Non-chemically Amplified Negative Molecular Resist Materials using Polarity Change by EUV Exposure

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We examined the synthesis, physical properties, and resist property of the molecular non-chemically amplified resist materials. By the condensation reaction of tri(4-hydroxyphenyl)methane (HPM) and various bisphenols (BisA, BisAF, HPE, and TDP) with 4-bromoethoxyphenyl methyl sulfide (BEPMS), the compounds (HPM-BEPMS, BisA-BEPMS, BisAF-BEPMS, HPE-BEPMS, and TDP-BEPMS) containing sulfide moieties were synthesized. These were reacted with silver trifluoromethanesulfonate and iodomethane, yielding corresponding compounds HPM-BEPMSion, BisA-BEPMSion, BisAF-BEPMSion, HPE-BEPMSion, and TDP-BEPMSion, respectively. They have good physical properties (solubility, film-forming ability, and thermal stability) and high negative-type resist sensitivity in an extreme ultraviolet (EUV) exposure tool, indicating these were good candidates to offer higher resolution resist patterns.

Keywords: Molecular resist, n-CAR, Extreme ultraviolet, Negative-type resist

1. Introduction
Development of large-scale integration using EUV lithography systems has been examined and just reached the early practical stage. However, a suitable resist material for EUV has been under consideration to offer higher resolution (R), lower roughness of resist pattern (L), and higher sensitivity under exposure tool (S). Then, there is still no resist material satisfying these three resist properties at the same time, i.e., the relationship of R, L, and S is well known as a trade-off issue [1]. At the present time, the chemically amplified resist (CAR) system has been useful method to form high-resolution resist patterns, and there are many reports concerning EUV resist materials [2]. Among them, the molecular resist materials have also been examined as higher resolution resist material and expected to improve the trade-off issue as mentioned above, due to that their sizes are smaller compared to those of polymers and they have also no molecular weight distribution. For example, Ueda et al. synthesized calix[4]resorcinarene with pendant t-butyloxycarbonyl group as a molecular resist and it’s a thin film could offer a resist pattern with 1.5 μm L/S using UV exposure tool [3]. Our research group has also reported the development of molecular resist materials based on ladder cyclic oligomer noria (“noria” = water wheel in Latin) [4-12], tannic acid derivative [13], and tellurium-containing materials [14, 15]. These molecular resists have been considered to achieve higher sensitivity, but their roughness of resist pattern could not improve. Very recently, the improving roughness of resist pattern would be the most important issue in the development of high-resolution resist material. Furthermore, the resolution of next generation EUV resist pattern has been expected to offer under about 15nm, which might not be applicable in CAR system, presumably because of that EUV exposure might cause some reactions to reach the unexposed area. Therefore, non-chemically amplified resist (n-CAR) system
has been attracting for next-generation EUV resist material [16 - 22]. Thakur et al. synthesized molecular n-CAR material having a fluorene skeleton in the aromatic core and introducing a sulfonium triflate group, and evaluated the resist performance using i-line, DUV, and electron beam (EB) as the exposure source. As a result, it showed 20 nm lines of resist patterns and LER was 5.69 ± 0.2 nm [23].

In this time, we synthesized the molecular resist materials containing sulfonium triflate skeletons which were expected to change polarity exposed by EUV light. The physical properties (solubility, film-forming, and thermal stability) and resist property (sensitivity) of synthesized molecular resist materials were examined to offer higher resolution in n-CAR system under EUV exposure tool.

2. Experimental

2.1. Materials

N,N-Dimethylformamide (DMF) and acetonitrile were dried with calcium hydride (CaH₂) and purified by distillation under reduced pressure. Chloroform (CHCl₃), hexane, diethyl ether, hydrochloric acid (HCl), potassium carbonate (K₂CO₃), cesium carbonate (Cs₂CO₃), tetrabutylammonium bromide (TBAB), 4-(methylthio)phenol, 1,2-dibromoethane, tri(4-hydroxyphenyl)methane (HPM), 2,2-bis(4-hydroxyphenyl)propane (BisA), di(4-hydroxyphenyl) ether (HPE), iodomethane (stabilized with Copper chip), silver trifluoromethanesulfonate, and propylene glycol monomethyl ether (PGME) were used as commercially available.

2.2 Measurements

Infrared (IR) spectra were taken with a JASCO FT/IR4200. The ¹H-NMR spectra were recorded on JEOL ECS-400K (400 MHz for ¹H-NMR) instruments in DMSO-d₆ and CDCl₃ with Me₄Si (TMS) as an internal standard. Thermal analysis was performed on a Shimadzu thermogravimetric analyzer (TGA) TGA-50/50H at a heating rate of 10 °C/min under nitrogen.

2.3 Condensation reaction of 4-(methylthio)phenol and 1,2-dibromoethane [synthesis of 4-bromoethoxyphenyl methyl sulfide (BEPMS)]

Typical procedure: A solution of 4-(methylthio)phenol (22.0 mmol, 3.12 g), K₂CO₃ (85.0 mmol, 11.71 g), in acetonitrile (75 mL) was stirred at 60 °C for 2 h. Then, 1,2-dibromoethane (69.0 mmol, 12.9 g) was added, and the reaction mixture was stirred at 60 °C for 24 h. After completion of the reaction, K₂CO₃ was separated from the reaction mixture by filtration on a membrane filter (Millipore LAWPO 4700 pore size 0.45 µm) and the resultant filtrate was evaporated under a rotary evaporator. The pure crystalline white solid of BEPMS was obtained after the purification of reaction mixture through silica gel column chromatography (Eluent: chloroform).

Yield = 1.43 g (28 %). IR (KBr, cm⁻¹): 2916 (ν -CH₂- of methylene), 1492 (ν C=C of aromatic), 1249 (ν -S-CH₃ of sulfide). ¹H-NMR (400 MHz, CDCl₃, TMS) δ (ppm): 2.38 (s, 3H, -CH₃), 3.74 (t, 2H, J = 5.6 Hz, -CH₂-), 4.24 (t, 2H, J = 5.6 Hz, -CH₂-), 6.89 - 7.19 (m, 4H, aromatic H).

2.4 Condensation reaction of BEPMS and HPM (synthesis of HPM-BEPMS)

Typical procedure: A solution of HPM (0.5 mmol, 0.146 g), tetrabutylammonium bromide (TBAB) (0.2 mmol, 0.064 g), and Cs₂CO₃ (2.0 mmol, 0.651 g), in DMF (7.0 mL) was stirred at 80 °C for 2 h. Then, BEPMS (2.0 mmol, 0.493 g) was added, and the reaction mixture was stirred at 80 °C for 24 h. The resulting mixture was poured into a large amount of 0.1 N hydrogen chloride solution to precipitate a solid, which was collected by filtration on a membrane filter (Millipore LAWPO 4700 pore size 0.45 µm) and washed with water. The obtained product was dried in vacuo at 60 °C for 24 h to afford a cream powder. Yield = 0.34 g (85 %). IR (KBr, cm⁻¹): 2916 (ν-CH₂- of methylene), 1492 (ν C=C of aromatic), 1239 (ν -S-CH₃ of sulfide). ¹H-NMR (400 MHz, CDCl₃, TMS) δ (ppm): 2.43 (s, 3H, -CH₃), 4.28 (s, 12H, -CH₂-), 5.40 (s, 1H, >CH-), 6.84 - 7.27 (m, 24H, aromatic H).

2.5 Condensation reaction of BEPMS and BisA (synthesis of BisA-BEPMS)

Reaction of BEPMS and BisA was carried out in the same way for the reaction of BEPMS and HPM. Yield = 0.85 g (80 %). IR (KBr, cm⁻¹): 2924 (ν -CH₂- of methylene), 1494 (ν C=C of aromatic), 1240 (ν -S-CH₃ of sulfide). ¹H-NMR (400 MHz, CDCl₃, TMS) δ (ppm): 1.62 (s, 6H, >CH₂-), 2.43 (s, 6H-CH₃), 4.27 (s, 8H, -CH₂-), 5.40 (s, 1H, >CH-), 6.84 - 7.27 (m, 16H, aromatic H).

2.6 Condensation reaction of BEPMS and BisAF
(synthesis of BisAF-BEPMS)

Reaction of BEPMS and BisAF was carried out in the same way for the reaction of BEPMS and HPM. Yield = 0.60 g (47 %). IR (KBr, cm⁻¹): 2924 (ν -CH₂- of methylene), 1494 (ν C=O of aromatic), 1240 (ν -S-CH₃ of sulfide). ¹H-NMR (400 MHz, CDCl₃, TMS) δ (ppm): 2.44 (s, 6H, -CH₃), 4.33 (s, 8H, -CH₂-), 6.88 - 7.34 (m, 16H, aromatic H).

2.7 Condensation reaction of BEPMS and HPE (synthesis of HPE-BEPMS)

Reaction of BEPMS and HPE was carried out in the same way for the reaction of BEPMS and HPM. Yield = 0.70 g (69 %). IR (KBr, cm⁻¹): 2924 (ν -CH₂- of methylene), 1494 (ν C=O of aromatic), 1240 (ν -S-CH₃ of sulfide). ¹H-NMR (400 MHz, CDCl₃, TMS) δ (ppm): 2.45 (s, 6H, -CH₃), 4.29 (s, 8H, -CH₂-), 6.86 - 7.28 (m, 16H, aromatic H).

2.8 Condensation reaction of TDP and BEPMS (synthesis of TDP-BEPMS)

Reaction of TDP and BEPMS was carried out in the same way for the reaction of BEPMS and HPM. Yield = 1.30 g (84 %). IR (KBr, cm⁻¹): 2921 (ν -CH₂- of methylene), 1490 (ν C=O of aromatic), 1238 (ν -S-CH₃ of sulfide). ¹H-NMR (400 MHz, CDCl₃, TMS) δ (ppm): 2.38 (s, 6H, -CH₃), 4.25 (s, 8H, -CH₂-), 6.91 - 7.28 (m, 16H, aromatic H).

2.9 Synthesis of HPM-BEPMSion

Typical procedure: A solution of HPM-BEPMS (0.10 mmol, 0.079 g) and silver trifluoromethane sulfonate (0.40 mmol, 0.10 g) in acetonitrile (5.0 mL) was stirred at room temperature. Then methyl iodide (0.4 mmol, 0.025 ml) added drop wise to the above reaction mixture over a period of 10min for 24 h in dark conditions. The resulting mixture was separated with membrane filter (Millipore LAWPO 4700 pore size 0.45 µm) and the obtained filtrate was evaporated under a rotary evaporator to obtain the solid HPM-BEPMSion. Yield = 0.103 g (81 %). IR (KBr, cm⁻¹): 2979 (ν C-H of methyl), 1725 (ν C=O of ester), 1205 (ν C-O of ether). ¹H-NMR (400 MHz, DMSO-d₆, TMS) δ (ppm): 3.17 (s, 9H, -CH₃), 4.33 (d, 12H, J = 8Hz, -CH₂-), 5.42 (s, >CH⁻), 6.86 - 7.98 (m, 24H, aromatic H).

2.10 Synthesis of BisA-BEPMSion

Reaction of BisA-BEPMS was carried out in the same way for the reaction of HPM-BEPMSion. Yield = 0.75 g (95 %). IR (KBr, cm⁻¹): 2935 (ν -CH₂- of methylene), 1499 (ν C=O of aromatic), 1255 (ν -S-CH₃ of sulfide). ¹H-NMR (400 MHz, DMSO-d₆, TMS) δ (ppm): 1.52 (s, 6H, -CH₃), 3.14 (s, 6H, -CH₃), 4.33 (d, 8H, J = 8Hz, -CH₂-), 6.60 - 7.96 (m, 16H, aromatic H).

2.11 Synthesis of BisAF-BEPMSion

Reaction of BisAF-BEPMS was carried out in the same way for the reaction of HPM-BEPMSion. Yield = 0.40 g (62 %). IR (KBr, cm⁻¹): 2935 (ν -CH₂- of methylene), 1499 (ν C=O of aromatic), 1255 (ν -S-CH₃ of sulfide). ¹H-NMR (400 MHz, DMSO-d₆, TMS) δ (ppm): 3.18 (s, 6H, -CH₃), 4.39 (d, 8H, J = 8Hz, -CH₂-), 7.04 - 7.97 (m, 16H, aromatic H).

2.12 Synthesis of HPE-BEPMSion

Reaction of HPE-BEPMS was carried out in the same way for the reaction of HPM-BEPMSion. Yield = 0.42 g (50 %). IR (KBr, cm⁻¹): 2924 (ν -CH₂- of methylene), 1499 (ν C=O of aromatic), 1255 (ν -S-CH₃ of sulfide). ¹H-NMR (400 MHz, DMSO-d₆, TMS) δ (ppm): 3.18 (s, 6H, -CH₃), 4.34 (d, 8H, J = 8Hz, -CH₂-), 6.71 - 7.98 (m, 16H, aromatic H).

2.13 Synthesis of TDP-BEPMSion

Reaction of TDP-BEPMS was carried out in the same way for the reaction of HPM-BEPMSion. Yield = 0.80 g (82 %). IR (KBr, cm⁻¹): 2939 (ν -CH₂- of methylene), 1495 (ν C=O of aromatic), 1253 (ν -S-CH₃ of sulfide). ¹H-NMR (400 MHz, DMSO-d₆, TMS) δ (ppm): 3.18 (s, 6H, -CH₃), 4.30 - 4.42 (m, 8H, -CH₂-), 6.92 - 7.97 (m, 16H, aromatic H).

2.14. Resist sensitivity

Solutions of synthesized molecular resist materials were filtered through a 0.20 µm PTFE syringe filter prior to spin-coating on 6-inch silicon wafers. Spin-coating was performed at 3300 rpm for 30 sec. to form thin films on the silicon wafers. Then these spin-coated films were prebaked at 90 °C for 60 sec. The film thickness was adjusted to 50 nm. The resulting films were exposed to EUV lithography (energetic EQ-10M). The area of exposure was approximately 1 × 1 cm². After the exposure, the silicon wafer was developed by dipping in deionized water at room temperature for 30 sec. then rinsed in deionized water before drying. The resist film thickness was measured with an ellipsometry to obtain sensitivity curves.
3. Results and discussion

3.1. Synthesis of molecular n-CAR materials

HPM-BEPMS\textsubscript{ion}, BisA-BEPMS\textsubscript{ion}, BisAF-BEPMS\textsubscript{ion}, HPE-BEPMS\textsubscript{ion}, and TDP-BEPMS\textsubscript{ion}

Condensation reaction of HPM and BEPMS was examined using cesium carbonate as a base in DMF at 80 °C for 24 h in the presence of TBAB as a catalyst, to give a corresponding compound HPM-BEPMS containing sulfide moieties in 85 % yield. Its structure was confirmed by \textsuperscript{1}H-NMR and FT-IR spectroscopy. In the same way, the reaction of various bisphenols (BisA, BisAF, HPE, and TDP) and BEPMS was performed to give the corresponding compounds BisA-BEPMS, BisAF-BEPMS, HPE-BEPMS, and TDP-BEPMS in 47 ~ 84 % yields. Next, the reaction of HPM-BEPMS with silver trifluoromethanesulfonate and iodomethane was carried out in acetonitrile at room temperature for 24 h, to give a corresponding compound HPM-BEPMS\textsubscript{ion} in 81 % yield. Its structure was confirmed by \textsuperscript{1}H-NMR and FT-IR spectroscopy. In the same way, BisA-BEPMS\textsubscript{ion}, BisAF-BEPMS\textsubscript{ion}, HPE-BEPMS\textsubscript{ion}, and TDP-BEPMS\textsubscript{ion} were synthesized in 50 ~ 95 % yields. These synthetic procedures are illustrated in Scheme 1.

3.2. Physical properties (solubility, film-forming ability, and thermal stability)

Physical properties of the synthesized molecular n-CAR materials HPM-BEPMS\textsubscript{ion}, BisA-BEPMS\textsubscript{ion}, BisAF-BEPMS\textsubscript{ion}, HPE-BEPMS\textsubscript{ion}, and TDP-BEPMS\textsubscript{ion} relevant to their applicability as EUV-resist materials were examined.

![Scheme 1. Synthetic procedure of molecular n-CAR materials HPM-BEPMS\textsubscript{ion}, BisA-BEPMS\textsubscript{ion}, BisAF-BEPMS\textsubscript{ion}, HPE-BEPMS\textsubscript{ion}, and TDP-BEPMS\textsubscript{ion}](image-url)
Solubility. HPM-BEPMSion, BisA-BEPMSion, BisAF-BEPMSion, HPE-BEPMSion, and TDP-BEPMSion were soluble in polar solvents such as water, DMSO, DMF, NMP, methanol, and acetone. Furthermore, they were soluble in PGME, which is usually used when the resist materials are spin-coated on the silicon wafer. They were also insoluble in non-polar organic solvents such as ethyl acetate, ethyl ether, CHCl3, toluene, hexane. These are summarized in Table 1.

Film-forming ability. The film-forming ability was examined by spin coating a solution of synthesized molecular resist materials 50 mg in PGME 1.0 ml on silicon wafer, and drying the wafer in vacuo at room temperature. All molecular resist materials showed good film-forming abilities.

Thermal stability. The thermal properties of the synthesized molecular resist materials were examined by means of TGA. The initial weight loss temperature was measured by means of TGA, to be in the range between 190 and 280 °C, which are also summarized in Table 1. These are adequate for application as photo-resist materials.

3.3. Resist sensitivity

Resist sensitivity of molecular n-CAR materials HPM-BEPMSion, BisA-BEPMSion, BisAF-BEPMSion, HPE-BEPMSion, and TDP-BEPMSion were examined using EUV exposure tool. Solutions of these compounds in PGME were spin-coated on silicon wafers to prepare thin films of about 50 ~ 80 nm thickness.

Next, the silicon wafer allows development by dipping in deionized water at room temperature for 30 sec. The value of the thickness of remained thin film was measured by means of ellipsometer after the lithography process. These results are illustrated in Fig. 1.

The thin films of HPM-BEPMSion, BisA-BEPMSion, BisAF-BEPMSion, and HPE-BEPMSion were fully insoluble in deionized water after 20, 18, 30, and 30 mJ/cm², respectively, i.e., E100 (value of resist sensitivity)’s were in the range between 18 and 30 mJ/cm². Furthermore, the photoresist contrast values γ could be extracted from these sensitivity curves and their values of HPM-BEPMSion, BisA-BEPMSion, BisAF-BEPMSion, and HPE-BEPMSion were 20.75, 6.91, 4.60 and 20.41 respectively. These are also summarized in Table 2. These results indicate that HPM-BEPMSion, BisA-BEPMSion, BisAF-BEPMSion, HPE-BEPMSion are applicable to negative type EUV.

Table 1. Solubility and thermal stability of molecular n-CAR materials HPM-BEPMSion, BisA-BEPMSion, BisAF-BEPMSion, HPE-BEPMSion, and TDP-BEPMSion

| (R)-BEPMSion | HPM | BisA | BisAF | HPE | TDP |
|--------------|-----|------|-------|-----|-----|
| water        | ++  | ++   | ++    | ++  | ++  |
| DMSO         | ++  | ++   | ++    | ++  | ++  |
| NMP          | ++  | ++   | ++    | ++  | ++  |
| DMF          | ++  | ++   | ++    | ++  | ++  |
| methanol     | ++  | ++   | ++    | ++  | ++  |
| acetone      | ++  | ++   | ++    | ++  | ++  |
| THF          | --  | --   | --    | --  | --  |
| ethyl acetate| --  | --   | --    | --  | --  |
| diethyl ether| --  | --   | --    | --  | --  |
| chloroform   | --  | --   | --    | --  | --  |
| toluene      | --  | --   | --    | --  | --  |
| hexane       | --  | --   | --    | --  | --  |
| PGME         | ++  | ++   | ++    | ++  | ++  |
| PGMEA        | --  | ++   | --    | ++  | ++  |
| 2.38wt% TMAH | ++  | ++   | ++    | ++  | ++  |

Table 2. E100 (value of resist sensitivity) and contrast value γ of HPM-BEPMSion, BisA-BEPMSion, BisAF-BEPMSion, HPE-BEPMSion, and TDP-BEPMSion

|            | E100 | γ    |
|------------|------|------|
| HPM-BEPMSion | 20   | 20.75|
| BisA-BEPMSion | 18   | 6.91 |
| BisAF-BEPMSion | 30   | 4.6  |
| HPE-BEPMSion  | 30   | 20.41|
| TDP-BEPMSion  | -    | -    |

Notes:

- ++: Soluble at room temperature. --: Insoluble in at room temperature. PEGME; Propylene glycol monomethyl ether. PGMEA; Propylene glycol monomethyl ether acetate. TMAH; Tetramethyl ammonium hydroxide.
- Td: Initial thermal decomposition temperature.
- E100: 20.75, 6.91, 4.60 and 20.41.
- γ: 20.75, 6.91, 4.60 and 20.41.
- a: Not determined.
resist materials. However, a good sensitivity curve could not be obtained in the case of TDP-BEPMSion. Presumably because of that transparency of TDP-BEPMSion might be low due to tellurium, which has high EUV absorption efficiency\(^{14,15}\).

4. Conclusion
In summary, we examined the condensation reaction of trisphenol (HPM) and various bisphenols (BisA, BisAF, HPE, and TDP) with BEPMS, and the corresponding compounds (HPM-BEPMS, BisA-BEPMS, BisAF-BEPMS, HPE-BEPMS, and TDP-BEPMS) containing sulfide moieties were obtained. The synthesized HPM-BEPMS, BisA-BEPMS, BisAF-BEPMS, HPE-BEPMS, and TDP-BEPMS were reacted with silver trifluoromethanesulfonate and iodomethane to give the molecular n-CAR materials HPM-BEPMSion, BisA-BEPMSion, BisAF-BEPMSion, HPE-BEPMSion, and TDP-BEPMSion. Their physical properties (solubility, film-forming ability, and thermal stability) could show good results, meaning that they are adequate for application as photo-resist materials. Furthermore, resist sensitivity of HPM-BEPMSion, BisA-BEPMSion, BisAF-BEPMSion, HPE-BEPMSion, and TDP-BEPMSion were examined using EUV exposure tool. All compounds except for TDP-BEPMSion could show the applicable to negative-type resist material, and their sensitivities (\(E_{100}\)) were in the range between 18 and 30 mJ/cm\(^2\).

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