Characterization of Solar Grade Silicon Contaminants

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ABSTRACT

The term 'Solar Grade Silicon (SoG)' has been used for many years but until recently, there were no specifications as to what this actually meant. Without specifications, suppliers of silicon have been using 'number of nines' purity as a way to define and differentiate their product. However the 'number of nines' reported is dependant on the measurement technique, and what that technique can and cannot measure. Purity can be adjusted to a wide range of values depending on what elements are included and excluded from the measurement. More importantly 'number of nines' does not differentiate between elements that are important for solar performance and those that are not.

In this work we show various methods for contaminant analysis including SIMS, ICP-MS, and GDMS. Some of these are official SEMI test methods for PV silicon; SIMS (PV25-1011), and GDMS (PV1-0211). We report on the strengths and limitations of each .

Keywords: solar-grade-silicon, contamination, sims, gdms, icp-ms.

1 INTRODUCTION

All solar technologies can benefit from contamination control. Generally the lower the contaminant level, the better the performance. This theme is reflected in 'Solar-Grade-Silicon' specifications reported in 'number of nines' or 'N's purity. Thus a nine-nines (9N) purity material should be 10x better than an 8N purity. There are a few problems with this method of specifying purity. First there is no agreement on what elements should or should not be included in the report of purity. Often the reported impurities reflect what the measurement technique can and cannot measure. However, the impurity measurement can be 'tweaked' by choosing what elements to included and exclude. An example is shown in Table 1 where adding up all measured contaminants and detection limits where the elements were not detected results in a reported purity of 7N. If we choose not to report the carbon level (outlined in bold), or if our analysis method cannot measure carbon (a common limitation) then purity can be reported as 8N. We could further 'improve' the reported purity by excluding Sb from the measurement. Thus it becomes important to know what elements are and are not reported in the measurement of purity.

Table 1: Impurities in solar-grade-silicon measured by Secondary Ion Mass Spectrometry (SIMS).

SIMS Bulk Analysis results				Detection limits
Elements	Conc.(at/cm3)	Conc.(ppbat)	Conc.(ppbwt)	Conc.(at/cm3)
B	4.9E+13	0.98	0.38	5E+12
Na	<4.0E+11	<0.008	<0.006	4E+11
Al	<6.0E+12	<0.12	<0.1	6E+12
P	7.2E+13	1.44	1.59	5E+12
Cr	<3.0E+11	<0.006	<0.01	3E+11
Fe	<1.0E+13	<0.20	<0.4	1E+13
Ni	<1.0E+14	<2.00	<4	1E+14
Cu	<1.0E+14	<2.00	<4	1E+14
Zn	<2.0E+14	<4.00	<9	2E+14
K	<4.0E+11	<0.01	<0.01	4E+11
C	<3.0E+15	<60	<25	3E+15
As	8.4E+13	1.68	4.54	5E+12
Sb	7.8E+13	1.56	6.76	1E+13

As we can see, the measurement of purity reported in 'nines' can be strongly influenced by the limitations of the measurement technique, and by what elements we choose to report. Thus the specification of 'solar-grade-silicon' in terms of nines purity has less value. Instead it makes more sense to have specifications for elements that have the strongest effect on PV material preformance. Some recent work on p-doped silicon wafers showed that iron and iron complexes had a significant affect on minority carrier lifetime while copper had far less affect [1]. Thus for p-type silicon the concentration of Fe is far more important than Cu.

The SEMI organization has recently released specifications for virgin silicon feedstock material (Solar Grade Silicon) defining 4 grades [2]. The specifications define upper limits of impurities for various elements, grouped by their function and importance on PV performance. There is no discussion of 'nines'.

The 4 grades of 'Solar Grade Silicon' have Specifications for:

1. Electron acceptors: B, Al
2. Electron donors: P, As, Sb
3. Transition and Post Transition Metals: Ti, Cr, Fe, Ni, Cu, Zn, Mo
4. Alkali and Earth Alkali Metals: Na, K, Ca
5. Atmospherics: H, C, O, Cl

These specifications are related to the performance of PV cells.

The SEMI organization has also recently released specifications for silicon wafers for use in photovoltaics [3]. There is recognition that oxygen, carbon and iron content

are important in the wafers. There is also recognition that total metal content may be important.

The first challenge for the analytical laboratory is to measure these contaminant levels accurately so that comparison to specifications has meaning. The second challenge is to measure the contaminant levels reproducibly so that comparison between samples and comparisons over time has meaning. The third challenge is to measure all of the elements in the Solar Grade Silicon specifications. Only one analytical technique can measure all of them.

The SEMI specifications for solar grade silicon feedstock includes a number of suggested measurement methods. In this work we will look at the strengths and limitations of four of these techniques; SIMS, GDMS, NAA and ICP-MS.

2 EXPERIMENTAL

2.1 Analytical Techniques

ICP-MS: Needs the sample dissolved into liquid form for analysis. Solution is vaporized, ionized in a plasma torch, and analyzed in a quadrupole mass spectrometer.

Strengths:

- Survey analysis technique.
- ppm to ppb detection limits depending on element.
- Relatively large sample size.
- Measures whole sample both inside and outside.

Limitations:

- Does not measure 'atmospheric' elements.
- Does not measure halides.
- Sample must be dissolved prior to analysis.
- Sample prep vulnerable to added contamination.
- Dedicated system required for best detection limit.
- P, an important dopant, can be difficult.
- Cannot measure H, C, N, O and Cl

Is ICP-MS Accurate? Liquid references are available from NIST. When contaminant concentrations are above 100ppm, then accuracy is +/- 5%. Lower concentrations +/- 30%.

Is ICP-MS Reproducible? This depends if the samples can be prepared in the same way each time. With proper control of the preparation method, precision is about +/- 5%.

Is sampling Representative? The sample size can be relatively large. Inhomogeneities in the sample will be evened out. The sample must be dissolved prior to analysis. This needs to be done without losing material and without adding material. With proper technique and procedures, the sample can be representative of the original material.

Does the sampling method change the sample? Yes and in a very fundamental way. We are converting a solid into a liquid.

Do we understand what is being measured? By dissolving the sample we are including contamination from the outside of the sample. It may be important to include surface contamination in which case sample handling is important. It may be important NOT to include surface contamination in which case sample cleaning or another analysis may be more suitable.

GDMS: Sample can be in its original form for analysis. Sample is exposed to a plasma where it is sputtered, ionized, and analyzed in a magentic sector mass spectrometer.

Strengths:

- Survey analysis technique
- Ppm to ppb detection limits depending on element.
- Sample does not need to be dissolved.
- Direct sampling of all forms of PV materials.
- Sample prep contamination rarely an issue.
- SEMI Standard Test Method for PV Si (SEMI PV1-0309)

Limitations:

- Smaller sample size that ICPMS
- Measures mostly the sample inside.
- Cannot measure H, C, N and O.

Is GDMS Accurate? With standards accuracy is +/- 10%. Without standards accuracy is +/- 30%.

Is GDMS Reproducible? Precision is +/- 5%.

Is sampling Representative? The sample size is smaller than ICP-MS. Smaller scale inhomogeneities will be evened out. GDMS is a direct sampling technique. The sample does not need to be altered before analysis.

Does the sampling method change the sample? No.

Do we understand what is being measured? Prior to data collection the sample is exposed to the glow discharge for a period of time. This removes the surface of a solid sample and removes some of the surface on particles, flakes and granules. GDMS is therefore sampling mostly bulk.

SIMS: For silicon feedstock analysis samples are cross-sectioned before analysis. Samples are then sputter etched causing some ionization of the sample material. Ions are then extracted and analyzed in a mass spectrometer

Strengths:

- ppm to ppt detection limits depending on element.
- DOES measure 'atmospheric' elements H,C,N,O.
- Sample does NOT need to be dissolved.
- Sample prep contamination is not an issue.
- Direct sampling of all forms of PV materials.
- Will sample all required elements in SEMI specifications for solar grade silicon.

Limitations:

- Measures the sample inside.
- Smaller sample size than GDMS
- A few elements at one time for best detection limit.
- Requires separate measurements for elements spoecified by SEMI for solar grade silicon.

Is SIMS Accurate? Accuracy depends on the quality of the standard. With NIST standards for B, P and As in Si, accuarcy is +/- 3%. With ion implant standards, +/- 15%. Without standards SIMS is not accurate.

Is SIMS Reproducible? Precision is +/- 5% to 10% depending on element.

Is sampling Representative? SIMS bulk measurement samples the interior and excludes the surface. Thus it is representative of the sample bulk. Analysis area is a few hundred microns. Measurement will not be representative if inhomogeneities occur over a larger scale. SIMS profiling can show changes from outside to inside.

Does the sampling method change the sample? SIMS is a direct sampling technique so the sample is not altered prior to analysis. Particle and granule type material are mounted and cross-sectioned prior to analysis.

Do we understand what is being measured? SIMS bulk measurement is true bulk, excluding and surface contamination contributions. SIMS profiling can be done from the outside in to see difference in exterior vs interior contamination.

2.2 Analysis

Comparative analysis was done on polysilicon feedstock material. Results were compared from SIMS and ICP-MS, and we compared results from SIMS and GDMS. We focused on elements that all techniques could measure.

3 RESULTS

3.1 Polysilicon Analysis by SIMS and ICP-MS

Polysilicon granules were analyzed by SIMS and ICP-MS looking for B, Al, P, Cu and Ni. Samples were prepared using standard sample preparation practices with the intention of analyzing the material 'as-is'. Results are shown in Table 2.

Table 2: Comparison of SIMS and ICP-MS impurity measurements from polysilicon. (ppma)

Element	SIMS 1	SIMS 2	ICP-MS 1	ICP-MS 2
	Samples cross-sectioned	Repeat	Samples as-received	Samples pre-cleaned
B	0.00047	0.00049	0.04	<0.01
Al	<0.0002	<0.0002	0.06	<0.01
P	0.0011	0.0011	<0.1	<0.1
Cu	<0.002	<0.002	<0.01	<0.01
Ni	0.021	0.020	0.14	0.02

- SIMS and ICP-MS measurements did not agree after the first comparative analysis (SIMS 1 and ICP-MS 1)
- The sample exterior was cleaned prior to repeat measurements.
- Repeat measurements showed much closer agreement (SIMS 2 and ICP-MS 2)

3.2 Polysilicon Analysis by SIMS and GDMS

Polysilicon granules were analyzed by SIMS and GDMS looking for B, Al, P, Cr, Fe, Ni and As. Samples were prepared using standard sample preparation practices with the intention of analyzing the material 'as-is'. Results are shown in Table 3.

Table 3: Comparison of SIMS and GDMS impurity measurements on polysilicon (ppma)

Element	SIMS	GDMS
B	1.1	0.8
Al	0.3	0.4
P	8.1	11.4
Cr	<0.000007	<0.01
Fe	<0.001	1.3
Ni	<0.008	<0.01
As	0.07	-

- SIMS and GDMS results agree for most elements except for Fe.
- Fe concentration is shown 3 orders of magnitude higher by GDMS.

One of the granules was then examined by SIMS depth profiling looking for Fe content as a function of depth from the surface to the interior of the granule. The results is shown in Figure 1.

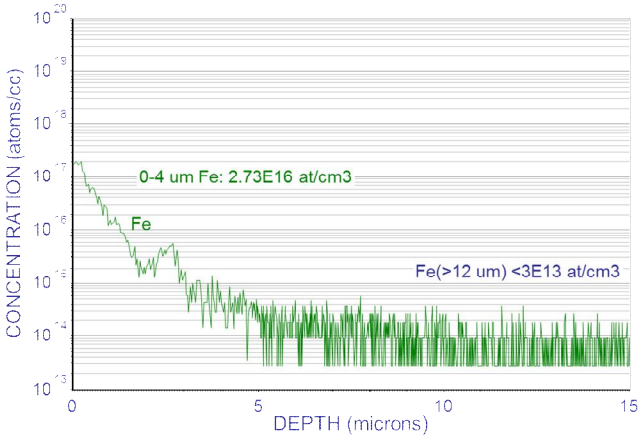

Figure 1: SIMS Fe depth profile on a granule surface. Surface Fe concentration is over 4 orders of magnitude higher than bulk concentration.

4 DISCUSSION AND CONCLUSIONS

4.1 Comparison of SIMS and ICP-MS Analysis on Polysilicon

Table 2 shows comparative analysis of selected elemental contamination from a polysilicon sample. The sample source was the same in both cases but initial results were quite different with ICP-MS showing significantly higher levels of contamination. SIMS sample preparation involves mounting and cross-sectioning granules before

analysis. SIMS is done on the interior surface of the granule only. ICP-MS sample preparation dissolves the entire sample in acid. Thus the analysis is done on material from the entire sample, interior and exterior. ICP-MS analysis was repreated but only after using an acid wash on the outside of the granules before dissolution. ICP-MS results on the pre-cleaned polysilicon showed results that were comparable with the SIMS results.

It is important to know when comparing results exactly what is being measured in each case. Often when techniques show different results, there is a good reason. In this case SIMS measures interior or 'bulk' contamination and ICP-MS includes contamination on the exterior as well as the interior.

4.2 Comparison of SIMS and GDMS Analysis on Polysilicon

Table 3 shows comparative analyiss of selected elemental contamination from a polysilicon sample. As in the previous case, the sample source was the same for both SIMS and GDMS. Results were very similar for all elements except Fe. Differences between results were again attributable to sample preparation and what each technique samples. SIMS sample prep was the same as before where granules are cross-sectioned and SIMS was done on the center of the granule. GDMS granule sample is pressed into untro-pure indium foil and plasma from the GDMS analysis cell removes a combination of granule exterior and interior. So it appeared that the difference in Fe measurement was due to differences in sampling. To check this theory a granule was SIMS depth profiled starting on the outside of a granule, profiling into the interior. This profile is shown in Figure 1 and reveals high Fe content on the exterior of the granule. GDMS sample some of the granule exterior so inclusion of exterior Fe content caused the difference in reported Fe impurity content.

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5 CONCLUSIONS

ICP-MS:

- Measures contamination on the interior and exterior of solar feedstock material.
- Cannot measure H, C, N, O, F and Cl.

GDMS:

- Measures contamination on the interior and to a lessor extent, the exterior of solar feedstock material.
- Cannot measure H, C, N and O.

SIMS:

- Measures contamination on the interior of solar feedstock material.
- Can measure a profile showing the change in contamination from exterior to interior.
- Measures all Semi spec solar grade silicon elements.
- Cannot measure all elements at the same time.

REFERENCES

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