Hydrogen bromide cylinder gas ppb-level

water vapor measurement

EXECUTIVE OVERVIEW

With continuing ITRS-driven requirements for lower impurities in essential raw materials, the precise measurement for water vapor concentration in hydrogen bromide is a specification essential for semiconductor fabrication. Cavity ring-down spectroscopy (CRDS) can measure water vapor impurity at part per billion (ppb) levels in HBr. However, two factors affect the accuracy of measurements from cylinder sources: the cylinder temperature and the sampling time. Appropriate data processing using thermodynamic principles provides accurate H_2O characterization while reducing measurement time by 50%.

The measurement of trace water vapor in corrosive gases such as hydrogen bromide (HBr) used in semiconductor manufacturing is essential to maintain process consistency and maximize device yields. Water vapor impurity not only causes corrosion of gas delivery systems, resulting in particle contamination and component failure, but also participates in wafer chemistries, potentially leading to electrical defects. CRDS has become the method of choice for water vapor impurity detection in corrosive gases [1–6].

CRDS for quality control of water vapor impurity in HBr cylinders requires using the instrumentation in production environments. Two factors greatly influence detection accuracy: cylinder temperature and sampling time. The water vapor concentration measured in a cylinder's gas phase is determined by the phase equilibrium between the gas and liquid phases. Considering an HBr cylinder containing trace amounts of water, where gas is being withdrawn at a relatively low flow rate and cylinder temperature is not fluctuating much during sampling, it is safe to ignore material loss and cylinder volume changes. Thus, the cylinder can be regarded as a two-phase two-component system; phase equilibrium is mostly dictated by cylinder temperature.

Jianlong Yao, Eric Olsen, Mark W. Rayner, Gianni D. Leonarduzzi, Matheson Tri-Gas Inc., Longmont, CO, United States

The water vapor concentration recorded by CRDS is influenced by the relatively slow equilibration time of water impurity in the sampling system and cavity. When flowing HBr gas through the sampling manifold and the CRDS instrument, it takes some hours of "wet-up" for the CRDS sample cell to reach dynamic equilibrium. Water vapor trace curves can be fitted with the proper equations to obtain the concentration value at equilibrium.

Within a certain temperature range, the gas-phase water concentration for cylinders can be normalized to corresponding levels at a chosen temperature by using thermodynamic principles. We modeled the equilibration process of water concentration in the sampling manifold and CRDS sample cavity, and used a set of water vapor readings recorded by CRDS in a limited time span to extrapolate the actual water concentration at equilibrium. This compensates for the equilibration effect in the sample manifold and cavity, and shortens measurement time.

Experimental

The experimental work was conducted using a Tiger Optics model MTO-1000 CRDS instrument, an HBr cylinder, a purified N_2 purge tee, a Matheson Tri-Gas model L-500 Nanochem Metal-X purifier, and a temperature tracking unit, which consisted of several thermocouples and an Omega model DC-3000 data logger. The thermocouples were placed at appropriate locations to track the temperature of the cylinder's liquid and gas sections, the gas lines, and the surrounding air. All the sample gas lines were heated to ~65°C using a PID controller to limit temperature variation in the sampling system.

Based on the ensemble Henry's Law, the final equation that models the water vapor concentration in the gas phase of an HBr cylinder can be approximately written as:

$$\ln [H_2O(g)] = -A/T + B$$

where $[H_2O(g)]$ is the water vapor concentration (ppb) in the gas phase of an HBr cylinder, T is cylinder temperature in Kelvin, coefficient A is mainly related to the vaporization energies of water and HBr from the liquid phase, and coefficient B is related to various correction terms, including initial water vapor content in the liquid phase, cylinder pressure, and deviation from ideal state.

To check the equation's validity, a series of HBr cylinders with low single-digit ppm water vapor levels were analyzed by CRDS in the 3°C to 32°C temperature range. A flow rate of ~1 slpm was used to limit the loss of material, and thus the perturbation of the system. Temperature was detected using thermocouples attached below the liquid level and on the outer surface of the HBr cylinder.

Figure 1a shows the water vapor level in HBr gas measured from a cylinder at ambient temperature over 9.5 hrs. Measurements were made from ~6:30 am to 4:00 pm, while the ambient temperature increased from ~20°C to 24°C. The water vapor reading followed the same trend, with higher concentrations measured as temperature increased. A plot of the natural logarithm of the gas-phase water vapor concentration vs. inverse temperature results in a straight line with a correlation coefficient of 0.9859 (**Fig. 1b**).

continued on page 48

 continued from page 46

More stringent CRDS H_2O measurements were performed for HBr cylinders equilibrated at fixed temperatures. The data set showed linearity with a correlation coefficient of 0.9726. Slopes (parameter A in the equation) for plots of all data sets from various cylinders were very close to one another, clearly confirming that coefficient A is a constant.

With the coefficient A value, for each CRDS water vapor concentration reading at temperature T2, one can calculate the corresponding coefficient B value. Then with both coefficient A and B values known, one can calculate the corresponding water vapor concentration at another temperature T1. The normalization result for the 9.5-hr trace obtained using this method is shown by the dark blue line of triangles in Fig. 1a. After normalization to 21°C,

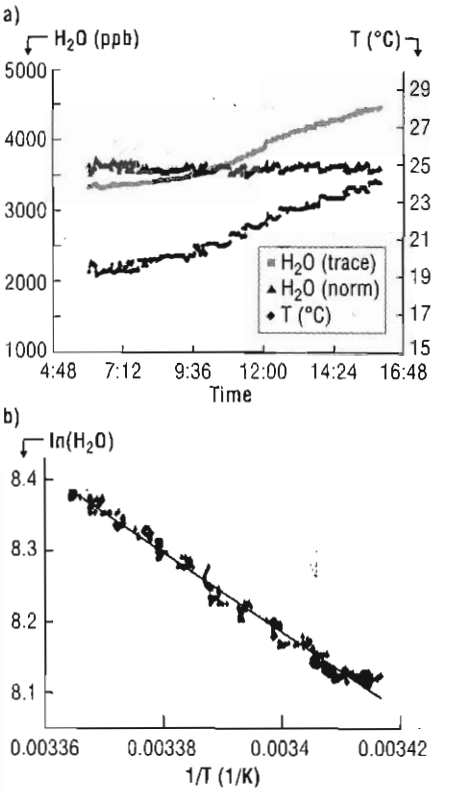


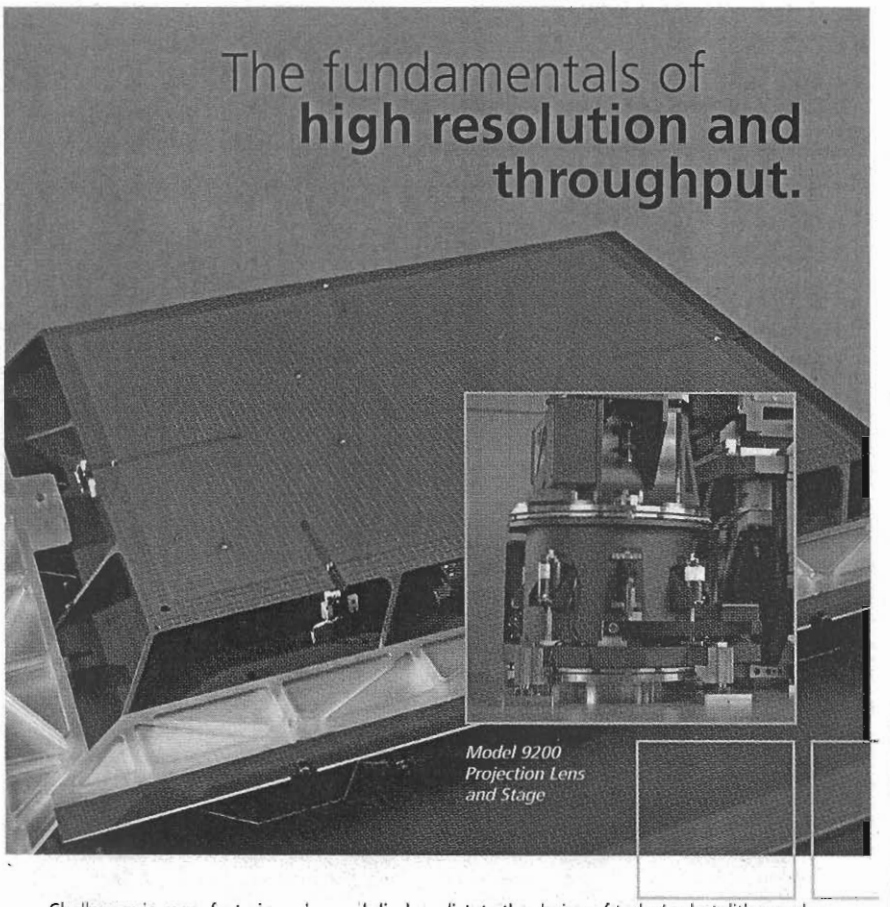
Figure 1. a) CRDS trace of water vapor concentration in an HBr cylinder (green) equilibrated with ambient temperature (dark blue), along with actual temperature (red), and **b)** a linear fit of the natural logarithm of water vapor concentration versus the inverse of cylinder temperature.

the recorded water vapor curve (green squares) becomes a straight line with nearly constant water vapor concentration.

Figure 2 shows a real-case scenario of a cylinder in a gas cabinet that is equilibrated with ambient temperature. As shown by the green line, after an initial "wet-up" stage, the CRDS trace of water vapor concentration continues to increase following the cylinder temperature during the course of analysis. Using this method, the water vapor concentration was also normalized to a steady level for a fixed temperature at 21°C (dark blue), except for the wet-up stage. These examples demonstrate that the modeling method employed and the vaporization energy related coefficient A generated are adequate for temperature normalization of the CRDS water vapor concentration data.

A typical CRDS water vapor trace has two sections: an initial "wet-up" section as water vapor in the sample gas wets the surfaces of the dry sampling manifold and CRDS cell, and a second equilibration

continued on page 50



Challenges in manufacturing advanced displays dictate the design of today's photolithography platforms. The demand for precision imaging and overlays requires high fidelity optics, laser metering, and an integrated alignment system.

But that's not enough. You also need enough throughput to keep up with today's exploding markets. And for that you need fast reticle exchange and real-time autofocus.

The result is high resolution down to 1.5 µm, high overlay accuracy, and improved throughput.

Contact us today. We understand the fundamentals.

Model 9200
PanelPrinter™

AZORES

1.978.253.6200
www.azorescorp.com

PanelPrinter™ is a trademark of Azores Corp.

 continued from page 48

section. The latter represents the water vapor varying gradually due to both further equilibration of water vapor in the system and the variation of cylinder temperature as a result of the variation of ambient temperature.

The red dashed line in Fig. 2 shows an exponential fit of the temperature normalized water vapor trace, which produces the final water vapor concentration at 21°C.

Assessment of models

Data were collected and processed for over 30 HBr cylinders either held at fixed temperature or allowed to fluctuate with ambient room temperature. Overall, both the temperature normalization and exponential fitting produce satisfying results. All the water vapor concentration traces can be normalized to steady levels at 21°C. This shows that the method and the vaporization energy-related coefficient A generated are adequate for temperature normalization of the CRDS water vapor data.

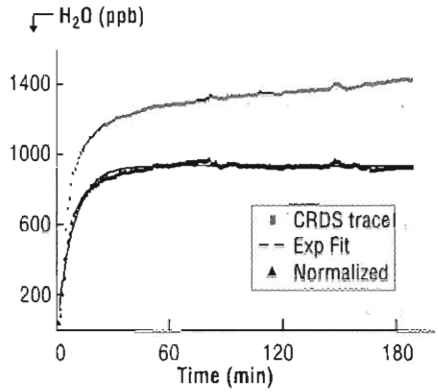


Figure 2. Temperature normalization (dark blue) and exponential fit (red) of water vapor trace (green) at ambient temperature by CRDS.

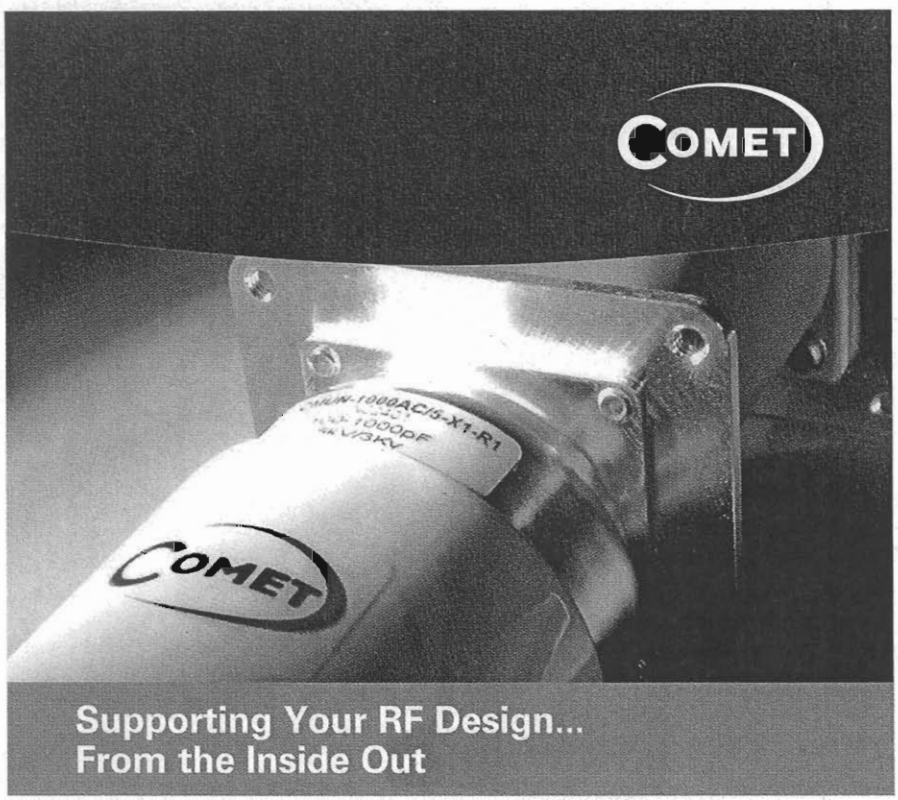
The exponential fit results give the final water vapor concentration at 21°C and the sampling system's wet-up trend from the start of the CRDS measurements. The latter is useful in judging how long the CRDS should be run for measuring water vapor in the HBr cylinder. A close analysis of the extrapolation results using data collected in various time spans suggests that the length of the CRDS measurement can be significantly reduced, while still allowing an accurate extrapolation of the exact water vapor concentration.

The differences between the 3-hr extrapolation results and those from shorter detection periods are presented for 24 cylinders in the **table** (see p. 52). The first column lists the extrapolated water vapor concentration values at 3 hrs detection. Columns 2–6 list the percentage differences between the 3-hr extrapolation results and those for shorter detection periods. The percent root-mean-square (RMS) deviation of the shorter period values from 3 hr results are listed in the last row. The results show only 3.38% and 5.39% RMS deviations from 3-hr analysis results for those of 2- and 1.5-hr runs. Depending on intended QC specifications, one can reduce the analysis time to 2 hrs or even shorter. This minimizes analysis time and material usage, both of which contribute to reducing costs.

Conclusion

With the two approaches developed in this work, we are able to detect the gas-phase

continued on page 52



Supporting Your RF Design...
From the Inside Out

Known the world over for our Vacuum Capacitor technology, COMET has the engineering and component manufacturing expertise to assist you with related RF competencies.

Invite us to support your sub-system design and manufacturing needs and we'll deliver solutions.

The X-perts for security, inspection, electronics and communication

COMET North America Inc., 76 Progress Drive, Stamford, CT 06902, USA
T +1 203 969 2161, F +1 203 969 2162, usa@comet.ch, www.comet.ch

 continued from page 50

The 3-hr CRDS extrapolated water vapor concentrations and their deviations for shorter sampling times

H_2O (ppm) at 3 hr	% difference from 3-hr result				
	2 hrs	1.5 hrs	1 hr	45 min.	30 min.
0.98	-0.61	-1.12	-3.57	-4.49	-2.45
0.822	-2.68	-5.35	-8.64	-12.65	-17.03
0.999	-5.11	-8.91	-10.21	-9.51	-5.31
0.897	-3.68	-4.24	-5.46	-4.46	-10.93
0.328	5.18	8.84	12.50	15.24	20.43
0.567	0.35	0.53	0.71	1.94	14.64
0.704	2.13	3.13	3.69	3.98	11.93
0.135	1.48	2.96	4.44	6.67	11.11
0.139	3.60	6.47	9.35	12.95	12.95
0.123	8.13	13.01	18.70	21.14	26.83
0.257	-2.72	-4.28	-6.23	-5.84	3.11
0.571	0.70	1.75	1.58	3.33	19.61
0.594	1.35	2.53	4.21	6.57	19.70
0.772	1.68	2.20	3.37	4.92	11.92
0.758	-0.40	-0.66	-0.40	0.13	3.03
0.162	3.70	6.79	11.73	17.90	54.94
0.579	5.53	8.98	12.44	14.16	17.44
0.536	1.31	1.49	-0.37	-2.05	-5.22
0.463	4.54	5.40	7.99	9.50	14.90
0.956	0.00	-0.42	0.84	2.30	14.44
0.745	-2.95	-3.76	-3.22	-1.88	1.61
0.777	3.60	5.15	6.44	6.44	13.26
0.957	0.947	0.937	0.925	0.919	0.909
0.943	0.944	0.944	0.928	0.916	0.911
RMS deviation (%)	3.38	5.39	7.60	9.28	17.60

water concentration in HBr cylinders in a relatively short time, normalize for temperature variation, and extrapolate the actual water vapor concentration to that at t_∞. This has enabled HBr QC processes to be optimized for production conditions, with resulting intrinsic improvements in 3σ values and cost of ownership reduction. ■

References

1. J. Yao, et al., *SEMI Technical Symp.: Innovations in Semi. Manufacturing, Session 108: Advances in Gas Analysis*, SEMICON West 2004, 2004.
2. K.W. Busch, M.A. Busch, Ed., "Cavity Ringdown Spectoscopy: An Ultratrace-Absorption Measurement Technique," *ACS Symposium Series 720*, Oxford University Press, Washington, DC, 1999.
3. G. Berden, et al., *International Reviews in Physical Chemistry*, 19, 565, 2000.
4. V. Vorsa, et al., *SEMI Workshop Proceedings: Advances in Detection of Trace Moisture in Specialty Gases*, SEMICON West 2003, San Francisco, CA, 2003.
5. V. Vorsa, et al., *Applied Optics*, Vol. 44, No. 4, 2005.
6. Y. Chen, et al., *PITTCON 2006*, Orlando FL, presentation # 1950-3, 2006.

JIANLONG YAO is a senior scientist at *Matheson Tri-Gas Inc., Advanced Technology Center (ATC), Longmont, CO, United States; ph 303/678-0700, e-mail jyao@matheson-trigas.com.*

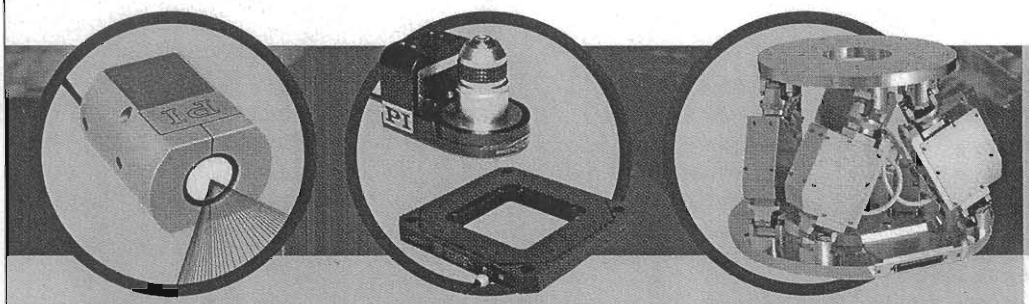
ERIC OLSEN is quality manager at Matheson Tri-Gas Inc. in Newark, CA.

MARK RAYNOR is R&D director at Matheson Tri-Gas ATC.

GIANNI D. LEONARDUZZI is director of marketing at Matheson Tri-Gas.

Nanopositioning Systems

PI
Piezo • Nano • Positioning



Fast Steering Mirrors
- 1 to 3 Axes
- Fixed Pivot Point
- Microsec Response

Piezo Flexure Stages
- 1 to 6 Axes
- Closed-Loop Control
- Sub-nm Precision

6-Axis Hexapods
- Sub-µm Precison
- Powerful 6-D Controller
- Vacuum Versions

PI is the Global Leader in Nanopositioning.
ISO 9001 since 1994.
30+ Years Experience.
Custom Designs.
Global Expert Support.
Get the 500 page PI catalog!

PI (Physik Instrumente) L.P.
Tel: (508) 832-3456
www.pi.ws/sst3n

Moving the NanoWorld | www.pi.ws

See us at SEMICON West, Booth 6149