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The use of proton-transfer reactions to detect low levels of impurities in bulk oxygen using an atmospheric pressure ionization mass spectrometer

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Abstract

Atmospheric pressure ionization mass spectrometry (APIMS) is being routinely used to quantify trace impurities in bulk gases used in the manufacture of semiconductor devices. APIMS has been successfully applied for the quantification of ppt levels of O_2, H_2O, CO_2, and CH_4 in Ar, N_2, and He. However, it has not been successfully used to quantify trace impurities in bulk O_2 because of the low ionization potential of O_2. APIMS relies on charge-transfer reaction between the ions of the bulk gas molecules and impurity molecules. As all the relevant impurity molecules have ionization potentials higher than that of O_2, APIMS has not been used to analyze for impurities in O_2. A recent publication describes the use of a clustering reaction, as opposed to a charge-transfer reaction, to detect trace levels of H_2O in bulk O_2. Clustering reactions have not been successfully used to detect CO_2, N_2, and CH_4 in bulk O_2 because the relevant cluster ions are very weak and are declustered in the low-pressure declustering region normally used in an APIMS. O_2 has a relatively low proton affinity, and protonated oxygen is expected to undergo proton transfer reactions with CO_2, N_2, and CH_4. We report the use of H_2, as a doping gas, in the source of an APIMS to facilitate the protonation of trace impurities in O_2. For safety considerations, a buffer gas like He or Ar has to be added to keep the concentration of H_2 below the lower explosion limit (LEL). Our results indicate a statistical limit of detection of 0.5 ppb for CH_4, 0.3 ppb for CO_2, and 1.2 ppb for N_2. (Int J Mass Spectrom 206 (2001) 7–12) © 2001 Elsevier Science B.V.

1. Introduction

Atmospheric pressure ionization mass spectrometry (APIMS) is being routinely used to quantify sub-ppb level impurities in inert gases being used in semiconductor processing. This technique is capable of achieving detection limits in the ppt range for O_2, H_2O, CH_4, and CO_2 in H_2, N_2, Ar, and He [1]. In the ionization source of an APIMS, a corona discharge operating at atmospheric pressure is used to create the primary ions of the gas being sampled. At such a high pressure, the mean free path is small and ion molecule reactions play a key role in ionizing the trace impurity atoms/molecules present in the sample gas. For impurities that can undergo fast charge-transfer reactions (rates of the order of 10^{-9} cm^3/sec) with the sample gas ions, APIMS can be used very effectively. This includes O_2, H_2O, CH_4, and CO_2 in bulk N_2, Ar, and He. If the sample gas is H_2, proton transfer reactions play a key role in the secondary ionization mechanism. In this case, the primary ion is H_3^+, and impurity

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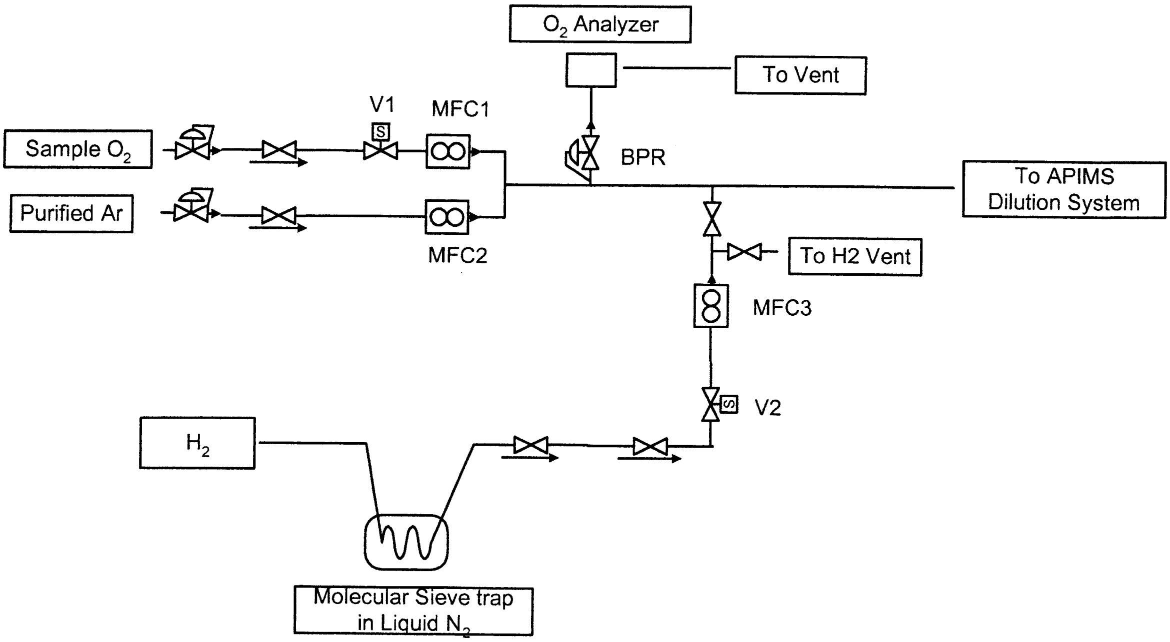

Fig. 1. Schematic of the gas inlet system. BPR, back pressure regulator; V1 and V2 are pneumatically actuated valves. A low-flow alarm on O_2 or a high-flow alarm on H_2 or a high O_2 concentration alarm will shut off V1 and V2.

molecules that can undergo fast proton transfer reactions can be detected as the protonated ion. Impurities that can be detected include N_2, H_2O, CO_2, and CO in H_2. APIMS has not been successfully used to analyze for trace impurities in bulk O_2 because of the fact that O_2 has a fairly low ionization potential, and consequently, O_2^+ cannot undergo charge transfer reactions with impurities of interest to the semiconductor industry. A recent publication reports the use of a clustering reaction to determine ppt levels of H_2O in O_2 [2]. Although N_2, CO_2, and CH_4 will also undergo clustering reactions with O_2^+ and O_4^+, these clusters are very weakly bound and, consequently, have not been successfully used to determine these impurities in O_2.

Oxygen has a very low proton affinity (100.9 kcal/mol), and the protonated oxygen molecule (O_2H^+) will undergo proton transfer reactions with impurity molecules with higher proton affinity. N_2 (118.2 kcal/mol), CO_2 (130.9 kcal/mol), CH_4 (132 kcal/mol), and H_2O (166.5 kcal/mol) will successfully undergo a proton-transfer reaction with protonated oxygen (O_2H^+) [3]. We report here the use of proton-transfer reactions to detect low levels of CH_4, CO_2, and N_2 in O_2 by using hydrogen as a dopant to facilitate such reactions.

2. Experimental

A VG APIMS coupled to an Air Products dilution system was used for the experiments. The APIMS uses a single quadrupole mass spectrometer coupled to a corona discharge source operating at atmospheric pressure. The dilution system uses dynamic dilution and is capable of generating dilution ratios as high as 10000 : 1 [4]. Hydrogen and oxygen will form an explosive mixture and, to keep the hydrogen concentration below the lower explosion limit (LEL), an inert gas like Ar or He was used as a buffer gas. Fig. 1 shows a schematic of the inlet system used to introduce the sample gas (O_2), the dopant gas (H_2), and the buffer gas (Ar or He) into the source of the APIMS. Hydrogen was purified using a molecular

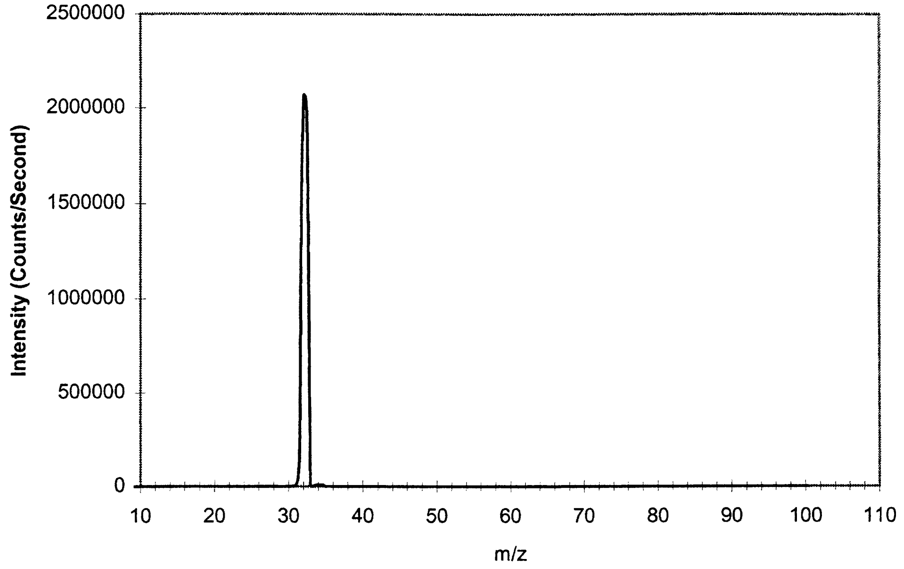

Figure 2(a)

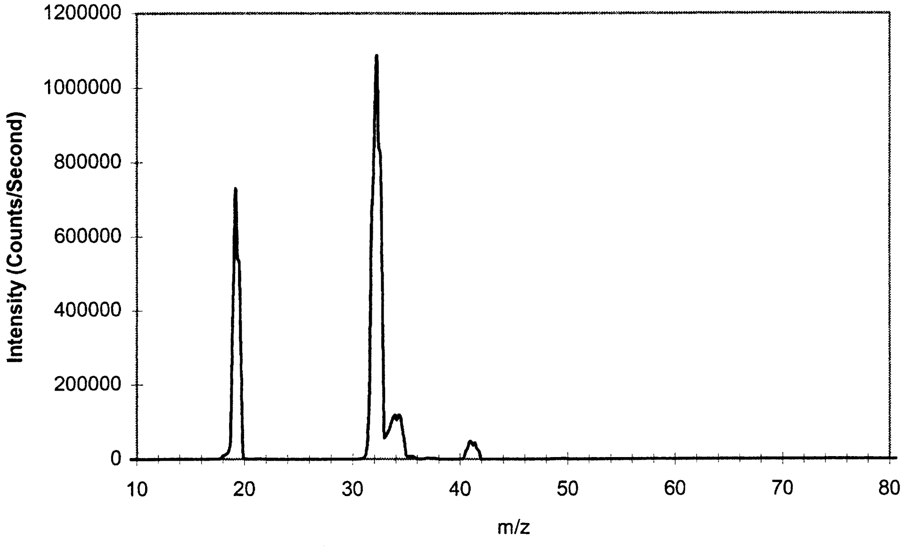

Figure 2(b)

Fig. 2. (*a*) Spectrum of 15% O_2 in purified Ar, (*b*) Spectrum of 0.17% H_2, 13% O_2 in Ar.

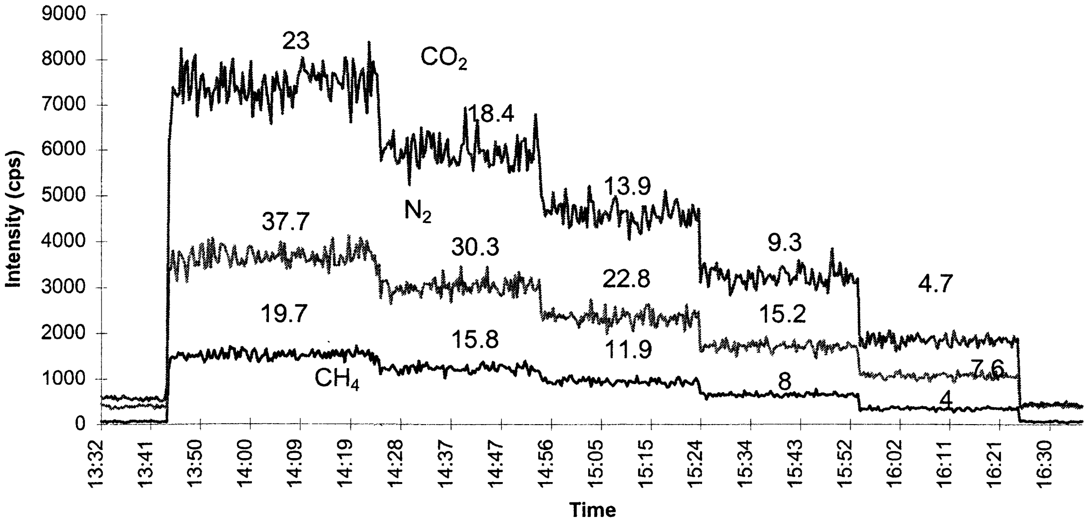

Fig. 3. Change in the intensities at m/z = 45 (CO_2H^+), m/z = 17 (CH_4H^+), and m/z = 29 (N_2H^+) as a function of the change in the concentrations of CO_2, CH_4, and N_2. The numbers indicate the concentration, in ppb, of the respective impurities.

sieve trap operating at liquid nitrogen temperatures, whereas the argon was purified using a heated getter purifier. Double-check valves were used to prevent O_2 from back diffusing into either the heated getter purifier or the molecular sieve trap. Safety features were incorporated into the system to automatically shut down the flow of O_2 and H_2 in case the O_2 concentration exceeded 20% or the H_2 concentration exceeded 4% of the total flow.

3. Results and discussion

Fig. 2a shows the APIMS spectrum of a mixture of 13% purified O_2 in purified Ar. The only peak visible is the O_2^+ peak at $m/z = 32$. As soon as the H_2 was added to this mixture, the peak at $m/z = 19$ (H_3O^+) appeared, indicating that H_2O is being produced in the source of the APIMS from a reaction of H_2 and O_2. Fig. 2b shows the APIMS spectrum of a mixture of

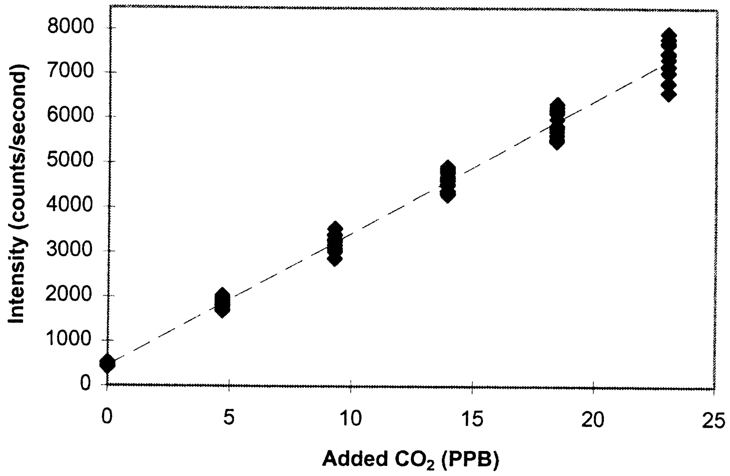

Fig. 4. Calibration curve for CO_2 at m/z = 45 (CO_2H^+).

Table 1
Calibration parameters using weighted least-squares analysis

Impurity	Intercept cps	Slope cps/ppb	LOD ppb
CO_2	457	298	0.3
N_2	413	86	1.2
CH_4	67	73	0.5

0.17% H_2, 13% O_2 in purified Ar. The major peak is still O_2^+ at $m/z = 32$. In addition to the peak at $m/z = 19$, there is a peak at $m/z = 41$ (ArH^+) and a peak at $m/z = 34$. Although there is an O_2 isotope ($^{16}O^{18}O^+$) at $m/z = 34$, it can not account for the intensity of the observed peak. The following reactions can occur in the ionization source to produce the observed peaks:

$$Ar + e^- \rightarrow Ar^+ + 2e^-,$$

$$Ar^+ + Ar + Ar \rightarrow Ar_2^+ + Ar,$$

$$Ar_2^- + O_2 \rightarrow O_2^+ + 2Ar,$$

$$Ar_2^+ + H_2 \rightarrow ArH^+ + H,$$

$$ArH^+ + H_2 \rightarrow H_3^+ + Ar,$$

$$O_2 + H + H \rightarrow HO_2,$$

$$H_3^+ + HO_2 \rightarrow H_2O_2^+ + Ar,$$

$$ArH^+ + H_2O \rightarrow H_3O^+ + Ar.$$

The peak at $m/z = 3$ (H_3^+) is not shown in the spectrum because of the inability of the mass spectrometer to resolve the peak at $m/z = 3$ from the on blast. In spite of the presence of a large peak at $m/z = 19$ (H_3O^+), the ArH^+ peak is still present. As ArH^+ can easily undergo proton transfer reaction with H_2, H_3^+ should also be present in the ionization source. Thus, proton transfer reactions should play a key role in ionizing impurities present in the source. Fig. 3 shows the change in the intensities at $m/z = 45$ (CO_2H^+), $m/z = 17$ (CH_4H^+), and $m/z = 29$ (N_2H^+) as a function of the change in the concentrations of CO_2, CH_4, and N_2.

Fig. 4 shows the calibration curve for CO_2. As can be seen from this figure, the variance increases with increasing concentration, indicating that a weighted linear model, with a weight inversely proportional to the variance, is the appropriate calibration model. Table 1 shows the statistical parameters obtained, using a weighted linear model, for the detection of CO_2, N_2, and CH_4 in O_2.

The statistical limit of detection is <1 ppb for CH_4 and CO_2 and slightly >1 ppb for N_2. To ascertain that the statistically derived LODs (based on a weighted linear model) were meaningful, low levels of CO_2

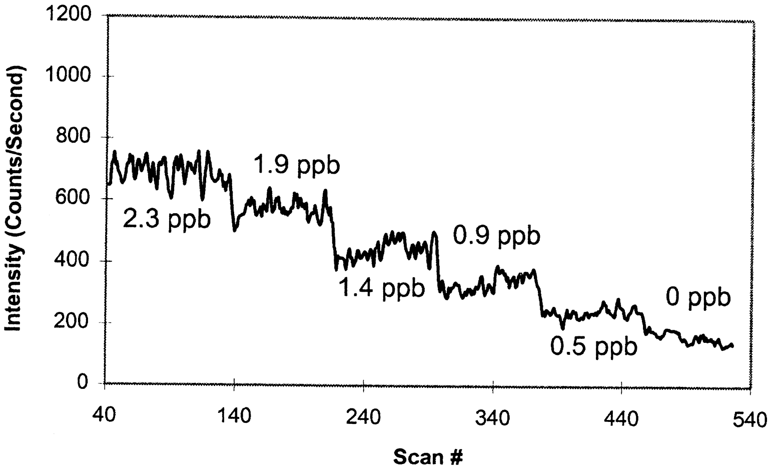

Fig. 5. Change in the response of the mass spectrometer at $m/z = 45$ (CO_2H^+) for changes of 0.4 ppb in the CO_2 concentration.

were added to the O_2 stream. Fig. 5 shows the response of the mass spectrometer at $m/z = 45$. As can be seen from the figure, changes in the CO_2 concentration of 0.4 ppb can be easily distinguished by the instrument.

4. Conclusion

This work shows that by adding small amounts of H_2 to a mixture of Ar and O_2, APIMS can be used to detect low levels of impurities in oxygen. Even though the presence of H_2 and O_2 in the discharge region produces H_2O, it is possible to detect low-level impurities using proton transfer reactions. We have also used He as the buffer gas to obtain similar performance. If the ionization and the reaction regions are separated, as reported by Irie et al. [5], it should be possible to avoid the production of H_2O. A mixture of Ar and H_2 can be used in the discharge region, whereas O_2 can be added to the interaction region. In such a scheme, it should also be possible to detect low levels of H_2O in O_2 at $m/z = 19$.

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