

Point-of-Use Sampling and Metal Analysis for Trichlorosilane

Dan Cowles and David Bollinger
Air Liquide America Corporation – Balazs Analytical Services
13546 North Central Expressway, MS 301
Dallas, TX
75243
dan.cowles@airliquide.com, david.bollinger@airliquide.com

Abstract

Highly reactive gases, such as trichlorosilane and hydrogen chloride, are crucial reagents in many semiconductor fabrication processes. The continuing challenge in delivering such gases to the point-of-use is to avoid contamination of the gases by metallic corrosion byproducts from tubing and components. Gas line corrosion results from intrusion of air or moisture due to leaks, cylinder change-outs, purifier exhaustion, or human error. When metal contamination is detected at the wafer, reactive gas delivery lines, along with the source cylinder, are often the first suspects in the investigation. Typical responses to metal contamination events include source cylinder replacement, change-out of expensive components or even whole sections of the gas delivery hardware, as well as time-consuming test wafer production and analysis. What is lacking is a flexible, safe method for reactive gas sample collection that can be used to isolate the contamination source in a distribution system.

This paper describes a point-of-use (POU) sampling/off-site analysis method for quantification of metal impurities in trichlorosilane (TCS). The sampling method described here is based on hydrolysis of TCS in aqueous HF. Analysis of metal impurities in the hydrolysis solution is achieved by inductively-coupled plasma mass-spectroscopy (ICP-MS).

Presented are results of laboratory sampling method development tests. Method detection limits are compared against typical TCS purity specifications. In addition, TCS hydrolysis chemistry is explained along with its impact on quantitative data analysis.

Introduction

TCS is a corrosive, liquefied gas widely used in the manufacture of semiconductor-grade silicon, and in the chemical vapor deposition (CVD) of epitaxial silicon. In these applications, TCS purity is essential since metallic and dopant impurities incorporated into silicon may alter device performance. In a fab, TCS is delivered to the tool either as a pressurized liquid, or diluted in a carrier gas, such as hydrogen. TCS sampling is particularly challenging as it is a flammable, highly reactive, and corrosive gas.

The literature related to TCS metals analysis focuses primarily on quantification of group III and group V elements: B, P, and As. Gas chromatography combined with a nitrogen-phosphorous detector (GC-NPD) was used [1] for direct analysis of PCl_3 and POCl_3 in liquid-phase TCS. More typically, the sample preparation and analysis steps are performed separately. A Teflon autoclave was used to

decompose TCS in aqueous HF, and the hydrolysis solution was analyzed by atomic emission spectroscopy and spectrophotometry [2]. In the same study, TCS hydrolysis was also carried out in an open vessel by addition of TCS to frozen distilled water. Similarly, TCS hydrolysis has been accomplished by addition of water to frozen TCS. [3]

Sample preparation involves capture of the metallic impurities and evaporation of the silicon matrix. Loss of analytes during sample preparation has been a major concern since many metal contaminants in TCS are in the form of volatile metal chlorides (e.g. AsCl_3 , BCl_3 , FeCl_3 ,...). Thus all the studies cited above, excepting the GC-NPD direct analysis, utilized complexing agents such as mannitol to stabilize volatile metals by the formation of non-volatile adducts. A more recent study utilized cuprous chloride (CuCl) to stabilize P and As impurities before evaporation of the TCS matrix and analysis by electrothermal vaporization (ETV) ICP-MS. [4]

Because use of adducting agents increases sample-handling complexity and cost, and because the metal content of supplemental reagents is variable and degrades detection limits for some elements, we do not use such reagents. Instead, our sample-handling procedures are tailored to avoid loss of volatile metal compounds.

The objective of this study is a method for sampling TCS gas or liquid in the fab for off-site analysis of metal impurities. Anticipated sampling points are: 1) the gas jungle of the process tool, 2) the valve manifold box, and 3) the TCS source gas cabinet. Availability of such an on-site sampling technique means that when metal contamination is detected on wafers, potential contamination sources can be isolated (or ruled out) in a timely and cost-effective manner.

Trichlorosilane Safety and Handling

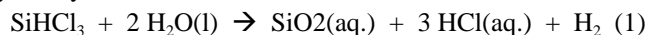
TCS handling is similar to that of dichlorosilane (DCS) except that TCS has a higher boiling point (31.8 °C vs. 8.2 °C). TCS is not pyrophoric in its pure form (autoignition temperature = 182 °C), however the flammability limits are wide: LEL = 1.2 %, UEL = 90.5 %. The flashpoint for TCS is low, but higher than that of DCS (-14 °C vs. -52.2 °C). In addition, TCS is particularly susceptible to ignition in air by static discharge [5]. TCS immediately hydrolyzes in the presence of moisture to form silica solids and hydrochloric acid (HCl), and thus is potentially very corrosive. Safe-handling of TCS requires a ventilated work-space, leak-free connections, and an inert gas purge of the sampling system both before and after TCS introduction.

Compound	Property	Value	Ref.
SiHCl ₃	b.p., 1 atm.(C)	31.8	6
"	Flash Point (C)	-14	7
"	Autoignition temp. (C)	182	5
"	LEL/UEL (%)	1.2 / 90.5	7
SiH ₂ Cl ₂	b.p., 1 atm.(C)	8.2	6
"	Flash Point (C)	-52.2	9
"	Autoignition temp. (C)	44	5
"	LEL/UEL (%)	4.1 / 98.8	8
SiHCl ₃ (g)	ΔH _f , 298 K, 1 atm. (kJ/mole)	-496.22	6
SiH ₂ F ₆ (aq.)	"	-2379.4	10
HF (aq.)	"	-334.0	11
HCl (aq.)	"	-167.2	12
H ₂ O (l)	"	-285.8	12

Table 1. Selected Physical and Chemical Data.

TCS Hydrolysis Chemistry

Quantitative metal analysis depends on an understanding of TCS hydrolysis chemistry. TCS reacts with water to yield hydrated silica:



This exothermic reaction yields a messy two-phase system consisting of SiO₂ solids in aqueous HCl. Aqueous hydrofluoric acid (HF) may be added to the solution to dissolve the solids and yield a homogenous liquid containing fluorosilicic acid, HF, and HCl:



Our sampling method combines these reactions in a single step:



with an associated reaction exothermicity of 381 kJ/mole. This hydrolysis chemistry enforces an upper limit on the quantity of TCS that can be consumed by a given volume and concentration of aqueous HF. Addition of TCS beyond the stoichiometric limit (i.e. after all HF has been consumed) results in the appearance of translucent solids (siloxanes). Although these solids can be later dissolved by adding more HF, in practice we stay well under the stoichiometric limit to minimize sample-handling steps. For 49% HF, the minimum sample dilution (assuming sampling is taken to the stoichiometric limit) is 2.7x (w/w). In practice, the typical sample dilution is 10x (w/w).

The hydrolysis chemistry described in equation 3 is utilized to calculate the quantity of TCS sampled, from the weight gain of the bottle. The weight gain is corrected for emission of hydrogen, but emissions of water vapor, HF, and HCl are assumed small and are ignored. It is important to note that use of the weight gain of the impinger to calculate the TCS sample weight makes precise sample flow control unnecessary.

The exothermicity of the hydrolysis chemistry is such that the solution temperature increases to approximately 70 °C, for a TCS sampling rate of 1 g/min, added to 400 mL of aqueous HF in a 500 mL impinger bottle. Relevant physical data and references are contained in Table 1.

TCS Sampling Method Development

A sampling system was erected in the lab for initial method development. The system comprises a TCS canister with vapor and liquid withdrawal ports, stainless steel, PTFE, and PFA hardware, a PTFE needle valve, and PFA tubing. The TCS canister, sampling apparatus, and abatement cell are contained in a gas cabinet. For liquid sampling, the inert gas charge in the as-received canister (typically 20 psig) provides a sufficient driving force. For gas-phase sampling, the liquid port is pressurized with 15 psig nitrogen and TCS-saturated nitrogen (estimated 30 % TCS by volume) is withdrawn from the gas port. Typically, TCS (gas or liquid phase) is sampled at 1 g/min. for 45 min. The sample bottle exhausts to an aqueous caustic scrubber. A sample blank is collected by passing nitrogen through the sampling system and bubbling through an identically prepared impinger for 45 min.

Sample pre-treatment and Metal Analysis Method

The 400-500 mL hydrolysis solution is slowly evaporated to near-dryness using a proprietary Air Liquide evaporation system specially designed to minimize metallic contamination during sample preparation. The sample is reconstituted with an aqueous solution of 2% HNO₃ [Fisher Optima grade] and 2% H₂O₂ [semiconductor grade] up to the original sample volume and analyzed by Dynamic Reaction Cell Inductively Coupled Plasma-Mass Spectrometry (DRC ICP-MS) (Perkin Elmer Elan 6000 DRC).

In Table 2, the method detection limit is calculated as the greater of 0.1 ppbw or the sample blank value. Note that although the DRC ICP-MS detection limit is 1-10 pptw for most elements, the effect of sample dilution and environmental contaminants leads to significantly higher method detection limits. Also note that the sampling portion of these laboratory-based tests was conducted in a non-cleanroom environment.

TCS Metal Analysis Results

Table 2 displays metal concentrations in liquid-phase and gas-phase TCS. The concentrations of iron, molybdenum, and tin are dramatically higher in the liquid phase, whereas the concentrations of titanium and chromium are slightly higher in gas-phase TCS.

Element	Det. Lim.	Blank	Gas 1	Gas 2	Liq. 1	Liq. 2
Fe	0.242	0.242	<0.242	<0.242	3.515	5.870
Mo	<0.1	<0.1	<0.1	<0.1	1.044	1.152
Cr	0.638	0.638	0.739	0.684	<0.638	<0.638
Zn	0.176	0.176	<0.176	0.247	<0.176	<0.176
Mg	0.198	0.198	<0.198	0.213	0.220	0.230
Sn	<0.1	<0.1	<0.1	<0.1	0.661	0.679
Ti	0.253	0.253	0.391	0.774	<0.253	<0.253
Ni	<0.1	<0.1	<0.1	<0.1	<0.1	0.109
Cu	<0.1	<0.1	<0.1	<0.1	<0.1	0.267
Al	0.154	0.154	0.185	0.168	<0.154	0.340
B	0.165	0.165	<0.165	<0.165	0.302	0.327
Ca	0.187	0.187	0.326	0.213	0.452	0.376
Na	0.154	0.154	<0.154	0.168	<0.154	<0.154
Mn	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
V	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
K	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Li	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Be	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ga	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ge	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
As	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sr	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zr	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Nb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Co	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ag	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cd	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
In	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ba	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ta	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Tl	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pb	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bi	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 2. TCS Metal Analysis Results (unit = ppbw)

Spike Recovery Results

The problem of volatile analyte loss during TCS sample handling is well recognized [1-4]. Thus it is important to confirm that our sampling and sample-pretreatment methods provide satisfactory analyte recovery. A spike recovery test was carried out as follows. Four sample bottles were prepared, each containing 400g aqueous HF at the normal sampling concentration. Two of the bottles were spiked with 80 ng/element for the 34 elements in Table 3; the other two bottles were unspiked controls. Each of the four bottles was then used to sample around 45 g liquid-phase TCS following the procedure described previously. Table 3 displays recovery percentages calculated by the relation:

$$SR_A (\%) = 100 \% * ([A]_{spike} - [A]_{unspiked}) / 200 \text{ pptw}$$

where,

$SR_A (\%)$ = percent spike recovery of element A

$[A]_{spike}$ = avg. concentration of A in spiked samples

$[A]_{unspiked}$ = avg. concentration of A in unspiked samples

200 pptw = parts-per-trillion-weight spike concentration

Our sampling and evaporation techniques yielded recoveries in the 83-115% range for all elements. The important take-home point is that excellent recoveries were obtained for dopant elements (B, As, Sb, and Ge) as well as for stainless steel components (Fe, Cr, Ni, Mn, and Mo) that

are typically found in TCS specifications. These data validate our sampling and pretreatment methods for these especially important elements. Phosphorus is another important TCS dopant element for which analysis and recovery at the 200 ppt level is still under development.

Element	SR (%)	Element	SR (%)
Li	92	Ga	94
Be	94	Ge	88
B	94	As	95
Na	91	Sr	90
Mg	93	Zr	90
Al	91	Nb	96
K	92	Mo	83
Ca	85	Ag	85
Ti	93	Cd	93
V	92	In	90
Cr	89	Sn	89
Mn	93	Sb	89
Fe	112	Ba	89
Co	97	Ta	88
Ni	115	Tl	89
Cu	97	Pb	91
Zn	97	Bi	88

Table 3. Spike Recovery Results

Comparison of Method Detection Limits with TCS Metal Specifications

Supplier specifications for metals in TCS are usually restricted to Fe, B, P, and/or ‘total donors’. They are expressed as ppba (parts-per-billion-atom) in an epitaxial silicon layer deposited from the gas. The silicon film is analyzed by photoluminescence spectroscopy. Table 4 compares industry standard TCS metal impurity specifications with our method detection limits. (Note that for this comparison no attempt was made to estimate the degree to which each metal impurity in TCS would be incorporated into the silicon film.) From these data, and from the data in Table 3, we conclude that our sampling method detection limits are sufficient to verify that a TCS sample is within specification for iron, (and therefore free from corrosion-related contamination) as well as for the dopants As, Sb, and Ge. The level of boron in the sample blanks is comparable to typical boron specs., and therefore sampling and analysis improvement is needed. Regarding phosphorous, further tests are in progress to improve the method detection limit.

Element	Spec. (ppba)	Sample Blank (ppbw)
Fe	5	0.2-1.2
B	0.1-0.3	0.1-0.2
P	1	-
Total Donor	0.8-1.5	-

Table 4. Detection Limits vs. TCS Metal Specs.

Conclusions

A method has been developed for sampling and analysis of metals in TCS. This method is not intended to supplant photoluminescence as a primary quality control test. Rather, the method should allow identification and quantification of metal contaminants in TCS at various points in a distribution system. Anticipated applications include trouble-shooting at the POU as well as qualification of new TCS piping systems. The next step of this work is field sampling. Additional studies will be completed in the future to apply this technique to other reactive gases.

Acknowledgments

The authors would like to thank Kohei Tarutani, Tracey Jacksier, Martine Carre, and Jean-Marc Girard for their valuable contributions to this project.

References

- [1] B.K. Shulte and L.W. Shive, *Anal. Chem.*, **54**, 2392 (1982).
- [2] I.V. Stolyarova, *J. Anal. Chem.*, **50**, 130 (1995)
- [3] J.S. Chen, H.M. Lin, and M.H. Yang, *Fresenius J. Anal. Chem.*, **340**, 357 (1991).
- [4] W.-C. Wei and M.-H. Yang, *Fresenius J. Anal. Chem.*, **353**, 167 (1995).
- [5] L.G. Britton and P. Taylor, *Semicond. Intl.*, 182, (May, 1991).
- [6] NIST Webbook, <http://webbook.nist.gov/chemistry/>
- [7] Air Liquide Material Safety Data Sheet– Trichlorosilane
- [8] Air Liquide Material Safety Data Sheet-Dichlorosilane
- [9] Praxair Material Safety Data Sheet – Dichlorosilane
- [10] *J. Phys. Chem. Ref. Data*, **11(2)**, 2-112 (1982).
- [11] JANAF Thermochemical Tables, *Nat. Stand. Ref. Data Ser.*, 37, (1971).
- [12] K.J. Laidler and J.H. Meiser, *Physical Chemistry*, p. 66 (1982).