Technology

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

MUKAI Yosuke* KAMEOKA Takashi* WATANABE Ryoma* KAGAWA Sota*

1. Introduction

Due to technological innovations in semiconductor devices (new structures and new film types), the volume of data handled has increased dramatically. As a result, the semiconductor and material markets are also expanding, driven by the growth in device performance through efforts to strengthen communication infrastructures and to reduce power consumption.

In particular, for higher integration of 3D-NAND memory, while further multi-layering and miniaturization are progressing, there is a movement to replace some of the tungsten (W) back-end-of-line material with molybdenum (Mo) as the material market expands.

This paper reports on the basic evaluation and elemental technology development for the development and commercialization of a supply system with molybdenum material (MoO_2Cl_2) targeting back-end-of-line processes using Mo for replacing W.

2. Physical properties and technical issues of MoO_2Cl_2

MoO_2Cl_2 represents molybdenum dichloride oxide, which has the molecular weight of 198.84 and is a yellowish-brown powder (Figure 1).

Figure 1. MoO_2Cl_2

MoO_2Cl_2 is filled into a special container, and is used by heating and vaporizing it. MoO_2Cl_2 readily reacts with moisture in the air, which forms a refractory hydrate. To maintain its quality, MoO_2Cl_2 needs to be kept out of contact with moisture during the handling processes thereof.

MoO_2Cl_2 is solid at room temperature and pressure and sublimates when heated. Figure 2 shows the saturated vapor pressure curve[1] of MoO_2Cl_2. Since deposition processes use MoO_2Cl_2 in gaseous form, technology to stably supply the sublimated MoO_2Cl_2 gas is essential.

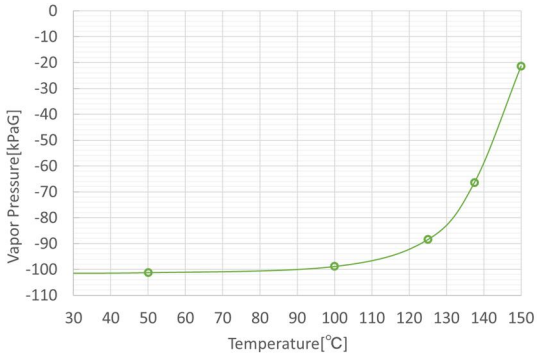


Figure 2. MoO_2Cl_2 saturated vapor pressure curve[1] of MoO_2Cl_2

3. MoO_2Cl_2 material quality control technology

3.1 MoO_2Cl_2 handling management standard

To establish management criteria for the MoO_2Cl_2 filling atmosphere, changes over time of MoO_2Cl_2 left statically in an atmosphere of a certain concentration of water vapor was evaluated by visual observation and XRD measurement. Figure 3 shows the results. The appearance of the MoO_2Cl_2 changes to green as the statically leaving time increases, indicating an increase in MoO_2Cl_2 hydrates. Experiments conducted with different moisture and oxygen concentrations during statically leaving revealed that these factors affect the rate of hydrate formation. Based on these results, we set the moisture concentration of <5ppm and oxygen concentration of <1ppm as the management criteria. We designed and

* Electronics Development Department, Tsukuba Laboratory, R&D Unit

installed a glove box capable of maintaining these management criteria, and established conditions for handling MoO_2Cl_2 while suppressing the formation of MoO_2Cl_2 hydrate, based on verification through similar statically leaving tests.

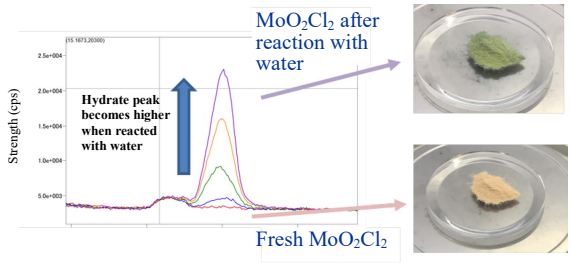


Figure 3. XRD measurement result and photos of MoO_2Cl_2 hydrate

3.2 Analysis of metallic impurities in MoO_2Cl_2

MoO_2Cl_2 may contain metallic impurities derived from raw material minerals or manufacturing. If metallic impurities are incorporated into the film during deposition, the expected performance of semiconductor devices cannot be obtained. To ensure product quality, we analyzed metallic impurities by ICP-MS. Analysis by ICP-MS requires hydrolysing MoO_2Cl_2 as a pretreatment. Therefore, we performed our own pretreatment with acid and used an Agilent 8900 ICP-MS, which is capable of high-sensitivity measurement, for the analysis. Table 1 shows the results of the actual analysis of metallic impurities in MoO_2Cl_2. As a result, it was judged that the analysis value of each metal impurity quantity could be used to confirm our standard (less than 100 ppb passed), indicating that high-sensitivity metal impurity analysis can be performed for quality assurance.

Table 1. Analysis results of metallic impurities in MoO_2Cl_2

Element	Measured value (wt.ppb)	Element	Measured value (wt.ppb)
Li	<1	Sr	<1
Be	<1	Zr	<1
B	<5	Nb	<1
Na	10	Ru	<1
Mg	12	Rh	<1
Al	15	Pd	<2
P	<27	Ag	<1
K	<4	Cd	10
Ti	10	In	4
V	8	Sn	5
Cr	1	Sb	<1
Mn	4	Cs	1
Fe	14	Ba	1
Co	<1	Hf	<1
Ni	18	Ta	<1
Cu	2	W	12
Zn	36	Re	1
Ga	<1	Ir	<2
Ge	2	Pt	<4
As	9	Au	5
Se	1	Pb	4
Rb	<1	Bi	16

Spike recovery tests were performed to verify the validity of the analysis, and the results are shown in Table 2. A spike recovery test performs the measurement of a sample (A) and a sample (B), which is prepared by adding a standard solution of known concentration to the sample (A), to check if the difference between A and B matches the known concentration of the added standard solution. When the standard solution (known concentration) and the concentration measured by ICP-MS are in perfect agreement, the recovery rate is 100%. As shown in Table 2, the accuracy (spike recovery rate), method accuracy, and measurement accuracy were all within the acceptable range of SEMI[2], and there was no interference caused by high concentration of Mo during the measurement. As a result, it was confirmed that the analysis results of metallic impurities shown in Table 1 is accurate.

Table 2. Spike recovery test results

Element	Sample 1 Recovery rate %	Sample 2 Recovery rate %	Recovery rate % Range	Sample 1 Relative standard deviation	Sample 2 Relative standard deviation
Li	115.0	114.0	1.0	0.3	0.5
Be	83.4	81.2	2.2	1.3	0.9
B	84.2	83.0	1.3	1.3	0.6
Na	109.6	109.7	0.1	0.8	0.9
Mg	104.5	105.4	0.9	0.8	0.5
Al	104.5	105.6	1.1	0.7	0.5
P	91.4	89.2	2.2	1.3	2.1
K	88.2	91.0	2.8	2.9	5.4
Ti	99.3	100.6	1.4	0.7	0.8
V	84.0	88.1	4.1	1.7	4.5
Cr	84.4	87.7	3.3	3.0	5.5
Mn	92.1	92.9	0.8	0.8	0.7
Fe	85.3	85.5	0.2	0.6	0.6
Co	91.3	91.3	0.0	0.6	0.7
Ni	88.3	88.2	0.1	0.9	1.6
Cu	84.5	84.1	0.4	0.6	1.0
Zn	90.4	87.8	2.7	0.5	1.0
Ga	100.8	100.7	0.1	0.9	0.4
Ge	89.6	88.2	1.4	0.5	0.7
As	84.1	81.5	2.6	0.7	0.5
Se	83.2	78.5	4.7	1.9	1.2
Rb	101.4	102.1	0.7	0.6	0.6
Sr	100.0	101.6	1.6	0.4	0.6
Zr	99.7	100.2	0.5	0.7	0.4
Nb	101.1	101.7	0.6	0.4	0.2
Ru	108.1	107.5	0.6	3.0	5.9
Rh	105.9	106.1	0.2	0.4	0.3
Pd	102.4	103.1	0.7	0.4	0.4
Ag	98.8	97.9	0.9	0.4	0.4
Cd	100.4	99.7	0.7	0.8	1.0
In	108.1	108.2	0.2	3.4	5.6
Sn	103.0	103.1	0.0	3.2	5.2
Sb	98.2	97.4	0.9	0.3	0.5
Cs	104.8	106.9	2.1	0.4	0.3
Ba	102.4	103.2	0.8	3.2	5.2
Hf	98.1	98.2	0.1	1.3	0.9
Ta	97.2	97.5	0.3	1.1	1.0
W	97.3	97.3	0.1	0.9	0.8
Re	99.7	99.7	0.1	1.2	1.2
Ir	98.4	98.7	0.3	1.0	1.1
Pt	95.5	94.9	0.6	1.4	1.0
Au	91.2	90.7	0.5	1.1	0.9
Pb	96.6	96.7	0.1	1.0	0.8
Bi	89.8	88.9	1.0	1.3	0.5

Item	Acceptance criteria	Result
Accuracy	Recovery rates of samples 1 and 2 are in the range of 75 to 125%	Acceptable
Method Accuracy	Recovery rate % range is less than 35	Acceptable
Measurement accuracy	Standard spike sample maximum relative standard deviation is less than 20	Acceptable
Interference check	Check that there is no interference	No interference

4. MoO_2Cl_2 container maintenance technology

We evaluated the cleaning process of an MoO_2Cl_2 filling containers (Figure 4). The cleaning process was divided into primary cleaning and secondary cleaning. The primary cleaning dissolves residues by batch cleaning three times with alkaline solution, the acceptable pH value of which was set to 12 or higher. The secondary cleaning rinses off the primary cleaning solution by flow cleaning with ultrapure water, the acceptable specific resistance value of which was set to 16 MΩ-cm or higher. Before and after the cleaning, visual checks were conducted, and MoO_2Cl_2 residue was observed visually before the cleaning, but not observed after the cleaning, indicating that the cleaning was complete (Figure 5).

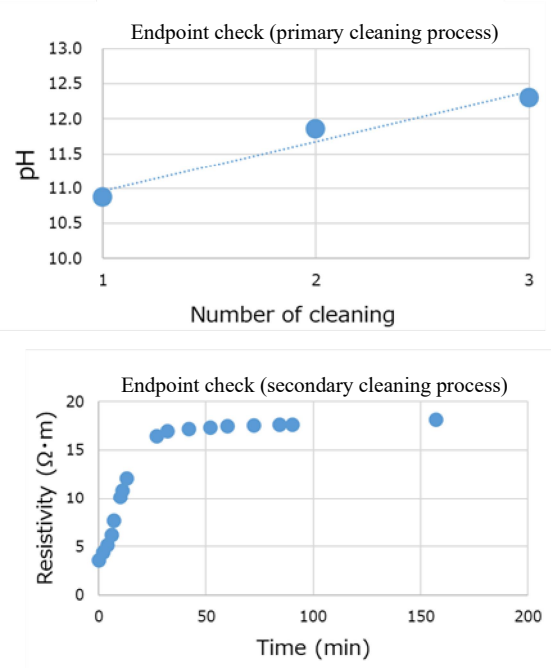
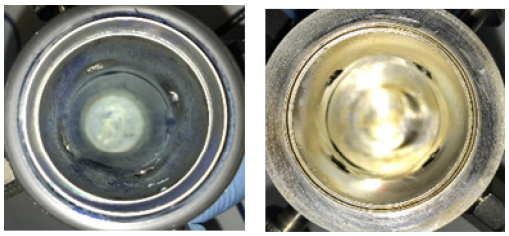


Figure 4. Container cleaning evaluation results



Before cleaning After cleaning

Figure 5. Visual check results

Based on the evaluation results shown in Figures 4 and 5, we constructed automatic container cleaning equipment in order to establish a container cleaning process for mass production (Figure 6). This equipment has made it possible to automatically complete the process from primary cleaning, secondary cleaning, to drying. In the future, we will conduct cleaning evaluations using the automatic container cleaning equipment.

Figure 6. Automatic container cleaning equipment

5. Evaluation of MoO_2Cl_2 gas supply technology

5.1 Optimization of container heating with heater

For stable supply of MoO_2Cl_2 gas, it is necessary to maintain the gas phase pressure in the container at a predetermined value, and in order to maintain the gas phase pressure, appropriate control of the amount of heating to the container is required. Therefore, as described in a previous report[3], we conducted simulations of multiple heater arrangements and the behavior of the gas phase pressure in the container with respect to the different heater arrangements. Based on the simulation results, we optimized the container heating method. It was indicated that stable supply can be achieved by using the type 1 heater arrangement and controlling on/off of the heater output (Figure 7).

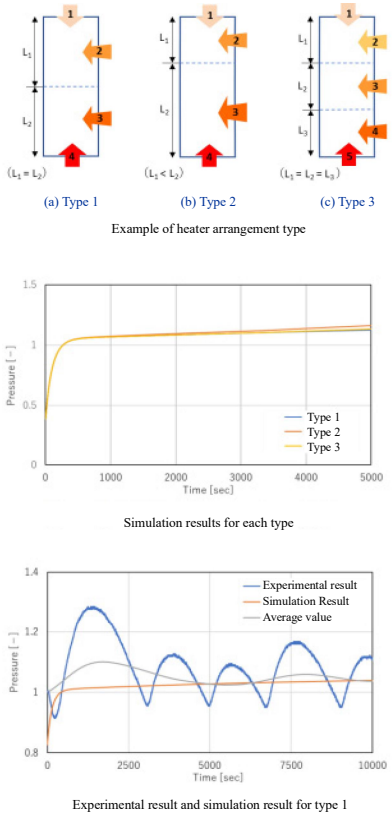


Figure 7. Container heater simulation results

5.2 Evaluation of gas supply

We conducted an MoO_2Cl_2 gas supply test with an MoO_2Cl_2 concentration of 100% and at a supply flow rate of 1000 sccm under conditions of repeated dose and stop that simulated an ALD (atomic layer deposition) process. Figure 8 shows the results. By controlling the container heating temperature in the range of 130°C to 200°C, the pressure in the material tank (blue on the right axis) was kept constant at -72 kPaG and stable supply at 1000 sccm (orange on the left axis) was achieved.

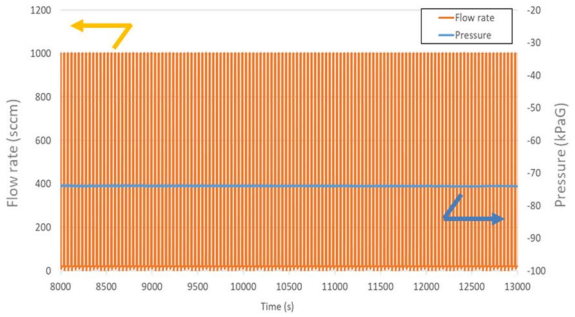


Figure 8. MoO_2Cl_2 gas supply evaluation result

6. Conclusion

We developed elemental technologies for handling MoO_2Cl_2, which is expected to be a next-generation material, and obtained the following results.

- We established a method for analyzing metallic impurities in MoO_2Cl_2, which enables us to ensure high quality materials containing less than 100 wt.ppb of metallic impurities.
- We established a handling management technology to maintain the quality of MoO_2Cl_2.
- We established container maintenance technology for returnable containers.
- We optimized the container heating method and established a technology for stable supply of MoO_2Cl_2 even at high flow rates.

Through the establishment of these technologies, we have built a system that can handle the entire process of MoO_2Cl_2 filling, supply, container maintenance, and quality control.

In the future, we will proceed with the development aiming at the commercialization of MoO_2Cl_2 materials and supply equipment.

Reference

1) H.W. Gaggeler et al., The Chemistry of Super-heavy Elements, pp. 251-253, 2003
2) SEMI C1-0704, Guide for the Analysis of Liquid Chemicals, pp. 7-8, 2004
3) Keisuke Aiba, Simulation of material gas supply system for semiconductors using surrogate model, Taiyo Nippon Sanso Technical Report No. 41 (2022)