Probing defects in silicon with positrons

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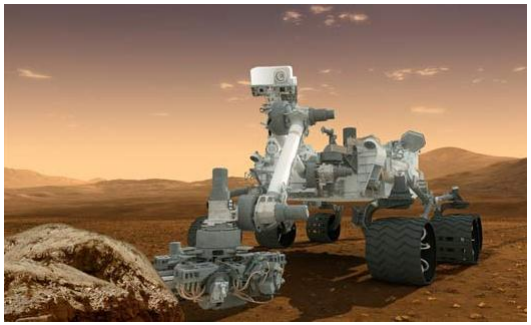
Defect detection in Silicon

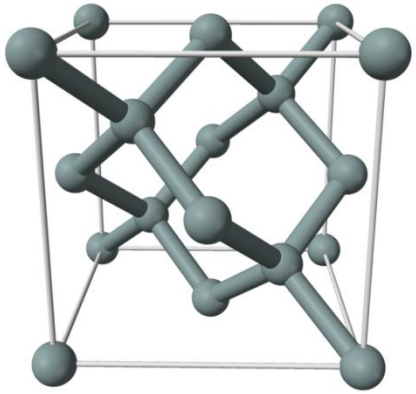
- as-grown bulk Si
- low-T electron irradiation
- Implantation
- plastic deformation

Silicon

- Si has changed the world …



- very advanced technology
- wafers up to 300 mm single crystals
- very pure material possible (Ge even better, but …)
- impurity level very low
- sensors can be integrated (T, p, …)
- no dislocations in the whole big wafer
- perfect material – really no defects ?



diamond lattice of Si

Defects in Silicon

Let us search …

SCIRUS
for scientific information only

1-10 of 411,699 hits for **silicon defects**

Defects seem to be important in Silicon

SCIRUS
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silicon defects positron

1-10 of 11,768 hits for **silicon defects positron**

Positron can obviously be useful…

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positron silicon (author:Coleman)

1-10 of 86 hits for **positron silicon (author:Coleman)**

SCIRUS
for scientific information only

silicon defects positron (author:Krause-Rehbe

1-10 of 30 hits for **silicon defects positron (author:Krause-Rehberg)**

Which Defects detectable by Positrons?

- In as-grown state not so many…

assuming $\mu = 1\times10^{16}\ s^{-1}$
⇨ [Vac] = $4\times10^{14}\ cm^{-3}$
⇨ corresponds to 10^{-8}

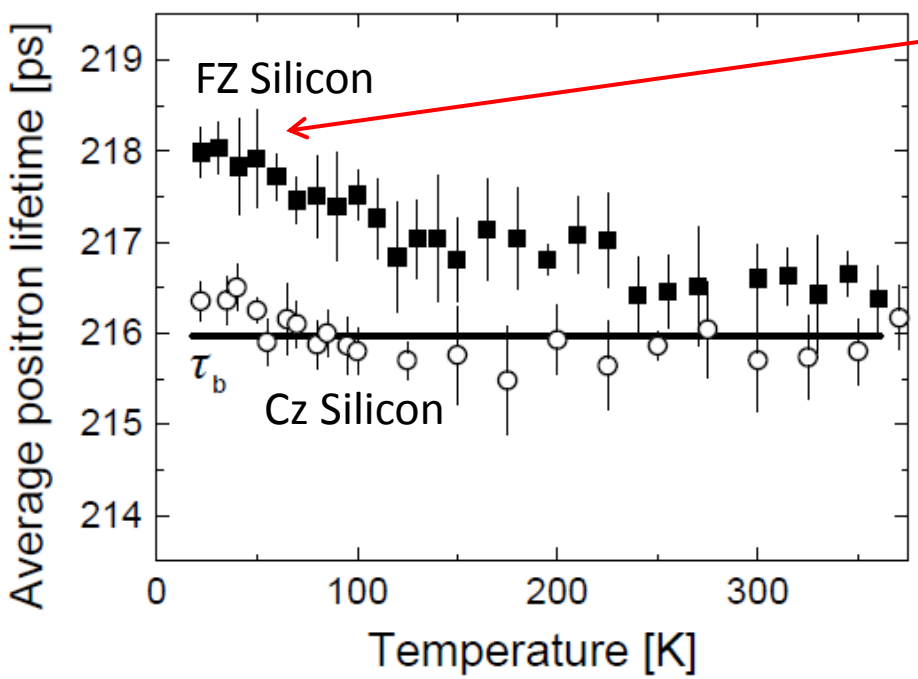


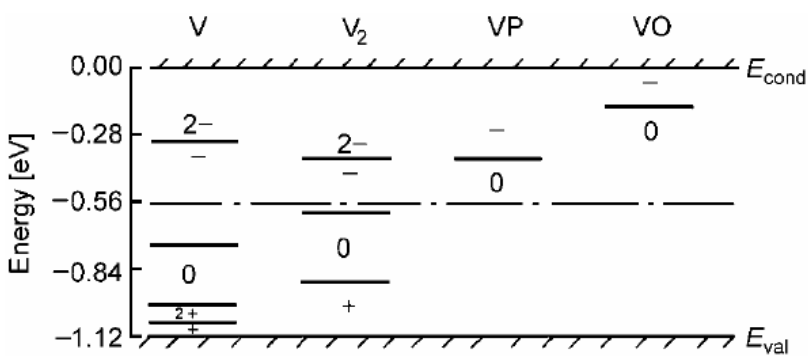
Fig. 4.1. Increase in the average positron lifetime with falling sample temperature in as-grown float-zone silicon (■). The results of a p-type boron-doped Si sample are shown for comparison (○). τ_b is the positron bulk lifetime. The data points were obtained from six measurements with 5×10^6 counts each (Gebauer et al. 1998a). The error bars correspond to the standard deviation of these measurements.

Participation in Avogadro project

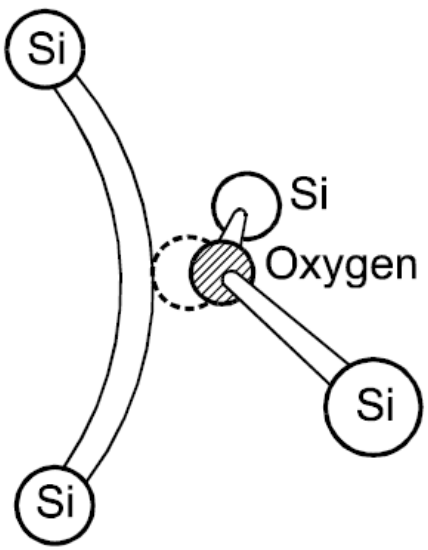
- can just 1 vacancy in 100.000.000 atoms be of interest?
- The **Avogadro project** produces a ball of Si as prototype kilogram (93.6 mm diameter)
- Yes – required accuracy should be 1×10^{-9}

No defects to play with?

- **Okay, we generate some defects ….**
  - low temperature electron irradiation ⇨ point defects
    - monovacancies (Frenkel pairs)
    - the A-center (VO) and V_xO_y clusters
    - the E-centers (dopant-vacancy complexes)
    - divacancies ⇨ stable up to 550 K
  - proton irradiation and ion implantation ⇨ vacancy cluster
  - plastic deformation at elevated temperatures
    - dislocation lines
    - vacancy clusters ⇨ generated by jog dragging



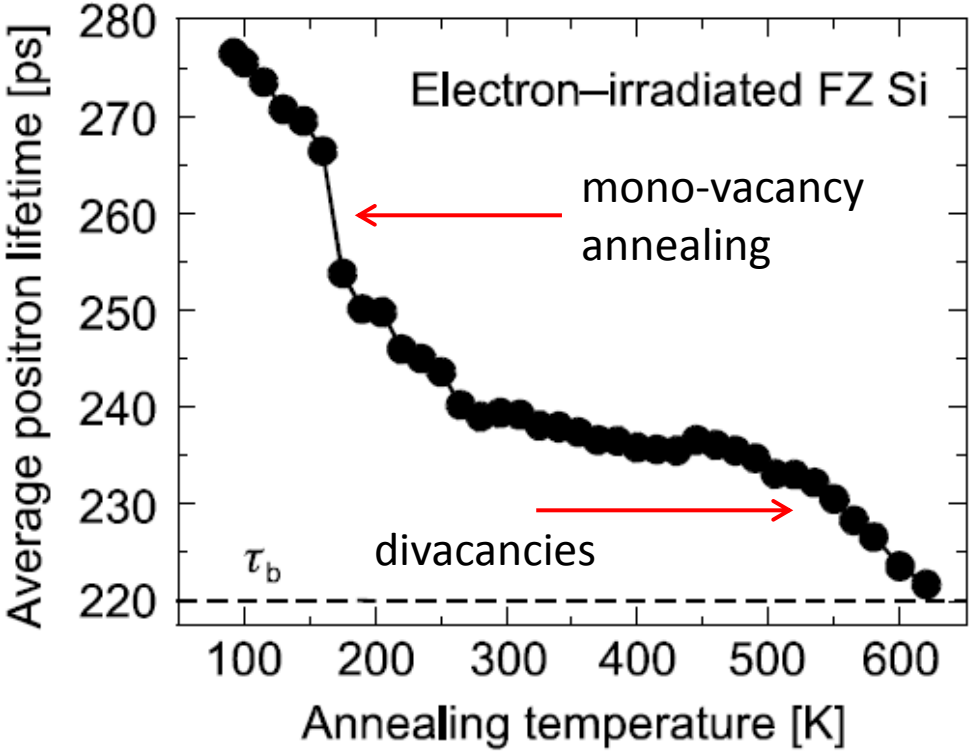
Energy-level scheme in the bandgap of silicon for various charge states of mono-vacancies and divacancies, vacancy–phosphorus pairs (*E* centers), and vacancy–oxygen pairs (*A* centers) according to Mascher et al. (1989b).



A-center in Si: almost no open volume of vacancy

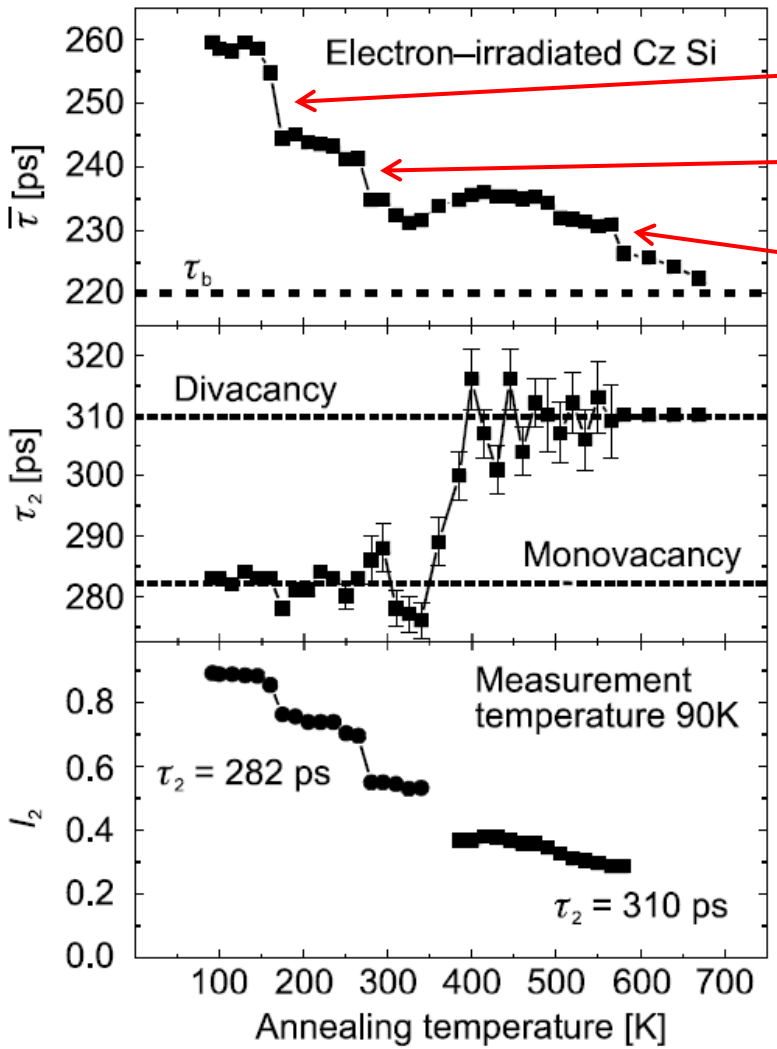
Low-temperature electron irradiation

- irradiation with 2 MeV electrons at 4K: production of Frenkel pairs
- for **FZ-Si things are still easy**



Change in the average positron lifetime with annealing temperature in electron-irradiated undoped float-zone (FZ) silicon. The irradiation was carried out with 2-MeV electrons at 4 K (1×10^{18} cm^{-2} dose). The positron measurement was performed at 90 K (Polity et al. 1998a). τ_b is the bulk lifetime.

Cz-Silicon



mono-vacancy

oxygen-related shallow positron trap

divacancies

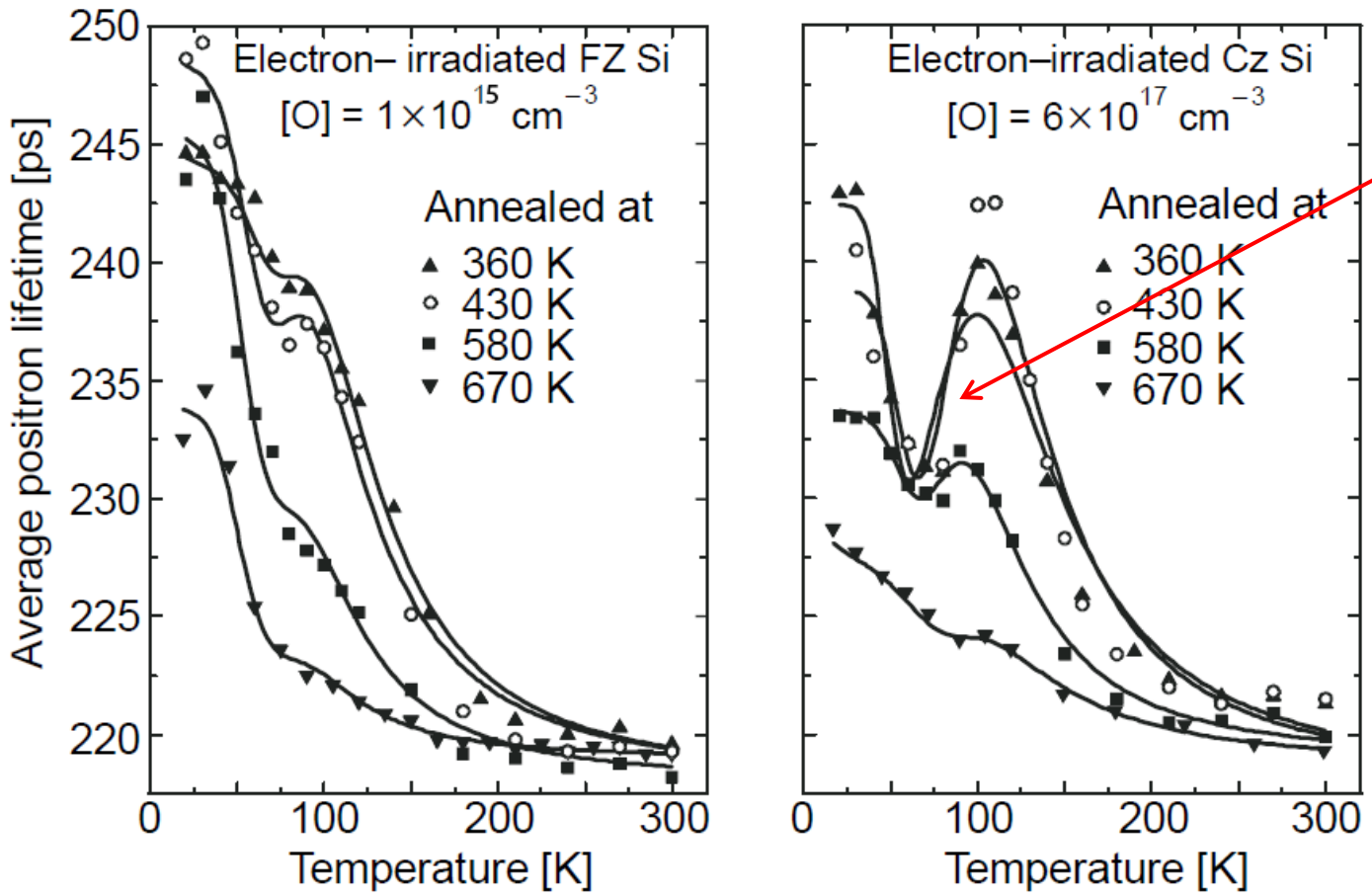
- difference between FZ and Cz silicon: [O]

  ≈ 10^{15} cm^{-3} ≈10^{18} cm^{-3}

- V-O (A-center) acts as shallow trap
- positron binding energy E_b = 48 ± 10 meV

Result of positron lifetime measurements in electron-irradiated Czochralski-grown (Cz) silicon (Polity et al. 1998a).

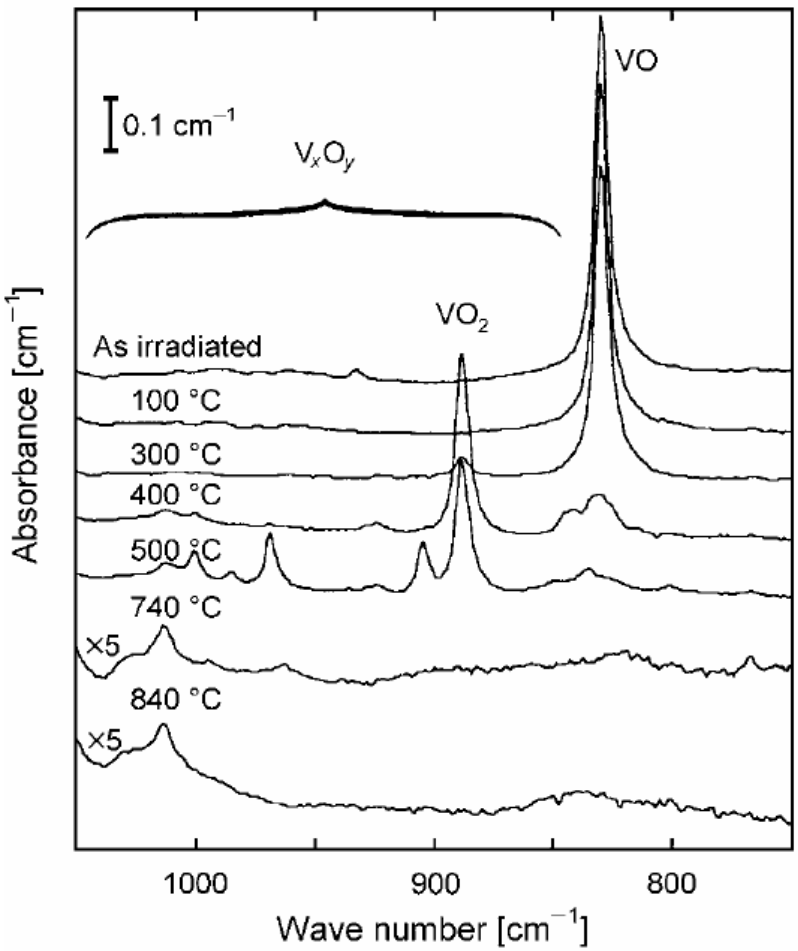
Low-temperature electron irradiation



- oxygen-related shallow positron trap
- weak effect in FZ-Si

Positron lifetime in float-zone (FZ) and Czochralski-grown (Cz) silicon irradiated with electrons at 4 K to a dose of 1×10^{18} cm^{-2} (Polity et al. 1998a).

V_x-O_y defects seen by IR absorption



Infrared absorption spectra of electron-irradiated Czochralski-grown silicon after isochronal annealing at the temperatures indicated. The disappearance of the VO center and the formation of VO_2 and higher V_xO_y complexes are monitored by the corresponding absorption bands (Ikari 1995).

- IR can detect the evolution from VO to V_xO_y
- VO anneals at about 350°C
- VO_2 is formed from VO between 100…300°C and disappears above 500°C

Isothermal annealing provide activation energies

International Workshop on Positron Studies of Defects (PSD 08) IOP Publishing
Journal of Physics: Conference Series **265** (2011) 012001 doi:10.1088/1742-6596/265/1/012001

Activation energies for vacancy migration, clustering and annealing in silicon

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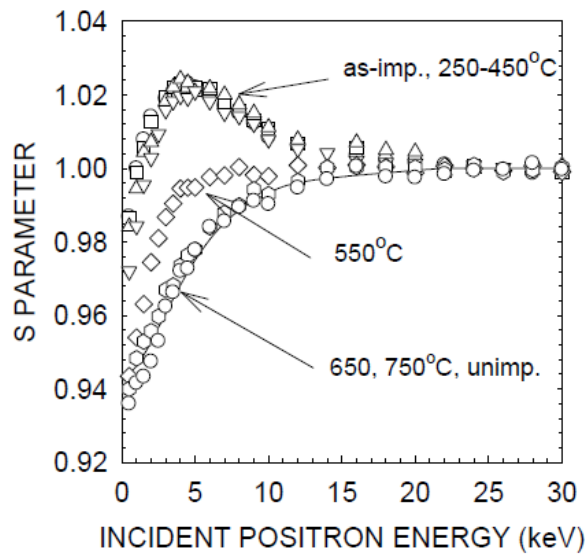
Abstract. A series of measurements have been performed at the University of Bath to study the evolution of vacancy-type structures in silicon. Isothermal annealing performed during positron beam-based Doppler broadening measurements have yielded activation energies for vacancy cluster formation and evaporation in silicon of approximately 2.5 and 3.7 eV, respectively. The clusters, which could predominantly be the stable hexavacancy, appear to form between 400-500°C, and anneal at ~ 600°C. A similar technique applied to low-temperature *in situ* measurements have yielded the migration energies for the silicon monovacancy and interstitial (of ~ 0.5 and 0.08 eV, respectively). Interesting observations of positronium formation at the surface of the samples studied during isothermal annealing are presented.

Isothermal annealing provide activation energies



- an annealing stage is seen between 500…650°C for 50 keV Si-self-implantation
- isothermal annealings allow Arrhenius-plots to determine the activation energies

Figure 1. $S(E)$ for FZ Si implanted with 50 keV Si^+ ions at $5\times10^{13}cm^{-2}$ and annealed at temperatures from 250 to 750°C [10].

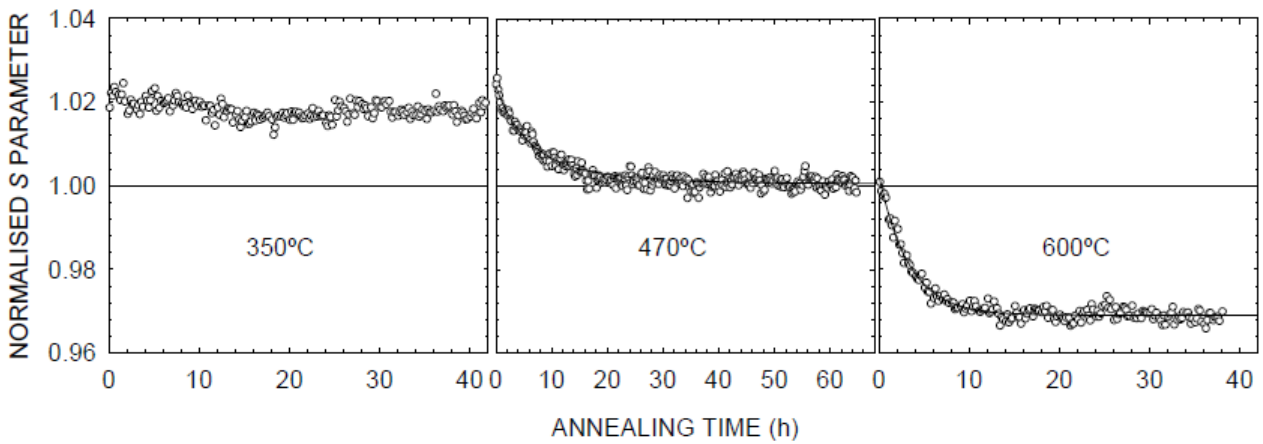


Figure 10. S(3.5 keV) vs annealing time for implanted epi Si at 350, 470 and 600°C. The solid lines through the points in are exponential fits. S values are normalised to that for bulk Si (i.e., unity – as shown in the graphs). Adapted from [23].

Mason R E and Coleman P G 2006 *Appl. Surf. Sci.* **252** 3228

Isothermal annealing provide activation energies

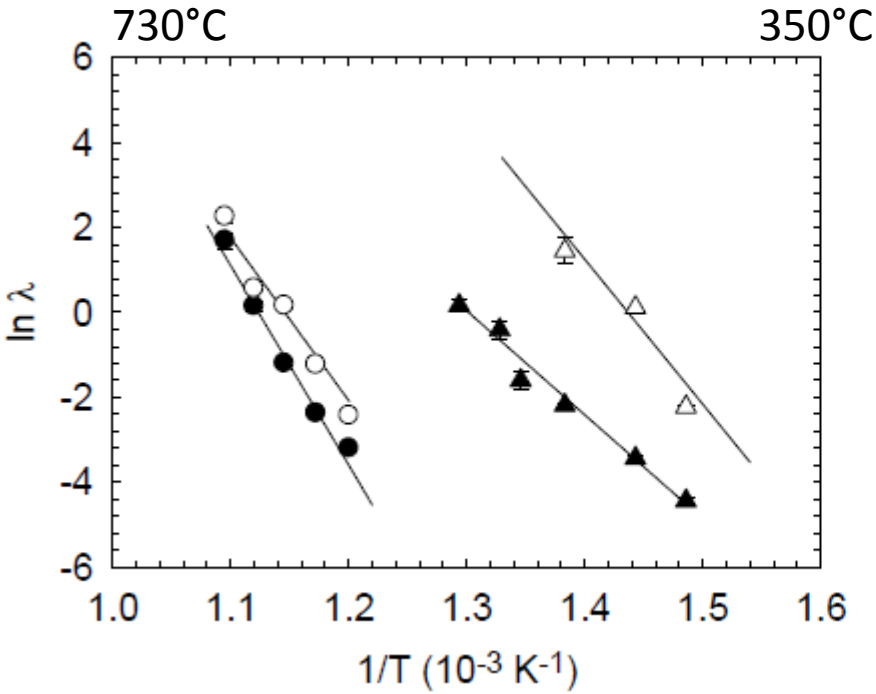


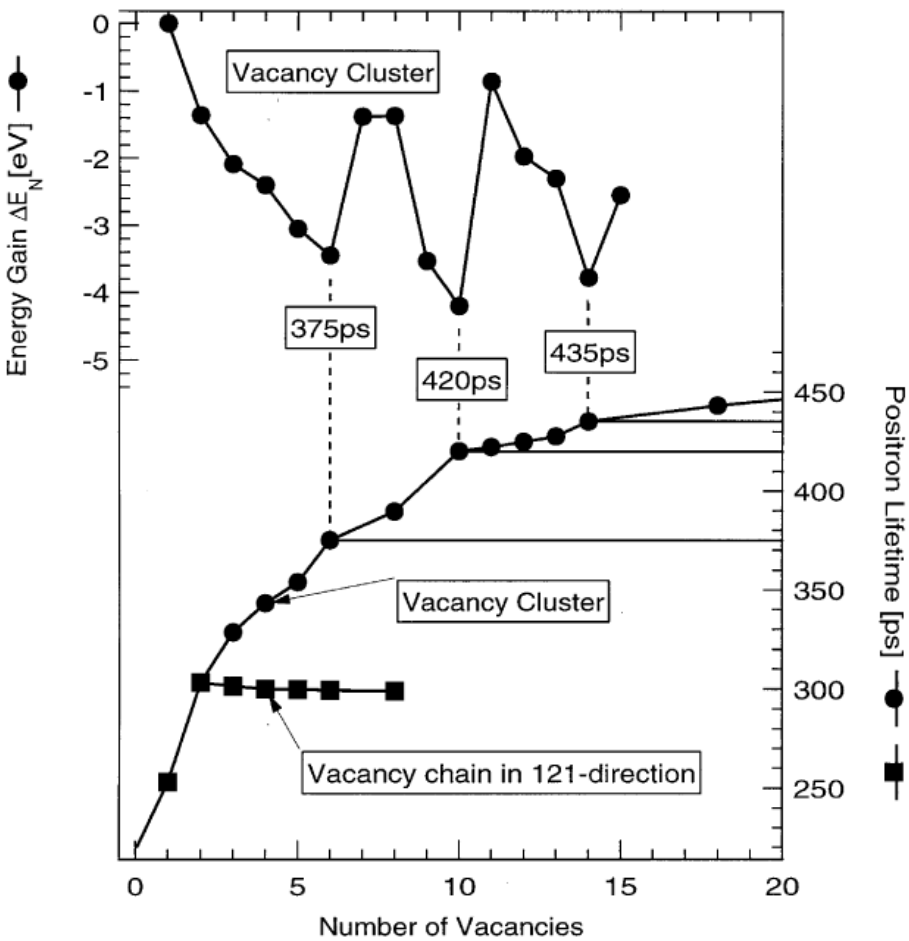
Figure 11. Arrhenius plots for epi and Cz-Si samples. The slopes of the fitted lines give activation energies for two vacancy evolution processes (lower temperatures, triangles and higher temperatures, circles). Solid symbols – epi-Si; open symbols – Cz Si. From [23].

- two different slopes were found in Cz-Si and in epi-layers (two modifications of vacancy clusters)

low-T value:	2.7 ± 0.7 eV	2.1 ± 0.2 eV	(probably transition V2 ⇨ V6)
high-T value:	3.6 ± 0.3	3.9 ± 0.3 eV	(probably hexavacancies)

Mason R E and Coleman P G 2006 *Appl. Surf. Sci.* **252** 3228

Magic numbers of vacancy clusters in Si



- simulations really show that V6, V10 and V14 are "magic numbers"
- stable vacancy clusters in Si
- lifetime measurement would be useful

Fig. 2. Energy gained by adding a monovacancy to an aggregate of $(N-1)$ vacancies in Silicon (upper part) and the corresponding positron lifetime (lower part) for unrelxed structures. Theoretical positron lifetimes for V_6, V_{10}, and V_{14} are indicated.

T.E.M. Staab, M. Haugk, A.Sieck, Th. Frauenheim, H.S. Leipner
Magic number vacancy aggregates in Si and GaAs: Structure and positron lifetime studies
Physica B **273-274** (1999) 501-504.

Isothermal annealing – Monovacancies

- Monovacancies anneal below RT – sample must be cooled during implantation and annealing
- He implantation of 20 keV was performed at 20 K ⇨ saturated trapping by V_1 at 130 nm depth
- two samples ⇨ undoped FZ-Si (very pure Si) and highly As-doped

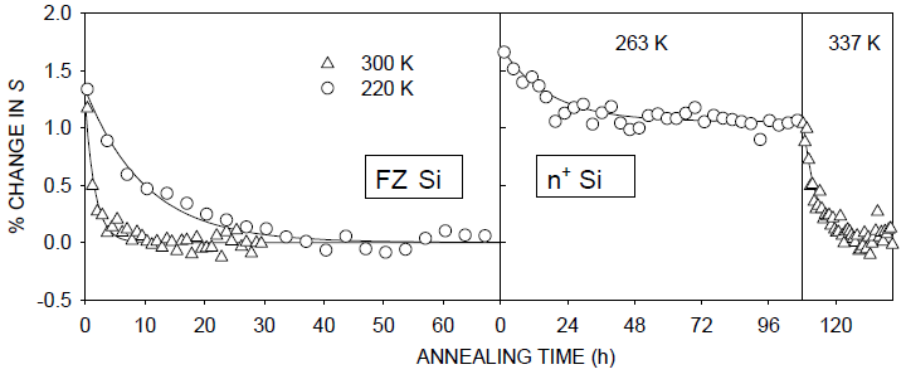
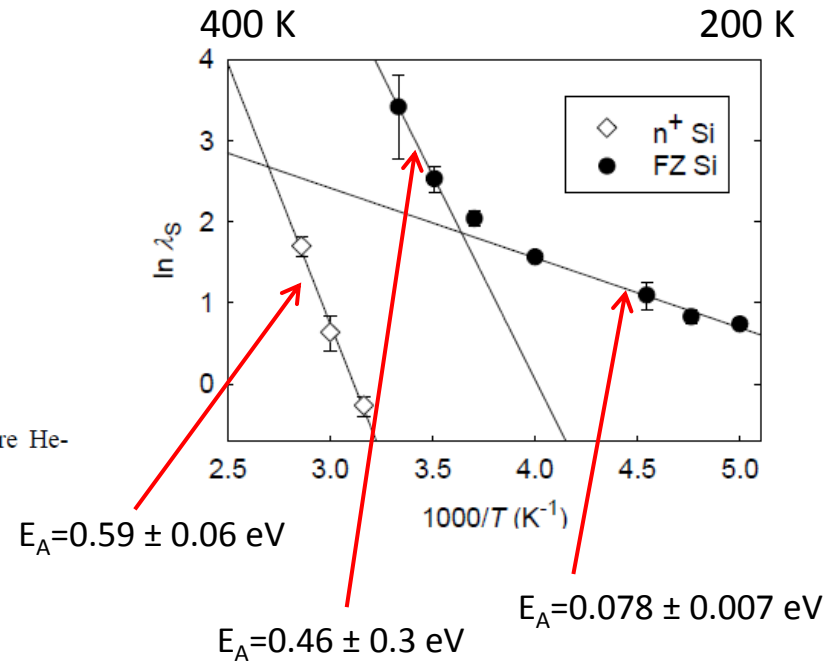


Figure 12. Percentage difference between S parameter at E = 3.5 keV for low-temperature He-implanted FZ and n^+ Si and its asymptotic value as a function of time at four temperatures.



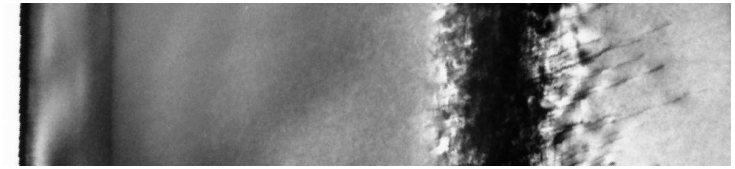
- E_A=0.078 ± 0.007 eV ⇨ disappearance of neutral V1 by interstitial migration
- E_A=0.46 ± 0.3 eV ⇨ disappearance of neutral V1 by vacancy migration
- E_A=0.59 ± 0.06 eV ⇨ annealing of V_{Si}-As E-centers

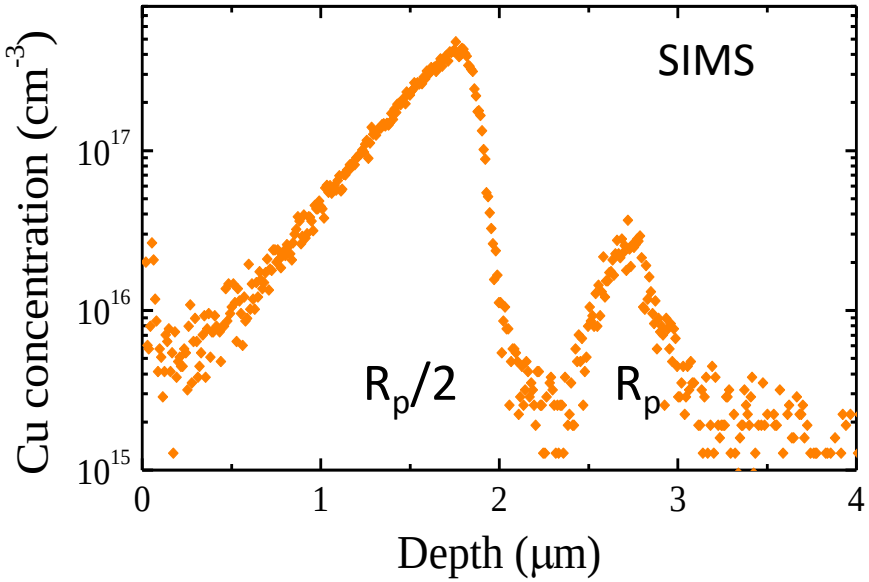
Coleman P G and Burrows C P 2007 *Phys. Rev. Lett.* **98** 265502

Defects in high-energy self-implanted Si: The Rp/2 effect

- after high-energy (3.5 MeV) self-implantation of Si ($5x10^{15}$ cm^{-2}) and RTA annealing (900°C, 30s): two new gettering zones appear at Rp and Rp/2 (R_p = projected range of Si^+)
- visible by SIMS profiling after intentional Cu contamination

TEM image by P. Werner, MPI Halle

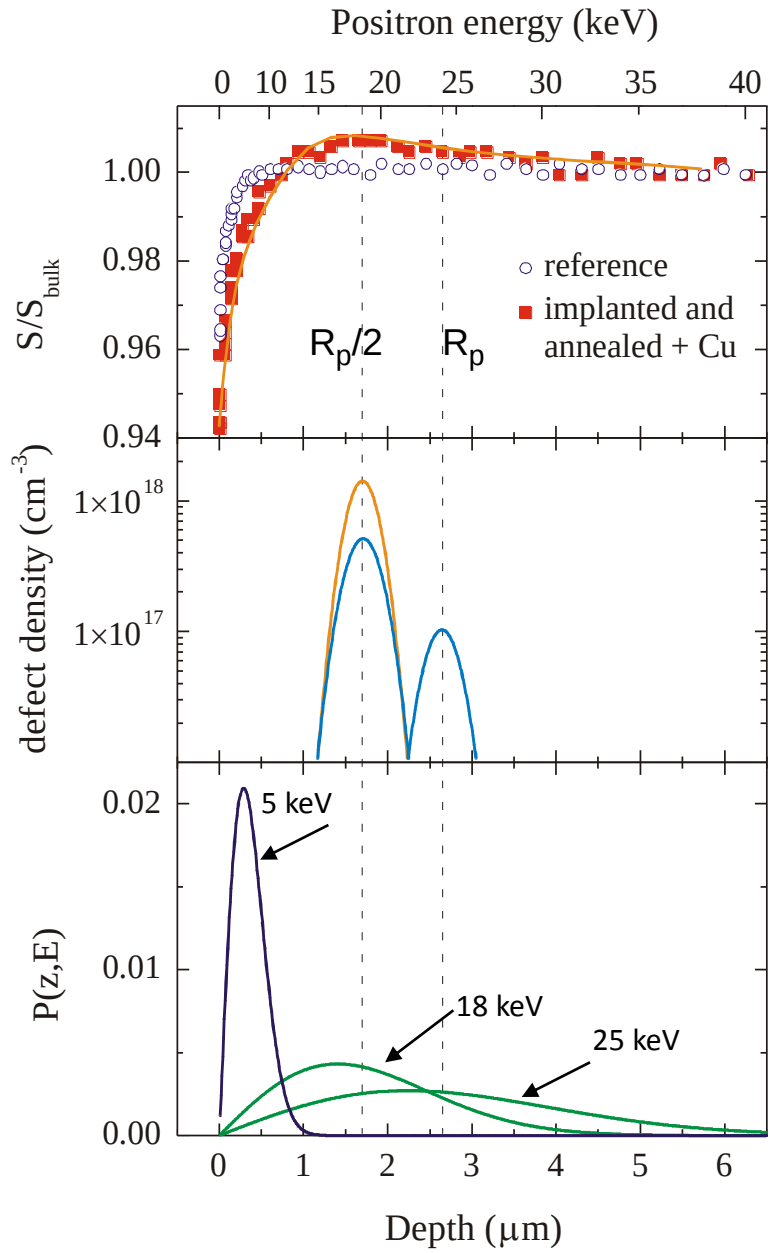




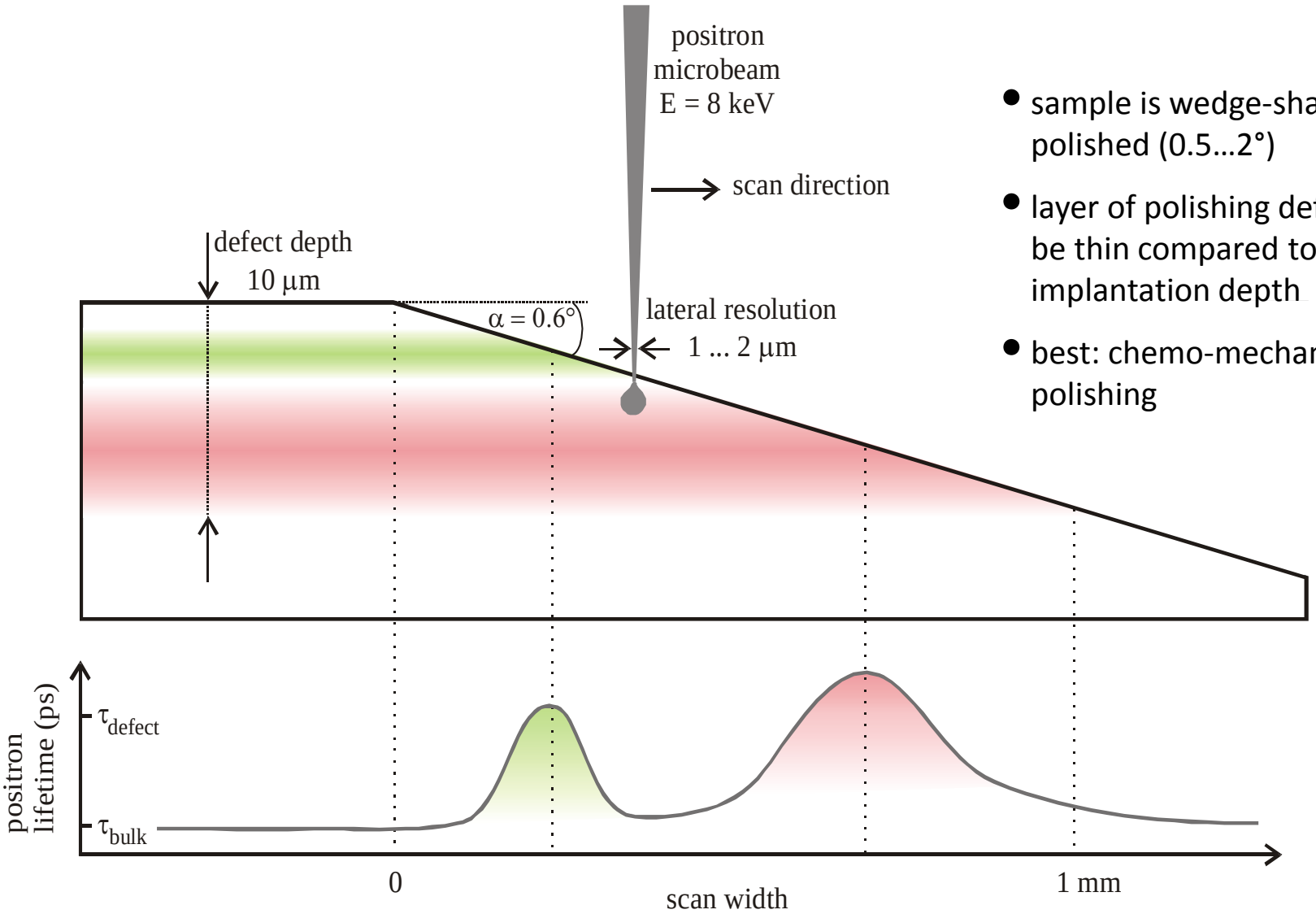
- at R_p: gettering by interstitial-type dislocation loops ⇨ formed by excess interstitials during RTA
- no defects visible by TEM at Rp/2
- What type are these defects?
- there was some debate:
  - interstitial type defects ?
  - vacancy-type defects?

Investigation of the Rp/2 effect by conventional VEPAS

- the defect layers are expected in a depth of 1.7 mm and 2.8 mm corresponding to E^+ = 18 and 25 keV
- implantation profile too broad to discriminate between the two zones
- simulation of S(E) curve gives the same result for assumed blue and yellow defect profile (solid line in upper panel)
- furthermore: small effect only
- no conclusions about origin of $R_p/2$ effect possible



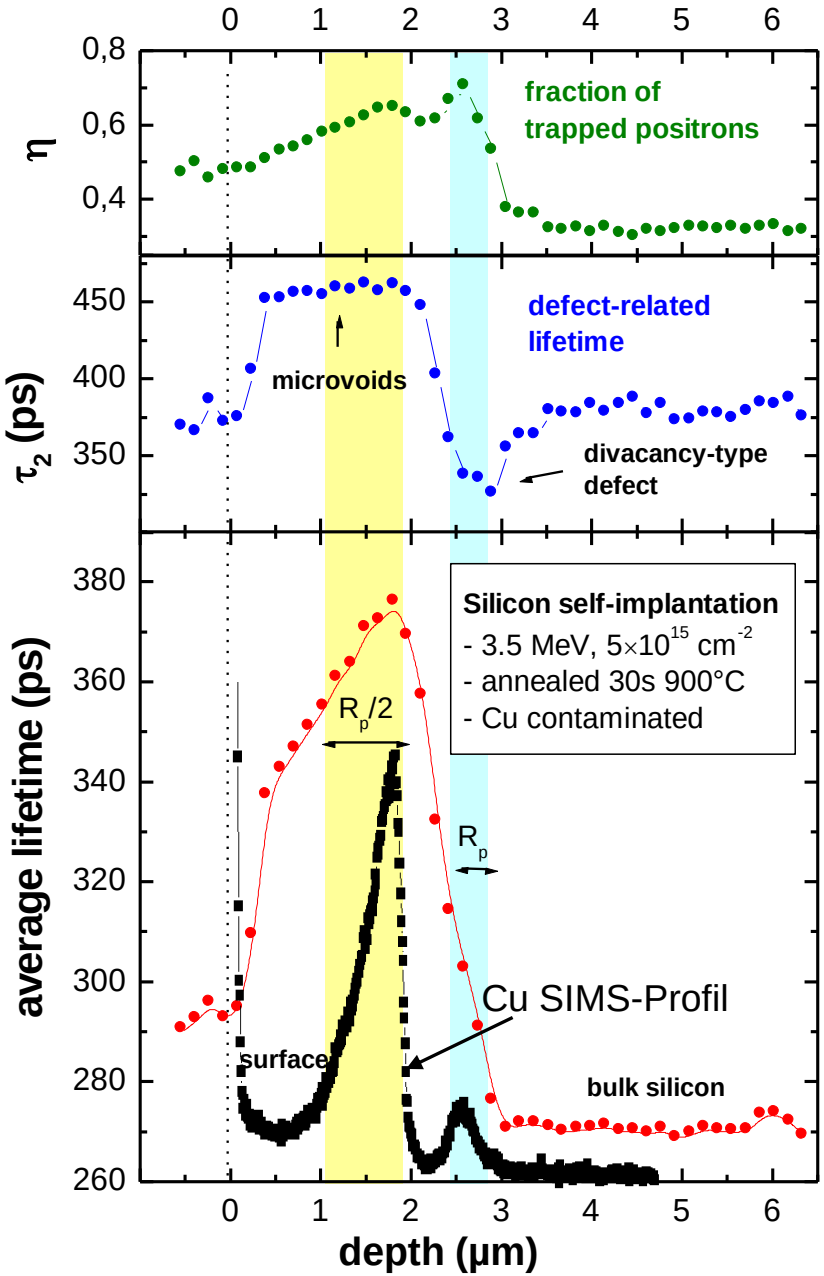
Enhanced depth resolution by using the Positron Microscope



- sample is wedge-shaped polished (0.5…2°)
- layer of polishing defects must be thin compared to e^+ implantation depth
- best: chemo-mechanical polishing

First defect depth profile using Positron Microscopy

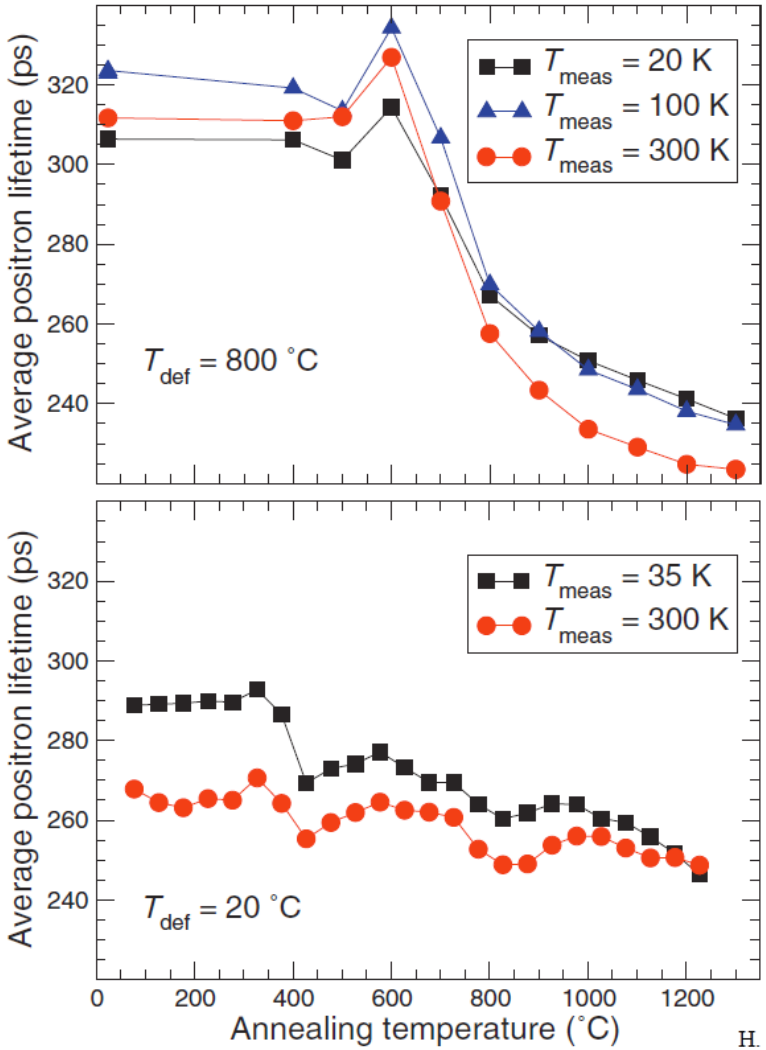
- 45 lifetime spectra: scan along wedge
- separation of 11 µm between two measurements corresponds to depth difference of 155 nm (α = 0.81°)
- beam energy of 8 keV: mean penetration depth is about 400 nm; represents optimum depth resolution
- no further improvement possible due to positron diffusion: L_+(Si @ 300K) » 230 nm
- both regions well visible:
  - vacancy clusters with increasing density down to 2 µm ($R_p/2$ region)
  - in R_p region: lifetime τ_2 = 330 ps; corresponds to open volume of a divacancy; must be stabilized or being part of interstitial-type dislocation loops
- excellent agreement with profile of gettered Cu



R. Krause-Rehberg et al., Appl. Phys. Lett. 77 (2000) 3932

Plastic deformation of Si

- p-doped FZ-Silicon was plastically deformed at RT (deformation 16%) and 800°C (7%)



- strong positron trapping is observed
- two or three lifetime components
- distinct component due to vacancy clusters

Average positron lifetime measured for the samples deformed at T_{def} = 800 °C (upper panel) and 20 °C (lower panel) as a function of the annealing temperature. The measurements have been carried out at different sample temperatures T_{meas}. The lines are drawn to guide the eye.

H. S. Leipner, Z. Wang, H. Gu, V. V. Mikhnovich Jr, V. Bondarenko, R. Krause-Rehberg, J.-L. Demenet, and J. Rabier
Defects in silicon plastically deformed at room temperature
phys. stat. sol. (a) 201, 9 (2004), 2021-2028

Plastic deformation of Si

Deformation at 800°C and 20°C

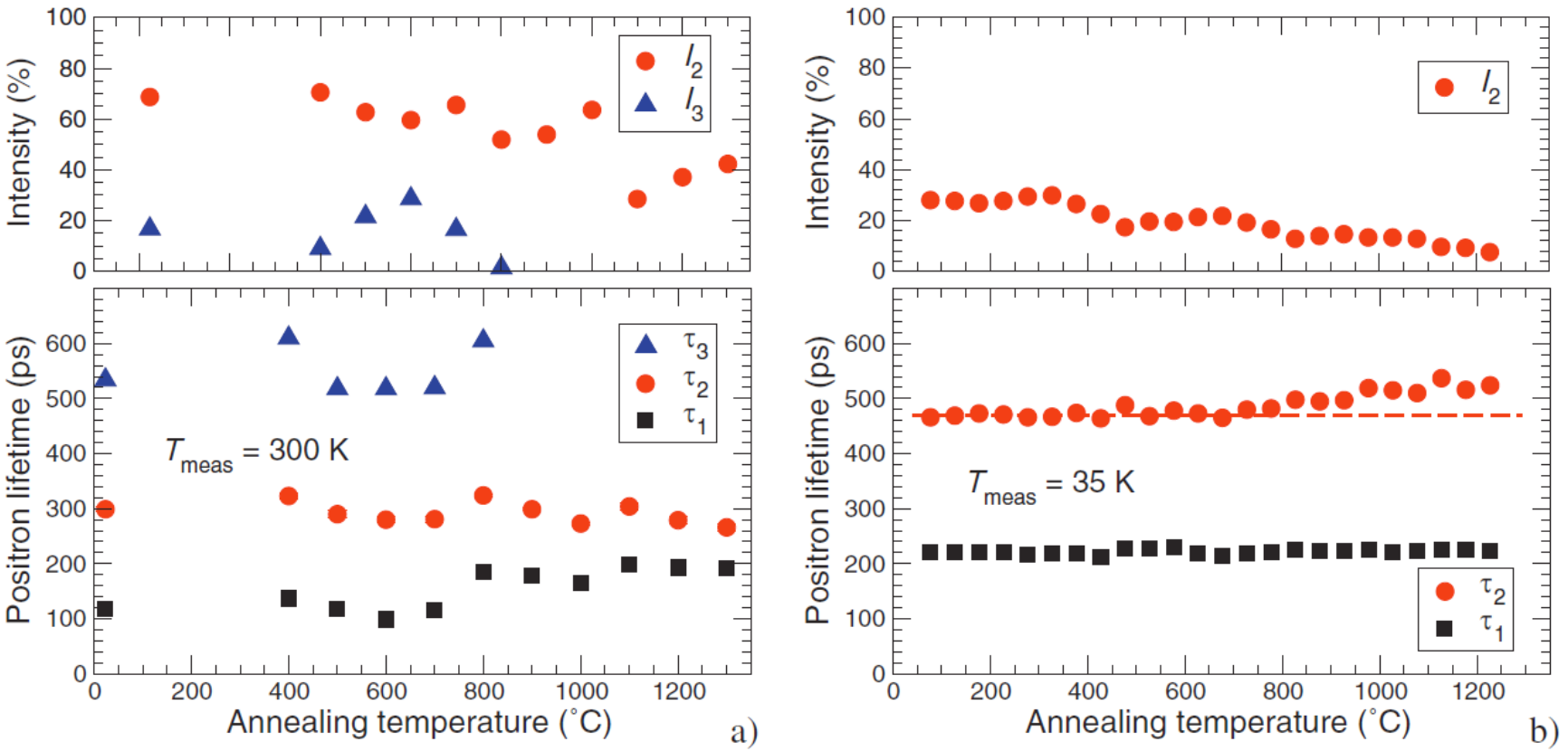
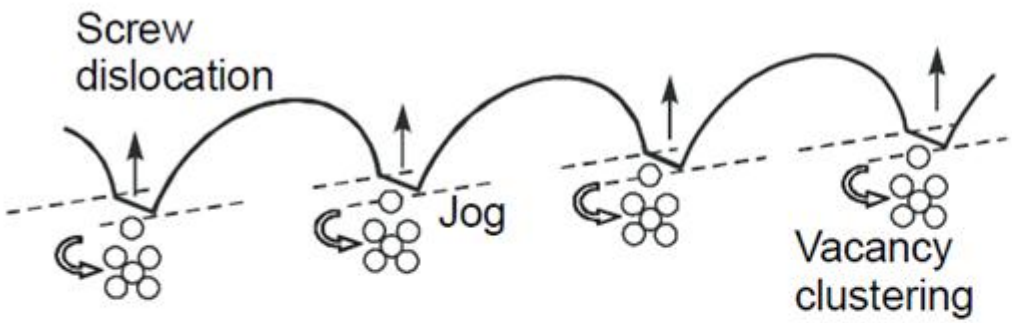


Fig. 6 (online colour at: www.interscience.wiley.com) Positron lifetime components and intensities for the sample deformed at 800 °C (a) and the sample deformed at 20 °C (b) as a function of the annealing temperature. For the high-temperature deformation, the lifetime τ_3 disappears after annealing at 800 °C and only a two-component decomposition is possible for higher temperatures. The sample temperature during the measurement T_{meas} was 300 K in (a) and 35 K in (b). The dashed line represents the mean value of the long-lived component at low annealing temperatures in the room-temperature-deformed sample.

Generation of vacancy clusters by plastic deformation – Jog dragging

two types of defects were found

- vacancy clusters (n > 10) produced by jog dragging
- monovacancy-type defect linked to dislocation lines (stable up to 1200°C)



Mechanism of the formation of vacancies by the dragging of non-glissile jogs along screw dislocations. Rows of vacancies are supposed to be unstable, and larger vacancy clusters are formed close to the edge-type jogs. The arrows indicate the direction of the non-conservative motion of the jogs.

Conclusion

- Si is still a very useful playground for defect studies by positrons
- in as-grown state positron can hardly detect something
- after irradiation, implantation and deformation ⇨ Positron annihilation is a very useful tool
- big differences for
  - FZ and Cz Silicon: vacancy-oxygen clusters V-O (A-center) and V_x-O_y
  - undoped and doped material: V_{Si}-dopant complexes (E-center)
- Deformation generated not only dislocations but also vacancy clusters: jog dragging process

Talk available: http://positron.physik.uni-halle.de

Thanks for your attention!