The Analysis of High purity Silicon wafers using Glow Discharge Mass Spectrometry

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Abstract: A new discharge cell has been developed that can accommodate flat samples such as Silicon wafers. Data will be presented to demonstrate the characterisation of this new cell. The effect of varying the plasma conditions will be discussed in terms of maximising the silicon ion yield and reducing molecular interferences, thus improving the sensitivity of the VG 9000 GDMS. As a results detection limits of the sub-ppb level are readily attainable for most elements, with an ultimate limit of detection being a few ppt.

Key Words: Silicon wafers, Glow Discharge, GDMS, Detection Limits, Elemental analysis.

Introduction

Glow Discharge Mass Spectrometry (GDMS) is now a established technique for the analysis of inorganic materials in conducting form. To date, the most frequent use of GDMS has been the analysis of high purity metals and alloys. Coburn and co-workers^{1,2} first demonstrated the potential of GDMS for analytical applications by showing that the ion signals in a glow discharge were representative of the metal cathode composition. The analytical considerations of GDMS have been explored extensively by Harrison and co-workers³⁻⁵ covering many ion source configurations.

One of the more successful configurations used to date is a pin-type glow discharge cell. This type of cell has traditionally been used on the VG 9000 glow discharge mass spectrometer⁶ for the analysis of conducting materials. Non-conducting powders have been analysed by compacting with a high purity conducting binder.

Ultra high purity silicon, however, possess a high resistivity (typically, a silicon wafer containing 10^{12} atoms cm^{-3} of p type impurities will possess a resistivity of 13×10^4 ohms cm), but will become insulating at the cryogenic temperatures often used in commercial Glow Discharge cells⁶. Calculations show that silicon cut into a pin 20mm in length by 2mm diameter would have a resistance of around 1.5×10^7 ohms, whereas the resistance of a wafer would be 3×10^7 ohms. Hence, using Ohm's law, that for a 1kV discharge, the maximum current that can be carried by a pin is 0.07 mA, and for a wafer 360mA. Typical currents experienced in a glow discharge source required to produce sufficient ion signal are in the 2-20mA range. It is clear that a pin sample would not allow sufficient current flow to sustain a suitable discharge. A silicon wafer, on the other hand, should present no such problems.

A new design of glow discharge cell has thus been developed that is capable of accommodating flat samples such as silicon wafers. This cell has been designed and characterised to maximise the silicon ion yield whilst minimising interferences from molecular ions and atmospheric contaminants. A two step analytical procedure was consequently adopted, enabling the analysis of a wide range of elements to be performed to ppb levels and lower.

Experimental

1. Instrumentation

The new glow discharge cell, designed to accommodate flat samples such as silicon wafers, is illustrated in Figure 1. The cell, constructed from tantalum, plugs into the source housing chamber of the mass spectrometer via a boron nitride disk, which allows thermal conduction to a liquid nitrogen ring whilst providing electrical insulation. The sample is held in a retractable sample holder and when in position the front plate, also constructed from tantalum comes into contact with the cell, and is held firmly in position by a spring loaded mechanism in the probe handle. The front plate of the sample holder is thus in direct electrical contact with the cell itself, which is held at anode potential.

Figure 1 - The new discharge cell developed for the analysis of flat samples

The sample, which acts as the cathode in the discharge, has to be insulated from the front plate. This is achieved by the use of alumina disks placed between the sample and front plate. The sample is held in place using a spring located in the sample holder. Electrical contact to the sample is made through this spring to the wall of the sample holder, which is in contact with a copper/beryllium contact, and is also insulated from the front plate.

2. Analytical Procedure

The glow discharge was initiated by applying a voltage of 2kV between the cell and sample in argon gas. (BOC Ltd, 99.9999%) held at a pressure of 4.5×10^{-5} m bar, as measured using an ion gauge situated above the cryo pump servicing the source housing. The discharge current recorded was 15 mA. Analysis of trace elements was performed under these conditions.

Once this analysis had been performed, the pressure of argon in the ion source was reduced (keeping the voltage constant) to produce a discharge current of 2mA.

Analysis of carbon and oxygen was then performed using these discharge conditions.

Results and Discussions

a) Analysis of important elements

The key elements of importance in the analysis of silicon are boron, aluminium, phosphorus and arsenic. Of the samples analysed three were characterised for phosphorous, by the technique of cryo photoluminescence). To determine low levels of phosphorous in silicon it is necessary to operate the mass spectrometer at high resolution (>4000), as shown in Figure 2. The peak on the left is due to phosphorous, at a measured concentration of 88 ppb a. The peak is clearly resolved from the interference peak on the right, due to $^{30}\text{SiH}^+$.

b) Survey Analysis

The VG 9000 is capable of analysis over the whole mass range, and can thus determine the concentrations of many other elements such as the transition metals and rare earths. The rapid survey analysis of a silicon wafer for these elements is given in Table 1 below.

Figure 2 - Spectrum of Phosphorous in Silicon

Table 1
Survey analysis of Sample A for Transition Metals and Rare Earth

Element	Concentrations	
	ppb atomic	atoms/cc
Ti	<0.4	<2E13
V	<0.3	<2E13
Cr	<0.4	<2E13
Mn	<0.4	<2E13
Fe	<1.5	<8E13
Co	<1.0	<5E13
Ni	<1.4	<7E13
Cu	<0.4	<2E13
Pr	<0.1	<5E12
Nd	<0.1	<5E12
Sm	<0.6	<3E13
Eu	<0.2	<1E13
Gd	<0.7	<4E13
Tb	<0.09	<5E12
Dy	<0.3	<2E13
Ho	<0.08	<4E12
Er	<0.3	<2E13
Tm	<0.08	<4E12
Yb	<0.5	<3E13
Lu	<0.1	<5E12

c) Determination of Carbon and Oxygen

It was observed that the contribution to the mass spectrum from atmospheric contaminants increased as the pressure was increased. To ensure that the C^+ and O^+ ions seen in the spectrum are due to C and O from the silicon wafer and not from the atmosphere, analysis of silicon for carbon and oxygen was performed under low pressures (7×10^{-6} mbar - resulting in a discharge current 2.0 mA for a 2kV discharge voltage).

A series of samples, previously characterised for carbon and oxygen by FT-IR measurements, were analysed to obtain calibration graphs for carbon and oxygen. The graphs so obtained (Figures 3a and b) are linear, and the relative sensitivity factors (RSF's - defined as the sensitivity of an element x relative to Si) are obtained from the slopes of the appropriate graph. The RSF's are 0.58 and 10.9 for carbon and oxygen respectively.

These RSF's can then be applied to the data obtained, to provide quantitative results. This is illustrated in Table 2, where three samples (previously characterised by FT IR measurements) were analysed for oxygen and one for carbon. The GDMS values are the mean of 4 analyses.

Table 2
Quantitative Determination of Carbon and Oxygen in Silicon Wafers

a) Oxygen

Sample	Characterised Value (ppm)	GDMS Value (ppm)
A	8.3	8.3 +/- 0.3
B	30.8	29.0 +/- 0.8
C	35.0	35.0 +/- 2.0

b) Carbon

A	0.56	0.68 +/- 0.2
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As can be seen, there is excellent agreement between the values obtained by GDMS and the values characterised by FT-IR measurements.

d) Detection Limits

Detection limits, defined as 2 sigma on the background noise of the mass of interest have been determined for some key elements in silicon wafers. These are listed in Table 3.

Table 3 - Detection Limits in Silicon Wafers

Elements	Limits of Detection (atoms/cc)
B ^a	5.0×10^{11}
Al ^b	4.0×10^{13}
P ^a	7.0×10^{11}
Cl ^b	5.0×10^{12}
Fe ^b	3.5×10^{12}
As ^a	3.5×10^{11}
U ^c	4.5×10^{10}

It can be seen from the data presented in Table 3 that the detection limits are typically in the $3\text{--}7 \times 10^{11}$ atoms/cc range. Detection limit for aluminium is limited by the tail from the silicon matrix peak at mass 28. The detection limit for iron is limited by the tail of the Si_2^+ peak. This, however, is much reduced when operating under high power conditions. The ultimate detection limit is 4.5×10^{10} atoms/cc for Uranium.

Conclusions

The new design of discharge cell has proved successful in the direct analysis of silicon wafers, to be performed using the VG 9000 glow discharge mass spectrometer.

Characterisation of this cell has shown that the silicon ion intensity is a maximum at high voltages and pressures whilst some ions may behave differently. The silicon dimer ion, for example, is found to decrease as the pressure is increased. This may reflect an increasing number of dissociative collisions that could occur with other particles in the discharge.

A refined analytical procedure has thus been developed based on these observations. This incorporates analysis of key elements to sup-ppb levels using high voltage and pressure followed by analysis of carbon and oxygen using lower pressure conditions.

Detection limits obtained by this GDMS technique are in the range from 0.001 to 0.1ppb atomic (5×10^{10} to 5×10^{12} atoms cm^{-3}) for the key elements studied.

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