# Development of non-flammable mixed refrigerant Joule-Thomson refrigerator for semiconductor etching process

**Cheonkyu Lee*, Jung-Gil Lee and Jin Man Kim**

Carbon Neutral Technology R&D department, Research Institute of Clean Manufacturing System, Korea Institute of Industrial Technology (KITECH), Cheonan, 31056, Republic of Korea

[C1Po2B]
[Non-Aerospace Coolers I: GM and JT Coolers]
Jul. 10, 2022 (Mon.) 14:00 ~ 16:00

## Introduction

- The etching process is a process of removing a desired part of the material deposited on the wafer using plasma, liquid, etc.
- Dry etching is applied to remove only the target area or structure. (Anisotropic etching, Fig. 1)
- As shown in Fig. 2, the semiconductor industry has developed into high-density and high-integration processes in order to respond to consumer demand for high-performance semiconductors especially high aspect ratio etching more than 40:1.

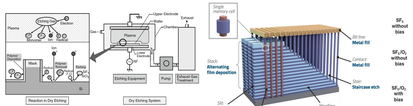

Fig. 1. Schematic of Dry etching



Fig. 2. 3D NAND structure

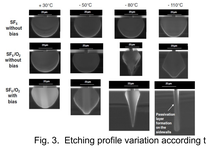

Fig. 3. Etching profile variation according to the wafer temperature

- It is expected that high-aspect-ratio etching can be achieved even with small plasma power by applying ultra-low temperature to the etching process. (Fig. 3)
- Cryogenic Etching or Ultra-low Temperature Etching is emerging as an etching process that can achieve a higher aspect ratio than the aspect ratio currently performed in high power etching at room temperature.
- A very low etching temperature of -100°C should be implemented, however, there is no cryogenic cooling system that can be used as an etching facility.
- Therefore, the low temperature chiller system to be applied to the semiconductor etching process was quantitatively analyzed based on the mixed refrigerant Joule Thompson refrigerator.

## Cycle configuration

- the cycle applying mixed refrigerant(MR) Joule-Thomson(JT) refrigeration cycle and the three-stage refrigeration cycle were compared in order to quantitatively compare the cryogenic refrigeration system.
- A single MR JT refrigeration cycle and a MR JT including pre-cooling refrigeration cycle were considered to figure out the maximum refrigeration efficiency (Coefficient of performance).
- R404A was applied as the working fluid of the precooling stage of the MR JT refrigeration cycle and that of the high temperature part of the three-stage refrigeration cycle.
- A schematic diagram of each refrigeration cycles are as shown in Fig. 4 to 6

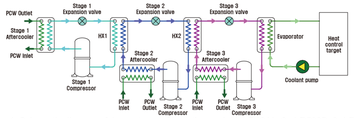


Fig. 4. Schematic diagram of three-stage refrigeration cycle(1st R404A, 2nd R508B, 3rd R14)

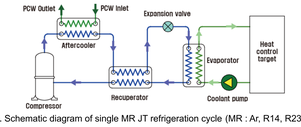


Fig. 5. Schematic diagram of single MR JT refrigeration cycle (MR : Ar, R14, R23, R218)

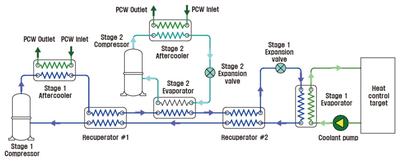


Fig. 6. Schematic diagram of MR JT refrigeration cycle with precooling stage (precool : R404A, MR: Ar, R14, R23, R218)

## Design constraints

Table 1. Design constraints of each refrigeration cycle

| Parameter | MR constraint | Precool | Three-stage refrigeration | Note |
|---|---|---|---|---|
| Refrigerant | Mixture of Ar, R14, R23, R218 | R404a | 1st : R404A<br>2nd : R508B<br>3rd : R14 | |
| Discharge pressure [kPa] | 1800 | 1250 (25 ℃) | Condensing pressure of each cycle<br>1st : 1250 (25℃)<br>2nd : 1485 (-18℃)<br>3rd : 2664 (-57℃) | |
| Suction pressure [kPa] | 400 | 220 | Evaporating pressure of each cycle<br>1st : 108 (-28℃)<br>2nd : 225 (-67℃)<br>3rd : 401 (-105℃) | |
| Pressure drop at HX [kPa] | 0 kPa | 0 kPa | 0 kPa | |
| Coolant inlet temperature [℃] | -95 | | | |
| Coolant outlet temperature [℃] | -100 | | | |
| Adiabatic efficiency of the compressor [%] | 50 | | | |
| Aftercooling(condensing) temperature [℃] | 25 ℃ | | | PCW |
| Minimum temperature approach [℃] | 5 | | 5 | |

- Entire refrigeration cycles were calculated by Aspen HYSYS v10 and Peng-Robinson Equation of State.
- The pressure drop in entire heat exchangers were neglected.
- Check all compositions at 0.1 intervals based on mole fraction in case of MR.
- The maximum COP were verified with aforementioned constraints.

$$COP = \frac{\dot{Q}_L}{\dot{W}_{in}} = \frac{\text{Cooling capacity}}{\text{Work input}}$$

## Cycle configuration selection

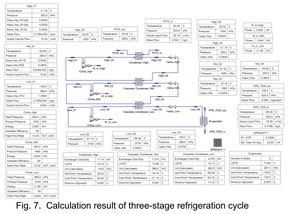

Fig. 7. Calculation result of three-stage refrigeration cycle

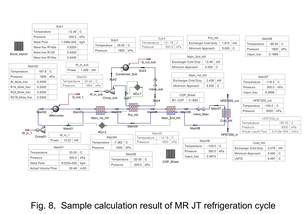

Fig. 8. Sample calculation result of MR JT refrigeration cycle with precooling stage

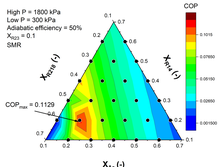


Fig. 9. Calculation result of Single MR JT cycle (R23 = 0.1)

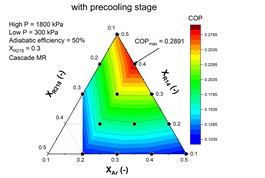


Fig. 10. Calculation result of MR JT cycle with precooling stage (R218 = 0.3)

- The maximum COP of the single stage MR JT refrigeration cycle was 0.113 at (Ar:R14:R23:R218 = 0.2:0.2:0.1:0.5).
- The maximum COP of the MR JT refrigeration with precooling cycle was 0.289 at (Ar:R14:R23:R218 = 0.2:0.4:0.1:0.3).
- if precooling is included, the efficiency can be increased more than 2 times compared to the single stage MR JT refrigeration cycle. It is assumed that the compressor efficiency is 50%, and COP enhancement might be limited if the efficiency of the scroll compressor lower than assumption.
- The COP of the three-stage refrigeration cycle is calculated as 0.229, this COP is lower than that of MR JT refrigeration cycle with precooling stage.

## Selected MR JT system

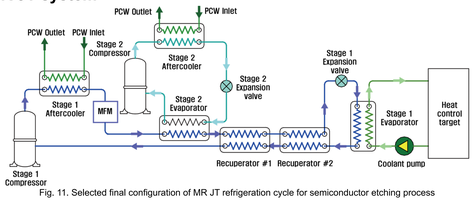


Fig. 11. Selected final configuration of MR JT refrigeration cycle for semiconductor etching process

- Figure 11 shows the schematic diagram of the final selected MR JT refrigeration system for the semiconductor etching process. (MR JT refrigeration cycle with precool)
- The detailed system constraints of the refrigeration cycle are described as Table 2.
- Design of Experiments(DOE) for mixture design were applied to optimize the composition of working fluid based on the trial and error.
- The detailed mixture compositions to optimize the MR JT refrigerator are shown as Table 3, and the cycle simulation program was developed based on the REFPROP V10.0, as shown in Figure 12.

Table 2. System constraints of designed MR JT refrigeration cycle

| Parameter | MR constraint | Precool | Note |
|---|---|---|---|
| Refrigerant | Mixture of Ar, R14, R23, R218 | R1234yf | |
| Discharge pressure [kPa] | 1800 | 1200 (25 ℃) | |
| Suction pressure [kPa] | 400 | 220 (-10℃) | |
| Pressure drop at HX [kPa] | 20 kPa for each pass | 20 kPa for each pass | |
| Coolant inlet temperature [℃] | -95 | | |
| Coolant outlet temperature [℃] | -100 | | |
| Adiabatic efficiency of the compressor [%] | 50 | | |
| Aftercooling(condensing) temperature [℃] | 25 | | PCW |
| Minimum temperature approach [℃] | 5 | | |

Table 3. Mixture composition to optimize the MR JT refrigeration cycle according to the DOE

| Run Order | Ar | R14 | R23 | R218 | Run Order | Ar | R14 | R23 | R218 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.25 | 0.35 | 0.1 | 0.3 | 19 | 0.2 | 0.4 | 0.25 | 0.15 |
| 2 | 0.15 | 0.35 | 0.35 | 0.15 | 20 | 0.2 | 0.3 | 0.35 | 0.15 |
| 3 | 0.25 | 0.25 | 0.35 | 0.15 | 21 | 0.25 | 0.4 | 0.15 | 0.2 |
| 4 | 0.15 | 0.2 | 0.35 | 0.3 | 22 | 0.25 | 0.175 | 0.35 | 0.225 |
| 5 | 0.15 | 0.4 | 0.3 | 0.15 | 23 | 0.25 | 0.225 | 0.225 | 0.3 |
| 6 | 0.25 | 0.4 | 0.1 | 0.25 | 24 | 0.175 | 0.4 | 0.125 | 0.3 |
| 7 | 0.25 | 0.4 | 0.2 | 0.15 | 25 | 0.2 | 0.15 | 0.35 | 0.3 |
| 8 | 0.2 | 0.4 | 0.1 | 0.3 | 26 | 0.205 | 0.325 | 0.235 | 0.235 |
| 9 | 0.15 | 0.4 | 0.15 | 0.3 | 27 | 0.2275 | 0.3375 | 0.1675 | 0.2675 |
| 10 | 0.25 | 0.1 | 0.35 | 0.3 | 28 | 0.1775 | 0.3375 | 0.2925 | 0.1925 |
| 11 | 0.15 | 0.375 | 0.325 | 0.15 | 29 | 0.2275 | 0.2875 | 0.2925 | 0.1925 |
| 12 | 0.15 | 0.4 | 0.225 | 0.225 | 30 | 0.1775 | 0.2625 | 0.2925 | 0.2675 |
| 13 | 0.15 | 0.275 | 0.35 | 0.225 | 31 | 0.1775 | 0.3625 | 0.2675 | 0.1925 |
| 14 | 0.15 | 0.3 | 0.25 | 0.3 | 32 | 0.2275 | 0.3625 | 0.1675 | 0.2425 |
| 15 | 0.25 | 0.375 | 0.1 | 0.275 | 33 | 0.2275 | 0.3625 | 0.2175 | 0.1925 |
| 16 | 0.225 | 0.4 | 0.1 | 0.275 | 34 | 0.2025 | 0.3625 | 0.1675 | 0.2675 |
| 17 | 0.225 | 0.375 | 0.1 | 0.3 | 35 | 0.1775 | 0.3625 | 0.1925 | 0.2675 |
| 18 | 0.225 | 0.325 | 0.275 | 0.15 | 36 | 0.2275 | 0.2125 | 0.2925 | 0.2675 |

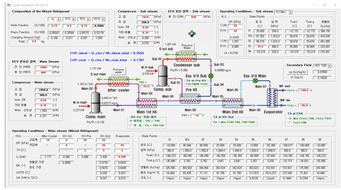

Fig. 12. developed MR JT cycle simulation program with REFPROP V10.0

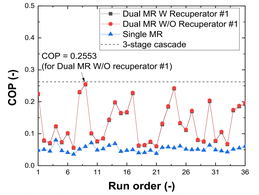


Fig. 13. Simulation results of MR JT refrigeration cycle with precool

- The maximum COP of the MR JT refrigeration cycle was obtained as 0.2553 with the mixture composition of Ar:R14:R23:R218 = 0.15:0.4:0.15:0.3 for aforementioned system configuration.
- Based on this result, we constructed a mixed refrigerant JT refrigerator.

## System schematic and preliminary result

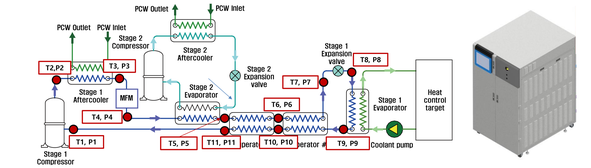


Fig. 14. Sensor position of the designed MR JT refrigeration cycle for preliminary scale

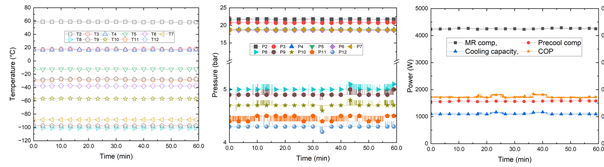


Fig. 15. Detailed system operation result of the MR JT refrigeration cycle for preliminary scale (0.5 kW)

- Figure 14 shows the sensor position of the MR JT refrigeration cycle for preliminary test (500 W class).
- Figure 15 depict the detailed system operation result of the MR JT refrigeration cycle of 500 W class preliminary test.
- Compressor work consumption of the stage 1 was measured 4.27 kW and that of stage 2 was obtained 1.56 kW, respectively. The cooling capacity of the system was obtained slightly higher than 1.10 kW.
- Thus, the COP of the MR JT refrigerator showed approximately 0.17 and therefore, it was confirmed to develop the MR JT refrigerator for semiconductor etching process.

## System Configuration

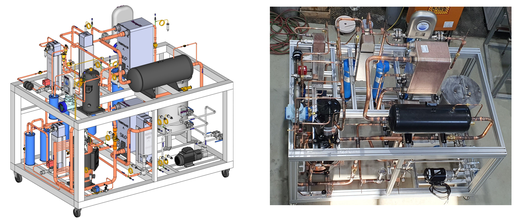

Fig. 16. System schematic and fabrication of MR JT refrigeration cycle for 2 kW cooling capacity

- Figure 16 depicts the schematic diagram and fabrication of the MR JT refrigeration cycle for 2 kW cooling capacity.

## Conclusion and future work

- Quantitative analysis of the COP of the various refrigeration cycle for cooling -100℃ were conducted to design a chiller for cryogenic etching process in this study.
- The COP of the MR JT refrigeration cycle with precooling stage was expected to reach more than twice that of the single stage MR JT refrigeration cycle, and is expected to meet more than 30% that of the three stage refrigeration cycle.
- The maximum COP of the designed MR JT refrigeration cycle was obtained 0.2553 and the composition of working fluid was Ar:R14:R23:R218 = 0.15:0.4:0.15:0.3.
- The preliminary system of MR JT refrigeration cycle was developed and it performed the COP of 0.17 and cooling capacity of 1.1 kW at –100℃ cooling temperature.
- A 2 kW mixed refrigerant JT refrigeration system is currently under construction, and an experiment will be conducted with the same refrigerant composition.

**Acknowledgements**

"This work was supported by the industrial Fundamental Technology Development Program (20014817, Development of ultra low temperature cooling system for semiconductor etching process with cooling capacity of 2 kW) funded by the Ministry of Trade, industry & Energy (MOTIE) of Korea"