SPECIAL REPORT

Parts-Per-Trillion Moisture Measurement Using Cavity Ring-Down Spectroscopy

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Introduction

Quantitative trace gas impurity detection is very important for many applications, such as spectroscopy, chemical analysis, medical diagnostics, environmental monitoring, and advanced contaminant control in industrial processes. For example, the advances in the semiconductor industry have resulted, in part, from a reduction in the maximum allowable impurity levels in gases by four orders of magnitude over the last two decades.

Indeed, maintenance of ultra-low contamination in semiconductor process gases is a critical factor in achieving acceptable product yields with ever-smaller geometry features in microchips. In particular, it has been established that moisture contamination levels of even a few parts per billion (ppb) can result in defects on silicon wafers.(1) Semiconductor manufacturers call on gas suppliers to guarantee moisture in semiconductor-grade gases at levels no greater than 1-10 ppb, with lower level requirements clearly on the horizon.

The demand for high purity gases by the semiconductor industry presents great challenges to both the gas manufacturers and analytical instrument makers. Not only must trace moisture in bulk gases, such as nitrogen, oxygen, hydrogen, helium, and argon be monitored, but also specialty gases, such as HCl, HBr, BF_3, AsH_3, CF_4, and many others. Many of these gases are highly corrosive, reactive, and toxic.

This challenge calls for trace gas measurement instruments that are sensitive, accurate, fast, and yet robust enough to stand up to corrosive gases. Existing instruments rarely satisfy all these requirements. Cavity Ring-Down Spectroscopy (CRDS) is one of the few laser-based techniques that can. The first commercial product based on the principle of Cavity Ring-Down Spectroscopy (CRDS), the MTO-1000-H_2O, has the capability to measure moisture down to 200 parts-per-trillion levels in inert, as well as corrosive and toxic gases with great speed and accuracy.

Principle of Cavity Ring-Down Spectroscopy (CRDS)

O'Keefe and Deacon developed the basic operating principle of CRDS in 1988.(2) Their work resulted in a technique that determines optical absorption based on time rather than intensity. The essential components in CRDS are the laser source, the optical cavity formed by a pair of highly reflective mirrors, and the light detector as shown in Figure 1.

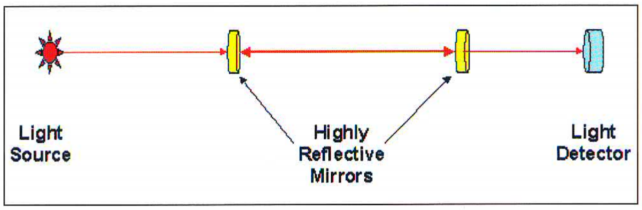

Figure 1. Cavity ring-down schematics.

In a cavity ring-down measurement, a fraction of radiation from a laser pulse is injected into the cavity and bounced back and forth by the highly reflective mirrors many times, leaking out a tiny amount of light upon each return. This light transmitting from the cavity constitutes the ring-down signal. It has an intensity envelope that is simply a first order exponential decay as depicted in Figure 2.

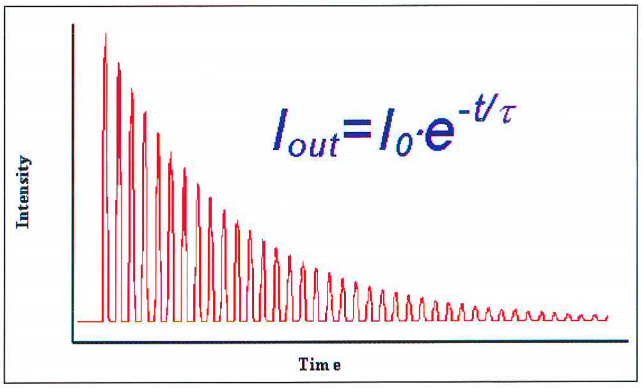

Figure 2. A ring-down signal from a pulsed laser.

This decay arises from losses in the optical cavity. When the cell is empty, the ring-down time, t_{empty}, is determined by the reflectivity of the mirrors (assuming the scattering and absorption are negligible compared to the transmission loss):

In practice, t_{empty} is measured not in a "true" empty cavity, but at a wavelength where there is no absorption from

$$\tau_{empty} = \frac{d}{c(1-R)}$$

the gas molecules inside the cavity. When the laser frequency n is on the peak of a specific absorption line by selected gas molecules inside the cell, the ring-down time, τ(ν), is determined, in addition, by the molecular absorption, which obeys Beer's Law,

$$\tau(\nu) = \frac{d}{c(1-R+\sigma(\nu)\cdot N\cdot d)}$$

In the above equations:

t_{empty} = ring-down time of the empty cavity.
τ(ν) = ring-down time at frequency n.
d = physical separation of the two cavity mirrors.
c = speed of light.
R = reflectivity of the mirrors (assumed to be the same for both mirrors).
σ(ν) = absorption cross section of the particular molecules that absorb light at frequency n.
N = number density, which is proportional to the absolute concentration.

CRDS measurement involves initial measurement of ring-down time t_{empty}, measured at a frequency away from molecular absorption, which is independent of frequency in the high reflective region of the mirrors, and the ring-down time τ(ν) at the peak frequency of molecular absorption. Molecular density N, which is easily converted to concentration, can be calculated from the following equation:

$$N = \frac{1}{c\cdot\sigma(\nu)}\cdot\left(\frac{1}{\tau(\nu)}-\frac{1}{\tau_{empty}}\right)$$

As shown above, trace gas concentration is determined by two "time" measurements. Thus, a calibration standard is unnecessary. The accuracy of the measurement depends on the accuracy of the molecular constant σ(ν), which is normally well determined by conventional absorption methods and published in the literature. If there is no difference between the t_{empty} and the τ(ν), then there are no molecules present. On the other hand, if the difference is large, then it means there are large concentrations of molecules there. The difference in the ring-down time, or more precisely, the inverse of time, which is the decay rate, measures the concentration level.

It should be pointed out that t_{empty} must only be measured once and is quite stable since it is determined by the reflectivity of the mirrors. Therefore, the trace gas concentration is determined by a single measurement of τ(ν), on the order of tens to hundreds of microseconds.

CRDS with Continuous Wave (CW) Lasers

The commercial development of CRDS was made possible by the use of continuous wave (CW) lasers as pioneered by Lehmann's group.[3,4] Compared to previously used pulsed lasers, CW diodes are much more compact, low cost, low power consuming, and often have narrower spectral width, offering higher resolution. By using single-mode, narrow spectral width DFB diode lasers, light can be coupled into the ring-down cavity more efficiently. When the light intensity inside the cavity quickly builds up to a sufficiently high level, it is abruptly deflected by an acousto-optical modulator (AOM), and the ring-down signal is measured. The diode laser then reverts back to the cavity, repeating another ring-down measurement cycle. A typical CW-CRDS system is depicted in Figure 3.

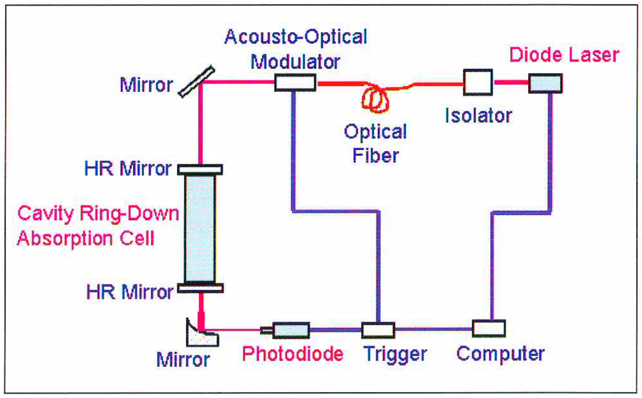

Figure 3. A typical CW-CRDS system.

CRDS Advantages

For gas analysis, CRDS affords certain unique advantages, chiefly speed of response, sensitivity, wide dynamic range, and freedom from costly, time-consuming calibration requirements. Based on Beer's Law of absorption, the sensitivity of absorption techniques can be improved by increasing the light pathlength in the sample cell. In conventional absorption spectroscopy, the intensity of light transmitted through a sample is compared to the transmission without the sample. The smallest number density that can be determined by this method is given by:

$$N_{min}=(\Delta I/I_0)_{noise}/(\sigma(\nu)\ L)$$

where $(\Delta I/I_0)_{noise}$ noise is the smallest fractional change in light intensity that can be detected. To maximize sensitivity, a molecular transition with a large s, as well as a long pathlength L, and the smallest possible $(\Delta I/I_0)_{noise}$ must be selected. The pathlength L in the conventional absorption method is limited by the physical size of the apparatus. The effective pathlength can be increased from 10 to 100 times the physical length using "multiple pass" cells, such as White[5] or Herriott[6] cells.

The sensitivity of conventional absorption techniques is often limited not only by the pathlength but is also limited by amplitude noise of light sources and the detection system. Moreover, any absorption external to the cell will interfere with the measurement accuracy. The absorption often occurring before and after the cell has to be taken into account. This is especially difficult for moisture measurement because its significant presence in air.

In particular, it has been established that moisture contamination levels of even a few parts per billion (ppb) can result in defects on silicon wafers.

CRDS, on the other hand, is unaffected by either the laser amplitude noise or the external absorptions since they do not contribute to the ring-down "time" we measure. Freedom from absorption interference outside the cell is a significant advantage of our technique in trace moisture measurement of ultra-high purity gases.

Another key benefit is CRDS' extraordinary sensitivity as determined by the pathlength the light traverses. Romanini and Lehmann[3] have shown that a ring-down cavity cell has an effective pathlength L=d/(1-R), where R is the reflectivity of the mirrors. Since mirrors are commercially available today with reflectivity on the order of 99.999%[7], the effective optical pathlength of the cell is increased by 105 times over the physical dimensions of the device. Thus, an absorption pathlength of 10,000 –100,000 meters is achieved in a cell of about one meter physical length, as illustrated in Figure 4. This translates into a moisture detection limit of 70 parts-per-trillion.

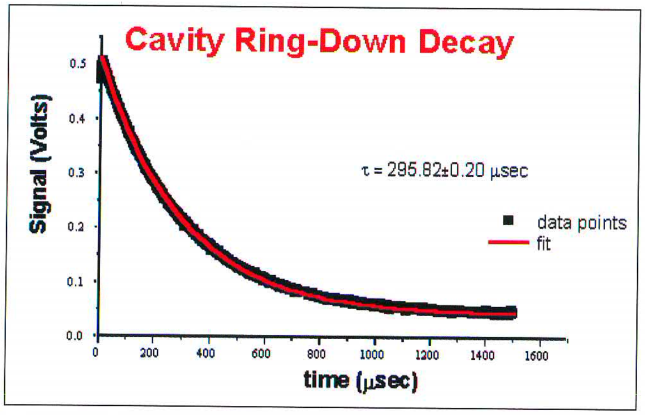

Figure 4. A CRDS decay curve indicating a pathlength of nearly 90 km.

The First CRDS Commercial Product: The MTO-1000-H2O

a. The setup

Figure 3 shows the component assembly schematic of a typical CRDS analyzer. The major components are a CW diode laser, a ring-down cavity sample cell with a pair of ultra-high reflectivity (HR) mirrors, and a photodetector that detects the light signal leaking out of the cell. Other components are mode-matching optics that include an input fiber optic coupler that directs light into the acousto-optical modulator (AOM), and a Faraday isolator to prevent light feedback to the diode laser.

The AOM acts to quickly deflect the laser from the cavity after it provides sufficient energy to generate a ring-down signal. A trigger located after the photodiode acts as an on-off switch to the AOM. An optical mirror placed after the cell focuses the light into the photodiode detector. Finally, a computer is used for data acquisition and transmission, as well as performing computational analysis. The literature contains various other schemes to replace the function of the AOM for temporarily switching the resonance off between the diode laser and the cavity mode to allow for a ring-down measurement.

Figure 5 shows the ring-down time measurement of water spectrum using the MTO-1000-H_2O. The spectrum was taken at 750 ppb moisture in a flowing N_2 carrier gas at 5 psi above atmosphere pressure.

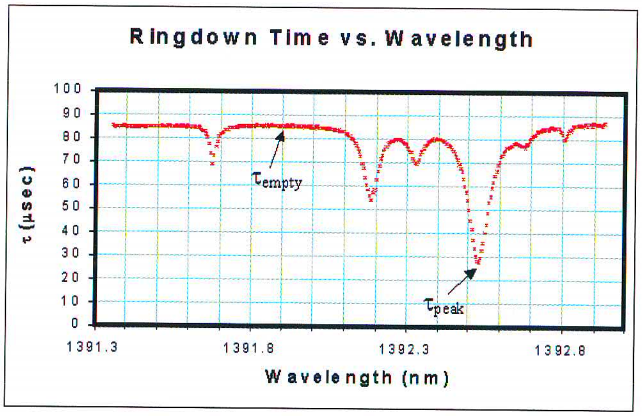

Figure 5. A water spectrum in flowing N_2 carrier gas. The wavelength positions of tempty

b. Sensitivity

Recently, an evaluation was conducted of the MTO-1000-H_2O against an Atmospheric Pressure Ionization Mass Spectrometer (APIMS), considered the most sensitive trace gas analytical instrument used by the gas industry. Results of the test showed that the MTO-1000-H_2O had a 99.96% correlation with the APIMS, with only a 35 ppt offset. The results are plotted in Figure 6. The dynamic range of the MTO-1000-H_2O is considerably wider than the APIMS. A recent test shows that the APIMS becomes saturated at moisture levels about 130 ppb, while the MTO-1000 can measure up to 2 ppm levels with the same settings.

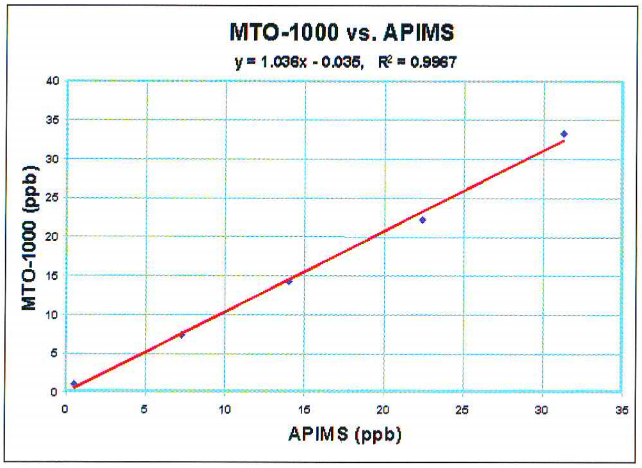

Figure 6. The MTO-1000-H_2O vs. APIMS.

The wide dynamic range of the MTO-1000-H2O is clearly seen in Figure 7, depicting a series of moisture intrusions using a moisture generator.

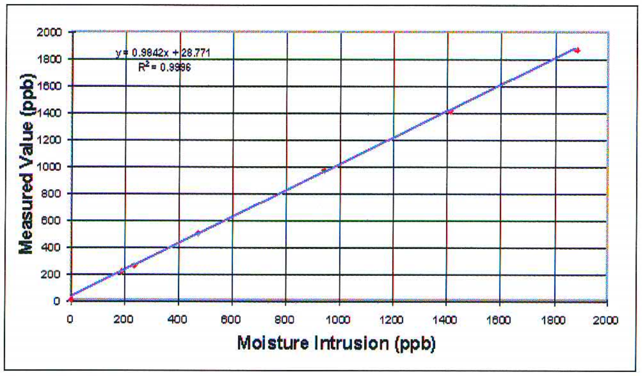

Figure 7. The MTO-1000-H_2O measurements of moisture intrusions.

c. Speed of response

Additional independent field tests conducted with the MTO-1000-H_2O demonstrate its responsiveness and its ablity to recover from a moisture intrusion, shown in Figure 8. In this test, two N_2 lines were consecutively flowed through the ring-down cavity cell, one containing 700 ppb of moisture and the othe is dry. The instrument responded quickly. The instrument dries down to 95% of the value in less than 4 minutes, and takes less than 2 minutes for intrusion.

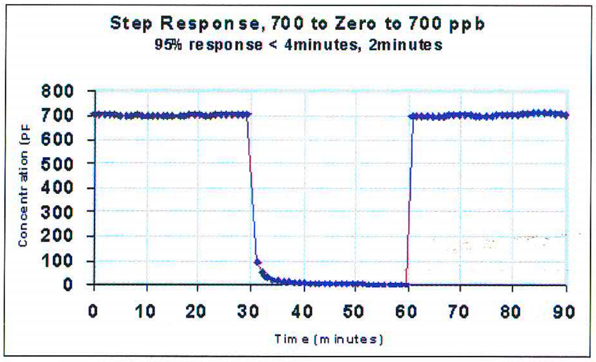

Figure 8. The MTO-1000-H_2O Response Curve.

Outlook

Beyond moisture, the CRDS MTO-1000 product series can easily be extended to the detection of scores of other contaminant species important in scientific analysis and process control. During 2002, Tiger plans to release several additional models of the MTO-1000 targeting CH_4, CO, and CO_2. In addition, its robust and flexible design lends itself to various configurations, including a split-architecture version under design for hazardous environments and tool and cart integration. In summary, cavity ring-down spectroscopy serves as a powerful analytical technique for trace gas analysis. It will find wide applications in trace gas detections within and beyond the semiconductor market. G&T

For gas analysis, CRDS affords certain unique advantages, chiefly speed of response, sensitivity, wide dynamic range, and freedom from costly, time-consuming calibration requirements.

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