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Synthesis of Silicon-based Polymer Films by Excimer Laser-induced Photo-reaction of Phenylsilane and Methylphenylsilane

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The synthesis of silicon-based polymer films was studied by excimer laser (248 nm)-induced photo-reaction of phenylsilane and methylphenylsilane at reduced pressure. IR and UV–VIS results showed that the films were composed of Si–C network structures with phenyl rings.

Keywords: excimer laser; silicon-based polymer; film; phenylsilane; methylphenylsilane; photo-reaction

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1 INTRODUCTION

Silicon-based polymers are promising new functional materials[1,2] Whereas polysiloxanes are already produced on an industrial scale and are used in various fields due to their excellent heat resistivity and chemical stability,[3] many other types of silicon-based polymers are yet to be studied. However, the methods of synthesis of silicon-based polymers and the kinds of monomer available are limited compared with those of carbon-based polymers.[4,5] Development of polymerization methods that are applicable to many types of monomers is desirable for the silicon-based polymers.

The excimer laser is a unique light source, which produces extremely strong ultraviolet light. It has been studied in various fields of application, such as micro-machining[6] and surface modification.[7] It is also a very promising tool for polymer-film synthesis.[8–13] Although many groups have reported on the synthesis of materials by photo-reaction induced by infrared lasers,[14–18] those induced by excimer lasers are relatively few.[19–25] In the present paper, we report on synthesis of silicon-based polymer films by excimer laser-induced photo-reaction of phenylsilane and methylphenylsilane.

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2 EXPERIMENTAL

Phenylsilane (PS) and methylphenylsilane (MPS) were obtained from Shin-Etsu Silicone. The experimental apparatus used for the film deposition is shown schematically in Fig. 1. The monomer vapor was introduced into the evacuated reactor, keeping a constant vapor pressure. Nitrogen gas flow (200 ml min^{-1}) introduced close to the quartz glass window prevented contamination of the windows by ablated materials and total pressure

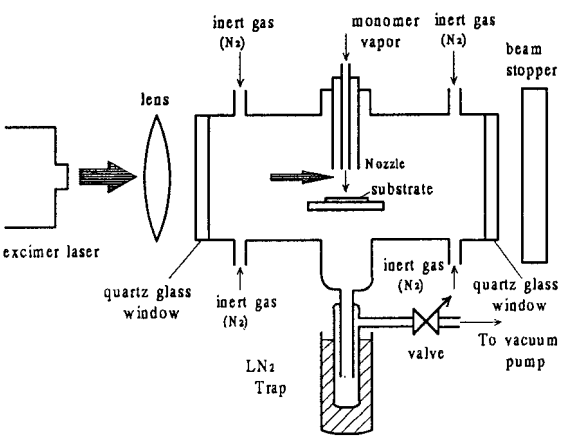

Figure 1 Schematic view of the excimer laser reactor.

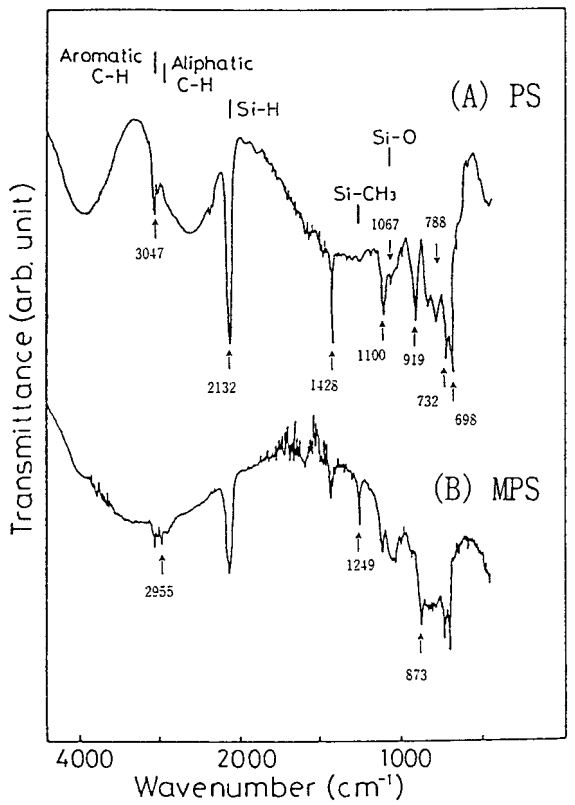

Figure 2 Typical IR spectra of the polymer films prepared with (A) PS (67 Pa, 15.5 W cm^{-2}, L_{ns} 10 mm) and (B) MPS (200 Pa, 20.6 W cm^{-2}, L_{ns} 10 mm).

was kept constant (400 Pa). A single-crystal silicon wafer or a quartz glass plate about 10 mm square was used as substrate for the depositing films. Focused excimer laser light (248 nm, 10 ns, 60 Hz, AQX-150, MPB) irradiated the monomer vapor just below the nozzle. The laser fluences ranged from 40 to 1067 mJ cm^{-2}. Polymeric films were formed on the substrate, depending upon the conditions. Vapor products and unreacted monomer were trapped by a liquid-nitrogen trap.

The chemical structure of the films was studied as a function of experimental conditions such as laser power density, nozzle–substrate distance (L_{ns}), and monomer vapor pressure, by Fourier transform infrared spectroscopy (FT-IR; Perkin-Elmer 1600), UV–VIS spectroscopy (UV; UV-1200, Shimadzu) and X-ray photoelectron spectroscopy (XPS; XSAM-800, Kratos). Charge shifts of the XPS spectra were observed for most samples because of their low electric conductivity and were corrected by the Au $4f_{7/2}$ peak (binding energy of 83.9 eV) from the small quantity of gold evaporated onto the film surface.

3 RESULTS AND DISCUSSION

Polymeric films were formed on the substrate, depending on the irradiation conditions, for both PS and MPS. For MPS, a laser power of about 15–20 W cm^{-2} and MPS pressure of 67 Pa were, suitable for polymeric film formation. Too high a laser power led to powder formation. The suitable laser power range depended on the pressure of the monomer, and its type.

Typical IR spectra of the film prepared with PS (A) and MPS (B) are shown in Fig. 2. The spectrum of the PS polymer contained bands of mono-substituted benzene (698 and 732 cm^{-1}), Si—phenyl (1100 cm^{-1}), aromatic ring stretching (1428 cm^{-1}), aromatic C—H (3047 cm^{-1}), Si—H (2132 cm^{-1}), Si—H_2 (919 cm^{-1}) and Si—O (1067 cm^{-1}).[26] The absorptions around 788 cm^{-1} can be assigned to 1,4-disubstituted benzene and Si—C. The spectrum of the MPS polymer exhibited Si—CH_3 (1249 cm^{-1}) and relatively strong aliphatic C—H (2955 cm^{-1}) bands reflecting the monomeric structure, in addition to those found for PS. It also exhibited a broad absorption around 800 cm^{-1}, which indicated the presence of a Si–C network structure in the polymer.

The IR spectra of MPS at different nozzle–substrate distances (L_{ns}) exhibited basically the same absorptions. However, the absorption intensities decreased with the increase in L_{ns}, indicating that the film thickness decreased with increasing L_{ns}.

The IR spectra of the PS and MPS polymer films did not depend on the monomer pressures, although absorption intensities increased with the pressure of MPS. In other words, the film thickness increased with increasing pressure of MPS.

The UV–Vis spectra of the PS and MPS polymer films, measured by the reflection method using an integrated sphere, are presented in Figs 3 and 4, respectively, together with the spectra of the corresponding monomers [in tetrahydrofuran (THF)]. The broad absorption bands of the polymer films must be due to the Si–C network structure, and the broader absorptions reflect well-developed Si–C network structures.[27]

Table 1 lists the XPS results of the polymer films of MPS. The Si 2*p* binding energies ranged from 99.4 to 100.1 eV and tended to shift to a slightly

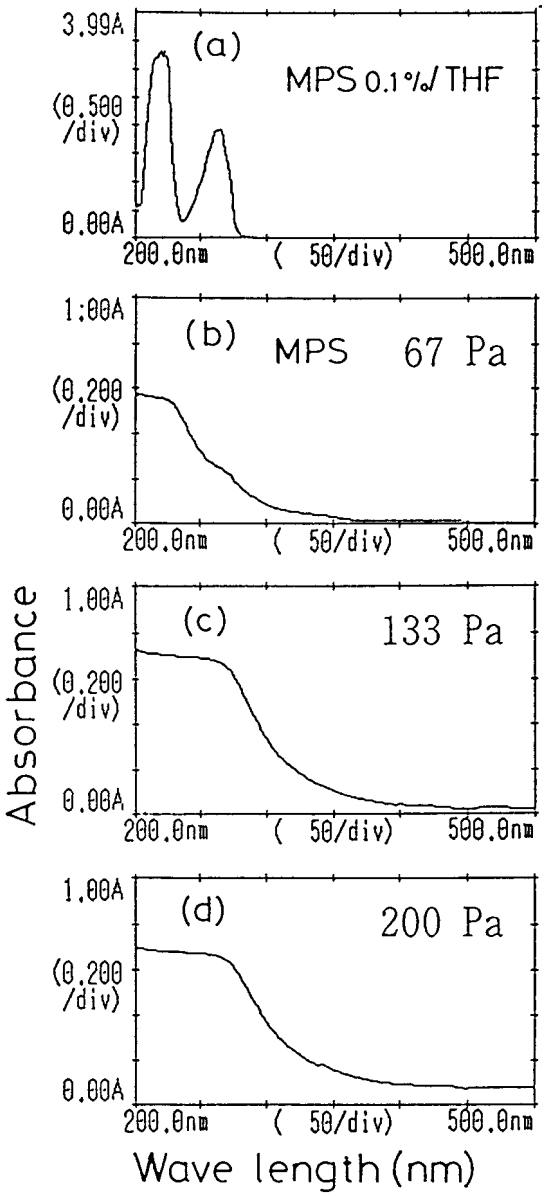

Figure 3 UV–VIS spectra of MPS monomer and the polymer films prepared from (a) 0.1% MPS solution in THF; (b) MPS at 67 Pa; (c) MPS at 133 Pa; (d) MPS at 200 Pa. Laser power 18.2–23.6 W cm^{-2}, L_{ns} 10 mm, irradiation time 30 min.

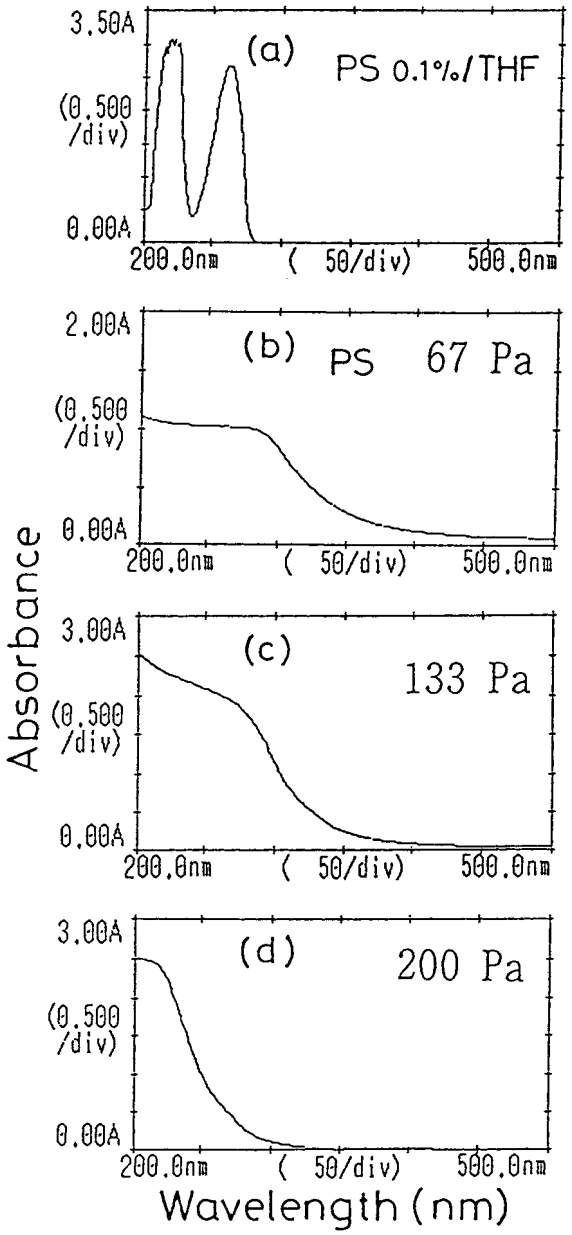

Figure 4 UV–VIS spectra of PS monomer and the polymer films prepared with (a) 0.1% PS solution in THF; (b) PS at 67 Pa; (c) PS at 133 Pa; (d) PS at 200 Pa. Laser power 13.4–16.0 W cm^{-2}, L_{ns} 10 mm, irradiation time 30 min.

higher energy as the laser power density increased. However, L_{ns} and the pressure of MPS did not affect the Si 2*p* binding energy. The Si 2*p* binding energy in the carbosilane structure ranges from 100.0 to 100.5 eV. For instance, the Si 2*p* binding energy of poly(diphenylsilylenemethylene) is 100.4 eV and that of poly(dimethylsilylenemethylene) is 100.5 eV. A lower binding energy ranging from 99.3 to 99.7 eV indicates a more silicon-rich structure, where the Si atom is surrounded by one Si and three C atoms.[12] Our experimental results

Table 1 XPS results of the polymer films from MPS.

Laser power density ($W\ cm^{-2}$)	Monomer pressure (Pa)	L_{ns}[a] (mm)	Si 2p		C 1 *s*		Atomic ratio	
			E_b[b] (eV)	FWHM (eV)	E_b (eV)	FWHM (eV)	C/Si	O/Si
22.8	200	10	100.1	2.7	283.4	1.7	7.2	0.9
20.6	133	10	100.1	2.8	283.5	1.8	6.8	0.8
17.5	67	10	100.1	2.4	283.6	1.6	7.7	0.5
13.8	200	15	99.9	2.5	283.3	1.8	7.8	0.9
15.0	200	10	99.5	2.5	283.0	1.8	7.5	0.7
13.1	200	7	99.4	2.4	283.2	1.6	7.0	0.6
MPS	—	—	—	—	—	—	7.0	—

[a] L_{ns}, nozzle–substrate distance.
[b] E_b, binding energy.

indicated that the polymer structure approached a carbosilane structure as the laser power density increased.

The C 1*s* binding energies ranged from 283.0 to 283.6 eV. The C/Si atomic ratios (6.8–7.8) were very close to that of MPS monomer (7.0). This means that the polymer structure essentially reflected the monomer structure; methyl and phenyl groups in the monomer were probably preserved in the polymer as side -chains. The O/Si atomic ratios in the range 0.5–0.9 indicated that the films were oxidized by exposing the polymer to the air.

The aging effect of the films was checked by IR and UV–VIS measurement. The IR spectrum of the film prepared with MPS at a pressure of 133 Pa was recorded after the film had been left in the ambient conditions for 60 days. The intensity of Si—O absorption ($1055cm^{-1}$) clearly increased after aging. In the UV–VIS spectra of the films prepared with MPS (Fig. 3) after they were exposed to the air for 55 days, the absorption edge shifted towards lower wavelength. For example, the sample of Fig. 3(d), with absorption up to 350nm, showed an absorption edge shift to around 300nm after aging. The reduction of UV absorption was probably due to the oxidation resulting in a polysiloxane structure.

4 CONCLUSIONS

Polymeric films were obtained by directly irradiating MPS and PS vapors with excimer laser light (248nm). IR and UV–VIS results showed that the films contained Si–C network structures with intact phenyl rings.

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