Optical Hyperdoping: Transforming Semiconductor Band Structure for Solar Energy Harvesting

3G Solar Technologies Multidisciplinary Workshop
MRS Spring Meeting
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Michael Brenner

Alan Aspuru-Guzik

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Eric Mazur


Experimental Approach to
selecting precursors for doping
Challenge : many precursors are
not very volatile

Harvard NSF SOLAR team

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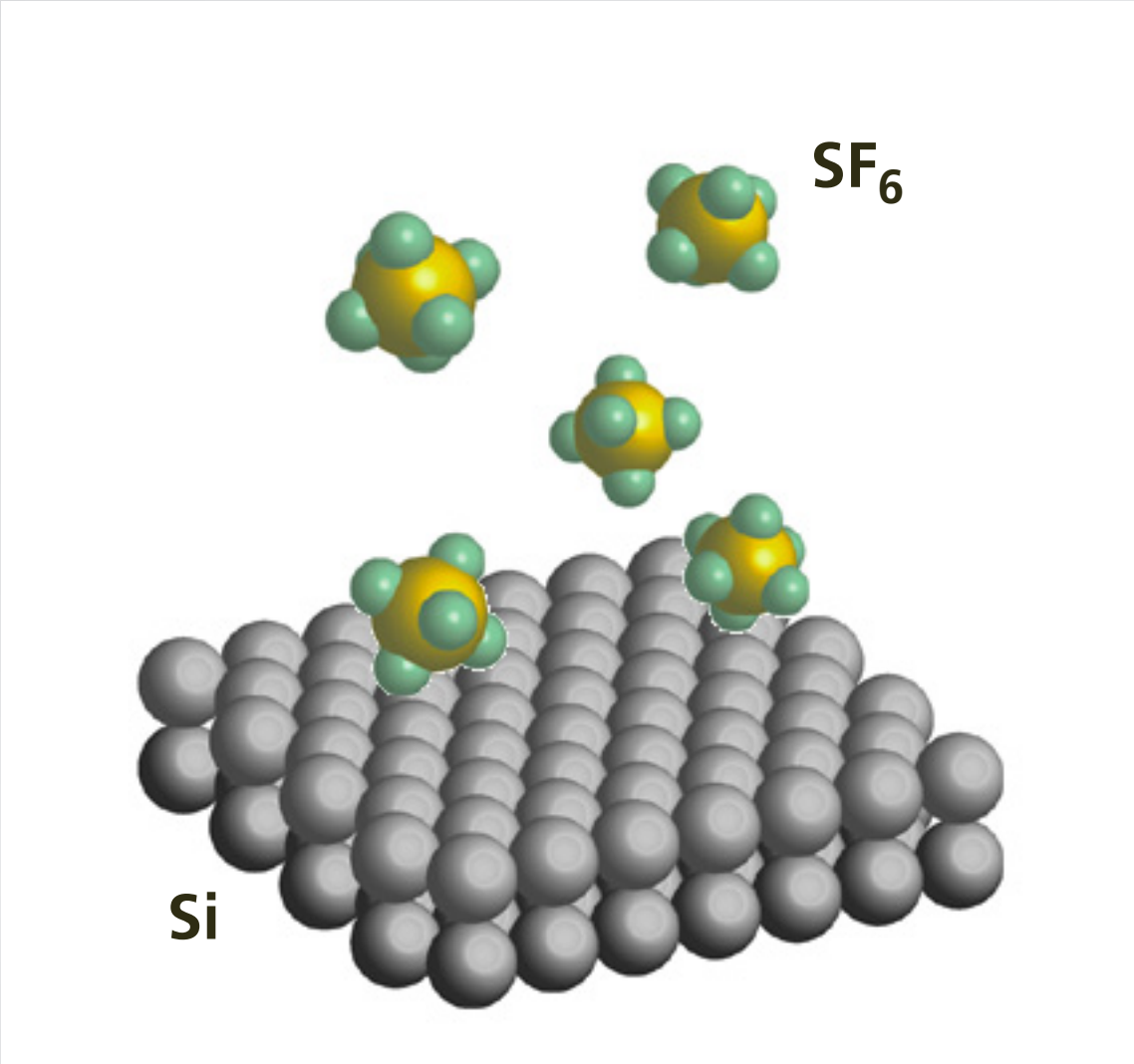
	Man Hong Yung (PD)
Brenner group:	Tobias Schneider (PD)
	Scott Norris (PD)
	Niall Mangan (GS)
Friend group:	Anne Co (PD)
	Stephen Jensen (GS)
Mazur group:	Meng-Ju Sher (GS)
	Yuting Lin (GS)
	Kasey Phillips (GS)

Introduction

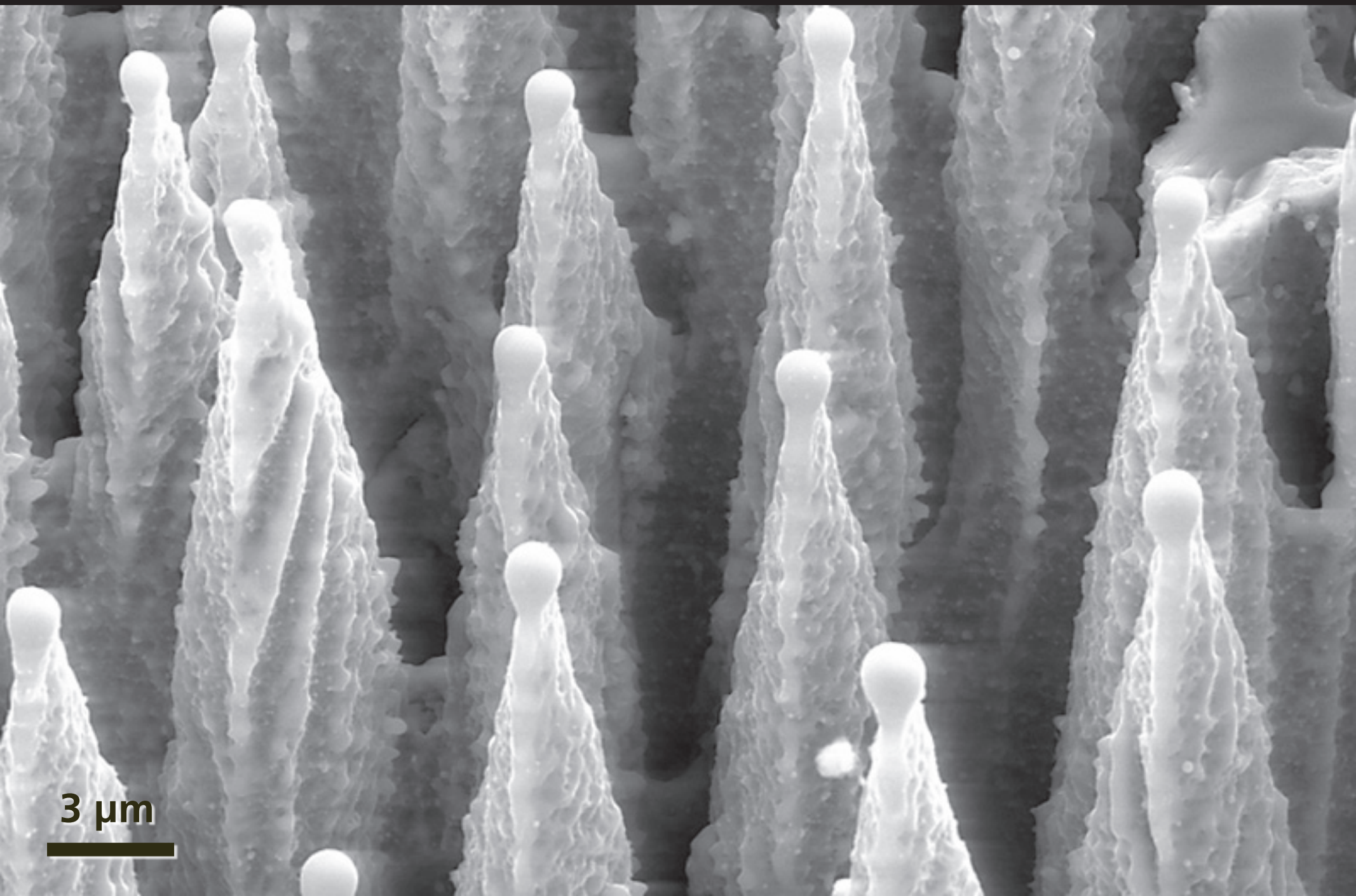


irradiate with 100-fs 10 kJ/m^2 pulses

Introduction

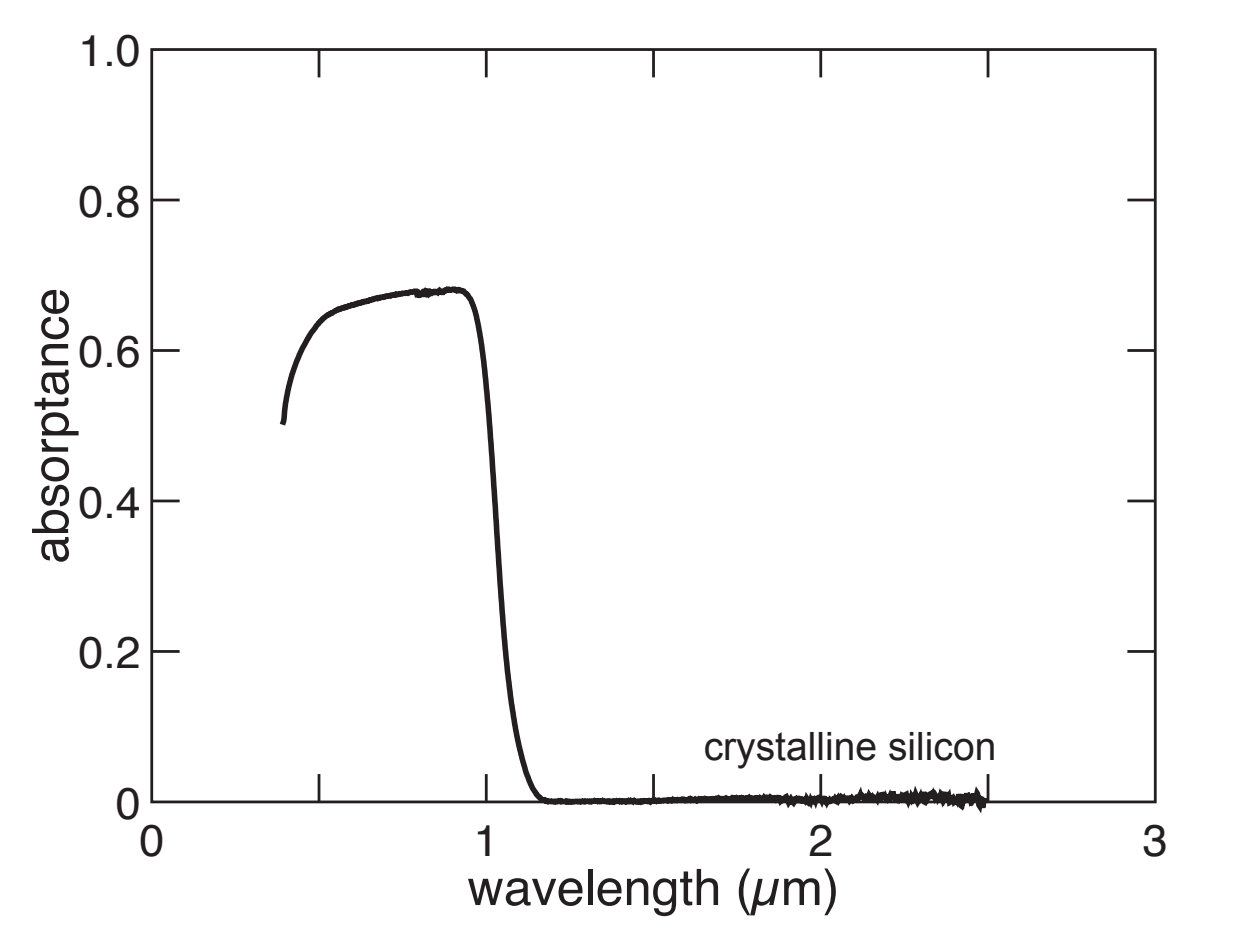
“black silicon”

Introduction



Introduction

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



Introduction

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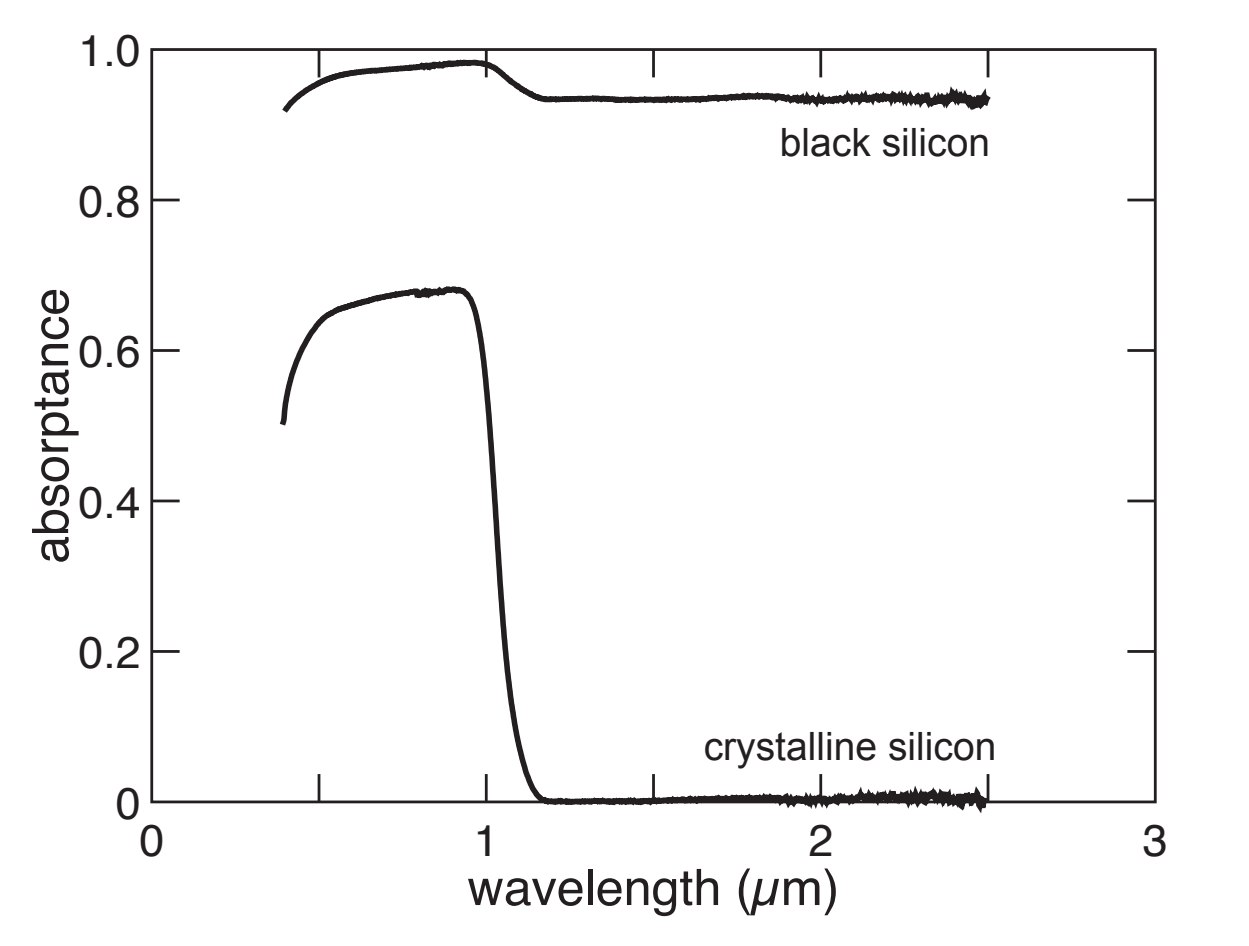

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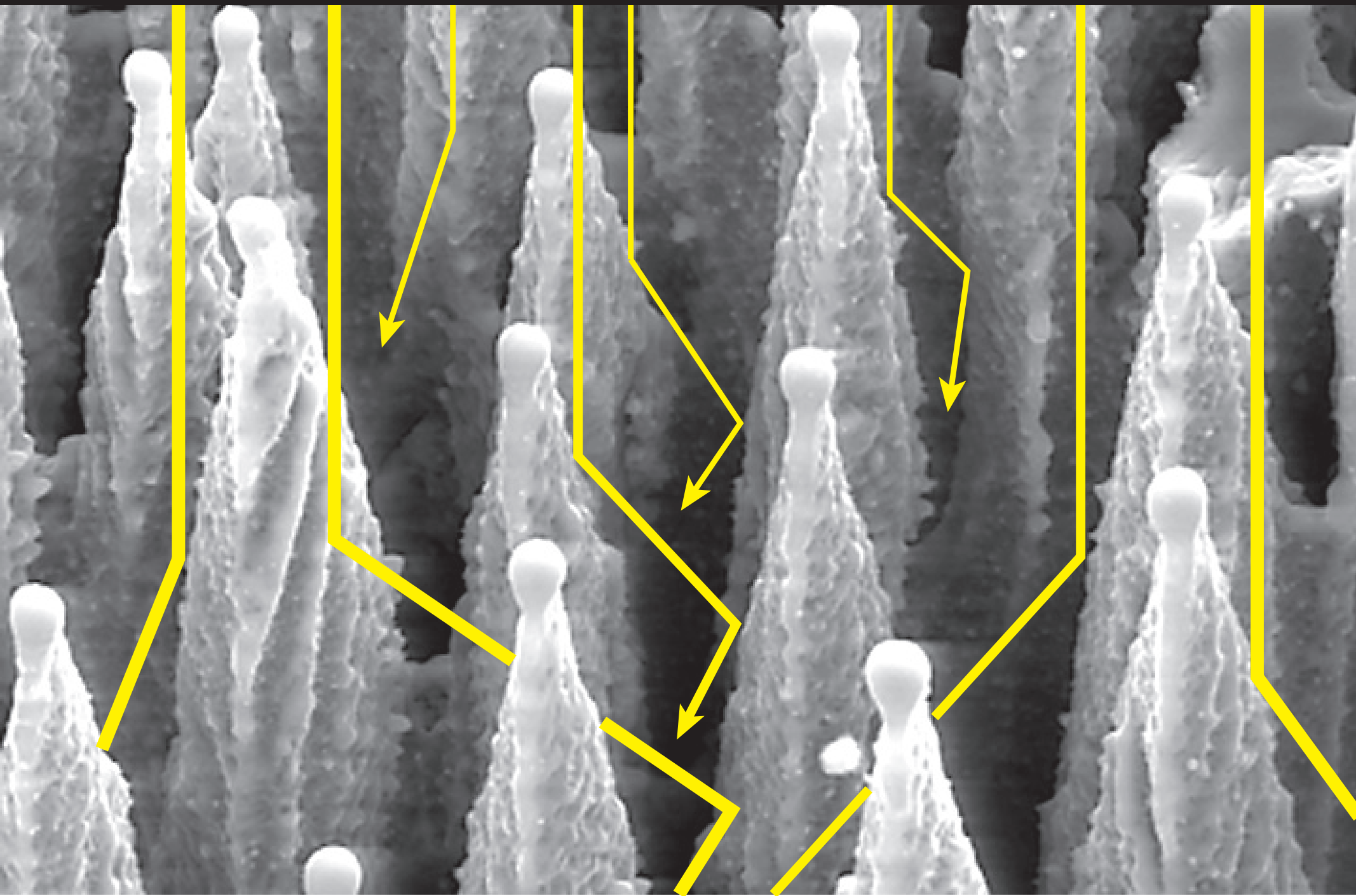

Introduction

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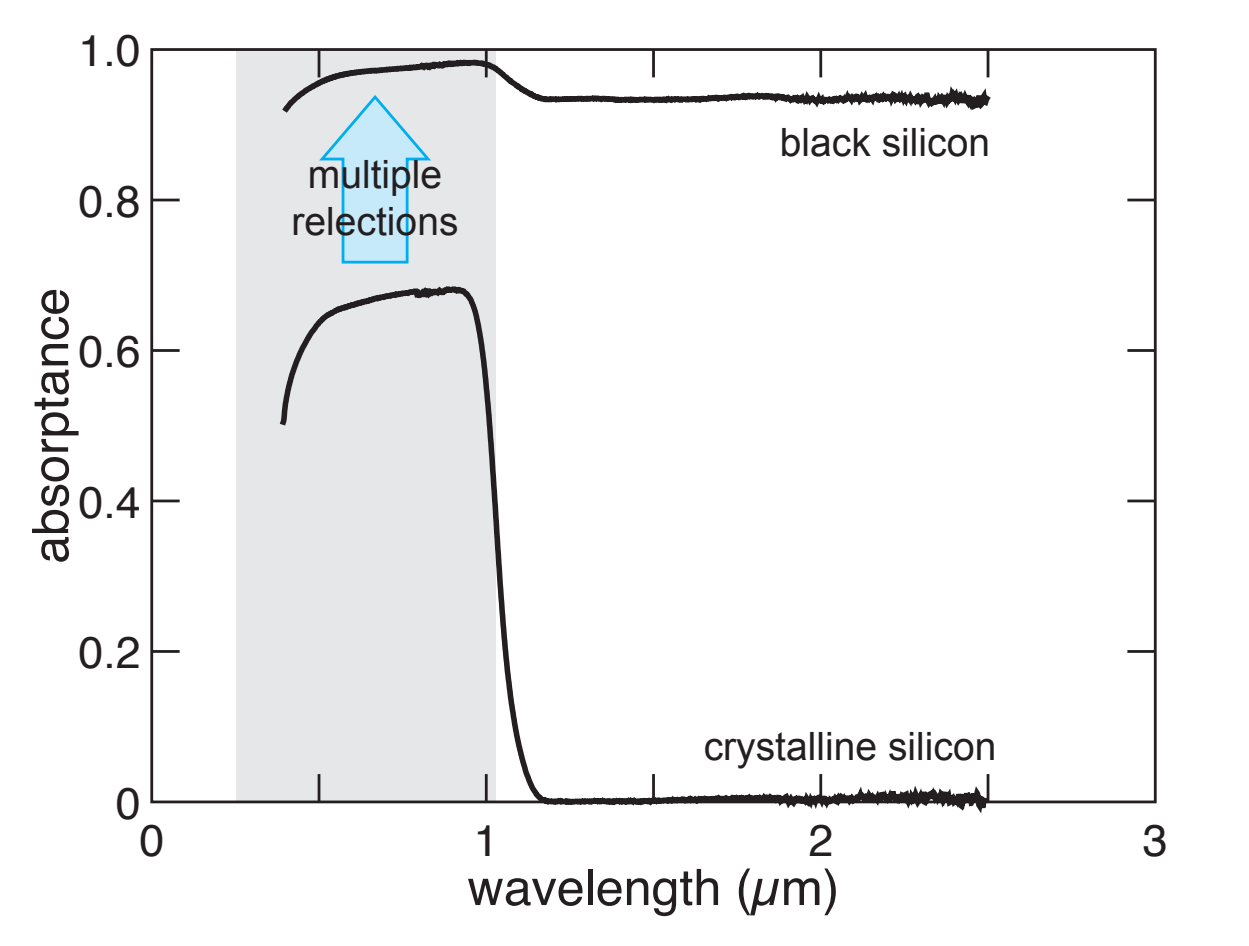


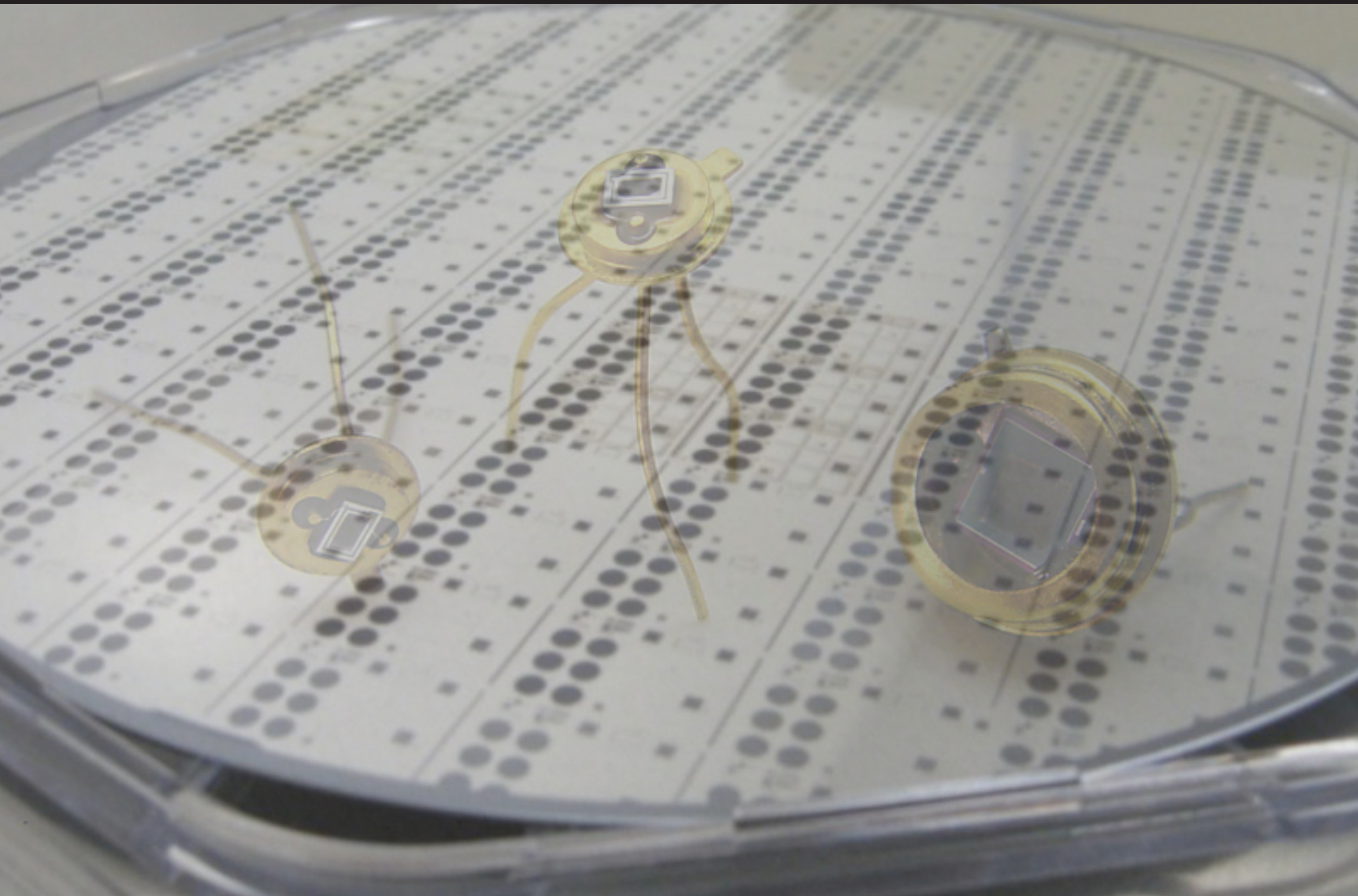
Introduction

band structure changes: defects and/or impurities

Introduction

optical hyperdoping puts 2% of sulfur in 200-nm surface layer

Introduction



Introduction

open questions

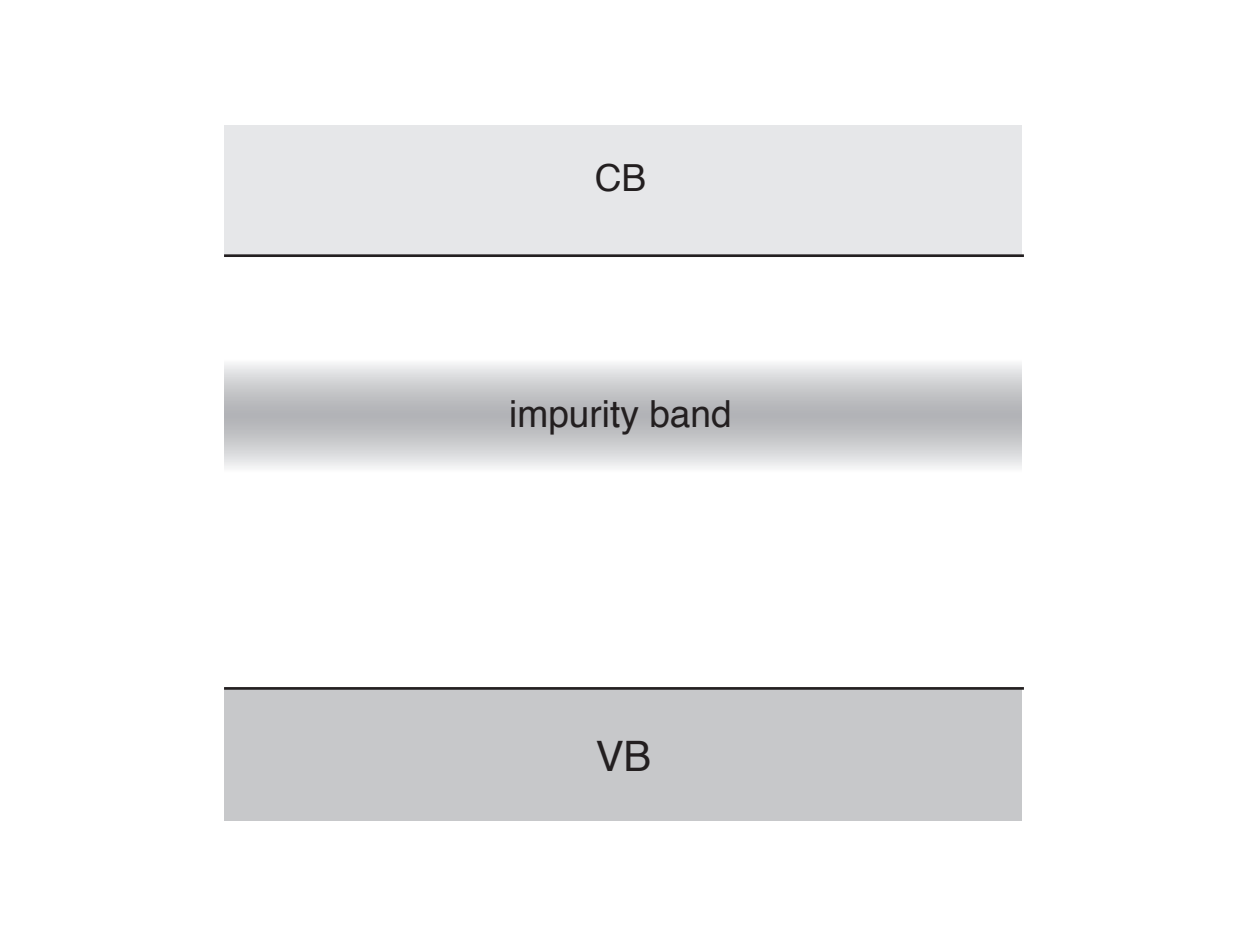
- how do the impurities get incorporated?
- can we use optical hyperdoping for solar cells?

Outline

- goals
- optimizing dopant profile
- intermediate band

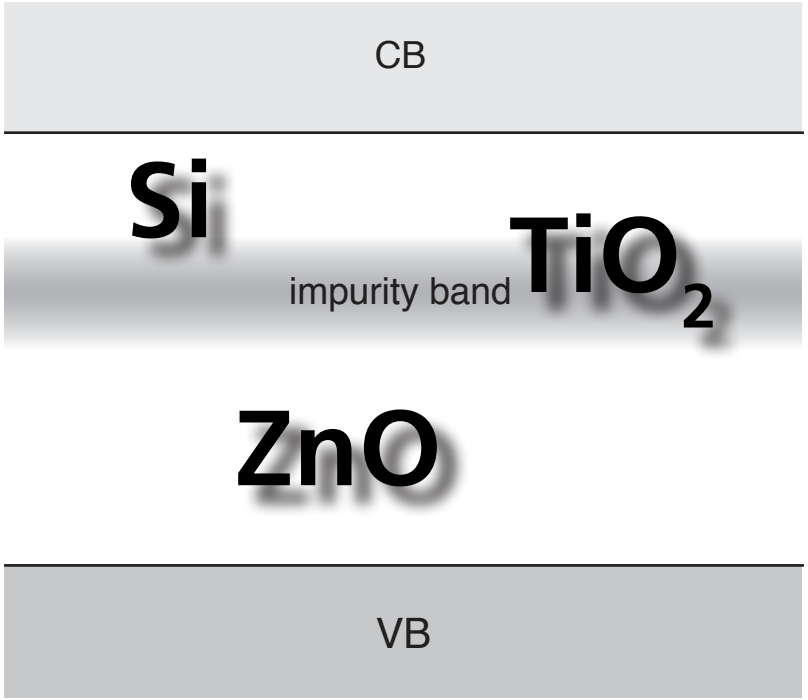
Goals

interesting properties due to intermediate band

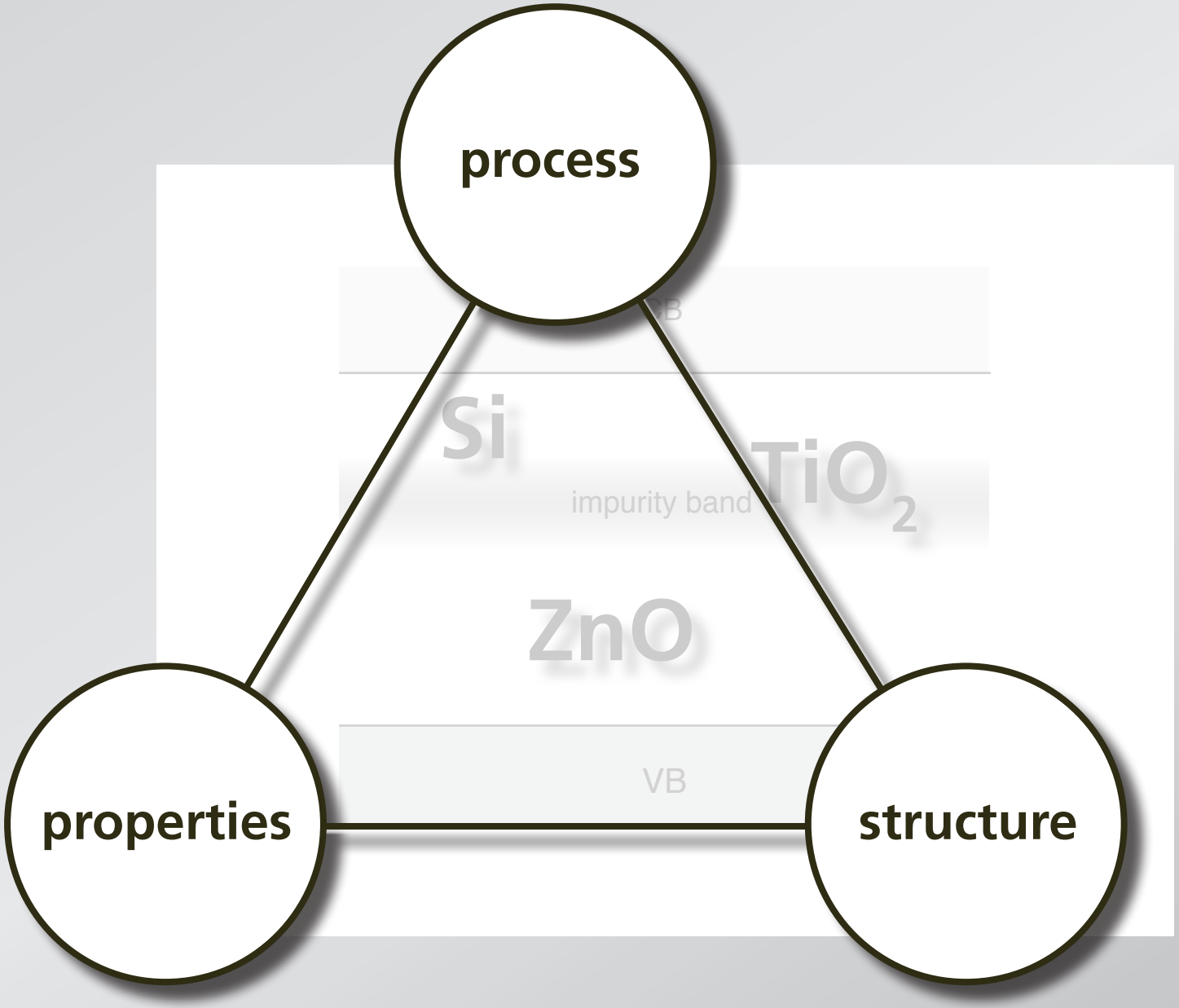


Goals

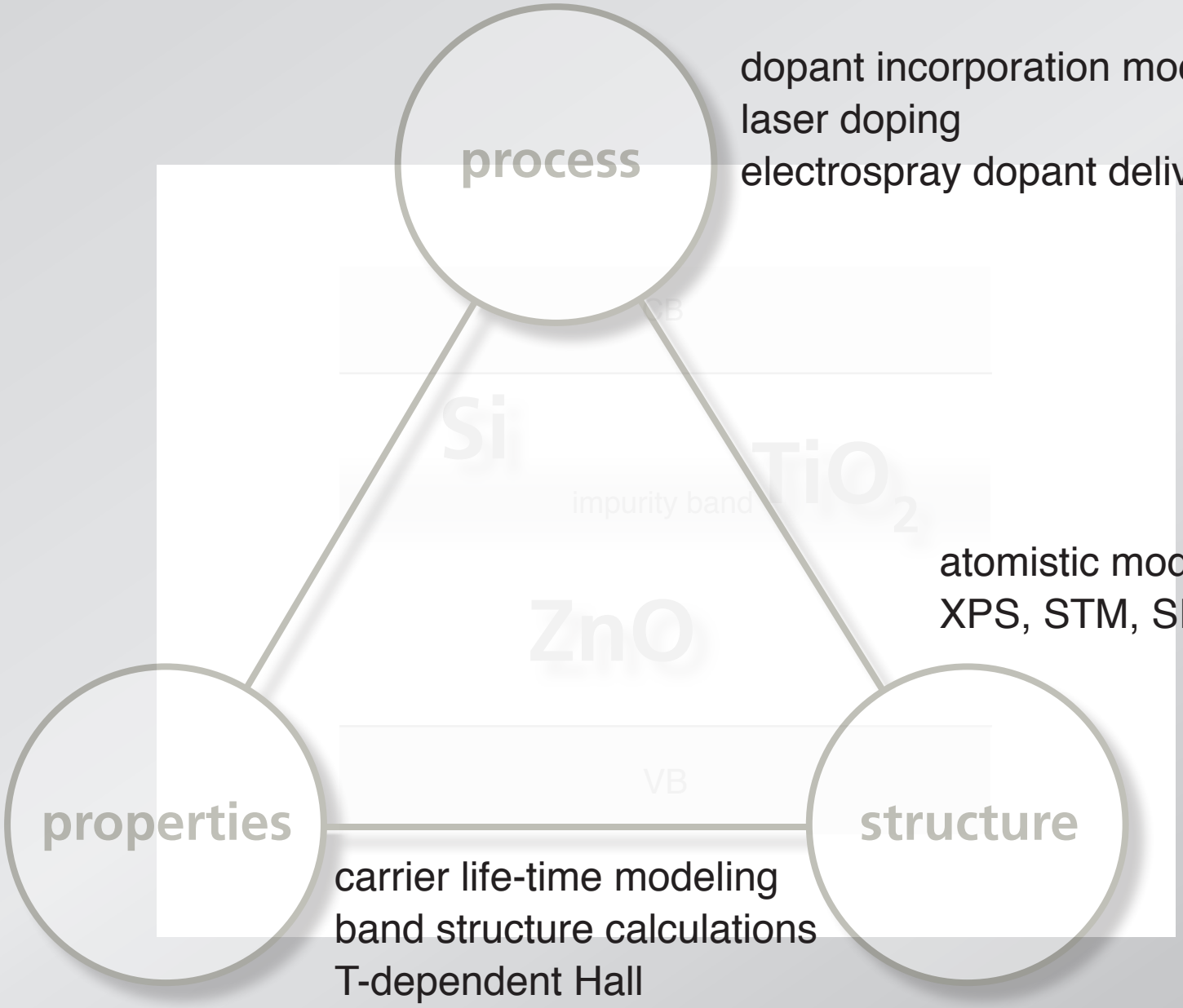
generalize



Goals


process
properties
structure
CB
Si
impurity band
TiO2
ZnO
VB

Goals



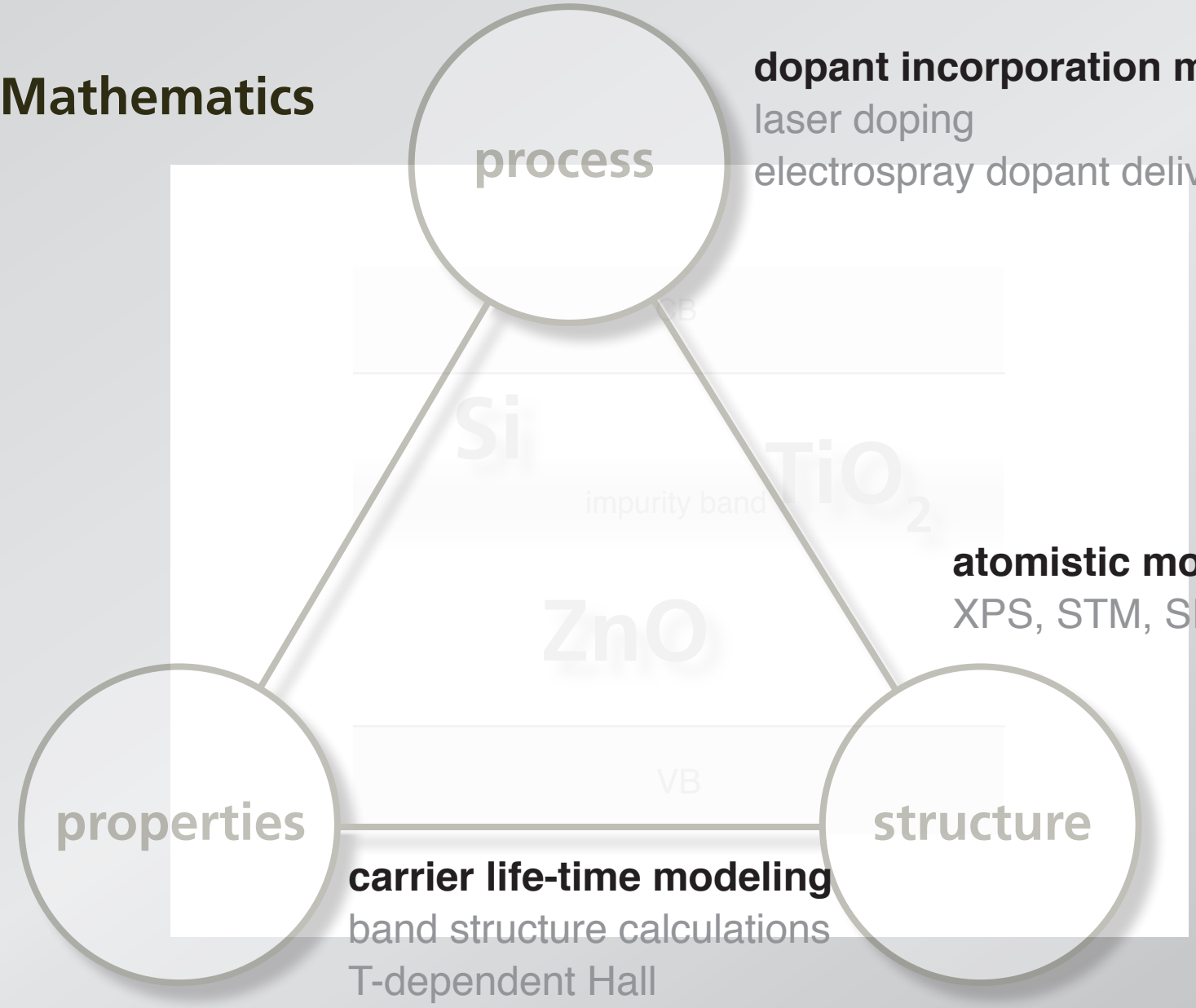
dopant incorporation modeling
laser doping
electrospray dopant delivery

atomistic modeling
XPS, STM, SIMS

carrier life-time modeling
band structure calculations
T-dependent Hall
IR spectroscopy

Goals

Mathematics



dopant incorporation modeling
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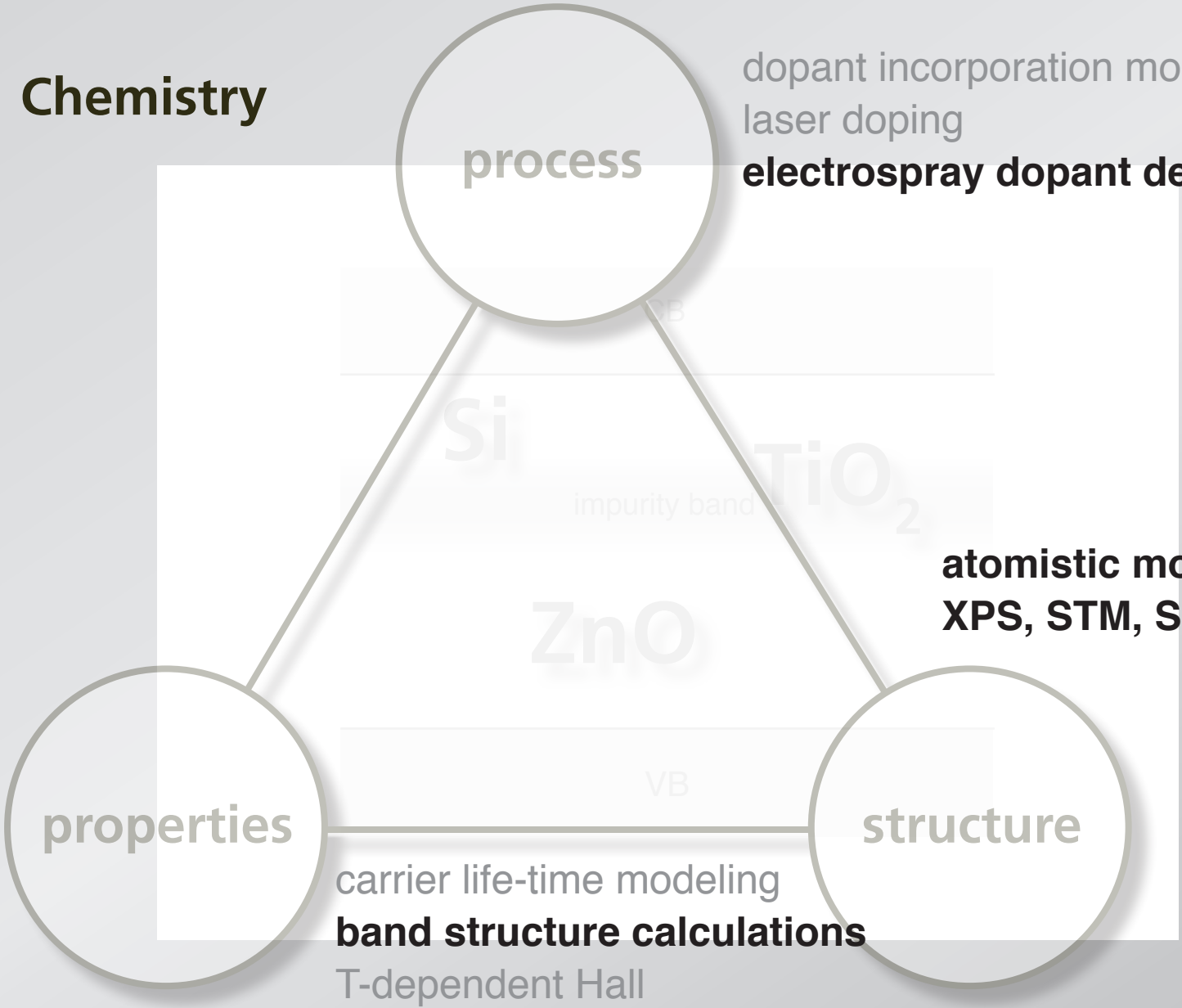
Goals

Chemistry



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atomistic modeling
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carrier life-time modeling
band structure calculations
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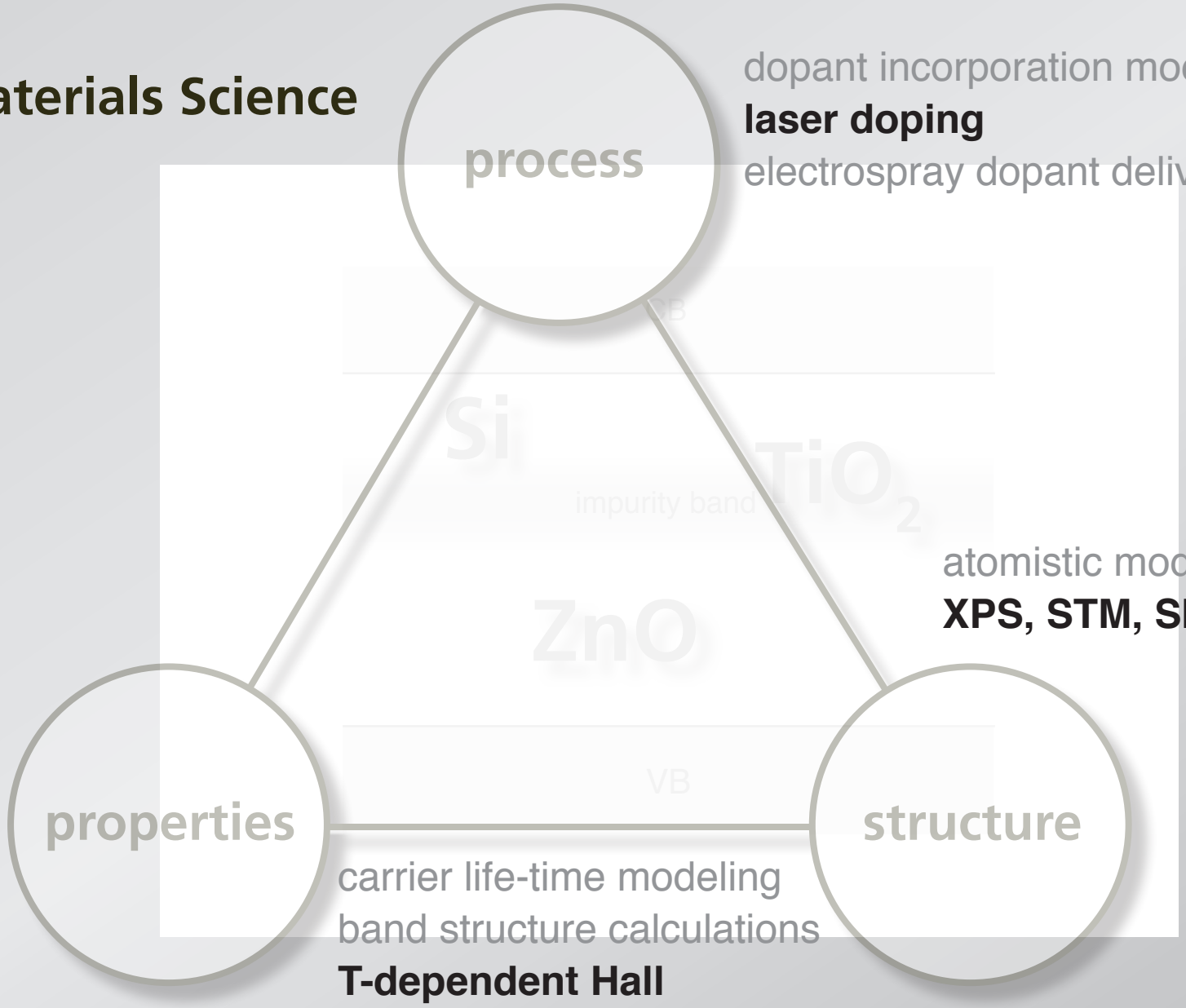
IR spectroscopy

Goals

Materials Science



dopant incorporation modeling
laser doping
electrospray dopant delivery

atomistic modeling
XPS, STM, SIMS

carrier life-time modeling
band structure calculations
T-dependent Hall
IR spectroscopy

Outline

- goals
- **optimizing dopant profile**
- intermediate band

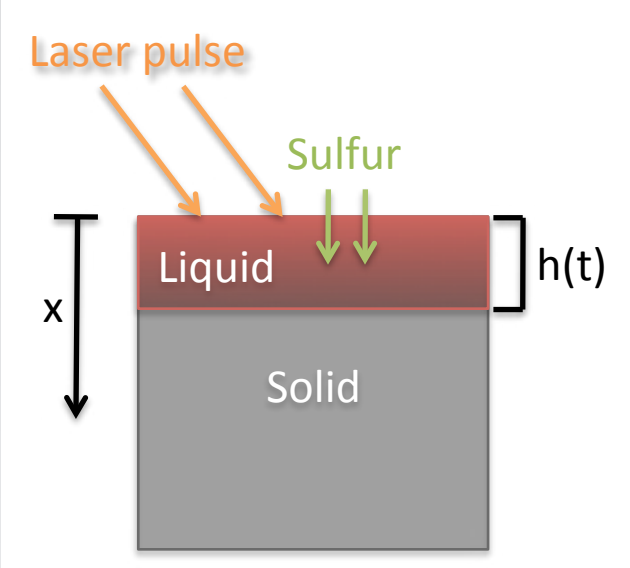
Optimizing dopant profile

Theoretical agenda

- explain enhanced doping
- optimize dopant profile for device design
- design process for optimal dopant profile

Optimizing dopant profile

why does enhanced doping occur?



physical mechanisms:

- melting and resolidification of thin layer
- sulfur diffusion into liquid silicon
- incorporation into solid during resolidification

Optimizing dopant profile

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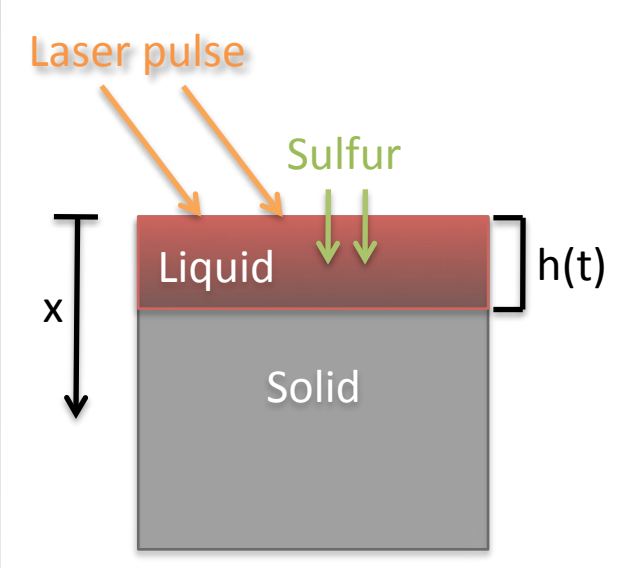


mathematical model:

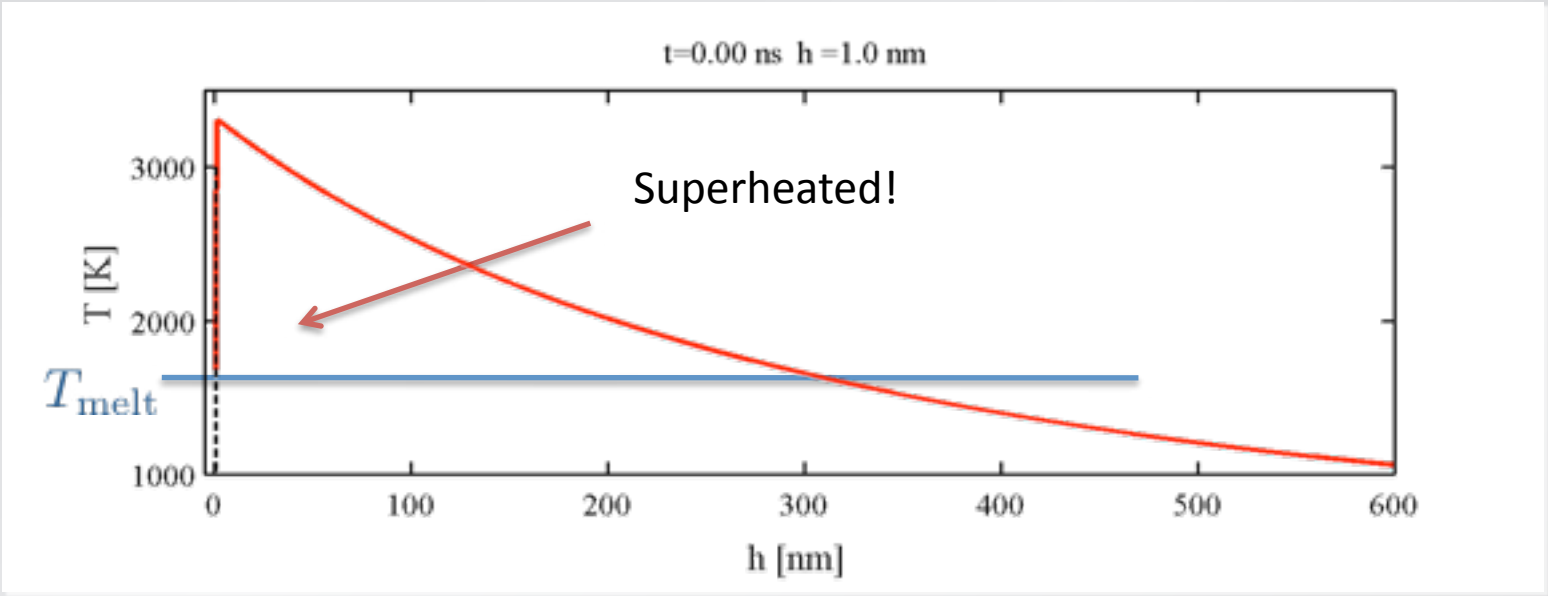
- calculate dynamics of two fields
- temperature $T(x,t)$
- sulfur concentration $c(x,t)$

Optimizing dopant profile

calculation step 1: temperature profile set up by laser

Optimizing dopant profile

calculation step 1: temperature profile set up by laser



Optimizing dopant profile

calculation step 2: solid melts, solute incorporated

Optimizing dopant profile

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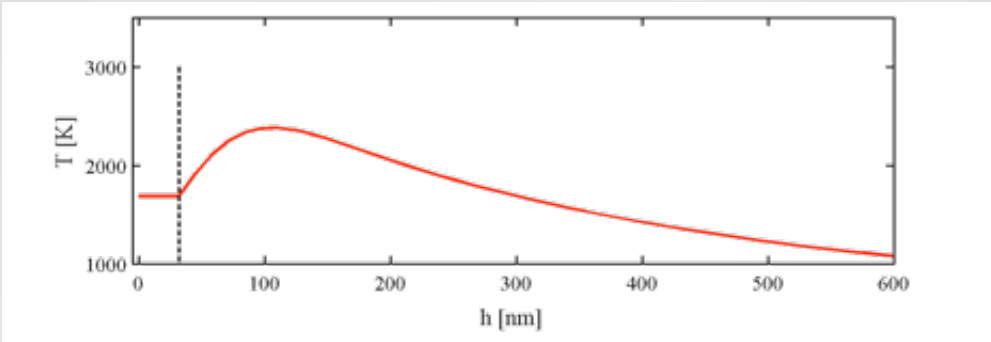
melting:

- heat diffusion $T_t = D_{th}\, T_{xx}$
- energy balance $L_V \dot{h} = [[-\kappa_T\, T_x]]$



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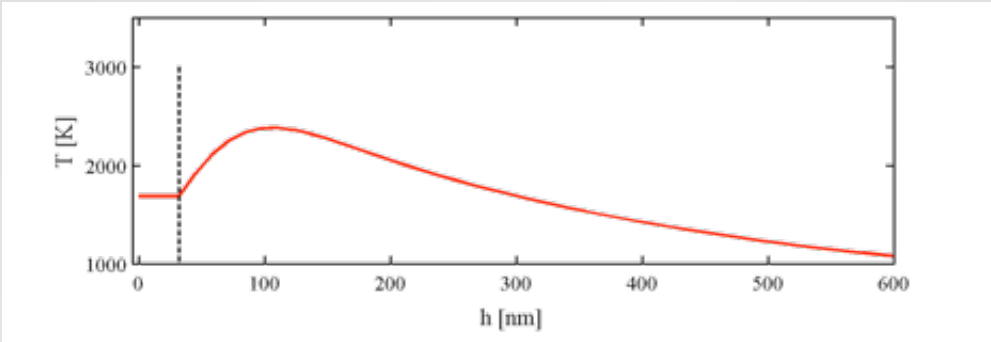
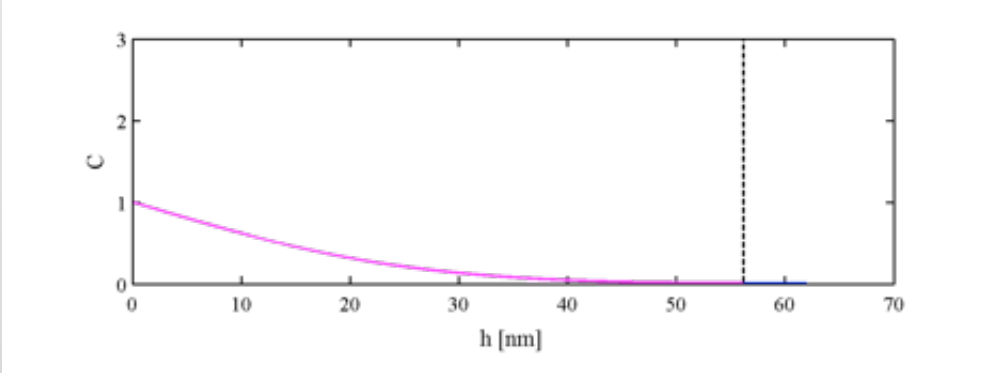


incorporation:

- solute diffusion $c_t = D c_{xx}$
- mass balance $[[c]]\dot{h} = [[-D\, c_x]]$



Optimizing dopant profile

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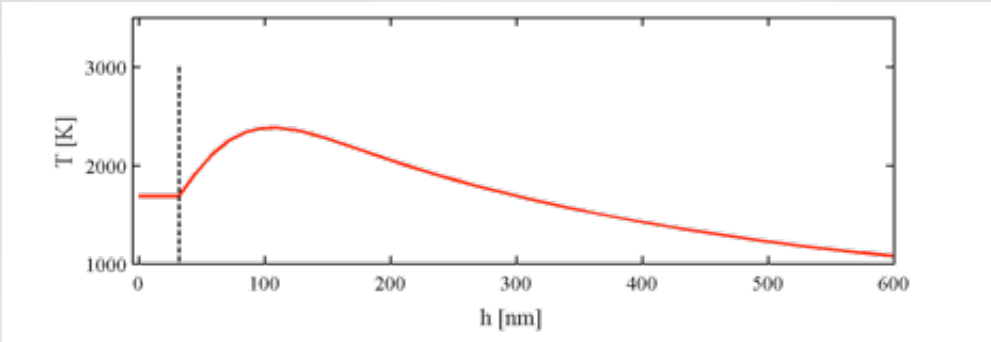

incorporation:

- solute diffusion $c_t = D c_{xx}$
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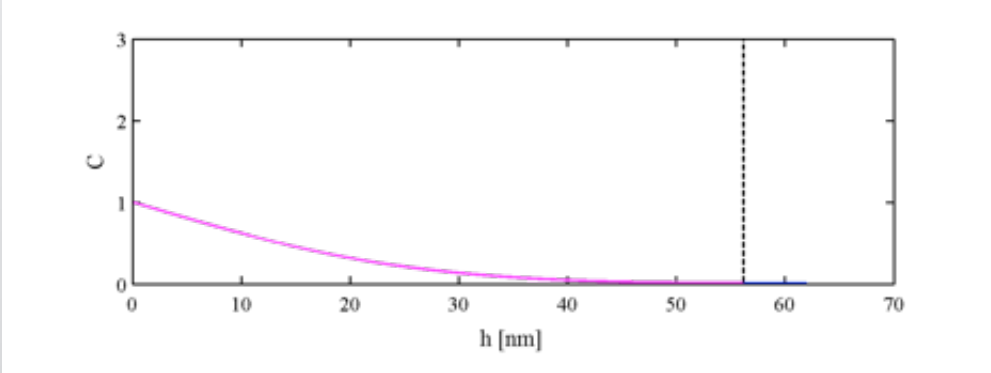
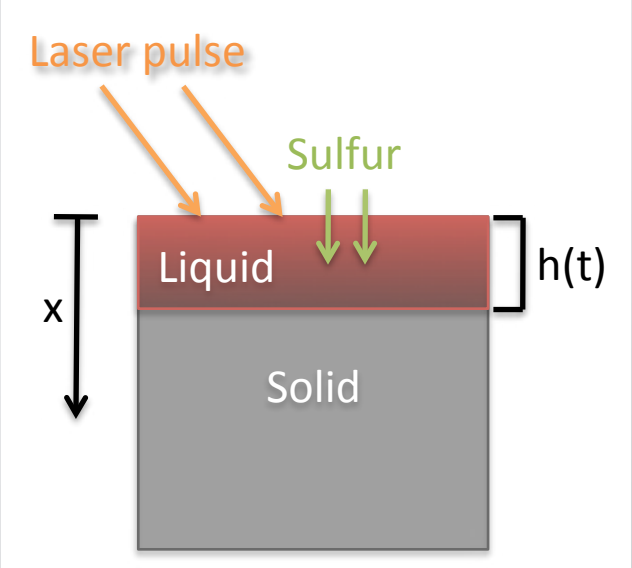
$$T = T_{\mathrm{melt}} + m c^L(h) - \mu \dot{h}$$



Optimizing dopant profile

boundary condition critically affects dopant profile



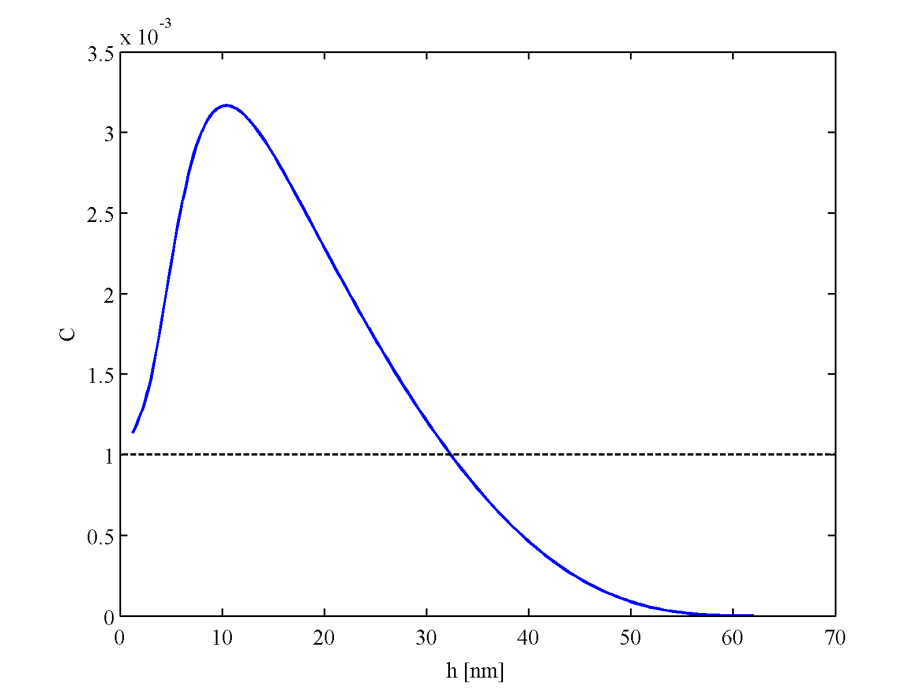
Optimizing dopant profile

two scenarios

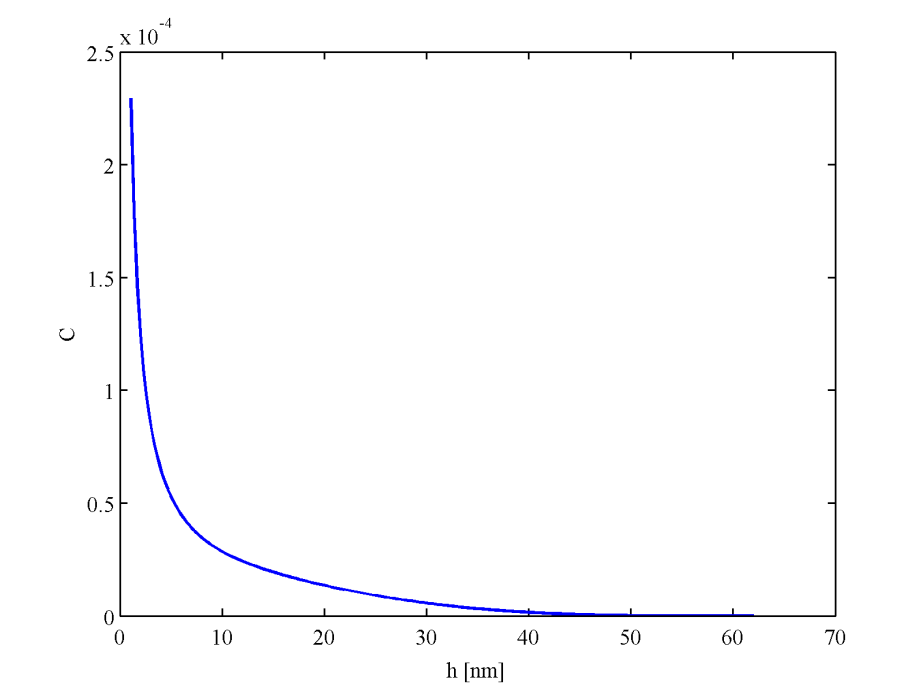
Optimizing dopant profile

two scenarios

constant concentration



constant sulfur flux



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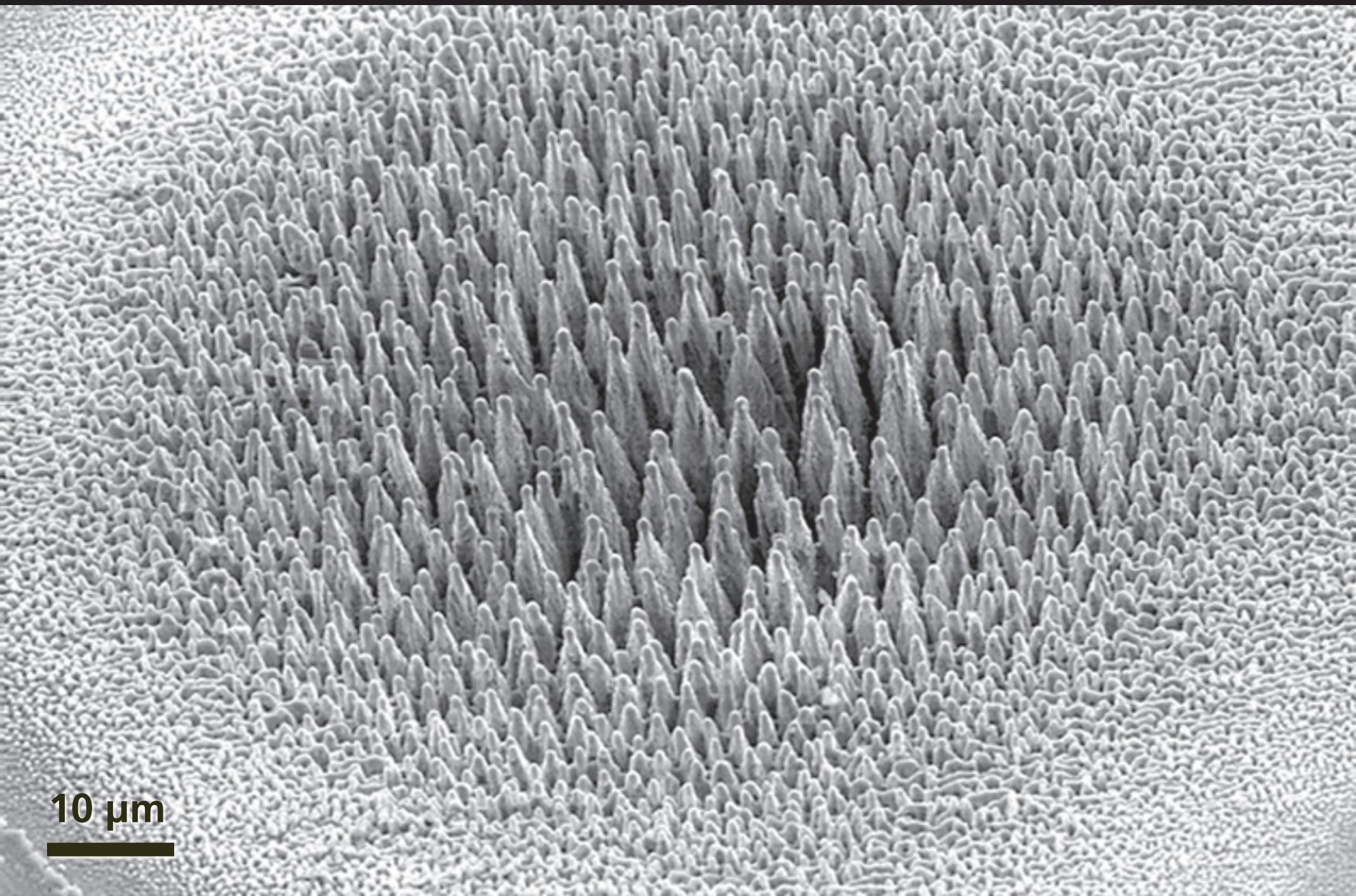

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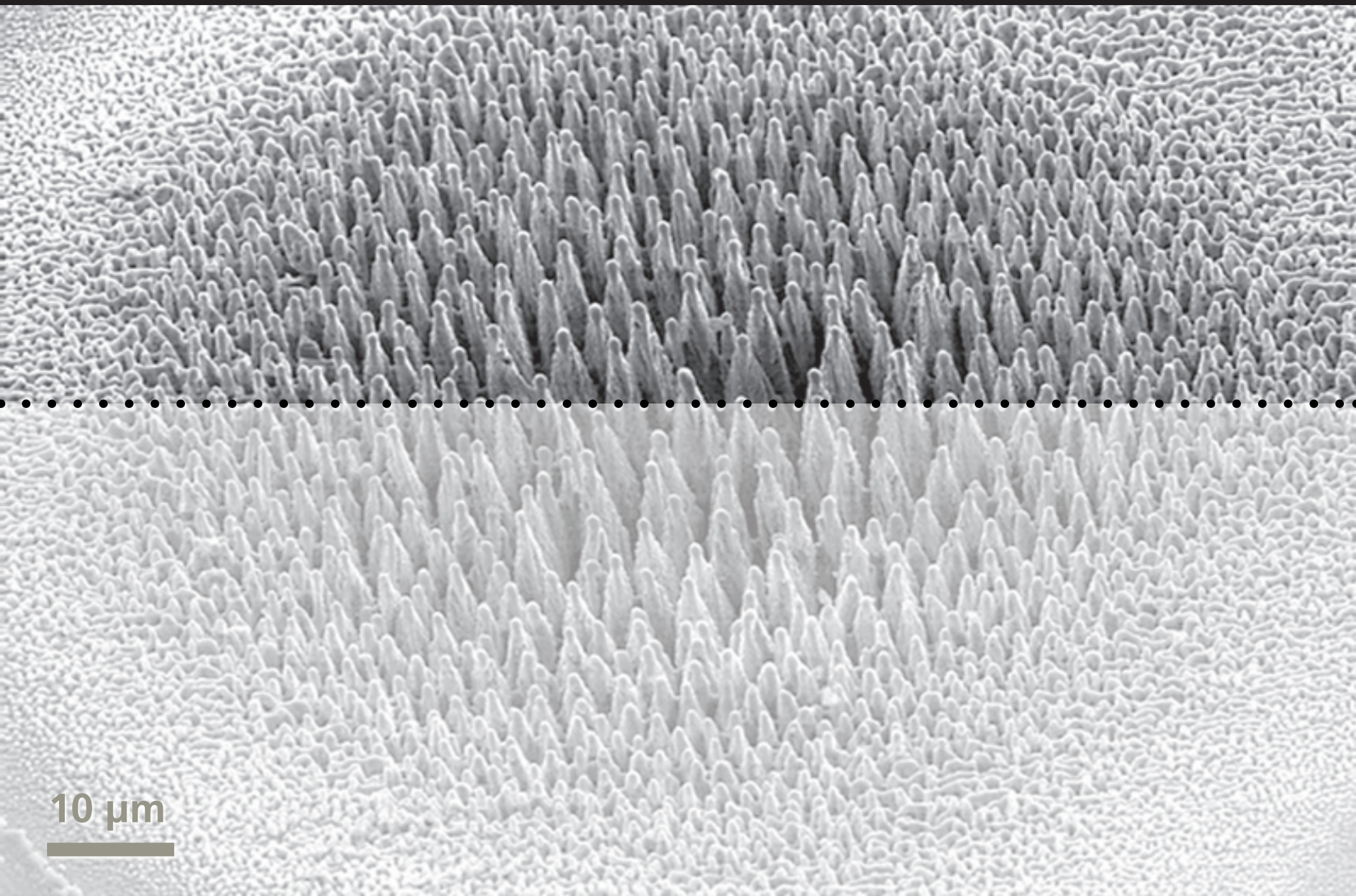

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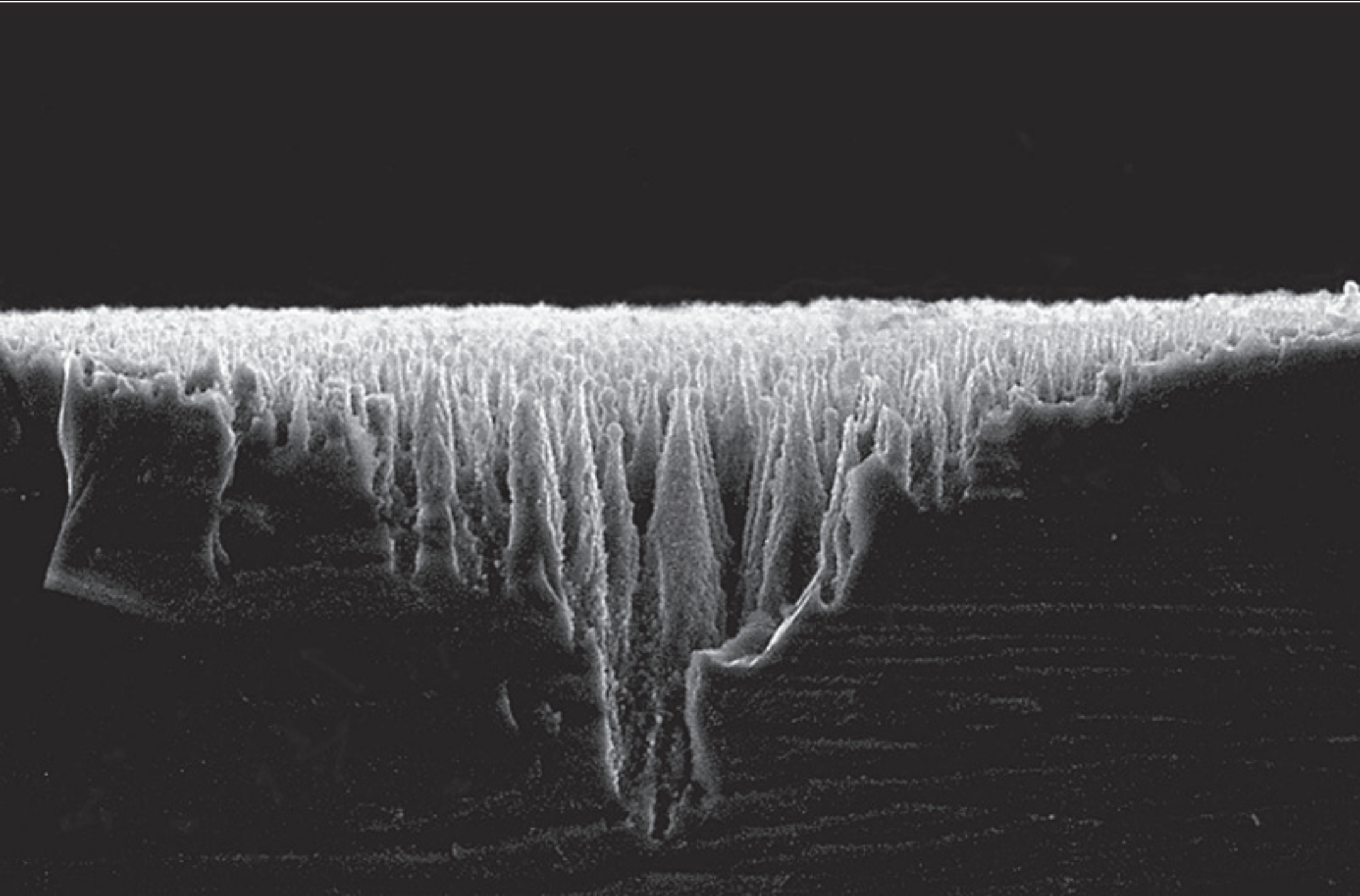

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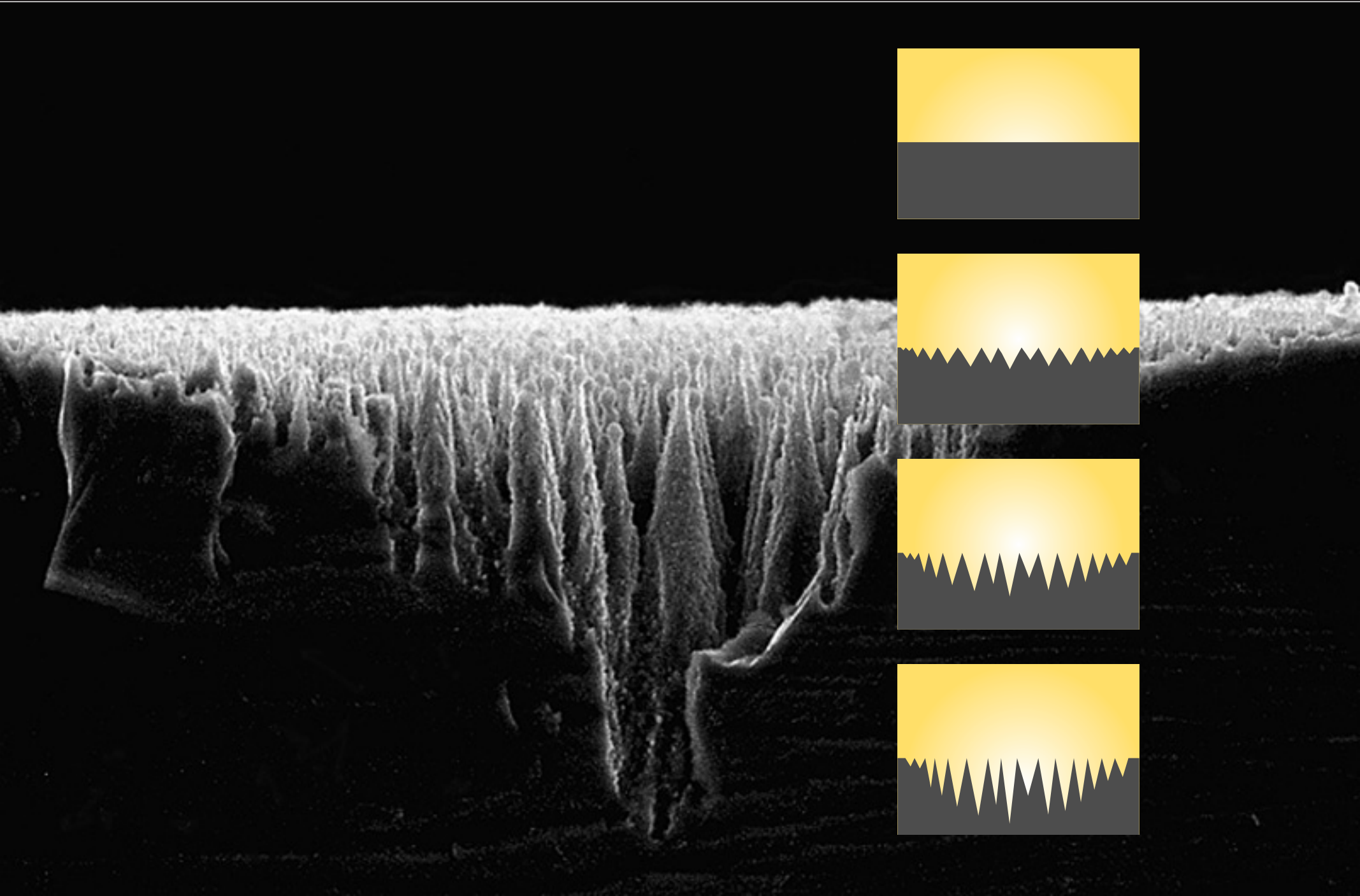

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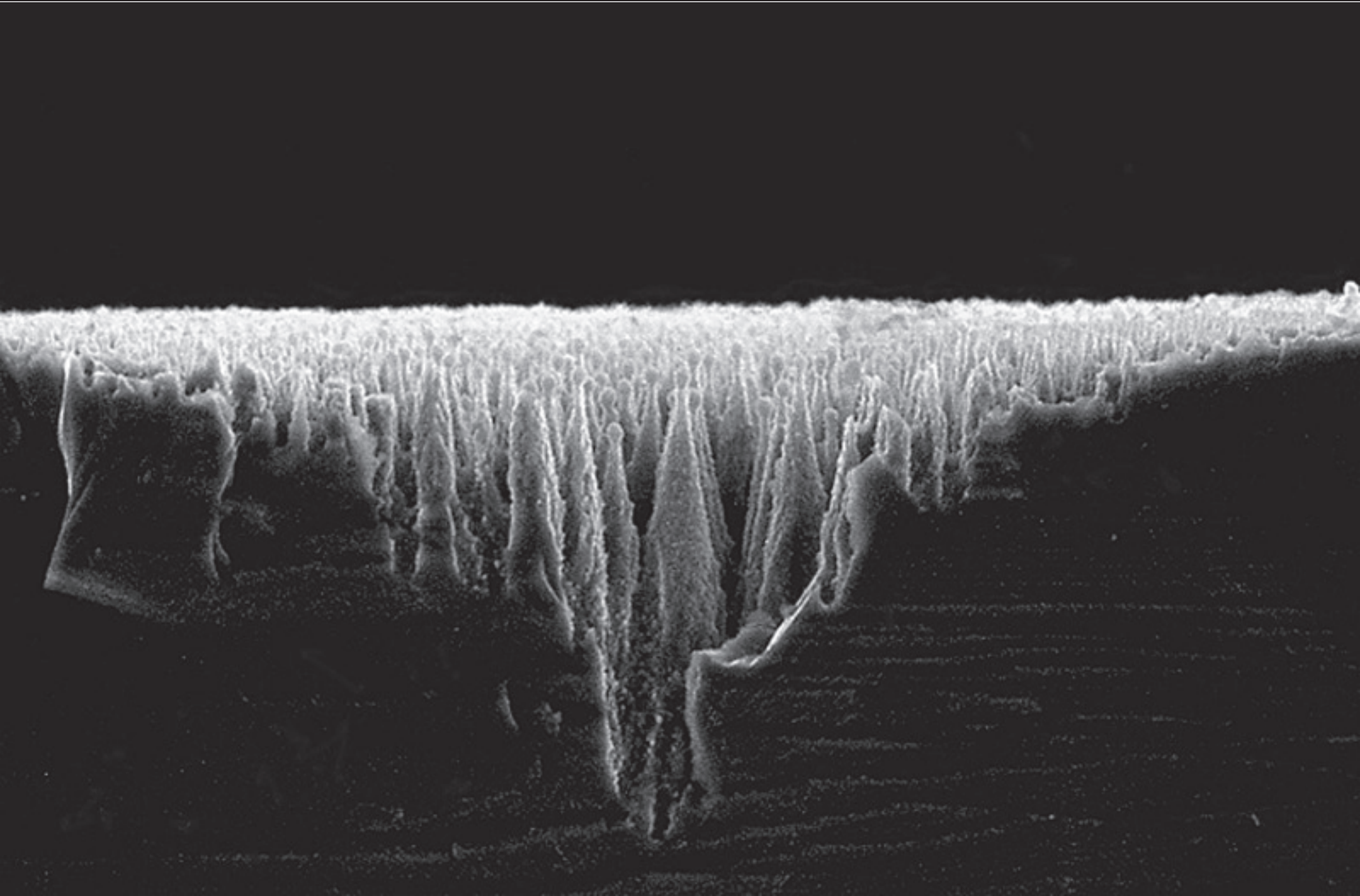

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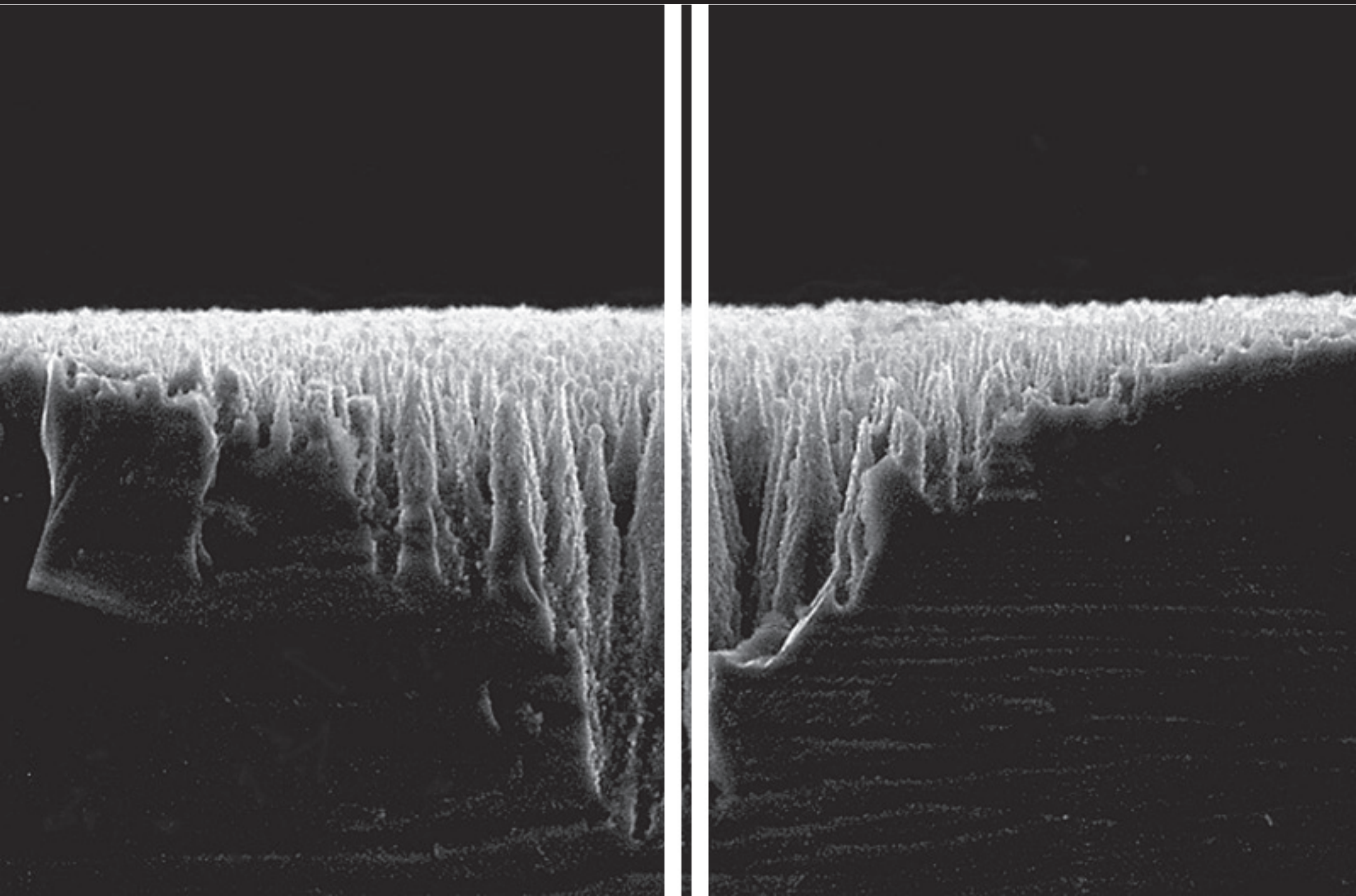

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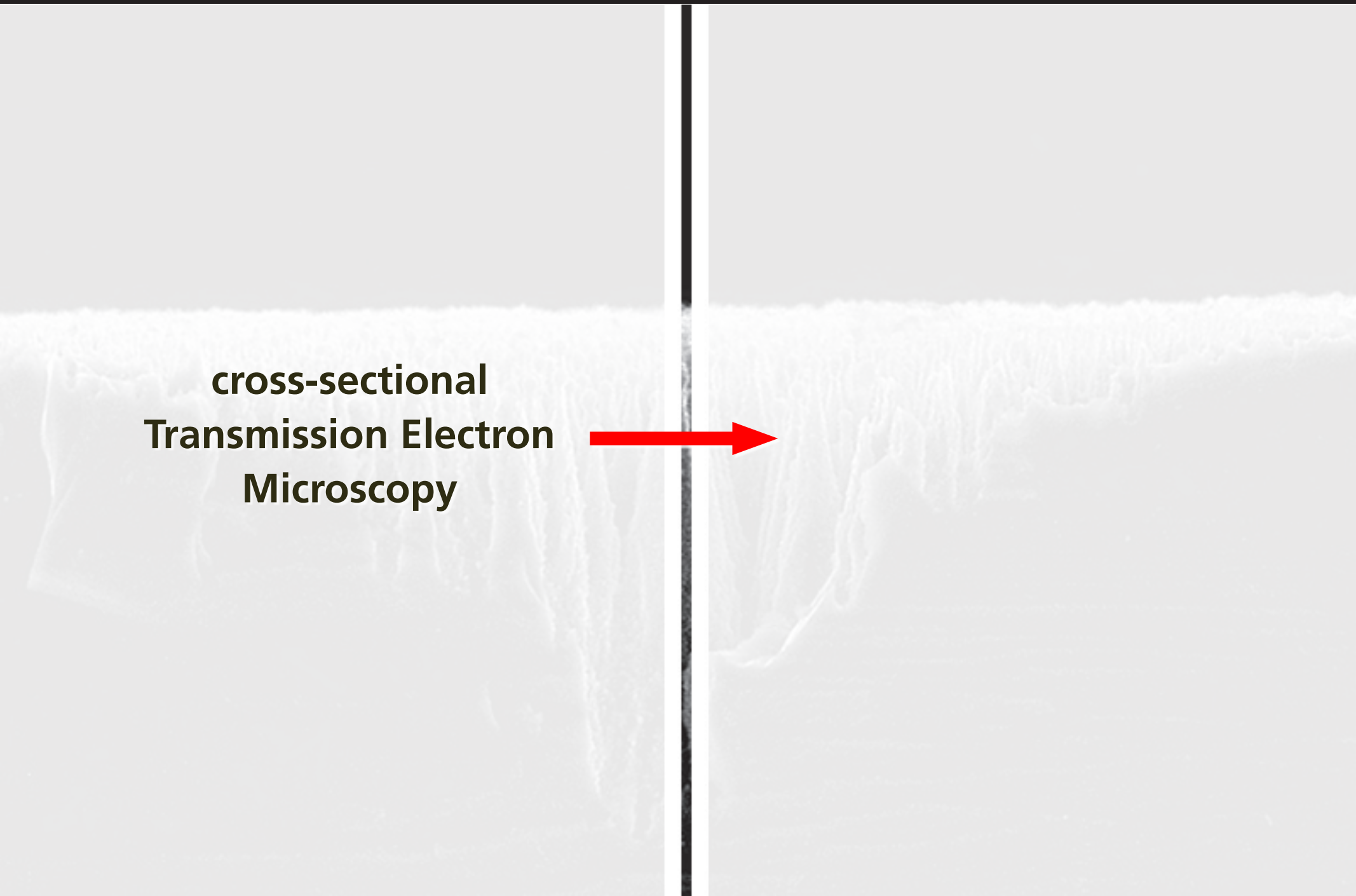

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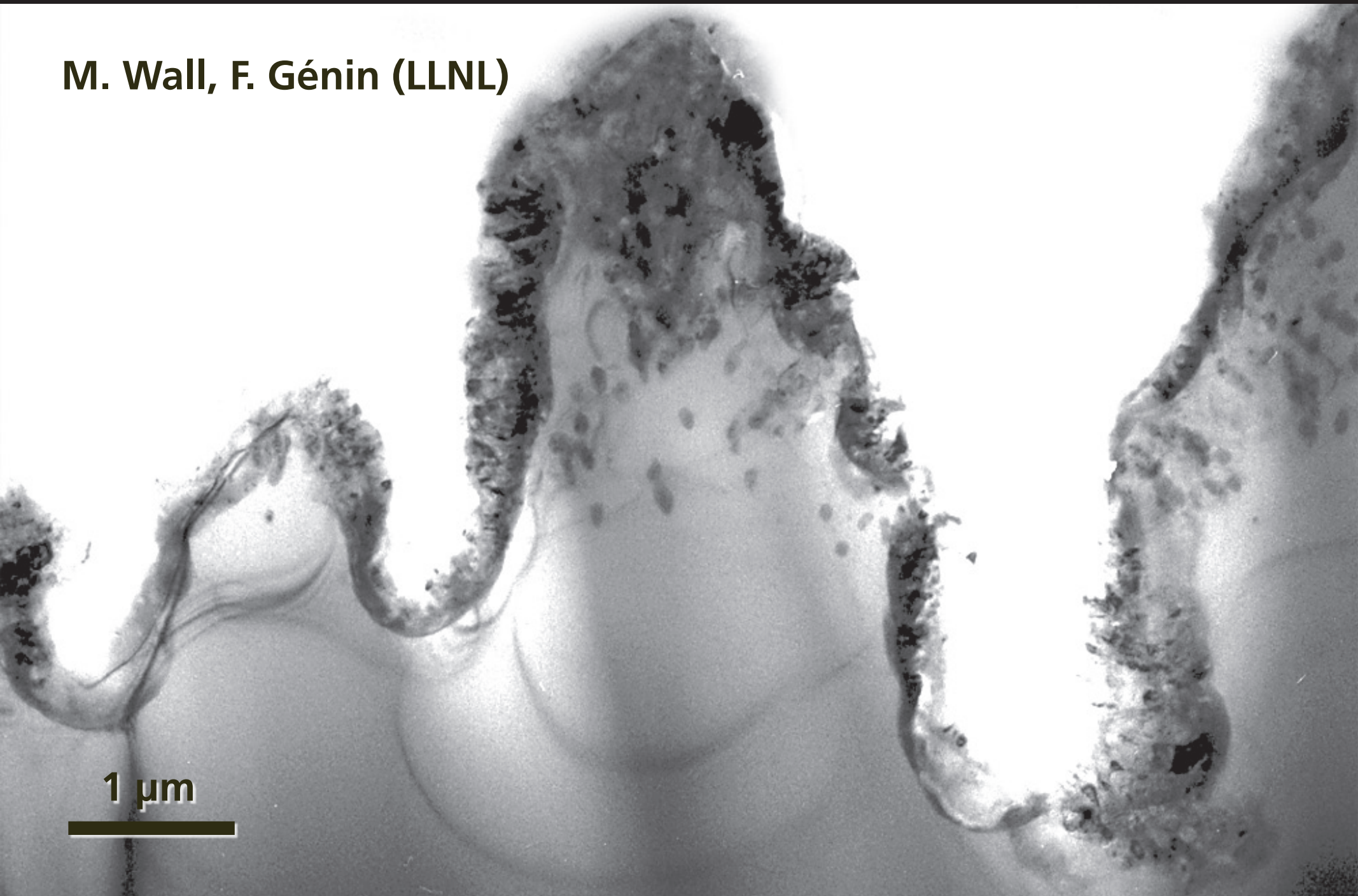
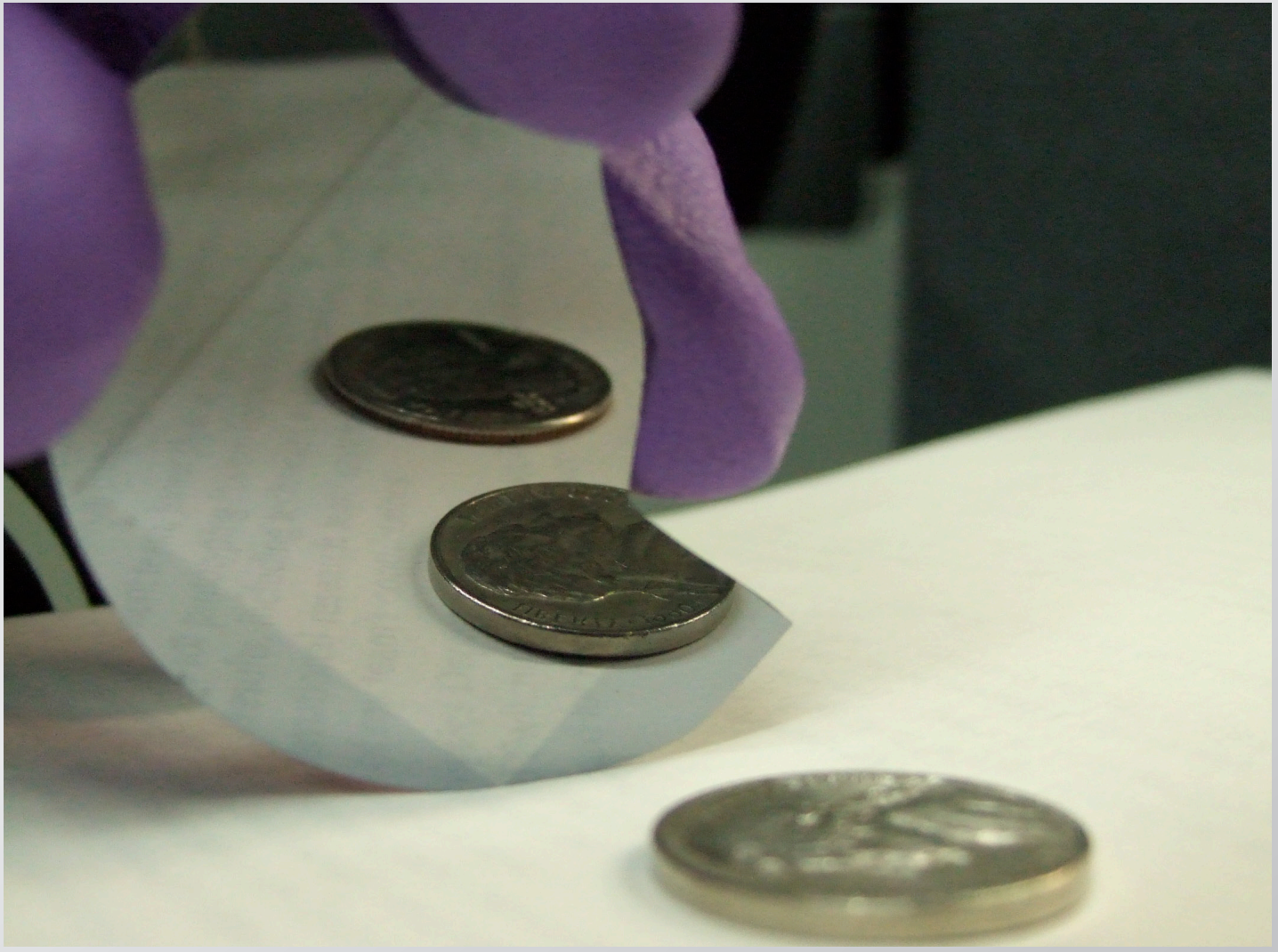


Optimizing dopant profile

decouple ablation from melting



Optimizing dopant profile

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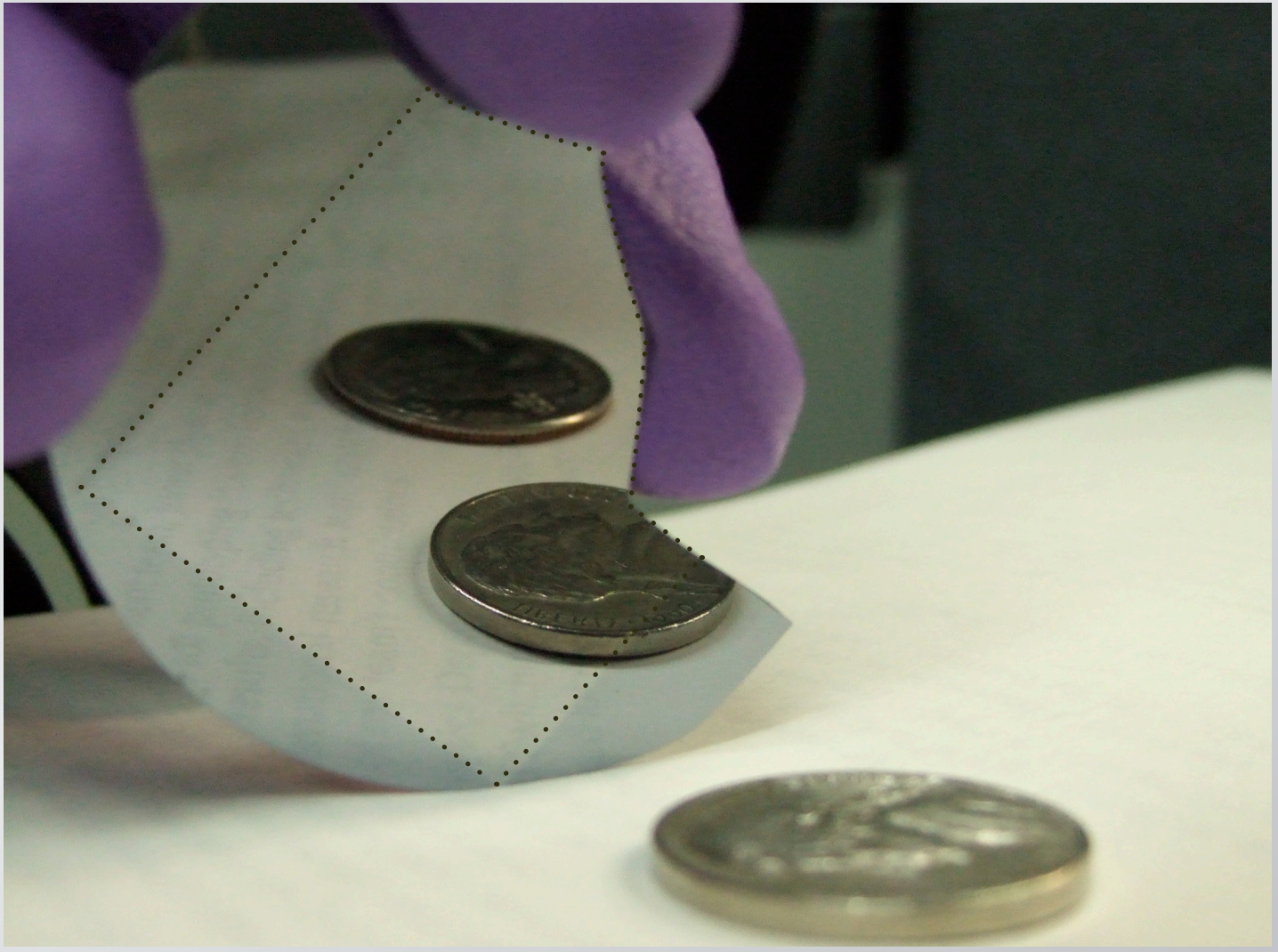

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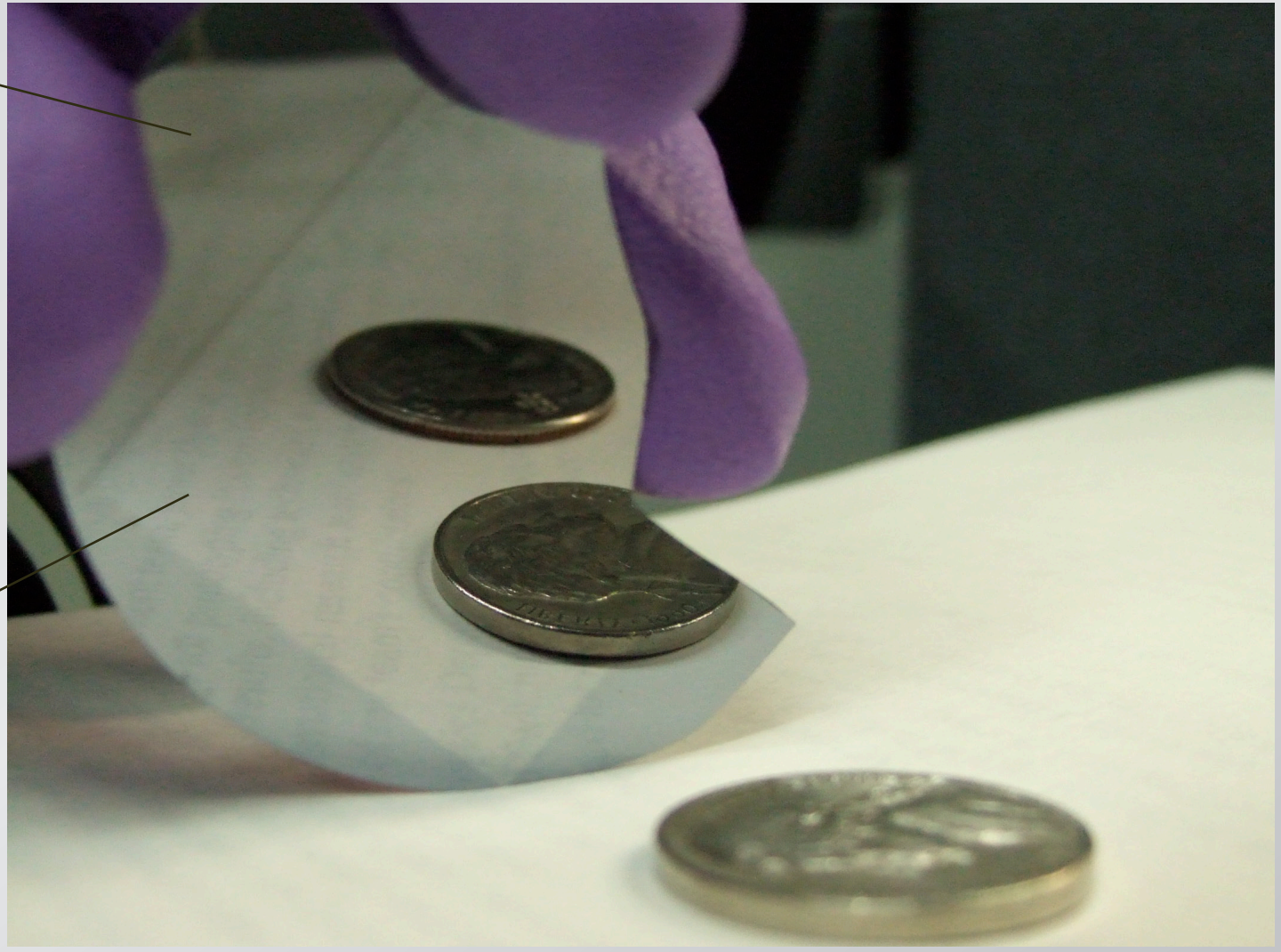

Optimizing dopant profile

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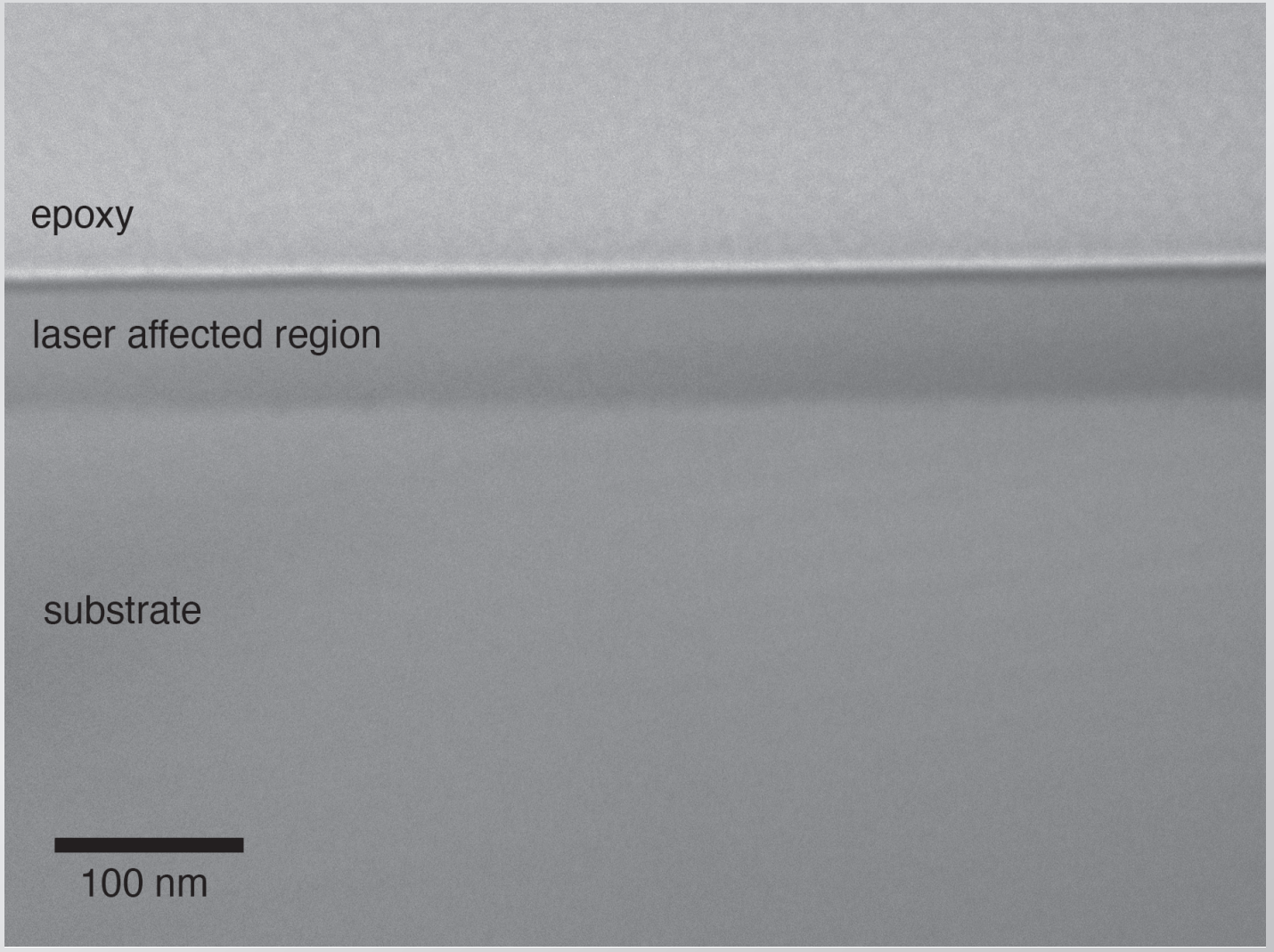
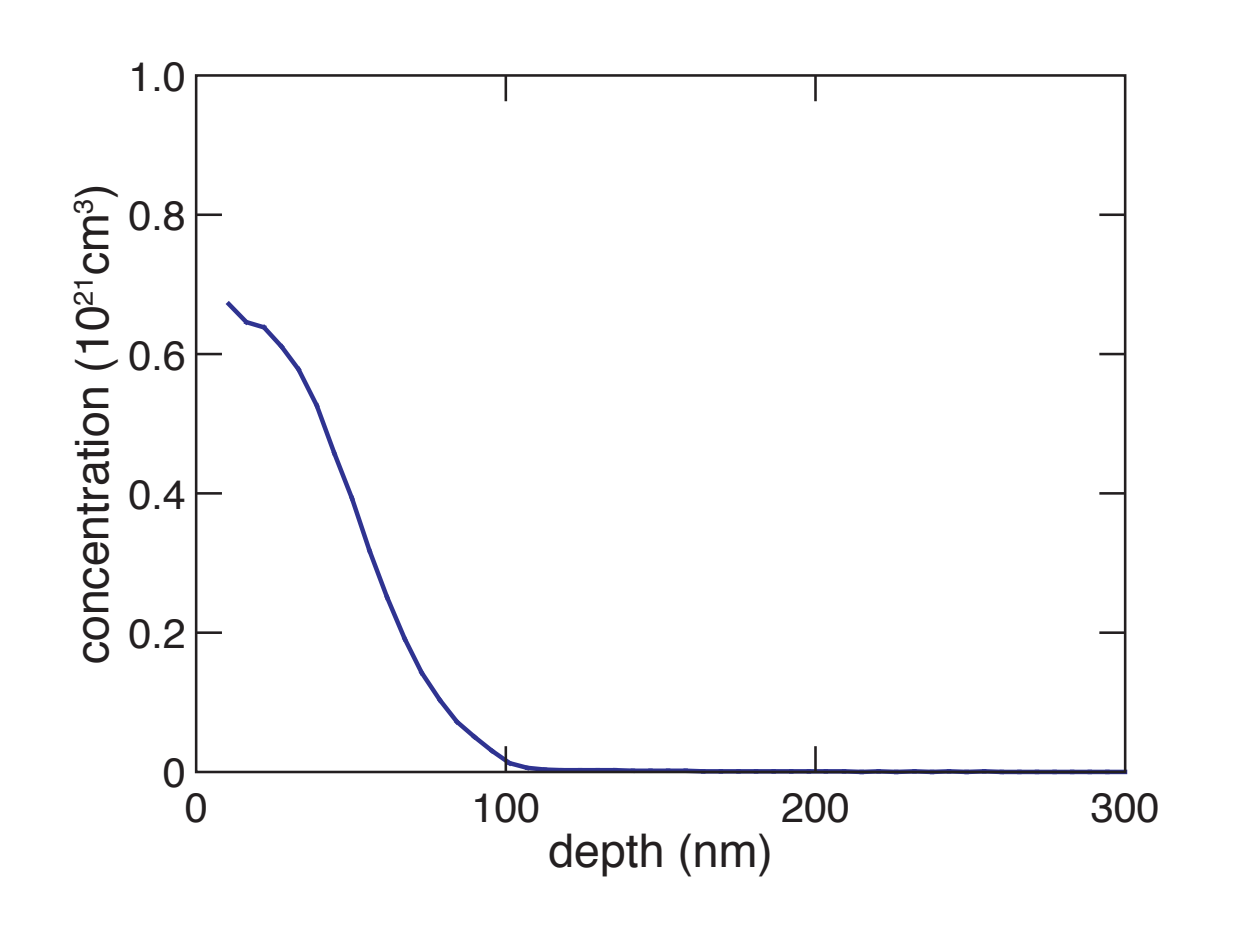


Optimizing dopant profile

secondary ion mass spectrometry



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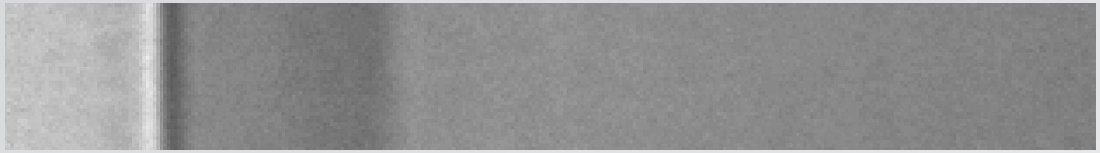
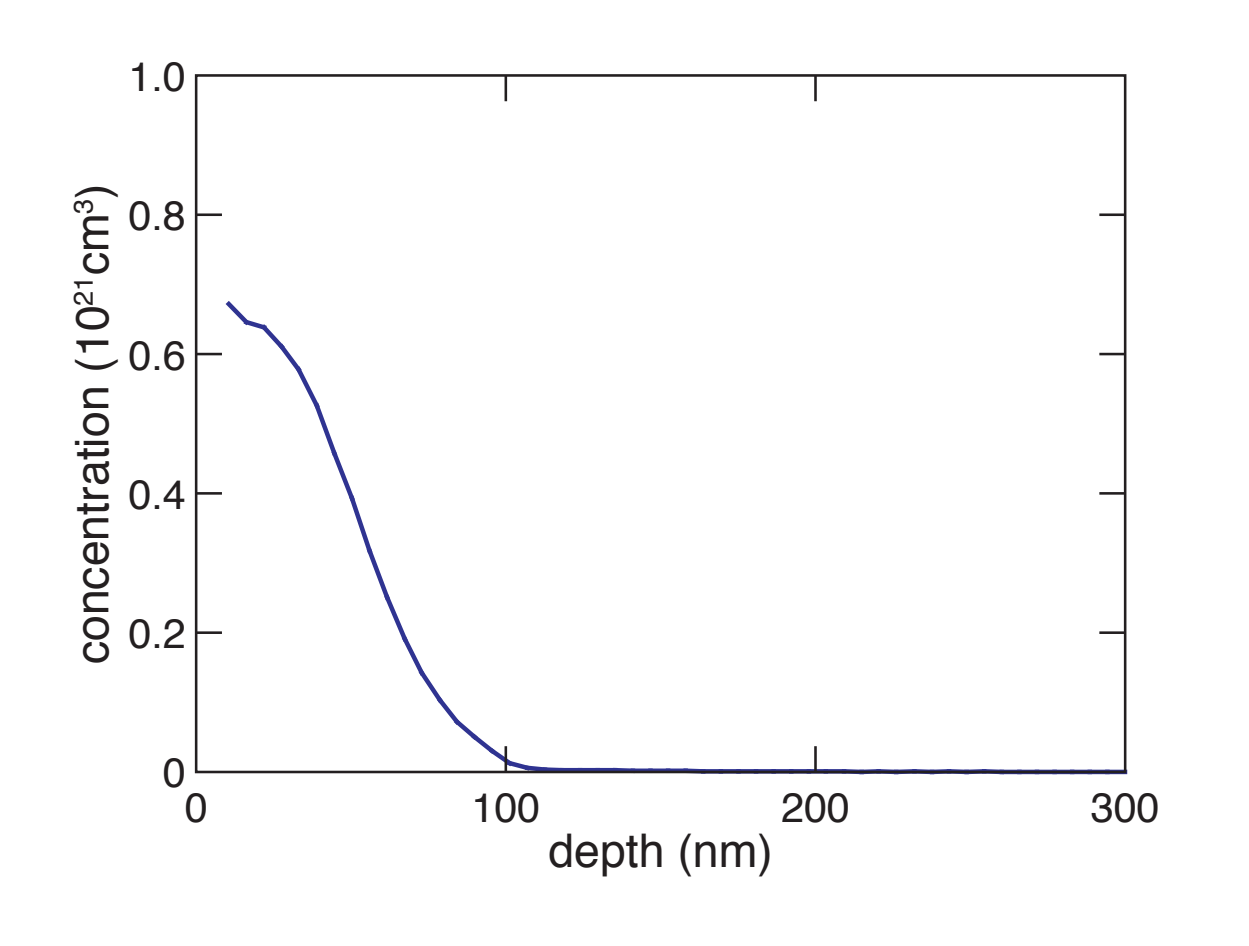




Optimizing dopant profile

appears to be closer to constant flux

Outline

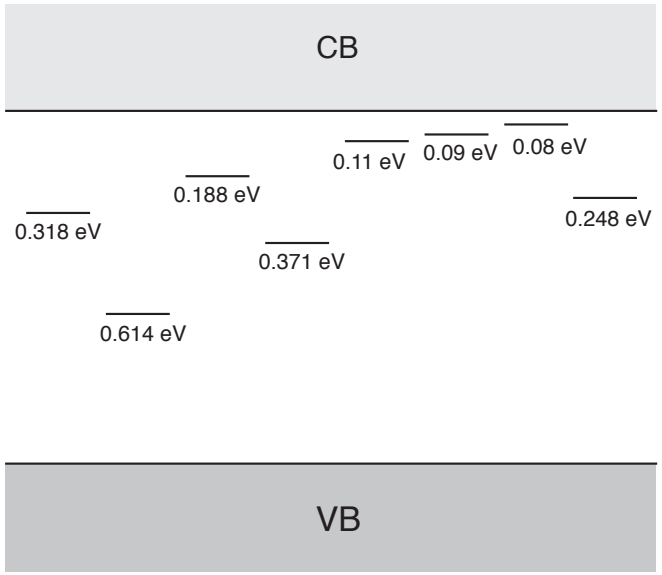
- goals
- optimizing dopant profile
- intermediate band

Intermediate band

what dopant states/bands cause IR absorption?

Intermediate band

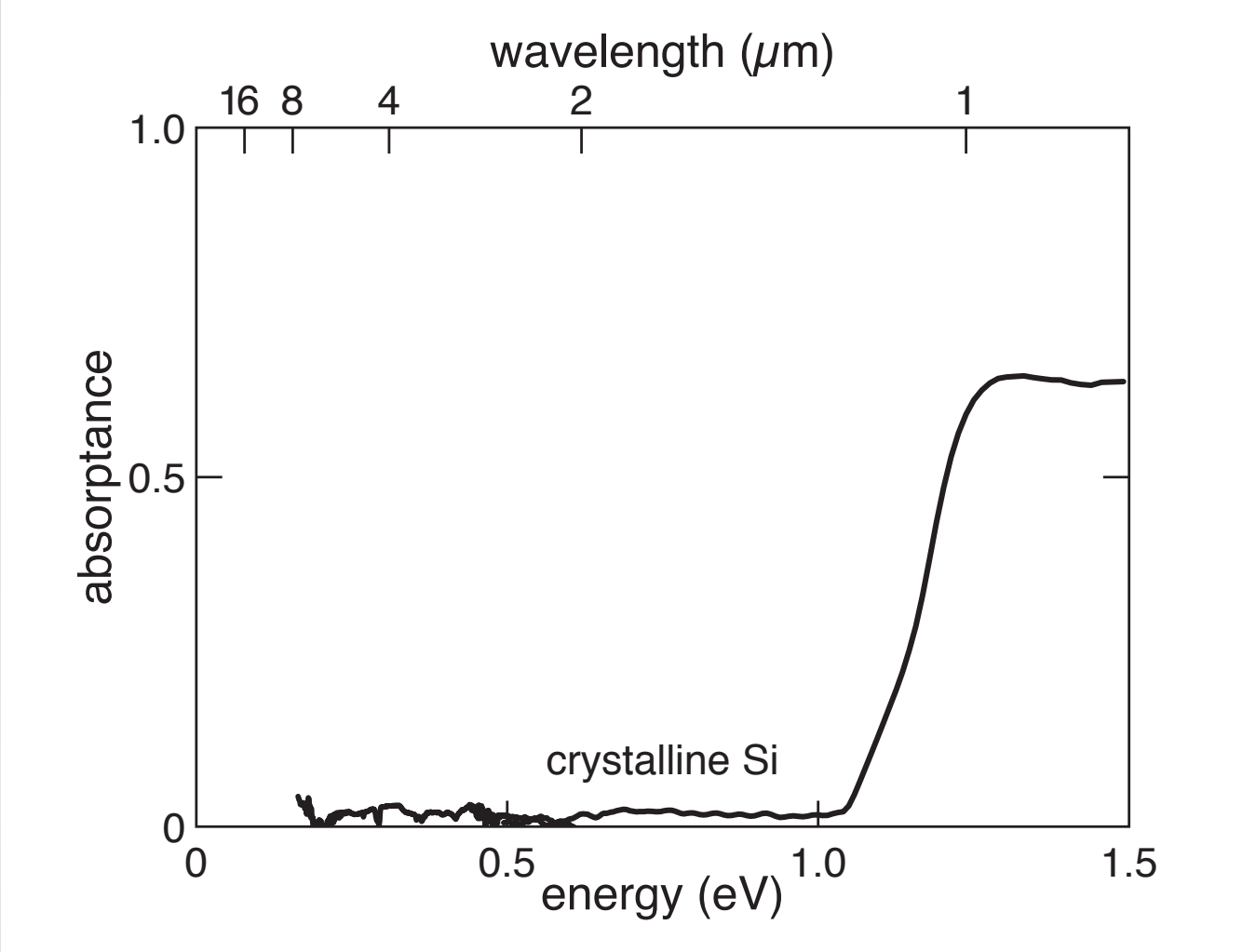
1 part in 10^6 sulfur introduces donor states in gap



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

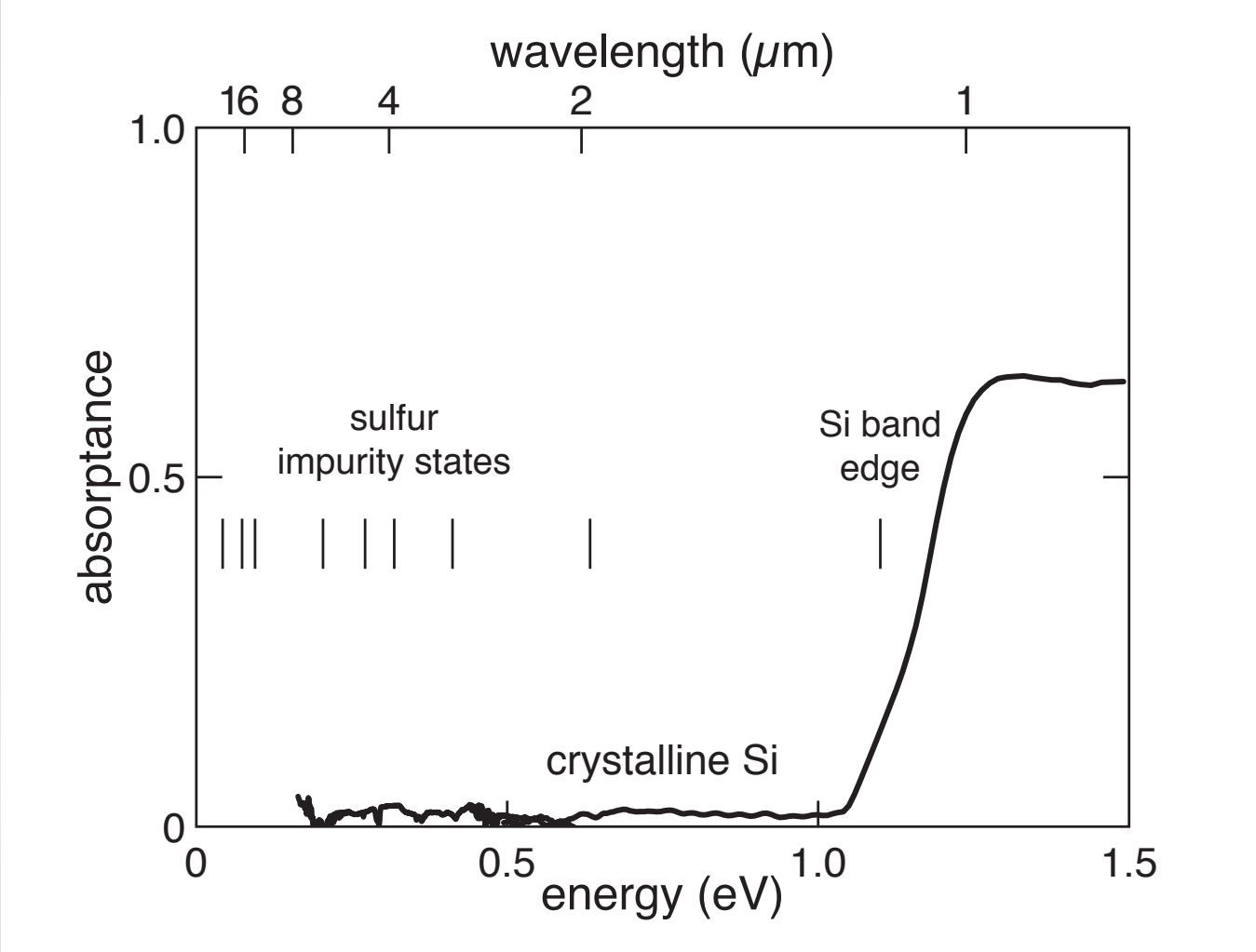
Intermediate band

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



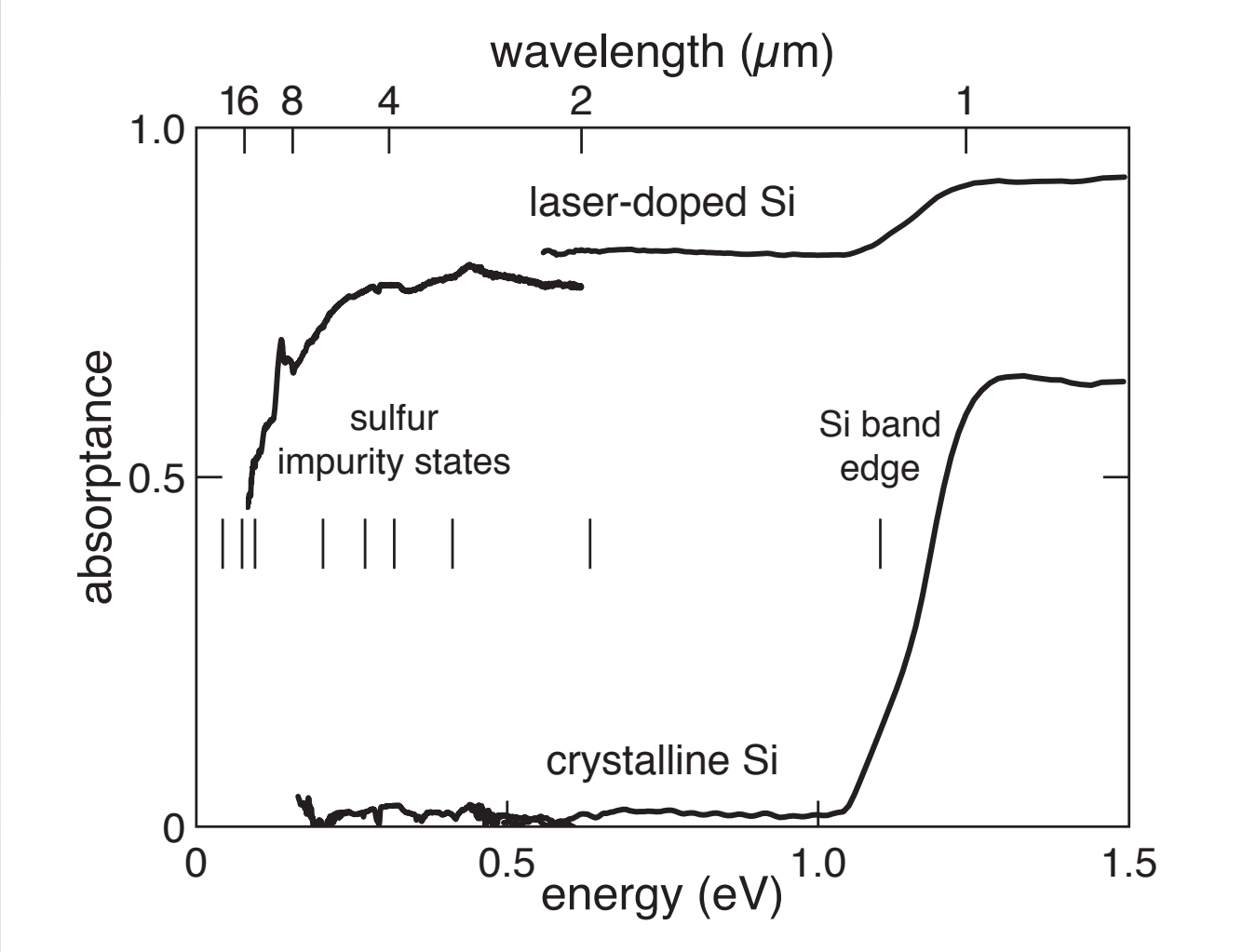
Intermediate band

10^{-6} sulfur doping



Intermediate band

laser-doped S:Si



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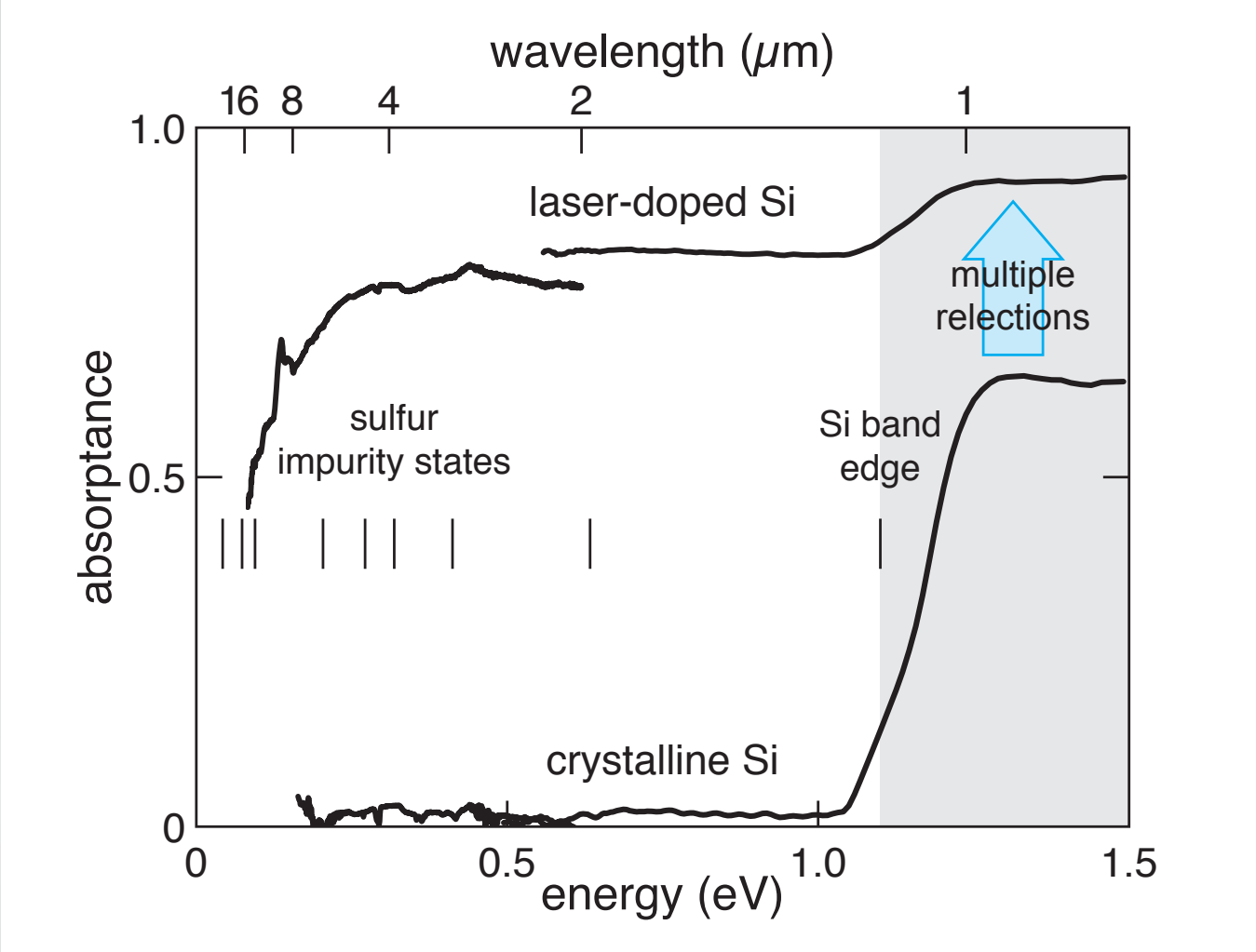

Intermediate band

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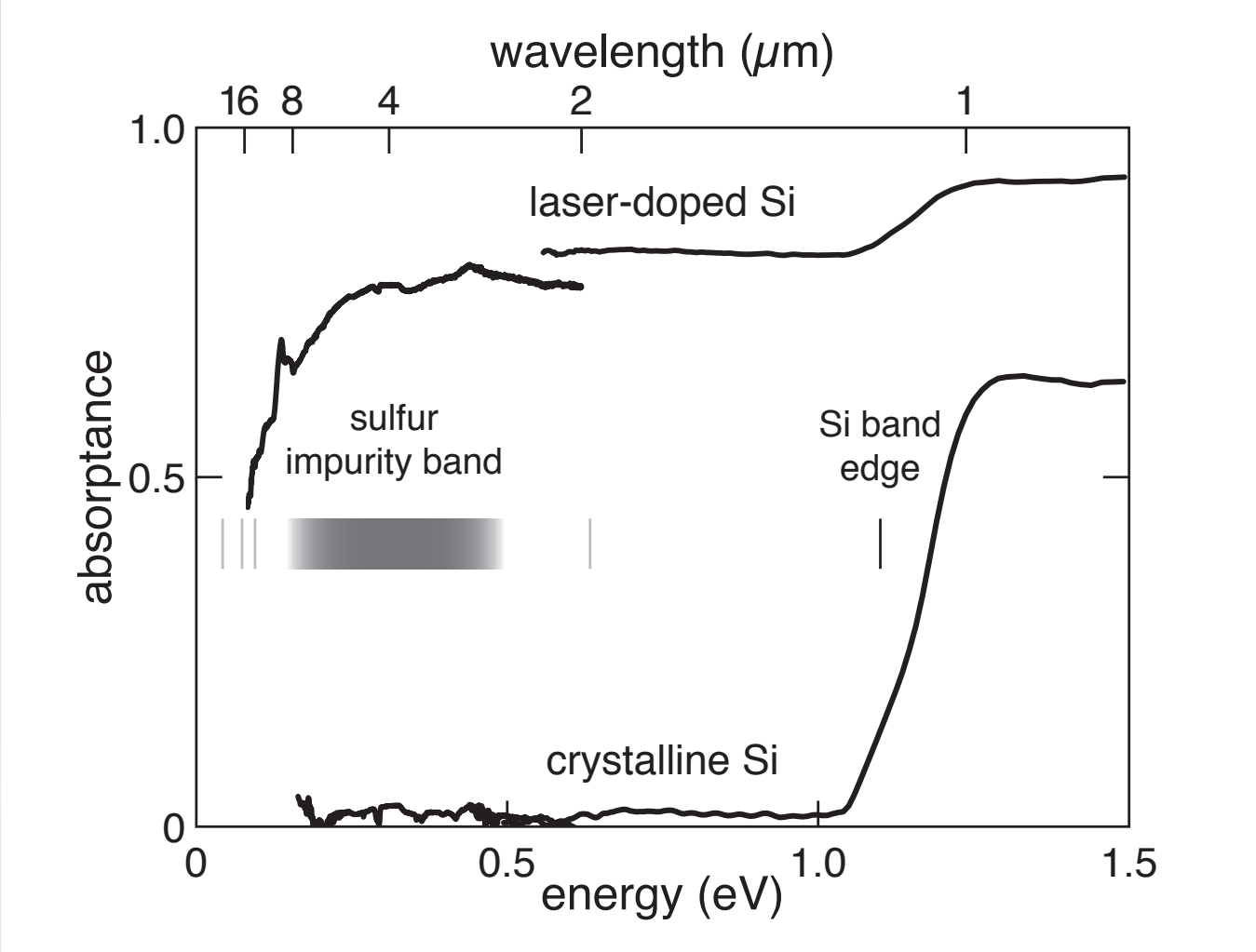
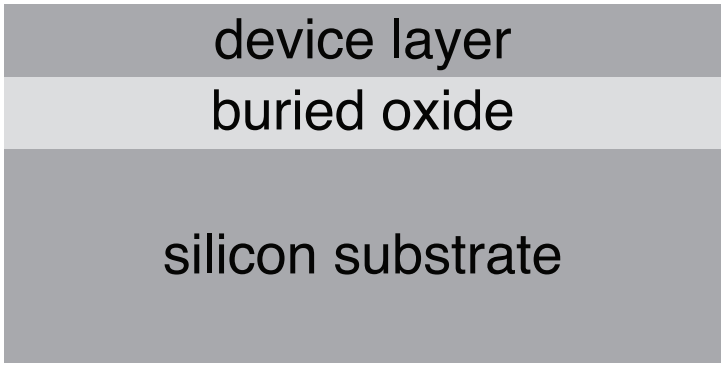


Intermediate band

isolate surface layer for Hall measurements



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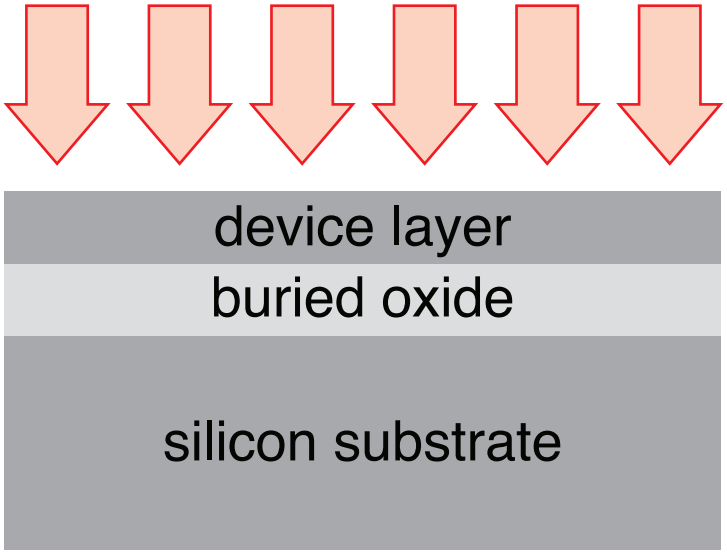

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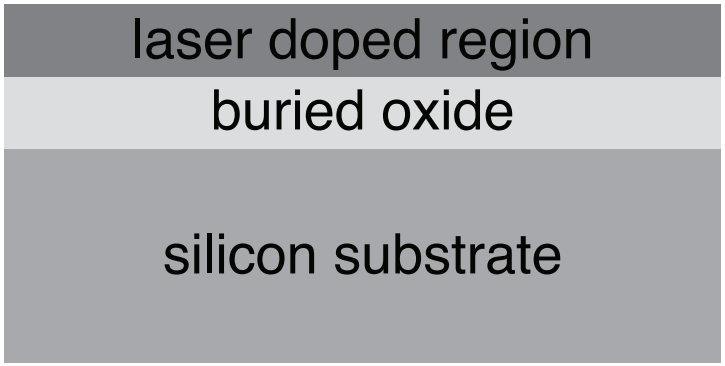

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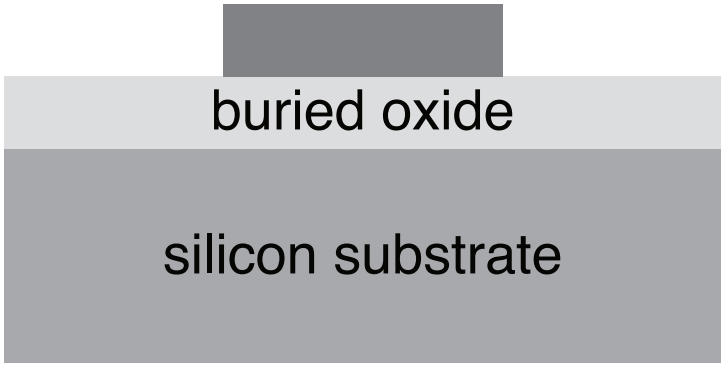
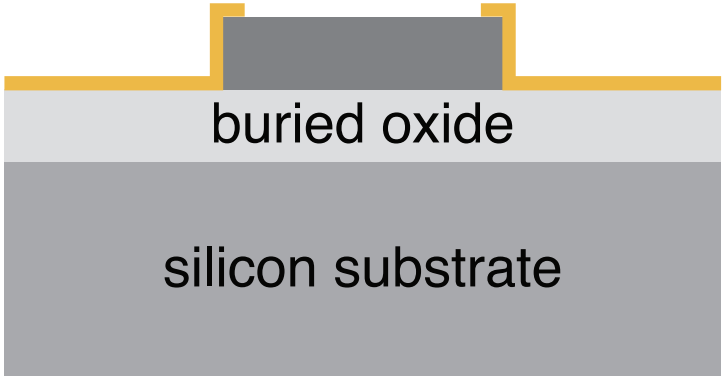
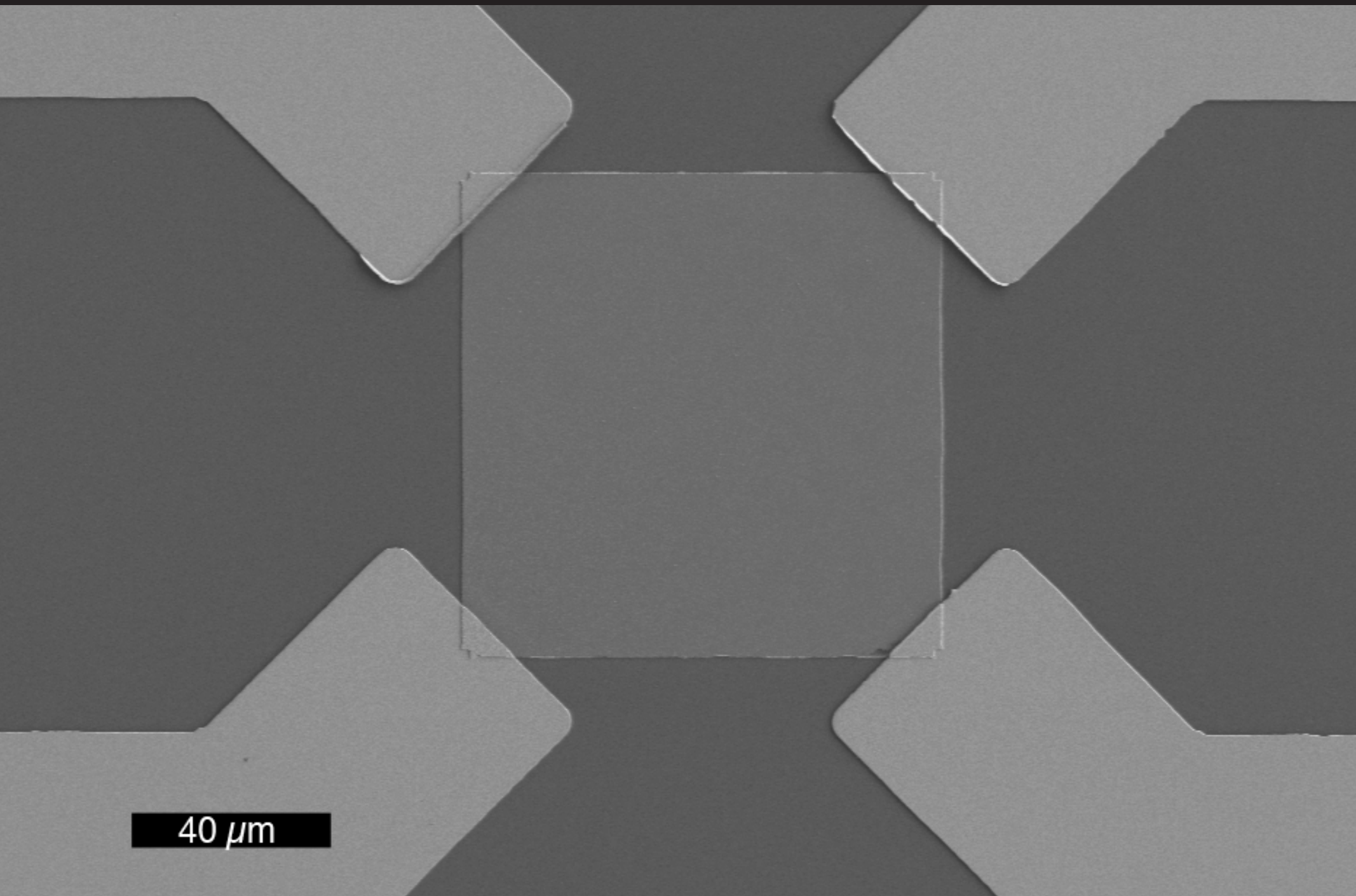


Intermediate band

isolate surface layer for Hall measurements

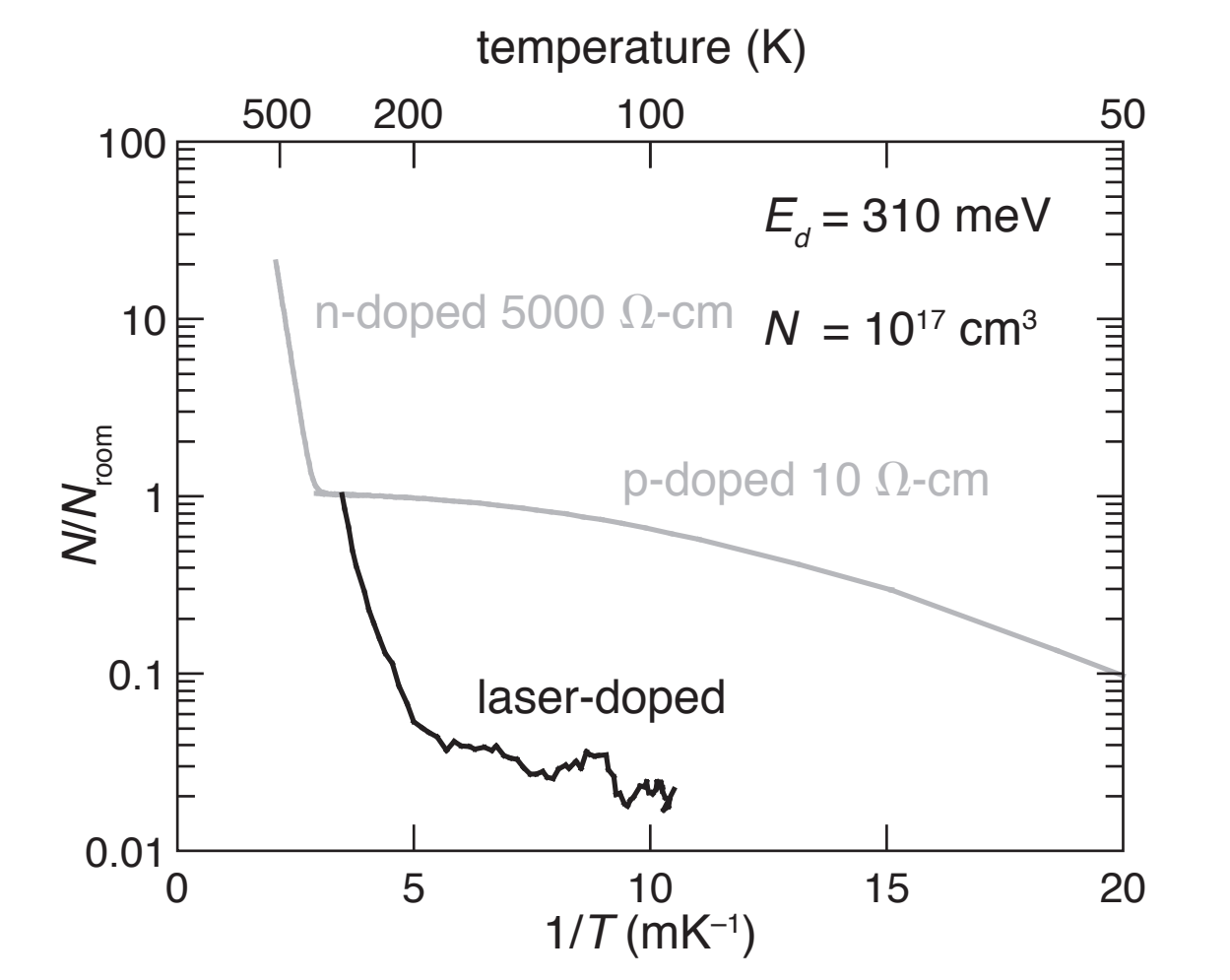


Intermediate band



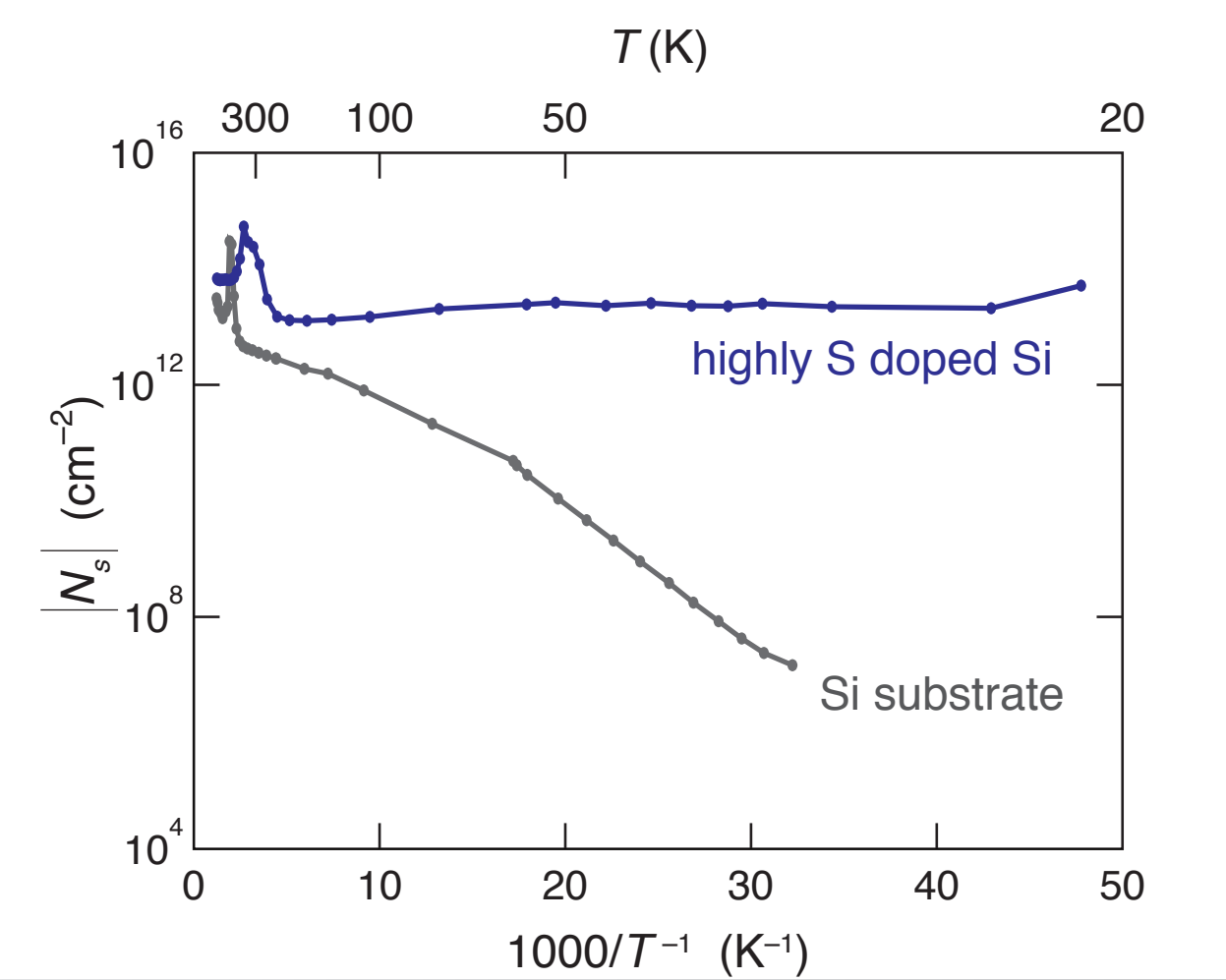
Intermediate band

Hall measurements



Intermediate band

transition to metallic behavior at high doping



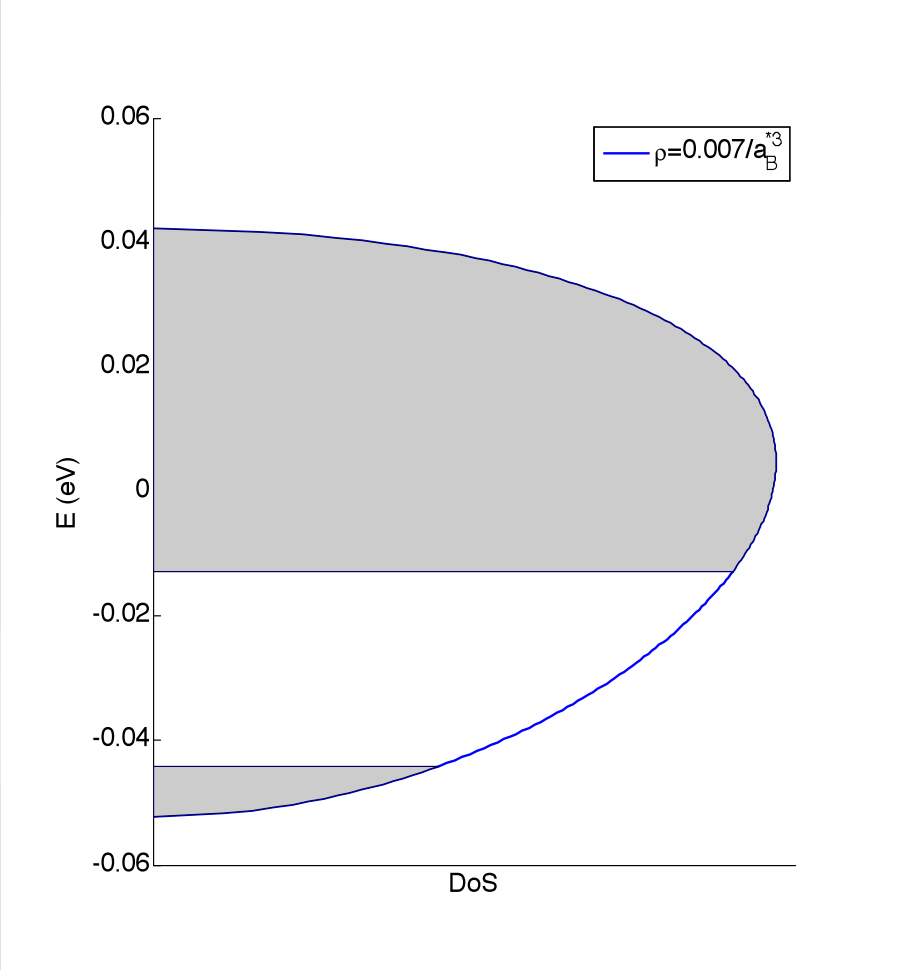
Intermediate band

can we understand this intermediate band

using atomistic modeling?

Intermediate band

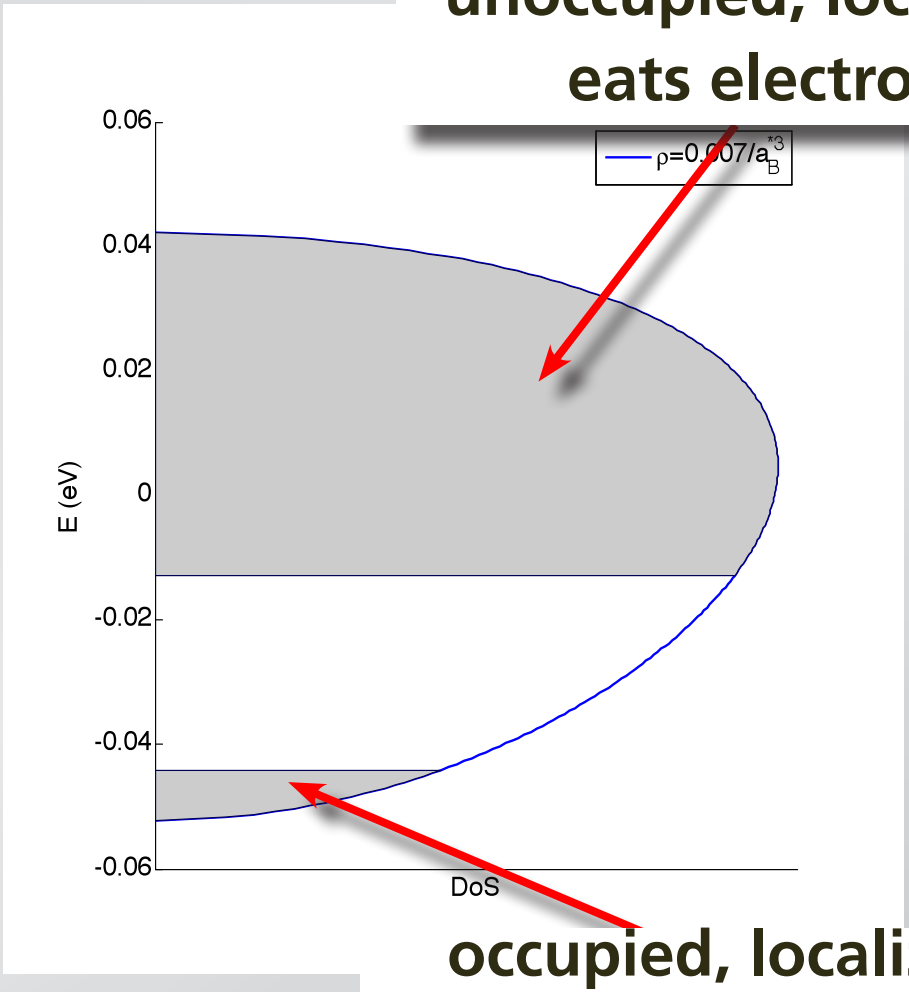
density of states



Intermediate band

density of states

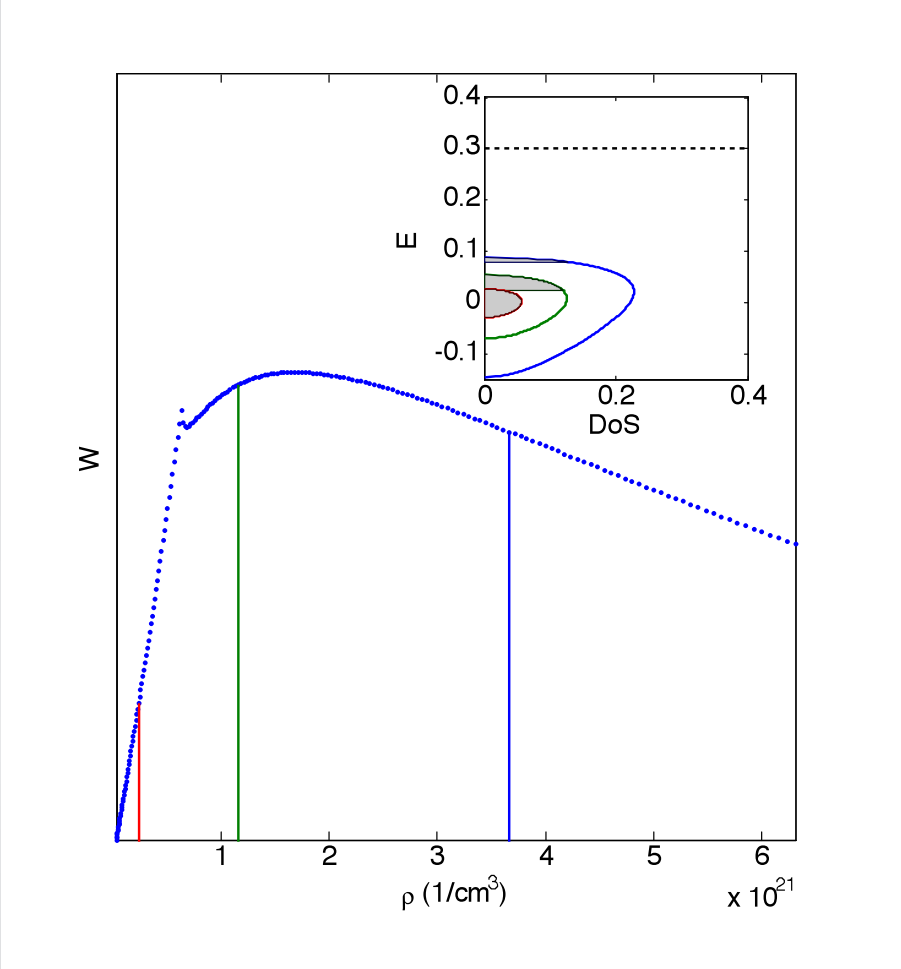
unoccupied, localized:
eats electrons



occupied, localized:
eats holes

Intermediate band

recombination rate

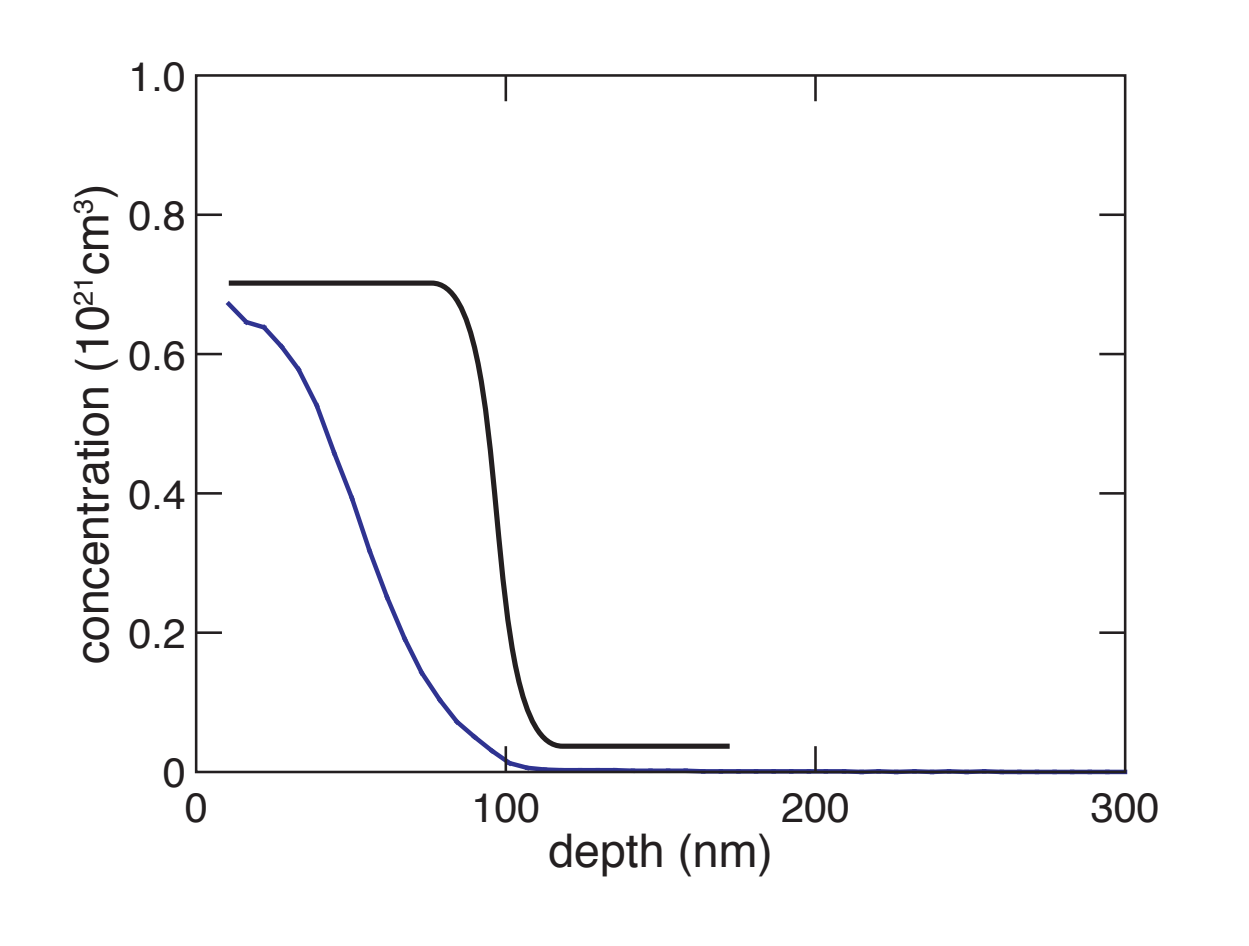


What's next?

change dopant/substrate combination

What's next?

optimal dopant profile is flat



What's next?

change incorporation process:

- electrospray
- pulse sequence design

Acknowledgments