Study of semiconductors with positrons

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Outlook:

- Introduction
- Positron trapping into defects
- Methods of positron annihilation
  - Positron lifetime spectroscopy
  - Doppler broadening spectroscopy
  - Coincidence Doppler broadening spectroscopy
Questions of semiconductor industry
- Defect types?
- Defect charge states?
- Defect concentrations?

Answers of positron annihilation
- Vacancy-like defects and defect complexes
  - Size of a vacancy (mono-, di-, vacancy cluster)
- Neutral or negatively charged vacancy-complexes
  - Positively charged defects are invisible
- Sensitivity limits $10^{14}$-$10^{19}$ cm$^{-3}$
Positron in condensed matter

\[ _{22}^{11}\text{Na} \rightarrow _{10}^{22}\text{Ne} + e^+ + \nu \]

\[ \gamma \rightarrow 1.27 \text{ MeV} \]

\[ 22 \text{Na} \]

\[ \tau_{1/2} = 3.7 \text{ ps} \]

\[ \beta^+ 90.4\% \text{, EC 9.5\%} \]

\[ \gamma 1274 \text{ keV} \]

\[ _{10}^{22}\text{Ne} \]

\[ _{11}^{22}\text{Na} \]

\[ E \approx 300 \text{ keV} \rightarrow k_B T \]

Thermalization

\[ \approx 3 \text{ ps} \]

Diffusion

\[ L_+ \approx 100 \text{ nm} \]

\[ 0.511 \text{ MeV} \]

\[ 100 \mu\text{m} \]

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Positron trapping - Vacancy

- Perfect lattice

Atom potential in GaAs (110) plane

Positron wave function in GaAs (110) plane

- Positrons are repelled by positive atom cores
Mono-vacancy

Vacancy represents a positron trap due to the missing nuclei (potential well for a positron)
Methods of positron annihilation

Sensitive to electron density distribution

- Positron Annihilation Lifetime Spectroscopy (PALS)

\[ L_+ = \sqrt{D} \tau_b \quad \lambda = \frac{1}{\tau_b} = \pi \cdot r_0 \cdot c \int \psi_+(\mathbf{r}) \psi_-(\mathbf{r}) \gamma d\mathbf{r} \]

\[ \tau_b \text{ – positron bulk lifetime} \quad \lambda \text{ - positron annihilation rate} \]

the lower the electron density is, the higher is the positron lifetime

Sensitive to electron momentum distribution

energy and momentum conservation leads to

- Angular Correlation of Annihilation Radiation (ACAR)
- Doppler Broadening of annihilation line Spectroscopy (DOBS)
  - Coincidence Doppler Broadening
Methods of Positron Annihilation

Positron lifetime spectroscopy

\[ E_1 = 0.511\,MeV + p_L c/2 \]

Diffusion
\[ L_+ \approx 100\,nm \]

Thermalization
\[ \approx 3\,ps \]
\[ E \approx 300\,keV \]
\[ \Theta = p_T/m_0c \]

\[ \Theta \equiv p_T / m_0c \]

Angular correlation of annihilation radiation

\[ E_2 = m_0 c^2 - p_L c/2 \]

Doppler broadening spectroscopy

\[ \gamma \]
\[ 1.27\,MeV \]

\[ ^{22}\text{Na} \]

\[ e^+ \]

\[ p \]

\[ p_T \]

\[ p_L \]
Technique of positron lifetime spectroscopy

PM – photomultiplier
SCA – Single Channel Analyzer
TAC – Time to Amplitude Converter
MCA – Multichannel Analyzer
Positron Annihilation Lifetime Spectroscopy (PALS)

- Probability $n(t)$ that $e^+$ is alive at time $t$:
  $$\frac{dn(t)}{dt} = -\lambda n(t) \quad n(0) = 1$$

- $\lambda$ - positron annihilation rate

- Positron lifetime spectrum in bulk:
  (no trapping of positrons)

  $\lambda_b = \frac{1}{\tau_b}$

  $n(t) = e^{-\lambda_{bulk} t}$

- $\lambda$ - slope of the exponential decay

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Positron Annihilation Lifetime Spectroscopy

- model of trapping into a defect
  - annihilation from bulk with \( \lambda_b = 1/\tau_b \) s\(^{-1} \)
  - trapping to vacancy-defect with \( K \) s\(^{-1} \)
  - annihilation from the defect with \( \lambda_d = 1/\tau_d \)
  - two-component lifetime spectrum

\[
N(t) = I_1 / \tau_1 \exp(-t / \tau_1) + I_2 / \tau_2 \exp(-t / \tau_2)
\]

- analysis by non-linear fitting

**Information**

- vacancy type (mono-, di-, vacancy cluster)
  \( \tau_2 \) – reflects the electron density
- defect concentration \( C \)

\[ K = \frac{I_2}{I_1} \left( \frac{1}{\tau_b} - \frac{1}{\tau_2} \right) \approx C \]
The Nature of EL2 defect in GaAs

- one of the most frequently studied crystal lattice defects at all
- responsible for semi-insulating properties of GaAs: large technological importance
- is deep donor, compensates shallow acceptors, e.g. C- impurities
- defect shows metastable state after illumination at low temperatures
- IR-absorption of defect disappears during illumination at $T < 100$ K
- ground state recovers during annealing at about $110$ K
- many structural models proposed Dabrowski, Scheffler and Chadi, Chang (1988): simple $\text{As}_{\text{Ga}}$antisite defect responsible
- must show a metastable structural change

(Dabrowski 1988, Chadi 1988)
in metastable state at low temperature: Ga vacancy
should disappear during annealing at about 110 K
confirmed by positron lifetime measurements
kinetics of recovery of ground state is identical for IR- und positron experiment: $E_A = (0.37 \pm 0.02) \text{ eV}$
evidence of the vacancy in metastable state confirms the proposed structural model

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Temperature dependence of positron trapping

Compensation in GaAs:S
- formation of $S_{\text{As}}$-$V_{\text{Ga}}$ complex
- increase of $\tau_{av}$ to low T is due to the trapping into negative shallow Rydberg potential of the defect

$V_+(r)$

$13.6a_0$

$4.8a_0$

$0.1\text{eV}$

$3.5\text{eV}$

$-\frac{1}{\varepsilon_0 r}$

- observed $S_{\text{As}}$-$V_{\text{Ga}}$ complex is negatively charged

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Positron trapping – shallow traps

- negative ions are also positron trapping centers due to small negative Coulomb potential
- term “shallow” relates to the positron binding energy (few meV).
- therefore the trapping is significant at low temperatures only
- the electron density is not reduced:
  \[ \tau_{st} = \tau_b \]

(J. Gebauer et al. 1997)

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Doppler effect

- Electron momentum in the propagation direction of a 511 keV $\gamma$-ray leads to Doppler broadening of the annihilation line.

\[ E_1 - E_2 = p_L c \]

Technique

- Technique involves using a 22-Na source and detecting the annihilation $\gamma$-rays with a Ge detector.

- The FWHM of the $\gamma$-ray line in GaAs is approximately 2.6 keV, while in $^{85}$Sr it is 1.4 keV.

- The energy of the $\gamma$-quanta is $E_1, E_2$.
Annihilation-Line Doppler broadening spectroscopy

Data Treatment
- Line Parameters
  - “Shape” parameter
    \[ S = \frac{A_s}{A_0}, \quad A_s = \int_{E_0-E_s}^{E_0+E_s} N_D dE \]
  - “Wing” parameter
    \[ W = \frac{A_w}{A_0}, \quad A_w = \int_{E_1}^{E_2} N_D dE \]

Information
- Both S and W are sensitive to the concentration and defect type
- W is sensitive to chemical surrounding of the annihilation site, due to high momentum of core electrons participating in annihilation
Coincidence Doppler broadening spectroscopy

- Both $\gamma$-quanta are detected
- Coincidence time is 0.5 $\mu$s
Doppler coincidence spectroscopy

- background is dramatically reduced by coincident detection of second annihilation $\gamma$-quantum
- this opens a possibility to investigate the high momentum part of the energy spectrum, i.e. annihilation with core electrons the atoms
- thus the chemical surrounding of a positron trap can be studied

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Doppler coincidence spectroscopy

chemical sensitivity of energy spectra

\[ \rho(p) [10^8 \text{ m}_0^2 \text{c}^{-1}] \]

\[ \frac{p_L(10^{-3} \text{ m}_0 \text{c})}{\rho(p)} \]

Electron momentum vs. \( p_L(10^{3} \text{ m}_0 \text{c}) \)

Ratio to bulk GaAs

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Nature of vacancy complexes in Si and Te doped GaAs

- Positron lifetime spectroscopy
- Doppler coincidence

\[ \tau_2 = 260 \text{ ps} \]
\[ \tau_2 = 253 \text{ ps} \]

**GaAs:Si**
**GaAs:Te**

**Measurement temperature**

\[ V_{Ga-Si_{Ga}} \text{ in GaAs:Si } \tau_2 = 260 \text{ ps} \]
\[ V_{Ga-Te_{As}} \text{ in GaAs:Te } \tau_2 = 253 \text{ ps} \]

Conclusion

- positron annihilation is a sensitive tool for investigation of vacancy-like defects in semiconductors.
- Information on type and concentration of vacancies can be obtained.
- Temperature dependence of positron trapping is governed by the charge state of the defects.
- Chemical surrounding of the annihilation site can be studied with the help of coincidence Doppler broadening technique.
- Positively charged defects are invisible for positrons.

This presentation can be found as a pdf-file on our Websites:

http://positron.physik.uni-halle.de
http://PositronAnnihilation.net
\[ \frac{22}{11} \text{Na} \rightarrow \frac{22}{10} \text{Ne} + e^+ + \nu \]

\( \tau_{1/2} = 3.7 \text{ ps} \)

\( \beta^+ 90.4 \%, \text{ EC} 9.5 \% \)

\( \gamma 1274 \text{ keV} \)

\( \beta^+ 0.06 \% \)

\( \frac{22}{10} \text{Ne} \)

\( \frac{58}{28} \text{Co} \)

\( \frac{26}{10} \text{Cu} \)

\( \frac{22}{11} \text{Na} \)

\( \frac{22}{10} \text{Ne} \)

\( \frac{64}{28} \text{Cu} \)

\( \frac{99}{28} \text{Co} \)

\( \frac{90.4}{100} \% \)

\( \frac{9.5}{100} \% \)

\( \frac{0.06}{100} \% \)

\( \frac{545}{100} \% \)

\( \frac{470}{99} \% \)

\( \frac{1340}{0.5} \% \)

\( \frac{\text{Maximum energy}}{\text{half-life}} \)

\( \frac{\text{radionuclide}}{\text{energy distribution after } \beta^+\text{-decay}} \)

\( \frac{\text{radionuclide}}{\text{moderation}} \)

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Conventional positron beam technique

- Monoenergetic positrons are used
- Magnetically guided

Disadvantages
- no simple lifetime measurements and bad lateral resolution (0.5-1 mm)
- defect studies by Doppler-broadening spectroscopy
- characterization of defects only by line-shape parameters or positron diffusion length
Information from Doppler-broadening spectroscopy

- Positron implantation profile
  Makhov function:

\[
P(z, E) = \frac{mz^{m-1}}{z_0^m} \left[ 1 - \left( \frac{z}{z_0} \right)^m \right]
\]

- S-E and S-W plots

- Positrons annihilation sites:
  - surface
  - bulk
  - vacancy defect

Ion implantation in Si

Defect density as a function of deposited ion energy

- \([\text{defect}] \sim \text{dose}^{0.5}\)
- valid for RBS- and positron data
- only exception: Si self-implantation
- can be explained: extra Si atoms are interstitials and kill vacancies that are seen by positrons but not by RBS


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Positron lifetime beam

- lifetime measurements are more difficult
- a system of chopper and bunchers: short pulses of monoenergetic positrons
- two systems are available till now:
  - Munich (Germany)
  - Tsukuba (Japan)

Lifetime measurements in SiC layer

SiC B/Si Implantation 1700°C annealed

- Si and B coimplantaion into SiC layers on Si
- Average positron lifetime behaves similar to S-parameter
- $\tau_2 = 300\pm6$ ps $\rightarrow$ small vacancy cluster defects


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**Scanning positron microscope**

- Variable energy micro-beam of monoenergetic positrons
- Lateral resolution of 2 µm is achieved
- Lifetime measurements at different beam energies are possible

Principle disadvantage: broad positron implantation profile at high energies

Electron and positron beam image of the surface of a test chip. Light area is SiO₂, dark area is platinum

Depth defect profiling with positron microbeam

- Energy is constant at 8 keV
- Sample is wedged at 0.6°
- Defect profile of 10 µm is “stretched” to 1 mm
- Depth resolution can be optimized

First time used to study Rp/2 effect in Si after self-implantation


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after high-energy (3.5 MeV) self-implantation of Si \((5 \times 10^{15} \text{ cm}^{-2})\) and RTA annealing (900°C, 30s): two new gettering zones appear at \(R_p\) and \(R_{p/2}\) (\(R_p\) – projected range of Si⁺)

visible by SIMS profiling after intentional Cu contamination

• at \(R_p\): gettering by interstitial-type dislocation loops (formed by excess interstitials during RTA)
• no defects visible by TEM at \(R_{p/2}\)
• What type are these defects?

Interstitial type \([3,4]\)

Vacancy type \([1,2]\)

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Both defect regions are gut visible

- vacancy clusters with increasing concentration up to 2 µm (Rp/2)
- in Rp region: lifetime $\tau_2 = 320$ ps; open volume corresponds to divacancy; defects are stabilized by dislocation loops

Very good agreement with the SIMS profile of in-diffused Cu
Lifetime measurements around a fatigue crack created in technical copper was measured

- $e^+$ Energy = 16 keV
- spatial resolution about 5 $\mu$m
- two lifetimes were observed:
  - 190 ps – dislocations
  - 360-420 ps – within 40 $\mu$m from the crack – vacancy clusters

have been for the first time microscopically observed