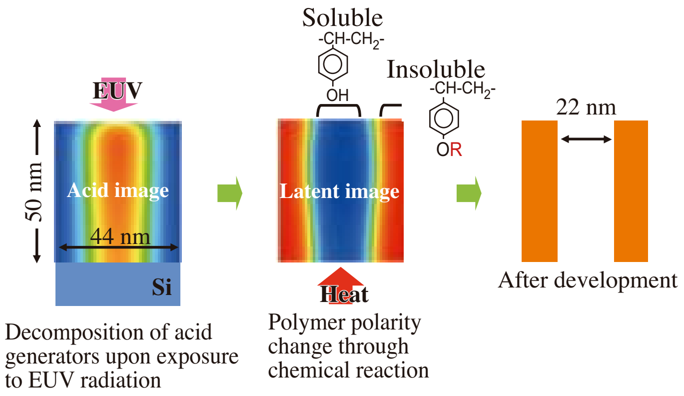
X-Ray Reflectivity Study on Depth Profile of Acid Generator Distribution in Chemically Amplified Resists

In the last half-century, integrated circuits have decreased in size at a remarkable speed with the progress in fabrication techniques. Their critical dimensions are still continuing to decrease in size. 22 nm patterns with line width roughness smaller than 2.2 nm are expected within 5 years. The exposure source for this sub-30 nm dimension is predicted to be extreme ultraviolet (EUV) radiation, where chemically amplified resists will be used to meet the sensitivity requirement for the mass production of semiconductor devices (Fig. 1). Chemically amplified resists, which consist of an acid generator and an acid-reactive polymer, utilize acid catalytic reactions for sensitivity enhancement. With the reduction in lateral dimension, the resist thickness has also been reduced and is projected to be 35 – 65 nm at the 22 nm node, according to the International Technology Roadmap for Semiconductors published by the Semiconductor Industry Association.

Below 100 nm thickness, the effects of resist interfaces become increasingly important. Surface effects such as acid generator segregation, T-top shape caused by an insoluble surface layer, and film loss during development have been reported. In addition to these factors common to deep UV (DUV), EUV, and electron beam (EB) resists, a strong absorption has to be taken into account in EUV resists. The absorption coefficient of typical polymers for EUV resists is approximately 4 μm^{-1}, which is 4 times higher than those of DUV resists and higher beyond comparison than those of EB resists. In addition, the enhancement of resist absorption has been proposed for the efficient use of the EUV energy. Therefore, the side wall profiles of patterned resists are a significant concern for EUV resists, which are affected by the depth profile of acid generator distribution.

In EUV resists for 22 nm patterning and below, a high concentration of acid generators is required [1]. When EUV photons enter resist materials, molecules are ionized and photoelectrons are emitted. The photoelectrons further induce ionization and generate secondary electrons. These secondary electrons sensitize acid generators. To suppress resolution blur caused by the secondary electron migration, the increase in the acid generator concentration is effective up to 30 wt%. In the development of EUV resists, the trade-off relationships among resolution, line edge roughness (LER), and sensitivity are the most serious problems. The enhancement of pattern formation efficiency is an essential solution to the trade-off problem. The increase in the acid generator concentration is also an effective method for enhancing the pattern formation efficiency. However, the increase in the acid generator concentration is likely to degrade the uniformity of acid distribution. Thus, the depth profile of acid generator distribution is an important issue for the development of EUV resists. The depth profile has been investigated by time-of-flight secondary ion mass spectrometry (TOF-SIMS) [2]. However, the depth resolution of TOF-SIMS is inadequate for its application to resist thicknesses corresponding to next-generation lithography. In this study, we have investigated the depth distribution of acid generators using X-ray reflectivity measurements [3-5].

Partially protected poly(4-hydroxystyrene) (PHS) was used as a model polymer of chemically amplified EUV resists. A tert-butyl (tBu) group was chosen as a protecting group to prevent the deprotection of the



Decomposition of acid generators upon exposure to EUV radiation

Polymer polarity change through chemical reaction

Fig. 1. 22 nm lithography for mass production of semiconductor devices (chemically amplified resist).

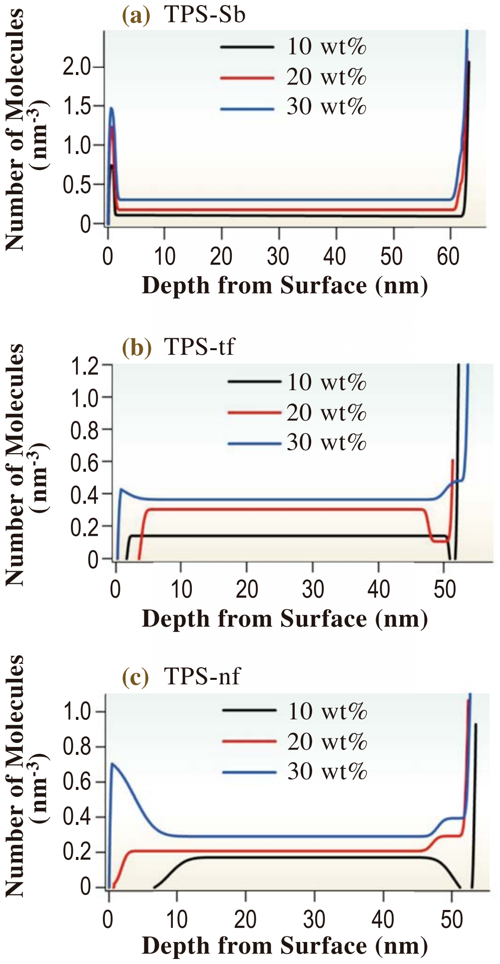


Fig. 2. Concentration profiles (molecule nm^{-3}) of **(a)** TPS-Sb, **(b)** TPS-tf, and **(c)** TPS-nf for 0, 10, 20, and 30 wt% concentrations in tBu-PHS films plotted *versus* distance from film surface.

polymer protecting group during X-ray exposure. 35% of the hydroxyl group was protected. Tryphenylsulfonium nonaflate (TPS-nf), triphenylsulfonium triflate (TPS-tf), and triphenylsulfonium hexafluoroantimonate (TPS-Sb) were used as acid generators. To obtain the density profiles of resist films, a monochrome X-ray from a synchrotron radiation source was irradiated at incidence angles of 0 to 4°. The experiment was performed at beamline **BL46XU**.

The depth profiles of the acid generator distribution reconstructed from the depth density profiles of resist films are shown in Fig. 2. In general, all three chemically amplified resist films showed a similar trend. As the acid generator concentration increased, the concentration at the interfacial areas increased. However, the details depended on the molecular structure of acid generators. The driving force for surface segregation is the difference in the interfacial tension between a small molecule and a polymer. Compounds with fluorinated groups generally give a low surface energy and preferentially segregate at interfaces. All the acid generators used in this experiment contain fluorine in their structures. Therefore, they all have a tendency to gather at the interfaces to lower the surface energy. However, tBu-PHS interacts with acid generators through hydrogen bonding. This strong ionic-dipole interaction between acid generators and the polar polymer tends to confine acid generators in the bulk of the film. Therefore, the depth distribution of acid generators is determined by the balance between the drive to reduce the surface energy by the segregation of fluorinated groups at the interfaces and ionic dipole interactions in the bulk of the film (Fig. 3).

The design of next-generation resist materials requires the control of the interaction between polymer and acid generators. SPring-8 is an effective tool for the analysis of state-of-the-art resist materials.

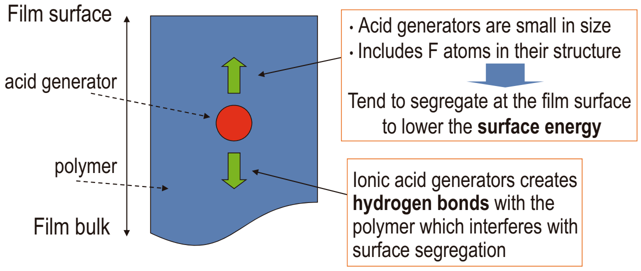


Fig. 3. Interaction of acid generators in chemically amplified resist films.

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