

The Importance of Organosilane Polymer Photo-Oxidation in Resist Pattern Fabrication

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Synopsis

The siloxane structure formed in photo-oxidized poly(methylphenylsilane) and poly(methylpropylsilane) is evaluated to clarify its effect on resist sensitivity. It is produced by 17–35 mol% where exposure energy corresponds to the resist sensitivity. This structure change enhances polymer solubility with the developer. Photo-oxidation reaction is found to be an important factor for fabricating organosilane polymer resist patterns.

INTRODUCTION

Organosilane polymers are susceptible to both photodegradation^{1,2} and photo-oxidation^{3,4} during the irradiation of ultraviolet (UV) light in air, and behave as positive-mode photoresists.^{5,6} Since organosilane polymers have high sensitivity to UV light and high durability to O₂ reactive ion etching, they can be applied to positive top-imaging resist materials in a two-level layer resist system.⁷ The mechanism of positive resist pattern formation of organosilane polymers has been thought to be according to the molecular weight decrease caused by photodegradation. However, the contribution of photo-oxidation to the resist characteristics has not been clarified.

The photo-oxidation reaction of organosilane polymers produces a siloxane structure. Then the main chain consists of a mixture of silane and siloxane segments. Since polysiloxanes usually reveal good solubility with organic solvents, the siloxane structure in photo-oxidized organosilane polymers is expected to influence solubility with the development solvents. As positive resist sensitivity generally depends on the solubility change of polymers with the development solvents, the resist sensitivity of organosilane polymers is thought to be influenced by the content of the siloxane structure.

This report discusses the effect of photo-oxidation on resist sensitivity. Poly(methylphenylsilane) (PMPS) and poly(methylpropylsilane) (PMPPrS) were investigated as typical organosilane polymers with and without phenyl pendant groups.

EXPERIMENTAL

Synthesis of PMPS and PMPPrS was carried out according to the previously published procedure.^{8,9} The high and low molecular weight portions of the bimodal molecular weight distribution of PMPPrS (abbreviated HMP and LMP, respectively) were fractionated. Molecular weights were measured by

gel permeation chromatography (GPC) with tetrahydrofuran (THF) as eluent. PMPS had a molecular weight of 38×10^3 and a polydispersity of 2.4, HMP had $3,900 \times 10^3$ and 2.8, and LMP had 19×10^3 and 1.9. Films of PMPS, HMP, and LMP were spin-coated $0.3 \mu\text{m}$ thick on the substrate through all the experiments. KRS-5 and silicon wafer were used as substrates for the infrared (IR) measurement and the resist characterization, respectively. The siloxane content was evaluated from IR spectra measured with a FT-IR spectrometer (Perkin Elmer). ESCA spectra were also measured to determine the chemical state of Si atoms in the polymer with a Shimadzu 760 spectrometer. Gold was thinly deposited on the film, and the binding energy in ESCA spectra was calibrated with the Au_{4f} core level signal. A spectro-irradiator (JASCO CMA-01) and Xe lamp (300 W) were used as light sources. Monochromatic light with 5 nm of full width at half maximum can be obtained with the spectro-irradiator. The resist sensitivity, the dose where the film thickness becomes to zero after development, was determined with cyclohexanol as a developer. Development and rinse were carried out at 25°C . PMPS, HMP, and LMP are insoluble to cyclohexanol. Their resist film thickness was constant in unexposed areas during development. The solubility of polymer films was examined by dipping them into solvents for 1 min.

RESULTS AND DISCUSSION

Figure 1 shows ESCA spectra of PMPS before and after irradiation of light from the Xe lamp in air. Before light irradiation, a Si_{2p} core level signal was observed at 100.4 eV. It was assigned to Si atoms forming silane bonds. However, after 1 min of light irradiation, a new peak appeared at 102.9 eV and the original peak at 100.4 eV decreased. The new 102.9 eV peak corresponds to Si atoms forming siloxane bonds. This suggests that the polymer main chain consists of silane and siloxane bonds. After 5 min irradiation, the original peak decreased considerably. This indicates that almost all surface Si—Si bonds were changed to siloxane bonds by light irradiation.

The ESCA spectra have the advantage of separation of silane and siloxane signals. However, they represent only the chemical structure of the film subsurface 100–200 Å thick, and do not exhibit the average structure of the whole film used here. On the other hand, the IR study can give information on the chemical structure averaged along the depth of the film, and is expected to coincide with resist characteristics. Therefore, the further study on the photo-oxidation was performed by IR measurement.

The IR absorption bands assigned to siloxane bonds of photo-oxidized PMPS and PMPrS appeared at 1050 cm^{-1} and 1040 cm^{-1} , respectively. The intensity of their absorption bands was saturated by irradiating light from the Xe lamp for 10 min in air. To determine the degree of photo-oxidation at this saturated state, the IR spectrum of the photo-irradiated PMPS was compared with that of poly(methylphenylsiloxane) (PMPSO) as shown in Figure 2. Photo-oxidation caused not only the increase of the absorption corresponding to siloxane bonds but also the change of the four strong absorption bands at $800\text{--}700 \text{ cm}^{-1}$, which are assigned to Si—C and phenyl groups. IR spectrum of sufficiently photoirradiated PMPS resulted in being very similar to PMPSO

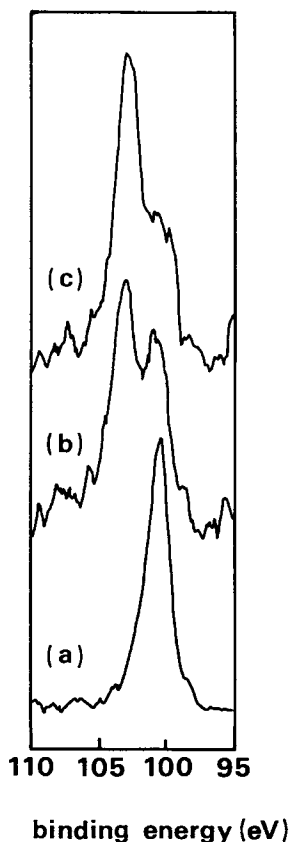


Fig. 1. ESCA spectra of poly(methylphenylsilane) film before and after the light irradiation from the Xe lamp in air. (a) Original polymer; (b) after irradiation for 1 min; (c) after irradiation for 5 min.

in terms of absorbance scale. This indicates that silane bonds in PMPS were almost completely changed to siloxane bonds by the light irradiation.

Assuming the extinction coefficient of the siloxane absorption band is constant regardless of the degree of photo-oxidation, siloxane content in the polymer film should be proportional to the siloxane absorption intensity in absorbance scale, because the Lambert-Beer's law is applicable. The siloxane absorption intensity was evaluated in terms of area obtained by subtracting the original spectrum from the photoirradiated one. The siloxane content, f , was obtained by normalizing the area with the IR spectrum of completely photo-oxidized film as a criterion.

Figure 3 shows the dose dependence of the siloxane content in PMPS oxidized by 254 and 330 nm light irradiation. PMPS was rapidly oxidized with 254 nm light irradiation and the siloxane content approached unity with the dose of 400 mJ/cm². On the other hand, the siloxane content was almost saturated at $f = \text{ca. } 0.4$ with 330 nm light irradiation over the dose of 700 mJ/cm². The absorption band at 330 nm, which is thought to be assigned to $\sigma-\sigma^*$ transition,¹⁰ is easily bleached by UV light irradiation.¹ The saturation

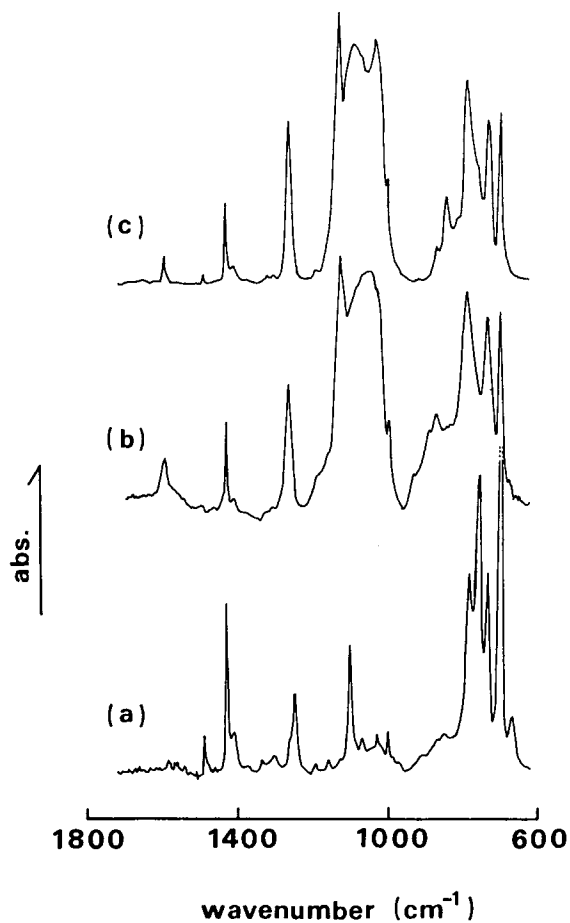


Fig. 2. IR spectra of (a) poly(methylphenylsilane), (b) sufficiently photo-oxidized poly(methylphenylsilane), and (c) poly(methylphenylsiloxane) in an absorbance scale.

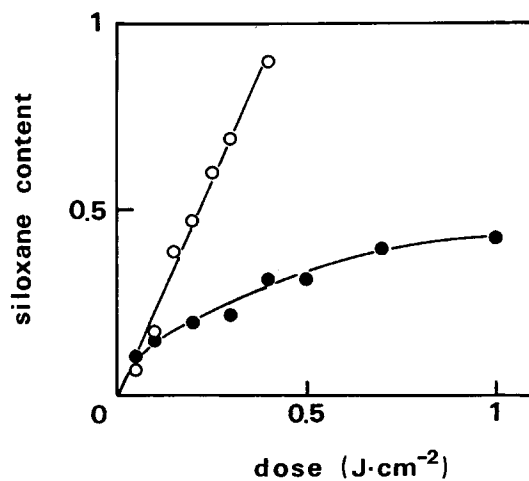


Fig. 3. Siloxane content produced in poly(methylphenylsilane) versus the dose. (○) 254 nm light irradiation; (●) 330 nm light irradiation.

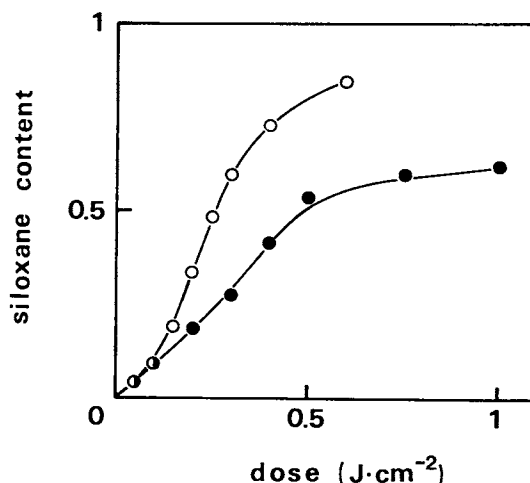


Fig. 4. Siloxane content produced in poly(methylpropylsilane) versus the dose. (○) 254 nm light irradiation; (●) 330 nm light irradiation.

of the siloxane formation is thought to arise from the decrease in polymer absorption at 330 nm caused by this. Figure 4 shows the dose dependence of the siloxane content in HMP. HMP was also rapidly oxidized by 254 nm light irradiation and the siloxane content was almost saturated at $f = \text{ca. } 0.6$ with 330 nm light irradiation. These curves for HMP agreed with those for LMP, and the rate of siloxane formation did not depend on the initial molecular weight. This is reasonably understood from the same photoreactivity of HMP and LMP.⁴

The siloxane contents and the molecular weights of PMPS and HMP after the light irradiation corresponding to the resist sensitivity are summarized in Table I. The siloxane structure formation and the molecular weight decrease were observed at the resist sensitivity. This means that both photo-oxidation

TABLE I
Resist Sensitivity and Molecular Parameters of Poly(methylphenylsilane) and Poly(methylpropylsilane) Films

	PMPS	HMP
Initial \overline{M}_w	38×10^3	$3,900 \times 10^3$
254 nm light irradiation		
D_0^a (mJ/cm ²)	180	130
$f(D_0)^b$	0.35	0.17
\overline{M}_w	11×10^3	11×10^3
330 nm light irradiation		
D_0 (mJ/cm ²)	400	300
$f(D_0)$	0.24	0.27
\overline{M}_w	9×10^3	12×10^3

^a Resist sensitivity determined with cyclohexanol as a developer.

^b Siloxane content at the resist sensitivity.

and photodegradation occurred. The siloxane contents were found to be $f = 0.17\text{--}0.35$ and the molecular weights were ca. 10×10^3 in these cases. LMP revealed that the f value and the molecular weight were 0.18 and 7×10^3 at the resist sensitivity, 160 mJ/cm^2 with 330 nm light irradiation. PMPS, HMP, and LMP show poor solubility with alcohols before light irradiation. However, after light irradiation, they revealed good solubility with alcohols, and their solubility came to resemble PMP SO. This improvement of the solubility is expected to be due to the existence of the siloxane structure.

The molecular weight of PMPS decreased to ca. $1/3$ of the initial polymer at the resist sensitivity, and HMP to ca. $1/300$. Since a decrease in molecular weight of the polymer generally improves solubility, photodegradation of organosilane polymers was expected to contribute to the improvement in the solubility. Actually, LMP can be developed at lower f value than HMP. If the solubility depended on only f value, the f values of LMP and HMP should be equal. Therefore, the decrease of molecular weight improves solubility in the case of organosilane polymers.

Before light irradiation, LMP reveals almost the same solubility as HMP. The molecular weight of LMP is a little higher than that of HMP at resist sensitivity. To investigate effects of molecular weight decrease and siloxane content on solubility, LMP was irradiated *in vacuo*. This condition allowed photodegradation but little photo-oxidation. After being exposed to 1 J/cm^2 of 330 nm light *in vacuo*, f value and molecular weight of LMP became 0.05 and 9×10^3 , respectively. This film revealed poor solubility with alcoholic solvents as summarized in Table II. Alkylsilane polymers were reported to undergo photovolatilization,³ however, the LMP film retained more than 90% of the initial thickness through irradiation *in vacuo*, evaluated from the intensity of IR absorption bands. Although the molecular weight of this sample was not larger than that of HMP irradiated with the dose at the resist sensitivity, it exhibited almost the same solubility as the original LMP. It was

TABLE II
Dependence of Poly(methylpropylsilane) Solubility on Siloxane Content and Molecular Weight

	HMP		LMP	
	Original polymer	at D_0^a	Original polymer	Irradiated <i>in vacuo</i> ^b
$\overline{M_w}$	$3,900 \times 10^3$	12×10^3	19×10^3	9×10^3
f	0	0.27	0	0.05
Solubility				
Methanol	X	X	X	X
Isopropyl alcohol	X	Δ^c	X	X
Amyl alcohol	X	\circ	X	X^d
Cyclohexanol	X	\circ	X	X

^a Irradiated at 330 nm by 300 mJ/cm^2 .

^b Irradiated at 330 nm by 1 J/cm^2 .

^c Thin layer still remained on the substrate, however, it was completely removed at the dose of 400 mJ/cm^2 .

^d The film became considerably thin.

not soluble with cyclohexanol, the development solvent, indicating that the development and the resulting resist sensitivity is seriously influenced by the existence of the siloxane structure in the polymer main chain. The photo-oxidation is considered to be an important factor for resist pattern fabrication of organosilane polymers.

CONCLUSION

The siloxane structure formed by the photo-oxidation reaction of PMPS and PMP_rS was evaluated and discussed with respect to their resist sensitivity. Silane bonds were completely changed to siloxane bonds by the sufficient light irradiation from Xe lamp. Using the completely photo-oxidized film as a criterion, the siloxane content in the polymer was evaluated on the basis of siloxane IR absorption intensity. Siloxane content rapidly increased and approached unity with 254 nm light irradiation. On the other hand, it was saturated at $f = 0.4-0.6$ with 330 nm light irradiation. With the dose corresponding to the resist sensitivity, 17-35 mol% of silane bonds changed to siloxane bonds. LMP film irradiated by 1 J/cm² of the 330 nm light *in vacuo*, which suffered sufficient molecular weight decrease but little photo-oxidation, was not soluble with the development solvent. Therefore, the photo-oxidation reaction is thought to be an important factor for the resist pattern fabrication of organosilane polymers.

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