MIZUHO

No. 215 (2023016)

October 10, 2023
Mizuho Bank Industry Research Department

# *Mizuho Short Industry Focus*

**Innovative Technology Series:[1]**

## Trends in High-End Photoresists –Strategic Direction for Japan to Remain Strong

**Arata Murashige**

[Summary]

- Technical progress in the semiconductor industry continues unabated, and the competition to develop next-generation technologies is intensifying. Japanese manufacturers hold a large share of the market for photoresists, which play a key role in miniaturization, one of the themes in semiconductor technological development.

- A photoresist is a circuit-forming material used in the photolithography process of semiconductor fabrication. Although Japanese photoresist manufacturers were latecomers to the market, they have been able to survive the competition by leveraging their superior technological capabilities. Historically, the miniaturization of front-end processes has been achieved by evolving exposure light sources to shorter wavelengths, but EUV lithography, which uses light with an extremely short wavelength of 13.5 nm, has been in practical use since 2019. Photoresists have been developed and improved in response to the evolution of exposure light sources.

- Resolution, line width - roughness and sensitivity are the primary criteria for evaluating photoresist performance, but there are trade-offs in the relationship between them. While it is considered to be extremely difficult to improve these trade-offs, various types of cutting-edge photoresists, such as PAG bound-CAR and Wet/Dry-MOR, are being developed as photoresists that can be used for semiconductor miniaturization that will evolve to 2 nm and 1.X nm in the future. Although PAG bound - CAR is a type of photoresist that is familiar to semiconductor fabricators and is attracting significant attention, the dispersion inhomogeneity of PAG polymers remains unresolved. Wet/Dry-MOR is considered to be superior to PAG bound-CAR in terms of resolution and in other aspects, but has issues such as the need to develop peripheral materials and equipment. Each type has its advantages and disadvantages, and at this point, it is unclear which type will become the de facto standard.

- In order for Japanese photoresist manufacturers to maintain their high technological capabilities and competitiveness and to continue leading the industry, they must assess areas to focus on and formulate appropriate strategies. One direction would be to allocate profits earned in the middle- to high-end areas, where each company's strengths can be leveraged. There are four specific strategies: (1) assess China as a market, (2) domestic coordination, (3) alliances, and (4) supply chain diversification. As for the environment surrounding the industry changes, there is the possibility that policy support will become essential. We hope that Japanese photoresist manufacturers will remain strong going forward through each company's continued R&D efforts and appropriate policy support.

[1] Series of reports highlighting areas of technology and innovation that can contribute to strengthening the competitiveness of Japanese industry and to solving social issues.

## 1. Introduction

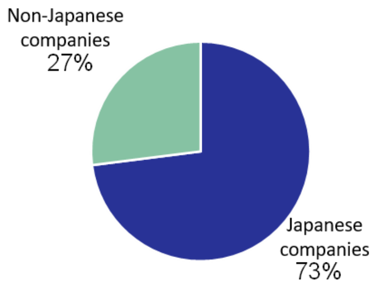
Growing importance of the semiconductor industry, and increased investment both domestically and internationally

The importance of semiconductors is increasing along with the digitalization of society. The technological progress of semiconductors continues unabated, and the competition to develop next-generation technologies is intensifying. Additionally, from the perspective of economic security, major countries are working to foster their own semiconductor industry by providing policy support worth trillions of yen. In response to these trends, major semiconductor fabricators, including TSMC from Taiwan, have announced large-scale capital and R&D investment plans and are increasing their presence in the industry.

Overview of photoresists, the key to front-end process technology development, and strategic directions for photoresist development

The development of next-generation semiconductor technologies includes miniaturization [2] in front-end processes [3] and 3D packaging [4] in back-end processes.[5] Japanese manufacturers are known to have a large share of the market for photoresists (Figure 1), which hold the technological key to realizing miniaturization. This paper provides an overview of the technological challenges facing photoresists and the R&D trends for cutting-edge products, and then examines the strategic directions for Japanese photoresist manufacturers to remain strong in the future, as well as the ideal form of policies to support semiconductor material manufacturers.

[Figure 1] Global Photoresist (Volume) Market Share (2022)




Source: Estimated by Mizuho Bank Industry Research Department

## 2. Overview of Photoresists

Photoresists are used in the lithography process in the semiconductor fabrication process

Semiconductors are fabricated by drawing a circuit pattern of minute semiconductor elements onto a glass substrate called a photomask, and then repeatedly transferring it via exposure to a photoresist coated on the surface of a silicon wafer to form an image of the circuit pattern (Figure 2).[6] This process is called photolithography, and the photoresist plays the role of protecting[7] necessary areas on the wafer to form circuits. Photoresists were developed by Kodak in the US in the 1950s. The first Japanese manufacturer of photoresists, Tokyo Ohka Kogyo, began development in 1962, followed by JSR, Sumitomo Chemical, Fujifilm, and Shin-Etsu Chemical. Although Japanese photoresist manufacturers were latecomers to the market, they have been able to survive by leveraging their superior technological capabilities.

[2] Reducing the size of the two-dimensional pattern created in the patterning process. Benefits include (1) reduced fabrication cost per transistor, (2) reduced power consumption, (3) increased operating speeds, and (4) increased functionality. In particular, an increase in the number of transistors arranged in the horizontal direction has a significant effect on improving computational processing performance per area.

[3] The process of processing and forming electronic circuits and electrodes on silicon wafers.

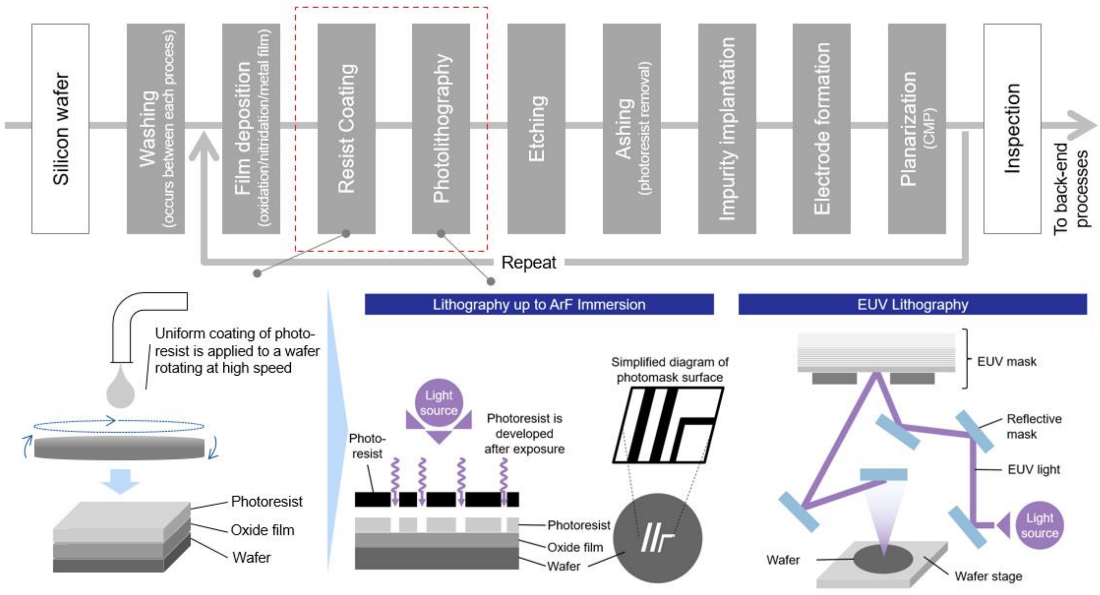
[4] Advanced packaging technology for semiconductor chips in which two or more layers of electronic components are stacked and then interconnected both vertically and horizontally to function as a single device.

[5] The process in which the hundreds of chips formed on a wafer are cut out one by one and then turned into final products.

[6] Note that EUV exposure and prior fabrication processes have different methods for forming the circuit patterns.

[7] Photoresists are classified into positive photoresists and negative photoresists depending on their reaction to exposure. With positive photoresists, exposure increases solubility and the exposed areas are removed after development, while with negative photoresists, exposure hardens the exposed areas and all but the exposed areas are removed after development. Negative photoresists were the mainstream when photoresists were first developed. However, negative photoresists have the problem of expanding after being developed, which tends to cause decreases in resolution. As such, the industry now primarily uses positive photoresists, which can be removed without chemical cleaning by irradiating the pattern with light after patterning.

[Figure 2] Overview of the Semiconductor Fabrication Process

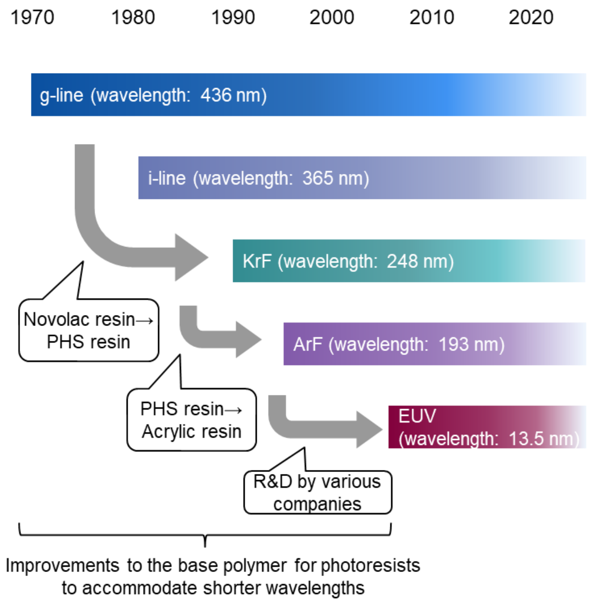



Source: Compiled by Mizuho Bank Industry Research Department based on Lasertec website, etc.

Photoresists have been developed and improved as semiconductor technologies have advanced

Moore's Law is a rule of thumb for predicting the technological evolution of semiconductors. This prediction about the future was proposed by Gordon Moore, co-founder of Intel (US), in 1965, when he stated that "the integration level of semiconductors doubles about every 18 to 24 months."[8] More than half a century after it was introduced, Moore's Law is still recognized by companies involved in semiconductor fabrication as an indicator of technological progress in the semiconductor industry. Miniaturization in front-end processes has a history of being achieved by evolving the exposure light source to one with a shorter wavelength, and EUV lithography, which uses light with an extremely short wavelength of 13.5 nm, has been in practical use since 2019. Photoresists have also been developed and improved in response to the evolution of exposure light sources (Figure 3).

[Figure 3] Roadmap for Exposure Light Sources and Photoresists




Note: EUV is stated as starting from the early 2000s, when research and development became active.
Source: Compiled by Mizuho Bank Industry Research Department based on Tokyo Ohka Kogyo website, etc.

8 When it was first proposed, the "integration level" was defined as the number of parts for all electronic components, including the resistors and other components that were mounted in an integrated circuit. However, as the integration level has increased, transistors have come to account for the majority of the electronic components, and today Moore's Law is defined by the number of transistors mounted in an integrated circuit.

## 3. Trends in High-End Photoresists

### (1) Specific Methods for Miniaturization

Future miniaturization will be achieved by decreasing $k_1$ and increasing NA in the Rayleigh equation

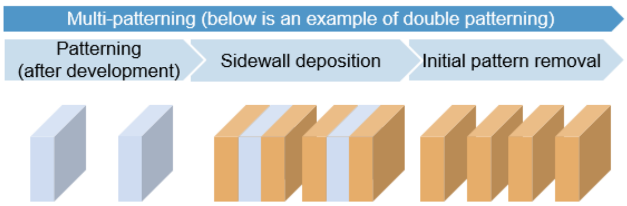
Semiconductor miniaturization is achieved by improving the resolution[9] (=shortening the resolvable dimension, i.e. making R smaller) expressed by the Rayleigh equation ($R = k_1 \times \lambda / NA$, with R: resolution, $k_1$: process coefficient, $\lambda$: wavelength, and $NA$: numerical aperture of the lens). In the future, further miniaturization is expected through EUV multi-patterning[10] (reducing $k_1$) and increasing $NA$, the numerical aperture of the lens (Figure 4). However, it is also expected that transistor structures will become more complex, and that the difficulty of fabricating semiconductors will increase (Figure 5). In order to realize complex structures formed on the nanometer scale, there are numerous challenges to be overcome by photoresists, exposure equipment, and semiconductor fabricators, but the challenges with photoresists are recognized as being the most difficult in the lithography process (Figure 6).

[Figure 4] Key Points in the Miniaturization Process

Rayleigh Equation $$R = k_1 \times \frac{\lambda}{NA}$$

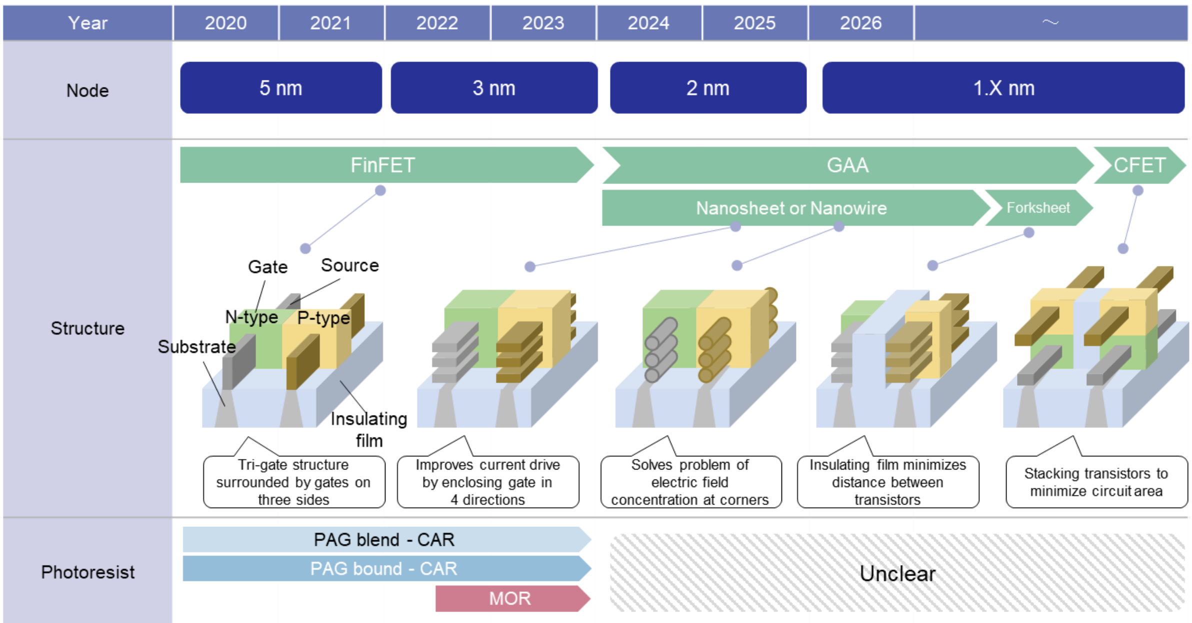
| Symbol | $R$ | $k_1$ | $\lambda$ | $NA$ |
|---|---|---|---|---|
| Meaning | Resolution | Process coefficient | Wavelength (fixed value) | Numerical aperture of lens |
| Target | Make smaller (=resolution ↑) | ↓ | - | ↑ |

| Symbol | Specific methods |
|---|---|
| $k_1$ | Improve the illumination optics of EUV scanners |
| | Improve the photoresist |
| | Introduce multi-patterning |
| | Improve the translation stage in EUV scanners (reduces overlay errors) |
| $NA$ | Increase the numerical aperture of the lens (effective for EUV where long exposure time is difficult) |




Source: Compiled by Mizuho Bank Industry Research Department based on ASML and Tokyo Ohka Kogyo websites, etc.

[Figure 5] Short- and Medium-Term Technology Roadmap




Source: Compiled by Mizuho Bank Industry Research Department based on ASML IR materials, etc.

---

9 Refers to the distance between two points that can be resolved and can also be thought of as the resolving power.
10 A technology that divides a single exposure into multiple patterns and then overlaps the patterns later.

[Figure 6] Difficulty Ranking for Solving Problems in Lithography Processes (as of 2019)

Photoresist | EUV pellicle | Photomask | Exposure machine

| Rank | 2015 | 2016 | 2017 | 2018 | 2019 |
|---|---|---|---|---|---|
| 1 | Reliable source operation with > 85% availability | Reliable source operation with > 85% availability | Resist resolution, sensitivity & LER met simultaneously | Resist resolution, sensitivity & LER met simultaneously | Resist resolution, sensitivity & LER met simultaneously |
| 2 | Resist resolution, sensitivity & LER met simultaneously | Resist resolution, sensitivity & LER met simultaneously | Reliable source > 250W operation with > 90% availability | Keeping mask defect free | Keeping mask defect free |
| 3 | Mask yield & defect inspection / review infrastructure | Keeping mask defect free | Keeping mask defect free | Reliable source > 250W operation with > 90% availability | Extension of EUV mask infrastructure for high NA requirements |
| 4 | Keeping mask defect free | Mask yield & defect inspection / review infrastructure | Mask yield & defect inspection / review infrastructure | Continue actinic PMI and new mask material development | System and power efficiency improvements for next generation tooling |

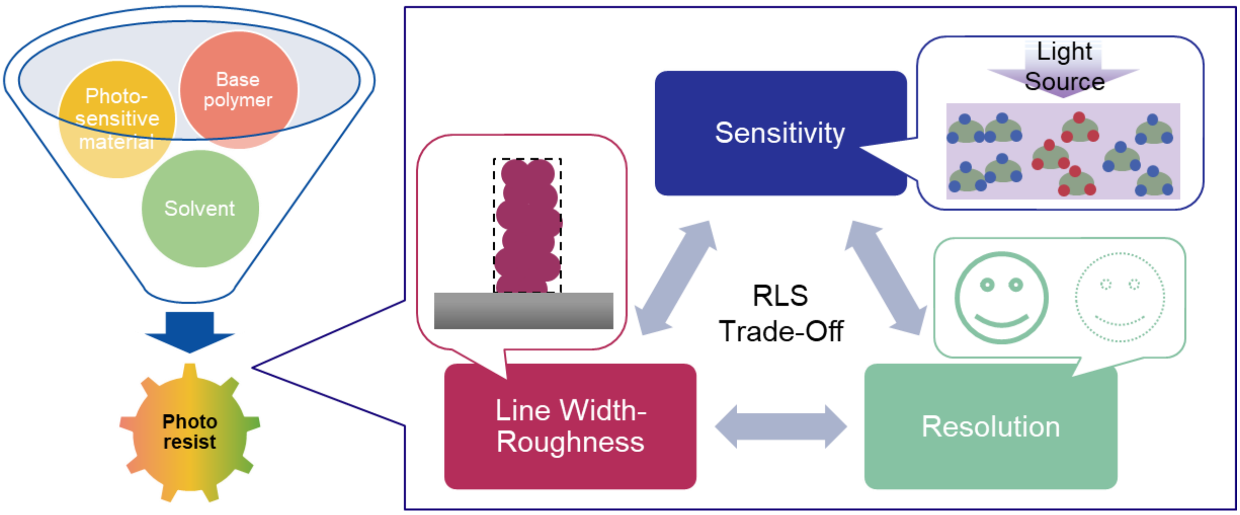
Source: Compiled by Mizuho Bank Industry Research Department based on materials published by the Semiconductor Equipment Association of Japan and the SPIE website.

### (2) Issues Facing Photoresists: The RLS Trade-Off

Improving on RLS trade-offs is a challenge for photoresist manufacturers

Photoresists are composed primarily of a base polymer, photosensitive material (hereinafter "PAG", an acronym for Photo Acid Generator), solvent, and sensitizer, and have contributed to the miniaturization of nm-scale circuit imaging by controlling the degree of dissolution in areas that are irradiated by the exposure light source. Resolution, line width – roughness and sensitivity[11] are the main criteria used to evaluate photoresist performance, and these are known to have a trade-off relationship (Figure 7).

[Figure 7] Overview of Photoresist Composition and Trade-Offs




Source: Compiled by Mizuho Bank Industry Research Department

Currently, mainstream CAR has issues such as poor resolution and non-uniform dispersion of the raw materials

The reaction mechanism for PAG blend[12]-positive CAR,[13] which is currently the mainstream photoresist, begins when the first incidence of a high energy ($h\nu$) EUV photon is applied to the photoresist, which ionizes the base polymer ($+I_e$) and emits secondary electrons. From the law of conservation of energy, the energy of the secondary electrons generated at this time is the energy of the photon reduced by the energy required to ionize the polymer ($h\nu - I_e$). The collisions caused by these movements are repeated, and when the energy of the secondary electrons decreases below a certain level and they collide with the PAG, acid is generated and breaks the bonds in the base polymer (Figure 8).

[11] Roughness is a phenomenon in which the edges of the resist deviate from a straight line to unevenness (Line Edge Roughness) or the line width of the resist deviates from an uneven line (Line Width Roughness).
[12] PAG is blended with other raw materials and is referred to as PAG blend for convenience.
[13] CAR is an acronym for Chemically Amplified Resist.

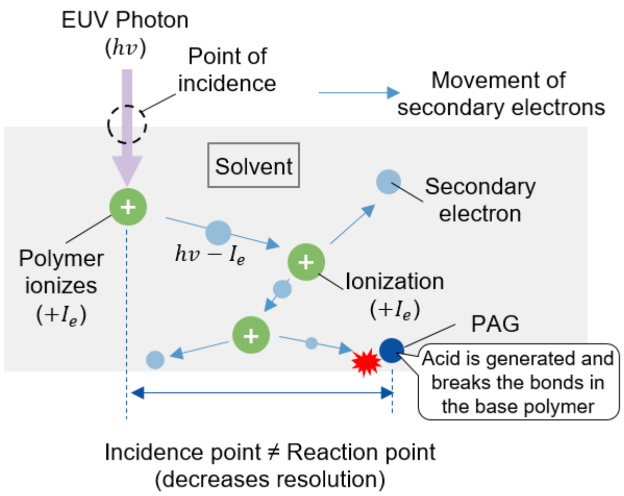
The lack of sensitivity that has resulted from the evolution of light sources has been addressed by the addition of more sensitizers, etc.

As light sources evolved from g/i line to KrF to ArF and then to EUV, the intensity of the light became weaker and the lack of sensitivity in lithography became more serious. However, the lack of sensitivity has been compensated for by adding more sensitizers to photoresists. Another reason why CAR is preferred is that adding heat treatment to the exposure produces the same processing results as exposure with sufficient light.

PAG blend-positive CAR has lower resolution due to the difference between the light incidence point and the acid generation point

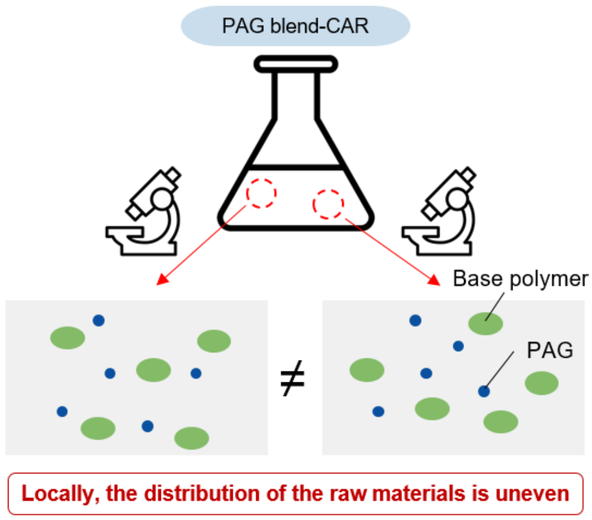
Due to the RLS tradeoff, increasing sensitivity will worsen roughness, and each company has tried to solve this problem by devising ways to minimize it. However, the problem with PAG blend-positive CAR is that the light incidence point and the acid generation point are different, which results in lower resolution. Additionally, the fact that the base polymer and PAG are not uniformly dispersed in the photoresist locally is also a factor causing the resolution to decrease. Due to these factors, it is very difficult for photoresist manufacturers to keep photoresist quality within a statistically acceptable margin of error over a certain period of time (Figure 9).

[Figure 8] Reaction Mechanism for PAG Blend-Positive CAR




Source: Compiled by Mizuho Bank Industry Research Department

[Figure 9] Raw Material Distribution for PAG Blend-Positive CAR




Source: Compiled by Mizuho Bank Industry Research Department

### (3) Overview of Various Cutting-Edge Photoresists

Photoresists thought to be able to support further miniaturization each have their own advantages and disadvantages

While it is considered to be extremely difficult to further improve the RLS trade-off in PAG blend-positive CAR photoresists, which have been the driving force behind miniaturization up until now, various types of cutting-edge photoresists are being developed as photoresists that can support future miniaturization evolving to 2 nm and 1.X nm (Figure 10). Each type has its own advantages and disadvantages, and at this point, it is unclear which type will become the de facto standard. The following is an overview of each type of photoresist.

[Figure 10] Overview of Various Cutting-Edge Photoresists

| Type | Major companies | Explanation | Advantages/disadvantages |
|---|---|---|---|
| PAG bound-CAR (positive) | Various Japanese photoresist manufacturers | • By bonding PAG to the main backbone of the base polymer, non-uniform dispersion between the base polymer and PAG is eliminated | • Is an improved version of PAG blend-CAR, and semiconductor fabricators are familiar with it<br>• Non-uniform PAG dispersion remains unresolved |
| Wet / Dry MOR (negative) | Wet: Inpria (US) (JSR subsidiary) | • Uses metal oxide reactions to form patterns by changing the solubility of exposed and unexposed areas | • Is a negative photoresist, so the point of incidence is the point of reaction, which realizes high resolution<br>• Removal requires chemical cleaning, which is more time-consuming than positive photoresists<br>• Quality control is difficult due to storage, process stability, and sensitivity to moisture, etc. |
| | Dry: Lam Research (US), Entegris (US), Gelest (US) | • Unlike Wet MOR, which uses a spin coating method, Dry MOR is deposited via CVD | • Superior to Wet MOR in terms of EUV light absorption rate and usage amount<br>• Dry development suppresses pattern collapse caused by the development solution or rinse solution<br>• Development of peripheral materials and equipment is essential |
| Main chain scission | Zeon | • Polymer is designed so that the main chain of the polymer breaks down into monomer units when irradiated by an electron beam | • The polymer, which is always present at any location, triggers a chemical reaction, making it easy to form fine, high-resolution patterns<br>• Development of peripheral materials and equipment is essential |
| Directed Self-Assembly (DSA) | JSR, Tokyo Ohka Kogyo, Merck (DE) | • Spontaneous assembly of molecules is promoted from a thermochemical perspective and applied to patterning | • Because it uses copolymerized polymer materials with the same molecular length, in principle there is no variation in width when three-dimensional structures are formed through self-assembly, and theoretically roughness does not occur<br>• Development of peripheral materials and equipment is essential |

Source: Compiled by Mizuho Bank Industry Research Department based on each company's IR materials, etc.

### (i) PAG bound-CAR

PAG bound-CAR addresses the problems with PAG blend-CAR

PAG bound[14]-CAR, in which PAG is bound to the main backbone of the base polymer (hereinafter "PAG polymer"), was developed with the aim of minimizing resolution degradation and non-uniform dispersion of raw materials, which are problems with PAG blend-CAR (Figure 11). Semiconductor fabricators who wish to continue using CAR that they are already familiar with are likely to adopt PAG bound-CAR in their 2 nm generation semiconductor fabrication recipes.

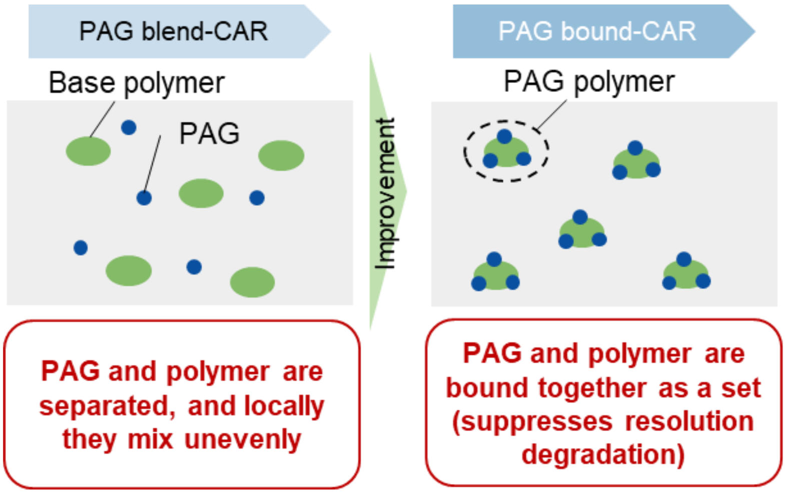
PAG bound-CAR requires high technical capabilities and know-how at the development and manufacturing stages

In order to meet the performance requirements of semiconductor fabricators, PAG bound-CAR requires even higher levels of technical capabilities at the development stage of PAG monomers, which are the precursor to PAG polymers. Furthermore, at the manufacturing stage, the chemical synthesis of PAG monomers by raw material manufacturers must be conducted under even more stringent environmental and reaction conditions than ever before. In order to minimize the risk of contamination with impurities, dedicated chemical synthesis kilns are required for each type of monomer/polymer that will be manufactured (multi-purpose use is not possible), and, while this is not limited to PAG bound-CAR, the investment burden and quality assurance risks for raw material manufacturers are also increasing (Figure 12) because they are being required to manufacture monomers, polymers, and solvents in smaller quantities, in more varieties, and under stricter conditions. In the Japanese photoresist industry, the fact that issues and risks related to chemical synthesis have been minimized through the relationships of trust that have been built via collaborations between photoresist manufacturers and raw material manufacturers will continue to be a source of competitiveness going forward.

---

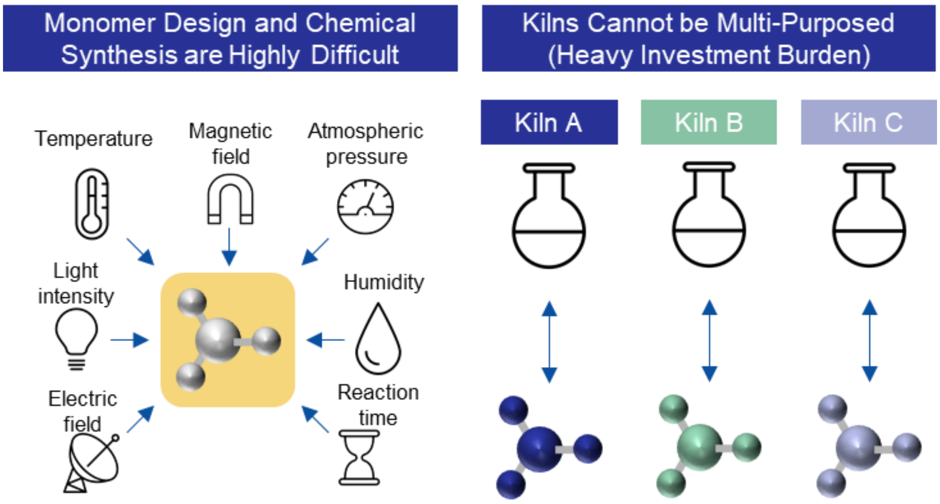
[14] The PAG is bound to a base polymer (Bind) and is referred to as PAG bound for convenience.

[Figure 11] Comparison of PAG blend-CAR and PAG bound-CAR




Source: Compiled by Mizuho Bank Industry Research Department

[Figure 12] Issues and Responsibilities Faced by Photoresist Manufacturers and Raw Material Manufacturers (Sources of Competitiveness)



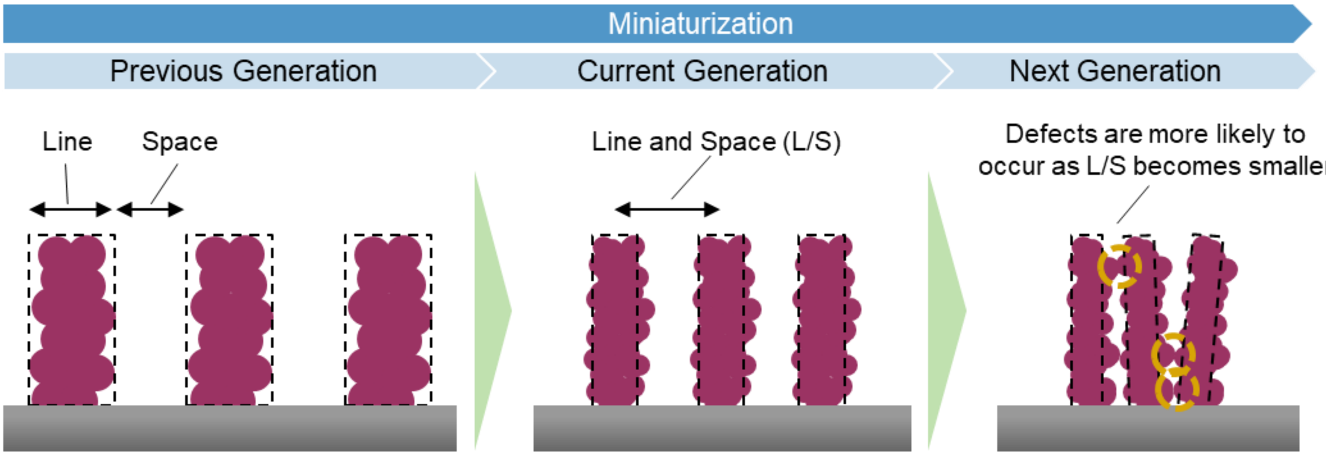

Source: Compiled by Mizuho Bank Industry Research Department

PAG bound-CAR does not eliminate the non-uniformity of the PAG polymer, and it is unknown if further miniaturization is possible

PAG bound-CAR minimizes non-uniformity between the base polymer and the PAG by introducing the PAG polymer. However, non-uniformity in the dispersion of the PAG polymer in the photoresist has not been resolved, and roughness, which is tolerated at the current 3 nm, may no longer be negligible as a cause of defects (such as pattern-to-pattern contact and pattern collapse) at 2 nm (Figure 13). Some are saying that CAR's support limit is 2 nm, and it remains to be seen to what extent PAG bound-CAR will be able to support L/S[15] reductions associated with future miniaturization.

[15] "Line" refers to pattern width, "Space" refers to the gap between patterns, and "Line and Space (L/S)" refers to the distance between the center of Lines.

[Figure 13] Diagram of Defect Occurrences due to Miniaturization




Source: Compiled by Mizuho Bank Industry Research Department

### (ii) Wet/Dry-MOR

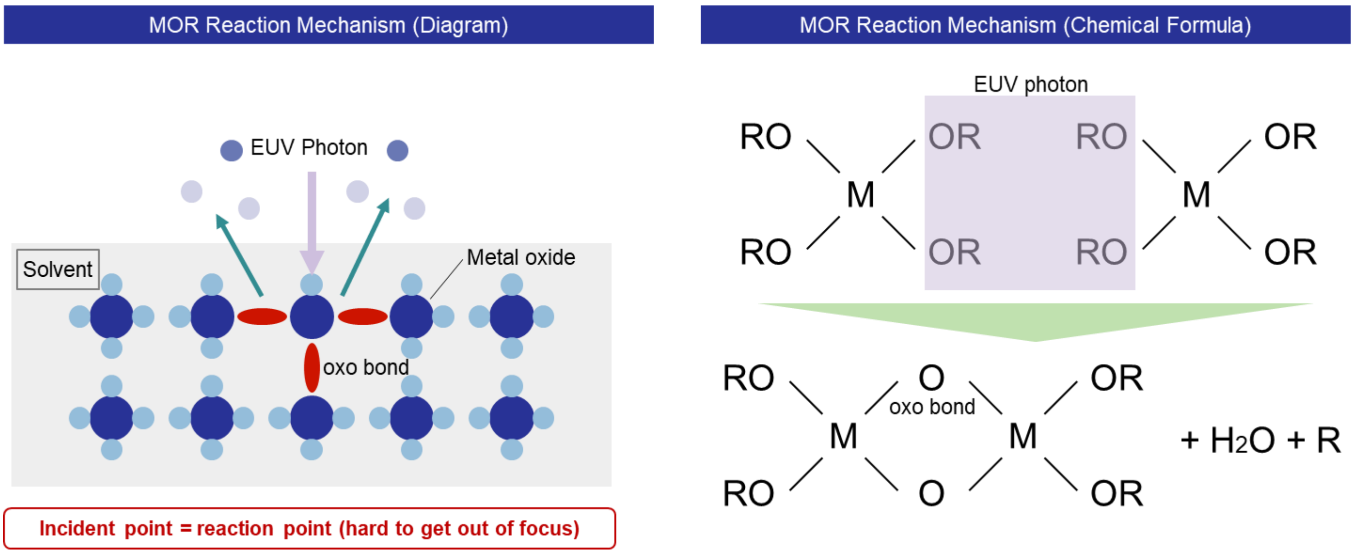
MOR is a negative photoresist containing metal oxides

Metal Oxide Resist (MOR), as the name suggests, is a photoresist containing metal oxide. MOR is a negative photoresist in which areas exposed to EUV light harden. There are both wet and dry MOR.

Wet-MOR is characterized by high resolution due to its high absorption rate for EUV light

First, the reaction mechanism for Wet-MOR is that oxo bonds occur in areas irradiated by EUV light, which results in hardening (Figure 14). In particular, Wet-MOR, which utilizes Sn (tin) and Hf (hafnium), is characterized by its high resolution due to its high absorption rate for EUV light. Although the hardened areas must eventually be removed via chemical cleaning, Wet-MOR has the advantage that resolution is less likely to be degraded due to the difference between the light incidence point and the reaction point, which has been an issue with PAG blend-positive CAR. Additionally, the high dry etching resistance[16] of Wet-MOR is another factor that is expected to contribute to future miniaturization. For Wet-MOR, the technical capabilities of Inpria (US), which has been conducting R&D since its establishment in 2007, are rated as being very high. The company was acquired by JSR in September 2021.

[Figure 14] Wet-MOR Reaction Mechanism




Note: M = metal (tin, etc.) and R = hydrocarbon group

Source: Compiled by Mizuho Bank Industry Research Department based on SPIE website, etc.

[16] The process of partially or completely removing a thin film by using an etching gas is called dry etching. The etching resistance of a photoresist is evaluated by its film reduction rate during etching, and the smaller the film reduction rate, the better the etching resistance.

With Dry-MOR, the photoresist agent is deposited via CVD

Conventional photoresists are liquid (hereinafter, liquid photoresists are described as Wet-Resist), and, after being dropped onto the center of a wafer, the Wet-Resist is evenly spread over the entire surface of the wafer via spin coating, which rotates the wafer at high speeds. Dry-MOR significantly differs from Wet-Resists in that it uses chemical vapor deposition (hereinafter "CVD"[17]) to deposit the photoresist agent (Figure 15).

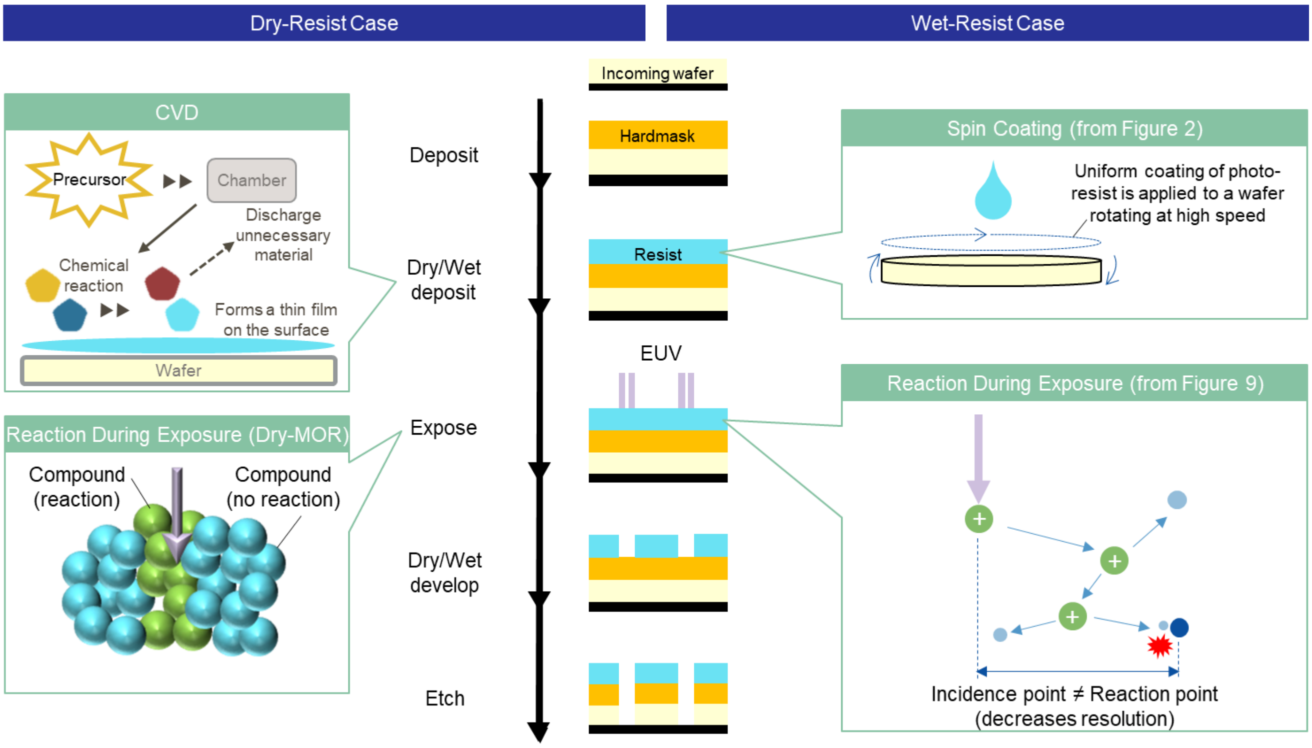
Dry-MOR makes it easy to improve RLS trade-offs and allows processes to proceed efficiently

According to Lam Research (US), Dry-MOR makes it easier to improve RLS trade-offs when compared to Wet-Resists, and is superior to Wet-Resists in terms of resolution, purity, and a wide process window.[18] Other Dry-MOR advantages include: the amount of photoresist used can be reduced compared to Wet-Resists, in which more than the required amount is dropped onto the surface of the wafer and then spread out to cover it; the amount of chemicals used in the Dry develop[19] process is less than in the Wet develop[20] process; and the electricity consumption can be reduced to efficiently perform the entire lithography process (Figure 16).

Lam Research, etc. have the lead in developing Dry-MOR

Dry-MOR was developed by Lam Research in 2020 in collaboration with ASML (NL) and IMEC[21] (BE). Lam Research, an equipment manufacturer, has announced that it will collaborate with Entegris (US) and Gelest (US) (a subsidiary of the Mitsubishi Chemical Group), who supply metallic precursor raw materials, as manufacturing partners for Dry-MOR.

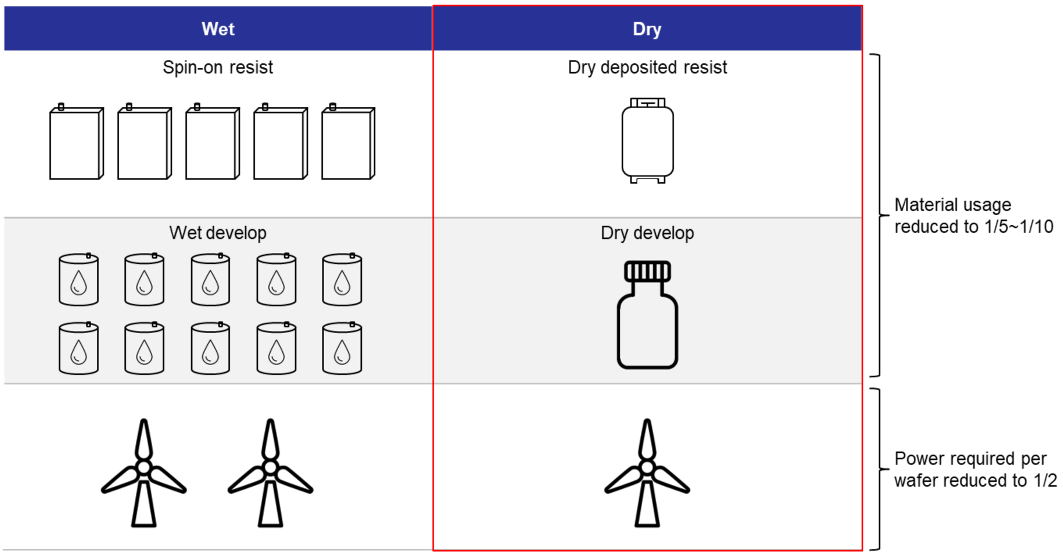
[Figure 15] Comparison of Wet/Dry Photoresist Coating/Photolithography Methods




Source: Compiled by Mizuho Bank Industry Research Department based on Lam Research IR materials

[17] CVD is a technology that is typically used in the deposition process of semiconductor fabrication, and its advantages include high deposition speed, large processing area, and high raw material utilization efficiency. The compounds used as raw materials to form thin films and wiring on wafers are called precursors, and metallic precursors are important in Dry-MOR.
[18] The range of permissible processing conditions to achieve the objectives of a certain process.
[19] Method of forming photoresist patterns using dry etching. Compared to Wet develop, the Dry develop method has the advantages of avoiding problems such as substrate reflection and a reduced probability of pattern collapse because no developing solution is used.
[20] Developing method that uses an alkaline developing solution or an organic developing solution as a chemical agent.
[21] Abbreviation for "Interuniversity Micro-Electronics Centre." IMEC is an independent research institute that was established in 1984 as an NPO by the Belgian and Flemish governments. IMEC started with approx. 70 researchers and now leads the technological development of next-generation semiconductors with a team of approx. 5,500 people from more than 95 countries around the world. Equipped with the latest equipment, clean rooms, and state-of-the-art facilities, IMEC attracts researchers from semiconductor fabricators around the world, including Intel (US) and Samsung (KR).

[Figure 16] Advantages of Dry-MOR




Source: Compiled by Mizuho Bank Industry Research Department based on Lam Research IR materials

**MOR is expected to contribute to resolving former challenges**

Although Wet/Dry-MOR are expected to make significant contributions to resolving issues such as the RLS trade-offs that are faced by CAR, which has been the de facto photoresist, it should also be noted that MOR photoresists have their own unique issues.

**MOR requires reliable residue removal**

Because Wet/Dry-MOR are photoresists containing metal, which can cause defects, a technical issue common to both of them is the need to reliably remove any residual photoresist.

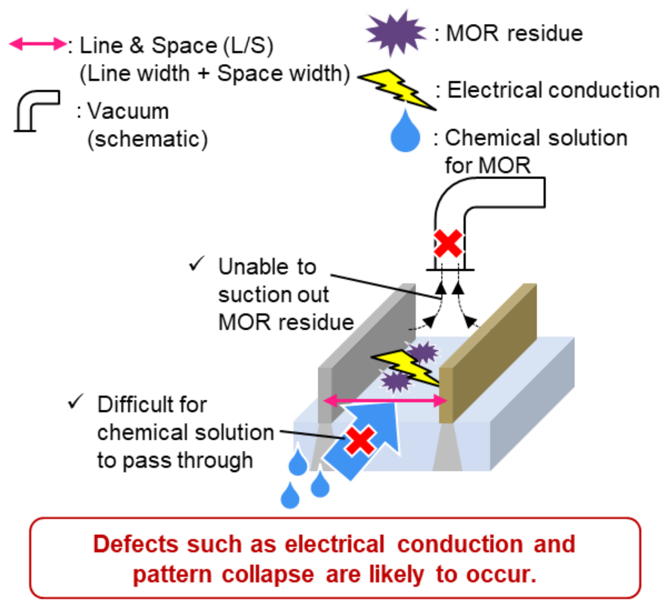
**Wet/Dry-MOR each have their own unique challenges**

A unique challenge for Wet-MOR is the use of chemical solutions for Wet development and cleaning, which can lead to pattern collapse due to the chemical agents flowing into small L/S (Figure 17). Unique challenges for Dry-MOR include the need to develop peripheral materials and equipment because it involves a new process of depositing the Dry-MOR via CVD, as well as the fact that it will take a long time for semiconductor fabricators to become proficient with the technology and achieve high yields (Figure 18).

**Wet/Dry-MOR require high sample evaluation**

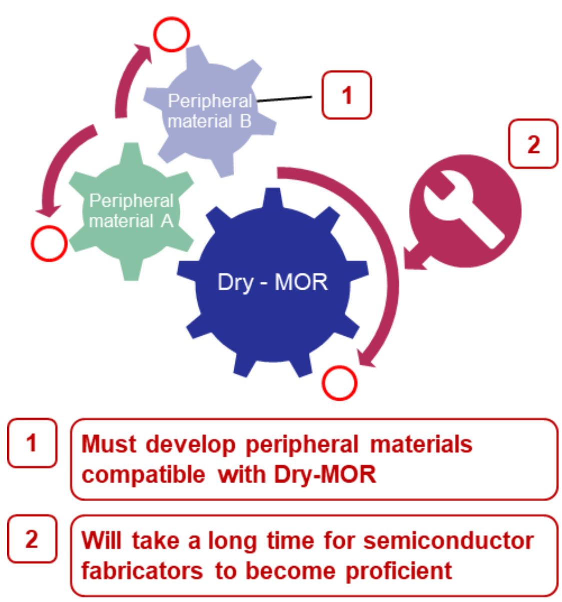
For both Wet/Dry-MOR, it is important to obtain high enough sample evaluations to overcome the psychological hurdles of semiconductor fabricators who wish to continue using familiar positive CAR, in which the irradiated portion dissolves.

[Figure 17] Wet-MOR Challenges




Source: Compiled by Mizuho Bank Industry Research Department

[Figure 18] Dry-MOR Challenges




Source: Compiled by Mizuho Bank Industry Research Department

(iii) Others (Main Chain Scission and DSA)

The advantage of Main Chain Scission is that it is easy to form fine, high-resolution patterns

Main Chain Scission and Directed Self-Assembly (DSA) have also been proposed as cutting-edge photoresists. Main Chain Scission is a photoresist in which the main chain of the polymer breaks down into monomer units when irradiated by an electron beam. Its advantage is that it is easy to form fine, high-resolution patterns because the polymer, which is always present at any location, triggers a chemical reaction. Main Chain Scission is being developed by Zeon.

The advantage of DSA is that, in theory, roughness does not occur

DSA is a photoresist that promotes the spontaneous assembly of molecules from a thermochemical perspective and is applied to patterning. Its advantage is that it uses copolymerized polymer materials with the same molecular length, so, when a three-dimensional structure is formed via self-assembly, in principle there is no width variation and, in theory, no roughness occurs.

Both Main Chain Scission and DSA have the same challenges as MOR

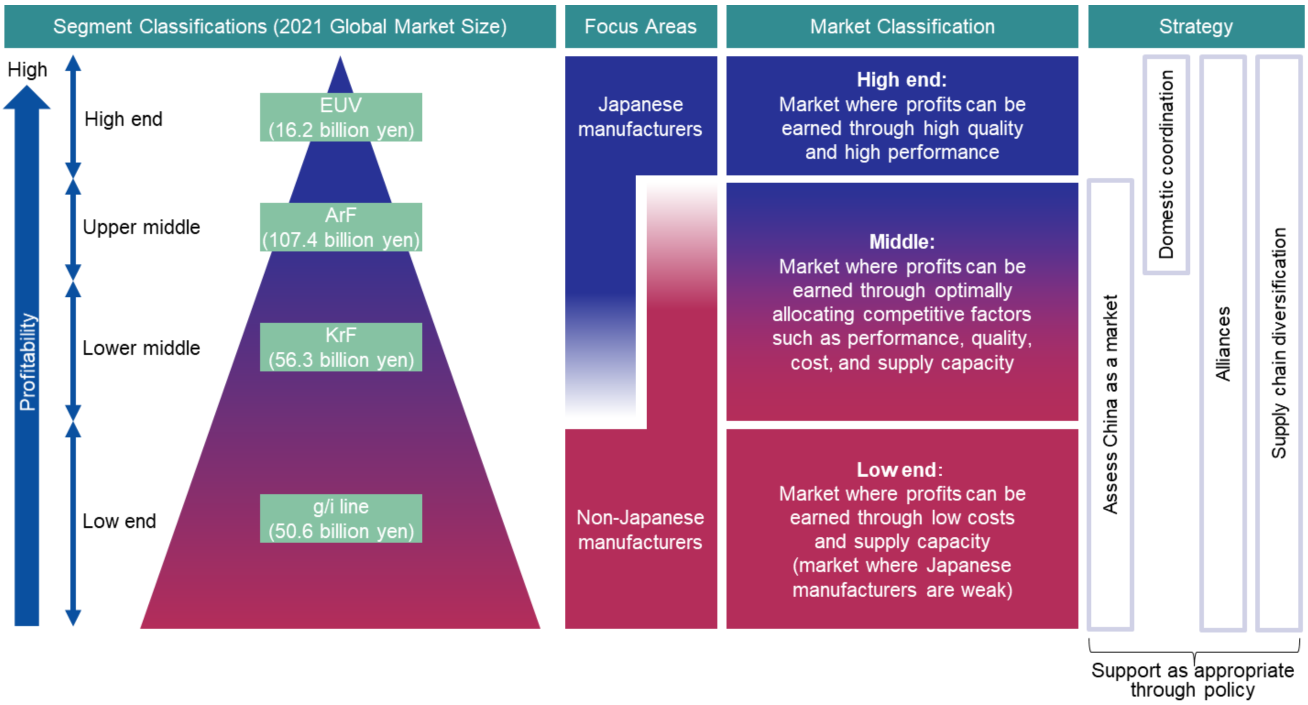
Both are expected to contribute to resolving the issues that CAR has been facing. However, as with MOR, not only do they face issues such as requiring the development of new processes and overcoming psychological hurdles from semiconductor fabricators who wish to continue using familiar CAR, but they also require the development of new peripheral materials and equipment and it is expected that it will take a long time for semiconductor fabricators to become proficient in using them and achieve high yields.

## 4. Ensuring that Japanese Photoresist Manufacturers Remain Strong at the High End

In order for Japanese photoresist manufacturers to remain strong, it is necessary to assess focus areas and develop appropriate strategies

To date, Japanese photoresist manufacturers have maintained high technological capabilities and competitiveness, and have led the industry. In order to continue doing so in the future, Japanese photoresist manufacturers need to assess areas to focus on and develop appropriate strategies. As mentioned earlier, although it is currently unclear which type of cutting-edge photoresist will become the de facto standard, one direction is to allocate the profits earned in the middle area to the high-end area where each company's strengths can be leveraged. In this section four specific strategies are discussed: (1) assess China as a market, (2) domestic coordination, (3) mergers and acquisitions, and (4) supply chain diversification. Examples of the kinds of policies required to implement these strategies are also provided (Figures 19 and 20).

[Figure 19] Focus Areas and Strategic Direction for Japanese Photoresist Manufacturers




Note: The 2021 global market size is quoted from the Fuji Chimera Research Institute's "Future Perspective and Reality of Cutting Edge / Noteworthy Semiconductor Related Market 2023"
Source: Compiled by Mizuho Bank Industry Research Department

[Figure 20] Concepts for Strategic Directions and Required Policies

| | Manufacturer's Strategic Direction | Concept | Required Policies |
|---|---|---|---|
| Protecting Technologies and Maintaining Competitiveness | 1 Assess China as a market | • EUV photoresist demand will not be created due to lack of access to EUV lithography equipment<br>• Chinese photoresist manufacturers will improve their technological capabilities through coordination with leading Chinese semiconductor fabricators<br>• Increasing exports of ArF photoresists, etc. will increase the risk of technology leakage; on the other hand, hesitating to export will mean missing out on a huge market<br>• It is important to earn solid profits in the Upper/Lower Middle segments while protecting cutting-edge technologies | • Careless export restrictions will increase the possibility that Chinese photoresist manufacturers will create innovative products on their own and build supply chains, thereby taking away market share from Japanese photoresist manufacturers<br>• The Japanese government also recognizes the fact that China functions as an enormous market, and is implementing appropriate policies through thorough dialogue with Japanese photoresist-related manufacturers |
| | 2 Domestic coordination | • State-of-the-art facilities and equipment are needed to coordinate with first-rate semiconductor fabricators; however, there are limits to investment by Japanese manufacturers alone<br>• Although it would be preferable to conduct coordination in Japan with its abundant human resources, the reality is that coordination is currently being conducted in Taiwan, South Korea, the US, and Europe | • Support for the creation of an environment of coordination in Japan by attracting the fabs and research institutes of first-rate semiconductor fabricators to Japan |
| Enhancing Technological Capabilities and Competitiveness | 3 Alliances | • Possibility of improving competitive advantage through technological fusion and expanding resources such as human resources and technology | • Strengthen R&D and seller negotiating power through expansion of scale, including the flexible application of antitrust laws, and friendly rivalries through intra-industry competition |
| | 4 Supply chain diversification | • There are cases where, from the perspective of economic rationality, procurement of raw materials for semiconductor materials is dependent on specific countries/regions | • Promote diversification of Japanese manufacturers' supply chains by providing short- and medium-term commercialization support through policies and subsidies |

Source: Compiled by Mizuho Bank Industry Research Department

(1) Assess China as a market: Business expansion will increase the risk of technology leakage, so it is necessary to carefully assess and respond

The first direction to be discussed will be (1) assess China as a market. As mentioned above, while Chinese manufacturers are expanding their market share in numerous functional materials, such as battery and display materials, Japanese manufacturers continue to maintain their market share in semiconductor materials, especially photoresists. However, it should be noted that China is making a concerted national effort to improve its semiconductor self-sufficiency rate. In October 2022, the US significantly tightened export regulations on high-end semiconductors and related technologies to China, and requested that Japan and the Netherlands, which are major producers in the semiconductor industry, comply with the regulations. Both countries agreed to do so. As a result, China is unable to obtain EUV lithography equipment, making it difficult for China to domestically fabricate high-end semiconductors. However, if yield and throughput[22] are ignored, then miniaturization is possible through multi-patterning using ArF exposure equipment, and in theory it is possible for China to domestically fabricate high-performance semiconductors. In fact, there are reports that China's SMIC is shipping 7 nm generation semiconductors that are positioned as high-end semiconductors, and that the competitiveness of China's YMTC is increasing in 3D NAND since changing course to stacking after miniaturization with ArF came to a halt.

Chinese demand is expected to continue to grow, but increasing export volumes may lead to increased risks of technology leakage

Japanese photoresist manufacturers have been exporting 16,000 tons/year of photoresists over the past 10 years, partly because Chinese photoresist manufacturers have not been able to meet China's strong domestic demand for photoresists in terms of quality and production capacity (Figures 21, 22, and 23). Although demand is expected to remain strong, if Japanese photoresist manufacturers increase exports to China of ArF photoresists, which are positioned in the middle segment, then it cannot be denied that the risk of technology leakage will increase. Additionally, it should also be noted that the technological capabilities of Chinese photoresist manufacturers, who coordinate with the aforementioned powerful Chinese semiconductor fabricators, are constantly improving, and such catch-up may lead to a decline in the market share of Japanese photoresist manufacturers.

[22] The number of wafers that can be processed per unit of time.

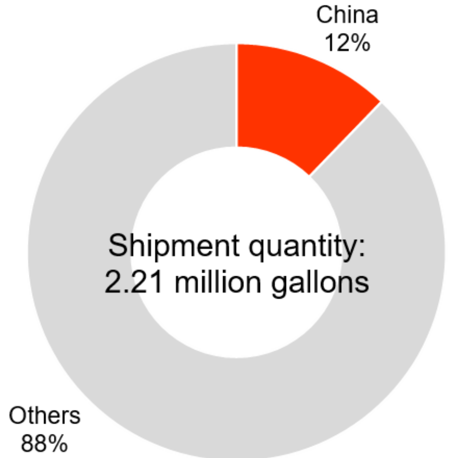
It is important to make solid profits in the Chinese market while protecting company technologies

However, if Japanese photoresist manufacturers hesitate to export to China in order to protect their own technologies, then that would mean missing out on an enormous photoresist market. Chinese manufacturers who are no longer able to obtain photoresists and their raw materials via imports may create innovative products on their own and build their own supply chains, potentially seizing market share from Japanese manufacturers. Therefore, we believe that it is important for Japanese photoresist manufacturers to capture the Upper/Lower Middle segment market and to make solid profits while maintaining their high-end technologies.

Requires appropriate policies through dialogue with photoresist-related manufacturers

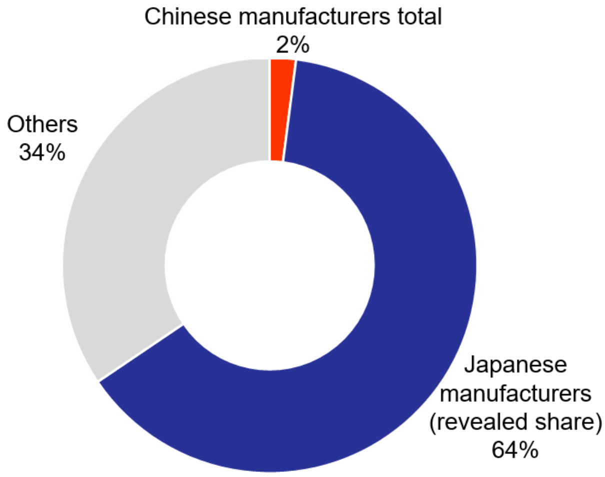
Although it is necessary for each country to implement regulations in line with each other for products that are at risk of being diverted for military purposes, the Japanese government should also recognize the fact that China functions as an enormous market and should engage in thorough dialogue with Japanese photoresist-related manufacturers to formulate with appropriate policies. On the other hand, when it comes to high-end technologies, there is an increasing need for manufacturers and the government to seriously work to prevent technology leaks. As an example of such initiatives, it goes without saying that Japanese photoresist manufacturers should seriously work to prevent engineers from going overseas by establishing remuneration systems that solidly reward engineers who have achieved results, and the government will also need to take strict measures to prevent information leaks from manufacturers and their employees.

[Figure 21] Breakdown of Global Photoresist Shipments (2020 Results)



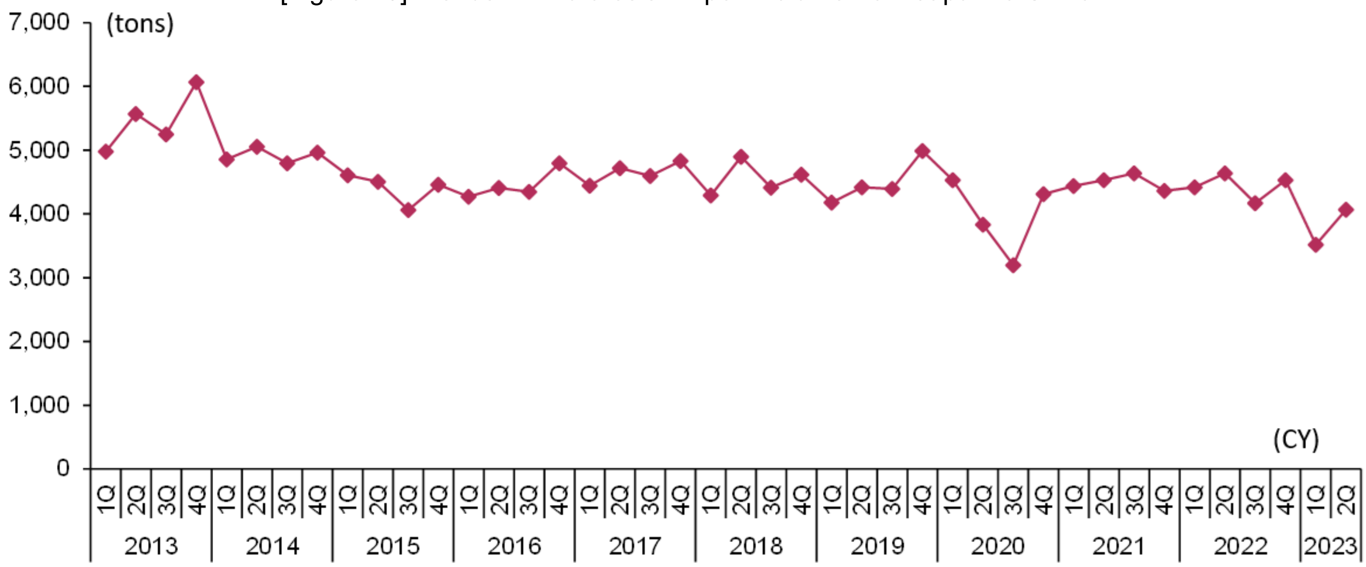

Source: Compiled by Mizuho Bank Industry Research Department based on "Latest trend survey of Chinese semiconductor manufacturers 2021" by the Fuji Chimera Research Institute

[Figure 22] World Photoresist Market Share (2020 Results)




Source: Compiled by Mizuho Bank Industry Research Department based on " Latest trend survey of Chinese semiconductor manufacturers 2021" by the Fuji Chimera Research Institute

[Figure 23] Trends in Photoresist Export Volume from Japan to China




Note: HS code is 370789, for "Photographic goods; chemical preparations other than sensitised emulsions"
Source: Compiled by Mizuho Bank Industry Research Department based on Global Trade Atlas

**(2) Domestic coordination: Implementing coordination with first-rate semiconductor fabricators in Japan**

The next direction to be discussed is domestic coordination. The types of photoresists that are expected to contribute to future miniaturization are highly likely to be accounted for, and a suitable amount of academic research results on them have been accumulated. In order to adopt them in next-generation semiconductor fabrication recipes, in addition to R&D for the photoresist itself, it goes without saying that coordination with semiconductor and equipment manufacturers will continue to be important, including various evaluations to maximize photoresist performance, as well as the development status of peripheral equipment and materials that are compatible with photoresists. Ideally, Japanese photoresist manufacturers should have their own equipment and continue to upgrade it to the latest models in order to coordinate with first-rate semiconductor fabricators who have complete sets of the equipment on a company scale that far exceeds that of their own companies.

**It is important to have close cooperation with semiconductor fabricators planning to introduce EUV exposure equipment**

However, realistically it is impossible for a single material manufacturer to have a lineup of the various types of equipment, including EUV exposure machines that cost tens of billions of yen each, and in some cases, they also lack the know-how to handle such equipment. Currently, in order to confirm the performance of their photoresists, Japanese manufacturers have no choice but to ship their cutting-edge photoresists by air to Taiwan, South Korea, the US, and Europe (IMEC), which have the EUV exposure machines and the know-how to use them. This means that some of the development status and technical capabilities of Japanese photoresist manufacturers cannot be kept within Japan. As such, one solution would be to closely work with Rapidus and Micron (US), which, with the support of the Japanese government, are planning to introduce EUV lithography equipment in Japan.

**Expectations for policies that foster Japan as a place for researching and developing cutting-edge semiconductors**

There are both pros and cons to providing huge subsidies to non-Japanese semiconductor fabricators, but we believe that the presence of EUV exposure equipment in Japan has the potential to contribute to maintaining and improving the competitiveness and technological capabilities of various semiconductor material manufacturers, including of Japanese photoresist manufacturers, which is a major advantage. We hope that policies will continue to foster Japan as a place where semiconductor fabricators, equipment manufacturers, and materials manufacturers work in unison to conduct R&D on cutting-edge semiconductors.

**There may be room for improvement in policy support that caters to Japanese manufacturers in need of support**

Incidentally, Japan's Ministry of Economy, Trade and Industry (METI) oversees the "Certification for Initiatives Related to Ensuring a Stable Supply of Semiconductors" as a subsidy for semiconductor materials, and the criteria for certifying subsidies for semiconductor materials is that "the scale of capital investment must be extremely large (in principle, business scale is 30 billion yen or more)." As shown in (Figure 19), business scale tends to be small in the High End because consumption is limited, but, considering that the companies are currently competing in a market worth 230 billion yen, there is a possibility that some photoresist manufacturers have given up on applying because they do not meet the criteria. If the barrier to application is high even for photoresist manufacturers, which have a relatively large market amongst semiconductor materials and for which Japanese manufacturers have a large market share, then the hurdles must be even higher for manufacturers of other semiconductor materials. As such, there is probably room for improvement in policies catering to Japanese manufacturers in need of support.

**(3) Alliances: Taking changes in the business environment into consideration, there is utility in reorganizing the Japanese semiconductor materials industry**

Semiconductor fabricators, equipment manufacturers, and material manufacturers have worked together in unison to develop semiconductor technologies. Amidst intensifying competition to develop next-generation technologies, the semiconductor fabricators that actually produce them are becoming more oligopolistic, and buyers' bargaining power is increasing. In response to these movements, non-Japanese material manufacturers are attempting to strengthen their competitiveness through mergers and acquisitions, and the bargaining power of Japanese material manufacturers is becoming weaker in relative terms. Examples include the acquisition of Versum Materials (US) by Merck (DE) in 2019, and the acquisition of CMC Materials (US) by Entegris (US) in 2021. The Japanese semiconductor materials industry has had little need for mergers and acquisitions due to factors such as the fact that each company, although small in size, has established a highly profitable model leveraging its superior technological capabilities. However, given the changing power balance among semiconductor fabricators, equipment manufacturers, and material manufacturers, as well as the prospect of increasingly heavy R&D and capital investment burdens for semiconductor material manufacturers to maintain and improve their competitive advantage, the benefits of restructuring the Japanese semiconductor materials industry, including the photoresist industry, can be seen.

By going private, JSR aims to become a leader in reorganizing the Japanese semiconductor material industry

Against this background, on June 26, 2023, JSR announced that it would accept an acquisition by the Japan Investment Corporation (JIC), a government-affiliated fund. With the backing of the government-affiliated fund, JSR is leading the reorganization of the Japanese semiconductor materials industry, and intends to increase its international competitiveness by gaining a large market share with a wide lineup of semiconductor materials, doing technological mergers with other companies, and enhancing its resources, which will enable it to acquire new human resources and technologies. JIC will provide an environment in which JSR can concentrate its management resources on the semiconductor materials business by going private, and by continuing to support the development of cutting-edge semiconductor materials, JIC hopes to strengthen the international competitiveness of the semiconductor industry being promoted by the Japanese government. However, it should also be noted that, because JSR has a first-rate market share in the photoresist industry, it would be reasonably difficult to consider the possibility of an industry reorganization that is in accordance with the Japan Fair Trade Commission's basic thinking.

It is important to balance strengthening seller bargaining power and R&D through expansion of scale with friendly rivalries through intra-industry competition

On the other hand, paradoxically, it is also true that Japanese manufacturers in the photoresist industry have continued to see success as a result of friendly rivalries between companies that have encouraged them to hone their technological capabilities in a fiercely competitive environment. If the competition amongst photoresist manufacturers subsides as a result of an industry reorganization, and if companies fall into innovation dilemmas wherein they lag behind in the development of innovative technologies as a result of focusing on customer service and improving existing products, then it cannot be denied that non-Japanese manufacturers could take advantage of that opening. It is important for Japanese manufacturers, including photoresist manufacturers, to maintain their technological superiority by both strengthening their bargaining power and their R&D by expanding their scale and by engaging in friendly rivalries via intra-industry competition.

(4) Supply chain diversification: From a viewpoint of economic rationality, diversify procurement networks for raw materials that are dependent on specific countries and regions

Although this is not a topic that is limited to photoresists, supply chain diversification is becoming increasingly important due to heightened interest in geopolitical risks and economic security, as exemplified by Russia's invasion of Ukraine and the friction between the US and China. Although it may be unavoidable in cases where raw materials are unevenly distributed in a particular country or region,[23] there is room for improvement in policy support in cases where there is a dependency on the raw materials from the perspective of economic rationality.[24] Improving stable supply capacity through diversification of raw material procurement networks should also contribute to improving seller bargaining power. Timely and appropriate policy support is needed not only for the downstream semiconductor industry, but also for the upstream semiconductor materials industry, with the aim being to maintain and improve competitiveness.

We hope that Japan will remain strong through each company's unflagging R&D and appropriate policy support

As mentioned at the beginning of this paper, with each country striving to develop and nurture its own semiconductor industry, it is not surprising that policy support for the development of cutting-edge products will become essential for Japanese photoresist manufacturers to maintain and improve their technological capabilities and competitiveness going forward. We hope that Japanese photoresist manufacturers will remain strong in the future through continued R&D and appropriate policy support.

Arata Murashige, Primary Materials Team,
Mizuho Bank Industry Research Department
arata.murashige@mizuho-bk.co.jp

---

[23] For example, 50% of the world's cobalt, which is used in some wiring layers, is dependent on the Democratic Republic of the Congo.
[24] For example, although Mexico and South Africa have relatively large reserves of fluorite, which is a raw material for fluorine-based materials, there is a dependence on China for cost and quality reasons.

# 【参考文献】


1. 新聞雑誌
   - ○ 化学工業日報社「金属レジスト　事業化へ前進」(2022 年 8 月 25 日・8 月 26 日)
   - ○ 株式会社産業タイムズ社「EUV リソグラフィー、マスクのインフラ整備着々」(https://www.sangyo-times.jp/scn/headindex.aspx?ID=2051)(2019 年 9 月 5 日)
   - ○ 株式会社産業タイムズ社「米国が考える対中半導体規制の次の一手」(https://www.sangyo-times.jp/article.aspx?ID=7809)(2022 年 8 月 12 日)
   - ○ 株式会社日本経済新聞社「中国への半導体輸出規制、米国が拡大　先端技術を広範に」(https://www.nikkei.com/article/DGXZQOGN07DZ90X01C22A0000000/)(2022 年 10 月 8 日)

2. 学術論文
   - ○ Sang-Kon Kim, Line-Edge Roughness from Extreme Ultraviolet Lithography to Fin-Field-Effect-Transistor: Computational Study, 2021(https://www.mdpi.com/2072-666X/12/12/1493)

3. 書籍
   - ○ 「2023 先端/注目半導体関連市場の現状と将来展望」(2023) 株式会社富士キメラ総研
   - ○ 「中国半導体メーカーの最新動向調査 2021」(2021) 株式会社富士キメラ総研

4. ホームページ(国内)
   - ○ 経済産業省「半導体の安定供給の確保に係る取組の認定について」(https://www.meti.go.jp/policy/economy/economic_security/semicon/index.html)(2023 年 9 月 22 日)
   - ○ 株式会社産業革新投資機構「JSR 株式会社に対する公開買付けの開始予定に関するお知らせ」(https://www.j-ic.co.jp/jp/news/pdf/20230626_JIC_PressRelease.pdf)(2023 年 9 月 22 日)
   - ○ JSR 株式会社「JICC-02 株式会社による当社株式等に対する公開買付けの開始予定に係る賛同の意見表明及び応募推奨に関するお知らせ」(https://ssl4.eir-parts.net/doc/4185/tdnet/2303298/00.pdf)(2023 年 9 月 22 日)
   - ○ JSR 株式会社「Inpria Corporation 全株式取得に関するお知らせ」(https://ssl4.eir-parts.net/doc/4185/ir_material_for_fiscal_ym1/106507/00.pdf)(2023 年 9 月 22 日)
   - ○ 株式会社 SCREEN セミコンダクターソリューションズ「初心者のための半導体入門」(https://www.screen.co.jp/spe/technical/guide/exposure)(2023 年 9 月 22 日)
   - ○ SEMI-NET「半導体用語集」(https://semi-net.com/word)(2023 年 9 月 22 日)
   - ○ 東京エレクトロン株式会社「パターニング技術による微細化への取り組み」(https://www.tel.co.jp/rd/highlights/20171208_001.html)(2023 年 9 月 22 日)
   - ○ 東京応化工業株式会社 HP(https://www.tok-pr.com/)(2023 年 9 月 22 日)
   - ○ 日経クロステック「まだ続く半導体微細化、最終到達点は「究極のトランジスタ」CFET」(https://xtech.nikkei.com/atcl/nxt/column/18/00001/07897/)(2023 年 9 月 22 日)
   - ○ 日清紡マイクロデバイス株式会社「第 2 回　半導体の微細化と半導体プロセス」(https://blog.nisshinbo-microdevices.co.jp/ja/process_2)(2023 年 9 月 22 日)
   - ○ 一般社団法人日本半導体製造装置協会「2019 年度報告 ウェーハプロセス専門委員会」(https://www.seaj.or.jp/activity/tech/file/2019wafer.pdf)(2023 年 9 月 22 日)
   - ○ 公益社団法人発明協会「フォトレジスト」(http://koueki.jiii.or.jp/innovation100/innovation_detail.php?eid=00061&age=stable-growth&page=keii)(2023 年 9 月 22 日)
   - ○ Bloomberg「中国最大の半導体メーカー、7nm製造技術確立か－米制裁対象」(https://www.bloomberg.co.jp/news/articles/2022-07-22/RFE9OQDWLU6801)(2023 年 9 月 22 日)
   - ○ レーザーテック株式会社「EUV マスク関連検査装置について」(https://www.lasertec.co.jp/ir/individuals/euv.html)(2023 年 9 月 22 日)

5. ホームページ(海外)
   - ○ ASML「Investor Day 2022」(https://www.asml.com/en/investors/investor-days/2022)(2023 年 9 月 22 日)
   - ○ Entegris「Entegris to Acquire CMC Materials to Create a Leader in Electronic Materials」(https://investor.entegris.com/news-releases/news-release-details/entegris-acquire-cmc-materials-create-leader-electronic)(2023 年 9 月 22 日)
   - ○ Lam Research「2020 Investor Day」(https://investor.lamresearch.com/events?item=37)(2023 年 9 月 22 日)
   - ○ Merck「Merck Completes Acquisition of Versum Materials」(https://www.merckgroup.com/press-releases/2019/oct/en/Versum-Closing-Press-Release-EN.pdf)(2023 年 9 月 22 日)
   - ○ SPIE「Novel metal-oxide photoresist materials for extreme UV lithography」(https://spie.org/news/6534-novel-metal-oxide-photoresist-materials-for-extreme-uv-lithography?SSO=1)(2023 年 9 月 22 日)

[Link to a survey]

Mizuho Short Industry Focus/215　2023　No.16　　Published on October 10, 2023



Edited/Published by Mizuho Bank Industry Research Department　1-3-3 Marunouchi, Chiyoda-ku, Tokyo　ird.info@mizuho-bk.co.jp