Why are so tiny defects important at all?
• Positron trapping by vacancies
• Other techniques of positron annihilation
• Vacancy clusters
Point defects determine optical and electronic properties of semiconductors

- Point defects determine electronic and optical properties
- Electric conductivity strongly influenced
- Doping of semiconductors (n-, p-Si)

- Point defects are generated by irradiation (e.g. cosmic rays), by plastic deformation or by diffusion, ...
- Metals in high radiation environment -> formation of voids -> embrittlement
- -> Properties of vacancies and other point defects must be known
- Analytical tools are needed to characterize point defects

Galliumphosphide

without vacancies transparent

with 0,001% vacancies opaque
1 vacancy in 100000 atoms
The positron lifetime spectroscopy

- positron wave-function can be localized in the attractive potential of a defect
- annihilation parameters change in the localized state
- e.g. positron lifetime increases in a vacancy
- lifetime is measured as time difference between appearance of 1.27 (start) and 0.51 MeV (stop) quanta
- defect identification and quantification possible
Positron lifetime spectroscopy

- positron lifetime spectra consist of exponential decay components
- positron trapping in open-volume defects leads to long-lived components
- longer lifetime due to lower electron density
- analysis by non-linear fitting: lifetimes $\tau_i$ and intensities $I_i$

Positron lifetime spectrum:

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right)$$

- trapping rate
- defect concentration

As–grown Cz Si
Plastically deformed Si

$\tau_2 = 320$ ps (divacancies)

$\tau_3 = 520$ ps (vacancy clusters)

$\tau_b = 218$ ps (bulk)
Vacancies in thermal Equilibrium

- Vacancy concentration in thermal equilibrium:
  - in metals $H^F \approx 1...4$ eV \Rightarrow at $T_m [1v] \approx 10^{-4}...-3$ /atom
  - fits well to the sensitivity range of positron annihilation

\[
C_{1v}(T) = \exp\left(\frac{S_{1v}^F}{k}\right) \exp\left(\frac{H_{1v}^F}{kT}\right)
\]

**Tungsten**

$H^F = (4.0 \pm 0.3)$ eV

(Ziegler, 1979)
Defects in Iron after tensile strength and fatigue treatment

• We performed an extensive study of defects in mechanically damaged iron and steel
• Positrons are very sensitive: detection of defects already in the Hooks range of the stress-strain experiment
• Vacancy cluster and dislocations are detectable in both cases

Somieski et al., J. Physique IV 5, C1/127-134 (1995)
in a metal: charge of a vacancy is effectively screened by free electrons
they are not available in semiconductors
thus, long-range Coulomb potential added
positrons may be attracted or repelled
trapping coefficient $\mu$ is function of charge state
Vacancies may be charged

For a negative vacancy:

- Coulomb potential is rather extended but weak
- it supports trapping only at low temperatures
- at higher temperatures: detrapping dominates and vacancy behaves like a vacancy in a metal or a neutral vacancy

Positive vacancies repel positrons

Puska et al. 1990
Theoretical calculation of vacancy levels in GaAs

- Theoretical description not simple
- relaxation of vacancy possible -> Jahn-Teller distortion / negative-U effect

Ionization levels of arsenic vacancies, gallium vacancies, and antisites according to theoretical calculations of (a) Baraff and Schlüter (1985a), (b) Puska (1989a), (c) Jansen and Sankey (1989), (d) Xu and Lindefelt (1990), (e) Zhang and Northrup (1991), and (f) Seong and Lewis (1995), (g) Zhang and Chadi (1990), (h) Pöykkö et al. (1997). $E_{\text{val}}$ and $E_{\text{cond}}$ are the edges of the valence and the conduction band, respectively.
Positron trapping by negative vacancies

- trapping process can be described quantitatively by trapping model
- Coulomb potential leads to Rydberg states
- from there: positrons may re-escape by thermal stimulation
- once in the deep state: positron is captured until annihilation
- detrapping is strongly temperature dependent

\[ \delta_R = \frac{\kappa_R}{\rho_v} \left( \frac{m^* k_B T}{2\pi \hbar^2} \right)^{3/2} \exp \left( - \frac{E_R}{k_B T} \right) \]

- \( E_R \) binding energy of positron in Rydberg state
- \( \rho_v \) vacancy density

Manninen, Nieminen, 1981
Negative vacancies show temperature-dependent positron trapping

- temperature dependence of positron trapping is rather complex

$$\kappa = \frac{\partial_R \rho_v \kappa_{R0} T^{-1/2}}{\partial_R \rho_v + \kappa_{R0} \left( \frac{m^* k_B}{2 \pi \hbar^2} \right)^{3/2} T \exp \left( -\frac{E_R}{k_B T} \right)}$$

- low temperature: $\sim T^{-0.5}$ due to diffusion limitation in Rydberg states
- higher $T$: stronger temperature dependence due to thermal detrapping from Rydberg state

Le Berre et al., 1995
Temperature-dependent positron trapping can be used to determine the charge state of vacancies. Trapping to positive vacancies is possible at elevated $T$, however, this has never been observed. An example is Positron trapping in e-irradiated Si. Trapping by negatively charged divacancies has been observed. (Mäkinen et al. 1989)
Sensitivity limits of PAS for vacancy detection

- **lower sensitivity limit** e.g. for negatively charged divacancies in Si starts at about $10^{15}$ cm$^{-3}$
- **upper limit**: saturated positron trapping
- defect identification still possible
- Then: only lower limit for defect density can be given
Negative ions act as shallow positron traps

- at low T: negatively charged defects without open volume may trap positrons
- “shallow” due to small positron binding energy
- annihilation parameters close to bulk parameters
- acceptor-type impurities, dopants, negative antisite defects
- thermally stimulated detrapping can be described by:

\[ \delta = \frac{\kappa}{\rho_{st}} \left( \frac{m^* k_B T}{2\pi \hbar^2} \right)^{3/2} \exp \left( -\frac{E_{st}}{k_B T} \right) \]

Saarinen et al., 1989
Shallow positron traps

- positron trapping model gets more complex
- however: trapping at shallow traps can be avoided at high temperatures
Effect of shallow positron traps

- Temperature dependence is characterized by competing trapping by vacancies and shallow traps.
- In GaAs:Si we observe $V_{Ga} - Si_{Ga}$ complexes at high temperatures.
- And $Si_{Ga}^{-}$ donors at low $T$ in addition (shallow traps).

J. Gebauer et al. 1997

Martin-Luther-Universität Halle
Identification of $V_{Ga}\text{-}Si_{Ga}$-Complexes in GaAs:Si

- Scanning tunneling microscopy at GaAs (110)-cleavages planes (by Ph. Ebert, Jülich)
- Defect complex identified as $V_{Ga}\text{-}Si_{Ga}$

Mono-vacancies in GaAs:Si are $V_{Ga}\text{-}Si_{Ga}$-complexes

Measurement of Doppler Broadening

- electron momentum in propagation direction of 511 keV $\gamma$-ray leads to Doppler broadening of annihilation line
- can be detected by conventional energy-dispersive Ge detectors and standard electronics
**Line Shape Parameters**

- **S parameter:**
  \[ S = \frac{A_S}{A_0} \]

- **W parameter:**
  \[ W = \frac{A_W}{A_0} \]

*W parameter mainly determined by annihilations of core electrons (chemical information)*
Doppler Coincidence Spectroscopy

- coincident detection of second annihilation $\gamma$ reduces background
- use of a second Ge detector improves energy resolution of system
Doppler Coincidence Spectra

\[ E_1 + E_2 = 2 \, m_0 \, c^2 = 1022 \, \text{keV} \]
• Chemical sensitivity due to electrons at high momentum (core electrons)
• A single impurity atom aside a vacancy is detectable
• Examples: $V_{Ga} – Te_{As}$ in GaAs:Te
Defects in electron-irradiated Ge

- Electron irradiation (2 MeV @ 4K) induces Frenkel pairs (vacancy - interstitial pairs)
- Steep annealing stage at 200 K
- At high irradiation dose: divacancies are formed (thermally more stable)

(Polity et al., 1997)
Low-temperature electron irradiation

- low-temperature electron irradiation was performed at 4K ($E_e = 2$ MeV)
- annealing stage of monovacancies at about 170 K
- moving $V_{Si}$ partly form divacancies
- divacancies anneal at about 550...650 K

GaAs: annealing under defined As-partial pressure

- two-zone-furnace: Control of sample temperature and As partial pressure allows to navigate freely in phase diagram (existence area of compound)

**GaAs: Annealing under defined As pressure**

**Si\(_{Ga}\)-V\(_{Ga}\)**

![Graph showing linear fit for Si\(_{Ga}\)-V\(_{Ga}\)](image)

**Te\(_{As}\)-V\(_{Ga}\)**

![Graph for Te\(_{As}\)-V\(_{Ga}\)](image)

**Thermodynamic reaction:**
\[
\frac{1}{4} \text{As}_4^{\text{gas}} \leftrightarrow \text{As}\_\text{As} + V\_\text{Ga}
\]

**Mass action law:**
\[
[V\_\text{Ga}] = K_{VG} \times p_{As}^{1/4}
\]

Fit: \([V\_\text{Ga}-\text{Dopant}] \sim p_{As}^n\)

\[\rightarrow n = 1/4\]

*J. Gebauer et al., Physica B 273-274, 705 (1999)*

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Comparison of doped and undoped GaAs

Thermodynamic reaction:

\[ \text{As}_\text{As} \leftrightarrow \text{V}_{\text{As}} + \frac{1}{4}\text{As}_4\text{gas} \]

Mass action law:

\[ [\text{V}_{\text{As}}] = K_{\text{VAs}} \times p_{\text{As}}^{-1/4} \]

Fit: \[ [\text{V-complex}] \sim p_{\text{As}}^n \]

\[ \rightarrow n = -1/4 \]

As vacancy

Bondarenko et al., 2003
Vacancy clusters in semiconductors

- vacancy clusters were observed after neutron irradiation, ion implantation and plastic deformation
- due to large open volume (low electron density) -> positron lifetime increases distinctly
- example: plastically deformed Ge
- lifetime: $\tau = 525$ ps
- reason for void formation: jog dragging mechanism
- trapping rate of voids disappears during annealing experiment

Krause-Rehberg et al., 1993
• there are cluster configurations with a large energy gain
• „Magic Numbers“ with 6, 10 und 14 vacancies
• positron lifetime increases distinctly with cluster size
• for $n > 10$ saturation effect, i.e. size cannot be determined

Lateral Resolution with Lateral Resolution with Positron-Scanning-Microscope

- lateral resolution 2 µm
- Positron lifetime spectroscopy
- However lateral resolution principally limited by positron diffusion ($L_+ \approx 100$nm)

W. Triftshäuser et al., NIM B 130 (1997) 265
Microhardness indentation in GaAs

- Comparison of SEM and Munich Positron Scanning Microscope

- problem here at the moment: intensity

- hope: strong positron source at FRM-II Garching or EPOS project in Rossendorf

Krause-Rehberg et al., 2002
• ELBE -> electron LINAC (40 MeV and up to 40 kW) in Research center Rossendorf (near Dresden)
• EPOS will be the combination of a positron lifetime spectrometer, Doppler coincidence, and AMOC
• User-dedicated facility
• main features:
  - ultra high-intensity bunched positron beam (E⁺=1…30 keV)
  - very good time resolution by using the unique primary time structure of ELBE
  - high quality spectra by lifetime and Doppler spectroscopy in coincidence mode
  - fast lifetime mode (single detector mode) for kinetic investigations
  - very high count rate (> 10⁶ s⁻¹) by multi-detector array
  - conventional source included for Doppler measurements (when primary beam is not available)
  - fully remote control via Internet by user
Schematic view of EPOS (ELBE Positron Source)
Variety of applications in all field of materials science:

- defect-depth profiles due to surface modifications and ion implantation
- tribology (mechanical damage of surfaces)
- polymer physics (pores; interdiffusion; ...)
- low-k materials (thin high porous layers)
- defects in semiconductors, ceramics and metals
- epitaxial layers (growth defects, misfit defects at interface, ...)
- fast kinetics (e.g. precipitation processes in Al alloys; defect annealing; diffusion; ...)
- radiation resistance (e.g. space materials)
- many more ...
Conclusions

• Positrons are a unique tool for characterization of vacancy-type defects in solids
• Positrons are sensitive for charge state of vacancies in semiconductors
• vacancy clusters can easily be observed by positron lifetime spectroscopy (appear after irradiation and plastic deformation)

This presentation can be found as pdf-file on our Website:
http://positron.physik.uni-halle.de

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