Thermolysis of Polymethacrylates for 193 nm Resist

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1. Introduction

ArF (193nm) lithography is a promising technology for producing fine patterns in microelectronic devices. Many types of resist materials for 193 nm lithography have been developed. However, a big concern is line edge roughness (LER) of resist patterns. Recently, several papers on the reduction of LER of resist patterns by plasma treatment prior to conventional etching of substrate have been published [1,2]. Since the ion energy and anisotropy is small during the plasma treatment process compared to a conventional etching process, the underlying substrate is not substantially etched. However, the reactive neutral species and reactive ions formed in the plasma sufficiently attack the resist patterns to give a smooth surface, and therefore this treatment process reduces LER of the resist patterns. It is known that the plasma exposure process includes thermal degradation of resist component with high content of oxygen atom [3,4]. Thus, it is important to investigate thermal degradation properties of 193 nm resists. Recently, we have reported the lithographic performance of 193 nm resists bearing methyl acetal and tertiary ester groups as blocking units [5-8]. The resist bearing methyl acetal protecting groups showed lower activation energy for the deprotection reaction, suggesting better control of acid diffusion and therefore better control of critical dimension (CD) of the resist patterns after development.

In this paper we report the thermal degradation of 193 nm resists, poly (2-adamantyl oxymethyl methacrylate-co- γ -butyrolactone methacrylate) and poly (2-methyl-2-adamantyl methacrylate-co- γ -

butyrolactone methacrylate). The degradation process of the resist film was studied by thermal desorption spectroscopy (TDS). Furthermore, the degradation profile was discussed in relation to the resist structure estimated by NMR spectroscopy.

2. Experimental

2.1. Materials

Methacrylic acid (MAA) was purchased from Wako Pure Chemical Industry. 2-Chloromethoxy adamantane was received from Idemitsu Kosan and used without further purification. 2-Methyl-2-adamantyl methacrylate (MAd) and γ -butyrolactone-2-yl methacrylate (GBL) were obtained from Osaka Organic Chemical Industry and used without further purification. Propylene glycol monomethyl ether acetate (PGMEA) was used as casting solvent for thin film preparation. Silicon wafer treated with hexamethyldisilazane was used.

Synthesis of 2-adamantyl oxymethyl methacrylate (AdOM) was carried out as follows. A tetrahydrofuran (THF) (200 mL) solution of MAA (6.9 g, 0.08 mol) and triethylamine (8.0 g, 0.08 mol) was stirred at room temperature for 1h. Then, a THF (50 mL) containing 2-chloromethoxy adamantane (15.0 g, 0.075 mol) was added to the solution, and the mixture was stirred for 12h at the same temperature. The reaction mixture was filtered, then evaporated and diluted with ethyl acetate, followed by a wash with water three times. Next, the solvent was evaporated and pure AdOM was then obtained as white solid after drying under a vacuum at 40 °C for 6 h. The yield was 18.1 g (96%). IR (KBr): 2907, 2854 (vC-H), 1725 (vC=O,

ester), 1638 ($\nu\text{C}=\text{C}$, vinyl), 1160, 1097 ($\nu\text{C}-\text{O}$, ester), 953 and 915 cm^{-1} ($\nu\text{O}-\text{C}-\text{O}$, ether). ^1H NMR (400 MHz, CDCl_3 , TMS): δ 1.48-1.51 (2H, m, 4-H, 9-H adamantyl), 1.65-1.73 (4H, m, 6-H, 6-H, 8-H, 10-H adamantyl), 1.77-1.88 (4H, m, 5-H, 7-H, 8-H, 10-H adamantyl), 1.95 (3H, s, $\text{CH}_2=\text{C}(\text{CH}_3)-$), 2.01-2.10 (4H, m, 1-H, 3-H, 4-H, 9-H adamantyl), 3.76 (1H, s, 2-H adamantyl), 5.50 (2H, s, $-\text{COOCH}_2\text{O}-$), 5.60 (1H, s, $\text{CH}_2=\text{C}(\text{CH}_3)-$), 6.12 (1H, s, $\text{CH}_2=\text{C}(\text{CH}_3)-$). ^{13}C NMR (400 MHz, CDCl_3 , TMS): δ 18.0 (CH_3), 27.3 (5-CH, 7-CH adamantyl), 31.3 (4- CH_2 , 9- CH_2 adamantyl), 32.5 (1-CH, 3-CH adamantyl), 36.4 (8- CH_2 , 10- CH_2 adamantyl), 37.4 (6- CH_2 adamantyl), 82.9 (2-CH adamantyl), 88.5 (COOCH_2O), 125.7 ($\text{CH}_2=$), 136.3 ($=\text{C}(\text{CH}_3)-$), 166.7 (carbonyl). Elemental analysis: calculated for AdOM $\text{C}_{15}\text{H}_{22}\text{O}_3$ (250.16): C, 71.97%; H, 8.86%; O, 19.17%. Found: C, 71.87%; H, 8.79%; O, 18.28%.

Polymethacrylates were prepared by the conventional radical polymerization at 60 °C for 6 h in THF using 5 mol% of 2,2'-azobisisobutyronitrile (AIBN) as an initiator (based on total monomer). Polymers were obtained as white powder after precipitating twice from methanol and drying in vacuum. The structure and properties of the polymers are shown in Scheme 1 and Table 1, respectively.

Scheme 1

Table 1. Characteristics of polymers.

Polymer	M_w	M_w/M_n	T_d (°C)
AdOM(55)-GBL(45)	14400	1.83	259
MAd(56)-GBL(44)	7400	1.60	221

T_d : temperature of 5 % weight loss measured by TGA.

2.2. Measurements

Compositions of AdOM(55)-GBL(45) and MAd(56)-GBL(44) were determined from the ^{13}C -NMR integration of the two signal areas for adamantyl ester and γ -butyrolactone ester at 30 °C using tetramethylsilane (TMS) as an internal standard in acetone- d_6 with a Jeol JNM-GX400-MHz spectrometer. Weight-averaged molecular weights (M_w) and molecular weight distribution (M_w/M_n) were estimated by gel permeation chromatography on a Tosoh Shodex GPC system calibrated with polystyrene standards.

1D $\{^1\text{H}, ^{13}\text{C}, \text{DEPT-45}, 90, 135$ (distortionless enhancement by polarization transfer)}, 2D $^1\text{H}-^1\text{H}$ correlation spectroscopy (COSY), and $^{13}\text{C}-^1\text{H}$ COSY NMR spectra for polymer structures were recorded at 40°C in 20% (w/v) mixed solution of CDCl_3 and acetone- d_6 (1:1, v/v) with a Jeol JNM-GX400-MHz spectrometer using different standard pulse sequences.

Dynamic thermogravimetric analysis (TGA) was performed on a Seiko Instrument TG/DTA6200 thermal analyzer under nitrogen atmosphere using a heating rate of 10 °C/min starting from the room temperature to 500 °C.

Thermal desorption spectroscopy (TDS) experiment was performed on an Esco EMD-WA1000S TDS system using an ultrahigh vacuum (UHV) chamber with a quadrupole mass spectrometer (QMS, Balzers QMG422) equipped with a 70 eV electron impact ion source. A sample film (250 nm thick) on silicon substrate was prepared by spin-casting of PGMEA solution of polymers. The sample film was baked at 100 °C for 60 s to remove the solvent PGMEA. TDS spectra were recorded from the signals of the QMS scans over 1-200 amu during linear heating of the sample stage from room temperature to 500 °C.

3. Results and Discussion

Structures of AdOM(55)-GBL(45) and MAd(56)-GBL(44) polymers were studied using NMR spectroscopy. AdOM(55)-GBL(45) (M_w 14400, M_w/M_n 1.83) indicated high syndiotacticity ($mm=4\%$, $mr=39\%$, $rr=57\%$). MAd(56)-GBL(44) (M_w 7400, M_w/M_n 1.60) gave low syndiotacticity and high isotactic MAD-MAD-MAD triads (32%).

Polymethacrylate with tertiary alkyl ester in the side chain forms olefin compounds via a six-membered ring transition in the primary pathway of the thermal decomposition and the stability of esters decreased in the order primary > secondary > tertiary [9-11]. Hence,

AdOM(55)-GBL(45) having primary ester units demonstrated higher thermal decomposition temperature ($T_d=259^\circ\text{C}$) compared to MAd(56)-GBL(44) ($T_d=221^\circ\text{C}$).

TDS of total mass scanning for 1 to 200 amu of volatile products from AdOM(55)-GBL(45) and MAd(56)-GBL(44) films is shown in Figure 1. Desorption peaks of the total mass fragments can be found at around 350 and 420 $^\circ\text{C}$ for AdOM(55)-GBL(45) film, and 230, 280, and 350 $^\circ\text{C}$ for MAd(56)-GBL(44) film, respectively.

TDS for the volatile species of fragment originating from the AdOM(55)-GBL(45) film heated at temperatures of 350 and 420 $^\circ\text{C}$ is shown in Figure 2. The volatile products were confirmed to be γ -crotonolactone (84 amu) [12,13] and adamantene (134 amu) [14] at 350 $^\circ\text{C}$. Deesterification of 2-adamantyl oxymethyl and γ -butyrolactone ester in the polymer side chain is proposed as shown in Scheme 2. Desorption of CO_2 (44 amu) and H_2O (18 amu) clearly showed that carbonyl decomposition and dehydration occurred at 420 $^\circ\text{C}$ rather than at 350 $^\circ\text{C}$.

Mass spectra for MAd(56)-GBL(44) film heated at 230, 280, and 350 $^\circ\text{C}$ are shown in Figure 3. As shown in Figure 3 (a), MAd(56)-GBL(44) film loses methylenadamantane (148 amu) [13] and H_2O (18 amu) at 230 $^\circ\text{C}$. Figure 3 (b) shows that carbonyl decomposition and dehydration occurred at 280 $^\circ\text{C}$. Deesterification of γ -butyrolactone ester occurred at 350 $^\circ\text{C}$ as shown in Figure 3 (c).

Figure 1. TDS of AdOM(55)-GBL(45) and MAd(56)-GBL(44) films.

Figure 2. Mass spectra of desorption species from AdOM(55)-GBL(45) film at (a) 350 $^\circ\text{C}$ and (b) 420 $^\circ\text{C}$.

Scheme 2

Figure 3. Mass spectra of desorption species from MAd(56)-GBL(44) film at (a) 230 $^\circ\text{C}$, (b) 280 $^\circ\text{C}$, and (c) 350 $^\circ\text{C}$.

Figure 4. H₂O released from AdOM(55)-GBL(45) and MAd(56)-GBL(44) films.

Desorption of H₂O (18 amu) from these polymer films is shown in Figure 4. In the AdOM(55)-GBL(45) film, the dehydration gradually started at around 370 °C and then a maximum dehydration peak was observed at 430 °C. MAd(56)-GBL(44) film showed two maximum peaks at around 240 and 385 °C. The dehydration temperature of AdOM(55)-GBL(45) film (peak at 430 °C) is higher than that of MAd(56)-GBL(44) film (second peak at 385 °C). This observation shows that anhydride formation between the neighboring carboxylic acids after deesterification in the AdOM(55)-GBL(45) film slowly occurred and was compared with that of MAd(56)-GBL(44) due to increase of syndiotactic cotacticity. This was consistent with the previous study on the rate of water loss of different stereoregularity of polymethacrylates [15]. Furthermore, in the MAd(56)-GBL(44) polymer film, deesterification of 2-methyl-2-adamantyl ester and dehydration (first peak at 240 °C) occurred almost simultaneous regardless of copolymer with GBL due to high isotactic MAd-MAd-MAd triads (32%).

In summary, TDS results of thermal degradation of AdOM(55)-GBL(45) and MAd(56)-GBL(44) films showed the thermal stability of each protecting group such as 2-adamantyl oxymethyl ester and 2-methyl-2-adamantyl ester, and is in

good agreement with TGA results. The stereoregularity of these polymers affected thermal degradation process (deesterification and dehydration) of the polymer film.

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