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# Synthesis and Property of Tannic Acid Derivatives and Their Application for Extreme Ultraviolet Laser Lithography System

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We synthesized tannic acid derivatives with pendant cyclohexyl acetal moieties (TA-CVE<sub>n</sub>), butyl acetal moieties (TA-BVE<sub>n</sub>), and adamantyl ester moieties (TA-AD<sub>n</sub>) by the reaction of tannic acid (TA) with cyclohexyl vinyl ether (CVE), butyl vinyl ether (BVE), and adamantyl bromo acetate (AD) in various feeds ratios. The synthesized TA-CVE<sub>n</sub>, TA-BVE<sub>n</sub>, and TA-AD<sub>n</sub> had good solubility, good film-forming ability, and high thermal stability relevant to application of photolithography materials. However, only TA-BVE<sub>97</sub> and TA-AD<sub>74</sub> can be used as positive-type photo-resist materials using 2.38 wt% TMAH aq. as developer due to the result of thickness loss property. Furthermore, their resist-sensitivity upon EUV exposure tool and etching durability were adequate and they have high potential as next-generation resist material for EUV photolithography.

**Keywords:** Tannic acid, Positive-type resist, Extreme ultraviolet laser

## 1. Introduction

The photolithography system has been advanced with use of various exposure sources, such as electron beam (EB), KrF excimer laser ( $\lambda = 248$  nm), ArF excimer laser ( $\lambda = 193$  nm), and extreme ultraviolet (EUV) laser ( $\lambda = 13.5$  nm). Very recently, it is expected that resist patterns of less than 16 nm can be achieved using EUV exposure system. However, there is a serious problem of the relationships among resist sensitivity upon EUV exposure, resolution, and roughness of the resist pattern, i.e., these are trade-off issue. To overcome this issue, various polymers and oligomers have been synthesized

and their resist properties have been examined to offer higher resolution resist patterns for EUV lithography system [1]. Our research group has also examined the synthesis of new resist materials based on a cyclic oligomer noria (noria = water wheel in Latin) [2], tube-type polymer botryosin (botryosin = bunch of grapes in Greek) [3], and hyperbranched polyacetals [4,5]. The resist properties of various noria derivatives with pendant *t*-butyl ester groups [6], *t*-butyloxycarbonyl groups [7], adamantyl ester groups [8 -10], cyclohexyl acetal moieties [11], and oxetanyl group [12], and botryosin derivative with haloalkyl groups [13] were examined, and

we found that the resist sensitivity to EUV increased with increasing pore size [14], indicating that the resist sensitivity might increase with decrease of density. Furthermore, hyperbranched polyacetals showed higher sensitivity compared to any other resist materials.

In the present paper, based on the idea that the hyperbranched might be suitable to provide next generation EUV resist material, we focused on the tannic acid. Tannic acid is one of the polyphenolic compounds and has 25 hydroxyl groups in it, which can be obtained by the extraction from plants, i.e., it is natural product and can be obtained easily as a commercially available. We examined the synthesis of tannic acid derivatives with pendant acetal moieties and adamantyl ester groups, and their physical properties and resist sensitivities to EUV exposure tool were examined relevant to next generation EUV resist material.

## 2. Experimental

### 2.1. Reaction of tannic acid (TA) and cyclohexyl vinyl ether (CVE)

A typical procedure; A solution of tannic acid (TA) (0.17 g, 0.1 mmol) and *p*-toluene sulfonate (PTS) (0.0125 g, 0.073 mmol) in THF (1.0 mL) was stirred at room temperature for 10 min. Then, cyclohexyl vinyl ether (CVE) (0.379 g, 3.0 mmol) was added, and stirring was continued. After 3 h,  $\text{NEt}_3$  (0.1 mL) was added. The resulting mixture was poured into a large amount of water. The insoluble product were collected by filtration with a membrane filter (Millipore LAWPO 4700 pore size 0.45  $\mu\text{m}$ ), and washed with water. The obtained product was dried *in vacuo* at 60 °C for 24 h to afford a white solid. Yield = 0.34 g (70%). IR (film,  $\text{cm}^{-1}$ ): 3254 ( $\nu$  O-H), 2935 ( $\nu$  C-H of methyl), 1597 and 1497 ( $\nu$  C=C of aromatic), 1040 ( $\nu$  C-O of acetal).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , TMS)  $\delta$  (ppm) = 1.03 ~ 1.83 (br,  $-\text{CH}_3$  and  $-\text{CH}_2-$  of cyclohexyl group), 3.52 ~ 4.21 (br,  $>\text{CH}$ ), 4.75 ~ 5.42 (m,  $\text{CH}_2=\text{CH}-$ ), 6.91 ~ 7.47 (m, aromatic proton), 9.65 (br, -OH).

### 2.2. Reaction of TA and butyl vinyl ether (BVE)

A typical procedure; A solution of tannic acid (TA) (17.02 g, 10 mmol) and *p*-toluene sulfonate (PTS) (1.25 g, 7.3 mmol) in THF (100 mL) was stirred at room temperature for 10 min. Then, butyl vinyl ether (BVE) (2.75 g, 27.5 mmol) was added, and stirring was continued. After 4 h,

$\text{NEt}_3$  (10 mL) was added. The resulting mixture was poured into a large amount of water. The insoluble product was collected by filtration with a membrane filter (Millipore LAWPO 4700 pore size 0.45  $\mu\text{m}$ ), and washed with water. The obtained product was dried *in vacuo* at 60 °C for 24 h to afford a white solid. Yield = 24.2 g (55%). IR (film,  $\text{cm}^{-1}$ ): 3407 ( $\nu$  O-H), 2958 ( $\nu$  C-H of methyl), 1599 and 1507 ( $\nu$  C=C of aromatic), 1077 ( $\nu$  C-O of acetal).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , TMS)  $\delta$  (ppm) = 0.97 ~ 1.42 (br,  $-\text{CH}_3$  and  $-\text{CH}_2-$  of butyl group), 3.50 ~ 3.52 (br,  $>\text{CH}$ ), 4.71 ~ 5.41 (m,  $\text{CH}_2=\text{CH}-$ ), 7.30 ~ 7.53 (m, aromatic proton), 9.69 (br, -OH).

### 2.3. Reaction of TA and adamantyl bromo acetate (AD)

A typical procedure; A mixture of TA (1.7g, 1.0 mmol),  $\text{K}_2\text{CO}_3$  (3.45 g, 25 mmol) and tetrabutylammonium bromide (TBAB) (0.8g, 2.48 mmol) in NMP (10 mL) was stirred at 80 °C for 2 h. Then, adamantyl bromo acetate (AD) (2.87 g, 10 mmol) solution in NMP (2 mL) was added slowly, and stirring was continued at 80 °C. After 24 h, the resulting mixture was poured into a large amount of 1N HCl aq. The insoluble product was collected by filtration with a membrane filter (Millipore LAWPO 4700 pore size 0.45  $\mu\text{m}$ ), and washed with water. The obtained residue was purified by silica-gel column chromatography eluted with ethyl acetate/ hexane (volume ratio 1/1) to obtain the white solid. Yield = 2.68 g (46%). IR (film,  $\text{cm}^{-1}$ ): 3275 ( $\nu$  O-H), 2958 ( $\nu$  C-H of methyl), 1734 ( $\nu$  C=O of ester), 1592 ( $\nu$  C=C of aromatic), 1188 ( $\nu$  C-O of acetal).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ , TMS)  $\delta$  (ppm) = 0.76 - 2.36 (m,  $-\text{CH}_3$  and  $-\text{CH}_2-$  of adamantane moiety), 3.88 ~ 4.23 (br,  $>\text{CH}$ ), 4.39 ~ 5.04 (m,  $-\text{O-CH}_2\text{-C(O)-}$ ), 5.28 ~ 5.78 (br,  $>\text{CH-}$ ), 6.62 ~ 7.68 (m, aromatic proton), 9.30 ~ 9.75 (m, -OH).

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

The solutions of TA-CVE, TA-BVE, and TA-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.

## 2.5. Resist sensitivity

The resist solutions were filtered through a 0.20  $\mu\text{m}$  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  $^{\circ}\text{C}$  for 60s. The film thickness was adjusted to about 100 nm. The resulting films were exposed to EUV lithography (energetic EQ-10M) [14]. The area of exposure was approximately  $1 \times 1 \text{ cm}^2$ . After the exposure, they were developed by dipping in TMAH solution at 23  $^{\circ}\text{C}$  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.

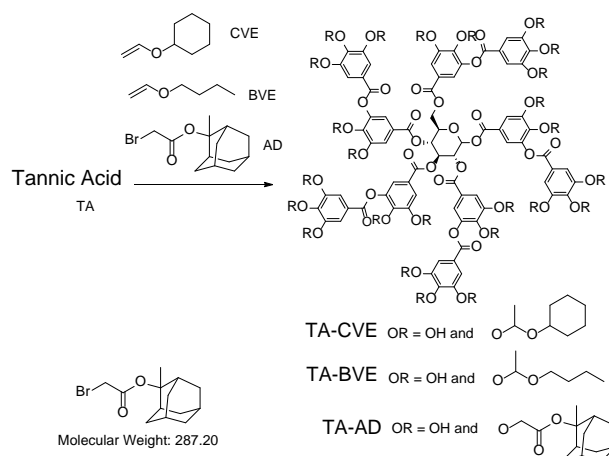
## 2.6. Etching durability

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  $\text{CF}_4$  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 and physical property of tannic acid derivatives with pendant acetal moieties

The reaction of tannic acid (TA) and cyclohexyl vinyl ether (CVE) was performed in the presence of pyridinium *p*-toluene sulfonate (PTS) as a catalyst in THF at 25  $^{\circ}\text{C}$  in various feeds ratios TA/CVE = 1/10, 1/15, 1/20, 1/25, and 1/30 (Scheme 1). The structures of the resulting products were confirmed by  $^1\text{H}$  NMR and IR spectroscopy, and the degree of introduction (DI) of CVE could be calculated by the integration ratios of the peaks at 6.91 ~ 7.47 ppm and 9.65 ppm in its  $^1\text{H}$  NMR spectrum, which are assignable to aromatic protons and hydroxyl groups, respectively. The corresponding tannic acid derivatives (TA-CVE) were obtained with DI = 32 ~ 94 %. In the same way as the mentioned above, the reaction of TA and butyl vinyl ether (BVE) was also examined in the feeds ratios TA/BVE = 1/27.5, 1/22.5, 1/17.5, 1/12.5, yielding corresponding TA derivatives TA-BVE with DI = 41 ~ 96%. These results are summarized in Table 1.



Scheme 1. Synthesis of TA derivatives (TA-CVE, TA-BVE, and TA-AD)

Table 1. Synthesis of TA-CVE and TA-BVE. <sup>a)</sup>

Run	Feed Ratios	TA Derivatives	DI <sup>b)</sup>
1	TA/CVE = 1/ 10	TA-CVE <sub>32</sub>	32
2	TA/CVE = 1/ 15	TA-CVE <sub>51</sub>	51
3	TA/CVE = 1/ 20	TA-CVE <sub>64</sub>	64
4	TA/CVE = 1/ 25	TA-CVE <sub>83</sub>	83
5	TA/CVE = 1/ 30	TA-CVE <sub>94</sub>	94
6	TA/BVE = 1/ 12.5	TA-BVE <sub>41</sub>	41
7	TA/BVE = 1/ 17.5	TA-BVE <sub>55</sub>	55
8	TA/BVE = 1/ 22.5	TA-BVE <sub>76</sub>	76
9	TA/BVE = 1/ 27.5	TA-BVE <sub>97</sub>	97

<sup>a)</sup> Condition; 3 mol % of pyridinium *p*-toluene sulfonate in THF at 25  $^{\circ}\text{C}$ . <sup>b)</sup> DI = degree of introduction is calculated by  $^1\text{H}$  NMR.

The synthesized TA derivatives TA-CVE and TA-BVE had good solubility and good film forming ability. TA-CVE and TA-BVE are expected to undergo solubility change in 2.38 wt% TMAH aq. due to decomposition of acetal units in the side-chain, acting as positive photo-resists, i.e., the unexposed part must remain on the silicon wafer after development. Therefore, thickness loss property of synthesized

TA-CVE and TA-BVE was determined by ellipsometry before and after soaking in 2.38 wt% TMAH aq. for 30 s. Except for TA-BVE<sub>97</sub> (DI = 97%), all thin films of TA-CVE and TA-BVE were lost after soaking. This means that only TA-BVE<sub>97</sub> (DI = 97%) can be used as positive resist material with 2.38 wt% TMAH aq. as the developer. In addition, thermal stability of TA-BVE<sub>97</sub> was determined by TGA, and thermal decomposition temperature ( $T_d^i$ ) was 120 °C.

### 3.2. Synthesis and physical property of tannic acid derivatives with pendant adamantyl ester groups

The reaction of TA and AD was performed using  $K_2CO_3$  as a base in the presence of TBAB as a catalyst in NMP at 80 °C in the feeds ratios TA/AD = 1/5 and 1/10 (Scheme 1). In the similar way for the synthesis of TA-CVE and TA-BVE, the resulting structures of TA-AD was confirmed by <sup>1</sup>H NMR and IR spectroscopy, and DI of AD was calculated to be 35% and 74%, respectively. These results are summarized in Table 2.

Table 2. Synthesis of TA-AD.<sup>a)</sup>

Run	Feed Ratios	TA Derivatives	DI <sup>b)</sup>
1	TA/AD= 1/ 5	TA-AD <sub>35</sub>	35
2	TA/AD = 1/ 10	TA-AD <sub>74</sub>	74

<sup>a)</sup> Condition;  $K_2CO_3$  as a base and TBAB as catalyst in NMP at 80 °C. <sup>b)</sup> DI = degree of introduction is calculated by <sup>1</sup>H NMR.

The synthesized TA-AD<sub>n</sub> (n = 35 and 74) had good solubility and good film forming ability. Furthermore, the thickness loss property of TA-AD<sub>n</sub> (n = 35 and 74) was examined, and only TA-AD<sub>74</sub> can be applicable to a positive resist material with 2.38 wt% TMAH aq. as the developer. TA-AD<sub>74</sub> has also high thermal stability and  $T_d^i$  was 168 °C.

### 3.3. Resist Sensitivity

From the mentioned above results on thickness loss properties after soaking in TMAH aq., the synthesized TA-BVE<sub>97</sub> and TA-AD<sub>74</sub> are applicable to positive type EUV lithography system. The resist-sensitivity of TA-BVE<sub>97</sub> and TA-AD<sub>74</sub> was examined under EUV exposure

tool. Solution of these materials in the presence of 10 wt% of triphenylsulfonium trifluoromethanesulfonate (TPS-Nf) as a PAG were spin coated on silicon wafer, preparing corresponding thin films with about 100 nm thickness. The postexposure baking (PEB) temperatures and time were 90 °C and 60 s, respectively. The value of the thickness of remained thin films was measured by means of ellipsometer after the lithography process. These results are depicted in Fig. 1.

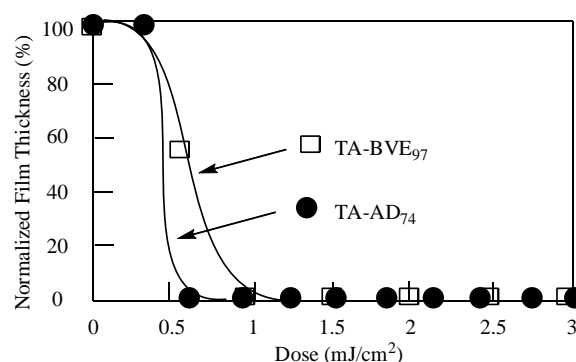


Fig. 1. Resist-sensitivity curves of resist materials based on TA-BVE<sub>97</sub> (□) and TA-AD<sub>74</sub> (●).

This result showed that the sensitivities ( $E_0$ ) of TA-BVE<sub>97</sub> and TA-AD<sub>74</sub> were 1.0 and 0.6 mJ/cm<sup>2</sup>, respectively. This means that TA-BVE<sub>97</sub> and TA-AD<sub>74</sub> have adequate high resist-sensitivity in EUV photolithography system, due to that main-chain scission also might proceed at the point of acetal bond in TA during EUV exposure process.

### 3.4. Etching durability

The etching durability of TA-BVE<sub>97</sub> and TA-AD<sub>74</sub> was examined using RIE plasma process. The plasma conditions were a 15 sccm  $CF_4$  gas flow, a 5 sccm Ar gas flow, and RF power of 100 W under 1.0 Pa pressure in the process chamber. Fig. 2 depicts the etching rate of the thin films prepared from TA-BVE<sub>97</sub>, TA-AD<sub>74</sub>, polymethyl methacrylate (PMMA), and poly(hydroxystyrene) (PHS). PMMA and PHS are typical polymers in the application of resist materials. It was observed that TA-BVE<sub>97</sub> and TA-AD<sub>74</sub> showed higher etching durability in the comparison of PMMA. This means that etching durability of TA-BVE<sub>97</sub> and TA-AD<sub>74</sub> are adequate for the EUV lithography system.

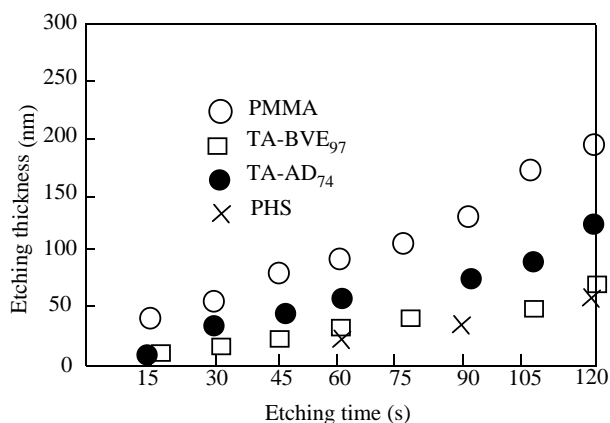


Fig. 2. Etching durability of the thin films on the silicon wafer prepared from TA-BVE<sub>97</sub> (□), TA-AD<sub>74</sub> (●), poly(methyl methacrylate)(PMMA) (○), and poly(hydroxystyrene)(PHS) (×).

#### 4. Conclusion

We synthesized tannic acid (TA) derivatives with pendant acetal moieties (TA-CVE<sub>n</sub> and TA-BVE<sub>n</sub>) and adamantyl ester groups (TA-AD<sub>n</sub>) by the reaction of TA with cyclohexyl vinyl ether (CVE), butyl vinyl ether (BVE), and adamantyl bromo acetate (AD) in their various feeds ratios. The physical properties such as solubility, film-forming ability, and thermal stability of TA-CVE<sub>n</sub>, TA-BVE<sub>n</sub>, and TA-AD<sub>n</sub> were examined relevant to the resist materials, and it was observed that these have good physical properties. However, among them, TA-BVE<sub>97</sub> and TA-AD<sub>74</sub> had good thickness loss property using 2.38 wt% TMAH aq. as the developer. Furthermore, resist-sensitivity upon EUV exposure tool and etching durability using RIE plasma process of TA-BVE<sub>97</sub> and TA-AD<sub>74</sub> were also examined, and these had high sensitivity and good etching durability for application as EUV photoresist materials. Further studies of their resist-patterning properties are under way using an EUV lithography exposure tool.

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