Advanced Photoresists: Development, Application and Market

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Abstract. Photoresist refers to the corrosion-resistant film material whose solubility changes when irradiated or radiated by ultraviolet light, electron beam, ion beam, X-ray, etc. Engraving technology is a micromachining technology that uses the solubility change of photoresist under ultraviolet light or electron beam to transfer the pattern designed on the mask to the exposed substrate. With the continuous improvement of light sources for semiconductor processing, from G line and I line to KrF(248 nm) and then to ArF(193 nm), the matching photoresist is constantly changing to meet the requirements of sensitivity, transparency and etching resistance. Nowadays, extreme ultraviolet (EUV) lithography has become recognized as the next-generation lithography technology. This paper mainly introduces the development history, classification and application of photoresists and the related characteristics, principles and process flow of photoresists in different periods and systems. At the same time, the market situation of photoresists at home and abroad is introduced and analyzed, and the prospect of domestic development is also discussed.

Keywords: Photoresists, corrosion-resistant, film material, ultraviolet.

1. Introduction

Photoresist (also known as photoresist) refers to a kind of material that undergoes chemical reaction under visible light, ultraviolet light, electronic beam, X-ray, ion beam, etc., to cross-link or degrade, thereby changing the solubility. Therefore, the photoresist is covered on the substrate to be etched, and by changing the solubility, part of the substrate is exposed and eroded, and part of the substrate is covered and protected, and finally, an etched substrate with a route is obtained. According to industry classification, the photoresist can be divided into flat panel display, PCB, semiconductor integrated circuit manufacturing, etc. The photoresists mainly used in the flat panel display industry include color and black photoresists, LCD touch screens, TFT-LCD positive photoresists, etc. The photoresists mainly used in the PCB industry include dry film photoresists, wet film photoresists and photosensitive solder resist inks. G-line photoresist, I-line photoresist, KrF photoresist and ArF photoresist are mainly used in the semiconductor integrated circuit manufacturing industry. This paper mainly introduces photoresists in the semiconductor integrated circuit manufacturing industry.

Photoresists can be divided into positive and negative adhesives. The basic technological process and principle of positive glue are as follows: firstly, the photoresist is coated on the substrate surface, and the light source selectively irradiates the photoresist, so that the irradiated part is degraded and the substrate is exposed, while the photoresist which has not received the illumination remains unchanged on the substrate surface. After etching, the substrate which is not covered with photoresist is eroded. Then remove the photoresist to obtain the etched substrate with circuits. The basic process flow and the principle of negative glue and positive glue are similar. The difference lies in that the part of negative glue irradiated by light is cross-linked, and the part that becomes insoluble plays an anti-erosion role, while the part that is not irradiated by light is not cross-linked, thus being easily dissolved and taken away so that this part of the substrate is exposed. The basic process is shown in figure 1[1].

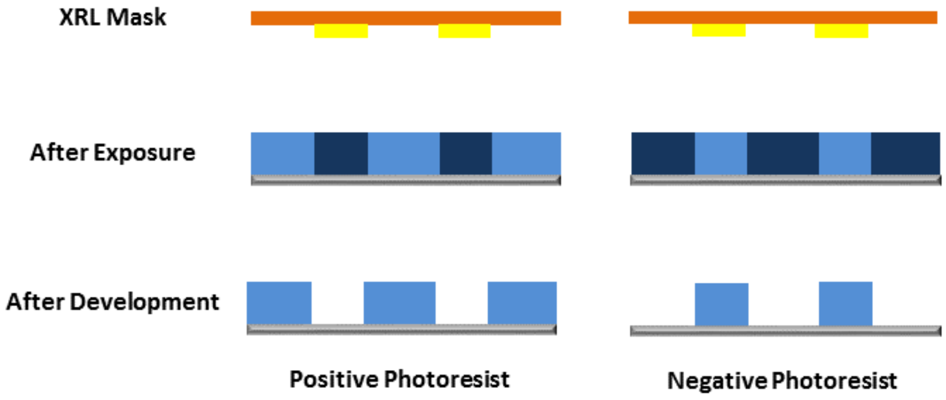

Figure 1. Lithographic patterning of positive and negative tone resists (Dark areas of the photoresist represent exposed resist).

2. History and advance of photoresist

Since its appearance in the 1950s, the photoresist has gone through six stages: full ultraviolet spectrum (300-450 nm), G line (436 nm), I line (365 nm), deep ultraviolet (DUV, 248 nm and 193 nm), extreme ultraviolet (EUV, 13.5 nm) and electron beam lithography[2-6]. However, the development of lithography technology with different wavelength light sources is actually due to the development of different lithography systems.

2.1. Ultraviolet photoresist

2.1.1. Ultraviolet negative photoresist

In 1954, Eastman-Kodak Company synthesized and prepared the earliest artificial photosensitive polymer photoresist-polyvinyl alcohol cinnamate photoresist system. Because the lithography system is easy to store, has good sensitivity and high resolution, and can be applied to fine circuit processing, it has become the first photoresist applied in the electronic industry. However, due to its poor adhesion to silicon wafers, it is limited in use.

Polyvinyl cinnamate and other photosensitive resins containing cinnamate functional groups need to absorb the spectrum between 230 nm and 340 nm, so they cannot be used directly. Appropriate sensitizers need to be added to extend the photosensitive wavelength to the long-wave direction, for examp

le, up to about 450 nm before being used normally. Figure 2 shows the structure of a sensitizer.

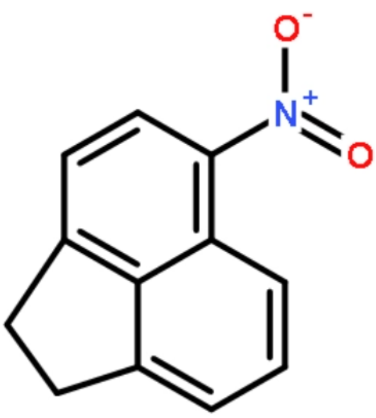

Figure 2. Structure of sensitizer 5-nitroacenaphthene.

In 1958, Kodak Company developed a cyclized rubber-diazo negative photoresist (the photosensitive range is 280~460 nm)[7]. The adhesive overcomes the defect of poor adhesion of polyvinyl cinnamate photoresist and has the advantages of fast photosensitive speed under the good adhesion of silicon wafers, thus becoming the main adhesive used in the electronic industry in the 1980s.

2.1.2. Ultraviolet positive photoresist

At present, the most widely used photoresist in the electronic industry is the o-diazonaphthoquinone-phenolic resin positive photoresist developed around 1960[8]. Compared with the cyclized rubber-diazo negative photoresist developed by Keda Company in 1958, the photoresist has a high resolution, good heat resistance, and convenient removal. However, it has the disadvantages of slow photosensitive speed, poor adhesion, and poor mechanical strength. Photopolymerization mechanism of this kind of photoresist: after UV irradiation, the o-diazonaphthoquinone compound in the exposed area undergoes photodecomposition, and after woff rearrangement, indene carboxylic acid is generated so that the film is dissolved in dilute alkaline water solution, while the unexposed part is insoluble in dilute alkaline water solution because it has not changed, and the unexposed area produces a positive image after alkaline water development[8]. At present, the widely used o-diazonaphthoquinone compounds are 214 o-diazonaphthoquinone sulfonates and 215 o-diazonaphthoquinone sulfonates,

O-diazonaphthoquinone-phenolic resin series UV positive photoresist can be divided into broad-spectrum UV positive photoresist, G-line positive photoresist and I-line positive photoresist according to different exposure machines. The microstructure of phenolic resin and sensitizer is slightly changed, so their performance, especially resolution, is different, which leads to their different uses. Wide-spectrum UV positive glue is used to fabricate 2~3 μm and 0.8~1.2 μm integrated circuits. G-line ultraviolet positive glue is exposed by G-line, which is used to fabricate 0.5~0.6 μm integrated circuits. I-line UV positive glue is exposed by I-line, suitable for fabricating 0.35~0.5 μm integrated circuits[9].

2.2. Deep ultraviolet photoresist

Deep ultraviolet photoresist has a higher resolution and sensitivity because of its smaller exposure wavelength and smaller diffraction effect and is widely used in the fabrication process of 22-0.25 μm integrated circuits. In principle, a deep ultraviolet photoresist is different from an ultraviolet photoresist. The deep ultraviolet photoresist is chemically amplified, and its principle mechanism is that under the action of light, acid is produced as a catalyst to catalyze cross-linking or degradation. After the reaction, the acid can be released again and continue to play a catalytic role. This forward mechanism makes the required energy smaller and makes the glue more photosensitive.

KrF, ArF and F2 rare gas excimer excited laser sources are the main light sources of deep ultraviolet photoresist with corresponding wavelengths of 248 nm, 193 nm and 157 nm, respectively.

2.2.1. 248 nm photoresist

The research of 248 nm photoresists started around 1990 and entered the mature stage in the middle and late 1990s. After research and test, poly (p-hydroxy styrene) and its derivatives became the film-forming resin of 248 nm photoresist. In this lithography system, a photoacid generator plays a key role in imaging. For example, a small number of alkaline substances in the air may neutralize some of the acid produced by the acid generator, thus affecting the catalysis of the acid, and the insufficient reaction may affect the film formation. Through technical improvement, the 248 nm photoresist technology has entered a mature stage, from the line width of 0.25 μm to the line width of 0.18-0.15 μm to the ability to produce 0.1 μm patterns.

2.2.2. 193 nm photoresist

Polymethacrylate has become the main research object because of its high transmittance at 193 nm, and the modified polymethacrylic acid with acid-sensitive alicyclic pendant group has become the main basic material of 193 nm photoresist. In practice, polar groups are introduced to improve adhesion, and polyvalent alicyclic rings improve dry etching. At first, the 193 nm photoresist can be used for 0.15 μm circuit fabrication and is now widely used in 0.13-0.1 μm related processes. There are also processes for 90 nm and 65 nm.

2.3. Advanced photoresist

2.3.1. EUV photoresist materials

The wavelength of the Extreme Ultraviolet Lithography (EUVL) light source is very short, only 13.5 nm. In the same volume and power density, compared with ArF light source, the photon number of the EUV light source is one-tenth less than that of the ArF light source. Therefore, it is required that high absorption elements (such as f, etc.) should be reduced as much as possible in the main material of EUVL, or the ratio of C/H should be increased[10]. At present, EUV lithography materials mainly include poly (p-hydroxy styrene) and copolymers, polycarbonate derivatives, polymer (or small molecule) -PAG system, Molecular glass system (MG), inorganic-organic nanocomposites, transition metal amorphous oxides and so on[11].

The high resolution of EUV lithography has been widely used. The supplier in mask aligner has exposed SRAM at 20nm, and 14 nm nodes, respectively, and the results are compared with those of 193i exposure. The resolution of EUV exposure is much better than that of 193i, even when using R&D equipment. The exposure focus depth of the 14 nm node pattern can reach more than 250 nm[12].

2.3.2. Electron beam photoresist

The most commonly used photoresist in electron beam lithography (EBL) is Polymethylmethacrylate (PMMA), which has the advantages of high resolution, strong adhesion, simple and mature process, and the disadvantages of low sensitivity and weak, dry corrosion resistance[10]. Chemical amplification photoresist makes up for the shortage of PMMA to a great extent. It has high sensitivity, which is conducive to improving the efficiency of electron beam exposure and has strong dry corrosion resistance, which is conducive to the subsequent semiconductor processing technology, so it has broad application prospects in semiconductor technology. The chemically amplified photoresist was originally developed for deep ultraviolet exposure, but some studies have shown that it also has high sensitivity, high contrast and high resolution when used in the electron beam exposure process[13-15].

3. Process of photoresist

The actual operation process of photoresists is complex, and different photoresists have many different operation steps and special treatment processes. Generally speaking, it can be divided into eight steps: substrate treatment, gluing and pre-baking, exposure, medium baking, display, post-baking, corrosion and glue removal, as shown in figure 3 below.

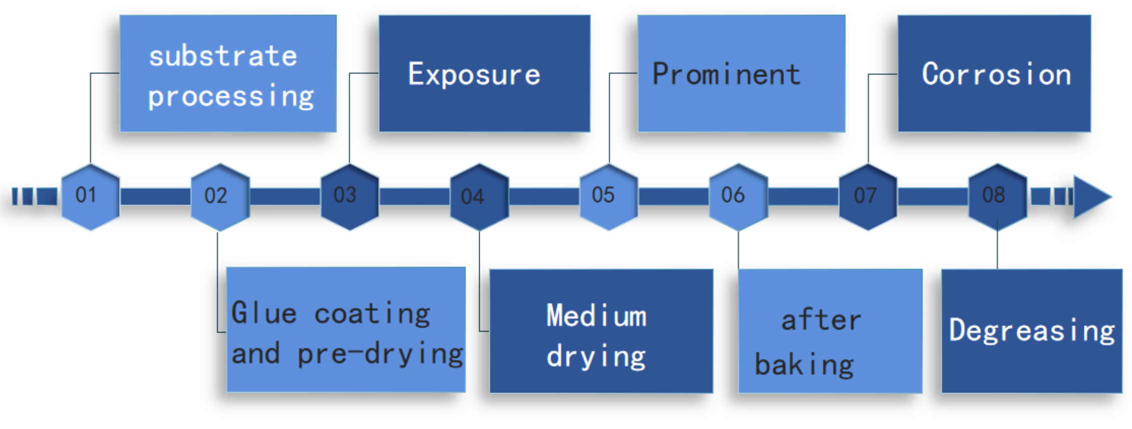

Figure 3. Process flow chart of photoresist.

3.1. Substrate processing

Substrate treatment refers to a certain substrate treatment before gluing to make the gluing better. Treatment methods include removing particles, drying, thickening, etc. Impurity particles on the surface of the substrate will affect the adhesion of the photoresist, thus damaging the precision and qualified rate of the lithography process, so the dust and impurity particles on the surface can be removed by nitrogen blowing and chemical wet cleaning. In addition, the surface may also contain moisture (hydrophilic surface), in which case it can be dried in advance to remove moisture. You can also modify the surface and do some tackifying treatment to better adhere to the photoresist and the substrate.

3.2. Glue coating and pre-drying

The purpose of gluing is to form a proper, uniform and defect-free adhesive film on the surface of the substrate. A commonly used coating method is rotary gluing.This method is that the glue is sprayed to the middle of the wafer, and then rotate at high speed to form a uniform glue film with proper thickness. After that, the solvent in the adhesive film is preliminarily removed so that the adhesive has firmly adhered to the substrate, and certain stress in the adhesive film is eliminated simultaneously.

3.3. Exposure

After the light source is aligned with the substrate, the pattern is transferred to the photoresist by the light source or electron beam. After a proper light retention time, the photoresist is fully reacted so that the film retention rate is as high as possible, and the approximately vertical sidewall of the adhesive film and the controllable line width with a low error is obtained.

3.4. Medium drying

Because of the standing wave effect, the sidewall of the photoresist will be rough and uneven, so it needs to be baked in the middle so that the polymer compounds at the sensitive and non-sensitive areas are redistributed and leveled, thus eliminating the problems caused by the standing wave effect.

3.5. Prominent

Showing means that after baking in the middle, the easily soluble part is dissolved with the developing solution, and the insoluble photoresist is kept so that the glue shows the pattern corresponding to exposure.

3.6. After baking

The purpose of post-baking is to completely evaporate the solution, solidify the adhesive film, achieve good adhesion of the substrate, enhance the mechanical strength such as the toughness of the adhesive film, and improve the etching resistance.

3.7. Corrosion

After the cured photoresist film is formed by post-baking, the exposed substrate is corroded, and the pattern is transferred to the substrate so that the substrate can get the grain corresponding to the glue film, and the part covered by the glue film is kept as far as possible from being eroded, thus obtaining the circuit substrate with clear grain.

3.8. Degreasing

And finally, removing the photoresist plays an anti-corrosion role in obtaining a pure substrate with a perfect surface and clear lines.

4. Photoresist market and prospect

4.1. International market

The photoresist is the material with the highest technical barriers in electronic chemicals, characterized by high purity requirements, complex production process, large investment in production and testing equipment, long technology accumulation period, etc., and belongs to a capital-technology intensive industry. The global market is monopolized by several large enterprises in Japan, the United States, Europe and other countries and regions. In the field of g/i line photoresist, the combined market share of Japanese and American enterprises exceeds 85%. International photoresists mainly include Japan JSR, Tokyo Yinghua, Dow Chemical, Fuji Electronic Material FujiFilm, Shinsuke Chemical, Merck, Sumitomo Chemical, Nissan Chemical, etc., with high market concentration [16].

According to the data in 2019, the top five manufacturers accounted for 87% of the global photoresist market. Japan accounted for four of the five companies, namely JSR, Tokyo Chemical Industry, Japan Shinsuke and Fuji Electronic Materials. The market share of these four companies reached 72%, and the total share of all Japanese companies exceeded 75%. In the subdivision field, the market share of Japanese manufacturers in the ArF, KrF and G-line /i-line photoresist market is 93%, 80% and 61%, respectively, showing strong control in the high-end market[17].

4.2. Domestic market

The research on photoresists in China began in the 1970s, and the initial stage was almost the same as the international level, almost at the same time as Japan's, but due to various reasons, the gap was getting wider and wider. At present, China has no technical advantage in this territory, and there is a big gap compared with the advanced international level, and the difference in products is about three generations or more[18]. In terms of industrial technical capability, international photoresist enterprises generally own series products such as I-line photoresist, KrF photoresist and ArF/ArFi photoresist, and are developing EUV photoresist established a comprehensive patent system and regional coverage for core products[18]. Domestic photoresist enterprises have only realized large-scale application in mid-range I-line photoresists, while KrF photoresist is in the small-scale application and serial development of products. The gap with the international advanced level photoresist is more than that three generations, with thin core patents and weak self-development ability.

There is a big gap between the overall technical level of China's local photoresist and the advanced international level, and the self-sufficiency rate is only about 10%, which is mainly concentrated in the PCB photoresist field with low technical content. In contrast, the self-sufficiency rate of semiconductor photoresists and LCD photoresists is low. The main domestic photoresist listed companies are Jingrui, Nanda Optoelectronics, Shanghai Xinyang and Beijing Kehuawei, etc.

Although China's photoresist industry is weak with poor rate, the industry is mainly concentrated in areas with relatively weak technology, and related research and industrialization are backward. The country has also issued many relevant policies in recent years to guide and support the development of the photoresist industry.

In September 2020, the National Development and Reform Commission, the Ministry of Science and Technology, the Ministry of Industry and Information Technology and the Ministry of Finance jointly issued the Guiding Opinions on Expanding Investment in Strategic Emerging Industries, Cultivating and Growing New Growth Points, and speeding up the strengths and weaknesses of the new materials industry. We will ensure the stability of the industrial chain supply chain in key areas such as large aircraft, microelectronics manufacturing and deep-sea mining and accelerate breakthroughs in areas such as photoresist, high-purity target materials, high-temperature alloys, high-performance fiber materials, high-strength and high-conductivity heat-resistant materials, corrosion-resistant materials, large-size silicon wafers and electronic packaging materials.

In November 2020, the national "14th Five-Year Plan" developed strategic emerging industries. It accelerated the expansion of a new generation of information technology, biotechnology, new energy, new materials, high-end equipment, new energy vehicles, green environmental protection, aerospace, marine equipment and other industries.

In addition, although China's photoresist industry is slightly backward, many enterprises are developing steadily. For example, Jingrui Co., Ltd., Nanda Optoelectronics Co., Ltd., Shanghai Xinyang and other enterprises have already produced IC photoresists. Jingrui Co., Ltd. has passed the online test of SMIC by participating in the National 02 Special Project and has achieved mass production of an I-line (365 nm) photoresist in China. Beijing Kehua, which Nanda Optoelectronics Co., Ltd., owns, has also completed the KrF(248 nm) photoresist production line with an annual production capacity of 10 tons with the support of Special Project 02.

5. Conclusion

Photoresist plays a very important role in our daily life invisibly. In the past 30 years, China's largest import commodity was crude oil. But in 2018, chips (integrated circuits) replaced oil and became China's largest import commodity. This year, according to data from the General Administration of Customs, China's chip imports reached US$ 312 billion. In 2019, it dropped slightly to US$ 305.5 billion but still firmly occupied first place in the import list. China's chips depend on imports, and lithography technology accounts for about 35% of the total chip manufacturing cost and 40%~60% of the total chip manufacturing time, which is the core technology in semiconductor manufacturing. As early as 1826, the first photo was born with photoresist material-photosensitive asphalt.

Later, in 1954, the famous Kodak Company synthesized the first photosensitive polymer, polyvinyl alcohol cinnamate, the first photoresist used in the electronic industry. In 1958, Kodak Company developed cyclized rubber-diazo photoresist. Because of its good adhesion on a silicon wafer, high sensitivity and strong resistance to wet etching, the adhesive became the main adhesive used in the electronic industry in the early 1980s. Then, around 1990, the 248 nm photoresist began to study and entered the mature stage in the late 1990s, and in 2002, the 193 nm photoresist entered the mature stage. In 2001, we began to study 157 nm deep-ultraviolet photoresists. In 2009, research and development of ultra-short ultraviolet photoresists began. It has been in contact with the electronics industry for more than 70 years, but its progress has greatly promoted the progress of the electronics industry and affected the progress of the whole society. Nowadays, lithography technology is still advancing by leaps and bounds. Each generation of more sophisticated and advanced lithography systems has driven the semiconductor and microelectronics industries. At present, Japanese and American enterprises monopolize the global semiconductor photoresist market. The photoresist is a high-tech barrier material with a complex production process and high purity requirement and needs long-term technical accumulation. However, China has a large demand for photoresists, relatively backward production capacity, relative lack of technology and talents, and more policies and capital investment. I believe that with the cooperation of technicians, government and enterprises, China's lithography technology will usher in a brand-new tomorrow.

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