Using tunable diode laser spectroscopy to detect trace moisture in ammonia

Detection of moisture contamination in hydride gases, such as ammonia used for epitaxial growth, has become a significant concern for manufacturers of III-V compound semiconductors. The presence of moisture in NH3 can negatively affect device properties, such as minority-carrier lifetimes and luminescent efficiency in light-emitting diodes. Tunable diode laser spectroscopy (TDLAS) has emerged as a potential solution for trace moisture detection in ultrahigh-purity gases. Tests show TDLAS is a viable on-line process analyzer in NH3 applications and an alternative to Fourier transform infrared (FTIR) spectroscopy.

Increased demand for ultrahigh-purity gases in compound semiconductor manufacturing has heightened the need for moisture detection during nitride film growth and other epitaxial process steps used to make III-V devices. For example, the presence of moisture in organometallic vapor phase epitaxy processes can negatively affect the photoluminescence properties of light-emitting diodes or vertical-cavity surface-emitting lasers [1, 2].

Currently, FTIR spectroscopy is the method of choice for trace moisture detection in these applications because of high sensitivity and maturity of those instruments [3, 4]. A state-of-the-art FTIR instrument was recently used to achieve low-moisture detection limits of 5 parts per billion (ppb) with a liquid N_2-cooled detector and 22ppb with a thermoelectrically cooled device [5]. To reach lower levels of moisture detection, fully optimized FTIR-based monitors require a long path-length cell, liquid N_2-cooled mercury-cadmium-telluride or indium antimonide detectors, narrow bandpass filters, and a sealed spectrometer purged with dry nitrogen. Typically, liquid N_2-cooled detector Dewars have to be refilled every 8 hrs, so for standalone production applications, additional automation would be required to maintain cooling.

Other emerging techniques based on infrared-light absorption with the potential for lower detection limits have been proposed, including cavity ringdown spectroscopy, intracavity laser spectroscopy, and TDLAS [6–8]. Each of these methods employs diode laser light sources with a very narrow wave range but high light intensity. A limiting factor for all three techniques is background interference due to the complexity of the IR spectra of hydride gases with absorbances throughout the infrared range. Because diode lasers are only capable of scanning a narrow wavelength range, a spectral window with minimal interference and relatively strong water-absorption lines is required. In inert gases, a TDLAS instrument has demonstrated sensitivity in the low parts-per-trillion (ppt) range by scanning a moisture line at ~1854nm. A prototype version of the inert-gas instrument has been developed using a different spectral range and modified data analysis to account for NH_3 background interference. Tests of the prototype instrument have shown sensitivity in the 10ppb range [7]. The Matheson Tri-Gas R&D facility has conducted additional tests of the prototype TDLAS instrument for sensitivity, accuracy, and stability of moisture measurements.

Probing NH3 performance

The tested prototype instrument (Delta F Model DF740) was designed for ammonia applications and was equipped with a Herriott cell with an internal volume of ~1 liter and a path length of 50m. The instrument's diode laser covers a spectral range between 1392.3–1392.8nm. Details of the operating principle of TDLAS are discussed by Hovde et al. [9]. During tests, the cell was maintained at a temperature of 45°C and the pressure was adjusted to 200torr for inert gases and 70torr for NH_3, using a needle valve and a diaphragm pump at the instrument outlet. An orifice at the gas inlet was used to limit the flow into the cell to 250sccm and to improve pressure stability. The detector did not require liquid N_2 cooling. The sample manifold included a Matheson Tri-Gas Nanochem OMA purifier to provide a zero reference NH_3 because the instrument did not include an internal purifier. Purge N_2 was purified using Nanochem OMX. The sample manifold was also modified for the addition of moisture without introducing N_2, as shown in Fig. 1. A diffusion vial placed in a heated vessel at constant flow rate, temperature, and pressure was used as moisture source for initial calibrations (not shown).
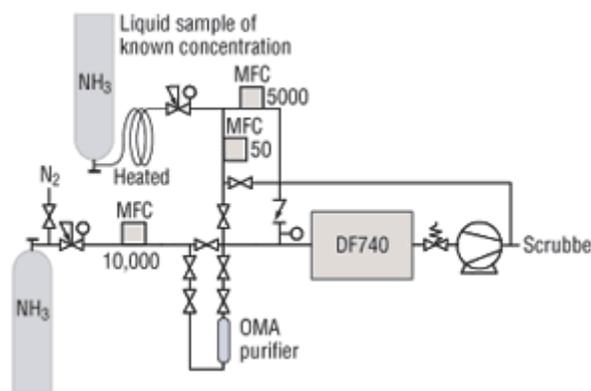
Figure 1. Manifold for verification of moisture response using total vaporization of a moisture-containing liquid NH$_3$ stream.

The diffusion vial was replaced with an inverted NH$_3$ cylinder, which contained 2.1ppm ±0.02ppm moisture in the liquid phase (measured by FTIR), and a heated line. To obtain humidified ammonia gas at stable concentrations reflecting the liquid-phase moisture content in the cylinder, the sample stream was completely vaporized at ~100°C and a gas flow rate of 1000sccm. A fraction of the vaporized ammonia was controlled by a mass flow controller (MFC) and diluted with purified NH$_3$ to obtain concentrations between 0 and 60ppb.

The installation of the instrument required an air supply line for internal pneumatic valves, connection of the supplied diaphragm pump to the gas outlet, and link to sample gas lines. After initiating the N$_2$ flow, background moisture levels of ~20ppb were reached. The background slowly decreased throughout the tests, likely due to residual outgassing from lines, valves, and other components. After several weeks of operation, moisture readings in N$_2$ reached ~2ppb. The instrument performed reliably during the test period.

Response to moisture

The moisture response of the instrument in nitrogen was within 9% of the added moisture content. This discrepancy was most likely caused by a combination of inaccuracies in the calibration setup and variations from instrument to instrument, as previously reported [7]. Introduction of purified NH$_3$ resulted in an offset of the reading of ~170ppb. Throughout the test period, the offset slowly decreased to ~140ppb (Fig. 2) with day-to-day fluctuations of 10–15ppb. No reason for the fluctuations was apparent. The offset could either be subtracted from consecutive data to obtain a baseline at 0ppb or a new background could be used by instructing the instrument to use data collected while flowing dry NH$_3$ as instrument background.
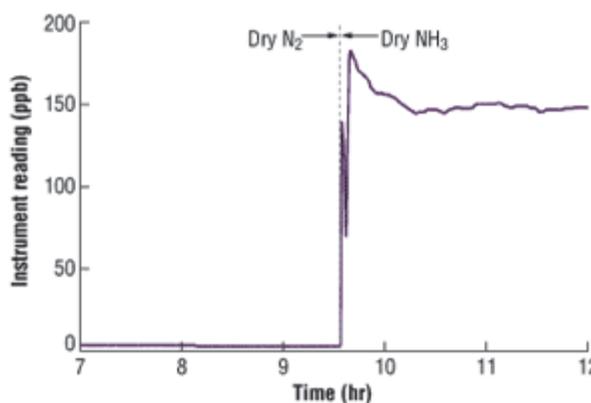
Figure 2. Moisture response during changeover from N$_2$ to NH$_3$.

The addition of moisture initially was performed by introducing increasing amounts of N_2 with a constant moisture concentration of ~0.7ppm to the purified NH_3 stream. Because the instrument response was about twice as high as expected, it was suspected that N_2 contributed to the overall reading due to line broadening of the NH_3 spectral features present as a background.
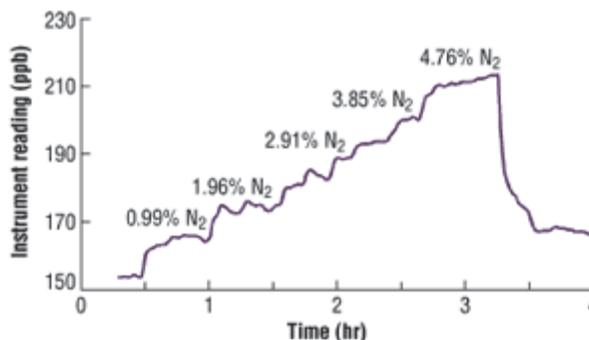
Figure 3. Response of instrument to N_2 addition in NH_3 without added moisture.

The overlaying spectral features of ammonia are significantly larger than moisture lines at low ppb concentrations. Small variations in the ammonia background, due to line broadening, can result in an artificial moisture response if the fitting software does not correctly account for those changes. The extent of the N_2 influence was determined by adding moisture-free N_2 to the dry NH_3 stream at concentrations similar to those used for adding moisture with a humidified nitrogen stream. The response to increasing N_2 concentration is linear with a slope of about 10ppb apparent moisture reading/percent of added nitrogen (Fig. 3).

N_2-free calibration
To avoid the apparent moisture response when adding N_2 to the purified NH_3 stream, an NH_3 cylinder containing 2.1ppm moisture in the liquid phase was inverted for liquid sampling [10]. A fraction of the vaporized stream was mixed with purified NH_3 to obtain concentrations between 10.4 and 51.2ppb without co-adding N_2. A linear response curve after correction for the NH_3 offset indicates analyzer readings that were ~1.2× higher than the true moisture content (Fig. 4). The slight overestimation is consistent with data published from a similar series of experiments by Wright and coworkers [7]. Those studies were performed by adding varying amounts of moisture in nitrogen while maintaining constant nitrogen concentrations. The discrepancies between the instrument readings and the true moisture content were attributed to inaccuracies of the pressure broadening coefficients used in the line profile fit by the TDLAS software. Improved fitting routines for better consistency are currently in development.
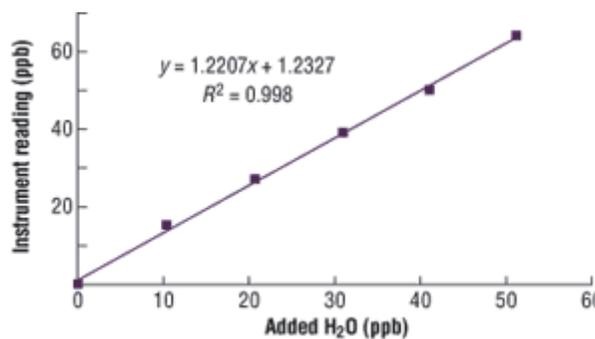
Figure 4. Moisture response of TDLAS in N_2-free NH_3.

The regression-based method detection limit (MDL) [11] calculated from the data in Fig. 4 amounts to 9ppb. The standard deviations of the readings are typically in the range of 2–4ppb over time periods of 0.5–1.5 hrs. Using the 3× standard deviation (3σ) IUPAC definition for detection limits, a similar sensitivity of ~9ppb can be determined from the signal noise and the slope.

Common to most spectroscopic trace-analysis methods is the need to subtract a clean background spectrum. The true moisture content of the purified ammonia cannot be measured directly because the spectral response is a combination of large ammonia background features and relatively small moisture lines. A residual moisture content of <10ppb is implied based on the purifier performance in inert gases where <100ppt can be obtained routinely.

The variance in moisture reading while purging the system with purified N_2 was ±0.7ppb over a period of three days. The instrument was optimized for ammonia and thus did not achieve the stability reported for instruments designed for inert applications using different spectral regions with detection limits in the 100ppt range. The application of different fitting routines to account for NH_3 interference also complicates the extraction of the true moisture concentration. The possibility of true moisture fluctuations due to residual outgassing of system components also cannot be ruled out.

Stability in ammonia

The instrument output during flow of purified NH_3 over a time period of ~15 hrs shows variations of ±5–10ppb with a standard deviation of 3.7ppb (Fig. 5). These data are consistent with data published in other studies [7]. Possible causes for the variations include instability in the laser output, and temperature drifts in the sample system and cell that cause changes in the adsorption equilibrium and changing background moisture.
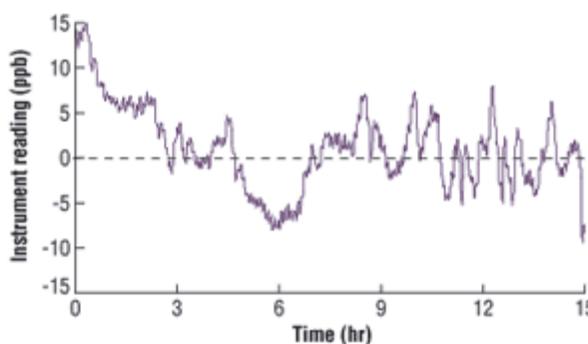
Figure 5. Stability of TDLAS moisture reading in Nanochem OMA-purified NH_3.

Under the assumption that the purifier removes moisture from the gas stream to <1ppb, residual moisture concentrations in the system should be significantly less than the observed fluctuations, and instrument instability appears to be more likely. Even though the room temperature fluctuated by as much as 10°F during some of the tests because of insufficient air-conditioning capacity, no direct correlation between instrument response and temperature was apparent.

Pressure dependency

The instrument is very sensitive to pressure. Operation at 70torr ±3torr is recommended for reliable readings in NH_3 [7]. Changes of 10torr at this pressure correspond to a change in moisture reading of ~10ppb. Increasing pressure results in decreasing readings and vice versa. As the pressure exceeds the recommended range, the readings deviate more dramatically from the true moisture content as the line-fitting routine ceases to account accurately for broadening effects. For example, lowering the pressure from 70 to 50torr resulted in ~250ppb increase in moisture response. Although the pressure during the test appeared to be stable within few torr, a pressure controller — instead of the supplied needle valve — is expected to improve instrument stability based on these observations.

Response time

The analyzer used a 1-liter gas cell that resulted in fast cell purge with a residence time of ~0.4 minutes in NH_3 service (pressure = 70torr, flow rate = 250sccm). Figure 6 illustrates the response time when bypassing the Nanochem OMA purifier using a gas stream containing about 160ppb moisture, which was obtained by total vaporization of the liquid phase of the NH_3 cylinder discussed previously. The time scale for dry-down of the instrument when redirecting the same gas stream through the OMA purifier was similar, and 90% of the final reading was reached within ~7 min.
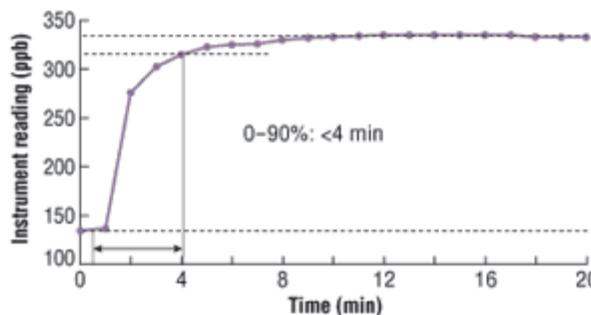
Figure 6. Equilibration time of TDLAS analyzer for a concentration change from Nanochem OMA-purified NH₃ to moisture-containing NH₃.

Conclusion

The tunable diode laser absorption spectrometer for moisture detection in NH_3 was sensitive at the low ppb range with a detection limit of 9ppb and long-term drifts of ±10ppb. The analyzer re-equilibrated to 90% of the final readings within few minutes after changes of the inlet concentration. The instrument response was linear and the true moisture content in nitrogen-free ammonia was overestimated by ~20%. The addition of nitrogen as typically required for moisture introduction resulted in false readings in the range of ~10ppb/% nitrogen added due to line-broadening of the strong ammonia spectral features.

Instrument tests have shown that TDLAS is viable for on-line monitoring of moisture levels in purified process gases, such as NH_3, for epi growth. The TDLAS prototype system was designed purely as a moisture analyzer, while most FTIR instruments offer multicomponent analysis. Additional cost issues must be weighed in on-line analyzer strategies, but TDLAS appears capable of addressing low-ppb requirements in purified NH_3 streams.

Acknowledgment

Nanochem is a registered trademark of Matheson Tri-Gas Inc.

References

1. D.D. Koleske, A.E. Wickenden, R.L. Henry, M.E. Twigg, *Journal of Crystal Growth*, 242, pp. 55–69, 2002.
2. G. Vergani, M. Succi, E.J. Thrush, J.A. Crawley, W. Van der Stricht, et al., *Proc. 43rd Annual Technical Meeting of the Institute of Environmental Sciences*, pp. 262–272, 1997.
3. H.H. Funke, B.L. Grissom, C.E. McGrew, M.W. Raynor, *Review of Scientific Instruments*, 74, pp. 3909–3933, 2003.
4. S. Salim, M.M. Litwin, J.P. Natwora, Jr., *Proc. Semicon West, Workshop on Gas Distribution Systems*, pp. D1–D17, 1998.
5. G..M. Mitchell, V. Vorsa, J.A. Milanowicz, D.J. Ragsdal, K.L. Marhefka, et al., *Gases and Technology,* 2, pp. 8–13, 2003.
6. S.-Q. Wu, J. Morishita, H. Masusaki, T. Kimishima, *Analytical Chemistry*, 70, pp. 3315–3321, 1998.
7. A.O. Wright, C.D. Wood, K.J. Reynolds, M.L. Malczewski, *MICRO*, 22, pp. 47–55, 2004.
8. R. Hardiman, D. McKee, K. Kimmerle, *Proc. Semicon West, STS: Innovations in Semiconductor Manufacturing, Session 106*, p. 101, 2003.
9. D.-C. Hovde, J.T. Hodges, G.E. Scace, J.A. Silver, *Applied Optics*, 40, pp. 829–839, 2001.
10. H.H. Funke, M.W. Raynor, B. Yucelen, V.H. Houlding, *Journal of Electronic Materials*, 30, pp. 1438–1447, 2001.
11. J.D. Hogan, ed., *Specialty Gas Analysis, A Practical Guide Book*, Wiley-VCH, New York, 1997.

Hans H. Funke *is a senior research scientist at the Advanced Technology Center of Matheson Tri-Gas Inc., 1861 Lefthand Circle, Longmont, CO 80501; ph 303/678-0700 ext. 323, fax 303/442-0711, e-mail hfunke@matheson-trigas.com.*
Andrew O. Wright *is a senior scientist in sensor development and support at Delta F Corp., 4 Constitution Way, Woburn, MA 01801-1087; ph 781/935-4600 ext. 272, e-mail andyw@delta-f.com.*
Solid State Technology October, 2004

Author(s) : Hans H. Funke Mark W. Raynor Andrew O. Wright Jianlong Yao