Characterization of point defects in ZnO crystals

J. Čížek, M. Vlček, P. Hruška, F. Lukáč, O. Melikhova, J. Valenta
Faculty of Mathematics and Physics, Charles University Prague, Czech Republic

W. Anwand
Helmholtz Zentrum Dresden-Rossendorf, Germany

F. Selim
Center for Photochemical Sciences, Bowling Green State University, USA

Ch. Hugenschmidt
Technical University München, Garching, Germany

W. Egger
Bundeswehr München, Neubiberg, Germany

Introduction

ZnO

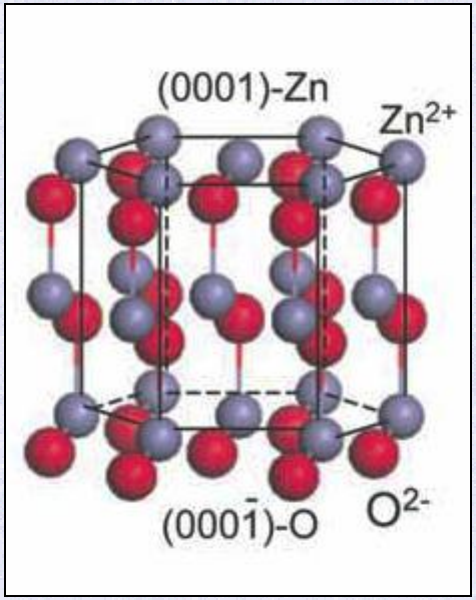
• wide band gap semiconductor E_g = 3.4 eV (λ = 365 nm) at room temperature

• 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

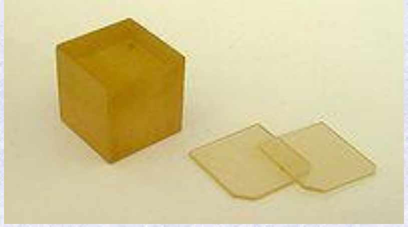
• high quality ZnO single crystals are commercially available



• main problem: doping asymmetry

- “natural” n-type doping

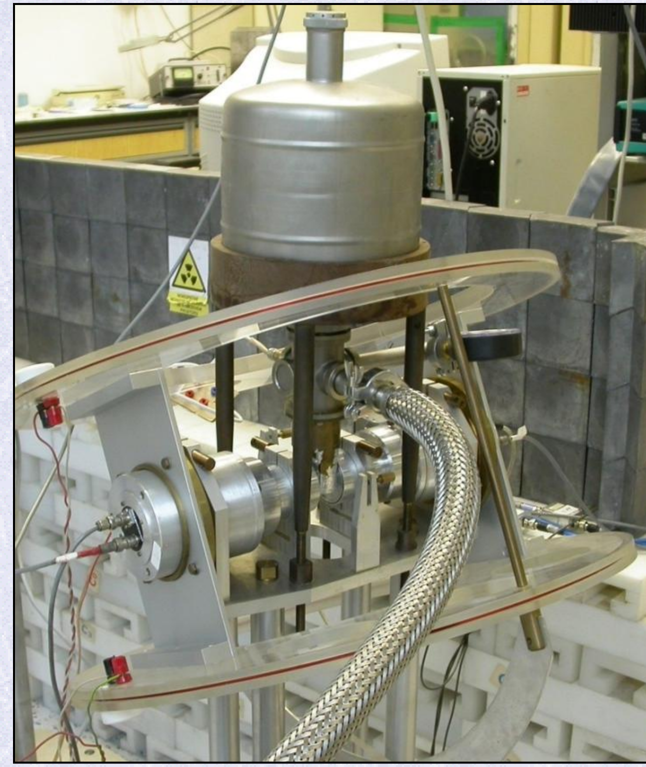
- p-type doping is very difficult

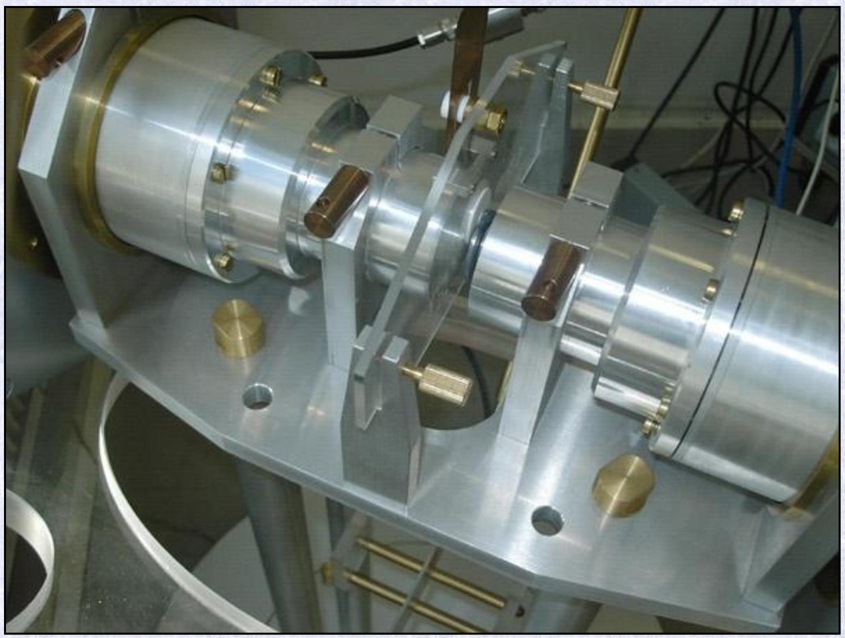


Positron annihilation spectroscopy

Bulk positron lifetime investigations

- 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





Positron annihilation spectroscopy

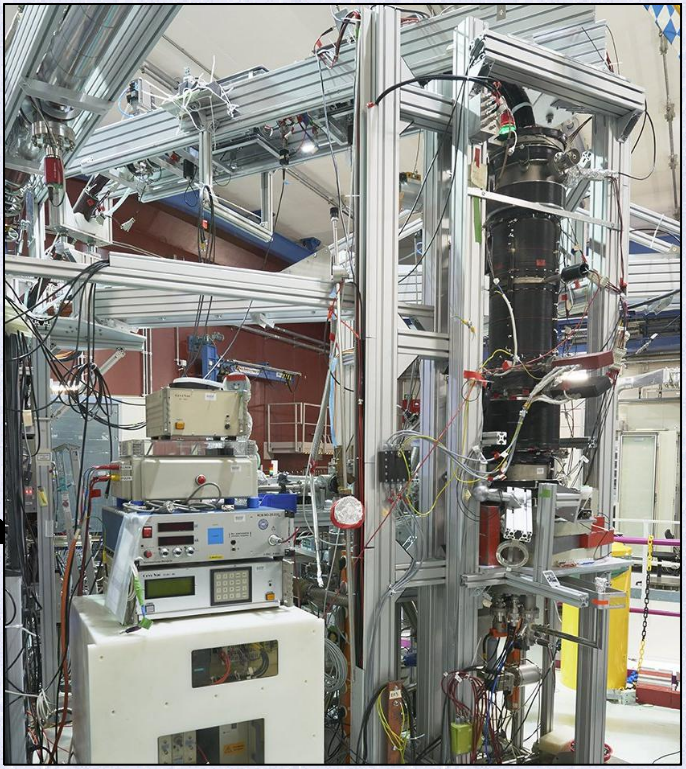
Bulk positron lifetime investigations

- 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

Positron back-diffusion measurement

- magnetically guided slow positron beam
- positron energy 0.030 – 36 keV
- HPGe detector with energy resolution 1.09$\pm$0.01 keV at 511 keV
- Doppler broadening of annihilation evaluated using *S*, *W* line shape parameters
- $> 7 \times 10^5$ counts in annihilation peak

Positron annihilation spectroscopy



Bulk positron lifetime investigations

- 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

Positron back-diffusion measurement

- magnetically guided slow positron beam
- positron energy 0.030 – 36 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
- $> 7 \times 10^5$ counts in annihilation peak

- pulsed low energy positron system (PLEPS)
- at high intensity positron source NEPOMUC (Munich)
- positron energy 0.5 -18 keV
- positron lifetime measurement (time resolution $\approx$300 ps)
- $> 5 \times 10^6$ positron annihilation events in each spectrum

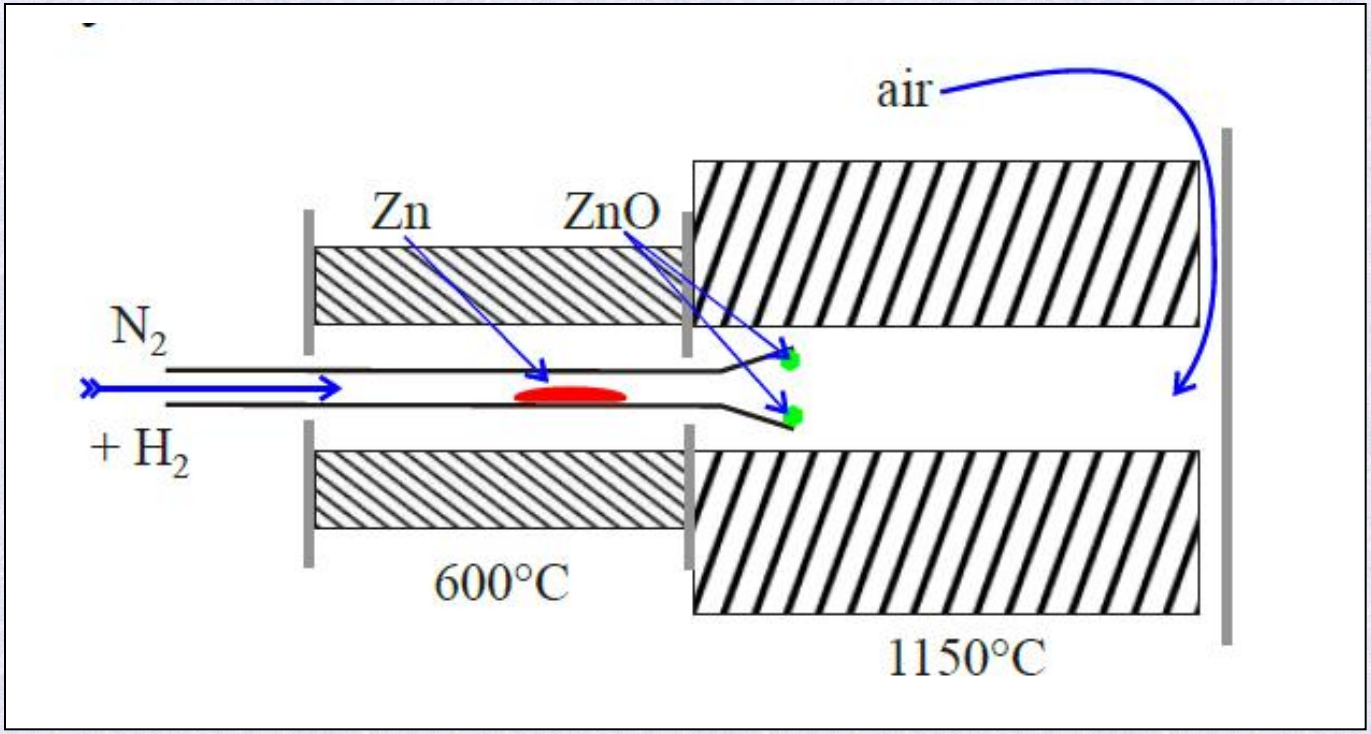
Growth of ZnO crystals

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

1. Chemically assisted vapor phase growth technique (CVT)
Eagle-Picher Inc., USA

• small crystals

• gas contamination (N_2, H_2)



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

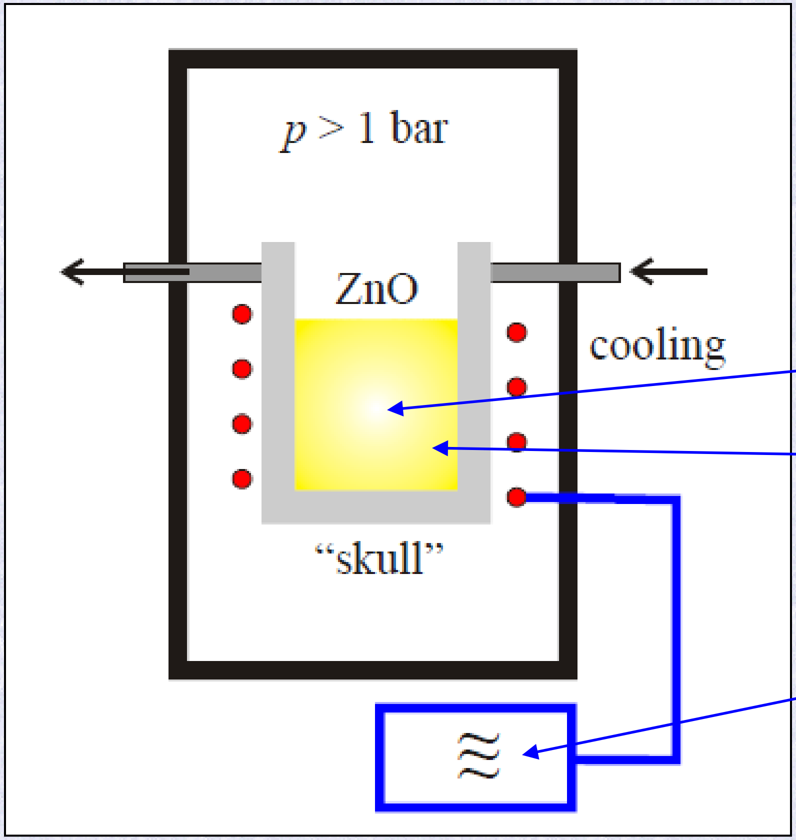
Growth of ZnO crystals

• 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“

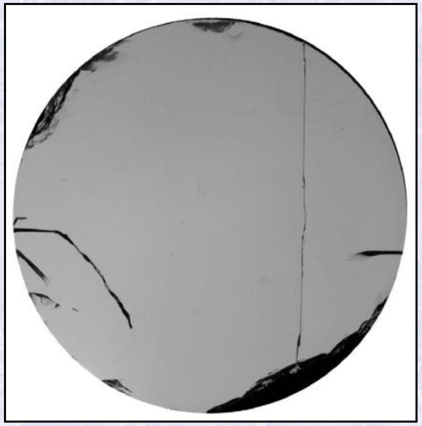
RF power

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

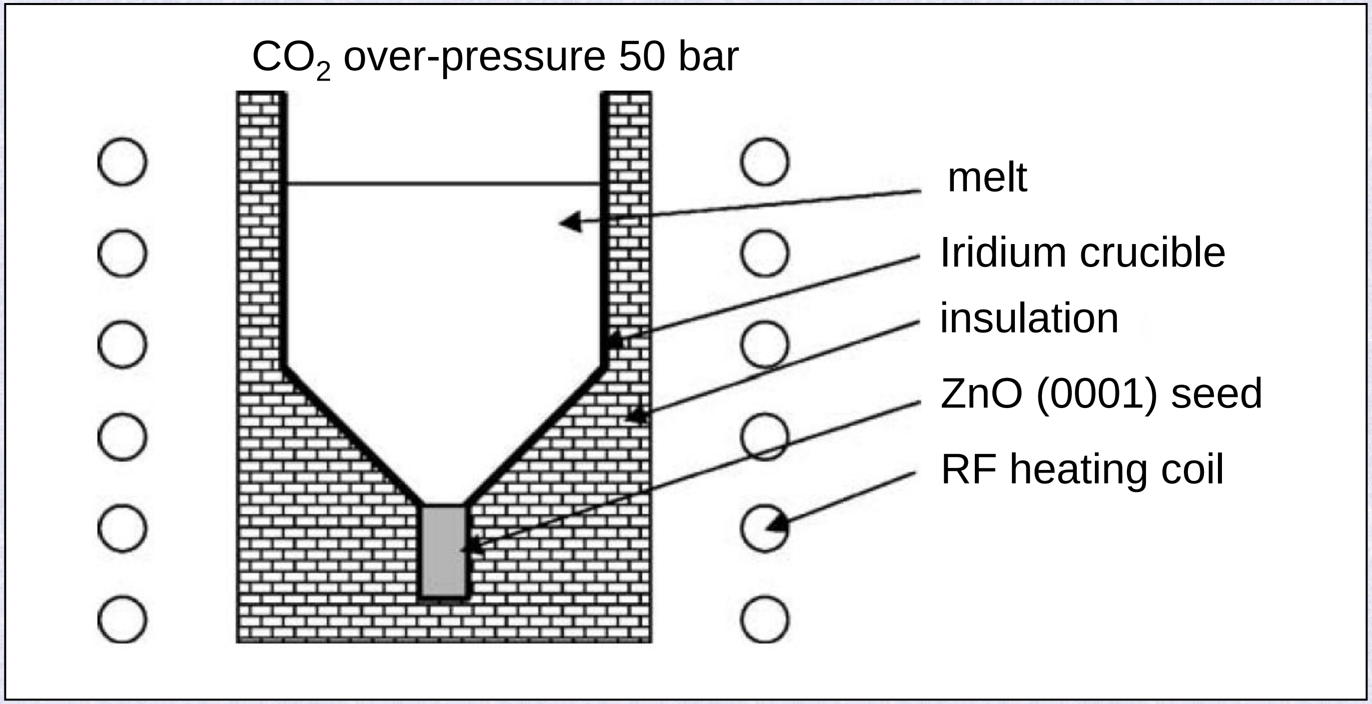
Growth of ZnO crystals

• 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)

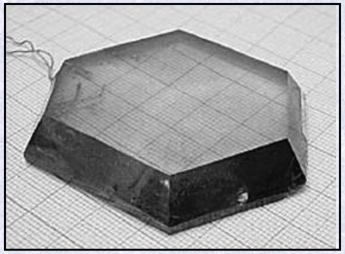
Growth of ZnO crystals

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

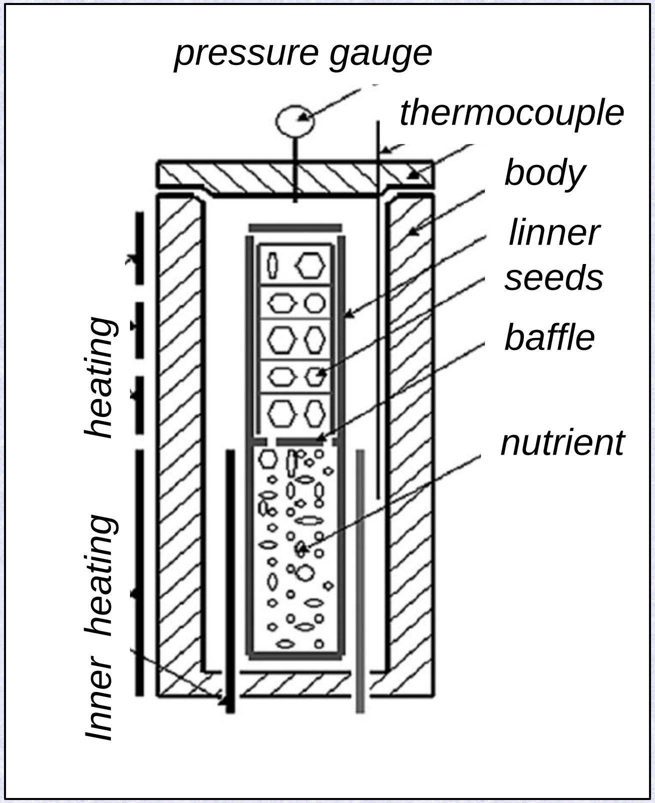
4. hydrothermal growth (HTG)

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

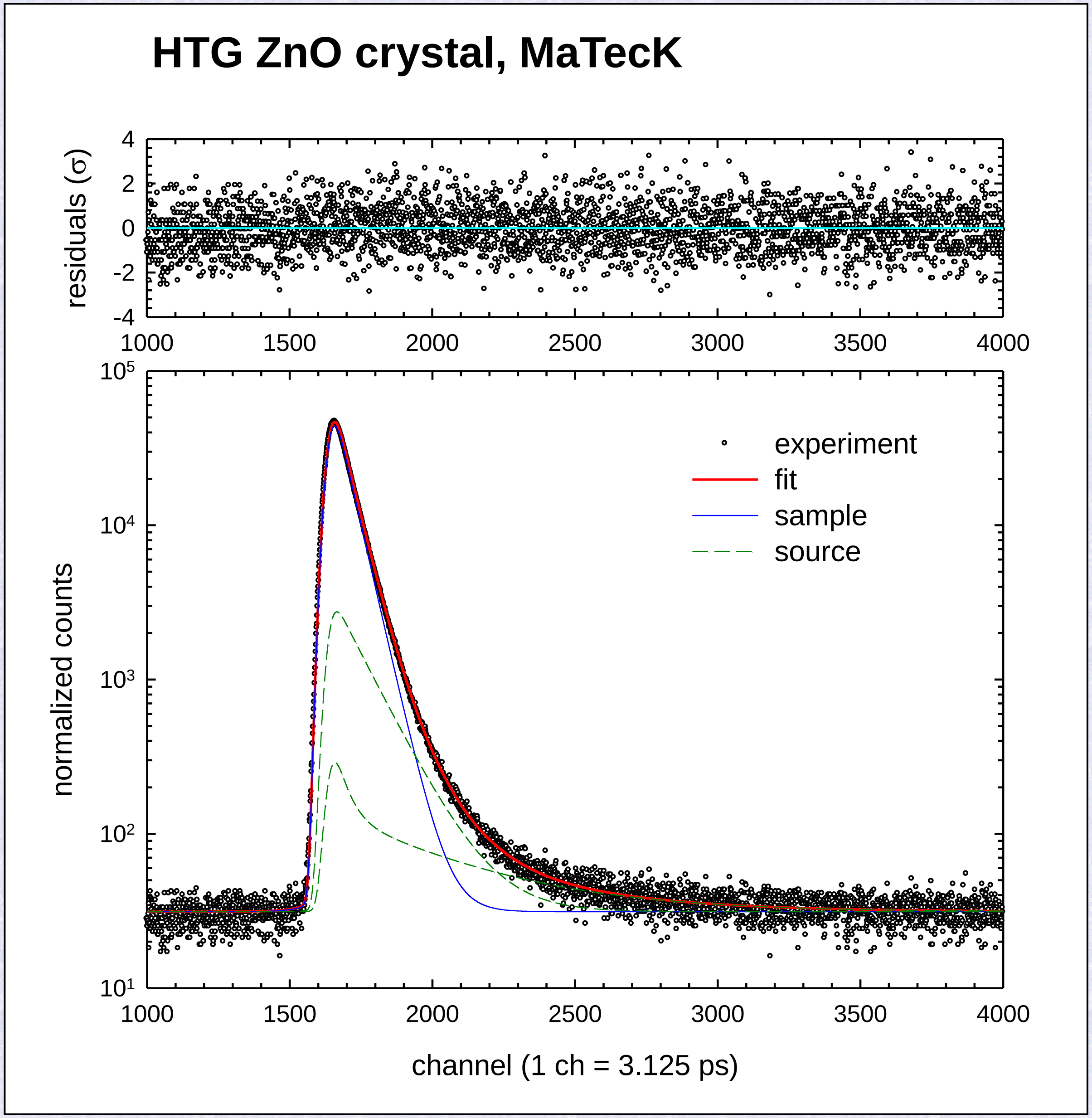
Bridgman growth (BG)

- Institut für Kristalzüchtung (IKZ), Berlin, Germany

Chemically assisted vapor phase growth technique (CVT)

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

Bulk Positron Lifetime Spectrum



single component

τ_1 = 180.7(3) ps, I_1 = 100 %

source contribution

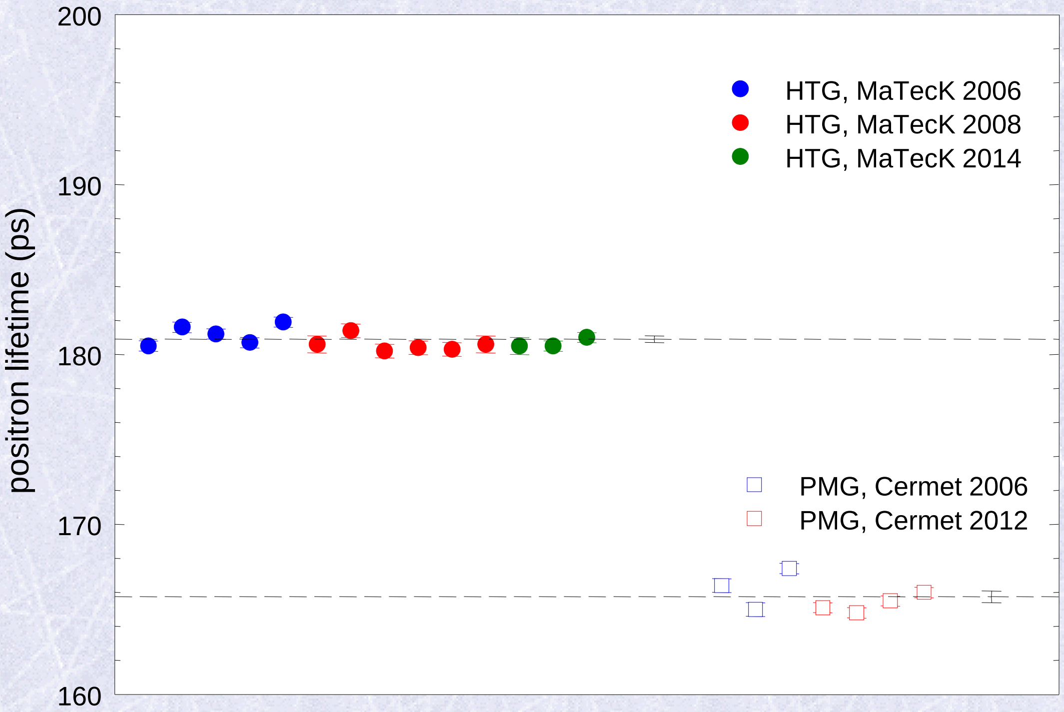
^{22}Na source deposited on 2 μm mylar foil

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
- no significant differences among samples prepared in various periods

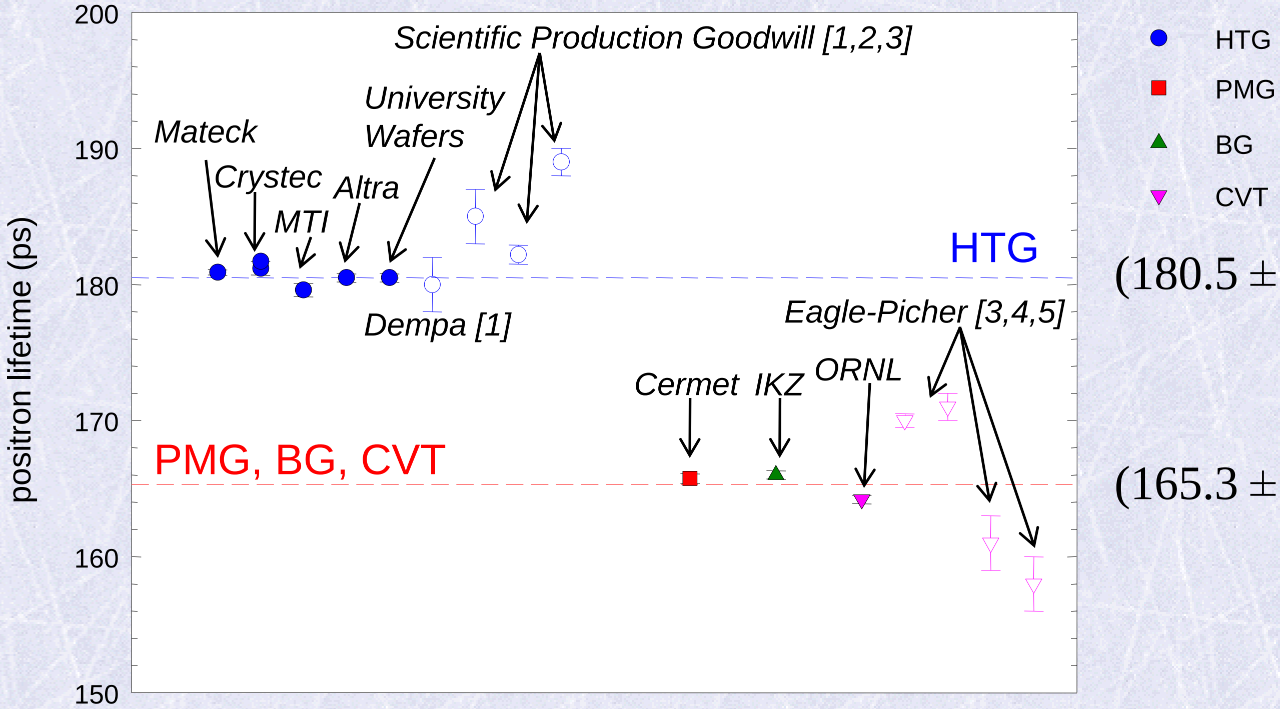


(180.9 ± 0.2) ps

(165.7 ± 0.4) ps

As-grown ZnO single crystals – comparison of growth techniques

- comparison of ZnO crystals prepared by various techniques
- two groups
  - → HTG ZnO crystals: lifetime ≈ 181 ps
  - → PMG, BG, CVT ZnO crystals: lifetime ≈ 165 ps



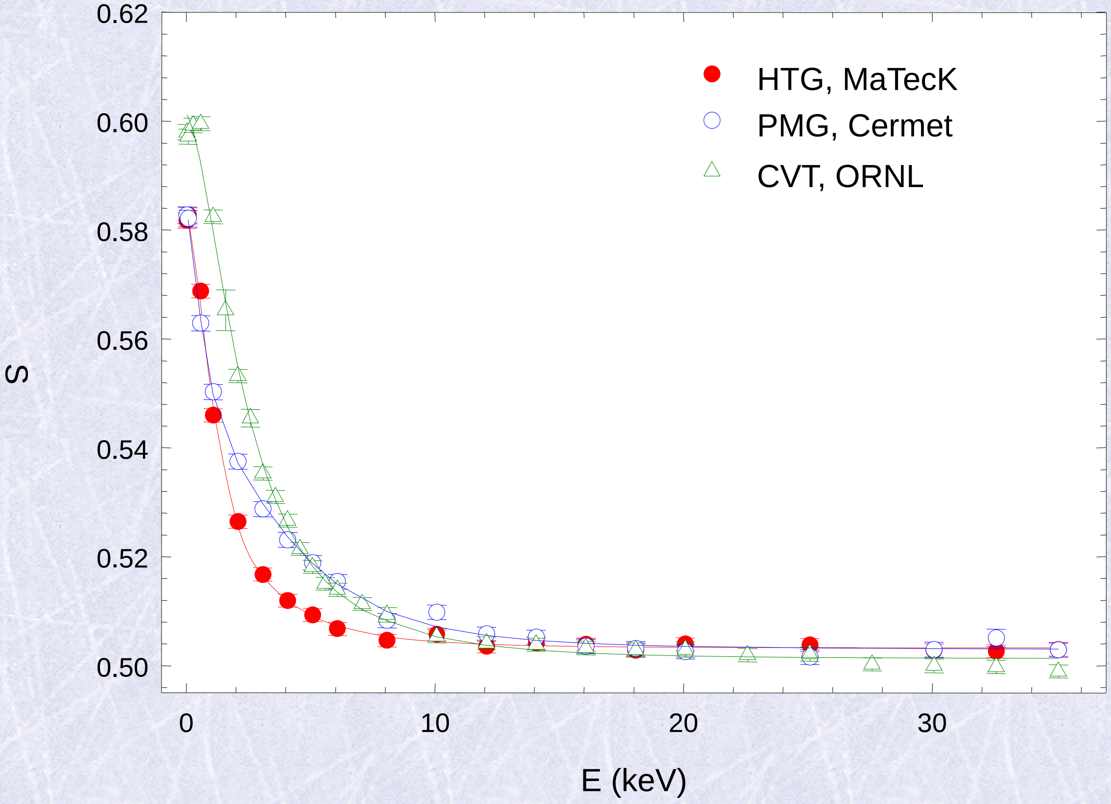
(180.5 ± 0.3) ps

(165.3 ± 0.6) ps

[1] F. Tuomisto, D.C. Look, Proc. SPIE 6474, 647413 (2007)
[2] Z.Q. Chen et al., Phys. Rev. B 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).

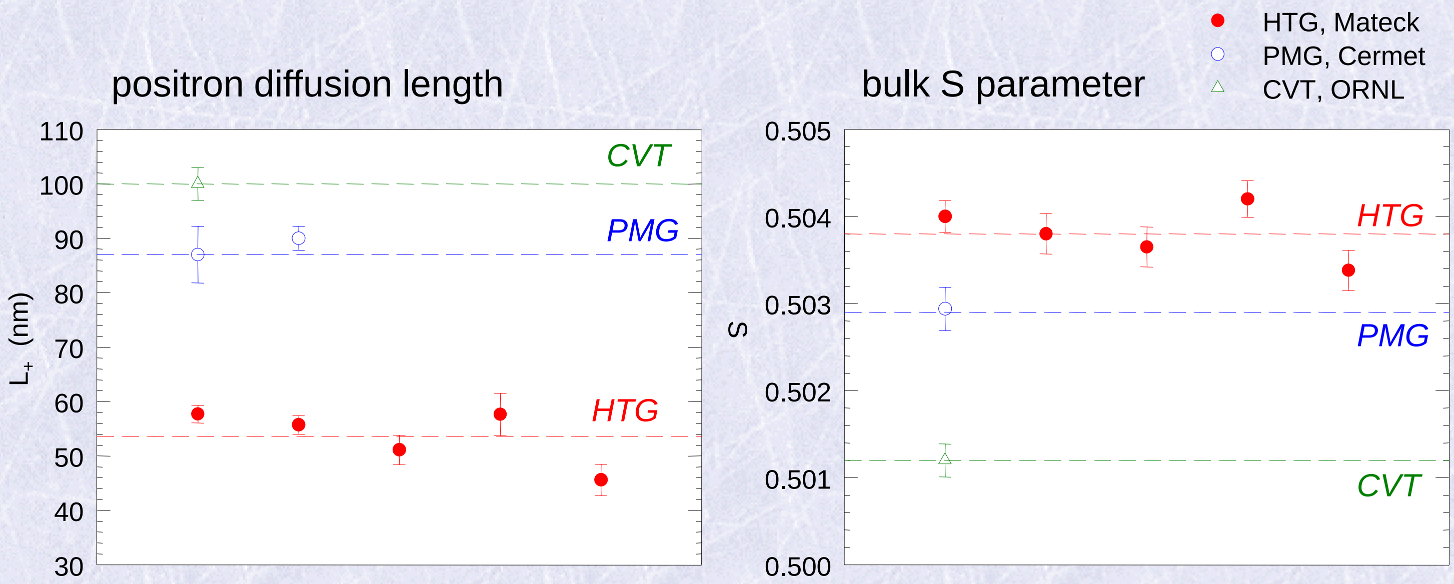
As-grown ZnO single crystals – comparison of growth techniques

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



As-grown ZnO single crystals – comparison of growth techniques

- positron back-diffusion measurement on slow positron beam
- comparison of ZnO crystals prepared by various techniques
- concentration of defects: CVT → PMG → HTG



Chemical Analysis of ZnO crystals

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

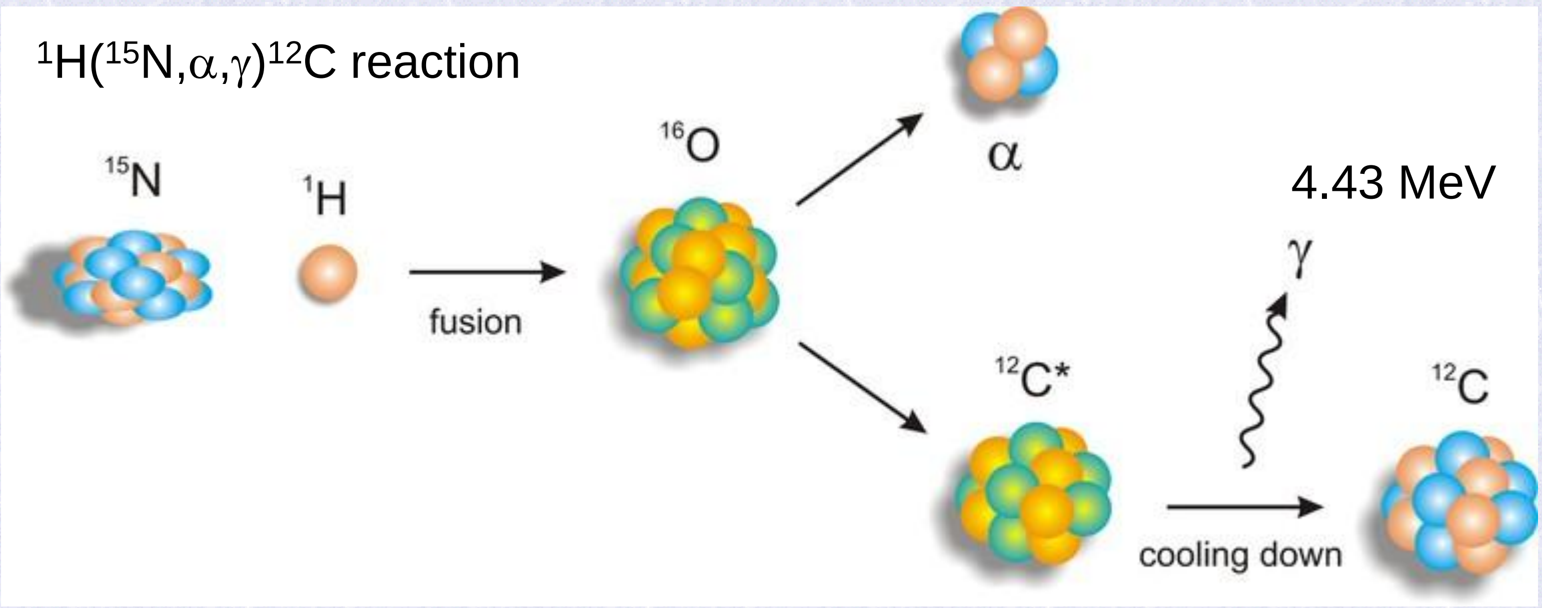
  atomic concentration (ppm = 10^{-4} at.%), sensitivity 0.01 ppm

Sample	Li	Mg	Al	Cr	Mn	Co	Ni	Cu	Ga	Ag	Cd
HTG MaTecK 2006	0.37	3.74		0.08	0.08	0.03	7.80	3.48	0.07	0.16	2.31
HTG MaTeck 2008			4.7		0.30	0.14	1.25	1.07			0.04
HTG Uni-Wafers	6.04				0.34	0.05	4.13	0.49	0.61	0.48	0.19
HTG Altramet	7.03				0.73	0.12	0.45	0.42	0.42	0.18	0.12
PMG Cermet							0.25	0.38	0.49	0.18	0.19
BG IKZ Berlin	0.16					0.01	0.14	0.73	0.68	0.19	

Determination of hydrogen concentration

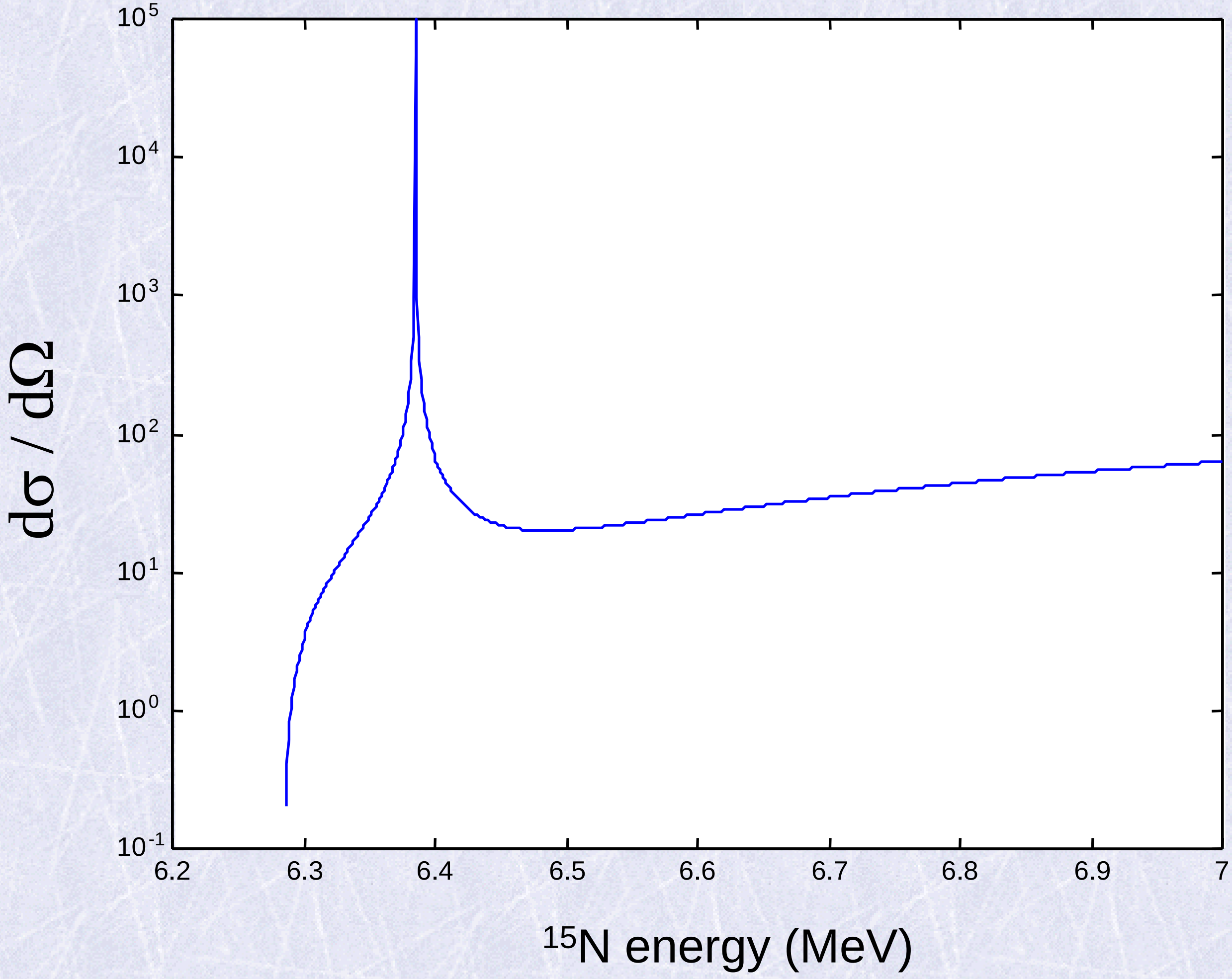
nuclear reaction analysis (NRA)

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



Determination of hydrogen concentration

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



Determination of hydrogen concentration

nuclear reaction analysis (NRA)

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

- **depth NRA scan**

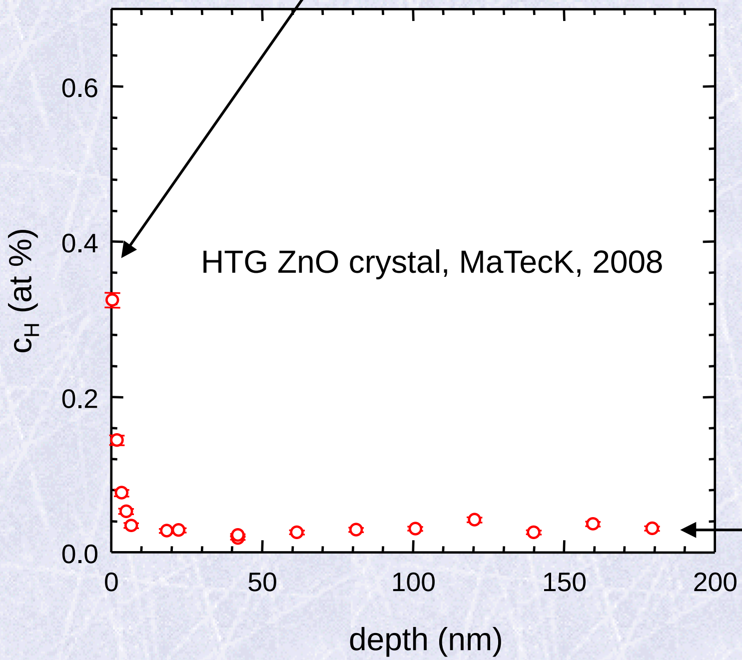
  - gradually increasing energy of ^{15}N ions: E = 6.4 – 7.1 MeV
  - detection depth in ZnO increasing from surface up to 300 nm
  - detection limit: 0.005 at.%

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

hydrogen adsorbed on surface



bulk value c_H = 0.03 at.%

Chemical Analysis of ZnO crystals

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

  atomic concentration (ppm = 10^{-4} at.%)

Sample	Li	Mg	Al	Cr	Mn	Co	Ni	Cu	Ga	Ag	Cd	H
HTG MaTecK 2006	0.37	3.74		0.08	0.08	0.03	7.80	3.48	0.07	0.16	2.31	700
HTG MaTeck 2008			4.7		0.30	0.14	1.25	1.07			0.04	300
HTG [illegible] Altramet	6.04				0.34	0.05	4.13	0.49	0.61	0.48	0.19	800
PMG Cermet							0.25	0.38	0.49	0.18	0.19	300
BG IKZ Berlin	0.16					0.01	0.14	0.73	0.68	0.19		400

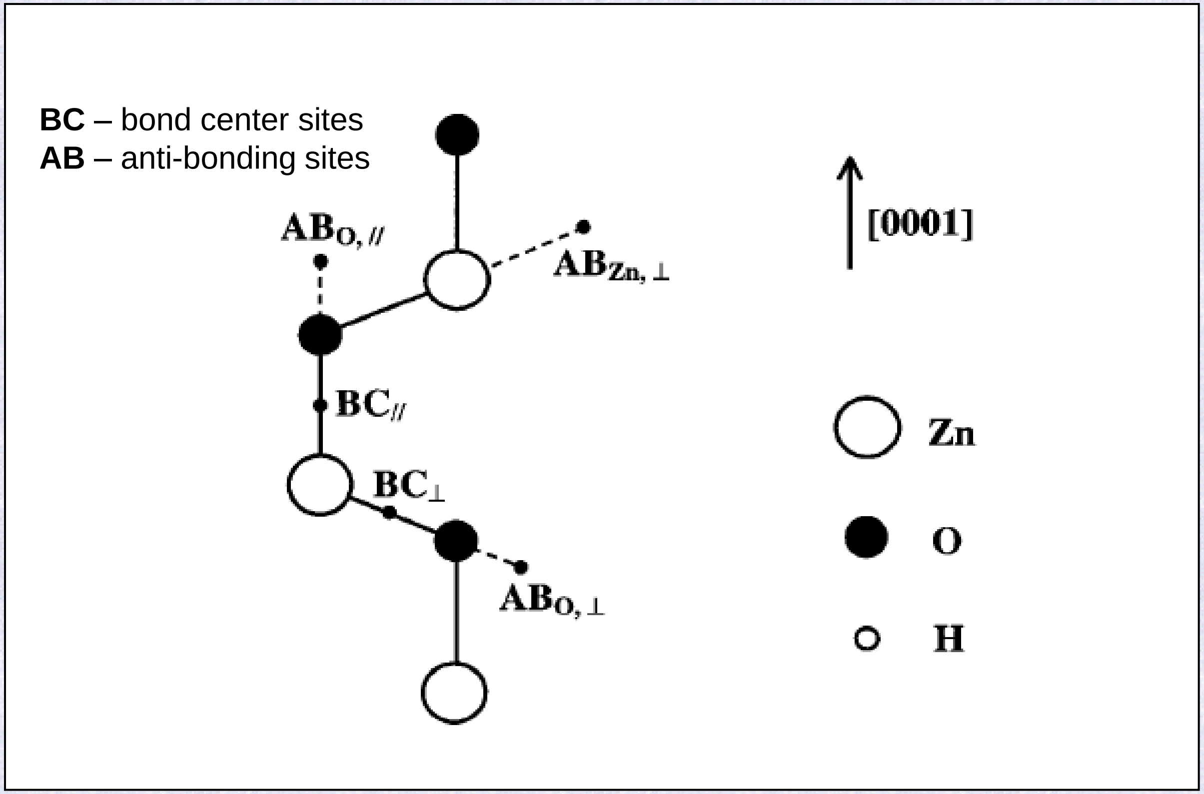
Hydrogen is the most important impurity in ZnO crystals

Hydrogen in ZnO

- Hydrogen is a shallow donor in ZnO

- *Van de Walle et al., PRL **85**, 1012 (2000)*

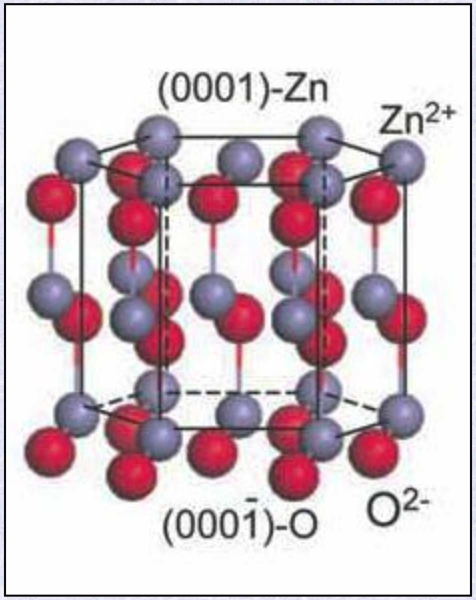
- *Janotti et al., Nature Mater. **6**, 44 (2007)*

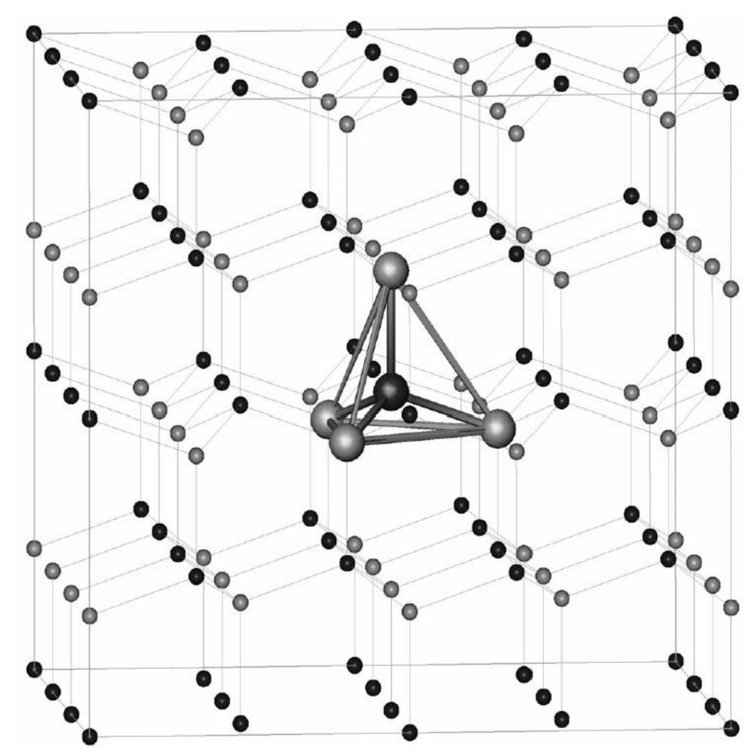


Theoretical calculations of positron lifetimes in ZnO

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





Theoretical calculations of positron lifetimes in ZnO

bulk ZnO lifetime

- **τ_B = 154 ps**, *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

- **τ_B = 157 ps**, *J. Kuriplach, B. Barbiellini, PRB 89, 155111 (2014)*

  - GGA ($\alpha = 0.05$) approach for electron-positron correlation
  - self consistent electron density and potential from WIEN2K
  - note that GGA approach with $\alpha = 0.22$ leads to $\tau_B = 177$ ps

- **τ_B = 155 ps**, *J. Kuriplach, private communication*

  - GGA (parameter-free model) *B. Barbiellini, J. Kuriplach PRL 114, 147401 (2015)*
  - self consistent electron density and potential from WIEN2K

Theoretical calculations of positron lifetimes in ZnO

Vacancies in ZnO

- 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

----------------> V_O is unable of positron trapping

----------------> V_{Zn} is deep positron trap

Theoretical calculations of positron lifetimes in ZnO

Vacancies in ZnO

- 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

F. Tuomisto et al., PRL 91, 205502 (2003)

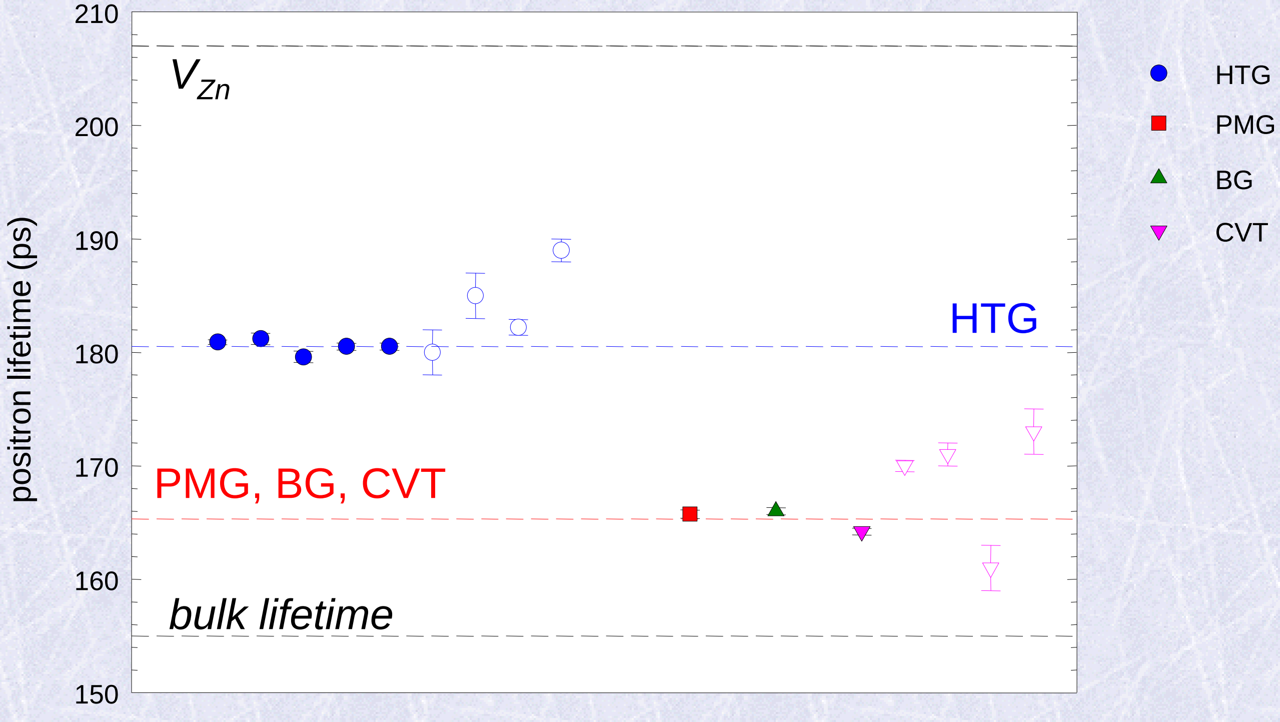
	τ (ps)	E_B (ev)	τ / τ_B	τ (ps)	τ / τ_B
e^-e^+ correlation	LDA (BN, $\varepsilon_\infty = 4$)			GGA ($\alpha = 0.22$)	
ZnO bulk	154	-	-	177	-
O-vacancy	154	~ 0.0	1.00	180	1.02
Zn-vacancy	207	1.11	1.34	237	1.34
Zn+O di-vacancy	253	1.87	1.64		

V_O is unable of positron trapping

V_{Zn} is deep positron trap

As-grown ZnO single crystals – comparison of growth techniques

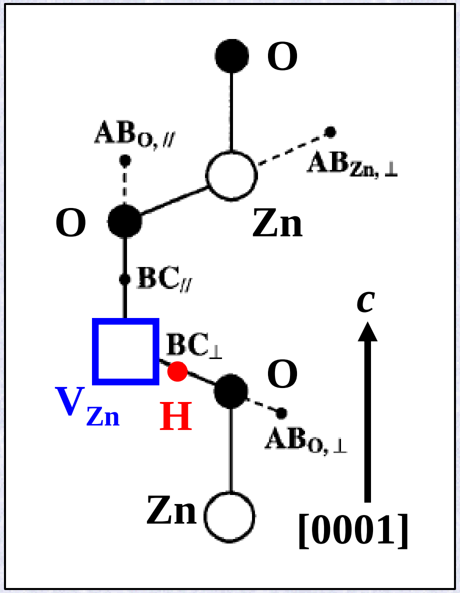
- comparison of ZnO crystals prepared by various techniques
- two groups
  - → HTG ZnO crystals: $\tau \approx 181$ ps $\longrightarrow$ $\tau_B < \tau < \tau_{\text{Zn-vacancy}}$
  - → PMG, BG, CVT ZnO crystals: $\tau \approx 165$ ps $\longrightarrow$ approaches τ_B

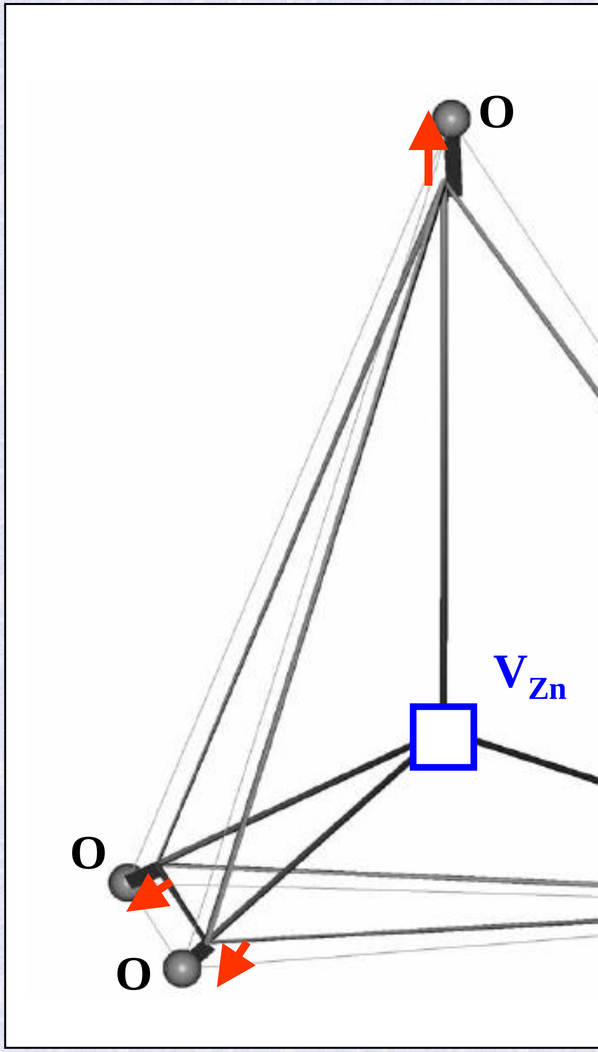


Complexes V_{Zn} + H

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

relaxation of O atoms and H

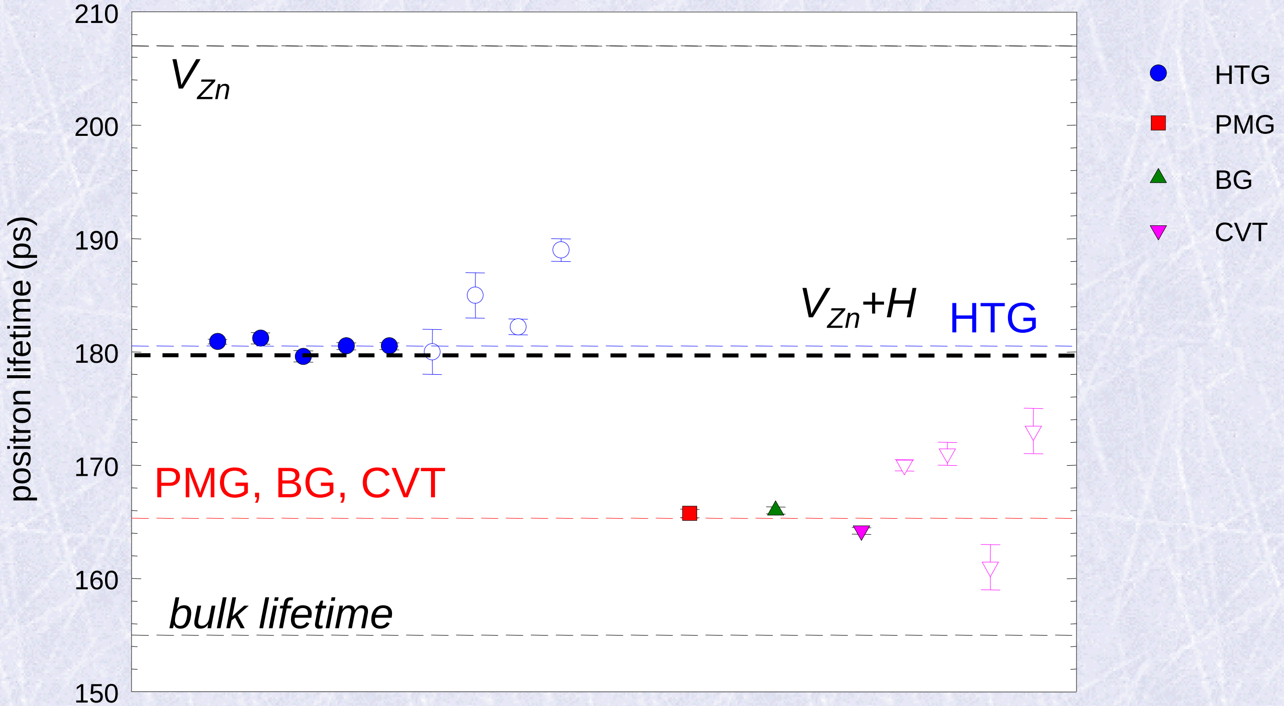




- outward relaxation of O atoms
- inward relaxation of H

As-grown ZnO single crystals – comparison of growth techniques

- comparison of ZnO crystals prepared by various techniques
- two groups
  - → HTG ZnO crystals: $\tau \approx 181$ ps → $\tau_B < \tau < \tau_{\text{Zn-vacancy}}$
  - → PMG, BG, CVT ZnO crystals: $\tau \approx 165$ ps → approaches τ_B
- HTG ZnO crystals: saturated positron trapping in V_{Zn}+H complexes



Estimation of V_{Zn+H} concentration

HTG ZnO, MaTecK

- estimation of V_{Zn}+H concentration

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

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

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

$\tau_B = 155\,\mathrm{ps}$

HTG ZnO

[V_{Zn}+H]

$\Rightarrow$ **$c_v \approx 0.002$ at.%**

(10^{18} cm^{-3})

simple trapping model

positron trapping rate

$K_v \approx 3 \times 10^{10}$ s^{-1}

$\Downarrow$

free positron component

$I_1 \approx 3$ %, $\tau_1 \approx 20$ ps

$\Downarrow$

too weak & short
to be resolved in PL spectrum

- hydrogen concentration (NRA)

$c_H = 0.03 – 0.07$ at.% $\rightarrow$ **[H] ≈ 20 [V_{Zn}+H]**

(3-6) $\times 10^{19}$ cm^{-3}

Li_{Zn} defect

HTG ZnO, MaTecK

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

Sample	Li	
HT-grown MaTecK 2006	0.37	**181.2(4) ps**
HT-grown MaTeck 2008		**180.6(3) ps**
HT-grown Uni-Wafers	6.04	**180.5(3) ps**
HT-grown Altramet	7.03	**180.7(3) ps**
PM-grown Cermet		
BG-grown IKZ Berlin	0.16	

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

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

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

$$\tau_B = 155\,\mathrm{ps}$$

HTG ZnO

$[V_{Zn}+H]$

$$\Rightarrow c_v \approx \mathbf{0.002\ at.\%}$$

$(10^{18}\ \mathrm{cm^{-3}})$

- Li concentration (ICPMS)

$$c_H = 0.00001 – 0.0007\ \mathrm{at.\%}$$

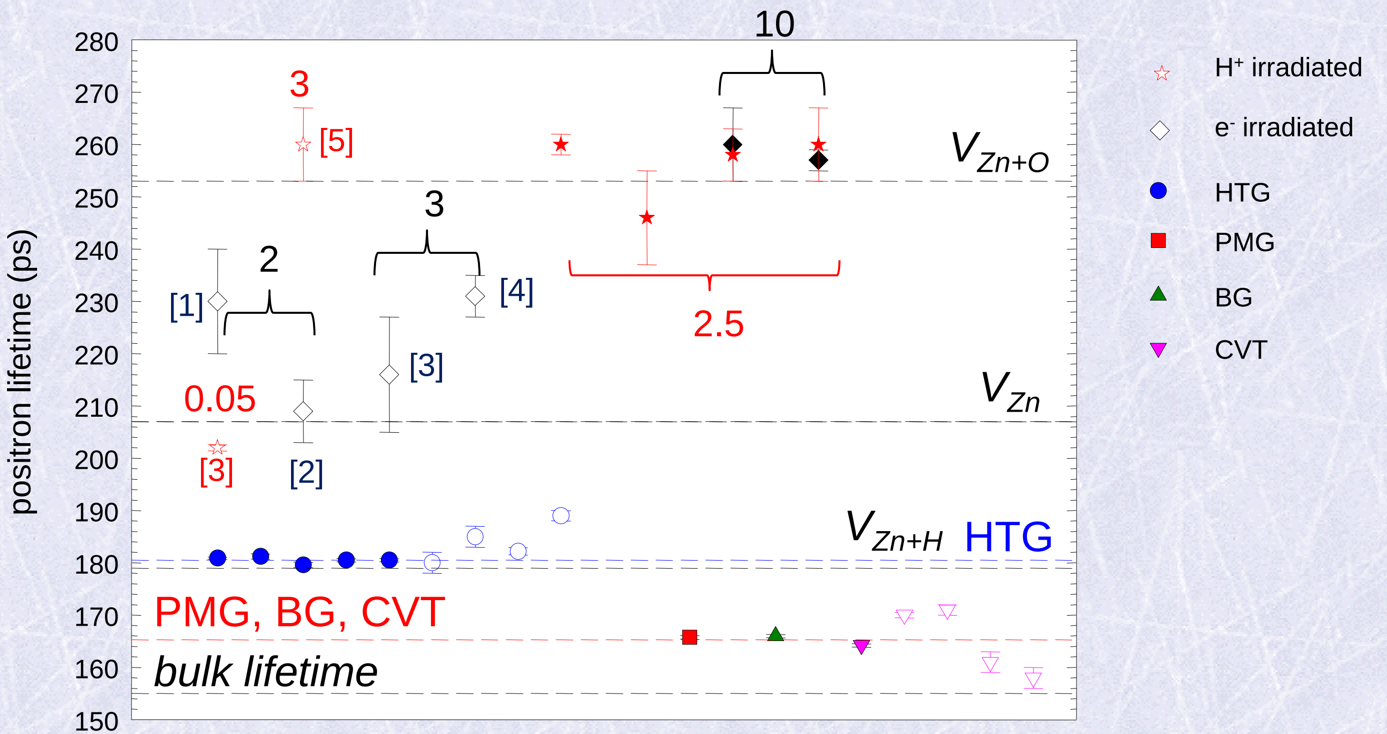
$$(0.01\text{-}6) \times 10^{17}\ \mathrm{cm^{-3}}$$

→ **[Li] is lower than concentration of positron traps**

→ **strong variations of [Li] but no variations of positron lifetime**

Irradiation-induced defects

- e^- irradiation: mixture of V_{Zn} and V_{Zn+O}
- fraction of V_{Zn+O} increases with increasing energy and fluence
- H^+ irradiation: for *E* > 1 MeV dominating defects V_{Zn+O}
- positron lifetimes: $V_{Zn} \approx 210$ ps, $V_{Zn+O} \approx 255$ ps



[1] F. Tuomisto et al. , PRL 91, 205502 (2003)
[2] S. Brunner et al., Mater. Sci. Forum 363-365, 141 (2001)
[3] Z.Q. Chen et al., PRB 77, 115213 (2005)
[4] Z.Q. Chen et al., PRB 75, 245206 (2007)
[5] S. Brunner et al., MRS proc. 540, 207 (1999)

Irradiation-induced defects

HTG ZnO, MaTecK

- electron irradiated E = 10 MeV, T < 100^{o}C

Fluence (cm^{-2})	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)
Electron irradiated E = 10 MeV, T < 100^{o}C				
1×10^{18}	182 ± 2	67 ± 2	256 ± 3	33 ± 2
2×10^{18}	181 ± 1	50 ± 2	254 ± 3	50 ± 2
Proton irradiated E = 2.5 MeV, T < 100^{o}C				
6×10^{15}	180 ± 1	75 ± 1	258 ± 5	25 ± 1
1×10^{16}	181 ± 1	71 ± 2	260 ± 2	29 ± 2

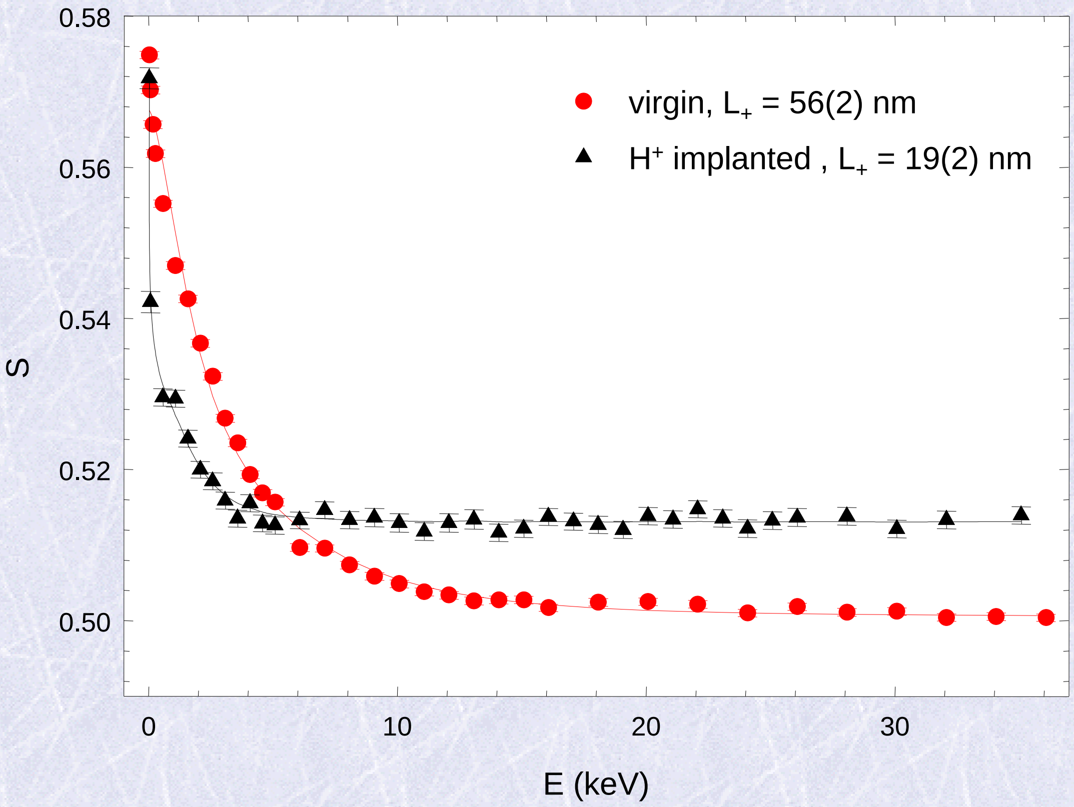
- simple trapping model: $$\tau_1 = \frac{1}{\tau_B^{-1} + K}$$

- no shortening of τ_1 testifies that it comes from trapped positrons

Irradiation-induced defects

HTG ZnO, MaTecK

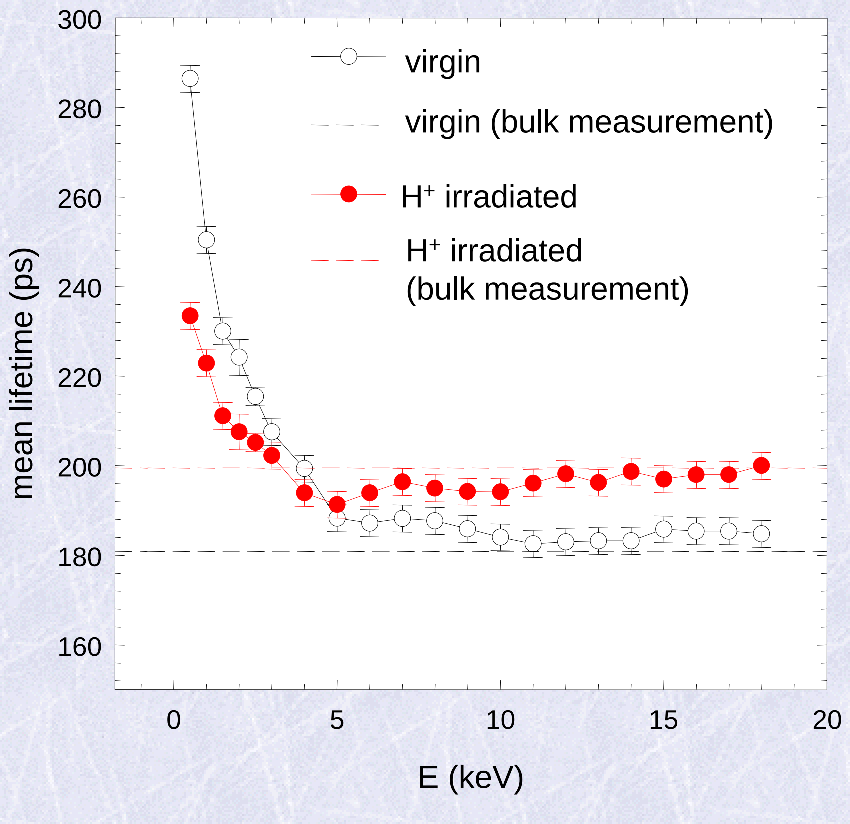
- H^+ irradiated E = 2.5 MeV, $F = 6 \times 10^{15}$ cm^{-2}, $T < 100^oC$
- shortening of L_+ and increase of S parameter due to radiation-induced V_{Zn+O}



Irradiation-induced defects

HTG ZnO, MaTecK – pulsed positron beam PLEPS (NEPOMUC, München)

- H^+ irradiated E = 2.5 MeV, $F = 6 \times 10^{15}$ cm^{-2}, $T < 100^{o}$C
- increase of the mean positron lifetime in bulk due to radiation-induced V_{Zn+O}

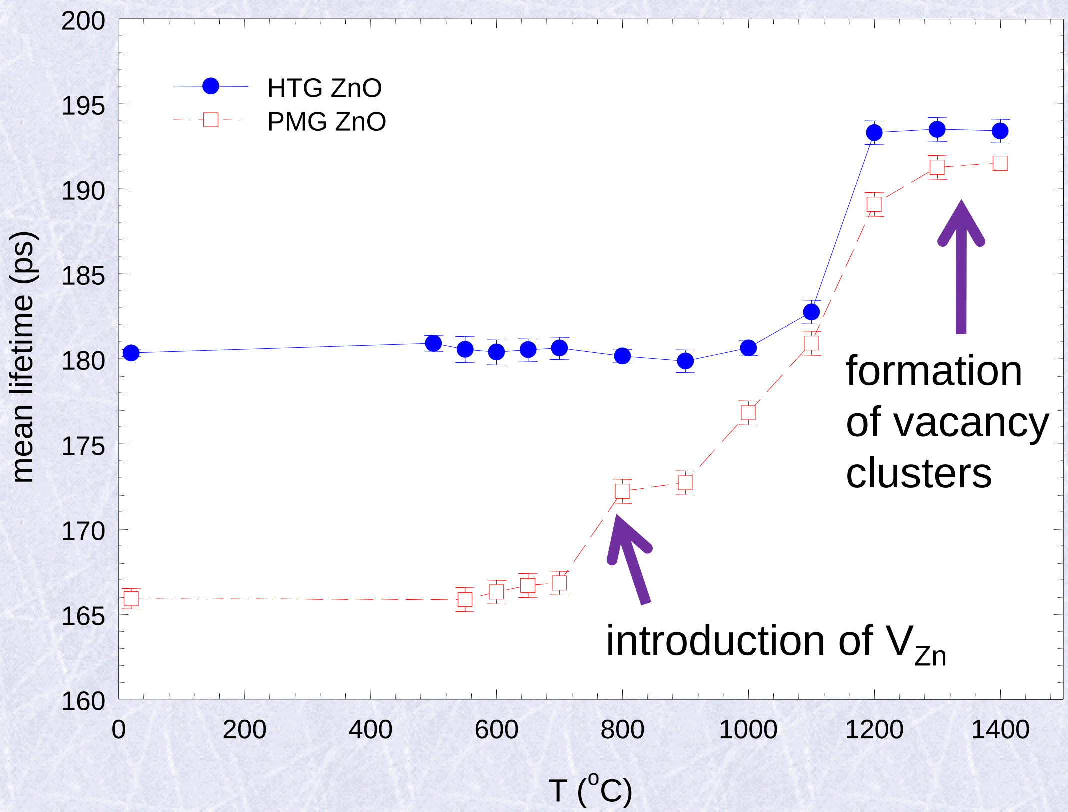


(199.5 ± 0.5) ps

(180.9 ± 0.4) ps

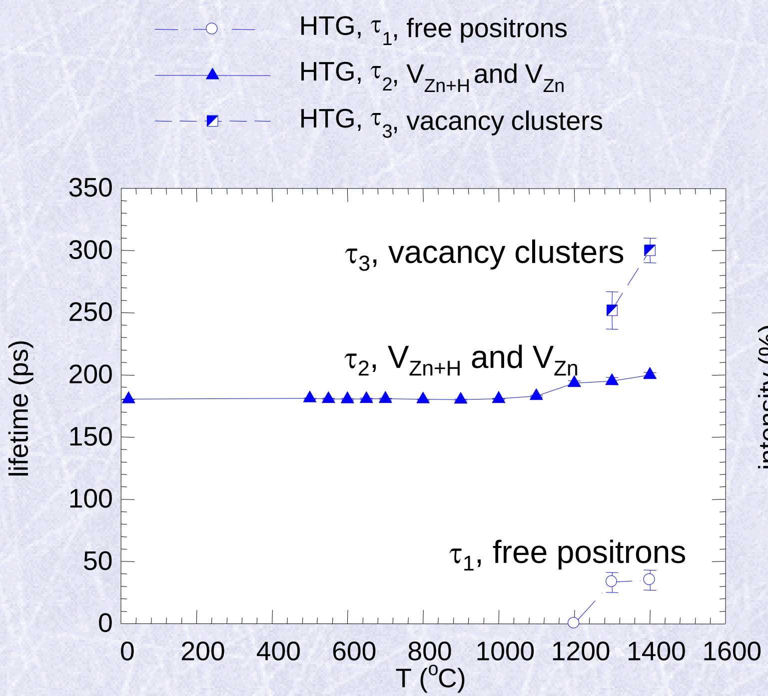
Annealing of ZnO crystals in air

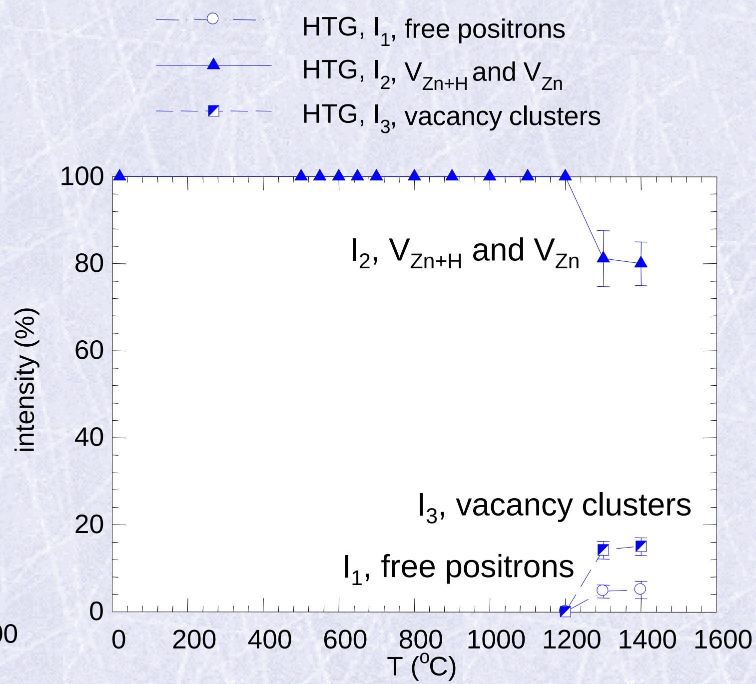
- ZnO easily decomposes to its components $ZnO \leftrightarrow Zn + \frac{1}{2} O_2$, $\Delta H = 350.5$ kJ/mol
- upon heating ZnO dissociates
- high vapour pressure of Zn and $O_2 \Rightarrow$ ZnO evaporation
- $p_{Zn} > p_{O2} \Rightarrow$ Zn evaporation is more intensive $\Rightarrow$ formation of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



Annealing of ZnO crystals in air

- decomposition of positron lifetime spectra
- HTG ZnO (MaTecK), PMG ZnO (Cermet)
- free positron component appeared at T > 1200°C

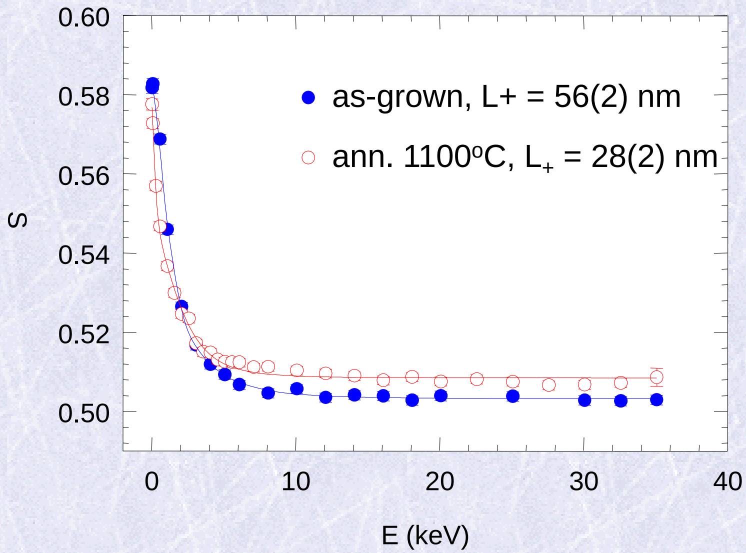




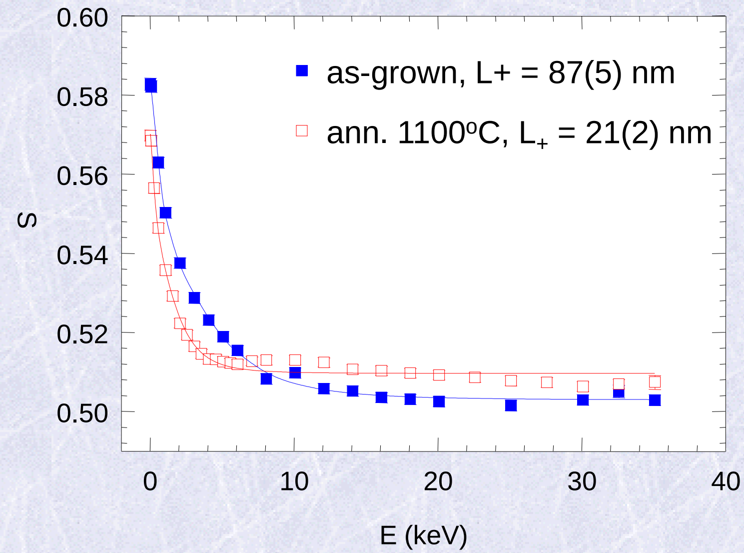
Annealing of ZnO crystals in air

- VEPAS results
- in both crystals annealing up to 1100°C led to shortening of L_+ and increase of S
- due to introduction of V_{Zn} and vacancy clusters

HTG ZnO (MaTecK)



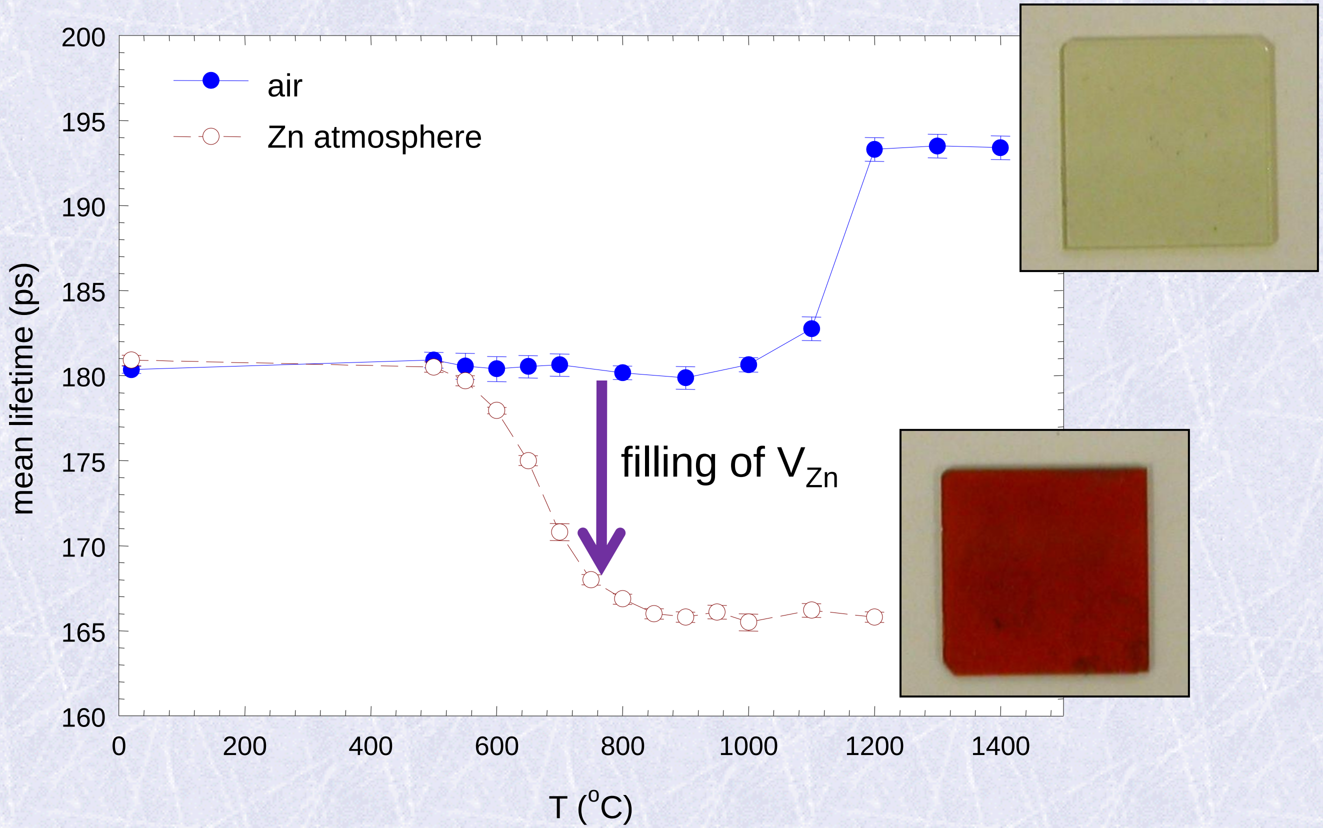
PMG ZnO (Cermet)



Annealing of ZnO crystals – air versus Zn atmosphere

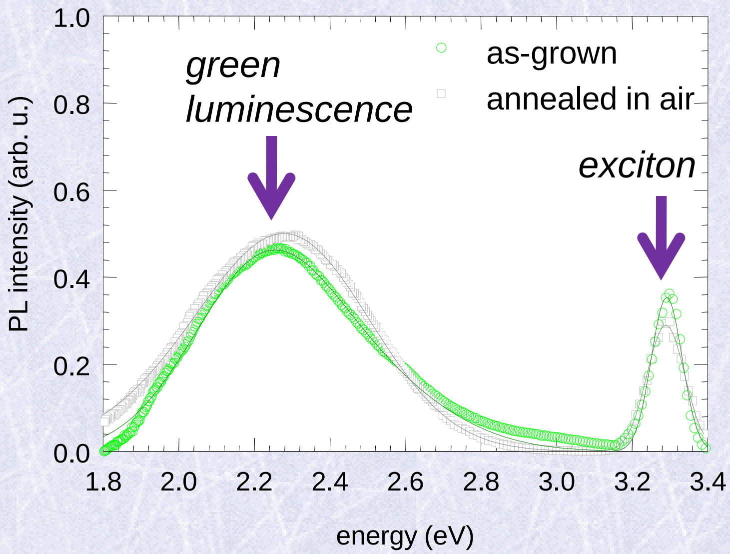
- HTG ZnO, MaTecK
- annealing in air → Zn evaporation → formation of V_{Zn}
- annealing in Zn overpressure → filling of V_{Zn}

  → creation of V_O → sample turns red



Annealing of ZnO crystals - photoluminescence

- HTG ZnO, MaTecK
- UV light excitation 325 nm (3.81 eV)
- UV exciton peak 3.29 eV (band-to-band transition)
- green emission 2.31 eV (defect-related inter-band transition)



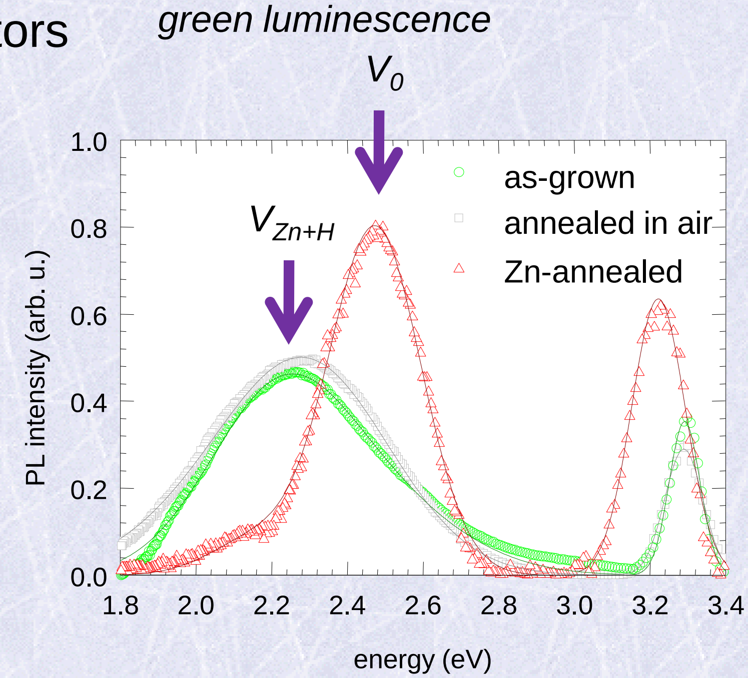
J. Čížek et al.,
APL 106, 251902 (2015)

Annealing of ZnO crystals - photoluminescence

- HTG ZnO, MaTecK
- UV light excitation 325 nm (3.81 eV)
- UV exciton peak 3.29 eV (band-to-band transition)
- green emission:

  2.31 eV V_{Zn+H} acceptors

  2.47 eV V_O centers



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

- annealing at 1000°C in Zn atmosphere → red shift of green emission 2.31 → 2.47 eV

Conclusions

- Hydrogen is the most important impurity in all ZnO crystals
- PMG, BG, and CVT ZnO crystals exhibit low concentration of defects and majority of positrons is annihilated in the free state
- bulk ZnO lifetime falls into the range 155 – 165 ps
- HTG ZnO samples contain V_{Zn}+ H complexes characterized by lifetime of 181 ps
- Electron and proton irradiation introduces
  - V_{Zn} characterized by lifetime ≈ 210 ps
  - V_{Zn+O} characterized by lifetime ≈ 255 ps
- Annealing in air introduced V_{Zn}
- Annealing in Zn atmosphere removed V_{Zn} but introduced V_O
- V_O turn the ZnO sample red