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Investigations into the Direct Analysis of Semiconductor Grade Gases by Inductively Coupled Plasma Mass Spectrometry*

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Silane is the main gas used in the field of electronics to produce compounds of silicon. The direct analysis of silane by inductively coupled plasma mass spectrometry has been found to be a practical proposition for both the measurement and indentification of elemental impurities at the sub-parts per billion level. Several steps, however, need to be taken to optimise commercial instrumentation further for this task. Firstly, in order to minimise the amount of matrix material being deposited on the sampler orifice, an alloy sample cone was used which operated at a higher temperature than that of the commercially available nickel cones; additionally, the optimum carrier gas flow-rate with silane was found to be significantly lower than that required to achieve maximum sensitivity in argon alone. This too reduced sample deposition around the orifice. A further increase in sensitivity was achieved when the argon carrier gas was supplemented by the addition of hydrogen; the detection limits for ^{75}As and ^{127}I were 0.55 and 0.65 p.p.b., respectively, with a precision of 2–5%. In order to quantify impurities in the silane two techniques were employed. The first used the silicon matrix as an internal standard and the second involved direct comparison with a calibration graph obtained by the addition of impurities to the silane.

Keywords: *Silane; inductively coupled plasma mass spectrometry; alloy cone; hydrogen addition; elemental analysis*

The trace element content of gases used as primary materials in the micro-electronics industry can have a detrimental effect on the quality of the end products. The sources of impurities are potentially multiple, ranging from impure raw materials to process hardware contamination. These impurities are primarily alkali metals, alpha-emitters, dopants and transition elements at sub-parts per billion levels. To date, no routine methods exist to analyse such gases directly for these elemental impurities and currently laboratories may use various indirect methods which can include hydrolysis or solvolysis[1] in order to effect an analysis. However, in methods dealing with organometallic gases for example, the chemistry is complex and the purity of the reagents used for hydrolysis is often poorer than the analyte gas with which they react. Hence, analytical measurements may be reagent blank limited at levels which often do not truly reflect the actual gas purity. A further disadvantage is that such indirect methods may only partially reflect the impurity composition of the gas.

Inductively coupled plasma mass spectrometry (ICP-MS) has the potential to analyse such gases directly and with sufficient sensitivity to negate the use of pre-analysis chemistry and hence yield a result indicative of actual gas impurity composition. Some unpublished work[2] has highlighted this potential and a direct correlation between ion mobility in gallium arsenide and the elemental content of the trimethylgallium (TMG) gas from which it was grown has now been tentatively proposed[3] from ICP-MS data.

The analysis of gases for trace elements is particularly difficult. However, the nature of the gases used for micro-electronics work further exacerbates such problems. The gases used are particularly difficult to handle. Silane (SiH_4) and organometallic gases such as TMG, trimethylaluminium (TMA) and dimethylzinc (DMZ) are pyrophoric and hence will spontaneously ignite in contact with air. The handling of such gases therefore requires highly specialised techniques and rigorous safety precautions must always be observed. It follows that analyses of these gases would only be carried out at facilities suitably equipped and experienced in such work.

In contrast to the analysis of liquids, no gas standards or reference materials exist for trace element content; however, it is possible to prepare gases with some elemental additions, but data on the stability of such gas mixtures have not so far been generally available.

The work described in this paper is concerned with the direct analysis of one of the most important of these gases, namely silane, by ICP-MS. This is the first paper to be published on the subject and as such considers basic instrumental performance with regard to silane analysis.

Experimental

ICP-MS

The investigations were carried out on a standard VG PlasmaQuad PQ2 Plus instrument (VG Elemental, Winsford, Cheshire, UK). To facilitate the introduction of gas samples, the conventional nebuliser and spray chamber were replaced by the gas handling rig shown in Fig. 1. The exit line of the gas

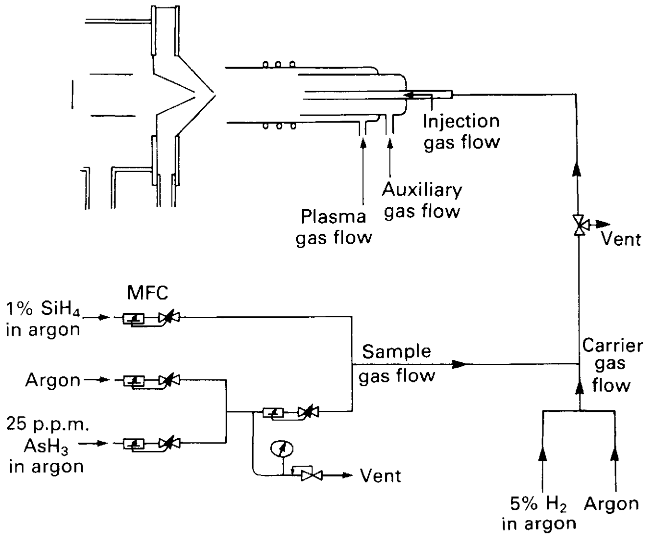

Fig. 1. Schematic diagram of the gas handling system

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rig was coupled directly to the central injector of the ICP torch.

Gases

The gas handling rig consisted of a gas mixing and dilution system with gas flow-rates controlled by mass-flow controllers. Using this system, mixtures of high-purity argon, SiH_4, hydrogen, arsine (AsH_3) and iodine (as CH_3I) could be mixed in precise amounts prior to introduction into the ICP. The argon plasma gas used was industrial grade liquid (99.995%) (L'Air Liquide, Paris, France).

Gas mixtures of SiH_4, AsH_3 and CH_3I in argon were in ultra high-purity argon (99.9999%) (L'Air Liquide, Alphagaz, St-Quentin-en-Yvelines, France). The standard gas mixtures from which analyte signals were obtained were from dilutions of 25 p.p.m. (v/v) each of CH_3I and AsH_3.

Results and Discussion

The aim of this work was to develop a method by which SiH_4 could be analysed directly for trace element content by ICP-MS. In order for this method to be viable, detection limits at low p.p.b. (atomic) levels for elements such as arsenic had to be achievable. As no prior knowledge of such an analysis existed, an investigation of all the relevant parameters was undertaken.

Signal Optimisation

To obtain the optimum conditions, the ICP parameters were investigated by measuring the response of ^{127}I both with and without SiH_4. Iodine-127 was chosen as the test element as it can be obtained in a readily manageable volatile form as CH_3I; further, ^{127}I can be detected sensitively by ICP-MS and is free of spectral interferences. The nebuliser gas was found to be the most critical parameter and the responses both with and without SiH_4 are shown in Figs. 2 and 3. Other optimum conditions were found to be similar to the normal typical operating conditions previously defined for this particular instrument and these are given in Table 1. It is clear that although very high sensitivity is achieved for 2 p.p.b. of ^{127}I using a high gas flow-rate of 1.3 l min^{-1} where no SiH_4 is present, the presence of 20 cm^3 min^{-1} of 1% SiH_4 in argon has shifted the maximum signal response to a lower value of *ca.* 0.70 l min^{-1}. It was also observed that at the high gas flow-rate, the presence of SiH_4 would cause suppression of the analyte signal compared with that in argon. However, at the lower optimum setting, the signal both with and without SiH_4 was essentially the same, although with the latter lower flow-rate the actual signal maximum obtained was one order of magnitude lower than the value achieved at the high gas flow-rate.

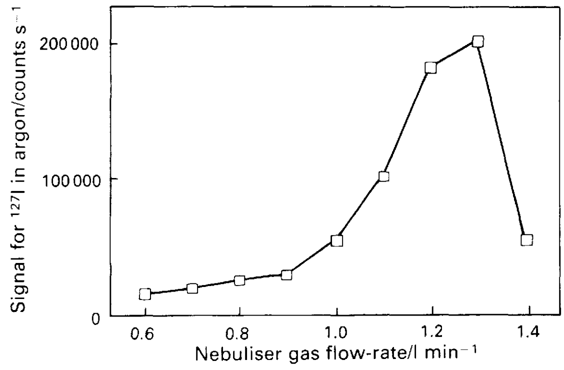

Fig. 2. Variation of ^{127}I signal with nebuliser gas flow-rate in pure argon

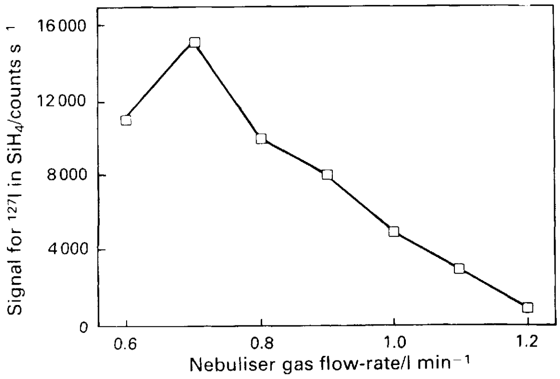

Fig. 3. Variation of ^{127}I signal with nebuliser gas flow-rate in the presence of 20 cm^3 min^{-1} of SiH_4 (1% in argon)

The presence of a heavy or refractory matrix in ICP-MS can cause some long-term degradation in the signal level due to deposition of matrix around the sampler and skimmer orifices. This has been reported by Hutton and Eaton[4] and also by Douglas and Kerr.[5] Silane can be considered to be such a matrix and products such as silica (SiO_2) or silicon (Si) may deposit around the samplers. One advantage of operating with lower gas flow-rates was that the reduction in signal with time was much improved as shown by comparing Figs. 4 and 5. At high carrier gas flow-rates, the signal fell dramatically over a very short period of time (<30 min) and this signal level could not be regained by re-optimisation of the ion optics. At lower flow-rates, it was concluded that the improved stability of the signal level is a result of less matrix material being deposited in a given time. However, there was some reduction in sensitivity over time.

Investigation of Alternative Cone Materials

To reduce deposition of the refractory matrix around the metal samplers further, alternative sampler materials were investigated. The sample cones used in commercial ICP-MS instruments are usually fabricated from nickel, copper or,

Table 1. Instrumental conditions

ICP—	
Nebuliser gas flow-rate	Variable, 0.5–1.50 l min^{-1}
Auxiliary gas flow-rate	0.5 l min^{-1}
Coolant gas flow-rate	13 l min^{-1}
Forward power	1.3 kW
Reflector power	<10 W (see text)
Mass spectrometer—	
Sampling distance	10 mm
Sample orifice	1.0 mm
Skimmer orifice	0.7 mm
Expansion pressure	2.5 mbar
Intermediate pressure	<1 × 10^{-4} mbar
Analyser pressure	2 × 10^{-6} mbar

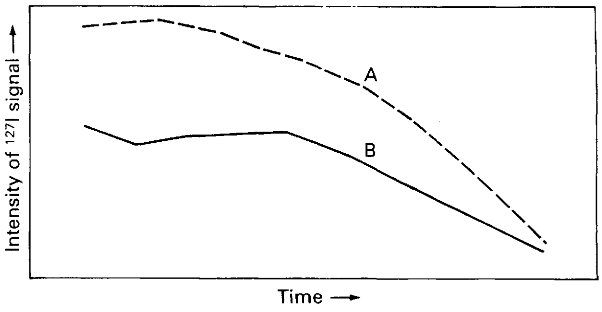

Fig. 4. Signal decay of 2 p.p.b. ^{127}I in 20 cm^3 min^{-1} SiH_4 (1% in argon) over several runs at a carrier gas flow-rate of 0.70 l min^{-1}. A, Run 1; and B, run 2

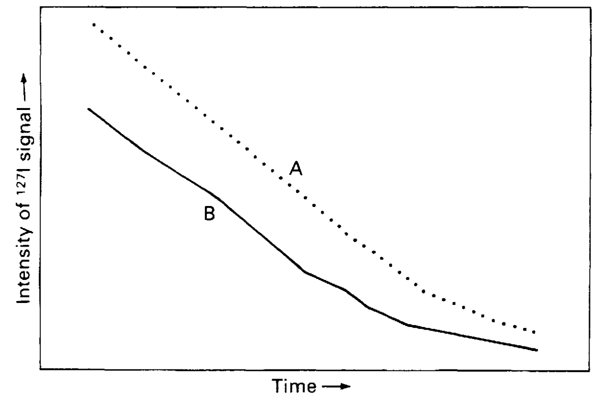

Fig. 5. Signal decay of 2 p.p.b. ^{127}I in 20 cm^3 min^{-1} SiH$_4$ (1% in argon) over several runs at a carrier gas flow-rate of 1.2 l min^{-1}. A, Run 1; and B, run 2

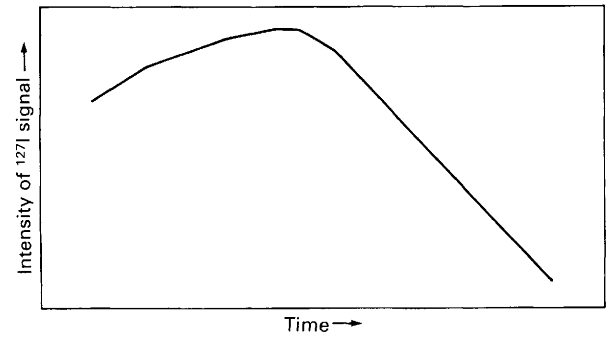

Fig. 6. Signal decay of 2 p.p.b. ^{127}I in 20 cm^3 min^{-1} SiH$_4$ (1% in argon) using nickel samplers (with SiH$_4$)

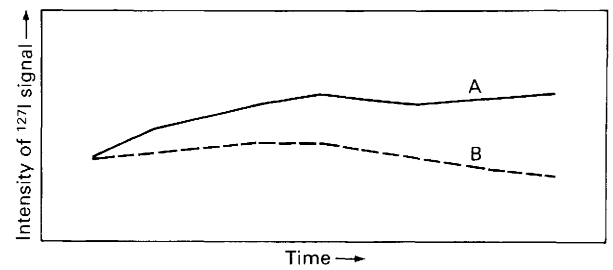

Fig. 7. Signal decay of 2 p.p.b. ^{127}I in 20 cm^3 min^{-1} SiH$_4$ (1% in argon) using alloy samplers. A, Without SiH$_4$; and B, with SiH$_4$

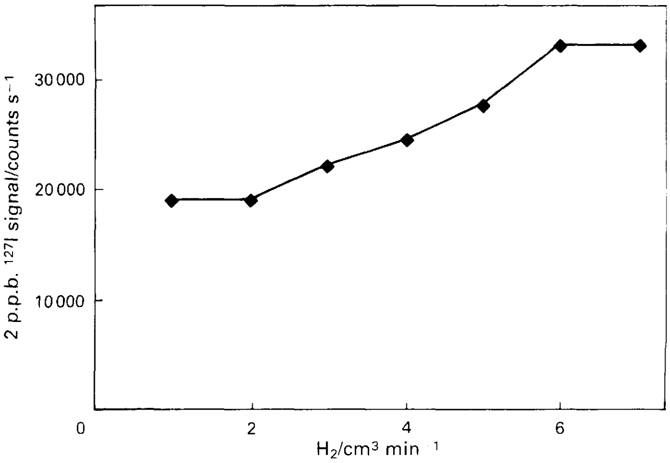

Fig. 8. Variation of the signal of 2 p.p.b. ^{127}I in 20 cm^3 min^{-1} SiH$_4$ (1% in argon) as a function of the addition of hydrogen to the carrier gas flow

more recently, platinum. These metals have a reasonable thermal conductivity and hence are not excessively degraded by the heat of the plasma. However there may be some advantages in operating with sample cones which run a little hotter, as in this manner, condensation of sample material may be expected to be reduced. In this study, cones fabricated from a high-temperature aerospace alloy were used. These cones operated visibly hotter than those of nickel with a dull-red glow observed around the tip of the cone when the plasma was operational. However, despite this, the signal stability was comparable to that with nickel cones and no apparent degradation of the cone material was observed. A comparison of the performance of these cones with those of nickel, when SiH$_4$ was injected, can be made from Figs. 6 and 7. There is little significant reduction in the signal when the alloy cone was used, indicating that the cone was operating at a sufficiently high temperature to minimise matrix condensation on it. Certainly visual inspection of the cone after this time confirmed that little or no silicon had been deposited. However, inspection of the skimmer cone indicated that this had now become a site for the matrix to deposit and that in the long term, deposition around the skimmer would be a source of signal degradation. Signal integrity could however be maintained for reasonably long working periods and this was considered to be a very positive step forward.

Investigation of the Addition of Hydrogen to the Plasma

It is known[6,7] that the addition of hydrogen is beneficial to the energy transfer processes between the bulk plasma and the central analyte channel. The plasma in this work does not have a water loading as it is dry. It was considered, therefore, that further improvements in sensitivity might be achievable were this dry plasma to be supplemented by an additional flow of hydrogen to the sample carrier gas. Hydrogen was added, up to a total flow-rate of 7.5 cm^3 min^{-1}, to the central injector and it can be observed from Fig. 8 that the signal level for 2 p.p.b. of ^{127}I was increased by over 70%. Also, signal reproducibility was improved and a detection limit for ^{127}I in 1% SiH$_4$ of 0.18 parts per trillion (p.p.t.) was obtained (this being calculated as 3σ of the background at mass 127), which is equivalent to *ca.* 0.65 p.p.b. in SiH$_4$ alone after dilution factors have been accounted for. However, as the flow-rate was increased, the reflected power also increased, and at 7.5 cm^3 min^{-1} of hydrogen a reflected power of *ca.* 30 W was obtained. Higher flow-rates of hydrogen were not investigated, therefore, as ultimately, some degradation in the performance of the r.f. generator could result.

Increased Silane Flow-rate

Optimisation of the system was carried out by using iodine as the test element and a SiH$_4$ flow-rate of 20 cm^3 min^{-1} (1% SiH$_4$) in argon. To investigate whether further detection limit improvements could be achieved, the SiH$_4$ flow-rate was gradually increased. Table 2 indicates the relationship between SiH$_4$ flow-rate (1% SiH$_4$) and the actual amount of silane at the injector of the ICP. In order to relate this value to the values observed in "normal" solution sample introduction, the value is given as "solution equivalent," this being the value that would be obtained if the SiH$_4$ were in aqueous solution (assuming a nebulisation efficiency of 1%). It is typical practice in ICP-MS to use a solution matrix concentration of about 2000 p.p.m., and in this work we are clearly operating up to several orders of magnitude higher than this. As it was considered that the system was operating close to its optimum, the test element was substituted by arsenic in the form of arsine (AsH$_3$), this being an important impurity in SiH$_4$. By increasing the SiH$_4$ flow-rate (at the injector) from a previous level of 20 cm^3 min^{-1} (equivalent to 285 p.p.m. of SiH$_4$ at the

Table 2. Silane concentration (1% in argon)

SiH_4 flow-rate/ cm^3 min^{-1}	SiH_4 at injector, p.p.m.	SiH_4 "solution equivalent," p.p.m.
10	140	14 000
20	290	29 000
50	710	71 000
100	1 400	140 000

Table 3. Detection limits for ^{75}As as a function of SiH_4 flow-rate

SiH_4 concentration at injector, p.p.m.	^{75}As detection limit in pure SiH_4, p.p.b.
290	1.1
710	0.43
1 400	0.55

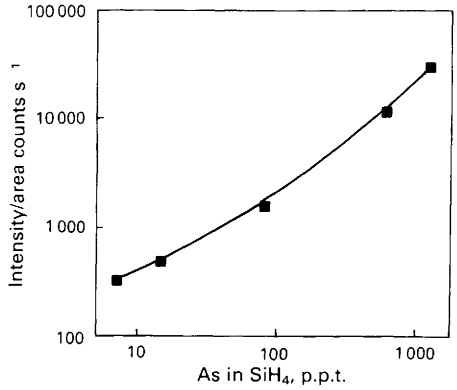

Fig. 9. Calibration graph for ^{75}As in 600 cm^3 min^{-1} of SiH_4. Obtained by variable additions of AsH_3 to silane

injector) to a level of 50 cm^3 min^{-1} (equivalent to 712 p.p.m. of SiH_4 at the injector) a 2–3-fold improvement in the detection limit of arsenic was obtained. Further increases in the SiH_4 flow-rate to 100 cm^3 min^{-1} (equivalent to 1425 p.p.m. of SiH_4 at the injector) resulted in poorer precision and significant signal decay was observed. The precision decreased from *ca.* 2 to >12%. A summary of these data is given in Table 3.

Quantification

Although the steps described previously have allowed SiH_4 to be introduced reproducibly into an ICP-MS instrument, the quantification of impurities merits further investigation.

The capability exists with the instrumentation used in this investigation to measure both trace and matrix components by utilising a dual-detection configuration consisting of both pulse counting and analogue modes. In this manner the trace components can be directly ratioed to the matrix element. By measuring the matrix ^{29}Si isotope (4.7% abundance) in analogue mode, values for ^{75}As, measured in pulse counting mode, were calculated to be 1.85 and 2.02 p.p.b. in repeat measurements, where a nominal value of 2 p.p.b. in 1% SiH_4 was expected. The internal ratio technique has been effectively used in laser ablation ICP-MS when no standard calibration reference materials are available and it was not unexpected that it should prove to be particularly effective in gas analysis. However, the gas dilution system used in this work also allowed variable independent additions of CH_3I and AsH_3 to be made to the SiH_4 and a linear calibration at the p.p.t. level was obtained for both elements. The calibration graph for As in SiH_4 is shown in Fig. 9 over 2–3 decades of concentration.

Conclusions

The direct analysis of SiH_4 by ICP-MS is a practical proposition; however, several steps need to be taken to modify the commercial instrumentation in order to obtain improved performance. The use of alloy cones in conjunction with optimal low carrier gas flow-rates substantially reduces the incidence of material deposition around the sampler orifice and hence improves long-term precision and sensitivity. The addition of hydrogen to the carrier gas further increases the analyte signal level; however, at flow-rates of hydrogen greater than 7.5 cm^3 min^{-1}, the reflected power was too high to be practicable on the current ICP configuration used.

Large amounts of SiH_4 matrix can be introduced into the ICP, in most instances up to several orders of magnitude more material than is usual in conventional solution sample introduction for ICP-MS. Detection limits of 0.55 p.p.b. for ^{75}As and 0.65 p.p.b. for ^{127}I in SiH_4 alone were routinely achieved with inter-sample precisions of 2–5%. Quantification of trace impurities in SiH_4 can be carried out either by ratioing to the silicon element of the matrix or by constructing a calibration in SiH_4 utilising the gas system described herein. Values for As in SiH_4 were found to agree well with expected values.

It is anticipated that the use of a high resolution magnetic sector based ICP-MS instrument[8] would lead to a further improvement in the detection limit.

References

1. Barnes, R. M., and Bertenyi, R., *Anal. Chem.*, 1986, **58**, 1734.
2. Streusand, B., Govorchin, S., and Hutton, R. C., paper presented at the 1st Durham Conference on Plasma Source Mass Spectrometry, Durham, 1988.
3. Streusand, B., paper presented at the 16th Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Chicago, IL, USA, October 1–6, 1989.
4. Hutton, R. C., and Eaton, A. N., *J. Anal. At. Spectrom.*, 1988, **3**, 547.
5. Douglas, D. J., and Kerr, L., *J. Anal. At. Spectrom.*, 1988, **3**, 749.
6. Murillo, M., and Mermet, J.-M., *Spectrochim. Acta, Part B*, 1989, **44**, 359.
7. Walters, P. E., and Barnardt, C. A., *Spectrochim. Acta, Part B*, 1988, **43**, 325.
8. Bradshaw, N., Hall, E. F. H., and Sanderson, N. E., *J. Anal. At. Spectrom.*, 1989, **4**, 801.

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