Organotin photoresists for extreme ultraviolet lithography

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Summary

Photoresists are photosensitive materials that are used to transfer patterns in photolithography. New types of photoresists are needed for the next generation of photolithography, which uses extreme ultraviolet radiation (EUV, wavelength 13.5 nm). Organotin materials have drawn great attention in the photoresist field, not only due to their potential in industrial application but also because of the interest from the fundamental point of view. This thesis focuses on two kinds of organotin materials as photoresists: the tin oxo cages and tin(II) carboxylates molecules. We study the interaction of EUV and short-wavelength (deep) UV (225 nm) photons with the two types of photoresist candidates.

Chapter 1 gives an overview of the subjects of photolithography and photoresists. The developments of photolithography and photoresists are briefly summarized. Some metal-containing photoresists and their proposed reaction mechanisms are discussed. The organotin type of photoresists is attractive for us as a prototype for the study of the chemical reactions on metal containing photoresists upon light exposure. This is important for understanding the principles of EUV-induced chemical reactions, and can form the scientific groundwork for the optimization of metal-containing photoresist performance in the next generation photolithography.

In Chapter 2, we introduce the experimental techniques we used throughout the thesis. Various X-ray photoelectron spectroscopy (XPS) techniques that we used receive special attention, because they uniquely enable the characterization of the chemical reaction in the photoresist thin films.

The DUV photon-induced chemical changes in tin oxo cages are studied in Chapters 3, 4 and 5 by using the HAXPES technique (Hard X-ray Photoelectron Spectroscopy). In Chapter 3, based on the HAXPES spectra from the tin oxo cages with hydroxide counterions (TinOH) upon DUV exposure, we find direct evidence indicating that the Sn-C bonds in the tin oxo cages are cleaved upon DUV exposure. By comparing the chemical reaction of the tin oxo cages under dry nitrogen (N_2) and air atmosphere, we find that the average photochemical reaction yield of TinOH at high conversion is higher under air than in an atmosphere of N_2, but rather low (~1 %) in both cases. A reaction mechanism of TinOH photoresist exposed to DUV is proposed.

In chapter 4 we show that not only photons introduce chemical changes in the photoresist. Thermal processes in air after exposure (baking processes) cause chemical reactions in the tin oxo cages which further reduce the solubility. These

reactions occur at temperatures where the intact non-exposed film is thermally stable, and can be used to enhance the sensitivity (see Chapter 6). The photochemical reactions under nitrogen probably lead to a partial reduction of the tin cage, while the baking processes lead to oxidation, and more cross-linking of the tin cages.

In Chapter 5, the relationship between the DUV photon absorption and chemical reaction yield in the photoresist is further investigated by comparing three types of tin oxo cages, which have the same cage structure but three different counterions (hydroxide (TinOH), acetate (TinA), trifluoroacetate (TinF)). The chemical reaction yields of the three cages were evaluated through XPS and UV-absorption spectra. The solubility changes in the resist layer were quantified by constructing dose-contrast curves. The sensitivities of TinOH and TinA are similar, and higher than that of TinF. This provides evidence that the anions must be involved in some stage of the chemical process that leads to solubility switching. Interestingly, the weaker basicity and hydrogen bonding ability of the trifluoroacetate anion compared to acetate and hydroxide is reflected in the Sn 3d XPS spectra.

The EUV patterning abilities of the tin oxo cages are investigated in Chapter 6 and Chapter 8. The tin oxo cages can generate negative tone patterns as discussed in Chapter 6. The pattern performances of the tin oxo cages with different counterions (TinA and TinOH) under EUV exposure are studied. The results indicate that the sensitivity and the quality of the patterns can be affected by the counterions (hydroxide (TinOH), acetate (TinA) and malonate (TinM)). A possible reason is their physical properties are modified by the counterion such as the solubility. The results of Chapter 5 (which were obtained after the results from Chapter 6 were published), however, show that there is an effect of the counterions on the chemical reactivity in the DUV photochemistry, and this difference may also affect the EUV-induced reactions. The sensitivity of the photoresist can be improved by optimizing the process conditions, such as film thickness, post-exposure baking (PEB) temperature and development conditions. The thermal stability of the TinOH powder is characterized by TGA measurement, and it is shown to be stable at least until 100 °C. By comparing the pattern performance under different PEB temperatures, 100 °C is chosen as the proper PEB temperature for the TinOH to generate negative tone patterns. We also observed that the sensitivity and pattern resolution of the TinOH photoresists are improved by adding a PEB step. After a partial optimization, we achieved a 22 nm half pitch pattern with 57 mJ cm^{-2} EUV dose by using TinOH as photoresist. A 30 nm half pitch pattern with 57 mJ cm^{-2} EUV dose is realized by using TinA as photoresist.

The EUV photon-induced chemical changes in the tin oxo cages are systematically investigated in Chapter 7. The reaction mechanism of the tin oxo cages under EUV

is compared with the mechanism under DUV exposure. Different forms of XPS combined with mass spectrometry are used to investigate the photon-induced chemistry in the photoresist films. The photoemission spectrum of TinOH with photon energies around 92 eV is reported for the first time, where we confirm that the core-level electrons from Sn 4d orbitals are an effective source of primary electrons under EUV exposure. The photolysis-outgassing products (gaseous compounds that are released from the film) under EUV exposure are characterized by an outgassing system in collaboration with IMEC. Butane, butene and butanal are generated if TinOH is exposed to EUV, which further confirms that the Sn-C bond can be cleaved upon EUV exposure, as deduced from our XPS analyses. The DUV/EUV exposed TinOH thin films were analyzed by means of XPS and mass spectrometry. The chemical reaction quantum yield was found to be higher with EUV exposure than with DUV exposure. A reaction mechanism of the tin oxo cages upon EUV exposure is proposed.

As an extension of the research of Chapter 6, we found that dual-tone patterns can be realized by using the tin oxo cages as photoresist under high PEB temperature (150 °C), and this phenomenon is further explored in Chapter 8. The normal (negative tone) pattern is observed for TinOH with PEB temperature below 150 °C as shown in Chapter 6. When the PEB temperature reaches 150 °C, however, varying the exposure dose can reverse the tone of the pattern. This dual tone phenomenon is observed with EUV and E-beam exposure. By analyzing the sample with TGA and XPS, we related this phenomenon to the water loss occurring on the unexposed TinOH at this temperature.

In Chapter 9, we study the possibility of using tin(II) carboxylate compounds as EUV photoresists. The patterning performance and the chemical reaction of tin(II) acetate and tin(II) ethylhexanoate thin films upon DUV/EUV irradiation are studied. The sensitivities of the two molecules under DUV/EUV exposure are demonstrated. Post application baking has significant effect on the molecular composition. Both of the two molecules show clear chemical changes upon light exposure. High quality pattern, however, could not (yet) be achieved by using these two materials as photoresist.