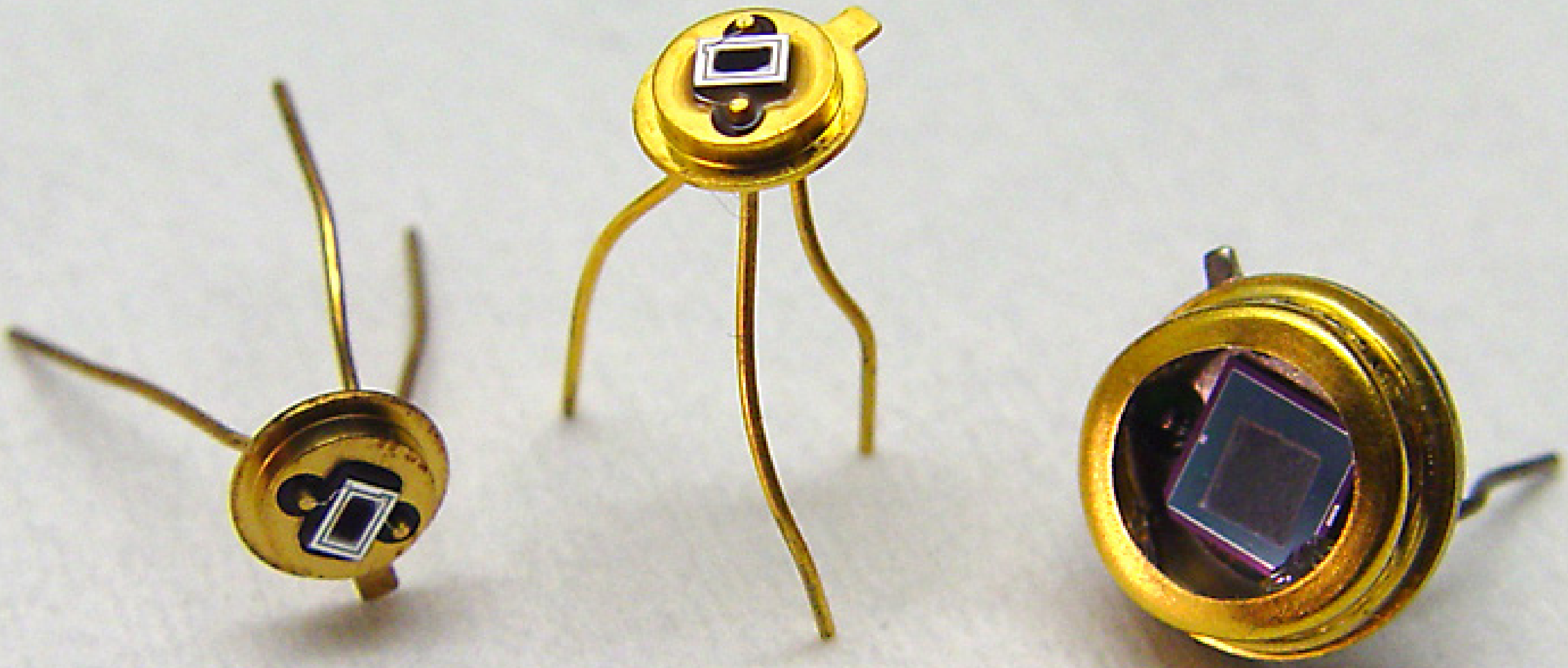
Laser doping and texturing of silicon for advanced optoelectronic devices



FiO/LS Conference
Laser Material Processing
Rochester, NY, 18 October 2016

Laser doping and texturing of silicon for advanced optoelectronic devices

@eric_mazur

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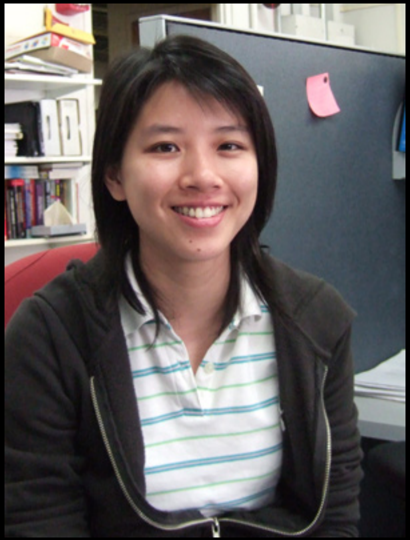
Renee Sher


Yu-Ting Lin


Kasey Philips


Ben Franta

eric_mazur

and also....

Hemi Gandhi
Alexander Raymond
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)

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

Dr. Martin Pralle (SiOnyx)
and everyone else at SiOnyx…

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

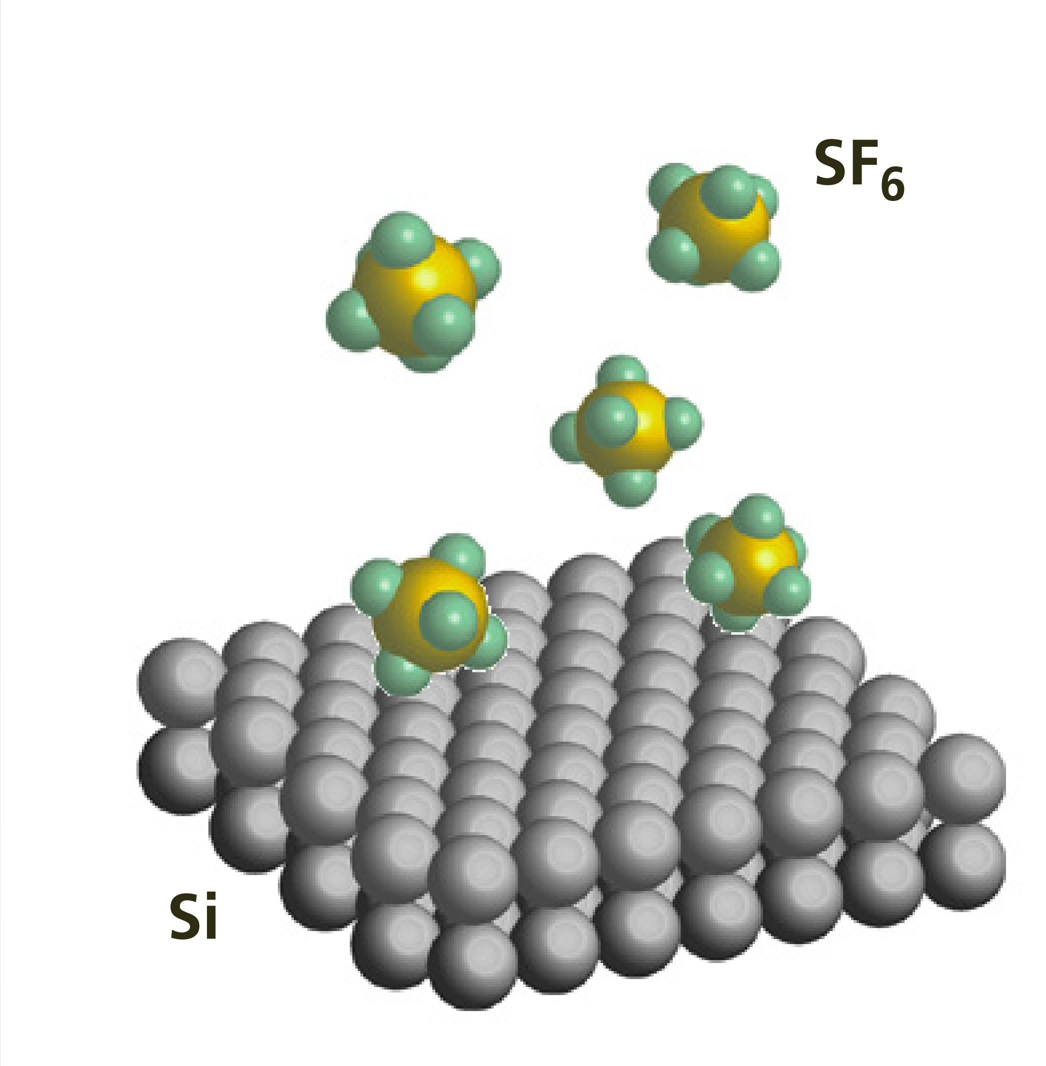
Prof. Augustinus Asenbaum (Vienna)

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

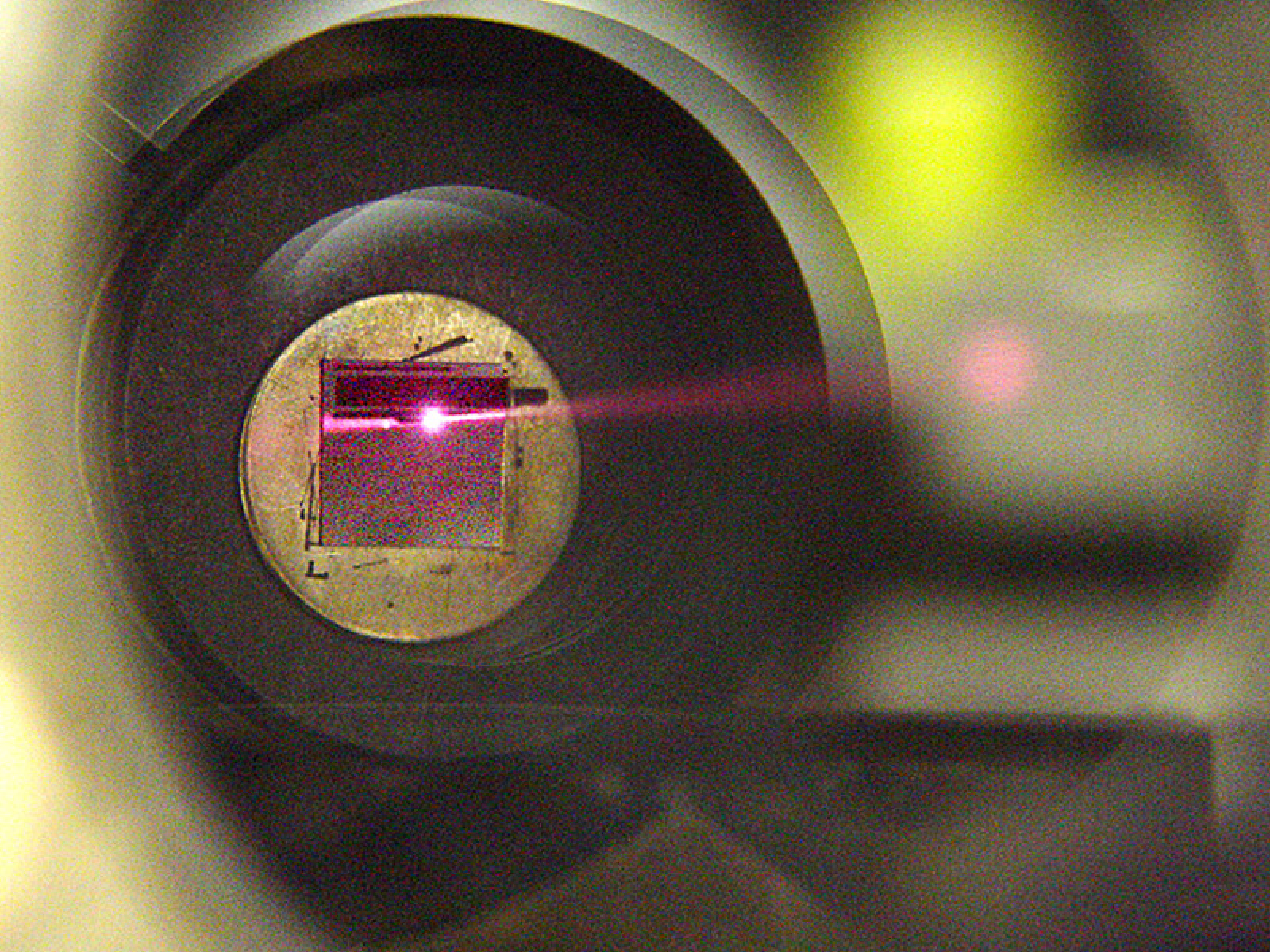
Dr. Richard Farrell (RMD)
Dr. Arieh Karger (RMD)
Dr. Richard Meyers (RMD)

Dr. Pat Maloney (NVSED)

Dr. Jeffrey Warrander (ARDEC)



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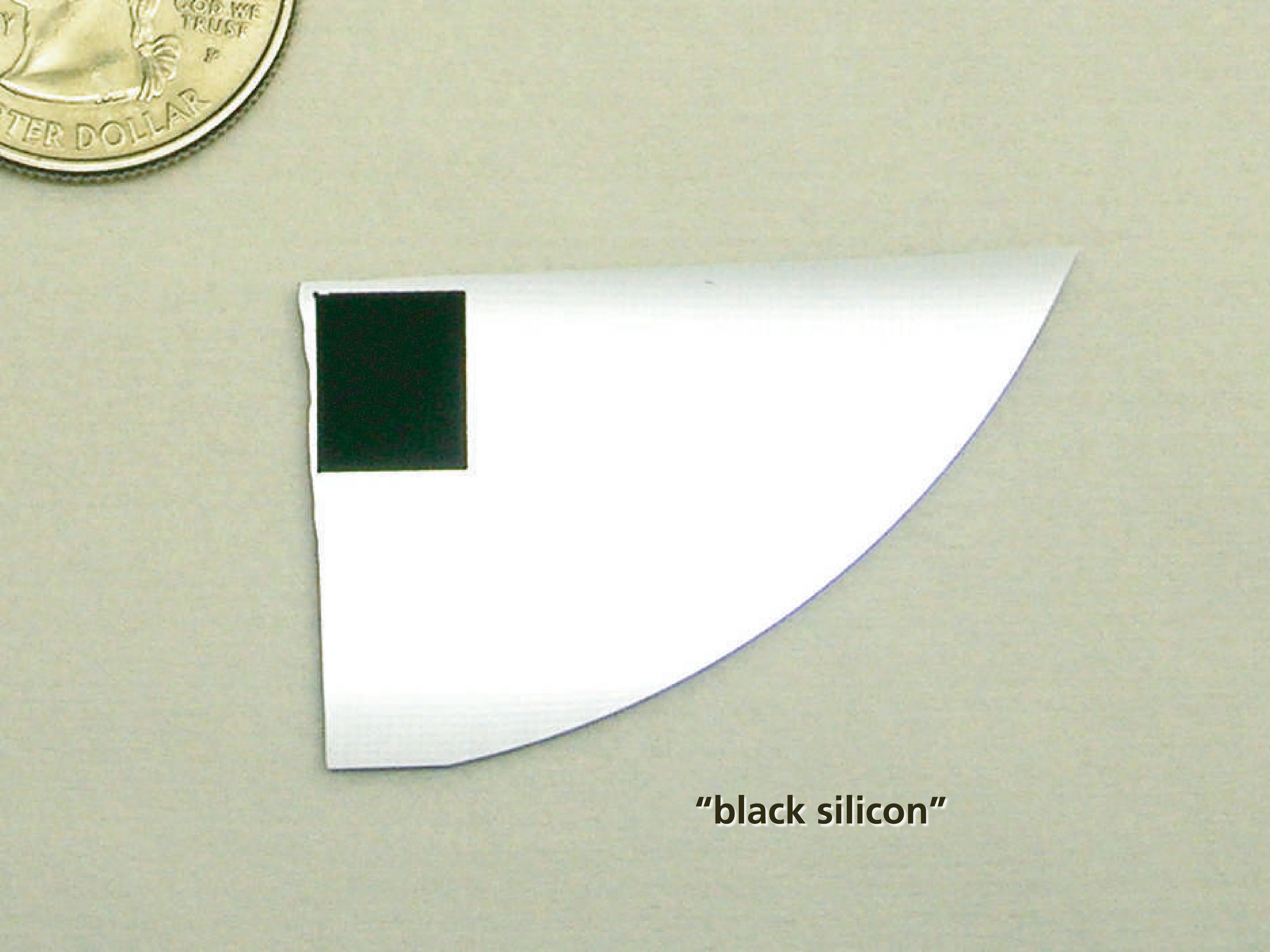
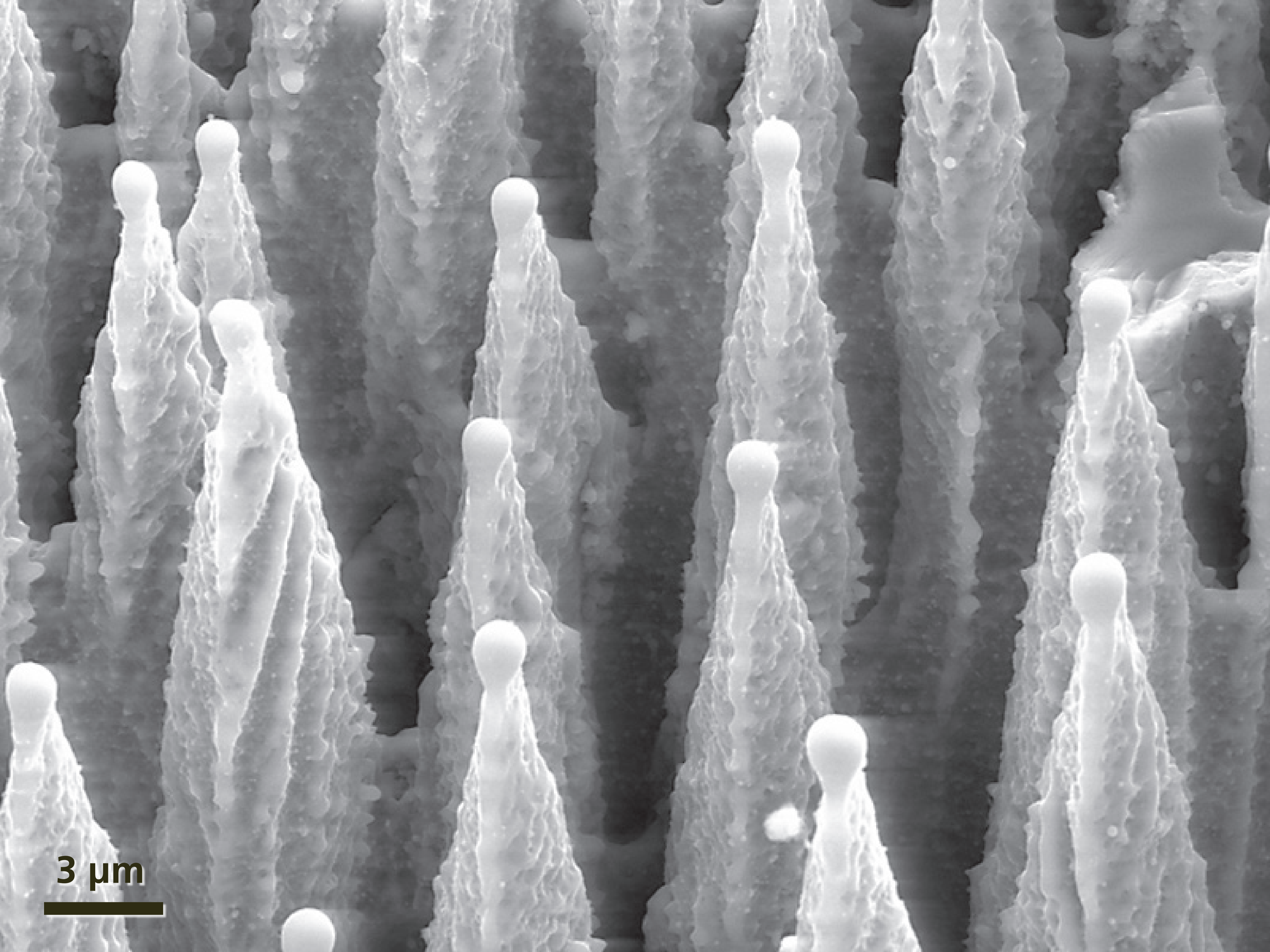
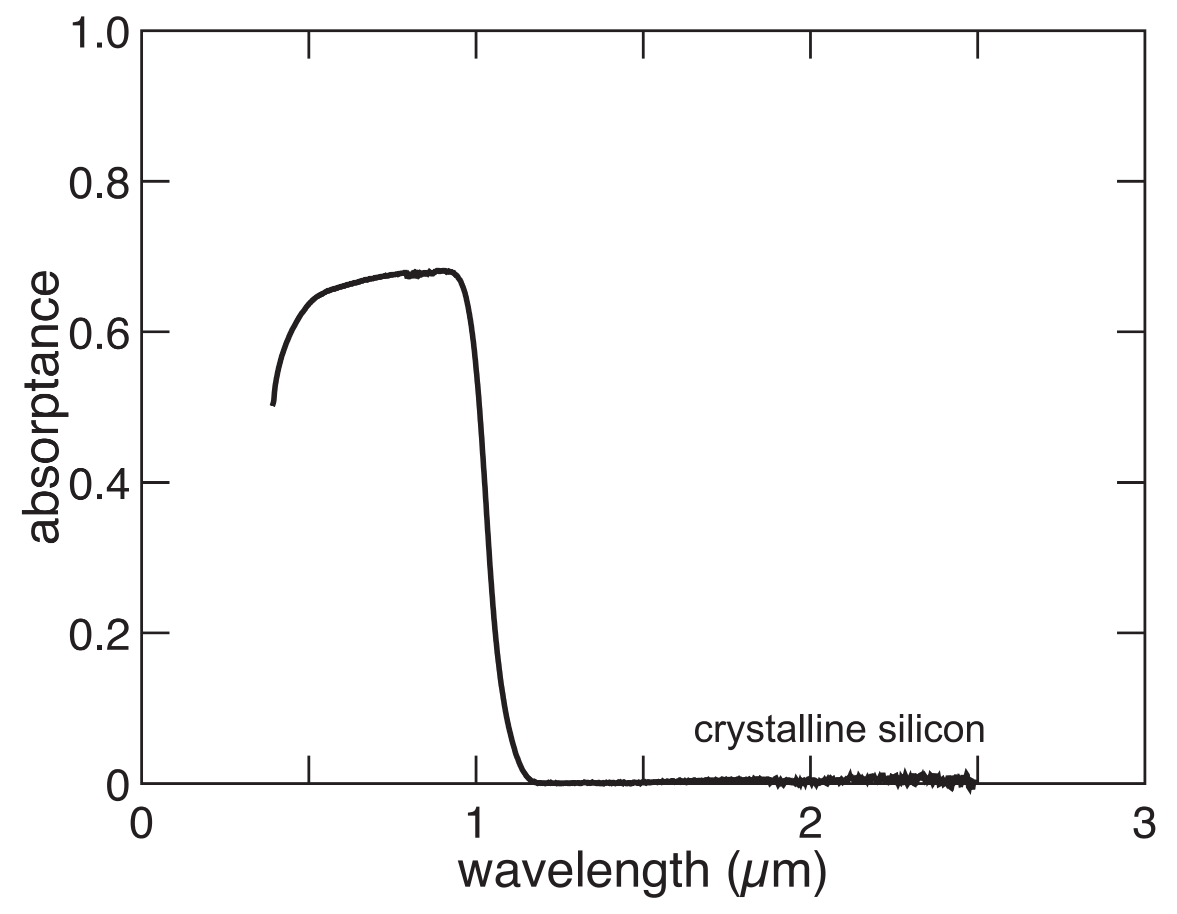


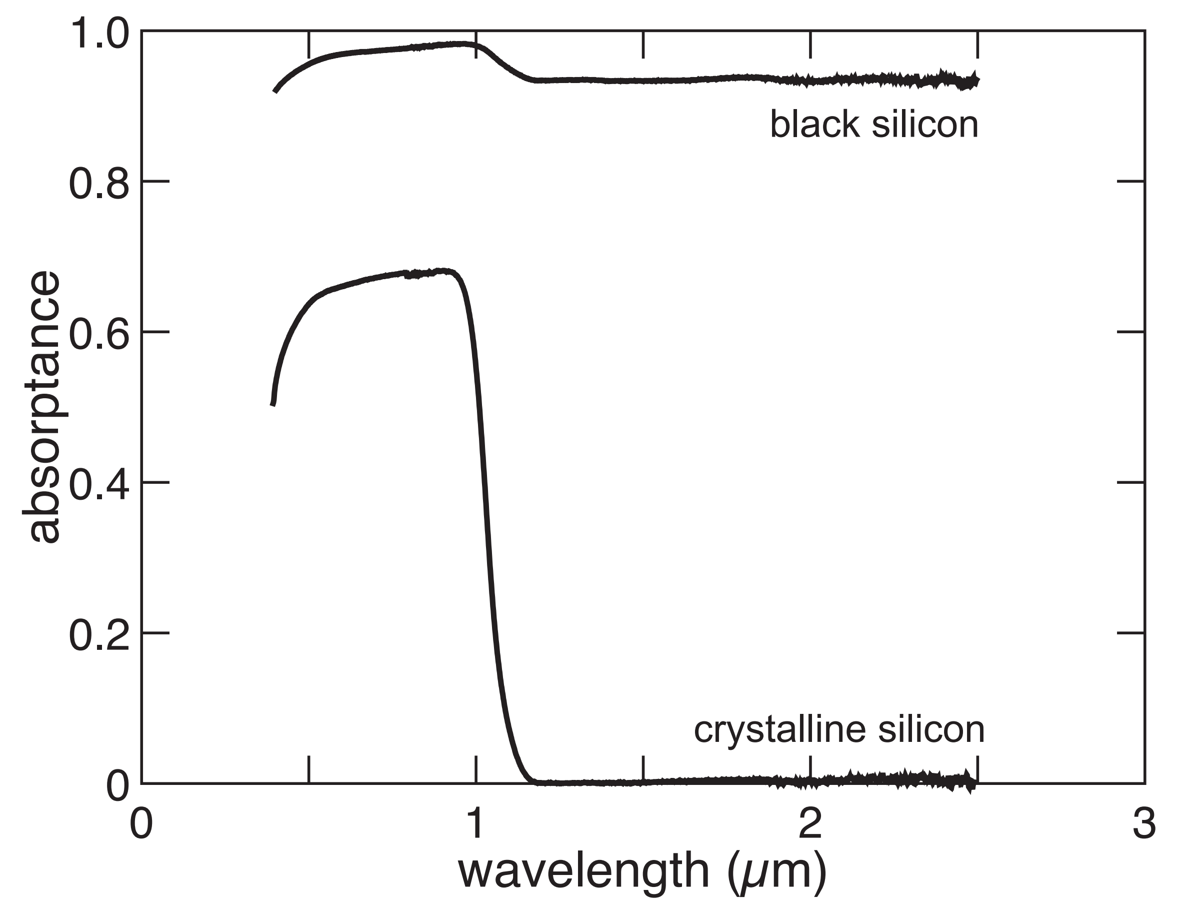
“black silicon”

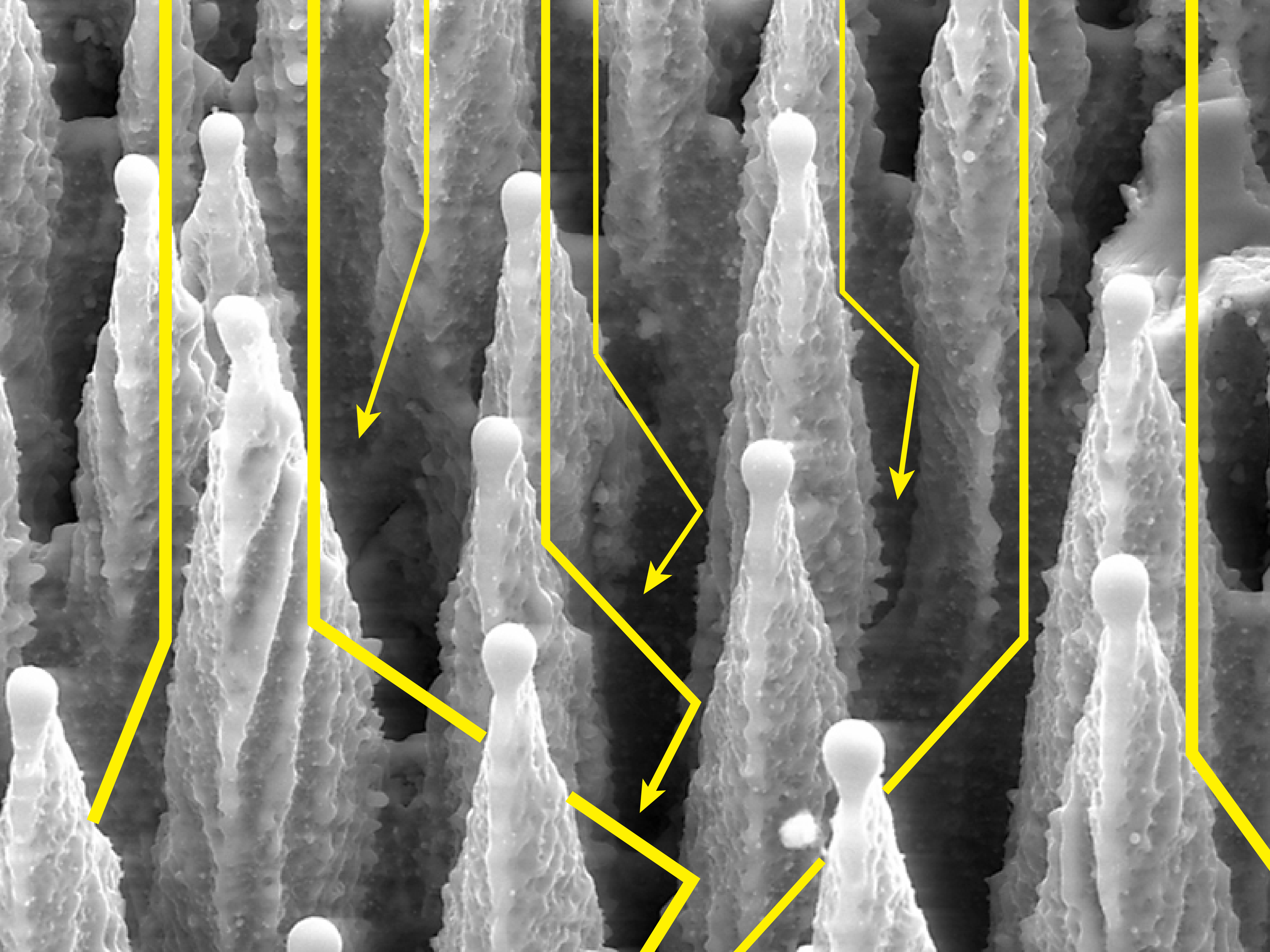

3 µm

absorptance (1 – R_{int} – T_{int})

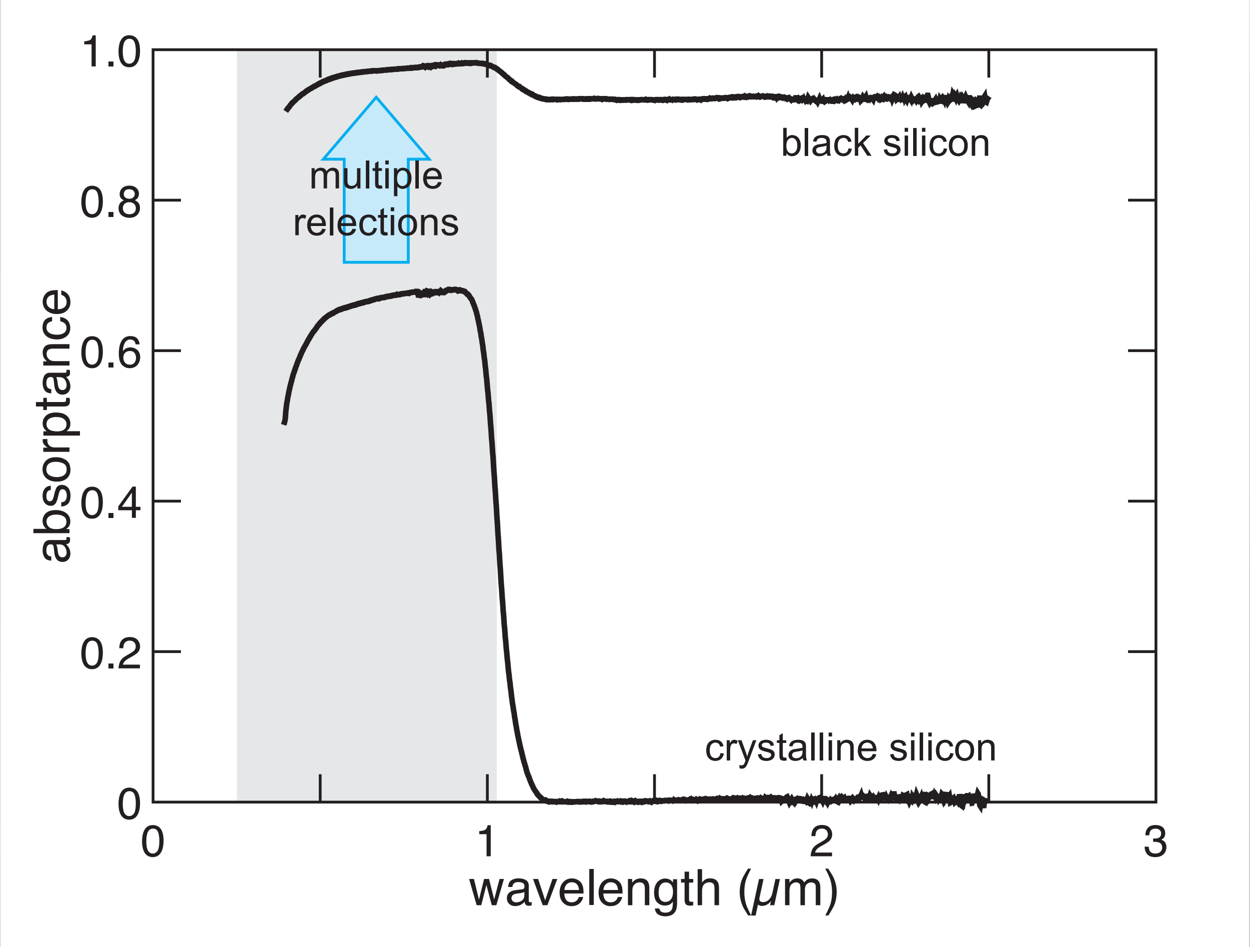


absorptance (1 – R_{int} – T_{int})

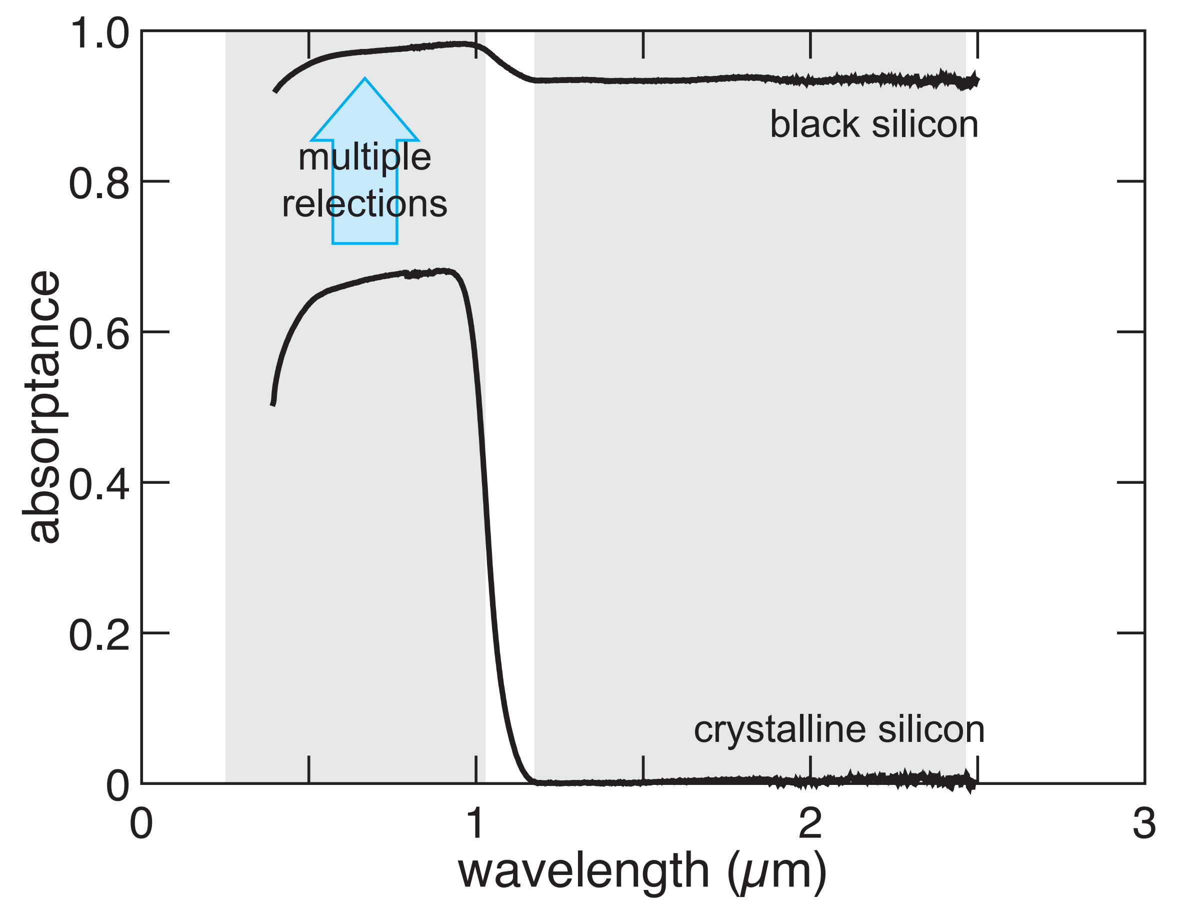




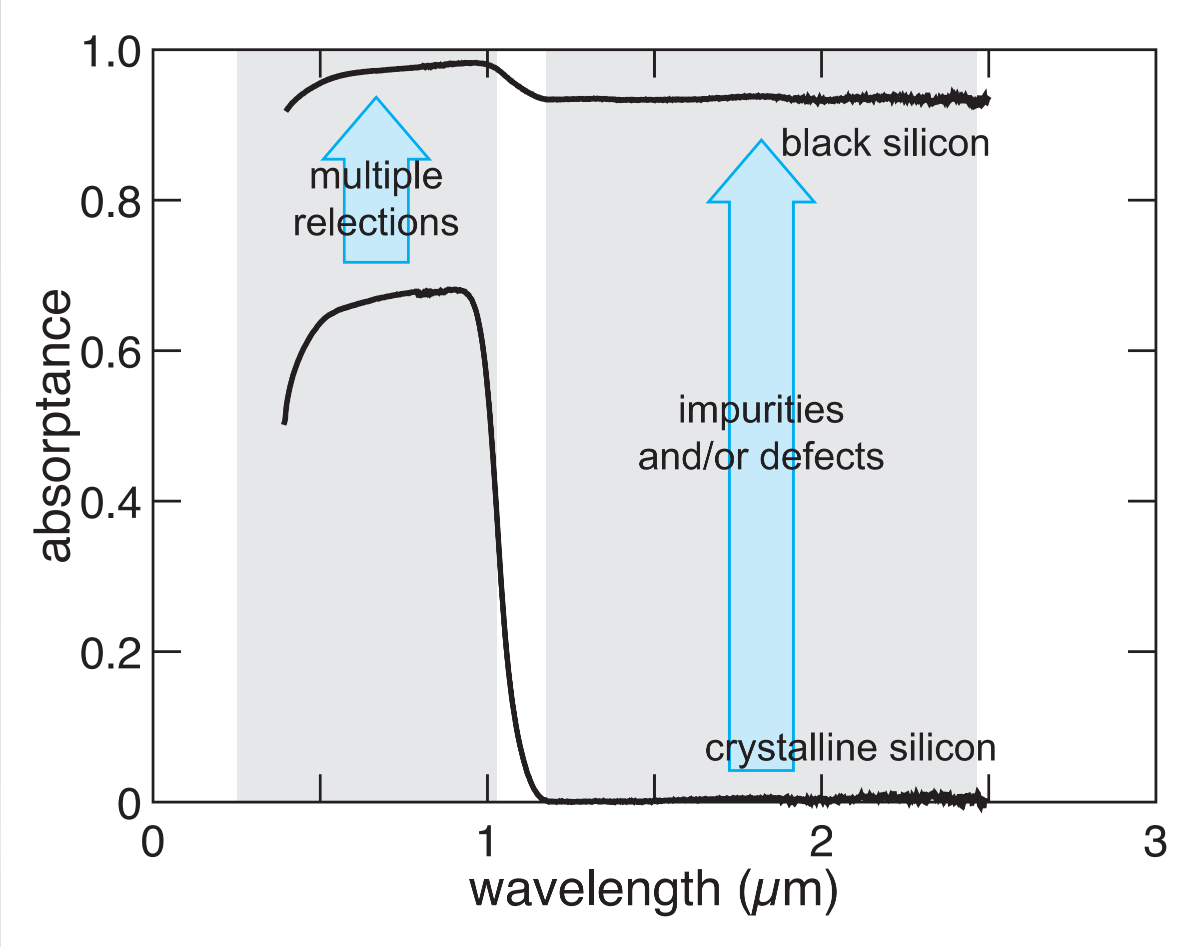
absorptance ($1 - R_{int} - T_{int}$)

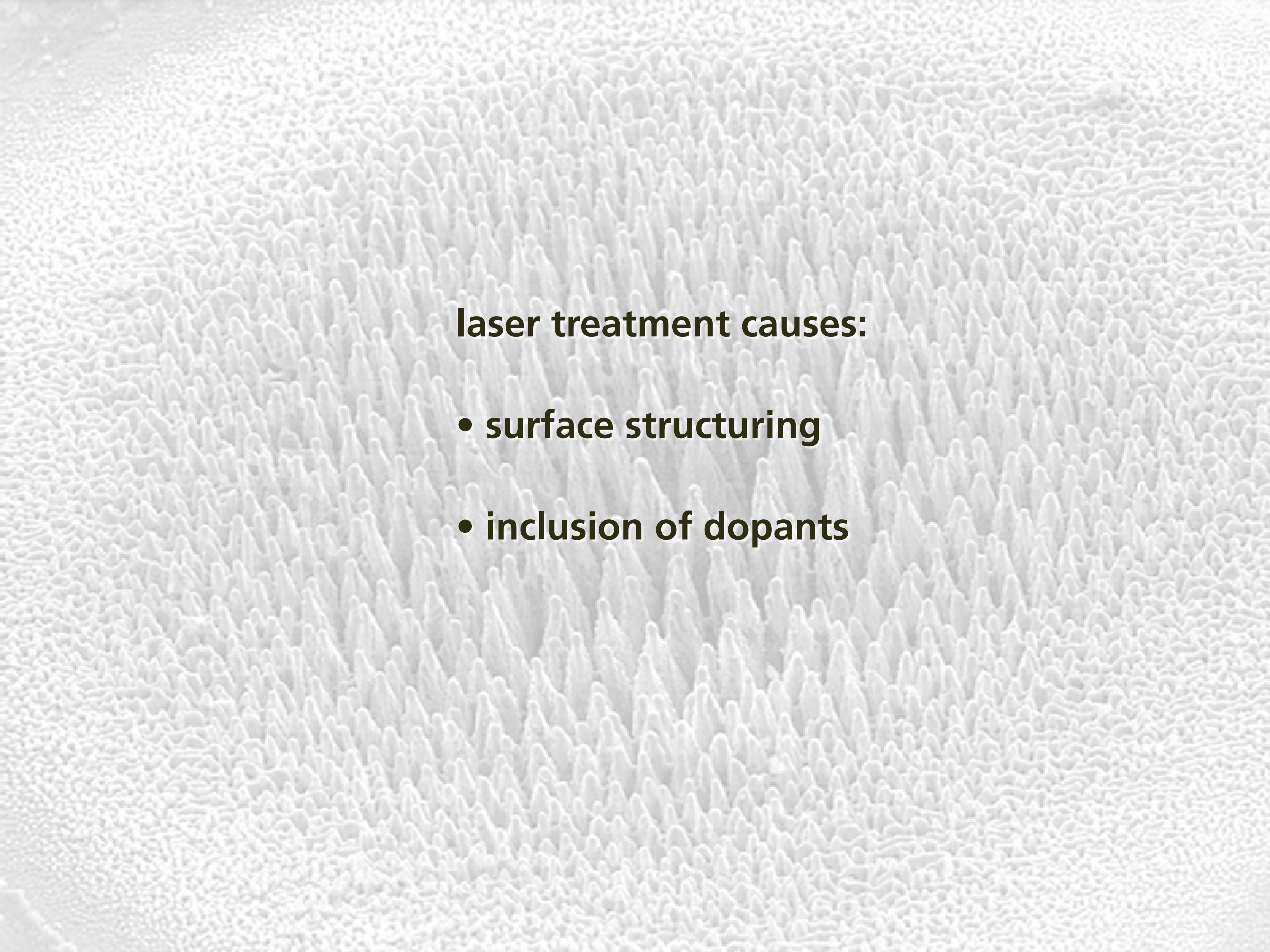


absorptance (1 – R_{int} – T_{int})



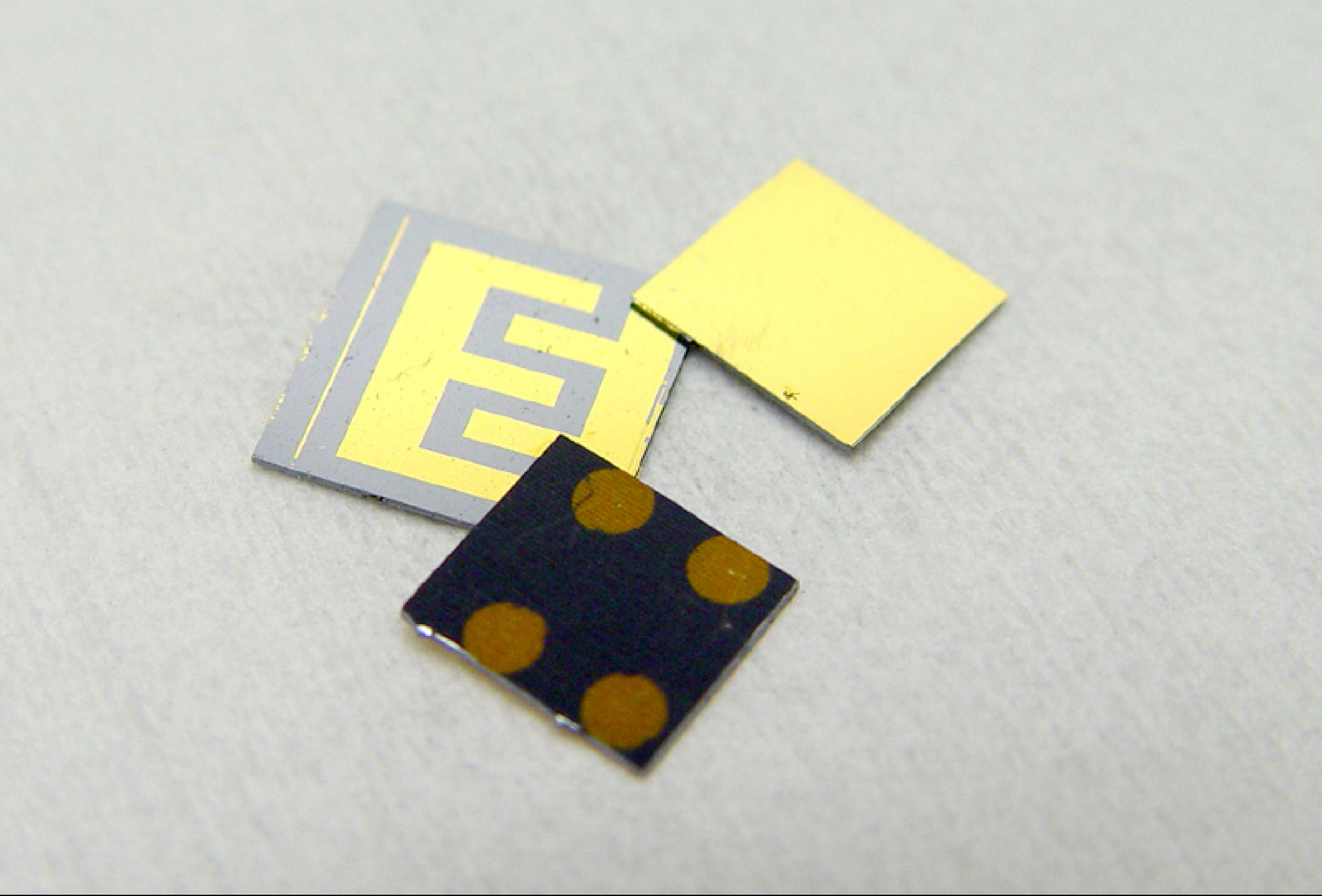
absorptance (1 – R_{int} – T_{int})



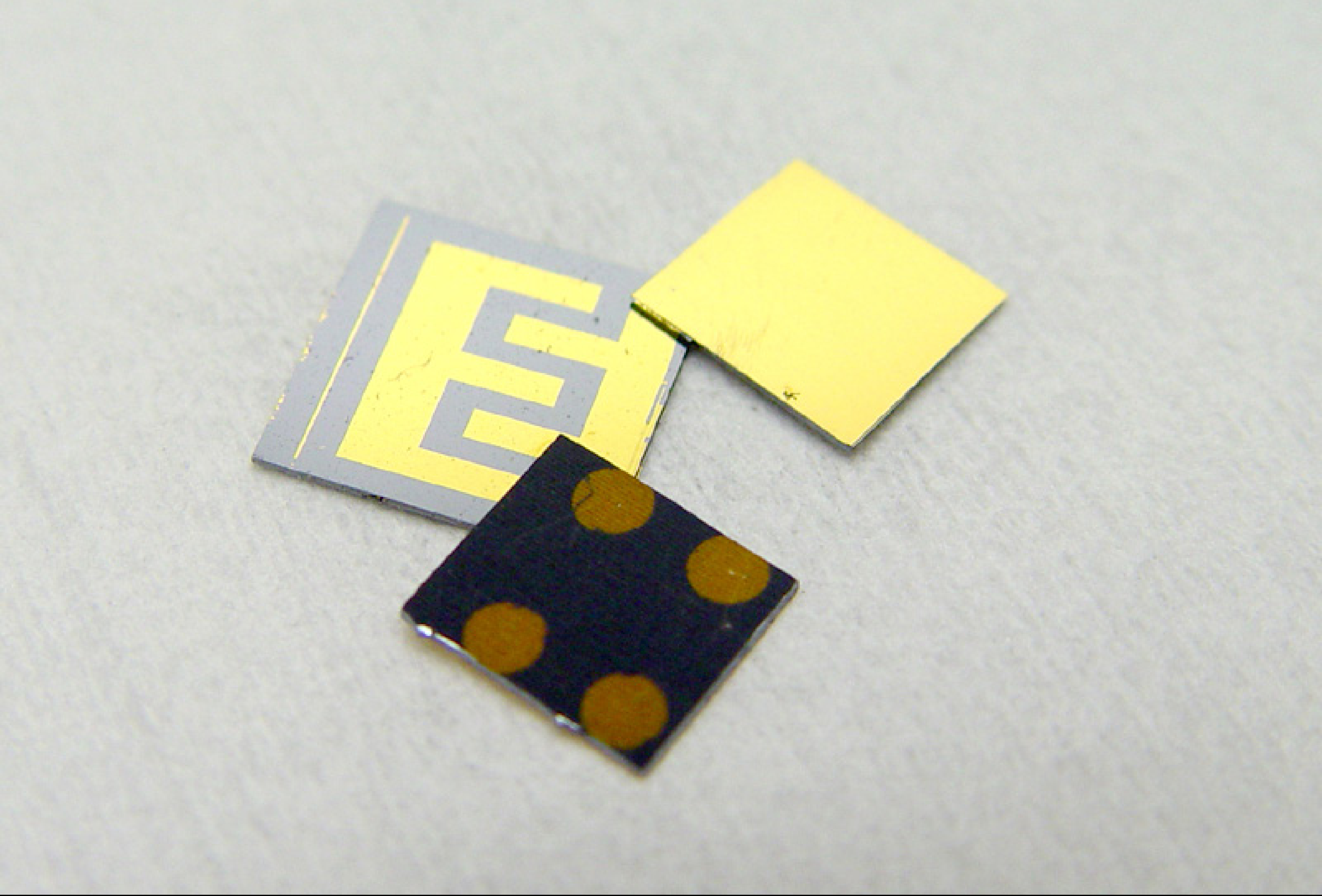


laser treatment causes:

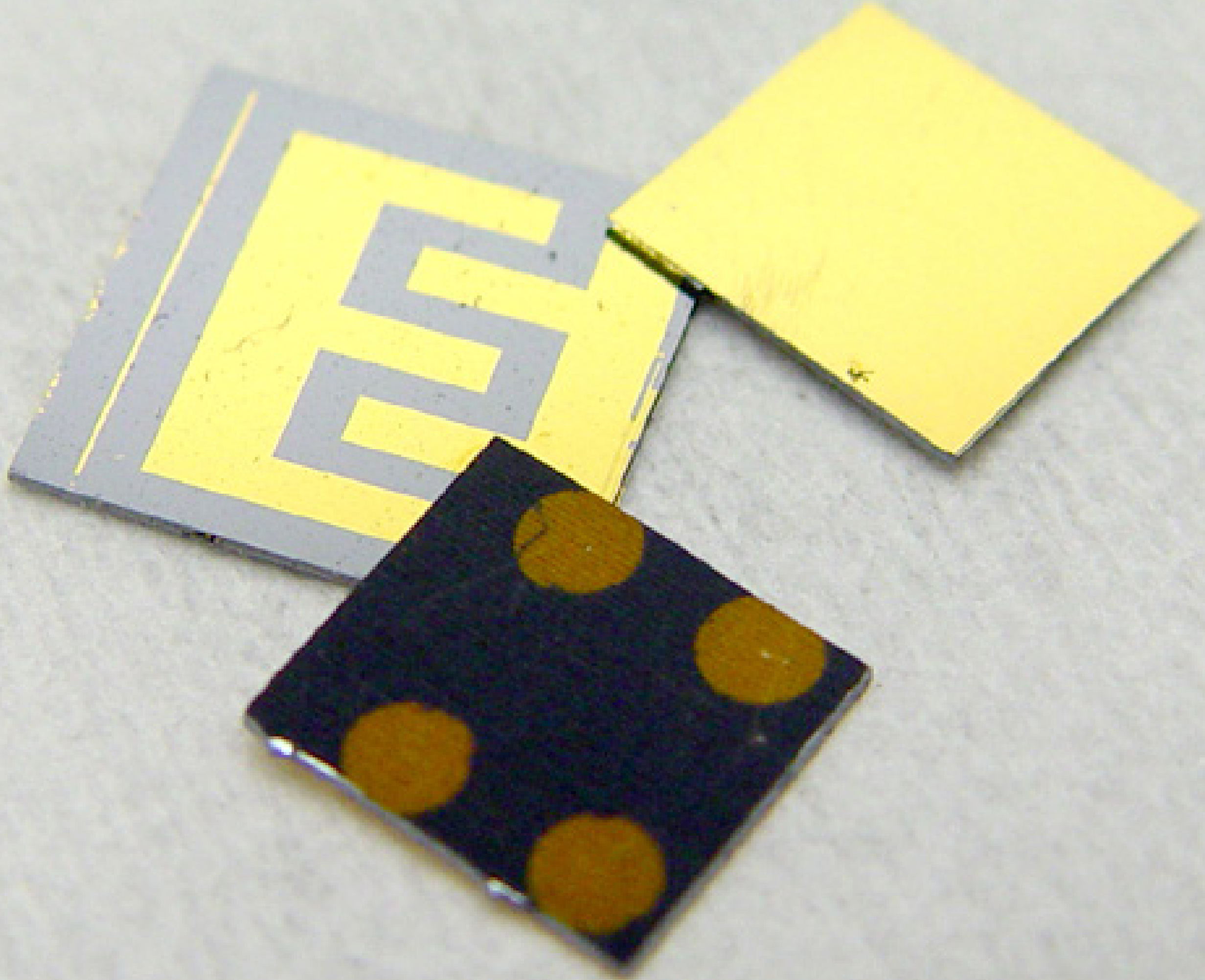
- surface structuring
- inclusion of dopants



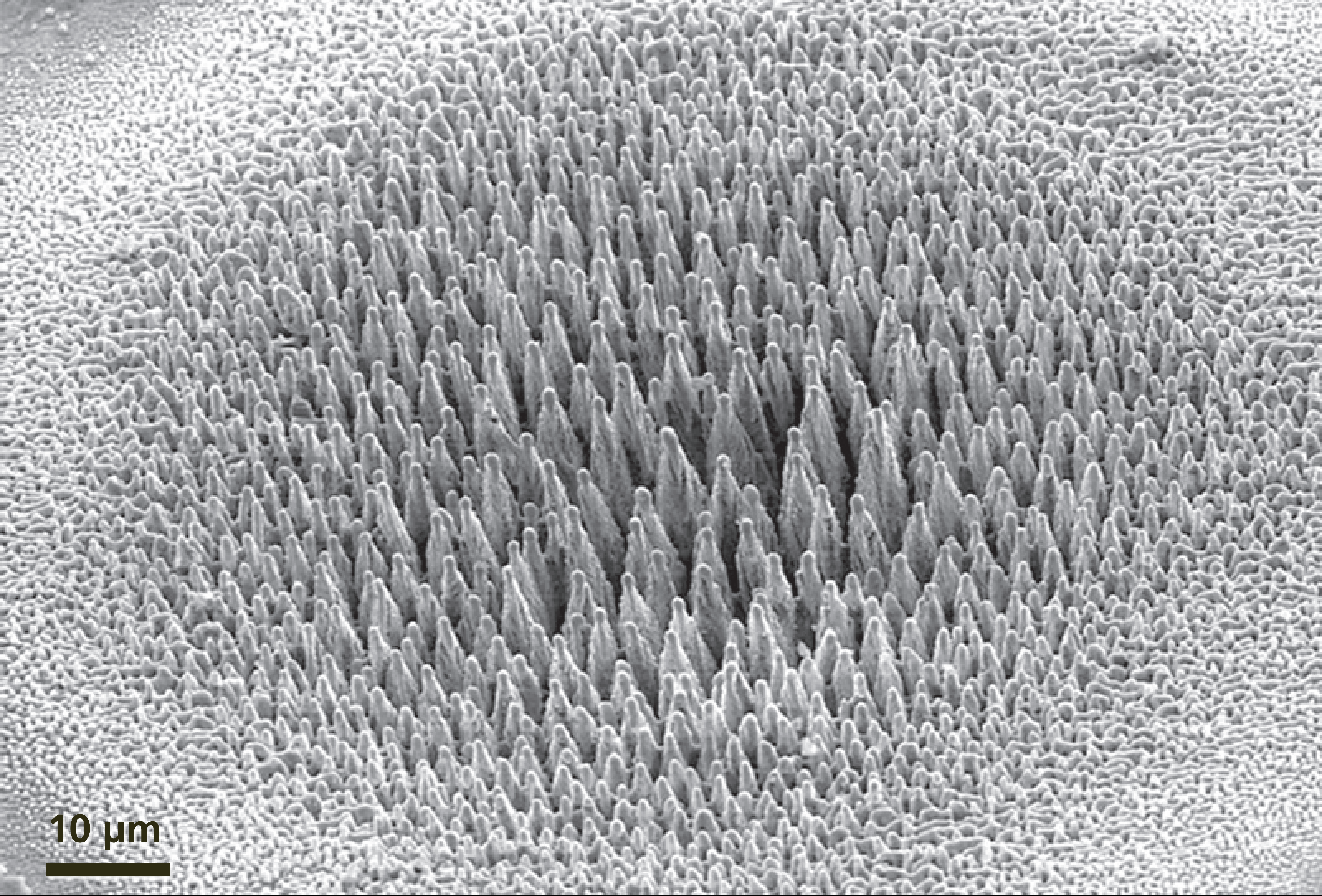
❶ properties



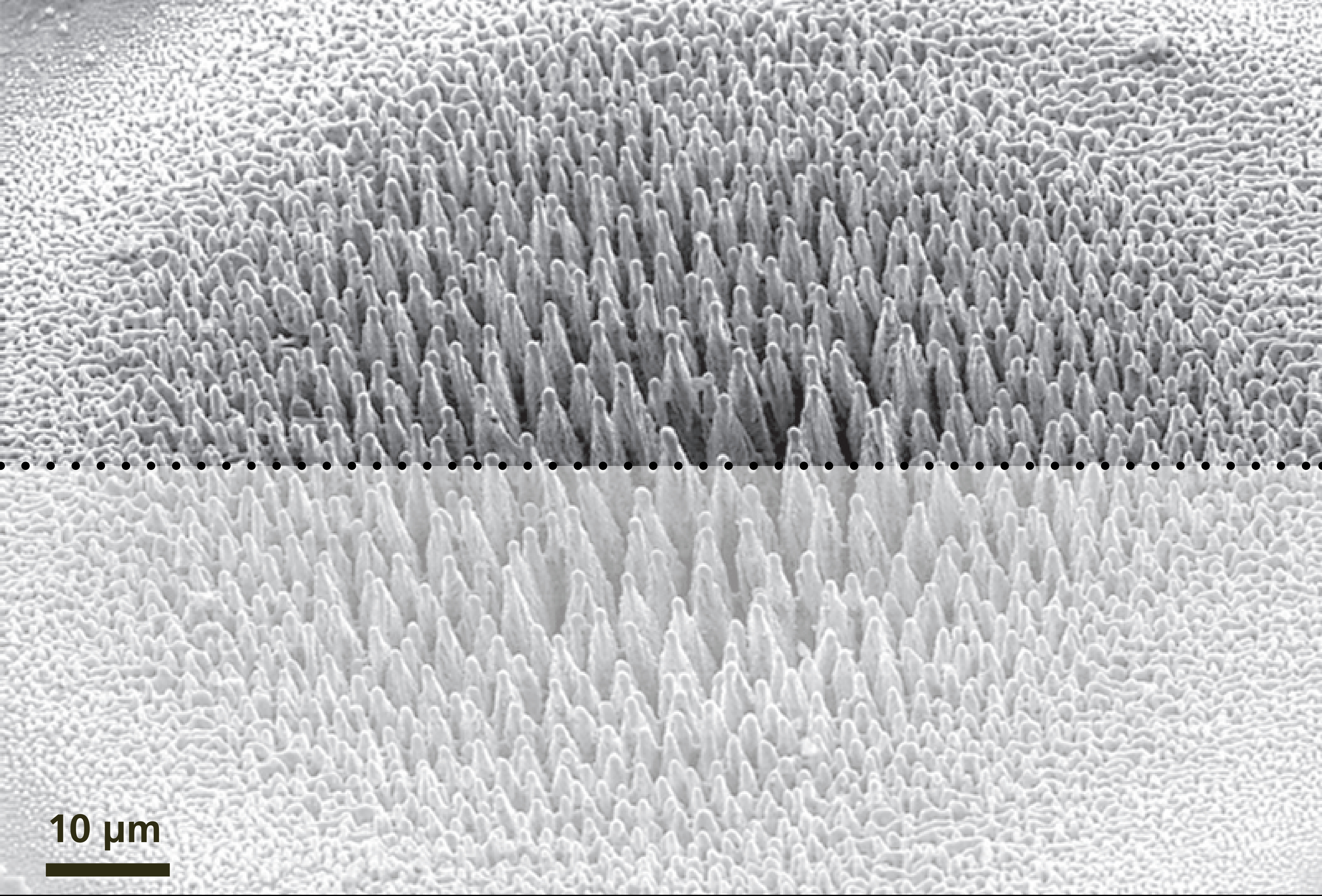
① properties ② intermediate band



① properties ② intermediate band ③ devices



1 properties



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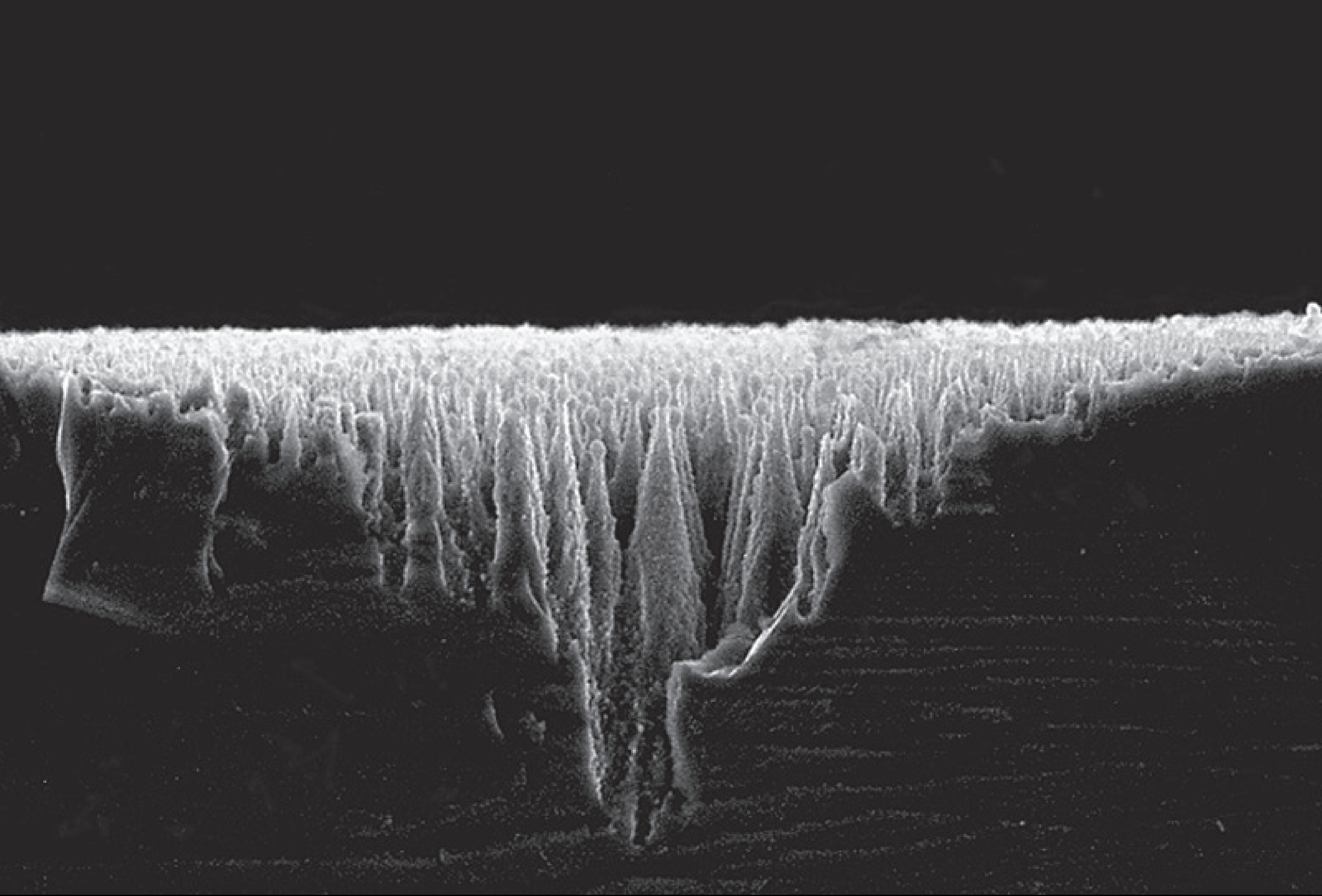

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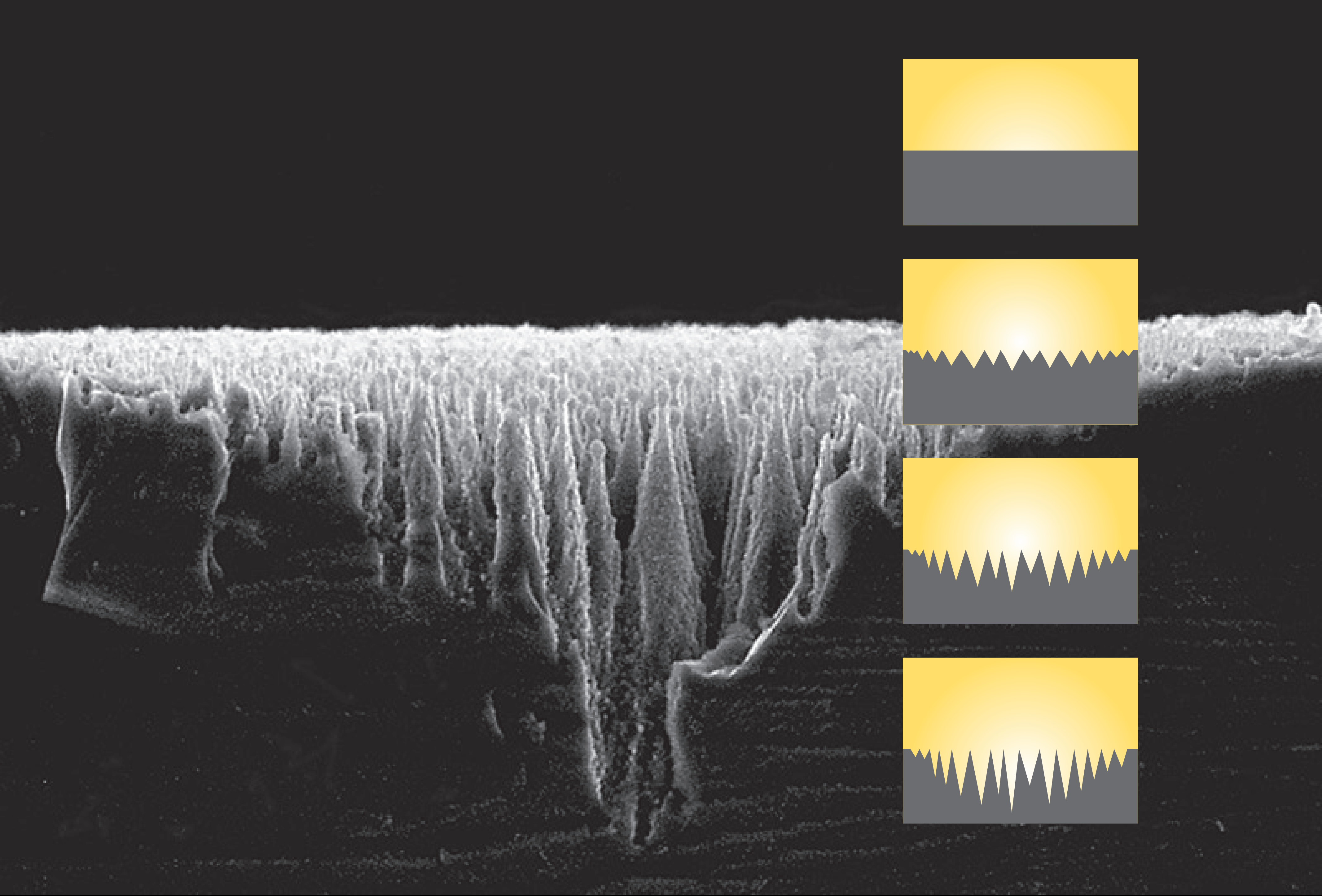

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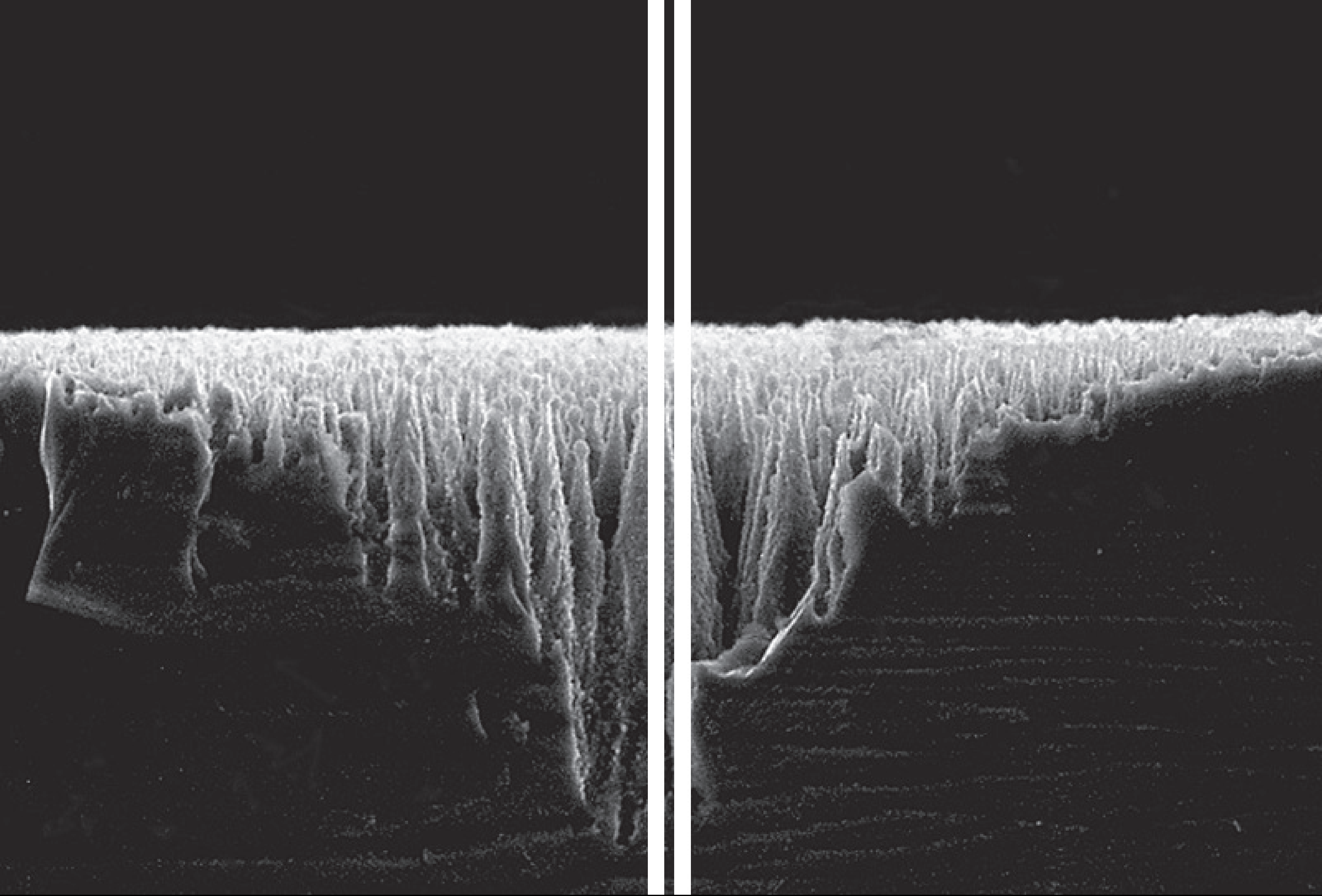
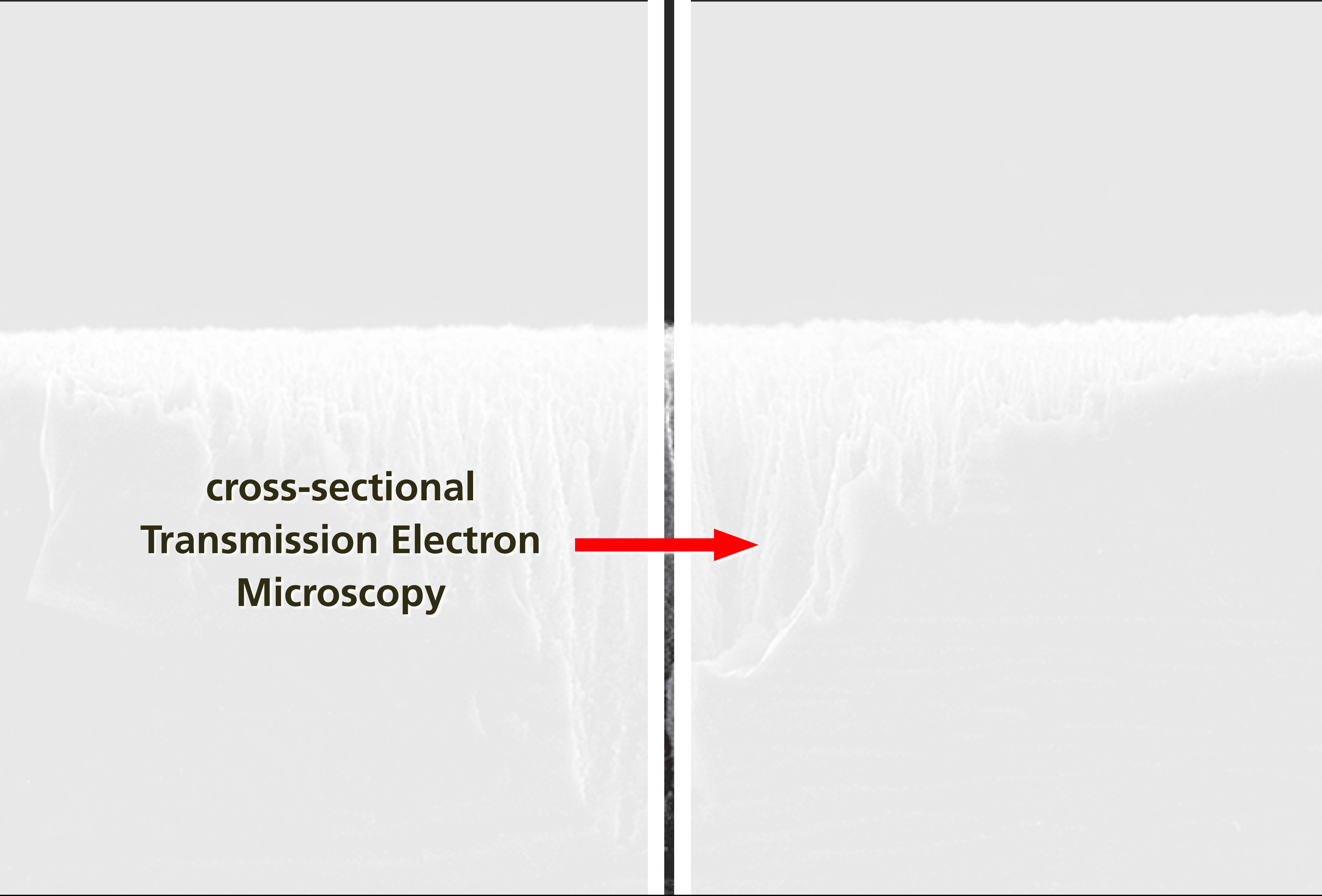
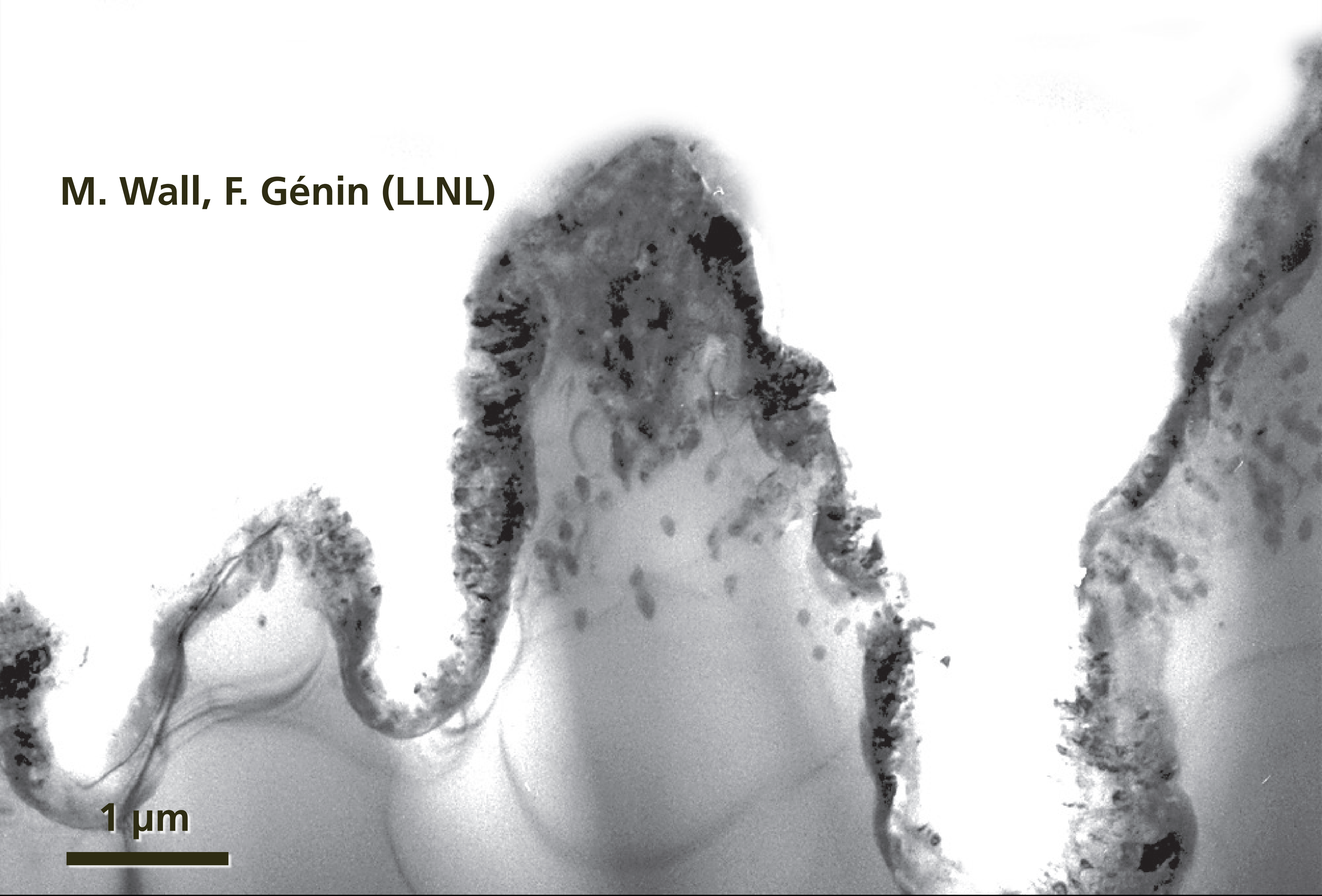


1 properties

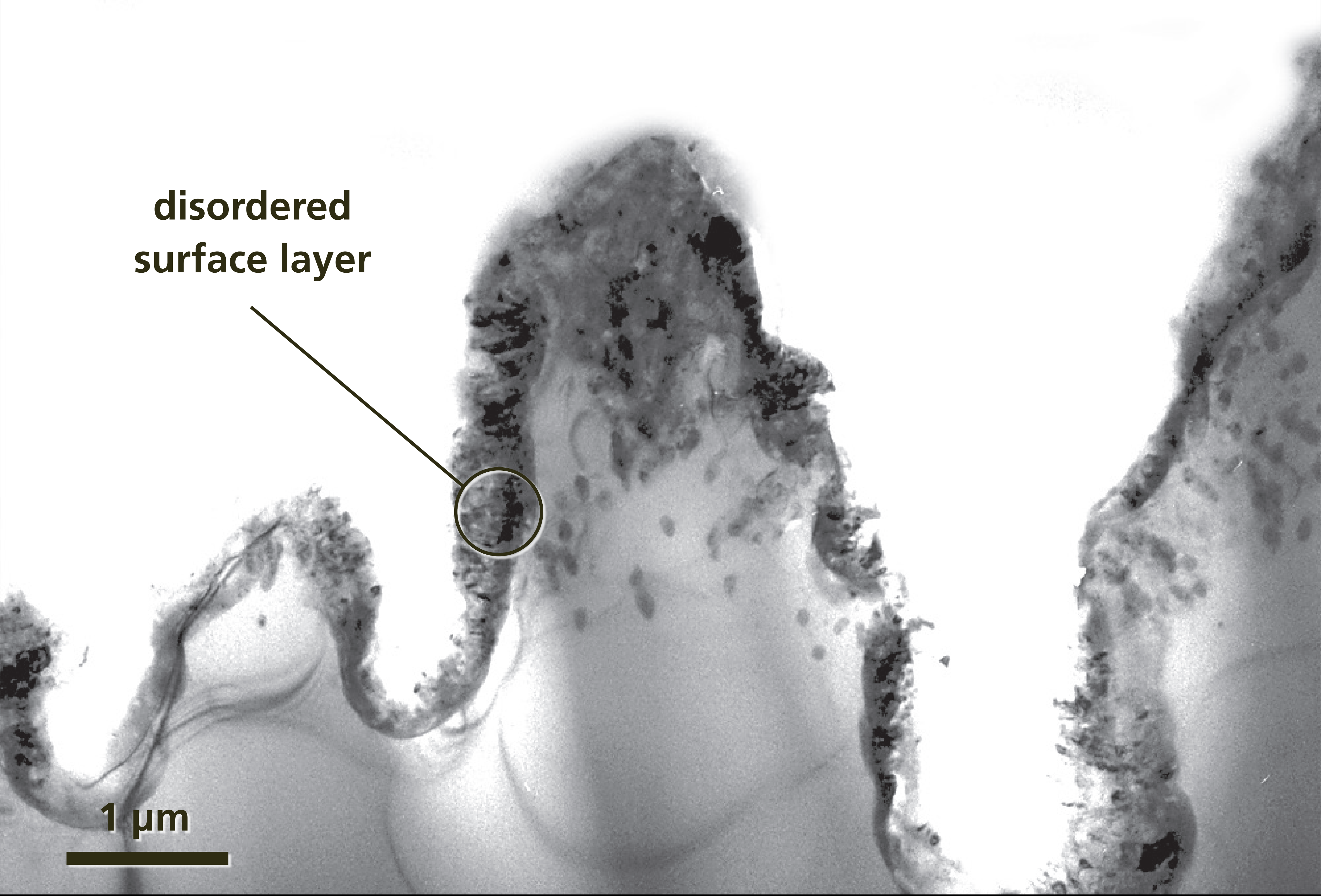


cross-sectional
Transmission Electron
Microscopy

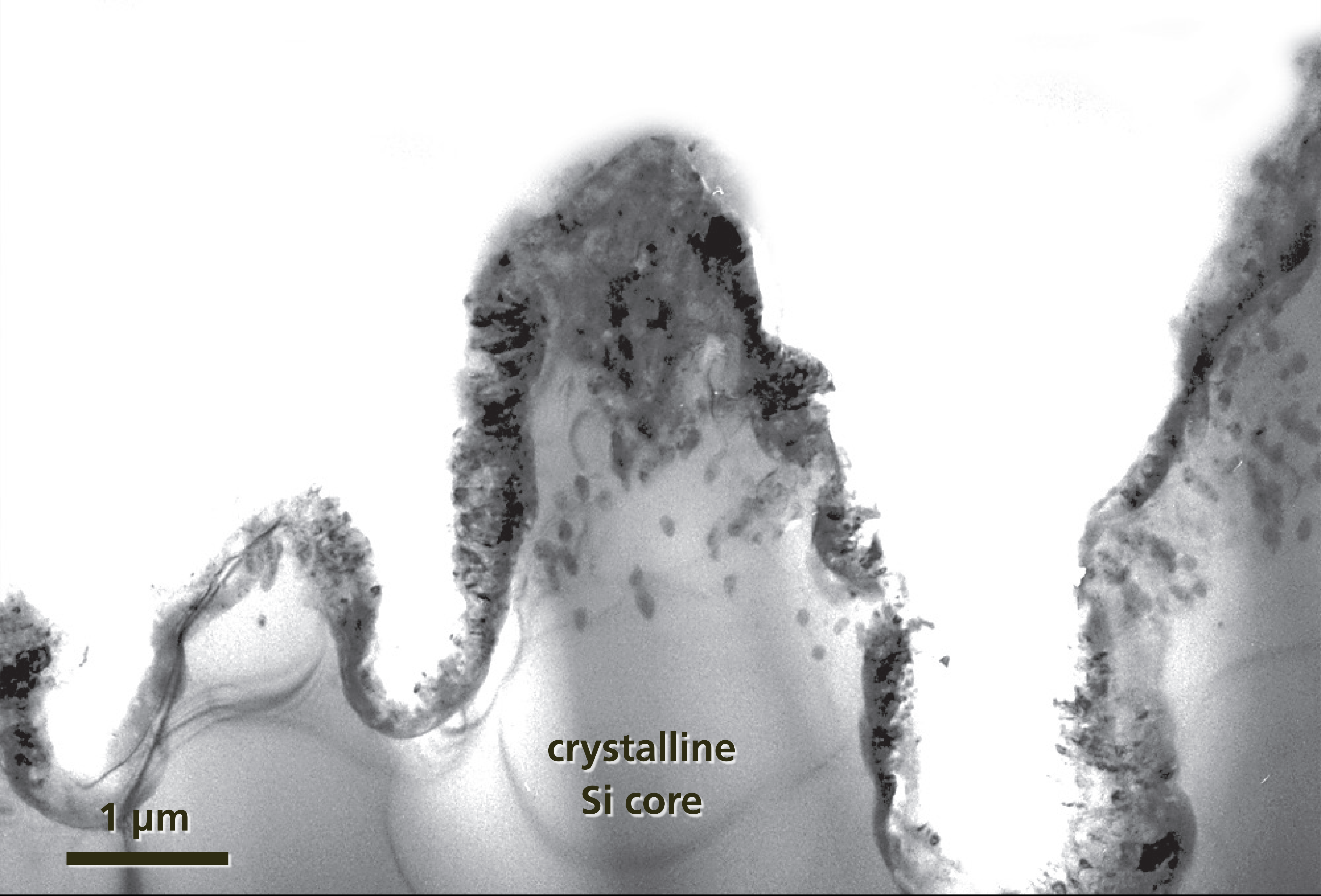
① properties



M. Wall, F. Génin (LLNL)



❶ properties



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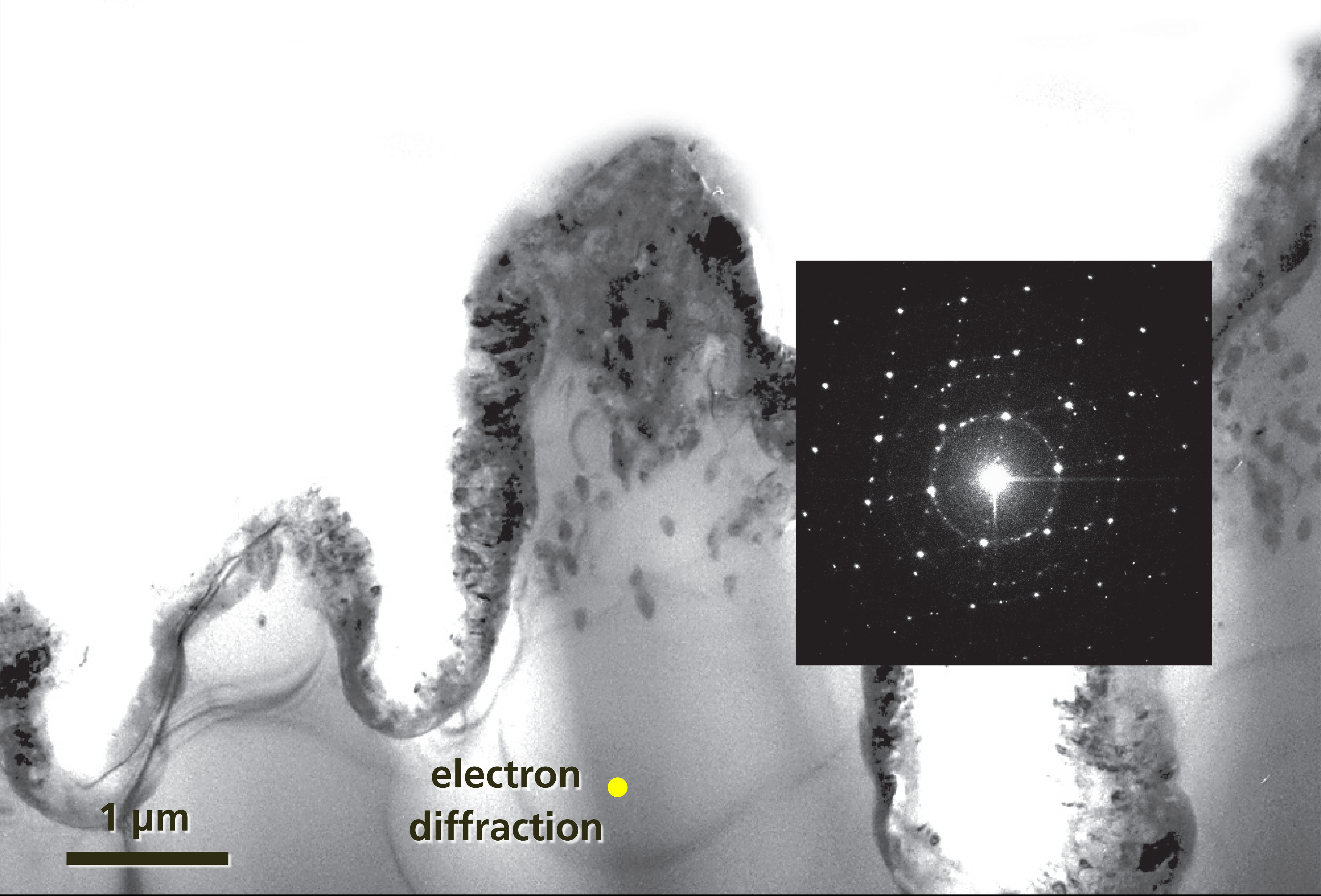
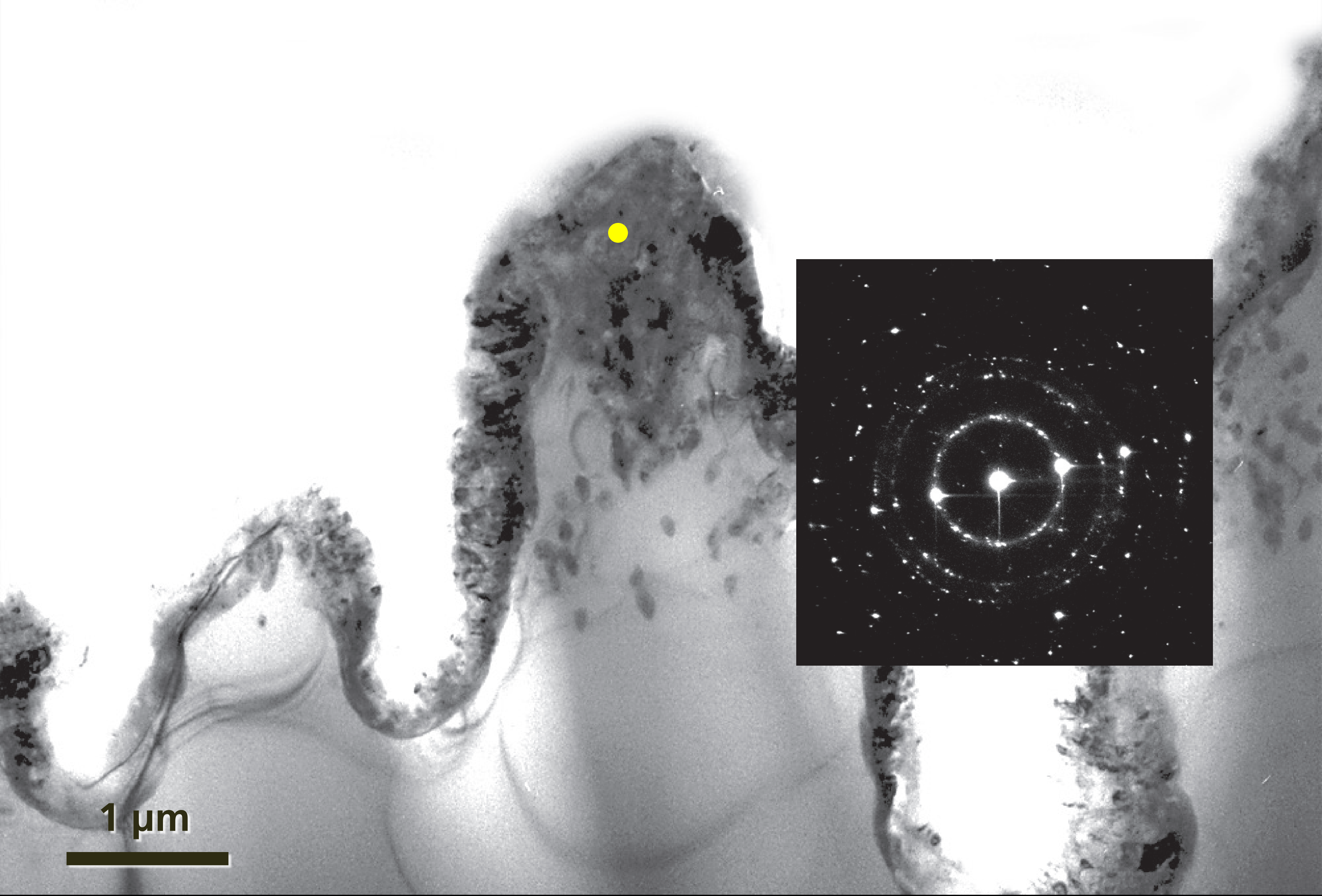
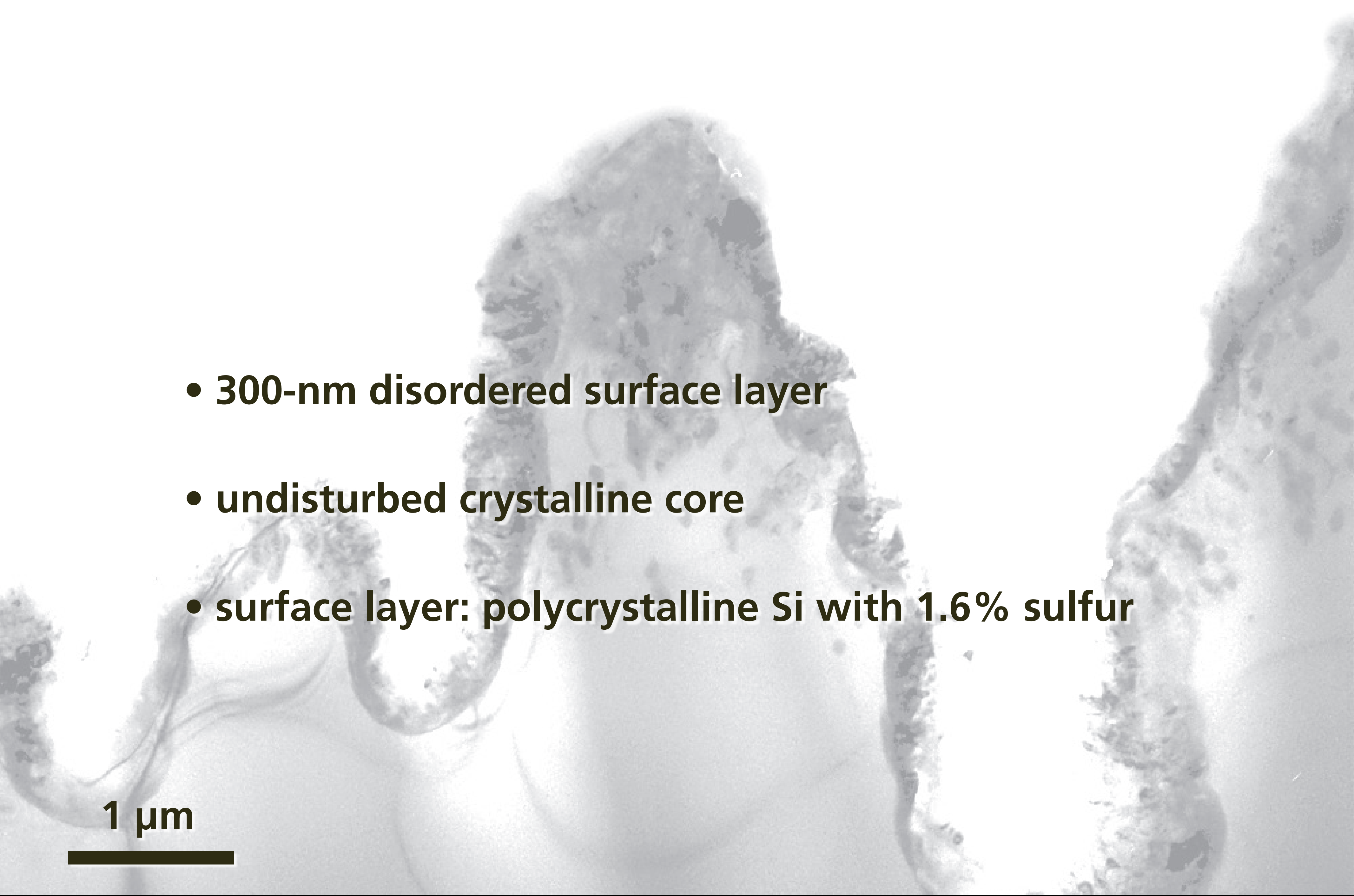


① properties


1 µm

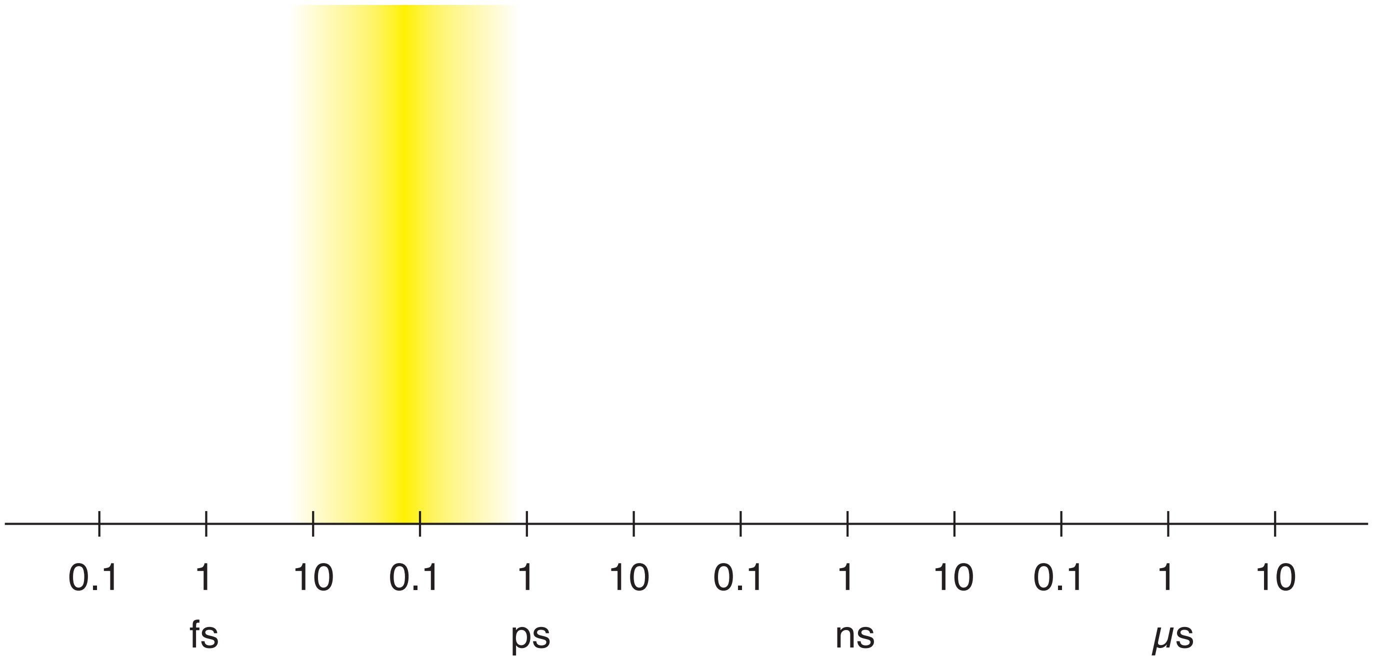


- 300-nm disordered surface layer
- undisturbed crystalline core
- surface layer: polycrystalline Si with 1.6% sulfur

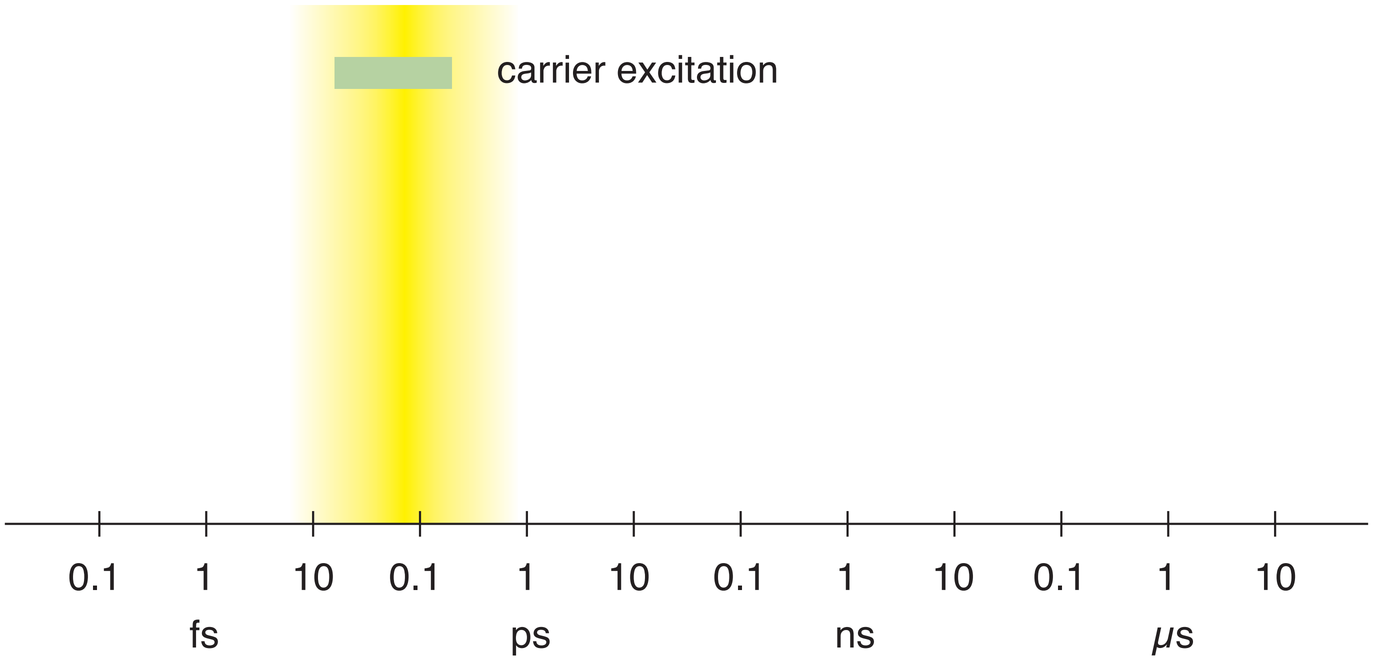
1 properties

two processes: melting and ablation

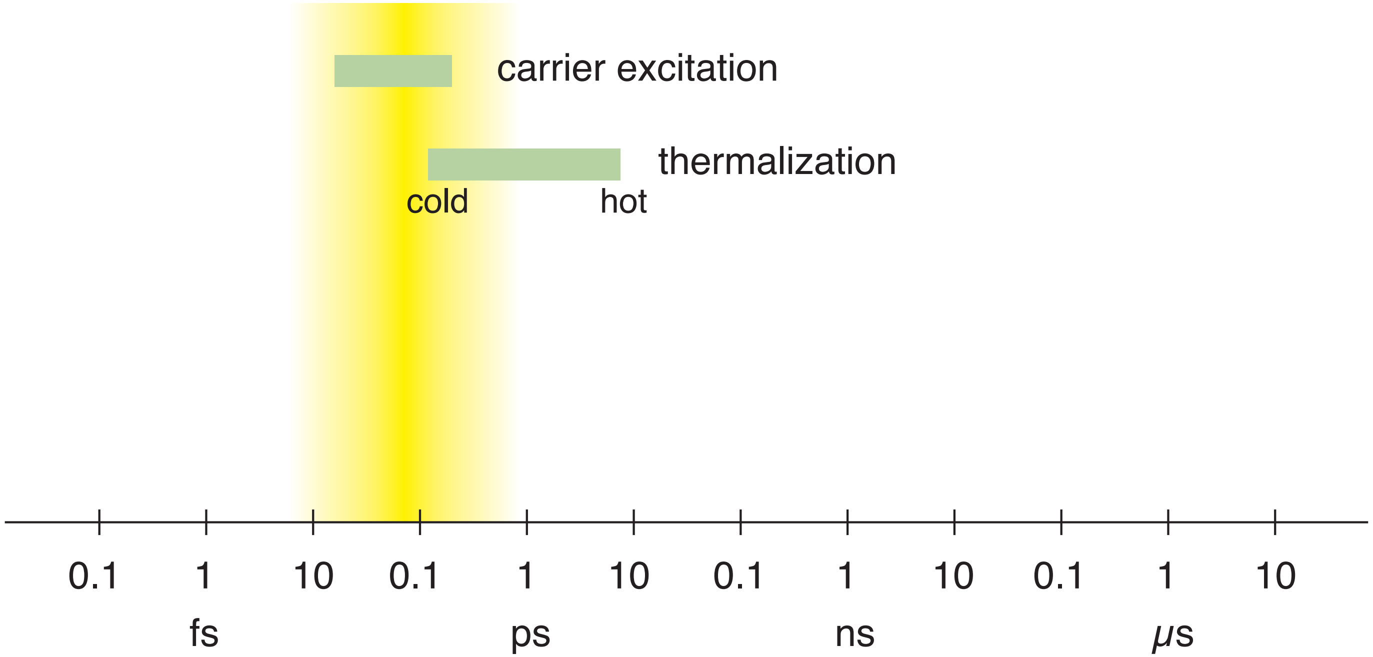
relevant time scales



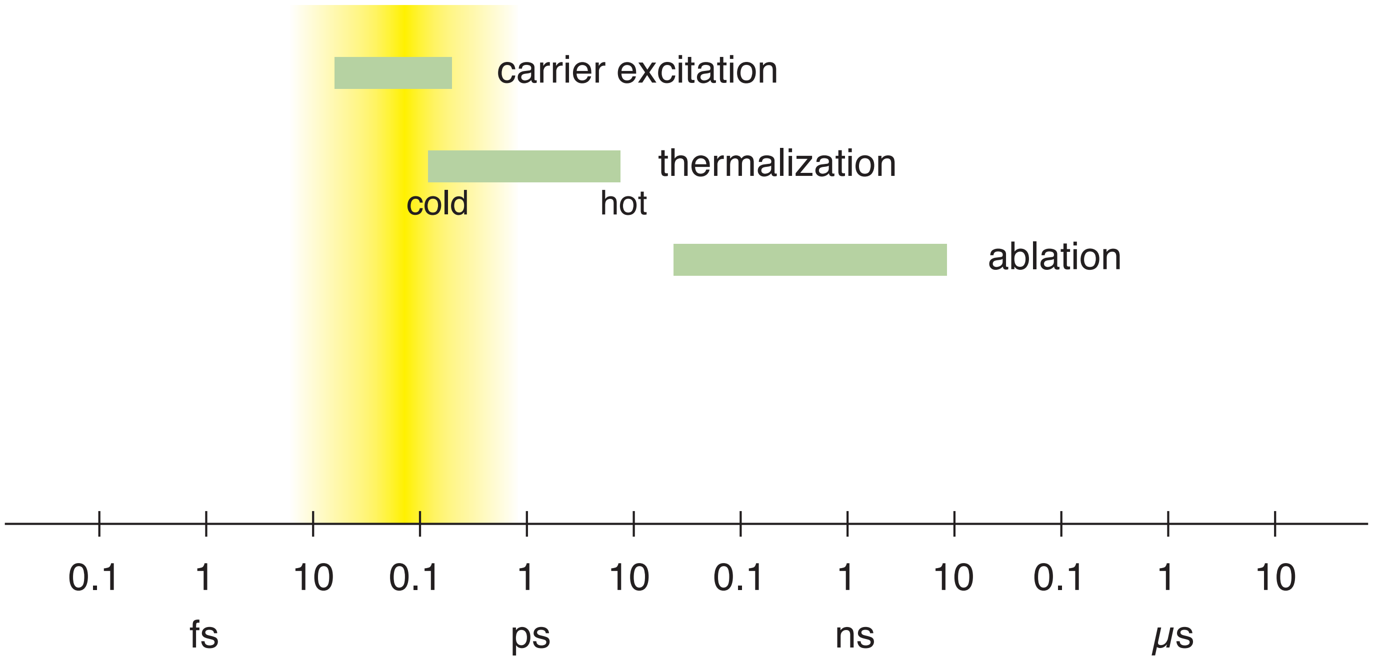
relevant time scales



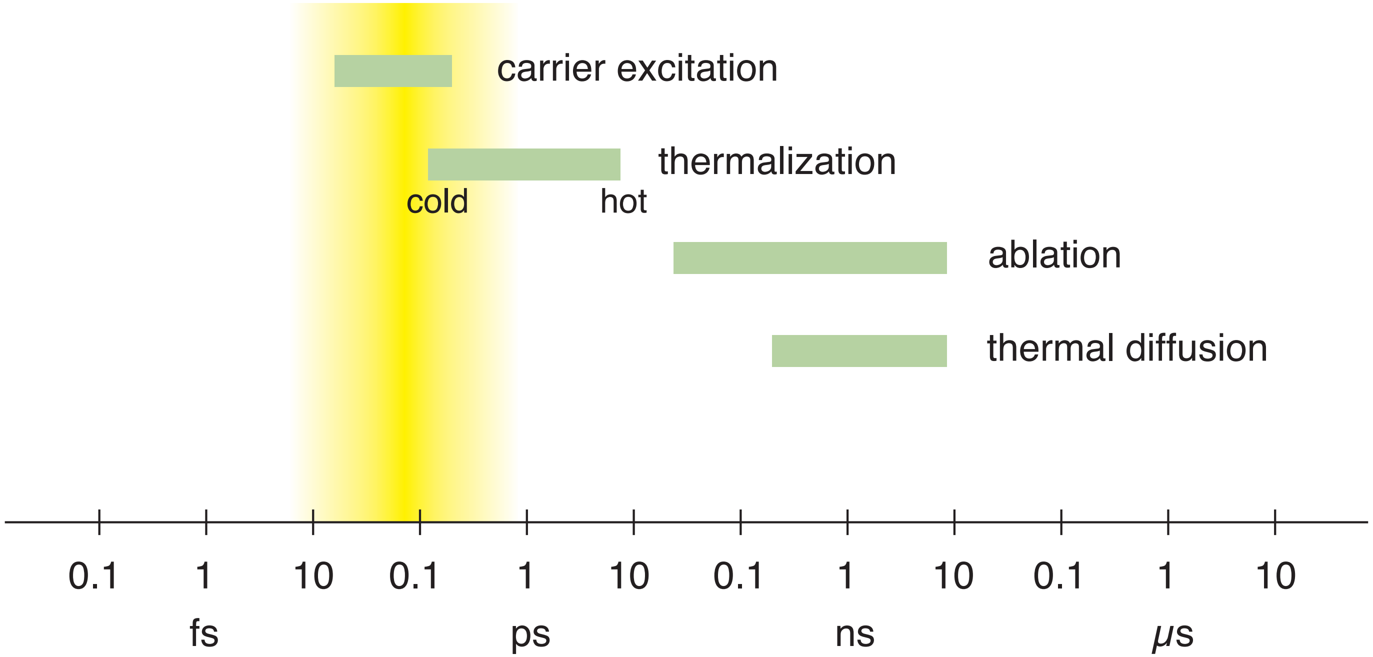
relevant time scales



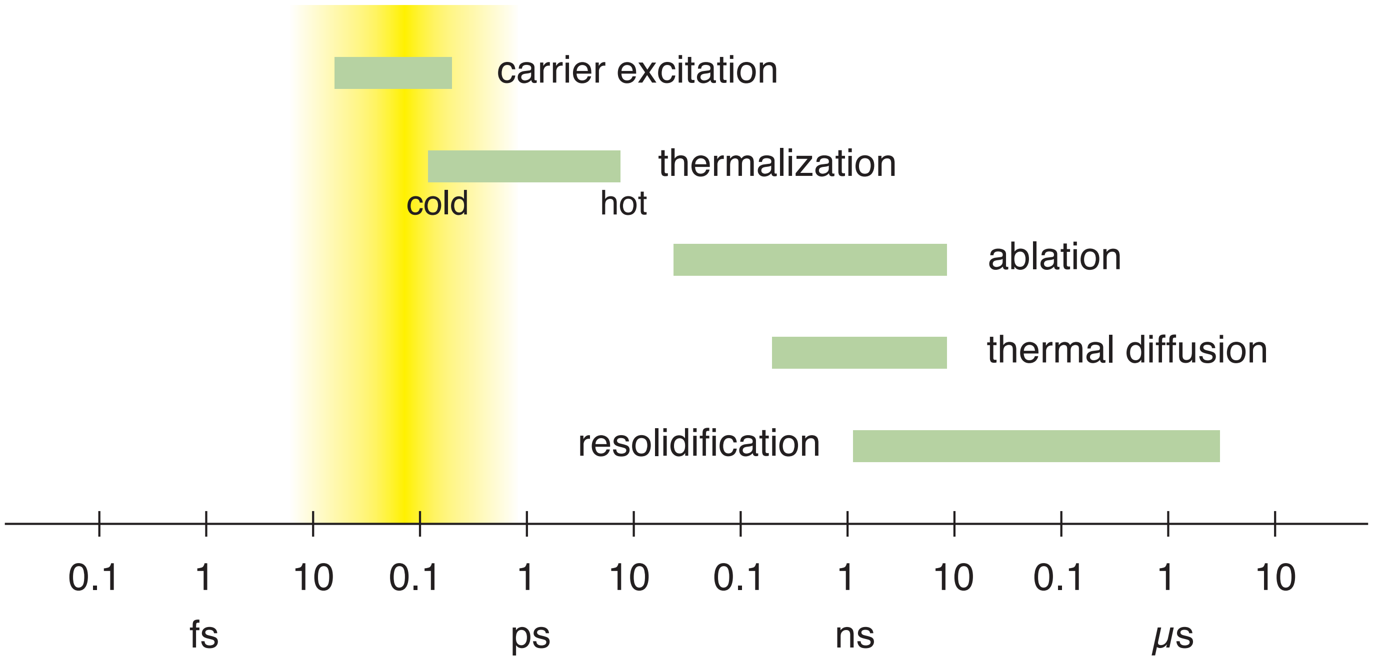
relevant time scales



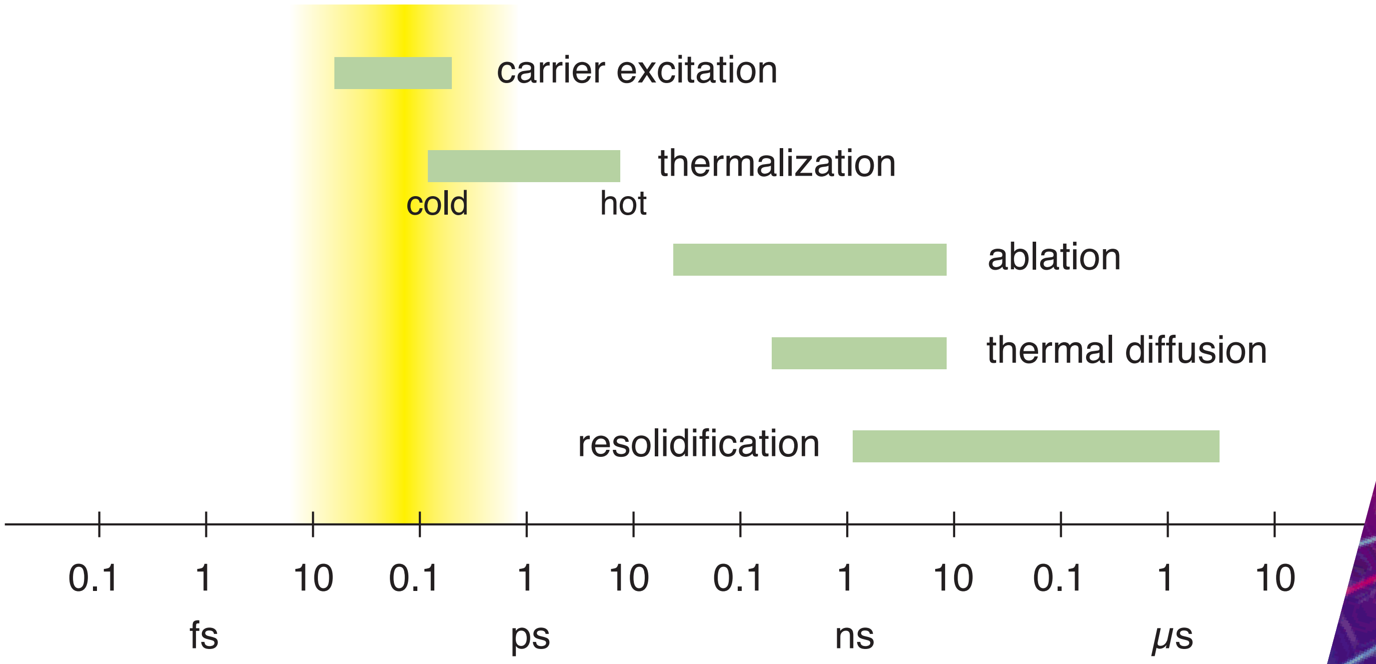
relevant time scales



relevant time scales

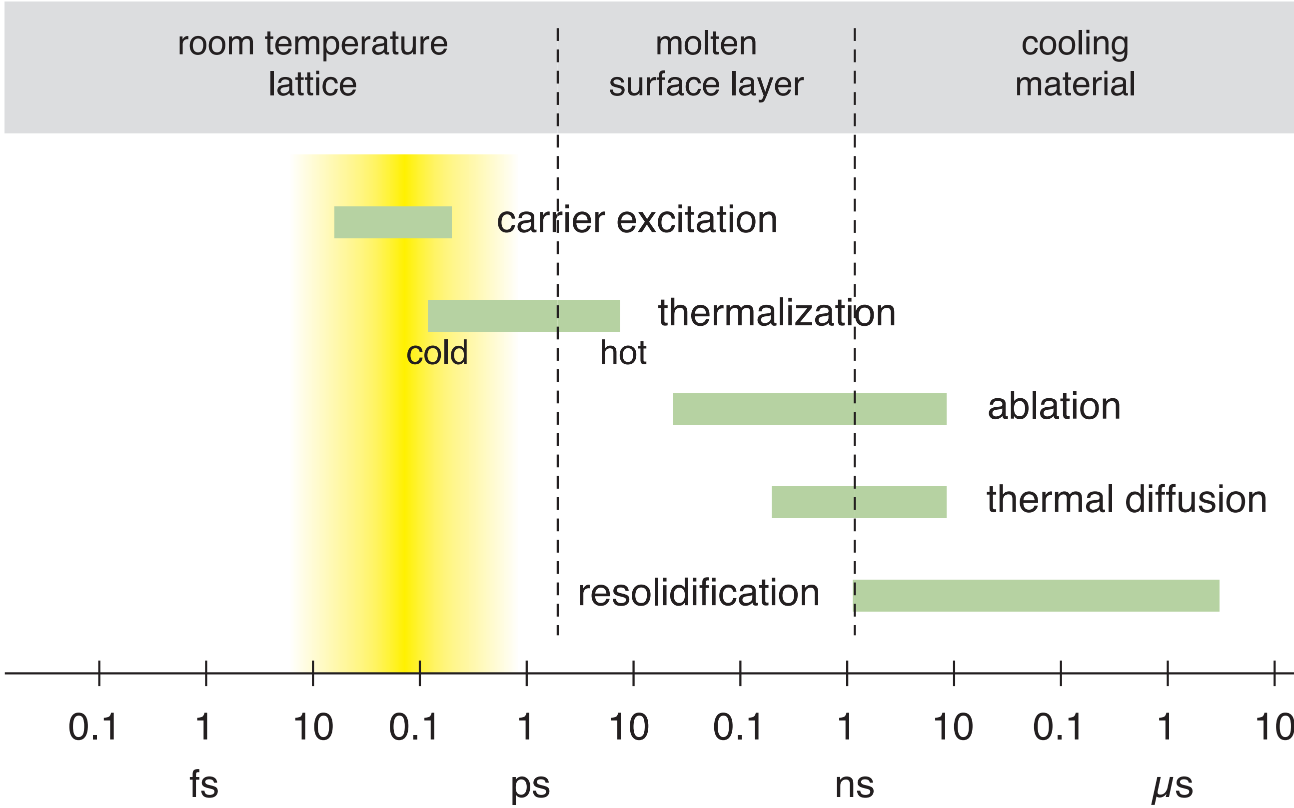


relevant time scales



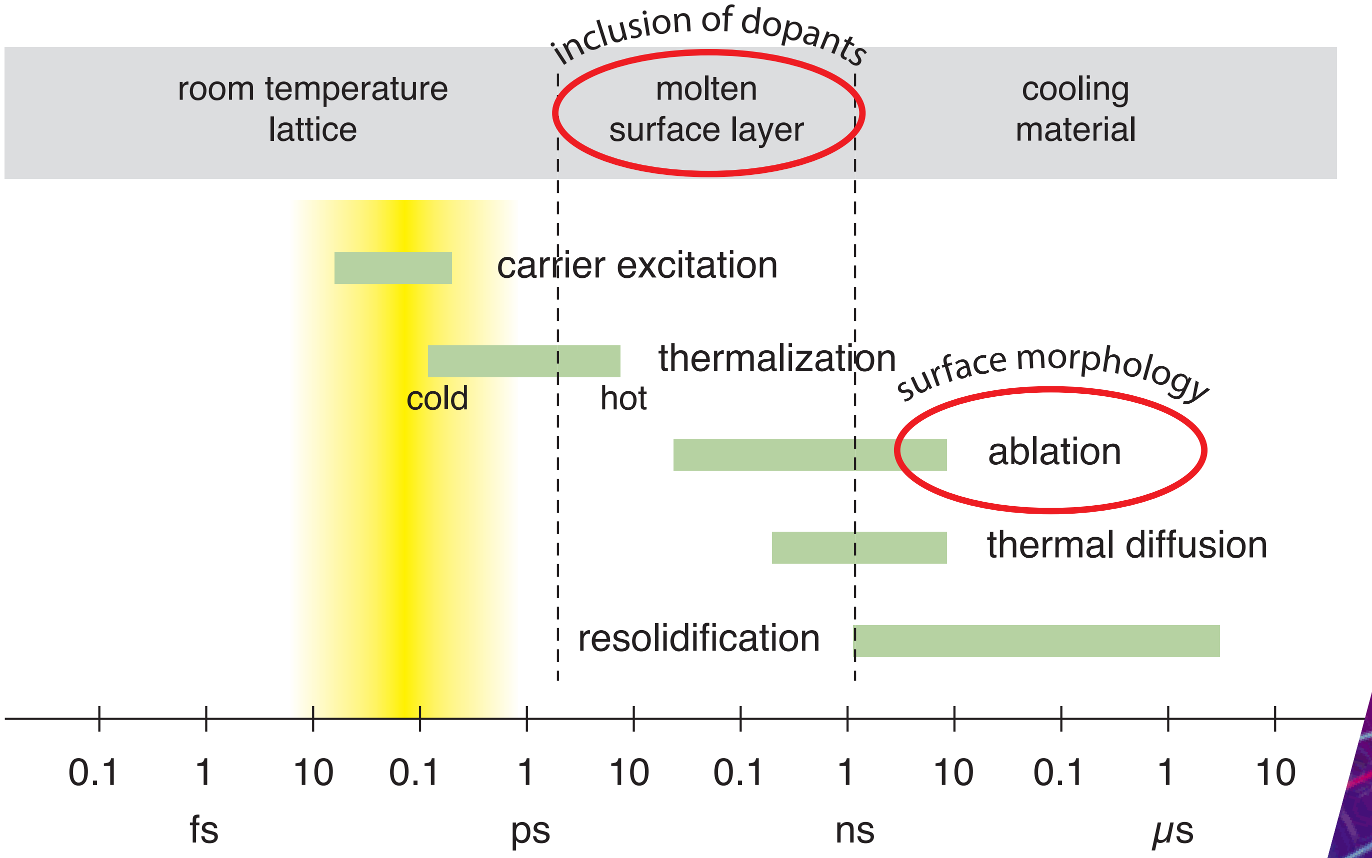
Nature Materials 1, 217 (2002)

relevant time scales



Nature Materials **1**, 217 (2002)

relevant time scales



inclusion of dopants

room temperature
lattice

molten
surface layer

cooling
material

carrier excitation

thermalization

cold

hot

surface morphology

ablation

thermal diffusion

resolidification

0.1 1 10 0.1 1 10 0.1 1 10 0.1 1 10

fs ps ns μs

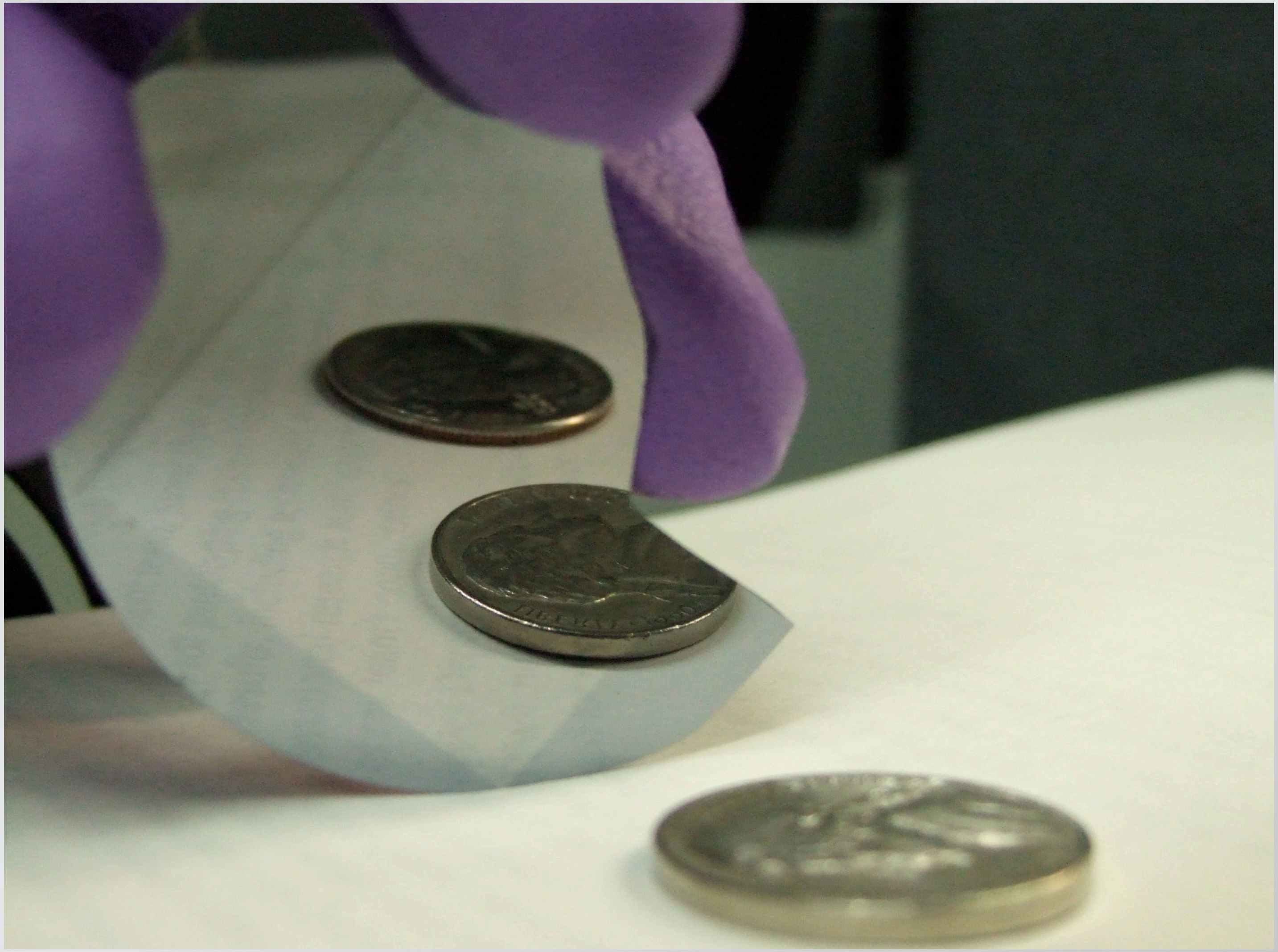
Nature Materials **1**, 217 (2002)

different thresholds:

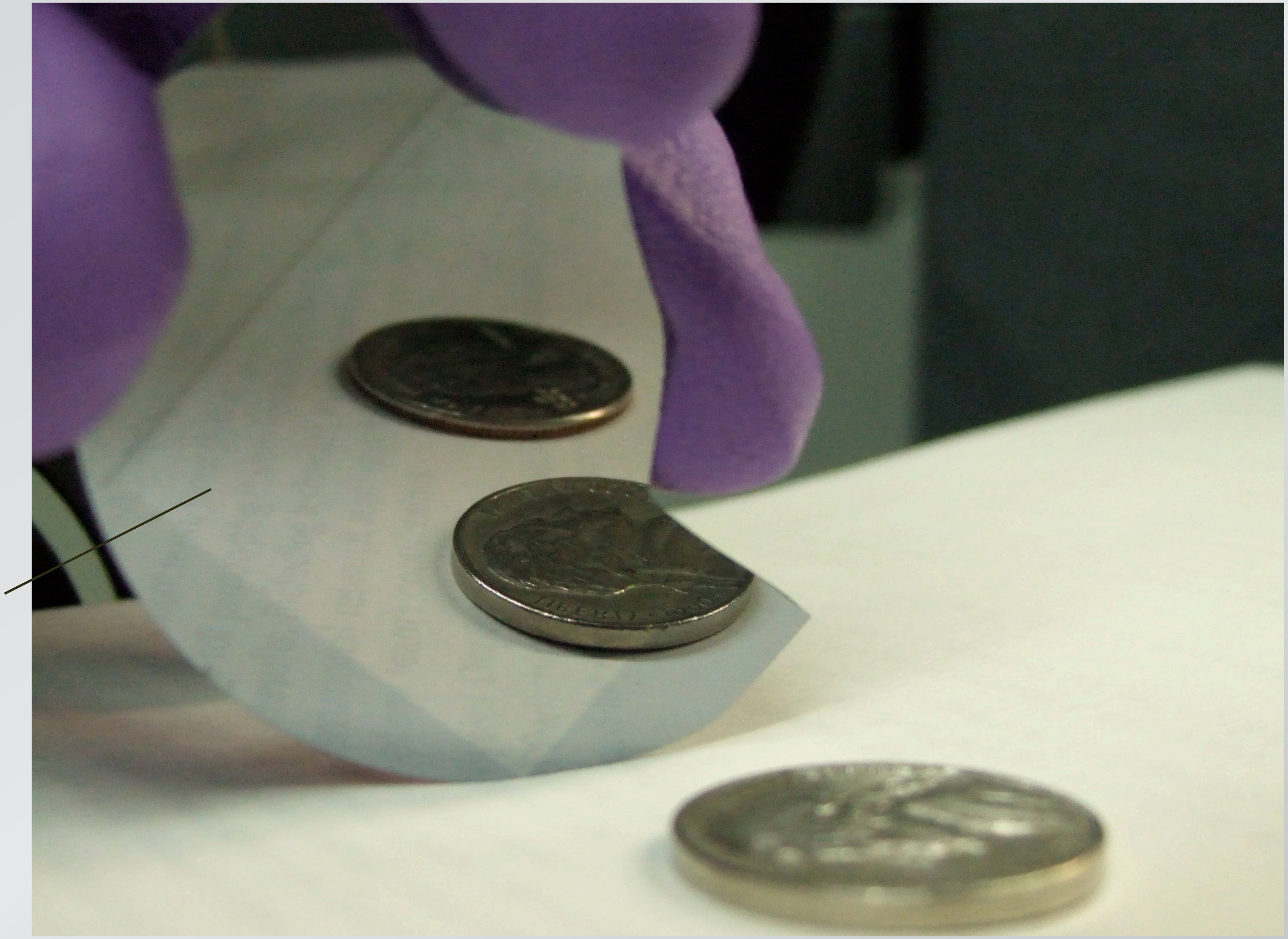
melting: 1.5 kJ/m^2

ablation: 3.1 kJ/m^2

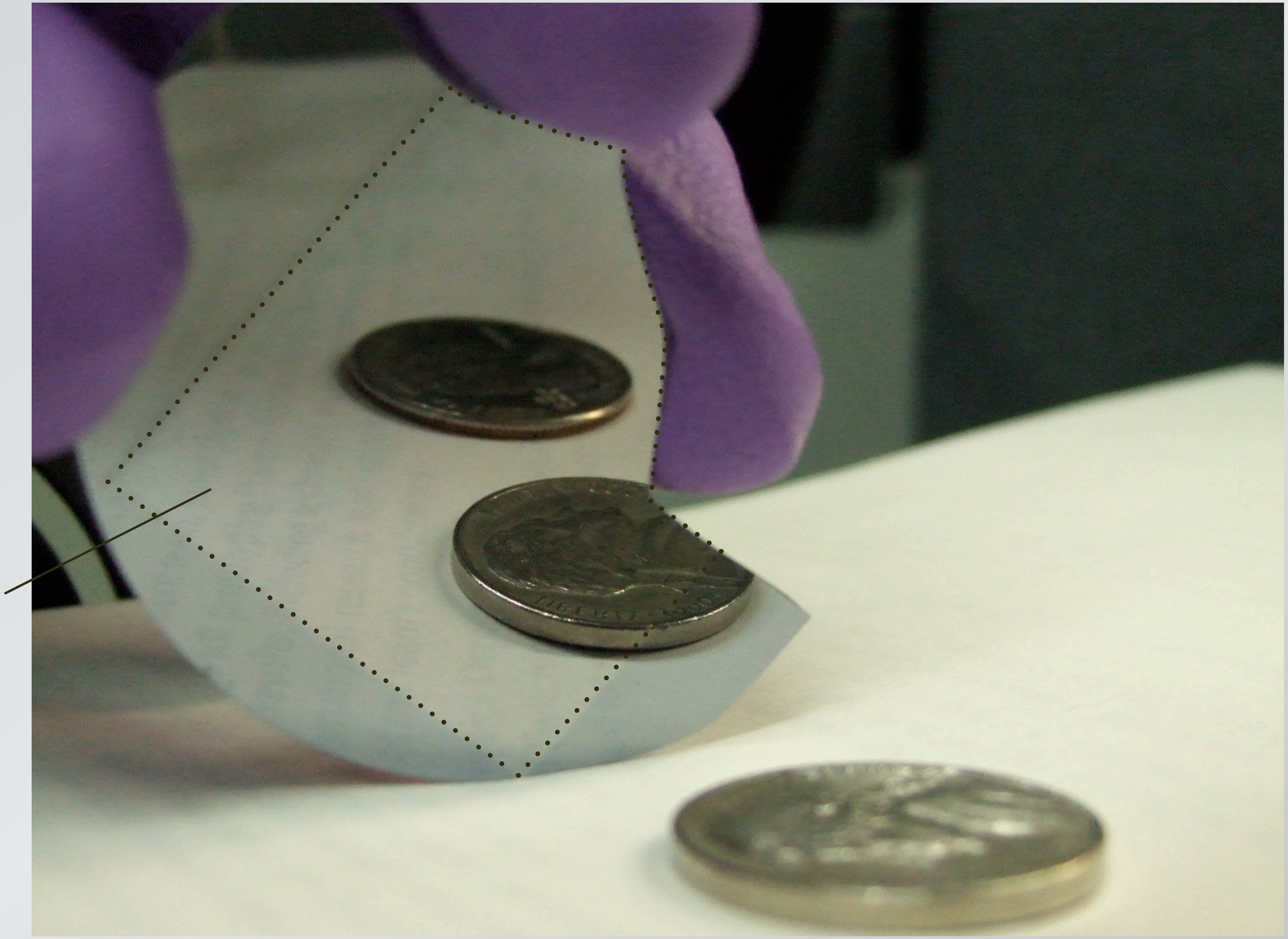
decouple ablation from melting



decouple ablation from melting

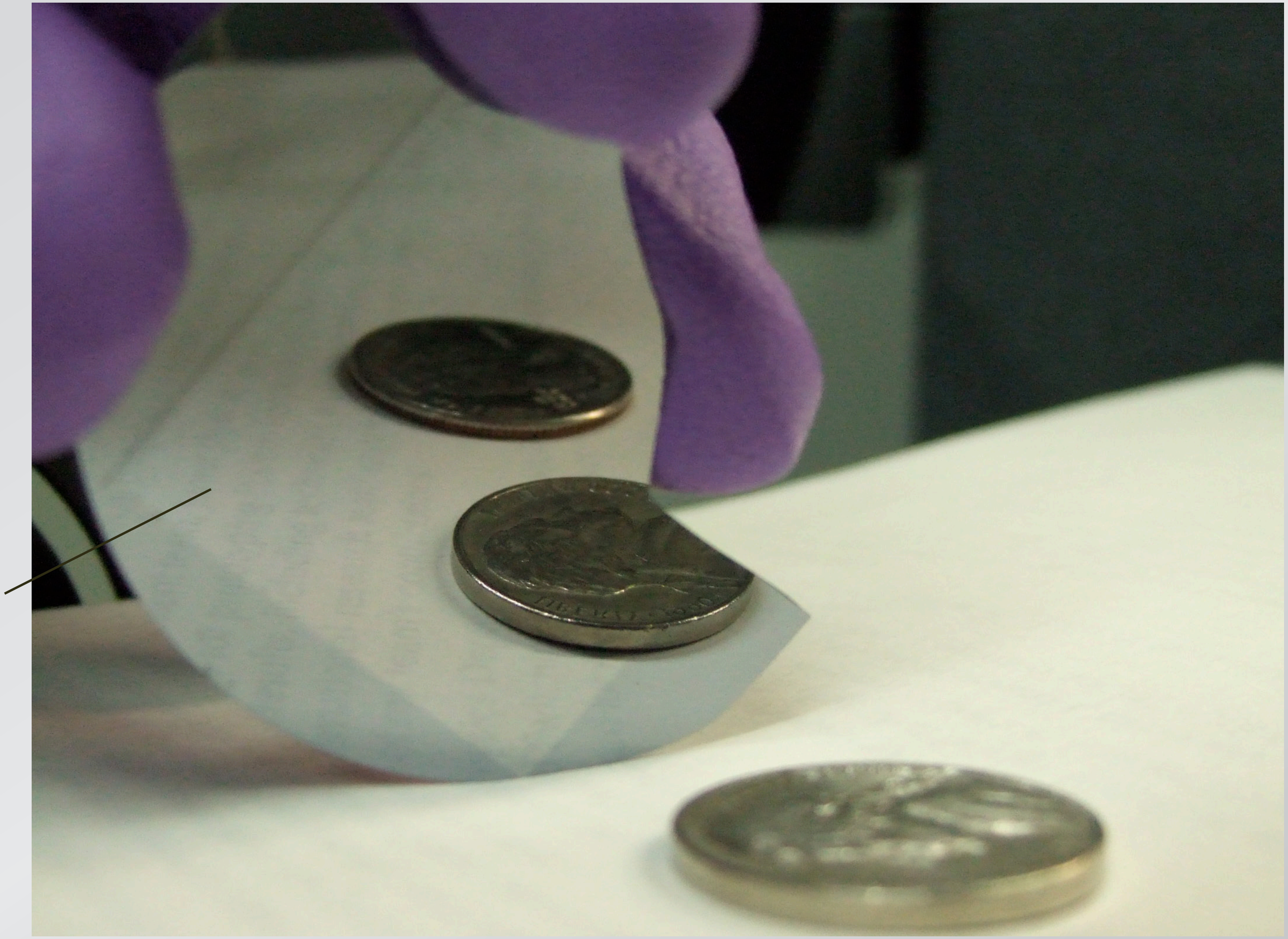


decouple ablation from melting



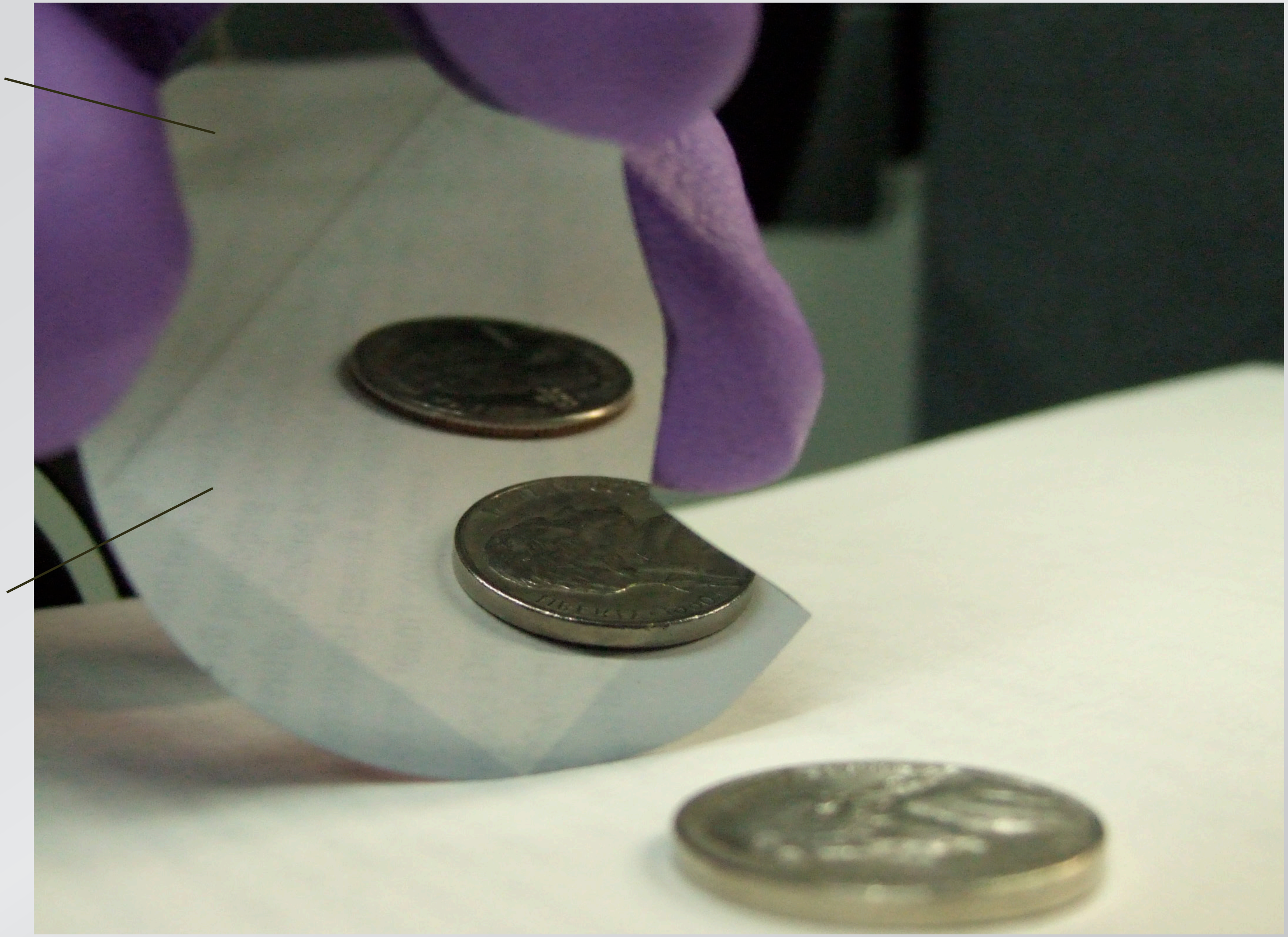
doped

decouple ablation from melting

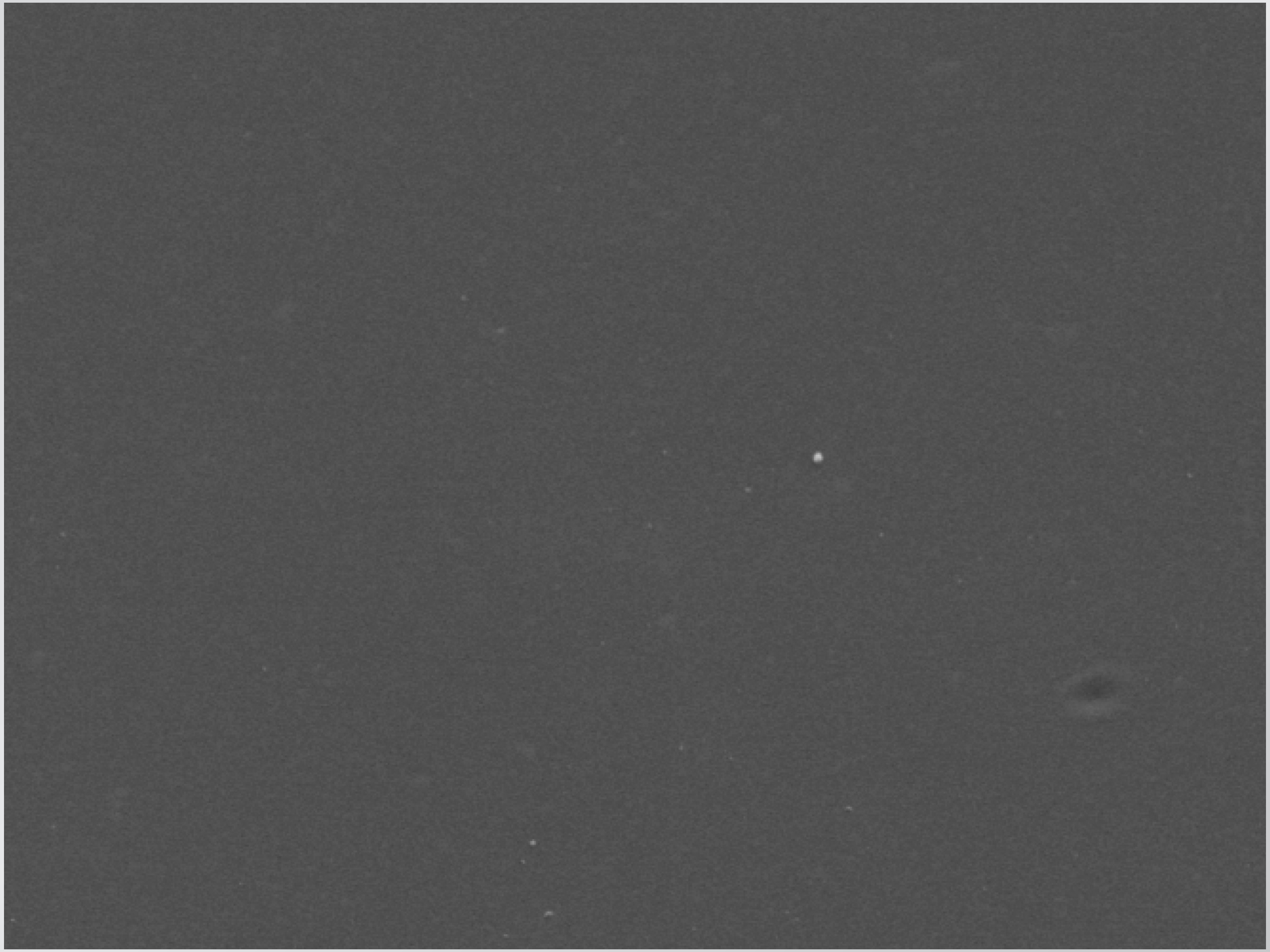


doped

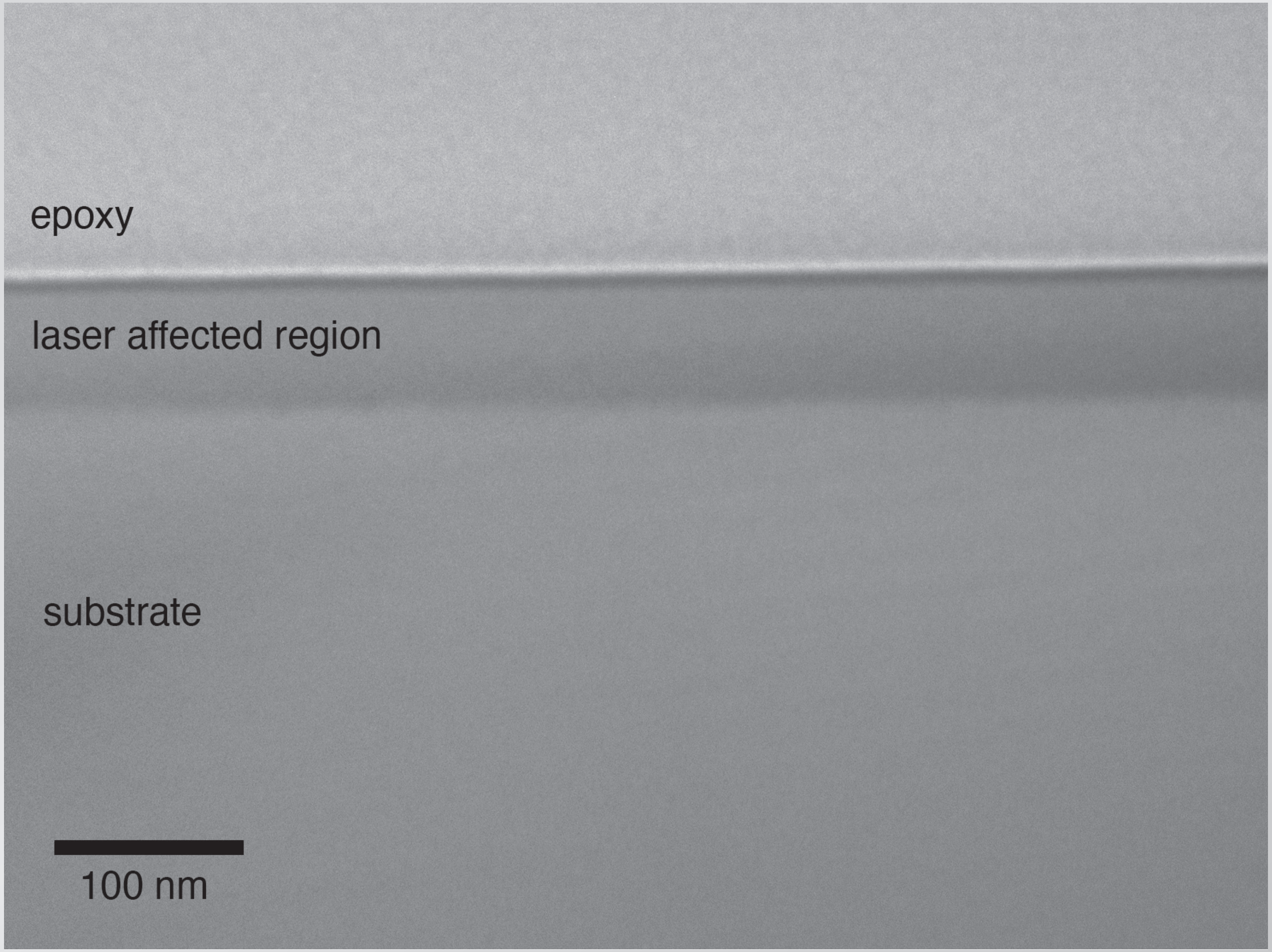
decouple ablation from melting



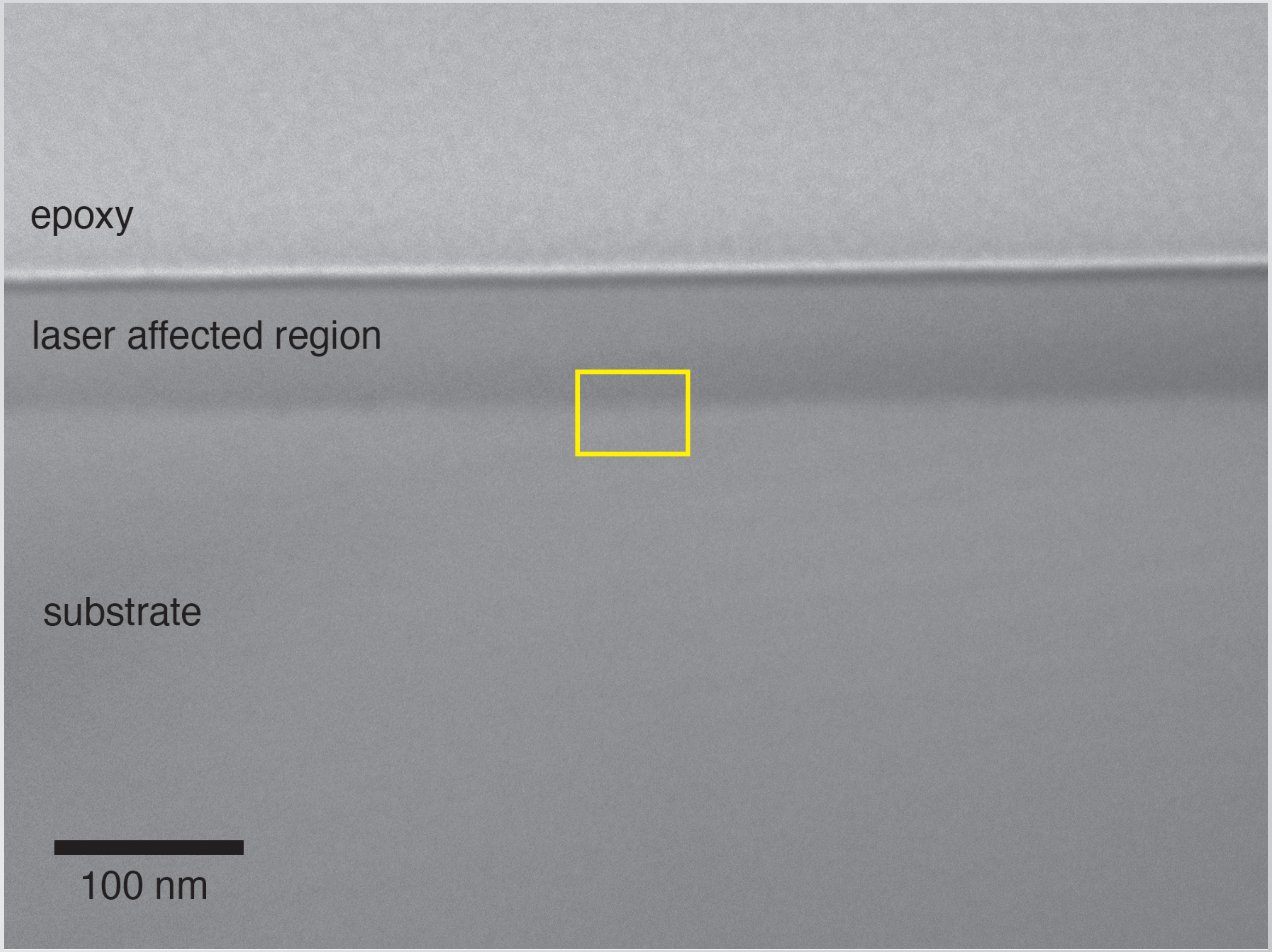
decouple ablation from melting



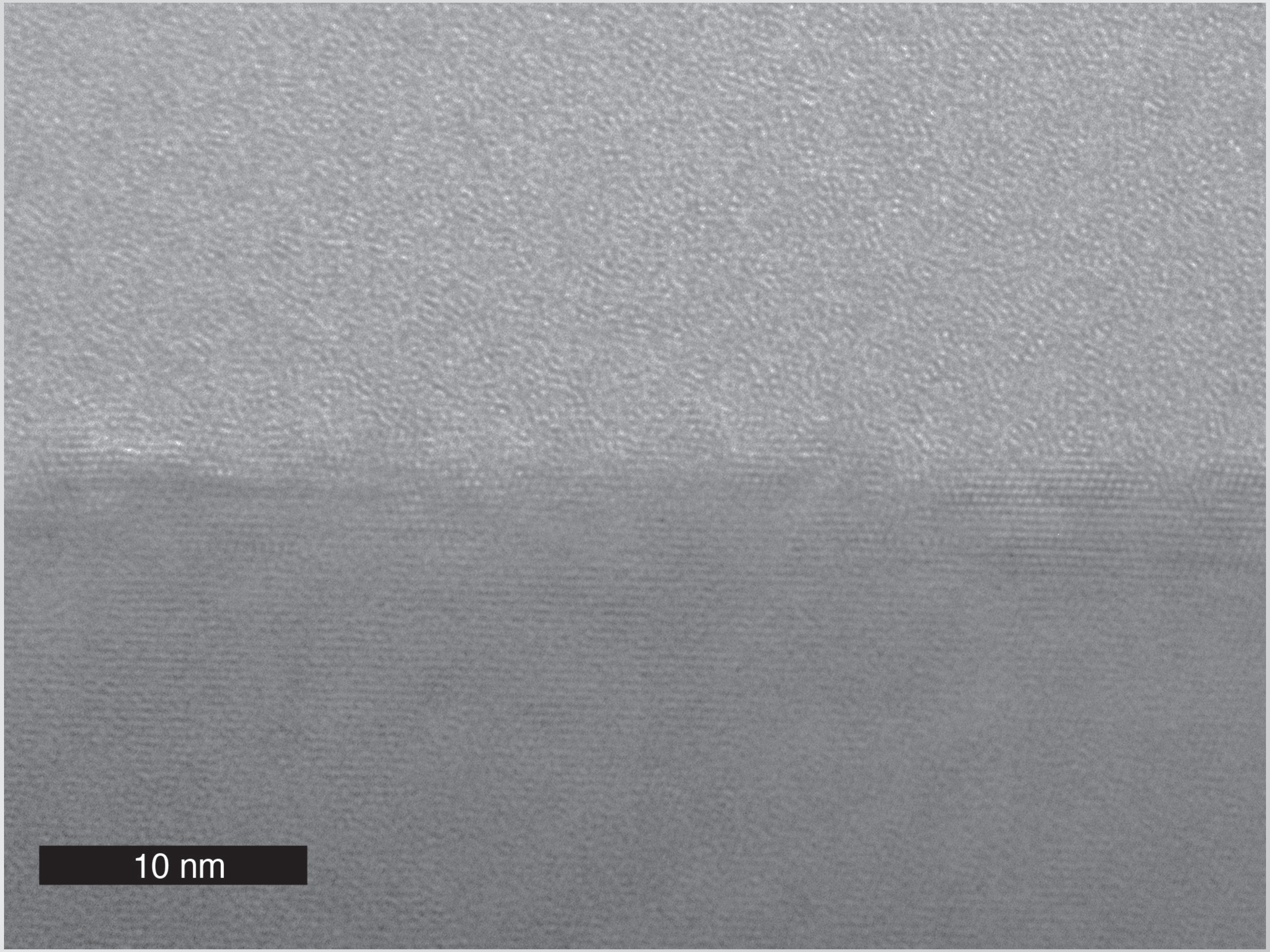
decouple ablation from melting



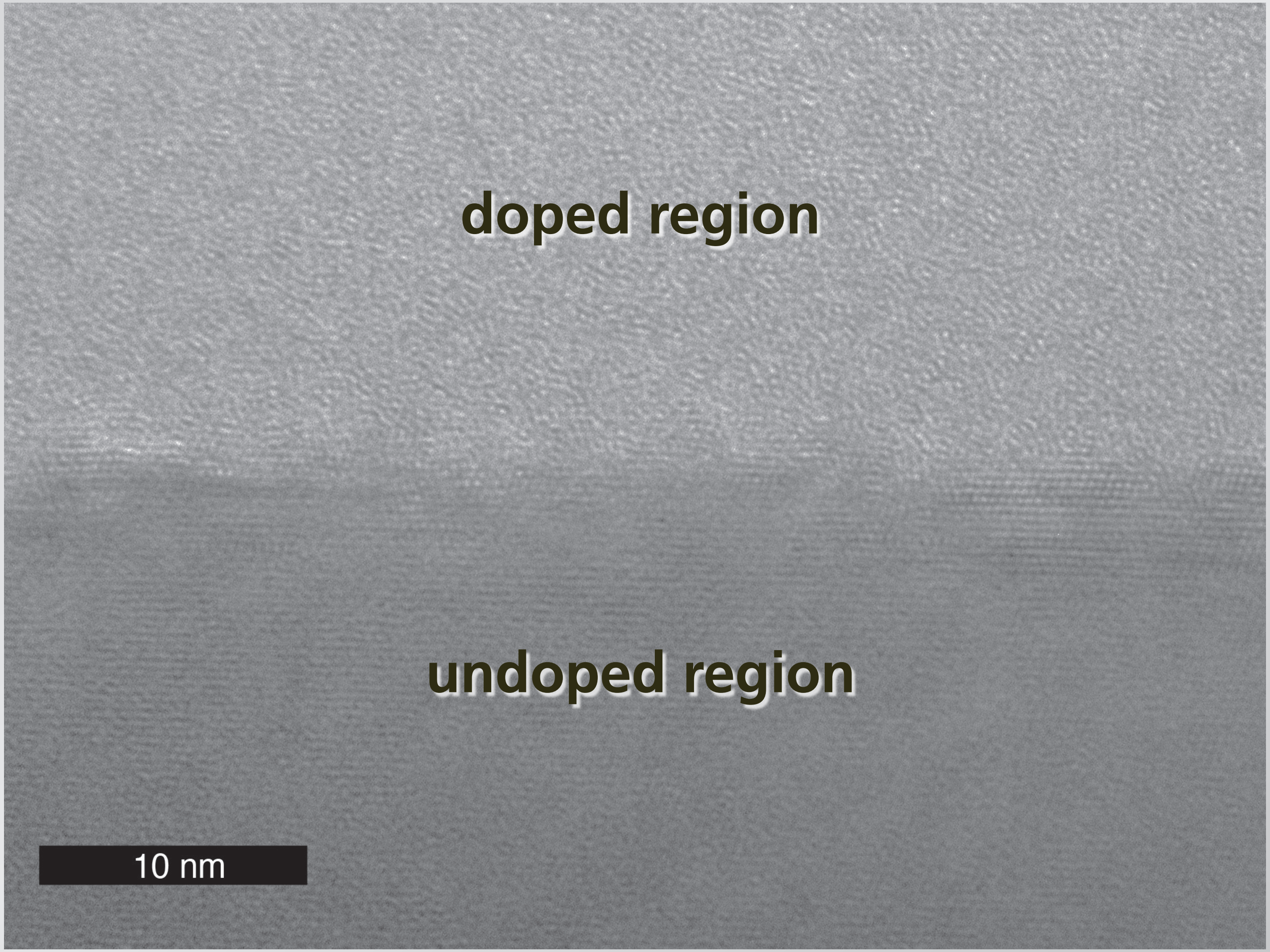
decouple ablation from melting



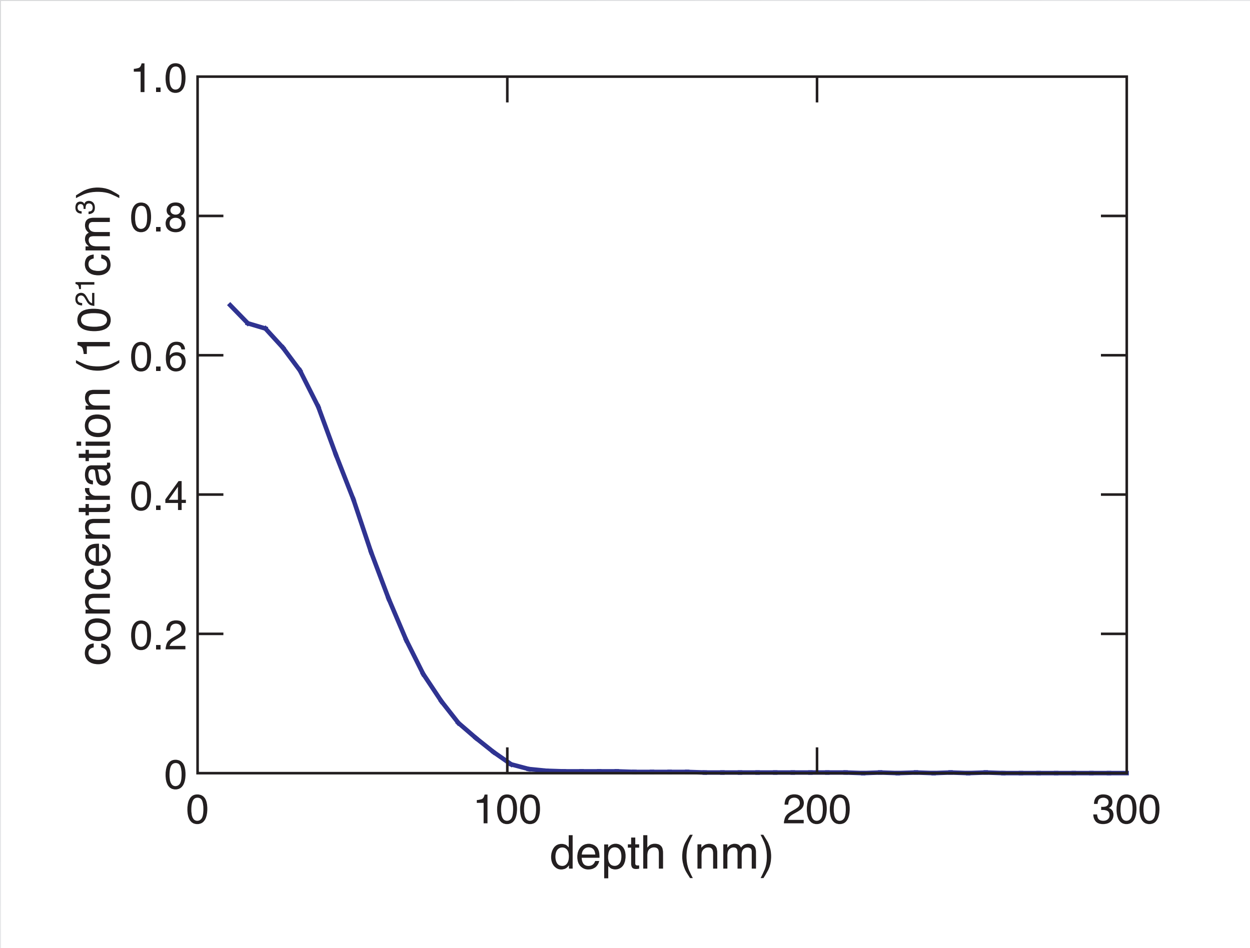
decouple ablation from melting



decouple ablation from melting

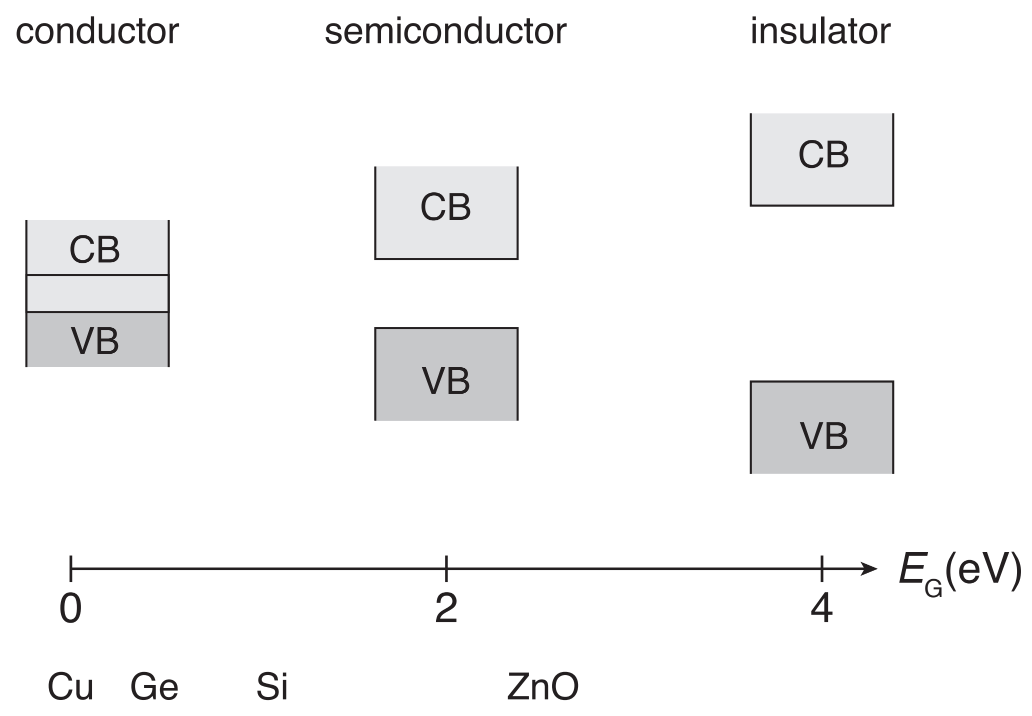


secondary ion mass spectrometry



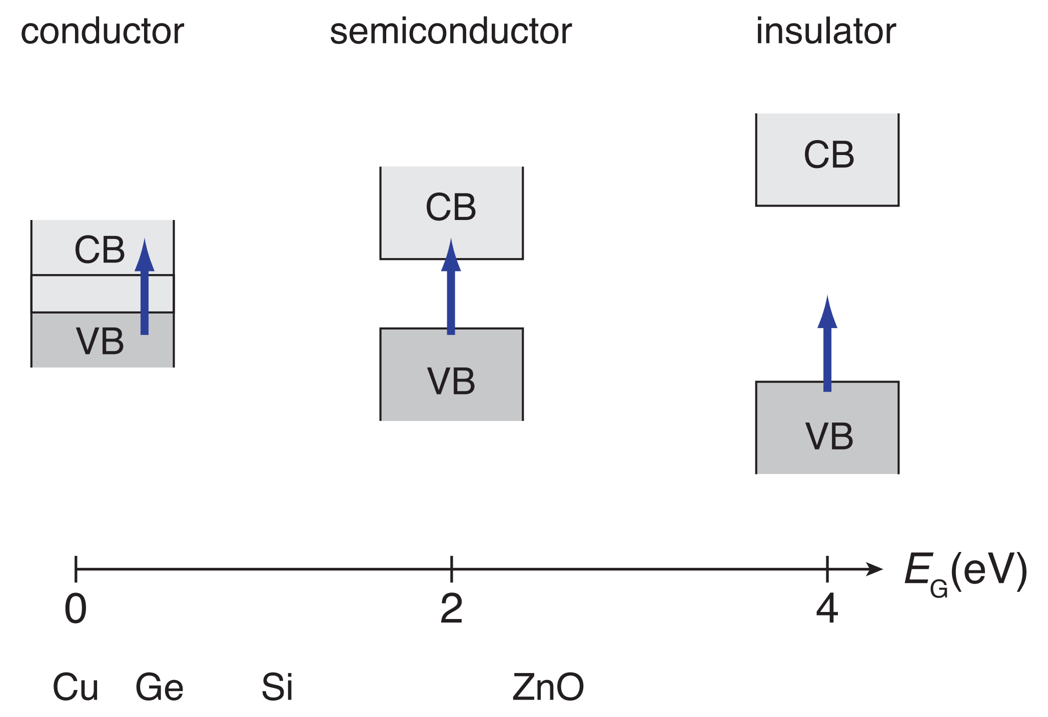
Things to keep in mind

- near unit absorption extending into IR
- surface structure due to ablation
- hyperdoping due to rapid melting and resolidification
- can decouple both processes

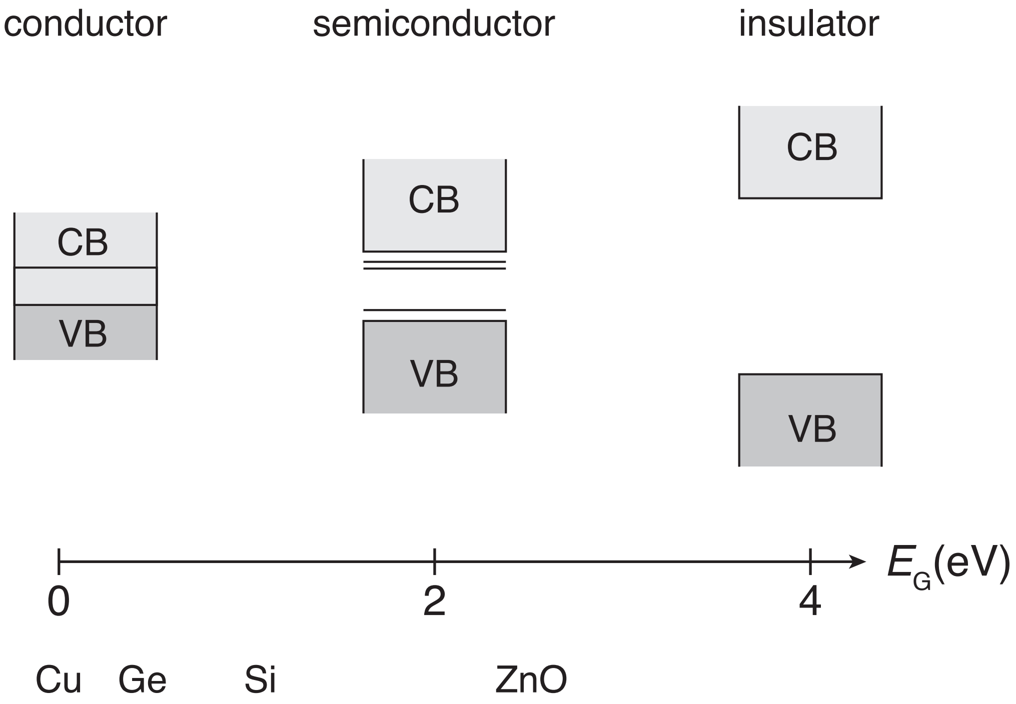


① properties ② intermediate band

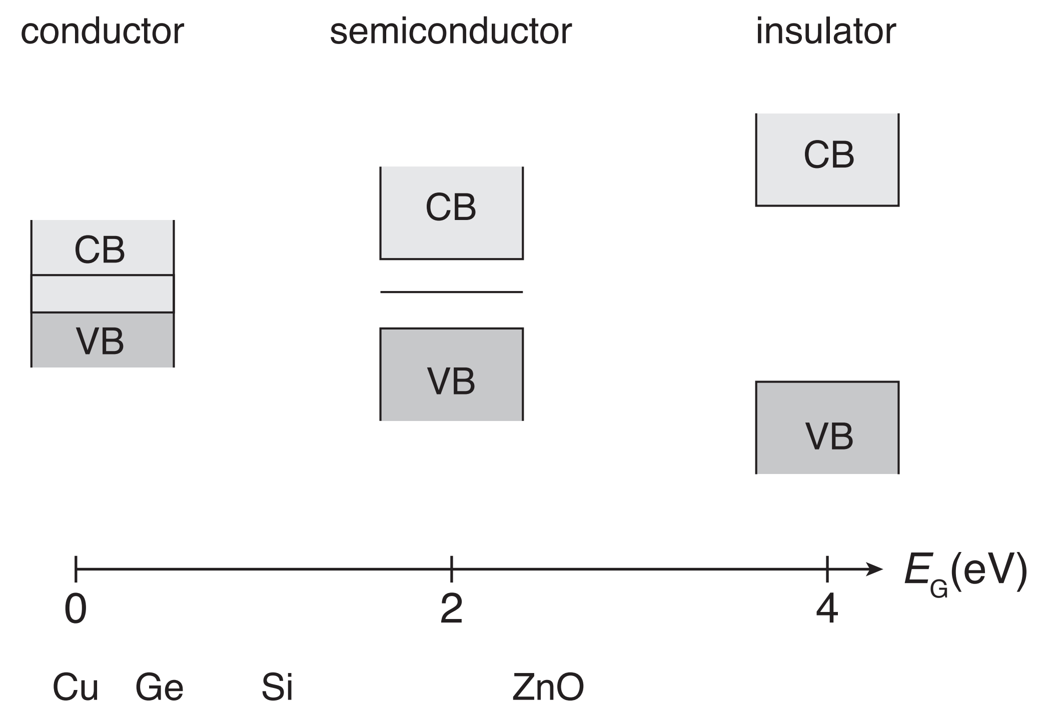
gap determines optical and electronic properties



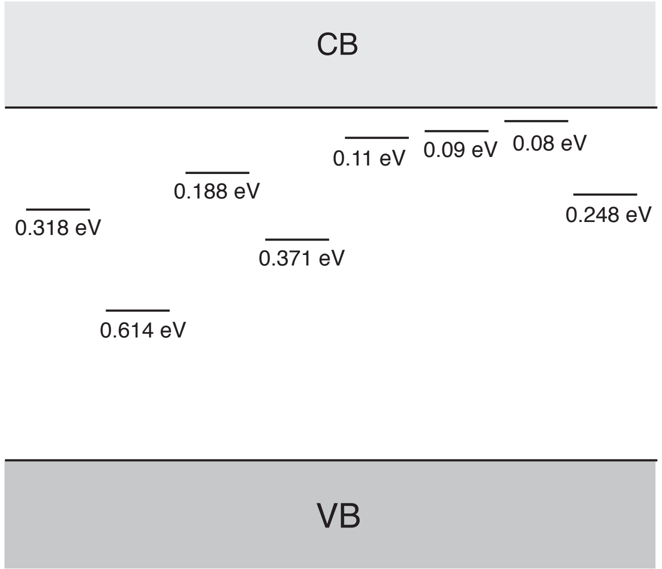
shallow-level dopants control electronic properties



deep-level dopants typically avoided

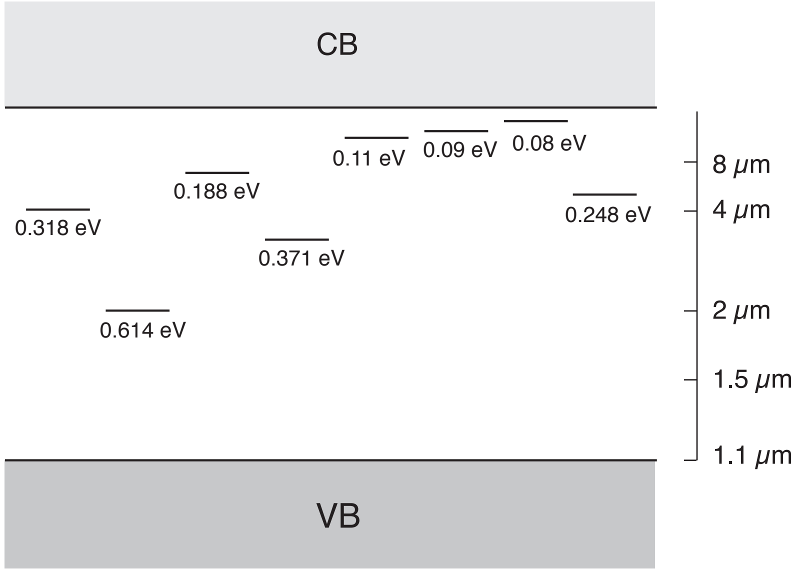


1 part in 10^6 sulfur introduces donor states in gap



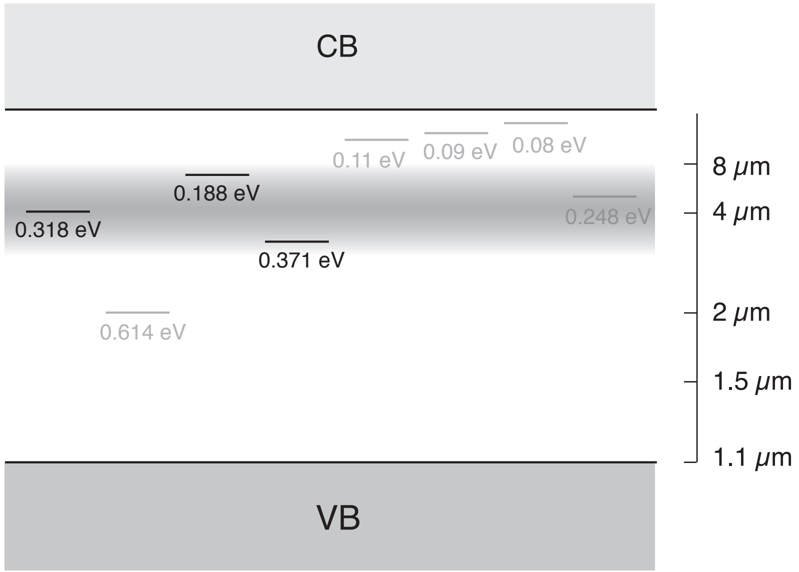
Janzén *et al.*, Phys. Rev. B 29, 1907 (1984)

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

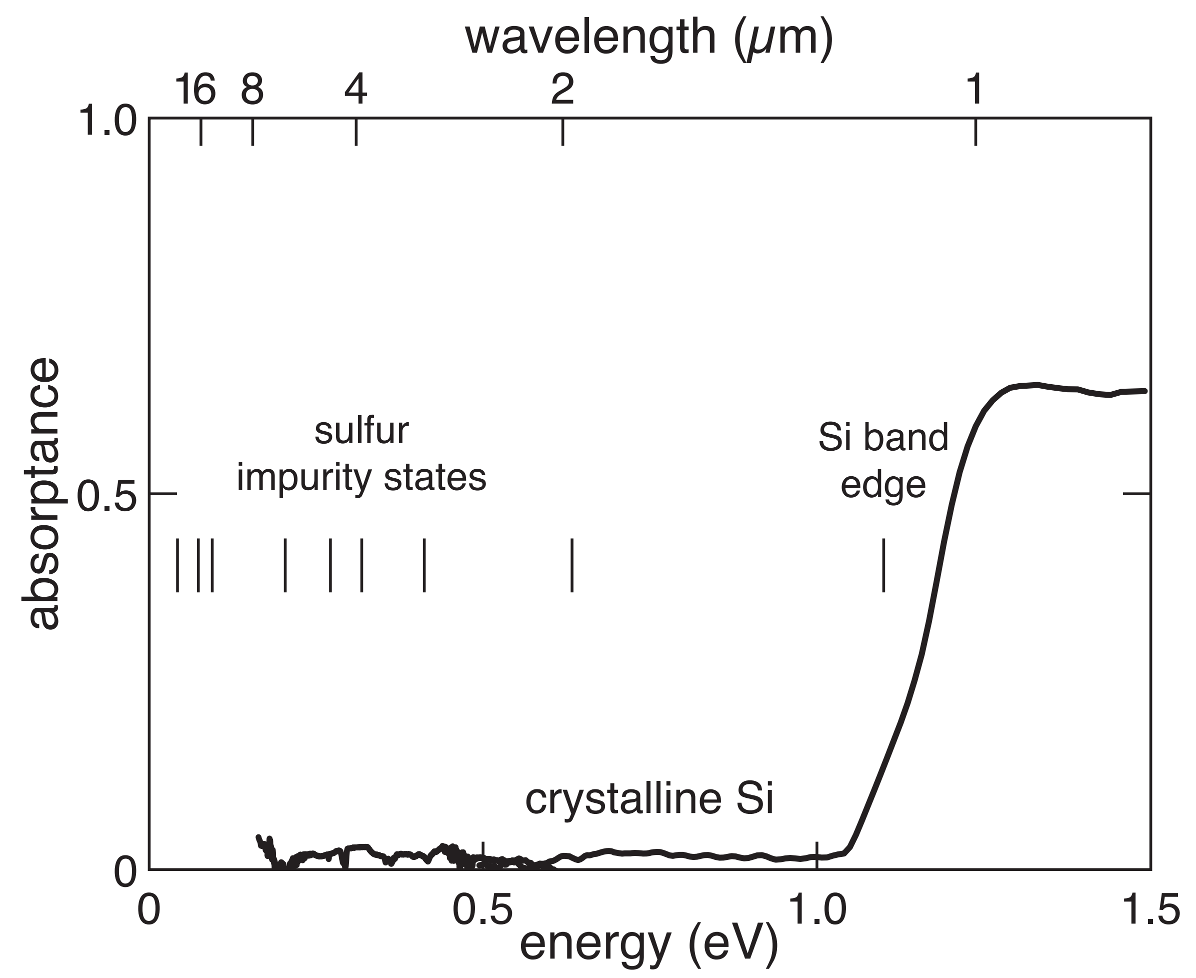


Janzén *et al.*, Phys. Rev. B 29, 1907 (1984)

at high concentration states broaden into band

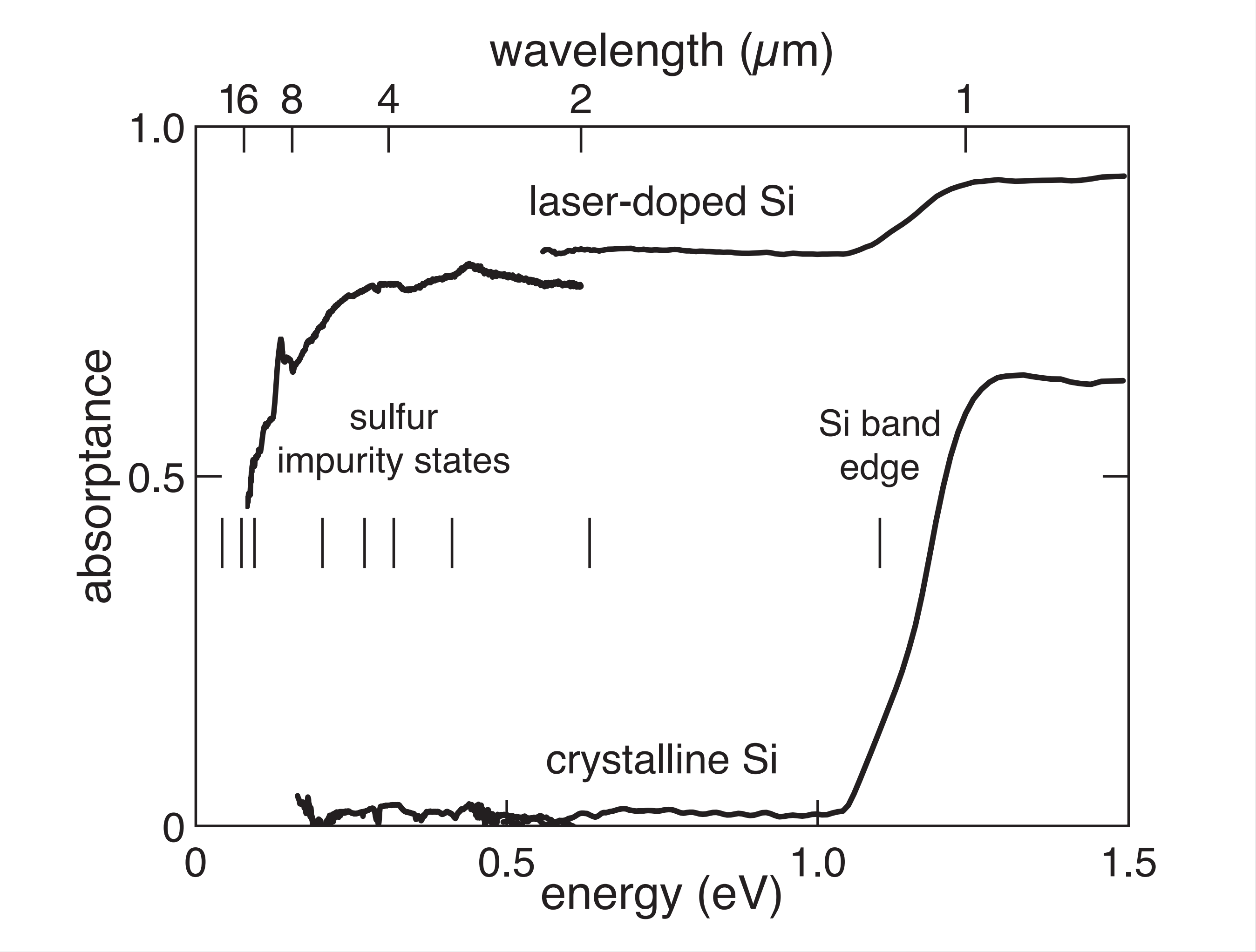


10^{-6} sulfur doping

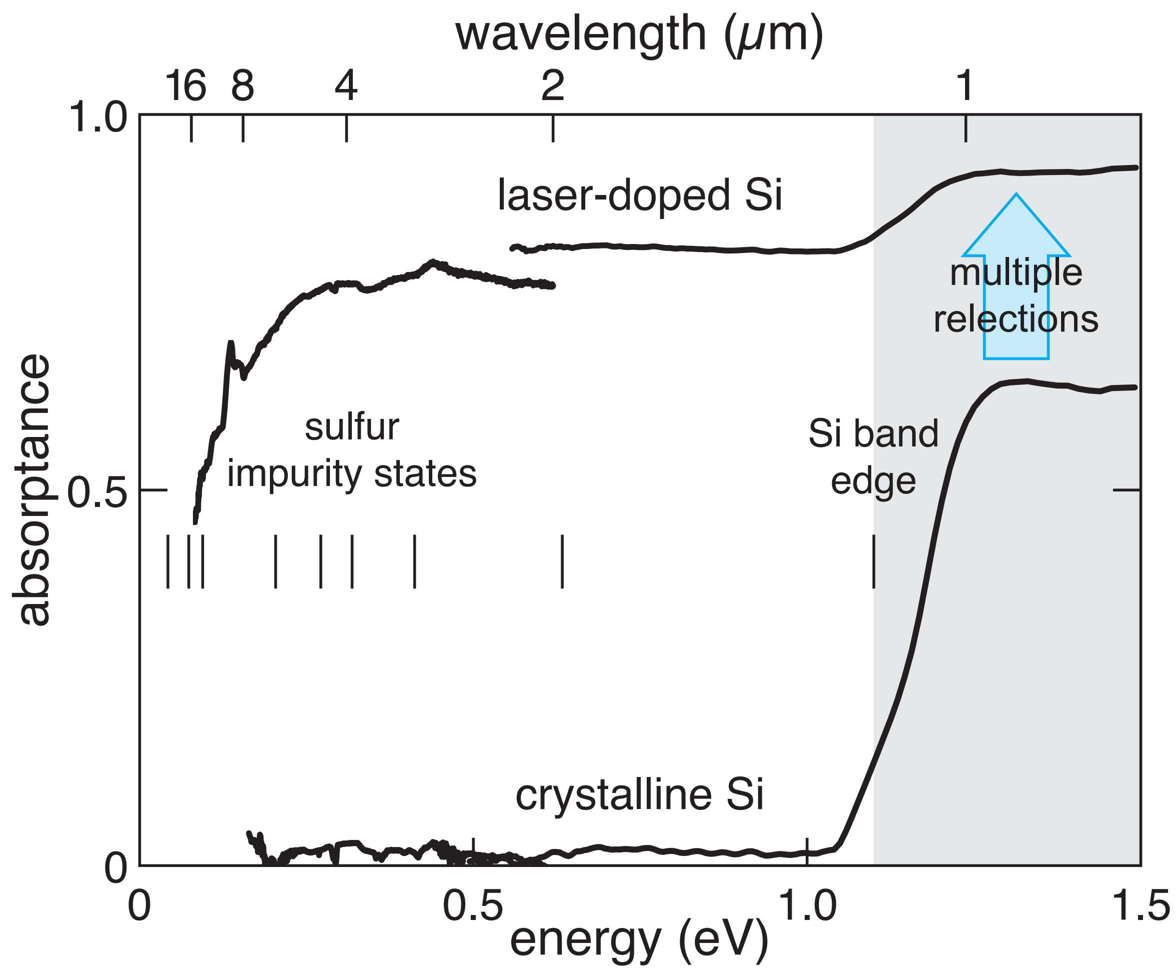


① properties ② intermediate band

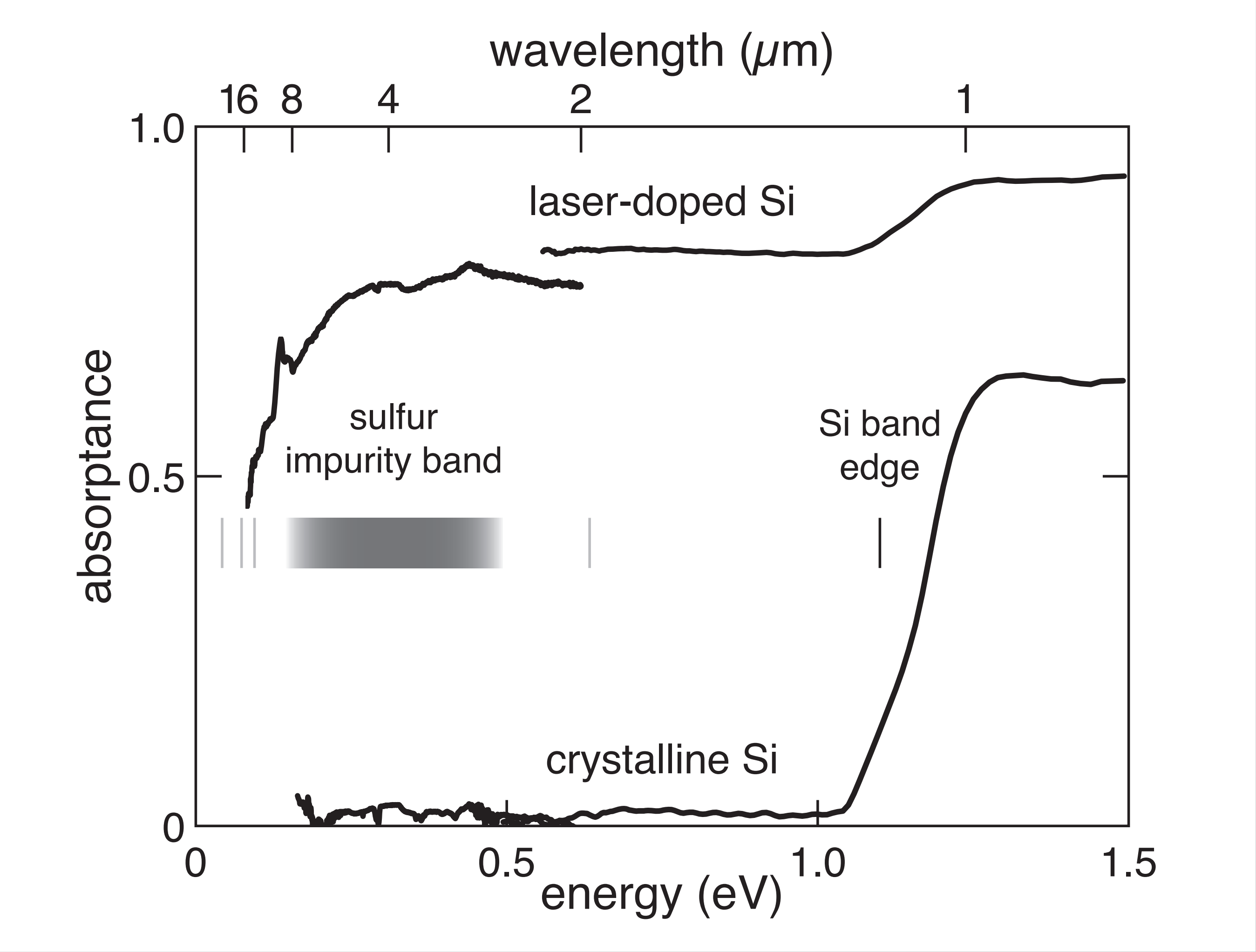
laser-doped S:Si



laser-doped S:Si

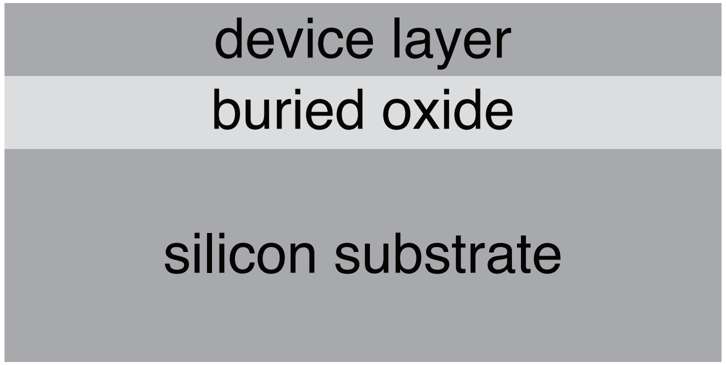


laser-doped S:Si

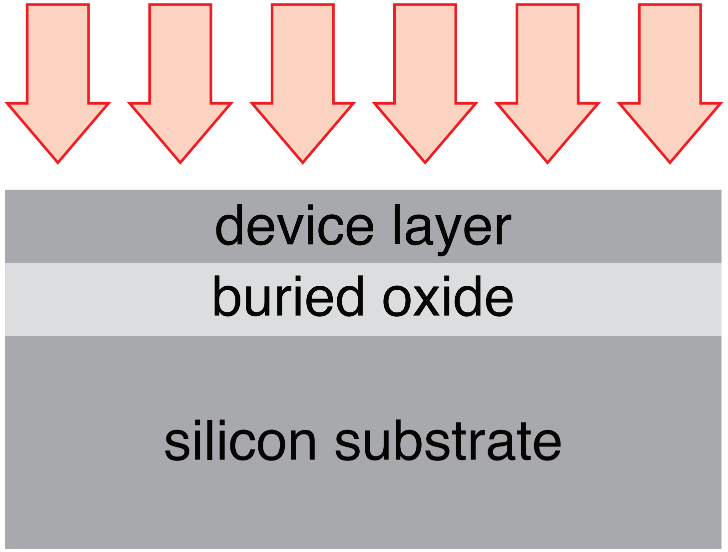


① **properties** ② **intermediate band**

isolate surface layer for Hall measurements



isolate surface layer for Hall measurements

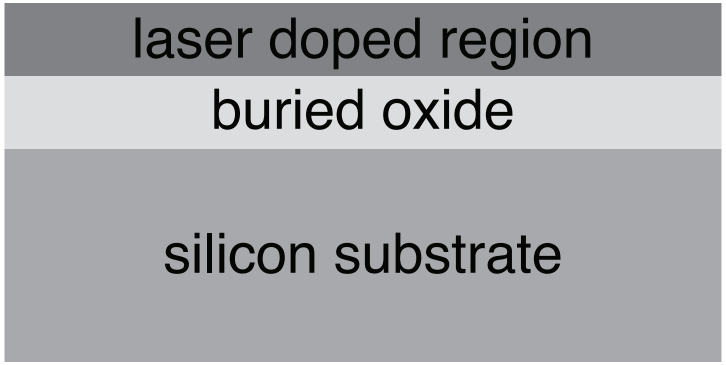


device layer

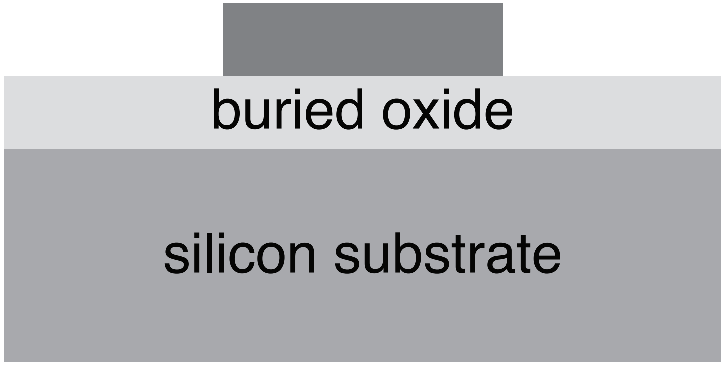
buried oxide

silicon substrate

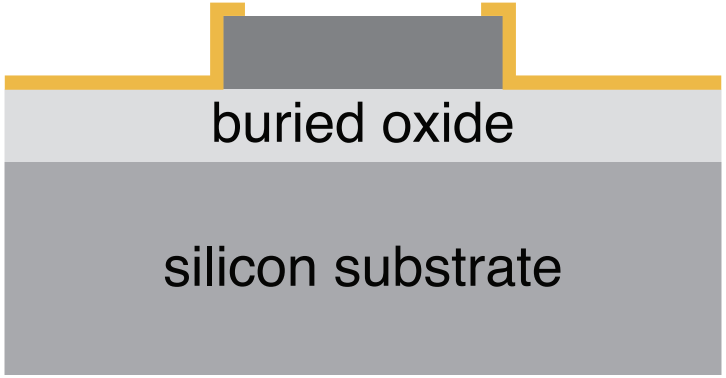
isolate surface layer for Hall measurements

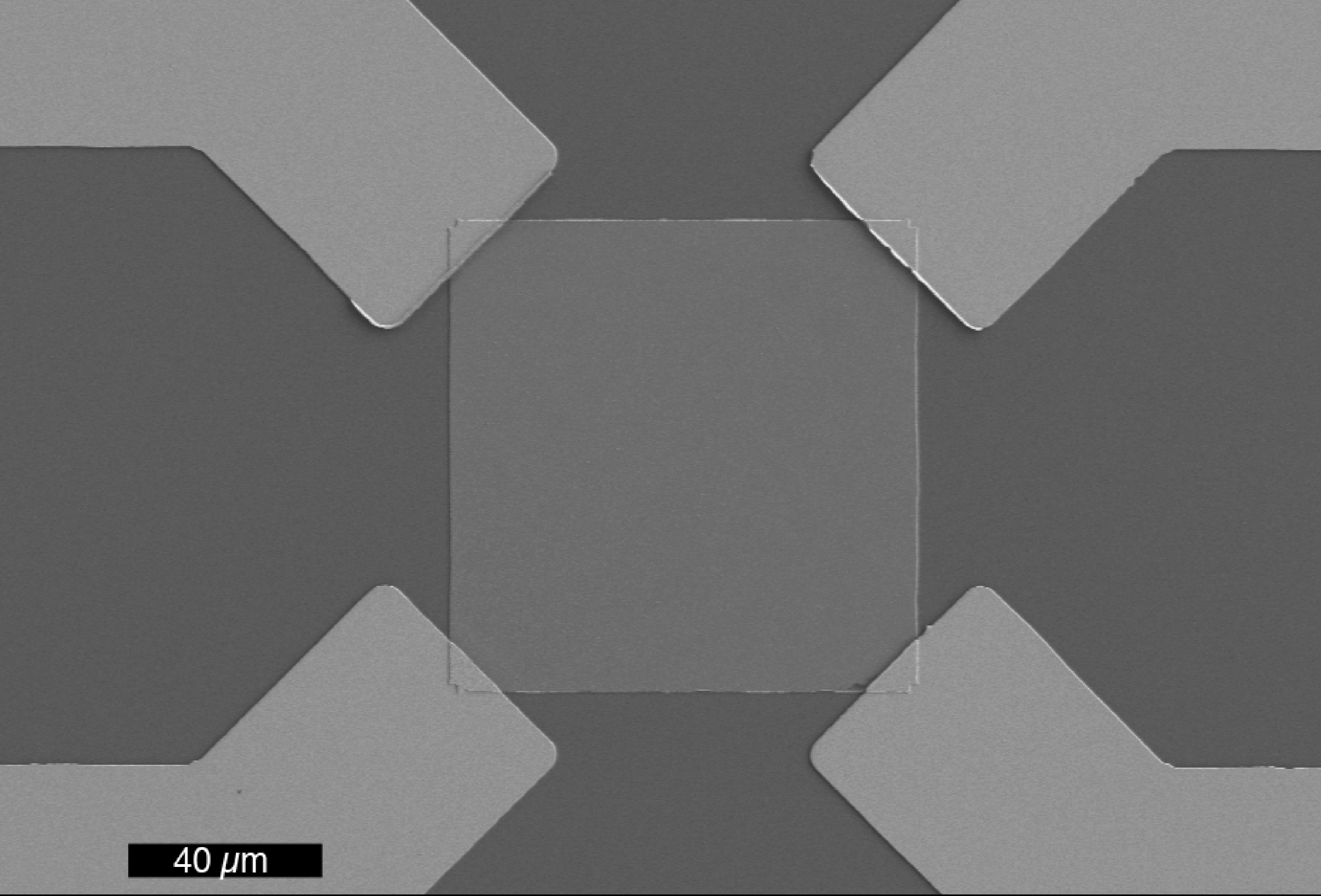


isolate surface layer for Hall measurements



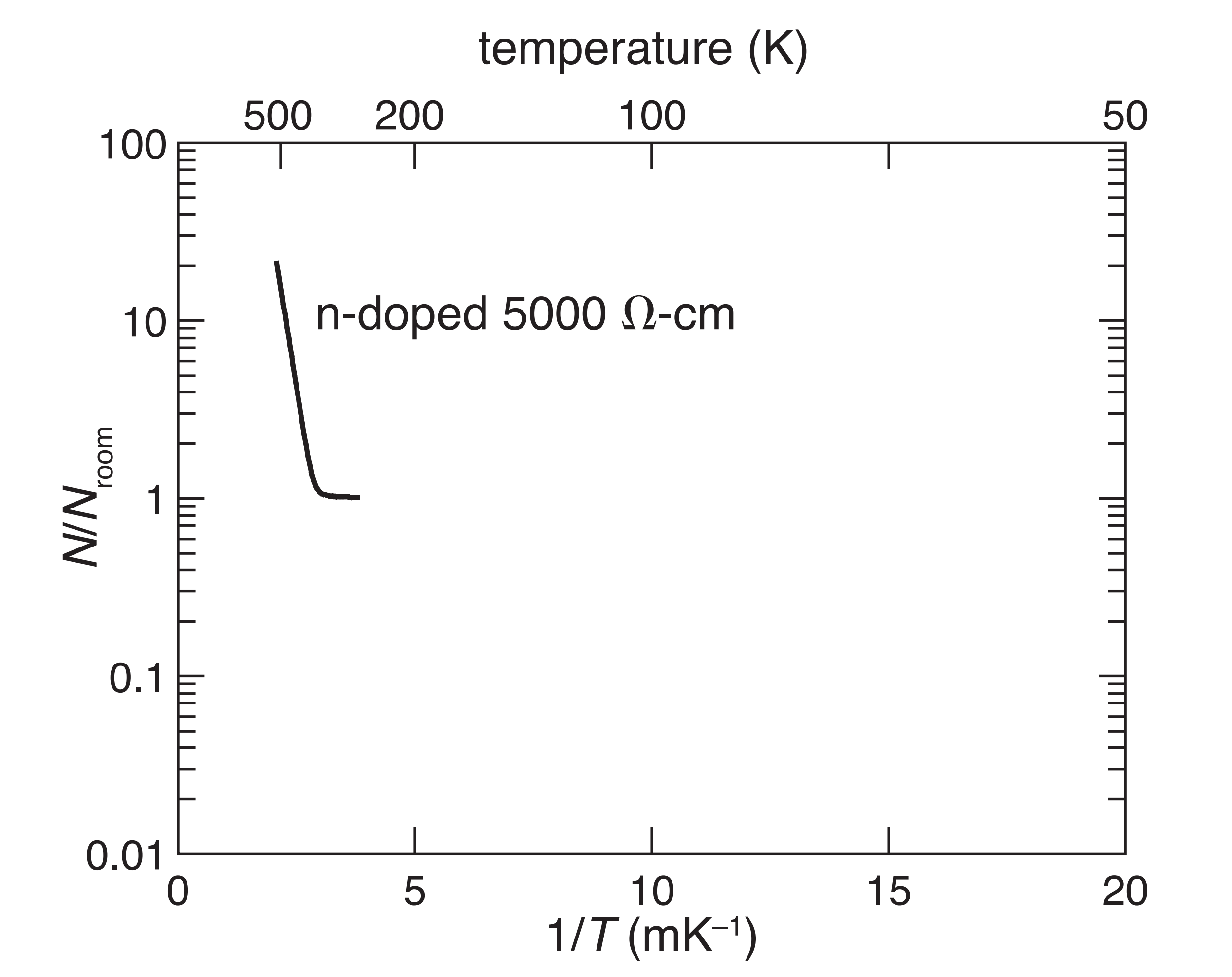
isolate surface layer for Hall measurements





① **properties** ② **intermediate band**

Hall measurements



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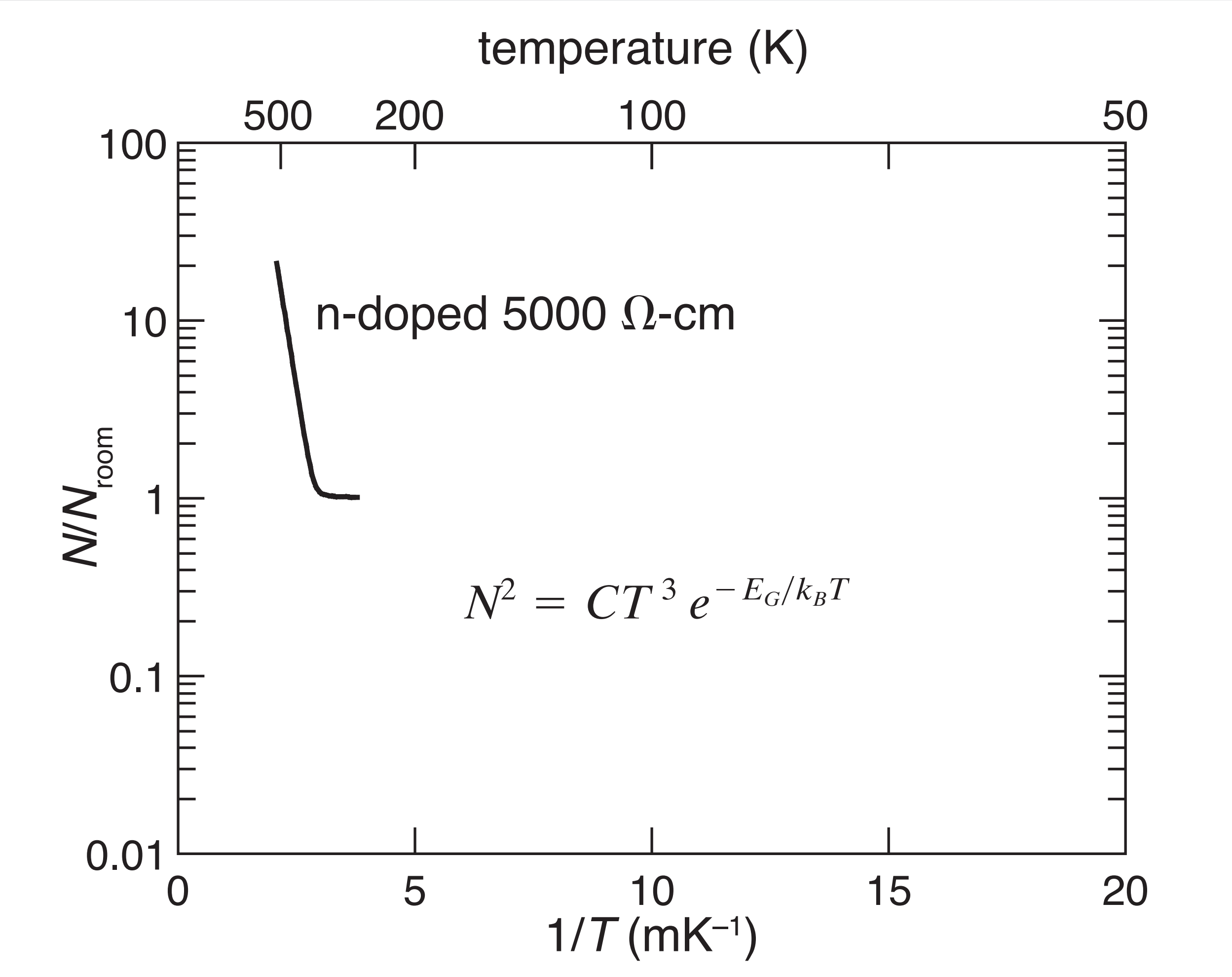
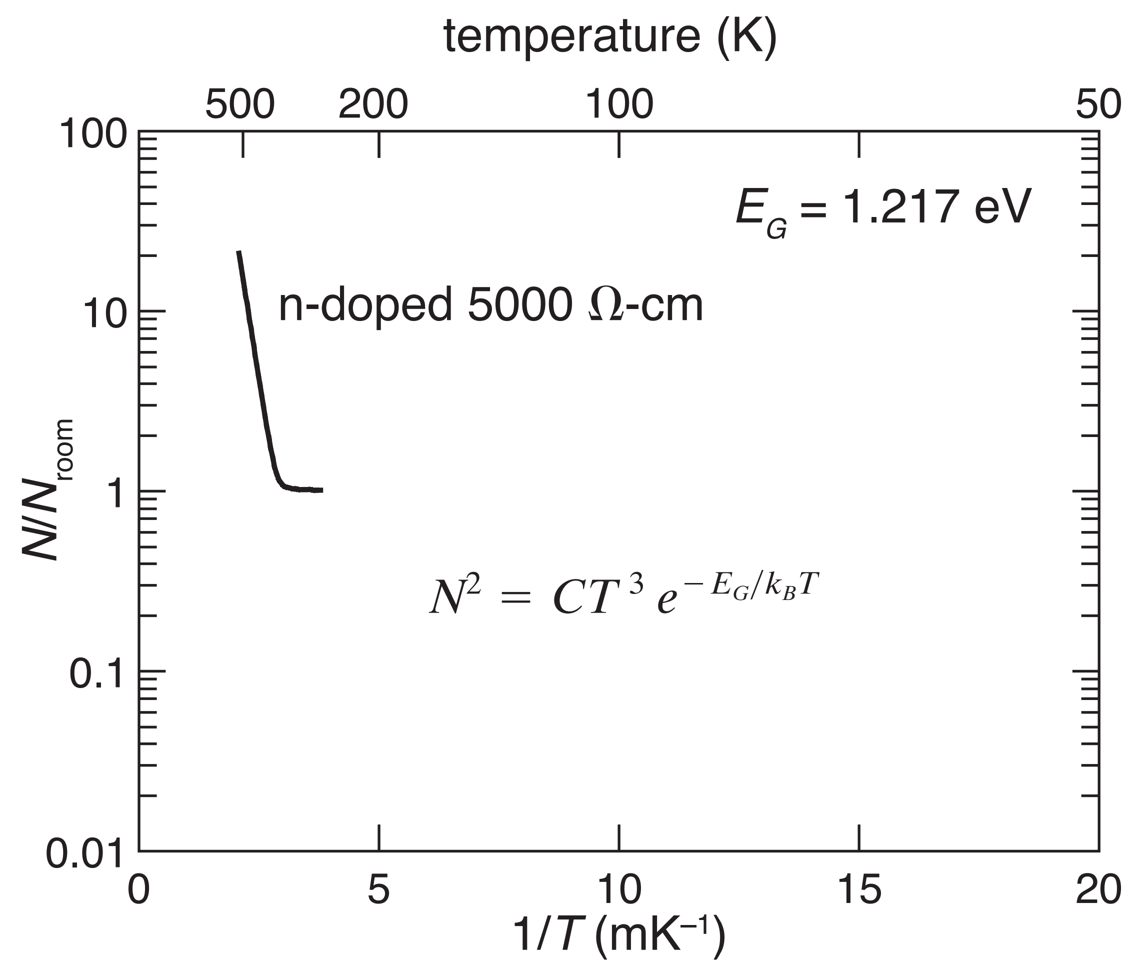
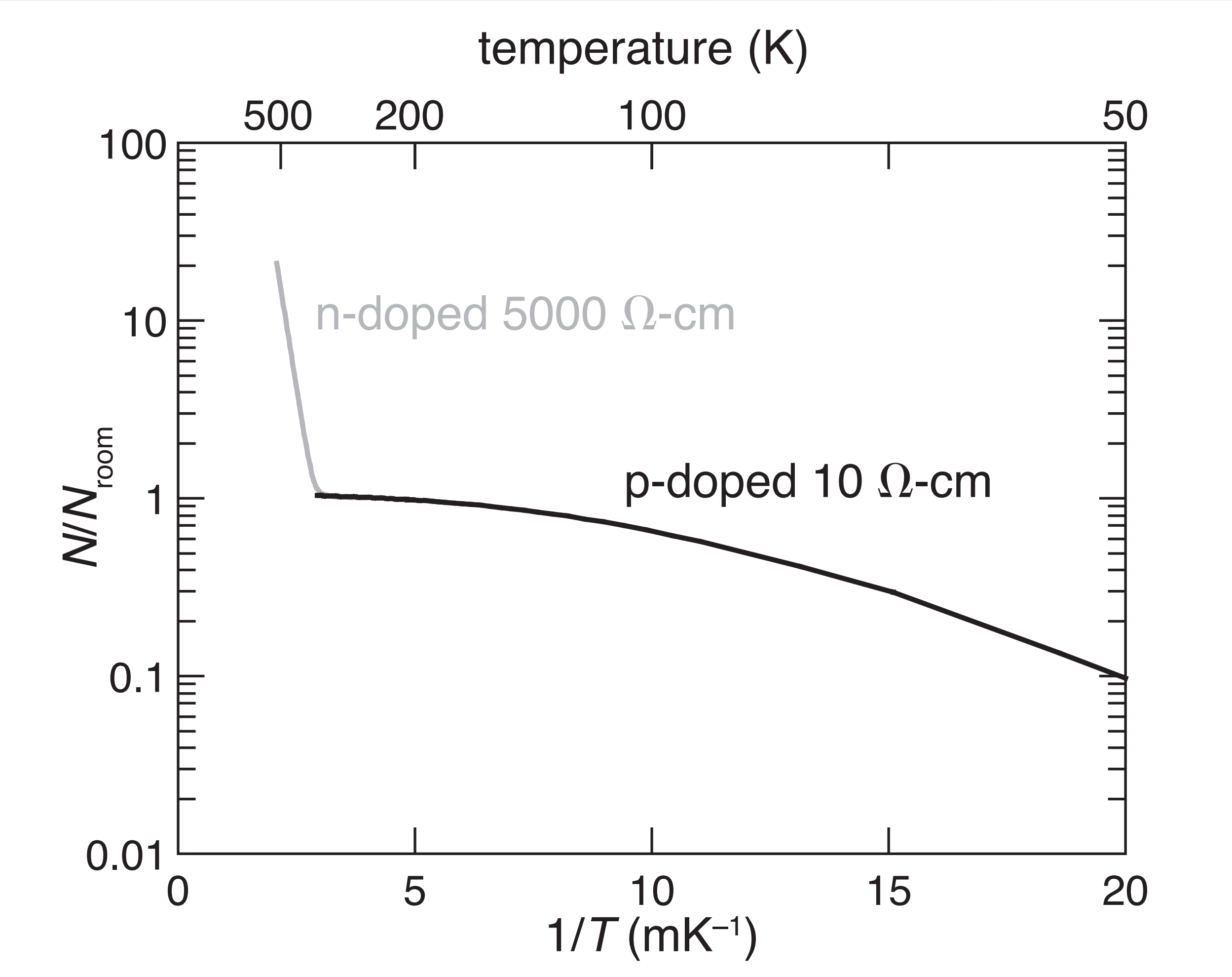


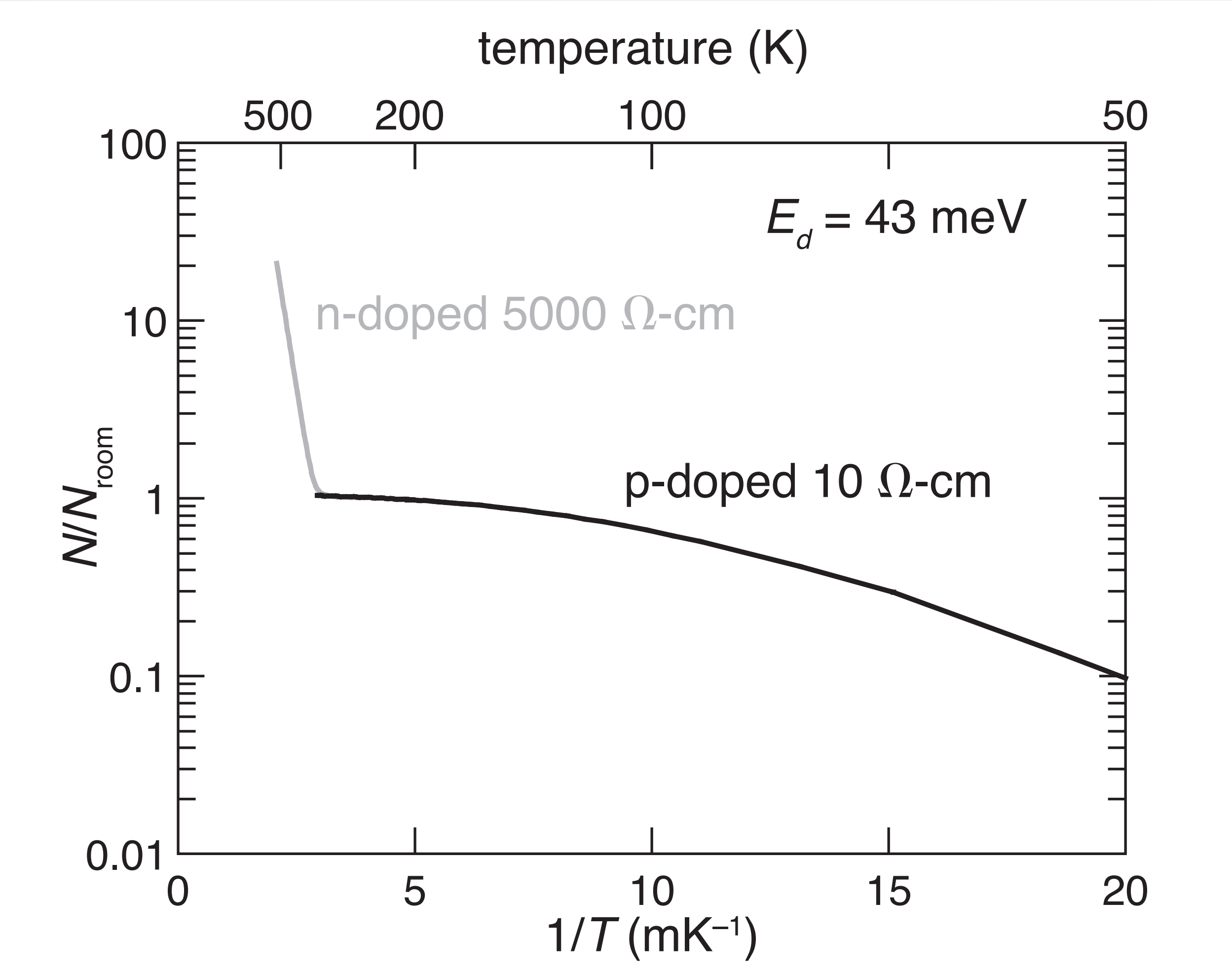
Hall measurements



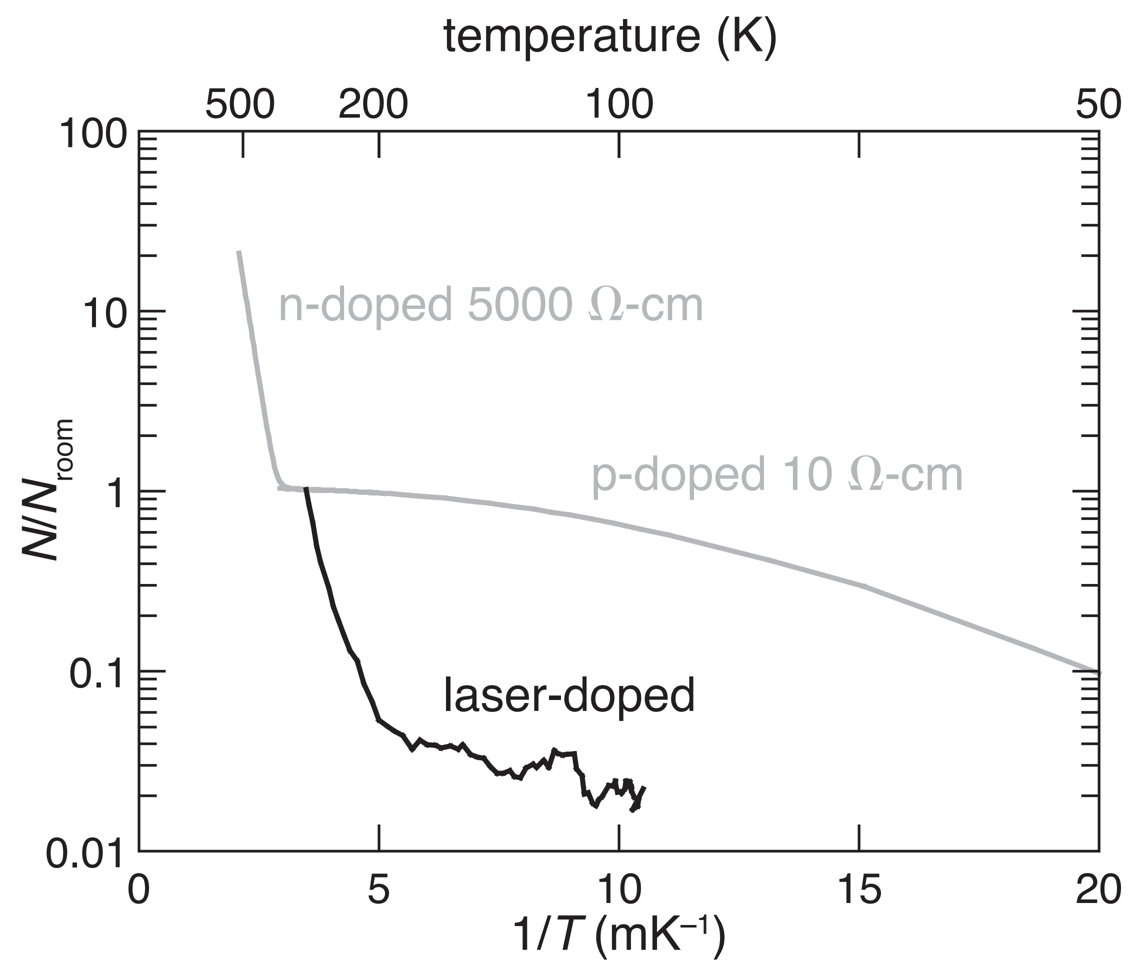
Hall measurements



Hall measurements



Hall measurements



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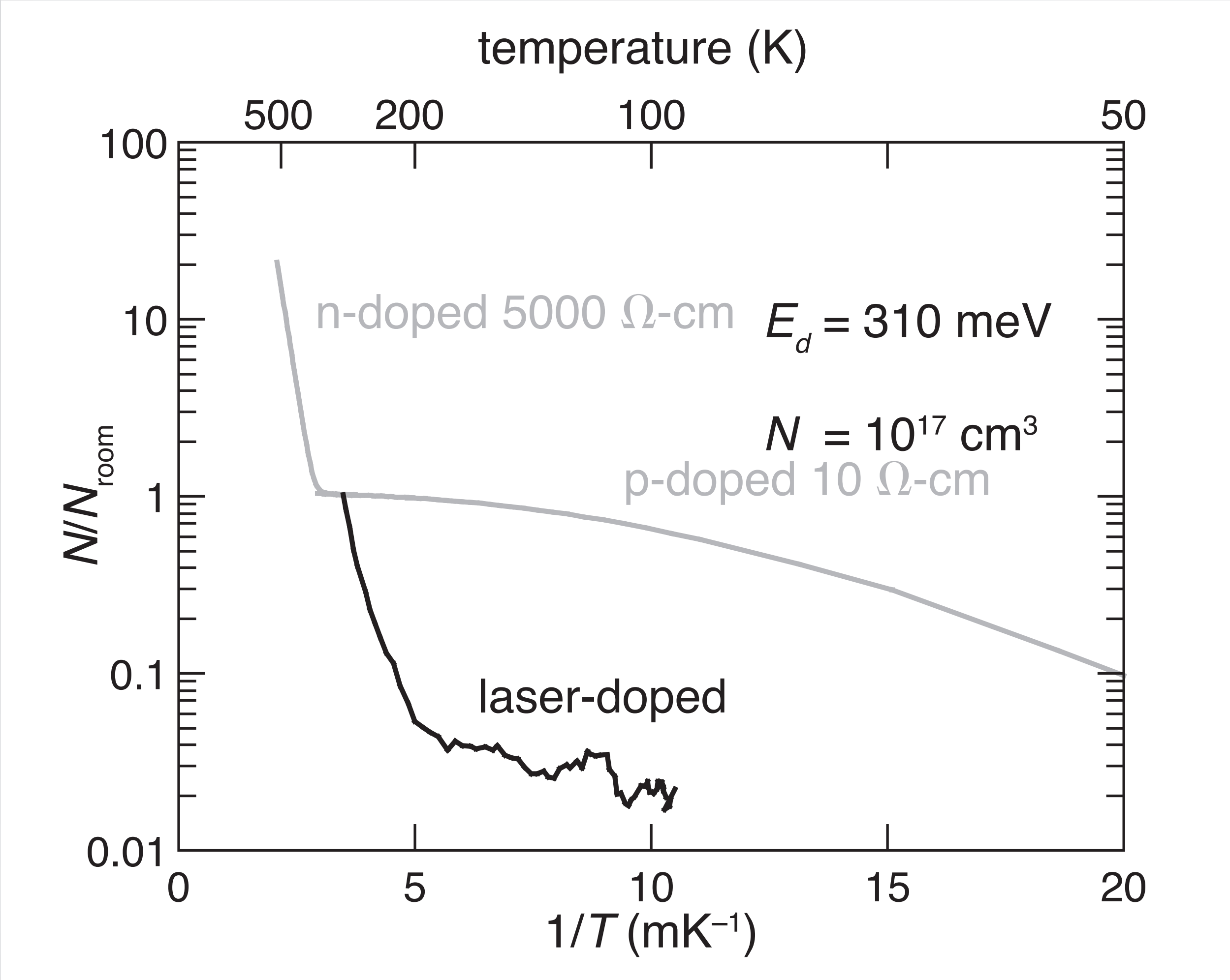
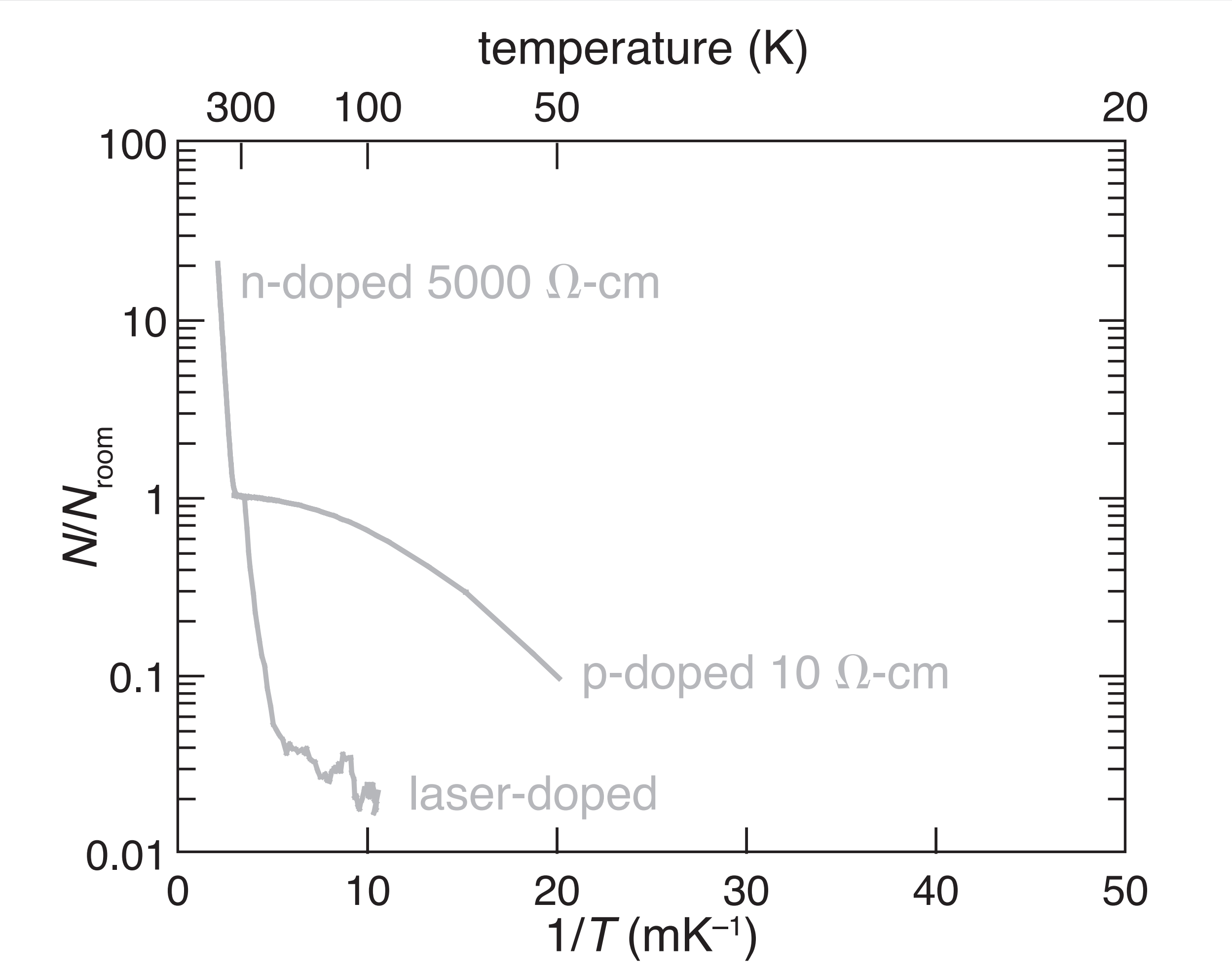
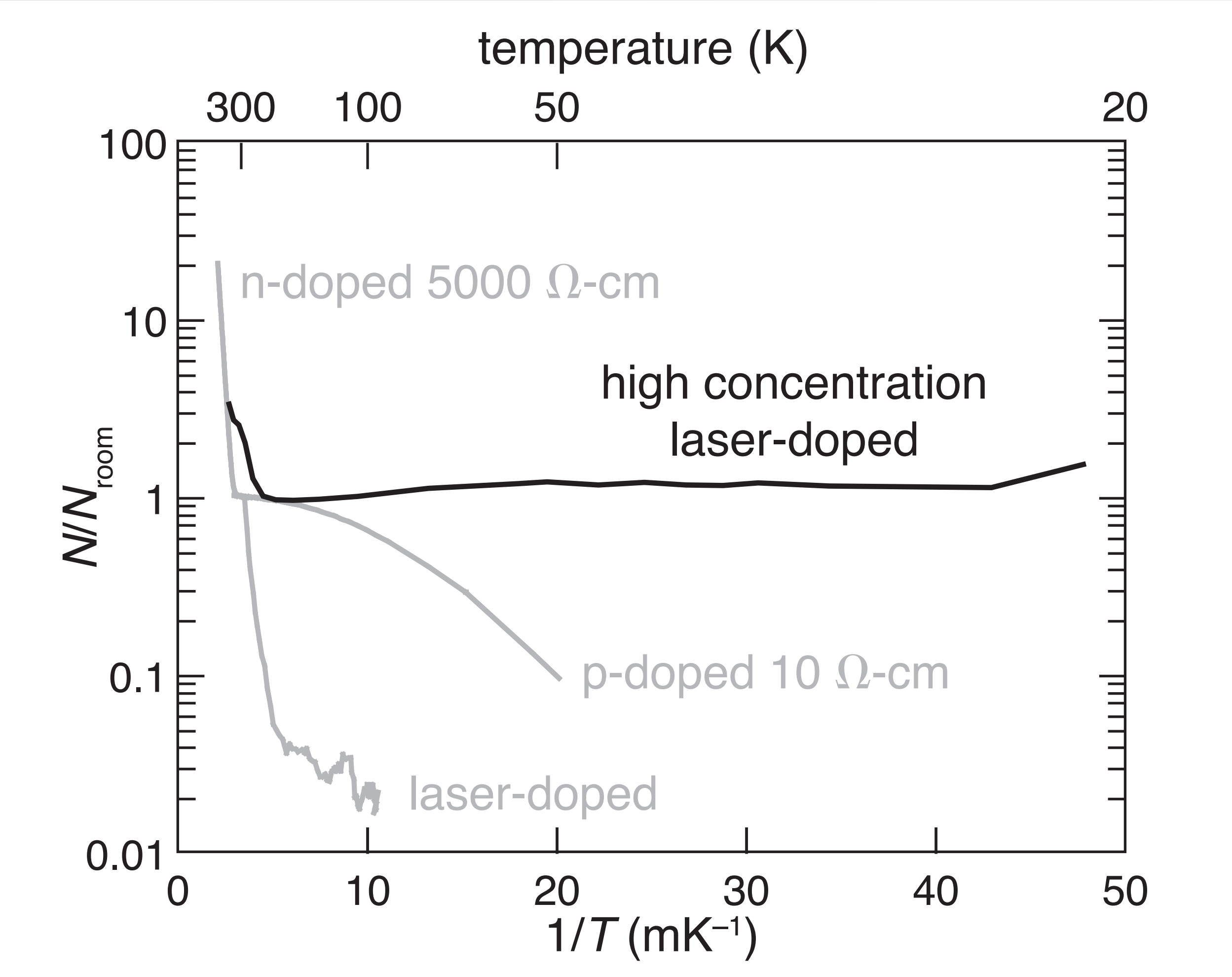


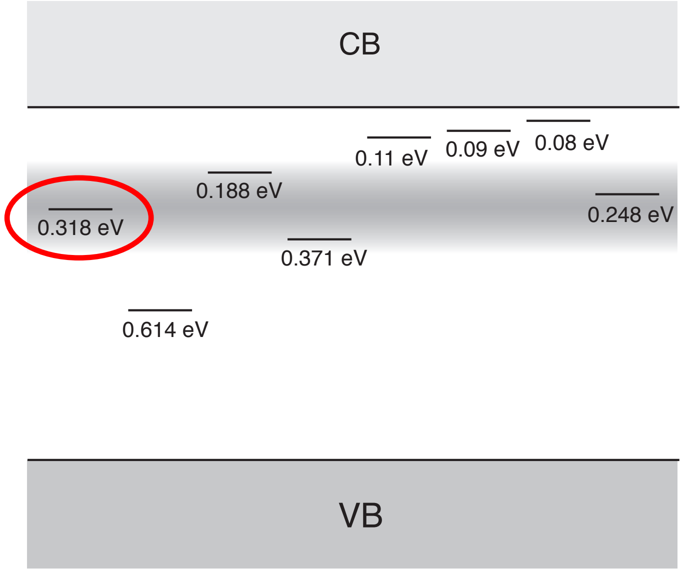
Hall measurements



Hall measurements



impurity (donor) band centered at 310 meV



PRL **108,** 026401 (2012) PHYSICAL REVIEW LETTERS week en
13 JANUARY 2012

Insulator-to-Metal Transition in Selenium-Hyperdoped Silicon: Observation and Origin

Elif Ertekin,[1,*] Mark T. Winkler,[2,†] Daniel Recht,[3] Aurore J. Said,[3] Michael J. Aziz,[3]
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(Received 14 October 2011; published 11 January 2012)

Hyperdoping has emerged as a promising method for designing semiconductors with unique optical and electronic properties, although such properties currently lack a clear microscopic explanation. Combining computational and experimental evidence, we probe the origin of sub–band-gap optical absorption and metallicity in Se-hyperdoped Si. We show that sub–band-gap absorption arises from direct defect-to–conduction-band transitions rather than free carrier absorption. Density functional theory predicts the Se-induced insulator-to-metal transition arises from merging of defect and conduction bands, at a concentration in excellent agreement with experiment. Quantum Monte Carlo calculations confirm the critical concentration, demonstrate that correlation is important to describing the transition accurately, and suggest that it is a classic impurity-driven Mott transition.

DOI: 10.1103/PhysRevLett.108.026401

PACS numbers: 71.30.+h, 61.72.sd, 73.61.Cw, 78.20.Bh

Of all the experimentally measurable physical properties of materials, electronic conductivity exhibits the largest variation, spanning a factor of 10^{31} from the best metals to the strongest insulators [1]. Over the last century, the puzzle of why some materials are conductors and others insulators, and the mechanisms underlying the transformation from one to the other, have been carefully scrutinized; yet even after such a vast body of research over such a long period, the subject remains the object of controversy. In 1956, Mott introduced a model for the insulator-to-metal transition (IMT) in doped semiconductors, in which long-ranged electron correlations are the driving force [2]. Hyperdoping (doping beyond the solubility limit) creates a new materials playground to explore defect-mediated IMTs in semiconductors. In this Letter, we identify a defect-induced IMT in silicon hyperdoped with selenium to concentrations exceeding 10^{20} cm^{-3} (compared to the ilibrium solubility limit [3] of about 10^{16} cm^{-3}) and we detailed nature of the transition with both tation. We find that the IMT is tion and most resembles ditionally, we

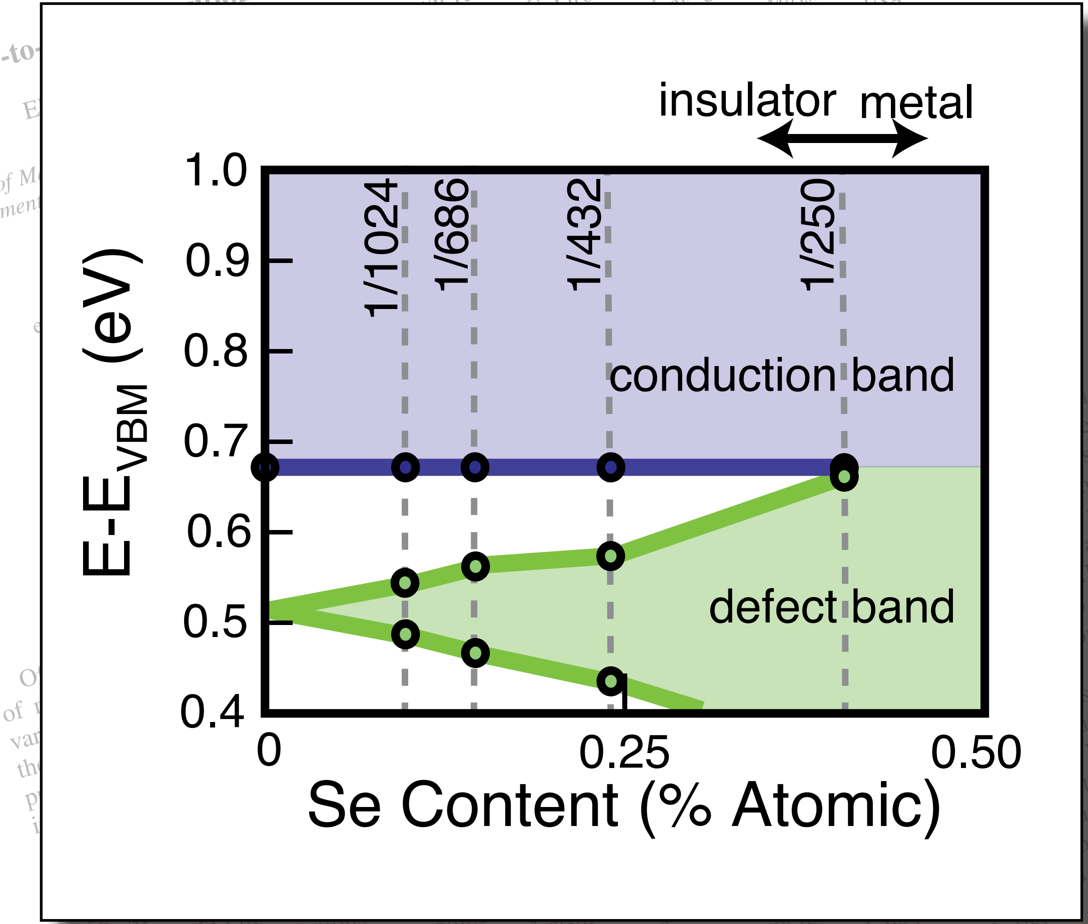
silicon appears to justify such interest. While isolated S and Se dopants are well-established deep double donors in silicon [3,14], the enhanced optical properties of hyper-doped silicon (in which these chalcogenic impurities are present at much higher concentrations) are not yet well understood. Further, unlike the prototypical system of phosphorus-doped silicon for which the IMT has been extensively studied and characterized [15,16], there are very few studies of an IMT resulting from deep defects such as chalcogens [17].

We prepared Se-doped silicon (Se:Si) samples using ion implantation followed by nanosecond pulsed-laser melting (PLM) and rapid resolidification. The PLM process enables chalcogen doping with concentrations exceeding 1% atomic; such samples exhibit unexplained optical properties including broad, featureless absorption of photons with energy lower than the band gap of silicon [9]. Silicon substrates (boron doped, $\rho \approx 25\ \Omega$ cm) were ion implanted with Se to nominal doses of 3×10^{15} and 1×10^{16} cm^{2} using an ion beam energy of 176 keV. The implanted samples were exposed to four laser pulses (fluences of 1.7, 1.7, 1.7 and 1.8 J cm^{-2}). This fluence regimen results in a slightly shallower dopant profile, and higher k Se concentration, than reported previously [18]. The is crystalline, extends approximately 350 nm electrically isolated from the nction formed between as measured

① properties ② intermediate band

DFT calculations

PRL 108, 026401 (2012) PHYSICAL REVIEW LETTERS week ending 13 JANUARY 2012



Ertekin *et al.*, Phys. Rev. Lett. 108, 026401 (2012)

① **properties** ② **intermediate band**

JOURNAL OF APPLIED PHYSICS **113**, 213501 (2013)

Emergence of very broad infrared absorption band by hyperdoping of silicon with chalcogens

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James S. Williams,[3] Malek Tabbal,[5] Dimitris G. Papazoglou,[6,7] Xi-Cheng Zhang,[8,a)]
and Michael J. Aziz[9]
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We report the near through mid-infrared (MIR) optical absorption spectra, over the range 0.05–1.3 eV, of monocrystalline silicon layers hyperdoped with chalcogen atoms synthesized by ion implantation followed by pulsed laser melting. A broad mid-infrared optical absorption band emerges, peaking near 0.5 eV for sulfur and selenium and 0.3 eV for tellurium hyperdoped samples. Its strength and width increase with impurity concentration. Its strength decreases markedly with subsequent thermal annealing. The emergence of a broad MIR absorption band is consistent with the formation of an impurity band from isolated deep donor levels as the concentration of chalcogen atoms in metastable local configurations increases. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4804935]

I. INTRODUCTION

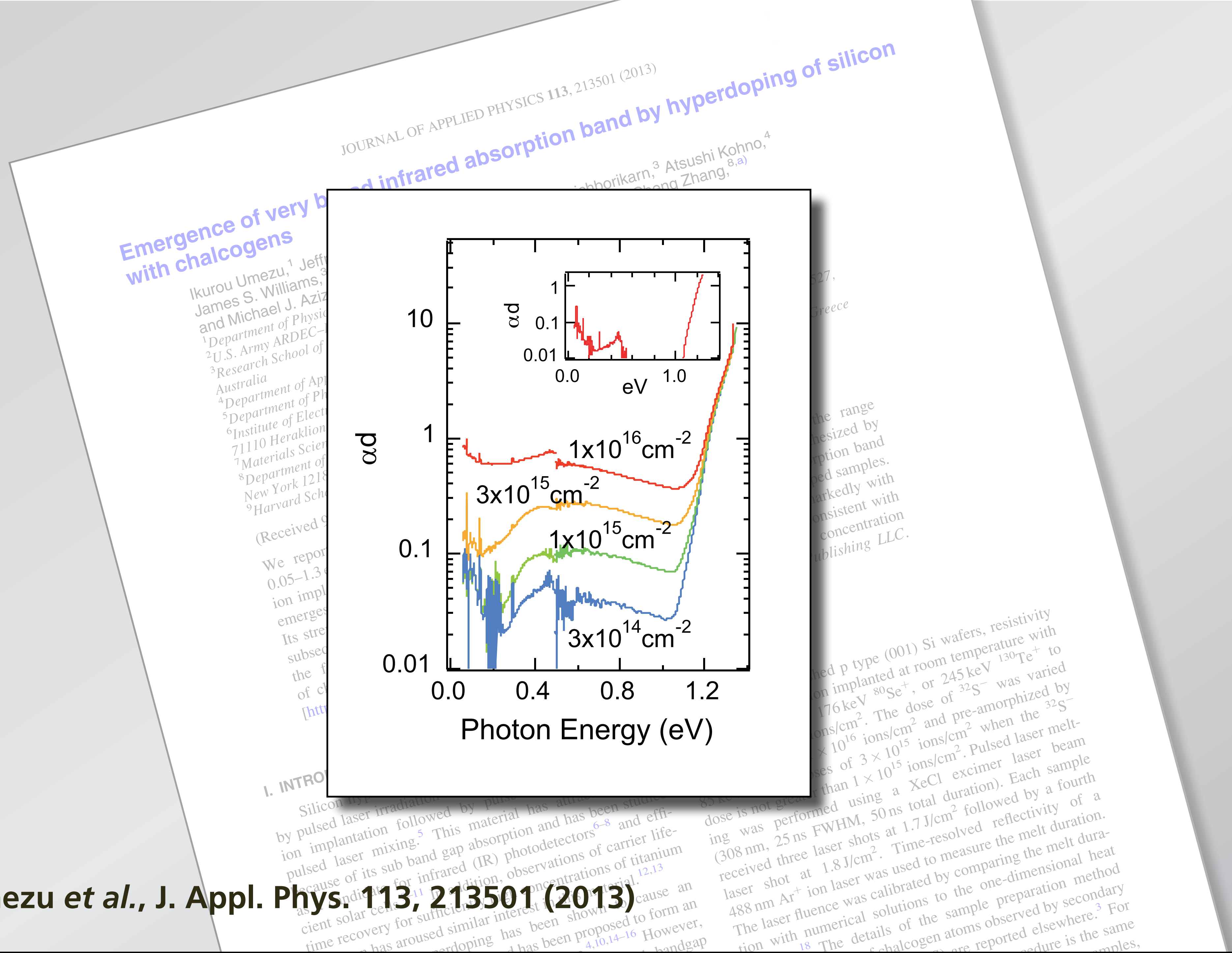
Silicon hyperdoped with chalcogens can be synthesized by pulsed laser irradiation in a sulfur-bearing atmosphere,[1,2] or ion implantation followed by pulsed laser melting,[3,4] or pulsed laser mixing.[5] This material has attracted interest because of its sub band gap absorption and has been studied as a candidate for infrared (IR) photodetectors[6–8] and efficient solar cells.[9–11] In addition, observations of carrier lifetime recovery for sufficiently high concentrations of titanium has aroused similar interest in this material.[12,13] erdoping has been shown to cause an has been proposed to form an [4,10,14–16] However, bandgap

II. EXPERIMENT

Double side polished p type (001) Si wafers, resistivity of 5–25 Ω cm, were ion implanted at room temperature with either 95 keV $^{32}S^-$, 176 keV $^{80}Se^+$, or 245 keV $^{130}Te^+$ to doses of 1×10^{16} ions/cm^2. The dose of $^{32}S^-$ was varied from 3×10^{14} to 1×10^{16} ions/cm^2 and pre-amorphized by 85 keV Si^- to doses of 3×10^{15} ions/cm^2 when the $^{32}S^-$ dose is not greater than 1×10^{15} ions/cm^2. Pulsed laser melting was performed using a XeCl excimer laser beam (308 nm, 25 ns FWHM, 50 ns total duration). Each sample received three laser shots at 1.7 J/cm^2 followed by a fourth laser shot at 1.8 J/cm^2. Time-resolved reflectivity of a 488 nm Ar^+ ion laser was used to measure the melt duration. The laser fluence was calibrated by comparing the melt duration with numerical solutions to the one-dimensional heat [18] The details of the sample preparation method chalcogen atoms observed by secondary) are reported elsewhere.[3] For edure is the same amples,

1 properties

2 intermediate band



Umezu *et al.*, J. Appl. Phys. 113, 213501 (2013)

① **properties** ② **intermediate band**

Understanding the Viability of Impurity-Band Photovoltaics: A Case Study of S-doped Si

by

Joseph Timothy Sullivan

Submitted to the Department of Mechanical Engineering
on May 18, 2013, in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

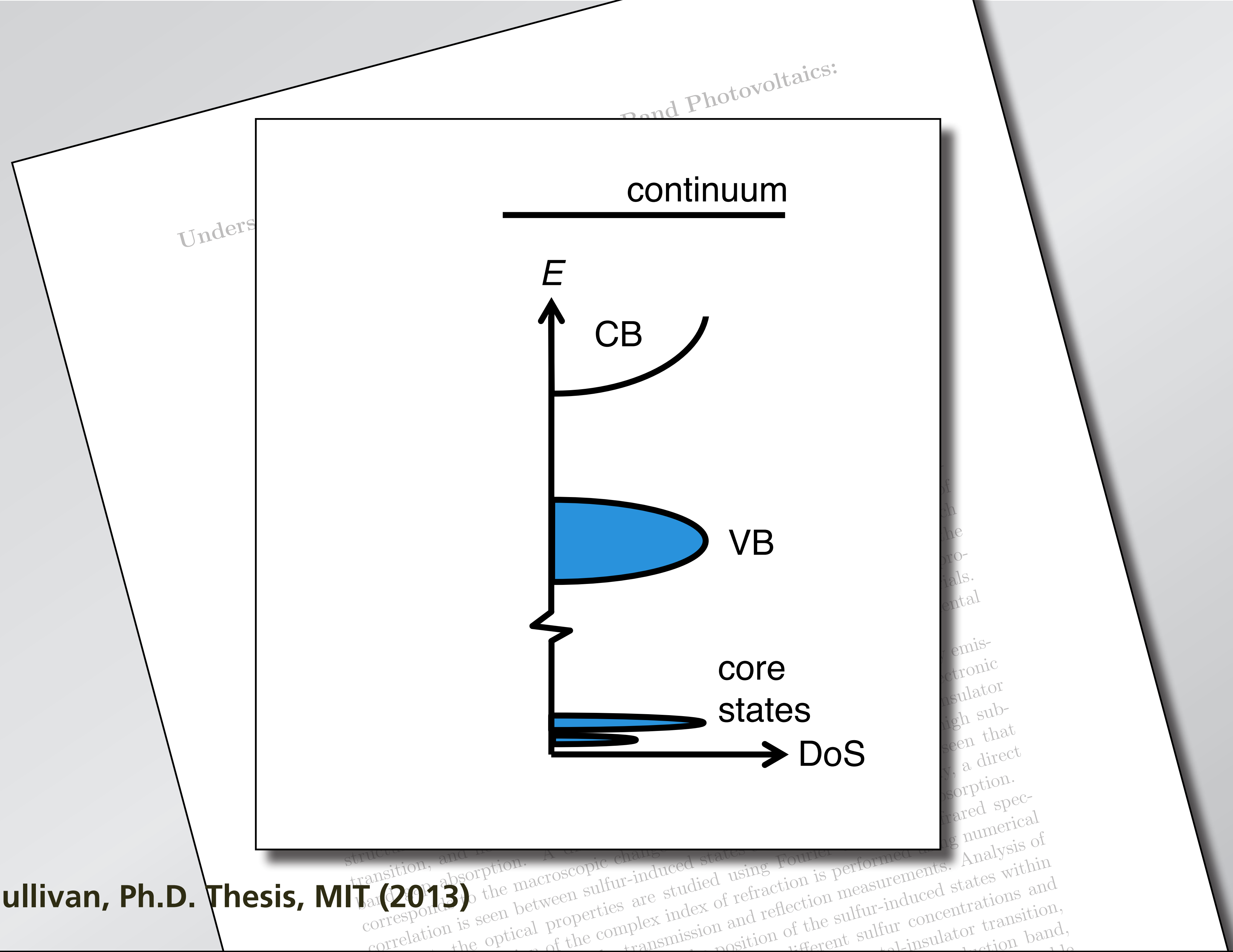
Abstract

This thesis explores the electronic structure, optical properties, and carrier lifetimes in silicon that is doped with sulfur beyond the equilibrium solid solubility limit, with a focus on applications as an absorber layer for an impurity-band photovoltaic device. The concept of an impurity-band material envisions the creation of a band of electronic states by incorporating high concentrations of deep-level dopants, which enable the generation of free carriers using photons with energy less than that of the band gap of the host semiconductor. The investigations reported in this thesis provide a framework for the appropriate selection of impurity-band candidate materials. The thesis is divided into three primary sections, one for each of three experimental techniques, respectively.

First, the electronic band structure is studied using synchrotron-based x-ray emission spectroscopy. These spectra provide the first insights into how the electronic structure changes as the sulfur concentration is increased across the metal-insulator transition, and how the electronic structure is linked to the anomalously high sub-band gap absorption. A discrete change in local electronic structure is seen that corresponds to the macroscopic change in electronic behavior. Additionally, a direct correlation is seen between sulfur-induced states and the sub-band gap absorption.

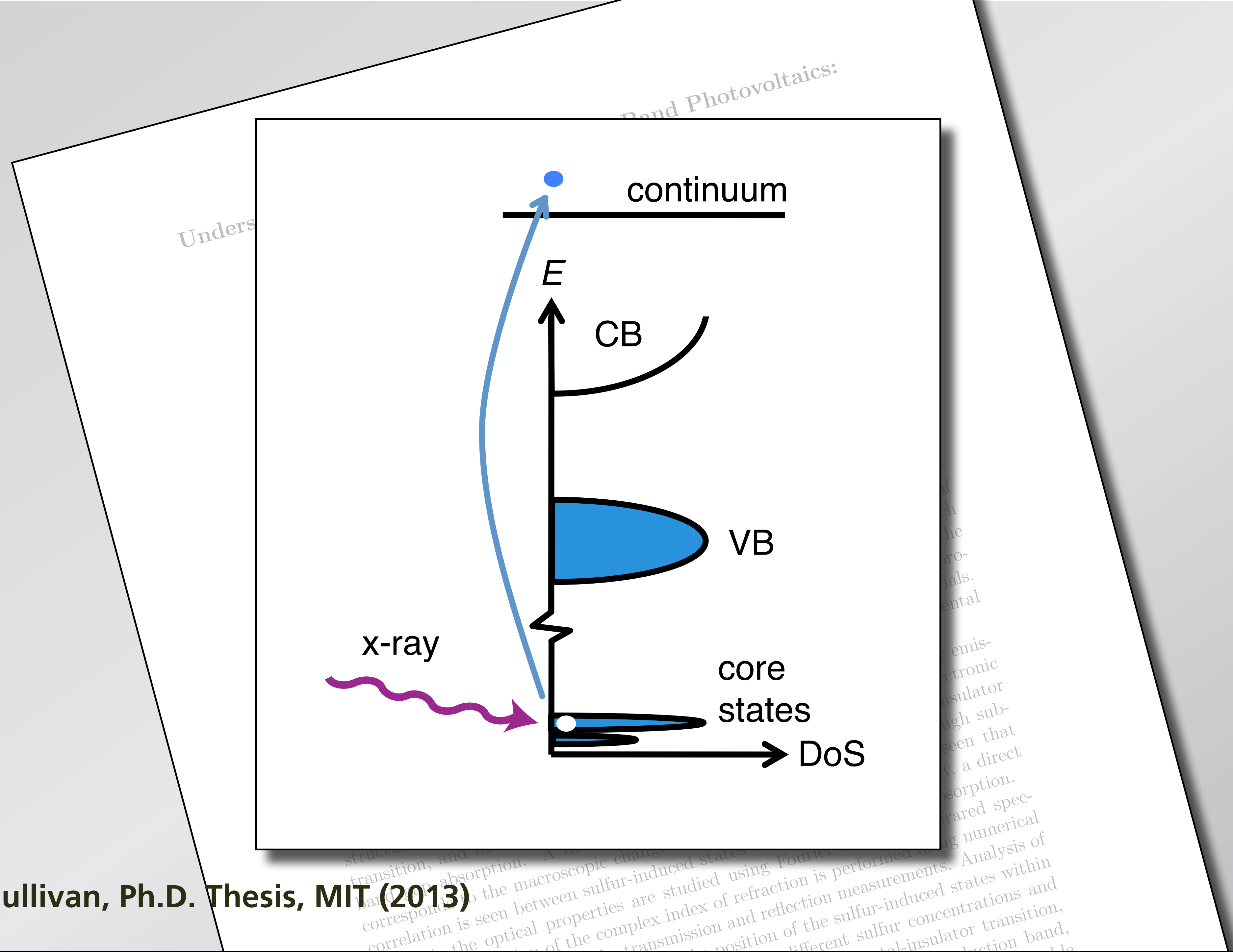
the optical properties are studied using Fourier transform infrared spec-
of the complex index of refraction is performed using numerical
transmission and reflection measurements. Analysis of
position of the sulfur-induced states within
sulfur concentrations and
transition,
band,

① **properties** ② **intermediate band**



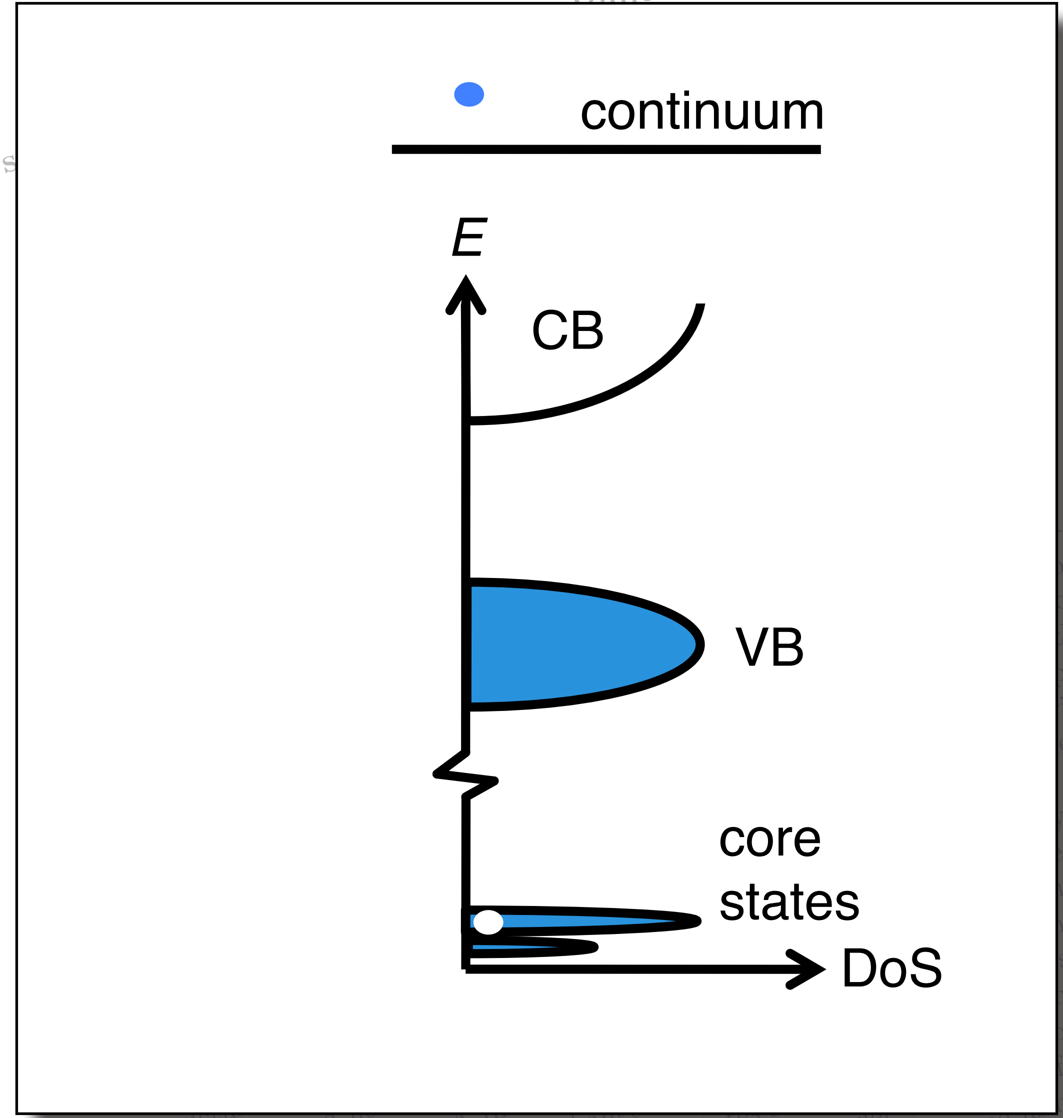
J. Sullivan, Ph.D. Thesis, MIT (2013)

① properties ② intermediate band

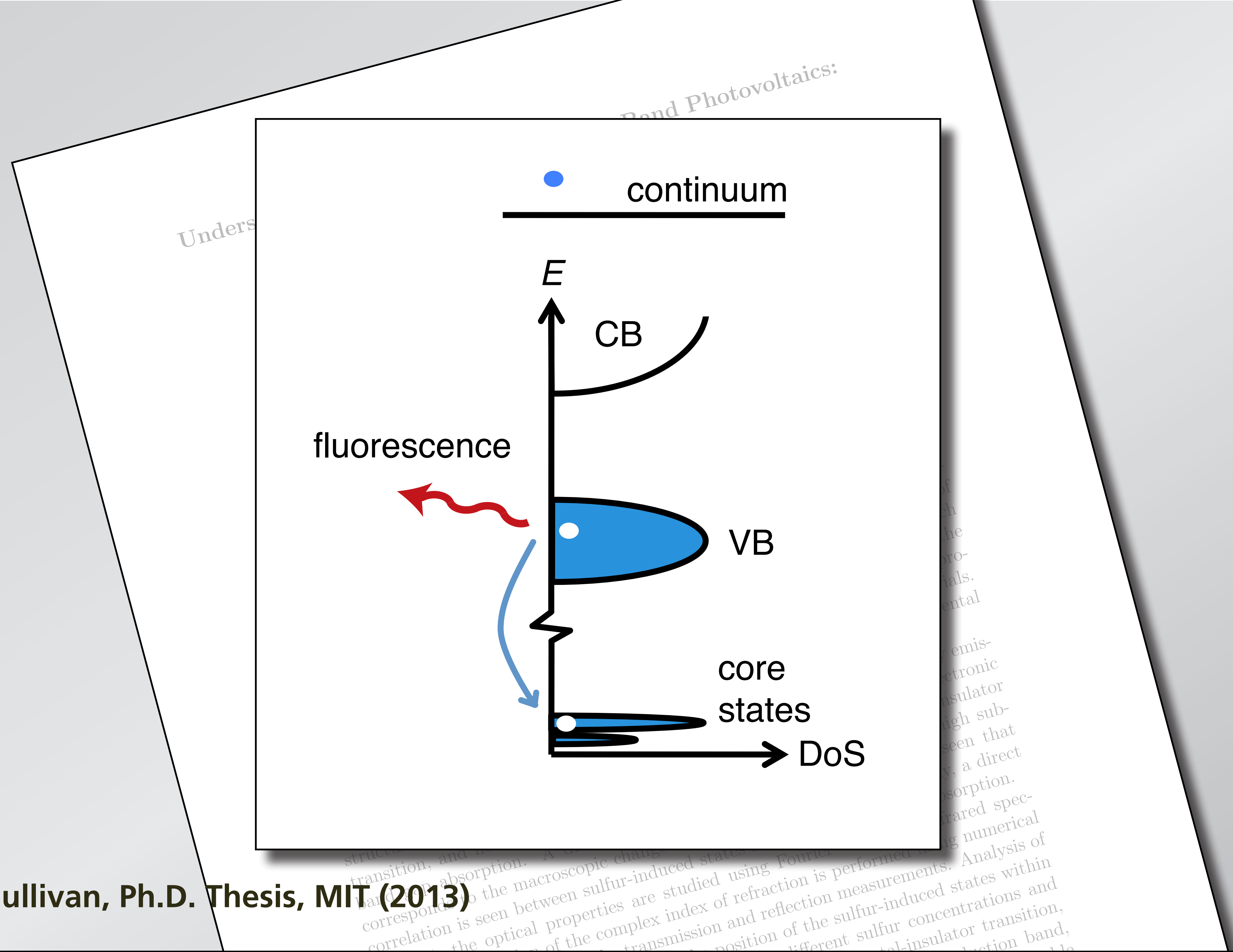


J. Sullivan, Ph.D. Thesis, MIT (2013)

① properties ② intermediate band

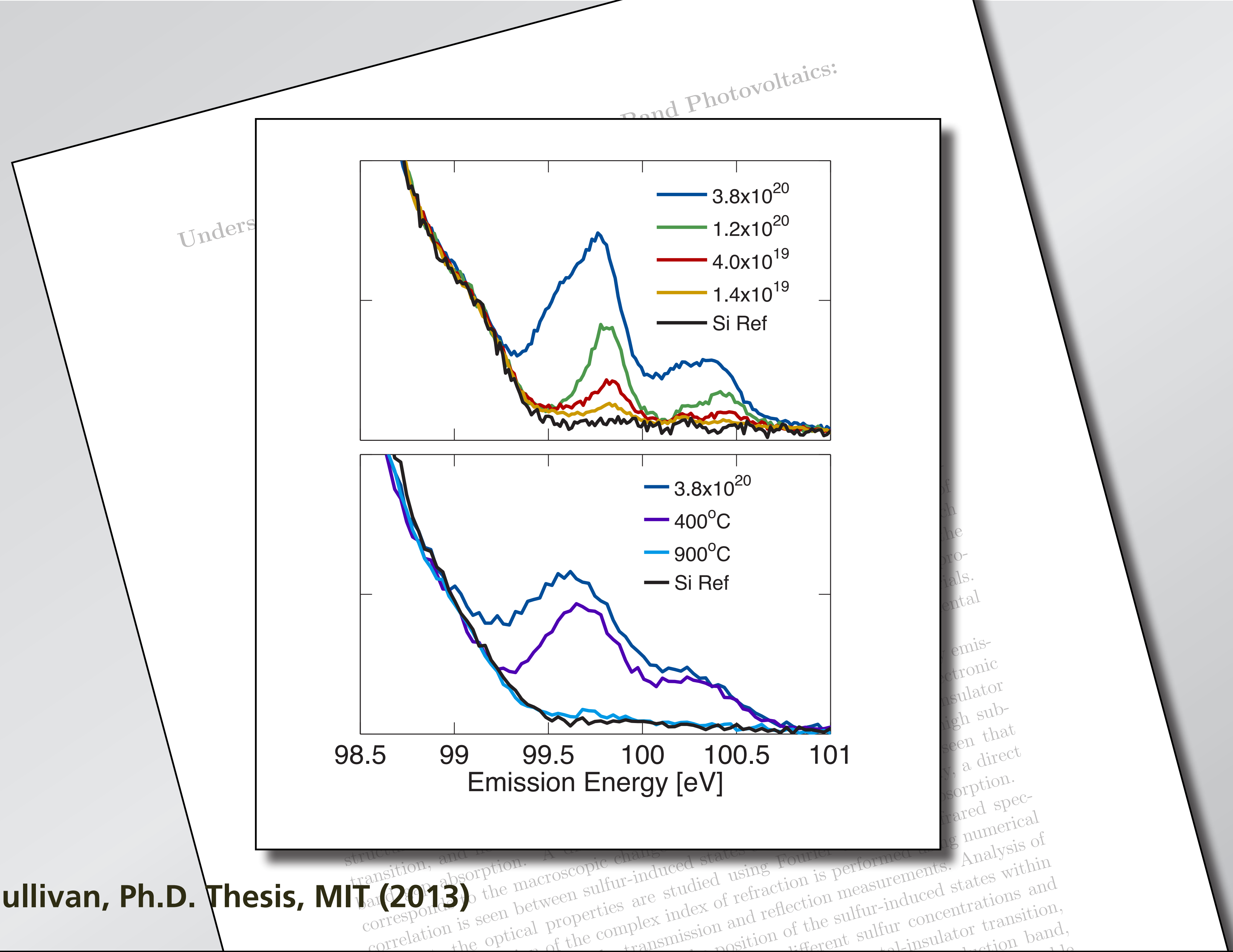


J. Sullivan, Ph.D. Thesis, MIT (2013)



J. Sullivan, Ph.D. Thesis, MIT (2013)

① properties ② intermediate band

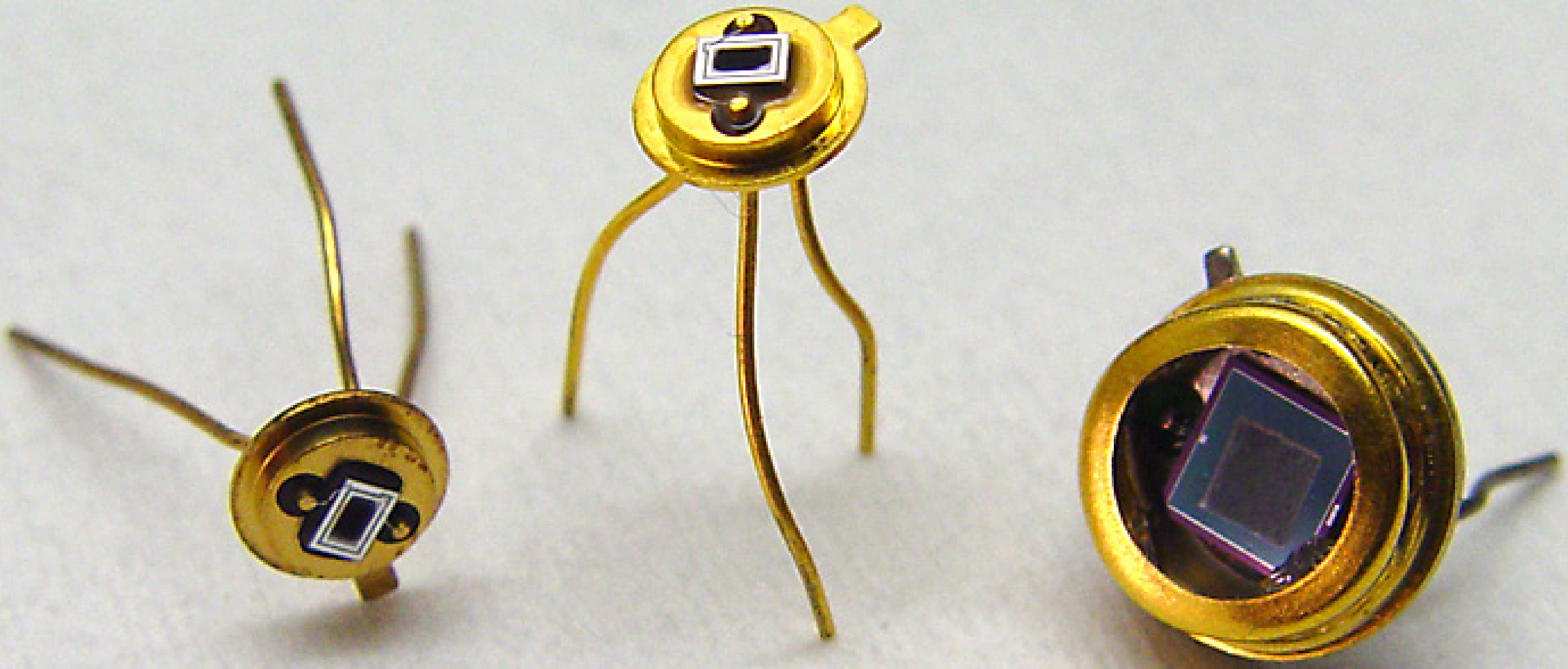


J. Sullivan, Ph.D. Thesis, MIT (2013)

① **properties** ② **intermediate band**

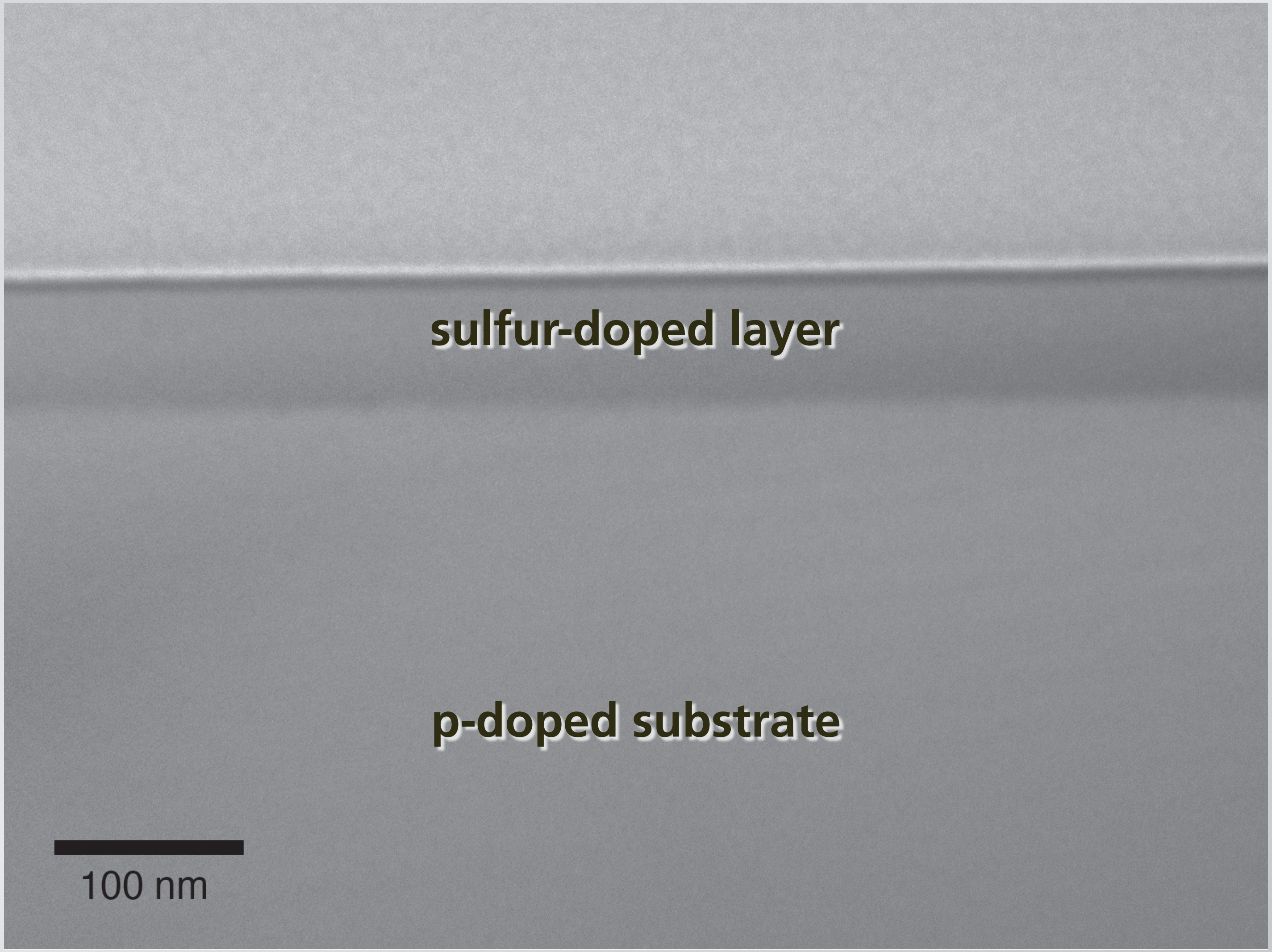
Things to keep in mind

- IR absorption rolls off around 8 µm
- consistent evidence of intermediate band formation
- IB forms at 0.1% at. doping, broadens at higher doping
- IB merges with CB at 0.4% at. yielding metallic behavior

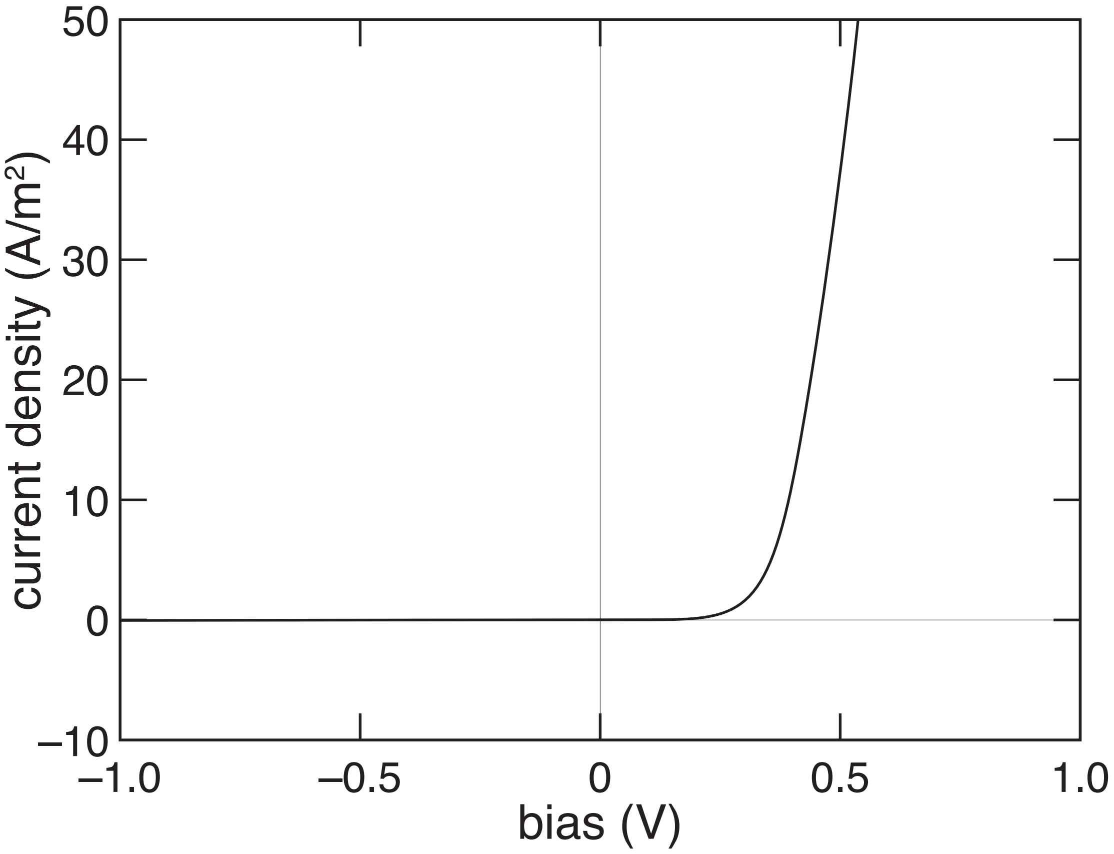


① properties ② intermediate band ③ devices

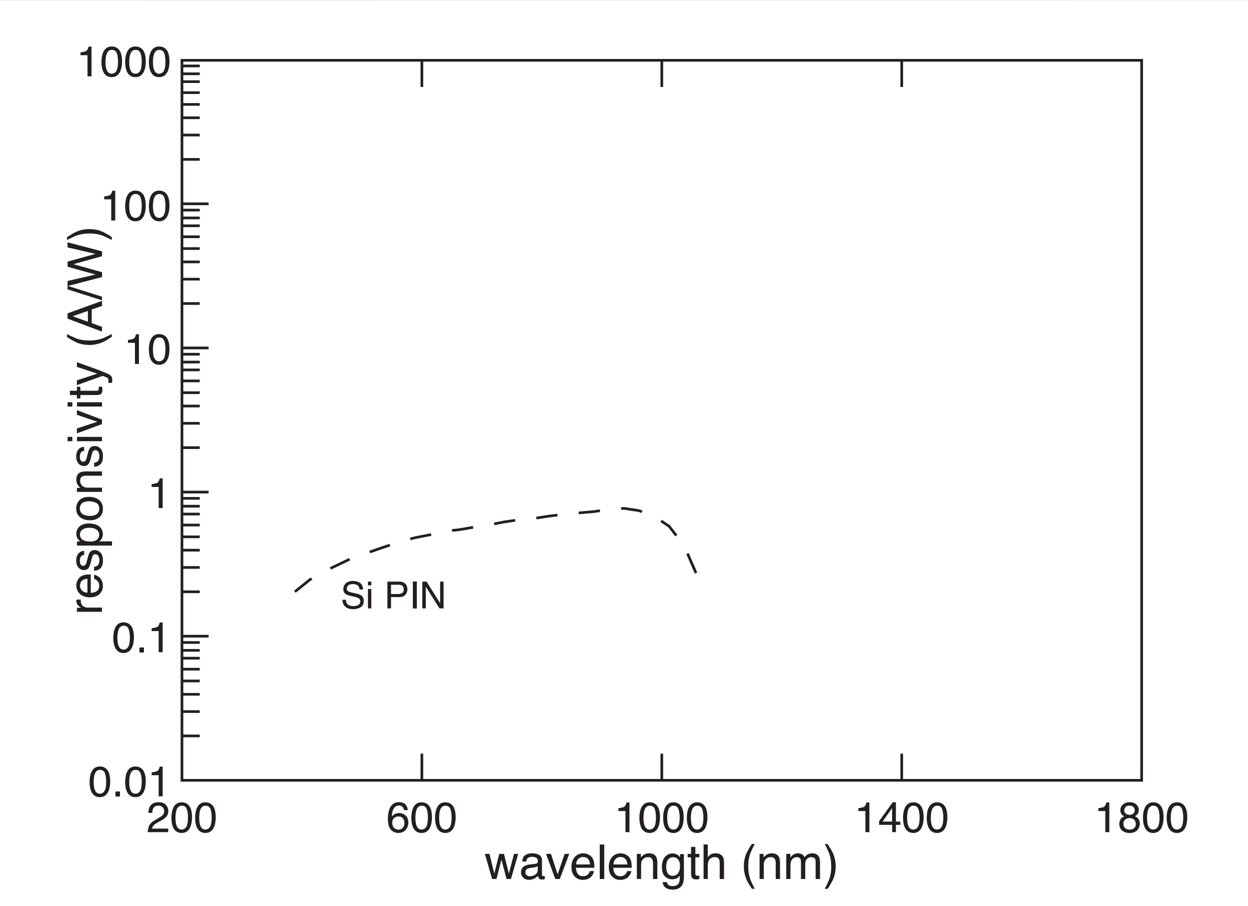
should have shallow junction below surface



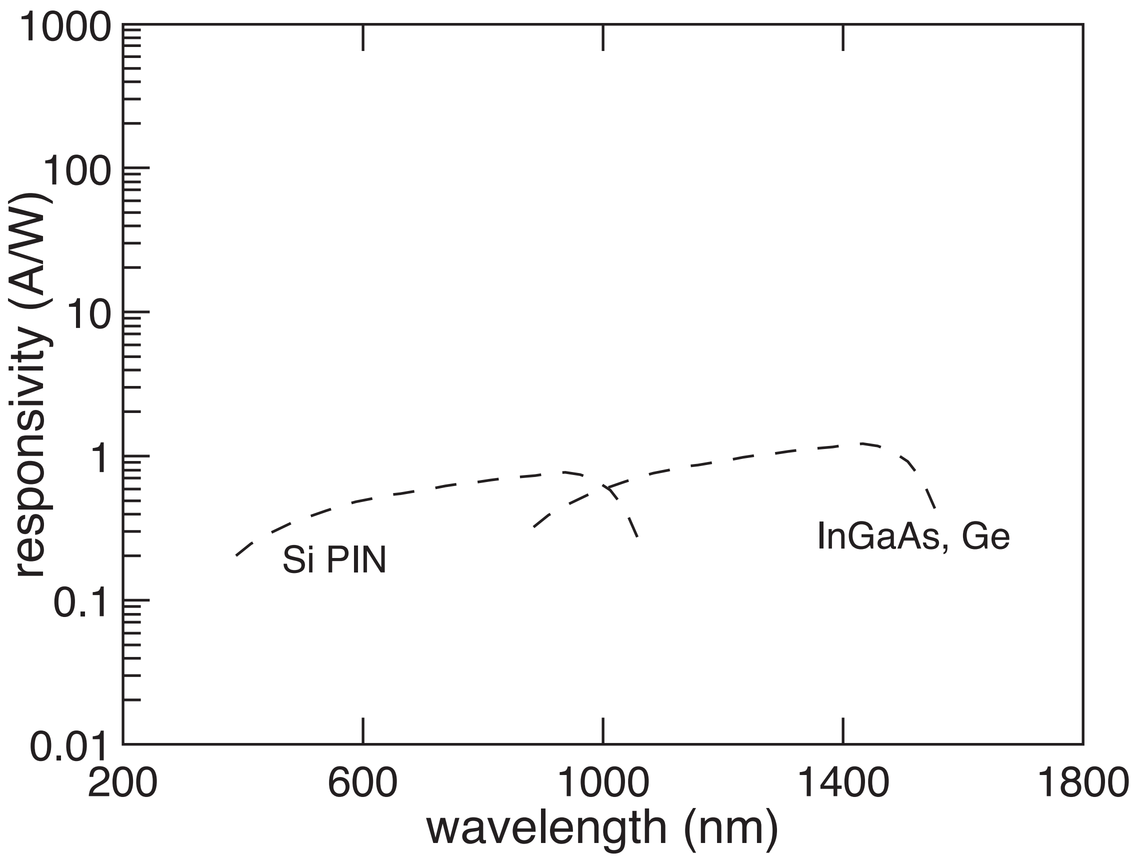
excellent rectification (after annealing)



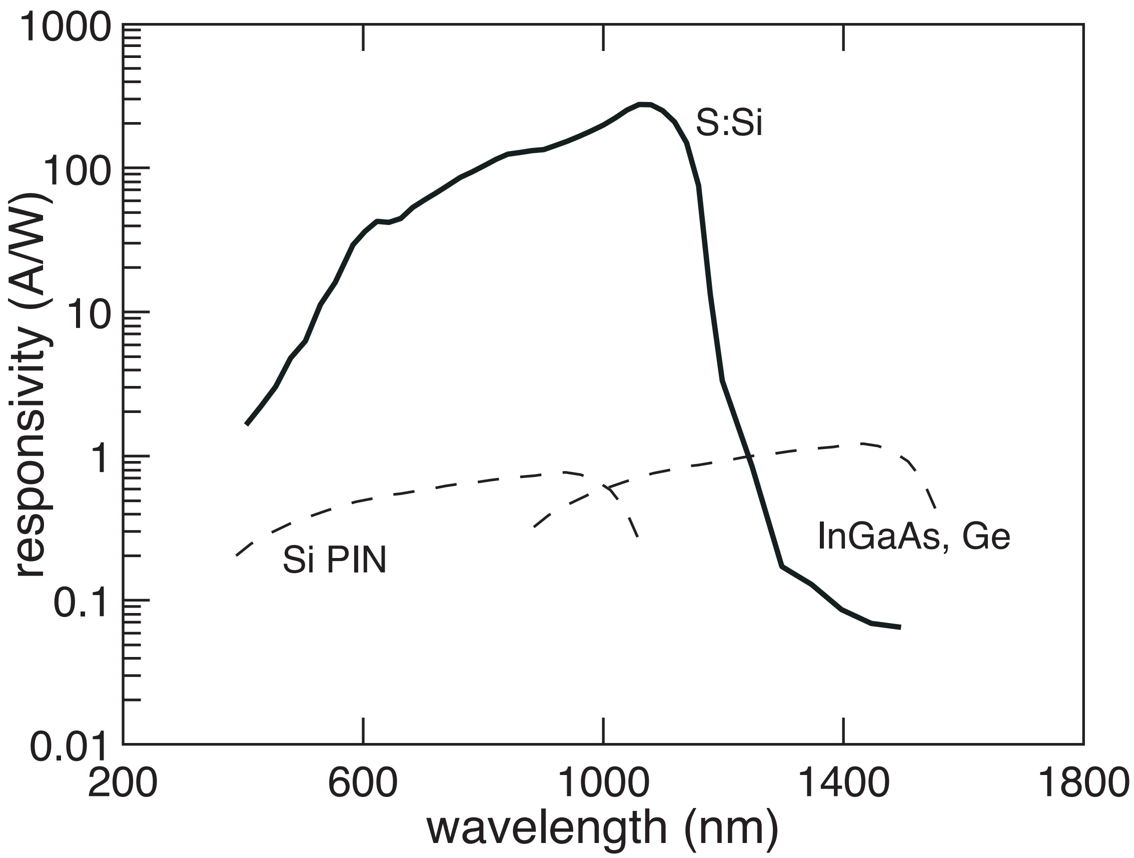
responsivity



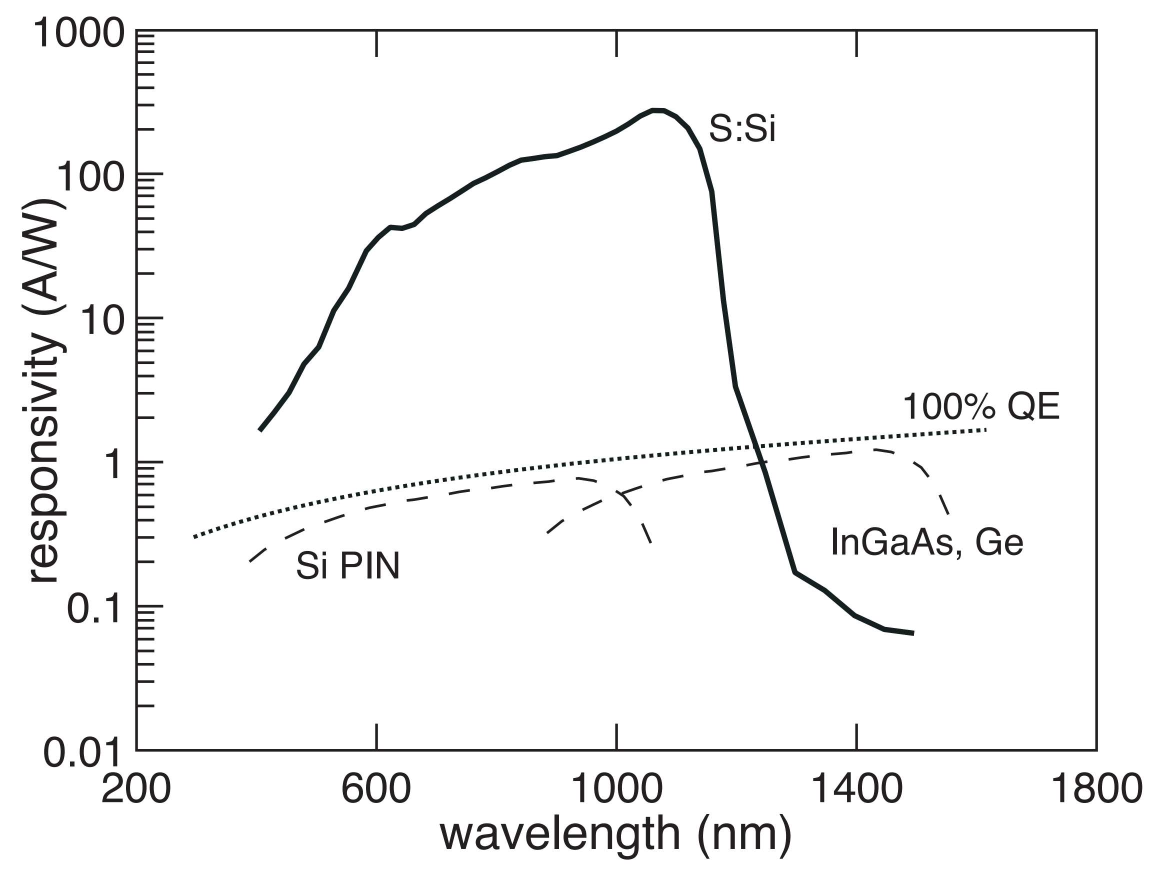
responsivity



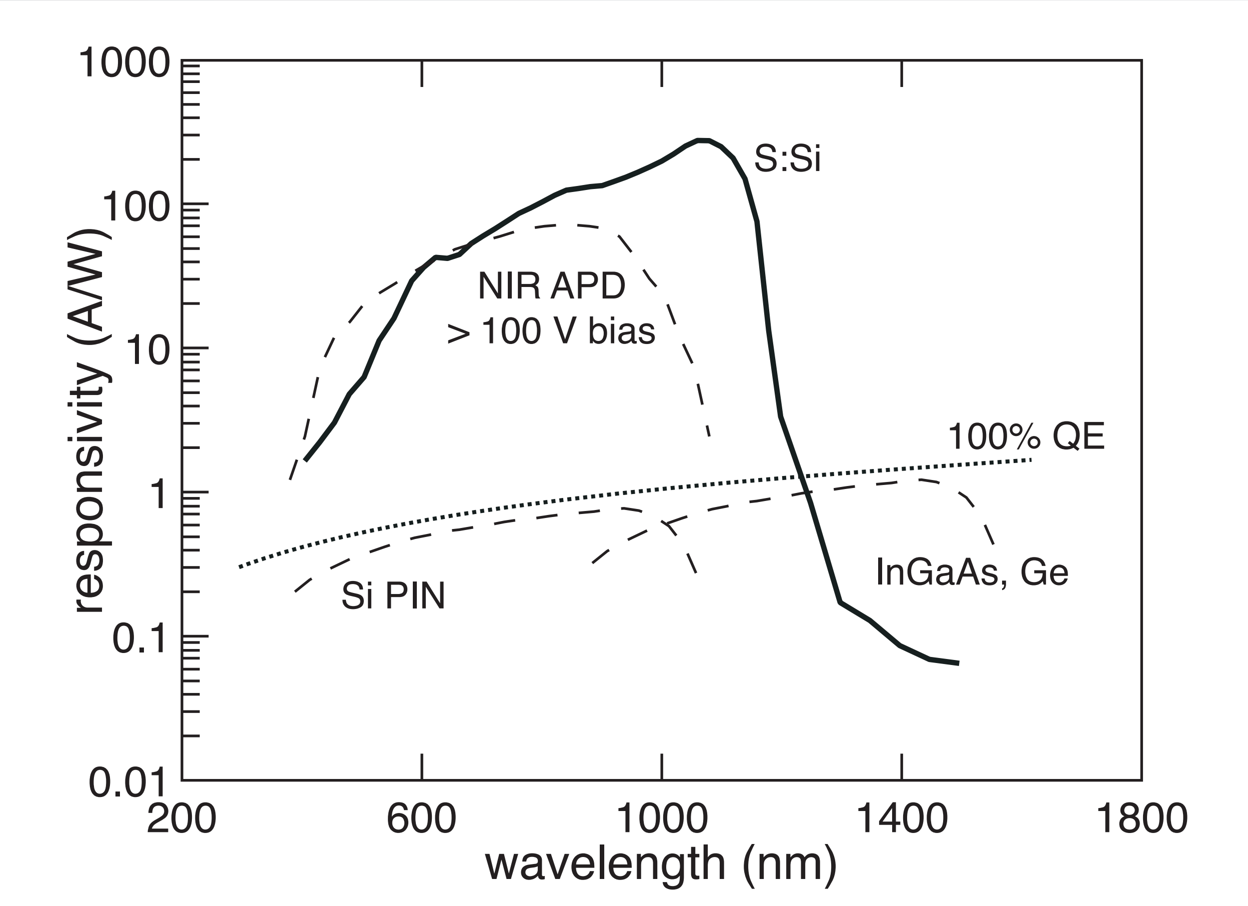
responsivity



responsivity

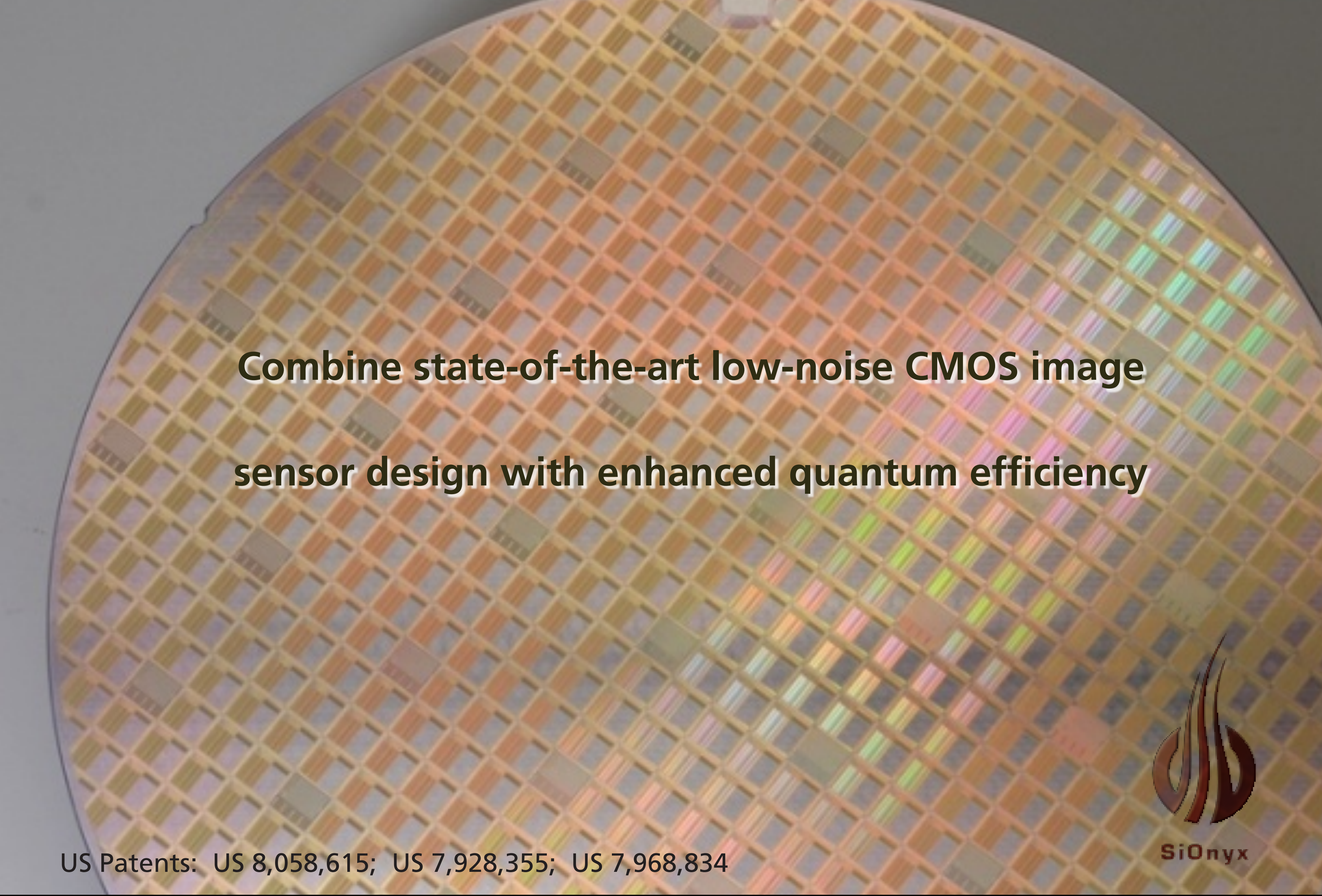


responsivity



- enhanced sensitivity
- extended IR response

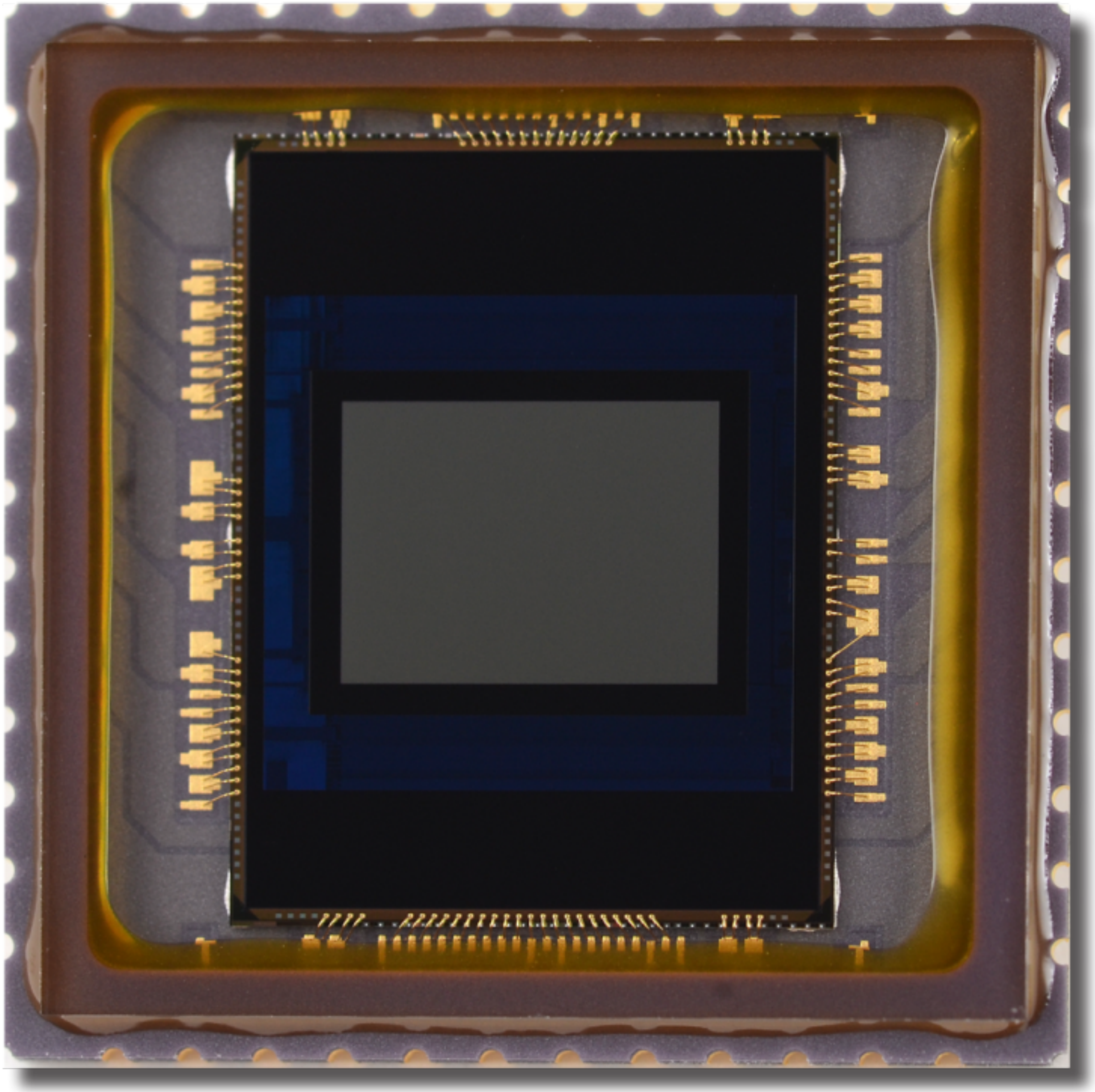
① properties ② intermediate band ③ devices



Combine state-of-the-art low-noise CMOS image sensor design with enhanced quantum efficiency

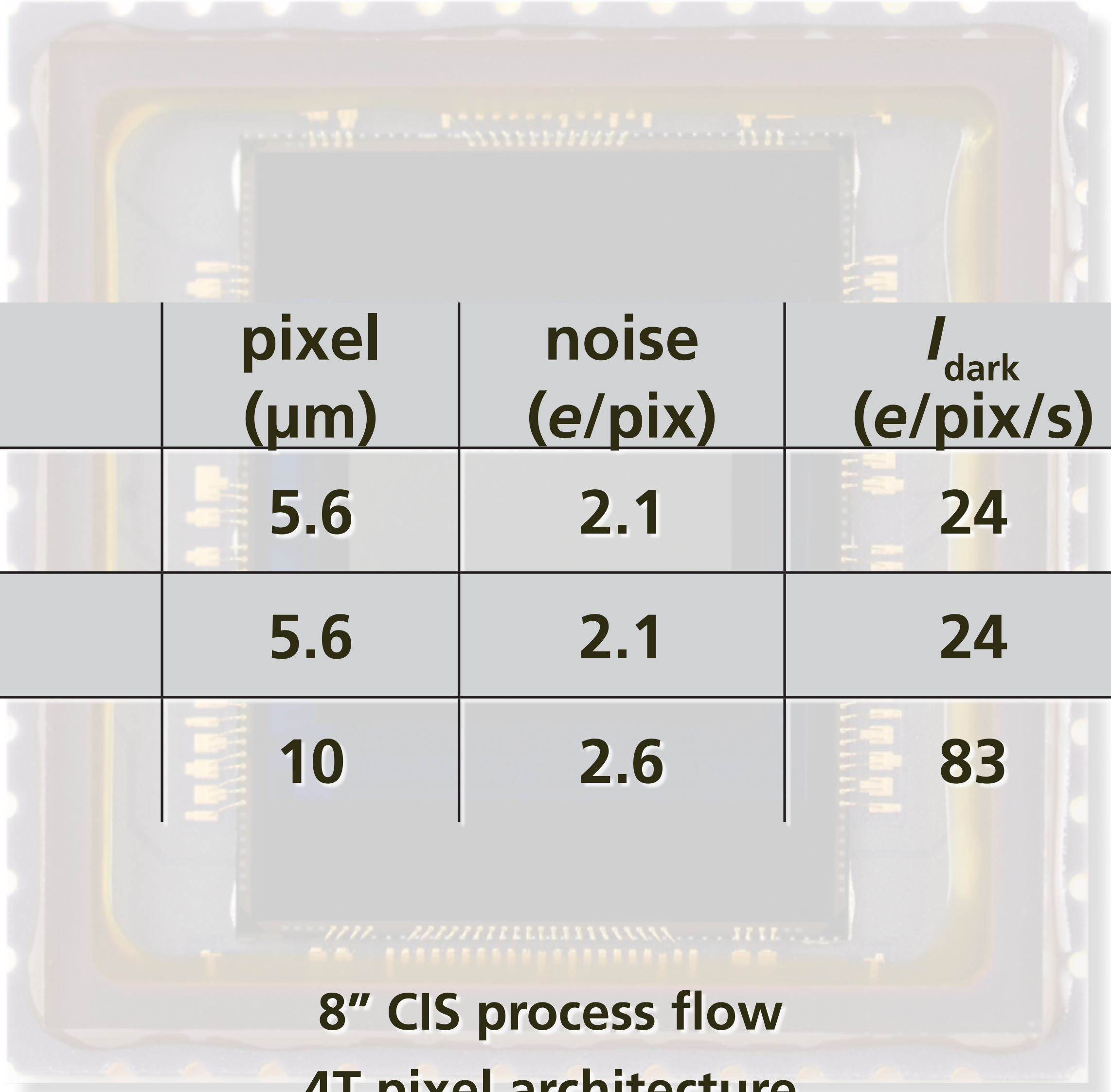
US Patents: US 8,058,615; US 7,928,355; US 7,968,834

SiOnyx



US Patents: US 8,058,615; US 7,928,355; US 7,968,834

SiOnyx

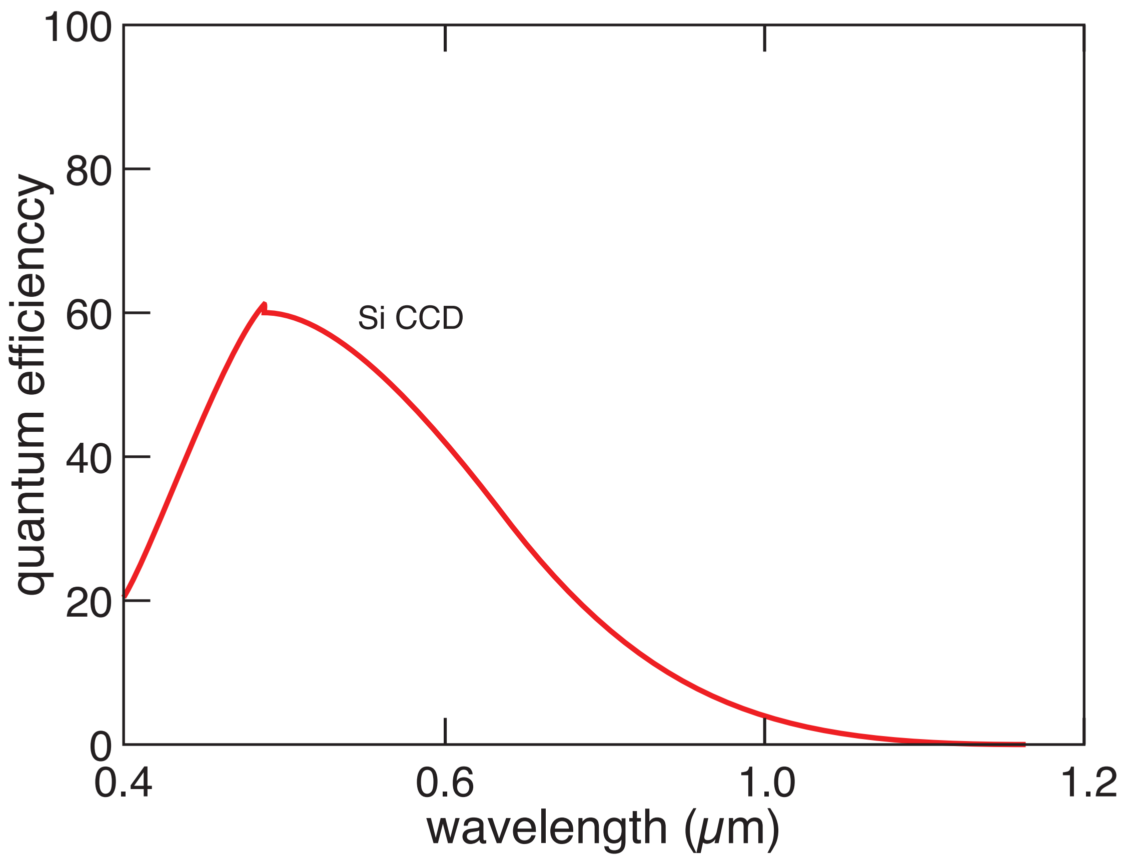


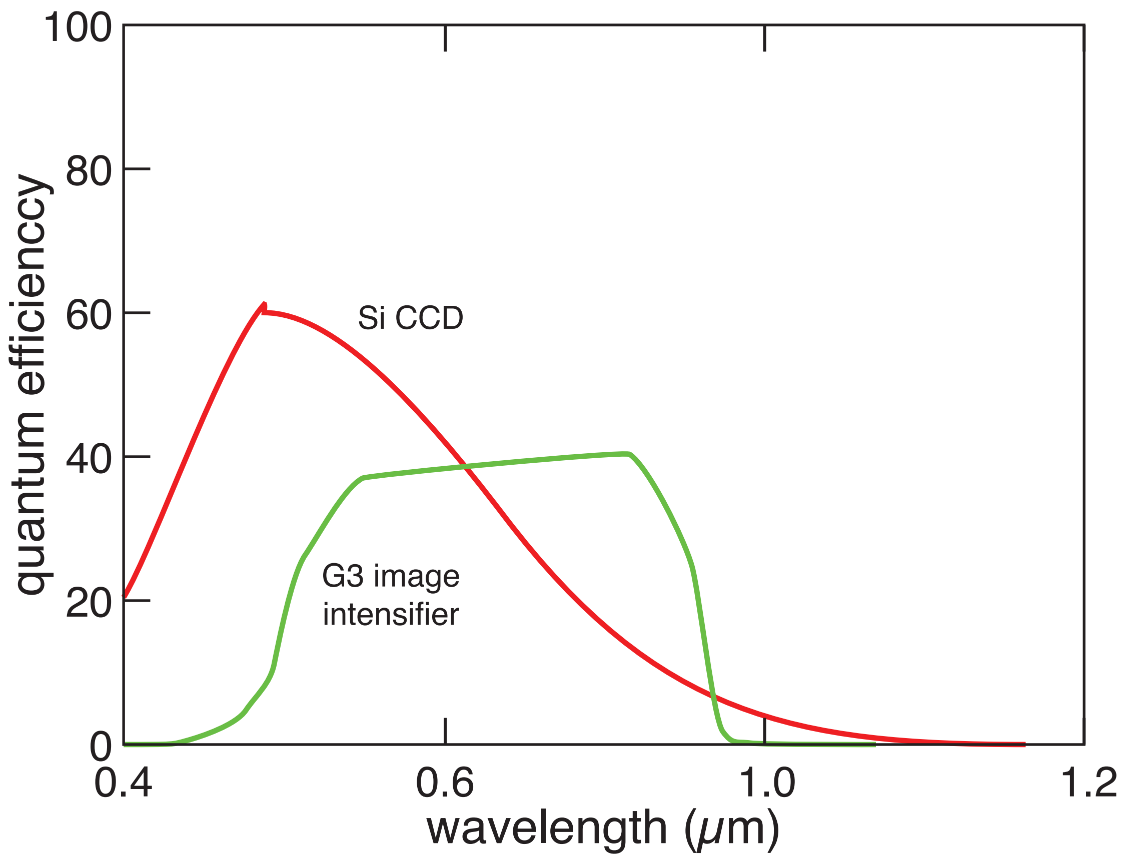
Resolution	pixel (μm)	noise (e/pix)	I_{dark} (e/pix/s)	P (mW)
872 x 654	5.6	2.1	24	300
1280 x 720	5.6	2.1	24	360
1280 x 1024	10	2.6	83	400

8" CIS process flow

4T pixel architecture

SiOnyx


100
80
60
40
20
0
quantum efficienccy
Si CCD
0.4
0.6
1.0
1.2
wavelength (μm)


100
80
60
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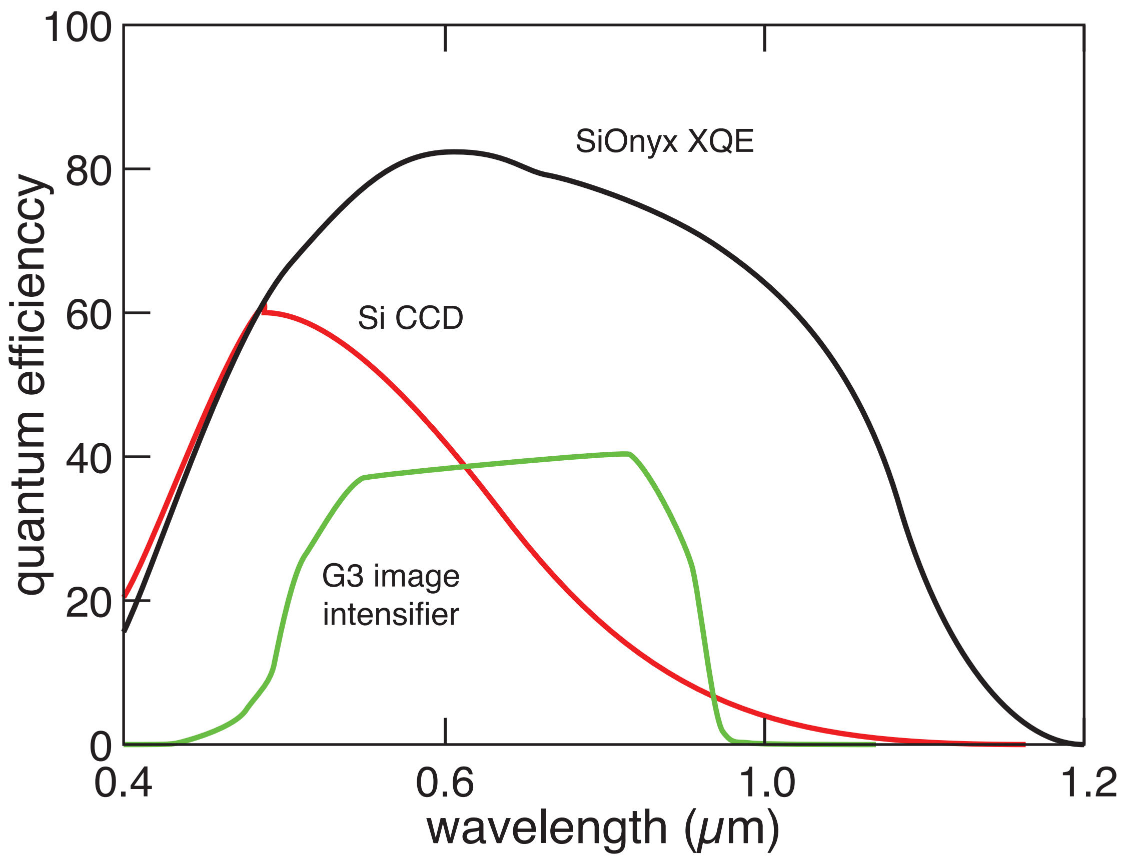
quantum efficienccy
Si CCD
G3 image
intensifier
0.4
0.6
1.0
1.2
wavelength (μm)

SiOnyx


100
80
60
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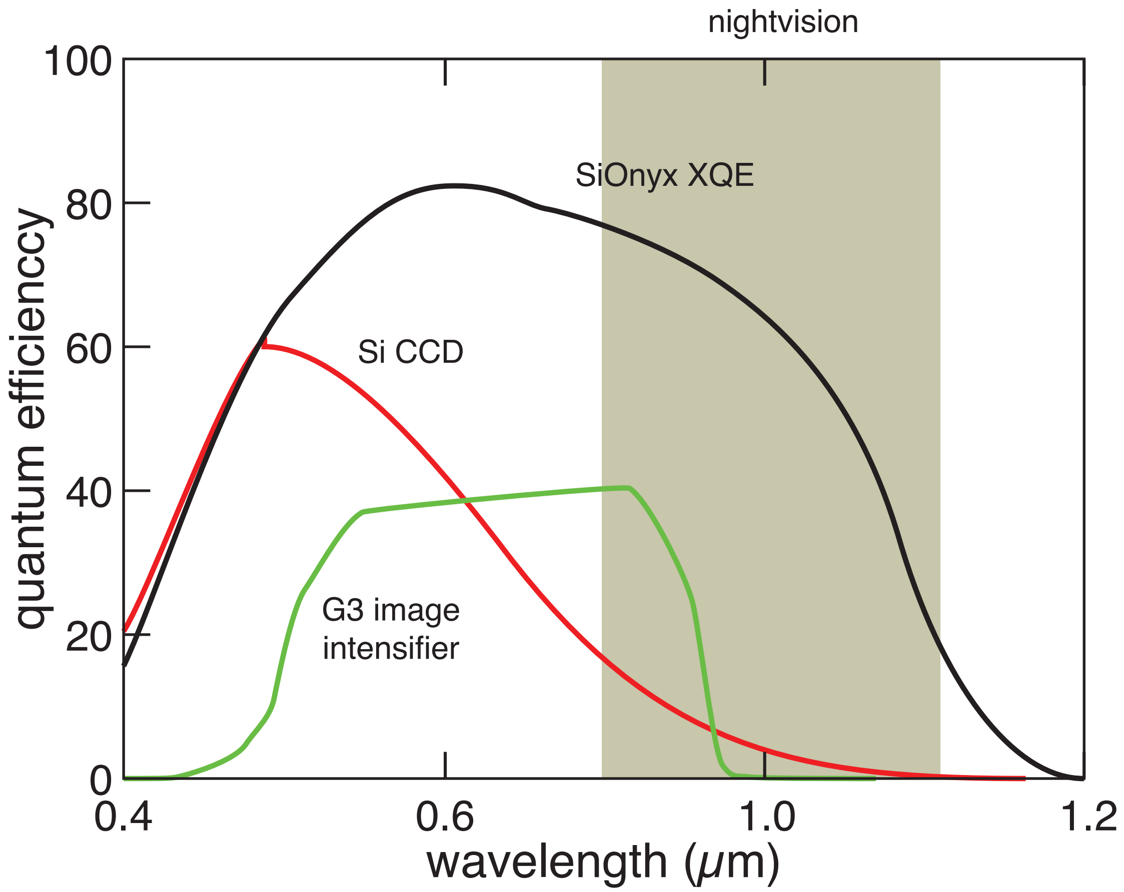
20
0
quantum efficiencY
0.4
0.6
1.0
1.2
wavelength (μm)
SiOnyx XQE
Si CCD
G3 image
intensifier

SiOnyx


nightvision
100
80
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40
20
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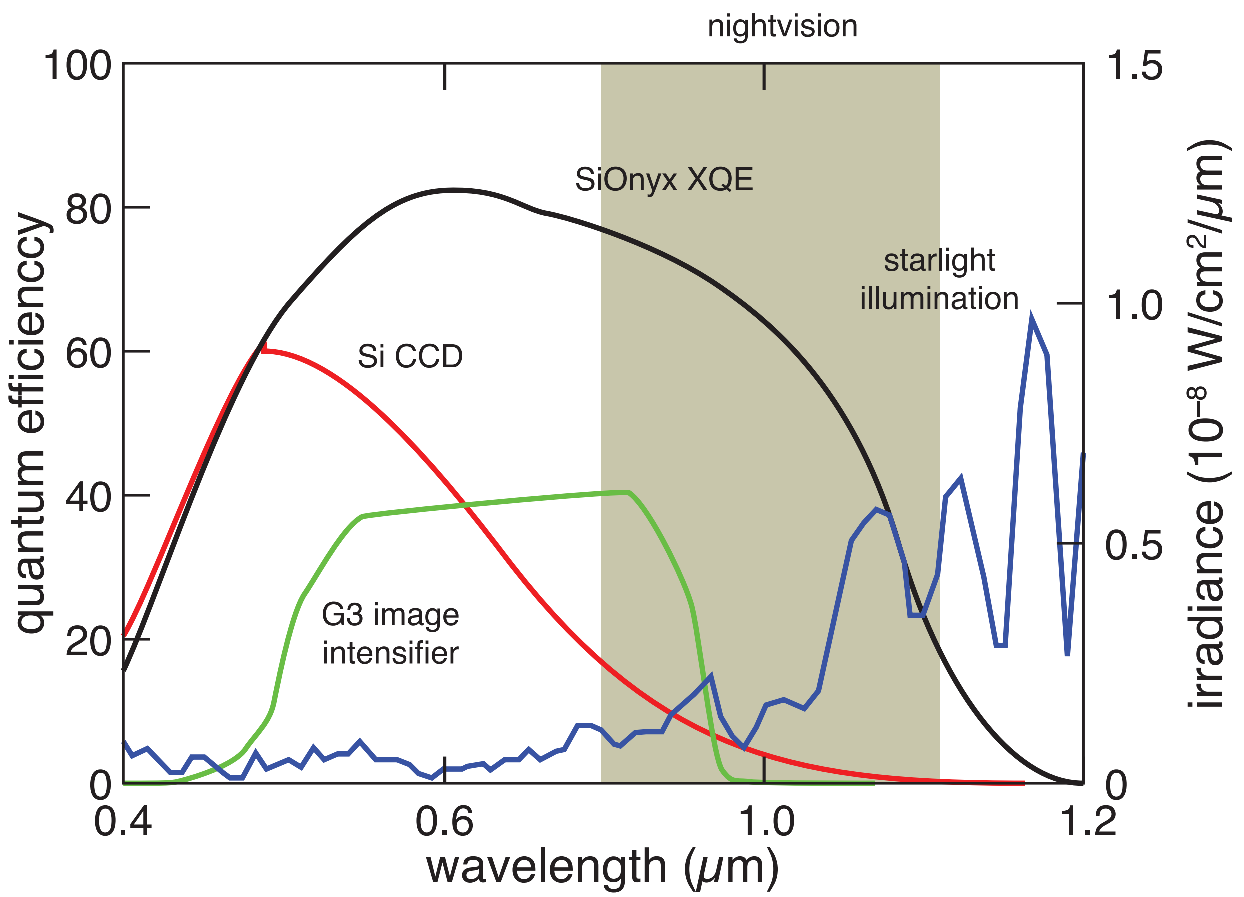
quantum efficiencсy
SiOnyx XQE
Si CCD
G3 image intensifier
0.4
0.6
1.0
1.2
wavelength (μm)

SiOnyx



SiOnyx

① properties ② intermediate band ③ devices

Things to keep in mind

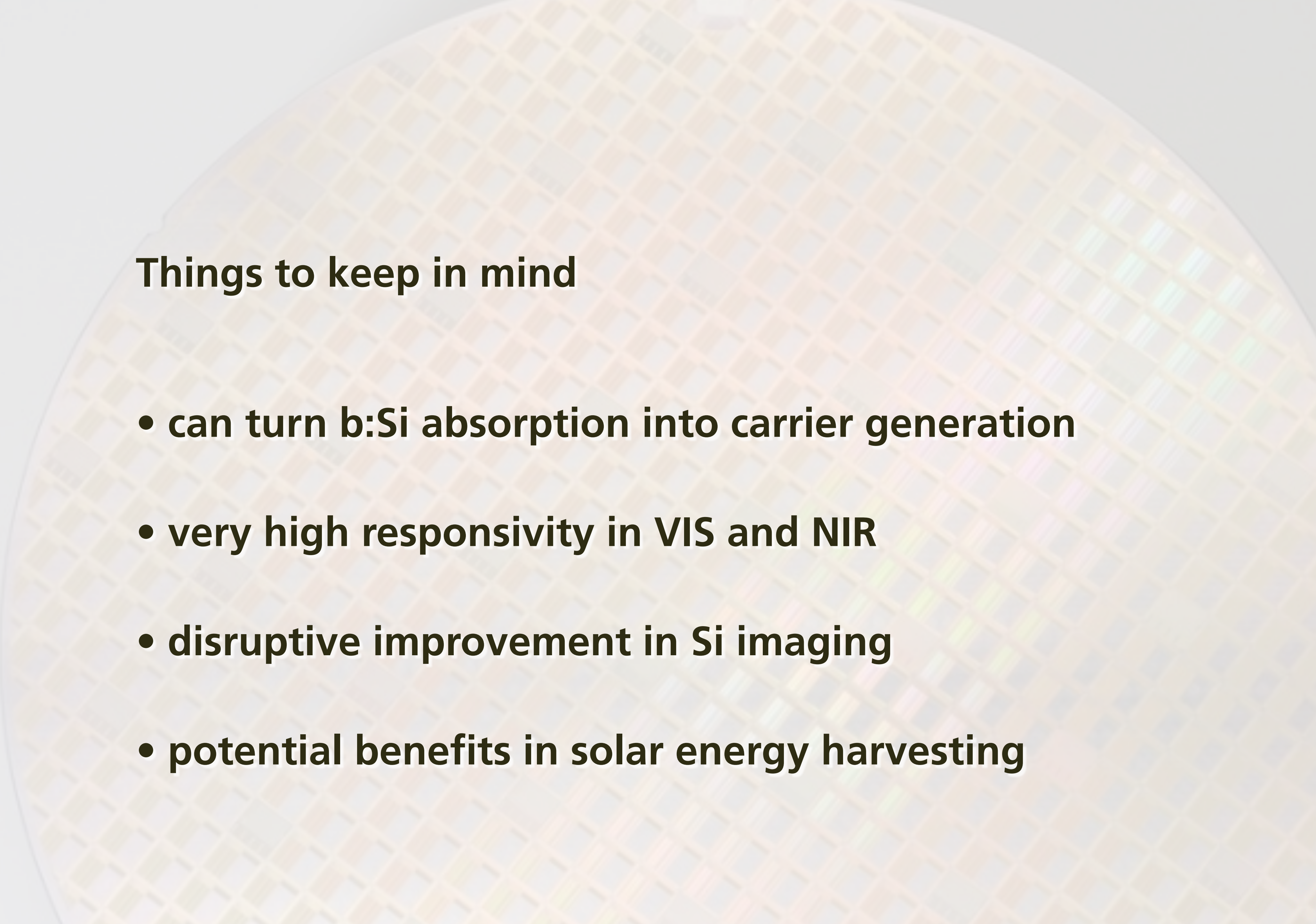
- can turn b:Si absorption into carrier generation

Things to keep in mind

- can turn b:Si absorption into carrier generation
- very high responsivity in VIS and NIR

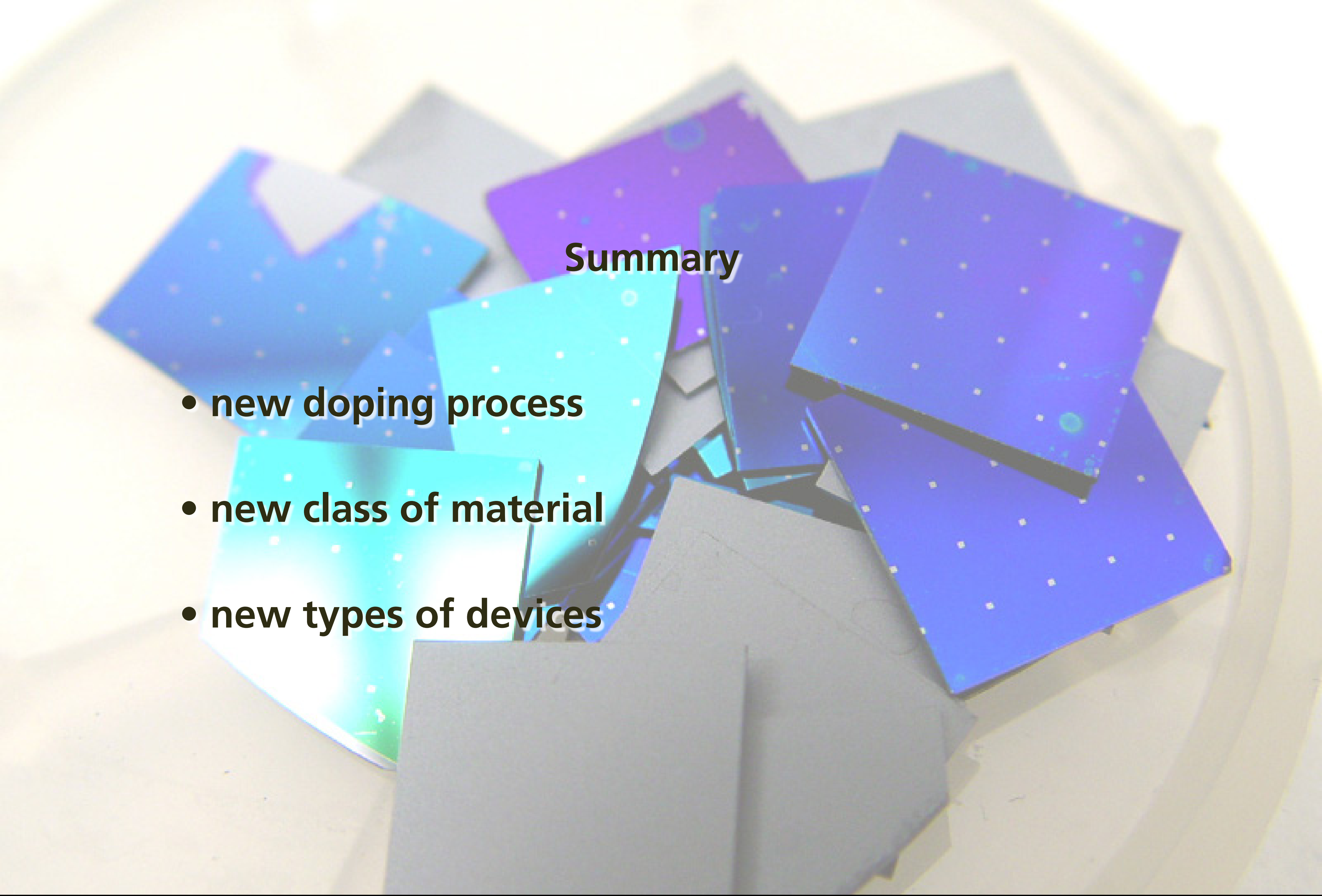
Things to keep in mind

- can turn b:Si absorption into carrier generation
- very high responsivity in VIS and NIR
- disruptive improvement in Si imaging



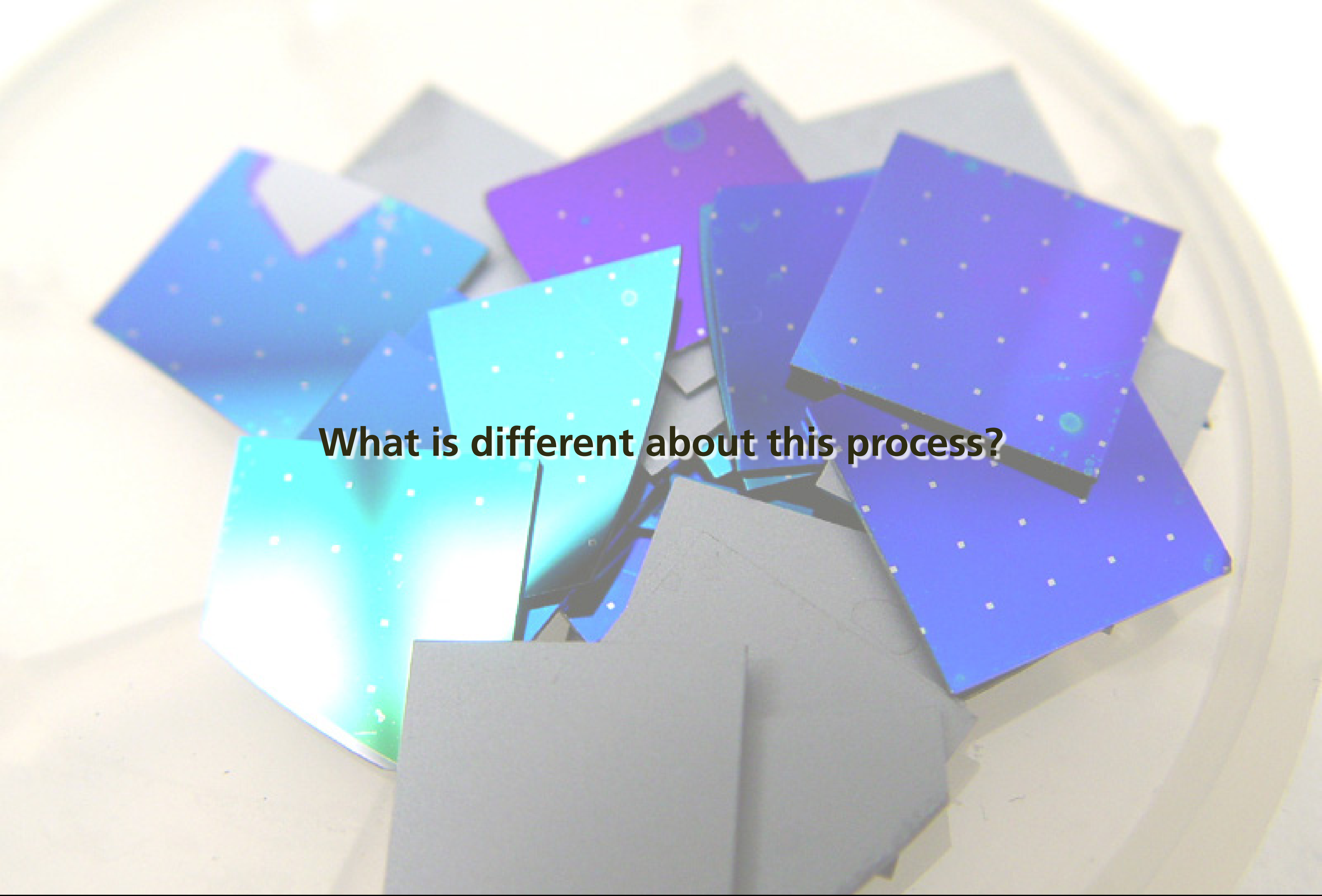
Things to keep in mind

- can turn b:Si absorption into carrier generation
- very high responsivity in VIS and NIR
- disruptive improvement in Si imaging
- potential benefits in solar energy harvesting



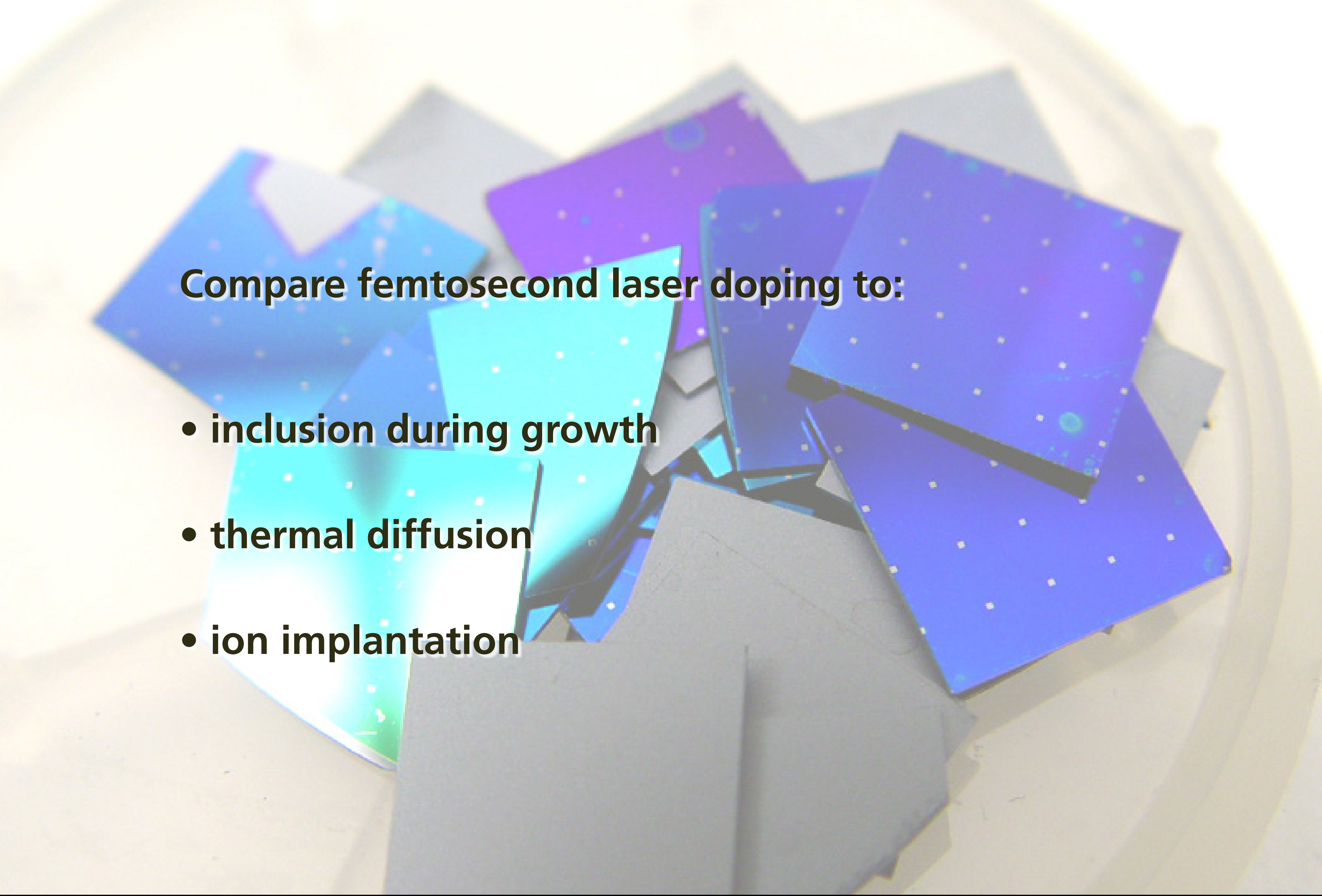
Summary

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



What is different about this process?

① properties ② intermediate band ③ devices



Compare femtosecond laser doping to:

- inclusion during growth
- thermal diffusion
- ion implantation

Funding:

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DARPA
Department of Energy
NDSEG
National Science Foundation

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