Organotin photoresists for extreme ultraviolet lithography

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Chapter 1

Introduction

1.1 Photolithography

Photolithography is a key technology that has enabled the rapid development of semiconductor industry during the past 60 years. It is a technique that enables geometric features to be transferred from a mask to a photo-responsive material (photoresists) deposited on a substrate.\textsuperscript{1} The typical photolithography process is illustrated in Scheme 1.1. The standard procedure is started with spin-coating a photoresist as a thin layer on the silicon substrate, and then exposing the photoresist thin film with an irradiation source, commonly ultraviolet light. The solubility of the photoresist is changed as a result of chemical reactions induced by the local exposure. In a development step, either the exposed part or the unexposed part can be removed by washing with a suitable solvent, generating positive tone or negative tone patterns, respectively. Using the protection by the photoresist, the pattern from the mask is transferred to the silicon substrate via an etching step.

\textbf{Scheme 1.1.} Fundamental photolithography procedure.
Optical lithography has been the dominant pattern transfer technology in the semiconductor industry for more than 5 decades because it can fulfill the requirement of high volume production of microelectronic components.\textsuperscript{2-4} In addition to the improvement of the throughput and decrease of the cost, another significant challenge in the semiconductor industry is the increasing transistor density per unit area, which implies that the feature size should become smaller and smaller. Until now, the shrinkage of the critical dimension (CD) of the device features has been able to match the International Technology Roadmap for Semiconductor (ITRS) and the famous Moore’s law.\textsuperscript{5-7} The number of transistors on a chip has been doubled on the average every 18 months. The minimum feature size that a projection system can print is given approximately by the Rayleigh equation:\textsuperscript{8}

\[ CD = \frac{k\lambda}{NA} \]  
(1.1)

In equation 1.1, CD is the critical dimension, $k$ is a coefficient that incorporates process-related factors, $NA$ is the numerical aperture of the optical system, and $\lambda$ is the wavelength of the projection light. During the past decades, the resolution (CD) has been systematically improved (CD became smaller) by optimizing the process factor $k$, which has reached its practical limit at $k = 0.25$, and by reducing the wavelength of the incident light.\textsuperscript{8} In the past decades, the wavelength used in optical lithography was continuously scaled down from 436 nm, 365 nm, 248 nm until 193 nm.\textsuperscript{3, 8, 9} The shorter wavelengths are dictated by the available light sources, which in practice are excimer lasers, KrF for 248 nm and ArF for 193 nm. A natural next choice would have been to turn to the F\textsubscript{2} laser at 157 nm, but this turned out to be problematic (the birefringence of the CaF\textsubscript{2} crystal lens, vacuum exposure, etc.).\textsuperscript{10} Instead, the 193 nm wavelength scanners where improved by using immersion lithography, which allowed to increase the numerical aperture from $NA = 0.93$ to $NA = 1.35$.\textsuperscript{11-14} With these improvements, the lower limit of the critical dimension is now $CD = 0.25 \times 193 / 1.35 = 36$ nm. To create smaller features, multiple patterning techniques are required. To avoid the added costs of these processes and to open a new path to smaller CD’s a significant step was needed. Extreme ultraviolet photolithography (EUVL), which uses 13.5 nm radiation, was developed to meet these challenges.\textsuperscript{9, 15, 16}

To achieve high quality patterns, the variation of the pattern feature is one of the most significant problems.\textsuperscript{17, 18} The variation of the line boundary of the resist pattern is called line edge roughness (LER).\textsuperscript{18} Kozawa et al. have investigated the reason for the LER.\textsuperscript{19} Almost all of the resists and process factors can affect the LER.\textsuperscript{19} At the beginning, the molecular size was considered to be the main reason for LER since it was considered the minimum dissolution unit.\textsuperscript{20} Later, Kozawa et al. found that the chemical inhomogeneity generated at the edge of the pattern
between the unexposed and exposed areas (or soluble and insoluble molecules) was the main concern.\textsuperscript{21, 22} Since the photon induced chemical reaction is a stochastic process, the inhomogeneity in the distribution of the soluble and insoluble molecules at the boundary leads to LER generation.\textsuperscript{21, 23} As the pattern resolution is aiming at approaching the atomic scale in EUV photolithography, the stochastic effects are becoming a more and more serious concern. The photon shot noise in particular is a fundamental physical limitation.\textsuperscript{22, 24} The difficulty to improve the resolution, LER and the sensitivity simultaneously is also known as the RLS trade-off, illustrated in Fig. 1.1.\textsuperscript{25, 26}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{resolution.png}
\caption{The resolution: LER: Sensitivity or RLS trade-off.}
\end{figure}

1.2 EUV photolithography

EUVL development has been initiated in the 1980s, and it was suggested to viably extend Moore’s law.\textsuperscript{27, 28} EUVL has many similarities with the previous generations of optical lithography technologies. The pattern resolution in EUVL still follows the Rayleigh equation. Since the wavelength used in EUVL is 13.5 nm it potentially supports the resolution of the pattern down to sub-10 nm in a single process step.\textsuperscript{16} It enables the feature size on the semiconductor chips to become smaller and smaller.\textsuperscript{29-31}

Yet, there are some important differences between the ultraviolet lithography technologies and EUVL, which are mainly due to the extremely short wavelength of 13.5 nm used in EUVL. One of the most significant differences is the EUV optics, which rely on reflection instead of traditional transmission optics. The schematic of current optical train in an ASML EUV photolithography machine is shown in Scheme 1.2.
In order to make EUVL a high-volume manufacturing tool for electronic devices, big efforts have been put in the EUV light source, optics, metrology, contamination control, masks and mask handling, and resists. Among these components, the photoresist is considered as one of the most critical issues in realizing EUVL in industry. In this thesis, we focus on the EUV photoresists.

![Scheme 1.2](image)

**Scheme 1.2.** Current optical train in ASML EUV photolithography machine (NXE: 3300/3350/3400).

### 1.3 EUV photoresist

A photoresist is a photo-responsive material of which the solubility can be switched by irradiation-induced chemical conversion, in many cases followed by a heat treatment. In the development of photolithography, each wavelength reduction has required the preparation of novel photoresists that are not only sensitive at the new wavelength, but also meet all of the requirements of an effective resist material. A good resist that is acceptable for high-volume manufacture must give good resolution, high solubility contrast, good etch resistance, high sensitivity and low outgassing. In order to continuously push the critical feature size down in EUV lithography, considerable efforts have been put in developing photoresists for the next generation EUV lithography.\(^{32}\)

EUV photoresists with high sensitivity are preferable, because the EUV exposure tools are currently photon limited. Thus the sensitivity of the photoresist plays an important role in EUVL. The shrinkage of the CD also places restrictions on the thickness of the photoresist. The aspect ratio is defined as the height divided by the width of the features being patterned. The aspect ratio of 2.5 or smaller has been acceptable. Higher aspect ratio starts to incur larger potential for pattern collapse.\(^{33}\)
For 15 nm features fabrication, a film thickness around 30 nm is routinely used. As a result, a high absorbance of the thin photoresist at 13.5 nm becomes the key factor for the sensitivity of the EUV photoresist. Ultra-high absorbance on the other hand should also be avoided because it leads to an insufficient penetration depth of the light so that the film cannot be completely exposed down to the substrate. It has been identified by Kunz et al. that ideal imaging is typically achieved for a film transmittance of 50 – 80%. Kozawa et al. reported that a minimum transmittance of 70% is required for vertical sidewalls. Based on the Lambert-Beer law, when a 30 nm film is used and the transmittance is 70%, the needed absorption coefficient of the photoresist is around 12 µm⁻¹. Because the source power of the current generation of EUVL machines is limited, and overall reflectivity of the EUV optics is relatively low, a resist sensitivity on the order of 10 – 15 mJ cm⁻² has been mentioned as a requirement to achieve the wafer throughput that would make EUV economical. But it may generate high LER under this low dose due to the photon stochastics. To search for proper materials with required absorption, the absorption cross section of different elements has been calculated from tabulated data, as shown in Fig. 1.2.

**Figure 1.2.** Atomic absorption cross-section at EUV (13.5 nm) of elements with atomic number Z from 1 to 86, from tabulated data. Figure from ref. 38.

Traditionally, the photoresists are polymer molecules, mainly containing carbon and oxygen atoms. After considering the EUV absorption cross-sections of the different elements illustrated in Fig. 1.2, metal-containing materials were investigated as photoresist for EUVL instead of traditional organic polymer type photoresist.
1.3.1 Chemically amplified photoresist

The current standard type of photoresists is the so-called chemically amplified photoresist (CAR), in which chemical amplification is accomplished by employing acid catalyzed deblocking of dissolution inhibiting groups. The strong acid required is generated by a local photochemical reaction of a compound called the photo-acid generator.\(^{41}\) Two of the common deprotection pathways are the conversion of carbonates or esters to phenolic or carboxylic OH. The typical photo-induced acid catalyzed deprotection chemistry (photoresist for 248 nm as an example) is shown in Fig. 1.3. The chemical reaction increases the fraction of free OH groups in the exposed part of the photoresist, which increases the solubility of the exposed part in aqueous base. The chemically amplified photoresists are widely used in 193 nm high-volume manufacturing lithography. For EUV lithography, researchers try to further adapt the CAR concept to develop EUV photoresists.\(^{42-44}\)

Since the absorptions of carbon and oxygen atoms are quite low at the EUV wavelength, in order to increase the sensitivity, it is important to improve the acid generation efficiency and catalysis as much as possible.\(^{45}\) The migration of the catalyst is an essential aspect of the chemical amplification mechanism, but the spreading of catalyst also leads to the decrease of resolution and increase of LER.\(^{46}\) To prevent the acid diffusion and improve the LER, base quencher was added into the photoresists thin film to react with the residual acid.\(^{47, 48}\)

**Figure 1.3.** Acid catalyzed deprotection chemistry (photoresist for 248 nm as an example). Figure from ref. 41.

The photoreaction mechanism of the CAR under EUV exposure was investigated by several groups.\(^{49-51}\) The main difference is that the photons give rise to molecular photochemistry during photolysis at 193 nm or even longer wavelength exposure. Under EUV (92 eV) exposure, primary photoelectrons are emitted from the valence band and the semi-core levels. These primary electrons have sufficient energy to
further ionize the photoresist molecules, generating secondary electrons, as shown in Fig. 1.4. Not only the photon-induced chemical reaction, but also the photoelectrons generated after the EUV photon absorption contribute to chemical conversion. The photoelectron generating mechanism under EUV is the same regardless of the type of photoresist. Because the photoelectrons diffuse within the photoresist, they induce the so-called secondary electron blur, which decreases the resolution and increases the line edge roughness of the EUV generated pattern.

Effort also needs to be put to improve the etching resistance of the organic polymer type photoresists. The final goal of the photoresist is to protect the underlying substrate from the etching. But with the resolution increasing, the film thickness of the resist has to be decreased to prevent pattern collapse. The thinner the organic photoresist film, the harder for the film thickness to protect the under-layer substrate from the etch process. To avoid these problems of organic polymer type photoresist, molecular organometallic photoresists started to be introduced.

**Figure 1.4.** Qualitative scheme depicting multiple electrons being created after the absorption of an EUV photon. Figure from ref. 52.

### 1.3.2 Metal containing photoresists

As an alternative to the traditional organic polymer type photoresist, which is mainly composed from carbon and oxygen atoms, the metal containing photoresist were introduced to EUVL. Based on the absorption cross sections at the EUV energy of 92 eV, shown in Fig. 1.2, metals can be expected to have much higher absorption than most of the organic photoresist under EUV exposure. Additionally, the metal containing photoresists also have higher mass density than the organic photoresist, which potentially decreases the secondary electron blur. Since this
type of photoresists are not blended with photoacid generators, acid diffusion is not a problem any more when the molecular metal containing photoresist is used.

The metal containing resist started to attract interest due to their high EUV absorption cross section, which can fulfill the absorption coefficient requirement of EUV photolithography. The hybrid metal containing type photoresists were introduced, firstly by Ober’s group at Cornell introduced the Hf- and Zr-containing type nanoparticles mixed with a photo-acid generator were tested as EUV photoresists. The properties of hybrid photoresist, their EUV patterning performance, and the chemical reaction mechanism were introduced with this work. Based on photolysis of the carboxylic group and surface charge change of the nanoparticles, the hydrodynamic size of the nanoparticles can be changed, therefore switching the solubility of the photoresist. It was shown that the Zr-/Hf-type nanoparticles give 25 times higher etching resistance than polymer type photoresists. Additionally, the sensitivity of these Zr- and Hf-type photoresists was demonstrated with high-resolution patterns with EUV doses as low as 4.2 mJ cm$^{-2}$. Hf-, Zr- and Ti-methacrylate clusters were introduced by Castellanos’s group as EUV photoresists. HfSOx cluster photoresist was introduced and the mechanism was studied by Herman and coworkers. They also use a sodium template butyltin cluster with β-Keggin, and butyltin oxo hydroxo, as model photoresists to investigate the patterning mechanism. Other molecular hybrid compounds inspired in metal organic frameworks comprising Zn-based dimers were introduced as EUV photoresist by Ober and coworkers. Brainard’s group explored a wide range of metal containing molecular type photoresists such as palladium and platinum containing molecules as positive tone photoresist, antimony molecule photoresist, tin molecule photoresists (negative tone). All the photoresist introduced above show good resolution and sensitivity performance. The US company Inpria was the first to develop inorganic photoresists for industrial application. The actual molecular structure was not disclosed, but it is known to be tin-based, and both patent descriptions and a publication suggest that it is like the tin cages discussed below. Several chemical structures of the metal containing photoresist mentioned above are shown in Fig. 1.5.

The absorption coefficients of different metal containing photoresists at the EUV energy were measured by Fallica et al. The advantage of the metal containing photoresist is a clear superiority over the organic type photoresist when we consider the EUV absorption ability, especially for the tin containing photoresists.

To improve the sensitivity of the EUV photoresist, except improving the EUV absorption, the photoresists also need to efficiently undergo photolytic conversion. The photolysis of the carboxylic group upon UV irradiation has been reported.
This mechanism has been observed in several EUV photoresist systems, such as Hf-, Zr- based nanoparticles, and Zr-, Hf- cluster, and L₂M(C₇O₄) type resist. Their performance under EUV exposure shows that the design based on the reaction mechanism is a good approach to create new EUV photoresist.

Figure 1.5. (a) Hf-, Zr- based nanoparticles from Ober’s group. (b) Hf-, or Zr cluster from Castellanos’ group. (c) Tin carboxylate molecule from Brainard’s group. (d) Pt based photoresist from Brainard’s group.

Above all, various metal containing photoresists were investigated as EUV photoresists. Not only the pattern performance under EUV lithography, most of the works also introduce the chemical reaction mechanism of the photoresist under EUV exposure. In addition to searching for the best pattern performance, we also would like to understand the reason behind. In this way, we might find a more efficient way to build more efficient EUV photoresists.

1.3.3 Tin-containing photoresists

Among all the metal containing molecules or complexes, the tin-containing molecules are probably the most attractive due to their potentially high EUV absorbances. The tin containing organic molecules are called organotin compounds if they contain at least one bond between tin and carbon. The organotin molecular complexes have been developed for decades. Their diversity of structures and
their suitability for construction of frameworks have attracted the attention of many research groups throughout the world. Various applications make use of organotin compounds, such as biocides, oil production, fracturing thickening agent, and green corrosion inhibitor.\textsuperscript{84-86} They also start to set their foot into the EUV photoresist field. Based on the expectation mentioned above, the metal carboxylate complexes can be good EUV photoresists, those tin oxo cages also can be used as EUV photoresist. Among all the organotin compounds, the tin containing cages as shown in Fig. 1.6, have attracted the attention from Brainard et al.\textsuperscript{70} The cages contain 12 tin atoms and twelve organic groups connected to the tin atoms, and also 20 oxygen atoms in the framework connecting the tin atoms. This tin oxo cage (with isopropyl R-groups) was first reported by Puff and Reuter.\textsuperscript{87} The synthesis method and the molecular structure were introduced and characterized carefully. This structure is stable and soluble in many media, it can be crystallized and its structure has been well characterized. But there was no specific property or potential application described for this interesting molecule until Brainard’s group introduced it as a metal-organic EUV photoresist.\textsuperscript{70} They used the 12-Sn and oxygen as the main framework, the counterion and the outer shell organic chain were exchanged. The conditions used to prepare this compound into EUV photoresists were tested and optimized. Clear patterns were achieved under EUV interference lithography and the lithographic performance of tin oxo cages with different organic groups and counterions was also tested and compared. They successfully employed the tin oxo cages as EUV photoresists. But the photochemical reaction mechanism upon EUV exposure was not clear.

Another kind of organotin molecule introduced by Brainard’s group into EUV photoresists are single tin atom containing organotin carboxylates.\textsuperscript{79} Twenty one compounds of the type $\text{R}_2\text{Sn(O}_2\text{CR')}_2$ were tested under EUV exposure.\textsuperscript{79} The photoreaction mechanism is clearer than in the case of the tin cages. Here it is mainly the decomposition reaction of the carboxylate and the Sn-C bond cleavage. They also found out the relationship between the hydrocarbon group size and the dose to gel value. Their results indicated that the sensitivity of photoresists showed strong correlation with the R groups, while the carboxylate groups were unlikely involved in the reaction upon EUV exposure. But when the R group is fixed, the higher the molecule weight of the R’ group, the lower the sensitivity of the photoresist, except the acrylate and methacrylate compound. Their sensitivity and high-resolution pattern ability under EUV exposure have been proven.

In this thesis, we study two kinds of tin compounds. The main subject is the organotin oxo cage as shown in Fig. 1.6. In addition we briefly explored low valent tin(II) carboxylates. The tin oxo cages were chosen due to their well-defined molecular structure, high EUV sensitivity, their easy synthesis and good pattern
ability which made them good to use as a model system to investigate the chemical reaction mechanism upon irradiation. In addition to EUV, we also use DUV as irradiation source to trace the photoreaction in the model EUV resist. In the last chapter we also explore tin(II) 2-ethylhexanoate and tin(II)acetate, which are formally not organotin compounds, and can be expected to react via different pathways. Tin(II) 2-ethylhexanoate has been applied for UV-assisted imprinting lithography.\textsuperscript{78} The photoreaction mechanism upon UV exposure has been described.\textsuperscript{78}

![Figure 1.6. Chemical structure diagram of the tin oxo cage \([(BuSn)_{12}O_{14}(OH)_{6}]\(OH\)\_2 with hydroxide as counterion.](image)

### 1.4 Aims and outline of this thesis

This thesis is the result of a research project in the Nanophotochemistry group at the Advanced Research Center of Nanolithography. In our group, we are aiming at investigating the photoreaction mechanism inside the photoresist for next generation photolithography. In this thesis, we used the tin oxo cages as a model compound and investigated the reaction mechanism of the photon-induced reaction. The possibility of using a small tin containing molecule as photoresist was also investigated.

In Chapter 2, we discuss the details of the experimental methods we used throughout this thesis. The chapter starts with sample preparation method and the way we used to characterize the pattern performance. It then shows the methods we used for characterizing the photon-induced chemical changes in the photoresist.

In Chapter 3, the photoreactions of the tin oxo cages with hydroxide group upon deep UV (225 nm) exposure under dry N\textsubscript{2} and air atmosphere are studied and compared by using hard X-ray Photoelectron Spectroscopy (HAXPES).
photoreaction mechanism in the tin oxo cages is proposed. XPS is demonstrated to be a valuable technique for investigating the chemical changes in the photoresist thin films. This work serves as a motivation for the following studies on the photoreaction mechanism in the photoresist thin films upon exposure.

In Chapter 4, the effect of thermal processing on the chemical reactions and reaction yield in the tin oxo cages are investigated, again using HAXPES. In addition to the photon-induced reaction, we prove that the chemical reactions in the bake processes also act as significant roles in the final performance of the photoresist.

In Chapter 5, we used three kinds of tin oxo cages, which have the same cage structure but three different counterions (hydroxide, acetate, trifluoroacetate), to investigate the relationship between photon absorption, chemical reaction and the solubility changes in the photoresist.

In Chapter 6, we study the pattern performance of the tin oxo cages under EUV exposure. Different process conditions are tested. Our results indicate that sensitivity and resolution are only meaningful for photoresist when the process conditions are optimized.

In Chapter 7, we investigate the photoreaction mechanism of tin oxo cages under EUV (13.5 nm) and DUV (225 nm) exposure. Different X-ray photoelectron spectroscopies combined with mass spectrometry methods are used to investigate the photon-induced chemistry in the photoresist films. To study primary reactions between photons and the tin oxo cage, the photoelectron spectrum with photon energy 92 eV was measured.

In Chapter 8, we describe the discovery of a dual-tone property of the tin oxo cages photoresist upon EUV and E-beam exposure. Additionally, we study the chemical reactions in the TinOH thin films under different conditions.

In Chapter 9, we study possibility of using the tin(II) carboxylate molecules as EUV photoresist. The patterning performance and the chemical reaction of the thin films upon EUV are studied.

1.5 References


59. L. Li, S. Chakrabarty, J. Jiang, B. Zhang, C. Ober and E. P. Giannelis, "Solubility studies of inorganic-organic hybrid nanoparticle photoresists with different surface functional groups", Nanoscale, 2016, 8, 1338-1343.


