Characterization of Contamination in PV Materials

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Summary

- Intro to EAG
- Contamination in PV materials
- Analytical methods
  - ICPMS, GDMS, SIMS
- c-Si
- Thin film
  - a-Si
  - CdTe
  - CIGS
- Conclusions

Who is Evans Analytical Group?

- Established in 1978
- 15 locations in 8 countries
- 30+ analytical techniques

- Origins in semiconductor industry support
- Very active in PV sector for many years
  - We have developed considerable expertise in measurement of contamination

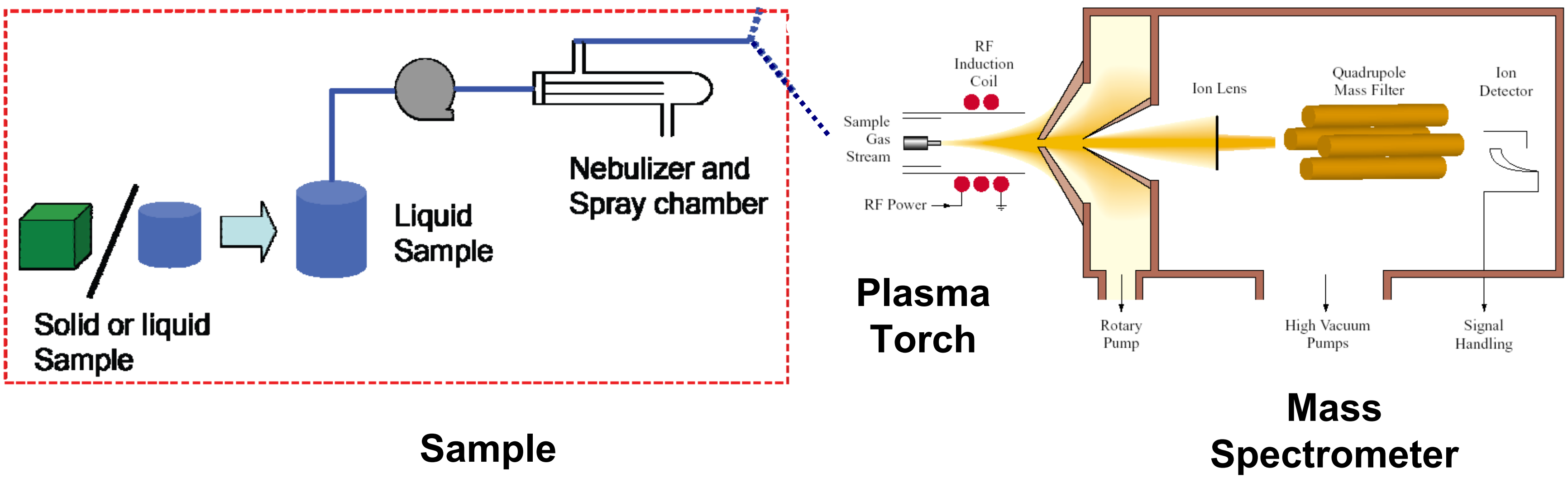
Contamination in Solar PV

- All solar technologies can be improved with contamination control.
- Each solar technology has different issues and different contaminants that are important.
- Some elements have known effects.
- Other elements little known effect.
- Some cell designs are more sensitive than others to the same elements.
- To be useful: measurements need to be ACCURATE.
- To be useful: measurements need to be REPRODUCIBLE.

Sampling and Measurement Issues

- Is sampling representative?
- Does the sampling method change the sample?
- Understand WHAT is being measured.
  - Inside/interior of sample?
  - Outside/exterior of sample?
  - Both?
- Understand the analytical method.

Inductively Coupled Plasma Mass Spectrometry

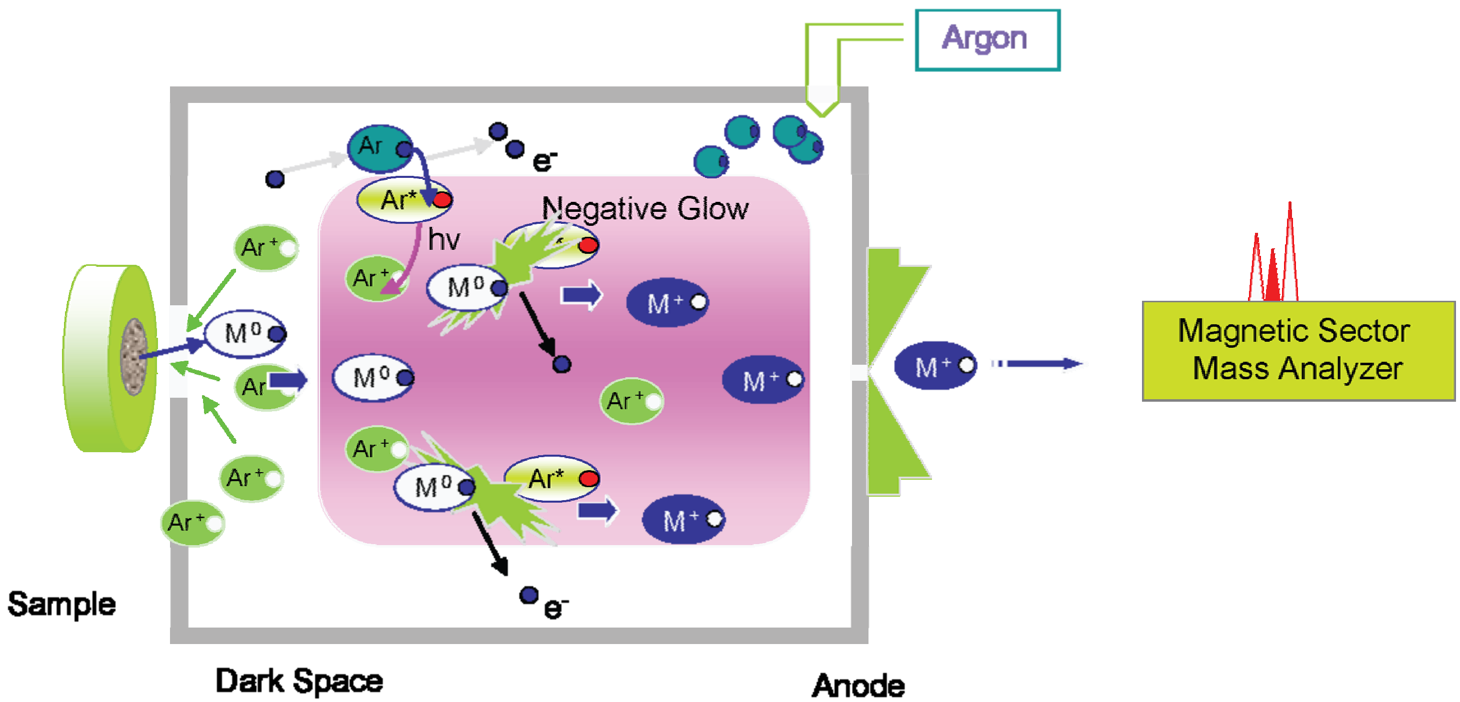


Sample Preparation

ICPMS

- Survey analysis technique.
- PPM to PPB detection limits, depending on element.
- Relatively large sample size.
- Measures whole sample both interior and exterior.
- Does not measure ‘atmospheric’ elements.
- P, an important dopant, can be difficult.
- Solid samples must be dissolved completely prior to analysis.
- Sample prep potentially vulnerable to added contamination.

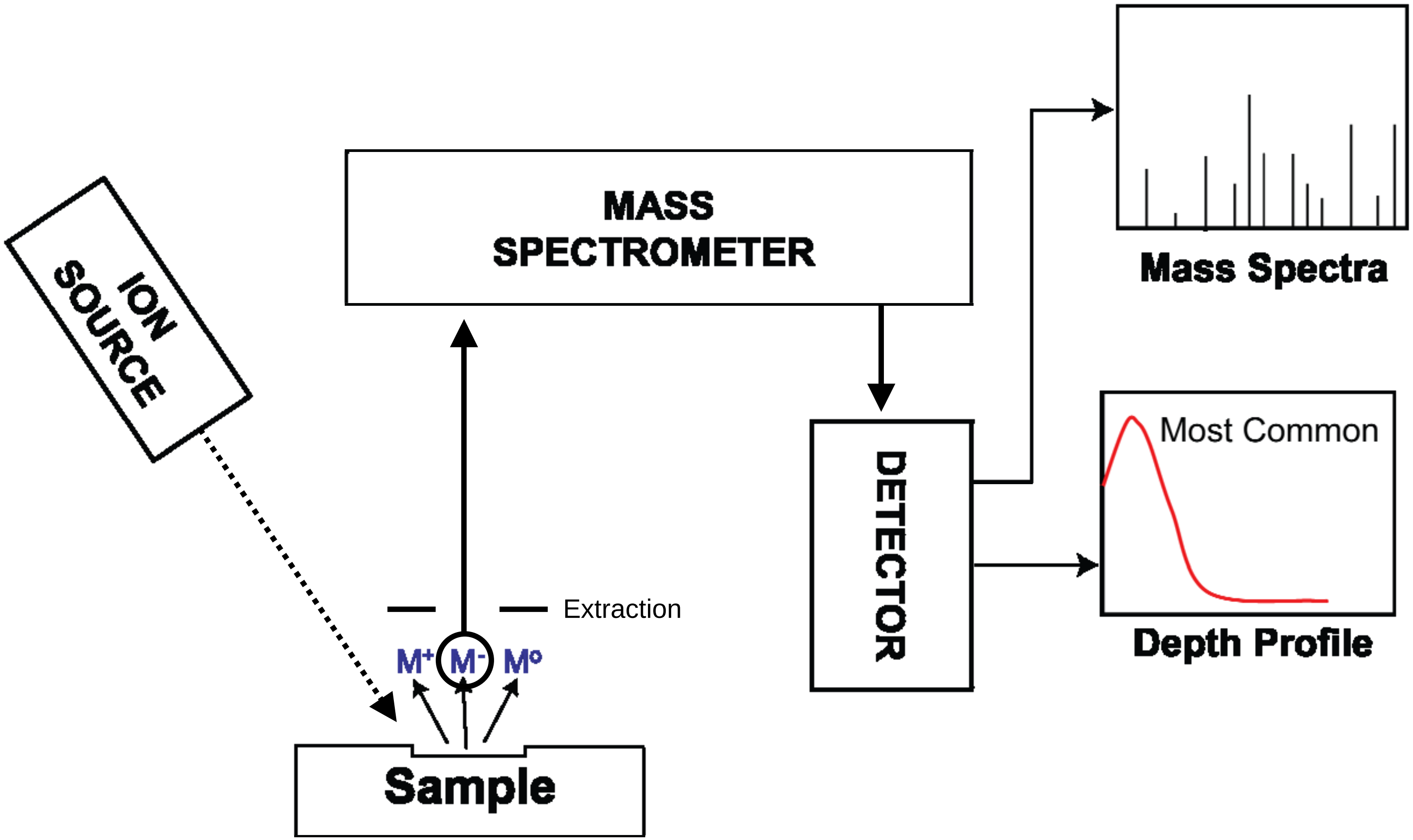
Glow Discharge Mass Spectrometry



GDMS

- Survey analysis technique
- PPM to PPB detection limits depending on element.
- Sample does NOT need to be dissolved.
- Direct sampling of all forms of solid PV materials.
- Sample prep contamination rarely an issue.
- SEMI Standard Test Method for PV Si (SEMI PV1-0309)
- Smaller sample size than ICPMS
- Measures mostly the sample interior.
- Does not measure ‘atmospheric’ elements.

Secondary Ion Mass Spectrometry



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 generally not an issue.
- Direct sampling of all forms of solid PV materials.
- Generally measures the sample interior.
- Smaller sample size than GDMS.
- A few elements at one time.

c-Si

e-Grade / UMG / Solar Grade

Silicon feedstocks

- A few years ago polysilicon was in short supply and very expensive.
- Solar cell makers resorted to using relatively low grade silicon - anything they could find
- Many new polysilicon producers have since come online, many with the goal of producing low cost high purity silicon using Siemens or ‘Modified’ Siemens process.

Contamination in Solar PV

- There are no standards that say what contaminants and what levels are acceptable
- Without standards materials for PV applications are 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!
  - Number of 'N's typically excludes atmospheric elements.

A typical bulk SIMS analysis of PV Si grown by Siemens Process

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**

- **Silicon has 7N purity considering all listed elements**
- **Silicon has 8N purity if we exclude carbon**

Contamination in Solar PV

- Materials specifications based on ‘N’s make it necessary to reduce contaminants that are not important for PV performance.
- Materials based on ‘N’s may be more expensive than they need to be.
- Rather than reducing all contaminants indiscriminately, wouldn’t it make sense to focus on the most important for PV performance?

Semi Committee on Solar Grade Silicon

Four grades of 'Solar Grade Silicon' are proposed 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

- Proposed specifications do not mention 'nines' or 'N's anywhere.
- Specifications related to the performance of PV cells.

Proposed Solar Grades

Grade	I	II	III	IV
Acceptors	< 2 ppba	< 20 ppba	< 300 ppba	< 1000 ppba
Donors	< 2 ppba	< 20 ppba	< 50 ppba	< 750 ppba
Total Al	-	-	-	< 1000 ppba
Bulk O	Not specified	Not specified	Not specified	Not specified
C	< 0.5 ppma	< 2 ppma	< 5 ppma	< 100 ppma
Transition Metals	< 10 ppba	< 50 ppba	< 100 ppba	< 200 ppba
Alkali and Earth Alkali	< 10 ppba	< 50 ppba	< 100 ppba	< 4000 ppba

- Proposal will be balloted in March 2011

UMG-Si

Upgraded Metallurgical Grade Feedstock

- Recently it appeared UMG silicon would not have a place vs. low cost Siemens process.
- Futher improvements in UMG quality and its inherent low costs have given it new life.
- Siemens process silicon: $50/kg
- UMG $15/kg – BUT need to know exactly what contaminants are present and how to handle them.

[B], [P], [C] and [O] by SIMS

- Low cost solar requires low cost analyses.
- A more cost effective 'all-in-one' SIMS measurement was developed for B, P, C and O.

Protocol	B	C	O	P
B,C,O,P together	1e14	2e16	5e16	2e14

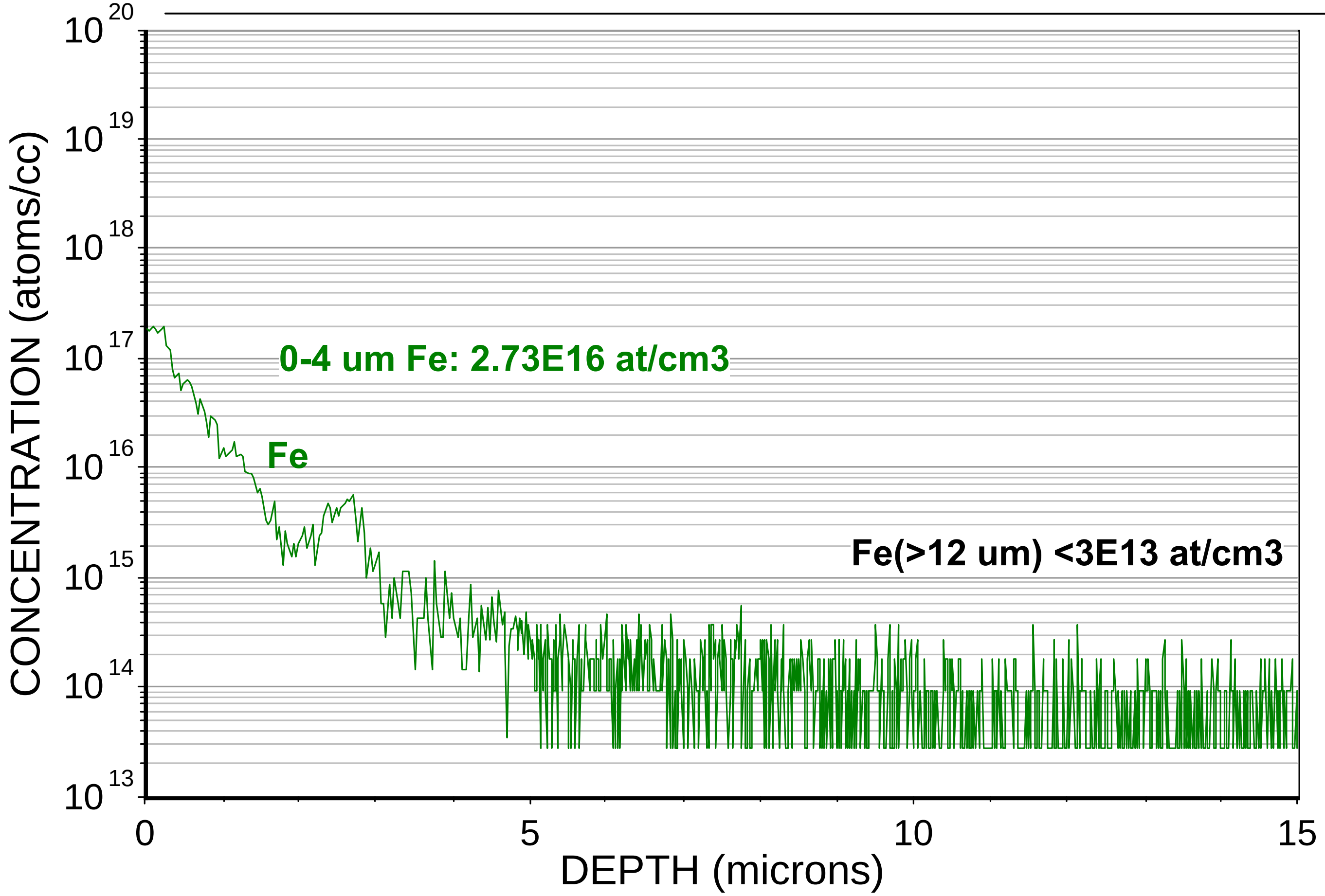
- Detection limits will be sufficient for Si solar wafers and UMG-Si.
- Measurement can be made on thin Si solar wafers or Si chunks/pieces.
- Precision should be sufficient (15-20%, 3 sigma).
- Proposed Semi Test Method in ballot.

Comparing Test Methods

	SIMS	GDMS
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

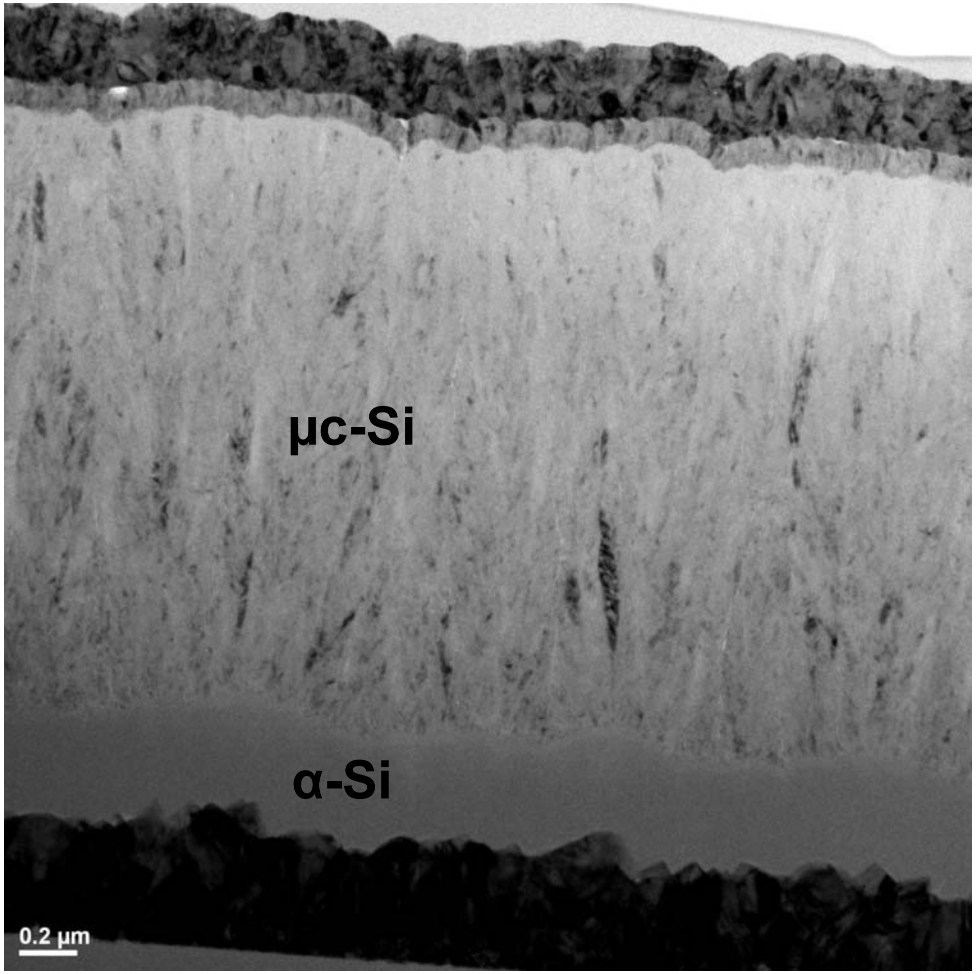


- GDMS measures both inside and outside the particles and some Fe surface contamination will be included.
- SIMS bulk measurement excludes the surface contamination.

α-Si

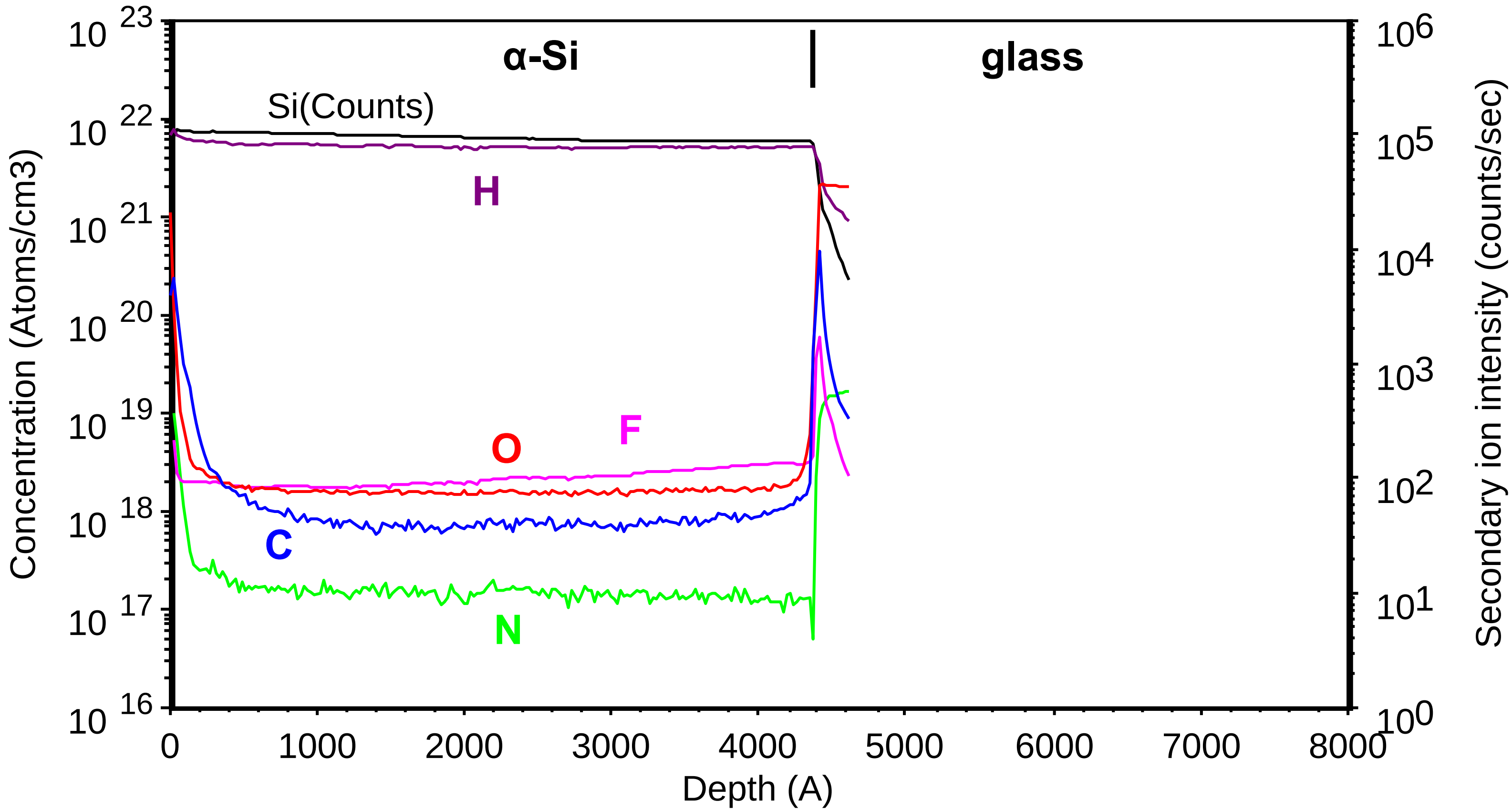
α-Si / μc-Si

α-Si/μc-Si Layer Structure



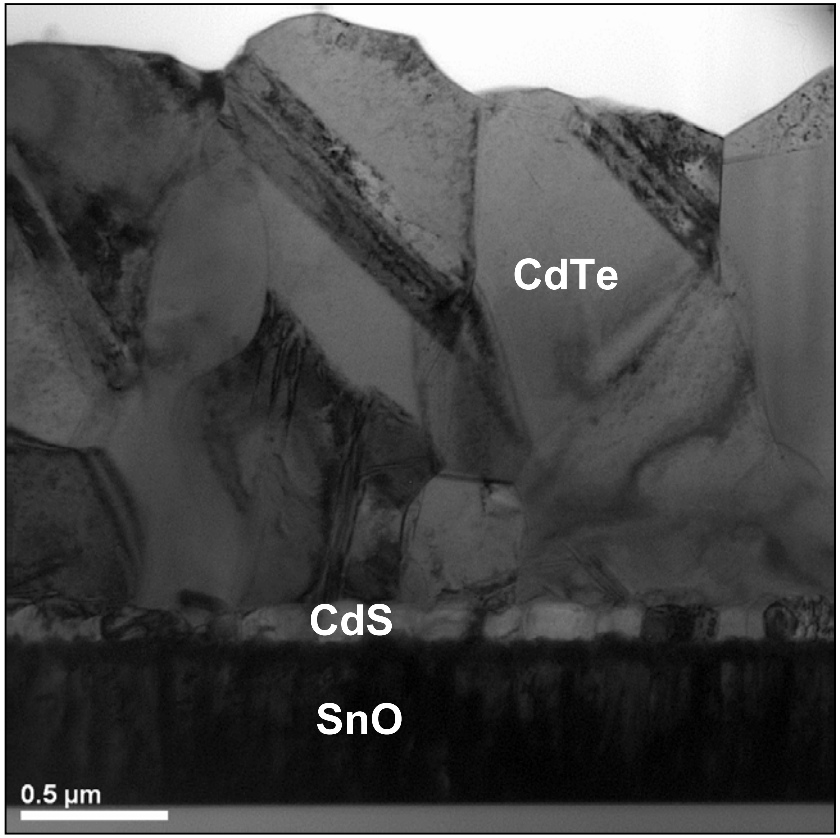
- Amorphous/μc silicon structure and high hydrogen content makes this technology less sensitive to metallic contaminants.
- H content may have a role in the Staebler-Wronski effect and can be measured.
- C, N and O may affect the bandgap and may influence the Staebler-Wronski effect. These can be measured along with H.

H and Contaminants in α-Si by SIMS



CdTe

CdTe Layer Structure

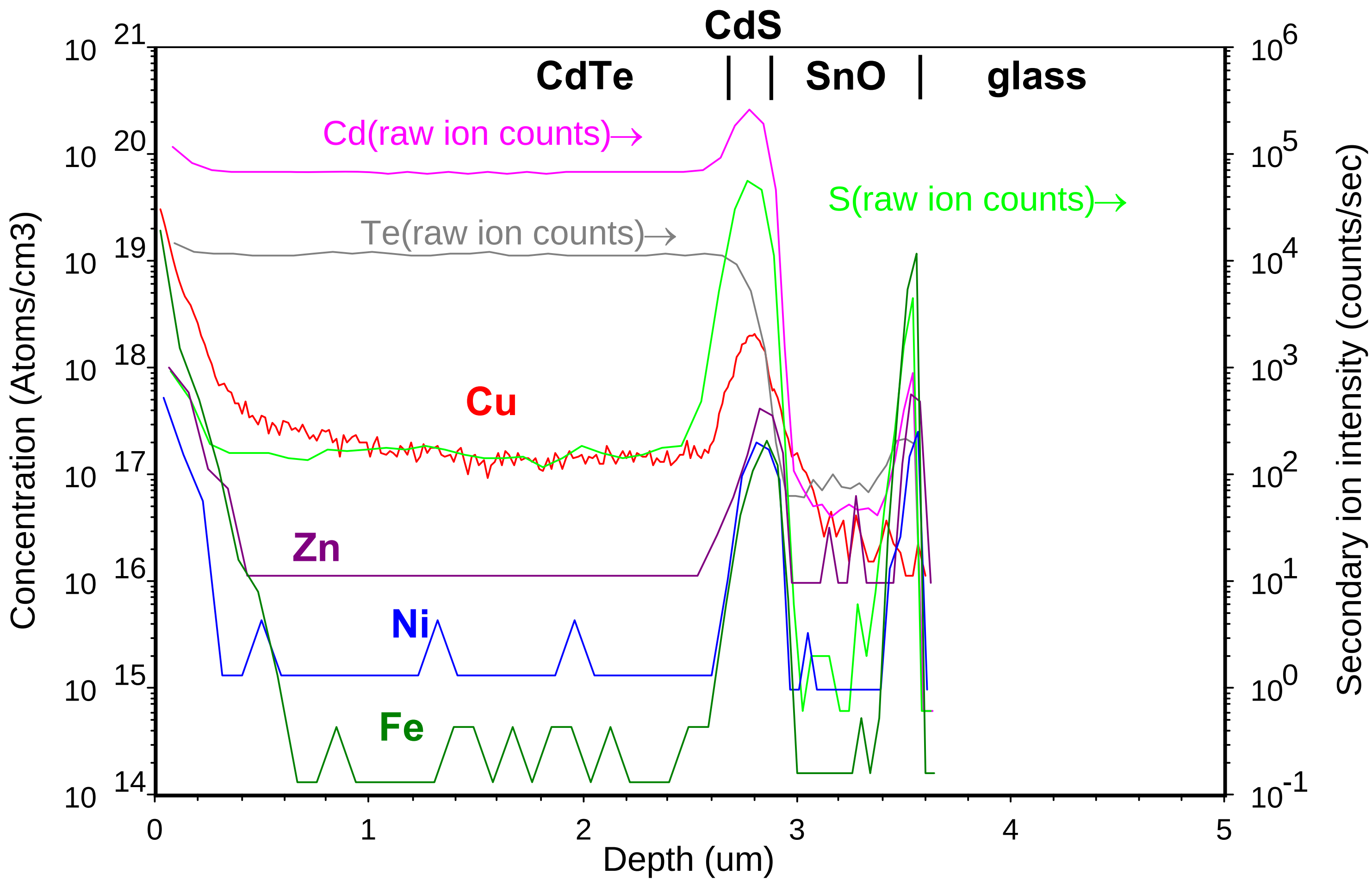


- There are no agreed upon standards for acceptable amounts of contaminants in CdTe
- Each company has their own specifications for contamination.
- Copper helps to make improved back contact and is expected through the CdTe film.

CdTe and CdS by GDMS

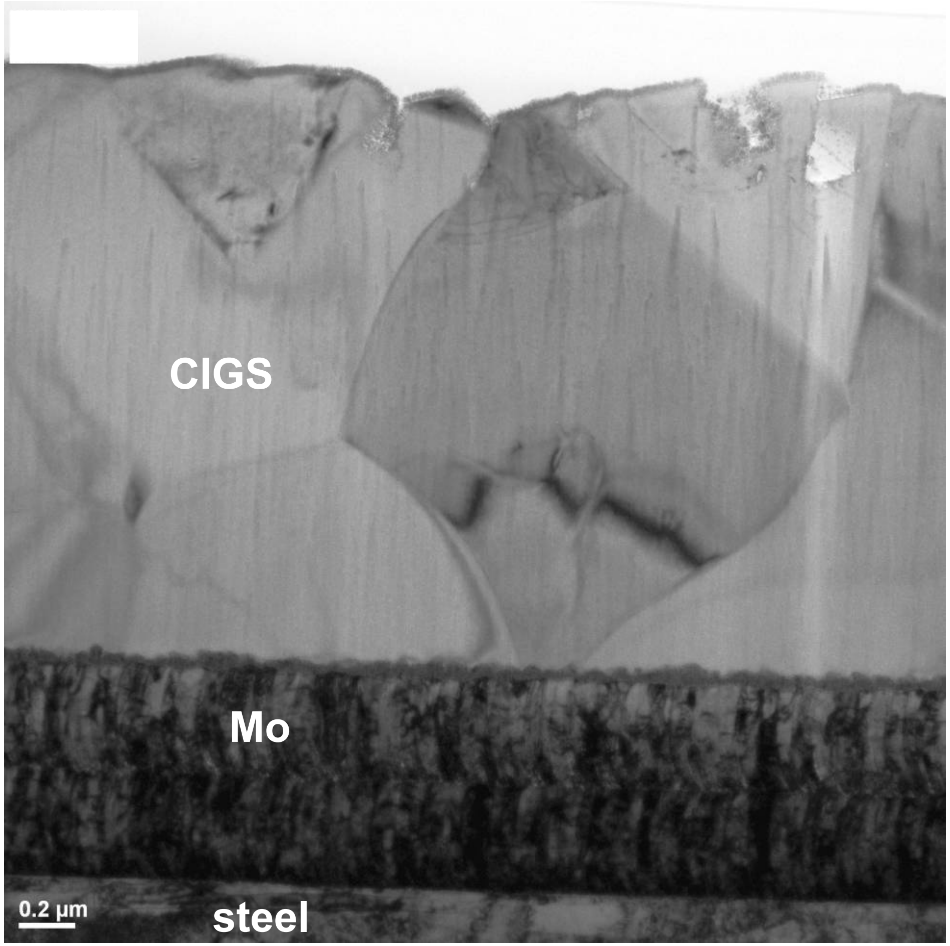
	CdTe powder		CdS powder	
	Detection Limit	Typical Result	Detection Limit	Typical Result
Element	ppba	ppba	ppba	ppba
B	10	100	30	250
Na	5	850	15	500
Mg	5	200	3	180
Al	4	150	15	740
Si	20	3500	15	15000
S	20	1800	-	-
Ti	3	20	10	40
Fe	10	1200	5	1100
Ni	2	120	1	110
Cu	2	75	1	70
Zn	10	60	550	<550
Se	150	1200	10	25
Pb	3	12	1	60

Metal Contaminants in CdTe/CdS/SnO by SIMS



$Cu_x(In_yGa_{(1-y)})_{(1-x)}Se_2$ (CIGS)

CIGS Layer Structure



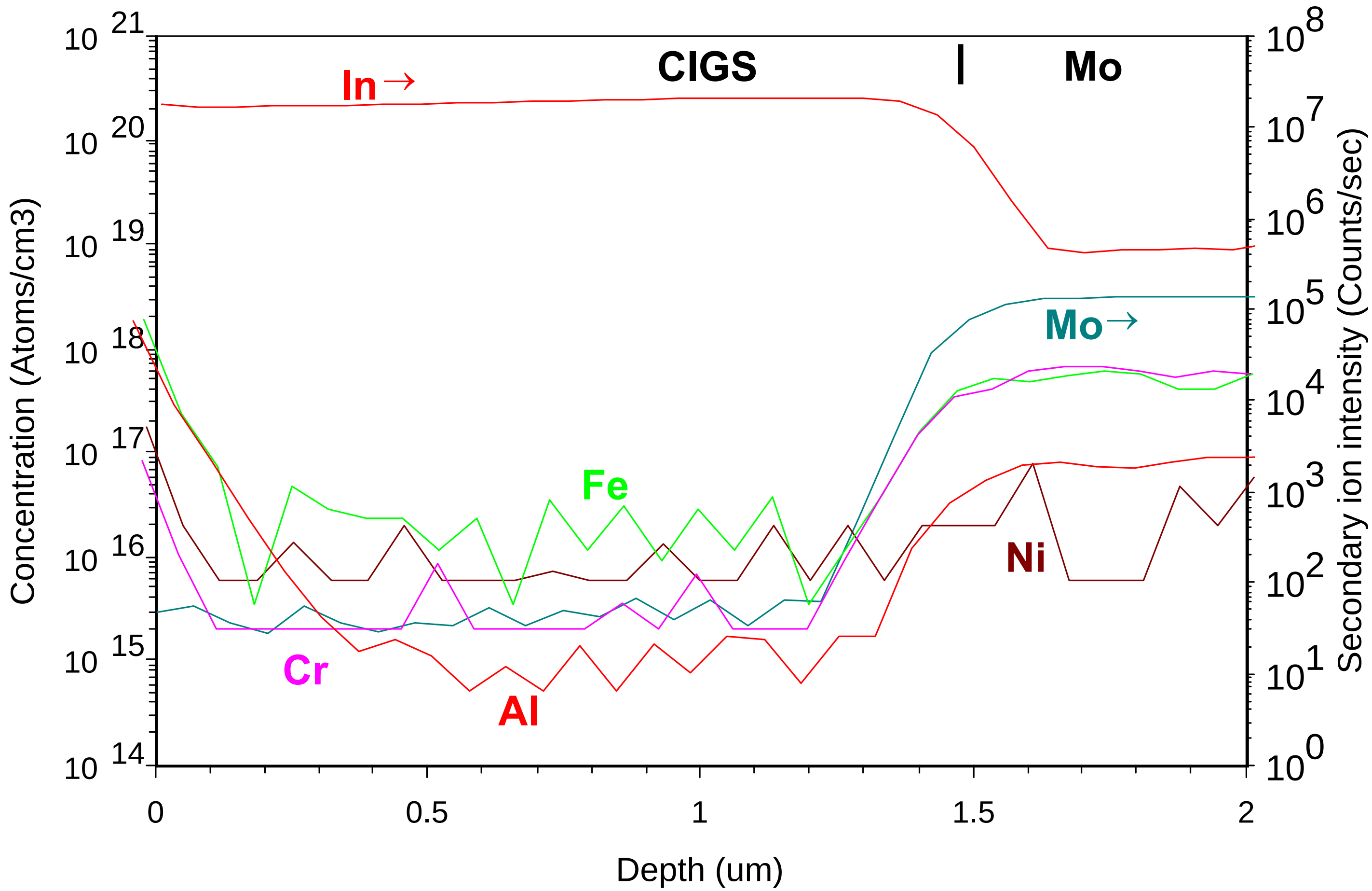
- Like CdTe, there are no agreed upon standards for acceptable amounts of contaminants in CIGS
- There is no agreement on which elements are most important
- Each company has their own specifications for contamination.

Analysis of CuInGa by GDMS

Element	Mass Fraction, ppmw	Element	Mass Fraction, ppmw	Element	Mass Fraction, ppmw
Li	< 0.001	Ga	Matrix	Nd	< 0.001
Be	< 0.001	Ge	< 1	Sm	< 0.001
B	11	As	0.19	Eu	< 0.001
C	-	Se	0.5	Gd	< 0.001
N	-	Br	< 0.05	Tb	< 0.001
O	-	Rb	< 0.005	Dy	< 0.001
F	< 0.1	Sr	< 0.001	Ho	< 0.001
Na	10	Y	< 0.001	Er	< 0.001
Mg	2.2	Zr	< 0.001	Tm	< 0.001
Al	4.8	Nb	< 0.5	Yb	< 0.001
Si	4.4	Mo	< 0.1	Lu	< 0.001
P	7.6	Ru	< 0.005	Hf	< 0.001
S	36	Rh	< 0.5	Ta	< 5
Cl	2.2	Pd	< 0.01	W	< 0.05
K	2.2	Ag	2.9	Re	0.02
Ca	2.8	Cd	< 1	Os	< 0.001
Sc	< 0.001	In	Matrix	Ir	< 0.005
Ti	0.03	Sn	27	Pt	< 0.05
V	0.12	Sb	0.05	Au	< 0.1
Cr	110	Te	0.45	Hg	< 0.01
Mn	1.1	I	< 0.005	Tl	0.43
Fe	70	Cs	< 0.005	Pb	2.8
Co	3.8	Ba	< 0.001	Bi	0.75
Ni	17	La	< 0.001	Th	< 0.001
Cu	Matrix	Ce	< 0.001	U	< 0.001
Zn	5.1	Pr	< 0.001		

72 elements in one measurement, most with 1ppb detection limit

Metal Contaminants in CIGS by SIMS



- Fe, Ni, Cr and Al are generally considered ‘important’
- Detection limit of 0.1-0.01 ppm for ‘all together’ measurement

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Conclusions

- Measure what matters
- Measure appropriately
- Full understanding of contaminant effects requires a detailed investigation of process steps
- Relating contaminant levels to performance is possible

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End