# Recent Innovations in ArF Sumiresist®

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With the increased development in electronic equipment in our highly information-oriented society, there have been significant advances in lithography. As a result, high-performance functions are required of the photoresists that play a critical role in lithography to control the feature size, line width roughness (LWR) and defects. We have been developing ArF photoresists since 1996, and this led to commercialization of the ArF photoresist PAR-101 in 1997. As critical dimensions get smaller, we have continued to put a great deal of effort into creating innovative materials and optimizing conditions in the photolithography process. The ArF Sumiresist® series is evolving to fill a variety of demands in the ArF photoresist market.

Introduction

With the rapid development of an advanced information-oriented society, there are demands for high-level functions and greater variety in electronic equipment. For example, the memory capacity required by mobile equipment (**Fig. 1**) such as digital audio players, mobile phones and car navigation systems just keeps moving along the line of exponential increases.
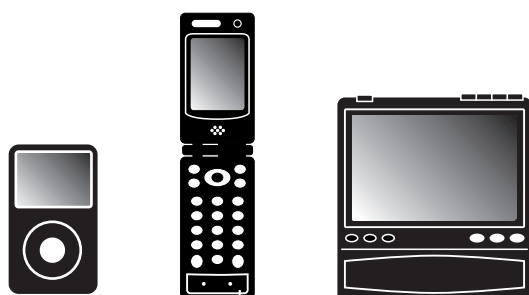
Fig. 1 Electronic Equipment

Therefore, there are increasing needs for related electronic materials and functions that exceed the capabilities of current materials. Among these, greater integration of the semiconductor devices that are indispensable for electronic equipment is very important. One of the fundamental technologies for creating circuit patterns on device substrates to achieve this increased integration is lithography.[1] Lithography is technology for forming very fine structural patterns obtained by exposure to electron beams, ultraviolet light and the like, and therefore, light sensitive materials called photoresists are used. According to the 2005 version of the International Technology Roadmap for Semiconductors (ITRS),[2] mass production of 65 nm and 45 nm node devices is planned for 2006 and 2009, respectively (**Fig. 2**). To respond to these demands, the development in lithography technology has been remarkable, and there is a great interest in research and development of photoresists, which are the materials for it.
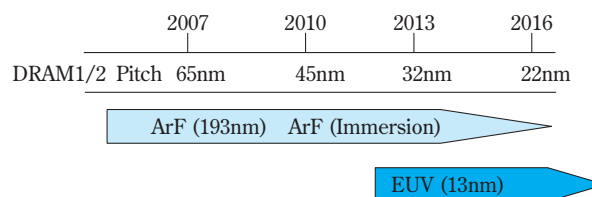

Fig. 2 Lithography Roadmap

We previously reported on photoresists and their development in the 2000 – No. 1[3] issue of SUMIKA, so we want to discuss the developments since then, particularly line edge roughness (LER) and line width roughness (LWR) which have come to the surface as new problems, as well as the problem of defects and newly developed photoresists.

Development of ArF Resist Resins

Development of ArF resists began at Sumitomo Chemical in 1996, and it was found that methacrylate ester copolymer resins exhibited good performance. Sumiresist® PAR-101 went on the market in 1997, ahead of other companies' products. We have already discussed this history in the earlier issue. Subsequently, we improved the methacrylate ester resins focusing on improving resolution with the further reductions in feature size, increasing etching resistance and solving the problems of LER, LWR and defects that have accompanied smaller patterns.

For the monomer units making up the resin, a deprotection reaction is brought about using a photoacid generator (PAG), and there are acid labile monomers where the polarity of the resin is changed and monomers with polar groups that adhere to substrates. Among these, the acid labile monomers are important, and various companies have developed various monomers up to this point.[4] Several examples are cited and described below (**Fig. 3**).
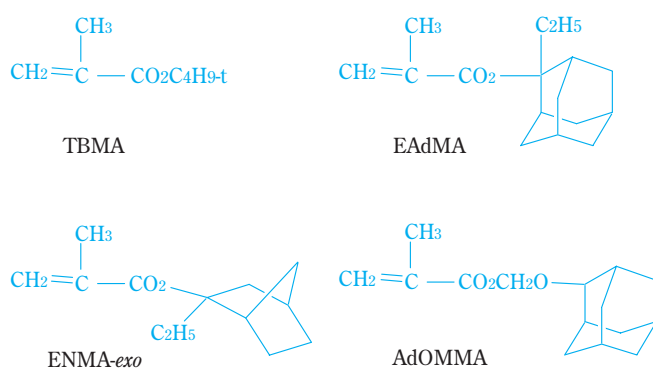
Fig. 3   Acid labile monomers

Acid labile *tertiary* esters are often used in protecting groups that undergo hydrolytic cleavage, but there are differences in reactivity in the various protecting groups, and ease of hydrolytic cleavage is

TBMA < EAdMA < ENMA-*exo*.

Hydrolytic cleavage is difficult with ENMA-*endo*, which is an isomer of ENMA-*exo*, and the configuration has a large effect. Furthermore, acetal structured AdOMMA, which undergoes hydrolytic cleavage more readily than *tertiary* esters, has been developed.[5], [6]

At Sumitomo Chemical, we have carried out opti-

mization of the methacrylate ester resin part with a large number of screenings and have developed resists with methacrylate ester monomers and resin compositions that have good performance in terms of resolution as well as LER and defects, which will be discussed in the following.

Recently, LER and LWR have become important problems with the surpassing of 100 nm nodes. LER is a value that indicates the unevenness in size on the sides of the pattern. LWR is the fluctuation arising because of the unevenness and affects the line width roughness in gate patterns. We can assume that it leads to problems in device performance.

At a DRAM half pitch (hp) of 65 nm, the permissible value for LWR is 3.4 nm (3σ); furthermore, at a half pitch of 45 nm, it becomes 2.4 nm (3σ), and there must be strict control of the pattern fluctuations. Since the C-C bond distance in chemical bonding is 1.5Å, the 2.4 nm (3σ) for LWR at a half pitch of 45 nm, it means that a size equal to 16 carbons becomes a problem, and we have reached the stage of control on the molecular level.

From the resist material side, we can cite various causes of LER, such as the molecular weight of the resin, dispersion, size of the aggregate, solubility characteristics, amine concentration in additives, diffusion length of acids arising from PAG and the like.[7], [8]

Given all of this, we carried out various investigations on resins. In investigations of the molecular weight of resins, there was poor solubility with resins having large molecular weights, so we carried out optimization. In addition, if the solubility of the resin is increased too much by introducing polar groups, the pattern collapses, so a better balance in the polarity of the resin as a whole is required. In terms of acid diffusion length, the diffusion length increases and LER improves with small acids such as trifluoromethanesulfonic acid, but there is a tendency for the resolution to get worse. Conversely, with large acids such as perfluorooctanesulfonic acid, the diffusion length is not very long and the resolution improves, but there is a tendency for LER to get worse. In other words, there is a trade-off relationship between acid diffusion length and LER, and the PAG molecular structure must be optimized.
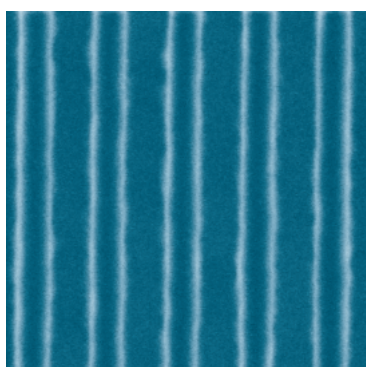
Not only are the materials, starting with the resin, optimized, but also the optimal conditions for the process must be found to derive better resist performance. It is not overstating it to say that resists come about because of an extremely delicate balance of the

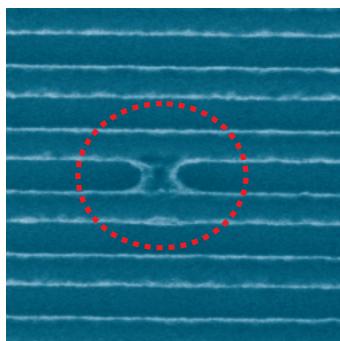various materials and process conditions.

By going through a process like this, we were able to develop Sumiresist® PAR-855 with its superior lithography performance for resolution, LWR and the like.

The photo is a top view SEM photograph of Sumiresist® PAR-855, and with the very good value of LWR 4.0 nm, the roughness of the side surface of the pattern (white part) is small (**Fig. 4**).

As the feature size becomes smaller, we have focused anew on the problem of defects. Examples of defects include micro bridge defects and satellite spot defects, and they are a problem in reducing yields in device production processes. The photo shows an

example of a micro bridge defect, and one can see that there is a connection like a small bridge between the pattern lines (**Fig. 5**).

One of the causes of defects is the solubility when the deprotected resin is developed. Deprotection reactions that change the polarity of the resin are very important. If the reaction is insufficient, defects are caused by the polymer gel not dissolving sufficiently in the alkaline developing solution and being left on the pattern. Therefore, as will be discussed later, we have worked on acid labile monomers and developed flexible monomers. Resins using these flexible monomers have protecting groups in positions outstretched from the main chain, so they are easily attacked by acids and the deprotection reaction proceeds smoothly. In addition, we can assume that the flexible monomer leads to a smooth disentanglement of polymer chains; therefore, the swollen polymer chain in the exposed area can be rapidly transferred to the bulk solution.

We have optimized other monomers with polar groups, investigated monomer ratios and optimized processes. As an example, the performance of Sumiresist® PAR-855 is shown in the photos below, and it is a resist with superior lithography performance where the nice square profile is maintained, and a large DOF and a small value for LWR are achieved. (**Fig. 6**).
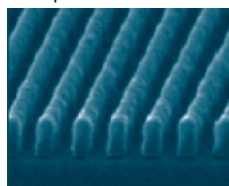
Fig. 4 Sumiresist®PAR-855 top view SEM image (70 nm Line & Space patterns, 140 nm pitch)

Fig. 5 Micro bridge defect (Top view SEM image, 100nm Line & Space patterns)

Sumiresist® PAR Series

1. Reflow Resist

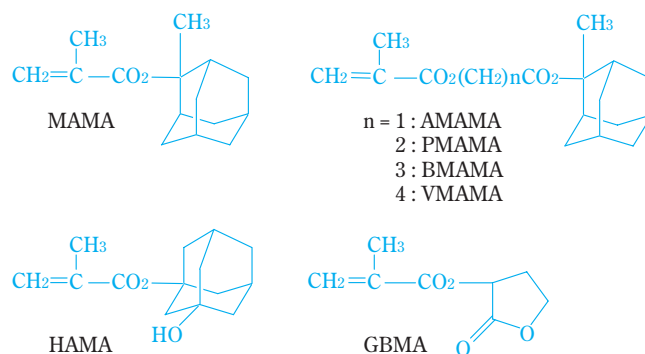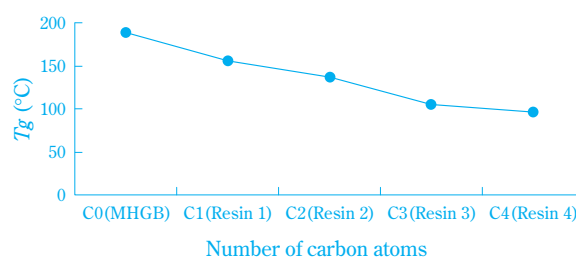Reflow technology is a resolution enhancement technique for forming fine patterns. This is a technique for heating a resist pattern that has been exposed and developed to the glass transition temperature (Tg) and further reducing the size of the pattern. Since normal methacrylate ester resins have a high Tg value, as in the Tg value for MHGB (MAMA/HAMA/GBMA = 50/24/25) in **Table 1** being in the vicinity of 190°C, for example, reflow processes are difficult when viewed in

65 nm Line & Space (1:1) (130nm pitch) Depth of Focus

| −0.20µm | −0.10µm | 0.00µm | +0.10µm | +0.20µm |

Fig. 6 Cross-section SEM image of Sumiresist®PAR-855

Table 1 The characteristics of the methacrylate polymers

Polymer	Monomers	Mw	PD	Tg (°C)
MHGB	MAMA/HAMA/GBMA	9400	1.59	188
Resin 1	AMAMA/HAMA/GBMA	11700	1.66	156
Resin 2	PMAMA/HAMA/GBMA	11700	1.84	137
Resin 3	BMAMA/HAMA/GBMA	14400	2.02	105
Resin 4	VMAMA/HAMA/GBMA	13400	1.86	96

Fig. 7 Methacrylate Monomers

**Fig. 8** Correlation of Tg with the number of carbon atoms

terms of mass production process conditions. In addition, the Tg value being the same as the decomposition temperature is also a factor that causes difficulty. Therefore, we investigated how to have a methacrylate ester resin structure with integrity that is flexible. Since ArF resist resins with methacrylate ester polymers as the main chains have adamantyl groups with their bulky ester groups, the Tg value is high because there is a hindered rotation around the main chain.

Therefore, we tried introducing methylene chains to the ester parts of acid labile monomers (MAMA) and investigated the relationship between the length and the resin Tg value. Using the methacrylate ester monomers shown in **Fig. 7**, we synthesized resins similar to MHGB. The chain was extended up to 4 carbons and the physical properties of the resin measured. When this was done, a linear relationship between the Tg value and the chain length was obtained, as is clear from Table 1 and **Fig. 8**, and we discovered that the Tg

value could be controlled freely.

Next, when the lithography performance of the resins with the extended chains was investigated, it was found that there was a tendency for performance to drop when there were too many carbons in the chains, making them too long, as is shown in the pho-
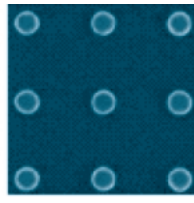

MHGB   Resin 1   Resin 2   Resin 3   Resin 4

Fig. 9 Comparison of 150nm 1 : 1 L/S of resists

MHGB   Resin 1   Resin 2   Resin 3   Resin 4
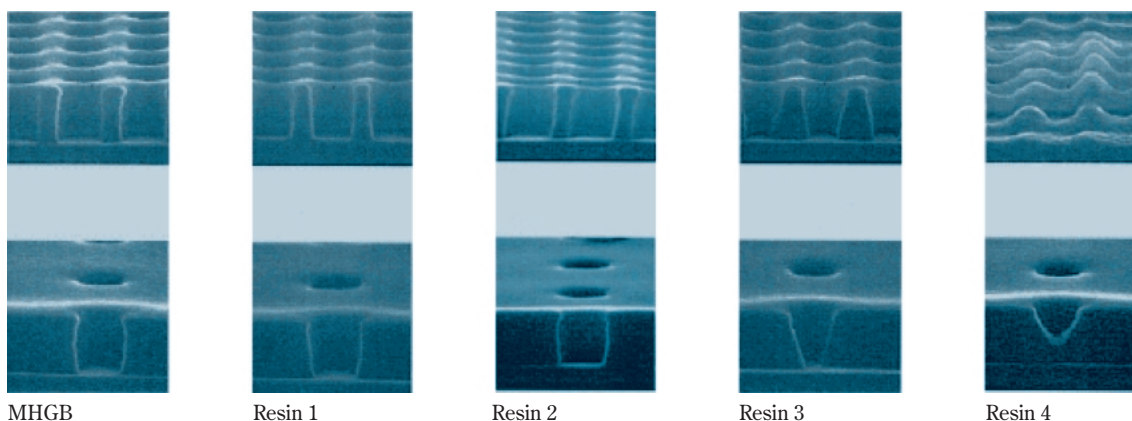
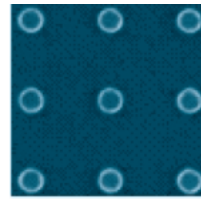**Fig. 10** Comparison of 180nm 1 : 0.5 and 1 : 3 contact holes of resists
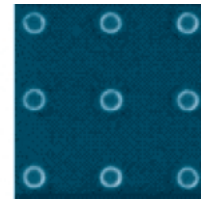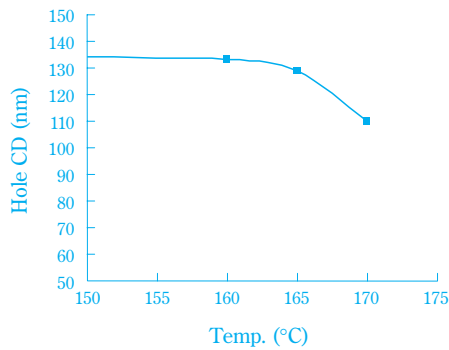
150nm Hole/600nm Pitch
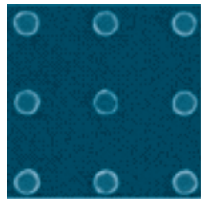
| No bake | 160°C/60sec | 165°C/60sec | 170°C/60sec |

Fig. 11   Thermal flow of contact holes with Resin 1

**Fig. 12**   CD change after thermal flow of Resin 1

tion of the resin, we found that the *Tg* caused no problems in processing. As is shown in the photo (**Fig. 11**) and graph (**Fig. 12**) of a hole pattern, this resist can form finer hole patterns in a state that maintains the true circular profiles in the reflow process.

Resists obtained by making use of this basic knowledge and further optimizing the resin and other additives have come onto the market as reflow Sumiresists®. [9]

tos in **Figs. 9** and **10**. When a thermal analysis of *Tg* and decomposition temperature for the resins with the increased number of carbons was conducted, we found that they were suitable for reflow processes because there was a clear gap between the *Tg* and the decomposition temperature. With optimization of the composi-

2. PAR Series Lineup

We have continued to press forward in the development of resist materials that meet market needs by making further use of the basic knowledge described above. As is shown in **Fig. 13**, the PAR series has currently been developed further into a lineup that brings together advanced ArF immersion exposure resists to further answer the needs of users.
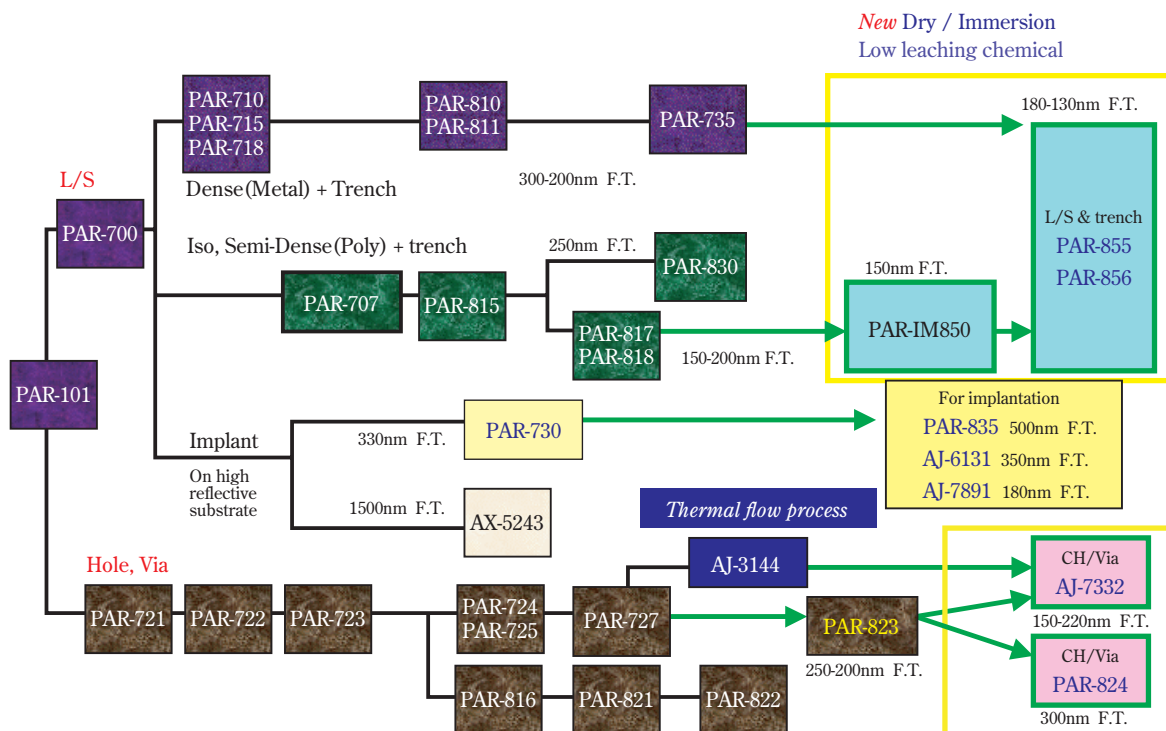
Fig. 13   Sumitomo positive tone ArF resist lineup

Conclusion

Sumitomo Chemical has been developing ArF resists since 1996, and Sumiresist® PAR-101 was marketed in 1997 ahead of other companies. Subsequently, we have developed resist materials and worked on the optimization of processes with the continued reductions in the feature size. We have thus marketed new products to answer the needs of the market. According the roadmap discussed above, ArF lithography is moving from dry exposure to ArF immersion exposure where pure water sticks between the lens and the wafer, and resists with even higher levels of performance are being required. We want to push even further forward with ArF resists that meet these needs of the market.

References

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