ENEA
ITALIAN NATIONAL AGENCY FOR NEW TECHNOLOGIES, ENERGY AND SUSTAINABLE ECONOMIC DEVELOPMENT

Porous Silicon growth on n- and p-type H+-irradiated silicon

Comunicazione

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TOP IMPLART

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Outline

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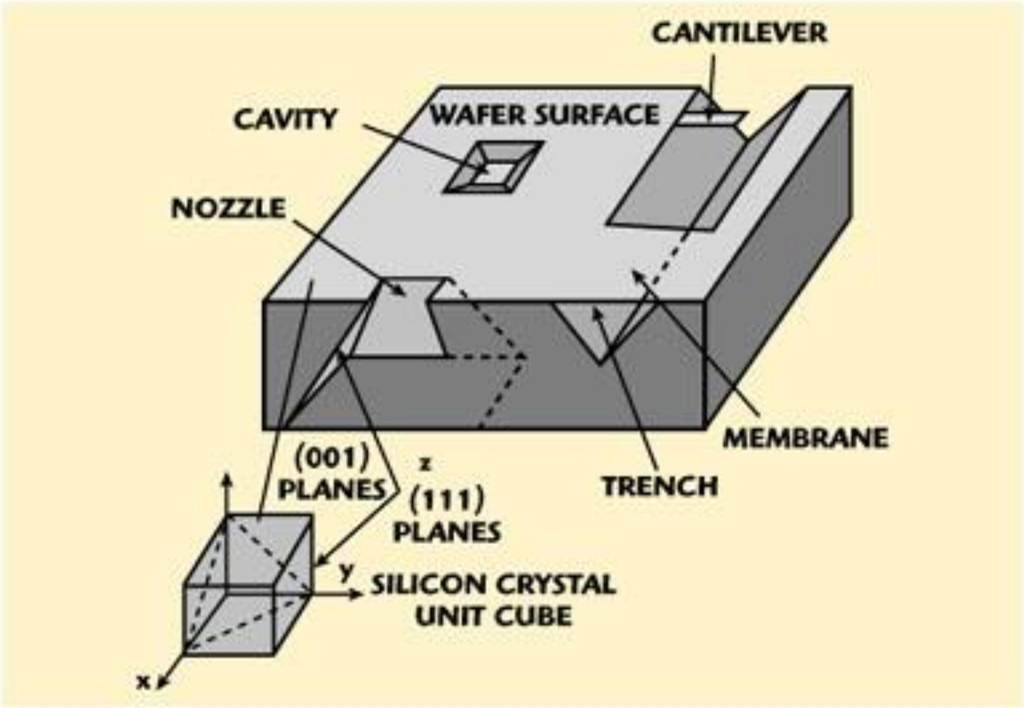
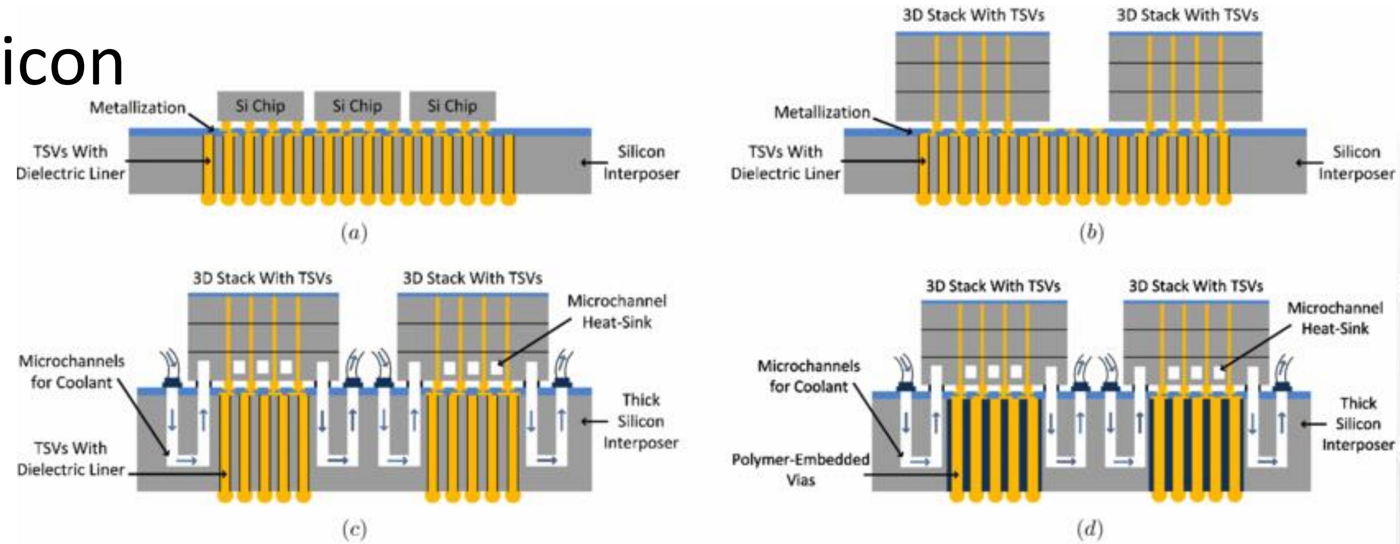
- Bulk micromachining of silicon
  - MEMS and Advanced IC packaging applications
  - Porous silicon based micromachining
- Porous Silicon growth on proton implanted silicon
- Uniform proton beam irradiation of silicon samples
  - TOP-IMPLART Proton LINAC
  - Experimental results
- Conclusions

Bulk Micromachining of Silicon

Bulk micromachining: realization of high aspect-ratio structures in the bulk of a silicon wafer.

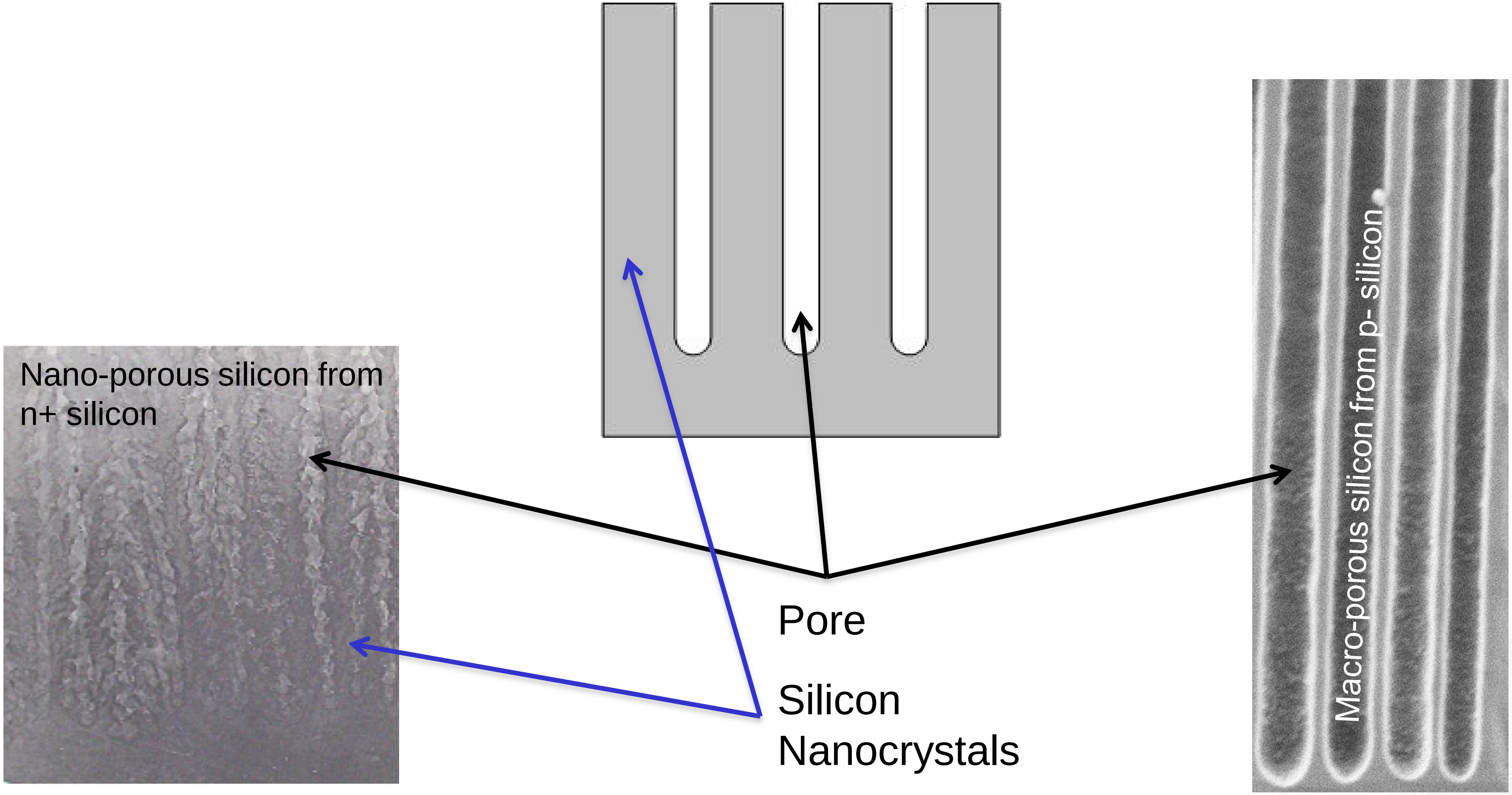
- Applications:
  - MEMS (Micro-Electro-Mechanical-Systems)
  - IC Packaging (Silicon Interposers)





Porous Silicon

- Porous silicon (PS or PSi) has been discovered in 1956 at Bell Labs by A. Uhlir and I. Uhlir and later rediscovered in the ’90 because of its photoluminescence properties.

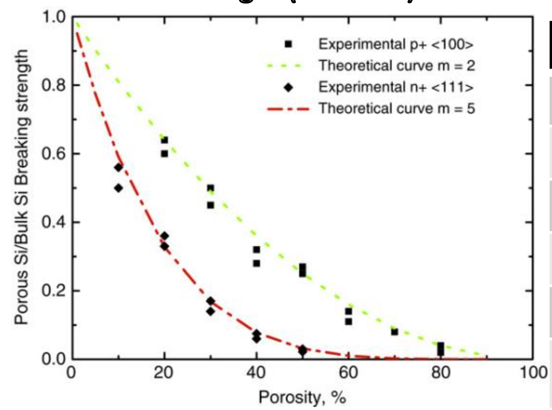


Porous Silicon Reference Card

Effect of anodization parameters on PSi (1nm/s per 1mA/cm2)

An increase of	Porosity	Etch. rate	E-polish. thr.
HF conc.	decrease	decrease	increase
Current density	increase	increase	-
Anod. time	increase	≈ constant	-
Temperature	-	-	increase
Doping (P-type)	decrease	increase	increase
Doping (N-type)	increase		-

Ultimate Strength (Balucani)

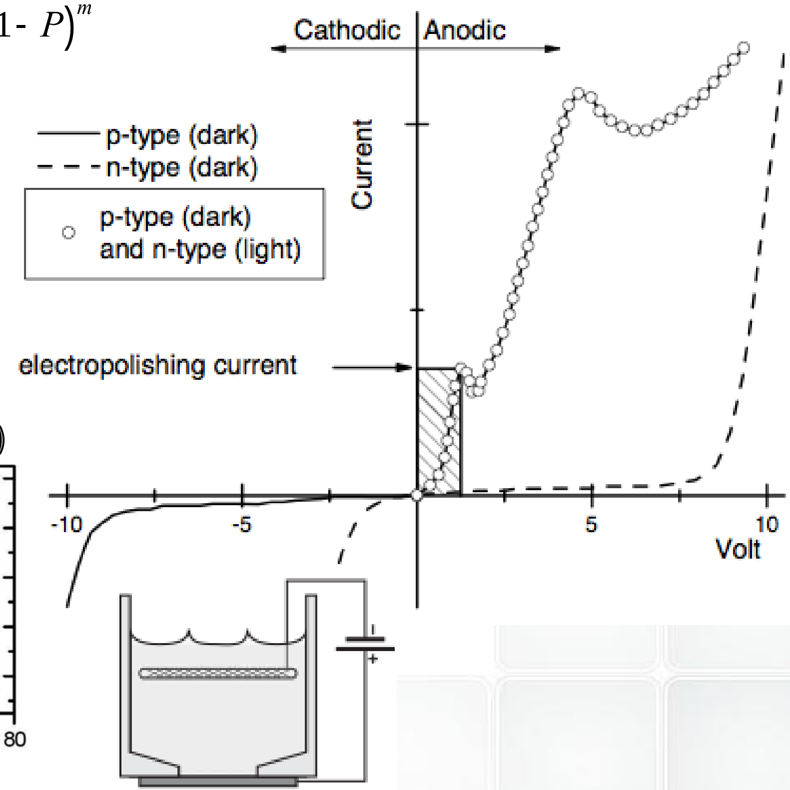


Model: $s = s_0 (1 - P)^m$

Silicon	m
p+ <100>	2
n+ <111>	5

Critical parameters

Parameter	Range (typ.)	Unit
HF Conc.	2-40	%wt
Current Density	0.5-150	mA/cm^2
Anodization time	5-1800	s
Temperature	250-300	K
Wafer ρ p-type	0.001-100	Ω•cm
Wafer ρ n-type	0.001-100	Ω•cm



Dielectric function of PSi (effective medium approximation)

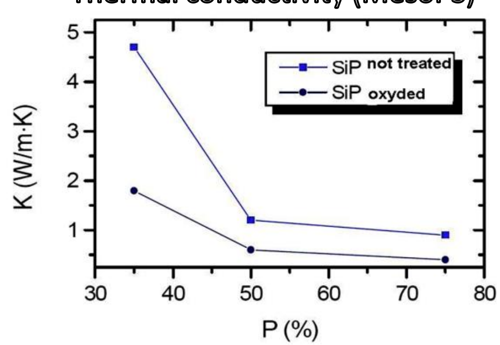
Theory	Formula
Bruggeman	$P\frac{\varepsilon_M - \varepsilon_{eff}}{\varepsilon_M + 2\varepsilon_{eff}} + (1-P)\frac{\varepsilon - \varepsilon_{eff}}{\varepsilon + 2\varepsilon_{eff}} = 0$
Maxwell - Garnett	$\frac{\varepsilon_{eff} - \varepsilon_M}{\varepsilon_{eff} + 2\varepsilon_M} + (1-P)\frac{\varepsilon - \varepsilon_M}{\varepsilon + 2\varepsilon_M}$
Looyenga	$\varepsilon_{eff}^{1/3} = (1-P)\varepsilon^{1/3} + P\varepsilon_M^{1/3}$

ε: Si permittivity, ε_{eff}: effective permittivity, ε_M: permittivity of host material (air), P: porosity

IUPAC classification

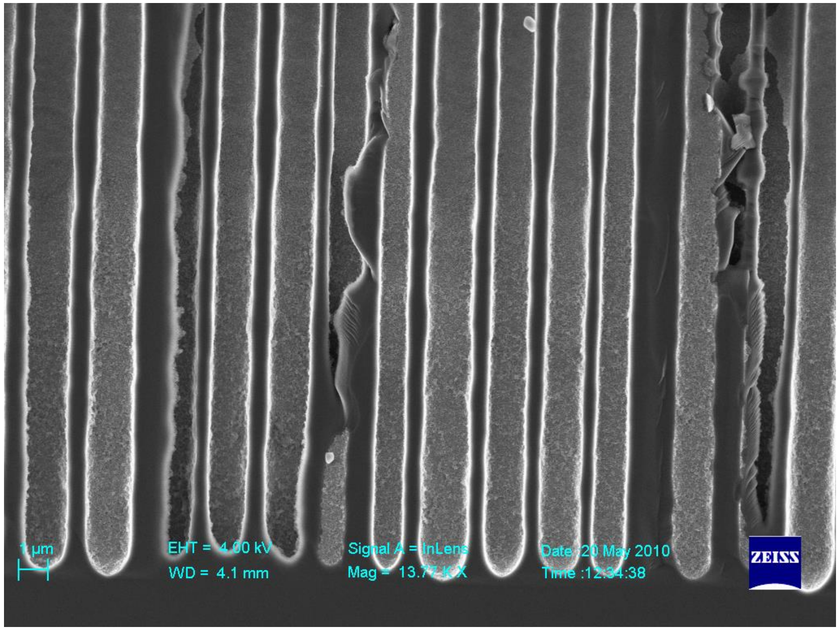
Pore width (nm)	Classification
≤2	Micro (nano) porous
2-50	mesoporous
>50	macroporous

Thermal conductivity (MesoPS)

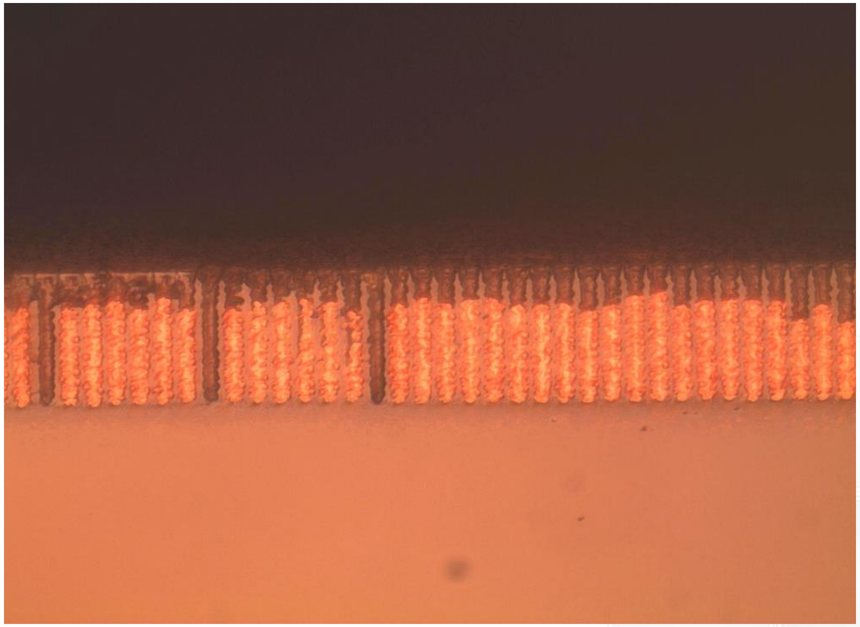


Porous silicon for bulk micromachining

- In bulk micromachining applications porous silicon is used as a scarificial layer that is etched away to reveal the structure.
- Extremely high selectivity of PS etching in comparison with bulk Si. *Etching ratio of PS to Si is 100000:1!*
- PS layers can be selectively etched by means of the structure sensitive mechanism.



High aspect ratio macro-pores, random order (M. Balucani, 2010)

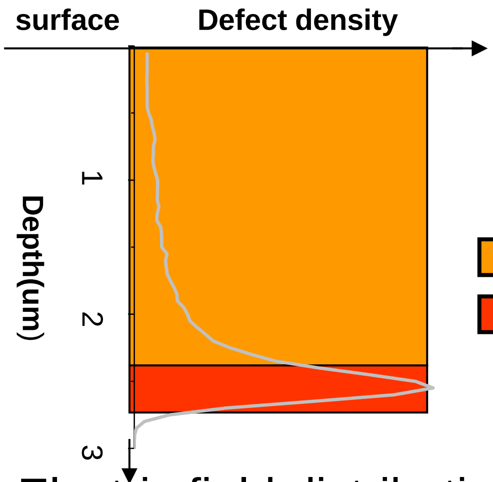


TSV structures filled with Cu formed from ordered macro PS (P. Nenzi et al., ECTC 2013)

Experiments on

POROUS SILICON GROWTH ON PROTON IMPLANTATED SILICON

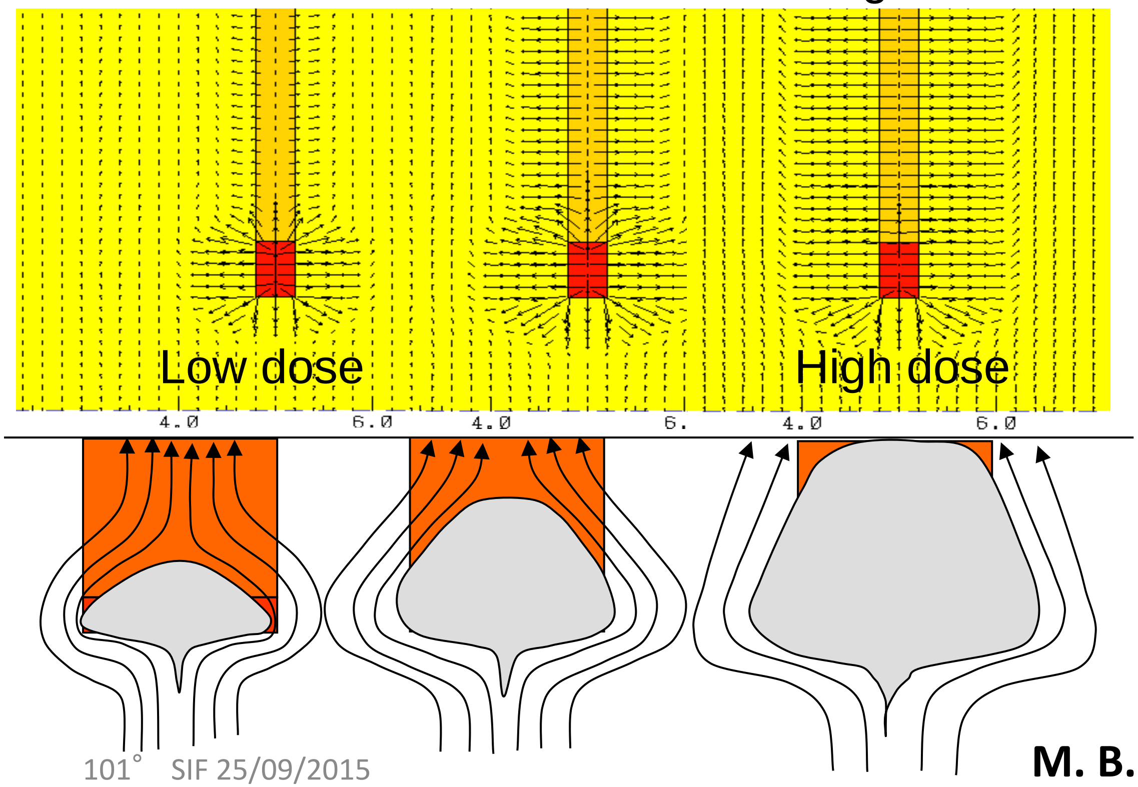
Porous silicon growth suppression over irradiated areas



Low defect region
High defect region

- Damage profile for protons with energy of 250 keV
- Damage profile almost constant for the first 2.2 μm (below surface)
- Tenfold (10x) defect density increase at the at the stopping range.

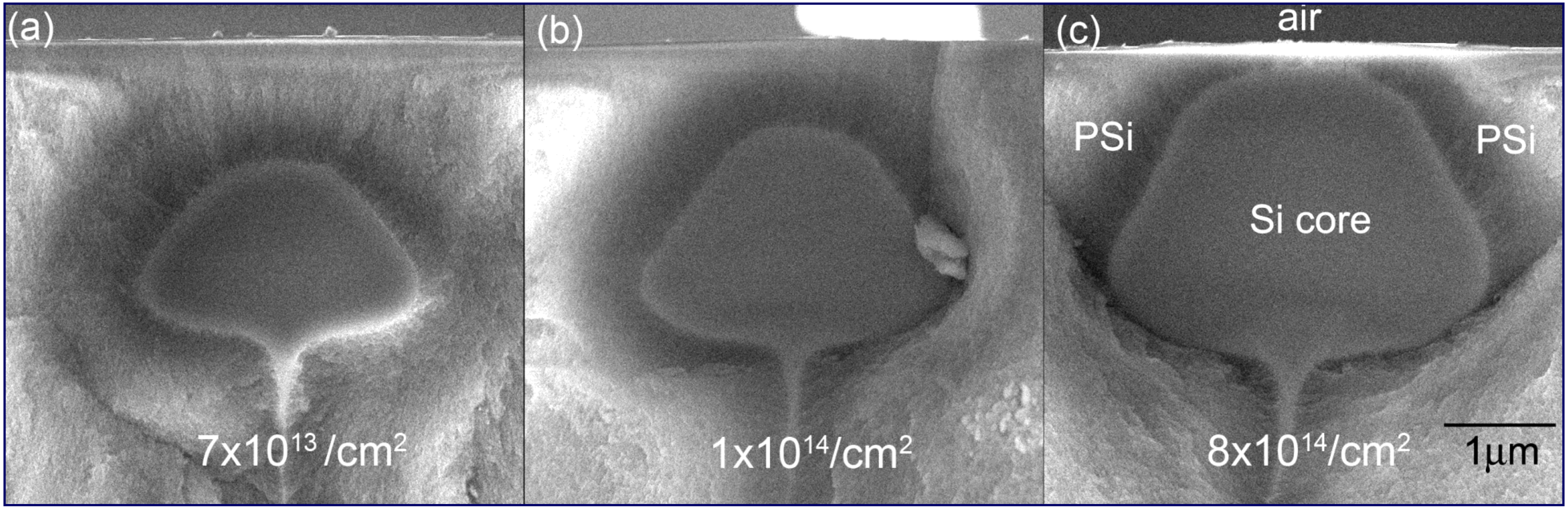
Electric field distribution with increasing dose

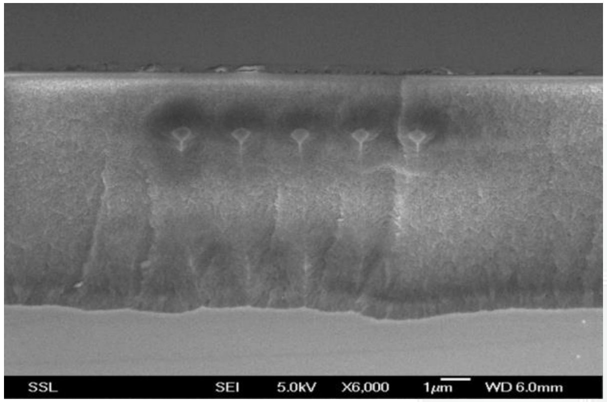


- The lateral electric field generated by implanted protons in the damaged regions causes a deflection of holes.
- Deflection increases near the highly defective region, corresponding to the stopping range.
- Hole current bends over the highly defective region.
- Porous silicon growth is suppressed only in the highly defective region at low doses ($<10^{14}$ /cm^2).
- Porous silicon growth is suppressed along all the particles path for high dose ($>10^{14}$/cm^2).

M. B. H. Breese at al., Phys. Rev B 73, 035428 2006

Porous silicon growth suppression over irradiated areas





E. J. Teo et al., Opt. Express 16 (2) 573-578

TOP – IMPLART experiment on

UNIFORM PROTON BEAM IRRADIATION OF SILICON SAMPLES

TOP-IMPLART proton LINAC

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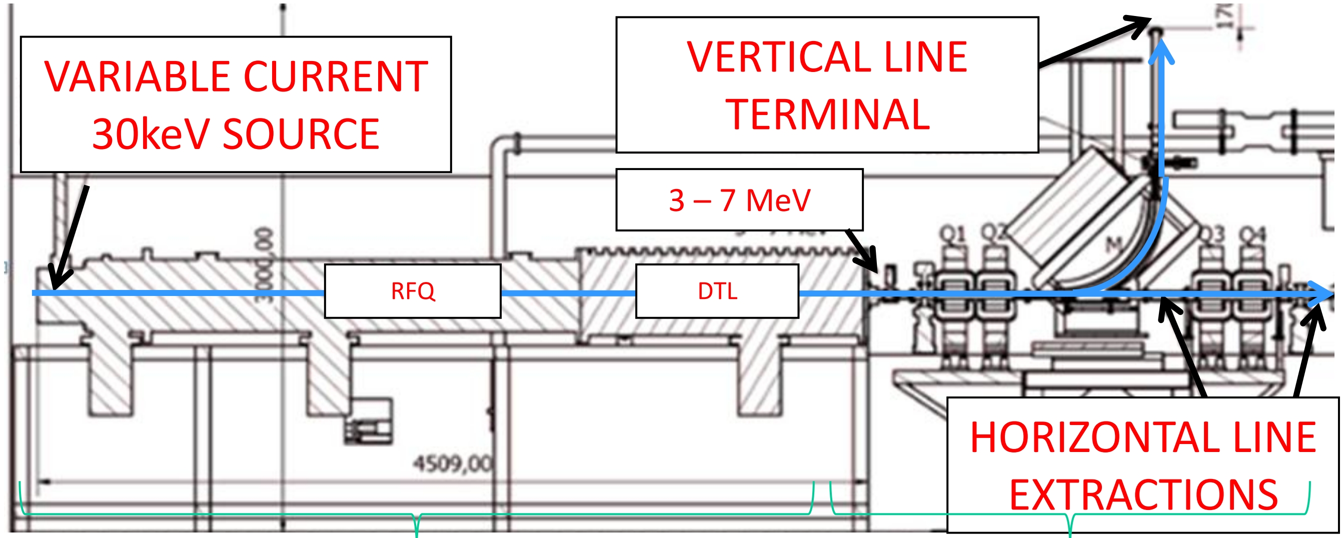
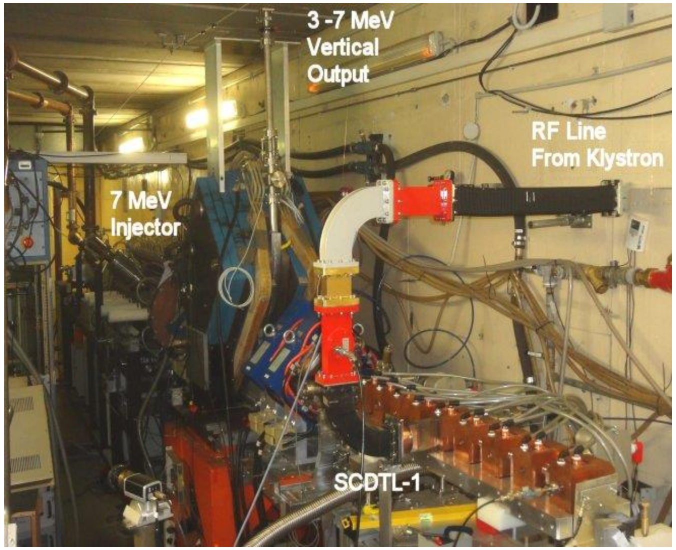
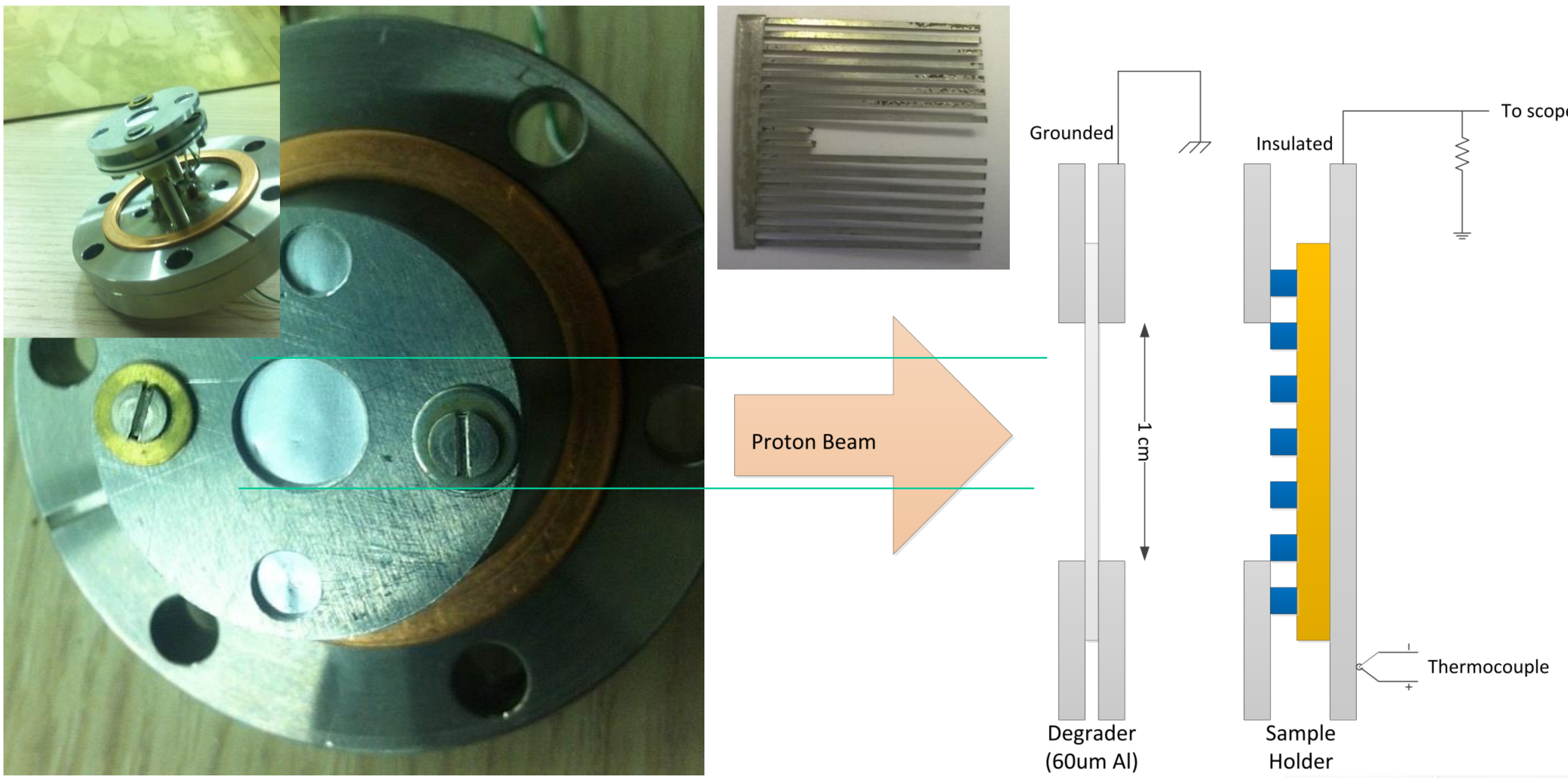




- TOP-IMPLART project is aimed to the development of a proton LINAC for Hadron therapy using compact S-band accelerating sections (SCDTL)
- The LINAC is under construction at ENEA C.R. Frascati by the APAM Laboratory
- The machine is now capable of delivering a pulsed proton beam with energies up to 18 MeV
- Lower energy beams can be obtained on a vertical line (radiobiology) or by degrading the energy of the main beam line

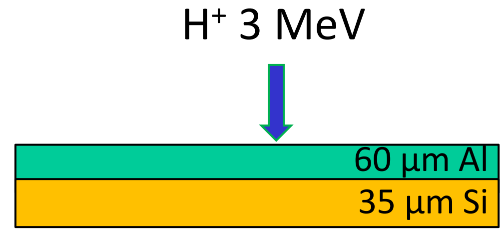
Experimental setup

- Silicon sample is masked with a 200μm thick molybdenum mask
- Silicon sample and mask are mounted on a custom designed holder and installed at the end of the accelerator pipe.
- Beam current and sample temperature have been recorded during the processes

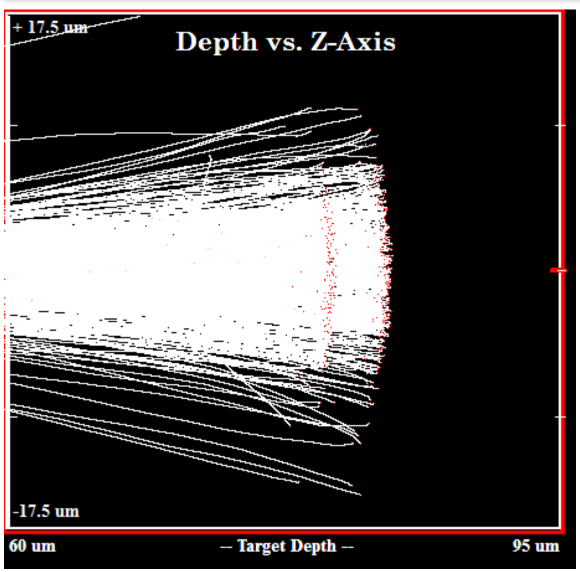


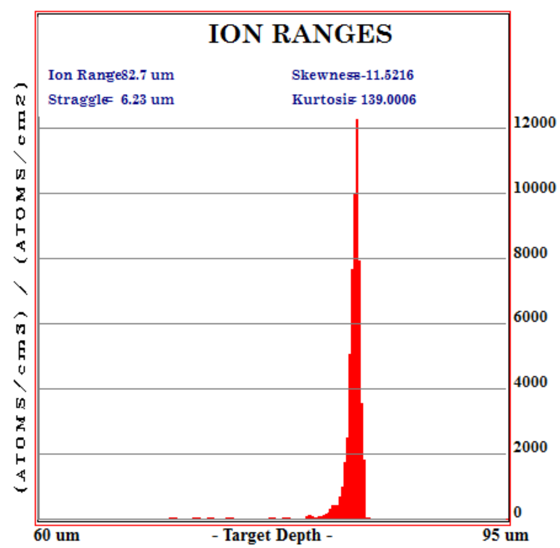
Experimental Conditions

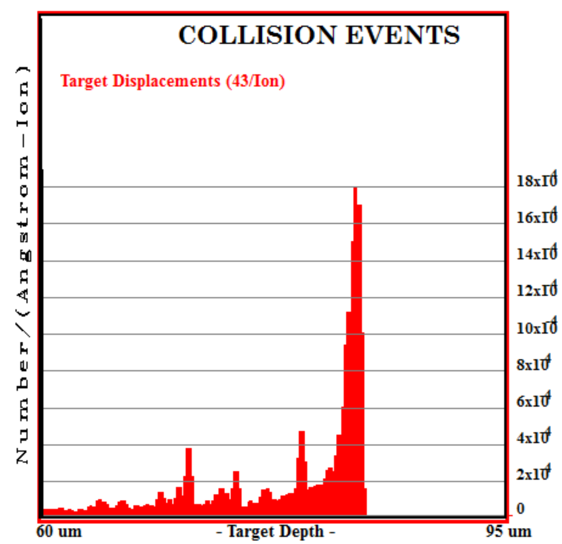
Parameter	Value	Units
Pulse length	98	µs
Pulse Repetition Frequency	30	Hz
Beam energy	1.8	MeV
Range in silicon	36.4	µm
Charge/pulse (average)	8.91×10^{-9}	C
Protons/pulse (average)	5.57×10^{10}	
Target fluence	5.00×10^{15}	cm^{-2}
Implantation peak	7.2×10^{19}	cm^{-3}
Exposure time (min) actual	(3600) 4500	s



- Target implantation depth: 30µm
- SRIM/TRIM code has been used to compute energy
- Accelerator minimum energy is 3MeV so an aluminum energy degrader (60µm thick) has been placed between the beam and the target to reduce it to 1.3MeV

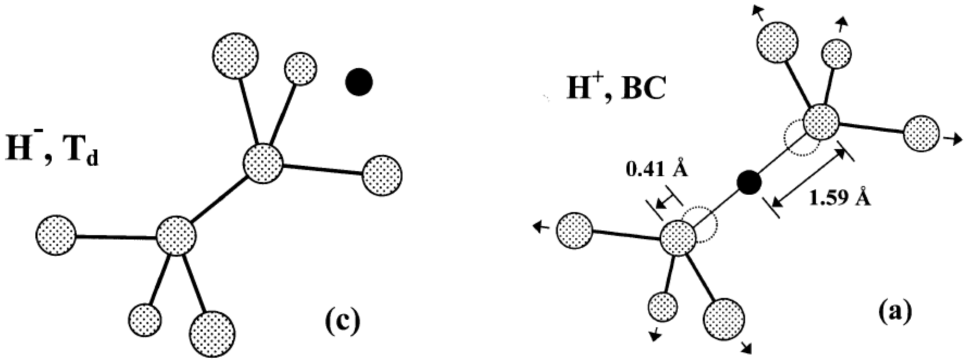






Expected results

Parameter	*p*-type	*n*-type
Resistivity	1-10 Ω·cm	20 Ω·cm
Dopant	Boron	Phosphorous



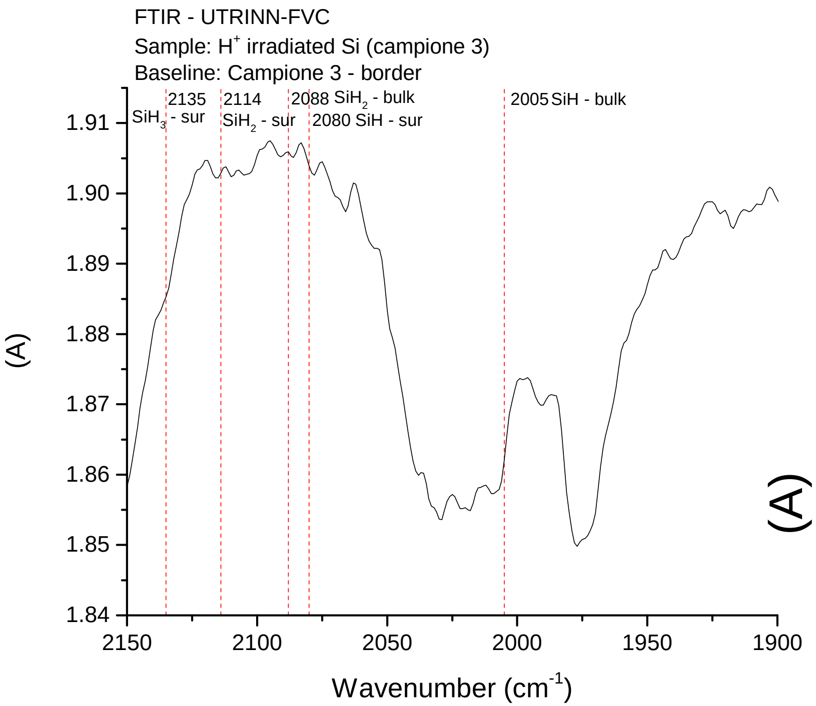
• Hydrogen is an amphoteric impurity that counteracts the activity of shallow dopants

• The most favorable state of hydrogen in p-type silicon is the H^+ state located in bond center. H^+ act as a donor that ***passivates*** ionized impurities (acceptors)

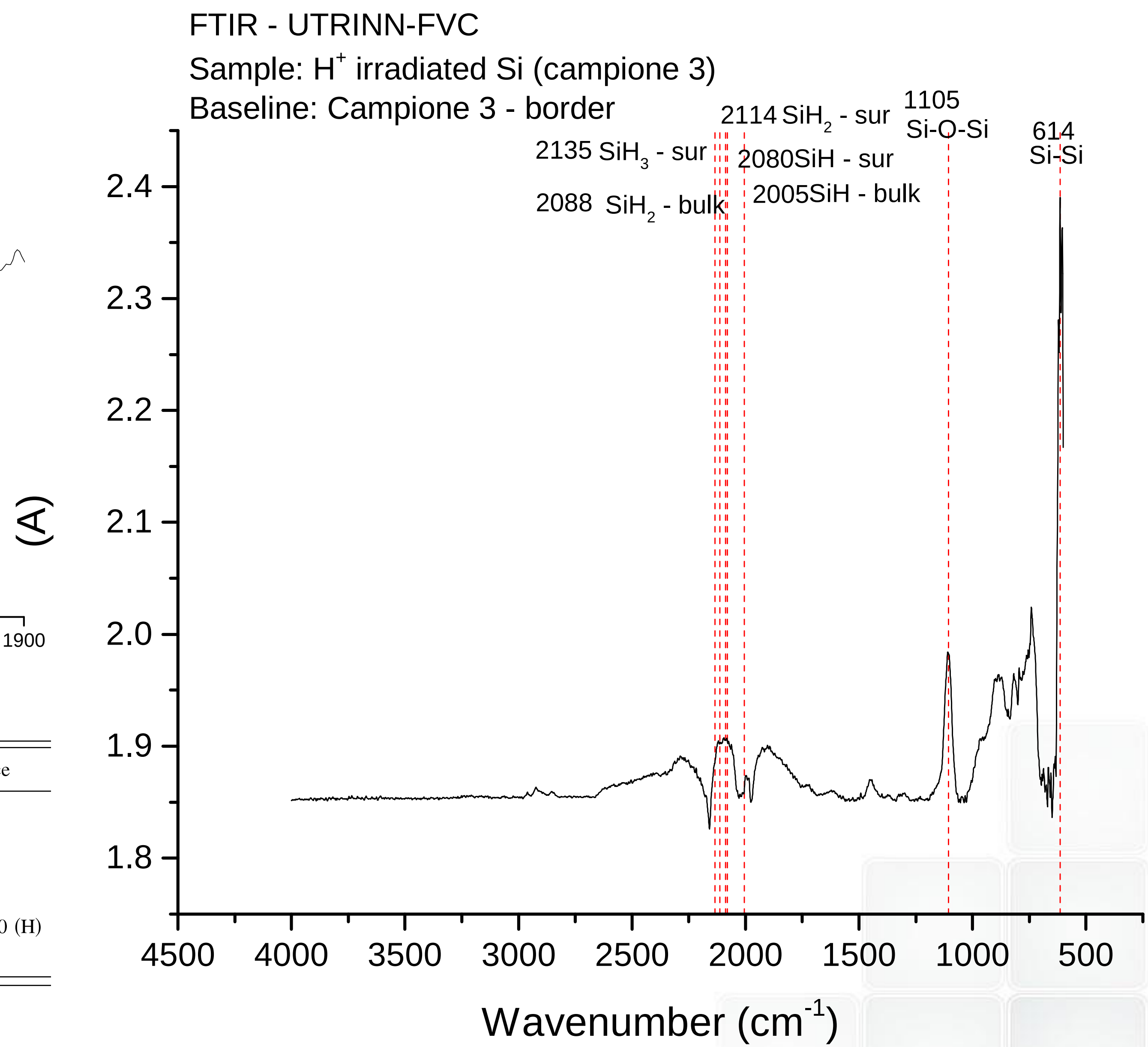
• The most favorable state of hydrogen in n-type is the interstitial H^- state. H^- acts as an acceptor that ***passivate*** donors.

• We expect to suppress porous silicon growth on implanted areas on p-type and promote growth on n-type

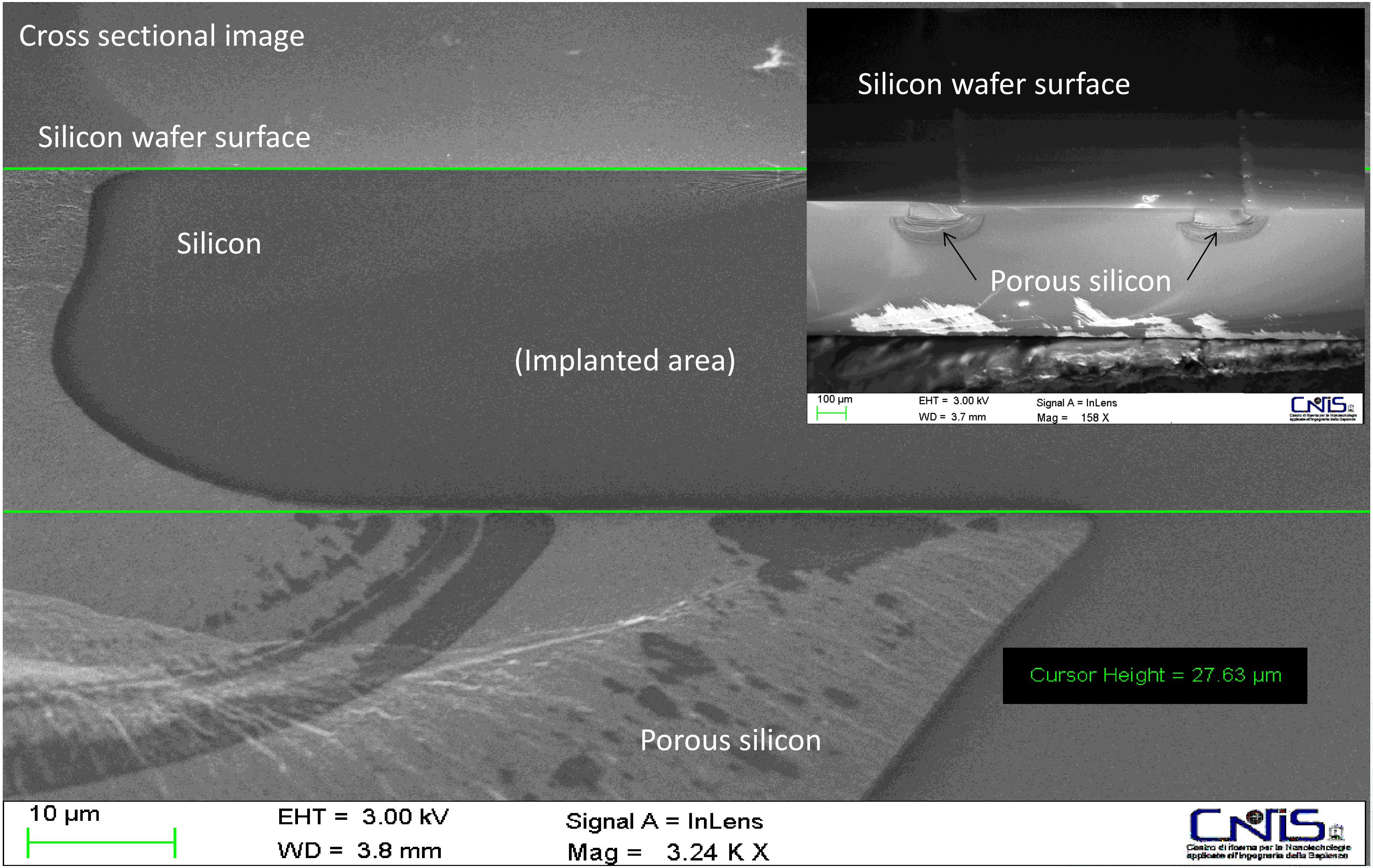
FTIR analysis



Hydride	Epitaxial	Interface	Bulk	Surface
SiH	2080 (B)	2005	2005 (A)	2080
SiH_2	2114 (D)	2088	2088 (C)	2114
SiH_3	2135 (E)			2135
$SiH_2(O_2)$			2190–2210 (F)	
$SiH(O_3)$			2250 (G)	2275–2290 (H)
FWHM	<30	~80	~80	<30

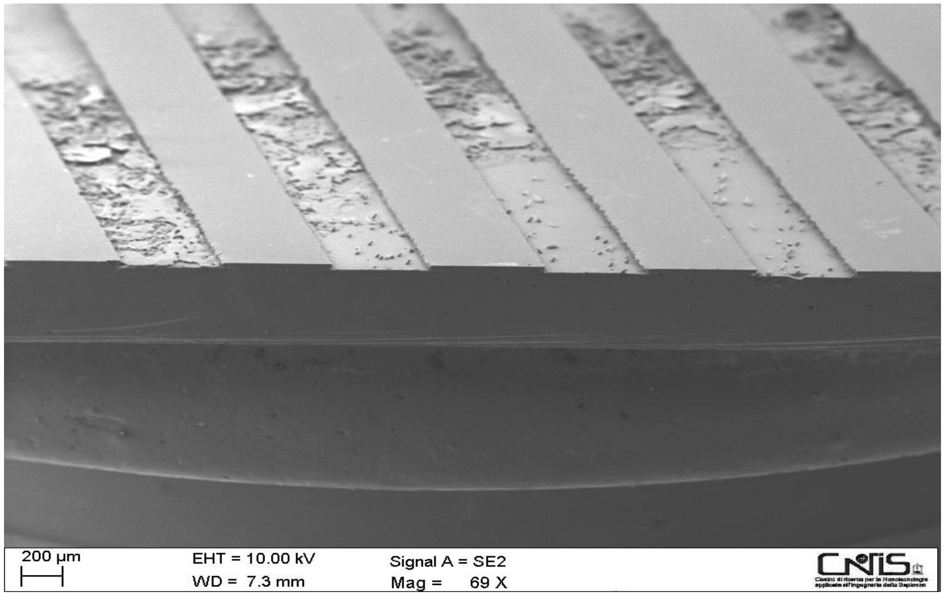


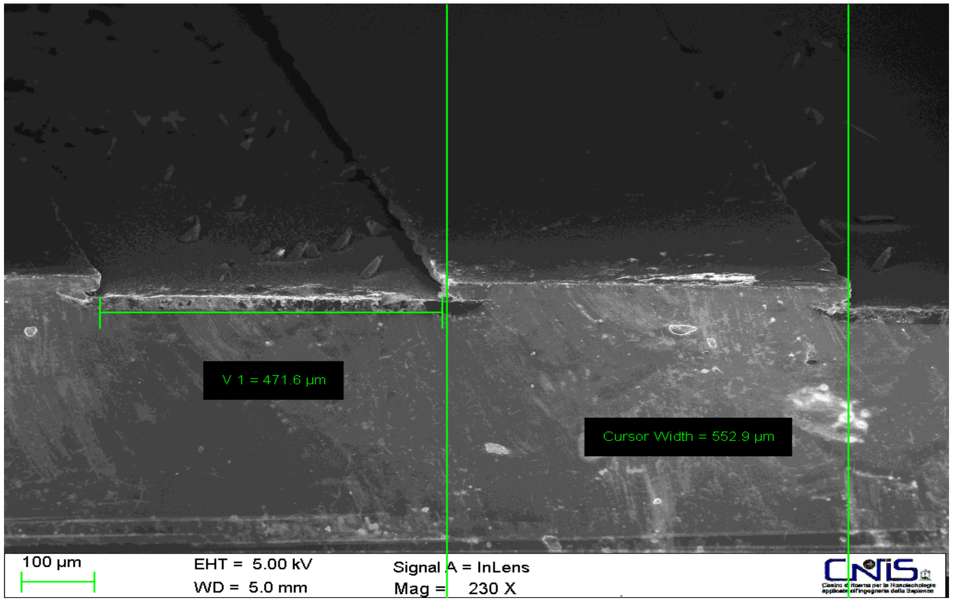
Exposed samples (p-type)



Exposed samples (p-type)

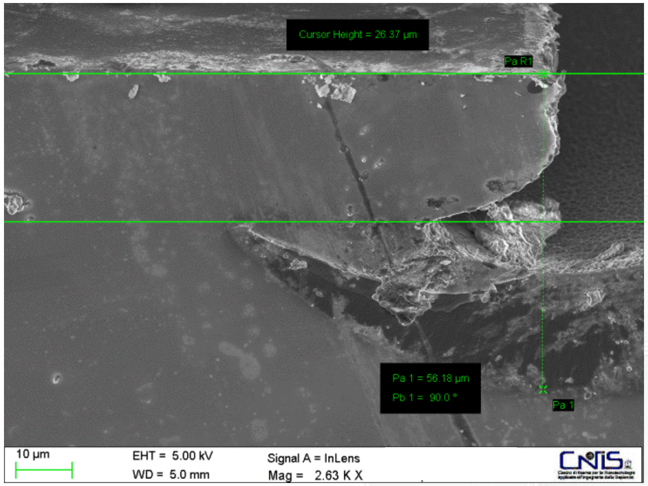
- Porous silicon has been removed with KOH etch to delineate the implanted areas





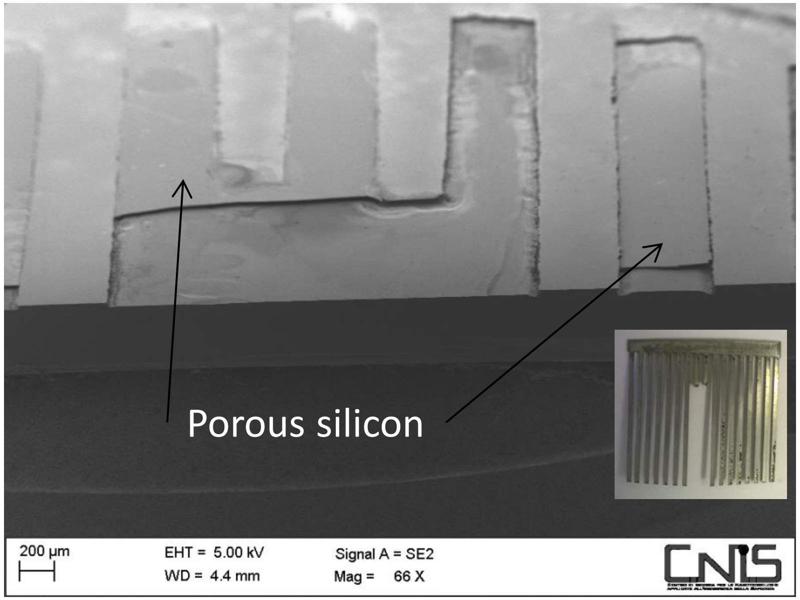
- Images shows the transferred pattern (lateral dimensions matches the maks (500µm finger, 500µm space)
- Porous silicon growth process:

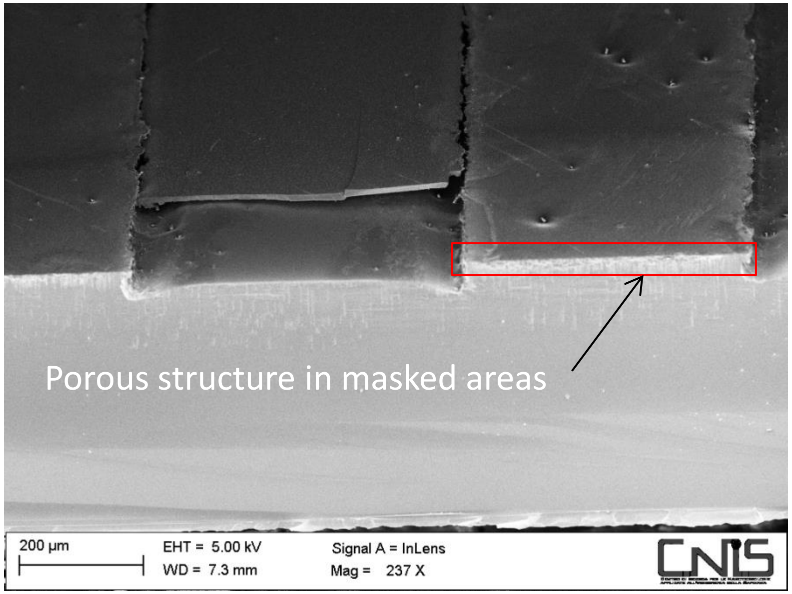
Parameter	*p*-type
Resistivity	1-10 Ω·cm
Dopant	Boron
Electrolyte	HF:IPA=1:1
Current density	20mA/cm^2
Environment	-



Exposed samples (n-type)

- Porous silicon has been removed with KOH etch to delineate the implanted areas



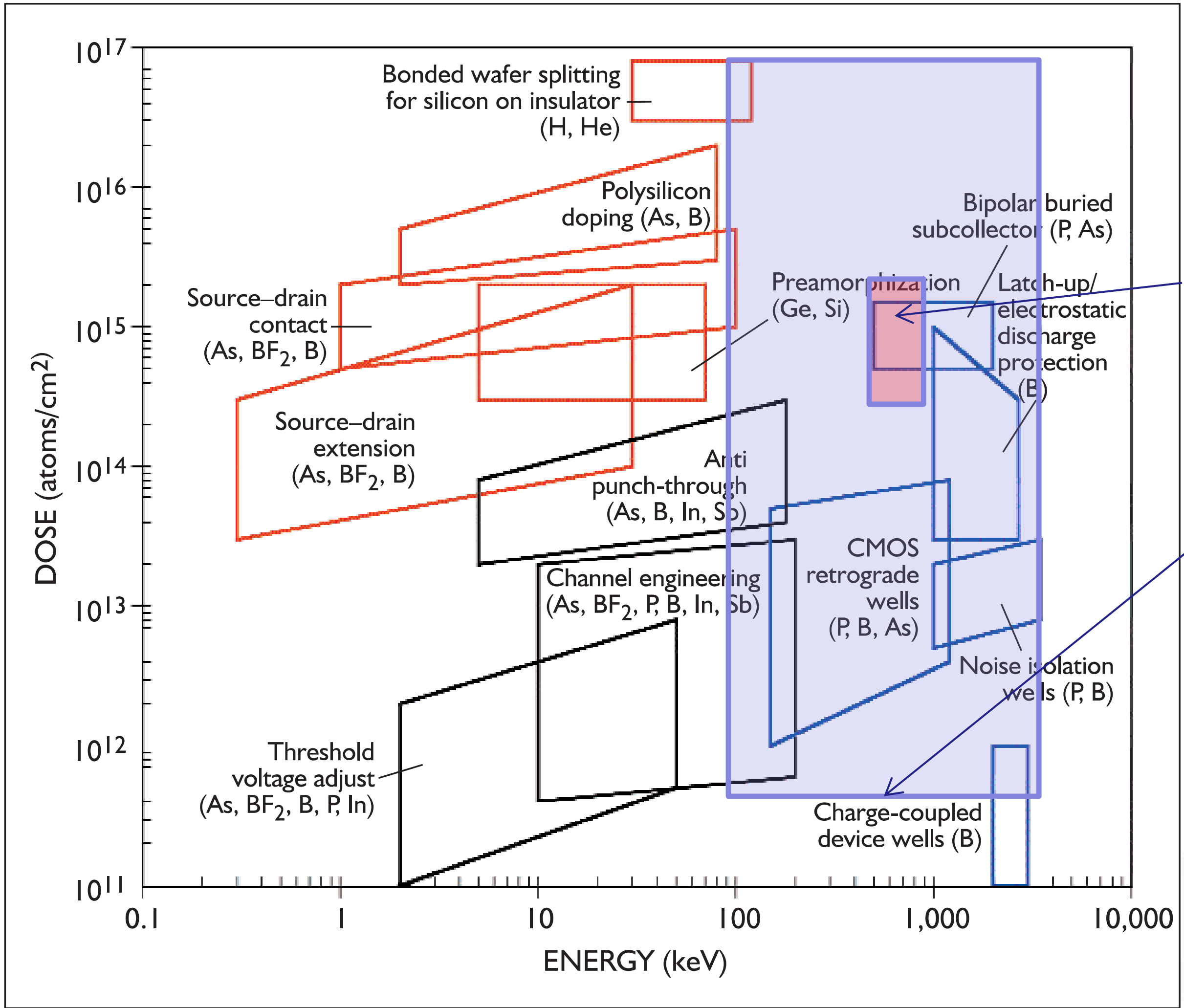


- As expected porous silicon growth has been obtained on implanted areas but results are not optimal as KOH etch does not completely removed the porous silicon layer.
- Porous structure is present in the non implanted areas also.
- Porous silicon growth process:

Parameter	*n*-type
Resistivity	20 Ω·cm
Dopant	Phosphorous
Electrolyte	HF:DI:IPA=1:3:1
Current density	30mA/cm^2
Environment	Dark

Conclusions

• TOP-IMPLART proton linear accelerator has been used to test uniform beam irradiation of silicon samples for potential applications to silicon bulk micromachining (MEMS, Advanced IC Packaging)
• New experiments will be carried on in 2015 and 2016 to investigate the benefits and limit of TOP-IMPLART LINAC use for semiconductor processing
• When energies higher than 11.6 MeV will be reached (next LINAC section) activities on the qualification of electronics components are planned



Current Experiments

TOP-IMPLART capability