

Ionic degradation products of ZEP520 resist film

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Introduction

ZEP520 (Nippon Zeon Co.) is a positive-tone electron-beam resist with comparable resolution to polymethylmethacrylate (PMMA). Chemical structure of this resist is alternating copolymer of α -chloromethacrylate and α -methylstyrene. This resist improves sensitivity and etch resistance compared with PMMA and thus has been widely used for device fabrication including zone plate optics. In higher-voltage e-beam exposure system, however, ZEP520 is needed to be improved contrast, enhanced reactive ion etching (RIE) resistance and improved sensitivity [1]. Line-edge roughness (LER) is also serious problem to reduce pattern size, which is caused by polymer aggregates in the size of 20-30nm [2]. To improve the performance of resist and design new resist, understanding of characteristics of ZEP520 is needed. In this study, ionic degradation products from ZEP520 thin film is measured using time-of-flight mass spectrometry for photon-stimulated ion desorption (TOF-PSID) near Cl K-edges.

Experimental

Measurements were performed at BL-27A with an energy width of 1 eV around Cl K-edge. TOF-PSID mass spectra were measured using a rotatable TOF spectrometer [3] combined with pulsed SR.

Results and discussion

Figure 1 shows TOF-PSID spectra, observed at 2814 eV, 2823 eV, 2830 eV and 2849 eV photon energy in an x-ray incident angle of 45°, together with a calculated mass scale. These energies correspond to off resonance, Cl 1s \rightarrow σ^* (Cl-C), Cl 1s \rightarrow σ^* shape resonance and continuum, respectively. H⁺ and CH₃⁺ ions were observed as major products above and below the Cl K-edge, while other product ions were observed only above the Cl K-edge. The features at m/z = 1, 2, 13, 14, 15, 27, 29, 35(37), 39, 41, and 43 were observed, which correspond to H⁺, H₂⁺, CH⁺, CH₂⁺, CH₃⁺, C₂H₃⁺, OCH⁺/C₂H₅⁺, Cl⁺, C₃H₃⁺, COCH⁺/C₃H₅⁺, and CH₃OC⁺/C₃H₇⁺, respectively. These ions are mostly cracking fragments of the α -chloromethacrylate unit and OCH⁺, COCH⁺, and CH₃OC⁺ ions are common products resulting from PMMA [4]. For heavier desorbing ions with m/z > 50 amu, m/z = 51(C₄H₃⁺) and aromatic fragments such as m/z = 77(C₆H₅⁺) and/or 78(C₆H₆⁺), 91(C₇H₇⁺) and/or 92(C₇H₈⁺), 104(C₈H₈⁺, monomer less CH₂), 116(C₉H₈⁺, monomer less H₂) and 129 (C₁₀H₉⁺) can readily be interpreted based on structure of the α -

methylstyrene unit. These desorbing ions are almost similar to those produced by laser ionization of poly α -methylstyrene [5]. In fact, only small amounts of ionic fragments larger than m/z > 50 were observed in PMMA [4]. Although the assignment of larger fragment ions remains obscure, it is clear that Cl atom-selective excitation produces main chain scissions. This finding implies a phenomenon that localized excitation forms ionic fragments produced by bond breaking of a remote site. The phenomenon is not a common reaction process of PSID since generally PSID occurs prior to energy redistribution over molecules of localized excitation (i.e. fast reaction) and Auger decay following core excitation also produces localized holes to the excited site, resulting in site-selective ionic fragmentations.

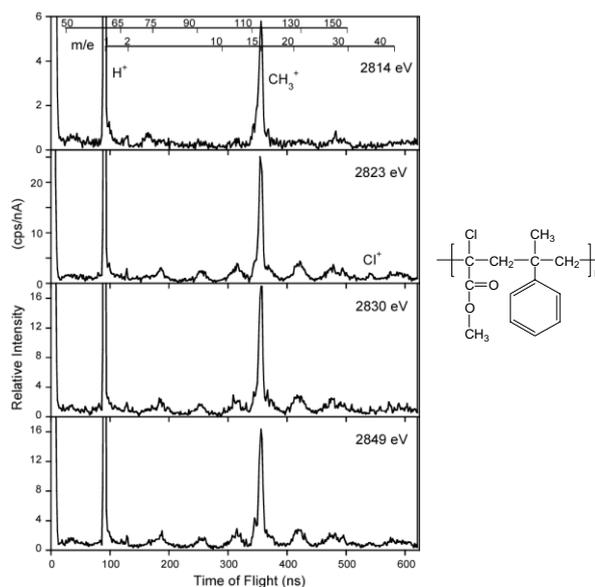


Fig. 1 Time of flight mass spectra for ion desorption from ZEP520 resist film.

References

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