PLASMA DEVELOPABLE PHOTORESISTS BASED ON SURFACE MODIFICATION

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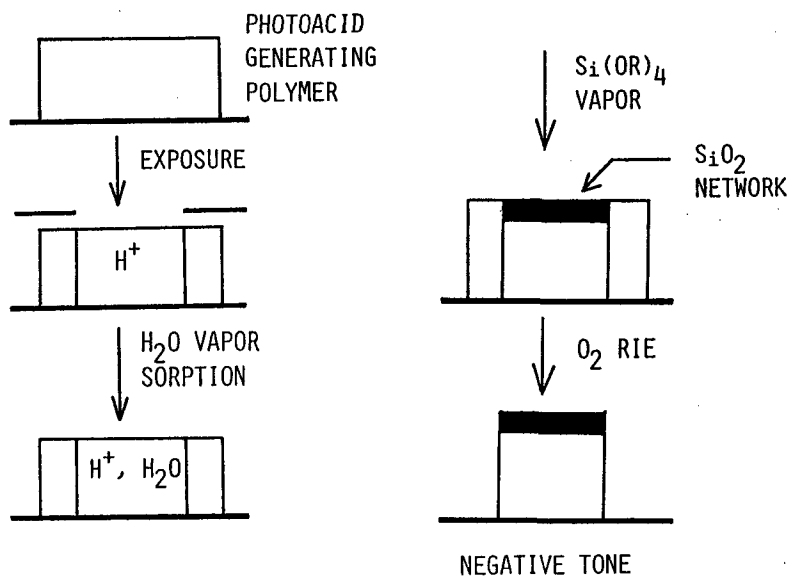Department of Applied Chemistry, College of Engineering,
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ABSTRACT

Copolymers of 1,2,3,4-tetrahydro-1-naphthylideneamino p-styrenesulfonate (NISS) and either methyl methacrylate, isopropyl methacrylate, or benzyl methacrylate were synthesized. When the UV irradiated polymer films were exposed to the vapor of tetraalkyl orthosilicates, silicon oxide was formed at the irradiated surface of the polymer films. No silicon oxide was formed at unirradiated areas. The silicon oxide formation rate was strongly affected by the structure of the methacrylate units in the polymers, the hydrolytic reactivity of the silicon compounds, the concentration of the silicon compounds in the vapor phase, and the number of photochemically formed p-styrenesulfonic acid units in the polymers. After UV irradiation and subsequent exposure to the vapor of tetraalkyl orthosilicates, the polymer films showed good etching resistance to an oxygen plasma.

INTRODUCTION

In the microlithographic process the use of deep UV light to provide higher resolution causes new problems due to decreased depth of focus and increased substrate reflectance. Plasma developable photoresist systems based on the surface modification are expected to reduce or eliminate these difficulties. Several approaches have been tried to accomplish the surface imaging system [1-7]. Scheme 1 shows the surface imaging system using photogenerated acid-catalyzed SiO_2 formation by the chemical vapor deposition (CVD) method. Upon irradiation with UV light the surface of polymers having imino sulfonate units becomes hydrophilic

PHOTOACID
GENERATING
POLYMER

EXPOSURE

H$^+$

H$_2$O VAPOR
SORPTION

H$^+$, H$_2$O

Si(OR)$_4$
VAPOR

SiO$_2$
NETWORK

O$_2$ RIE

NEGATIVE TONE

Scheme 1

because of the formation of sulfonic acid. Water sorption from the atmosphere occurs at the top surface of the irradiated films. When the irradiated surface is exposed to the vapor of alkoxysilanes at 30 °C, a silicon oxide network is formed at the near surface of the polymers. No silicon oxide network is formed at unirradiated areas because the

$$n \; Si(OR)_4 \; + \; 2n \; H_2O \; \xrightarrow{\;H^+\;} \; n \; SiO_2 \; + \; 4n \; ROH \qquad (1)$$

photochemically formed sulfonic acid units are necessary for the silicon oxide formation by hydrolysis and subsequent polycondensation reactions of alkoxysilanes [8,9]. This system gives a negative tone image by oxygen plasma etching.

Polymers bearing pendant 1,2,3,4-tetrahydro-1-naphthylideneamino p-styrenesulfonate (NISS) units were synthesized and they were utilized in the surface imaging resist system using CVD method. The NISS units in the polymers can form p-styrenesulfonic acid units upon UV irradiation as shown in Scheme 2 [10]. This paper describes the photochemistry of NISS units in polymers, the water sorption to the irradiated polymer surface, the formation of silicon oxide networks at the irradiated polymer surface, and the etching resistance to an oxygen plasma for the

polymer films which are irradiated and subsequently exposed to the vapor of alkoxysilanes.

R: CH_3, $i-C_3H_7$, $CH_2C_6H_5$
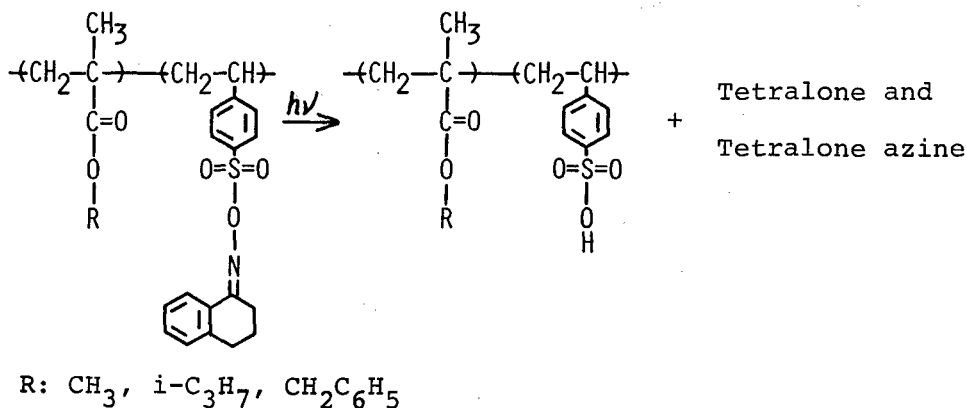
Scheme 2

EXPERIMENTAL PROCEDURES

The copolymers were prepared by the radical copolymerization of 1,2,3,4-tetrahydro-1-naphthylideneamino p-styrenesulfonate (NISS) and methacrylates with azobis(isobutyronitrile) (AIBN) as an initiator. Synthesis of NISS has been reported elsewhere [11]. The characteristics of poly(methyl methacrylate-co-NISS) (PMANI), poly(isopropyl methacrylate-co-NISS) (PPRNI), and poly(benzyl methacrylate-co-NISS) (PBZNI) are shown in Table 1. Tetramethyl orthosilicate (TMOS), tetraethyl orthosilicate (TEOS), tetra-n-propyl orthosilicate (TPOS), methyltrimethoxysilane (MTMOS), and methyltriethoxysilane (MTEOS) were reagent grade and used without further purification.

Water sorption in the polymer films was measured by using a laboratory-constructed piezoelectric apparatus. The AT-cut quartz crystal with gold electrodes (Webster Electronics, WW1476) had a resonance frequency of 10.000 MHz. With this crystal, a frequency shift of 1 Hz corresponded to a mass change of 0.84 ng. Polymers were deposited onto the quartz crystal (1.2 cm diameter) by casting from chloroform solution. The area coated with the polymer film was usually 0.19 cm^2. Irradiation of the polymer films was carried out with 254-nm light.

TABLE 1

Characteristics of Polymers

Polymer	R^a	M_n $\times 10^{-4}$	M_w/M_n	NISS Content in Polymer (mol %)	T_g^b (°C)	T_d^c (°C)
PMANI(A)	CH_3	7.0	3.0	25	–	–
PMANI(B)	CH_3	10.0	2.5	15	–	132
PMANI(C)	CH_3	11.5	2.0	8	114	–
PPRNI	$i\text{-}C_3H_7$	13.1	1.9	15	105	149
PBZNI	$CH_2C_6H_5$	15.5	2.3	18	83	147

a See Scheme 2.

b Glass transition temperature.

c Decomposition temperature of NISS units in polymers from DSC.

To measure the deposition of SiO_2 at the polymer surface, the polymer films (8.8 X 22 mm) were prepared on glass plates (8.8 X 50 mm) by casting from chloroform solution and drying under vacuum at room temperature. The polymer weight on the glass plate was usually 2×10^{-4}g (thickness $\approx$ 1 μm). After exposure with 254-nm light, the glass plate coated with polymer film was placed at the center of a 500 mL of glass vessel which had gas-inlet and -outlet valves. Water (50 mL) was placed at the bottom of the vessel and equilibrated for 10 min prior to introduction of the vapor of alkoxysilanes. During the SiO_2 network formation nitrogen gas (50 mL/min) flowed through a bubbler which contained liquid alkoxysilanes. The bubbler and reaction vessel were placed in a thermostatic oven at 30 °C. The amounts of SiO_2 formed at the near surface of the polymer were determined from the difference between the weight of the sample plate before and after exposure to the vapor of the silicon compounds.

Oxygen plasma etching was carried out at room temperature using a laboratory-constructed apparatus where the oxygen plasma was generated using two parallel electrodes and RF power supplies. The typical etching conditions were as follows: 20W power (13.56MHz), power density of 1.0 W/cm^2, 30-125 mTorr, and oxygen flow of 1 sccm. The self-biasing voltage was -40 V.

RESULTS AND DISCUSSION

It has been reported that upon irradiation with UV light the cleavage of -O-N= bonds in imino sulfonates and the subsequent abstraction of hydrogen atoms from residual solvent in the polymer film or from polymer molecules leads to the formation of sulfonic acid, azines and ketones as shown in Scheme 2 [10]. The polymers showed absorption peak at 254 nm. The absorbance at 254 nm decreased with irradiation time due to the cleavage of -O-N= bonds of NISS units in the polymers and an isosbestic point was observed at 305 nm. The slight increase in absorbance above 300 nm was due to the formation of tetralone azine. In our system photolytic decomposition of NISS units in polymers was complete after exposure of 250 mJ/cm^2. The quantum yields (Φ) for the photolysis of NISS units in the polymer films at 254 nm were 0.33, 0.31, 0.36, 0.26, and 0.38 for PMANI(A), PMANI(B), PMANI(C), PPRNI, and PBZNI, respectively. They were not strongly dependent on either structure of the methacrylate unit or the NISS content of the polymers.

Water sorption began the moment that the polymer film was irradiated with 254-nm light. It increased with irradiation time and more gradually increased after irradiation until sorption equilibrium was established. Figure 1 shows the relationship between water sorbed and the weight of the irradiated polymer film (area=0.19 cm^2) on the quartz crystal. The water sorption for all polymers examined increased with increasing polymer weight and reached a constant value at high polymer weight. A saturation phenomenon for the water sorption was observed above ca. 1000 ng (thickness=51 nm) for the irradiated polymers. Thus the water sorption occurs at very surface of the polymer films. Although the water sorption increased with increasing p-styrenesulfonic acid units formed photochemically, the hydrophobic nature of the methacrylate ester groups decreased the water sorption.

In the presence of water and strong acids, the hydrolysis and subsequent polycondensation reactions of $Si(OR)_4$ or its homologues lead to the formation of silicon oxide or polysiloxane networks as shown in eq (1), which is well known as the sol-gel process for the silica glass formation [8,9]. When the irradiated polymer films bearing NISS units were exposed to the vapor of $Si(OR)_4$ or $CH_3Si(OR)_3$ at 30 °C, SiO_2 or polysiloxane was formed in the near surface region of the films, which
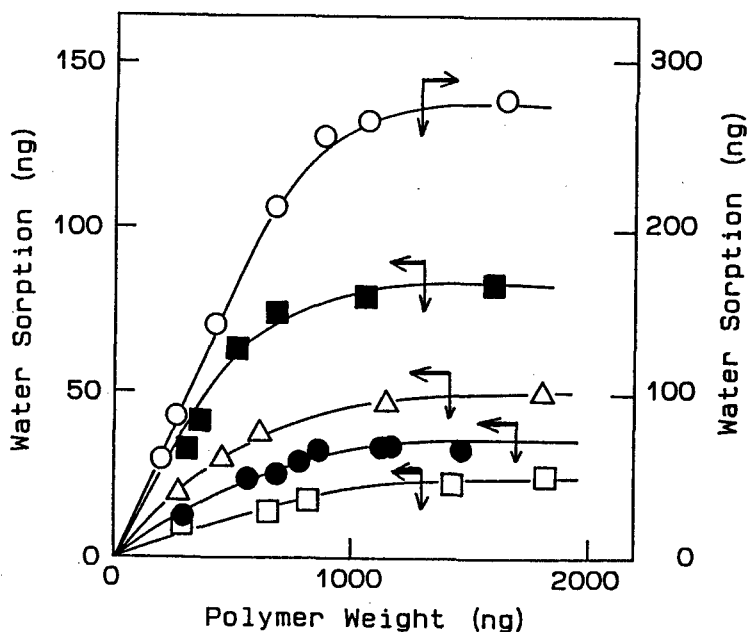
FIGURE 1. Water sorption at 95% RH into polymer films irradiated with 42 mJ/cm^2 of 254-nm light at 25 $^\circ$C. Polymer: (O) PMANI(A), (■) PMANI(B), (△) PMANI(C), (●) PPRNI, (□) PBZNI.

was confirmed by IR analysis. The irradiated PMANI(A) film exposed to TMOS vapor showed new peaks at 1080 (Si-O-Si), 940 (Si-OH), and 3300 cm^{-1} (Si-OH). The presence of Si-OH peaks suggests that the polycondensation reaction of Si(OH)$_4$ does not occur completely and silanol groups still remain in the film. No SiO$_2$ formation was observed in the unirradiated areas of the polymer films, since the styrenesulfonic acid units formed photochemically are essential to catalyze the hydrolysis of the silicon compounds. SiO$_2$ formation increased with increasing irradiation time and decreased in the order PMANI(A) > PMANI(B) > PMANI(C). This means that the SiO$_2$ formation rate is proportional to the number of sulfonic acids formed photochemically in the polymer matrix. Figure 2 shows the influence of methacrylate structure on SiO$_2$ formation at the irradiated polymer surface. The NISS content of the three polymers was almost the same. SiO$_2$ formation decreased in the order PMANI(B) > PPRNI > PBZNI, the same trend observed in water sorption experiments. Thus the SiO$_2$ formation rate is strongly affected by the amount of water sorbed in
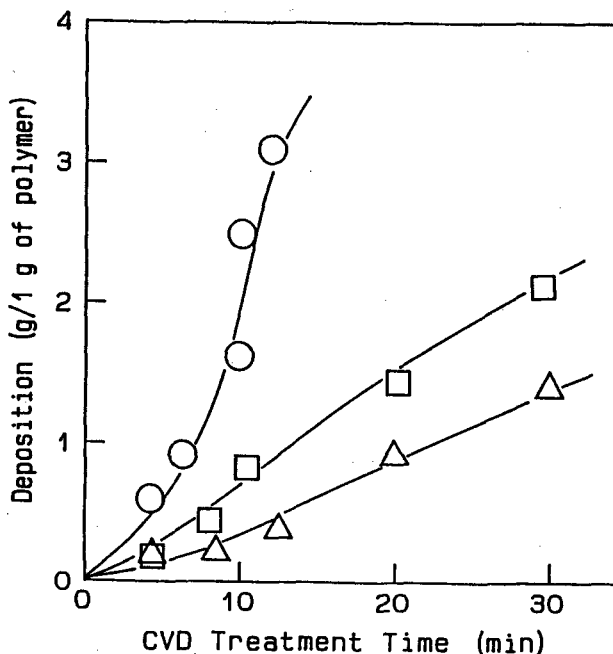
FIGURE 2. Effect of the polymer structure on the SiO_2 deposition using TMOS at 30 °C. Polymer : (◯) PMANI(B), (▢) PPRNI, (△) PBZNI. Exposure dose: 62 mJ/cm^2. Relative humidity: 95%. Polymer weight: 2×10^{-4}g. Surface area: 1.9 cm^2.

the irradiated polymer surface. Figure 3 shows the effect of silicon compound structure on SiO_2 or polysiloxane formation in irradiated PMANI(B) film. The formation rate decreased in the order MTMOS > TMOS > MTEOS > TEOS > TPOS. SiO_2 formation using TPOS was negligibly small under present conditions. It was confirmed that the SiO_2 or polysiloxane formation rate in the irradiated polymer surface was determined by both the rate of acid-catalyzed hydrolysis of alkoxysilanes and concentration of alkoxysilanes in the vapor phase.

SiO_2 formation using TMOS vapor increased with increasing polymer film thickness and showed a saturation at thicknesses above ca. 400 and 800 nm for PMANI(A) and PMANI(C), respectively. This roughly corresponds to the penetration depth of 254-nm light. This means that TMOS diffused into the polymer film and the hydrolysis and subsequent polycondensation reactions occurred beneath the film surface and at the
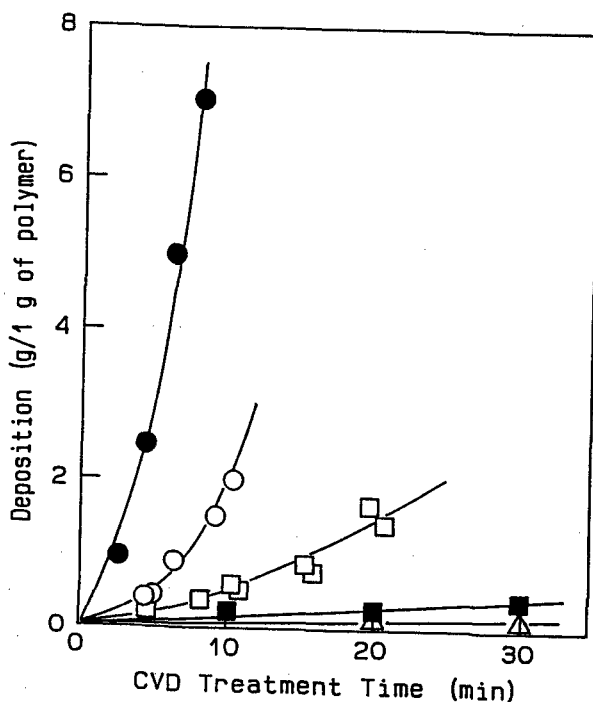
FIGURE 3. Effect of silicon compound structure on the SiO_2 deposition in irradiated PMANI(B) film at 30 °C. Silicon compound : (●) MTMOS, (○) TMOS, (☐) MTEOS, (■) TEOS, (△) TPOS. Exposure dose : 62 mJ/cm^2. Polymer weight : 2X10^{-4}g. Surface area : 1.9 cm^2. Relative humidity: 95%.

film-air interface. The depth of the SiO_2 formation layer was beyond the depth of the water sorption layer ($\approx$ 50 nm) of the irradiated polymer films (see Figure 1). The methanol liberated during the hydrolysis of TMOS in the film may help the diffusion of water in the film by destroying the "hydrophobic barrier" of the photochemically formed 1-tetralone and/or 1-tetralone azine.

Figure 4 shows the effect of CVD treatment time on the oxygen plasma etching of the irradiated PMANI(A) film. The etching rate of PMANI(A) was 0.1 µm/min in the present etching conditions. The typical curve for the etching with oxygen plasma was observed for the PMANI(A) film which was irradiated and subsequently exposed to the vapor of MTEOS for 15 min. The etching rate can be divided into three different regions that occur

in sequence: initial rapid region, very slow region, and rapid region which was almost equal to the etching rate for PMANI(A) film. The period where the etch resistance to oxygen plasma can be observed increased with CVD treatment time of the irradiated films. The initial rapid region corresponds to the process that polymers are etched to make SiO_2 layer acting as etch barrier to oxygen plasma. In the very slow region SiO_2 layer is working as a good etch barrier, where the etching rate was 100 times slower than that of PMANI(A) film. The latter rapid region shows the etching of PMANI(A) layer after the removal of SiO_2 layer by oxygen plasma etching.
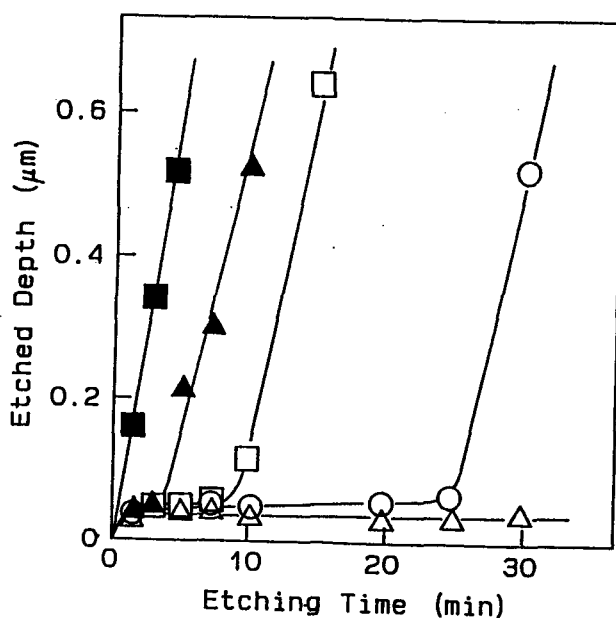

FIGURE 4. Effect of CVD treatment time on the oxygen plasma etching of the PMANI(A) films which were irradiated with dose of 171 mJ/cm^2 and subsequently exposed to the vapor of MTEOS at 30 °C and 58% RH. CVD treatment time: (■) 0, (▲) 10, (□) 13, (O) 15, (△) 20 min.

CONCLUSIONS

Polymers bearing 1,2,3,4-tetrahydro-1-naphthylideneamino p-styrene-sulfonate (NISS) unit, which forms p-styrenesulfonic acid upon UV irradiation, were synthesized by the copolymerization of NISS and either

methyl methacrylate, isopropyl methacrylate, or benzyl methacrylate. When the UV-irradiated polymer films were exposed to the vapor of tetraalkyl orthosilicates under humid conditions at 30 °C, SiO_2 networks were formed at the surface. The factors affecting the rate of SiO_2 formation were studied. The polymer films obtained after UV irradiation and subsequent exposure to the vapor of alkoxysilanes showed a good etching resistance to oxygen plasma. It is suggested that the preliminary results point out the potential for application of this system as plasma developable resists using surface modification.

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