Dipartimento di Fisica e Astronomia Galileo Galilei

Pulsed Laser Melting of polycrystalline Silicon for photovoltaic applications

Master Degree in Physics

Course: Introduction to Research Activities

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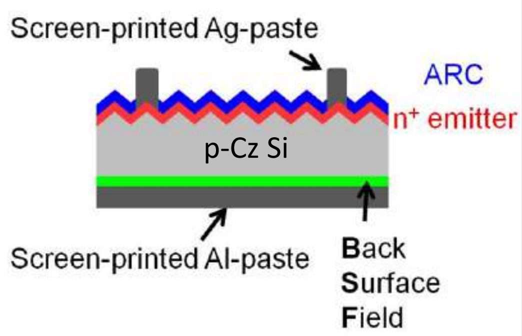
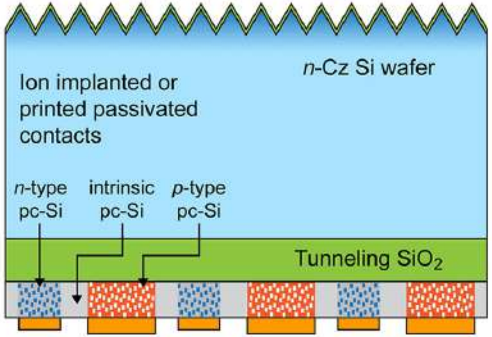
Matr. 1225015

Motivations

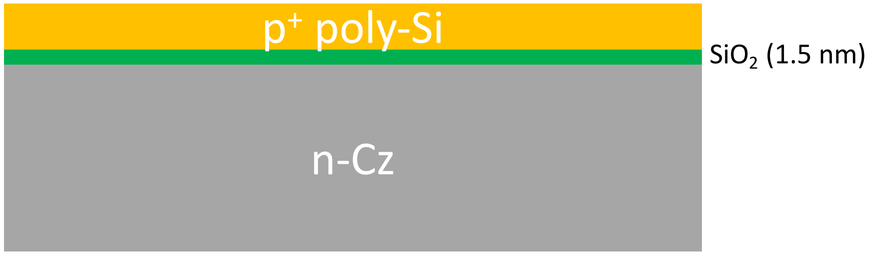
Current technology is limited by:
- Light shadowing by surface contacts
- Charge carrier recombination at the metal – semiconductor interface
- …

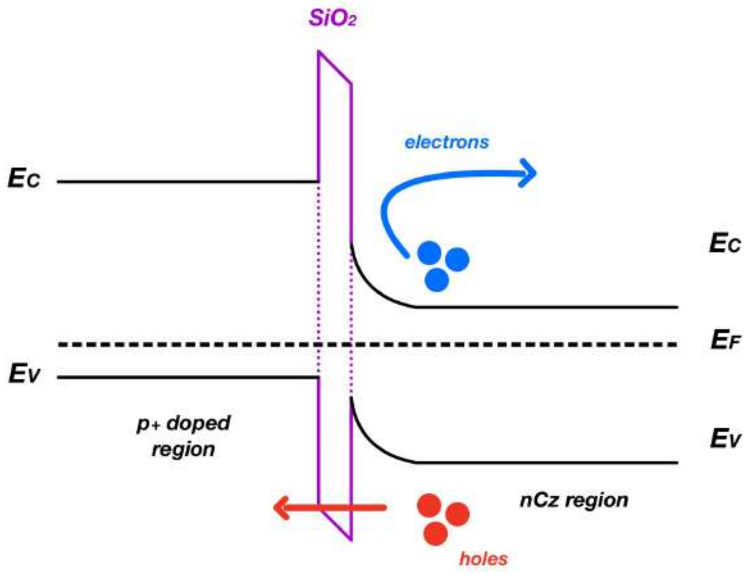


Future trend:
- Interdigitated Back Contact solar cells (IBC)
- with passivated contacts:
  - a-Si/c-Si heterojunctions *or*
  - polycrystalline silicon (poly-Si) on oxide (POLO)



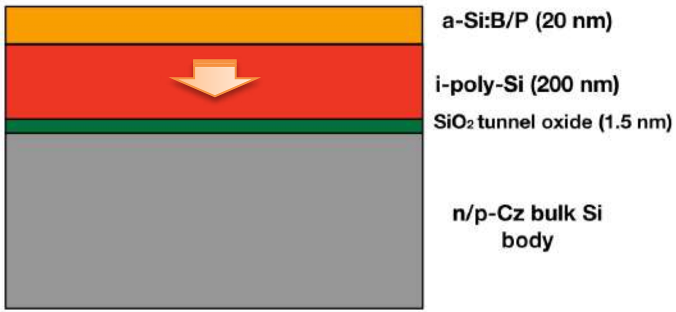
The role of tunnel oxide passivation

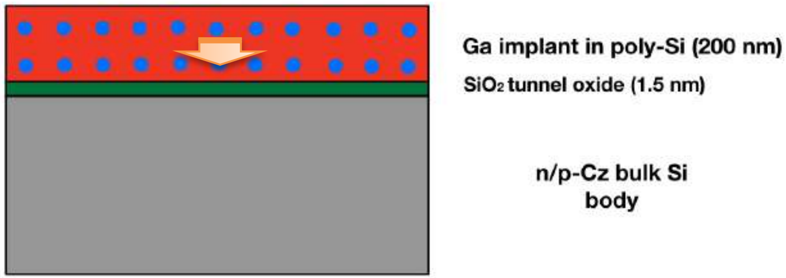




The SiO_2 tunnel oxide layer passivation allows current flow with a higher probability for one type of carriers (holes) than the other (electrons) → Surface recombination phenomena probabilities are reduced → Photovoltaic cell efficiency increases

Fabrication of passivated contacts with SiO_2





<u>Processes</u>:

- SiO_2 deposition
- Intrinsic Poly-Si deposition
- Dopant deposition (a-Si doped with B or P) or implantation (Ga)
- Thermal annealing (RTP or furnace)

<u>Results/issues</u>:

- Good passivation for n-type dopants (P)
- *Issue*: Oxide damaging and contamination with B
- Research in progress with Ga ion implanted in poly-Si (promising)

This work:

- **Investigate Pulsed Laser Melting (PLM) as alternative annealing technique for efficient contact formation while preserving the tunnel SiO_2**

Pulsed Laser Melting

Heat diffusion

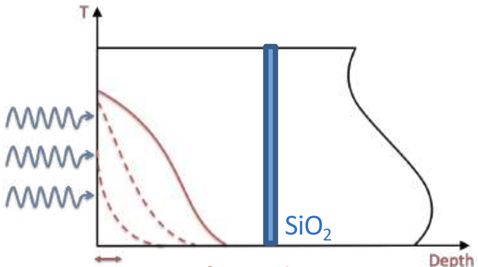
$$\frac{\delta T}{\delta t} = D\nabla^2 T + \frac{A}{\rho C}$$

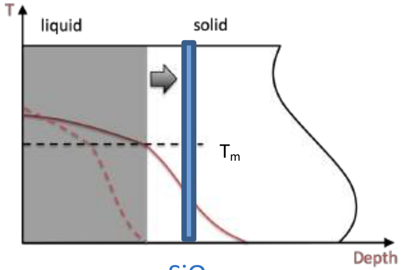
Melting

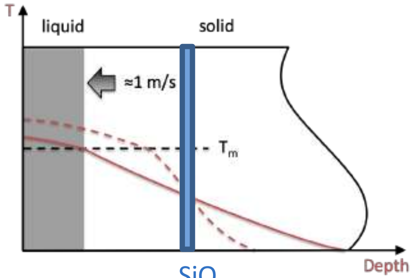
Epitaxial regrowth velocity

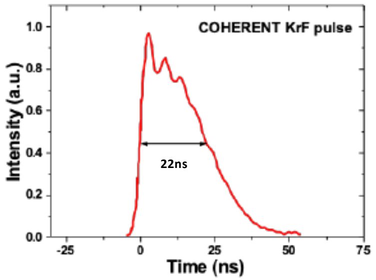
$$v_r = \frac{k}{\Delta H \rho}\frac{\delta T}{\delta z}$$

Dopant incorporation







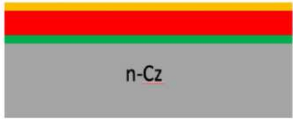


KrF Laser at DFA, 248 nm, 22 ns pulses

Workplan

Substrates provided by NREL labs:

- Poly-Si with P, B or Ga (implanted)
- n-Cz or p-Cz substrates
- Polished or rough surface



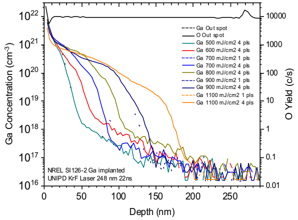
Processes:

- KrF Laser at DFA, 248 nm, 22 ns pulses. PLM processes with 300-1100 mJ/cm^2 and 1 to 8 pulses

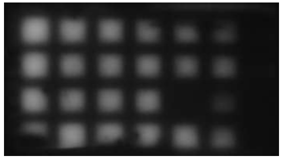
Characterization:

- Electrical characterization (VdP-Hall)

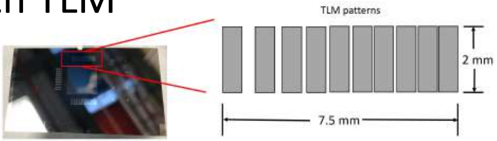
- Chemical concentration profiling (SIMS)



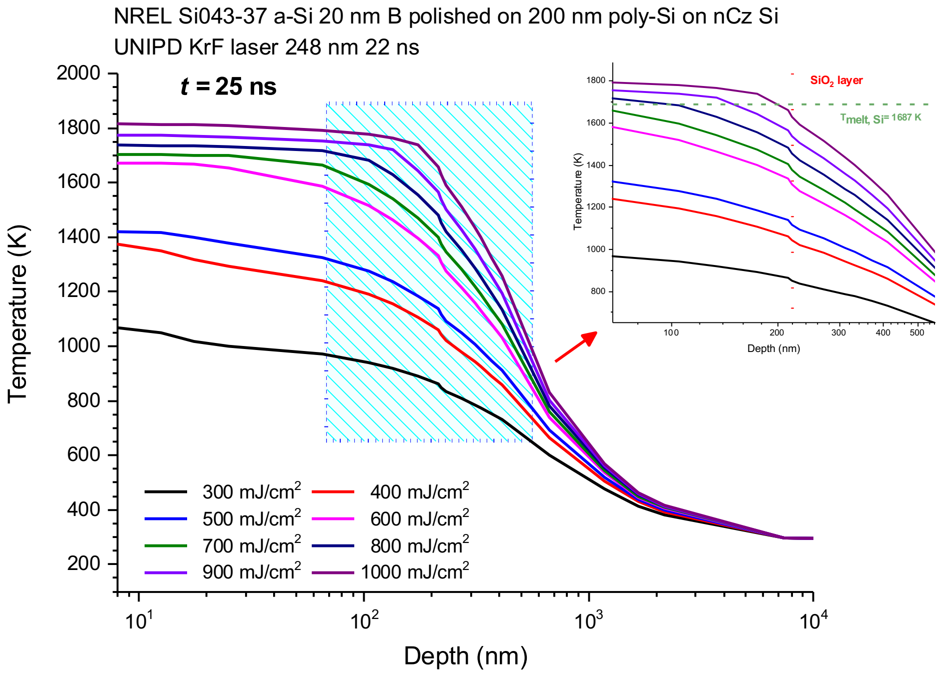
- Photoluminescence imaging (@NREL)

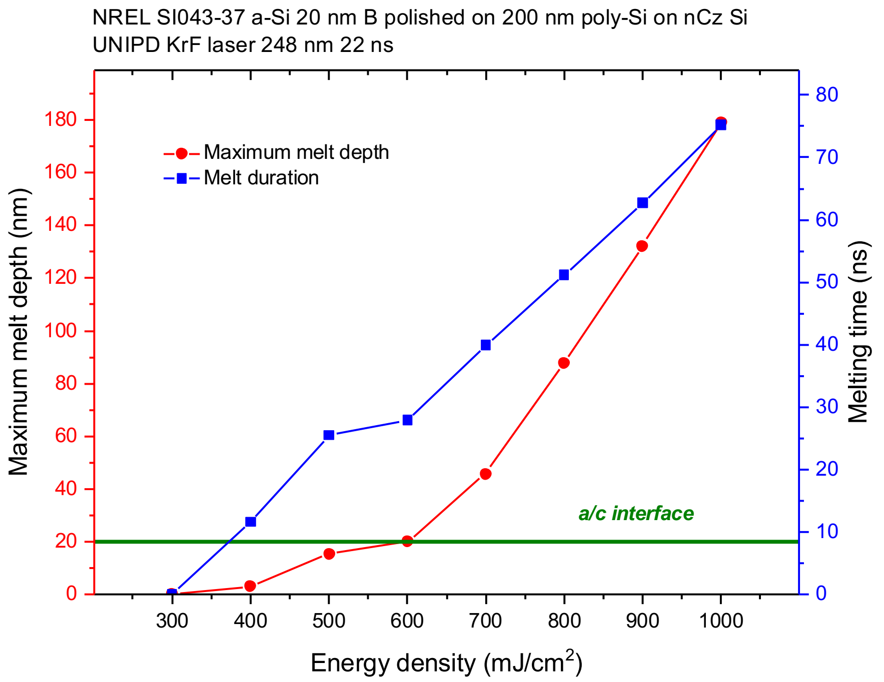


- Contact resistance with TLM (@NREL)



Simulations with LIMP (*Laser Induced Melting Predictions*) code





- Simulation of heat diffusion in a sequence of layers with known thickness and properties
- Useful as a preliminary study for the identification of the ED range of interest (min value for the dopant activation, max imposed by the apparatus limits)

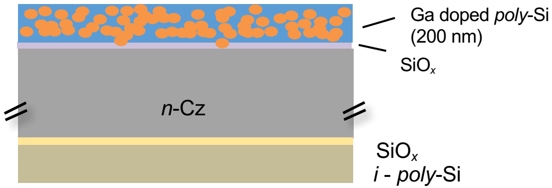
First batch samples structures (B, P, Ga doped poly-Si – polished surface)

Single side polished nCz Si samples:

- Intrinsic poly-Si grown on 1.5 nm SiO_2 tunnel oxide by LPCVD
- P, B deposition by CVD
- Ga^{69} ion implantation (10 keV, $6 \cdot 10^{15}$ cm^{-2}) in poly-Si

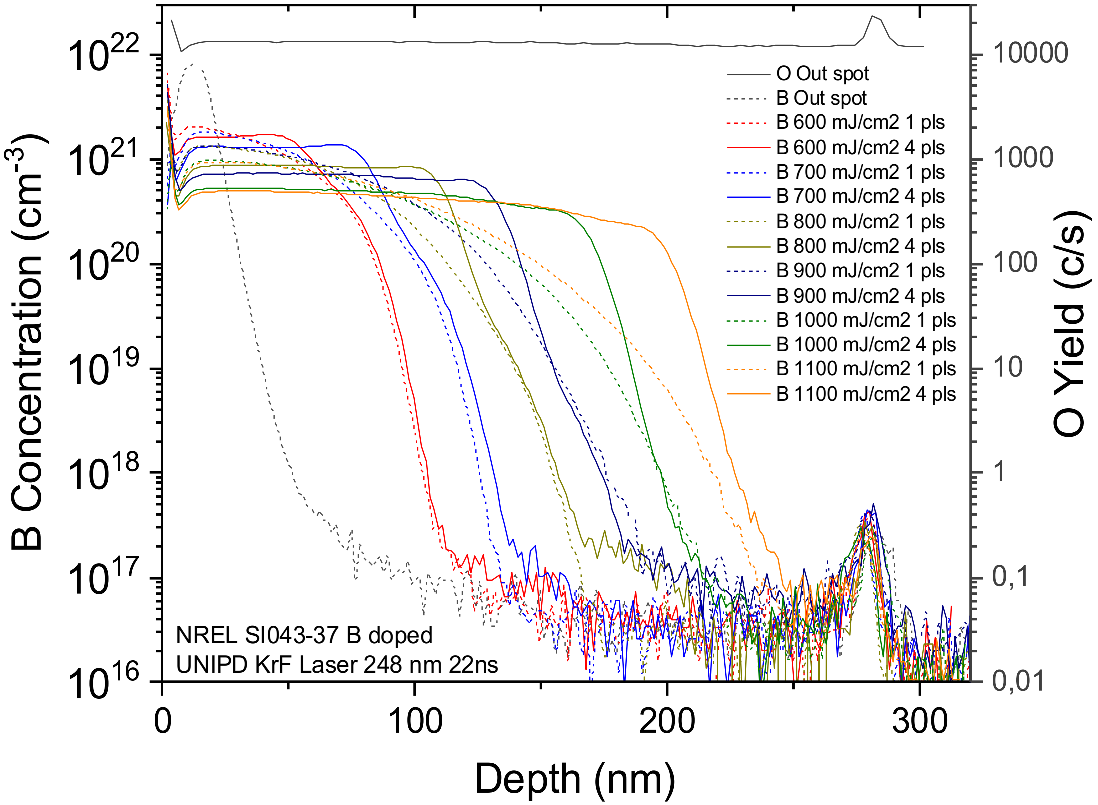
- Energy density (ED): 400-1000 mJ/cm^2; Pulses: 1-2-4-8

- Energy density (ED): 400-1100 mJ/cm^2; Pulses: 1-2-4-6

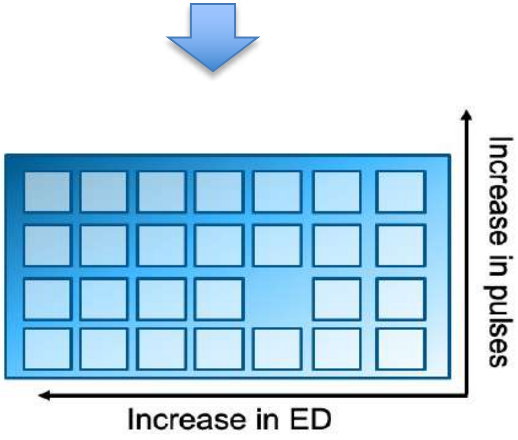


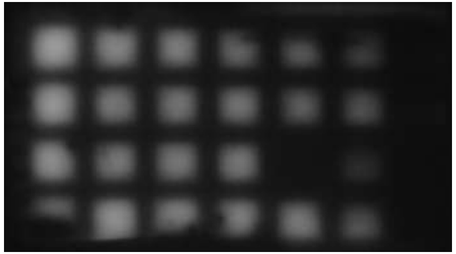
- Polished n-Cz wafer with symmetric poly-Si/SiO_x (1.5 nm)
- Energy density (ED): 300-1100 mJ/cm^2; Pulses: 1-2-4-6

B doped Si – SIMS profiles / PL

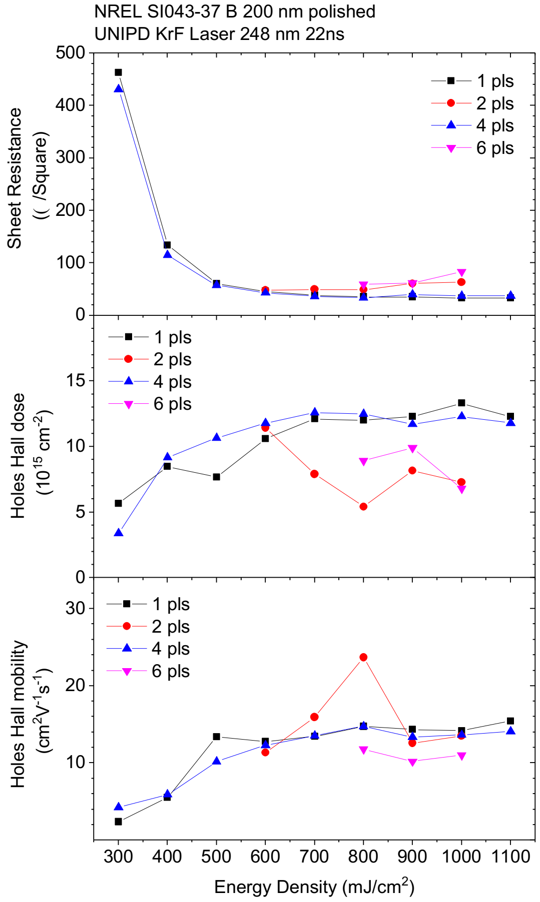


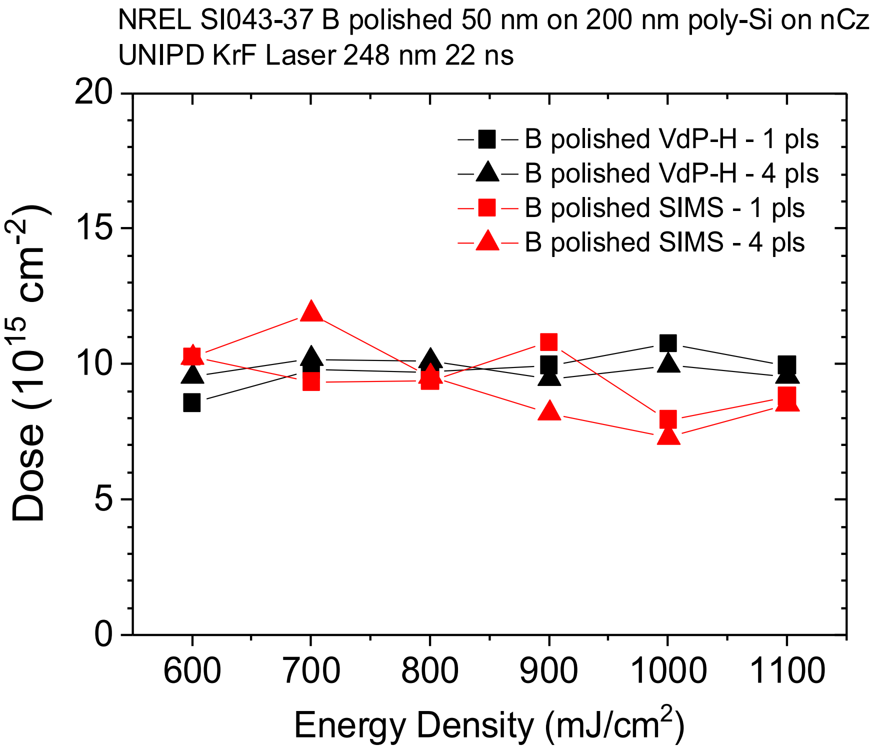
Photoluminescence measurements (NREL)





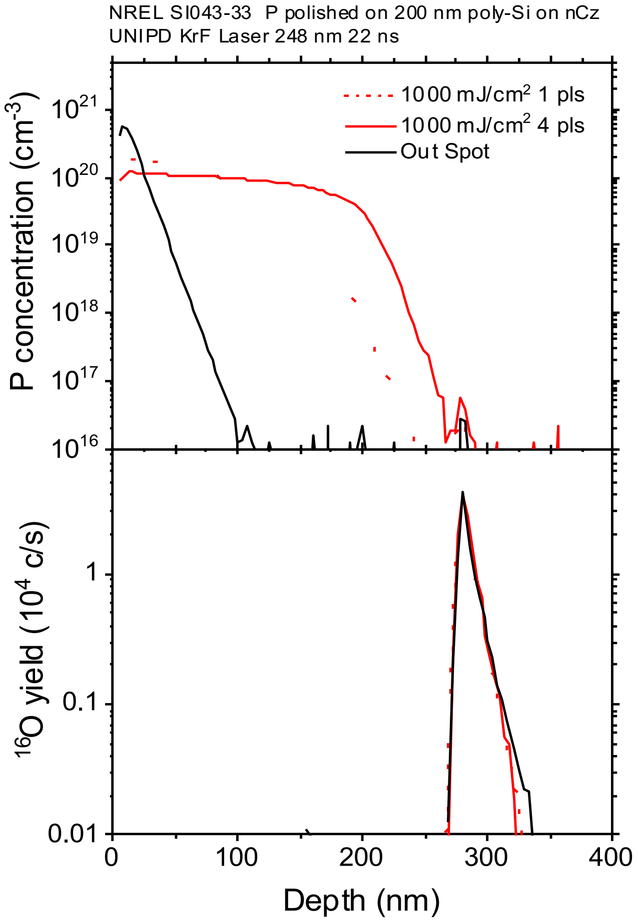
B doped Si – VdP-Hall electrical measurements / Dose



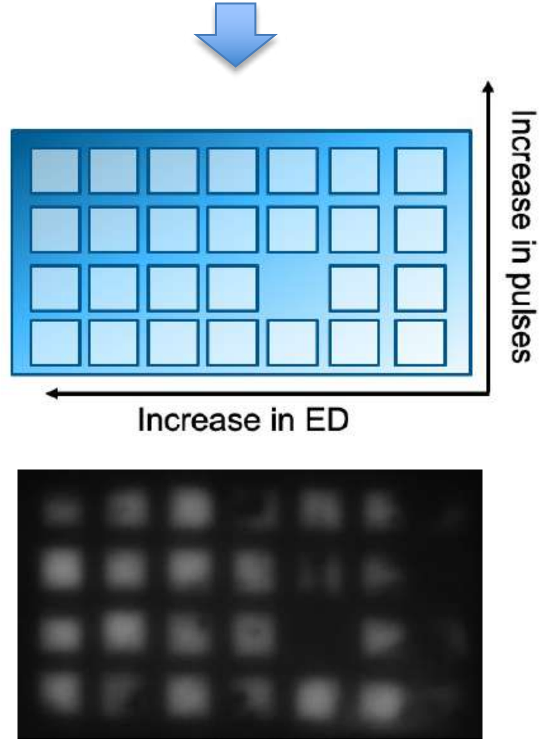


Hall scattering factor for holes applied to carrier dose and mobility : γ_H=0.81 *(Mirabella APL 2008)*

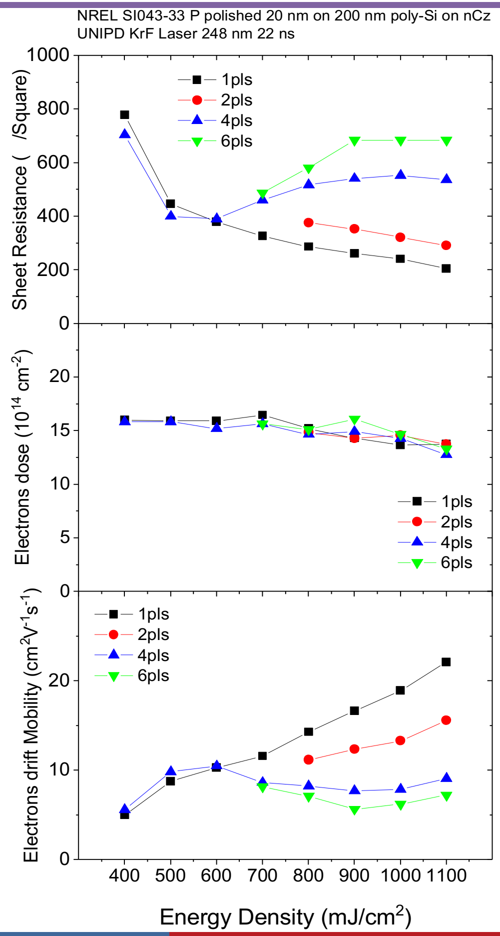
P doped Si – SIMS profiles / PL

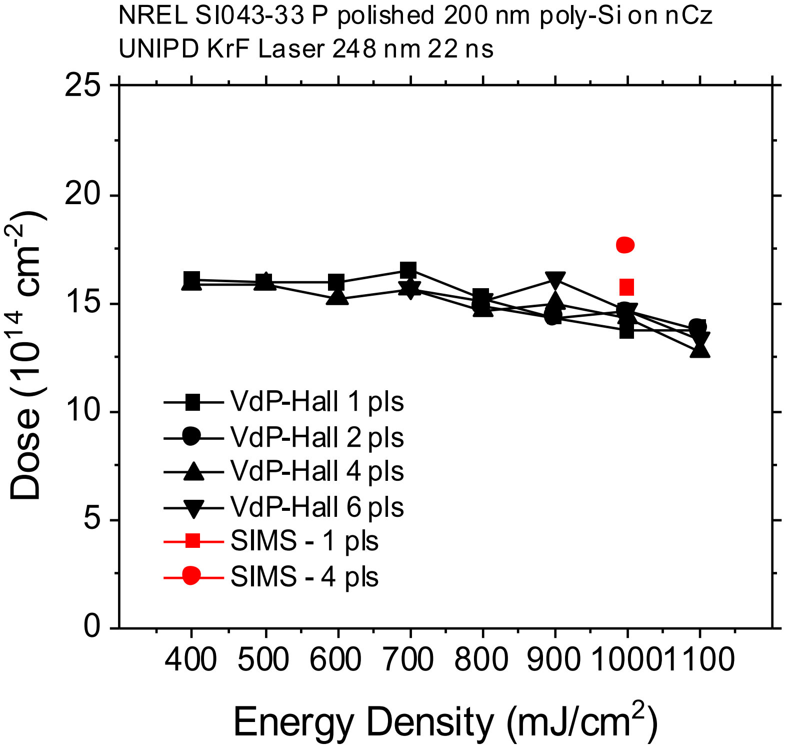


Photoluminescence measurements (NREL)



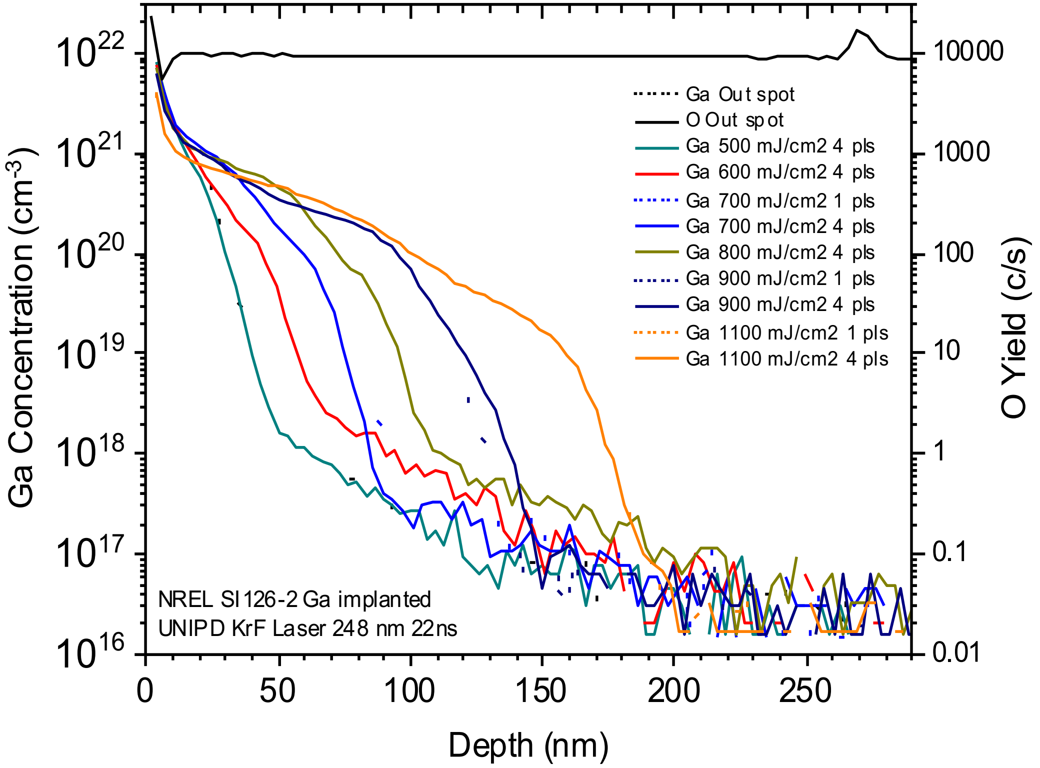
P doped Si – VdP-Hall electrical measurements / Dose



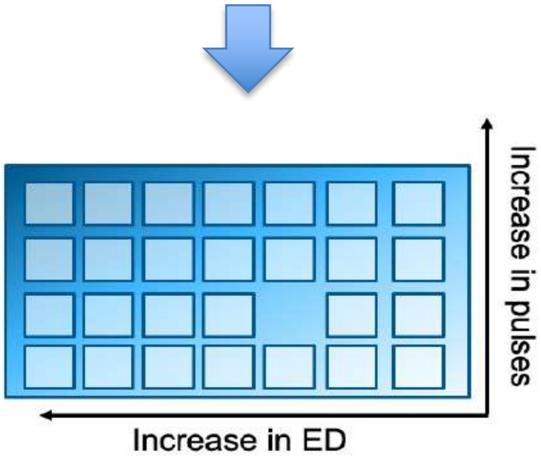


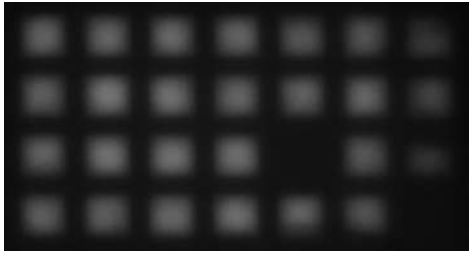
Hall scattering factor for electrons applied to carrier dose and mobility : γ_H=0.9 *(del Alamo JAP 1985)*

Ga doped Si – SIMS profiles / Dose

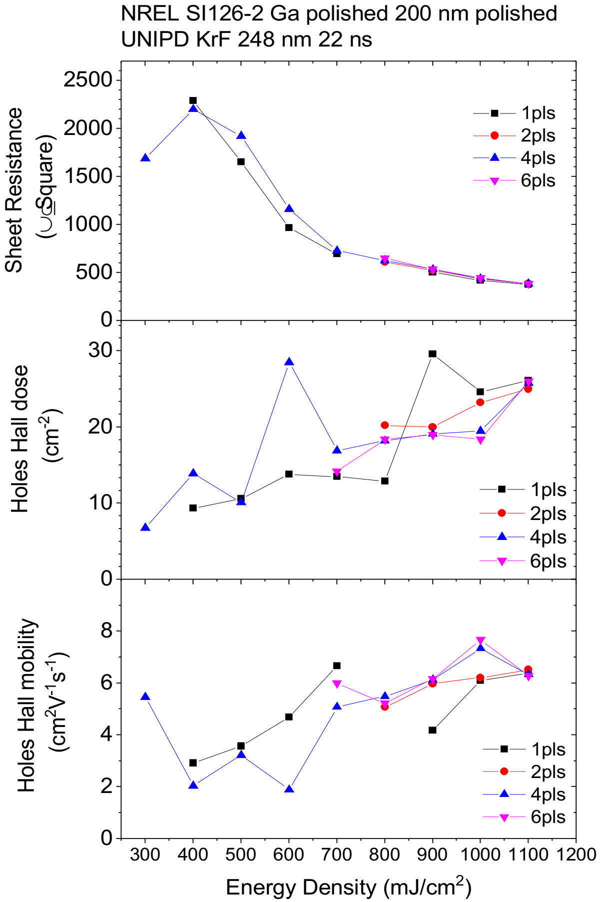


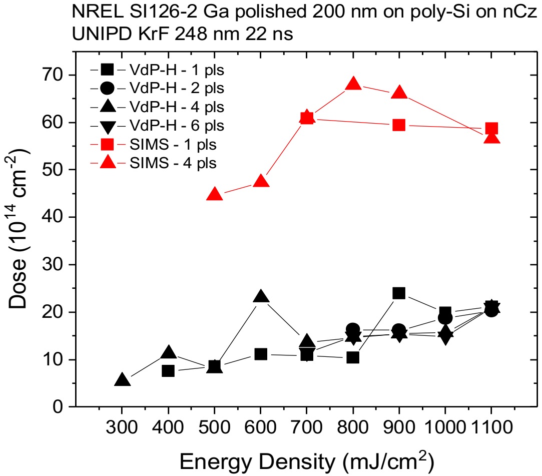
Photoluminescence measurements (NREL)

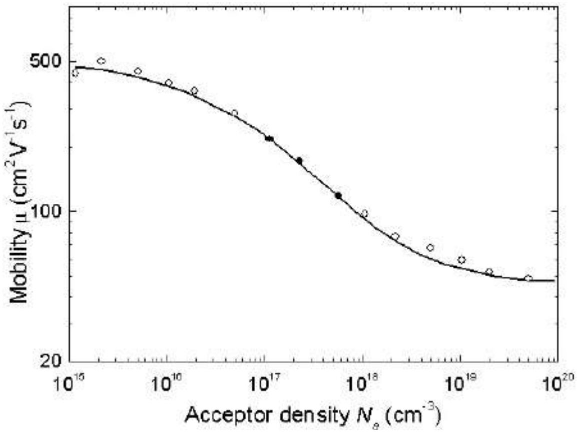




Ga doped Si – VdP-Hall (UNIPD and NREL)



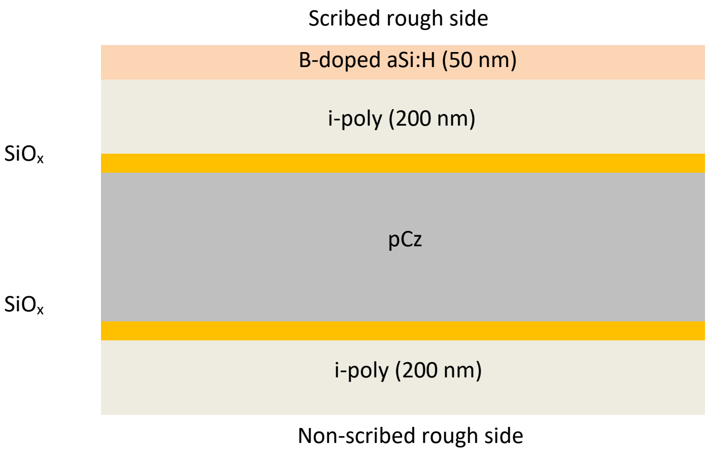


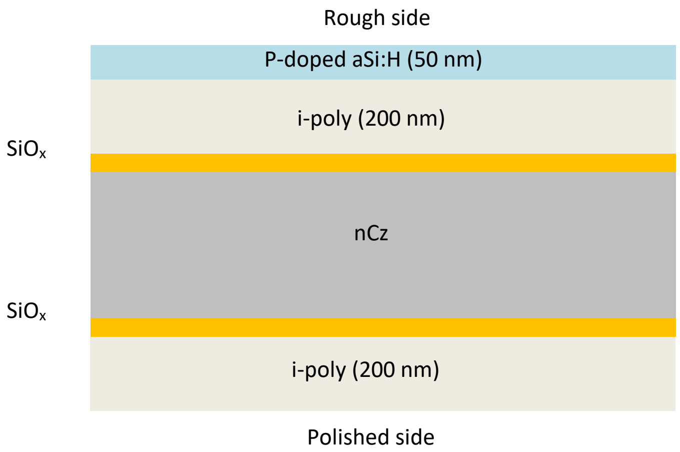


Jacoboni, C., C. Canali, G. Ottaviani, and A. A. Quaranta, *Solid State Electron.* **20, 2**(1977) 77-89.

Hall scattering factor for holes applied to carrier dose and mobility : γ_H=0.81 *(Mirabella APL 2008)*

Second batch samples structures (B, P doped poly-Si – rough surface)

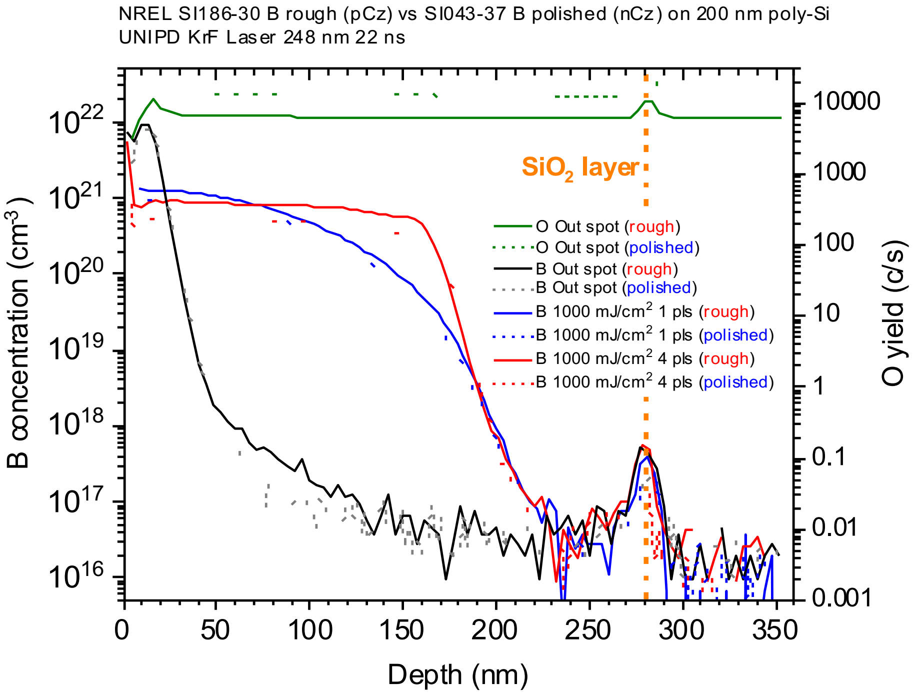




- Energy density (ED): 400-1000 mJ/cm^2; Pulses: 1-2-4-8

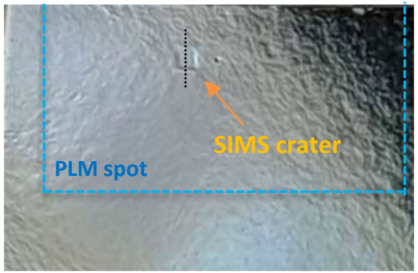
- Energy density (ED): 400-1000 mJ/cm^2; Pulses: 1-2-4-8

SI186-30 B rough 200 nm pCz vs SI043-37 B polished 200 nm nCz – SIMS

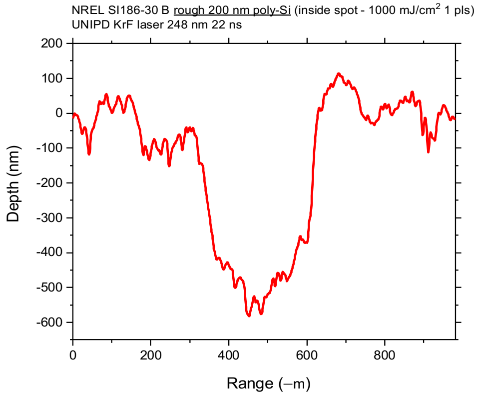


- Rough surfaces provide similar results with respect to the previous polished samples
- Crater depth measurements give SiO_2 depth values in agreement with previous Si043 samples, but with much larger errors, therefore SiO_2 depth value estimated in previous samples (281 nm) has been assumed for SIMS depth calibration.
- Higher B dose (+30%), in agreement with Hall measurements.
- Note that the B outspot thickness agrees with the 20 nm thickness of the previous samples, i.e. is much lower than the nominal 50 nm thickness (see slide n. 2).

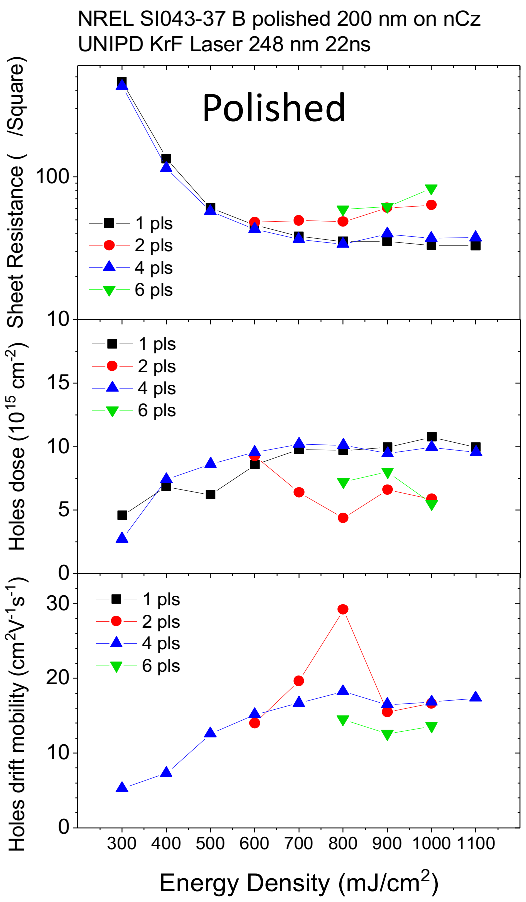
#71-1000 mJ/cm^2 1 pls

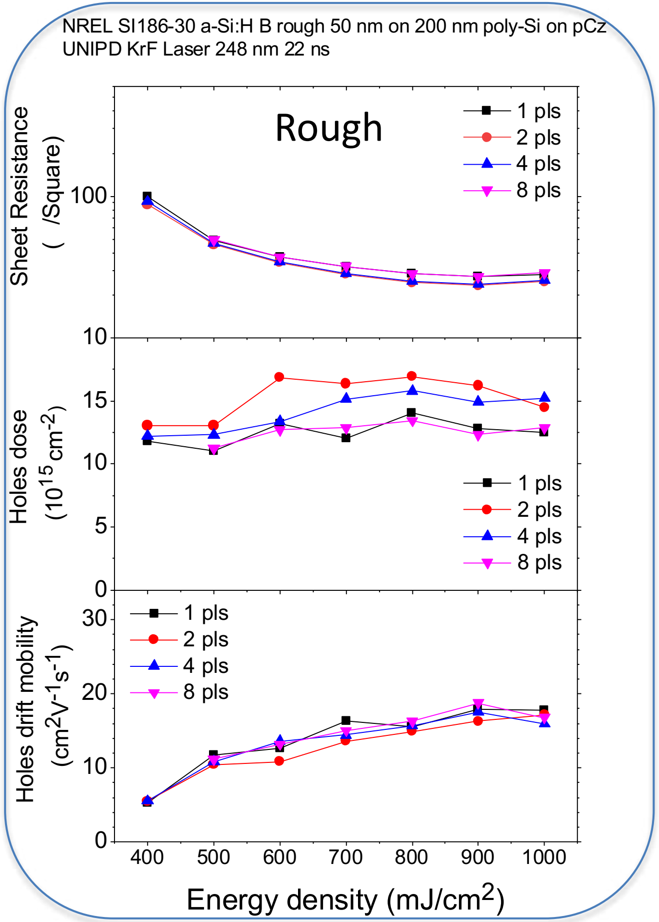


SIMS crater profilometer scan

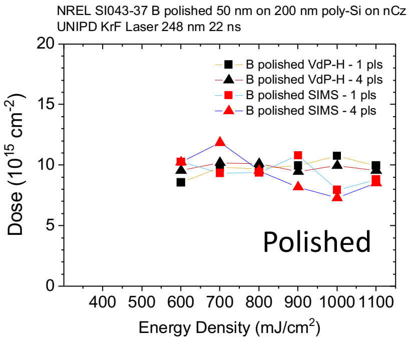


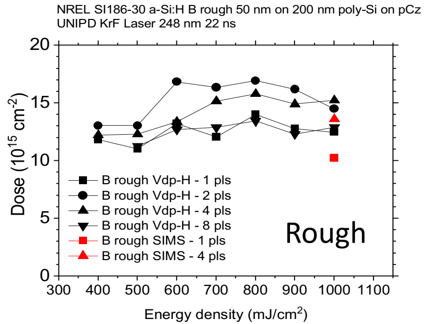
SI186-30 B rough 200 nm pCz vs SI043-37 B polished 200 nm nCz – VdP-Hall





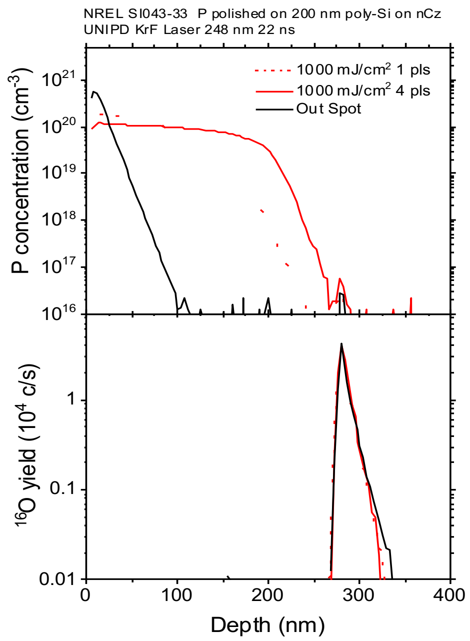
- <u>Hall scattering factor for holes applied to carrier dose and mobility : γ_H=0.81</u> *(Mirabella APL 2008)*
- Good reproducibility. No significant role of rough surface
- Higher dose in rough sample.
- Full dopant activation.



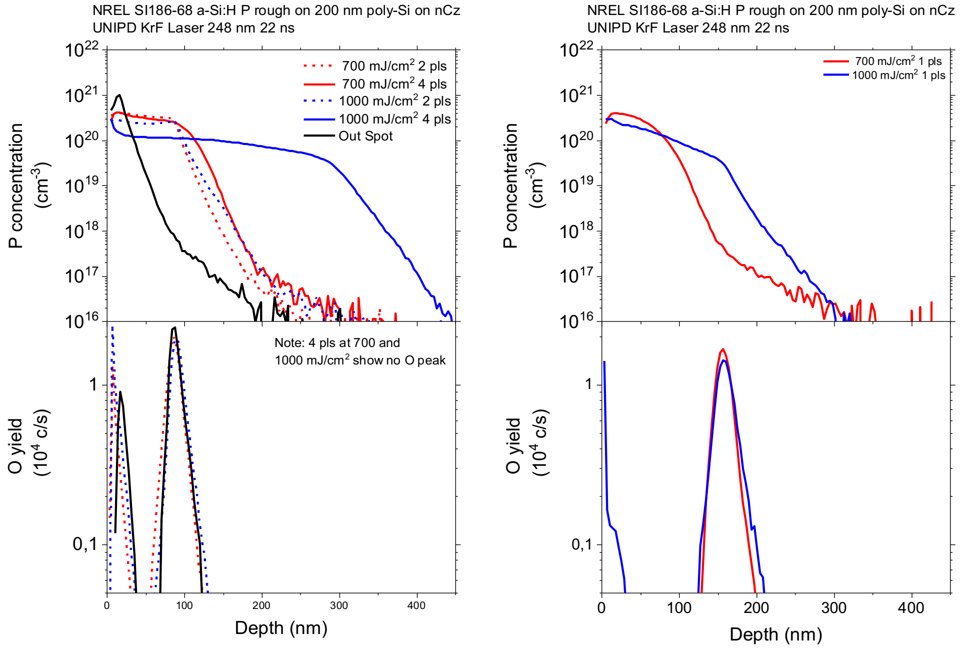


SI186-68 P rough 200 nm poly-Si nCz vs SI043-33 P polished 200 nm nCz – SIMS

Polished

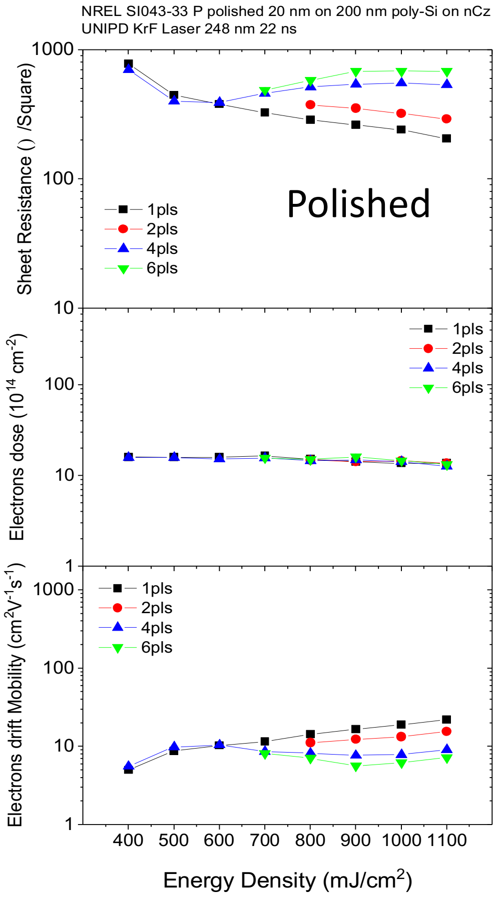


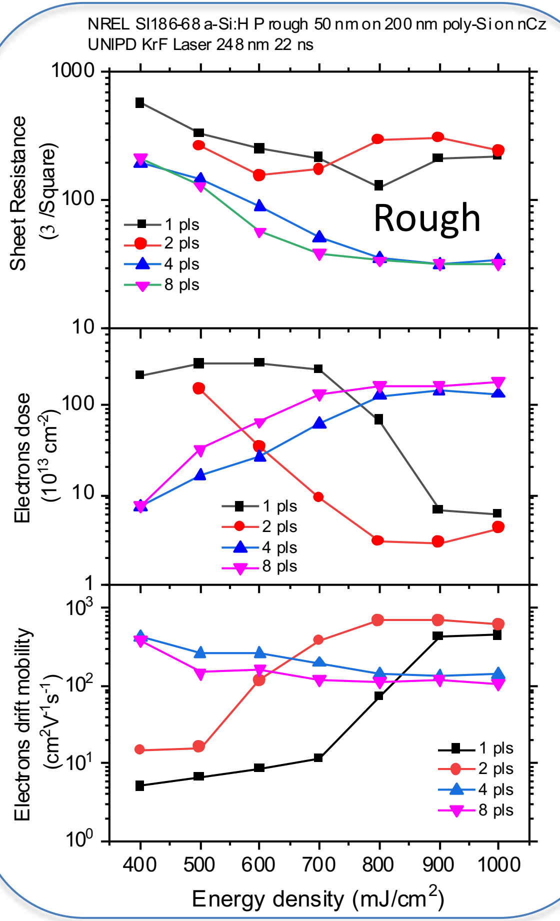
Rough



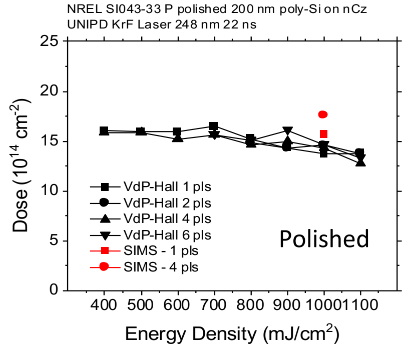
- Poly-Si thickness much lower than in polished samples, and not uniform (1 pls row shows larger thickness than other processes)
- After 4 pulses, the SiO_2 seems to be destroyed (O peak disappeares)
- *Note: we observed that the sample is considerably more rough than the rough B sample*

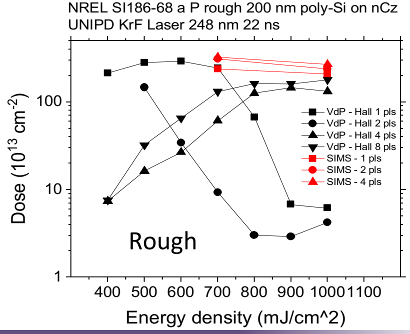
SI186-68 P rough 200 nm poly-Si nCz vs SI043-33 P polished 200 nm nCz – VdP-Hall



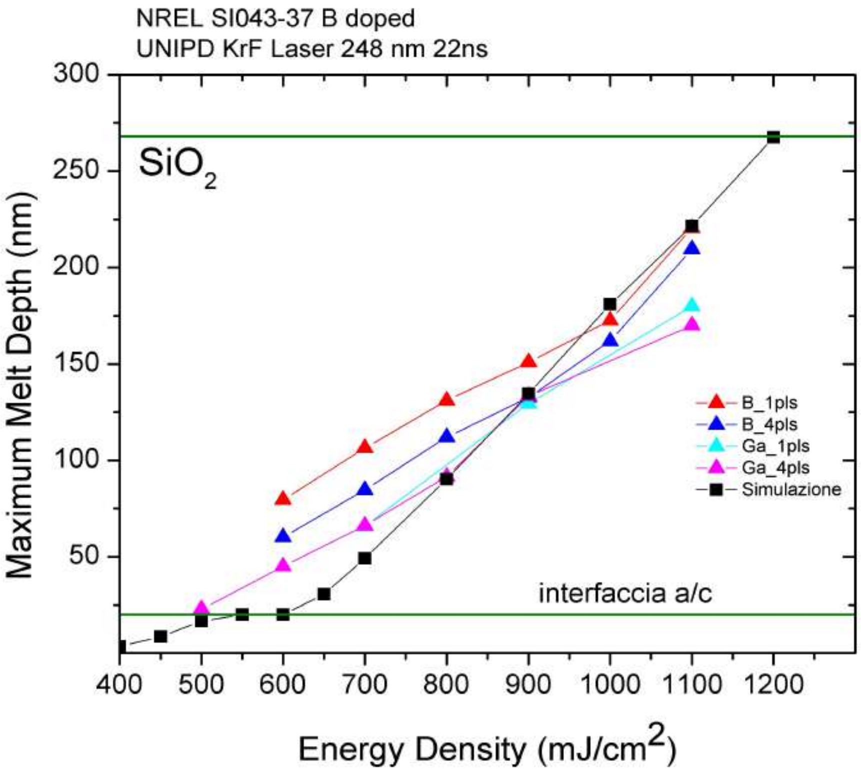


- <u>Hall scattering factor for electrons applied to carrier dose and mobility : γ_H=0.9</u> *(del Alamo JAP 1985)*
- Anomalous behavior for Rough sample. It might be related to the too thin and not uniform poly-Si layer (see SIMS data)





LIMP simulations



<u>No agreement between experimental points trend and simulation predictions</u>

- c-Si substrate used in simulation macros, but poly-Si in actual experiments
- Probably reflectivity and fusion enthalpy values are not sufficiently accurate.

<u>Comparison between simulation and c-Si substrate sample experimental data</u>

<u>Necessity of creation and implementation of a new poly-Si layer material in LIMP macros</u>

Conclusions

Promising doping method

- Excellent dopant confinement with high active concentrations
- Low carrier recombination and low contact resistivity

Reduced mobility due to use of poly-Si instead of c-Si

Poly-Si reduces Ga dopant activation

- Less activated percentage than Ga in c-Si
- Probable major interaction of poly-Si defects with Ga atoms

Perspectives

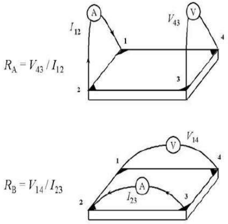
- Investigate and optimize reduced poly-Si thickness samples (100 nm instead of 200 nm)
- Investigate defects (TEM) and correlate them with electrical properties and PLM dynamics
- Improving LIMP macros:
  - Comparison with experiments performed in c-Si
  - PLM dynamics predictions
  - Implementation of poly-Si material
- Production of a high efficiency PV device

Laboratories and experimental measurements

UNIPD DFA Laser Processing Laboratory

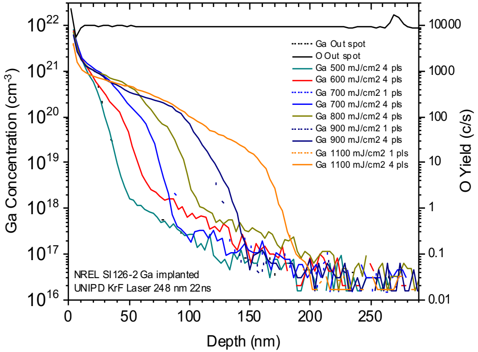
Van der Pauw measurements

- Sheet Resistance
- Holes/Electrons Hall dose (areal density)
- Hall mobility
- Dopant activation



SIMS measurements

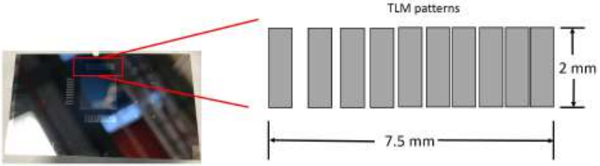
- Concentration profiling
- Dose
- Maximum melt depth (MMD)



NREL Laboratories

Photoluminescence imaging (PL)

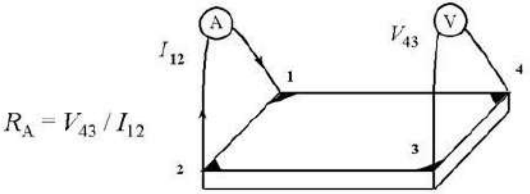
Trasmission Line Measurement (TLM)

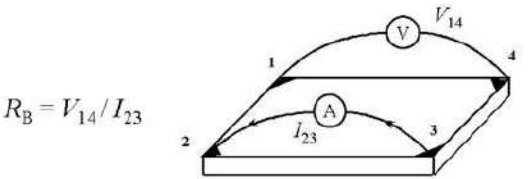


Van der Pauw-Hall electrical measurements

- Van der Pauw technique
  - Measurement of the *sheet resistance* R_S through a four-point probe apparatus. It can be derived from the relation:

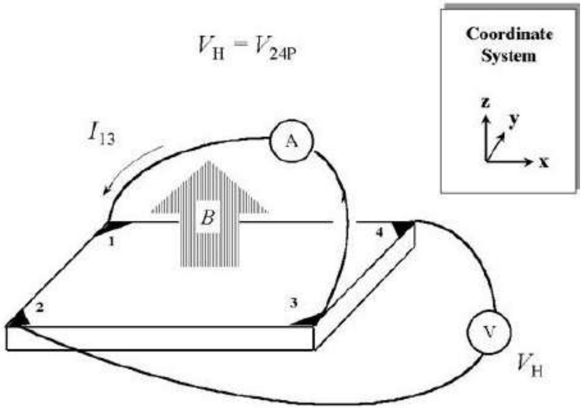
$$e^{-\frac{\pi R_A}{R_S}} + e^{-\frac{\pi R_B}{R_S}} = 1$$





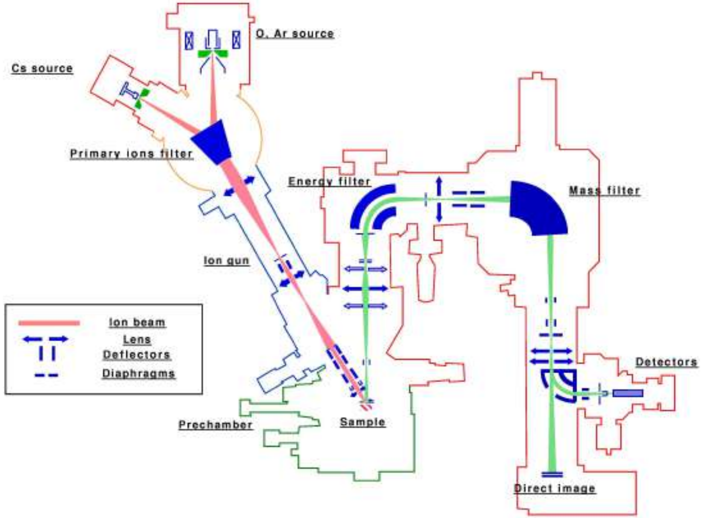
- Hall effect
  - On the same geometry as before, a constant magnetic field perpendicular to the sample is applied in order to obtain the *Hall dose* (sheet density) n_S and the carriers' *Hall mobility* μ

$$n_S = \frac{IB}{qV_H} \qquad \mu = \frac{1}{qn_S R_S}$$

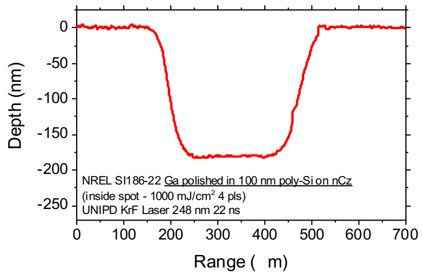


SIMS/profilometer measurements

- Detection of impurities in a matrix with concentrations down to parts per billion
- By means of reference samples with known dopant concentration it is possible to calibrate the concentration profile as the depth increases
- A profilometer is necessary to measure the SIMS crater depth in order to obtain the correct profile plot



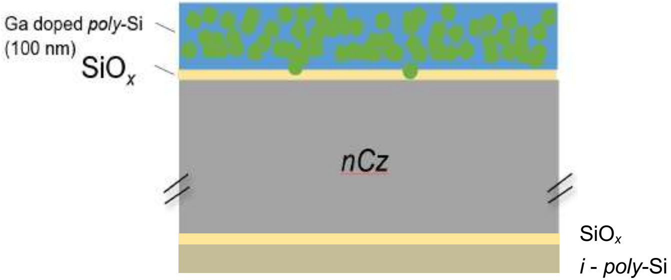
Schematics of the Cameca IMS 4f used for the acquisition of all the depth profiles

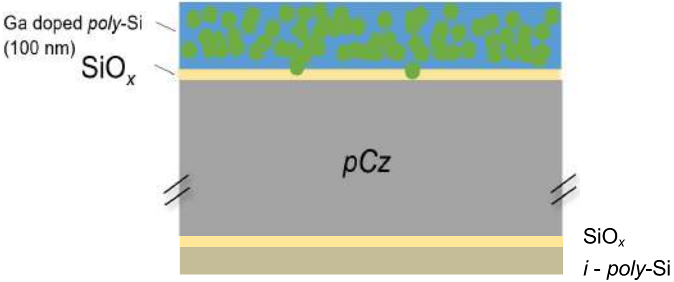


SIMS crater profilometer scan

Third batch samples structures

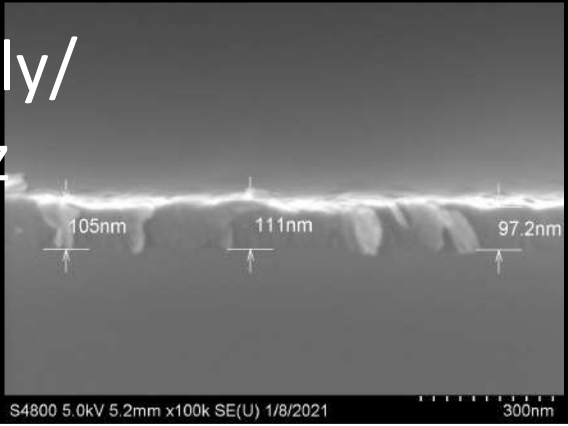
100 nm i-poly-Si on nCz and pCz single side polished samples for laser anneal

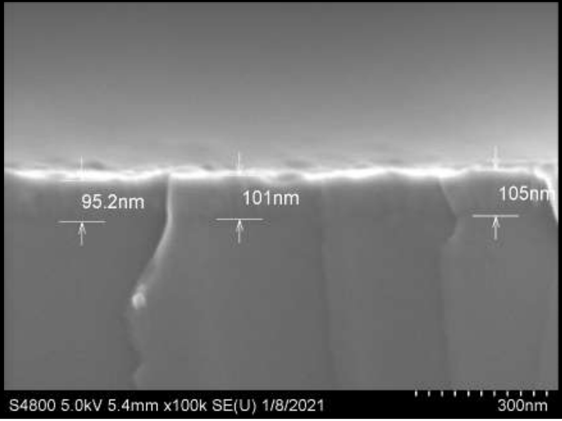


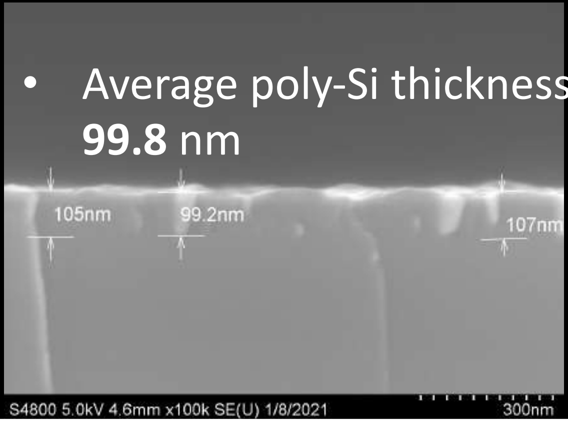


Post TMAH etch

ipoly/
nCz

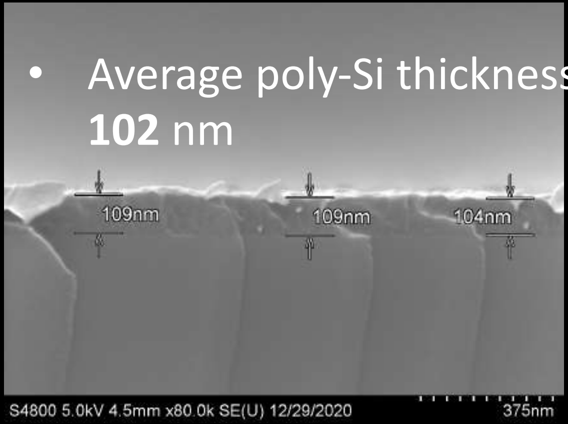






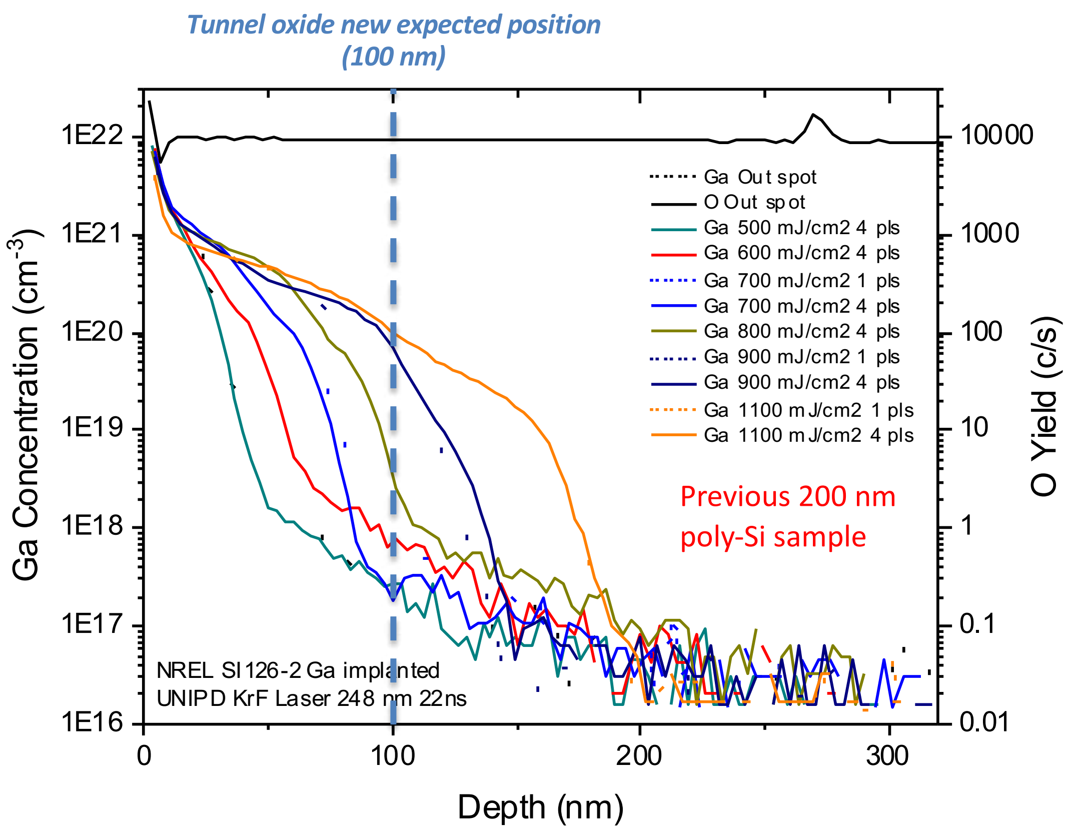
- Average poly-Si thickness **99.8** nm

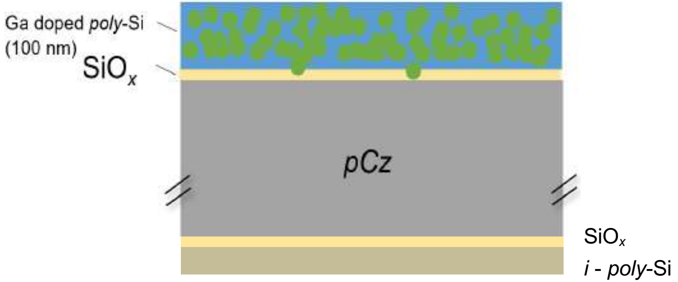
ipoly/
pCz



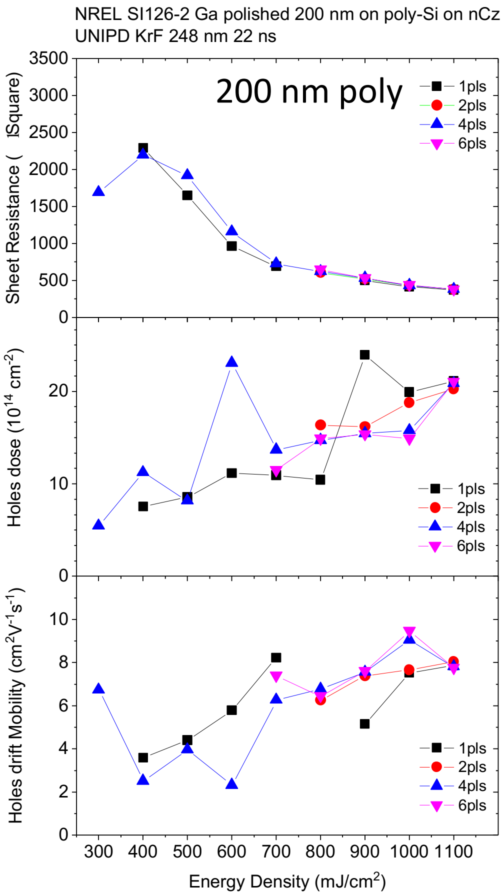
- Average poly-Si thickness **102** nm

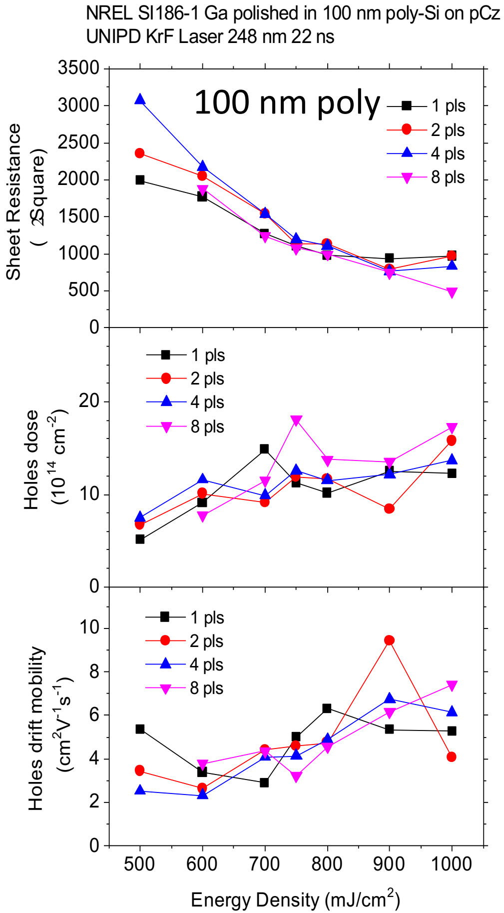
2. 100 nm i-poly on nCz and pCz single side polished samples - PLM process plan



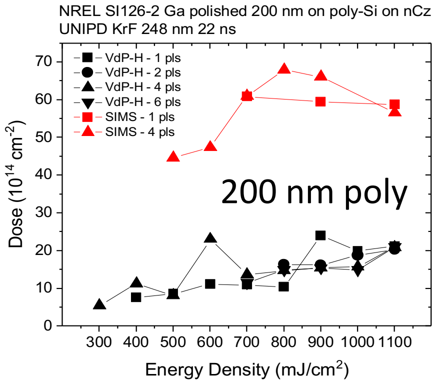


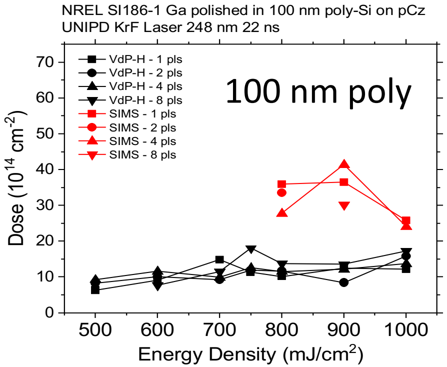
SI186-1 Gallium in 100 nm poly pCz – VdP-Hall





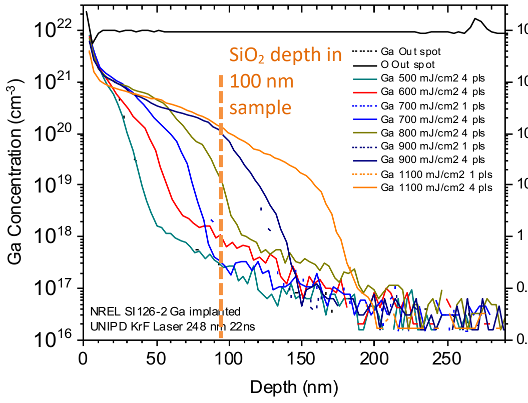
- Hall scattering factor for holes applied to carrier dose and mobility : γ_H=0.81 *(Mirabella APL 2008)*
- Similar electrical behavior as in 200 nm poly-Si sample.
- Lower doses (both Hall and SIMS) in 100 nm samples.

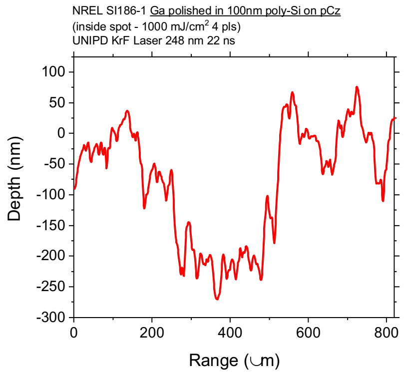




SI186-1 Gallium in 100 nm poly pCz - SIMS and surface profiles

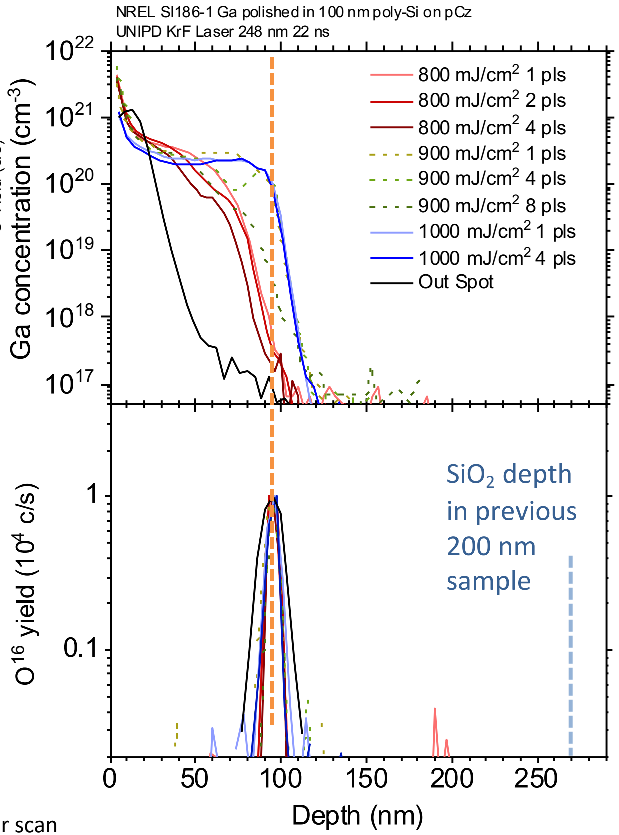
200 nm nCz





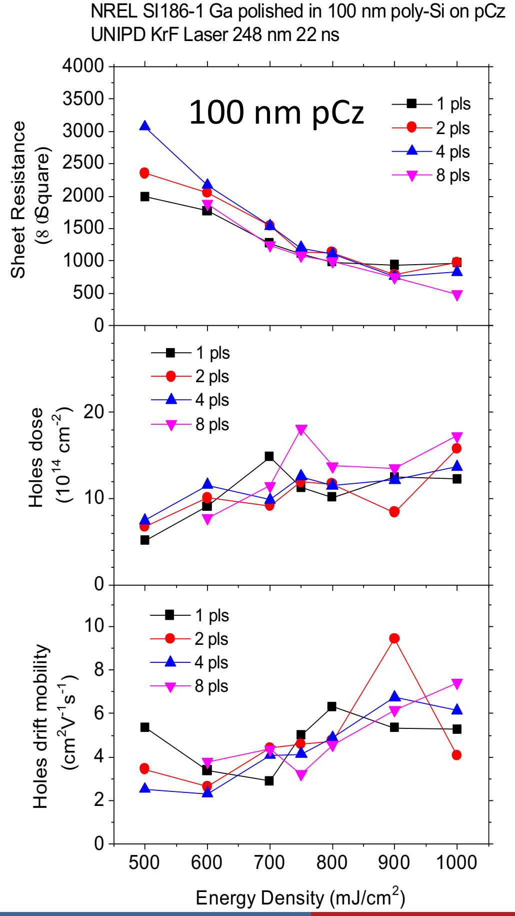
SIMS crater profilometer scan

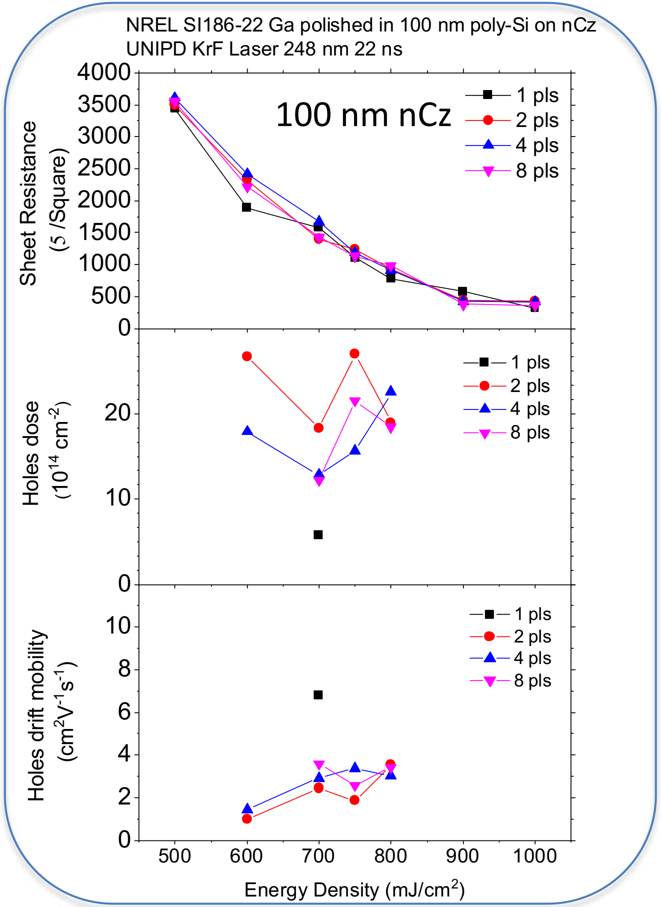
100 nm pCz



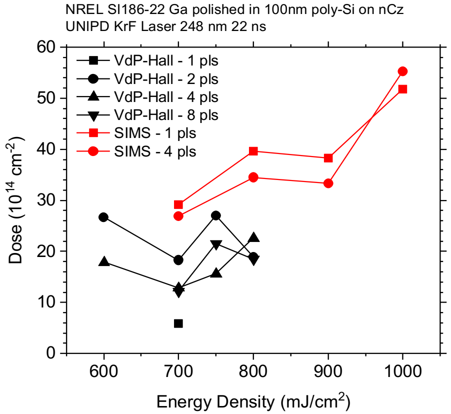
- <u>SiO_2 seems to provide an efficient barrier for Ga diffusion, without Ga segregation within the oxide.</u>
- According to previous data on 200 nm poly, at 900 and 1000mJ/cm² the Maximum Melt Depth (MMD) is expected to go well beyond the SiO_2 depth. O peak remains sharp even after PLM suggesting that SiO_2 is always preserved during PLM. We don't know if SiO2 acts also as a barrier for melting or just as a barrier for diffusion.
- At 800 mJ/cm2 the maximum melt depth seems well below the SiO2 depth
- At 1000 mJ/cm2 Ga freely diffuse within the entire poly-Si thickness, without segregation nor diffusion.
- 900 mJ/cm2 shows an intermediate behavior, with Ga segregating close to the SiO2 (but not within) and eventually towards the surface with increasing the number of pulses
- *Note that the surface is rough at variance with the nominally polished surface.*

SI186-22 Gallium in 100 nm poly nCz – VdP-Hall

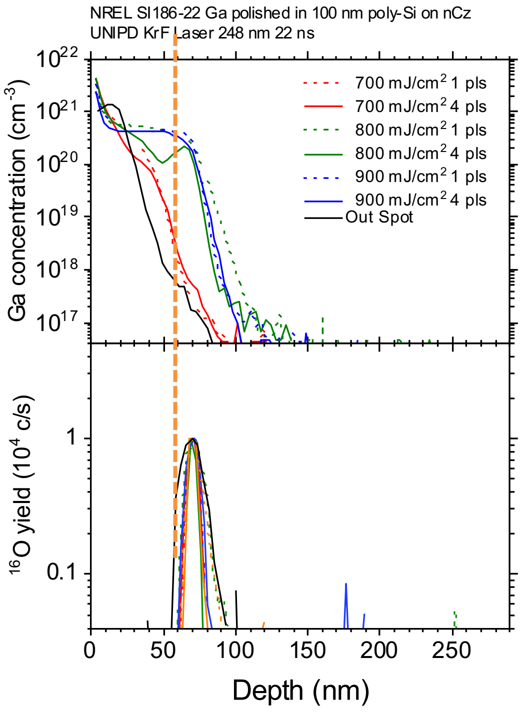


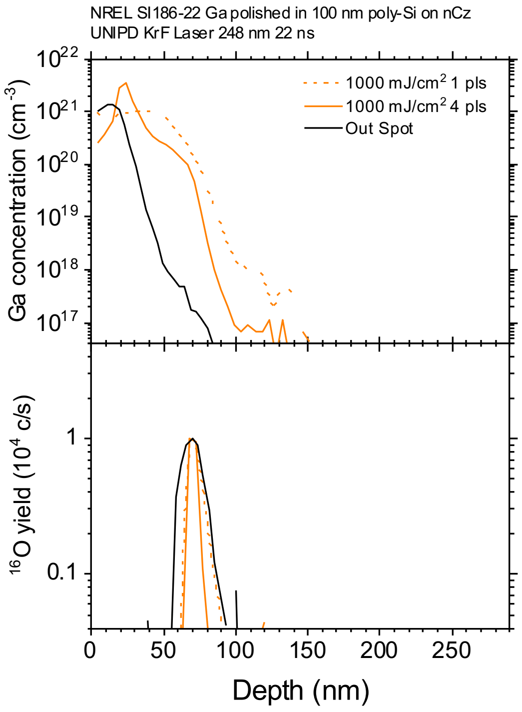


- <u>Hall scattering factor for holes applied to carrier dose and mobility : γ_H=0.81</u> *(Mirabella APL 2008)*
- Sheet resistances in nCz and pCz samples are quite similar
- On the contrary, only few spots in nCz give reasonable Hall data, even if they are quite scattered. The other spots give negative values. The reason might be the much lower poly-Si thickness (see SIMS) and the n-type substrate (SiO2 is not an efficient barrier for carriers?...)

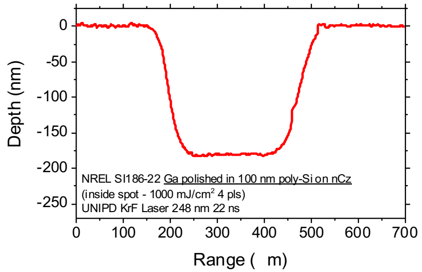


SI186-22 Gallium in 100 nm poly nCz - SIMS and surface profiles





- Similar behavior as in pCz sample, with SiO_2 appearing to be a barrier for Ga diffusion/melting.
- The sharpness of the O peak after PLM seems to be similar as in nCz sample, suggesting a similar behavior of the SiO_2 layer.
- Except for:
  - The SiO_2 depth (68 nm) in nCz samples lower than in pCz (95 nm).
  - Anomalous behavior at 1000 mJ/cm2
- *Note that the surface in this case is confirmed to be polished, even if with slightly higher roughness than in a polished, not-etched poly-Si.*



SIMS crater profilometer scan