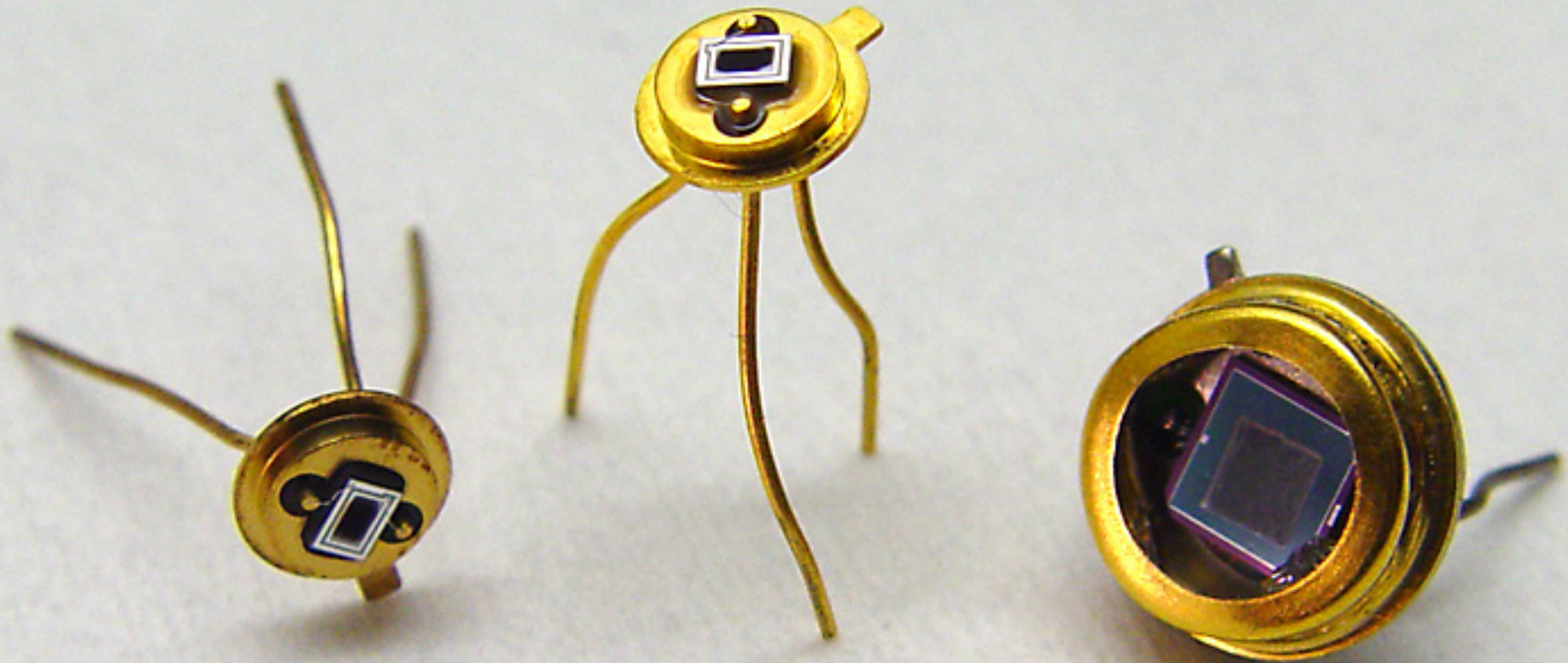


Laser doping and texturing of silicon for advanced optoelectronic devices



Institute of Atomic and Molecular Sciences
Academia Sinica
Taipei, Republic of China, 29 January 2016



Laser doping and texturing of silicon for advanced optoelectronic devices



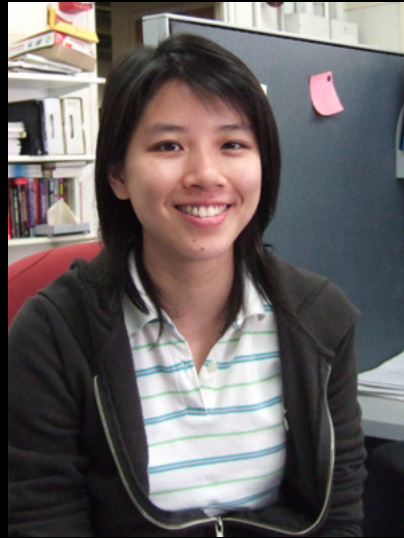
@eric_mazur

Institute of Atomic and Molecular Sciences
Academia Sinica
Taipei, Republic of China, 29 January 2016





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

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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)

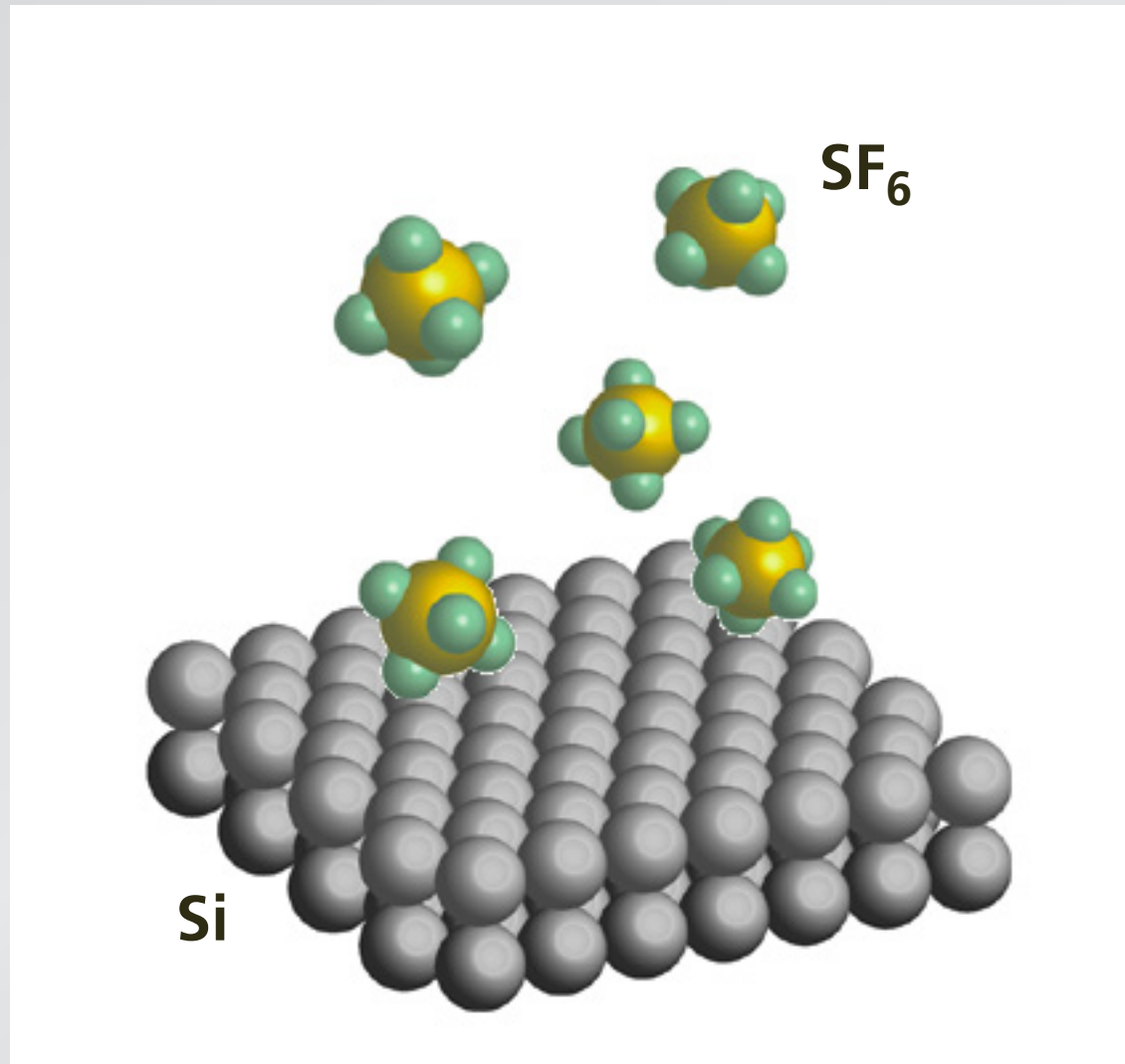
Prof. Augustinus Asenbaum (Vienna)

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

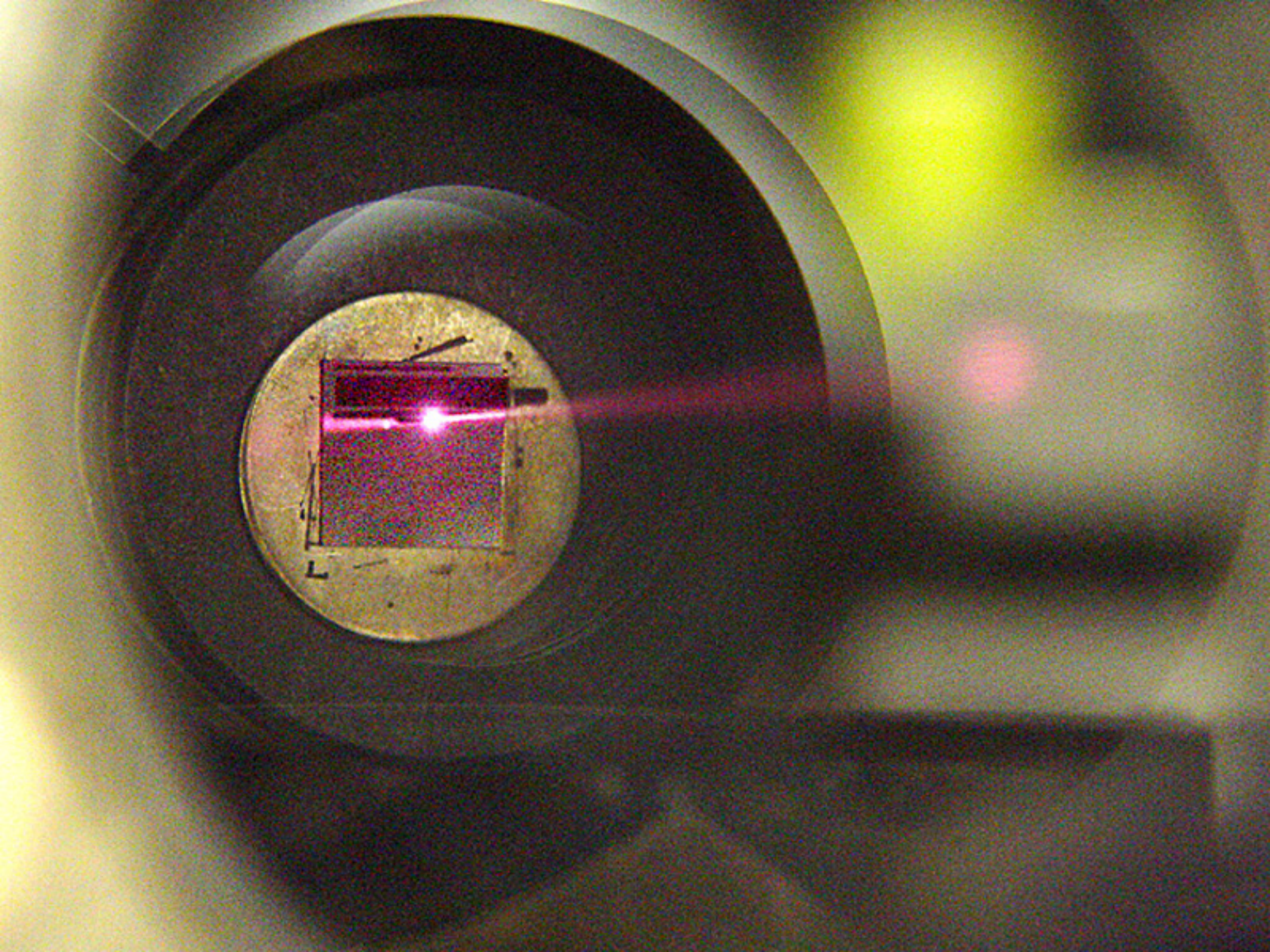
Dr. Richard Farrell (RMD)
Dr. Arie Karger (RMD)
Dr. Richard Meyers (RMD)

Dr. Pat Maloney (NVSED)

Dr. Jeffrey Warrander (ARDEC)

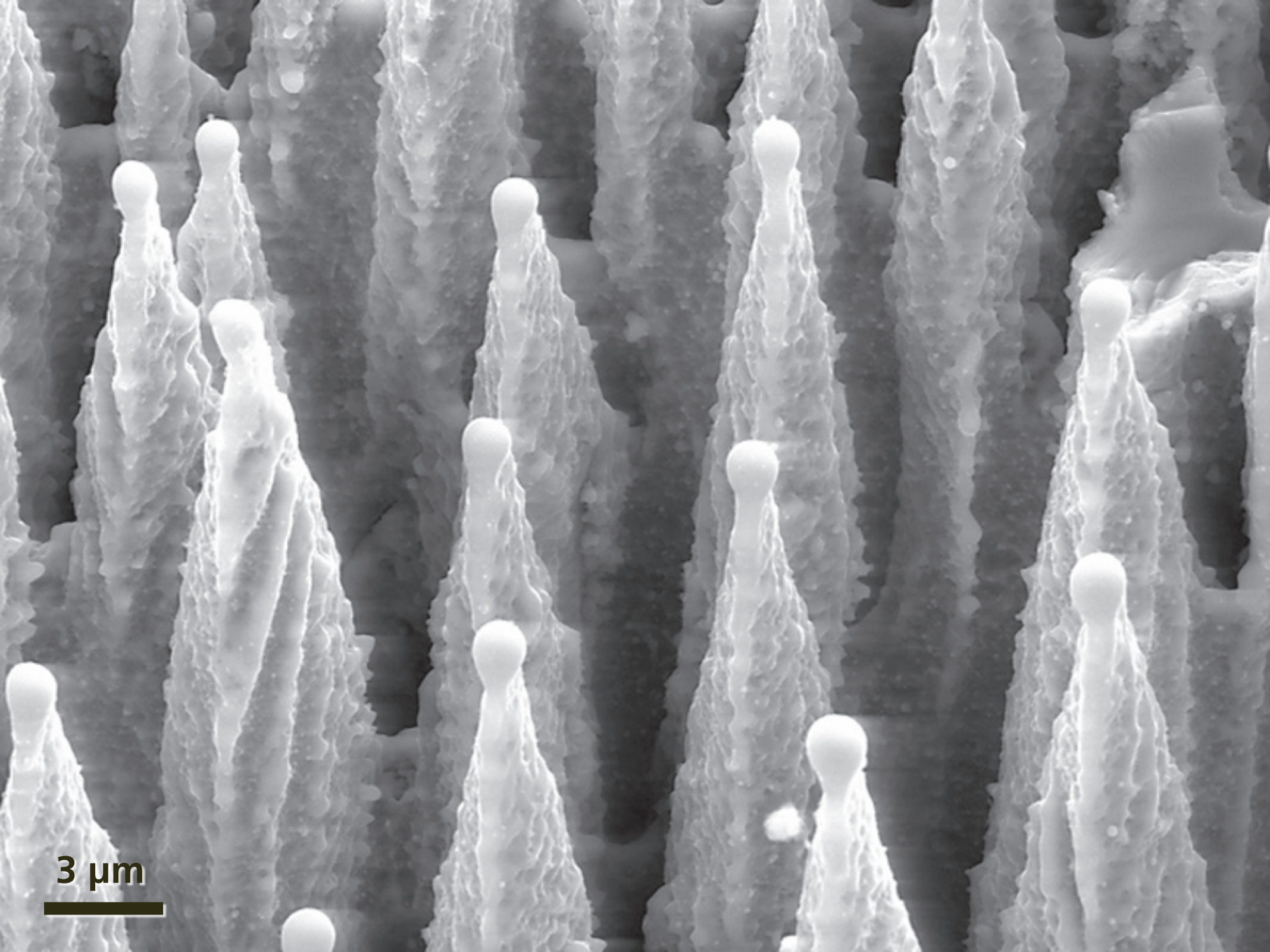


irradiate with 100-fs 10 kJ/m² pulses



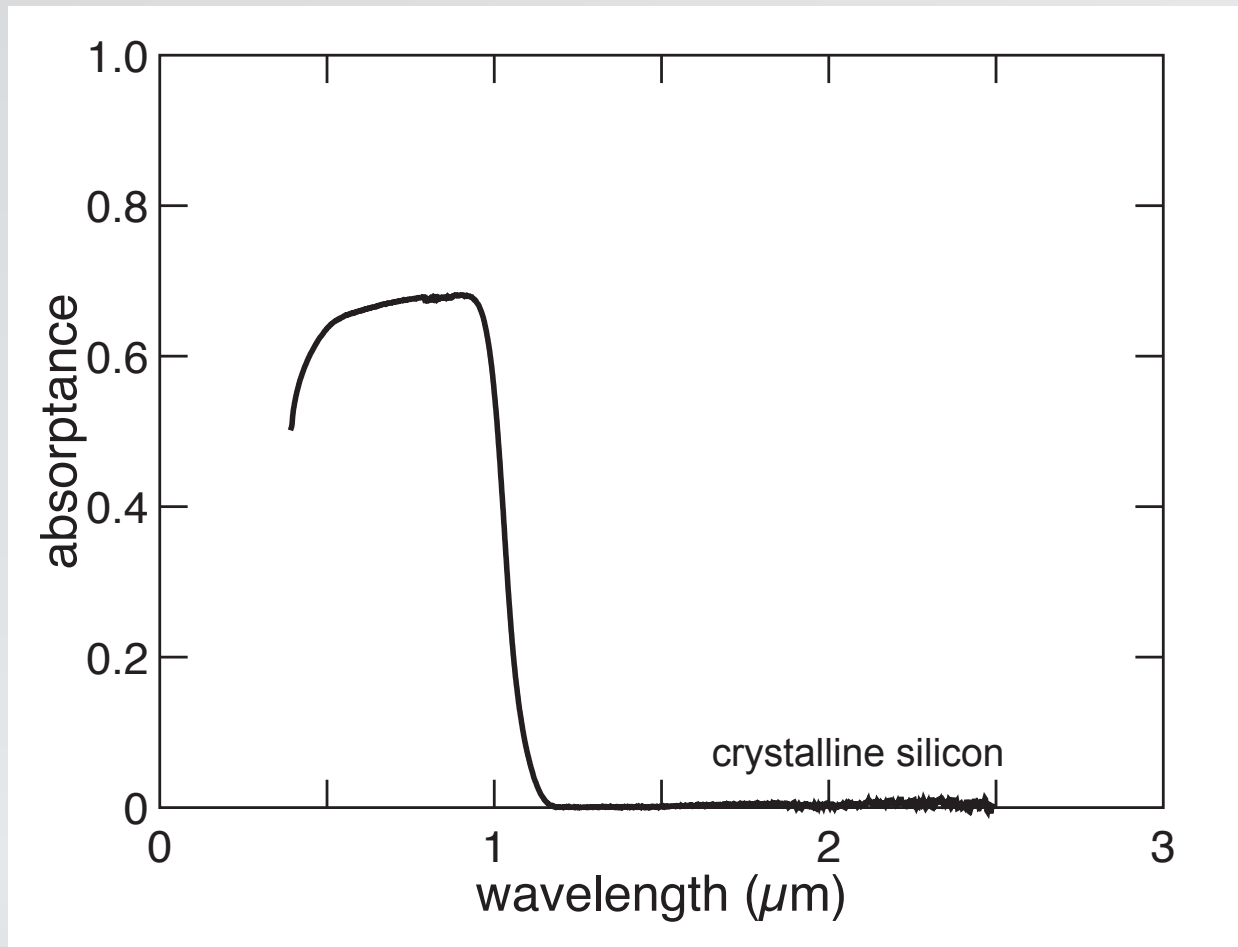


"black silicon"

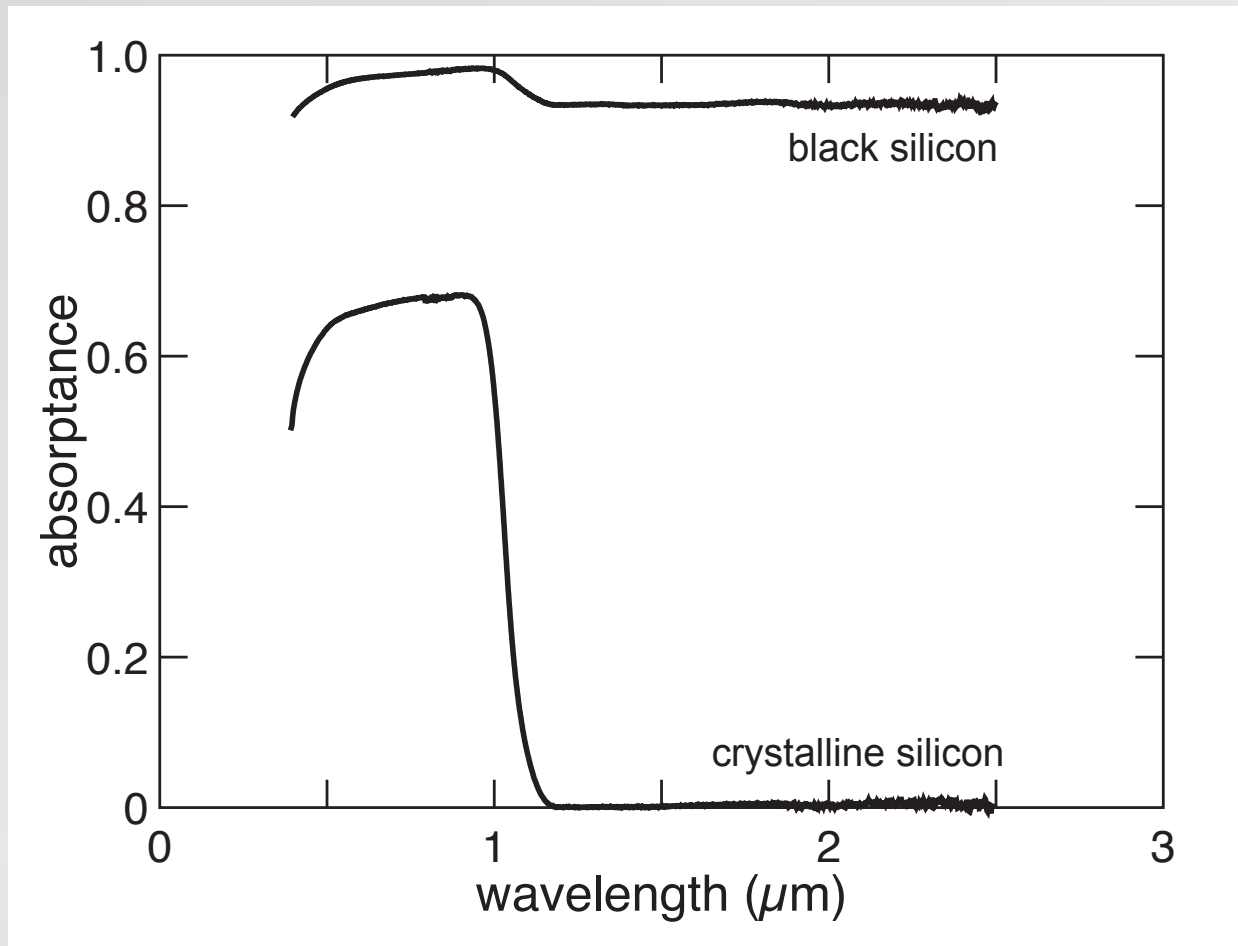


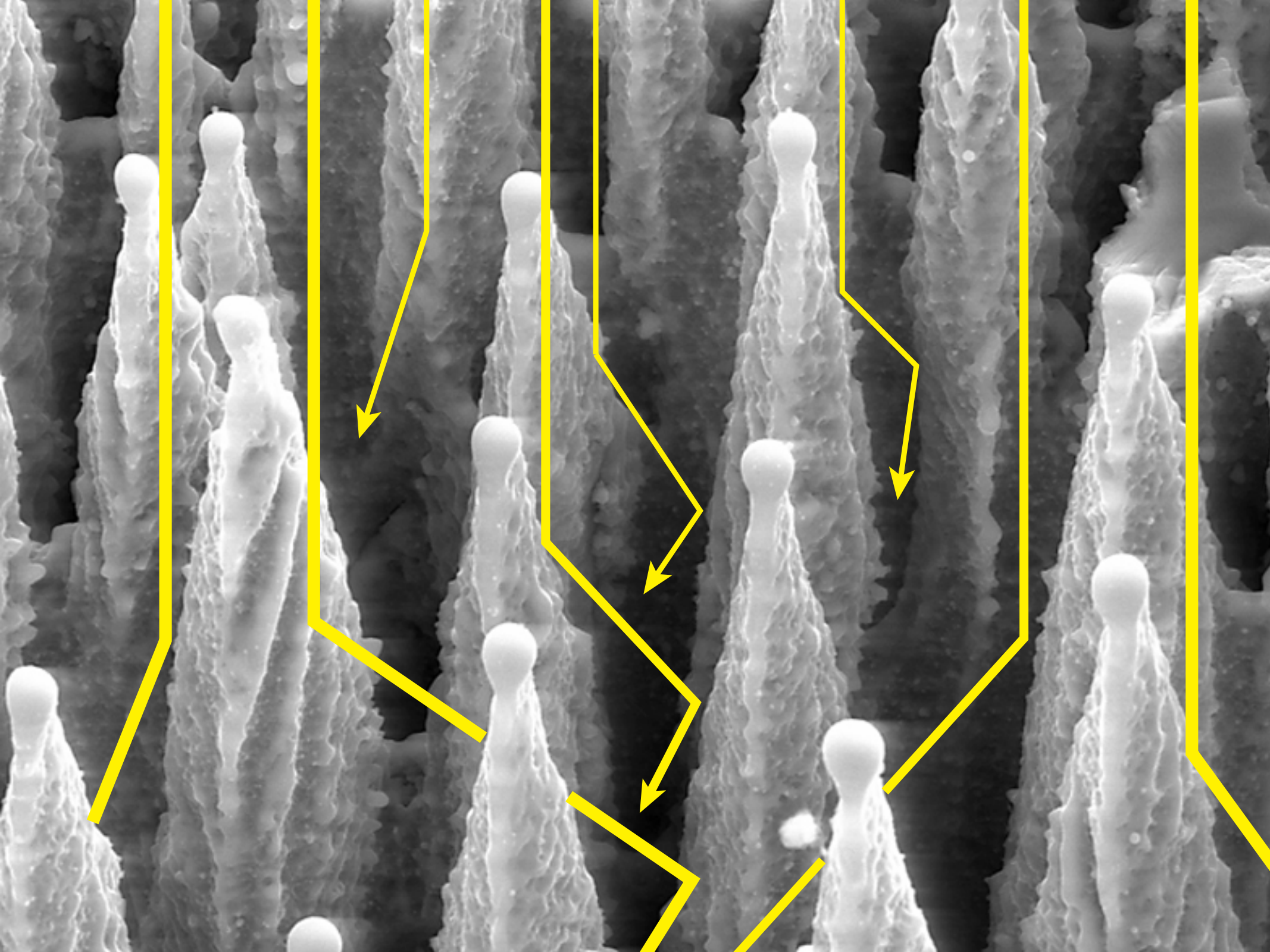
3 μm

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

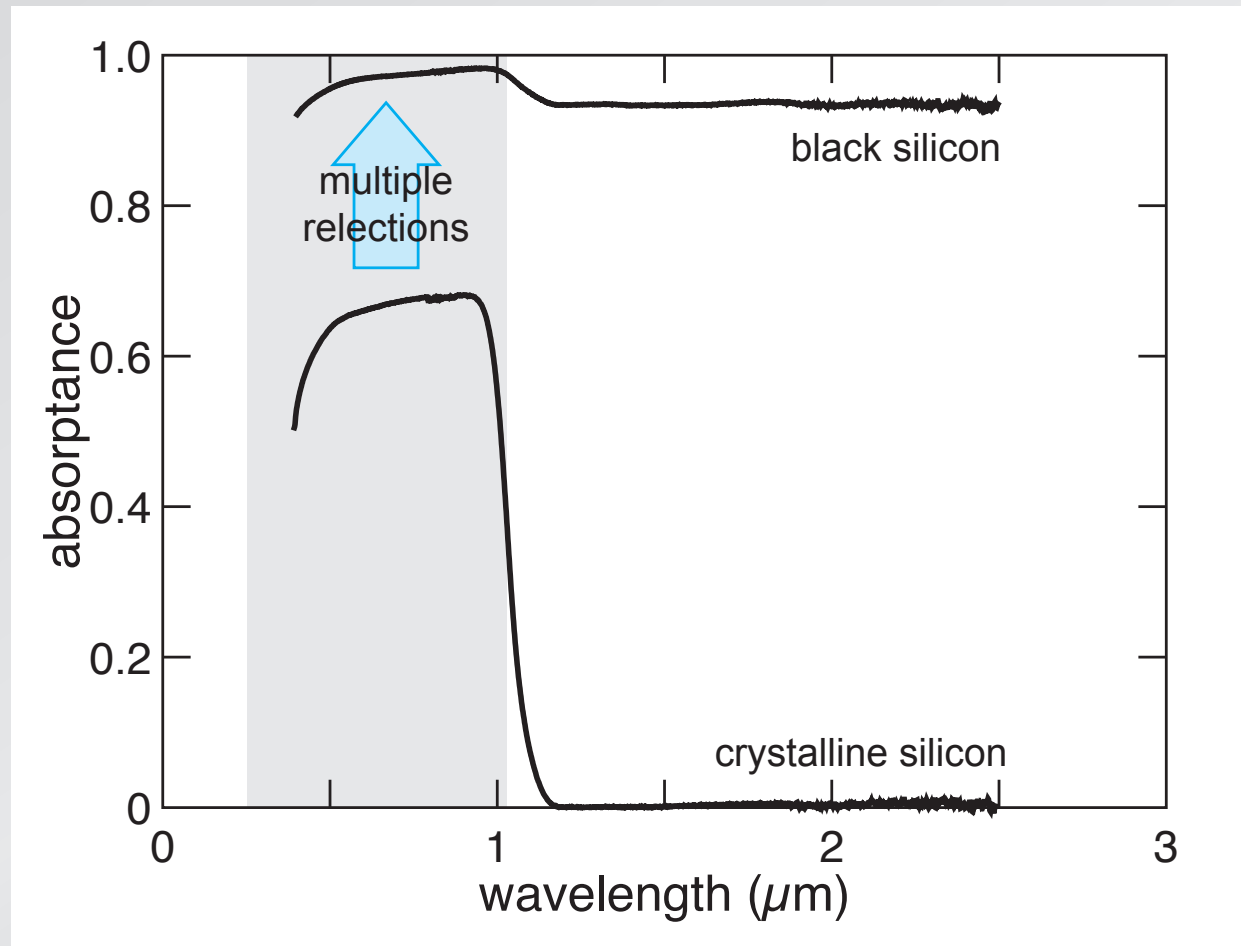


absorptance ($1 - R_{int} - T_{int}$)

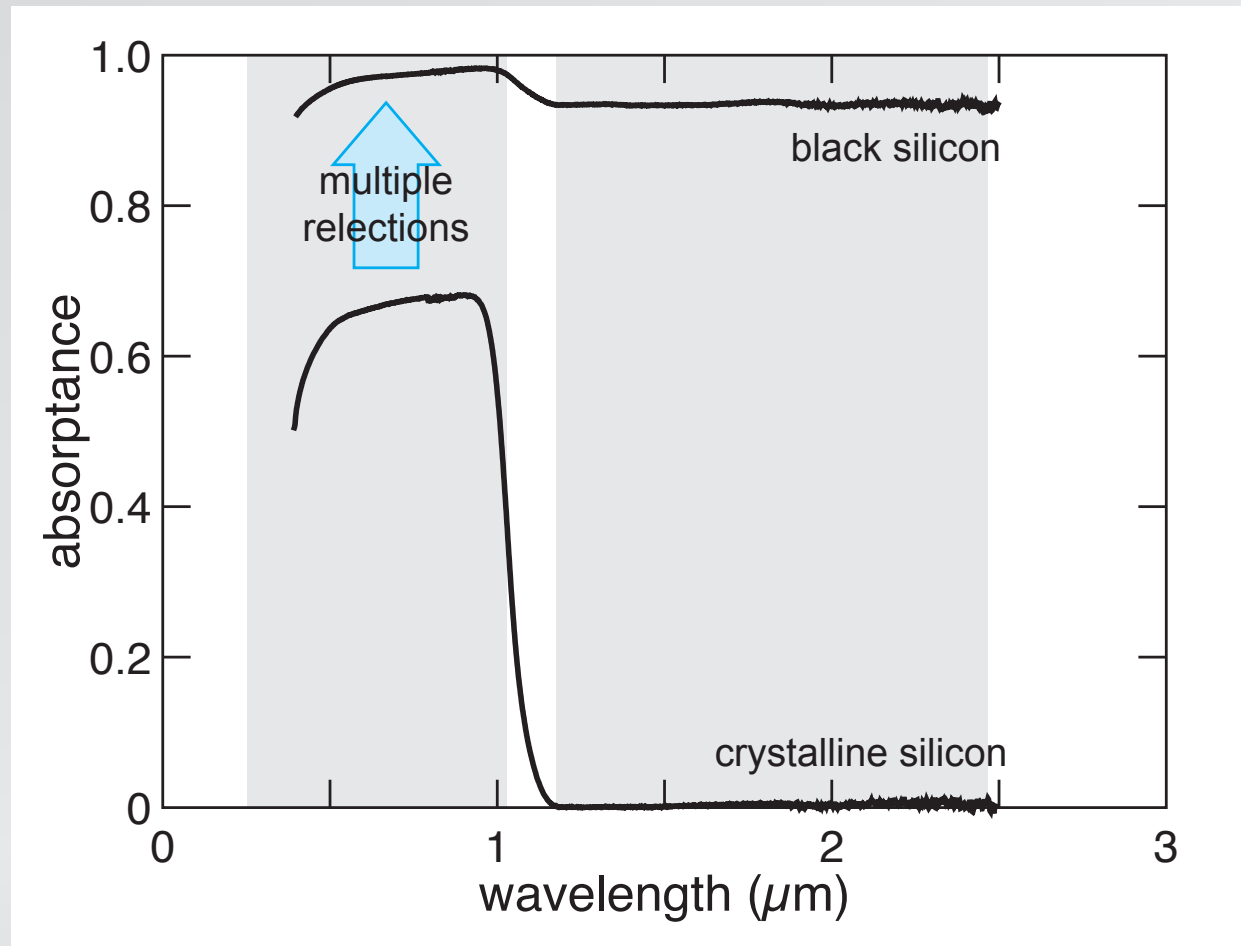




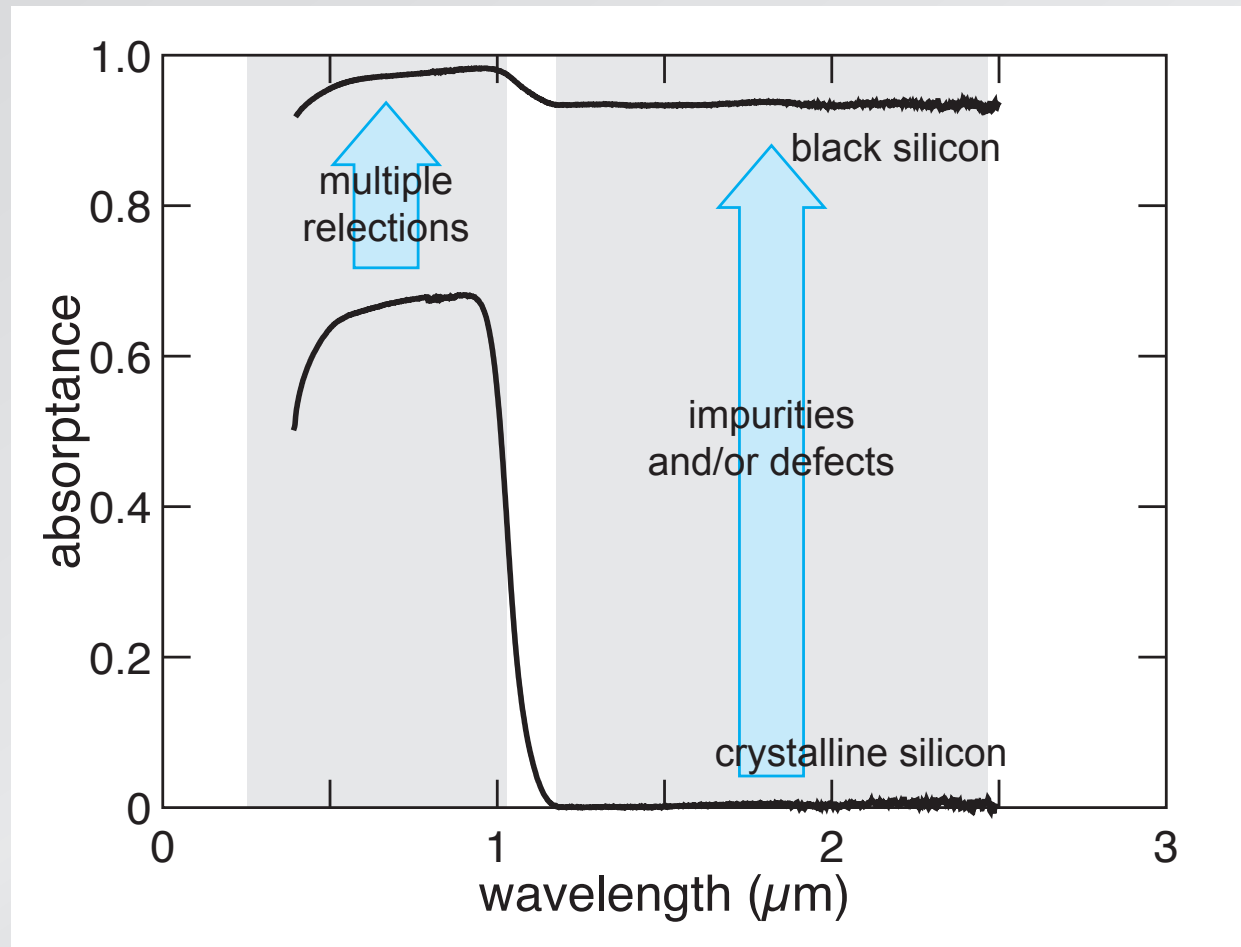
absorptance $(1 - R_{int} - T_{int})$



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



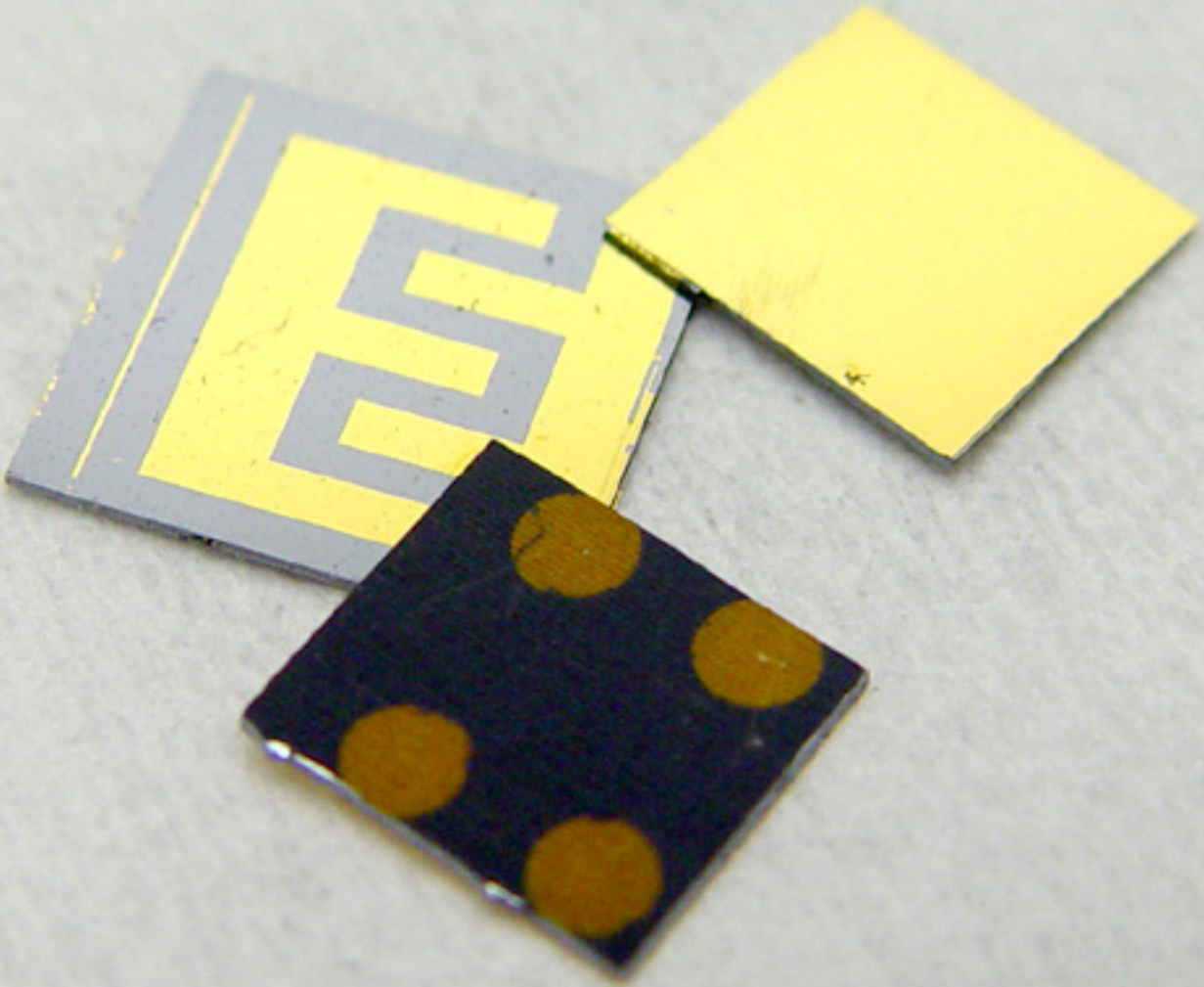
absorptance ($1 - R_{int} - T_{int}$)

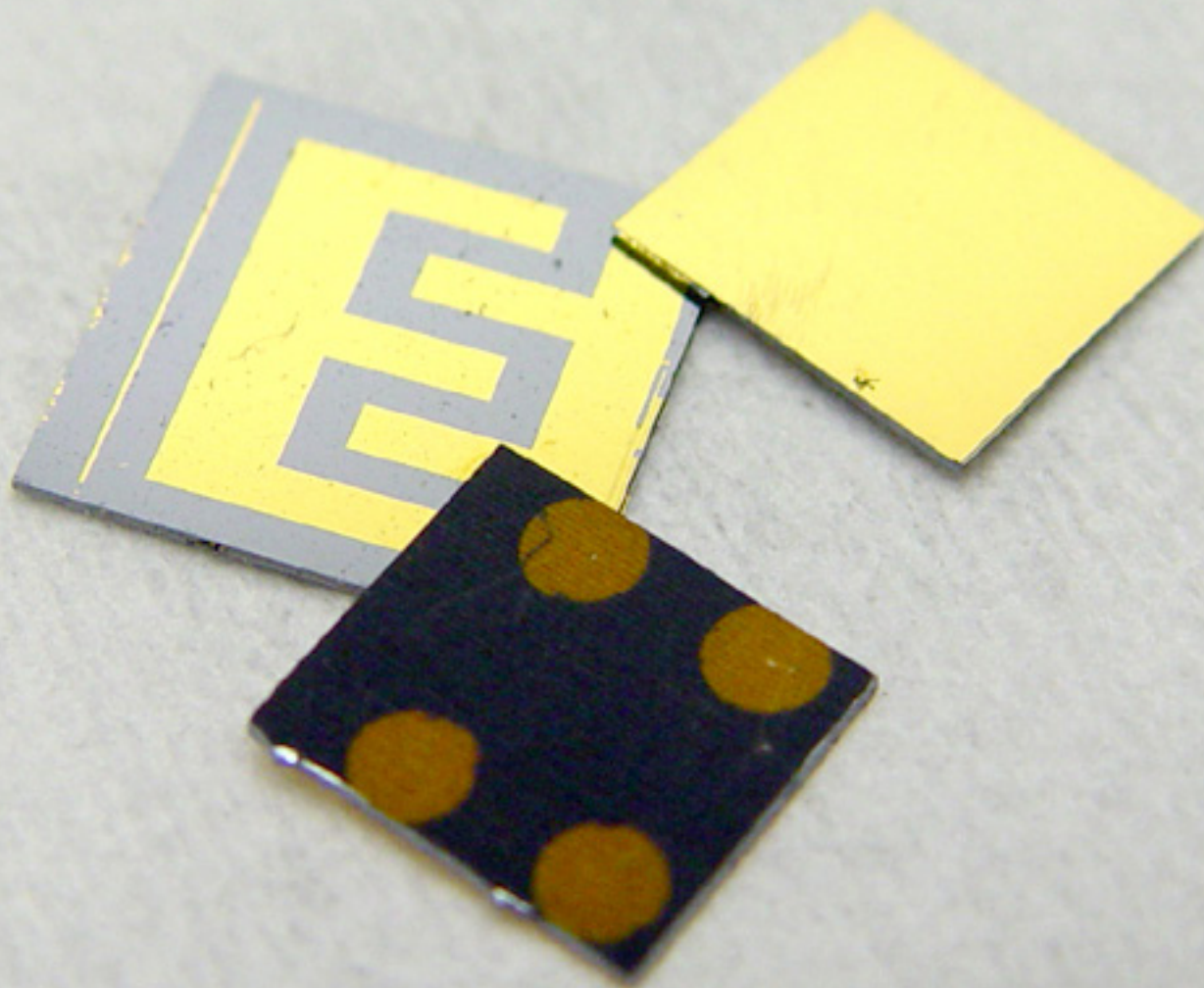


A scanning electron micrograph (SEM) showing a surface with a dense, regular array of small, conical structures. The structures are arranged in a grid-like pattern, with each structure being a small, rounded cone. The background is a smooth, light-colored surface. The overall appearance is that of a highly ordered, nanostructured surface.

laser treatment causes:

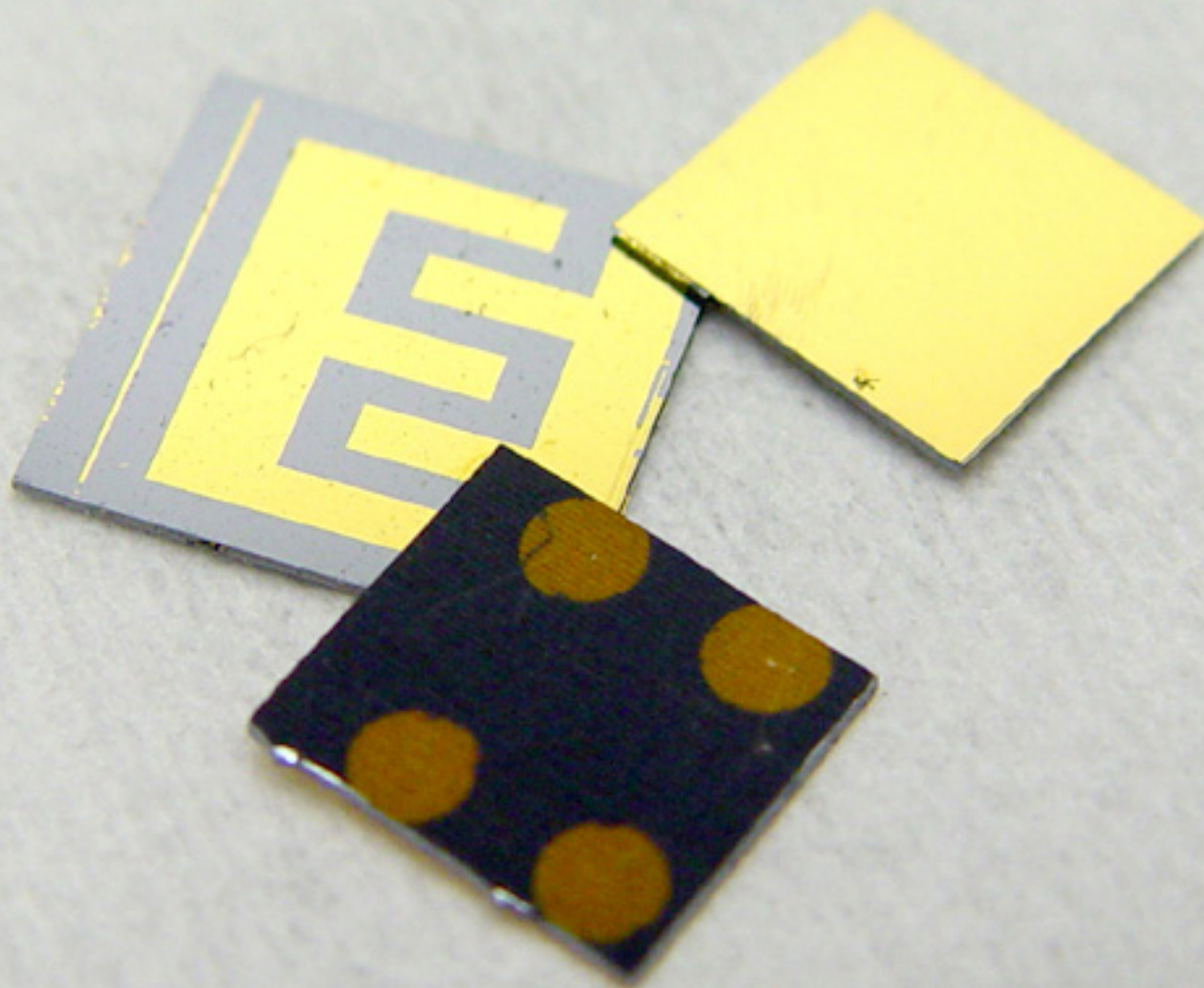
- **surface structuring**
- **inclusion of dopants**





1 properties

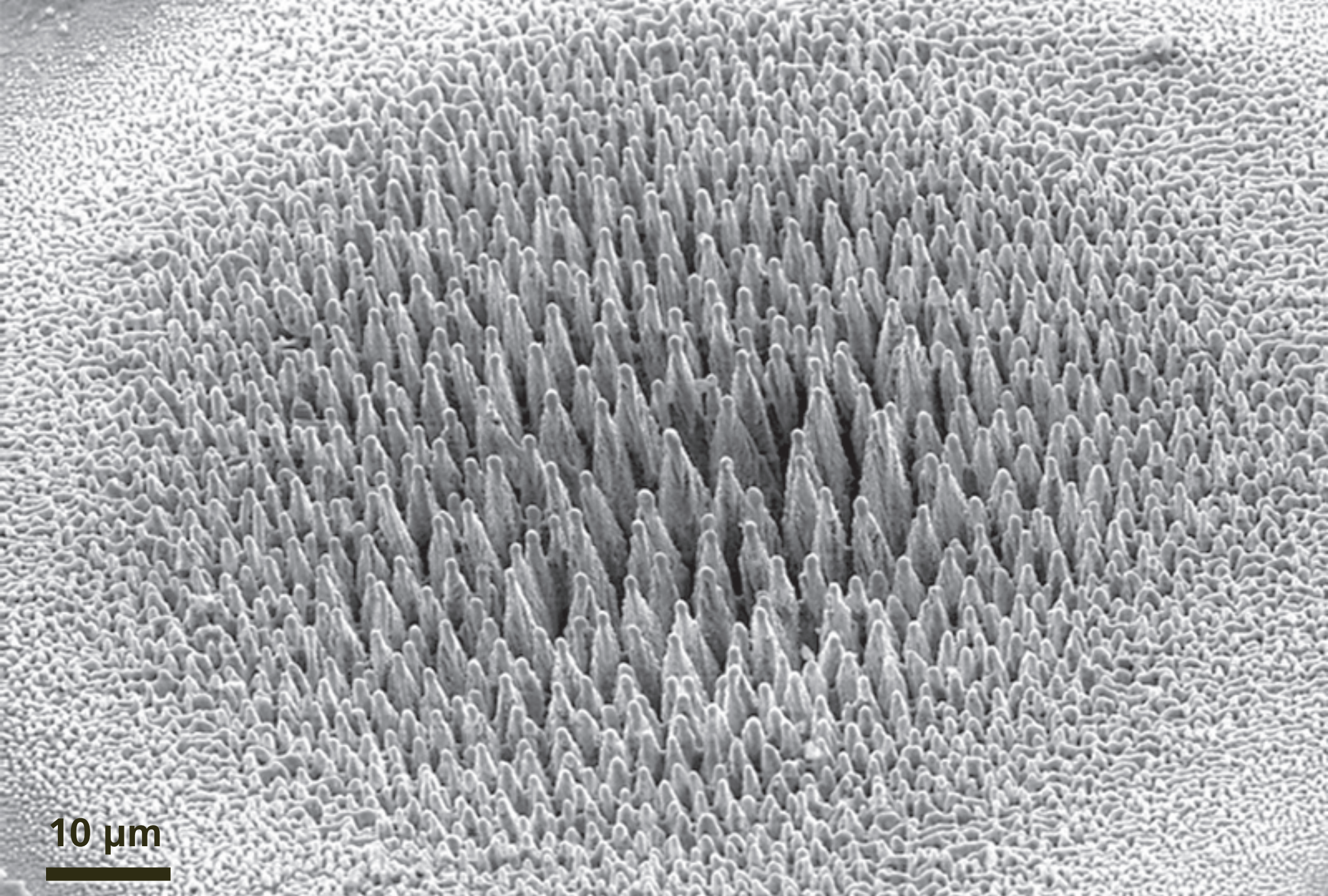
2 intermediate band



1 properties

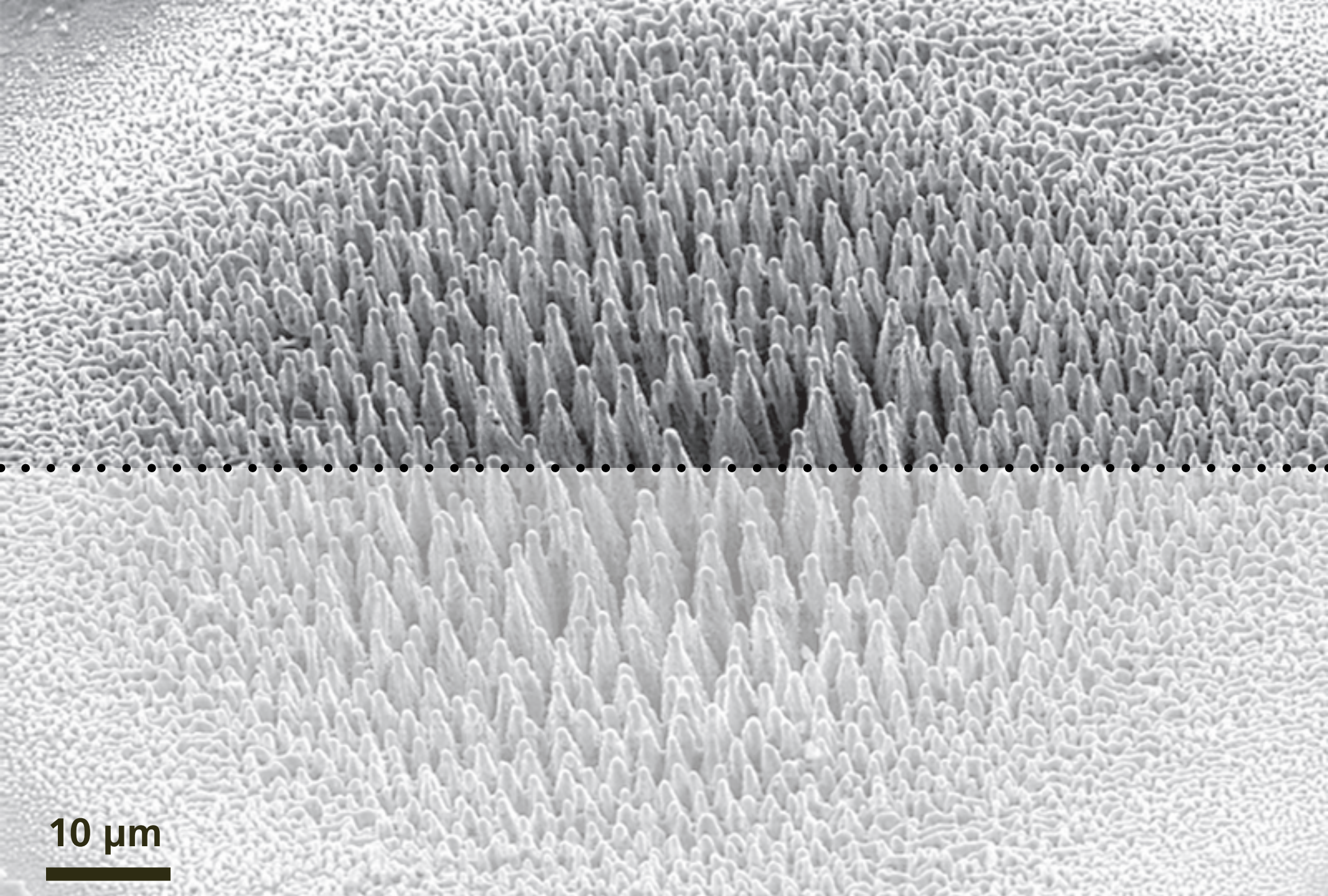
2 intermediate band

3 devices



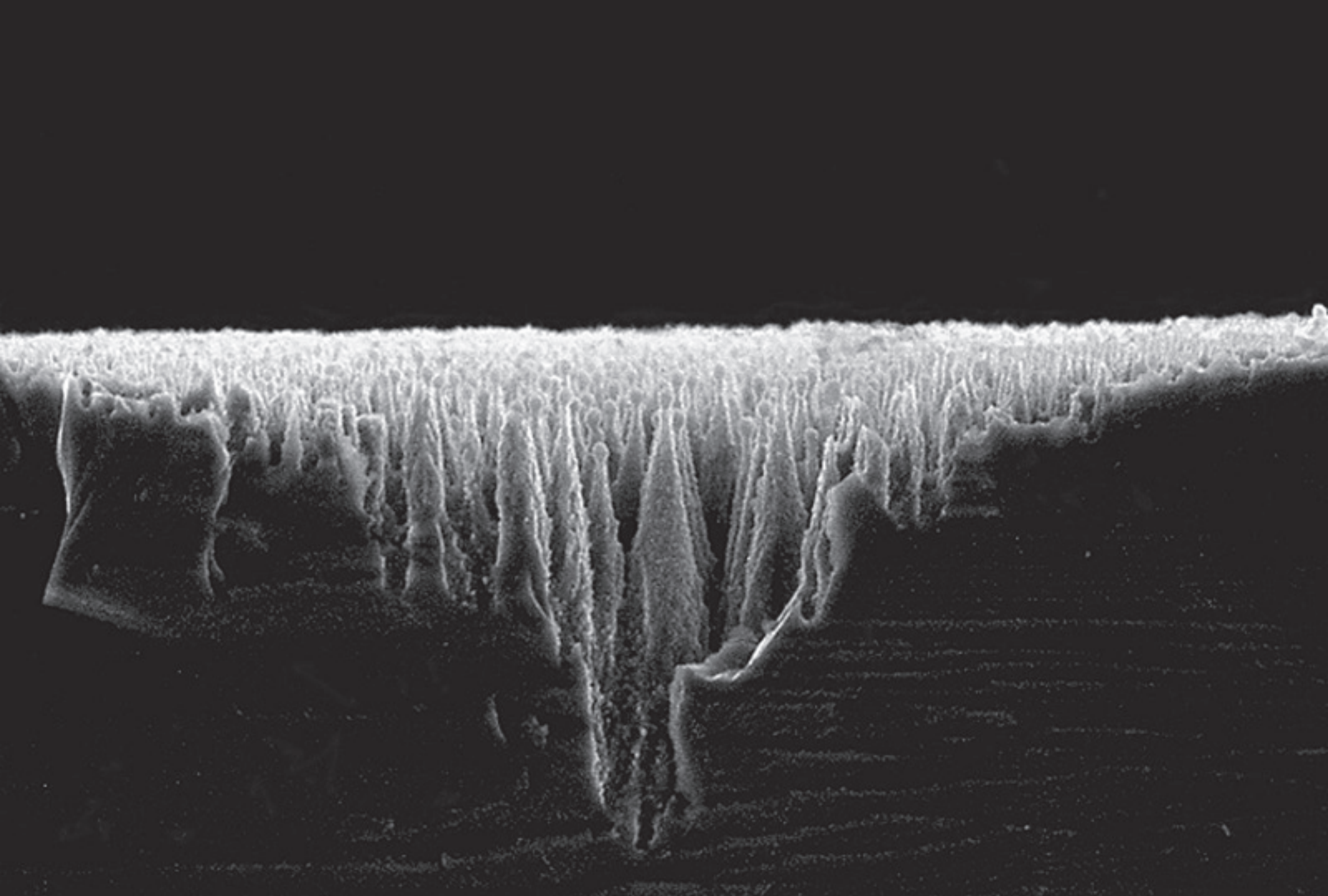
10 μm

1 properties

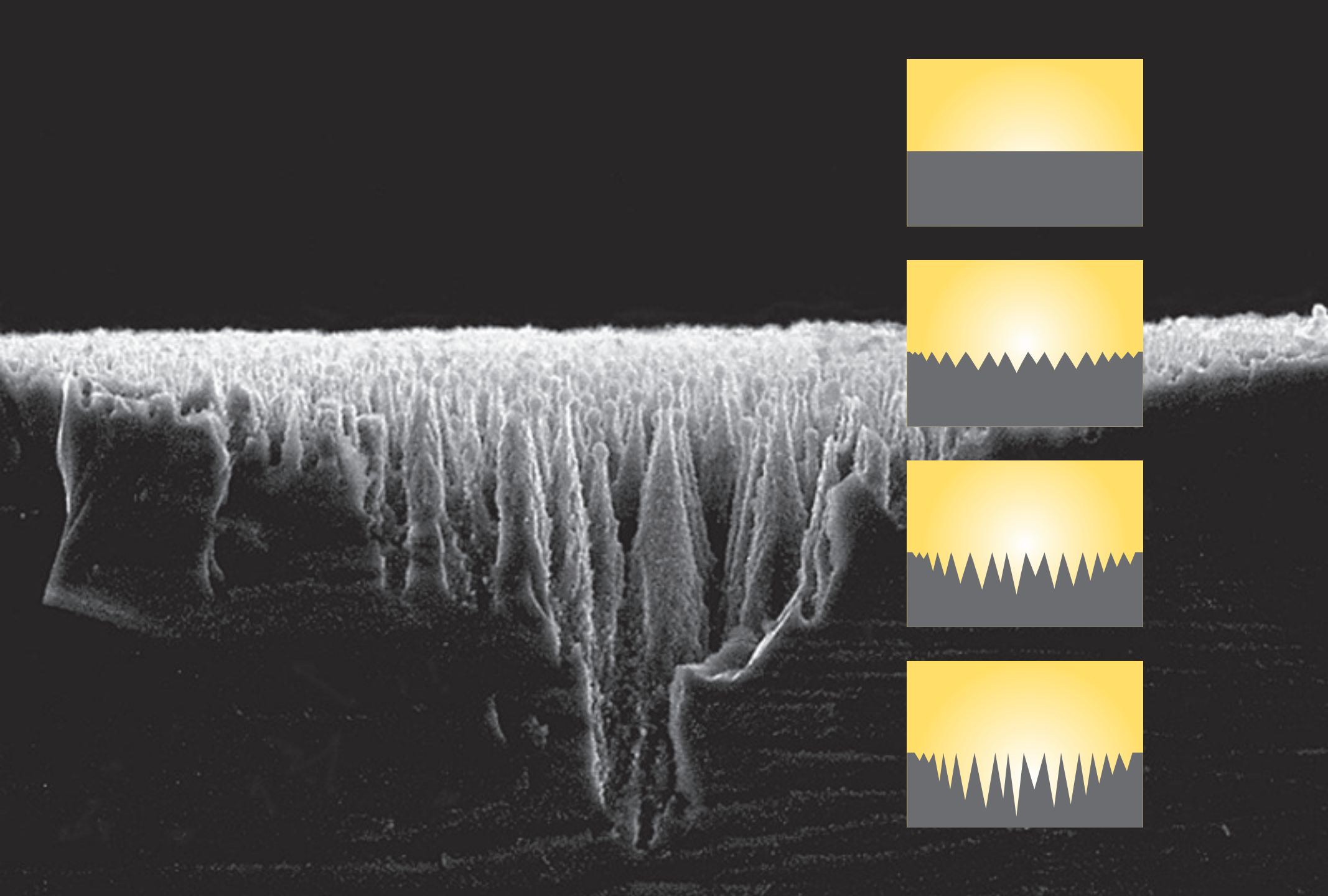


10 μm

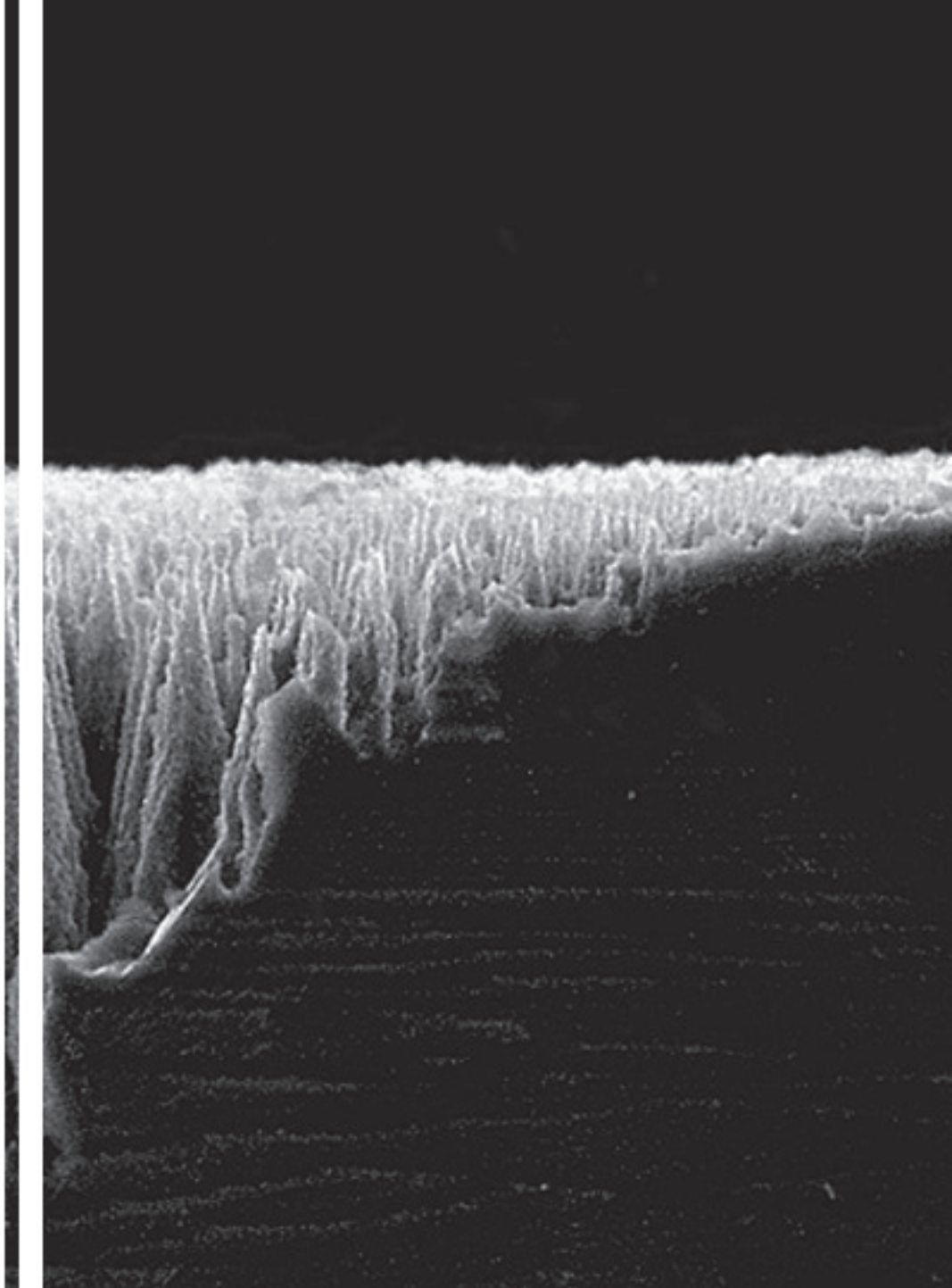
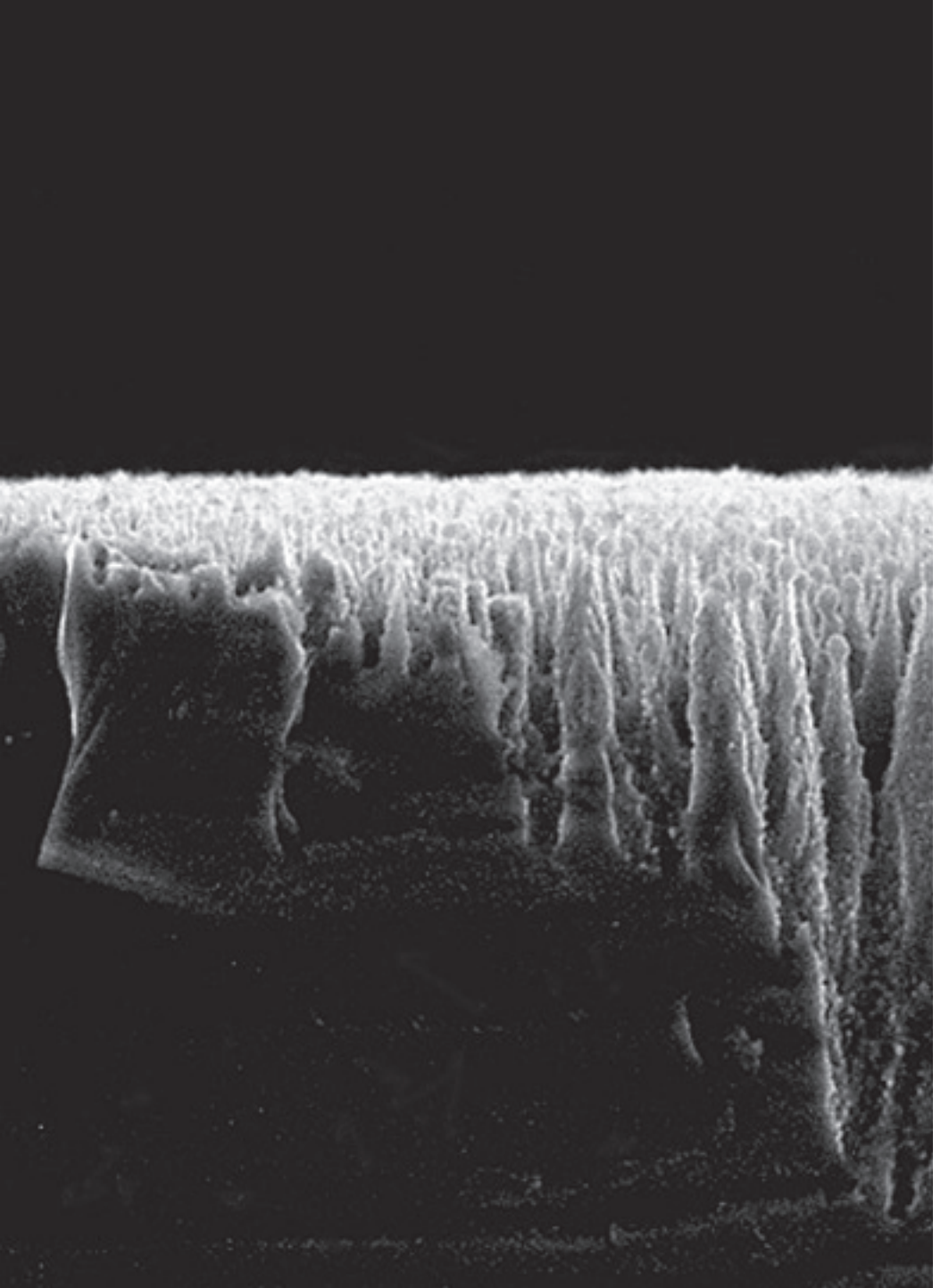
1 properties



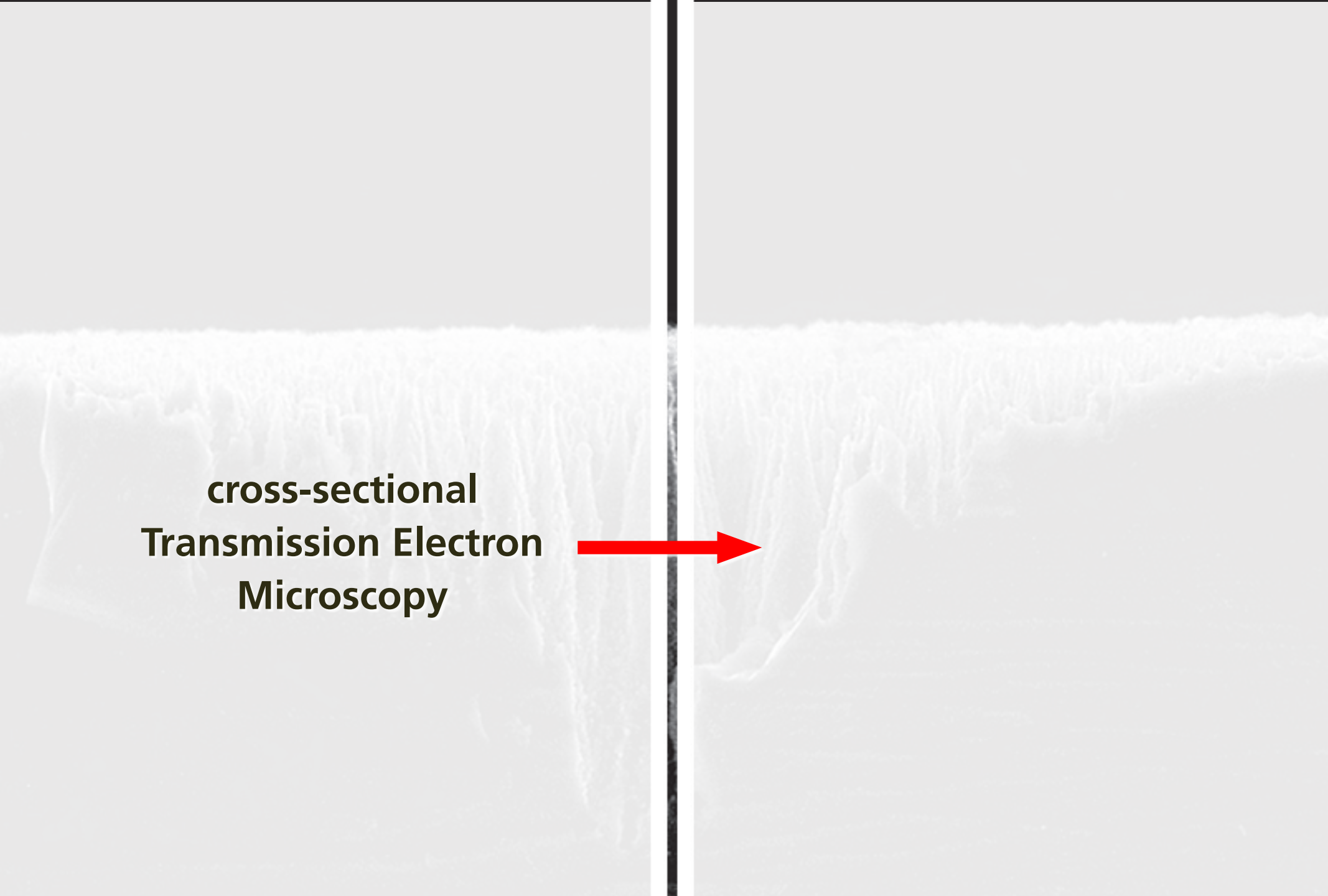
1 properties



1 properties

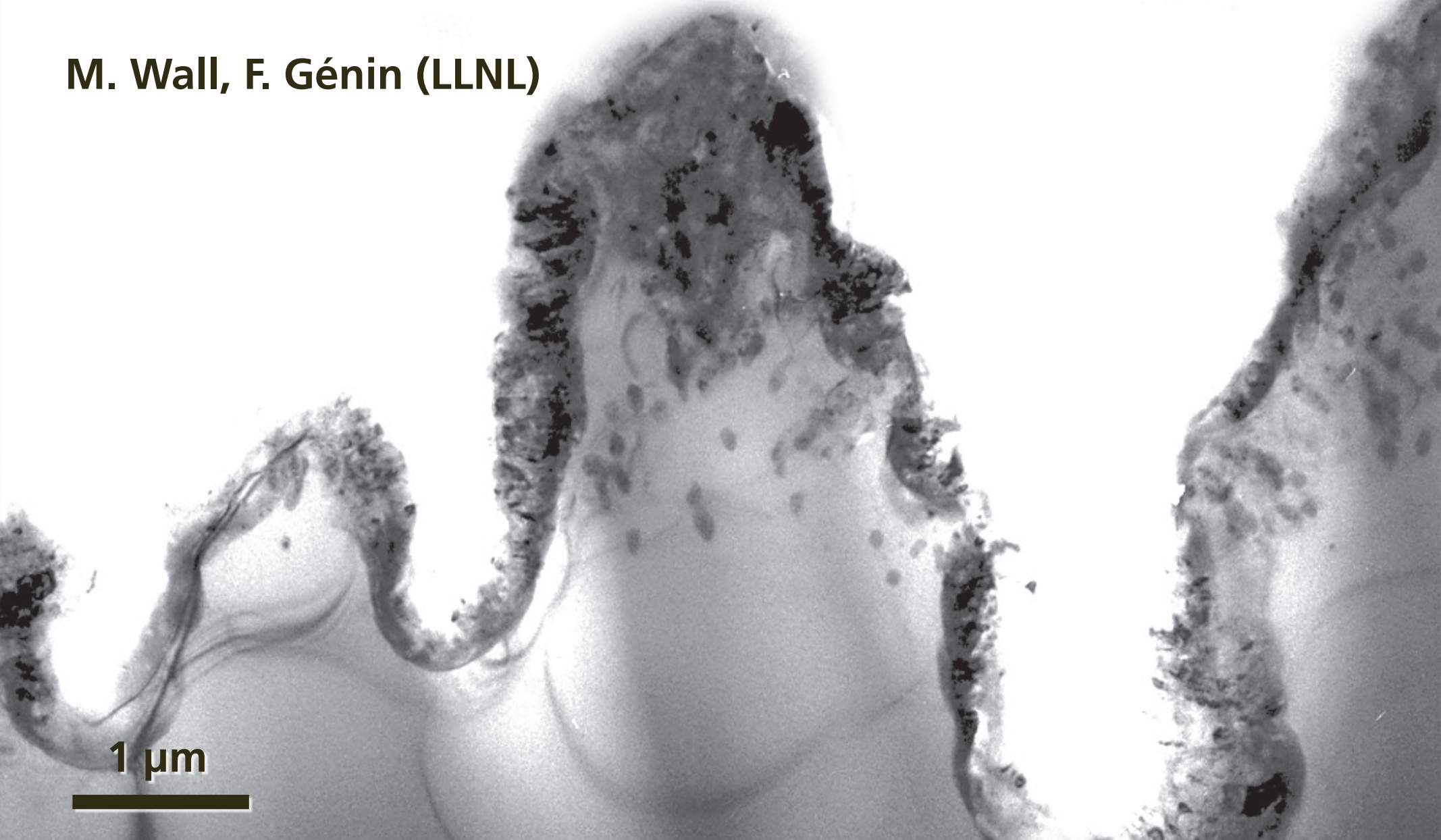


1 properties



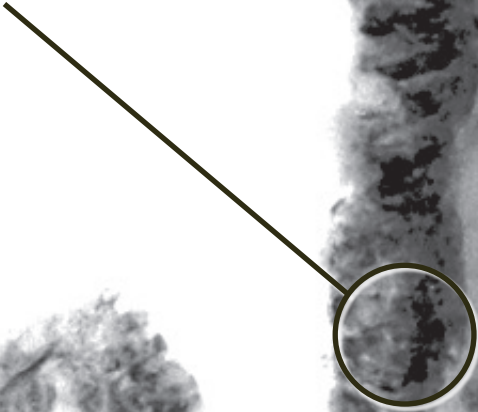
**cross-sectional
Transmission Electron
Microscopy**

M. Wall, F. Génin (LLNL)

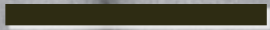


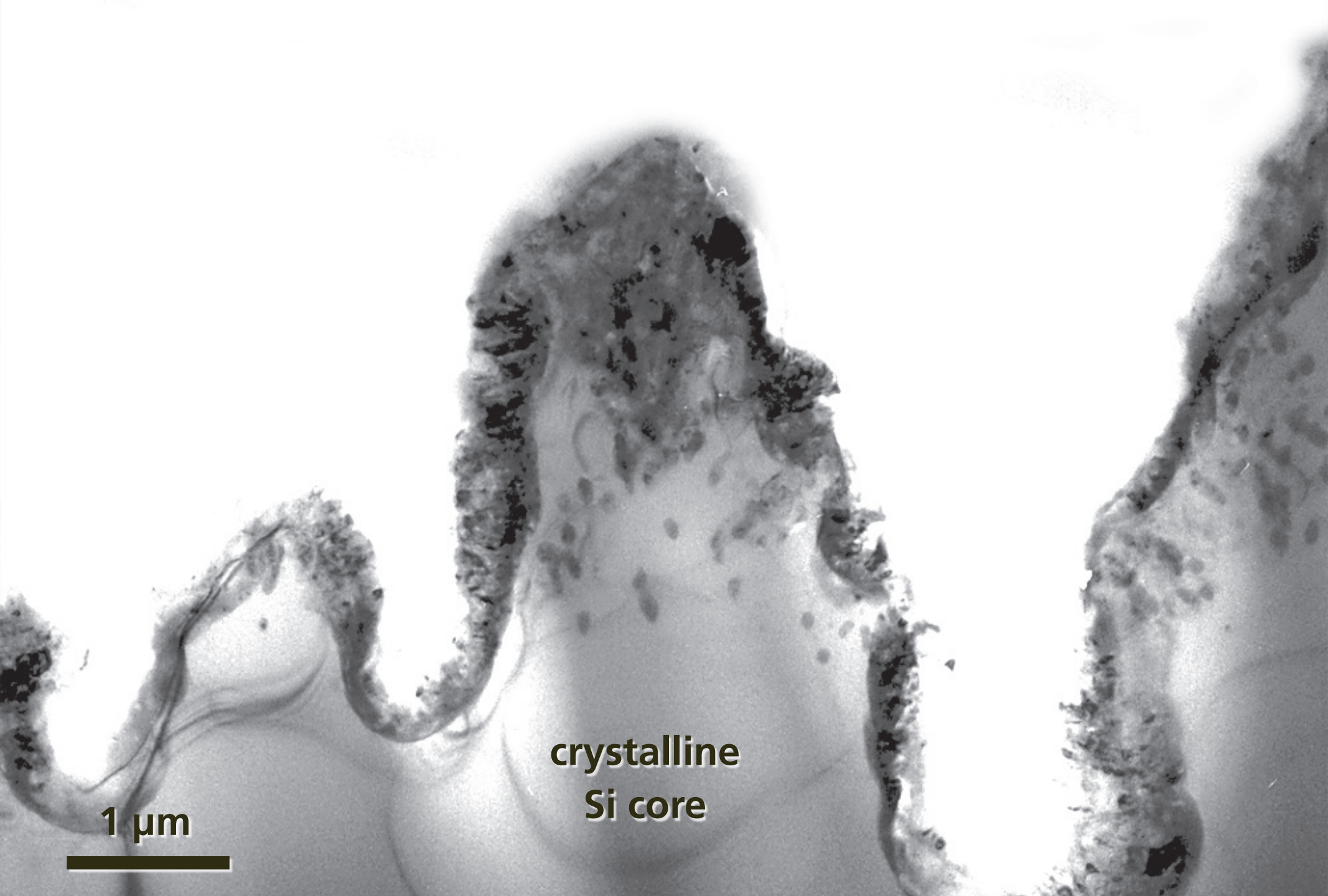
1 μm

**disordered
surface layer**



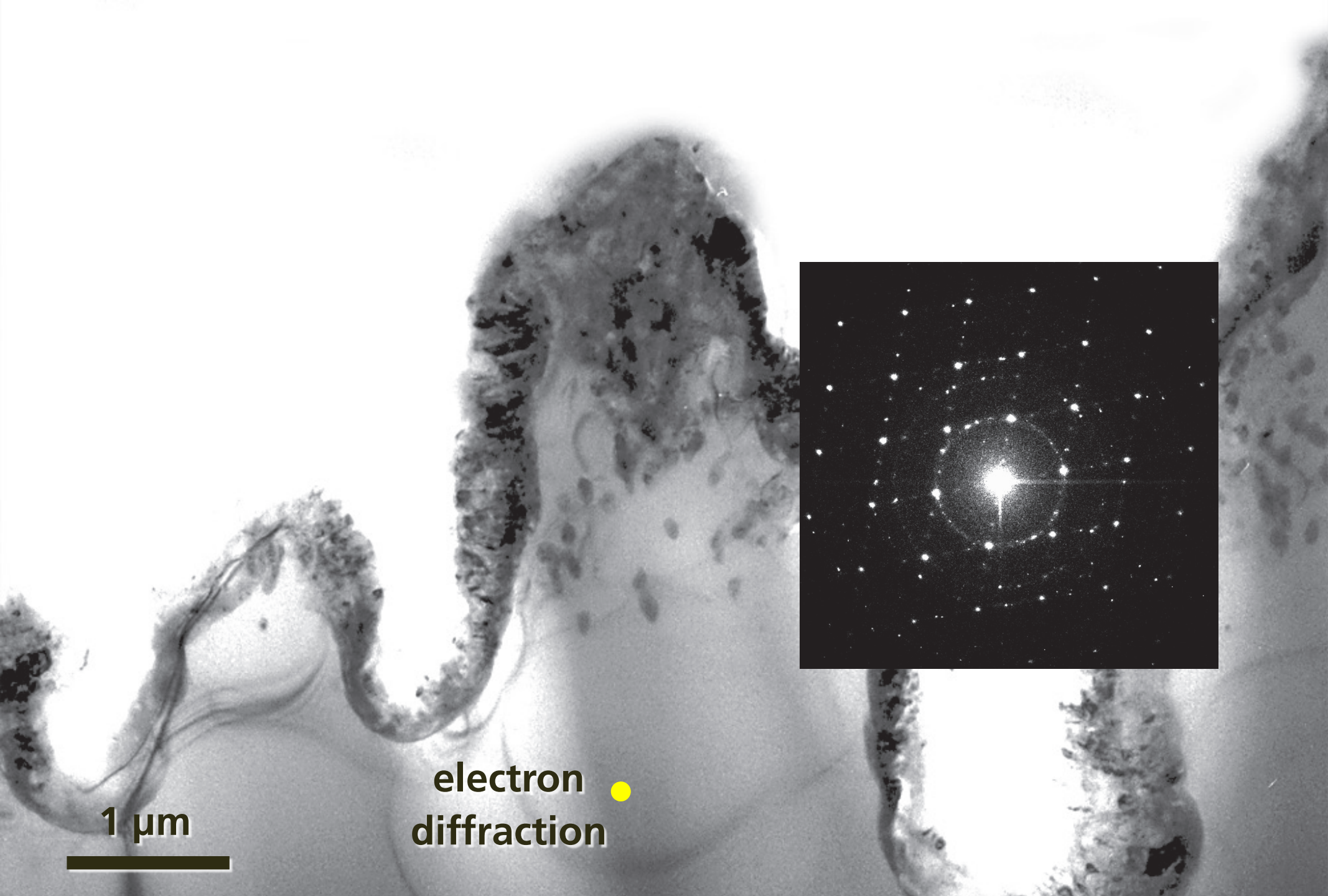
1 μm





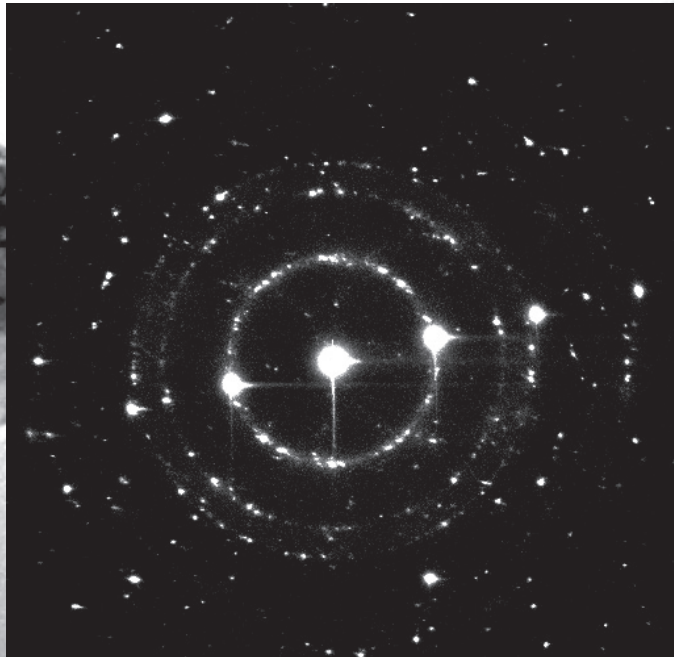
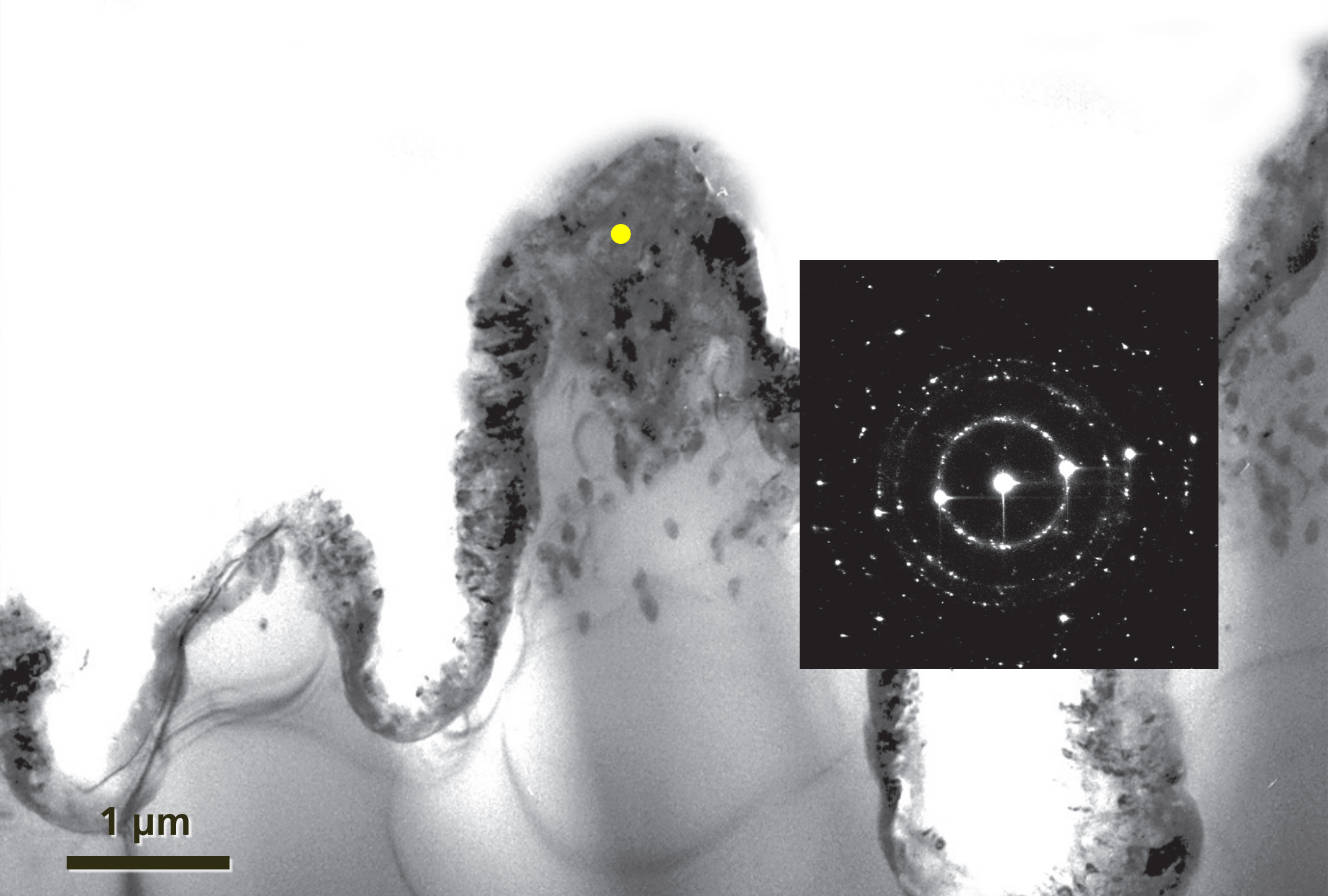
1 μm

crystalline
Si core

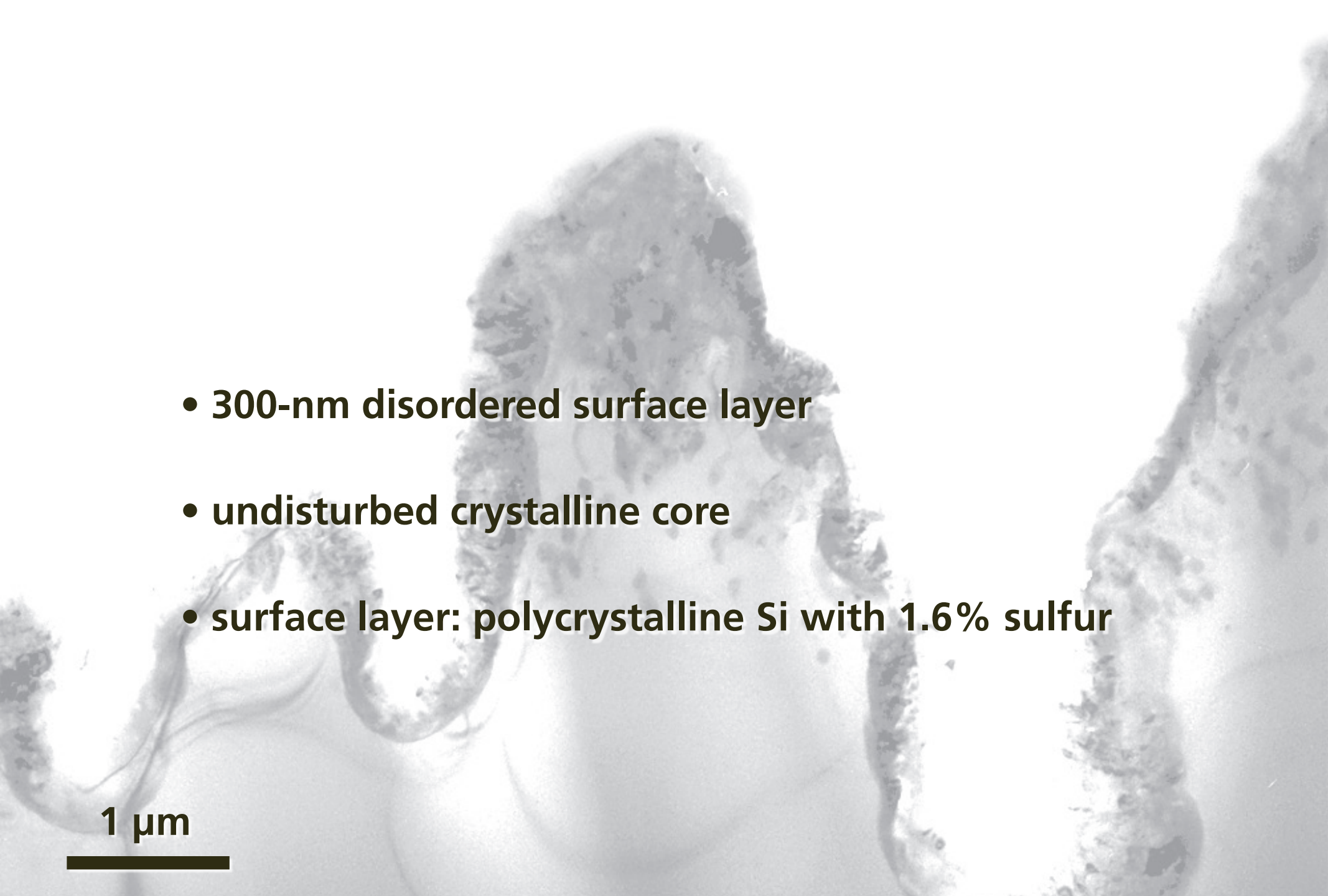


1 μm

electron •
diffraction



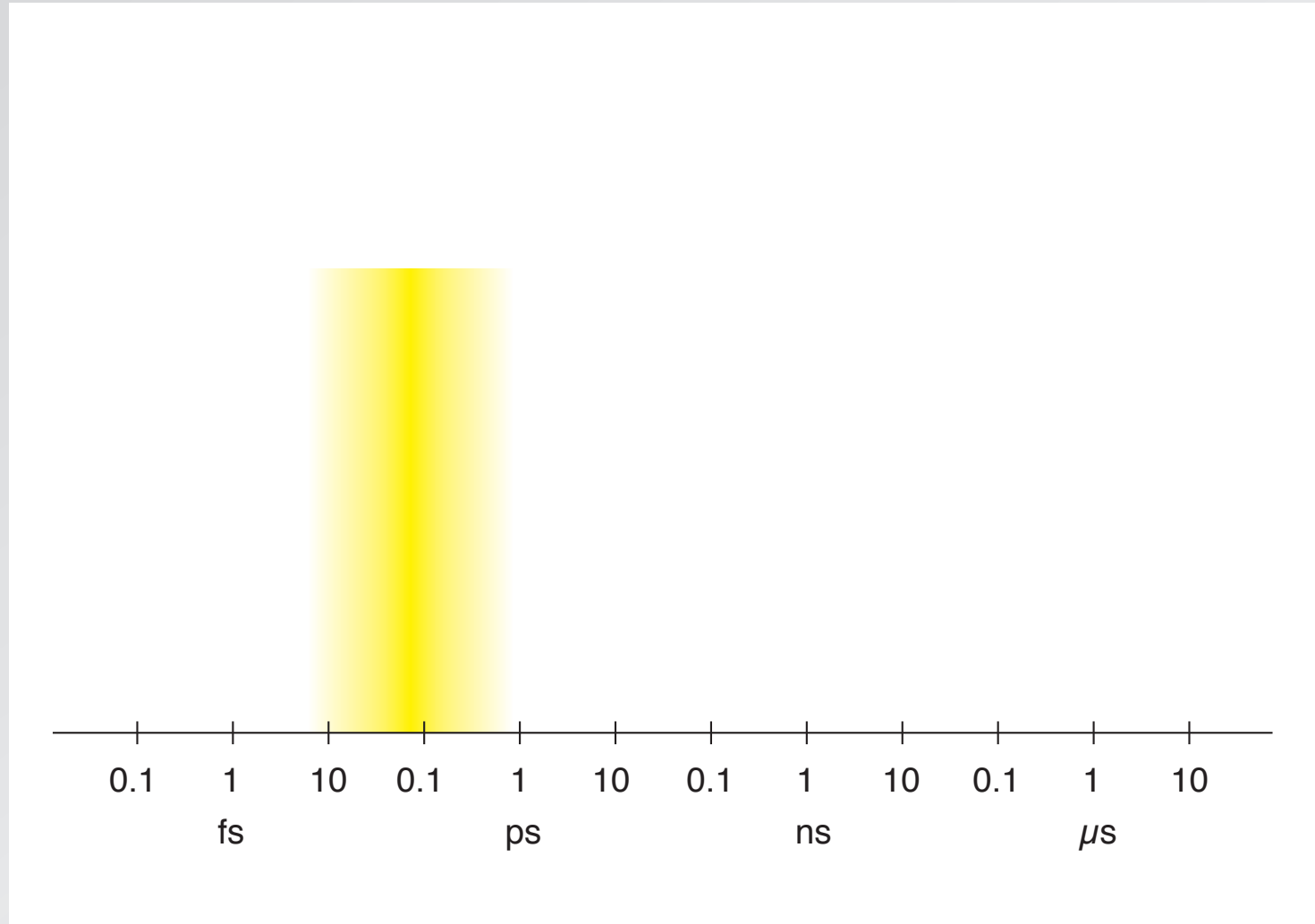
1 properties

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

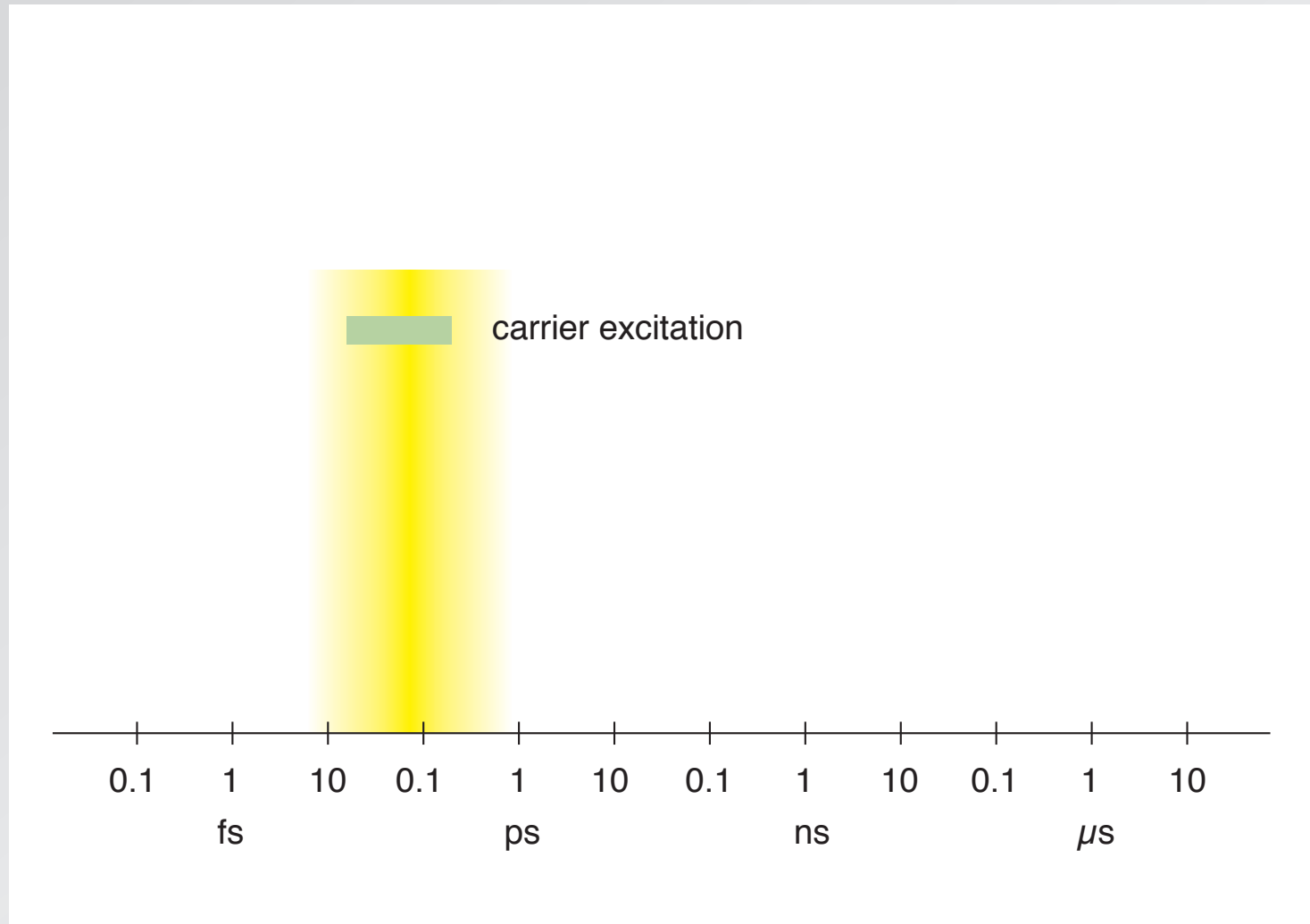
1 μm

two processes: melting and ablation

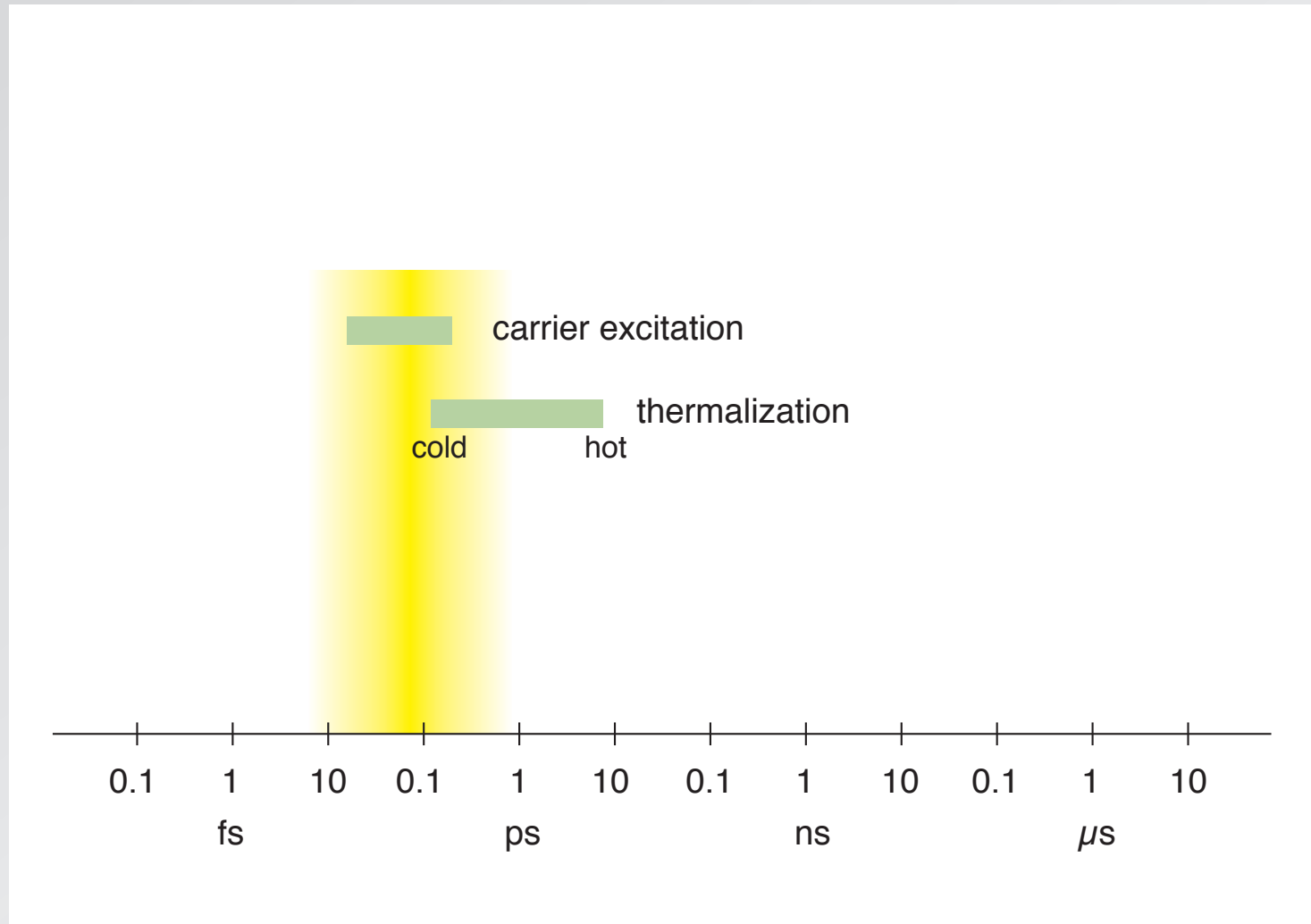
relevant time scales



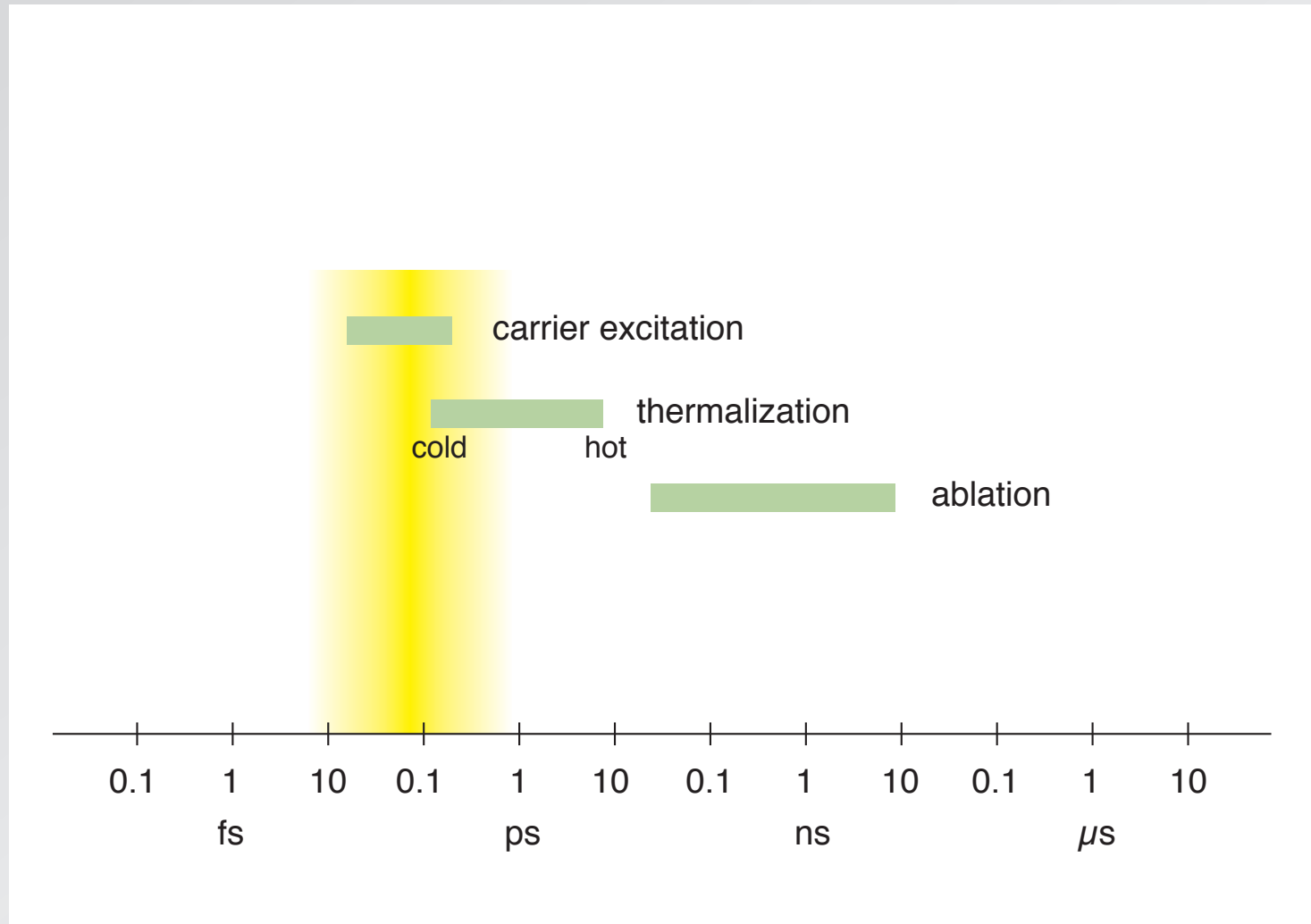
relevant time scales



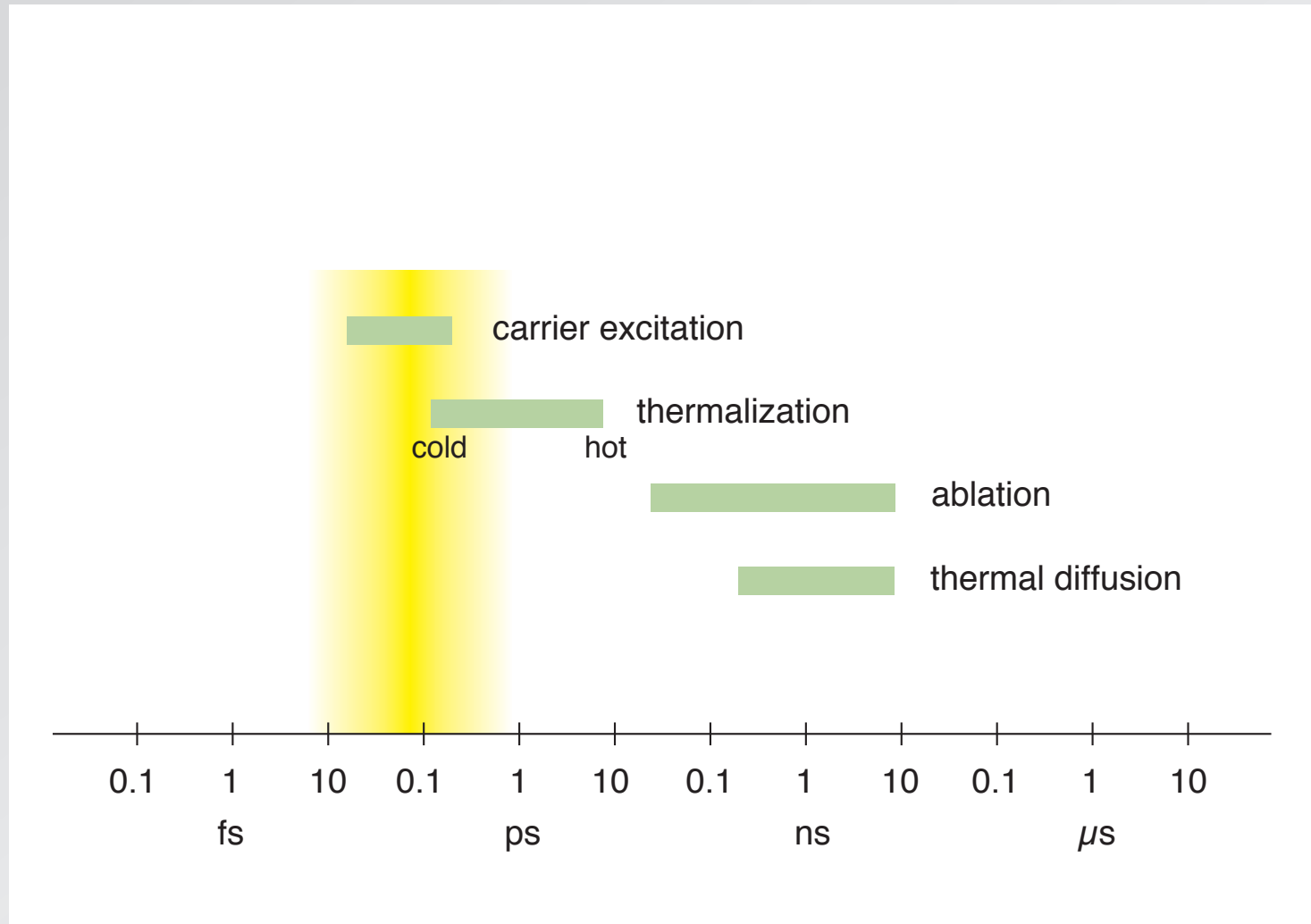
relevant time scales



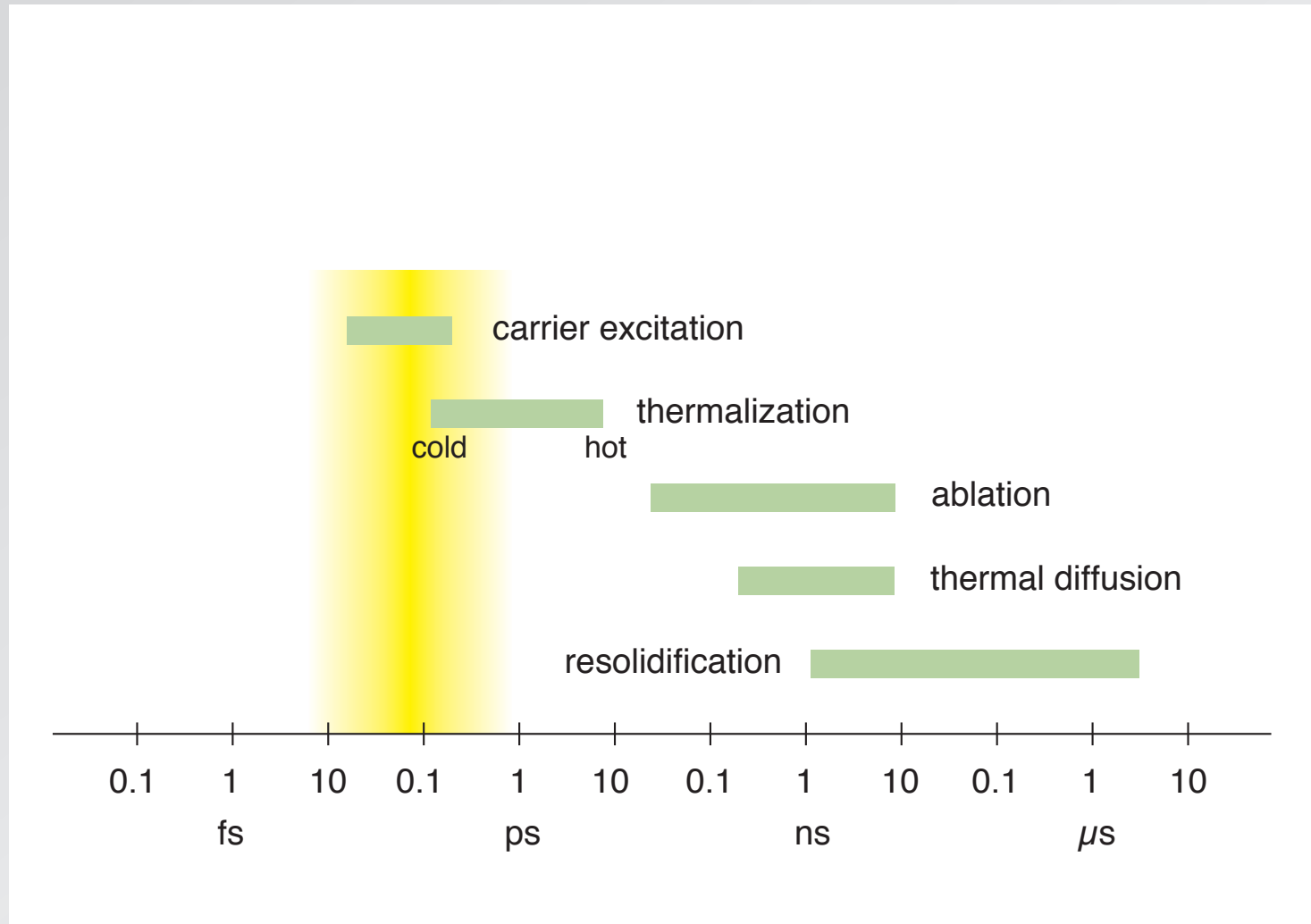
relevant time scales



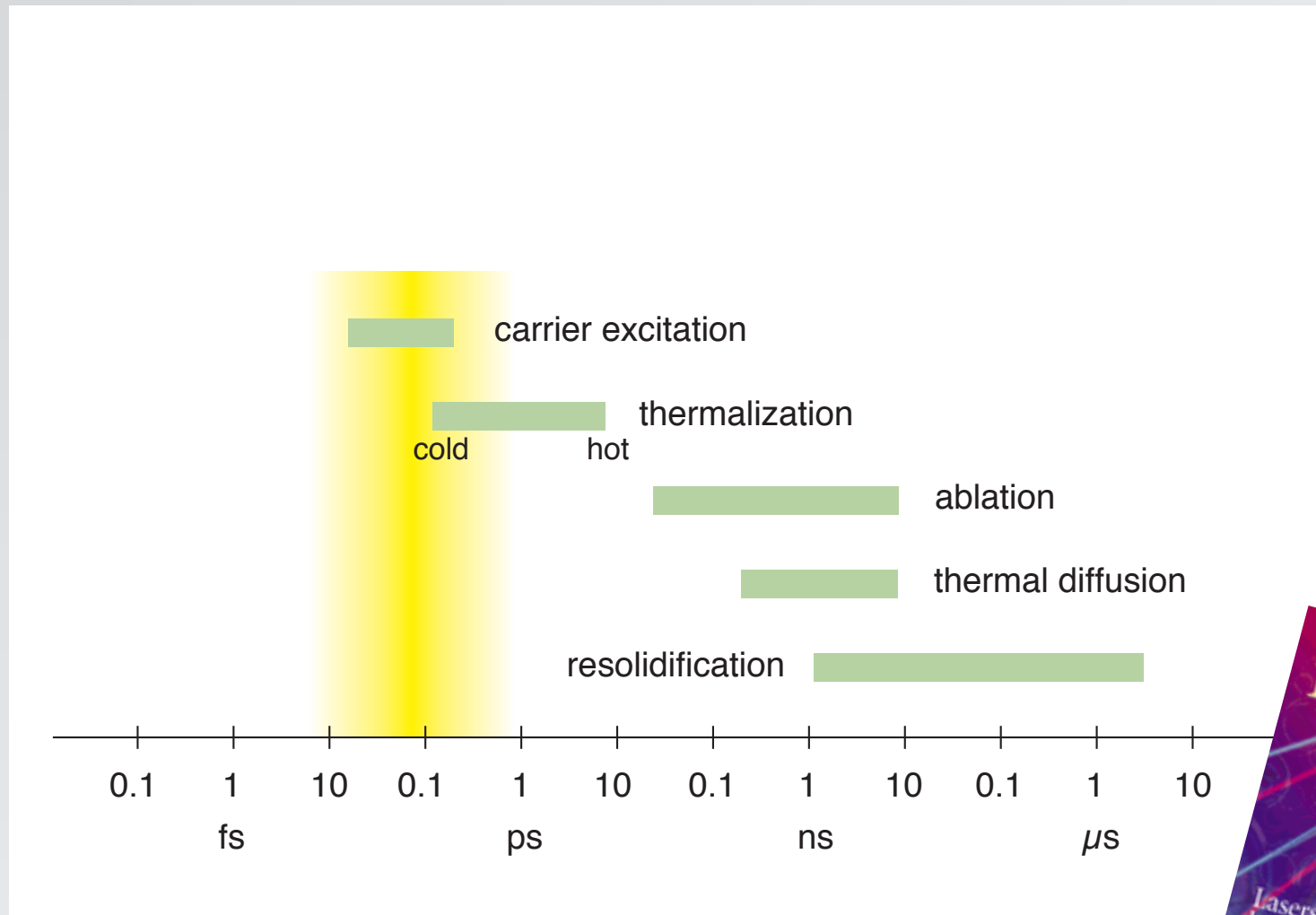
relevant time scales



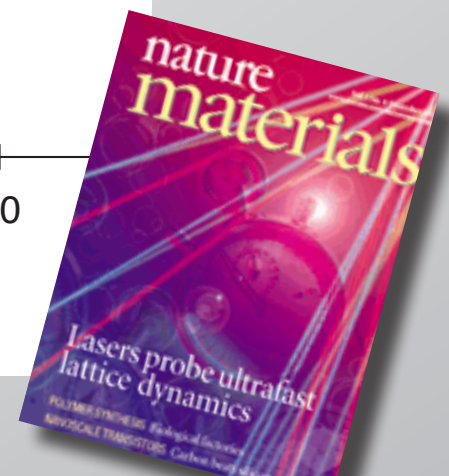
relevant time scales



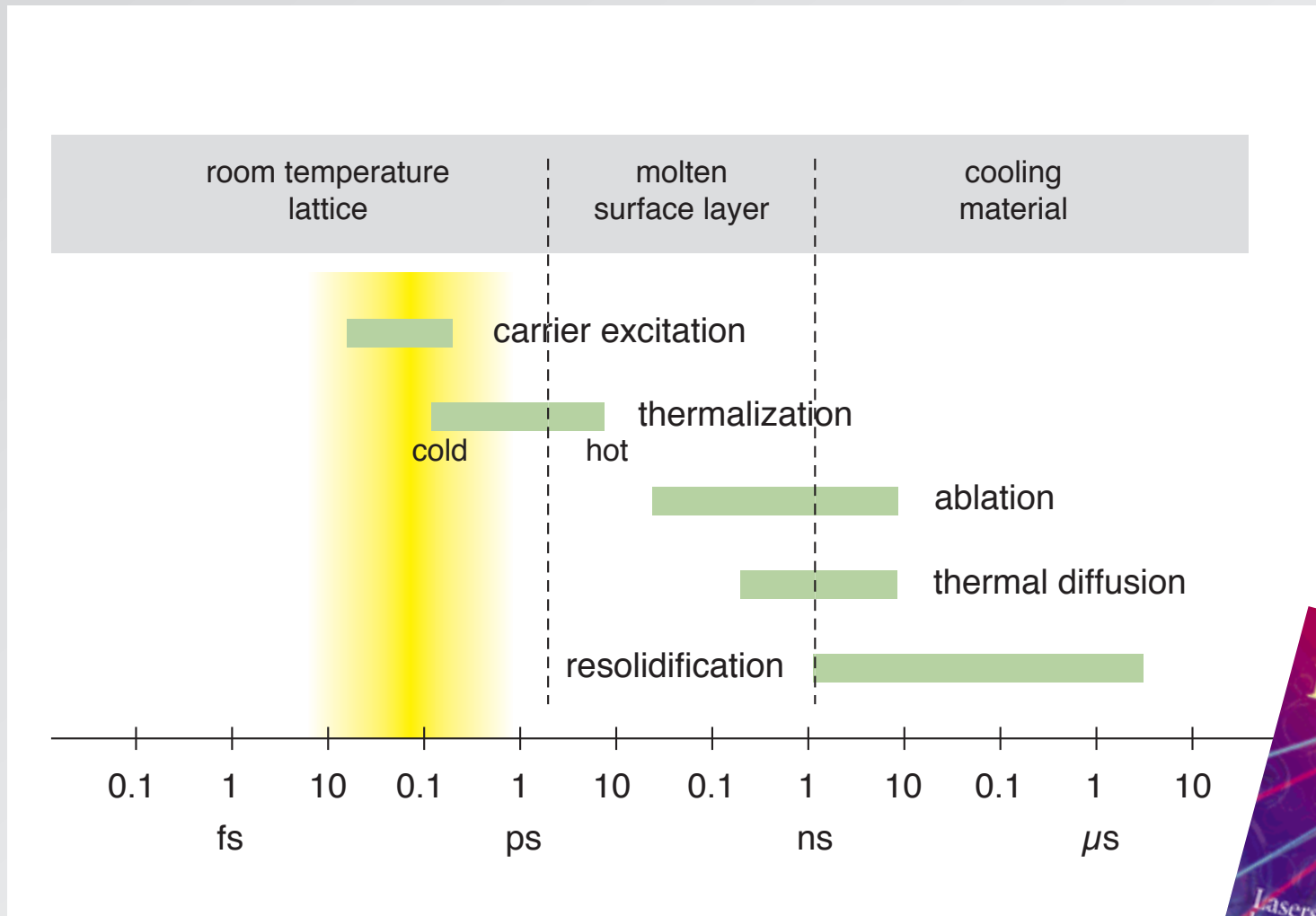
relevant time scales



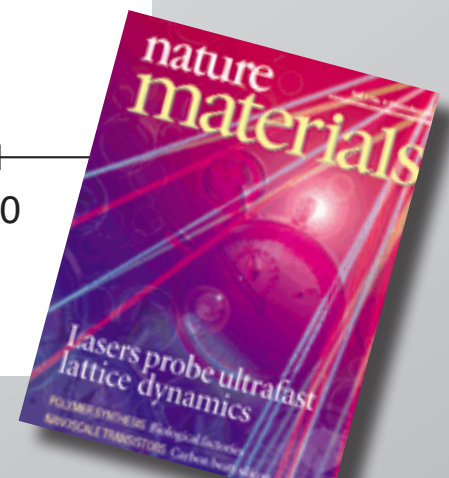
Nature Materials 1, 217 (2002)



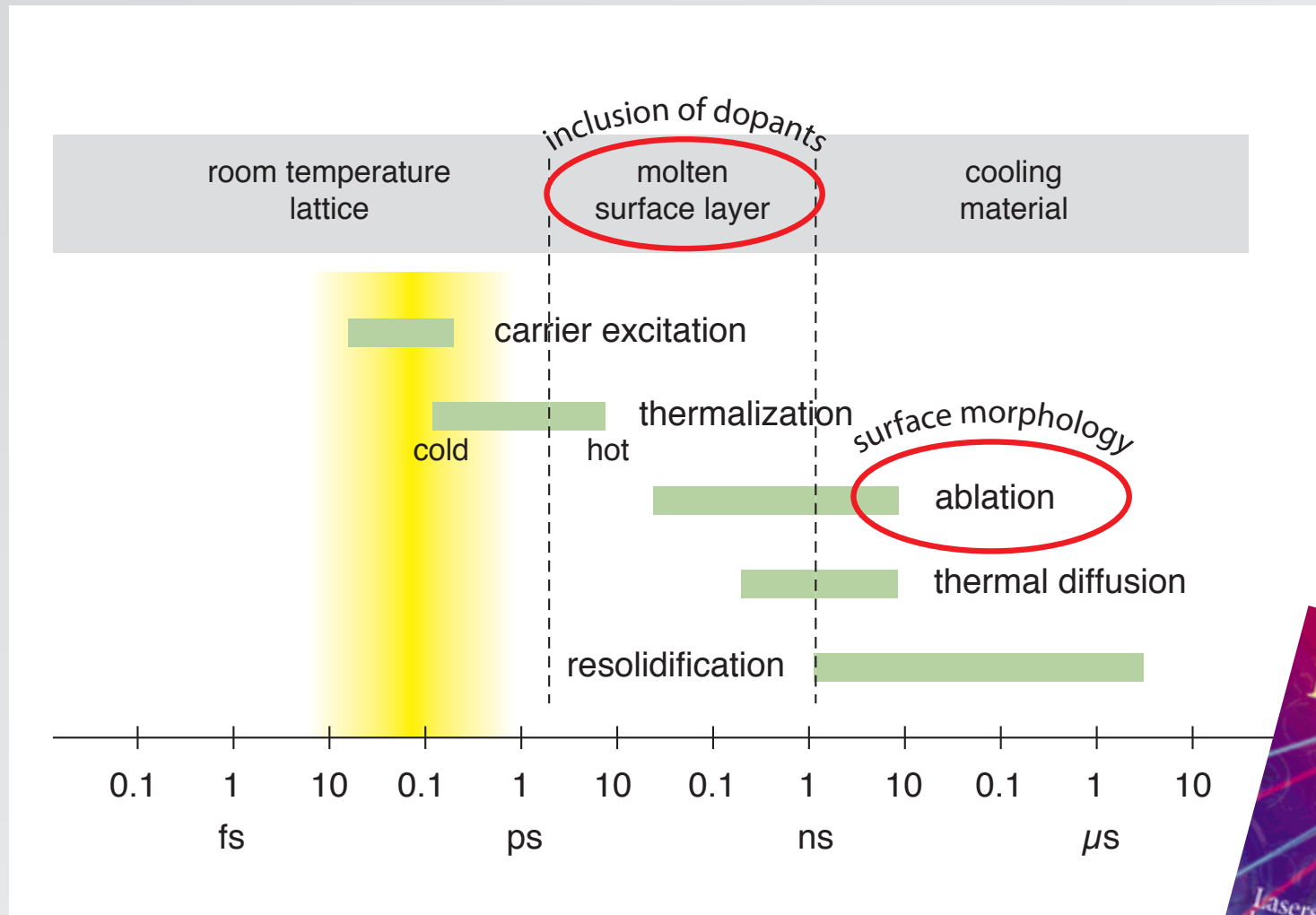
relevant time scales



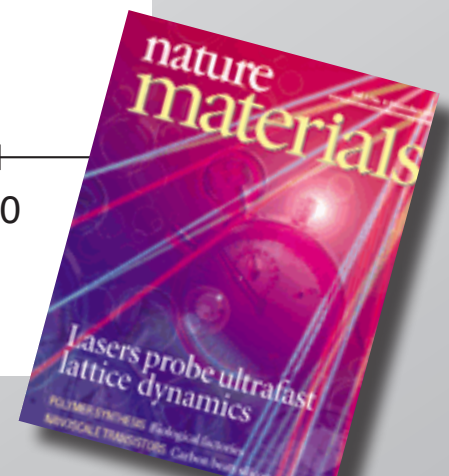
Nature Materials 1, 217 (2002)



relevant time scales



Nature Materials 1, 217 (2002)

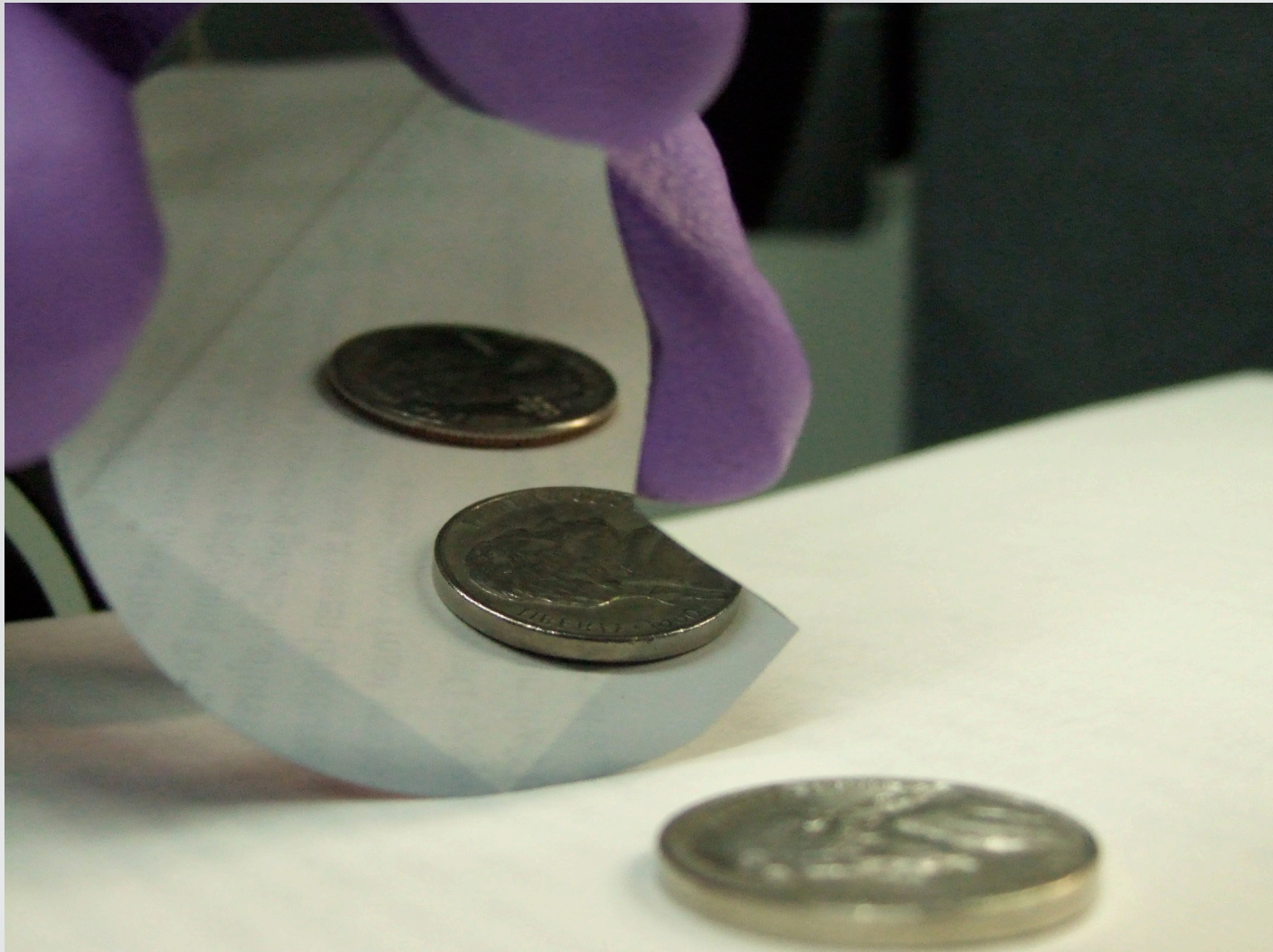


different thresholds:

melting: 1.5 kJ/m²

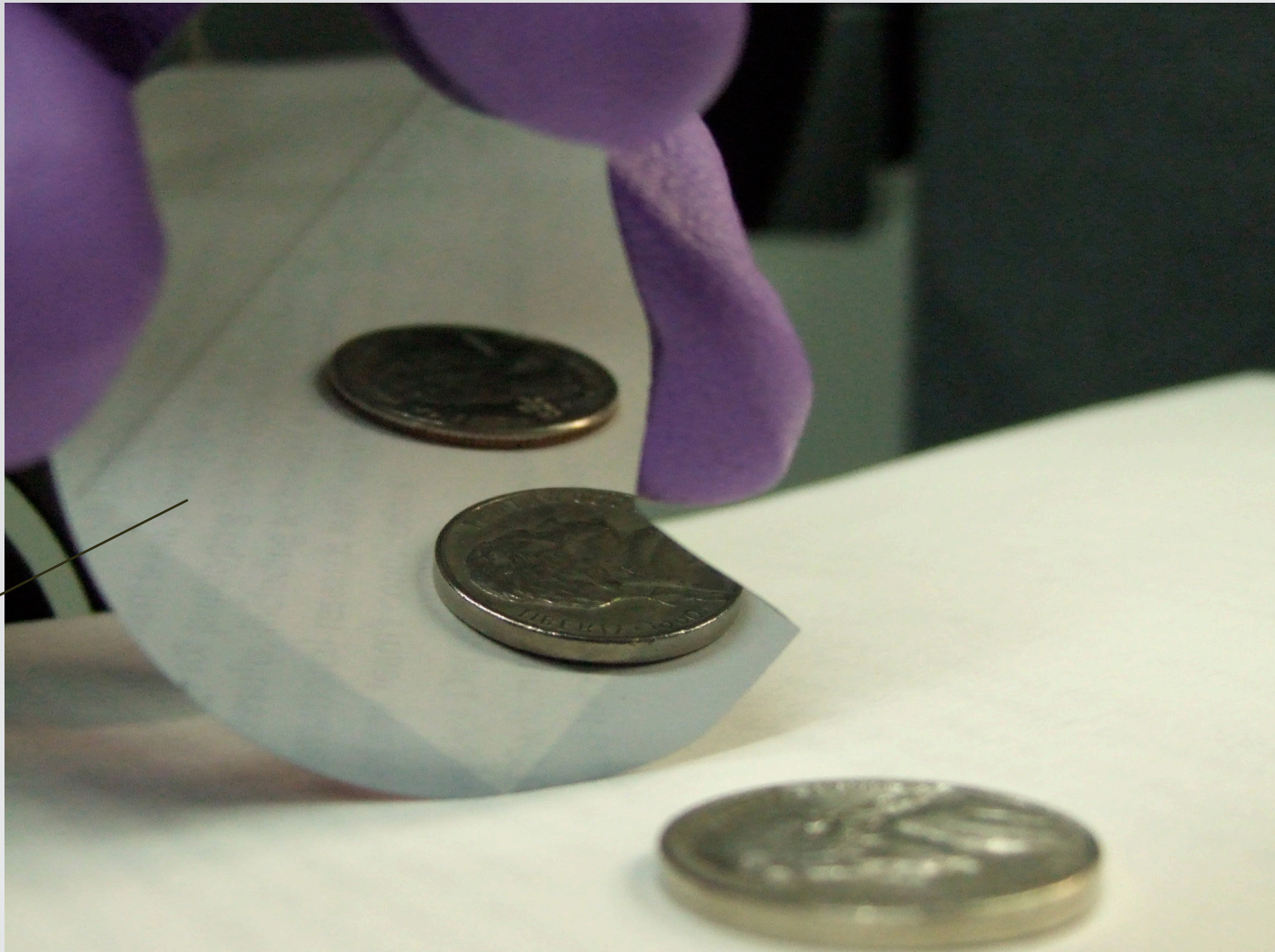
ablation: 3.1 kJ/m²

decouple ablation from melting

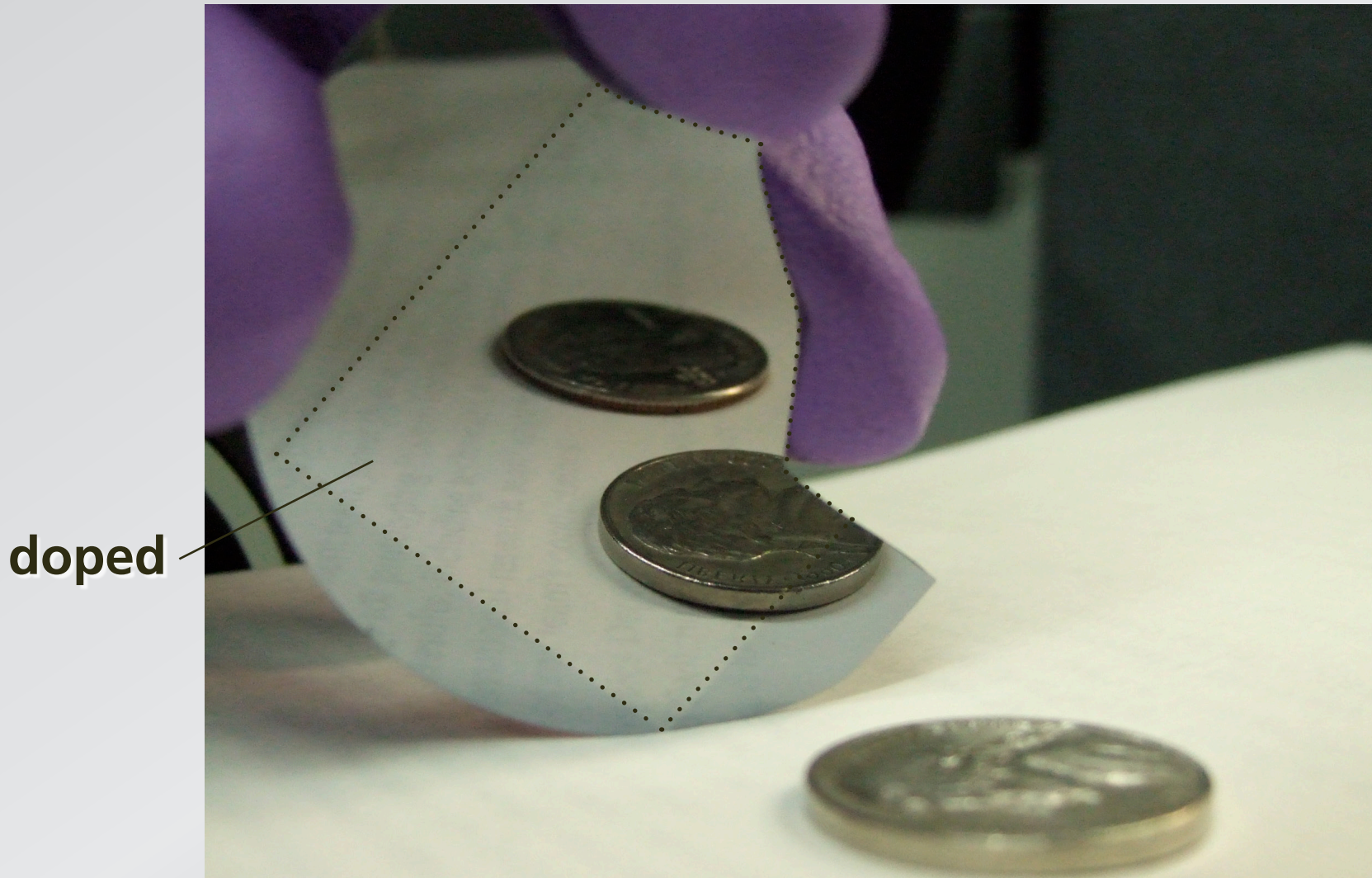


decouple ablation from melting

doped

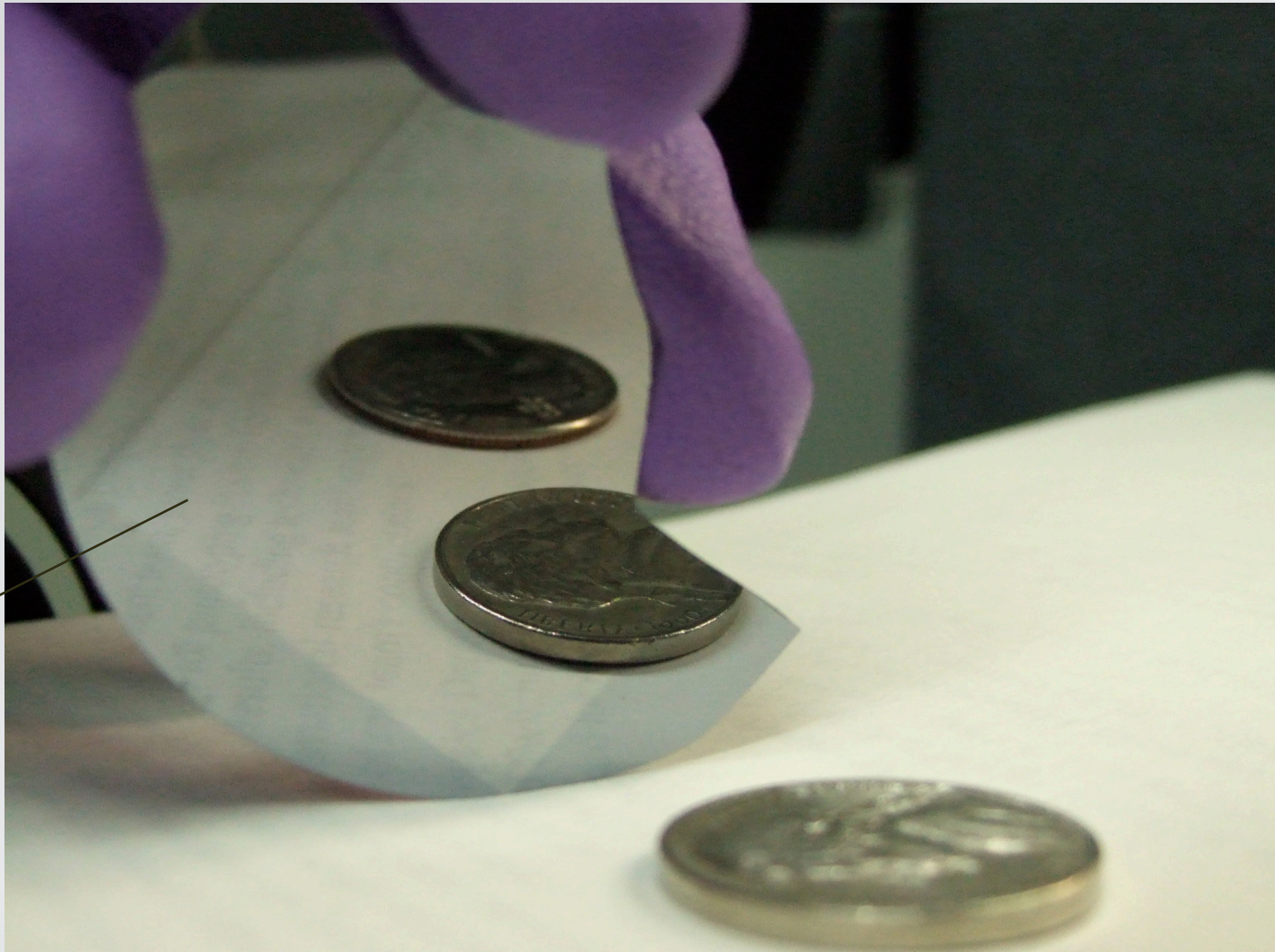


decouple ablation from melting



decouple ablation from melting

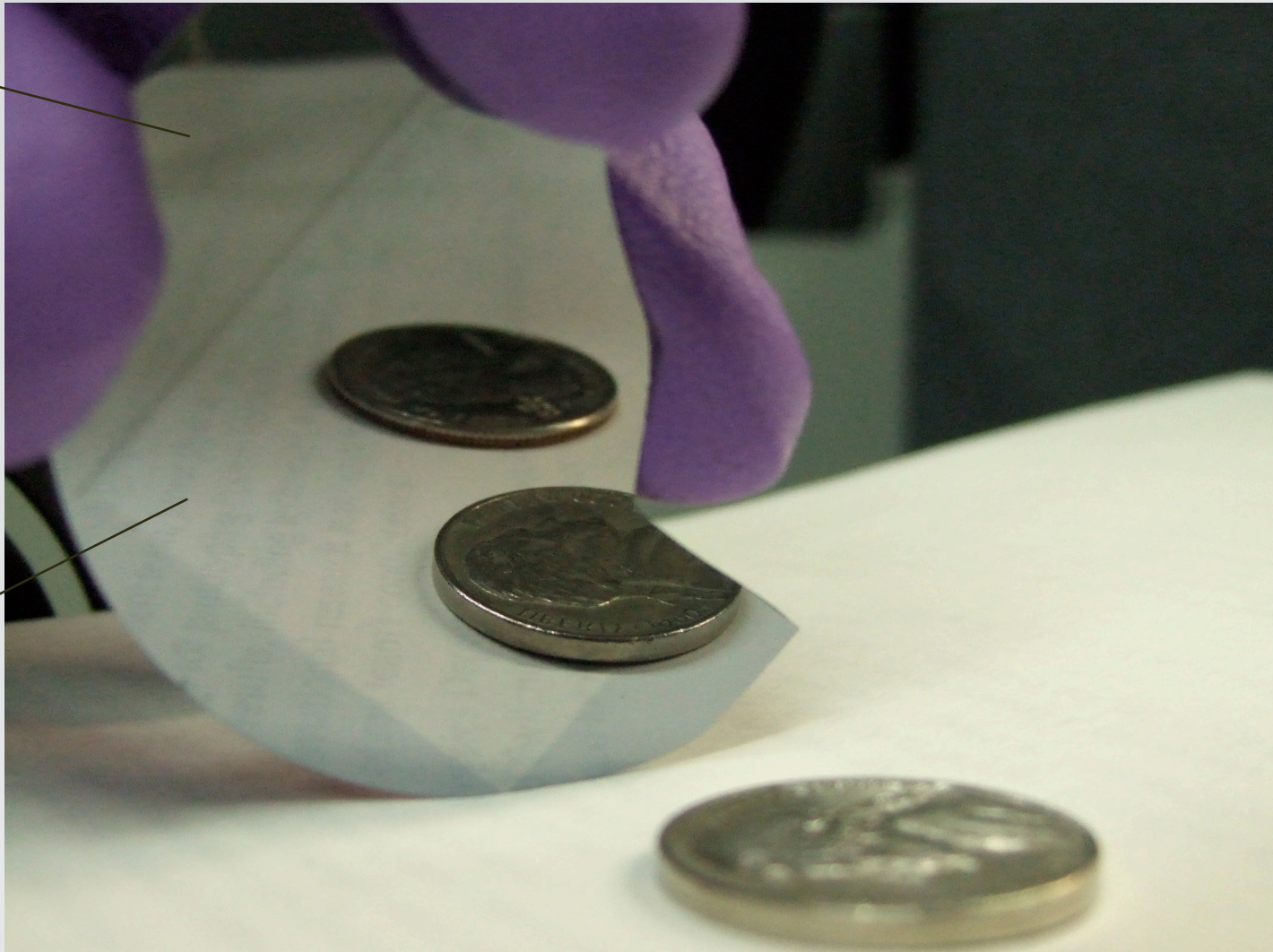
doped



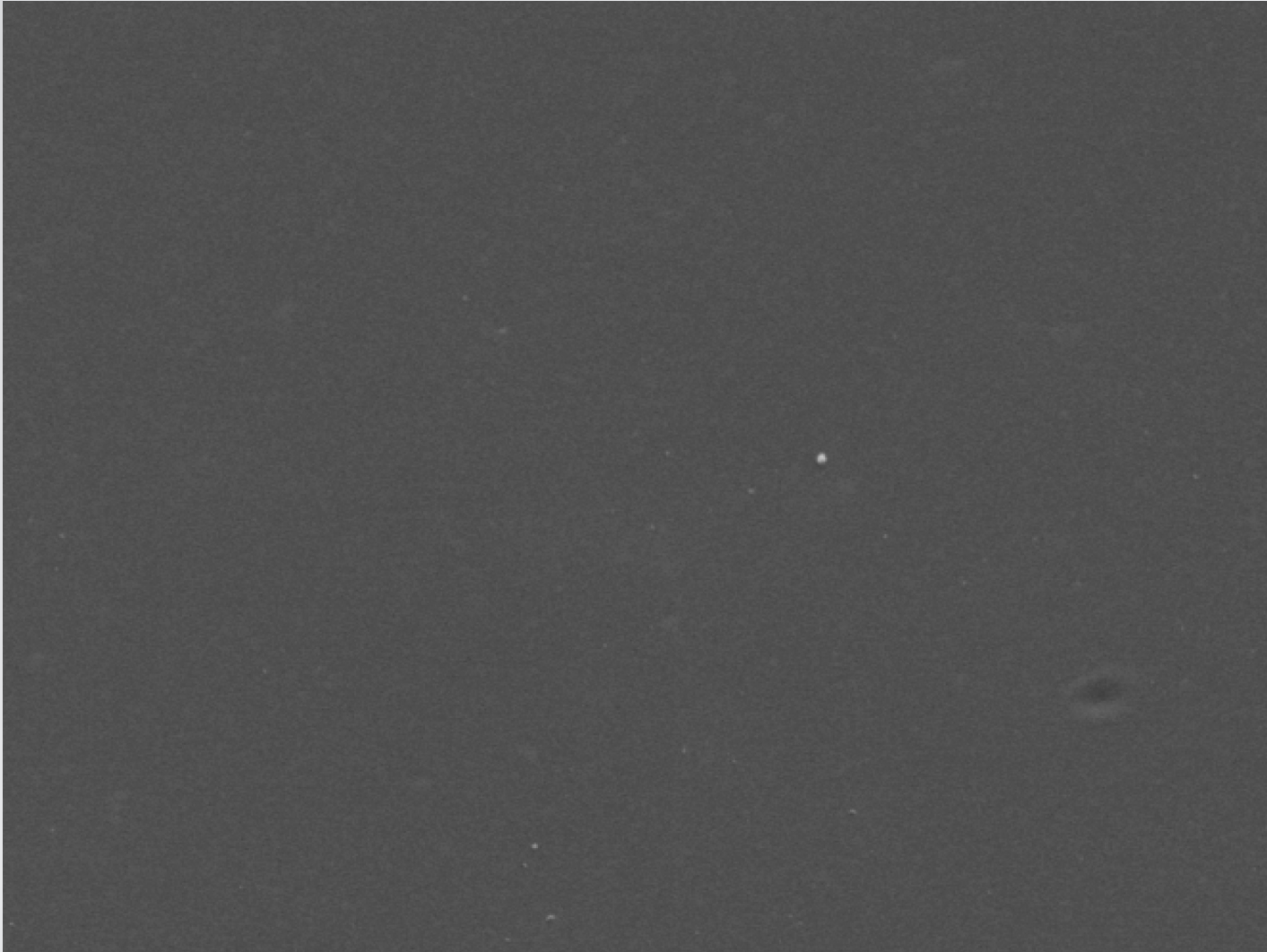
decouple ablation from melting

undoped

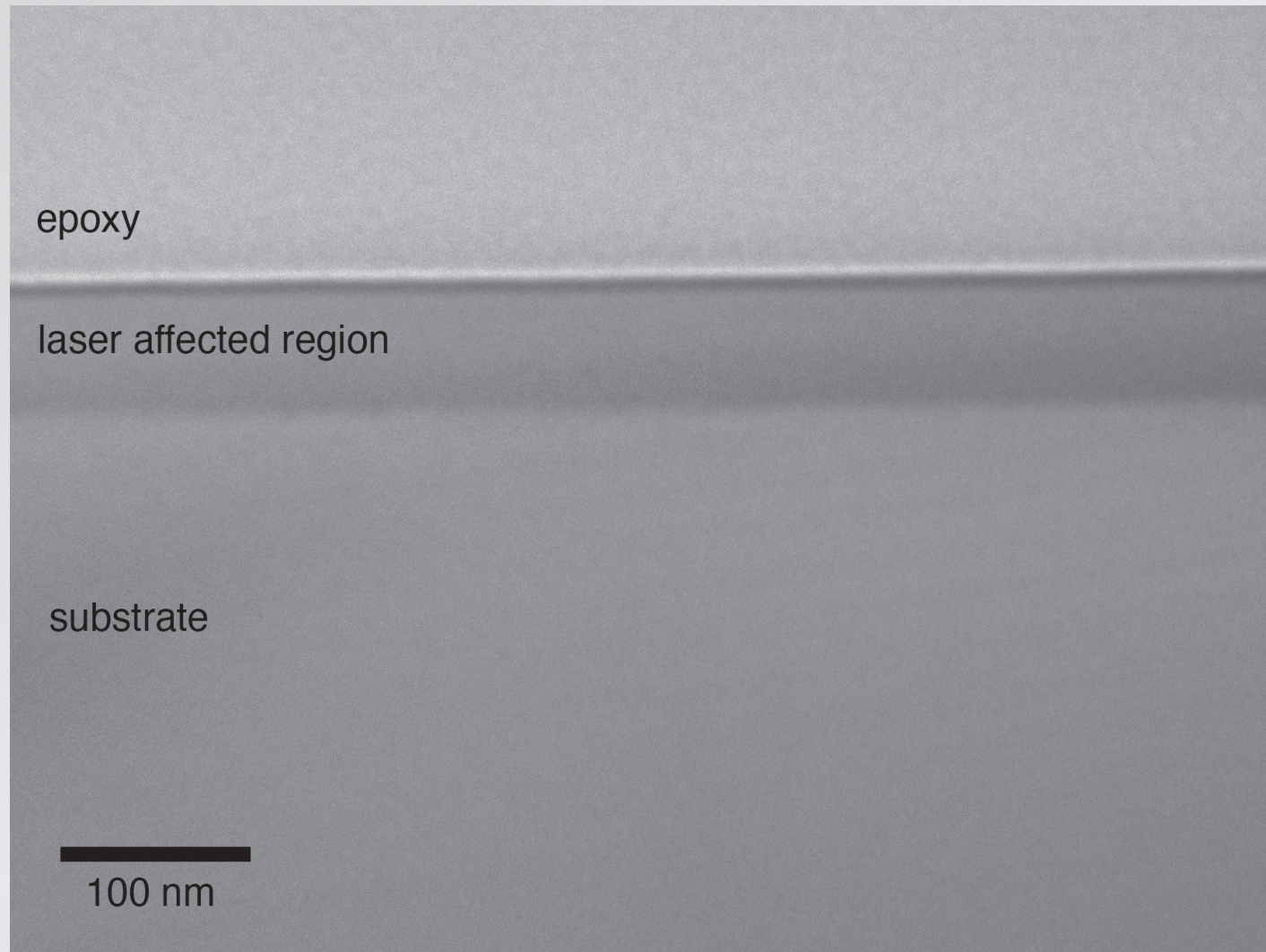
doped



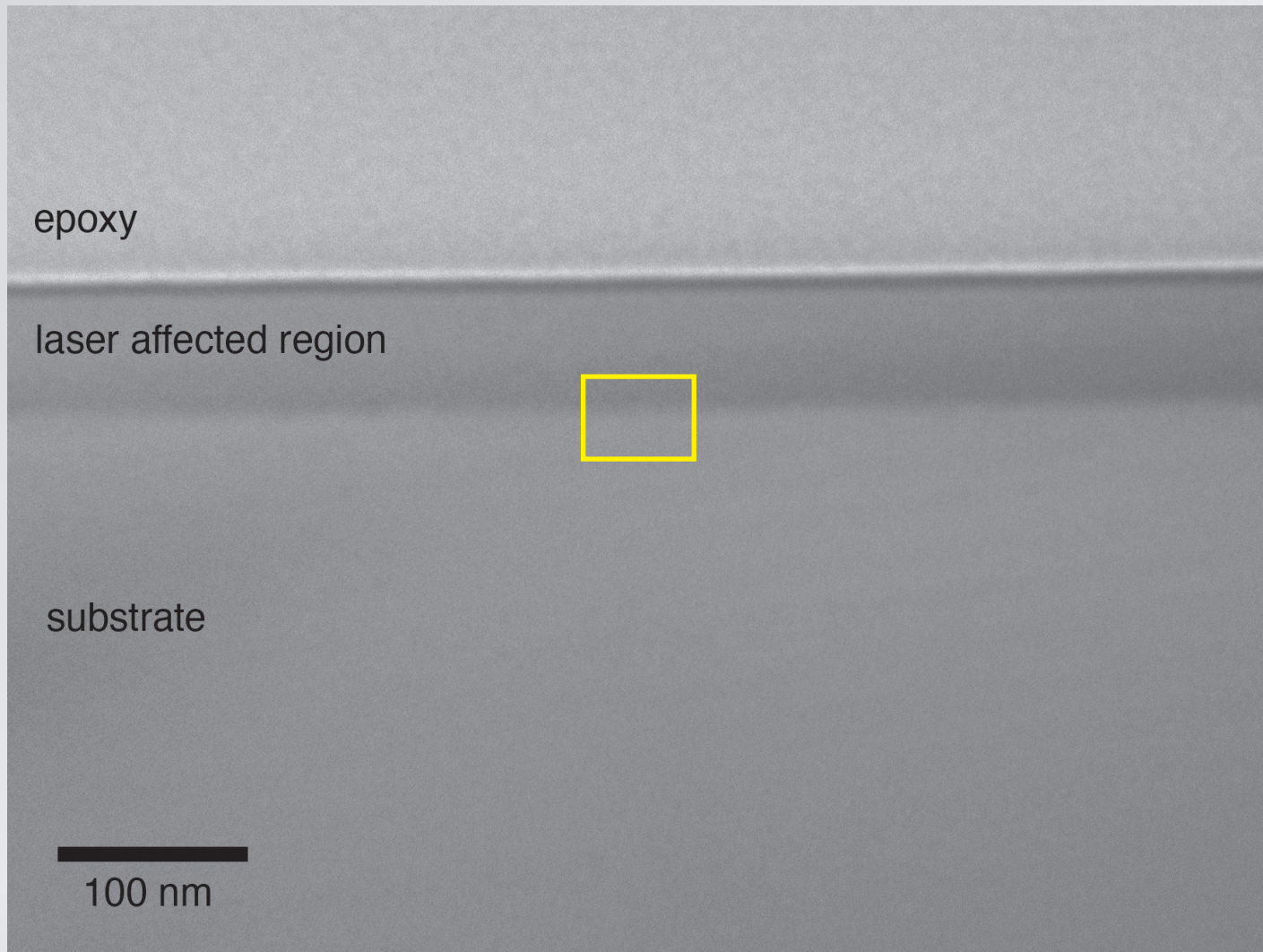
decouple ablation from melting



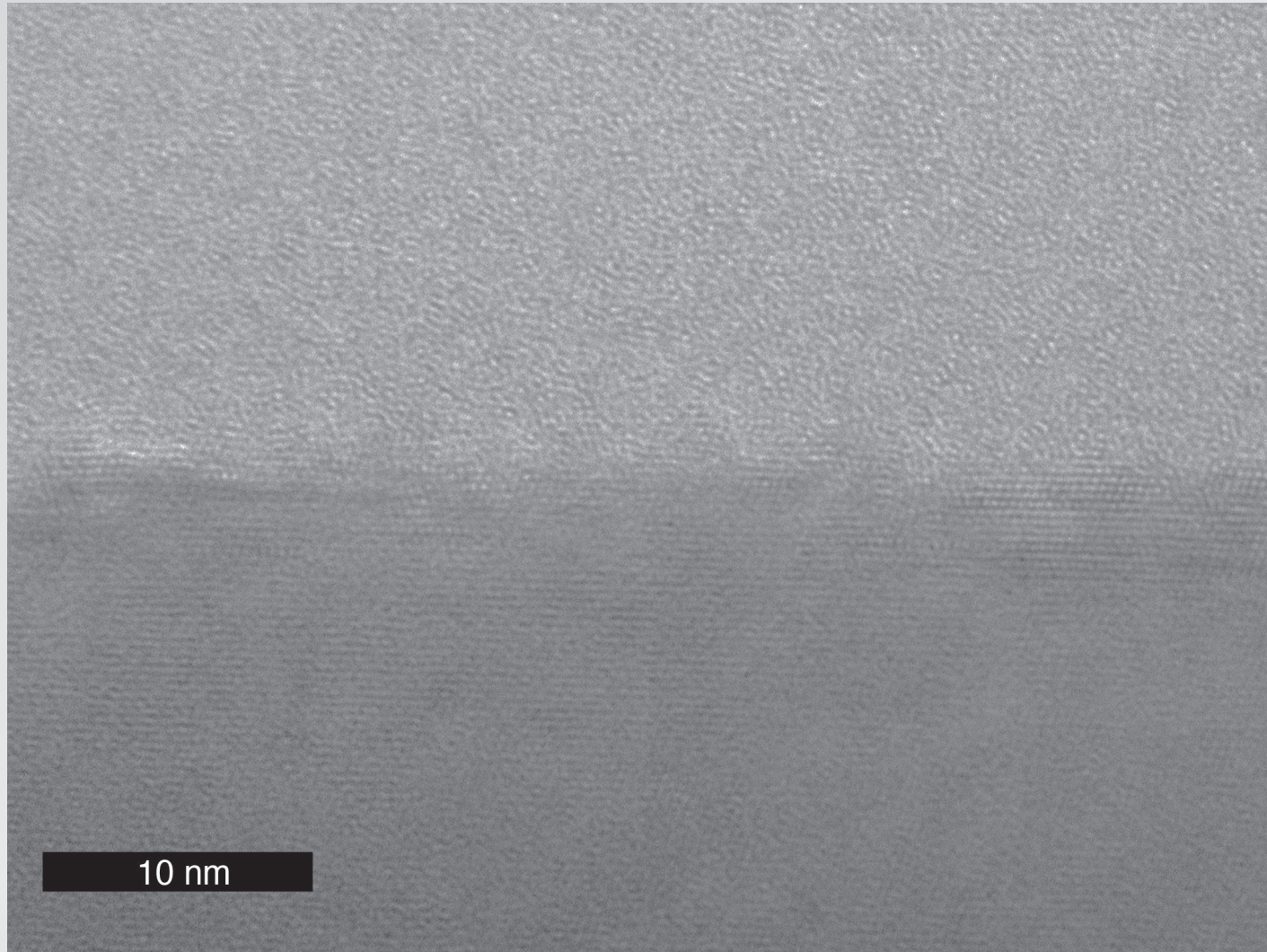
decouple ablation from melting



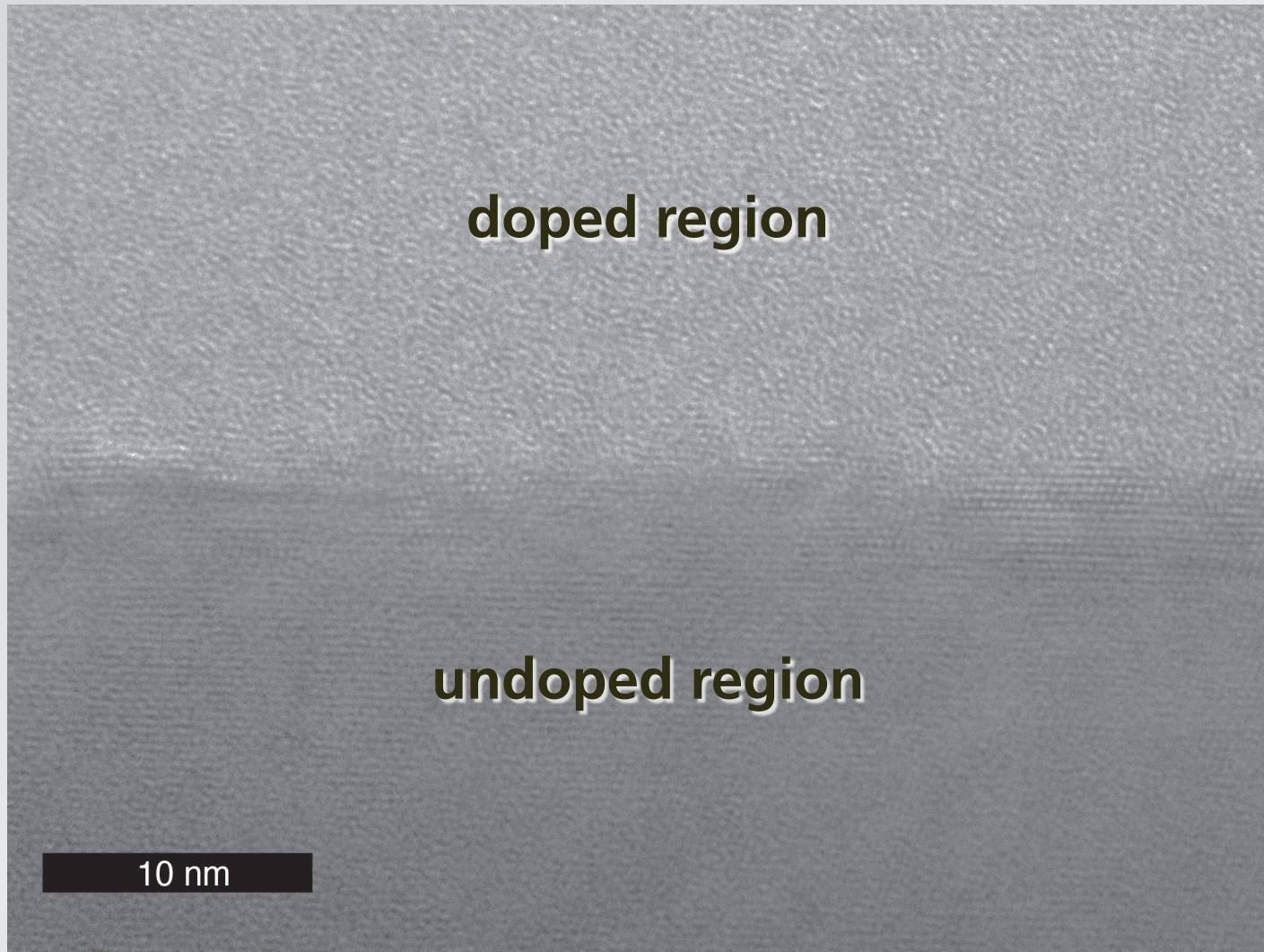
decouple ablation from melting



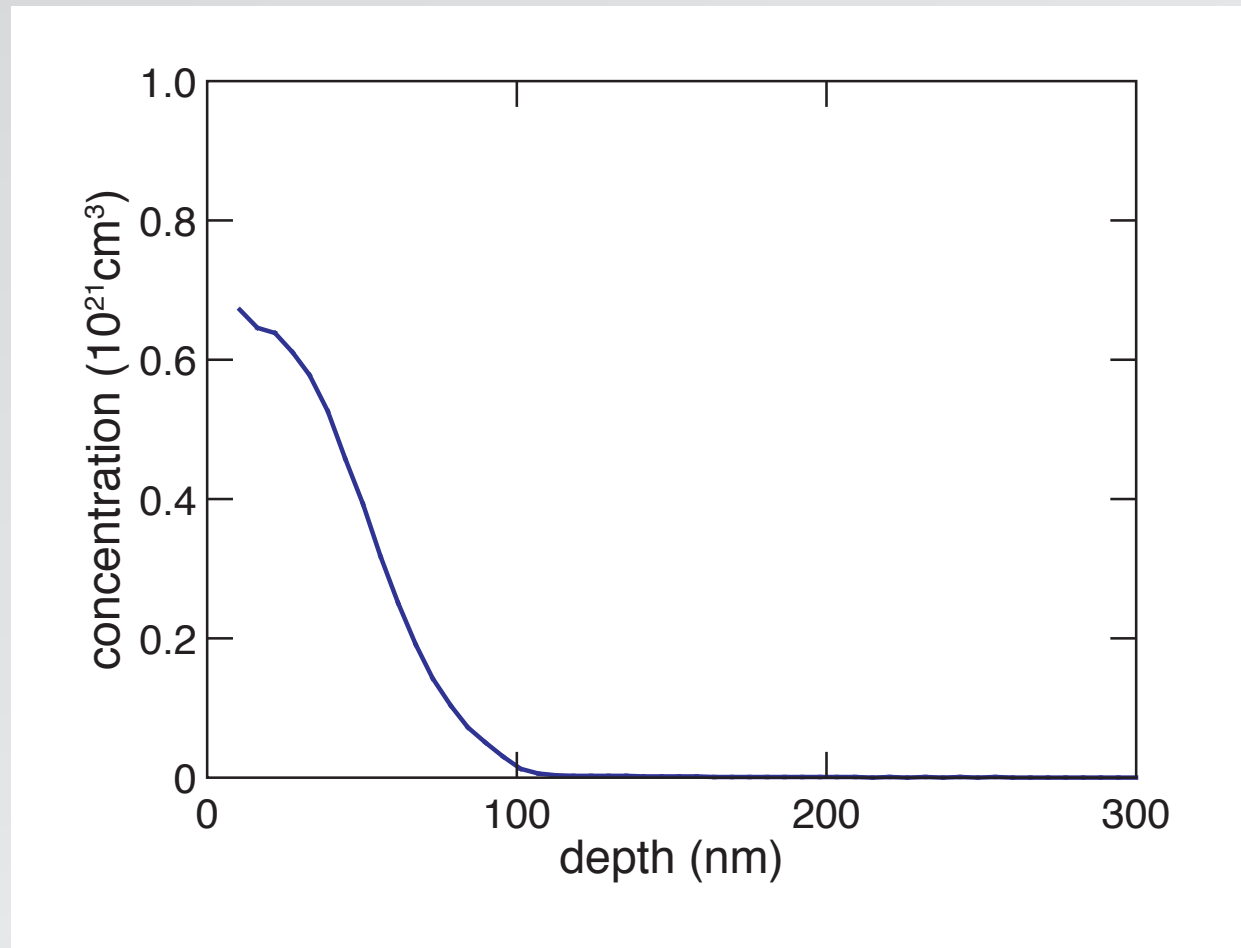
decouple ablation from melting



decouple ablation from melting

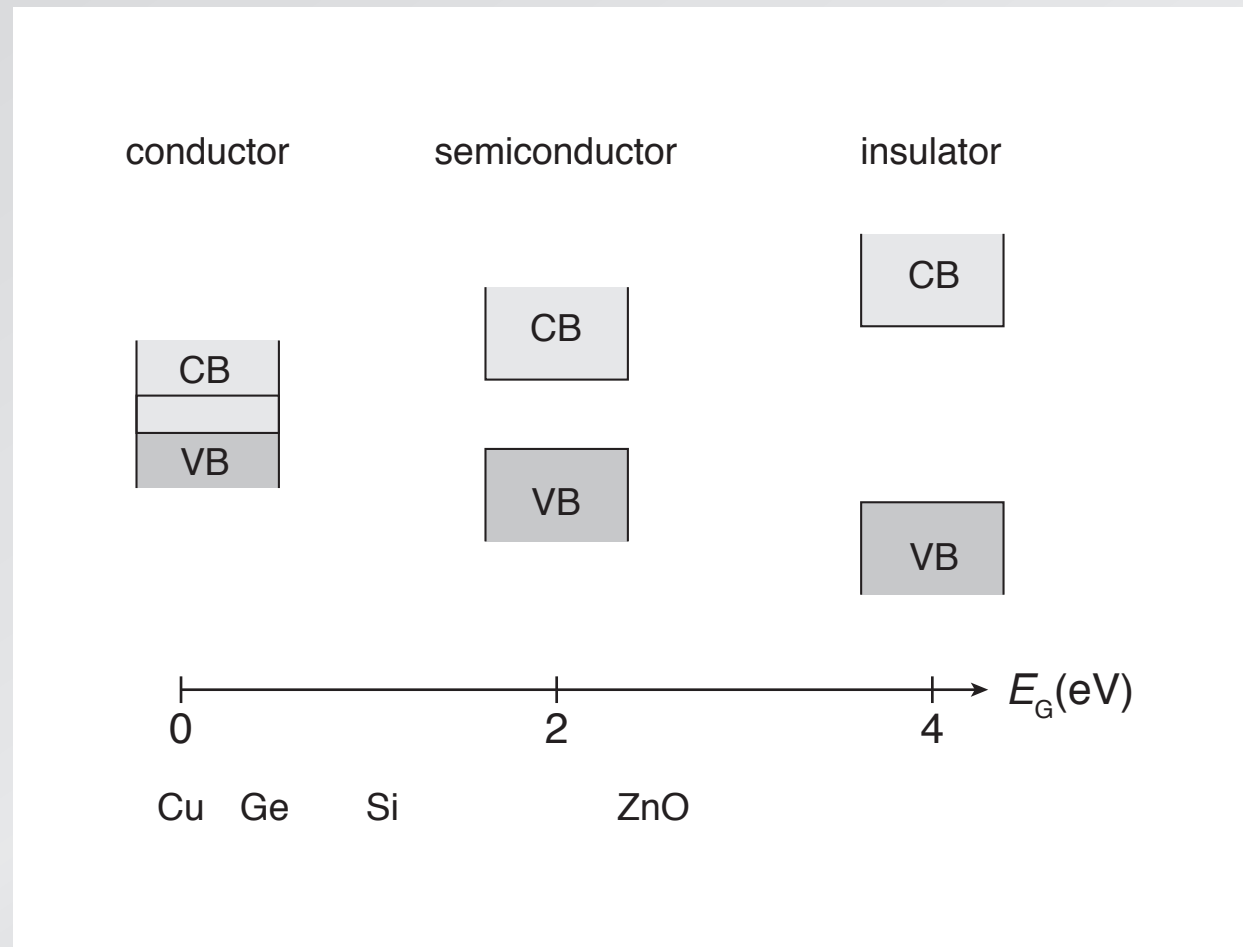


secondary ion mass spectrometry



Things to keep in mind

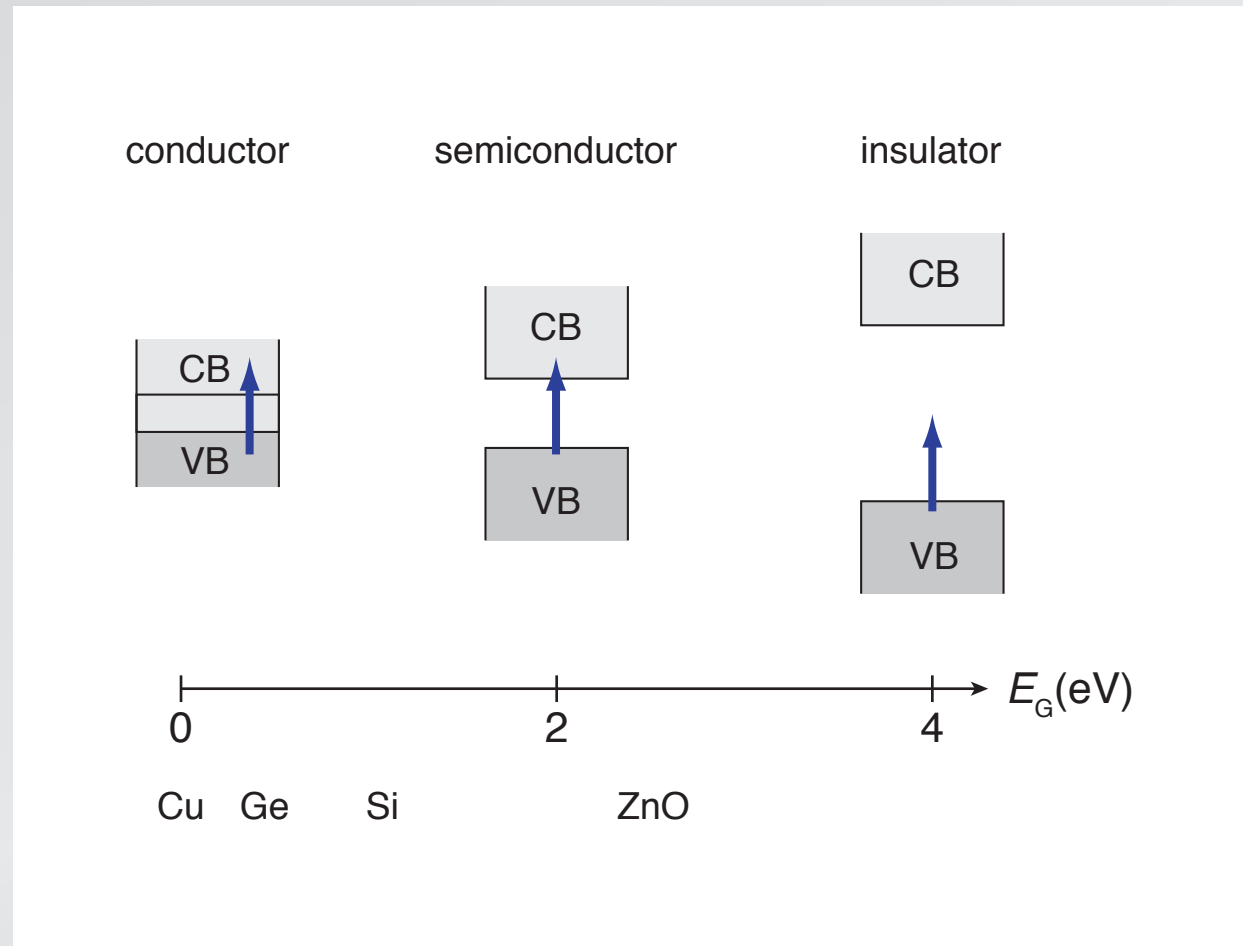
- near unit absorption extending into IR
- surface structure due to ablation
- hyperdoping due to rapid melting and resolidification
- can decouple both processes



1 properties

2 intermediate band

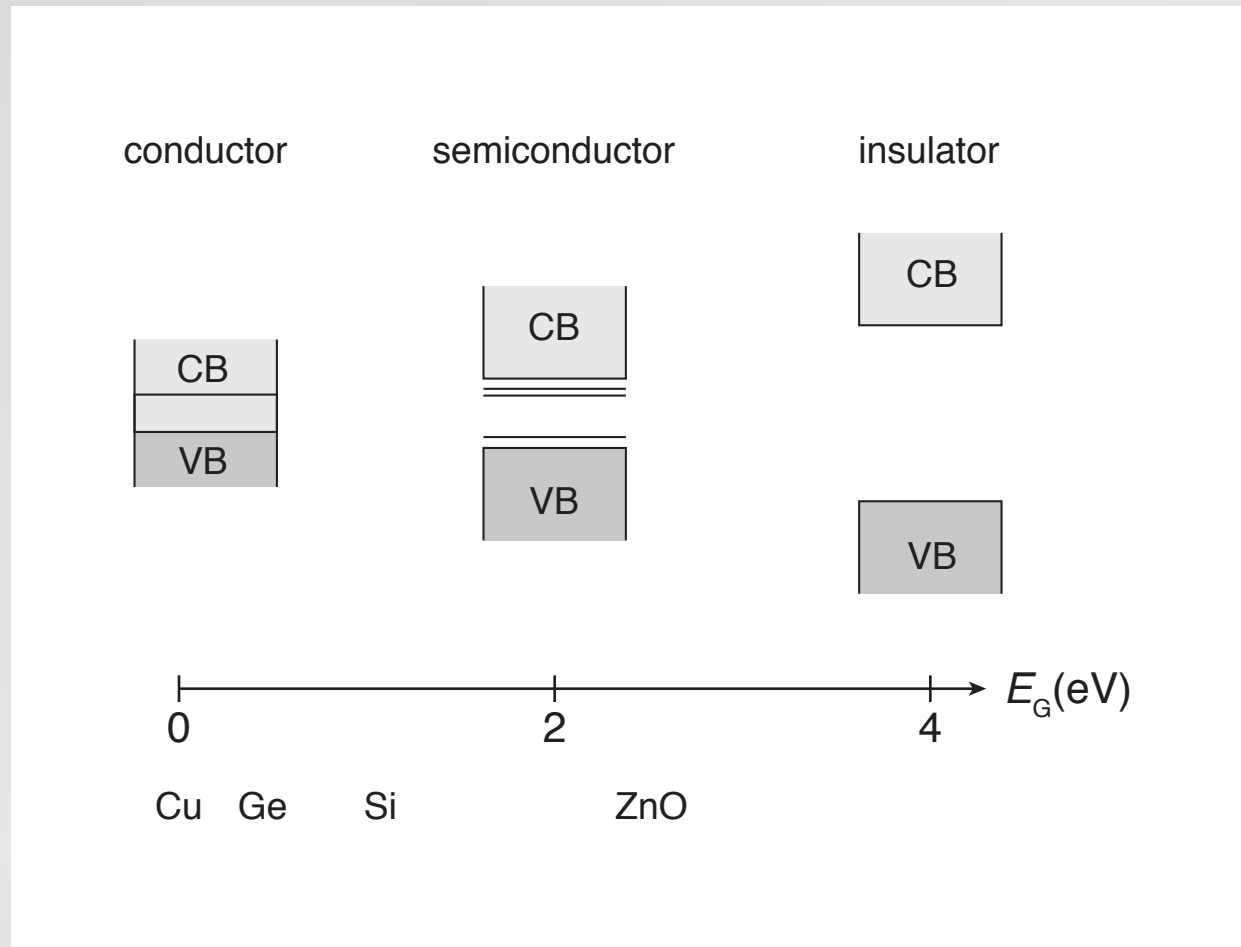
gap determines optical and electronic properties



1 properties

2 intermediate band

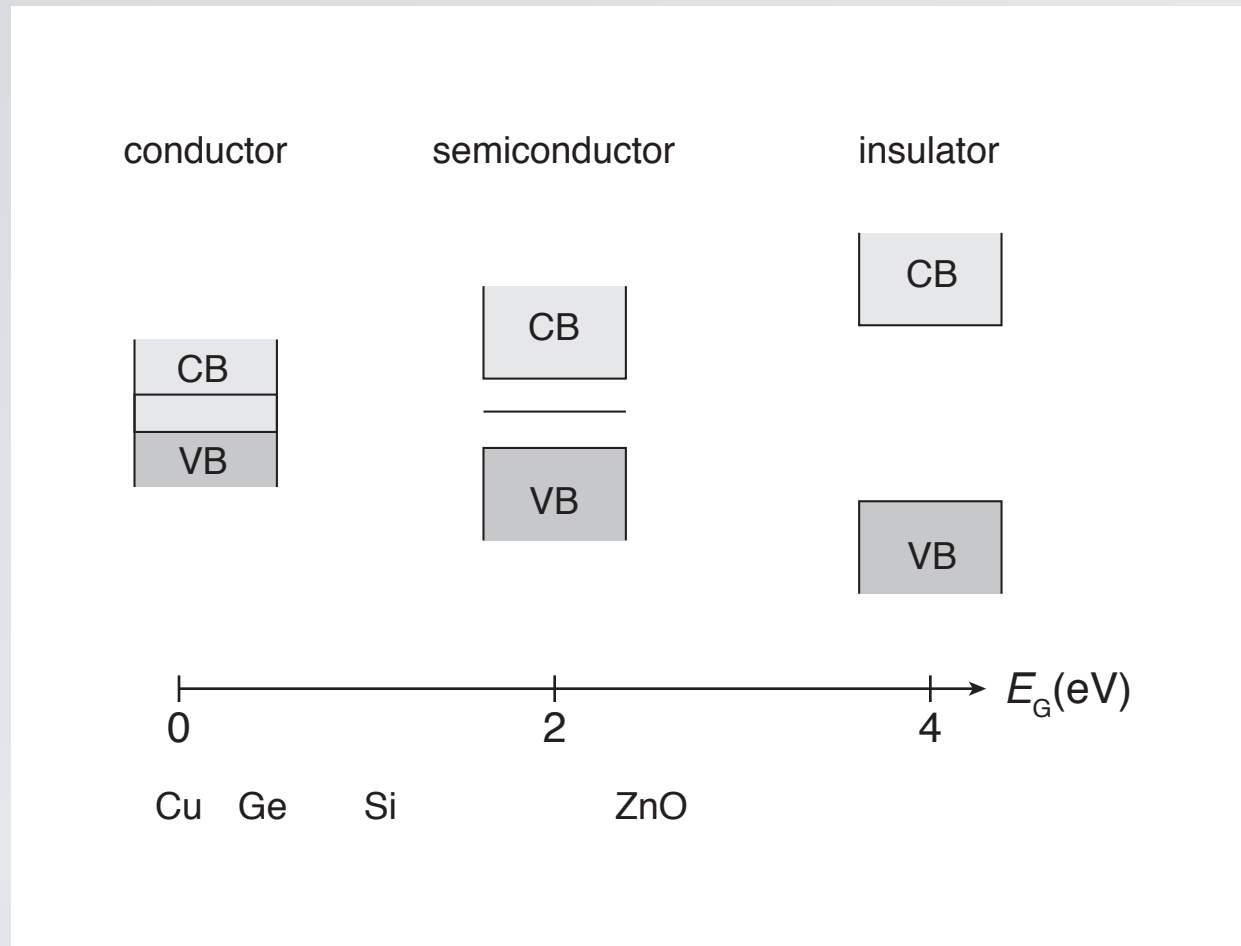
shallow-level dopants control electronic properties



1 properties

2 intermediate band

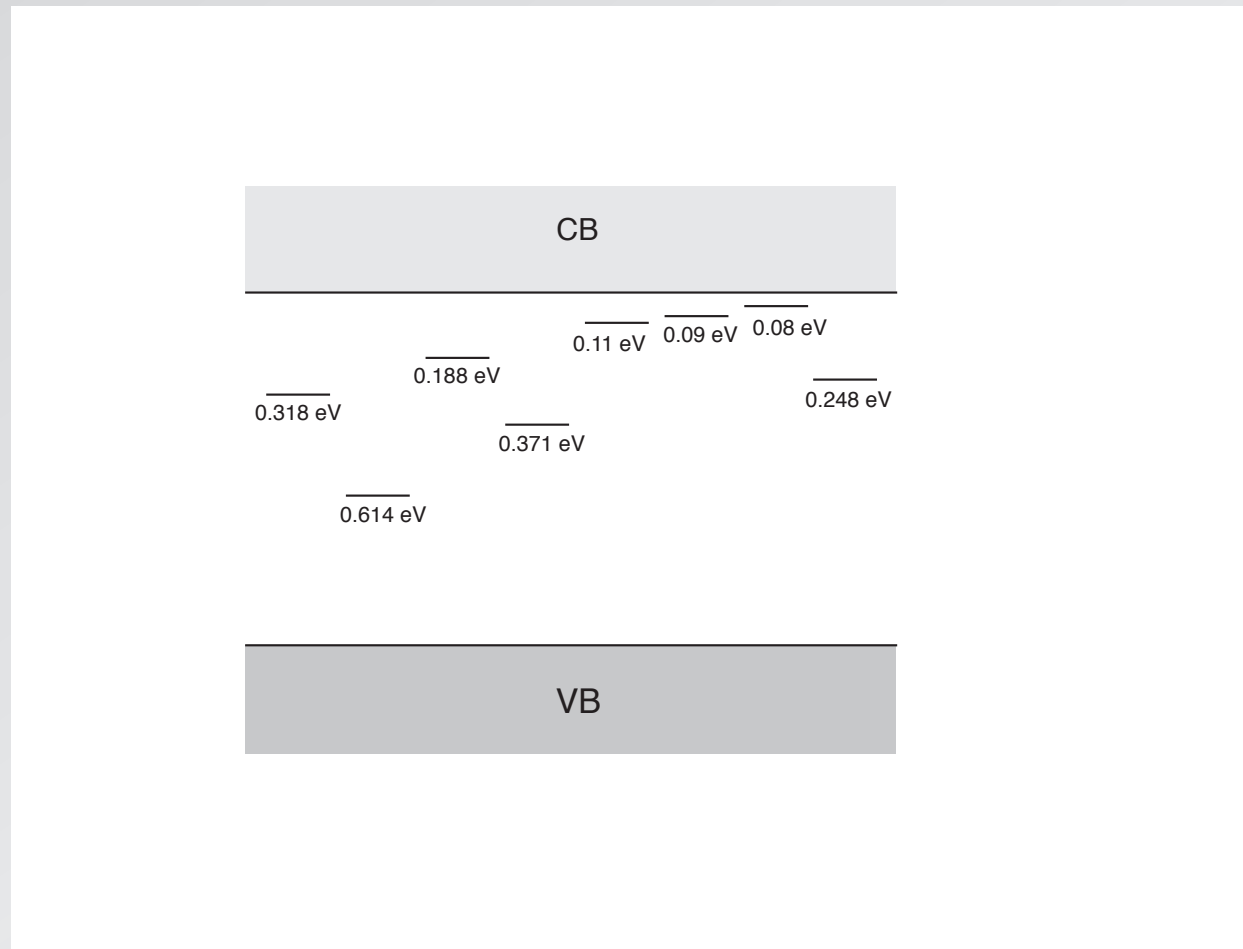
deep-level dopants typically avoided



1 properties

2 intermediate band

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

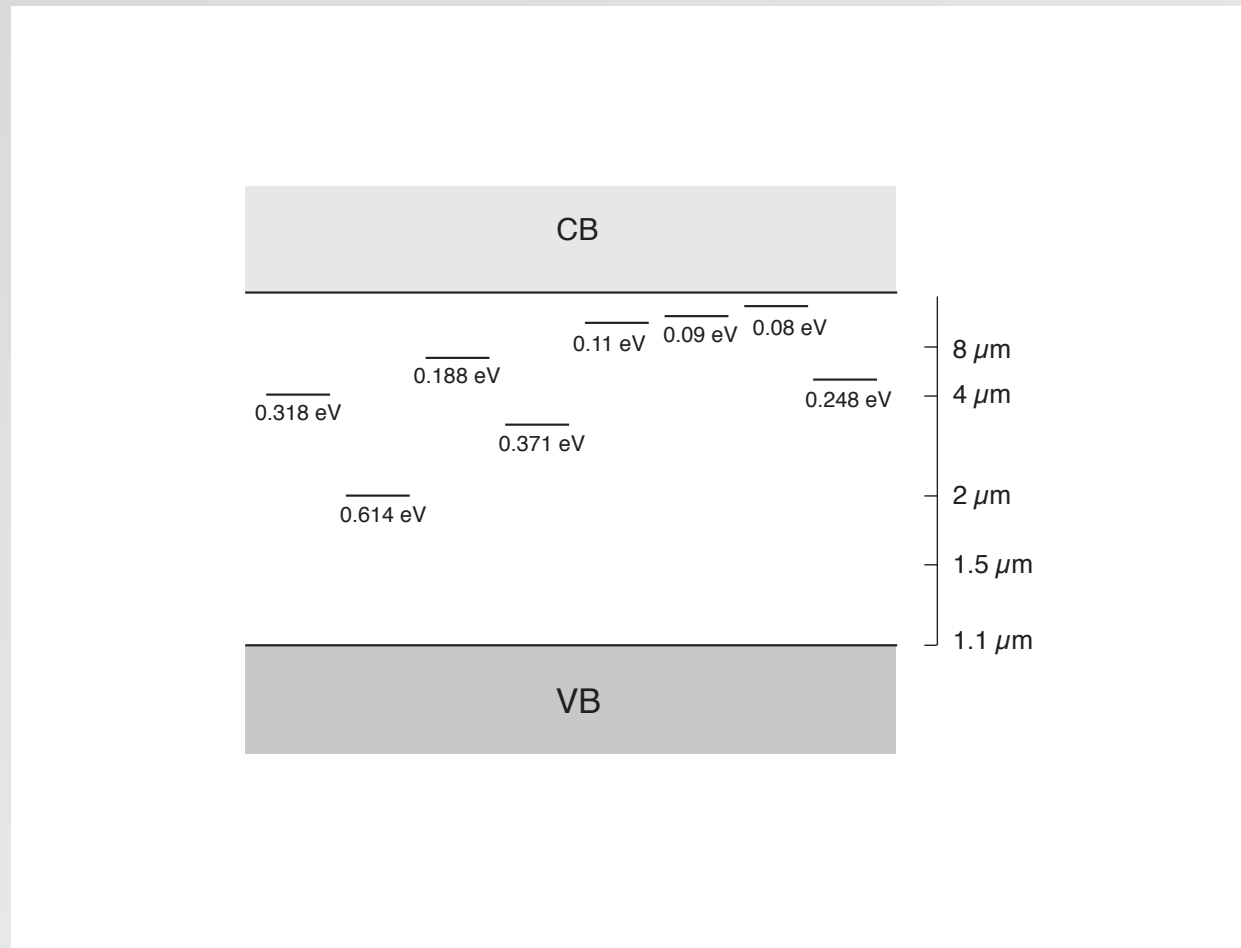


Janzén *et al.*, Phys. Rev. B 29, 1907 (1984)

1 properties

2 intermediate band

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

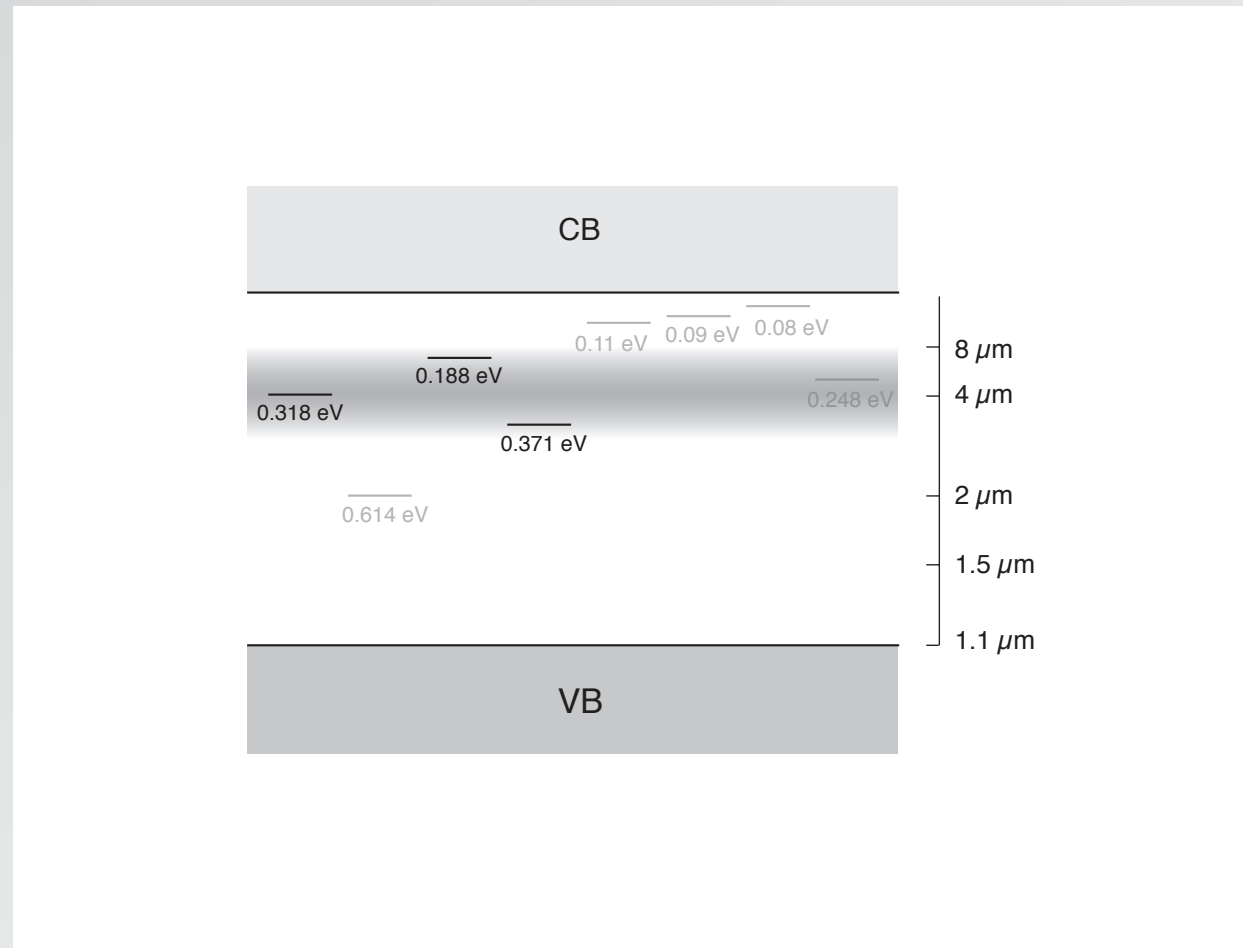


Janzén *et al.*, Phys. Rev. B 29, 1907 (1984)

1 properties

2 intermediate band

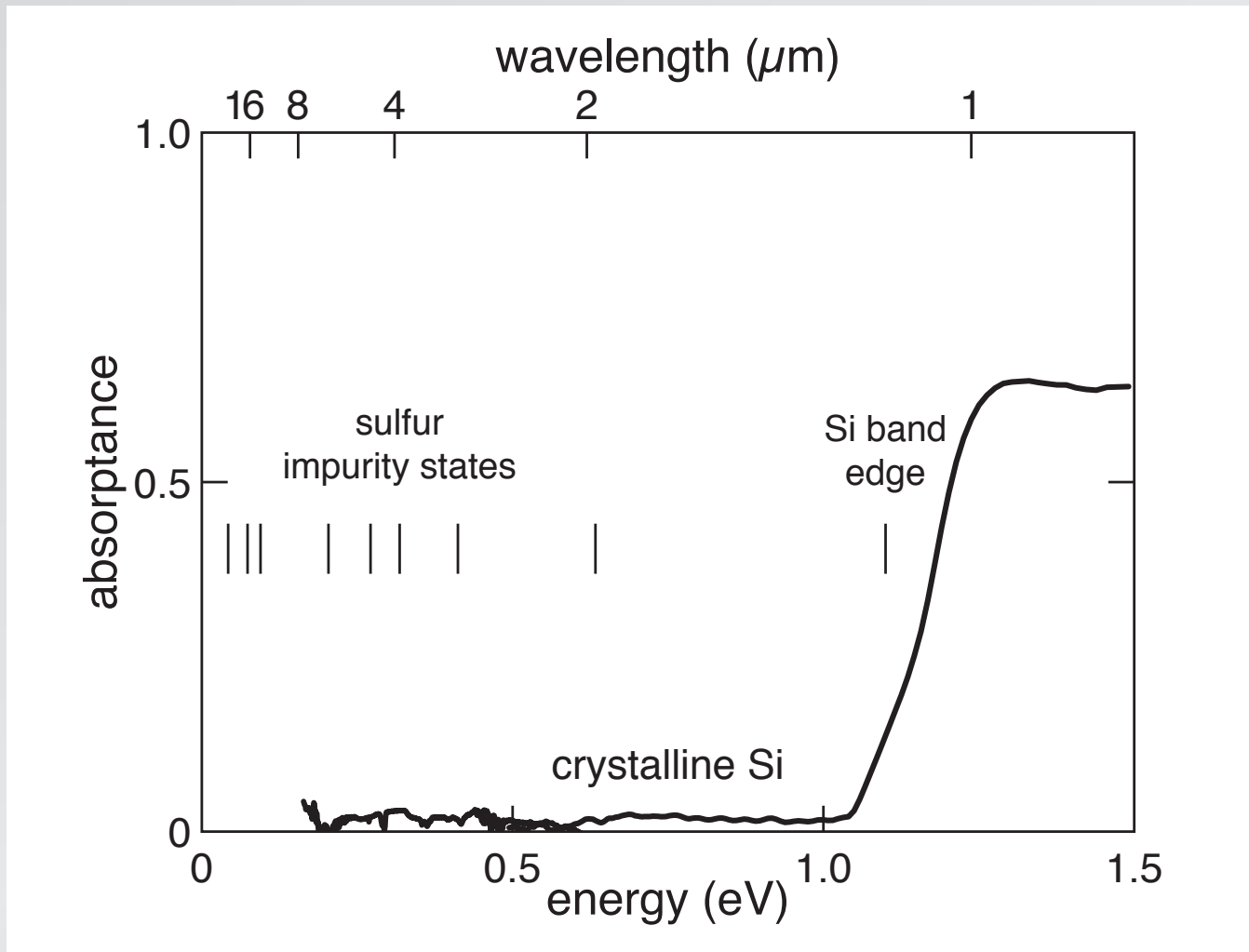
at high concentration states broaden into band



1 properties

2 intermediate band

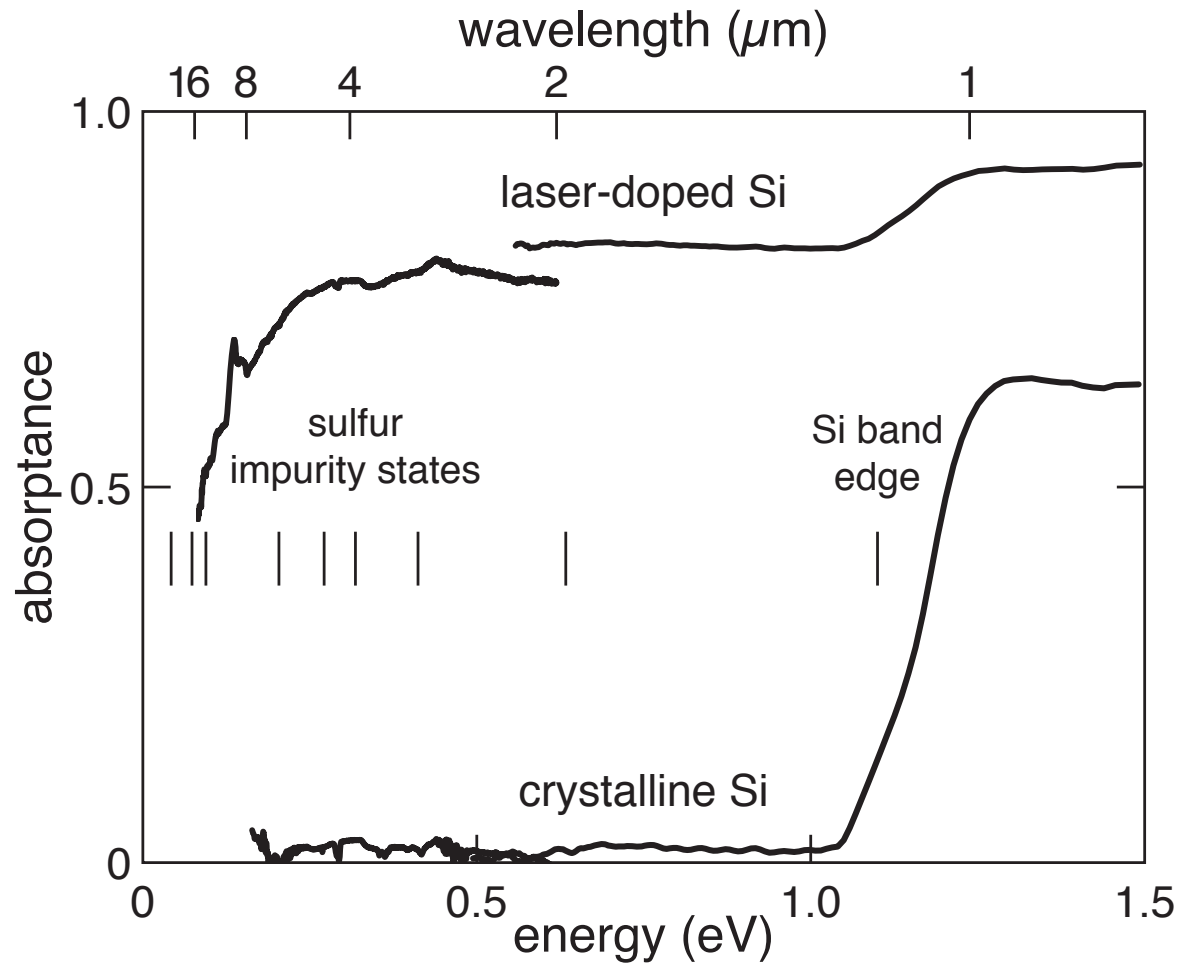
10^{-6} sulfur doping



1 properties

2 intermediate band

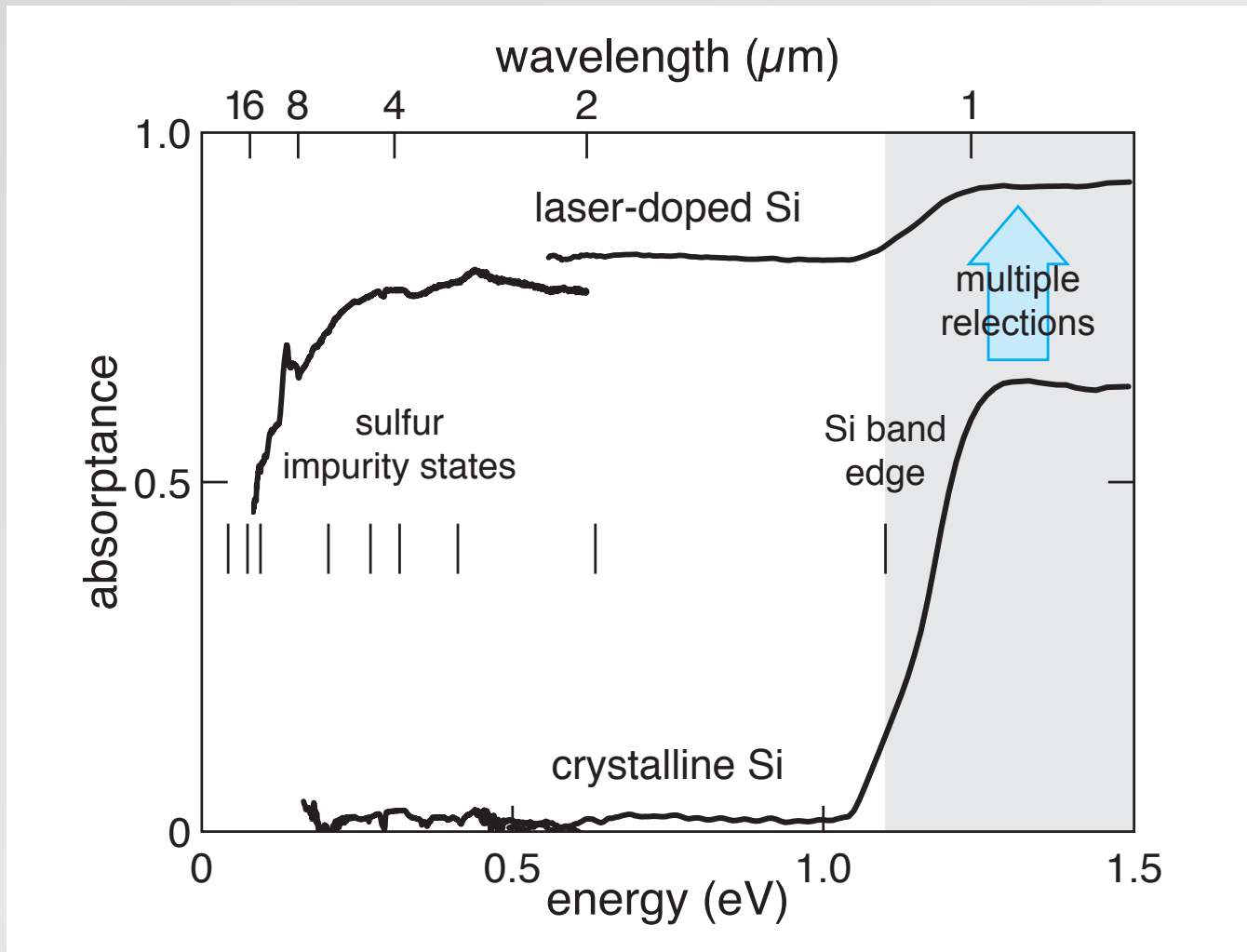
laser-doped S:Si



1 properties

2 intermediate band

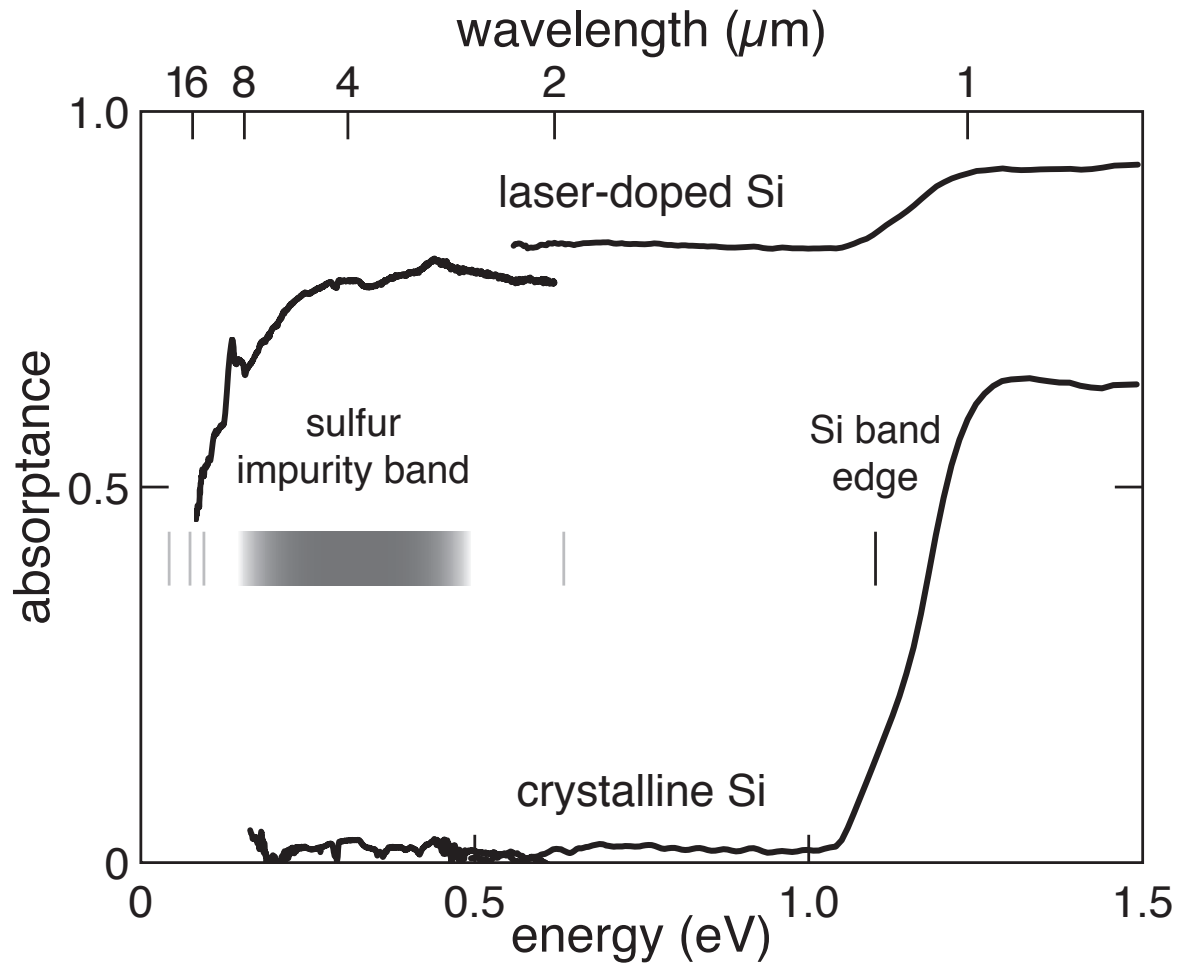
laser-doped S:Si



1 properties

2 intermediate band

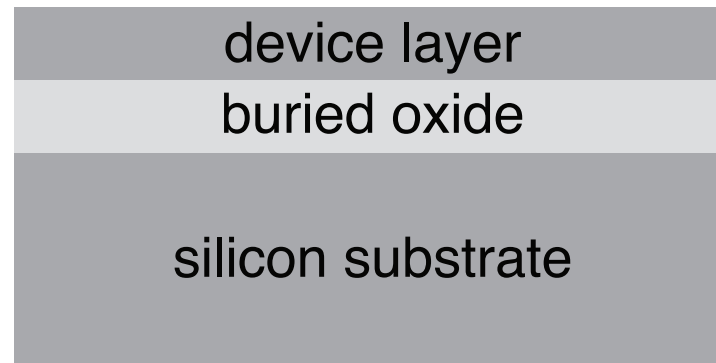
laser-doped S:Si



1 properties

2 intermediate band

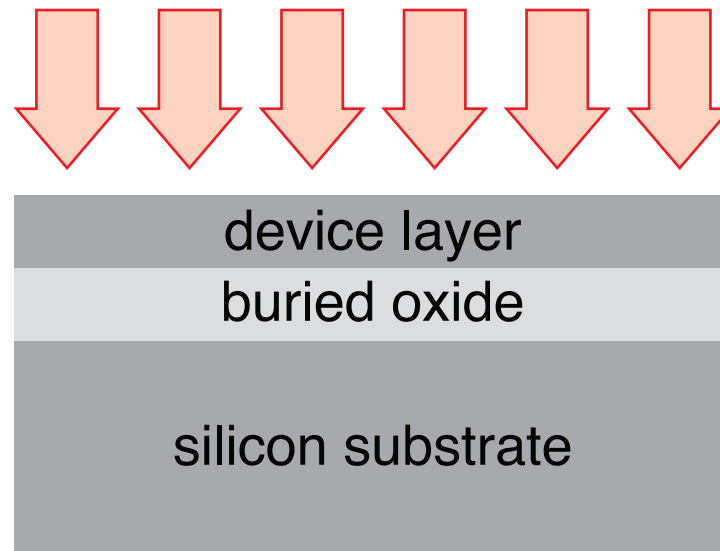
isolate surface layer for Hall measurements



1 properties

2 intermediate band

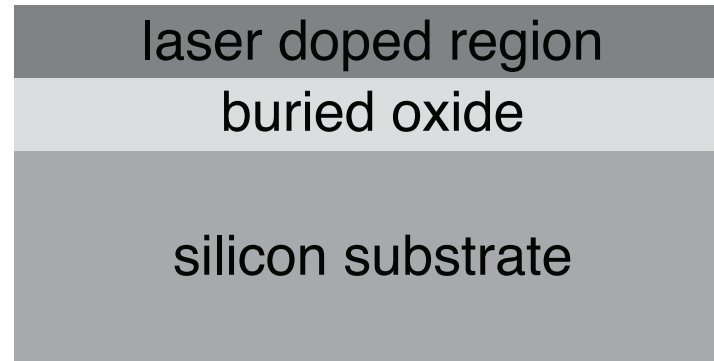
isolate surface layer for Hall measurements



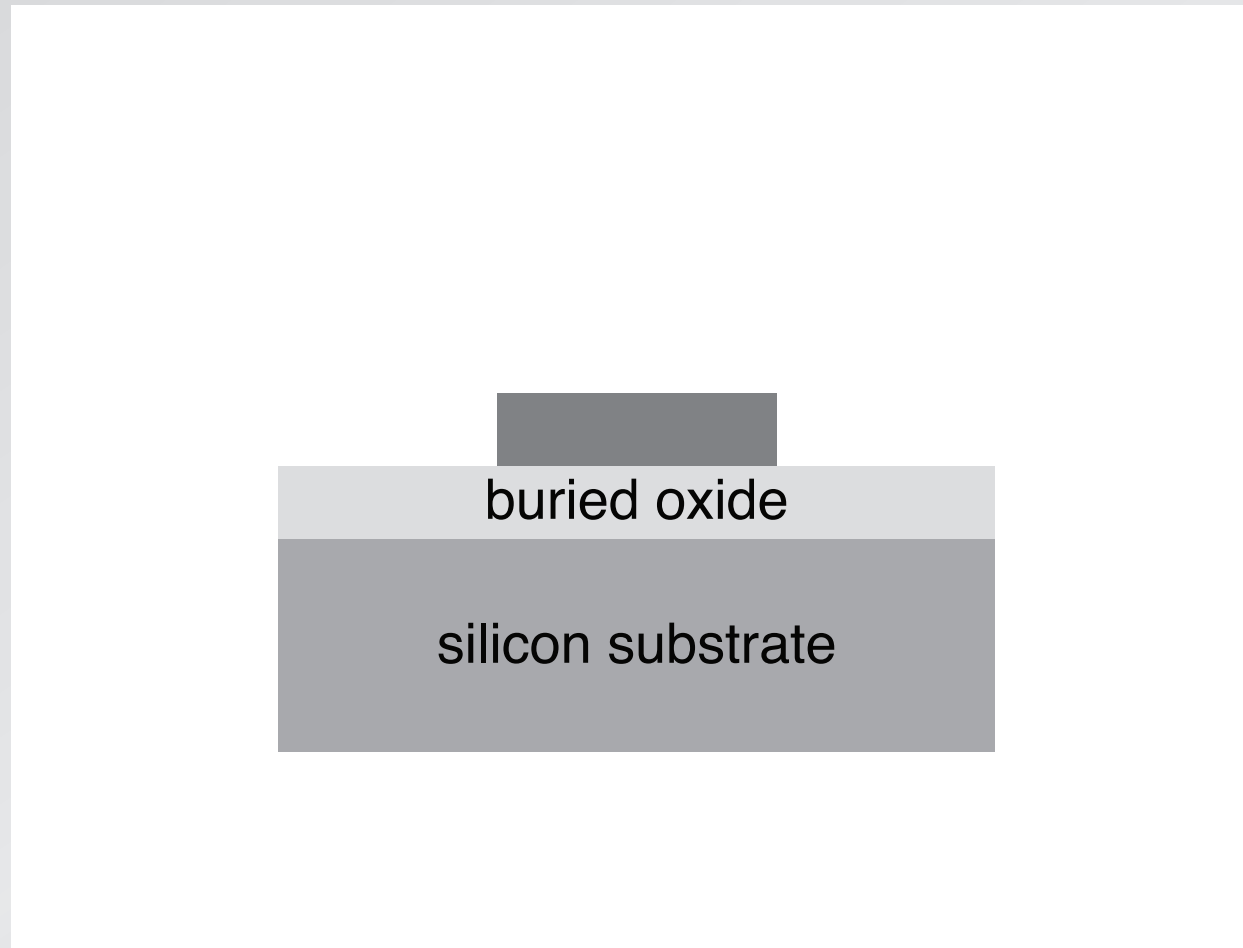
1 properties

2 intermediate band

isolate surface layer for Hall measurements



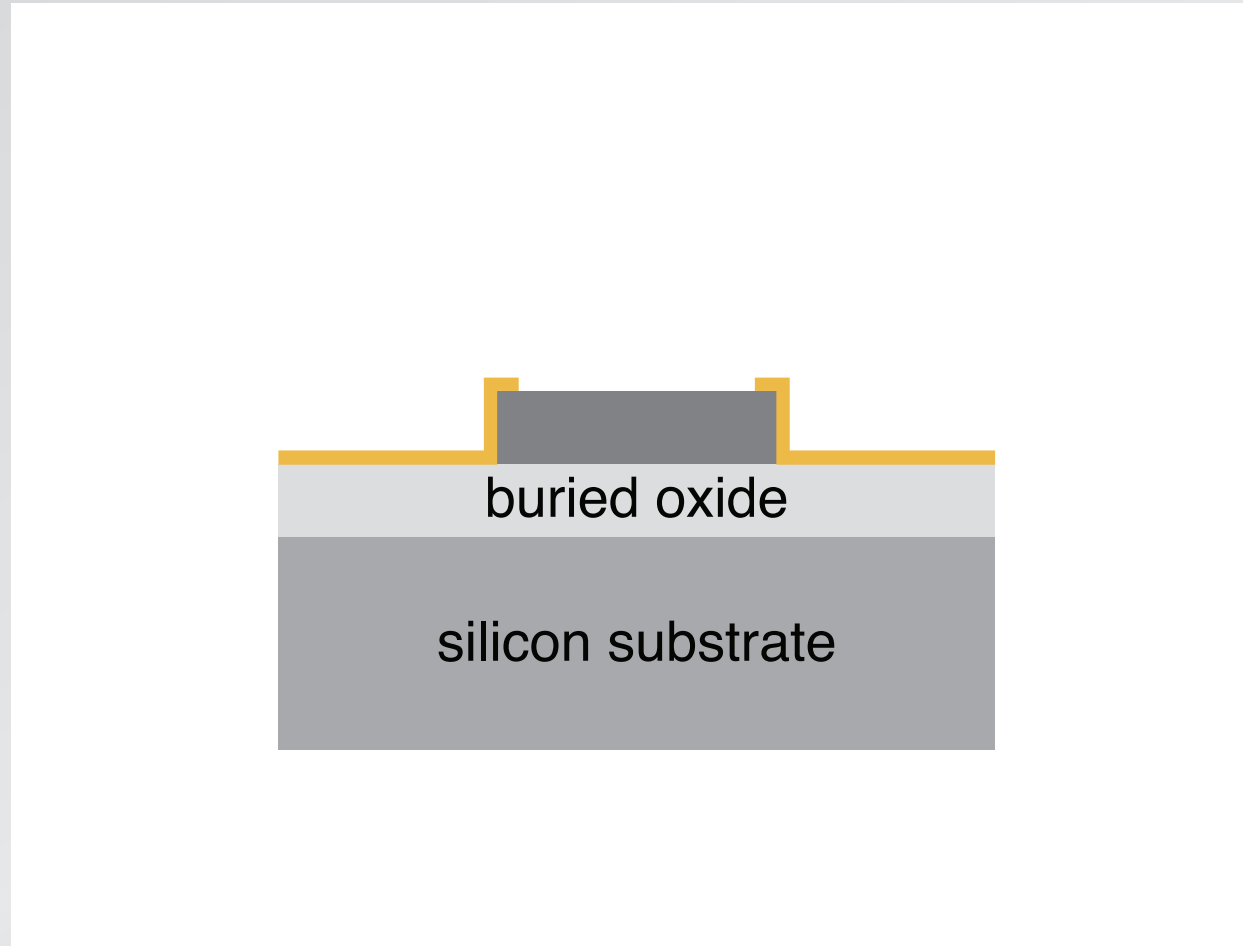
isolate surface layer for Hall measurements



1 properties

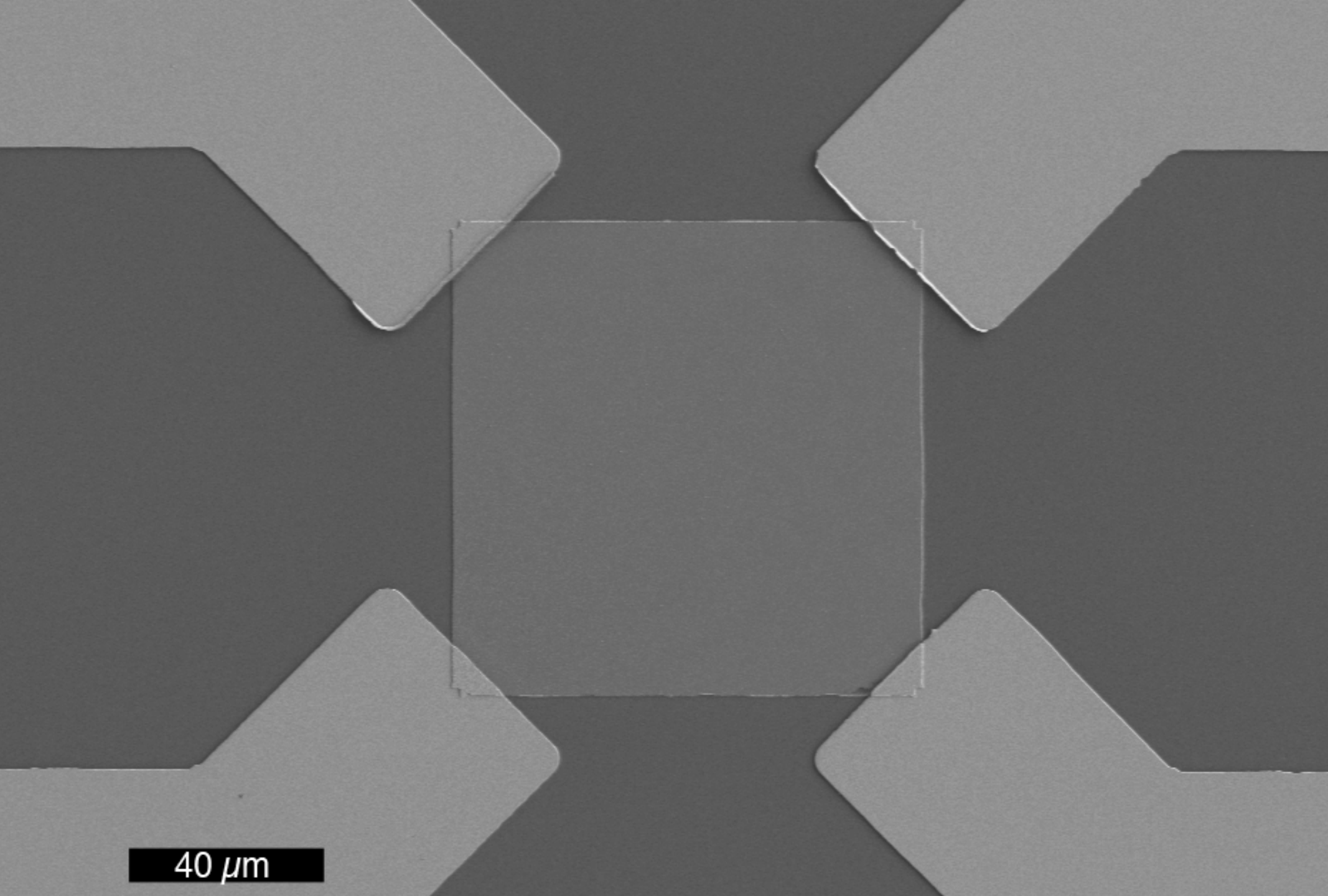
2 intermediate band

isolate surface layer for Hall measurements



1 properties

2 intermediate band

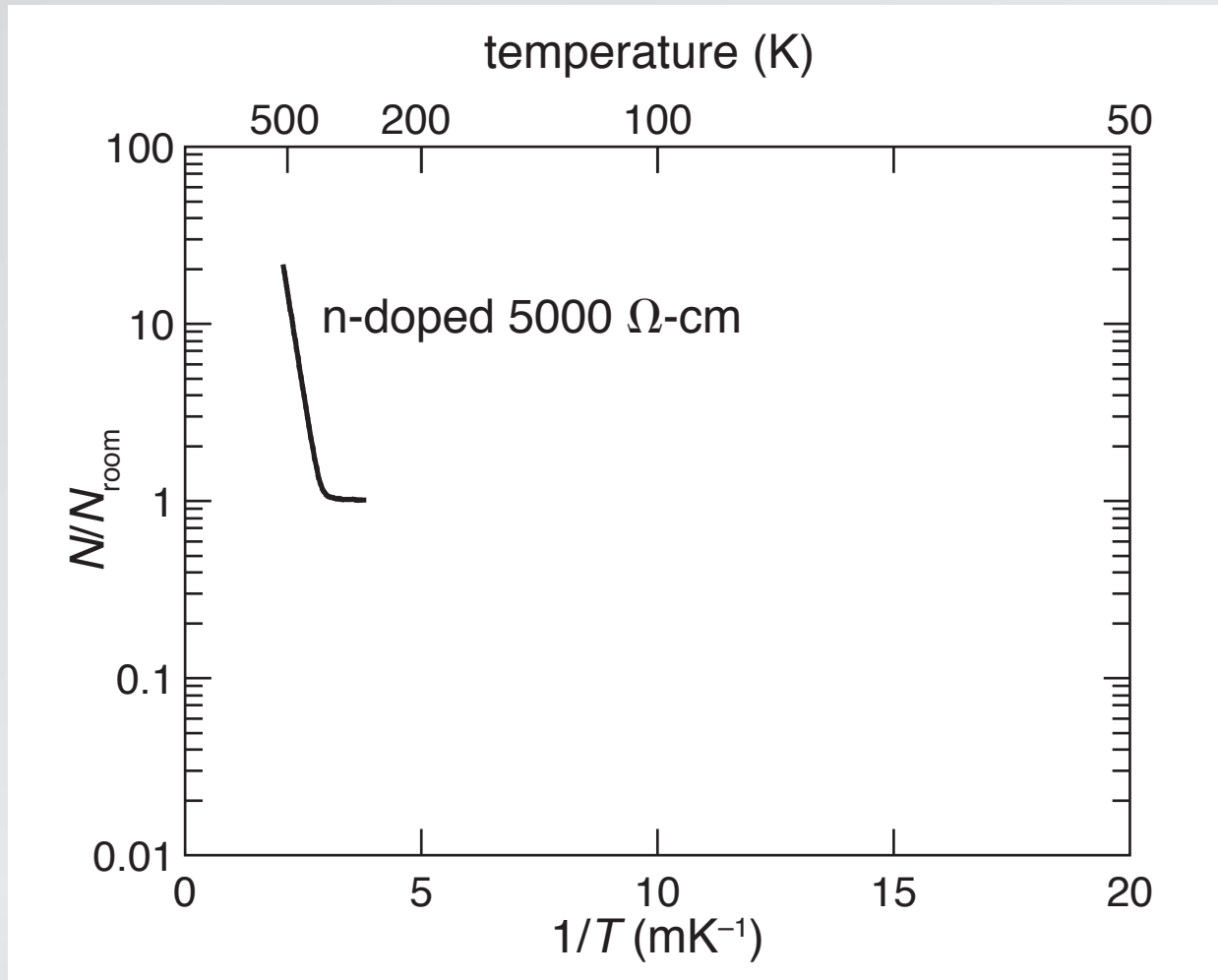


40 μm

1 properties

2 intermediate band

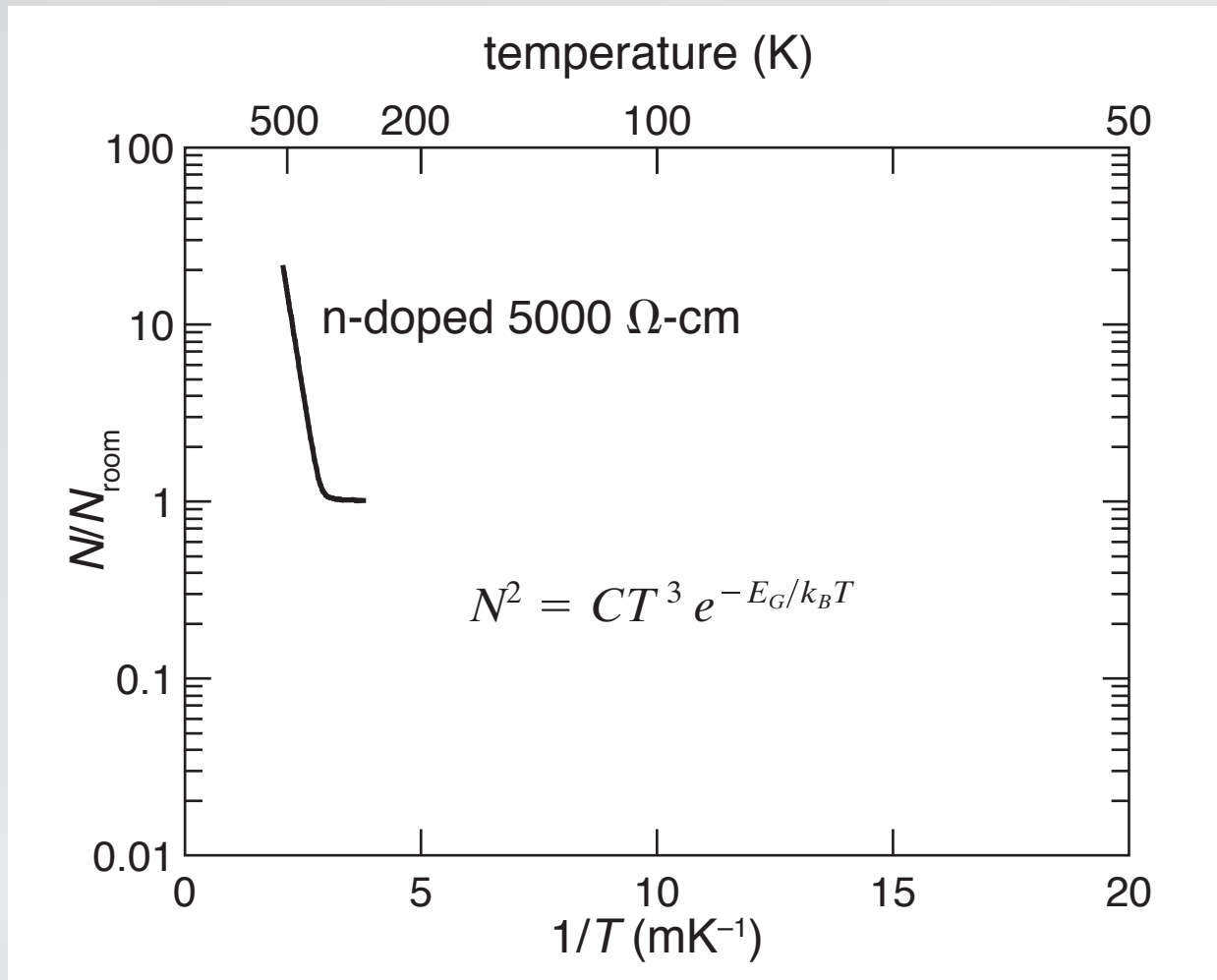
Hall measurements



1 properties

2 intermediate band

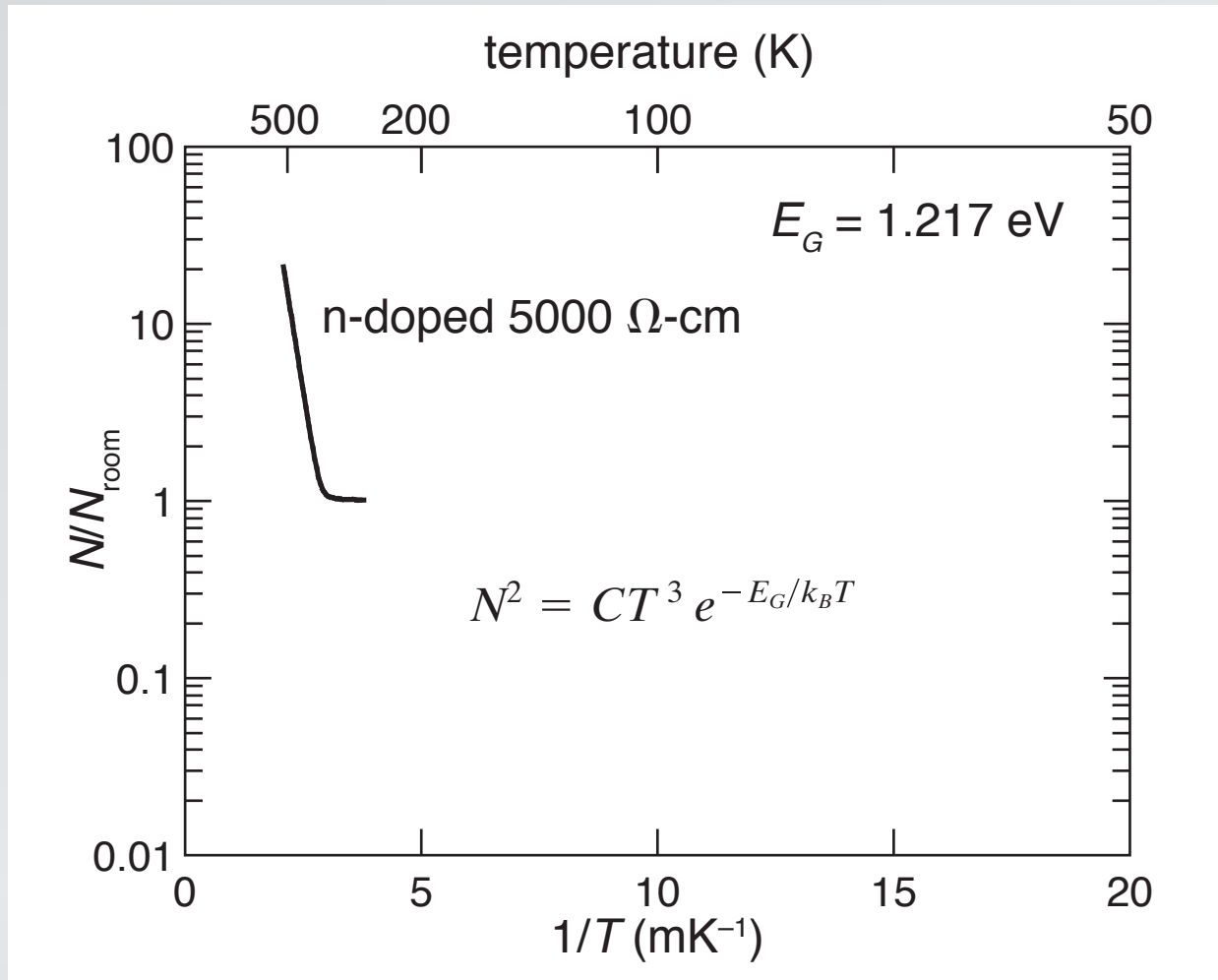
Hall measurements



1 properties

2 intermediate band

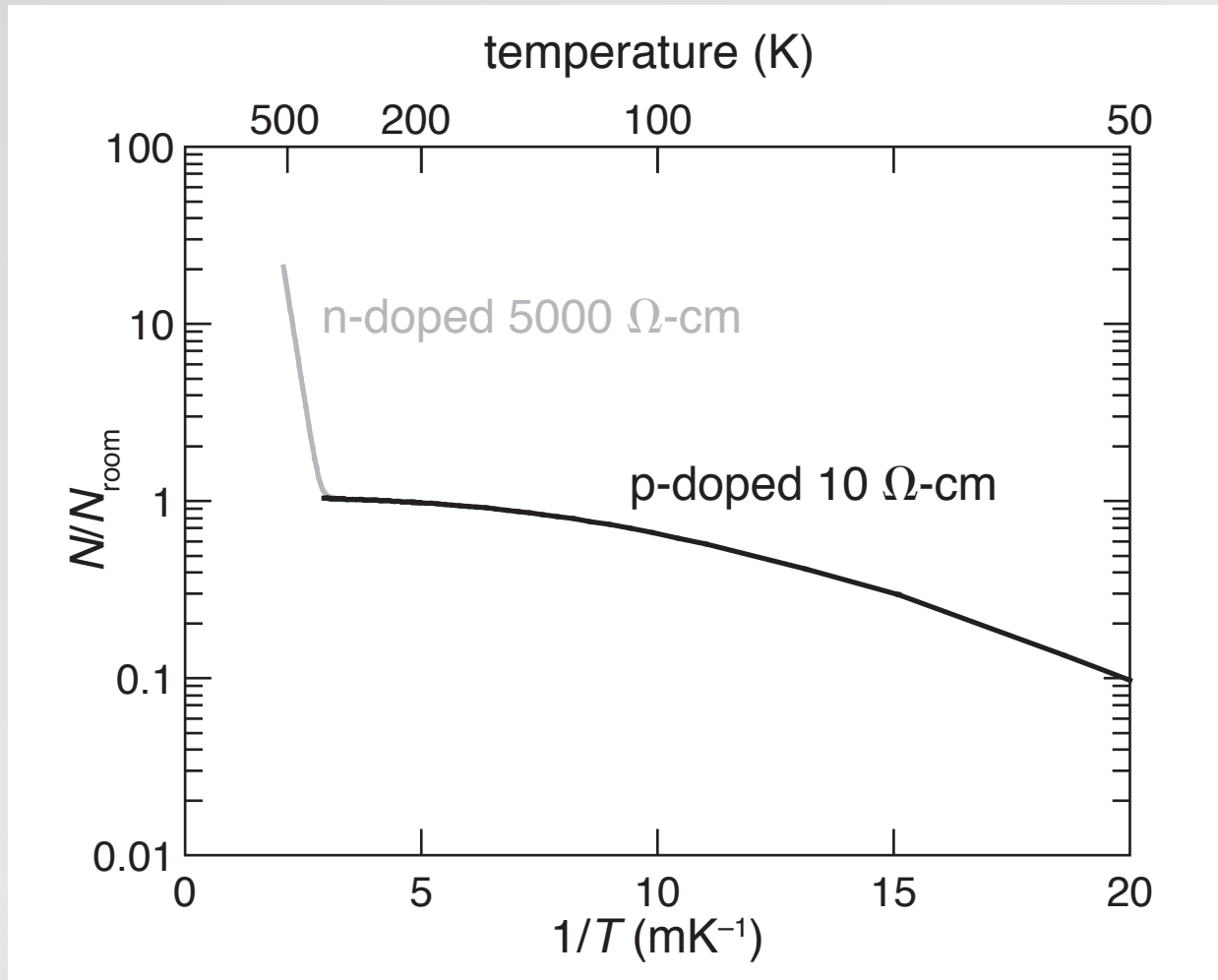
Hall measurements



1 properties

2 intermediate band

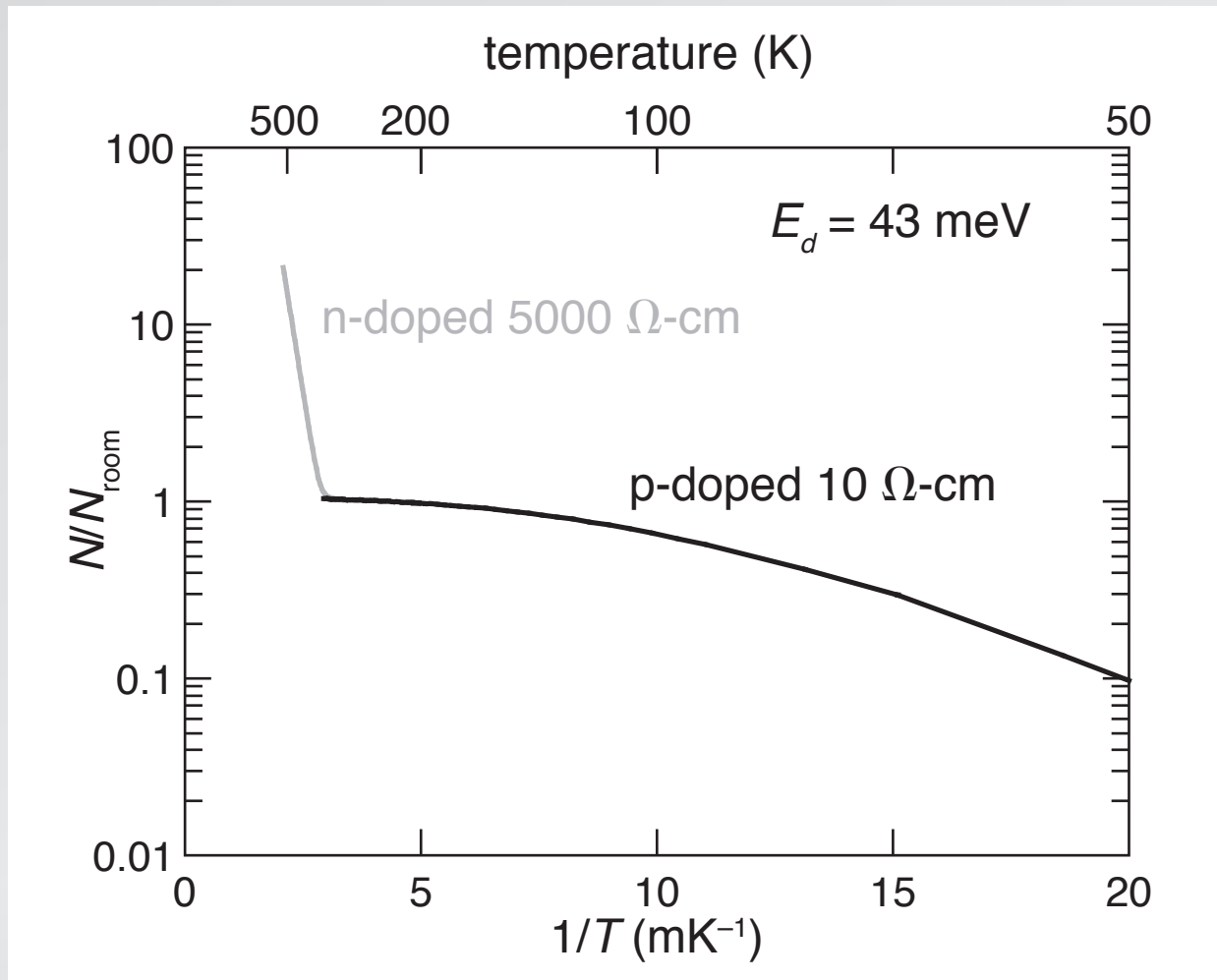
Hall measurements



1 properties

2 intermediate band

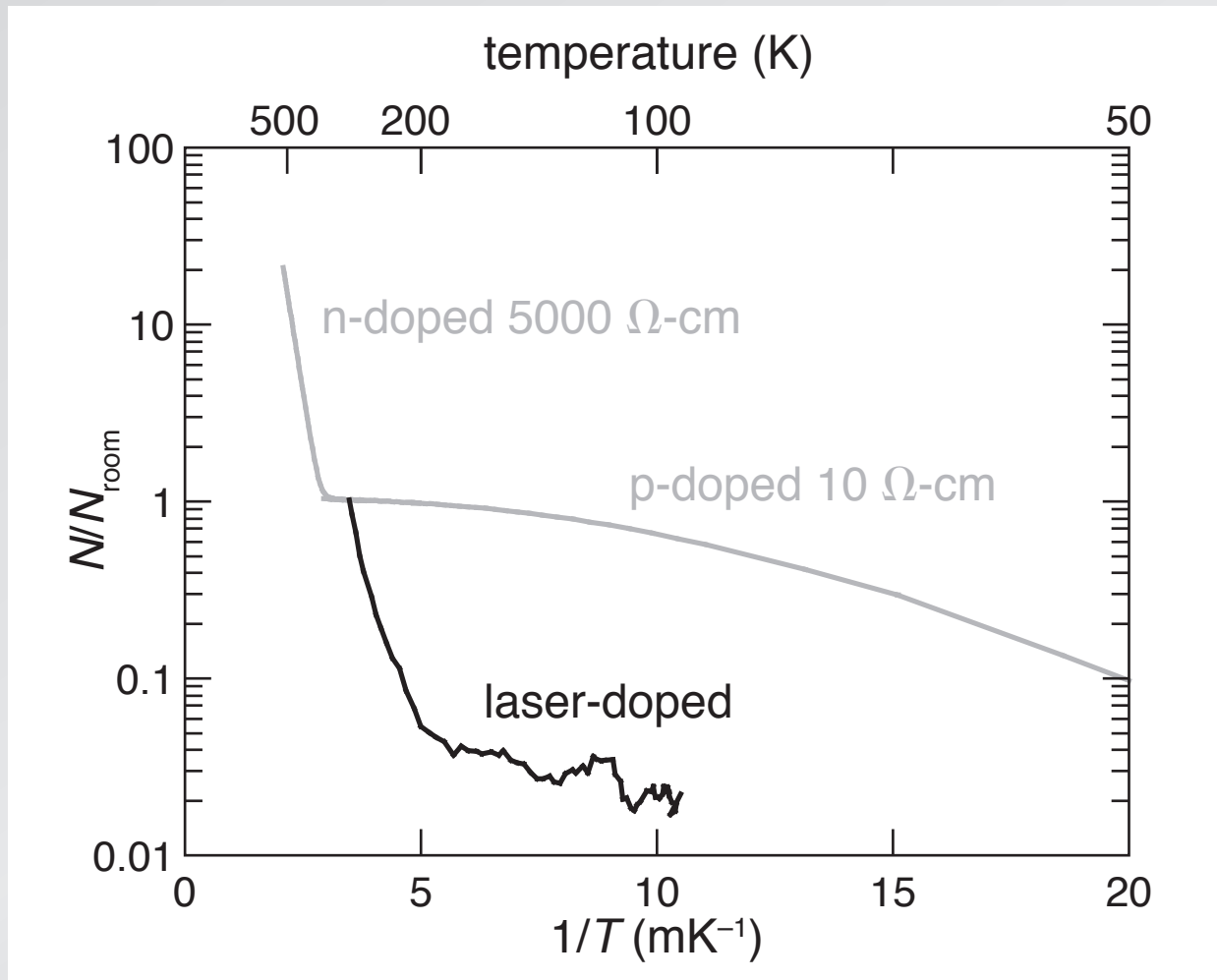
Hall measurements



1 properties

2 intermediate band

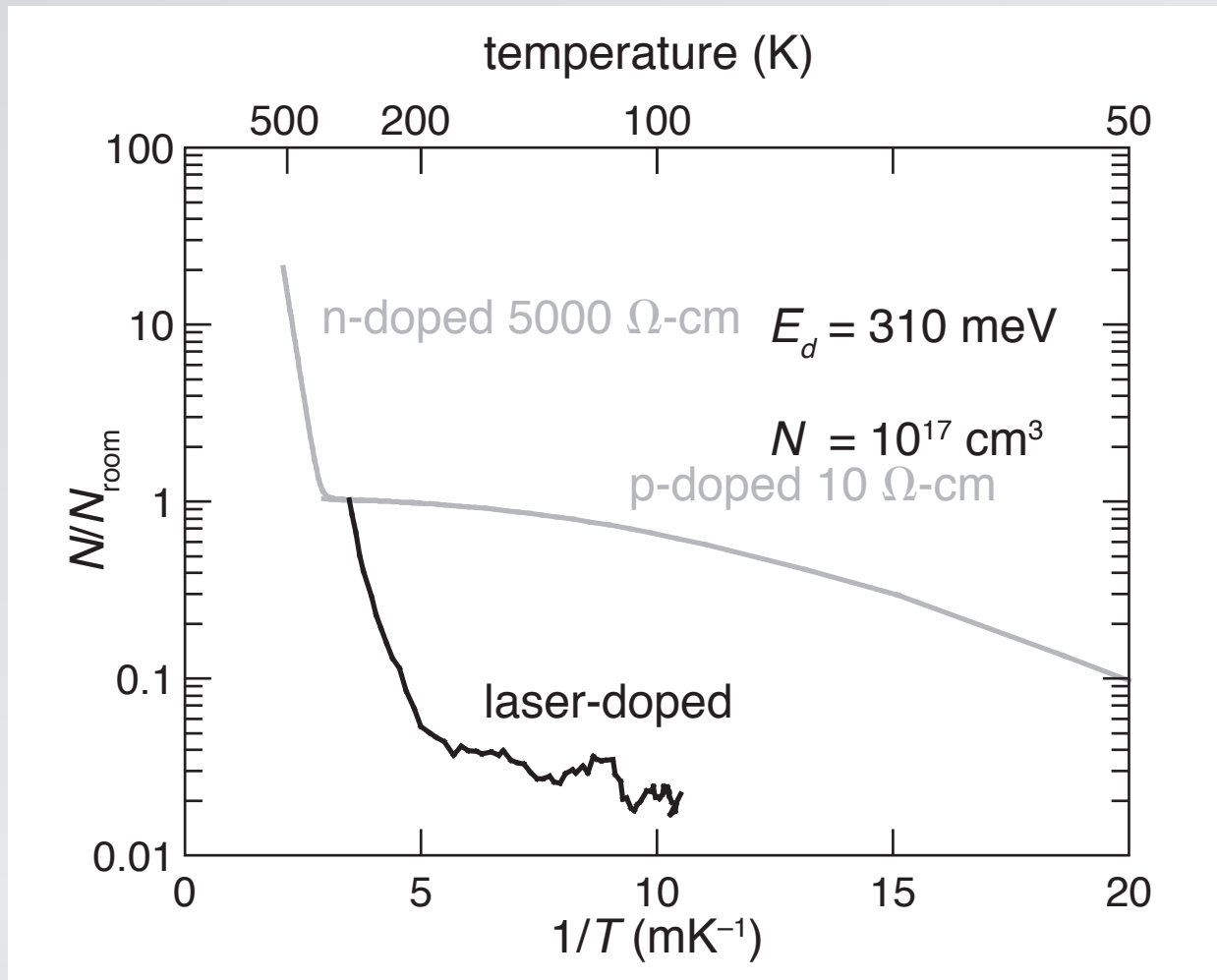
Hall measurements



1 properties

2 intermediate band

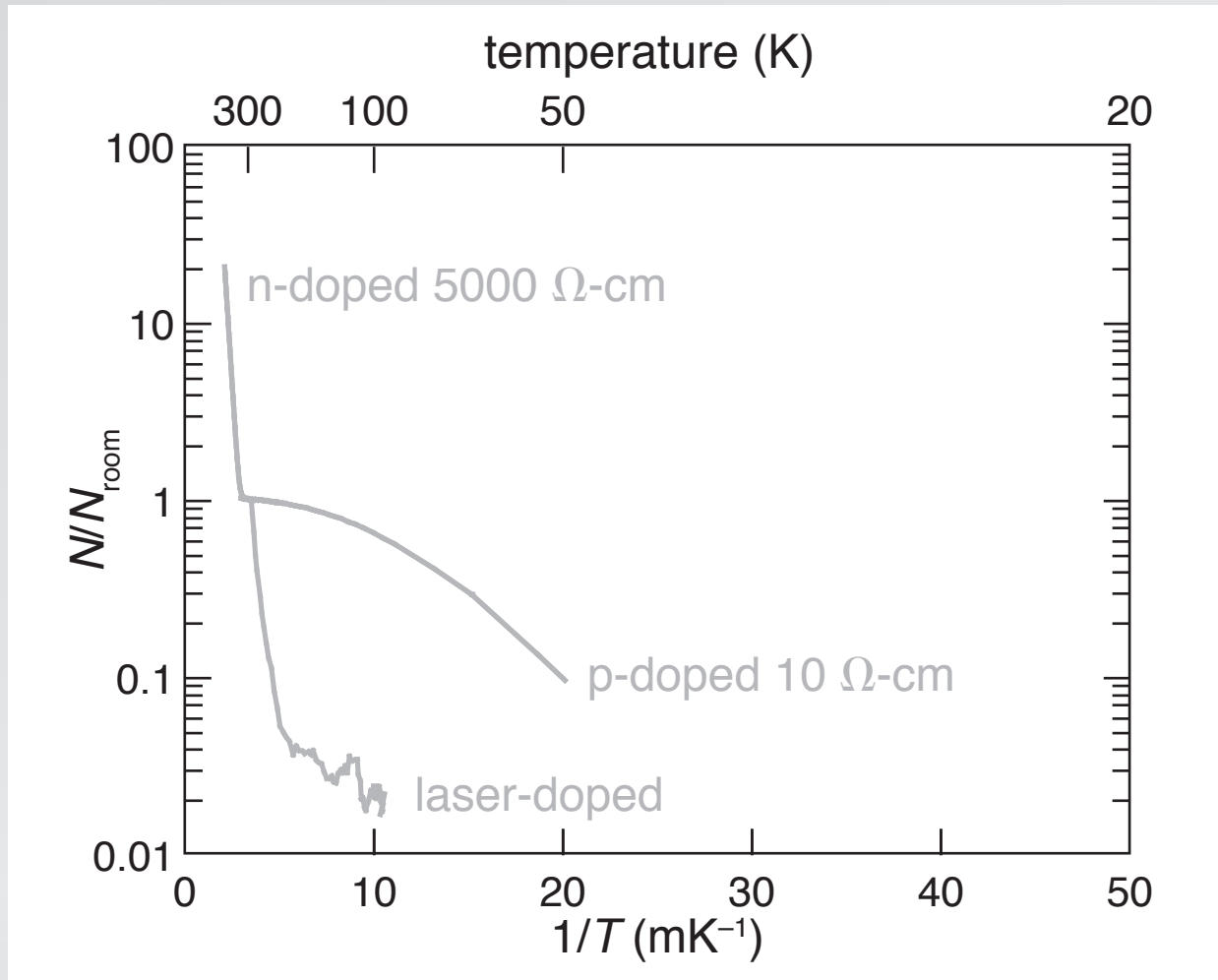
Hall measurements



1 properties

2 intermediate band

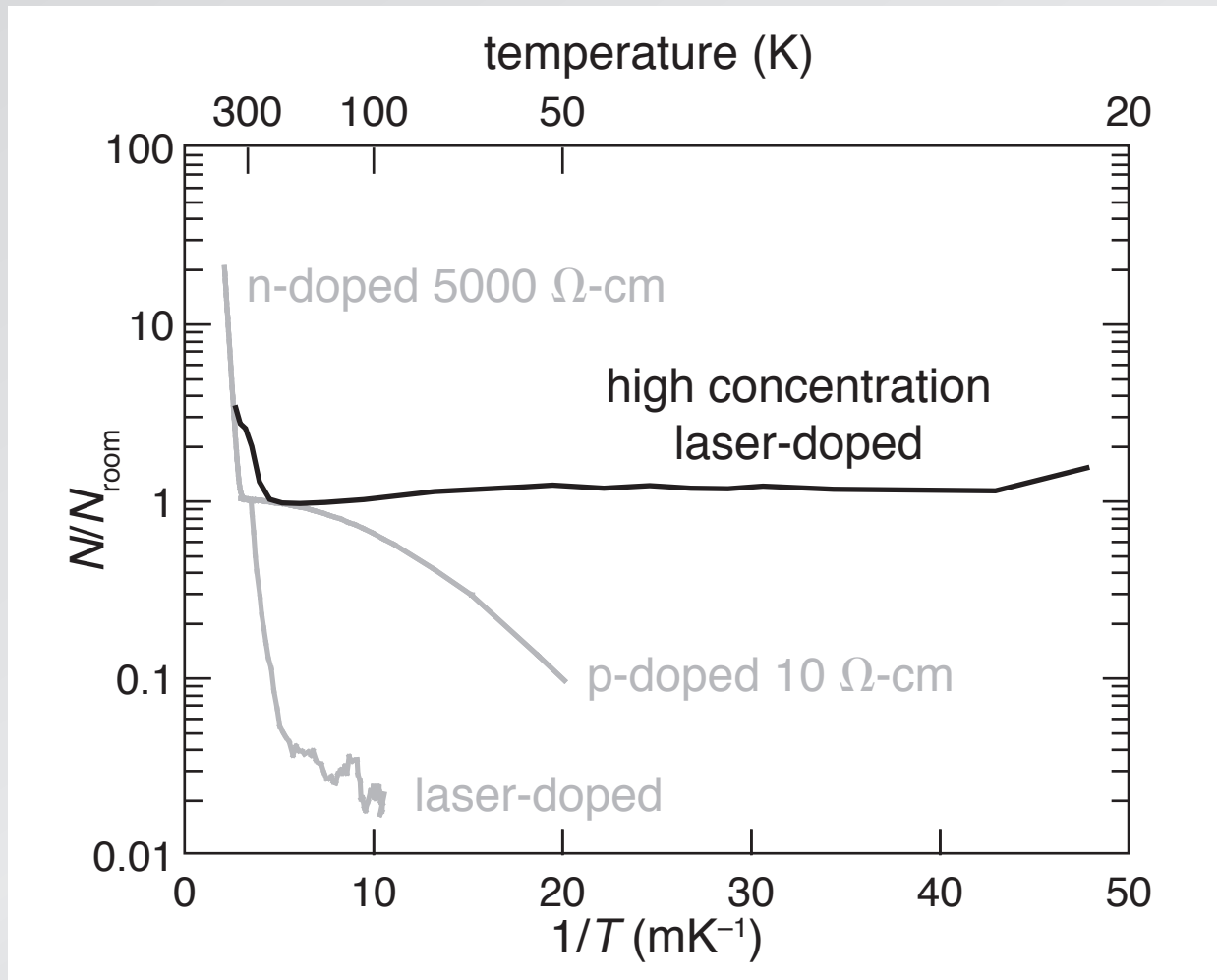
Hall measurements



1 properties

2 intermediate band

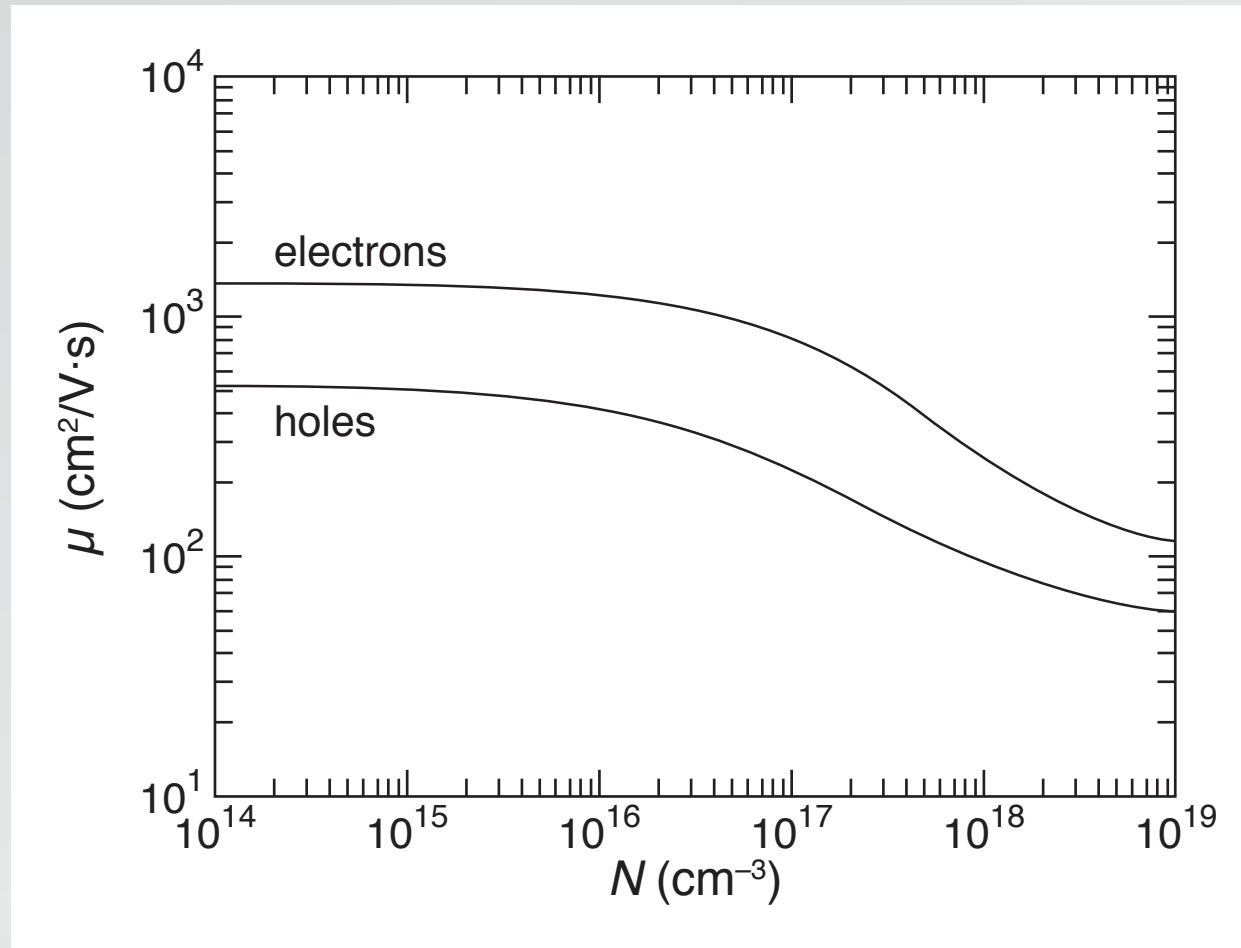
Hall measurements



1 properties

2 intermediate band

majority carrier mobility

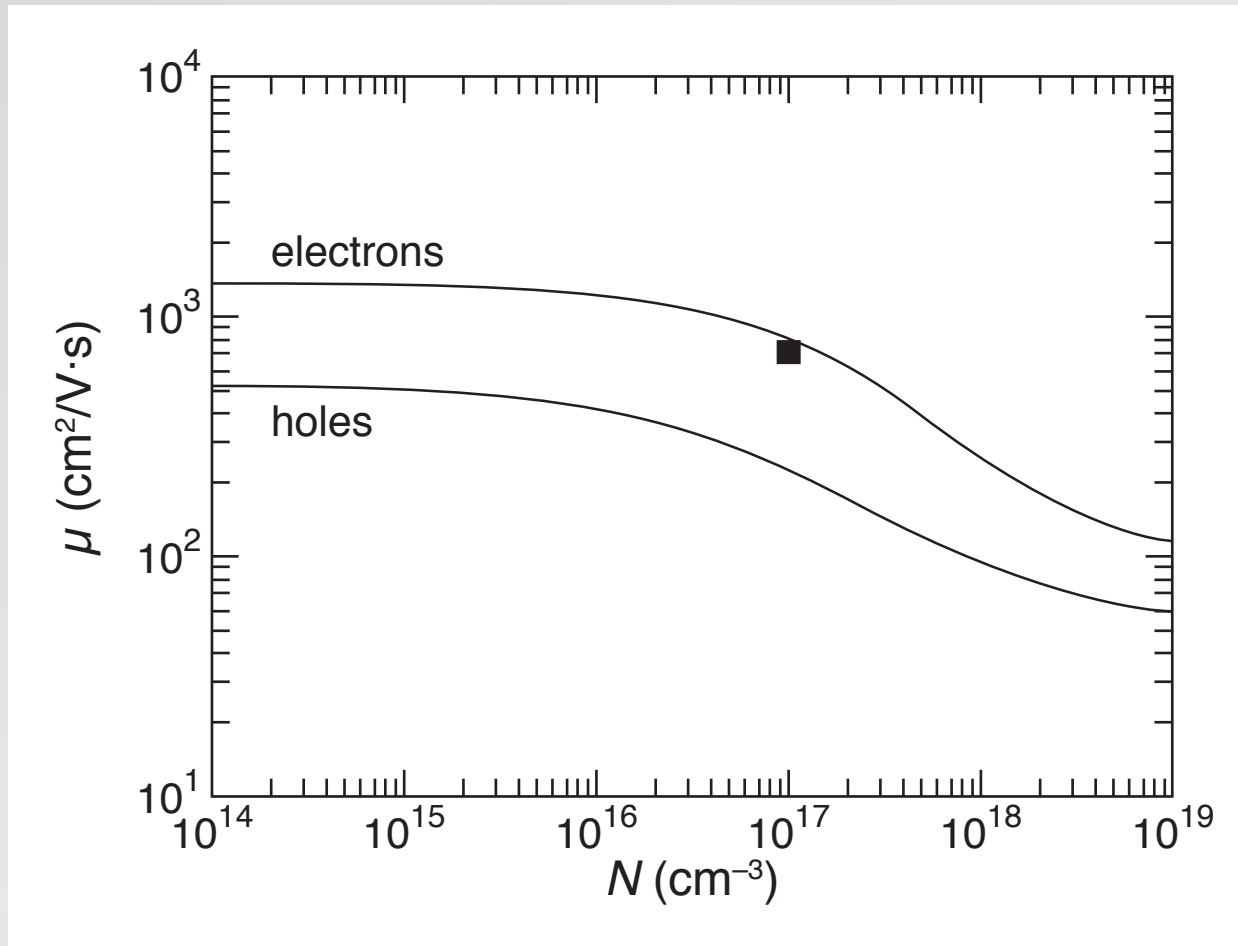


Caughey *et al.*, Proc. IEEE 55, 2192 (1967)

1 properties

2 intermediate band

majority carrier mobility

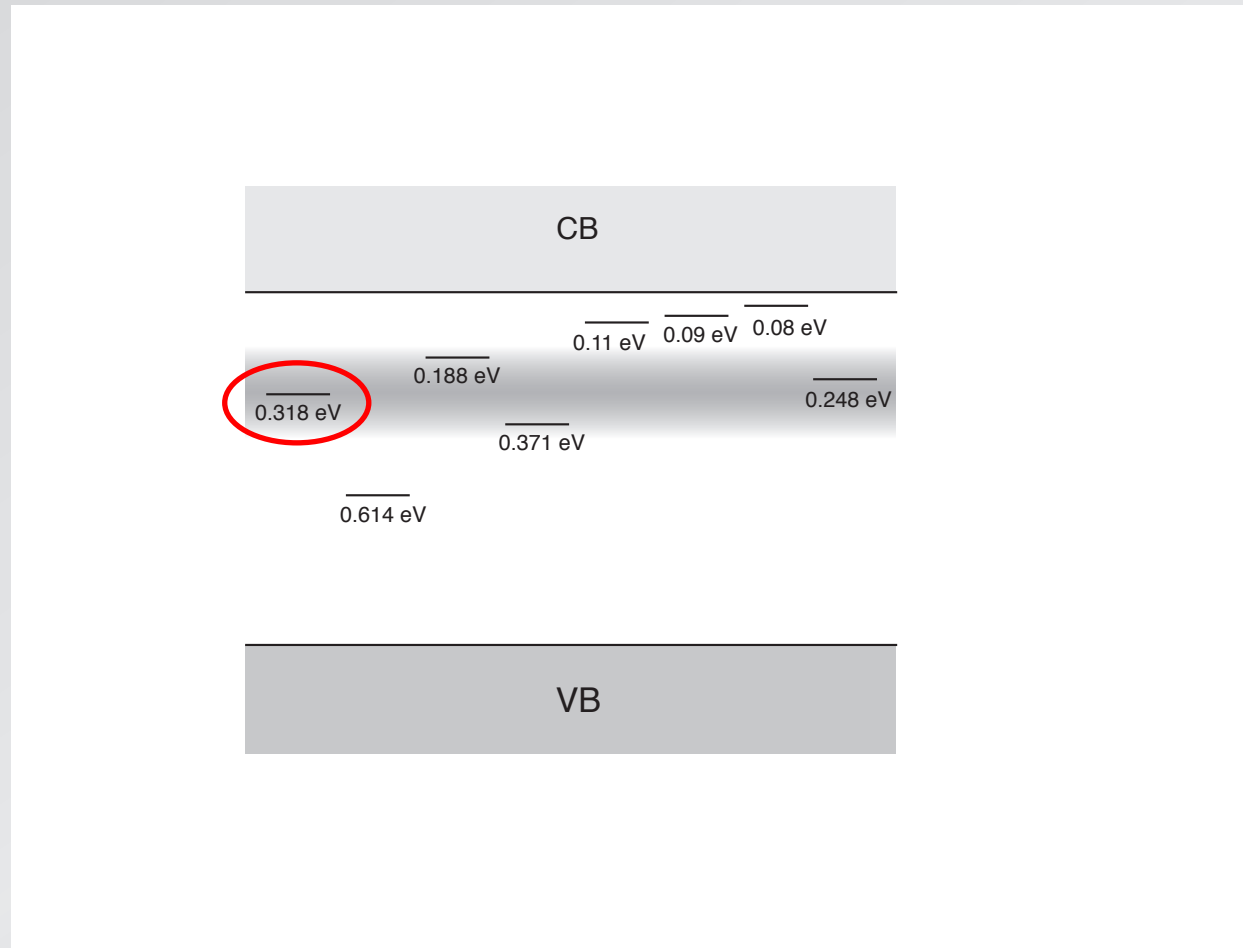


Caughey *et al.*, Proc. IEEE 55, 2192 (1967)

1 properties

2 intermediate band

impurity (donor) band centered at 310 meV



1 properties

2 intermediate band

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

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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.

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

DOI: 10.1103/PhysRevLett.108.026401

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 equilibrium solubility limit [3] of about 10^{16} cm^{-3}) and we detail the nature of the transition with both experimental and theoretical methods. Additionally, we

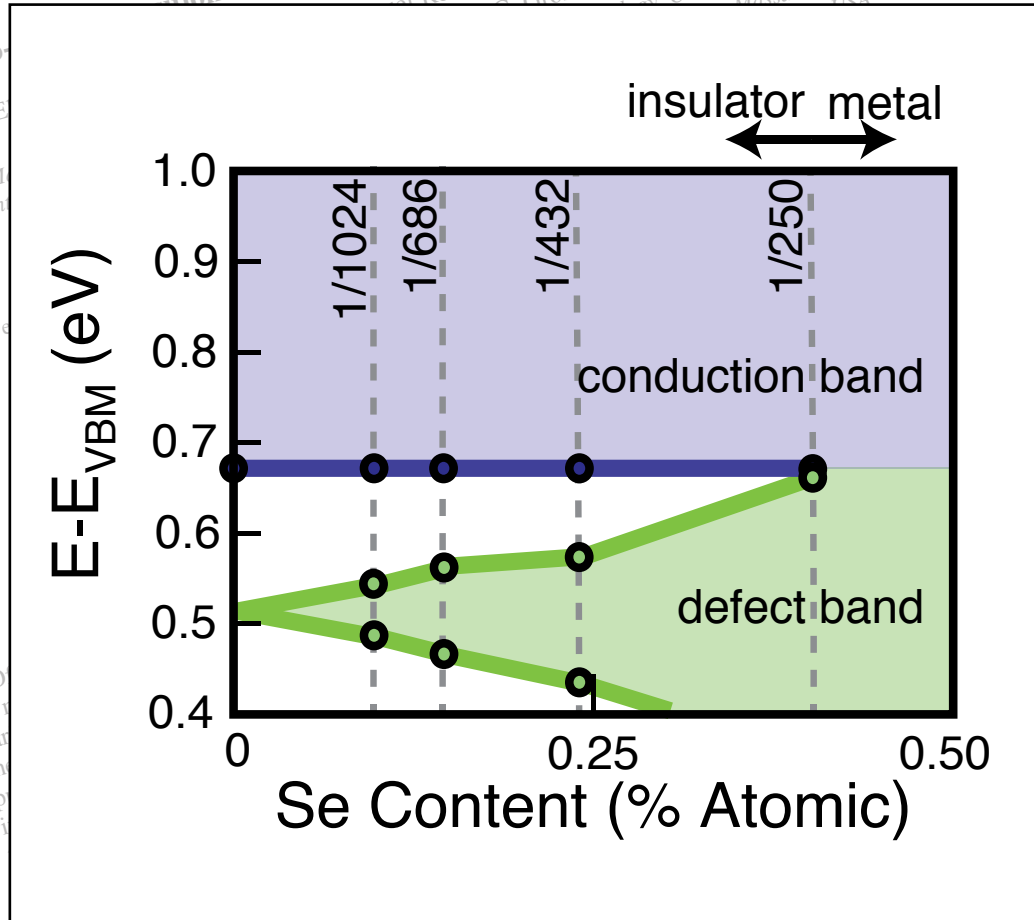
silicon appears to justify such interest. While isolated S and Se dopants are well-established deep double donors in silicon [3,14], the enhanced optical properties of hyperdoped silicon (in which these chalcogenic impurities are present at much higher concentrations) are not yet well understood. Further, 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, $\rho \approx 25 \text{ } \Omega \text{ cm}$) were ion implanted with Se to nominal doses of 3×10^{15} and $1 \times 10^{16} \text{ cm}^{-2}$ 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 Se concentration, than reported previously [18]. The electrically isolated from the crystalline, extends approximately 350 nm between electrically isolated from the measured

1 properties

2 intermediate band

DFT calculations



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

1 properties

2 intermediate band

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

Ikurou Umezu,¹ Jeffrey M. Warrender,² Supakit Charnvanichborikarn,³ Atsushi Kohno,⁴ James S. Williams,³ Malek Tabbal,⁵ Dimitris G. Papazoglou,^{6,7} Xi-Cheng Zhang,^{8,a)} and Michael J. Aziz⁹

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³Research School of Physics and Engineering, The Australian National University, Canberra, ACT 0200, Australia

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(Received 9 September 2012; accepted 29 April 2013; published online 3 June 2013)

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.

I. INTRODUCTION

Silicon hyperdoped with chalcogens can be synthesized by pulsed laser irradiation in a sulfur-bearing atmosphere,^{1,2} 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}

Hyperdoping has been shown to cause an intermediate bandgap^{4,10,14–16} However, the details of the hyperdoping mechanism has been proposed to form an intermediate bandgap.¹⁷ The details of the hyperdoping mechanism has been reported elsewhere.³ For the samples, the details of the hyperdoping mechanism is the same.

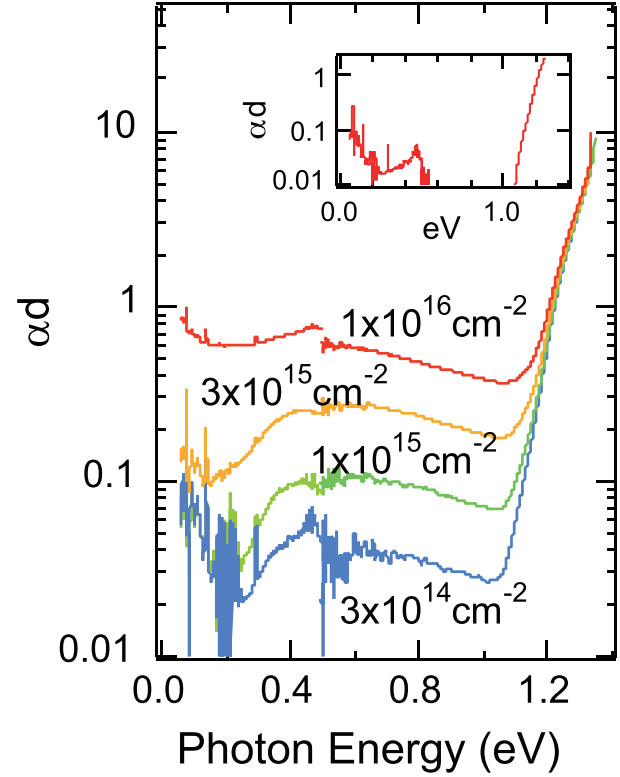
II. EXPERIMENT

Double side polished p type (001) Si wafers, resistivity of 5–25 Ω cm, were ion implanted at room temperature with either 95 keV ³²S⁻, 176 keV ⁸⁰Se⁺, or 245 keV ¹³⁰Te⁺ to doses of 1 × 10¹⁶ ions/cm². The dose of ³²S⁻ was varied from 3 × 10¹⁴ to 1 × 10¹⁶ ions/cm² and pre-amorphized by 85 keV Si⁻ to doses of 3 × 10¹⁵ ions/cm². 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/cm² followed by a fourth laser shot at 1.8 J/cm². 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 method of chalcogen atoms observed by secondary ion mass spectrometry.¹⁸ The details of the sample preparation method are reported elsewhere.³ For the samples, the details of the hyperdoping mechanism is the same.

Emergence of very broad infrared absorption band by hyperdoping of silicon

Ikuro Umezu,¹ Jeffrey Williams,² and Michael J. Aziz³
¹Department of Physics, MIT
²U.S. Army ARDEC, Ft. Belvoir, Illinois
³Research School of Engineering, Australian National University

Shrikant, Atsushi Kohno,⁴ and Shuang Zhang,^{5,a)}



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

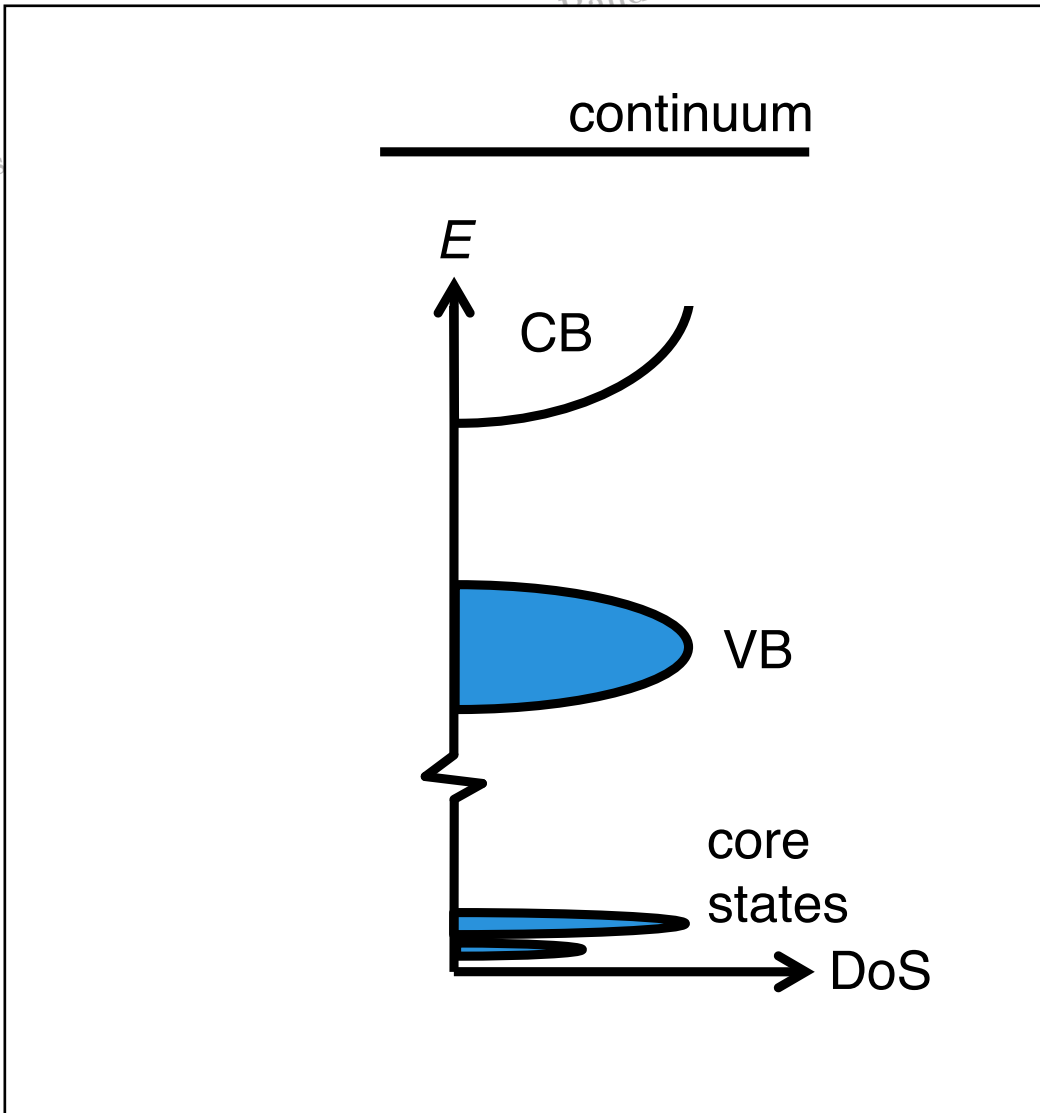
This thesis explores the electronic structure, optical properties, and carrier lifetimes in silicon that is doped with sulfur beyond the equilibrium solid solubility limit, with a focus on applications as an absorber layer for an impurity-band photovoltaic device. The concept of an impurity-band material 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 spectroscopy. The complex index of refraction is performed using numerical simulation. The position of the sulfur-induced states within the band structure is determined by transmission and reflection measurements and the position of the sulfur-induced states within the band structure is determined by transmission and reflection measurements and the position of the sulfur-induced states within the band structure is determined by transmission and reflection measurements.

1 properties

2 intermediate band

Unders

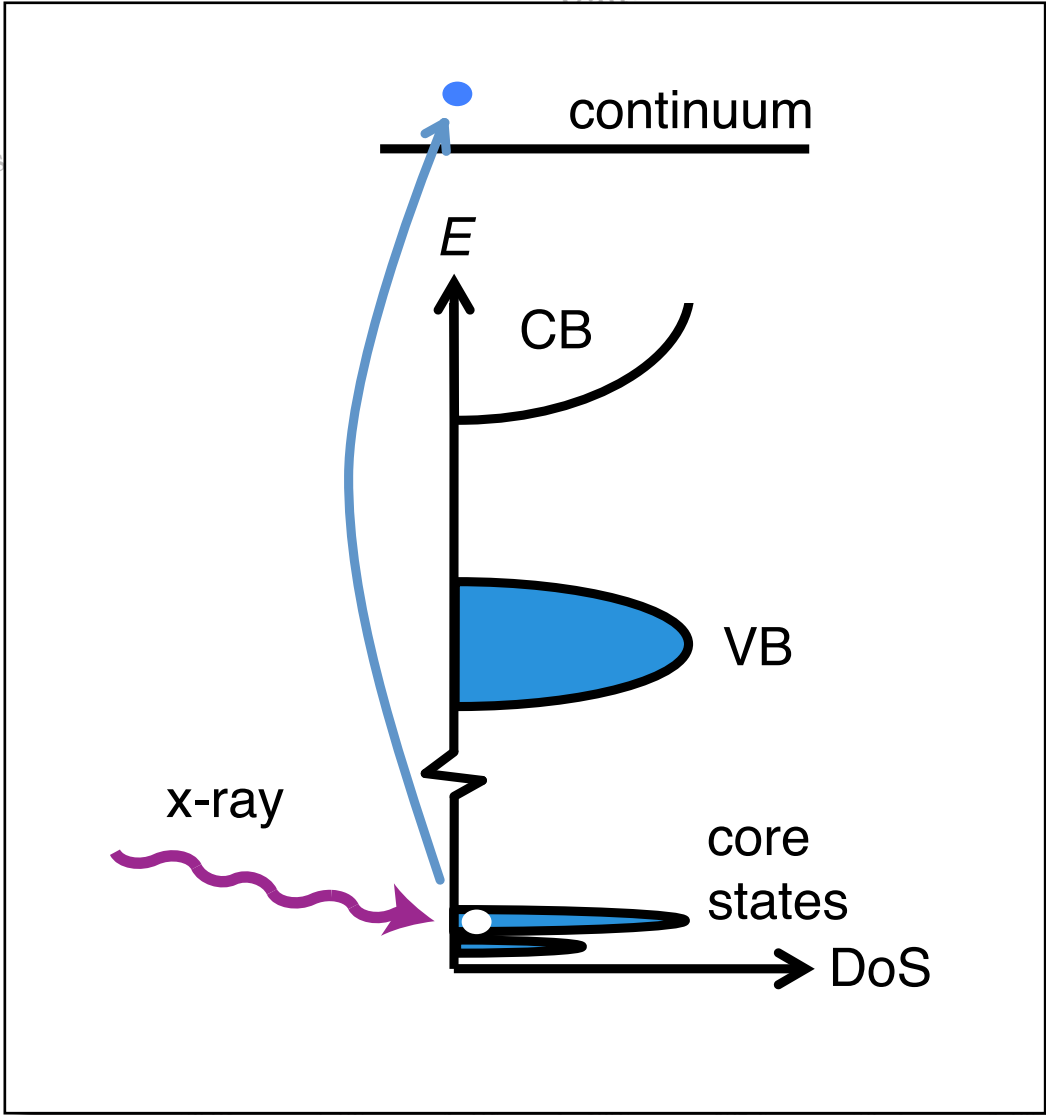


J. Sullivan, Ph.D. Thesis, MIT (2013)

1 properties

2 intermediate band

Unders

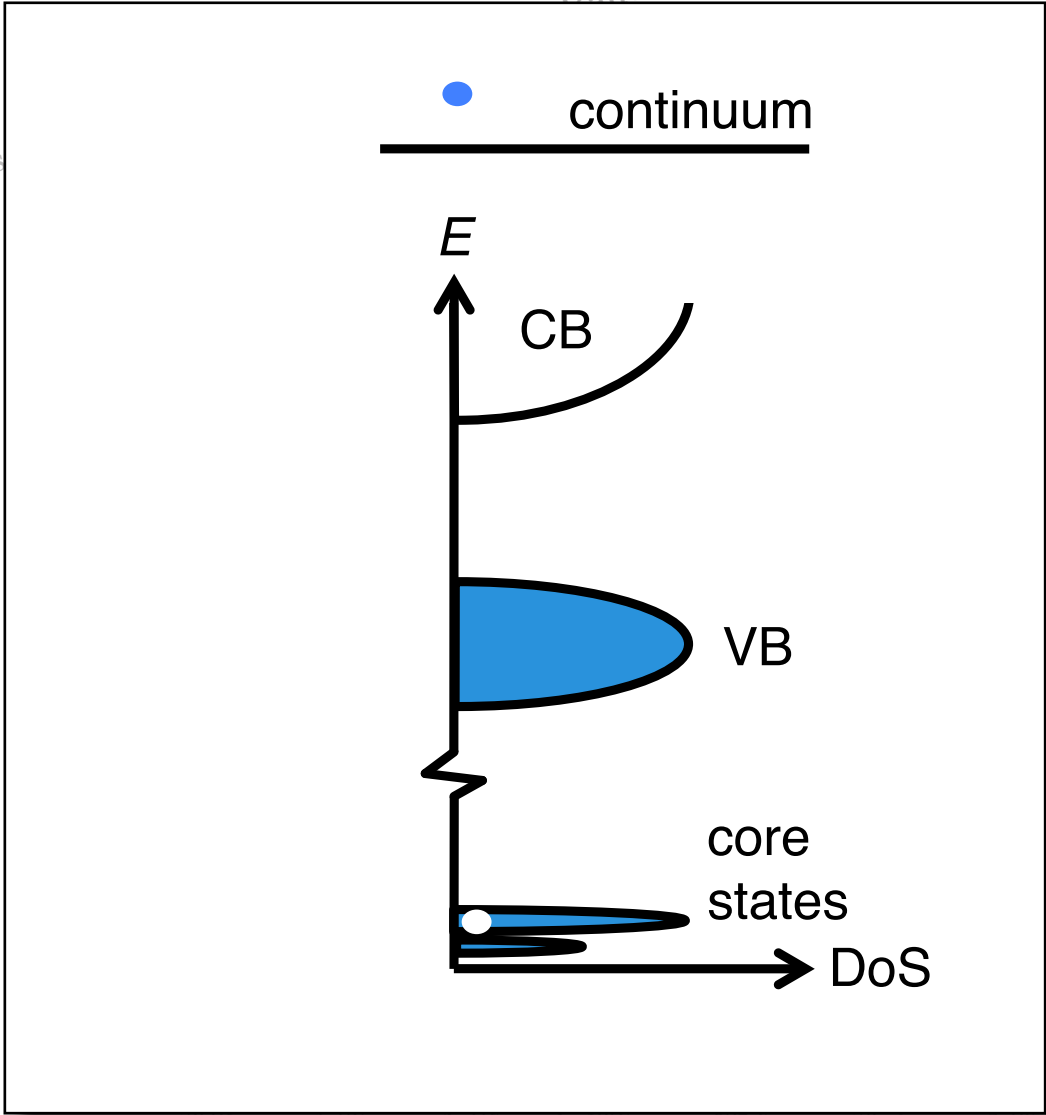


J. Sullivan, Ph.D. Thesis, MIT (2013)

1 properties

2 intermediate band

Unders

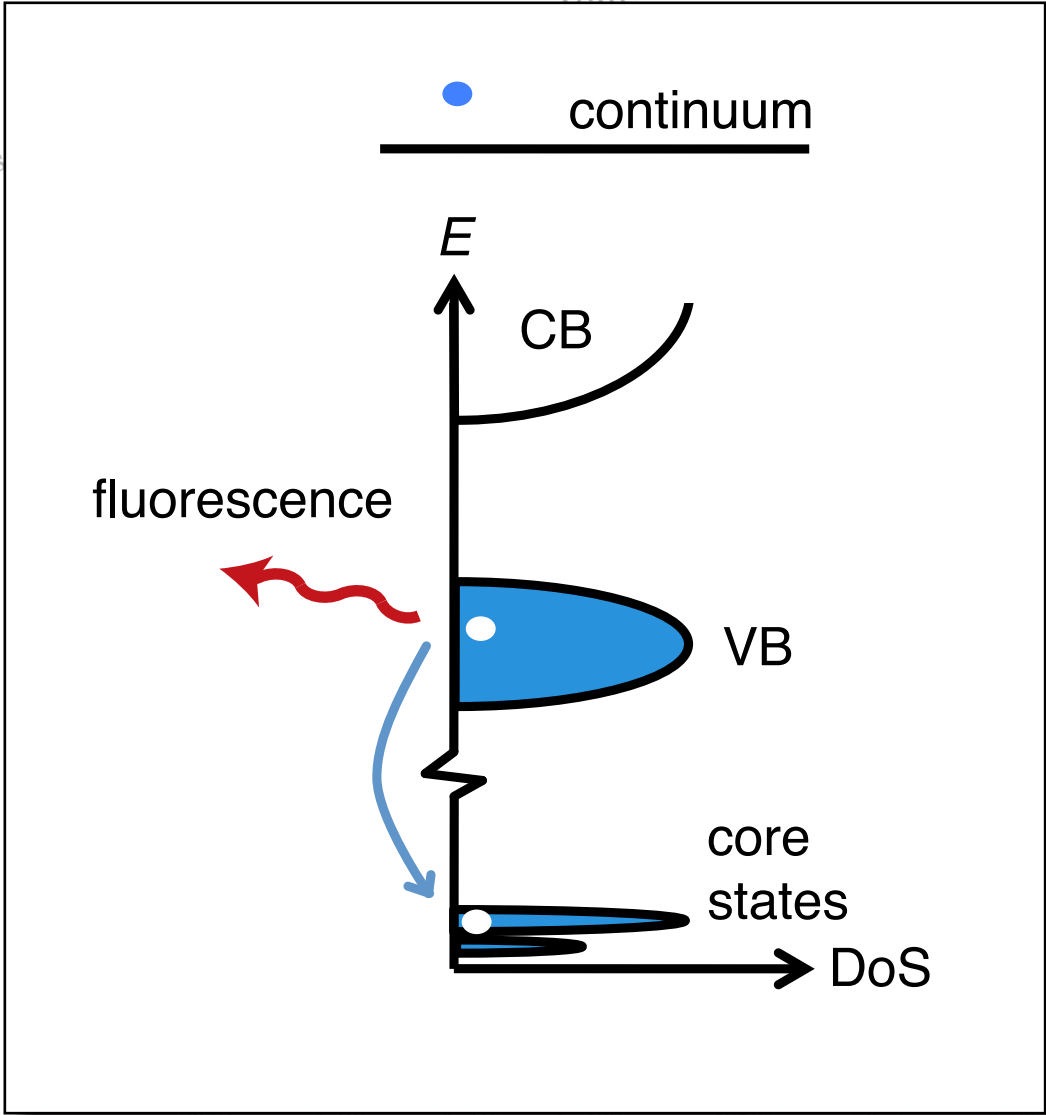


J. Sullivan, Ph.D. Thesis, MIT (2013)

1 properties

2 intermediate band

Unders

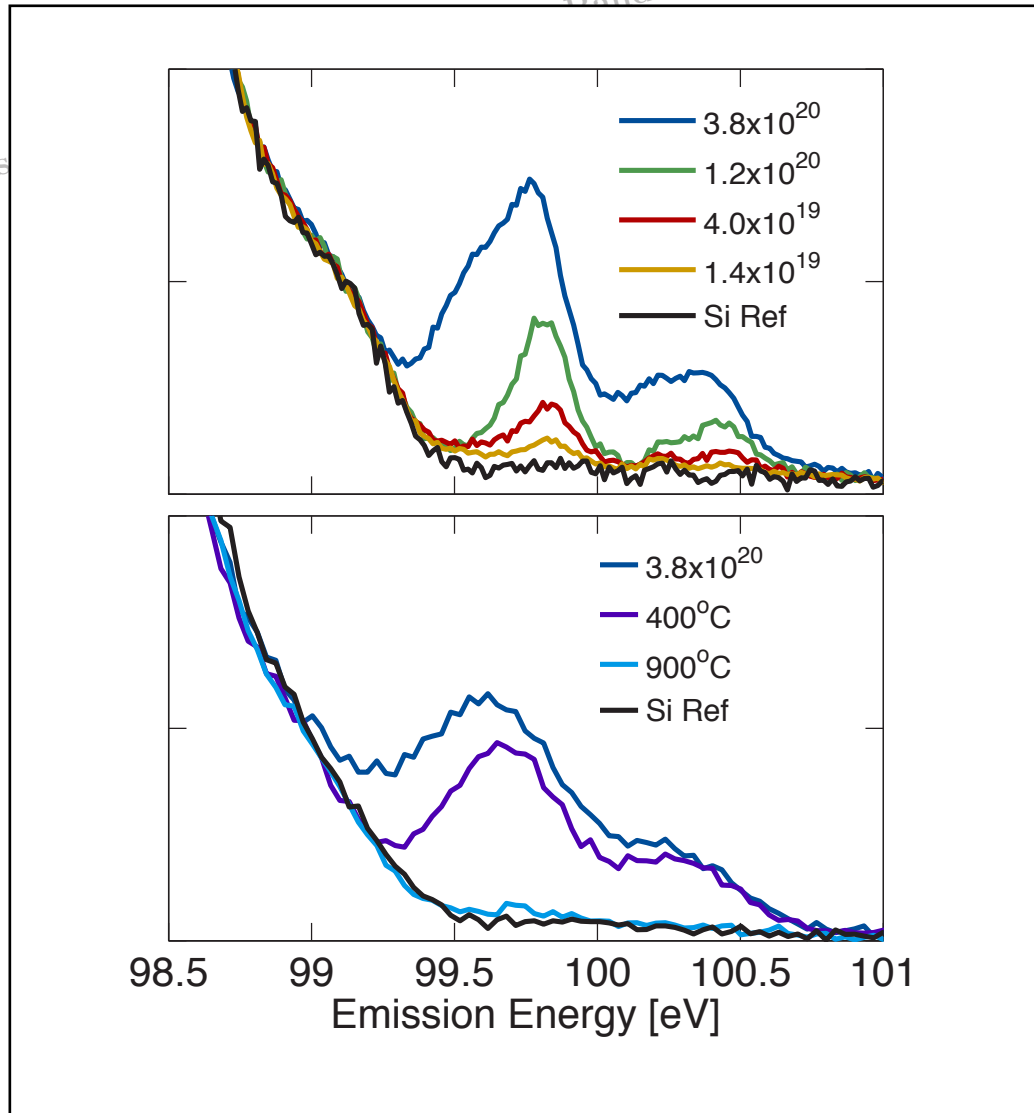


J. Sullivan, Ph.D. Thesis, MIT (2013)

1 properties

2 intermediate band

Unders



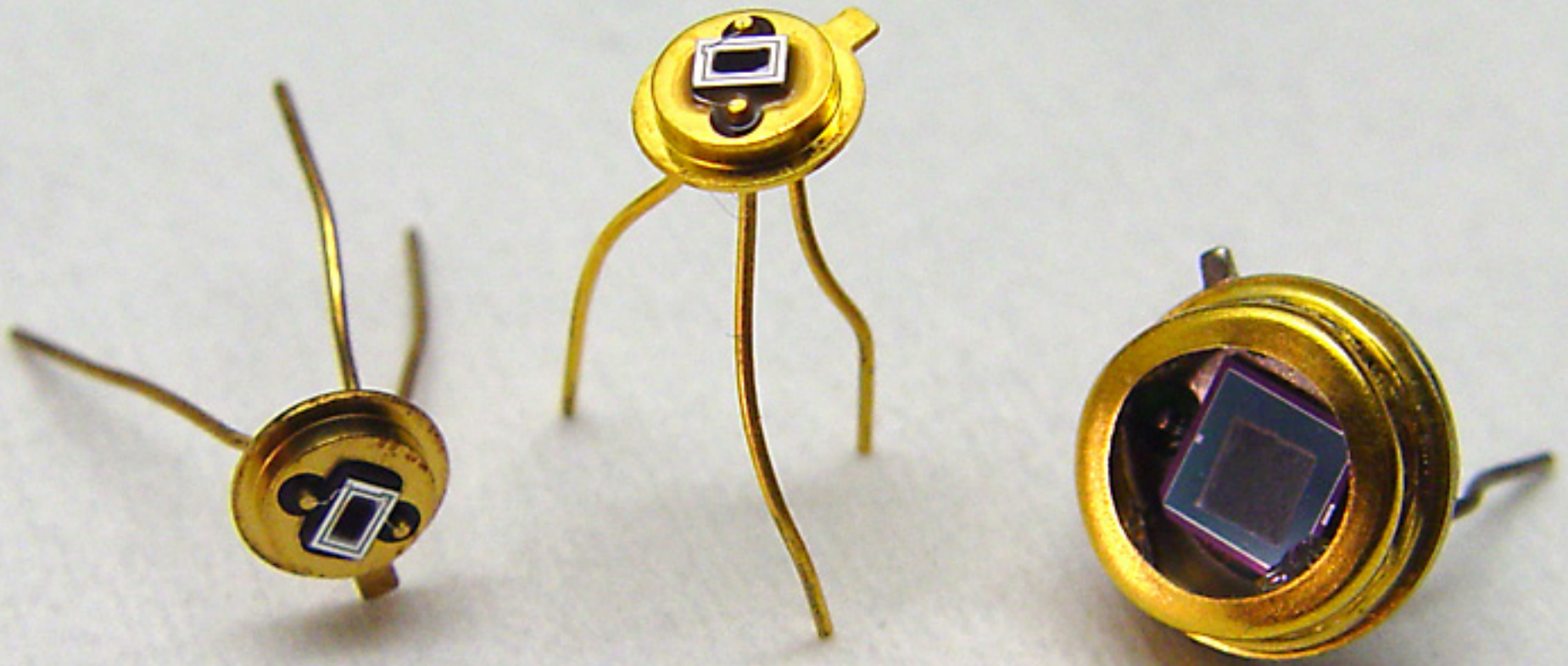
J. Sullivan, Ph.D. Thesis, MIT (2013)

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

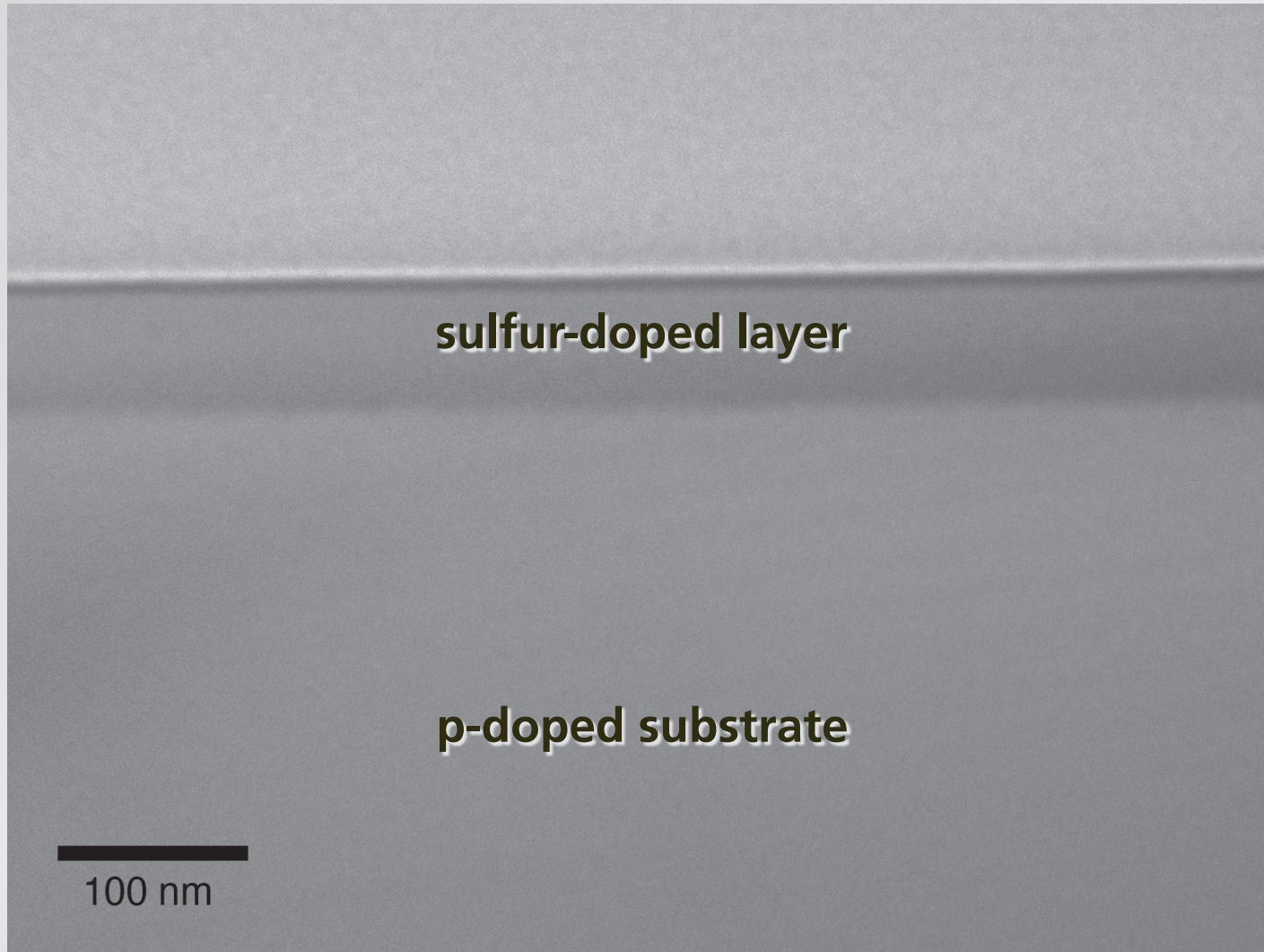


1 properties

2 intermediate band

3 devices

should have shallow junction below surface

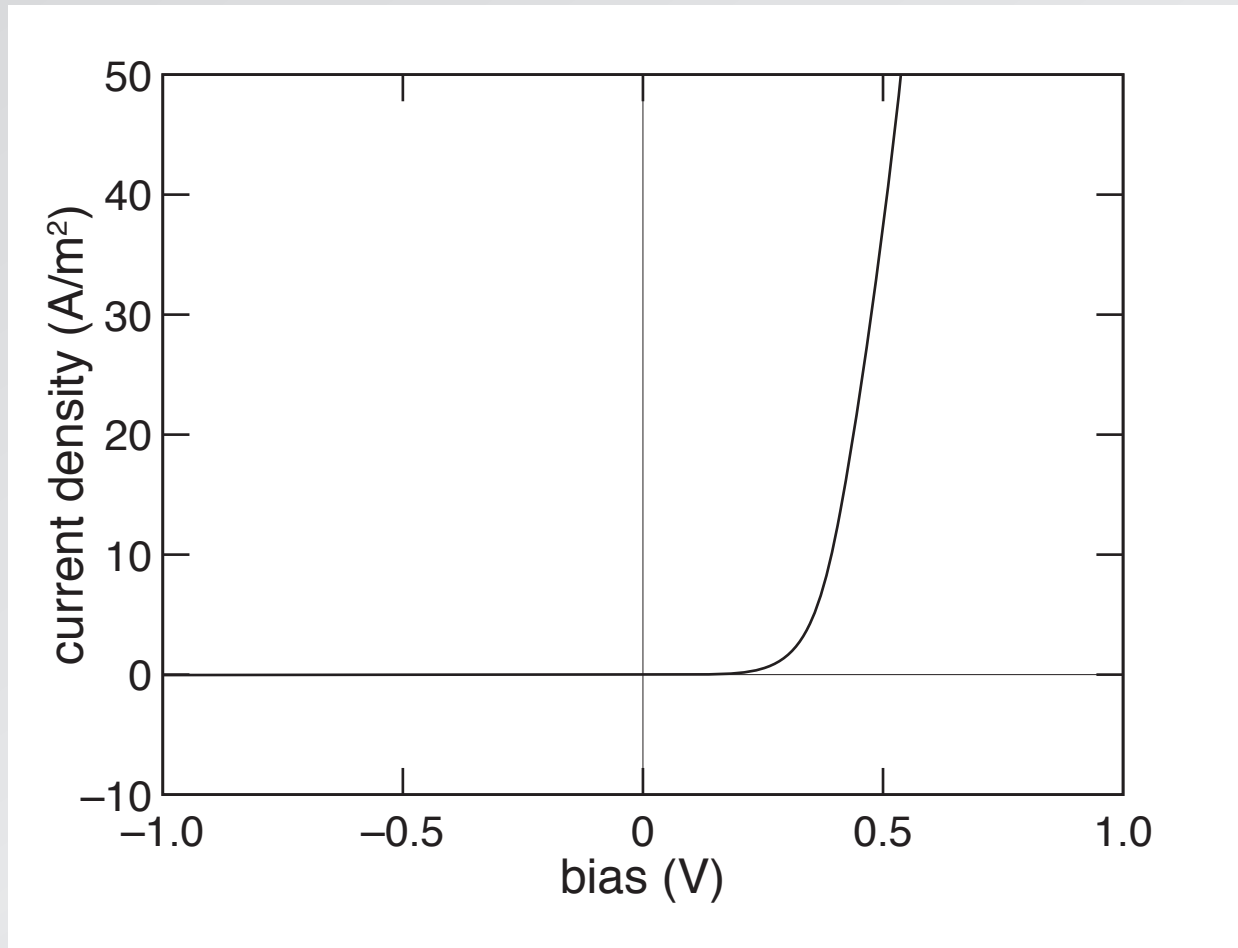


① properties

② intermediate band

③ devices

excellent rectification (after annealing)

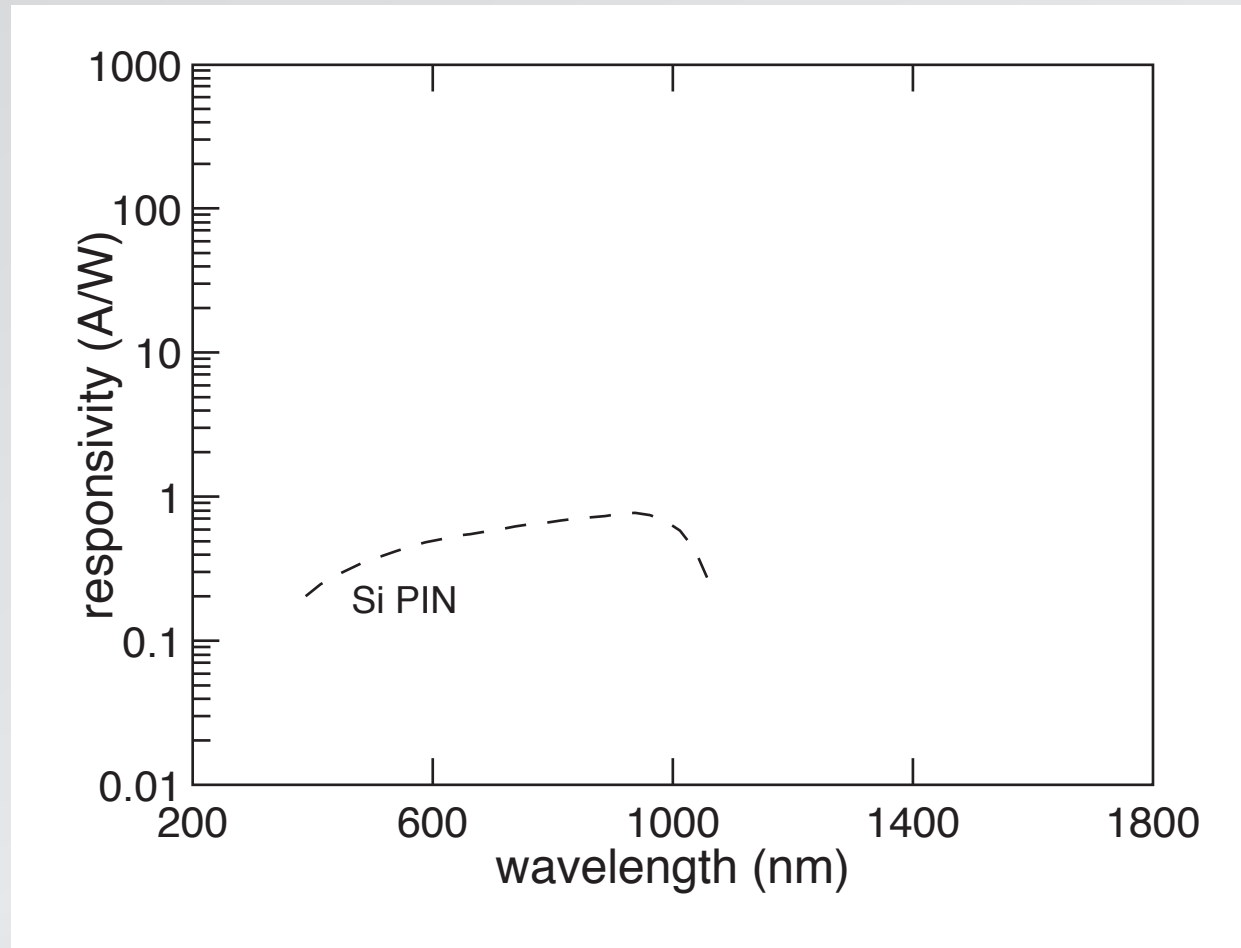


1 properties

2 intermediate band

3 devices

responsivity

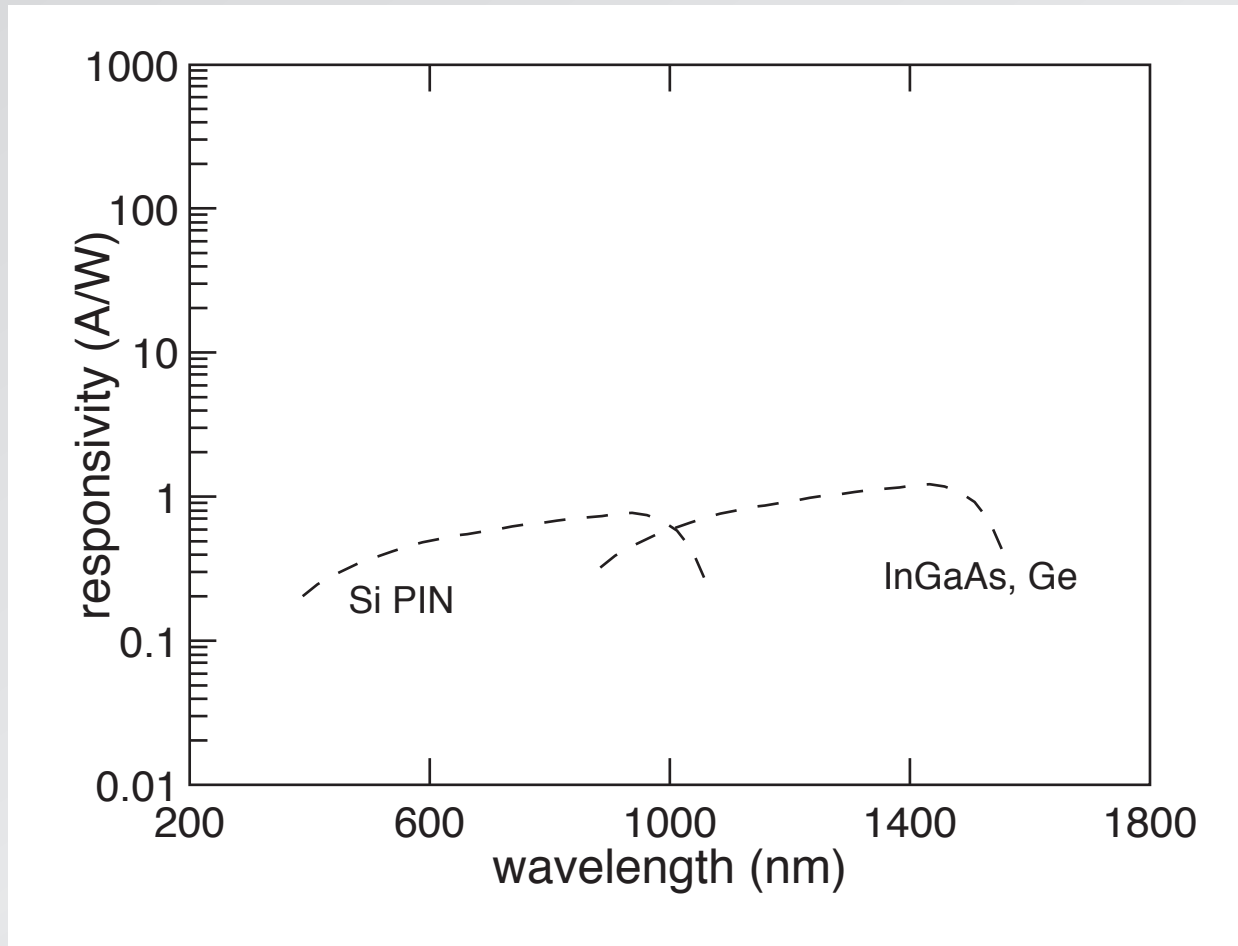


1 properties

2 intermediate band

3 devices

responsivity

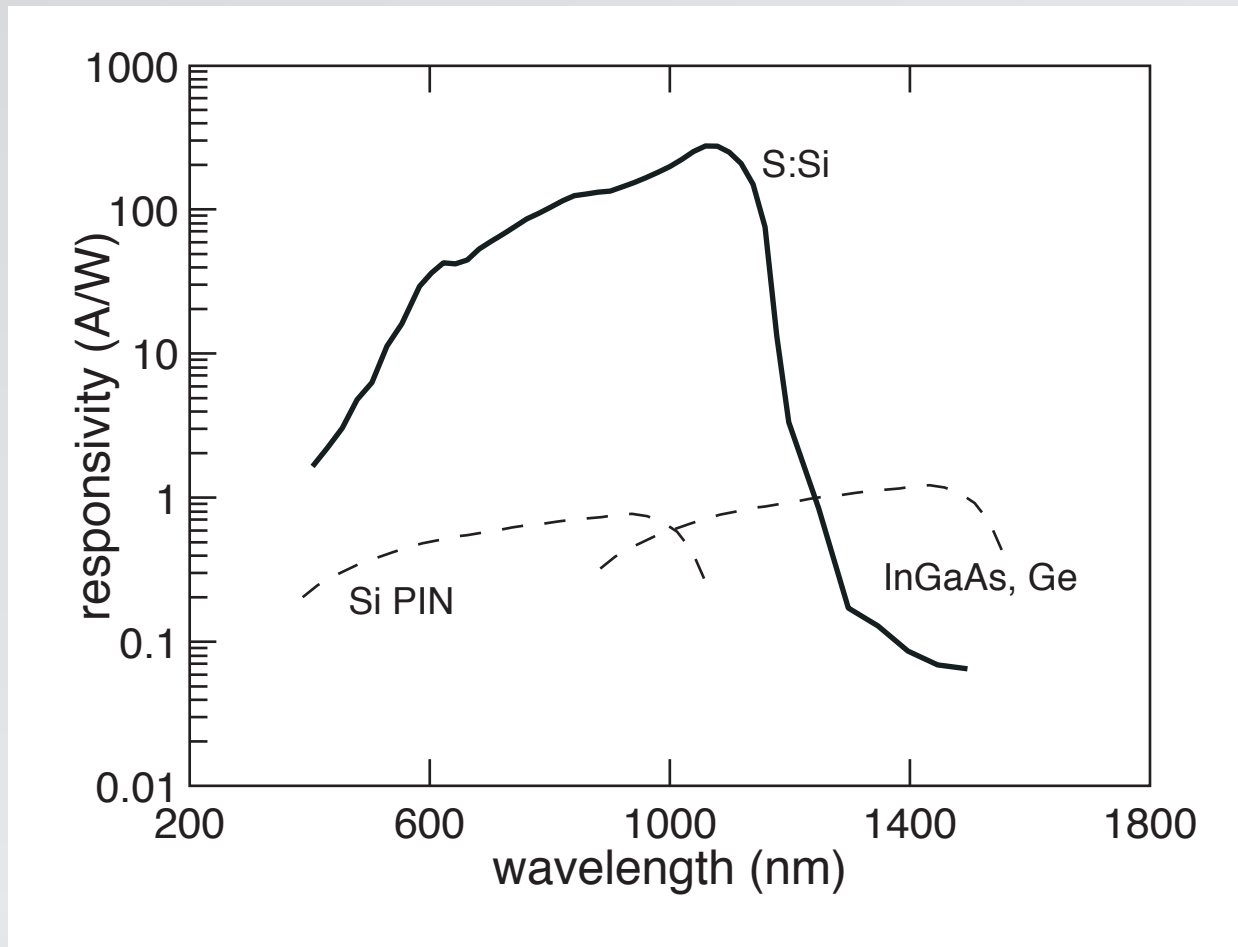


1 properties

2 intermediate band

3 devices

responsivity

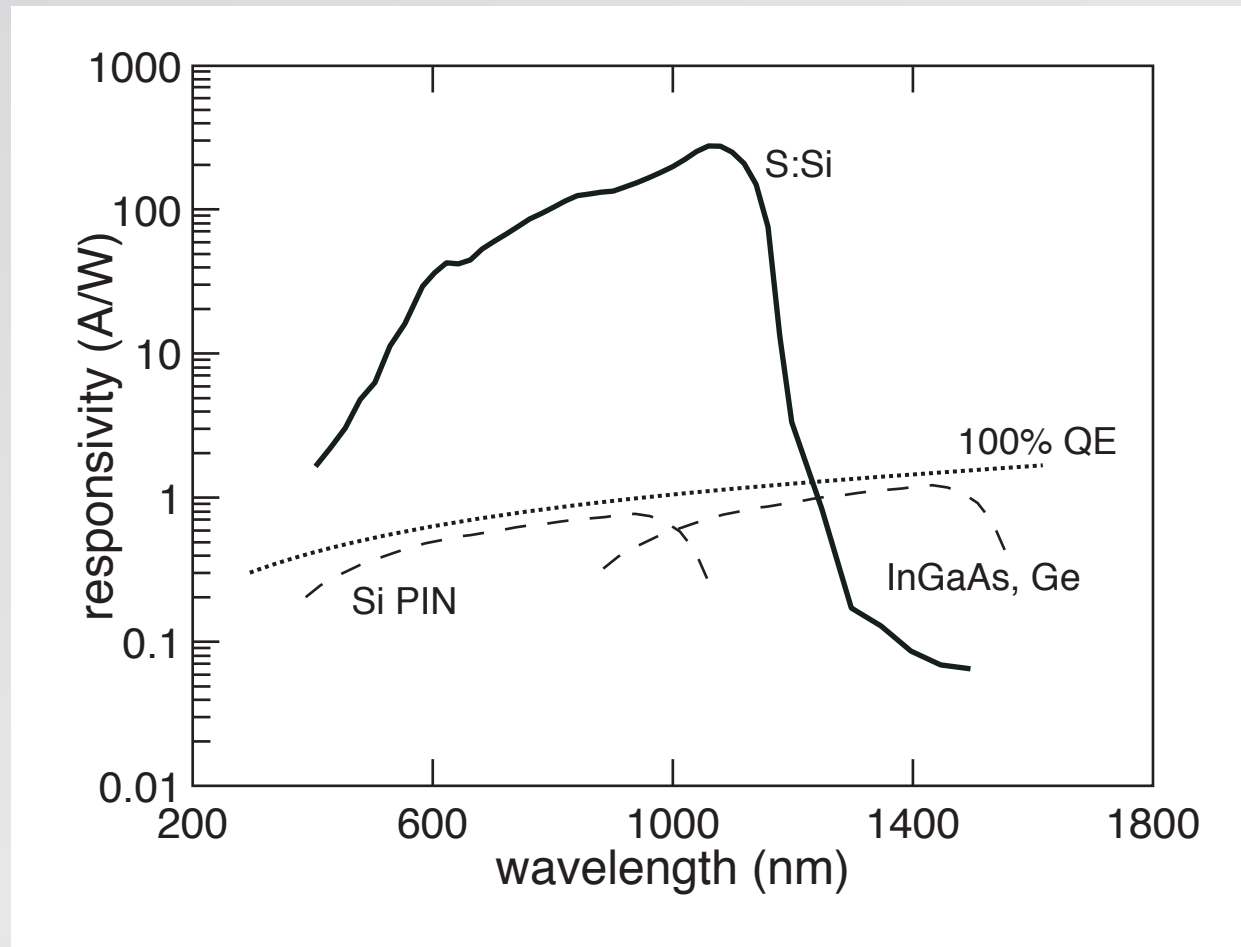


1 properties

2 intermediate band

3 devices

responsivity

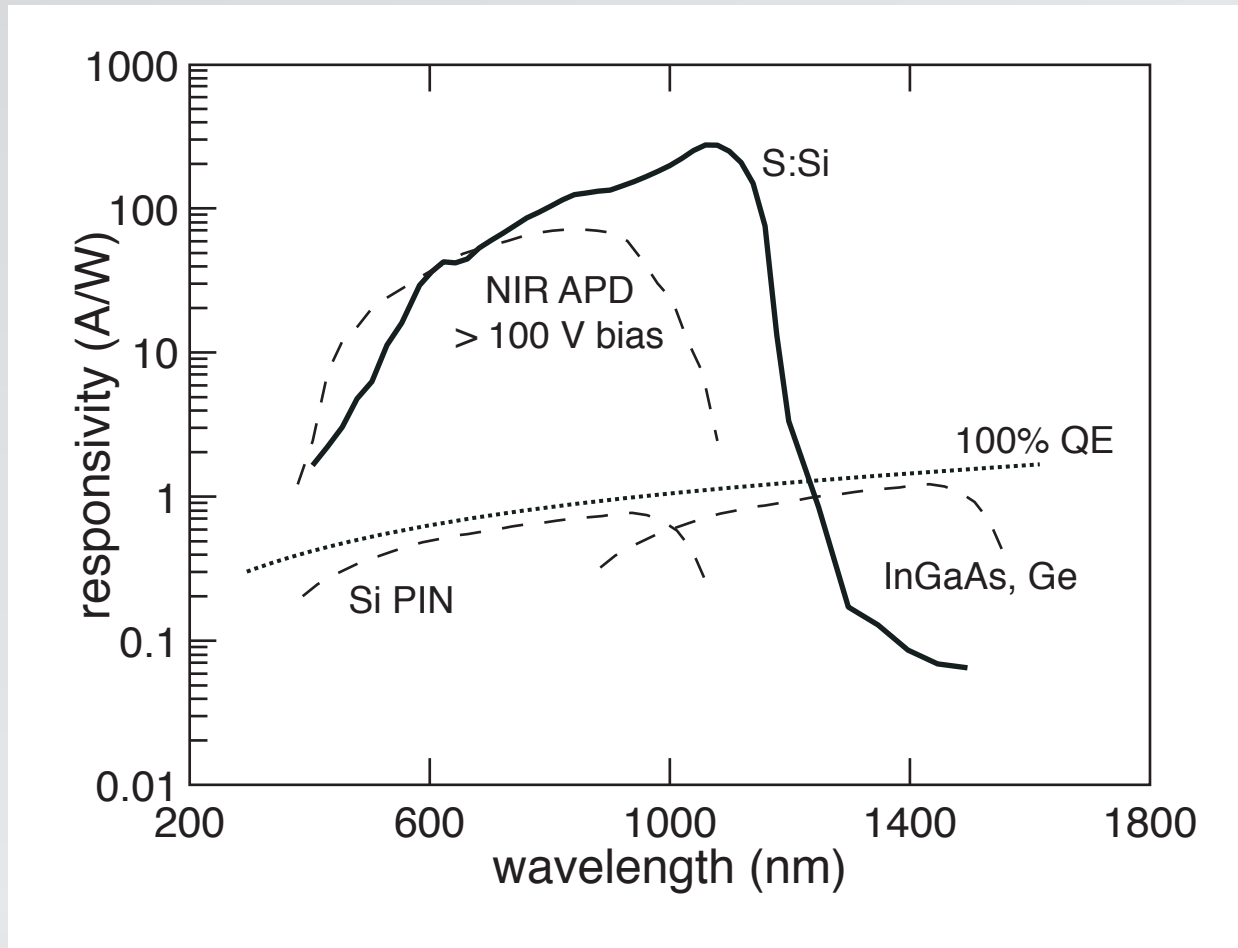


1 properties

2 intermediate band

3 devices

responsivity



1 properties

2 intermediate band

3 devices

- **enhanced sensitivity**
- **extended IR response**

near-IR is next wave in imaging!

1 properties

2 intermediate band

3 devices



gesture recognition

image: fastcolabs.com

1 properties

2 intermediate band

3 devices



night vision

wikimedia.org

1 properties

2 intermediate band

3 devices

biometrics



image: kusic.ca

1 properties

2 intermediate band

3 devices

robotics

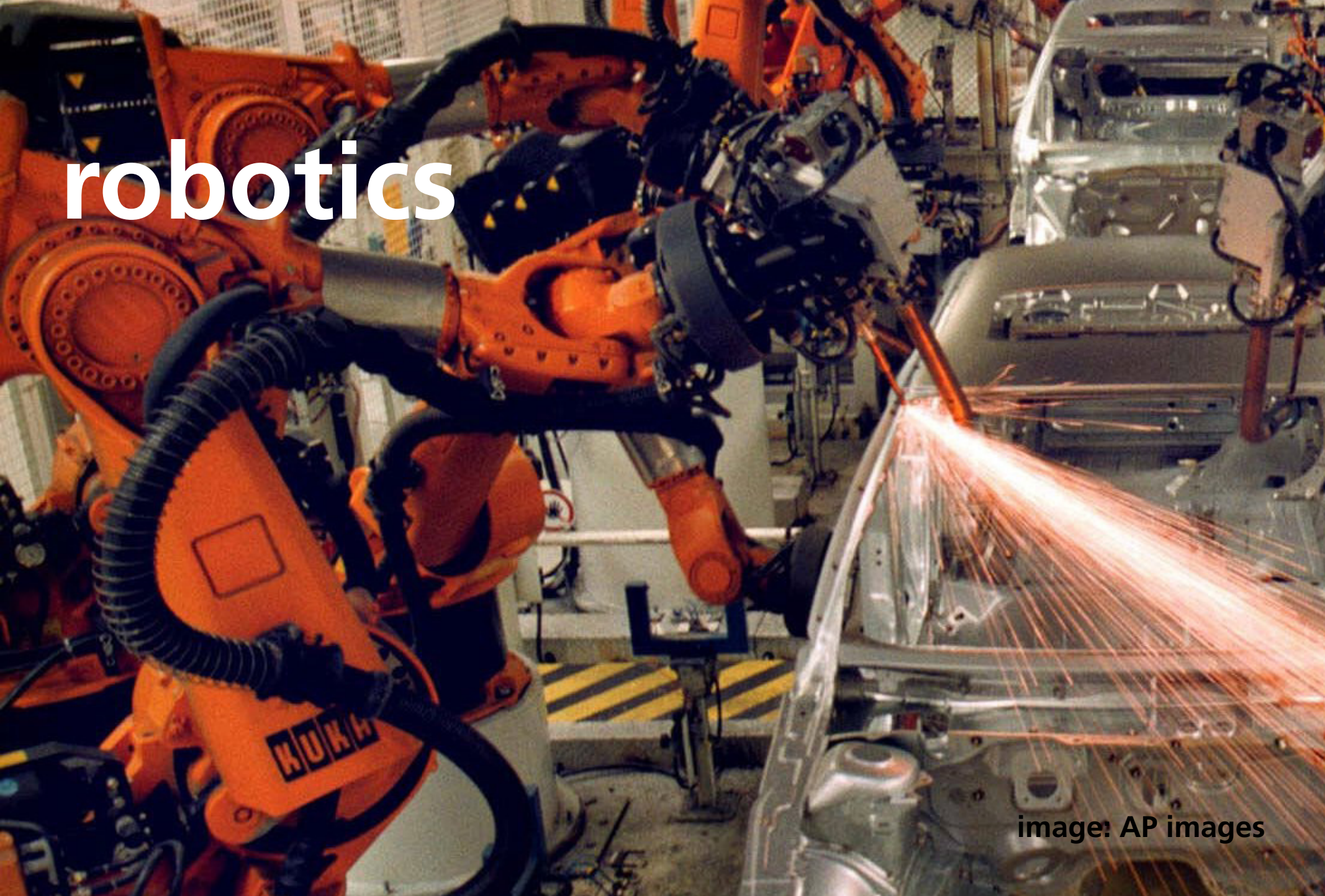
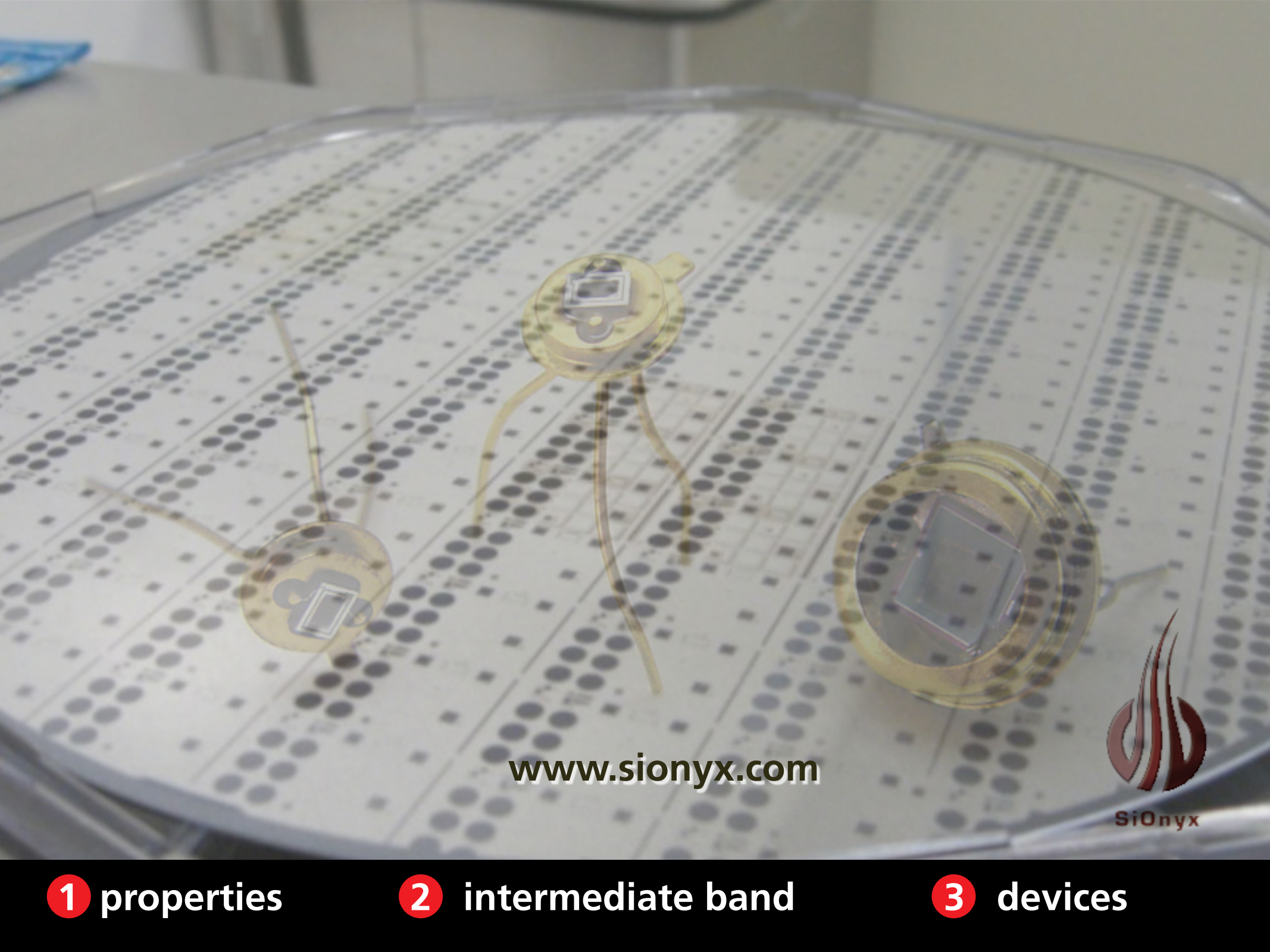


image: AP images

1 properties

2 intermediate band

3 devices



www.sionyx.com

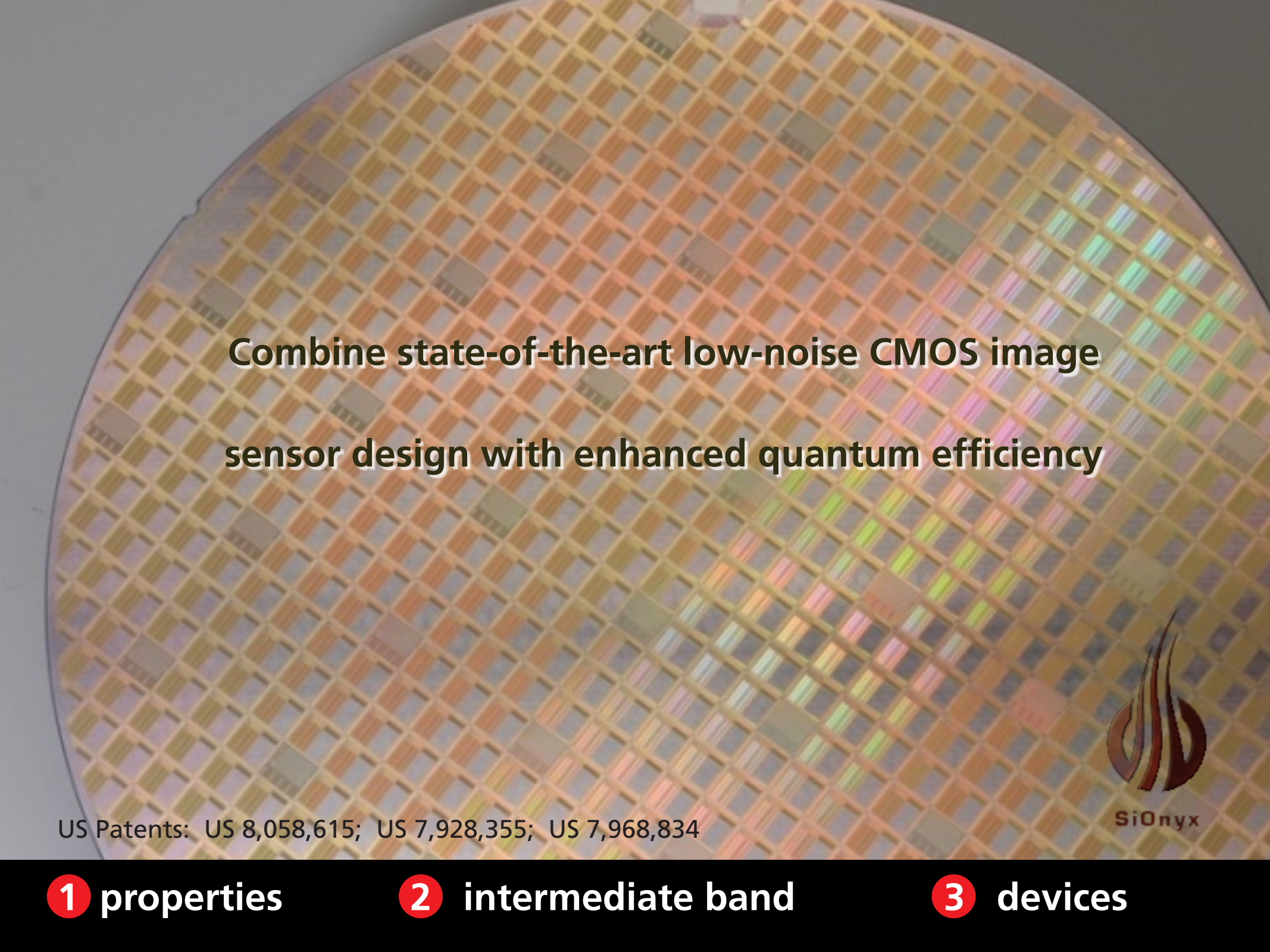


SiOnyx

1 properties

2 intermediate band

3 devices



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



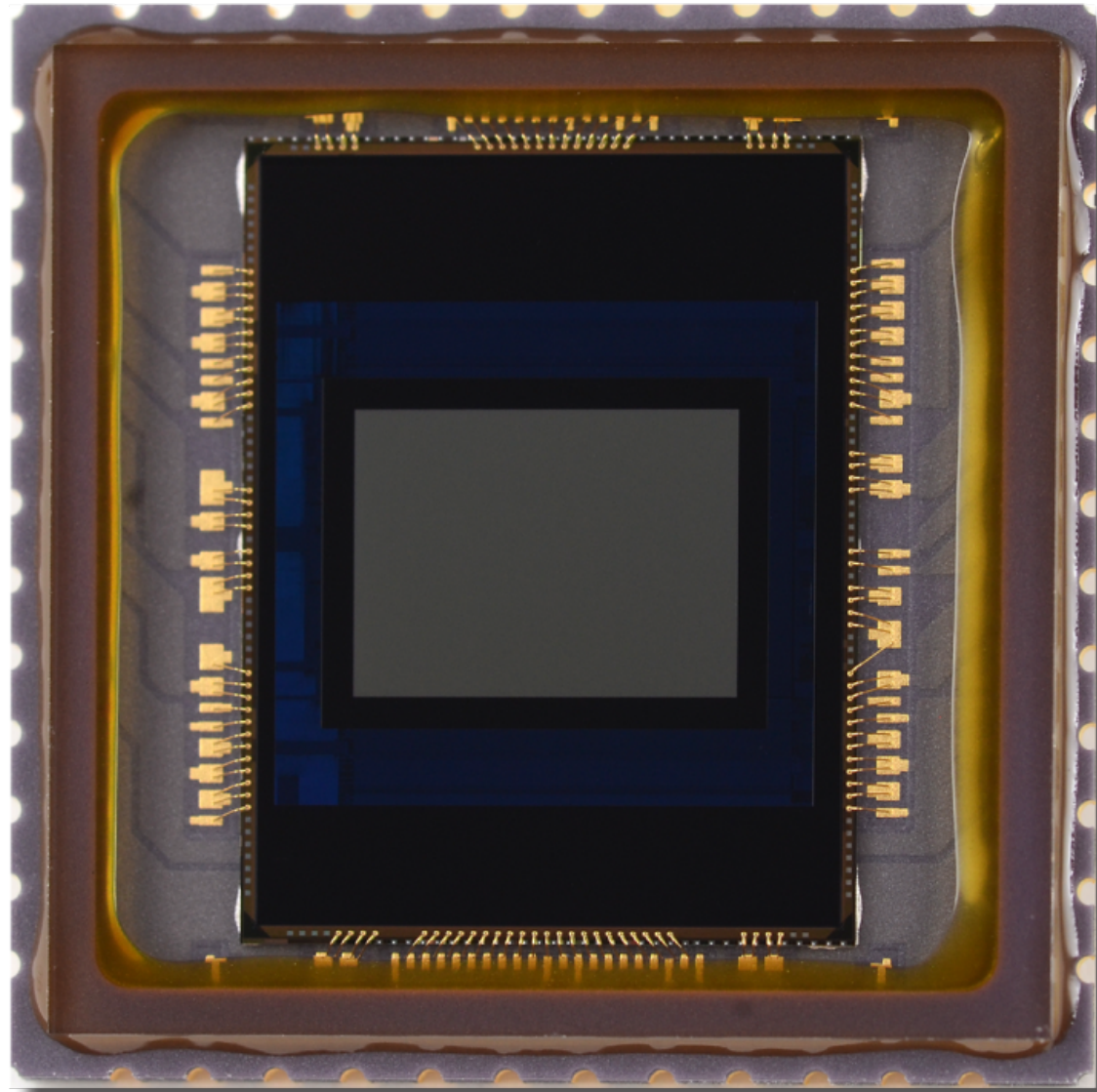
SiOnyx

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

1 properties

2 intermediate band

3 devices



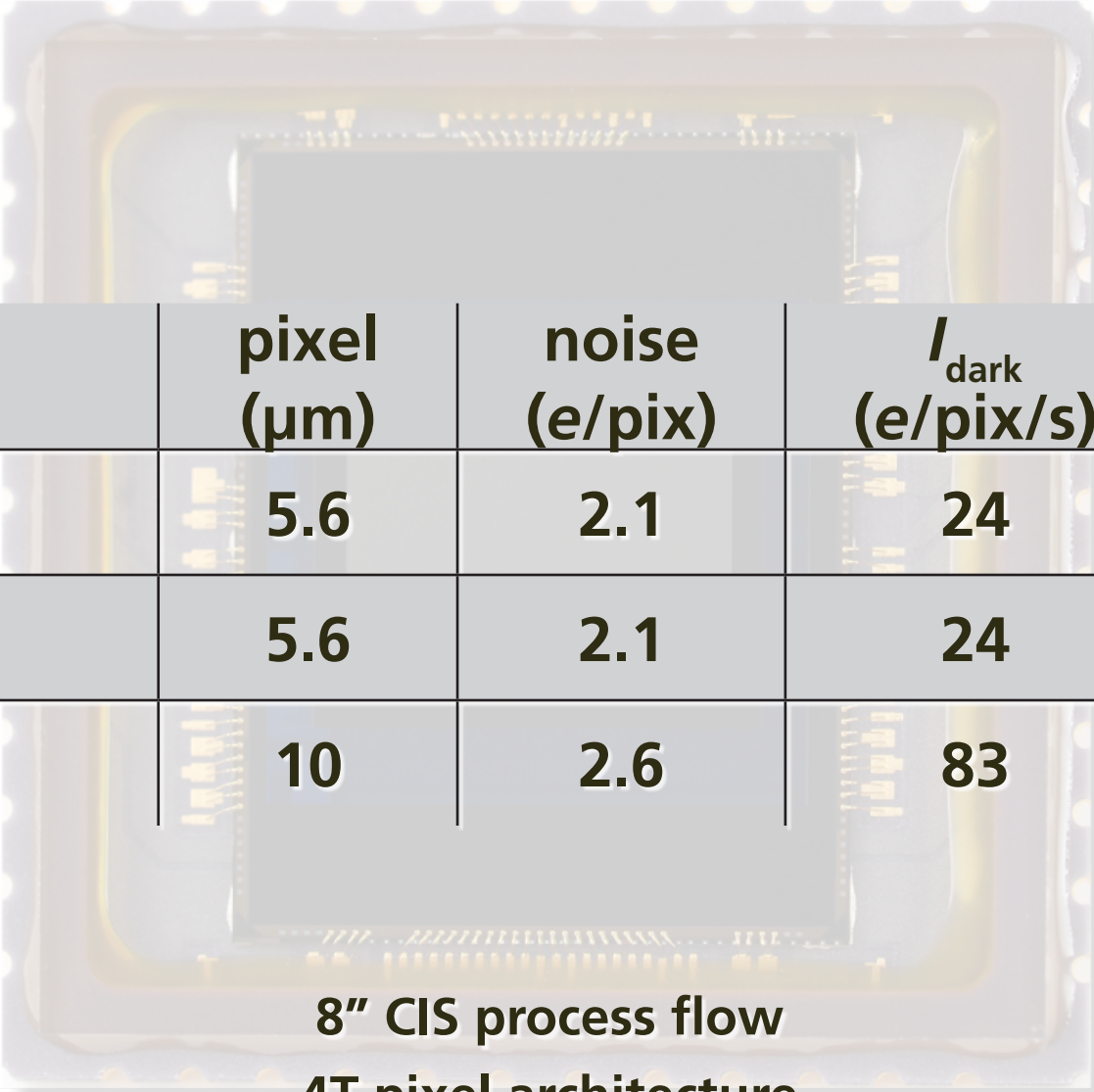
SiOnyx

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

1 properties

2 intermediate band

3 devices



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

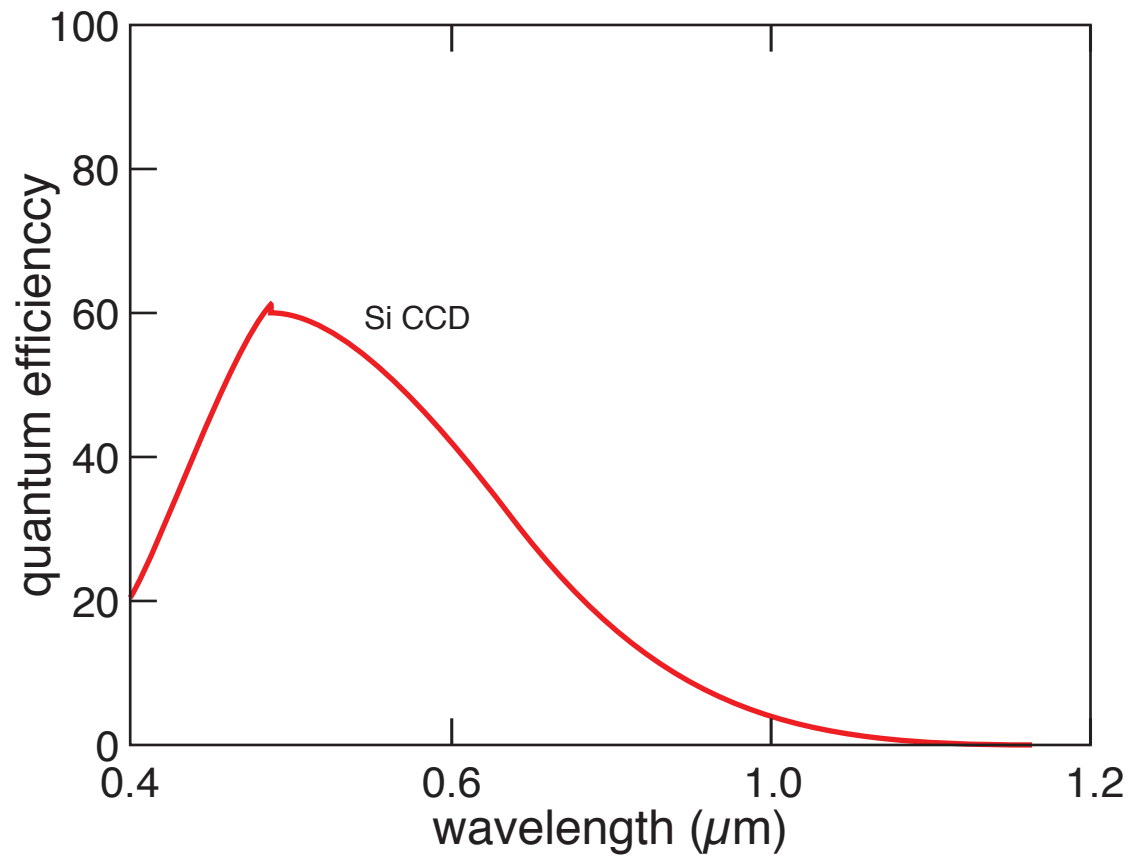
8" CIS process flow
4T pixel architecture



1 properties

2 intermediate band

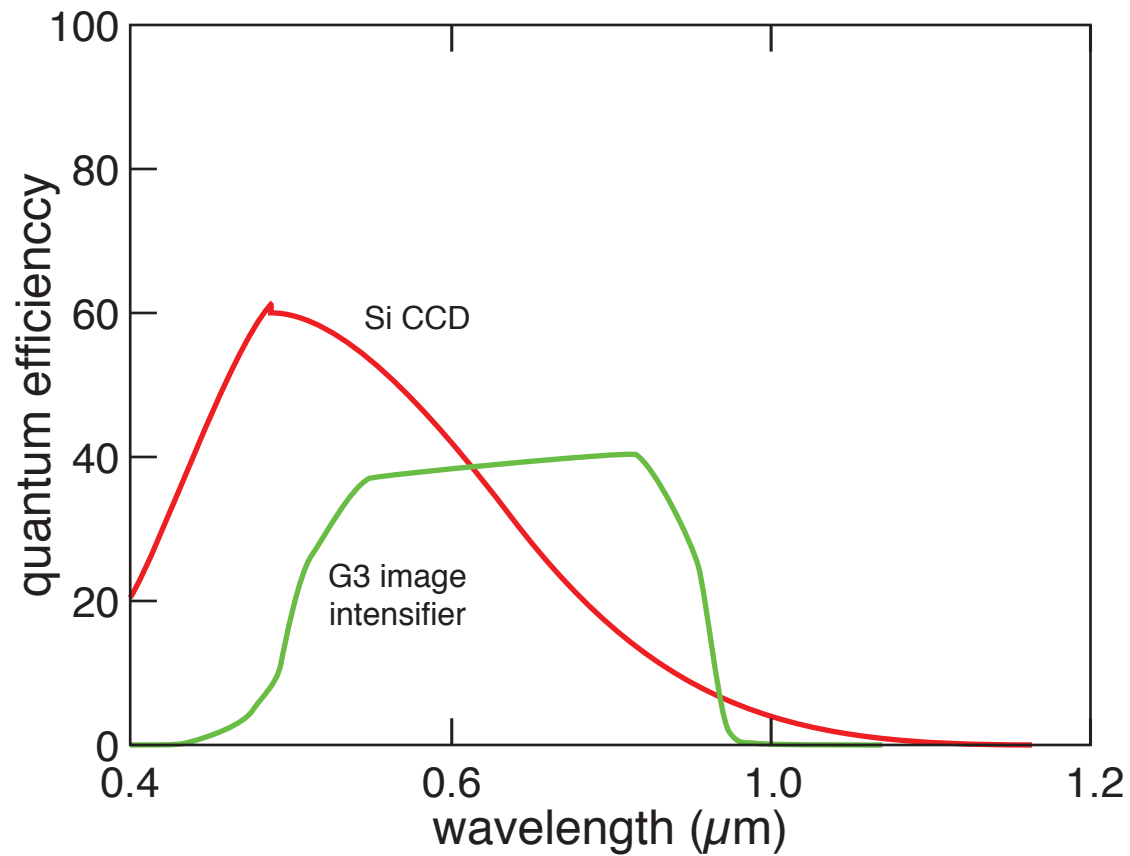
3 devices



1 properties

2 intermediate band

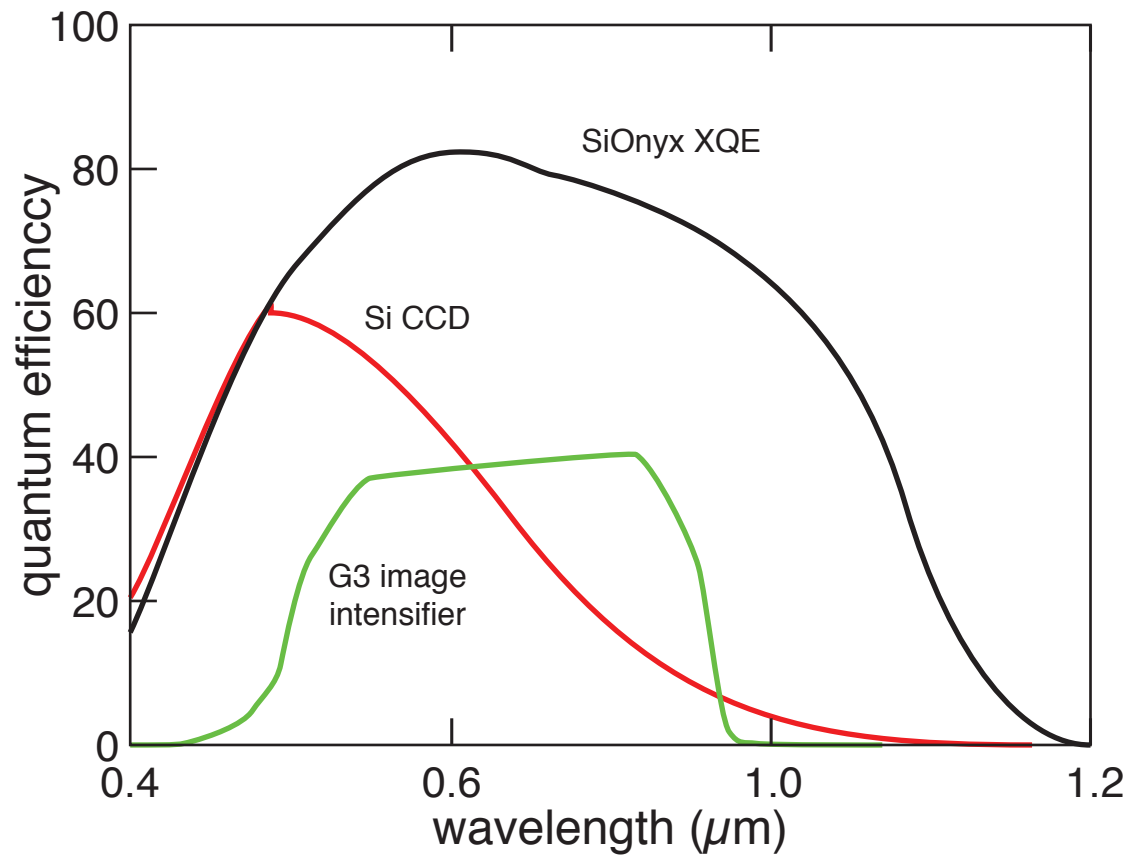
3 devices



1 properties

2 intermediate band

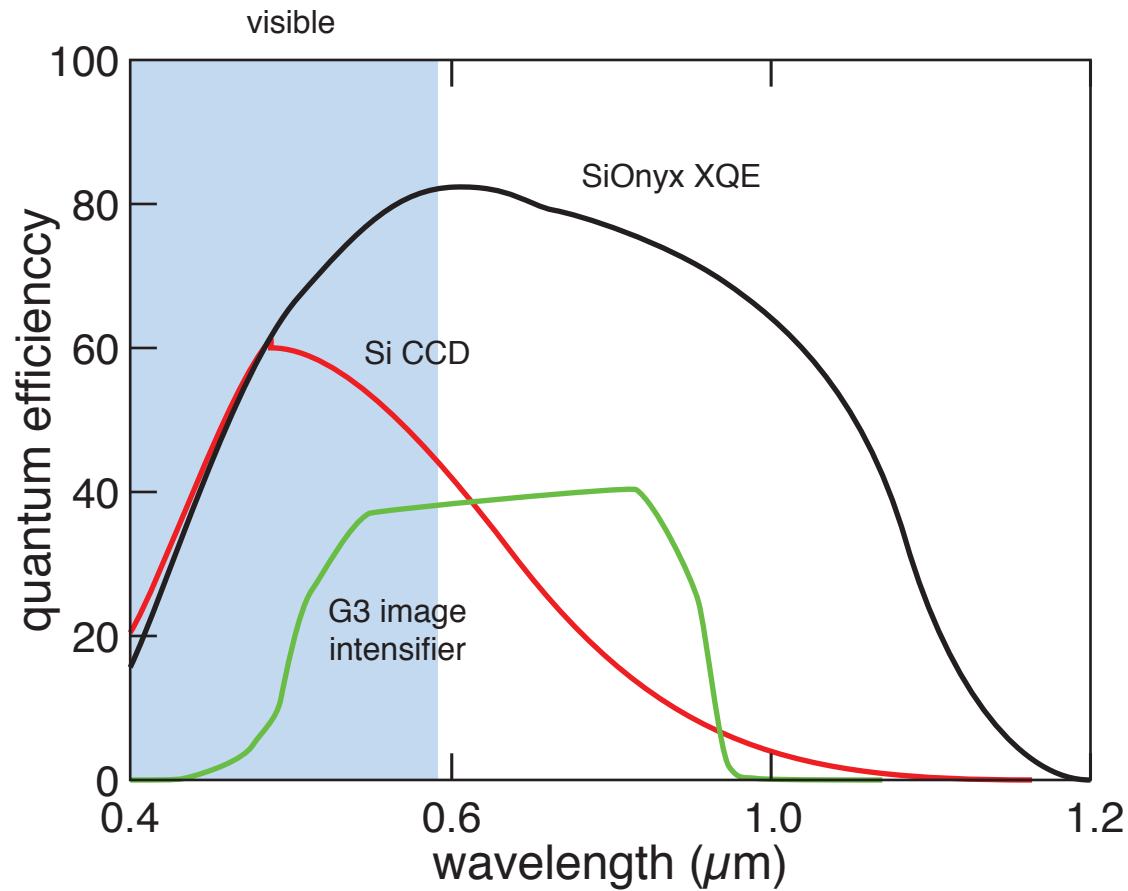
3 devices



1 properties

2 intermediate band

3 devices



1 properties

2 intermediate band

3 devices

no compromises in visible



Sony color CCD



1 properties

2 intermediate band

3 devices

no compromises in visible



Sony color CCD



SiOnyx XQE sensor

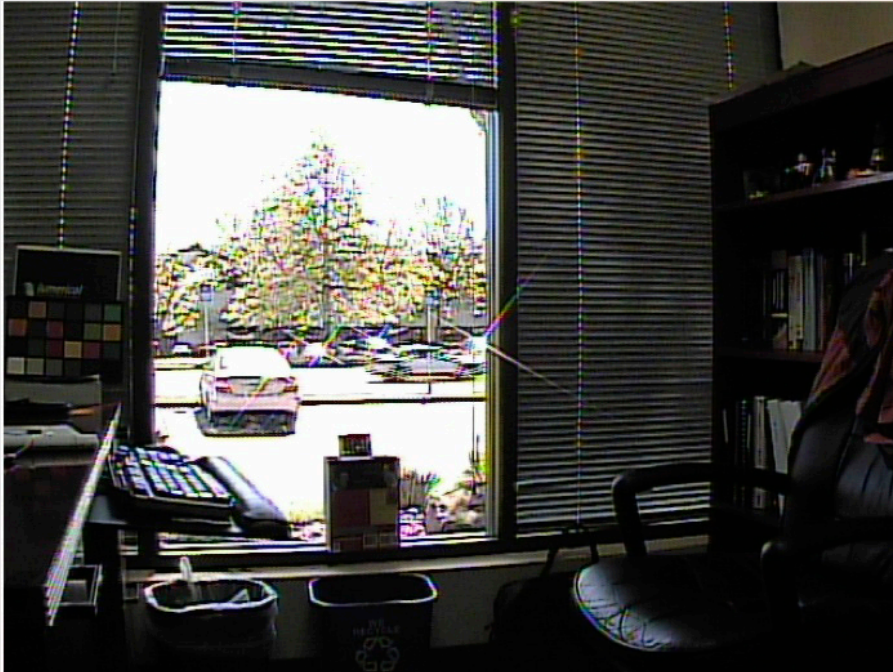


1 properties

2 intermediate band

3 devices

90+ dB dynamic range



Sony color CCD



1 properties

2 intermediate band

3 devices

90+ dB dynamic range



Sony color CCD



SiOnyx X1 sensor

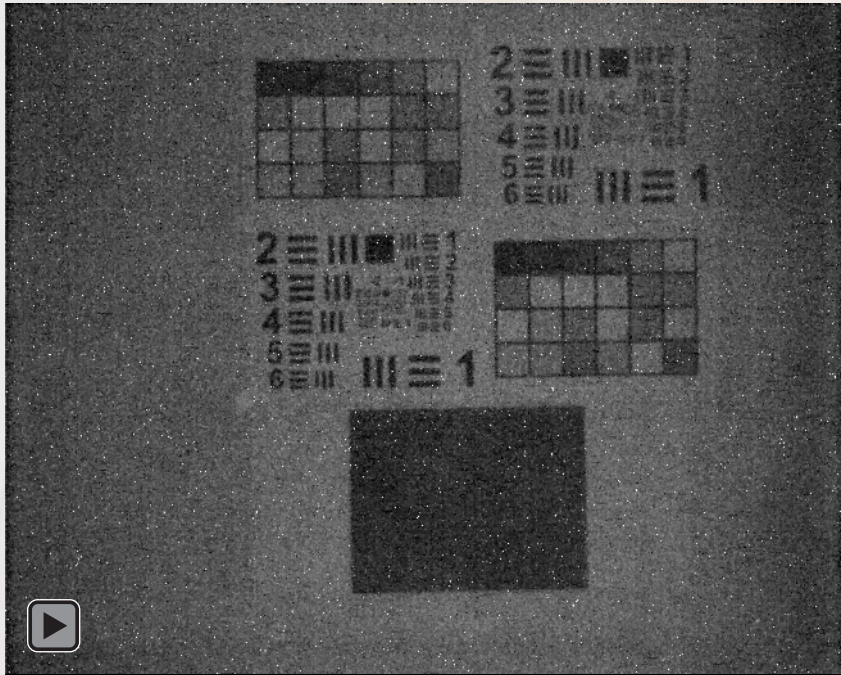


1 properties

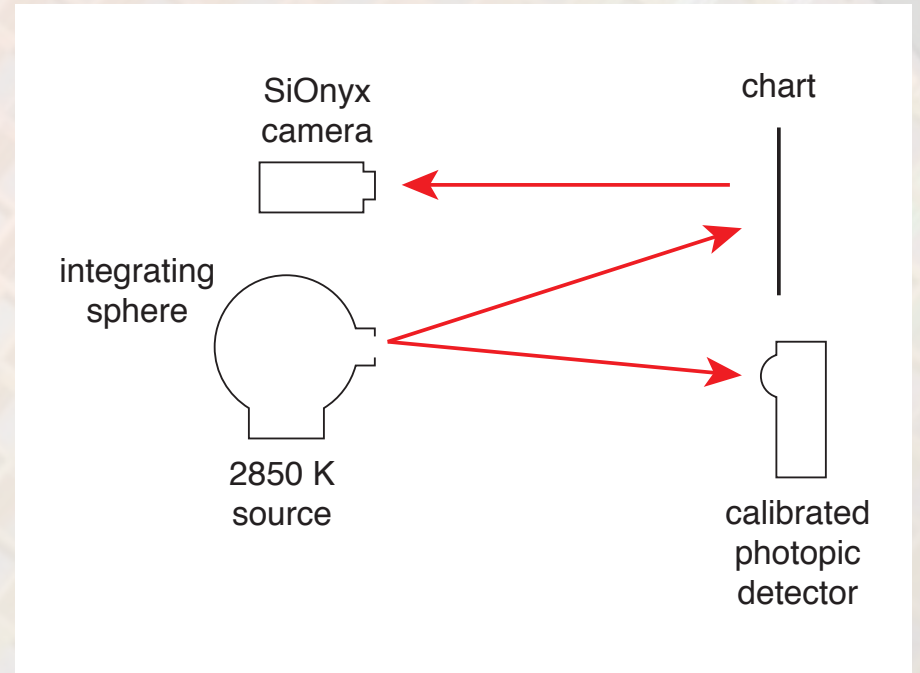
2 intermediate band

3 devices

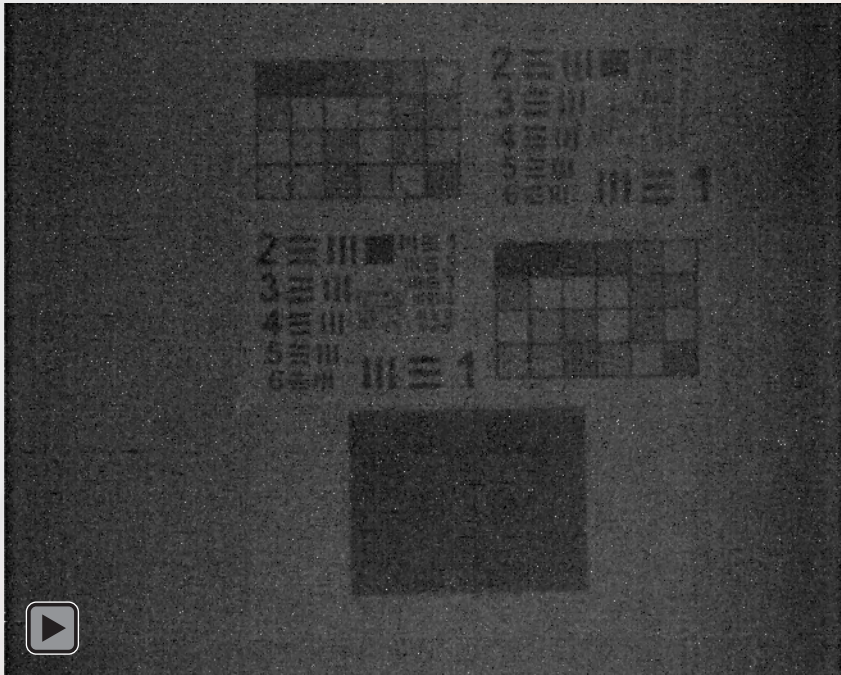
0.9 mlux irradiance from 2850 K source



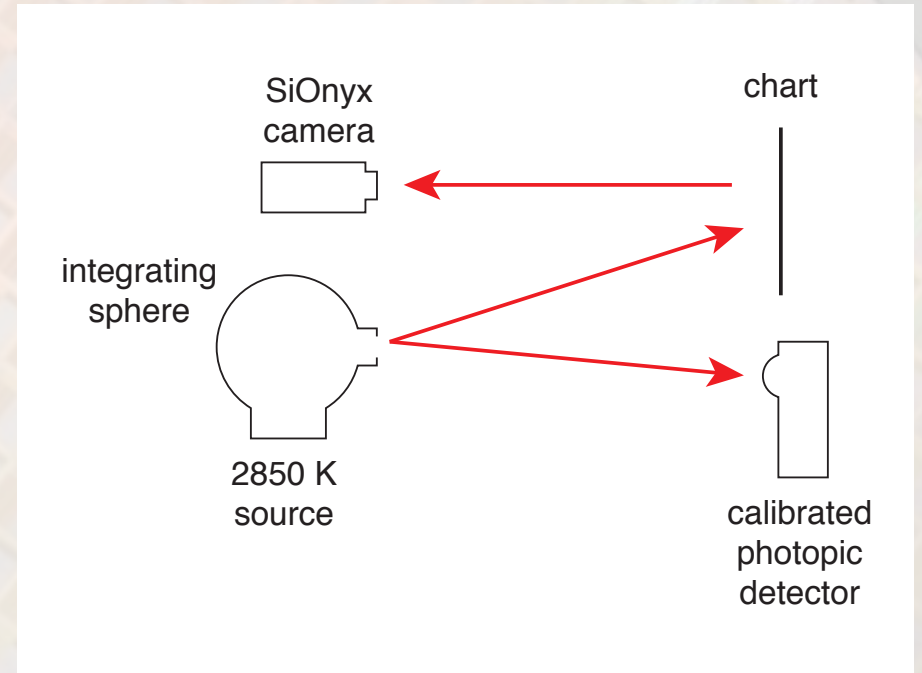
SiOnyx (50 mm, F1.4, 30 fps)

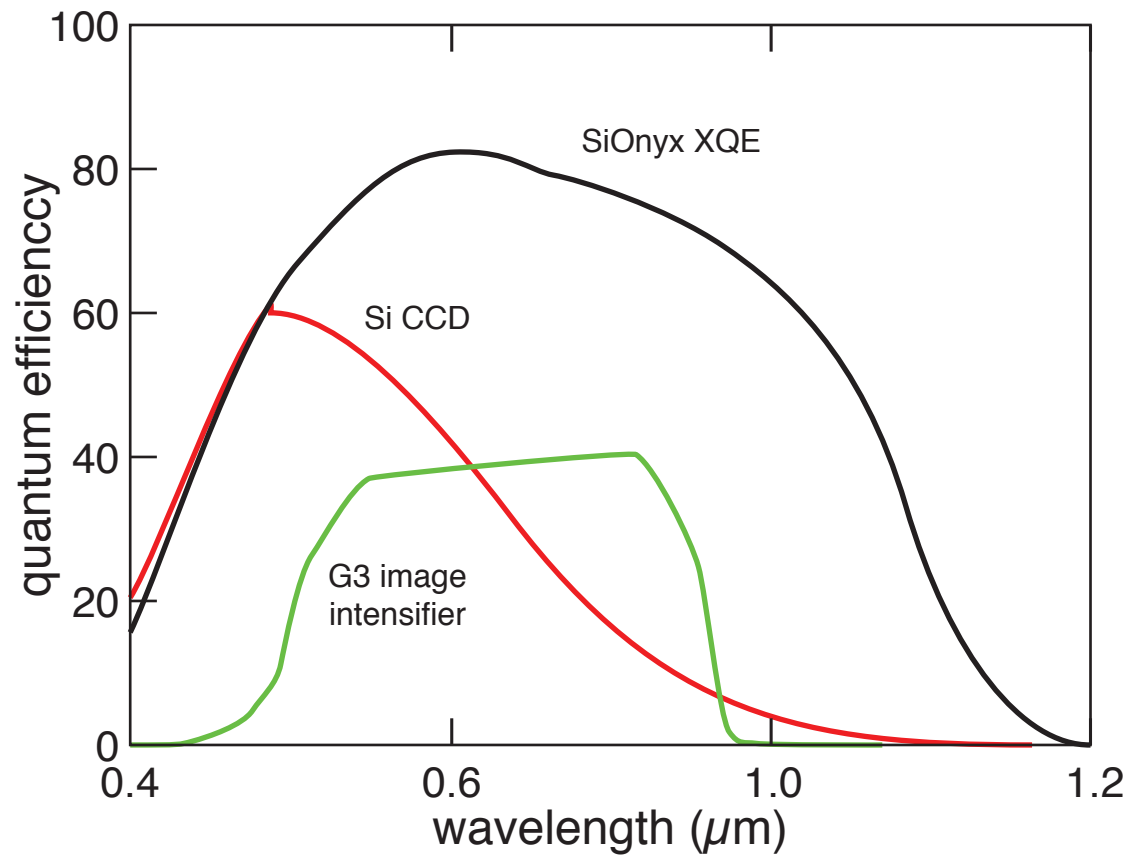


0.9 mlux irradiance from 2850 K source



SiOnyx (50 mm, F1.4, 60 fps)

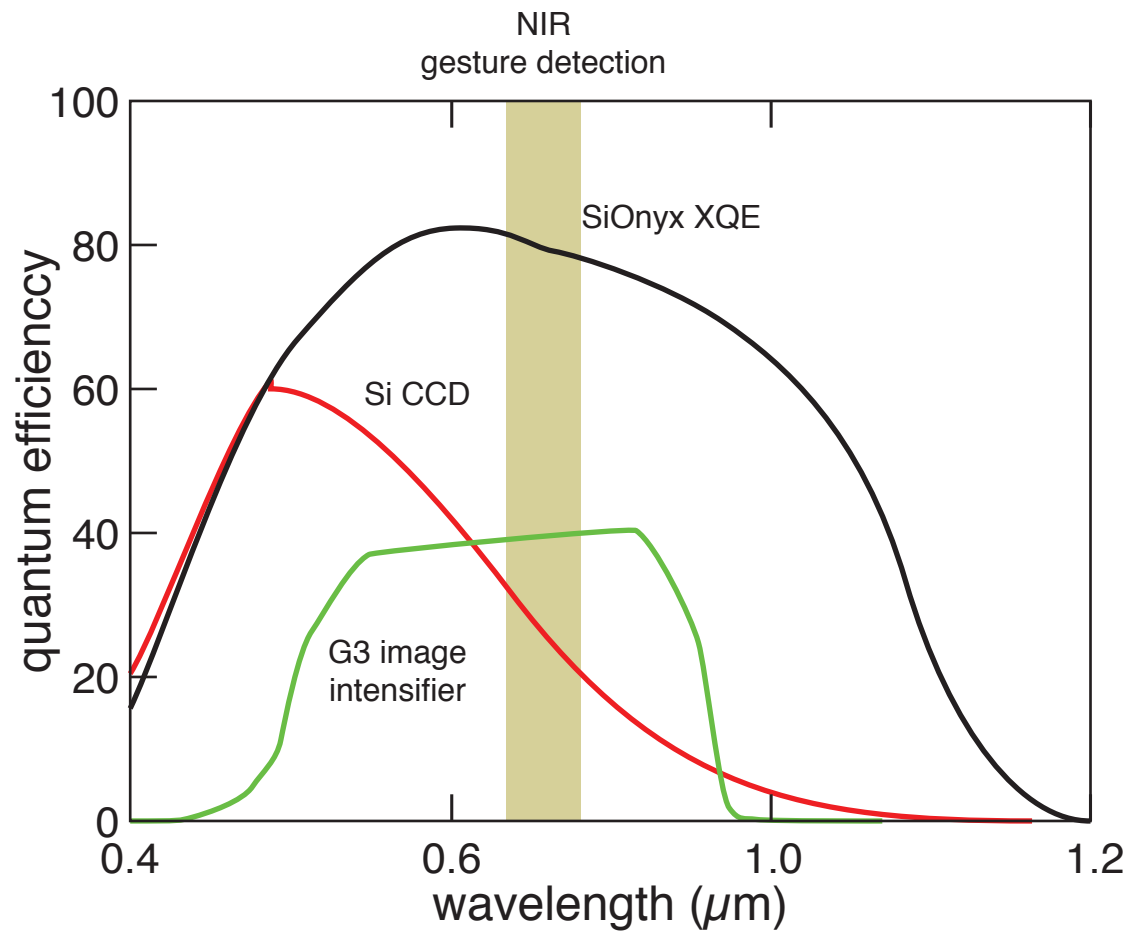




1 properties

2 intermediate band

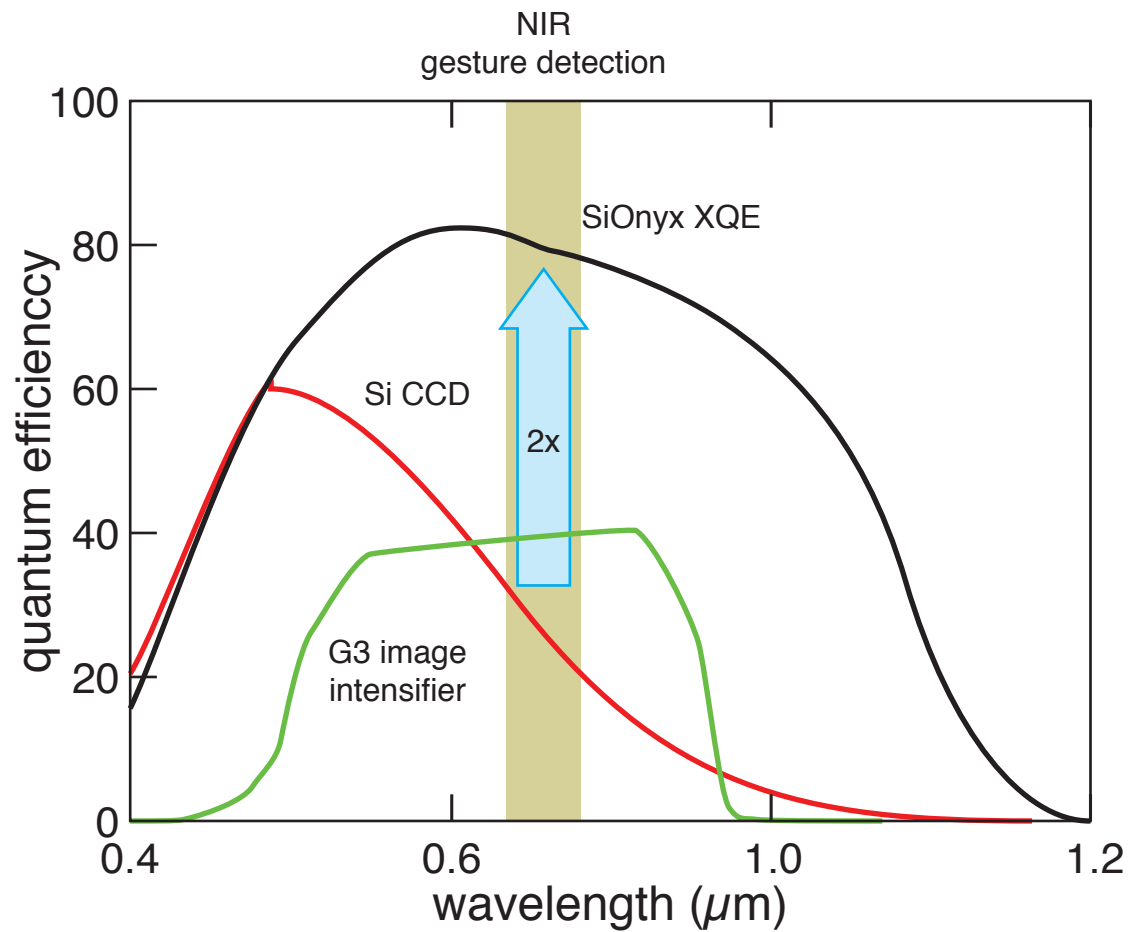
3 devices



1 properties

2 intermediate band

3 devices



1 properties

2 intermediate band

3 devices

3D imaging for gesture user interface (850 nm)

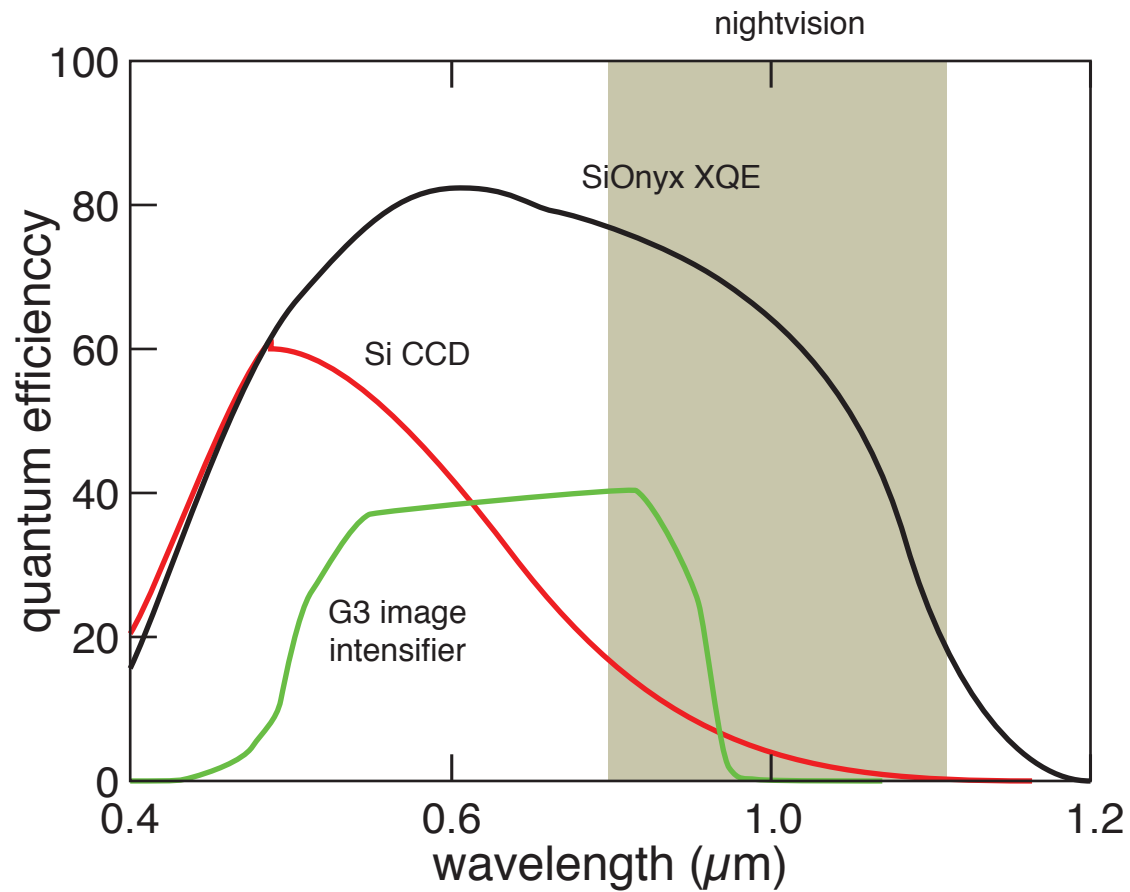


SiOnyx XQE



standard CCD

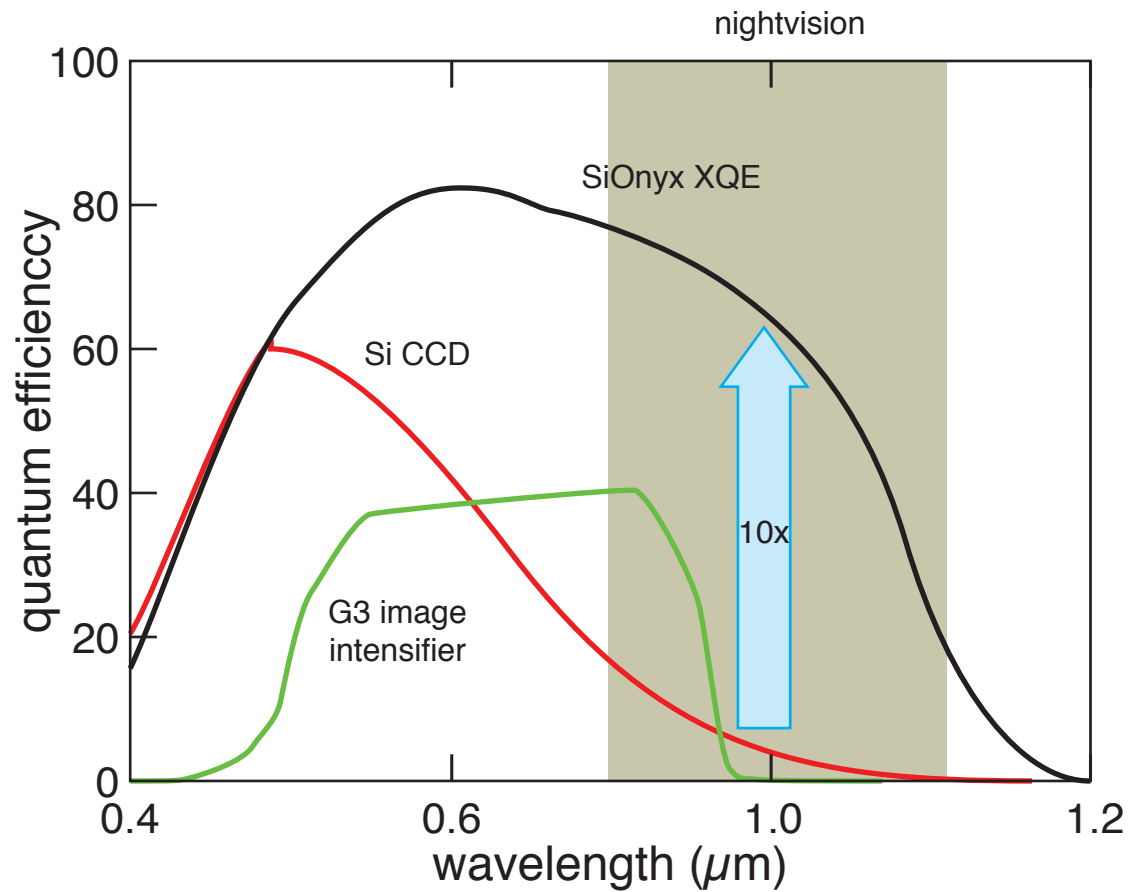




1 properties

2 intermediate band

3 devices

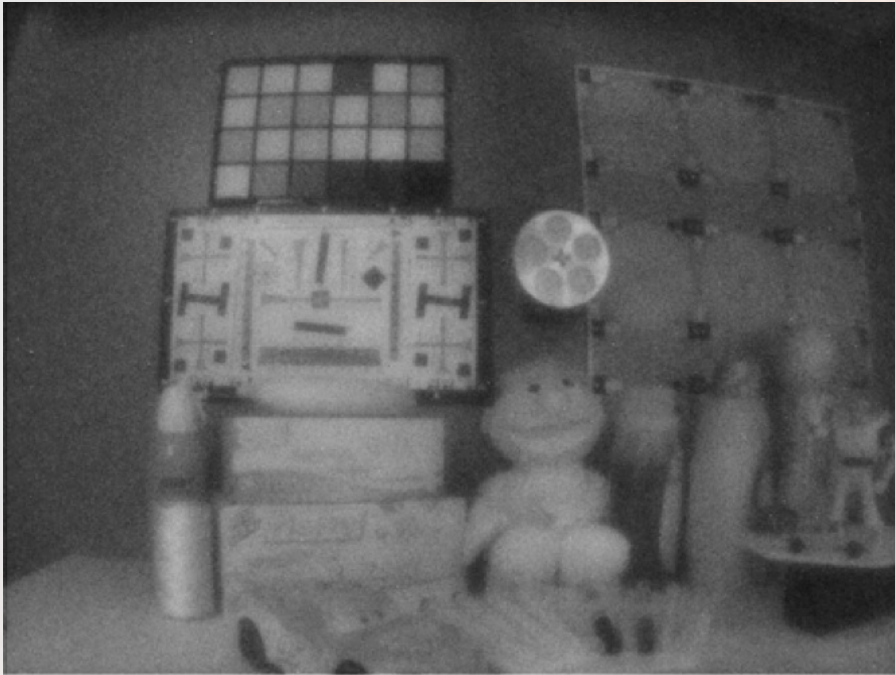


1 properties

2 intermediate band

3 devices

dark room 1050 illumination



SiOnyx (F1.4, 33 ms, 24x)

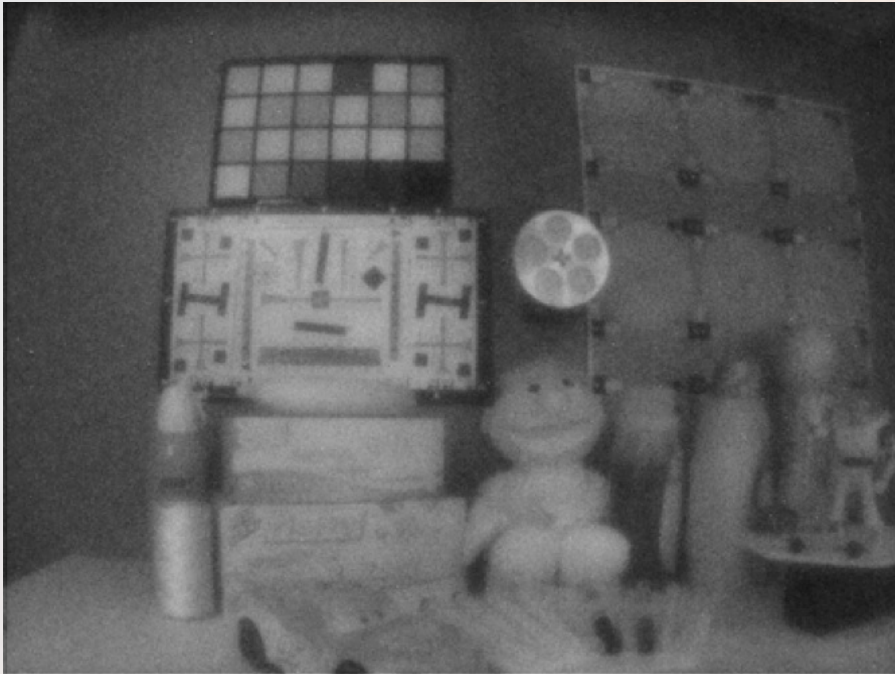


1 properties

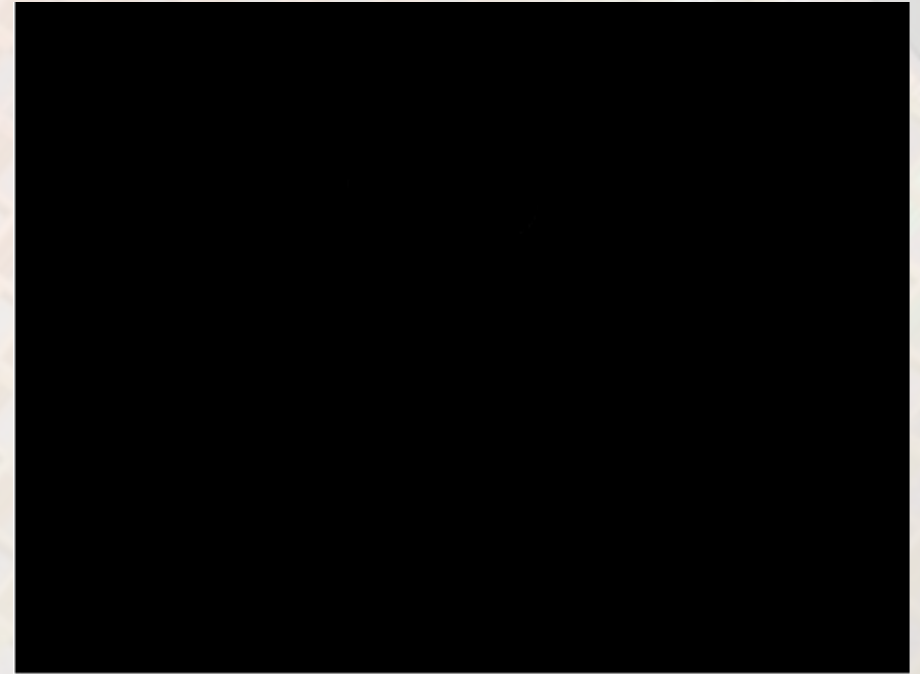
2 intermediate band

3 devices

dark room 1050 illumination



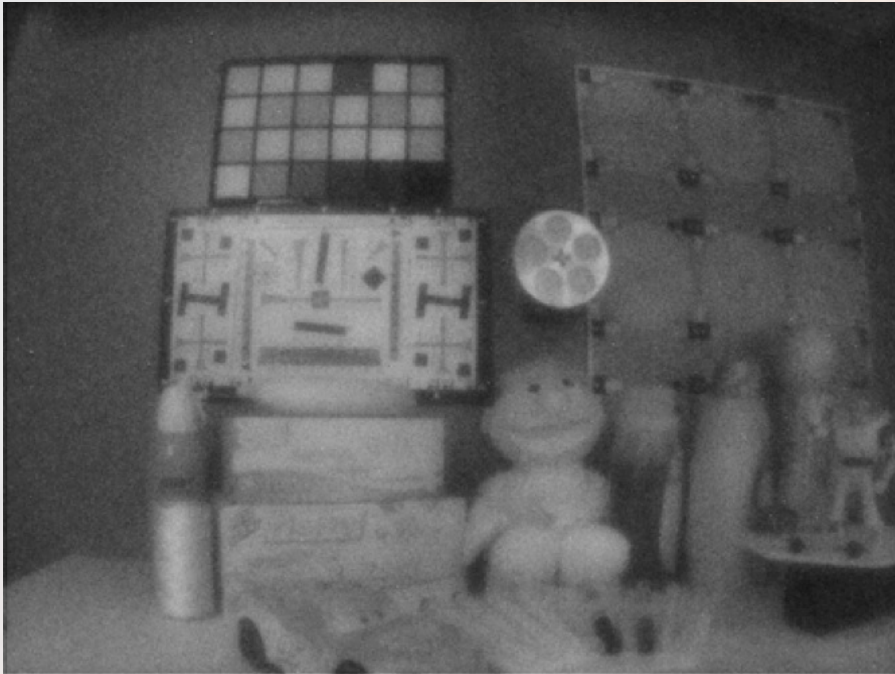
SiOnyx (F1.4, 33 ms, 24x)



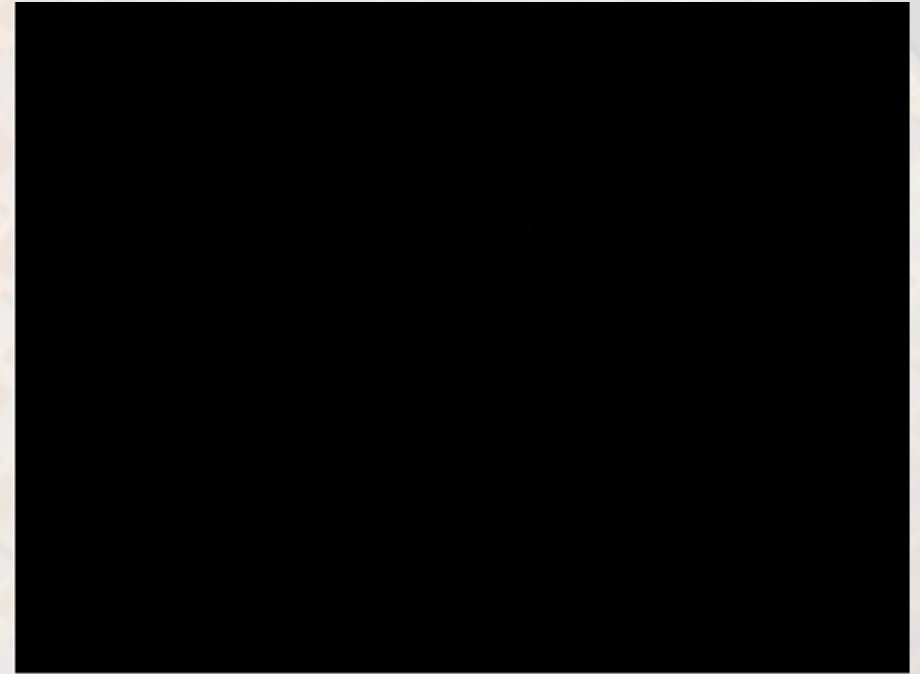
reference (F1.4, 33 ms, 24x)



dark room 1050 illumination



SiOnyx (F1.4, 33 ms, 24x)

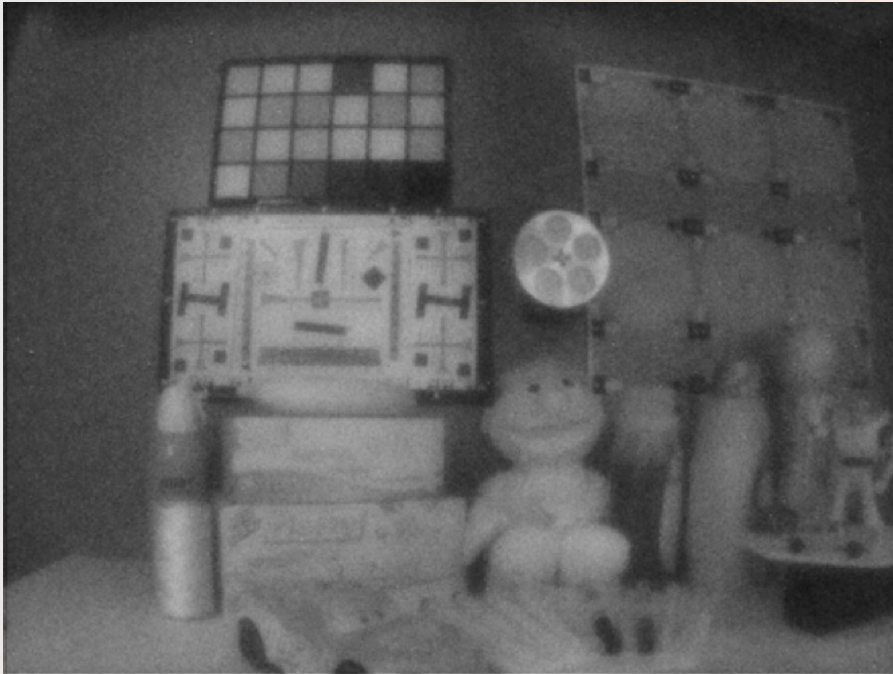


reference (F1.4, 33 ms, 24x)

no image processing



dark room 1050 illumination



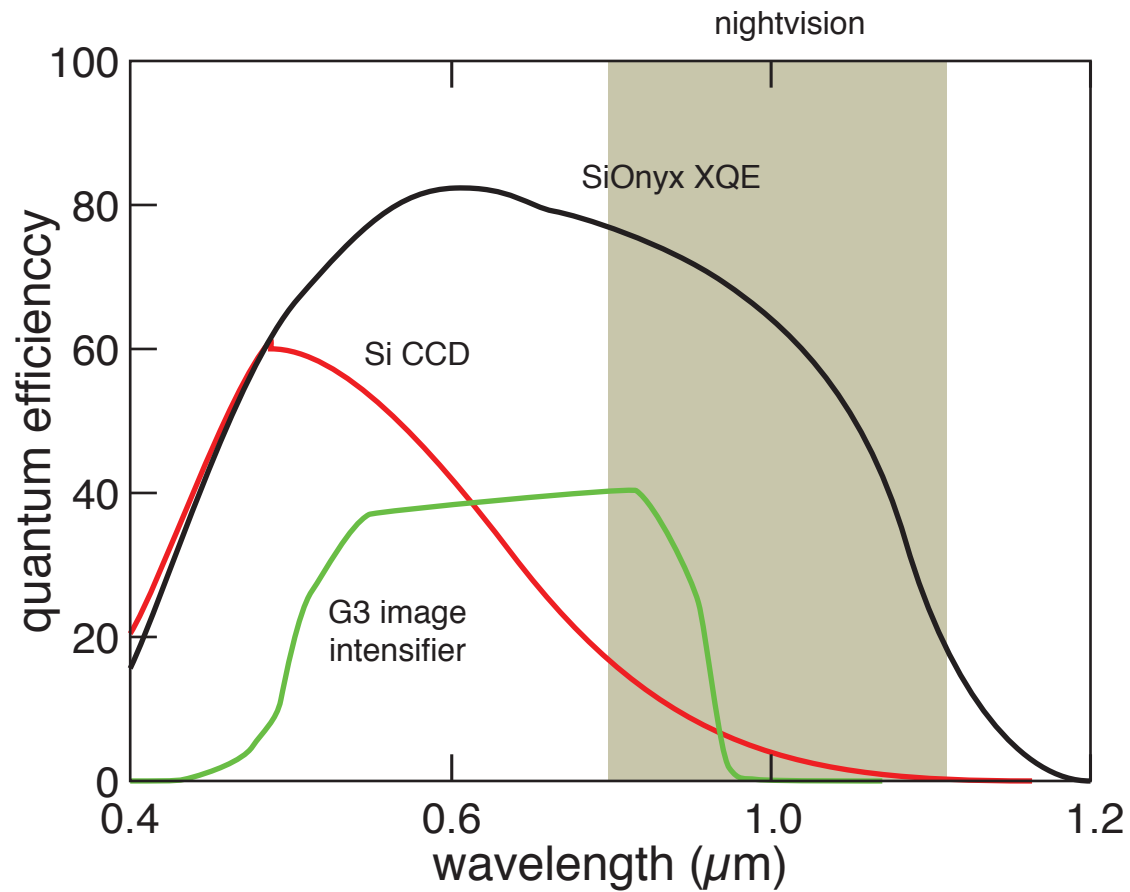
SiOnyx (F1.4, 33 ms, 24x)



reference (F1.4, 33 ms, 24x)
2x DIGITAL GAIN ADDED

no image processing

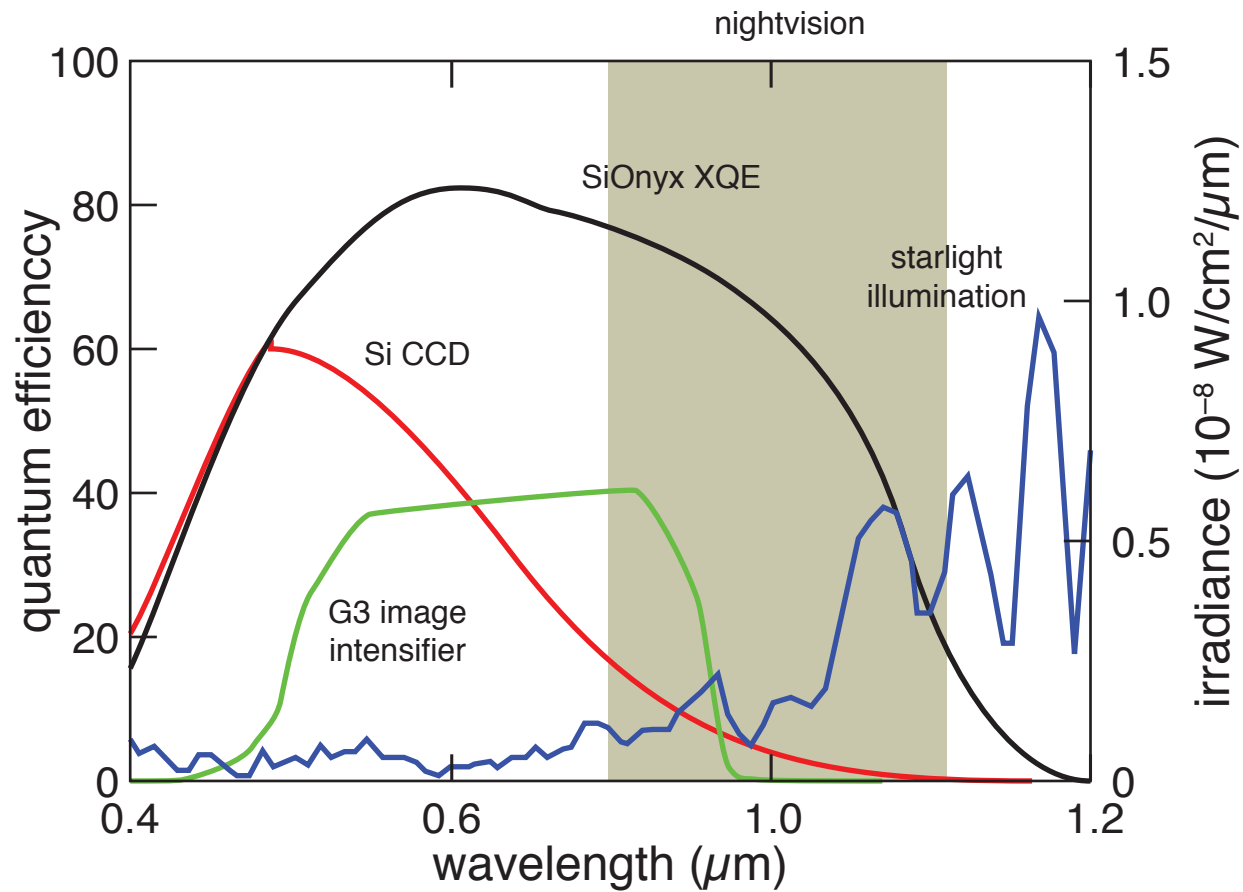




1 properties

2 intermediate band

3 devices



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

1 properties

2 intermediate band

3 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**

1 properties

2 intermediate band

3 devices



Funding:

Army Research Office

DARPA

Department of Energy

NDSEG

National Science Foundation

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SiOnyx