Structural, compositional and defect studies on hadron irradiated B-doped silicon diodes

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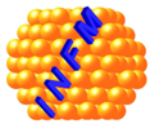
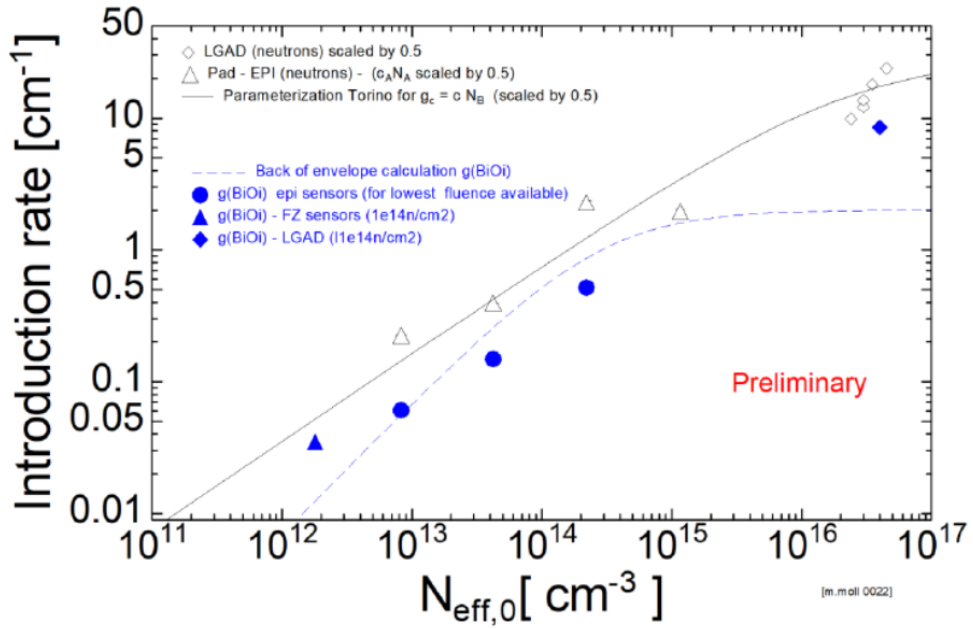


Outline

- Motivation
- Samples
- Impurity content – new employed technique (LA-ICP-MS)
- Structural damage after high fluences (10^{19} n/cm^2)
- Defect investigation- update generation rates

Motivation: “Acceptor removal rate” in p-type Silicon and the BiOi defect

- Compare [BiOi] introduction to “acceptor removal rate”



Large differences between *macroscopic* and *microscopic* results

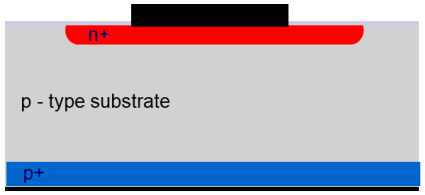
- **strong scattering of data**, different measurement techniques used; different devices; different Silicon (e.g. [O], [C])
- **differences up to 4 times** between BiOi defect generation rate and the acceptor removal rate as determined from C-V measurements

Possible explanations:
- Different devices and producers, sensors with different amount of impurities
- Differences in the time scale of measuring CVs and perform microscopic defect investigations (bistability of BiOi)
- Formation of other defects containing B or/and of other type of defects acting as donors.

start a systematic study on defect engineered Si (same processing, different B doping, comparison EPI, FZ and CZ technology), *all the experiments done in same place, with the same set-up/procedures*

Investigated p-type Samples

PiN pads, all produced and processed by CiS, Germany and few PiN and LGADs from CNM



50 µm thick P-type substrate:

- EPI, 50 ohm cm (4 samples)
- EPI, 250 ohm cm (4 samples)
- CZ, 100 ohm cm (4 samples)
- EPI, 1000 ohm cm (4 samples)
- FZ high resistivity (4 samples)
- LGAD FZ diodes highly irradiated (10^{17} and 10^{19} n/cm^2)
- PiN and LGAD FZ diodes irradiated with10^{14} and 10^{15} n/cm^2

Irradiation
(eq. fluences <$1.3x10^{13}$ n/cm^2)

23 GeV protons (p):
(2 samples of each type, 2 fluences)

1MeV neutrons (n):
(2 samples of each type, 2 fluences)

Type of investigations

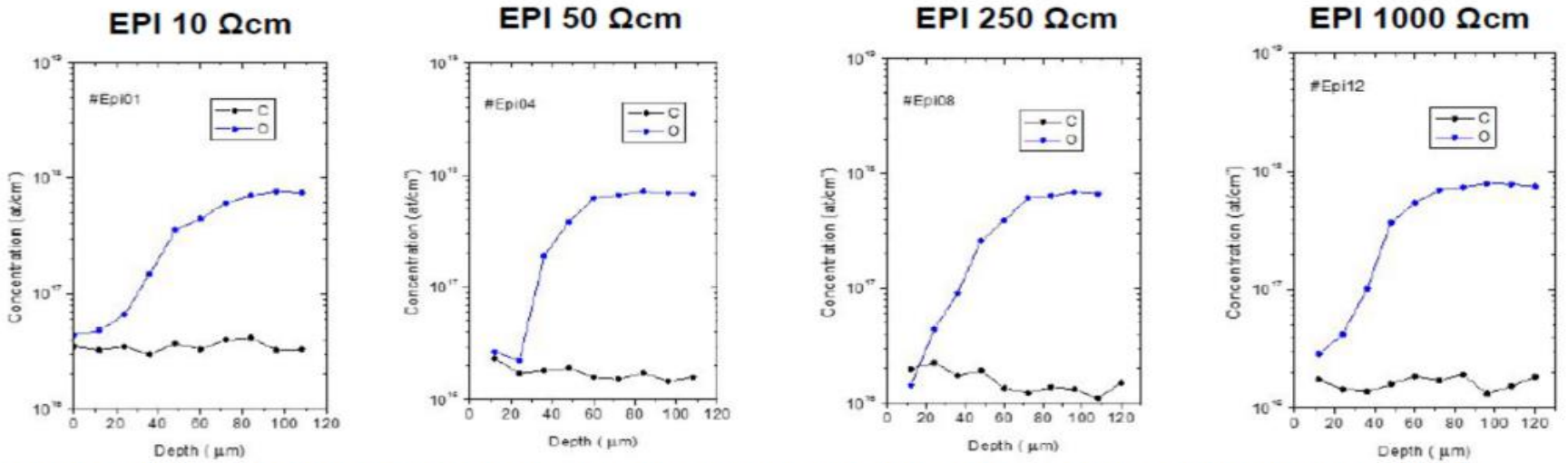
- Analyses for determining the impurity content in the investigated materials (SIMS and LA-ICP-MS, both distructive methods)
- Analyses of structural damage in highly irradiated samples (10^{17} and 10^{19} n/cm^2) by TEM
- Electrical characterization of samples irradiated with 10^{10} – $1.3x10^{13}$ n/cm^2 (DLTS), similar equiv. fluences for neutrons and protons

Impurity content – e.g. SIMS in EPI grown on CZ substrate

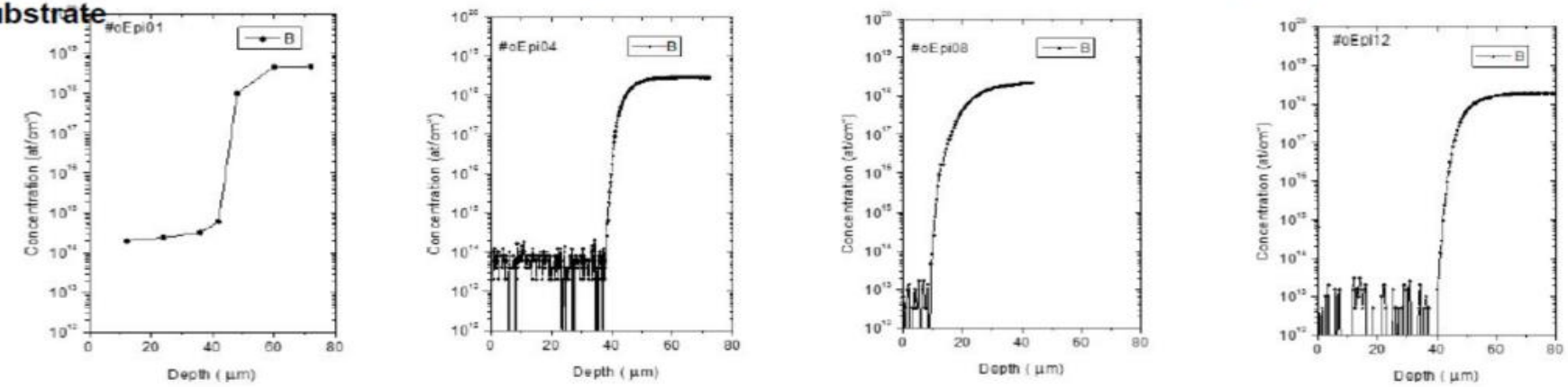
SIMS measurements results

(SIMS Laboratory at Institute of Physics PAS, Warsaw, Poland)

Detection limit of SIMS >10^{14} cm^{-3}



Oxygen, Carbon and Boron concentration profiles measured with SIMS on 50 um EPI layer grown on Cz substrate



- Similar Carbon content in EPI and CZ substrate. [C] in EPI and CZ materials ~ $1.3x10^{16}$ cm^{-3} and in FZ ~ 10^{15} cm^{-3}.
- 40 times more O in Cz than in EPI layer
- **[B] content could be detected by SIMS only in the CZ substrate** (~$2x10^{18}$ cm^{-3}) for EPI diodes with resistivities< 50 ohmcm.

LA–ICP–MS

Our institute LA-ICP-MS set-up

What LA-ICP-MS is?

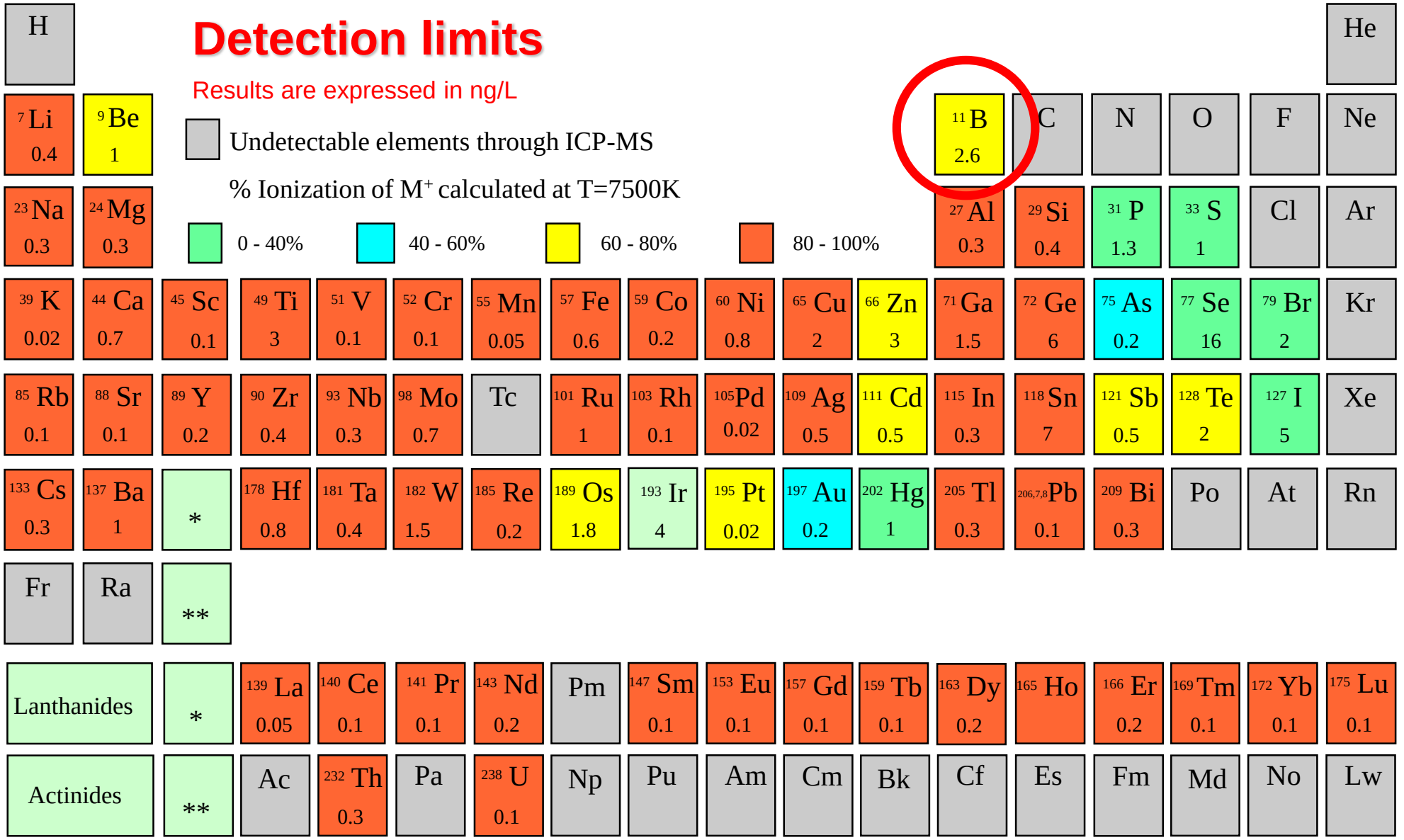
It is an analytical technique for the

- Determination of Elements using
- Mass Spectrometry of Ions generated by an
- Inductively Coupled Plasma

LA-ICP-MS analytical benefits

- Rapid multi-element quantitative analysis
- Quite low detection limits
- Wide dynamic range
- Rapid semi-quantitative analysis
  - can be used for “screening” purposes
- Isotopic analysis
- Spectral simplicity

What elements can be detected using the LA-ICP-MS technique?



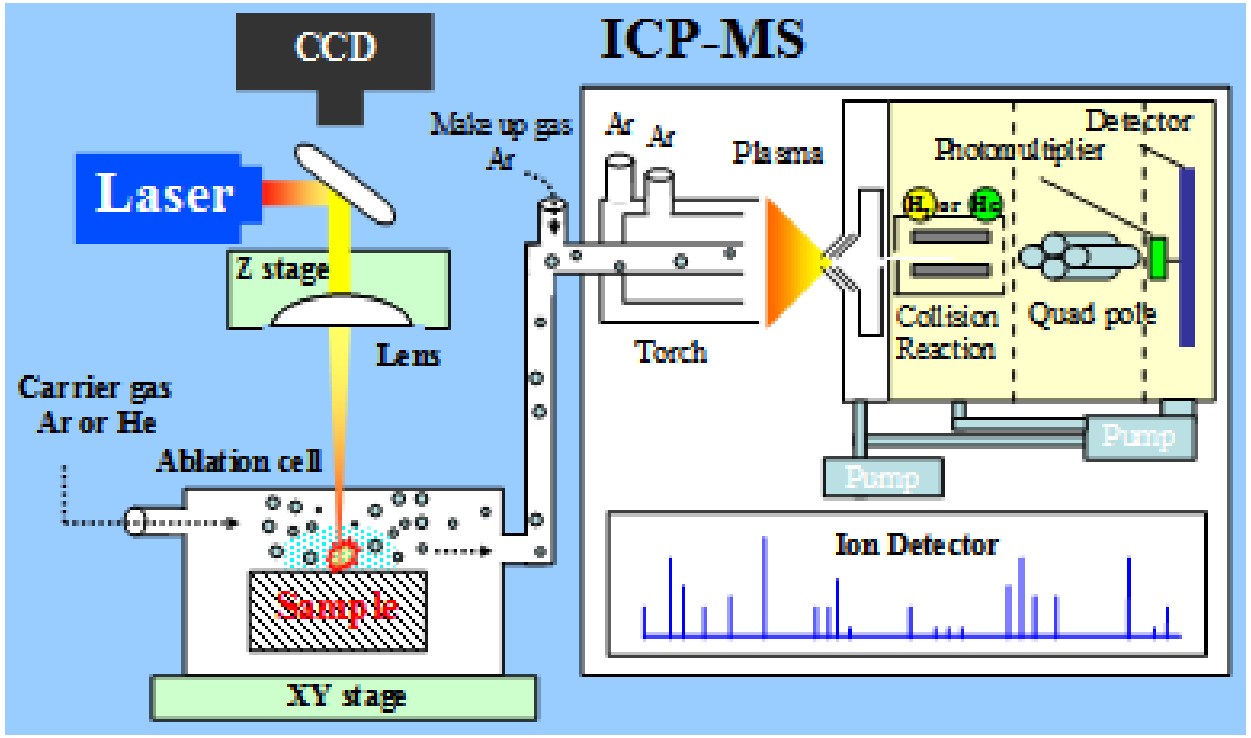
LA-ICP-MS vs. ICP-MS: benefits and drawbacks

- Compared to solution nebulization ICP-MS (the "classical" operation procedure), LA-ICP-MS can provide *in situ* and high-resolution elemental/isotopic compositions of solid samples with lower sample consumption and more efficiency (**less than 3 min for a single-point analysis**);
- The application of **LA-ICP-MS can avoid the sample-digestion-related problems** e.g., incomplete digestion of some minerals, poor stability/memory effect of some elements in dilute acid solutions, as well as the strong interferences from oxides and hydrides;
- **LA-ICP-MS suffers from severe matrix effects**—as do all solid mass spectrometric techniques—as a result of the varying ablation yields associated with differences in the material properties between the solid standards and the samples;
- For conventional quantification techniques, **a matrix-matched standard is typically required** to calibrate the laser ablation processes and the ICP response;
- Because of the limited availability of standards, **matrix-matched synthetic laboratory standards are always needed** to produce calibration curves for quantification purposes;
- The preparation of synthetic laboratory standards is often **the most time-consuming step** in solid state mass spectrometry, it is not feasible for all types of samples, and it can lead to homogeneity problems.

Synthetic laboratory standards preparation and LA-ICP-MS calibration procedures

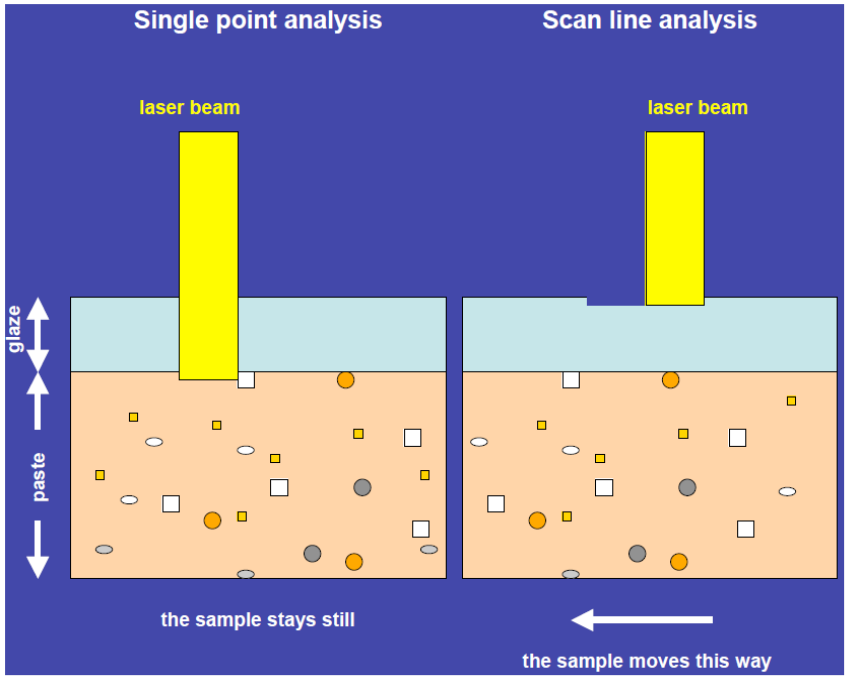
- **To avoid boron contamination**, **only** **PTFE** vessels and **polyethylene** containers were used
- **Platinum-coated Si-wafer** (Si/450 nm SiO_2/15 nm TiO_2/100 nm Pt) were sliced into 15 mm × 15 mm pieces and **truly washed/cleaned** prior to use as support for the boron-containing standards
- The **"standard materials"** used for performing the calibration were prepared by using **only** certified reagents:
  - ✓ **ultrapure water** (type 1: conductivity of 0.055 µS/cm and a resistivity of 18.2 MΩ·cm at 25 °C);
  - ✓ **polyvinyl alcohol** (United States Pharmacopeia Reference Standard) hydrated overnight before deposition;
  - ✓ **boron** certified reference material (CRM) 1000 mg/L (certified value and uncertainty 996.2 ± 2.5 mg/L);

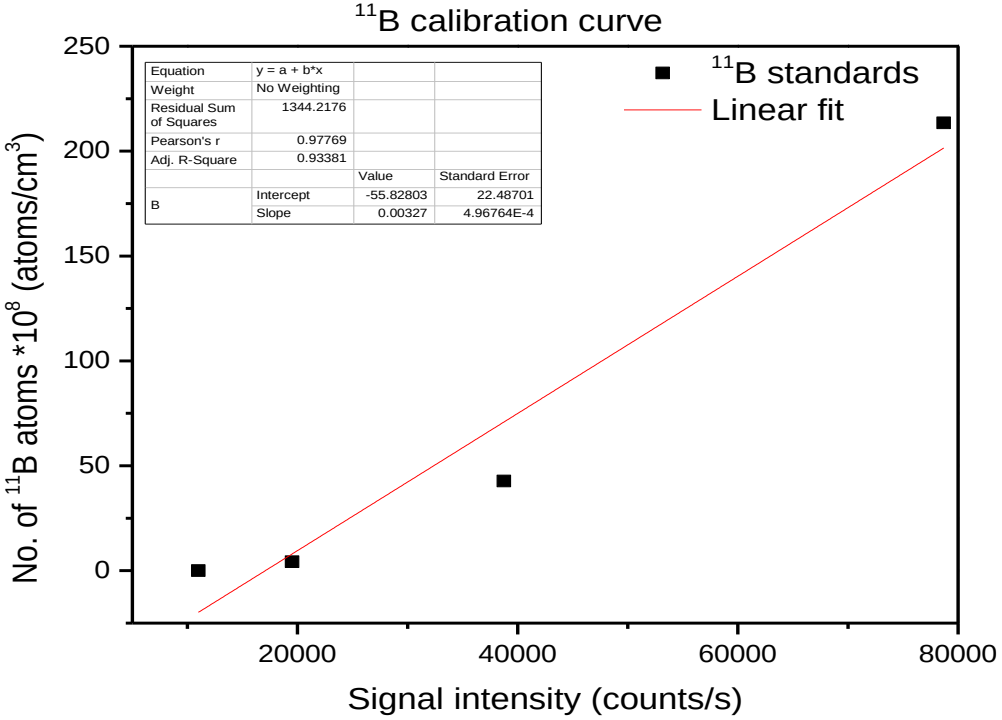
✓ **Deposition parameters**:
- **1000 rpm** for **60 seconds**
- drying **80 °C** for **10 min**
- at least **25 deposition steps**

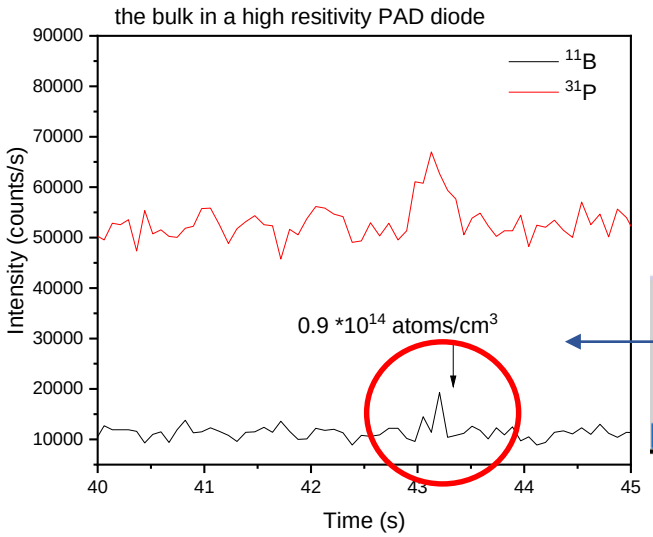


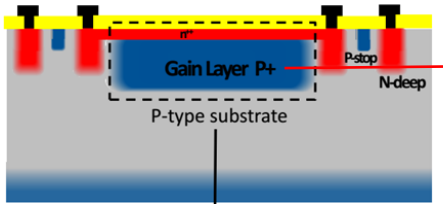
https://www.jfe-tec.co.jp/en/battery/analysis/material/la-icp-ms.html

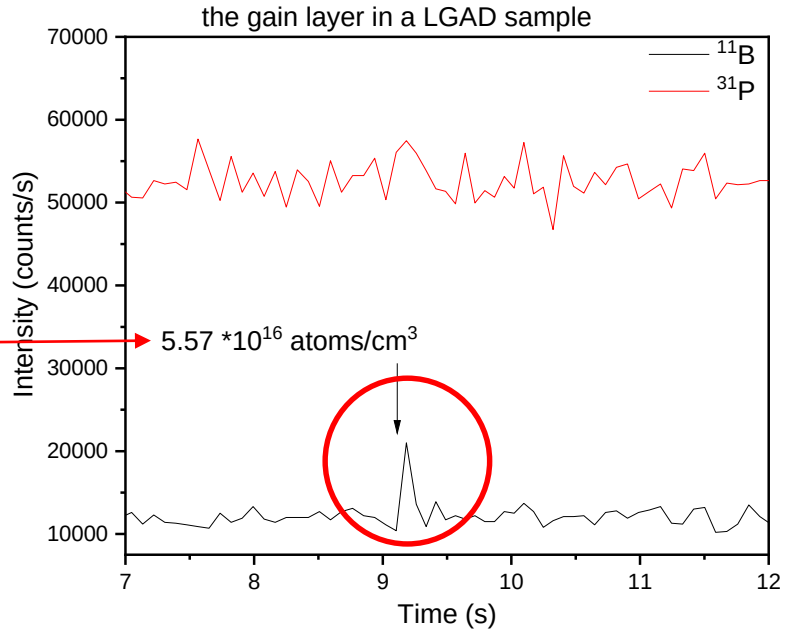
Our results







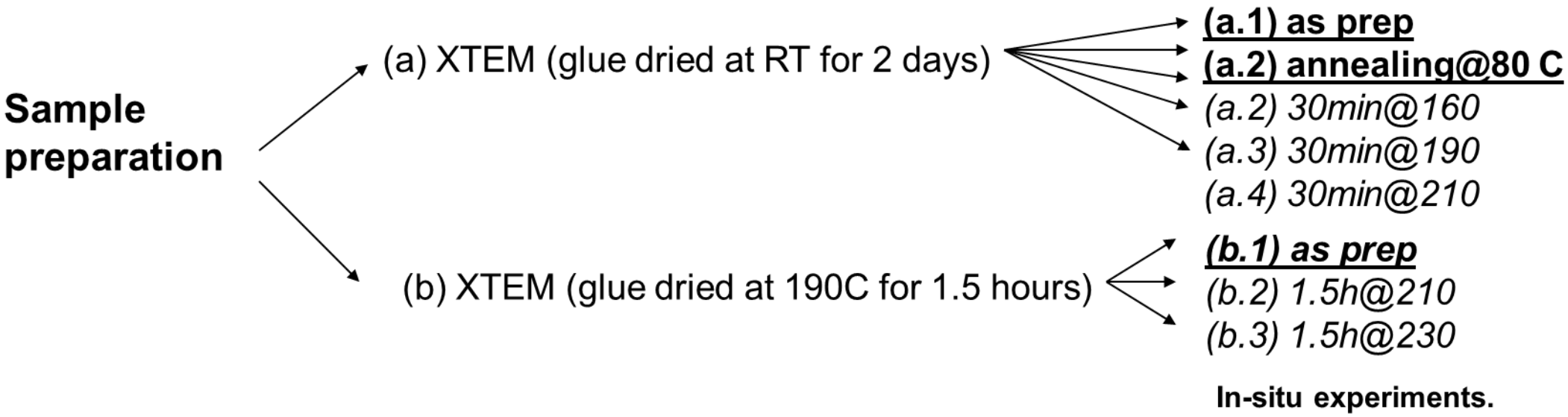




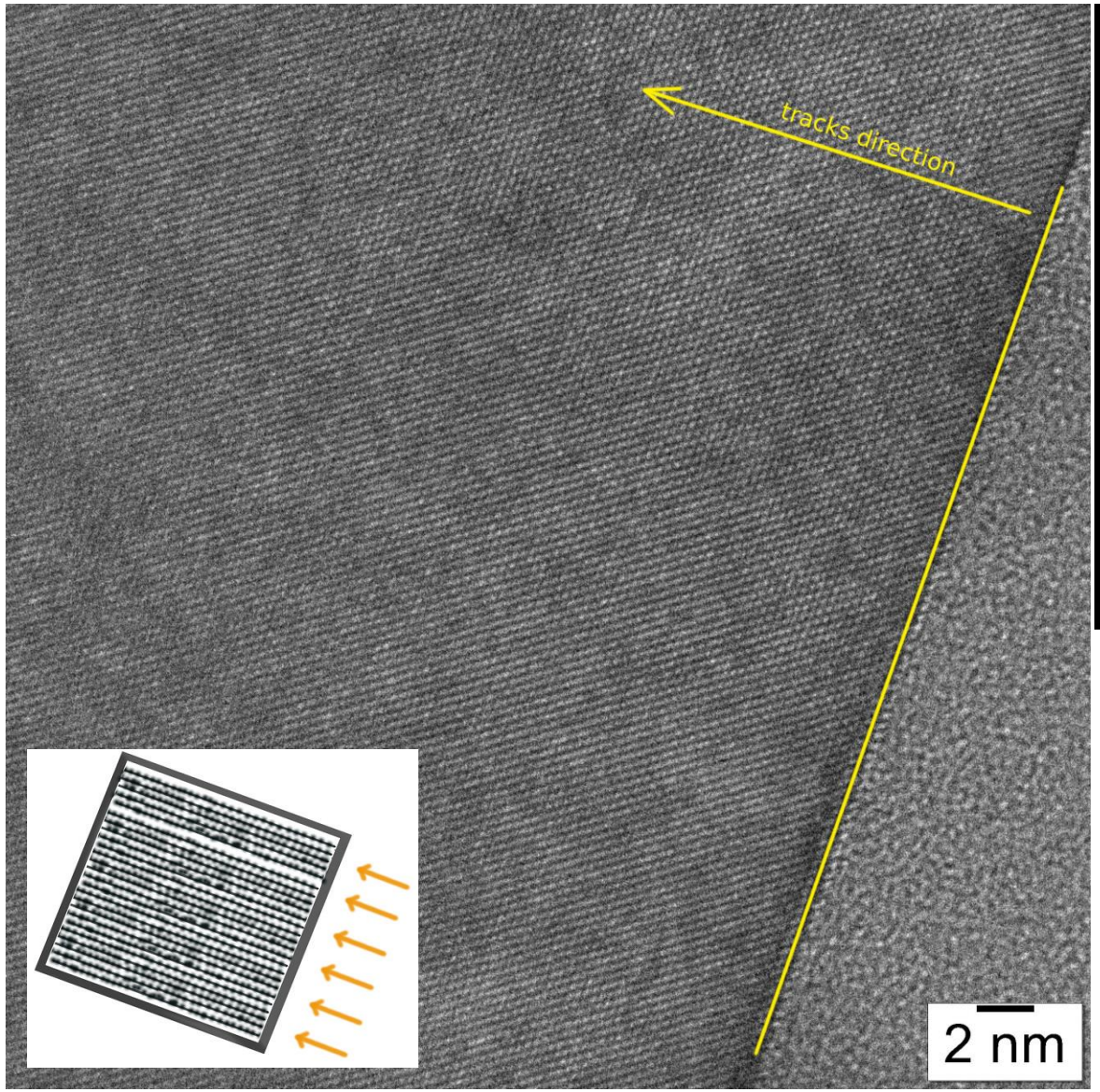
Both P and B exist in the bulk of Si

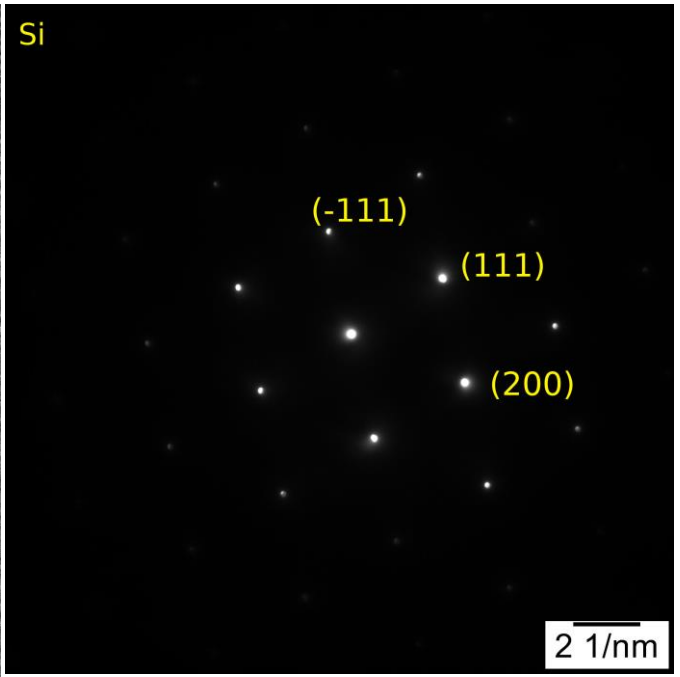
Structural damage -HRTEM investigations

- Equipment: **JEOL 2100** Transmission Electron Microscope
- Operation Mode: CTEM/HRTEM @ 200kV. (80kV not appropriate for this situation)
- Sample: **LGAD** irradiated with 10^{19} n/cm^2

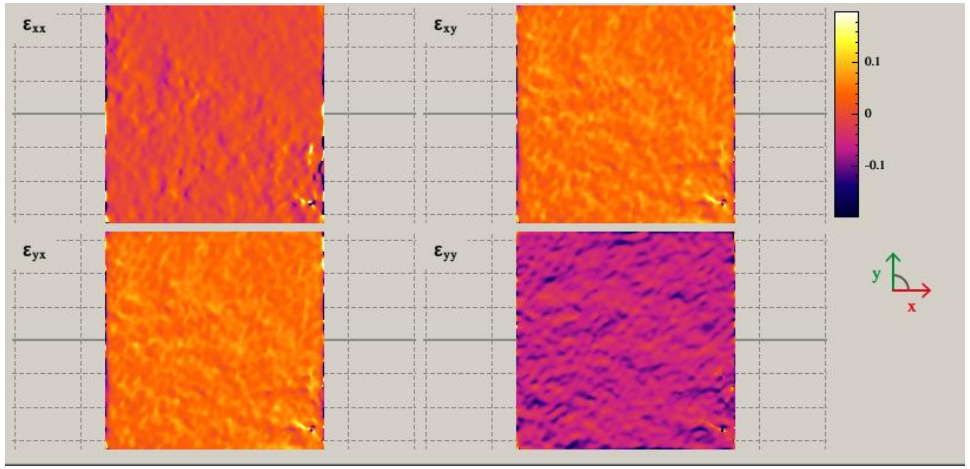


a1) as prepared samples irradiated with 10^{19} 1MeV n/cm^2





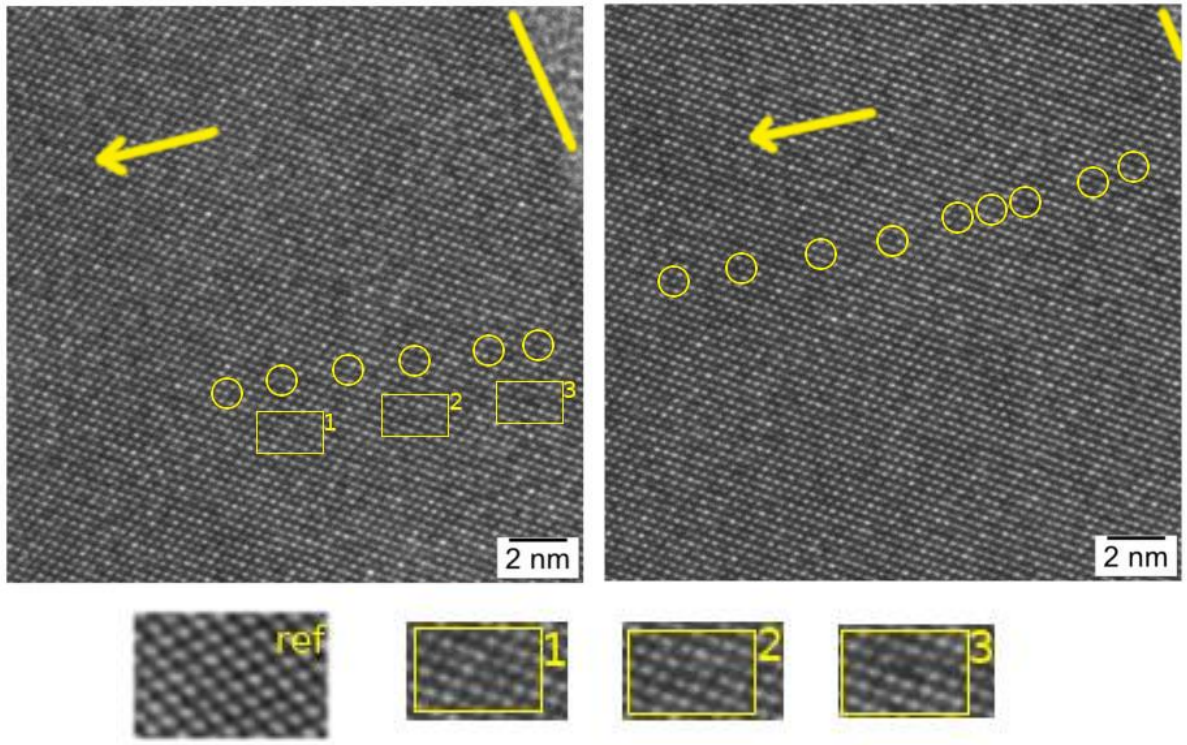
- HRTEM image (left) and SAED (right).
- Some defects/ cluster of defects seem to group along tracks normal to the film surface (inset).
- Strain maps on HRTEM image (down)
- Monocrystalline Si has been identified in SAED



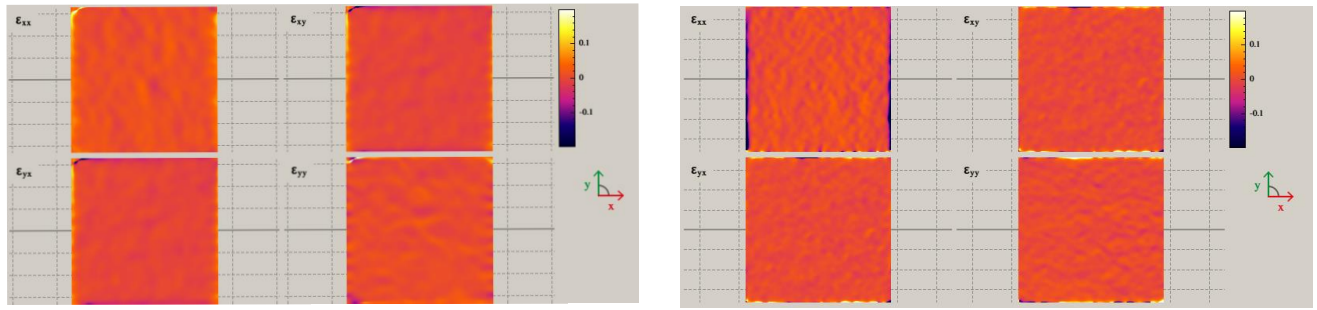
HRTEM showing point-defects (i.e vacancies, interstitials)

Before focusing e-beam

After focusing e-beam

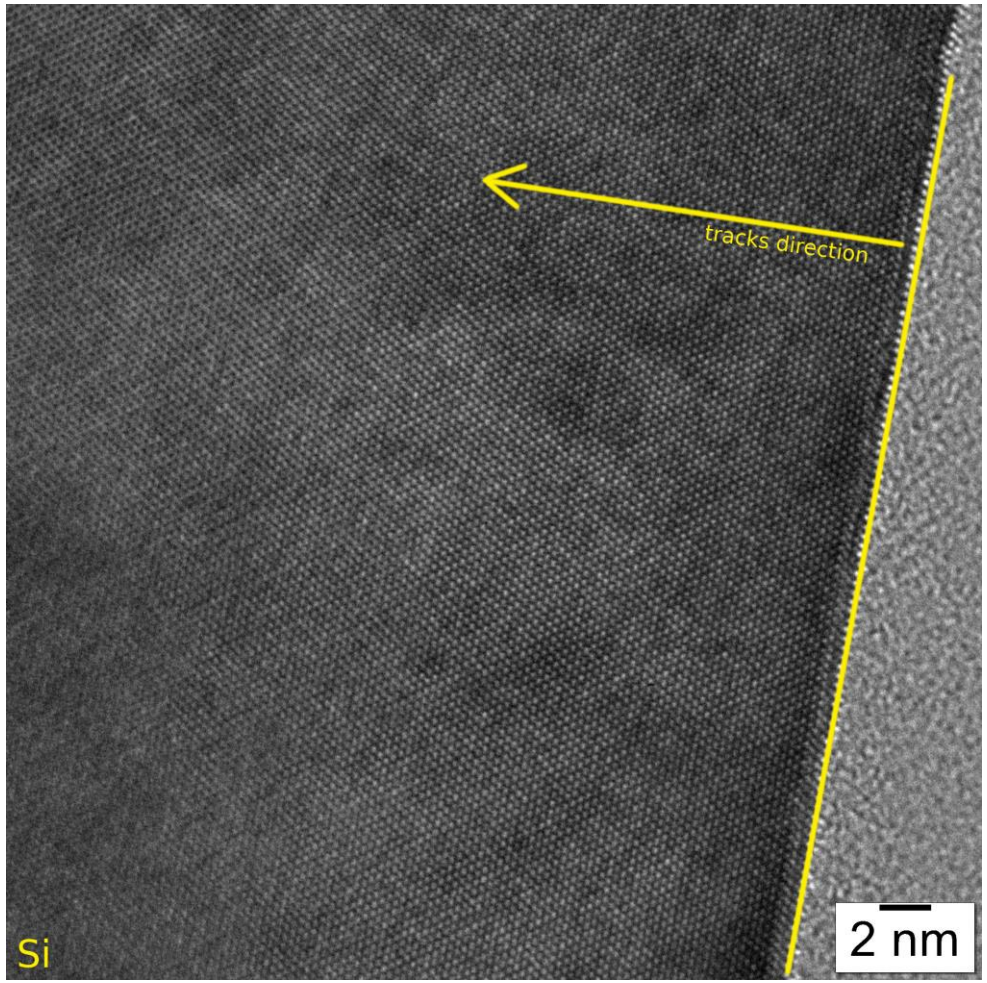


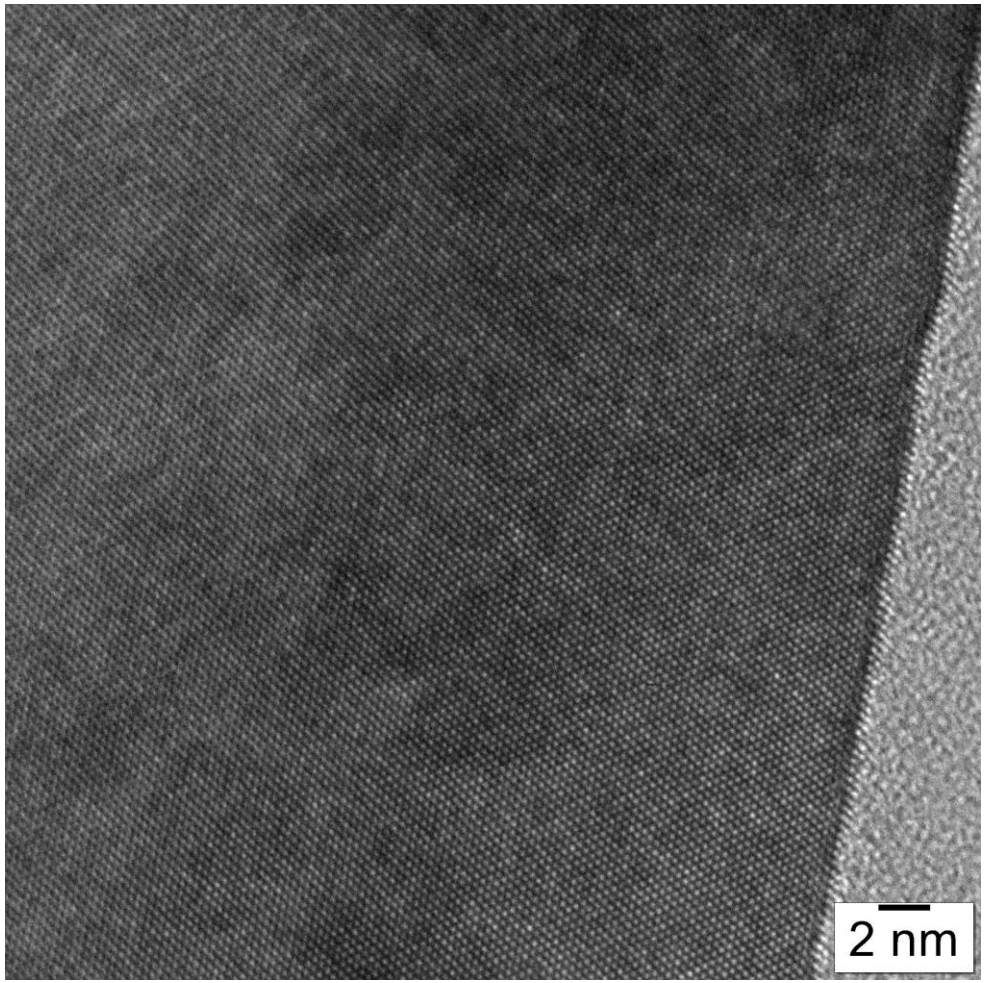
Strain maps: no dislocations, stacking faults



- **Tracks** have no footprint in strain maps=> no extended defects in the crystallographic sense (dislocations, stacking faults)
- **Point defects** (vacancies and/or interstitial) seem to group along tracks normal to film surface.
- **No beam damage** is observed in this case even at 200kV (a low beam dose was used).
- **Strain maps**: no extended defects in the crystallographic sense (dislocations, stacking faults)

a2) sample annealed at 80 C for 3 months





HRTEM images. Tracks normal to the film surface are still observed. No structural changes observed due to annealing at moderate temperatures.

Electrical characterization of radiation induced defects

- ***Trapping parameters**:* activation energy (E_t) and capture cross sections for electrons and holes ($\sigma_{n,p}$)
- ***Defect type*** (donor or acceptor) and charge state(s)
- ***Defect concentration*** (N_t); generation rate ($g=N_t/\Phi_{eq}$)

Needed for estimating the impact of each defect on the electrical performance of the device

$$\Delta LC(T) = q \times A \times d \times N_t \frac{e_n(T) e_p(T)}{e_n(T) + e_p(T)}$$

with

$$e_n(T) = v_{th,n}(T) \times \sigma_n(T) \times N_C \times \exp\left(-\frac{E_c - E_t}{k_B T}\right)$$

$$e_p(T) = v_{th,p}(T) \times \sigma_p(T) \times N_V \times \exp\left(-\frac{E_t - E_V}{k_B T}\right)$$

$$\Delta N_{eff}^{acceptor}(T) = -n_t^{acceptor}(T) = -N_t^{acceptor} \frac{e_p(T)}{e_n(T) + e_p(T)}$$

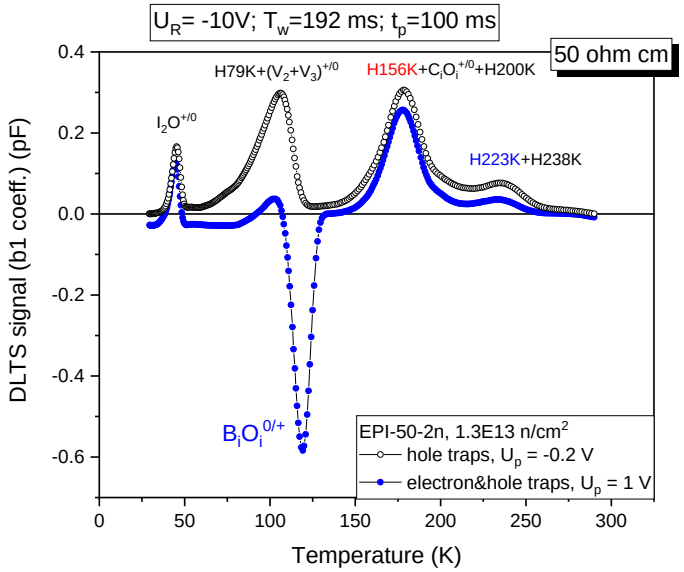
$$\Delta N_{eff}^{donor}(T) = +p_t^{donor}(T) = +N_t^{donor} \frac{e_n(T)}{e_n(T) + e_p(T)}$$

$$N_{eff}(T) = N_d + \sum_i p_{t,i}^{donor}(T) - \sum_j n_{t,j}^{acceptor}(T)$$

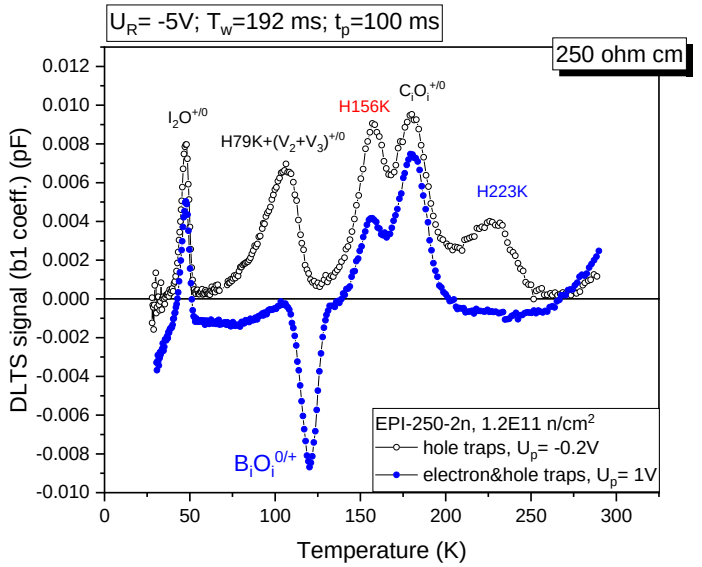
Electrical characterization -typical DLTS spectra

EPI diodes, 50 µm thick

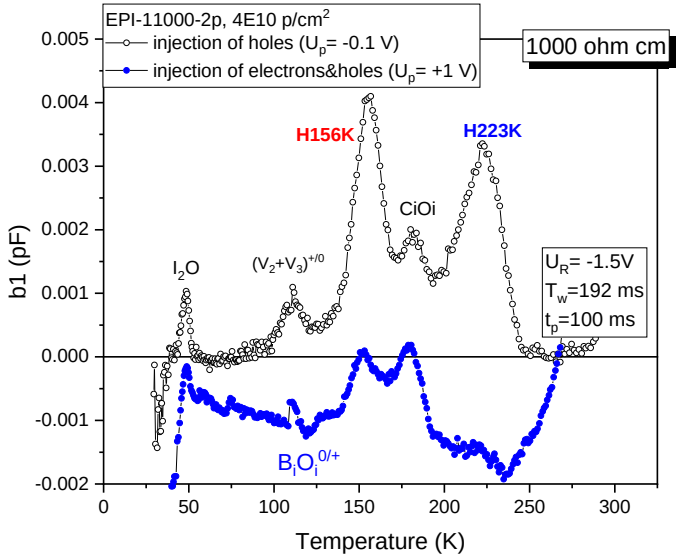
Low resistivity



Medium resistivity



High resistivity



Several yet un-identified defects (traps for holes - H79K, H156K, H223K and H238K)

H156K and H223K – well separated in diodes of medium and high resistivity (analyses possible with old capacitance meter in the DLTS setup)

H156K: E_a^{H156K}= 0.291 eV; σ_h = 4.8x10^{-16} cm^2

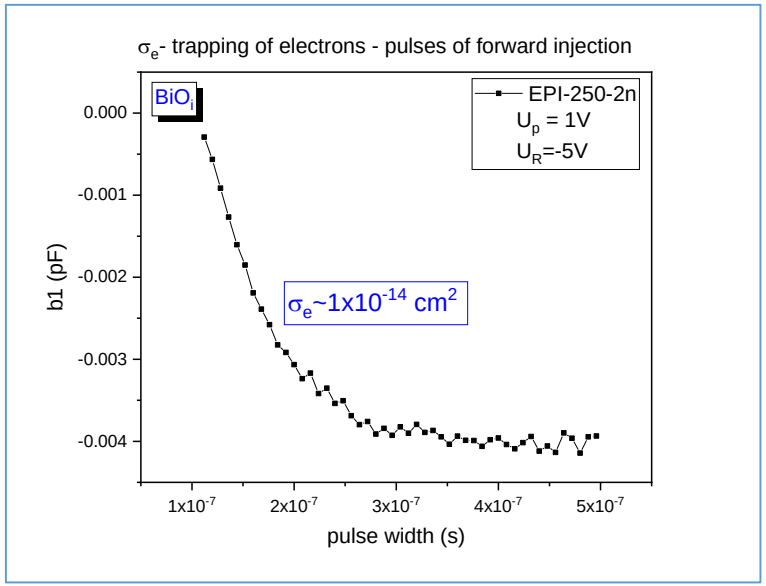
H223K: E_a^{H223K}= 0.363 eV; σ_h = 1.7x10^{-17} cm^2

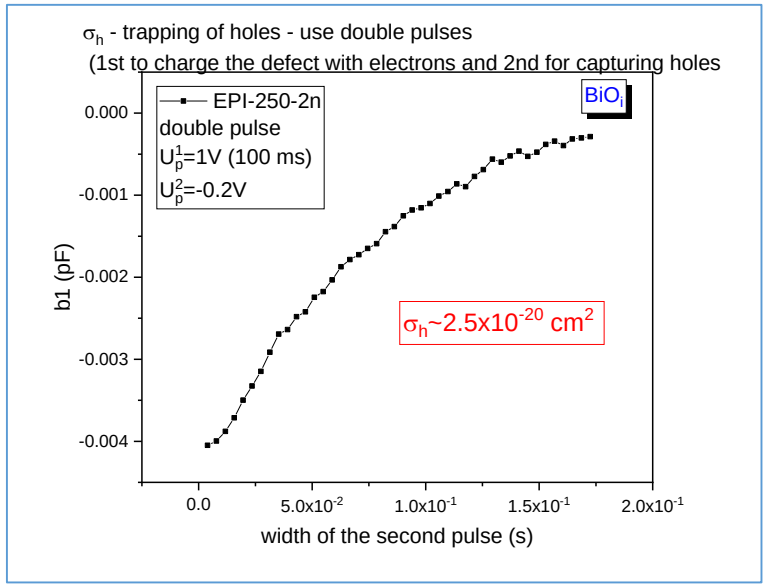
Electrical characterization –BiOi defect

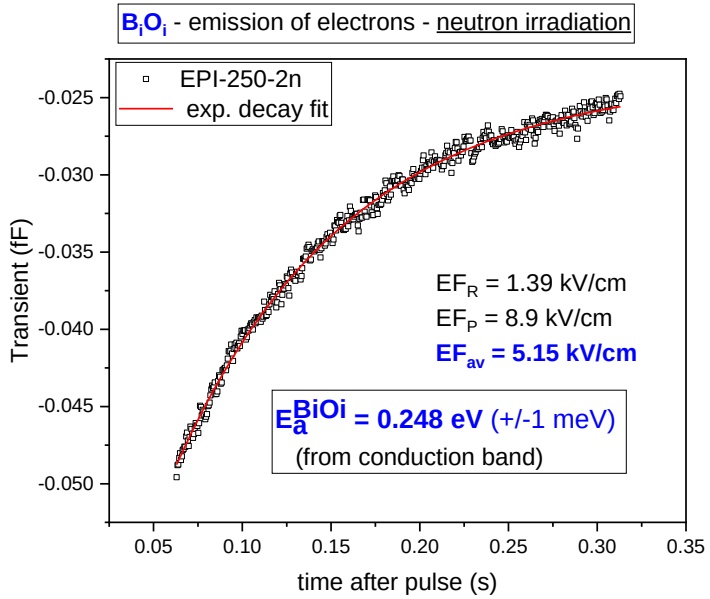
Direct measurement of <u>both capture cross sections</u> (for e and h) (errors up to 20%)

- By measuring the amplitude of the emission transient as function
- of the filling pulse duration at constant temperature

<u>Activation energy</u> (errors up to 5%) – from direct analyses of transients at 120 K and exponential decay fit (using as input the measured $\sigma_e=10^{-14}$ cm^2 at the same T)



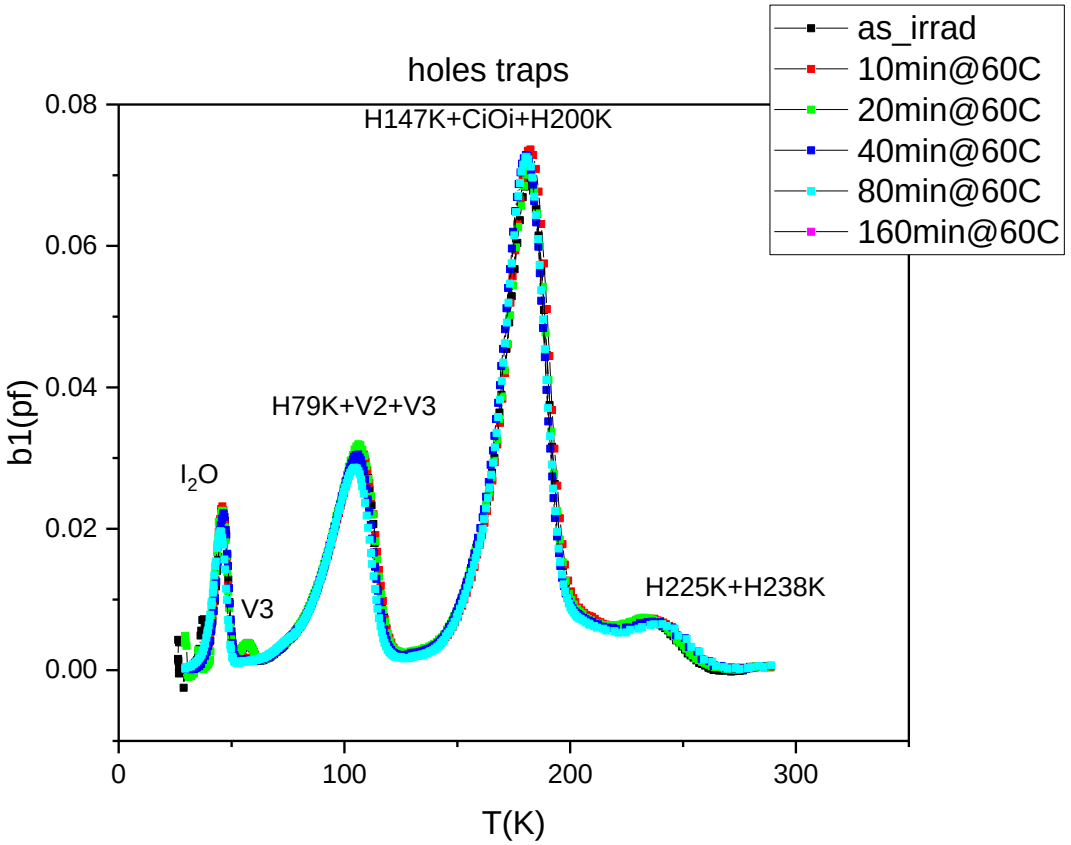


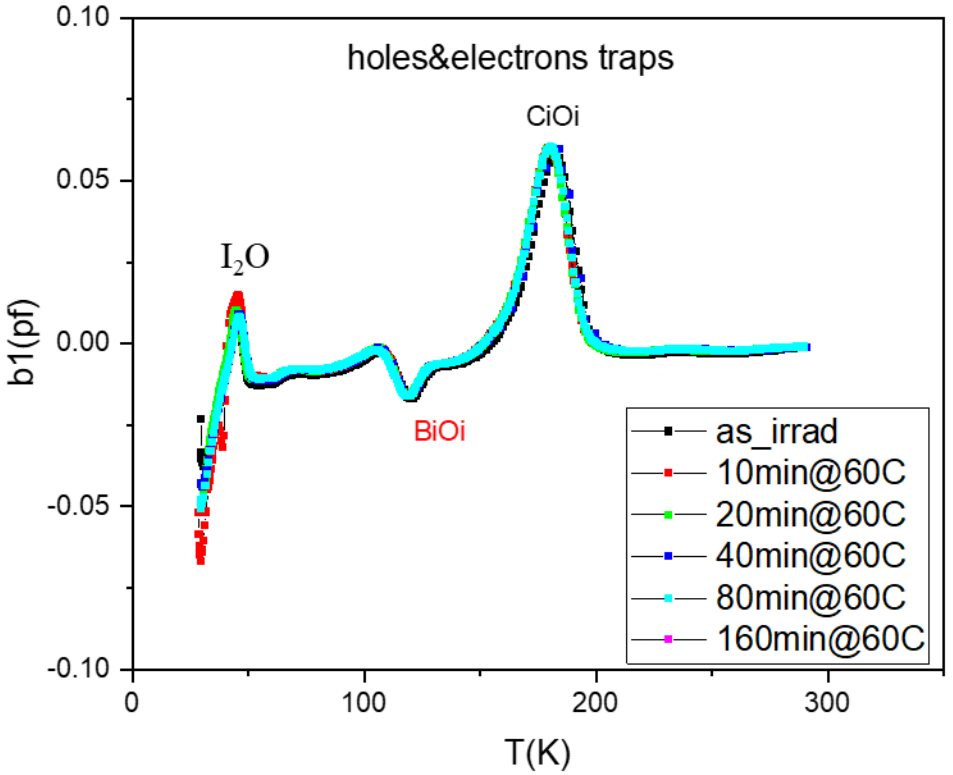


With these values it can be calculated the inpact of BiOi defect on Neff and LC

- It contributes in full concentration with positive charge to Neff at RT
- Insignificant contribution to LC at RT ~0.002%LC

Annealing at 60^0 C



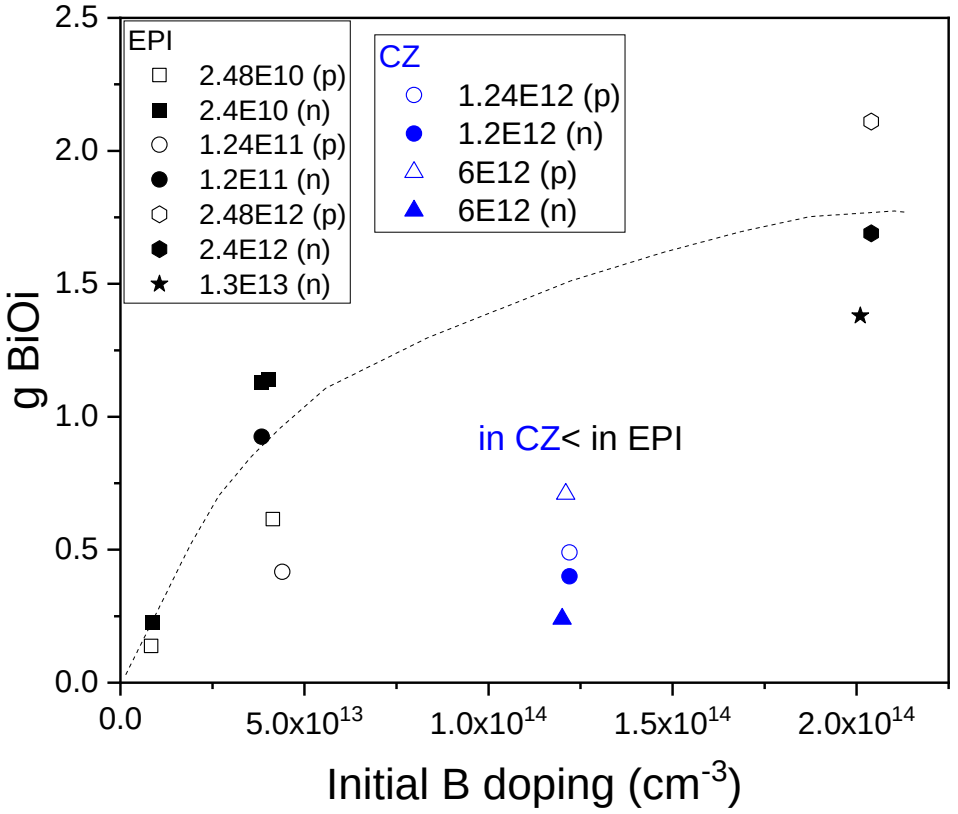


- No change in BiOi
- V_3 anneals out by changing its configuration from the one visible in the DLTS spectra to another one with insignificant impact on the device electrical properties.
- I_2O anneals slowly out

B_iO_i generation rate – a real puzzle !

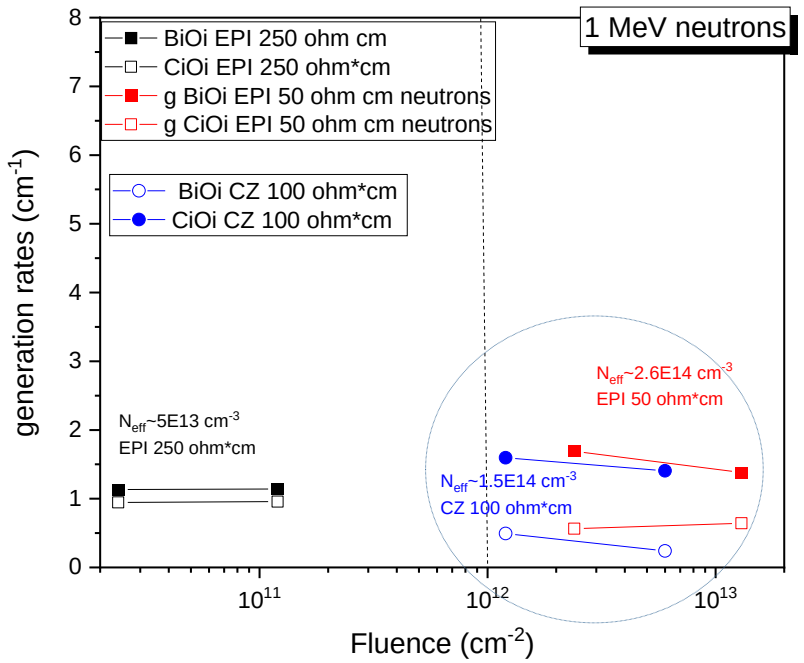
All the experiments done on samples processed in the same way, measured in same place, with the same set-up/procedures

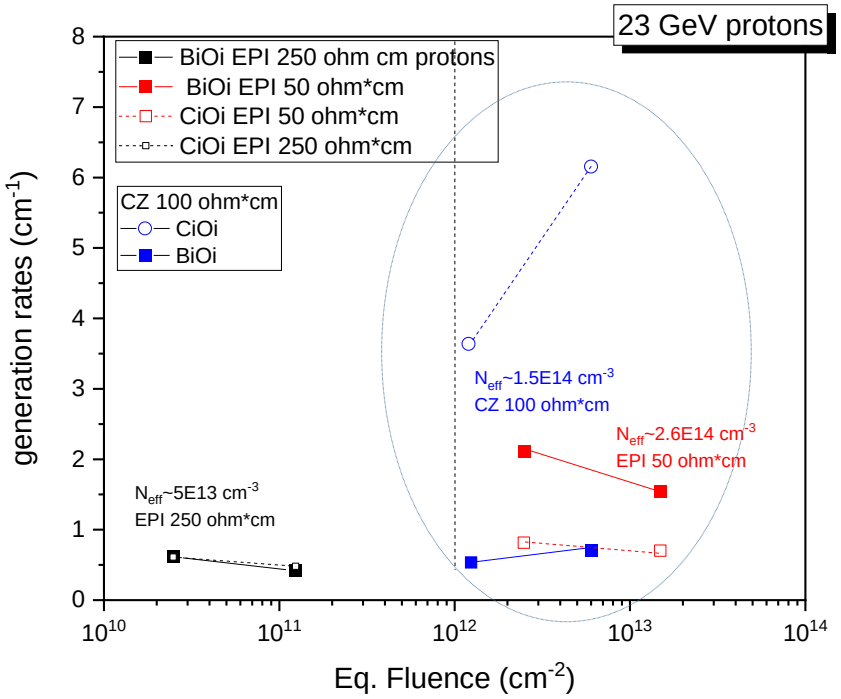
Dependence on doping



- Nonlinear even at low irradiation fluences when defect concentrations are small
- Large differences between proton (open symbols) and neutron irradiation (filled symbols) for the same equivalent irradiation fluence and material (e.g. **EPI**) for fluences above 10^{12} cm^{-2}
- Large differences between EPI and CZ materials

Dependence on the fluence – different in CZ and EPI, although the C content is the same in EPI and CZ substrate and only O is larger in CZ than in EPI





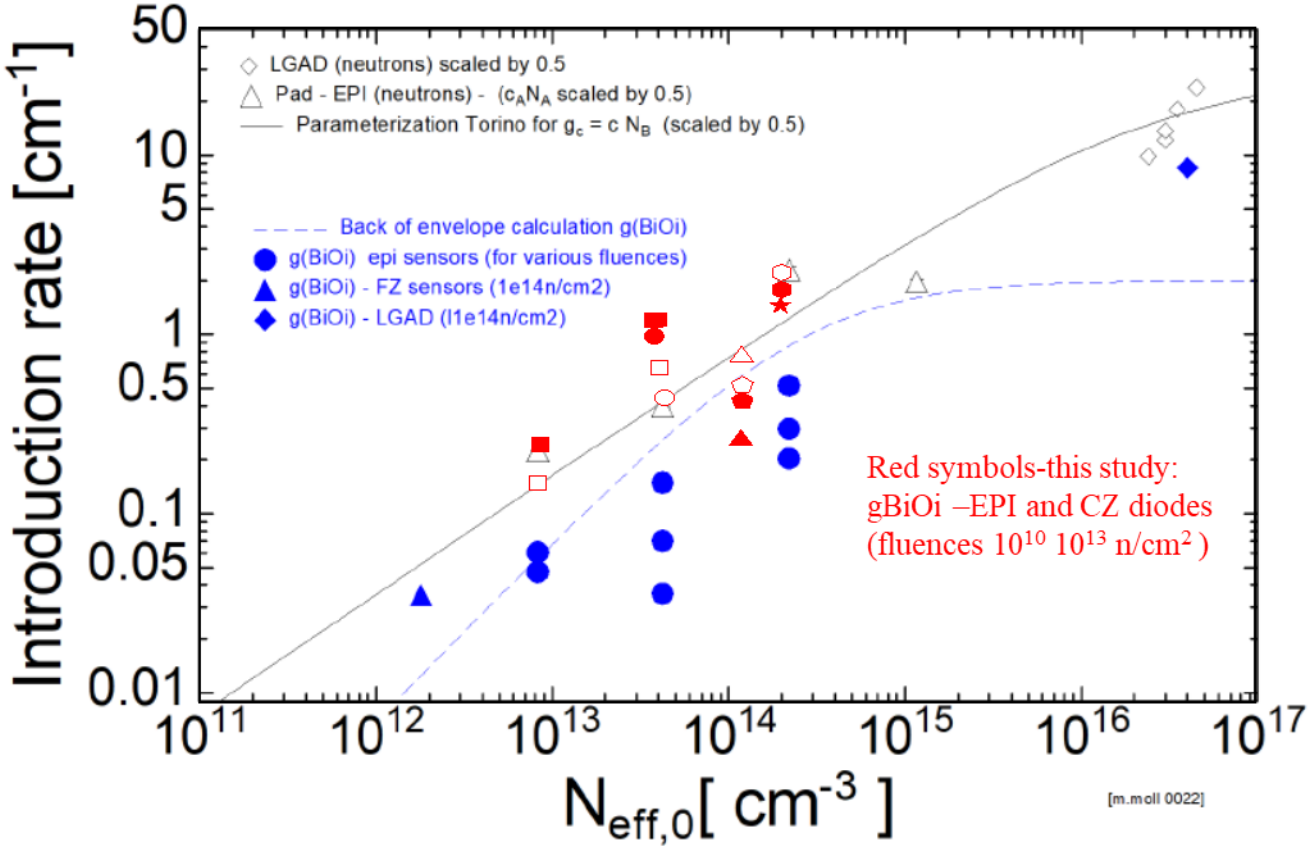
The BiOi generation rate is also varying with the fluence (above 10^{12} cm^{-2}) for the same type of irradiation and material impurity content:

- after ***neutron irradiation*** it ***decreases*** for all the materials
- after ***proton irradiation*** it ***decreases*** in EPI and ***increases*** in CZ

For similar fluences range and B doping – the generation rate of BiOi is larger in EPI than in CZ material (the opposite stands for the CiOi defect) for both type of irradiations – a result suggesting that either the C content in CZ diodes is not the same as in CZ substrate of EPI diodes (SIMS on 100 Ωcm CZ diodes should be performed) or there is another competitor for interstitials or O in CZ material, beside B and C – *new topic of investigation.*

Where stands our results on defect engineered Si samples ?

(all processed by CiS and *all the experiments done in same place, with the same set-up/procedures)*



- **The large data scattering is a real fact!**
- **Determined most likely by differences in C content in the samples (not yet measured) or/and the existence of other competing defect reaction paths**

Summary and further work

- **Impurity content and structural damage**
  - *LA-ICPMS technique more sensitive than SIMS*
  - *Structural damage has a preferential starting direction of propagation in the bulk of Silicon*
- **Trapping parameters of several defects induced by irradiation**
  - *BiOi, H156K and H223K, concentrations and generation rates*
- **The generation of BiOi defects depends on:**
  - ***B doping*** *– the prime factor in generating the BiOi defect*
  - ***Impurity content (C and O content)*** *– Large differences between EPI and CZ of similar B doping*
  - ***type of irradiation*** *- Large differences between* ***p/n*** *irradiation even for the same equivalent fluence (above* 10^{12} cm^{-2}*) and impurity content (B, C and O) in the material*
  - ***irradiation fluence*** *– Large differences in the defect generation rates even when use the same type of irradiation and material*
- **The large data scattering is a real fact** ***determined most likely by variations in impurity content (especially C, not always measurable) and/or the existence of additional (not yet accounted) competitive defect reaction paths***

- **Experiments at elevated temperatures for monitoring the defect reactions and get the necessary input for modelling the defect kinetics controlled by impurities.**
- **More diodes, including LGADs, to be measured – preferable in series of diodes produced in the same way.**
- **Investigation of HVCMOS samples – as soon as we get them**

Thank you for your attention !