Synthesis and Property of Tellurium-Containing Molecular Resist Materials for Extreme Ultraviolet Lithography System

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We examined the synthesis and resist properties of tellurium-containing molecular resist materials. By the condensation reaction of anisol, phenol, and 2-phenylphenol with tellurium tetrachloride (TeCl4), dichloro di(4-hydroxyphenyl) telluride (CHPT), dichloro di(4-hydroxy-3-phenylbenz) telluride (CHBT), di(4-hydroxyphenyl) telluride (HPT), and di(4-hydroxy-3-phenylbenz) telluride (HBT) were synthesized. These were reacted with 2-methyl-2-adamantyl bromo acetate, yielding corresponding compounds CHPT-AD, CHBT-AD, HPT-AD, and HBT-AD, respectively. By the examination of resist properties (thickness loss property, resist sensitivity, and etching durability), CHBT-AD could be a good candidate for higher resolution EUV resist material.

Keywords: Metal resist, Molecular resist, Tellurium, Extreme ultraviolet light

1. Introduction

Photoresist materials have been developed based on polymers containing photo-reactive groups in their side chains or main chains for KrF and ArF resist systems [1]. Recently, the resist patterns resolution of about 20 nm have been developed for an ArF immersion resist system [2]. Furthermore, in order to improve the resolution of the resist pattern, development of new exposure systems and resist materials have been investigated. Among them, extreme ultraviolet (EUV) light is attracting attention as potential candidate for a new exposure system [3]. In this system, development of a 10 nm node resist pattern has been required and there are certain issues that must be overcome to realize the EUV photo-resist system. In order to construct higher resolution, it is necessary to increase the sensitivity in the exposure dose. At the present time, a chemically amplified resist system is considered to be most effective as a method for increasing sensitivity [4]. When the node width of resist pattern is reduced by increasing exposure dose, the resist pattern roughness (Line Edge Roughness: LER or Line Width Roughness: LWR) becomes worse significantly. That is, the relationship among the resolution of resist pattern, sensitivity of exposure dose, and LER (LWR) is a trade-off.

While the molecular resist material has been considered as a higher resolution resist material and might overcome the trade-off issue as mentioned above, presumably because of that they have no molecular weight distribution and smaller sizes compared to those of polymers. Then various molecular resist materials based on phenol resins,
calixarenes, noria, and fullerene were synthesized and their resist properties were examined [5]. However, no resist material has yet been developed that completely meets the requirements to offer high resolution EUV resist pattern.

Very recently, synthesis of some metal-containing resist materials have been reported, anticipating that they can show good etching property, higher resist-sensitivity, and higher resolution resist property using EUV resist system [6-10]. In our previous report, we designed a tellurium-containing polymer with pendant adamantly ester groups, anticipating that they could show good resist properties in EUV exposure tool. However, their synthetic methods are not suitable for industrial application [11].

In this paper, we examined the synthesis of certain tellurium-containing molecular resist materials and their resist properties (thickness loss property, resist sensitivity, and etching durability) were examined.

2. Experimental

2.1. Materials

1-Methyl-2-pyrrolidone (NMP) was dried with calcium hydride (CaH2) and purified by distillation under reduced pressure. Tetrahydrofuran (THF) was dried with sodium and benzophenone and purified by distillation under nitrogen atmosphere. Carbon tetrachloride (CCl4), chloroform (CHCl3), dichloromethane (CH2Cl2), ethyl acetate, hexane, acetonitrile, potassium carbonate (K2CO3), magnesium sulfate (MgSO4), tellurium tetrachloride (TeCl4), anisole, phenol, 2-phenylphenol, sodium ascorbate, copper, 2-methyl-2-adamantyl bromo acetate (ADBAc), tetrabutylammonium bromide (TBAB), propyleneglycol methyl ether acetate (PGMEA), tetrachloride (TeCl4) (Synthesis of CHPT), boron tribromide (BBr3), and tetramethylammonium hydroxide (TMAH) 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 with Me4Si (TMS) as an internal standard for 1H NMR. 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 anisol and tellurium tetrachloride (TeCl4) (Synthesis of CMPT)

Typical procedure: A mixture of anisol (32.4 g, 300 mmol) and tellurium tetrachloride (TeCl4) (8.03 g, 30 mmol) was stirred at 160 °C for 6 h. Then, the resulting mixture was poured into large amount of hexane to precipitate the solid, which was dried in vacuo at 25 °C for 24 h. The obtained solid was purified by recrystallization using acetonitrile. The resulting solid was precipitated and was dried over in vacuo at 25 °C, to give corresponding red solid [dichloro di(4-methoxyphenyl) telluride (CMPT)]. The structure was confirmed by IR and 1H NMR spectroscopy. Yield = 3.99 g (40%). MP = 182.7 ~ 184.2 °C. IR (KBr, cm-1) : 3000 (ν C-H), 2838 (ν C-H of methoxy), 1400 ~ 1500 (ν C of aromatic), 1263 (ν C-O of methoxy). 1H NMR (400 MHz, DMSO-d6, TMS) δ (ppm) : 7.15 (d, J = 60 Hz, 4H, aromatic H), 7.90 (d, J = 60 Hz, 4H, aromatic H).

2.4. Reaction of CMPT and boron tribromide (BBr3) (Synthesis of CHPT)

Typical procedure: CMPT (3.8 g, 9.60 mmol) was dissolved in CH2Cl2 and 50 mL of BBr3 was added slowly. The resulting solution was stirred at -20 °C for 48 h. Then, the mixture was poured into large amount of 1N HCl aq. to precipitate the solid, which was purified by recrystallization using the mixture of ethyl acetate and hexane. The resulting solid was precipitated and was dried over in vacuo at 25 °C, to give corresponding colorless solid [dichloro di(4-hydroxyphenyl) telluride (CHPT)]. Yield = 1.44 g (39%). MP = 212.0 ~ 214.4 °C. IR (KBr, cm-1) : 3400 (ν -OH), 2835 (ν -OH), 7.51 (d, J = 60 Hz, 4H, aromatic H), 7.10 (d, J = 60 Hz, 4H, aromatic H).

2.5. Condensation reaction of 2-phenylphenol and TeCl4 (Synthesis of CHTB)

Typical procedure: A mixture of 2-phenylphenol (0.24 g, 1.4 mmol) and TeCl4 (0.27 g, 1.0 mmol) in CCl4 (5 mL) was stirred under reflux for 6 h. Then, insoluble product was collected by filtration with a membrane filter (Millipore LAWPO 4700 pore size 0.45 μm), and washed with CH2Cl2. The obtained product was dried in vacuo at 25 °C for 24 h to afford a light yellow compound. This product was mixed with 2-phenylphenol (1.70 g, 10 mmol) and was stirred at 170 °C for 24 h. The resulting mixture was dissolved in ethyl acetate and poured
into large amount of hexane to precipitate the red solid, which was purified by recrystallization using the mixture of CHCl₃ and hexane. The resulting solid was precipitated and was dried over in vacuo at 25 °C, to give corresponding solid [dichloro di(4-hydroxy-3-phenylbenz) telluride (CHPT)]. Yield = 0.20 g (3.0%). IR (KBr, cm⁻¹): 3350 (ν O-H), 1300 ~ 1500 (ν C-C of aromatic). ¹H NMR (400 MHz, DMSO-d₆, TMS) δ (ppm): 7.01 ~ 8.51 (m, 16H, aromatic H), 10.6 (s, 2H, -OH).

2.6. Condensation reaction of 2-phenylphenol and TeCl₄ (Synthesis of CHPT)

**Typical procedure:** A mixture of phenol (7.62 g, 42 mmol) and TeCl₄ (8.16 g, 30 mmol) in CCl₄ (24 mL) was stirred under reflux for 3 h. Then, the resulting precipitate was filtered and washed with CH₂Cl₂, to obtain a light yellow solid. The resulting solid was prepared in the mixture of ethyl acetate (30 mL) and aqueous solution of sodium ascorbate (20.1 g, 99 mmol) in water (35 mL) was added. The resulting mixture was stirred at room temperature. After 6 h, ethyl acetate (30 mL) was added and the organic phase was washed with water 15 times. The combined organic phase was dried over anhydrous MgSO₄ for 30 min, and removed solvent by evaporator. Next, copper powder (11.4 g, 180 mmol) was added in the obtained solid in ethyl acetate. The resulting mixture was stirred under reflux for 24 h. After filtration of insoluble part, the solution was passed through Celite (40 mm × 100 mm) and resulting solution was concentrated by means of rotary evaporator to obtain a solid CHPT-AD. Yield = 0.88 g (42%) IR (KBr, cm⁻¹): 3400 (ν O-H), 1500 (ν C-H of aromatic), 700 (ν C-C of aromatic). ¹H NMR (400 MHz, DMSO-d₆, TMS) δ (ppm): 6.82 ~ 7.84 (m, 16H, aromatic H), 9.81 (s, 2H, -OH).

2.7. Condensation reaction of 2-phenylphenol and TeCl₄ in the presence of sodium ascorbate (Synthesis of HBT)

**Typical procedure:** Reaction of 2-phenylphenol (0.24 g, 1.4 mmol) and TeCl₄ (0.27 g, 1.0 mmol) was carried out in the same way as the reaction of phenol and TeCl₄ to give [di(4-hydroxy-3-phenylbenz) telluride (HBT)]. Yield = 0.19 g (42%) IR (KBr, cm⁻¹): 3400 (ν O-H), 1500 (ν C-H of aromatic), 700 (ν C-C of aromatic). ¹H NMR (400 MHz, DMSO-d₆, TMS) δ (ppm): 7.01 ~ 8.51 (m, 16H, aromatic H), 10.6 (s, 2H, -OH).

2.8. Reaction of CHPT and ADBAc (Synthesis of CHPT-AD)

**Typical procedure:** A mixture of CHPT (0.39 g, 1.0 mmol), K₂CO₃ (0.22 g, 2.2 mmol) using TBAB (0.064 g, 0.2 mmol) as a catalyst in NMP (5.0 mL) was stirred at 25 °C for 2 h. Then, ADBAc (0.63 g, 2.2 mmol) was added in the resulting solution and was stirred at 100 °C for 24 h under nitrogen atmosphere. The resulting mixture was poured into large amount of 1N HCl aq. to precipitate the solid, which was dried in vacuo at 25 °C for 24 h. The residue was purified by silica gel column chromatography eluted with mixture of ethyl acetate and hexane (4/1), followed by concentration using rotary evaporator to obtain a solid CHPT-AD. Yield = 0.05 g (6.0%). IR (KBr, cm⁻¹): 2900 (ν C-H), 1700 (ν C=O of ester), 1500 (ν C-H of aromatic), 1300 (ν C-O of ether). ¹H NMR (400 MHz, DMSO-d₆, TMS) δ (ppm): 1.20 ~ 3.63 (br m, 34H, -CH₃, -CH₂-, >CH- of adamantyl), 4.62 (s, 4H, O-CH₂-C-), 6.81 (d, J = 40 Hz, 4H, aromatic H), 7.72 (d, J = 40 Hz, 4H, aromatic H), 6.82 ~ 7.84 (m, 16H, aromatic H), 9.81 (s, 2H, -OH).

2.9. Reaction of CHBT and ADBAc (Synthesis of CHBT-AD)

**Typical procedure:** Reaction of CHBT (0.53 g, 1.0 mmol) and ADBAc (0.63 g, 2.2 mmol) was carried out in the same way as the synthesis of CHPT-AD. Yield = 0.52 g (55%). IR (KBr, cm⁻¹): 2900 (ν C-H), 1753 (ν C=O of ester), 1500 and 800 (ν C-H of aromatic). ¹H NMR (400 MHz, DMSO-d₆, TMS) δ (ppm): 1.10 ~ 2.52 (br m, 34H, -CH₃, -CH₂-, >CH- of adamantyl), 4.80 (s, 4H, O-CH₂-C-), 7.01 ~ 8.02 (m, 16H, aromatic H).

2.10. Reaction of HPT and ADBAc (Synthesis of HPT-AD)

**Typical procedure:** Reaction of HPT (1.58 g, 5.0 mmol) and ADBAc (4.29 g, 15 mmol) was carried out out in the same way as the synthesis of CHPT-AD. Yield = 1.02 g (74%). IR (KBr, cm⁻¹): 2900 (ν C-H), 1753 (ν C=O of ester), 1487 (ν C=C of aromatic), 1103 (ν C-O of ester). ¹H NMR (400 MHz, DMSO-d₆, TMS) δ (ppm): 1.43 ~ 2.17 (br m, 34H, -CH₃, -CH₂-, >CH- of adamantyl), 4.73 (s, 4H, O-CH₂-C-), 6.82 (d, J = 40 Hz, 4H, aromatic proton).
7.56 (d, J = 40 Hz, 4H, aromatic proton).

2.11. Reaction of HBT and ADBAc (Synthesis of HBT-AD)  
Typical procedure: Reaction of HBT (0.68 g, 1.5 mmol) and ADBAc (0.94 g, 3.3 mmol) was carried out in the same way as the synthesis of CHPT-AD. Yield = 0.69 g (53%). IR (KBr, cm⁻¹): 2900 (ν C-H), 1700 (ν C=O of ester), 1300 (ν C=C of aromatic), 1101 (ν C-O of ester). ¹H NMR (400 MHz, DMSO-d₆, TMS) δ (ppm): 1.20 ~ 2.20 (br m, 34H, -CH₃, -CH₂-, >CH- of adamantyl), 4.50 (s, 4H, O-CH₂-C-), 6.70 ~ 7.71 (m, 16H, aromatic proton).

2.12. Thickness loss property on the silicon wafer after soaking in tetramethylammonium hydroxide (TMAH) aq.

The solutions of CHPT-AD, CHBT-AD, HPT-AD, and HBT-AD in propylene glycol monomethyl ether acetate (PEGMEA) were spin-coated on the silicon wafer to prepare corresponding thin films with about 50 nm thickness. The value of thickness of the thin films was determined by ellipsometry before and after soaking in TMAH aq. for 30 sec.

2.13. Resist sensitivity

The resist solutions were filtered through a 0.20 μm PTFE syringe filter prior to spin-coating on silicon wafers which were primed with hexamethyldisilazane (HMDS). Spin-coating was performed at 3000 rpm for 30 s to form thin films on the silicon wafers. Then these spin-coated films were prebaked at 90 °C for 60 s. The film thickness was adjusted to about 100 nm. The resulting films were exposed to EUV lithography (energetic EQ-10M) [12]. The area of exposure was approximately 1 × 1 cm². After the exposure, they were developed by dipping in TMAH solution at 23 °C for 30 s and then rinsed in deionized water before drying. The resist film thickness was measured with an ET200 surface profiler to obtain sensitivity curves.

2.14. Etching durability

The etching rates of the thin films on the silicon wafers were determined using a reactive ion etching (RIE) plasma process. The plasma conditions were a 15 sccm CF₄ gas flow, a 5 sccm Ar gas flow, and an RF power of 100 W. The pressure in the process chamber was 1.0 Pa.

3. Results and discussion

3.1. Synthesis of tellurium-containing compounds CHPT and CHBT

The reaction of anisol and tellurium tetrachloride (TeCl₄) was carried out at 160 °C in bulk for 6 h, to give dichloro di(4-methoxyphenyl) telluride (CMPT) in 40% yield. Next, the synthesized CMPT was treated with BBr₃ to afford dichloro di(4-hydroxyphenyl) telluride (CHPT) in 39% yield (Scheme 1[A]). Their structures were confirmed by ¹H NMR and IR spectroscopy. Furthermore, reaction of 2-phenylphenol and TeCl₄ was examined by the two-step reactions. In the first step, an intermediate product could be obtained, and target product dichloro di(4-hydroxy-3-phenylbenz)telluride (CHBT) could be synthesized in 12% yield by the second step reaction (Scheme 1[B]).

3.2. Synthesis of tellurium-containing compounds HPT and HBT

Reaction of phenol and TeCl₄ was carried out using sodium ascorbate and copper powder, to give the di-(4-hydroxyphenyl) telluride (HPT) in 3% yield. In the same way, the reaction of 2-phenylphenol and TeCl₄ afforded the corresponding compound di(4-hydroxy-3-phenylbenz) telluride (HBT) in 42% yield (Scheme 2).
3.3. Synthesis of tellurium-containing compounds containing adamantyl ester groups (CHPT-AD, CHBT-AD, HPT-AD, and HBT-AD)

Reaction of CHPT and ADBAc was carried out using K₂CO₃ as a base in the presence of TBAB as a catalyst, yielding a corresponding compound containing adamantyl ester groups CHPT-AD in 6.0% yield. In the same way for the synthesis of CHPT-AD, CHBT, HPT and HBT were reacted with ADBAc, to give corresponding CHBT-AD, HPT-AD, HBT-AD in 55, 24, and 53% yields, respectively (Scheme 3 [A] and [B]).

![Scheme 3. Synthesis of CHPT-AD, CHBT-AD, HPT-AD, and HBT-AD.](image)

Furthermore, thermal stability of these synthesized compounds CHPT-AD, CHBT-AD, HPT-AD, HBT-AD was determined by thermogravimetric analysis (TGA), and their initial decomposition temperatures (T_d) were in the range between 106 and 174 °C. These were also soluble in common organic solvents such as DMSO, DMF, THF, CHC₁₃, propylene glycol monomethyl ether acetate (PGMEA), and propylene glycol monomethyl ether (PEGME). Their film-forming ability was confirmed by the spin-coating on silicon wafers from the solutions in PGMEA, and it was observed that corresponding thin films with about 100 nm could be obtained.

3.4. Thickness loss property on the silicon wafer after soaking in 2.38 wt% TMAH aq. solution

Next, the value of thickness of the thin films on the silicon wafer was determined by ellipsometry before and after soaking in 2.38 wt% TMAH aq. for 30 sec., anticipating that they are applicable to positive-type resist materials. These results are summarized in Table 1. The ratios of decrease of the thickness of CHPT-AD and HPT-AD were 100 and 96%, respectively. On the other hand, these of CHBT-AD and HBT-AD were 4.0% and 5.0%, respectively. These results mean that CHBT-AD and HBT-AD can be used as positive resist materials with 2.38 wt% TMAH aq. as the developer. This means that the thickness loss property was consistent with the structure of the resist materials, i.e., phenylbenz moieties could improve their properties.

| Compounds     | CHPT-AD | CHBT-AD | HPT-AD | HBT-AD |
|---------------|---------|---------|--------|--------|
| Thickness lost | 100%    | 4.0%    | 96%    | 5.0%   |

*a* Determined by ellipsometry.

3.5. Resist sensitivity

From the mentioned above results on thickness loss property after soaking in 2.38 wt% TMAH aq., CHBT-AD and HBT-AD are applicable to positive-type photo lithography system. Then, their resist sensitivity was examined using an EUV exposure tool. Solutions of CHBT-AD and HBT-AD in the presence of 10 wt% of TPS-Nf as a PAG were spin-coated on silicon wafers to prepare thin films of about 66 nm thickness in the absence of a quencher. The postexposure baking (PEB) temperature and time were 90 °C and 90 s, respectively. The thickness of the films was measured with an ellipsometer after the lithography process. These results are shown in Fig. 1.
Although, thin film of HBT-AD remained fully after the lithography process with 10 mJ/cm² EUV-exposure dose, the thin film of CHBT-AD was fully soluble in aqueous alkaline solution after 4.0 mJ/cm² EUV-exposure dose, i.e., \(E_0\) (value of resist sensitivity) = 4.0 mJ/cm². Generally, an \(E_0\) value of less than 10 mJ/cm² is required for EUV lithography. Therefore, CHBT-AD could appear to have adequate resist sensitivity for application as EUV photoresist systems.

3.6. Etching durability

We next examined the etching durability of CHBT-AD, which showed the higher resist sensitivity using EUV exposure tool, as described above. The plasma conditions were 15 sccm CF₄ gas flow, 5 sccm Ar gas flow, and RF power of 100 W under 1.0 Pa pressure in the process chamber. Figure 2 shows the etching rates of thin films prepared from CHBT-AD, accompanied with poly(methyl methacrylate) (PMMA) and poly(hydroxystyrene) (PHS) as typical resist materials. The thin film of CHBT-AD showed exceptionable etching durability, similar to that of PHS. The values of etching rate (nm/min) were 38 (CHBT-AD), 97 (PMMA), and 36 (PHS), respectively.

![Fig. 2. Etching durability of the thin films on the silicon wafer prepared from CHBT-AD, poly(methyl methacrylate) (PMMA), and poly(hydroxystyrene) (PHS).](image)

**4. Conclusion**

In summary, we examined the condensation reaction of anisol, phenol, and 2-phenylphenol with tellurium tetrachloride (TeCl₄), yielding corresponding bisphenols CHPT-AD, CHBT-AD, HPT-AD, and HBT-AD containing tellurium and adamantyl groups. Their physical properties (solubility, film-forming ability, thermal stability) could show good results, indicating that they were applicable to positive-working resist materials. Furthermore, its resist properties (thickness loss property after soaking in 2.38 wt% TMAH aq. solution, resist sensitivity under EUV exposure tool, and etching durability using a reactive ion etching plasma process) were also examined and CHBT-AD could show good results, indicating that the CHBT-AD was good candidate for higher resolution EUV resist materials. Furthermore, patterning property of electron beam (EB) and EUV exposure tools are under investigation.

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