

Trace water detection in semiconductor-grade phosphine gas*

K. A. Bertness, S. Y. Lehman,^[a] J. T. Hodges^[b], H.H. Funke, M.W. Raynor^[c]

^[a] National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80305, USA

^[b] National Institute of Standards and Technology, 100 Bureau Dr., Gaithersburg, MD 20899, USA

^[c] Matheson Tri-Gas Advanced Technology Center, Longmont, CO, 80501, USA

Abstract. We are applying cavity ring-down spectroscopy (CRDS) to measure water concentrations in nitrogen and, for the first time to our knowledge, in phosphine. Semiconductor-grade phosphine cylinders from different suppliers contained water in the several ppm range. Moisture levels were also measured with in-line, point-of-use purifiers from different manufacturers. To date, the lowest water mole fraction measured in this system is $(150 \pm 30) \times 10^{-9}$ (150 ppb) in a nitrogen matrix. At our present signal-to-noise levels our detection limit is approximately 30×10^{-9} . We also present material studies of AlInP grown with characterized phosphine in a gas-source molecular beam epitaxy machine.

1. Introduction

We report on the first measurements of water concentration as an impurity in phosphine gas using the cavity ring-down spectroscopy (CRDS) technique [1, 2]. CRDS offers high sensitivity and high accuracy without requiring calibration with gas mixtures or the control of water vapor concentrations outside the active gas cell. The lowest detectable concentration of our instrument is approximately 50×10^{-9} moles of water per mole of PH_3 , and the accuracy at the $\mu\text{mole/mole}$ level is $\pm 10\%$ or better. In this experiment, a CRDS system was constructed so as to share a PH_3 gas line with a gas-source molecular beam epitaxy (MBE) machine. Water is a detrimental impurity in III-V semiconductors, particularly those containing Al [3]. Nevertheless, we have found that unpurified PH_3 containing $18.0 \pm 1.7 \mu\text{mol/mol}$ of water produced only a small increase in the amount of oxygen incorporated into AlInP as grown by gas-source MBE.

2. Experiment

A simplified diagram of our experimental set-up is given in Fig. 1. The active region of the ring-down cavity is formed by two high-efficiency mirrors of nominal reflectance 0.999985 mounted in a sealed volume. A piezoelectric transducer is used for precise translation of one cavity mirror, thus enabling the consistent excitation of a specific cavity mode as the laser frequency is tuned. A tunable, continuous-wave, single-mode external-cavity diode laser emitting in the spectral range 920 nm to 940 nm is used as a probe laser. Ring-down signals are measured by use of a Si-PIN photodetector with 200 kHz bandwidth. When the detector indicates that the cavity is in resonance and filling with light, the laser beam into the cavity is rapidly switched off with an acousto-optic modulator (AOM), thus initiating the passive exponential decay of recirculating light within the ring-down cavity. The time constant of this decay is limited by the optical losses in the mirrors and is reduced as a consequence of light absorption by gas molecules within the ring-down cavity. Spectral scans are achieved by tuning the diode laser and cavity together to maintain excitation of the fundamental Gaussian transverse mode. CRDS measurements were normally made with a nominal gas flow rate of $10 \text{ standard cm}^3 \text{ min}^{-1}$ and nominal cavity pressure of 13.33 kPa (100 Torr). The data in this paper were all acquired for the water absorption line at 935.68451 nm (10687.36 cm^{-1}), one of the strongest lines in this wavelength neighborhood. The cavity is also equipped with a diffusion tube and mixing manifold containing mass flow controllers (MFC) to generate variable concentrations of water in PH_3 by adding nitrogen doped with water to the gas stream. $\text{Al}_{0.58}\text{In}_{0.42}\text{P}$ layers were grown using gas-source MBE at a growth temperature of approximately 480 °C. PH_3 was thermally decomposed upon entry into the MBE chamber by passing the gas through a ceramic tube heated to 1050 °C.

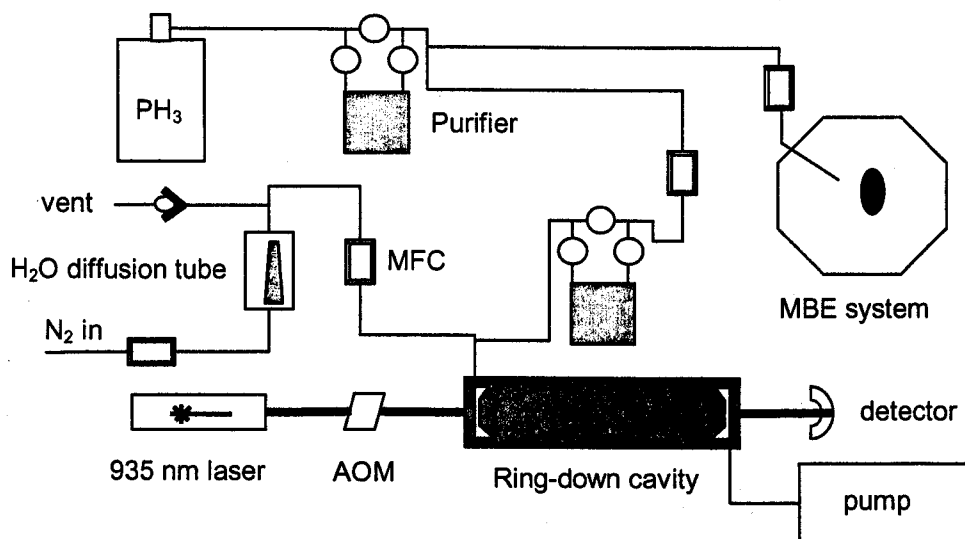


Fig. 1. Diagram of ring-down cavity and gas handling system.

3. Results

By measuring the decay lifetime as a function of frequency in the vicinity of a water absorption line, we can calculate the water concentration in the cavity[1]. Because water is present in the atmosphere, the cavity walls and any tubing exposed to air will absorb water that must be removed to obtain the lowest background levels. Fig. 2 shows the water absorption peak before and after extensive purging and modest heating of the cavity. The integrated area under the loss per pass peak is directly proportional to the water concentration. The initial water concentration in the cavity was $1.4 \pm 0.2 \mu\text{mol/mol}$, which decreased to $0.15 \pm 0.03 \mu\text{mol/mol}$ with purging. Fig. 2 also shows that smaller water concentrations would be detectable; we estimate the detection limit of the system to be approximately one-third of the lowest concentration measured in Fig. 2, or 50 nmol/mol . This limit is slightly higher than the 10 nmol/mol obtained using Fourier transform infrared spectroscopy (FTIR)[4], while retaining the advantages of CRDS, namely operation without the need for calibration and the insensitivity to water vapor outside the active gas cell.

The results of water measurements in PH₃ are given in Fig. 3, where the loss per pass as a function of frequency is plotted for PH₃ delivered straight from the cylinder to the cavity and for PH₃ purified using the purifier next to the cylinder in Fig. 1. The vertical scale for Fig. 3 is larger than for Fig. 2. The peaks at approximately -700 MHz and $+3000 \text{ MHz}$ appear to be weakly absorbing PH₃ lines. These peaks are present at the same intensity levels regardless of the water concentration. Cylinders with special low-quantity fills were purchased from more than one vendor, and all cylinders tested contained water at the several $\mu\text{mol/mol}$ level.

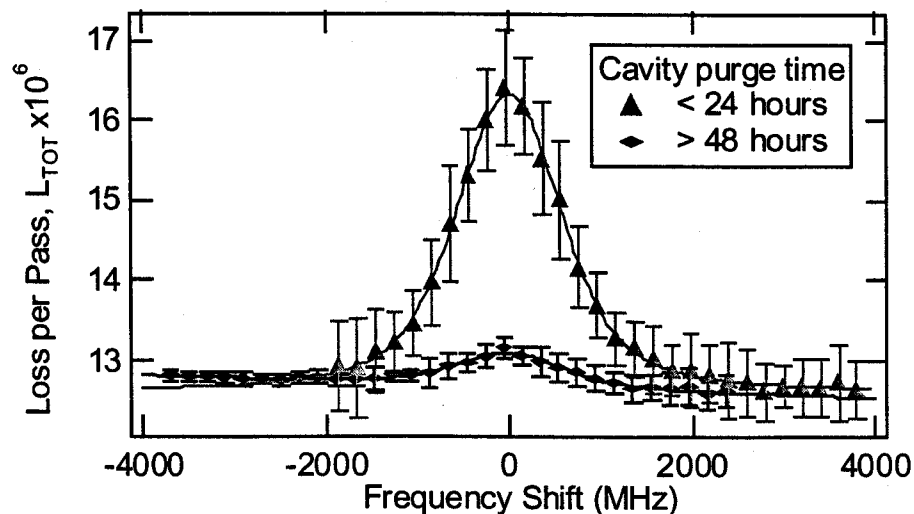


Fig. 2. CRDS data for dry nitrogen flowing through the cavity. Increased purge time reduces the water background in the cavity. Zero frequency shift corresponds to line center of the 10687.36 cm^{-1} H₂O absorption transition.

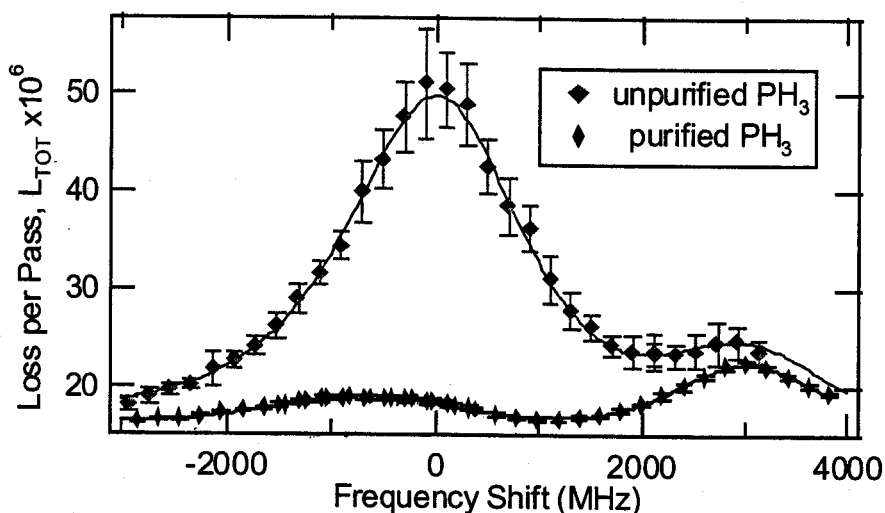


Fig. 3. CRDS data for phosphine gas with and without in-line purification. The water concentrations for the two conditions are $0.0 (+1.4 / -0)$ $\mu\text{mol/mol}$ and 18.0 ± 1.7 $\mu\text{mol/mol}$, respectively.

The PH_3 cylinder used to acquire the data in Fig. 3 was also used to grow two epitaxial layers of $\text{Al}_{0.58}\text{In}_{0.42}\text{P}$ in a single growth run, one layer with and one layer without PH_3 in-line purification. The layers were separated by a GaAs spacer layer, and the PH_3 line was purged thoroughly between AlInP layer growth to assure that the gas reaching the growth chamber reflected the water concentration at the purifier manifold. The layers were analyzed by a commercial secondary-ion mass-spectroscopy service. The oxygen concentration in the layer grown with purified PH_3 was 1.5×10^{17} O atoms/ cm^3 , indicating reasonably good material quality[5-8]. Somewhat surprisingly, the oxygen background increased by only 2×10^{16} O atoms/ cm^3 when unpurified PH_3 was used. Because organometallic vapor phase epitaxy is generally thought to require water impurity levels below 1 $\mu\text{mol/mol}$ to obtain material of good quality, these results imply that the gas-source MBE process is less sensitive to contamination. This insensitivity may come from the high-temperature cracking of the gas upon entry into the vacuum chamber.

4. Conclusions

These results demonstrate the first successful application of CRDS to the measurement of water as an impurity in PH_3 and nitrogen. Cylinders from more than one vendor were found to contain water at the several $\mu\text{mol/mol}$ level. The use of conventional purifiers reduced the water concentration below the sensitivity of our CRDS system. Our materials quality results suggest that materials grown by gas-source MBE are largely insensitive to water contamination.

5. Acknowledgments

This work was supported in part by the Advanced Technology Program, administered by the National Institute of Standards and Technology for the U.S. Department of Commerce.

Footnote

* This paper is a contribution of an agency of the U.S. government and is not subject to copyright.

References

- [1] van Zee RD, Hodges JT, Looney JP 1999 *Appl. Optics* **38**(18) 3951-3960.
- [2] Romanini D, Kachonov AA, Sadeghi N, Stoeckel F 1997 *Chem. Phys. Letters* **264** 316-322.
- [3] Bertness KA, Kurtz SR, Asher SE, Reedy RC, Jr. 1999 *J. Cryst. Growth* **196** 13-22.
- [4] Funke HH, Raynor MW, Yücelen, Houlding VH 2001 *J. Electron. Mat.* **30**(11) 1438-1447.
- [5] Kondo M, Okada N, Domen K, Sugiura K, Anayama C, Tanahashi T 1994 *J. Electron. Mat.* **23**(3) 355-358.
- [6] Suzuki M, Itaya K, Nishikawa Y, Sugawara H, Okajima M 1993 *J. Cryst. Growth* **133** 303-308.
- [7] Nishikawa Y, Suzuki M, Ishikawa M, Kokubun Y, Hatakoshi G-c 1992 *J. Cryst. Growth* **123** 181-187.
- [8] Hafich MJ, Woods LM, Kim HS, Patrizi GA, Robinson GY 1993 *J. Cryst. Growth* **127** 995-8.