Selective and Homo Emitter Junction Formation Using Precise Dopant Concentration Control by Ion Implantation and Microwave, Laser or Furnace Annealing Techniques

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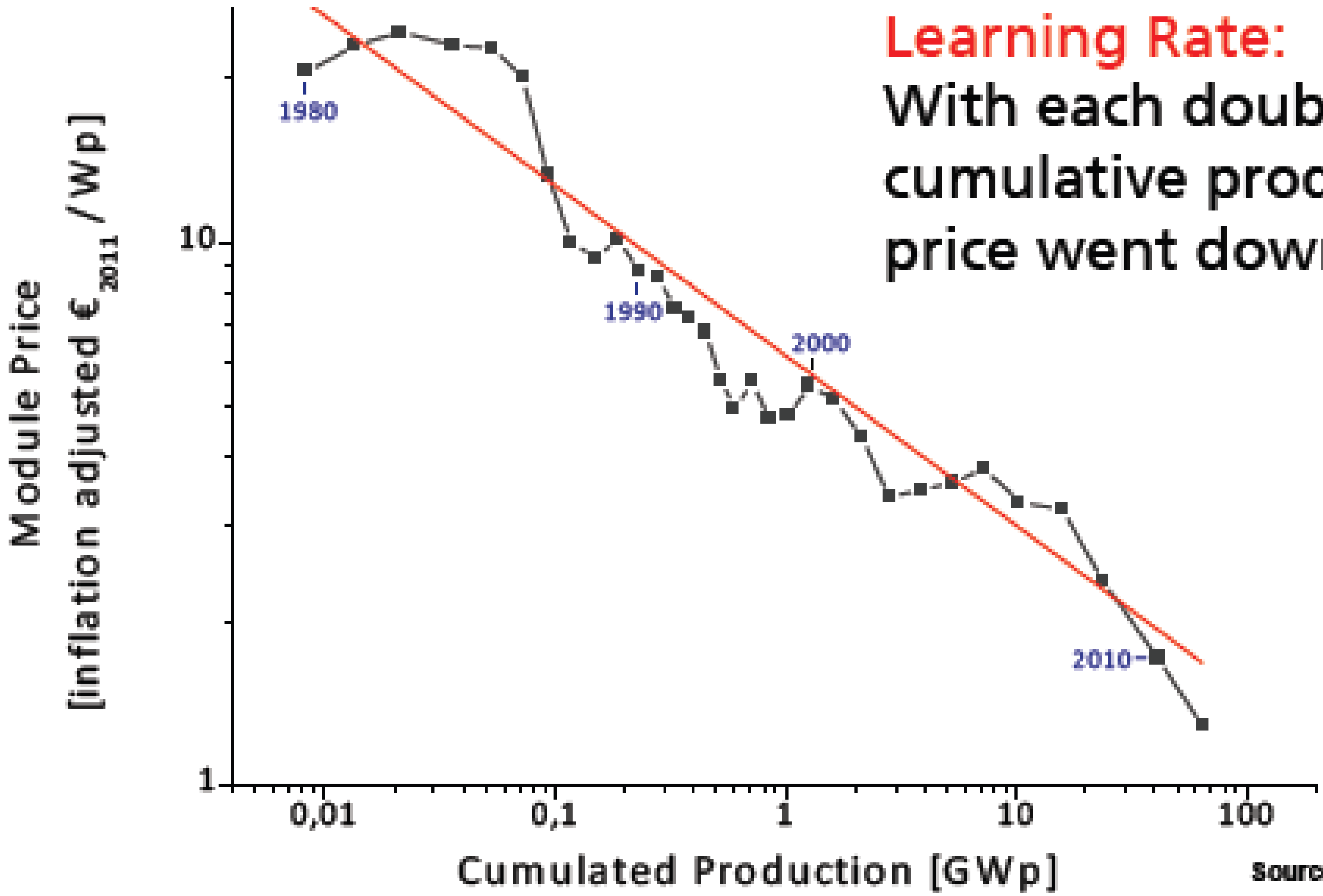
Outline

- Introduction
- Experimentation
- Results
  - Boron implantation
  - Phosphorus implantation
- Summary
- Acknowledgements

Price Learning Curve (all c-Si PV Technologies)



Learning Rate:
With each doubling of cumulative production, price went down by 20%!

Source: Navigant Consulting; EuPD Module price (since 2006)
Design: PSE AG 2012

E. Weber, F-ISE, PVSC-2012

Fraunhofer

At SNEC May 2012 price reported down to $0.67/W!

Solar Cell Dopant Methods

Solar PSG & BSG Dopant Source

- Phosphorus
  - POCl3 Furnace ~850C
  - Phosphorus Acid Spray on Dopant
  - Phosphorus Spin on Dopant
- Boron
  - BBr3 Furnace ~950C
  - BCl3 Furnace
  - Boron Spin on Dopant

Solar Implanted Dopant Source

- **Varian/AMAT (Sept 2010) 1100wph**
  - **Solion-Blue ribbon beam implanter 320mm beam so only (2x3 wafer tray)**
  - **Next Gen will be from FPD implanter**
- **Intevac (Sept 2011) 2400wph**
  - **ENERGi implanter: in-line design, 3 wafers across**
- **Amtech/Kingstone (May 2012) >1600wph**
  - **IonSolar 480mm beam so 3-across tray**

Figure 8. Intevac's ion implantation tool for manufacturing solar cells.


Figure 1. Photograph of Kingstone's solar ion implanter "IonSolar" with automation EFEM. Footprint: 4.9m×3.6m.

25th European Photovoltaic Solar Energy Conference and Exhibition /
5th World Conference on Photovoltaic Energy Conversion, 6-10 September 2010, Valencia, Spain
2DV.1.3

WHY IMPLANT? 1980s switched from POCl3 diffusion furnace to implant!

EMITTER FORMATION USING ION IMPLATATION METHOD FOR FABRICATION OF CRYSTALLINE SILICON SOLAR CELLS

Minsung Jeon, Joonsung Lee, Hoon Oh, Jongkeun Lim, Myungik Hwang, Jaewon Seo, Sangkyun Kim, Wonjae Lee, Eunchol Cho
Photovoltaic Technology Research Department, Electro-Mechanical Research Institute,
Hyundai Heavy Industries Co. Ltd., 102-18 Mabuk-dong, Giheung-gu, Yongin-si, Gyeonggi-do 446-716, Korea

ABSTRACT: In this implantation method phosphosilicate glass necessary after fabric and their characterist efficiency by increas cell efficiencies of > emitter have been acl

Table II: Comparison of the I-V parameters of ion implanted emitter solar cells on p-type Cz wafer with and without laser isolation. The reference cell is $POCl_3$-diffused emitter solar cell with laser isolation. All the value of ion implanted samples is average of 8 solar cells.

	I_{sc} [A]	V_{oc} [mV]	FF [%]	$E_{ffi.}$ [%]
Ref.	8.73	621.3	78.66	17.85
w/ isol.	8.66	627.5	78.50	17.86
w/o isol.	8.82	629.8	78.34	18.21

+0.01%
+0.36%

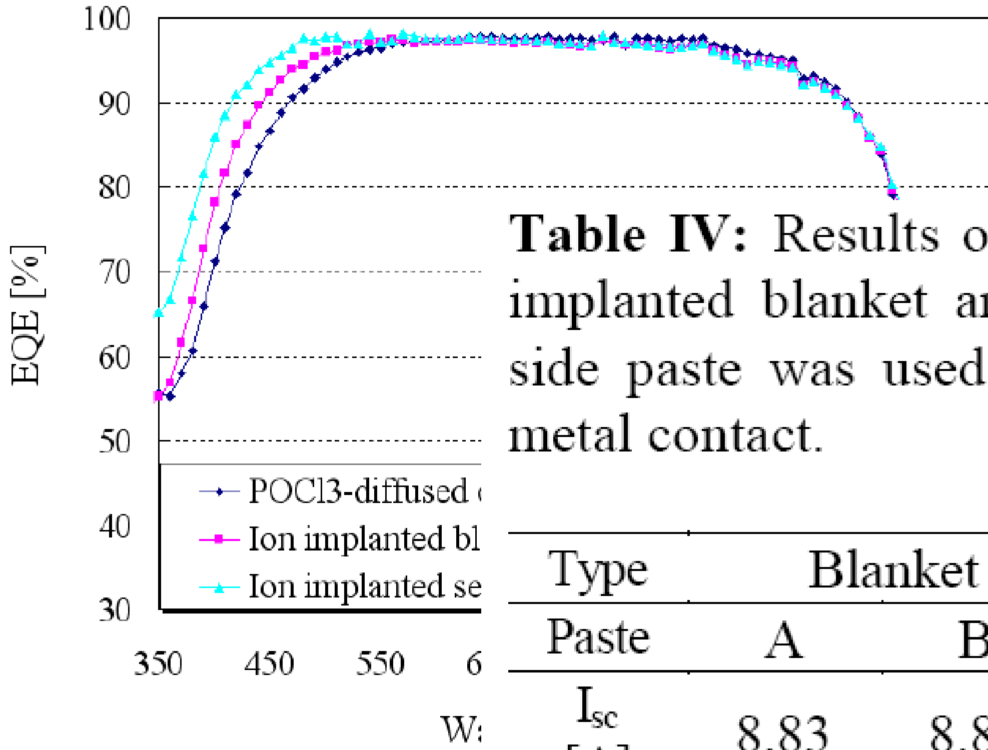


Figure 5: Comparison of th
(EQE) for a $POCl_3$-diffu
implanted blanket emitter
emitter solar cell.

Table IV: Results of the fabricated solar cells with ion implanted blanket and selective emitter. Same Al back side paste was used. All the samples have 3-bbr front metal contact.

Type	Blanket emitter			Selective emitter		
Paste	A	B	C	A	B	C
I_{sc} [A]	8.83	8.86	8.86	8.86	8.97	8.94
V_{oc} [mV]	630.2	629.5	629.8	631.8	636.6	636.7
FF [%]	78.82	78.92	78.51	78.65	77.54	77.9
Effi. [%]	18.35	18.42	18.32	18.42	18.53	18.55
Rs [mΩ]	3.28	2.71	3.21	3.24	4.01	3.54
R_{sh} [Ω]	37.04	55.11	44.54	52.06	36.28	28.46

+0.1%

J.O.B. Technologies (Strategic Marketing, Sales & Technology)

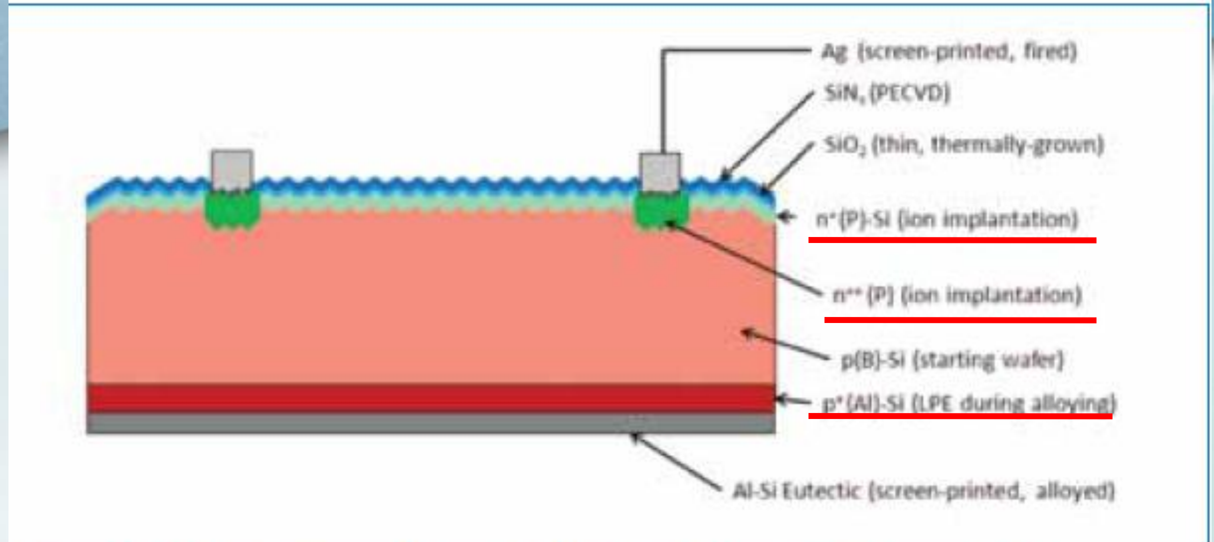


Figure 10. Cell structure with ion-implanted selective emitter instead of a homogeneous emitter.

Phos-implanted Selective Emitter Improved Cell Efficiency By Only 0.1-0.2%!

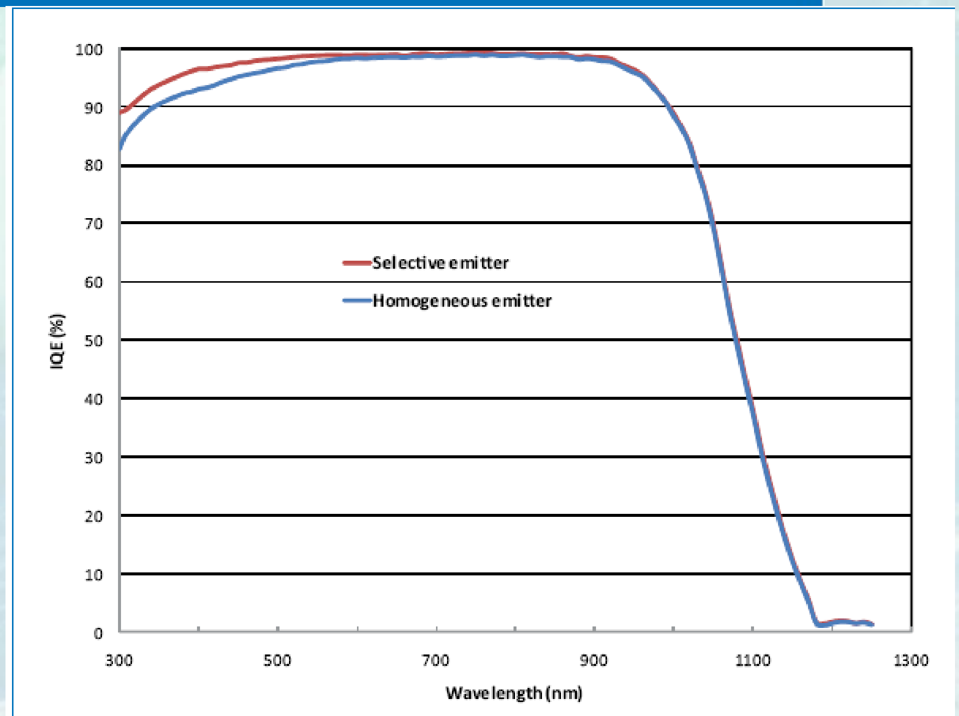


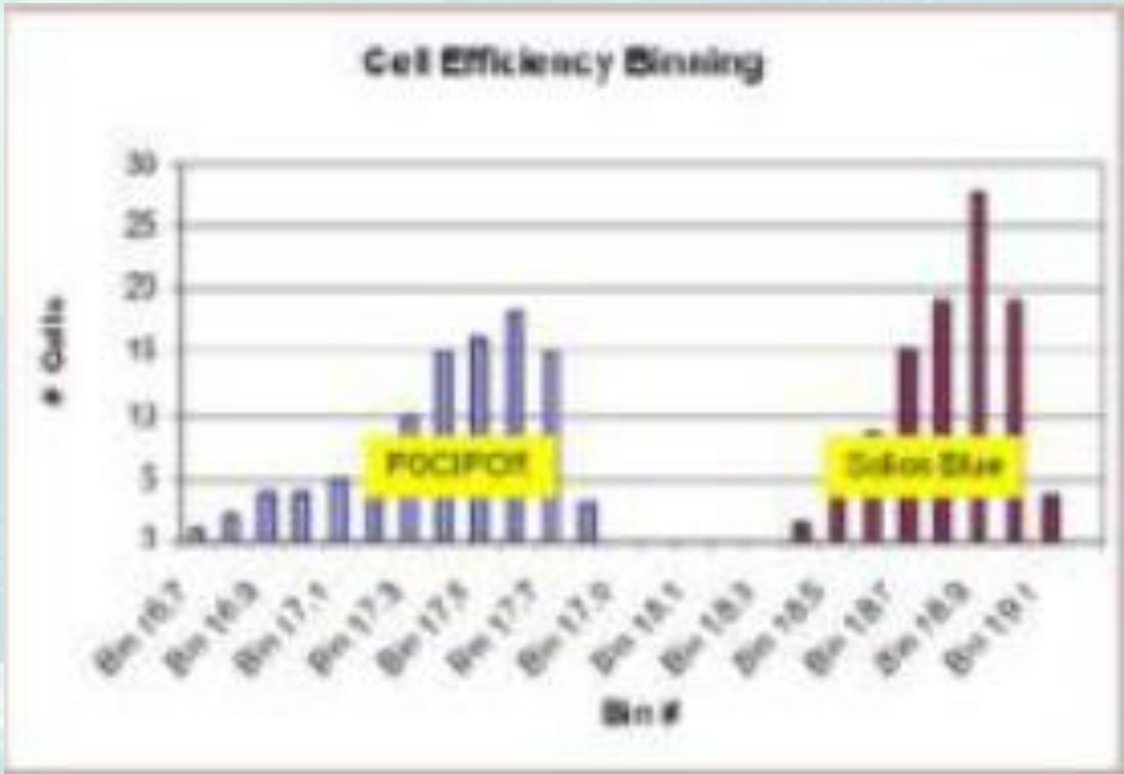
Figure 11. Measured IQE for cells having a homogeneous emitter and a selective emitter.

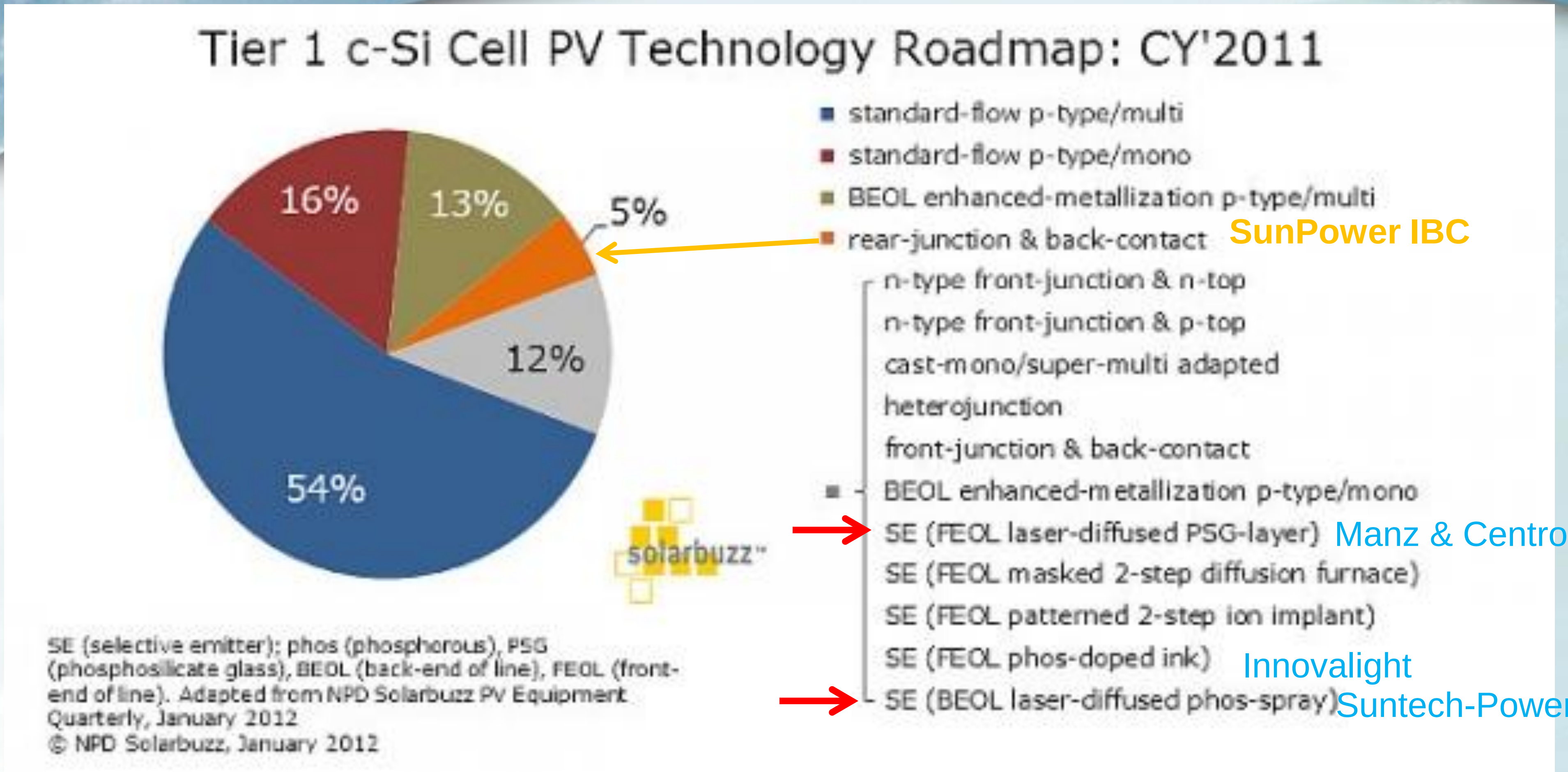
J.O.B. Technologies (Strategic Marketing, Sales & Technology)

Condition	Hyundai	Suniva	Innovalight	Suntech
Std POCl3	17.85%	18.0%	17.95%	17.8%
P-implant wLaser Isolation	17.86% **+0.01%**			
P-implant w/o Isolation	18.21% **+0.35%**	19.0% **+1%**		
	18.36%			
Selective E P-implant	18.50% **+0.14%**	19.1% **+0.1%**		
total	=+0.65%	=+1.1%		
SE Paste			18.9% **+1.0%**	
SE-Laser Melt				19.2% **+1-2%**

EIPBN Plenary talk 3: Mark Pinto, GM of Applied EES/Solar group on “Silicon Photovoltaics: Accelerating To Grid Parity”. He said **Implant improving wafer binning**.

PVSC-2012 Paper 881: Paul Sullivan of **AMAT/VSE** on “Ion Implantation for PV”. Today with the Solion they are at 50mA so throughput is ~1100wph with uniformity of <3%, Rs<3%, wafer breakage of <0.2% and uptime of >90%. He showed the results reported by Astronergy on their Nova-cell which was reported at the May SNEC vTech seminar. Nova-cell using implant emitter is at 19.3% efficiency with tight binning which is a +0.87% efficiency advantage compared to $POCl_3$ at 18.4%.





Many Different Options For Selective Emitter

-Phos Ink Paste

-Phos silicon etch back of screen printed WAX

-Localized Laser Melt (LLM) or Laser Doped Selective Emitter (LDSE)

Innovalight Selective Emitter Si-Ink Doping

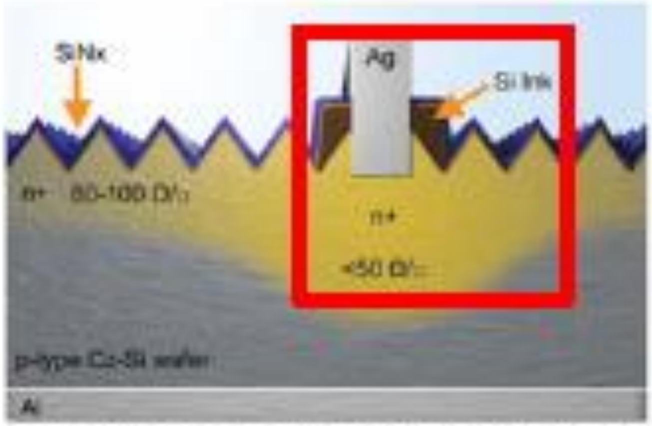


Figure 1: Cross section of Cougar cell architecture using Innovalight Silicon Ink (drawing not to scale)

Fig.16: Innovalights SE silicon ink.

Cell Structure		Voc (mV)	Jsc (mA/cm^2)	FF (%)	Efficiency (%)
Cougar	Average (100 cells)	0.637	37.6	78.9	18.9
Reference	Average (100 cells)	0.621	36.5	79.2	17.95

Table 1: Average values of four I-V parameters for Cougar cells against reference homogeneous emitter cells. Data confirmed by ISE CalLab in Freiburg, Germany

Fig.17: Improved cell efficiency by 1%.

2E20/cm3=>3E15/cm2 <50Ω/□.

2E19/cm3=<1E15/cm2 >120Ω/□.

EF: Xj=0.3um

SE: Xj=0.7um

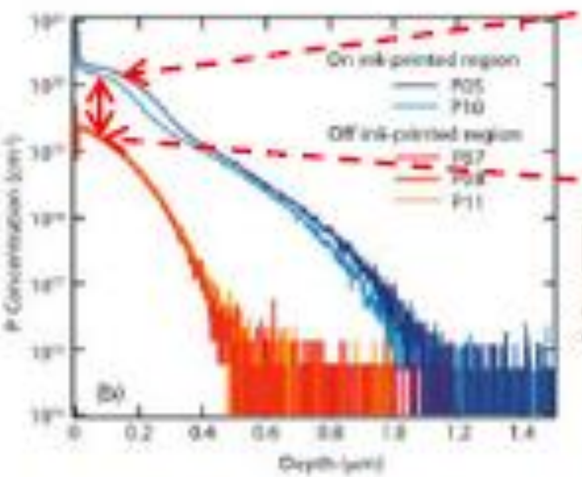


Fig.18: Note the higher P level in SE regions.

Figure 1: Typical internal quantum efficiency (IQE) curves for the Cougar selective emitter structure and a reference homogeneous emitter cell

Fig.19: Improved blue light IQE.

Applied now also offers this with Honeywell paste press-release Feb 22, 2011.

Dupont purchases Innovalight July 2011

Paper 882: M. Nejati of **MAGI Solar** on "Etching Paste for Innovative Solar Cell Applications". They reported on a new paste that etches oxide or PSG at 60nm/min at room temperature! So they did a 2-step $POCl_3$ doping for SE for 100Ω/□ and 50Ω/□ emitter regions. For 50Ω/□ homo emitter they reported cell efficiency of 18.3% +/- 0.4% while SE 50Ω/□ and 100Ω/□ efficiency of 18.8% +/-0.2% for a 0.5% efficiency improvement and tighter distribution/binning also! So not only implant for tighter binning! Fig.9 below shows the scatter plot for 600 homo emitter wafers and 200 SE wafers while Table I summaries the results.

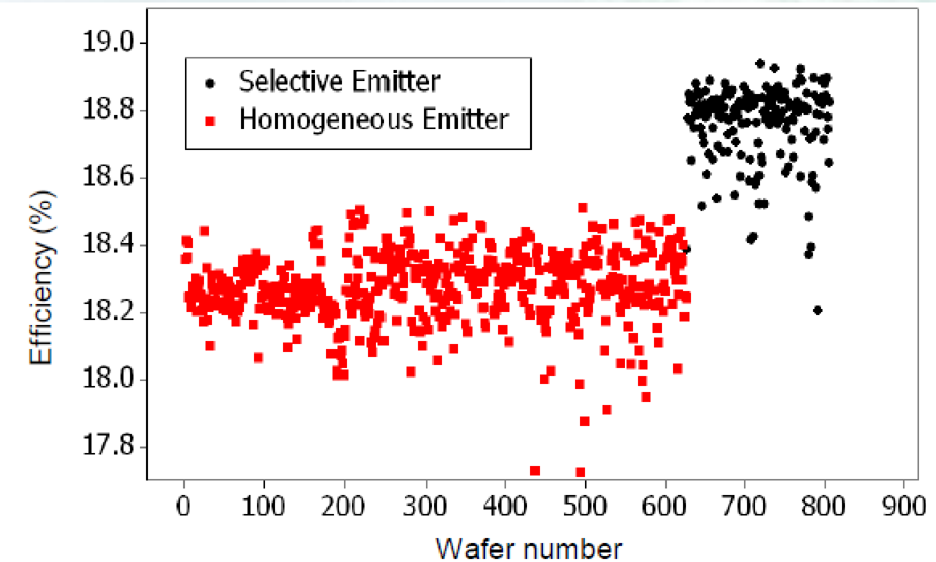


Fig. 9. Scatter plot of the conversion efficiencies (%) of selective emitter vs homogeneous emitter.

TABLE I

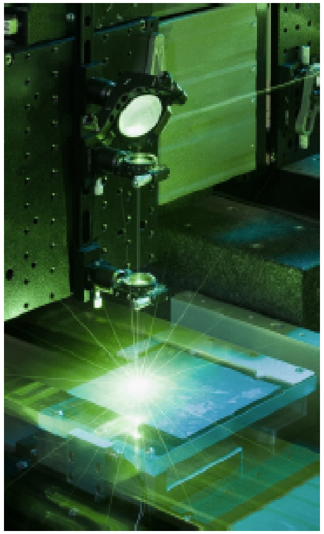
AVERAGE I-V CHARACTERISTICS OF SOLAR CELLS WITH DIFFERENT EMITTER STRUCTURES.

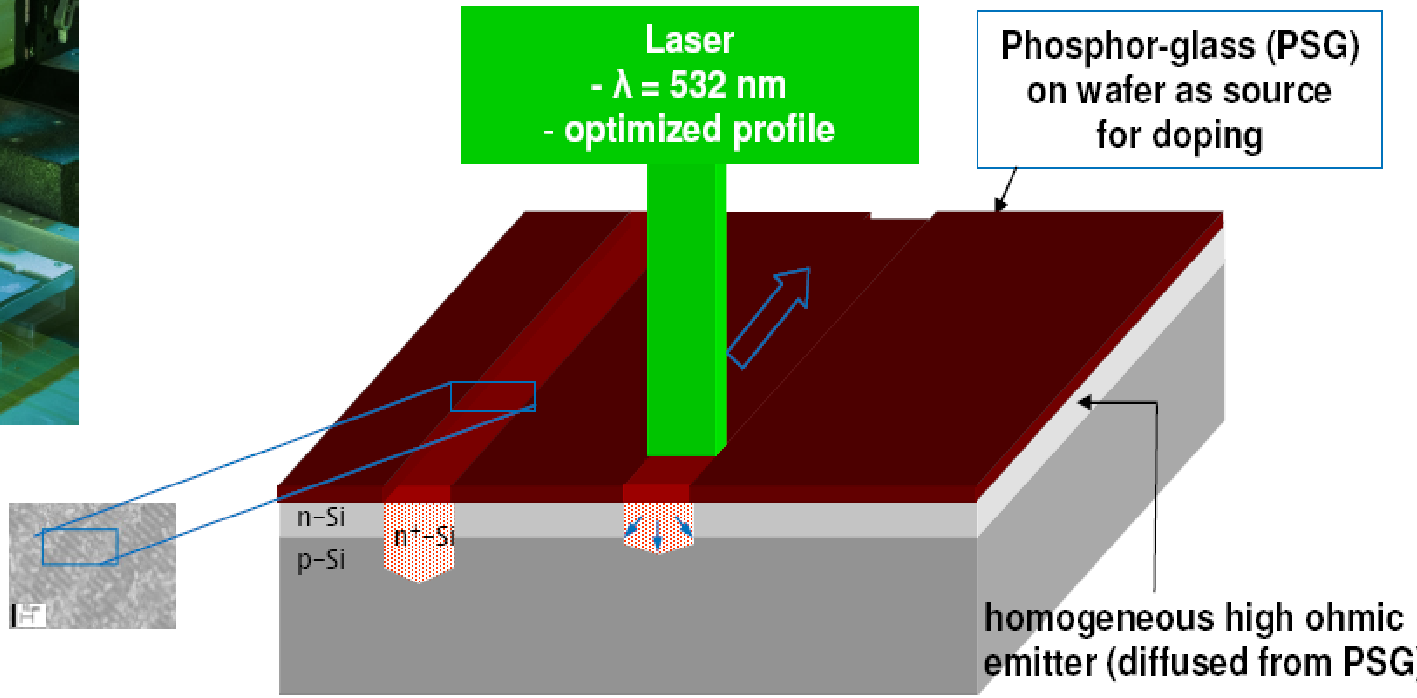
Average Parameter	Selective emitter	Homogeneous emitter	Δ
Efficiency (%)	18.79	18.27	+ 0.52
FF (%)	79.45	79.07	+ 0.38
J_{SC} (mA/cm^2)	37.08	36.83	+ 0.25
V_{OC} (mV)	638	627	+ 11

Tighter Binning Too!

Efficiency: selective emitter cell I

Laser process provides additional doping from PSG glass





Only one laser process step added to mainstream cell process.

Optimisation of laser process (power/profile/pulse, no defects in silicon…) essential

LLM used for both c-Si and multi-Si Solar Cells!

PVSC-2011: #617 & 627 Centrotherm LDSE of 18.9% (EF=120Ω/□, SE=30 Ω/□ no change in P-SIMS)

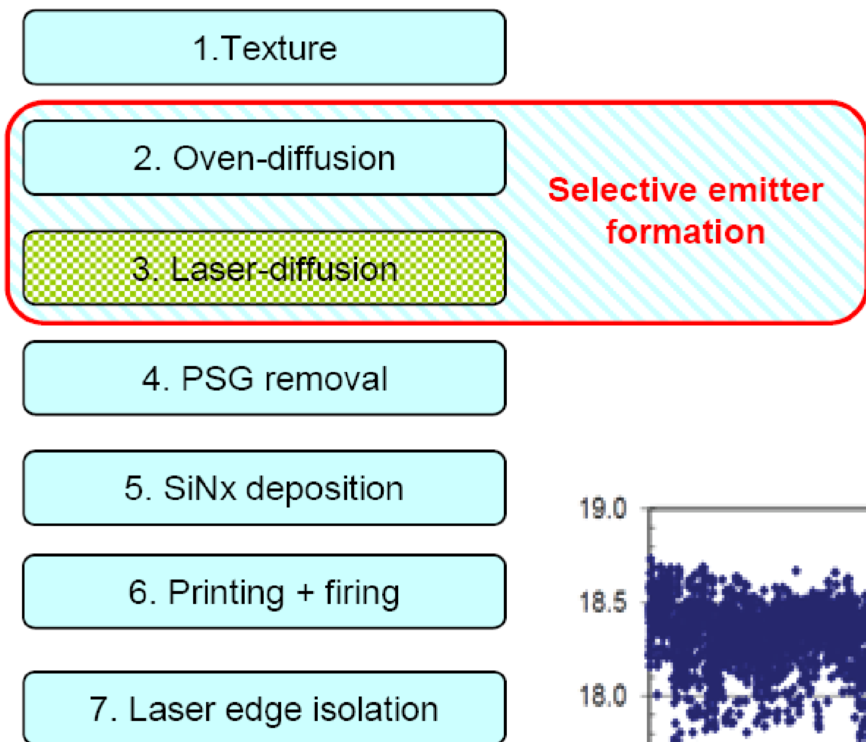
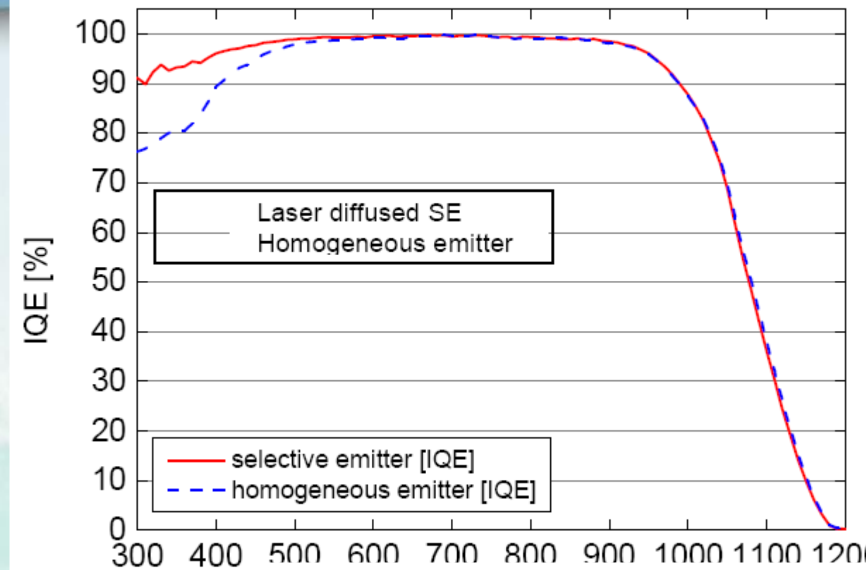
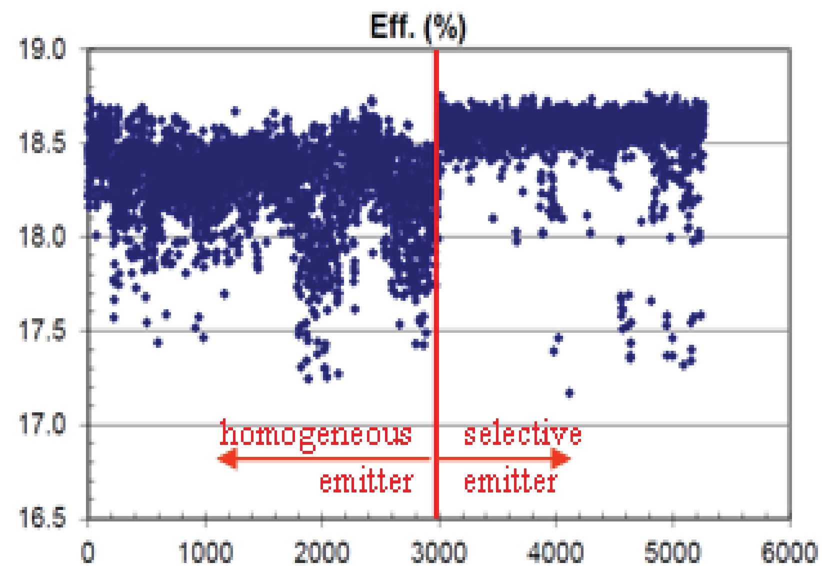
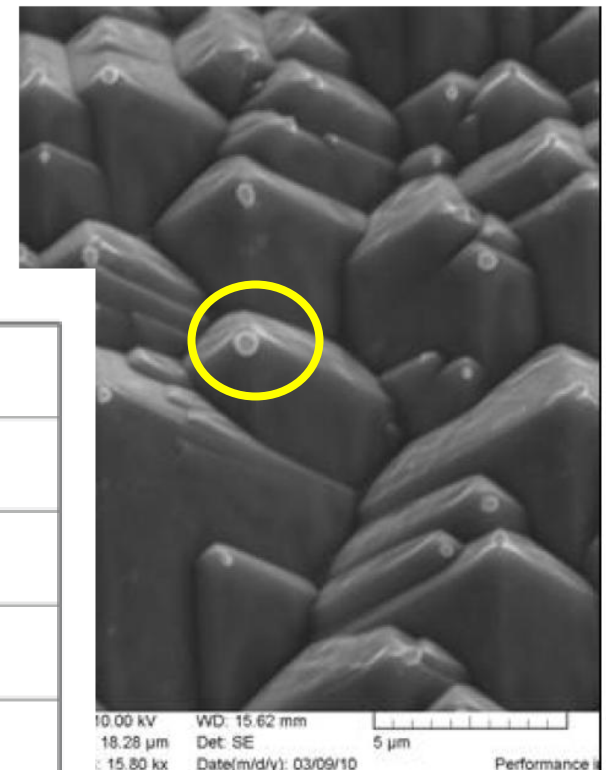


Fig. 3: Schematic overview of la
emitter process as implement
turn-key lines. The selectiv
consists of both an oven-diffus
emitter. After oven-diffusion
emitter is applied by structurin
in a grid-like pattern.

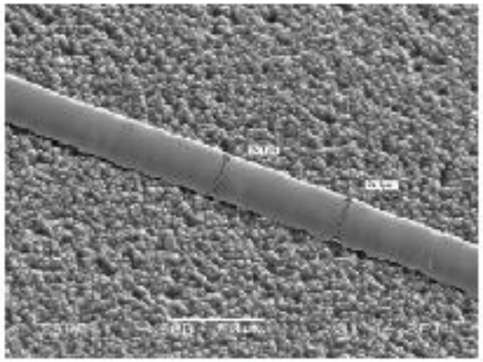




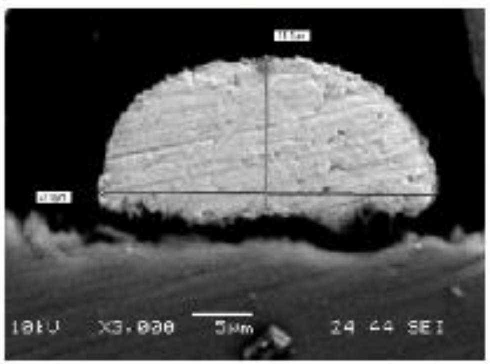


2: Wafer surface after laser treatment. Only the
s of the pyramids were slightly molten.

Suntech's Pluto Cell



(a)



(b)

Figure 3: (a) Typical metal finger for the PLUTO cell demonstrating line width, height and aspect ratio the same as routinely achieved by the PERL cell using photolithographic and masking techniques. (b) Shows the cross-section of a typical PLUTO metal line.

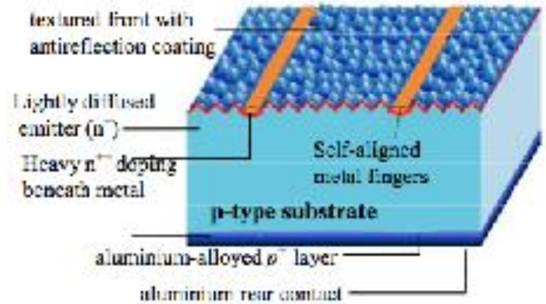


Figure 6: Schematic of the simplified PLUTO solar cell with screen-printed and fired rear aluminium contact and front metal lines only 20-25 microns wide.

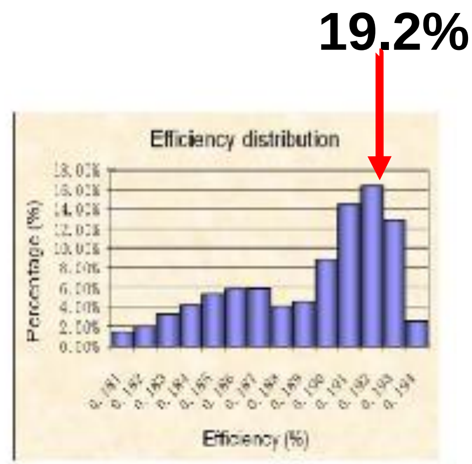


Figure 8: Typical efficiency distribution for a single-day's production of the 34MW PLUTO production line following 6 months of operation. The bimodal distribution has been shown to be caused by wafers fitting into two distinct categories based on quality.

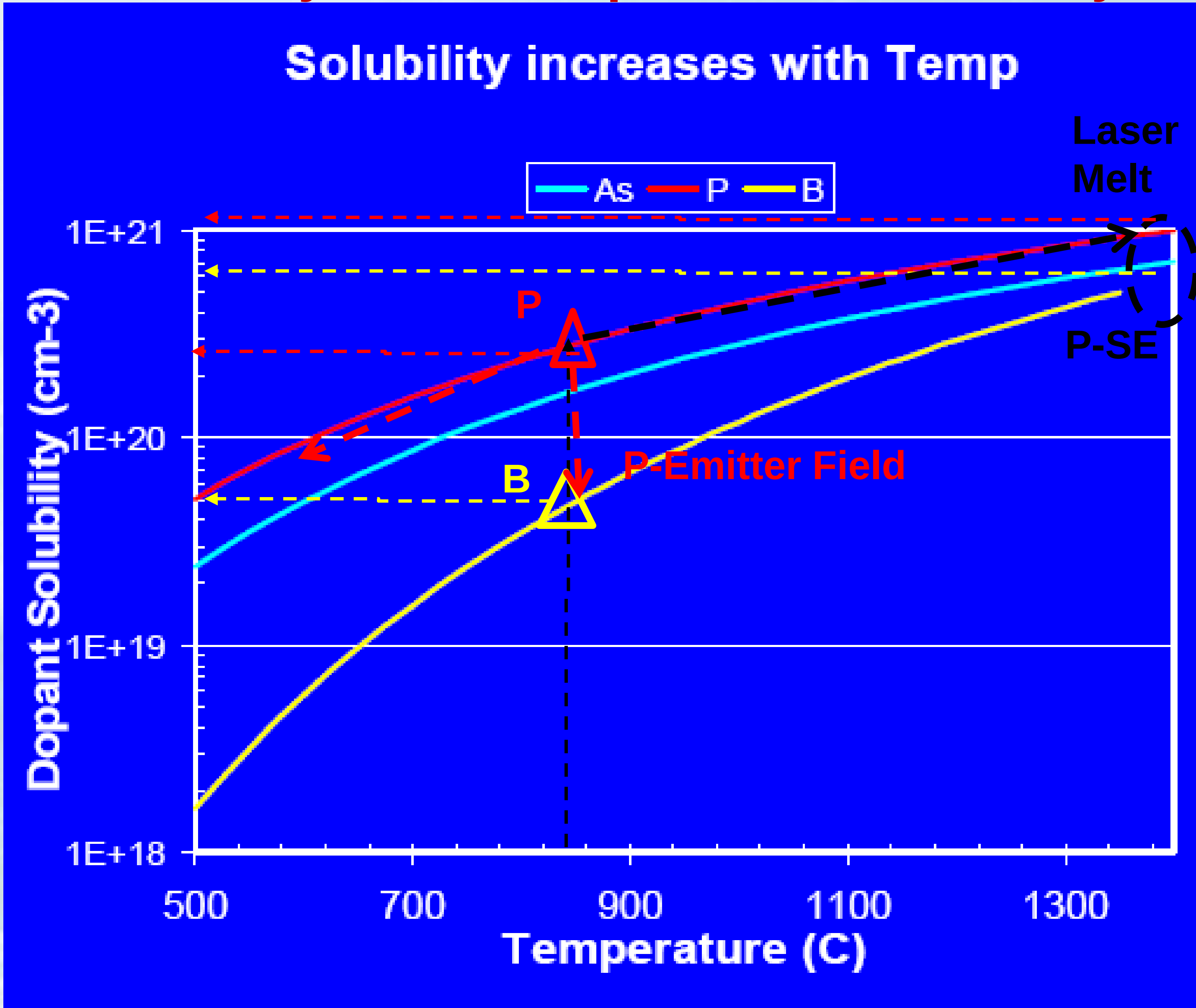
Process features

- Selective emitter
- Fine grid lines with high aspect ratio (enabling close spacing to minimize ohmic losses with selective emitter)
- Relatively little added cost over conventional process
- 1-2% absolute efficiency gain

From Shi, Wenham and Ji, 2009 IEEE PVSEC, Philadelphia

Use Phosphoric Acid deposition over SiN and then laser ablation of the selective emitter fingers

Introduction: Many Different Options For Selective Emitter But Localized Laser Melt Annealing Will Achieve Highest Dopant Activation Efficiency Due To Dopant Solid Solubility Limit In Silicon!



Excess Phos as Interstitials or Cluster Precipitates?

Kennel, Intel, IEEE/RTP 2006

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  - Boron implantation
  - Phosphorus implantation
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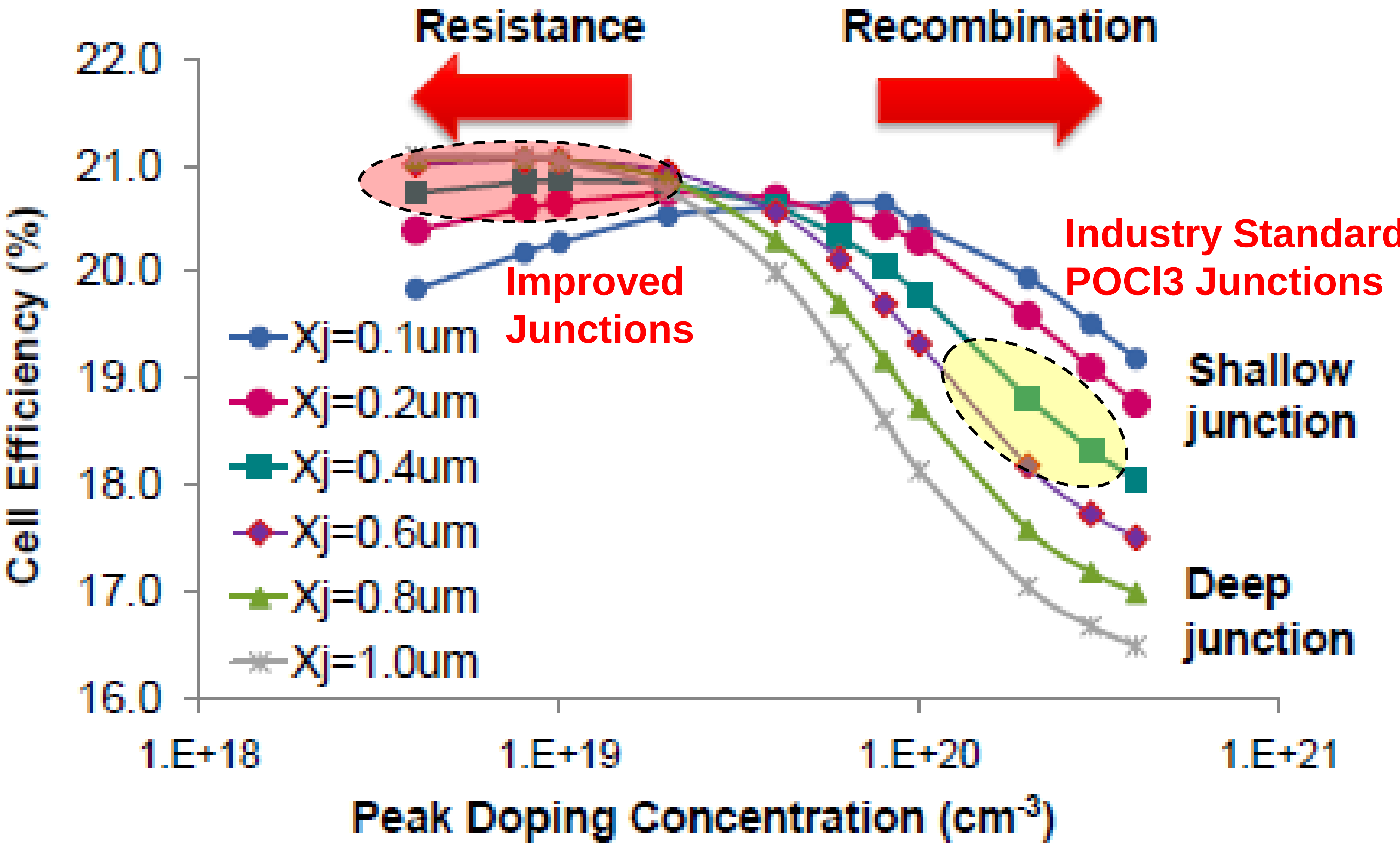
Activity

- Implant Matrix by Kingstone (King-Core) in China
- Furnace Anneal Junction Simulations by Synopsys
- Localized Laser Melt Annealing by Jenoptiks/Innovavent GmbH in Germany
- Furnace Anneals, POCl3, BBr3 & ECV analysis by Tempress in the Netherlands
- Low Temperature Microwave Annealing by National Nano Device Lab in Taiwan
- SIMS analysis by Evans Analytical Group



Resistance
Recombination
22.0
21.0
20.0
19.0
18.0
17.0
16.0
Cell Efficiency (%)
Improved
Junctions
Industry Standard
POCl3 Junctions
Xj=0.1um
Xj=0.2um
Xj=0.4um
Xj=0.6um
Xj=0.8um
Xj=1.0um
Shallow
junction
Deep
junction
1.E+18
1.E+19
1.E+20
1.E+21
Peak Doping Concentration (cm-3)

Experimentation

Species	Dose	Energy	Microwave	750C	850C	1050C	Laser=1J	3J	5J	6.7J
B	3E14	15keV	X	X	X	X	X	X	X	X
B	3E14	30keV	X	X	X	X	X	X	X	X
B	1E15	15keV	X	X	X	X	X	X	X	X
B	1E15	30keV	X	X	X	X	X	X	X	X
B	3E15	15keV	X	X	X	X	X	X	X	X
B	3E15	30keV	X	X	X	X	X	X	X	X
B	1E16	15keV	X	X	X	X	X	X	X	X
B	1E16	30keV	X	X	X	X	X	X	X	X
P	3E14	15keV	X	X	X	X	X	X	X	X
P	3E14	30keV	X	X	X	X	X	X	X	X
P	1E15	15keV	X	X	X	X	X	X	X	X
P	1E15	30keV	X	X	X	X	X	X	X	X
P	3E15	15keV	X	X	X	X	X	X	X	X
P	3E15	30keV	X	X	X	X	X	X	X	X
P	1E16	15keV	X	X	X	X	X	X	X	X
P	1E16	30keV	X	X	X	X	X	X	X	X
$POCl_3$ →							X	X	X	X
BBr_3 →							X	X	X	X

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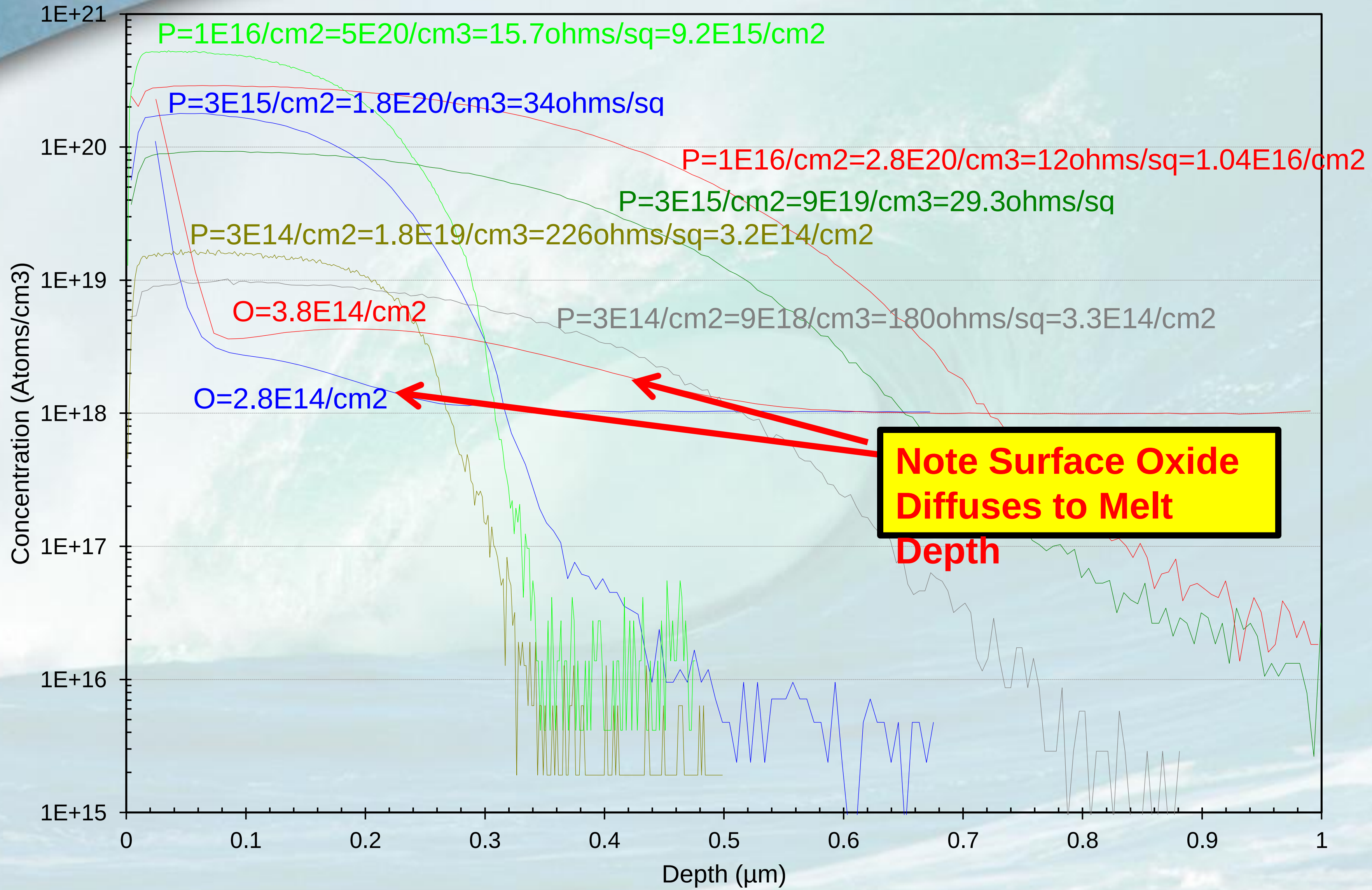
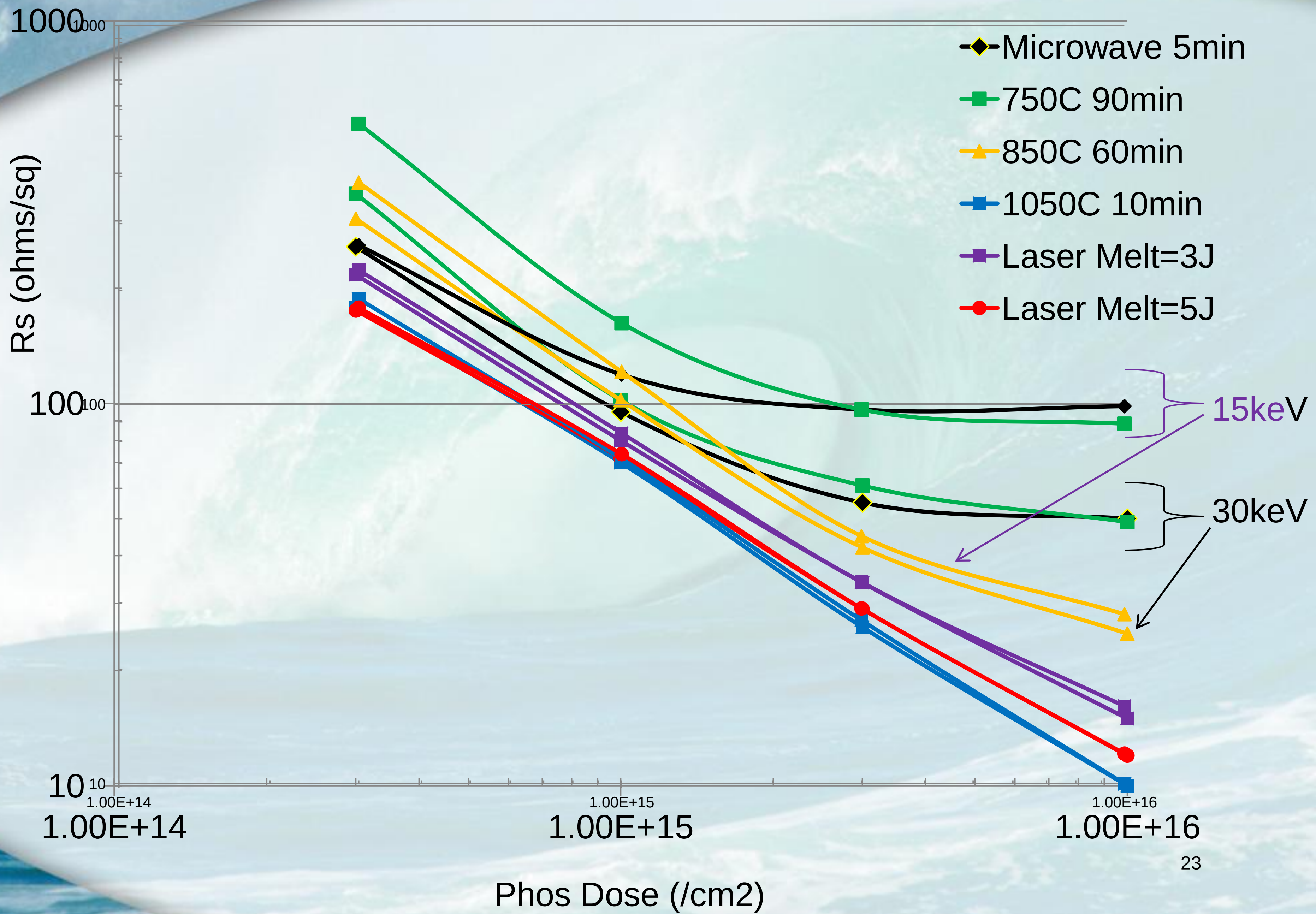
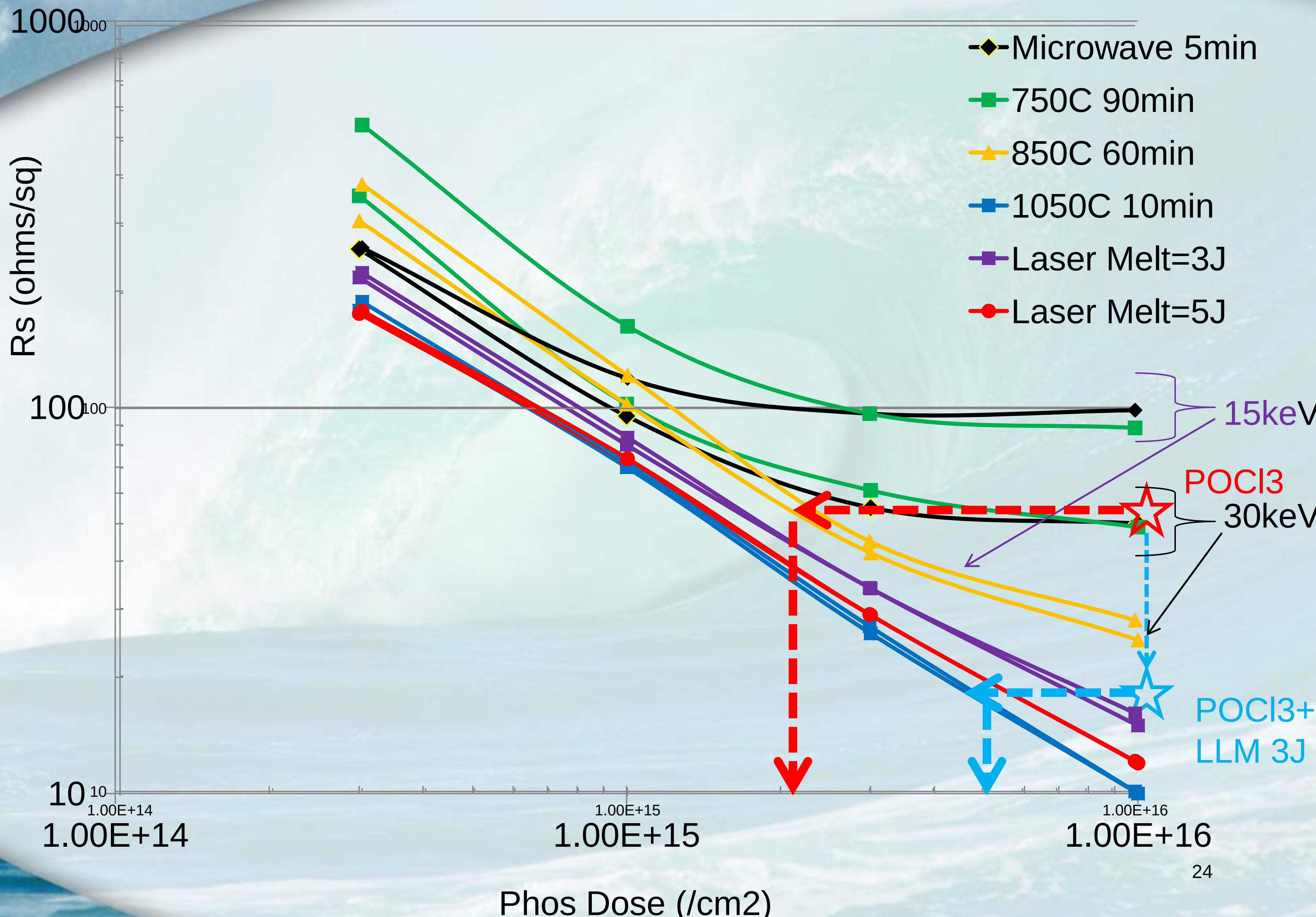


1E+21
1E+20
1E+19
1E+18
1E+17
1E+16
1E+15
Concentration (Atoms/cm3)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Depth (µm)
P=1E16/cm2=5E20/cm3=15.7ohms/sq=9.2E15/cm2
P=3E15/cm2=1.8E20/cm3=34ohms/sq
P=1E16/cm2=2.8E20/cm3=12ohms/sq=1.04E16/cm2
P=3E15/cm2=9E19/cm3=29.3ohms/sq
P=3E14/cm2=1.8E19/cm3=226ohms/sq=3.2E14/cm2
O=3.8E14/cm2
P=3E14/cm2=9E18/cm3=180ohms/sq=3.3E14/cm2
O=2.8E14/cm2
Note Surface Oxide Diffuses to Melt Depth

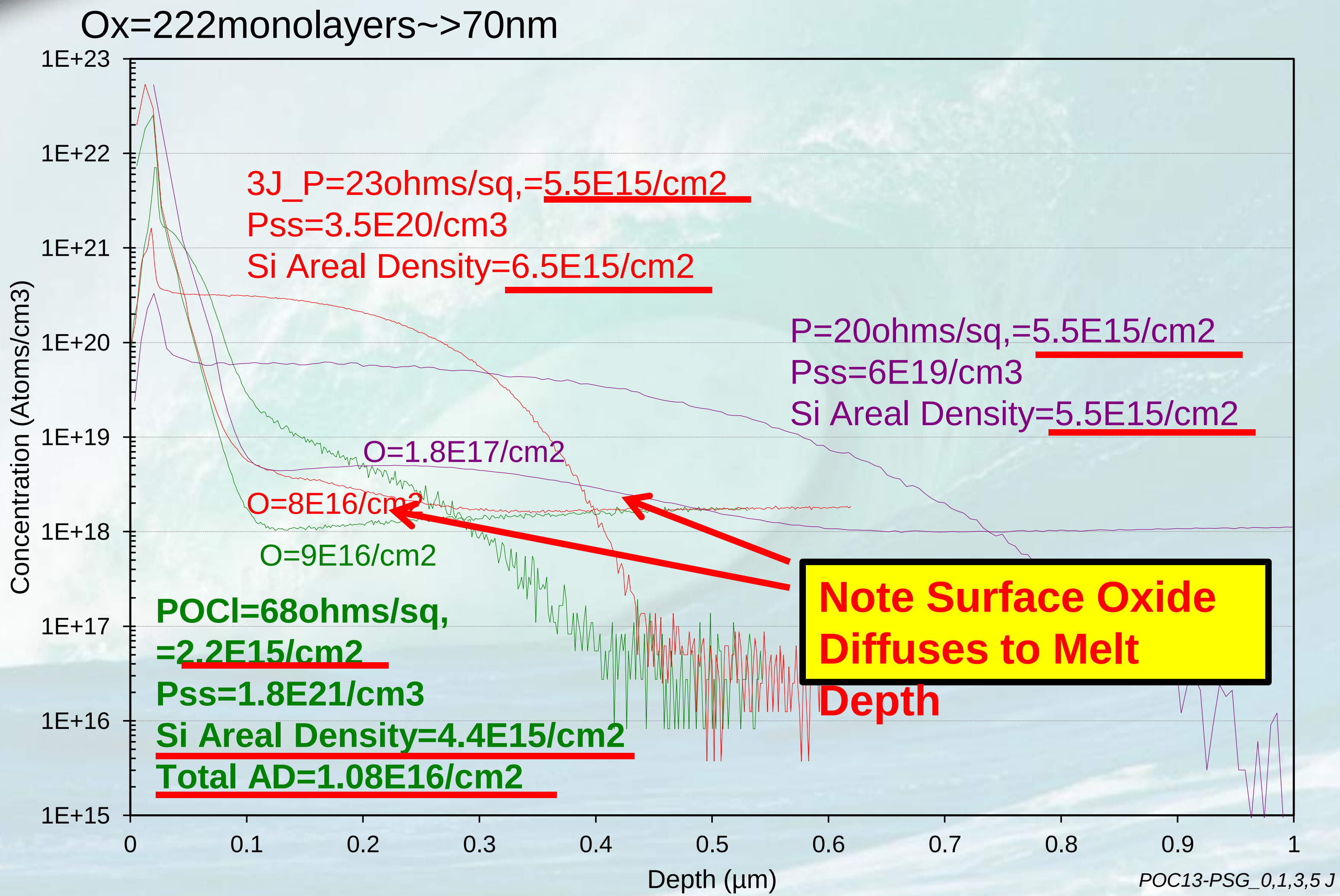
Phos Implant 15keV & 30keV

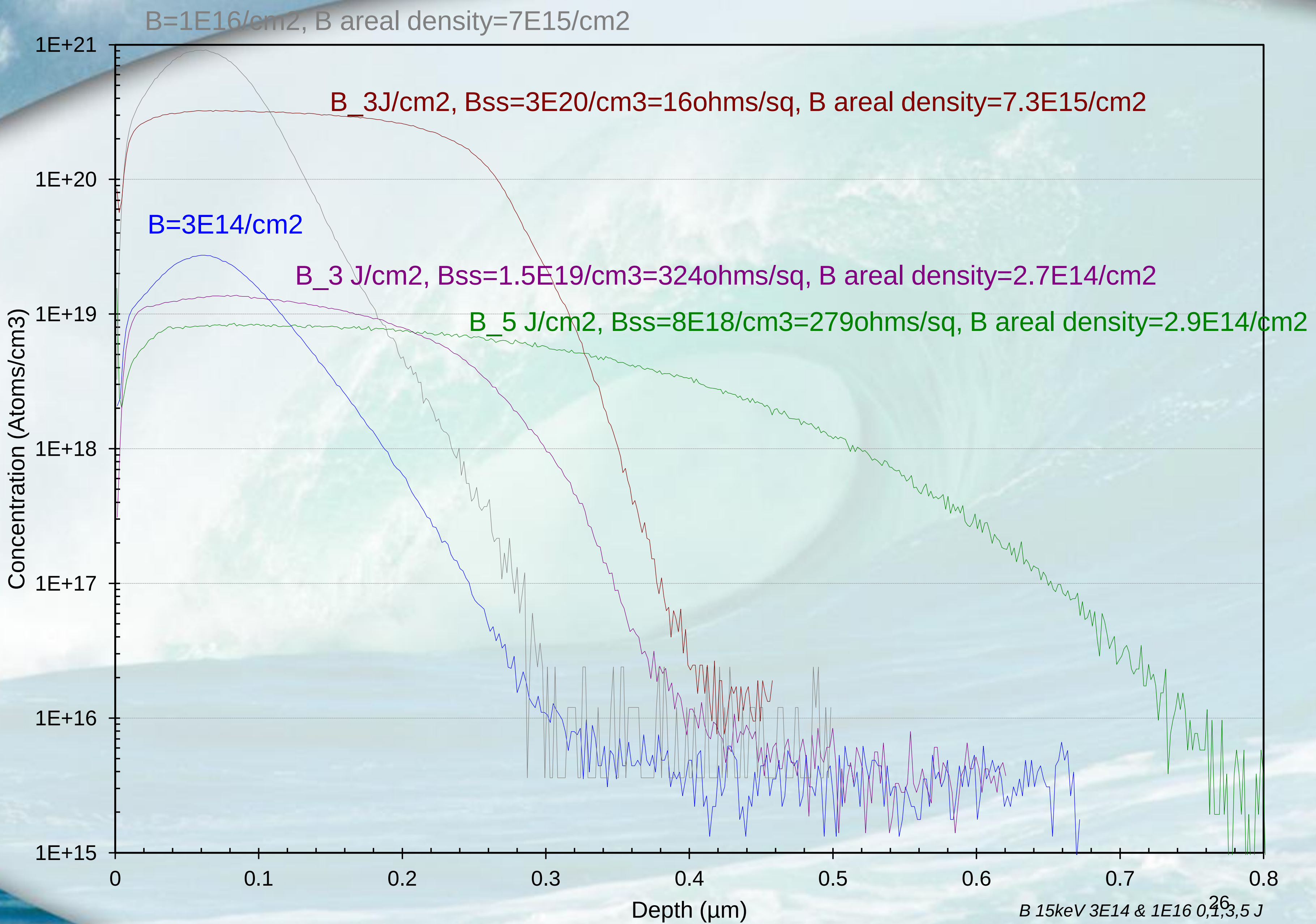


Phos Implant 15keV & 30keV

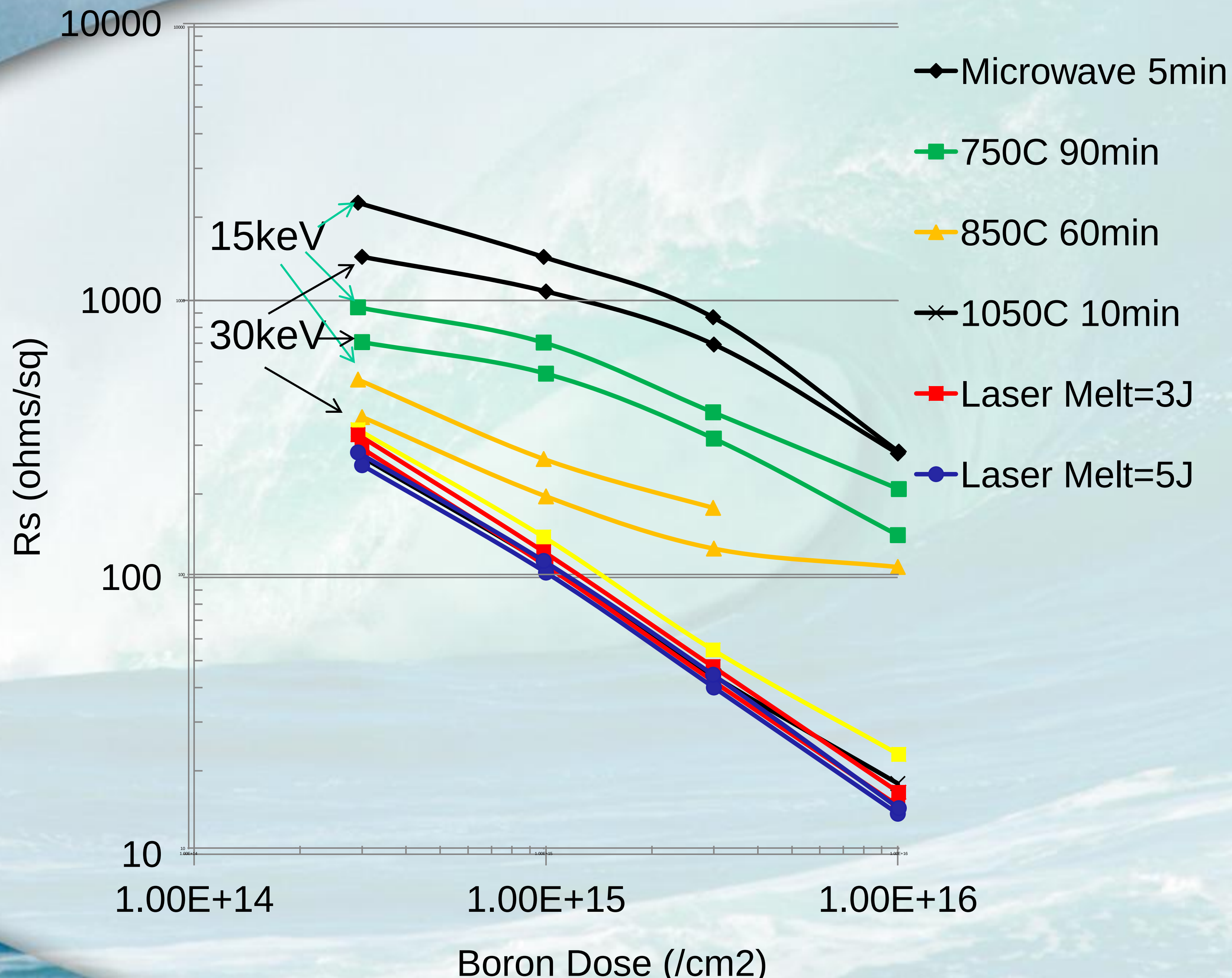


POCl3 Laser SIMS Results

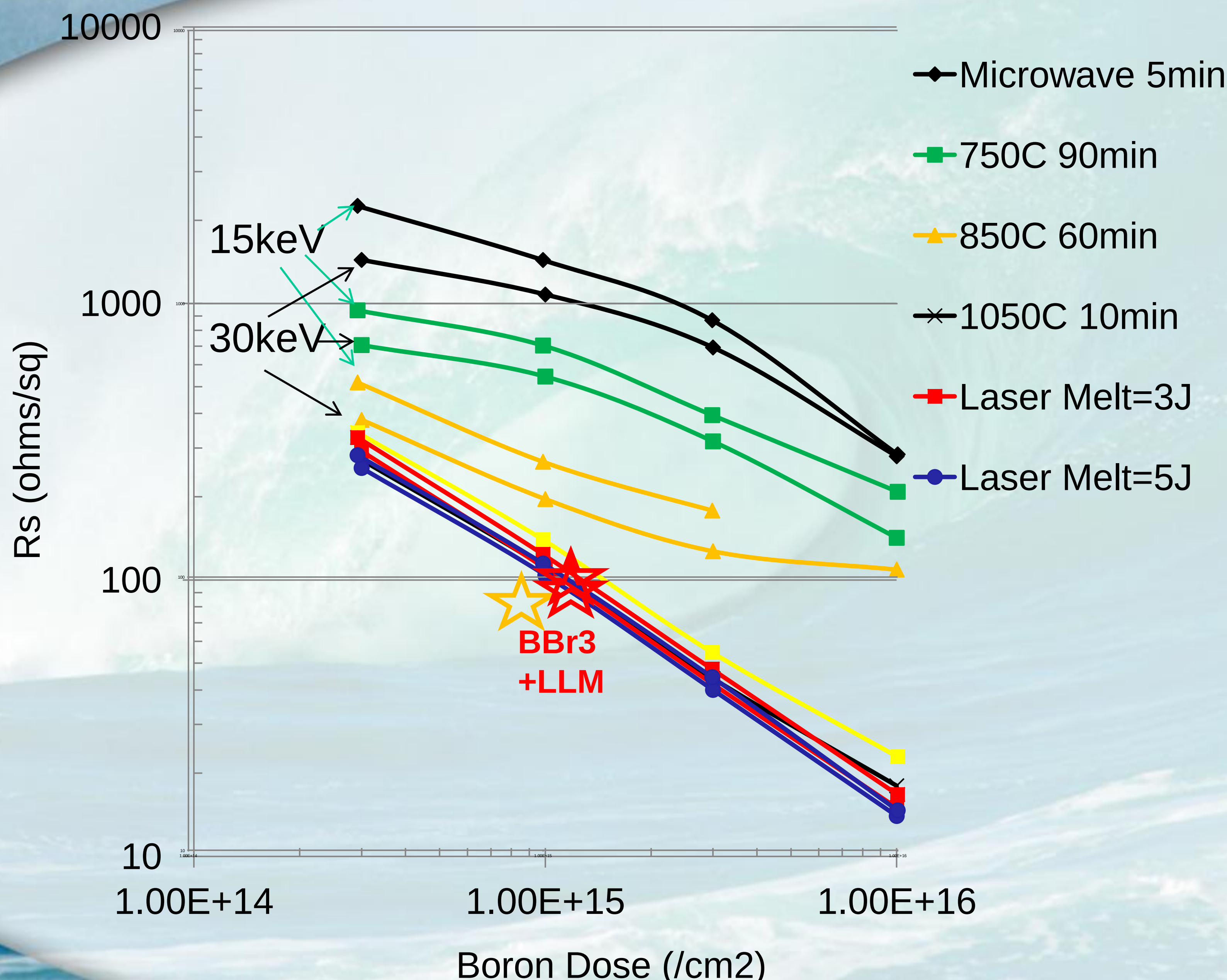


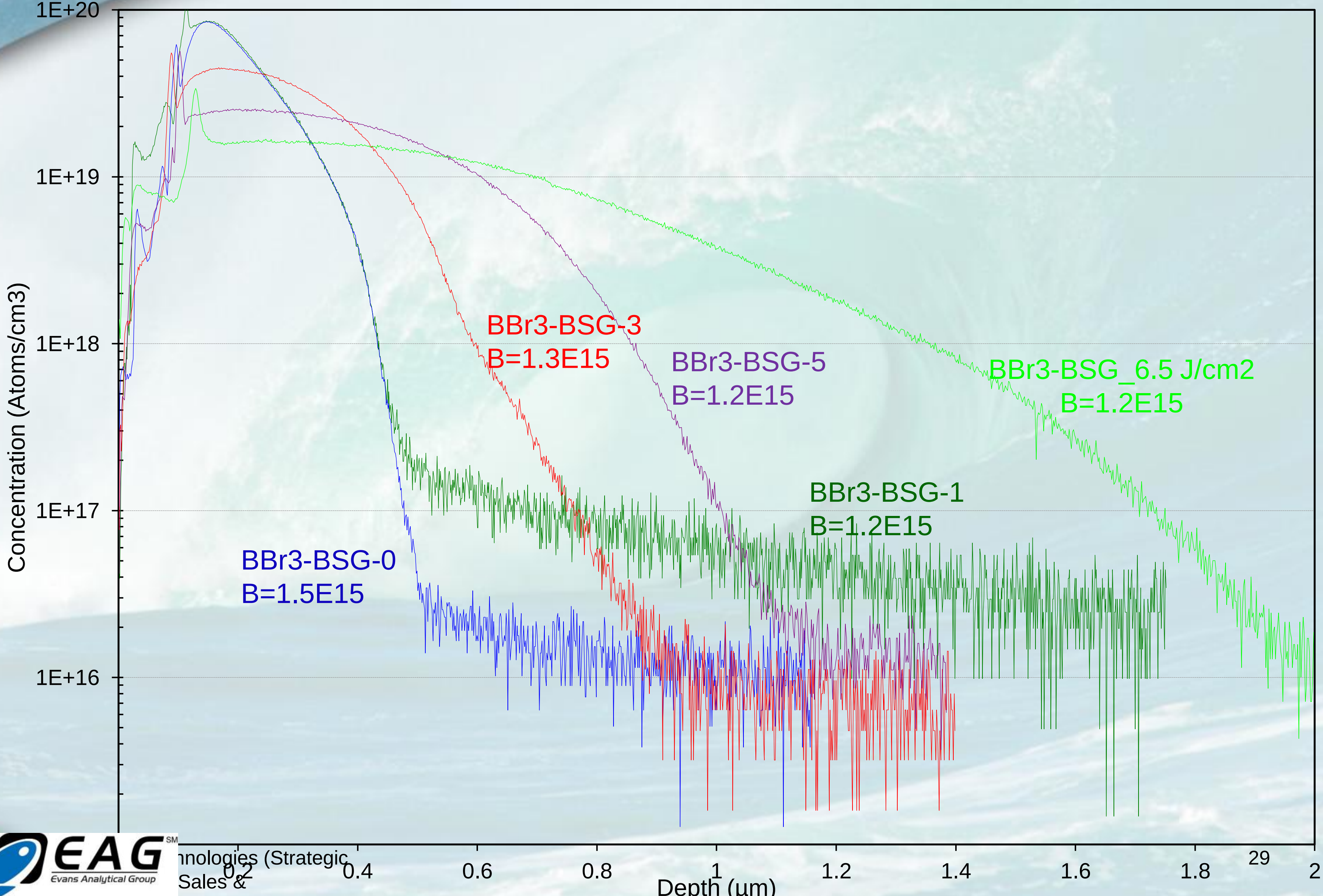

B=1E16/cm2, B areal density=7E15/cm2
B_3J/cm2, Bss=3E20/cm3=16ohms/sq, B areal density=7.3E15/cm2
B=3E14/cm2
B_3 J/cm2, Bss=1.5E19/cm3=324ohms/sq, B areal density=2.7E14/cm2
B_5 J/cm2, Bss=8E18/cm3=279ohms/sq, B areal density=2.9E14/cm2
Concentration (Atoms/cm3)
1E+21
1E+20
1E+19
1E+18
1E+17
1E+16
1E+15
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
Depth (µm)
B 15keV 3E14 & 1E16 0,1,3,5 J

Boron 15keV & 30keV Implant



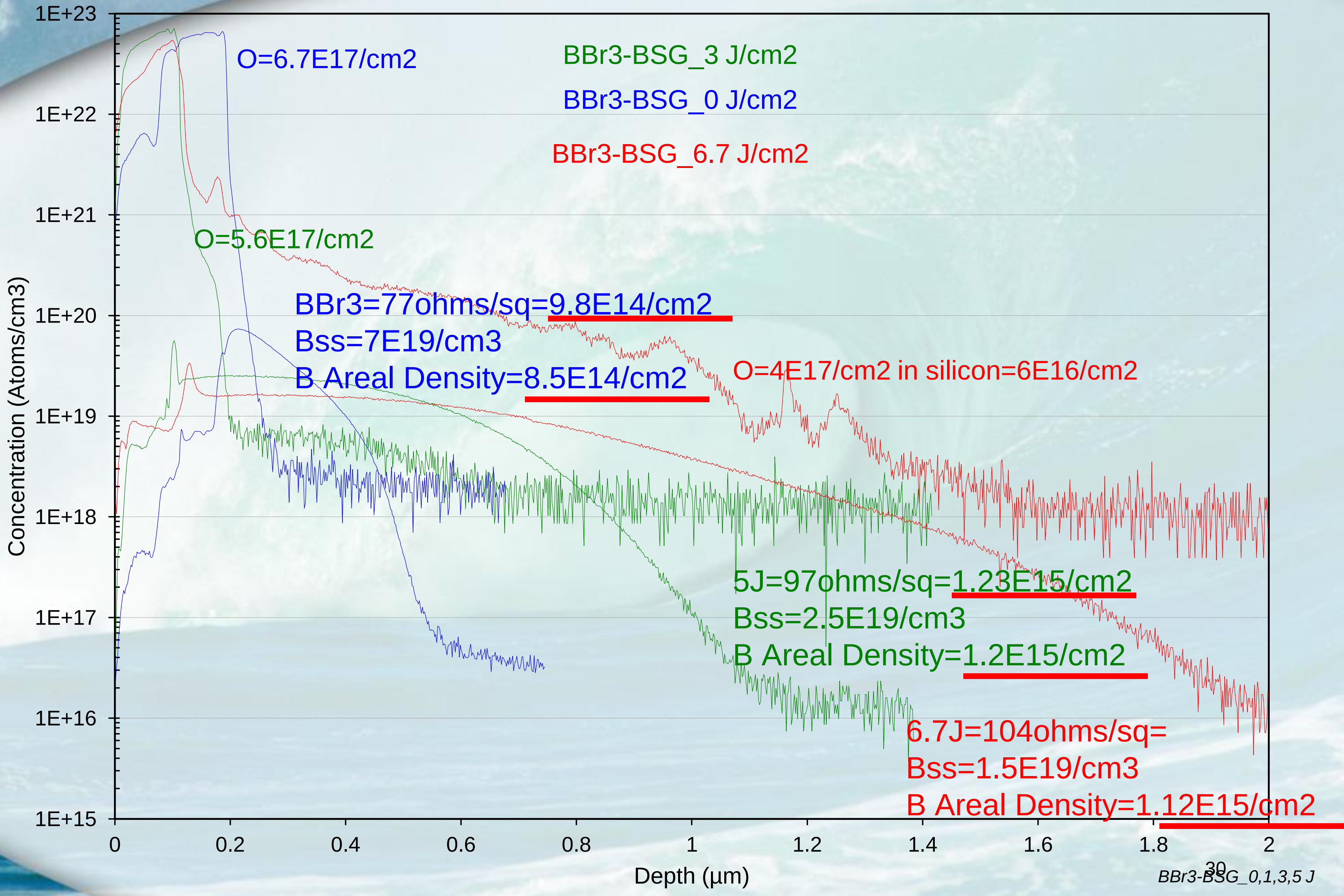
Boron 15keV & 30keV Implant





1E+20
1E+19
1E+18
1E+17
1E+16
Concentration (Atoms/cm3)
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
Depth (µm)
BBr3-BSG-3
B=1.3E15
BBr3-BSG-5
B=1.2E15
BBr3-BSG_6.5 J/cm2
B=1.2E15
BBr3-BSG-1
B=1.2E15
BBr3-BSG-0
B=1.5E15

Ox~580nm



1E+23
1E+22
1E+21
1E+20
1E+19
1E+18
1E+17
1E+16
1E+15
Concentration (Atoms/cm3)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
Depth (µm)
O=6.7E17/cm2
BBr3-BSG_3 J/cm2
BBr3-BSG_0 J/cm2
BBr3-BSG_6.7 J/cm2
O=5.6E17/cm2
BBr3=77ohms/sq=9.8E14/cm2
Bss=7E19/cm3
B Areal Density=8.5E14/cm2
O=4E17/cm2 in silicon=6E16/cm2
5J=97ohms/sq=1.23E15/cm2
Bss=2.5E19/cm3
B Areal Density=1.2E15/cm2
6.7J=104ohms/sq=
Bss=1.5E19/cm3
B Areal Density=1.12E15/cm2
BBr3-BSG_0,1,3,5 J

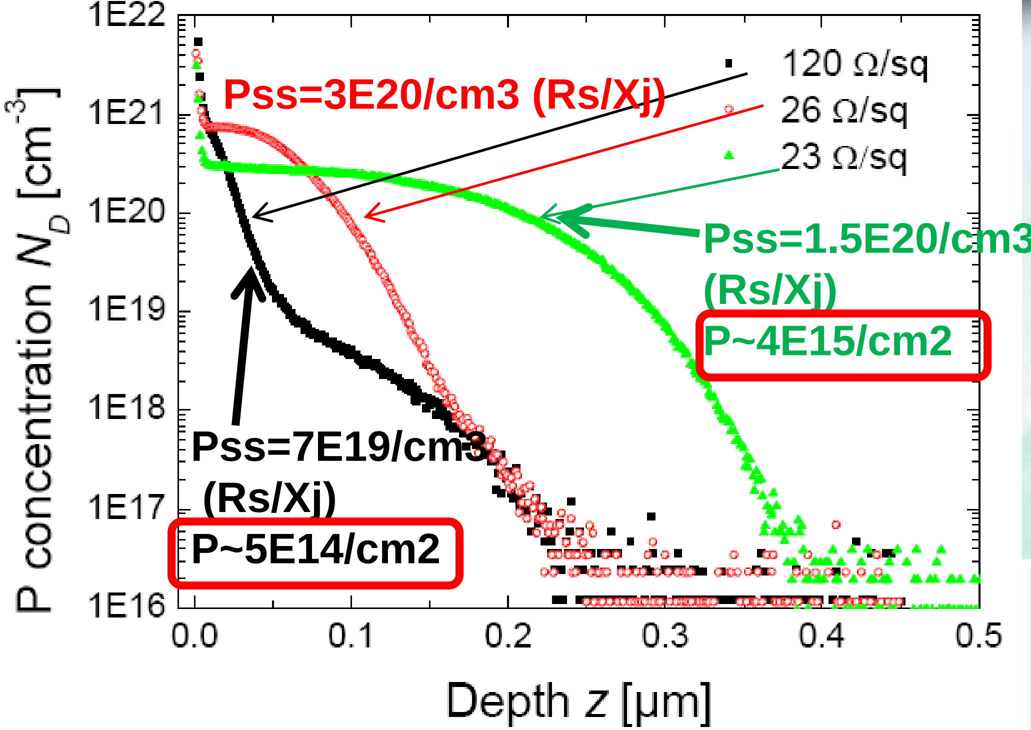


Figure 4: SIMS Profiles of the selective laser doped areas. For comparison, the shallow emitter with a sheet resistance of 120 Ω/sq emitter is also included.

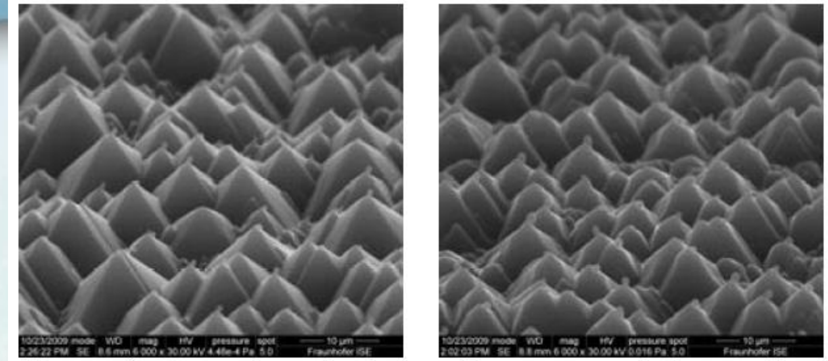


Figure 4: Scanning electron microscope pictures of laser processed samples. Although a slight change of the surface can be seen, the general shape of the pyramids is preserved. Left: random pyramid surface irradiated with 2.0 J/cm²: 41 Ω/sq at R_W = 11.8%; Right: irradiated with 3.5 J/cm²: 18 Ω/sq at R_W = 13.2%

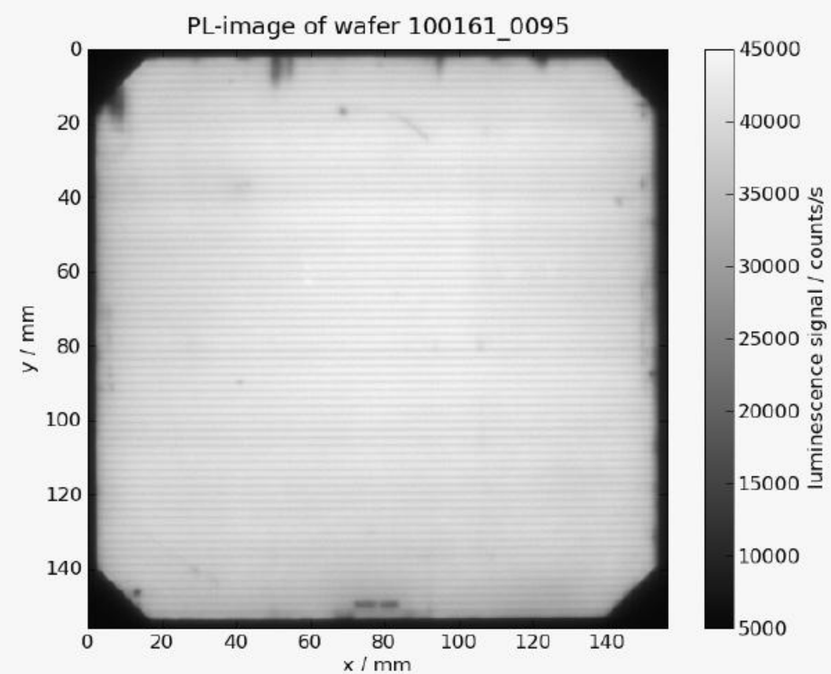
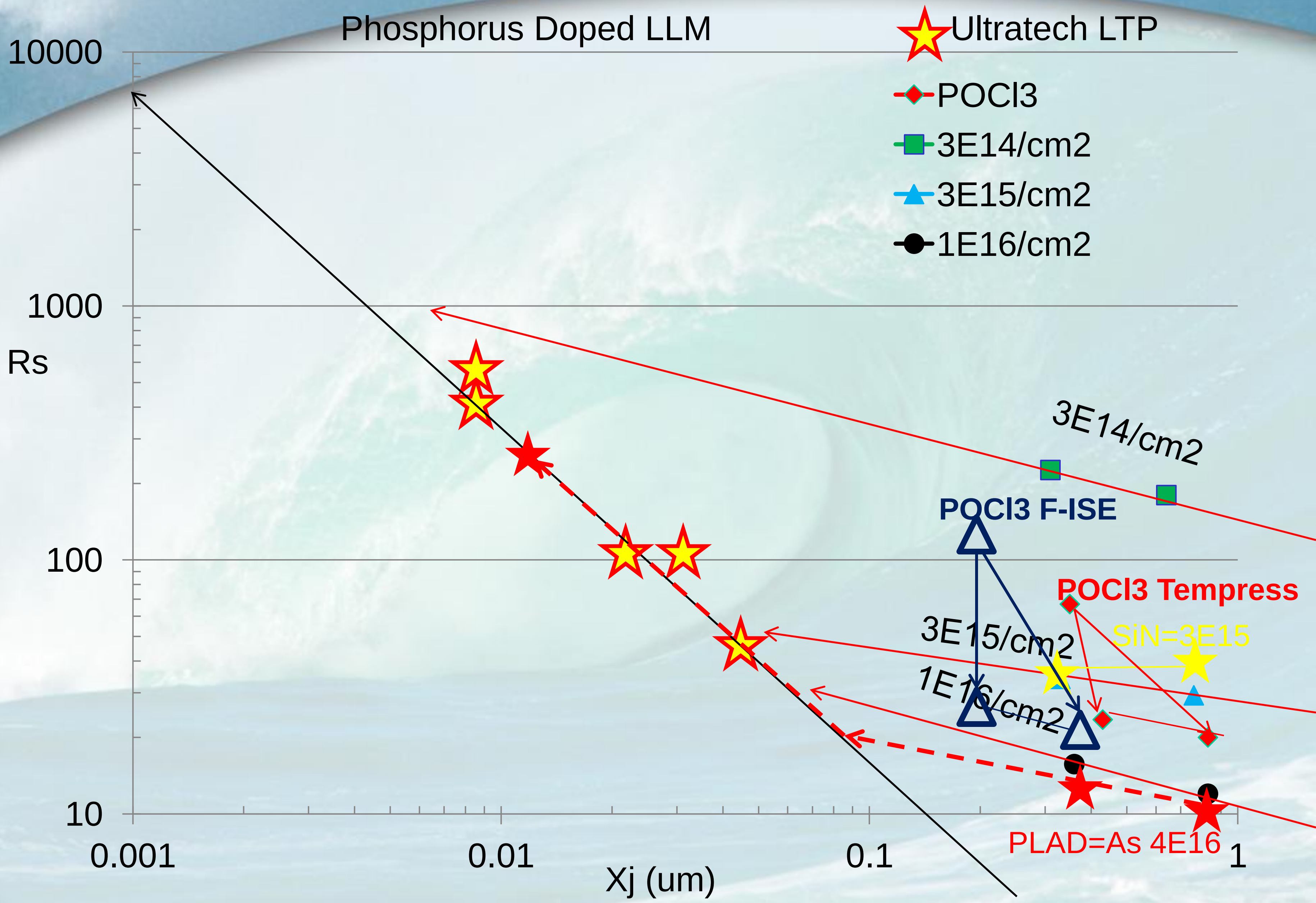


Figure 8: Photoluminescence pictures of the doping on a full 156x156 mm² wafer. The 70 highly doped finger are visible and have a uniform appearance.

LDSE
F-ISE & Jenoptiks

PVSC-2010 Hawaii



Borland et al., to be published EU-PVSEC Sept. 24, 2012

PVSC-2011 paper #321

Hameiri of Univ. of New South Wales [7] reported **inconsistent B-SOD concentration results**, 4% B-SOD Rs was 10 Ω/□, 8% was 80 Ω/□ and 10% was 38 Ω/□ suggesting poor B concentration control and precision with their Filmtronics B-SOD.

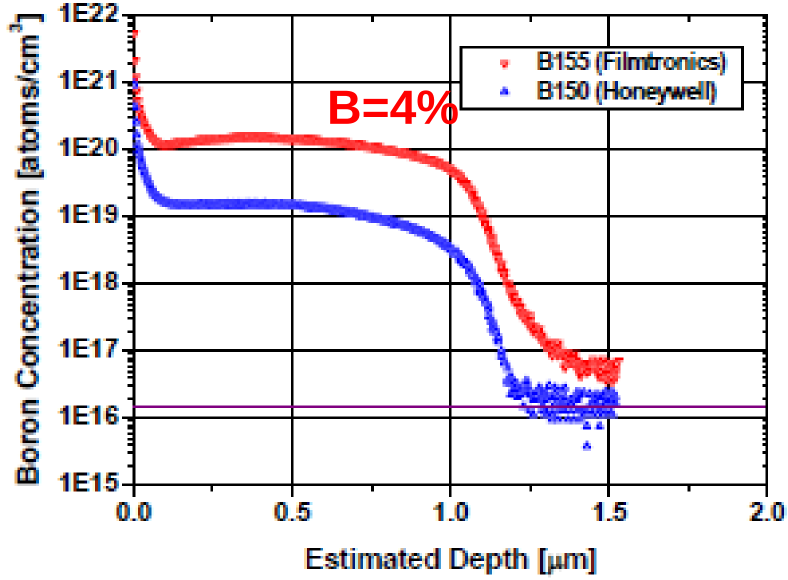


Figure 2: SIMS measurements of two different boron SODs. The solid line represents the background boron level of the substrate.

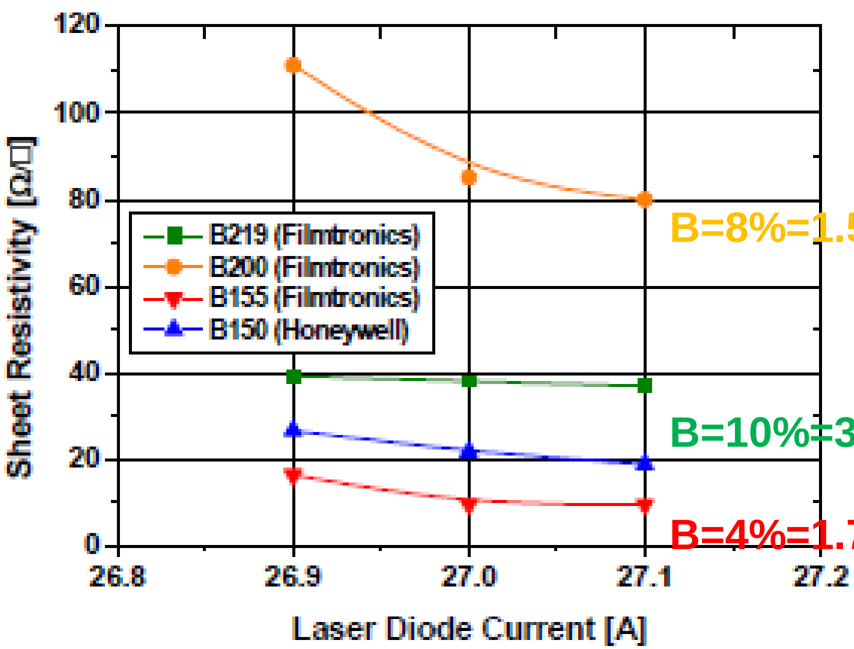
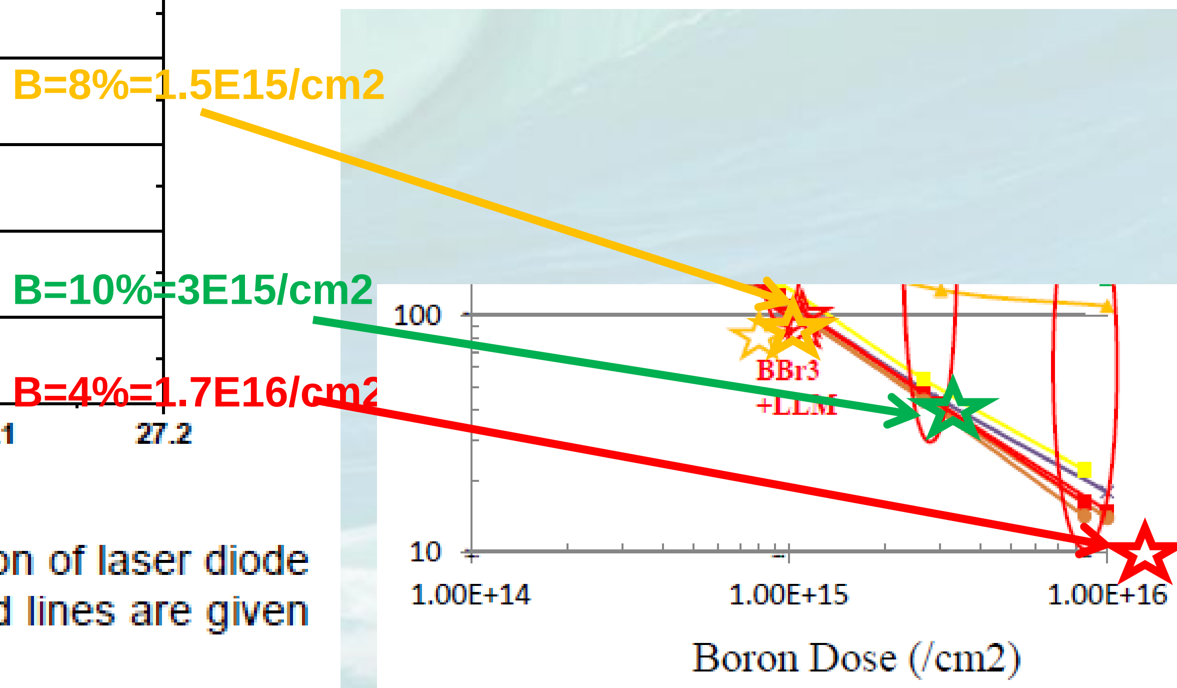
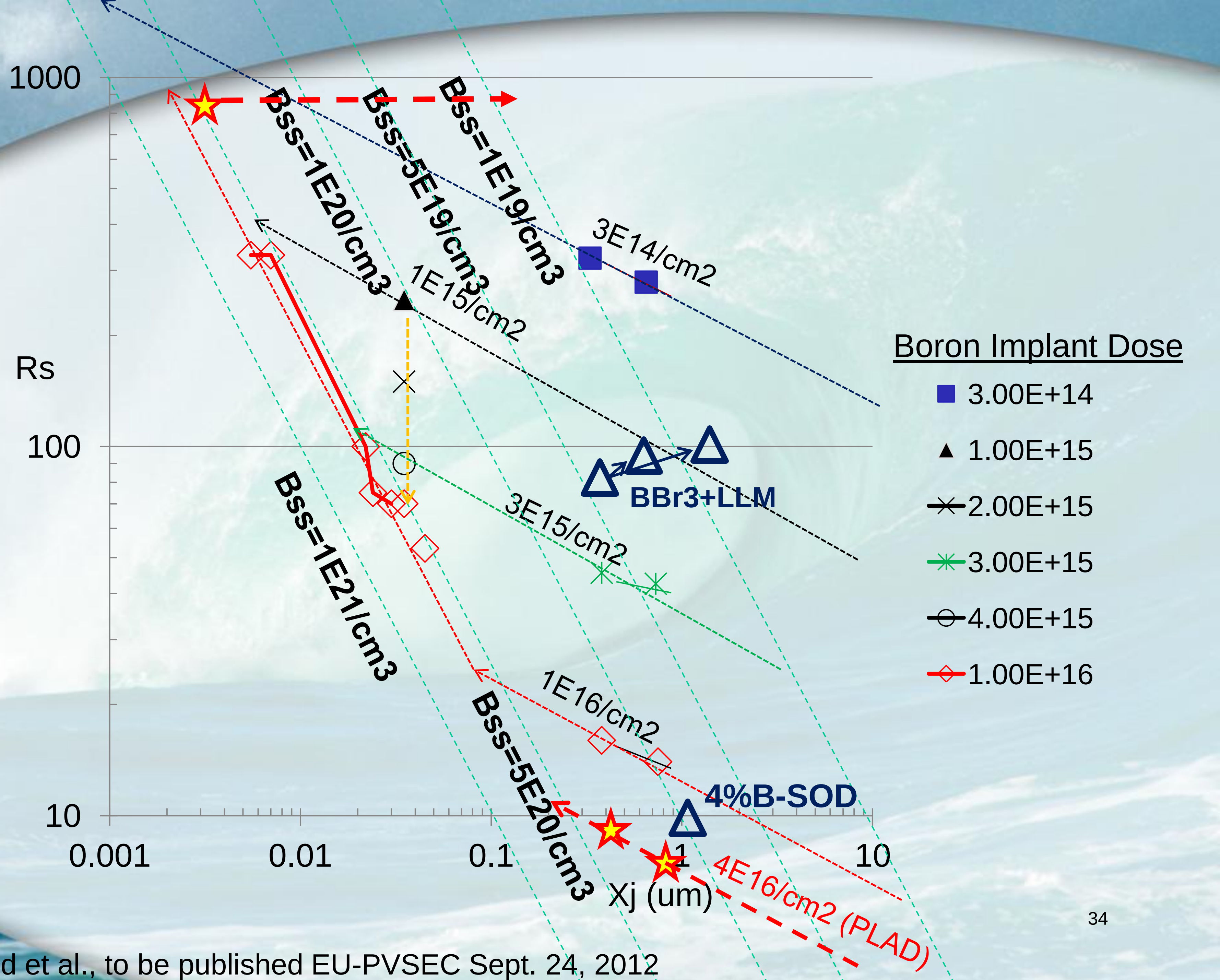


Figure 1: Sheet resistivity as a function of laser diode current for the four boron SODs. Solid lines are given as a guide for the eye.





Borland et al., to be published EU-PVSEC Sept. 24, 2012

- Summary of Part 1 Test
  - We achieved precise surface dopant concentration and activation control using ion implantation with various annealing techniques from 4E18/cm^3 (2200Ω/□) with an implant dose of 3E14/cm^2 to 5E20/cm^3 (12Ω/□) with a dose of 1E16/cm^2. $POCl_3$ solid phase diffusion dopant activation was only 15% efficient while liquid phase diffusion was 45%. To see the full benefit of localized laser melt annealing for selective emitter to maximize dopant activation based on solid solubility limit higher selective emitter P and B dopant sources should be investigated in the future with an equivalent concentration of **2-3E16/cm^2** range for highest efficiency dopant activation with Rs 3-6Ω/□ with laser melt liquid phase dopant diffusion. This will realize a Pss limit of ~1.5E21/cm^3 and a Bss limit of ~6E20/cm^3.
  - **Part 2: EU-PVSEC Sept. 24, 2012**

N-SIMS Analysis of Laser Ablation

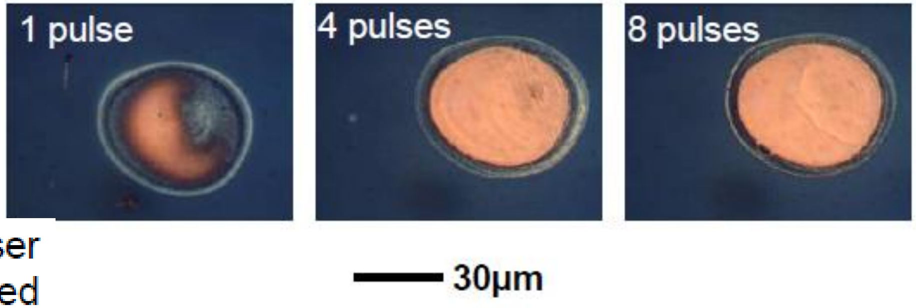


Fig. 5. Micrographs of laser drilled holes with different pulses used.

In order to easily characterize the profiles of the laser drilled contact openings, in this paper we use polished silicon wafers with an 80nm thick PECVD silicon nitride dielectric layer. The silicon wafer is heavily arsenic doped with a bulk resistivity of about 0.0015 Ω·cm. Hence the

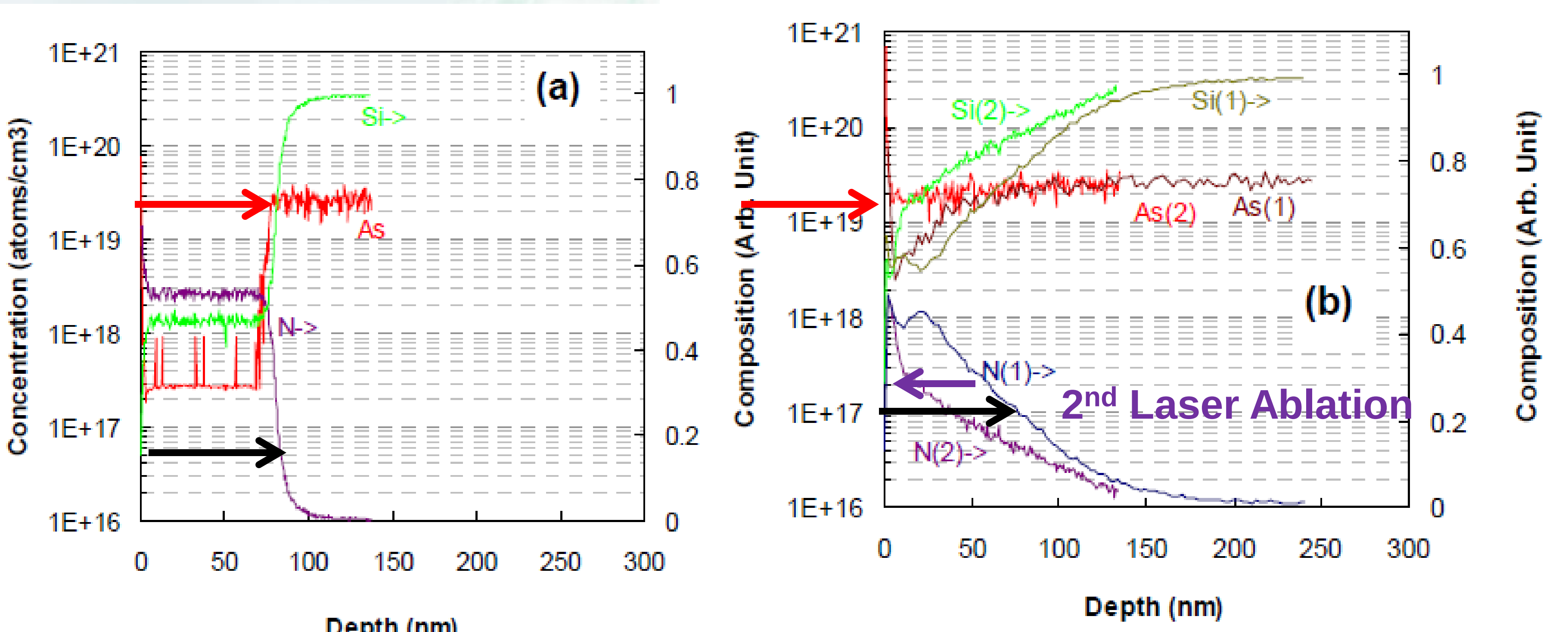


Fig. 6. SIMS element analyses at the area without holes (a), or at the area with holes drilled by one or two laser pulses (b).

Baomin Xu, PARC, EU-PVSEC Sept 2011

Comparison of $POCl_3$ & BBr_3 Furnace Diffused Dopant Sources to Phosphorus & Boron Implant and Plasma Dopant Sources Using Localized Laser Melt (LLM) Selective Emitter Formation Either Before or After SiN/ARC

John Borland[1], John Chen[2], Peter Oesterlin[3], Peter Venema[4], Henri Geerman[4], Yao-Jen Lee[5], Peter Zhao[6], Larry Wang[6], Baomin Xu[7], Shu Qin[8]

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[2]Kingstone, Shanghai, China

[3]Innovavent GmbH, Gottingen, Germany

[4]Tempress Systems B.V., Vaassen, the Netherlands

[5]National Nano Device Labs, Hsinchu, Taiwan

[6]EAG, Sunnyvale, California, USA

[7]PARC, Palo Alto, California, USA

[8]Micron Technology, Boise, Idaho, USA

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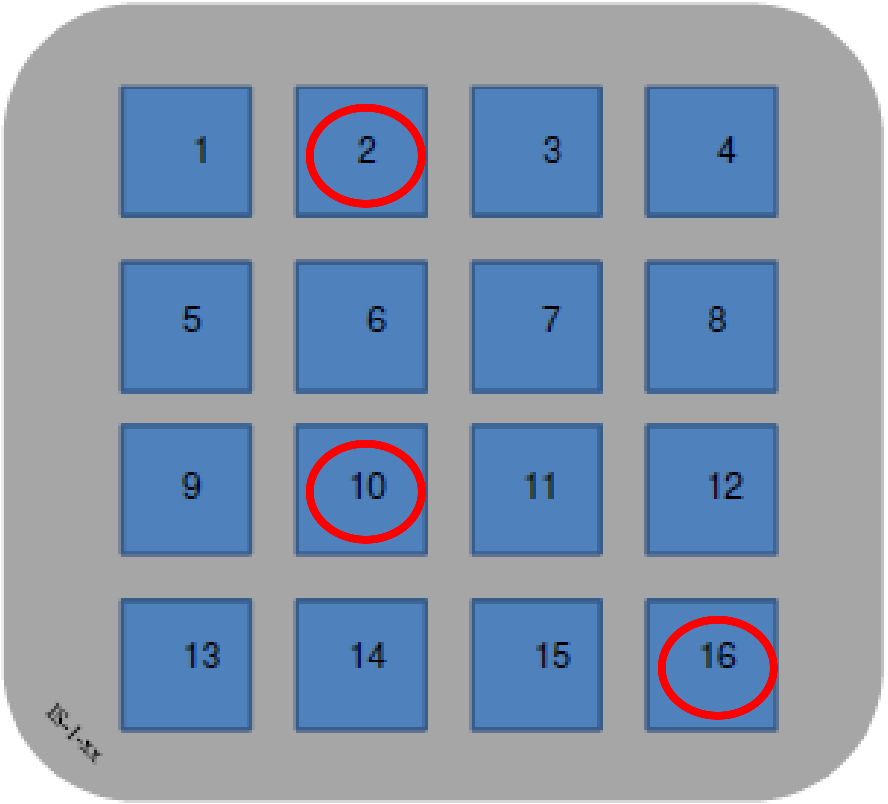
Implant SiN/ARC Dopant Source:

Species	Dose	Energy	Laser= 1J	3J	5J	6.5J	RTA	MWA
SiN/B	3E15	15keV	X	X	X	X	X	X
SiN/P	3E15	15keV	X	X	X	X	X	X
p-control SiN wafer			X	X	X	X		
n-control SiN wafer			X	X	X	X		
B-PLAD	4E16	10kV	X	X	X	X	X	X
As-PLAD	4E16	10kV	X	X	X	X	X	X



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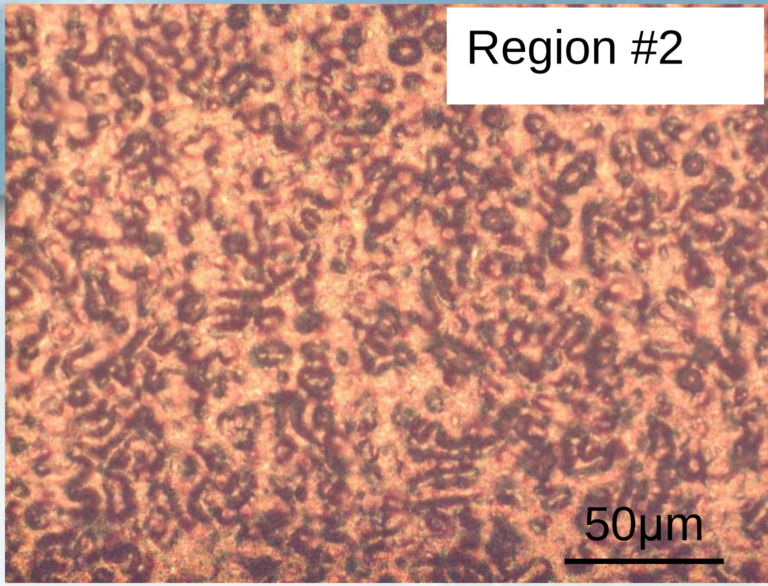
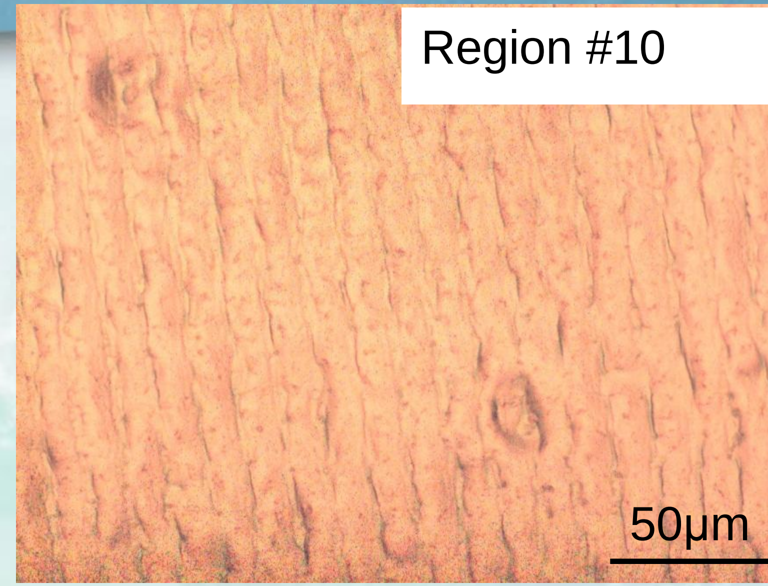
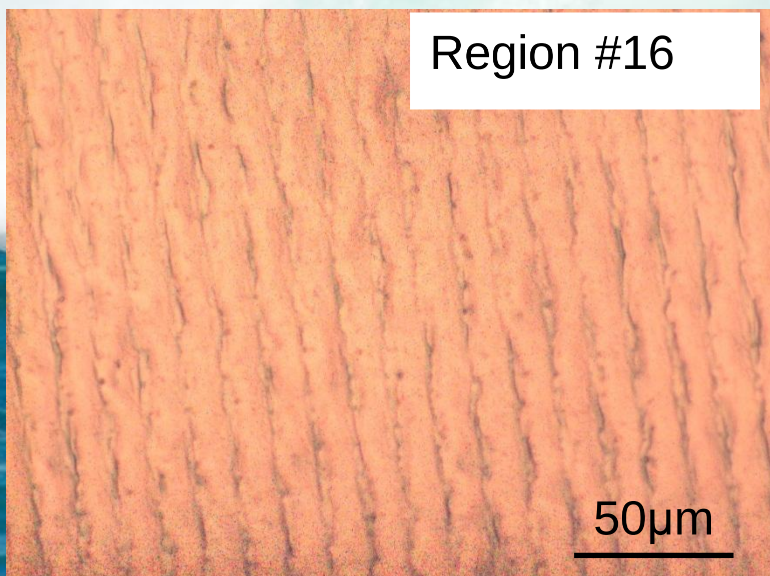
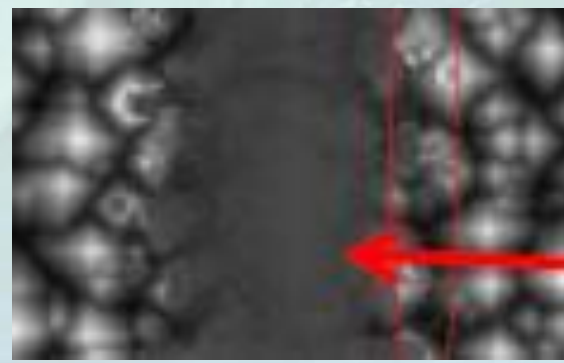
area	energy density (J/cm²)		area	energy density (J/cm²)
1	2.75		9	4.75
2	3.0		10	5.0
3	3.25		11	5.25
4	3.5		12	5.5
5	3.75		13	5.75
6	4.0		14	6.0
7	4.25		15	6.25
8	4.5		16	6.5

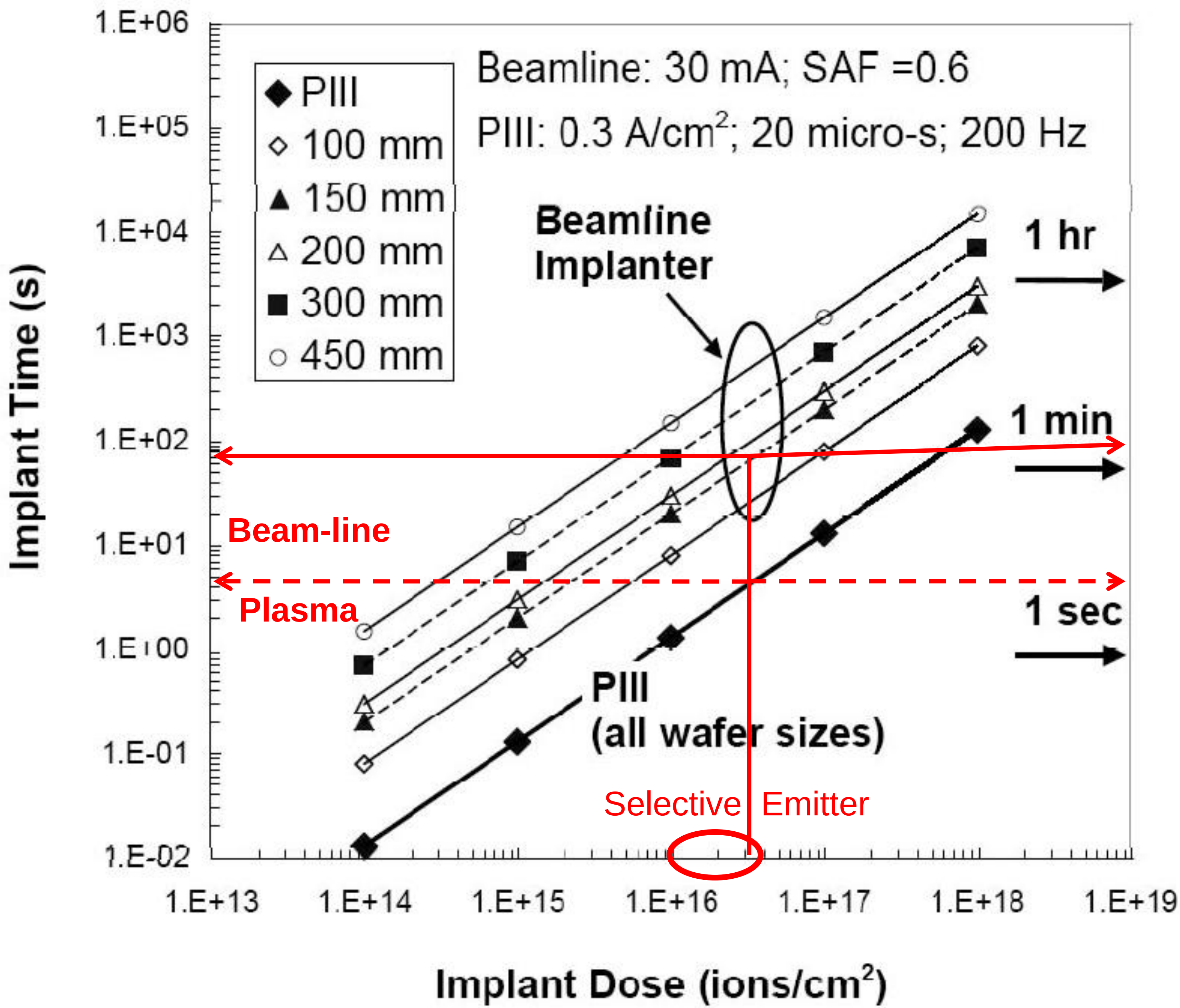




Sample N-3







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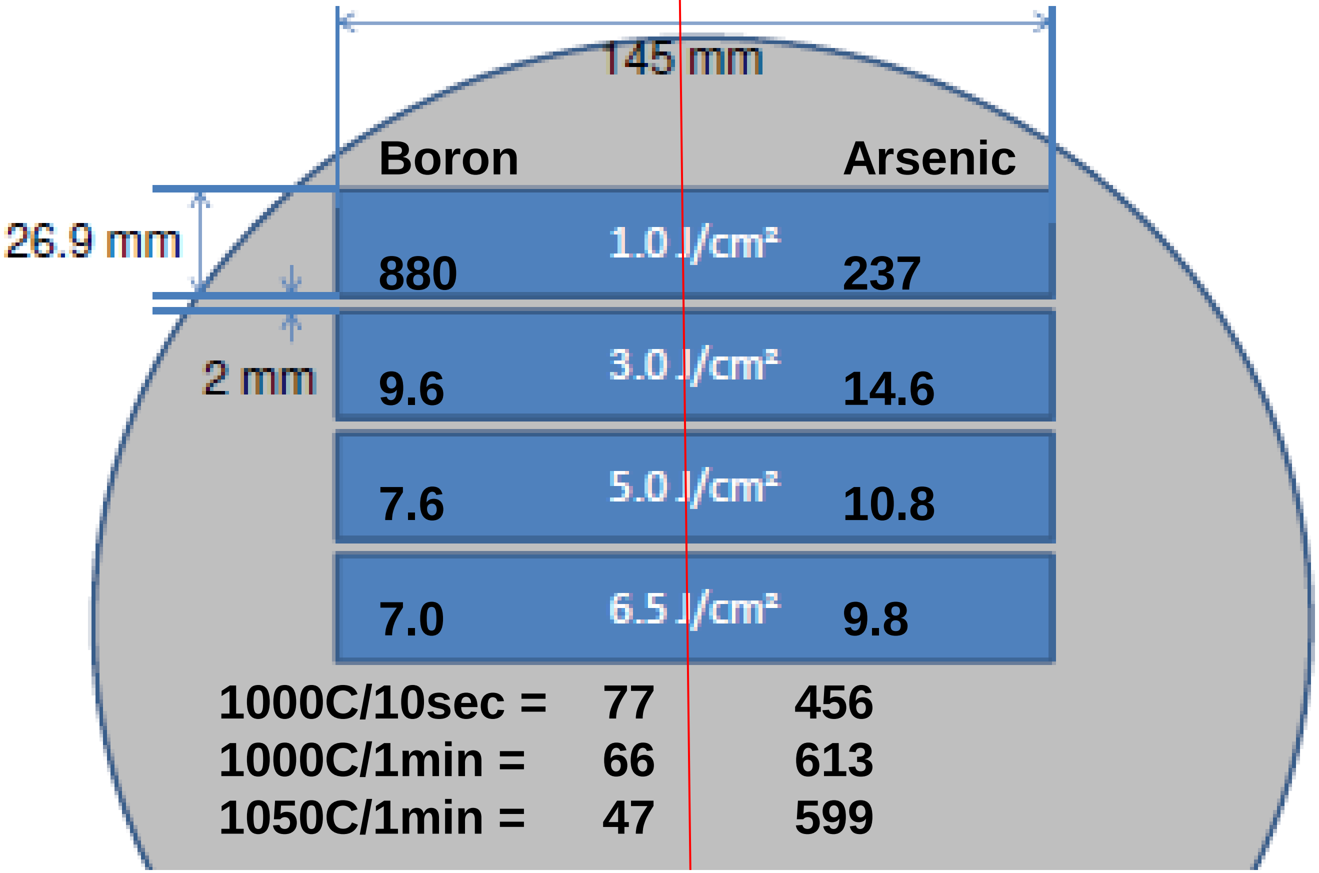
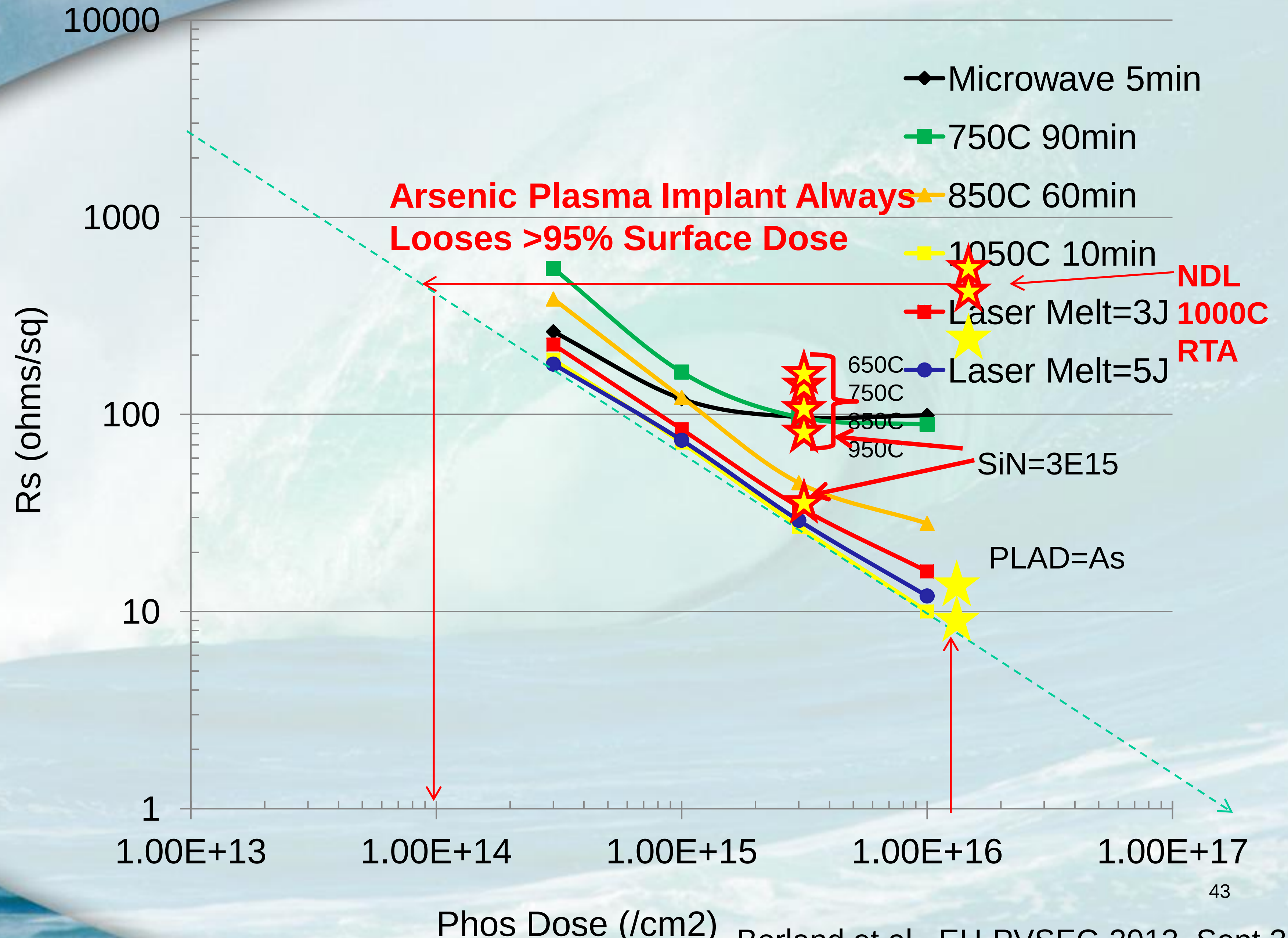


Processing parameters

wavelength	515nm
pulse duration	300ns
beam shape	line
line size	1.6mm x 30µm FWHM
intensity distribution	top-hat (long dimension) x Gaussian (short dimension)
scan direction	perpendicular to the 1.6mm dimension
scan overlap	80% of 30µm FWHM
energy densities	see sketch of wafer

Phos Implant



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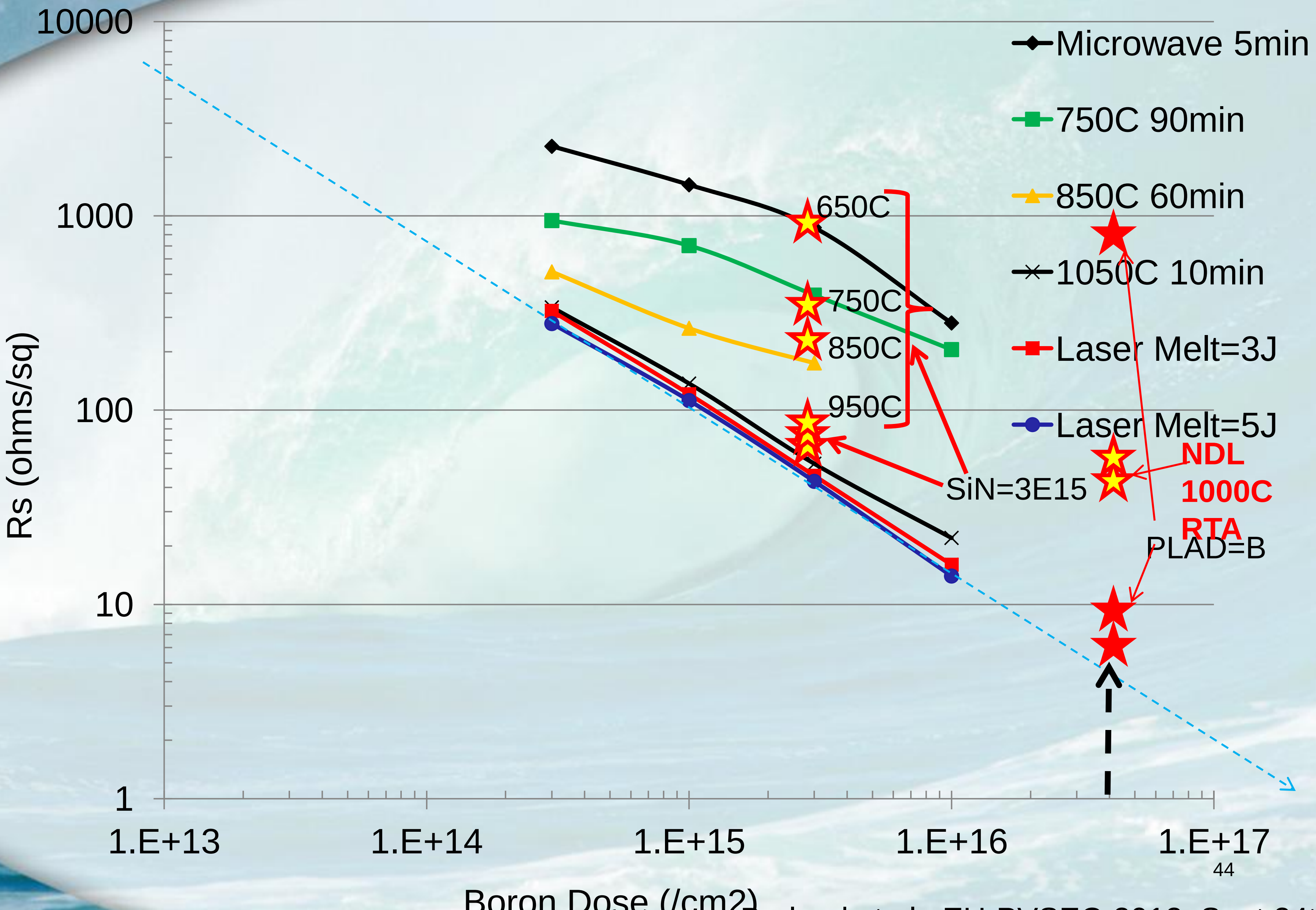
Boron 15keV Implant



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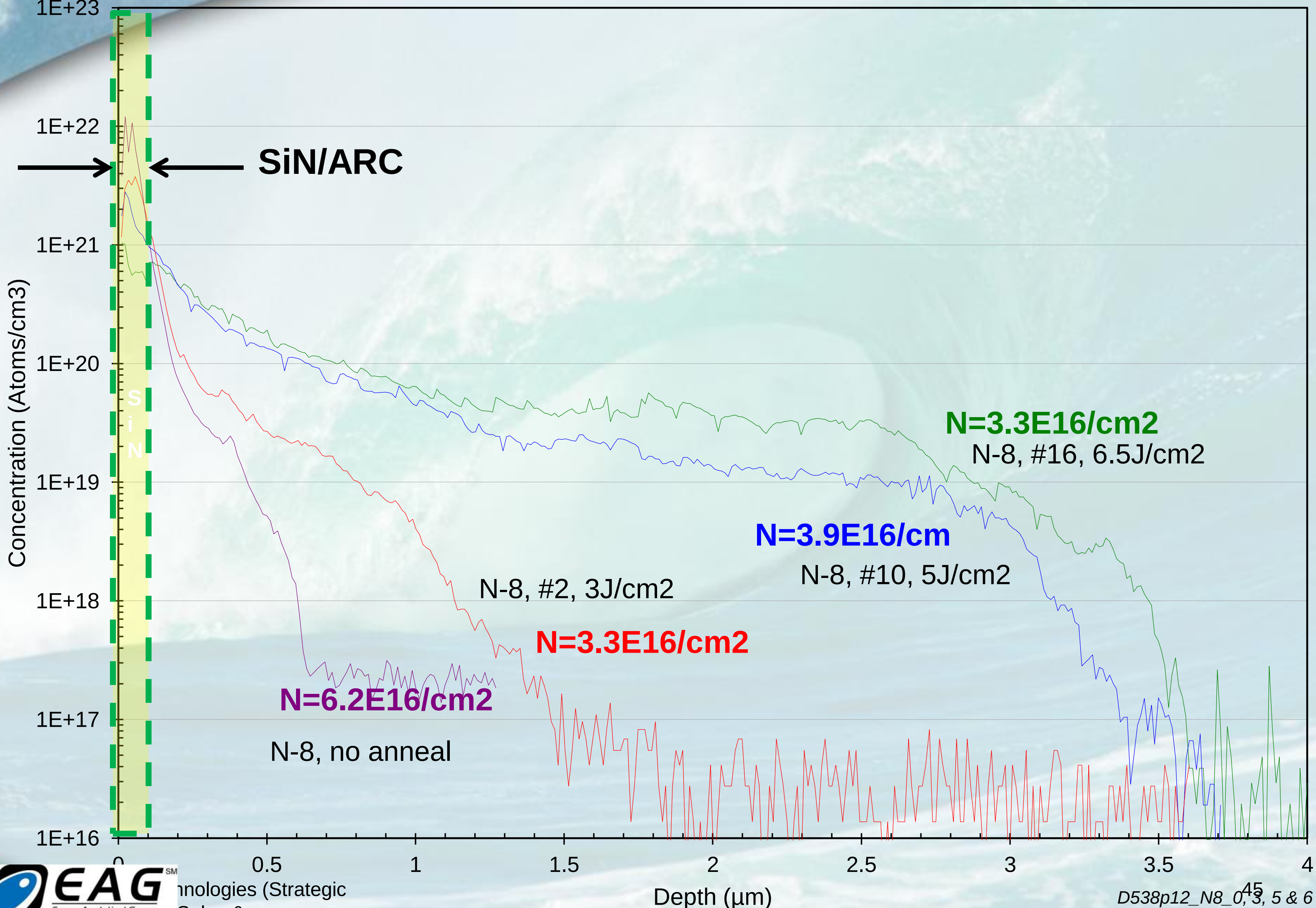
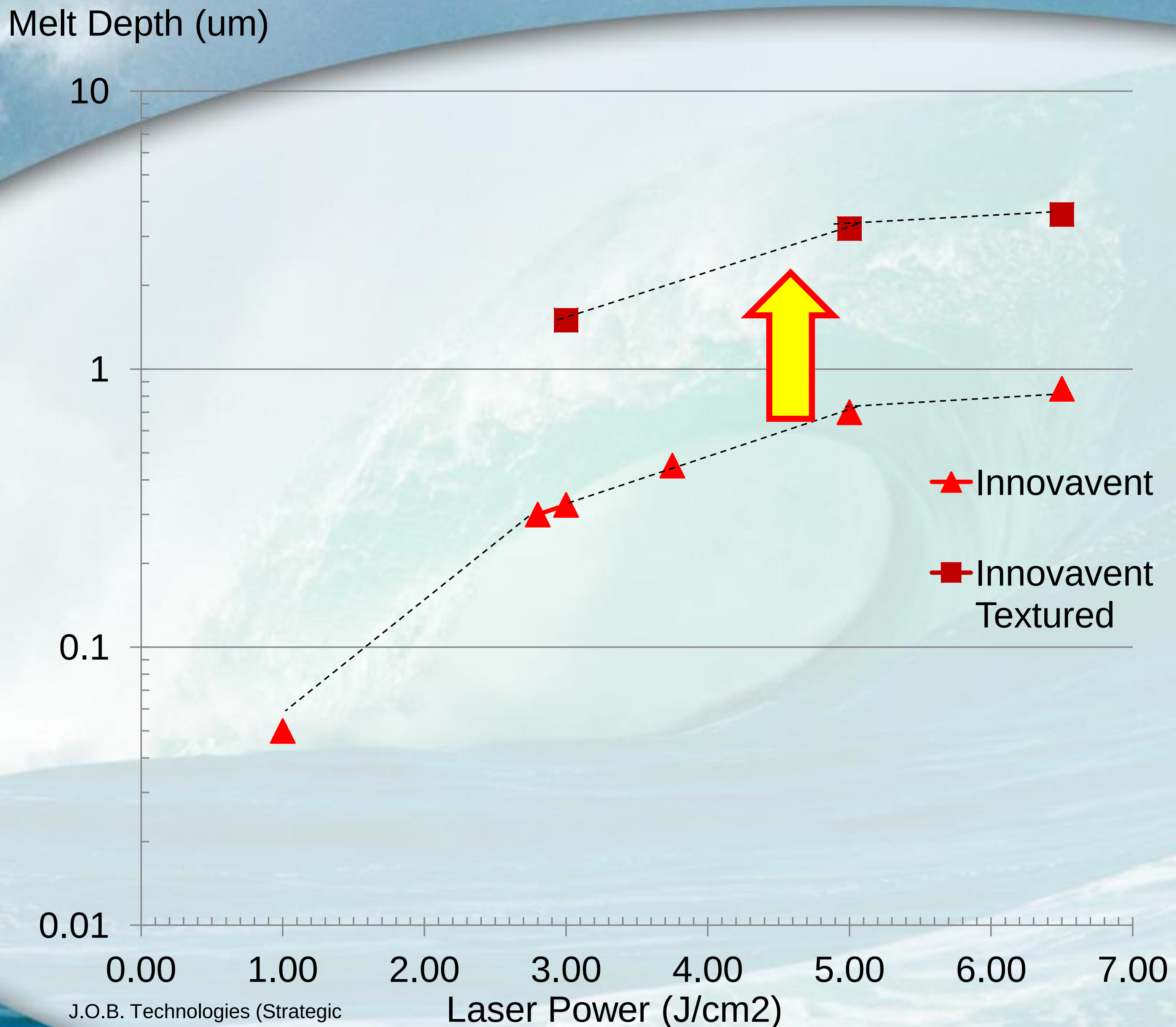
Boron Implant/SiN Wafer Nitrogen SIMS Areal Density



D538p12_N8_0, 3, 5 & 6



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