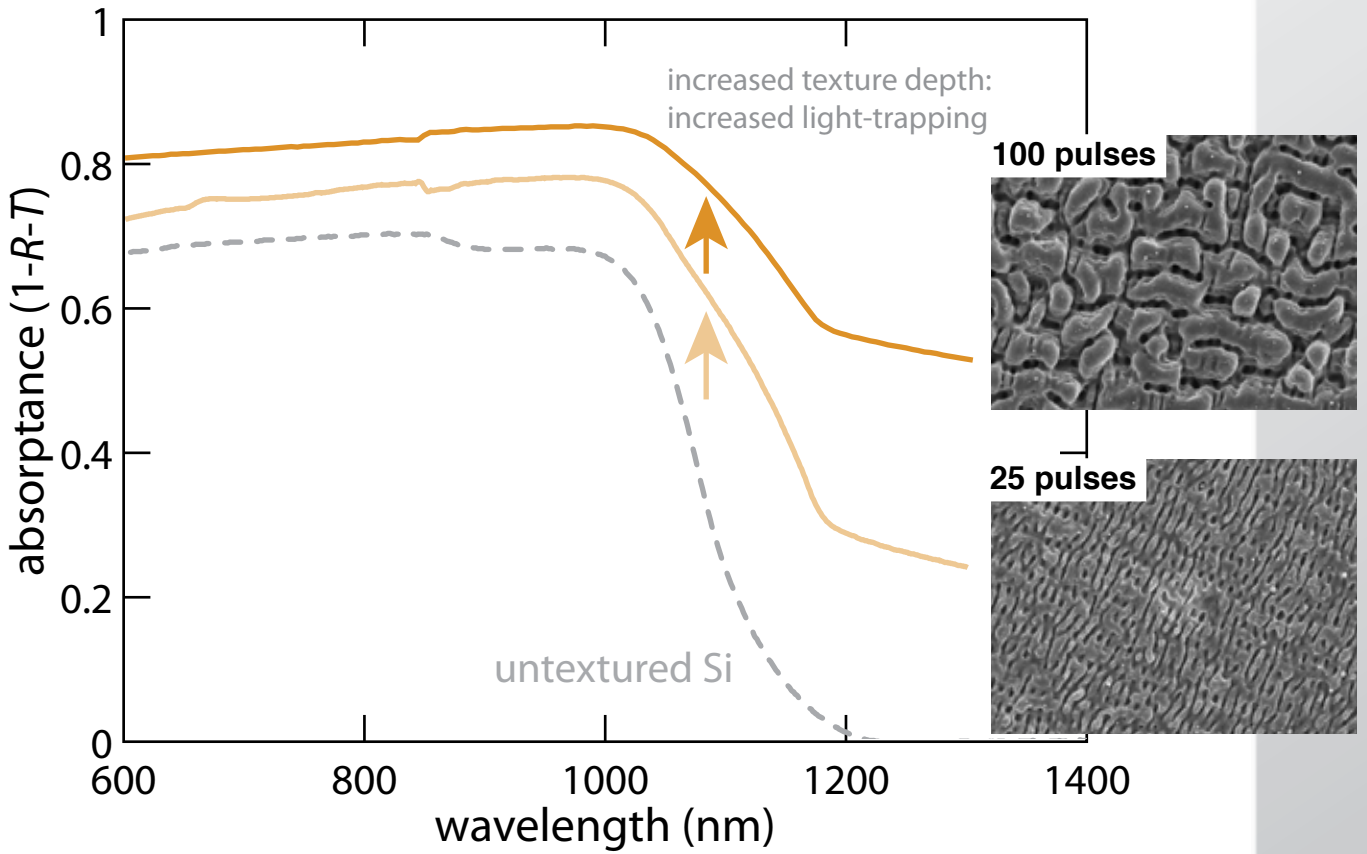

Using ultrafast laser processing,
texture sizes are easily tunable.

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Challenge:
Independent control of texture width and height.

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texture sizes are easily tunable.

Challenge:
Independent control of texture width and height.

Bigger challenge:
Controlling laser-induced damage.

1 Si texturing

2 Si doping

Hyperdoping with deep-level states
produces a dopant band
and infrared absorption.

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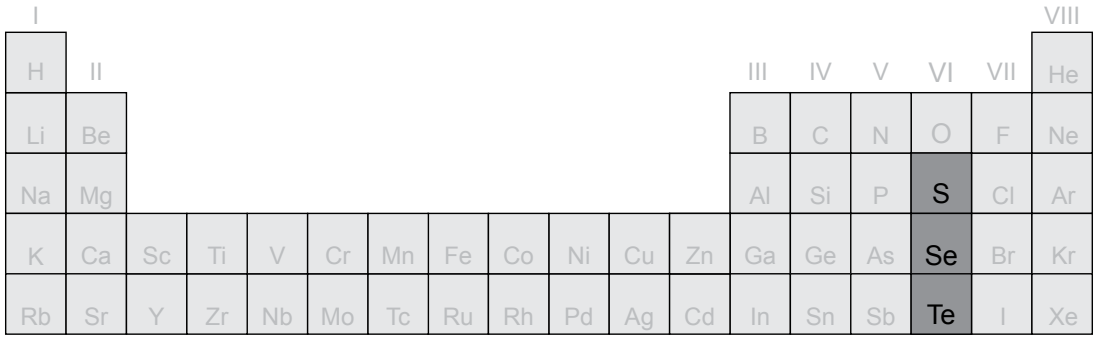
and infrared absorption.

Dopant band can be tuned
with thermal treatments.

we dope silicon with heavy chalcogens

Dopants:



Substrates:

Si

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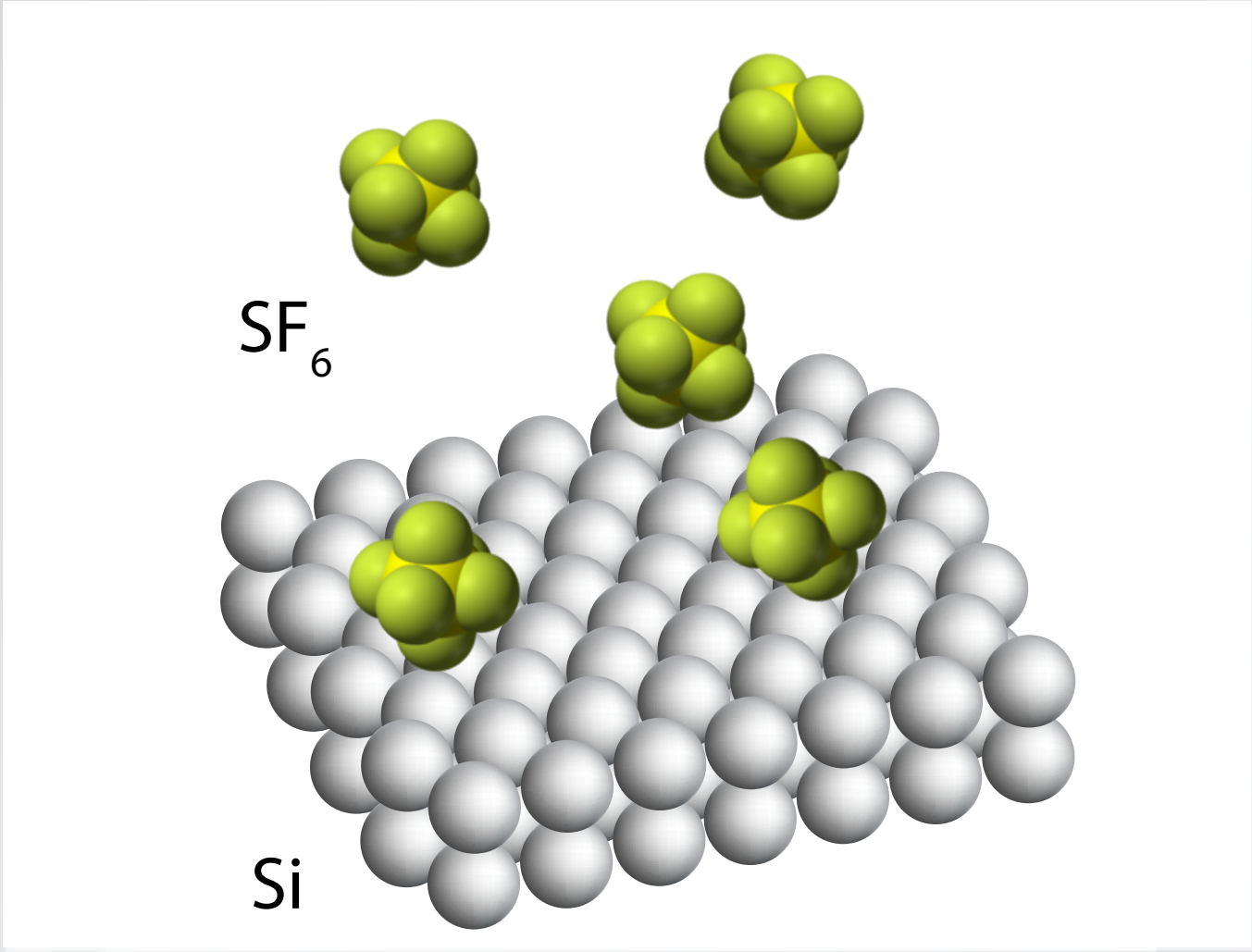
2 Si doping



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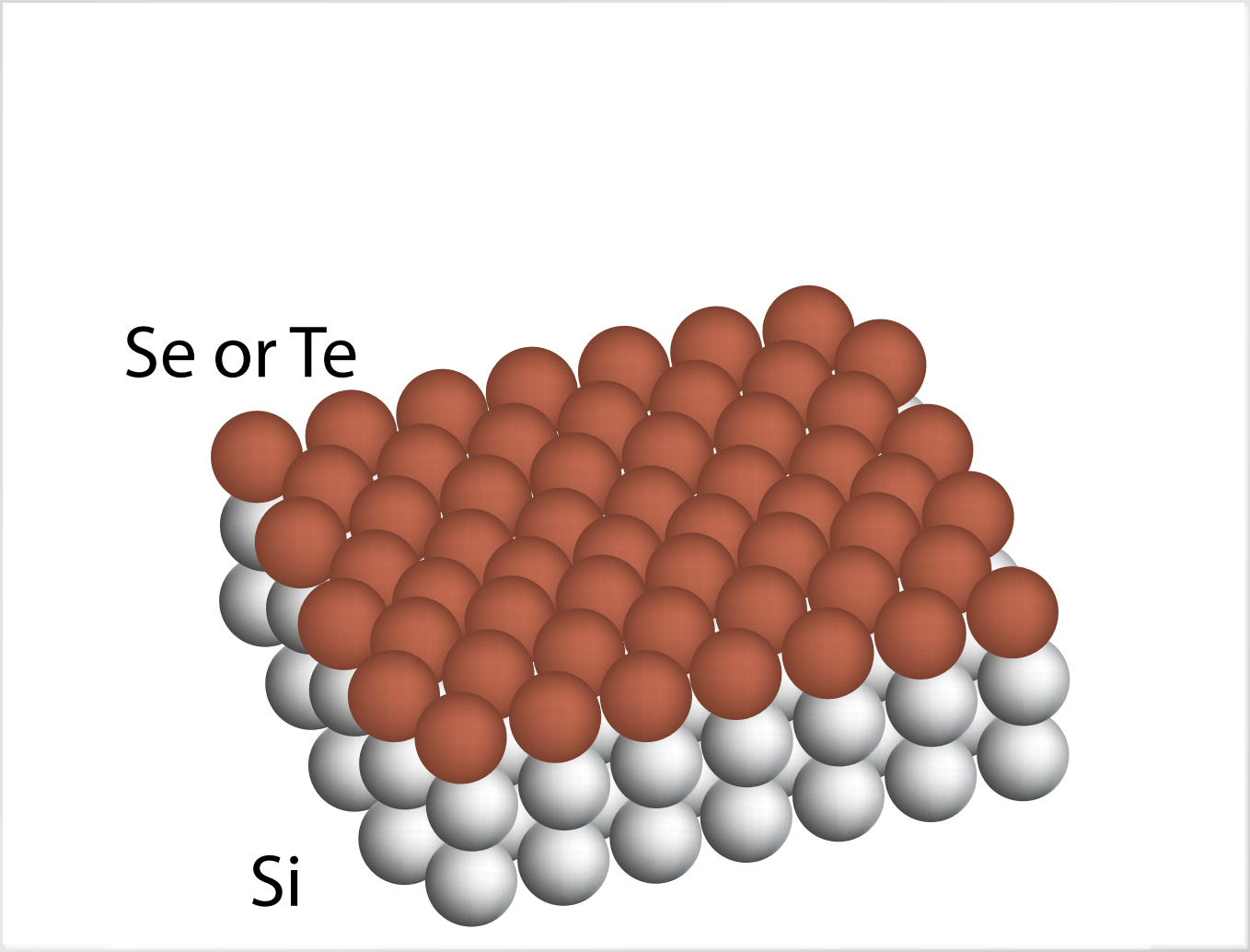
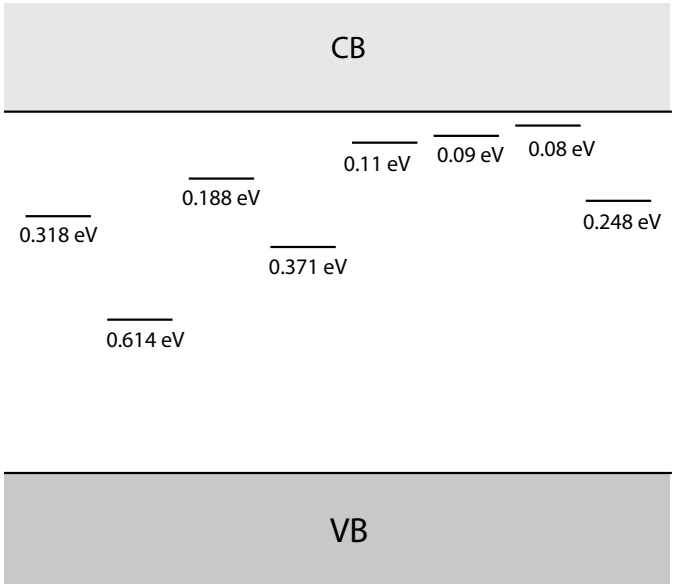


1 Si texturing

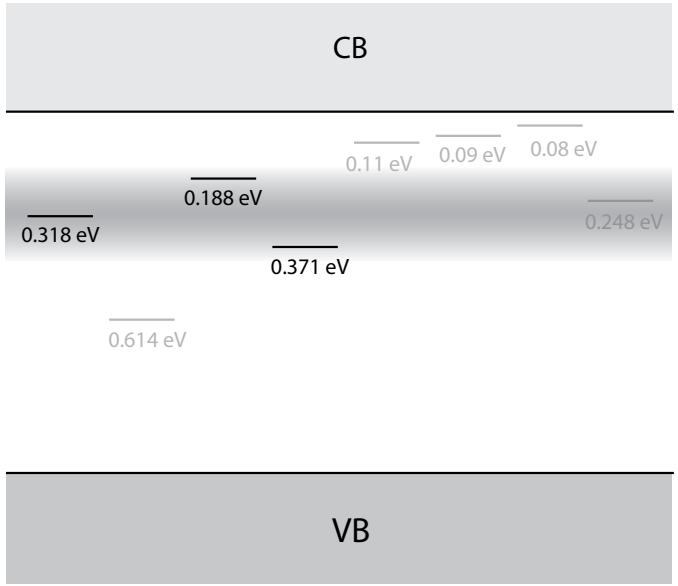
2 Si doping

equilibrium doping leads to isolated defects



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

hyperdoping leads to an extended band



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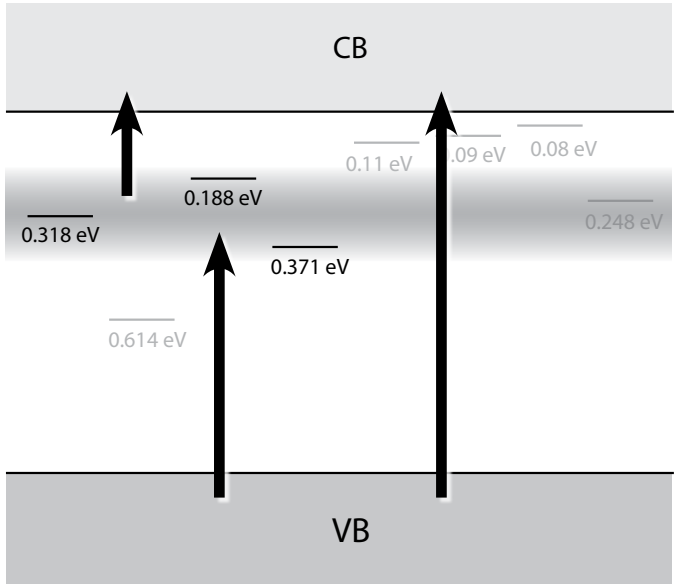

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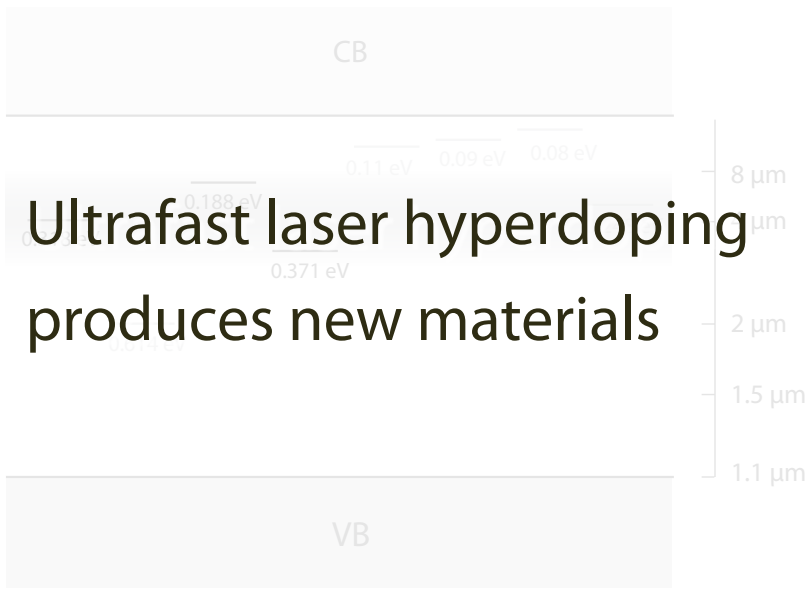
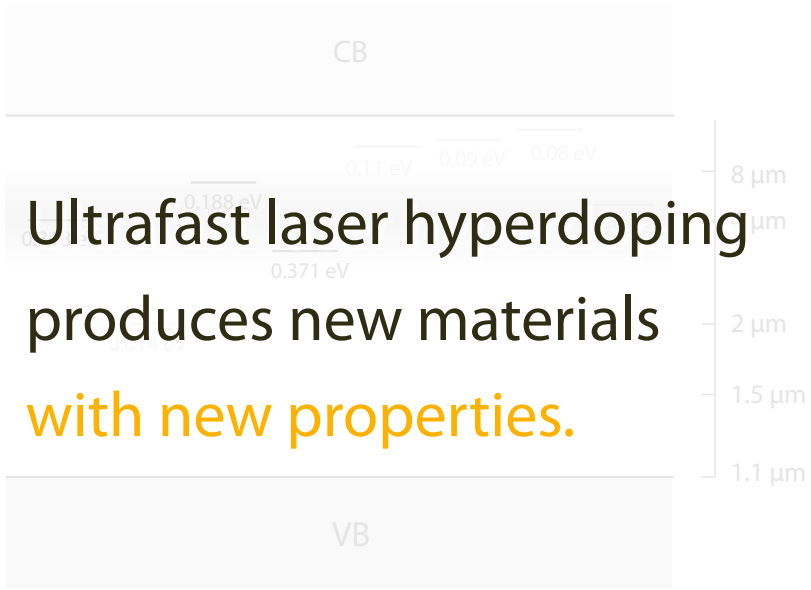


Ultrafast laser hyperdoping produces new materials

1 Si texturing

2 Si doping

hyperdoping leads to an extended band



Ultrafast laser hyperdoping produces new materials with new properties.

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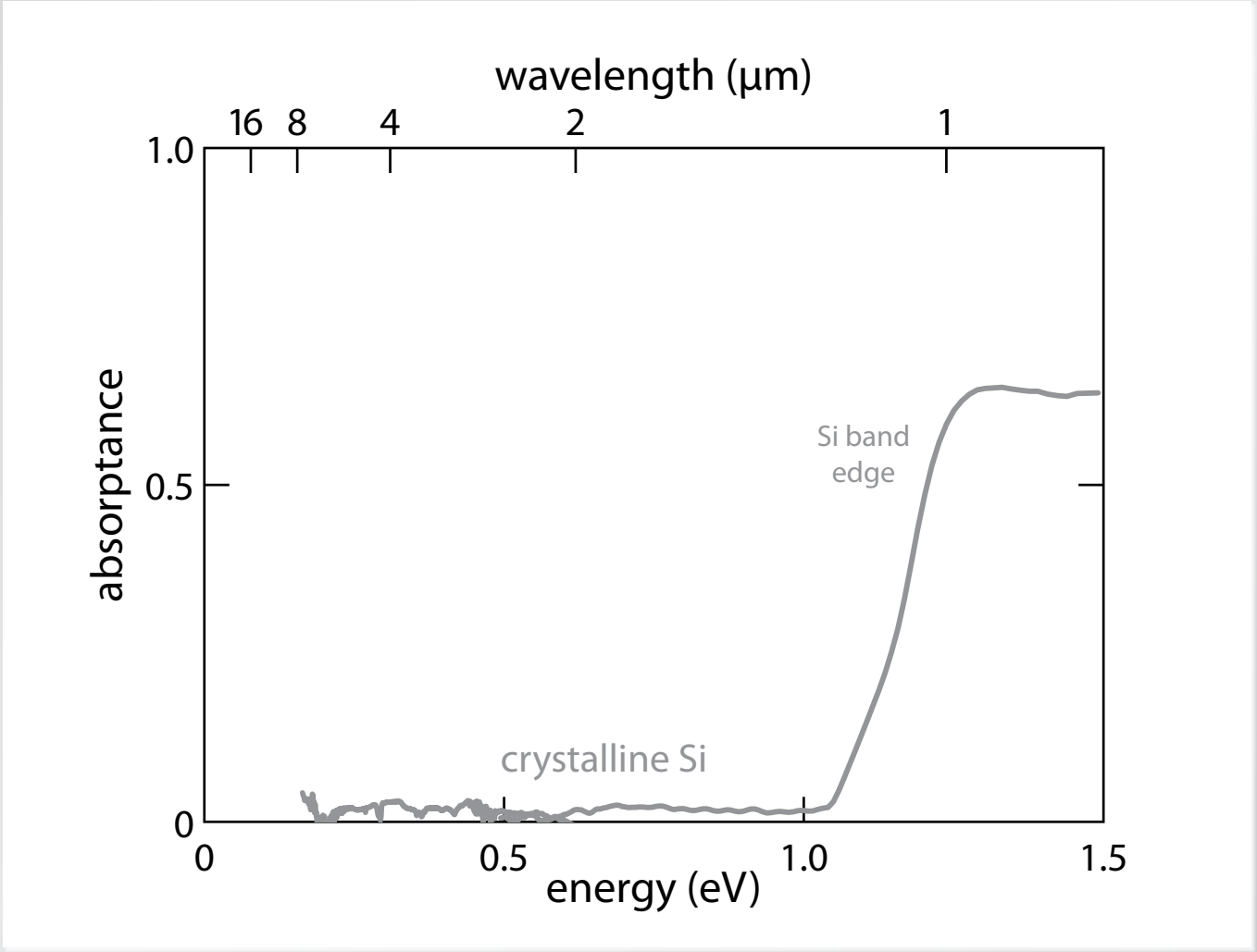
2 Si doping

chalcogen-hyperdoped silicon absorbs in the infrared



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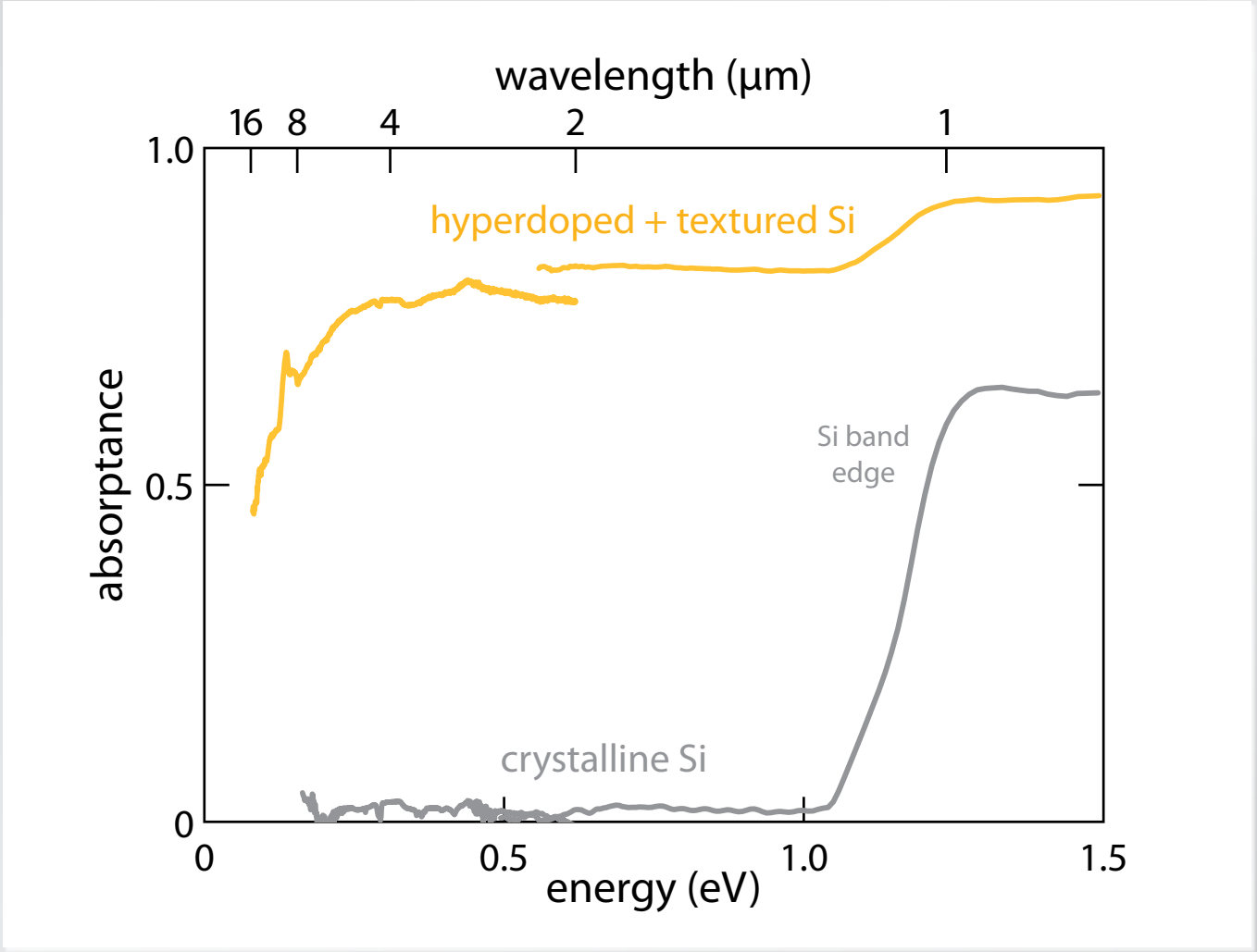

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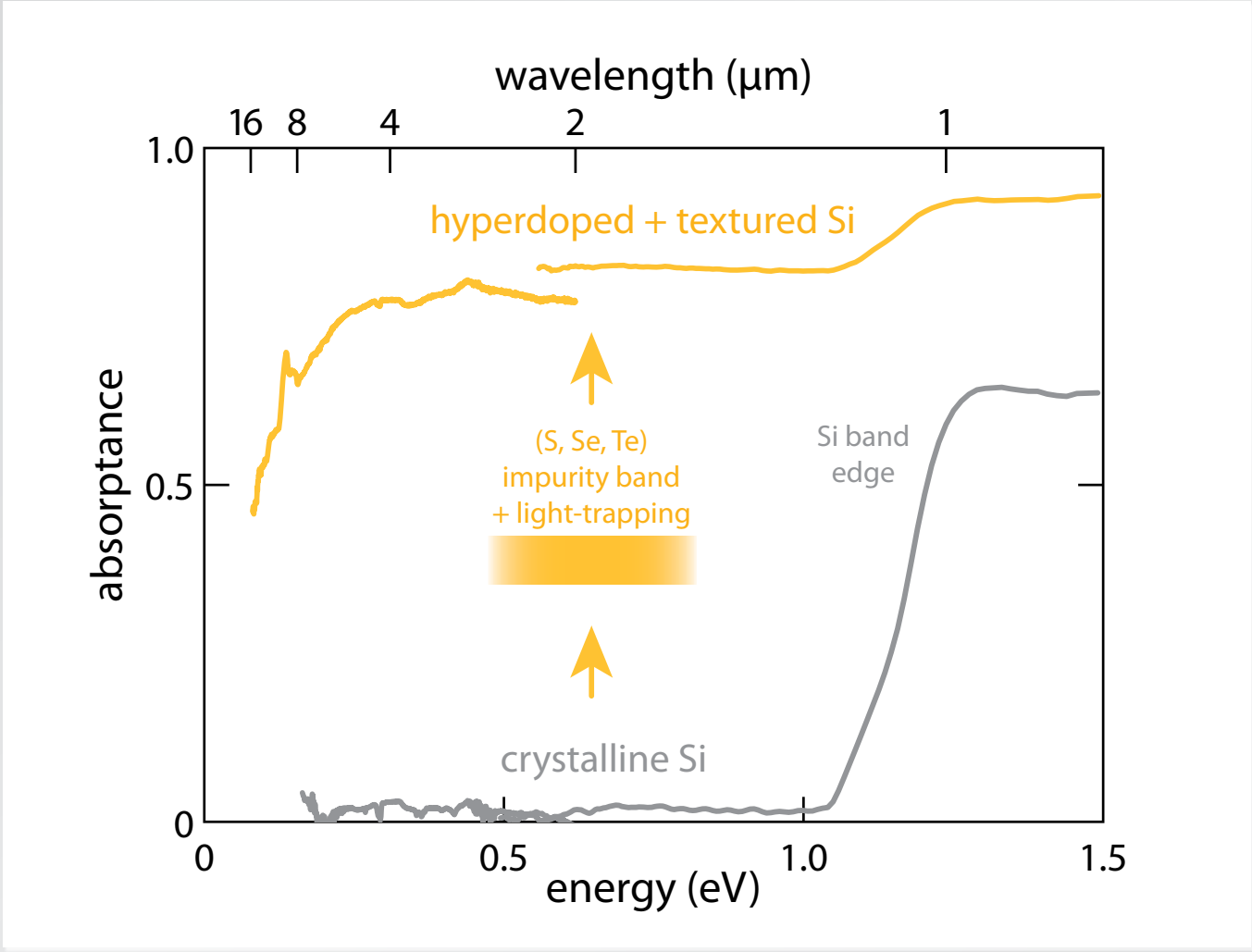

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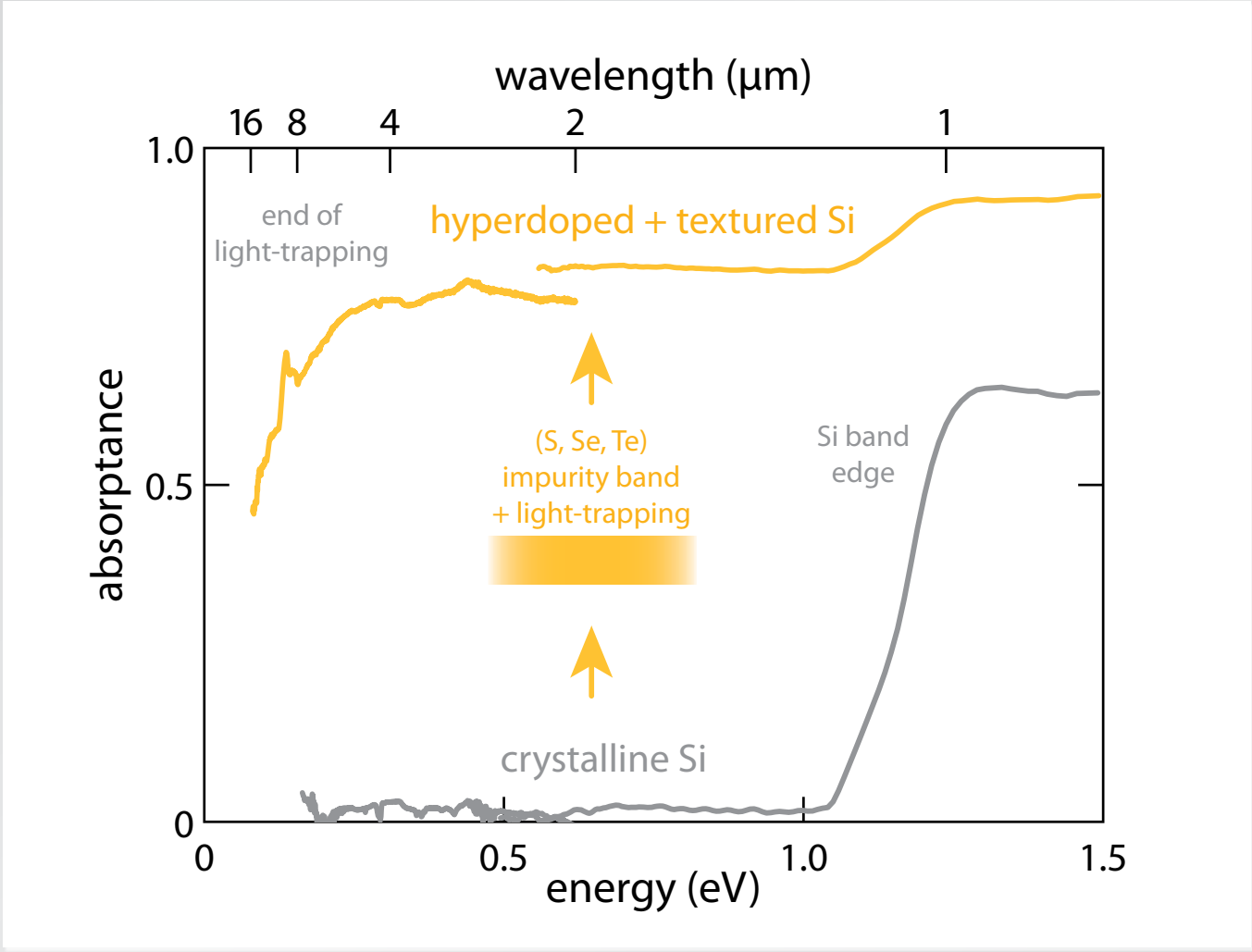

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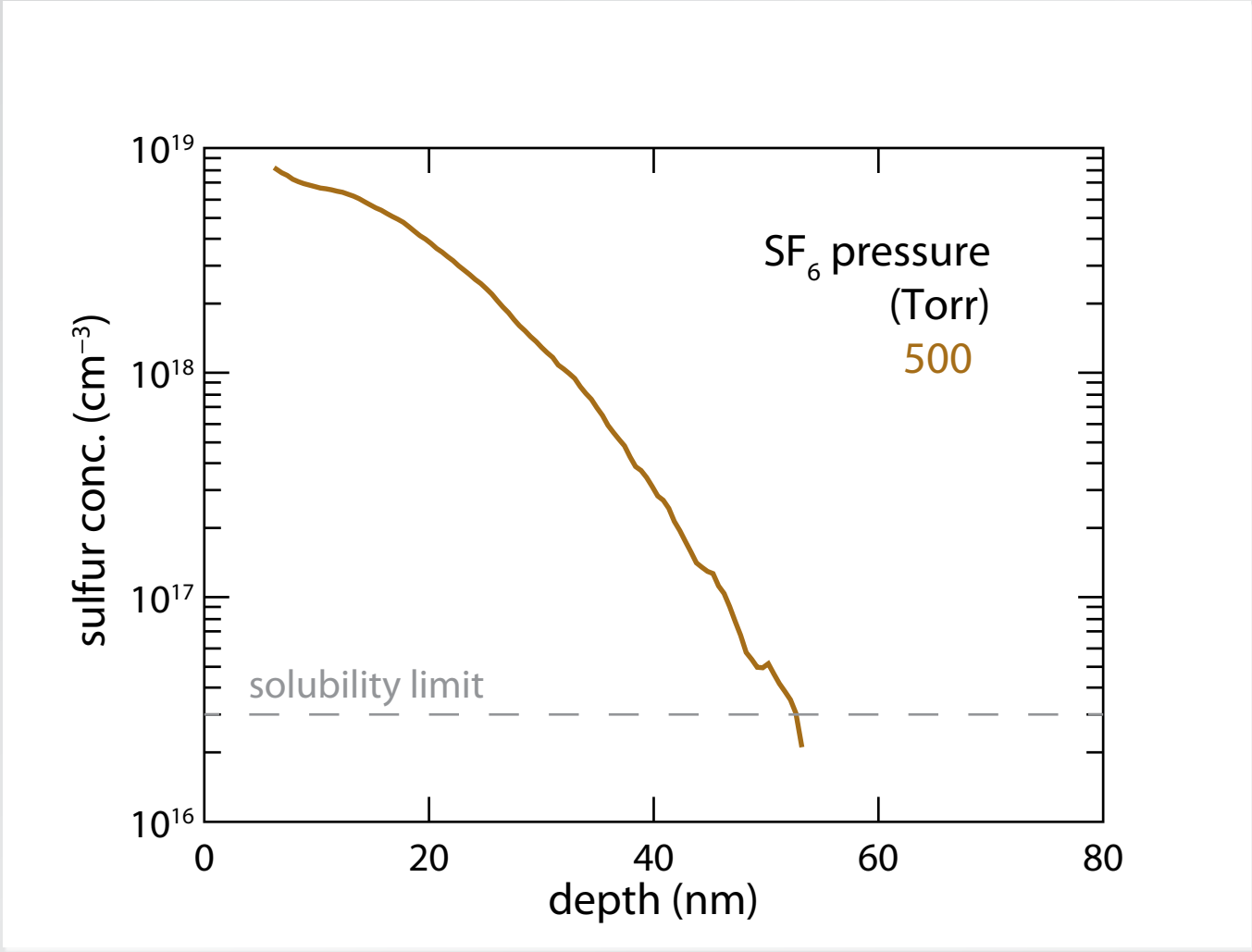
2 Si doping

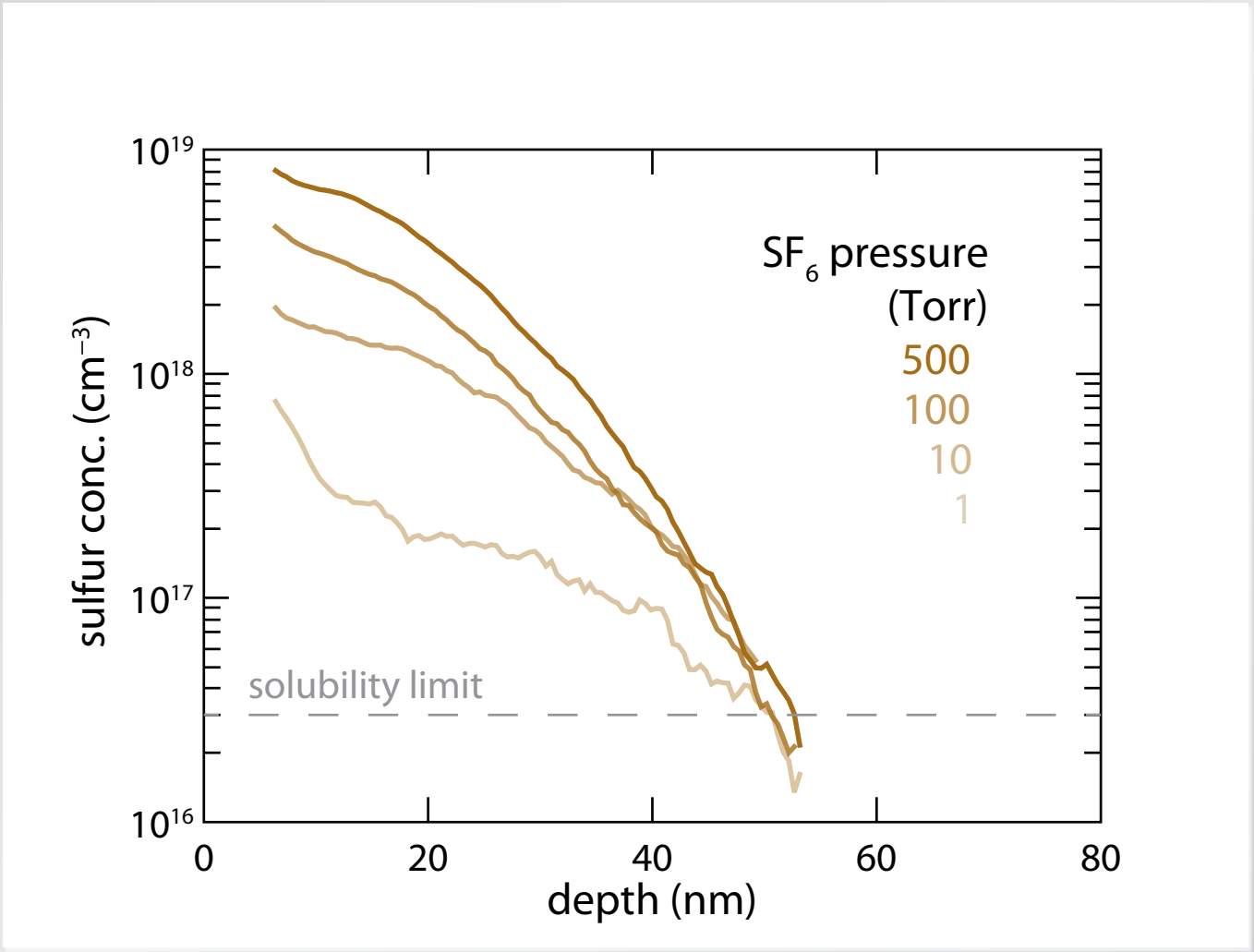
silicon is doped beyond its solubility limit



1 Si texturing

2 Si doping

dopant concentration controlled with gas pressure



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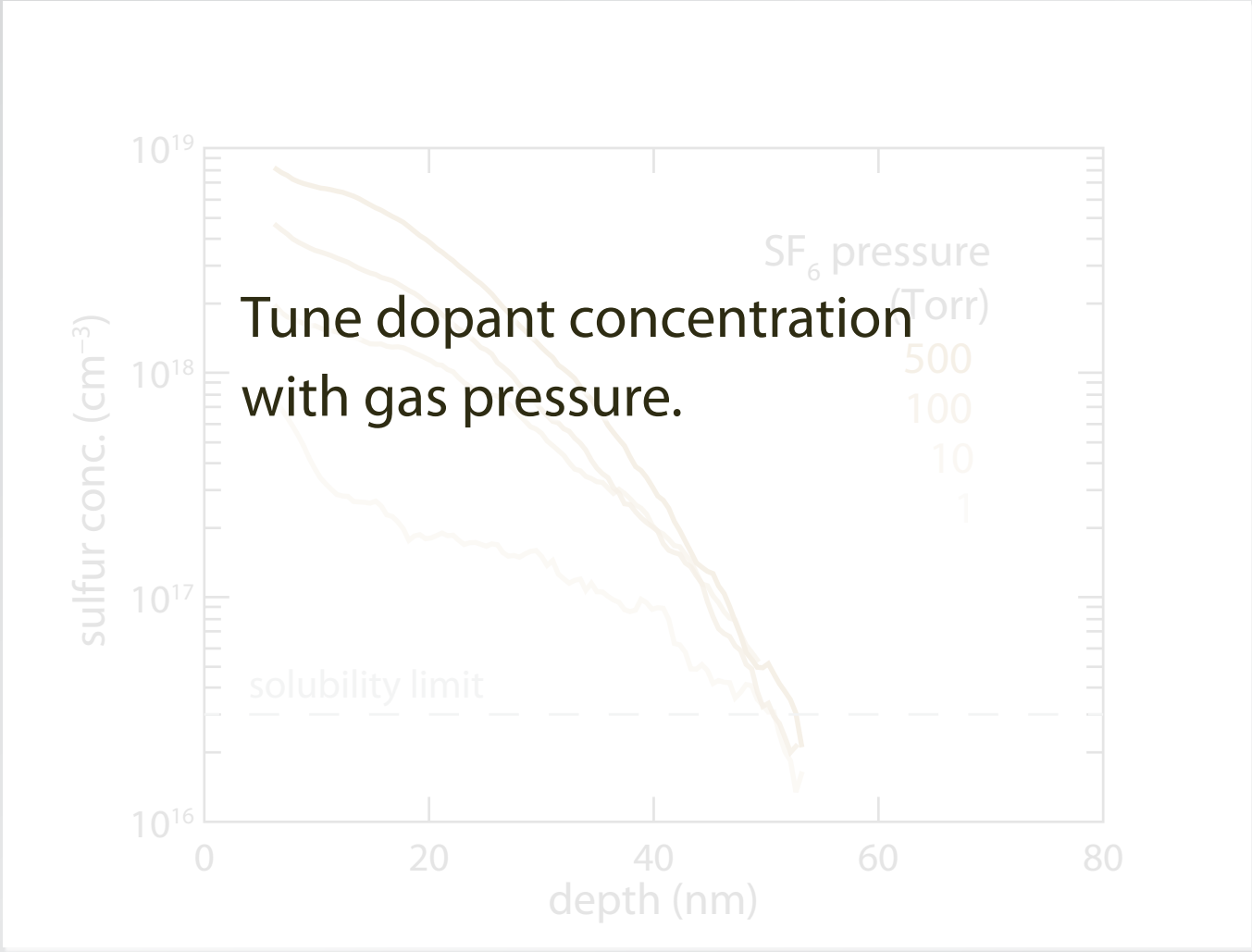

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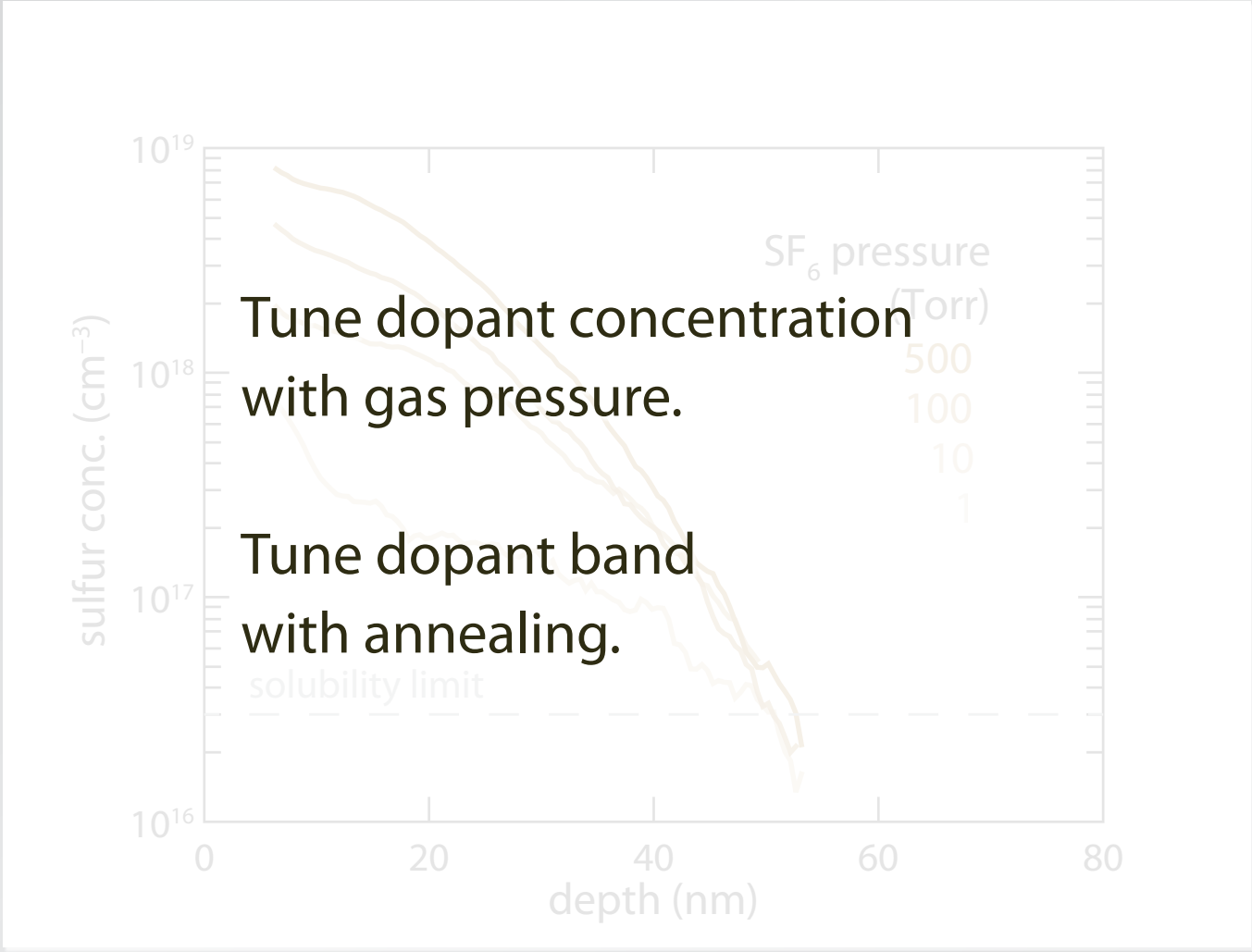
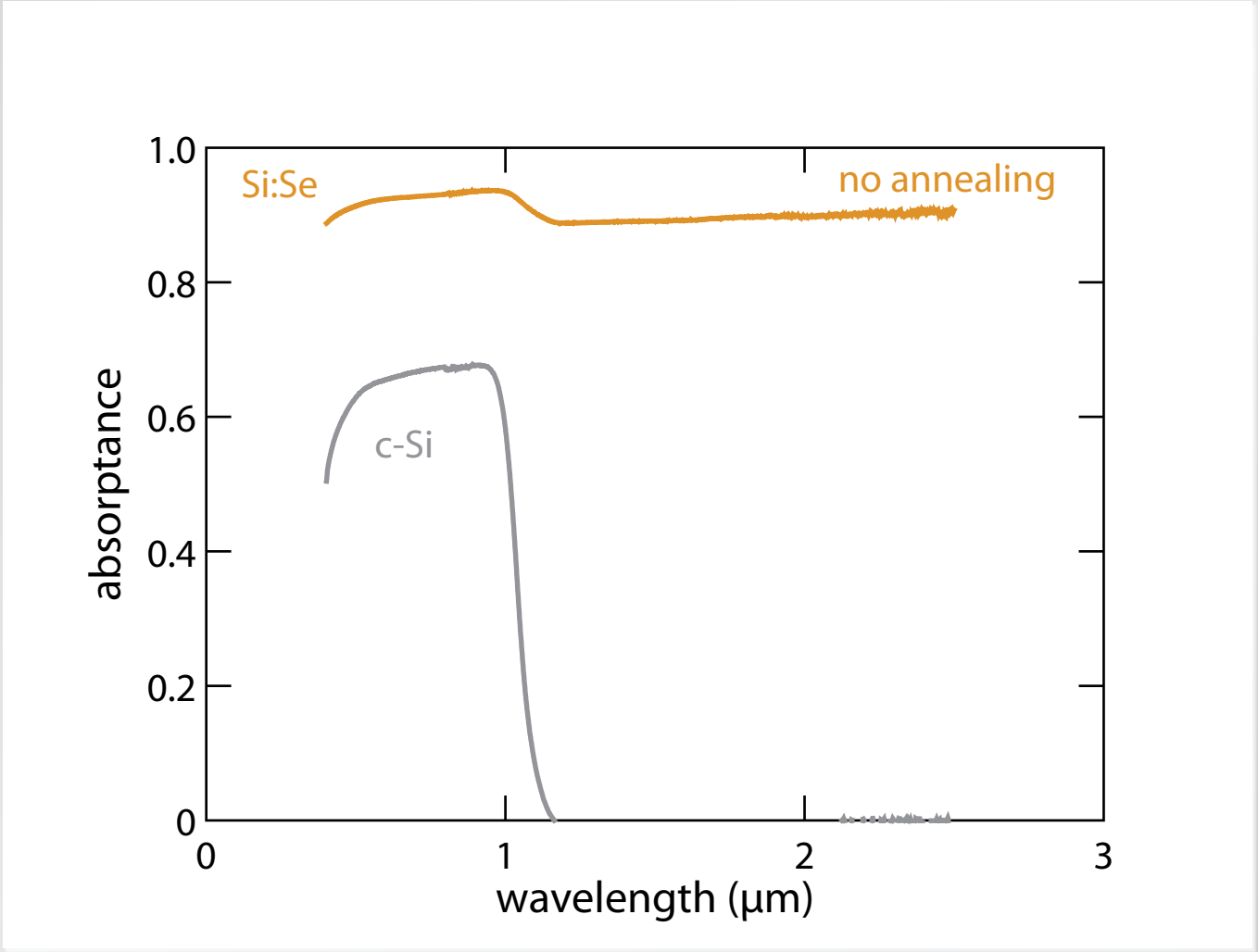


annealing causes deactivation of infrared absorption



Tull et al., Appl. Phys. A (2009)

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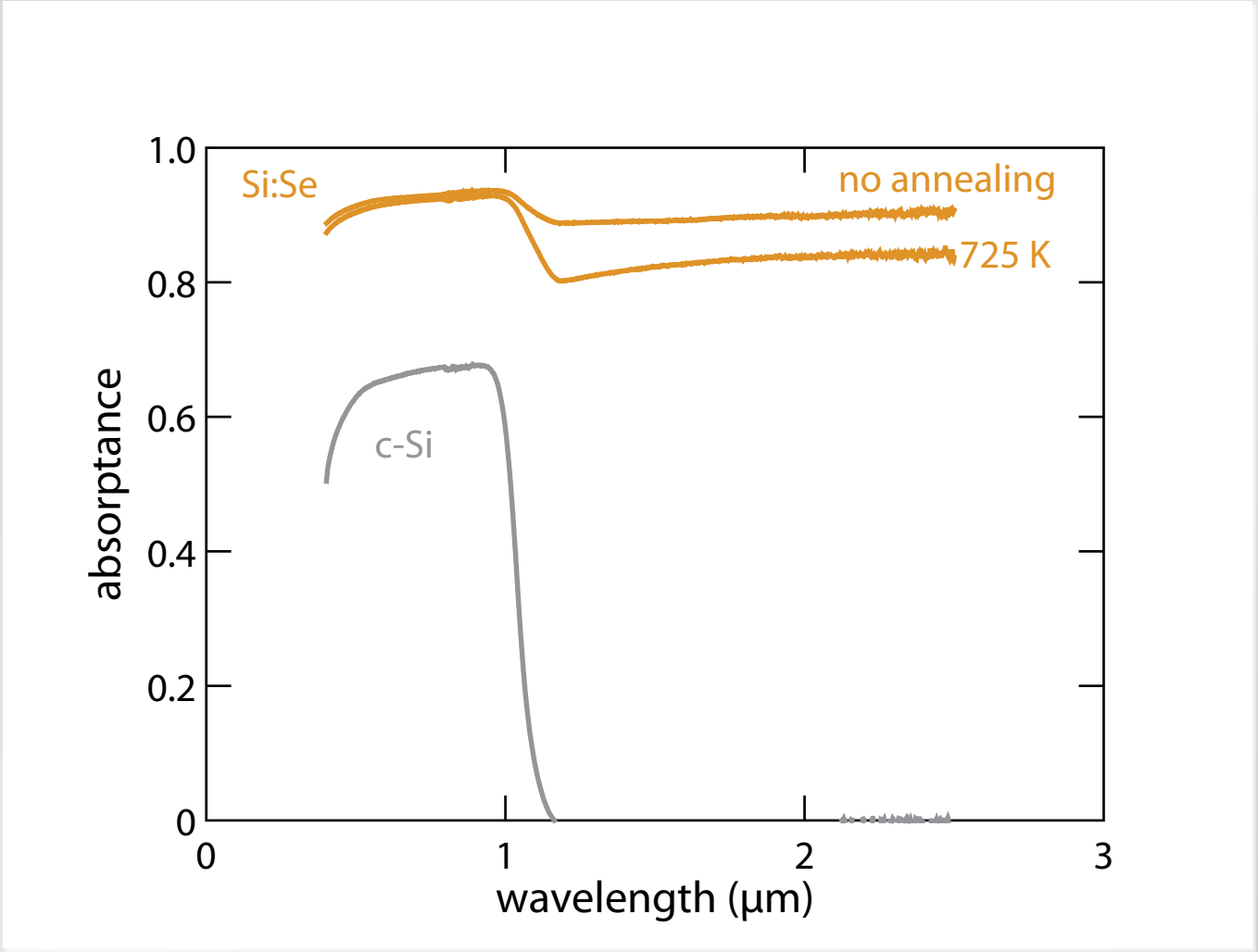

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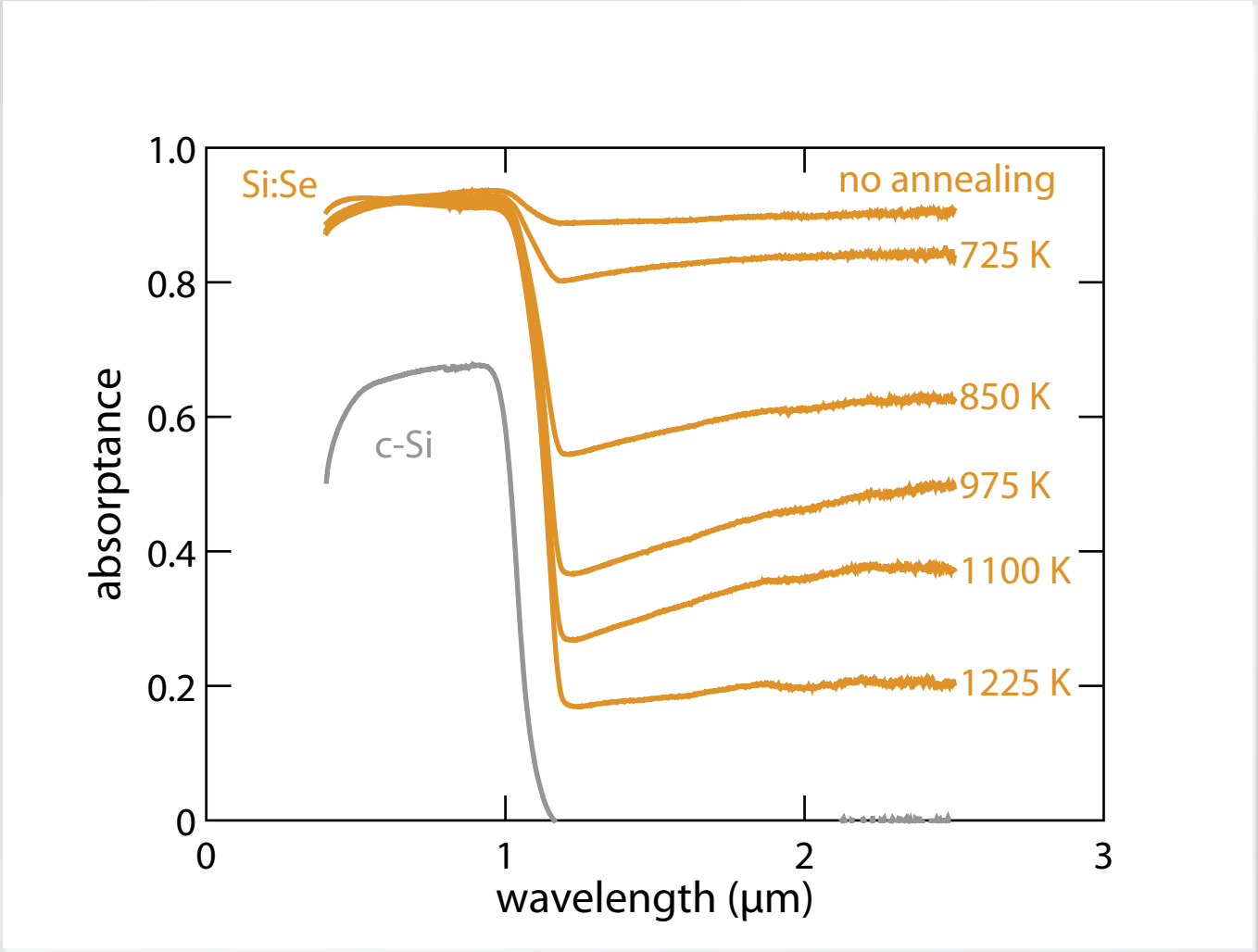

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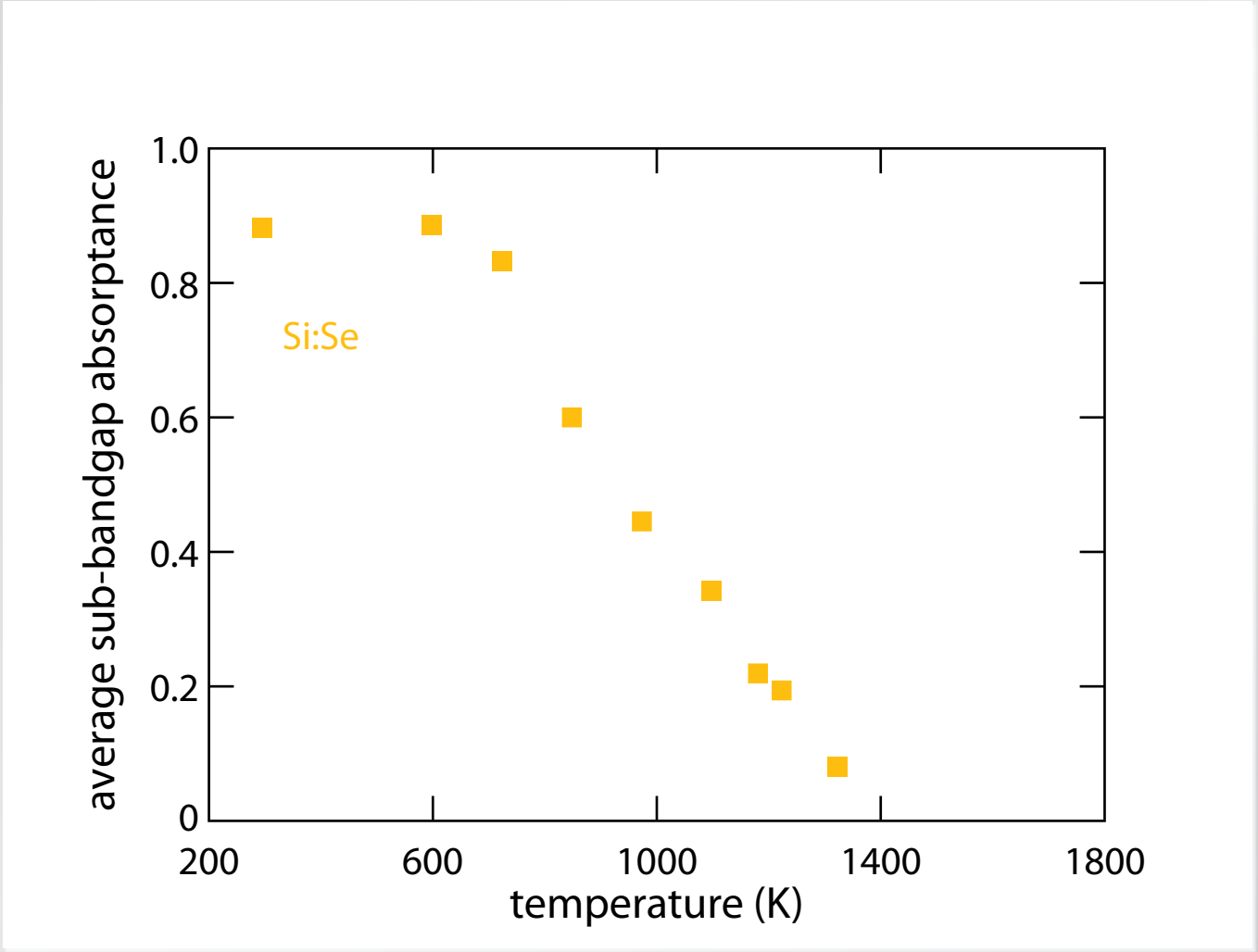
1 Si texturing **2 Si doping**

annealing causes deactivation of infrared absorption



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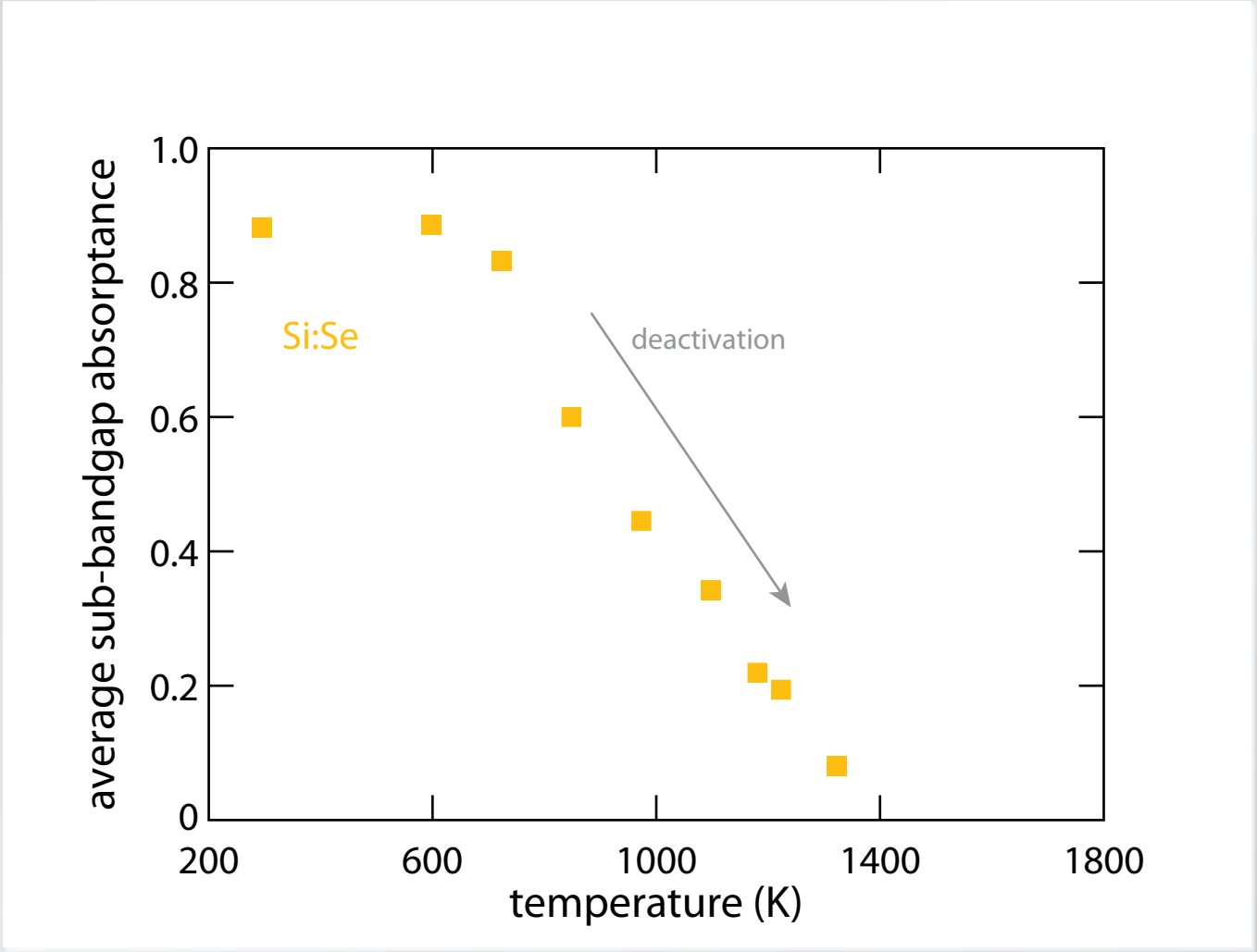

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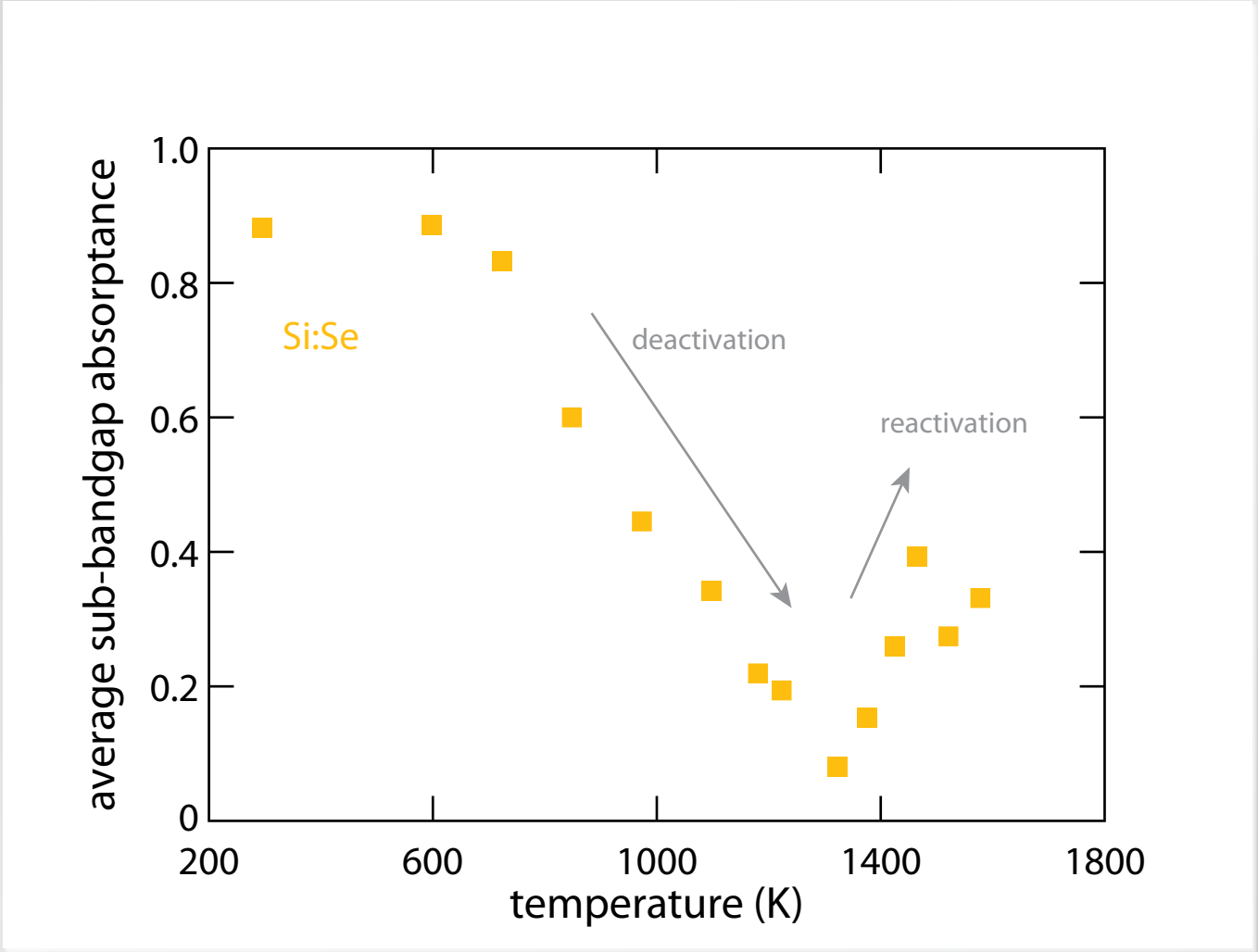
high-temp. annealing causes reactivation of infrared absorption



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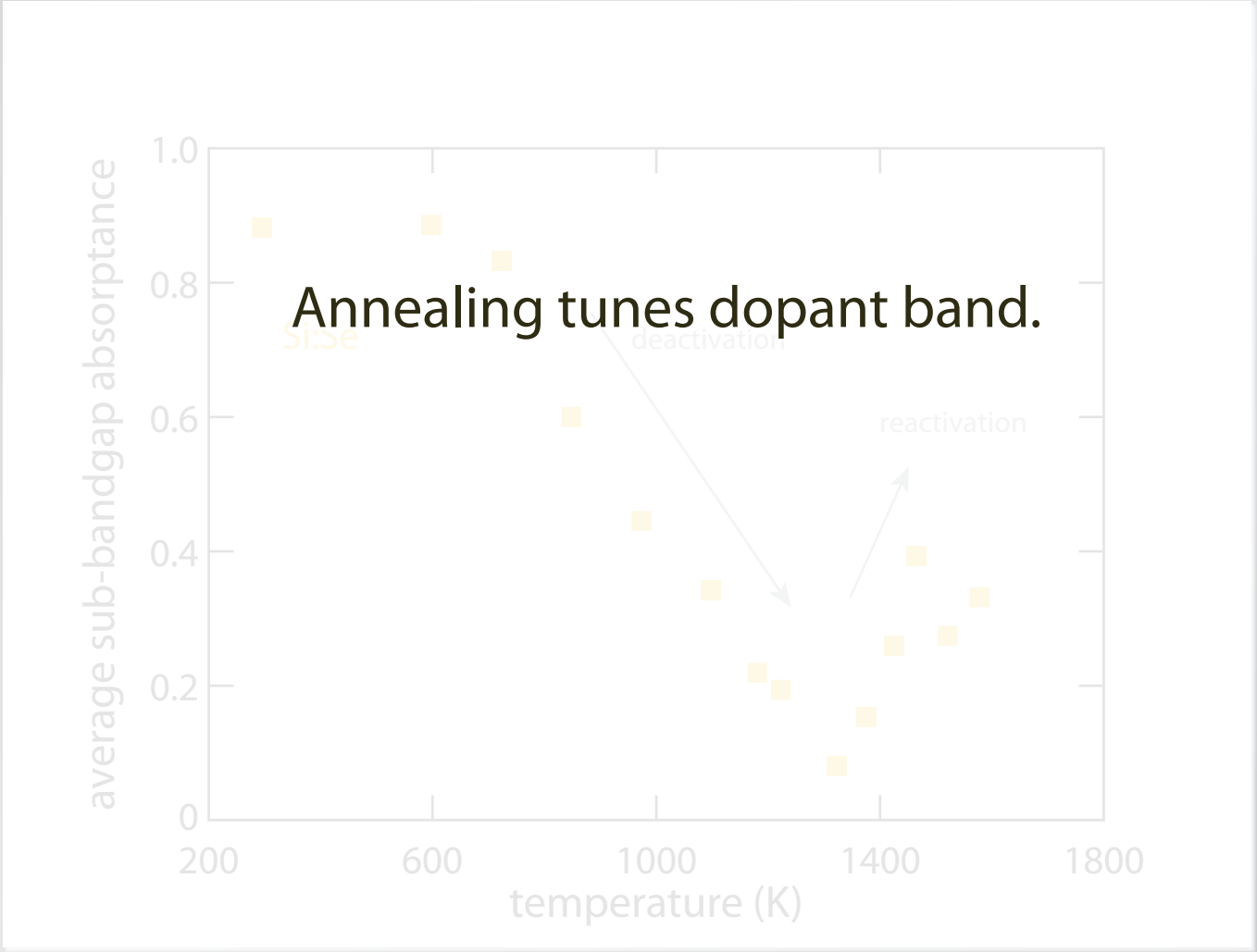

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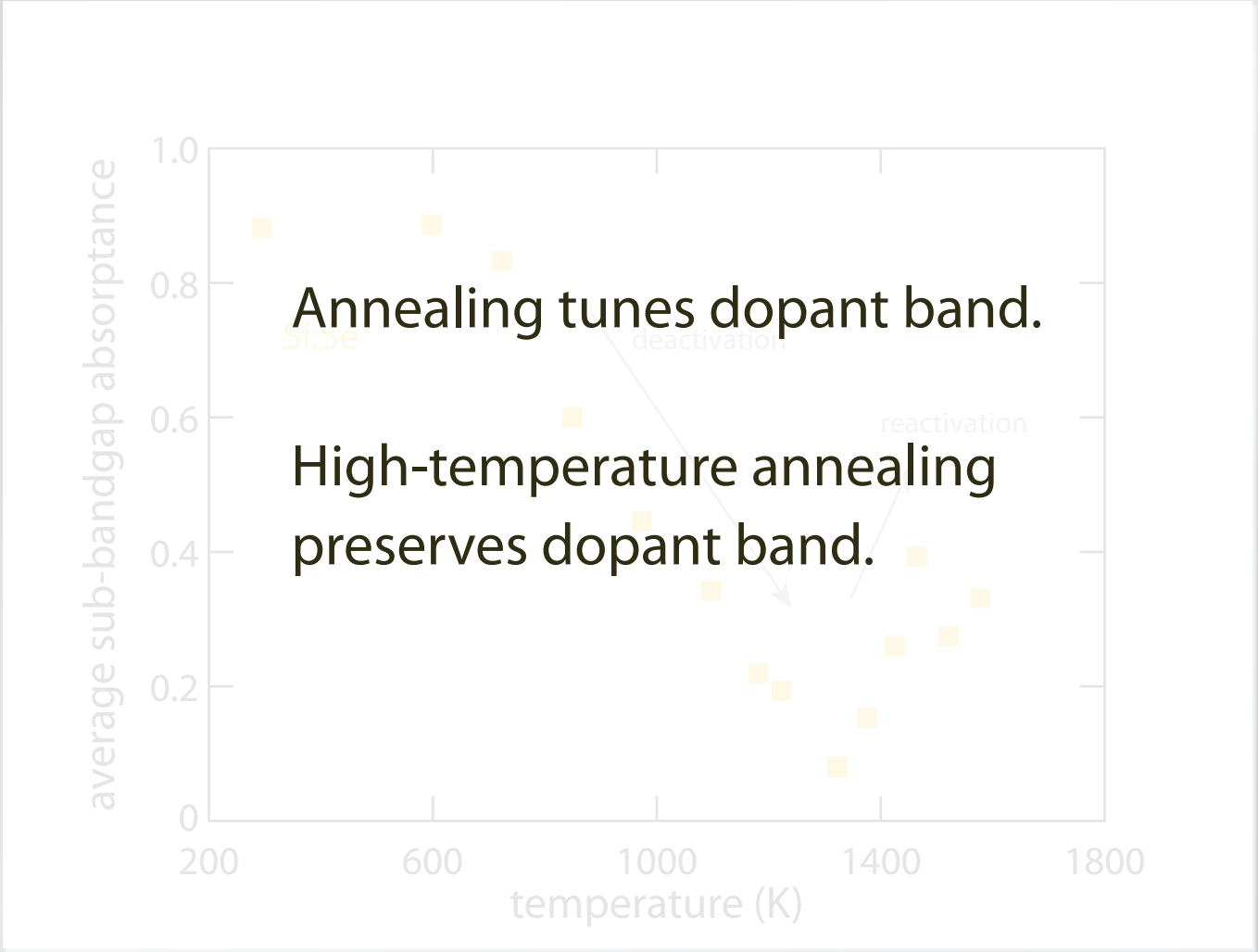


1. Tull et al., Appl. Phys. A (2009)
2. Newman et al., Appl. Phys. Lett. (2011)

We can:

create a dopant band in silicon
with fs-laser hyperdoping.

tune the dopant band in silicon
with thermal treatments.

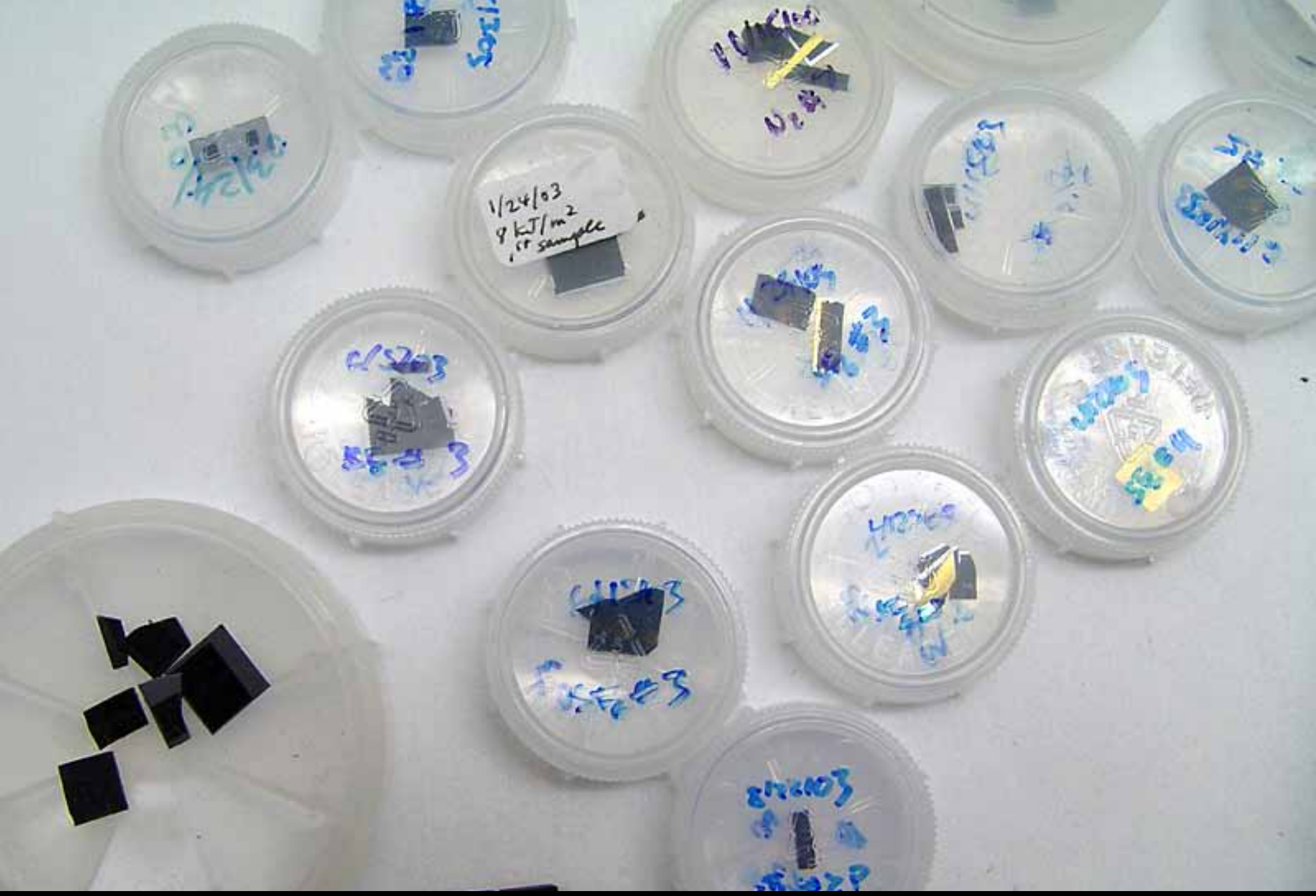
Challenge:

Creating an ideal dopant band

for photovoltaics.

Challenge:
Creating an ideal dopant band
for photovoltaics.

Bigger challenge:
Controlling carrier recombination
induced by the dopant band.

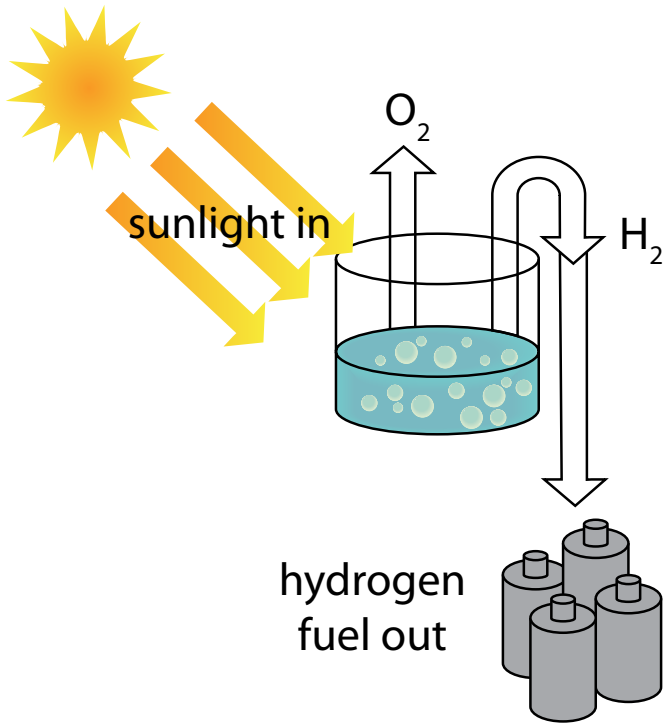


1 Si texturing

2 Si doping

3 TiO_2

water splitting



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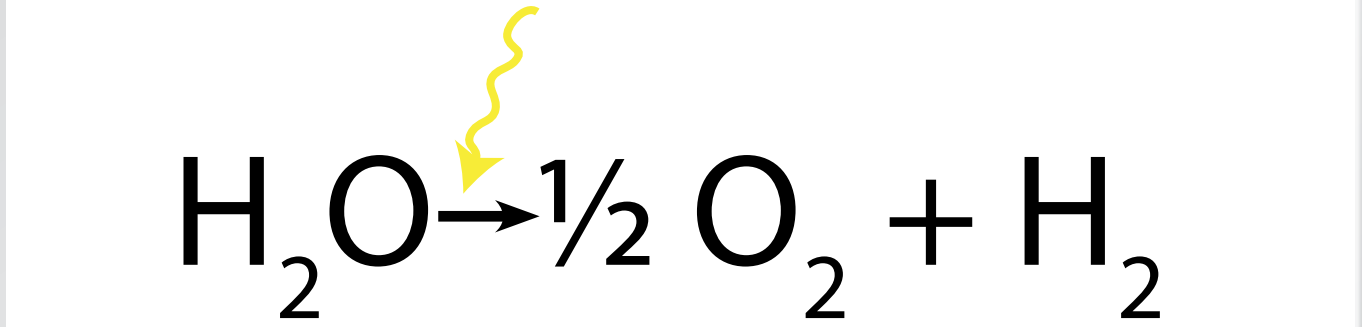

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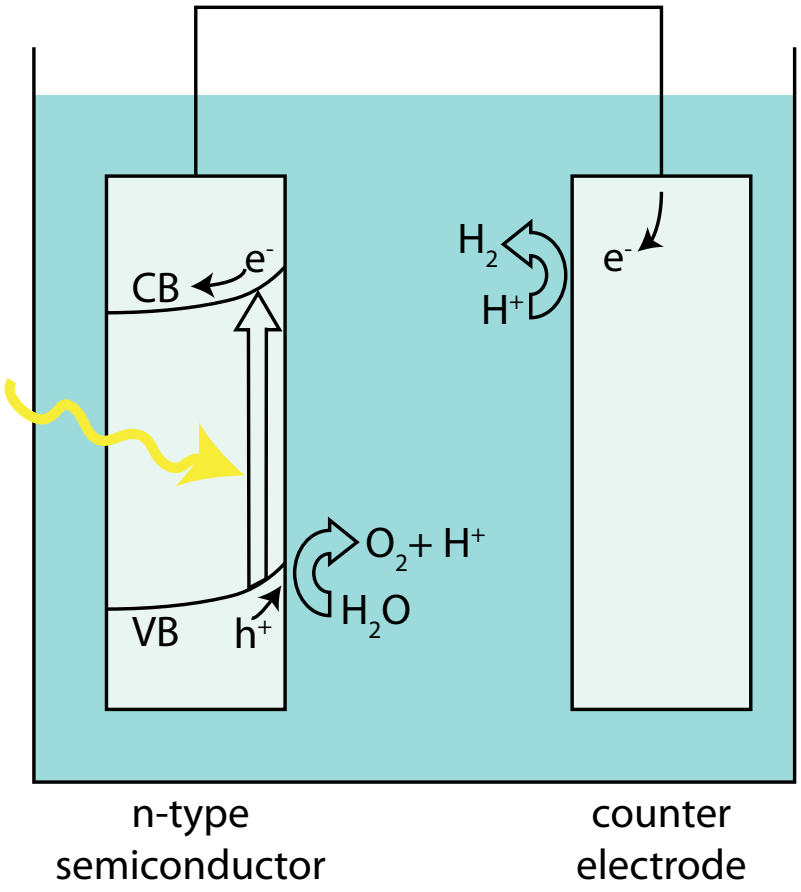

Bard and Fox, Acc. Chem. Res. (1995)

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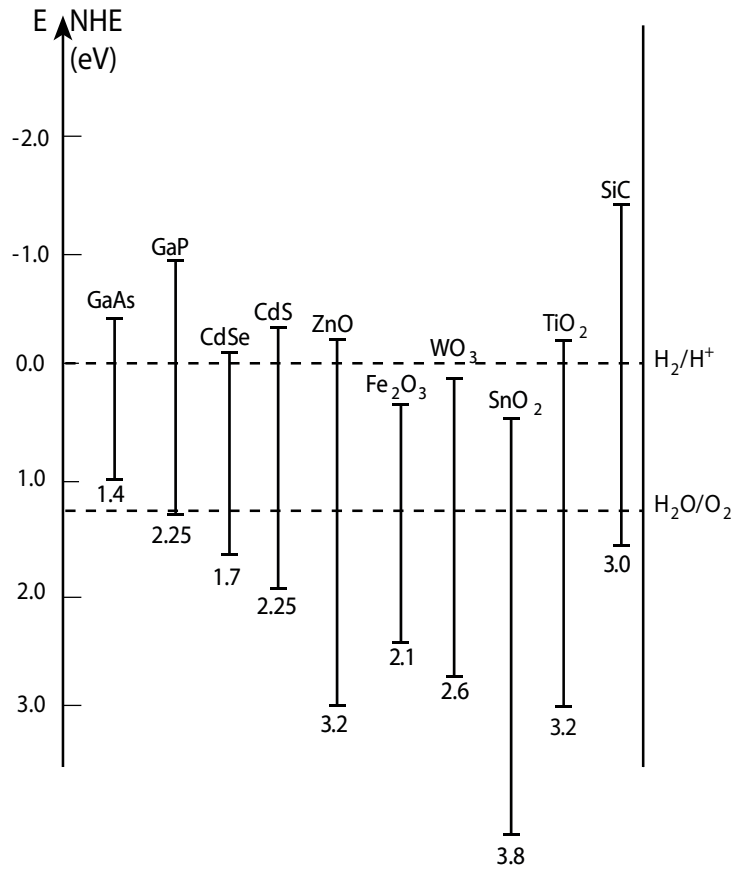
3 TiO_2

water splitting



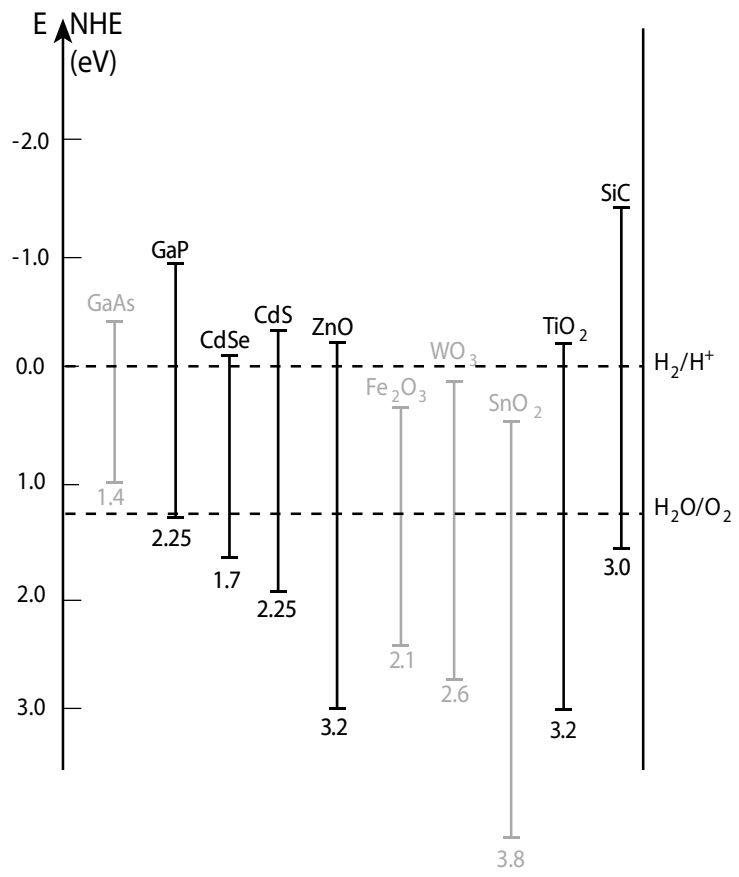
Graetzel, Nature (2001)

1 Si texturing

2 Si doping

3 TiO_2

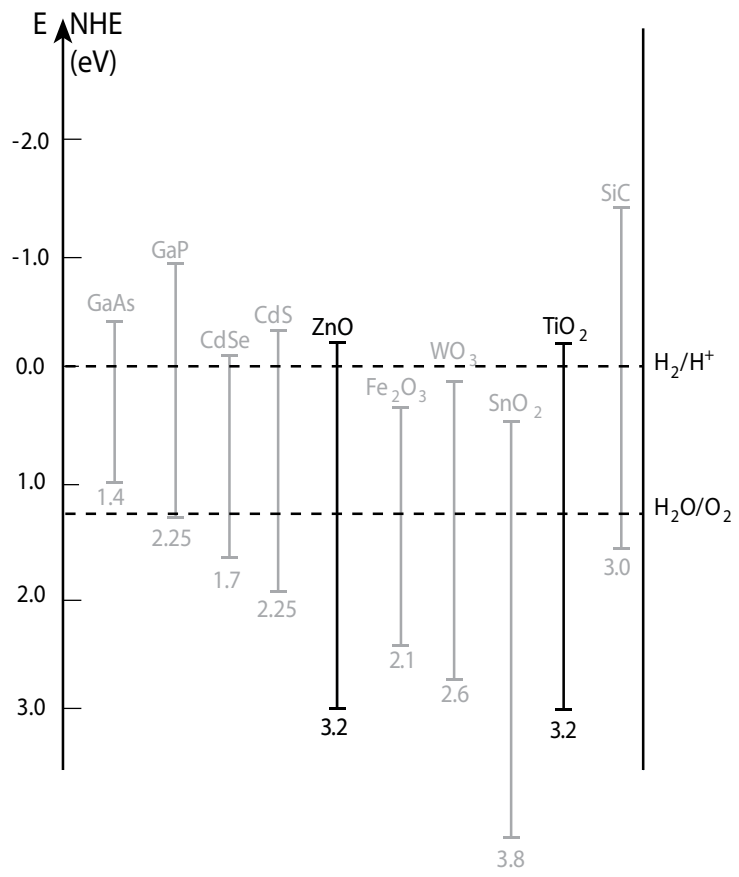
water splitting



Graetzel, Nature (2001)

1 Si texturing **2 Si doping** **3 TiO_2**

water splitting



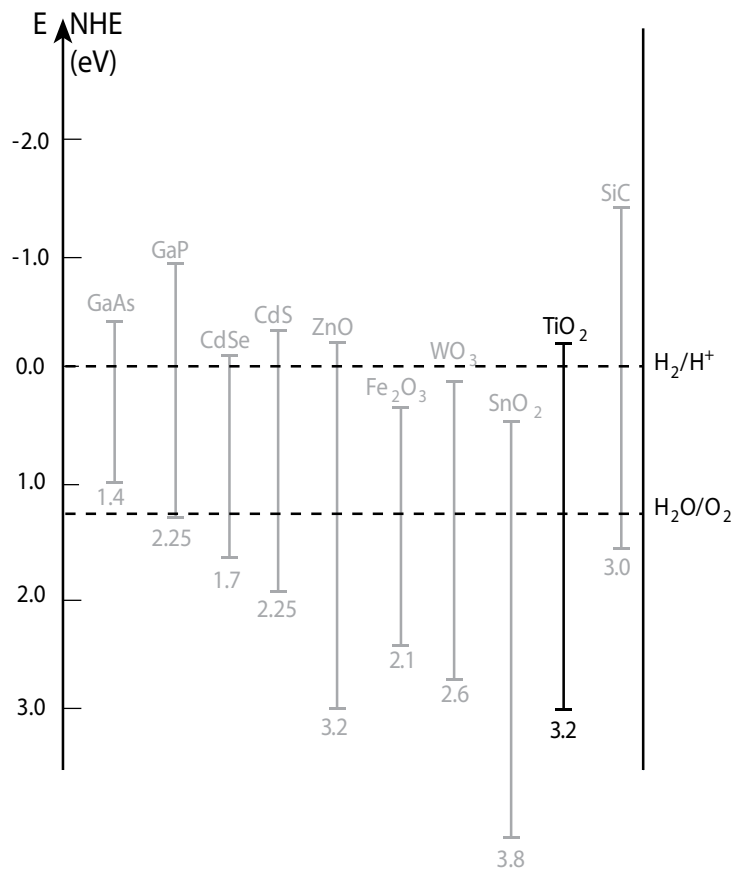
Graetzel, Nature (2001)

1 Si texturing

2 Si doping

3 TiO_2

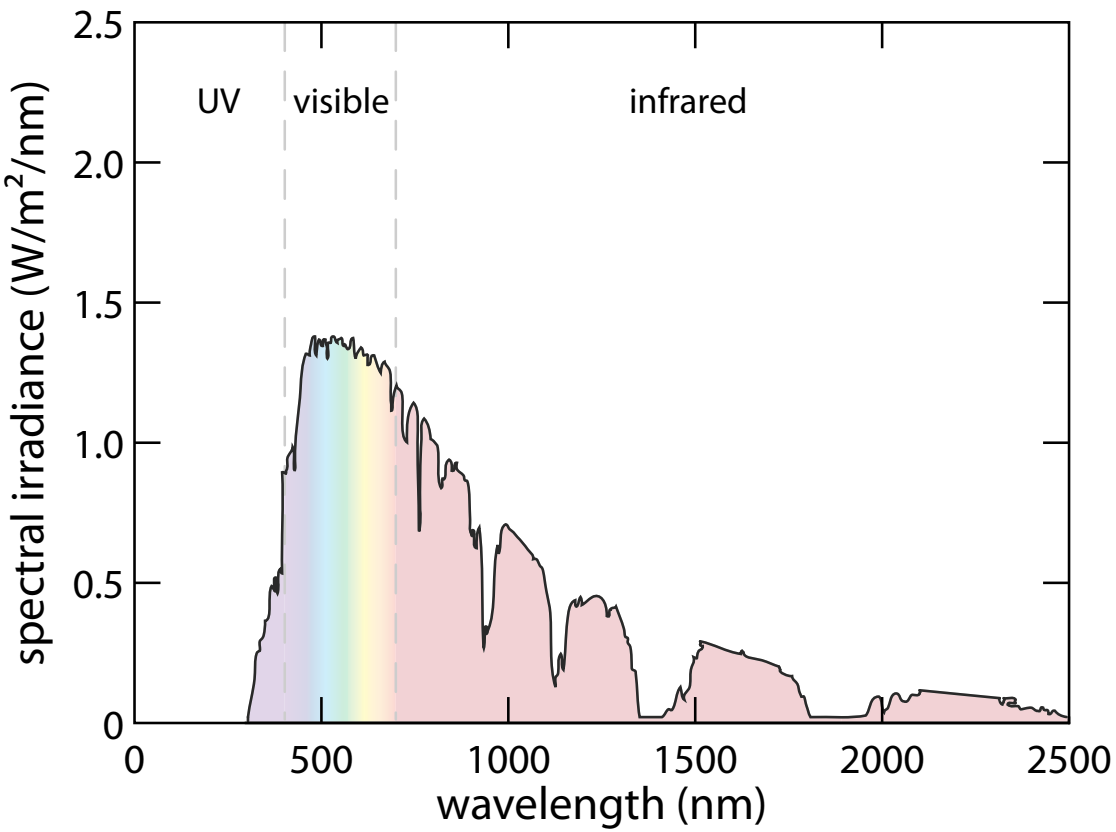
water splitting



Graetzel, Nature (2001)

1 Si texturing **2 Si doping** **3 TiO_2**

solar spectrum

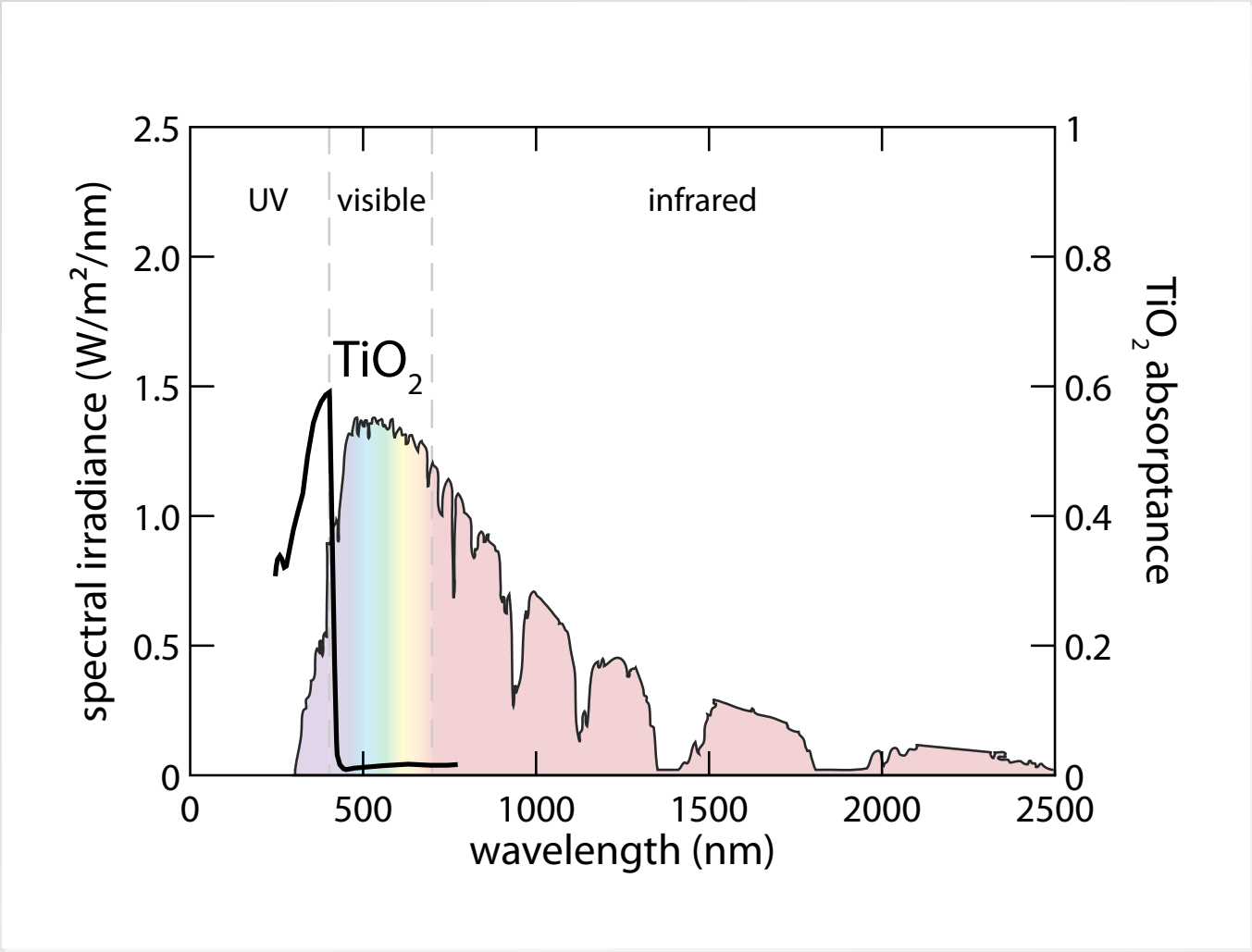


1 Si texturing

2 Si doping

3 TiO_2

solar spectrum

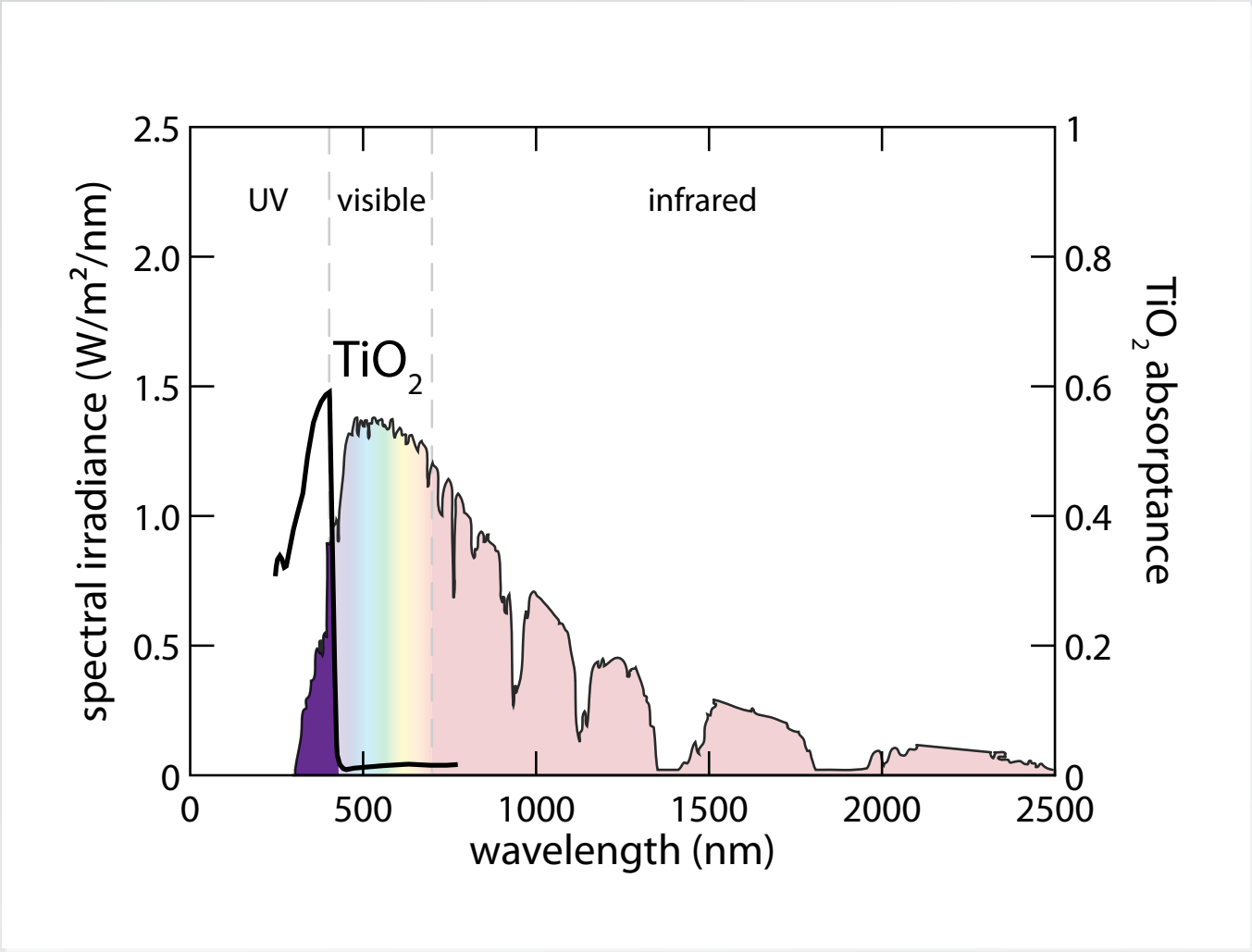


1 Si texturing

2 Si doping

3 TiO_2

solar spectrum

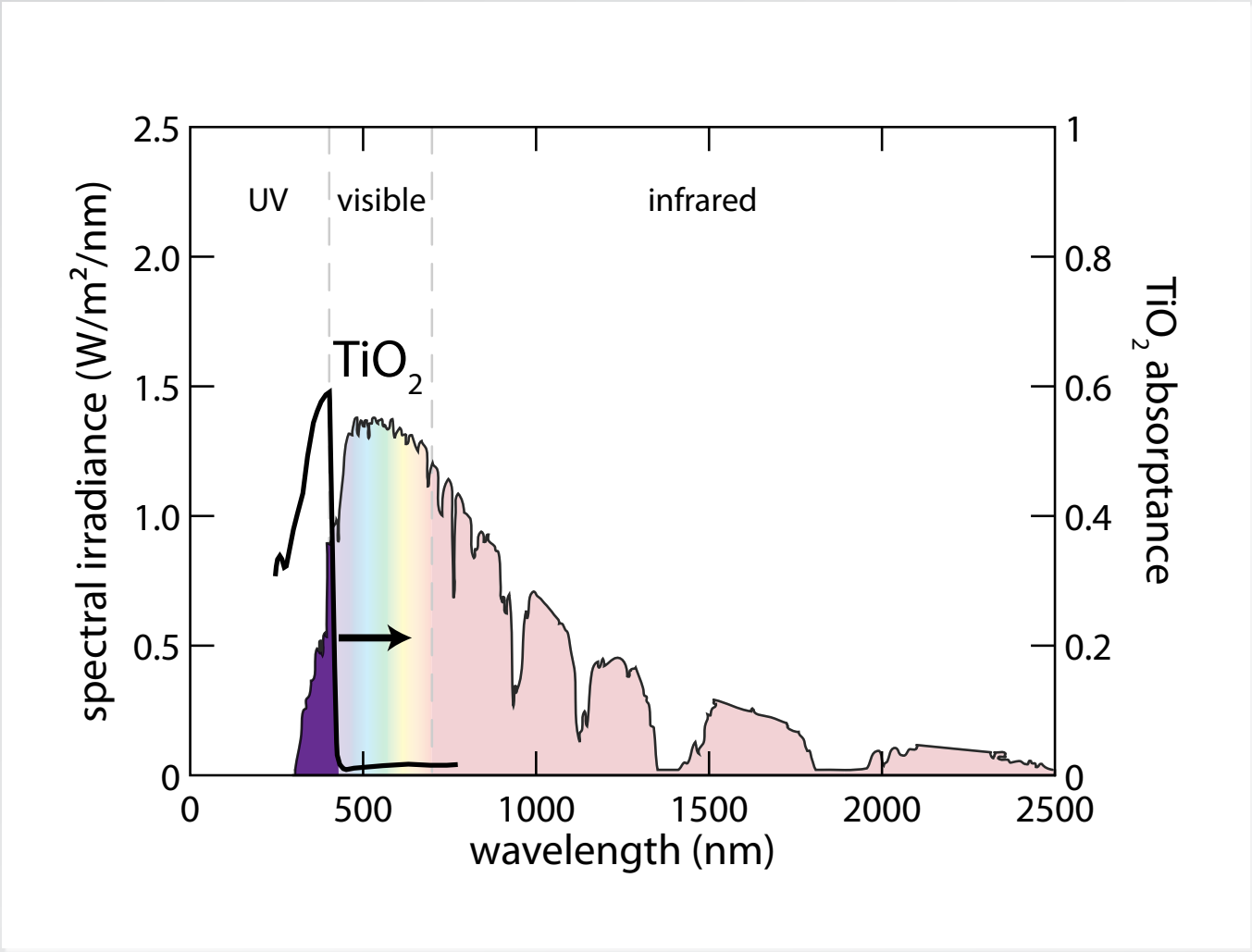


1 Si texturing

2 Si doping

3 TiO_2

solar spectrum



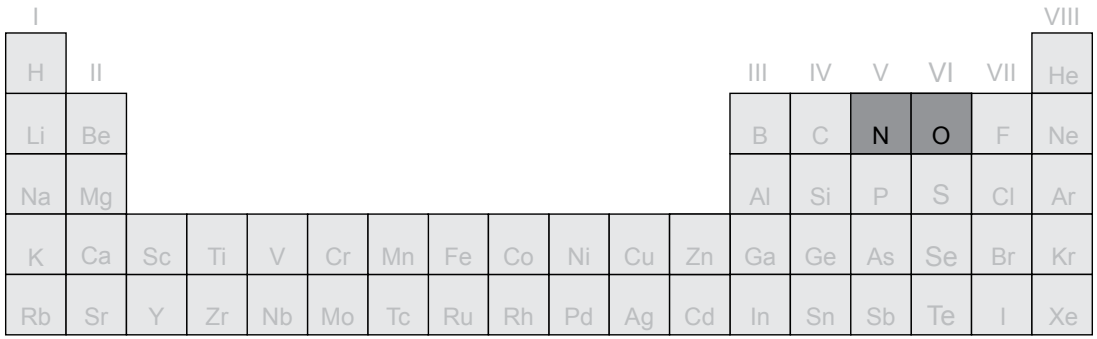
1 Si texturing

2 Si doping

3 TiO_2

substrate/dopant combinations

Dopants:



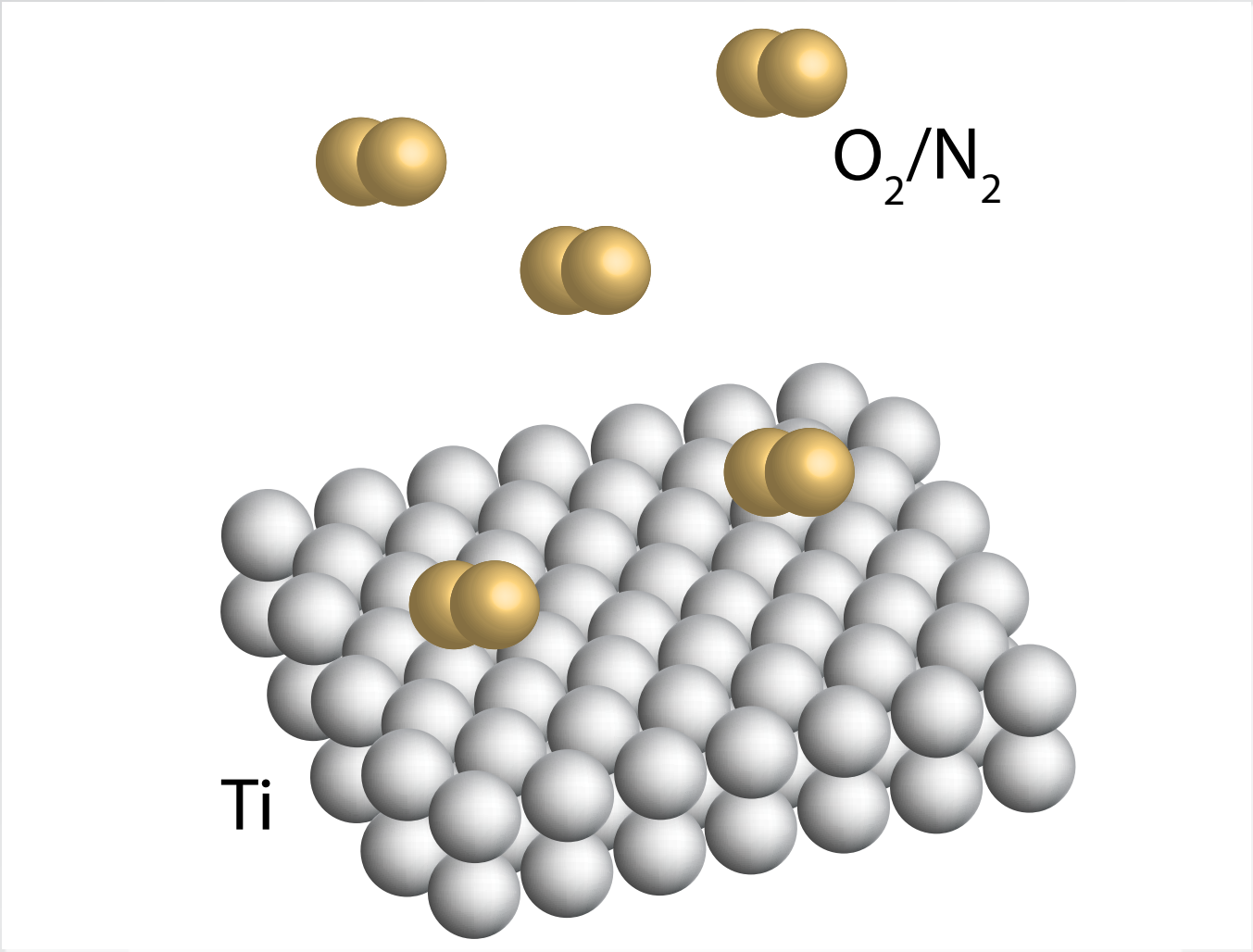
Substrates:

Ti

1 Si texturing

2 Si doping

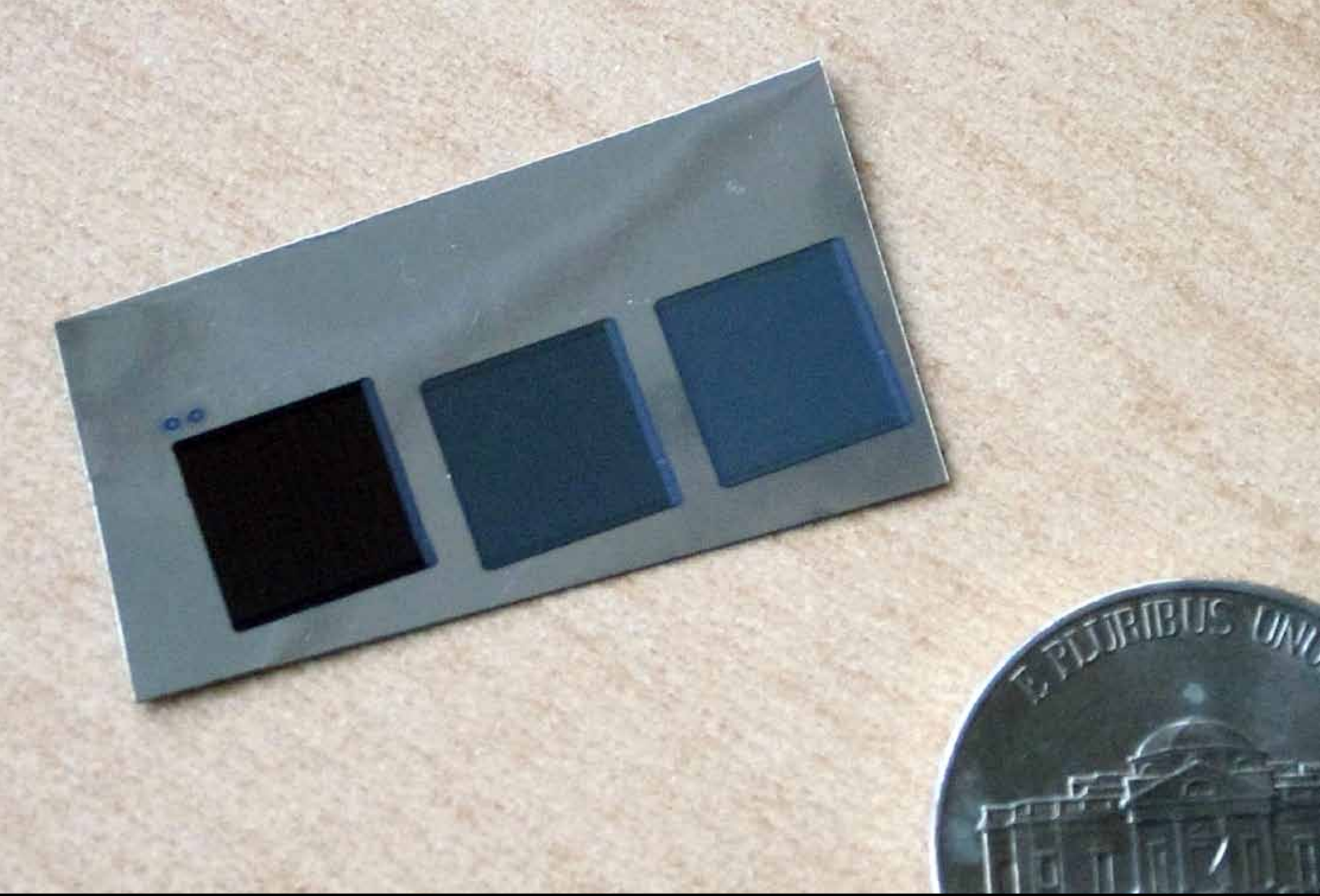
3 TiO_2



1 Si texturing

2 Si doping

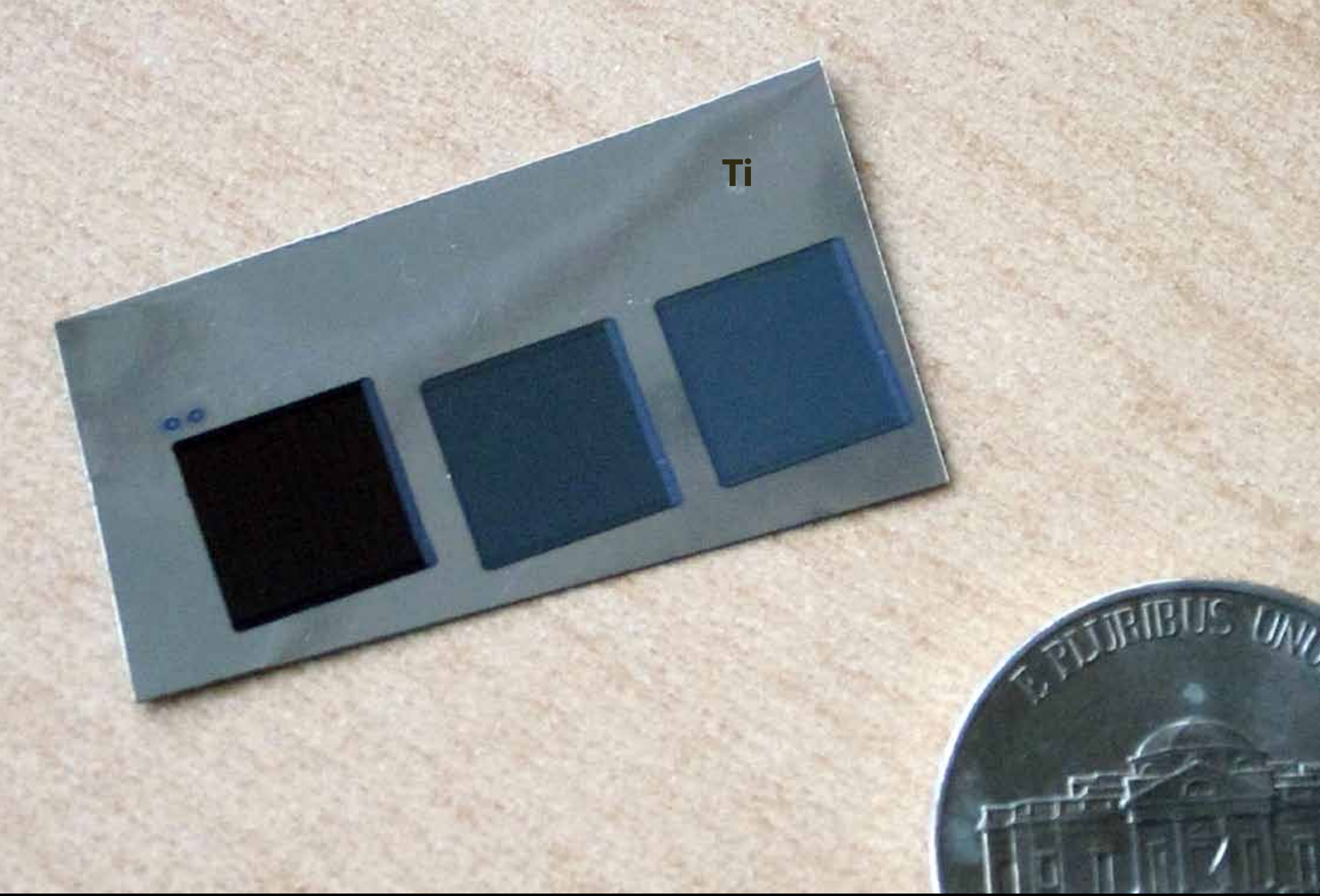
3 TiO_2



1 Si texturing

2 Si doping

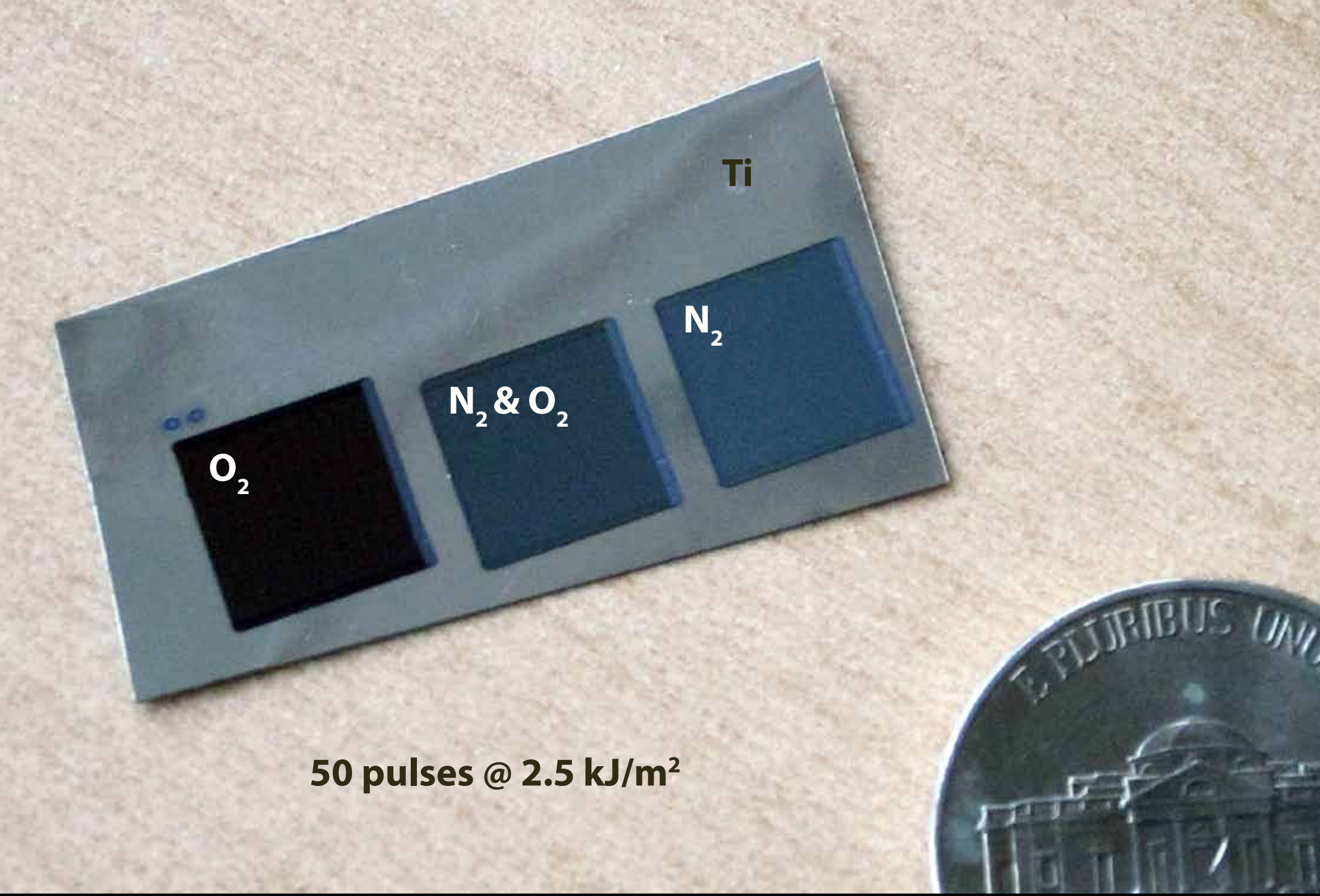
3 TiO_2



1 Si texturing

2 Si doping

3 TiO_2

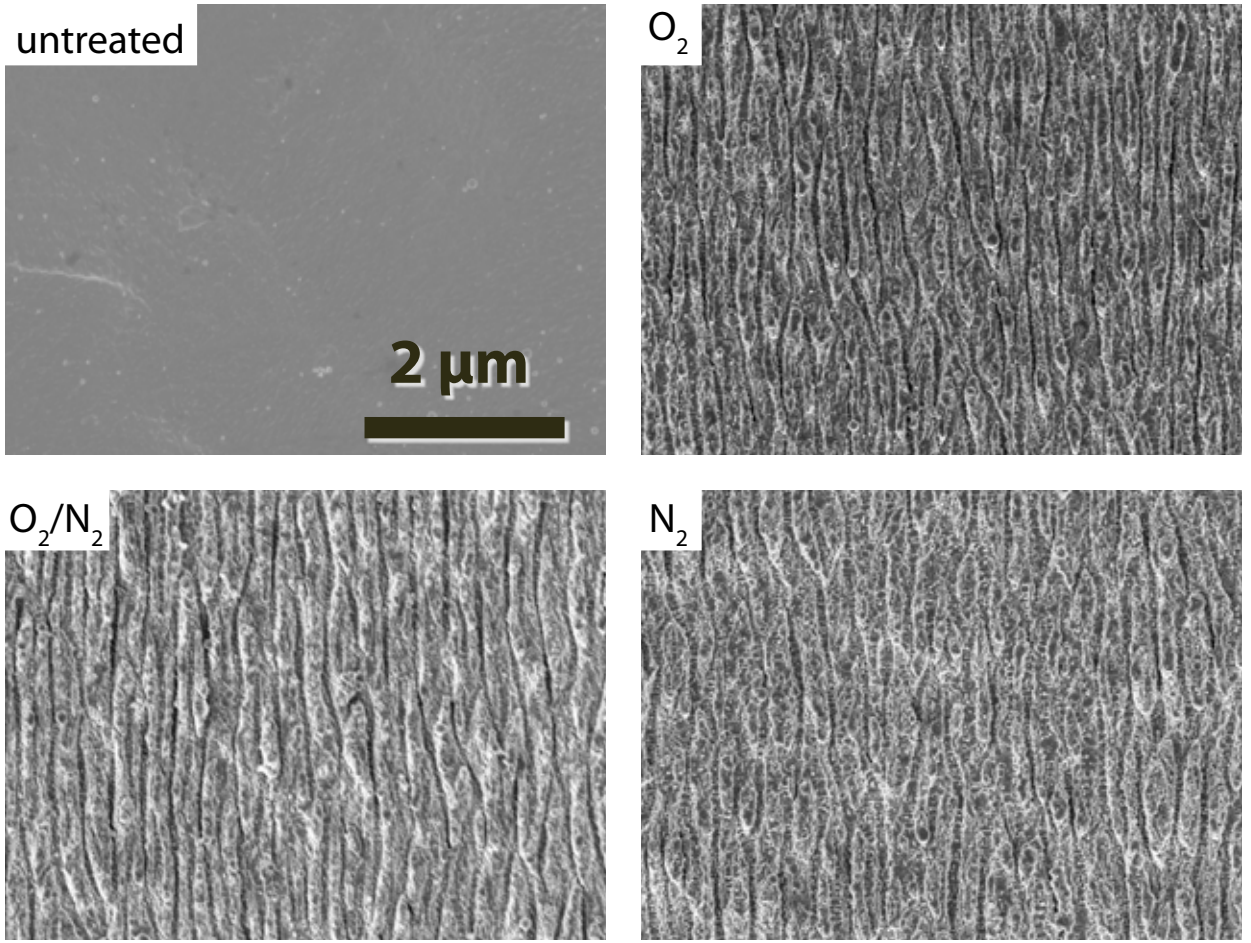


1 Si texturing

2 Si doping

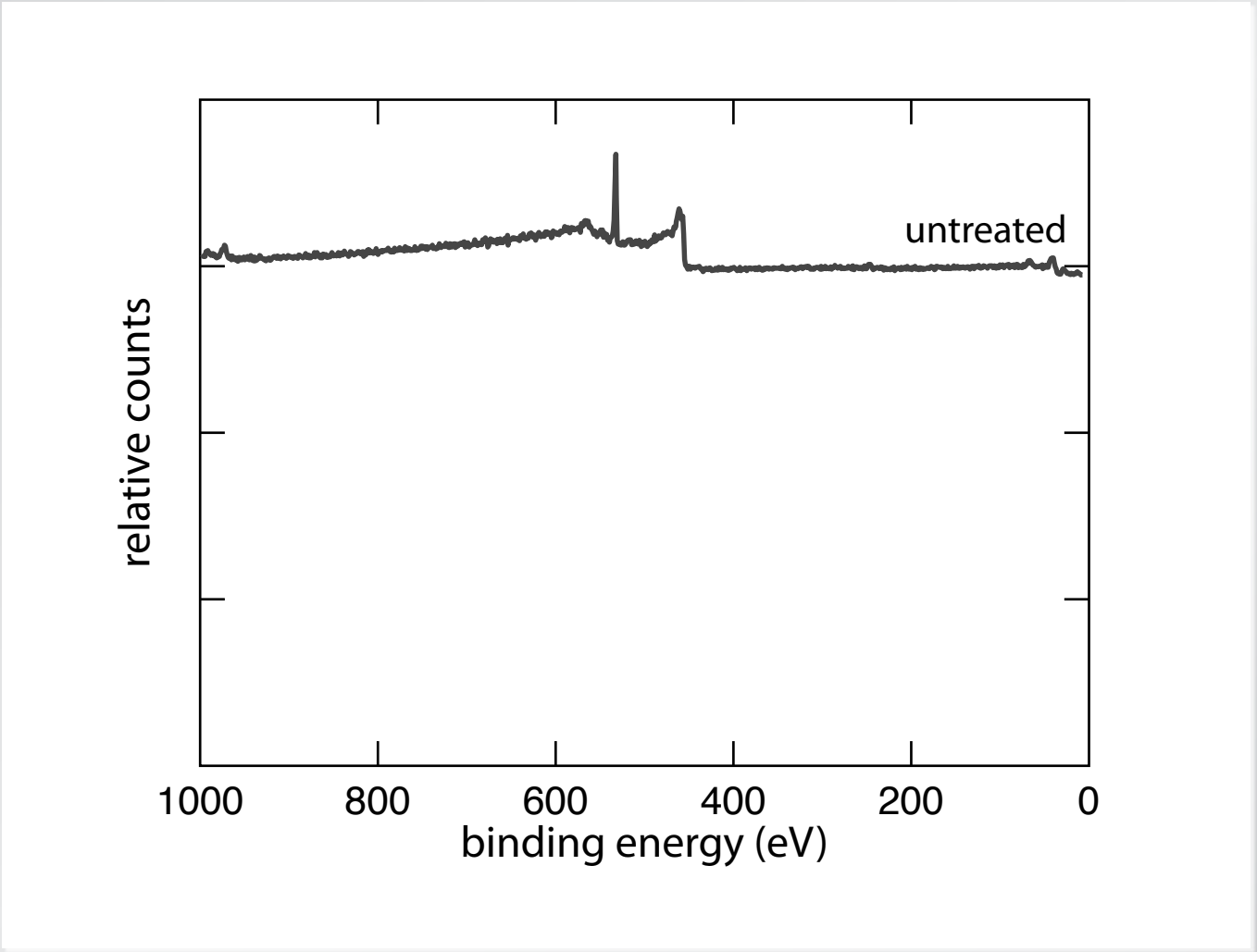
3 TiO_2

50 pulses @ 2.5 kJ/m²



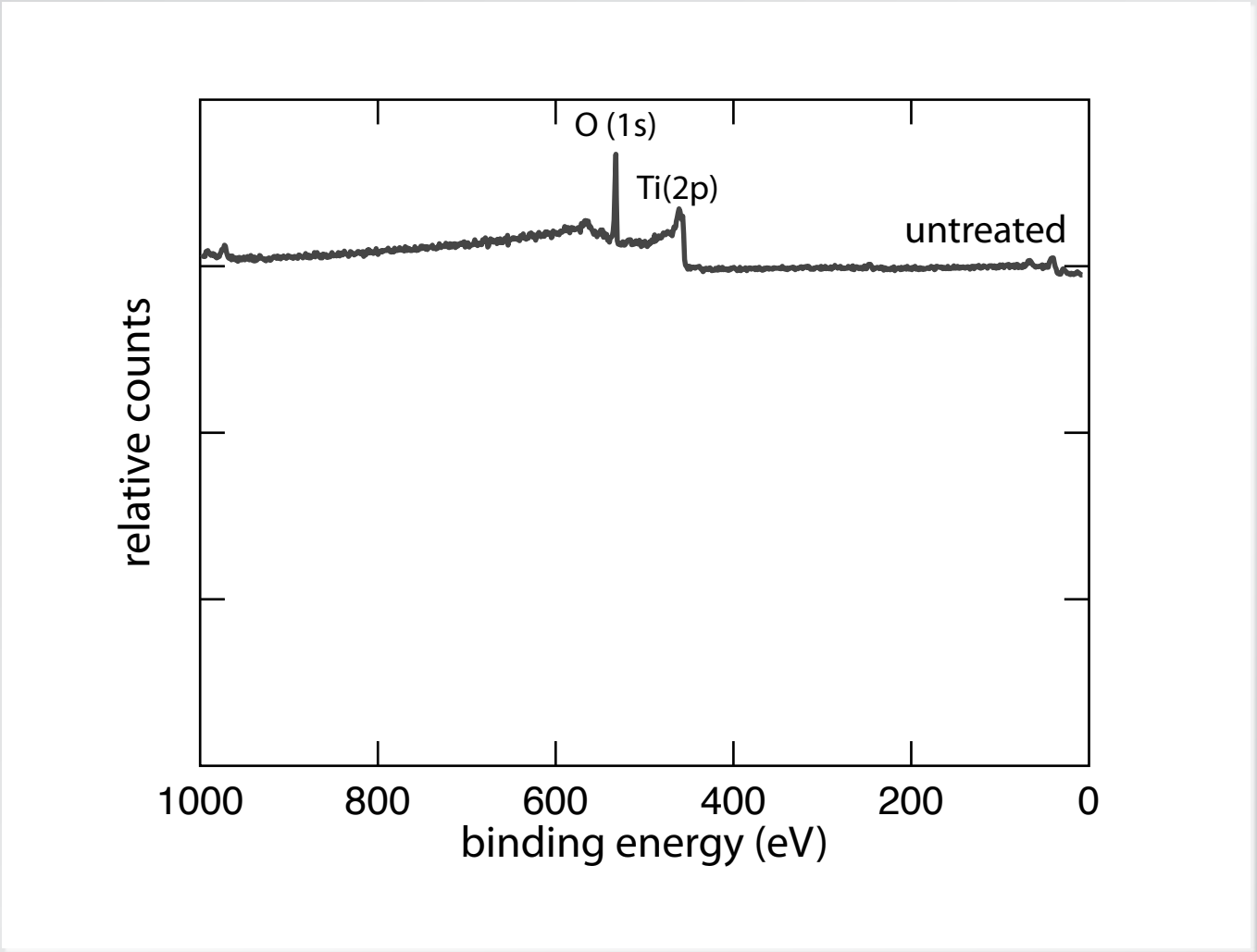
Landis E., Phillips K. et al., J. Appl. Phys. in print (2012)

X-ray photoelectron spectroscopy



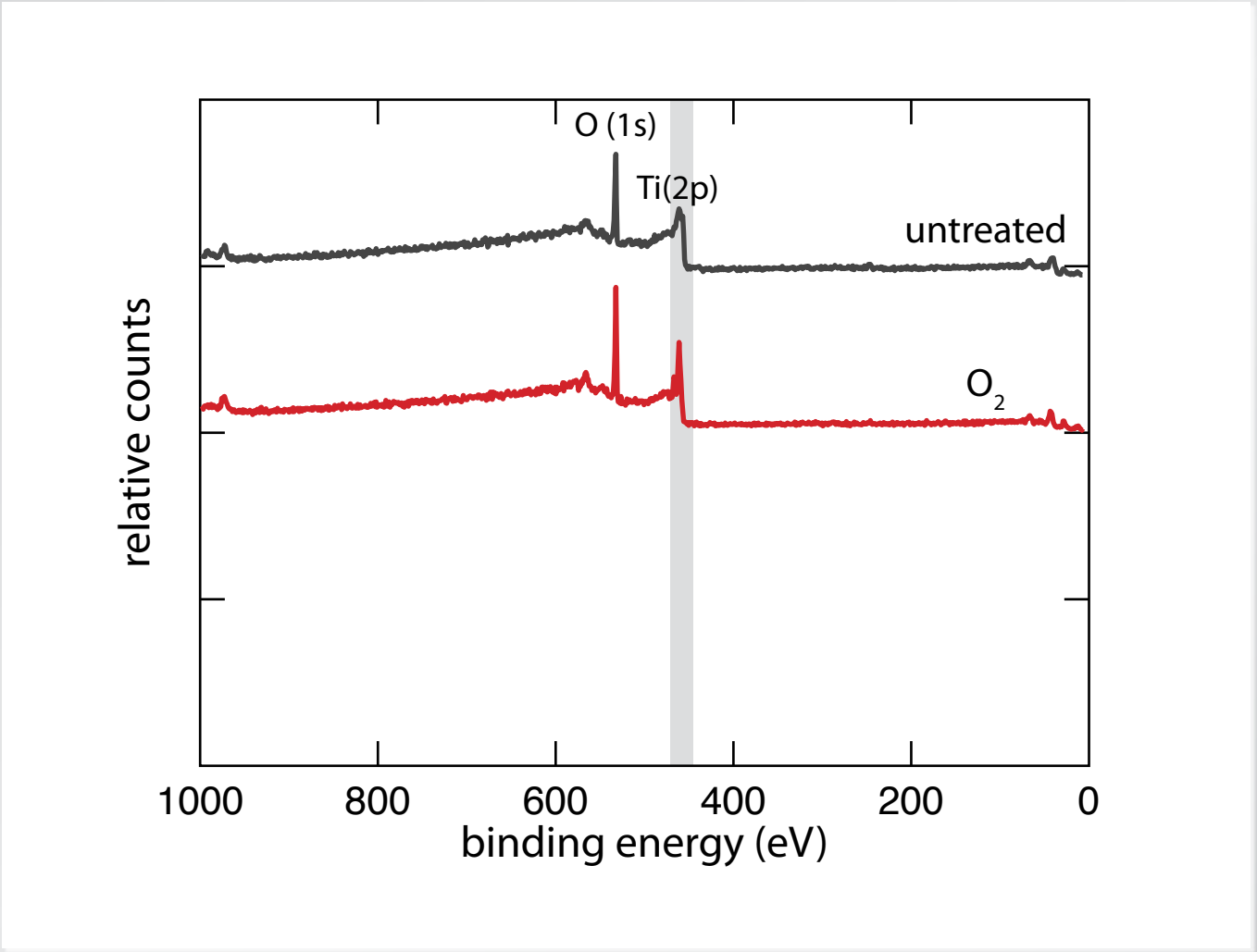
Landis E., Phillips K. et al., J. Appl. Phys. in print (2012)

X-ray photoelectron spectroscopy



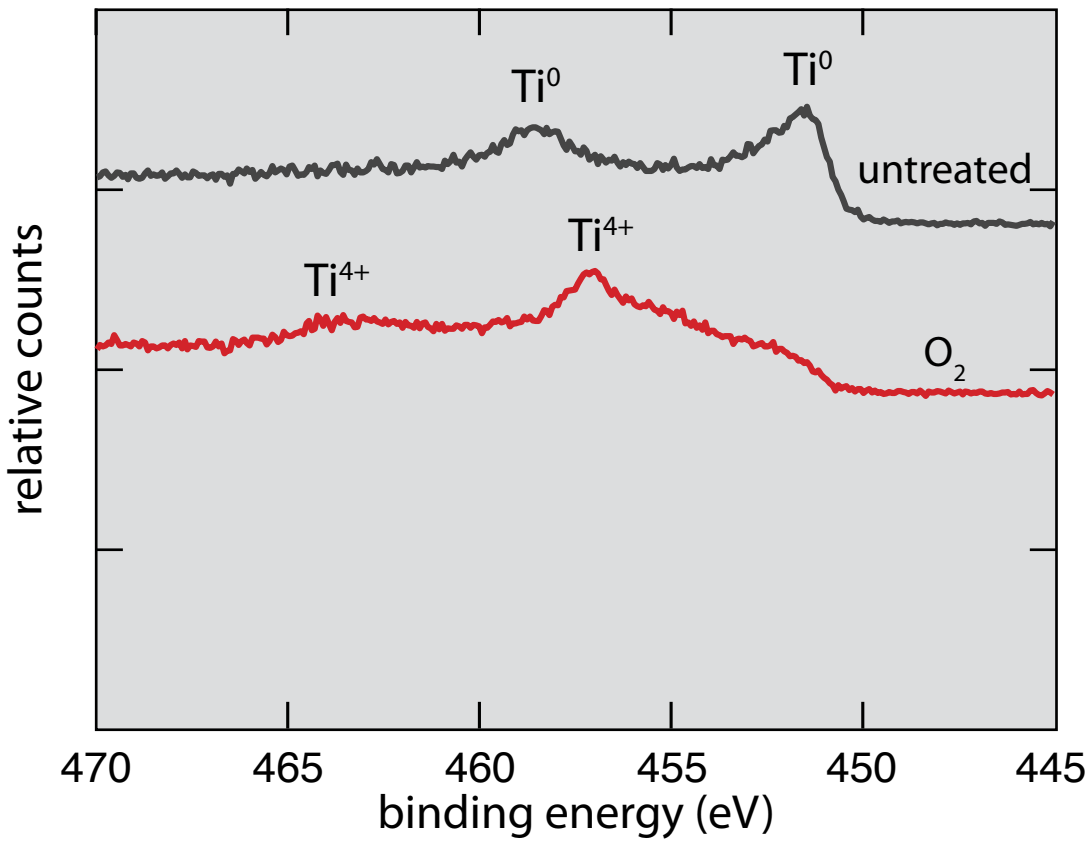
Landis E., Phillips K. et al., J. Appl. Phys. in print (2012)

X-ray photoelectron spectroscopy



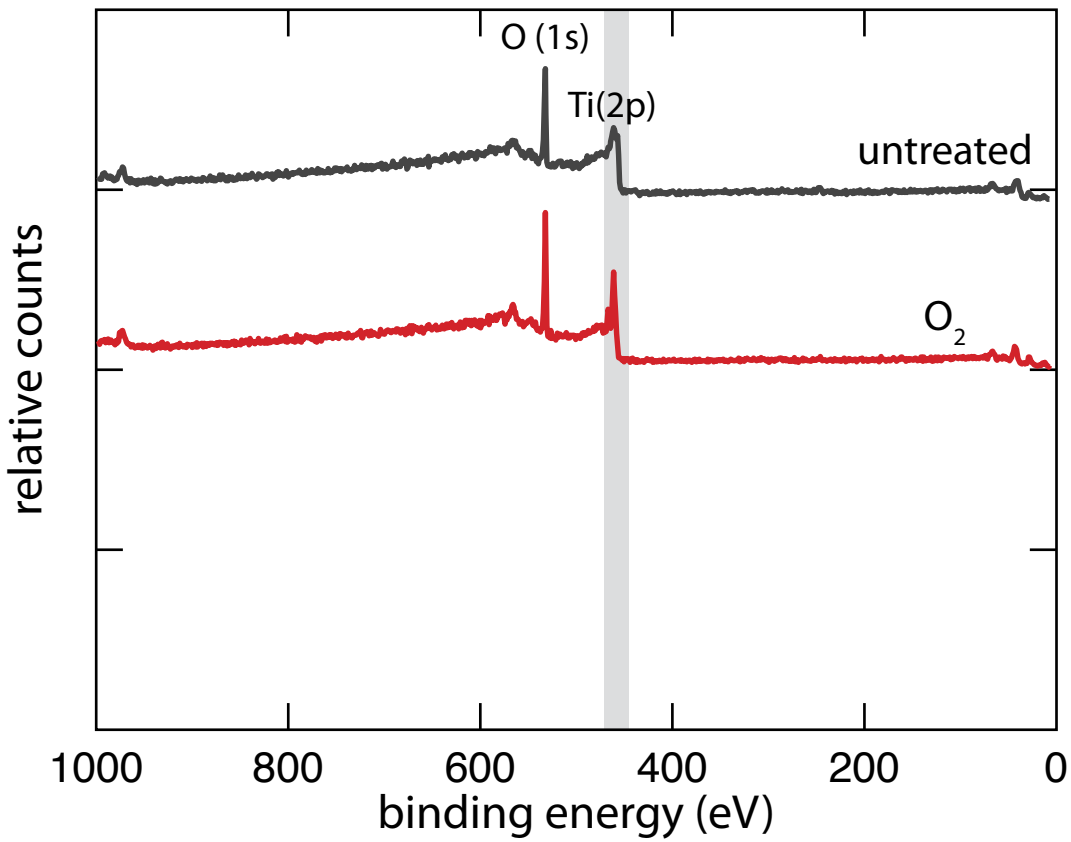
Landis E., Phillips K. et al., J. Appl. Phys. in print (2012)

we form TiO_2 in the presence of oxygen



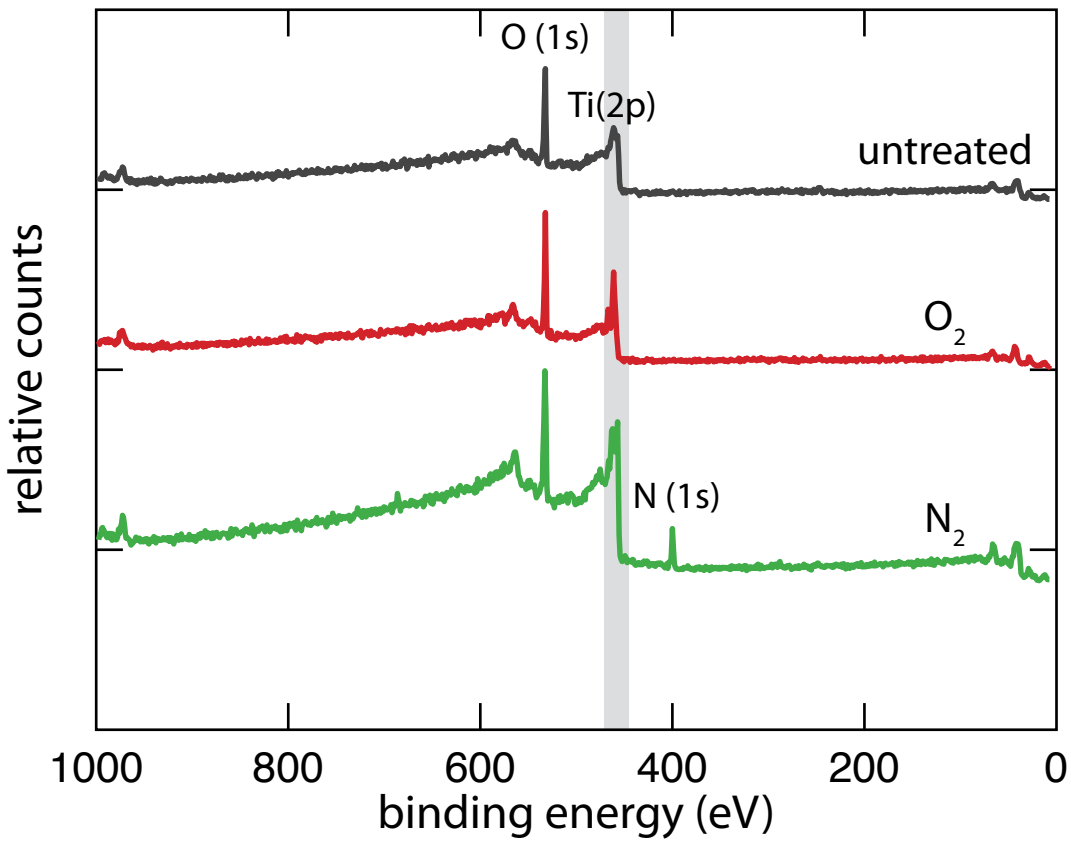
Landis E., Phillips K. et al., J. Appl. Phys. in print (2012)

we form TiO_2 in the presence of oxygen



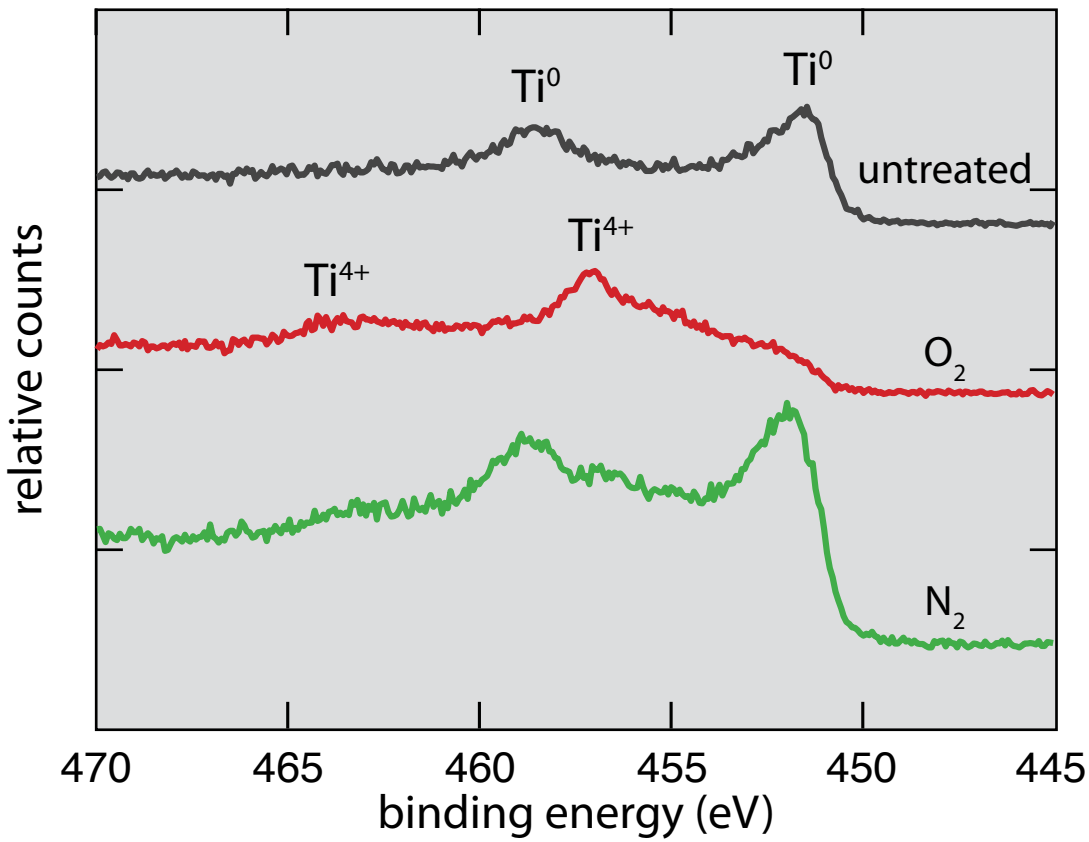
Landis E., Phillips K. et al., J. Appl. Phys. in print (2012)

nitrogen peak means TiN formed



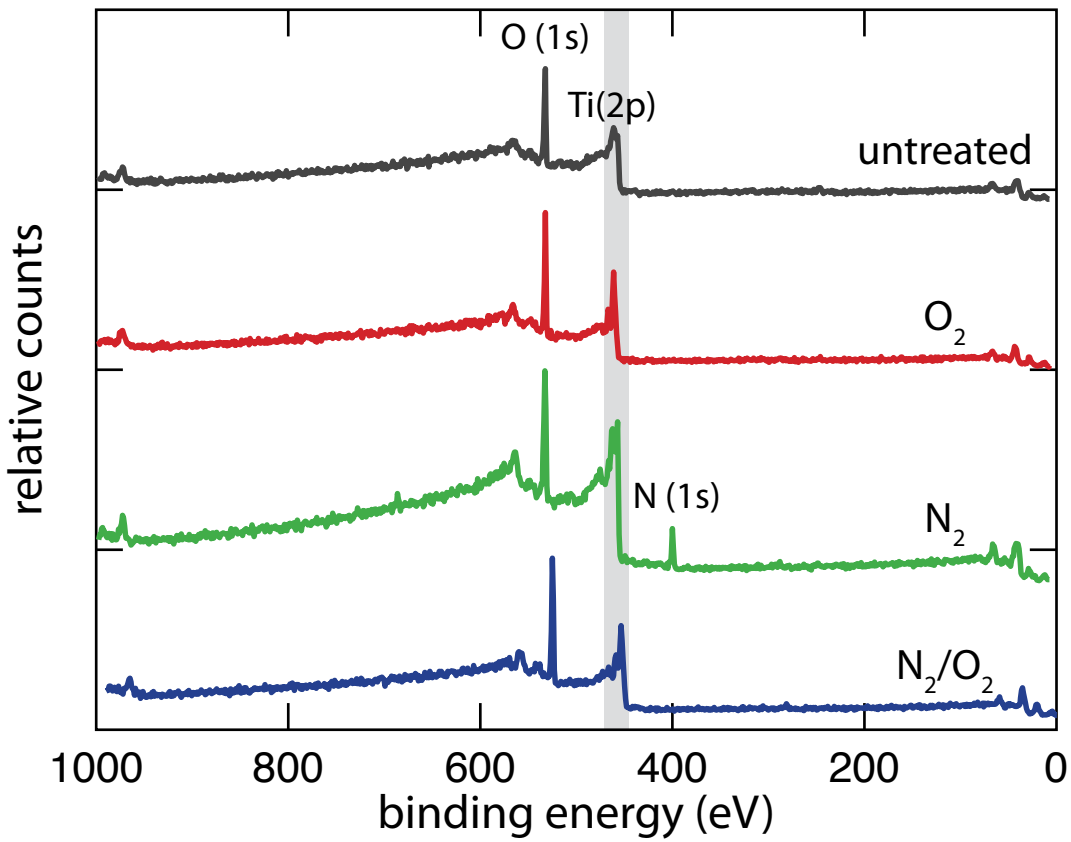
Landis E., Phillips K. et al., J. Appl. Phys. in print (2012)

non-stoicimetric TiN formed



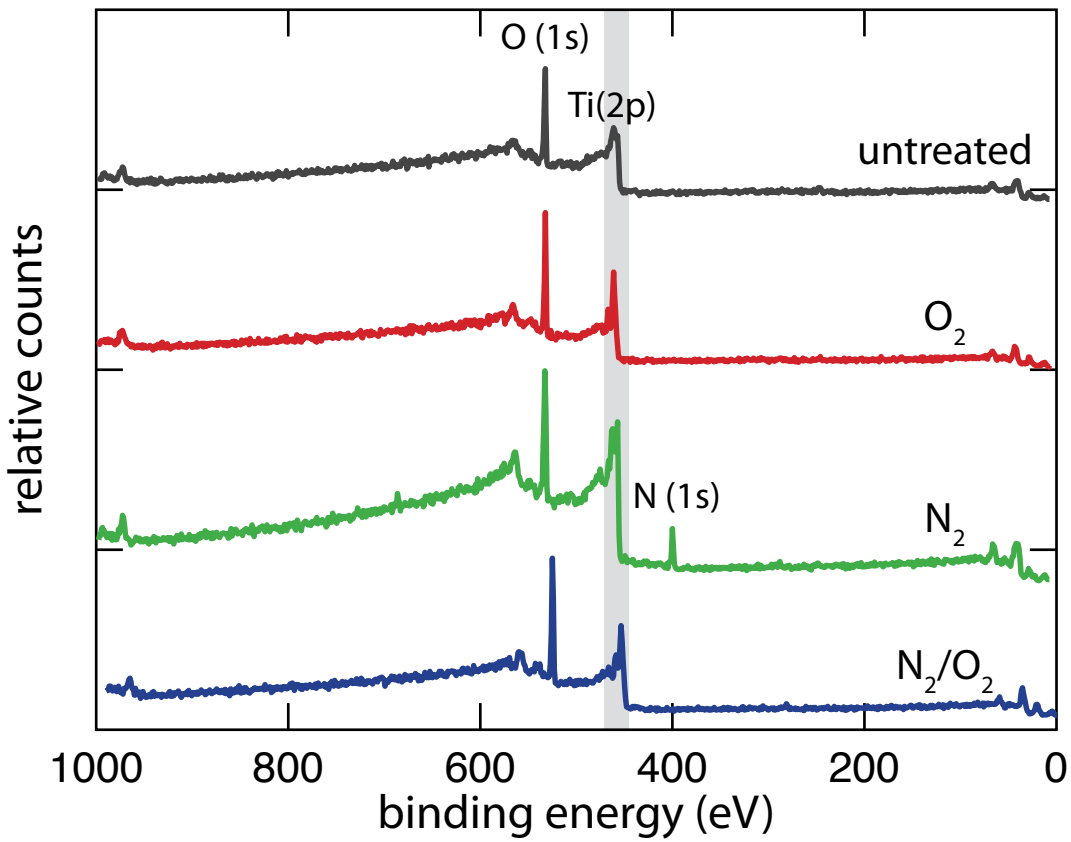
Landis E., Phillips K. et al., J. Appl. Phys. in print (2012)

with both nitrogen and oxygen



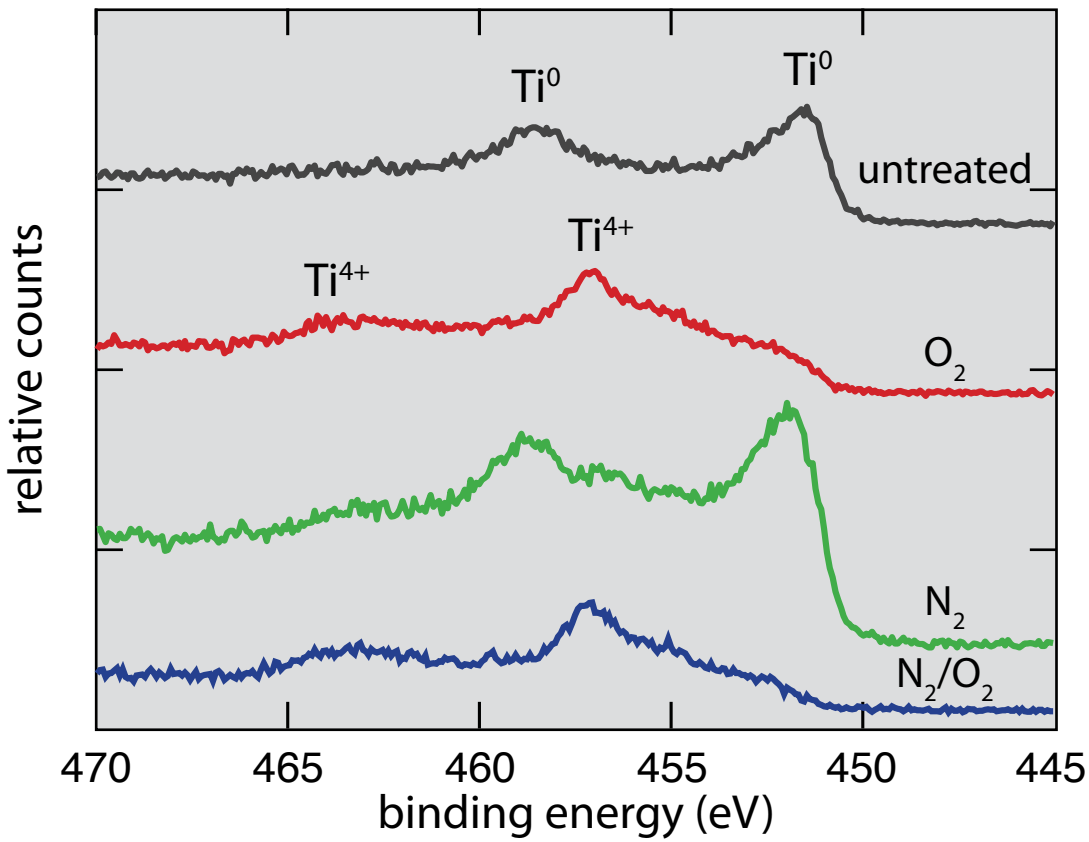
Landis E., Phillips K. et al., J. Appl. Phys. in print (2012)

1% oxygen prevents nitrogen incorporation



Landis E., Phillips K. et al., J. Appl. Phys. in print (2012)

nitrogen and oxygen together form TiO_2

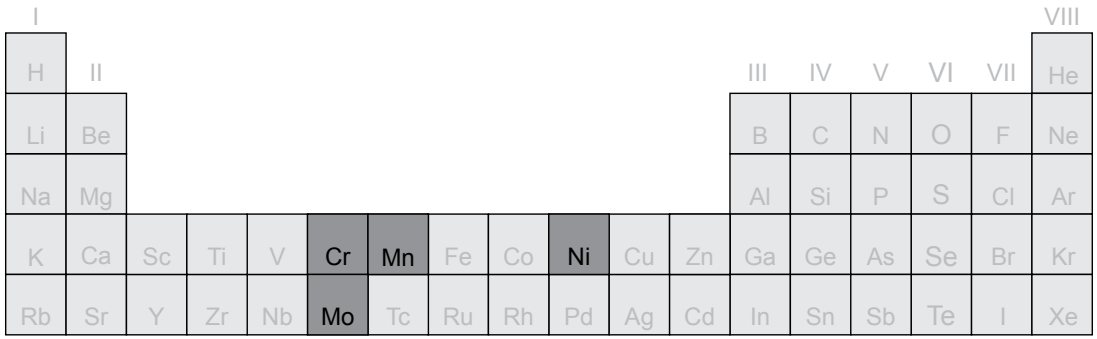


Landis E., Phillips K. et al., J. Appl. Phys. in print (2012)

can incorporate N_2 or O_2 but not both

substrate/dopant combinations

Dopants:



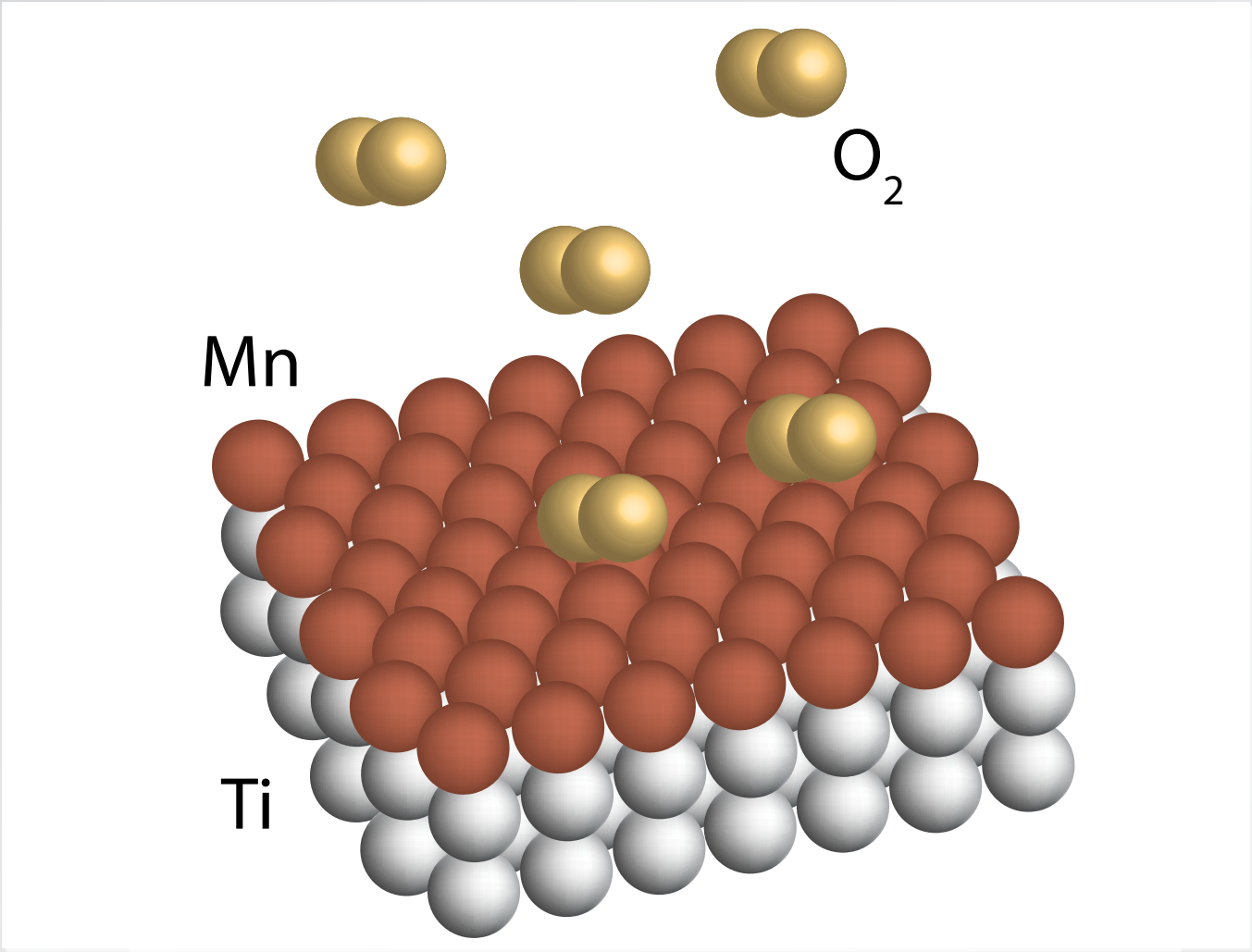
Substrates:

Ti

1 Si texturing

2 Si doping

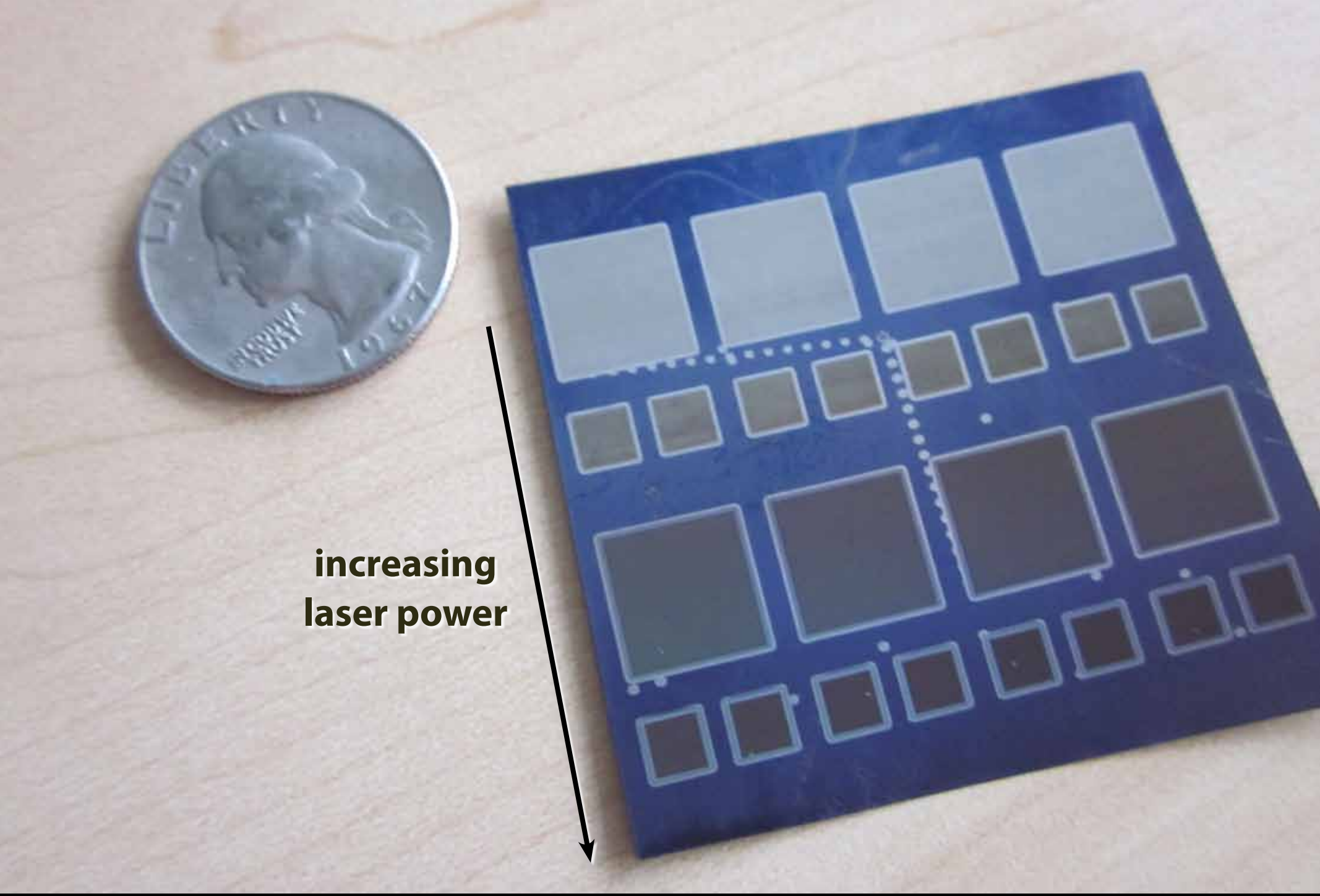
3 TiO_2



1 Si texturing

2 Si doping

3 TiO_2

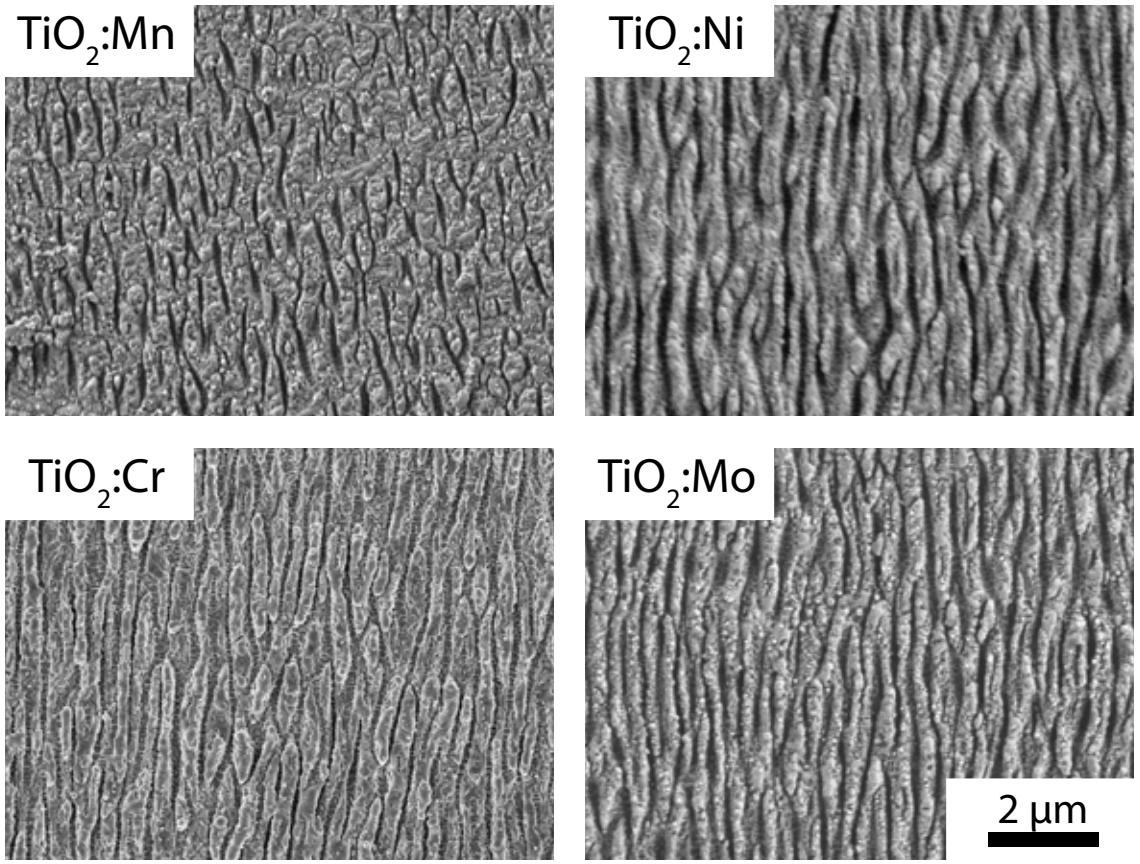


1 Si texturing

2 Si doping

3 TiO_2

similar surface structures

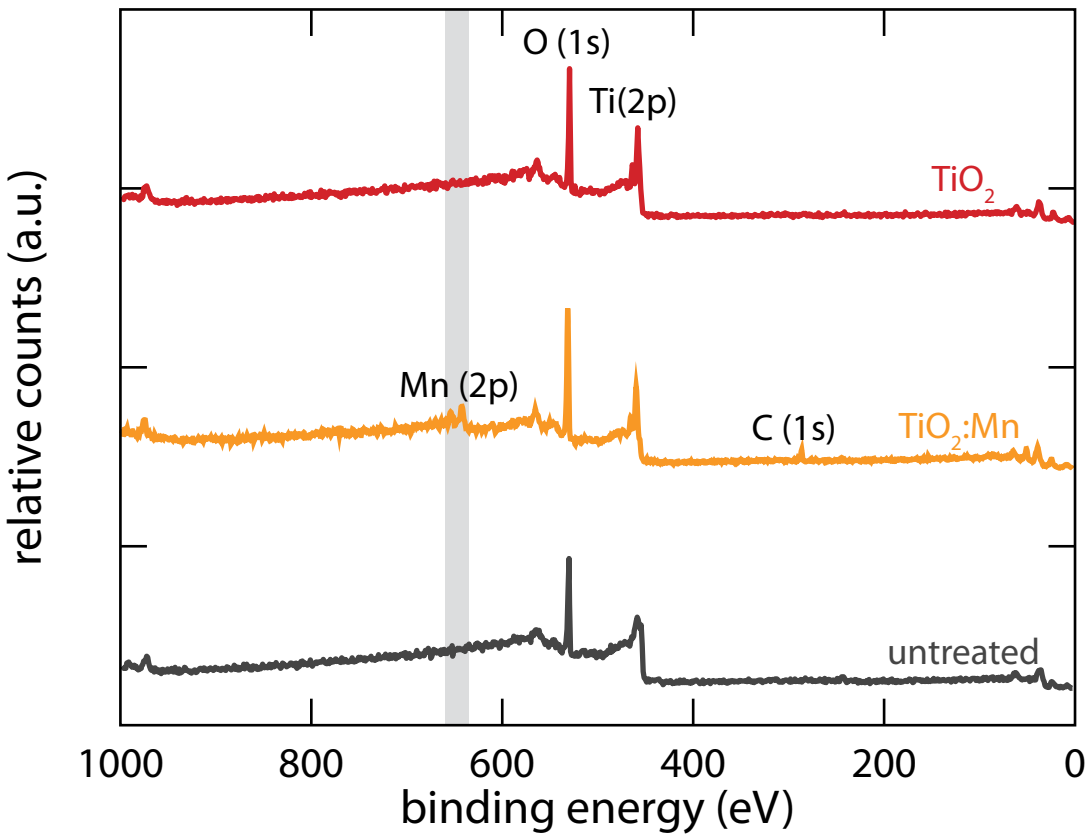


1 Si texturing

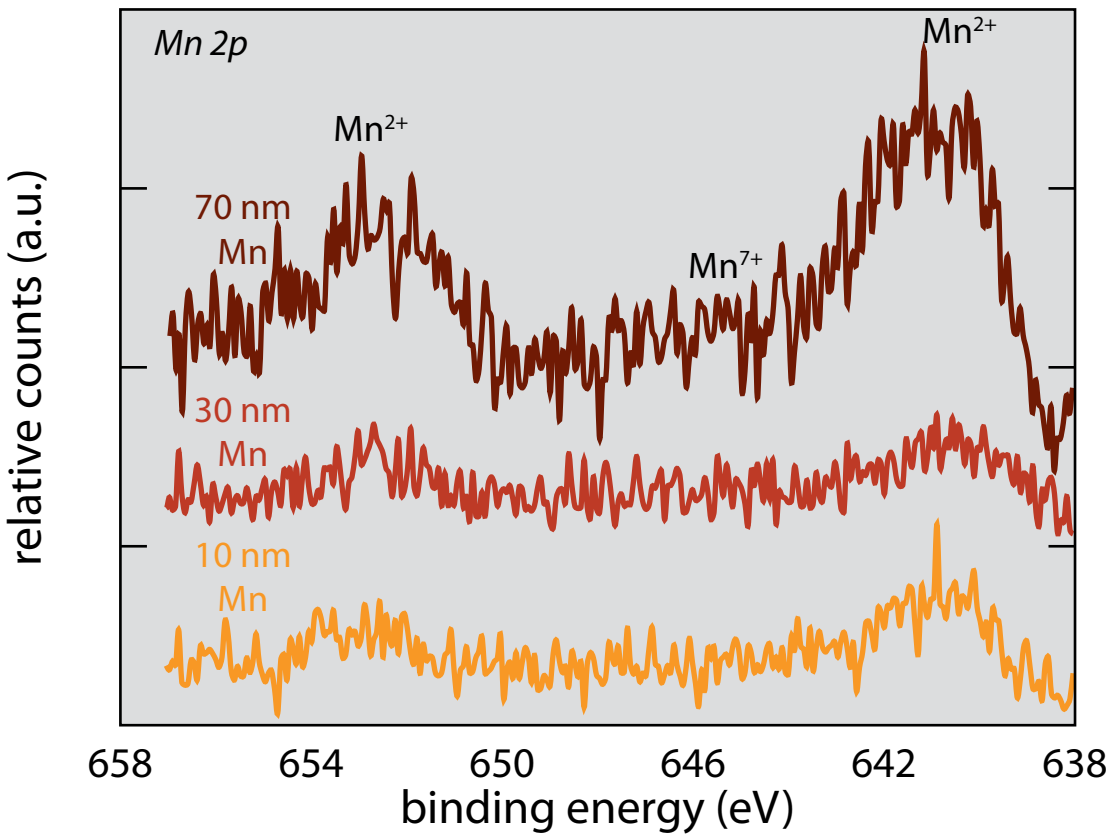
2 Si doping

3 TiO_2

both manganese and oxygen incorporated



both manganese and oxygen incorporated

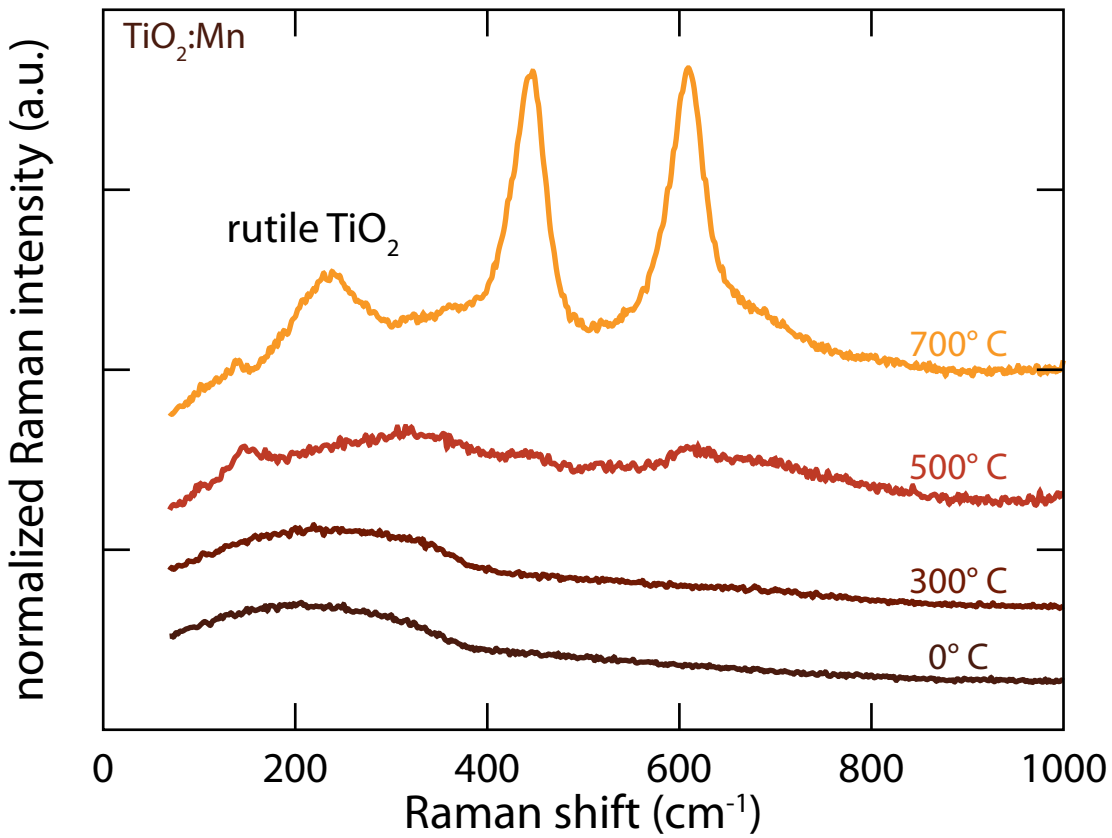


1 Si texturing

2 Si doping

3 TiO_2

we form rutile TiO_2 when annealed



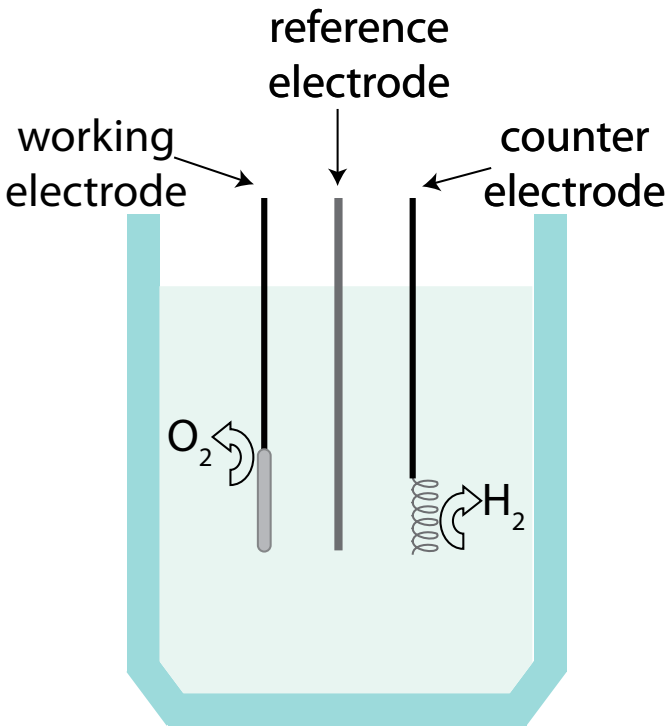
1 Si texturing

2 Si doping

3 TiO_2

can incorporate a variety of transition metals in TiO_2

then measure photoelectrochemical response

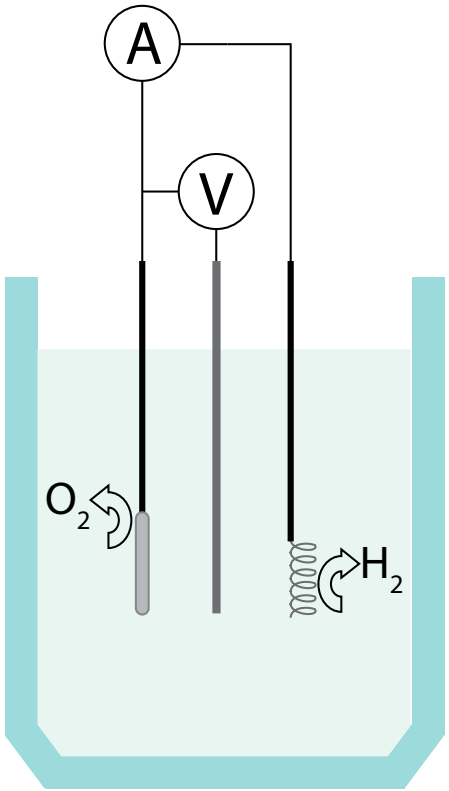


1 Si texturing

2 Si doping

3 TiO_2

then measure photoelectrochemical response



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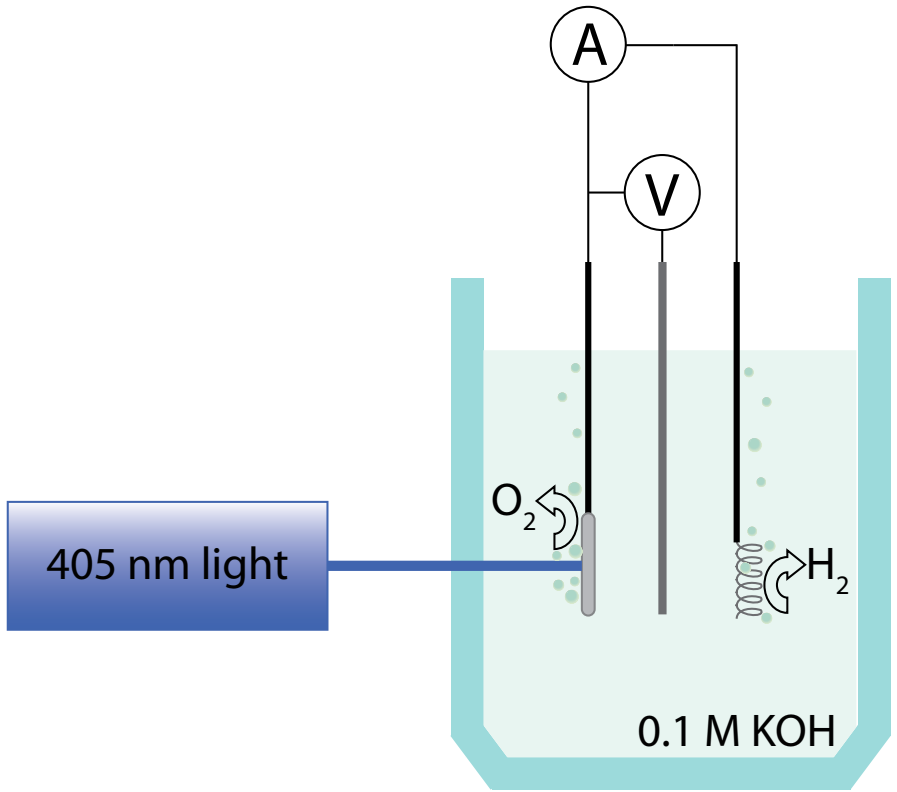
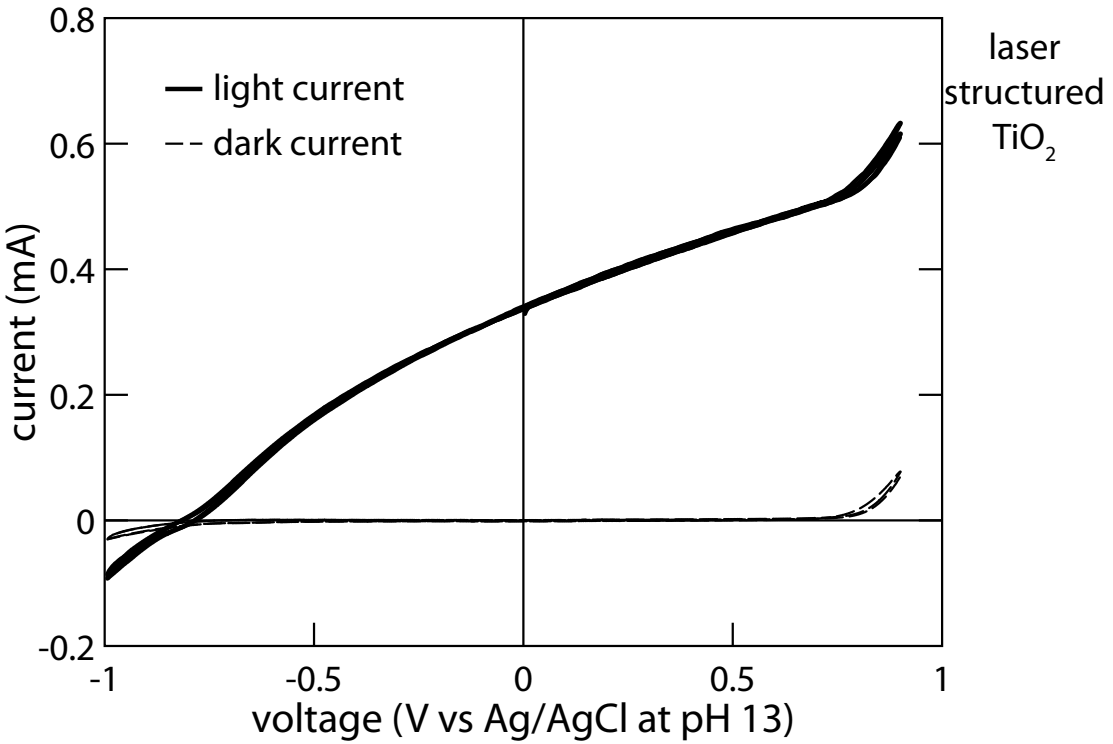


1 Si texturing

2 Si doping

3 TiO_2

water oxidation

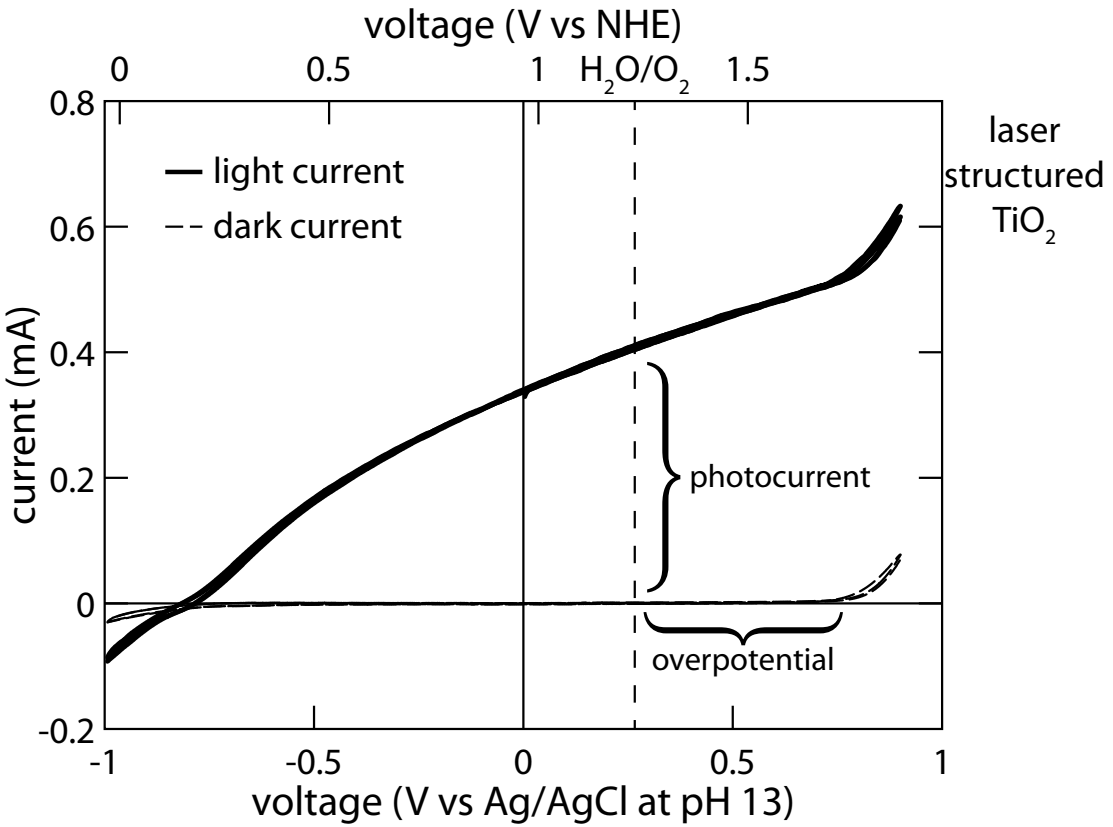


1 Si texturing

2 Si doping

3 TiO_2

water oxidation

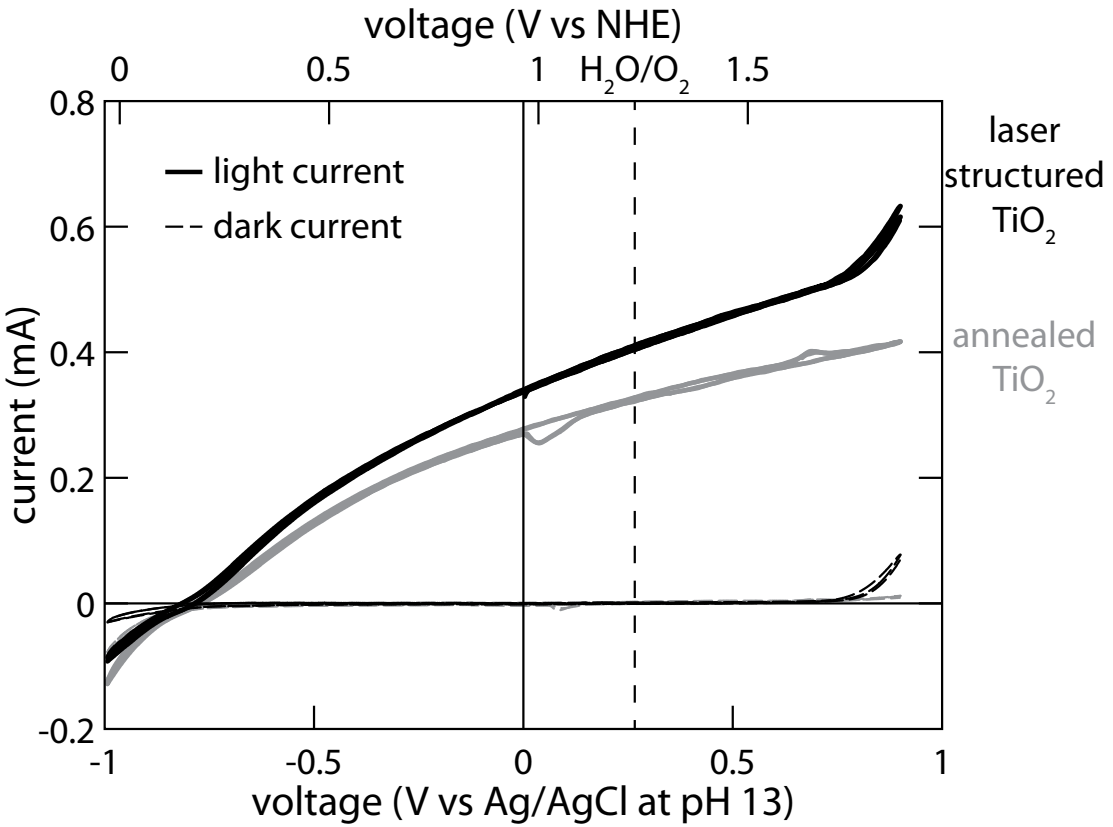


1 Si texturing

2 Si doping

3 TiO_2

water oxidation

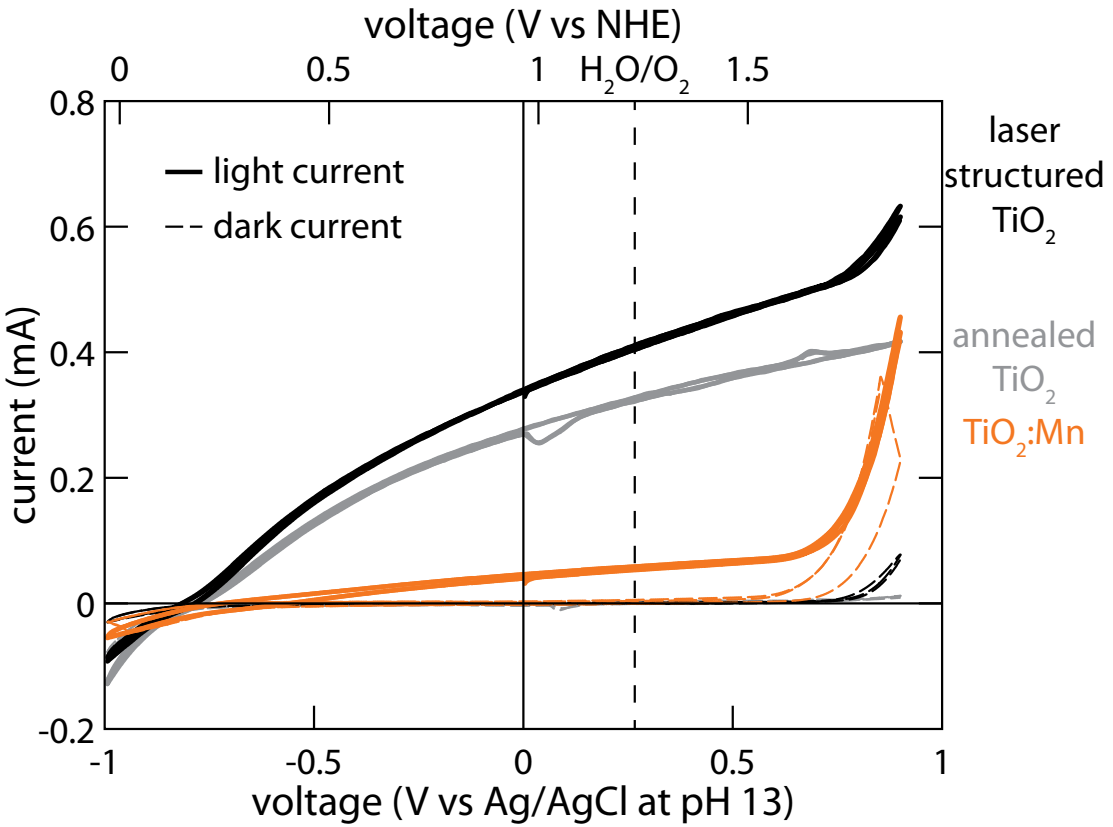


1 Si texturing

2 Si doping

3 TiO_2

water oxidation

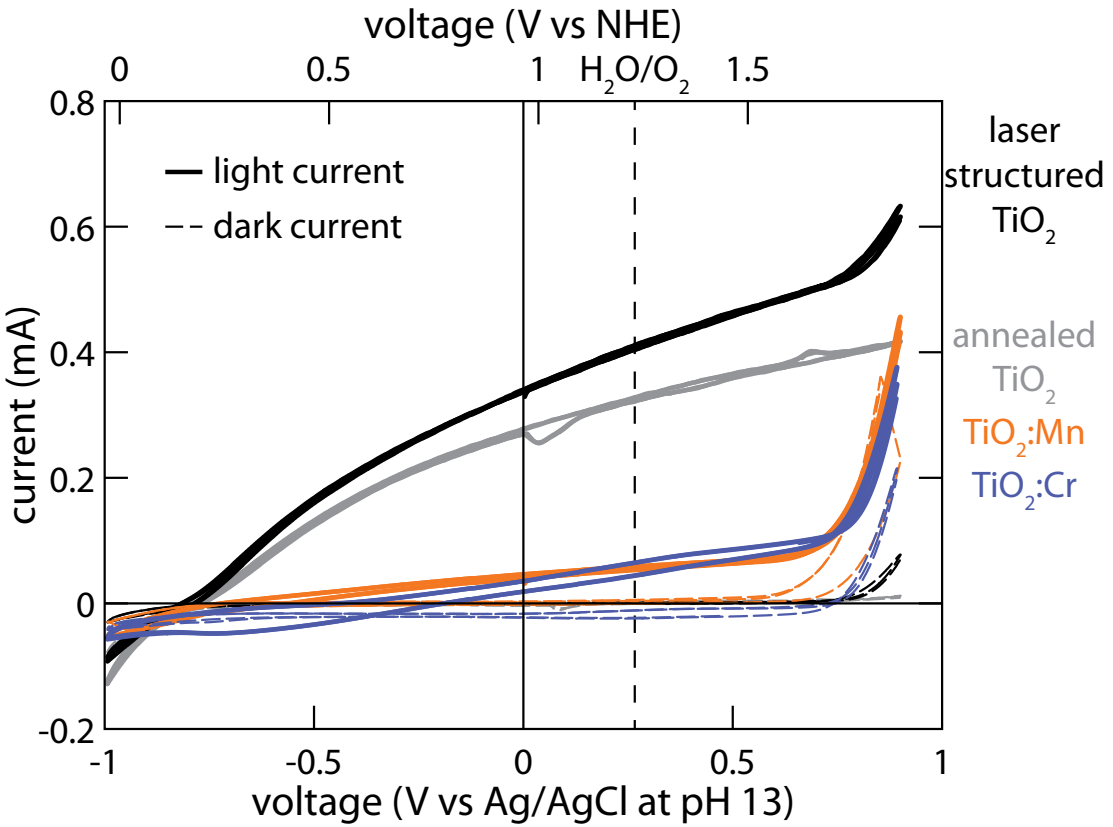


1 Si texturing

2 Si doping

3 TiO_2

water oxidation

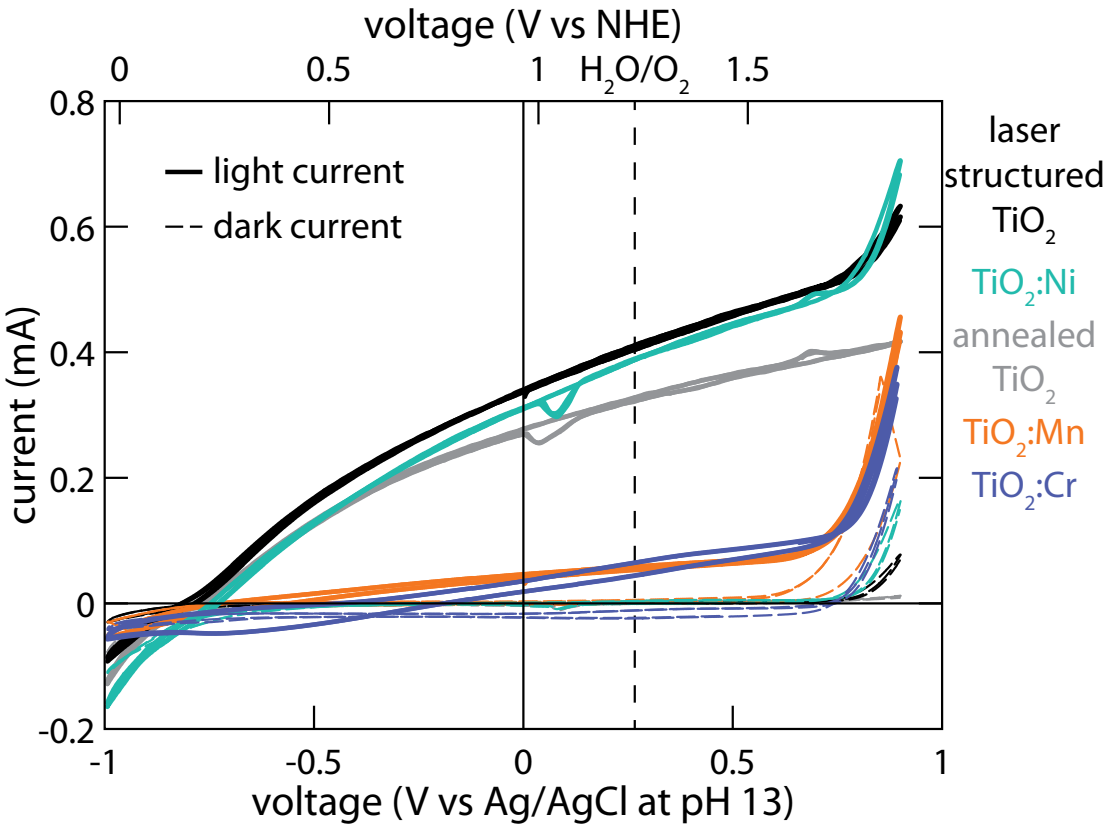


1 Si texturing

2 Si doping

3 TiO_2

water oxidation



1 Si texturing

2 Si doping

3 TiO_2

Produce nanostructured and doped TiO_2

Oxidize water with laser-structured samples

Produce nanostructured and doped TiO_2

Oxidize water with laser-structured samples

Future work: Extend to other oxides
and optimize dopants

Thank you!

Army Research Office
DARPA
Department of Energy
NDSEG
National Science Foundation

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