

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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ABSTRACT: Secondary Ion Mass Spectrometry (SIMS) can be used to quantitatively measure bulk dopants, oxygen and carbon, and metals at exceptionally low levels in both crystalline and polycrystalline Si for PV. The approach is to use CAMECA magnetic sector SIMS instruments and protocols which are optimized for these bulk measurements. Accuracy is traceable to NIST SRMs for B, P, and As, and ion implanted reference standards for other elements. Traditional analytical methods have their strengths but also their limitations. For dopants, resistivity is affected by compensation of other dopants, and low temperature FTIR and PL require the growth of a single crystal ingot slug. For oxygen and carbon, FTIR is limited to interstitial oxygen and substitutional carbon in single crystal Si. SIMS and Glow Discharge Mass Spectrometry (GDMS) overcome these limitations, but SIMS has lower detection limits and better precisions which may be needed in some cases.

Keywords: silicon, impurities, qualification and testing, SIMS

1 INTRODUCTION

The most common impurities of interest in PV silicon feedstock and wafers are the dopants (mainly B and P), the atmospherics (mainly O for p-type Si, and C), and the transition metals (mainly Fe). Other elements that may be critical include, but are not limited to, Al, Ca, Ti, Cu, Ni, and N. A wide range of analytical techniques are used for detecting impurities in PV Si, some more appropriate than others depending on the purity level and on the solar cell design, but each with its strengths and weaknesses [1].

Two analytical techniques which require little to no sample preparation that may introduce or remove impurities of interest and which have excellent detection limits in PV Si are High Mass Resolution Glow Discharge Mass Spectrometry (GDMS) and Secondary Ion Mass Spectrometry (SIMS).

GDMS is best suited for “6N” upgraded metallurgical grade (UMG-S) and when a survey of a large number of impurities is of interest. GDMS accuracies for the two most important dopants, B and P, are now traceable to NIST SRMs, but the accuracies for other impurities are within a factor of about 2x. GDMS precisions are ~ 10% for high levels of impurities and ~ 25% for low levels of impurities. See reference [2] in these proceedings for further details on GDMS.

SIMS is best suited when improved detection limits, accuracy, and precision are of interest, but also when only a few elements are of interest. SIMS is not cost effective compared to GDMS for a survey of a large number of elements. SIMS accuracies for all impurities are traceable to reference materials, and precisions are typically less than 10% because reference materials can be analyzed *in situ* with the test samples. The SIMS detection limits are even good enough for some Solar Grade Silicon made by Siemens-type processes. Table I lists SIMS detection limits for selected impurities in silicon. Figures 1 through 3 show the excellent long term repeatability for the SIMS measurement of B (7.5%), P (4%) and O (5%).

Table I: SIMS detection limits (DL) for selected impurities in PV Silicon. Units are atoms/cm³ (ppb wt). He through W are measured using an O₂⁺ primary beam, and H through Au are measured using a Cs⁺ primary beam.

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

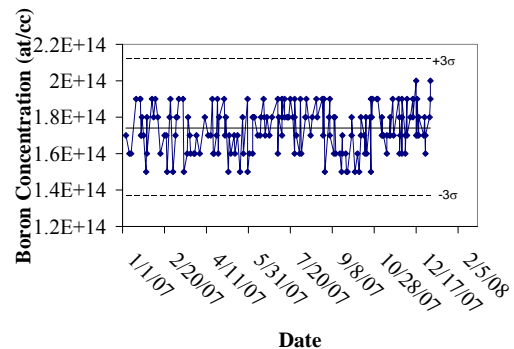


Figure 1: SIMS B bulk measurement in Si – long term repeatability

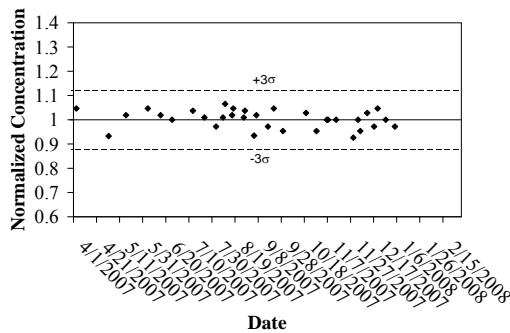


Figure 2: SIMS P implant dose measurement in Si – long term repeatability

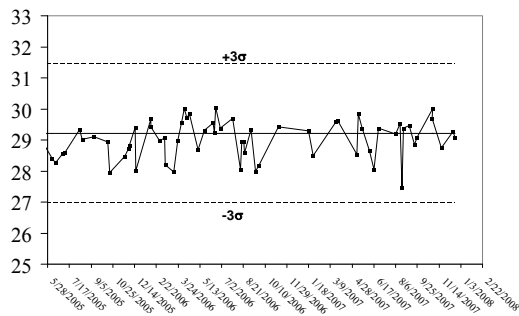


Figure 3: SIMS O bulk measurement in Si – long term repeatability [Oxygen in units of ppma; dates range from 5/28/2005 to 2/22/2008]

2 APPLICATION – PV SI POWDERS

PV Si can come in many forms, including wafers, ingot tails, chunks, granules, flakes and powders. SIMS bulk analysis can be performed on powder samples, if the size of the particle is larger than ~ 300 microns. Table II shows SIMS bulk analysis results for C, O, B, Al, P, Cr, Fe, Ni and As analyzed on ~ 400 micron particles from Si powder sample. Five conditions were used in this analysis. In this particular sample, C, O, B, Al, P and As are detected. The Cr, Fe and Ni are below detection limits. Note that an acid digestion followed by ICPMS would not detect the oxygen and carbon content in this feedstock.

Table II: SIMS analysis of powder PV Si feedstock

	atoms/cm ³	ppm wt
B	1.40E+17	1.1
C	1.10E+18	9
O	2.65E+18	30
Al	1.60E+16	0.3
P	3.64E+17	8.1
Cr	<2E12	<7E-5
Fe	<1E14	<0.004
Ni	<4E14	<0.016
As	1.60E+15	0.07

3 APPLICATION – DISTRIBUTION OF IMPURITIES IN UMG-Si BRICKS

3.1 Representative sampling?

The analysis of PV Si is only one part of the problem for evaluating feedstock. *Representative* sampling and process stability of the silicon feedstock are also part of the problem, and a procedure to validate the statistical process control of the analytics is also critical.

The worldwide shortage of polysilicon for mono-crystalline and multi-crystalline Si PV has resulted in R&D and now commercialization of upgraded metallurgical silicon (UMG-Si) which has higher levels of impurities than traditional Siemens-based polysilicon but which can be used successfully in some PV solar cell designs. In the early days of Siemens-based polysilicon (over 30 years ago) companies had to determine the uniformity of impurities in the large polysilicon rods in order to know how to characterize the impurities for an individual polysilicon rod. In other words, where and how many samples must be taken from the polysilicon rod and analyzed in order to provide a *representative* level of impurities for the polysilicon rod and eventually for the *process*? The following preliminary experiment was completed in support of one UMG-Si manufacturer in order to determine if this kind of study will be necessary for UMG-Si.

3.2 Experimental Samples

This particular UMG-Si process results in large, rectangular bricks of silicon for shipping. Samples were taken from three UMG-Si bricks as follows. Ten (10) samples were taken sequentially down the Edge Vertical of one brick. Ten (10) samples were taken sequentially down the Center Vertical of one brick. Ten (10) samples were taken across the Center Horizontal of one brick.

3.3 SIMS analysis procedures and precisions

All 30 sample pieces (~ 5 mm x 7 mm) were polished on one side. SIMS analyses were performed at two or more locations, ~ 150 microns apart, on each sample (polished face). Average concentrations of impurities from two or more locations were averaged and reported for each sample.

B, Al, Ca and Fe: These elements were analyzed using oxygen beam sputtering and positive ion detection (O-SIMS). B was analyzed using maximum transmission. Al was analyzed using Medium Mass Resolution. Ca and Fe were analyzed using High Mass Resolution.

C, O and P: These elements were analyzed using Cs beam sputtering and negative ion detection (Cs-SIMS). C and O was analyzed using best detection sensitivity (low background). P was analyzed using High Mass Resolution.

All quantifications are based on EAG reference materials (standards). The B and P standards are calibrated to NIST standard reference materials, and are accurate to within 1-3%. The Al, C, O, Ca and Fe standards are Ion implanted reference materials which are accurate to within 10-15%.

Analysis precision was as follows. B control (2.9E16/cc) samples were measured together with all samples in B measurements. The analysis precision (1σ) was 3.5%. For all other elements, multiple pieces of

standards were measured. The analysis precisions (1σ) were 3-8%.

3.4 Results - Boron

Table III shows the data for B measurements in the 20 samples taken from the Center Vertical and Center Horizontal of two of the UMG-Si bricks. The left hand column lists data for samples taken from the Center Vertical of a brick. The sample number sequence (1 through 10) is the sequence of samples taken from the top to bottom of the brick. The average of the 10 samples taken from the center vertical is $3.71E17/cc$ and the relative standard deviation (RSD) of the 10 samples is 6.0%. However, the standard deviation is misleading because the B values of the 10 samples in sequence are not random. There is a B trend from top to bottom of the as shown the by the % deviation from average for each of the 10 samples. The range (maximum/ minimum) of B is about 1.2x. As stated earlier the analysis precision for B is small (3.5 %) compared to the trend.

Table III: Boron distribution (units of atoms/cm³)

Center Vertical			Center Horizontal		
Sample Sequence			Sample Sequence		
Sample No	Average	Deviation from Ave	Sample No	Average	Deviation from Ave
1	3.59E+17	-3.4%	1	2.30E+17	-12.7%
2	3.37E+17	-9.2%	2	2.90E+17	10.3%
3	3.58E+17	-3.6%	3	2.76E+17	4.9%
4	3.48E+17	-6.3%	4	2.25E+17	-14.6%
5	3.85E+17	3.8%	5	2.69E+17	2.3%
6	3.72E+17	0.4%	6	2.86E+17	8.6%
7	3.90E+17	5.0%	7	2.26E+17	-14.1%
8	4.14E+17	11.5%	8	3.00E+17	14.1%
9	3.79E+17	2.0%	9	2.84E+17	8.0%
10	3.67E+17	-1.1%	10	2.43E+17	-7.6%
Average	3.71E+17		Average	2.63E+17	
RSD	6.0%		RSD	11.1%	
Max/Min	1.2x		Max/Min	1.3x	
Trend?	yes		Trend?	no	

The far right set of data (Center Horizontal Sequence) are taken from the sequence of 10 samples taken horizontally across the center part of a UMG-Si brick. The average is $2.6E17/cc$, about 29% lower than the average of the 10 samples taken vertically from the center, and the RSD of 11.1% is about twice that of the RSD of the vertical sequence. The B across the center does not show a clear trend, unlike the other sequence. The range is 1.3x.

Not shown in Table III are the Edge Vertical sample data. This material is normally cut and excluded from the bricks. The data for the Edge Vertical samples show an average boron concentration of $5.06E17/cc$, an RSD of 18.7%, a range of 1.8x and a trend in the same direction as for the Center Vertical samples. Basically the Edge Vertical part of the brick have boron concentrations that vary much more than the other samples.

In summary, there are real distributions of B in the UMG-Si bricks, but as we will see next, on a relative basis the B is more uniform than the P.

3.4 Results – Phosphorus

The P data are shown in Table IV. The P RSDs are higher than the B RSDs. The trends are similar to the

boron. The Edge Vertical data is not shown, but like the boron, it is much more variable than the Center Vertical and Center Horizontal data.

Table IV: Phosphorus distribution (units of atoms/cm³)

Center Vertical			Center Horizontal		
Sample Sequence			Sample Sequence		
Sample	Average	Deviation from Ave	Sample	Average	Deviation from Ave
1	2.30E+17	-25.3%	1	1.43E+17	-27.5%
2	2.90E+17	-6.0%	2	2.00E+17	1.3%
3	1.95E+17	-36.7%	3	2.05E+17	3.8%
4	1.98E+17	-35.9%	4	1.36E+17	-31.0%
5	4.07E+17	32.0%	5	2.05E+17	3.9%
6	3.45E+17	12.0%	6	2.03E+17	3.0%
7	3.20E+17	3.9%	7	1.36E+17	-31.1%
8	4.00E+17	29.9%	8	3.37E+17	70.9%
9	3.55E+17	15.3%	9	2.49E+17	26.4%
10	3.45E+17	12.0%	10	1.55E+17	-21.4%
Average	3.08E+17		Average	1.97E+17	
RSD	25.3%		RSD	31.5%	
Max/Min	2.1x		Max/Min	2.5x	
Trend?	yes		Trend?	no	

3.5 Results – Aluminum

The Al data are shown in Table V. Again we see similar trends compared to the boron and phosphorus, but the range (3.8x) along the Center Horizontal is larger than for the other two elements. The Edge Vertical data has even greater variability.

Table V: Aluminum distribution (units of atoms/cm³)

Center Vertical			Center Horizontal		
Sample Sequence			Sample Sequence		
Sample	Average	Deviation from Ave	Sample	Average	Deviation from Ave
1	6.53E+16	-10.5%	1	1.08E+16	-56.7%
2	5.24E+16	-28.3%	2	3.00E+16	21.0%
3	6.50E+16	-11.0%	3	2.71E+16	9.1%
4	6.33E+16	-13.3%	4	1.32E+16	-47.0%
5	6.75E+16	-7.5%	5	2.84E+16	14.3%
6	7.74E+16	6.0%	6	3.45E+16	39.1%
7	8.61E+16	17.9%	7	1.39E+16	-44.0%
8	8.05E+16	10.3%	8	4.07E+16	63.9%
9	8.27E+16	13.3%	9	3.11E+16	25.2%
10	9.01E+16	23.4%	10	1.87E+16	-24.8%
Average	7.30E+16		Average	2.48E+16	
STD	16.5%		STD	40.7%	
Max/Min	1.7x		Max/Min	3.8x	
Trend?	yes		Trend?	no	

3.6 Results – Carbon

The C data are shown in Table VI. The carbon distribution down the Center Vertical is different than for B, P and Al in that there is no trend. The variability is high.

3.7 Results – Oxygen

The O data are shown in Table VII. As with C there are no trends. The variability is less than for the carbon, but significant. SIMS profiles and images (not shown here) reveal the oxygen has large precipitates while the carbon does not.

Table VI: Carbon distribution (units of atoms/cm³)

Center Vertical			Center Horizontal		
Sample Sequence			Sample Sequence		
Sample	Average	Deviation from Ave	Sample	Average	Deviation from Ave
1	6.21E+17	-25.5%	1	8.80E+17	-1.1%
2	9.83E+17	17.9%	2	1.10E+18	23.9%
3	6.23E+17	-25.3%	3	8.85E+17	-0.6%
4	6.41E+17	-23.1%	4	6.67E+17	-25.1%
5	9.86E+17	18.3%	5	6.90E+17	-22.5%
6	1.03E+18	23.0%	6	7.47E+17	-16.1%
7	9.41E+17	13.0%	7	6.37E+17	-28.5%
8	1.06E+18	27.3%	8	1.60E+18	79.4%
9	8.10E+17	-2.8%	9	1.01E+18	13.4%
10	6.41E+17	-23.1%	10	6.90E+17	-22.5%
Average	8.33E+17		Average	8.90E+17	
RSD	22.3%		RSD	32.9%	
Max/Min	2.3x		Max/Min	2.5x	
Trend?	no		Trend?	no	

Table VII: Oxygen distribution (units of atoms/cm³)

Center Vertical			Center Horizontal		
Sample Sequence			Sample Sequence		
Sample	Average	Deviation from Ave	Sample	Average	Deviation from Ave
1	2.20E+18	9.3%	1	2.21E+18	21.8%
2	1.70E+18	-16.6%	2	2.11E+18	16.6%
3	2.55E+18	27.5%	3	1.74E+18	-4.1%
4	1.70E+18	-16.6%	4	1.69E+18	-6.9%
5	1.73E+18	-15.3%	5	1.96E+18	8.0%
6	1.90E+18	-6.2%	6	1.76E+18	-2.8%
7	1.75E+18	-14.0%	7	1.41E+18	-22.1%
8	1.95E+18	-3.9%	8	1.31E+18	-27.9%
9	1.70E+18	-16.6%	9	2.55E+18	40.9%
10	2.15E+18	6.7%	10	1.39E+18	-23.5%
Average	1.93E+18		Average	1.81E+18	
RSD	14.9%		RSD	22.1%	
Max/Min	1.5x		Max/Min	1.9x	
Trend?	no		Trend?	no	

3.8 Results – Ca and Fe

No Ca (<2E12/cc) or Fe (<mid E13/cc) were detected, even in the Edge Vertical Samples.

3.9 Summary of impurity distribution

Table VIII shows a summary of all the data, even the Edge Vertical data. Ca and Fe were not detected.

3.10 Discussion and conclusions on impurity distribution

Some of the trending data (i.e., present for dopants B, P, and Al, but not present for C and O) along the Center Vertical may be due to impurity segregation as the brick was cooled, even though this was not cooled by a direct-solidification process often used to make blocks for wafer slicing. We do not know how the cooling occurred, or how the cooling occurred with respect to the sample sequences. The purpose of this study was to demonstrate how SIMS can provide distribution information. The UMG-Si manufacturer could use the data coupled with

their process knowledge to interpret the data from a process standpoint, and from the standpoint of how to sample the material to establish if they were doing *representative sampling*.

The Center Horizontal data do not suggest impurity segregation, but do reveal a wide range of variability depending upon the specific elements. The SIMS precisions are good enough to establish this variability is real.

We conclude that SIMS can provide useful information on the distribution of impurities in UMG-Si bricks. Another conclusion is that the total volume of the analysis (for SIMS it is small) is not critical in that a larger analysis volume would not make the measurement/sampling more representative, because the dimensions over which there are significant changes in concentration are much, much larger than any analytical volume technique available other than maybe NAA.

Table VIII: Summary of impurity distributions units of atoms/cm³)

	B	P	Al	C	O
Edge Vertical					
Ave	5.06E+17	2.96E+17	3.04E+17	9.42E+17	1.62E+18
RSD	18.7%	61.9%	119.0%	26.5%	37.0%
Max/Min	1.8x	4.5x	12.2x	1.9x	4.2x
Trend?	yes	yes	yes	no	yes
Center Vertical					
Ave	3.71E+17	3.08E+17	7.30E+16	8.68E+17	1.93E+18
RSD	6.0%	25.3%	16.5%	29.4%	14.9%
Max/Min	1.2x	2.1x	1.7x	2.3x	1.5x
Trend?	yes	yes	yes	no	no
Center Horizontal					
Ave	2.63E+17	1.97E+17	2.48E+16	8.90E+17	1.81E+18
RSD	11.1%	31.5%	40.7%	32.9%	22.1%
Max/Min	1.3x	2.5x	3.8x	2.5x	1.9x
Trend?	no	no	no	no	no

4 REFERENCES

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