Photoresist Fabrication for High-NA EUV Lithography: Material and Mechanism

Herong Xu*

School of the Gifted Young, University of Science and Technology of China, Hefei, China

*Corresponding author: xuherong@mail.ustc.edu.cn

Abstract. Extreme ultraviolet (EUV) lithography is critical for the semiconductor industry nowadays. However, high-numerical aperture (NA) EUV systems face challenges in many areas, especially in photoresists. This paper reviews requirements and recent progress in EUV photoresists for high-NA EUV lithography. The key needs for photoresists include high resolution, low stochastic defects, minimal pattern collapse, and high sensitivity. Proposed solutions involve new photoresist materials and mechanisms, such as metal-containing photoresists, non-chemically amplified photoresists and tin-oxo cages photoresists. Basic fabrication and processing procedures are also discussed. Other than photoresists, the weak EUV light source also heavily restrains the development of photoresists. In the future, improvements in EUV light sources and patterning techniques will further help high-NA EUV photoresist development. In summary, the realization of high-NA EUV lithography system depends critically on the breakthrough of photoresists, while solutions are emerging to meet demanding requirements from various directions. Overall, these results shed light on guiding further exploration of next generation lithography.

Keywords: Lithography; high-NA; EUV lithography; photoresists.

1. Introduction

Lithography has been used to fabricate semiconductor chips over the past few decades, and has become one of the most important technologies for mankind today. Since contact lithography was invented in the 1960s, scientists have been trying to achieve smaller critical dimension (CD). In 1973, Perkin-Elmer introduced the Micralign projection scanner with a numerical aperture of 0.167, which combines projection printing and positive photoresist. Same year, Canon introduced the first proximity aligner. In 1975, IBM demonstrated step & repeat printing using a wavelength of 405nm (h-line) at a NA of 0.32. After that, in 1978, GCA introduced the first step-and-repeat system (stepper) with a NA of 0.28 using a wavelength of 436 nm (g-line). Nikon shipped first i-line (365nm) stepper in 1984 and the first KrF (248nm) stepper in 1988. The first step-and-scan tool, Micrascan, was developed by Perkin-Elmer in 1990. This new system combined large field size and low overlay errors together with a resolution of 0.5 μm, thus improved productivity [1]. In 1995, Nikon introduced their first scanner with 0.25 μm resolution using 248 nm deep ultraviolet (DUV) generated by an excited krypton fluoride (KrF) laser [2]. The argon fluoride (ArF) laser at a wavelength of 193 nm was firstly applied to ASML's first ArF scanner in 1998. Due to the limit of the resolution at 193nm water immersion, shorter wavelength is significantly needed for higher resolution. In 2013, ASML started a new era of extreme ultraviolet exposure tool, when they introduced the first NXE:3100. It has a NA of 0.25 and reached a resolution of 27nm using 13.5nm EUV light. The most advanced lithography system currently is the TWINSCAN NXE:3600D, from ASML, which has a NA of 0.33 and 13nm resolution, and can produce 5 and 3 nm logic nodes. ASML has been pushing limit to high-NA EUV lithography, and chose 0.55NA as goal, which may achieve 8nm resolution.

Another important component in lithography is photoresist, which also experienced rapid development since the 1950s. In addition, its development highly corresponds to the development of lithography system. In 1954, Kodak synthesized and prepared the first artificial photosensitive polymer photoresist. As a kind of ultraviolet negative photoresist, the polyvinyl alcohol cinnamate photoresist system, absorbs between 230 nm and 340 nm and must be extended to over 450nm before use. Although it has good sensitivity and high resolution, its weak adhesion to silicon wafer limits its

application in industry. Sooner in 1958, Kodak developed a new negative photoresist called cyclized rubber-diazo, which has better adhesion, and preserves the advantages of polyvinyl cinnamate at the same time, thus was widely used in 1980s. The photoresist that is most commonly used in electronic industry is the o-diazonaphthoquinone-phenolic resin UV positive photoresist developed in 1960s. Comparing it with the negative photoresist cyclized rubber-diazo that mentioned above, a conclusion can be made that this positive photoresist has its advantages in high resolution, good heat resistance and easy removal. However, it also has some disadvantages, such as poor adhesion, weak mechanical strength, and slow photosensitive speed. As resolution goes higher, DUV lithography machine is needed. As a result, DUV photoresist must meet the requirements of smaller exposure wavelength and smaller diffraction effect with higher resolution and sensitivity. To achieve the goal, scientists discovered a new principle and developed chemically amplified photoresist. This new photoresist is much more sensitive, so it can be applied to smaller wavelength like 248nm, 193nm, 157nm and even EUV with some modification. Just as the development of lithography tool, 248nm photoresist poly (p-hydroxy styrene) was the first DUV photoresist that come to use in 1990s. As for 193nm photoresist, polymethacrylate attracted a lot of attention because of its extraordinary transmittance at 193nm. When it comes to EUV, things become quite different, since the wavelength of EUV light is so short, only 13.5nm. Under the same condition of volume and power, the EUV light contains only less than one-tenth photon number comparing to 193nm ArF light. As a result, high absorption elements should be removed as much as possible, otherwise increasing the ratio of C/H is of great importance [3].

In this paper, photoresist for high-NA system is discussed to study its current status and to promote the research on photoresist. The rest of this paper is divided into five sections. First, an introduction of photoresist is shown, following with its requirements for high-NA system. Then, the material and mechanism of photoresist are discussed. The final part is about some limitations and outlooks.

2. Basic Descriptions of Photoresist

Photoresist is of great importance to lithography. It is a kind of light-sensitive material, consists of a polymer, a solvent, and a photoactive compound. Each of them plays a specific role during the lithography process. In the case of the positive photoresist, the photoactive component can prevent the polymer from dissolving into the solvent before it exposed to light. After the photoactive material receiving light, it breaks down into small parts, allowing the polymer in the photoresist to spread into the solvent and forming thin layers over the wafer. Then it comes to the development part, only the area that experienced exposure can be removed, other parts which was protected by masks or covers can remain. After that, the pattern on the mask creates a copy onto the wafer precisely, which allows the process to continue. For example, the polymer can be novolac resins, with a photoactive material of diazonaphthoquinone (DNQ), dissolving in aqueous alkali [4].

However, things are quite opposite for the other type of photoresist. For negative photoresist, exposure may cause crosslinking in the photoresist. So, the exposed part of the negative photoresist can remain on the wafer. Then, during the development process, the developer solution dissolves the area that didn't receive light. As a result, masks for negative photoresist should use the inversed version of the pattern that needs to be transferred to the wafer. Example of negative photoresist is SU-8 which uses bisphenol A novolac epoxy resin as polymer. Depending on the formulation, the organic solvent can be chosen from gamma-butyrolactone (GBL) or cyclopentanone, using mixed Triarylsulfonium/ hexafluoroantimonate salt as the photoactive material.

Just as previously discussed, the mechanisms of positive and negative photoresist have a lot of differences which can lead to different usage scenarios. Both of them have their advantages. For the positive photoresist, advantages of it are better resolution, higher contrast, lower defect rate, convenient removal, and thermal stability. For the negative photoresist, advantages are higher sensitivity, better adhesion to silicon, lower cost, and faster process. All properties must be considered

in industry production. The result of the exposure of both type of photoresists is presented in Fig. 1 [5]. As shown in the Fig. 1, using the same mask can produce complementary patterns.

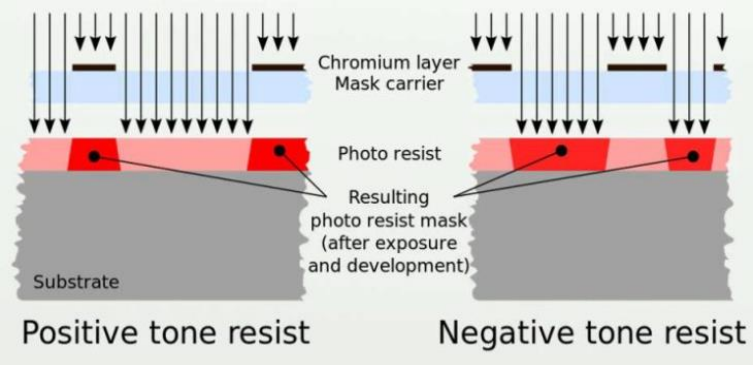

Fig. 1 Negative and positive photoresists are exposed using the same mask.

3. Requirements for High-NA EUV System

Photoresists have been a limit for EUV lithography for a long time, as the requirements for high-NA EUV technology become harder, the situation will be more difficult. Many new challenges in high-NA EUV lithography system have appeared as ASML and Zeiss pushing forward their researches. A summary of the key challenges of high-NA EUV lithography has been listed [6]. Among all of the crucial challenges of high-NA EUV lithography, the problem with photoresists lies in the first place. Conclusions can be made that in order to produce the photoresist suitable for high-NA EUV lithography, it must achieve necessary resolution requirements, low levels of stochastic defects, low levels of pattern collapse. In addition, reducing exposure doses is very helpful to increase throughput while saving the cost in mass production. In the following parts of this chapter, problems with resolution would be talk about firstly. Continuing with low defect rate causing by stochastic phenomena and pattern collapse. Last one should be high sensitivity which can reduce exposure doses.

3.1. Resolution

During the early stage of EUV lithography, it is discovered that the limitation for resolution was photoacid diffusion. Photoacid is a product generated by the decomposition of photoacid generators (PAGs). PAGs can be classified as a type of photoactive material which are mainly used in chemical amplified resists (CARs). Although CARs have appeared for long time, some enhanced versions of CARs are promising to be the photoresist for high-NA EUV lithography. The mechanism of photoacid diffusion can be explained by random walk. For a single photoacid molecule, its trail follows random walk. Statistically, if there is a large number of molecules, the total behavior of them looks like a blur similar to Fig. 2 [6].

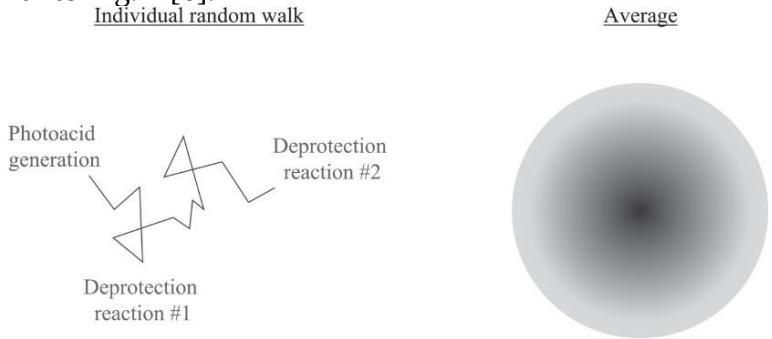

Fig. 2 Random walk one photoacid molecule. The average effect is blur.

Besides the photoacid diffusion, the resolution of EUV photoresists can also be restrained by photoelectron and secondary electron blur [7]. At first, the EUV photons are absorbed by molecules in the photoresist. Due to the high energy of the photons, photoelectrons can be emitted from those molecules, leading to ionization and electronic excitation of other molecules. If the photoelectrons

have enough energy, they can cause ionization and electronic excitation again, creating secondary electrons. It has been reported that the inelastic mean free path of electrons with the energy about 92eV is less than 1 nm [8,9]. As a result, the process of ionization and electronic excitation caused by either photoelectrons or secondary electrons occurs only near the molecules that absorb EUV photons. Therefore, the existence of high energy electrons is of great concern to EUV lithography. However, there are more than one kind of molecules can generate electrons. Under most situations, both polymers and PAGs can do that. The absorption in polymers is not expected to happen, one possible approach is through the fluorination of polymers [10]. This method can greatly improve the performance of the photoresist.

3.2. Defects

The line edge roughness (LER) is also an important factor to the performance of EUV lithography. Since the exposure dose of EUV need to be very small, shot noise can make great contributions to LER. Just as mentioned above, while using CARs, photoelectron and secondary electron blur can cause LER. Both effects are basically quantum phenomenon, which cannot be predicted, making it harder to control. It is reported that LER of EUV can reach about 2.58 nm, with the local CD of 5nm to 30nm [11]. One possible thing is that the size of molecules may affect LER under this scale. As for high-NA EUV, the demand of pattern size should be higher, making higher requirements for LER. In addition, CARs may face pattern collapse issue under small pitches. Scientists have been trying to reach below 12-nm half pitch, but keep facing problems. However, if the size of pattern keeps shrinking, the risk of having pattern collapse will become a big trouble. Using other kinds of material to make photoresists can avoid this, for example, Bespalov reported that tin oxo cages materials can form cross-linked network which can enhance its structure [12].

3.3. High Sensitivity

High-NA EUV is expected to have an exposure dose of over 80 mJ/cm^2 [13]. This prediction is very convincing because ASML has reached the exposure dose of 60 mJ/cm2 as reported in 2021, just as the prediction. If ASML combine the 80 mJ/cm^2 exposure dose and the 500W EUV light source they invented together, the throughput of high-NA system will increase a lot (100 wafers/hr), comparing to that of the 0.33NA system under the same situation (80 wafers/hr), according to Fig. 3 [14]. The curves are based on the circumstance when the high-NA system has already gained 2x increase in wafer stage, 4x increase in mask stage, while exposing half field rather than full field of 0.33NA using the same mask. However, this number of throughputs still remains a distance to the limit of the current 0.33NA system. Either more powerful EUV light source, or lower exposure dose can improve the throughput. There is still a long way to go, but applying new photoresist with high sensitivity, may dramatically reduce the requirement for exposure dose, offering relax to the demands of source power.

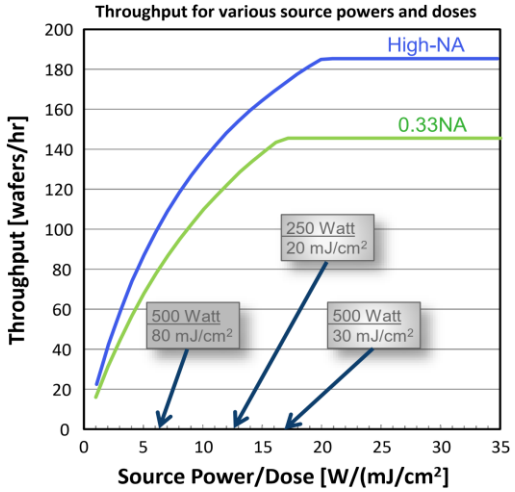

Fig. 3 Throughput curves for the NXE:3400C compared with the high-NA system.

4. Materials and Fabrication of Photoresist

4.1. Materials of Photoresist

CARs mainly consist of polymers, PAGs, and base quencher molecules. After exposed to light, the PAGs can generate acid, which can change the solubility of the polymers in the following post-exposure bake (PEB) step. There are several possible ways to achieve that, changing hydrophilicity, making crosslinking and back bone scission. However, when it comes to the EUV light, traditional CARs are mainly transparent, since their absorptivity to the EUV photons is quite low. Obviously, adding elements with higher absorptivity to the EUV photons into CARs, can greatly help to improve their sensitivity to EUV. The chart of atomic cross sections at 92 eV is shown in Fig. 4 [15]. As can be seen, among hydrogen, carbon and oxygen, the cross section of oxygen is much higher than others. Which leads to the method of increasing the amount of oxygen atoms to improve sensitivity. Furthermore, adding atoms with higher absorptivity, such as Zn, Sn, is proved to be much more helpful. In 2018, Yamamoto et al. reported the mechanism of the metal sensitizer added into CARs to improve the sensitivity. However, it turns out that the increase in sensitivity is resulted from not higher EUV photon absorption but higher acid yield and electron efficiency. They improved 43% of sensitivity along with a reduction in LWR simultaneously [16].

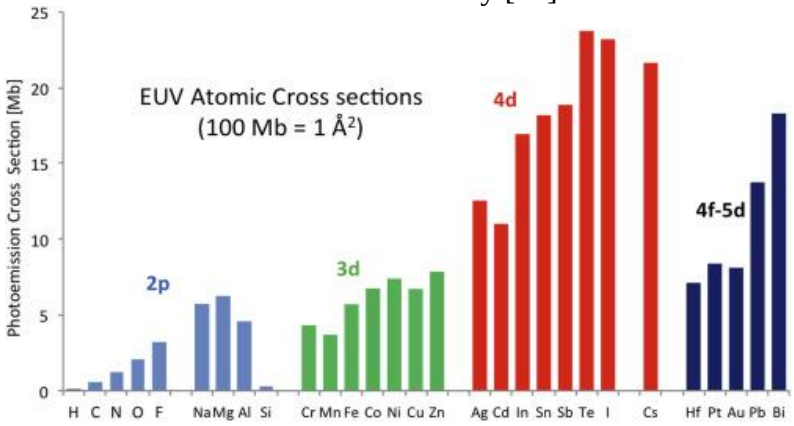

Fig. 4 Calculated atomic cross sections at 92 eV in Mb (mega barn).

One important reason for LER in CARs is blur. Moreover, acid diffusion can also influence resolution. As a result, to improve performance, materials for non-chemical amplified resists are needed the be developed. To give an example, the chain-scission reaction of polymethylmethacrylate (PMMA) resists perform good resolution and LER [17]. Even though PMMA finds a solution for LER and acid diffusion, it still faces problems like poor sensitivity and low etch resistance. Many approaches have been introduced to fix them. For example, Sharma et al. developed a new type of non-CARs which has an excellent sensitivity of about 11.3 mJ/cm^2 while avoiding acid diffusion and blur [18, 19]. Just as mentioned above, new types of photoresists are required to have higher sensitivity, and adding high EUV absorptivity atoms like Zn, Sn can be a solution. Recently, tin oxo cage materials attract a lot of interests, among them a type of Tin-OH material will be discussed [12]. Tin-OH refers to tin-oxo cage compound with hydroxide counterions which has been discovered to have response to very low energy electrons. It was reported that for the electron energy lower than 2 eV, small scale of crosslinking can be triggered. For those energy above 2 eV, the material can also crosslink and finally form a denser film.

4.2. Fabrication of Photoresist

The fabrication of many types of photoresists shares similar procedures. Same as mentioned above, the materials in photoresists are mainly polymer, solvent, and photoactive compound. It is obvious that polymer and photoactive compound need to be dissolved into the solvent. During this process, heating and stirring many be helpful to acceleration. Next step is spin-coating the photoresist to a cleaned and treated wafer. This process needs to be executed at a high temperature in order to

evaporate solvent making the photoresist firm enough to carry on. Until now, the photoresist is totally ready for exposure and forming pattern to the wafer. After the photoresist is prepared properly, the main procedures of lithography process can finally begin.

5. Mechanism of Lithography

Before exposure, the pattern on the mask must be aligned to the previous pattern using alignment marks [20]. In this process, the alignment is not perfect which can cause overlay in patterns. Many devices need several masks to from layers to operate, so the overlay factor is significant to them. One thing that need to be mentioned is that for the first layer, there is no previous alignment mark, so this procedure requires the alignment marks on the wafer.

After alignment, the mask is in the right place for exposure. Light pass through or be blocked due to the pattern on the mask. After that, photons in the light interacts with the light sensitive materials in the photoresist, changing its structure. For the positive photoresists, this change will make it soluble in the developer in the next step. On the other hand, the negative photoresist can be converted into a firm material preventing it from dissolving into the developer. The exposure process aims at creating pattern in the photoresist. However, the standing wave effect makes its side rough [12]. This effect results from the reflection of the substrate material. The reflected light interferes with the incident light creating a standing wave pattern inside the photoresist. This pattern happens in the whole exposure area and causes the sidewall uneven. During the baking process, the photoactive compound diffuses under high temperature, flatten the edge of the photoresist. Fig. 5 show the progress of the photoresist in the post exposure bake process [20]. For CARs, this process can change the solubility of the polymers under high temperature by the acid generated before.

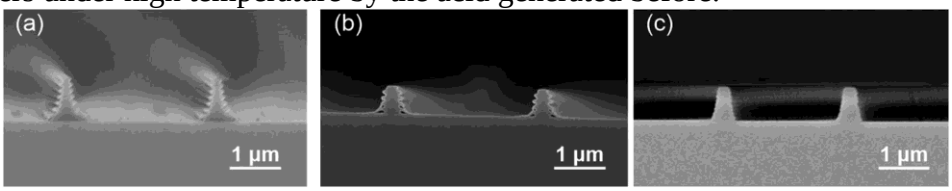

Fig. 5 SEM images of the developed photoresist patterns under different post baking conditions (a) without post baking, (b) post baked at 100 °C for 1 min, and (c) post baked at 100 °C for 3 min.

During the development process, the proper part of the photoresist is removed. Developer is applied to dissolve the soluble part of the photoresist, which means the exposed part of the positive photoresist or the unexposed part of the negative photoresist. After that, the pattern needed can be seen from the rest of photoresist. After development, the rest part also needs to be baked in order to get rid of the solvent and enhance the structure of the photoresist [3]. If not, the photoresist cannot be firm enough to maintain itself during the next pattern transfer process. Pattern transfer can be classified into three types, etching, deposition and doping. Among them etching is most common way in semiconductor industry. Etching can be divided into wet etching and dry etching. Wet etching often uses acid while dry etching uses plasma. After etching, the desired pattern is cut into the wafer and the lithography process can finally come to an end. The last step is cleaning up the photoresist. After the rest of the photoresist is removed, the wafer can continue with other process.

6. Limitations & Future outlooks

For the photoresists, there still lies many limitations to meet the requirement of high-NA EUV lithography. The most important thing should be the trade-off relationship among resolution, LER and sensitivity. Resolution is needed to fabricate advanced devices using high-NA EUV lithography, which shows a demand of low LER. However, the poor power of EUV light source can only provide very low exposure doses without limiting throughput which may cause photon shot noise. Photon shot noise is a great contribution to LER. So, improvements in sensitivity and low defects of photoresist are needed since it is hard to raise the power of EUV light source when maintaining

throughput. Moreover, throughput is also a critical factor for factories to take consideration of purchase which makes higher requirements for sensitivity.

The solutions are likely to be found soon. For photoresists, the tin-oxo cage compound has unique property in high sensitivity just as mentioned above, and might be the final solution for high-NA EUV lithography system. New mechanisms like that are significant to producing new types of photoresists. For light source, ASML has already achieved 500 W power scale with their laser-produced plasma (LPP) light source and is expected to reach 800 W in the high-NA EUV lithography system. If 800 W or higher power of light source can be applied, the requirements for photoresists can be relaxed and can reach higher throughput. Many efforts are also made towards new types of light source to break the power limitation of LPP light source. New methods of patterning have also been hopefully to provide alternative ways in making high-NA EUV lithography system.

7. Conclusion

High-NA EUV lithography is essential for continued scaling of semiconductor devices. However, it faces critical challenges in terms of photoresist performance. The key requirements for EUV photoresists include high resolution, low line edge roughness, low defects from stochastic effects and pattern collapse, and high sensitivity to reduce exposure doses. Meeting these requirements will require innovative new photoresist materials and mechanisms. Metal-containing photoresists can increase EUV absorptivity and sensitivity. Non-chemically amplified photoresists avoid acid diffusion and blur to improve resolution and line edge roughness. In a specific example, tin oxo cages utilize low energy electrons to provide both high resolution and sensitivity. Significant research remains to develop photoresist formulations and chemistries that can optimize across all metrics. Fabricating and processing these next-generation photoresists will require adapting many standard procedures like spin-coating, exposure, baking and development. The successful development of high-NA EUV photoresists will further depend on concurrent advances in other areas. The most important thing is that light sources must continue improving power scale. Advanced pattern methods can make great contributions to throughput as well. In conclusion, high-NA EUV lithography is extremely challenging but within reach. Further breakthroughs in EUV photoresists will play a key role in its realization. With ongoing research and development, new photoresists, light sources, and pattern methods can together enable this technology. High-NA EUV will be critical for progress in the semiconductor industry and advanced technology.

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