Measurement and Control of Trace Moisture in Corrosive Gases

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Abstract

Measurement and control of trace moisture in corrosive gases used in etch and other semiconductor manufacturing steps is important to minimize line corrosion, maintain process consistency and maximize device yields. A commercial cavity ring-down spectrometer (MTO-1000, Tiger Optics) specifically designed for corrosive gas analysis has been investigated for trace moisture detection in nitrogen, chlorine and hydrogen bromide with regards to accuracy, sensitivity, linearity, response time and durability. The instrument response to moisture level between 0 and 2 ppm were linear and the instrument equilibrated within 20 minutes to 90% of the final readings after concentration changes between ca.100 ppb and 3 ppm. The analyzer demonstrated good corrosion resistance over the test period and was capable of moisture detection at low ppb levels. The capability of a point-of-use purifier (Nanochem Metal-X) to remove moisture from both HBr and Cl_2 to <0.1 ppm was verified with the instrument.

Introduction

The presence of trace impurities such as moisture in process gases for semiconductor manufacturing is known to negatively affect device quality. Moisture not only causes corrosion in gas delivery systems that can lead to particle contamination and equipment failure, but also participates in wafer surface chemistry and thus leads to electrical defects and other undesirable side effects. Additionally, moisture concentrations from liquefied gas sources potentially are not stable throughout the lifetime of the source (1,2), and can cause process instabilities. These factors have resulted in a growing demand for more sensitive and reliable analytical instrumentation that is capable of measuring trace moisture in gas production and purification processes, as well as for on-line monitoring of gases supplied to process tools. Furthermore, efficient purifier materials are required for removal of trace moisture from gases at the point-of-use.

Various instrumental and sensor-based techniques for measurement of trace moisture in electronic specialty gases have recently been reviewed (3). Spectroscopic methods are widely accepted and also viewed as the most promising candidates for the next generation of real-time trace moisture analyzers for several reasons. Optical techniques are non-destructive and only require optical access to the reactive or corrosive gas. Further, they usually provide rapid response times, high sensitivity and selectivity and are suitable for on-line monitoring applications. Among these is cavity ring-down spectroscopy (CRDS), which has recently been adopted in commercial instrumentation. Reports of optimized sensitivity studies in the literature show that the CRDS analyzer, when used in inert gas service, is capable of sub-ppb moisture detection (4,5). CRDS studies in corrosive gases such as HCl with single-digit ppb level detection limits have also been reported (6).

In this work, the performance of a commercial CRDS analyzer (Tiger Optics MTO-1000) has been investigated for the analysis of moisture in chlorine and hydrogen bromide analysis. The accuracy, linearity, response time and durability of the instrument was measured. In addition, the performance of a point-of-use purifier for moisture removal to <100 ppb was verified using this instrument.

Operating Principles

CRDS is based on the absorption of IR radiation and has been explored for detection of moisture at sub-ppb to ppm levels (4-12). Figure 1 shows a schematic diagram of the main instrumental components and operating principles of the CRDS system. Some of the components in the commercial instrument tested in this work are shown in the photograph in Figure 2. The instrument operates by directing an IR laser beam into the ring-down cavity equipped with highly reflective mirrors that contains the sample gas. As the cavity fills with light, an increasing amount of the light leaks through the mirror into the photodiode detector. At a predetermined intensity of light reaching the detector, the laser beam is interrupted and the ring-down decay lifetime of the cavity is recorded. The moisture concentration in a sample gas is calculated from the following equation(4, 8):

$$N = (1/\tau(\nu) - 1/\tau_{empty}) / (c\,\sigma(\nu))$$

c is the speed of light, N is the molecular density of moisture, σ is the absorption cross section of water molecule in cm^2, $\tau(\nu)$ is the sample gas ring-down time, τ_{empty} is the ring-down time without moisture present, and ν is the laser light frequency. The effective path-length is of the order of kilometers, which results in high sensitivity.

The Tiger Optics CRDS analyzer is capable of scanning the spectrum between 1390-1395 nm by regulating the temperature of the laser diode. The two moisture lines that can be used for quantification in this range are at 1391.67 and 1392.54 nm, corresponding to a laser diode temperature of 21.15 and 29.64 °C, respectively. These lines arise from rotational transitions $(6,6,0 \leftarrow 6,6,1)$ and $(2,0,2 \leftarrow 3,0,3)$ in the $\nu1 + \nu3$ $(1,0,1 \leftarrow 0,0,0)$ vibrational

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band of water molecules (13, 14). As spectra take several hours to scan, they are not routinely measured. However, these data can be used to accurately confirm the moisture concentration and account for any matrix gas absorbance that may affect the moisture readings in normal operation.

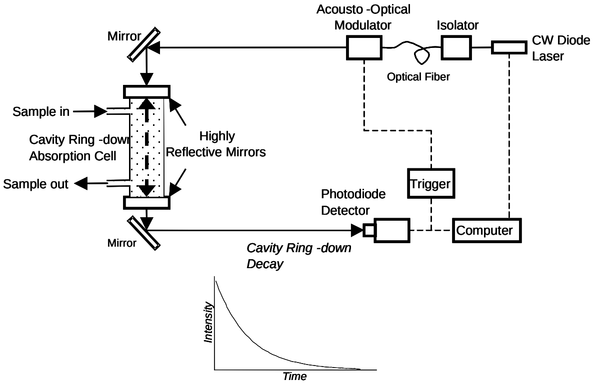

Figure 1. Schematic diagram of CRDS instrument.

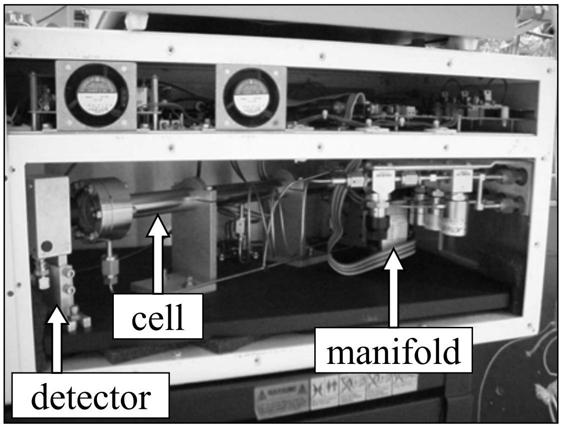

Figure 2. Internal view of the Tiger Optics MTO-1000 CRDS instrument.

For routine moisture analysis, the instrument monitors the ring-down time at 1392.53 nm at a predetermined interval. Prior to initiating a run, the ring-down time at 1391.3 nm corresponding to a laser temperature of 17.8 °C (where water does not absorb) is measured. This is used to calculate the baseline at 1392.53 nm. The baseline is employed as a reference against which total moisture measurements in the cavity are subsequently made. Because the ring-down is only dependant on the moisture present inside the gas cell, the measurements are unaffected by external humidity and purge of the optical bench as often used in FTIR is not necessary.

Figure 3 shows two spectra that were collected in Cl_2 and HBr matrix and that cover the two moisture lines at 1391.67 and 1392.53 nm at a concentration of 900 ppb and 2300 ppb respectively. The straight baseline of the Cl_2 spectrum indicates minimal interference from the matrix gas and single-point baseline correction is justified. The HBr spectrum showed a curved baseline in the H_2O spectral region that initially resulted in an offset of the readings. The data processing routines were modified to account for the baseline features.

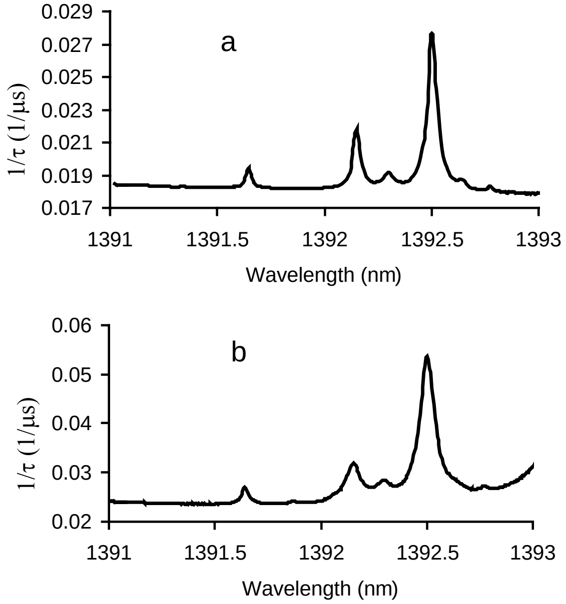

Figure 3. CRDS spectra showing moisture bands in (a) Cl_2 and (b) HBr matrices.

Experimental

The instrument used in this work (MTO 1000, Tiger Optics, Warrington, PA) had been in prior corrosive gas service but was certified to be in good working order by the manufacturer. A schematic of the manifold used for verifying the calibration of the CRDS instrument, gas sample analysis and purifier evaluation is shown in Figure 4. Calibrations were performed by adding nitrogen that was humidified with a moisture generator (Span Pac 261, Kin-Tek, LaMarque, TX) to the HBr or Cl_2 sample gas. The output from the moisture generator was verified using a chilled mirror hygrometer (CR-3, Buck Research, Boulder, CO). The addition of N_2 to the sample gases caused a baseline shift, and was compensated by a baseline-tune. Ring-down measurements were performed at a flow rate of 1 slpm and a cavity pressure of 4 psig.

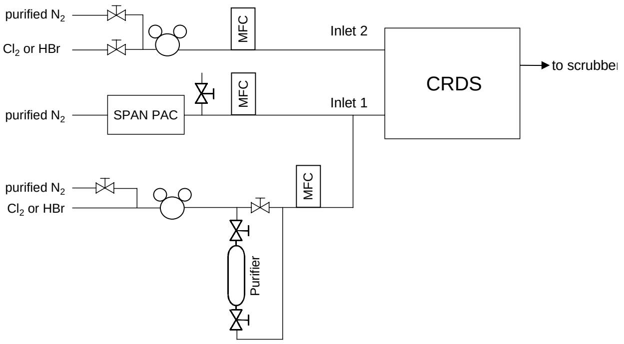

Figure 4. Schematic diagram of the CRDS sampling manifold.

Using the instrument, the moisture removal efficiency of a 500 ml Nanochem Metal-X purifier (Matheson Tri-Gas) was evaluated with moisture challenges of ~2.3 ppm in HBr and ~0.9 ppm in Cl_2 matrix at 40 psig and a flow rate of 1250 sccm. The purifier was also used to generate dry gas for the instrument testing.

Results

Instrument Response

Figure 5 shows a plot of instrument moisture reading versus actual moisture concentration in N_2 that was used to verify that the analyzer was calibrated correctly. The instrument moisture reading agreed well with the actual moisture concentration in the 0-2 ppm range investigated. The correlation coefficient was 0.9999. A 5.0 ppb regression based (weighted least squares) detection limit was calculated from the calibration data (15), which is approximately two to three times higher than the practical detection limit previously reported by Hardiman and coworkers (10). This is likely because the instrument had been exposed to corrosive environments prior to the tests and was not fully optimized for highest sensitivity in inert gases.

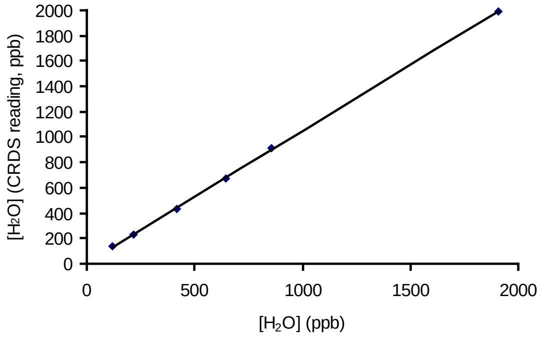

Figure 5. Plot of instrument moisture reading versus actual moisture concentration in N_2.

Figure 6a shows the moisture response of the CRDS instrument to different moisture levels with time in chlorine. The response curve generated from these data in Figure 6b was also linear with a correlation coefficient of 0.9998. However, in contrast to measurements in N_2, the instrument overestimated the actual moisture concentration by ~16% in Cl_2. This discrepancy is likely caused by spectral parameters such as broadening coefficients in the instrument software that were not optimized for moisture detection in Cl_2. A detection limit of 11.3 ppb using weighted least squares method was calculated from the data.

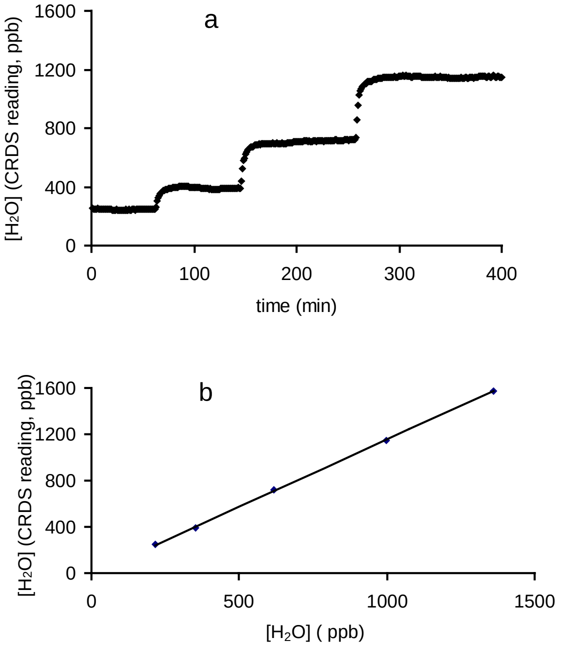

Figure 6. (a) Moisture response of the CRDS instrument with time during calibration of moisture in Cl_2, and (b) Plot of instrument moisture reading versus actual moisture concentration in Cl_2.

Cylinder Analysis

The MTO 1000 has been used to analyze moisture in several HBr and Cl_2 cylinder sources. Figure 7 shows an example of such analysis for a Cl_2 cylinder that contained ~104 ppb moisture in the gas phase. The sample gas was passed through a Nanochem Metal-X purifier and after the system was dried below ~50 ppb, the purifier was bypassed to obtain the gas phase moisture concentration in the cylinder.

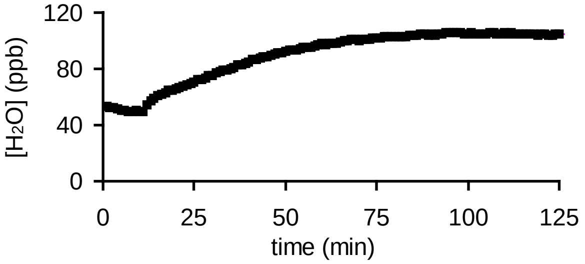

Figure 7. CRDS measurement of moisture in gas phase Cl_2 from cylinder source.

Response Time

The analysis of purified and humidified sample streams that were introduced through two instrument inlets was used to characterize the response time of the instrument to changes in moisture level. Figure 8 shows the response to ppm changes of moisture in nitrogen. The readings reached 90% of the final value in <5 minutes, confirming earlier work by Yan and coworkers(4).

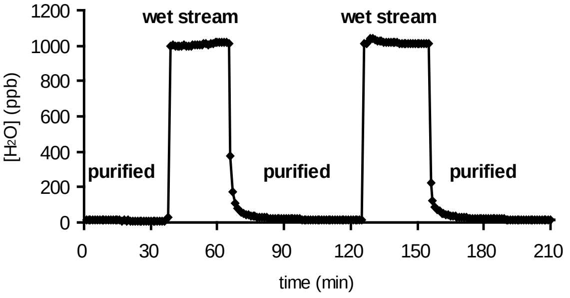

Figure 8. Response of the CRDS instrument to changes in moisture concentration when switching from a dry (Nanochem OMX purified) nitrogen stream to a stream containing 1 ppm moisture.

For both Cl_2 and HBr, the instrument response to moisture changes was slower and equilibration to 90% of the final readings were obtained within ~20-25 minutes. Dry-down times typically were a few minutes longer then the time required for wetting the system. Two examples in Cl_2 and HBr are shown in Figure 9. A humidified HBr stream with a concentration of 2.3 ppm was used to challenge a 500 mL Nanochem Metal-X purifier. The moisture level was reduced to 83 ppb within 3 hours. The Metal-X purifier material was also effective in removing moisture in Cl_2 where a 900 ppb challenge resulted in outlet concentrations of 72 ppb after about 3 hours of gas flow. Reducing the moisture concentration in process gases to these levels will significantly reduce line corrosion and improve process stabilities.

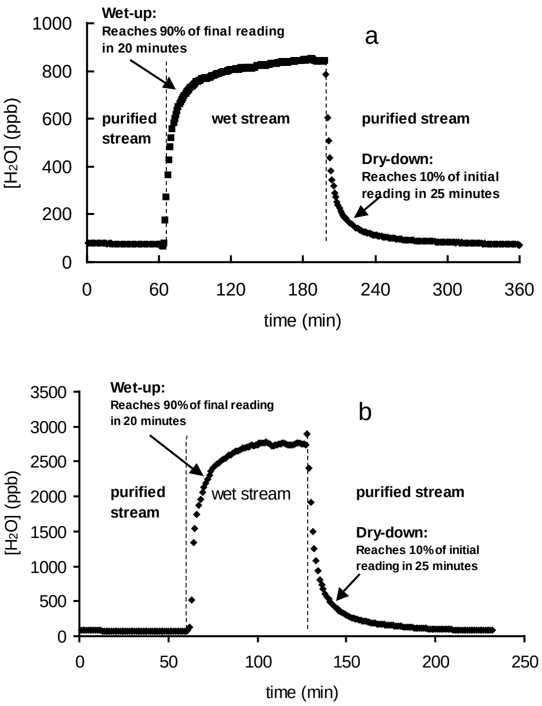

Figure 9. Moisture in Metal-X purified and humidified gas streams from two inlets during purifier testing: (a) Cl_2 and (b) HBr.

Resistance to Corrosive Gases

The CRDS instrument was used in HBr and Cl_2 service for about 6 months. The ring-down time slowly decreased during this time period likely due to decreasing mirror reflectivity. This behavior is shown in Figure 10 at a laser diode temperature of 17.8 °C (1391.3 nm) in both nitrogen and HBr. Because measurements were not continuous and were performed with different corrosive and inert gases, the decreasing ring-down time only illustrates a general trend in loss of performance. The data cannot be used for quantitative predictions. As the ring-down time decreased the sensitivity decreased accordingly. The instrument accuracy was not affected by this change and the slope of the calibration for the different gases remained constant. The loss in mirror reflectivity might be due to deposition products from the sample gases. Etching of the mirror surface is less likely since exposure to liquid HBr for 6 month by the manufacturer did not show any degradation. The time-frame of mirror degradation is significantly lengthened in comparison to long path-length FTIR cells where unacceptable reflectivity loss in HBr was observed within few days to weeks.

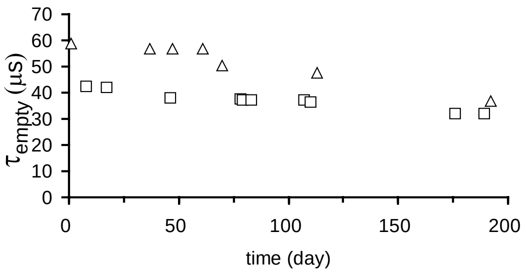

Figure 10. Decay of ring-down time in nitrogen (Δ) and HBr (□) over a test period of 6 months.

Conclusions

Measurement of moisture in Cl_2 and HBr at ppb to ppm level was explored using a Tiger Optics CRDS MTO-1000 analyzer. The CRDS instrument operated reliably and was found to be suitable for cylinder analysis, on-line monitoring applications and purifier evaluations. For example, a Nanochem Metal-X purifer was shown to remove moisture at the ppm level in Cl_2 and HBr to less than 100 ppb. The instrument is sensitive to low ppb moisture with linear response in the tested range of 0-2 ppm. The instrument has been shown to withstand the corrosive effects of gases such as HBr and Cl_2 over a test period of 6 months. The response in Cl_2 and HBr is approximately 4 times slower than in N_2 matrix and therefore sufficient equilibration time is required to obtain reliable results in the corrosive gases. Linear response to actual moisture concentration was obtained in all gases, but the presence of background interference and other spectroscopic artifacts such as line broadening due to additional components in the gas stream resulted in different slopes depending on the sample gas. This illustrates the need for appropriate data analysis and calibration procedures if accurate concentration readings are required.

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