Point defects in ZnO single crystals and their thermal stability

J. Čížek, P. Hruška, J. Valenta, E. Belas, A. Musiienko, O. Melikhova

Faculty of Mathematics and Physics, Charles University Prague, Czech Republic

M. Elsayed, R. Krause-Rehberg

Helmholtz Zentrum Dresden-Rossendorf, Germany

W. Anwand, M.O. Liedke

Helmholtz Zentrum Dresden-Rossendorf, Germany

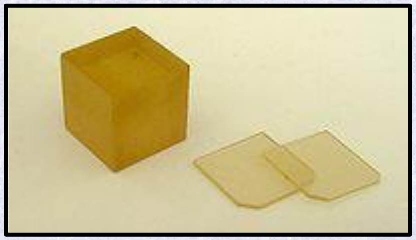
F. Selim

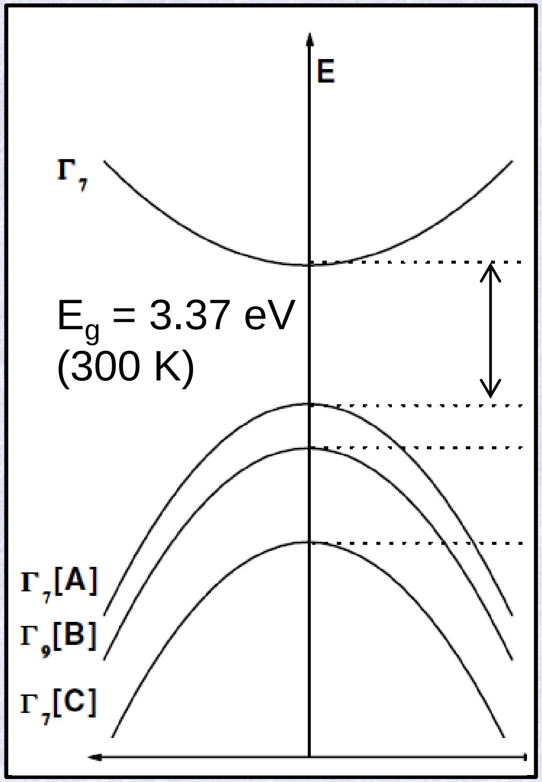
Center for Photochemical Sciences, Bowling Green State University, USA

Introduction

ZnO

- wide band gap semiconductor E_g = 3.37 eV (λ = 368 nm) at room temperature
- large exciton binding energy 60 meV
- promising material with many applications mainly in optoelectronics (transparent electronics, UV light emitting diodes, lasers, gas sensors)
- transparent conductive electrode for solar cells
- better resistance against radiation than GaAs or Si
- high quality ZnO single crystals are commercially available
- main problem: doping asymmetry
  - "natural" n-type doping
  - p-type doping is very difficult

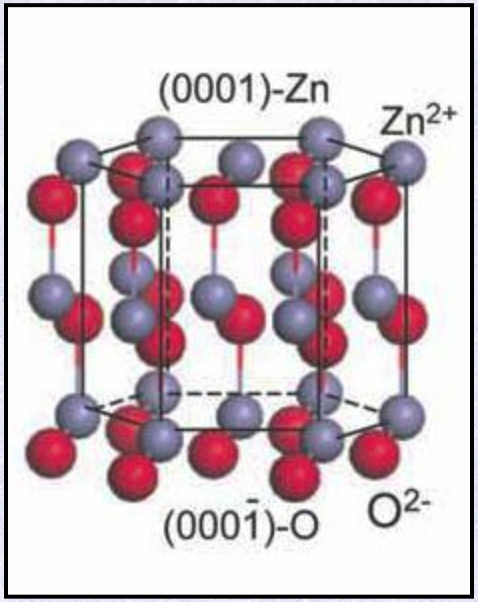


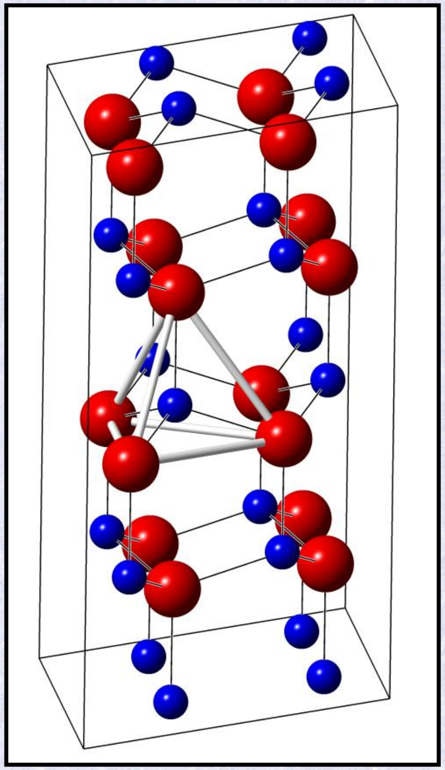


Theoretical calculations of positron lifetimes in ZnO

ZnO

- Wurtzite structure
- *a* = 3.25 Å, *c* = 5.12 Å
- Zn atoms in tetrahedral co-ordination
- Zn *d*-electrons hybridize with O *p*-electrons





Growth of ZnO crystals

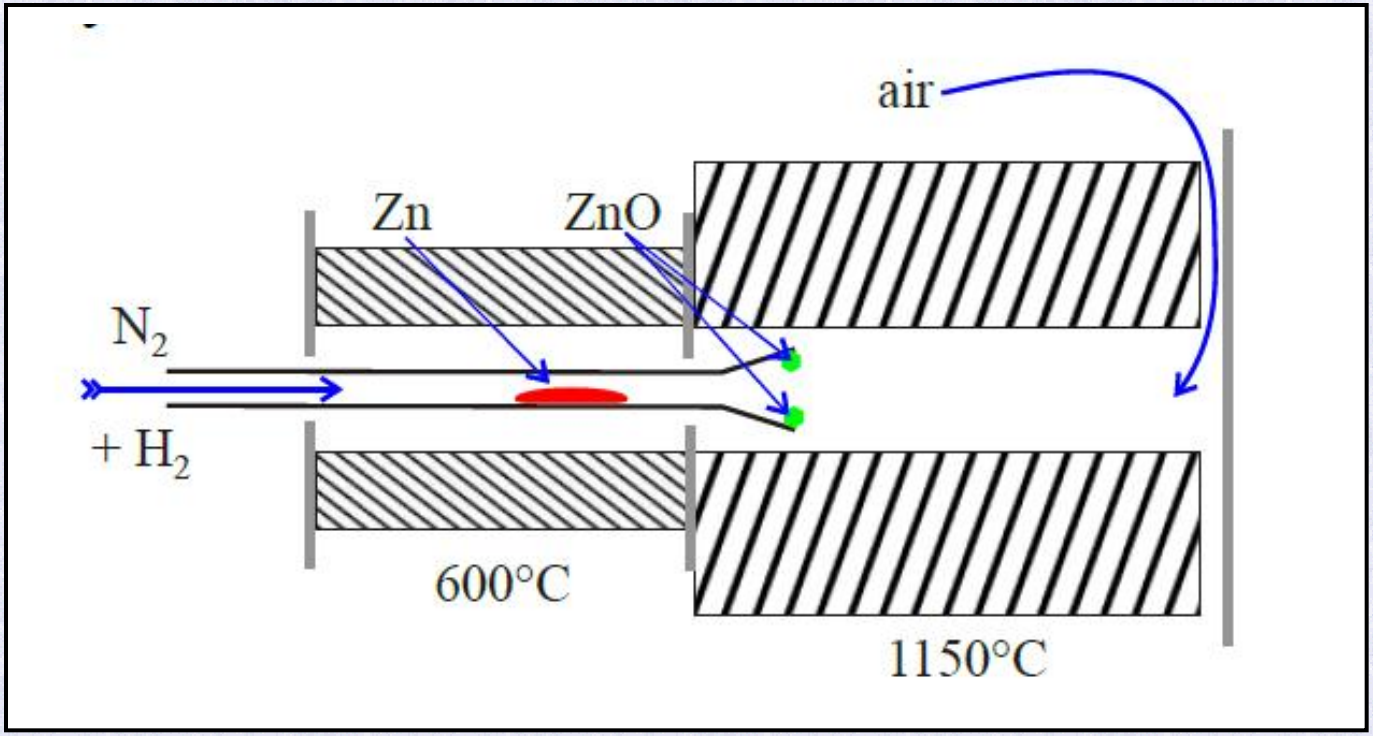
• ZnO melting temperature $T_m \approx 1975^oC$, vapor pressure 1.06 bar

1. Chemically assisted vapor transport (CVT)

Eagle-Picher Inc., USA

• small crystals

• gas contamination (N_2, H_2)



K.Grasza et al., J. Cryst. Growth ***310****, 1823 (2008)*

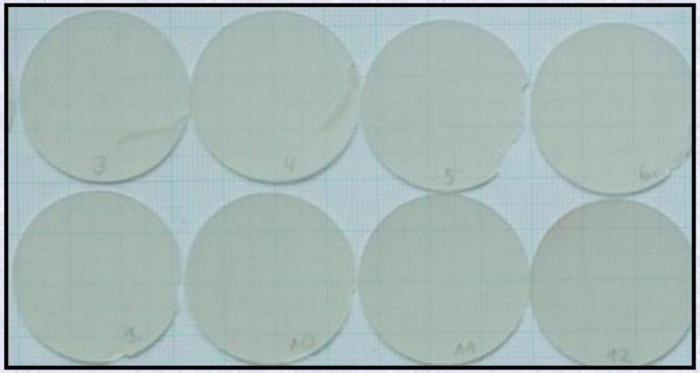
Growth of ZnO crystals

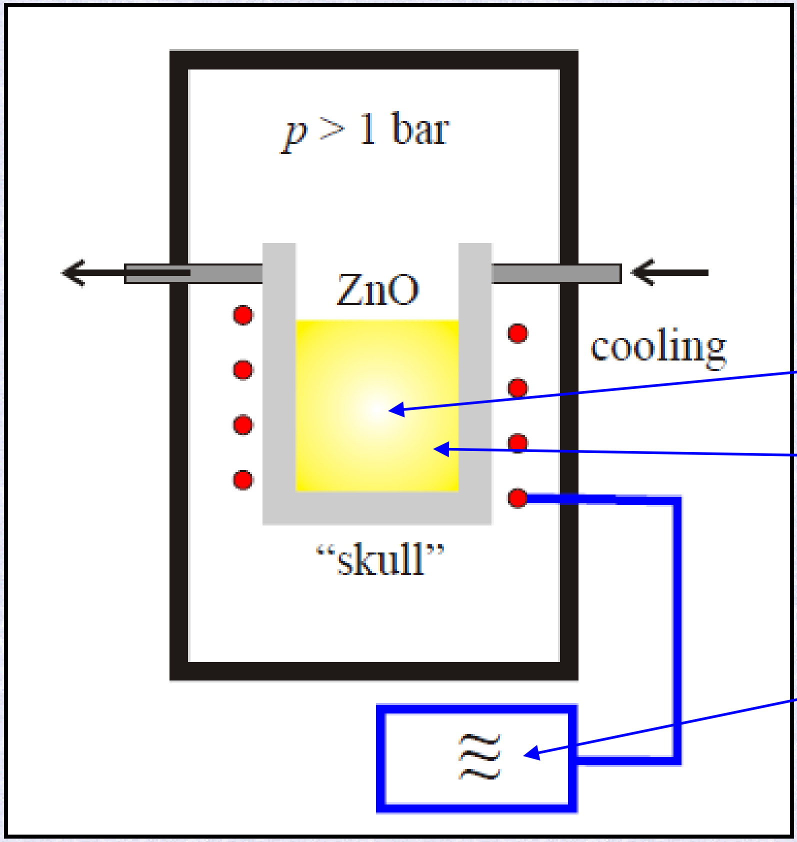
• ZnO melting temperature $T_m \approx 1975^oC$, vapor pressure 1.06 bar

2. pressurized melt growth (PMG) "skull growth"
Cermet Inc., USA

• very pure environment – growing crystal is in contact with ZnO only

• temperature gradients





zone of growth

cooled ZnO powder "skull"

RF power

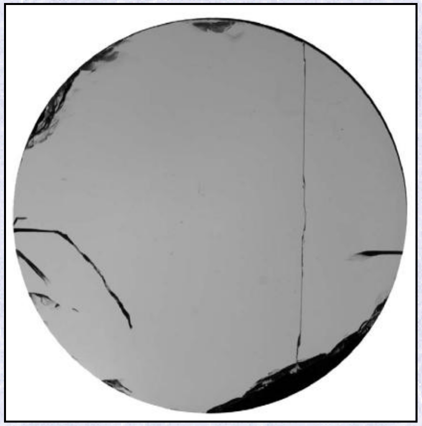
D.C. Reynolds et al., J. Appl. Phys. ***95****, 4802 (2004)*

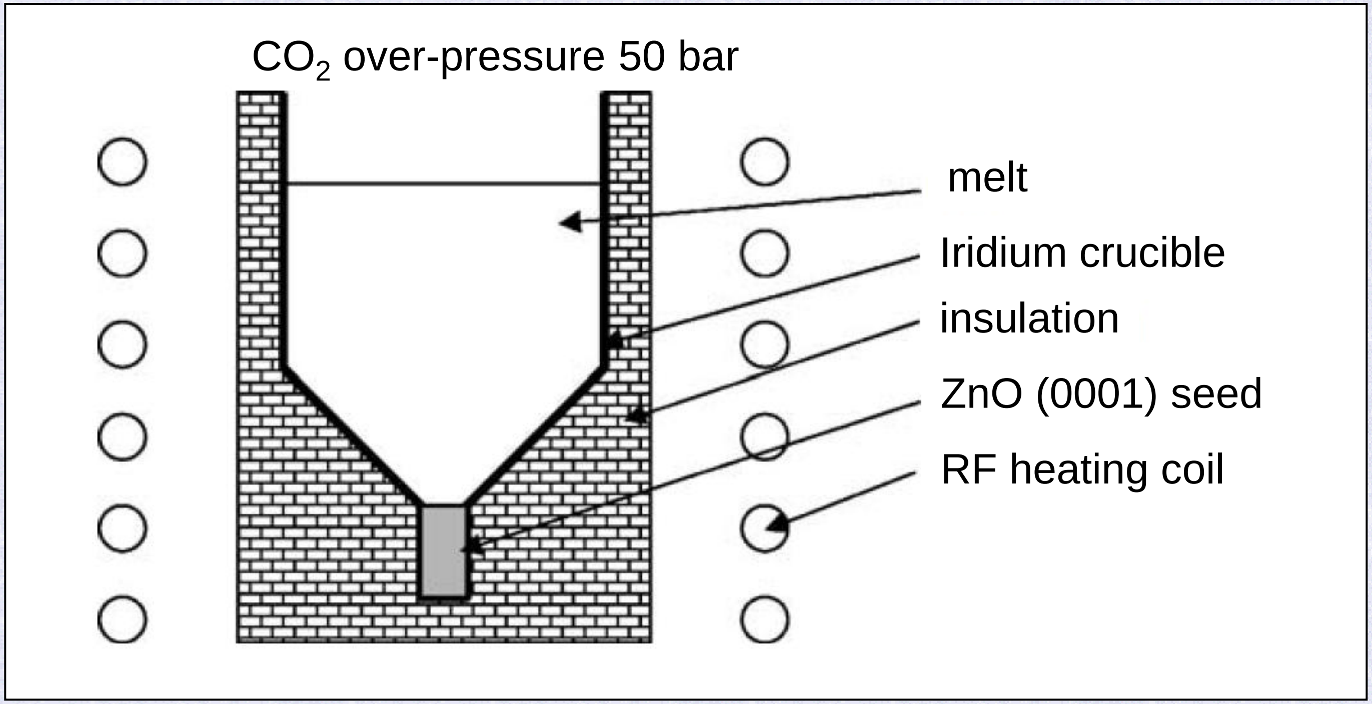
Growth of ZnO crystals

• ZnO melting temperature $T_m \approx 1975^oC$, vapor pressure 1.06 bar

3. Bridgman growth (BG)
Institut für Kristalzüchtung (IKZ) Berlin

• problem with suitable crucible material





D. Schulz et al., J. Cryst. Growth ***296****, 27 (2006)*

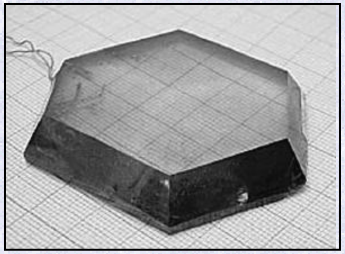
Growth of ZnO crystals

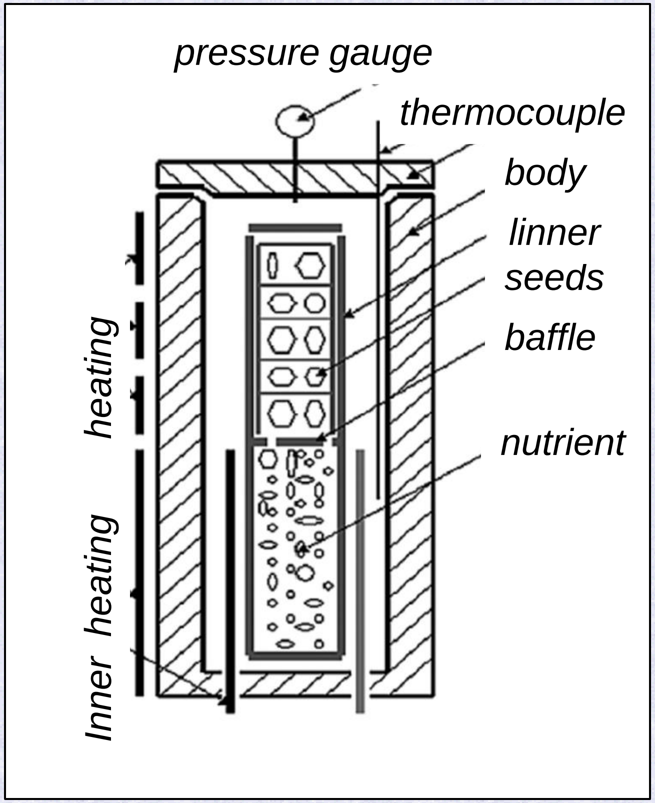
• ZnO melting temperature $T_m \approx 1975^oC$, vapor pressure 1.06 bar

4. hydrothermal growth (HTG)

MaTecK (Germany), CrysTec (Germany), Altramet(USA), MTI (USA), ...

- from aqueous alkaline solutions
- concentrated KOH / LiOH solution
- nutrient (Zn salt + hydroxide) is heated in Ti or Ag lined autoclave ($T \approx 370^oC$, $p \approx 220$ bar)
- small temperature gradient transports zincates from solution to the growing zone
- enable to growth large crystals (diam. ≈100 mm, length ≈1 m)





- main problem is contamination by impurities
- most common method for production of commercial ZnO crystals

*L.N. Dem'yanets, V.I. Lyutin, J. Cryst. Growth **310**, 993 (2008)*

ZnO single crystals studied

Hydrothermal growth (HTG)

- MaTecK GmbH, Jülich, Germany
- CrysTec GmbH, Berlin, Germany
- MTI Corp., Richmond, CA, USA
- Atomergic Chemetals Corp. (Altra), Farmingdale, NY, USA
- University Wafers, South Boston, MA, USA

Pressurized melt growth (PMG)

- Cerment Inc., Atlanta, GA, USA

Bridgman growth (BG)

- Institut für Kristalzüchtung (IKZ), Berlin, Germany

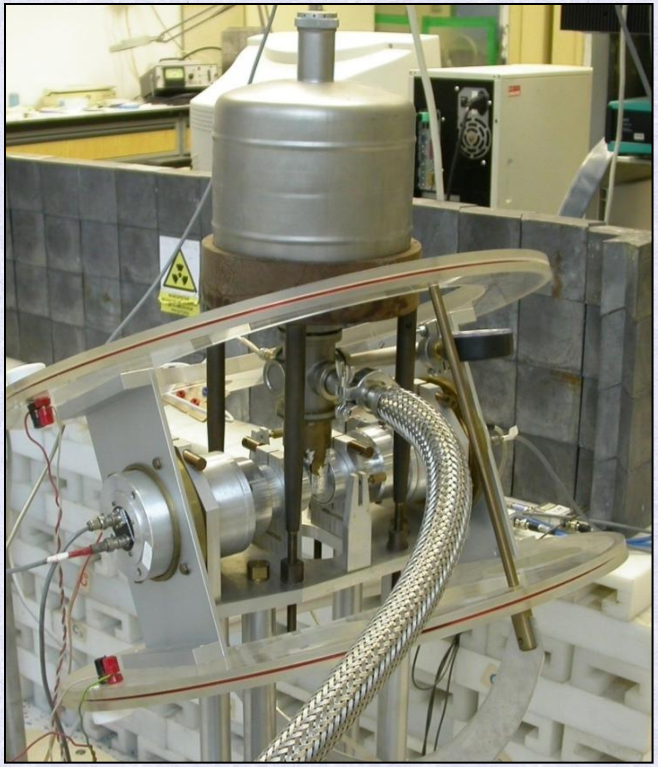
Chemically assisted vapor phase growth technique (CVT)

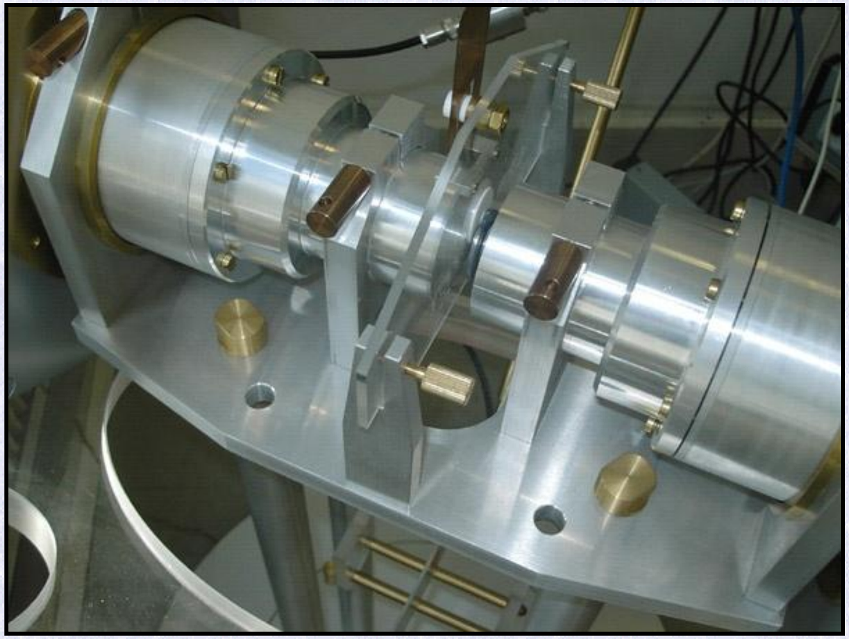
- Oak Ridge National Laboratory (ORNL), TN, USA

Positron lifetime spectroscopy

- digital positron lifetime spectrometer
- photomultipliers Hamamatsu H3378
- BaF_2 scintillators
- timing resolution 145 ps (FWHM ^{22}Na)
- effective coincidence count rate 100 s^{-1}
- >10^7 positron annihilation events in each spectrum

*F. Bečvář et al., Nucl. Instrum. Methods A **539**, 372 (2005)*

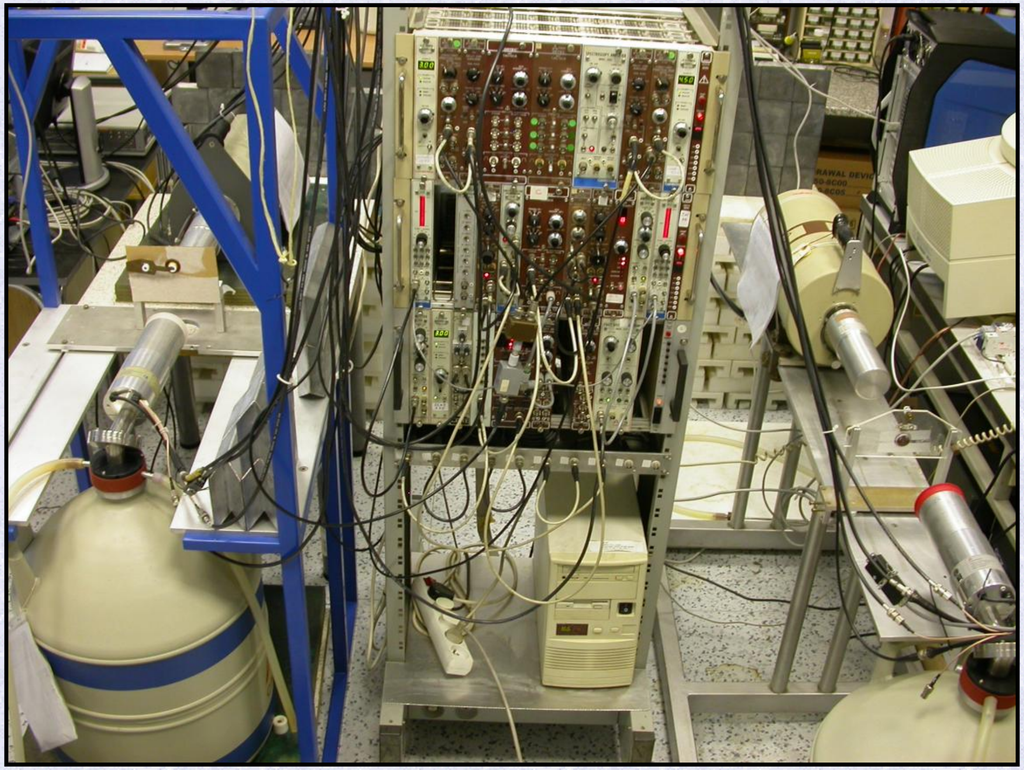


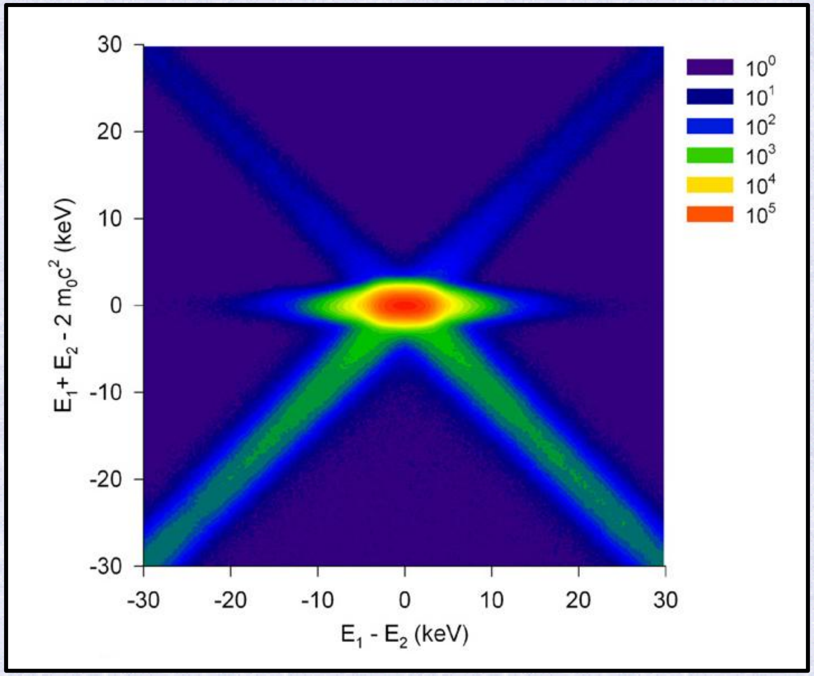


Coincidence Doppler broadening

- digital CDB spectrometer
- two HPGe detectors
- resolution 0.9 keV at 511 keV
- peak-to-background ratio 10^6
- $>10^8$ positron annihilation events in each spectrum

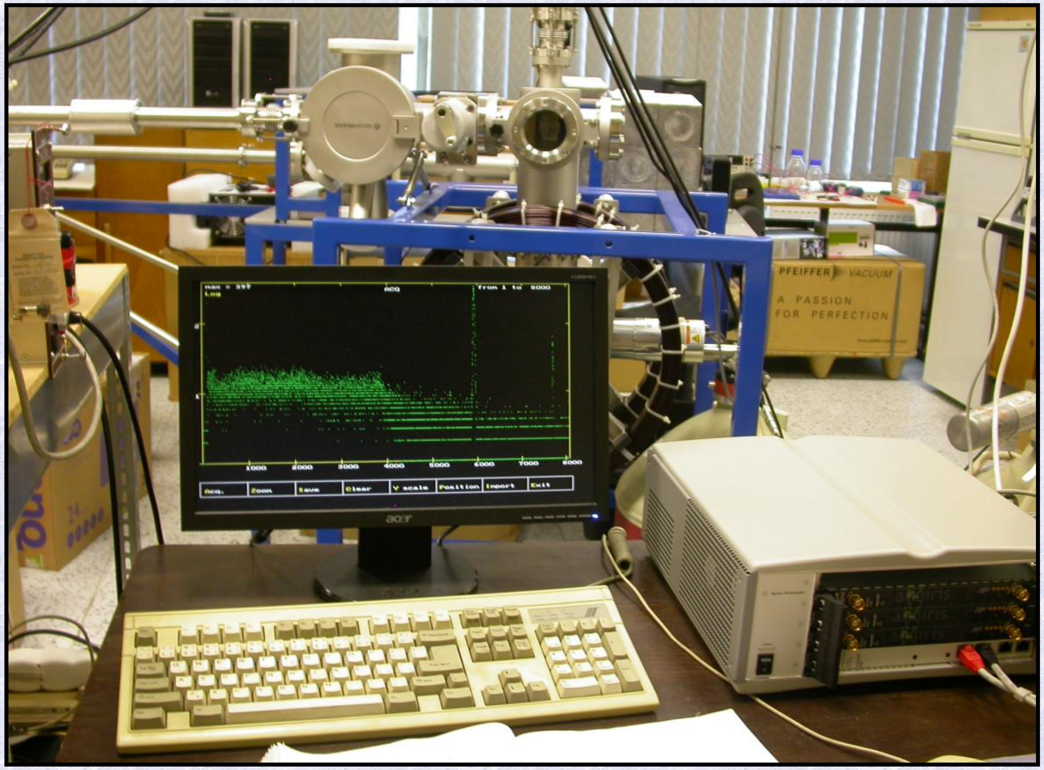
*J. Čížek et al., Nucl. Instrum. Methods A **623**, 982 (2010)*

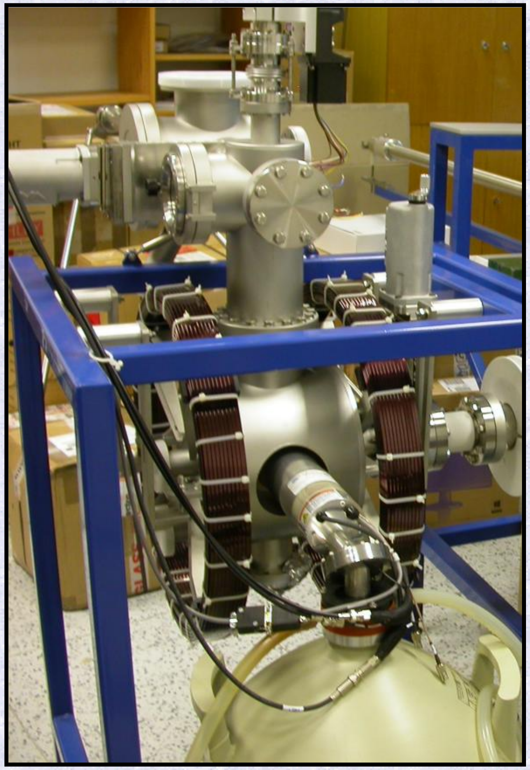




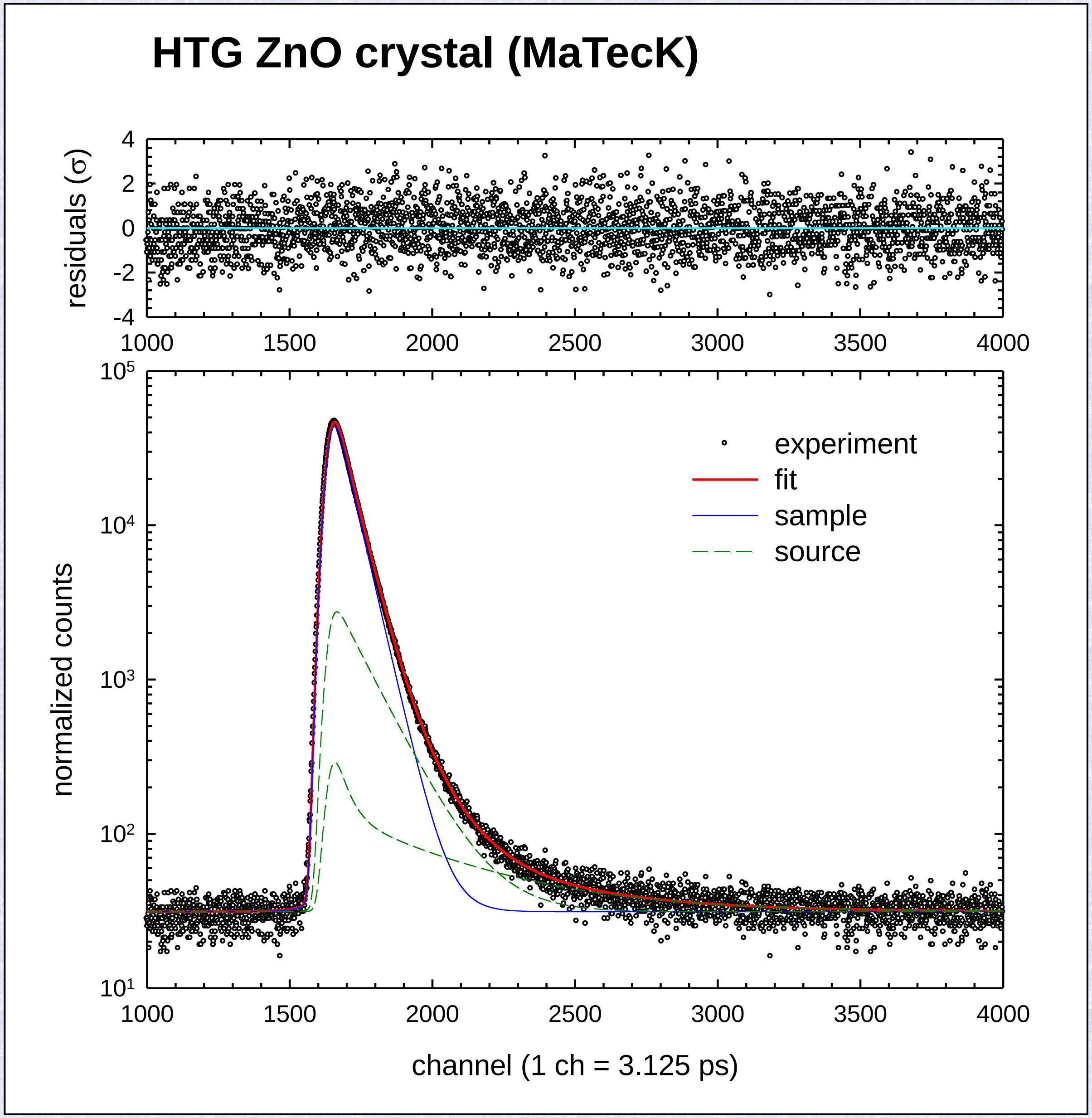
Positron back-diffusion

- magnetically guided slow positron beam
- positron energy 0.050 – 35 keV
- HPGe detector with energy resolution 1.09±0.01 keV at 511 keV
- Doppler broadening of annihilation evaluated using *S*, *W* line shape parameters
- > 7 × 10^5 counts in annihilation peak





Positron Lifetime Spectrum



single component

τ_1 = 180.7(3) ps, I_1 = 100 %

source contribution:

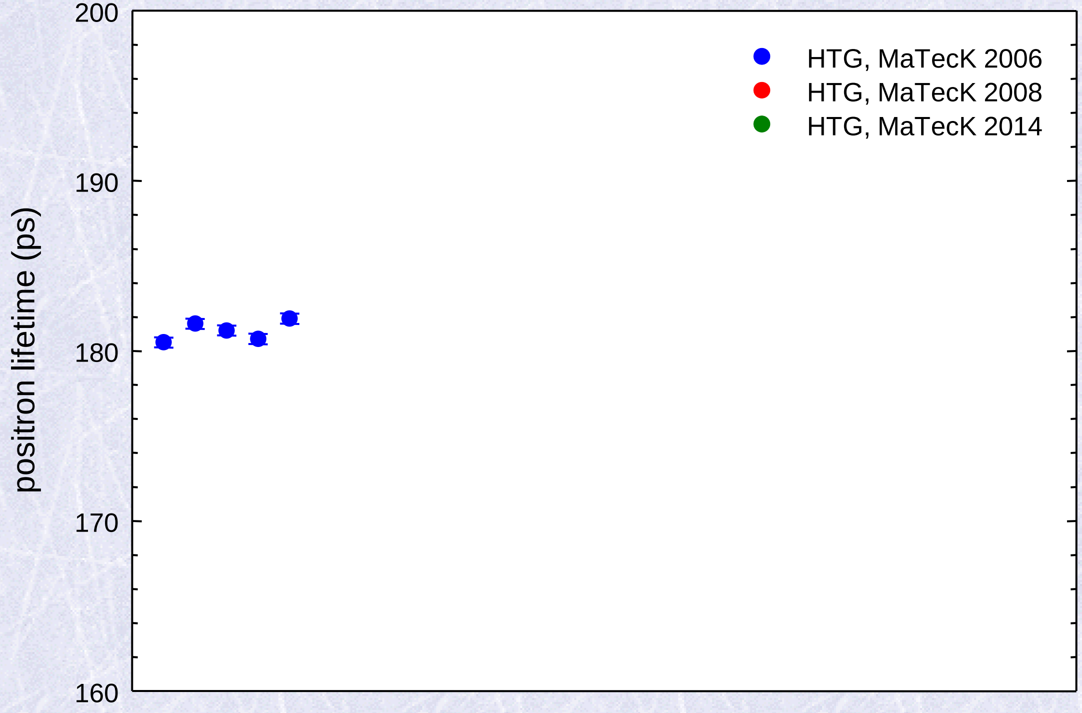
^{22}Na source deposited on 2 μm mylar foil

τ_{s1} = 368 ps, I_{s1} = 9 %

τ_{s2} = 1.26 ns, I_{s2} = 1 %

As-grown ZnO single crystals - reproducidibility

- comparison of sample batches from various periods



J. Čížek et al., J. Phys. Conf. Ser. ***791****, 012017 (2017)*

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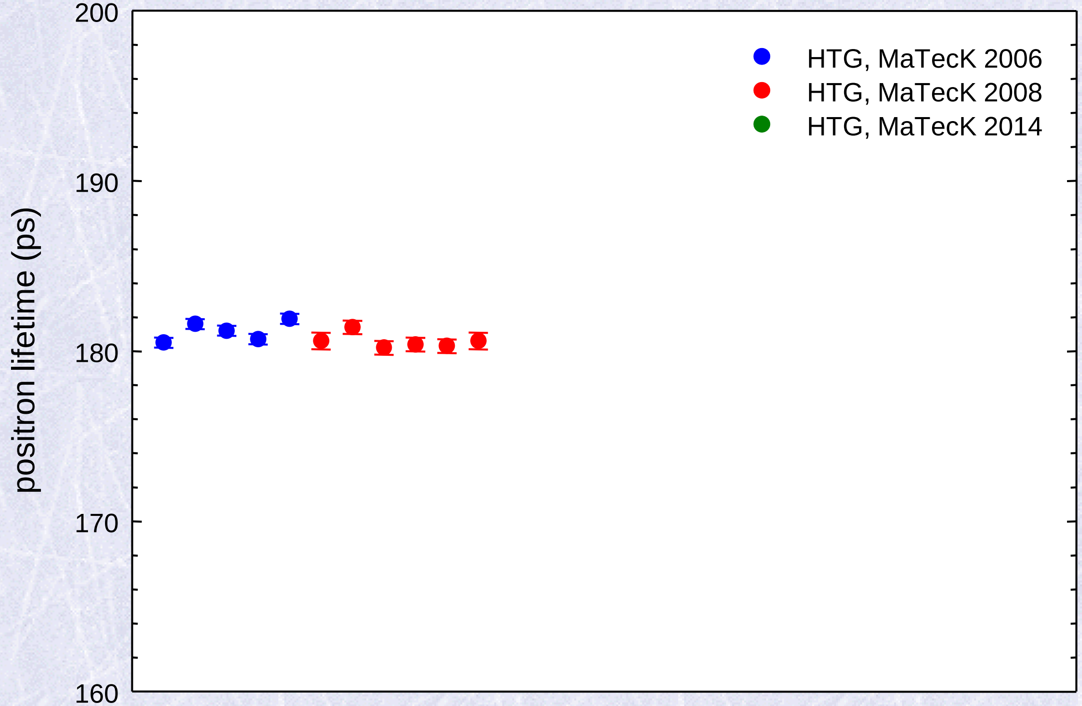

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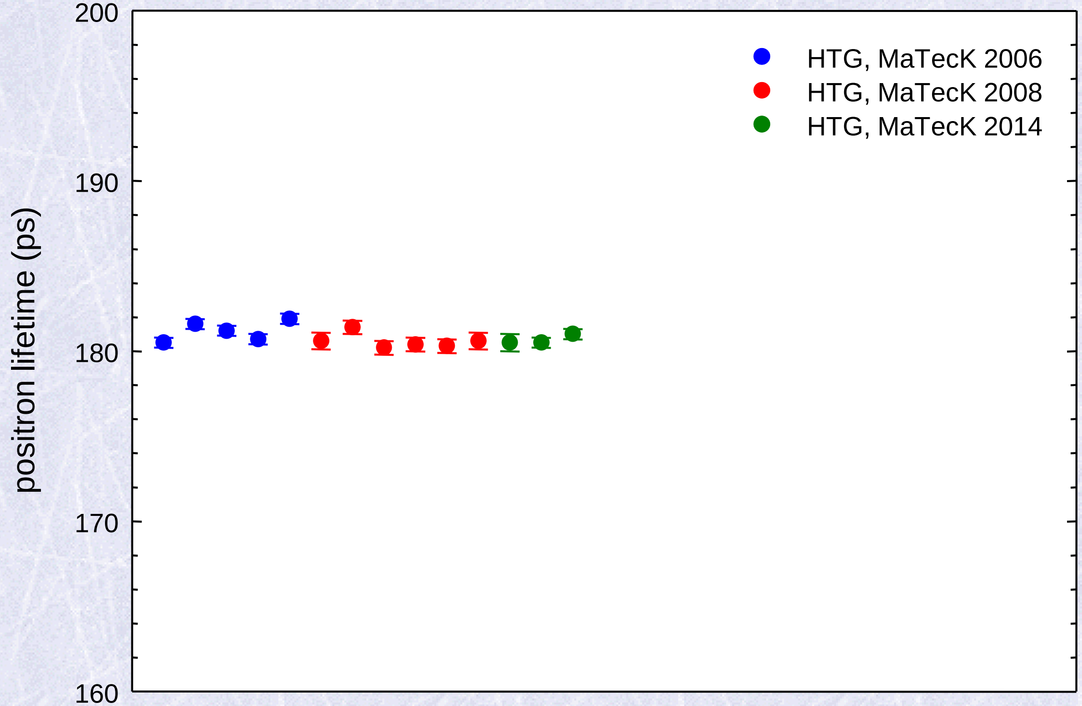

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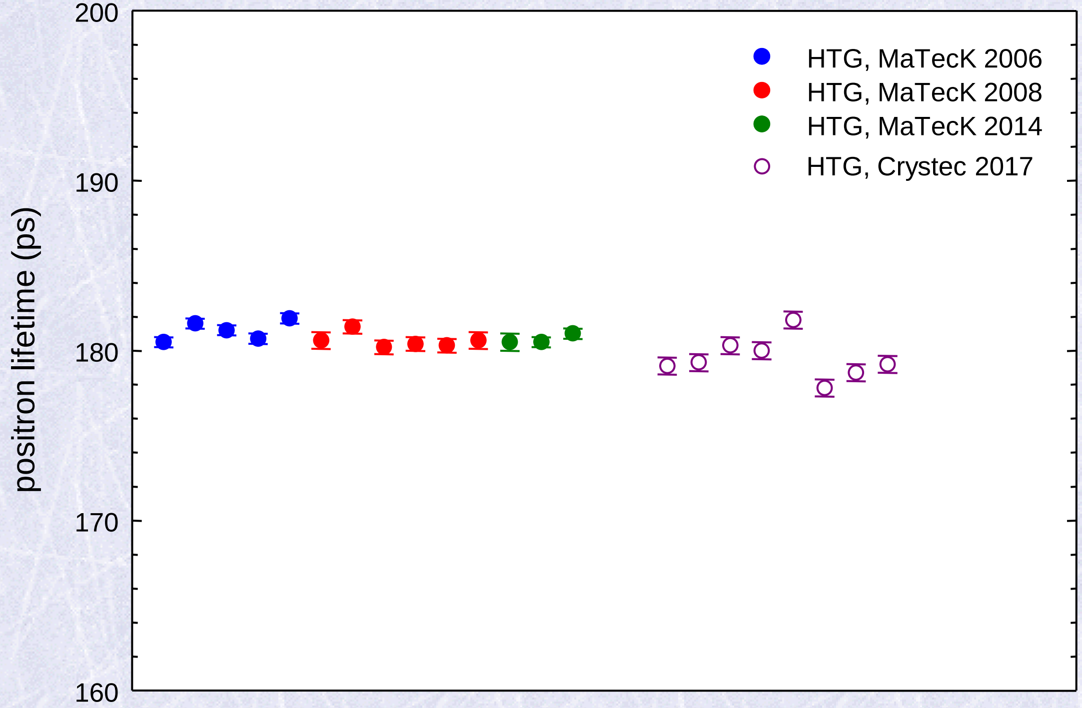

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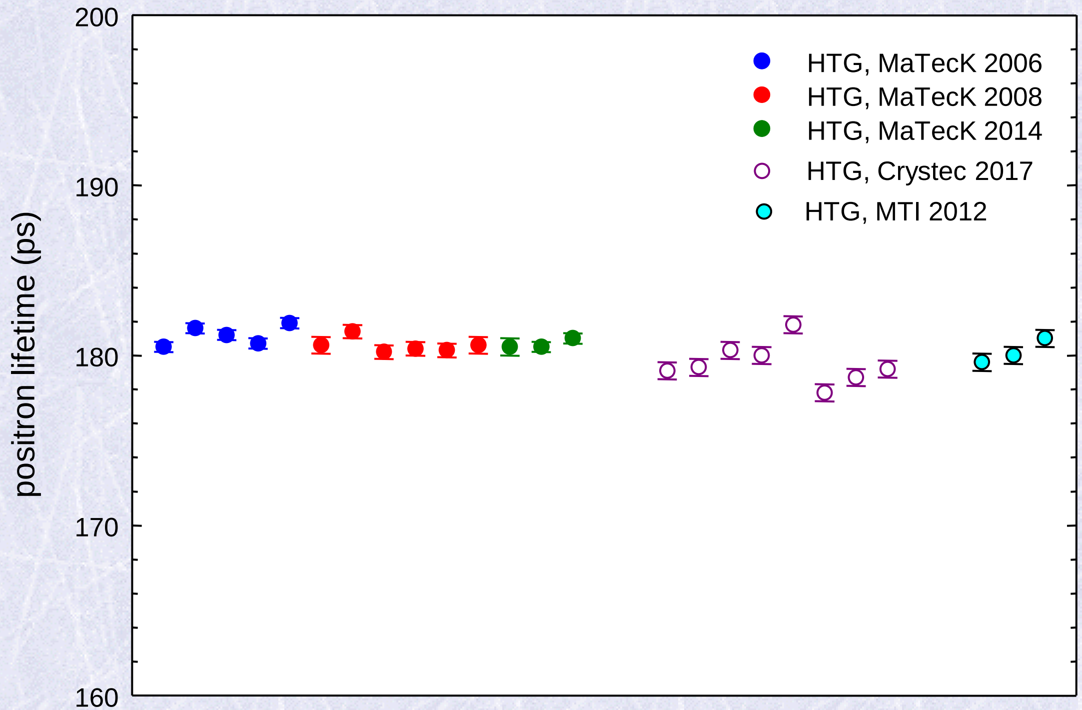

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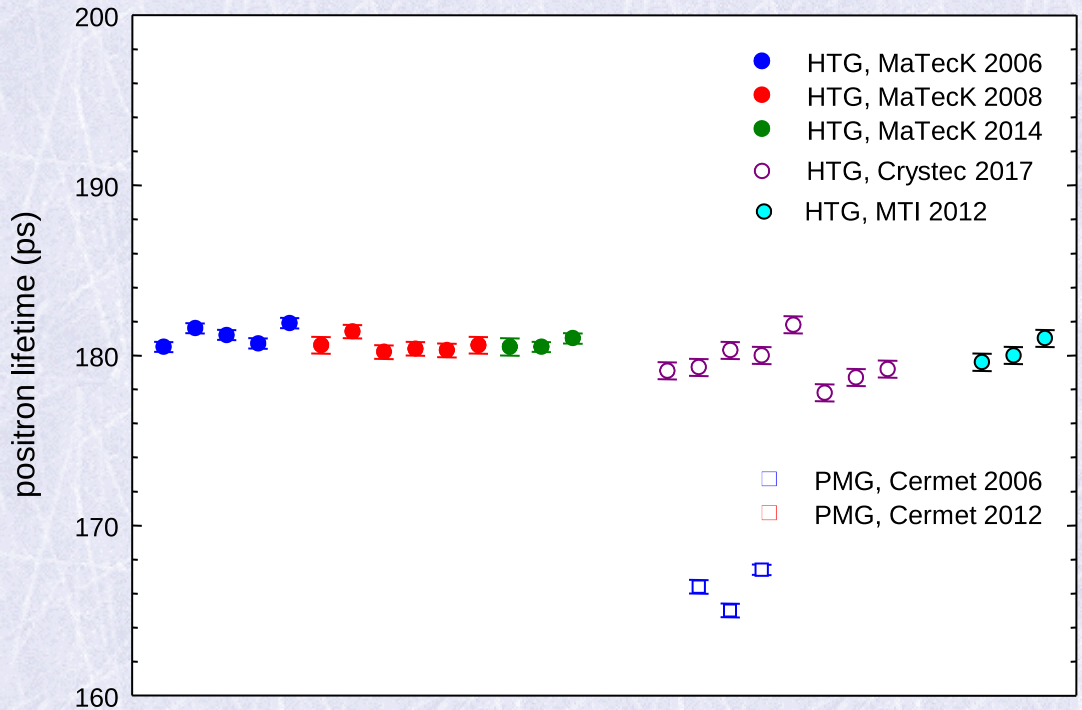

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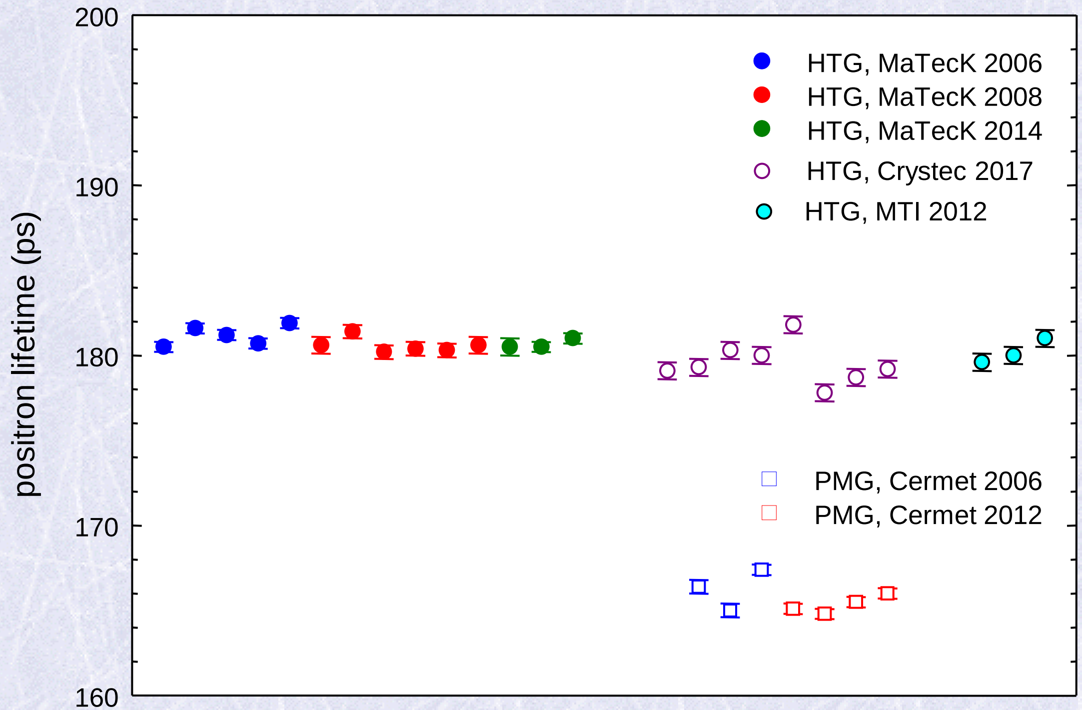

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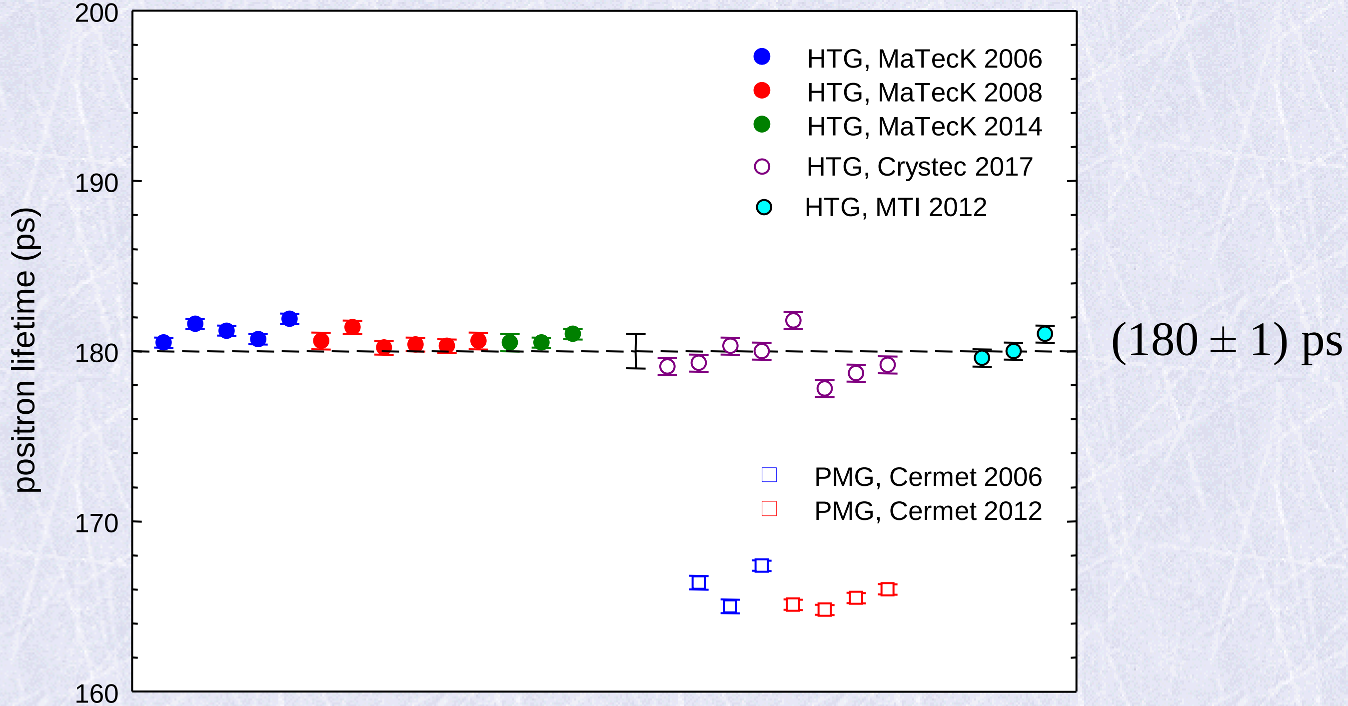

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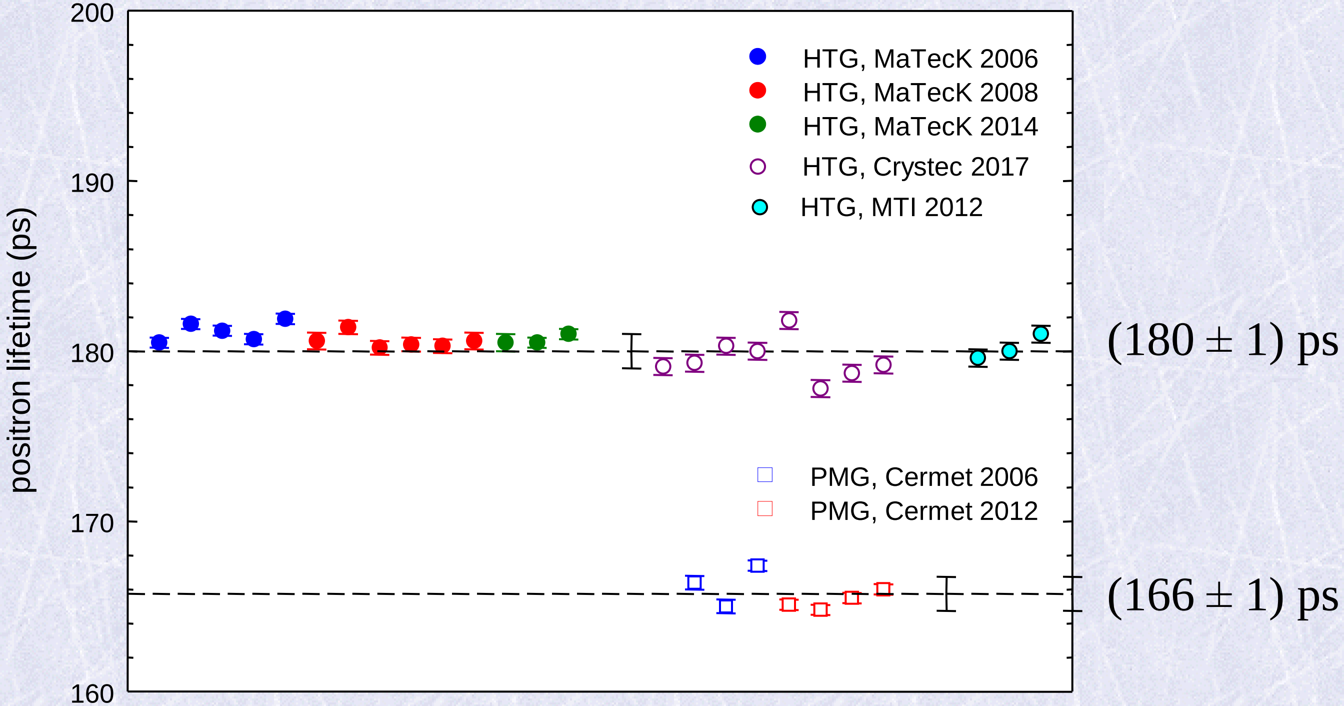

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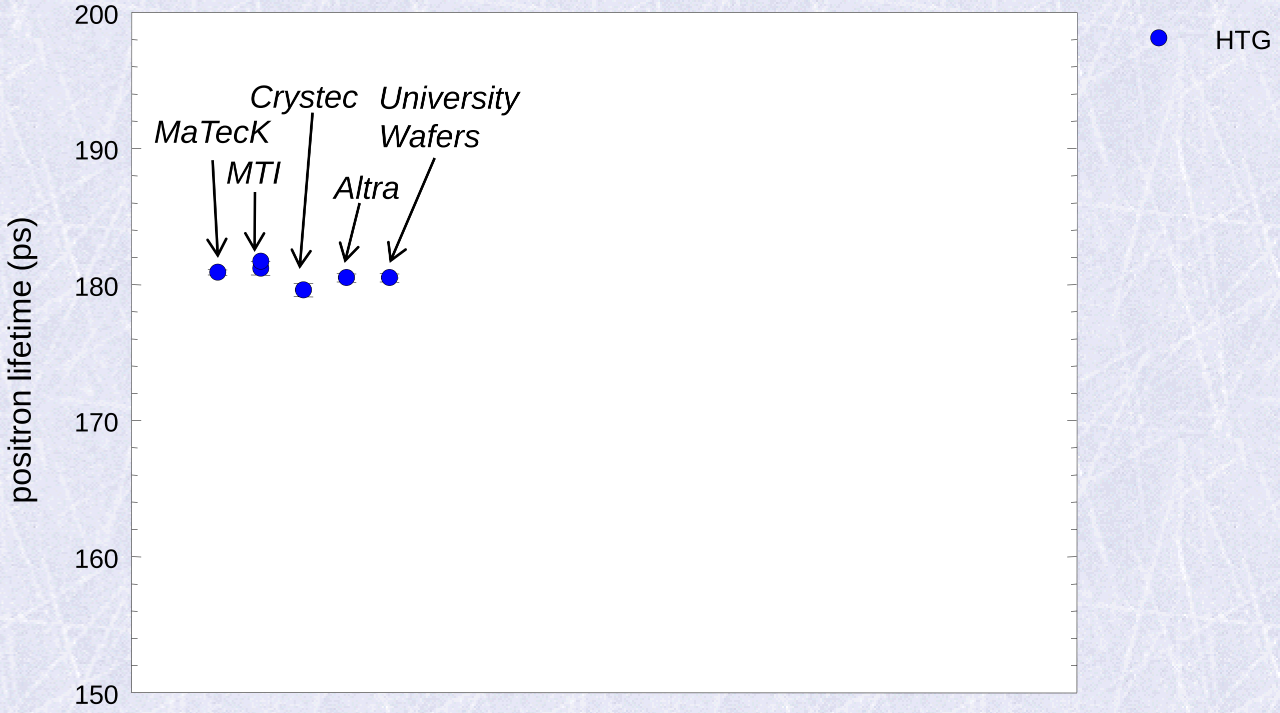
As-grown ZnO single crystals – comparison of growth techniques

• comparison of ZnO crystals prepared by various techniques



F. Lukáč et al., Acta Physica Polonica A ***125***, *748 (2014)*

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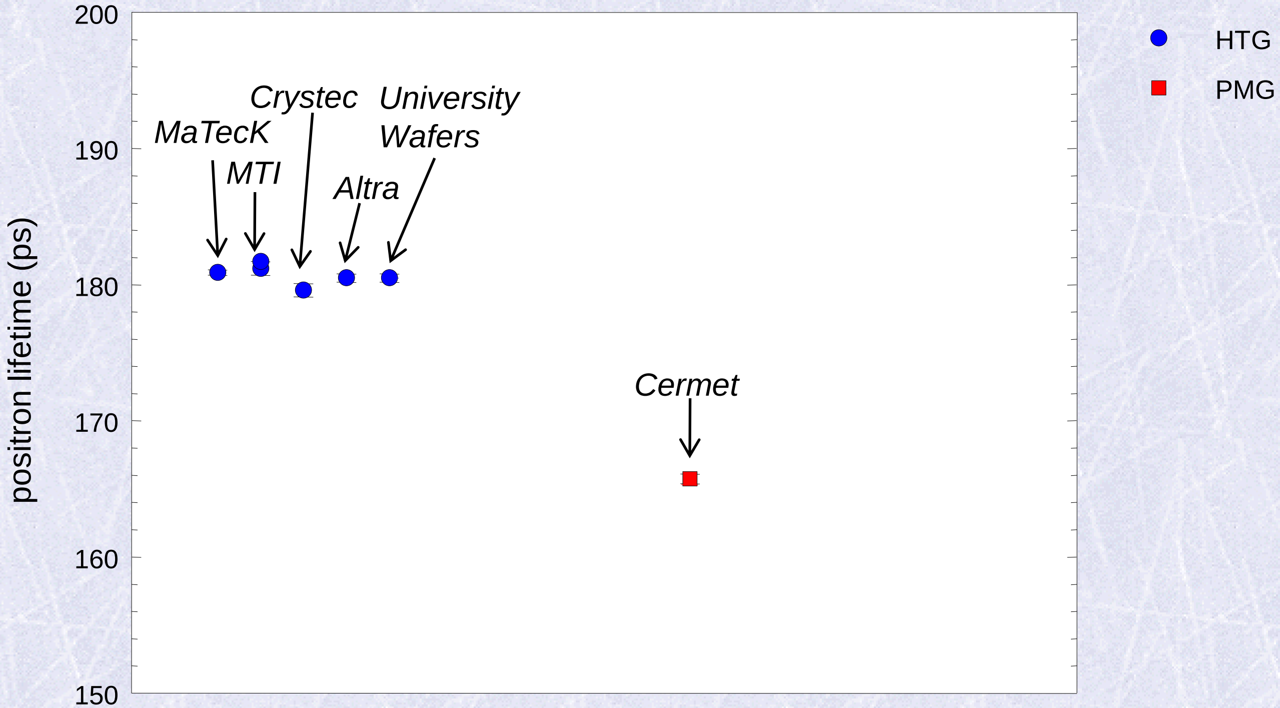

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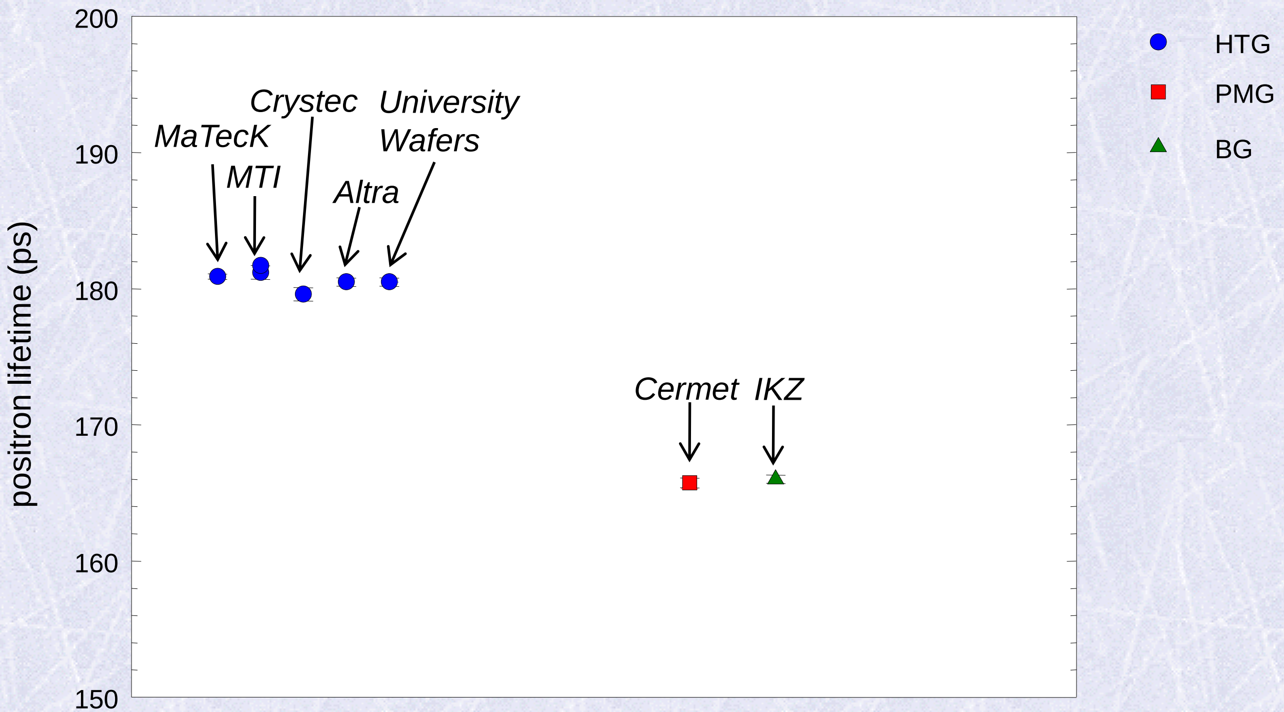

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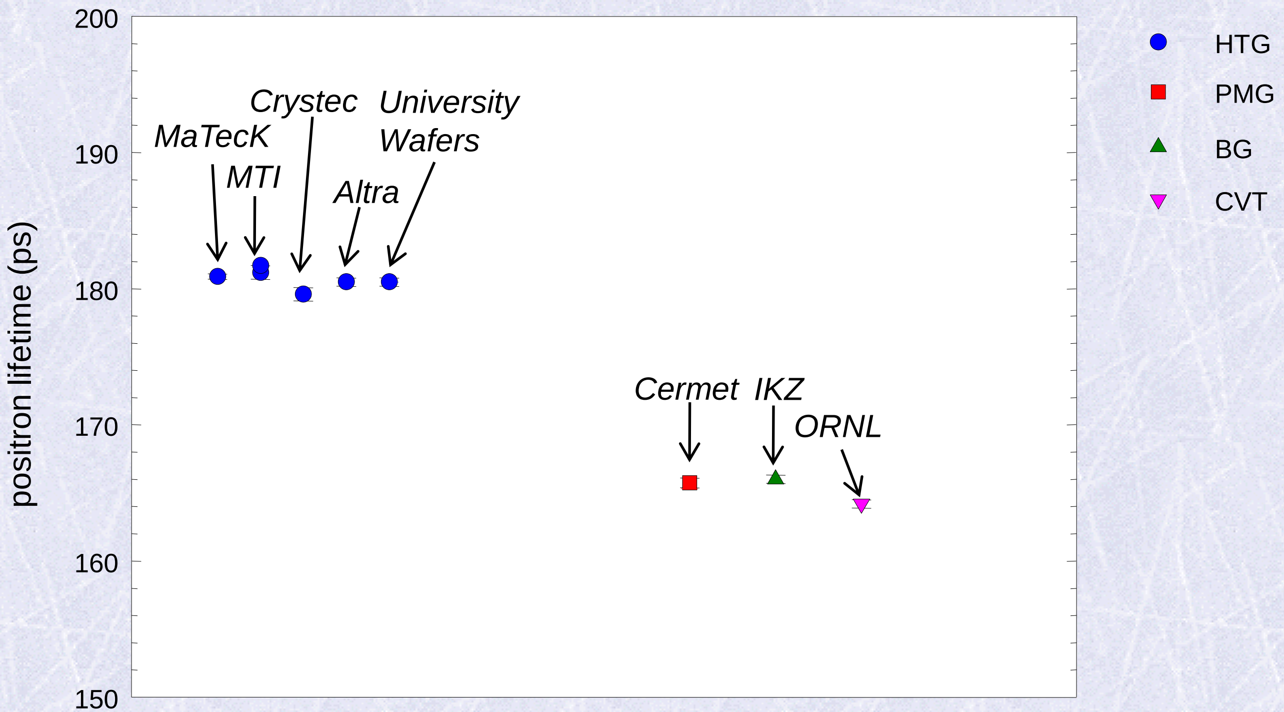

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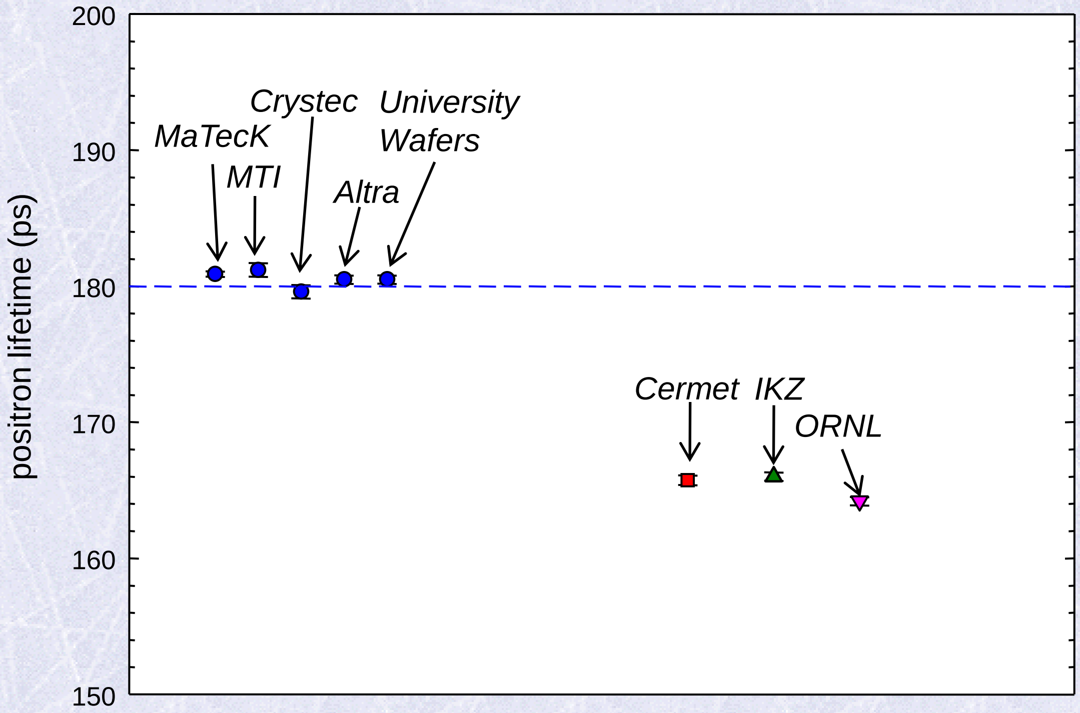
- two groups → HTG ZnO crystals: lifetime ≈ 180 ps



(180 ± 1) ps

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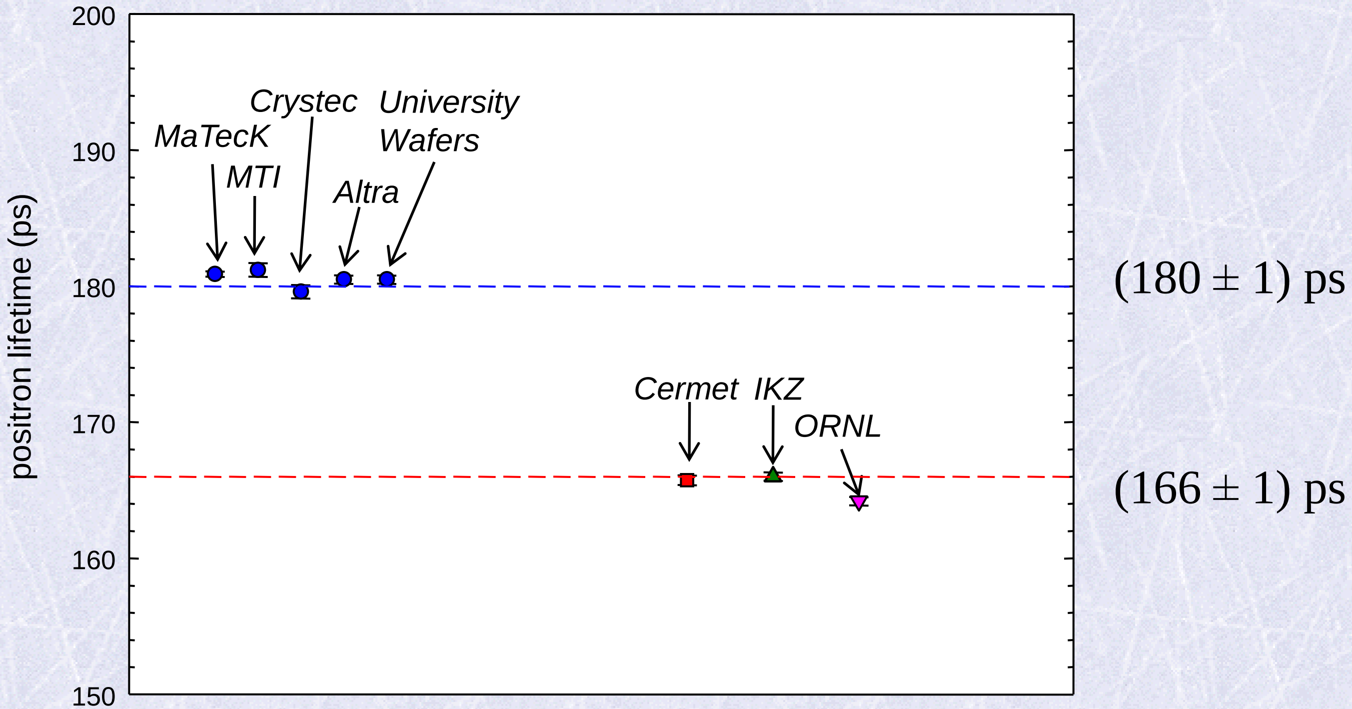
- two groups
  - → HTG ZnO crystals: lifetime ≈ 180 ps
  - → PMG, BG, CVT ZnO crystals: lifetime ≈ 166 ps



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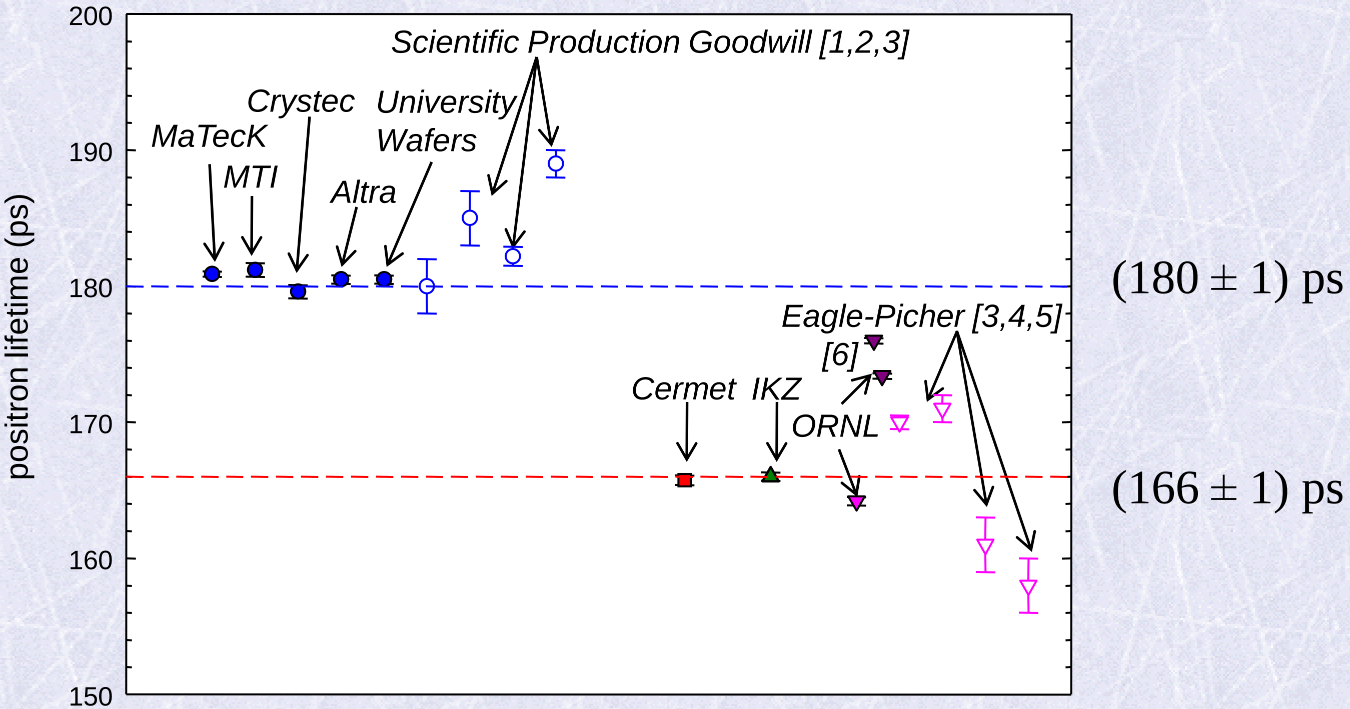
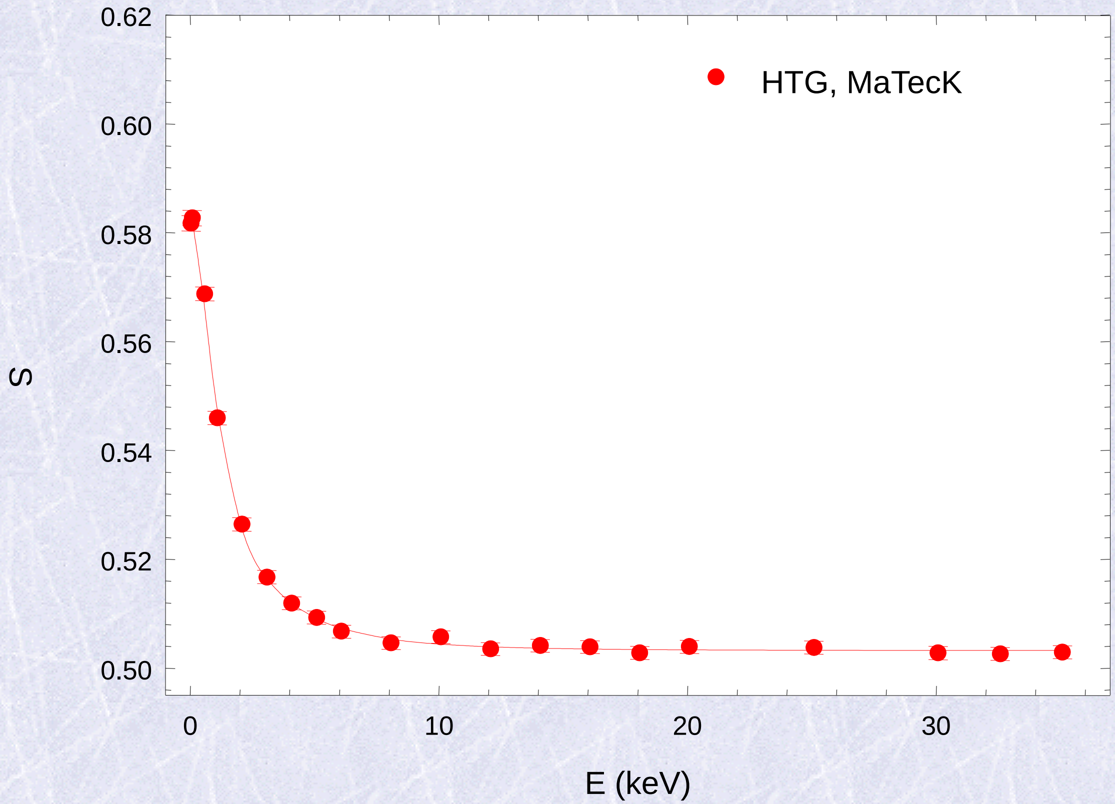


[1] F. Tuomisto, D.C. Look, Proc. SPIE **6474**, 647413 (2007)
[2] Z.Q. Chen et al., PRB **71**, 115213 (2005)
[3] Z.Q. Chen et al., JAP **94**, 4807 (2003)
[4] F. Tuomisto et al., PRL **91**, 205502 (2003).
[5] S. Brunner et al., Mater. Sci. Forum **363-365**, 141 (2001).
[6] J. Ji et al. Sci. Reports **6**, 31238 (2016).

As-grown ZnO single crystals – comparison of growth techniques

- positron back-diffusion measurement using slow positron beam
- comparison of ZnO crystals prepared by various techniques



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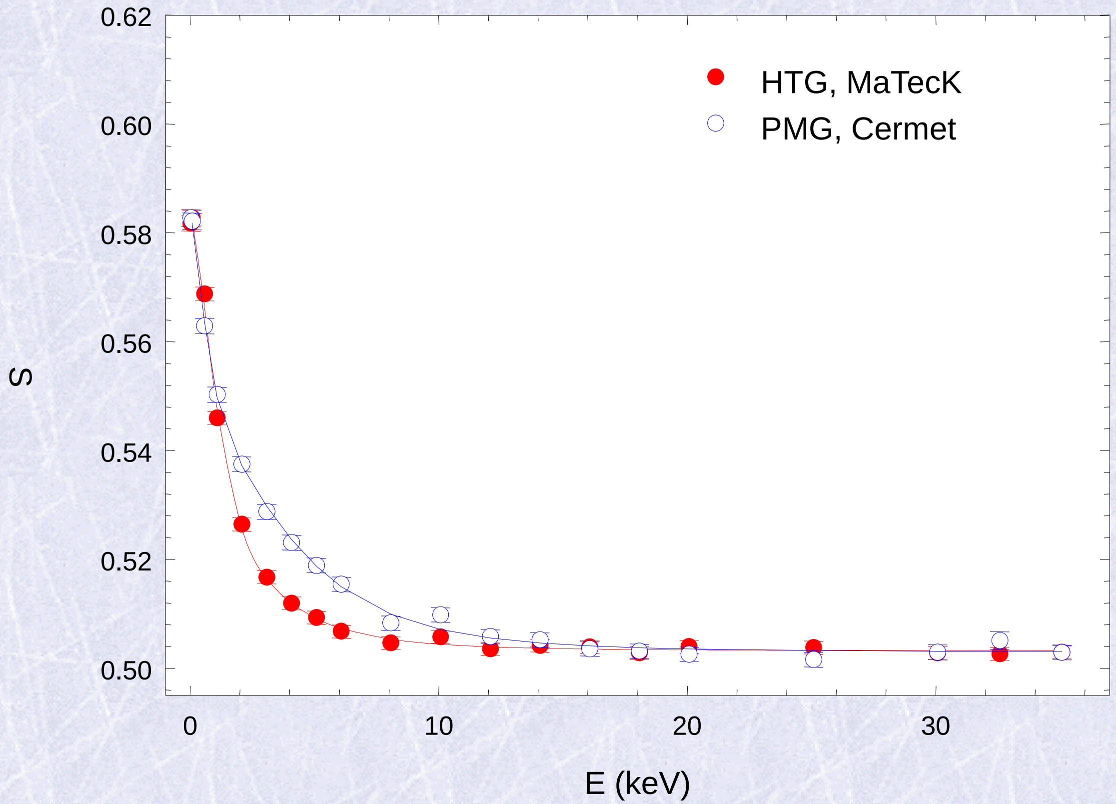

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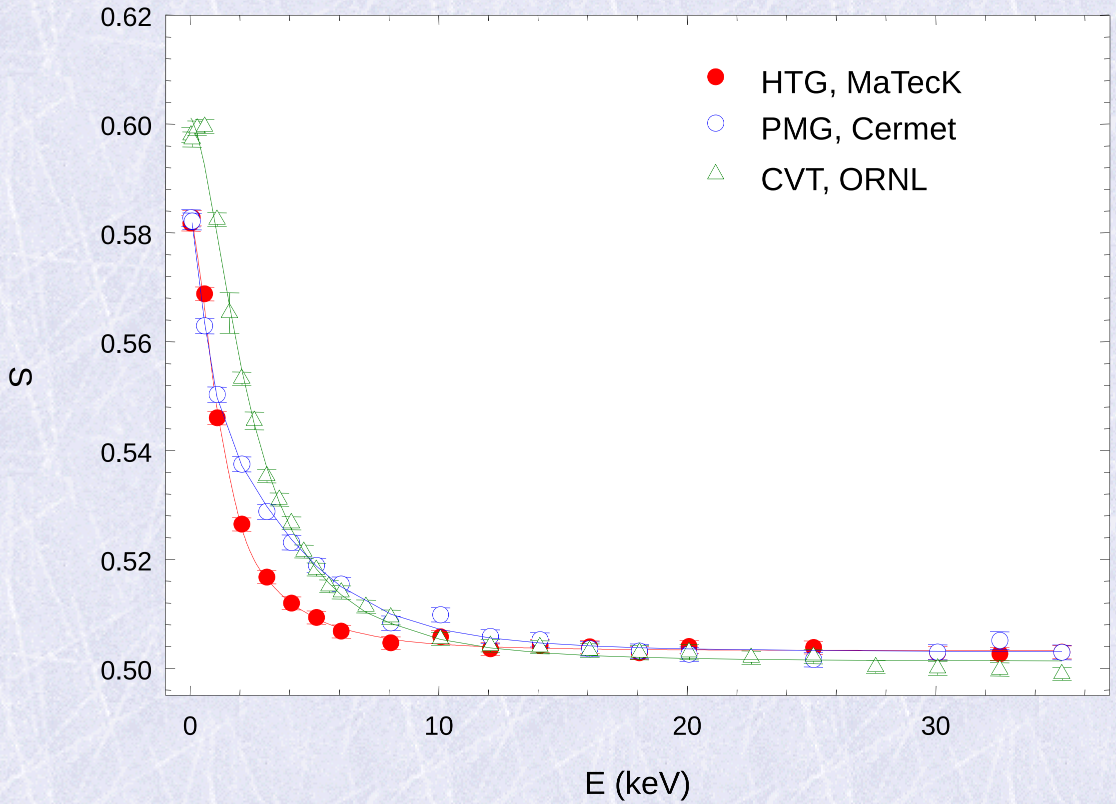

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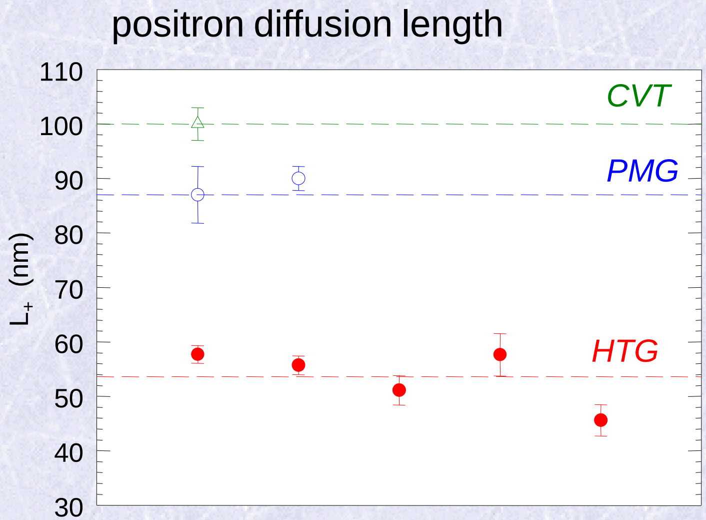
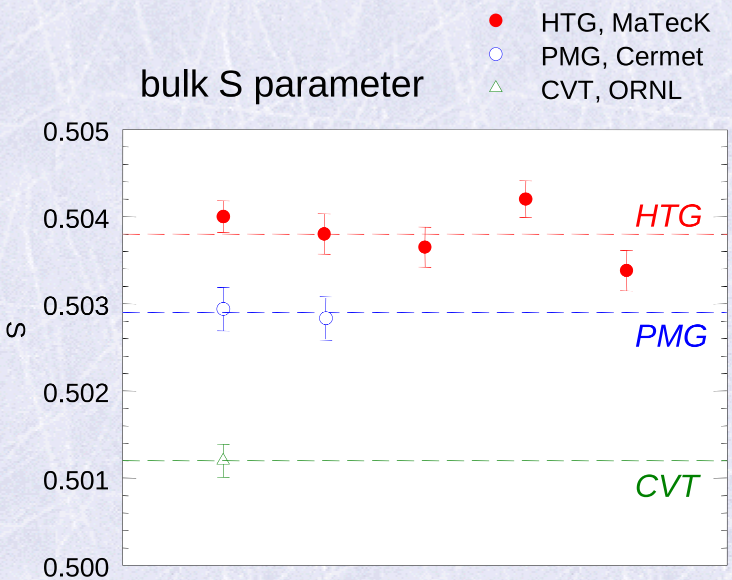
As-grown ZnO single crystals – comparison of growth techniques

- positron back-diffusion measurement using slow positron beam
- comparison of ZnO crystals prepared by various techniques
- concentration of defects: CVT → PMG → HTG
- HTG crystals from various producers (MaTecK, Crystec, MTI,…) are comparable





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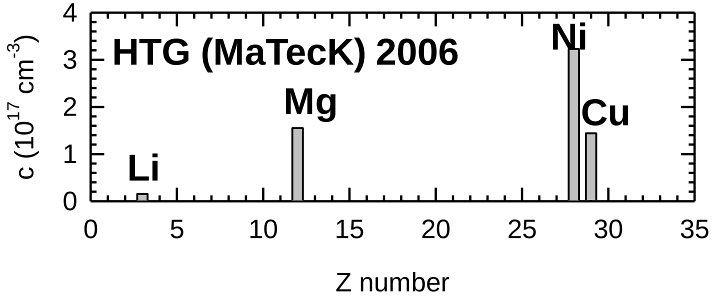
Chemical Analysis of ZnO crystals

- Inductively Coupled Plasma Source – Mass Spectrometry (ICP-MS)
- Glow discharge Mass Spectrometry (GDMS) sensitivity 5 ppb (2×10^{14} cm^{-3})



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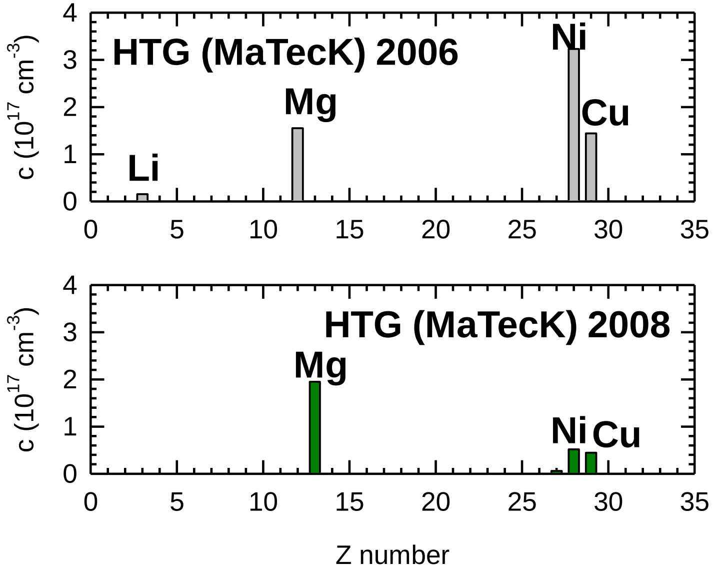

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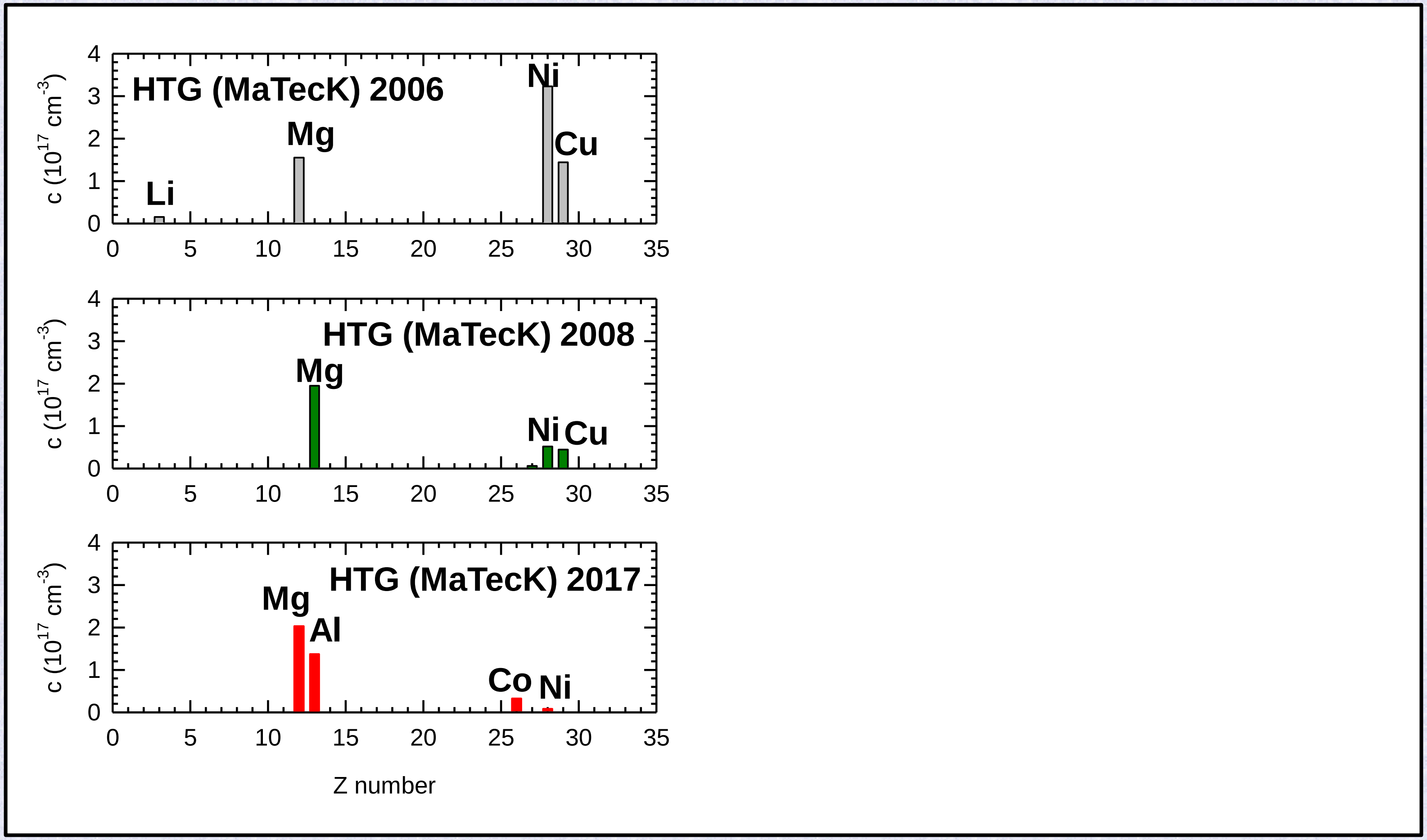

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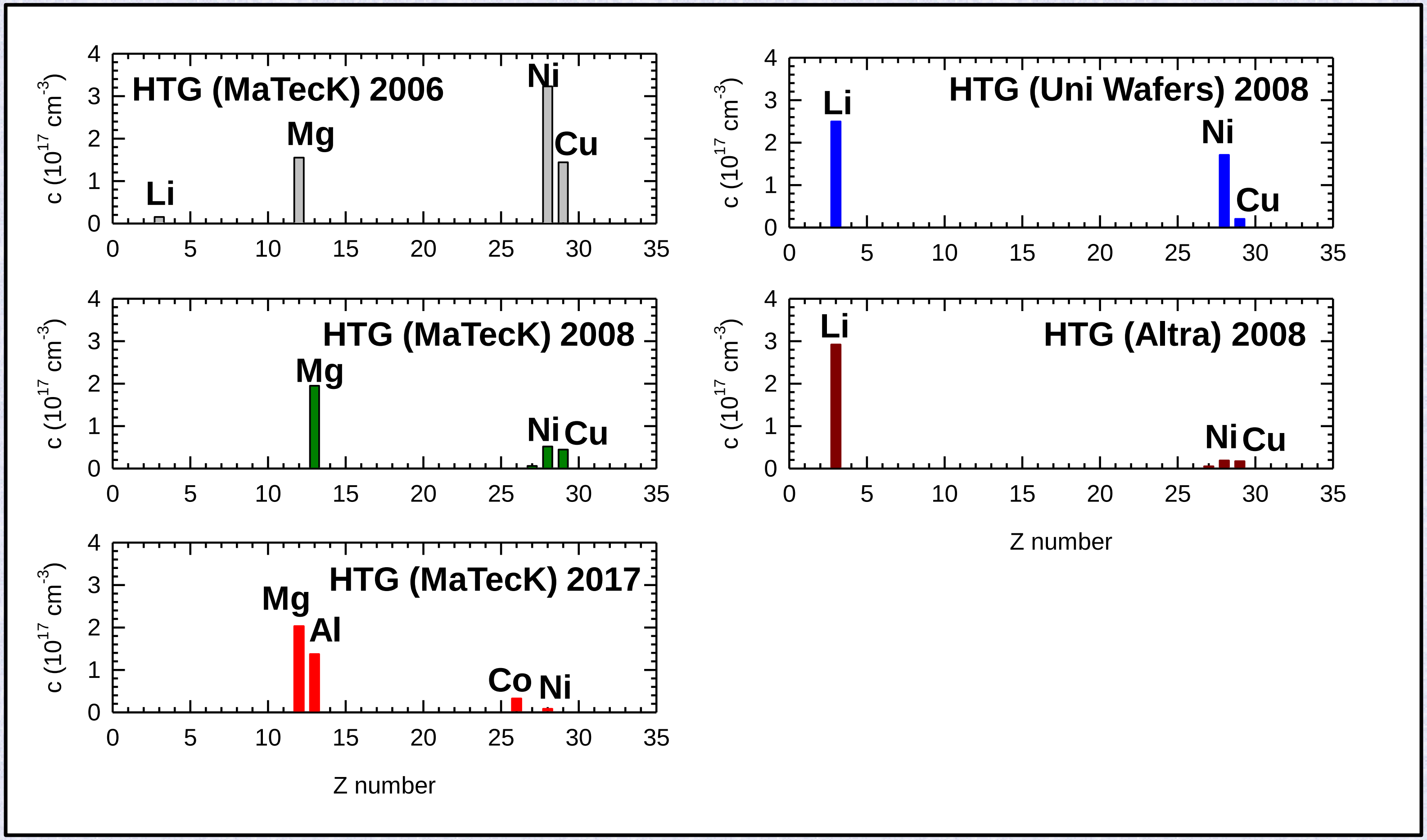

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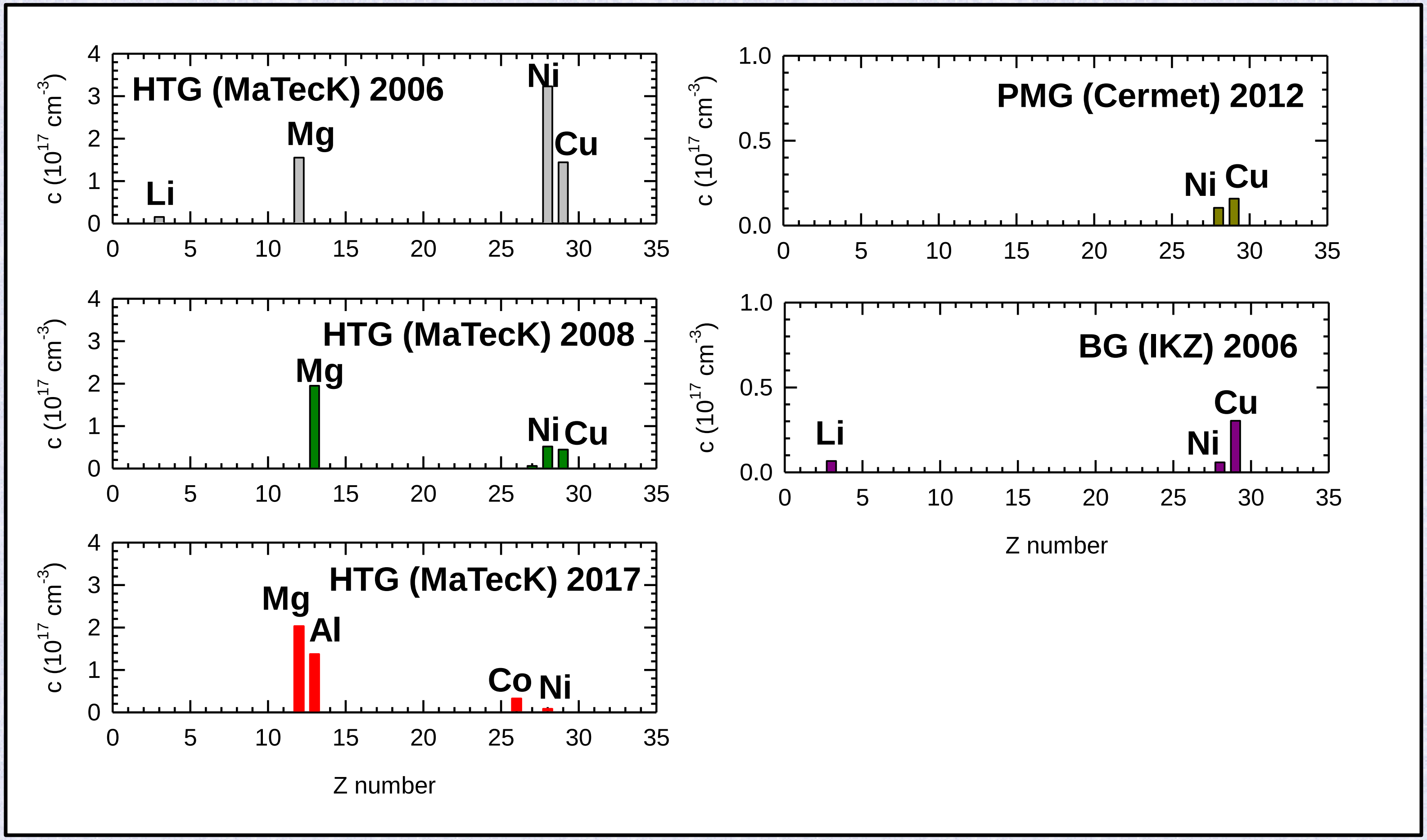
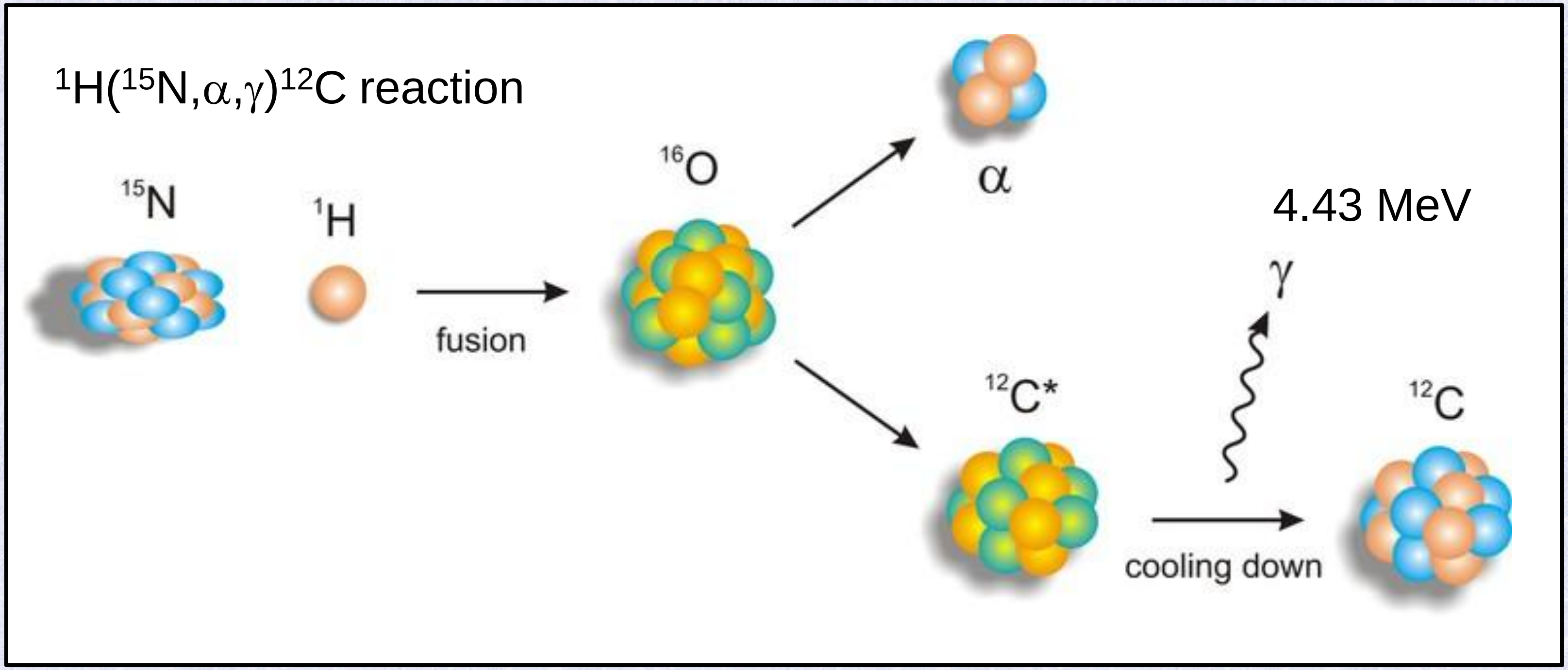


Determination of hydrogen concentration

nuclear reaction analysis (NRA)

$^{15}N + {}^{1}H \rightarrow {}^{12}C + {}^{4}He + \gamma$ rays ⟶ reaction γ rays energy: 4.43 MeV



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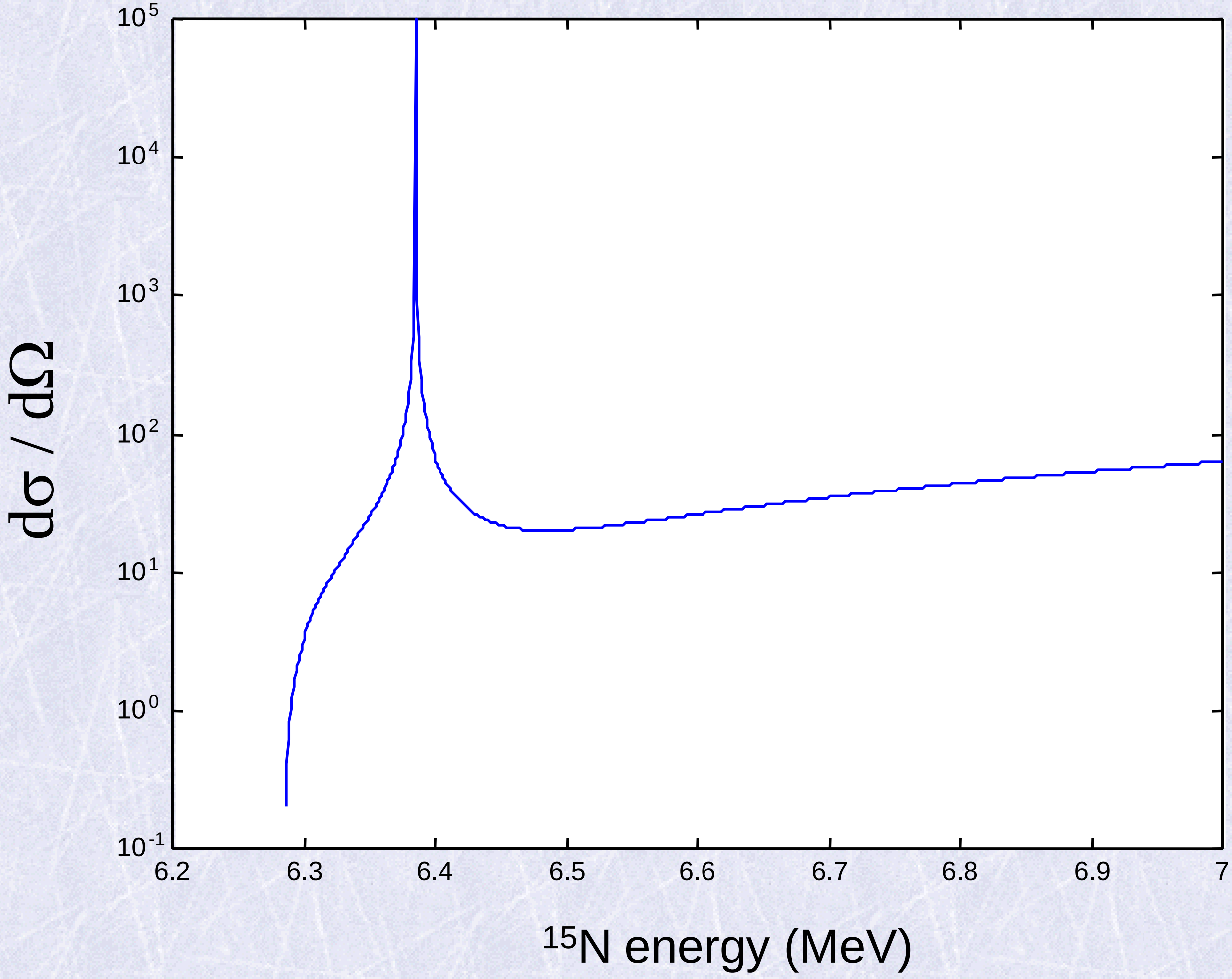

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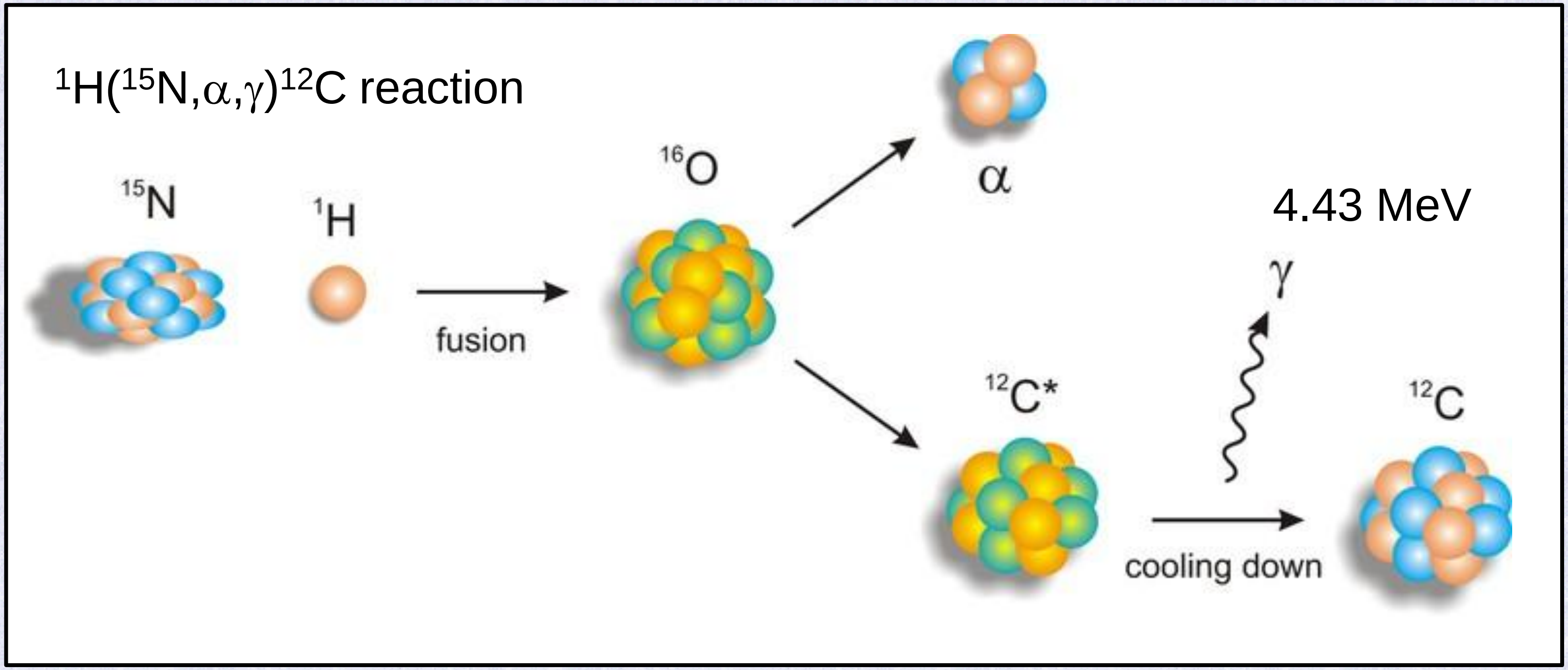
$^{15}N + {}^{1}H \rightarrow {}^{12}C + {}^{4}He + \gamma$ rays ⟶ reaction γ rays energy: 4.43 MeV

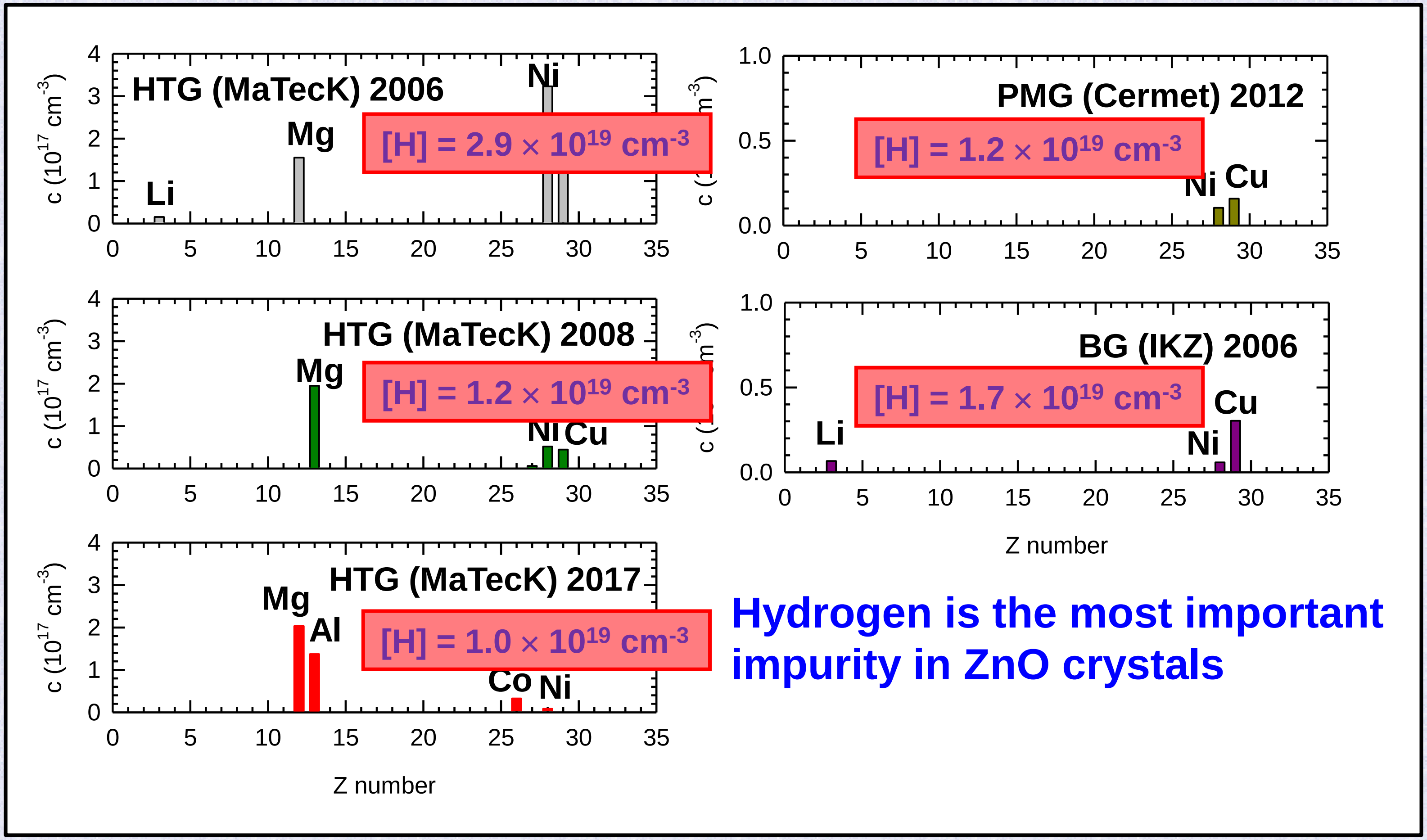


- **depth NRA scan**
  - gradually increasing energy of ^{15}N ions: E = 6.4 – 7.1 MeV
  - detection depth in ZnO increasing from surface up to 300 nm
  - detection limit: 5 ppm

Chemical Analysis of ZnO crystals

- Inductively Coupled Plasma Source – Mass Spectrometry (ICP-MS)

- Nuclear reaction analysis (NRA)

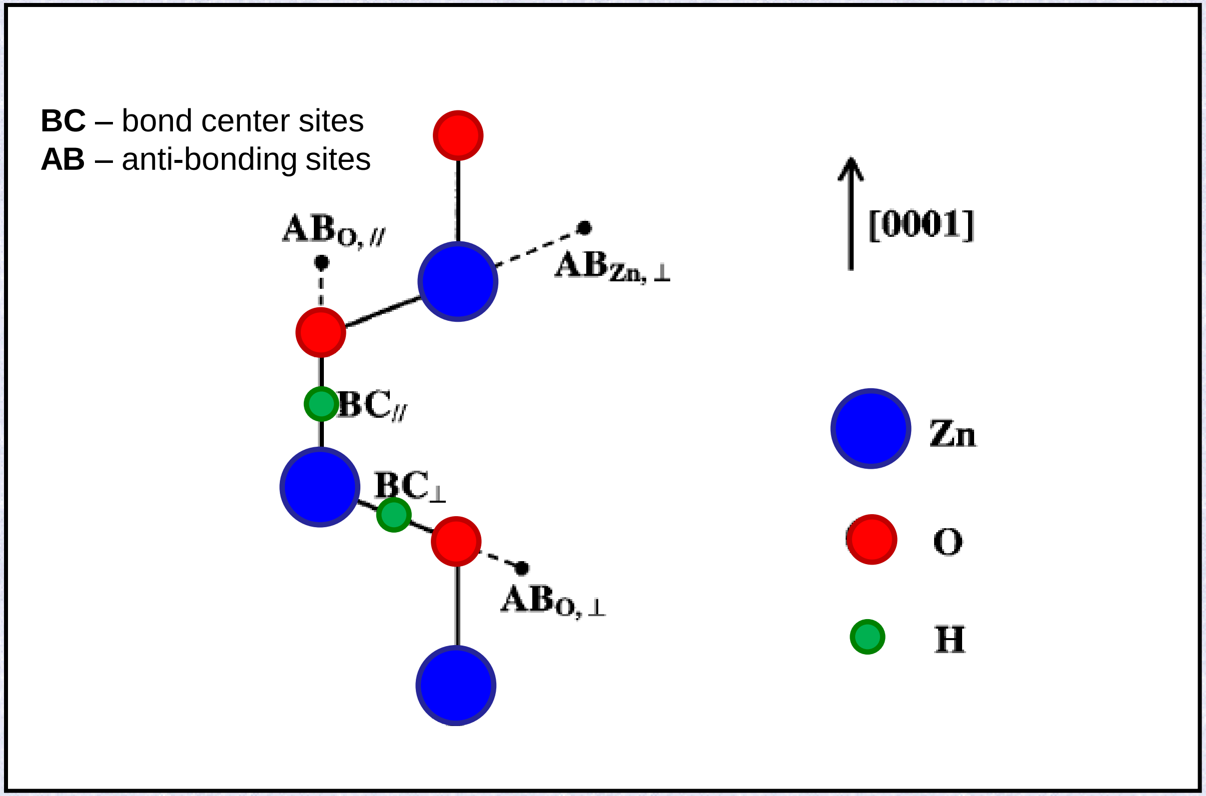


Hydrogen is the most important impurity in ZnO crystals

J. Čížek et al., J. Alloys Compd. ***580****, S51 (2013)*

Interstitial hydrogen in ZnO

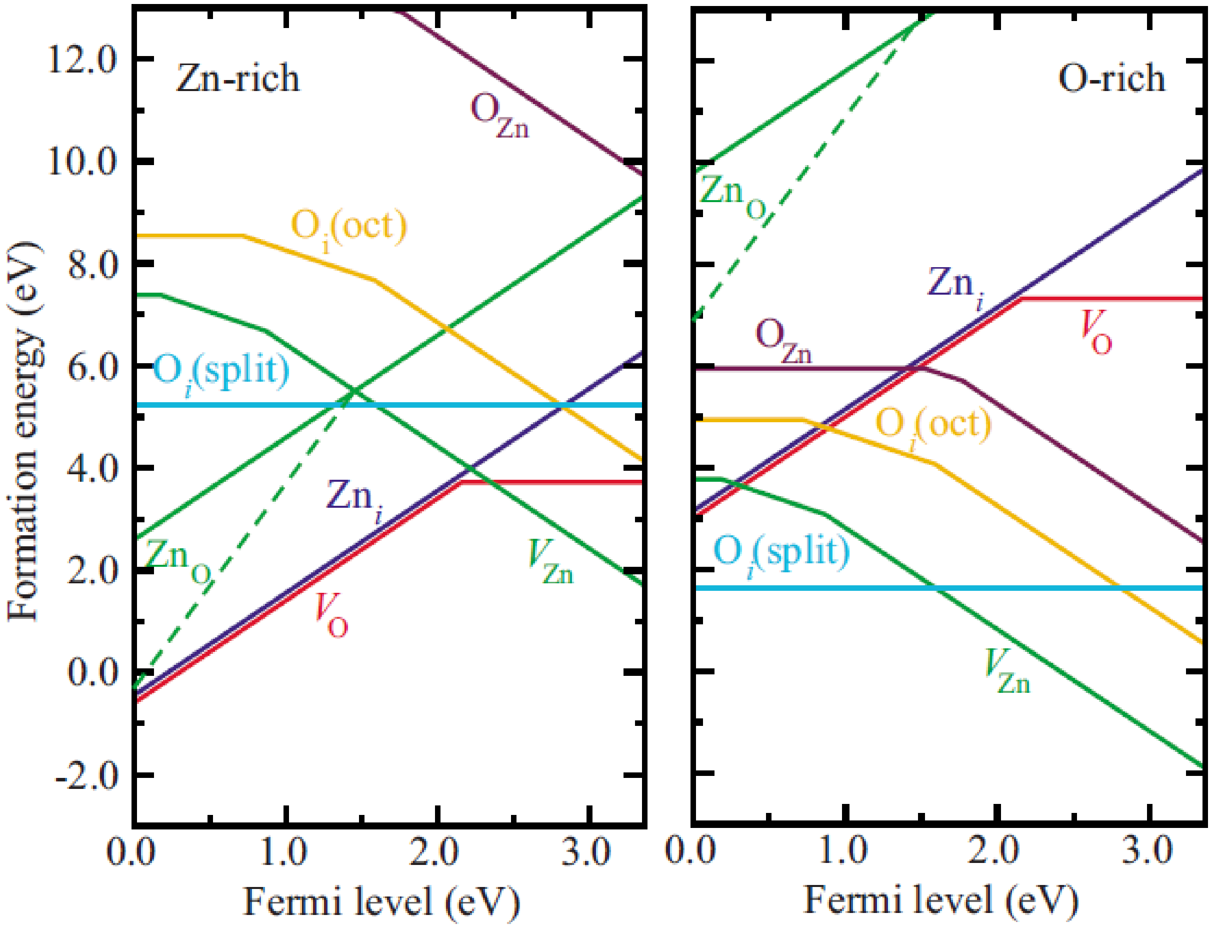
- Hydrogen occupies bond centered (BC) sites in ZnO lattice
- *Van de Walle et al., PRL* ***85****, 1012 (2000)*
- *Janotti et al., Nature Mater.* ***6****, 44 (2007)*



Points defects in ZnO

*A. Janotti, C.G. Van de Walle, PRB **76**, 165202 (2007)*

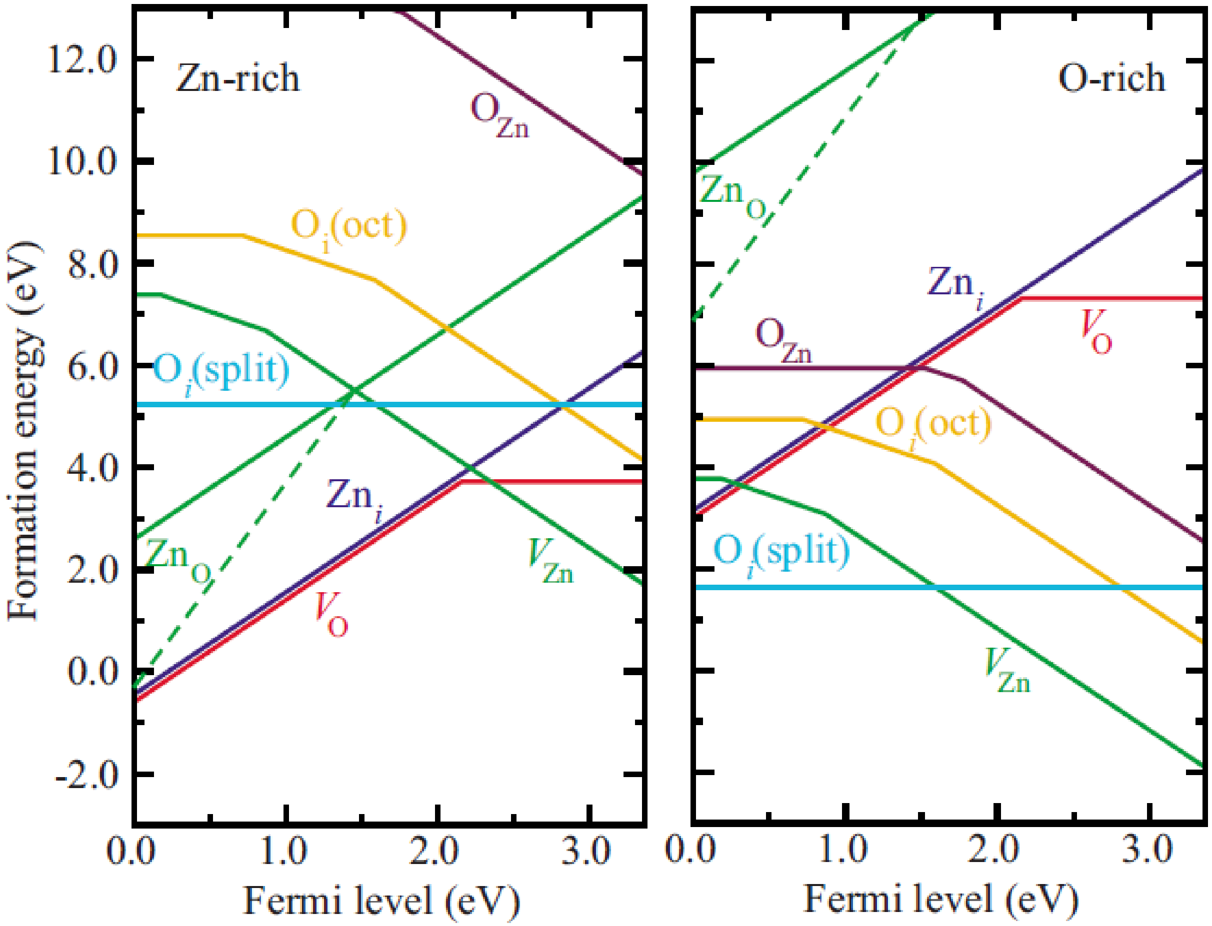
- calculated formation energies of intrinsic points defects in ZnO



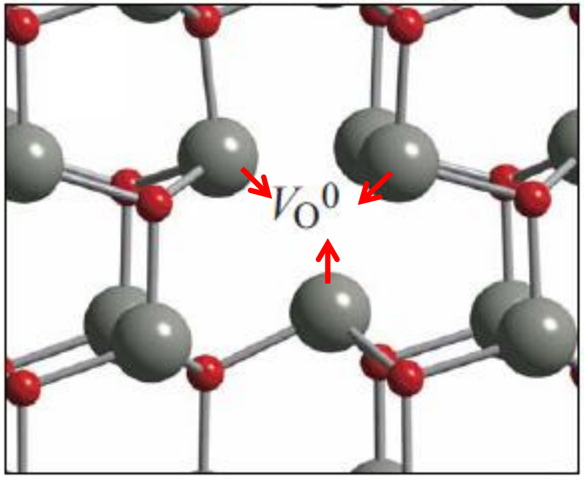
Oxygen vacancy (V_O)

*A. Janotti, C.G. Van de Walle, PRB **76**, 165202 (2007)*

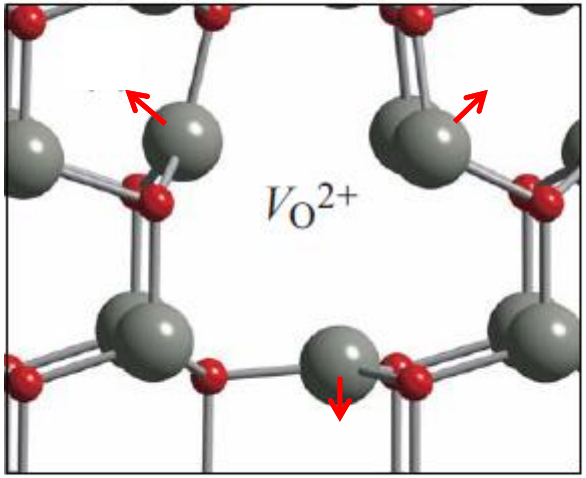
- V_O^+ is thermodynamically unstable (negative U-centre)



V_O^0 12% inward relaxation



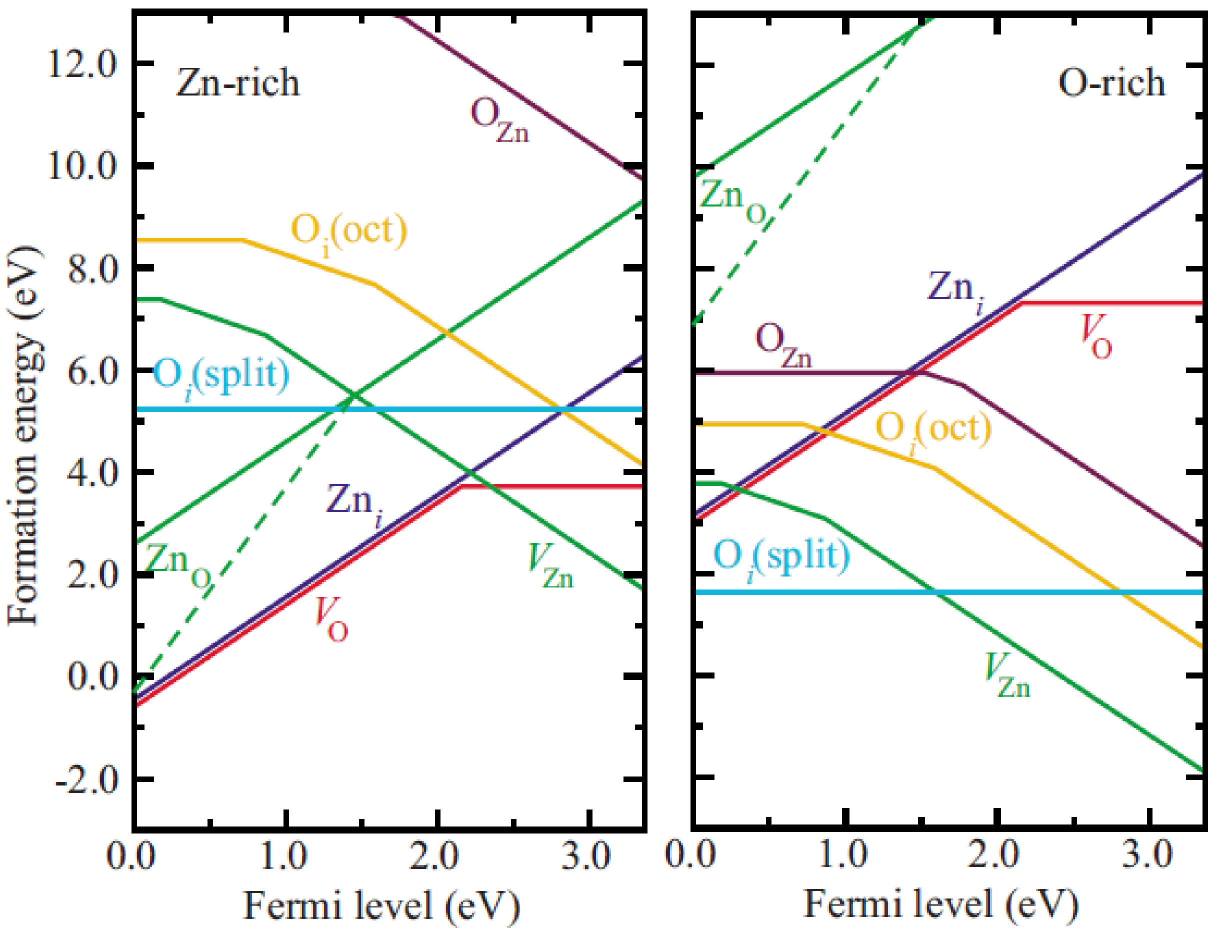
V_O^{2+} 23% outward relaxation



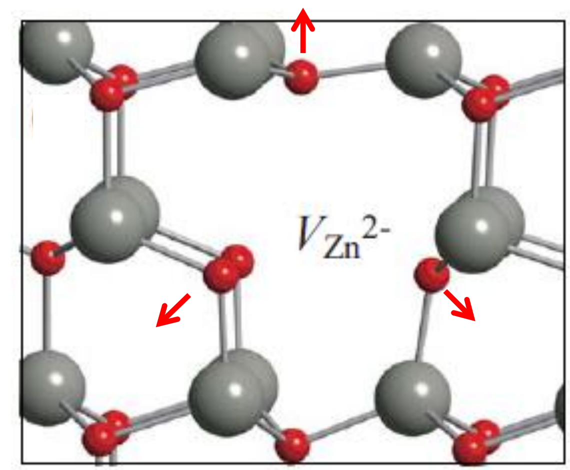
Zinc vacancy (V_{Zn})

*A. Janotti, C.G. Van de Walle, PRB **76**, 165202 (2007)*

• low formation energy in n-type ZnO in O-rich conditions



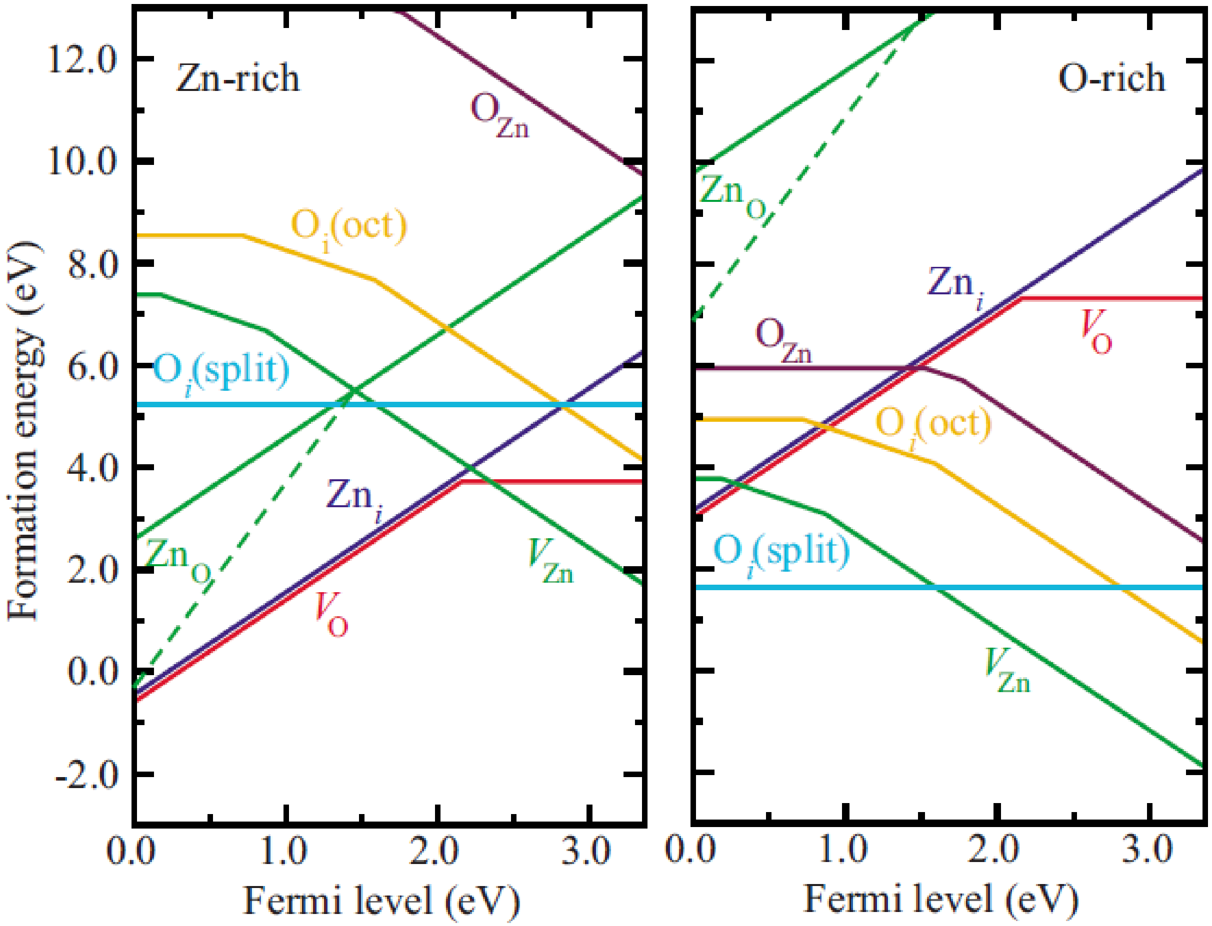
V_{Zn} 10% outward relaxation



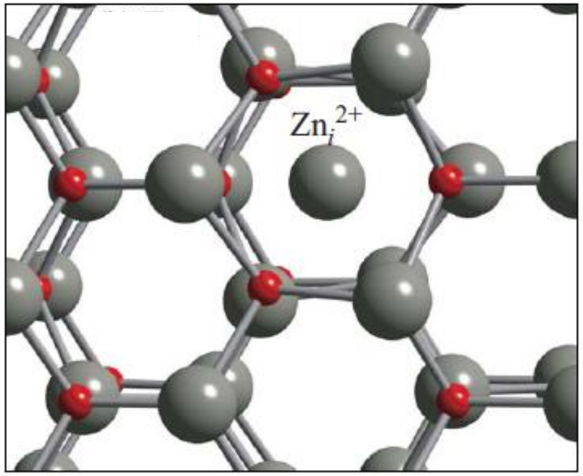
Zinc interstitial (Zn_i)

*A. Janotti, C.G. Van de Walle, PRB **76**, 165202 (2007)*

• high formation energy in n-type ZnO even in Zn-rich conditions



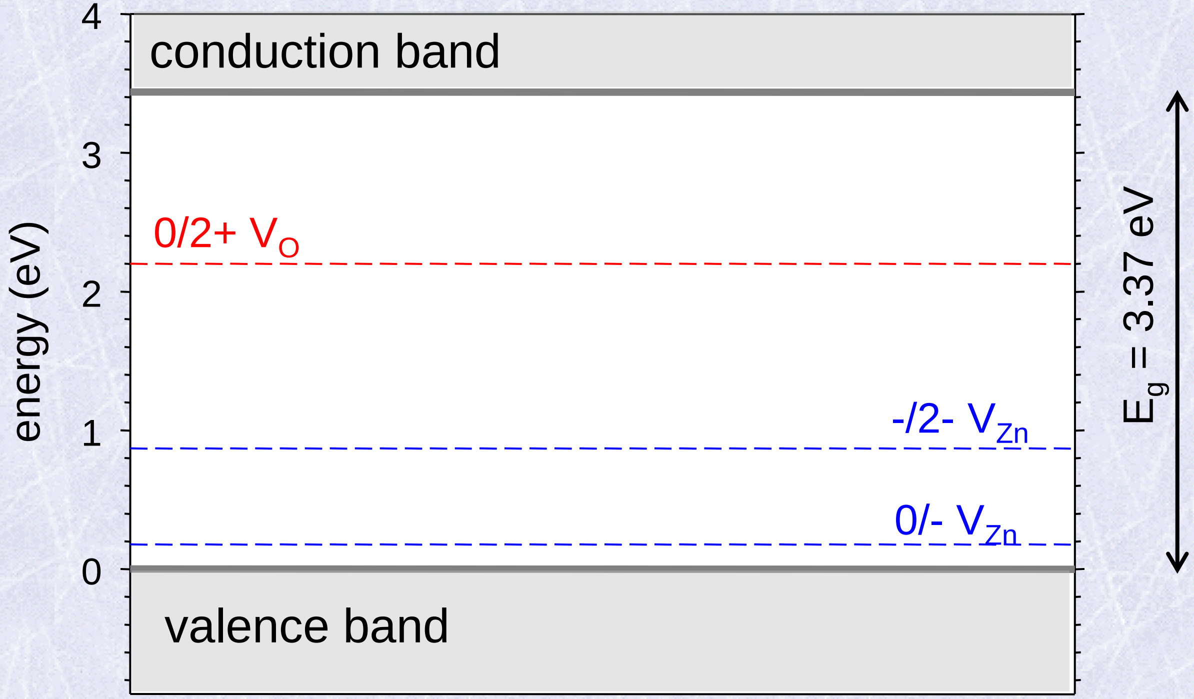
octahedral interstitial site
in the "channel" along the c-axis



Points defects in ZnO

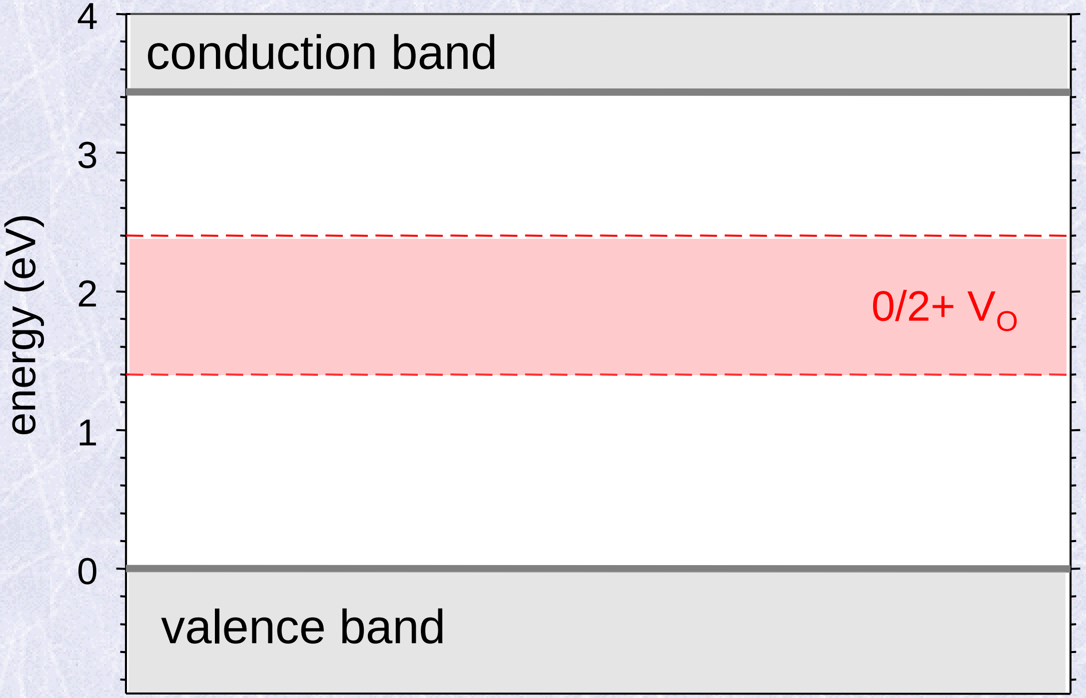
• calculated defect charge transition levels

*A. Janotti, C.G. Van de Walle, PRB **76**, 165202 (2007)*



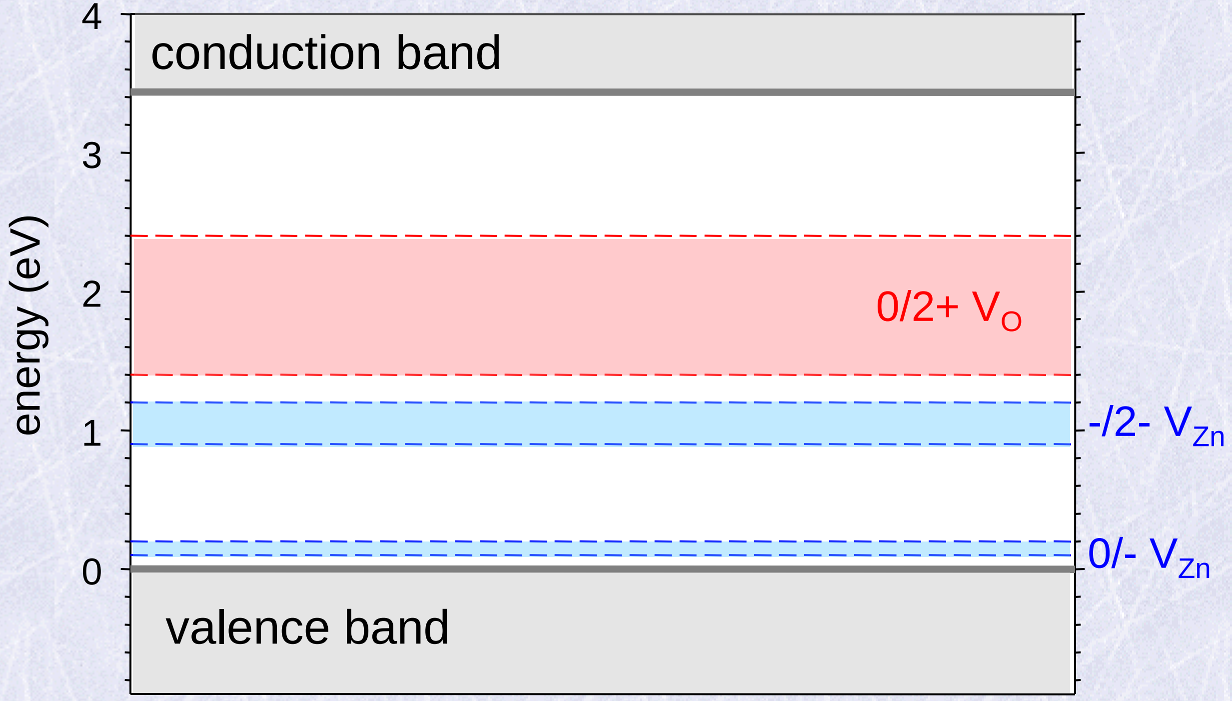
Points defects in ZnO

- calculated defect charge transition levels
- V_O is deep donor



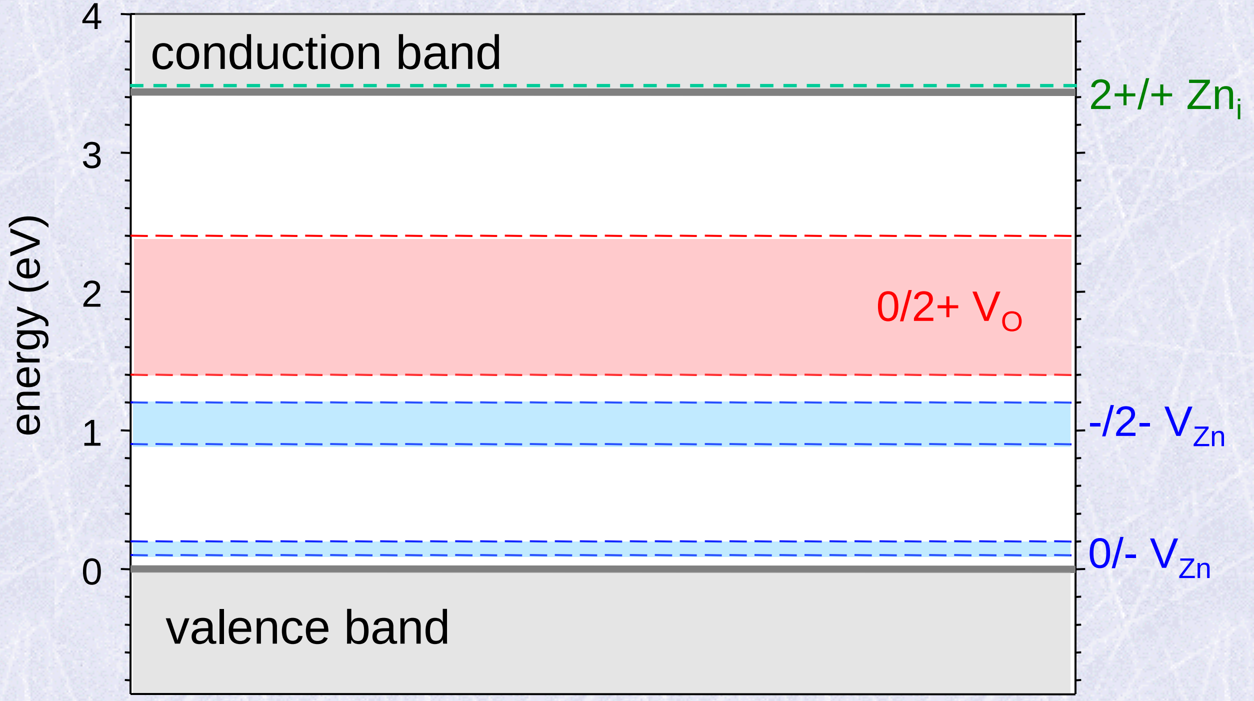
Points defects in ZnO

- calculated defect charge transition levels
- V_O is deep donor
- V_{Zn} is deep acceptor



Points defects in ZnO

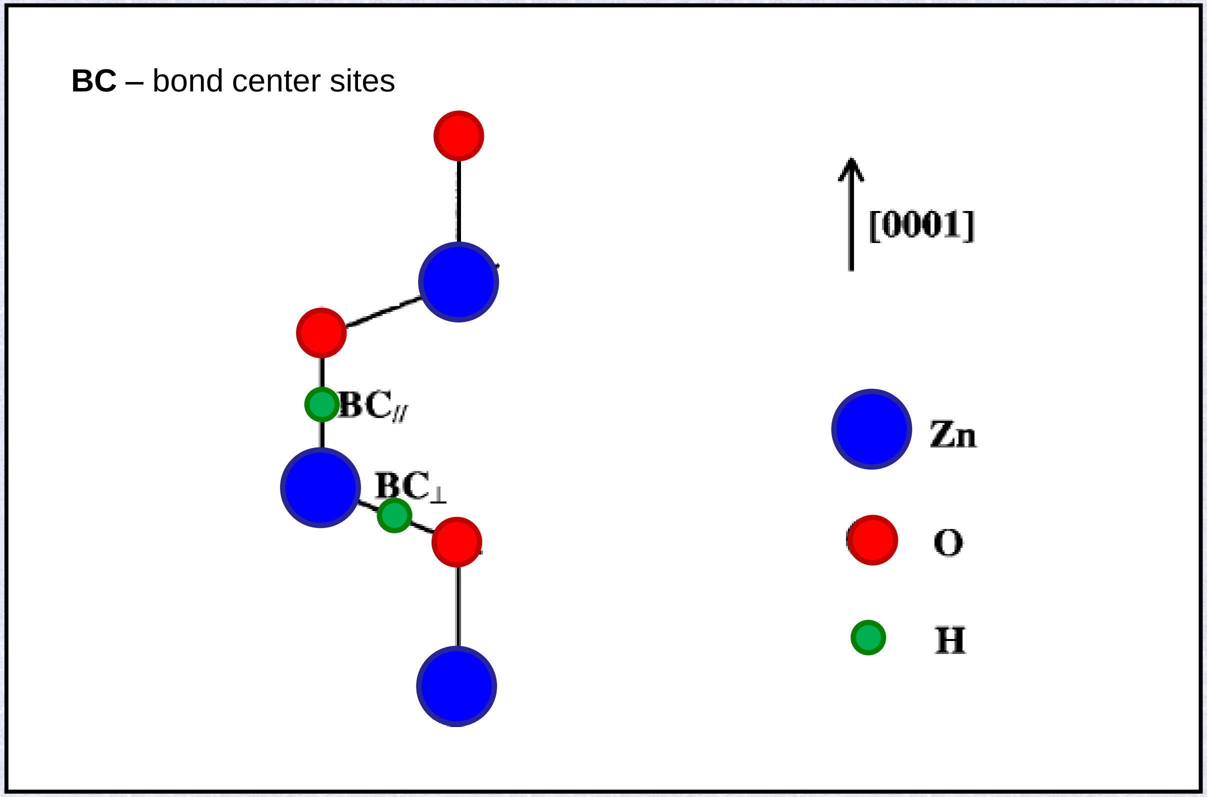
- calculated defect charge transition levels
- V_O is deep donor
- V_{Zn} is deep acceptor
- Zn_i is shallow donor

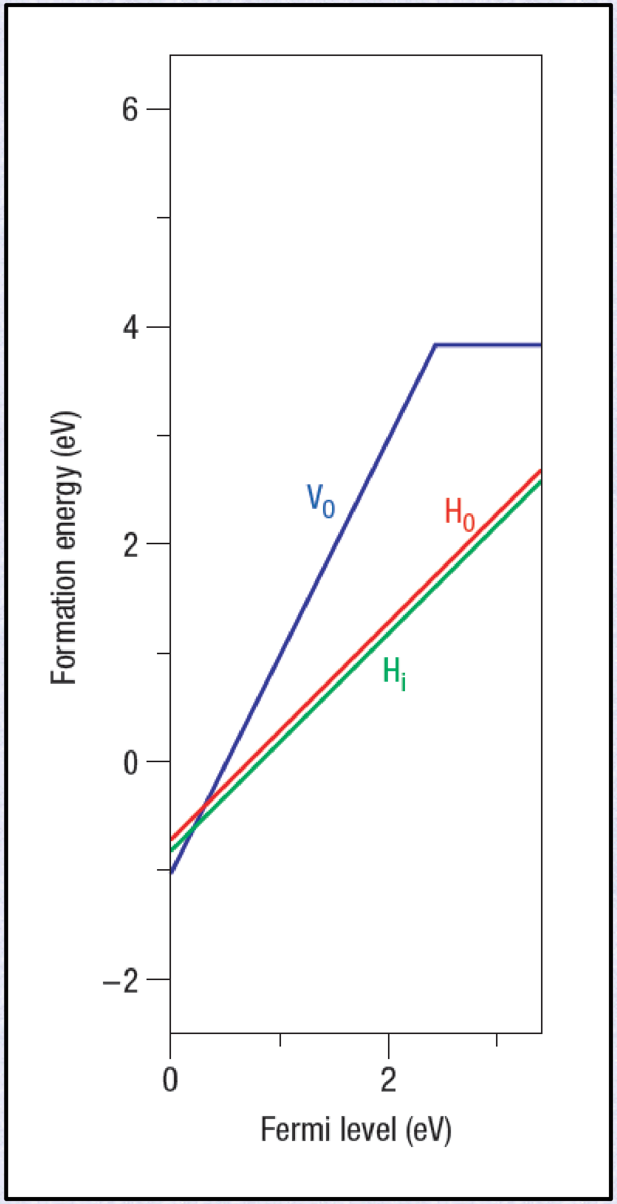


Hydrogen in ZnO

A. Janotti, Ch. Van de Walle, Nature Mater. ***6****, 44 (2007)*

- interstitial hydrogen in ZnO is shallow donor
- hydrogen is in H^+ charge state





Theoretical calculations of positron lifetimes in ZnO

Vacancies in ZnO *G. Brauer et al., PRB **79**, 115212 (2009)*

- LDA (Boroński-Nieminen) approach for electron-positron correlation
- with correction for incomplete positron screening, $\varepsilon_\infty = 4$
- self consistent electron density and potential from VASP
- relaxed geometry of vacancies determined by VASP
- positron-induced forces were taken into account

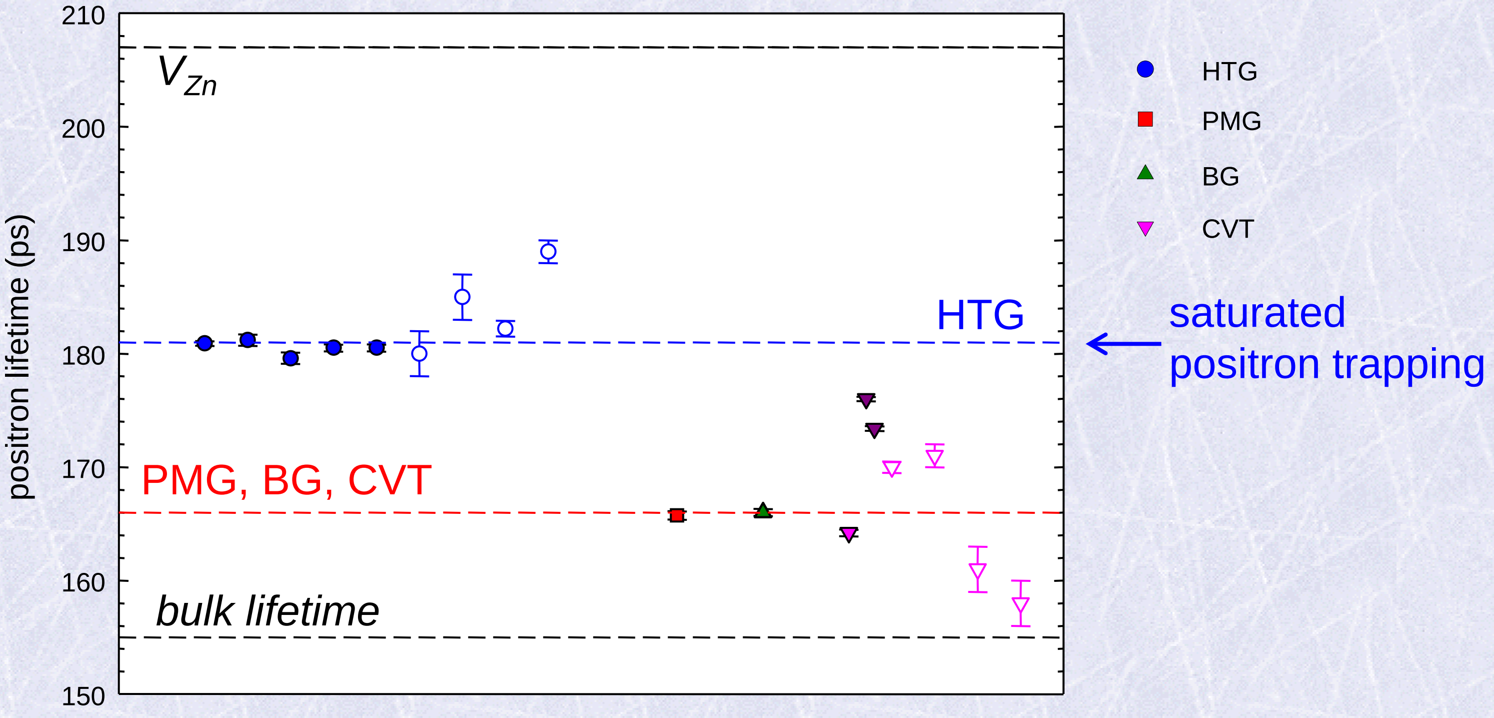
	τ (ps)	E_B (ev)	τ / τ_B
e^-e^+ correlation	LDA (BN, $\varepsilon_\infty = 4$)		
ZnO bulk	154	-	-
O-vacancy	154	~ 0.0	1.00
Zn-vacancy	207	1.11	1.34
Zn+O di-vacancy	253	1.87	1.64

O-vacancy → V_O is unable of positron trapping

Zn-vacancy → V_{Zn} is deep positron trap

As-grown ZnO single crystals – comparison of growth techniques

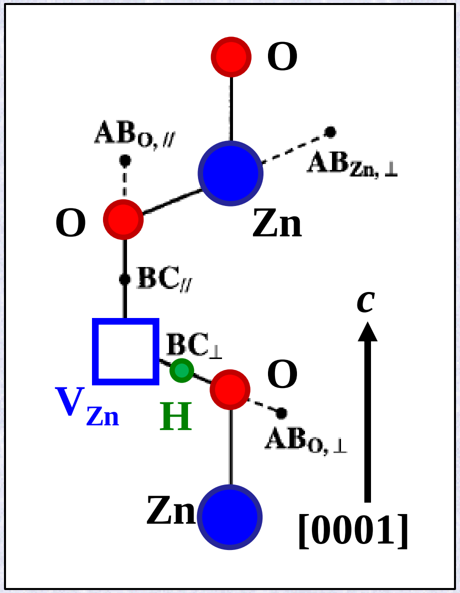
- comparison of ZnO crystals prepared by various techniques
- two groups
  - HTG ZnO crystals: $\tau \approx 180$ ps $\longrightarrow$ $\tau_B < \tau < \tau_{\text{Zn-vacancy}}$
  - PMG, BG, CVT ZnO crystals: $\tau \approx 166$ ps

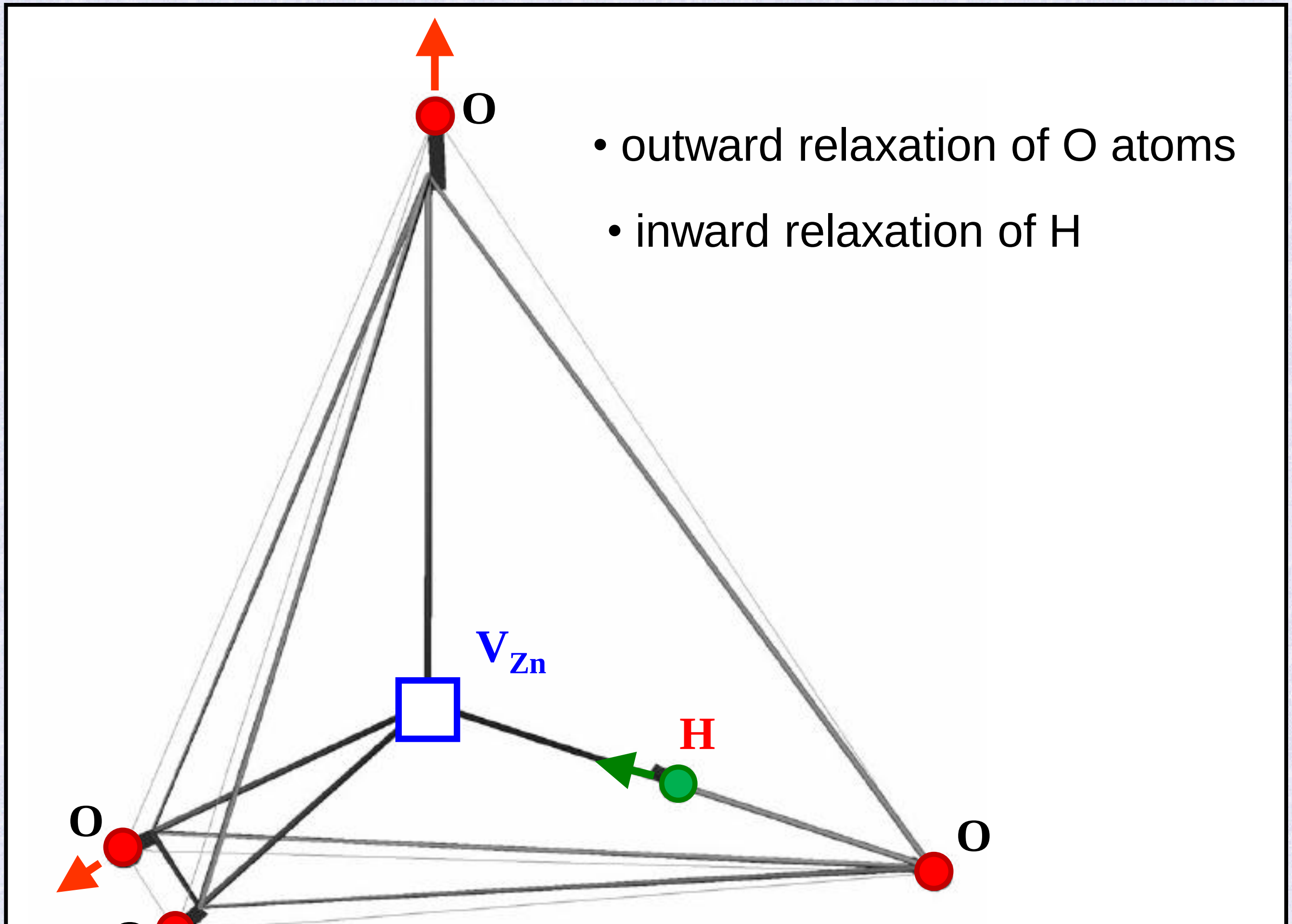


Complexes V_{Zn} + H

Calculated lowest energy configuration: V_{Zn} + 1H, $BC_{\perp}$ site, τ = 179 ps

relaxation of O atoms and H

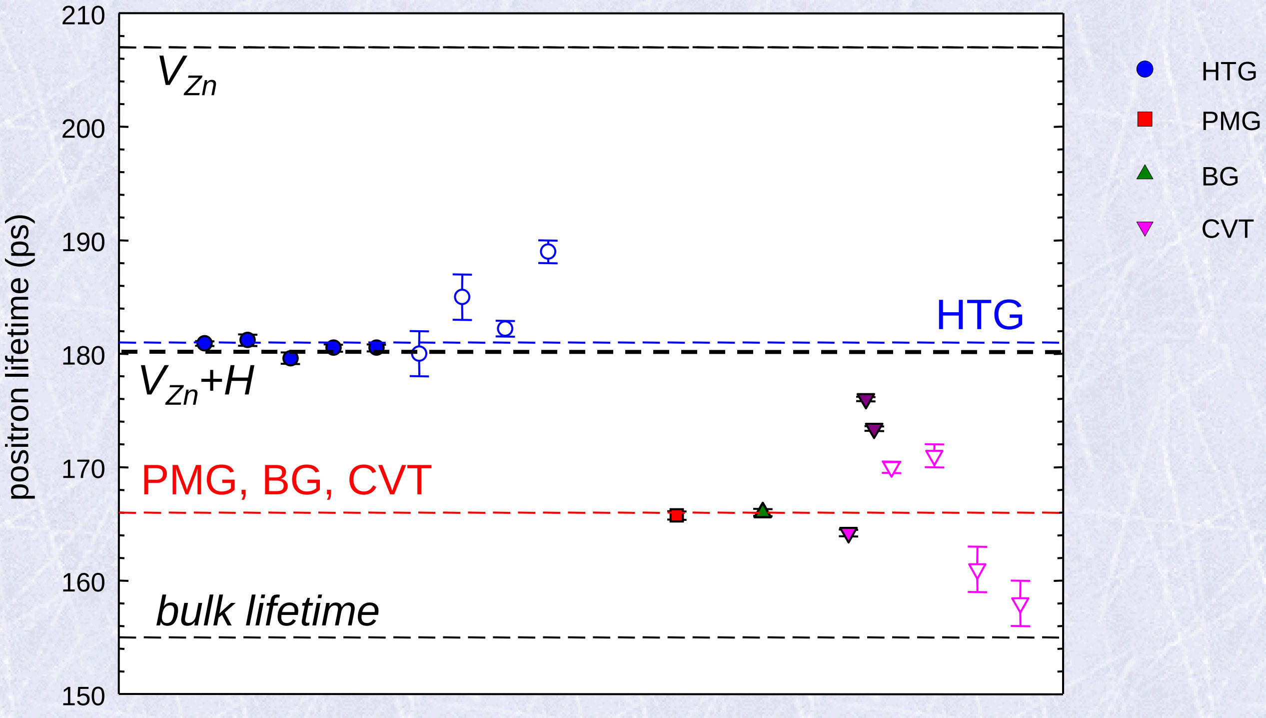




*G. Brauer et al., PRB **79**, 115212 (2009)*

As-grown ZnO single crystals – comparison of growth techniques

- comparison of ZnO crystals prepared by various techniques
- two groups
  - → HTG ZnO crystals: $\tau \approx 180$ ps ⟶ V_{Zn}+H complexes
  - → PMG, BG, CVT ZnO crystals: $\tau \approx 166$ ps



Estimation of V_{Zn+H} concentration

HTG ZnO, MaTecK

- estimation of V_{Zn}+H concentration

$$c_V = \frac{1}{\nu_v}\frac{1}{\tau_B}\left(\frac{L_{+,B}^2}{L_+^2} - 1\right)$$

$L_{+,B} \approx 100\,\text{nm}$ (CVT ZnO)

$\nu_v \approx 10^{15}\,\text{at.s}^{-1}$

$\tau_B = 154\,\text{ps}$

HTG ZnO

[V_{Zn}+H]

$\Rightarrow$ **$c_v \approx 10$ ppm**

(4×10^{17} cm^{-3})

simple trapping model

positron trapping rate
$K_v \approx 2 \times 10^{10}\ \text{s}^{-1}$

$\Downarrow$

free positron component
$I_1 \approx 4\ \%,\ \tau_1 \approx 30\ \text{ps}$

$\Downarrow$

too weak & short
to be resolved in PL spectrum

- hydrogen concentration (NRA)

[H] = (1-3) × 10^{19} cm^{-3} $\rightarrow$ **[H] ≈ 50 [V_{Zn}+H]**

*J. Čížek et al., J. Phys. Conf. Ser. **791**, 012017 (2017)*

Li_{Zn} defect

HTG ZnO, MaTecK

- positron trapping in negatively charged substitution Li (Li_{Zn})
  *K.M. Johansen et al., PRB **83**, 245208 (2011)*

$$c_V = \frac{1}{\nu_v}\frac{1}{\tau_B}\left(\frac{L_{+,B}^2}{L_+^2} - 1\right)$$

$L_{+,B} \approx 100\,\mathrm{nm}$ (CVT ZnO)

$\nu_v \approx 10^{15}\ \mathrm{at.s^{-1}}$

$\tau_B = 154$ ps

HTG ZnO

$[V_{Zn}+H]$

$\Rightarrow$ **$c_v \approx 10$ ppm**

($4\times10^{17}\ \mathrm{cm^{-3}}$)

Sample	[Li] $10^{17}\ \mathrm{cm^{-3}}$	
HT-grown MaTecK 2006	1.5	**181.2(4) ps**
HT-grown MaTecK 2008	0.02	**179.6(3) ps**
HT-grown MaTecK 2017	0.008	**180.1(3) ps**
HT-grown Uni-Wafers	2.5	**180.5(3) ps**
HT-grown Altramet	2.3	**180.7(3) ps**
PM-grown Cermet	0.004	
BG-grown IKZ Berlin	0.06	

- Li concentration (ICPMS,GDMS)

$[Li] = (0.008\text{-}2.5) \times 10^{17}\ \mathrm{cm^{-3}}$

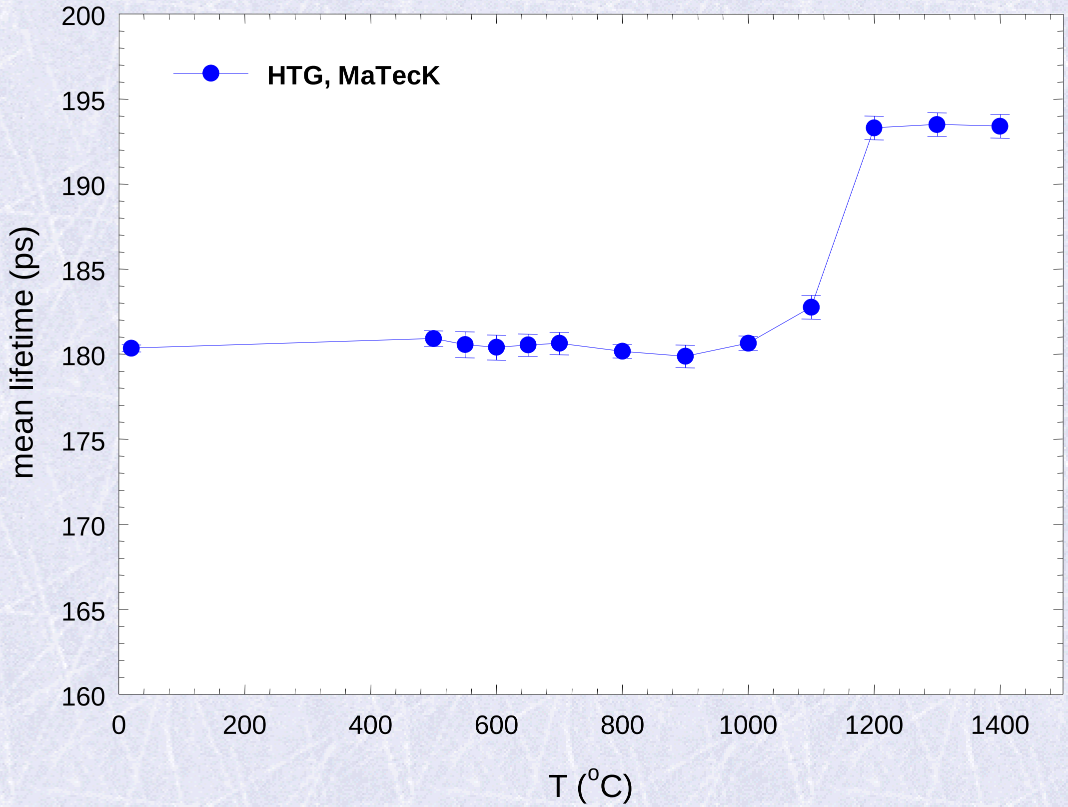
$\rightarrow$ **lower than concentration of positron traps**

$\rightarrow$ **strong variations of [Li]**
but no variations of positron lifetime

Annealing of ZnO crystals in air

- ZnO easily decomposes to its components $ZnO \leftrightarrow Zn + ½ O_2$, $\Delta H = 350.5$ kJ/mol
- upon heating ZnO dissociates
- high vapour pressure of Zn and $O_2 \Rightarrow$ ZnO evaporation
- $p_{Zn} > p_{O2} \Rightarrow$ Zn evaporation is more intensive $\Rightarrow$ formation of V_{Zn}

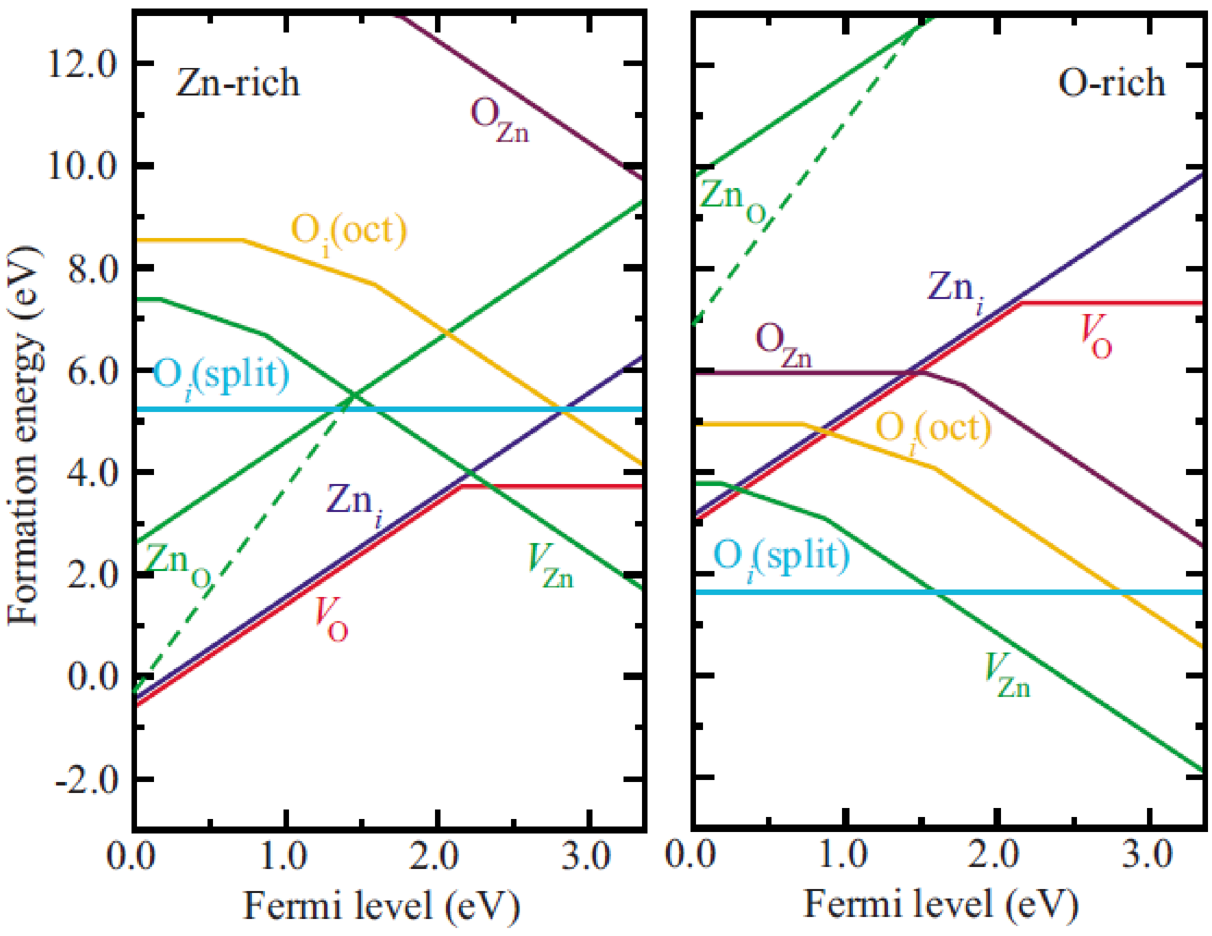
HTG, MaTecK



Points defects in ZnO

*A. Janotti, C.G. Van de Walle, PRB **76**, 165202 (2007)*

• calculated formation energies of intrinsic points defects in ZnO



Annealing of ZnO crystals in air

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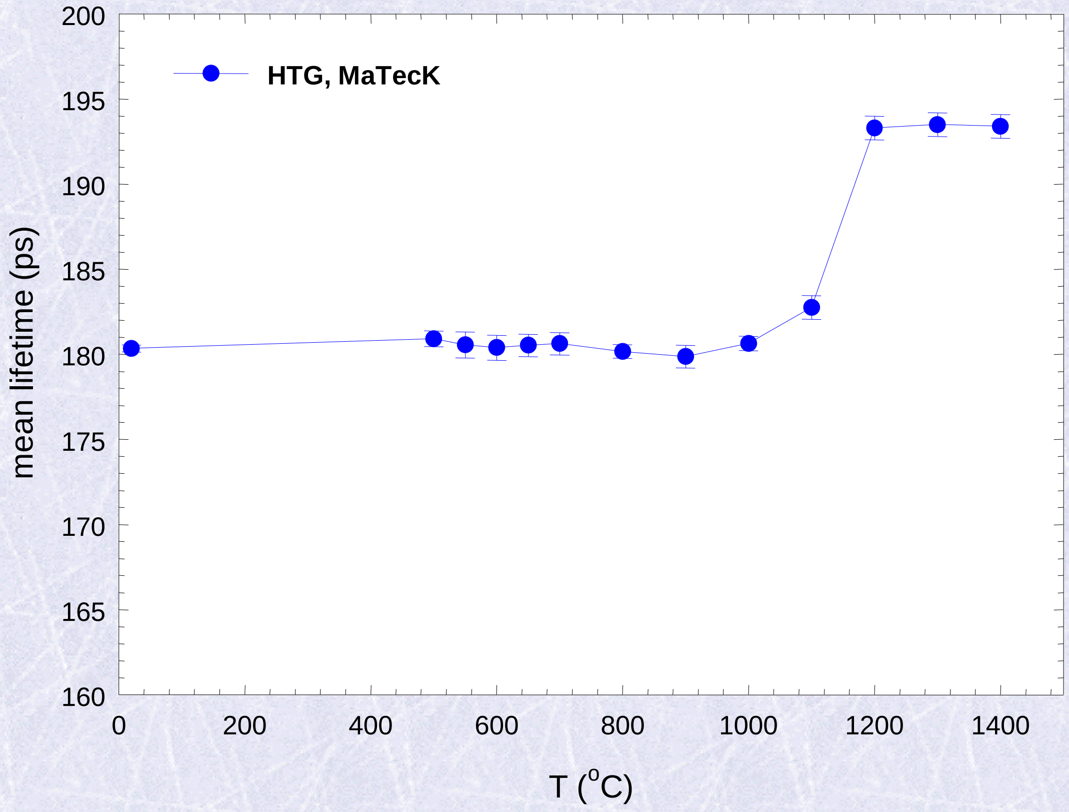
HTG, MaTecK



Annealing of ZnO crystals in air

- ZnO easily decomposes to its components ZnO $\leftrightarrow$ Zn + ½ O_2, ΔH = 350.5 kJ/mol
- upon heating ZnO dissociates
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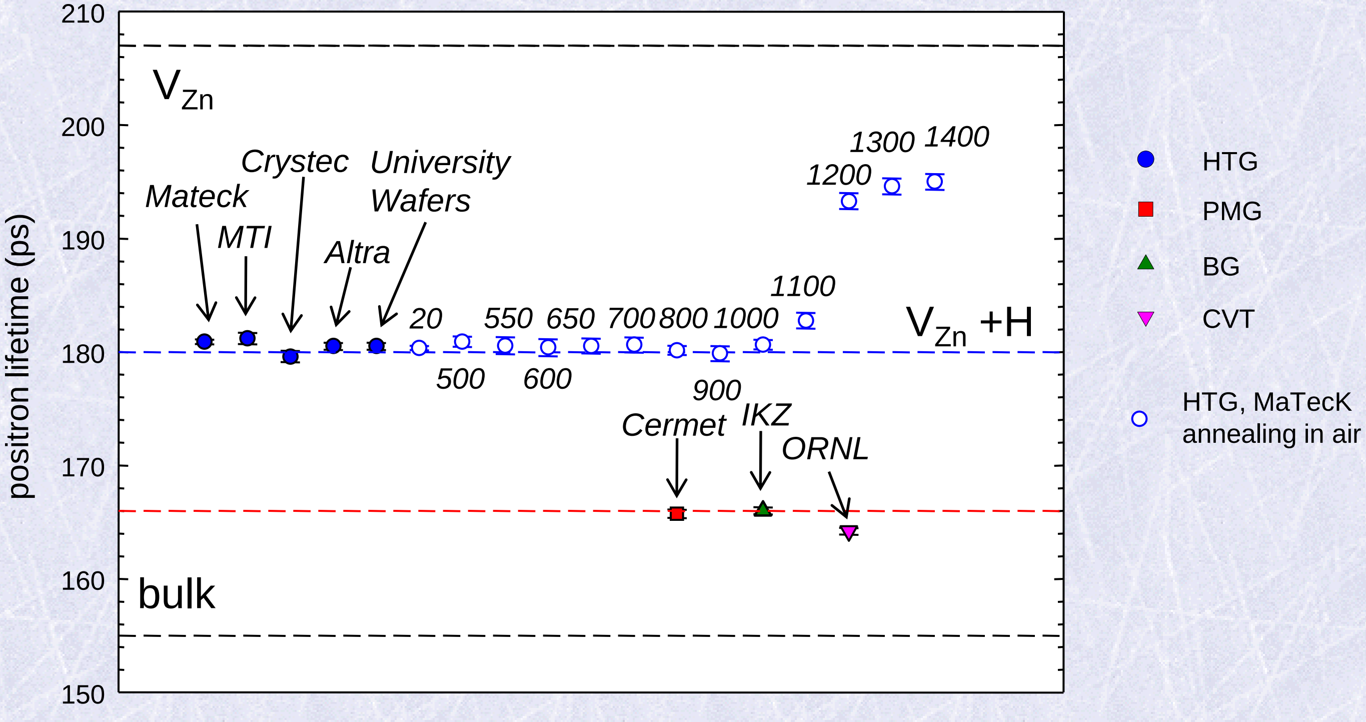
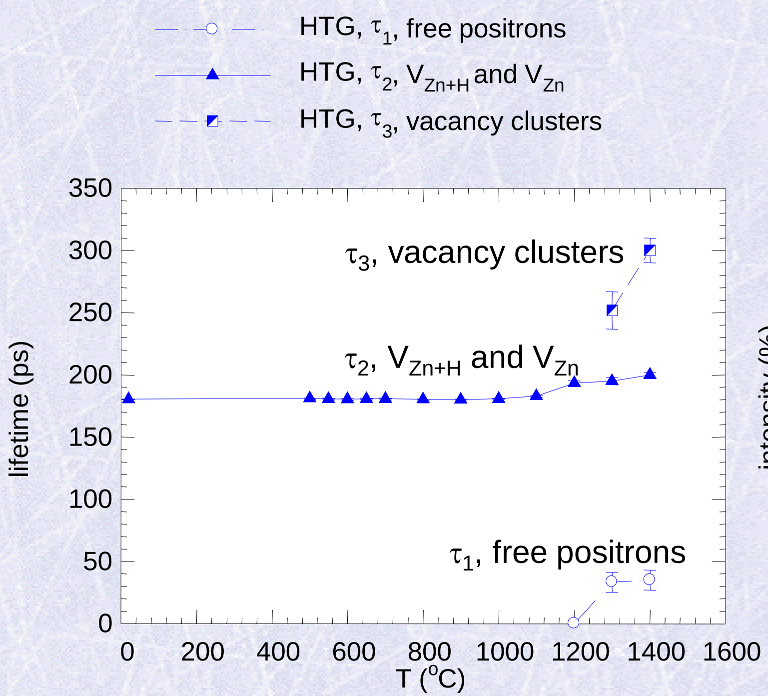
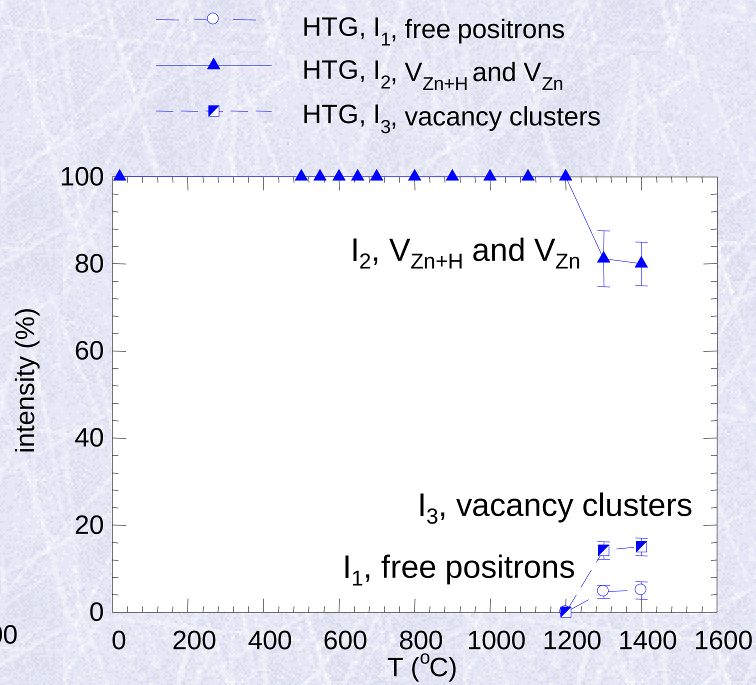
- $p_{Zn} > p_{O2}$ $\Rightarrow$ Zn evaporation is more intensive $\Rightarrow$ formation of V_{Zn}



Annealing of ZnO crystals in air

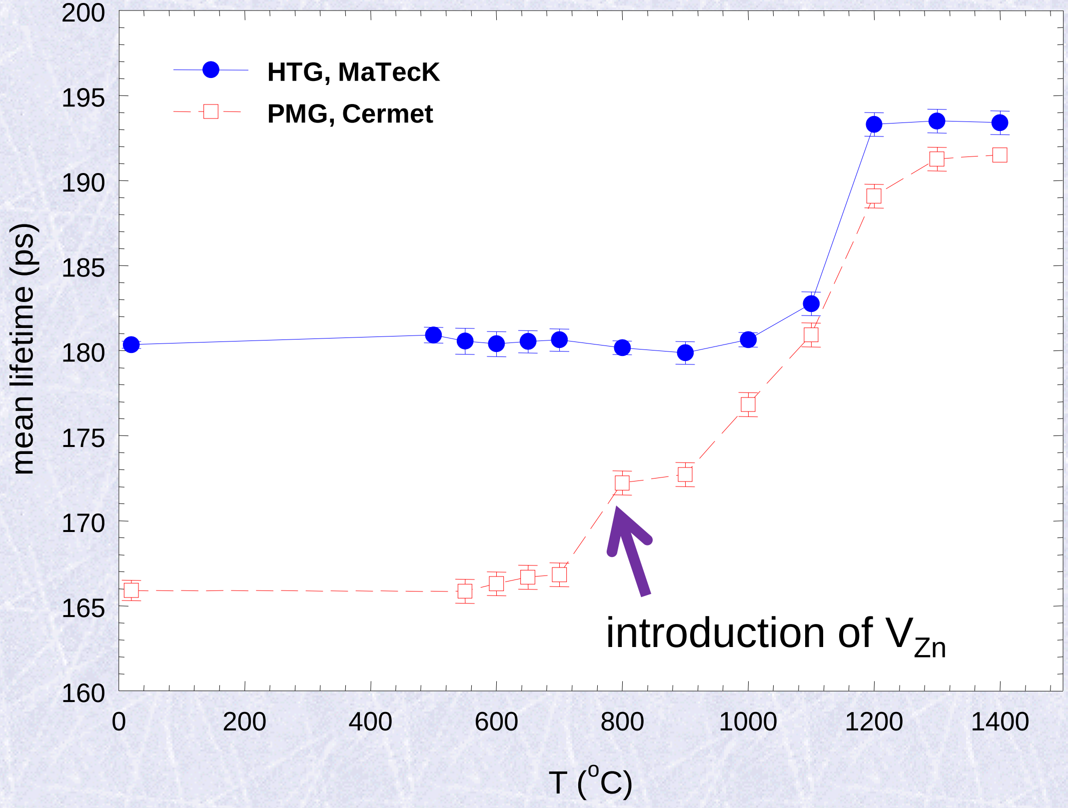
- HTG ZnO (MaTecK)
- decomposition of positron lifetime spectra
- free positron component appeared at T > 1200°C when V_{Zn} agglomerate to clusters





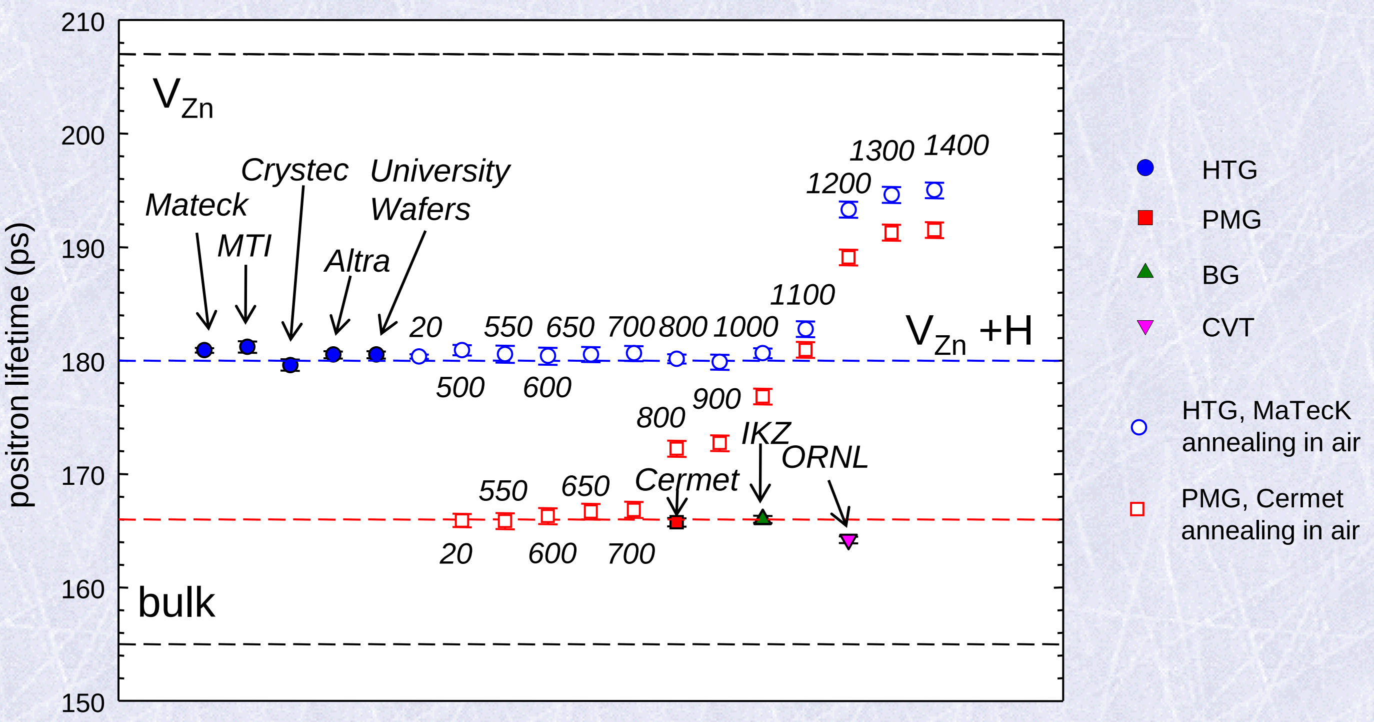
Annealing of ZnO crystals in air

- ZnO easily decomposes to its components   ZnO $\leftrightarrow$ Zn + ½ O_2, ΔH = 350.5 kJ/mol
- upon heating ZnO dissociates
- high vapour pressure of Zn and O_2 $\Rightarrow$ ZnO evaporation
- $p_{Zn} > p_{O2}$ $\Rightarrow$ Zn evaporation is more intensive $\Rightarrow$ formation of V_{Zn}



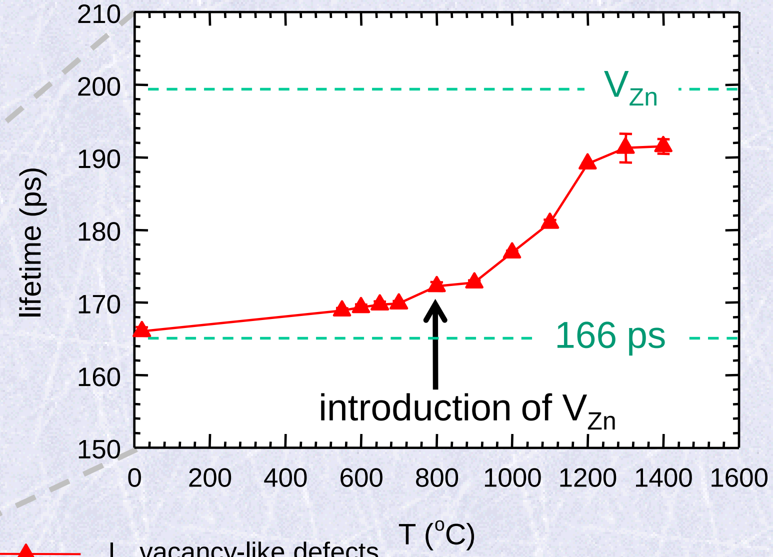
Annealing of ZnO crystals in air

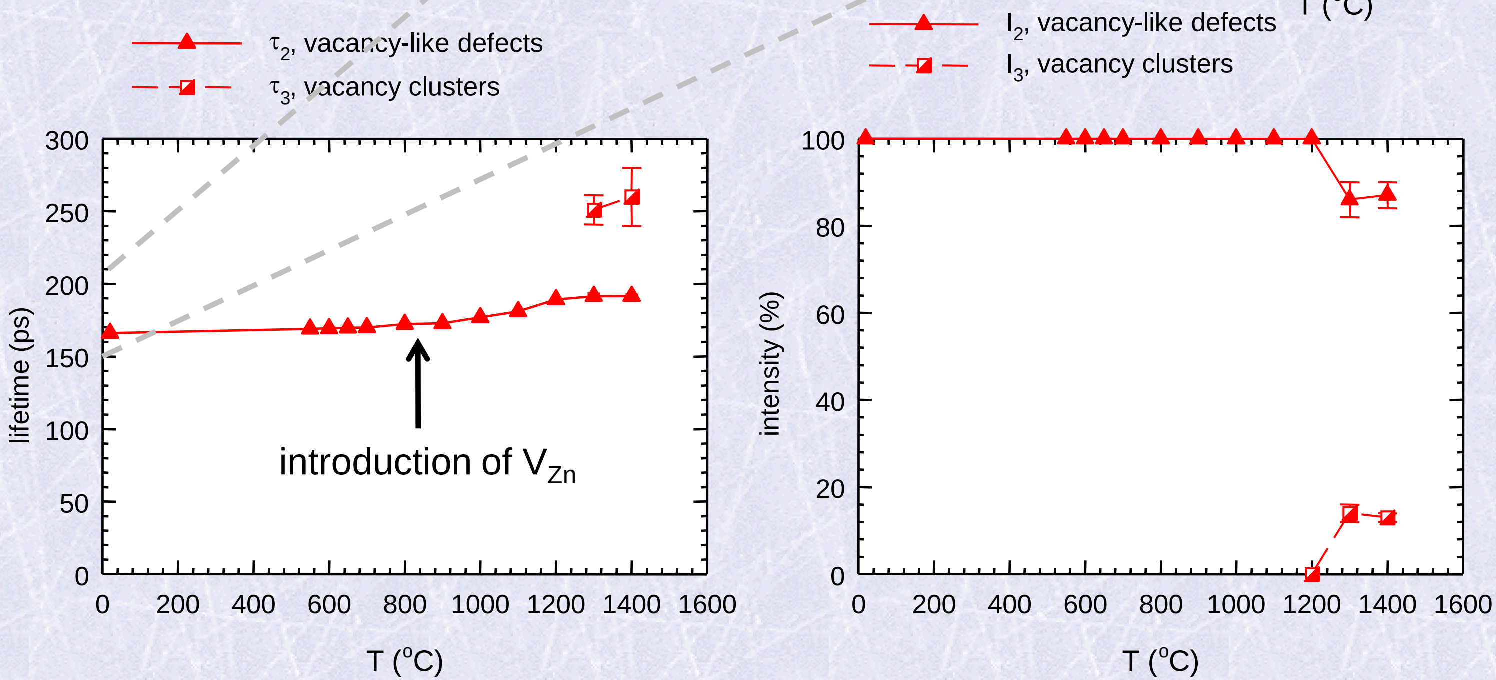
- ZnO easily decomposes to its components $ZnO \leftrightarrow Zn + \frac{1}{2} O_2$, $\Delta H = 350.5$ kJ/mol
- upon heating ZnO dissociates
- high vapour pressure of Zn and $O_2 \Rightarrow$ ZnO evaporation
- $p_{Zn} > p_{O2} \Rightarrow$ Zn evaporation is more intensive $\Rightarrow$ formation of V_{Zn}



Annealing of ZnO crystals in air

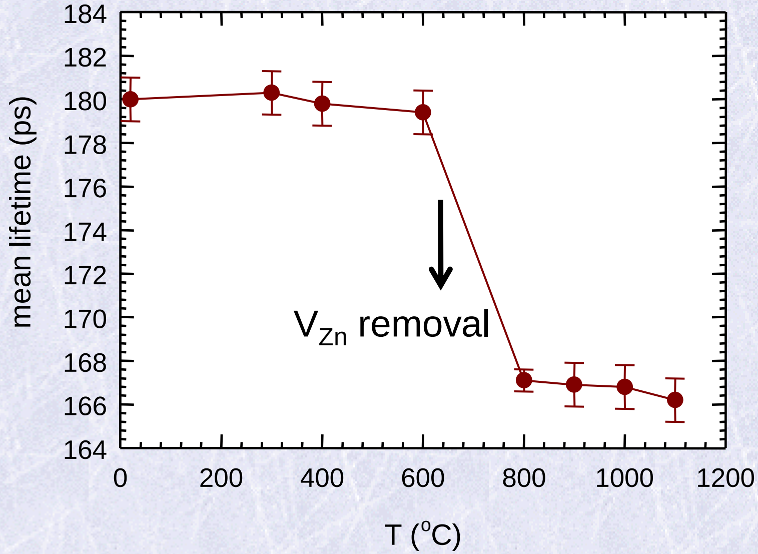
- PMG ZnO (Cermet)
- decomposition of positron lifetime spectra
- V_{Zn} introduced at T > 800°C
- T > 1200°C agglomeration of vacancies

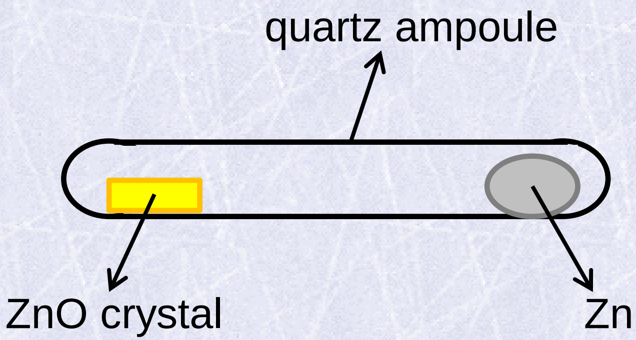


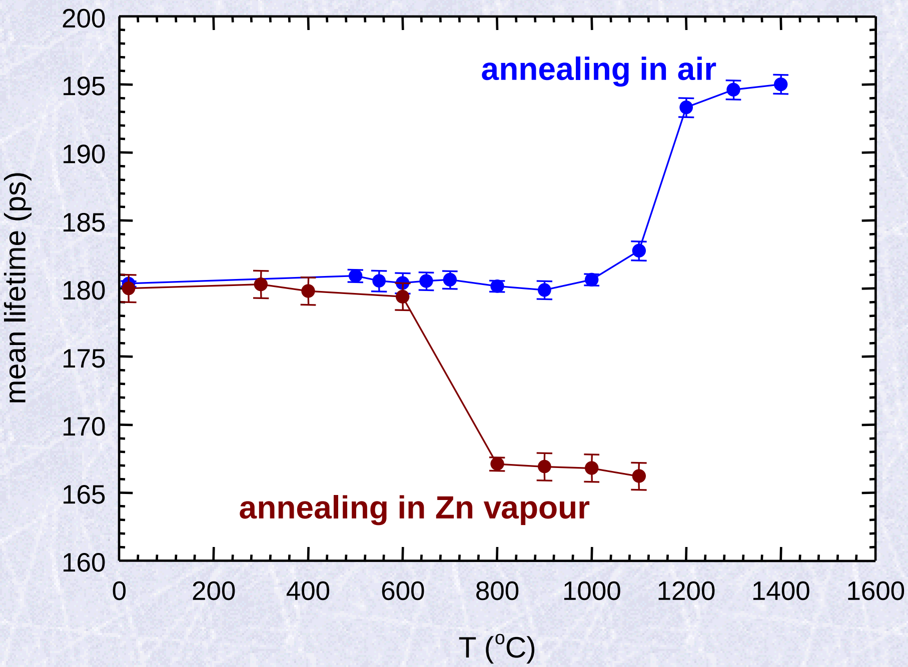


Annealing of ZnO crystals in Zn vapour

- HTG ZnO (MaTecK)
- annealing in evacuated ampoule with metallic Zn at various temperatures for 12 h



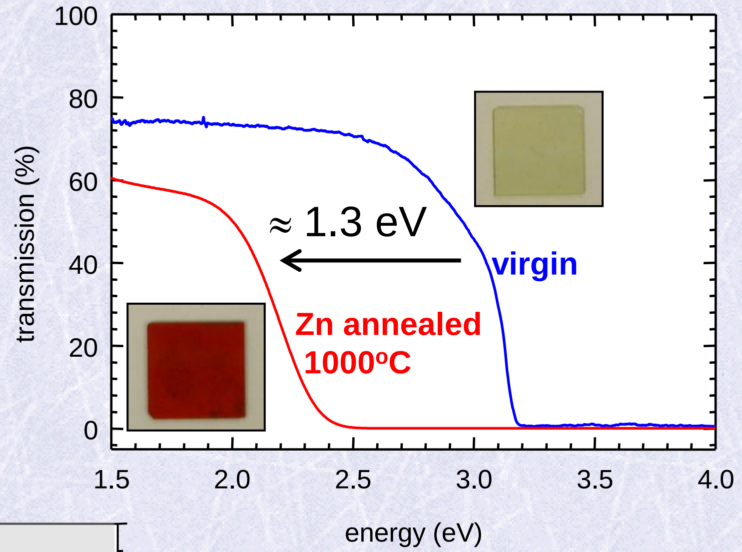




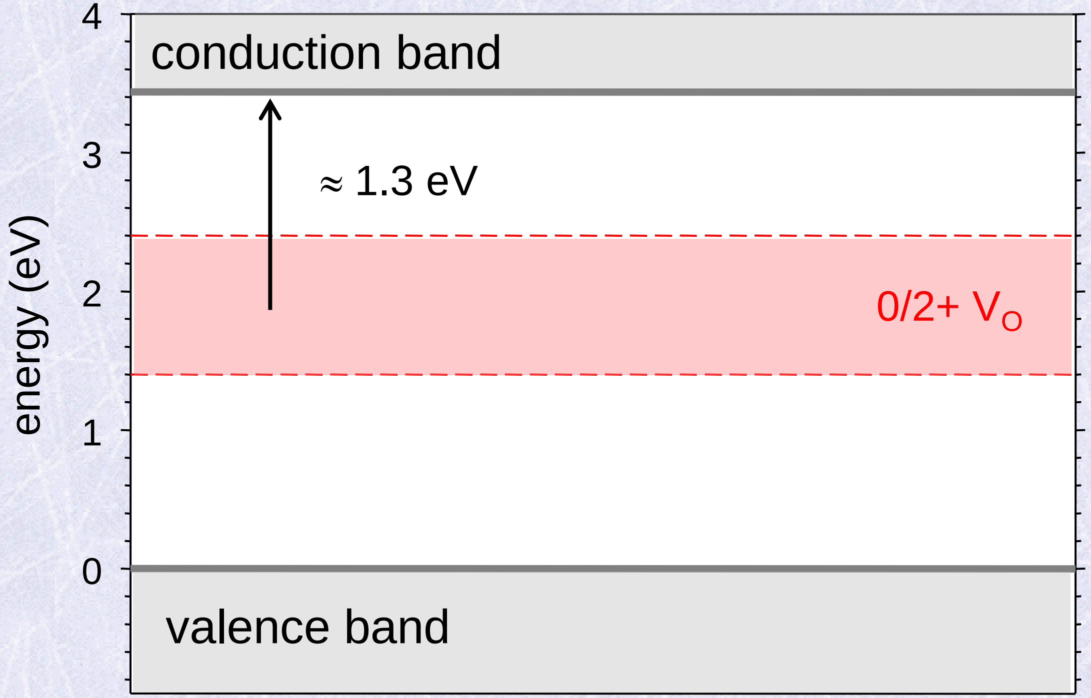
*J. Čížek et al., APL **106**, 251902 (2015)*

Points defects in ZnO

- HTG ZnO (MaTecK)



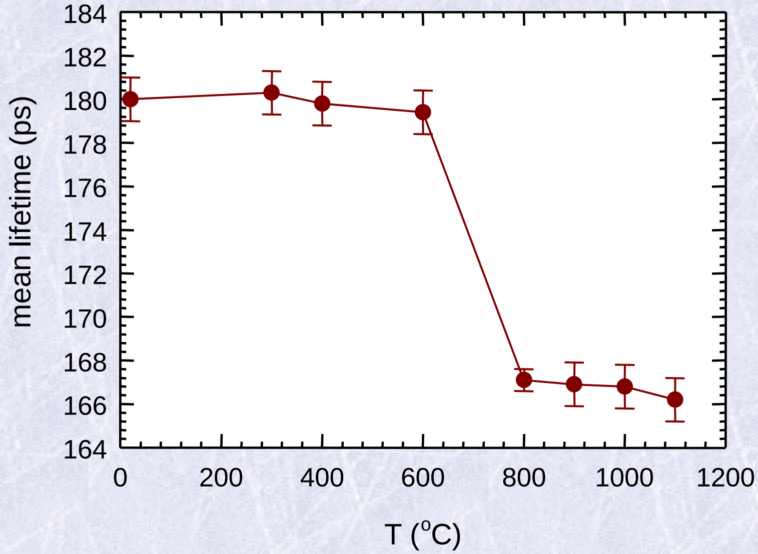
- calculated defect charge transition levels
- V_O is deep donor

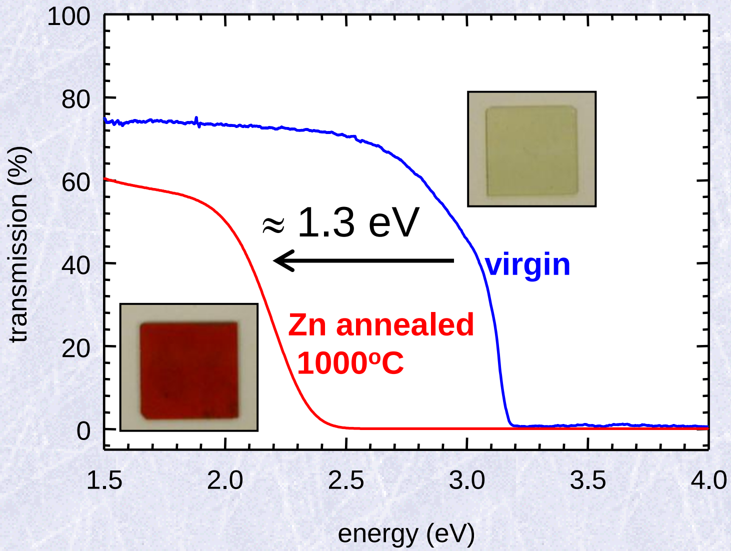


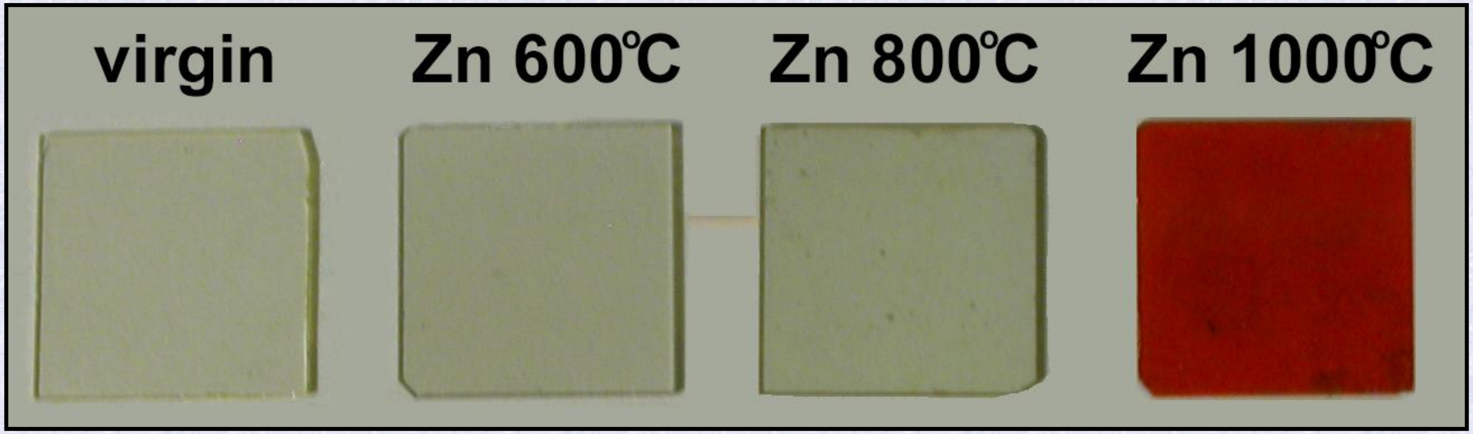
*J. Čížek et al., APL **106**, 251902 (2015)*

Annealing of ZnO crystals in Zn vapour

- HTG ZnO (MaTecK)
- annealing in evacuated ampoule with metallic Zn at various temperatures for 12 h



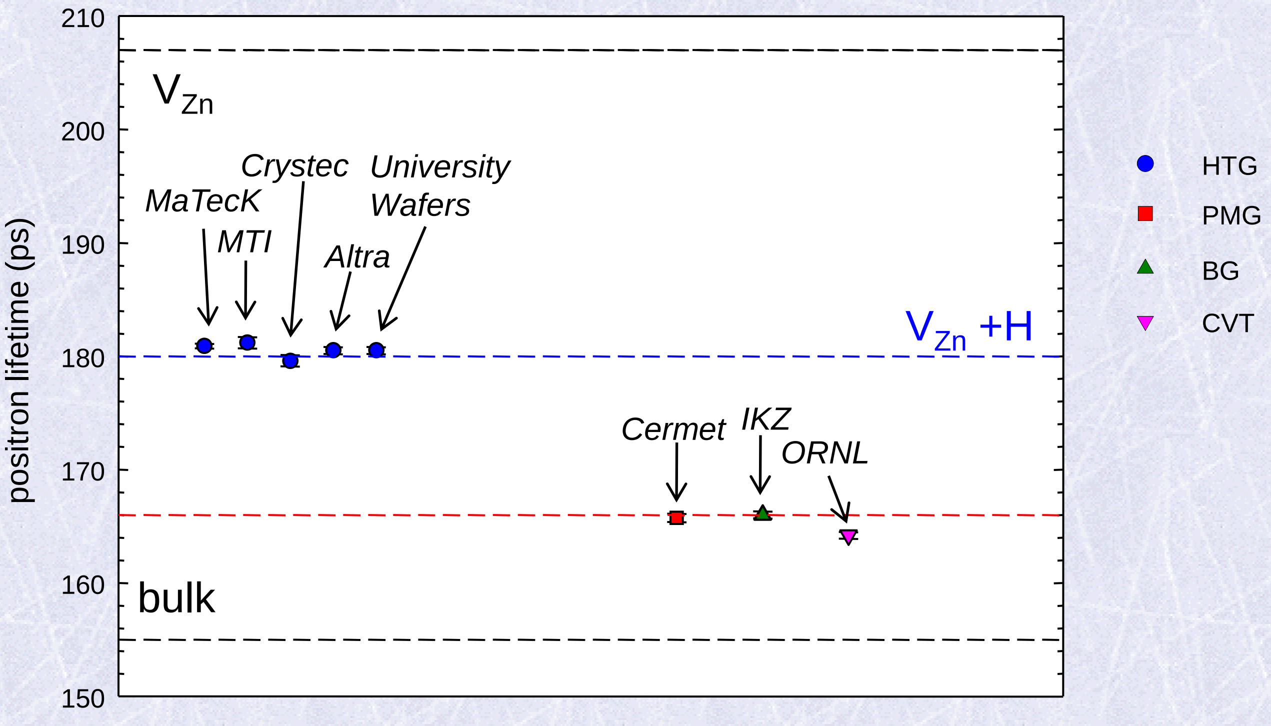




*J. Čížek et al., APL **106**, 251902 (2015)*

Annealing of ZnO crystals in Zn vapour

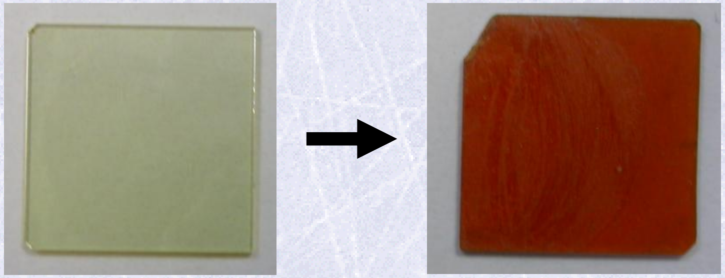
- HTG ZnO (MaTecK)
- annealing in evacuated ampoule with metallic Zn at various temperatures for 12 h

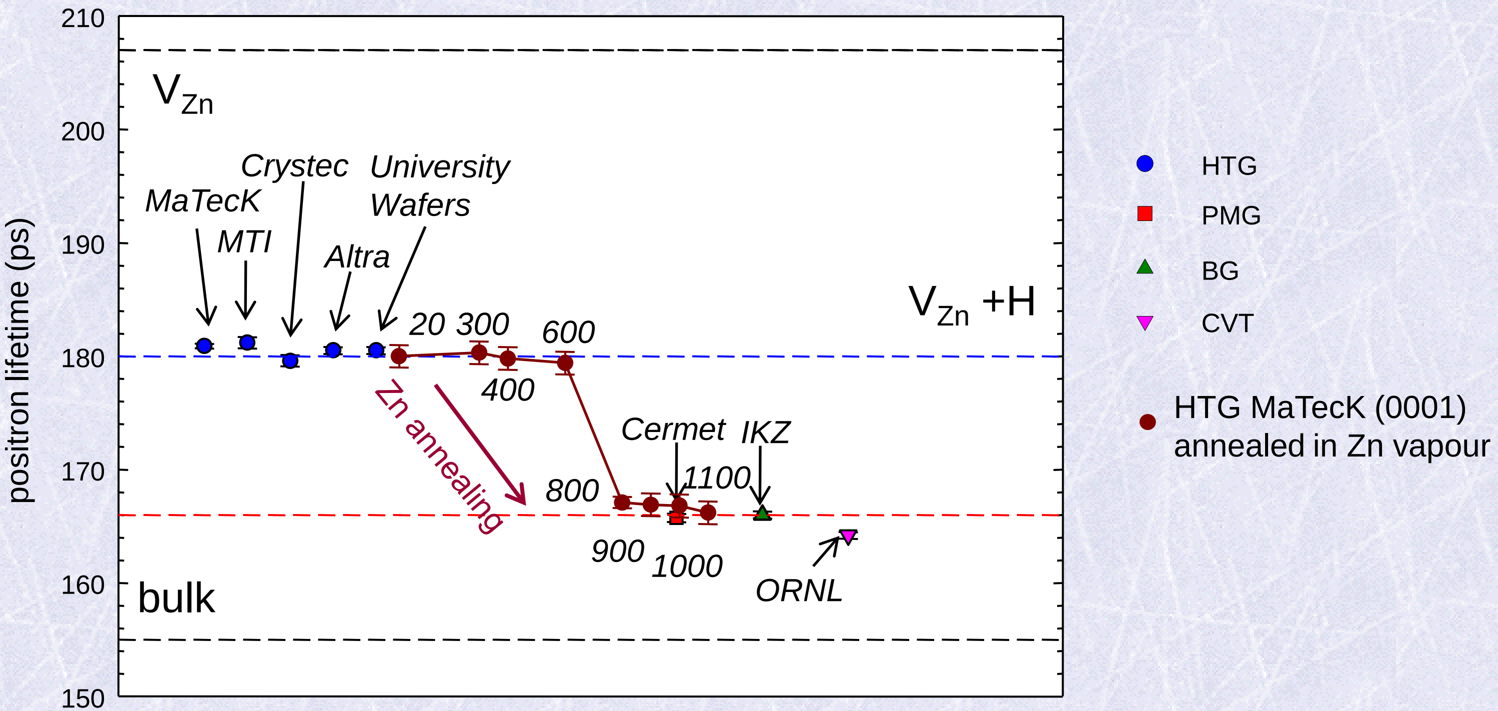


Annealing of ZnO crystals in Zn vapour

- HTG ZnO (MaTecK)

virgin | 1000ºC/12 h (Zn)

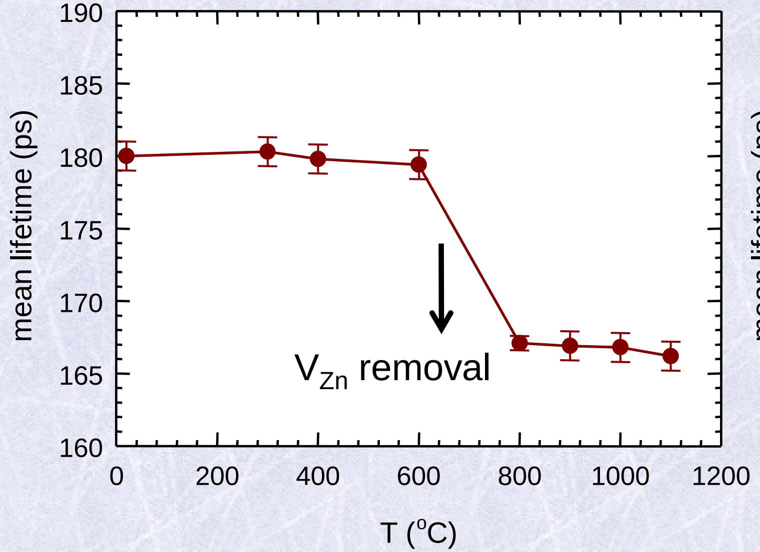




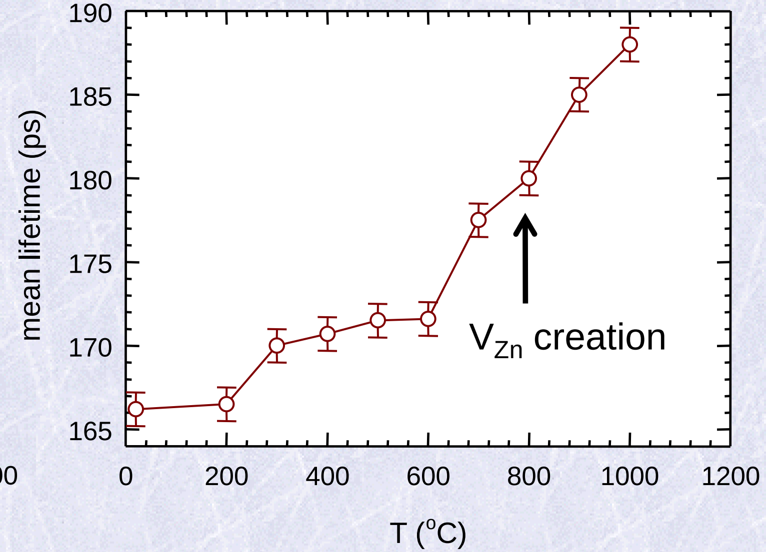
Annealing of ZnO crystals in Zn vapour

- HTG ZnO (MaTecK)
- annealing in evacuated ampoule with metallic Zn at various temperatures for 12 h
- post-annealing in air at various temperatures for 12 h

Zn-annealing

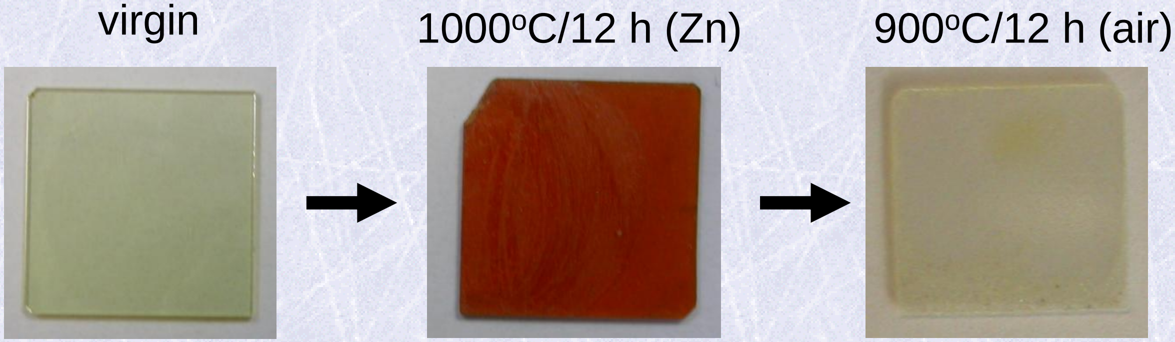


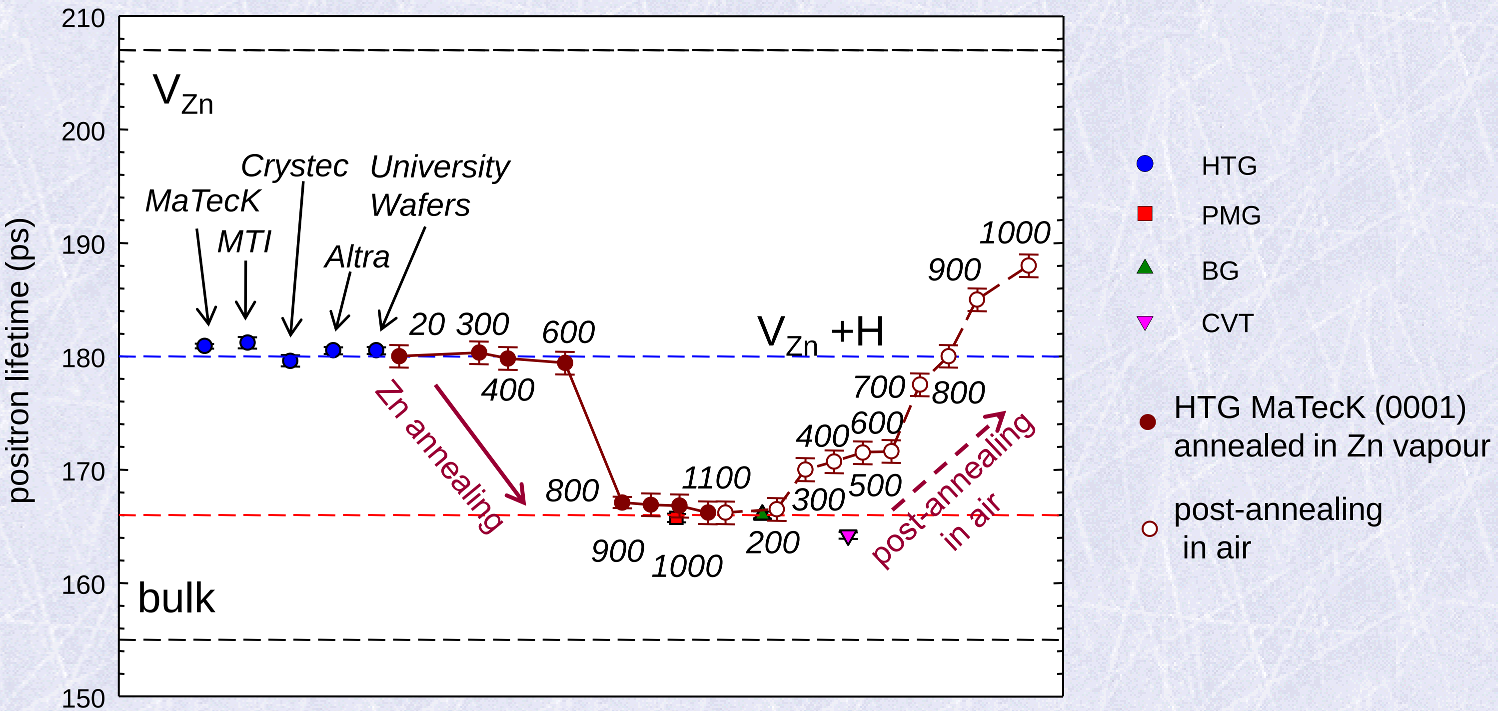
post-annealing in air



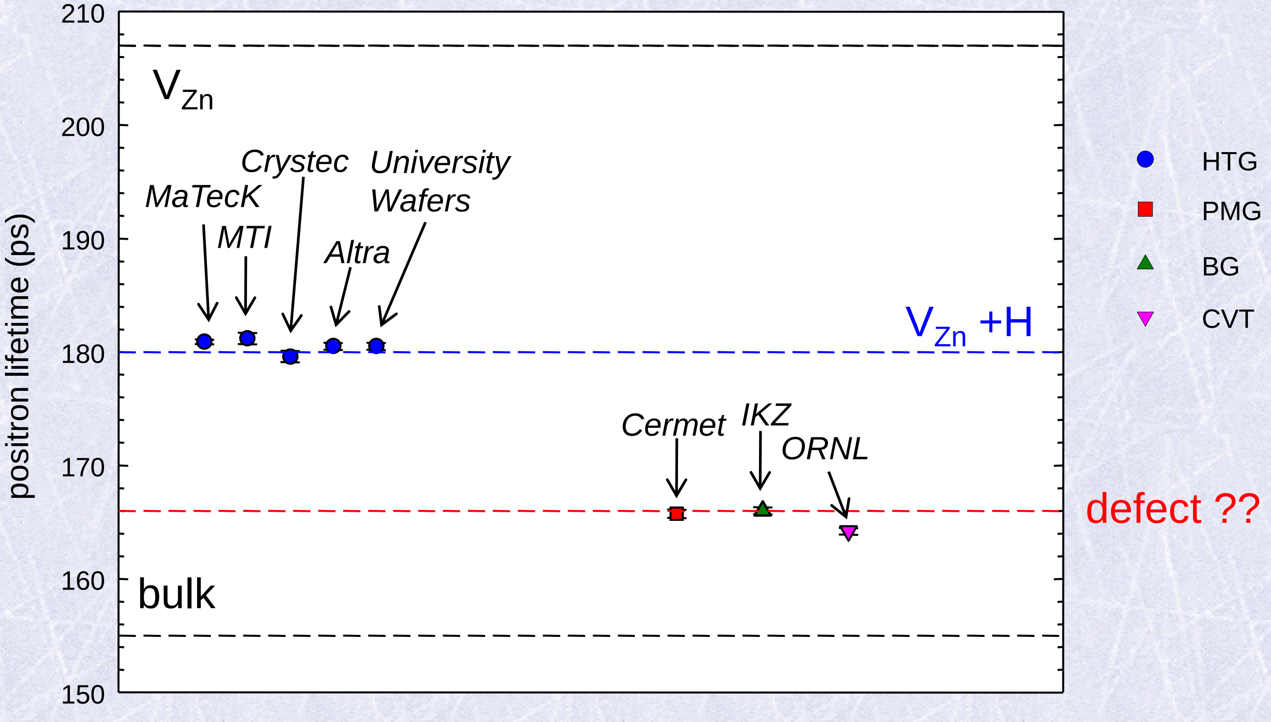
Annealing of ZnO crystals in Zn vapour

- HTG ZnO (MaTecK)





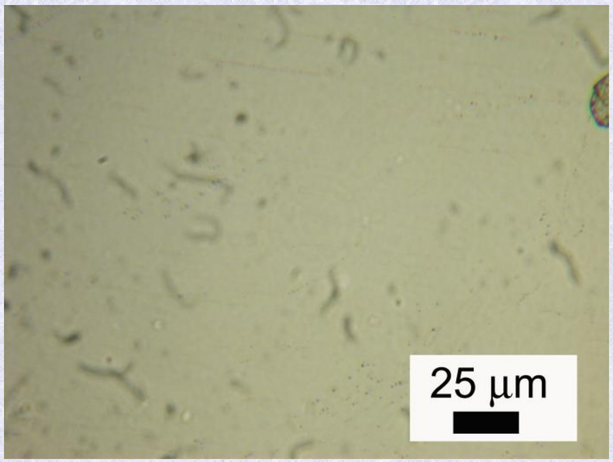
ZnO crystals grown by various methods



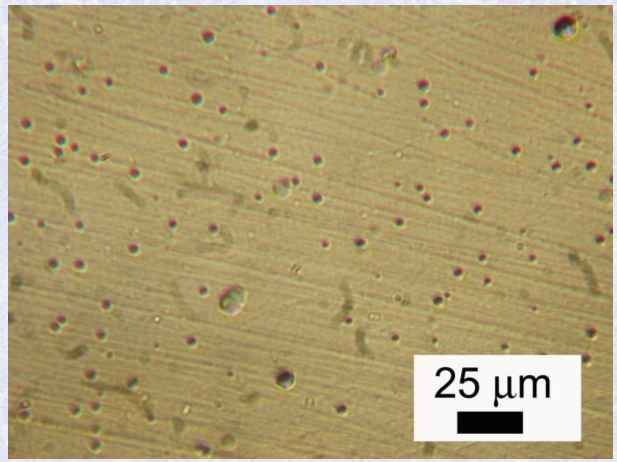
Dislocation density in ZnO crystal

- etch pitting (H_3PO_4 + glycerine 1:2)
- **PMG (Cermet)**

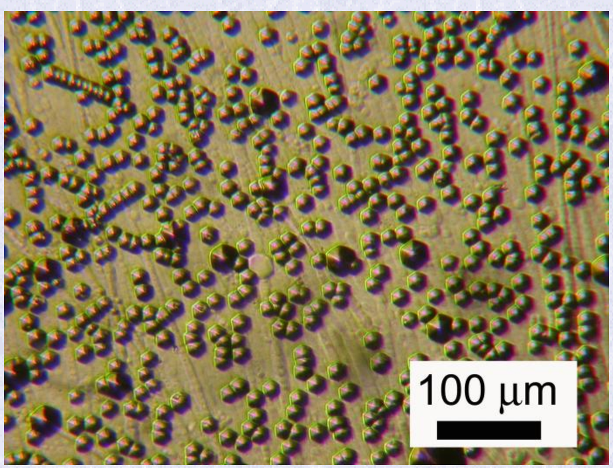
virgin



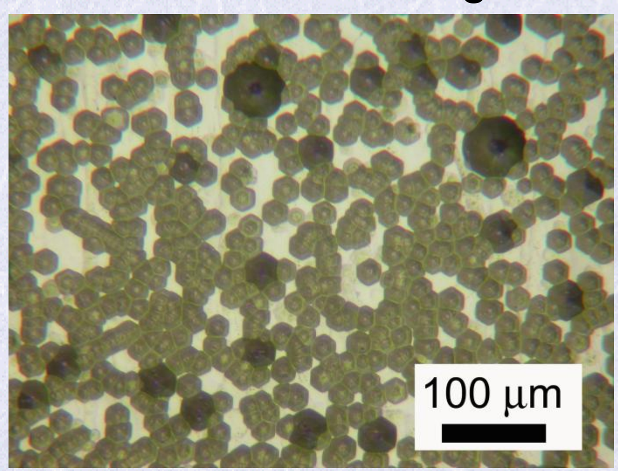
15 min etching



75 min etching



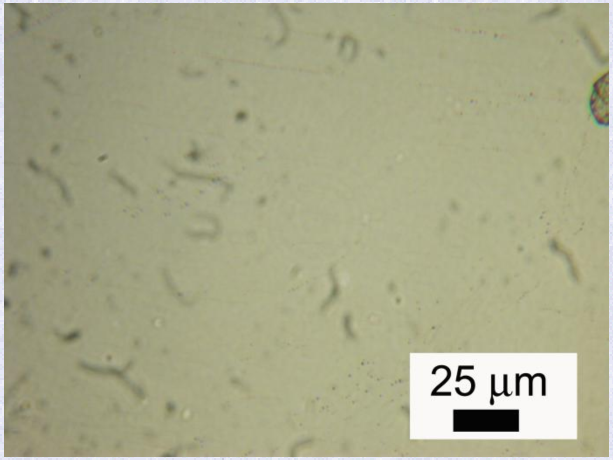
165 min etching



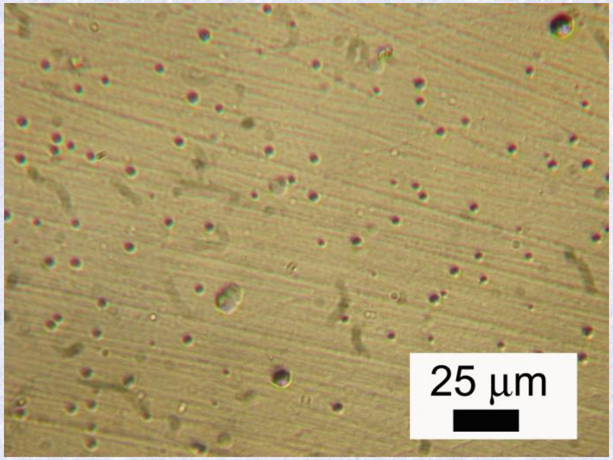
Dislocation density in ZnO crystal

- etch pitting (H_3PO_4 + glycerine 1:2)
- **PMG (Cermet)**

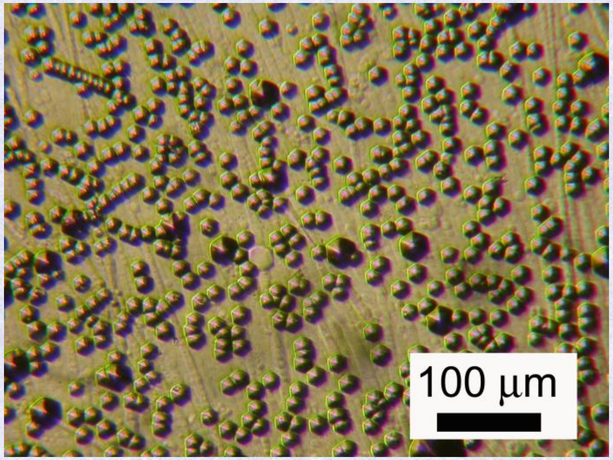
virgin



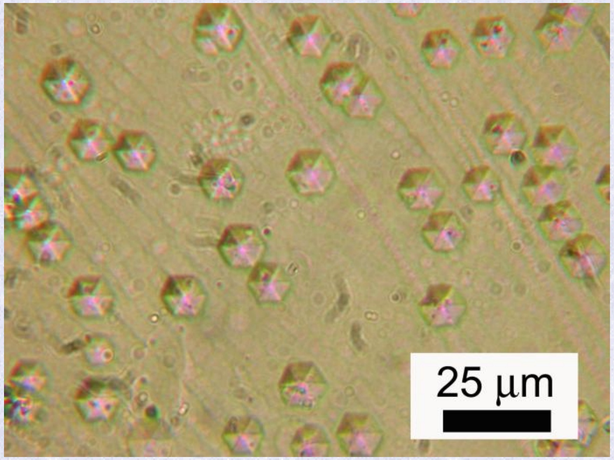
15 min etching



75 min etching



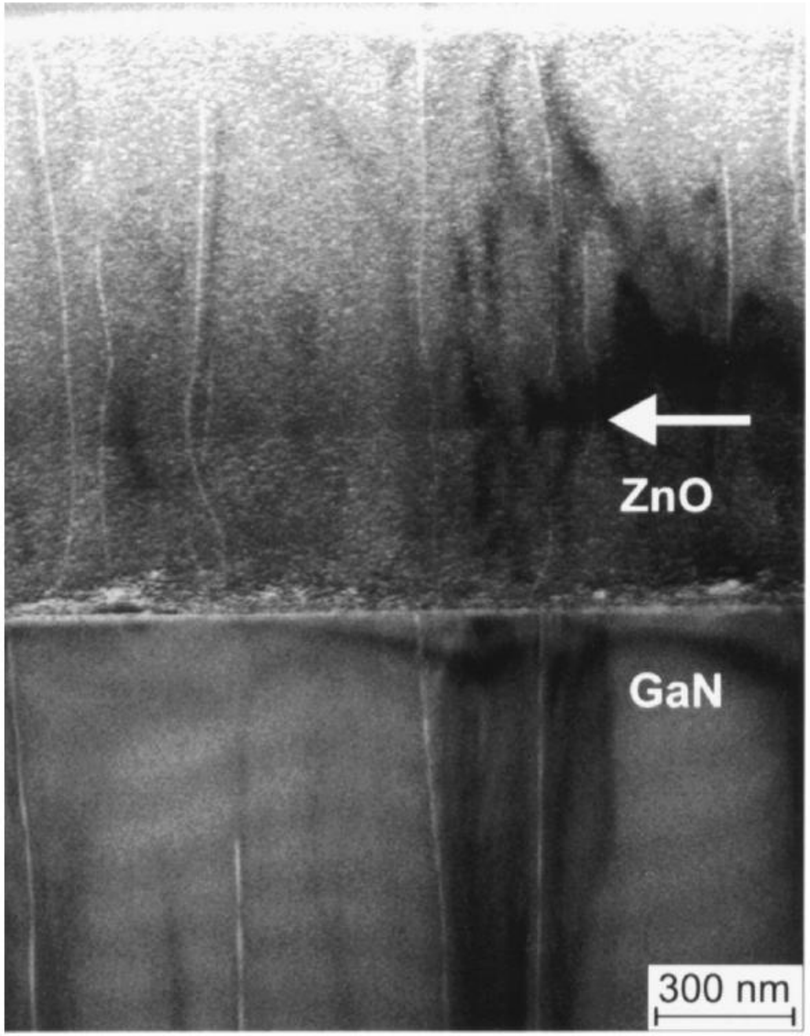
detail of etch pits

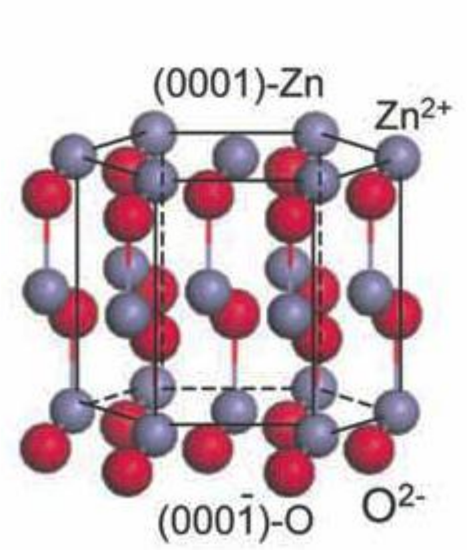


- dislocation density $\rho_D \approx 3 \times 10^{10}$ m^{-2}
- too low to explain saturated trapping of positrons

Stacking faults in ZnO

- epitaxial ZnO film grown by metalorganic vapour phase epitaxy (MOVPE)
- TEM image in cross-section of the film

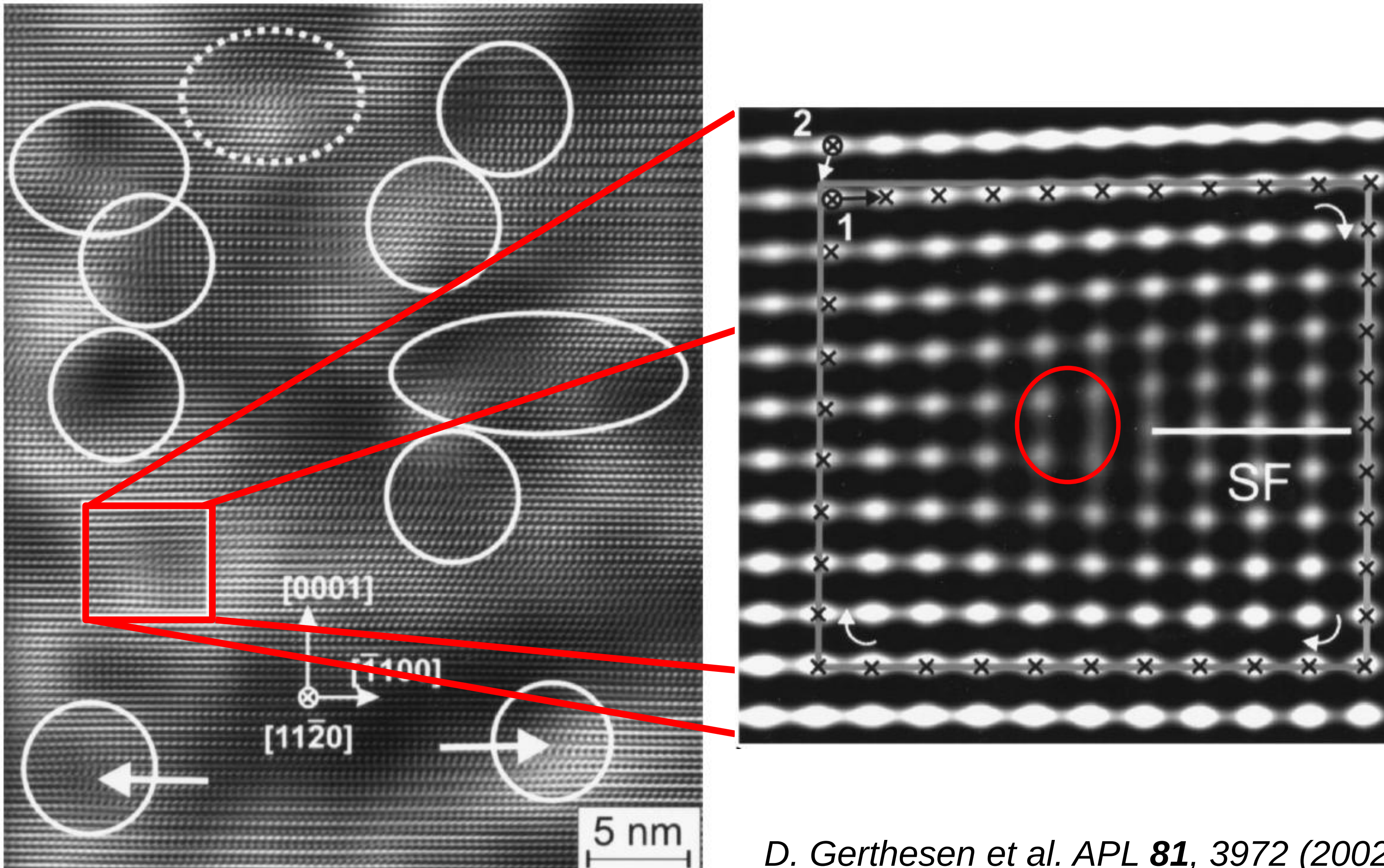




*D. Gerthesen et al. APL **81**, 3972 (2002)*

Stacking faults in ZnO

- epitaxial ZnO film grown by metalorganic vapour phase epitaxy (MOVPE)
- HRTEM image in cross-section of the film

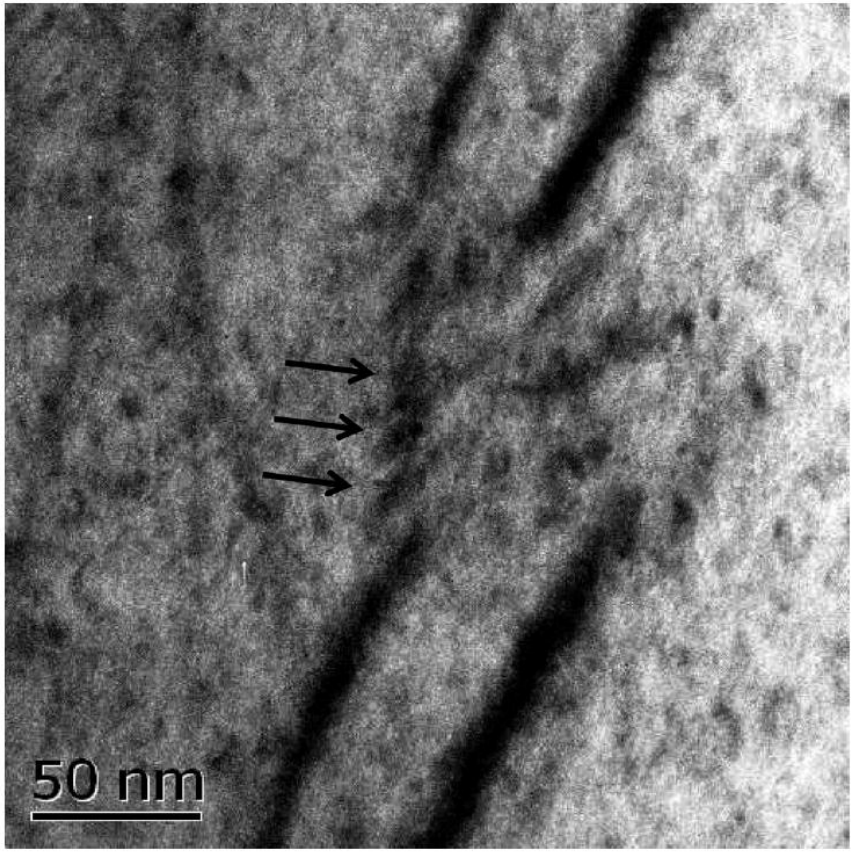


*D. Gerthesen et al. APL **81**, 3972 (2002)*

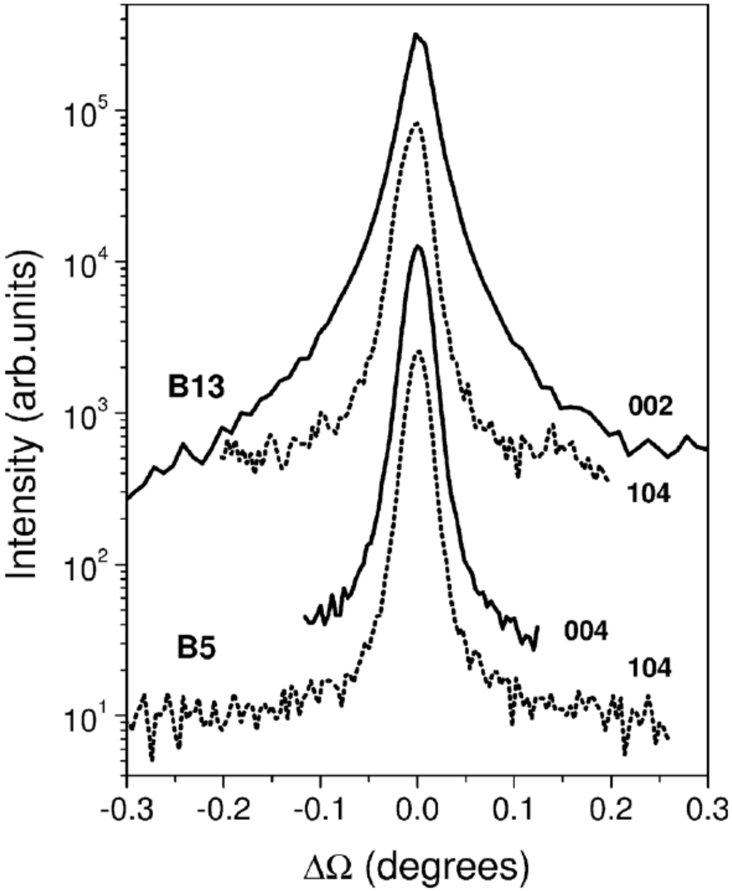
Stacking faults in ZnO

- lifetime of 166 ps: positron trapping at misfit defects associated with stacking faults
- BG (IKZ), virgin

bright field TEM micrograph

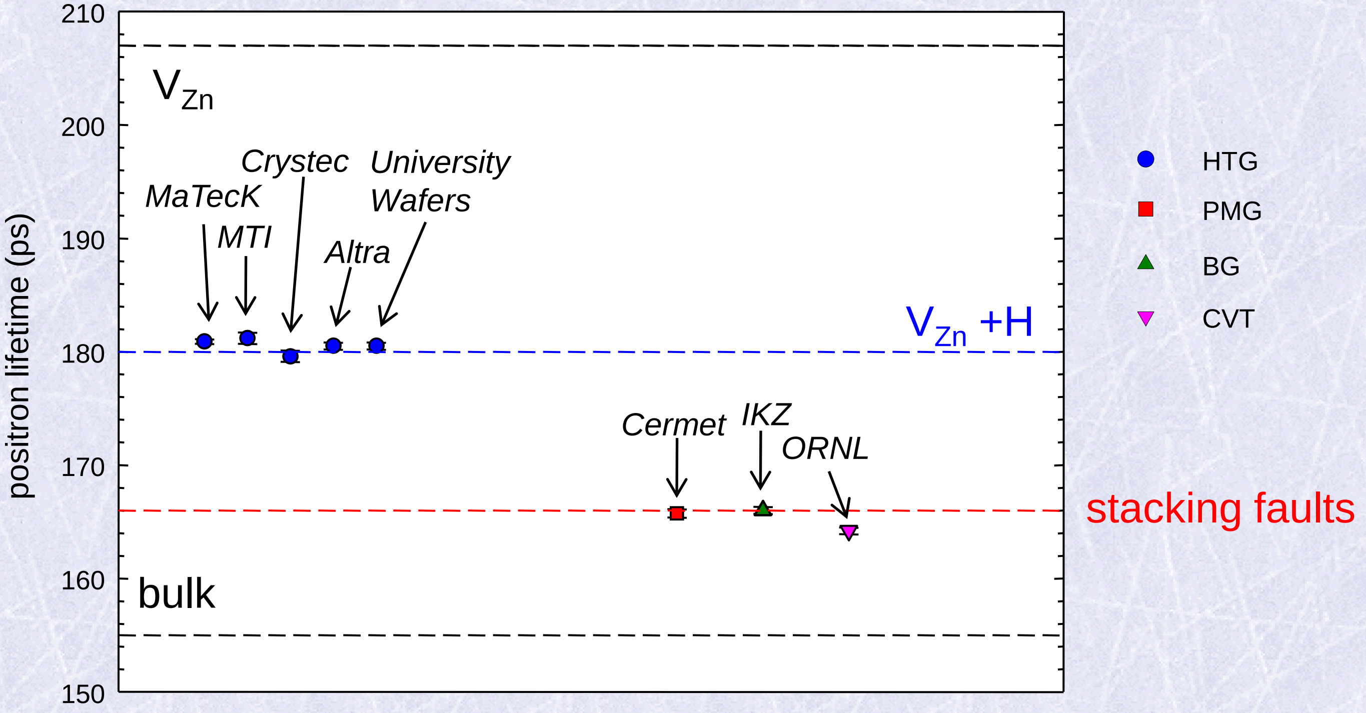


X-ray diffraction profiles



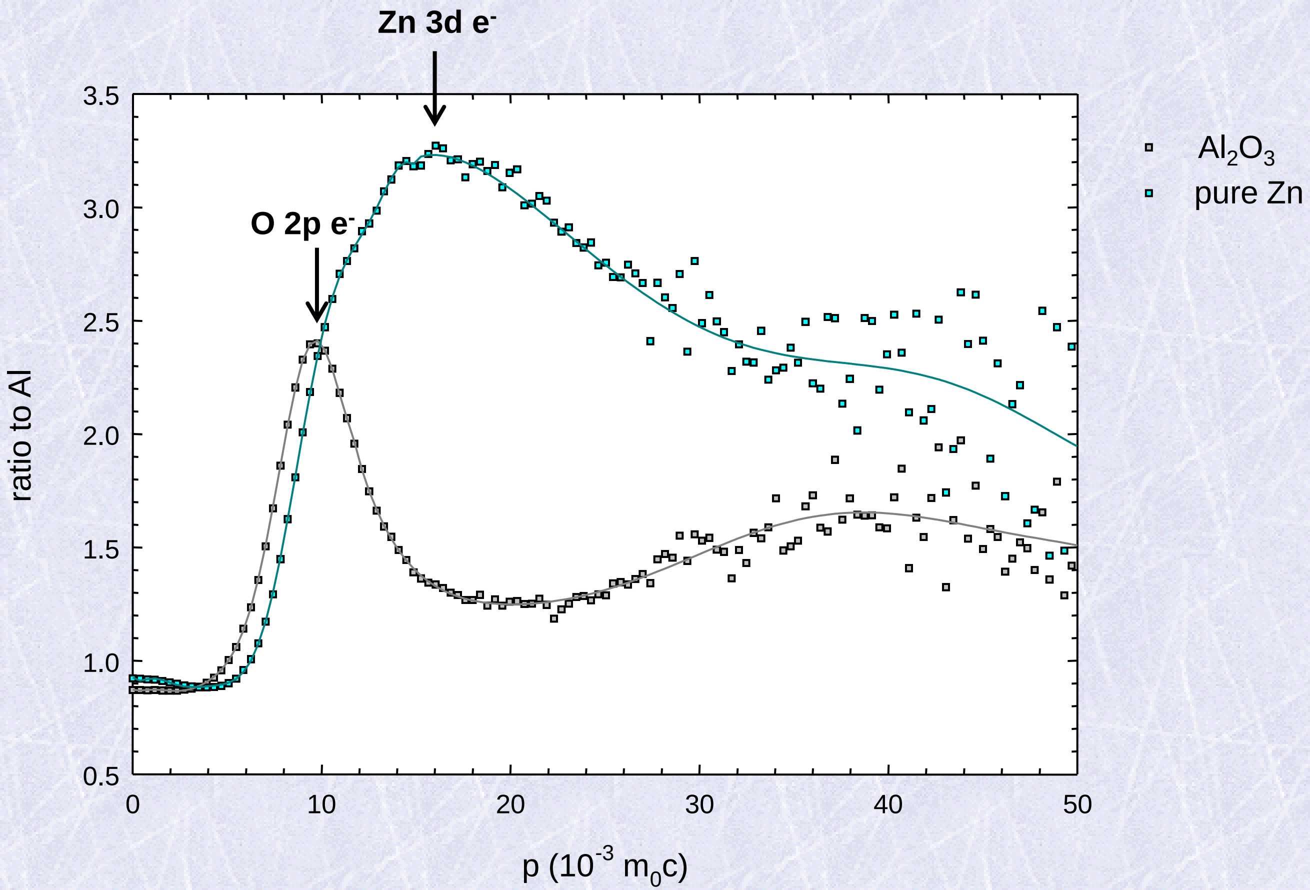
W. Anwand et al. JAP ***109****, 063516 (2011)*

ZnO crystals grown by various methods



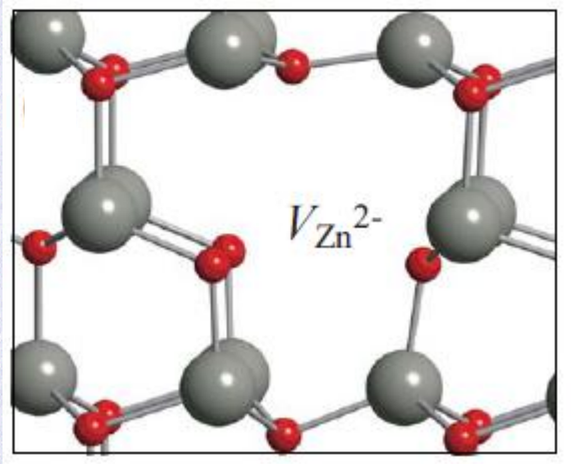
CDB results

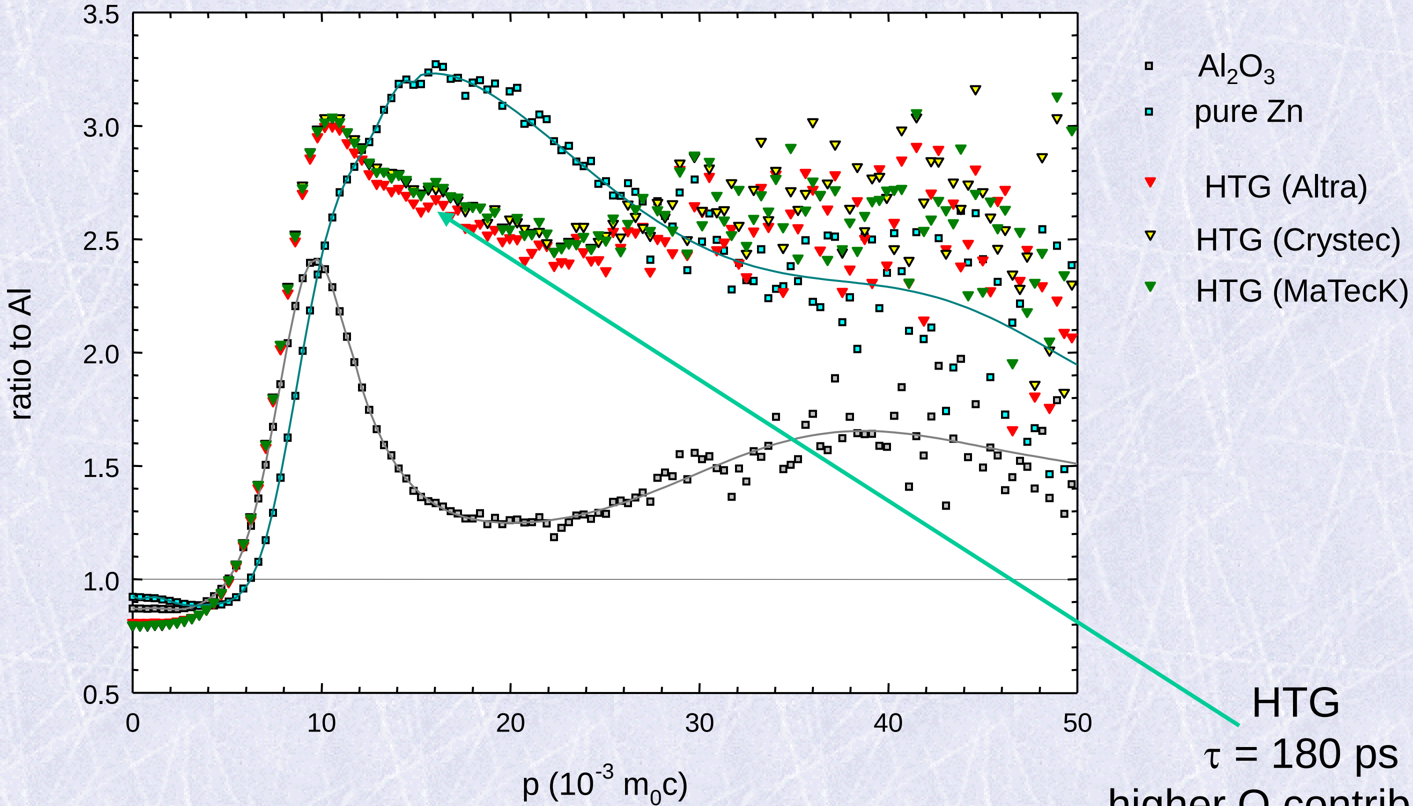
- reference samples (pure Zn and Al_2O_3)



CDB results

- virgin ZnO crystals grown by various methods
- dominating O contribution in HTG crystals is consistent with e^+ trapping in V_{Zn}+H

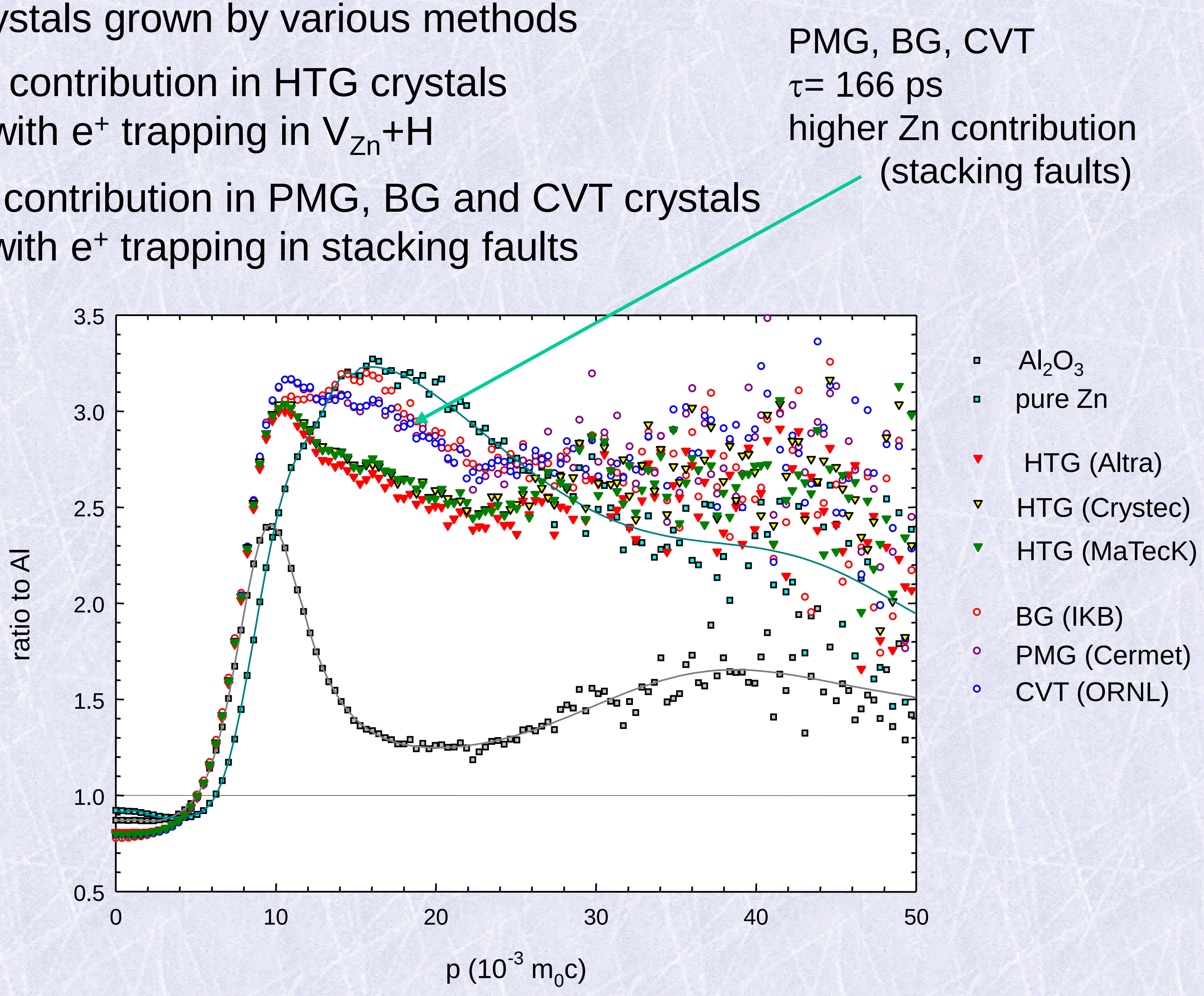




HTG
τ = 180 ps
higher O contribution
(V_{Zn}+H)

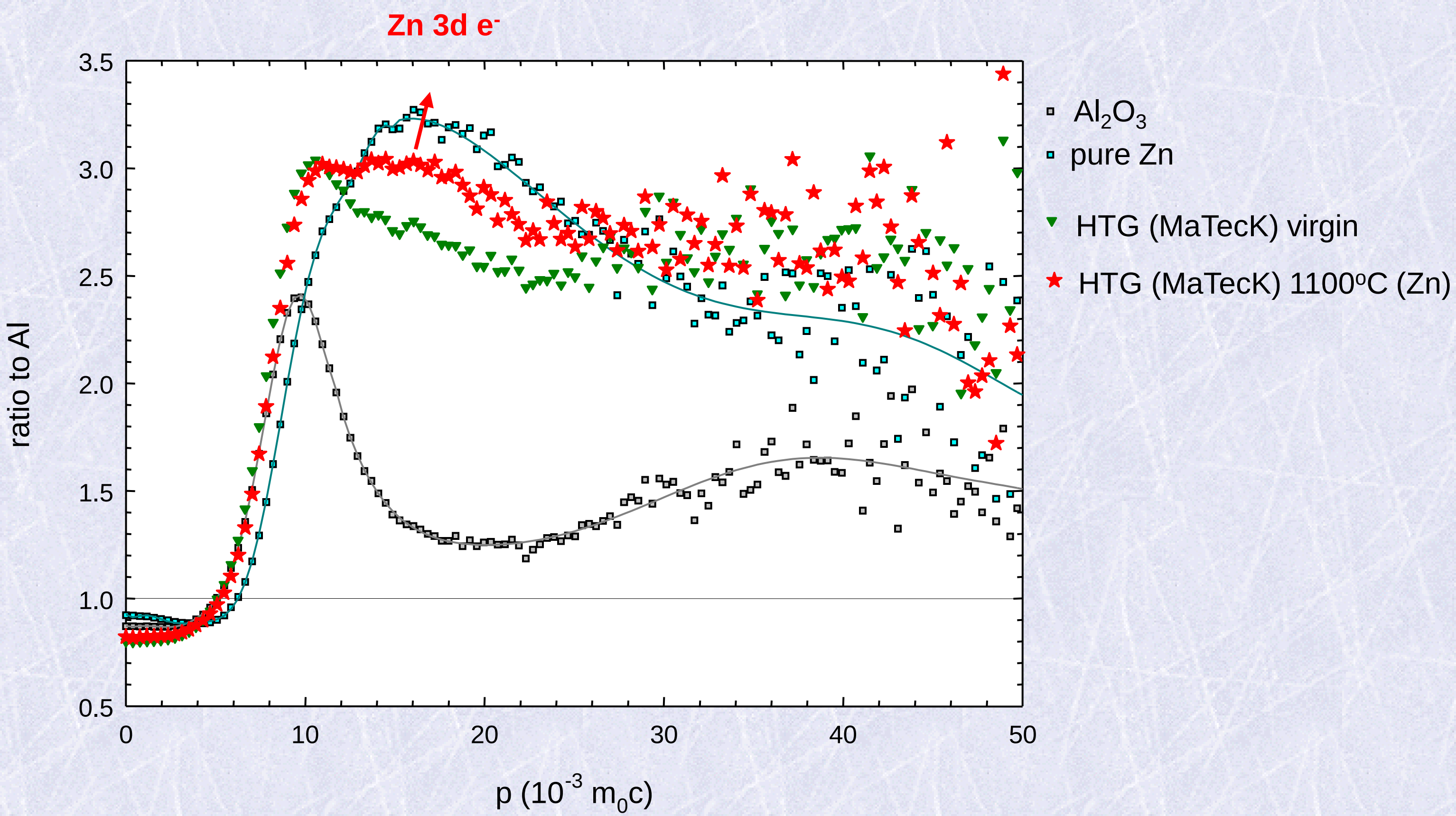
CDB results

- virgin ZnO crystals grown by various methods
- dominating O contribution in HTG crystals is consistent with e^+ trapping in V_{Zn}+H
- enhanced Zn contribution in PMG, BG and CVT crystals is consistent with e^+ trapping in stacking faults



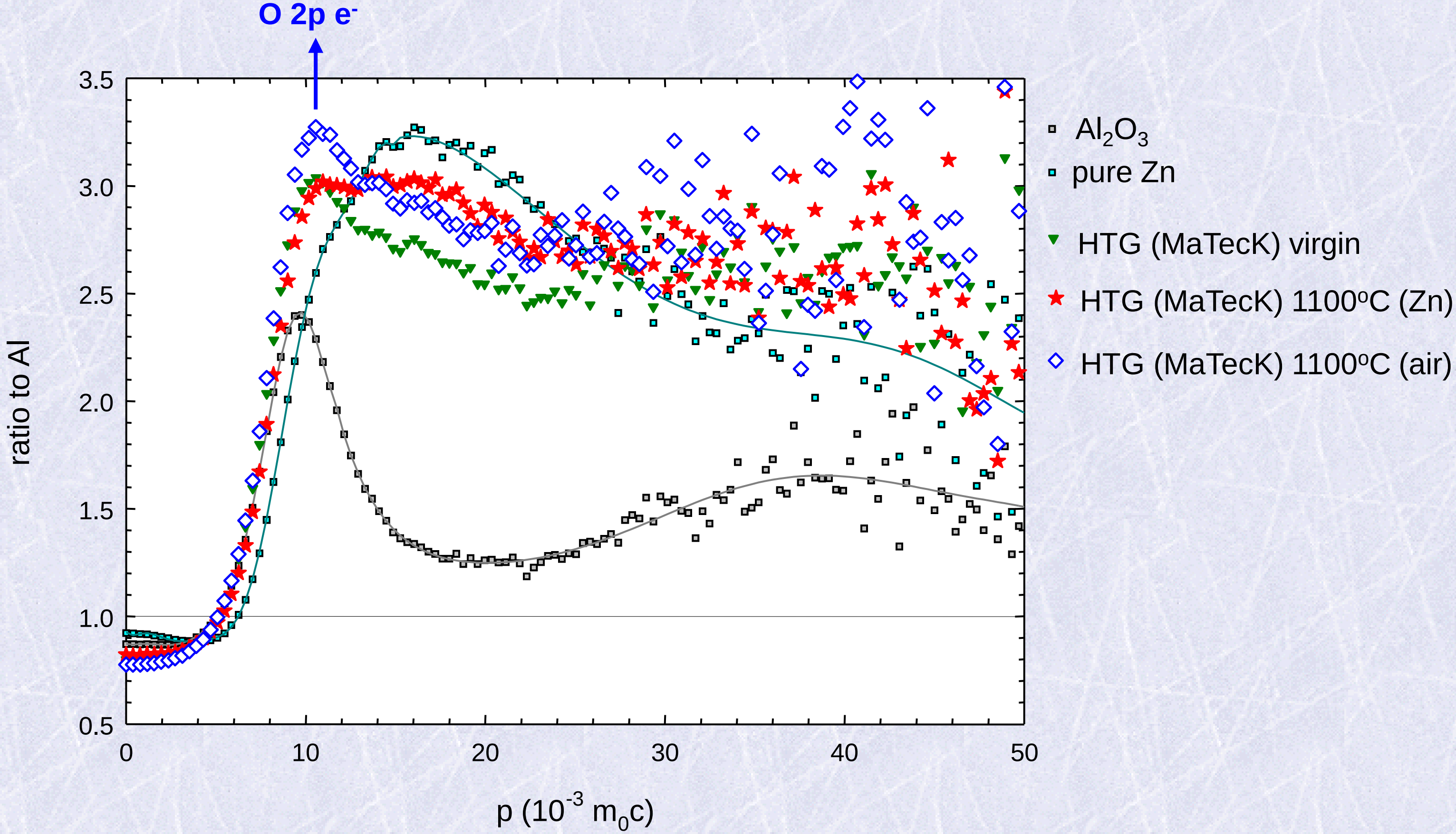
CDB results

- HTG ZnO - effect of annealing
- annealing in Zn vapour → increase of Zn contribution (removal of V_{Zn})



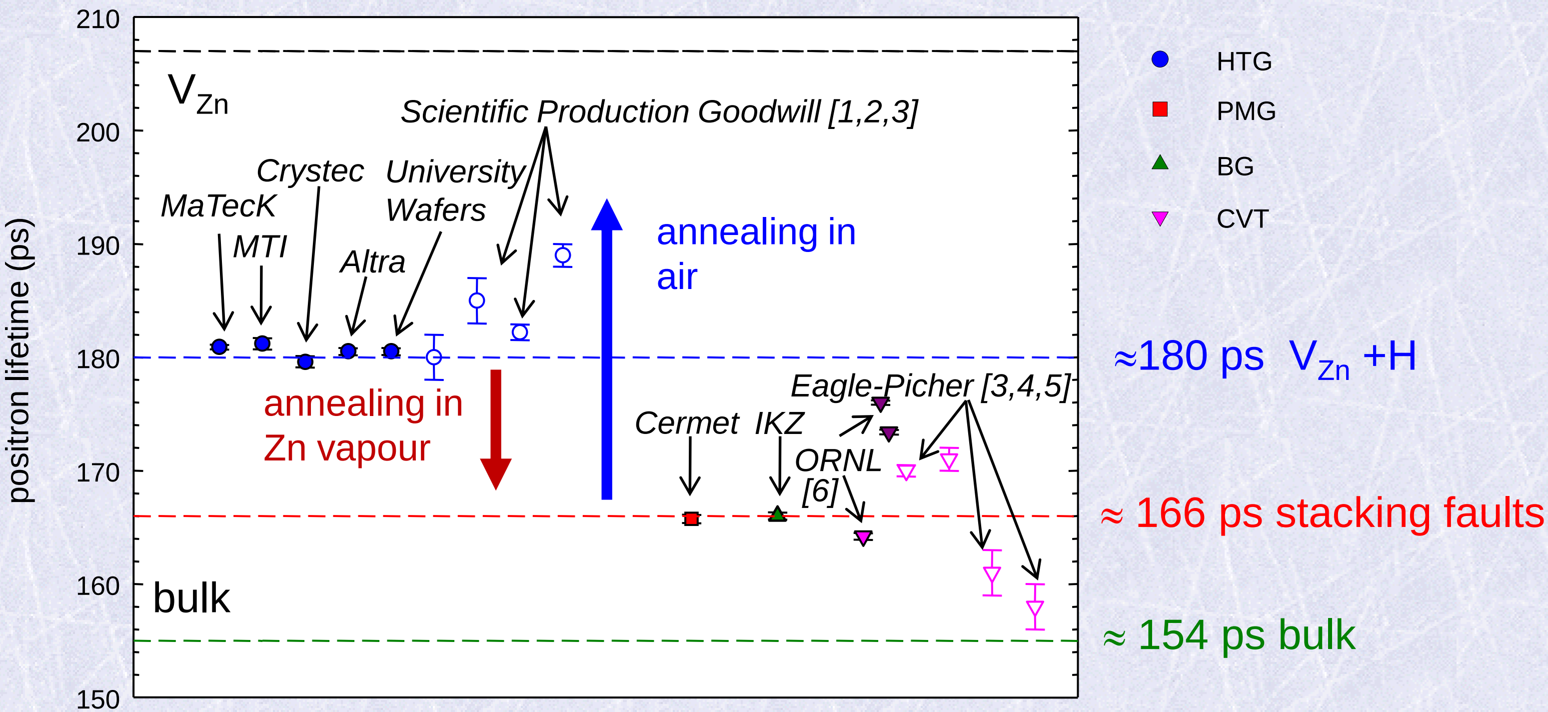
CDB results

- HTG ZnO - effect of annealing
- annealing in Zn vapour → increase of Zn contribution (removal of V_{Zn})
- annealing in air → increase of O contribution (creation of V_{Zn})



Conclusions

- HTG crystals – saturated trapping in V_{Zn+H}
- PMG, BG crystals – saturated trapping in stacking faults
- annealing in air creates V_{Zn}
- annealing in Zn vapour removes V_{Zn} and introduces V_O



[1] F. Tuomisto, D.C. Look, Proc. SPIE **6474**, 647413 (2007)
[2] Z.Q. Chen et al., PRB **71**, 115213 (2005)
[3] Z.Q. Chen et al., JAP **94**, 4807 (2003)
[4] F. Tuomisto et al., PRL **91**, 205502 (2003).
[5] S. Brunner et al., Mater. Sci. Forum **363-365**, 141 (2001).
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SLOPOS -15

Prague, Czech Republic

September 2-6, 2019

See you in Prague