Technology

Supply technology for high-purity solid-state precursor MoO_2Cl_2 for semiconductors

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1. Introduction

In recent years, as IoT and AI have become increasingly widespread, the volume of data handled across society has grown dramatically. Semiconductor devices, which support this massive data processing, are required to achieve both high processing performance and low power consumption.

Amid these technological trends, 3D NAND memory continues to evolve through higher stacking and further miniaturization, and attempts are being made to replace part of W (tungsten), a conventional wiring material, with Mo (molybdenum)1, 2). As a representative Mo wiring material, MoO_2Cl_2 (molybdenum dichloride oxide) is being investigated. When using this material in the deposition process, high quality and a stable supply are essential in order to obtain sufficient device performance.

To meet these requirements our company are developing quality control and supply technologies for MoO_2Cl_2. To date, we have advanced technology development across multiple stages, including filling, delivery, container management, and analysis (Fig. 1)3). This report describes our initiatives to establish robust quality control technologies by leveraging these core capabilities, as well as our efforts in the design of supply equipment and the manufacturing of high-purity MoO_2Cl_2.

2. Technological Challenges of MoO_2Cl_2

To design and manufacture equipment capable of a stable supply of high-quality MoO_2Cl_2, the technological challenges regarding the material container and the material supply mechanism are presented below.

a) Material Container

MoO_2Cl_2 is a sublimable compound, and for use it is filled into a dedicated container and vaporized by heating. Since MoO_2Cl_2 exhibits corrosiveness, there is a concern regarding the contamination of metal impurities due to corrosion of the container's inner surface during heating. Therefore, a corrosion-resistant inner surface treatment technology to suppress this is required. Furthermore, since high concentrations of highly volatile metal impurities are detected in the gas phase during thermal vaporization, a purification technology to reduce these impurities in advance is essential for the application of MoO_2Cl_2 to semiconductor processes.

b) Material Supply

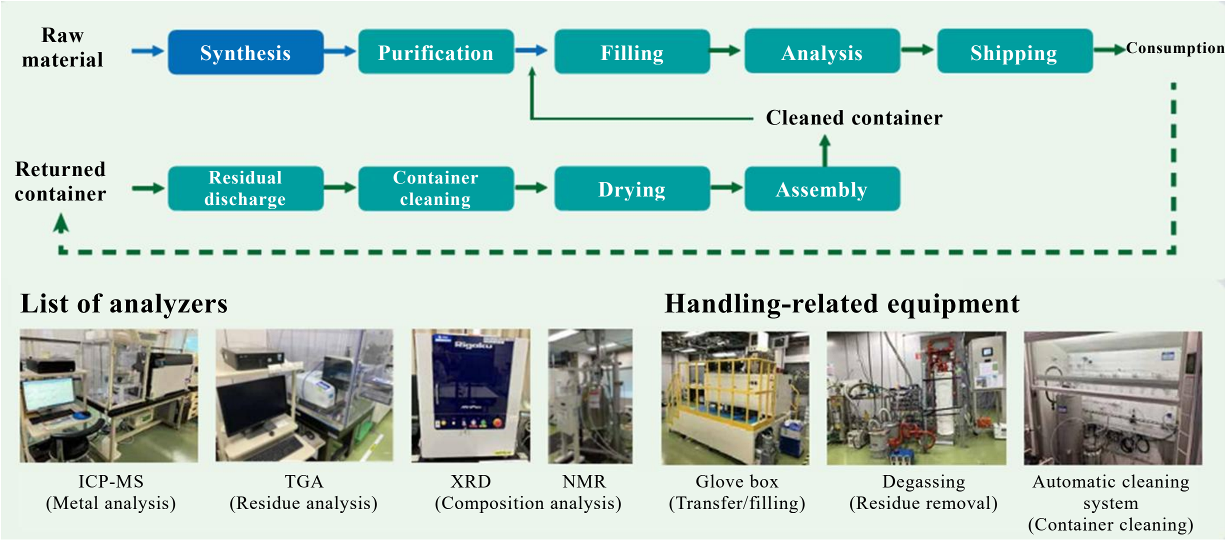

Fig. 1 Development of filling, supply, container management, and analysis technologies for our solid materials

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In order to stably supply vaporized MoO_2Cl_2, it is necessary to maintain the gas phase pressure inside the container within a predetermined range. This requires a supply mechanism that stabilizes the supply pressure by appropriately controlling the amount of heat applied to the container.

3. MoO_2Cl_2 Material Quality Control Technology

3.1 Countermeasure against Corrosion by MoO_2Cl_2

We evaluated the effectiveness of the container's inner surface treatment against MoO_2Cl_2. In performing this evaluation, assuming repeated use of the container in actual operation, we conducted a test in which heating and cleaning cycles were repeated more than ten times to thereby verify the effectiveness and durability of the treatment.

The concentration of metal impurities contained in MoO_2Cl_2 after the repeating test was measured using an inductively coupled plasma mass spectrometer (ICP-MS). Fig. 2 shows the results of the metal analysis. Without the inner surface treatment, high concentrations of metal components derived from stainless steel, such as Fe, Ni, and Cr, were detected. In contrast, with the inner surface treatment, it was confirmed that their concentrations remained below 100 wt.ppb, which is our control standard for semiconductor process materials, even in the repeating test.

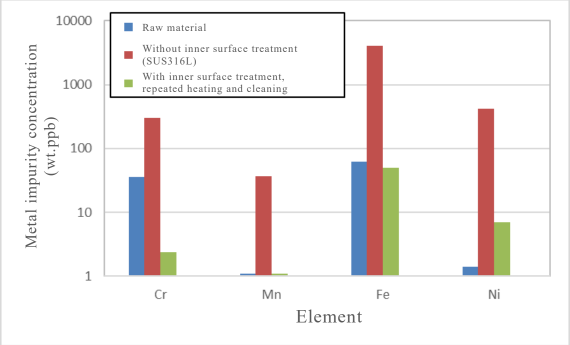


Fig. 2 Metal impurity concentrations in the raw material and MoO_2Cl_2 after the repeating test

Fig. 3 shows SEM images of the container's inner surface before and after the repeating test. Even after the test, no peeling or degradation of the inner surface treatment layer was observed, and no significant changes in the appearance of the container were observed.

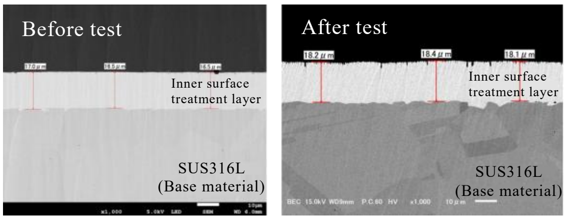


Fig. 3 Cross-sectional images of the container's inner surface before and after the test

Based on the above results, it was found that this inner surface treatment technology demonstrates sufficient corrosion resistance and durability against MoO_2Cl_2. It should be noted that the use of Hastelloy (C-22) containers is currently under consideration, not limited to the inner surface treatment.

3.2 MoO_2Cl_2 Purification Process

MoO_2Cl_2 contains metal impurities derived from the raw minerals or the manufacturing process. If these metal impurities are incorporated into the film during deposition, the produced semiconductor device cannot exhibit the expected performance. To reduce these impurities, our proprietary purification process was applied.

Table 1 shows an example of the metal impurity analysis results after purification. Through this purification process, the concentrations of impurities such as V and As were significantly reduced, and the concentrations of the elements shown in Table 1 were achieved to be less than 100 wt.ppb, which is our internal control standard for semiconductor process. This has led to the establishment of a manufacturing technology for high-purity solid-state MoO_2Cl_2 precursor suitable for semiconductor process.

Table 1 Example of metal impurity concentrations in the gas phase before and after purification

Element	Unit	Before purification (Gas phase)	After purification (Gas phase)	Analysis method
Na	wt.ppb	<30	<30	ICP-MS
Mg	wt.ppb	<60	<60	ICP-MS
Al	wt.ppb	<50	<50	ICP-MS
K	wt.ppb	<40	<40	ICP-MS
V	wt.ppb	**273**	<50	ICP-MS
Cr	wt.ppb	<50	<50	ICP-MS
Mn	wt.ppb	<30	<30	ICP-MS
Fe	wt.ppb	71	<50	ICP-MS
Co	wt.ppb	<20	<20	ICP-MS
Ni	wt.ppb	<40	<40	ICP-MS
Cu	wt.ppb	<30	<30	ICP-MS
Zn	wt.ppb	<50	<50	ICP-MS
As	wt.ppb	**626**	<40	ICP-MS
Ag	wt.ppb	<50	<50	ICP-MS
Sn	wt.ppb	**191**	<40	ICP-MS
Sb	wt.ppb	<30	<30	ICP-MS
Ba	wt.ppb	<30	<30	ICP-MS
W	wt.ppb	<50	<50	ICP-MS
Re	wt.ppb	<30	<30	ICP-MS
Bi	wt.ppb	<30	<30	ICP-MS

4. MoO_2Cl_2 Supply Unit Design

4.1 Evaluation of MoO_2Cl_2 Flow Rate Stability

We evaluated the flow rate stability during MoO_2Cl_2 supply. The test was conducted under the conditions of a MoO_2Cl_2 concentration of 100% and a supply flow rate of 1000 sccm, with repeated supply and stop cycles simulating ALD (Atomic Layer Deposition) processes.

As shown in Fig. 4, this supply mechanism employs a pressure feedback system that monitors the supply pressure and performs PID control of the container temperature based on that pressure.

As shown in Fig. 5(a), without pressure feedback, the supply pressure tends to decrease as the material is supplied. On the other hand, as shown in Fig. 5(b), with this control applied, the supply pressure is maintained approximately constant, enabling stable gas supply. This mechanism has made it possible to stably supply the material down to a residual amount well below 10%, which is our exchange criterion for specialty material liquefied gases.

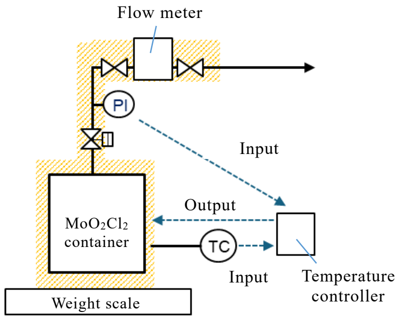
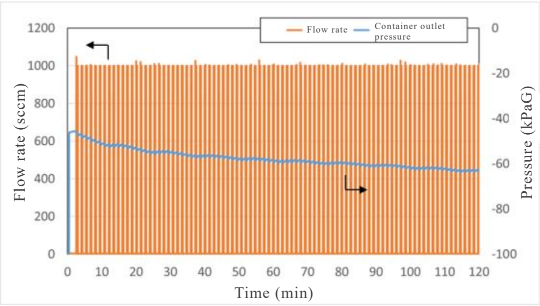


Fig. 4 Pressure feedback control system

(a) Without pressure feedback



(b) With pressure feedback

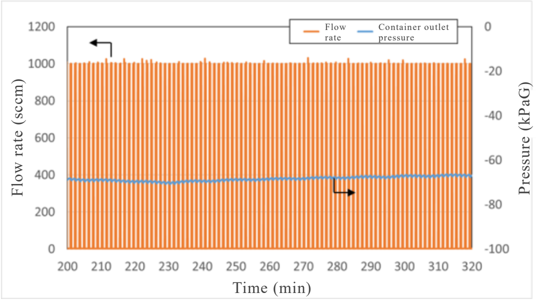


Fig. 5 Container outlet pressure and flow rate with and without feedback control

4.2 Temperature Uniformity of the Supply Container

In order to stably supply MoO_2Cl_2, it is necessary to heat the inside of the container uniformly and efficiently. Accordingly, we evaluated the temperature distribution inside the container by simulation when the solid material and the supply container are heated. As an example of the simulation, Fig. 6 shows the temperature distribution results with and without a heat transfer plate inserted inside the container. The simulation results clarified the tendency of the heat transfer plate position that enables heating the inside of the container more efficiently. This indicated that by placing the heat transfer plate at an appropriate position, the temperature uniformity of the entire container is enhanced and the heat transfer efficiency is improved.

As mentioned above, since the current container's residual limit is 10% or less, optimizing the internal structure and heat transfer plate placement based on these results is expected to further improve material utilization efficiency.

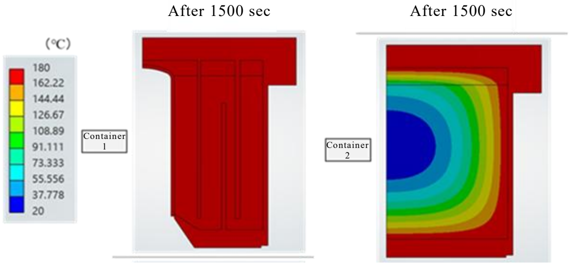


Fig. 6 Example of temperature simulation inside the container

5. Efforts toward MoO_2Cl_2 Manufacturing

Toward the commercialization of MoO_2Cl_2, the operation of MoO_2Cl_2 production facilities at the Taiyo Nippon Sanso JFP Mie Plant is scheduled to begin in October 2026 (Fig. 7). The planned production capacity of this facility is 12 t/year.

Fig. 7 Taiyo Nippon Sanso JFP Mie Plant

Fig. 8 shows the external and internal views of the MoO_2Cl_2 supply unit. This supply unit possesses excellent temperature uniformity and traceability, and by combining it with the aforementioned pressure feedback control, stable gas supply is made possible. Furthermore, as a result of adopting a configuration featuring two systems, each equipped with a large container with a capacity of 40 L or more, long-term continuous operation has been achieved while avoiding downtime during container replacement. Future plans involve proceeding with various performance evaluations and reliability verifications, with the goal of designing a next-generation model capable of both self-pressure supply and carrier gas supply to multiple chambers.

Fig. 8 MoO_2Cl_2 supply unit

6. Conclusion

Regarding MoO_2Cl_2, which is expected to be a next-generation material, we developed core technologies for material quality control and supply, and obtained the following results.

- It was confirmed that by applying containers with corrosion-resistant inner surface treatments, it is possible to suppress the contamination of metal impurities derived from the container even after repeated use. This led to the establishment of a corrosion countermeasure technology for MoO_2Cl_2.
- Applying a proprietary purification process reduced the metal impurity concentrations in the gas phase to less than 100 wt.ppb, which is our control criterion. This led to the establishment of a manufacturing technology for high-purity MoO_2Cl_2 suitable for semiconductor applications.
- A stable MoO_2Cl_2 gas supply technology was established using a supply mechanism that employs a pressure feedback control system.
- Temperature uniformity within the container was improved by optimizing the internal structure of the supply container, indicating the potential for improving material utilization efficiency.

In the future, we will proceed with reliability evaluations of these technologies toward the start of mass production facilities at the Taiyo Nippon Sanso JFP Mie Plant and the advancement of supply unit functionality, aiming to expand their applications to next-generation semiconductor processes.

References:

1) Lam Research, "Wordline Metallization – Transitioning to Molybdenum"
2) Nikkei Electronics, May 2024 issue
3) Y. Mukai, "Supply Technology for High-Purity Solid-State Precursor MoO_2Cl_2 for Semiconductors," Taiyo Nippon Sanso Technical Report, No. 42, 2023