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Parts-per-trillion sensitivity for trace-moisture detection using wavelength-meter-controlled cavity ring-down spectroscopy

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ABSTRACT
We introduced frequency-control and temperature-control systems in wavelength-meter-controlled cavity ring-down spectroscopy. The frequency-control system shifted the wavelength of the probe laser from 1393 nm to 696.5 nm where no strong absorption lines of water exist, and therefore, it could avoid measurement errors in laser frequency due to residual moisture in the built-in Fizeau interferometer of a wavelength meter. We verified the hypothesis that the nonuniform reflectivity of the mirror surface contributes to fluctuations in the ring-down time observed with multi-transverse-mode CRDS signals. The fluctuations due to this effect were greatly suppressed by the temperature-control system. Using this system, we could improve the minimum detectable absorption coefficient by three times on average and also improve the experimental standard deviations of the averages by nine times compared with those without the system. We measured near-infrared spectra of residual moisture in dry nitrogen at an approximately 1 nmol/mol (1 ppb) level and performed least-squares fitting of the averaged spectrum. The standard deviation of the residuals of the fitting was 6.6 × 10⁻¹² cm⁻¹, corresponding to a mole fraction of water of 6.3 pmol/mol (6.3 ppt).

I. INTRODUCTION

The demand for accurate measurement of trace moisture in high-purity industrial gases at a level of 10 nmol/mol (10 ppb) or lower has been increasing in the semiconductor industry. Cavity ring-down spectroscopy (CRDS)1–5 has been a powerful technique for such measurements.6–9 CRDS uses a high-finesse optical cavity (optical resonator) with high-reflectivity mirrors and can thus obtain a very long effective pathlength, making this technique highly sensitive. However, one issue in using a high-finesse cavity is that the frequency of the probe laser must be accurately and precisely controlled to match the resonant frequency of the cavity; CRDS can perform measurement only when the frequency of a laser matches the resonant frequency of the cavity. The width of the resonant frequencies becomes narrower as the reflectivity of the mirrors becomes higher, so it becomes more difficult to efficiently match the laser frequency to the resonant frequency with a higher reflectivity. Various techniques have been developed to overcome this issue.10–16

In our previous study, we proposed a relatively simple technique for CRDS with a high-finesse cavity to fulfill the resonant condition. First, we stabilized the resonant frequencies of the cavity with reference to the frequency of a helium–neon (He–Ne) laser, which is known as “frequency-stabilized CRDS (FS-CRDS),” developed by Hodges et al.17 Second, we controlled the frequency of the probe laser to match a resonant frequency using a high-resolution wavelength meter. This technique, referred to as the “wavelength-meter-controlled” technique, does not require a narrow linewidth probe laser such as an external cavity diode laser, electronics for the fast feedback loop, wavelength modulation, and cavity length modulation, which are commonly used to couple a laser with a high-finesse cavity. In our previous study, we evaluated the performance of the wavelength-meter-controlled CRDS using a primary trace-moisture standard. The measured values with our CRDS were in good agreement with the certified values.
agreement with the values of the trace-moisture standard in the range of 13 ppb–157 ppb. We measured a near-infrared spectrum of the trace moisture and obtained a standard deviation corresponding to 12 pmol/mol (12 ppt) for the fitting residuals of the spectrum.

However, there remained two challenges in our previous system: it is always necessary to correct errors in the laser frequency measured using a wavelength meter, and there are fluctuations in the ring-down time, \( \tau \), owing to temperature fluctuations of the cavity. In the present study, we adopted a new frequency-control system and a precise temperature-control system to address these two challenges.

II. EXPERIMENTAL SETUP

The experimental setup used in this study was essentially the same as that used previously except the frequency-control and temperature-control systems. The length of the cavity, \( L \), was 70.9 cm, and the reflectivity of the mirror, \( R \), was 0.999 978 1. A distributed feedback (DFB) laser at 1393 nm was used as the probe laser. The details of the frequency-control and temperature-control systems will be described in Sec. III.

III. RESULTS AND DISCUSSION

In wavelength-meter-controlled CRDS, the frequency of the laser is controlled to match a resonant frequency of the cavity on the basis of the frequency measured by a wavelength meter. However, in our previous study, we found systematic errors in the frequency measurement due to dispersion (change in the refractive index) caused by residual moisture in the built-in Fizeau interferometer of the wavelength meter. The residual moisture could not be removed by purging the inside of the wavelength meter with dry nitrogen because the built-in Fizeau interferometer consisted of a glass vacuum cell. The errors were particularly significant near the center of the water absorption lines, leading to a mismatch between the frequency of the probe laser and the resonant frequency. As a consequence, the repetition rate of \( \tau \) measurement (the number of ring-down times measured per unit time) was considerably reduced. Therefore, we had to measure the systematic errors as a function of frequency in advance and make corrections in the CRDS experiment. The red dots and black dots in Fig. 1, respectively, show the repetition rates obtained with and without the correction as a function of wavenumber. While the black dots near the center of the strongest water absorption line at 7181.14 cm\(^{-1}\) are lower than 10 Hz, the red dots are always higher than 60 Hz. This indicates that the repetition rates can be improved by correcting the errors.

However, the magnitudes of the systematic errors may vary with time because of, for example, a change in the vapor pressure of the residual moisture inside the Fizeau interferometer owing to the water adsorption/desorption. When this happens, the numerical values of the errors measured in advance are no longer accurate. This is a reason why the red dots shown in Fig. 1 are not stable in the entire range; the numerical values changed during the measurement. In addition, measurement of the systematic errors takes more than 8 h, so it is difficult in practice to regularly remeasure them. To overcome this challenge, in this study, we introduced a new system of controlling the laser frequency using a periodically poled lithium niobate (PPLN) waveguide module (WH-0696-000-F-B-C, NTT Electronics). The laser light was divided into two using a fiber coupler; one was used for the probe laser, and the other was guided to the PPLN. The PPLN converted the frequency of the laser at 1393 nm into that at 696.5 nm, and this doubled frequency was measured using the wavelength meter. The absorption strengths of water molecules at around 696.5 nm are three orders of magnitude weaker than those at around 1393 nm, and therefore, the measurement results are not affected by the residual moisture.

The frequency of the probe laser can easily be calculated by dividing it by two. The blue dots, shown in Fig. 1, are the repetition rates obtained using the new system. We could measure \( \tau \) rapidly and stably in the entire measurement region even without correction. The average and standard deviation of the repetition rates were 146 Hz and 10 Hz, respectively. It appeared that the highest repetition rate is currently limited by the performance of a personal computer used for the real-time analysis of \( \tau \). When we measured the number of the trigger signals used for switching off the laser using a universal counter, it was higher than 400 Hz, implying the potential improvement of the repetition rate. A small dip near 7181.14 cm\(^{-1}\) was caused by a decrease of the cavity transmission power due to absorption by atmospheric moisture, which can be reduced by introducing a better drying system for the optical path outside the cavity.

The second challenge is fluctuations in \( \tau \) due to the temperature fluctuations of the cavity. \( L \) may vary owing to thermal expansion produced by ambient temperature fluctuations. In wavelength-meter-controlled CRDS, it is necessary to stabilize \( L \) using the frequency-stabilized technique. In this technique, a piezoelectric actuator (PZT) connected to the mirror mount is used to stabilize \( L \). However, it is not easy to attach the mirror mount to the cavity so that the direction of the motion of the PZT is perfectly parallel to the optical axis of the cavity, and the direction of the motion can be slightly deviated from the optical axis. Hence, the point at
which the laser light reflected on the mirror surface changes with the mirror motion, and the reflectivity at the new point may be different from that of the original point owing to the nonuniform reflectivity of the mirror surface. This means that the reflectivity varies with the mirror motion, and therefore, the effective path-length also varies, leading to the fluctuations in $\tau$. This situation is evidenced in Fig. 2(a), where the red line and black line are the voltage applied to the PZT ($V_{PZT}$) to stabilize $L$ and $\tau$, respectively. $\tau$ was measured at 7180 cm$^{-1}$, where no strong absorption line of water exists. $V_{PZT}$ varied with time to compensate for the change in $L$ due to the thermal expansion of the cavity. $\tau$ also varied synchronously (in the antiphase) with $V_{PZT}$, suggesting a change in $R$ with time because $L$ was kept constant by the frequency-stabilized technique [note that $\tau$ is given by $L/c(1 - R)$, where $c$ is the speed of light]. In order to verify that this phenomenon was caused by the motion of the PZT, we manually changed $V_{PZT}$ and observed the change in $\tau$ in synchronization with $V_{PZT}$. In contrast, $V_{PZT}$ and $\tau$ were very stable after the introduction of a temperature-control system, as shown in Fig. 2(b). The system consisted of a heating wire, temperature sensor, and temperature controller. The heating wire was tightly wrapped around the cavity and was covered with aluminum foil to ensure homogeneous heating. The temperature of the cavity was kept constant at around 26 °C using the temperature controller by controlling the current applied to the wire heater.

In order to evaluate the effectiveness of the temperature-control system, a minimum detectable absorption coefficient (MDAC), defined by $\Delta a_{\text{min}}(\tau_N) = \sigma(\tau_N) / (c \tau_N)^2$, was investigated for cases with and without the temperature-control system, where $\tau_N$ is the average of $N$ measurements of $\tau$. $\tau_N$ and $\sigma(\tau_N)$ are the average and standard deviation of $m$ sets of $\tau_N$, respectively. This experiment was repeated 20 times for $N = 10^4$ (70 s on average) and $m = 10$. The results are shown in Fig. 3, where the blue and red circles represent the averages of the 20 repeated data with and without the temperature-control system, respectively, and the error bars are the experimental standard deviations of the averages. Using this system, we could improve the MDAC by three times on average and also improve the experimental standard deviation of the average by nine times compared with those without the system.

It is important to again emphasize the fact that the fluctuations in $\tau$ were attributable to the nonuniformity of $R$ on the mirror surface but not to the change in $L$. The change in $\tau$ is given by $\Delta \tau = [\Delta L/L + \Delta R/(1 - R)] \times \tau$, where $\Delta X$ is the change in a quantity $X$. The maximum change in $V_{PZT}$, observed as shown in Fig. 2(a), is 31 V, corresponding to $\Delta L = 3.8 \mu$m, according to the specification of the PZT used in this study (S-314.10, PI-Japan Co., Ltd.). This corresponds to $\Delta \tau = 0.0006 \mu$s when $L = 70.9 \, \text{cm}$ and $\tau = 107.7 \, \mu$s and does not explain the maximum value of $\Delta \tau = 0.95 \, \mu$s, as observed in Fig. 2(a), indicating that $\Delta \tau$ observed was attributable to the other parameter, that is, $R$. $\Delta \tau$ corresponds to $\Delta R = 0.000 \, \text{002}$ when $R = 0.999 \, 978 \, 1$, and it seems difficult to attain the uniformity of $R$ much better in other levels than in this level. This finding suggests that a temperature-control system will be effective to reduce $\Delta \tau$ even for FS-CRDS that precisely stabilizes $L$. The interpretation on the nonuniformity of $R$ on the mirror surface was also supported by the difference in $\tau$ observed between the TEM$_{00}$ and TEM$_{01}$ modes. Laser lights with these two modes in the cavity have different intensity patterns on the mirror surface, and, therefore, may have different effective mirror reflectivities. In fact, we observed a significant difference in $\tau$ between the two modes by 30% relative. This corresponds to $\Delta R = 0.000 \, 007$, indicating the nonuniformity in $R$ at this level. The numerical value of $R$ also depends on the laser frequency, and this is a primary cause of the baseline slope often observed in CRDS spectra. The difference in resonant frequency between TEM$_{00}$ and TEM$_{01}$ modes was 86 MHz in this study, and $\Delta \tau$ due to the frequency dependence of $R$ is estimated to be only 0.0002 $\mu$s, which does not explain the relative difference of 30% stated above. This means that fluctuations in $\tau$ observed with multimode excitation of the cavity originates in the nonuniformity of $R$ rather than the frequency dependence of $R$. This verifies the hypothesis suggested by Cormier et al. in Ref. 20, where they supposed that the fluctuations in $\tau$ observed with multimode signals were attributable to the different effective

![FIG. 2. Fluctuations in the cavity length-stabilization piezo voltage $V_{PZT}$ (red line) and ring-down time $\tau$ (black line) with time observed (a) without and (b) with the temperature-control system.](image)

![FIG. 3. The averages of the MDAC for the 20 repeated data with (blue) and without (red) the temperature-control system; the error bars are the experimental standard deviations of the averages.](image)
Finally, we measured near-infrared spectra for dry nitrogen at atmospheric pressure, as shown in Fig. 4, which is the average of 166 spectra recorded for 22 h. Each spectrum consists of 274 spectral points, and each spectral point is the average of 100 ring-down time measurements. Peaks seen in the black line of the lower figure are attributable to the rotation-vibration transitions of residual moisture in dry nitrogen at an approximately 1 ppb level. The averaged spectrum was analyzed using least-squares fitting with Lorentzian functions (red peaks in the figure) and a linear baseline (not shown); the residuals obtained from the fitting are shown in the upper figure. The standard deviation of residuals was $6.6 \times 10^{-12} \text{ cm}^{-1}$, corresponding to a mole fraction of water of 6.3 ppt for the water absorption line at 7181.14 cm$^{-1}$, demonstrating parts-per-trillion sensitivity attained by wavelength-meter controlled CRDS with the frequency-control and temperature-control systems developed in this study.

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