Photomask and Photoresist

78

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Contents

Abstract

The photolithography is the most critical step for the IC fabrication, among which the photomask and photoresist are the necessary materials. The photomask is commonly used as the printing master plate on the photolithography process. The

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mask pattern can be transferred on the substrates with the help of the photoresist. The basic knowledge on the photomask, photoresist, phase-shift mask, DUV lithography photomask, and DUV photoresist has firstly been introduced in this chapter. With the development of lithography technology, extreme ultraviolet (EUV) and mask technology have attracted most attention, concerning the EUV lithography photomask and photoresist. Then, next-generation lithography materials have also been prospected. Moreover, photosensitive polyimides, antireflection coating, and ancillaries have also been illustrated.

Keywords

Photolithography · Photomask · Photoresist · Phase-shift · Extreme ultraviolet mask technology · Photosensitive polyimides, antireflection coating · Ancillaries

Requirements of Photomask Materials and Development for ICs

Photomask, also called mask, is a typically transparent fused silica plate covered with patterns defined with an absorbing film, commonly used as printing master plate on photolithography processes in IC fabrication. In mass production, the more correct term is usually photo-reticle or simply reticle. A set of photomasks, each defining a pattern layer, is individually selected for exposure. In double patterning (DP) techniques, a mask would correspond to a subset of the layer patterns.

The photomask manufacturing process is to convert the original layout data, designed by integrated circuit design engineers for wafer manufacturing, into recognizable data formats for laser pattern generators or electron-beam exposure equipment, so that the original layout can be exposed by the above-mentioned equipment on the photosensitive material-coated photomask substrate. After a series of processing processes, such as developing and etching, the graphics are fixed on the substrate material. It is then followed with inspection, repair, cleaning, and coating; the mask product is formed and delivered to the IC Fab for wafer manufacturing.

There is always a long story behind each technology node. The earliest IC of China was made by traditional photography for pattern transfer, that is, spraying black paint on the Cu plate paper, manual engraving, then photographing with the camera. At that time, PR was coated on glass substrates and should be used immediately before drying, so this is called wet plate process. Later, ultrafine Ag emulsion plate was developed, which is made by uniformly coating Ag halide emulsion (photo-sensitive body) dispersed in gelatin as carrier on a clean and flat photomask glass substrate. It replaced old wet plate process. Meanwhile, lithography process has gradually developed from the initial manual alignment and vacuum pressure imaging to contact lithography technology, which would reach 1 um resolution by using ultrafine latex dry plate process. Dry plate mask has been used for a long time for discrete devices and MSI (medium- and small-scale integration) ICs because of its high sensitivity (to visible light, I line, and G-line), high resolution, and high contrast.

Contact photolithography mask includes vacuum contact, soft contact, hard contact, and so on. The mask is directly in contact with the PR layer to achieve the graphics transfer. Direct contact ensures the reproduction quality of imaging process; avoids introducing any possible errors of pattern zoom; and has advantages in specific application areas. Even at 20–22 nm high-tech nodes, NIL (nanoimprint lithography) [1, 2] has once become a research hotspot, which can be regarded as an advanced contact mask technology. But in general, due to high contamination during direct contact of PR to the mask surface, accumulated wear defects would inevitably affect the lifetime of the mask. Therefore, contact masks are gradually replaced by projection lithography masks with high durability, high resolution, and easy cleaning in IC industry.

The application of projection lithography mask is also transplanted from the printing plate-making technology in printing industry, that is, through the projection exposure with a prism system in a lithographic lithography machine, the cold light pattern is transferred to the wafer, thus avoiding the pollution caused by the direct contact between PR and mask. Early projection lithography masks also used the same 1:1 pattern transfer ratio as contact lithography masks. With the widespread application of microlithography technology, they have been developed into reticle masks, which can be subdivided into 5:1 projection and 4:1 projection in proportion. In addition, projection lithography masks sizes also can be distinguished as 2.5 inches (or 2.5″), 4″, 5″, 6″, 7″, 9″, etc. (1″ = 25.4 mm). Mask shapes can be divided into two types: circular and square, of which square shapes are the most common. At present, the 4:1 projection 6″ square mask is the mainstream for IC lithography.

Projection photolithography masks can also be classified by the material category, including binary, phase shift mask, and opaque Mo-Si binary on quartz glass, etc. Moreover, since image distortion induced by projection lithography exposure, i.e., optical proximity effect error at different densities, it is increasingly necessary to simulate the optical proximity effect correction (OPC) in advance and compensate such image distortion with data model. The associated mask has been defined as optical proximity effect correction (OPC) mask. In recent years, with the maturing of extreme ultraviolet (EUV) lithography, the related EUV mask technology has attracted most attention by IC technology researchers.

Photomask Substrate Material

Photomask substrate material is a basic material of photomask products, mainly refers to glass substrate coated with opaque material and photo-sensitive material. Substrate material must have good optical transmittance characteristics, thermal and chemical stability, smooth surface, no sand inclusions, translucent points, bubbles, or any other minor defects. Photomask substrate materials include white crown soda-lime glass, low-expansion borosilicate glass, and quartz glass. **(1) White crown soda-lime glass** is a kind of substrate material with good mechanical and optical properties, easy processing, and low cost. Although its thermal expansion coefficient (TEC) is relatively higher, the price is only about one-third of that of low thermal expansion glass. Therefore, it has been widely used as photomask substrates, which account for more than two-third of total photomask substrate application. The photomask made of white crown glass is mainly used for micro-fabrication of discrete devices and MSI ICs. **(2) Low-expansion borosilicate glass** has better temperature and optical properties than white crown soda-lime glass. Its TEC is less than half of white crown glass and its transmittance is very high. Even though its price is slightly higher than that of white crown glass, it is only one-third of that of quartz glass, so it has attracted much market attention and occupies a large application field. This material can ensure the dimensional accuracy of photomask and is suitable to make master masks or relatively high-precision masks. The consumption of low expansion borosilicate glass substrate accounts for about one-fourth of the total amount of photomask substrates. **(3) Synthetic high purity quartz glass** is a kind of high purity silica in glass state. It has excellent optical properties, i.e., very high transmittance above 90% especially in short wavelength exposure and its TEC only 1/20 of white crown glass. It is superior to the former two materials in thermal and chemical stability, absolutely excellent as the photomask substrate material. It is widely used in the photomask fabrication of ultra-fine and large-scale ICs. The composition, transmittance, and characteristics of Photomask Glass Substrate Material are shown in Tables 78.1, 78.2, and 78.3.

Table 78.1 Composition of photomask glass substrate material

Components	Alkali-lime glass		NA	LE	QZ
	SLW	SL			
SiO_2	73%	70%	55%	60%	100%
B_2O_3	–	–	–	5%	–
Al_2O_3	1%	–	14%	15%	–
Na_2O	15%	8%	–	1%	–
K_2O	1%	9%	–	1%	–
RO	10%	13%	31%	18%	–

Table 78.2 Transmittance characteristics of photomask glass substrate material

Wavelength	SL	LE	QZ
400 nm	92%	92%	92%
350 nm	85%	90%	92%
300 nm	2%	17%	92%
250 nm			91%
200 nm			90%

Table 78.3 Characteristics of photomask glass substrate material

Item	Characteristic	Condition	Unit	SLW	SL	NA	LE	QZ
Temperature characteristics	Coefficient of thermal expansion	50–200 °C		94×10^{-7}	98×10^{-7}	43×10^{-7}	37×10^{-7}	5×10^{-7}
Humidity characteristics	Annealing point	–	°C	542	533-	730	686	1120
Optical characteristics	Refractive index			1.52	1.52-	1.57	1.53	1.46
Chemical stability	Weightlessness	Di-water 100°C1h	%	0.050	0.058	0.014	0.015	0.000
	Weightlessness	1/100 N NHO_3 100°C1h	%	0.028	0.023	0.040	0.030	0.000
	Weightlessness	5% NaOH, 80°C1h	Mg/mm^2	0.13	0.14	0.10	0.31	0.17
Mechanical properties	Density		g/cm^3	2.50	2.56	2.87	2.58	2.20
	Elastic modulus		kgf/mm^2	7000	7341	9420	7540	7413
	Shear modulus		kgf/mm^2	2870	2980	3730	3250	3170
	Poisson ratio			0.22	0.23	0.25	0.16	0.58
	Knoop hardness		kgf/mm^2	540	530	650	657	615
	Grind hardness			88	88	160	209	210
Electrical characteristics	Surface resistance		Ω	6×10^{4}	1×10^{10}	1×10^{11}	1×10^{12}	1×10^{19}
	Bulk resistivity		Ω·cm	1×10^{12}	1×10^{16}	1×10^{14}	1×10^{16}	1×10^{18}

Photoresist Applied Chrome Thin-Film Photo-Plate [3, 4]

The uniform chromium (Cr) plate photomask is a uniform Cr plate formed by evaporating or sputtering a 0.1 μm thick Cr monoxide (CrO) film on the flat photomask substrate and then coated with a layer of photoresist (PR) or electron-beam (e-beam) resist (EBR). It has the characteristics of high sensitivity, high resolution, and low defect density and is an ideal photo-sensitive blank plate to fabricate micro-photomask patterns. The photosensitivity and resolution of the Cr plates are entirely determined by the type and variety of PR or e-beam resist coated, and the required photomask can be obtained by lithography process. In the era of contact lithography technology, the use of ultrafine latex dry plate process has the advantages of easy production and low cost, but also has the shortcomings of soft film surface, easy to scratch, contamination, cleaning treatment difficulties, short service lifetime and other weaknesses. Relatively, the manufacturing process of uniform Cr plate is more complex, difficult, and costly, but it has the advantages of high resolution, low defect, wear resistance, easy cleaning, and longer service lifetime. It is suitable for making high-precision and ultra-fine graphics. Now it has replaced the contact latex mask and become the mainstream key material of IC photomasks. After etching the Cr layer, a homogeneous Cr mask can generate a simple binary image composed of black-and-white areas. Therefore, this mask type is also called a binary mask (or Binary Intensity Mask, BIM). As the traditional penetrating mask, its exposure principle is shown in Fig. 78.1. The black area is completely opaque, and the white area is transparent. For example, in the exposure of chemically amplified photoresist, the laser beam passes through the mask to the corresponding position of the Si wafer, causing PR reaction to produce photo acid, which is removed or retained by subsequent development process (depending on whether the PR is positive or negative) to form an image. The optical range of the uniform Cr mask is very wide, covering G-lines, I-lines, and DUV (Deep Ultraviolet,

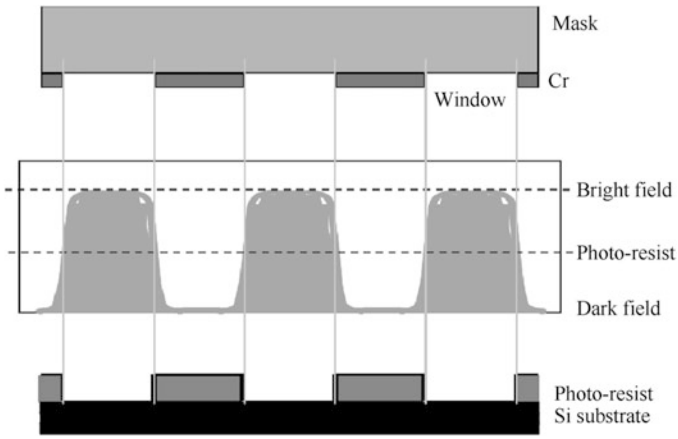

Fig. 78.1 Working principle of UV exposure using the uniform Cr photomask

including KrF wavelength 248 nm and ArF wavelength 193 nm). The wavelength of laser light source determines the minimum resolution of the technical nodes.

Phase-Shift Mask (PSM)

When the feature size and spacing of the IC pattern reach the wavelength limit of the exposure light source, the adjacent light intensity of the adjacent patterns on the traditional uniform chrome-plated plate will be superimposed with each other by the optical diffraction, resulting in insufficient projection contrast and poor imaging. In order to increase the limit of exposure resolution, the phase-shift masks (PSM) are used to improve the contrast of light intensity by using complementary optical phase difference or phase shift. In addition, the traditional opaque Cr metal layer can be replaced with a material that is not completely opaque (such as Mo-Si), which has a certain transmittance and a phase shift difference of 180°. This type mask is called a half-tone mask (HTM).

The application of phase shift mask (PSM) started with deep ultraviolet (DUV) lithography technology [5, 6]. Due to different exposure wavelengths of lithography (KrF at 248 nm and ArF at 193 nm), KrF or ArF phase shift mask with 180°phase compensation transmittance is used at 248 nm or 193 nm wavelengths, respectively. ArF PSM mask mentioned here can also be used for immersion ArF lithography that can extend integrated circuit technology nodes below 10 nm.

According to different forms of optical compensation, PSM can be divided into Alternate Phase Shift Mask (Alt-PSM) and Attenuated Phase Shift Mask (Att-PSM). These two different exposure principles are shown in Fig. 78.2. (1) The Alt-PSM is equivalent to alternatively adding a phase shift dielectric layer (as phase shifter) between adjacent transparent regions to offset the diffraction between neighboring light beams, thus enhancing the exposure resolution. In addition, this phase shifter layer can also be achieved by alternatively etching different depths between adjacent transparent regions of quartz substrates. (2) Att-PSM directly replaces the conventional opaque Cr layer by a translucent molybdenum-silicon (Mo-Si) layer with phase opposite to the transparent region, partially compensating the interaction

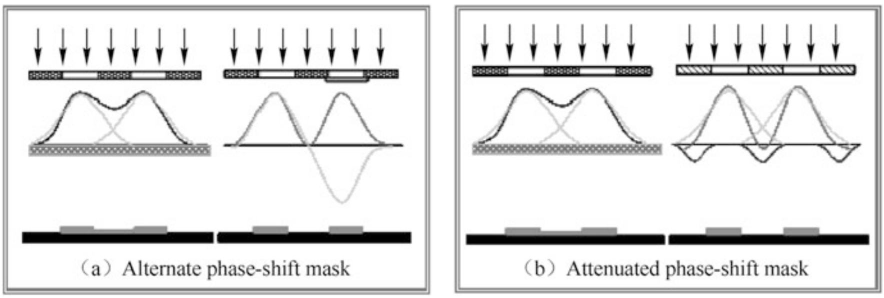

Fig. 78.2 Working principles of alternate phase-shift mask and attenuated phase-shift mask

between adjacent light beams to improve the exposure resolution. The corresponding fabrication process is simpler than that of Alt-PSM. Table 78.4 shows the characteristics of Att-PSM masks of HOYA Company in Japan.

Opaque-Mo-Si-on-Glass (OMOG), which is developed on the basic structure of Att-PSM blank material, is a kind of black-and-white mask similar to binary mask, also known as Super Binary Intensity Mask (SBIM). The original phase shift layer of Mo-Si compound is treated to be completely opaque and no longer has the function of shift compensation, and the ultra-thin Cr layer in the middle of blank is mainly used as the pattern transfer layer (hard mask). Unlike the conventional binary mask, the black areas of OMOG are an opaque thin Mo-Si compound material rather than a chrome layer, which can effectively reduce mask 3D errors. Moreover, the ultra-thin Cr middle layer can support thinner photoresist to achieve higher exposure limitation

Table 78.4 Characteristic specifications of HOYA PSM optical blank

Characteristic Specifications			AXQ 6025 2C	AXQ 6025 0.5 T
Quartz	Thickness/mm		6.35 ± 0.10	6.35 ± 0.10
	Flatness/μm		≤2.0	≤0.5
Cr	Type		AR8	TF11
	Thickness	Average/nm	105 ± 5	48 ± 5
		Uniformity/nm	≤5	≤5
	Reflectivity	Average	(12.5 ± 1.0)% @365 nm	(19.5 ± 1.0)% @193.4 nm
		Uniformity	≤1.0%	≤1.0%
	Defectivity		Pinhole-free (≥3.0 μm)	Pinhole-free (≥1.0 μm)
Mo-Si	Type		K63A	A61A*
	Phase shift	Average	(181 ± 2°) @248.4 nm	(181 ± 2°) @193.4 nm
		Uniformity	≤2.5°	≤2.5°
	Transmittance rate	Average	(5.3 ± 0.3)% @248.4 nm	(6.1 ± 0.3)% @193.4 nm
		Uniformity	≤0.2%	≤0.2%
	Thickness	Average/nm	93	69.5
		Uniformity/nm	2.6	2.5
	Reflectivity		18%@248.4 nm	20%@193.4 nm
	Defectivity		Pinhole-free (≥1.0 μm)	Pinhole-free (≥0.15 μm)
Photoresist	Type		FEP171	FEP171
	Thickness	Average/nm	400 ± 10	200 ± 10
		Uniformity/nm	≤7	≤7
	Defectivity		0.3 ~ 1.0 μm: ≤17 1.0 ~ 2.0 μm: ≤2 ≥2.0 μm: 0	0.2 ~ 0.3 μm: ≤20 0.3 ~ 1.0 μm: ≤10 ≥1.0 μm: 0

and minimize the micro-deformation errors introduced by etching process, as well as obtain better critical dimensional uniformity and graphic fidelity. Therefore, under allowed exposure limit of lithography, a smaller mask error effect factor (MEEF) can be achieved for superior lithographic quality and product yields.

Extreme Ultraviolet Lithography Photomask

Extreme ultraviolet photolithography (EUV) technology [7, 8] (wavelength at 13–15 nm, generally 13.5 nm) has been developed for many years and finally used at 7 nm node manufacturing since 2019. Considering its very short exposure wavelength and strong material absorption in EUV exposure environment, traditional penetrating lithography mask is no longer applicable; instead, reflective masks with multilayer stacked structure of reflective optical system (e.g., intermediate layers, top cover layer (Ru), and absorption layer TaN, etc.) are used. Intermediate layer of EUV mask is a multilayer structure composed of Mo and Si with high reflectivity to EUV radiation. As the EUV radiation at about 13 nm is similar to X-ray characteristics, there is minimum distortion of pattern transfer during reflective lithography, so that high-quality pattern resolution could be achieved. A comparison between the penetrating and EUV reflective masks is shown in Fig. 78.3.

EUV mask requires high thermal stability and anti-radiation technology due to the large amount of energy accumulation in lithography process [8]. However, it is still unavailable for EUV reflective masks to be protected by traditional pellicle mounting, there are difficulties in mask storage, transportation, and exposure

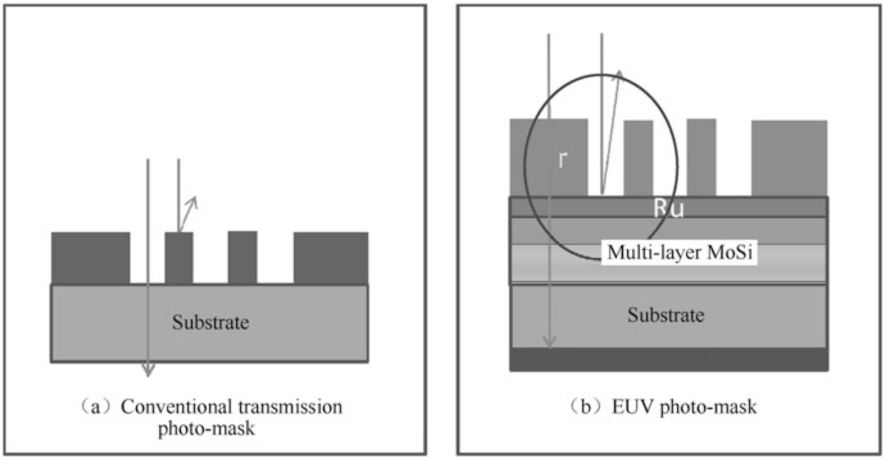

Fig. 78.3 Comparison of conventional transmission photomask and EUV photomask

process. Currently, the application of EUV masks is combined with photomask inspection, cleaning, and repair equipment to avoid defects on the chip caused by contamination or other reasons during the exposure process. As a result, the maintenance cost of related process, masks, and equipment is very high. It demands the R&D for more durable pellicle techniques.

EUV lithography technology was originally considered for 65 nm technology node in 2005, but the development is slow especially the EUV light sources for sufficient power and reliability due to various technical challenges. After years of efforts, the EUV lithography technology is finally used in IC manufacturing at 7 nm node in 2019 and is expected to be continuously progressing for the future 5 nm node and beyond.

Hard Mask

Hard mask refers to all kinds of hard semiconductor processing materials used in etching process to replace polymers or other organic "soft" anti-etching materials (e.g., PR). This concept, in fact, belongs to different technological field in semiconductor industry compared with photomasks in microlithography technology. Figure 78.4 shows an application of hard mask materials. As the feature size of semiconductor chips is shrinking, the sharp increase in the height-to-width ratio (that is, aspect ratio) of PR makes the etching more difficult, and the etching deviation, uniformity, and sidewall angle are difficult to control. Thus, a relatively thinner hard mask layer is introduced as an intermediate transition layer for pattern transfer, the etching process is transformed into a double process step from PR layer to hard mask and then to etching layer. This can eliminate difficulties in the etching process and achieve nearly ideal etching results. Currently, it is a common and mature etching technique in IC manufacturing. Generally, hard mask layer is formed by chemical vapor deposition (CVD) or physical vapor deposition (PVD). There are many kinds of hard mask materials, including amorphous carbon material, silicon dioxide, silicon nitride, etc., which are characterized by thinner thickness and better etching resistance.

The hard mask corresponds to the soft mask material, which is generally a thick adhesive layer, and is commonly called photoresist directly. In addition, in some cases, because the finished chrome photomask material is hard, it is sometimes called a hard mask material.

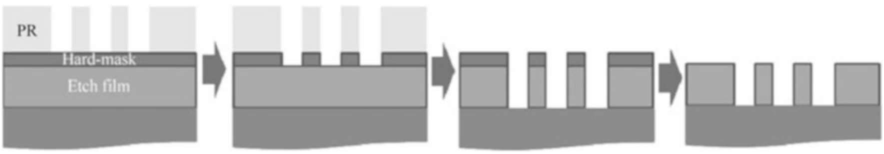

Fig. 78.4 Application of thin hard mask

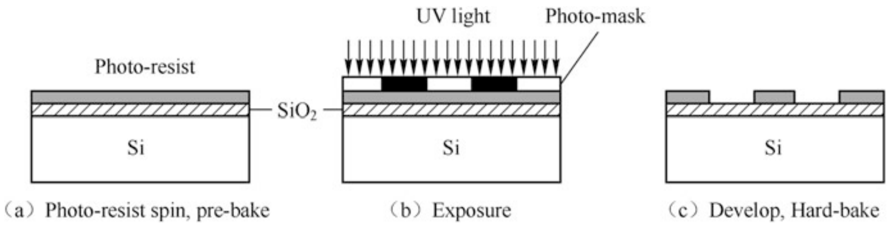

Fig. 78.5 Working principle of photoresist

Photoresist [9, 10]

Photoresist (PR) is a photo-sensitive material, in which the photoactive compound will undergo chemical reactions under the irradiation of light, resulting in a change in the dissolution rate of the material. Its main role is to transfer the pattern from the reticle to the substrate. As shown in Fig. 78.5, the complete process can be comprised of the following steps: (1) Apply the PR to the substrate, the excess solvent is removed through a soft bake step. (2) The substrate is exposed through a reticle, so that chemical reactions occur in the photosensitive components of photoresist on the exposed region. (3) Post-exposure baking is performed, and finally, the PR is selectively removed by a developer (for a positive PR, the exposed region is removed; for the negative PR, the unexposed region is removed). Thus, the pattern transfer from the reticle (mask) to the substrate is realized.

The components of the photoresist (PR) mainly include the resin, the photo-sensitive component, the trace additive, and the solvent. The resin provides mechanical properties and etch resistance; the photo-sensitive component undergoes chemical reactions under illumination, causing the dissolution rate to change; the trace additive may includes dyes, cross-linkers, etc., to improve the performance of the PR. The solvent is used to evenly dissolve these solid materials. Currently widely used PR can be classified into conventional PR and chemically amplified PR according to the photo-chemical reactions. Lithography can also be divided into ultraviolet (UV), deep ultraviolet (DUV), extreme ultraviolet (EUV), electron beam, ion beam, and X -ray according to the wavelength of light. PR is more accustomed to use its wavelength or light source to name it as shown in Table 78.5.

UV Photoresist

UV photoresist (PR) refers to a PR sensitive to a wavelength between 280 nm and 450 nm. According to the wavelength of light, it can be classified into UV broadband, G-line (436 nm), and I-line (365 nm) PRs. The resolution of I-line PR can reach 0.35 μm, which is the workhorse in microelectronics and ICs. Also, the most versatile type of PR is.

Table 78.5 Photoresist types, application fields, and characteristics reference table [9, 10]

Photoresist type		Application field	Feature description
Ultraviolet broad-spectrum photoresist	Ultraviolet broadband positive photoresist	Semiconductor discrete device	The manufacture of devices such as diodes and triodes. The process line width is large (>5 μm), which requires excellent process window of the photoresist. A phenolic resin is used as a resin, and a compound having an absorption peak at long wavelength is used as a photosensitive component.
Ultraviolet broad-spectrum photoresist	Ultraviolet broadband positive photo resist	Integrated circuit package	Bumping, rewiring RDL (redistribution layer), silicon TSV (through silicon via), and other processes. A thicker photoresist film thickness (20–100 μm) is required, and the photoresist is required to have a fast photospeed or good resistance to the plating solution. Resolution requirements are not high (>10 μm).
		LED light-emitting diode	Positive photoresists for LED chip fabrication are similar to those used in semiconductor discrete devices.
		LCD liquid crystal display	For LCD Array, touch panel manufacturing, according to different applications, it is divided into positive photoresist for TN/STN-LCD and TFT-LCD. The former has lower resolution requirements (>15 μm), while resolution for the later application is high (>5 μm), and it requires good coating performance and faster photospeed (100 ms).
	Ultraviolet broadband negative photoresist	Semiconductor discrete device	The cyclized rubber is used as a resin, and the double azide compound is a cross-linking agent, which has low resolution (>5 μm), but needs to have good wet etch resistance.
		Integrated circuit package	Used in bumping, rewiring (RDL), and other processes, is an acrylate based negative photoresist. It has good light transmittance and can maintain good profile and high photospeed under a thick film thickness; the resolution requirement is not high (>5 μm).

(continued)

Table 78.5 (continued)

Photoresist type		Application field	Feature description
		LED light-emitting diode	Used in LED chip manufacturing, mainly use phenolic resin as resin. It is generally used in the lift-off process to form electrode. This type of photoresist has inverted trapezoidal profile, high sensitivity (<250 ms), and high resolution (2–3 μm).
		MEMS microelectromechanical system	Such photoresists mainly use epoxy resin as a resin, the resolution requirement is not high (>10 μm), the thickness requirement is 20–100 μm, it has large aspect ratio, good thermal stability, and excellent mechanical properties.
G-line (436 nm) photoresist	G-line positive photoresist	Semiconductor discrete device	The manufacture of devices such as diodes and triodes. A phenol resin is used as a resin, and a compound having an absorption peak near the G-line is a photosensitive component. The resolution is higher than UV broadband photoresist, which can reach the micron level.
		Integrated circuit package G	Bumping, rewiring RDL (redistribution layer), silicon TSV (through silicon via) and other processes. A thicker photoresist film thickness (20–100 μm) is required, and the photoresist is required to have a fast photospeed or good resistance to the plating solution. Resolution requirements are not high (>10 μm).
G-line (436 nm) photoresist	G-line positive photoresist	LED light-emitting diode	LED chip manufacturing, use phenolic resin as resin, film thickness is within 2 ~ 3 microns, and the resolution is around 5 micron.
		LCD liquid crystal display	High-generation TFT-LCD manufacture, use phenolic resin as resin, a compound has absorption peak around 436 nm used as photosensitive component, resolution (<5 μm), require good slit coating performance and fast photospeed (100 ms).

(continued)

Table 78.5 (continued)

Photoresist type		Application field	Feature description
		Integrated circuit (IC) G-line positive photoresist	For non-critical layers of low-end integrated circuit processes, G-line positive photoresists require higher resolution (approximately 1.0 μm) and good process window, especially exposure latitude (EL) and depth of focus (DOF), with both dry etch resistance and implant resistance.
	G-line negative photoresist	LED, integrated circuit	G-line negative photoresist is similar to ultraviolet broadband negative photoresist, use phenolic resin as resin. The main difference is that the photo-acid generator has stronger absorption at 436 nm.
I-line (365 nm) photoresist	I-line positive photoresist	Integrated circuit (IC)	Like the G-line photoresist, based on Novolac/DNQ system, which is characterized by high resolution. The main difference from the G-line photoresist is that the photosensitive component's absorption peak is around 365 nm, and the phenolic resin structure is also different; I-line photoresist with 0.5 μm resolution for non-critical layers; high-resolution I-line photoresist with a resolution of 0.35 μm for critical layers; thick film photoresist (thickness 3–5 μm) for passivation layer.
		TFT-LCD	Similar to G-line photoresist, it is based on Novlac/DNQ system, which is used to fabricate LCD arrays. The resolution requirement is not critical, around 2 μm, but the uniformity of the coating, trace metal, and particle requirements are higher than normal TN/STN-LCD photoresist, photospeed requirement is less than 70 mJ.
		LED substrate	The patterned sapphire substrate (PSS) process has been widely adopted in LED fabrication. This advanced process requires an I-line stepper, and thus, an I-line photoresist is used. Requires photoresist to have strong

(continued)

Table 78.5 (continued)

Photoresist type		Application field	Feature description
			resistance to dry etching, resolution 1 ~ 2 μm.
	I-line negative photoresist	Integrated circuit (IC), LED	A negative photoresist platform based on phenolic resin. Compared with the broadband negative photoresist, the absorption peak of the photo-acid generator is around 365 nm.
DUV (248 nm) photoresist	DUV (248 nm) positive photoresist	Integrated circuit manufacturing	KrF positive photoresist is sensitive to KrF (248 nm) wavelength, use hydroxyl styrene polymer as the resin, and a photo-acid generator with absorption peak around 248 nm used as photosensitive component, and the acid generated by PAG acting as catalyst and thus has a chemical amplification effect. This type of photoresist is characterized with fast photospeed (~30 mJ), high resolution (down to 110 nm), can be used in 0.13 μm–0.35 μm technology node, combined with resolution enhancement technology, can be used in 0.11 μm or even 90 nm technology node.
DUV (248 nm) photoresist	DUV (248 nm) negative photoresist	Integrated circuit manufacturing	KrF negative photoresist is similar as KrF positive photoresist, the main difference is that the photo-acid generated by the photo-acid generator catalyzes the cross-linking reaction in the exposed area, thus form a negative pattern; the resolution can also reach 0.13 μm; mainly used in some special processes.
ArF (193 nm) photoresist	ArF positive photoresist (dry)	Advanced integrated circuit manufacturing	ArF positive photoresist is sensitive to ArF(193 nm wavelength), use acrylic polymer as the resin and a rigid molecular group is introduced to increase the etch resistance and a photo-acid generator with absorption peak around 193 nm used as photosensitive component, and the acid generated by PAG acting as catalyst and thus has a chemical amplification effect. This type of photoresist is characterized with

(continued)

Table 78.5 (continued)

Photoresist type		Application field	Feature description
			fast photospeed (~30 mJ), high resolution, can be used for 65 nm–90 nm, combined with resolution enhancement technology, can be used in 45 nm process; another requirement is line width uniformity (LWR) <4 nm.
	ArF positive photoresist (immersion)	Advanced integrated circuit manufacturing	ArF immersion photoresist is similar as ArF positive photoresist, the resin and photo-acid generator structure need to be further optimized to achieve higher resolution ~38 nm, and the photo-acid generator absorption peak is still near 193 nm, still using chemical amplification technology. Fast photospeed (~30 mJ), combined with resolution enhancement technology, can be used in 32/28 nm technology node; if multiple patterning technology is used, 20 nm/14 nm process can be realized; another requirement is line width uniformity (LWR) <2.5 nm.
EUV (13.5 nm) photoresist	EUV (13.5 nm) positive photoresist	Advanced integrated circuit manufacturing	EUV is an exposure light source, which uses chemical amplification technology. Unlike traditional 248 nm and 193 nm photoresists, all components in the photoresist are absorbed by EUV, and the acid generation mechanism is more complicated. The photoresist has a lower outgassing during exposure. As a candidate for next-generation lithography, EUV photoresists are expected to be used in process nodes of 10 nm and below.
Electron-beam photoresist	Electron-beam photoresist	Lithography mask fabrication	An electron beam is used as an exposure light source, and an acrylic resin is a film-forming resin. The resolution is up to nanometer, and the photospeed requirement is 30–60 $\mu C/cm^2$.

UV Broadband PR

It refers to a class of photoresist with the full spectrum of a high-pressure mercury lamp as the exposure wavelength; it has relatively lower resolution and mainly used for discrete devices, ICs and LED chips, LCD, and touchscreen manufacturing. UV broadband PR is divided into positive and negative PRs. (**a**) **Broadband UV-positive PR** mainly uses Novolac/DNQ system. The photo-sensitive component (as photosensitizer) can form hydrogen (H) bonds with the phenolic resin to reduce its dissolution rate in the developer. Under the light exposure, photosensitizer can form carboxylic acid with phenolic resin and promotes the dissolution rate of phenolic resin, thus form dissolution rate contrast between exposed and unexposed area. According to the different applications, the types of phenolic resins, photosensitizer, and additives in UV broadband positive photoresist are also different. Such PR can be used in many applications such as semiconductor discrete devices, IC packages, LEDs, and LCDs. Discrete devices mainly refer to a diode, triode, power bipolar, power MOSFETs, etc. Semiconductor packaging PR is mainly used in the bumps process (i.e., bumping), redistribution layer (RDL), and through-Si-via (TSV). In these processes, the resolution of PR is not critical (>10 μm), but thicker (20–100 μm) PR and much faster photospeed are required. At the same time, the photoresist is required to have a high sensitivity and is not corroded by the plating solution. PR for light-emitting diode (LED) is similar to PR for discrete device manufacturing, except that the LED manufacturing uses a dry etch process and requires the PR with good etch resistance. PR for liquid crystal display (LCD) can be divided into different applications for TN/STN-LCD and TFT-LCD. Due to the different process requirements, the composition of the two photoresist is different. The resolution of the PR for TN/STN-LCD manufacturing process is relatively low (>15 μm) and uses sodium hydroxide/potassium hydroxide (NaOH/KOH) as a developer. The TFT-LCD manufacturing process requires a high resolution (>5 μm) for the PR with a good coating performance and a fast photospeed. (**b**) **Broadband negative PR** has three main types: One is conventional negative PR, in which cyclized rubber acts as the resin and azides as photosensitizer and cross-linker. The second type PR is based on the chemically amplify mechanism (CAM)PR to use phenolic resin as film-forming resin. It belongs to the negative photoresist from the reaction mechanism, but the supporting reagent used is the same as the positive photoresist. The third type is based on the free radical polymerization or ring-opening cross-linking mechanism to use acrylate or epoxy resin as film-forming resin. It is characterized with good transparency and fast photospeed. These negative photoresists are mainly used for discrete devices, IC packaging, LEDs, and MEMS in the fabrication process. Broadband negative PR for discrete devices is a conventional negative PR. It uses cyclized rubber as resin and azide as cross-linker, in which the resolution is not critical, but need good wet etch resistance. Broadband negative PR for IC packaging is based on acrylate polymer. It has good transparency, allowing it to form good profile and faster photospeed at thicker PR films. The UV broadband negative PR used for LED chip fabrication is based on phenolic resin, which is mainly used to form the electrode in lift-off process. This photoresist has inverted trapezoidal profile and is characterized with fast photospeed and good resolution. The UV broadband negative PR for the MEMS fabrication is based on epoxy resin. This kind of photoresist has high cross-link density which can form a high aspect ratio profile with excellent thermal and mechanical properties.

G-Line (436 Nm) PR

G-line (436 nm) PR refers to a PR using 436 nm wavelength light as the exposure light source and can be classified into positive and negative PRs. G-line positive PR is similar as UV broadband PR, i.e., it is based on Novolac/DNQ platform and usually using stepper as the exposure tool. The main difference between G-line and UV broadband PR is that the photosensitizer for G-line must have strong absorption at 436 nm. Also, G-line PR has certain requirements for the content of metal ions (fewer metal ions) as needed for IC manufacturing. G-line positive PR for discrete devices is similar to UV broadband positive PR but better resolution and process window due to changes in exposure mode. G-line positive PR for IC processes requires higher resolution (about 1.0 μm) and greater process window especially in exposure latitude (EL) and depth of focus (DOF). Due to the use of dry etching and ion implantation in IC manufacturing, the photoresist is required to have better etching resistance. G-line negative PR uses phenolic resin as film-forming resin and is mainly used in the lift-off process of integrated circuit manufacturing and LED chip manufacturing. The composition is similar to the UV broadband negative PR with the main difference in the stronger absorption at 436 nm by photo-acid generator.

I-Line (365 Nm) PR

I-line PR refers to PR using 365 nm wavelength light as the exposure light source. It is the main type of PR in the IC manufacturing with resolution up to 0.35 μm. It is widely used in 6″ and below wafer fabrication lines. I-line also has a significant portion of layers in 8" IC manufacturing. Like the G-line PR, the I-line positive PR is a Novolac/DNQ system with higher resolution (than G-line). The main differences of I–line PR from G-line PR are the chemical composition and structure of phenolic resins, photosensitizers, and additives. In addition to p-cresol and m-cresol, a third structural unit is introduced into the phenolic resin to improve the contrast between the exposed and unexposed areas, as well as the molecular weight distribution of the resin is narrower by the fractionation technique. The distribution of light intensity in the photoresist is more uniform by using the photosensitizer skeleton with better light transmission, and by using additives such as dissolution promoters or dissolution inhibitors, the sensitivity of the photoresist can be controlled more precisely. The I-line PR for ICs and advanced packaging processes can be divided into three categories, i.e., standard I-line PR with a resolution of 0.5 μm for non-critical layers, high resolution of 0.35 μm for critical layers, and thick film PR (film thickness 3–5 μm) for passivation layer. I-line positive PR is also widely used in patterned sapphire substrate (LED PSS) process for LED fabrications in which the PR is required to have strong resistance to dry etching by improving the mechanical properties of the PR resin. On the other hand, the PSS process requires higher resolution and better sensitivity of the photoresist (R < 1.5 μm, E_{op} < 150 mJ). The negative PR of I-line mainly includes the negative system of phenolic resins. It is mainly used in the lift-off process of IC and LED chip manufacturing. Compared with UV broadband negative photoresist, the photo acid-producing agent in I-line negative photoresist has stronger absorption at 365 nm.

Deep UV Photoresist (DUV Photoresist)

DUV photoresist (PR) refers to PR using wavelength between 180 nm and 260 nm light as exposure source. It can be subdivided to KrF (248 nm) and ArF (193 nm) PRs depending on the wavelength of light sources. For ArF PR, it can be further divided to ArF PR and ArF immersion PR based on the exposure tool types. The resolution of KrF PR is around 130 nm and ArF PR is around 45 nm. If using multi patterning technology (MPT), the resolution of ArF immersion PR can reach 7 nm and ArF PR is a key material for advanced IC manufacturing at 14 nm node and beyond. **(1) KrF PR** refers to the PR using KrF laser as the exposure light source. It is the first PR using chemical amplification mechanism (CAM) [11, 12] with main components of polymer, photo-acid generator, additive, and solvent. Upon exposure, photo-acid generator generates photoacid, and then, the photoacid catalyzes the de-blocking or cross-link reaction of the polymer during the post-exposure bake (PEB); this reaction achieves a difference in dissolution rate between exposed area and unexposed area, thus transfer the pattern to the substrate in the following development process. This CAM gives KrF PR higher sensitivity (30–50 mJ) and good resolution (0.13–0.35 μm) and if combined with resolution enhancement techniques (RET), it can be used at 90 nm technology node. KrF PR use polyhydroxystyrene as polymer, sulfonium, or iodonium as photo-acid generator (PAG). For positive photoresist, the photoacids generated in the exposed area can catalyze the de-blocking reaction of polymers to form phenolic hydroxy or carboxylic acids which makes the polymer easy to be dissolved in the developer. For negative photoresist, these photoacids generated in the exposed area can catalyze the cross-link reaction of polymers to form dense cross-link structures that are hardly dissolved in the developer. **(2) ArF PR** is a photoresist with ArF laser as exposure light source, which also uses chemical amplification technology. That is, the photoacid generated by the photoacid generator under 193 nm light catalyzes the de-blocking or cross-link reaction on the film-forming resin during the post-exposure bake (PEB) process. This reaction results in a difference in dissolution rate between the exposed and non-exposed areas and then transfers patterns to the substrate in the following development process.

ArF PR can be further divided into ArF dry PR and ArF immersion PR based on the exposure tool type. ArF dry PR can be used in 90 nm, 65 nm, and 45 nm technology nodes. ArF dry PR use PMMA type polymer as resin, iodonium, or sulfonium as photo acid generator (PAG). It works on the same principle as KrF (248 nm) photoresist. For positive ArF dry PR in the PEB step, PAG generates photoacid to catalyze the chain scission reaction of polymer, and then form carboxylic acid to make the exposed area more soluble in the base developer, while for negative ArF dry PR in the PEB step, the photoacid can catalyze the cross-link reaction to form dense cross-link network leading to the exposed area hard to be dissolved in developer.

ArF immersion PR is similar as ArF dry PR, but the difference is that in immersion lithography, water is filled between lens and PR, so it is necessary to ensure that the components in the photoresist are not dissolved by water, and the contact angle between the photoresist and water should be as large as possible to improve the throughput of the lithography process. To meet the above performance requirements, it can be achieved by adding a top coating in the process and using macromolecular photo acid generators and additives in the photoresist. 193 nm immersion lithography is widely used in IC manufacturing at 32 nm, 28 nm, 14 nm, as well as 10 nm nodes and beyond.

EUV Photoresist [10]

EUV photoresist (PR) refers to PR using EUV (13.5 nm) as exposure light source. Currently, the main focus is to further improve the PR sensitivity, reduce line edge roughness, and outgassing of the PR system. Based on ITRS, for high volume manufacture, EUV PR need to meet: (1) high resolution, (2) fast photospeed, (3) low line edge roughness and less outgassing, and no contamination to exposure system. As a next-generation lithography, EUV is already used in manufacturing for 7 nm node and beyond.

EUV PR can be classified to chemical amplification (CA) [11, 12] system, molecular glass, and metal oxide types: **(1) Conventional CA type PR** is characterized with high photosensitivity as an advantage for EUV lithography (with limited source power). However, it has line edge roughness issues caused by the acid diffusion and the resolution not meeting requirements; and it is subject to further optimization. **(2) Molecular glass** was developed to solve the issues of chemical amplification PR, in which the main component is small molecules with protective groups. It can form homogeneous and non-crystalized photoresist films by the spin-coating method and perform good thermal stability (>150 °C), but molecular glass PR suffers from pattern collapse especially for small features. Therefore, it needs further optimization. **(3) Metal oxide type PR** has higher density and better absorption cross section for EUV light, it also performs less outgassing, no contamination to exposure system, and high etch resistance during the pattern transfer step. However, the photosensitivity of this type of PR is very slow and need further optimization. Fig. 78.6 illustrates a common EUV MG/PAG bonded structure.

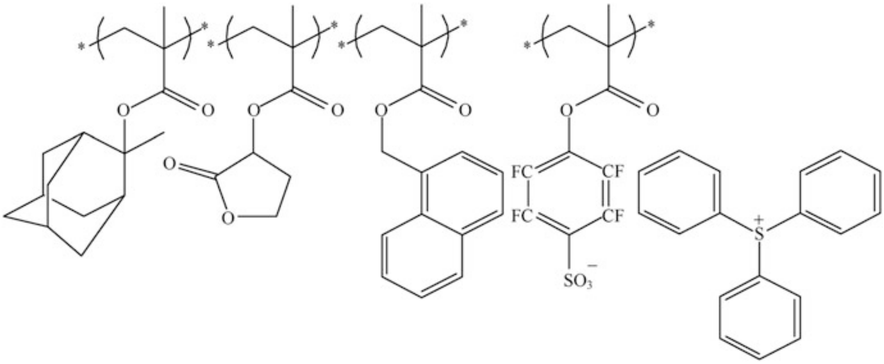

Fig. 78.6 A common EUV MG/PAG bonded structure

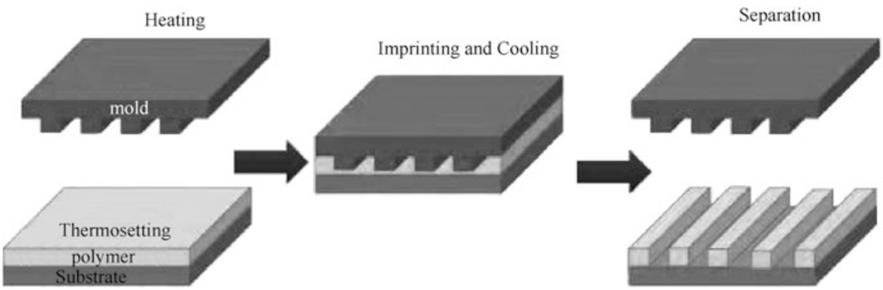

Fig. 78.7 Heat curing nanoimprint schematic

Next-Generation Lithography Materials [10]

The following is photoresist (PR) materials for next-generation lithography, including nanoimprint materials, block copolymers for directed self-assembly process, and electron-beam PRs.

Nanoimprint PR [13, 14]

Nanoimprint PR includes two types of PRs, i.e., thermal curing and UV curing types shown as in Figs. 78.7 and 78.8 respectively. The thermal curing type uses a stamp to transfer the pattern and followed by thermal curing the PR, then use dry etch to transfer the pattern to substrate. Another type is UV curing type which uses a UV light to cure the PR and then uses the dry etch to transfer the pattern to the substrate. The main components of nanoimprint PR include acrylate polymer, photo-initiator, cross-linker, additives, and solvent.

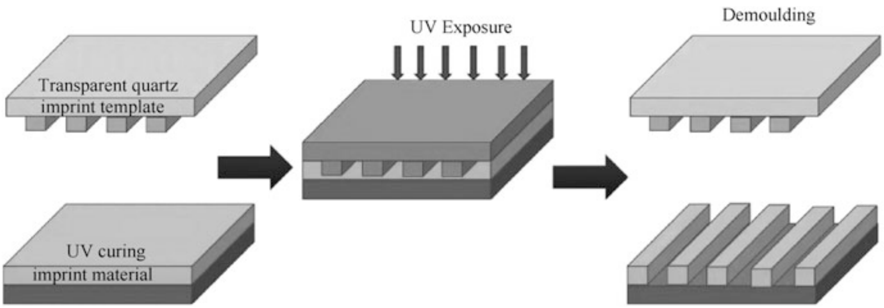

Fig. 78.8 UV-curable curing nanoimprint schematic

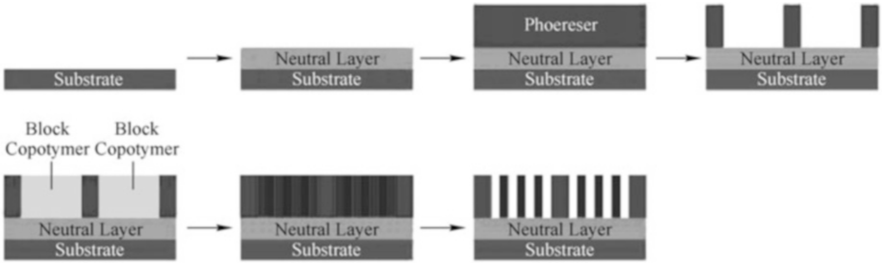

Fig. 78.9 Graphics-based self-assembly

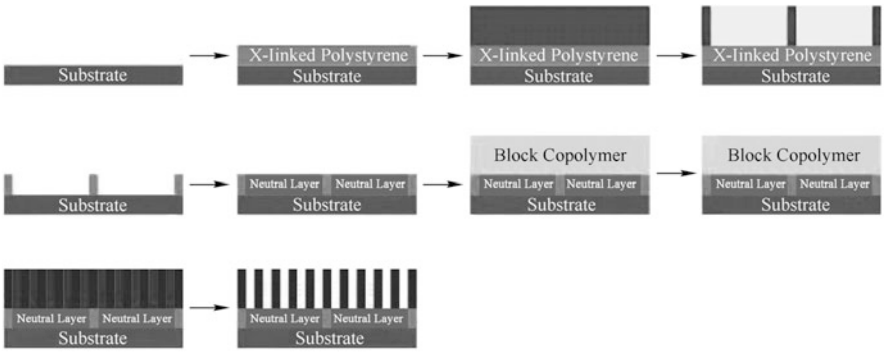

Fig. 78.10 Self-assembly based on chemical substrate

Directed Self-Assembly of Block Copolymer (DSA BCP)

Directed self-assembly use the polarity differences between the two segments of block copolymer to form ordered structures. Based on the phase separation condition, it can be classified to grapho-epitaxy and chemo-epitaxy as illustrated in Figs. 78.9 and 78.10, respectively. The basic principle of self-assembly is to induce fragments with different properties to arrange themselves by physical and chemical methods, and achieve the purpose of photolithography according to different etching rates of different fragments. The main focus is to design the block copolymer with necessary polarity and etch rate differences. DSA is reported to be used in quantum devices, magnetic storage, nanowire, and photonics applications.

Electron-Beam (e-Beam) PR

Electron-beam photoresist (e-beam PR) refers to PR using electron beam as exposure source. Due to its short wavelength, high energy, and small beam size, electron-beam lithography can perform excellent resolution and has been widely used in mask manufacture. PMMA type resin is the main component of e-beam PR. It undergoes the chain scission when bombarded by electrons, which makes the exposure area easy to be dissolved by the developer. The main challenge of e-beam lithography is low throughput caused by its direct write nature, not suitable for the mass production of ICs. There are studies of multiple e-beam (multibeam) lithography which may improve the throughput of e-beam lithography.

Photo-Sensitive Polyimides

Photosensitive polyimide (PSPI) resin is a polymer chain with imide ring and photosensitive group, which has excellent thermal stability and good mechanical, electrical, chemical, and photosensitive properties of organic materials. PSPI resin can be cross-linked or decomposed under ultraviolet, X-ray, electron-beam, or ion-beam irradiation, and can form thin-film patterns on the surface of the substrate through the mask plate. At the same time, because the process of using PSPI resin to form film patterns on the substrate is relatively simple, the production cost is low. Therefore, the PSPI resin has been widely used in the manufacture and packaging of VLSI, micromachinery, and other fields. For example, the photo-patterned and thermally cured PSPI film can act as a thermal stable and electric insulating dielectric layer in the multilayer structure or a passivation coating layer for ICs. PSPI should possess not only the great film properties (e.g., mechanical strength and toughness, electric insulating and dielectric properties, dimensional, and adhesive properties), but also photolithographic performance (e.g., photosensitivity, resolution, developing and rinsing, imidization temperatures, etc.).

According to the convex and concave shapes of the photolithographic images obtained after exposure, PSPI can be divided into negative-tone (n-type PSPI) and positive-tone (p-type PSPI) similar to standard PRs. The general photo-patterning process involves four steps: (1) Spin-coating PSPI resin onto the substrate surface such as Si wafer; (2) Prebaking and exposing to UV light (I-line and/or G-line) through a mask, transferring the pattern information to the PSPI layer; (3) Developing; either the exposed or unexposed area is selectively removed by dissolution to form a patterned layer; (4) Thermal curing; the developed pattern on exposed PSPI was converted into the polyimide one.

After the UV exposure, the cross-linking reaction occurred on the exposed zone of n-type PSPI resin, and the solubility of the exposure zone in the developer decreased significantly. Therefore, after the exposed PSPI was developed and cured, the convex lithographic pattern could be obtained. On the contrary, for p-type PSPI resin, the solubility of the exposure zone in the developer is significantly enhanced due to the chain scission reaction. Thus, after the development and curing steps, concave lithographic pattern can be obtained.

According to the different preparation methods, negative PSPI resin can be divided into ester n-type PSPI, ionic n-type PSPI, and self-sensitizing n-type PSPI. Most of n-type PSPI are based on polyimide precursor poly(amic ester) (PAE) in which photo-reactive methacrylate groups are linked to the carboxylic acids through the ester linkage via the covalent bond (ester n-type PSPI) or acid-amine ion linkage via the ionic bond (ionic n-type PSPI). The photo-chemistry mechanism of pattern formations is different. In the case of ester n-type PSPI, methacrylate groups can react in a radical polymerization by UV irradiation. Conversely, a "charge separation" mechanism is considered in the ionic n-type PSPI, in which charge-transfer complexes are formed between the poly-amic acid and the photo-radical initiator in the exposed area upon UV exposure. The photo-radical initiator is usually photo-acid generator (PAG) or photo-base generator (PBG), which can photo-chemically generate a strong acid or a base upon UV irradiation. Then at relatively low temperatures, heat treatment can perform the conversion from the precursor to a robust structure. In addition, the self-sensitized PSPI resin is cross-linked by the substituted alkyl group on the amido group in the main chain of the polyimide resin and the carbonyl group of the benzophenone structural unit, thus reducing the solubility of the resin in the solution developer, so as to obtain the convex lithographic pattern.

According to the different kinds of photosensitizers, positive PSPI resins can be divided into o-nitrobenzyl ester PSPI, cyclobutylamine resin PSPI, and diazonaphthoquinone sulfonate PSPI. **(1) o-nitrobenzyl ester PSPI resin:** The working principle is that the o-nitrobenzyl ester photosensitive groups are decomposed into carboxylic acids and aldehydes under the ultraviolet light, and the polyamide ester resin connected with o-nitrobenzyl ester photosensitive groups on the main chain can transform the ester group into carboxylic group after the UV exposure, which significantly improves its solubility in alkaline aqueous developer. After the alkaline solution development and curing, the exposed region is completely dissolved while the unexposed region is preserved, thus forming a positive convex lithographic pattern. **(2) Cyclobutylimide resin PSPI:** The working principle is that polyimide resin containing cyclobutyl group is decomposed by the light irradiation, so that the solubility of the exposure zone in the organic developer is enhanced, therefore, a positive convex lithographic pattern is obtained. **(3) Diazonaphthoquinone sulfonate PSPI resin:** It is composed of polyamide ester resin and photosensitizer which can form organic carboxylic acid compound under the light irradiation. That is, with the UV light irradiation, the diazonaphthoquinone sulfonate group (DNQ) decomposes to form organic indenic acid, which obviously enhances the solubility of the resin in the exposure area with the alkaline aqueous developer, so as to obtain a positive convex lithographic pattern. PSPI have been extensively employed in the micro-electronic manufacturing and packaging (e.g., passivation and buffer coating layer on ICs, interlayer dielectric layers in multilayer structures, BGA/CSP/WLP, etc.), as well as buffer-stress coatings in IC packaging by EMC.

Antireflection Coating [15, 16]

Antireflection coating refers to a thin coating under or over PR layer; it was used to reduce the reflected light at interfaces of PR/air and PR/substrate for suppressing the influence of standing wave effect on the photoresist **(1) The top antireflection coating (TARC)** is coated at the top of the PR. The main function of the TARC layer is to eliminate the light reflected from the top surface of the photoresist, prevent the impurities in the air from diffusing into the photoresist, reduce the influence of the film thickness on the performance of the photoresist, and improve the uniformity of the line width of the photoresist. Its performance requirements include matching the refractive index of the photoresist and being easily soluble in the developer. **(2) The bottom antireflection coating (BARC)** [17] is coated under the PR for reducing light reflection at the substrate/PR interface. Barc layer can prevent the diffusion of impurities on the substrate to the photoresist, and its performance requirements include high absorption coefficient, insolubility in the photoresist solvent, and lower etching rate than the photoresist.

Antireflection coating is generally used with 248 nm DUV photoresist or 193 nm DUV photoresist, usually composed of polymer resin, dye, thermal acid generator, solvent, and so on. However, the composition of the antireflection coating used for 248 nm and 193 nm photoresist is different, and the absorption peak of the dye used is also different.

Ancillaries

Ancillaries refer to chemicals used with PR in the lithography process of integrated circuits. It mainly includes adhesion promoter, thinner, edge bead remover (EBR), developer, and stripper. **(1) Adhesion promoter:** HMDS (Hexamethyl disilylamine) is a main chemical applied to substrate before photoresist coating. It will turn the substrate surface from hydrophilic to hydrophobic by reacting with the surface hydroxyl on substrate, thus improving the adhesion property of photoresist to the substrate, as well as reduce adhesion-related defects and improve the wet etch resistance. **(2) Thinner:** Thinner is a chemical used to dilute PR, mainly for adjusting PR viscosity to obtain different film thickness. The main component is PR solvent, like PGMEA, PGME, EL, MAK, etc. **(3) Edge bead remover (EBR):** It refers to chemicals used to clean the edge and backside of wafers. During spin coating, PR will become thicker at wafer edge and even splash to the backside of the wafer. If not cleaned properly, these PR will move with wafers in the following steps and increase particles and contamination to both wafers and tools. Main components of EBR are solvents such as PGMEA, PGME, EL, etc. It needs to match the solvents used in photoresist. The edge bead remover can dissolve the photoresist quickly and has the characteristics of high purity and low particle content. **(4) Developer:** Developer refers to chemical used to remove the unwanted PR on the wafer. For positive PR, the developer is aqueous organic basic solution such as TMAH, NaOH; for cyclized rubber-based type negative PR, developer is organic solvents. **(5) Stripper:** Stripper refers to chemicals used to remove PR after development and subsequent processes such as wet etch, dry etch, implantation, etc. These process steps may cause structural changes in the photoresist and result in difficult to remove PR; thus, stripper needs to have strong solubility to PR. Its basic components are organic solvent and organic amine additives, commonly used stripping solvents include N-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and so on.

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