Characterization of Solar Grade Silicon Contaminants

Gary Mount

Evans Analytical Group

Contamination and Solar PV

- All solar technologies can be improved with contamination control.
- Each solar technology has different contaminants that are important.
- Some elements have known effects on PV performance.
- Other elements little known effect.
- Some cell designs are more sensitive than others to the same elements.

Contamination SoG Si Standards

- Standards are just emerging that specify contaminants and what levels are acceptable
- Without industry standards materials for PV applications have been described in terms of 'nines' or 'N's (example: 99.99999% pure or 7 nines)
- Number of 'N's does not discriminate between elements that are important and those that are not.
- Number of 'N's excludes elements the measuring technique cannot measure!!
  - For example: Number of 'N's typically excludes atmospheric elements.

Playing Games with 'Nines'

SIMS Bulk Analysis results				Detection limits
Elements	**Conc.(at/cm3)**	**Conc.(ppba)**	**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**

- **This silicon has 7N purity considering all listed elements**

xclude Carbon

Playing Games with 'Nines'

SIMS Bulk Analysis results				Detection limits
Elements	**Conc.(at/cm3)**	**Conc.(ppba)**	**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
			<25	3E+15
As	**8.4E+13**	**1.68**	**4.54**	**5E+12**
Sb	**7.8E+13**	**1.56**	**6.76**	**1E+13**

- **This silicon has 8N purity of we exclude Carbon**

Contamination in Solar PV

- Materials specifications based on only ‘N’s make it necessary to reduce all contaminants including those that are not important for PV performance.
- Materials based on ‘N’s may not emphasize the important elements enough.
- Materials based on ‘N’s may be more expensive than they need to be.
- For solar PV the contaminants that are most important for performance should be emphasized.

Transition Metal Impurity Affect on Lifetime

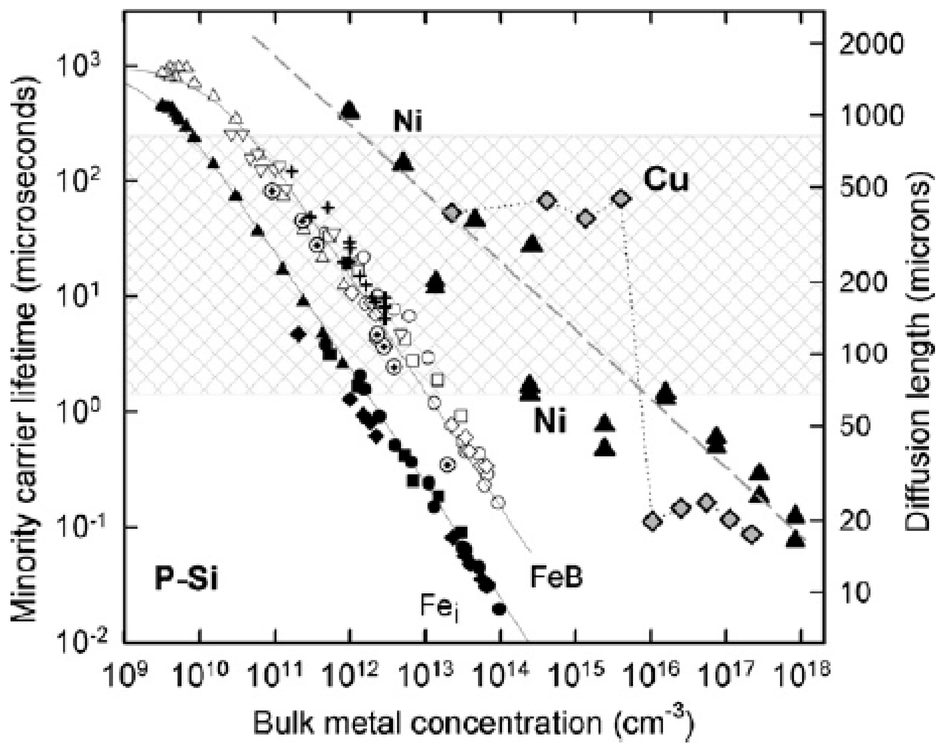


Fig. 2. Impact of iron, copper, and nickel on minority carrier diffusion length in single-crystalline silicon. The shaded area represents a typical range of minority carrier diffusion lengths in multicrystalline silicon solar cells.

Control of metal impurities in "dirty" multicrystalline silicon for solar cells

A.A. Istratov[a,b,*], T. Buonassisi[a,b,1], M.D. Pickett[a,b], M. Heuer[a,b], E.R. Weber[a,b]

[a] *Department of Materials Science, University of California, Berkeley, CA 94720, USA*
[b] *Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

Received 26 May 2006; accepted 16 June 2006

- This work investigated Fe, Ni and Cu.
- Fe had the most effect on lifetime while Cu had less effect.
- This work suggests specifications for solar silicon should emphasize Fe more than Cu.

Semi Committee on Solar Grade Silicon

The Semi organization has developed specifications for solar grade silicon.

There are 4 grades of 'Solar Grade Silicon' with Specifications for:

1. Acceptors: B, Al
2. 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

- The specifications do not mention 'nines' anywhere.
- Specifications are related to the performance of PV cells.

SEMI PV17-0611 Specifications

Grade	I	II	III	IV
Acceptors B,Al	< 1 ppba	< 20 ppba	< 300 ppba	< 1000 ppba
Donors P,As,Sb	< 1 ppba	< 20 ppba	< 50 ppba	< 720 ppba
Bulk O	Not specified	Not specified	Not specified	Not specified
C	< 0.3 ppma	< 2 ppma	< 5 ppma	< 100 ppma
Transition Metals Ti,Cr,Fe,Ni,Cu,Zn,Mo	< 10 ppba	< 50 ppba	< 100 ppba	< 200 ppba
Alkali and Earth Alkali Na,K,Ca	< 10 ppba	< 50 ppba	< 100 ppba	< 4000 ppba
Total H	Low enough so that particles do not explode on heating			
Total Cl	Low enough so that particles do not explode on heating			

Measuring Contamination

Analytical Techniques

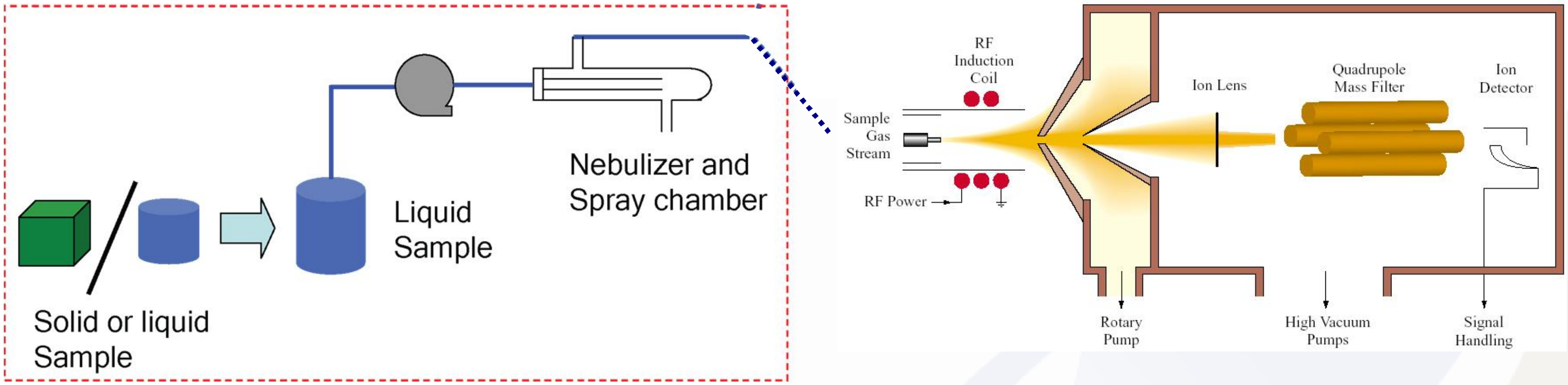
Methods of Measuring Contamination

- There are many methods for measuring contamination in silicon.
- Each has advantages and limitations.
- Detection limits need to be sufficient to report intended level of purity.
- Accuracy is important for comparison to specifications.
- Reproducible measurements are needed for comparison to previous analysis.
- Elements that have high background or cannot be measured need to be specified.

Methods of Measuring Contamination

- In this presentation we look at:
  - ICP-MS (Inductively Coupled Plasma Mass Spectrometry)
  - SIMS (Secondary Ion Mass Spectrometry)

ICP-MS: Description of Technique



ICP-MS

- Survey analysis technique.
- ppm to ppb detection limits depending on element.
- Relatively large sample size.
- Measures whole sample both inside and outside.
- Does not measure ‘atmospheric’ elements.
- P, an important dopant, can be difficult.
- Sample must be dissolved prior to analysis.
- Sample prep vulnerable to added contamination.
- Dedicated system required for best detection limit.

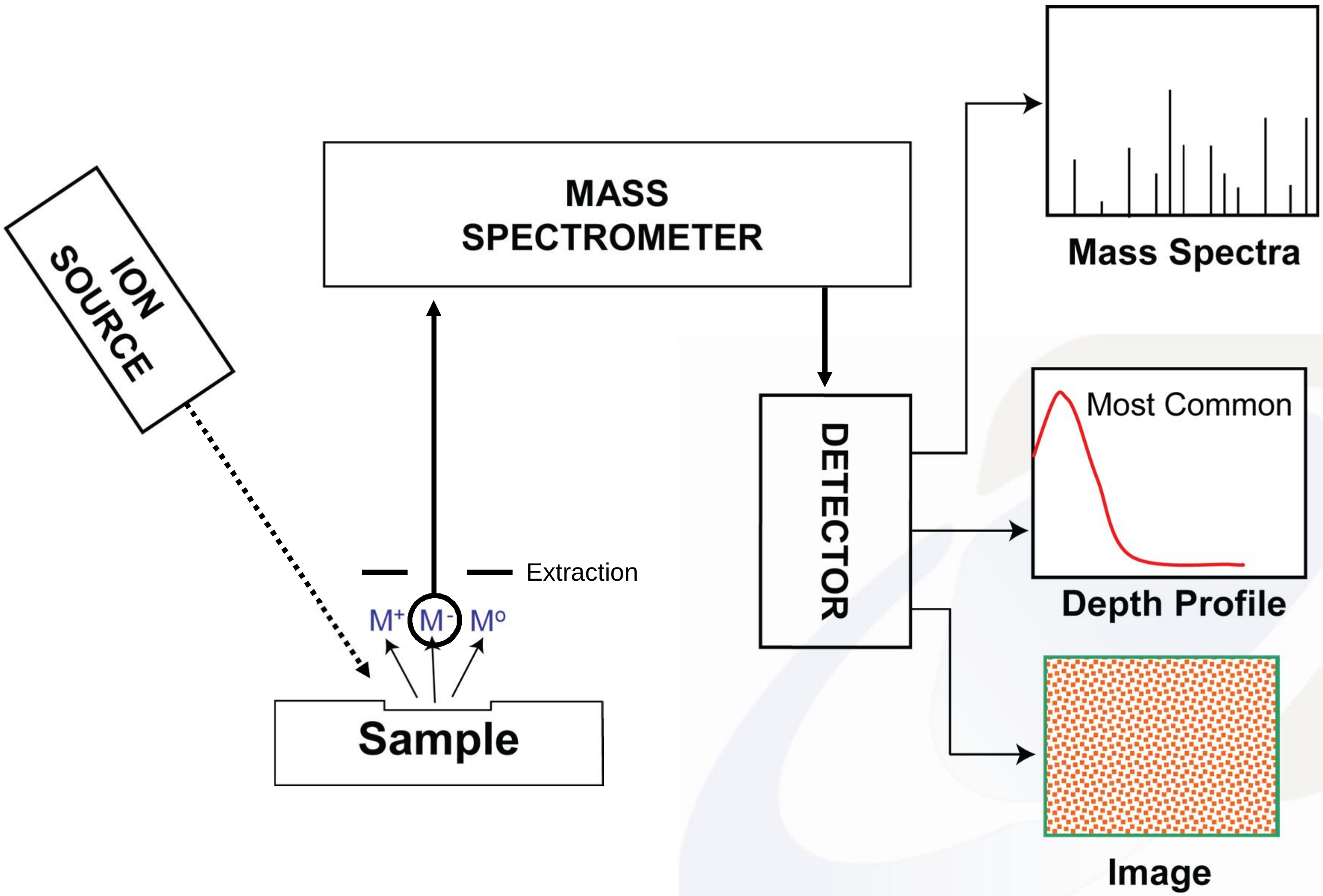
Measurement Issues: ICP-MS

- 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. Precision is about +/- 5%.
- Is sampling Representative?
  - The sample size can be relatively large. Inhomogeneity 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.

Measurement Issues: ICP-MS

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

SIMS Technique



SIMS

- 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.
- Measures the sample inside.
- Smaller sample size than ICP-MS
- A few elements at one time for best detection limit.

Measurement Issues: SIMS

- Is SIMS Accurate?
  - Accuracy depends on the quality of the standard. With NIST standards for B, P and As in Si, accuracy 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 inhomogeneity occurs over a larger scale.
  - SIMS profiling can show changes from outside to inside.

Measurement Issues: SIMS

- 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.
- 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.

Case Study: Contamination in Powders

ICP-MS and SIMS

Comparing Test Methods

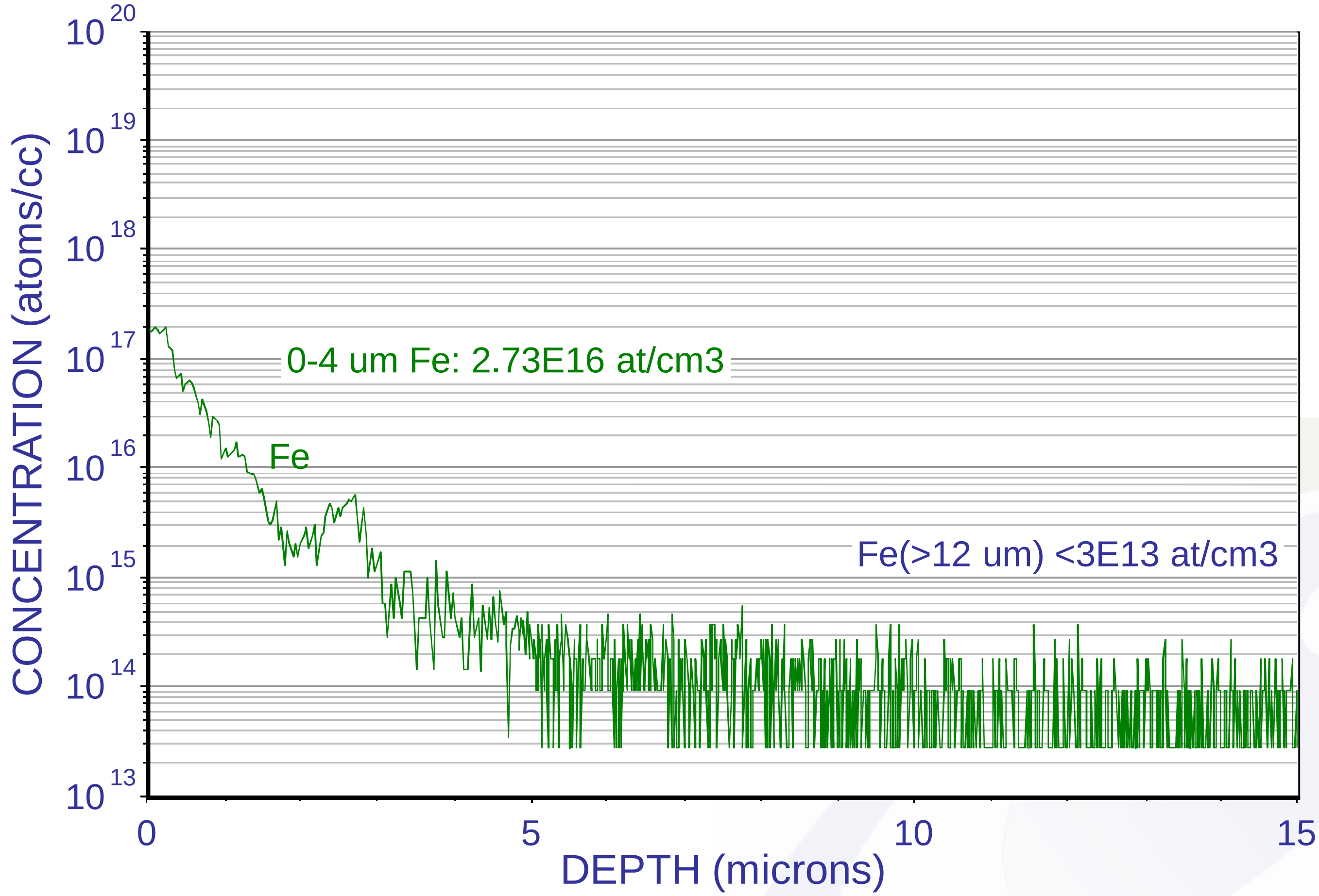
	SIMS	ICP-MS
B	1.1	0.8
C	9	-
O	30	-
Al	0.3	0.4
P	8.1	11.4
Cr	<7E-5	<0.01
Fe	<0.001	1.3
Ni	<0.008	<0.01
As	0.07	-

Comparing Test Methods

	SIMS	ICP-MS
B	1.1	0.8
C	9	-
O	30	-
Al	0.3	0.4
P	8.1	11.4
Cr	<7E-5	<0.01
Fe	<0.001	1.3
Ni	<0.008	<0.01
As	0.07	-

- Test results from different methods often show different results.
- Fe shows great differences, why?

SIMS Profile on Granule



- GDMS measures both inside and outside the particles and some Fe surface contamination will be included.
- SIMS bulk measurement excludes the surface contamination.

Summary

- 'Number of Nines' can be a misleading measure of purity.
- Progress has been made defining what is meant by 'Solar Grade Silicon' with values relevant to PV performance.
- Contamination measurement techniques can show different numbers from the same material. We must understand what is being measured.