Moisture Measurements in Semiconductor Process Gases Using Cavity Ring-Down Spectroscopy*

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Introduction

"CRDS has become more common as stable, tunable lasers have become readily available in small sizes and at modest cost."

In this article we present recent research results applying cavity ring-down spectroscopy (CRDS) to the measurement of water vapor in N_2 and PH_3. In addition to being the first reported application of this technique to phosphine gas, we have what we believe is a unique capability to correlate H_2O impurity level with the materials properties of epitaxial AlInP grown with PH_3. Our instrument is sufficiently stable and responsive to allow real-time monitoring of H_2O concentrations as well. Our current sensitivity is 10 nmol/mol (ppbv) of water in nitrogen gas, which rises to approximately 200 nmol/mol in PH_3 owing to interference from weak PH_3 absorption lines in the vicinity of the 936 nm water absorption lines. Because the absorption strength of the lines is well known, the method has excellent accuracy without the need for calibration with reference gas mixtures.

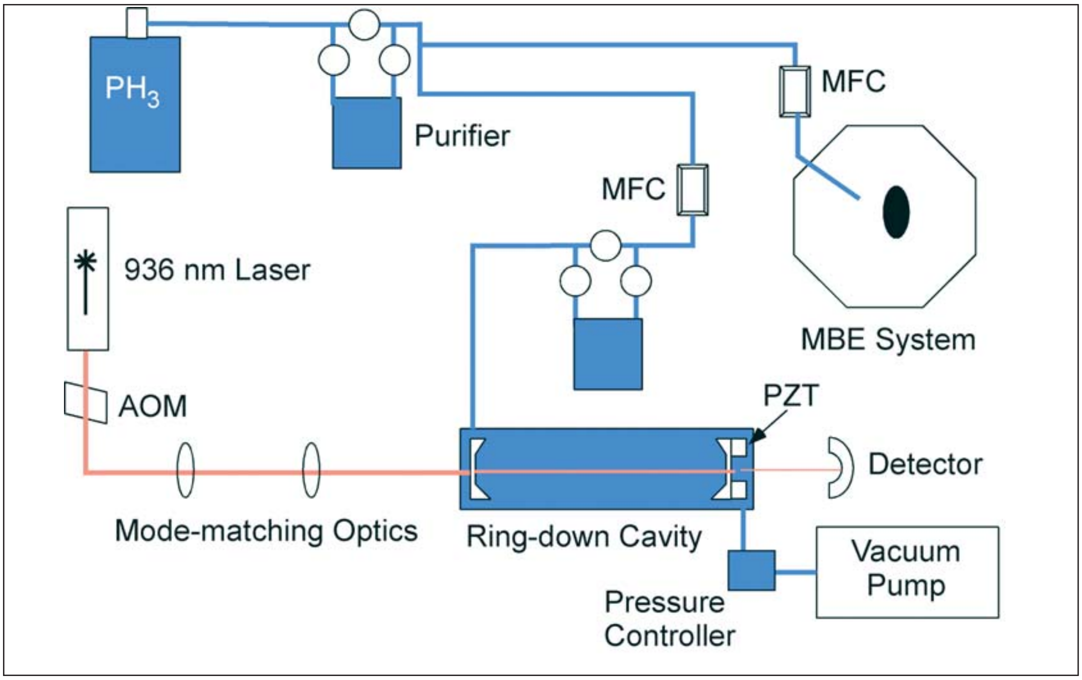

Figure 1: Simplified schematic of the experimental apparatus.

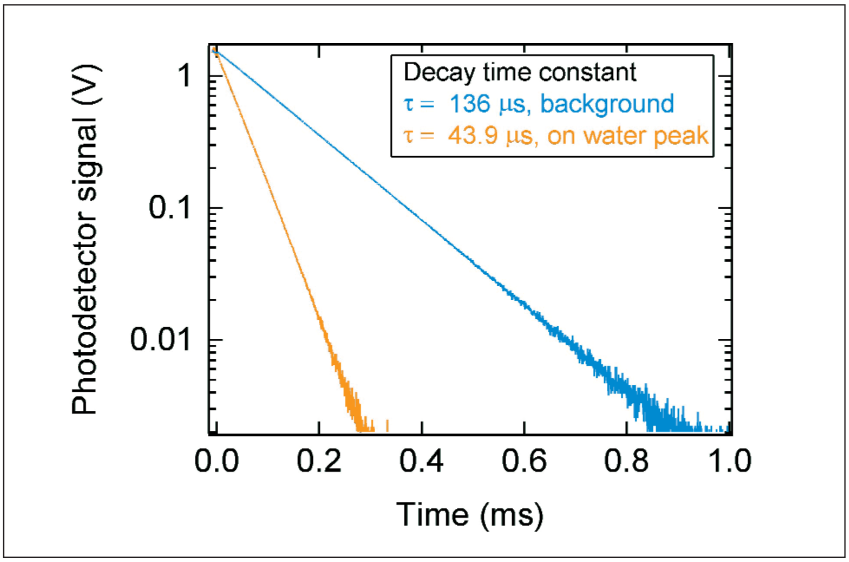

Figure 2: Examples of ring-down intensity decay signals for laser tuned to the H_2O absorption peak (red curve) and far from the peak (blue curve).

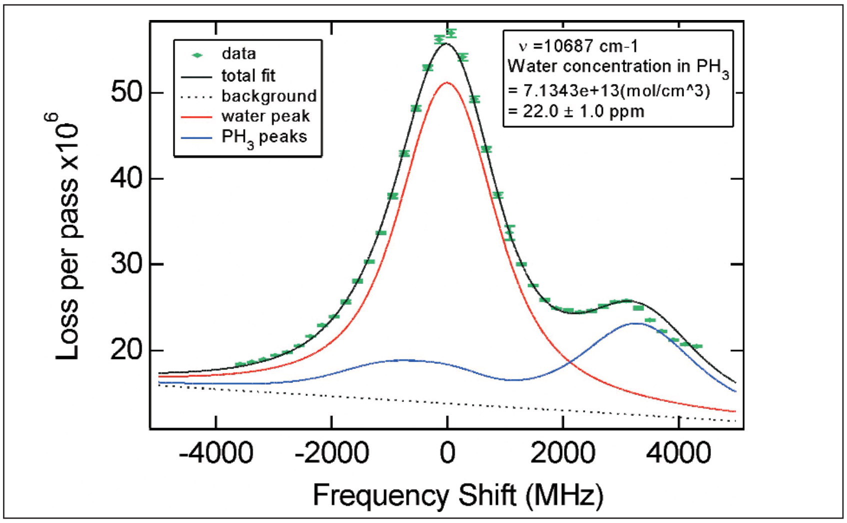

Figure 3: Loss spectrum for H20 in PH3 without in-line purification.

CRDS [1-5] has become more common as stable, tunable lasers have become readily available in small sizes and at modest cost. The basic principle of the technique is as follows. The passive decay of light intensity in a resonant optical cavity occurs at a rate determined by the total cavity losses. For single-mode excitation the intensity follows an exponential time dependence characterized by a single time constant. Consequently, the absorption spectrum of a gas within a resonator can be determined by measuring the wavelength or frequency dependence of the cavity time constant (which is inversely proportional to the total losses). The principal losses include absorption in the cavity (given by the product of absorber number density and its absorption cross-section), and transmission, scattering and absorption by the cavity mirrors.

In practice, a resonant optical cavity (i.e., the ring-down cavity) is formed with two (or more) high reflectivity dielectric mirrors. Laser light is sent into the cavity through one of the mirrors, and the cavity fills with light only when the laser frequency is resonant with a cavity mode. The light intensity in the cavity is monitored by measuring the optical power leaking out the mirror at the other end of the cavity. When the monitoring photodetector senses a strong build-up of light intensity in the cavity, the laser light is switched off to initiate the passive decay of energy from the ring-down cavity.

By probing a distinct absorption transition of H_2O, the transition line shape and peak area can be measured and related simply to the H_2O concentration. When expressed as a mole fraction x_w (in typical units of nmoles of H_2O per mole of host gas, commonly referred to as "ppb" or "ppbv"), the H_2O concentration is given by $x_w = (A_{peak}/LS) * (k_bT/P)$, where A_{peak} is the area under the loss vs. frequency curve for the H_2O line, L is the cavity length, S is the line strength of the H_2O peak, k_b is the Boltzmann constant, T is the gas temperature and P is the gas pressure.[2] A_{peak} is determined by fitting the peak with a Voigt function combined with appropriate background loss subtraction.

Experiment

A simplified schematic of the equipment used in this experiment is given in Fig. 1. PH_3 flows from a cylinder through mass flow controllers (MFCs) to both the ring-down cavity and the gas-source molecular beam epitaxy (MBE) machine, with optional purifiers placed in two locations. The laser source is an external-cavity diode laser operating near 935.7 nm in order to probe a water absorption line with a center at 935.68 nm or 10687.36 cm^{-1}. The total cavity volume is approximately 200 cm^3, and a typical operating pressure is 13.3 kPa (100 Torr). Ring-down signals are initiated by altering the state of the acousto-optic modulator (AOM) so that the laser input to the cavity is switched off. The cavity length is adjusted with the piezoelectric transducer (PZT) mount used for the right-hand mirror. The PZT voltage is controlled with

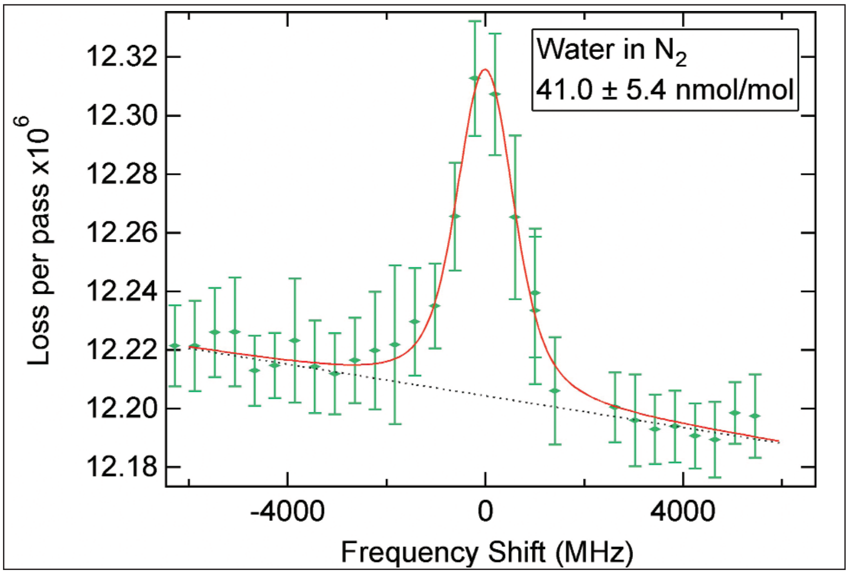

Figure 4: Loss spectrum for H_2O in N_2 showing that the lowest detectible concentration is about 10 nmol/mol.

a feedback loop based on the measured transmission of a 633-nm wavelength HeNe laser beam traveling into the cavity from the right (not shown).

A pair of 100-cm radius-of-curvature mirrors separated by 74.1 ± 0.2 cm form the ring-down cavity. The mirrors have a dielectric coating with reflectivities of 0.99999 and 0.95, near 936 nm and 632 nm, respectively. The effective interaction length at 936 nm is > 120 km by virtue of the extraordinarily low-loss mirrors employed. The mirror alignment and external optics are adjusted so that the fundamental transverse mode (a simple Gaussian cross-section) is the dominant mode excited as the laser frequency is tuned.

In order to take a spectrum, the laser is tuned through successive longitudinal mode orders of the fundamental transverse mode. This set of longitudinal modes forms a comb of frequencies with a spacing equal to the cavity free spectral range of 202 MHz. The feedback system discussed above provides active control of the cavity length and locks absolute cavity eigenfrequencies to 2 MHz. The frequency comb provides a well-defined frequency axis for the measured spectra, independent of probe laser tuning and drift. The absolute frequency of the laser is determined with a wavemeter in order to unambiguously locate and assign the H_2O absorption transition being probed.

Moisture Measurements in PH_3 and N_3

Typical ring-down signals from our system are shown in Fig. 2, with the red curve taken at a frequency at the peak of the water absorption line and the blue curve taken at a frequency far from the peak. Both curves have been corrected for the background noise in the detector. These data were taken with PH_3 flowing through the cavity at 62 ± 3 standard cm^3 min^{-1}(sccm). The total optical losses per pass are 57 x10^{-6} and 18 x10^{-6}, respectively, for the peak water absorption (red) and the background (blue) curves.

The full loss spectrum vs. frequency shift relative to the H_2O line center is given in Fig. 3. The water concentration is determined by taking the area of the Voigt function fit to the water peak, as described above, and for this data set yields a water concentration of 22.0 ± 1.0μmol/mol (ppmv). Also evident in this spectrum are two or three PH_3 peaks. The peak at negative frequency shift appears to consist of two closely spaced peaks, one very near the water line. This "near-zero-shift" peak is also present when purified PH_2 is flowing through the cavity, when the water concentration is expected to be

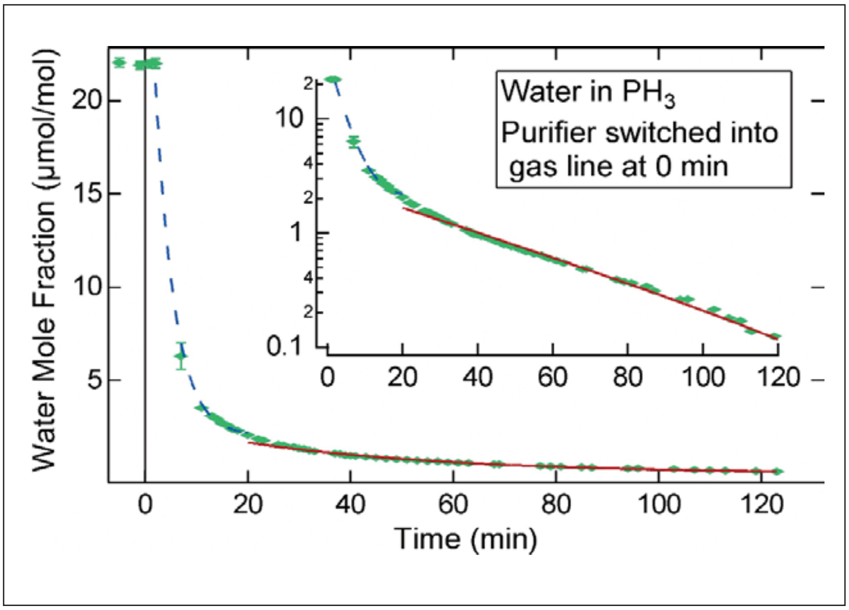

Figure 5: Real-time measurements of H_2O in PH_3 as a purifier is switched into the gas stream.

below the detection limit of our instrument, but it is still possible that this peak represents residual water. These background peaks make it difficult to reach the ultimate sensitivity of the instrument in PH_3.

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Fig. 4 shows that a peak corresponding to 41.0 ± 5.4 nmol/mol (ppbv) is readily resolved by the instrument when the host gas is N_2, where the lower detectability limit is about 10 nmol/mol. In PH_3, the lower detectability limit is currently about 200 nmol/mol, though it should be possible to reduce this with further refinement of the PH_3 background subtraction.

Real-time Measurements and Materials Correlations

Although the width of the water absorption line and hence the ratio of its area to its peak height both vary with pressure and matrix gas, when these conditions are held constant the water concentration can be extracted from the peak height alone. Fig. 5 illustrates real-time monitoring of the moisture content of PH_3 as a purifier is switched into the gas line approximately 6 m upstream of the ring-down cavity. After a short time delay for purified gas to begin to reach the cavity, the moisture content drops rapidly as the gas volume in the cavity is replaced with purified gas. The gas volume purge takes about 20 minutes at a flow rate of 62 ± 3 sccm. This initial rapid decay is followed by a slower decay that continues for over 120 minutes. This decay is attributed to desorption of water from the tubing and cavity walls, a process that is clearly not yet fully complete after two hours.

One of the more surprising results of our studies to date has been that AlInP grown by gas-source MBE is not very sensitive to water contamination in PH_3.[1] To test the correlation, two layers of p-type $Al_{0.58}In_{0.42}P$ were grown, one with and one without an in-line purifier in the PH_3 line. The unpurified PH_3 was measured to have an H_2O concentration of 18.0 ± 1.5 μmol/mol, while H_2O concentration in the purified PH_3 was found to be no greater than the detection limit of 200 nmol/mol. The layers were nearly identical in their oxygen content as measured by SIMS, with O concentrations of 6.7×10^{17} and 5×10^{17} cm^{-3}, respectively.[6] Both layers also showed excellent and nearly identical photocurrent response in an illuminated electrochemical cell.[1]

Future Directions

We have demonstrated that ring-down cavity spectroscopy can be applied to real-time measurement of H_2O as an impurity in PH_3 and N_2 gases, with excellent sensitivity and accuracy. Our next steps include measuring pressure-broadening coefficients to allow extraction of H_2O concentrations from losses at the peak frequency alone under a number of operating conditions. We plan to pursue further improvements in lower detection limits by mapping out background peaks and moving to a longer wavelength region where the absorption strength of H_2O lines is greater. This experiment makes conflicting demands on the laser source, with ideal behavior including tunability over several GHz and linewidth of the order of a kHz. As laser technology develops further, the practical range and durability of these types of instruments will improve dramatically.

Acknowledgment

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