Technology

High-Purity Hydrazine Vapor Delivery System

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1. Introduction

Demand for semiconductors has continued to grow along with the evolution of information technologies such as generative AI and edge computing. The increasing demand for semiconductors is supported by semiconductor scaling including miniaturization, and various materials and process technologies have been developed and commercialized to realize the semiconductor scaling. Especially in recent years, while further miniaturization of semiconductors is more and more difficult, semiconductor scaling by stacking has been promoted.

The issues in stacking semiconductor devices include lowering the temperature, improving the film quality, and increasing the throughput during the film formation process of silicon nitride and titanium nitride films [1]. To solve these issues, hydrazine, which has higher reactivity than ammonia, an existing nitridation source, is attracting attention [2]. In this context, RASIRC has commercialized BRUTE® Hydrazine so as to safely handle hydrazine [3]. On the other hand, a technology to stably delivery hydrazine vapor at high concentrations is required at semiconductor manufacturing sites.

Therefore, using our proprietary gas handling technology, we have developed a high-purity hydrazine vapor delivery system (hereinafter referred to as the “developed delivery system”) that can be applied to semiconductor manufacturing processes. This paper reports on the developed delivery system.

2. Issues in delivery technology of BRUTE® Hydrazine

2.1 Features of BRUTE® Hydrazine

Anhydrous hydrazine is severely restricted for international transportation due to its toxicity and flammability. To address this issue, we have been distributing BRUTE® Hydrazine (hereafter called BH), a liquid mixture of anhydrous hydrazine and a non-volatile organic solvent. In a BH container, only vaporaized hydrazine exists in the headspace, and by using a carrier gas or vacuum transport to deliver this to a film forming chamber or the like, we have made it possible to use high-purity hydrazine vapor in semiconductor processes [3].

2.2 Need for delivery system

While the new process using high-purity hydrazine vapor by use of BH has attracted much attention, there are some issues in terms of stable delivery. For example, since BH is a mixture of non-volatile solvent and hydrazine, the hydrazine vapor pressure decreases with the consumption of hydrazine according to Raoult's law (Figure 1). In the case of delivery using a carrier gas, the decrease in vapor pressure leads to a decrease in the concentration of hydrazine vapor in the reaction gas.

Because of these characteristics, a system is essential that is capable of delivering high concentration hydrazine vapor stably from BH in semiconductor mass production processes, where delivering material gas at a stable concentration is indispensable.

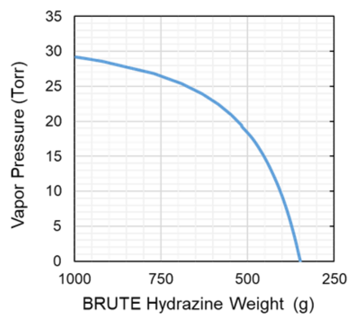

Figure 1 Dependence of vapor pressure on remaining BRUTE® Hydrazine

3. Features of the hydrazine vapor delivery system

Figure 2 shows the appearance of the high-purity hydrazine vapor delivery system we have developed. In this system, up to two BH containers can be connected thereto. By using one of the containers as the container for supply and the other as the one for standby, downtime when replacing the container can be minimized. The valve operation is interlocked with a leak detector to automatically shut off the vapor delivery in case of leakage. Furthermore, the inside of

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the system is always maintained at a negative pressure by an exhaust duct, preventing fire and exposure to workers caused by leakage. Thus, the developed delivery system has the same safety mechanism as cabinets for specialty gases in semiconductor manufacturing, and allows safer use of high-purity hydrazine gas.

Figure 2 Appearance of developed high-purity hydrazine vapor delivery system

The following paragraphs present the delivery stability of the developed delivery system.

First, we investigated the behavior of hydrazine concentration without the developed delivery system for the purpose of comparison: a BH container was heated to 40°C and a carrier nitrogen gas was introduced at a flow rate of 3 slpm from the inlet of the container. The container pressure was kept constant by a pressure regulator at its outlet, and hydrazine was delivered along with the carrier gas. Then, a Fourier transform infrared spectrometer (FTIR) was connected in the posterior side to the pressure regulator and the concentration of hydrazine was measured. Figure 3 shows behaviors of the hydrazine concentration generated from the BH container when its residual volume was 900 g and 500 g out of 1000 g. As expected from Raoult's law, the concentration of hydrazine when the residual volume was 500 g was less than half of the concentration when the residual volume was 900 g. In addition, in both cases where the residual volume was 900 g and 500 g, the concentration of hydrazine was high immediately after the start of the carrier gas supply, and gradually decreased and stabilized.

This behavior is considered to be due to the fact that the concentration of hydrazine in the gas phase gradually increases until it saturates while there is no carrier gas flow in the container (during shutdown), and that the saturated vapor of hydrazine is delivered along with the carrier gas immediately after the start of hydrazine generation. In contrast, during continuous hydrazine generation, the evaporation rate of hydrazine is slower with respect to the flow rate of the carrier gas, and therefore it is considered that non-saturated hydrazine vapor is delivered along with the carrier gas.

Next, we investigated the behavior of hydrazine concentration when using the developed delivery system. The developed delivery system has a mechanism to control the container pressure in order to generate a predetermined concentration of hydrazine. In this investigation, the hydrazine concentration was set at 5%, and a FTIR connected to the outlet of the developed delivery system was used to check if the hydrazine delivery was stable. The evaluation was conducted under the conditions where BH containers were heated to 40°C and the carrier nitrogen gas flow rate was set to 3 slpm. Figure 4 shows behaviors of the hydrazine concentration when BH containers whose residual volume was 900 g and 500 g were used. It was confirmed that 5% hydrazine was delivered regardless of the residual volume. It was also confirmed that high-concentration hydrazine discharge immediately after the start of generation did not occur and hydrazine could be delivered at a stable concentration for approximately one hour. In this way, by using the developed delivery system, stable and reproducible delivery of hydrazine is possible regardless of the usage conditions (such as gas delivery ON/OFF timing) of the semiconductor manufacturing equipment.

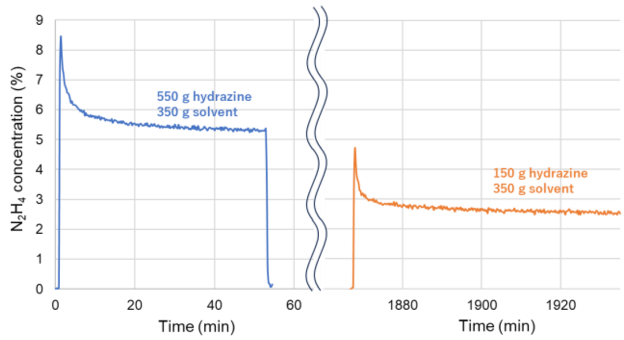

Figure 3 Behaviors of hydrazine concentration when the developed delivery system is not used

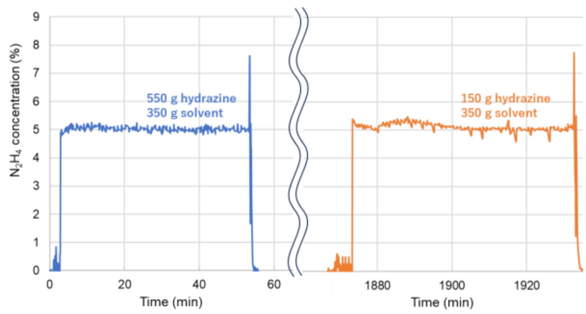

Figure 4 Behaviors of hydrazine concentration when the developed delivery system is used

4. Conclusion

The high-purity hydrazine vapor delivery system we have developed to meet the requirements of semiconductor mass production processes can stably deliver nitrogen/hydrazine mixture gas using hydrazine concentration control technology based on the control of the BH container internal pressure. Also, the developed delivery system has the same safety measures as those used for semiconductor material gas cabinets, so it can safely handle hydrazine gas.

Reference

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