QUADRUPOLE MASS SPECTROMETRY
TECHNICAL INFORMATION

Application of the DQ100 High Performance Mass Spectrometer System to Plasma Enhanced Chemical Vapour Deposition (PECVD) Process Gas Analysis

The design and performance of a diamond (PECVD) process gas analysis system is described. Diamond film quality can be controlled by monitoring the plasma reaction products. Impurity gases can be determined to ppm levels and lower. The key features of the system are low detection limits for impurities, fast response time and an inert heatable all glass inlet.

Introduction

In diamond growth a methane and hydrogen gas mixture is used to form a plasma discharge from which diamond film is deposited on a heated electrode. The operating pressure is in the range 20 to 400 Torr and the ratio of the partial pressure of methane to hydrogen is between 0.1 and 10%. The quality of diamond film depends on impurities in the process gas mixture and also on the operating conditions in the plasma reactor. Process impurities and plasma reaction products can both be determined using gas analysis. Impurities in the process can arise from many sources.

1. Air leaks from atmosphere to the process gas through gaskets, fittings, regulator valves or gas delivery lines.

2. Virtual air leaks from fittings inside the process vacuum chamber which can trap gas when the chamber is vented.

3. Residual water vapour in the process chamber or gas inlet lines.

4. Solvents used to clean parts of the vacuum system or substrates for example acetone, alcohol, freon, trichloroethane.

5. Backstreaming from the vacuum pumping system contributes high molecular weight hydrocarbon contamination.

6. Outgassing from part of the process cycle for example when a substrate heater is brought to temperature or when the plasma discharge is initiated.

In PECVD gas molecules are ionised and dissociated. The dissociated products then recombine to form new reaction products which can be detected by gas analysis. In diamond deposition using a methane in hydrogen discharge acetylene is a known reaction product.

As plasma discharge power increases methane is consumed and acetylene is generated. The ratio of acetylene to methane is an indication of diamond film quality high ratios producing graphitic films and can be used as a process monitor.

The requirements of a gas analysis system for PECVD can be summarised:

1. Low detection limits for the common gases and higher molecular weight impurities in a hydrogen stream.
2. Short resident time in the inlet allowing fast response and reducing the probability of surface reactions.
3. Heatable inlet to prevent gas adsorption.
4. Compact design easily attached to a PECVD vacuum system.
5. Flexible acquisition, display and storage of mass spectral data.

System Design

The DQ100 system can be divided intro three components: the gas inlet, mass spectrometer and vacuum system. (Figure 1)

The gas inlet system uses an all glass jet separator to reduce the process pressure from 20-400 Torr and produce a molecular beam in the mass spectrometer ion source. The jet separator acts as a momentum analyser which enriches the number density of the higher molecular weights as they are transferred to the vacuum chamber. This approach provides a high dynamic measurement range for higher molecular weight gases and process reaction

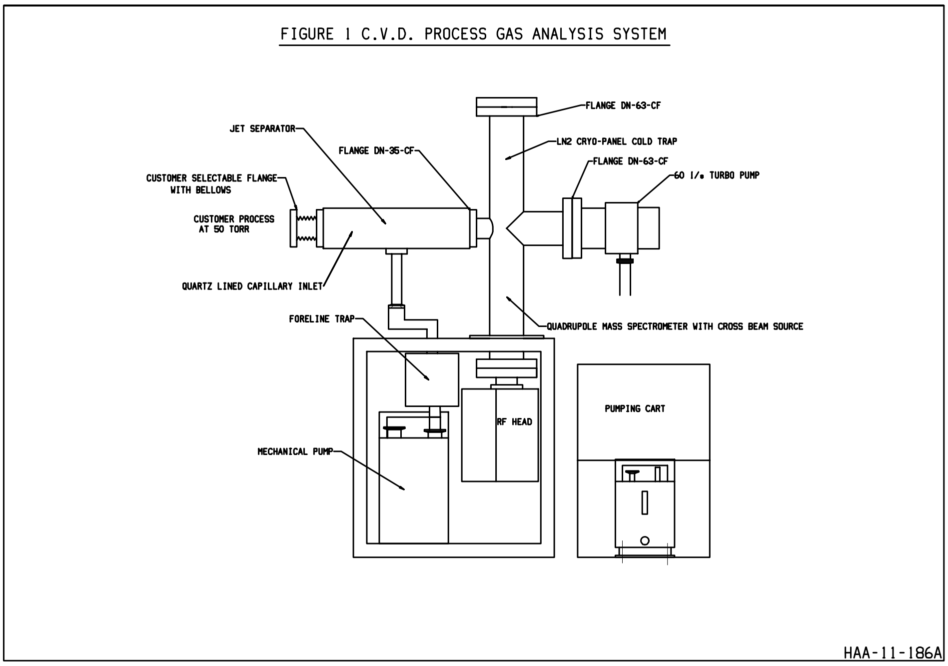

Figure 1. DQ100 Gas Analysis System

products. The jet separator comprises two accurately aligned opposing glass jets, the volume around the jets is pumped by a mechanical pump.

The mass spectrometer uses an electron impact ion source with a crossed electron - molecular beam configuration to produce positive ions in a high pressure ionisation volume. This technique means that ionisation takes place at high pressure with simultaneously high pumping speed in the ion source region realising a low background low memory effect spectrum and overcoming the inherent disadvantage of a closed ion source. The vacuum system is pumped by a 60 litre/sec turbomolecular pump backed by a mechanical pump. For high dynamic range measurements cryopanels are mounted around the ion source and reduce the background pressures for high molecular weights to the 10^{-11} to 10^{-12} Torr range.

The mass spectrometer is available with four mass range options 100, 200, 300 and 320 amu. A continuous dynode electron multiplier CDEM is recommended for fast scanning high dynamic range work. These spectrometers have a minimum detectable partial pressure of 5 x 10^{-14} Torr for m/e 28 and retain high scanning speeds when working in the more sensitive pressure ranges resulting in ppm analysis with fast acquisition. Mass spectral data can be acquired in several ways: SURVEY or BAR mode allows acquisition of complete mass spectra over predefined mass and pressure ranges. TREND or MID mode allows multichannel peak jumping appropriate for long term process monitoring. PROFile mode is used to check mass resolution.

Data can be hard copied direct to a dot matrix printer or can be stored to disc for recall and display using a PC. Data formats are compatible with LOTUS 1-2-3, SIGMAPLOT and others. In addition the instrument can be directly connected via RS232 to a remote computer for data analysis and display.

Impurity Determination

Figure (2) shows a spectrum of 1% methane in hydrogen, with a reactor pressure of 30 torr.

The spectrum is shown on two pressure ranges differing by a factor of 10. The higher sensitivity spectrum shows an air component (m/e 28, 32) at 0.03% caused by an impurity in the methane and hydrogen gas stream.

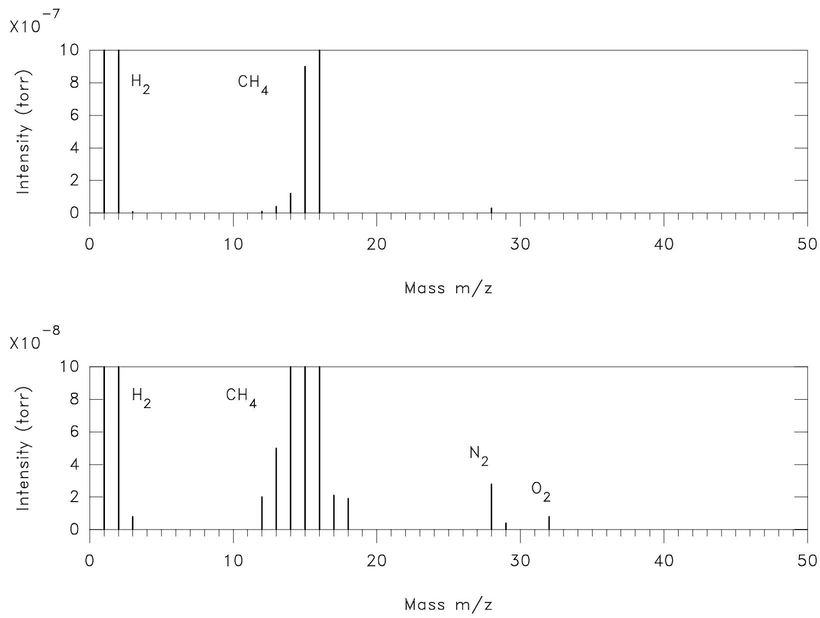

Figure 2. Spectrum of 1% methane in hydrogen

	Parent Gas	Fragment	m/z	Detection level (ppm)
Common Gases	Water Vapour	H_2O	18	5
	Nitrogen/Carbon Monoxide	N_2/CO	28	10
	Oxygen	O2	32	1
	Argon	Ar	40	0.1
	Carbon Dioxide	CO_2	44	2.5
Solvents	Alcohol	C_2H_5O	45	0.02
	Acetone	$(CH_3)_2CO$	58	0.01
	Freon	CF_3	69	0.01
	Freon	$CClF_2$	85	0.01
Reaction Products	Acetylene	C_2H_2	26	0.5
		C_2H_x	27,29,30	0.5
		C_3H_x	37,38,39,40,41 42,43	0.5

Table 1. Detection Levels of Gases of Interest

Table 1 shows the detection limits for various gases of interest and are in the ppm range for all gases of interest. The detection limit for oxygen and most of the C_2H_X and C_3H_X components is in the ppb range.

Figure (3) is a spectrum showing the detection of a high molecular weight impurity gas in the hydrogen/methane mixture. Mass 85 and 87 are the characteristic peaks of FREON 12 with the spectrum showing an indicated freon level of around 300 ppb identified as an impurity in the hydrogen gas supply.

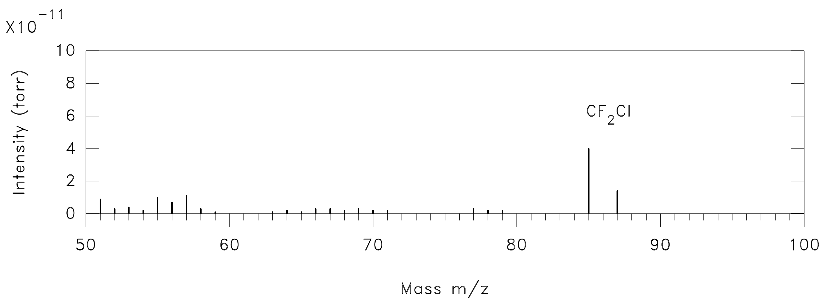

Figure 3. Detection of a 300 ppb FREON impurity

Reaction Products

Spectra from a diamond PECVD reactor showing the formation and detection of reaction products are shown in figure 4.
Several hydrocarbon species of the form C_2H_x are formed by dissociated and recombination in

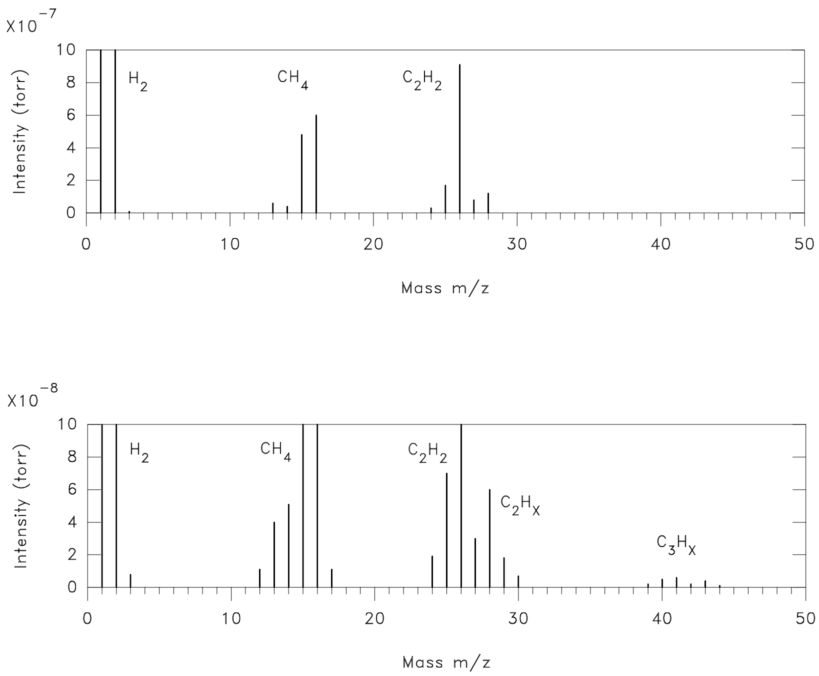

Figure 4. Reaction Products in a methane/hydrogen plasma

the plasma. The most significant reaction product is acetylene with a characteristic mass at m/z 26. Other reaction products of the form C_3H_x are also formed but the probability of formation is much lower.

The ratio of acetylene to methane is a function of microwave power coupled into the reactor, increasing microwave power in the reactor reduces the methane abundance by dissociation acetylene increases by the recombination of methane fragments. Figure 5 shows a typical characteristic. These curves can be used to test process reproducibility and that the plasma-microwave power coupling is consistent.

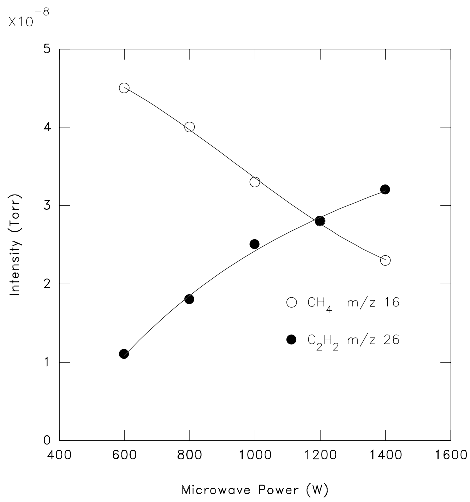

Figure 5. Variation of methane and acetylene with indicated microwave power (Discharge pressure 30 torr, 0.5% CH_4 in H_2)

The time variation of the concentrations of hydrogen, methane and acetylene is shown in figure 6. Long term trend monitoring of parent gas and reaction product ratios gives a quality control fingerprint for a particular film growth.

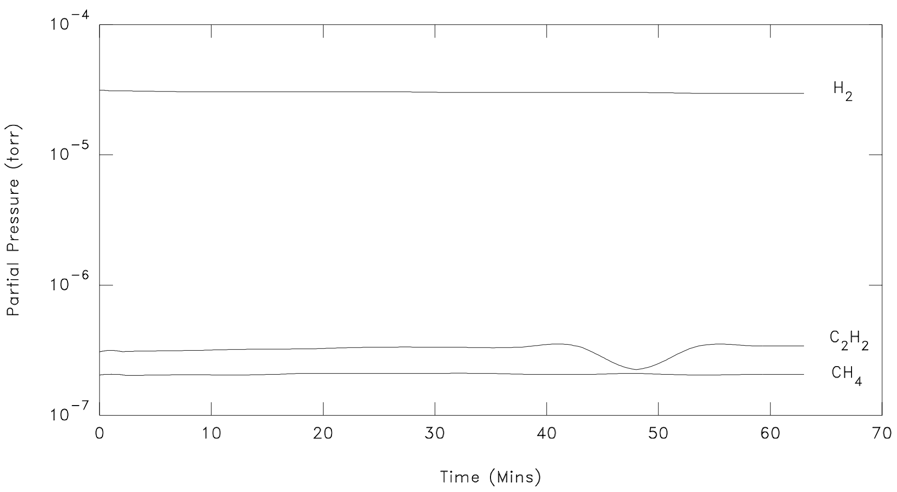

Figure 6. Time Variation of hydrogen, methane and acetylene application areas

Conclusion

This article shows that the DQ100 can be used in three application areas:

1. Measurement of impurity gases to ppm and ppb levels.

2. Characterisation of the system in terms of reaction product concentration determination measurement against microwave input power.

2. Long term trend monitoring of reaction products and impurities as a quality control 'signature'.

The benefits of using the technique as a diagnostic are improved reproducibility and better quality control of deposited films.

Acknowledgements

Thanks to Barry C. Farnsworth, GTE Laboratories, Inc for the data presented in this article.

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