Quick External Leakage Inspection Method for Gas Supplying System in Semiconductor Facility Using Atmospheric Pressure Ionization Mass Spectrometer

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Semiconductor fabrication field requires screening technology, for external air leakage inspection in a clean room gas delivery system which can inspect all inspection points in one gas line in one process. Recent advances in welding technology have meant that the occurrence of a leak at welding point is now extremely uncommon. Inspection costs of a gas delivery system can therefore be decreased by applying such a screening process. The detection sensitivity required for screening of the air component is ppt level or below.

The atmospheric pressure ionization mass spectrometer (APIMS) was applied to the screening process using the argon carrier gas. Trace nitrogen which previously could not be detected by the APIMS, could be detected by mixing hydrogen in the argon gas. The detection sensitivity was increased over 100 times compared to the oxygen detection since there is a large amount of nitrogen in air and the proton transfer reaction for nitrogen ionization having a larger rate constant than the charge transfer reaction for oxygen ionization. N_2H^+ intensity shows a sudden increase with H_2 concentration because the rate constant, in the rate-determining step for N_2H^+ formation in higher H_2 concentrations, is larger than that in the lower H_2 concentrations. The optimum H_2 concentration is 3–10% for obtaining the higher sensitivity.

It is expected that the application of APIMS technique will greatly reduce the costs associated with the leak inspection.

1. Introduction

Since the presence of trace gaseous impurities has been shown to degrade device performance and reduce device yield,¹⁾ advanced integrated circuit technology requires high-purity levels of gases (total impurity concentration below 1 ppb) used in the fabrication of the sub-micron devices. To obtain such highly purified gases at use points, it is essential to remove the air leakage into the gas supplying system.

In general, an external leakage has been inspected using a helium leak detector, with a sensitivity of 10^{-11} atm·cc/s level corresponding to 1 ppt of impurity level.²⁾ However, the inspection using the helium leak detector is a highly expensive process. For the high sensitive detection of a small leakage using a helium leak detector, the points to be inspected are covered with a bag filled with helium gas. Furthermore, a high vacuum must be established inside the gas line. This operation is extremely

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cumbersome and time-consuming. In a clean-room, many gas lines are over 50 m in length and each gas line has many points which must be inspected; that is, welding points and connectors in pipes, valves, pressure regulators, mass flow controllers and purifiers.^{3), 4)} To carry out inspection of these great number of points in a clean-room is an extremely expensive process.

The number of leak points and leak volume has been decreased to a great extent by the development of leakage-free connectors⁴⁾ and the advanced welding technology.⁵⁾ However, inspection must still be carried out for all welding points and connectors in the gas lines, since it is difficult to completely eliminate the external leakage due to scratches caused by particles rolled into the sealing surface of a connector or human error in welding.

If the inspection can be carried out in two steps as described below, it would become extremely economical. Firstly, the gas line having the external leakage is screened by inspecting all points in one gas line in a lump sum. Secondly, the leak point is determined by inspections for all points in the gas line screened. Since most gas lines have no external leakage, the number of check points can be decreased by the screening. Screening can be achieved by detecting air leaked into the gas line.

For screening, although using a mass spectrometer with an electron impact ion source (EIMS) is one possibility, the use of an atmospheric pressure ionization mass spectrometer (APIMS) is preferred from reasons of common use in the gas purity evaluation in the semiconductor fabrication⁶⁾⁻¹⁴⁾ and of a low EIMS sensitivity.

For the detection of air with the APIMS, the use of argon, a common carrier gas in a clean-room, is adequate to distinguish the air component, such as nitrogen or oxygen. However, the detection sensitivity for oxygen in argon gas may be low¹⁵⁾ due to the slow reaction of Ar_2^+ with O_2 ¹⁶⁾ and the smaller content of oxygen in air compared to nitrogen. Previously, trace nitrogen could not be detected in argon gas due to the almost equal ionization potentials of argon and nitrogen. However, nitrogen can be effectively detected by mixing hydrogen gas using a proton transfer reaction between ArH^+ or H_3^+ and N_2 which has large rate-constant.¹⁶⁾ Due to the larger component of N_2 in air, the increase of the detection sensitivity for a small external leakage can be expected.

This paper describes how the APIMS can be successfully applied to the inspection of external leakage by detecting nitrogen using the large rate-constant proton transfer reaction.

2. Experimental

Figure 1 illustrates a schematic diagram of the apparatus for the experiment. It consists of a gas supply system, an APIMS and a helium leak detector.

The APIMS used was a single quadrupole mass spectrometer, covering 1–360 daltons (Hitachi Tokyo Electronics, UG240-P). It consists of an ionization chamber operated at atmospheric pressure, a differential pumping region at 10 Pa, where cluster ions are dissociated by the collision-induced dissociation method, and an analyzing region at 10^{-4} Pa. Primarily, ions are produced by corona discharge with a needle electrode. The discharge current was 1 μA . The distance between the needle electrode and the first aperture electrode was 4 mm. The ion source temperature was kept at

Fig. 1. Schematic diagram of the apparatus.

120°C. The drift voltage applied between the first and second aperture electrode was fixed at 30 V, providing maximum total ion current to the collector.

SUS316L-EP (electropolished) pipe (O.D. 1/4") was used throughout the piping system. A connector with an external leak was installed in the gas supply system. To assess the relationship between the leak volume and the ion intensity, the leak volume was changed using seven connectors. The connectors were leak-free MCG fittings (leak volume below the detection limit of 2×10^{-11} atm·cc/s with a helium leak detector)²⁾ from Toyoko Kagaku Co., Ltd., and were prepared by scratching with a micro-needle. The helium leak volume for the seven connectors were 7×10^{-6} , 4×10^{-6} , 4×10^{-7} , 2×10^{-7} , 4×10^{-8} , 8×10^{-9} , and 4×10^{-10} atm·cc/s, respectively. The leak volumes were evaluated using the helium leak detector installed in the gas supply system. The pressure in the gas supply system was 10^{-4} Pa, with helium leak detector installed. The leak volume for air, with the carrier gas flowing, was calculated from a calibration curve¹³⁾ for oxygen or nitrogen concentration in the carrier gas. The pressure in the gas supply system with the carrier gas flowing was 1.01 kg/cm².

To detect oxygen, argon carrier gas was supplied into the supply system. The argon gas flow rate was controlled by a mass flow controller. Oxygen included in the argon gas through the leaking connector, was detected by the APIMS. Since oxygen ion intensity is influenced by water, water was removed by an alloy getter type purifier from Saes Getters Co., Ltd. and a molecular sieve trap.

To detect nitrogen in the form of N_2H^+ , an argon carrier gas with hydrogen was supplied into the gas supply system. The hydrogen concentration in the mixed carrier gas was changed by controlling argon and hydrogen flow rates using mass flow controllers, to determine the optimum hydrogen concentration for high sensitivity. N_2H^+ intensity is also influenced by the coexisting water.¹⁴⁾ Thus water was removed using the purifier and a molecular sieve trap.

3. Results and Discussion

3.1 Detection of oxygen

For detection of oxygen in the extremely trace-level air leaked in the piping system from the atmosphere, oxygen concentration in the argon carrier gas must be controlled

Fig. 2 The APIMS spectra for argon gas at flow rate of 1 L/min: (a) background, (b) argon gas passed through a connector with a leak rate of 4×10^{-7} atm·cc/s.

Fig. 3. O_2 intensity vs. the leak rate.

to trace-levels as oxygen concentration determines the detection limit. Figure 2(a) illustrates the APIMS mass spectrum for highly purified argon gas. Major ions as Ar^+ at m/z 40 and Ar_2^+ at m/z 80 and ultra-trace ions as H_2O^+ at m/z 18, O_2^+ at m/z 32, and CO_2^+ at m/z 44, are observed. The concentration of water, oxygen and carbon dioxide are estimated to be 200, 12, and 20 ppt, respectively, from the calibration curve for each component.^{13), 15)} The extremely low concentrations of these components are attributed to the use of highly purified argon gas supplied from a clean room high grade argon gas line, and purification by the alloy getter. In the detection of oxygen for external leakage inspection, the oxygen background concentration of 12 ppt, that is 1.2×10^{-12} A, corresponds to the detection limit.

Figure 2(b) gives a spectrum obtained for argon carrier gas flowing through the piping system with the 4×10^{-7} atm·cc/s leak rate connector installed. The flow rate of the carrier gas is 1 L/min. Peaks for water and oxygen are higher than those in Fig. 2(a). This result indicates that atmospheric air leaks into the gas through the small scratch when the gas flows in the narrow pipe, even when inside pressure of the pipe is at atmospheric pressure. The air leak rate calculated from the oxygen concentration in Fig. 2(b) is about 8×10^{-9} atm·cc/s. Converting this value to the helium leak rate, the value is one-tenth of the value obtained using the helium leak detector. The difference in the leak rate is caused by the difference in the internal pressure of the pipe, *i.e.*, the low pressure (10^{-4} Pa) when using the helium leak detector and the atmospheric

pressure when using the argon carrier gas. It appears that the ratio 1/10 is large, concerning the large pressure difference. External leakage is caused by the back diffusion and the aspiration (*i.e.*, suck-in of air due to the Bernoulli's theorem) when gas flows at a high speed through the pipe having a small aperture. If external leakage by the back diffusion is the main reason, the leak rate for the argon carrier gas may be smaller. It seems, therefore, that the air is aspirated into the pipe by gas flowing under the conditions in this experiment.

Figure 3 illustrates the relationship between leak rate for the helium leak detector and the ion intensity detected by the APIMS under the condition of 1 L/min argon gas flow rate. The ion intensity of oxygen in the argon gas is given by the equation¹⁷⁾

$$I = a(1 - e^{-kbt}), \quad (1)$$

where I is oxygen ion intensity; a is constant; k is rate constant when O_2^+ is produced from Ar_2^+ ; b is oxygen concentration, and t is reaction time. In Eq. (1), the ion intensity is approximately proportional to concentration, when b is less than 100 ppb. Thus the ion intensity is proportional to the leak rate of the air in this concentration range. In Fig. 3, however, the ion intensity is not completely proportional to the leak rate for the helium leak detector. This result indicates that the aspiration effect increases with decreases in aperture size of the leakage.

In Fig. 2(a), the detection limit was determined to be 1.2×10^{-12} A oxygen ion intensity. The signal to noise ratio (S/N) for this ion intensity is about 2. The detection limit can therefore be decreased by only 1.5×10^{-8} atm·cc/s, even if the background oxygen concentration in the argon gas is decreased. Although this detection limit is extremely high compared to 2×10^{-11} atm·cc/s for the helium leak detector,²⁾ this level of noise is to be expected in daily inspection. When carried out under laboratory conditions, however, the noise level for the APIMS has been reported at one-seventieth of that in this experiment.¹⁸⁾ However, the same precautionary measures are not applied on facility lines as in the laboratory, and therefore an easier method for decreasing the detection limit must be considered.

In APIMS, the oxygen ion in argon is produced by the following reactions¹⁶⁾:

where k is the rate constant for each reaction. Since the rate constant in reaction (4) is small, the detection sensitivity of oxygen in argon gas is low. Thus, if a reaction having a larger rate constant is applied to the detection of the air component, an increase in detection sensitivity is expected.

3.2 Detection of nitrogen

In order to increase the detection sensitivity of the air component, the detection of nitrogen was investigated. Since nitrogen and argon have the same ionization potential, trace nitrogen can not be ionized by a charge transfer reaction in the argon gas. However, nitrogen can be ionized by a proton transfer reaction when hydrogen is present in the carrier gas. An increase in detection sensitivity can then be expected

Fig. 4. The APIMS spectra for argon gas with 3% hydrogen content at flow rate of 1 L/min: (a) background, (b) gas passed through a connector with a leak rate of 4×10^{-7} atm·cc/s.

since air includes higher concentrations of nitrogen than oxygen, and the proton transfer reaction generally has a large rate constant (*i.e.*, collision rate).

Figures 4(a) and (b) illustrate the background spectrum for the argon carrier gas with 3% hydrogen and the spectrum when the carrier gas was passed through the connector with a leak rate of 4×10^{-7} atm·cc/s, respectively. In Fig. 4(a), nitrogen ion is not observed. However, in Fig. 4(b), N_2H^+ at m/z 29 is observed and the ion intensity is obviously stronger than the O_2^+ intensity in Fig. 2(b). These results indicate that the trace nitrogen can be detected with a high sensitivity by the presence of hydrogen.

The high sensitivity for nitrogen is due to the high rate reaction brought about by the presence of hydrogen. It appears that nitrogen is ionized by following reactions¹⁶⁾:

$$k = 8 \times 10^{-10} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1} \quad (13)$$

$$k = 2 \times 10^{-9} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}. \quad (14)$$

The complex ionization process is shown in Fig. 5. As can be seen in Fig. 5, N_2H^+ is produced from ArH^+ and H_3^+ . These reactions have large rate constants.

Figure 6 illustrates the total ion and N_2H^+ intensity changes with hydrogen concentration. N_2H^+ intensity increases with hydrogen concentration, and maximum sensitivity is obtained around 10% hydrogen concentration.

Figure 6 indicates that the increase of N_2H^+ intensity is due not only to the increase in total intensity. This can be seen through the sudden increase of the N_2H^+ intensity with the increase of the hydrogen concentration. This effect is not observed for total ion intensity. It appears that the N_2H^+ production process changes with changes in hydrogen concentration. Figure 7 illustrates the calculated and experimental ion intensity changes for ArH^+ and H_3^+ with hydrogen concentration. The experimental data is approximately fits the calculated curve. As can be seen in Fig. 7, H_3^+ intensity increases with hydrogen concentration, and its relative intensity is over 90% at 10% hydrogen concentration. This result indicates that N_2H^+ is mainly produced from H_3^+ in the high hydrogen concentration, (*i.e.*, reaction (14') in Fig. 5), and from ArH^+ in low hydrogen concentration, (*i.e.*, reaction (13') in Fig. 5). The rate-determining step occurring before reaching reaction (14') is reaction (12), and for reaction (13') is reaction (10). Reaction (12) has a larger rate constant than reaction (10). Therefore, the sudden increase of the

Fig. 5. The ionization sequence for the production of N_2H^+ .

Fig. 6. The ion intensity changes with hydrogen concentration.

Fig. 7. The calculated and experimental ArH^+ and H_3^+ intensity changes with hydrogen concentration.

Fig. 8. N_2H^+ intensity change with the carrier gas flow rate (carrier gas: argon with 0.1% hydrogen content).

Fig. 9. N_2H^+ intensity change with the leak rate.

N_2H^+ intensity is observed with the increase of the hydrogen concentration.

H_3^+ does not appear to be produced from Ar_2H^+ . Ar_2H^+ is observed, even at 3% hydrogen concentration as shown in Fig. 4. With the APIMS, for impurity concentrations over 100 ppm, the impurity ion intensity is almost 100%.¹³⁾ The proton affinity of argon may be increased by the clustering.

To increase the detection sensitivity for the external leakage, the effect caused by decreasing the carrier gas flow rate below the standard APIMS rate of 1 L/min^{6)~14)} was also investigated. Figure 8 illustrates N_2H^+ intensity change with the carrier gas flow

rate. N_2H^+ intensity increases with decreasing the flow rate, thus indicating that air concentration is increased by decreasing the flow rate. Figure 9 illustrates the relationship between the leak rate and the N_2H^+ intensity under the condition of 200 cc/min flow rate. The argon carrier gas includes 3% hydrogen. The detection limit was estimated to be 5×10^{-11} atm·cc/s, which is approximately equal to the detection limit for the helium leak detector.

4. Conclusions

The detection limit for the external leakage of the air could be decreased to 5×10^{-11} atm·cc/s by the detection of nitrogen using the high-rate reactions by mixing hydrogen with argon carrier gas. The detection limit corresponds to 1 ppt or below for an air leak in a clean room gas line. APIMS technique investigated in this paper can therefore be usefully applied to the external leakage inspection.

Gas line construction cost for a clean room is generally about 3 billion yen, and external leakage inspection cost is about 0.3 billion yen. Since the number of the inspections can be decreased by 1/10 using APIMS technique for screening, external leakage inspection cost may be decreased by 1/2. Semiconductor manufacturers generally have over 30 clean rooms and the life span of one gas line is about 10 years. Thus a manufacturer may invest close to 1 billion yen/year in inspection cost alone. Applications of APIMS technique to the external leakage inspections may save 0.5 billion yen/year.

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