Dissolution Characteristics of Acidic Groups for 157-nm Resist

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1. Introduction

In 157-nm lithography, the choice of resist polymers is very much restricted in terms of transparency, because most common hydrocarbon polymers strongly absorb at 157 nm. Thus, fluoropolymers have been intensively studied because of their high transparency at 157 nm [1-6]. In addition to good transparency, the most important property for high-resolution capability is good dissolution characteristics [7]. Good solubility in the standard developer, 2.38wt% tetramethyl ammonium hydroxide (TMAH) aqueous solution, is a requirement for resist polymers used in the semiconductor industry. In the currently used resists, the solubility in TMAH solutions is provided by phenolic moiety or carboxylic acid. A hexafluoroisopropanol (HFA) as a new acidic group, which has a pKa similar to that of phenol [8], is used for 157-nm resist polymers because of its high transparency. The HFA group can be attached to styrene (St) and norbornene (Nb). 4-(1,1,1,3,3,3-Hexafluoro-2-hydroxypropyl) styrene (HFASt) or \( \alpha, \alpha \)-bis(trifluoromethyl)-bicyclo[2.2.1]hept-5-ene-2-ethanol (HFACH2Nb) can be easily copolymerized by radical reaction with 2-trifluoromethylacrylate (\( \alpha \)-CF3MA) [1]. We found that vinyl sulfonyl groups exhibited extremely high transparency at 157 nm and reported that copolymers with HFASt worked as resists [9, 10]. These copolymers were also synthesized easily by radical copolymerization. The ease of synthesis of polymer is an important thing from a viewpoint of material cost and quality stability. Then we think that these polymers are desirable as 157-nm resist polymers.

In this study, we measured the dissolution rates of conventional resist polymers for the g/i-line, 248 and 193 nm, and polymers containing the HFA group or the vinyl sulfonyl group in various concentrations of TMAH solution. We compared and studied each dissolution characteristic.

2. Experimental

The conventional alkaline soluble resist polymers used in this study were novolak resin, poly(p-hydroxystyrene) (PHS), the copolymer of methacrylic acid and methacrylate (Poly(MAA/MA)), and the alternating copolymer of norbornene-5-carboxylic acid and maleic anhydride (Poly(NbCOOH/MaAn), as shown in Fig. 1. The homopolymers of HFASt...
(Poly(HFASc)) and HFACH2Nb (Poly(HFACH2Nb)) are shown in Fig. 2. We used the copolymers of 2-trifluoromethylacrylic acid and HFASt (Poly(αCF3MAA/HFASt), 2-trifluoromethylacrylic acid and HFACH2Nb (Poly(αCF3MAA/HFACH2Nb), vinyl sulfonoyl fluoride and HFASt (Poly(VSO2F/HFASt), and vinyl sulfonic acid and HFASt (Poly(VSO2OH/HFASt) as alkaline soluble polymers containing fluorine or sulfonoyl for the 157-nm resist, as shown in Fig. 2. Poly(MAA/MA) and Poly(NbCOOH/MaAn) were obtained by exposing the commercial available 193-nm resists with ArF excimer laser. Poly(VSO2OH/HFASt), Poly(αCF3MAA/HFASt), and Poly(αCF3MAA/HFACH2Nb) were obtained by exposing the resist protected with a certain acid labile group by F2 laser, respectively. The molecular weights of theses polymers are shown in Table 1.

Table 1. Molecular weights of polymers used in this study.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Mw</th>
<th>Mw/Mn</th>
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<tbody>
<tr>
<td>Novolak</td>
<td>6400</td>
<td>6.0</td>
</tr>
<tr>
<td>PHS</td>
<td>1000</td>
<td>1.1</td>
</tr>
<tr>
<td>Poly(HFASc)</td>
<td>13300</td>
<td>1.7</td>
</tr>
<tr>
<td>Poly(HFACH2Nb)</td>
<td>3500</td>
<td>1.3</td>
</tr>
<tr>
<td>Poly(αCF3MAA/HFASt)</td>
<td>15600</td>
<td>1.8</td>
</tr>
<tr>
<td>Poly(αCF3MAA/HFACH2Nb)</td>
<td>13500</td>
<td>1.4</td>
</tr>
<tr>
<td>Poly(VSO2F/HFASt)</td>
<td>24000</td>
<td>1.5</td>
</tr>
<tr>
<td>Poly(VSO2OH/HFASt)</td>
<td>22800</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The polymer and resist films coated on a silicon wafer were baked at 100°C for 60 s. The 157-nm or 193-nm exposure was carried out with an F2 laser exposure system "VUVES-4500" produced by Litho Tech Japan [11]. The polymer and resist films were developed with 0.60, 1.19, 2.38, and 5.00 wt% TMAH aqueous solution at 23°C.

The dissolution rates of polymers and resists in a developer were measured with a high-speed development-rate measurement system "RDA-800" (Litho Tech Japan) [12]. The development end-point can be detected for at least 0.02 seconds by using this system.

3. Results and Discussion
3.1. Dissolution Rates of Polymers with Various Acidic Groups

The dissolution rates of various polymers in 2.38 wt% TMAH solution are shown in Fig. 3. In conventional resist polymers, the dissolution rate of novolak resin was very low, 11 nm/s, that of PHS was 1150 nm/s, and that of Poly(MAA/MA) with carboxylic acid was a very high 2120 nm/s. In the HFA containing homopolymers, the rate of Poly(HFASc) was equal to that of PHS. This result is to be expected because HFA has a pKa similar to that of phenol. On the other hand, the rate of Poly(HFACH2Nb) was low, 45 nm/s, and similar to that of Poly(NbCOOH/MaAn). It is thought that the low rate of these polymers is due to the hydrophobicity of norbornene. Poly(VSO2OH/HFASt) bearing a sulfonic acid has a very high dissolution rate that is similar to that of Poly(MAA/MA) bearing carboxylic acid. The rates of Poly(αCF3MAA/HFASt) and Poly(αCF3MAA/HFACH2Nb) were 2380 nm/s and 970 nm/s, respectively. In copolymers consisting of alkaline soluble components, the
dissolution rate of the copolymer is equal to that of the component with higher rate. In Poly(VSO2F/HFASt), the rate was lower than that of Poly(HFASt). The vinyl sulfonyl fluoride unit inhibits the dissolution of the HFASt unit. The sulfonyl group has a large dissolution inhibition effect, as is well known in diazonaphthoquinone-based resists [13].

3.2. Dissolution Kinetics

We measured the dissolution rates in 5.00wt%, 2.38wt%, 1.19wt%, and 0.60wt% TMAH solutions. Figures 4 and 5 show the dependence of the dissolution rate on the TMAH concentration for both of conventional resist polymers and the 157-nm resist polymers, respectively. From Fig. 4, the dependence of polymers with carboxylic acid, such as Poly(MAA/MA) and Poly(NbCOOH/MaAn), was smaller than those of polymers (novolak and PHS) with the phenol group. From Fig. 5, the dependence of Poly(VSO2F/HFASt), Poly(αCF3MAA/HFASt) and Poly(αCF3MAA/HFAch2Nb), which contained sulfonic acid or carboxylic acid, was small.

In general, the rate of chemical reaction is proportional to the concentration of reactants, each raised to some power,

\[ \text{Rate} = k [A]^a [B]^b \cdots \]

where \( k \) is the rate constant and the exponents \( a \) and \( b \) are known as the reaction orders in \( A \) and \( B \), respectively. This relation indicates that a plot of the log of the chemical reaction rate versus the log of the concentration of reactant would provide useful information, such as the reaction order, etc. As a dissolution phenomenon is a kind of chemical reaction, this relation could be applied to the dissolution phenomenon of resist polymer in a developer [14].

In Figs. 4 and 5, it can be seen that the log of the dissolution rates of each polymer increased linearly with the increasing log of the concentration of TMAH in the range of about 0.6wt% ~ 2.38wt%. From the slopes of the straight lines in Figs. 4 and 5, the reaction orders for dissolution in the TMAH solution can be estimated. Figure 6 shows the reaction order for...
the dissolution of various polymers. The reaction order for dissolution shows the degree of deprotonation [15]. The degree of deprotonation of vinyl sulfonic acid was very high which was similar to that of methacrylic acid. That of HFASt was between that of PHS and methacrylic acid. The degree of deprotonation of HFACH2Nb was smaller than PHS.

4. Conclusions
We studied the dissolution characteristics of 157-nm resist polymers containing the HFA group and the vinyl sulfonyl group. It was suggested from our results that HFASt and vinyl sulfonic acid are excellent acidic groups for use with 157-nm resists.

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References