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Impurity Measurement in Specialty Gases Using Atmospheric Pressure Ionization Mass Spectrometer with Two Compartments Ion Source

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1. Introduction

Highly purified specialty gases are required for semiconductor manufacturing. The conventional atmospheric pressure ionization mass spectrometer(APIMS) is able to detect in bulk gases such as nitrogen(N_2) and argon(Ar) in part per billion(ppb) order[1,2]. But impurities measurement technology for ensuring a detection sensitivity of a ppb has not been developed in specialty gases. We have newly established a technology for measuring impurities in specialty gases using APIMS with two compartments ion source with detection limit around 0.1 to 1 ppb[3].

2. Experiment

Fig.1 shows schematic diagram of APIMS with two compartments ion source. Ar gas and specialty gas are introduced to the first and second ionization compartments, respectively. Ar⁺ ion generated by corona discharge in the first ionization compartment is sent out to the second ionization compartment. Ar+ ion reacts with specialty gases including impurities of unknown concentration to exchange ion, because ionization energy is larger than specialty gases such as methane(CH₄), monosilane(SiH₄), and germane(GeH₄). Impurity ions are generated in it, too. Fig.2 shows ion-molecule reaction model in two compartments ion source.

Fig.3 shows experimental flow. Using this system, we have obtained impurity calibration curve in specialty gases. Moreover, we have examined adsorbing property of disiloxane(SiH₃-O-SiH₃), by flowing SiH₄ from the upstream of the stainless steel tube.

3. Results and Discussion

Fig.4 shows spectrum of SiH₄ gas measured by APIMS. The vertical axis shows relative ion intensity, horizontal axis shows mass number. In the spectrum of SiH₄ gas, it has been defined that moisture(H₂O) is observed with mass numbers of 49,67 and 81 and SiH₃-O-SiH₃ is observed with mass numbers of 77 and 109 experimentally. But in SiH₄ cylinder in the market available, H₂O cannot exist as a H₂O molecule. Because H₂O reacts with SiH₄ and SiH₃-O-SiH₃ in order to obtain the SiH₃-O-SiH₃ calibration curve, SiH₄ gas and H₂O gas was made to react completely in the reactor to produce SiH₃-O-SiH₃ gas as follow reaction(equal(1)).

 $2SiH_4 + H_2O \rightarrow SiH_3 - O-SiH_3 + 2H_2$

Formula(1) indicates that the H_2O volume introduced in the reactor and generated SiH_3 -O-SiH₃ volume are in the

proportion of one to one. Therefore, additional H_2O was regarded as SiH₃-O-SiH₃ concentration and a SiH₃-O-SiH₃ calibration curve was obtained from the relationship between additional H_2O and SiH₃-O-SiH₃ ion intensity measured by APIMS. Fig.5 shows SiH₃-O-SiH₃ calibration curve by using reaction SiH₄ and H₂O. It is obvious that total SiH₃-O-SiH₃ ion intensity is proportional to adsorbed H₂O less than 5x10⁻⁹mol. In the case of more than 5x10⁻⁹mol, generated amount of SiH₃-O-SiH₃ is exceeds upper limit of APIMS, so SiH₃-O-SiH₃ ion intensity is detected lower than actual generation rate. From this calibration curve, 150ppb concentration of SiH₃-O-SiH₃ was included in this SiH₄ cylinder,

Using this SiH₄ cylinder, SiH₃-O-SiH₃ adsorption was investigated to flow SiH4 gas through electro-polish stainless steel(SUS316L-EP) tube from upstream at 25°C. The diameter of the tube is 1/4 of an inch and the length is 2 meter. Fig.6 shows time dependence of SiH₄ and ion intensity measured SiH₃-O-SiH₃ by APIMS. SiH₂-O-SiH₂ is detected 9 minutes later, after SiH₄ gas is detected. This means that SiH₃-O-SiH₃ adsorbs onto inner surface of stainless tube. Since SiH₄ flow rate, SiH₃-O-SiH₃ concentration and surface area of tube are known, adsorbed amount of SiH₃-O-SiH₃ molecules per unit area is obtained. Equilibrium adsorbed amount for 150ppb SiH₃-O-SiH₃ in SiH₄ to the SUS316L-EP tube was 7.3x10¹²molecules/cm². Thus, SiH₃-O-SiH₃ has strong adsorption, it is worried to become a factor of the oxygen defect in film decomposition.

Fig.7a shows a spectrum of GeH₄ gas from a cylinder while Fig.7b shows a spectrum of purified GeH₄ gas measured by APIMS. Main peak of mass number 77 and 153 are correspond to GeH₅⁺ and GeH₄·GeH₅⁺ respectively. When comparing Fig.7a and 7b, it is found that ion intensity of peaks with mass number of 95, 114, gets higher in the spectrum in Fig.7a. These mass numbers are H₂O-related peak clustered with GeH₄, because these get higher with H₂O injection into purified GeH₄ gas. We have clarified that H₂O concentration in GeH₄ from cylinder is 2000ppb and purified GeH₄ is less than 1ppb from H₂O calibration curve. Another mass number is not detected. Thus, main impurity in GeH₄ is H₂O. Similar results is obtained in CH₄ gas(Fig.8). Main impurity in CH₄ is also H₂O and smaller ethane.

4. Conclusions

By using APIMS with two compartments ion source, we clarified impurities in specialty gases at 0.1 to 1 ppb order.

(1)

Main impurity is SiH_3 -O-SiH₃ in SiH₄ and H₂O in CH₄, GeH₄. Moreover, we have clarified that SiH₃-O-SiH₃ has the strong adsorption.

References

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Fig.1 Schematic of APIMS.



Fig.2 Schematic diagram of ion-molecule reaction.



experimental system.









Fig.5 Calibration curve between integrated SiH₃·O·SiH₃

ion intensity and amount of adsorbed H₂O.



Fig.6 Time dependence of SiH4 and SiH3-O-SiH3 ion intensity.



Fig.8 Mass spectrum of CH4 gas.