Application Note
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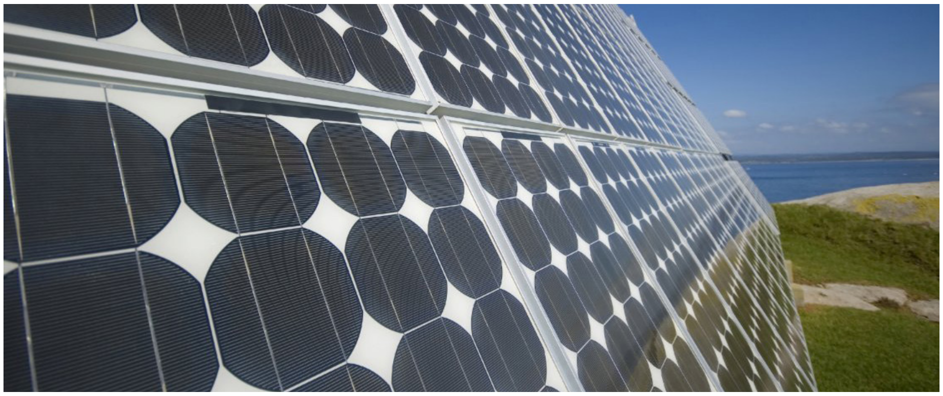
Trace Elemental Analysis of Trichlorosilane by Agilent ICP-MS



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Verified for Agilent 7900#200 ICP-MS

Abstract

Metallic impurities in trichlorosilane (TCS), an intermediate product used in the production of photovoltaic (PV) silicon, must be strictly controlled in order to produce the high purity PV silicon necessary for the manufacture of solar cells. A successful analytical method was developed, featuring measurement of impurities in TCS using an Agilent ICP-MS, following a sample preparation approach developed by Agilent. A spike recovery test demonstrated the validity of the method for 33 elements including boron and phosphorus, and two TCS samples were also analyzed. The ability to analyze TCS allows PV silicon manufacturers to check the TCS intermediate chemical for metallic impurities prior to the manufacture of PV silicon.

Introduction

The search for alternative energy resources is continuing due to the exhaustion of natural fossil fuel resources and their contribution to global warming, together with associated geological, environmental, and political concerns. Among the many alternative methods of generating electricity, solar power or photovoltaic (PV) is a booming industry with enormous increases in capacity each year. Photovoltaic panels, which are generally silicon wafer-based, convert energy from the sun into electricity, but the efficiency of this process is relatively low. Improving conversion efficiency and reducing production costs are key goals within the industry. The metallic impurity level in the polycrystalline silicon (polysilicon) used in the manufacture of the wafers that go into the PV panels must be strictly controlled, as impurities degrade the conversion efficiency. An effective method for the analysis of PV grade silicon by ICP-MS has already been developed by Agilent (*1*). In an effort to further increase device efficiency, PV silicon manufacturers want to measure impurities in the chemicals used in the manufacture of polysilicon. This application note describes the use of an Agilent ICP-MS with Octopole Reaction System (ORS) for the analysis of TCS. TCS is commonly used in the manufacture of ultrapure polysilicon.

Experimental

Instrumentation

A standard Agilent 7700s* ICP-MS was fitted with an Agilent Inert Sample Introduction kit. The kit consisted of a PFA concentric nebulizer, PFA double pass spray chamber and a demountable torch with 2.5 mm inner diameter platinum injector.

The Agilent ICP-MS have a wide range of available interference removal technologies. In addition to conventional no gas mode, the instruments can be operated in cool plasma mode and in ORS mode, which provides effective interference removal in both collision mode using an inert cell gas (He), and in reaction mode using a reactive cell gas (such as H_2). The ICP-MS includes an ORS cell that features a longer, smaller internal diameter octopole, operating at higher frequency than in previous ORS versions. The ORS can also be operated at higher cell gas flow rates and with higher bias voltages, which promotes greater collision energy. In combination, these features give improved interference removal efficiency in both collision and reaction modes.

The interference removal approach is selected depending on the analytical requirement. For this application, ultimate sensitivity is required for all analytes and therefore the most effective interference removal mode is required for every analyte/ interference. A data acquisition protocol featuring four steps was used, and all instrument operating parameters are given in Table 1. During method development, some analytes were run in multiple modes, and the mode that gave the best detection limits in the sample matrix was determined for each analyte.

Table 1. ICP-MS operating conditions.

	Method step			
	Step 1	**Step 2**	**Step 3**	**Step 4**
Plasma	Cool	Normal		
RF power (W)	600	1600		
Sample uptake rate (µL/min)	~160 (free aspiration)			
Sampling depth (mm)	16	8		
Carrier gas flow rate (L/min)	0.7			
Makeup gas (L/min)	0.8	0.5		
He cell gas flow rate (mL/min)	0		5	2
KED (V)	13	3		135

Analytes:	Step 1	^{7}Li, ^{23}Na ^{24}Mg, ^{27}Al, ^{39}K, ^{40}Ca, ^{55}Mn, ^{56}Fe, ^{63}Cu, ^{71}Ga
	Step 2	^{10}B, ^{138}Ba, ^{178}Hf, ^{181}Ta, ^{182}W
	Step 3	^{48}Ti, ^{51}V, ^{52}Cr, ^{59}Co, ^{60}Ni, ^{64}Zn, ^{75}As, ^{88}Sr, ^{90}Zr, ^{93}Nb, ^{98}Mo, ^{107}Ag, ^{114}Cd, ^{118}Sn, ^{121}Sb, ^{205}Tl, ^{208}Pb, ^{209}Bi, ^{232}Th, ^{238}U
	Step 4	^{31}P

**The 7700s has been superseded by the Agilent 7900 #200 instrument.*

The analytes measured in each step in the final method are also shown in Table 1. Step 1 employed cool plasma mode, and all remaining steps used normal or hot plasma. Step 2 used conventional no gas mode, Step 3 used He collision mode, and Step 4 was a modified He collision mode optimized for phosphorus determination. In the past, P has been measured indirectly as $^{31}P^{16}O$ at *m/z* 47, using cool plasma or O_2 cell gas. The improved performance of the ORS enables a greater reduction of the interferences $^{15}N^{16}O$ and $^{14}N^{16}O^{1}H$ that overlap P at mass 31, lowering the detection limit of P in He collision mode by a factor of 50, and making direct measurement of P possible at the required levels. Switching between modes is fully automated and all analytes were measured with a single visit to the sample vial, which helps to minimize sample contamination. The small size of the ORS cell allows for very fast switching between modes, so the additional time required for multimode operation is minimized. The total analysis time was eight minutes per sample.

Sample preparation

Trichlorosilane (TCS) is an intermediate compound used in the manufacture of high purity polysilicon. Since TCS is a volatile liquid that can easily be purified by distillation, it can be made from low-grade metallurgical grade silicon, purified, and then converted to high purity polysilicon. TCS is liquid at room temperature with high volatility (BP 31.8 °C). It easily decomposes to SiO_2 in air by hydrolysis, as shown below:

$$SiHCl_3 + 2H_2O \rightarrow SiO_2 + 3HCl + H_2$$

The direct sampling and on-line ICP-MS analysis of TCS in the manufacturing line is not feasible, because SiO_2 would deposit in the transfer tube and on the ICP-MS sample introduction and interface components. In addition, TCS must be chilled and handled in an inert environment to avoid evolution of HCl gas, and so an ICP-MS inside a clean mini-environment would need to be installed at each sampling point. The only practical approach is therefore to transfer liquid TCS to the lab for analysis. In this work, liquid TCS was transferred to a clean laboratory following appropriate safety precautions, and analyzed after careful sample preparation using the following procedure: Liquid TCS was converted to SiO_2 via gentle hydrolysis in an inert gas atmosphere, dissolved in HF solution and Si removed (as SiF_4 gas) by heating to dryness. The dry residue was then re-dissolved in 0.4% HCl solution before analysis by ICP-MS.

WARNING

Chemical Hazard

As with all sample preparation methods that utilize HF, use great care when handling the acid. Use all appropriate personal protective equipment and follow all appropriate safety procedures.

For more information of safe handling of TCS, please contact your local Agilent Applications team.

Calibration standards

External calibration in a matrix of 0.4% HCl was used for quantification of the trace elements. Since the Si matrix is removed during the sample preparation, the sample residue re-dissolved in 0.4% HCl, is essentially free of any matrix. Four multielement calibration standard solutions were prepared at 0, 1, 2, and 5 ppb in 0.4% HCl. No internal standardization was used, to avoid the possibility of adding contamination.

Results and Discussion

Detection limits

Detection limits (DLs) were calculated from 3 sigma of the calibration blank and are shown in Table 2. Low ppt DLs for V and As demonstrate the efficient removal of the ClO (on 51V) and ArCl (on 75As) polyatomic interferences in the HCl matrix. Also the phosphorus DL of 0.1 ppb shows the effectiveness of the optimized He collision mode parameters used in Step 4 for the removal of NO/NOH on P. DLs in the original sample were also calculated, by multiplying by a dilution factor of 7.5*, and all DLs were under 1 ppb in the original TCS sample.

Quantitative analysis

Table 2 also shows the results from the quantitative analysis of two TCS samples, after reagent blank subtraction. Sample A was a high purity TCS sample obtained from a semiconductor company and stored in a glass vial. Sample B was also obtained from a semiconductor company, but shipped in a stainless steel pressure vessel.

**Agilent ICP-MS users requiring more detailed information on TCS sampling and analysis should contact their local Agilent ICP-MS applications team.*

As is clearly shown in Table 2, Sample B contained significantly higher levels of Fe, Ni and Cr than Sample A, indicating metallic contamination from the steel container. Sample A was found to be of high purity with only four elements above 1 ppb in the original sample.

Table 2. Detection limits and quantitative analysis.

m/z	Element	DL (final solution) (ppb)	DL (original sample) (ppb)	Analysis — Sample A (ppb)	Analysis — Sample B (ppb)
7	Li	0.0003	0.002	0.007	0.007
10	B	0.08	0.60	1.4	5.5
23	Na	0.002	0.01	0.53	15
24	Mg	0.001	0.010	2.5	1.4
27	Al	0.006	0.04	0.75	8.5
31	P	0.1	0.7	2.7	4.2
39	K	0.02	0.15	0.23	3.6
40	Ca	0.006	0.05	0.83	26
48	Ti	0.001	0.008	0.08	2.3
51	V	0.008	0.06	0.08	0.6
52	Cr	0.02	0.12	0.12	22
55	Mn	0.001	0.008	0.01	1.6
56	Fe	0.01	0.08	1.9	180
59	Co	0.0001	0.001	0.02	0.3
60	Ni	0.001	0.008	0.08	14
63	Cu	0.002	0.01	0.08	0.8
64	Zn	0.001	0.01	0.38	3.5
71	Ga	0.001	0.006	0.01	0.03
75	As	0.02	0.14	0.14	0.02
88	Sr	0.0001	0.0004	0.01	0.1
90	Zr	0.0002	0.001	0.08	1.0
93	Nb	0.0002	0.001	0.007	0.02
98	Mo	0.0003	0.002	0.08	1.3
107	Ag	0.004	0.03	0.03	0.02
111	Cd	0.0001	0.001	0.007	0.04
118	Sn	0.003	0.02	0.38	1.7
121	Sb	0.001	0.01	0.08	0.5
138	Ba	0.0002	0.002	0.007	1.4
181	Ta	0.0001	0.0004	0.007	0.2
182	W	0.0003	0.002	0.007	0.3
208	Pb	0.0002	0.002	0.007	0.8
232	Th	0.0001	0.001	0.007	0.007
238	U	0.0001	0.0002	0.007	0.007

Recovery test

In order to test the recovery efficiency of the method, and in particular to check for loss of volatile elements during the sample preparation procedure, a high purity sample of TCS was purchased (Tokyo Chemical Industry Co. Ltd., Tokyo, Japan). The TCS sample was divided into four aliquots, each containing 1.5 g of TCS, and sample preparation was performed as previously described. After hydrolysis and HF addition, but prior to the heating step to remove Si, one of the aliquots was spiked at the 5 ppb level with a multielement standard (Spex, Metuchen, NJ, USA). The samples were then evaporated to dryness and the dry residue was taken up in 0.4% HCl and analyzed. Figure 1 shows the recoveries achieved for the 5 ppb spiked sample. All elements gave good recoveries, including B, which can be problematic due to its volatility, demonstrating the validity of both the sample preparation and analytical methods.

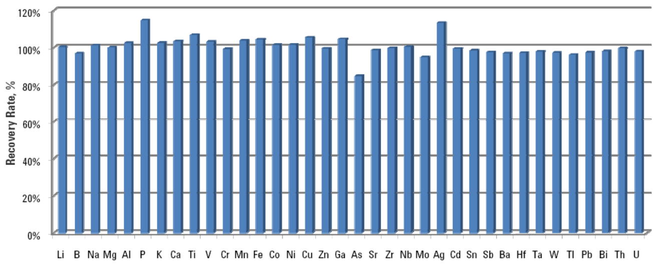

Figure 1. 5 ppb spike recovery test in TCS, confirming no loss of volatile elements during sample evaporation, and accurate recovery (between 80 and 120%) for all analytes.

Conclusions

Trichlorosilane has been successfully analyzed using the Agilent ICP-MS, following a sample preparation approach developed by Agilent. The ORS cell improves He collision cell performance significantly, achieving a DL of 0.1 ppb for phosphorus from a direct measurement at *m/z* 31. A spike recovery test demonstrated the validity of the sample preparation and analytical methods for all elements including boron. The ability to analyze TCS allows PV silicon manufacturers to check the TCS intermediate product for metallic impurities prior to the manufacture of PV silicon.

References

1. Ultratrace Analysis of Solar (Photovoltaic) Grade Bulk Silicon by ICP-MS. Agilent Application Note, 5989-9859EN, Oct 2008.

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7900#200 ICP-MS

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