Technology

# Development of continuous measurement type gas concentration monitor

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## 1. Introduction

The global market of the semiconductor industry is increasing every year and is expected to reach one trillion dollars by 2030 [1]. As for technological trends, semiconductor devices are expected to become increasingly miniaturized and multi-layered to achieve higher integration [2), 3)], which will boost the demand for highly reactive gaseous substances (gases: $B_2H_6$ etc., precursors: liquids and solids) that are needed for production of such devices. Highly reactive gases are thermally unstable and generate trace amounts of impurities over time, making them difficult to supply the target concentration accurately and stably. In order to solve this problem, continuous in-line concentration monitoring is necessary, and gas concentration monitors using infrared rays or ultrasonic waves are generally used. However, current gas concentration monitors have problems in measurement accuracy in consideration of the amount of impurities and in measurement sensitivity responding to the measurement pressure, and therefore, need to be further improved in terms of performance.

Therefore, we have been working on the development of a gas concentration monitor using vacuum ultraviolet and deep ultraviolet light, which has not been studied extensively, for the purpose of monitoring concentrations of various gases with high accuracy and high sensitivity. This paper reports basic evaluation results of this development.

## 2. Fabrication of gas concentration monitor

### 2.1 Prediction of optical absorption wavelengths using quantum chemical calculations

Semiconductor process gases consist mainly of a mixture of highly reactive gas (sample gas) and inert gas (base gas). In order to understand the wavelength bands at which optical absorption occurs in the sample gas and base gas, the optical absorption wavelengths of various highly reactive gases and base gases were calculated using quantum chemical calculations (density functional method). Figure 1 shows the simulated results.

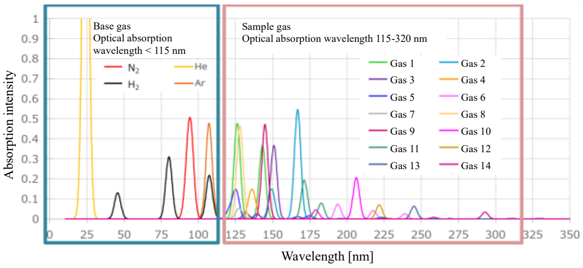


Figure 1　Prediction of optical absorption wavelengths of various gases

As a result of the simulation study, it was predicted that the base gases $N_2$, $H_2$, He, and Ar had their optical absorption band below 115 nm, and the sample gases, which were the measurement targets, had them in the range of 115 to 320 nm (= vacuum ultraviolet and deep ultraviolet region).

### 2.2 Fabrication of gas concentration monitor

According to 2.1, it was predicted that the concentration of only sample gas without interference from the base gas can be measured by using light having wavelengths between 115 nm and 320 nm. Based on this prediction, we designed and fabricated a gas concentration monitor that uses light having wavelengths between 115 nm and 320 nm (Figure 2).

Figure 2　Gas concentration monitor prototype

## 3. Basic verification of gas concentration monitor

### 3.1 Check for interference from base gas

To confirm the consistency between the theoretical calculation results obtained in 2.1 and the gas concentration monitor, we compared its response intensities in a vacuum

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condition and in a base gas -present condition. Figure 3 shows the results.

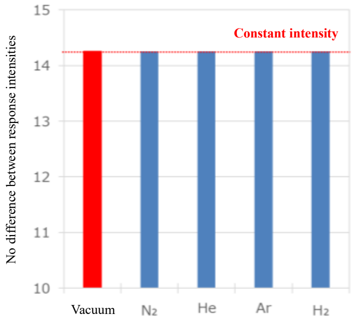


Figure 3 Comparison of vacuum and base-gas conditions

As a result of the verification, no difference between the response intensities in the vacuum condition and in the base gas-present condition was observed. This indicates that the quantum chemical calculation is valid and that the sample concentration can be measured without interference from the base gas.

### 3.2 Evaluation of gas concentration monitor sensitivity

This section shows the results of actual concentration measurements using the sample gas 4 in Figure 1 as an example of the evaluation.

A 1% sample gas 4 was diluted with $N_2$ and the peak intensities for various concentrations were measured. The gas cell pressure was set to 50, 100, and 150 kPaA, and calibration curves were prepared for each (Figure 4).

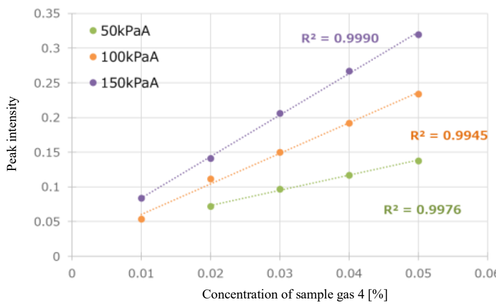


Figure 4 Measurement results of sample gas 4

All the calibration curves for each pressure condition resulted in $R^2$ values of greater than 0.99 and exhibited good linearity.

In addition, the slope of each calibration curve was plotted against each measured pressure to check their correlations (Figure 5).

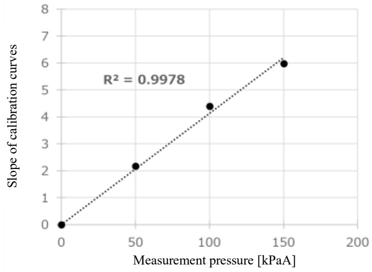


Figure 5 Comparison of measured pressure and calibration curve slope

The resulted $R^2$ value was greater than 0.99, indicating a linear pressure dependence. Using the approximate equations obtained in Figure 4 and Figure 5 to calculate the minimum measurement pressure, it is estimated that 1% sample gas 4 at a pressure as low as 0.7 kPaA can be measured.

## 4. Evaluation of gas concentration monitor stability

We evaluated the stability of the response intensity of the gas concentration monitor by operating it for about 50 hours while periodically introducing sample gases. This section shows the results of this evaluation using the sample gas 7 shown in Figure 1 as an example.

For this evaluation, the average value of the sample gas concentrations at which the baseline response intensity stabilized was taken as 0% concentration, and the response intensity was converted to concentration using the calibration curve of the sample gas 7. Figure 6 shows the result of the evaluation for about 50 hours.

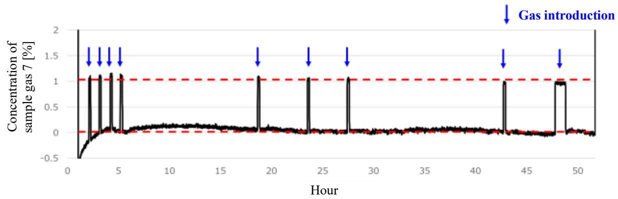


Figure 6 Stability evaluation

Both the baseline and the concentration indication tended to stabilize after about 5 hours. Also in the subsequent measurement, the baseline and the concentration indication remained stable, with fluctuations of ±5% or less for the 1%-concentration sample gas 7. Therefore, it was confirmed that the developed gas concentration monitor also has excellent stability.

## 5. Verification of measurement of three-component gas mixture

### 5.1 Prediction of optical absorption wavelengths of three-component gas mixture

Figure 7 shows the results of calculating the optical absorption wavelengths of each component of a three-component gas mixture (component A + component B + $N_2$) according to the calculation method described in 2.1.

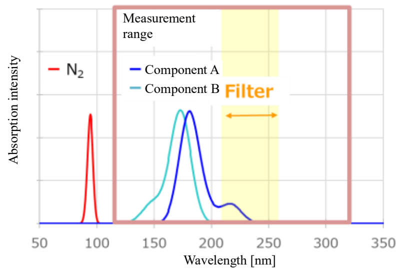


Figure 7 Prediction of optical absorption wavelengths of three-component gas mixture

As a result of the simulation study, both the component A and the component B have optical absorption within the measurement wavelength range (between 115 nm and 320 nm), and it is predicted that the component A will be interfered by the component B if measurement is made without any modification. To solve this problem, we installed a optical filter (center wavelength: 240 nm) that transmits light of 240 nm, the wavelength band in which only the component A is detected, in the gas cell before measurement.

### 5.2 Performance verification of optical filter

We measured a 25% component B + $N_2$ gas mixture using a gas concentration monitor with a optical filter installed that had been calibrated with component A (Figure 8).

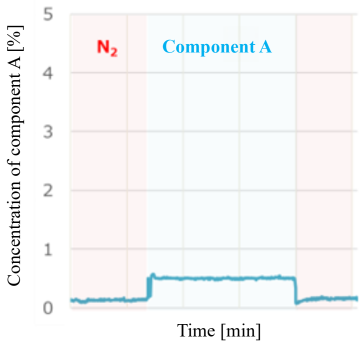


Figure 8 Measurement result of component B

The measurement result showed that there was a slight interference from component B, but the interference to component A from the 25% introduced concentration of component B was reduced to less than 1%. The reason for the slight detection is probably the effect of a half-width of several tens of nm that exists with respect to the optical filter with a center wavelength of 240 nm.

Next, we measured a 3.1% component A + 13.1% component B + $N_2$ gas mixture using the gas concentration monitor with a optical filter installed similarly (Figure 9).

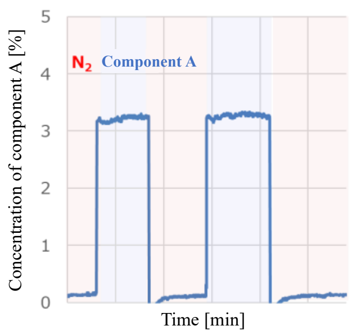


Figure 9 Measurement result of three-component gas mixture

This measurement of a 3.1% component A + 13.1% component B + $N_2$ gas mixture resulted in a concentration indication of about 3.1%. The result shown in Figure 8 indicates that installing the optical filter with a center wavelength of 240 nm allowed only the optical absorption of component A to be captured, with no interference from component B.

Then we created a calibration curve by varying the concentration of the component A. As a result, the $R^2$ value was greater than 0.99, showing good linearity (Figure 10). These results indicate that the selective use of a optical filter makes it possible to measure the concentration of the target component only with high precision, without being affected by impurities.

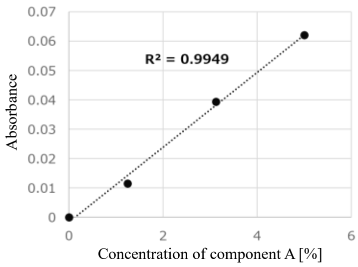


Figure 10 Calibration curve of component A

## 6. Conclusion

We developed a gas concentration monitor using vacuum ultraviolet and deep ultraviolet light and this paper presented the development results below.

- Simulation study allowed for the prediction of optical absorption wavelengths of base gases and highly reactive gases, and consistency with actual measurements was demonstrated using a prototype gas concentration monitor.
- The sensitivity level capable of measuring pressures below 1 kPaA, depending on the sample species, was demonstrated.
- It was demonstrated that both the baseline and concentration readings stabilized in approximately 5 hours and that stable measurements were possible after that.
- It was demonstrated that the installation of an appropriate optical filter eliminates the interference from components other than the measurement target, allowing for highly accurate measurement of the concentration of only one component.

This paper presented basic evaluations of the developed gas concentration monitor. In the future, we plan to further improve its accuracy and sensitivity, and to evaluate its long-term stability. Gas concentration monitors must be gas-calibrated, and therefore we, as an industrial gas manufacturer with excellent gas handling capabilities, will work on their development to enable them to measure a wider range of gas types.

Reference

1) WSTS, Gartner, SEMI, Forecast, 4Q23
2) Michael Lercel (ASML), “Lithography and Patterning for 3nm node and beyond”, SemiconWest , 2022.
3) Pieter Schuddinck(imec), “PPAC of sheet based CFET configurations for 4 track design with 16nm metal pitch”, VLSI, T10-2, 2022.