Multispur in chemically amplified electron beam resists

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When ionizing radiations such as extreme ultraviolet (EUV) radiation and electron beam (EB) enter materials, ion pairs are generated through the ionization. The space where this ion pair occupies is called a spur. The ionized molecule with positive charge (radical cation) and the electron with negative charge interact with each other through the electric field. When spurs are overlapped, the electron dynamics significantly changes and affects a chemical yield and distribution. A single spur model has been reported to well reproduce the acid yields generated in resist films upon exposure to 75 keV electron beam.[1] The acid generation efficiency per ionization is 0.74 in a poly(4-hydroxystyrene) (PHS) film with 10 wt% triphenylsulfonium triflate (TPS-tf). Upon exposure to EUV, a single EUV photon generates 4.2 ion pairs on average in resist films. Because the inelastic mean free path of <92.5 eV electrons is less than 1 nm, these ion pairs are narrowly distributed around the EUV absorption point. The ion pairs are overlapped and affect each other because the thermalization distance of electrons reaches 3-7 nm. This configuration of ion pairs referred to as a multispur decreases acid generation efficiency to 0.62 per ionization.[2] The acid generation efficiency in PHS films has been experimentally evaluated to be 2.5 per photon at 10 wt% acid generator loading, which is equivalent to 0.62 per ionization.[3]

Although the acid yield is well approximated by a single spur model, the real distribution is obviously not a single spur in EB resists considering electron energy loss function. In this study, the distribution of intermediate species in EB resists was investigated by a Monte Carlo simulation. The results were compared with the distribution in EUV resists. The effects of the initial configuration of intermediate species on acid yields are discussed.

In this study, we simulated acid generation in PHS films with 10 wt% TPS-tf using the inelastic mean free path, electron energy loss function, photoelectron emission spectra and a diffusion equation. Figure 1 shows the typical configuration of ionized molecules and thermalized electrons. The distribution of overlapped spurs in EB resists is shown in Fig. 2 together with that in EUV resists. The average number of ion pairs in an isolated space is 1.5 in EB resists. The relationship between the average number of ion pairs and the acid generation efficiency (per ionization) is shown in Fig. 3. The acid generation efficiency was decreased with the increase in the average number because of the strong electric fields generated by plural cations and the cross recombination. The strong electric fields accelerate the recombination between cations and electrons and decrease the probability of the reaction of acid generators with electrons. The acid generation efficiency was calculated to be 0.70 per ionization (0.74 for a single spur model). The fact that ion pairs are overlapped indicates an inhomogeneous distribution of intermediate species. However, the subsequent proton migration moderates this inhomogeneity in chemically amplified EB and EUV resists.

References 1. T. Kozawa et al., J. Vac. Sci. Technol. **B24**, 3055 (2006). 2. T. Kozawa et al., J. Vac. Sci. Technol. **B25**, 2481 (2007). 3. R. Hirose et al., Jpn. J. Appl. Phys., Part 2 **46**, L979 (2007).

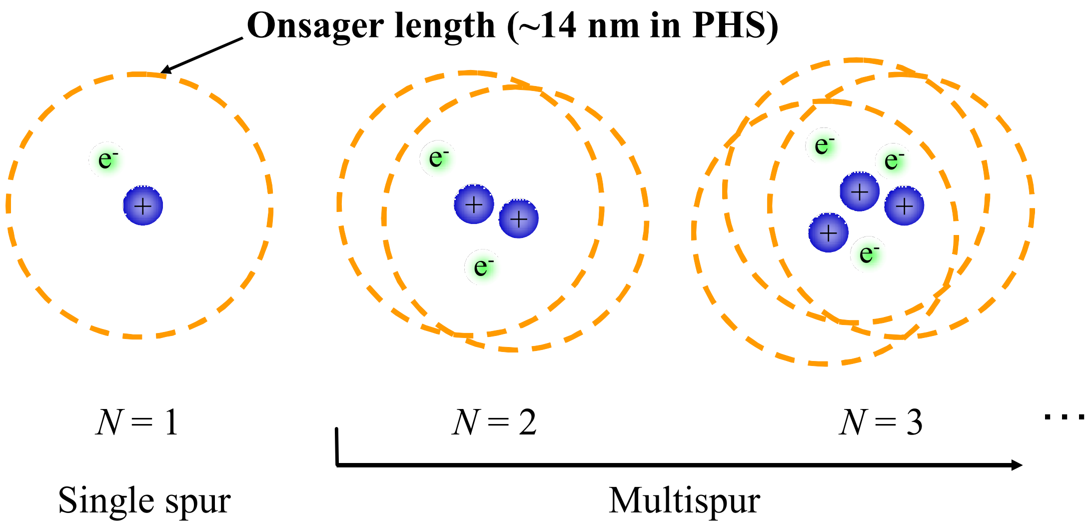

Fig. 1. Typical configuration of ionized molecules (parent radical cations) and thermalized electrons. Onsager length is defined as a length at which the thermal energy of electron corresponds to the Coulomb potential. Onsager length is approximately 14 nm in PHS.

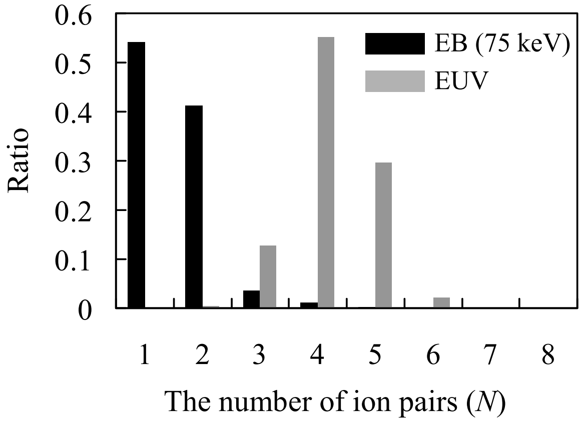

Fig. 2. Distribution (histogram) of overlapped spurs in EB and EUV resists. The average number is 1.5 for EB and 4.2 for EUV. The energy of incident electrons is 75 keV.

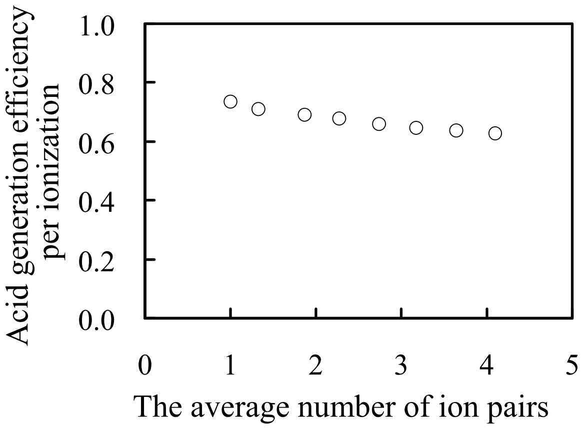

Fig. 3. Relationship between the average number of ion pairs and acid generation efficiency (per ionization).