Deposition of polysiloxane films using CO_2 laser evaporation assisted by remote O_2 plasma and its transformation to silicon oxide films

Shuzo HATTORI[1], Toshiaki FUJII[2], Tsuneki YOKOI[2],
Mineo HIRAMATSU[2], Masahito NAWATA[2],
Masaru HORI[3] and Toshio GOTO[3]

[1]*Nagoya Industrial Science Research Institute,*
Naka-ku, Nagoya 460 JAPAN
[2]*Meijo University, Tempaku-ku, Nagoya 468 JAPAN*
[3]*Nagoya University, Chikusa-ku, Nagoya 464-01 JAPAN*

A simple deposition system using cw CO_2 laser for preparation of polysiloxane and silicon oxide films was demonstrated. CO_2 laser evaporation technique was applied to the deposition of polysiloxane thin films and remote microwave O_2 plasma during deposition was used for improving the hardness of formed polysiloxane film and eventually for transforming to the silicon oxide. The effects of O_2 plasma produced oxygen radicals on the properties of polysiloxane films were also investigated from XPS, FT-IR, and PyGC analyses.

Introduction

Polysiloxanes comprising an alternate silicon and oxygen skeleton have been widely used in industry as fluids, elastomers and resins. Polysiloxanes which perform chemically intermediate behavior between organic and inorganic material have many excellent characterizations including thermal and chemical stability, electrical property and durability. Polysiloxane thin films can be applied to the surface modifications for optical material and electronic device.

Up to now, the structures of a variety of polysiloxanes have been investigated by using pyrolysis gas chromatography (PyGC) and mass spectrometry (MS) [1, 2]. As for the preparation of silicon oxide films from several siloxane monomers, hexamethyldisiloxane (HMDSO) has been used as source materials for SiO_2 film using RF plasma polymerization or CVD methods [3]. Recently, Joubert *et al.* have demonstrated the transformation of polysiloxane to silicon oxide films by photon process using excimer lasers [4].

In the present work, laser evaporation technique was applied to the formation of polysiloxane thin films. A continuous wave (cw) CO_2 laser beam was used as the heat source for the material release from polysiloxane bulk target surface. During deposition oxygen radicals generated by the remote microwave O_2 plasma was introduced in order to improve the hardness of the formed polysiloxane film and to transform the film from polysiloxane to silicon oxide. The effects of oxygen radicals on the composition and properties of the films were investigated from X-ray photoelectron spectroscopy (XPS), fourier transform infrared spectroscopy (FT-IR), and PyGC analyses.

Experimental

Figure 1 shows the film deposition system using laser evaporation assisted by remote O_2 plasma. The system is composed of a deposition chamber, a continuous wave (cw) CO_2 laser (10.6 μm) for material release from polysiloxane target, and a remote microwave (2.45 GHz) O_2 discharge as a source of oxygen radicals. The cw CO_2 laser beam was introduced into the deposition chamber through a ZnSe window and irradiated the surface of the polysiloxane target directly, resulting in degradation of the surface of polysiloxane bulk target into a variety of siloxane oligomers. O_2 gas was introduced through a quartz tube of 10 mm diameter penetrating a microwave discharge cavity and was pumped out using rotary pump. The microwave power was supplied to the discharge cavity through a coaxial cable. The oxygen radicals generated by the remote microwave O_2 plasma were poured onto the substrate. During deposition the microwave power was maintained at 100 W and the O_2 pressure inside the deposition chamber was kept at 2.7 Pa. Control of the amount of oxygen radicals poured onto the substrate was performed by changing the distance between the microwave discharge cavity and the substrate. Silicon (100) and aluminum were used as the substrate. They were mounted at a distance of 10 cm over the polysiloxane target. Substrate heating was performed using a halogen lamp which was placed at a distance of 3 cm from the substrate. The substrate temperature was controlled by varying the applied voltage of the halogen lamp and was monitored with a thermocouple in contract with the surface of the substrate. The volume of the polysiloxane vapor evaporated from the surface of the target was controlled by varying the irradiation power of the CO_2 laser.

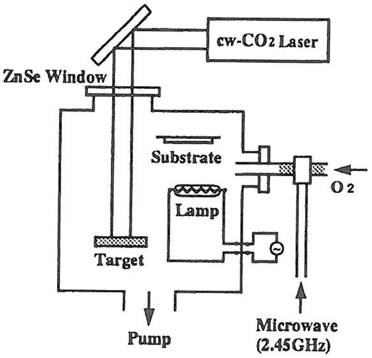

Fig. 1. Schematic diagram of film deposition system using CO_2 laser assisted by remote microwave O_2 plasma.

A powder of a polysiloxane sample with the glass transition point (*Tg*) of 80-90 ℃ was compressed into the disk target. That sample contained methyl and phenyl groups as functional group and its molecular weight was about 2100.

The structures of the deposited polysiloxane films were analyzed by FT-IR and XPS. The film thickness was measured from the observation of SEM image of the cross section of the film or using a tally step. The molecular weight of film was measured by PyGC.

Results and discussion

The film deposited at the CO_2 laser power of 5 W and at room temperature without the assistance of oxygen radicals was uniform and transparent, but not hard. When the CO_2 laser power increased above 5 W, such films were not formed due to excess polysiloxane vapor. With the assistance of oxygen radicals, on the other hand, films deposited at room temperature in the CO_2 laser power range of 5-12 W were not uniform nor transparent due to high rate reaction of siloxane oligomers with oxygen radicals. The film deposited without the assistance of oxygen radicals at substrate temperatures above the glass transition point *Tg* of target was not uniform nor transparent in the CO_2 laser power range investigated. With the assistance of oxygen radicals, however, films deposited at substrate temperatures above *Tg* were transparent, smooth, hard, free from pinholes and strongly adherent throughout the surface of films. These results suggest that substrate heating over the softening point of target is required in order to obtain uniform, transparent and hard polysiloxane thin films.

Figure 2 shows the CO_2 laser power dependence of the deposition rate of the film deposited at the substrate temperature of 100 ℃ and the substrate-cavity separation of 30 cm. The deposition rate increased at first gradually and then more rapidly with increase of laser power.

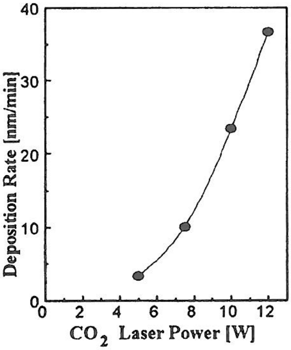

Fig. 2. CO_2 laser power dependence of deposition rate at the substrate temperature of 100 ℃ and the substrate-cavity separation of 30cm.

The atomic compositional analysis was carried out using XPS spectra. The C/Si and O/Si ratios of the film were obtained from the ratio of the intensities of the C (1s), O (1s) and Si (2p), corrected using the relative intensity factors. Figure 3 shows the C/Si and O/Si ratios of the film as a function of the CO_2 laser power. Films were deposited at the substrate temperature of 100 ℃ and the distance of 30 cm between substrate and microwave discharge cavity. The C/Si and O/Si ratios of the pure polysiloxane bulk were 4.9 and 1.0, respectively, which are indicated by the horizontal lines in Fig. 3. In the case of the film deposited at the CO_2 laser power of 5 W with the assistance of oxygen radicals, the C/Si and O/Si ratios of the film were 1.7 and 2.4, respectively. As shown in Fig. 3, as the CO_2 laser power increased, the C/Si ratio of the film increased and the O/Si one decreased. At the CO_2 laser powers above 10 W these ratios of the film were similar to those of polysiloxane bulk. Without the assistance of oxygen radicals, on the other hand, the C/Si and O/Si ratios of the deposited films were almost the same value as those of polysiloxane bulk.

Figure 4 shows the FT-IR spectra of (a) the polysiloxane bulk target and (b) the film deposited with the assistance of the oxygen radicals at the CO_2 laser power of 10 W, the substrate temperature of 100 ℃ and the substrate-cavity separation of 30 cm. The FT-IR spectrum (a) of polysiloxane bulk target have shown peaks of the strong Si-O-Si stretching mode in the range of 1000-1100 cm^{-1}, the $Si-CH_3$ (SiMe) symmetry bending mode around 1260 cm^{-1} and the $Si-C_6H_5$ (SiPh) bending mode around 1425 cm^{-1}. Peaks which appeared in the FT-IR spectrum (b) of the film deposited at the CO_2 laser power of 10 W are similar to those of polysiloxane bulk.

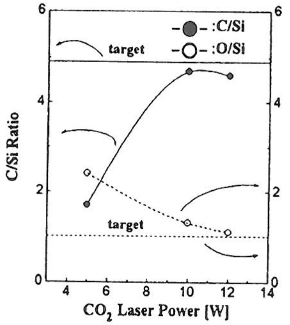

Fig. 3. CO_2 laser power dependence of the C/Si and O/Si ratios of the film at the substrate temperature of 100℃ and the substrate-cavity separation of 30cm.

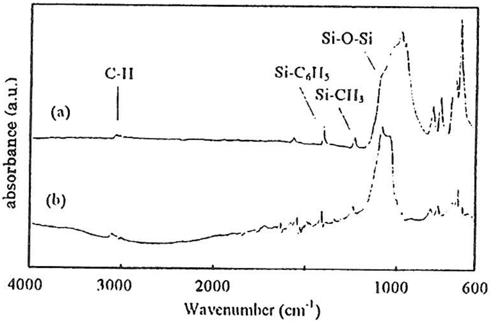

Fig. 4. The FT-IR spectra of (a) polysiloxane bulk target and (b) the film deposited with the assistance of oxygen radicals at the CO_2 laser power of 10W, the substrate temperature of 100℃ and the substrate-cavity separation of 30cm.

From the PyGC measurement, the molecular weight of the film deposited at the CO_2 laser power of 10 W, the substrate temperature of 100 ℃ and the substrate-cavity separation of 30 cm was about 32000, which resulted in the hard films. On the other hand, the molecular weight of the film deposited without the assistance of oxygen radicals was only 1100, which was smaller than that of polysiloxane bulk sample. Consequently, the highly crosslinked polysiloxane films were obtained with the assistance of oxygen radicals.

In the case of the film deposited at high CO_2 laser powers and long separation between substrate and microwave discharge cavity, it is expected from the results in Figs. 3 and 4 that repolymerization of siloxane oligomers mostly proceeded to reconstruct polymer film like bulk target because of the large density of siloxane oligomers relative to the oxygen radicals. In other words, a only small part of the methyl and phenyl groups of the siloxane oligomers would be replaced by oxygen on the depositing surface, resulted in a moderately crosslinked polysiloxane structure during deposition.

As shown in Fig. 3, the composition of the film deposited at low laser power was rather different from that of polysiloxane bulk. Especially, carbon content of the film decreased remarkably compared with the film deposited at higher laser power, probably because of the excess oxygen radicals for the siloxane oligomers produced by the CO_2 laser irradiation. In addition, carbon content of the film decreased furthermore by shortening the distance between substrate and microwave discharge cavity. Accordingly, for the purpose of obtaining silicon oxide films by using CO_2 laser evaporation assisted by oxygen radicals, hereafter the substrate-cavity separation was kept at 15 cm, which was the shortest in the present system, in order to increase the amount of oxygen radicals poured onto the substrate. In between these two extreme case, continuous change of film property in terms of grade of oxidation and extent of crosslinking was observed according to the laser power and oxygen radical concentration.

Figure 5 shows the substrate temperature dependence of the deposition rate of the film deposited at the CO_2 laser power of 5 W and the substrate-cavity separation of 15 cm. The deposition rate decreased at first rapidly and then more gradually with increase of substrate temperature.

Figure 6 shows the C/Si and O/Si ratios of the films as a function of the substrate temperature. Films were deposited at the CO_2 laser power of 5 W and the distance of 15 cm between substrate and microwave discharge cavity. The C/Si ratio of the film decreased with the increase of the substrate temperature, and it was less than 0.2 at the substrate temperature of 250 ℃. On the other hand, the O/Si ratio of the same film decreased at first and then became almost constant at 1.6.

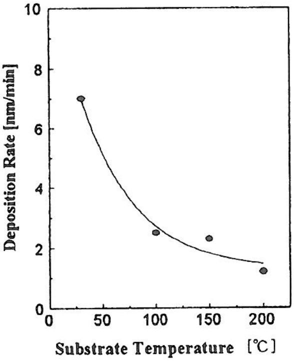

Fig. 5. Substrate temperature dependence of deposition rate at the CO_2 laser power of 5W and the substrate-cavity separation of 15cm.

Figure 7 shows the FT-IR spectra of the films deposited with the assistance of the oxygen radicals at the substrate temperature of (a) 30 ℃ and (b) 200 ℃. During deposition, the CO_2 laser power was 5 W, and the distance between substrate and microwave discharge cavity was 15 cm. In the case of the film deposited at 30 ℃, absorption peaks of C-O bond and O-H bond as well as Si-O-Si stretching mode appeared in the FT-IR spectrum (a). The peaks of O-H and C-O bonds in the film deposited at low substrate temperatures were attributed to the reaction of methyl and phenyl groups of siloxane oligomers with oxygen radicals. On the other hand, in the case of the film deposited at 200 ℃, the absorption peaks of O-H and C-O bonds disappeared in the FT-IR spectrum (b). In addition, the absorption peak of Si-O-Si stretching mode in spectrum (b) was narrower than that in spectrum (a).

In the case of low CO_2 laser powers and the short separation between the substrate and the microwave discharge cavity, a large amount of the oxygen radicals to the siloxane oligomers would have the sufficient ability of oxidation of CH groups. Accordingly, results in Figs. 6 and 7 suggested that in the case of the films deposited at low substrate temperatures the rupture of C-C and C-H bonds in the methyl and phenyl groups of siloxane oligomers would be most likely to occur by the oxygen radicals, resulting in the production of C-O and O-H bonds of the film. It is also expected that at high substrate temperatures the rupture of the Si-C bond in the siloxane oligomers would be likely to occur, resulting in the production of Si-O bond by the reoxidation of silicon after the removal of CH groups and then carbon-deficient films. As a result, the formation of a network of Si-O chains would proceed for the film at high substrate temperatures with the assistance of excess oxygen radicals. Namely, the transformation from polysiloxane to silicon oxide films could be performed effectively by a combination of thermal and radical oxidation processes. The low deposition rate at high substrate temperatures shown in Fig. 5 might be attributed to the removal of the residual CH groups from the film surface or in gas phase.

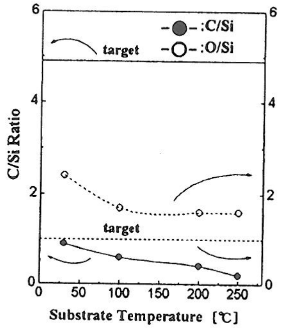

Fig. 6. Substrate temperature dependence of the C/Si and O/Si ratios of the film at the CO_2 laser power of 5W and the substrate-cavity separation of 15cm.

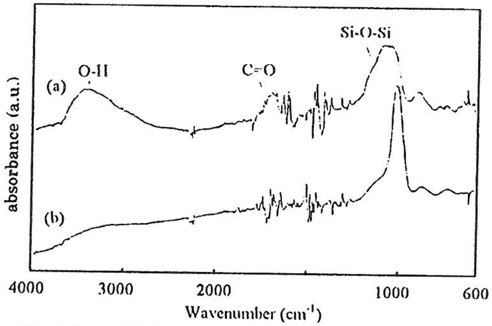

Fig. 7. The FT-IR spectra of the film deposited with the assistance of oxygen radicals at the CO_2 laser power of 5W, the substrate-cavity separation of 30cm and (a) the substrate temperature of 30℃, (b) the substrate temperature of 200℃.

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