CHEMICAL MODIFICATION OF POLYMER SURFACE USING 185-nm LIGHT

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Photolithographic processes that use surface imaging techniques have been studied [1]. The predominant approach involves post-exposure silylation of an organic polymer film [2]. Polymer films bearing phenolic -OH groups are irradiated, followed by selective silylation of the unexposed areas to provide sufficient plasma etch resistance for pattern transfer. In contrast to the silylation process, the selective deposition of metal oxides on the irradiated surface has been studied [3,4]. Recently we have reported a plasma-developable photoresist system based on photoinduced acid-catalyzed polysiloxane formation at irradiated polymer surface bearing photoacid generating moieties by a chemical vapor deposition (CVD) method using alkoxysilane vapor [5]. In this paper we report new photoacid generators sensitive to 185 nm-light and formation of polysiloxanes at the irradiated polymer surface containing those photoacid generators by CVD method using alkoxysilane vapor.

Four types of photoacid generators shown in Scheme 1 were synthesized from acetone oxime or N-hydroxysuccinimide and corresponding sulfonyl chlorides. The procedure for the preparation of **1a** was as follows: To a solution of acetone oxime (2.0 g, 27.4 mmol) in pyridine (22 ml) below 5 °C was slowly added methanesulfonyl chloride (3.5 g, 30.7 mmol). The reaction was continued with vigorous stirring at 15 °C for 4 hr. The reaction mixture was poured into 242 ml of ice-cold 5% HCl and extracted with chloroform. After washing the chloroform layer thoroughly with water, the chloroform layer was dried over K₂CO₃ and evaporated under reduced pressure. After recrystallization from n-heptane, pure product was obtained in 45% yield. Identification of the compound was done from elemental analysis, ¹H-NMR, and FT-IR spectra. **2a** was prepared by the same procedure (yield; 33%). According to the literature [6], **1b** and **2b** were prepared in 23 and 45% yield, respectively. Characteristics of the photoacid generators are shown in Table 1. Thermal decomposition temperatures (T_d) for **1b** and **2b** were

higher than those for **1a** and **2a**. Poly(methyl methacrylate) (PMMA) ($M_n=107000$, $M_w/M_n=2.0$) was prepared by the conventional radical polymerization of methyl methacrylate. Alkoxysilanes were of reagent grade and used without further purification. Sample films were spin-cast onto glass plates or Si wafers from diglyme solution. Irradiation was carried out at 185 nm under high vacuum (< 0.03 Torr) using low-pressure Hg lamp.

Scheme 1

Table 1 Characteristics of photoacid generators

Photoacid generator ^{a)}	T_m (°C) ^{b)}	T_d (°C) ^{c)}	ϵ (l / mol cm) ^{d)}	
			193 nm	248 nm
1a	46	135	1900	0
1b	154	208	11500	100
2a	84	139	3100	10
2b	91	228	9800	80

a) See Scheme 1. b) Melting point. c) Thermal decomposition temperature from DSC measurement. d) In Acetonitrile.

It has been reported that upon irradiation imino sulfonate compounds form sulfonic acid along with ketone and azine [7]. N-Hydroxyimide sulfonates are known to be photolyzed to form sulfonic acid and imide [8]. Molar extinction coefficients (ϵ) of **1b** and **2b** at 193 nm were larger than those of **1a** and **2a**. All photoacid generators used here showed no significant

absorption peaks at longer wavelength than 260 nm. Fig. 1 shows the relationship between exposure dose and acid generation. PMMA films (thickness $\sim 1 \mu\text{m}$) containing 10 mol% of the photoacid generators were irradiated at 185 nm. **1b** and **2b** were poorly soluble in PMMA film. The sample film was stripped from the Si wafer with tetrahydrofuran (THF) and added to a stock solution of tetrabromophenol blue mono sodium salt (TBPB) in THF. The amount of acid in the film could be determined by monitoring the absorbance change of the TBPB indicator at 412 nm. The acid generated in the irradiated film increased with exposure dose and reached constant value above 1 J/cm^2 . The yield of acid generated from the photoacid generators was 25-40%. The efficiency of acid generation for **1b** and **2b** was slightly higher than that for **1a** and **2a**. The structure of sulfonyl moiety in the photoacid generators did not significantly affect the efficiency of acid generation.

In the presence of water and strong acids such as sulfonic acid, alkoxy silanes can be converted to polysiloxanes. When the irradiated film containing **1a**, **1b**, **2a**, or **2b** was exposed to the vapor of $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ at 30°C , polysiloxanes were formed at the surface region of the films, which was confirmed by FT-IR analysis. The modified films showed new peaks at 3320 (Si-OH), 1270 (CH_3 -Si), and 1180-1000 cm^{-1} (Si-O-Si). Formation of polysiloxane networks by the CVD treatment occurs at air-film interface and beneath the film surface. Relationship between polysiloxane formation and film thickness was studied. The amount of polysiloxanes formed at the irradiated film increased with film thickness and reach a constant value at the thickness above $0.5 \mu\text{m}$, suggesting that the maximum thickness of polysiloxane-PMMA

composite layer is about 0.5 μm . Fig. 2 shows polysiloxane formation at the irradiated film surface containing 10 mol% of **1a** and **2a**. The amount of polysiloxanes formed was estimated from the enhanced absorbance at 1035 cm^{-1} due to Si-O-Si. **2a** was more effective for the formation of polysiloxanes than **1a**. The amount of acid formed photochemically in the film was almost the same for **1a** and **2a**. Since methanesulfonic acid generated in the film by the photolysis of **1a** is liquid at ambient temperature, it may move to the film surface, causing a rapid formation of polysiloxane networks at very top surface. This prevents the diffusion of alkoxysilane vapor into the film.

Figure 1. Photoinduced generation of acid from **1a** ($\square$), **1b** ($\circ$), **2a** ($\diamond$), and **2b** ($\triangle$) in PMMA film.

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Figure 2. Polysiloxane formation at the irradiated film surface containing 10 mol% of **1a** ($\circ$) and **2a** ($\square$). Exposed dose; 600 mJ/cm^2 .