Molecular Design of o-Nitrobenzyl Phenol Ether for Photo-deprotection Resist; Challenge to half-pitch 22 nm using Near-field Lithography

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Polyhydroxystyrenes protected with three kinds of o-nitrobenzyl (NB) group are synthesized: 4,5-dimethoxy NB group (DNB), 4-monomethoxy NB group (MNB) and α-methyl 4,5-dimethoxy NB group (ADNB). Their solutions are formulated as photo-deprotection resists for the near-field lithography (NFL). These resists are evaluated in terms of the fundamental lithographic performances using the propagation i-line light, followed by the NFL experiments. The ADNB has the highest photosensitivity and the DNB provides the resist patterns of the smallest line edge roughness (LER). Hp 22 nm L/S pattern of 10 nm deep is fabricated on the top portion of a single-layer of DNB. Hp 32 nm L/S pattern of 10 nm thick is transferred to the 100 nm thick bottom-layer resist through the tri-layer resist process.

Keywords: near-field light, photolithography, o-nitrobenzyl ether, chemically amplified resist, tri-layer resist process, electro-magnetic analysis

1. Introduction

As nano-scale fabrication techniques for manufacturing of a wide variety of optical and electronic devices, scanning probe lithography [1], nano-imprint lithography [2] and step and flash imprint lithography [3] are widely studied.

A contact photolithography technique that uses near-field light was proposed, namely near-field lithography (NFL) [4-7]. Near-field light is a localized one that exists on the surface of illuminated materials thereby concentrating in a much smaller volume than can be achieved by the ordinary lithography techniques. Since a conventional mercury lamp can be applied as a light source, the NFL is expected to provide a low-cost and small-footprint printing tool.

In our previous paper [8-10], we reported the fabrication of resist patterns of hp 32 nm and 100 nm deep, using the NFL with the positive-tone i-line sensitive CAR (iCAR) through the tri-layer resist process. Figure 1 shows the tri-layer resist process, which is necessary to obtain higher aspect resist patterns than the near-field region depth estimated to be within 10–30 nm.

In terms of line edge roughness (LER), the iCAR patterns showed superior performance to those of commercially available novolak type i-line photoresists [7]. However, its LER was still as large as 13 nm (3σ) on the pattern, which is obviously insufficient for the specification required for hp 22 nm node.

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It is widely known that the diffusion of the photo-generated acid in CARs during post-exposure bake (PEB) is one of the causes of the insufficient LER and limits the ultimate lithographic resolution. Typical diffusion length of the acid has been estimated to be 11~25 nm [11,12].

We developed a positive-tone photoresist system based on photolysis of o-nitrobenzyl (NB) phenol ether shown in Scheme 1, in order to obtain finer resist patterns than that of CARs [13].

Scheme 1. Photo-deprotection reaction of o-nitrobenzyl phenol ether [16].

The photo-deprotection reaction of NB ether or ester have been applied to the photo-sensitive polyimides [14], the photo-acid generators [15], the caged compounds [16] and the drug delivery system [17]. The NB ether and ester regenerate reactive functional group such as carboxylic acid, sulfonic acid, phosphoric acid, and phenolic acid after UV exposure.

In our previous paper [13], we introduced the lithographic results obtained with the polyhydroxystyrene (PHS, Mw = 4,100, Mw/Mn = 1.1) whose 39% of the hydroxyl groups were protected by 4,5-dimethoxy-2-nitrobenzyl group (DNB-39). Scheme 2 shows the molecular structure and its photolysis.

Scheme 2. Photolysis of photo-deprotection resist

The resist patterns of DNB-39 had lower LER than that of the iCAR in hp 32 nm L/S pattern thanks to the photo-deprotection system without the acid diffusion although the DNB-39 had a lower γ-value than the iCAR as shown in Figure 2.

Figure 2. AFM images depicting hp 32 nm top-layer photoresist patterns of (a) iCAR and (b) DNB-39. The exposure doses were 201 and 1208 mJ/cm², respectively. Scale bars of both images are 500 nm.

In return, DNB-39 had six times lower photosensitivity than that of the iCAR although we employed 4,5-dimethoxy NB group in order to give the polymer a high absorption to the i-line light. The low throughput enlarges the cost of ownership (CoO), i.e. reduces the attraction of the NFL as a low-cost lithography.

It has been known that the photolysis rates of NB ether or ester vary with the molecular structures of NB groups. For example, A. R. Katritzky et al. reported that 4-monomethoxy NB phenol ether decomposed 2~3 times more rapidly than 4,5-dimethoxy NB phenol ether under irradiation at 363 nm due to the electronic characteristics of the benzylic carbon [16]. K. Yamaguchi et al. reported that the photolysis rates of NB carboxylate derivatives were in the order of α-methyl 4,5-dimethoxy NB carboxylate > 4,5-dimethoxy NB carboxylate > NB carboxylate under the irradiation at 364 nm [17]. Note that these compounds bearing the NB groups were synthesized for bio-chemical materials, not for photoresist materials.

We synthesized PHSs protected with 4,5-dimethoxy NB group (DNB), 4-monomethoxy NB group (MNB) and α-methyl 4,5-dimethoxy NB group (ADNB). The molecular structures were shown in Scheme 3. They were evaluated with respect to the lithographic performance in order to optimize the molecular structure for the NFL of low CoO and high resolution.

Scheme 3. Molecular structures of NB protected PHSs
In this paper, we report the result of the synthesis, the evaluation of the fundamental lithographic features of these NB type photo-deprotection resists (PDR), followed by the fabrication of sub-45 nm patterns using the NFL.

2. Experimental

2.1. Materials for Synthesis

PHS was obtained from Nippon Soda. 4,5-Dimethoxy-2-nitrobenzyl bromide (DNB-Br) and 4-Methyl-3-nitroanisole were purchased from Sigma-Aldrich. 3,4-Dimethoxyacetophenone and N-bromosuccinimide (NBS) were purchased from Tokyo Chemical Industry Co., Ltd. NaH and NaBH₄ was purchased from Kanto Chemical Co., Ltd. Benzoyl peroxide was purchased from nacalai tesque Co., Ltd.

All the commercially available compounds, except for NaH, were used without further purification. NaH with mineral oil was rinsed with dry hexane and dried under reduced pressure.

2.2. Equipment

¹H-NMR spectral data were obtained with a JEOL AL400 (400 MHz) spectrometer. Chemical shifts are reported as δ values in ppm relative to TMS. The absorption spectra in UV-visible region and the thickness of the resist were recorded and measured using a spectroscopic ellipsometer (J. A. Woollam M-2000). The resist pattern was observed using an atomic force microscope (AFM, Digital Instruments D3000) and a scanning electron microscope (SEM, Hitachi S5000H). An RIE machine (ULVAC NE-550) was used in the transfer process.

2.3. Synthesis

2.3.1. Synthesis of NB Bromides

4-Monomethoxy-2-nitrobenzyl bromide (MNB-Br) was synthesized through the bromination reaction shown in Scheme 4 and characterized using NMR, as reported by A. R. Katritzky et al. [16].

\[
\begin{align*}
\text{4-methyl-3-nitroanisole} & \rightarrow \text{4-methyl-3-nitrobenzyl bromide} \\
(\text{2-nitro-4-methoxytoluene}) & \text{(MNB-Br)}
\end{align*}
\]

Scheme 4. Synthesis of MNB-Br

\[\alpha\text{-methyl 4, 5-dimethoxy -2- nitrobenzyl bromide (ADNB-Br) was synthesized as shown in Scheme 5. To an ice-cooled concentrated nitric acid aq. was added dropwise 3,4-dimethoxyacetophenone (250 g, 1.4 mol, 1.0 eq.) at 0°C. This brown solution was stirred at room temperature overnight. To ice water (5 L) was added the resulting solution. The precipitation was filtered, washed with water and dried. 4, 5-dimethoxy -2- nitroacetophenone (DNMA) was obtained as a yellow solid (161 g, 0.72 mol, 52% yield). To an ice-cooled solution of DMNA (98.0 g, 0.44 mol, 1.0 eq.) in dry MeOH (15 L) was added dropwise NaBH₄ (46.6 g, 1.2 mol, 2.8 eq.), was stirred for 0.5 h at 0°C and 1 h at room temperature. The yellow solution was concentrated by a rotary evaporator. After the addition of water (15 mL) to the yellow residue, the suspension was extracted with CHCl₃ (7.5 L x 3). The combined CHCl₃ layers were dried over MgSO₄, filtered and concentrated by a rotary evaporator to obtain a brown solid (115 g). All process was carried out in a dark room by NARD Institute, Co., Ltd.]

All process was carried out in a dark room by NARD Institute, Co., Ltd.
The PHSs protected with NB groups were synthesized from PHS and nitrobenzyl bromides (NB-Br) synthesized or purchased as described above, through Williamson-type etherification reaction as depicted in Scheme 6.

Scheme 6. Synthesis of polymers

To a solution of PHS (7.0 g, 58.3 mmol, 1.0 eq) in dry DMF were added NaH (out of oil) and NB-Br at 50 °C with stirring. This mixture was stirred for 4 h at the same temperature. To the resulting solution was added 10 % NH4Cl aq. (175 mL) and extracted by EtOAc (150 mL × 3). The combined organic solution was washed with water (150 mL × 8), brine (150 mL) and dried by Na2SO4. The solvent was evaporated and to the residue was added AcOEt (10 mL). This viscous oil was decanted twice with toluene and the residual viscous oil was dissolved in AcOEt (140 mL). The oil was reprecipitated with hexane (2.1 L), filtered, dried under reduced pressure at 50°C for 24 h to obtain as a pale brown solid. An identical procedure was repeated with variations in the amounts of NB-Br and NaH added to obtain the full series of polymers. The amounts of NB-Br and NaH added are described in Table 1 in the results and discussion section.

DNB. \(^1\)H NMR (400 MHz, DMSO): δ = 8.99 (br s, 1H, PhOH), 7.75-6.12 (br m, ArH), 5.42-5.05 (br s, 2H, OCH2), 3.91-3.67 (br s, 6H, 2 × CH3O), 2.4-0.75 (br m, ArCHCH2)

MNB. \(^1\)H NMR (400 MHz, DMSO): δ = 9.00 (br s, 1H, PhOH), 7.61-6.10 (br m, ArH), 5.25 (br s, 2H, OCH2), 3.83 (br s, 3H, CH3O), 2.4-0.75 (br m, ArCHCH2)

ADNB. \(^1\)H NMR (400 MHz, DMSO): δ = 8.99 (br s, 1H, PhOH), 7.62-5.96 (br m, ArH + OCH), 3.81-3.78 (br s, 6H, 2 × CH3O), 2.25-0.60 (br m, ArCHCH2).

The protective ratios were determined from the ratio of the peak intensities of CH3O and ArH.

All process was carried out in a dark room by NARD Institute, Co., Ltd.

2.4. Resist Materials

The PDR solutions were formulated by dissolving PHSs protected with NB groups into propylene glycol monomethyl ether acetate (PGMEA) making 1.25 ~6.66 wt% solutions. Spin on glass (SOG) material (Honeywell T-03AS) thinned with PGMEA was used as a SOG layer. Thermosetting phenol resin (Shipley AR2450) thinned with PGMEA was used as a bottom resist layer. The solution was filtered through 0.45-mm filter prior to coating.

2.5. Preliminary Lithographic Evaluation

The photoresist solutions were spin-coated onto 1, 1, 1, 3, 3, 3-hexamethyl disilazane (HMDS) primed silicon wafers, then baked at 90 °C for 90 s.

2.5.1. Dissolution Rate

The dissolution rate of the photoresist to the developer was determined by measuring the thickness of the film before and after dipping the substrate into the developer for a certain time.

2.5.2. Sensitivity Curve

30 nm thick photoresist layers on the Si wafers were exposed to the propagation light of i-line through a gray scale mask. The exposed wafers were developed in 2.38 wt% tetramethyl ammonium hydroxide (TMAH) aqueous solution for 10 s followed by rinse with distilled water for 20 s.

2.6. Near-field Lithography

The prototype NFL machine [7] equipped with a mercury lamp and an i-line band pass filter was used. A near-field photomask, which had 50 nm thick amorphous Si (α-Si) film as an absorber and 400 nm thick Si3N4 film as a transparent substrate, was used [8]. Hp 22~32 nm L/S patterns were fabricated in the absorber using electron-beam (EB) lithography. The transmittance of the Si3N4 film was 30 % at 365 nm. The intensity of light was measured to be 200 mW/cm² on the photomask. The exposed wafers were developed in 2.38 wt% TMAH aqueous solution for 10 s followed by rinse with distilled water for 20 s.

2.7. Single-layer Resist Process

The photoresists were spin-coated on HMDS primed Si wafers and baked at 90 °C for 90 s to provide 130 nm thick layer, then the near-field exposure and the development was carried out as schematically shown in Scheme 7.
Scheme 7. Single-layer resist process

2.8. Tri-layer Resist Process

The AR2450 was spin-coated on a bare Si wafer and baked at 200 °C for 600 s to provide a 100 nm thick film. The T-03AS was spin-coated on the AR2450 layer and baked at 200 °C for 600 s to provide a 20 nm thick film. After the T-03AS layer was primed with HMDS, the photoresists were spin-coated on the T-03AS layer and baked at 90 °C for 90 s to provide 10~20 nm thick top-layer photoresist.

The NFL patterns lithographically fabricated in the top-layers were transferred by the two-step reactive ion etching (RIE) process; into the SOG layer with fluoride-based gas plasma and into the bottom-layer with oxygen-based gas plasma.

2.9. Electro-magnetic analysis

We conducted a computer simulation using finite-difference time domain (FDTD) method for an analytical study of near-field light around the near-field mask. The model was as follows; i-line light (λ = 365 nm in a vacuum) was generated from a plane wave source placed in the silicon nitride layer. The light illuminated the a-Si layer over the resist layer on silicon substrate.

Complex refractive indexes used were 1.9 for silicon nitride, 3.90 +2.66i for a-Si, 1.69 +0.09i for resist materials and 6.53 +2.61i for c-Si substrate.

3. Results and Discussion

DNB polymers of 16, 20, 26 and 39% protective ratio (DNB-16, -20, -26 and -39, respectively), MNB polymers of 19, 22, 27 and 29% protective ratio (MNB-19, -22, -27 and -29, respectively) and ADNB polymers of 16, 20, 28 and 32% protective ratio (ADNB-16, -20, -28 and -32, respectively) were obtained as shown in Table 1.

Table 1. Resulting protective ratio of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Added amount (eq.; relative to PhOH)</th>
<th>Resulting protective ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DNB-16</td>
<td>0.25 NaBr 0.30 NaH</td>
<td>15.7</td>
</tr>
<tr>
<td>DNB-20</td>
<td>0.30 NaBr 0.35 NaH</td>
<td>19.8</td>
</tr>
<tr>
<td>DNB-26</td>
<td>0.35 NaBr 0.40 NaH</td>
<td>26.4</td>
</tr>
<tr>
<td>DNB-39</td>
<td>0.47 NaBr 0.53 NaH</td>
<td>38.8</td>
</tr>
<tr>
<td>MNB-19</td>
<td>0.25 NaBr 0.30 NaH</td>
<td>18.9</td>
</tr>
</tbody>
</table>

We prepared films of the PDRs by spin-coating the solutions of the polymers and then measured the dissolution rate of each PDR to the developer. The results are shown in Figure 3.

![Figure 3. Development rates of NBPs](image)

The dissolution rates lower than 0.1 nm/s were obtained with all of the PDRs of the protective ratio higher than approximately 22%.

Although the ADNBs are expected to have higher hydrophobicity than the DNB because of the presence of the α-methyl group, the ADNBs had the highest dissolution rates especially at the high protective ratio. This means that the unexposed area in the ADNB pattern has low durability to the developer.

The absorption spectra of the polymers of the 26~28% protective ratios are shown in Figure 4.

![Figure 4. Absorption spectra](image)

The extinction coefficient of the MNB-27 was the smallest in the three polymers at 365 nm. The
small absorption of the MNB was considered to be the result of the small conjugated system due to the lack of one electron-donating group.

We measured the sensitivity curves of the PDRs to the i-line propagation light. That of the iCAR was also measured for comparison. The results are shown in Figure 5 and Table 2.

![Sensitivity curves](image)

Figure 5. Sensitivity curves. Initial thicknesses are 30 nm for all.

<table>
<thead>
<tr>
<th></th>
<th>Extinction Coefficient @ 365 nm</th>
<th>Sensitivity (mJ/cm²)</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>DNB-39</td>
<td>0.086</td>
<td>846</td>
<td>1.19</td>
</tr>
<tr>
<td>DNB-26</td>
<td>0.074</td>
<td>541</td>
<td>1.10</td>
</tr>
<tr>
<td>MNB-27</td>
<td>0.021</td>
<td>1058</td>
<td>0.88</td>
</tr>
<tr>
<td>ADNB-28</td>
<td>0.059</td>
<td>264</td>
<td>0.79</td>
</tr>
<tr>
<td>iCAR</td>
<td>0.0086</td>
<td>35</td>
<td>3.09</td>
</tr>
</tbody>
</table>

The positive-tone resist system of the MNB and ADNB was demonstrated by this result for the first time. All the PDRs required 7.5~30.1 times as high exposure doses as that for the iCAR. Moreover, their γ-values were smaller than that of the iCAR. We previously reported [13] that the DNB-39 provided patterns of smaller LER despite the lower γ-value than the iCAR, because of the advantage of the acid diffusion free system. We suppose that the γ-value is worth consideration only when comparing the photoresists of the same photo-reaction system.

The ADNB-28 had the highest photosensitivity and the smallest γ-value. Although the ADNB-28 had 0.8 times as small absorption as the DNB-26 at 365 nm, the ADNB-28 showed 2.0 times higher photosensitivity. It can be said that the ADNB-28 had a 2.6 times higher quantum yield than the DNB-26 with considering the extinction coefficients of the both polymers, which is consistent with the result of the corresponding NB esters studied by K. Yamaguchi et al [17].

The MNB-27 required twice as high exposure dose as that for the DNB-26, as opposed to the result reported by Katritzky et al. The contradiction might be caused by the difference of the states: liquid and solid, however, the reason cannot be concluded presently. The quantum yield of the MNB-27 was estimated to be 1.8 times higher than that of the DNB-26.

The photosensitivity of the DNB-39 was lower than that of the DNB-26, as a matter of course. The DNB-39 had the highest γ-value of 1.19 among all the PDRs evaluated in this paper.

We carried out the single-layer resist process for the NFL using the PDRs. High aspect patterns cannot be obtained with the single-layer resist process, however, this makes it possible to evaluate the resolution ability of photoresists for the NFL without pattern stripping [13].

An electro-magnetic analysis using FDTD method was conducted prior to the NFL experiment. The light intensity distribution around the near-field mask is depicted as a contour plot in Figure 6.

![Contour plot](image)

Figure 6. Contour plot of light intensity distribution around hp 45 nm L/S near-field photomask calculated using FDTD method, where (a) a silicon nitride layer, (b) an a-Si layer with 30 nm wide apertures and (c) a photoresist of 130 nm thick.

The simulation result indicated that the near-field light was generated within 25 nm from the apertures, that is, 5~25 nm deep resist pattern would be fabricated on the top portion of 130 nm thick single-layer.

Hp 45 nm L/S patterns of 5~20 nm deep were obtained with all the PDRs as expected from the simulation result. Deeper patterns were obtained with higher exposure doses. AFM images of around 10 nm deep patterns are shown in Figure 7.
The ADNB-28 provided the 10 nm deep pattern with the least exposure dose as expected from the sensitivity curves obtained with the propagation light.

The LER on the ADNB-28 patterns were larger than the others. The low durability to the developer of the unexposed area clarified in Figure 3 as well as the low $\gamma$-value were considered to result in the large LER.

The resist patterns with the smallest LER were obtained with DNB-39. The highest $\gamma$-value as well as the high durability to the developer contributed to the small LER pattern.

We tried to fabricate patterns finer than hp 45 nm L/S using DNB-39. Hp 32 and 22 nm patterns are shown in Figure 8.

Figure 7. Hp 45 nm patterns of the PDRs. Scale bars of all images are 500 nm.

This result indicated that the NFL technique with the PDRs had potential resolution of hp 22 nm and below.

Then, we employed the tri-layer resist process in order to fabricate deeper patterns than the near-field region. 10 nm thick DNB-39 spin-coated on the SOG layer was exposed to the near-field light. AFM images of the top-layer resist patterns are shown in Figure 9.

Figure 8. (a) hp 32 nm and (b) hp 22 nm patterns fabricated on the top portion of the single-layer of DNB. The exposure dose was 1400 mJ/cm² for each. The pattern depths were 15 and 10 nm, respectively. Scale bars of both images are 500 nm.

Figure 9. AFM images of (a) hp 32 nm and (b) hp 27 nm L/S top-layer photoresist pattern. The exposure was 1200 mJ/cm² for each. The thickness of the top-layer was 10 nm. Scale bars of both images are 500 nm.

Stripping of the top-layer resist pattern was observed in the hp 27 nm L/S pattern. The adhesiveness of the top-layer photoresist pattern to the SOG might be too weak to maintain hp 27 nm L/S patterns on the SOG.

Then we conducted the pattern transfer process.
from the hp 32 nm L/S DNB-39 top-layer resist pattern of to the 20 nm thick SOG layer, followed by the subsequent transfer process to the 100 nm thick bottom-layer resist from the SOG layer. The 10 nm thick DNB-39 pattern shown in Figure 9 was successfully transferred into the bottom-layer as shown in Figure 10.

The line width was approximately 25 nm. The LER value (3σ) was estimated to be 4.3 nm from the top view image.

As of this writing, we are dealing with the adhesiveness issue of PDR patterns.

4. Conclusion

PHSs protected with the three kinds of NB group (DNB, MNB and ADNB) were synthesized and the solutions were prepared as PDRs for the NFL by dissolving them into the organic solvent. Their fundamental lithographic performances were evaluated using the i-line propagation light. The ADNB-28 had the highest photosensitivity and the highest quantum yield, while its γ-value was the smallest. DNB-39 had the highest γ-value of 1.19.

The NFL experiments were conducted upon these PDRs. Patterns with the lowest LER were obtained with the DNB-39 due to its high γ-value and high durability to the developer. Hp 22 nm L/S pattern of 10 nm deep was fabricated on the top portion of the single-layer of 130 nm thick DNB-39.

Hp 32 nm L/S pattern of 10 nm deep was successfully transferred into the 100 nm thick bottom-layer resist through the tri-layer resist process. The adhesiveness of the DNB-39 to the SOG should be improved to fabricate high-aspect patterns finer than hp 27 nm L/S.

References