Technology

Trace Moisture Monitor Used of Metal Organic Frameworks.

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1. Introduction

We provide high-purity gases used in semiconductor manufacturing and many other industries. One of the quality control items for such high-purity gases is moisture content, and we use a trace moisture monitor as a control instrument. If a high-purity gas is contaminated with moisture, the moisture becomes a hydroxide group during the reaction process and is eventually incorporated as oxygen, causing deterioration of product performance and yield. For example, it is known that residual trace moisture at the sub-ppm level can significantly reduce the brightness of gallium nitride-based LEDs [1]. Since a large amount of moisture exists in the atmosphere, it can easily become mixed in and is difficult to remove. In addition, the adsorptive property of moisture is strong because of its high polarity, so moisture needs to be removed by heating while circulating a large amount of purge gas if enters in the piping. Therefore, in order to maintain product performance, it is important to have a monitoring technology that can immediately determine the quantity of the trace moisture concentration in the high-purity gas used in the manufacturing process and provide feedback to the user, and a trace moisture monitor with excellent detection sensitivity and response speed is required. Metal organic frameworks (MOFs) with porous structures, which are formed by coordination bonds between metal ions and organic ligands and easily synthesized, are expected to be an applied technology for adsorption in gas storage and gas separation, and various studies have been conducted. Focusing on the gas adsorption function of MOFs, we developed a trace moisture measurement system using MOFs as a moisture sensitive agent in collaboration with Kumamoto University, which has been researching sensing technology for trace moisture in gases [2),3)], and established a trace moisture monitor based on this system.

This paper describes the basic principle of this trace moisture monitor and the improvements made to the size and performance of the trace moisture monitor reported in a previous paper [4] (hereafter referred to as the previously reported prototype).

2. Basic principles of measurement

Cu-BTC, one of the MOFs used as a moisture sensitive agent in this trace moisture monitor, is formed from copper ions (Cu^{2+}) and 1,3,5-benzene tricarboxylic acid (BTC). Cu-BTC adsorbs and desorbs water molecules at room temperature and quickly reaches adsorption/desorption equilibrium in accordance with the moisture concentration in the gas. Cu-BTC also shows a change in the absorbance at a specific wavelength according to the adsorption and desorption of water molecules. By optically detecting this change in the absorbance, the moisture concentration can be measured. Since this basic principle is simpler than other trace moisture monitors, it is expected that an inexpensive and compact measurement system can be realized. Figure 1 shows the structure of Cu-BTC and the change in the absorbance due to moisture adsorption and desorption, and Figure 2 and Figure 3 show the appearance of the moisture monitor unit and the previously reported prototype, respectively.

Although the previously reported prototype has achieved a certain level of performance, there were issues with the convenience and portability at the user site due to its large size, so we set a target to develop a trace moisture monitor with further improved performance and less than half the size of the previously reported prototype.

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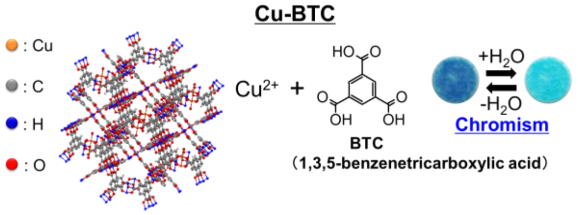

Figure 1. Structure of Cu-BTC and change in color of moisture sensitive agent

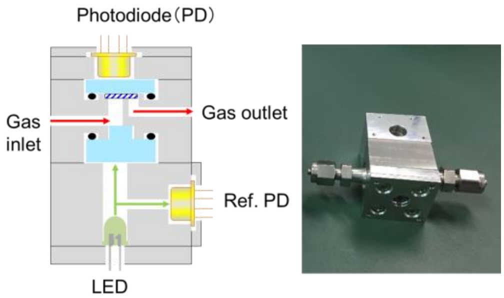

Figure 2. Appearance of moisture monitor unit

Figure 3. Previously reported prototype
H = 150 mm, W = 480 mm, D = 330 mm (including display and moisture monitor unit)

3. Performance improvement of moisture sensitive agent

3.1 Performance improvement study

As a method to improve the performance of the moisture sensitive agent, we reviewed the MOF synthesis method and studied various MOF synthesis conditions. We compared the response intensity to moisture obtained in the evaluation in 3.2 for each condition under which the moisture sensitive agent was produced.

3.2 Performance evaluation method

The performance evaluation was conducted by introducing N_2 gas (wet gas), which the moisture concentration is adjusted by diluting N_2-based moisture standard gas (manufactured by Taiyo Nippon Sanso JFP) with N_2 gas purified to less than 0.1 ppb moisture (dry gas), into this trace moisture monitor using the evaluation line shown in Figure 4. As a measurement device for comparison, we used a cavity ringdown spectroscopy (CRDS), which is known as a highly sensitive and fast-response moisture monitor [5] although it is expensive and has a large size. This technical introduction reports the results of response speed evaluation, step response evaluation, and repetition response evaluation.

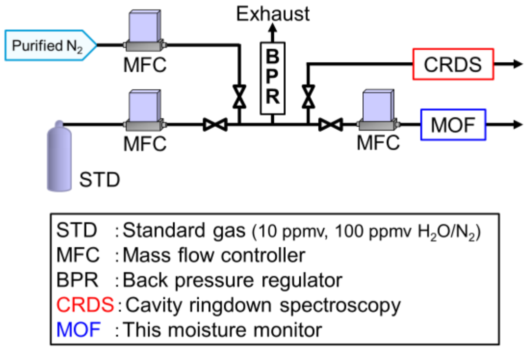

Figure 4. Evaluation line

4. Verification with improved prototype

4.1 Evaluation of improved moisture sensitive agent

Figure 5 shows the result of the evaluation of the response intensity to a moisture concentration of 10 ppm using the moisture sensitive agent produced under the synthesis conditions studied in various ways (hereafter referred to as the improved agent 1 and the improved agent 2).

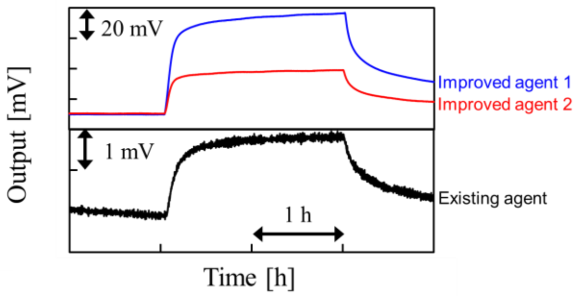

Figure 5. Response intensity of moisture sensitive agent produced under synthesis conditions

Both improved agents 1 and 2 showed 10 times more intense moisture response than the existing moisture sensitive agent synthesized for the detecting component of the previously reported prototype, and the improved agent 1 is particularly good in terms of the response intensity. The response intensity and the lower limit of detection are correlated, and the improvement of the response intensity makes it possible to produce a high-sensitivity trace moisture monitor. Figure 6 shows crystal SEM images of the improved agent 1 and the existing synthesized moisture sensitive agent.

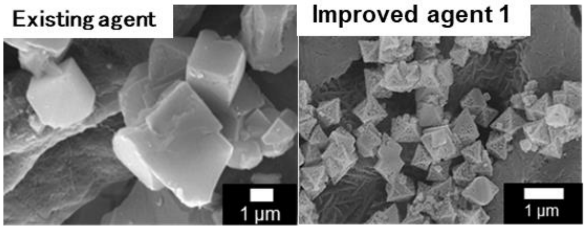

Figure 6. Crystal SEM images of existing agent and improved agent 1

Compared to the existing agent, the crystals of the improved agent 1 have smaller grain size and form more regular crystals. The intense response shown by the improved agent 1 in Figure 5 is assumed to be due to the fact that the crystals obtained by synthesis have become finer and the surface area of the crystals for the same moisture sensitive agent has increased, resulting in an increase in the amount of moisture adsorbed and the surface area of the crystals transmitted relative to the area of light irradiated from the LED, enabling higher sensitivity detection of a change in the color of Cu-BTC in response to moisture. From this result, we determined that the synthesis conditions of the improved agent 1 were optimal. Therefore, it is possible to provide a trace moisture monitor with higher sensitivity than the previously reported prototype by adopting the improved agent 1. However, the increase in response intensity leads to an increase in noise in the calculation of the lower detection limit. We will incorporate measures to reduce the increased noise in the future into the trace moisture monitor to further improve sensitivity.

4.2 Fabrication of improved prototype and its basic evaluation

To solve the issue of the previously reported prototype described in 2, we considered a package that focused on convenience and portability, and built a new prototype (hereafter referred to as the improved prototype). Figure 7 shows the external appearance of the built trace moisture monitor.

Figure 7. Improved prototype
(Main unit: H = 180 mm, W = 100 mm, D = 90 mm
Display: H = 50 mm, W = 90 mm, D = 100 mm)

The improved prototype consists of a main unit and a separate display for easy installation into user's facilities in order to allow users to replace their existing trace moisture monitors. In addition, the size of the improved prototype, including the display, was reduced to less than one-third of that of the previously reported prototype so that it can be easily transported to the user site. We evaluated the response speed to moisture, step response, and repeatability of the improved prototype shown in Figure 7, using the moisture sensitive agent (improved agent 1) employed in 4.1 for the detection part.
Table 1 compares the response intensity ratio, size, response speed, and repeatability between the improved and previously reported prototypes for performance evaluation.

Table 1. Performance comparison between improved prototype and previously reported prototype

	Previously reported prototype	Improved prototype
Response intensity ratio	1	More than 10 times
Body size (mm)	H=150, W=480, D=330	Main unit H=180, W=100, D=90 Display H=50, W=90, D=100
Response speed (90% response time)	Equivalent to CRDSs	Equivalent to CRDSs
Coefficient of variation	0.9	0.7

Colored column: Advantages

Figure 8 shows the peak rise behavior of the improved prototype when wet gas containing 1 ppm moisture is introduced.

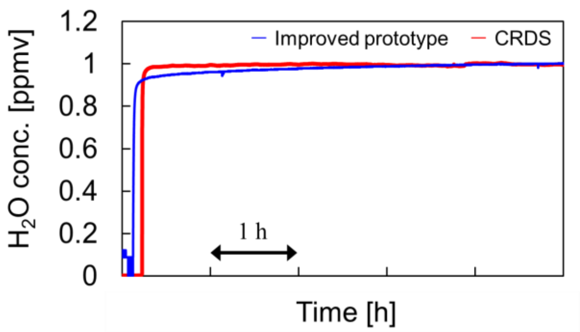

Figure 8. Response speed evaluation of improved prototype

After the dry gas was switched to the wet gas, the improved prototype's moisture indication value increased, and its 90% response time, at which the indication value reaches 90% of the wet gas concentration, was 10 minutes. This means the improved prototype has about the same response speed as that of CRDSs in terms of the 90% response time. The response speed of the previously reported prototype was also comparable to that of the CRDS in terms of the 90% response time. Therefore, it can be said that this trace moisture monitor can detect moisture at the same speed as CRDSs in processes affected by trace moisture contamination.

Figure 9 shows the result of evaluating the step responses when moisture was added to dry gas so that the moisture concentration ranged from 0.1 to 2 ppm. Figure 10 shows the result of evaluating the repetitive response of the improved prototype by introducing dry gas and wet gas containing 0.1 ppm moisture at regular intervals.

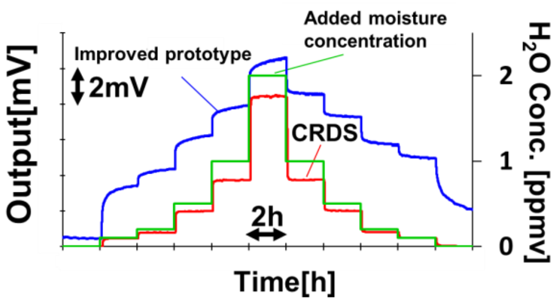

Figure 9. Evaluation of step response of improved prototype

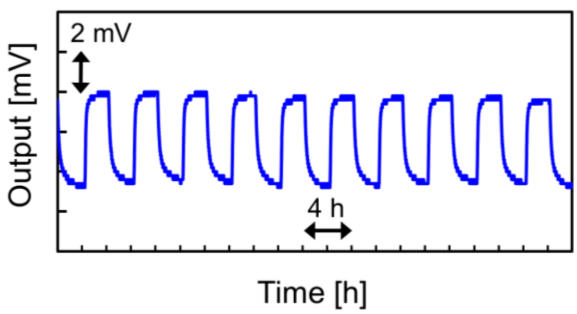

Figure 10. Evaluation of repetitive response of improved prototype

Figure 9 shows that the improved prototype has a step response with response intensity corresponding to the added moisture concentration (right-side vertical axis value), similar to CRDS. Figure 10 shows that the improved prototype has a stable repetitive response. As shown in Table 1, the improved prototype's coefficient of variation of response intensity is smaller than the previously reported prototype's, which means that the improved prototype is able to determine the quantity of trace moisture with higher accuracy. This confirms that the improved prototype with the high-sensitivity moisture sensitive agent employed this time is sufficiently practical for trace amount moisture analysis.

5. Conclusion

By improving the synthesis conditions of the moisture sensitive agent and the body size, we have been able to increase the response intensity to more than 10 times of that of the previously reported prototype and to reduce the body size to less than one-third, as shown in Table 1. In addition, by reducing the coefficient of variation, we have realized more accurate quantity determination of trace moisture.

We confirmed that the improved prototype is a trace amount moisture monitor with excellent sensitivity and response speed, as well as stable and repeatable response. In particular, the response speed is as high as that of CRDSs, so the application to cases that require control of trace moisture concentration is also possible. In the future, we will evaluate the improved prototype in field tests to prepare for bringing it to market, and work on the development of an improved monitor with higher sensitivity.

References

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