Notes

Comparison of Sampling Techniques for the Analysis of Particulate Metal Impurities in Gases

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Purity requirements for the gases used in the semiconductor manufacturing process are becoming increasingly stringent as the feature sizes of electronic devices decrease. Trace level metallic contamination is one of today's concerns since such elements can create critical defects in the devices. Metal impurities in gases are typically analyzed with indirect methods by first extracting the metallic impurities from the gas into the liquid media. This liquid is subsequently analyzed by sensitive metal analyzers such as ICP-AES, ICP-MS, GF-AAS (graphite furnace atomic absorption spectrometry) or MIP-MS (microwave induced plasma mass spectrometry). The sampling of metal impurities from the gas is carried out usually by passing a gas through a sampling filter (filtration method) or by bubbling the gas in a liquid in an impinger (impinger method).^{1,2} Quantitative collection efficiency of metal impurities is usually assumed to be 100% by these sampling methods. However, this efficiency is difficult to verify because metal standards are not readily available in gas phase. In spite of such a limitation, the indirect methods have the advantage that they can be applied to a wide variety of gases, and the sampling device is portable. In recent years, attempts have been made to inject the sample gas directly into the plasma of ICP-AES^{3,4}, ICP-MS⁵, MIP-AES⁶ or MIP-MS to determine the metal impurities in gases. However, the types of gas which can be introduced into such plasma-based analyzers are limited because of problems in plasma stability or material compatibility.

Particle counting can be considered as an alternative monitoring technique for metals in particulate form in the gas stream.⁷ Correlation, however, is not well established between the metal analysis results either by an indirect or a direct method and the particle counting results obtained for the same gas.

In the present study, the sampling efficiencies of the filtration and the impinger method are compared using NaCl particles in Ar or N₂ gas. NaCl particles in Ar stream were also directly introduced into the plasma of an ICP-MS to evaluate its capability for determination of particulate metal impurities in gas phase. All the above

results of the metal analysis were compared with the particle counting results.

Experimental

A schematic diagram of the experimental setup for the comparison of various sampling methods is shown in Fig. 1. NaCl particles were generated in a high purity Ar or N₂ stream by a particle generator equipped with a cross flow nebulizer (Standard particle generator, RION). A 5 w/v% aqueous solution of NaCl was used as a source of NaCl. The nebulizer gas (N₂ or Ar) of the particle generator was first bubbled through deionized (DI) water prior to entering into the nebulizer. This is to provide constant moisture in the nebulizer gas so as to avoid precipitation of NaCl at the nebulizer tip.

The particle size distribution was monitored for over 24 h as shown in Fig. 2, by a LPC (laser particle counter, CGS-200, Particle Measuring Systems Inc.) whose minimum detectable particle diameter is 0.2 μm with 50% counting efficiency. The cell flow rate is 20 ml min⁻¹ at the sample gas pressure.

Fig. 1 A schematic diagram of sodium chloride particle introduction into a laser particle counter, sampling filters and an impinger.

Fig. 2 Size distribution of sodium chloride particles.

The gas lines were all made by PFA (tetrafluoroethylene-perfluoroalkylvinylether copolymer) components. The distance between the particle generator and each sampling device was made the same. While the gas was sampled with the three devices, the particles were measured simultaneously. The sampling was made seven times with various sampling durations ranging from 30 min to 2500 min.

An impinger made of PTFE (polytetrafluoroethylene) or PFA contained 100 ml DI water to absorb the NaCl particles. A PTFE filter or a PC (polycarbonate) filter of 0.2 μm in pore size and 47 mm in diameter (Nihon Millipore) was set in each filter holder to trap NaCl particles. The gas flow rate through the filters or the impinger was 1 l min⁻¹. After the collection of NaCl particles on the filters, the filter was removed from each holder and placed in a polyethylene flask separately under clean room conditions. Then DI water was added over the filter in the flask in order to wash out NaCl from the filter. After ultrasonic treatment of the flask for 20 min, the Na contents washed from filter were determined by flame emission spectrometer (5100PC, Perkin Elmer). The Na amounts washed from the blank filters without any prewashing were separately determined to be 13.2 ng ml⁻¹ ($n=3$, for polycarbonate filters) and 1.2 ng ml⁻¹ ($n=3$, for PTFE filters) by GF-AAS (5100ZL AAS, Perkin Elmer). These blank levels are negligibly small compared with the Na amounts detected in the washing solution of the filter after the sampling. The Na amount in the impinger solution was also determined by the flame emission spectrometer.

Figure 3 shows a setup used to evaluate direct analysis of NaCl particles in Ar gas by ICP-MS (Fisons, VG Plasma Trace 1). The gas line was connected to both the torch of ICP-MS and a CNC (condensation nucleus particle counter, Model 3851, KANOMAX). The minimum detectable diameter of the CNC is 0.05 μm with 50% counting efficiency. The number of NaCl particles were also counted by the LPC described above. The signals at m/z 23 (Na) observed by ICP-MS and the particle counts were accumulated for 1 min, and the measurement was repeated ten times. Signal intensity was determined by integration of the peak area.

Fig. 3 A schematic diagram of direct analysis of sodium chloride particles in argon gas by ICP-MS. MFC1 - MFC3 indicate mass flow controllers.

Fig. 4 Correlation between particle counts by laser particle counter and sodium amounts trapped by metal impurity sampling methods: ●, bubbling; □, filtration with polycarbonate filter; ▲, filtration with PTFE filter.

Results and Discussion

Comparison of the sampling efficiency between filtration and bubbling

Figure 4 shows the comparison of the results of the three sampling devices. Since the flow rates through the three devices and the particle counter were different, the results were all normalized to 1 l min⁻¹ for comparison.

The Na amounts collected by the three sampling methods were proportional to the total particle number measured by the LPC (Fig. 4). When we assume that all the particles are spherical with the bulk NaCl density, the Na amount calculated from the total particle number is three orders of magnitude smaller than the Na amounts determined by indirect metal analysis methods in all the cases. This discrepancy might have been due to the mean diameter of the generated NaCl particles being smaller than the minimum detectable diameter of the LPC. Therefore, the particle counter was used mainly to monitor the stability of size distribution and the number of the particles from the particle generator. The generated particle concentration ($>0.2 \mu\text{m}$) was

typically in the level of 10^6 particles l^{-1} . The distributions of the size and the number of the particles were stable throughout the sampling.

In six out of seven experiments, the Na amount trapped by the impinger was larger than the amounts trapped by the two filters. This indicates that the recovery of filtration might be lower than that of the impinger method. This can be due to penetration of a part of the particles through the filter membrane or by some reproducibility problem of wash out of the particles from the membrane. Those two factors may contribute to the uncertainty of the results by filtration.

The Na amount trapped by the PC filter is larger than that by the PTFE filter in five experiments. One of the reasons may be a difference in the recovery ratio of the particles from hydrophobic membrane (PTFE) compared with hydrophilic one (PC) with ultrasonic DI water washing.

The Na amounts obtained by filtration using PTFE or PC sampling filters and by impinger methods showed deviations from 10% to 50% of the averages. The differences among the results of the three methods were smaller than these deviations.

Direct analysis of NaCl particles in Ar gas by ICP-MS

Analytical results by indirect methods often may not reflect actual gas purity, due to the uncertainty of sample preparation and reagent blank. In addition, these methods require long sampling time to achieve low wt.ppt of detection limit, the level which is demanded in the present electronics field. Direct analysis of metal impurity in gases by ICP-MS has advantages because it needs no sample pretreatment, and can allow real time monitoring of impurities in gases.

In order to examine the capability of direct analysis of particles in gases by ICP-MS, and compare with indirect methods, the Ar stream with NaCl particles was directly introduced into the plasma of ICP-MS, and Na signal intensity was determined. The particles were diluted by

Fig. 5 Correlation between particle counts by condensation nucleus counter and sodium peak intensity by ICP-MS.

Ar gas (Fig. 3) with dilution factors of about 800, 400, 270 and 200. The dilution was necessary to avoid signal saturation. Both CNC and a LPC were used in parallel with ICP-MS to detect particles in the stream. The particle counts were changed when the flow from the particle generator was diluted by the above factors (Fig. 3).

The signal intensity of Na peaks after background subtraction and the particle counts by CNC showed a correlation (Fig. 5). LPC could not detect a sufficient number of particles within 10 min when the dilution factor was >200 . This also indicated that the majority of the generated particles are smaller than the detectable size of LPC. The scanned profile of the Na signal appeared as a main ordinary peak like that obtained in solution analysis with many superimposed spike signals (Fig. 6). These spikes may correspond to the particles entering into the ICP-MS torch during the mass scanning.

The previous experiment by the impinger method

Fig. 6 Peak profiles of sodium chloride particles with direct analysis of argon gas by ICP-MS, peak profiles at 153 counts l^{-1} (left) and 1630 counts l^{-1} (right) by a condensation nucleus counter.

determined that $3.3 \mu\text{g l}^{-1}$ of Na was introduced when the particle concentration of $1.4 \times 10^6 \text{ l}^{-1}$ ($>0.2 \mu\text{m}$) was obtained by LPC. When the dilution factors were 200 and 130, particle concentrations ($>0.2 \mu\text{m}$) by LPC were 330 and 820 l^{-1} , respectively. These corresponded to 0.8 and 1.9 ng l^{-1} of Na in this experimental condition. Pg l^{-1} order of detection limits by 1 min signal accumulation can be expected for ICP-MS from the observed signal intensity and 3σ of background signal. Determination of metal impurity at this level within 1 min is difficult to achieve reliably with indirect methods.

These results indicate two advantageous aspects of the direct analysis of metallic impurities in gases by ICP-MS: high sensitivity and real-time elemental monitoring. These advantages are very attractive, especially for the analysis of high purity semiconductor process gases, because the required purity levels and particle size control.

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