Unmanageable Defects in Proton-Irradiated Silicon: a Factual Outlook for Positron Probing

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Recent papers: Solid State Phenomena, 205 – 206 (2013) 317

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Material(i) and Motivation(ii)

Silicon Crystal Grown by the Floating-Zone Technique

Proton irradiation (MeV energies) is effective way of modifying properties of semiconductors

(i) Initial material :

Oxygen [O] ≈ 10^{16} cm^{-3}, carbon lean [C_i]≈ 10^{15} cm^{-3} *n*-FZ-Si

- **Moderately doped silicon *n*-FZ-Si([P]=7×10^{15} cm^{-3}) is of special interest owing to its wide use in various applications**

Knowledge about the radiation hardness of Si is indispensable

***(ii)* • *Reliable data* on RD created in *silicon of n-type* is scarce.**

- **Which defects are produced in this material of silicon under irradiation with 15 MeV protons at RT?**

Recent data: unmanageable thermally stable electrically neutral (or even electricaly inactive) point defects were revealed

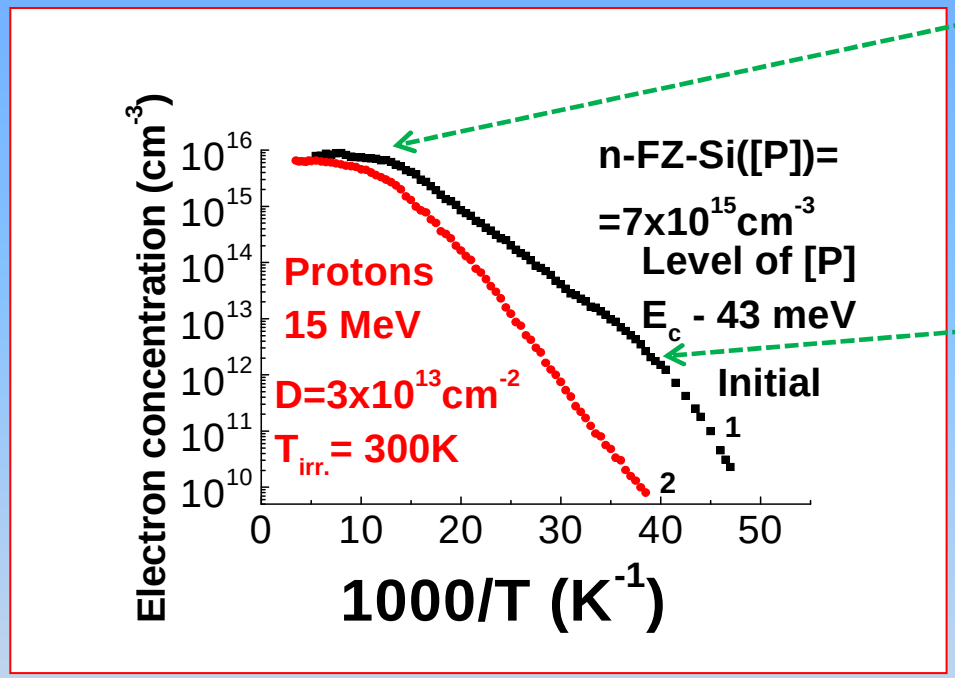
Arutyunov et al.,Solid State Phenomena, 178 – 179 (2011) 313

Emtsev et al. Fiz. Tekh. Poluprov. 46 (2012) 473

We are to discuss possible configuration of these defects in silicon

Characterization: Hall's measurements

and removal of carriers from conduction band of silicon *n*-FZ-Si([P]) irradiated with 15 MeV Protons



High-temperature region

1000/T ≤ 15:

$N_d - N_a \approx f\{n(1/T)\} \approx$ const.

Low-temperature "exponential" impurity ionization region region

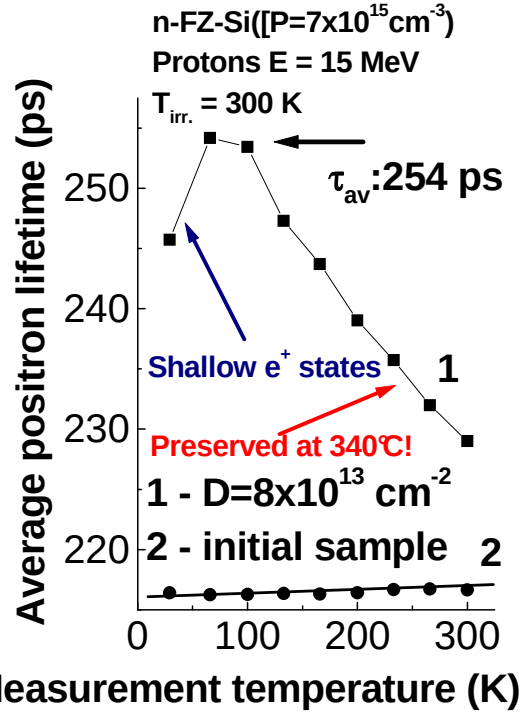
1000/T ≥ 15:

$N_d / N_a \approx \varphi\{n(1/T)\}$ (degree of compensation)

This system of equation allows one to determine N_d and N_a separately and, thus, one can estimate the rate of introduction of donor and acceptor states

- **Concentration of defects has been estimated using these data; Values have been applied for analysis of results obtained by PALS**
- **Removal rate of electrons: ≈ 110–120 cm^{-1} (15 MeV H$^+$) and ≈ 0,11 cm^{-1} (1 MeV electrons)►tecnological advantage of H$^+$ beams**

Temperature Dependency of e^+ Lifetime In Silicon *n*-FZ-Si([P]) Irradiated with 15 MeV Protons



- τ_{av} - strong T-dependency indicates effective positron-phonon interaction
- Value of e^+ lifetime suggests forming the defects of a vacancy type:

τ_{av} (100K) ~ 254 ps (Dose=$8x10^{13}cm^{-2}$)

- Shallow e^+ state (s): $E_{st} \approx 0.2 - 0.6$ meV (R.Krause-Rehberg and H.Leipner, 1999)

- We expected: ► isochronal annealing of E-centers and V_2 had to be completed at regular temperature 280 °C – 300 °C ► τ_{av} (T) had to decreases.
- We have found: T-dependency of τ_{av} (T ≥ 85K) is observed in the course of annealing up to unexpectedly high temperature $T_{ann.} \approx 500$ °C

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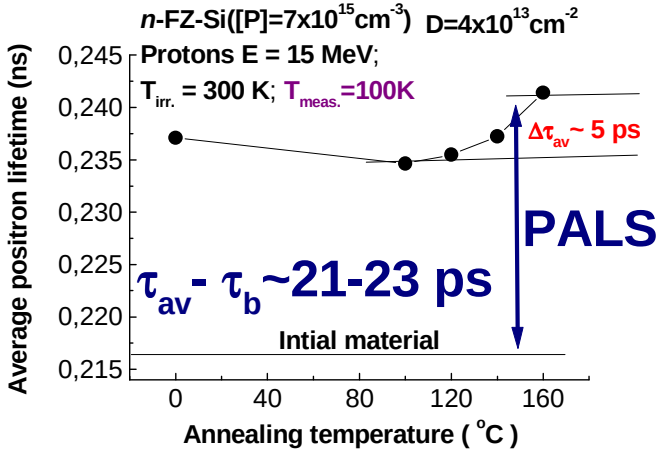
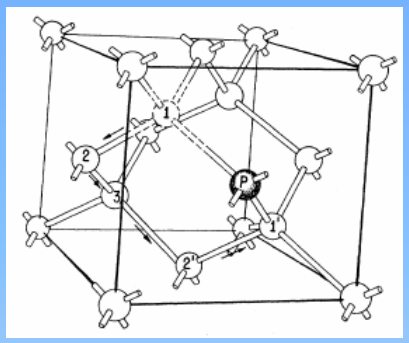
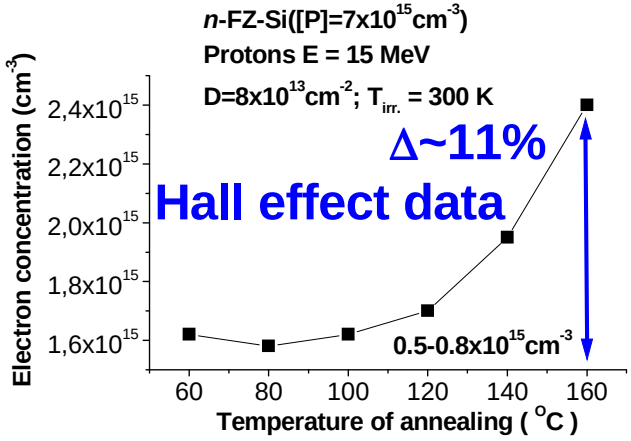
1st Stage: Annealing of *E*–centers in Silicon *n*-FZ-Si([P]) Irradiated with 15 MeV Protons





E-centers:
$E_b(0/-) \approx E_c - 0.41$ eV
Negatively charged in investigated n-FZ-Si([P])



- The annealing of E–centers affects average positron lifetime insignificantly ($\Delta \approx 5$ ps)
- Electrons return to conduction band: concentration changes by $\approx (0.5–0.8)\times10^{15}$ cm^{-3} (Δ ~11%)

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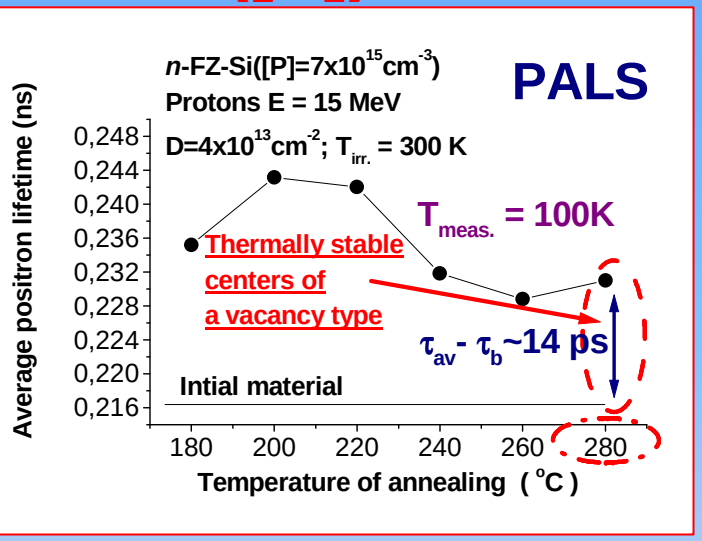
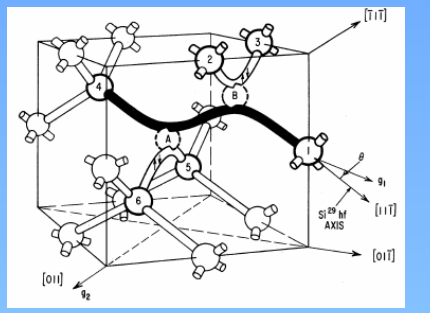
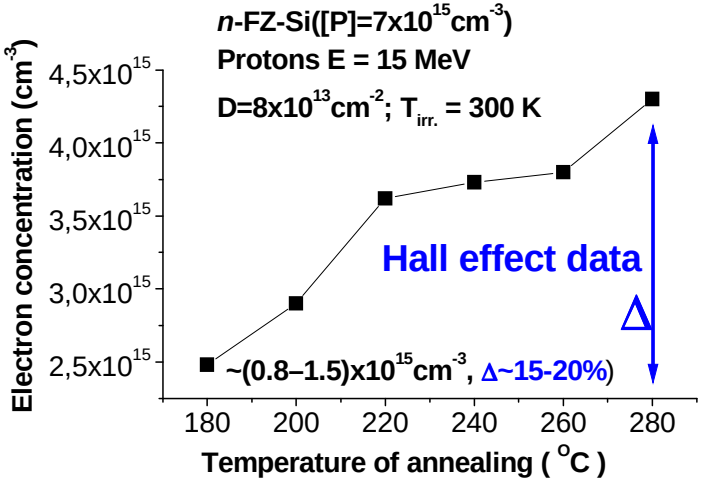
2nd Stage: Annealing of Divacancies in *n*-FZ-Si([P]) Irradiated with 15 MeV Protons





Divacancy:
E_b(-/--)≈ E_c – 0.23 eV
E_b(0/-)≈ E_c – 0.41 eV
Negatively charged in investigated n-FZ-Si([P]){D=4×10^{13} cm^{-2}}: ~70% of V_2^{--} and ~30% of V_2^- of total population
For D=8×10^{13} cm^{-2} : ~50% of V_2^- and ~50% V_2^{--}



- **At 280 ºC average positron lifetime is by ~ 14 ps larger than the value characteristic of non-irradiated silicon**
- **This fact indicates thermally stable centers of a vacancy type (E-centers, V_2 were eliminated from the sample at 1st and 2nd stages of isochronal annealing)**
- **Electron concentration changes by ≈(0.8–1.5)×10^{15}cm^{-3} (>15-20%)**

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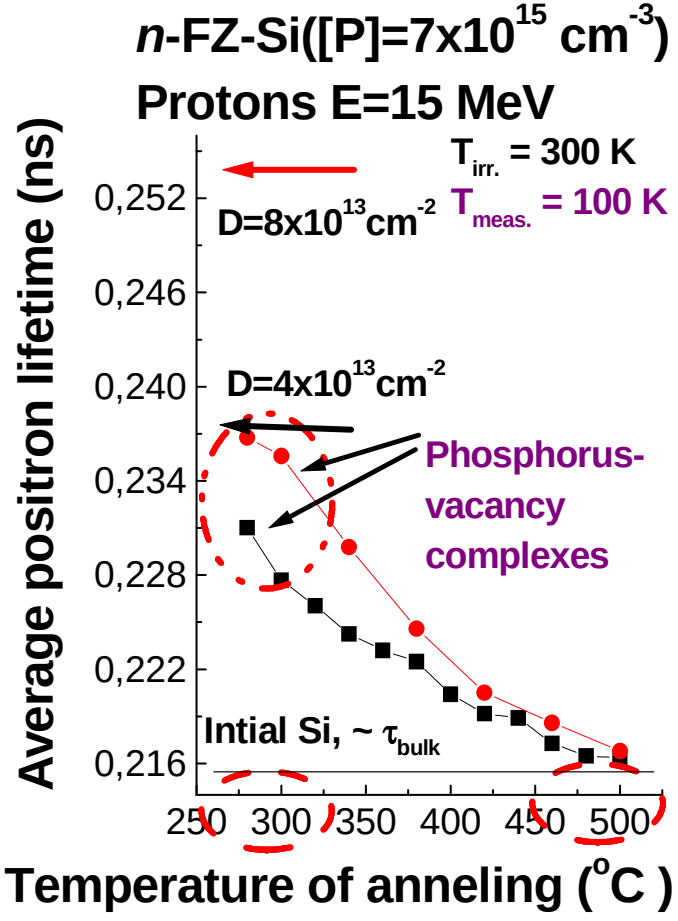
3rd Stage: Annealing of Thermally Stable Centers in Si of *n*-type Irradiated with 15 MeV Protons



- **Data of measurements of Hall effect indcate that:**
  - centers include atoms of phosphorus
  - centers are electrically neutral (or electrically inactive). They are deep donors having levels $E_{DD} > E_c - 0.24$ eV
- **Positron annihilation data indicate that:**
  - *deep donors are hidden at 1st and 2nd stages of the isochron. annealing*
  - deep donor has an open volume and it is a phosphorus-vacancy complex
  - deep donor attracts e^+ effectively
  - the annealing of deep donors results in restoring average positron lifetime: (from 232-236 ps to 216–217 ps ,by ~20 ps), ΔT_{ann} = 280 ºC to ~ 500 ºC

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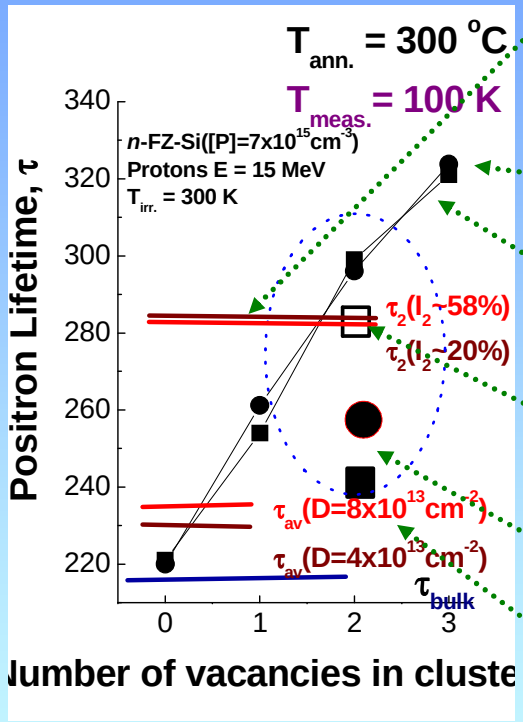
Number of Vacancies In Phosphorus-Vacancy Complex
Silicon of *n*-type irradiated 15 MeV protons



Horizontal lines: this work, two doses

- Long positron lifetime τ_2 is close to numbers of vacancies from 1 to 2 (elipsoid includes the results of calculations obtained by different authors)

calc., **Hakala et. al, PRB,** 57 (1998) 7621;

- **Line-and-squares (unrelaxed cluster):**

calc., **Staab et. al, PRB** 65 (2002) 115210;

- **Line-and-dots (unrelaxed cluster):**

Kuriplach et al., PRB 58 (1998) 10475;

- **Inward relaxation: big open square**

Makhov et al., PRL 92 (2004) 255504;

- **Inward relaxation big dot**

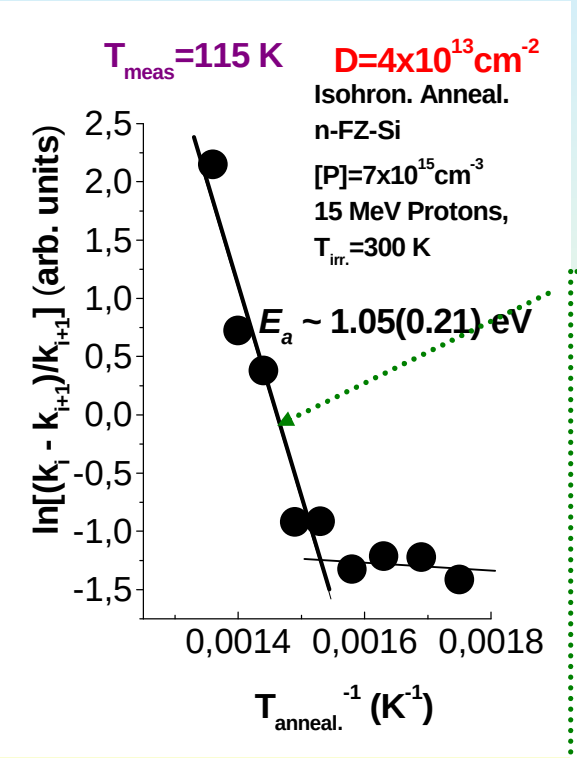
Staab PRB 65 (2002) 115210;

- **Inward relaxation big square**

Vacancy-phosphotrus complex (deep donor) includes, at least, 2 vacancies

Arutyunov et. al J. Phys.: Condens. Matter 28 (2013) 035801; Solid State Phenomena 205 – 206 (2013) 317

Entropy S_m and Activation Energy E_a of Annealing Of Deep Donors Of Radiation Origin In Silicon of *n*-type Irradiated With 15 MeV Protons



$$\ln\left[\frac{k_i - k_{i+1}}{k_{i+1}}\right] \cong A + \frac{E_a}{K_B T_i}$$

$$A \cong \ln\frac{K_0}{\alpha} \cong \ln\left[\exp\left(\frac{S_m}{K_B}\right) \cdot 4\pi r_0 \cdot N_d \cdot (0.5a)^2 \cdot \nu_0\right]$$

- **$E_a \approx 1.05(0.21)$ eV $S_m \approx 2–3k_B$, D=4·10^{13}cm^{-2}**

Similar value E_a~ 1 eV was found for neutral V_2 (EPR, Watkins 1964 138 A543)

The value of configurational entropy S_m indicates decomposition of point (not a large-scale) defect of a vacancy type.

- **Annealing ► 1st order of reaction γ=1**

Interval of annealing 320- 460ºC: ($\nu_0 \leq 10^{13}$ s^{-1})

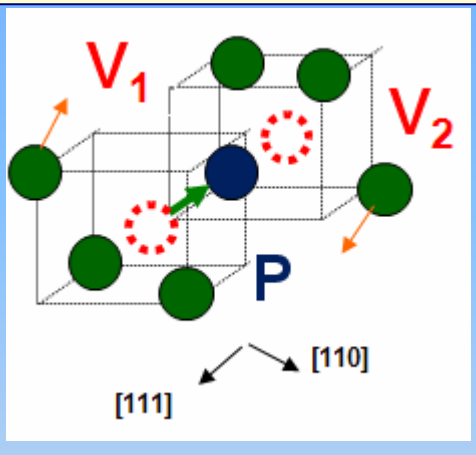
Equation of kinetics of chemical reaction

$$\varphi(T_a) = \gamma \ln C_0 - \ln(dk / dT_a) = A + E_a / k_B T_a$$

$$N_{deep\ donors} \times const \cong k = \lambda_0 \frac{\lambda_{av} - \lambda_0}{\lambda_d - \lambda_{av}} = \lambda_0 \frac{I_d}{1 - I_d}$$

Arutyunov et al., Solid State Phenomena, 205 – 206 (2013) 317; ibid. 178– 179 (2011) 313

Formal configuration of deep donor center *detected* in silicon of n-type {*n*-FZ-Si ([P])} irradiated with protons 15 MeV



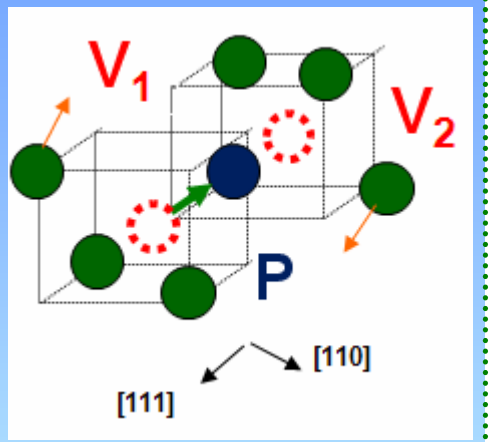
VPV

- Two vacancies (dashed circles) are in close proximity to atom of phosphorus P. Nearest atoms of Si participate in closing bonds. The 5th electron of P atom is on the deep donor level: VPV
- Decomposition of deep donor center restores impurity atom of phosphorus as a shallow donor in Si: 1 e^- per 1 centre (Hall effect data)

Relaxation is not shown, red arrows show possible shift of the atoms of Si, green arrow shows the shift of vacancy towards the atom of phosphorus P

- Configuration of 2 *semi-vacancies* *tied to P- impurity atom* was considered for the *E*-center (Tolpygo et al. 1973 Sov. Phys. Solid. State 15 740); *semi-vacancy pair* was discussed by Masters (1973 Sol. St. Comm. 9 283)

Conclusion



e^+ lifetime ~ 280–300 ps
$E_a \approx 0.84 - 1.26$ eV
$S_m \approx 2–3kB$

Sol. St. Phenom. (2013): Phonon-assisted trapping of e^+, cross-section obeys to ~T^{-3} law
$\sigma+ \approx 3 \cdot 10^{-12}$ cm^2 (66K) – $2 \cdot 10^{-13}$ cm^2 (266 K)

- **Deep donors of radiation origin have been revealed in silicon of *n*-type conductivity (*n*-FZ-Si([P]) irradiated with 15 MeV protons)**
- **Being thermally stable they are hidden at early stages of isochronal annealing whereas E-centers and divacancies disappear.**
- **Data obtained by PALS spectroscopy: Configuration of deep donor consists of 2 vacancies and one atom of phosphorus**
- **Anealing of deep donors ranges temperatures from ~320℃ to 700℃**
- **Ab intio calculations are needed (to shed the light on details of configuration of this defect)**