



Quantitative Measurement of Dopants (sub-ppba),
Oxygen and Carbon (sub-ppma), and Metals (sub-ppma)
in PV Si Feedstock and Wafers by SIMS

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Glow-Discharge Mass Spectrometry (GDMS)

- useful for survey of most elements in periodic table with DLs in pptwt range; good for 6N Upgraded Metallurgical Grade Si
- measurement independent of chemistry and electronic state
- minimal sample prep (mechanical)
- all forms of PV Si including chunks, granules, flakes and powders
- SEMI Standard Test Method under development for PV Si (SEMI Draft Doc. 4558)

GDMS Detection Limits

Element	ppm wt	Element	ppm wt	Element	ppm wt	Element	ppm wt
Li	< 0.001	Cu	< 0.01	Te	< 0.01	Lu	< 0.005
Be	< 0.001	Zn	< 0.05	I	< 0.01	Hf	< 0.01
B	36	Ga	< 0.05	Cs	< 0.001	Ta	< 100
F	< 1	Ge	< 0.05	Ba	< 0.01	W	< 0.05
Na	< 0.01	As	< 0.05	La	< 0.01	Re	< 0.01
Mg	< 0.005	Se	< 0.01	Ce	< 0.005	Os	< 0.01
Al	< 0.01	Br	< 0.01	Pr	< 0.005	Ir	< 0.01
Si	Matrix	Rb	< 0.01	Nd	< 0.005	Pt	< 0.01
P	< 0.01	Sr	< 0.01	Sm	< 0.005	Au	< 0.1
S	< 0.1	Y	< 0.01	Eu	< 0.005	Hg	< 0.01
Cl	< 0.05	Zr	< 0.01	Gd	< 0.005	Tl	< 0.01
K	< 0.05	Nb	< 0.01	Tb	< 0.005	Pb	< 0.01
Ca	< 0.05	Mo	< 0.05	Sm	< 0.005	Bi	< 0.01
Sc	< 0.001	Ru	< 0.01	Eu	< 0.005	Th	< 0.005
Ti	< 0.005	Rh	< 0.01	Gd	< 0.005	U	< 0.005
V	< 0.005	Pd	< 0.01	Tb	< 0.005		
Cr	< 0.01	Ag	< 0.01	Dy	< 0.005		
Mn	< 0.005	Cd	< 0.05	Ho	< 0.005		
Fe	< 0.05	In	< 0.01	Er	< 0.005		
Co	< 0.005	Sn	< 0.01	Tm	< 0.005		
Ni	< 0.01	Sb	< 0.01	Yb	< 0.005		

- all elements in periodic table, including B, P, O, C and Fe
- useful when a small number of elements are of interest (not a survey technique)
- can measure wafers, chunks, granules, flakes, powders, etc
- DLs in 8-11N range for most elements; useful for PV Si made by Siemens process
- high accuracy (all elements traceable to reference materials)
- precisions under 10%
- no sample prep

Secondary Ion Mass Spectrometry (SIMS)

SIMS Detection Limits in Si

Atoms/cm ³ (ppb wt)					
O ₂ ⁺ primary beam			Cs ⁺ primary beam		
He	1E17 (286)	Cr	3E11 (0.01)	H	5E16 (36)
Li	5E11 (0.003)	Mn	2E12 (0.1)	C	2E15 (30)
B	1E12 (0.008)	Fe	1E13 (0.4)	N	5E13 (0.5)
Na	5E11 (0.001)	Ni	1E14 (4)	O	5E15 (60)
Mg	1E12 (0.02)	Cu	1E14 (4)	F	1E14 (1)
Al	5E12 (0.1)	Zn	1E14 (6)	P	1E13 (0.2)
K	5E11 (0.001)	Mo	1E14 (7)	S	2E14 (10)
Ca	2E12 (0.08)	In	1E13 (0.8)	Cl	5E14 (23)
Ti	1E12 (0.03)	W	5E13 (7)	As	1E13 (0.5)
				Ge	5E13 (2.6)
				Sb	1E13 (0.8)
				Au	1E13 (1.4)

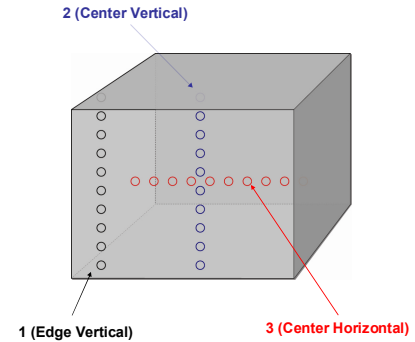
Case Study: Uniformity Study of B, Al, P, C, O, Ca and Fe in PV Si (UMG-Si 5N) by SIMS

Experimental: Three large bricks were made from melted UMG-Si. The cooling was not a direct solidification process, though there may still be unintentional segregation of impurities from cooling. 10 samples for SIMS analysis were taken from each of the three bricks as shown in the left side schematic, for a total of 30 test samples. SIMS precisions for the analyses were less than 10%.

Black circles represent samples from Sample 1, numbered #1 to #10 from top to bottom. The location is close to left hand side of the sample.

Blue circles represent samples from Sample 2, numbered #1 to #10 from top to bottom. The location is in the middle between left and right.

Red circles represent samples from Sample 3, numbered #1 to #10 from left to right. The location is in the middle between top and bottom.



B Uniformity

B Data (units of atoms/cc)

Edge Vertical Sample Sequence			Center Vertical Sample Sequence			Center Horizontal Sample Sequence		
Sample	Average	Deviation from Ave	Sample	Average	Deviation from Ave	Sample	Average	Deviation from Ave
1	4.40E+17	-13.1%	1	3.59E+17	-3.4%	1	2.30E+17	-12.7%
2	4.24E+17	-16.3%	2	3.37E+17	-9.2%	2	2.90E+17	10.3%
3	4.42E+17	-12.6%	3	3.58E+17	-3.6%	3	2.76E+17	4.9%
4	4.08E+17	-19.4%	4	3.48E+17	-6.3%	4	2.25E+17	-14.6%
5	5.17E+17	2.1%	5	3.85E+17	3.8%	5	2.69E+17	2.3%
6	5.34E+17	5.5%	6	3.72E+17	0.4%	6	2.86E+17	8.6%
7	4.64E+17	-8.3%	7	3.90E+17	5.0%	7	2.26E+17	-14.1%
8	5.26E+17	3.9%	8	4.14E+17	11.5%	8	3.00E+17	14.1%
9	5.95E+17	17.6%	9	3.79E+17	2.0%	9	2.84E+17	8.0%
10	7.17E+17	41.7%	10	3.67E+17	-1.1%	10	2.43E+17	-7.6%
Average	5.06E+17		Average	3.71E+17		Average	2.63E+17	
RSD	18.7%		RSD	6.0%		RSD	11.1%	
Range	1.8x		Range	1.2x		Range	1.3x	
Trend?	yes		Trend?	yes		Trend?	no	

Boron distributions at different locations are fairly uniform. With exception of #10 in sample #1- taken at corner - the variation from average are within ±20%

P Uniformity

P Data (units of atoms/cc)

Edge Vertical Sample Sequence			Center Vertical Sample Sequence			Center Horizontal Sample Sequence		
Sample	Average	Deviation from Ave	Sample	Average	Deviation from Ave	Sample	Average	Deviation from Ave
1	1.58E+17	-46.8%	1	2.30E+17	-25.3%	1	1.43E+17	-27.5%
2	1.65E+17	-44.4%	2	2.90E+17	-6.0%	2	2.00E+17	1.3%
3	1.83E+17	-38.2%	3	1.95E+17	-36.7%	3	2.05E+17	3.8%
4	1.72E+17	-41.8%	4	1.98E+17	-35.9%	4	1.36E+17	-31.0%
5	1.99E+17	-32.8%	5	4.07E+17	32.0%	5	2.05E+17	3.9%
6	2.47E+17	-16.4%	6	3.45E+17	12.0%	6	2.03E+17	3.0%
7	3.68E+17	24.4%	7	3.20E+17	3.9%	7	1.36E+17	-31.1%
8	2.52E+17	-14.9%	8	4.00E+17	29.9%	8	3.37E+17	70.9%
9	5.04E+17	70.3%	9	3.55E+17	15.3%	9	2.49E+17	26.4%
10	7.15E+17	141.6%	10	3.45E+17	12.0%	10	1.55E+17	-21.4%
Average	2.96E+17		Average	3.08E+17		Average	1.97E+17	
RSD	61.9%		RSD	25.3%		RSD	31.5%	
Range	4.5x		Range	2.1x		Range	2.5x	
Trend?	yes		Trend?	yes		Trend?	no	

P distributions at different locations are less uniform compared with B. The variation are in 30-40% range in most cases.

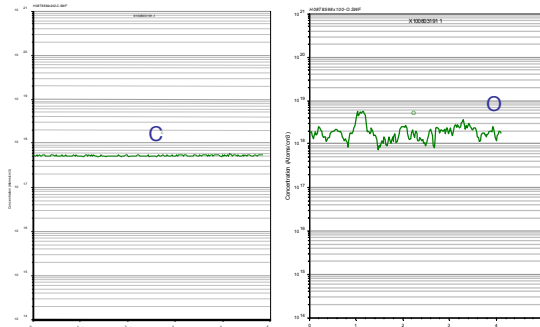
O Uniformity

O Data (units of atoms/cc)

Edge Vertical Sample Sequence			Center Vertical Sample Sequence			Center Horizontal Sample Sequence		
Sample	Average	Deviation from Ave	Sample	Average	Deviation from Ave	Sample	Average	Deviation from Ave
1	1.91E+18	17.9%	1	2.20E+18	9.3%	1	2.21E+18	21.8%
2	1.71E+18	5.2%	2	1.70E+18	-16.6%	2	2.11E+18	16.6%
3	2.19E+18	34.9%	3	2.55E+18	27.5%	3	1.74E+18	-4.1%
4	2.35E+18	45.1%	4	1.70E+18	-16.6%	4	1.69E+18	-6.9%
5	1.95E+18	20.4%	5	1.73E+18	-15.3%	5	1.96E+18	8.0%
6	2.16E+18	33.0%	6	1.90E+18	-6.2%	6	1.76E+18	-2.8%
7	1.22E+18	-25.0%	7	1.75E+18	-14.0%	7	1.41E+18	-22.1%
8	1.26E+18	-22.5%	8	1.95E+18	-3.9%	8	1.31E+18	-27.9%
9	1.00E+18	-38.0%	9	1.70E+18	-16.6%	9	2.55E+18	40.9%
10	5.19E+17	-68.0%	10	2.15E+18	6.7%	10	1.39E+18	-23.5%
Average	1.62E+18		Average	1.93E+18		Average	1.81E+18	
RSD	37.0%		RSD	14.9%		RSD	22.1%	
Range	4.2x		Range	1.5x		Range	1.9x	
Trend?	yes		Trend?	no		Trend?	no	

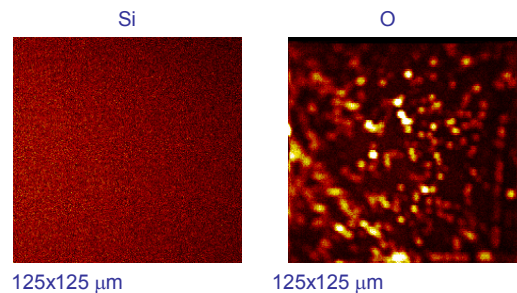
O concentration variation are in 30-60% range. The distribution of O with depth is not uniform – it shows large variation – precipitates

O Uniformity in PV Si



The C and O profiles from the same location. The O profile shows large variation in concentration (0.1 to 0.5 μm precipitates). FTIR can not provide accurate measurement on this type of sample

O Uniformity in PV Si – SIMS Image



SIMS images show O is not uniform in micron scale.

Summary of Results

Sample Sequence	B	P	Al	C	O	Ca	Fe
Edge Vertical							
Ave (atoms/cc)	5.06E+17	2.96E+17	3.04E+17	9.42E+17	1.62E+18	<2E12	< mid E13
RSD	18.7%	61.9%	119.0%	26.5%	37.0%		
Range	1.8x	4.5x	12.2x	1.9x	4.2x		
Trend?	yes	yes	yes	no	yes		
Center Vertical							
Ave (atoms/cc)	3.71E+17	3.08E+17	7.30E+16	8.68E+17	1.93E+18	<3E12	< mid E13
RSD	6.0%	25.3%	16.5%	29.4%	14.9%		
Range	1.2x	2.1x	1.7x	2.3x	1.5x		
Trend?	yes	yes	yes	no	no		
Center Horizontal							
Ave (atoms/cc)	2.63E+17	1.97E+17	2.48E+16	8.90E+17	1.81E+18	<3E12	< mid E13
RSD	11.1%	31.5%	40.7%	32.9%	22.1%		
Range	1.3x	2.5x	3.8x	2.5x	1.9x		
Trend?	no	no	no	no	no		

Conclusions

1. Impurity distributions in UMG-Si bricks are not uniform.
2. The range of non-uniformity is element dependent.
3. Boron is the most uniform of the elements studied.
4. Some impurities in some sections show trends that may be caused by segregation.
5. Data can be used to improve the UMG-Si process.
6. Data can be used to determine what material to exclude (e.g., edge).
7. Data can be used to select where representative samples should be taken.
8. Sampling volume for techniques such as SIMS, GDMS or ICPMS is not relevant.

EAG Recommendations for PV Si Impurity Analysis

- How pure is your Si, what kind of impurities? – **GDMS**
- Best detection limits and accuracy analysis of specific elements – **SIMS**