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Photolithography and Photoresist

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Synonyms

EB lithography; EUV lithography; Litho; Lithography; Resist; Resist material; UV lithography

Definition

Photolithography is a process to construct patterns using photoresist on a substrate by the exposure with a laser.

Introduction

Figure 1 depicts the process of photolithography system. The solution of photoresist is spin coating on the silicon wafer to form a thin film. The thin film was exposed by a laser and developed with a solvent to give two types of resist patterns: positive tone and negative tone. A positive tone can be obtained by that the exposed parts are soluble, and a negative tone can be done by that the exposed parts are insoluble in a developer.

Moore's law for the development of photolithographic technology predicts an exponential increase of microelectronic component densities as shown in Fig. 2 [1].

To achieve increased densities, new photolithography systems employ electron beams (EBs) and short-wavelength lasers, such as g-line ($\lambda = 436$ nm), i-line ($\lambda = 365$ nm), KrF ($\lambda = 248$ nm), ArF ($\lambda = 193$ nm), and extreme ultraviolet (EUV) ($\lambda = 13.5$ nm). At the same time, the appropriate photoresist materials have been developed according to the progress of photolithography systems. When designing photoresist materials for lithography systems, the requirements of their properties are as follows: (1) transparency in the laser, (2) good solubility and good film-forming ability to form thin film, (3) good photochemical reactivity, (4) sufficient mechanical integrity of the pattern, and (5) high etch resistance. The polymers based on phenol resins, polystyrenes, and polymethacrylates (polyacrylates) were modified with photoreactive groups and applied as photoresist in each photolithography systems [2, 3]. It was also reported that molecular photoresist materials based on low-molecular-weight phenol resins and cyclic oligomers were examined to offer higher-resolution resist patterns [4]. Furthermore, the chemical amplification resist system using a photoacid generator has offered enhanced photosensitivity by the exposure of a laser [5].

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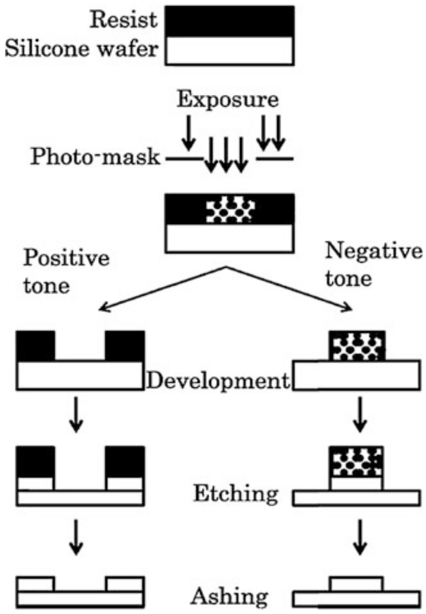

Fig. 1 Photolithography process

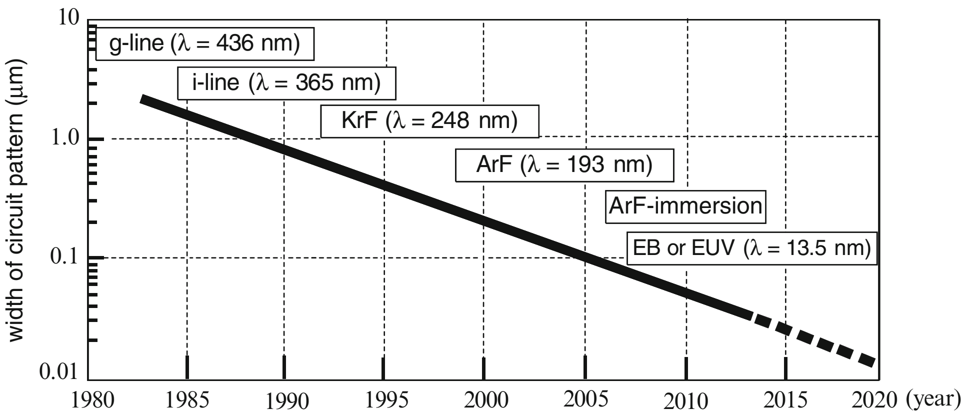

Fig. 2 Moore's law (development of IC chip)

Chemical Amplification Photolithography System

Typical photoresist using chemical amplification photolithography system is shown in Fig. 3. This polymer contains *t*-butyloxycarbonyl (BOC) groups in the side chain. When the thin film prepared by the solution of photoresist material and photoacid generator (PAG) was irradiated by a laser, PAG decomposed to produce an acid H^+ at first. This H^+ attacks to a BOC group to give a new H^+ accompanying with carbon dioxide and isobutylene. The H^+ can be amplified one after another deprotection reaction. As a result, the chemical reaction can occur under low exposure dose of a laser, i.e., the sensitivity of photoresist increases.

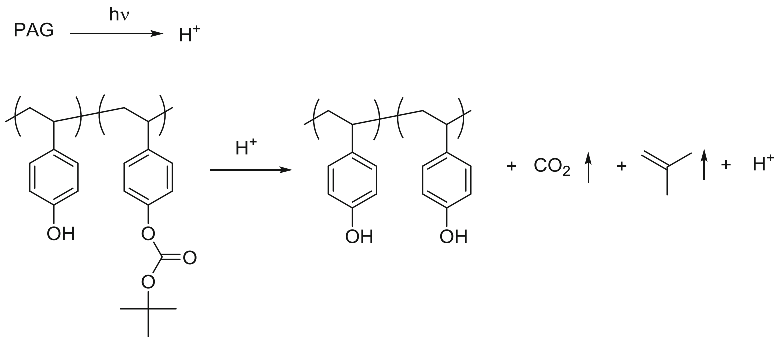

Fig. 3 Chemical amplification system using photoacid generator

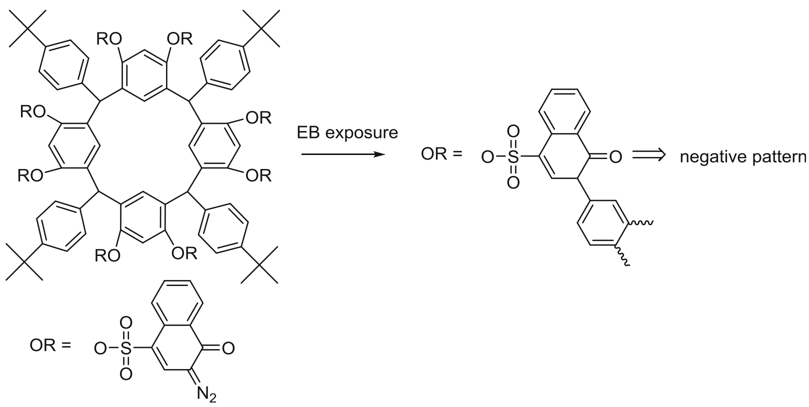

Fig. 4 Negative resist based on calixarene

Molecular Photoresist

Molecular resist materials have been employed in EB and EUV lithography systems. Most of them have hydroxyl groups in the side chain, due to that they are expected to provide good film-forming ability and good adhesion to the substrate, owing to its hydrophilicity. At first, some calixarene derivatives showed high-resolution pattern using point beam EB irradiation [6, 7].

Ober et al. reported the synthesis of *p*-*t*-butylcalix [4] resorcinarene derivatives with pendant diazonaphthoquinone moieties, and a negative pattern with 60 nm resolution could be obtained by EB exposure system without chemical amplification (Fig. 4) [8].

Ueda et al. also reported a negative EB resist pattern using the mixture of calix [4] resorcinarene (CRA), 4,4′-methylenebis[2,6-bis(hydroxymethyl)phenol](MBHP) as a cross-linker and a photoacid generator. A clear pattern with 1.0 μm resolution could be obtained by i-line exposure system (Fig. 5) [9].

Hattori et al. reported the synthesis and EB resist pattern using a truxene derivative with pendant adamantyl ester groups (Fig. 6), and a clear 22 nm resolution pattern was obtained with an EB exposure system [10].

Oizumi et al. reported the synthesis of fullerene derivatives with pendant *t*-BOC and *t*-butyl ester groups and examined their patterning properties with an EUV lithography system (Fig. 7) [11]. A 45 nm-hp pattern as positive-type resist was obtained at EUV exposure dose of 12.5 mJ/cm^2, and resolution of up to 26 nm-hp could be obtained as positive tone.

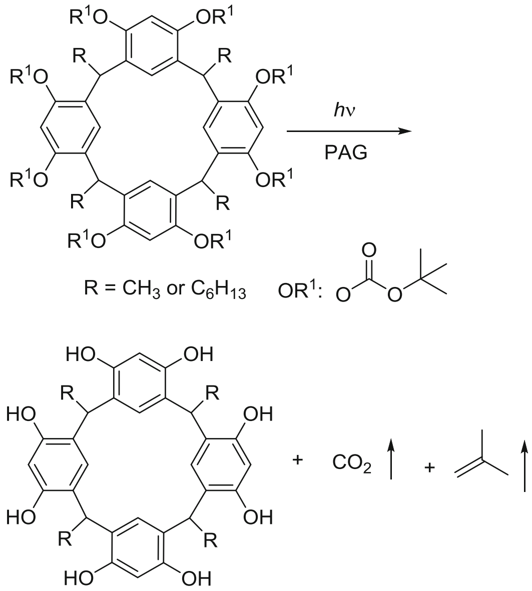

Fig. 5 Positive resist based on calix[4]resorcinarene

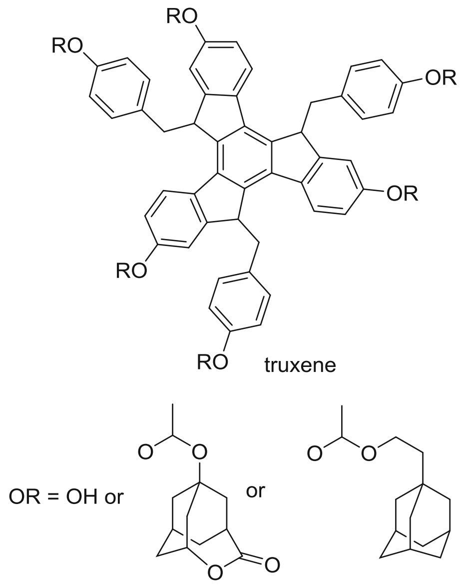

Fig. 6 Positive resist based on truxene

Kudo et al. reported the synthesis of noria (waterwheel-like ladder cyclic oligomer) derivatives with pendant photodegradable groups as EB and EUV resist materials (Fig. 8). Noria derivatives containing *t*-butoxycarbonyl groups [12] and *t*-butyl ester groups [13] showed clear line-and-space patterns with resolutions of 50 ~ 70 nm in an EB resist system. The noria derivative containing adamantyl ester group (noria-AD) showed a clear line-and-space pattern with a resolution of 26 nm at an EUV exposure of 14.5 mJ/cm^2 [14].

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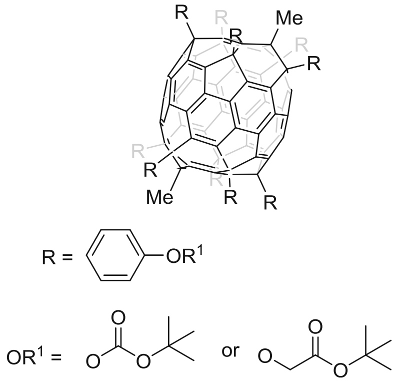

Fig. 7 Positive resist based on fullerene

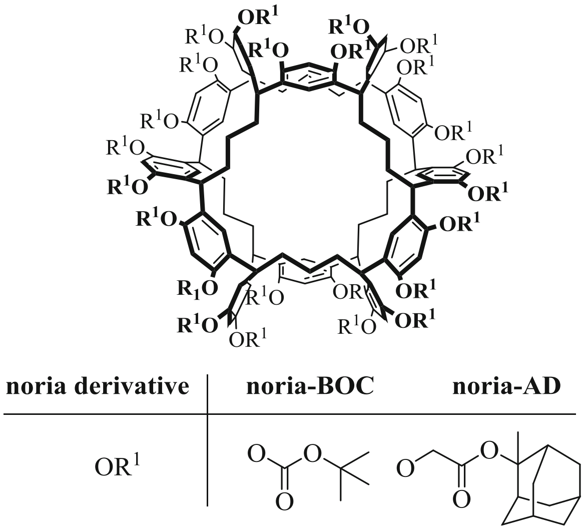

Fig. 8 Positive resist based on noria

Henderson et al. reported the synthesis of a photoacid-generator (PAG)-bonding molecular resist, tris[4-(*t*-butoxycarbonyloxy)-3.5-dimethylphenyl]sulfonium hexafluoroantimonate, and examined its patterning properties using EB and EUV exposure (Fig. 9) [15, 16]. The sensitivity and line-edge roughness (LER) were improved compared to those of non-PAG-bonding molecular resist, and a 50 nm resolution was obtained in the EB system.

Next-Generation Photolithography and Photoresist

In next-generation lithography systems, EB or EUV exposure systems are expected and a resolution of better than 15 nm is required. To obtain such high resolution, the photoresists must be very sensitive to exposure tool. However, high sensitivity is associated with increased roughness [line-edge roughness (LER) or line width roughness (LWR)], which is unfavorable for high resolution. That is, there is a trade-off of three factors: resolution of the resist pattern, LER value of the resist

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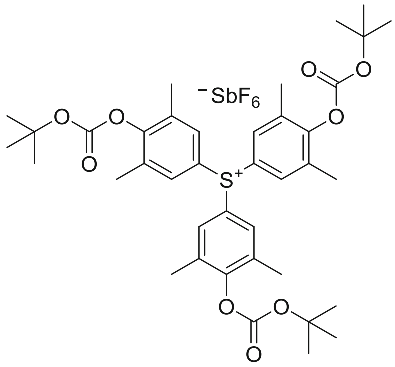

Fig. 9 PAG-bounding molecular resist

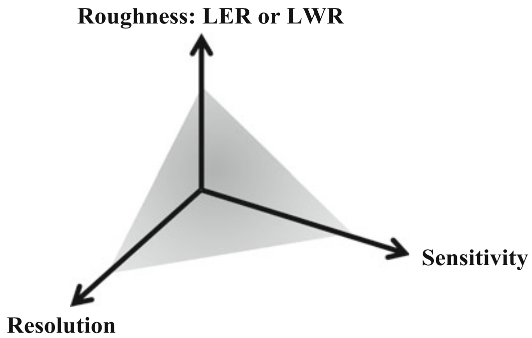

Fig. 10 Trade-off between sensitivity, line roughness, and resolution of resist pattern

pattern, and sensitivity of the photoresist, as shown in Fig. 10. To overcome this trade-off, the development of new photoresist material has been required.

Summary

Various photoresists based on polymers and low-molecular-weight compounds have been investigated in attempts to obtain very high-resolution resist patterns in the next photolithography systems. However, there is a trade-off among characteristic properties such as resolution, line-edge roughness, and sensitivity of the photoresist. At such high resolution, the line-edge roughness of the resist pattern remains the most significant problem. Synthesis of new photoresist and improvement of exposure system must be investigated together to accomplish the problem.

Related Entries

► Photoinitiated Polymerization
► Photoresponsive Polymer

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