NanoSPV - SPM Technique for the Quantitative Measurement of Minority Charge Carrier Diffusion Lengths with High Spatial Resolution

European Photovoltaic Solar Energy Conference and Exhibition (EU PVSEC),

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F. Stumpf [ab], M. Rommel [a], A.J. Bauer [ab], L. Frey [ab], F. Hitzel [c], A. Stadelmann [c], T. Bartel [d]

[a] Fraunhofer Institute for Integrated Systems and Device Technology IISB, Erlangen, 91058, Germany
[b] Graduate School in Advanced Optical Technologies SAOT, Erlangen, 91052, Germany
[c] DME Nanotechnologie GmbH, Braunschweig, 38106, Germany
[d] Silicor Materials, Berlin, 12489, Germany

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Outline

- Motivation
- Theoretical Background
- Process of Quantification
- Measurements and Results
- Summary and Outlook

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Motivation

- Driven by PV – Industry

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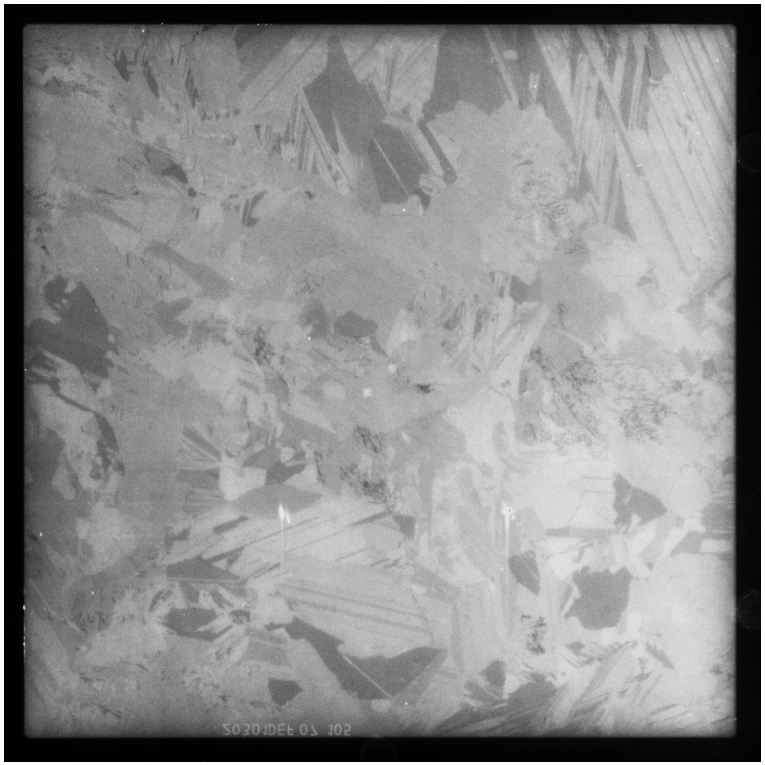
Motivation

- Commonly used techniques
  - Photoluminescence (PL)
  - Microwave Photoconductive Decay (µ - PCD)
  - Surface Photovoltage (SPV)



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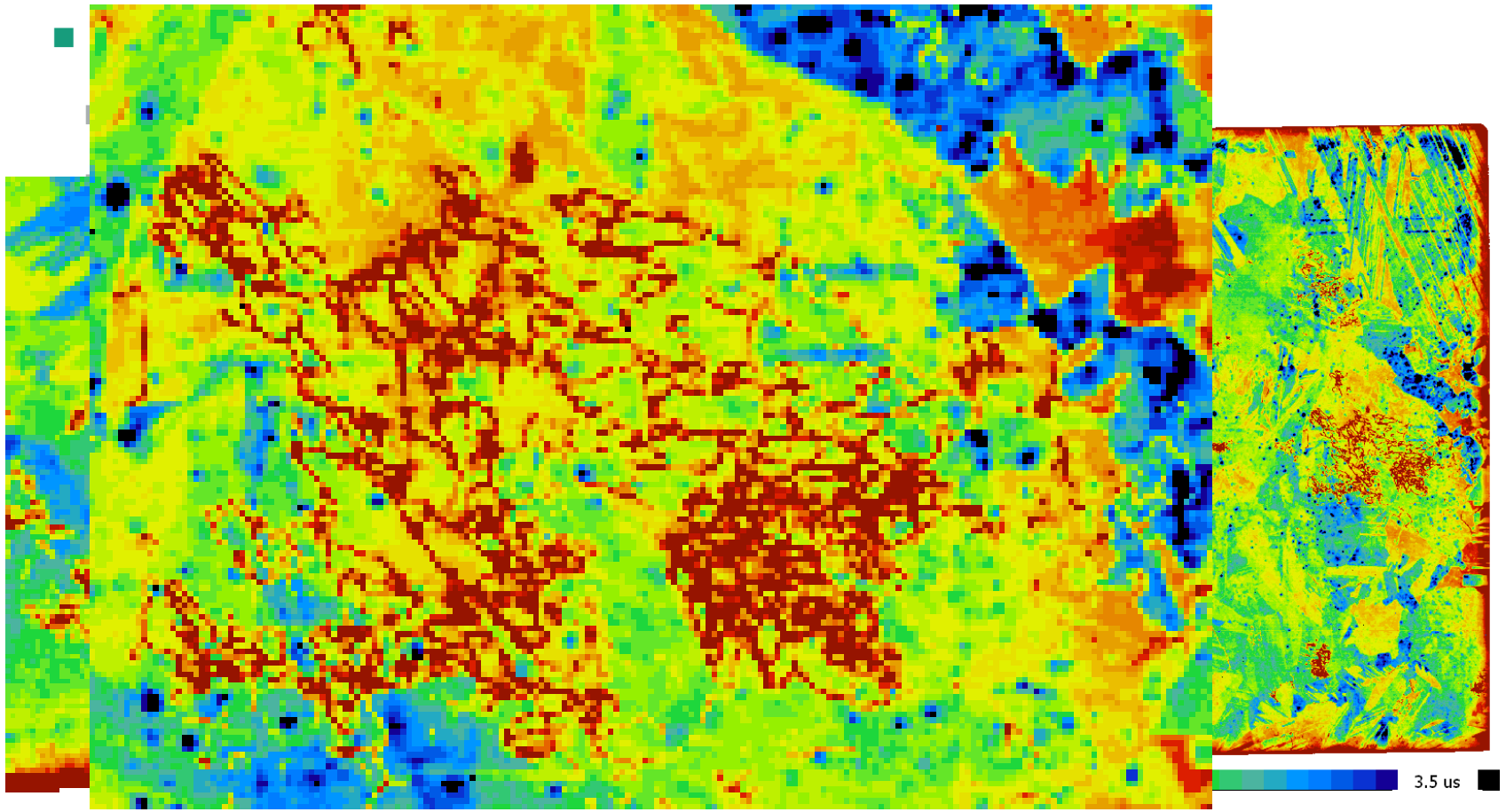
SAOT

Fraunhofer
IISB

Motivation



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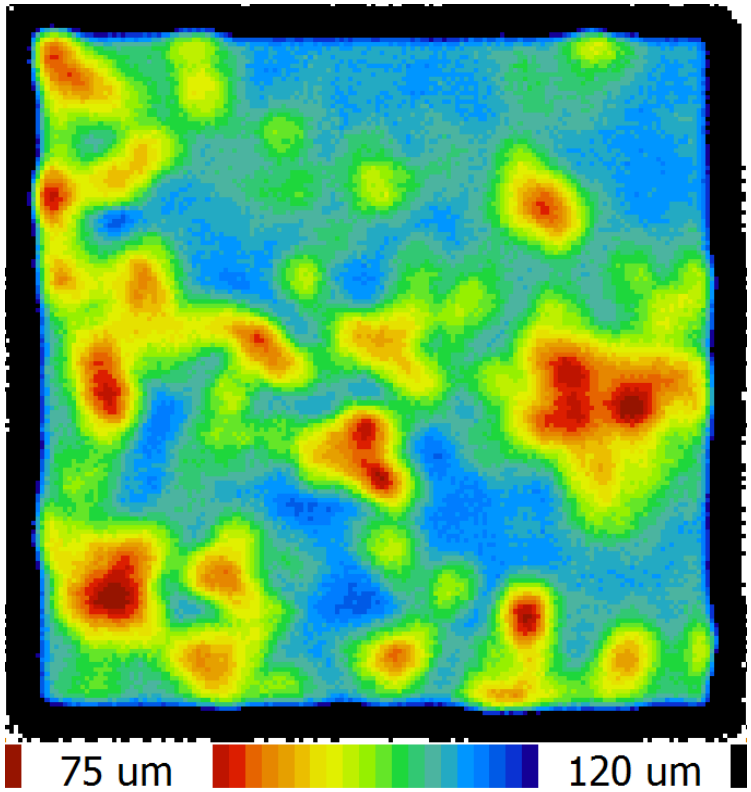
Motivation

- Commonly used techniques
  - Photoluminescence (PL)
  - Microwave Photoconductive Decay (μ - PCD)
  - Surface Photovoltage (SPV)

Scan head diameter 8 mm
Measurement raster 1 mm

Hard to compare with μ-PCD and PL due to worse resolution and different injection levels



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Motivation

- Lateral resolution is not sufficient to explicitly allocate the cause of short diffusion lengths to grain boundaries or bulk material
- Requirements for production:
  - No additional sample preparation
  - Ambient conditions
  - High spatial resolution
- Combine SPV with KPFM
  - SPV is limited by the diameter of the macroscopic Kelvin Probe

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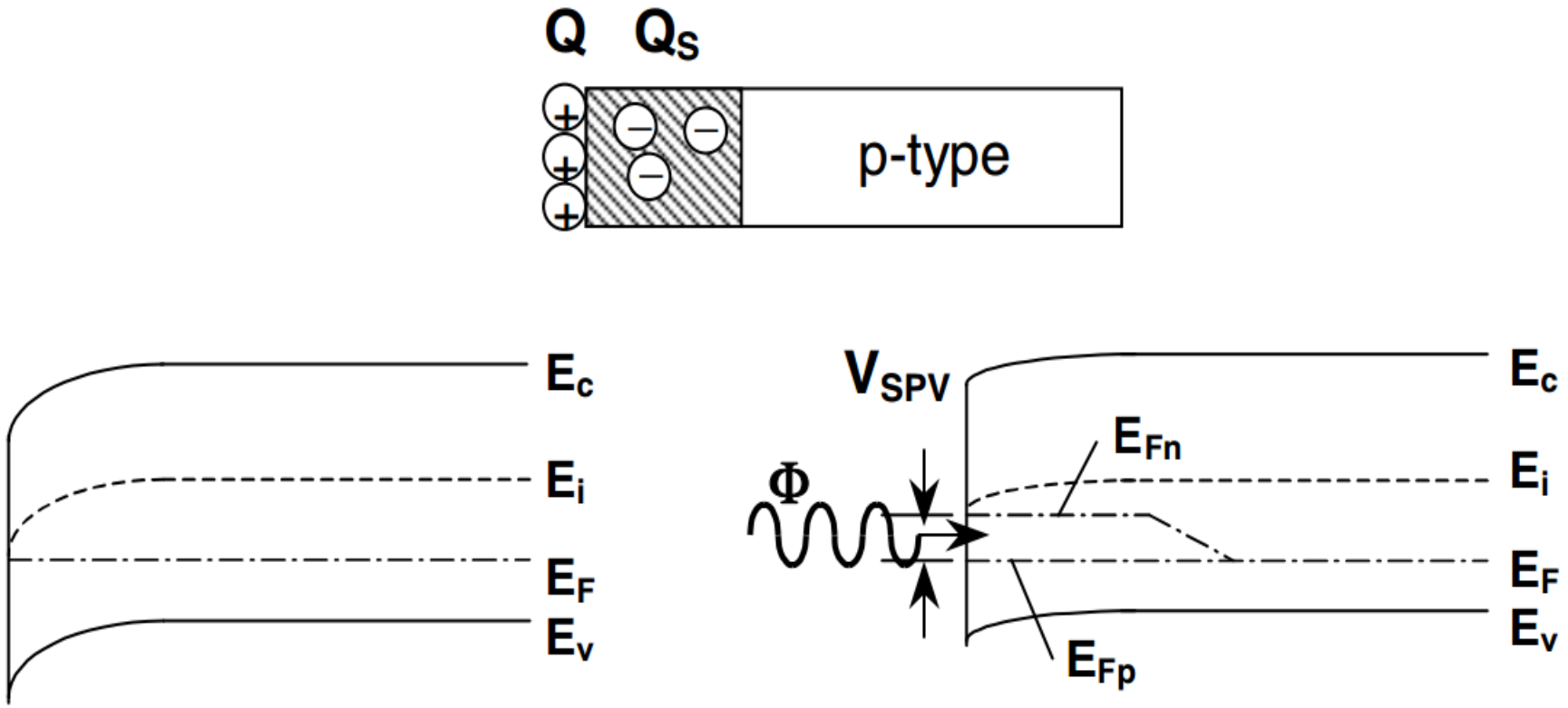
Theoretical Background

Surface Photovoltage



D. Schroder: Surface voltage and surface photovoltage: history, theory and applications, Meas. Sci. Technol. **12** (2001) R16-R31

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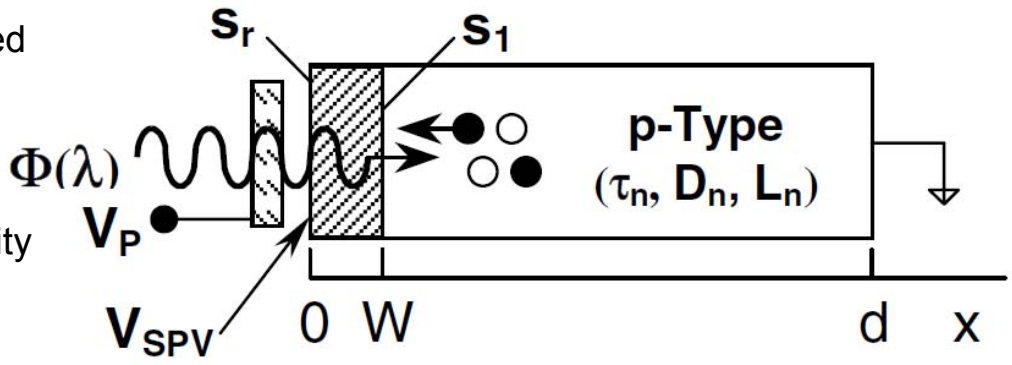
Theoretical Background

Surface Photovoltage

- Electron – hole – pairs are generated
- Miniority carriers diffuse and drift towards surface -> SPV
- SPV ~ excess minority carrier density Δn(W)



$$\Delta n(W) = A\left[\left[K_1 sinh\left(\frac{d-W}{L}\right) + K_2 cosh\left(\frac{d-W}{L}\right) + e^{-\alpha d}\left[K_3 sinh\left(\frac{W}{L}\right) + K_4 cosh\left(\frac{W}{L}\right)\right]\right] \cdot \left[\left(\frac{s_1 s_2 L}{D} + \frac{D}{L}\right) sinh\left(\frac{d}{L}\right) + (s_1 + s_2) cosh\left(\frac{d}{L}\right)\right]^{-1} - e^{-\alpha W}\right]$$

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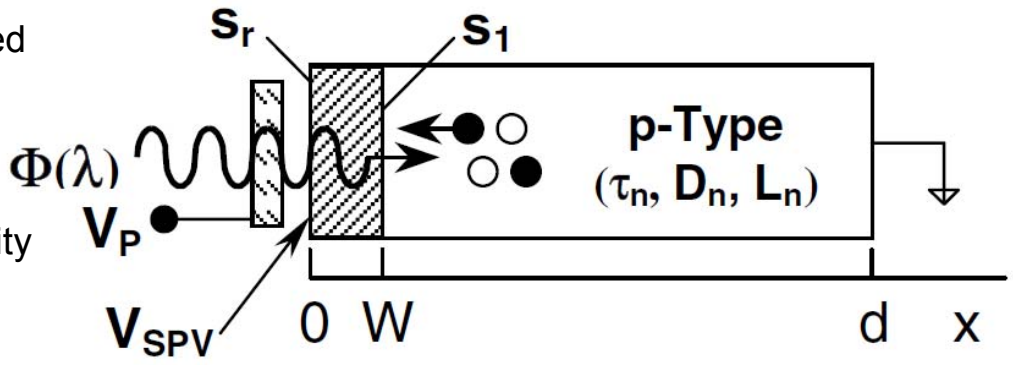

with $A = (1 - R)\Phi \propto \tau/(\propto^2 L^2 - 1)$

$$K_1 = \frac{s_1 s_2 L}{D} + s_2 \propto L \qquad K_3 = \frac{s_1 s_2 L}{D} - s_1 \propto L$$

$$K_2 = s_1 + \propto D \qquad K_4 = s_2 - \propto D$$

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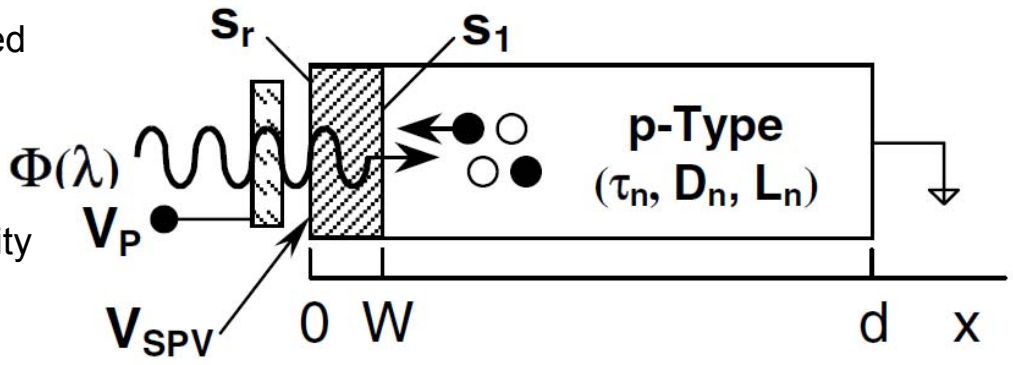

- Assumptions: $d - W \approx d$; $d - W \gg L$; $\propto (d - W) \approx \propto d \gg 1$; $\propto W \ll 1$; $s_2 \to \infty$

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Theoretical Background

Surface Photovoltage

- „law of junction“ relates surface voltage to excess carrier density at x = W for $V_s < 0.5\ kT\ /q$

$$\Delta n(W) = n_0(\exp\left(\frac{qV_s}{kT}\right) - 1) \approx n_0 qV_s/kT$$

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Theoretical Background

Surface Photovoltage

- Assumptions:
  - Low injection levels: $D_n = const$
  - Diffusion length $L_n = const$
  - Restricted wavelength range and bare surface: $R = const$
  - If $\Delta n(W) = const$ during measurement: $s_1 = const$

- Only variables left are α and Φ

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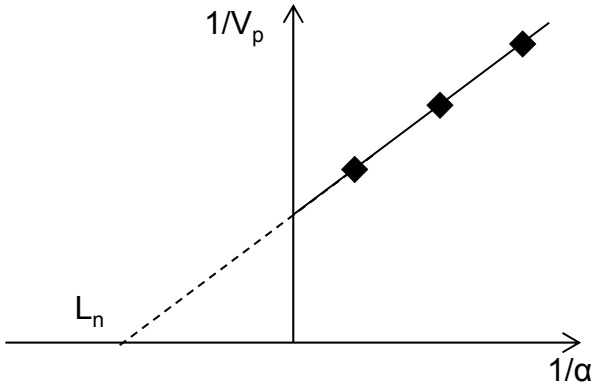
Theoretical Background

Surface Photovoltage

Constant photon flux density Φ

$$\frac{1}{V_p} = \frac{n_0(s_1 + \frac{D_n}{L_n})}{(\frac{kT}{q})(1-R)\Phi} \frac{(Ln + \frac{1}{\alpha})}{L_n}$$

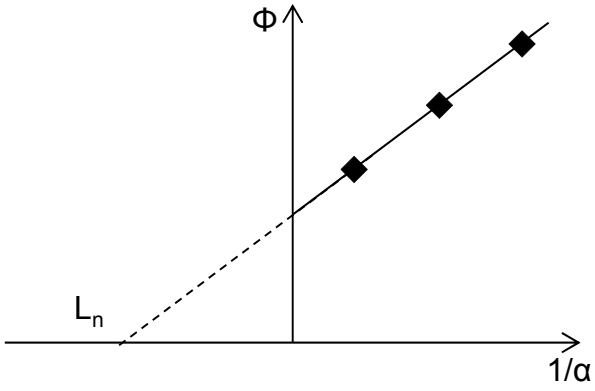
$$= C_1(Ln + \frac{1}{\alpha})$$



constant surface photovoltage V_p

$$\Phi = \frac{n_0 V_p(s_1 + \frac{D_n}{L_n})}{(\frac{kT}{q})(1-R)} \frac{(Ln + \frac{1}{\alpha})}{L_n}$$

$$= C_2(Ln + \frac{1}{\alpha})$$



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Process of Quantification

Reference Samples

- 25 SPV-Wafer (6“, boron doped, 10 Ωcm, 625 µm)
- 20 nm Oxide
- 20 Wafer (#06-#25) : Fe-Implantation (180 keV), 5 Wafer per dose:
  - Doses: $2 \cdot 10^{10}$ cm^{-2}, $6{,}75 \cdot 10^{10}$ cm^{-2}, $2 \cdot 10^{11}$ cm^{-2}, $6{,}75 \cdot 10^{11}$ cm^{-2}
    (homogeneous Distribution in 625 µm Wafer:
    → **ca. $3.2 \cdot 10^{11}$ cm^{-3}, $1.1 \cdot 10^{12}$ cm^{-3}, $3.2 \cdot 10^{12}$ cm^{-3}, $1.1 \cdot 10^{13}$ cm^{-3}**
  - RTA: 0) purge (30 s, 15 slm N_2), a) 400°C (5 slm N_2),
    b) 10s Ramp up 800°C (2/2 slm O_2/N_2), c) 2s bei 800°C (2/2 slm O_2/N_2),
    d) 6s Ramp up 1100°C (1/1 slm O_2/N_2), e) 45s bei 1100°C (1/1 slm O_2/N_2),
    f) 12s Ramp down 400°C (2/2 slm O_2/N_2), g) cool (ca. 120 s 15 slm N_2)
    → 4x for #06, #07, #11, #12, #16, #17, #21, #22
    → 6x for #08, #09, #13, #14, #18, #19, #23, #24
- Forming Gas Anneal (430 °C, 30 min., 0,47 l H_2 / 10 l N_2)

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Process of Quantification

Reference Samples

$$L = \sqrt{D\tau}$$

Diffusion length measurement: L_{before}

↓

Fe-B Dissociation (optical)

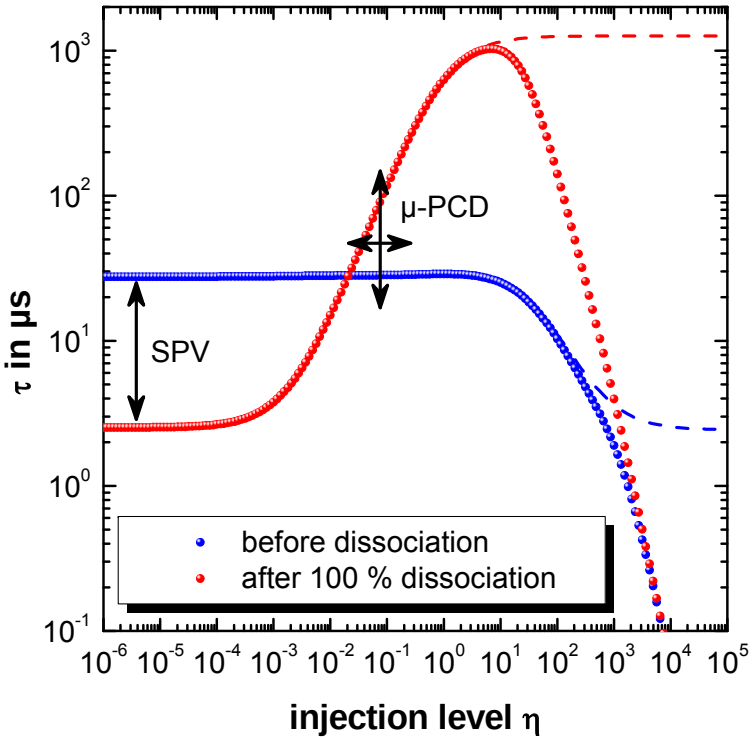
↓

Diffusion length measurement : L_{after}

↓

Calculation: $$N_{Fe} = C \cdot \left(\frac{1}{L_{after}^2} - \frac{1}{L_{before}^2} \right)$$

$N_{Fe} \approx 7.5 \cdot 10^{11}$ cm^{-3}



C = $1.06 \cdot 10^{16}$ µm^2/cm^3, Zoth, Bergholz, J. Appl. Phys. **67**, 6764 (1990)

Rommel et al., Diffusion and Defect Data Pt. B: Solid State Phenomena 82-84, 373-380 (2002)
Rommel et al., Journal of the Electrochemical Society 155 (2), H117-H123 (2008)

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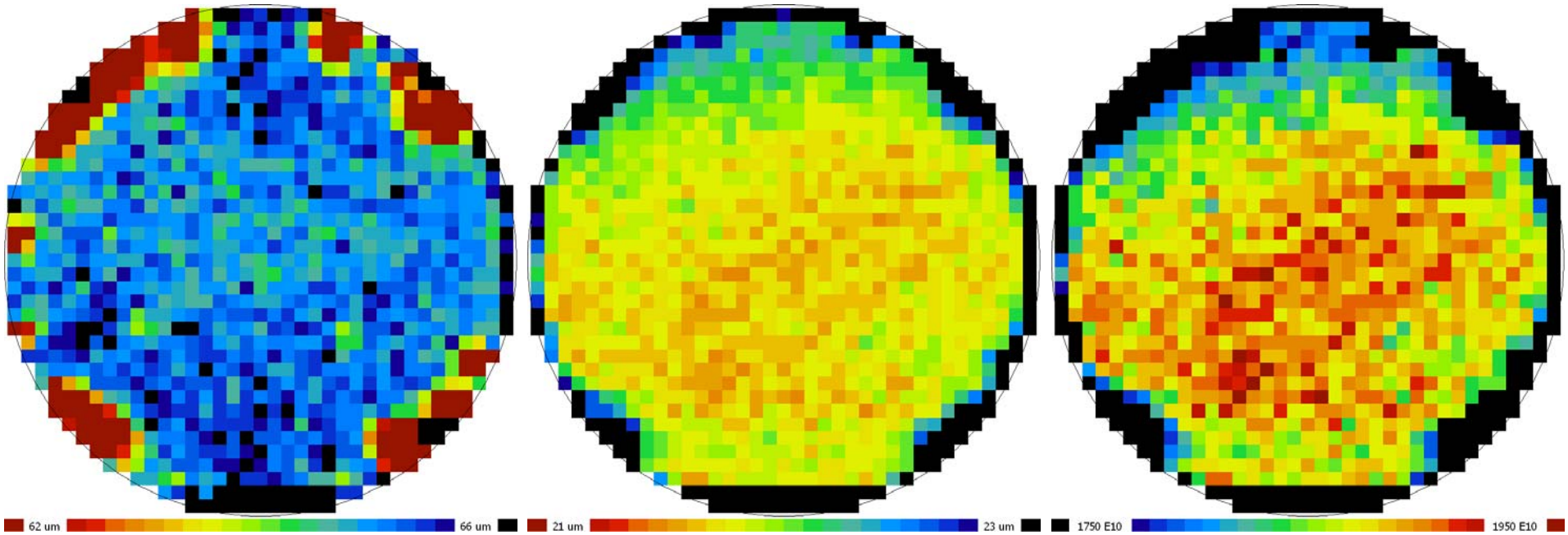
Process of Quantification

Reference Samples

#22: $6.75 \cdot 10^{11}$ cm^{-2}



NanoSPV Fe 22 before | NanoSPV Fe 22 after | NanoSPV Fe 22

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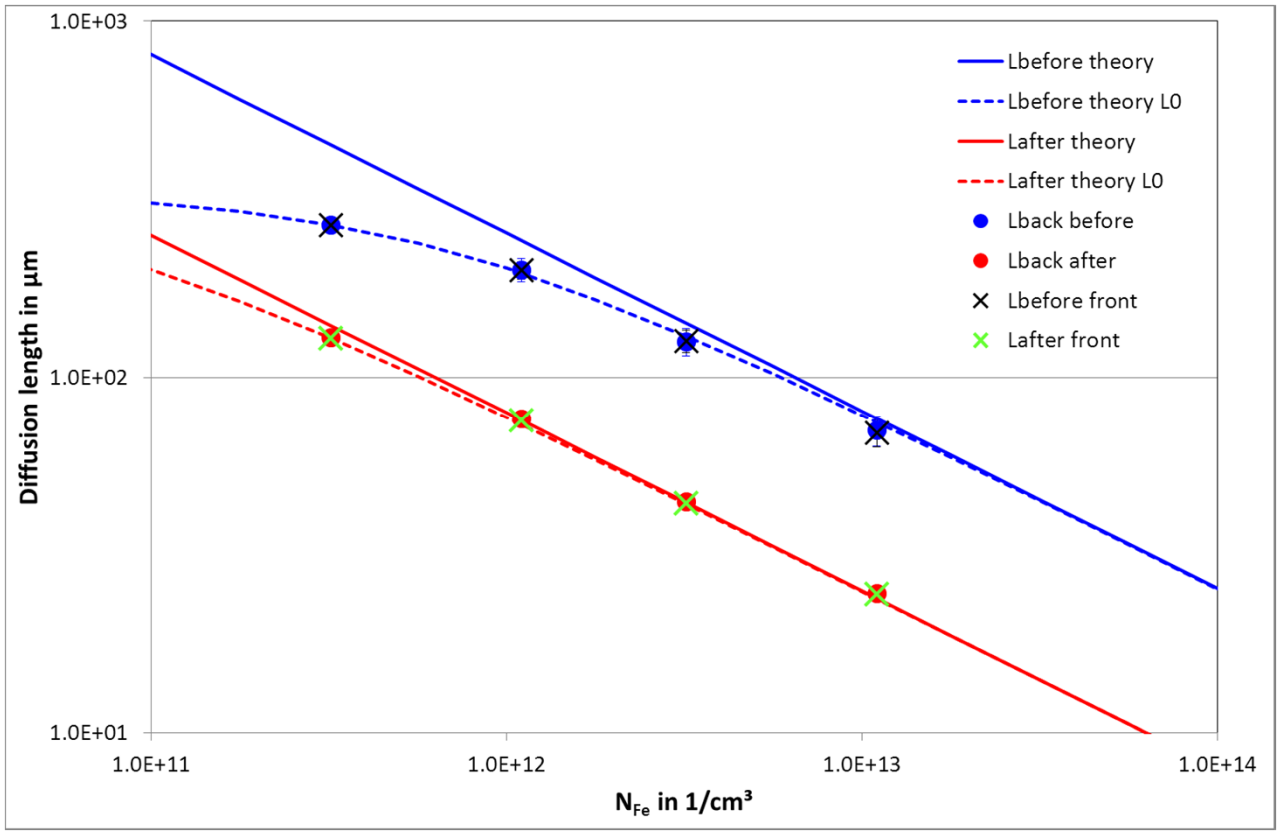
Process of Quantification

Reference Samples



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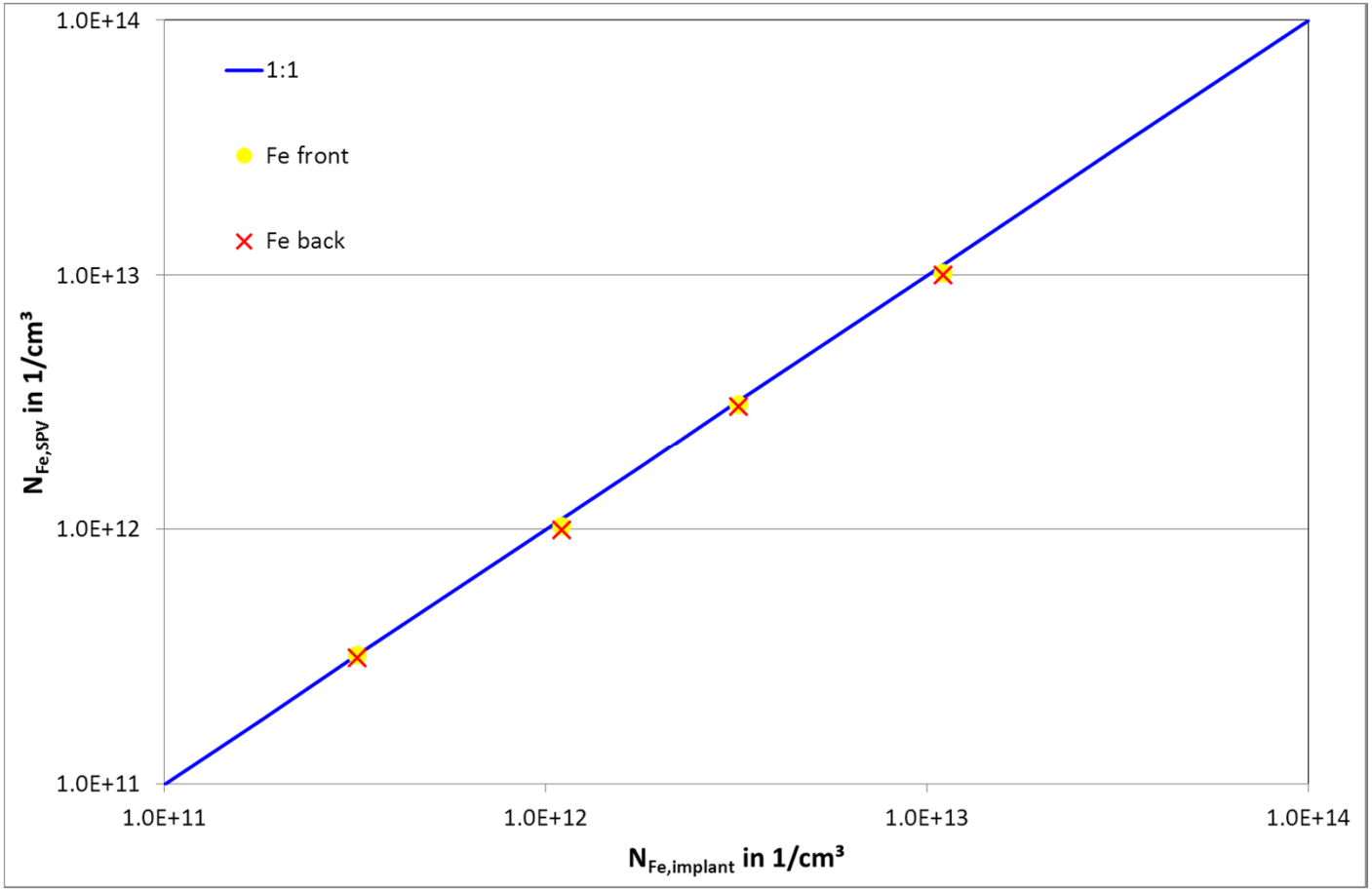

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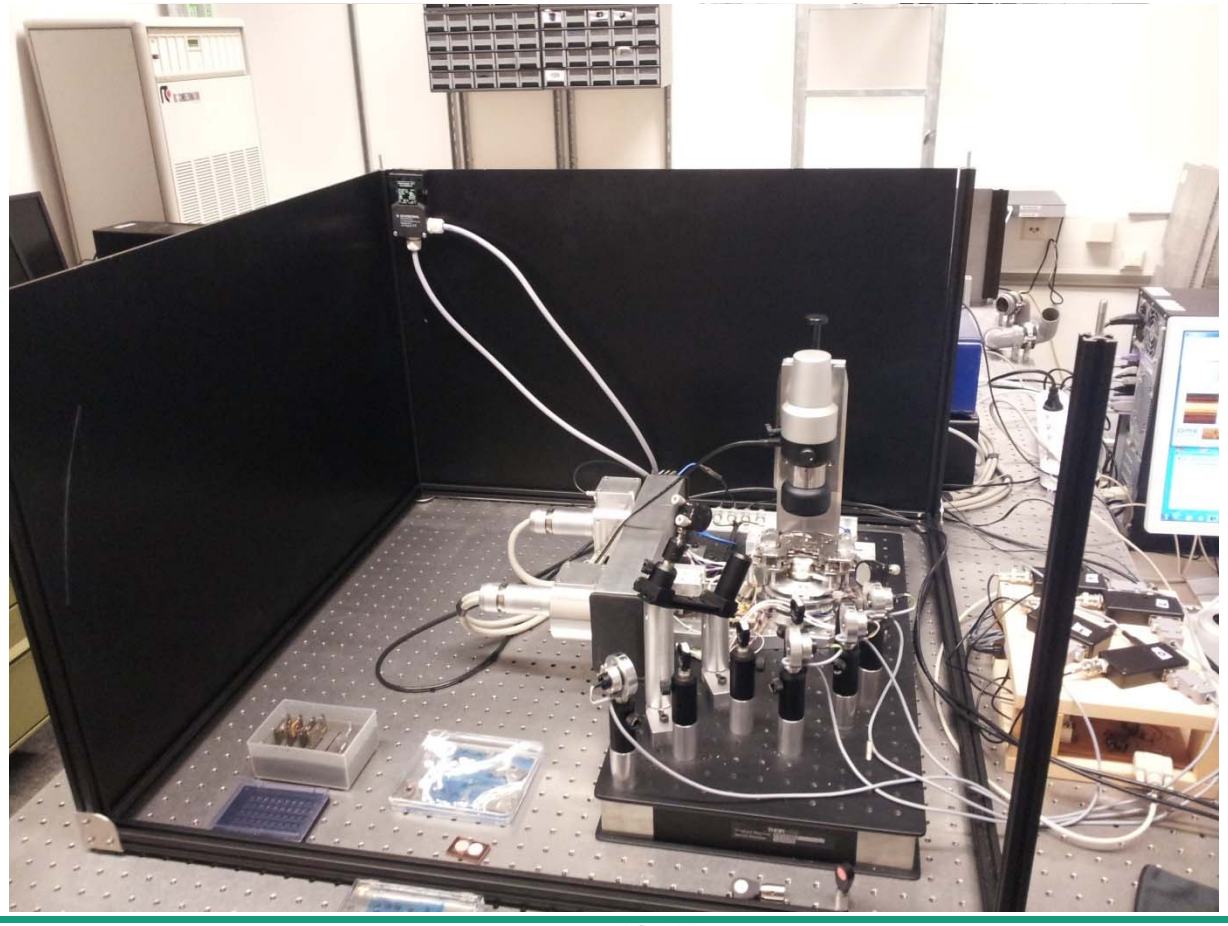
Measurements and Results

Setup



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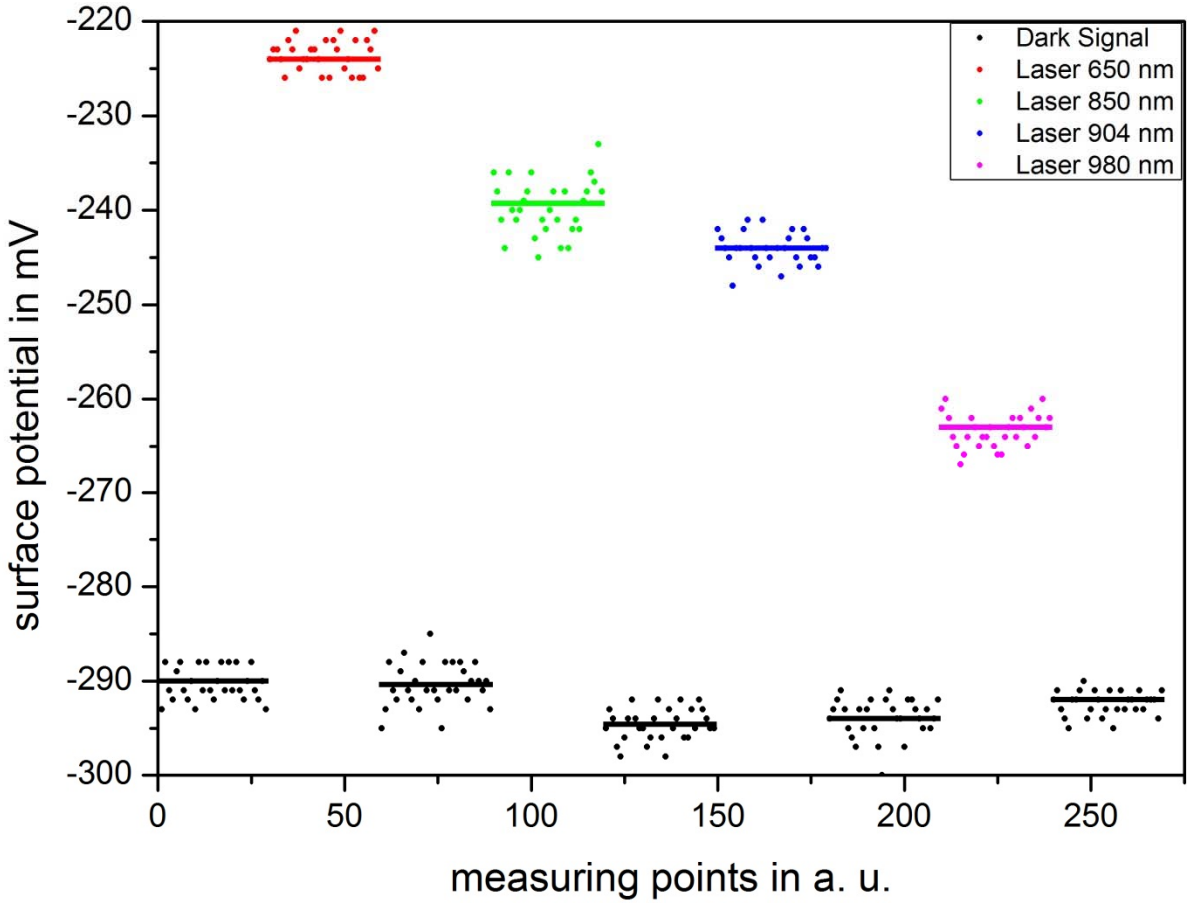
Measurements and Results

Single Point Measurement – Fe $1.1 \cdot 10^{13}$ cm^{-3}



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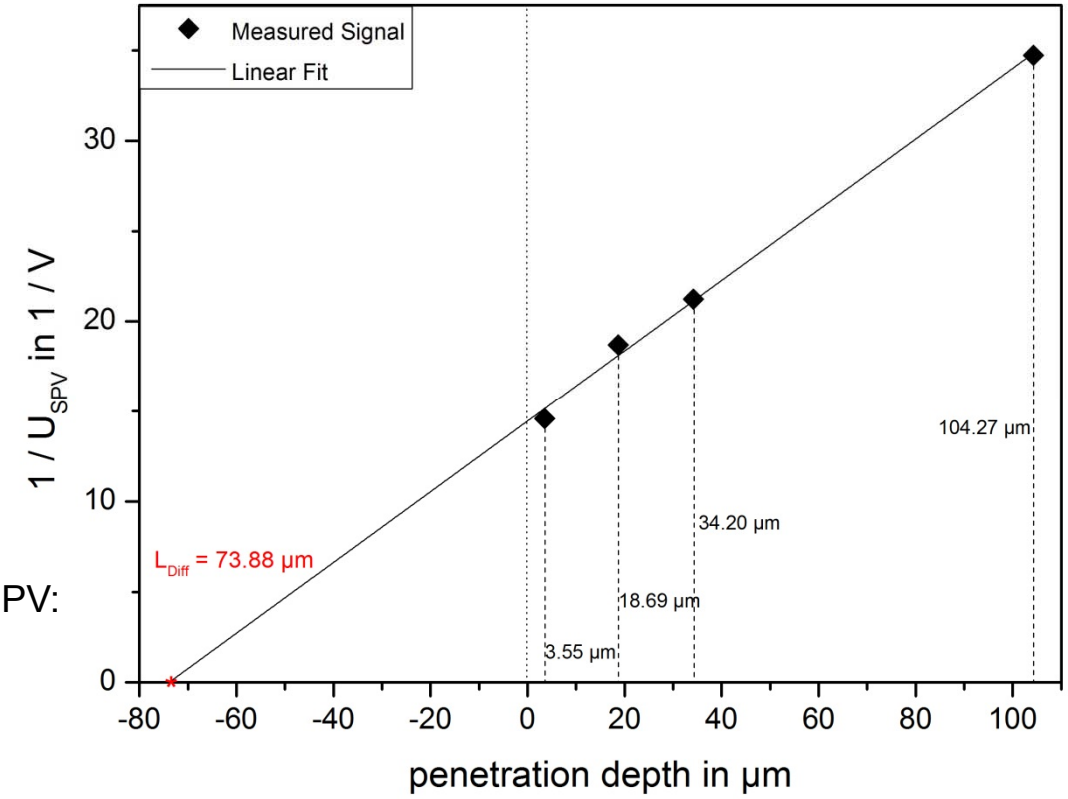
Measurements and Results

Single Point Measurement – Fe $1.1 \cdot 10^{13}$ cm^{-3}

Macroscopic SPV:
L_n = 72.75 µm



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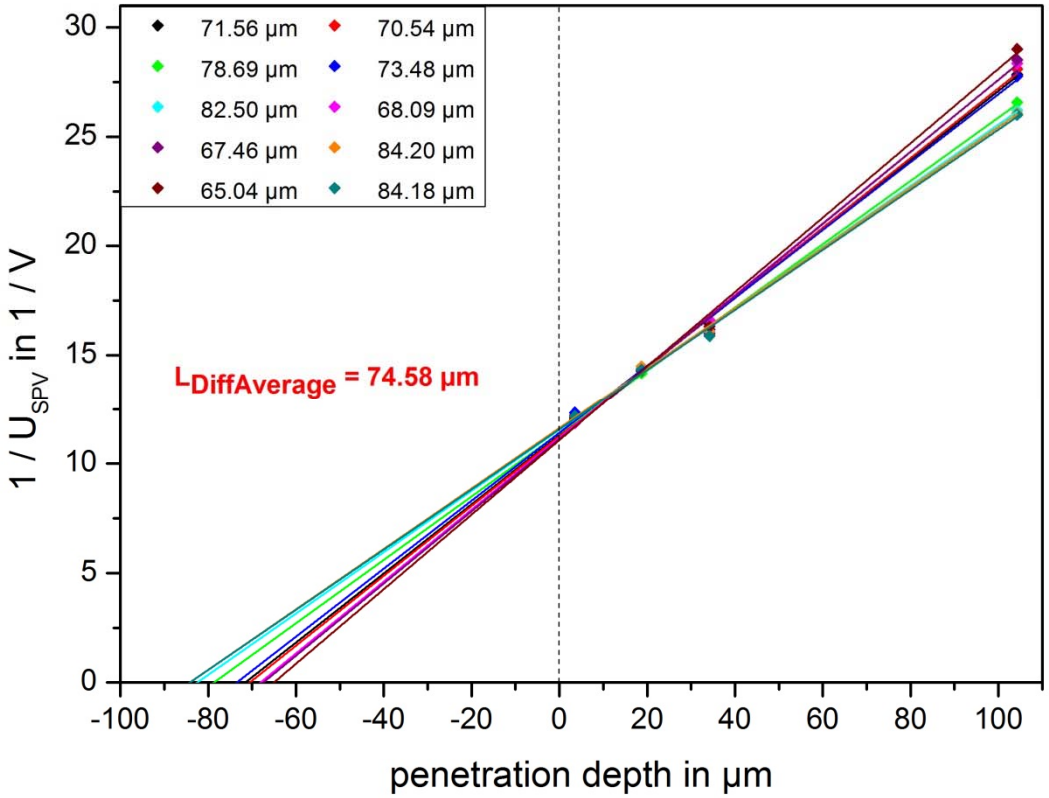

Macroscopic SPV:
L_n = 72.75 µm

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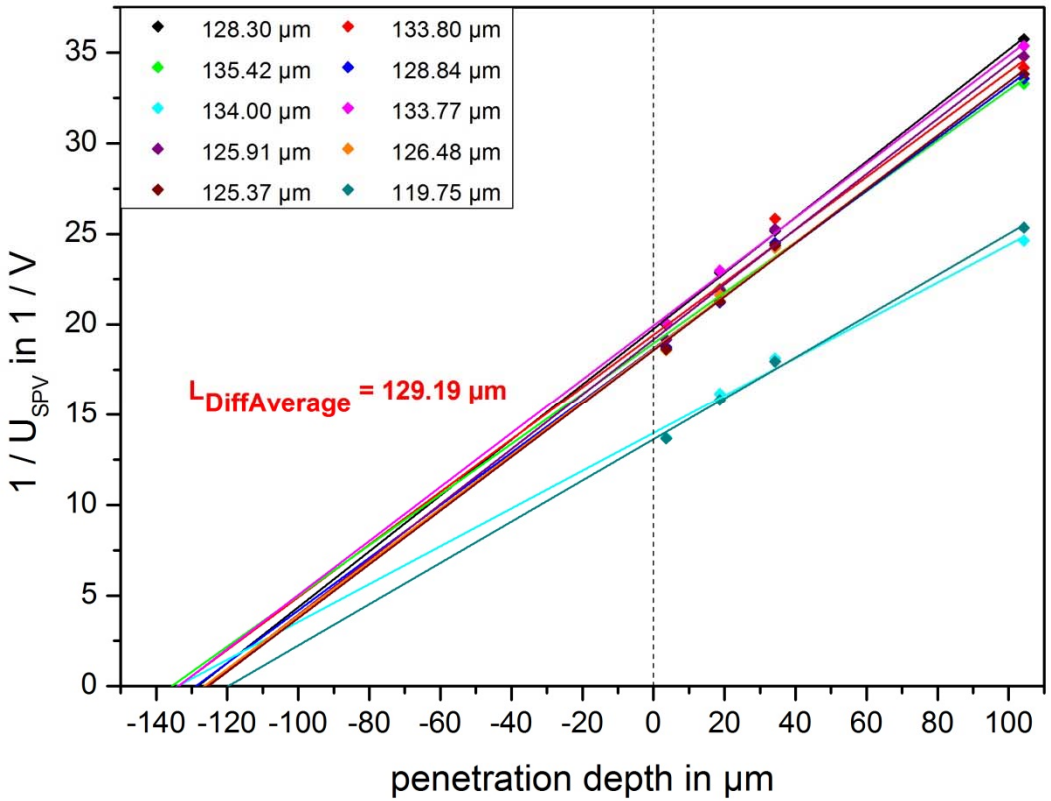
Measurements and Results

Single Point Measurement – Fe $3.2 \cdot 10^{12}$ cm^{-3}



Macroscopic SPV:
L_n = 127.62 µm

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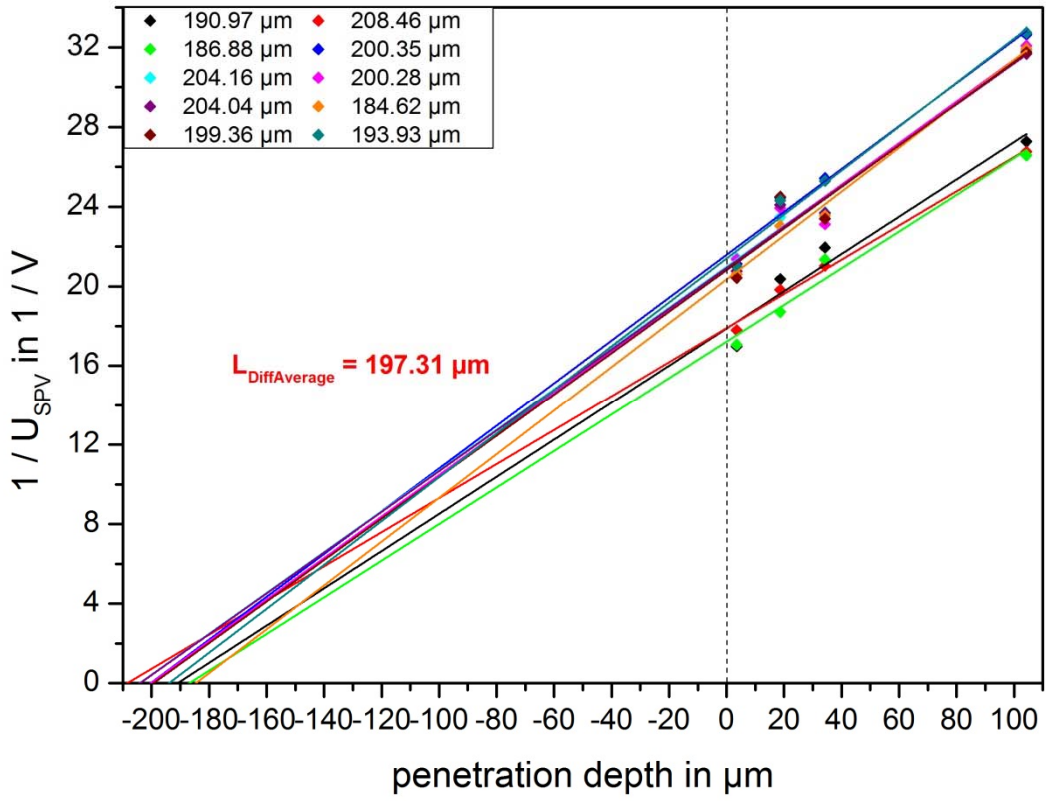
Measurements and Results

Single Point Measurement – Fe $1.1 \cdot 10^{12}$ cm^{-3}



Macroscopic SPV:
L_n = 198.35 µm

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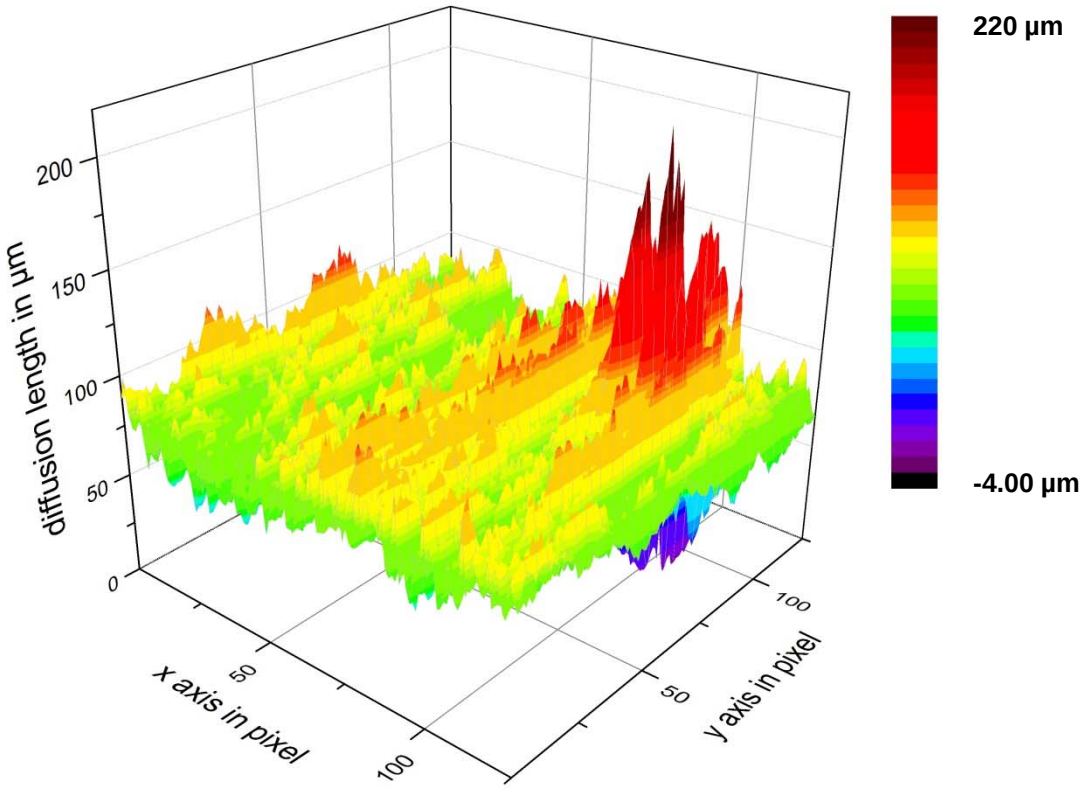
Measurements and Results

AFM Map – Fe $1.1 \cdot 10^{13}$ cm^{-3} – 5 µm x 5µm



$L_{Maximum}$: 219.15 µm
$L_{Minimum}$: -3.19 µm
$L_{Average}$: 78.07 µm
L_{Median}: 76.56 µm

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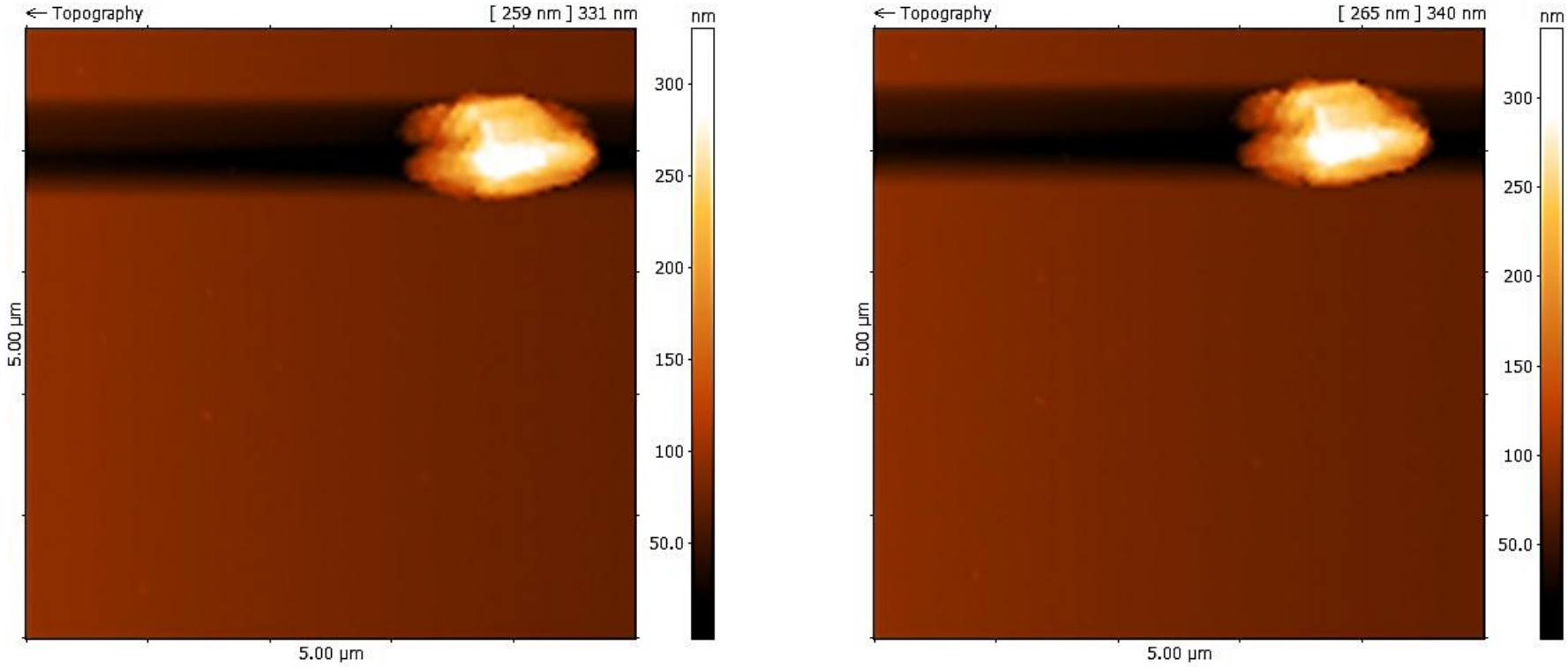
Measurements and Results

AFM Map – Fe $1.1 \cdot 10^{13}$ cm^{-3} – 5 µm x 5µm

Dark Signal



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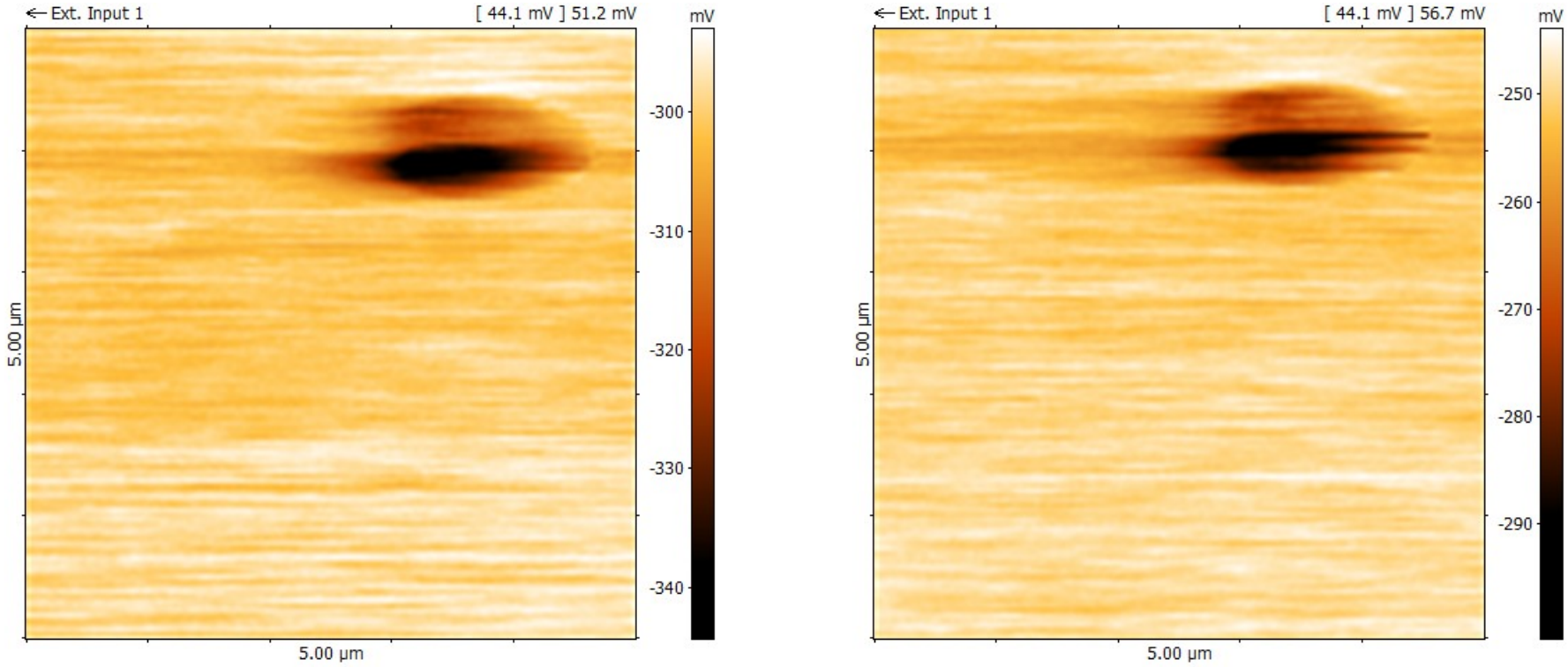

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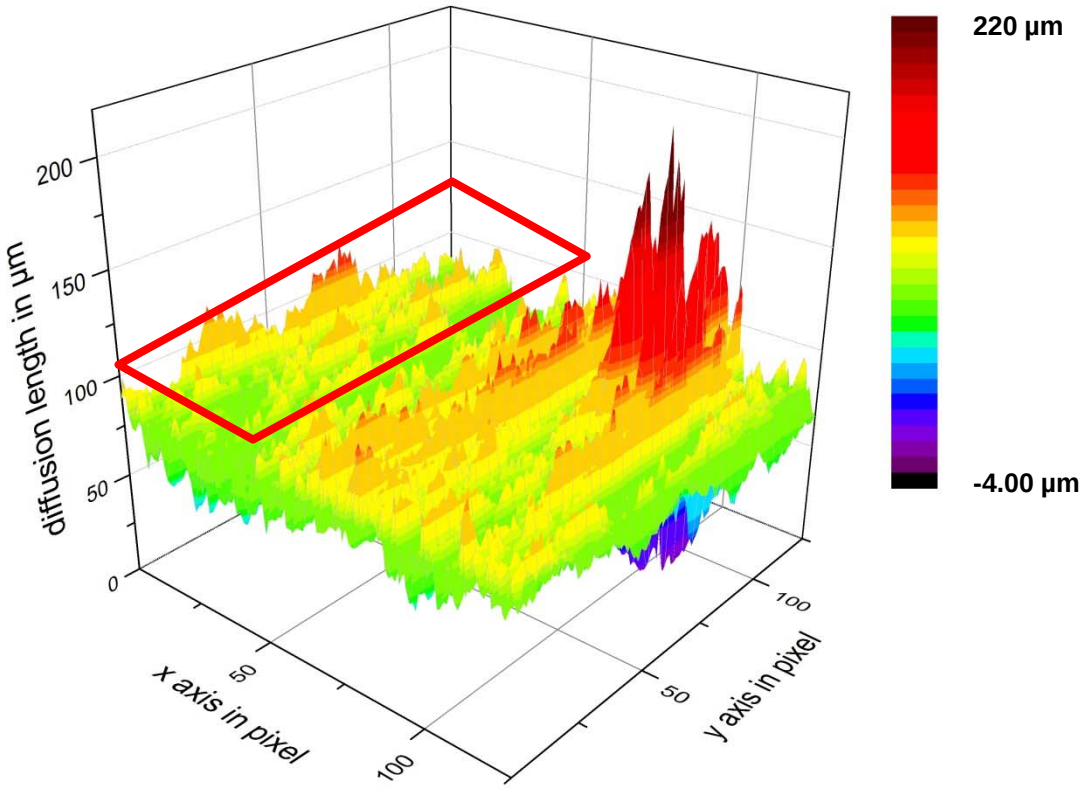

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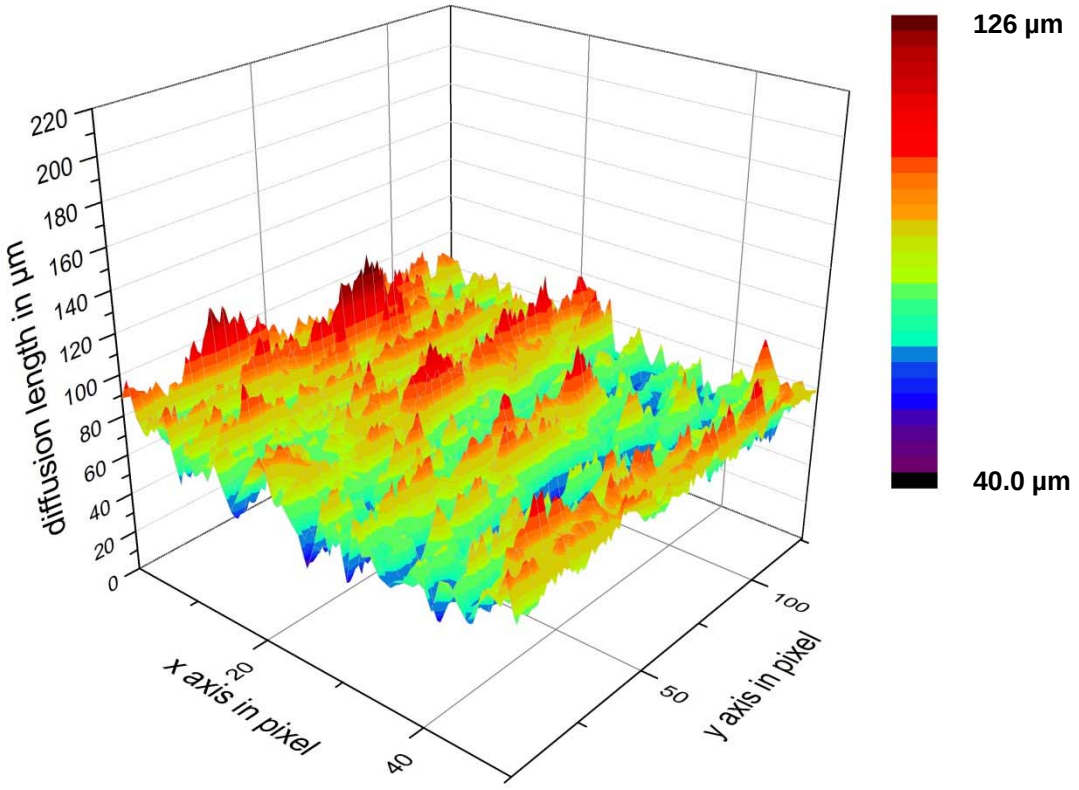

$L_{Maximum}$: 126.20 µm
$L_{Minimum}$: 41.01 µm
$L_{Average}$: 72.34 µm
L_{Median}: 71.66 µm

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Summary and Outlook

- Quantitatively proven that NanoSPV is comparable to macroscopic tools
- Increase stability of measurement (photon count and AFM drift)
  - Currently at project partner for updates
- Measure poly- and microcrystalline samples

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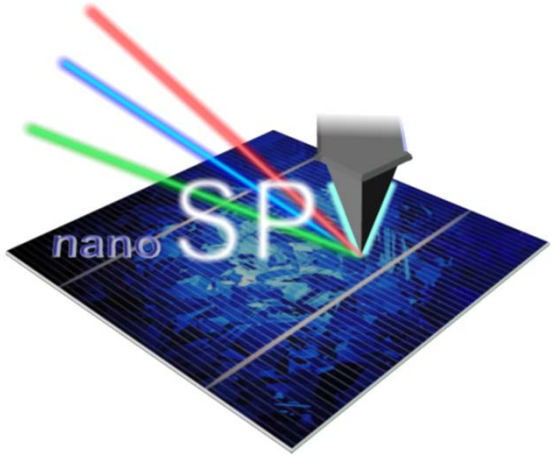
Acknowledgements

- Sponsored by BMBF: „KMU-innovativ“, FKZ 13N11890

- Poly-Si samples provided by CaliSolar GmbH (Silicor Materials)

Thank you for your attention!



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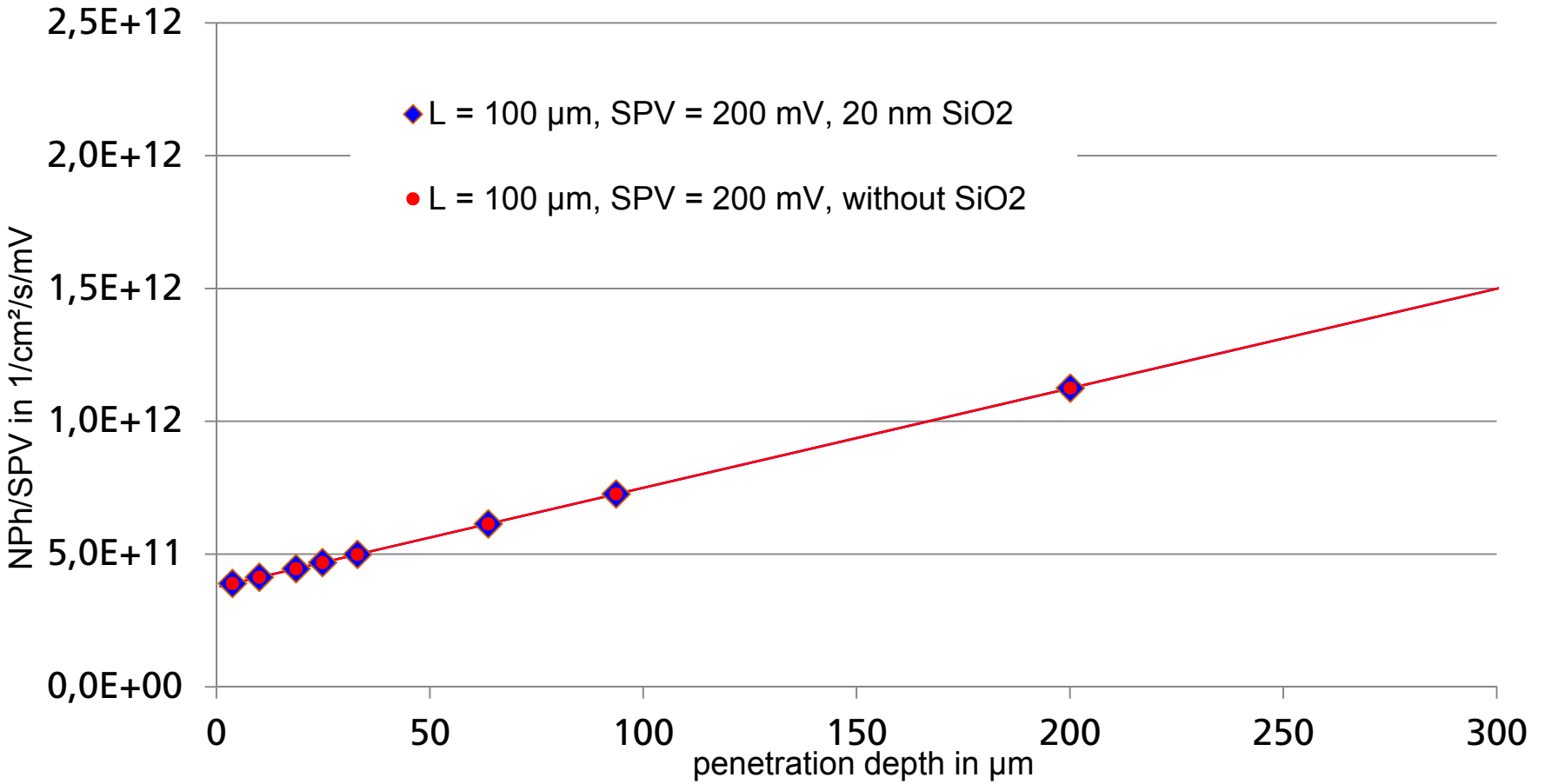
Surface Photovoltage

Same SPV - Signal



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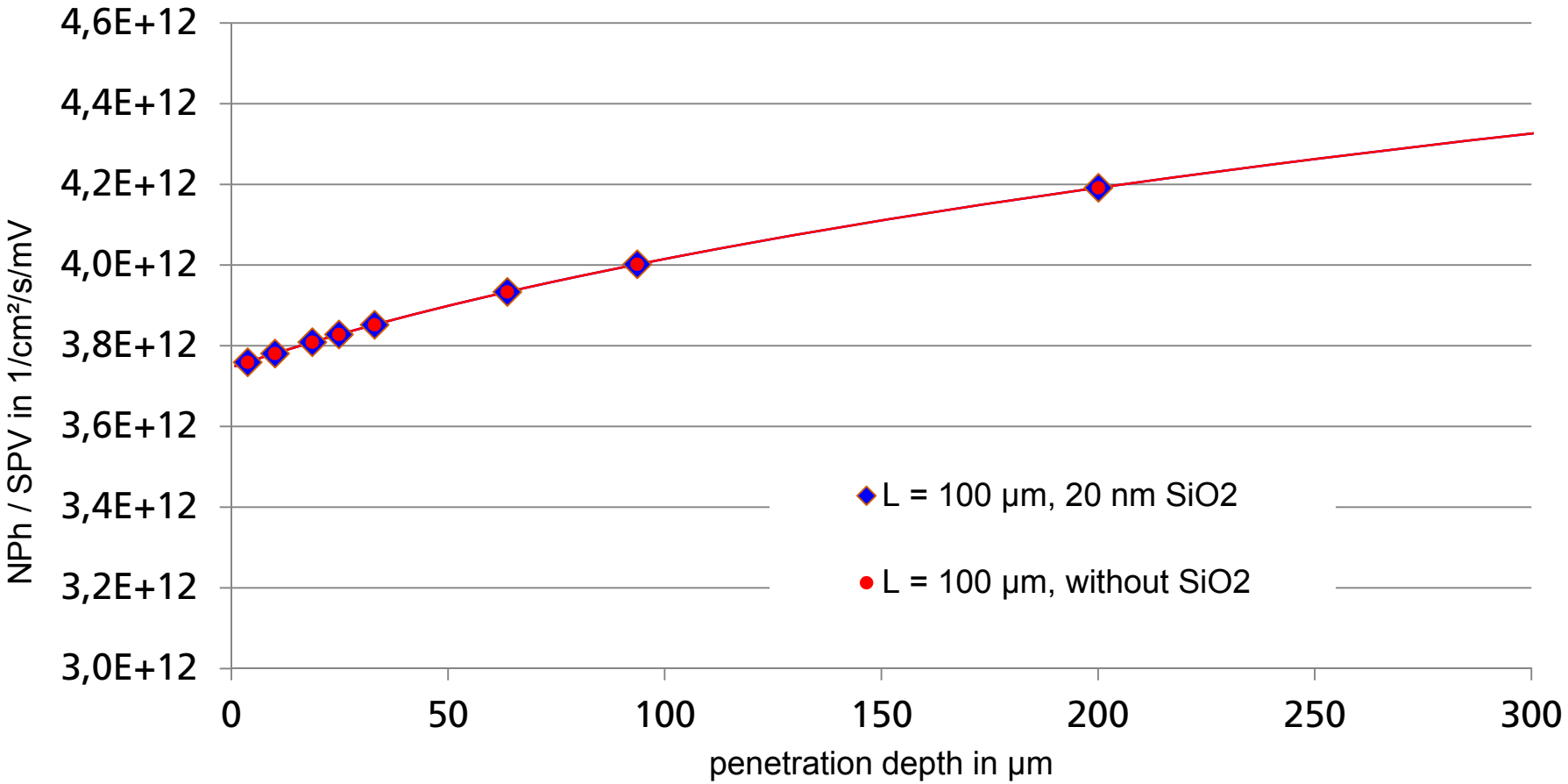
Surface Photovoltage

Same Photon Count



GEFÖRDERT VOM
Bundesministerium für Bildung und Forschung