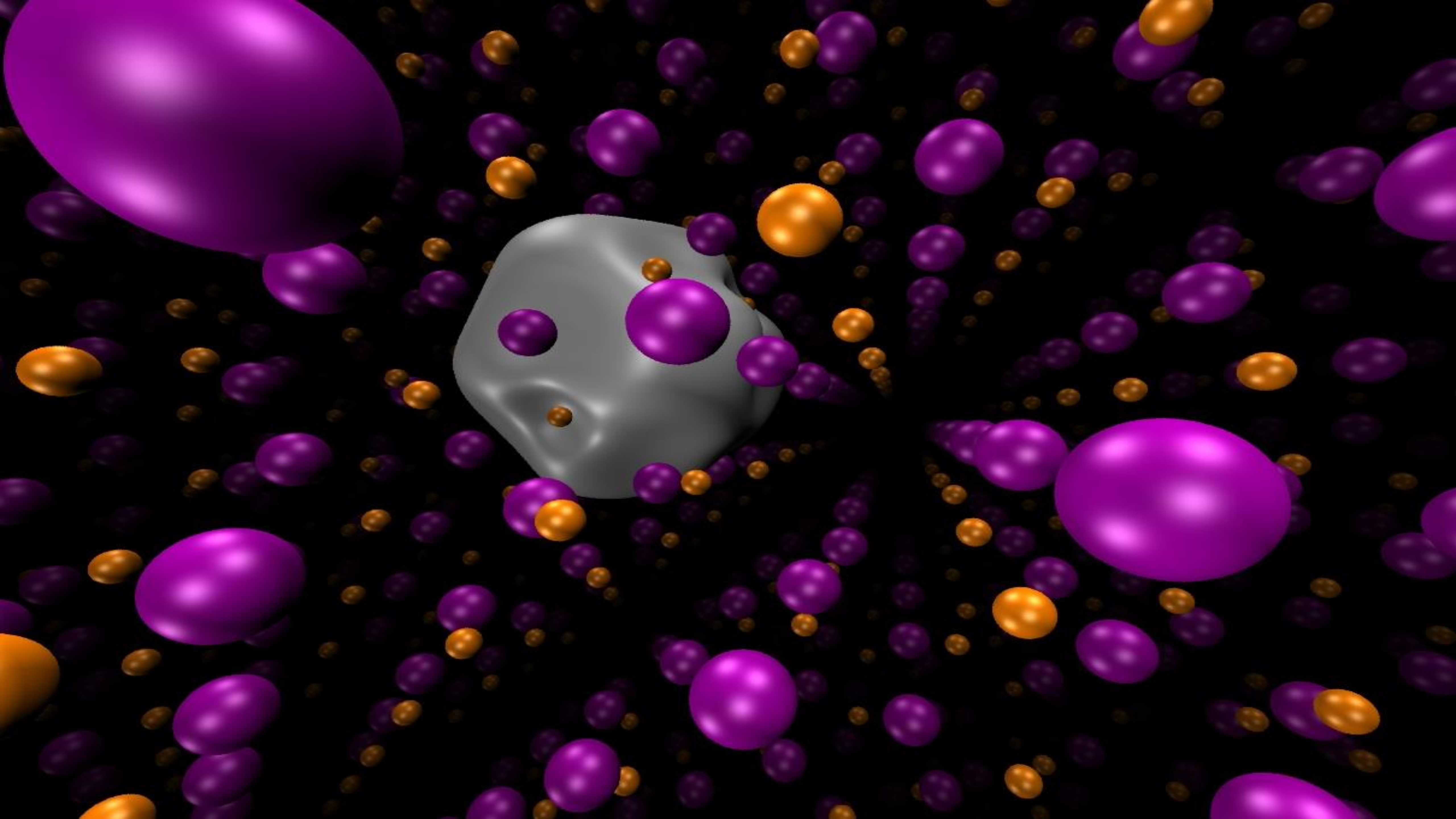


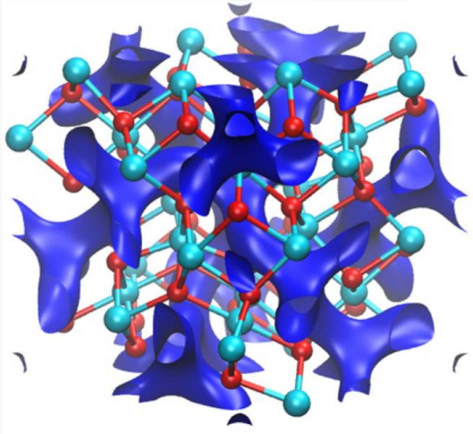
POSITRON ANNIHILATION

PROBING THE ATOMIC AND ELECTRONIC STRUCTURES OF CONDENSED MATTER

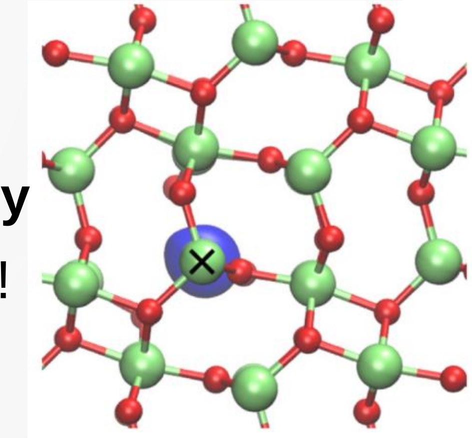
Filip Tuomisto
Department of Physics, University of Helsinki, Finland

CONTENTS

WHY DO WE DO POSITRON ANNIHILATION EXPERIMENTS?



- Because in solids, positrons want to go where there aren’t any atoms!
  - interstitial space
  - **vacancies!**
- Happy additional property: positrons are pretty insensitive to most other stuff
- Hence: **selective sensitivity to vacancy defects**
  - identification, concentration
  - bulk crystals, thin films, any conductivity
  - sensitivity to charge: negative, neutral (positive invisible)
- **Somewhat (”second order”) sensitive to other interruptions of periodicity**
- Fun in semiconductors: sensitivity to negative charge temperature-dependent!
  - manipulation: illumination, bias, magnetic fields, etc.



POSITRON-ELECTRON ANNIHILATION

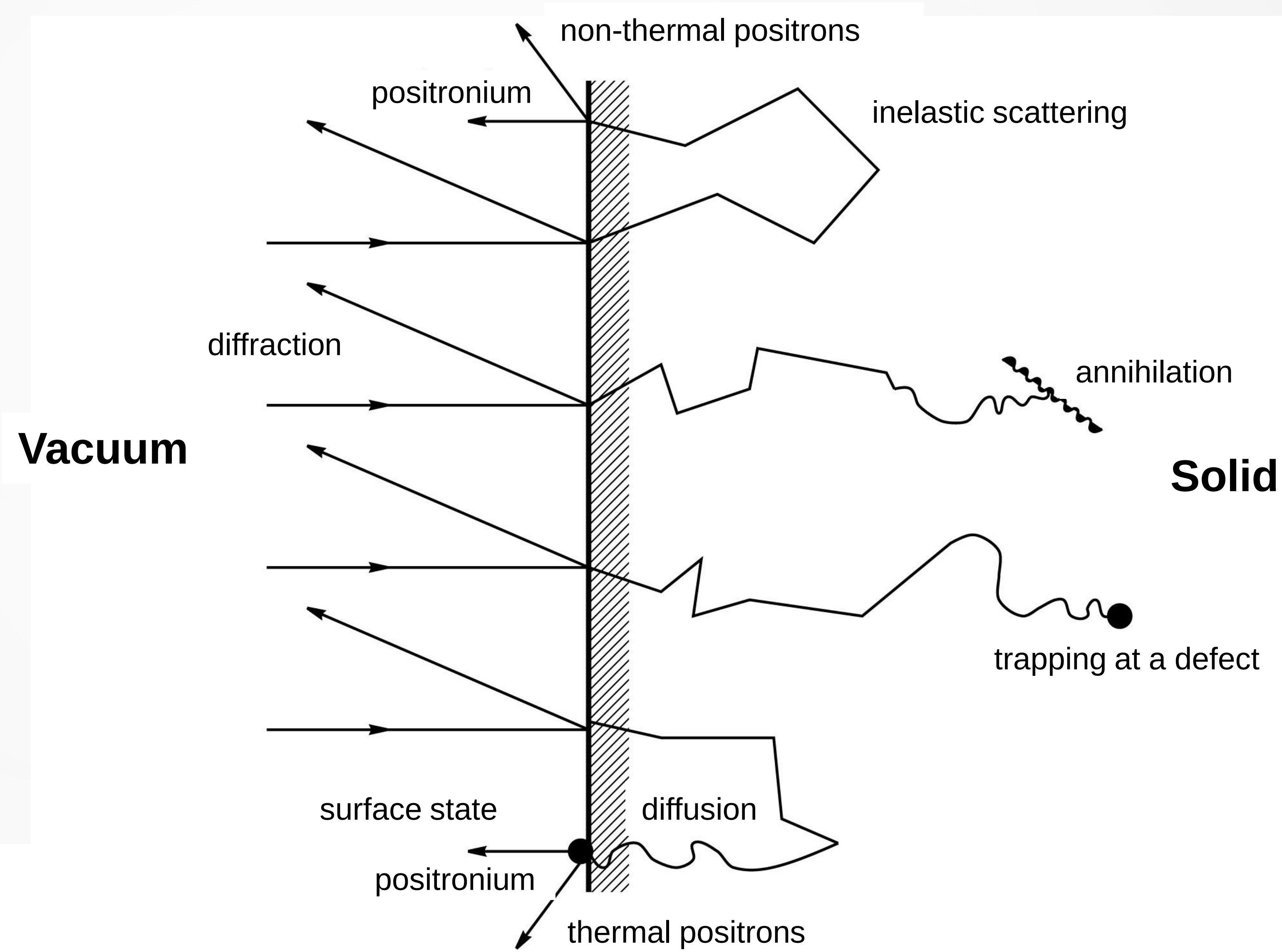
- By far most probable in solids: annihilation of the ”free” positron with an electron, both almost at rest. Produces two gamma photons of ~511 keV each, lifetime in the range 100 – 500 ps

- Other possibility: formation of the $e^+ - e^-$ bound state called positronium (Ps)
  - $^1S_0$ state (para-positronium, p-Ps): two gamma photons, lifetime of the bound state 125 ps
  - $^3S_1$ state (ortho-positronium, o-Ps): three (or more) gamma photons, lifetime of the bound state 142 ns (in practice always so-called pick-off annihilation, lifetime 500 ps – 60 ns)
  - Ps^- (positron + two electrons): two gamma photons, lifetime 500 ps

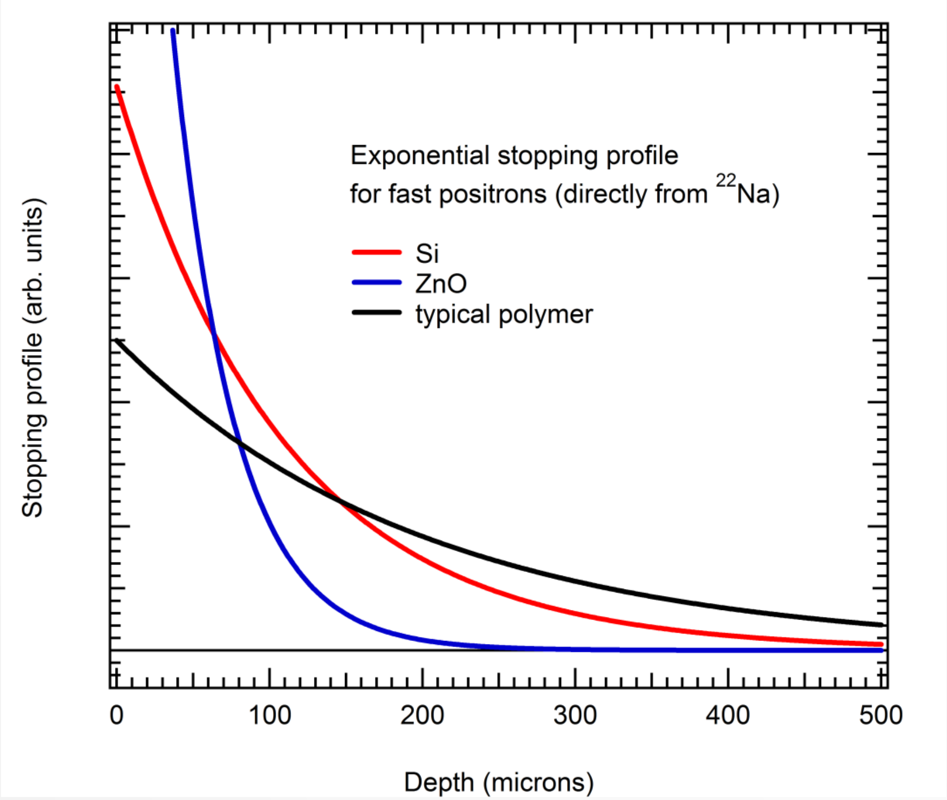
POSITRON-SOLID INTERACTIONS

Stopping and thermalization are the same as for energetic electrons: ionization, band-to-band excitation, phonon emission

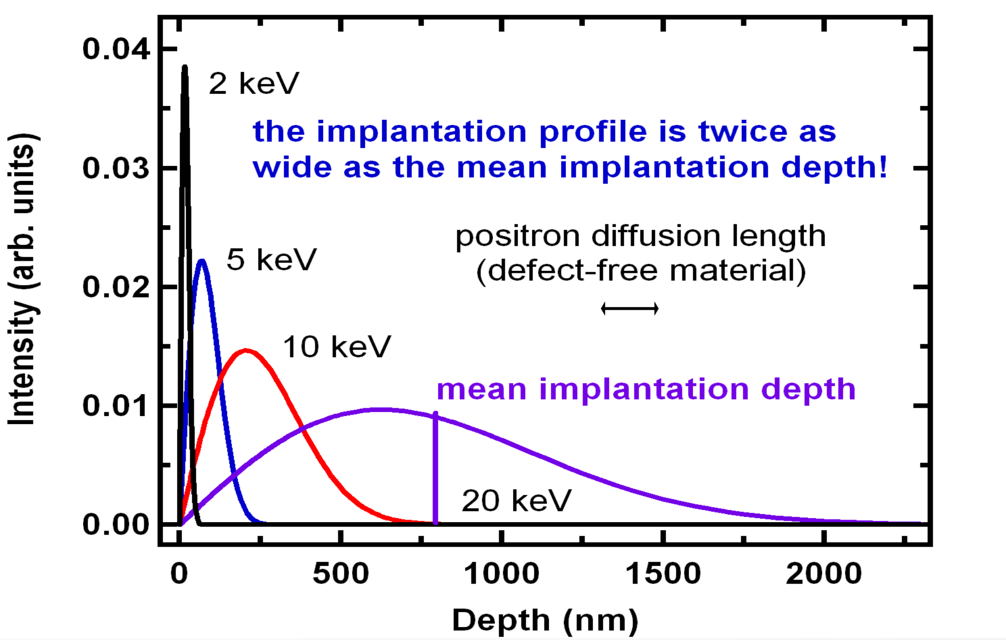
Timescale for stopping and thermalization (at RT): a few picoseconds



FAST VS. SLOW POSITRONS



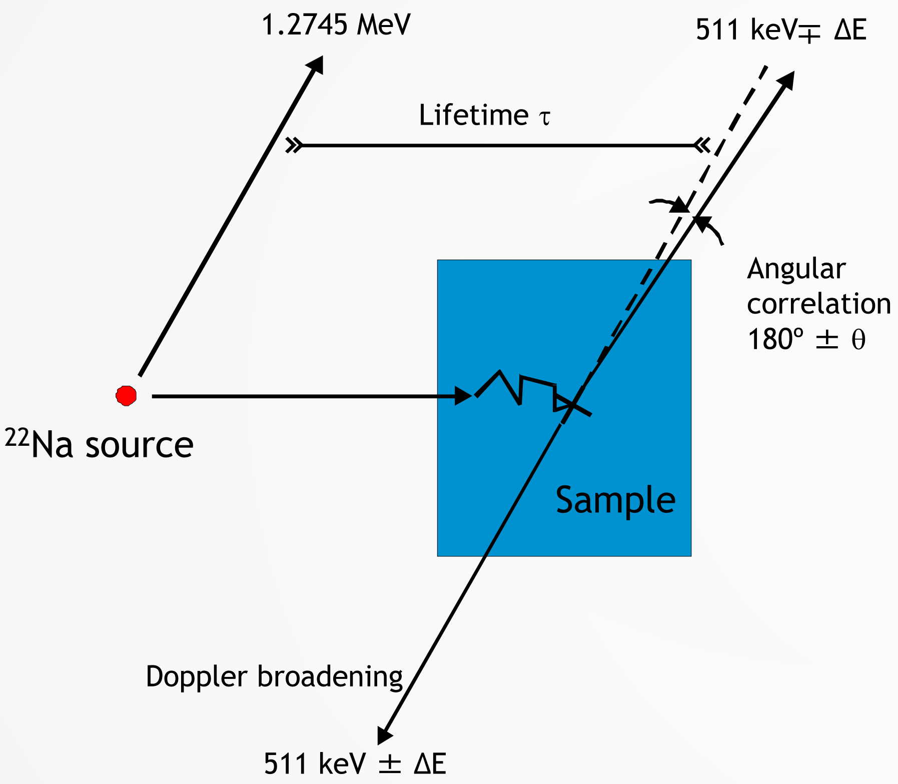
A tunable monoenergetic positron beam can be used to measure a depth profile at distances 0 - 5 μm from the surface of a solid

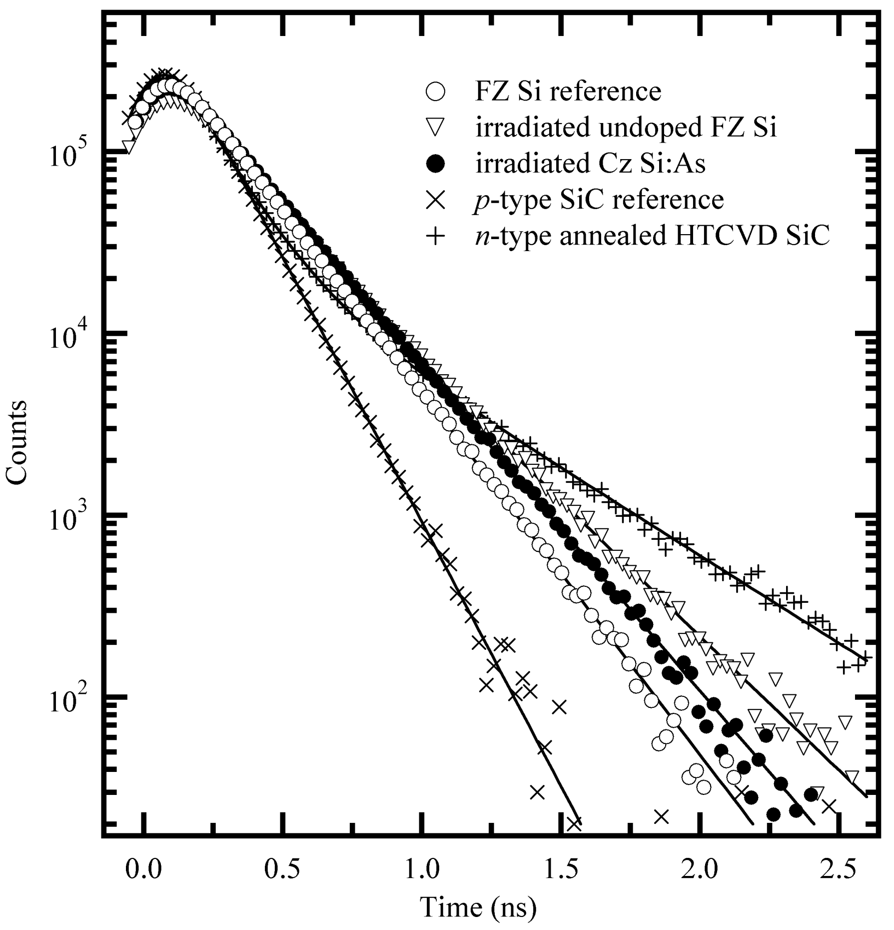


POSITRON STATE(S) IN A SOLID

- Important: single-particle physics! (both in theory and in experiments)
- In a periodic lattice (perfect crystal), the thermalized positron will be in a Bloch-like delocalized state
  - In fact, this is the closest you can get to the textbook example of a Bloch state in real life (single particle in a static periodic potential)!
- Interruptions in the periodicity can lead to the localization (trapping) of the positron
  - In particular, missing atoms (vacancies) are efficient traps!
  - Competition between annihilation from the delocalized (”free”) state and trapping (+subsequent annihilation from the trapped state)
- Can be modeled from first principles

POSITRON LIFETIME EXPERIMENT



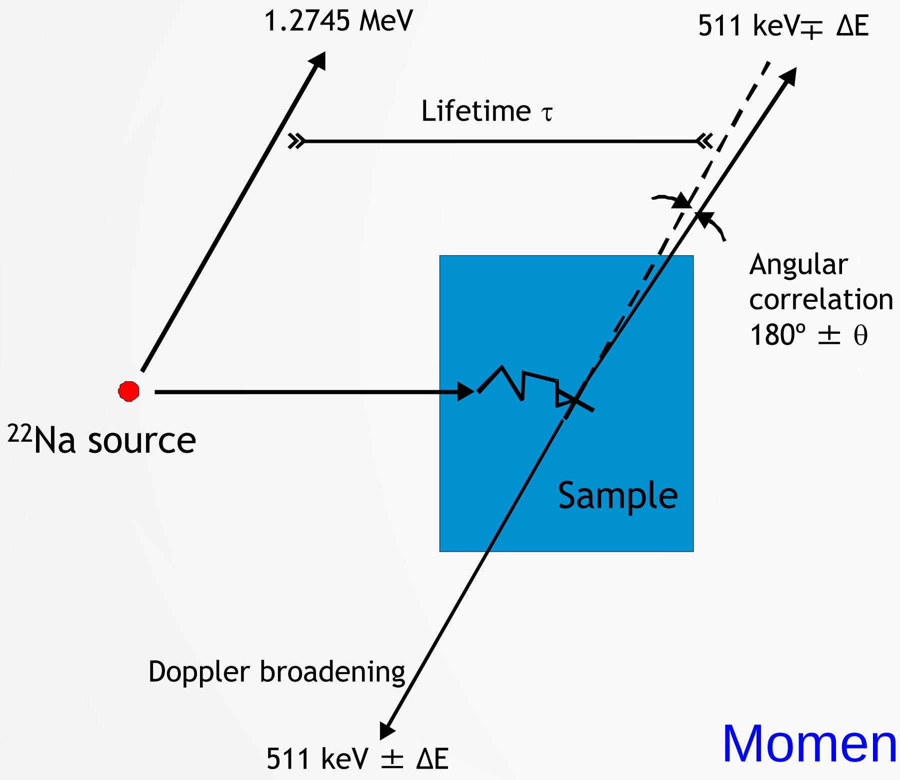


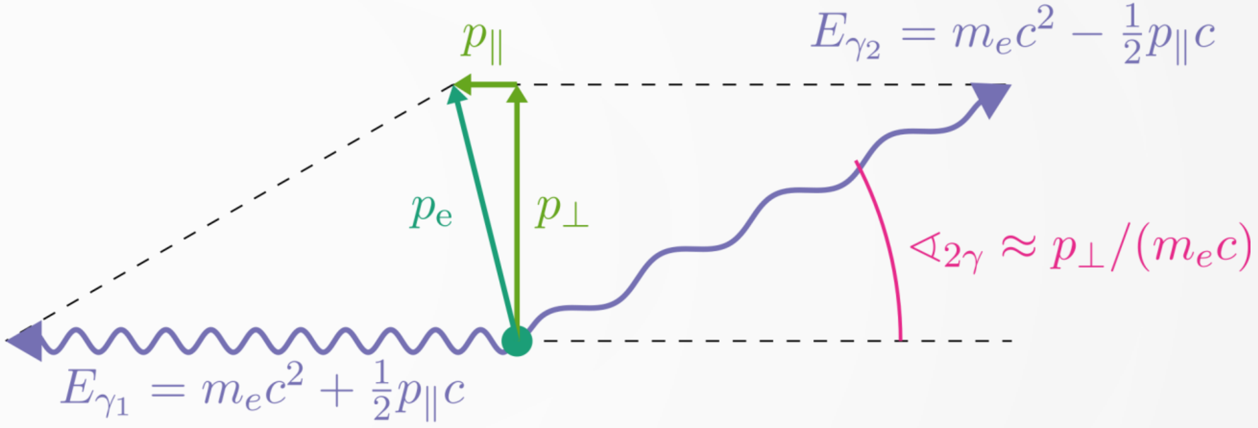
Positron lifetime:

$$1/\tau = \lambda = \pi r_0^2 c \int d\mathbf{r} \left|\Psi_+(\mathbf{r})\right|^2 n(\mathbf{r}) \gamma[n(\mathbf{r})]$$

$$N(t) = \sum_i I_i \mathrm{e}^{-t/\tau_i} \qquad \tau_{\mathrm{ave}} = \sum_i I_i \tau_i$$

DOPPLER BROADENING EXPERIMENT



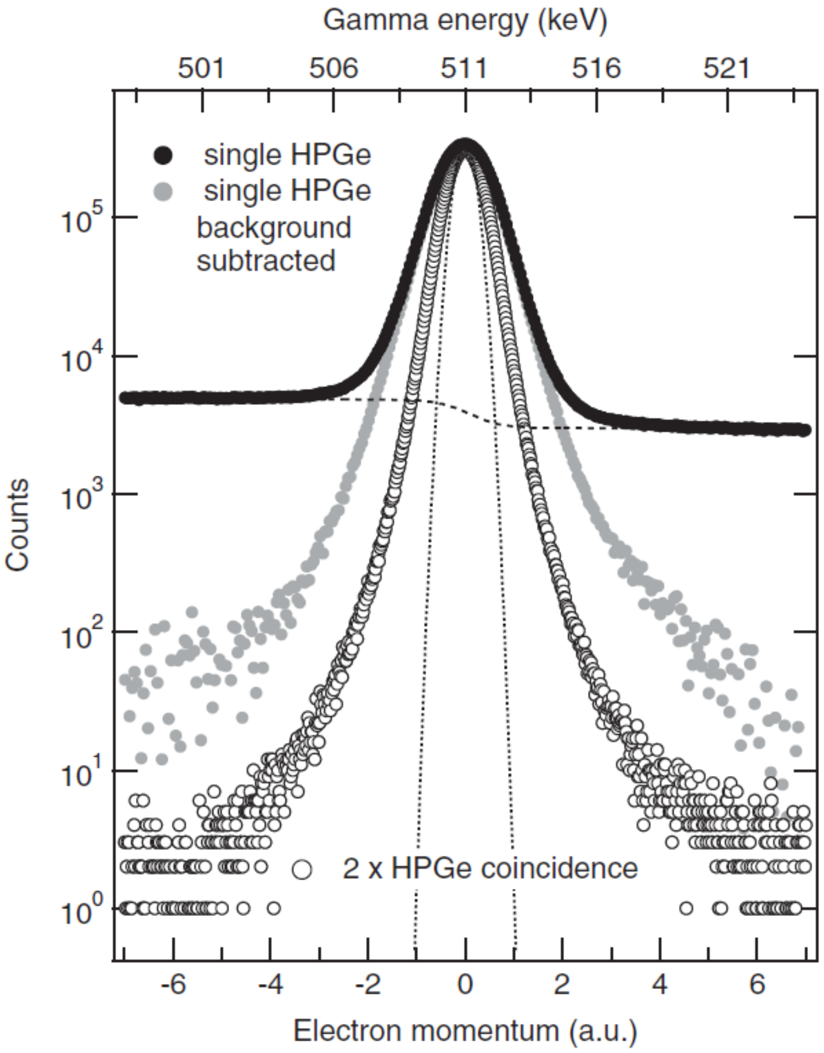


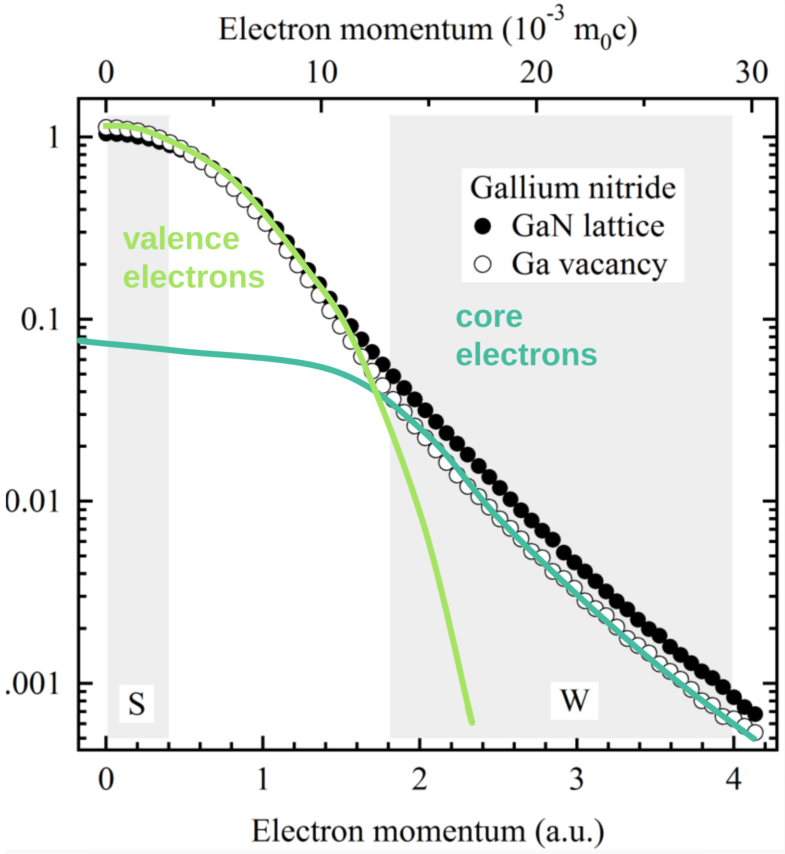
$p_L = 2\,\Delta E\ /\ c$ $\quad$ $(\Delta E = ½\, p_L\, c)$

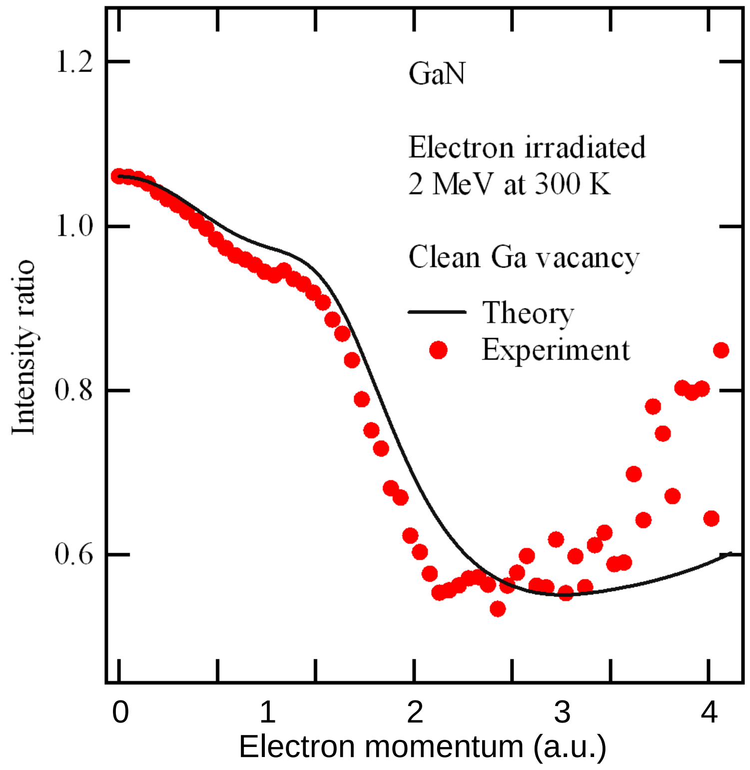
Momentum distribution (Doppler & ACAR):

$$\rho(\mathbf{p}) = \frac{\pi r_0 c}{V} \sum_i \left| \int d\mathbf{r} e^{-i\mathbf{p}\cdot\mathbf{r}} \Psi_+(\mathbf{r}) \Psi_i(\mathbf{r}) \sqrt{\gamma(\mathbf{r})} \right|^2$$

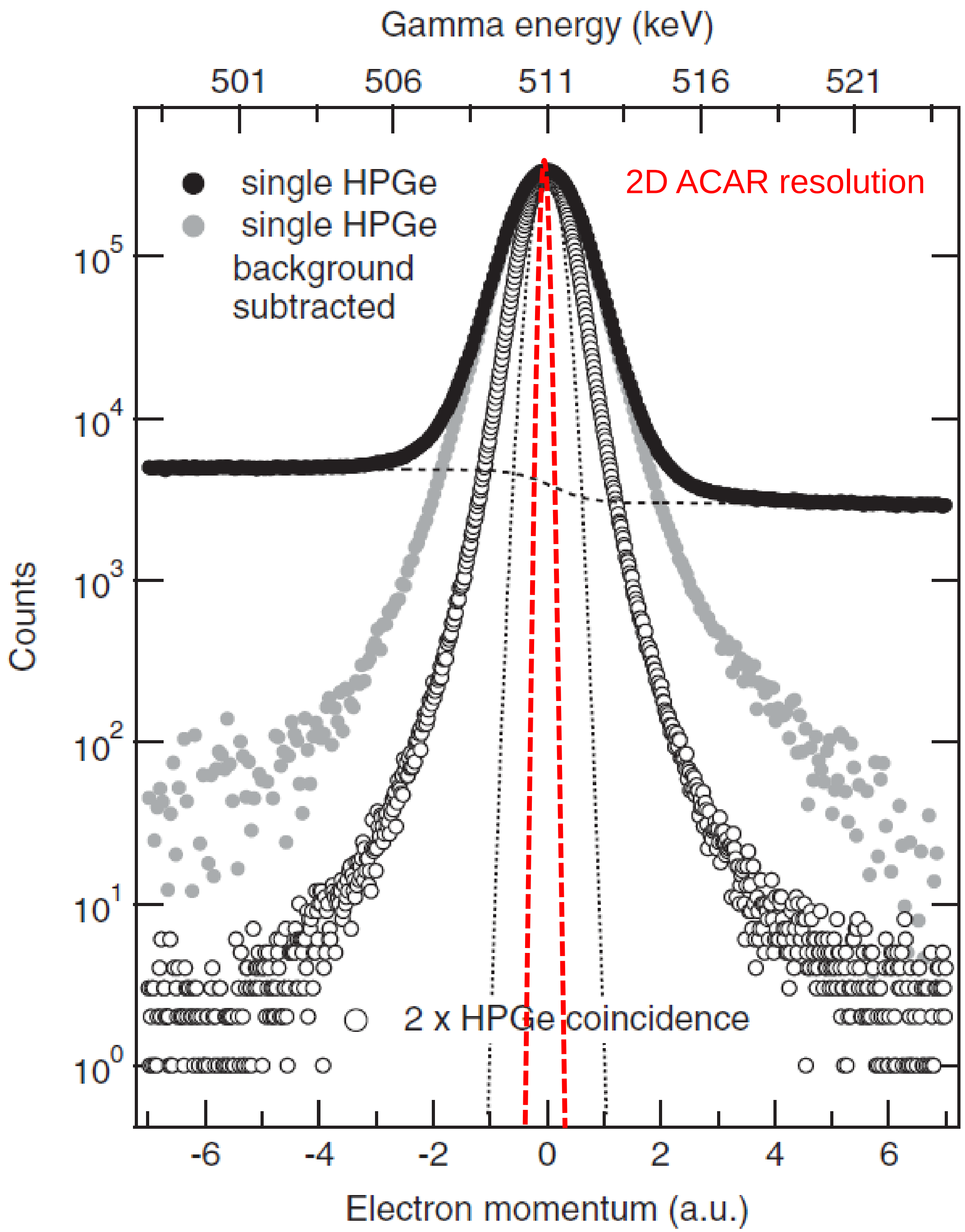
DOPPLER BROADENING EXPERIMENT

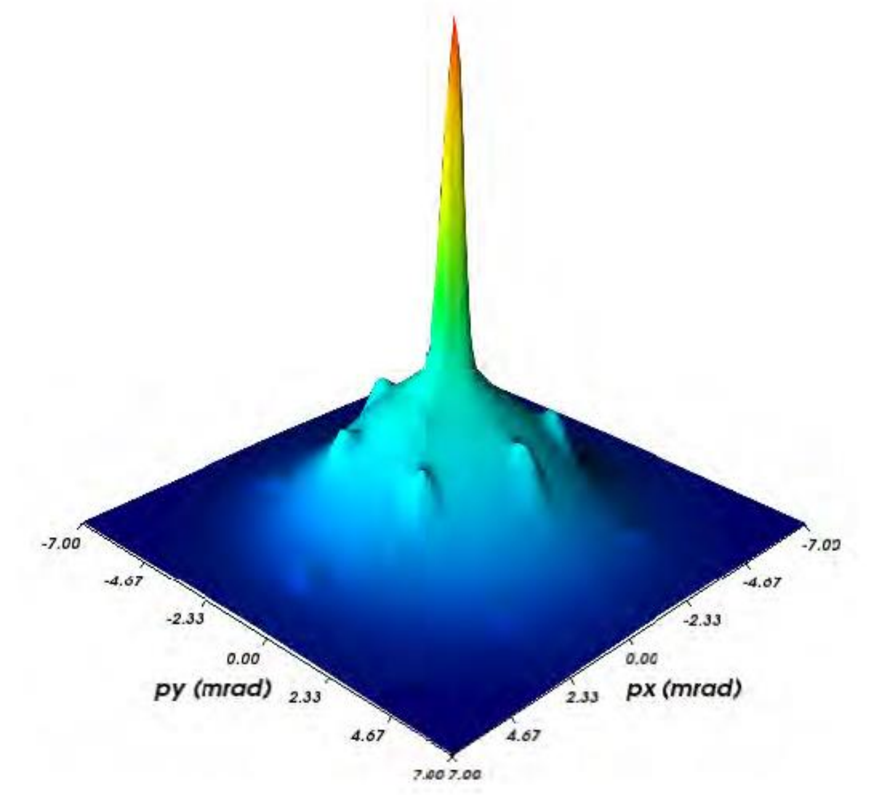






2D ACAR VS. DOPPLER





c. Surface plot of the 2D-ACAR spectrum for α-quartz.

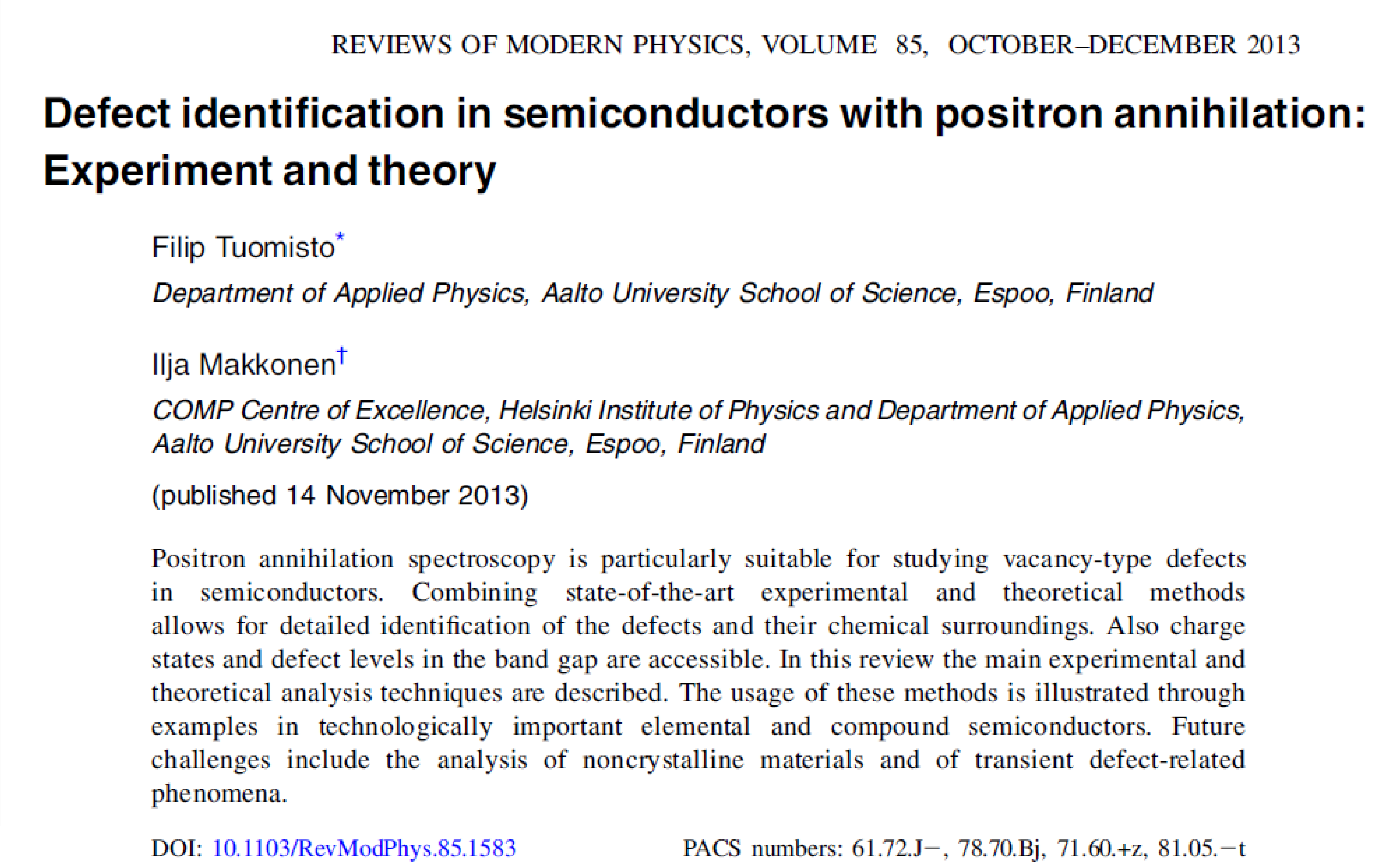
Hubert Ceeh, PhD thesis, TUM, 2015

DOPPLER VS. ACAR

- Doppler: resolution not that good, but **sufficient for defect studies**. HPGe detectors have high efficiency and can be placed close to the samples → **high count rates**, allows ”scanning”

- ACAR: **excellent resolution**, **allows for, e.g., Fermi surface mapping** in metals (also spin-dependence). Count rates low – traditional trade-off between resolution and count rate

IF YOU HAVE TROUBLE FALLING ASLEEP AT NIGHT…



REVIEWS OF MODERN PHYSICS, VOLUME 85, OCTOBER–DECEMBER 2013

Defect identification in semiconductors with positron annihilation: Experiment and theory

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(published 14 November 2013)

Positron annihilation spectroscopy is particularly suitable for studying vacancy-type defects in semiconductors. Combining state-of-the-art experimental and theoretical methods allows for detailed identification of the defects and their chemical surroundings. Also charge states and defect levels in the band gap are accessible. In this review the main experimental and theoretical analysis techniques are described. The usage of these methods is illustrated through examples in technologically important elemental and compound semiconductors. Future challenges include the analysis of noncrystalline materials and of transient defect-related phenomena.

DOI: 10.1103/RevModPhys.85.1583 PACS numbers: 61.72.J−, 78.70.Bj, 71.60.+z, 81.05.−t

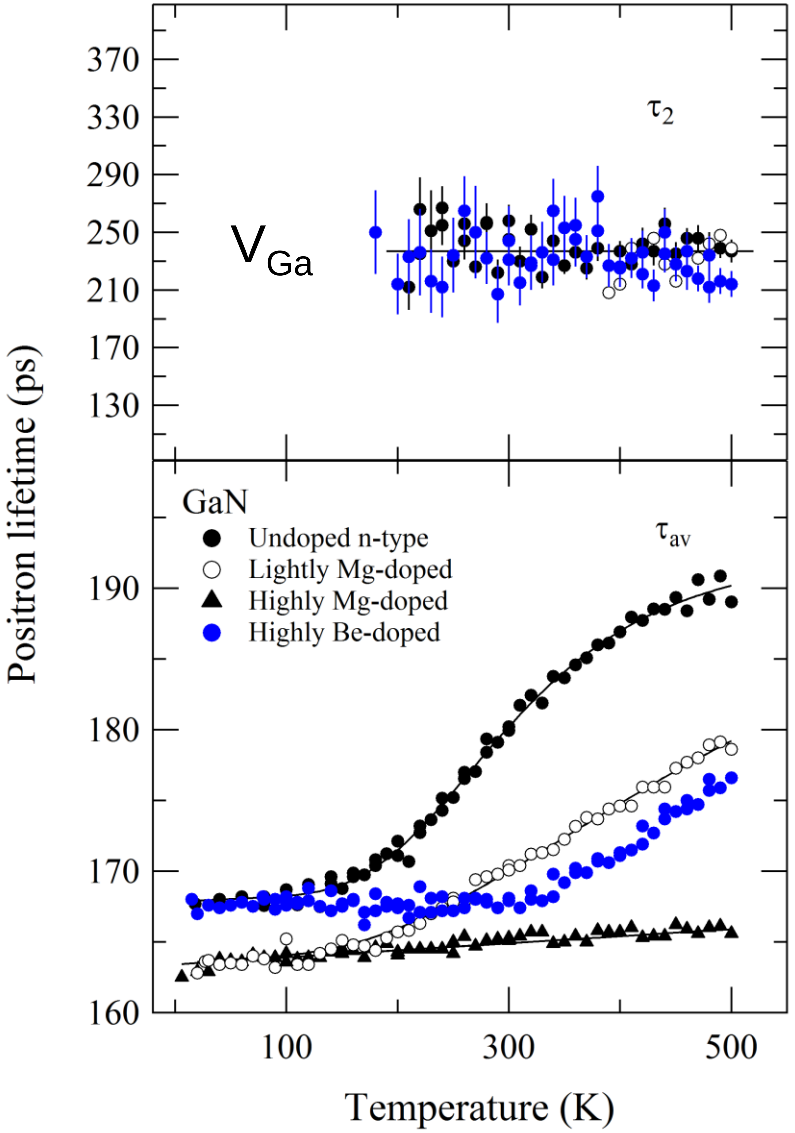
EXAMPLES

ELECTRICAL COMPENSATION IN GaN

HNP grown single crystals of GaN

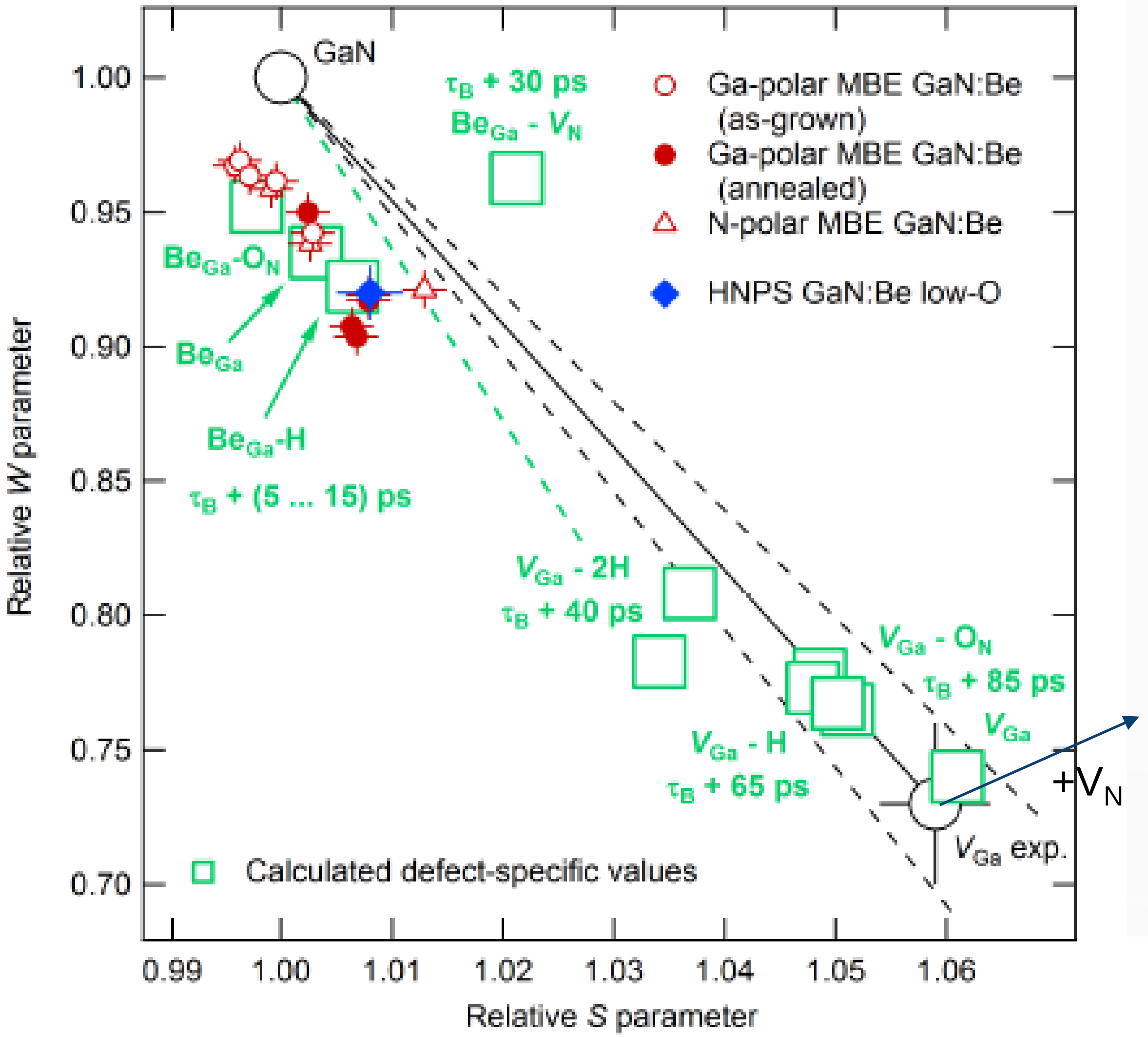
- O content ~10^{19} cm^{-3}, n-type (O is a donor)
- Mg content ~10^{17} cm^{-3} in undoped
  - Lightly doped: ~10^{19} cm^{-3}
  - Highly doped: ~10^{20} cm^{-3}
- Fitting of the T-dependent trapping model (undoped):
  - Negative Ga vacancies 7 × 10^{16} cm^{-3}
  - Negative ions 3 × 10^{17} cm^{-3} (E_b = 70 meV)

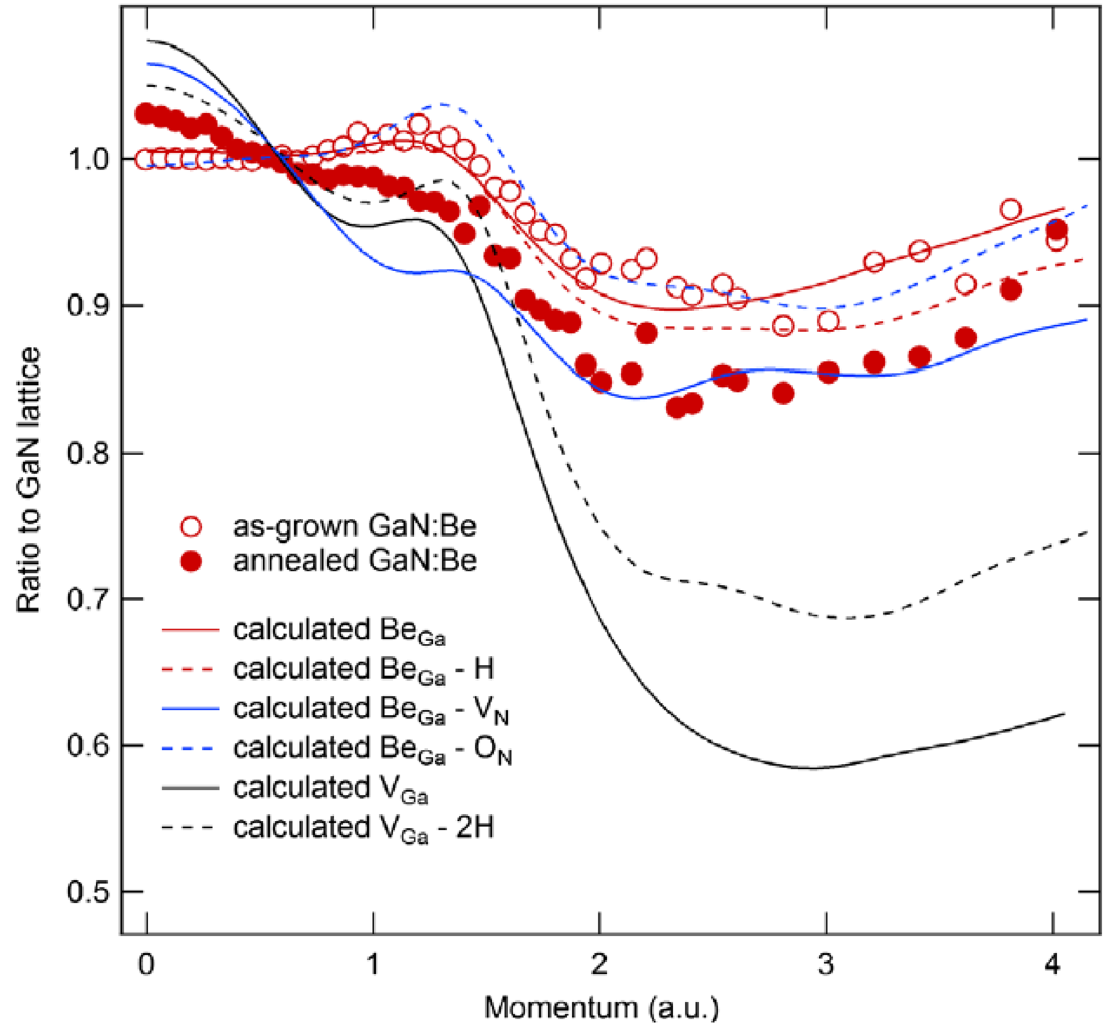
[dozens of studies]



[F. Tuomisto *et al.*, Phys. Rev. Lett. **119**, 196404 (2017)]

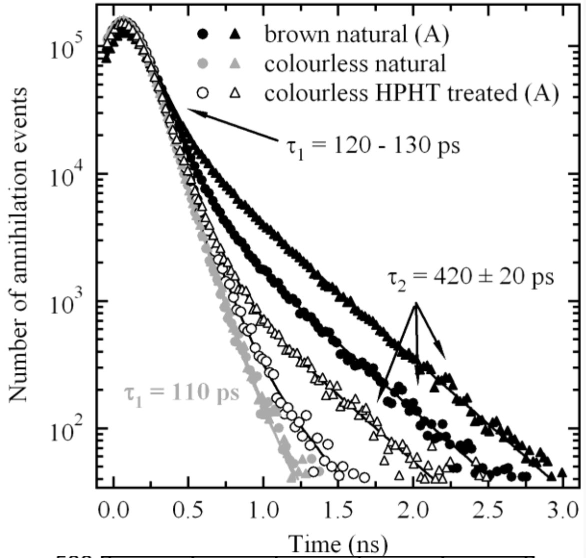
GaN: vacancies and Be_{Ga}

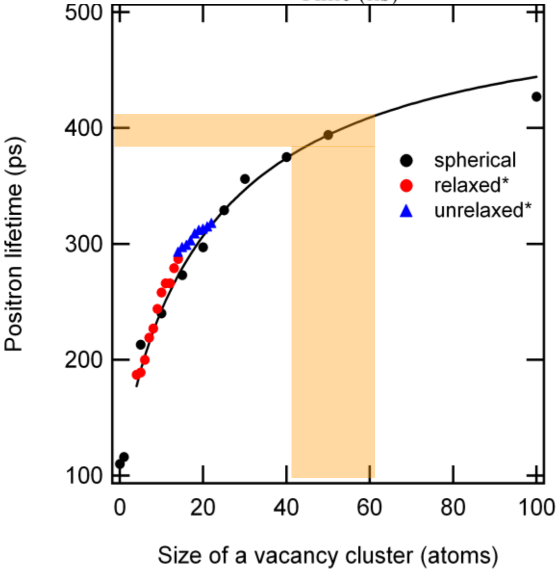


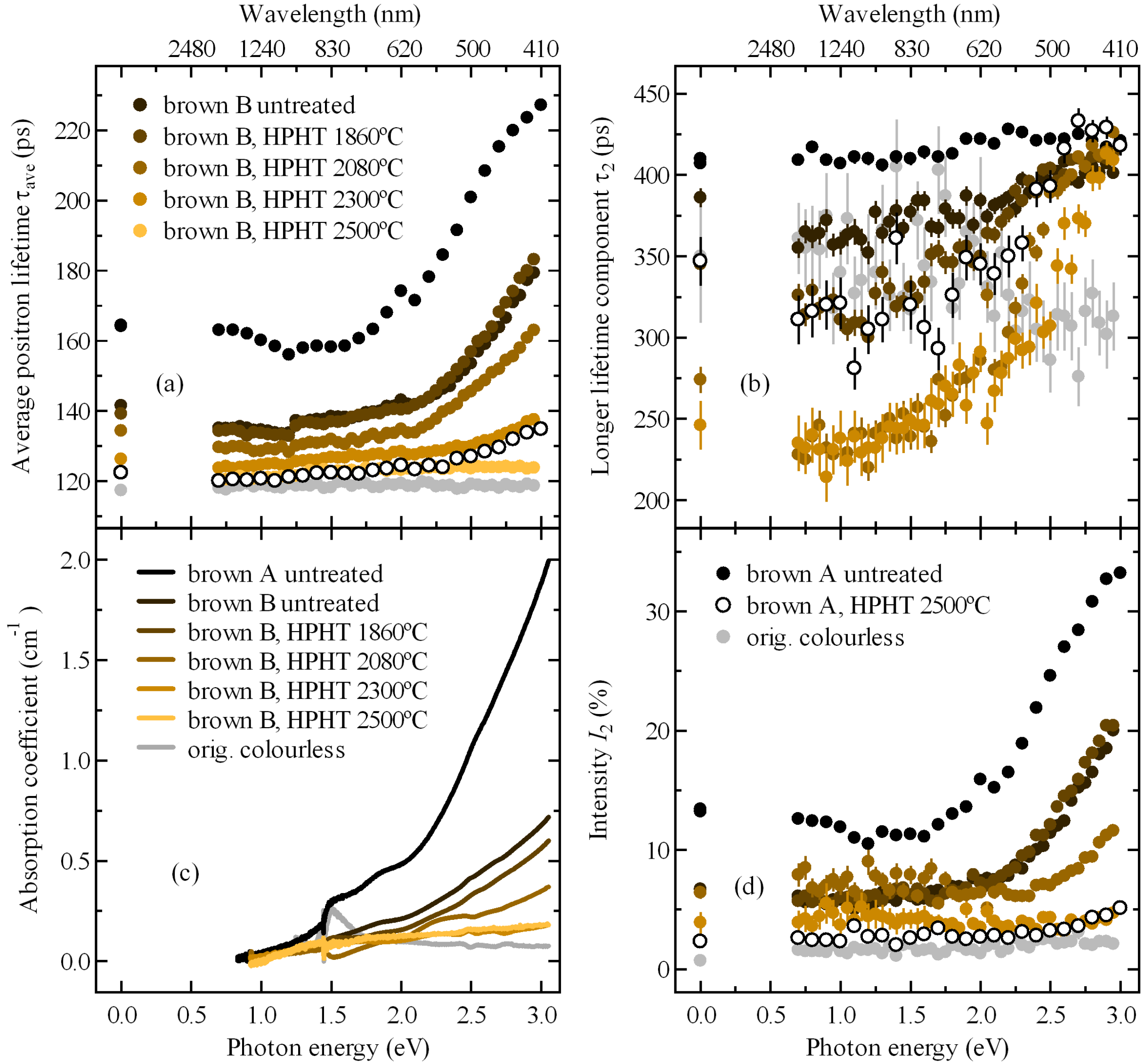


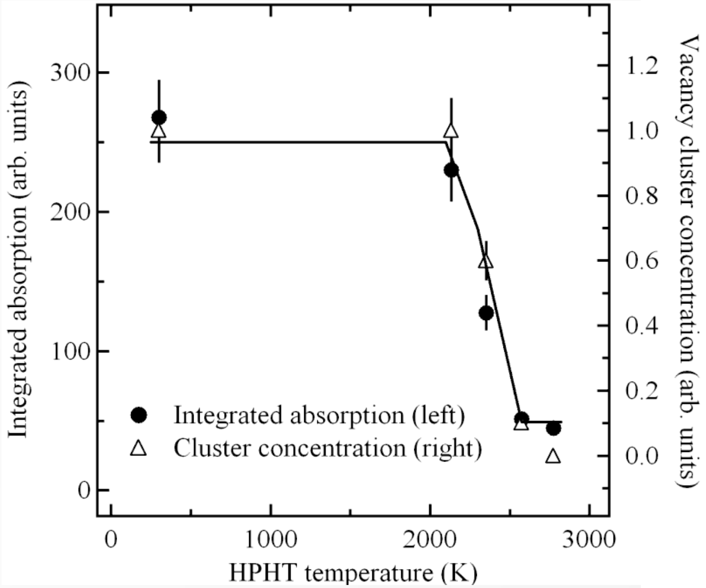
[J.-M. Mäki et al., JPCM **21**, 364216 (2009)]

TYPE IIA NATURAL DIAMOND



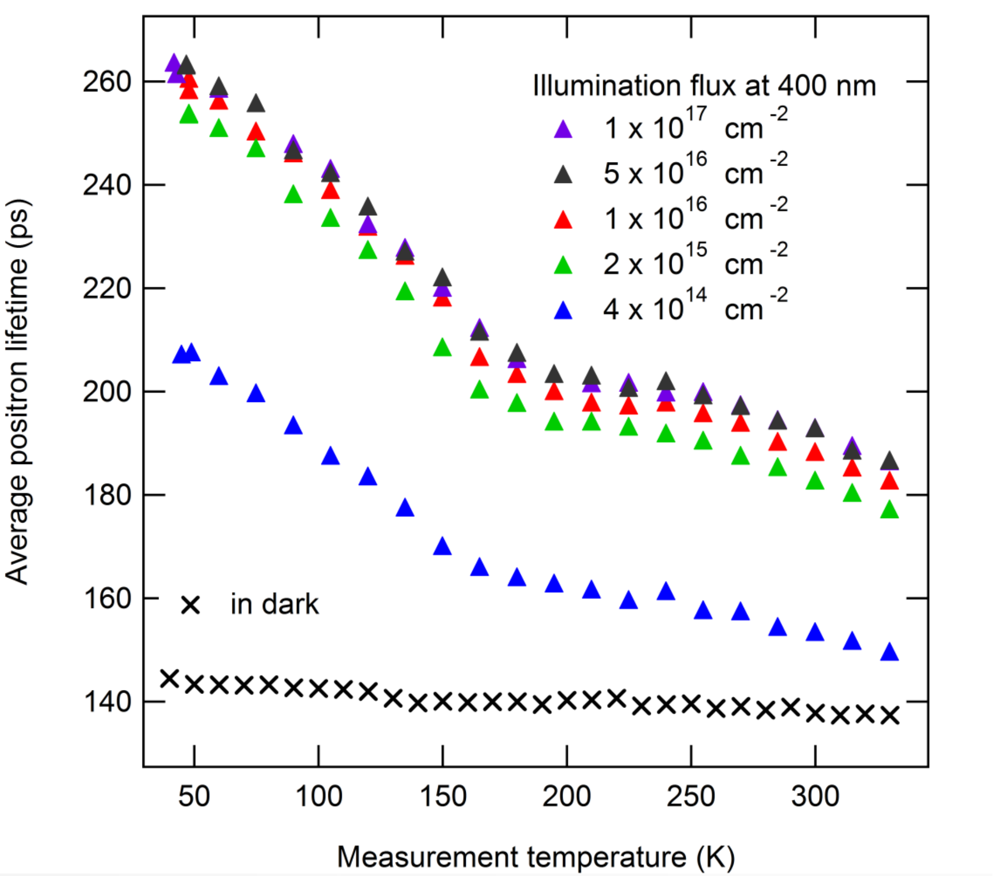


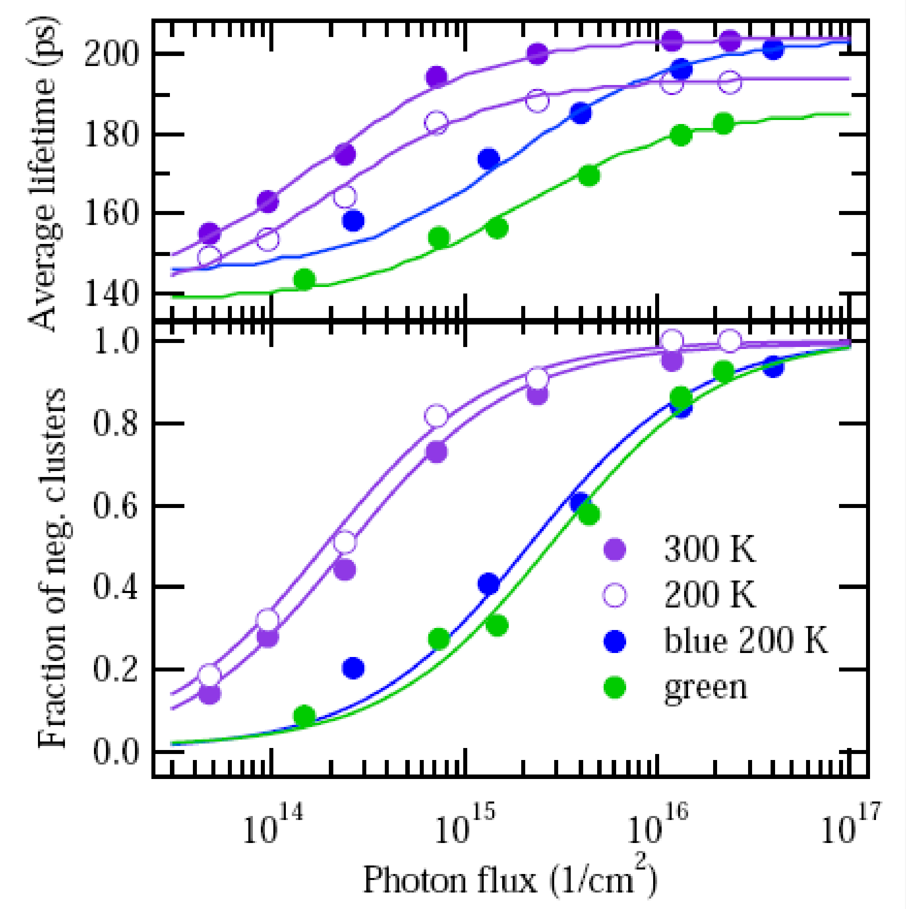




[J.-M. Mäki et al., PRL **107**, 217403 (2011)]

ILLUMINATION POWER DEPENDENCE

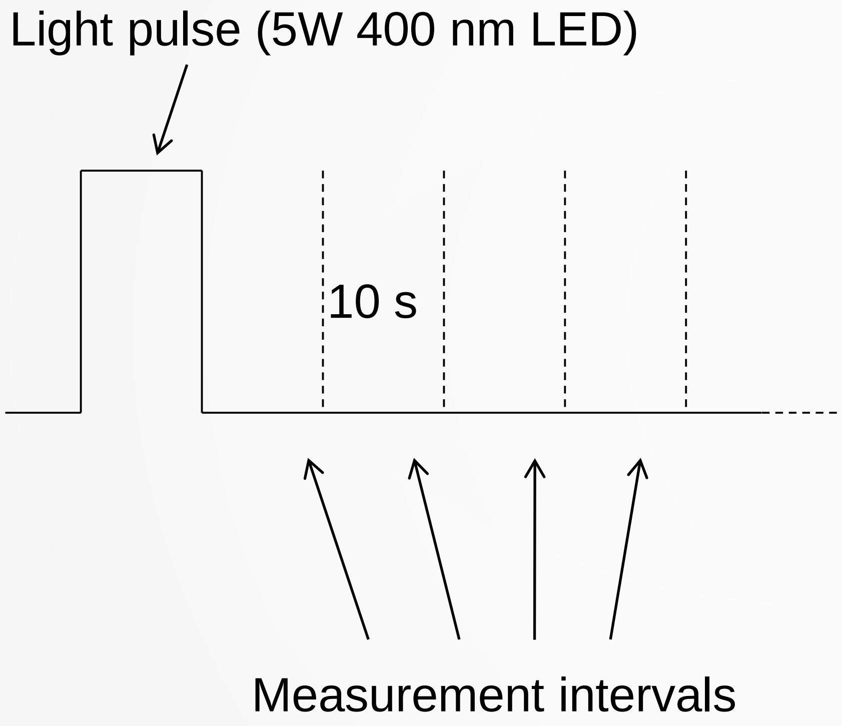




Important: Fraction of negative clusters directly from experimental data

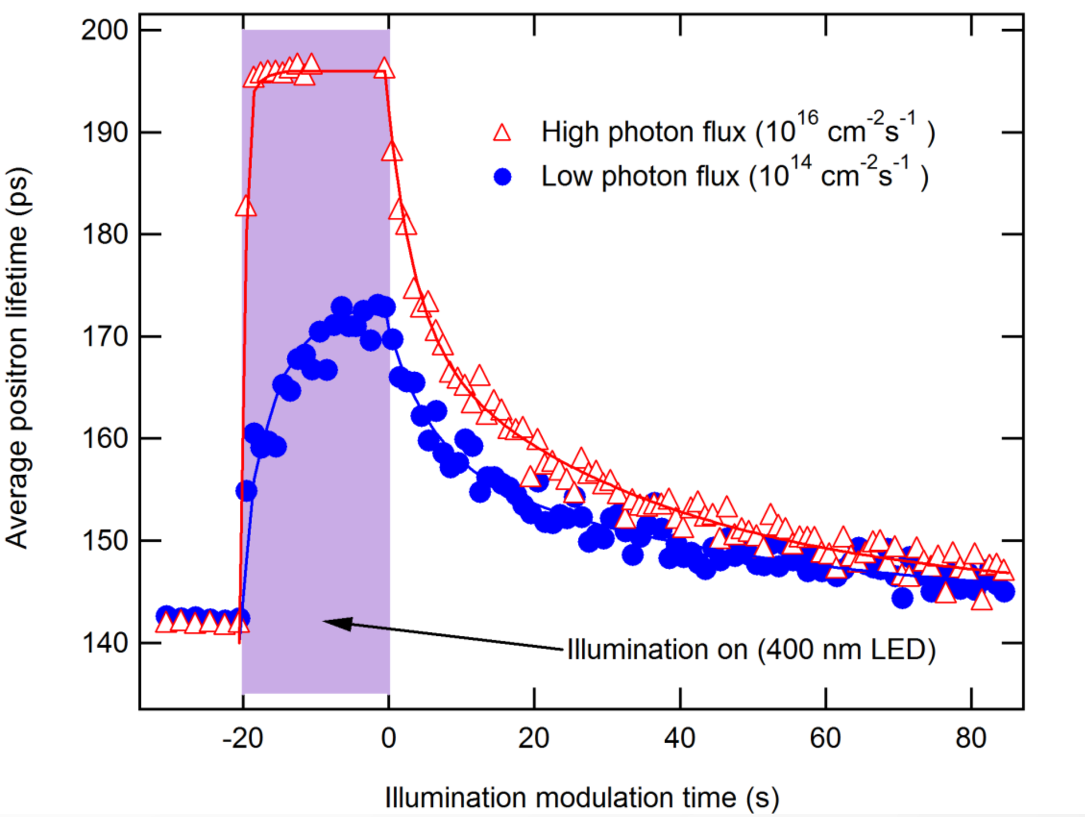
$$\frac{[V^-]}{[V^0_{\text{dark}}]} = \frac{I_2/I_1 - (I_2/I_1)^0}{(I_2/I_1)^- - (I_2/I_1)^0}$$

OPTICAL TRANSIENT POSITRON SPECTROSCOPY!


Light pulse (5W 400 nm LED)

10 s

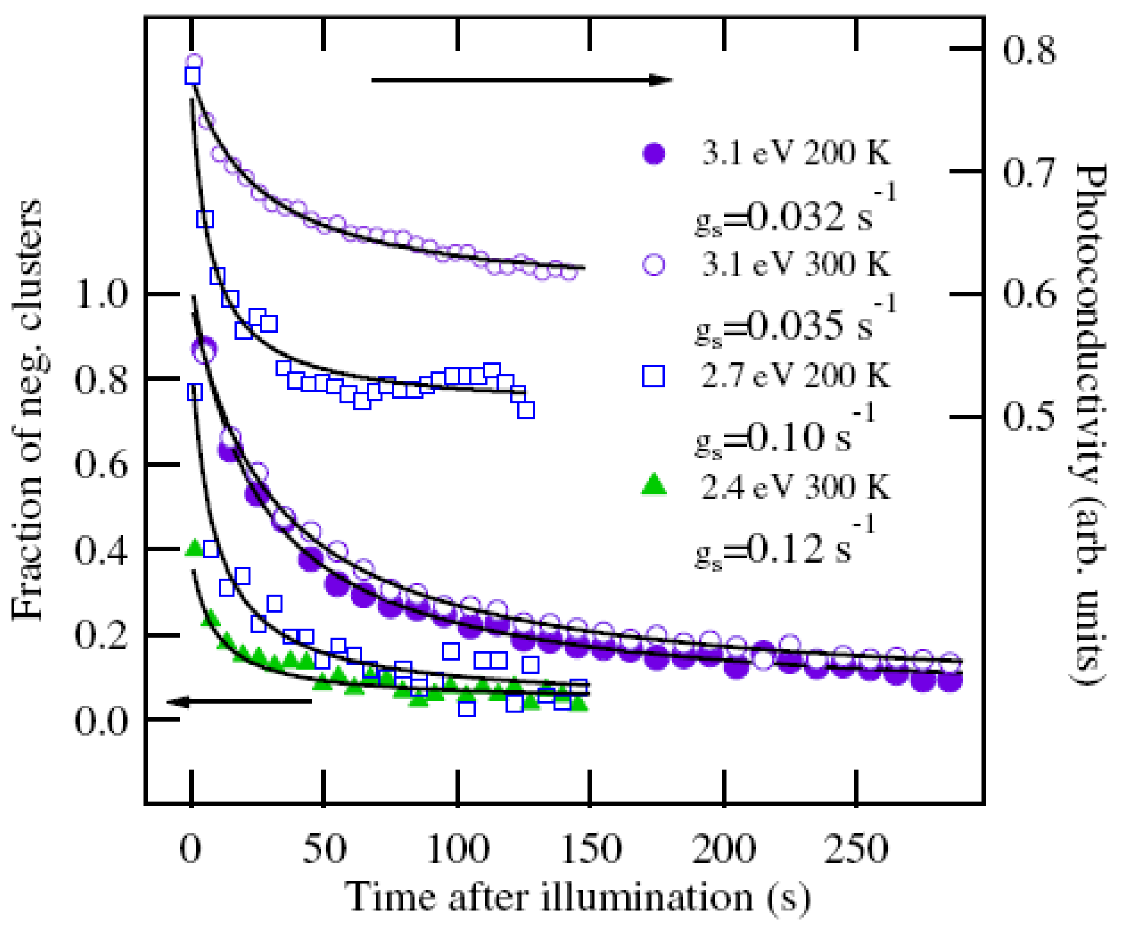
Measurement intervals



Benefits: optical constants of identified defects, self-consistent defect density determination (positron trapping coefficient not needed)

[J.-M. Mäki et al., PRL **107**, 217403 (2011)]
[J.-M. Mäki et al., NJP **14**, 035023 (2012)]

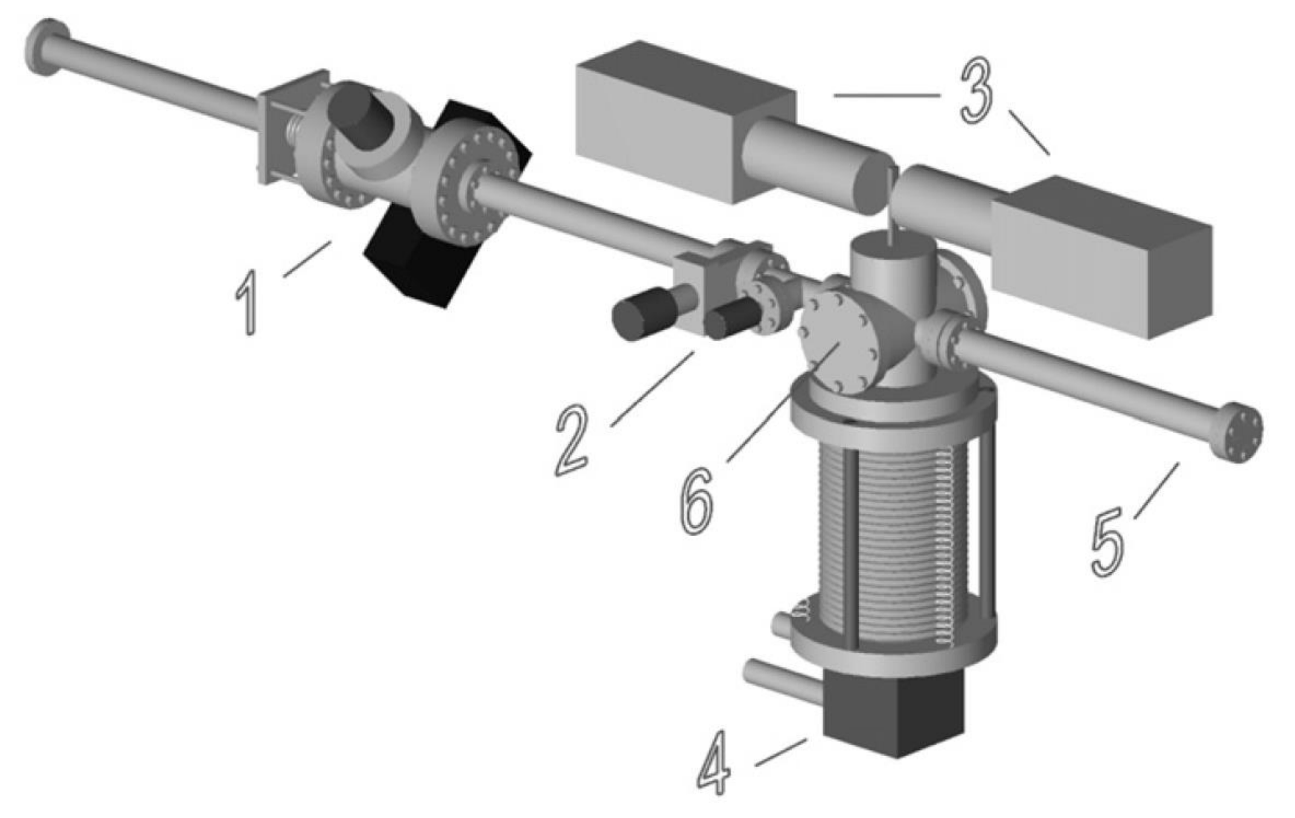
PHOTOCONDUCTIVITY?



The free holes created by illumination by the same wavelengths disappear at the same rate as the negative charge leaves the vacancy clusters!

FREEZE-IN OF RADIATION DAMAGE

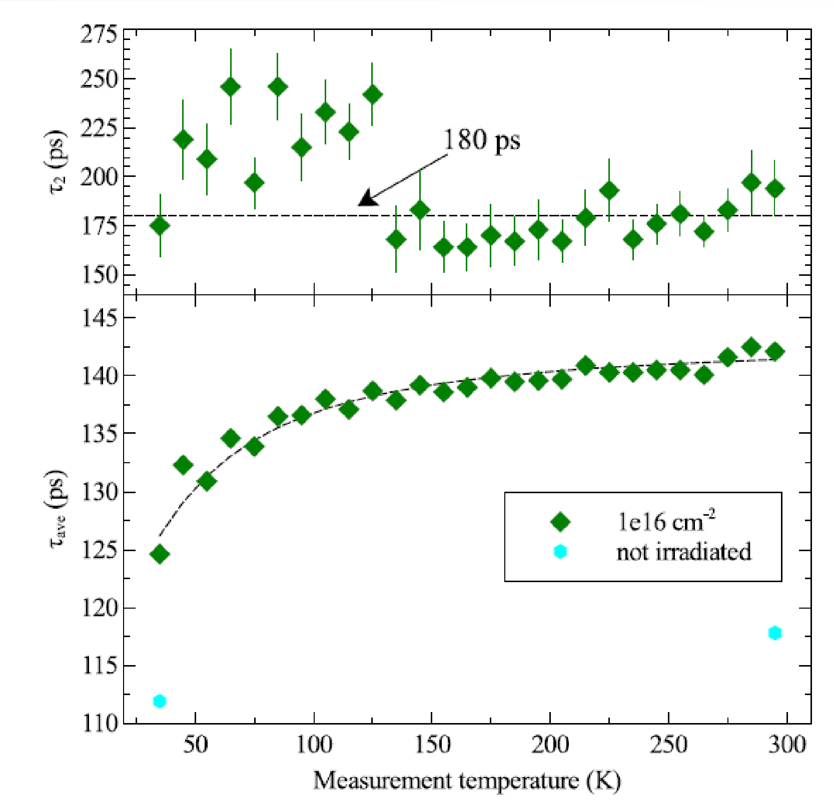
[S. Väyrynen et al., NIMA **572**, 978 (2007)]



- ion irradiation (e.g., 10 MeV protons) at low T (down to ~10 K)
- in situ positron lifetime experiments
- heating up to RT

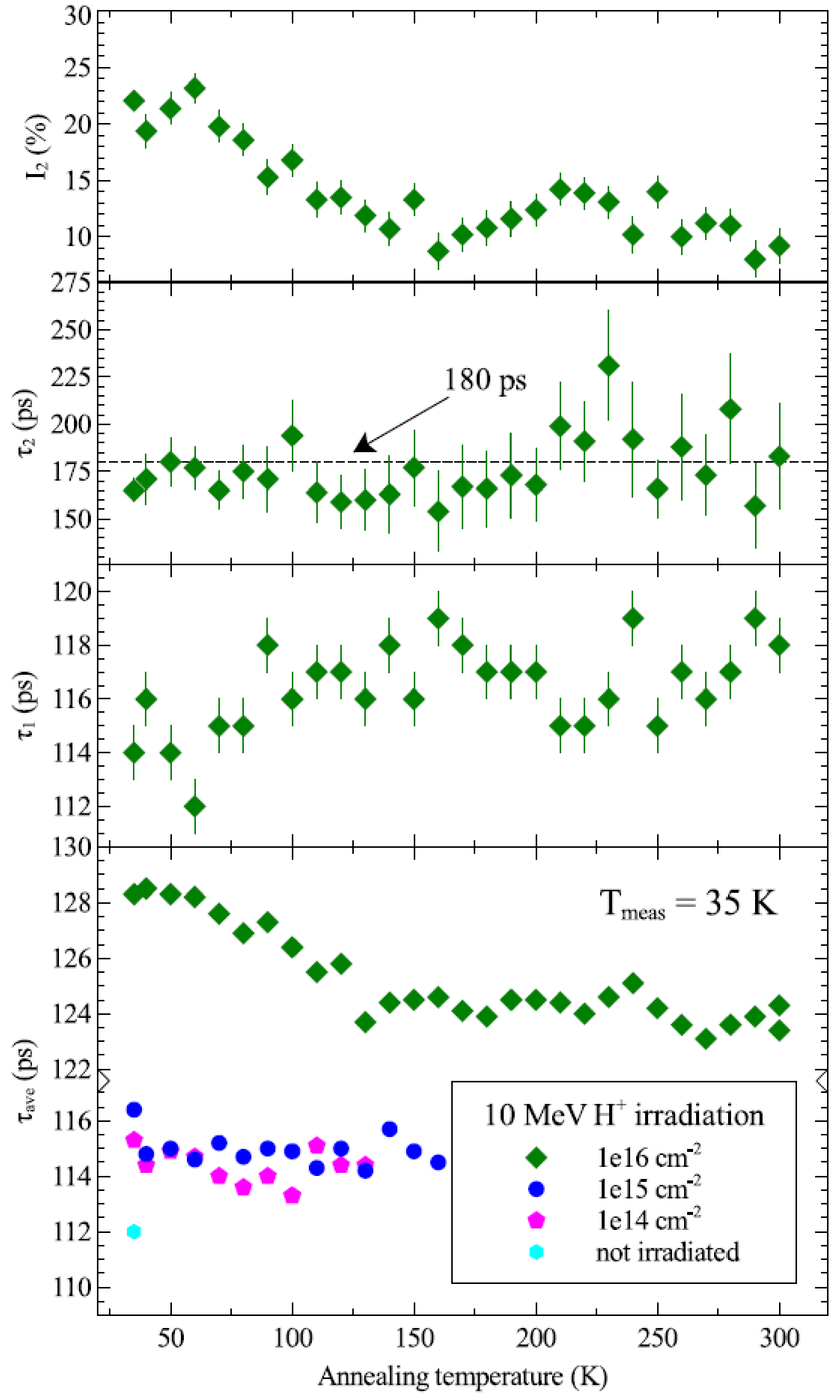
TUNGSTEN

[J. Heikinheimo et al., APL Mater. 7, 021103 (2019)]



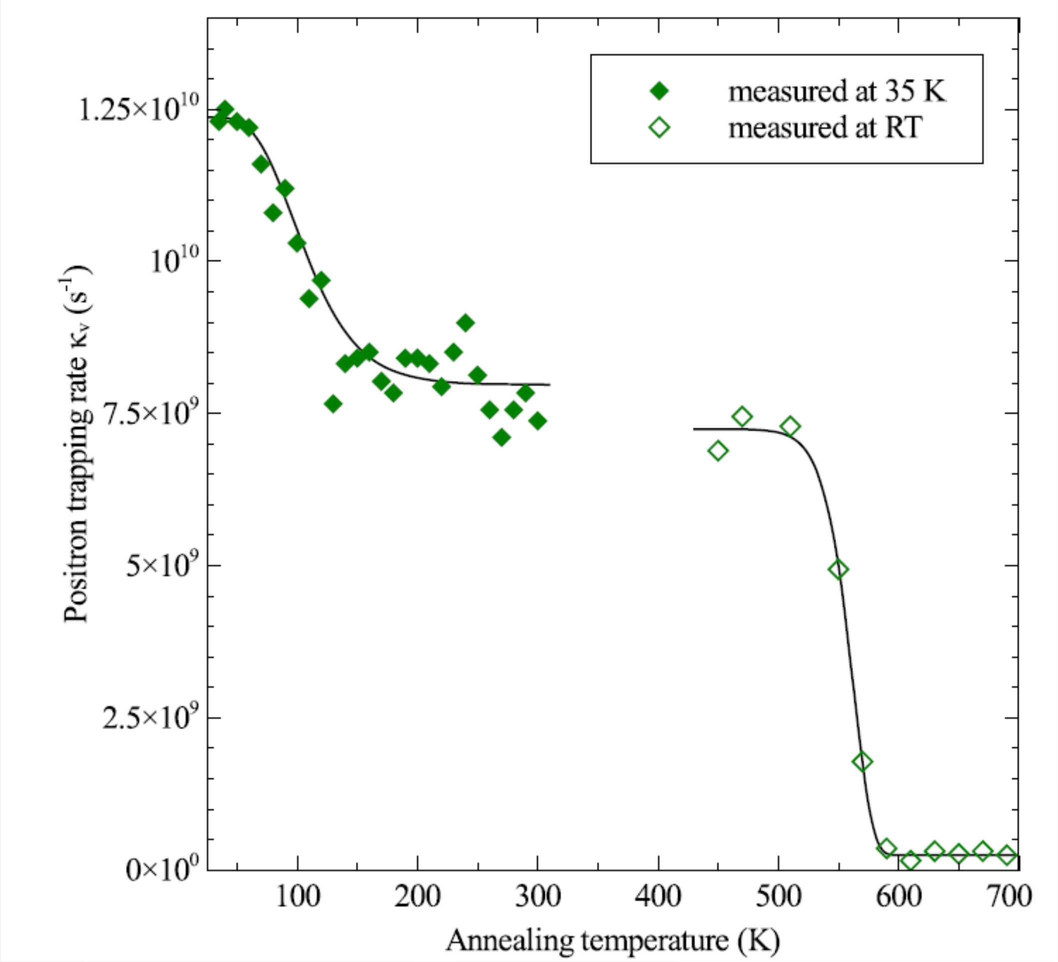
180 ps: monovacancies

T behavior (left): dislocations (not a surprise)



DAMAGE RECOVERY

[J. Heikinheimo et al., APL Mater. 7, 021103 (2019)]



Vacancy migration barrier: 1.85 ± 0.05 eV

Vacancy production rate: 80 cm^{-1} (SRIM predicts ~1000 cm^{-1})

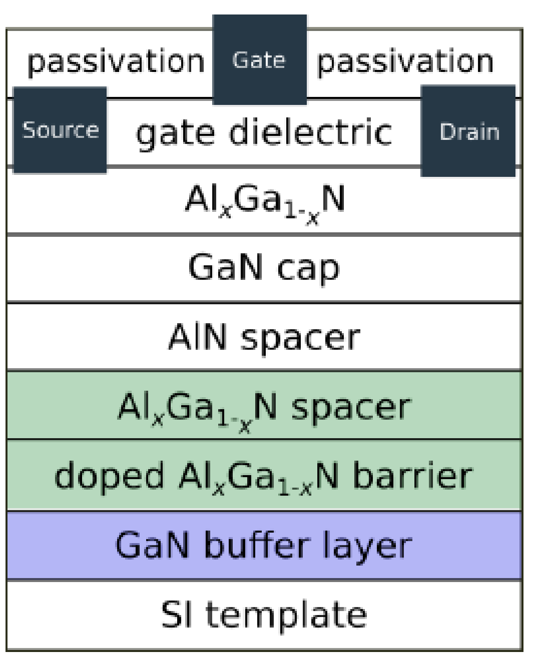
This means very efficient Frenkel pair recombination, placing an upper bound for the SIA migration barrier of 0.1 eV

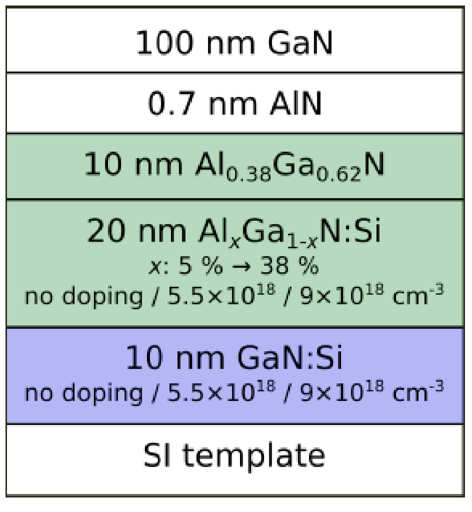
Recovery at 50-100 K: SIA migration through release from impurities and structural defects, activation energies in the range 0.1 – 0.4 eV

INTERFACES?

DEVICES: N-POLAR GaN/AlGaN HEMT-LIKE STRUCTURES

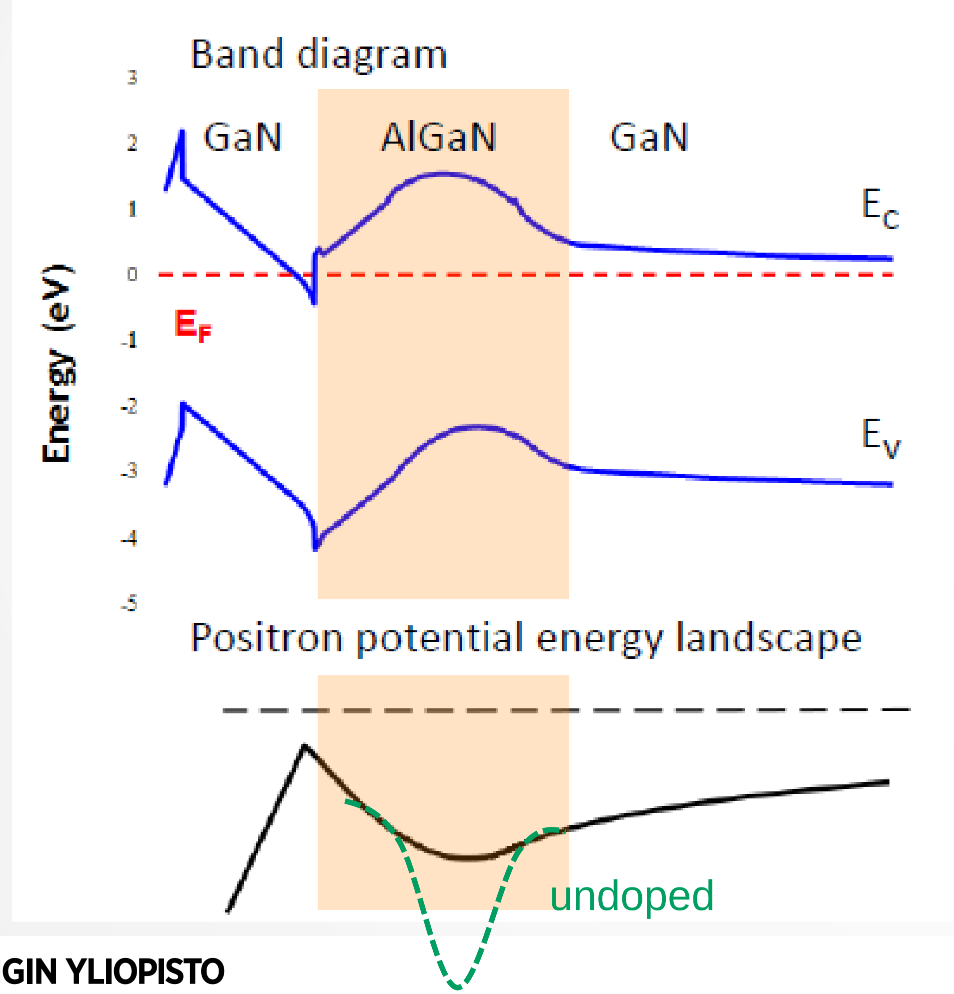
- N-polar GaN/AlGaN high electron mobility transistors
  - This polarity is beneficial for enhancement-mode and highly scaled transistors, and sensors
- A carrier trap forms at the bottom AlGaN/GaN interface and causes current collapse in unoptimized HEMT structure
  - Can be overcome by doping (in addition to grading the Al content of) the AlGaN layer, but what is the nature of this trap?





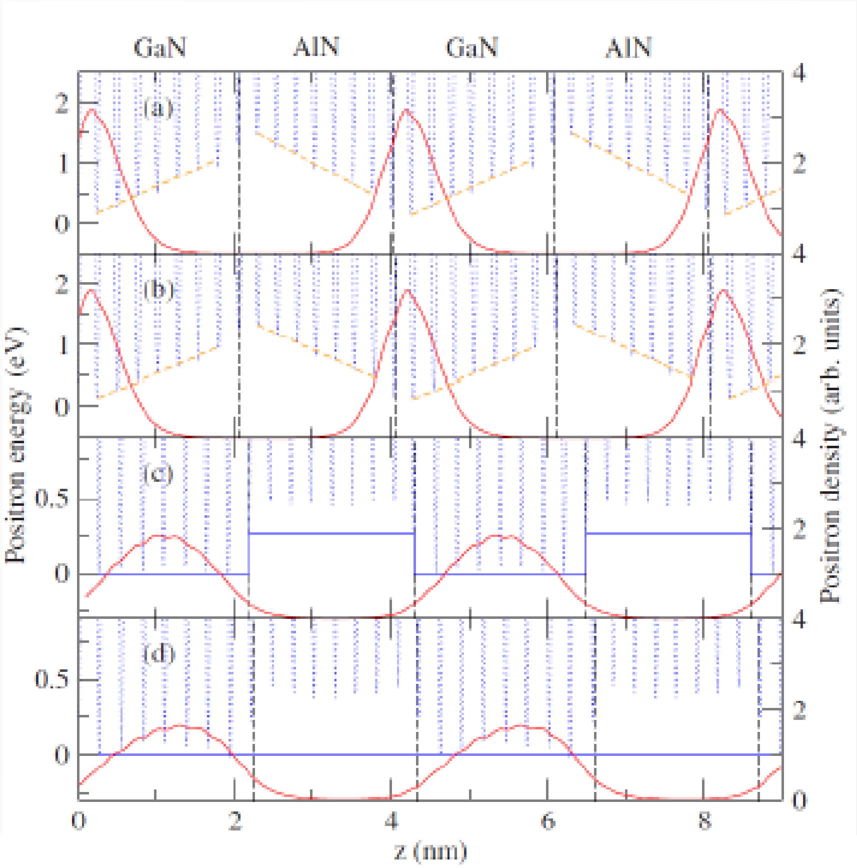
[V. Prozheeva et al., Phys. Rev. Applied **13**, 044034 (2020)]

SHOULD POSITRONS CARE ABOUT THE INTERFACE OF INTEREST?

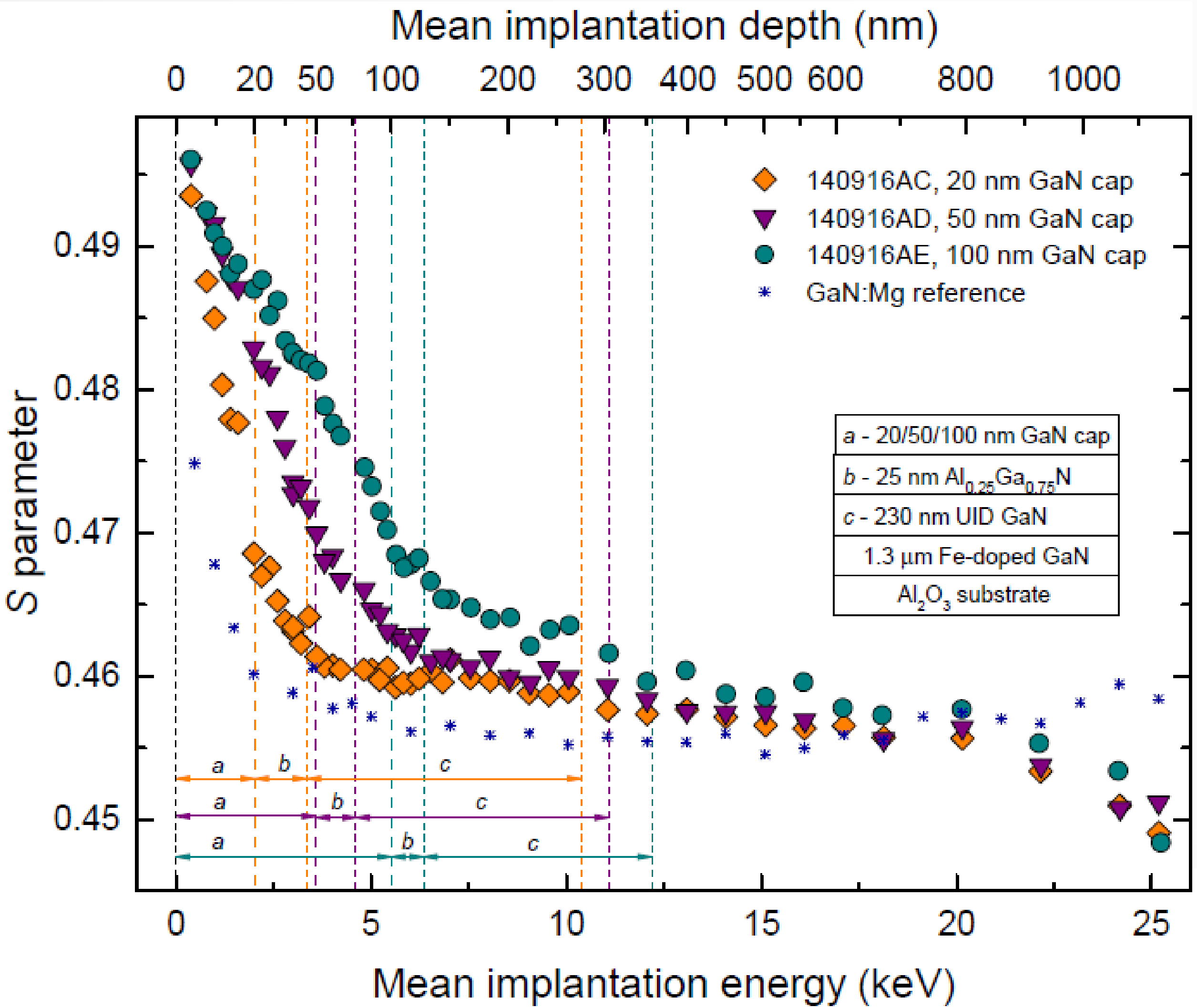


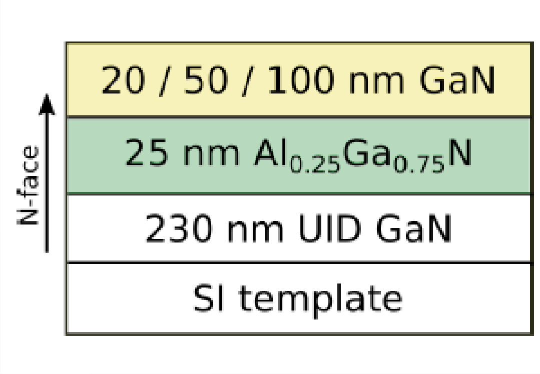
Yes!

[I. Makkonen *et al.*, PRB **82**, 041307 (2010)]



OPTIMIZE THE CAP THICKNESS





N-face

20 / 50 / 100 nm GaN

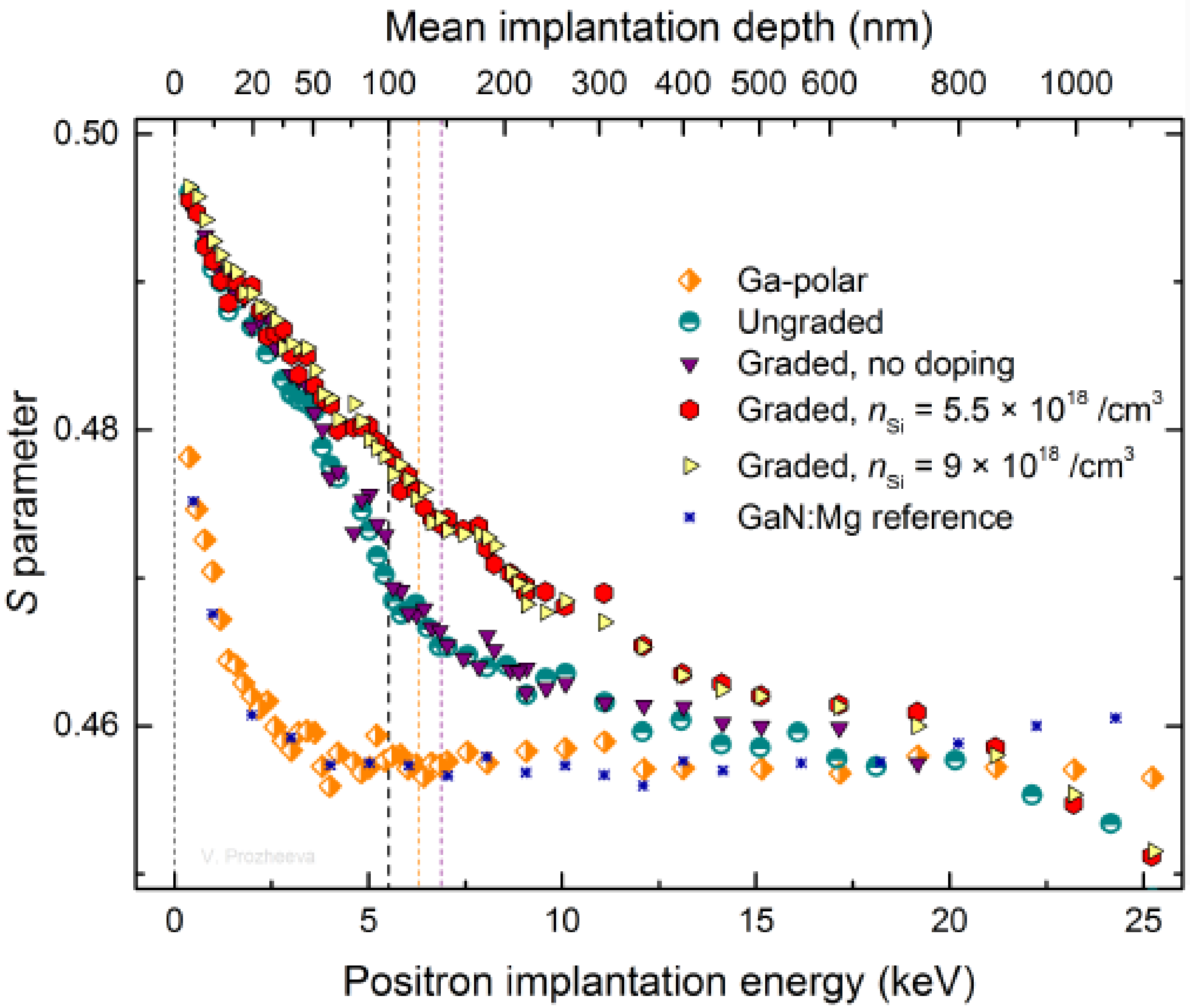
25 nm $Al_{0.25}Ga_{0.75}N$

230 nm UID GaN

SI template

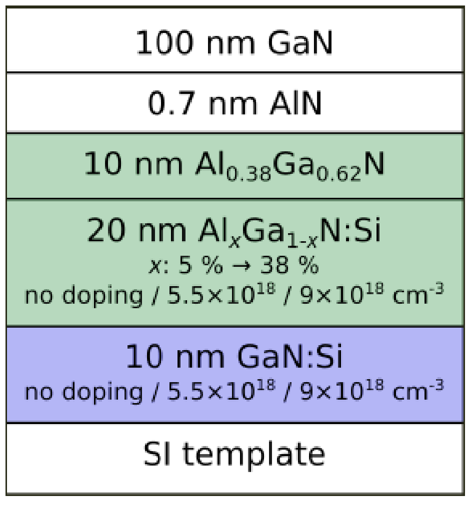
It would seem that with a 100 nm cap it is possible to see some structure in the S-E curve!

N-POLAR HEMT + Ga-POLAR TEST STRUCTURE



Distinct difference between undoped and doped structure!

Ga-polar: nothing is seen, in line with electric fields


100 nm GaN

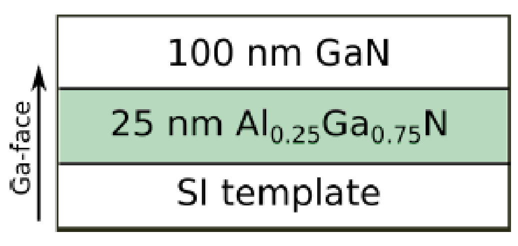
0.7 nm AlN

10 nm $Al_{0.38}Ga_{0.62}N$

20 nm $Al_xGa_{1-x}N:Si$
x: 5 % → 38 %
no doping / 5.5×10^{18} / 9×10^{18} cm^{-3}

10 nm GaN:Si
no doping / 5.5×10^{18} / 9×10^{18} cm^{-3}

SI template

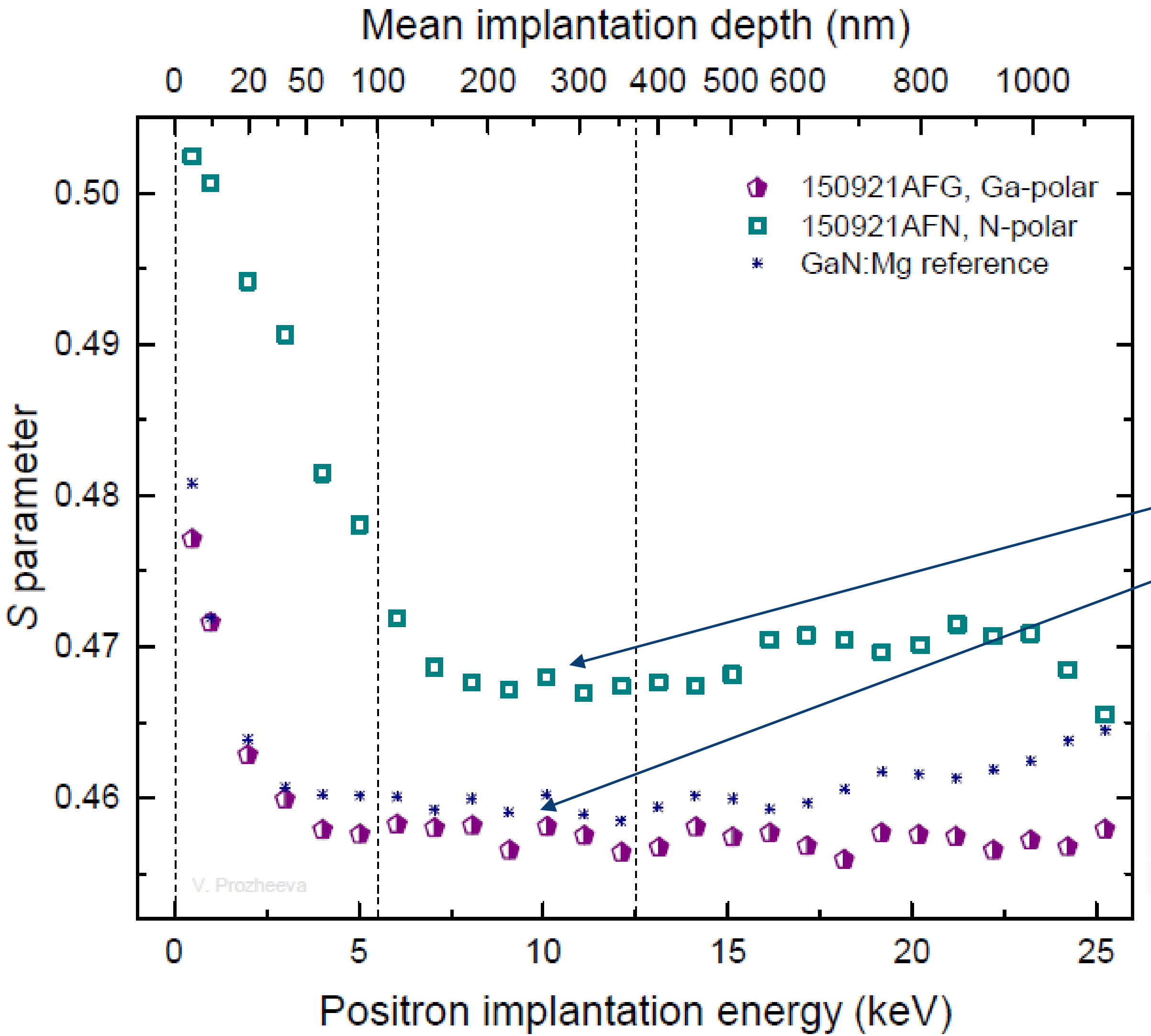


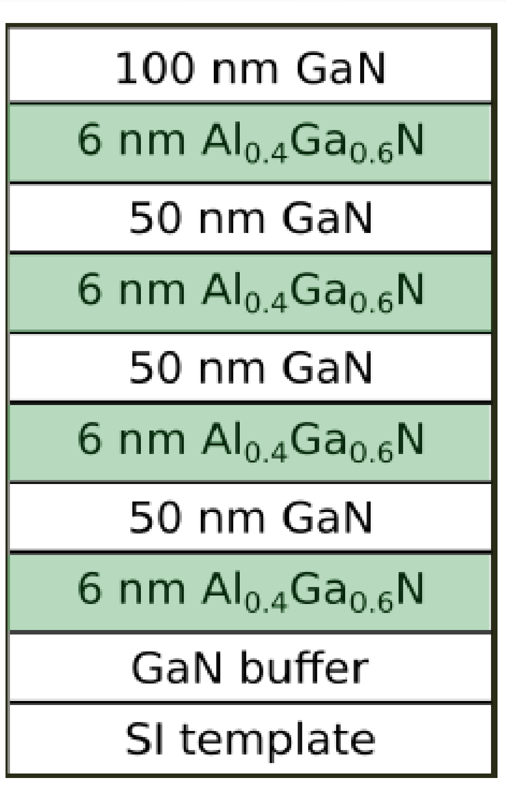
100 nm GaN

25 nm $Al_{0.25}Ga_{0.75}N$

SI template

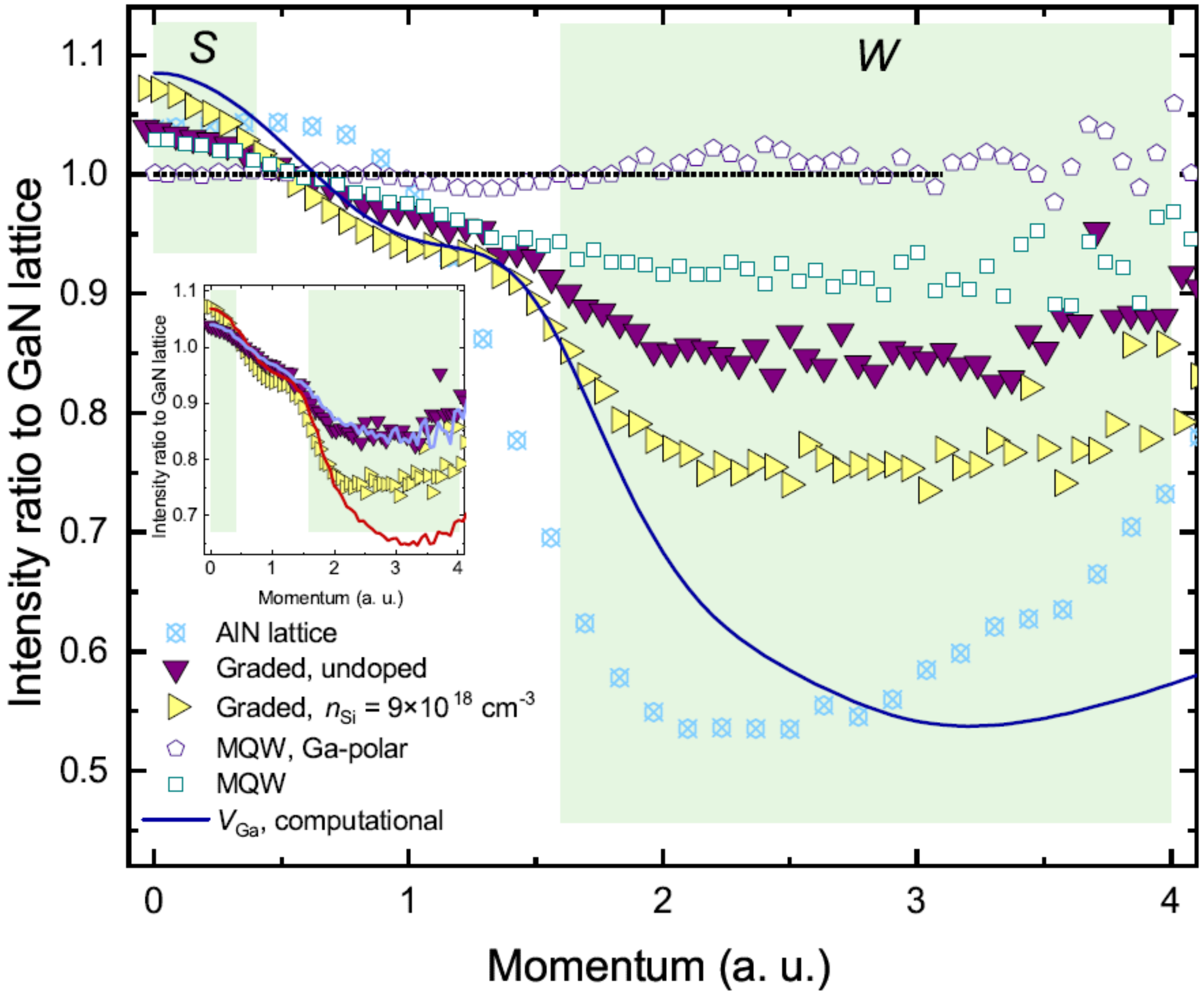
MORE TEST HETEROSTRUCTURES: MQW





AlGaN/GaN bottom interface clearly different from the GaN/AlGaN ”top” interface!

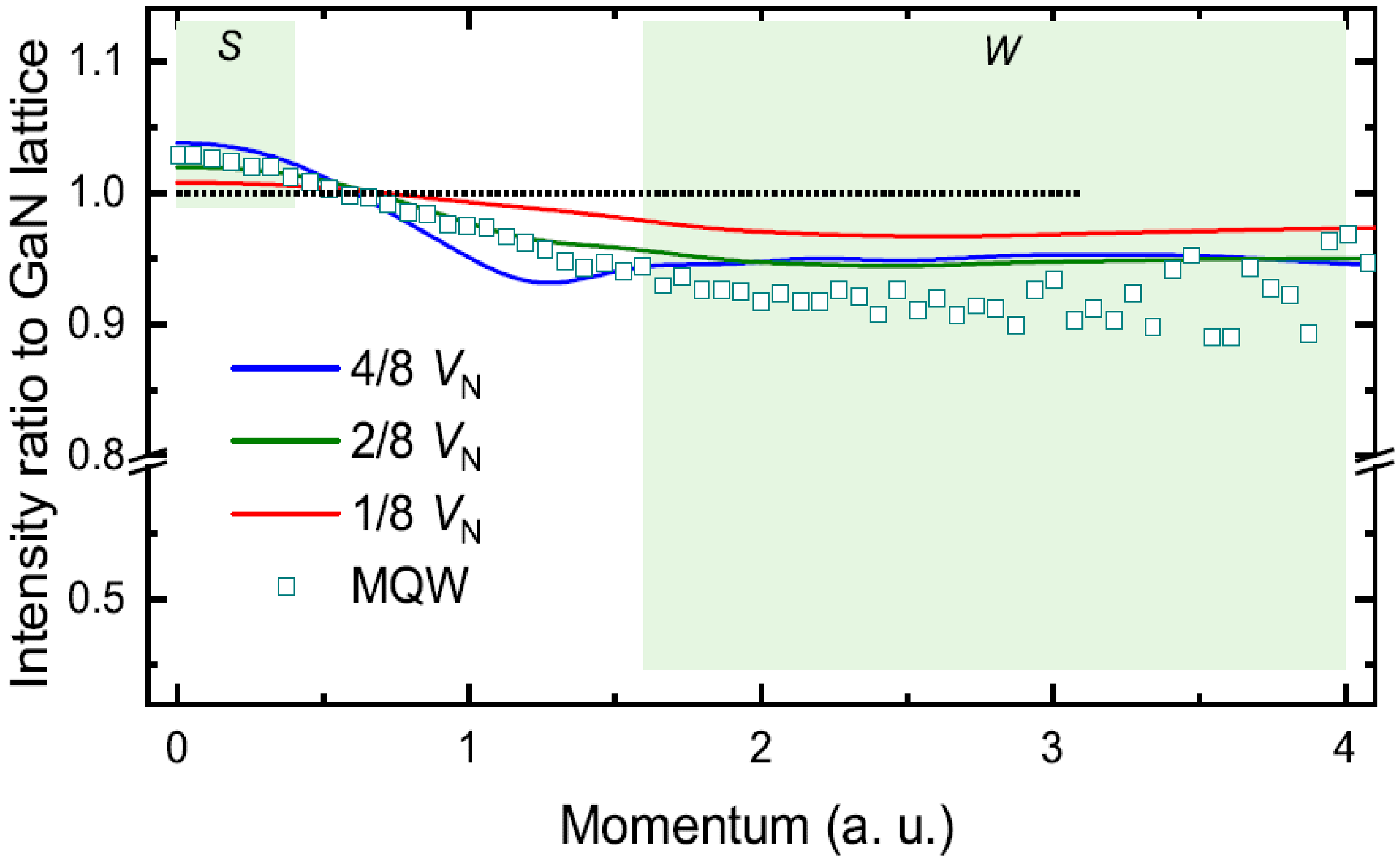
HELP FROM COINCIDENCE DOPPLER?



Data taken from doped and undoped HEMTs at 6-7 keV can be represented (fairly closely) by a linear combination of ”interface” from test structure and V_{Ga}:

in the undoped structure the ”interface” produces 80% of the signal while in the doped only 25-30%.

NATURE OF THE TRAP?



The trap at the interface cannot be an ionized donor – positrons would be repelled. Possibly a neutral donor capable of trapping holes?

”interface” data consistent with N vacancies at the interface!

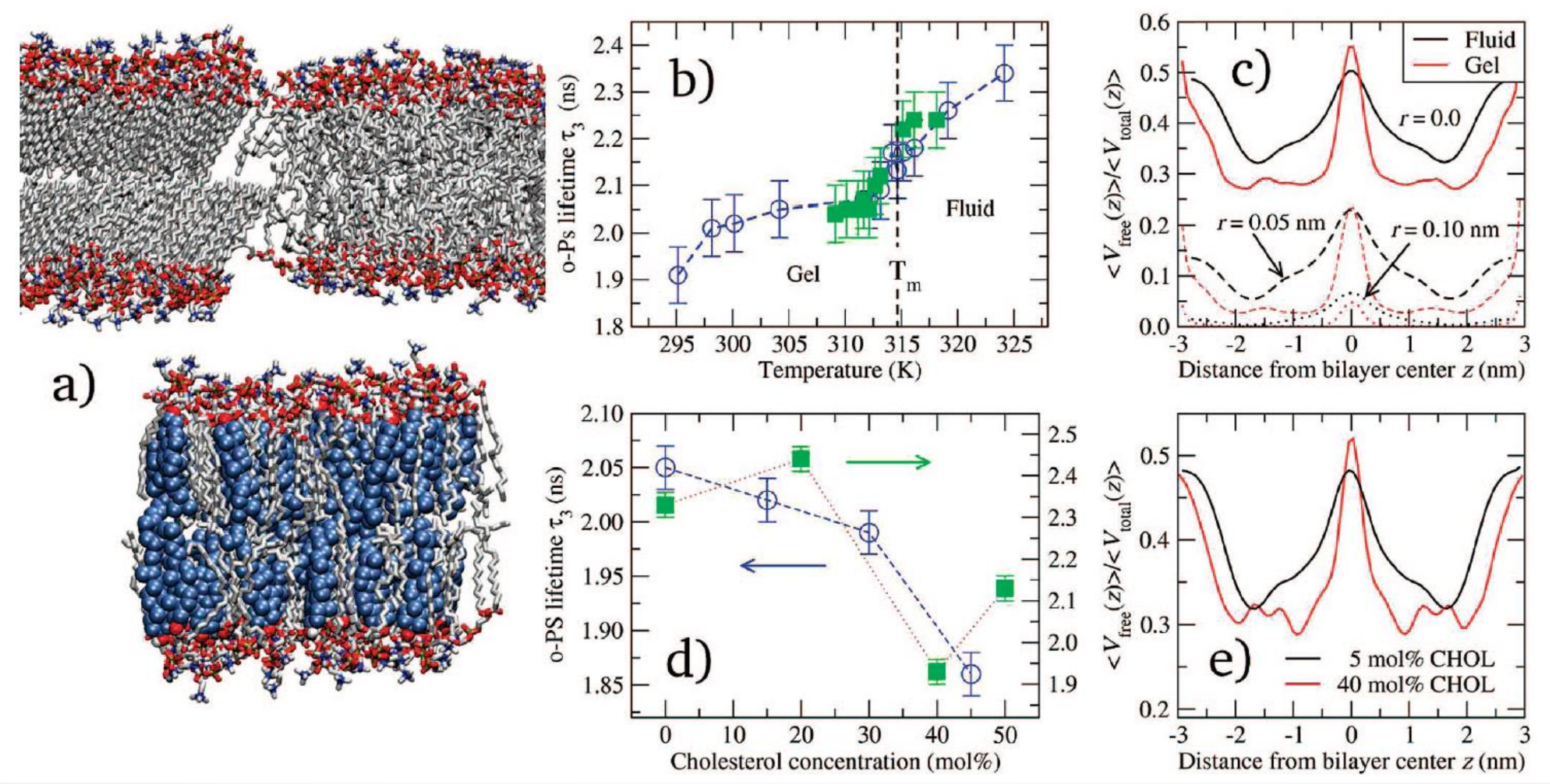
Note that N vacancies will not trap positrons elsewhere in the structure!

Direct observation of N vacancies!

Effect in calculations requires 2 N vacancies at the interface – corresponds to a sheet concentration of about 10^{14} cm^{-2}

Positron and Positronium Chemistry: Eds. Y. C. Jean, P. E. Mallon, and D. M. Schrader, World Scientific 2003

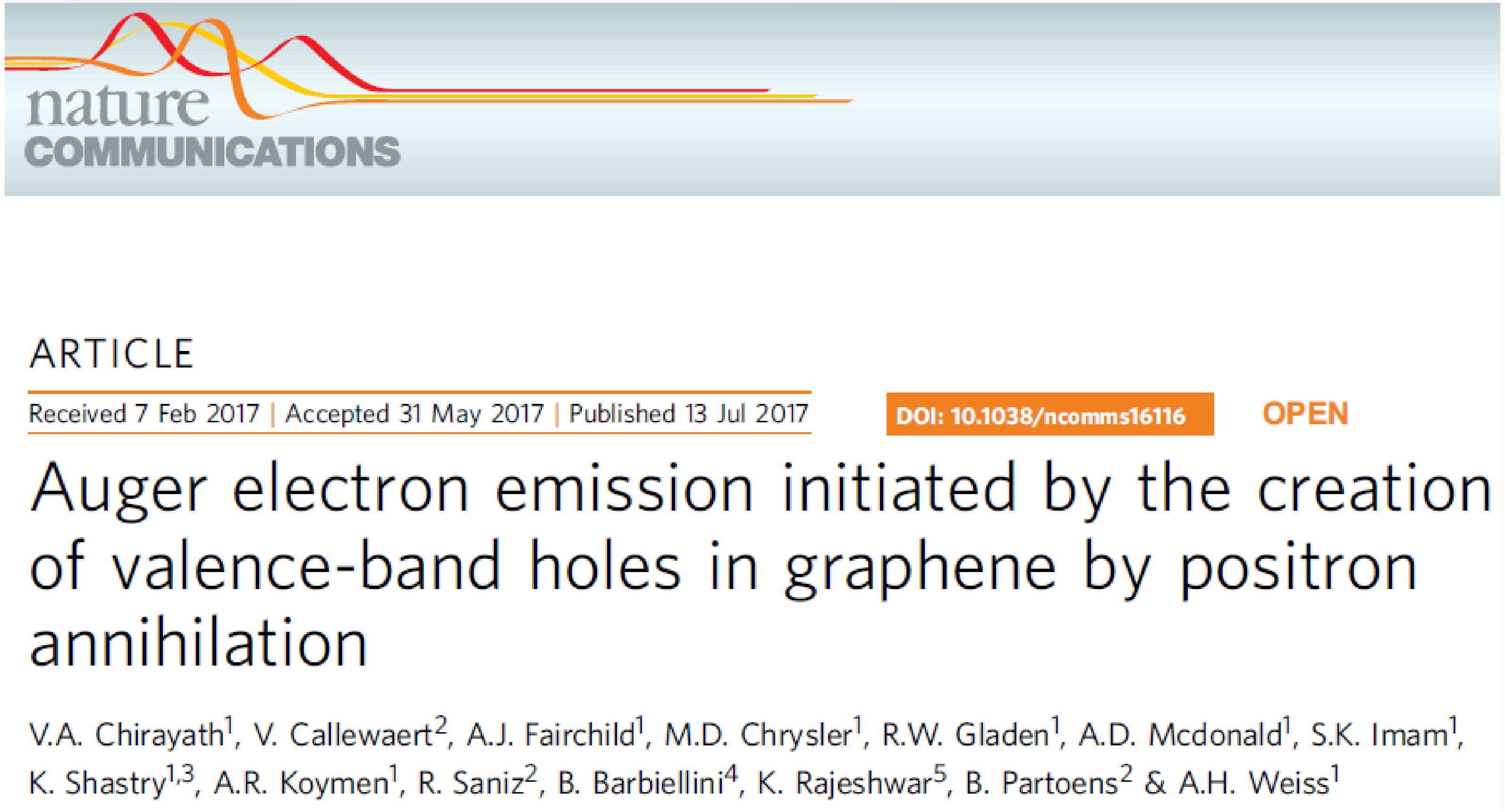
SOFT MATTER: OPEN VOLUME ”POCKETS”



[P. Sane et al., JPCB **114**, 1811 (2009).]

SURFACES?

POSITRONS AT SURFACES: AUGER



nature
COMMUNICATIONS

ARTICLE

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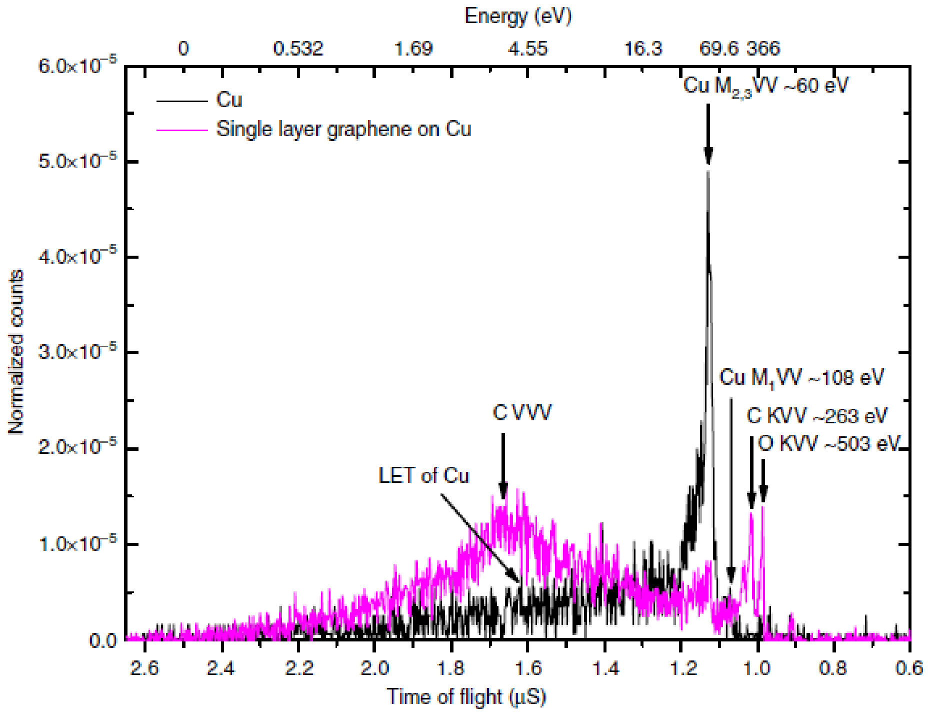
OPEN

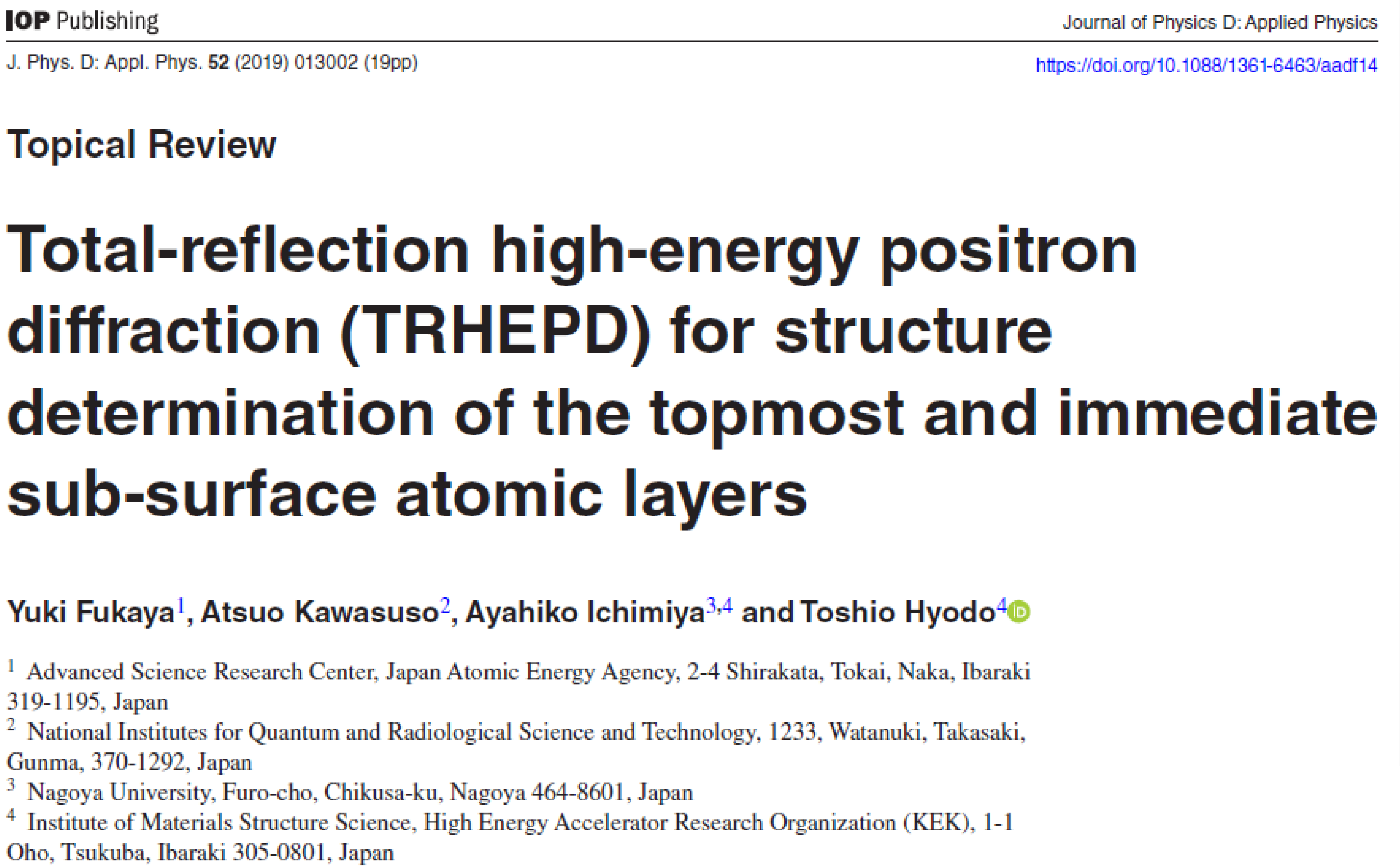
Auger electron emission initiated by the creation of valence-band holes in graphene by positron annihilation

V.A. Chirayath[1], V. Callewaert[2], A.J. Fairchild[1], M.D. Chrysler[1], R.W. Gladen[1], A.D. Mcdonald[1], S.K. Imam[1], K. Shastry[1,3], A.R. Koymen[1], R. Saniz[2], B. Barbiellini[4], K. Rajeshwar[5], B. Partoens[2] & A.H. Weiss[1]

Super surface sensitive
No secondary electron background



POSITRONS AT SURFACES: RHEPD



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Topical Review

Total-reflection high-energy positron diffraction (TRHEPD) for structure determination of the topmost and immediate sub-surface atomic layers

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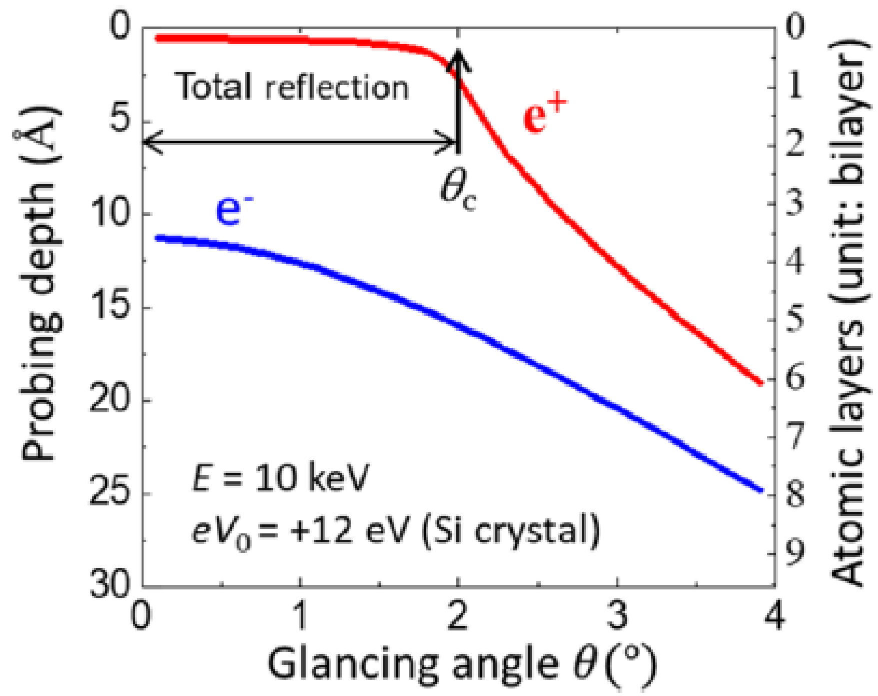

Figure 3. Probing depths of the positron and electron beam with an energy of 10 keV into the surface of a Si crystal as functions of the glancing angle. Red and blue lines indicate the positron and electrons beams, respectively.

SUMMARY

- Positron annihilation spectroscopy is a practical method for studying open volume defects in semiconductors and metals (concentration range 10^{15} – 10^{19} cm^{-3})
- At its best in identifying and quantifying **cation vacancies** and **vacancy-impurity complexes** in compound semiconductors (lifetime + Doppler + theory)
- Also: mono- and di-vacancies as well as vacancy-impurity complexes in elemental semiconductors and metals, vacancy-solute complexes in alloys, etc.
- Sample state manipulation allows for determining the physical characteristics of the identified defects (electrical activity, transition levels, migration barriers, etc.)
- Bulk crystals, thin films can be studied, conductivity (or not) not an issue
- Angular correlation experiments: Fermi surface analysis
- For surfaces, use ”fancy” methods such as PA-induced Auger or RHEPD