Nonequilibrium materials: using ultrashort laser pulses to change band structures

2016 SPIE Defense + Commercial Sensing Meeting
Ultrafast Bandgap Photonics Conference
Baltimore, MD, 18 April 2016

Introduction

SCIENCE

4 May 1979, Volume 204, Number 4392

Laser Annealing of Ion-Implanted Semiconductors

C. W. White, J. Narayan, R. T. Young

Impurities can be implanted in the near-surface region of solids by a process in which the impurity ions are accelerated in an electrostatic field to a desired energy and then made to impinge on the solid targets. This process, known as ion implantation, has made a significant impact [illegible] industry, where it is used to dope semiconductors.

is often accompanied by undesirable consequences such as precipitation of dopants in the implanted region, degradation of certain electrical properties, decomposition of the substrate in the case of compound semiconductors, and usually only partial removal of lattice damage in the implanted layer.

Recently, interest (*1*) has been gener-

gion which are necessary for annealing the lattice damage; yet, the absorbed photon energy is insufficient to raise the temperature of the undamaged substrate significantly above ambient, and hence the deleterious effects of high temperatures in this region are circumvented. Another advantage for some applications is that laser annealing can be carried out in air because the surface region subjected to high temperatures cools so rapidly that introduction of significant amounts of impurities from the atmosphere is minimized. This should be a particularly attractive feature for highly automated device fabrication. A third, and potentially very important, advantage of laser annealing is that it enables highly localized annealing to be performed simply by focusing the incident laser light to the desired dimensions (*21*). This may permit the "writing" of regions of localized electrical activity on an ion-implanted wafer and could have profound implications for device process-

Summary. The physical and electrical properties of ion-implanted silicon annealed [illegible] radiation are described. Particular emphasis is placed on the [illegible] be achieved with laser annealing to those [illegible] applications of these tech-

work performed at [illegible] Laboratory (ORNL) on the characterization of ion-implanted silicon annealed by radiation from pulsed ruby la- particular emphasis on [illegible] with

C.W.White, J.Narayan, R.T.Young, *Science* 204, 461–468 (1979)

Introduction

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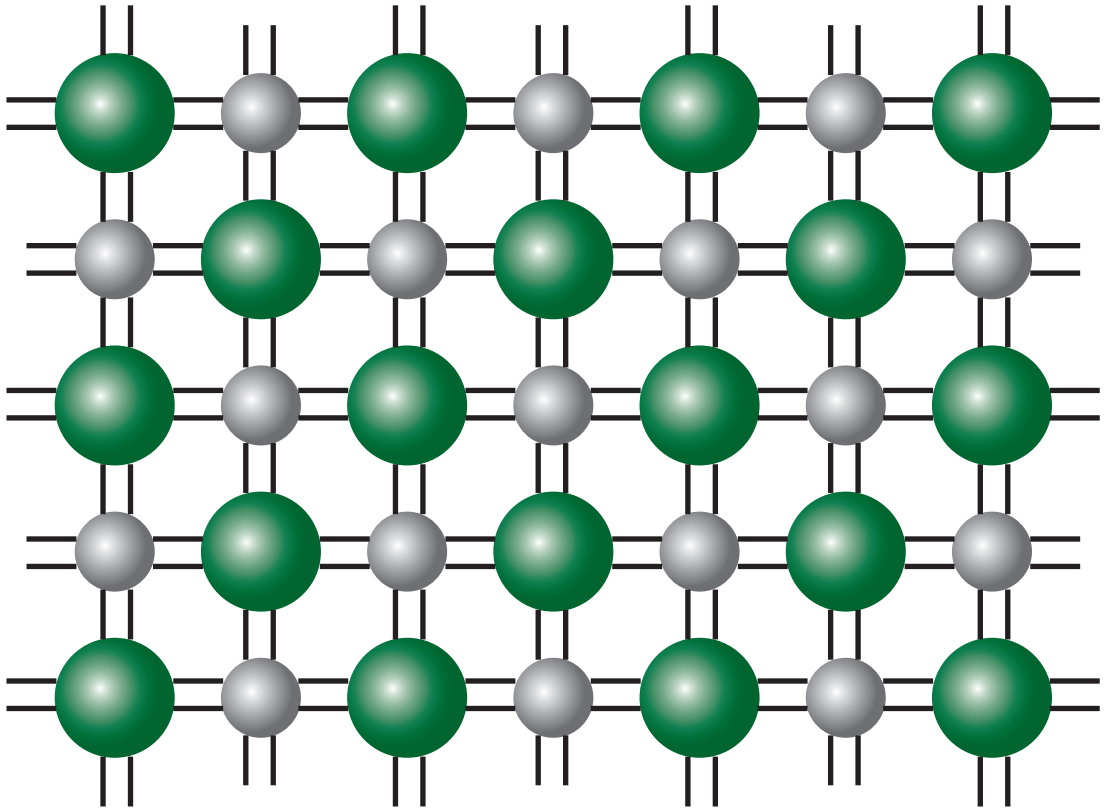
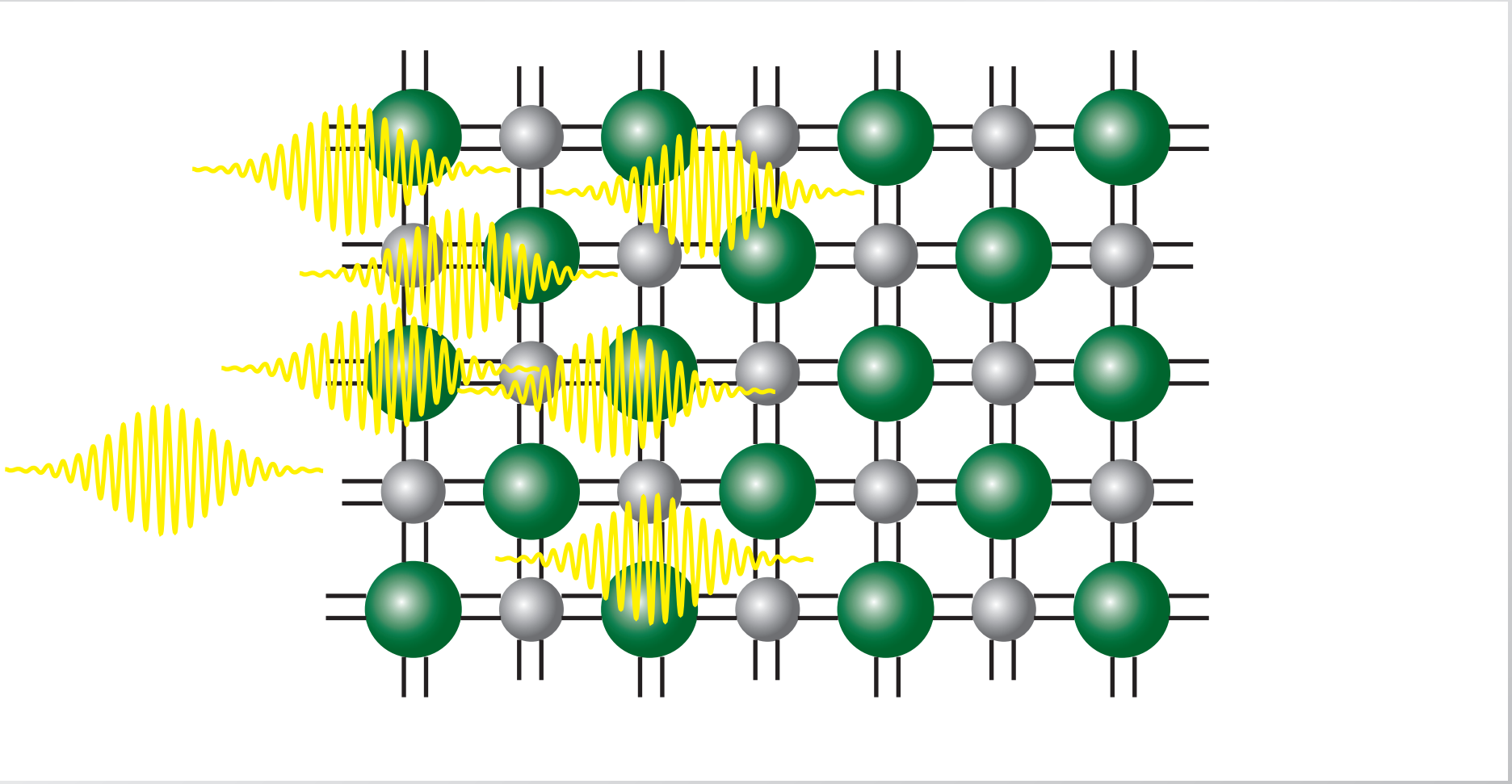


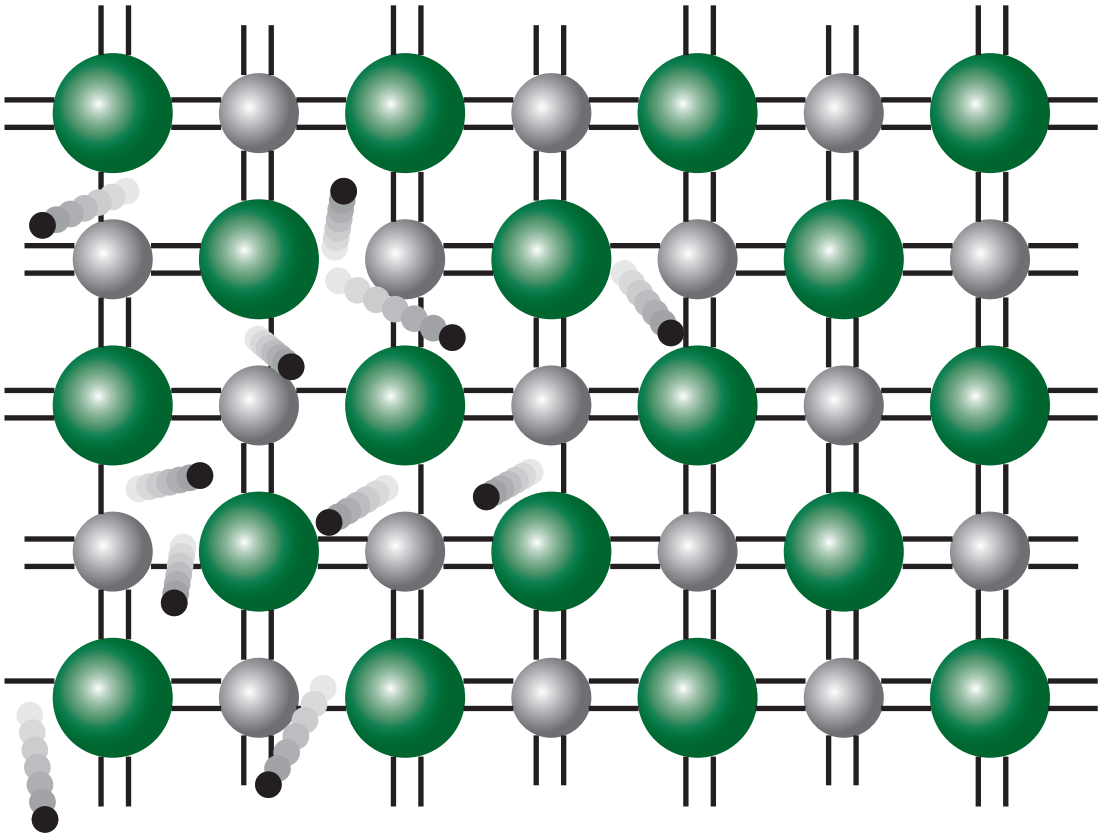
Introduction

photons excite valence electrons…



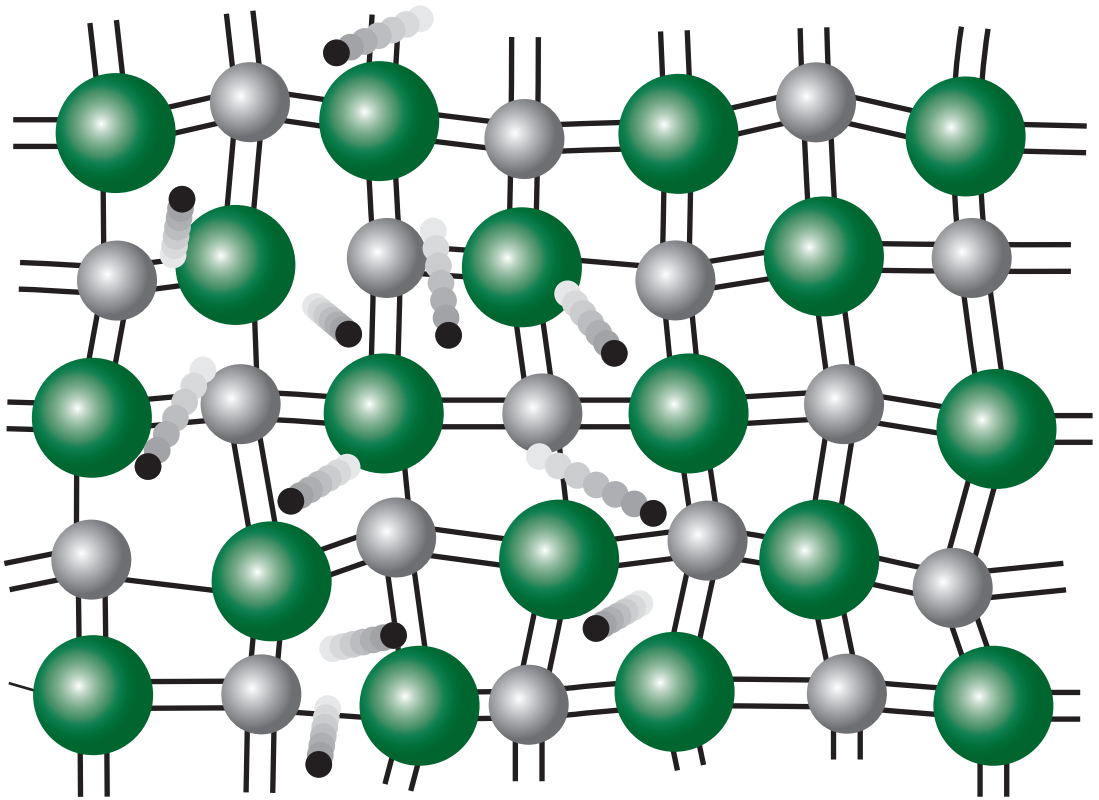
Introduction

…and create free carriers…



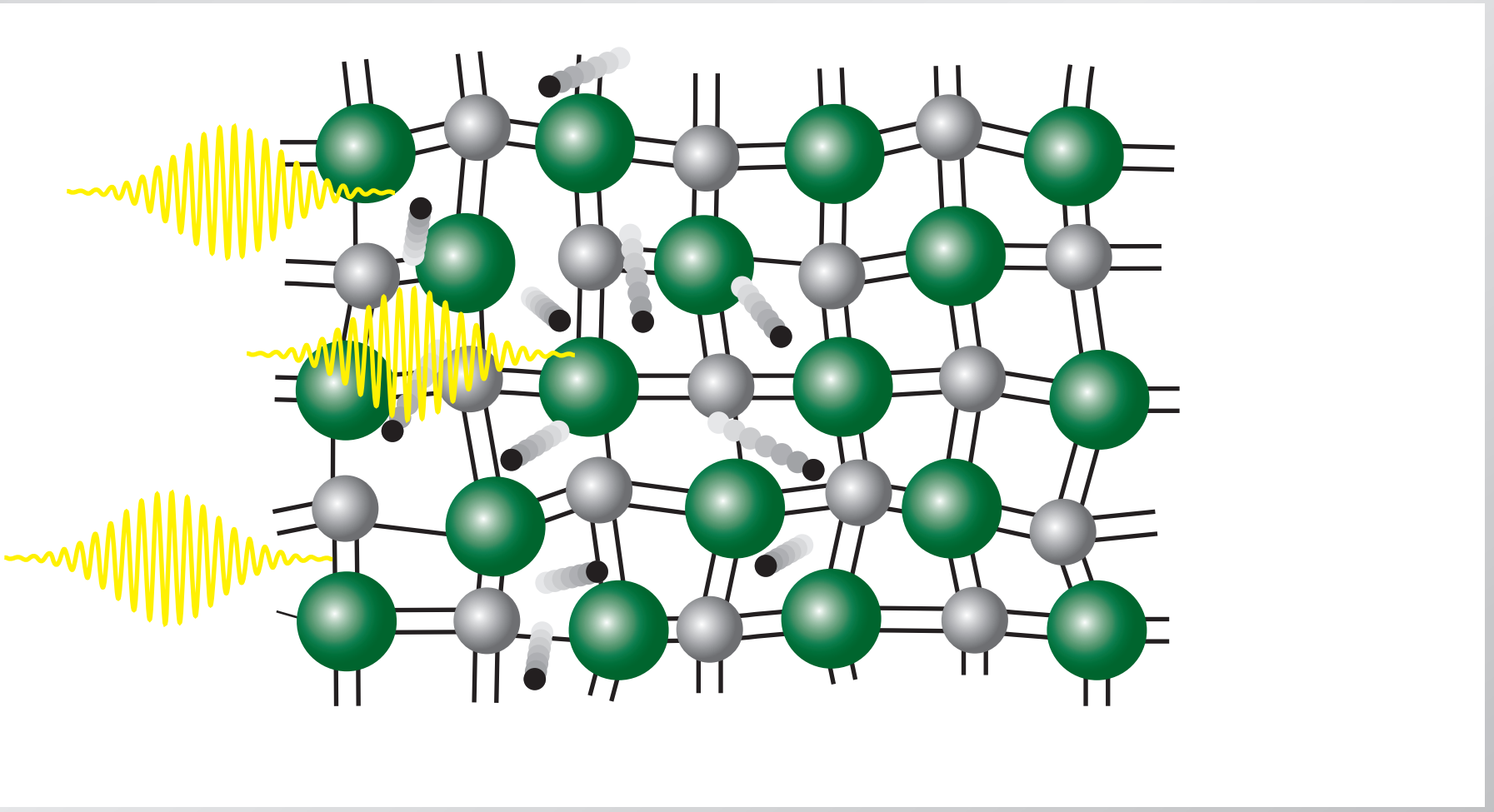
Introduction

…causing electronic and structural changes…



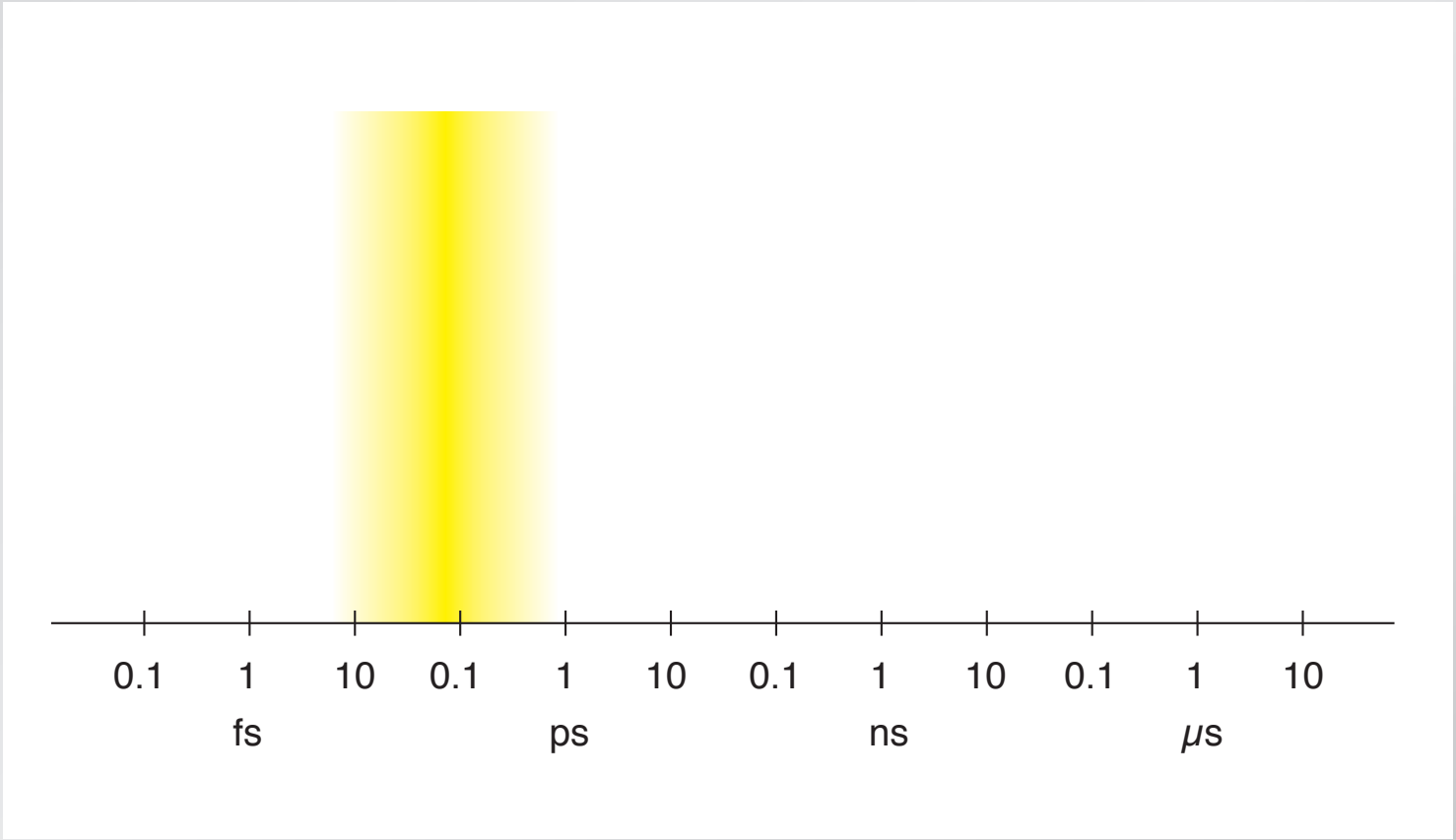
Introduction

…which we can detect with a second laser pulse.



Introduction

relevant time scales



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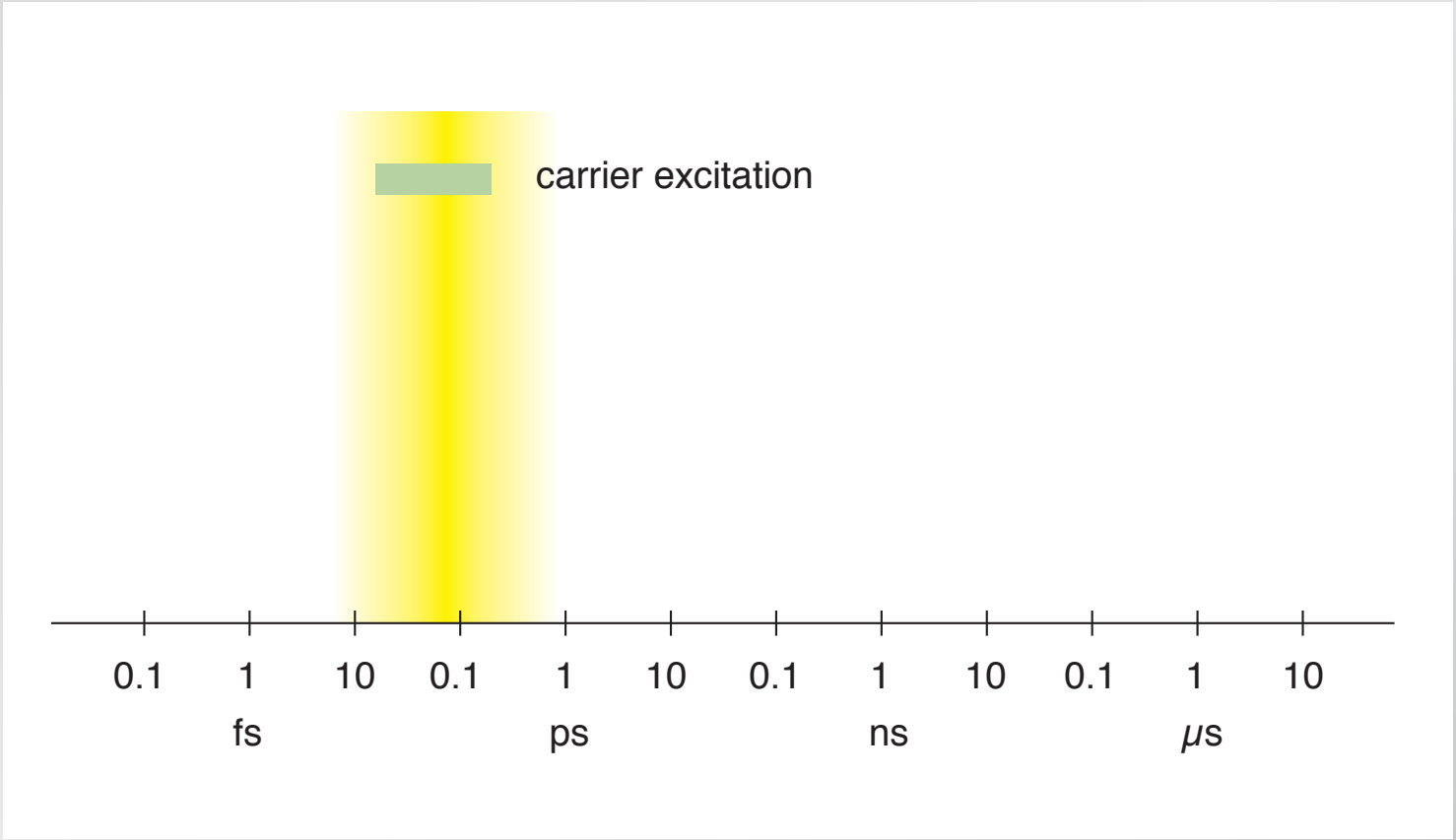

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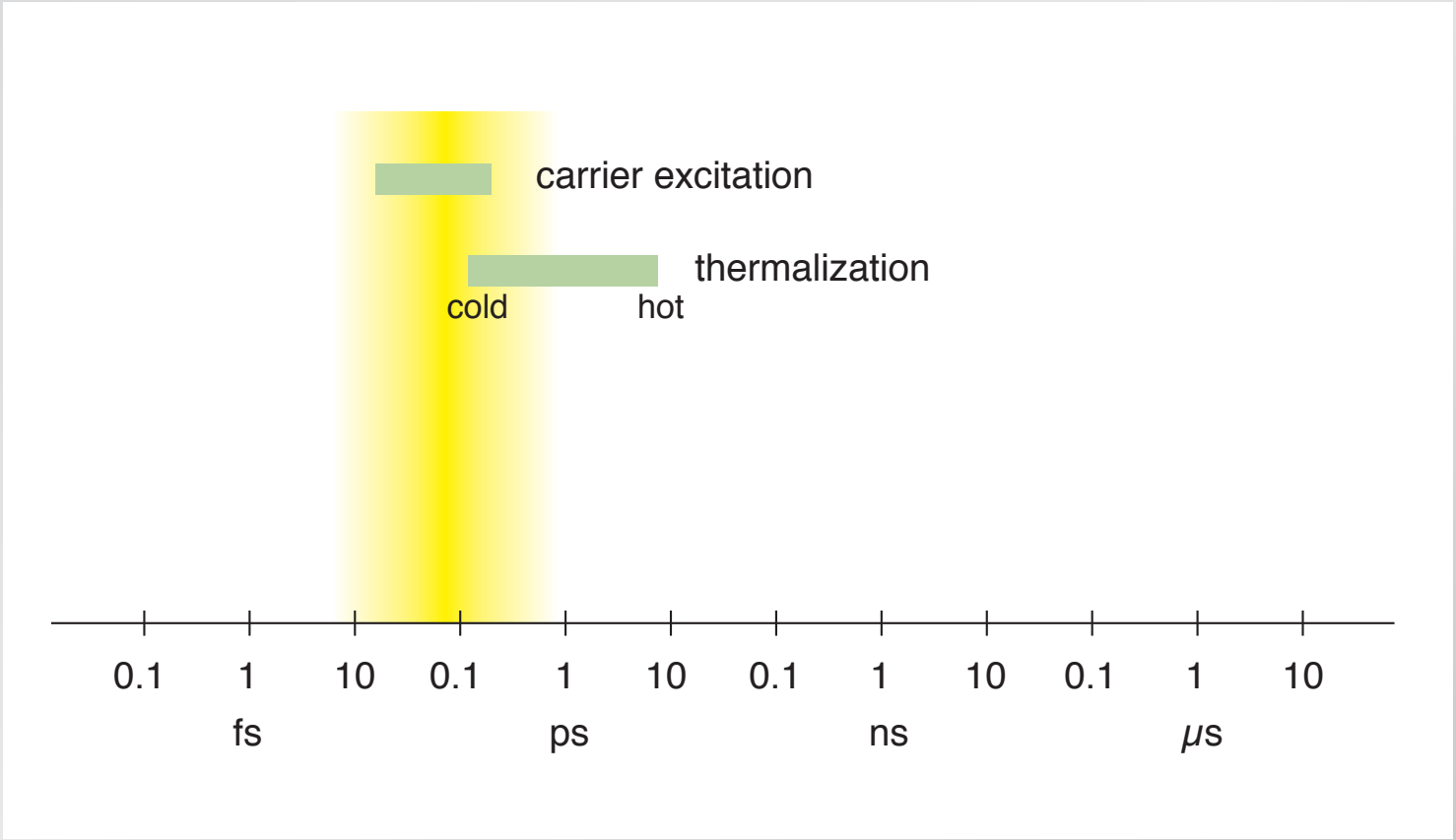

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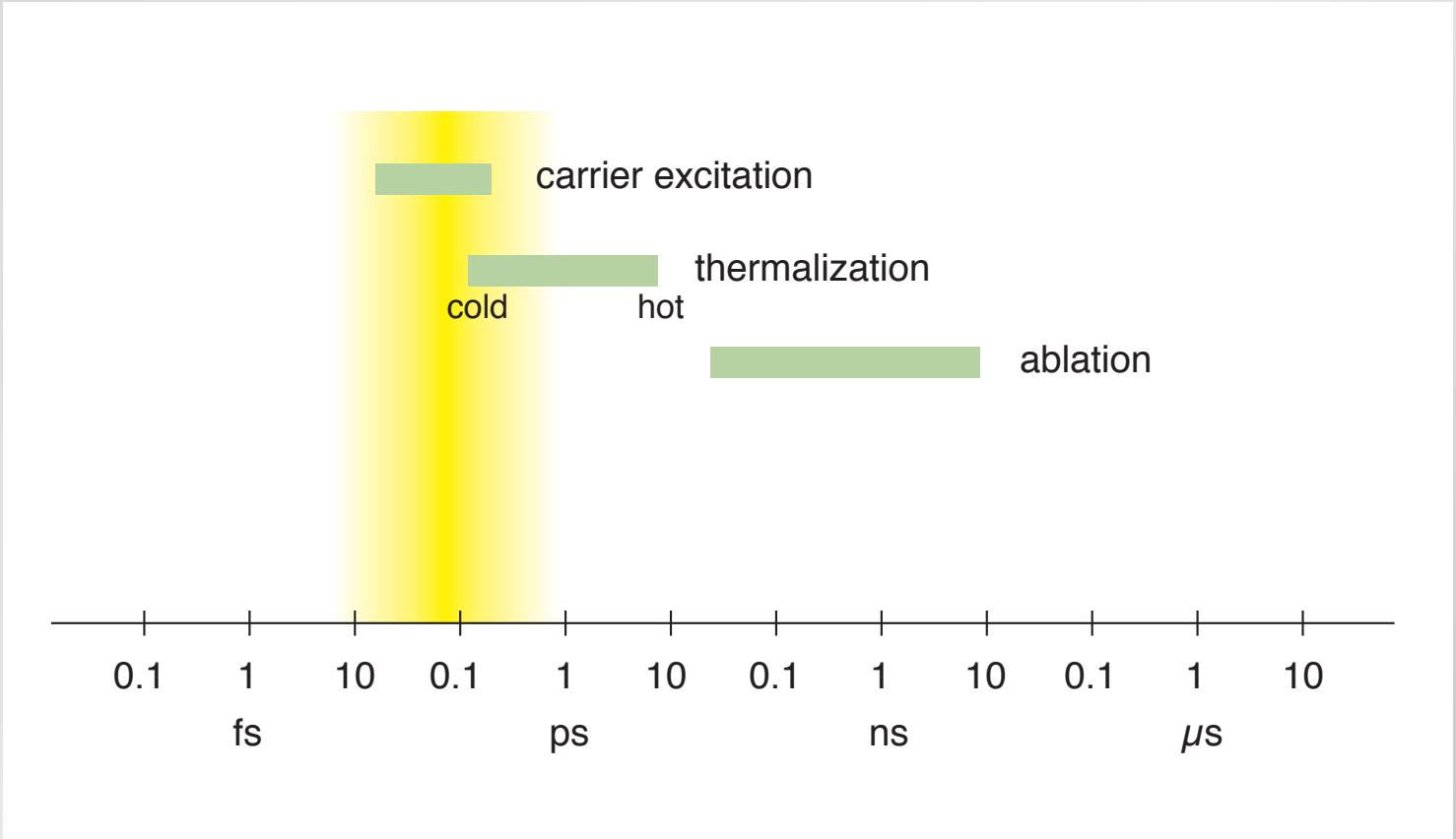

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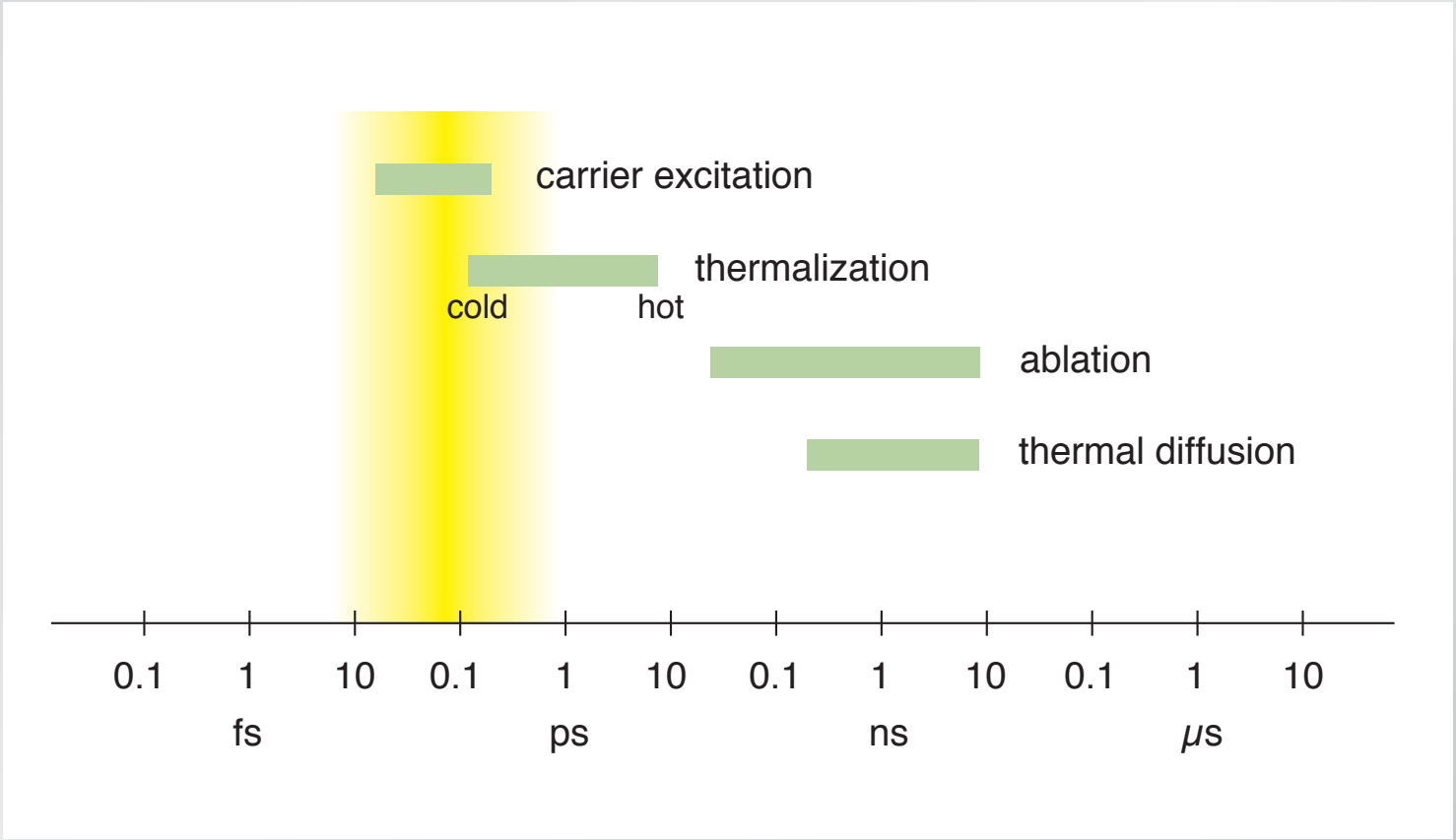

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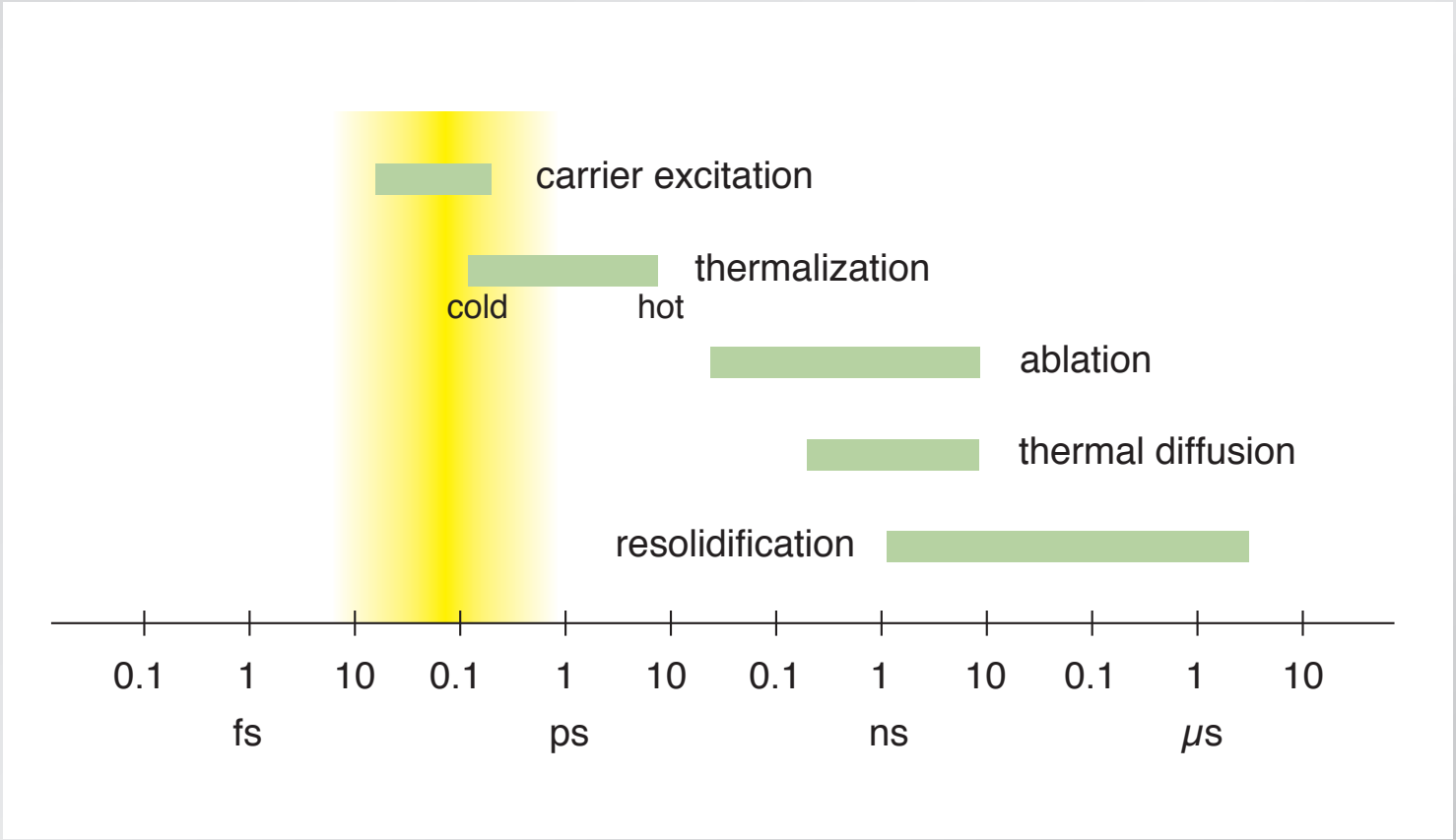

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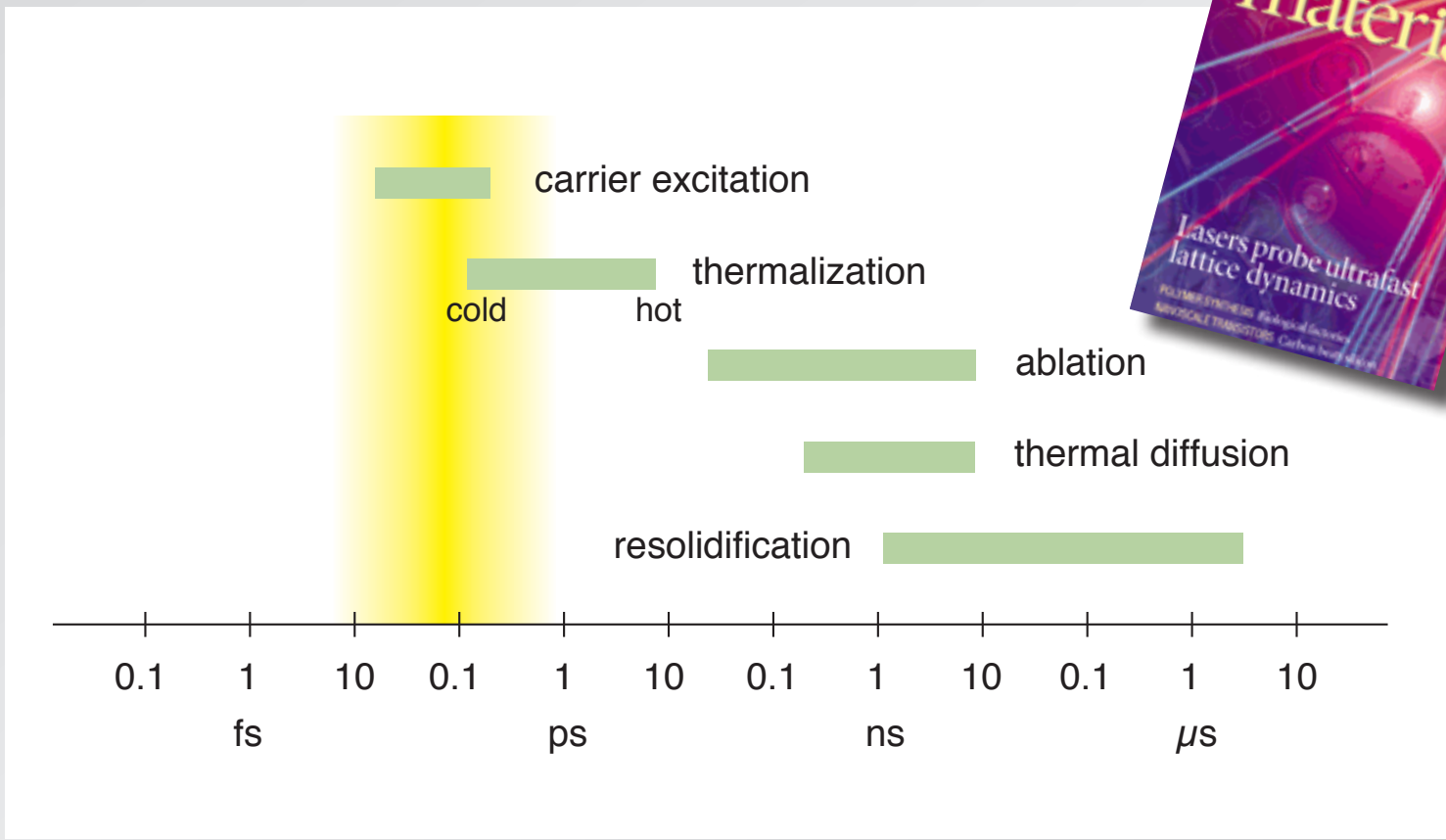


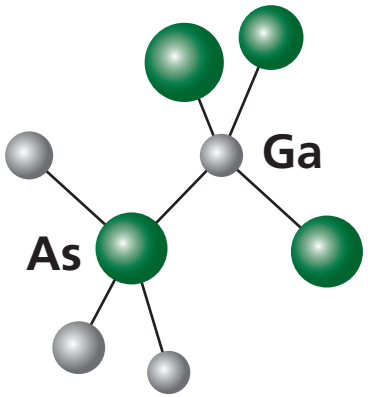
Nature Materials **1**, 217 (2002)

Outline

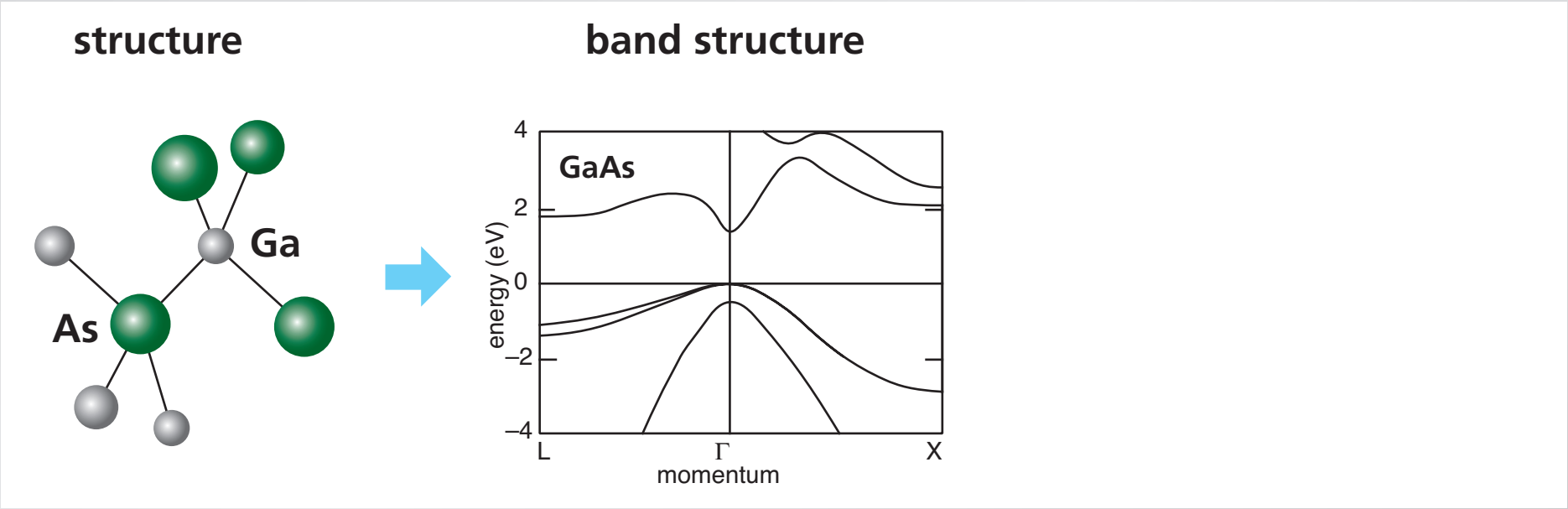
- transient band structure changes
- creating an intermediate band
- semiconductor to metal transition

Transient band structure changes

structure



Transient band structure changes



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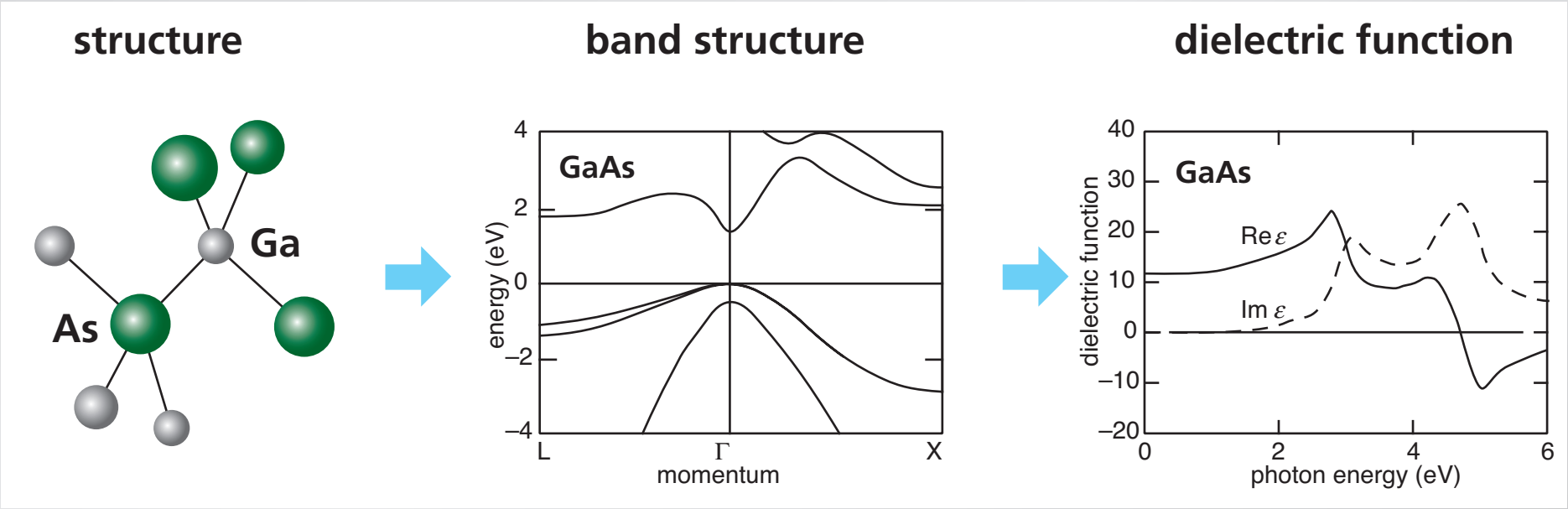

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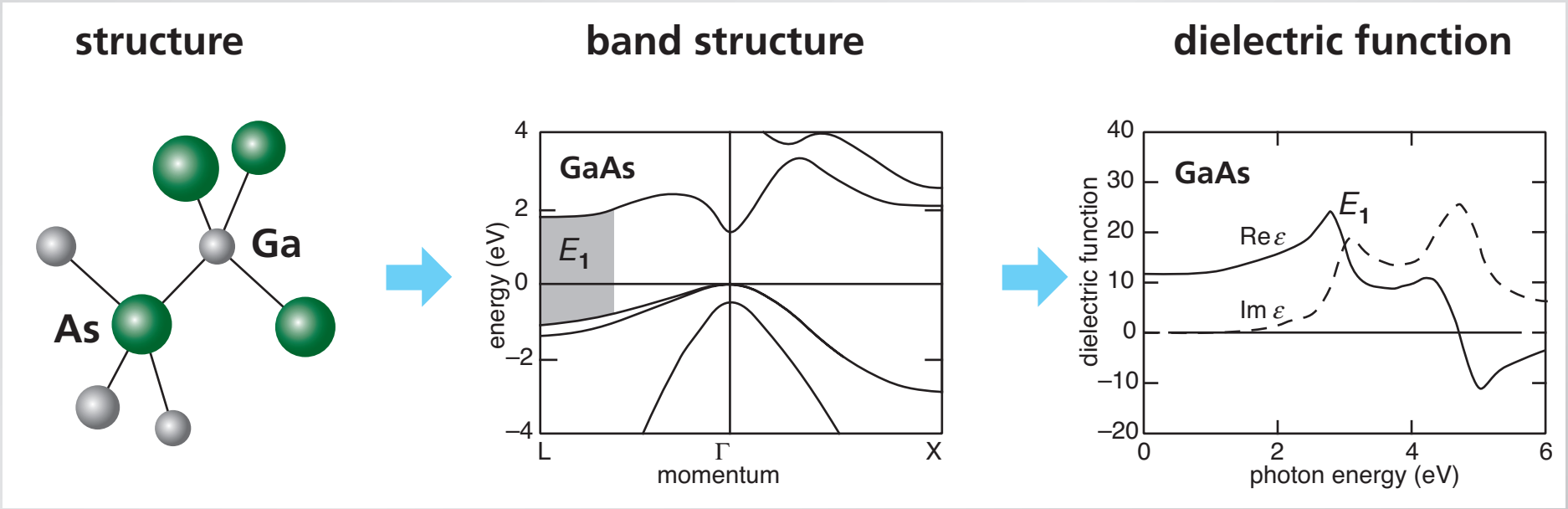

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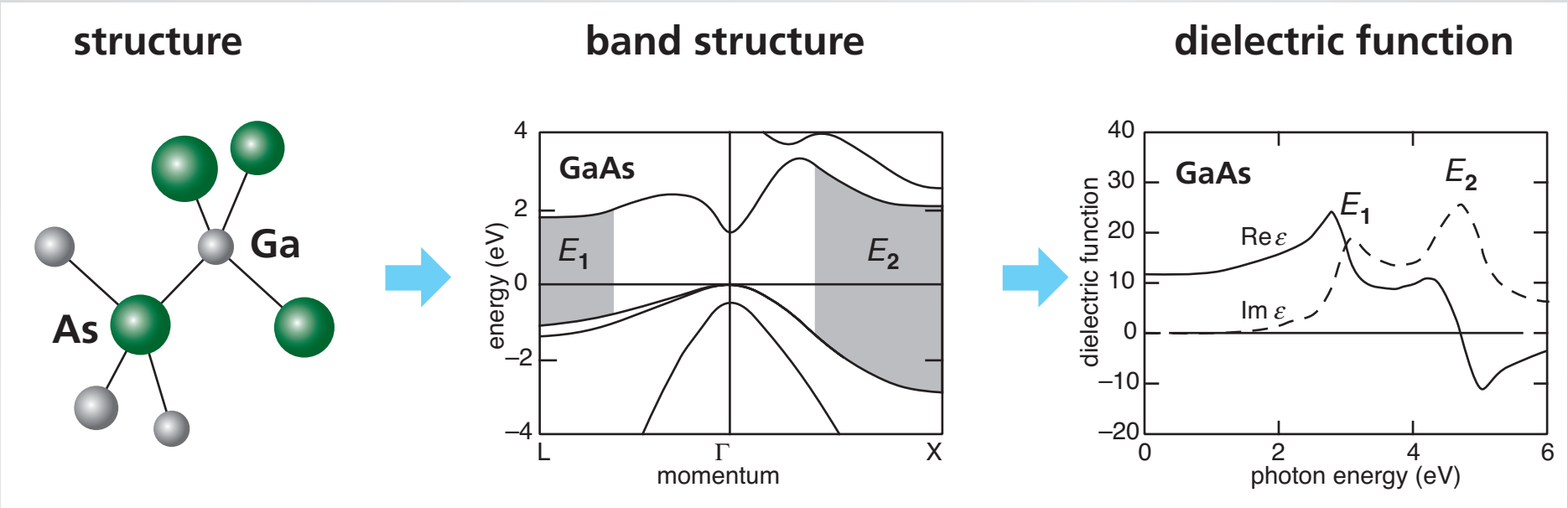

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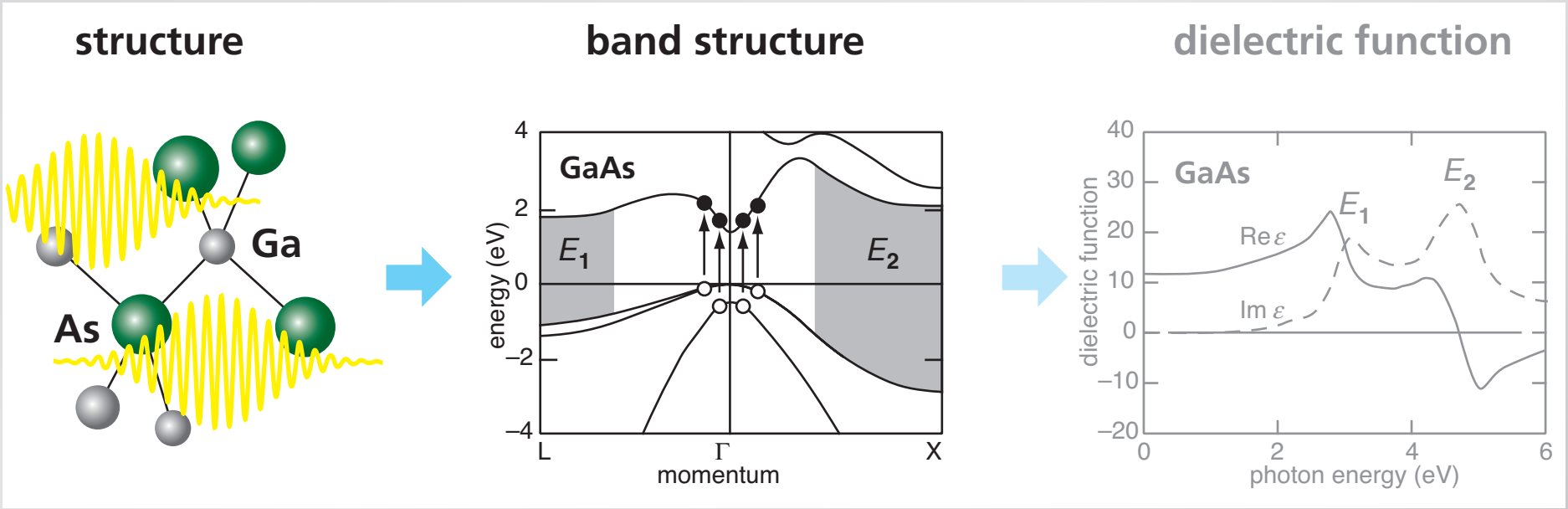

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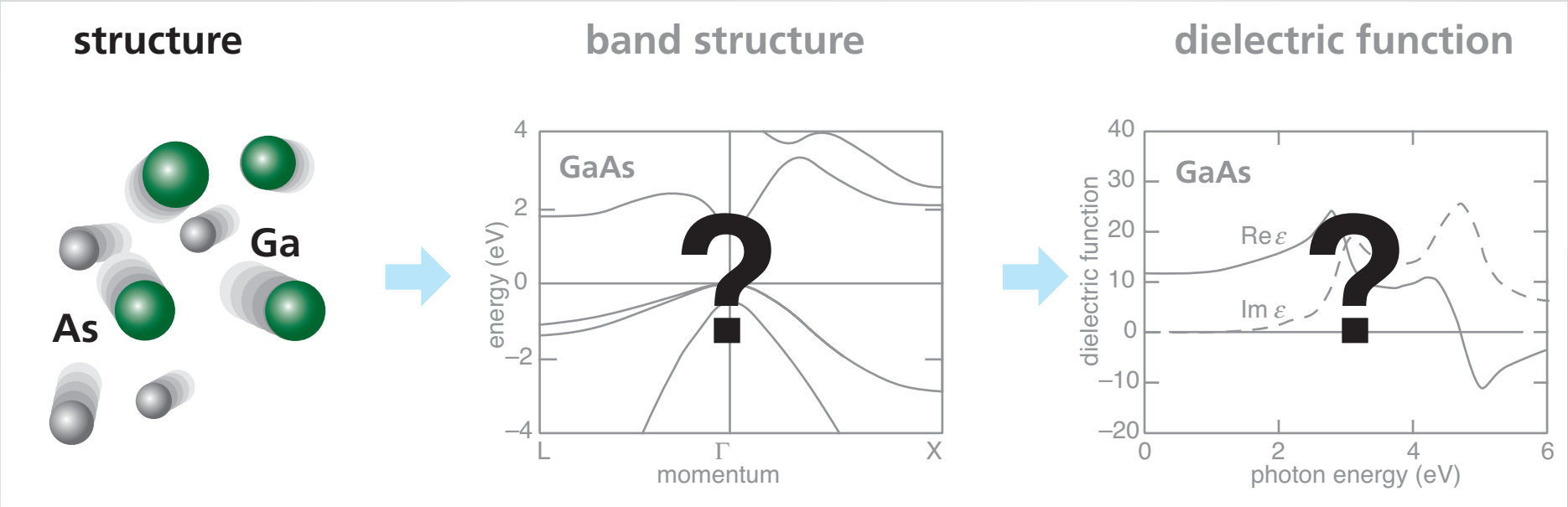

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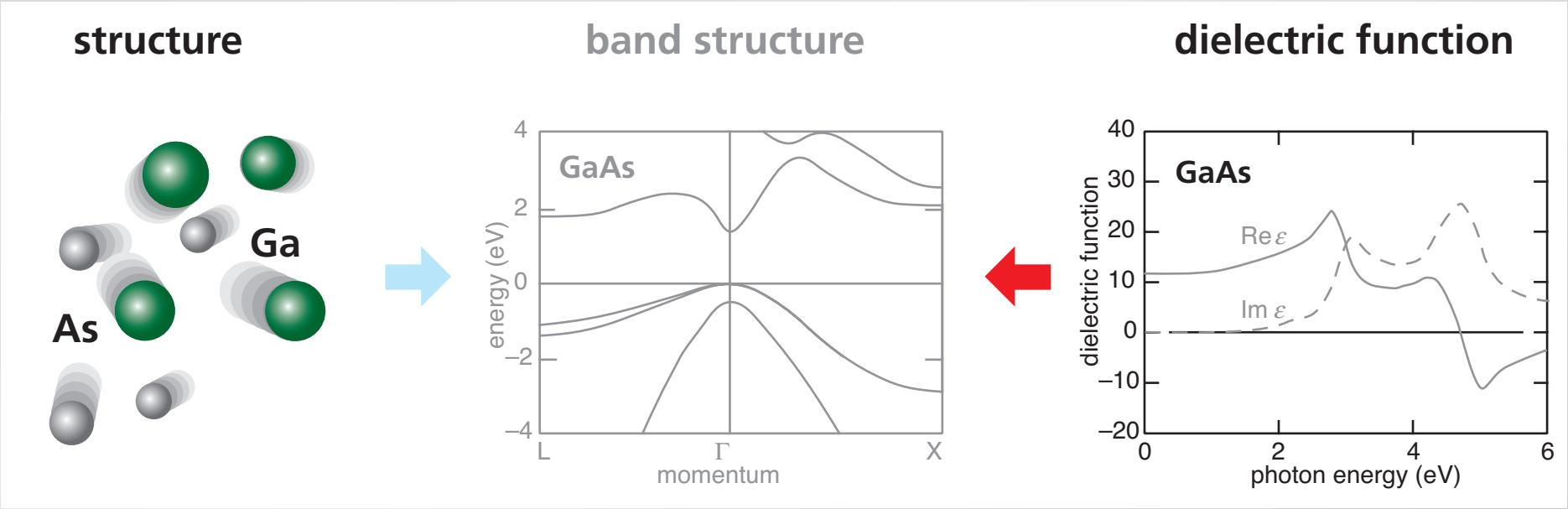

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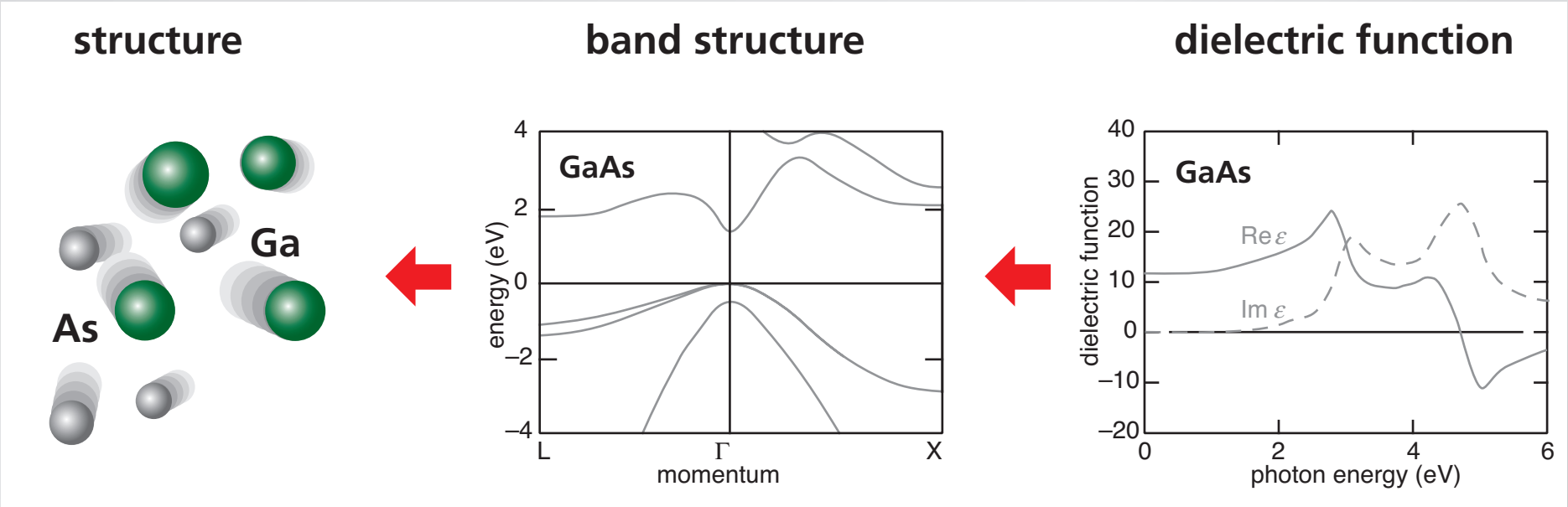

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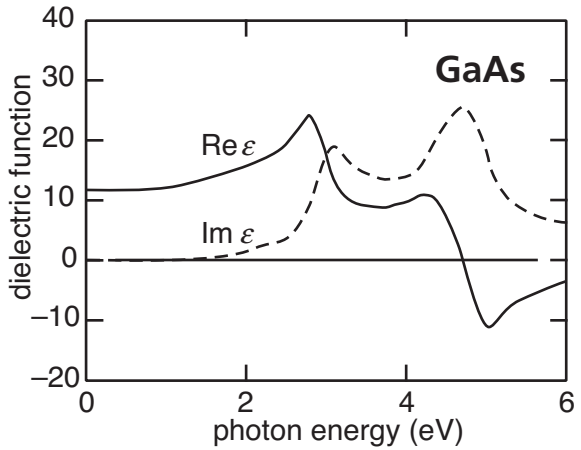

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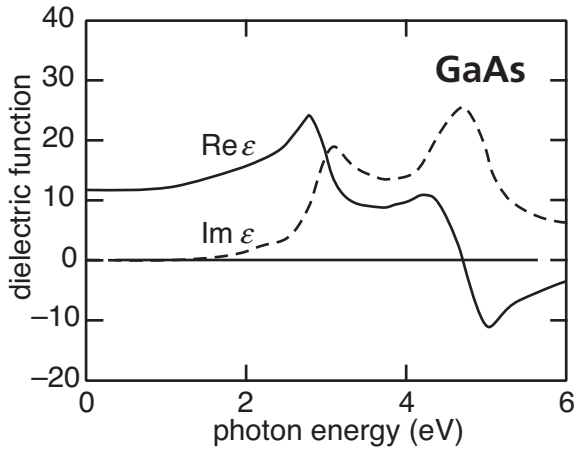

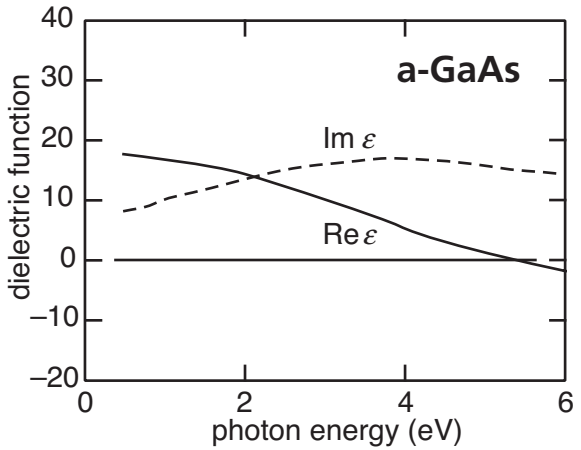

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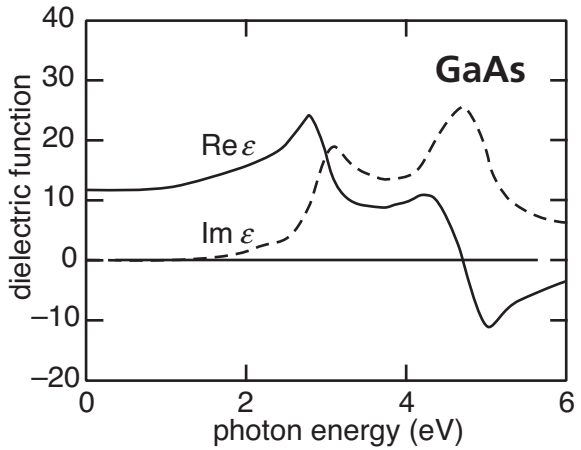

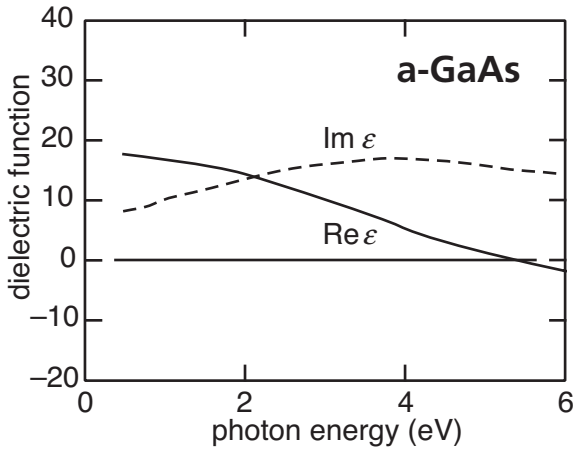

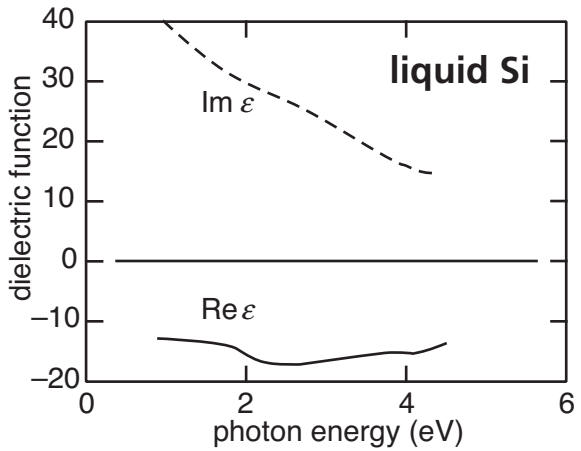

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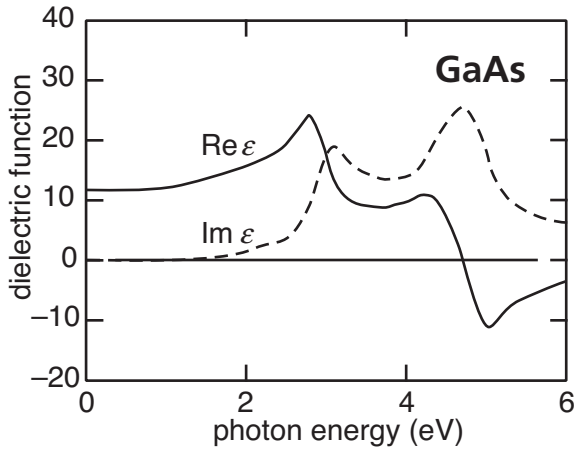
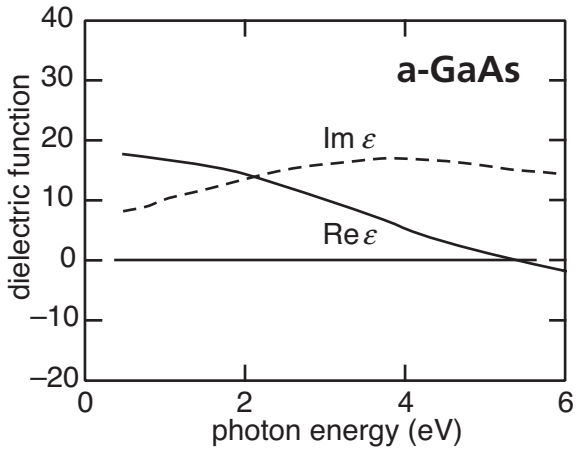
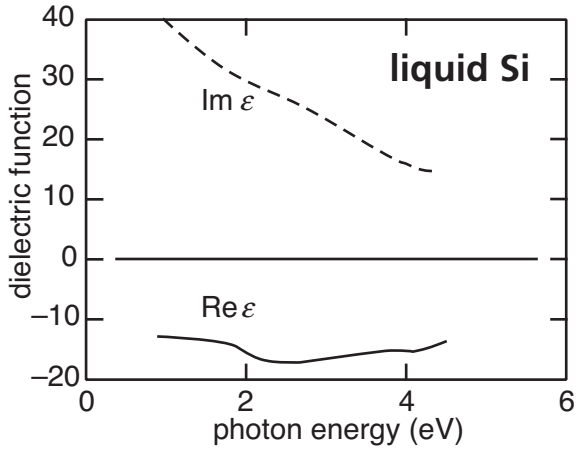
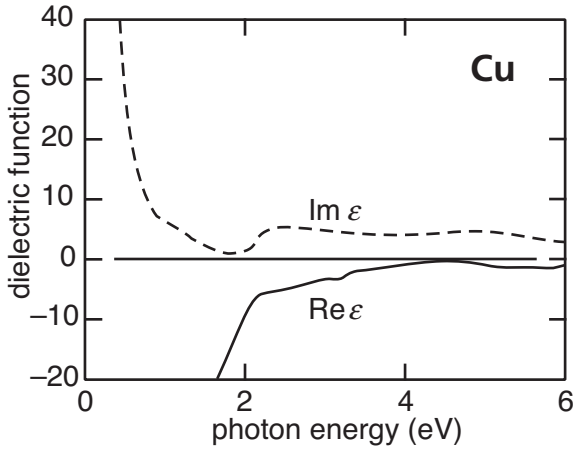


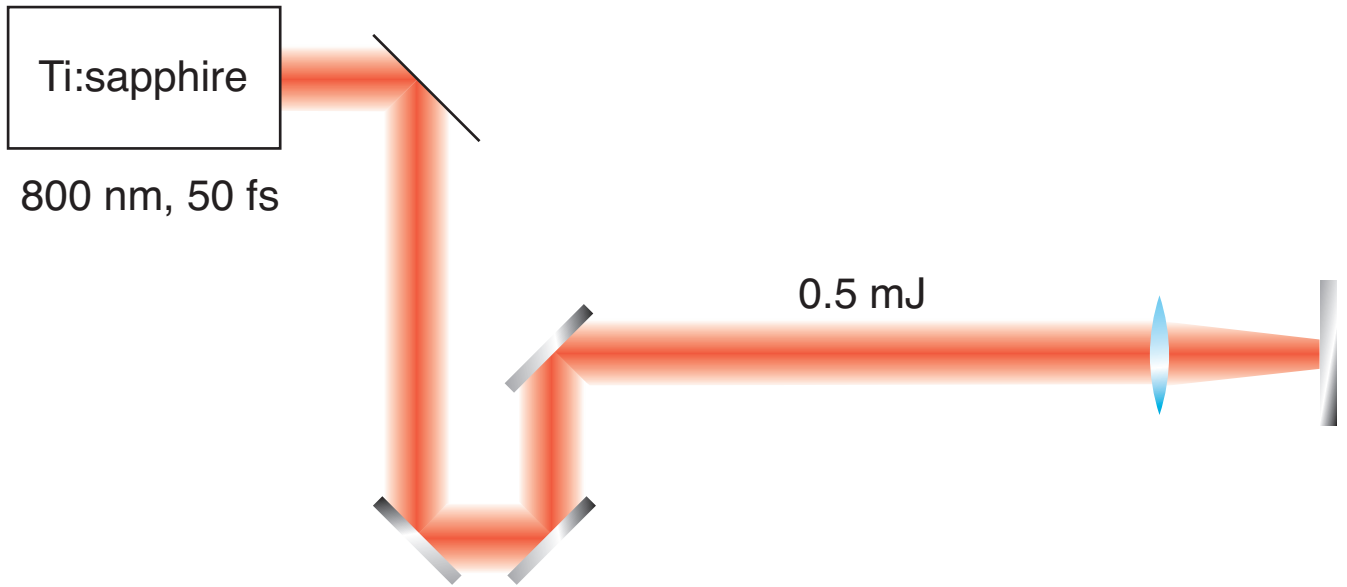






Transient band structure changes

time-resolved dual-angle reflectometry



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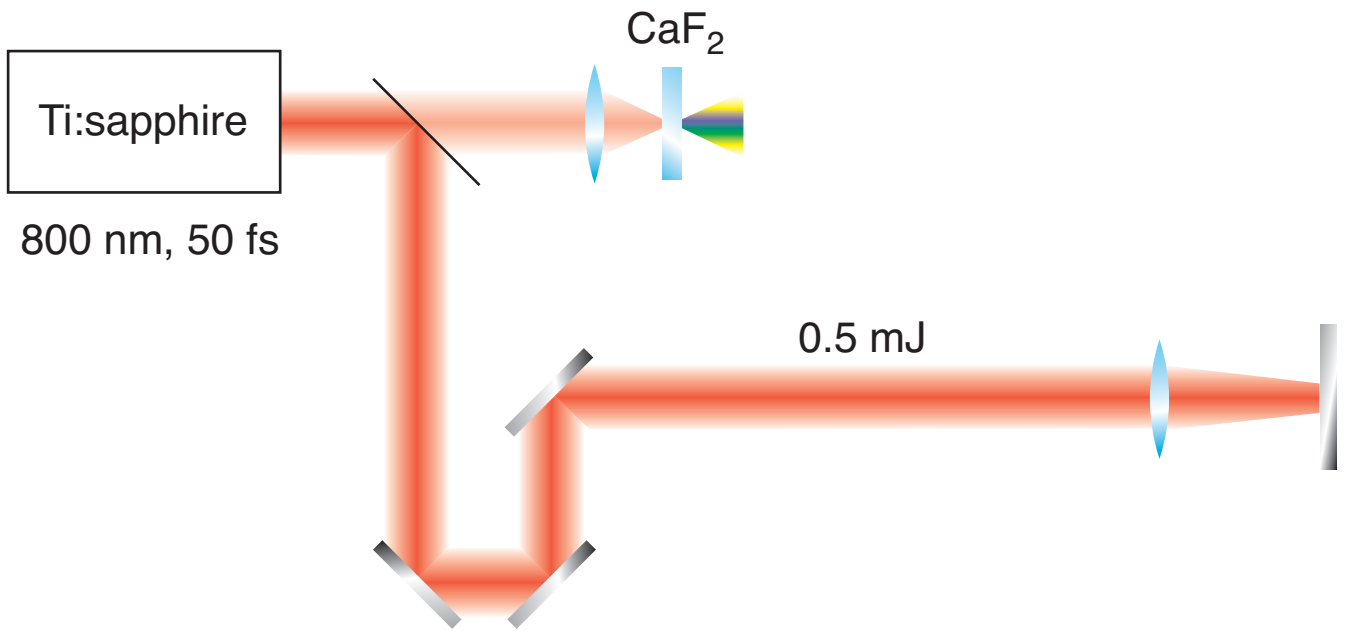

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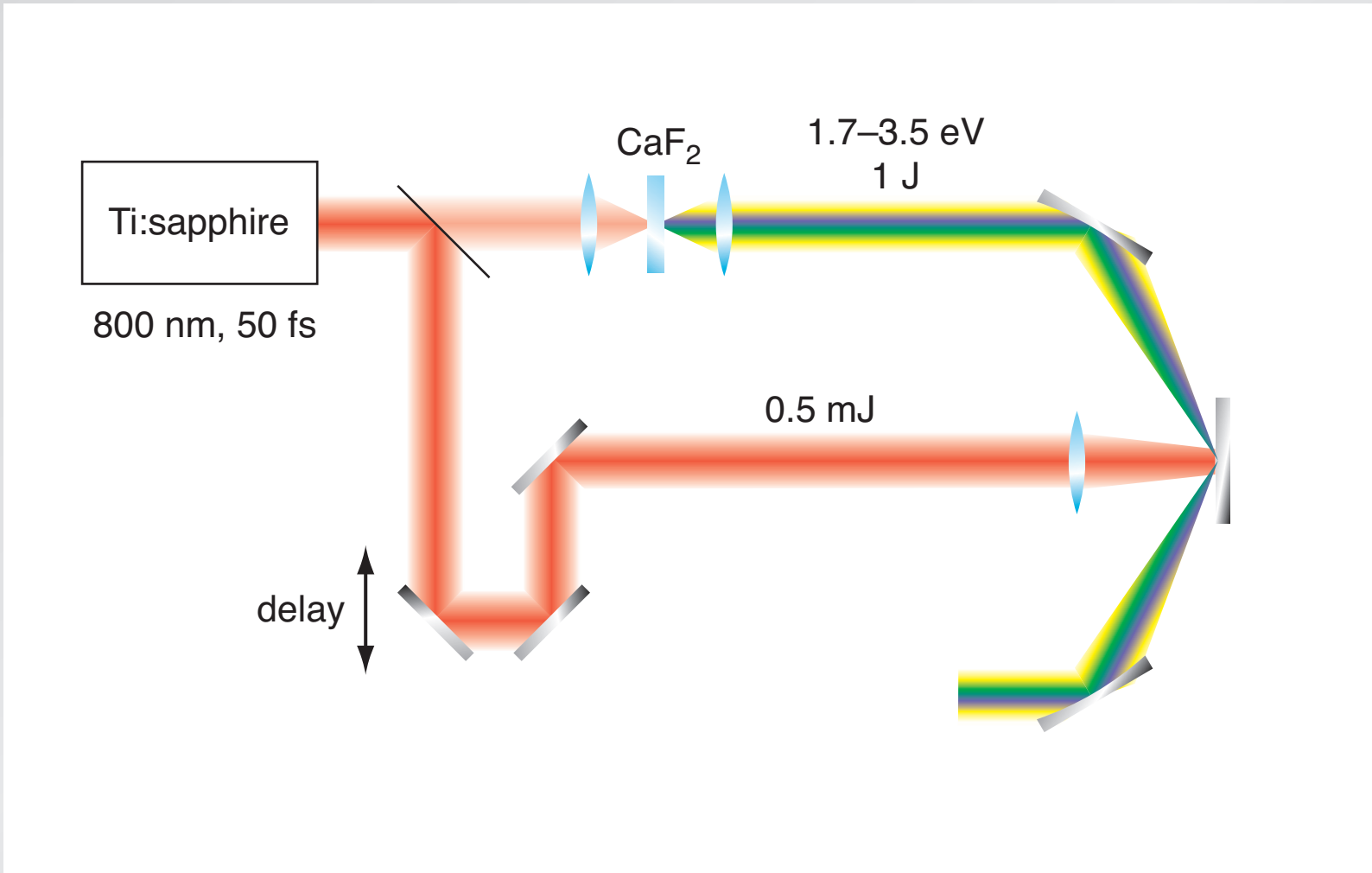

Transient band structure changes

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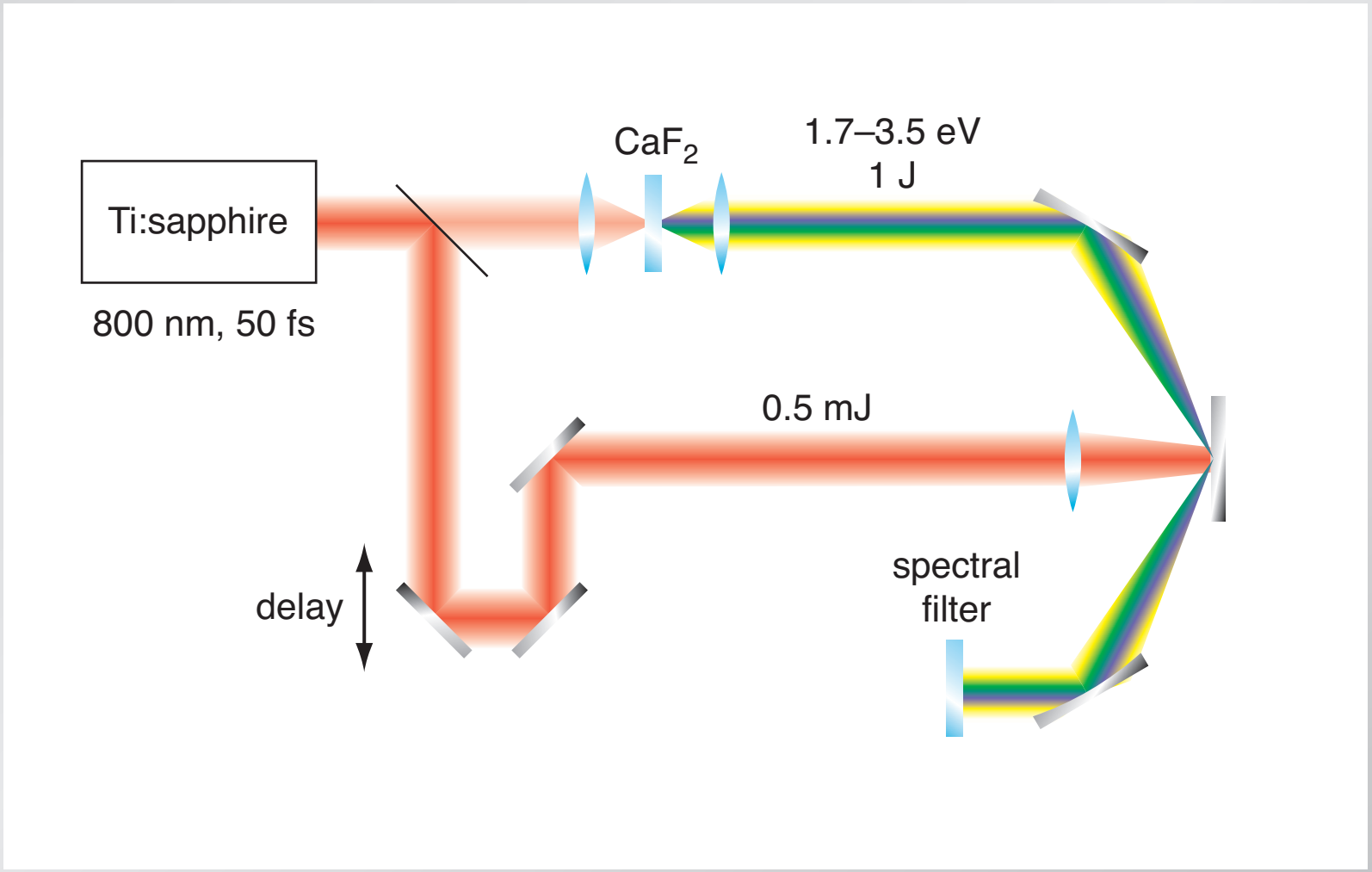

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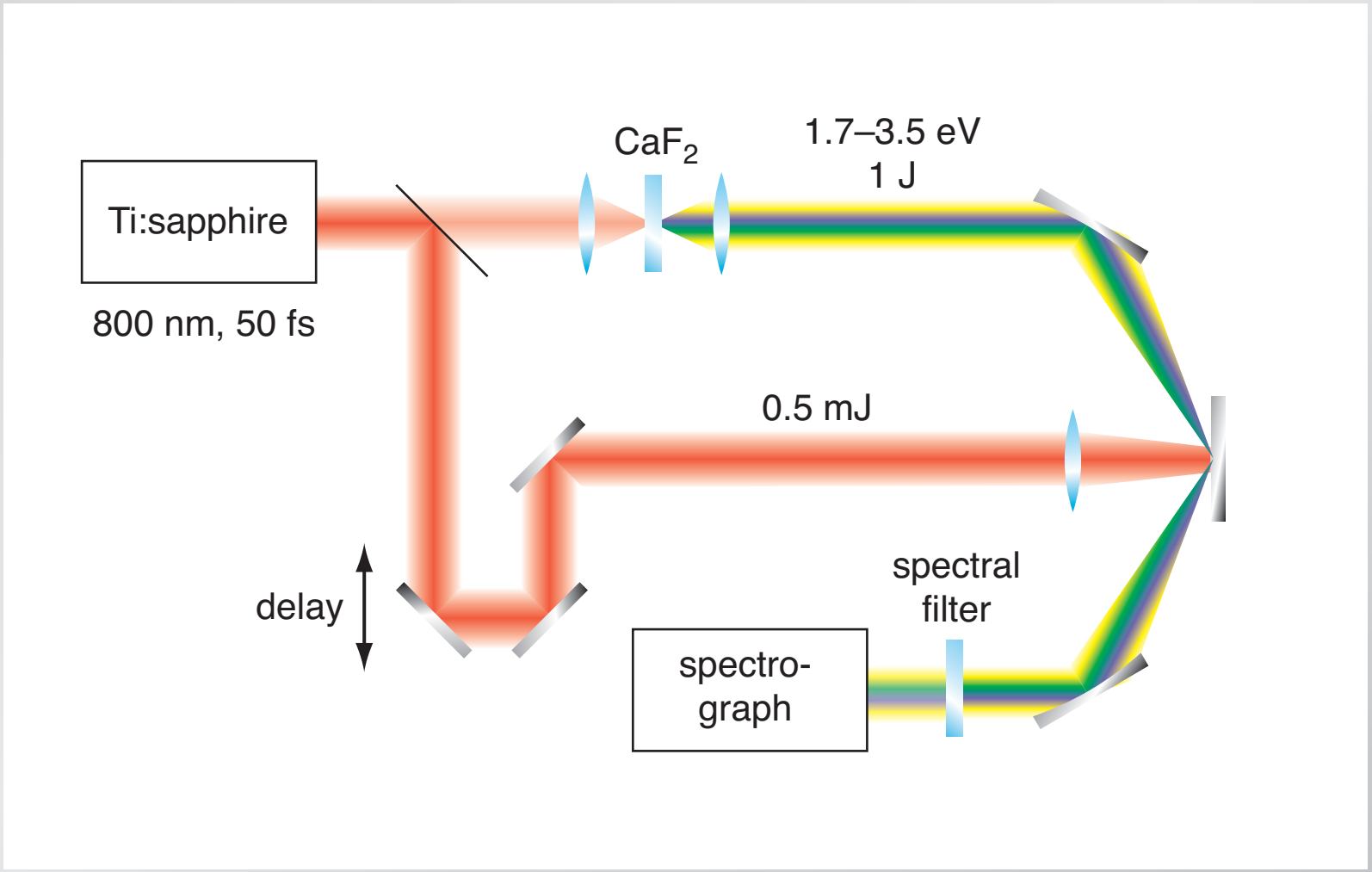

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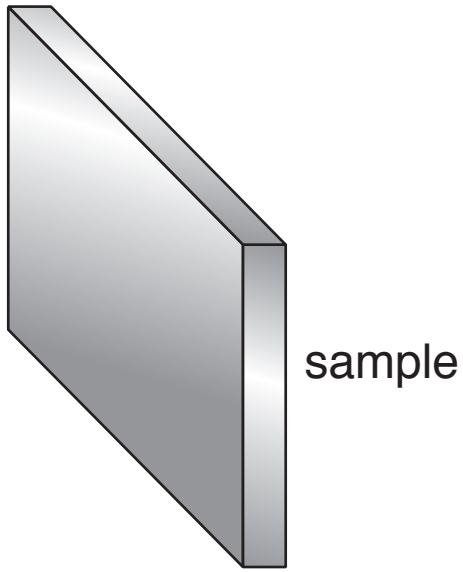
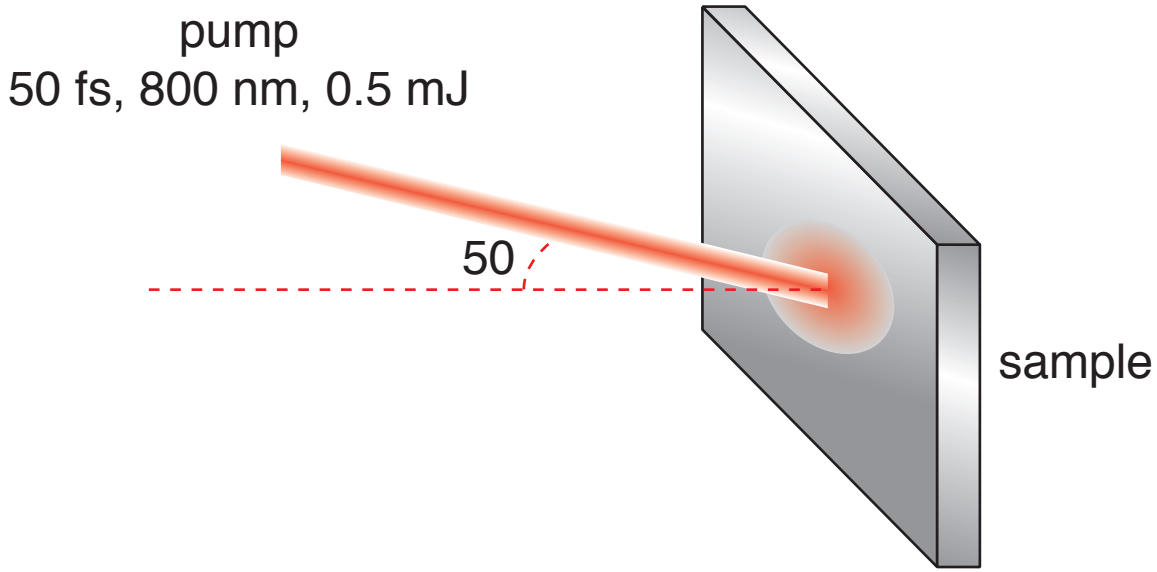


Transient band structure changes

time-resolved dual-angle reflectometry



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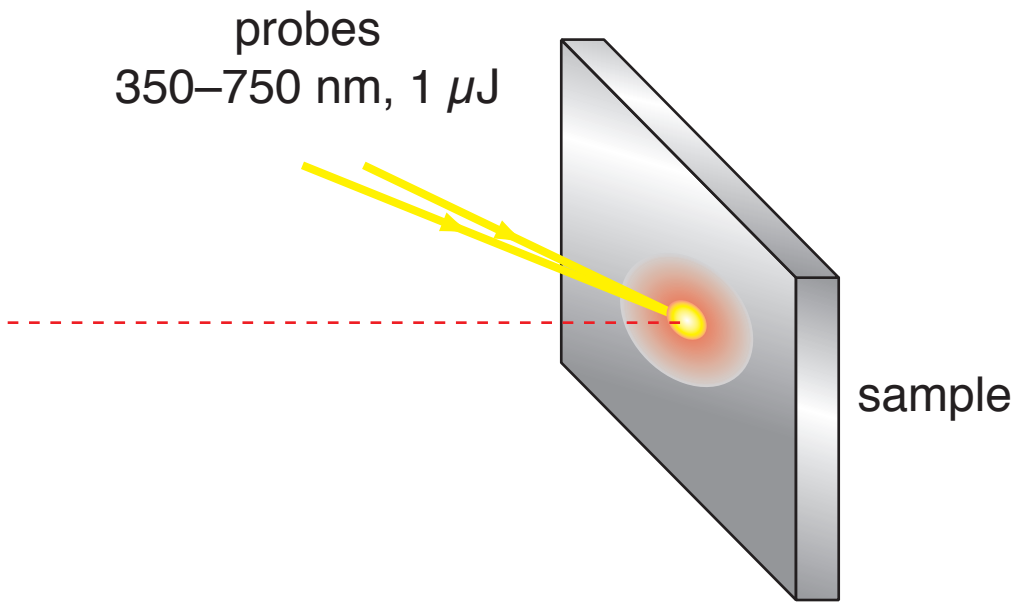
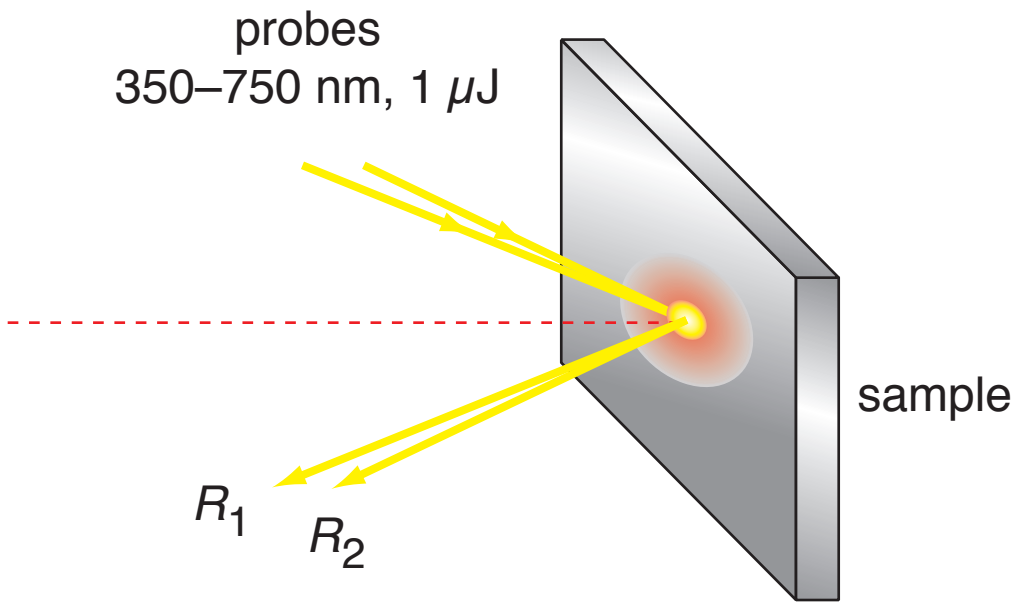


Transient band structure changes

time-resolved dual-angle reflectometry



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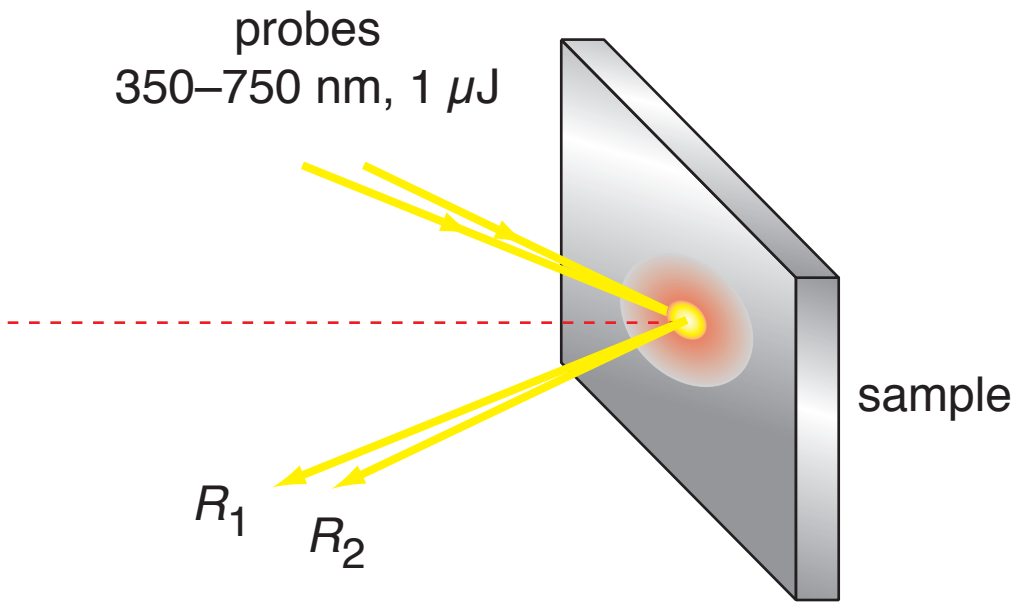
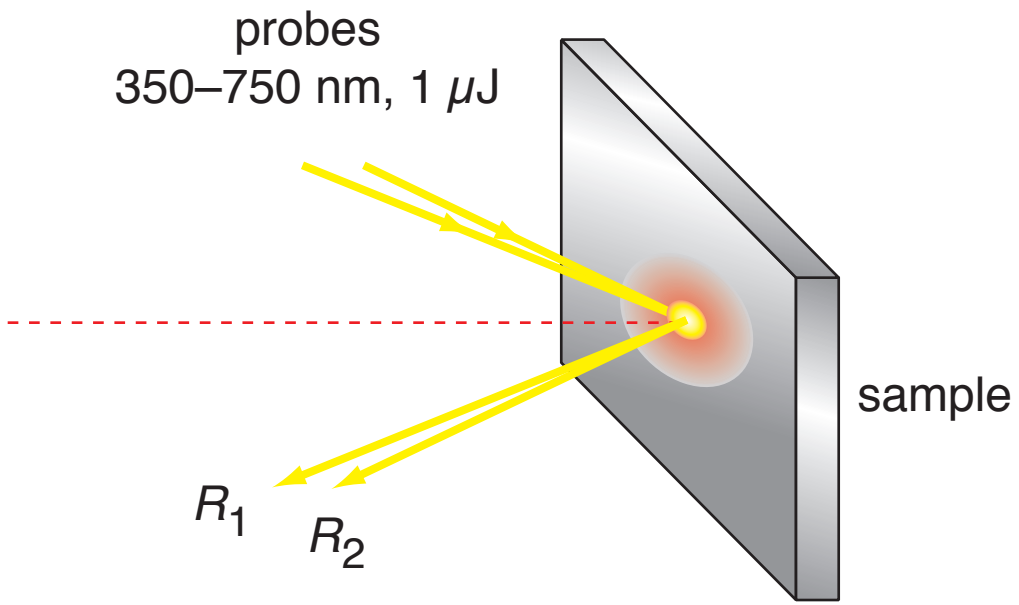


Fresnel equations

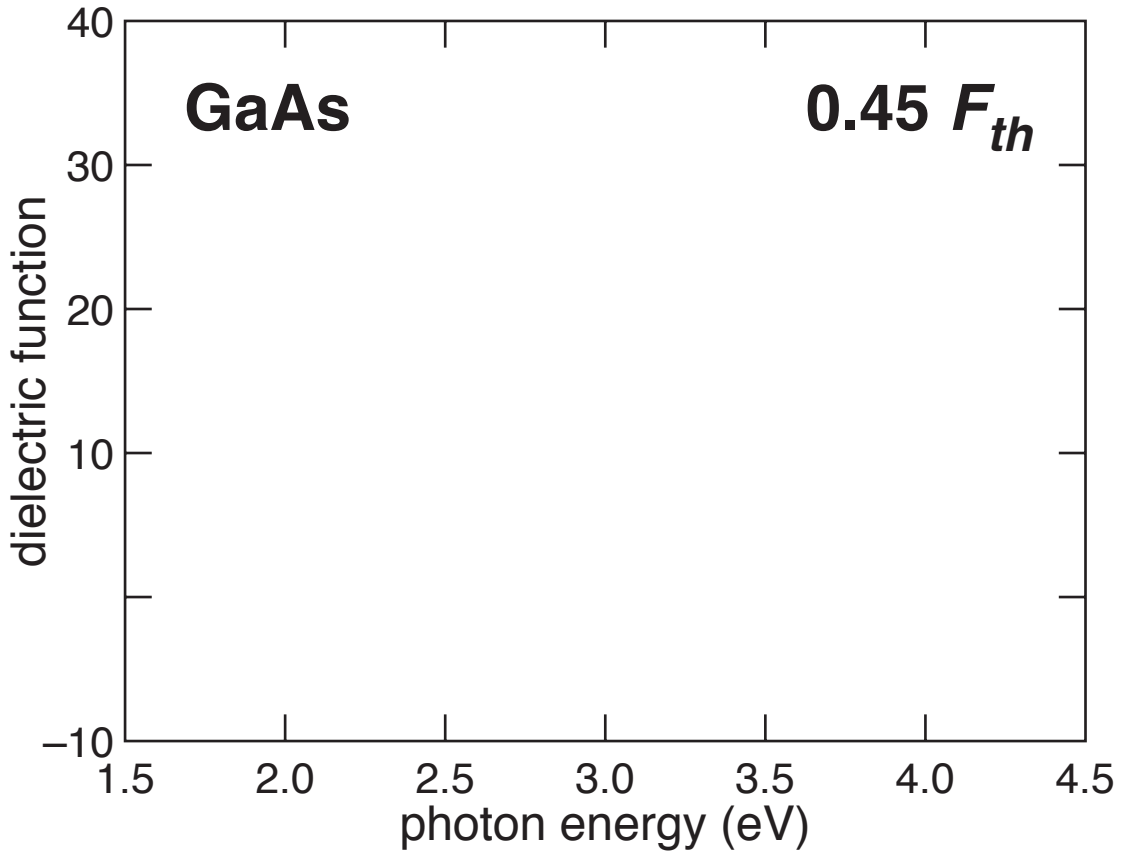
Transient band structure changes

time-resolved dual-angle reflectometry



Fresnel equations → Re $\varepsilon(\omega)$, Im $\varepsilon(\omega)$

Transient band structure changes



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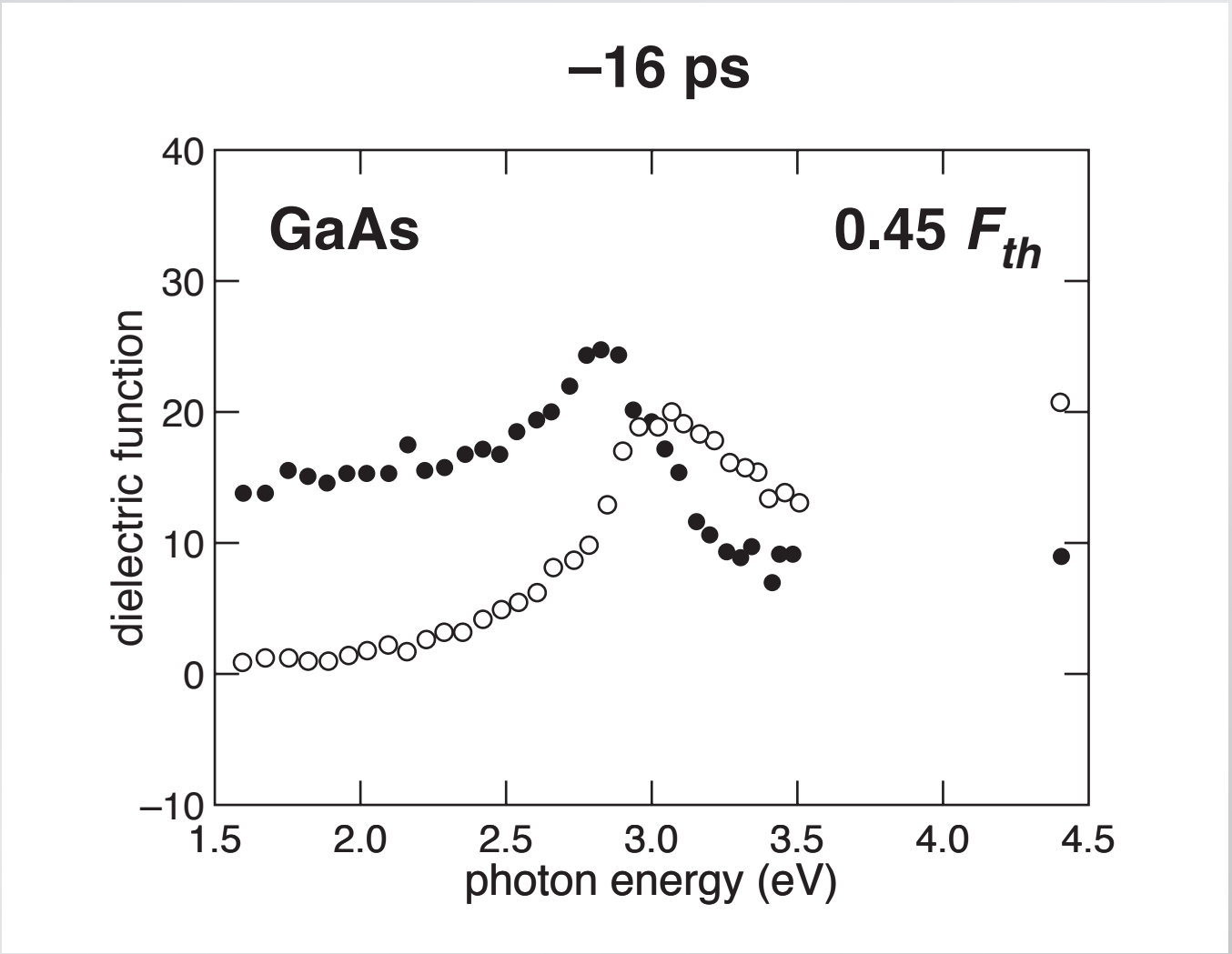

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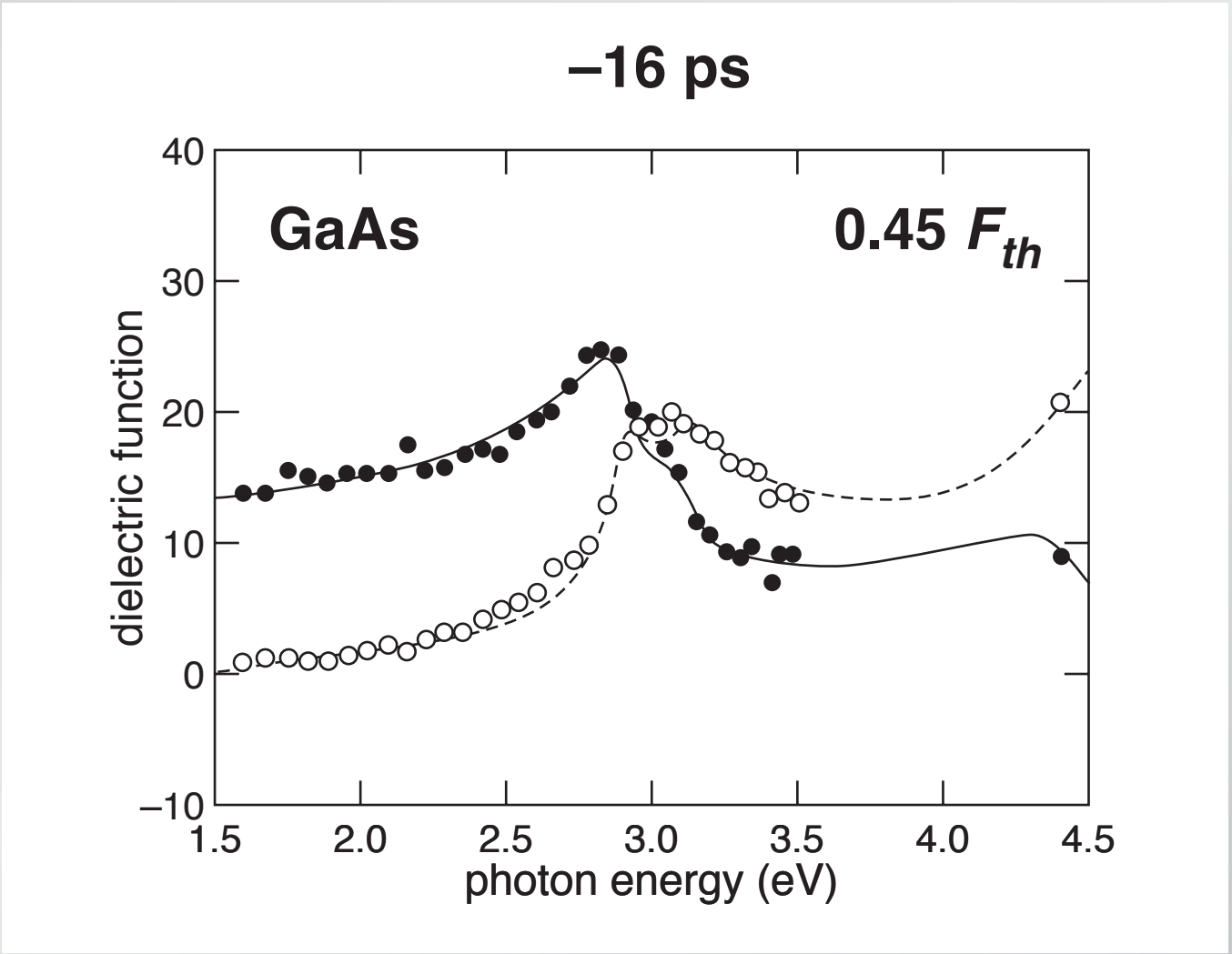

E.D. Palik, *Handbook of Optical Constants of Solids* (Academic Press, 1985)

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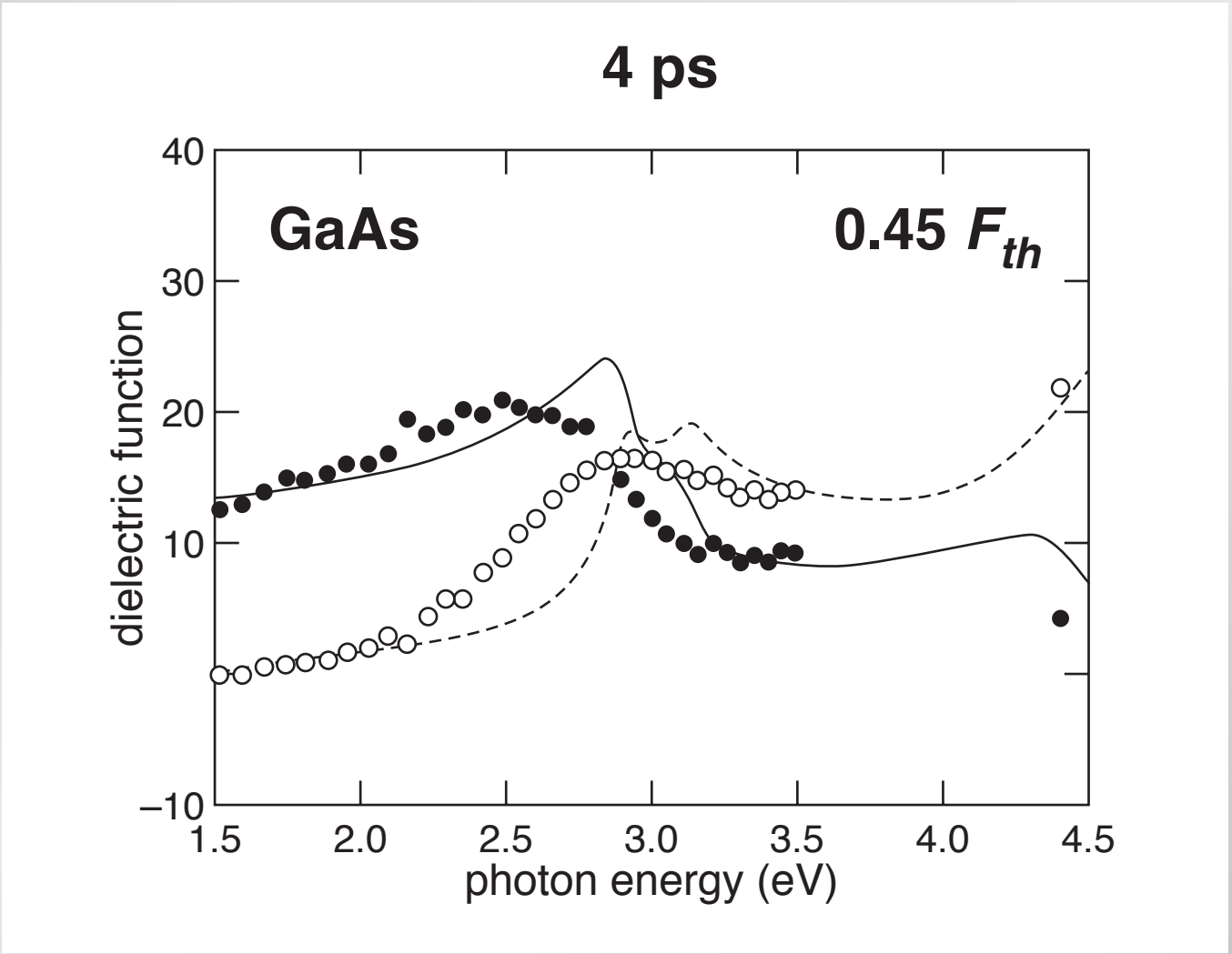

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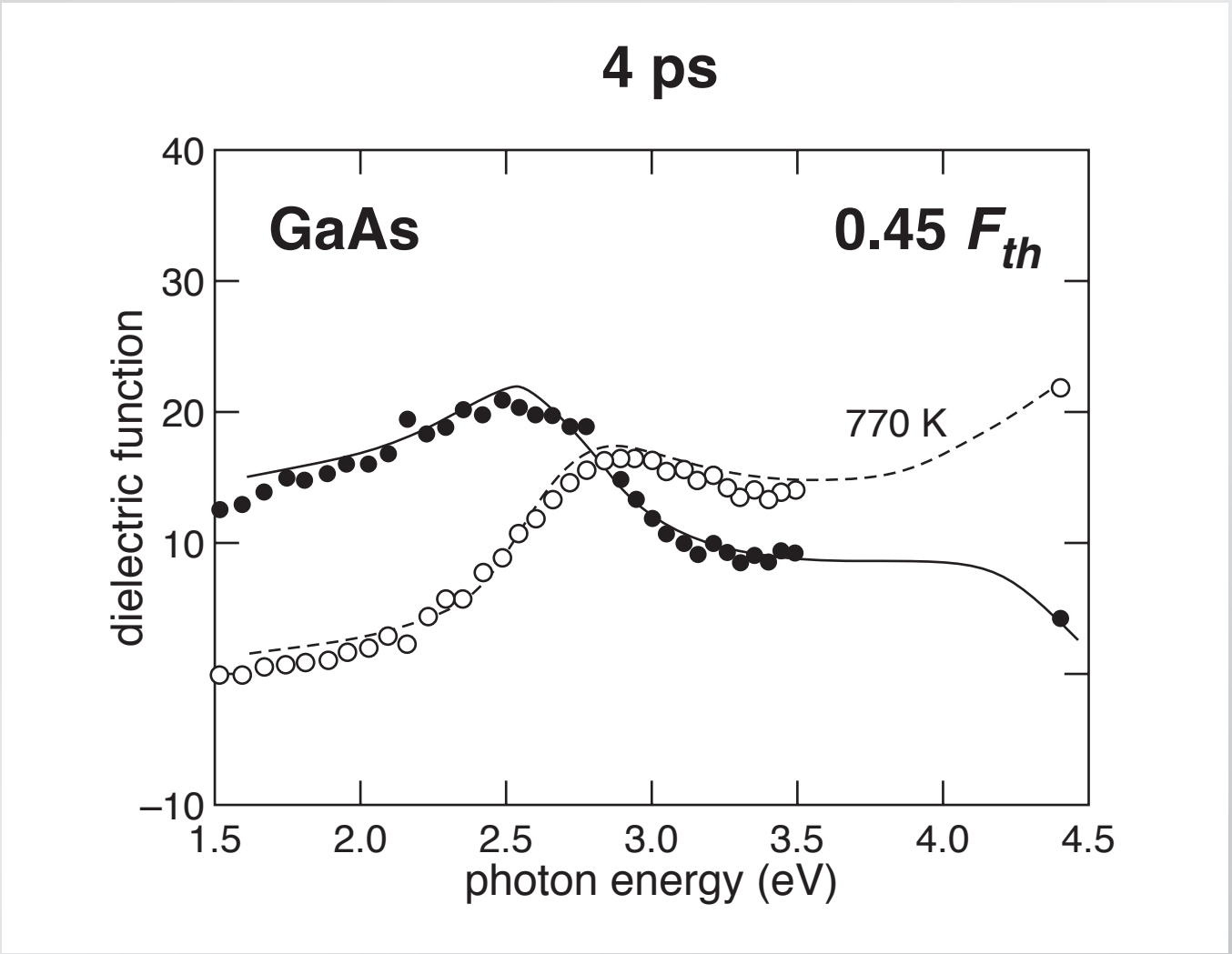

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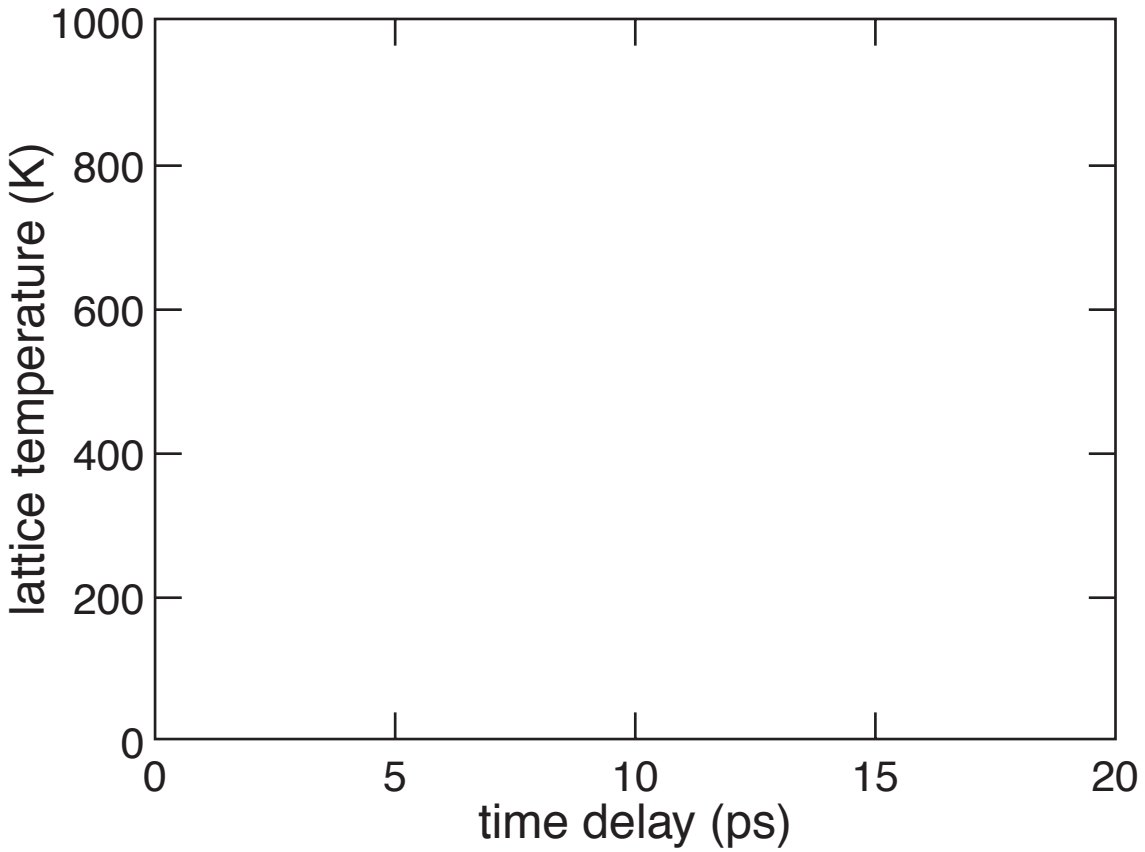

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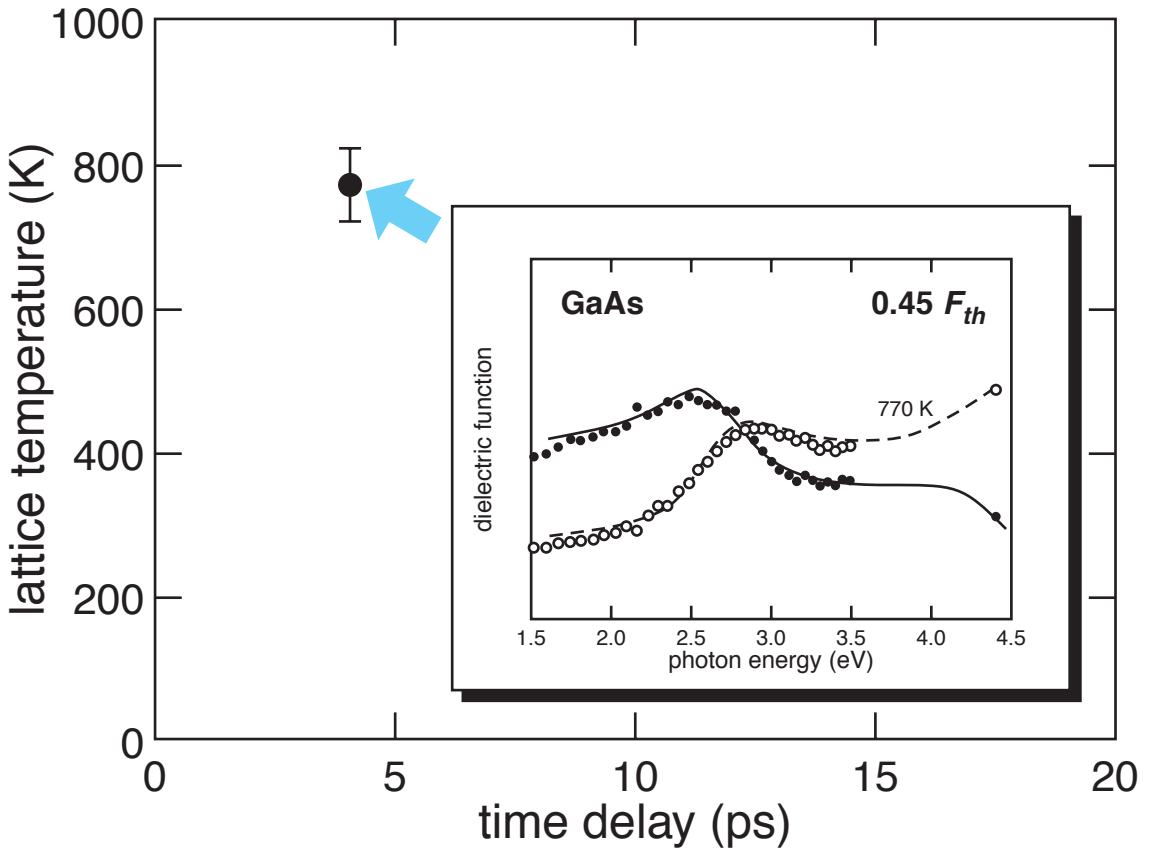
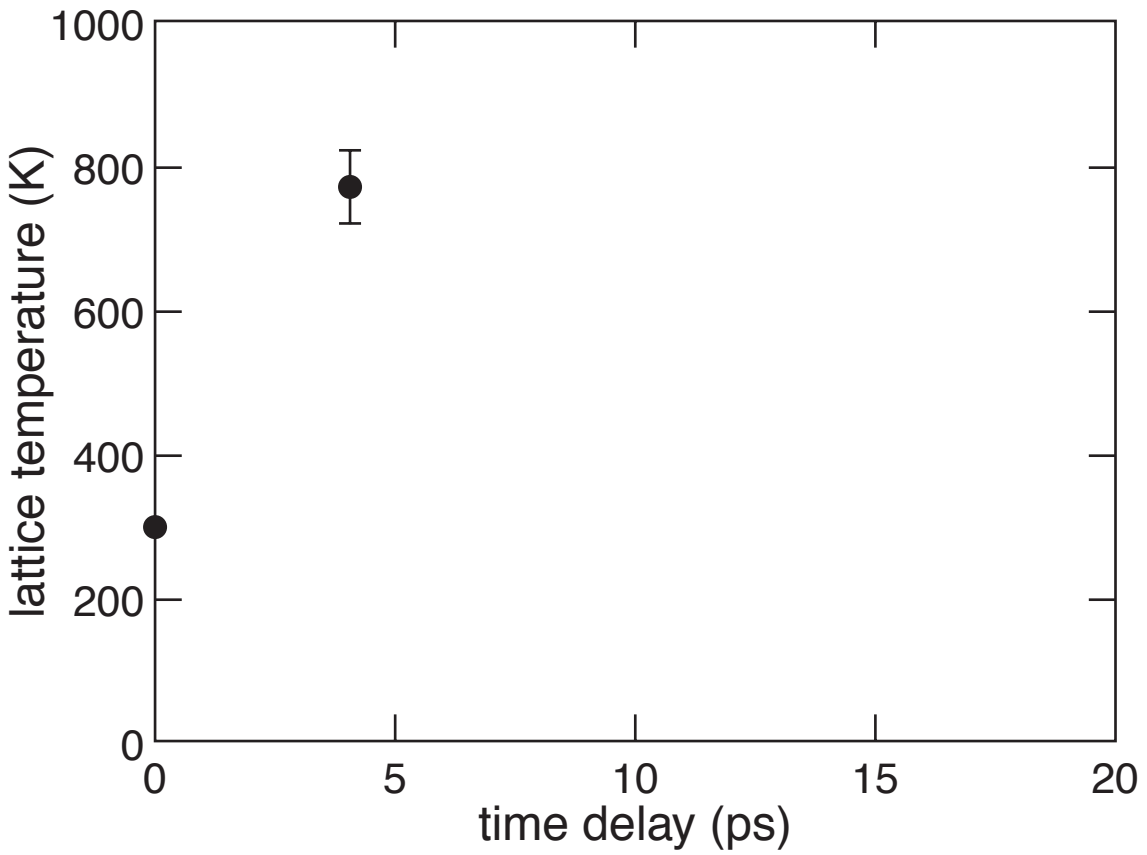
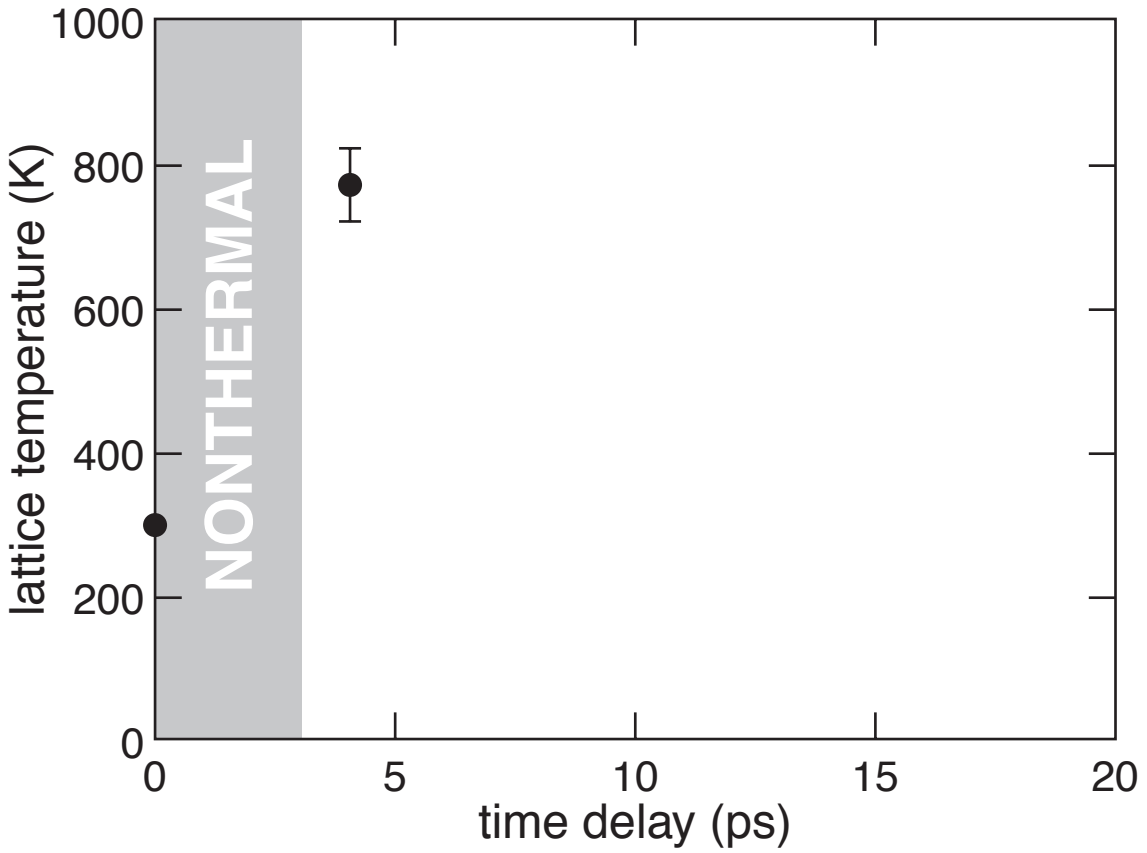


Transient band structure changes



Transient band structure changes



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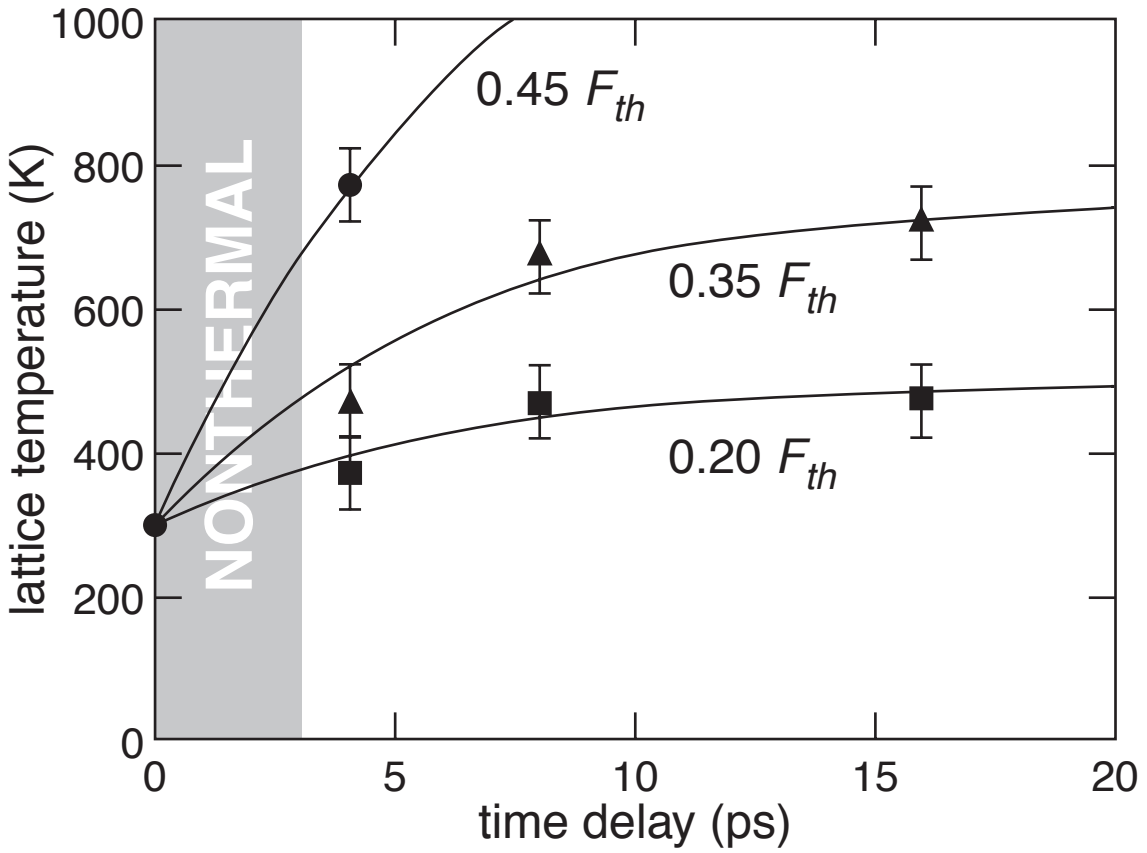

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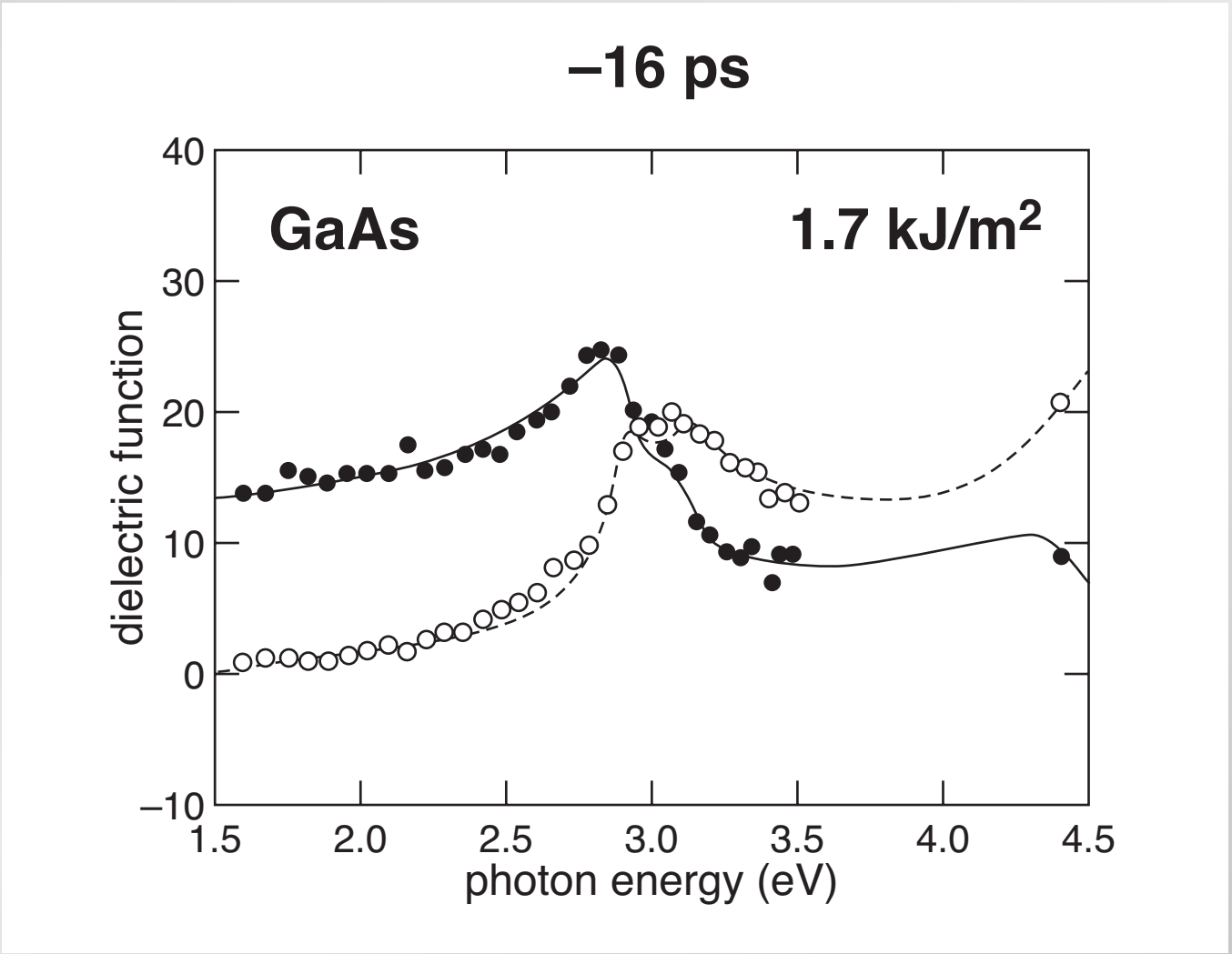

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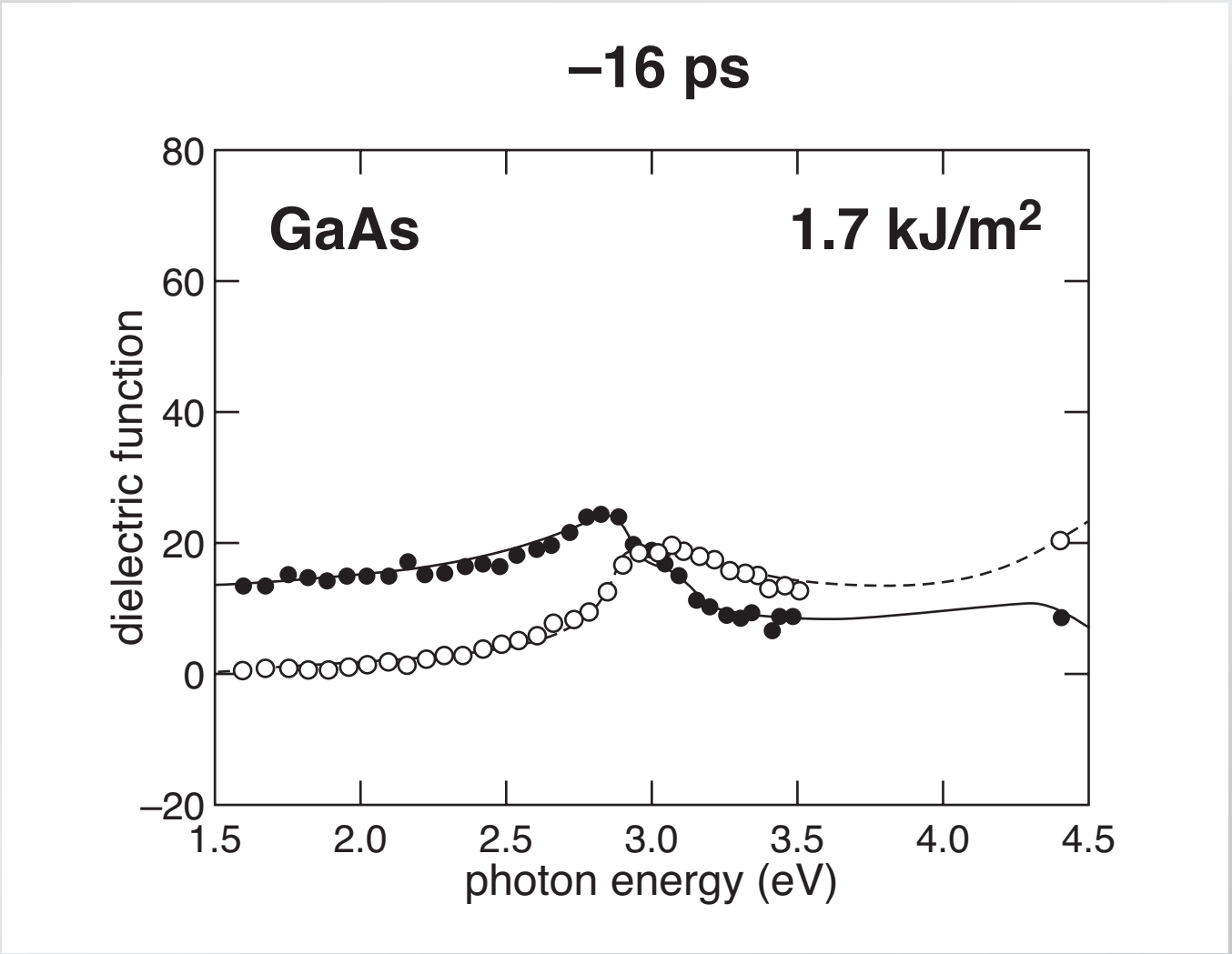

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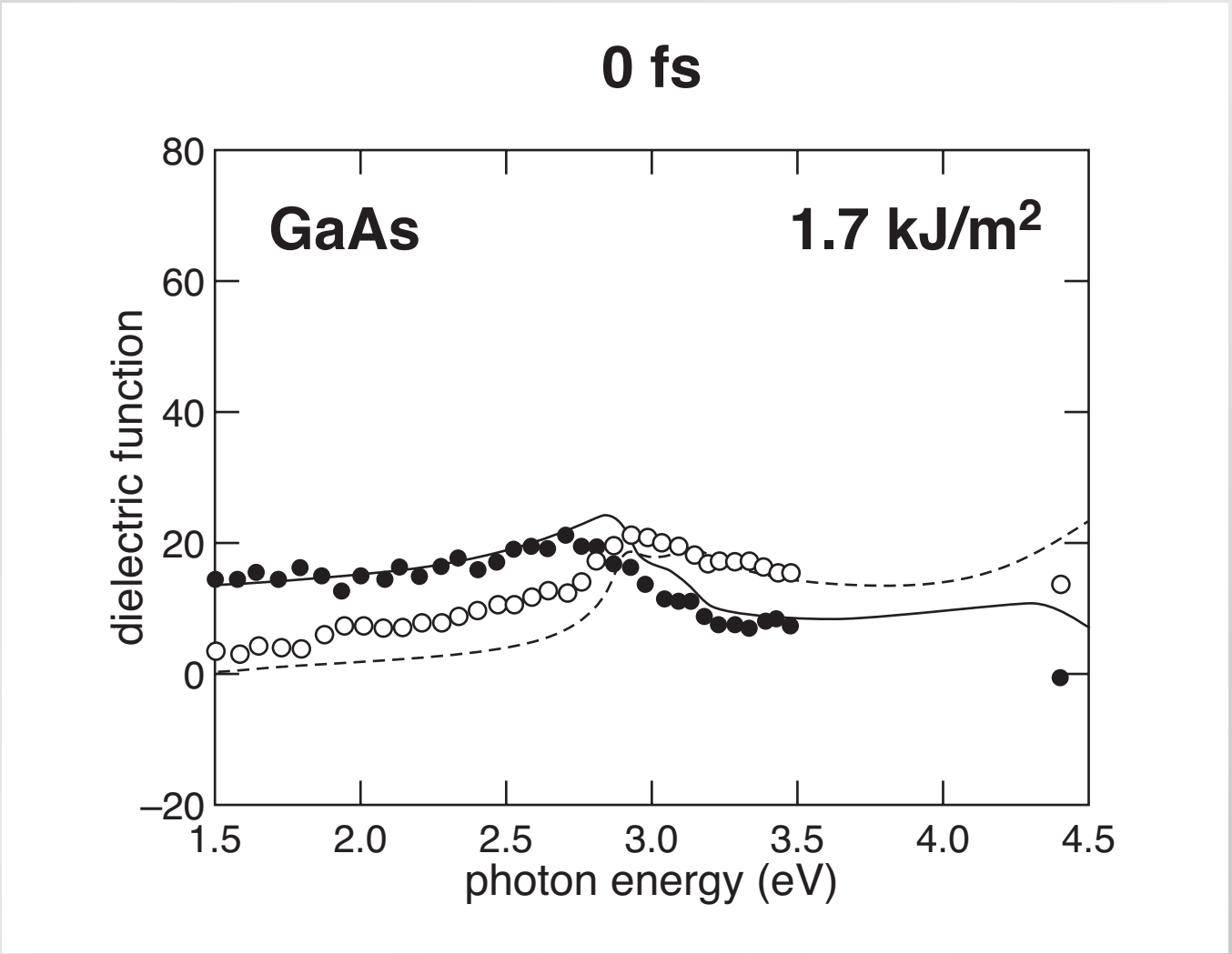

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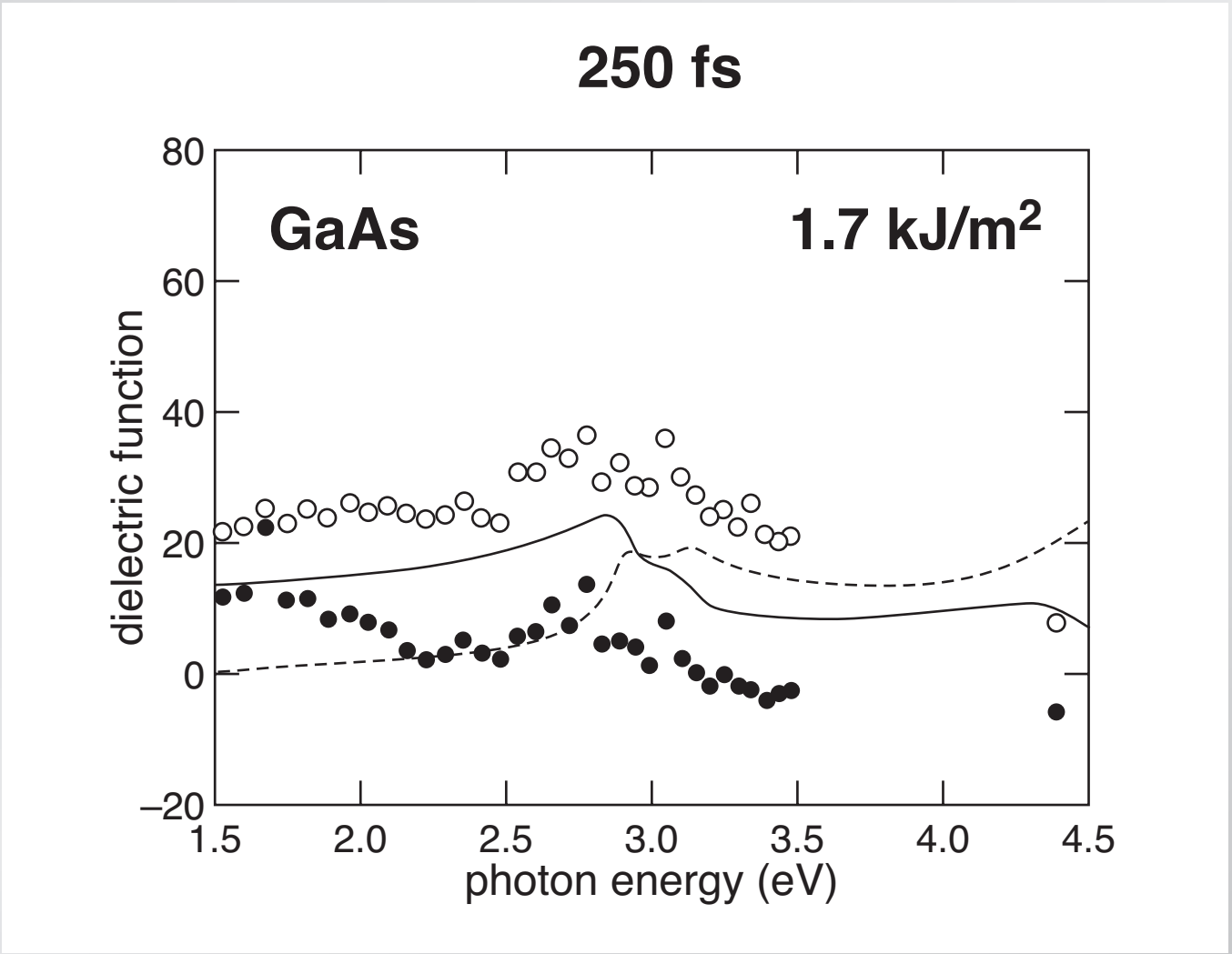

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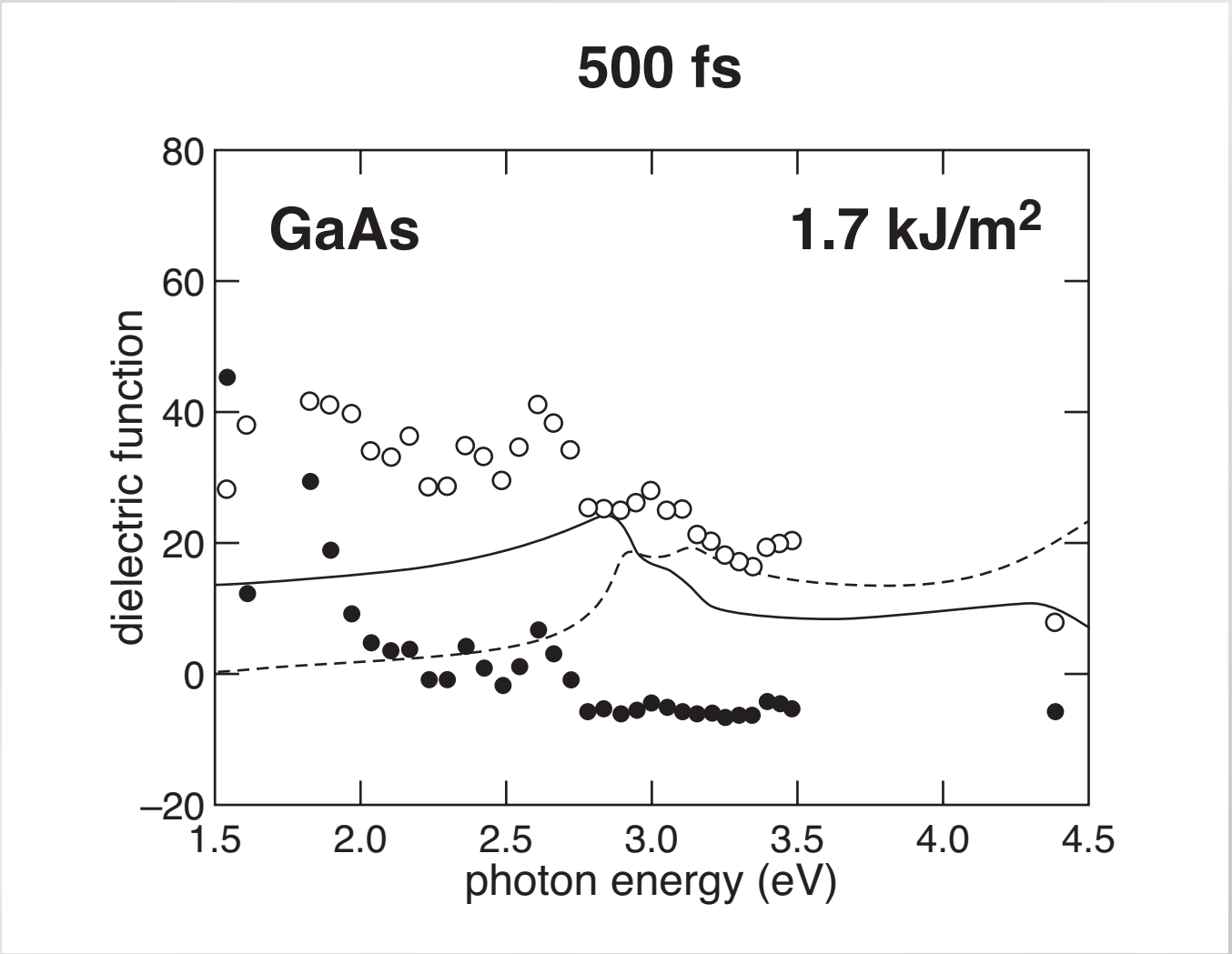

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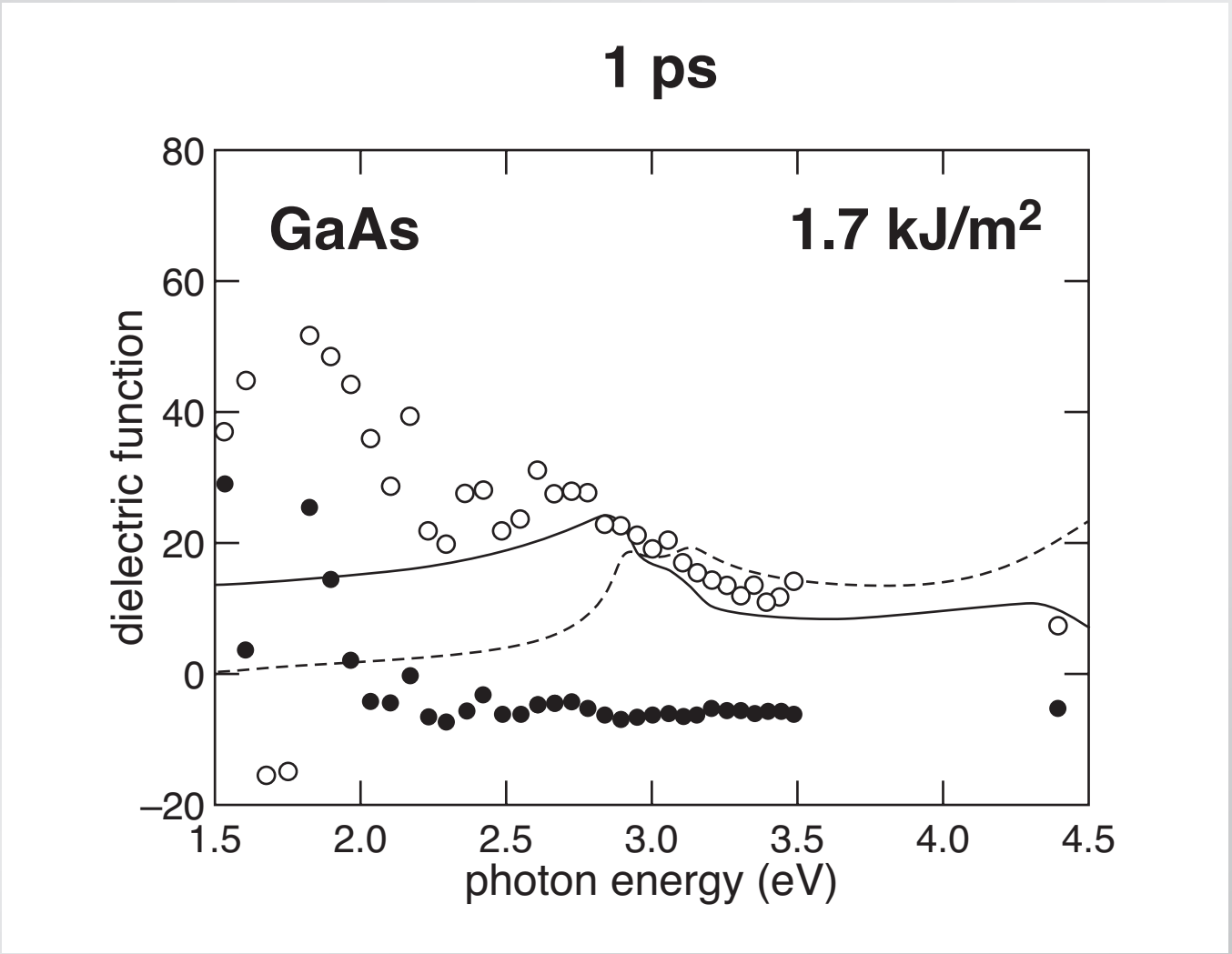

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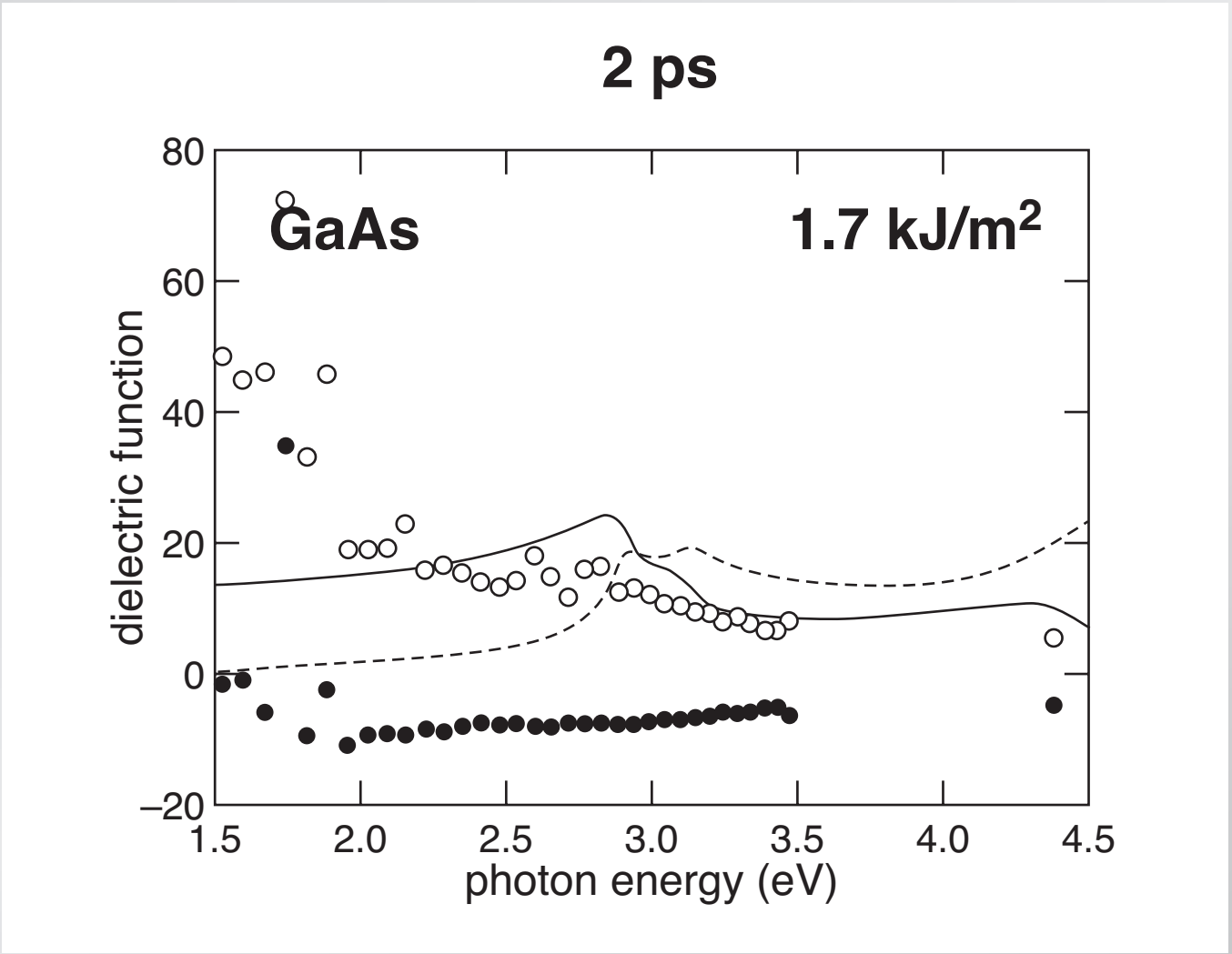

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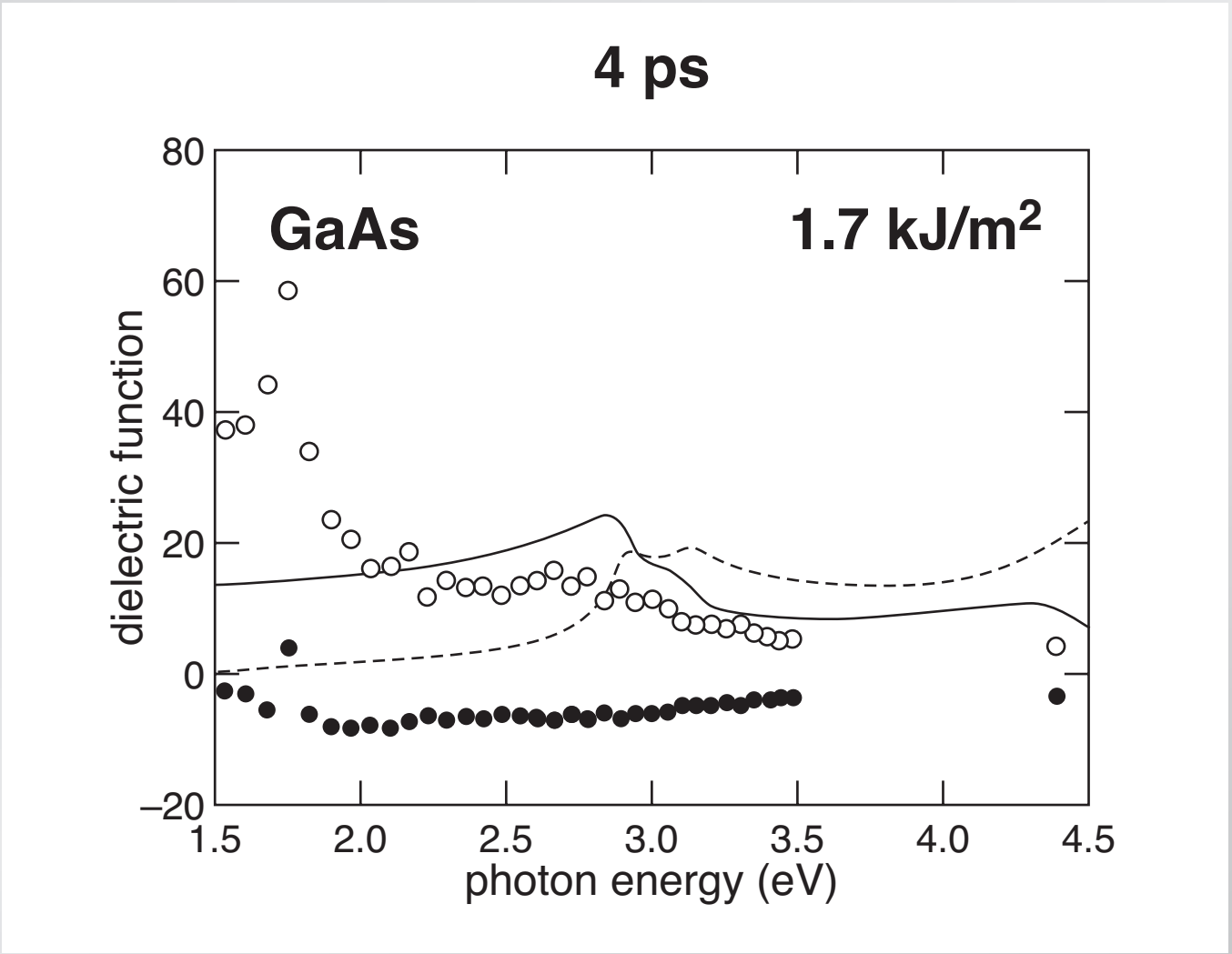

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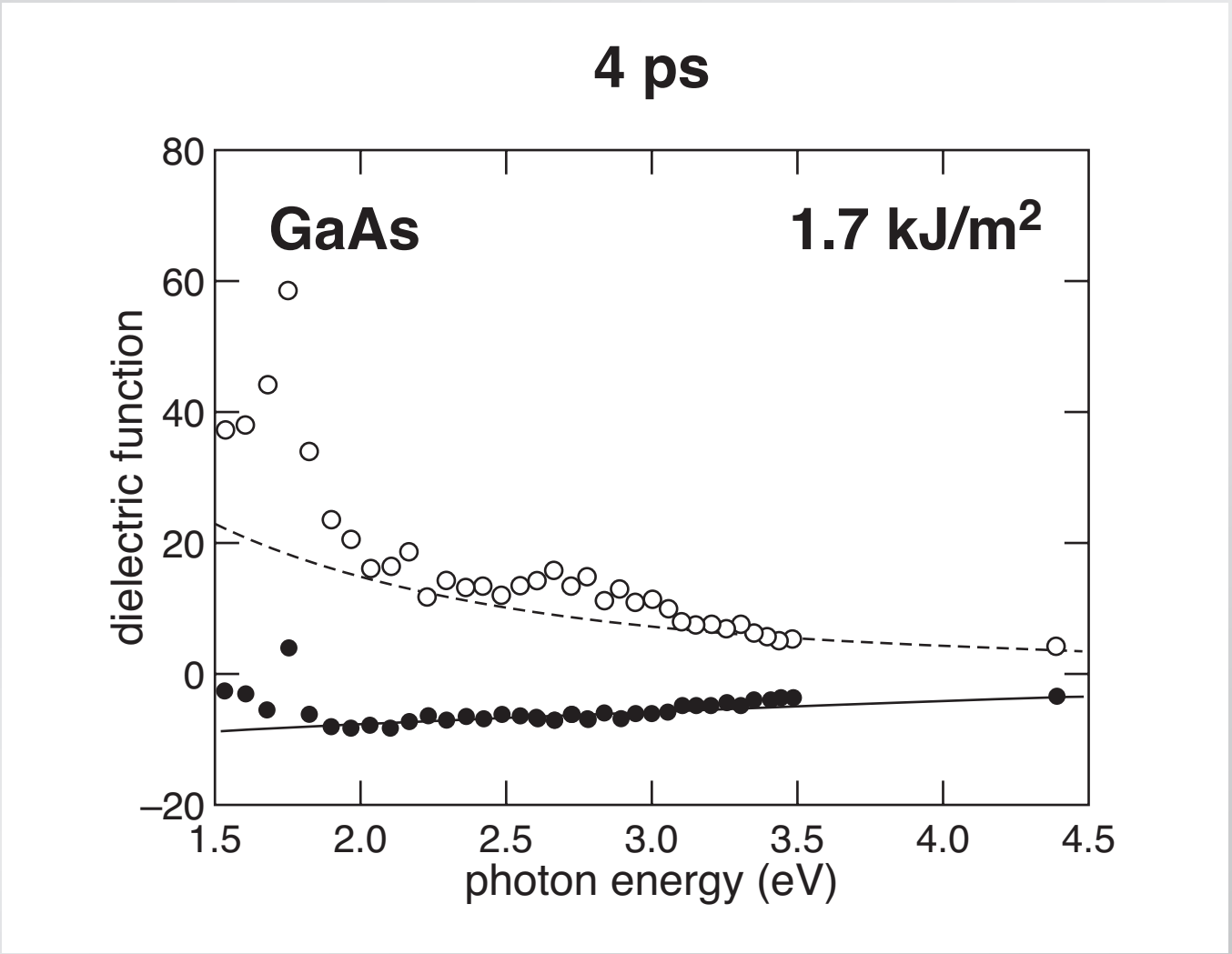


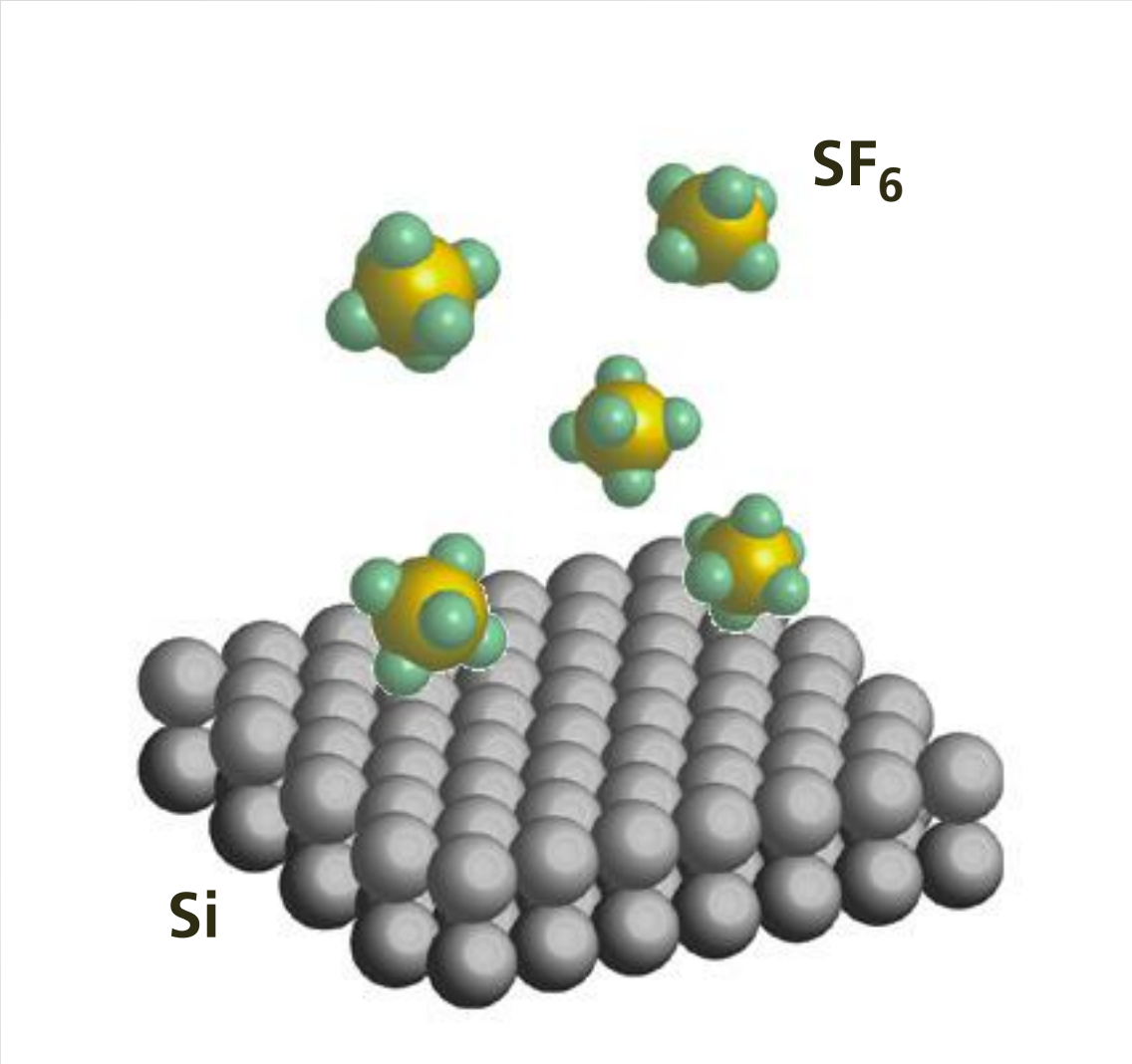
Transient band structure changes

can observe dielectric to metallic transition

Outline

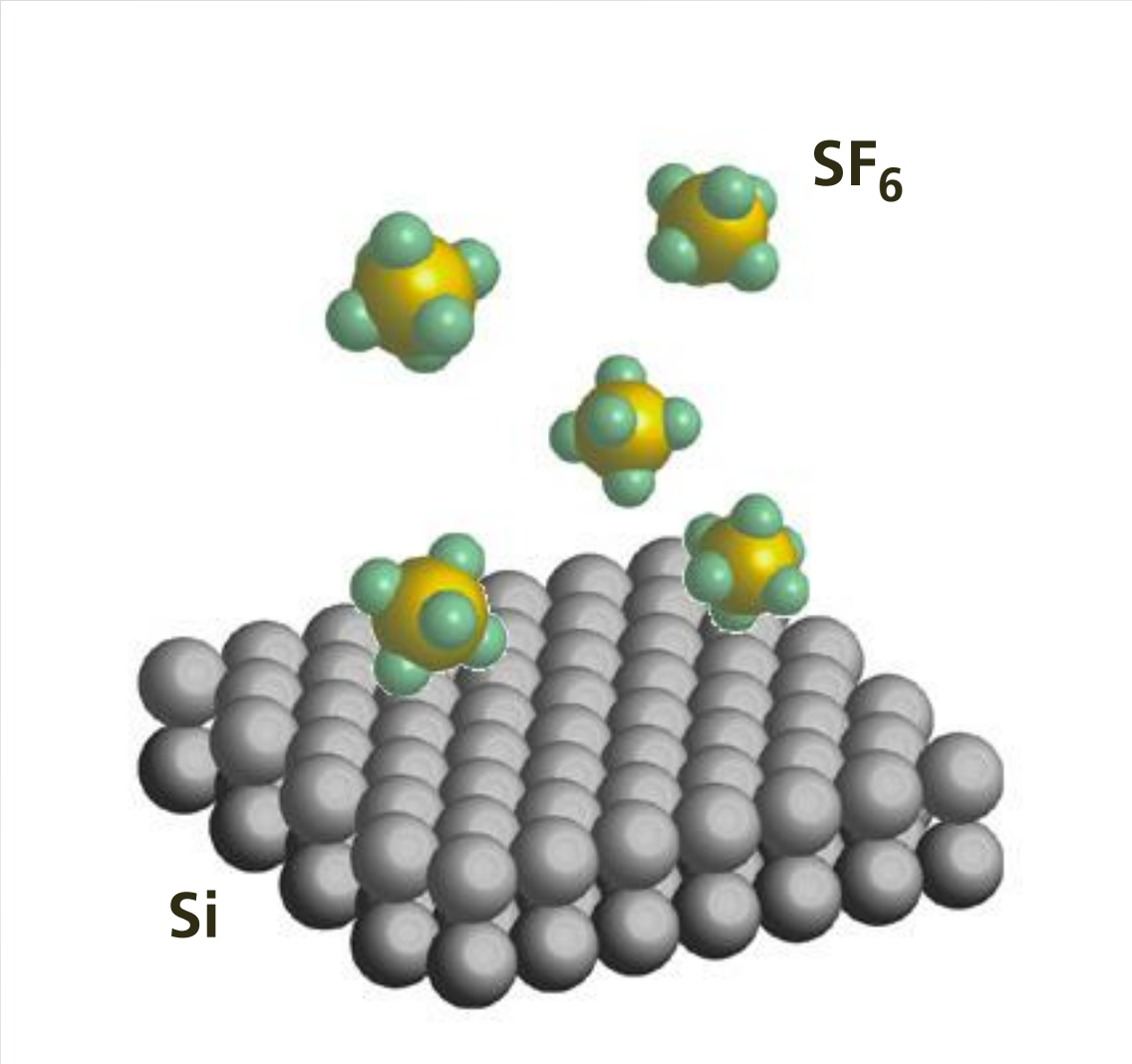
- transient band structure changes
- **creating an intermediate band**
- semiconductor to metal transition

Creating intermediate band



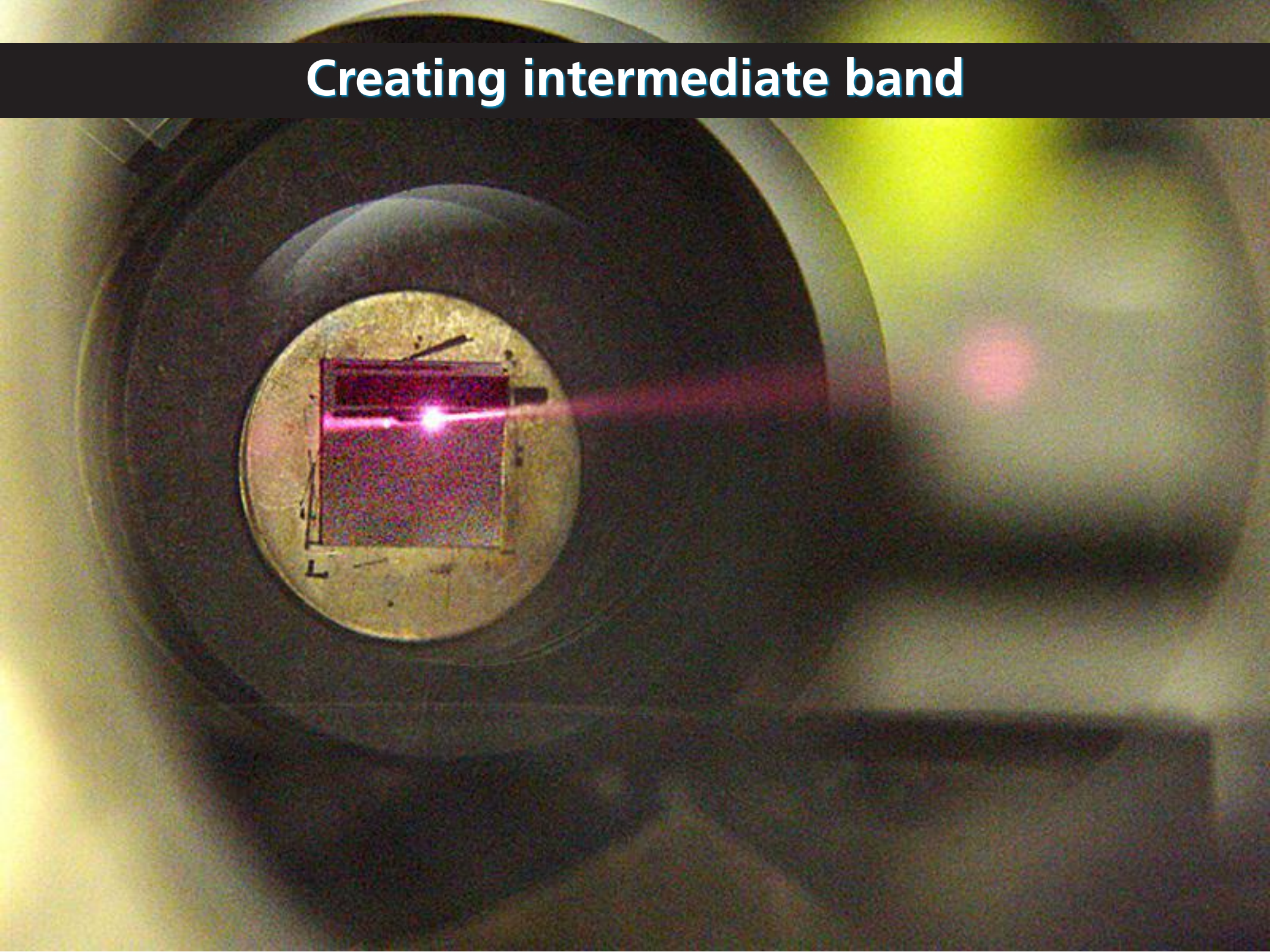
capturing dopants with fs pulses

Creating intermediate band



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

Creating intermediate band

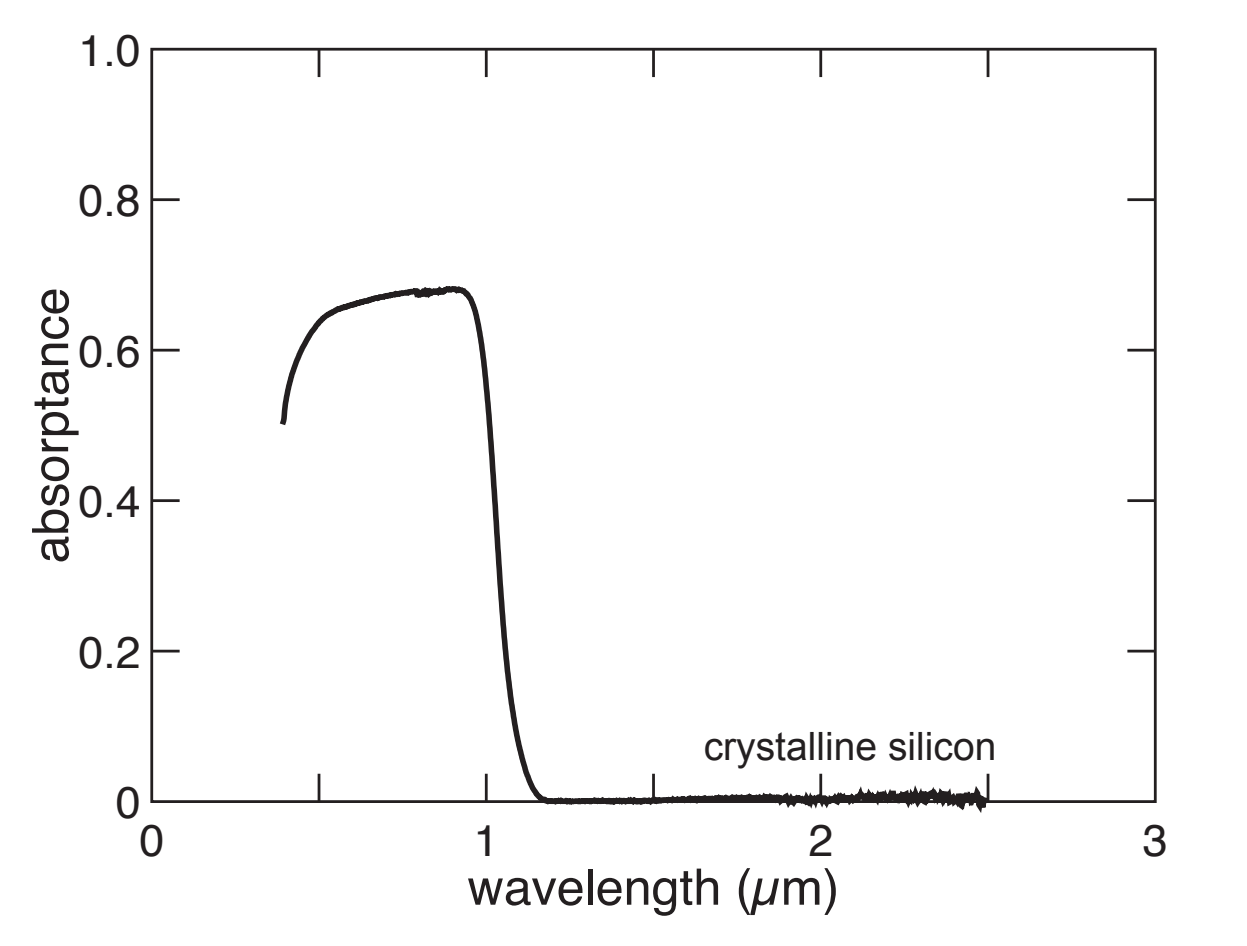


Creating intermediate band

Creating intermediate band

Creating intermediate band

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



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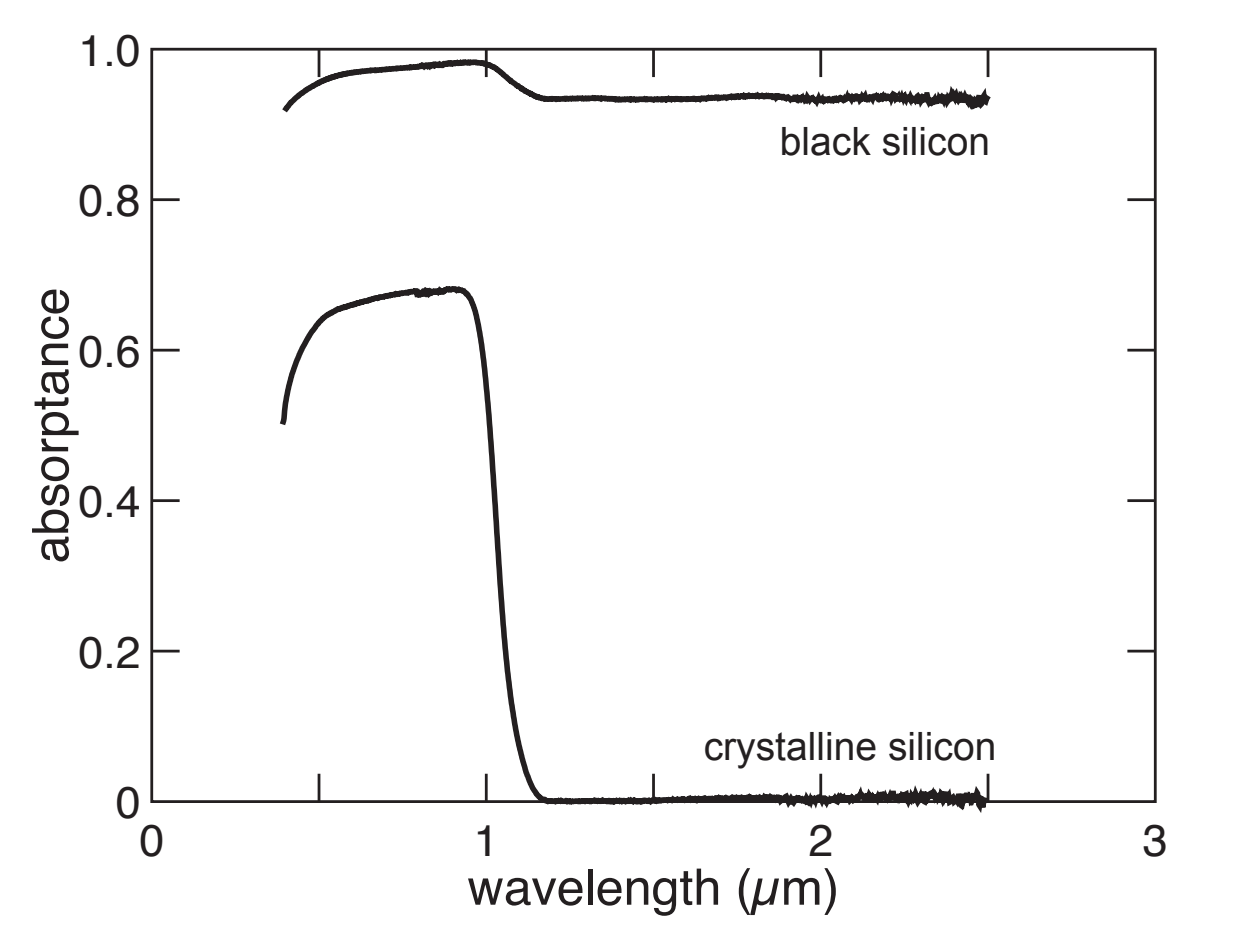
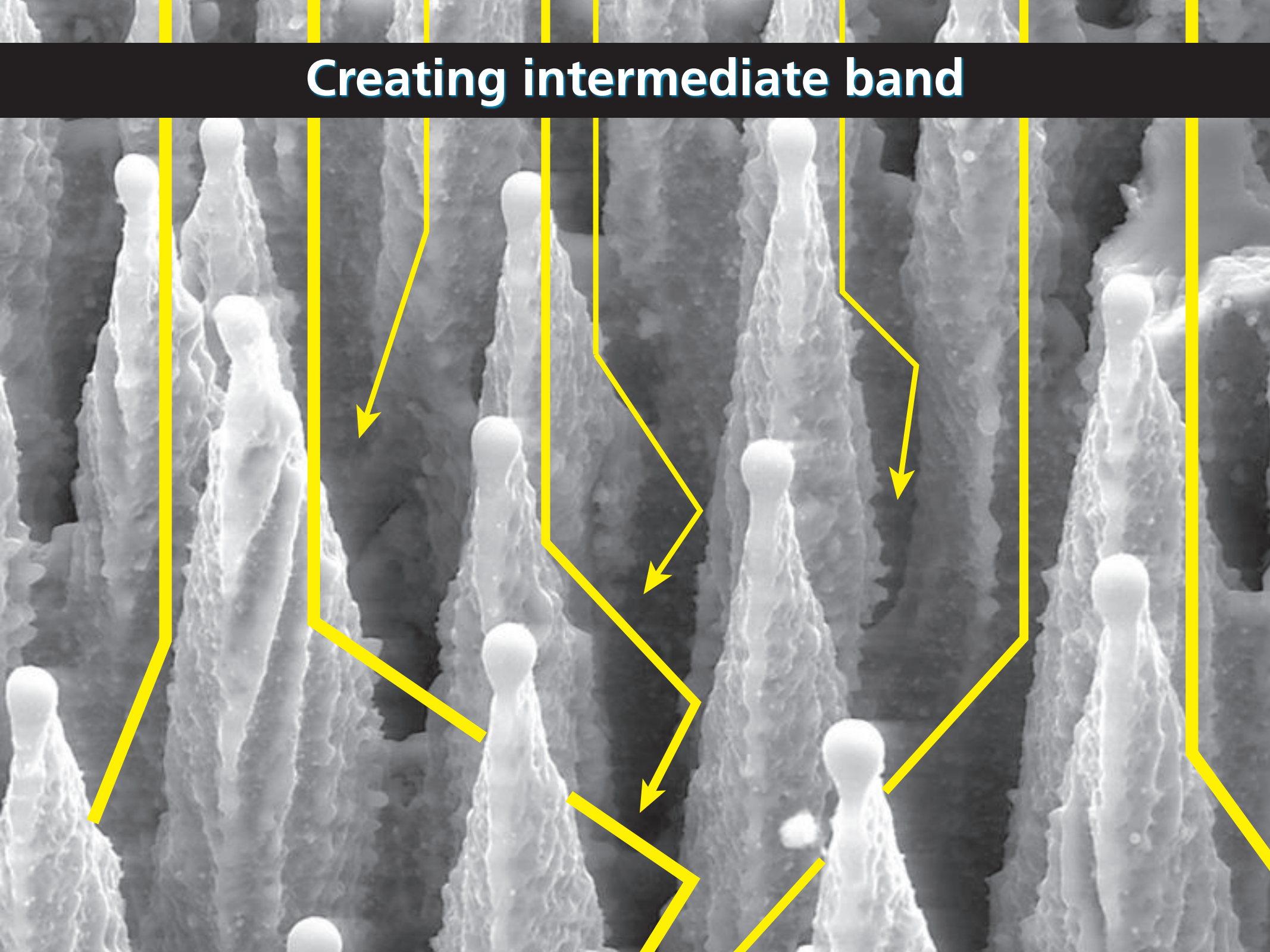
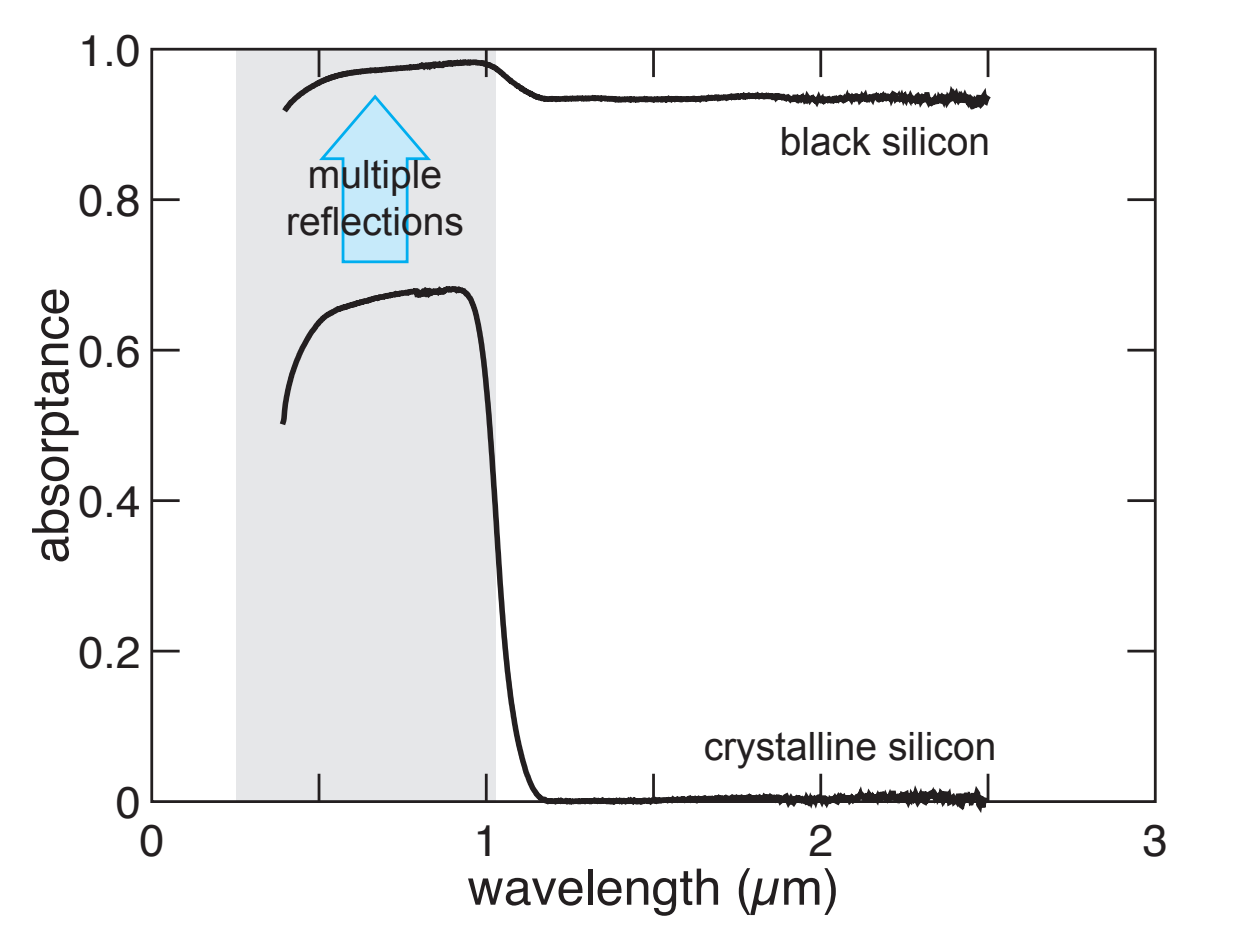



Creating intermediate band

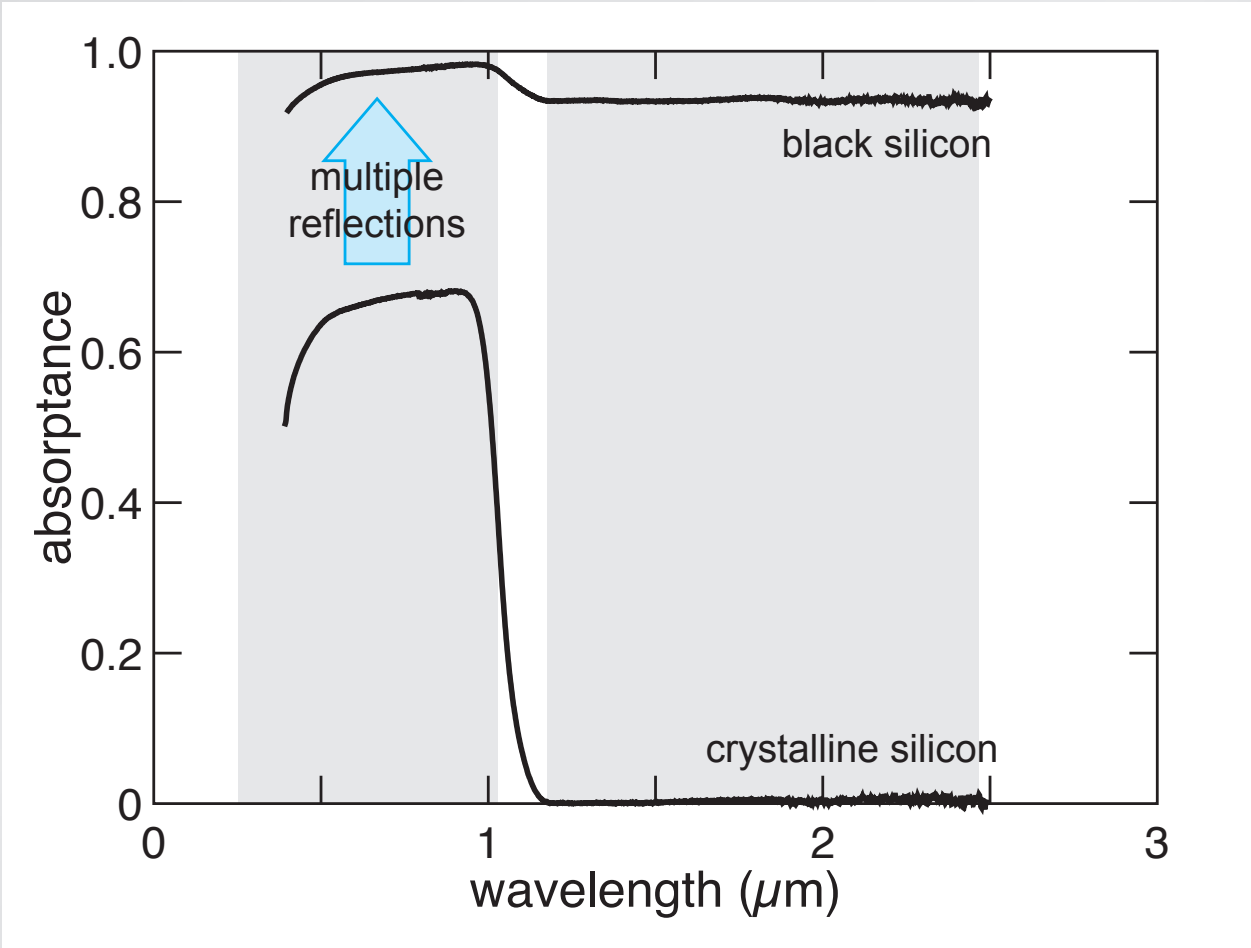
Creating intermediate band

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



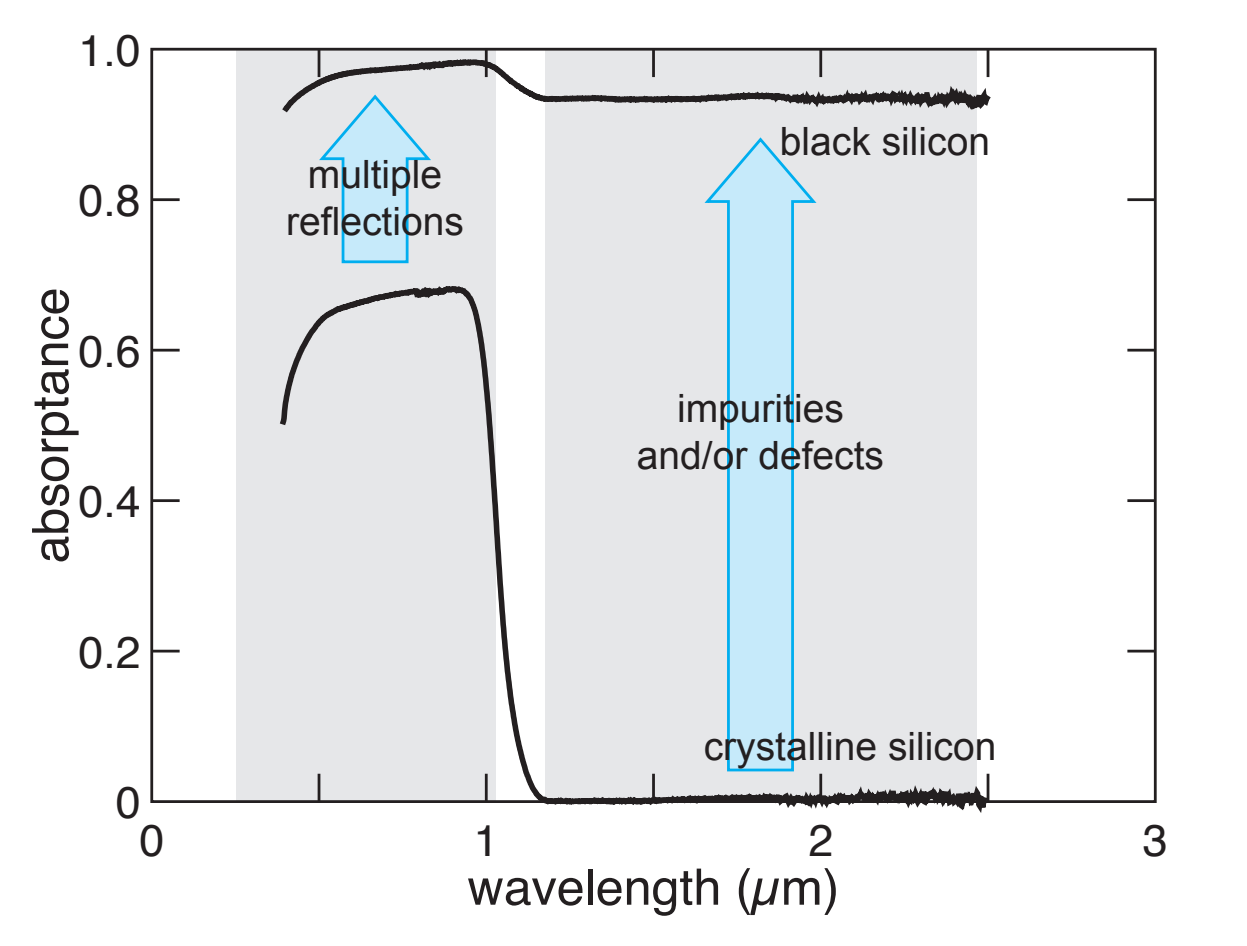
Creating intermediate band

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



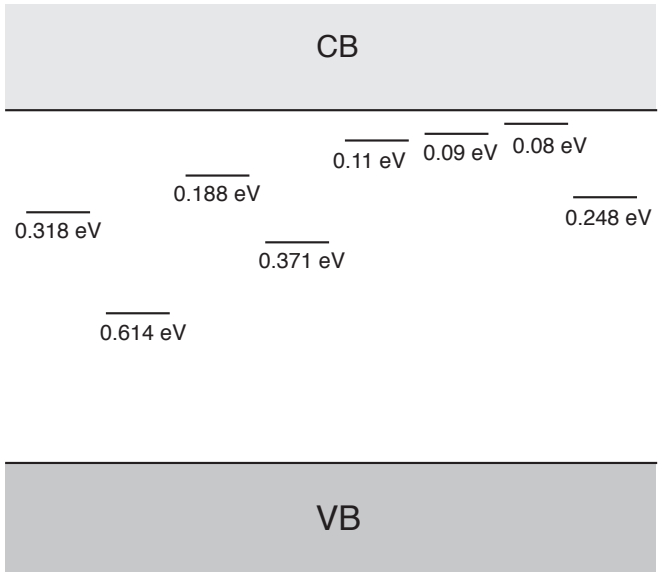
Creating intermediate band

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



Creating intermediate band

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



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

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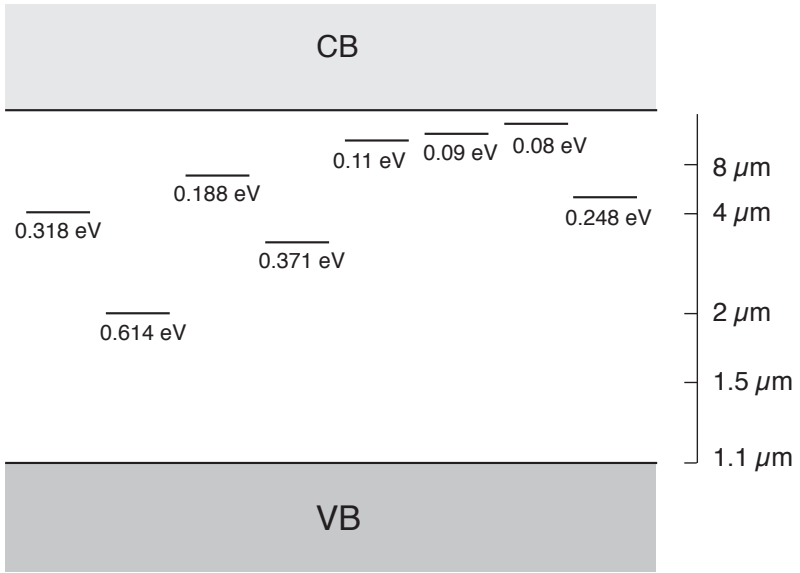

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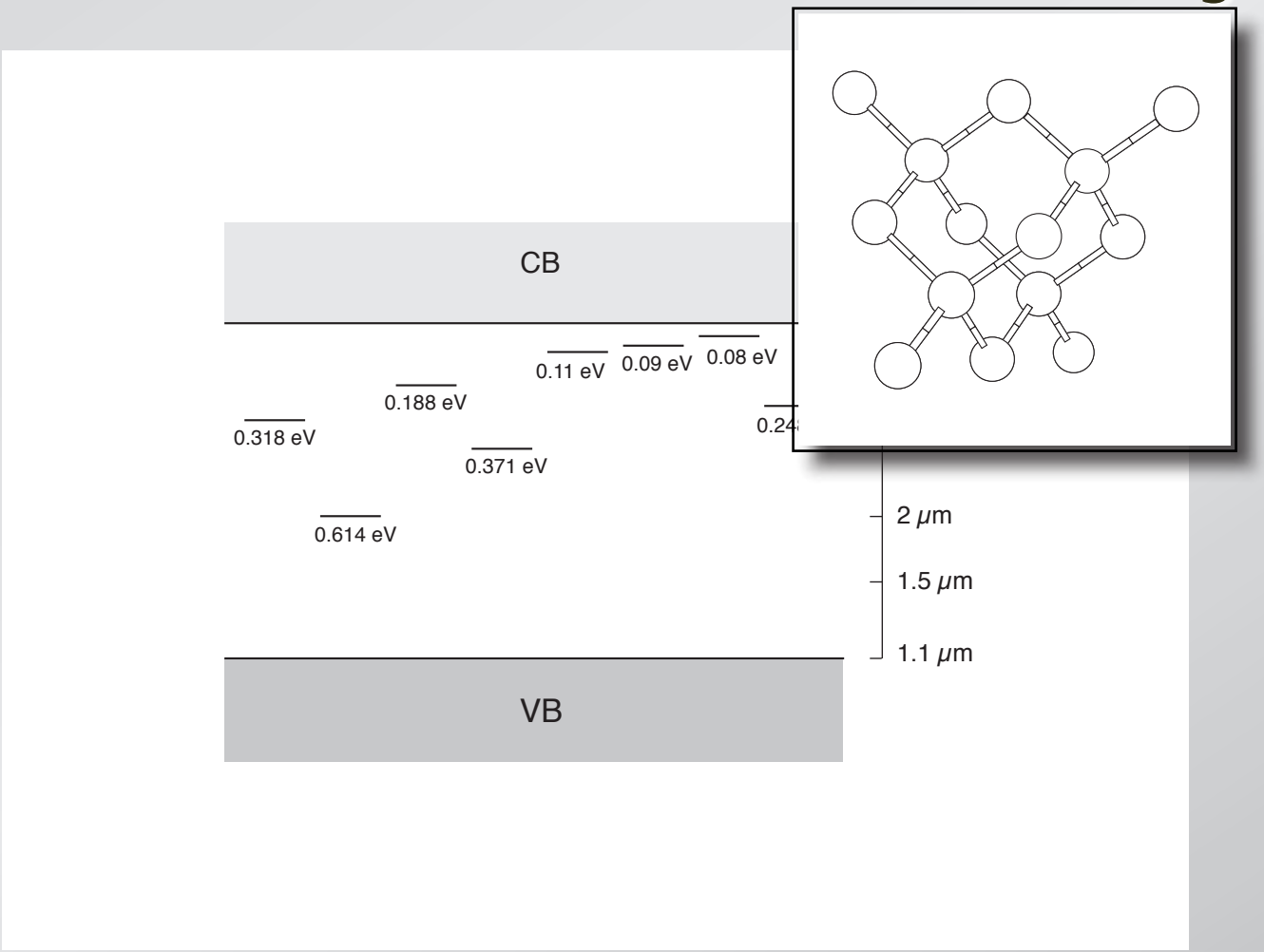

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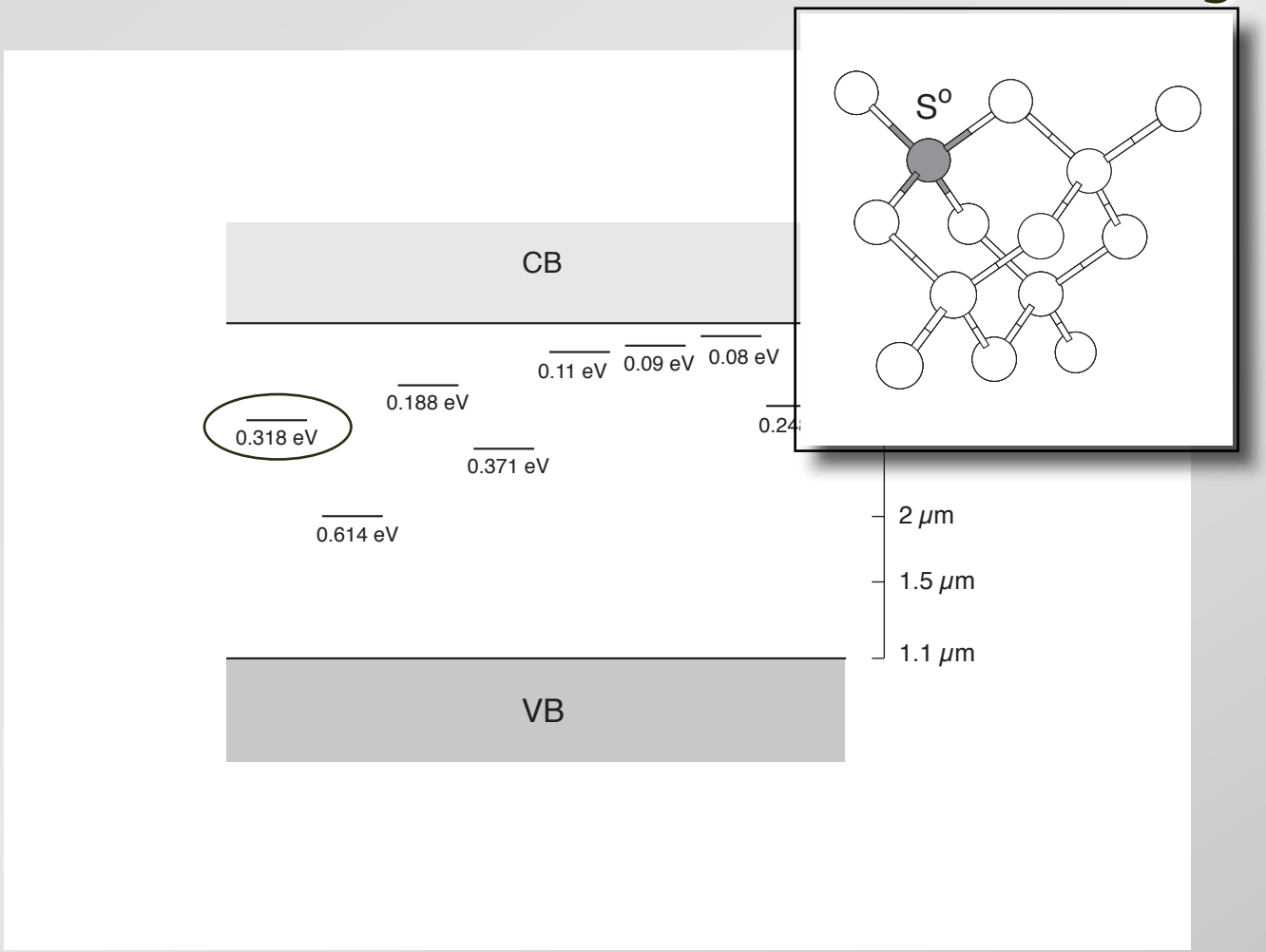

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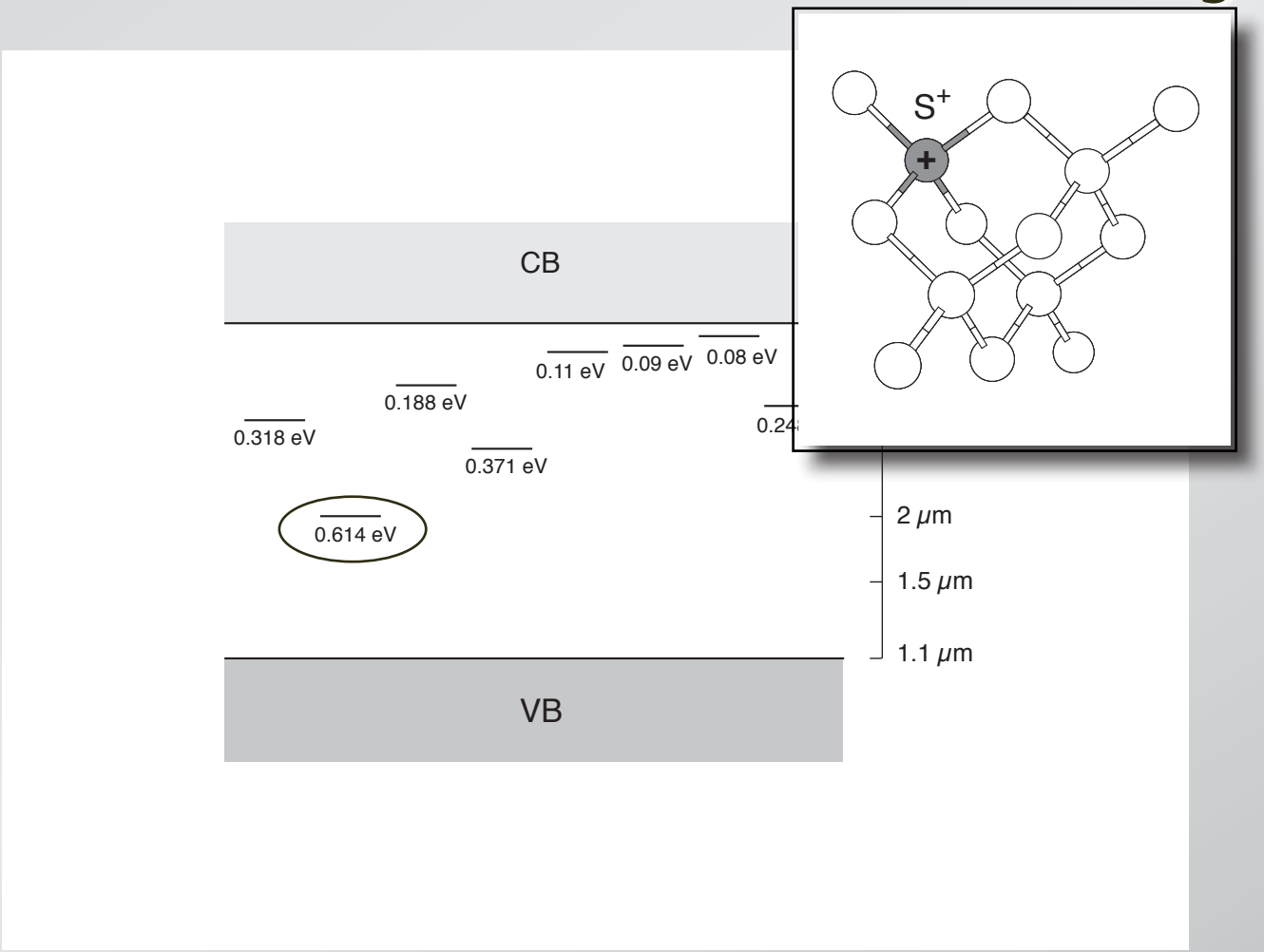

Janzén *et al.*, Phys. Rev. B 29, 1907 (1984)

Creating intermediate band

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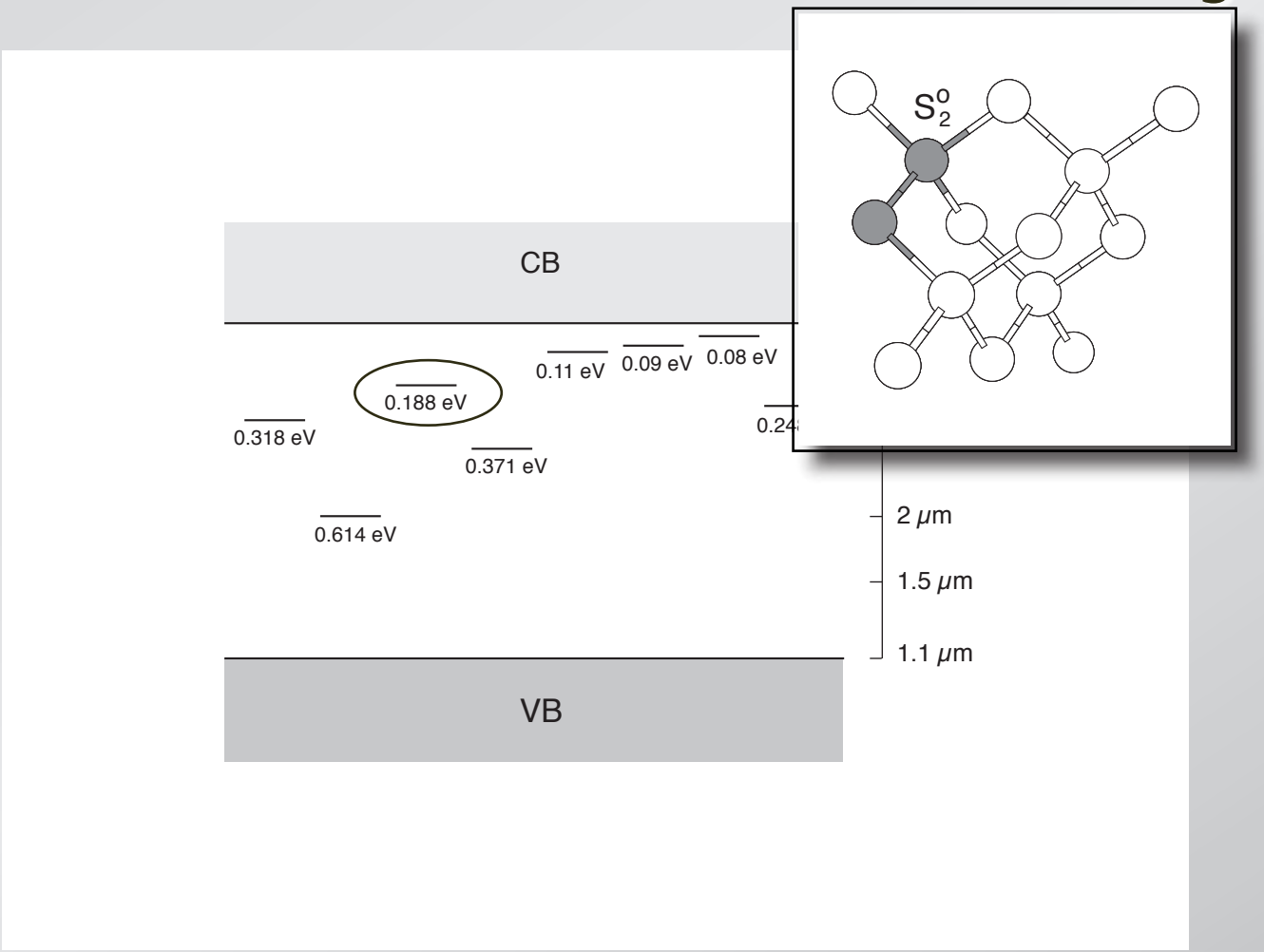

Janzén *et al.*, Phys. Rev. B 29, 1907 (1984)

Creating intermediate band

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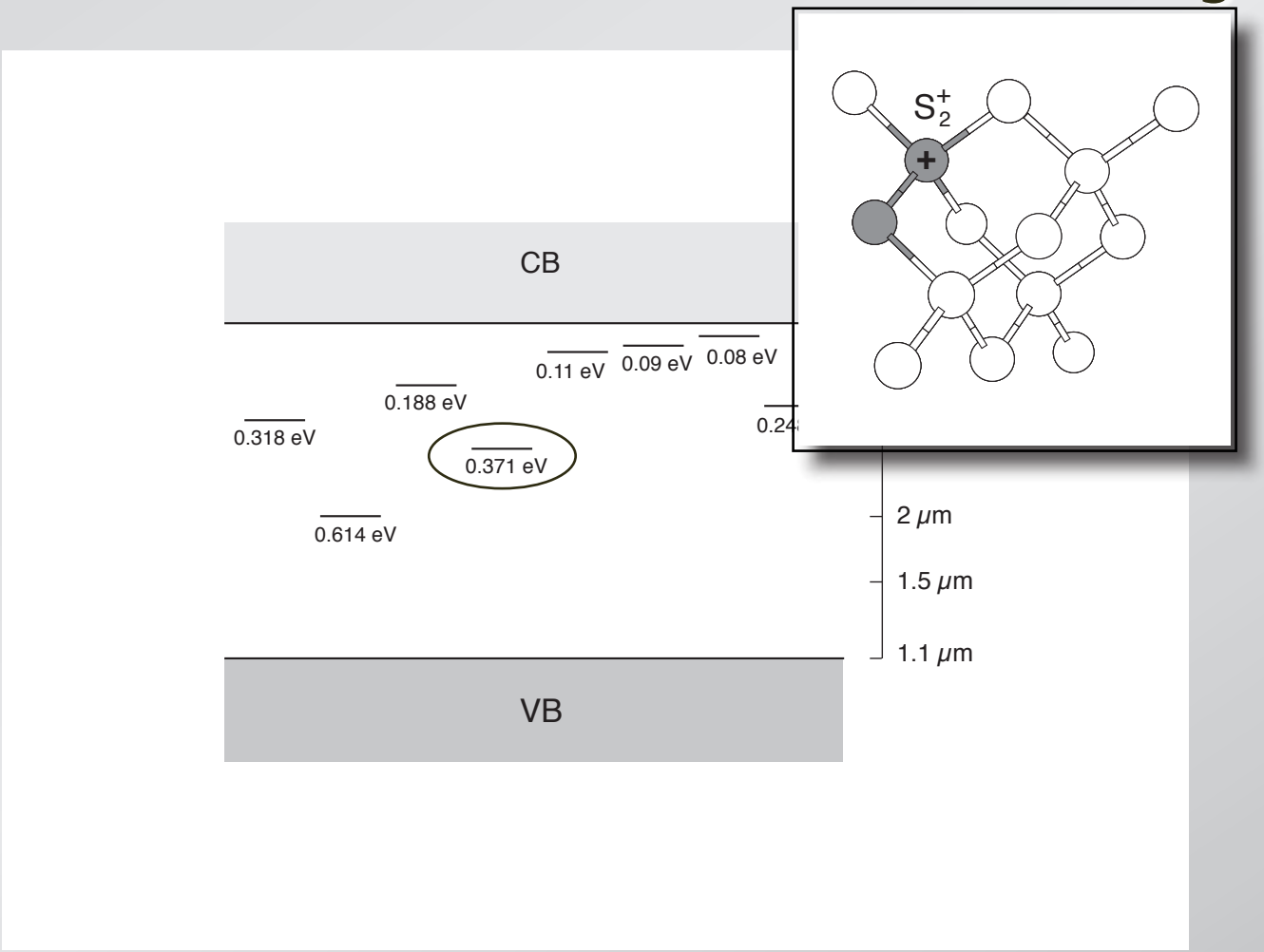
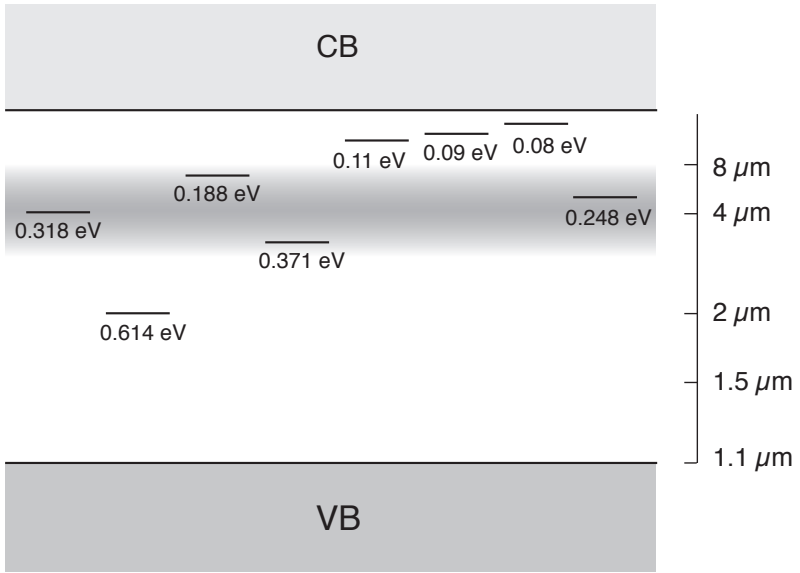


Janzén *et al.*, Phys. Rev. B 29, 1907 (1984)

Creating intermediate band

at high concentration states broaden into band



Creating intermediate band

Outline

- transient band structure changes
- creating an intermediate band
- **semiconductor to metal transition**

Semiconductor to metal

PRL 108, 026401 (2012) PHYSICAL REVIEW LETTERS

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

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Tonio Buonassisi,[2] and Jeffrey C. Grossman[1,2,‡]

[1]*Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge Massachusetts 02139, USA*
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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.

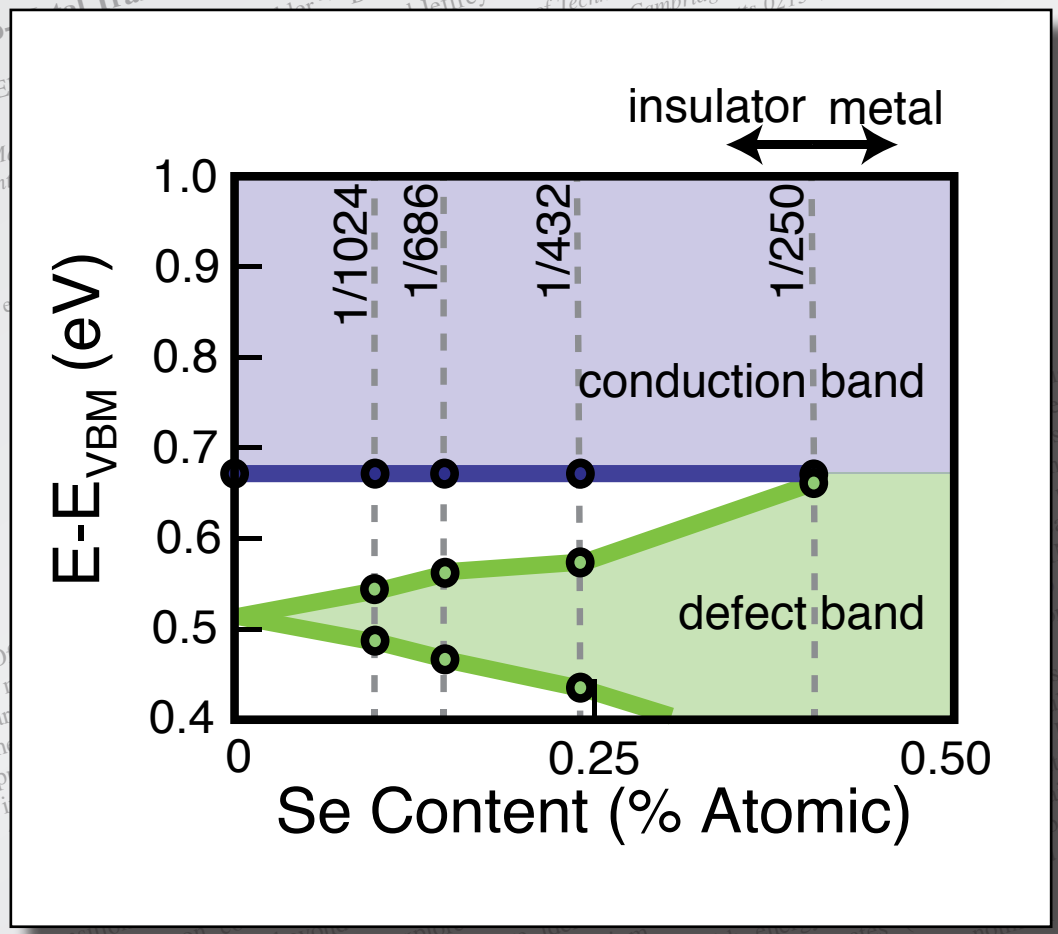
DOI: 10.1103/PhysRevLett.108.026401 PACS numbers: 71.30.+h, 61.72.sd, 73.61.Cw, 78.20.Bh

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 equilibrium solubility limit [3] of about 10^{16} cm^{-3}) and we explore the detailed nature of the transition with both experiment and computation. We find that the IMT is [illegible] electron correlation and most resembles [illegible] Mott transition. Additionally, we [illegible] at the IMT yields [illegible] efficient in 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, $\rho \approx 25\ \Omega\,\mathrm{cm}$) 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 peak Se concentration, than reported previously [18]. The Se-rich layer is crystalline, extends approximately 350 nm [illegible] surface, and is electrically isolated from the [illegible] by the rectifying junction formed between [illegible]-depth profile was measured [illegible] [17,18]. Sample [illegible] described

Semiconductor to metal

DFT calculations



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

Semiconductor to metal

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

Emergence of very broad infrared absorption band by hyperdoping of sili 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. Aziz[9]

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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*.

[http://dx.doi.org/10.1063/1.4804935]

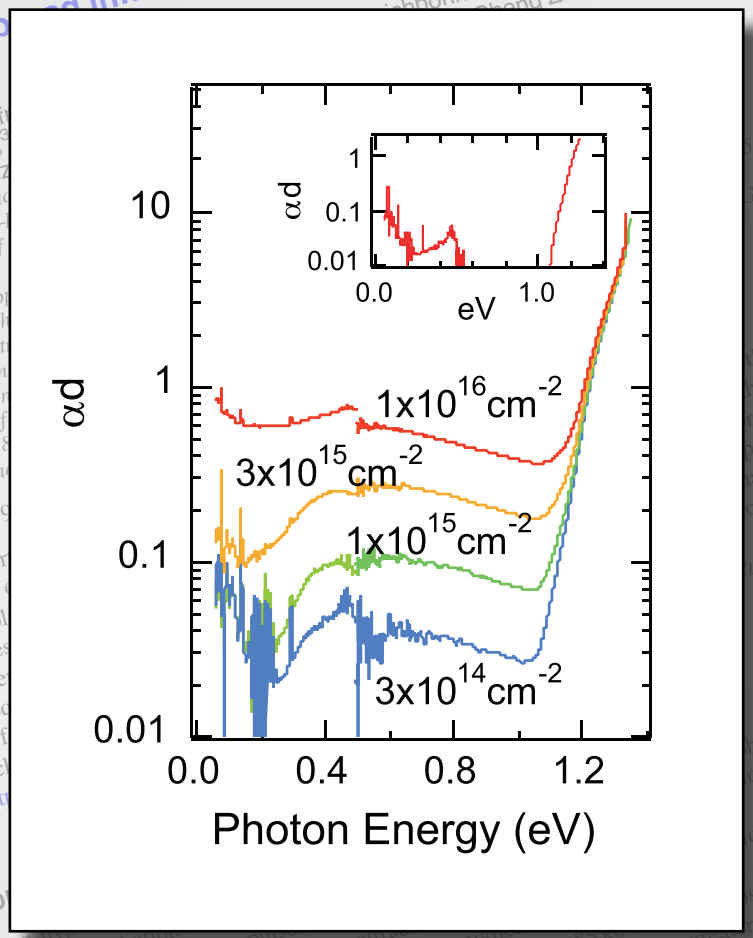
I. INTRODUCTION

Silicon hyperdoped with chalcogens can be synthesized by pulsed laser irradiation in a sulfur-bearing atmosphere,[1,2] 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 in silicon has aroused similar interest in this material.[12,13] Chalcogen hyperdoping has been shown to cause an metal transition and has been proposed to form an the silicon band gap.[4,10,14–16] However, causing the sub-bandgap for this is that

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. 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 equation.[18] The details of the sample preparation method and depth profiles of chalcogen atoms observed by secondary ectrometry (SIMS) are reported elsewhere.[3] For the synthesis procedure is the same for sulfur doped samples, what higher flu-

Semiconductor to metal



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

Semiconductor to metal

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

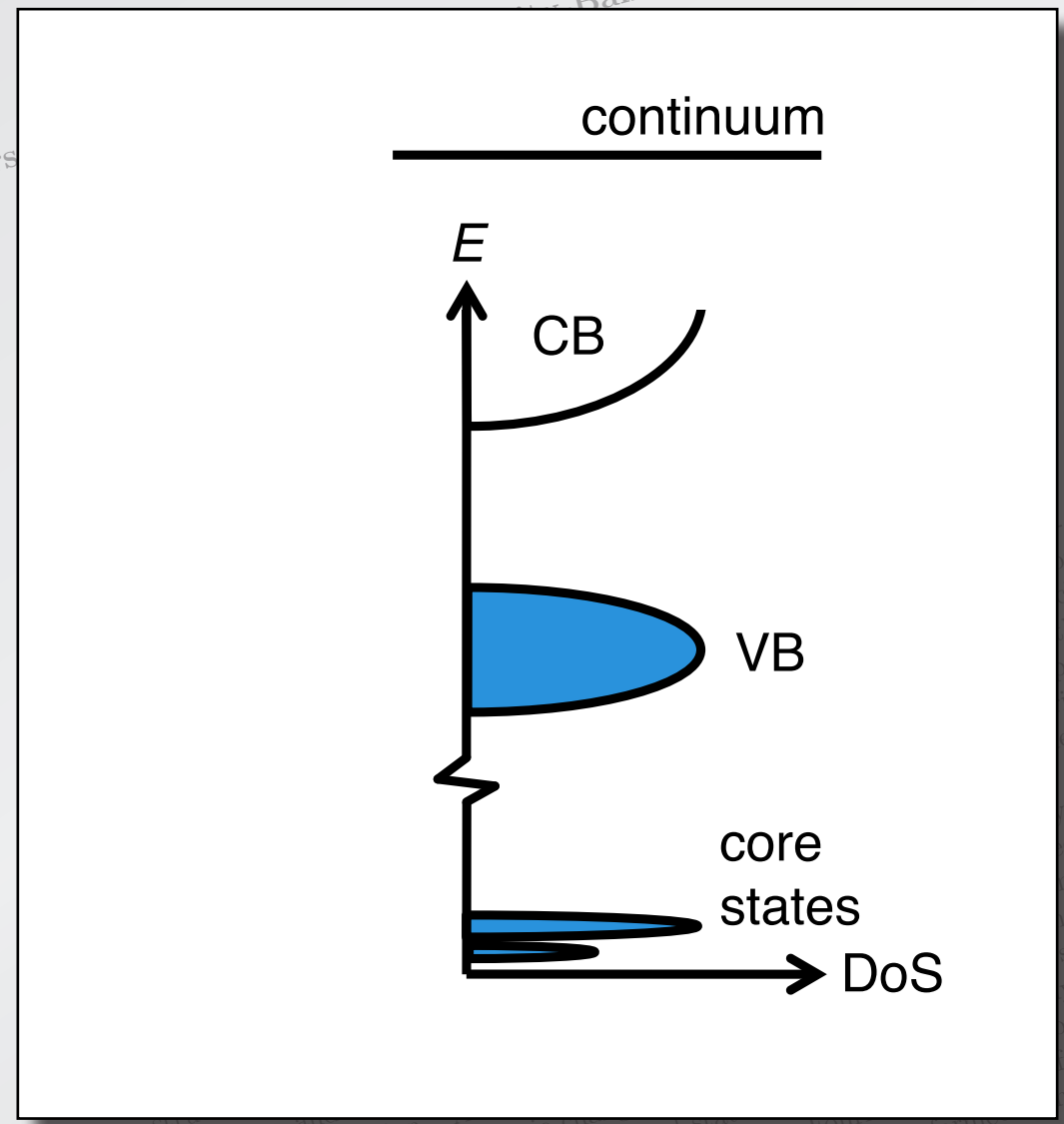
Abstract

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.

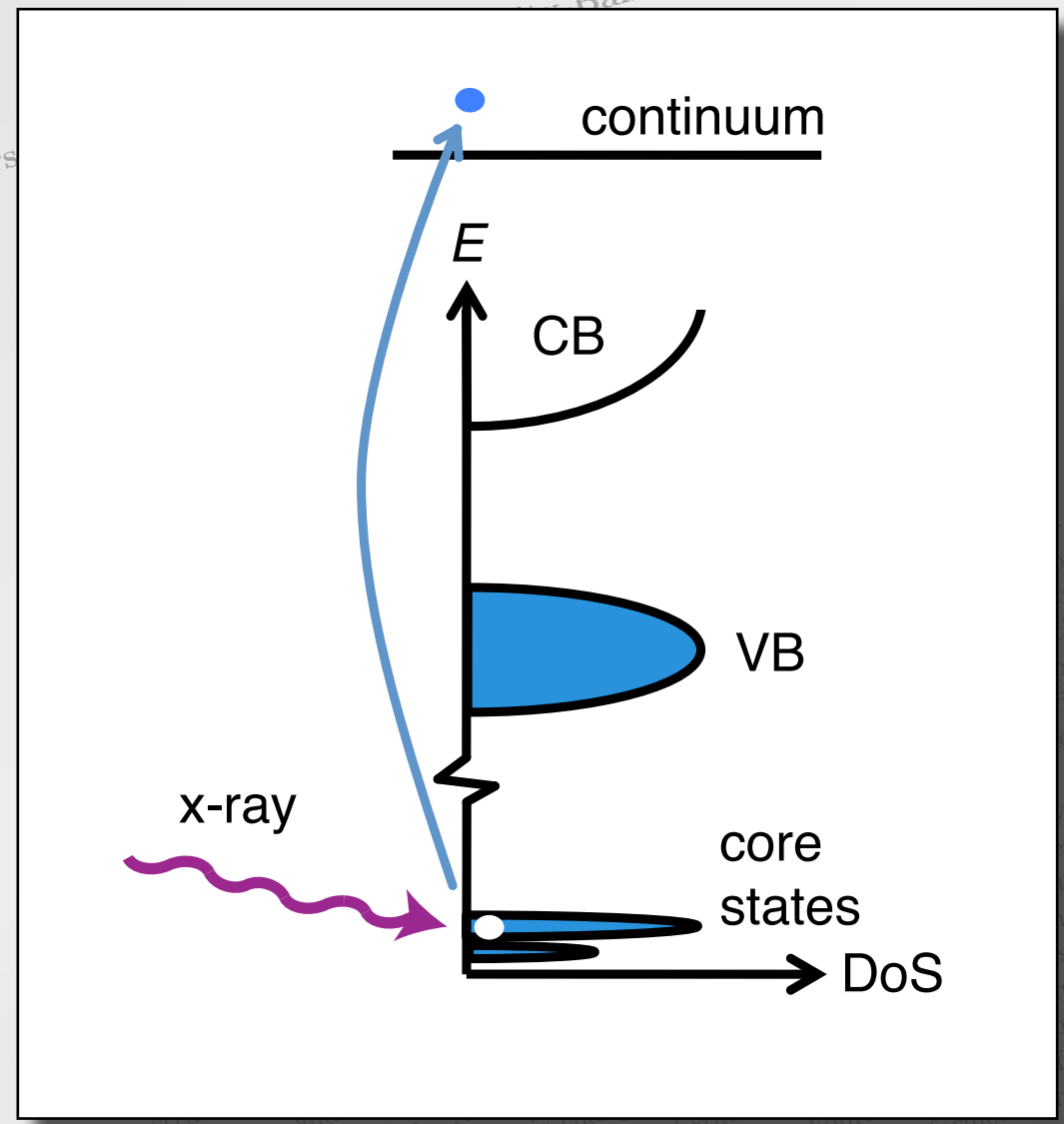
Next, the optical properties are studied using Fourier transform infrared spectroscopy. Extraction of the complex index of refraction is performed using numerical simulate both the transmission and reflection measurements. Analysis of determines the position of the sulfur-induced states within section for different sulfur concentrations and above the metal-insulator transition, with the conduction band, ucture unsuitable

Semiconductor to metal



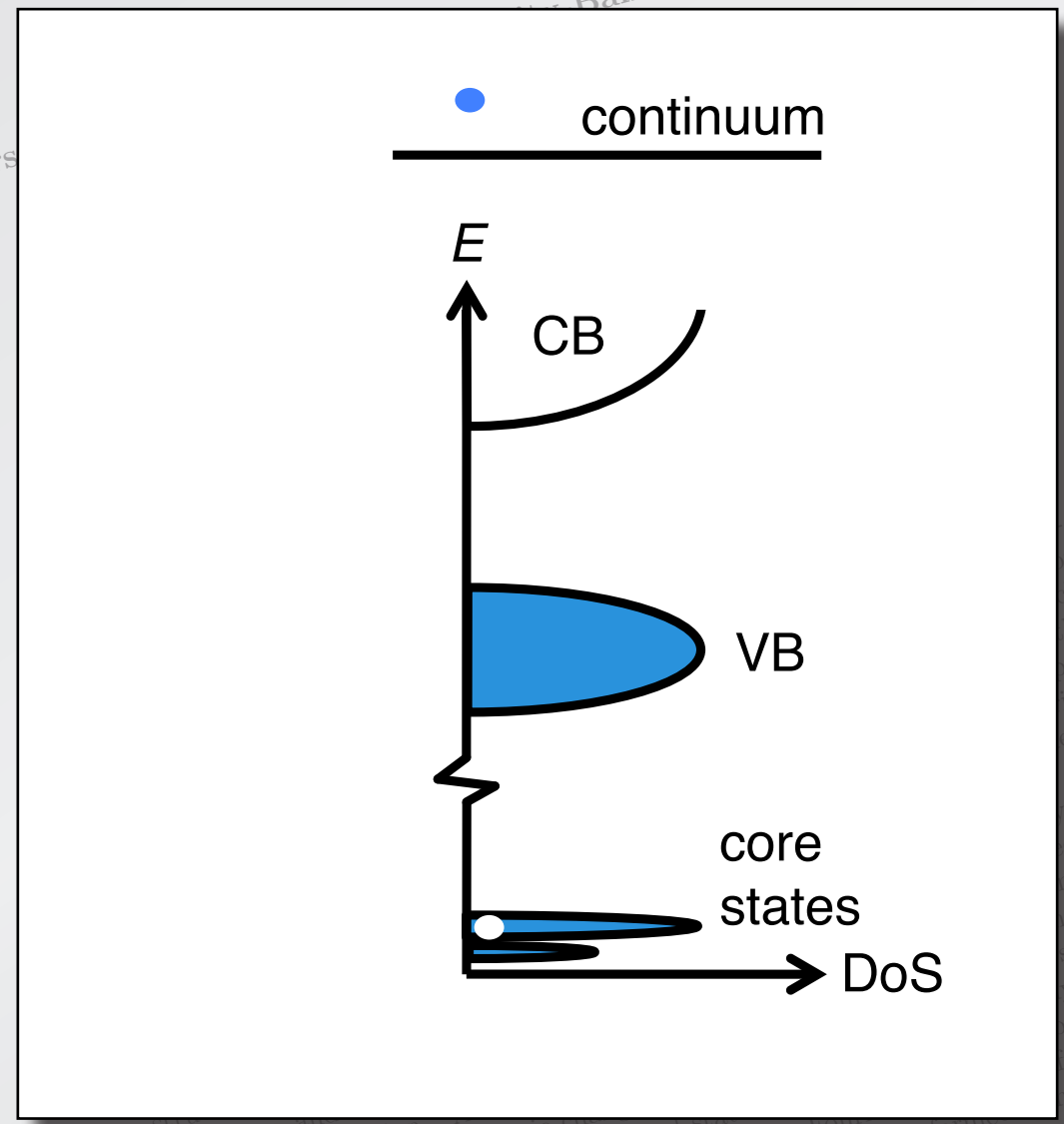
J. Sullivan, Ph.D. Thesis, MIT (2013)

Semiconductor to metal



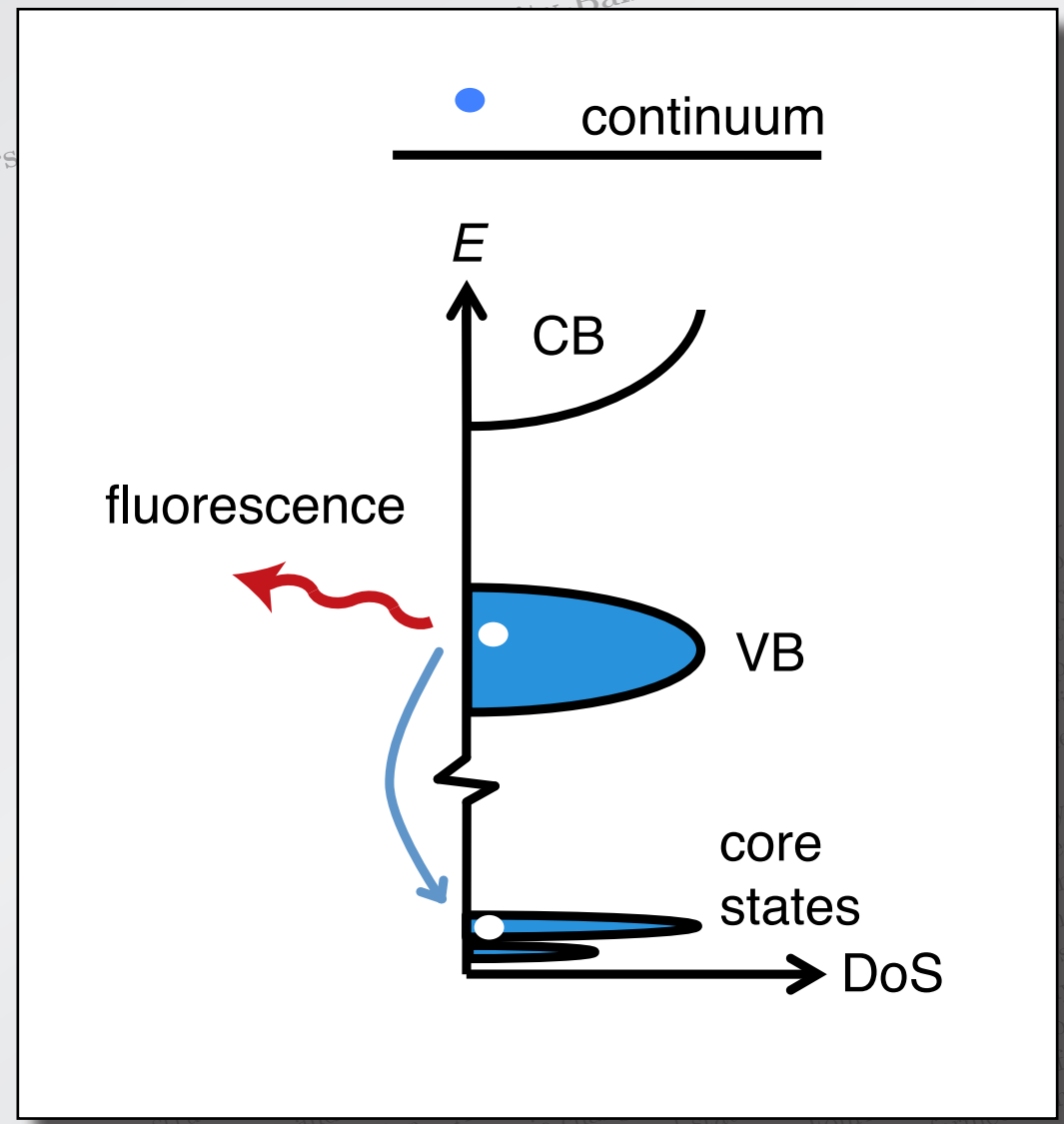
J. Sullivan, Ph.D. Thesis, MIT (2013)

Semiconductor to metal



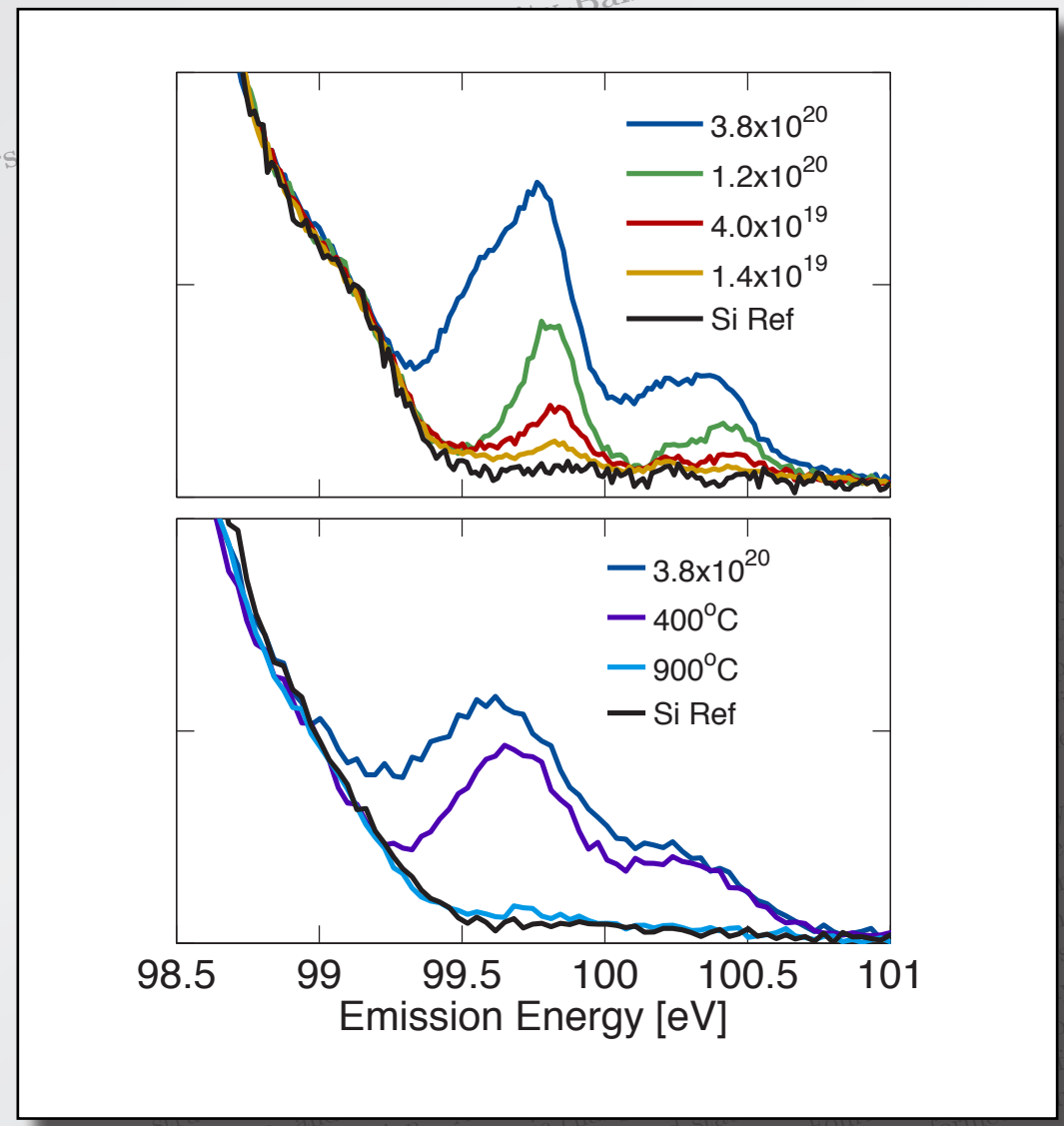
J. Sullivan, Ph.D. Thesis, MIT (2013)

Semiconductor to metal



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

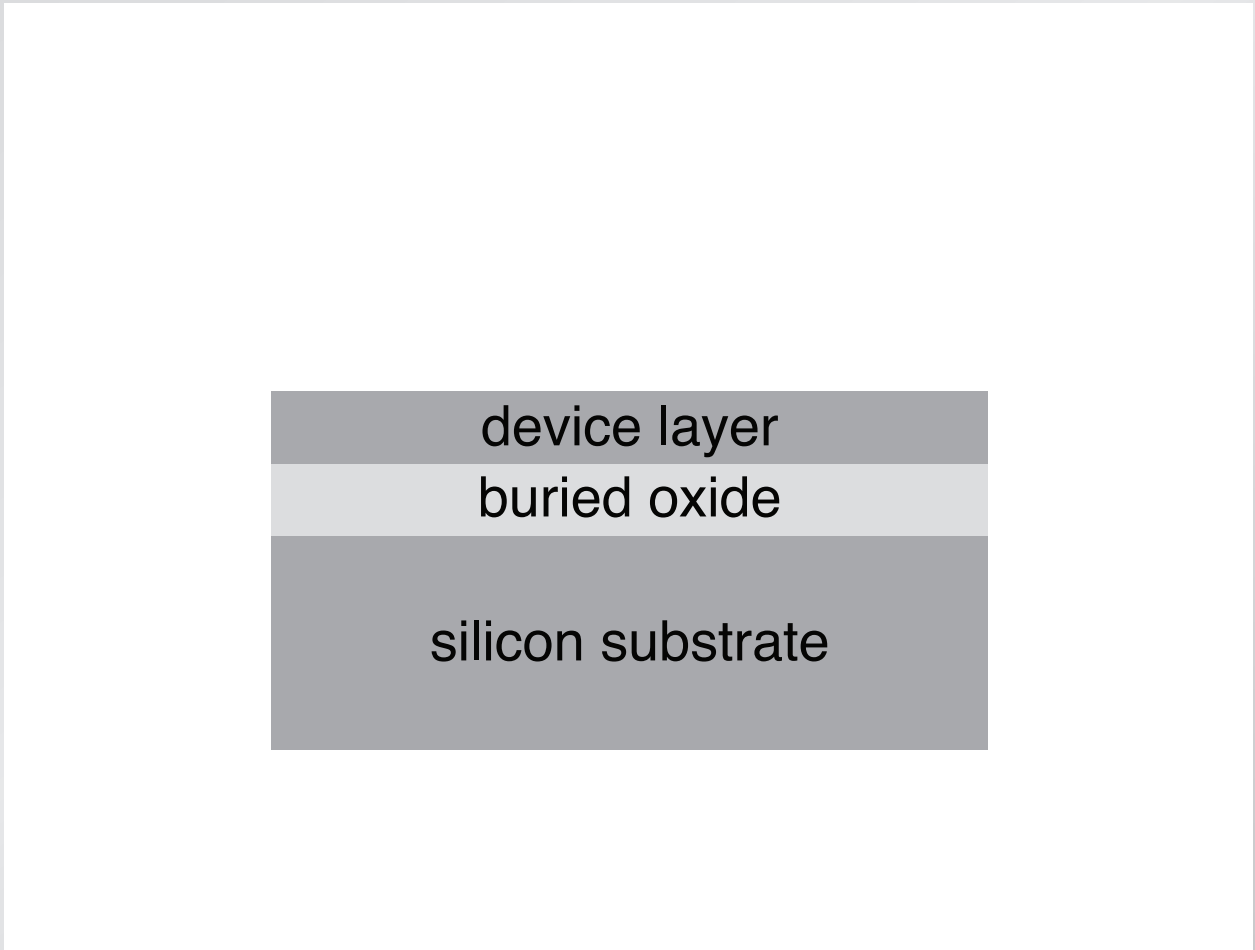
Semiconductor to metal



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

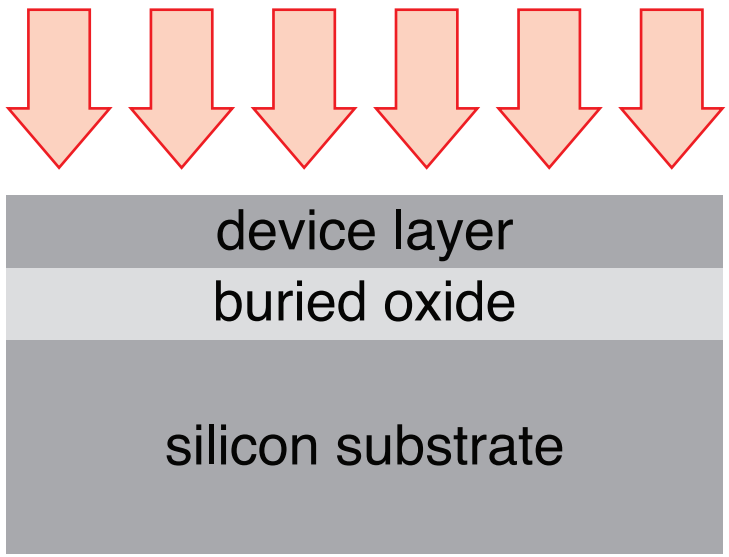
Semiconductor to metal

isolate surface layer for Hall measurements



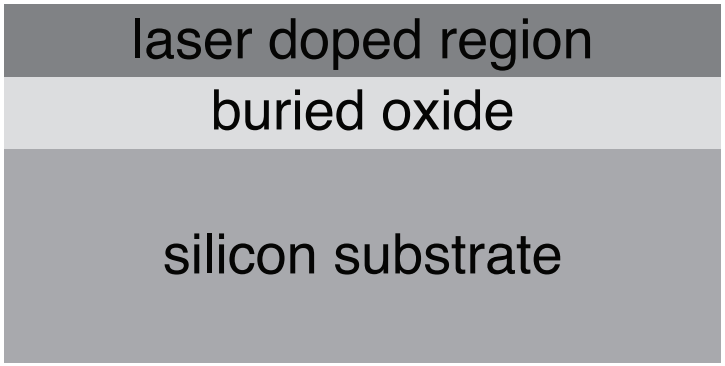
Semiconductor to metal

isolate surface layer for Hall measurements



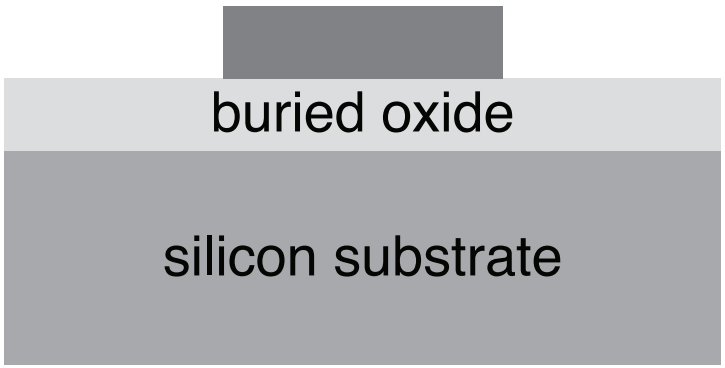
Semiconductor to metal

isolate surface layer for Hall measurements



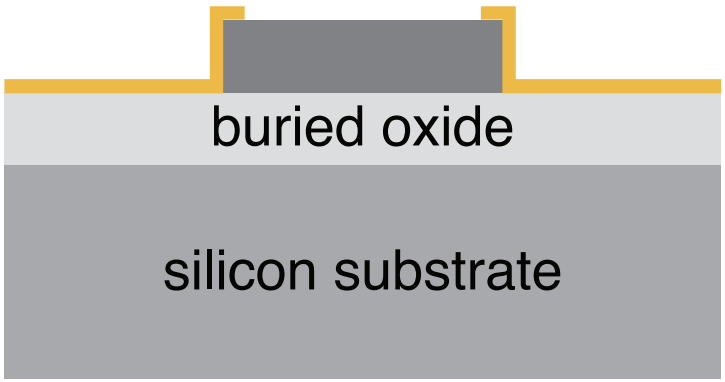
Semiconductor to metal

isolate surface layer for Hall measurements



Semiconductor to metal

isolate surface layer for Hall measurements



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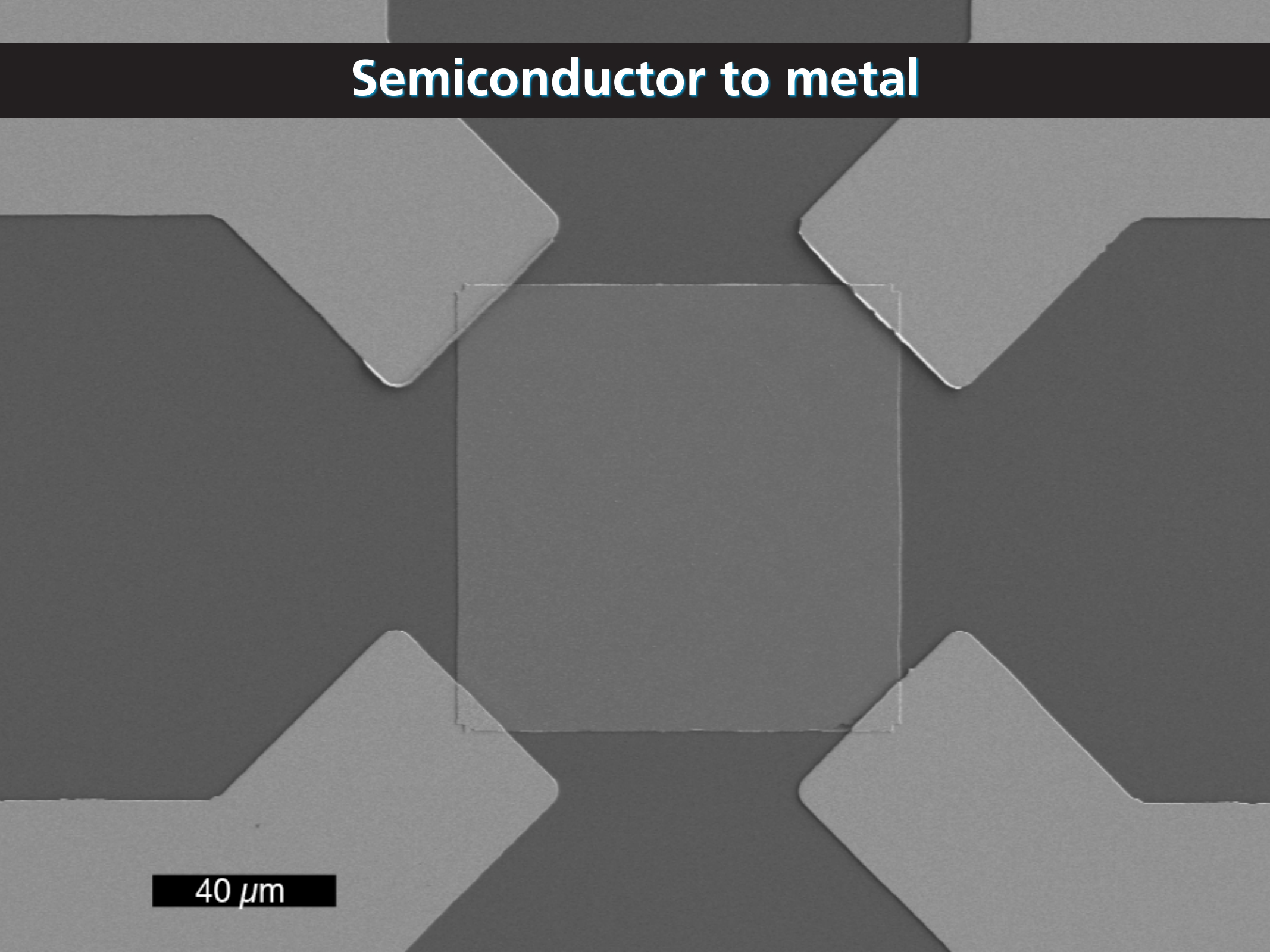
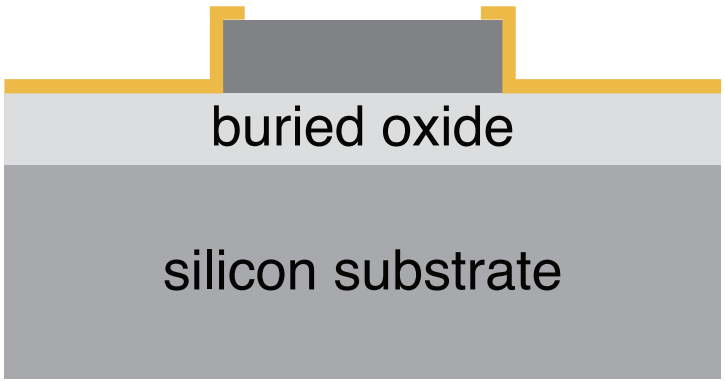
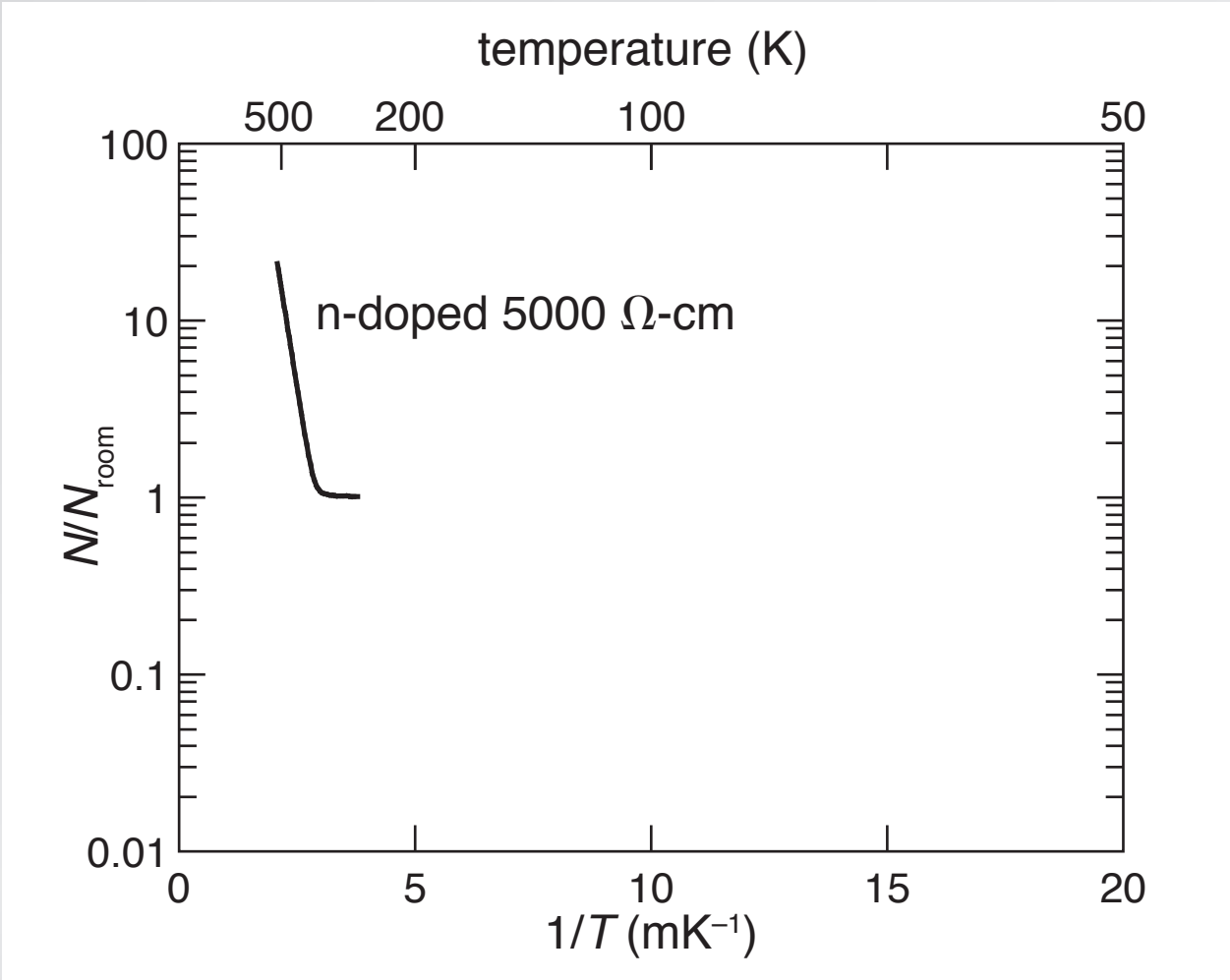


Semiconductor to metal

isolate surface layer for Hall measurements



Semiconductor to metal



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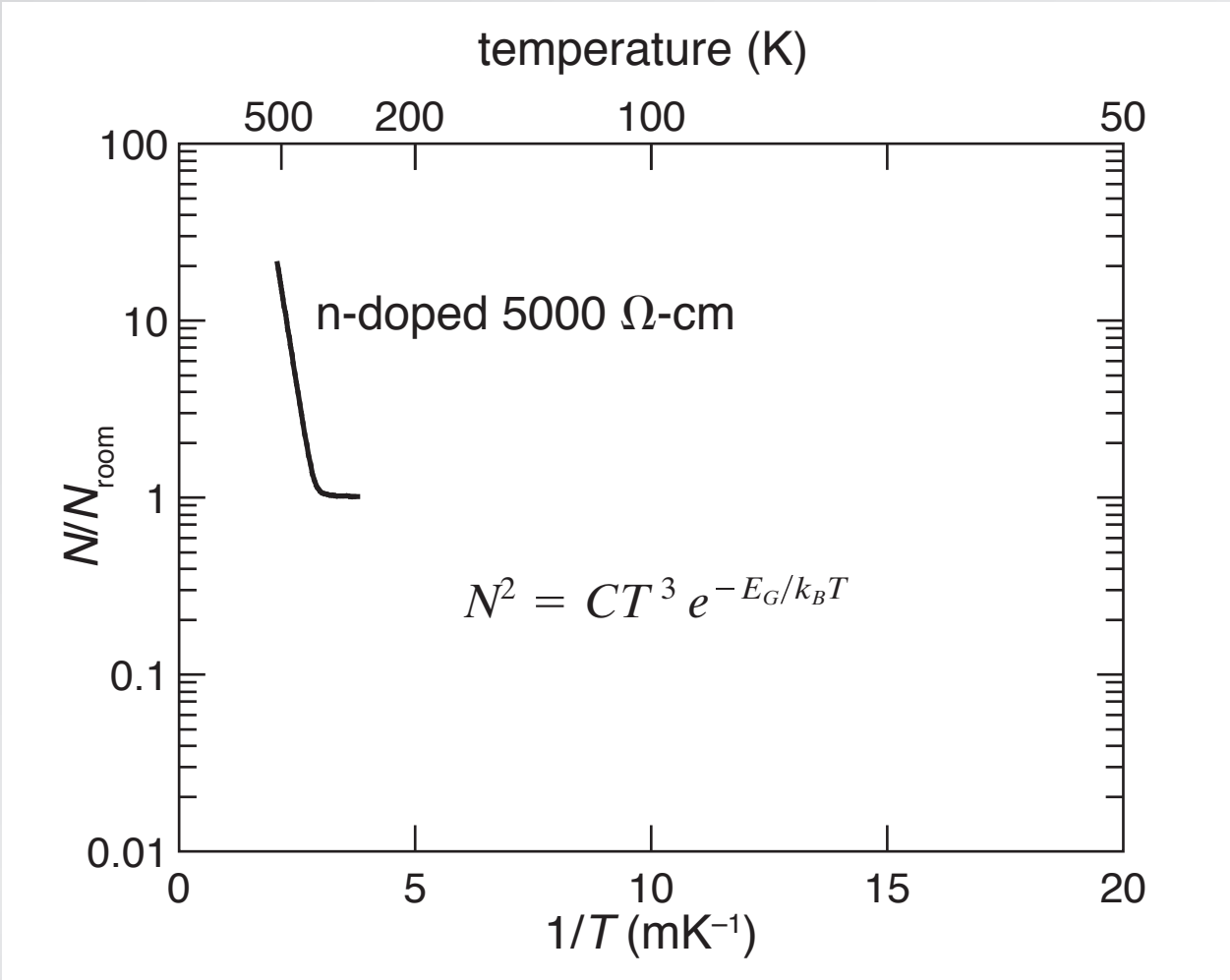

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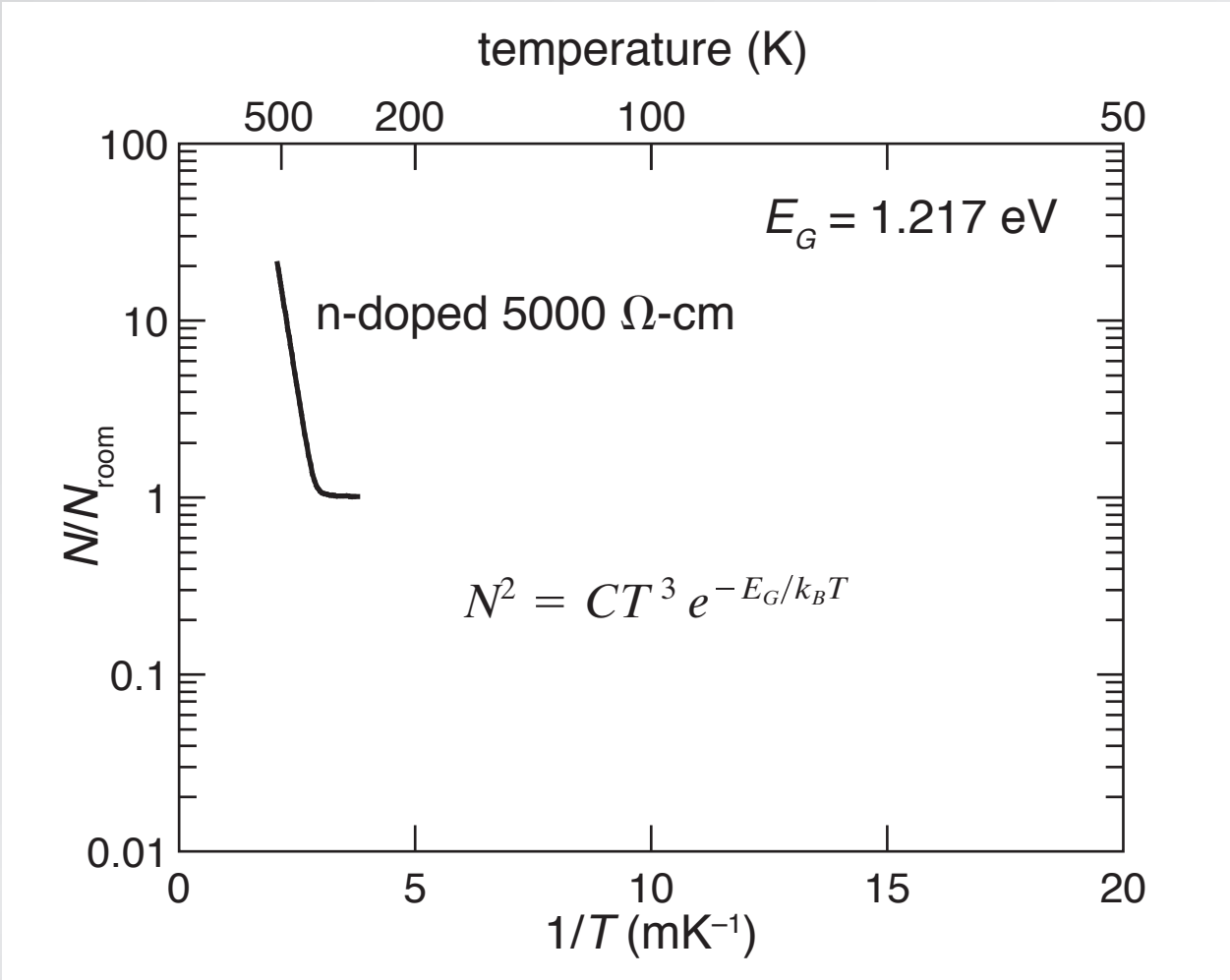

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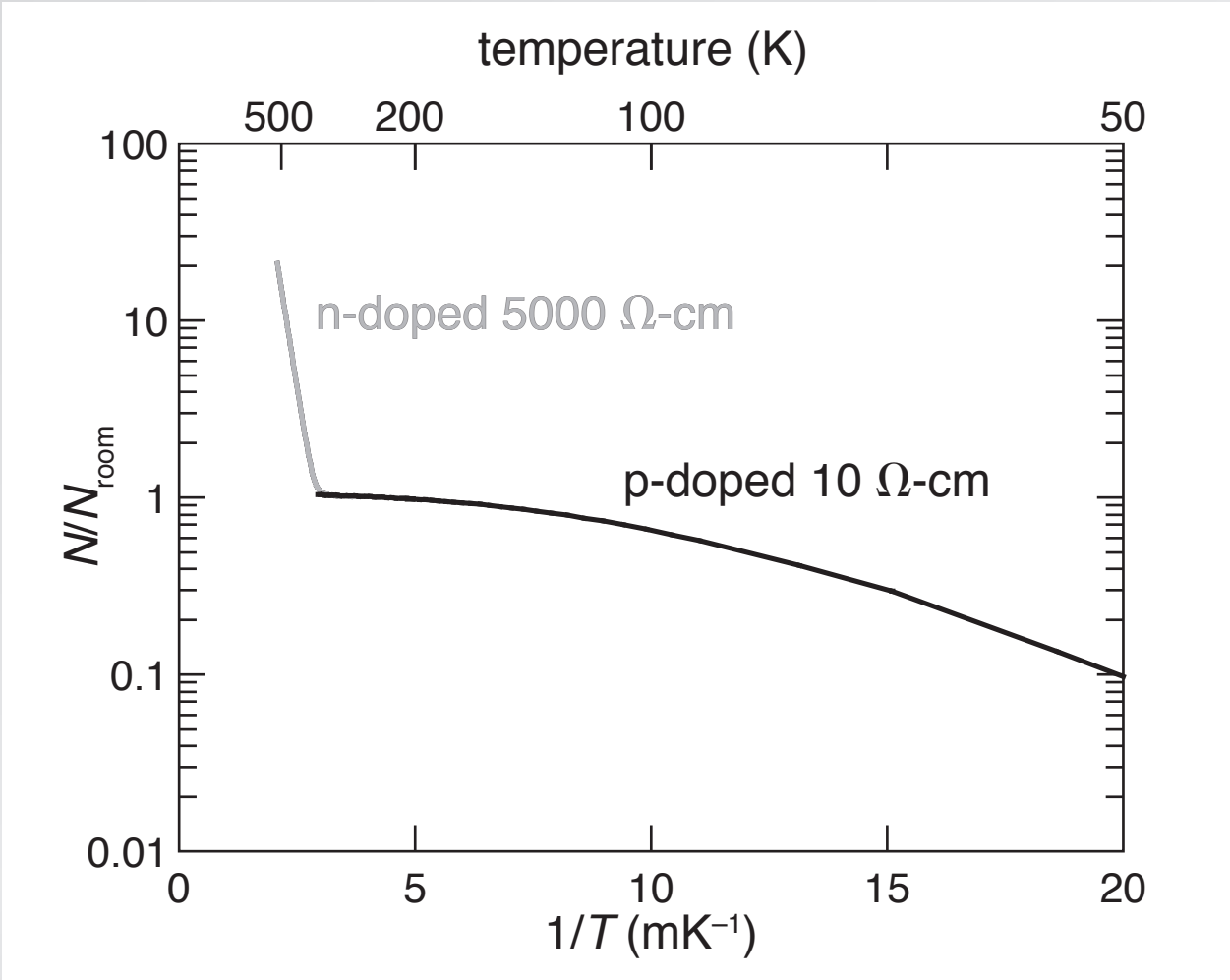
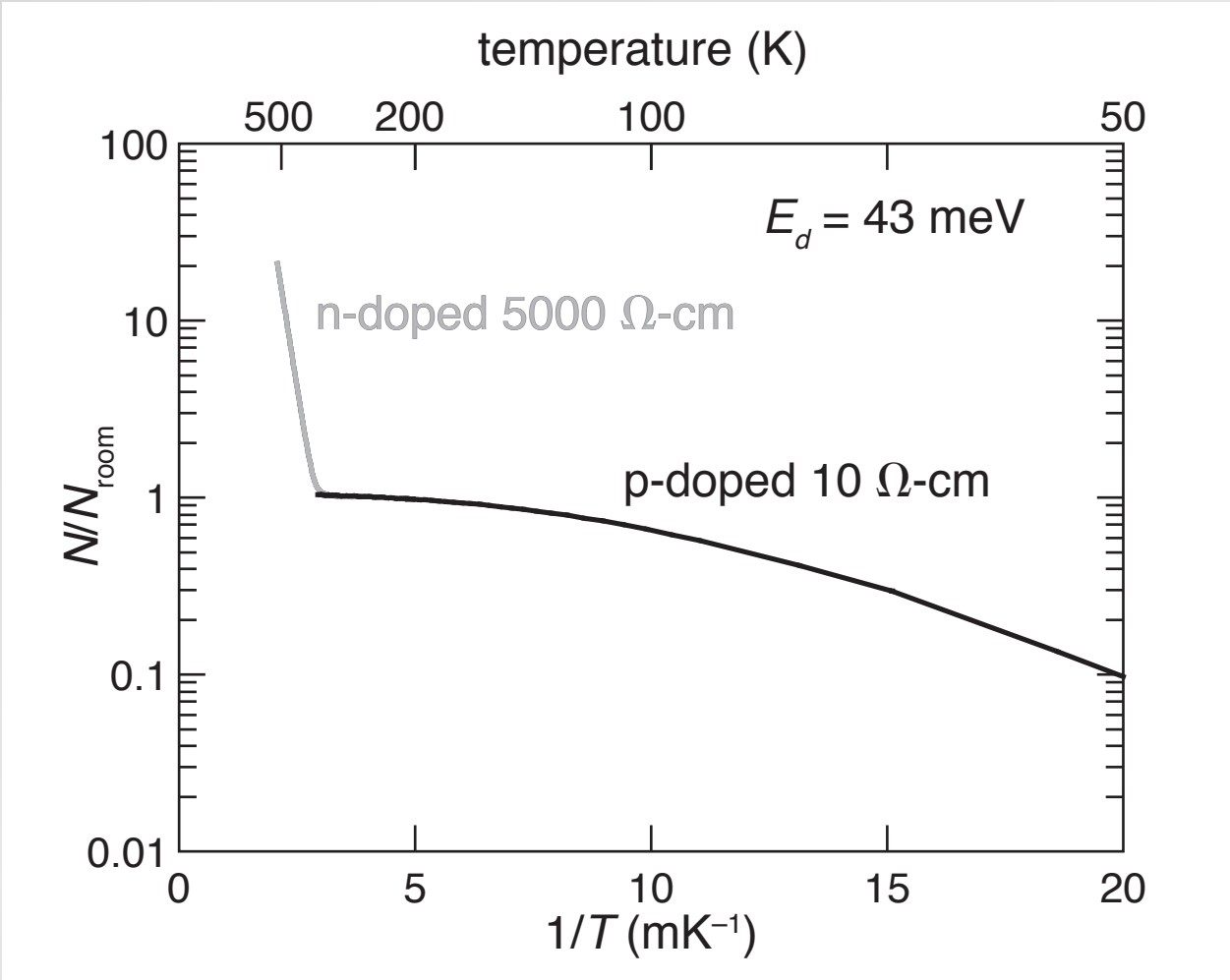


Semiconductor to metal



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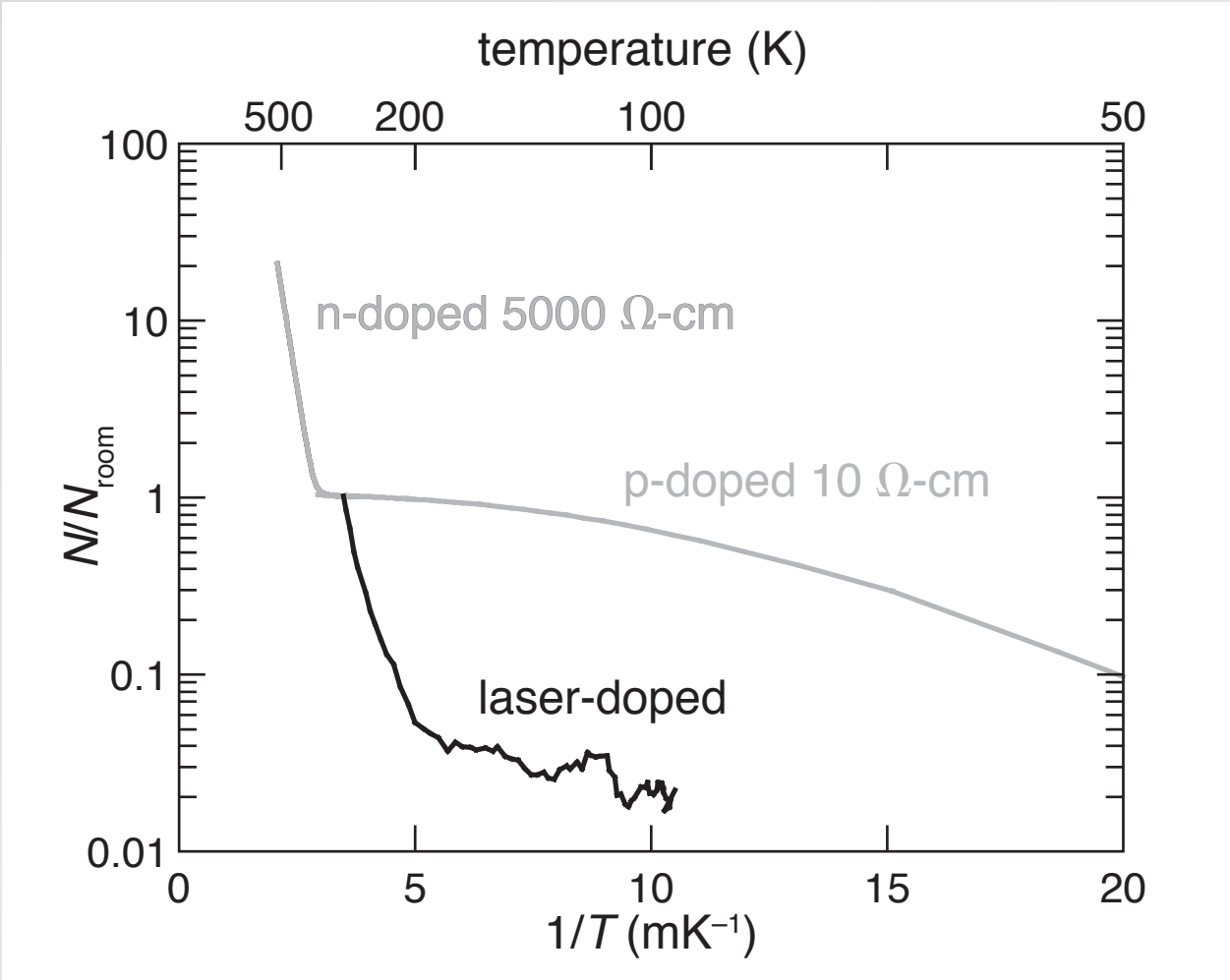

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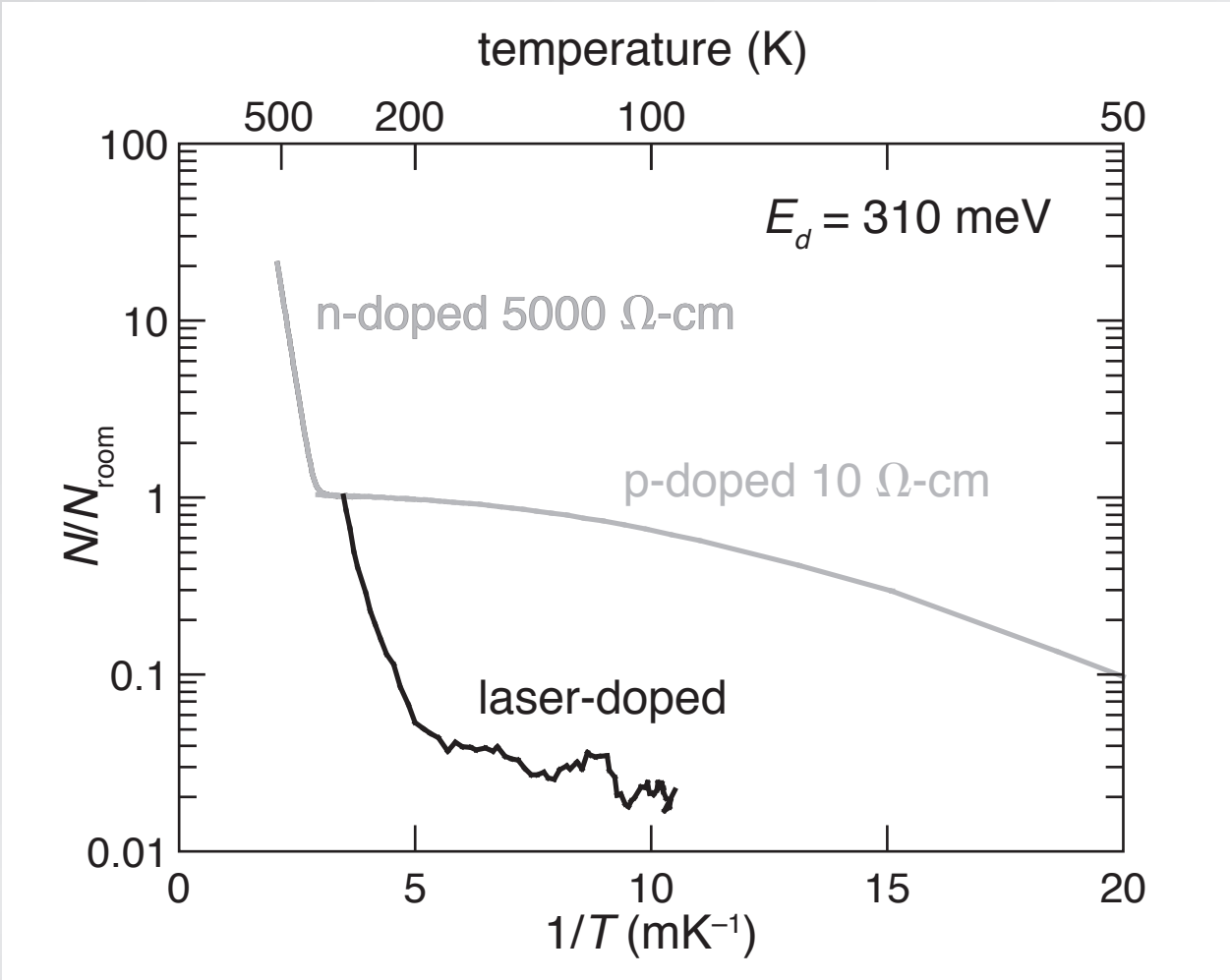

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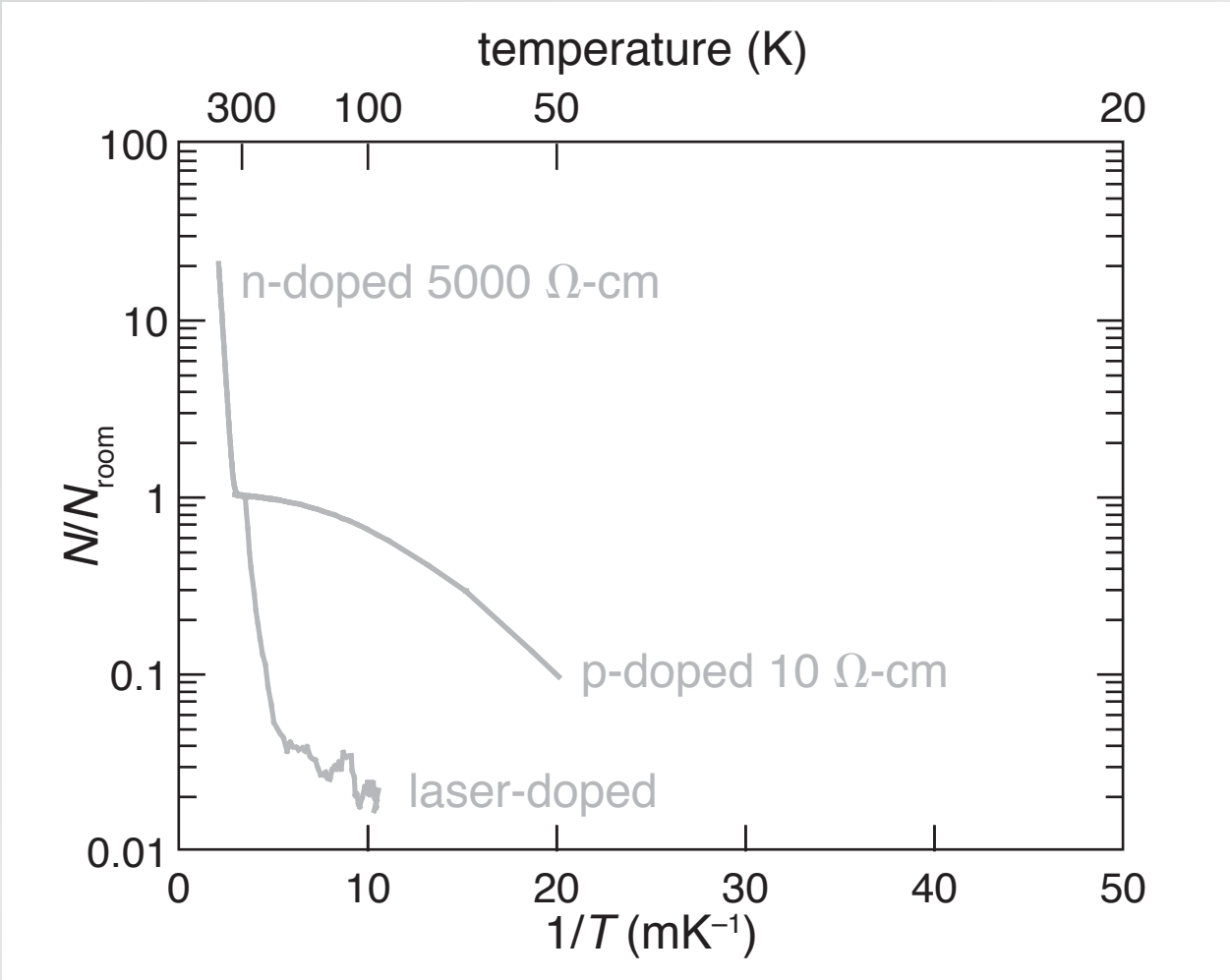

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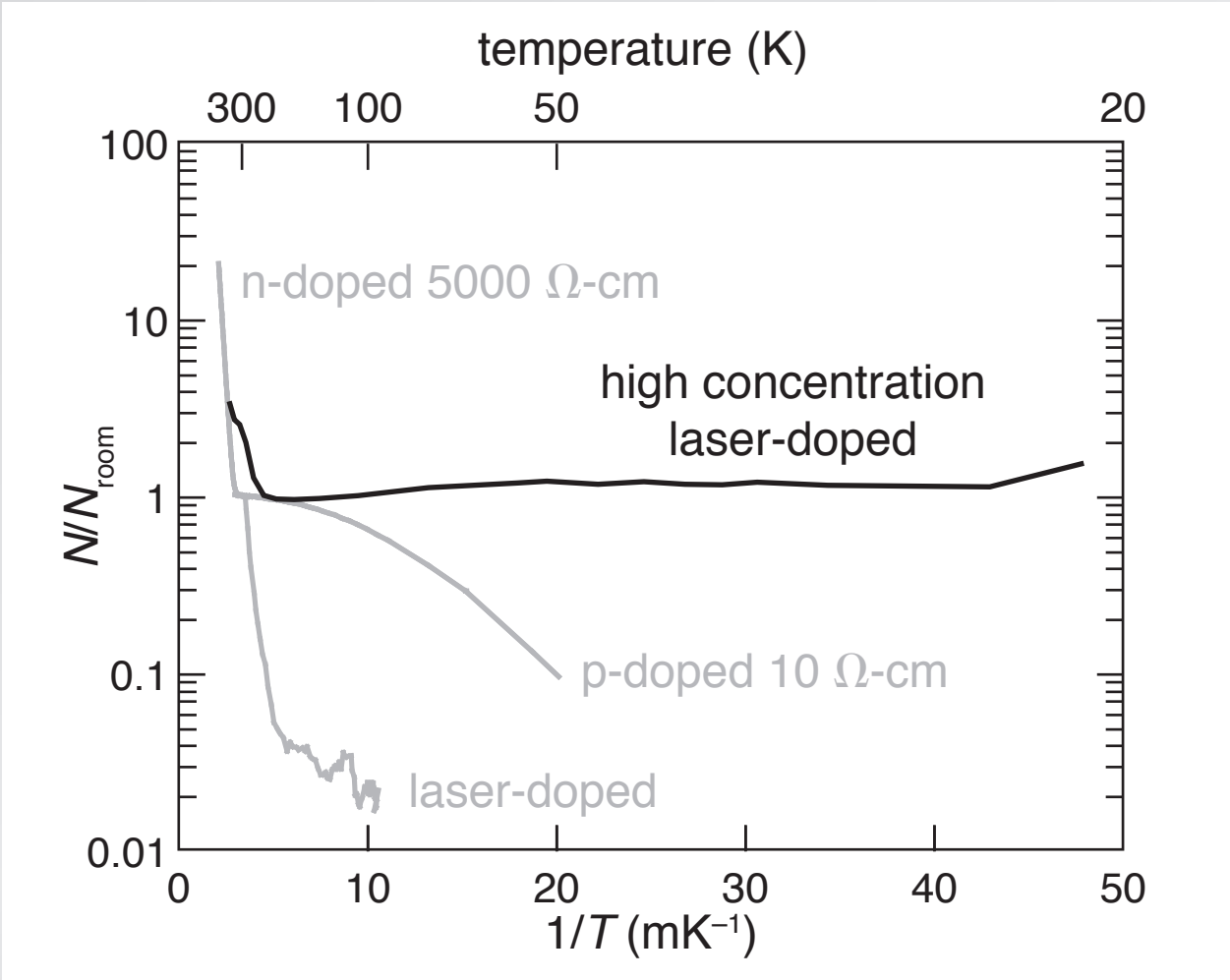

Conclusion

- transient and metastable band structure changes
- both due to fs-induced nonequilibrium state
- a new way of manipulating band structure

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Dr. Jeffrey Warrander (ARDEC)

Funding:

Army Research Office
DARPA
Department of Energy
NDSEG
National Science Foundation

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