A Study of an Organic Bottom Antireflective Coating for 157-nm Lithography

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In 157-nm lithography, an organic bottom-antireflective-coating (BARC), which has been mainly used as an antireflective technology in KrF or ArF lithography, is needed to reduce reflection from the substrate under the resist. To apply a conventional BARC to 157-nm lithography, the BARC thickness must be less than that used in KrF or ArF lithography. This is because conventional BARCs have a lower dry-etching rate than resists with a fluorinated polymer resist for 157-nm lithography and the thickness of the remaining resist after BARC dry-etching may be greatly reduced. Moreover, the substrate reflection under a conventional thin BARC cannot be completely controlled since the k -value of the extinction coefficient at a 157-nm wavelength is small. Therefore, a BARC material for 157-nm lithography must have a higher k -value at the 157-nm wavelength, a higher dry-etching rate than resists with a fluorinated polymer, good matching between the fluorinated resist and the BARC material to ensure a good resist pattern shape, and low outgassing from the BARC material during exposure. In this paper, we evaluate newly developed BARC materials for 157-nm lithography. We found that the k -value of one new BARC material (NCA660) was 0.41 (1.6 times that of a conventional BARC (DUV30J; Brewer Science, Inc)), and the ratio of the dry-etching rate to that of a KrF resist was 2.0 (twice that of DUV30J). These improvements were achieved by introducing a chromophore containing an I-atom of halogen into a heterocyclic polymer. Furthermore, the film thickness loss (used to evaluate outgassing from this BARC material when irradiated by 157-nm light) was close to 0 nm (irradiation condition: 100 mJ/cm²), and a resist pattern with no footing was obtained in four typical kinds of fluorinated resist on this BARC material. We concluded that this BARC material was suitable for 157-nm lithography.

Keywords: Bottom-antireflective-coating, 157-nm lithography, halogen atom, optical constants, dry-etching rate, outgassing, resist pattern shape, fluorinated resist

1. Introduction

To fabricate sub-65-nm node semiconductor devices, 157-nm lithography is the most promising technology. 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 mainly used as the antireflective technology in KrF or ArF lithography, is needed to reduce reflection from the substrate under the resist. Generally, to be used for a lithographic technology, a BARC film must have suitable optical constants (refractive index n and extinction coefficient k) and a high dry-etching rate, and must permit

formation of a footing-free pattern shape at the bottom of the resist pattern on the BARC. Moreover, for a BARC to be used in 157-nm lithography, outgassing from the BARC material under 157-nm irradiation must be kept low. To apply a conventional BARC to 157-nm lithography, the BARC thickness will have to be less than the BARC thickness used in KrF or ArF lithography. This is because conventional BARCs have a lower dry-etching rate than resists with a fluorinated polymer resist [1–10] for 157-nm lithography and the thickness of the remaining resist after BARC dry-etching may be greatly reduced. Moreover, the reflection from the substrate under a conventional

thin BARC cannot be completely controlled since the k -value of the extinction coefficient at a 157-nm wavelength is small. Therefore, a BARC material for use in 157-nm lithography must have a higher k -value at the 157-nm wavelength, a higher dry-etching rate than that of resists with a fluorinated polymer, good matching between the fluorinated resist and the BARC material to ensure the proper resist pattern shape, and low outgassing from the BARC material. However, there have been few reports regarding BARC materials for 157-nm lithography [11].

In this paper, we report on a newly developed BARC material for 157-nm lithography. To make the k -value of the BARC polymer higher, we attached a halogen atom to the polymer side-chain, because the absorption peak is shifted to a longer wavelength by introducing a halogen atom into a BARC polymer [12] and we think that the absorption of the polymer at a 157-nm wavelength becomes greater. We evaluated materials with three kinds of main-chain polymer and side-chain chromophore containing a halogen atom with respect to four criteria: the optical constants, the dry-etching rate, the pattern shape, and the amount of outgassing. As a result, we obtained a BARC material suitable for 157-nm lithography.

2. Experimental

2.1 Materials

The main-chain polymers that we evaluated as BARC materials were acrylic, novolak, and heterocyclic polymers. The side-chain chromophores were a chromophore containing either a Br- or an I-atom. The 157-nm light was absorbed strongly by these chromophores containing a halogen atom. A newly developed BARC material (NCA660) consists of chromophore with an I-atom attached to a heterocyclic polymer. The casting solvent of NCA660 was a mixed solvent of propylene-glycol-methyl-ether-acetate (PGMEA) and propylene-glycol-methyl-ether (PGME). A conventional BARC based on a novolak polymer, DUV30J (Brewer Science, Inc.), was used as the reference samples in the evaluation.

The evaluated resists were based on three kinds of main-chain fluorinated polymer and one side-chain fluorinated polymer. The casting solvent of all the fluorinated resists was PGMEA. The base developer was aqueous 2.38-wt% tetramethylammonium hydroxide (TMAH) solution supplied by Tokyo Ohka Kogyo Co., Ltd.

2.2 Optical constant measurement

To evaluate the optical properties of the BARC materials at a 157-nm wavelength, we measured the optical constants (refractive index n -value and extinction coefficient k -value) of the polymers on a VUV-VASE spectroscopic ellipsometer (J.A. Woollam Co., Inc.). The various polymers tested as BARC materials were coated onto silicon wafers, and baked at 205°C for 60 s in a Clean Track ACT-8 system (Tokyo Electron Co.).

2.3 Dry-etching rate measurement

We measured the dry-etching rate of polymer films coated onto silicon wafers to a thickness of 200 nm. Etching under the organic BARC / hard mask (HM) dry-etching conditions was done using a Unity etcher (Tokyo Electron, Ltd.). The etching gases were mixed gases containing CF_4 and O_2 . The dry-etching rates were calculated using the thickness measurements obtained before and after the dry-etching. The film thicknesses were measured with an interferometer. A KrF resist based on poly (p-hydroxypolystyrene) (PHS) was used as a standard dry-etching material together with the polymer samples.

2.4 Outgassing measurement

Flood exposure to evaluate the BARC film thickness loss under 157-nm irradiation was done using the VUVES-4500 system (Lithotech Japan Co.). Measuring the film thickness loss is an easy method to determine the amount of outgassing from a BARC material. The BARC polymers were coated onto a silicon wafer. The flood exposure dose was from 0.1 to 300 mJ/cm^2 .

2.5 Imaging experiment

To evaluate the matching between the resist and BARC material, we patterned the fluorinated resists on BARC with a 157-nm laser microstepper (numerical aperture (NA) = 0.85; Exitech, Ltd.) with an alternating phase-shift mask (alt-PSM). The exposed resists were developed in the 2.38% TMAH solution using a puddle-development-process for 60 s after post-exposure baking at 110°C for 60 s in the ACT-8 system. For lithographic evaluation, we obtained resist-pattern micrographs using an S-5000 scanning electron microscope (Hitachi Co.).

3. Results and discussion

3.1 Optical constant

We evaluated the change in the optical constants brought about by introducing a chromophore with a Br- or I-atom into three kinds of BARC polymer.

Figure 1 shows the dependence of the extinction coefficient k on the wavelength (from 145 to 240 nm) for the three kinds of BARC polymer – (a) acrylic polymer, (b) novolak polymer, (c) heterocyclic polymer – with the chromophore containing a Br- or I-atom. The k -value of the three polymers without a chromophore was about 0.2 at a 157-nm wavelength. However, when a chromophore containing a Br- or I-atom was

introduced, the k -value of all three polymers rose above 0.2. We think that the increased absorption at a 157-nm wavelength in all of these polymers was that the main absorption peak at a wavelength shorter than 157-nm wavelength was shifted to a longer wavelength by the introduction of a chromophore with a halogen atom such as a Br- or I-atom.

Figures 2 and 3 show the dependence of the refractive index n and the extinction coefficient k at a 157-nm wavelength on the halogen atom content for the three kinds of polymer.

The n -values of the three polymers at a 157-nm wavelength increased with a rising halogen atom

Fig. 1. Dependence of the extinction coefficient k -value on the wavelength (from 145 to 240 nm) for the three kinds of BARC polymer – (a) acrylic polymer, (b) novolak polymer, and (c) heterocyclic polymer – with chromophores containing Br- or I-atoms.

Fig. 2. Dependence of the refractive index n on the halogen atom content for three kinds of polymer – (a) acrylic polymer, (b) novolak polymer, and (c) heterocyclic polymer – with chromophores containing halogen atoms.

Fig. 3. Dependence of extinction coefficient k on the halogen atom content for three kinds of polymer – (a) acrylic polymer, (b) novolak polymer, and (c) heterocyclic polymer – with chromophores containing halogen atoms.

content, except when the I-atom was introduced into the acrylic polymer. We found that the n -value was proportional to the halogen atom content. Thus, we can adjust the n -value of a BARC material by changing the halogen content of the polymer.

The k -values of the three polymers at a 157-nm wavelength also increased with a rising halogen atom content. The change in the k -value with the halogen atom content was greater when we introduced the I-atom rather than the Br-atom, because the main absorption peak of polymer with the I-atom shifted to a longer wavelength than was the case with the Br-atom. We found that the k -value was proportional to the halogen atom content as was the case with results for n -value. Thus, we can also adjust the k -value of a BARC material by changing the halogen content of the polymer.

Figure 4 shows the extinction coefficient k , calculated from the approximated line of Fig. 3, for the three kinds of polymers with chromophores

Fig. 4. Extinction coefficient k , calculated from the approximated line of Fig. 3, for three kinds of polymers – acrylic polymer, novolak polymer, and heterocyclic polymer – with chromophores containing a Br- or I-atom content of 0 or 50 %.

containing a Br- or I-atom content of 0 % or 50 %. The k -value of DUV30J is shown for reference. Regardless of the kind of polymer, the k -value at a 157-nm wavelength was increased by introducing a chromophore with a halogen atom to the polymer. If the content of halogen atom was the same in each BARC polymer, the attachment of the I-atom to the chromophore more effectively increased the absorption of the BARC polymer than the case with the Br-atom. The k -value of the heterocyclic polymer containing a chromophore with an I-atom content of 50 % was the highest (0.43) among the three polymers.

3.2 Dry-etching rate

We also evaluated the change in the dry-etching rate ratio brought about by introducing a chromophore with a Br- or I-atom into the three BARC polymers.

Figure 5 shows the dependence of the dry-etching rate ratio to a KrF resist for each BARC polymer on the halogen atom content. The etching rate ratio rose for all of the polymers as the halogen atom concentration increased. The change in the etching rate ratio with the halogen atom content was greater when the Br-atom was introduced rather than the I-atom, unlike the trend for the k -value, because the reactivity of the Br-atom to another atom is higher than that of the I-atom. We found that the etching rate ratio was proportional to the halogen atom content, as was the case with results for the k -value. Thus, we can also adjust the etching rate ratio of a BARC material by changing the halogen content of the polymer.

Figure 6 shows the dry-etching rate ratio, calculated from the approximated line of Fig. 5, for the three kinds of polymers with chromophores containing the Br- or I-atom at a weight percentage

Fig. 5. Dependence of the dry-etching rate ratio of the BARC polymer to a KrF resist on the halogen atom content for three kinds of polymer – (a) acrylic polymer, (b) novolak polymer, and (c) heterocyclic polymer.

of 0 % or 50 %. The dry-etching rate ratio of DUV30J is shown for reference. Regardless of the polymer, the dry-etching rate ratio of the polymer at a 157-nm wavelength was increased by introducing a chromophore with a halogen atom to the BARC polymer. With the same halogen atom content in each BARC polymer, the Br-atom more effectively increased the etching rate ratio of the polymer than the I-atom. As for the heterocyclic polymer, which had the highest etching rate of the polymer itself among the three polymers, the etching rate ratio of the polymer with a Br-atom content of 50 % was the highest (2.1) and that of polymer with a I-atom content of 50 % was the second highest (2.0).

Table 1 summarizes the halogen atom concentrations and the dry-etching rate ratios of the BARC polymer to a KrF resist needed to obtain an extinction coefficient k of 0.35 [11] for the three polymers as calculated from each

Fig. 6. Dry-etching rate ratio, calculated from the approximated line of Fig. 5, for three kinds of polymers – acrylic, novolak, and heterocyclic – with a chromophore containing a Br- or I-atom content of 0 % or 50 %.

Table 1. Halogen atom concentration and dry-etching rate ratio of the BARC polymer to a KrF resist needed to obtain an extinction coefficient k of 0.35 for the three kinds of polymer (calculated from each approximated line shown in Figs. 3 and 5).

		BARC Polymer			DUV30J
		Acrylic	Novolak	Heterocyclic	
Chromophore with Br-atom	Concentration of Br-atom (wt%)	62	62	79	-
	Dry-etching rate ratio	2.2	1.7	2.5	1.0
Chromophore with I-atom	Concentration of I-atom (wt%)	33	33	29	-
	Dry-etching rate ratio	1.4	1.1	1.8	1.0

approximated line shown in Figs. 3 and 5. To obtain a dry-etching rate ratio of more than 1.7 [10] (the etching rate ratio of a main-chain fluorinated polymer), an acrylic polymer with a chromophore containing the Br-atom, a novolak polymer with Br-atom, a heterocyclic polymer with the Br-atom, or a heterocyclic polymer with the I-atom were required. However, since the maximum halogen atom content in each polymer is about 40 to 50 % in polymer synthesis, the heterocyclic polymer with the I-atom is the most attractive as a BARC material for 157-nm lithography.

3.3 Outgassing from a BARC material

We evaluated the outgassing from the three kinds of polymer with a chromophore containing a halogen atom.

Figure 7 shows the dependence of the film thickness loss for a BARC-polymer on the exposure dose for (a) the three polymers without a chromophore, and (b) a heterocyclic polymer with a chromophore containing the Br- or I-atom. In Fig. 7(a), the film thickness loss of the acrylic polymer increased as the exposure dose rose, and a loss of more than 3 nm at 100 mJ/cm² was observed. In contrast, the film thickness loss of the novolak polymer and heterocyclic polymer was close to 0 nm even at 100 mJ/cm². Because the novolak and heterocyclic polymers both have a ring-shaped structure, these polymer structures were stable under 157-nm irradiation. Therefore, we concluded that a BARC polymer for 157-nm lithography would need to have a polymer structure having a ring-shaped structure. As shown in Fig. 7(b), the film thickness loss of the heterocyclic polymer

with a chromophore containing the halogen atom

suitable optical constant, dry-etching rate, and

Fig. 7. Dependence of film thickness loss for BARC-polymer on exposure dose for (a) three kinds of polymer without chromophore, and (b) a heterocyclic polymer with a chromophore containing Br- or I-atom.

Fig. 8. Lithographic results of 100-nm line-and-space patterns for three kinds of main-chain fluorinated resists (main-chain F resist-A, F resist-B, and F resist-C) and one side-chain fluorinated resist (side-chain F resist) on a heterocyclic polymer containing a chromophore with a Br content of 40 % or an I-atom content of 50 %.

was close to 0 nm even at 100 mJ/cm², and we observed no outgassing from this polymer. Therefore, we found that the heterocyclic polymer structures with a chromophore containing the halogen atom are also stable under 157-nm irradiation.

3.4 Lithographic performance

We evaluated the lithographic performance of various fluorinated resists on a BARC polymer with a chromophore. We had earlier found that the shape at the bottom of a resist pattern on a BARC polymer depends on the kind of BARC polymer side-chain, rather than the kind of polymer main-chain. Here, we evaluated the lithographic performance of various fluorinated resists on a heterocyclic polymer containing a chromophore with the Br- or I-atom, which had each shown a

Fig. 9. Lithographic results of 80-nm to 60-nm line-and-space patterns for main-chain F resist-B on a heterocyclic polymer containing a chromophore with an I-atom content of 50 %.

Table 2. Evaluation results for a heterocyclic polymer with a chromophore containing the Br-atom at a 40 % content, a heterocyclic polymer with chromophore containing the I-atom at a 50 % content (NCA660), and DUV30J as a reference.

BARC			n-value	k-value	Etching rate ratio (vs. KrF resist)	Resist pattern shape
Polymer	Chromophore					
Heterocyclic	With Br-atom of 40 %	—	1.7	0.29	2.0	small footing
Heterocyclic	With I-atom of 50 %	NCA660	1.61	0.41	2.0	no footing
Novolak	Without halogen atom	DUV30J	1.54	0.25	1.0	no footing

outgassing.

Figure 8 shows the lithographic results for three kinds of main-chain fluorinated resists (main-chain F resist-A, F resist-B, and F resist-C) and one side-chain fluorinated resist (side-chain F resist) on a heterocyclic polymer containing a chromophore with a Br-atom content of 40 % or an I-atom content of 50 %. These results were obtained using a microstepper with a 0.85 NA. Since the transparency of each resist differed from 1.0 to 3.0 (μm^{-1}) greatly, 100-nm line-and-space (L/S) patterns were evaluated to make the optical contrast of the 157-nm light sufficiently high. The resist pattern shapes of the heterocyclic polymer with the Br-atom show a small footing shape in the main-chain F resist-A, -B, and -C samples. On the other hand, the pattern shapes on the heterocyclic polymer with the I-atom show no footing shape in any of the fluorinated resists and match those on DUV30J as the reference BARC. Also, the pattern shapes of the heterocyclic polymer with the I-atom did not depend on the combination of the resist and BARC material. Therefore, the matching of the heterocyclic polymer with the I-atom with various fluorinated resists is better than that of the heterocyclic polymer with the Br-atom. Furthermore, we evaluated the lithographic performance of smaller size patterns for the fluorinated resist on the heterocyclic polymer with the I-atom.

Figure 9 shows the lithographic results of 80-nm, 70-nm, and 60-nm L/S patterns for main-chain F resist-B on a heterocyclic polymer containing a chromophore with an I-atom content of 50 %. We obtained a 60-nm L/S pattern with no footing at a 150-nm film thickness.

3.5 Comparison of heterocyclic polymers containing a Br- or I-atom chromophore

Table 2 summarizes our evaluation results for the heterocyclic polymer with a chromophore

containing a Br-atom with a weight percentage of 40 %, the heterocyclic polymer with a chromophore containing the I-atom with a weight percentage of 50 % (named NCA660), and DUV30J as a reference. The halogen atom content of both materials was the maximum value for each polymer in the polymer synthesis.

With respect to the optical constants and the resist pattern, NCA660 was superior. As for the dry-etching rate ratio to KrF resist, NCA660 was almost the same as the other polymer. By introducing a chromophore with the I-atom into the heterocyclic polymer, we could obtain a k-value of 0.41 (1.6 times that with DUV30J) and a dry-etching rate ratio of 2.0 (twice that with DUV30J). We could achieve the conditions of having a k-value more than 0.35 and a dry-etching rate ratio more than 1.7 for a BARC material of 157-nm lithography. Also, we were able to form resist patterns with no footing when using four typical kinds of fluorinated resist on this BARC material.

4. Conclusions

We have developed a BARC material (NCA660) for 157-nm lithography. Introducing a chromophore with an I-atom content of 50 % into a heterocyclic polymer enabled us to obtain a k-value of 0.41 (1.6 times that of a conventional BARC (DUV30J)) and a ratio of the dry-etching rate to that of a KrF resist of 2.0 (twice that of DUV30J). Furthermore, the film thickness loss (by which we evaluated outgassing from this BARC material when it was irradiated by 157-nm light) was close to 0 nm (irradiation condition: 100 mJ/cm²), and a resist pattern with no footing was obtained with four typical fluorinated resists used in 157-nm lithography on the BARC material. We concluded that this BARC material was suitable for 157-nm lithography.

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