

Solar Grade Feedstock Evaluation Using GDMS and SIMS

R. S. Hockett, Chief Scientist, Evans Analytical Group, Sunnyvale, CA, USA
dhockett@eaglabs.com

Abstract

This paper is an expansion of a paper presented at the 18th NREL Workshop on Crystalline Silicon Solar Cells & Modules: Materials and Processes, Vail, CO, August 3-6, 2008. The NREL Workshop paper reviewed analytical techniques that may be used to evaluate solar grade Si feedstock, and presented data on the application of SIMS in characterizing the impurity content (B, P, Al, C, O, Ca and Fe) of UMG-Si bricks that were formed for shipment (not a direct solidification process). This paper expands the NREL Workshop paper by including SIMS data of C, O and N at two sequential *commercial* process steps:

- (a) feedstock: 7N (modified Siemens) and 5N feedstock (UMG-Si)
- (b) wafers: cut and etched, from direct solidification bricks grown from 7N and 7N/5N (80:20) feedstock

Introduction, background, caveats, and cautions

This paper is an overview of analytical techniques for evaluating silicon solid material that is used to manufacture crystalline or micro-crystalline silicon solar cells. In any overview of a technical field, the author's experience and expertise leads to emphasis on some topics, less on others and benign neglect on some. I claim nothing less. I worked for some years as a senior research group leader for analytics in a silicon substrate company (the predecessor to MEMC), and for twenty years in managing instrumental analytics as an international commercial service business at the Evans Analytical Group (previously known as Charles Evans & Associates). As such I do not have expertise on the use of wet chemistry or optical/electrical characterization techniques for silicon. I also have been active for many years in the development of ASTM and SEMI test methods in the area of semiconductor silicon, but again this was related to instrumental analytics. I am presently Chairman of the SEMI Europe PV Analytical Test Methods Task Force and Co-Chairman of the SEMI North American PV Analytical Test Methods Task Force, both under SEMI PV Standards. This experience emphasizes test methods and techniques that can be used in the commercial world of industry, and de-emphasizes innovative analytics that may not have reach commercialization (for example, in universities or research institutes.)

Before delving into specific analytical techniques, it is important to understand that an analytical technique that is used in the commercial materials world is only part of the problem of evaluating silicon feedstock. *Representative* sampling (cf. ASTM Practice E 122, ANSI/ASQC Z1.4-1993) and process stability of the silicon feedstock are also part of the problem, and a procedure to validate the measurement capability (SEMI E89), statistical process control of the total measurement, and the effects on costs (SEMI M56-0307) are also critical. None of these issues are simple.



The broader picture

Test method is only one part of the PV Si feedstock evaluation

1. Representative sampling ([ASTM Practice E 122](#))
 2. Process stability
 3. Validation of measurement capability ([SEMI E89](#))
 4. Statistical process control of the measurement
 5. Cost effect of the measurement (product errors due to measurement variability and bias) ([SEMI M56](#))
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One last caveat – there is no clear definition in the PV industry on what defines PV Si Feedstock (or Solar Grade Silicon), and various analytics may or may not be appropriate depending up how one makes that definition. There are even loosely termed “grades” of solar grade silicon. The PV industry, as it stands today, is a very new industry, and as such there is much unknown, some would call chaos. But it is producing product which is being used worldwide. This is what we, as analysts, have to work with today. This can be fun.



One last caveat

The terms “PV Si Feedstock” or “Solar Grade Silicon” do not have consensus definitions

→ An analytical technique may be appropriate for low (or high) levels of impurities in silicon

→ An analytical technique may be appropriate for some impurities (but not others) in silicon

What needs to be evaluated in Feedstock Evaluation?

The answer to this is universally (to my knowledge) – impurities, and “elemental” impurities, not impurities in compounds or various chemical states. The reason for this is that PV Si feedstock is converted into crystalline or multi-crystalline material through a high temperature process (solid silicon melts at 1420 °C) whereby chemical bonding in the original feedstock is lost.

The specific elemental impurities that need to be evaluated in feedstock depends, to some extent, upon the process to make the solar wafer and the solar cell design and processing. However, the list of impurities always includes the following: dopants (mainly B and P), atmospheric (mainly O and C) and transition metals (especially Fe). But beyond the usual suspects, the list can be expanded to almost the entire periodic table of elements (conversion of metallurgical grade silicon into “upgraded” metallurgical grade silicon for PV Si feedstock may result in many different impurities beyond the usual suspects.)



What needs to be evaluated?

Elemental Impurities

- Dopants (mainly B and P)
- Atmospheric (mainly O in p-type Si, and C)
- Transition metals (mainly Fe)

- BUT...
Some PV Si feedstock has a broad range of other impurities (other metals, other dopants, Ge, etc.)

The solar cell design may be more tolerant of some impurities (higher impurity levels, or elements).

Review of analytical techniques

The definition of an analytical technique for feedstock evaluation includes the sample preparation, not just the direct analysis. The reason is that the sample preparation may change the concentrations of the impurities of interest, or the sample preparation may create a chemical state of an impurity that is useful, or not, in the analysis. An example would be to take the feedstock and grow a multi-crystalline block that could be analyzed using resistivity, lifetime techniques, or FTIR. The process of growing the block may introduce impurities, such as O, C, N, and Fe, or even dopants such as Al. Or, the process may result in a mix of chemical states for O which can affect the FTIR measurement, or thermal donors related to O which will affect resistivity. The “analysis” which includes the sample preparation would have to be controlled and monitored in such a way that these artifacts do not result in misleading data. For these kinds of reasons, we will comment on the sample preparation as part of the analytical technique.



The definition of an analytical technique for PV Si Feedstock must include the sample prep

→ Sample prep may add, or remove, impurities before the analysis

→ Sample prep may create a chemical state or electronic state of the impurity which is useful, or not, for the analytical technique

At first thought the simplest approach to feedstock evaluation is to convert the silicon feedstock into a form whereby resistivity, lifetime and FTIR can be measured. If the new form is a single-crystal of Si grown by the Float-Zone process (SEMI MF1723-1104, SEMI MF1708-1104) followed by a thermal donor annihilation process and a 2 mm slug is cut from the ingot, then resistivity measurement provides the net carrier concentration, lifetime gives an indirect measure of the impurities, and FTIR (SEMI MF1188, SEMI MF1391) provides interstitial O concentration and substitutional C concentration. Lifetime (SEMI MF28) can provide a qualitative measure of some metals, and SPV (SEMI MF391) can provide a quantitative measure of Fe in p-type (B-doped) silicon. Low temperature FTIR (SEMI MF1630) or PL (SEMI MF1398) can provide B, P and Al concentrations. One must take into account the segregation coefficients of impurities through the FZ ingot (SEMI MF 1723-1104). This kind of collective analysis was common for Siemens polysilicon evaluation in the 1980's and may still be today. The sample preparation process could be done cleanly, and the O and C tended to form chemical states accessible to FTIR. For very high purity Siemens polysilicon this works well. It should be noted that the very high purity Siemens polysilicon had extremely low concentrations of dopants and metals.



Example suite of techniques

- Convert the PV Si feedstock into a single crystal 2mm thick test sample (SEMI MF1723, SEMI MF1708) followed by thermal donor annihilation (TDA)
 - Resistivity vs position in ingot (SEMI MF43) and type (SEMI MF42) – net carrier concentration, dopant concentration (SEMI MF1723)
 - Lifetime (SEMI MF28) – scattering from metal concentration
 - SPV for Fe in p-type (B doped) (SEMI MF391)
 - FTIR – O_i (SEMI MF1188) and C_s (SEMI MF1391)
 - Low T FTIR – B, P, Al (SEMI MF1630)
 - PL – B, P, Al (SEMI MF1398)
-

However, there are issues with this suite of techniques. The test method (SEMI MF1630) for low temperature FTIR is limited to 5 ppba of electrically active impurity and the test method (SEMI MF1398) for PL also has some upper limits ($1 \times 10^{15}/\text{cm}^3$). These upper limits in concentrations restrict these techniques from being useful for a range of higher impurity PV Si Feedstock. Resistivity by itself cannot provide dopant concentration if there is compensation from different dopants. Lifetime is not element specific, and SPV misses other metals, so the actual concentration of metals is not known. In upgraded metallurgical grade silicon, Ge at the ppm wt level may affect the thermal donor annihilation.



Issues: Example suite of techniques

- Convert the PV Si feedstock into a single crystal 2mm thick test sample followed by thermal donor annihilation (TDA) – **Ge may alter TDA**
- Resistivity vs position in ingot, and type – net carrier and dopant concentration
- Lifetime – scattering from metal concentration – **not element specific**
- SPV for Fe in p-type (B doped) – **miss other metals**
- FTIR – O_i and C_s
- Low T FTIR – B, P, Al – **limited to < 5 ppba**
- PL – B, P, Al – **limited to < $1 \times 10^{15}/\text{cm}^3$**

One can go through a similar sample preparation as above via a Cz crystal growth process, but O is introduced from the crucible and the low temperature FTIR and PL have the same constraints as described above.

One can follow a similar sample preparation but using a multi-crystalline growth process like direct solidification. In this case O, C, N and Fe may be introduced, and the O, C and N may form precipitates that are not quantifiable by the FTIR. If there is more than one dominant dopant, resistivity will not give the correct dopant concentration. If one knows the impurity segregation coefficients and measures the resistivity as a function of position along the growth axis of the multi-crystalline ingot, in principle the dopant concentrations can be determined. One needs to truly know the segregation coefficients which are a function of the growth rate, and all contributions from thermal donors need to be eliminated. Artifacts from the multi-crystalline nature of the material that can affect the resistivity need to be eliminated.

Lifetime measurements provide an indirect measure of contamination, at least for those which are strong scatters of minority carriers, but identification of specific metals or their concentrations are not possible except for Fe in B-doped silicon using SPV. Although lifetime is an indirect measure of contamination, for many solar cell designs this parameter is key even if the specific elements are not known. The downside is that a low lifetime does not identify how to improve the feedstock quality.

Accuracy of the FTIR [O] is compromised by the reflectivity of the sample backside compared to the BLANK.



2nd Example suite of techniques

- Convert the PV Si feedstock into a multi-crystalline test sample by DS followed by thermal donor annihilation - **Contaminants may be introduced**
- Resistivity and type – net carrier and dopant concentration - **segregation coefficients vary with growth rate; need to know all the dopants; must do TDA**
- Lifetime – scattering from metal concentration – **and defects and compensating dopants, not element specific**
- SPV for Fe in p-type (B doped) – **miss other metals; thin wafers**
- FTIR – O_i and C_s – **O and C precipitates; backside reflection**
- Low T FTIR – B, P, Al – **bulk defects? limited to < 5 ppba**
- PL – B, P, Al – **bulk defects? limited to < 1x10¹⁵/cm³**

The next series of analytical techniques do not require a conversion of the feedstock into ingot or block form.

Neutron Activation Analysis (NAA) is the most sensitive instrumental analysis technique for bulk analysis of moderate to high-Z impurities, and can make measurements on any form of the feedstock (Huber *et al*, J. Radio. & Nucl. Chem. 169, p. 93, 1993). The technique requires access to a neutron source which makes it restricted in location, and the nuclear decay times for analysis are quite long, so that analysis results can take one or more months to achieve. Thus, this technique though the most sensitive has limited use commercially. NAA is used for IC-grade polysilicon analysis for metals because of its very high sensitivity and the ability to quantify individual elements. Detection limits for the dopants B, P and Al are not useful.

Another analytical technique that was developed for the IC-grade polysilicon is acid extraction followed by atomic absorption spectroscopy (SEMI MF1724) or ICPMS. This method was developed to test for metals on the surface of the polysilicon and was not intended as a bulk analysis. It could be applied to any polysilicon form, such as chunks, granules, or powders. The test method describes the use of blanks and controls that are critical to identifying interferences, and this method requires a high skill in order to avoid contamination. The downside of this test method is that it does not measure the bulk impurity levels, and detection of P, S, O, C and N are not useful. It is possible to do a variant of this method by digesting the entire sample (a small sample) and then analyzing the solution by ICPMS. Memory effects can be a problem if both very pure and very dirty samples are to be monitored, and the inability to detect P at reasonable levels is a limitation because of a mass interference from residual silicon and hydrogen. The SEMI PV Committee approved on Oct. 15, 2008, a new work item under the PV Analytical Test

Methods Task Force group to develop an international test method for bulk-digestion ICP-MS of PV Si feedstock.

Instrumental Gas Analysis, or Gas Fusion, requires the feedstock to be shaped into a cylinder for insertion into the instrument which heats the sample such that gases (O, C, N, H) from the sample are emitted and analyzed. One must note that the gaseous species can derive from the sample surface or its bulk, but emission from the bulk does not depend upon chemical state. Detection limit for O is 1 ppmwt which is useful. If the sample is a very fine polysilicon powder with a high surface to volume ratio, the surface O may introduce a bias.

The last two techniques are Glow Discharge Mass Spectrometry (GDMS) and Secondary Ion Mass Spectrometry (SIMS), both of which are direct sampling techniques, require no conversion of the feedstock form, and samples of all forms can be analyzed – chunks, granules, powders, or wafers. Samples may require no “preparation”, or simple mechanical shaping. Both techniques can be used to analyze all elements in the periodic table (but detection limits or precisions may not be useful for all elements or “grades” of feedstock), and the analysis is independent of the chemical or electronic state of the impurity.

An international standard test method (SEMI PV1-0309) for GDMS as applied to PV Si feedstock passed international ballot and was approved on Oct. 15, 2008, by the SEMI PV Committee.

SIMS has been used in the IC silicon industry for over 20 years (for example, ASTM test methods F 1528, F 2139, F 1366, and F 1617). SIMS can in principle achieve better precisions than GDMS.

The GDMS survey method is most cost effective (compared to SIMS) when many impurity elements (up to 73) are of interest, while SIMS is the test method of choice when best accuracy and detection limits of dopant elements - such as B and P – are needed. SIMS also provides the best detection limits and analysis precision for atmospheric species, such as C, O, N and H.

GDMS analysis of PV Si

Cathodic sputtering is used for GDMS analysis. The cathode/sample is bombarded by positive ions formed in the glow-discharge. Argon is typically used as the discharge gas. Argon positive ions are accelerated towards the cathode (sample) surface with energies from hundreds to thousands of eV resulting in erosion and atomization of the upper atom layers of the sample. This bombardment produces surface erosion, layer by layer. Atoms, electrons and ions are removed from the surface of the cathode/sample. This sputtered material then participates in ionization caused by collisions in the discharge. Analyte ions generated from the sputtered area are measured after being mass separated in a mass spectrometer. The ions are converted into concentrations, typically in unit of parts per million in weight (ppm wt), based on element dependent calibration factors.



Other Techniques - GDMS

- **High Resolution 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 International Standard Test Method (SEMI PV1-0309)

Traditional GDMS calibrations for silicon are traced back to NIST SRMs of metallurgical grade silicon or steels. To improve the accuracy for the dopants B and P, EAG has developed protocols that trace the B and P calibration to NIST SRMs of B and P in silicon.

GDMS techniques can be used to quantitatively measure the elemental impurity concentrations in 6N or 99.9999% pure materials and cleaner. The GDMS survey methods are the most cost effective especially when many impurity elements (up to 73) are of interest.

The table below shows GDMS results of ultra-high purity “IC grade” boron-doped Si ingot. Only B was detected in this BLANK sample. The B detection limit in Si is 0.001 ppm wt.

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		

The weaknesses of GDMS are that it is not useful for detecting O, C or N, and apart from the dopants B and P, the accuracy of the quantification is within a factor of 2x without reference materials. The precisions range from 10% for high levels of impurities, to 25% for low levels. This technique is useful for upgraded metallurgical silicon where a wide range of impurities may be present, but not for Siemens-based polysilicon due to detection limits.



Other Techniques - GDMS

- **High Resolution Glow Discharge Mass Spectrometry (GDMS)**

- not useful for O, C or N

- accuracy tied to reference materials; B and P traceable to NIST SRMs, other elements within factor of 2x

- precisions range from 10% for high levels to 25% for low levels

- not useful for Siemens-based PV Si (8N and purer)

SIMS analysis of PV Si

Secondary Ion Mass Spectrometry (SIMS) analysis provides a more accurate quantitative measurement for impurities in PV Si at the sub-6N level (sometimes needing high mass resolution). Unlike Neutron Activation Analysis (NAA) which takes a few months to complete the analysis, SIMS can be accomplished within a few hours. SIMS can measure all elements of the periodic table, but is especially good for dopants (B, P, As, Sb, Al, In) independent of electrical activity and for atmospherics (H, O, C, N)

independent of their chemical state. The cost of SIMS for a few elements is low, but because it is an element specific technique the cost can become prohibitive for a large number of elements. GDMS is recommended when the number of elements of interest is more than a few.



Other Techniques - SIMS

- **Secondary Ion Mass Spectrometry (SIMS)**
 - all elements in periodic table, including B, P, O, C, Fe, (and N)
 - 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
-

During a SIMS analysis, the samples are sputtered by a focused energetic primary ion beam, either oxygen (O_2^+) or cesium (Cs^+). Secondary ions formed during the sputtering process are accelerated away from the sample surface. Secondary ions are energy separated by an electrostatic analyzer and mass separated based on their mass/charge ratio by a magnetic mass analyzer. Oxygen (O_2^+) beam sputtering is used to enhance ion yield of electropositive species (boron and metal elements); cesium (Cs^+) beam sputtering is used to enhance ion yield of electronegative species (P, As, Sb and atmospheric species).

By choosing the proper primary beam and using optimized instrument conditions, SIMS can provide excellent detection limits at sub-ppm to ppt level. The table below shows SIMS detection limits at bulk mode in Si for selected elements. Please note that units used in the table are atoms/cm³ and parts per **billion** in weight (ppb wt).



SIMS detection limits in Si

Atoms/cm³ (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)

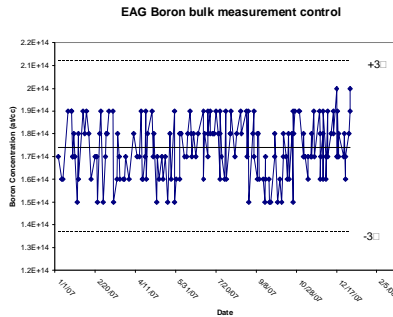
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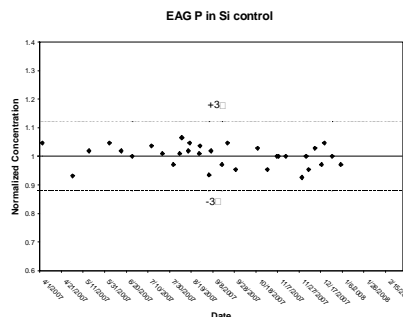
SIMS is both accurate by using traceable reference materials and precise using highly developed protocols and instrumentation. For the dopants B, As, and P in silicon there are even NIST certified reference materials. Long term precisions for bulk analysis of B and P in Si are shown in the following figure. Even at very low 10¹⁴/cm³ concentration level of B (0.001 ppm wt), SIMS analysis can achieve long term reproducibility of 7.5 %



Long-term reproducibility



Stdev (1s) =7.5%



Stdev (1s) =4%

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(1 σ).

PV Si can come in many forms, including powders. SIMS can be used to measure wafers, chunks, granules, flakes or even powders if the size of the powder is greater than 300 um.

Results below were obtained from powder Si sample (see figure below) with the impurities in individual powder pieces, as shown in the following table. The analyses were performed using five analytical conditions.

Element	Ppm wt	Element	ppm wt
B	1.1	Cr	<7E-5
C	9	Fe	<0.001
O	30	Ni	<0.008
Al	0.3	As	0.07
P	8.1		



The primary downside to SIMS is the complexity of protocol development and instrument optimization required to reach the detection limits listed above, and it is expensive when a large number of elements need to be monitored.



Other Techniques - SIMS

- **SIMS**

- **protocol development and instrument optimization for very low detection limits**

- **expensive when a large number of elements is of interest**

In conclusion, GDMS can provide high sensitivity survey and total elemental impurity mass concentrations analysis. SIMS can be used for accurate, precise, and localized measurement of selected impurities in PV Si.

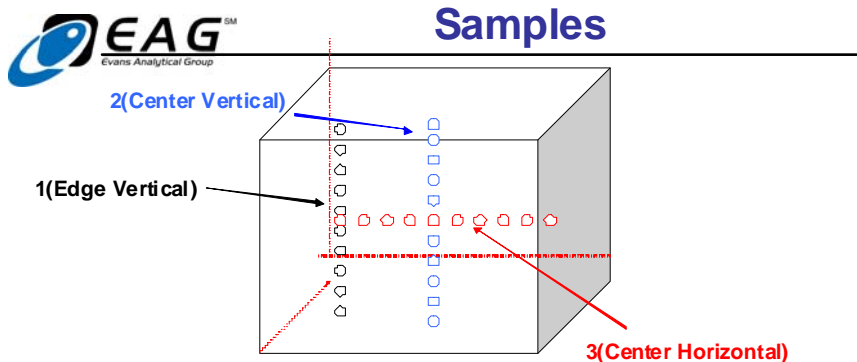
Case Study: Uniformity Study of B, Al, P, C, O, Ca and Fe in Upgraded Metallurgical Silicon (UMG-Si) by SIMS

In the beginning of this paper we mentioned that the analysis 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. The conclusion was this kind of study will be very important.

Experimental Design

This particular UMG-Si process (not direct solidification) for shipping material results in a large, rectangular block of silicon. Samples were taken from three UMG-Si blocks in locations as illustrated in the following figure.



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 left to right. The location is in the middle between top and bottom

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

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%.

Results

The following table shows the data for B measurements in the 30 samples taken from three UMG-Si blocks. Concentration units are atoms/cc. The left hand column lists data for samples taken on the edge of a block. This material is normally cut from the UMG-Si block and excluded from use. The sample number sequence (1 through 10) is the sequence of samples taken from the top to bottom of the edge. The average of the 10 samples taken from the edge is 5.06E17/cc and the relative standard deviation (RSD) of the 10 samples is 18.7%. 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 edge as shown the by the % deviation from average for each of the 10 samples. The range (maximum/ minimum) of B is about 1.8x. As stated earlier the analysis precision for B is small (3.5 %) compared to the trend.

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	

The middle set of data (Center Vertical Sequence) are taken from the sequence of 10 samples taken vertically down the center part of a UMG-Si block. The average is 3.7E17/cc, about 27% lower than the average of the 10 samples taken from the edge, but more importantly the RSD of 6.0% is one third of the RSD of the edge sequence. The B down the center is more uniform than on the edge. The range is 1.2x. There appears to also be a trend.

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 block. 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 two sequences. The range is 1.3x.

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

The P data are shown in the following table. The averages of the P sequences are closer together than the B, but the RSDs are higher. Two of the sequences have trends.

P Data (units of atoms/cc)

Edge Vertical			Center Vertical			Center Horizontal		
Sample Sequence			Sample Sequence			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	

A summary table for the impurity elements is shown below.

Summary of Results

<u>Sample Sequence</u>	<u>B</u>	<u>P</u>	<u>Al</u>	<u>C</u>	<u>O</u>	<u>Ca</u>	<u>Fe</u>
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 from the Summary Table:

- Impurity distributions in UMG-Silicon blocks or bricks formed for shipping are generally not uniform. (These are not grown by a direct solidification process.)
- The range of non-uniformity is element specific
- Boron in this study is the most uniformly distributed element in UMG-Silicon

- Some impurities in some sections show trends (not random distribution) – most likely process dependent
- Sensitive analytical measurements can help manufacturers to improve their processes
- Analytical results can be used to determine, for instance, what material to exclude (e.g., edge)
- Analytical results can be used to select where representative samples should be taken.
- Sampling volume for techniques such as SIMS, GDMS or ICPMS is not relevant

In summary, SIMS can be used to study the uniformity of impurities in UMG-Si, and thereby provide a metric to improve uniformity. In addition, SIMS can help determine where and how many samples need to be analyzed to give a *representative* level of impurities. Lastly, this study reveals that the analytical volume in an analysis (which varies between SIMS, GDMS, ICPMS) does not determine whether one technique can give a *more representative* level of impurities.

Case Study: SIMS data of C, O and N at two sequential *commercial* process steps: Feedstock and Wafer

Oxygen, carbon and nitrogen are important elements in silicon photovoltaic (PV) technology.

- Oxygen forms a BO_x defect in p-type Si wafers which are used in most Si solar cells, and this defect is responsible for the initial light-induced degradation of solar cell efficiency. Controlling the oxygen concentration below some prescribed level is one approach to reduce this efficiency loss. The SEMI PV wafer standard M6-0707 prescribes that the oxygen concentration should be below $8 \times 10^{17}/\text{cm}^3$ in multi-crystalline wafers and $1 \times 10^{18}/\text{cm}^3$ in single crystal wafers.

Oxygen can enter the silicon from a variety of paths, such as,

- (1) the crucible material used in Cz-pullers and in direct solidification furnaces;
- (2) the process of making Si feedstock bricks if it some kind of oxide liner is used in the brick formation; or
- (3) the process for upgrading metallurgical-grade silicon as feedstock for Si solar wafers.

The measurement of oxygen in silicon at levels of $8 \times 10^{17}/\text{cm}^3$ implies the detection limit should be below $8 \times 10^{16}/\text{cm}^3$. The chosen analytical method can depend upon the form of the silicon to be tested. For example, FTIR can be used for single crystal silicon wafers according to SEMI MF1188-1107. However, this method has some special challenges for multi-crystalline wafers in that there may

be considerable oxygen precipitation which is not quantified by FTIR, and the backside IR reflectance is most likely not matched to the BLANK silicon wafer used in the method, thus giving a bias error the determination of the oxygen content. If the oxygen needs to be measured in feedstock bricks, chunks, granules or flakes, FTIR is not appropriate.

SIMS can measure the oxygen concentration in all these forms of silicon. [SIMS has been used for over 20 years to measure [O] in heavily-doped single crystal electronic-grade silicon according to SEMI MF1366-1107, and a variant of this method can be used for non-wafer physical forms as well.]

- Carbon can form SiC-type defects in including filaments in multi-crystalline PV Si. These defects can cause local shunting behavior and may affect minority carrier lifetime. But another reason to limit the carbon concentration is the formation of rod-like SiC defects in multi-crystalline PV blocks that can break wire saws used to slice the wafers. The SEMI PV wafer standard prescribes that carbon concentration should be below $1 \times 10^{18}/\text{cm}^3$ in multi-crystalline wafers and $5 \times 10^{17}/\text{cm}^3$ in single crystal wafers.

Carbon can enter the silicon from a variety of paths, such as,

- (1) the crucible material used in Cz-pullers or other furnaces;
- (2) from the open ambient in direct solidification furnaces;
- (3) the process of making feedstock bricks if an open ambient is used in the cooling; or
- (4) the process for upgrading metallurgical-grade silicon for Si PV.

The measurement of carbon in silicon at levels of $5-10 \times 10^{17}/\text{cm}^3$ implies a desired detection limit of $5-10 \times 10^{16}/\text{cm}^3$. The chosen analytical method can depend upon the form of the silicon to be tested. For example, FTIR can be used for single crystal silicon wafers according to SEMI MF1391-1107. However, this method has some special challenges for multi-crystalline wafers in that the reference substrate is to be the same thickness as the solar wafer and have a carbon content below 2×10^{15} and the test method is limited to resistivity above 3 ohm-cm for p-type wafers which is higher than Si solar wafers. If the carbon needs to be measured in feedstock bricks, chunks, granules or flakes, FTIR is not appropriate.

SIMS can measure the carbon concentration in all these forms of silicon. [SIMS has been used for over 15 years to measure [C] in heavily-doped single crystal electronic-grade silicon, and this method works for all forms of silicon.]

- Nitrogen can form nitride-type defects in multi-crystalline PV Si. These defects may affect minority carrier lifetime. But there is another more fundamental reason to measure nitrogen in PV Si. Nitrogen can have an important effect on the Si vacancy and Si interstitial concentrations in silicon, and these point defect concentrations affect the diffusion of metal contaminants. The diffusion of metals is important in the segregation of metals in direct solidification furnaces, in gettering schemes (such as phosphorus gettering), and in other processes designed to deactivate metals from being minority carrier lifetime degraders.

The main recognized source of nitrogen in silicon is the nitride release liner in multi-crystalline furnaces, but there may also be nitrogen introduced from the less expensive crucibles used in PV Si. Residual nitrogen may also be present in UMG-Si.

The measurement of nitrogen in silicon at levels of $1 \times 10^{16}/\text{cm}^3$ implies a desired detection limit of $1 \times 10^{15}/\text{cm}^3$. The chosen analytical method can depend upon the form of the silicon to be tested. For example, FTIR can be used for single crystal silicon wafers but the quantification is complicated by the many forms of nitrogen in silicon. If the nitrogen needs to be measured in feedstock bricks, chunks, granules or flakes, FTIR is not appropriate.

SIMS can measure the nitrogen concentration in all these forms of silicon. [SIMS has been used for over 15 years to measure [N] in single crystal electronic-grade silicon (SEMI MF2139-1103), and this method works for all forms of silicon.]

In the following case study, SIMS measurements of C, O and N were made on various silicon materials in the process of making Si solar cells. First, two sources of Si feedstock were analyzed: (a) polysilicon from a modified Siemens process, called “7N” Si feedstock here, and (b) upgraded metallurgical grade silicon (UMG-S), called “5N” Si feedstock here. The “N” is an abbreviation of “9”, so that 7N means the material was 7 “nines” pure (99.99999%), and 5N means the material was 5 “nines” pure (99.999%). The 7N purity was limited by Cl and H in the bulk. These two silicon feedstocks represent two ways (and purity and cost) for manufacturing the purified Si fed into direct solidification furnaces that melt and regrow the silicon into very large multi-crystalline blocks. After the blocks are grown, they are cut into subsections called bricks from which Si solar wafers are then cut. Lastly, the Si solar wafer is converted into a Si solar cell using various depositions and thermal processing. To save costs sometimes the 7N (higher cost, higher purity) and 5N (lower cost, lower purity) are mixed in some predetermined proportion in the direct solidification furnace.

In this study they were mixed in the following proportion: 7N:5N of 80:20, or 7N:5N of 100:0 (no mixing) in two direct solidification furnace runs to make two blocks. For each block 16 bricks were cut out, and solar wafers were sliced from the bricks and polish etched. The slicing was done perpendicular to the solidification direction. Slices from three of the 16 bricks were taken for measurements: corner brick, center brick, and side brick.

SIMS measurements were made on the following eight samples:

7N Si feedstock: 7N PV Si

5N Si feedstock: 5N PV Si

Wafer from the corner brick of 7N grown block: 7N-Corner

Wafer from the center brick of 7N grown block: 7N-Center

Wafer from the edge brick of 7N grown block: 7N-Edge

Wafer from the corner brick of 7N:5N (80:20) block: 7N:5N-Corner

Wafer from the center brick of 7N:5N (80:20) block: 7N:5N-Center

Wafer from the edge brick of 7N:5N (80:20) block: 7N:5N-Edge

Carbon and oxygen measurements of wafers were done on two separate days and two separate pieces.

The SIMS results are shown in the following table. The two columns for [C] and for [O] represent repeat measurements several months apart.

	units of atoms/cc				
	[C]	[C]	[O]	[O]	[N]
7N PV Si	<5E15		<1E16		3.E+14
5N PV Si	3.7E+17		2.0E+18		5.5E+15 N precipitates
Detection Limit	5.E+15		1.E+16		2.E+14
7N-Corner	5.6E+17	5.4E+17	1.1E+17	1.1E+17	1.3E+16
7N-Center	6.3E+17	7.8E+17	7.7E+16	8.2E+16	1.1E+16
7N-Edge	4.8E+17	6.0E+17	8.4E+16	7.1E+16	9.6E+15
Detection Limit	2.E+16	3.E+16	2.E+16	2.E+16	7.E+14
7N:5N Corner	3.9E+17	4.3E+17	1.6E+17	1.5E+17	1.1E+16
7N:5N Center	4.0E+17	5.8E+17	1.6E+17	2.0E+17	1.4E+16
7N:5N Edge	4.4E+17	5.4E+17	1.4E+17	1.2E+17	1.2E+16
Detection Limit	2.E+16	3.E+16	2.E+16	2.E+16	7.E+14
	7N/5N ratioed to 7N				
Corner	0.70	0.80	1.45	1.36	0.85
Center	0.63	0.74	2.08	2.44	1.27
Edge	0.92	0.90	1.67	1.69	1.25

Discussion:

The 7N PV Si (modified Siemens process) has no detectable [C] or [O] below $5 \times 10^{15}/\text{cm}^3$ and $1 \times 10^{16}/\text{cm}^3$ respectively. This is as expected for a Siemens-based polysilicon process.

The 7N PV Si does have detectable [N] which is about an order of magnitude higher than found in electronic grade Si substrates.

The 5N PV Si which is an upgraded metallurgical grade silicon (UMG-Si) does have much higher levels of C, O and N, and there are nitrogen precipitates, presumably silicon nitride. We have tested other UMG-Si which was cooled in non-silicon nitride forms and not detected nitrogen above $1 \times 10^{15}/\text{cm}^3$, so this N may come from a furnace liner. The carbon levels in the 5N PV Si are below the SEMI PV Si wafer specification of for mc-Si wafers, but the oxygen level is not.

The direct solidification of 7N into blocks for Si wafers adds C, O and N far above the original 7N feedstock, but the C and O are still less than the SEMI PV Si solar wafer specification. The 7N-Edge brick has slightly less C, O and N than the 7N-Center or 7N-Corner bricks. (NOTE: the 7N-Edge brick was cropped from the original 7N block.) There is no SEMI specification for nitrogen in PV Si wafers, but the $\sim 1 \times 10^{16}/\text{cm}^3$ [N] level is high and presumably comes from the silicon nitride liner in the direct solidification furnace, but this level of nitride is about the same for all three bricks which are located in different places of the block. This suggests that from the standpoint of C, O and N, the higher purity C, O and N in 7N PV Si is overkill, i.e. the subsequent processing adds much higher levels of C, O and N.

What happens then if the 7N and 5N are mixed 80/20? Compared to the pure 7N case, the carbon is reduced but the oxygen and nitrogen are increased. Note that we do not have a 5N control. The block grown from 7N feedstock and the block grown from 7N/5N feedstock were grown in different direct solidification furnaces. The unexpected C reduction from mixing pure 7N with dirty 5N feedstock may be due to differences in the C contamination from the different furnaces.

This study does not draw any conclusions on other elements, such as dopants and metals.

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