PROCESS GATES

Spectroscopy exposes trace-water contamination in process gases

A highly sensitive optical technique known as cavity ring-down spectroscopy can reveal minute levels of water contamination in MOCVD process gases such as arsine and can demonstrate the true benefit of point-of-use purification, say **Jun Feng** and **Mark Raynor** from Matheson Tri-Gas and **Yu Chen** from Tiger Optics.

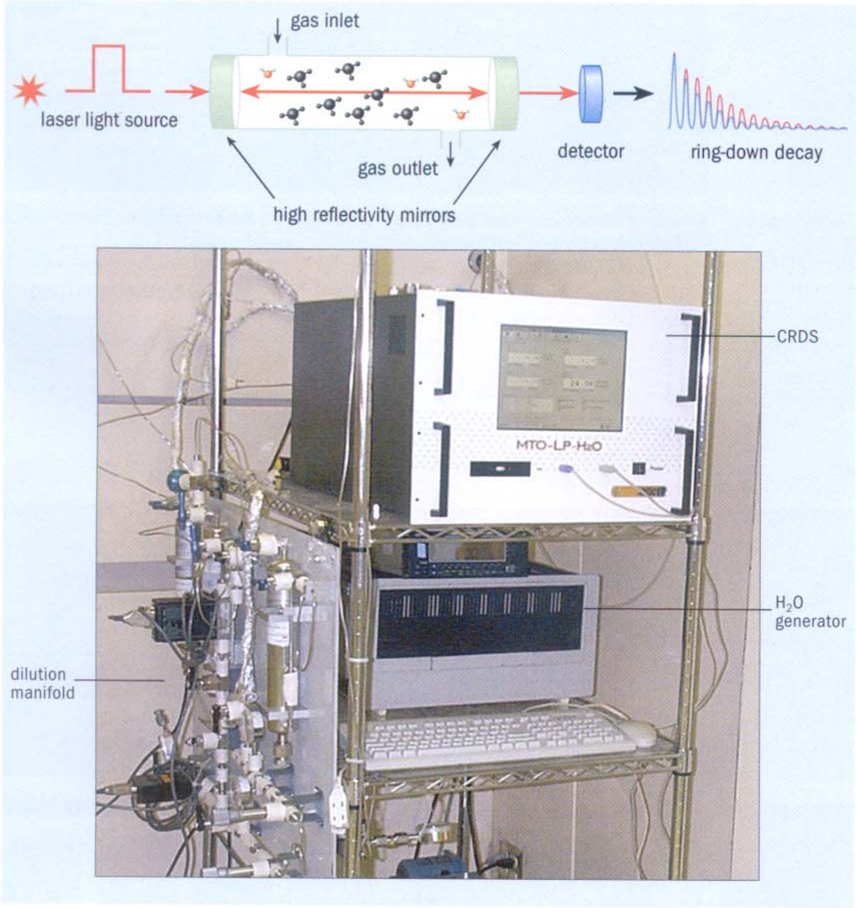


Fig. 1. Cavity ring-down spectroscopy can expose incredibly low levels of water in arsine and phosphine gases. The approach is based on injecting laser light into a cavity and measuring the decay signature of the small proportion of light that escapes when the laser is turned off.

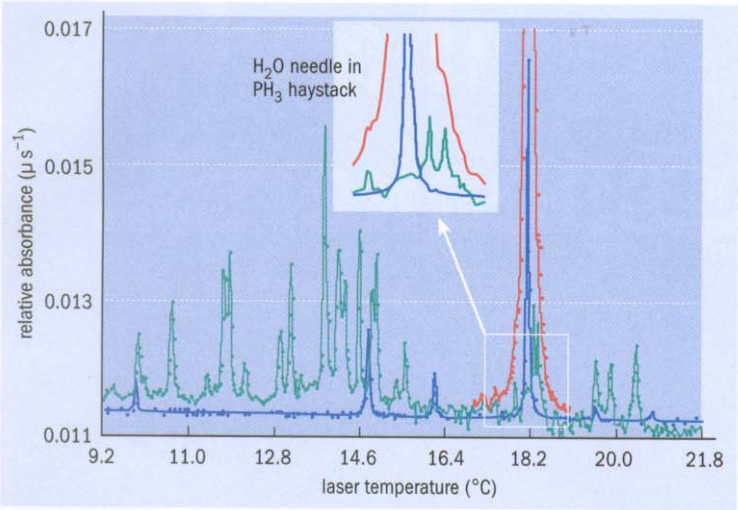
Finding an affordable and reliable means of measuring trace contaminants in the MOCVD process gas arsine poses a considerable challenge. But earlier this year, that is just what Matheson Tri-Gas set out to do when it embarked on a collaboration with Tiger Optics, a pioneer of continuous-wave cavity ring-down spectroscopy (CRDS), which is a new laser-based technique for gas analysis.

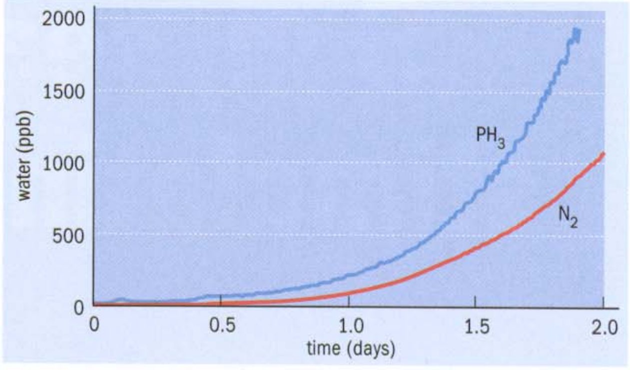
By developing techniques to measure and control water contamination in arsine and phosphine, the partnership has found a route to manufacturing better-performing devices. This is because traces of water vapor and oxygen are the enemy of III-V devices, killing photoluminescence and degrading other properties. Oxygen is incorporated into epilayers from various sources, including incomplete purging of atmospheric contaminants from the tool, unwanted methoxide species that can be found in the organometallic precursor, and oxygenated impurities, such as water, which are present in the hydride gas. Even water levels of single-digit parts per billion (ppb) can cause marked damage to AlGaAs films. It is this molecule, rather than oxygen, that is often targeted by process engineers because water's ubiquitous nature makes it the hardest impurity to control.

To date, manufacturers seeking to confirm the purity of their MOCVD process gases, in particular arsine, have had few viable options. Based on their low cost and ease of use, capacitance sensors have commonly been employed for online water monitoring in this application. But these are far from ideal because they can drift and they are insensitive to low ppb levels. So chip manufacturers prefer to qualify their MOCVD process gases by measuring the performance characteristics of a test device, such as photoluminescence, carrier concentration and mobility. This approach may become less popular, however, if highly sensitive laser spectroscopy techniques, such as CRDS, become more widely used to monitor process lines.

Matheson turned to Tiger Optics in the hope that its CRDS gas monitor might lend itself to trace-water detection in MOCVD hydride gases. With its proven stability and wide dynamic range, the CRDS technique uses laser light to provide optical excitation of gases in a stable cavity resonator formed between two highly reflective mirrors (figure 1). The light that is injected into the cavity reflects back and forth many times and builds up in intensity. However, with each reflection a very small fraction of light leaks out to a detector. The so-called ring-down signal is measured when the light source is abruptly turned off. If the light is also absorbed by water in the cavity, it will decrease the decay time for this signal. The water concentration can then be calculated from the ring-down time measurements made on and off the water line.

The CRDS technique has strengths that include a sensitivity to water at levels of single-digit ppb or bet-





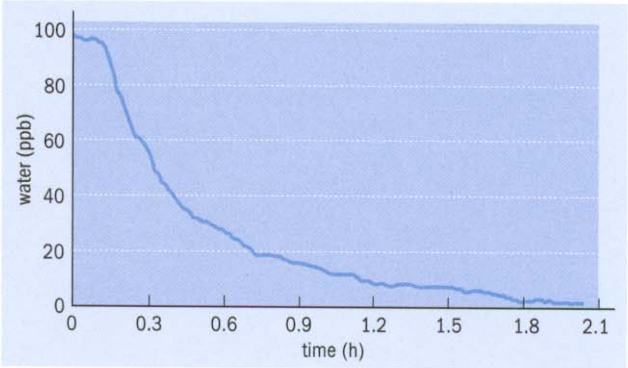


Fig. 2. (above) Water has a very strong absorption peak that is sufficiently removed from those of phosphine to allow detection in the spectral range between 1300 and 1400 nm. The prominence of this peak can be seen in the three different absorption spectra: 120 ppb water in N_2 (blue); dry PH_3 (green); and 1.5 ppm water in PH_3 (red). **Fig. 3.** (above right) Stagnant conditions can lead to a substantial build-up in the concentration of water vapor in both nitrogen and phosphine process gases over the course of a couple of days. **Fig. 4.** (right) Purifying arsine with an in-line Matheson Tri-Gas Nanochem ASX-II purifier at a flow rate of 800 cm^3/min can drive down water levels from 100 ppb to less than 5 ppb within two hours, with a pay-off in higher wafer yield.

ter, due to a measurement technique that creates an effective path-length of typically tens of kilometers. CRDS also has a high degree of selectivity, thanks to the use of a high-resolution laser and the option to conduct measurements at low pressure.

Nevertheless, one of the major challenges of trace-water vapor measurements in hydride gases is identifying a suitable wavelength where water absorbs but the matrix gas (arsine, phosphine, ammonia) doesn't. There is so much interference that the proverbial needle in a haystack comes to mind. Hydride gases have absorbances in many regions of the electromagnetic spectrum, which mask many of the absorption peaks of water at low ppb levels. Therefore, it is extremely difficult to detect the presence of trace water in a hydride gas.

To find a suitable wavelength for water detection in each hydride gas, Tiger Optics characterized and tested 10 custom diode laser sources in the 1.3–1.4 μm spectral range. Figure 2 shows a water absorption line that corresponds to a laser operating at 18.12 °C. This peak is sufficiently resolved from the PH_3 matrix absorbances to enable the single-digit ppb detection of water.

Matheson had thus unlocked the door to detecting low levels of water contamination and it followed this up by testing the technology's suitability for use in a commercial product. This involved tests for accuracy, linearity, sensitivity, limit of detection and response time on a Tiger Optics' MTO-LP-H_2O CRDS analyzer. Matheson Tri-Gas Ultima grade arsine and phosphine, which were passed through Nanochem ASX-II and PHX purifiers, were used as the diluent gases, and a certified water generator and dilution manifold were used to spike water vapor into the diluent gas at various concentrations (figure 1).

Matheson's tests verified that CRDS is a key technology for monitoring trace water vapor in hydride gas streams and for evaluating the dry-down of process gas lines. Measurements revealed that the concentrations of water-spiked gas measured by CRDS agreed to within 2% with the values intentionally added through the dilution manifold. The instrument can detect water down to single-digit ppb concentrations, is sensitive to changes in water concentration of less than 1 ppb and provides a linear response to the presence of water in the tested range of tens to hundreds of ppb.

The CRDS technique also reveals that even when a system has been thoroughly leak-checked and purged extensively with a dry gas stream, out-gassing of water from metal surfaces can continue for long periods and may build up if the gas flow is stopped for any reason. According to our tests, this contamination can reach levels of a 1000 or more ppb after two days under stagnant conditions (figure 3). Notably, the water levels increase more rapidly in phosphine than in nitrogen.

This high water-level implies that the high-purity process gases, which are mandatory for oxygen-sensitive MOCVD processes, must be used in conjunction with a line purge when hydride gas is not flowing. To minimize any water variations further, point-of-use purification should be employed in the line close to the tool. In tests using a Nanochem ASX-II purifier to remove water from an arsine line, this approach reduced water concentration in arsine to less than 5 ppb within two hours (figure 4). Such a reduction in water contaminants should have a pay-off in improved yields and higher device performance, and it makes an investment in process gas purity highly worthwhile.

About the authors

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