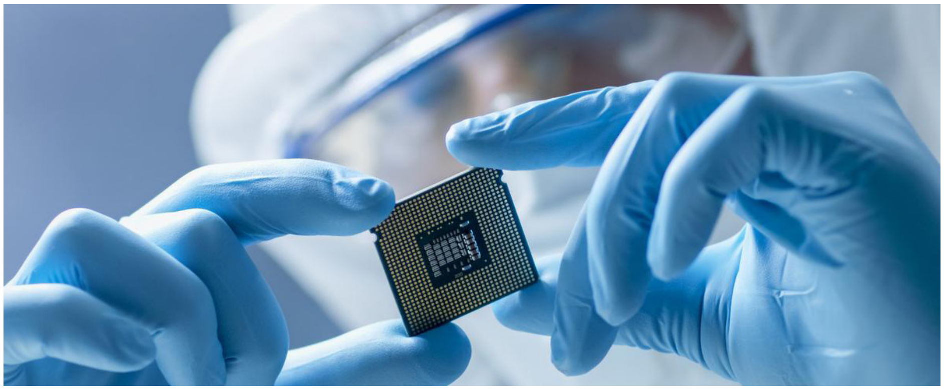
Application Note

Semiconductor

Determination of Trace Impurities in Electronic Grade Arsine by GC-ICP-QQQ

Sub-ppb detection limits for hydride gas contaminants using a single column, single injection volume, and multi-tune method



Authors

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Introduction

Most electronic devices use silicon-based semiconductors. However certain applications can benefit from alternative semiconductor materials, such as III-V compound semiconductors. These compounds are made of elements from groups III and V of the periodic table, usually Al, Ga, or In combined with N, P, As, or Sb. The appeal of these compounds is that they have much higher “carrier mobility” than silicon, which means they offer high performance and greater chip density with lower power consumption and less heat generation. These are critical factors in microelectronics, leading to increased use of III-V compound semiconductors in high electron mobility transistors (HEMT) and field effect transistors (FET).

Unlike Si semiconductors, III-V compound semiconductors are also able to emit light, which makes them essential for the large and growing field of optoelectronics. Light emitting diodes (LED) are widely used in lighting, displays, illuminated switches, and infrared remote controls. Other III-V compound semiconductor devices include vertical-cavity surface-emitting lasers (VCSEL), which are used in optical fiber communications.

Among the most widely used III-V compounds are gallium arsenide (GaAs), aluminum gallium arsenide (AlGaAs), and indium gallium arsenide nitride (InGaAsN), all of which require arsine gas as a precursor for manufacture.

Dopants are added deliberately to modify the electrical properties of semiconductor materials, but incorporation of unwanted dopant elements into III-V compound semiconductor structures can be problematic, even at trace levels (*1*). The unwanted dopants will introduce energy levels in the energy gap of the semiconductor, altering the electrical and optical properties of the semiconductor substrate through an increase in electron mobility, leakage current, or photoluminescence.

For example, n-type dopants such as Ge, Si, P, and S increase leakage current and reduce the gain of transistors. Therefore, it is critical to determine the concentration of germane (GeH_4), silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) impurities in arsine to prevent them affecting the performance of the final device. There may be some slight variation in the gas purity levels required for the manufacture of each type of device, but, in general, process gases need to be free of dopant impurities. Because Ge is of particular concern in the manufacture of many devices, there is a need to measure GeH_4 impurities at or below single digit ppb levels in arsine. However, the ability to detect such low level impurities requires a highly sensitive analytical method.

Gas chromatography (GC) coupled with ICP-MS is currently the only technique capable of measuring germane in arsine at sub-ppb levels (*2–4*). The non-atmospheric molecular impurities typically determined by GC-ICP-MS are H_2S, SiH_4, PH_3, and GeH_4. Occasionally, stibine (SbH_3), hydrogen selenide (H_2Se), and stannane (SnH_4) are also of interest.

The goal of this work was to measure as many of the critical hydride gas impurities as practically possible in arsine, using a single GC-ICP-MS injection and a multi-tune "time program" acquisition method. This approach avoids the need to use different detectors, columns, methods, and even instruments to cover the full range of impurities.

Experimental

Sample and standard preparation

Standards of SiH_4, PH_3, GeH_4, and H_2S were made using a 10 ppm standard mixture (Custom Gas Solutions, Durham, NC, USA) and dynamically diluting it to a value of 24 ppb using a UHP-MMSD dilution system (CONSCI, Pasadena, TX). Standards for H_2Se, SbH_3, and SnH_4 are difficult to obtain due to the labile nature of these compounds. Only qualitative retention time standards were made using hydride generation with sodium borohydride. Although H_2Se, SbH_3, and SnH_4 can be determined by GC-ICP-MS, they were not studied quantitatively in this investigation.

Instrumentation

An Agilent 7890B GC was used for the separation of impurities in arsine and an Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) was used as the detector. The standard Agilent GC-ICP-MS interface was modified using a high flow Deans switch, as shown in Figure 1. This configuration allowed the arsine matrix to be vented at its elution time, preventing the matrix from entering the ICP-MS torch. The column was selected based on a previous study that used an Agilent 8800 ICP-QQQ (*3*). The GC operating parameters are given in Table 1.

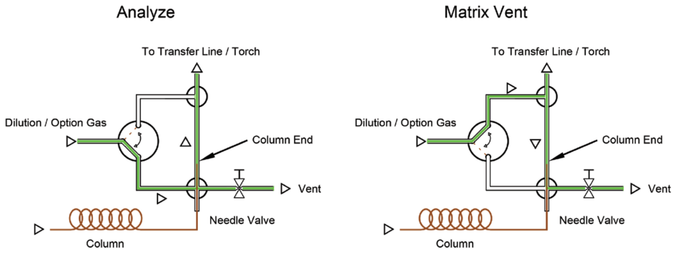

Figure 1. Schematic of the Deans switch used to vent arsine eluted by the GC column, preventing the matrix from being passed to the 8900 ICP-QQQ.

Table 1. GC operating parameters.

Parameter	Setting
Column	Two 100 m x 0.53 mm x 5.0 µm DB-1
Carrier Gas (psig Ar)	20
Oven Temperature (°C)	30 (isothermal)
Sample Size (µL)	60
Transfer Line Temperature (°C)	120

Standard instrument operating parameters for the ICP-MS recommended by Agilent were used. To optimize the ICP-QQQ, a standard containing 5 ppm sulfur hexafluoride, xenon, and krypton in argon (CSI Gas, Texas City, TX) was used. The standard was introduced into the argon dilution gas flow path at 2 mL/min and the signal at *m/z* 32 was maximized. The S, Kr, and Xe peaks were used to optimize torch position and confirm mass calibration.

As described in a previous study (*3*), Agilent ICP-QQQ instruments feature two identical, full-sized quadrupole mass filters (Q1 and Q2), situated either side of the Octopole Reaction System (ORS) collision/reaction cell (CRC). This configuration enables double mass selection (MS/MS), which is vital for successful interference removal using reactive cell gases. Like Q2, Q1 operates in a high vacuum region, so it provides excellent resolution and abundance sensitivity while also maintaining high transmission. This allows precise selection of the ions that enter the cell, ensuring the reactions used to remove interferences on analyte ions are consistent and predictable. A reactive cell gas such as hydrogen, oxygen, or ammonia is used to react with either the interfering ion or the analyte ion (M^+) to attain interference-free measurement. Analytes are measured in 'on-mass' or 'mass-shift' mode. When the cell gas reacts with the interferent, but not the analyte ion, the analyte is measured at its natural mass (on-mass) and the interference ions are removed by Q2. When the analyte ion reacts more readily with the cell gas than the interference ions do, the analyte forms a reaction product ion e.g. MH^+ or MO^+. These product ions are then measured at a new mass, away from the interfering ion overlaps.

The ICP-QQQ can also be operated in no gas mode or the ORS cell can be pressurized with a collision gas, such as helium (He). He mode removes many common polyatomic ion interferences by kinetic energy discrimination (KED) or by collision-induced dissociation (CID).

Compared to the 8800 ICP-QQQ used in the previous study (*3*), the 8900 uses newer technology, such as an ORS^4 cell, which provides higher sensitivity and lower backgrounds. In addition, the 8900 #100 (Advanced Applications) model used in this work includes inert, low sulfur and silicon argon gas lines, which reduce instrumental backgrounds for these elements. To identify the best method conditions for the application, three different MS/MS tune modes were investigated: no gas, hydrogen, and oxygen with and without a mass-shift. Instrument operating conditions are listed in Table 2.

Table 2. ICP-QQQ operating parameters.

Parameter	No Gas	H_2	O_2
RF Power (W)	1450		
Sampling Depth (mm)	3		
Dilution Gas Flow (L/min)	0.7		
Extract 1 (V)	−20		
Extract 2 (V)	−250		
Kinetic Energy Discrimination (V)	5	2	−7
Cell Entrance (V)	−50		
Cell Exit (V)	−80	−70	
Cell Gas Flow Rate	NA	2 mL/min	0.6 mL/min (40% of full scale)

Method development

The method conditions that provided the best detection limits (DLs) for each compound are summarized using bold text in Table 3. The DLs were calculated from signal-to-noise value multiplied by three (as described later). For analytes where the background noise is low due to the absence of interferences (e.g. ^{74}Ge), single digit ppt level DLs were easily achieved using GC-ICP-QQQ operating in no gas, H_2, or O_2 mode. For analytes that are prone to higher backgrounds, such as ^{31}P, ^{32}S, and ^{28}Si, lower DLs were achieved using a reactive cell gas method. The presence of CO_2, N_2, and O_2 in the argon supply and from air entrainment into the plasma leads to the formation of spectral interferences. These interferences include $^{12}C^{18}OH^+$, $^{14}N^{16}OH^+$, $^{15}N_2H^+$, $^{15}N^{16}O^+$ and $^{13}C^{18}O^+$ on $^{31}P^+$, $^{16}O_2^+$ and $^{14}N^{18}O^+$ on $^{32}S^+$, and $^{12}C^{16}O^+$ and $^{14}N_2^+$ on $^{28}Si^+$. P and S react quickly with O_2, so both analytes were measured as reaction product ions, $^{31}P^{16}O^+$ and $^{32}S^{16}O^+$, at *m/z* 47 and 48, respectively, in mass-shift mode. H_2 cell gas provided effective removal of the background interferences at mass 28, allowing on-mass measurement of $^{28}Si^+$ at *m/z* 28.

The measurement of different analytes in different reaction modes is simple to set up and run using a single multi-tune method on the 8900. In the acquisition method, the cell gases and measurement modes are switched automatically during the analysis, giving a fast and automated analysis using the optimum mode for each analyte. Switching conditions during the run allows the analyst to use the best cell conditions, as well as increase the analyte acquisition times to improve sensitivity.

Increasing the injection volume would provide even lower DLs for all compounds except for H_2S. A 60 µL (or smaller) sample size is needed for the separation of H_2S from the arsine matrix.

Table 3. Comparison of GC-ICP-QQQ method conditions for each gas mode.

	No Gas				
	Mass	Integration Time (s)	Area of 24 ppb Standard	S/N	3 sigma DL, ppbv
Silane	28 > 28	0.2	165967	14	5
Germane	74 > 74	0.2	447435	8260	0.01
Phosphine	31 > 31	0.2	32118	870	0.08
Hydrogen sulfide	32 > 32	0.2	234053	175	0.41
	Hydrogen				
	Mass	**Integration Time (s)**	**Area of 24 ppb Standard**	**S/N**	**3 sigma DL, ppbv**
Silane	28 > 28	0.2	**79068**	**42**	**1.7**
Germane	74 > 74	0.2	272006	8300	0.01
Phosphine	31 > 31	0.2	17919	650	0.11
Hydrogen sulfide	32 > 32	0.2	145124	180	0.40
	Oxygen				
	Mass	**Integration Time (s)**	**Area of 24 ppb Standard**	**S/N**	**3 sigma DL, ppbv**
Silane	28 > 28	0.2	51499	34	2
Silane	28 > 44	0.2	34201	37	2
Germane	74 > 74	0.2	**422359**	**8000**	**0.01**
Germane	74 > 90	0.2	15577	1240	0.06
Phosphine	31 > 31	0.2	0	0	NA
Phosphine	31 > 47	0.2	**29011**	**1500**	**0.05**
Hydrogen sulfide	32 > 32	0.2	22579	13	6
Hydrogen sulfide	32 > 48	0.2	**218640**	**290**	**0.24**

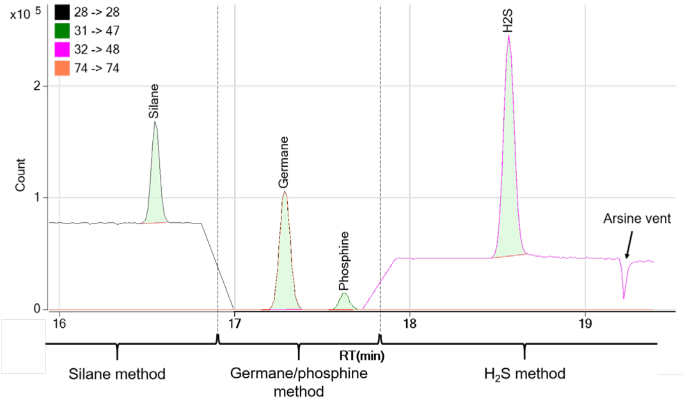

Figure 2. Overlaid chromatograms of SiH_4, PH_3, H_2S, and GeH_4 in arsine by GC-ICP-QQQ obtained using a multi-tune method.

Multi-element analysis of SiH_4, PH_3, H_2S, and GeH_4

Since the best sensitivity (peak area) was obtained using different cell gas conditions for each analyte compound, a time program method was used where the acquisition conditions were changed during the run. The optimized single-method parameters are given in Table 4 and the chromatograms are shown in Figure 2. If analysts preferred to simplify the analysis and use a single cell gas, O_2 would provide acceptable data, with some loss of sensitivity compared to the multi-tune method.

Table 4. Multi-tune method parameters.

	Acquisition Time (s)	Retention Time (s)	Gas Mode	Q1 -> Q2	Integration Time/Mass (s)
Silane	1008	992	H_2	28 -> 28	0.8
Germane	77	1037	O_2	74 -> 74	0.2
Phosphine		1057	O_2	31 -> 47	0.4
Hydrogen sulfide	89	1112	O_2	32 -> 48	0.8

Table 5. DLs for SiH_4, GeH_4, PH_3, and H_2S.

	Mass	Integration Time (s)	Gas Mode	Area of 24 ppb Standard	S/N	3 sigma DL, ppbv
Silane	28 > 28	0.8	H_2	308146	140	0.51
Germane	74 > 74	0.2	O_2	438374	8000	0.01
Phosphine	31 > 47	0.4	O_2	60451	4700	0.02
Hydrogen sulfide	32 > 48	0.8	O_2	883099	490	0.15

Results and discussion

The DLs reported for SiH_4, GeH_4, PH_3, and H_2S (Table 5) were determined using the chromatograms (Figure 2) that were obtained using the parameters outlined in Table 4. The ICP-MS MassHunter software signal-to-noise (S/N) tool was used. The software divides the concentration of the analyte by the S/N value followed by multiplication by three to determine the DL. The EPA protocol MDL and a Student T-test could have been applied if a standard 10 times or less than the expected DL had been available (*5*). That level standard was not available for this work.

Other compounds of potential interest in the quality control testing of arsine including H_2Se and SbH_3 eluted well beyond the arsine retention time (not shown in Figure 2). The relative retention time of SnH_4 and arsine prevented SnH_4 from being separated on a boiling point column, so an Agilent Select Low Sulfur column (p/n CP8575) was used instead. DLs for SnH_4, H_2Se, and SbH_3 were estimated at 1 ppb or lower, based on their relative response in aqueous samples and their first ionization potentials.

Conclusion

GC-ICP-QQQ was used to separate and measure all hydride gas contaminants in arsine at or below single digit ppbv levels. Germane, which is probably the most critical contaminant in semiconductor-grade arsine, was determined at low ppt levels. Measurements of SiH_4, PH_3, H_2S, GeH_4, H_2Se, and SbH_3 were performed using a single GC column and a single injection.

The best detection limits for all compounds were achieved by operating the 8900 ICP-QQQ in MS/MS mode with H_2 and O_2 cell gases. Using a single multi-tune method allowed us to maximize signal averaging, and therefore achieve low DLs with a single injection.

The determination of dopants/contaminants in arsine provides extra process control to aid in the quality of the manufacturing process, thus improving the yield and performance of micro-electronic and opto-electronic devices.

References

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WARNING **Chemical Hazard**

This method does not address safety issues associated with its use. It is the responsibility of the analyst to use all appropriate personal protective equipment and follow all appropriate safety procedures.

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DE.9781365741

Printed in the USA, September 30, 2020
5994-2213EN

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