Synthesis and Property of Tellurium-Containing Polymer for Extreme Ultraviolet Resist Material

Mari Fukunaga¹, Hiroki Yamamoto², Takahiro Kozawa², Takeo Watanabe³,
and Hiroto Kudo^{1*}

¹*Faculty of Chemistry, Materials and Bioengineering, Kansai University, 3-3-35,
Yamate-cho, Suita-shi, Osaka, 564-8680, Japan*

²*Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka,
Ibaraki, Osaka 567-0047, Japan*

³*Center for EUVL, LASTI, University of Hyogo, 3-1-2 Kouto, Kamigori, Ako-gun,
Hyogo 678-1205, Japan*

*kudoh@kansai-u.ac.jp

Synthesis, physical properties, and resist properties of tellurium containing polymer with pendant adamantyl ester groups poly(Re-co-Te)-AD were examined, relevant to the application of resist material for extreme ultraviolet laser photolithography (EUVL) system. A tellurium containing polymer with pendant hydroxyl groups poly(Re-co-Te) was synthesized by the condensation reaction of resorcinol (Re) and tellurium tetrachloride (TeCl₄), followed by the condensation reaction with adamantyl bromo acetate to give a corresponding polymer poly(Re-co-Te)-AD. Their physical properties (solubility, film-forming ability, thermal stability) and resist properties (thickness loss property after soaking in 2.38 wt% TMAH aq. solution, out-gassing on EUV exposure tool, and resist sensitivity under EUV exposure tool) were also examined.

Keywords: Tellurium, Synthesis, Adamantyl ester, Extreme ultraviolet, Resist

1. Introduction

Development of a new resist material is an important key component of extreme ultraviolet laser lithography (EUVL) system. When designing resist materials for photo-lithography system, the transparency of the materials has been a key consideration in general. In the case of EUVL, the absorbance of the materials is independent of the molecular skeleton and can be calculated from the atomic composition [1,2]. Hydrogen, carbon, nitrogen, and oxygen show low absorptions, and many organic compounds have been synthesized and their resist properties were examined for EUVL system. However, very recently, some metal-containing materials have been used as a novel EUVL resist material, which the metal can show high absorptions of EUV laser. It is noteworthy that these metal-containing materials showed good etching property, higher resist-sensitivity, and higher resolution resist property using EUVL system [3-9].

In this paper, we designed a tellurium-containing polymer for EUVL resist material, due to its higher absorption of EUV laser. Engman et al. reported the condensation reaction of phenol and TeCl₄ was performed to give a di(4-hydroxyphenyl)telluride, i.e., phenol and TeCl₄ could perform as an A₁-type monomer and B₂-type monomer, respectively, as shown in Scheme 1 [A] [10]. Also, we examined the polycondensation reaction of resorcinol (Re) as a A₂-type monomer and TeCl₄ as a B₂-type monomer, yielding a tellurium-containing polymer poly(phenylene telluride) [poly(Re-co-Te)] with pendant hydroxyl groups, as shown in Scheme 1 [B]. Then, the reaction of poly(Re-co-Te) and adamantyl bromo acetate was performed to give a corresponding polymer [poly(Re-co-Te)-AD] with pendant adamantyl ester (AD) groups. Furthermore, physical properties and resist properties of poly(Re-co-Te)-AD were examined for the application of EUV-resist material.

Scheme 1. Condensation reaction of phenol and resorcinol with TeCl_4 .

2. Experimental

2.1. Synthesis of tellurium-containing polymers with pendant hydroxyl groups [poly(Re-co-Te)]

Typical procedure: A mixture of resorcinol (0.551 g, 5.0 mmol) and tellurium tetrachloride (TeCl_4) (4.04 g, 15 mmol) in CCl_4 was stirred under reflux for 24 h. Then, the resulting precipitate was filtered and washed with CH_2Cl_2 (40 mL), to obtain a solid. The resulting solid was prepared in the mixture of ethyl acetate (15 mL) and aqueous solution of sodium ascorbate (6.54 g, 33 mmol) in water (11.5 mL) was added. The resulting mixture was stirred at room temperature. After 24 h, ethyl acetate (30 mL) was added and the organic phase was washed with water 15 times. The combined organic phase was dried over with anhydrous MgSO_4 for 30 min, and removed solvent by evaporator. Next, copper powder (3.81 g, 60 mmol) was added in the obtained solid in ethyl acetate (15 mL). The resulting mixture was stirred under reflux for 24 h. After filtration of insoluble part, the solution was passed through Celite (40mm $\times$ 100 mm) and resulting solution was concentrated by means of rotary evaporator. Then, the obtained residue was poured into large amount of CHCl_3 to precipitate the solid, which was dried *in vacuo* at 25 °C for 24 h. The molecular weight of the product was estimated by means of SEC, and the structure was confirmed by IR spectroscopy and ^1H NMR spectroscopy. Yield = 0.90 g. IR (KBr, cm^{-1}): 3271 (ν O-H hydroxyl group), 1778 (ν C-H of aromatic), 1604 (ν C=C aromatic). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, TMS) δ (ppm): 6.17 ~ 7.24 (m, aromatic protons), 8.53 ~ 10.27 (m, -OH).

2.2. Synthesis of tellurium-containing polymer with pendant adamantyl ester groups

[poly(Re-co-Te)-AD]

Typical procedure: A mixture of poly(Re-co-Te) ($M_n = 2,400$, $M_w/M_n = 1.06$) (0.35 g), adamantyl bromo acetate (ADBAC) (0.95 g, 3.3 mmol), and K_2CO_3 (0.46 g, 3.3 mmol) using TBAB (0.032 g, 0.1 mmol) as a catalyst in NMP was stirred at 100 °C for 24 h. Then, the obtained residue was poured into large amount of 1 N HCl aq. to precipitate the solid, which was dried *in vacuo* at 25 °C for 24 h. The molecular weight of the product was estimated by means of SEC, and the structure was confirmed by IR spectroscopy and ^1H NMR spectroscopy. The degree of introduction ratio (DI) of adamantyl ester moieties was calculated by the integration ratios of aromatic protons and remained hydroxyl protons, to be DI = 95%. Yield = 0.83 g [poly(Re-co-Te)-AD] (DI = 95). IR (KBr, cm^{-1}): 2912 (ν C-H of adamantyl group), 1750 (ν C-H of aromatic), 1603 (ν C=C aromatic). ^1H NMR (400 MHz, $\text{DMSO}-d_6$, TMS) δ (ppm): 6.29 ~ 7.37 (m, aromatic protons), 9.40 (m, -OH).

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

The solutions of poly(Re-co-Te)-AD in propylene glycol monomethyl ether acetate (PGMEA) 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.

2.4. Out-gassing

Out-gassing from resists was measured by means of residual gas analysis (RGA) and the witness sample (WS) method at the BL3 station in the NewSUBARU synchrotron radiation facility in Hyogo University [11]. A Ru (5 nm)-capped Mo/Si multilayer mirror was used as the WS-plate, which was placed opposite the resist-coated wafer. Illuminating light was reflected off WS before reaching the wafer. At the wavelength of 13.5 nm, the illumination intensity was 267 mW/cm^2 on the WS, and 85 mW/cm^2 on the resist surface. The exposure chamber was pumped to ultrahigh vacuum in the range between 2×10^{-6} and 4×10^{-6} (Pa) before the exposure to ensure a clean and well-defined analysis environment. The EUV-exposed wafer was developed with 2.38 wt % TMAH aq. for 30 sec. to confirm that the resist had been

completely exposed.

2.5. 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 sec. to form thin films on the silicon wafers. Then these spin-coated films were prebaked at 150 $^{\circ}\text{C}$ for 60 sec. The film thickness was adjusted to 100 nm. The resulting films were exposed to EUV lithography (energetic EQ-10M) [12]. The area of exposure was approximately $1 \times 1 \text{ cm}^2$. After the exposure, they were developed by dipping in THF at 23 $^{\circ}\text{C}$ for 30 sec and then rinsed in deionized water before drying. The resist film thickness was measured with an ET200 surface profiler to obtain sensitivity curves.

3. Results and discussion

3.1. Synthesis of tellurium-containing polymers with pendant hydroxyl groups [poly(Re-co-Te)]

The reaction of resorcinol (Re) and tellurium tetrachloride (TeCl_4) was carried out in the feeds of $\text{Re}/\text{TeCl}_4 = 1/0.5, 1/2, 1/3$, and $1/4$ in ethyl acetate and DMF using sodium ascorbate and copper, to give the corresponding polymers. These conditions and results are summarized in Table 1. When this reaction was performed in DMF, the corresponding polymer was insoluble in common organic solvents (Run 3 in Table 1). In the case of ethyl acetate, the polymers with $M_n = 1,960 \sim 2,800$ were obtained in 3 ~ 77 % yields, respectively (Runs 1, 2, 4 and 5 in Table 1). The structure of the obtained soluble polymers was confirmed by ^1H NMR spectroscopy. The peaks at 6.17 ~ 7.24 and 8.53 ~ 10.27 ppm were seen, which were assignable to aromatic protons and hydroxyl groups. This means that condensation reaction of Re and TeCl_4 proceeded to give corresponding polymers poly(Re-co-Te) in 8 ~ 77 % yields, as shown in Scheme 1 [B]. As the result, the appropriate condition for the synthesis of poly(Re-co-Te) was performed in the feed of $\text{Re}/\text{TeCl}_4 = 1/3$ in ethyl acetate (Run 4 in Table 1), yielding poly(Re-co-Te) with $M_n = 2,560$ ($M_w/M_n = 1.33$) in 77% yield.

3.2. Synthesis of tellurium-containing polymer with pendant adamantyl ester groups [poly(Re-co-Te)-AD]

The condensation reaction of synthesized

Table 1. Polycondensation reaction of resorcinol and TeCl_4 ^a

Run	Feed Ratio	Solv.	Yield (%)	M_n^b (M_w/M_n)
	Re / TeCl_4			
1	1.0 / 0.5	EtAc	3	1,960 (1.10)
2	1.0 / 2.0	EtAc	8	2,400 (1.06)
3	1.0 / 2.0	DMF	62	- ^c
4	1.0 / 3.0	EtAc	77	2,560 (1.33)
5	1.0 / 4.0	EtAc	42	2,800 (1.36)

^aConditions; Resorcinol (5.0 mmol), sodium ascorbate (30 mmol), copper powder (60 mmol) in 15 mL of solvent.

^bEstimated by SEC based on polystyrene standards; LiBr and phosphoric acid solution in DMF (20 mM).

^cNot determined.

poly(Re-co-Te) (Run 2 in Table 1) and adamantyl bromo acetate (ADBAC) was carried out using K_2CO_3 as a base in NMP at 100 $^{\circ}\text{C}$ for 24 h in the feed of poly(Re-co-Te) / ADBAC = 1.0 / 2.2, to afford corresponding polymer poly(Re-co-Te)-AD with $M_n = 2,580$, $M_w/M_n = 1.09$ in 84 % yield (Scheme 2).

Scheme 2. Reaction of poly(Re-co-Te) and ADBAC.

The DI of AD groups was calculated by the peaks at 6.29 ~ 7.37 ppm assignable to aromatic protons and 9.40 ppm of hydroxyl groups, to be 95 %. By the control of feed ratios of poly(Re-co-Te) and ADBAC, the corresponding poly(Re-co-Te)-AD with DI = 20 % and 50 % could be obtained in 55 and 60 % yields. These conditions and results are summarized in Table 2. Furthermore, thermal stability of the synthesized polymers was determined by thermo gravimetric analysis (TGA), and their initial decomposition temperatures (T_d^1) were in the range between 100 and 155 $^{\circ}\text{C}$. These polymers were also soluble in common organic solvents such as DMSO, DMF, THF, CHCl_3 , and propylene glycol monomethyl ether acetate (PGMEA). Their film-forming ability was confirmed by the

spin-coating on silicon wafers from the polymers solutions in PGMEA, and it was observed that corresponding thin films with about 100 nm could be obtained from their solutions in PGMEA. Furthermore, poly(Re-co-Te)-AD (DI = 20) and poly(Re-co-Te)-AD (DI = 50) were soluble in 2.38 wt% TMAH and poly(Re-co-Te)-AD (DI = 95) was insoluble. These results indicate that poly(Re-co-Te)-AD (DI = 95) can be applicable to positive-type photoresist material.

Table 2. Condensation reaction of poly(Re-co-Te) and ADBAc^a

Run	Feed Ratio	DI ^b (%)	Yield (%)	T _d ^{ic}
	Poly(Re-co-Te) / ADBAc			
1	1.0 / 0.5	20	55	100
2	1.0 / 1.1	50	60	116
3	1.0 / 2.2	95	84	155

^aConditions; K₂CO₃ (3.3 mmol), TBAB (0.1 mmol) in NMP at 100 °C for 24h. ^bDI = degree of introduction of adamantyl ester group. ^cT_dⁱ: Initial decomposition temperature determined by TGA.

3.3. 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 was determined by ellipsometry before and after soaking in 2.38 wt% TMAH aq. for 30 sec., anticipating that poly(Re-co-Te)-AD (DI = 95) is applicable to positive-type resist materials. In the case of the thin film of poly(Re-co-Te)-AD (DI = 95), the thickness loss was not observed.

3.4. Out-gassing

From the mentioned above results on thickness loss property after soaking in 2.38 wt% TMAH aq., poly(Re-co-Te)-AD (DI = 95) is applicable to positive-type photo lithography system. Then, its out-gassing was examined under EUV exposure tool. Solution of poly(Re-co-Te)-AD (DI = 95) was spin coated on silicon wafer to prepare corresponding thin films with 89 nm thickness. The post exposure baking (PEB) temperature and time was 130 °C and 60 sec., respectively. The change of partial pressure inside the exposure chamber was determined by quadrupole mass spectrometer (QMS) before and after exposed EUV light (Fig. 1). This result means that this polymer produced smaller amounts of fragments and would be suitable as a

EUV resist material.

Fig. 1. Out-gassing of poly(Re-co-Te)-AD (DI = 95).

3.5. Resist sensitivity

The resist sensitivity of poly(Re-co-Te)-AD was also examined under EUV exposure tool. Solution of this polymer in the presence of 10 wt% of Triphenylsulfonium nonafluoromethanesulfonate (TPS-Nf) as a PAG were spin coated on silicon wafer to prepare corresponding thin films in the absence of a quencher with 89 nm thickness. The post exposure baking (PEB) temperature and time was 130 °C and 60 sec., respectively. The value of the thickness of remained thin film was measured by means of ellipsometer after the lithography process. Figure 2 shows sensitivity curve of poly(Re-co-Te)-AD (DI = 95). Thin film of poly(Re-co-Te)-AD (DI = 95) was completely soluble in alkali aqueous solution with 2.5 mJ/cm² exposure dose. From this sensitivity curve, the sensitivity and contrast of poly(Re-co-Te)-AD (DI = 95) were 2.5 mJ/cm² and $\gamma = 5.6$, respectively. The sensitivity of poly(Re-co-Te)-AD were higher than those of cyclic oligomer such as Noria-AD (7 mJ/cm²) and Noria-OMe-AD (7 mJ/cm²) [13]. This

Fig. 2. Sensitivity curve of poly(Re-co-Te)-AD (DI = 95).

result shows that this polymer have high sensitivity in EUV photoresist system.

4. Conclusion

In summary, we examined the condensation polymerization of resorcinol (Re) and tellurium tetrachloride (TeCl_4) using sodium ascorbate and copper in ethyl acetate, to give the corresponding tellurium containing polymer with pendant hydroxyl groups poly(Re-co-Te) with $M_n = 2,560$ and $M_w/M_n = 1.33$ in 77 % yield. Next, the condensation reaction of poly(Re-co-Te) and adamantyl bromo acetate was performed, yielding corresponding polymers with pendant adamantyl ester groups poly(Re-co-Te)-AD. Their physical properties (solubility, film-forming ability, thermal stability) were examined relevant to the application of positive-working resist materials. Furthermore, its resist properties (thickness loss property after soaking in 2.38 wt% TMAH aq. solution and out-gassing on EUV exposure tool) and resist sensitivity under EUV exposure tool were also examined. These results mean that the synthesized poly(Re-co-Te)-AD can be good candidate for higher resolution EUV resist materials. Furthermore, etching durability using a reactive ion etching plasma process, patterning property of electron beam (EB) and EUV exposure tools are under investigation.

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