DECOMPOSITION PRODUCTS OF EBR-9
BY
X-RAY AND EB EXPOSURE

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1. Introduction

Poly (1,1,1-trifluoroethyl-2-chloroacrylate) is widely used for photomask making as a positive
tone EB resist (EBR-9, Toray), but its mechanism of decomposition is not well known. So as a part
of a photochemical study of EBR-9, we have conducted an experimental investigation using
Electron Spectroscopy for Chemical Analysis (ESCA or XPS). This method which uses X-ray
exposure, can give the in-situ information on the photochemical dynamics of the reactions of this
resist by X-ray. In this letter, we assign the EBR-9 spectrum of ESCA at the first stage. Then we
discuss about the kinetics of decomposition caused by the X-ray exposure. We also discuss about
the decomposition products of EBR-9 by EB exposure.

2. Experimental

EBR-9 was spin coated on the Si wafer and then prebaked in a convection oven at 190 °C for 15
minutes. The resist film thickness was 0.5 µm.

For the analysis of decomposition products by EB exposure, the resist films on Si wafer was
exposed at 20 kV, 1 - 25 µC/cm² of EB dose (beam current 10 nA). EB exposure of the resist was
done by ERE 301 (Elionix) system.

ESCA 750 (Shimazu) with a Mg Kα₁,₂ X-ray source was used for this ESCA measurement. X-
ray power of 7 kV, 30 mA was used for the measurement and each elemental peak was taken as
quickly as possible. Relative sensitivity factors determined from the standard samples in this ESCA system, were used to calculate atomic ratios from peak area ratios.

3. Results and Discussion

The C1s spectrum for EBR-9 is shown in fig. 1. It is separated to five peaks which have nearly the same intensities, depending on the five carbon atoms affected by their chemical bonds with different atoms respectively (the notation numbers of five carbon atoms are defined in fig. 1). From their chemical shift, the five peaks have been assigned as shown in fig. 1.

Fig. 2 shows the C1s spectrum for EBR-9 after 180 minutes X-ray irradiation. The intensities of the five peaks are clearly changed from fig. 1. This spectral change suggests that there exist mainly two kinds of side chain (-Cl and -COOCH2CF3) eliminations by X-ray exposure, and the Cl elimination rate is faster than that of the alkyl side chain: The #1, #2 and #3 peaks corresponding to the carbon atoms of the alkyl side chain decrease the ratios, keeping nearly equal intensities one another. The #4 peak intensity, corresponding to the density of carbon atoms which combine with Cl atoms, decreases further than those of #1, #2 and #3 peaks. Only the #5 peak corresponding to carbon atoms with only C-C and/or C-H bonds increases. Fig. 3 shows the log changes in the peak ratios of Cl[-COOCH2CF3] (equal to #1 + #2 + #3 ratios) and C[Cl-Cl] (#4 ratios) and in the atomic ratios of F/C, O/C and Cl/C for the X-ray irradiation time. As each set of plots shows linearity, these elimination reactions are concluded to be first order reactions. Table 1 lists the slope and the intercept values of these plots. As O/C slope is good agreement with Cl[-COOCH2CF3] slope, O elimination must be due to that of alkyl side chain only. The slope of F/C is slightly larger than that.

![Fig. 1: C1s spectrum for EBR-9.](image1)

![Fig. 2: C1s spectrum for EBR-9 after X-ray exposure for 180 minutes.](image2)
of Cl(-COOCH2CF3), so the additional elimination pathway of F can be elucidated. From the value of each slope, the ratios of elimination reaction rate constants of Cl, Cl(-COOCH2CF3) and F (additional) are evaluated to be 5.7 / 1 / 0.2.

The intercept value represents the atomic ratio before X-ray irradiation. The values of Cl/C and O/C agree with the stoichiometric ratios of EBR-9, but that of F is slightly large (see Table 1). The information which can be observed by ESCA is usually in the depth of 10 nm because the photoelectron mean free path in such organic material is about 10 nm. The difference between the intercept value and stoichiometric ratio can be due to the surface structure. Fig. 4 shows the changes in the peak ratios of F/C, Cl/C, O/C for the photoelectron emitting angle θ. (Those ratios are normalized at θ=90° generally used in the present experiments. The value of sin θ is proportional to the mean depth where ESCA observes the area.) The segregation of F atom is clearly observed at the surface.

Fig. 5 shows the changes in the ratios of F/C, Cl/C and O/C after EB exposure at various dose, the ratios are normalized by those of the control sample. Their elimination reactions increase as the

Table 1 The values of the slope and intercept of Cl/C, O/C F/C and Cl(-COOCH2CF3)

<table>
<thead>
<tr>
<th></th>
<th>Slope (x 10^3, /min)</th>
<th>Intercept</th>
<th>Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl/C</td>
<td>23.02 ± 2.01</td>
<td>0.208 ± 0.088</td>
<td>0.2</td>
</tr>
<tr>
<td>O/C</td>
<td>4.21 ± 0.60</td>
<td>0.400 ± 0.062</td>
<td>0.4</td>
</tr>
<tr>
<td>F/C</td>
<td>4.91 ± 0.22</td>
<td>0.627 ± 0.021</td>
<td>0.6</td>
</tr>
<tr>
<td>Cl(-COOCH2CF3)</td>
<td>3.83 ± 0.21</td>
<td>0.605 ± 0.020</td>
<td>0.6</td>
</tr>
</tbody>
</table>
dosage increases in the range of $1 \sim 25 \mu\text{C/cm}^2$, however those reaction mechanisms are more complicated than the case of X-ray irradiation. These are obviously not the first order reactions. And the relations in this range could be described as straight lines when the EB dose plot in log scale, but the F/C and O/C ratios at $1 \mu\text{C/cm}^2$ are not changed from those of the control sample. At the dose of $5 \mu\text{C/cm}^2$ which is a usual dose used for EB delineation of EBR-9, the elimination ratios of F, Cl and O are estimated to be $3 \sim 7\%$. Fig. 6 shows the changes in normalized peak ratios of F/C, Cl/C and O/C at $5 \mu\text{C/cm}^2$ EB exposure for the photoelectron emitting the angle $\theta$. The segregation of F atom is also observed as in the case of fig. 4, and still more elimination of O atom caused by EB exposure is clearly observed at the surface.

![Fig. 5 The changes in the ratios for EB dose.](image1)

![Fig. 6 The changes in the ratios for photoelectron emitting angle $\theta$.](image2)

The elimination behavior is very different each other in X-ray and EB exposure. In the case of X-ray, the dynamics are simply described as first order reactions, but those of EB are more complicated. We think that the dynamics of EB and the resist interactions are not different from those of X-ray primarily, but the other reaction mode is predominant or added in the EB exposure. The heat mode reaction may be possible to occur, depending on the current density of EB irradiation. The contamination on the sample should do the serious damage to the ESCA analysis, but it must be negligible in the present experiments, because O/C atomic ratio decreases and F/C increases at the top surface (see fig. 4 and 6), even though the O or C atomic ratio should increase if the contamination occurs in the laboratory. The study of the reaction caused by the heat of exposure will be needed for more precise understanding of EBR-9 decomposition.