Application of a New BARC Material for 157-nm Lithography


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We developed NCA660 as a bottom-antireflective-coating (BARC) for 157-nm lithography last year. The NCA660 characteristics, such as the k-value, dry-etching rate, and film thickness loss, were optimized to meet the target for 157-nm lithography. In this paper, we discuss our evaluation of resist pattern profiles on BARC with various chemophores. We have found that the position of the hydroxyl group in the chromophore is the key to providing an inactive surface, which does not degrade the resist profile, and NCA660 has the optimum chemical structure in terms of the resist pattern profile. In addition, we attempted resist pattern profile control by using NCA660 with acidic additives, and confirmed that this method is quite effective. We concluded that NCA660 is the most suitable BARC for 157-nm lithography and has a wide range of application.

Keywords: Bottom-antireflective-coating (BARC), 157-nm lithography, Resist pattern profile, Surface free energy

1. Introduction

157-nm lithography is the most promising process for fabricating semiconductors with feature sizes of 65 nm and below. As 157-nm lithography is required for more precise critical-dimension (CD) control in fabricating gate patterns, an organic bottom-antireflective coating (BARC), which has been commonly used in KrF or ArF lithography, is needed to reduce reflection from the substrate under the resists. The BARCs used in KrF or ArF lithography are not usable in 157-nm lithography because the optical constants and etching rates of 157-nm resists differ greatly from those of KrF or ArF resists. Thus, we developed the NCA660 BARC optimized for 157-nm lithography last year. NCA660 consists of a heterocyclic polymer as a main-chain polymer and an o-hydroxybenzoic acid decorated with iodine as a chromophore. This indicates that the outgassing rate from NCA660 will be quite low. Furthermore, resist pattern profiles without footing were obtained with typical fluorinated 157-nm resists on NCA660. As a result, we concluded that NCA660 was suitable for use as a BARC and started mass-synthesis for 157-nm lithography [1,2]. We have already succeeded in synthesizing NCA660 in a gallon unit, and we are evaluating various items for practical application.

In our previous paper, we clarified the relationship between the structure of NCA660 and its characteristics, and showed that the resist pattern profile was slightly affected by the halogen species in the chromophore.

In this paper, we discuss the relationship between the resist pattern profile and the chemical structure of the chromophore. Moreover, we report results from resist pattern profile control by introducing acidic additives.

2. Experimental

2.1 Materials

NCA660 consists of a heterocyclic polymer as a main-chain polymer and an o-hydroxybenzoic
2.2 Contact angle and surface free energy

To evaluate the surface conditions of the BARCs, we measured the contact angle and surface free energy. We measured the contact angles of H$_2$O, diiodomethane (CH$_2$I$_2$), bromonaphthalene (Br-NAD), and a standard developer (2.38 wt% tetramethyl ammonium hydroxide aqueous solution) on the BARC surfaces by using the CA-W150 contact angle measuring system (Kyowa Interface Science Co., LTD). We measured contact angles at 3, 5, and 7 s after drop and averaged the three data. Surface free energy was calculated by Owen's approximation from the contact angles of H$_2$O and CH$_2$I$_2$ on the BARCs.

2.3 Imaging experiment

To evaluate the resist pattern profile on the BARC films, we patterned the resists with a 157-nm microstepper (numerical aperture (NA) = 0.85 or 0.9; Exitech, Ltd.) with an alternating phase-shift mask. The resist thickness and process conditions for pre-bake, post-exposure-bake, and development were optimized for each resist in an ACT-8 in-line coater/developer system (Tokyo Electron Ltd.). For lithographic evaluation, we obtained resist pattern micrographs using an S-5000 scanning electron microscope (Hitachi, Ltd.).

2.4 Measurement of optical constant and dry etching rate

We measured the optical constants of the BARCs coated on silicon wafers with a VUV-VASE spectroscopic ellipsometer (J. A. Woollam Co., Inc.). We measured the dry-etching rate of the BARCs under the organic BARC/SiN hard mask dry-etching conditions using a Unity II dry-etching system (Tokyo Electron Ltd.). The etching gas was a mixture of CF$_4$ and O$_2$. The relative etching rates were calculated based on the etching rate of a KrF resist.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>A (NCA660)</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Halogen</td>
<td>Iodine</td>
<td>Bromine</td>
<td>none</td>
<td>Bromine</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Hydroxyl</td>
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<tr>
<td>Structure</td>
<td></td>
<td></td>
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</tbody>
</table>

Fig. 1 Chemical structure of NCA660.

Fig. 2 Chemical structure of evaluated chromophore.
3. Results and discussion

3.1 Effect of halogen atom

Figure 3 shows the k-value and dry-etching rate ratio for each BARC. The results for DUV30J (Brewer Science, Inc.), which is a commonly used BARC for KrF lithography, are also shown for reference. The 100-nm line-and-space (L/S) resist patterns replicated on each BARC are also shown in Fig. 3.

First, we evaluated chromophores A, B, and C to compare the effect of the halogen species. The k-values and the dry-etching rates were directly related to the halogen species. The resist pattern profiles on these BARCs had a small amount of footing. Although the order regarding footing was B > A > C, the differences were small. Incidentally, the BARC with chromophore C is not usable because the k-value and dry-etching rate do not meet the target for 157-nm lithography.

3.2 Isomeric effect

Next, we evaluated chromophores D, E, and F of α-, m-, and p-hydroxybenzoic acid, respectively, to investigate the isomeric effect. These samples had similar k-values and dry-etching rates because they did not contain halogen atoms. As mentioned, the resist pattern profile on the BARC with chromophore C (o-hydroxybenzoic acid) had little footing. In contrast, the resist pattern profile on the BARC with chromophore E (m-hydroxybenzoic acid) had a large amount of footing. Although the sample with chromophore E was exposed with a 10% higher exposure dose than the sample with chromophore C, the residue remaining at the bottom of the spaces was not cleared (Fig. 3). As for the sample with chromophore F, the L/S pattern was not replicated because the resist film of the exposed area had disappeared.

The resist pattern profile on the BARC with chromophore D (m-hydroxybenzoic acid with bromine) showed moderate footing.

From these results, we can conclude that the position of the hydroxyl group is a leading cause of resist footing on the BARCs with hydroxybenzoic acid.

3.3 Contact angle and surface free energy

The measured contact angles and the surface free energies calculated from the contact angles of H₂O and CH₃I are summarized in Table 1. Note that the contact angles of the developer changed more drastically than those of the other liquids. We plotted the contact angles of the developer versus those of H₂O in Fig. 4, and categorized the BARCs

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>A (NCA660)</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>DUV30J</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>67.7</td>
<td>68.4</td>
<td>64.5</td>
<td>57.4</td>
<td>50.7</td>
<td>52.9</td>
<td>67.7</td>
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<tr>
<td>CH₃I</td>
<td>21.9</td>
<td>28.7</td>
<td>34.1</td>
<td>33.6</td>
<td>31.7</td>
<td>35.3</td>
<td>23.5</td>
</tr>
<tr>
<td>Br-NAD</td>
<td>4.6</td>
<td>12.5</td>
<td>10.7</td>
<td>12.3</td>
<td>17.5</td>
<td>23.8</td>
<td>4.5</td>
</tr>
<tr>
<td>Developer</td>
<td>68.2</td>
<td>65.1</td>
<td>58.1</td>
<td>55.5</td>
<td>23.3</td>
<td>26.4</td>
<td>68.5</td>
</tr>
</tbody>
</table>

Table 1 Contact angle and surface free energy on each BARC.

Surface free energy (dyne/cm²)  | 51.0 | 48.7 | 49.9 | 53.0 | 56.3 | 54.2 | 50.5 |

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into three groups in the figure. The group having high contact angles for both H$_2$O and the developer (chromophores A, B, and C) produced patterns with little footing. In contrast, the group having low contact angles (chromophores E and F) led to patterns with a large amount of footing. Chromophore D, which leads to moderate footing, had intermediate contact angles. The difference between chromophores D and E is the presence of bromine. This suggests that the bromine weakened the influence of neighboring hydroxyl groups.

Concerning the three-dimensional molecular structure, the hydroxyl group sits outward in BARCs with p- and m-hydroxybenzoic acid, while it sits inward in BARCs with o-hydroxybenzoic acid. Thus, at the surface of the BARC films, the hydroxyl groups sit toward the outside in the BARCs with p- and m-hydroxyl groups and increase the surface free energy and acidity. On the contrary, the o-hydroxyl groups sit toward the inside and do not affect the surface condition of the BARC films.

3.4 Relationship between the surface condition and the resist profile

As shown in Fig. 4, there is a clear correlation between the surface conditions of the BARC films and the resist profiles. We speculate that the quenchers and photo-acid generators (PAGs) in the resist interacted with a BARC surface that had high surface free energy or high acidity, and the resist pattern profile changed depending on the chromophores in the BARCs. To verify the interaction between the BARC surface and the PAG or quencher, we evaluated the resist pattern profiles using resists with or without a quencher on various BARCs. The base resin of the resist was main-chain fluorinated polymer, the PAG was triphenylsulfonium nonaflate (TPSNf), and the quencher was tributylamine. The resist solutions were dissolved in 2-heptanone (MAK) at 7 wt%. We evaluated three kinds of BARCs with chromophores C, D, and E; these chromophores had low, medium, and high surface free energies, respectively.

Figure 5 shows the resist profiles of 100-nm L/S patterns. The resist pattern profiles on the BARC with chromophore C showed no footing with or without the quencher. The resist pattern profiles on the BARC with chromophore D showed a large amount of footing with the quencher, but no footing without the quencher. The resist pattern profiles on the BARC with chromophore E showed moderate footing with and without the quencher.
From these results, we developed the interaction model shown in Fig. 6. The low acidity and low surface energy surface of the BARC with chromophore C cause the BARC to be inactive (Fig. 6(a)), and it does not interact with either quencher or PAG. The surface of the BARC with chromophore D has moderate acidity and moderate surface free energy, so it interacts with the quencher but not with the PAG. The surface of the BARC with chromophore E has high acidity and high surface free energy, so it interacts with both the PAG and the quencher (Fig. 6(b)).

As shown in Table 1, NCA660 has an o-hydroxybenzoic acid with iodine as a chromophore, so the surface free energy and acidity of NCA660 are low enough to prevent interaction with the resist. The contact angle and surface free energy of NCA660 are close to those of DUV30J, which we have used as a reference in the evaluation of the resist pattern profiles. Thus, NCA660 has the most suitable properties for use with 157-nm resists.

3.5 Resist pattern profile control by acidic additives

Although NCA660 in combination with several common 157-nm resists enables good resist profiles, footing profiles were observed with some resists. For example, some 157-nm resists with low transparency produced tapered shapes on NCA660. We tried to better control the resist pattern profiles in these cases by adding acidic additives. We evaluated the relationship between the resist pattern shapes and the additive contents in NCA660.

Based on a screening test, we decided to use triphenylsulfoniumtriflate (TPSTf), which is generally applied to 157-nm resists, as an additive [3,4]. We made four samples with 0, 1, 2.5, or 5 wt% TPSTf added to the base polymer, and evaluated the resist pattern profiles for three kinds of 157-nm resist on each BARC sample. The resist profiles of 100-nm L/S patterns are shown in Fig. 7. The resist pattern profile on NCA660 with no TPSTf showed a tapered profile, and the degree of taper depended on the TPSTf content – as the TPSTf content increased, the profile changed from a tapered shape to an inversely tapered shape.
Figure 8 shows the k-value and the dry-etching rate ratio as a function of the TPSTf content. As the TPSTf content rose, the k-value and the dry-etching rate ratio fell. Because the k-value of TPSTf is about half that of NCA660 [5], the k-value of NCA660 with TPSTf dropped. However, the drop for NCA660 with 5 wt% TPSTf was about 1%, which is not a concern. The dry-etching rate ratio of NCA660 with TPSTf also dropped, because TPSTf has a benzene ring. This drop for NCA660 with 5 wt% TPSTf was about 10%.

![Graph showing relationship between TPSTf content, k-value, and dry-etching rate.](image)

**Fig. 8 Relationship between the TPSTf content and the k-value and dry-etching rate.**

Our results show that the PAG addition is an effective means of resist pattern control. However, the PAG content must be optimized because the dry-etching rate was significantly lowered by TPSTf addition. Therefore, we are now developing new acidic additives that can be used to control the resist profile without sacrificing the dry-etching rate.

4. Conclusions

We have evaluated the relationship between resist pattern profiles and the chemical structure of NCA660. NCA660 consists of a heterocyclic base polymer and a chromophore that is an o-hydroxybenzoic acid decorated with iodine. We found that the position of the hydroxyl group in the chromophore is the key to providing an inactive surface, and NCA660 has the optimum structure for producing good resist pattern profiles.

Moreover, to further control the resist pattern profile, we evaluated the effect of acidic (TPSTf) addition. We are now developing new additives because TPSTf addition lowers the dry-etching rate of NCA660.

References