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Effect of polymer addition and temperature on the structure of silicon-based polymer films deposited by excimer laser ablation of hexaphenyldisilane

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Abstract

The effects of the cooling target, heating substrate, and the addition of polysilanes were studied to control the film structure and properties of silicon-based polymer films synthesized by laser ablation deposition of hexaphenyldisilane (HPDS). The cooling target reduced the thermal effect, and the resultant film structure differed from that without cooling. The film structure was changed by the heating substrate and exhibited significant microhardness, while the thermal stability was not improved. The addition of polysilanes, in particular poly(dimethylsilane) (PDMS), was very effective in developing the Si–C network structure in the resultant films. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Silicon-based polymer; Hexaphenyldisilane; Poly(dimethylsilane); Laser ablation; Film

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1. Introduction

Laser ablation has many characteristic advantages for material syntheses, such as the stoichiometrical transfer of material and the capability for reactive deposition in ambient gases [1], and laser ablation phenomena of various polymer materials have been extensively investigated by practical and fundamental interests. The deposition of thin polymer films by laser ablation is a promising new method for preparing thin films of hard-to-process materials. Much attention has been paid to the change in surface morphology [2], the electric properties of the remaining polymer materials, and the machining process of the polymer [3]; many papers have been written concerning laser ablation deposition of carbon-based polymers such as poly(tetrafluoroethylene) (PTFE) [4–6], poly(methylmethacrylate) (PMMA) [4], and poly(acrylonitrile) (PAN) [7]. Nishio et al. [8] recently studied the effect of temperature control of substrates during laser ablation of 3,4,9,10-perylenetetracarboxylic dianhydride. Tsuboi and Itaya [9] investigated an anthracene photosensitizer during laser ablation of polystyrene at 351 nm.

However, there are few papers that discuss the laser ablation deposition of silicon-based polymers, although the ablation behavior and ablated fragments have been analyzed with several kinds of polysilane [10–12]. Silicon-based polymers are expected to become new functional materials [13,14]. Many silicon-based polymers besides polysiloxanes are being studied to determine their synthesis method and properties on a laboratory scale. The synthesis method of silicon-based polymers and the types of available monomers are limited compared with those of carbon-based polymers. Polymerization techniques that apply to many kinds of monomers are sought in the field of silicon-based polymers. Pulsed-laser ablation deposition is one promising method of synthesizing silicon-based polymer films. We studied the synthesis of silicon-based polymer films by plasma polymerization [15] and laser ablation deposition [16,17]. We demonstrated that silicon-based polymer films could be synthesized by laser ablation deposition of hexaphenyldisilane (HPDS), which is difficult to polymerize by conventional chemical methods because of its insolubility in organic solvents. It is very important to control the chemical structure of the products in the case of laser ablation deposition of organic materials. If organic materials are ablated under severe conditions, such as high fluence or high photon energy, they decompose to very small fragments or elements, and the resulting films are no longer organic. It is necessary to retain the desired parts and remove or decompose the

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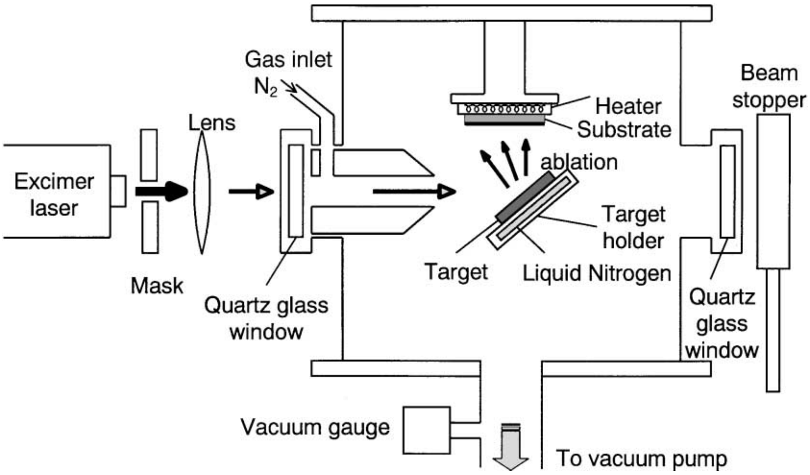

Fig. 1. Schematic view of the experimental apparatus for pulsed-laser ablation deposition.

unwanted parts of the organic source materials during ablation, which leads to obtaining the desired product structure. Therefore, the ablation conditions and mechanisms must be investigated. In this paper, effects of the cooling target, heating substrate, and polymer addition on the structure and the properties of films deposited by excimer laser ablation of HPDS.

2. Experimental

The experimental apparatus used for the film deposition is schematically shown in Fig. 1. The commercial HPDS powders were purified by rinsing twice in tetrahydrofuran (THF), to remove the soluble component in the reagent and were then dried in a vacuum and darkness at a temperature of 313 K. In some experiments, poly(dimethylsilane) (PDMS, Mn = 2000) and poly(methylphenylsilane) (PMPS, Mn = 54 000) were mixed with HPDS powder using a mortar. The powder pellets were made by a tablet die with a diameter of 20 mm. The pellet was fixed on a target holder at the center of the vacuum chamber. The target was cooled by liquid nitrogen in some experiments. A single-crystal silicon wafer about 20 mm^2 was used as a substrate and placed on a substrate holder opposite the target. In some experiments, the substrate was heated up to 573 K. The distance between the target and the substrate was 20 mm. The vacuum chamber was evacuated to a background pressure of 4.0×10^{-3} Pa. Nitrogen gas was then introduced from the gas inlet at the window to prevent contamination by the ablated materials, and to keep a constant pressure of 3.0 Pa. The target was irradiated with an excimer laser light (248 nm, AQX-150, MPB) through the quartz glass window at an incident angle of 40° with respect to the target.

The chemical structure of the films was studied by Fourier transform infrared spectroscopy (FT-IR, Perkin-Elmer 1600) and X-ray photoelectron spectroscopy with a monochromated Al Kα X-ray (XPS, VG, Escalab 220XL). 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 from the small quantity of gold evaporated onto the film surface. The thickness of the films was measured by stylus profilometry.

The thermal stability of the deposited films was evaluated by thermogravimetry (TG, MAC, TG-DTA2000). The experimental parameters were as follows: heating rate, 5 K/min; cooling rate, 20 K/min; maximum temperature, 1073 K; ambient gas, argon gas flow of 50 $\text{cm}^3\,\text{min}^{-1}$. The sample weight was 0.5–2.0 mg. Since it was difficult to measure the TG behavior of the films themselves, the films were scraped with a thin knife and the resultant powders were put into the TG crucible. The Vickers microhardness was measured by a microhardness tester (MHT-4, Paar) with loads of 0.5–5 g.

3. Results and discussions

3.1. Effect of cooling target

The synthesis of silicon-based polymer films by laser ablation of HPDS was investigated in a previous study [17]. The film structure and properties depended on the ablation conditions, particularly the laser fluence and repetition rate. Some deposited films contained an HPDS monomer, depending on the condition. Simple evaporation or decomposition of the HPDS monomer from the target could occur by the thermal effect of the target, since HPDS evaporates or decomposes at 623 K. Cooling the target may suppress the thermal effect of the target.

The HPDS target was cooled by liquid nitrogen and ablated by 248 nm at 2 Hz, 135 $\text{mJ}\,\text{cm}^{-2}$, and the deposited film was formed on a substrate. A bluish-green luminescence with a long lifetime was observed on the irradiated surface during laser ablation, and the laser plume above the

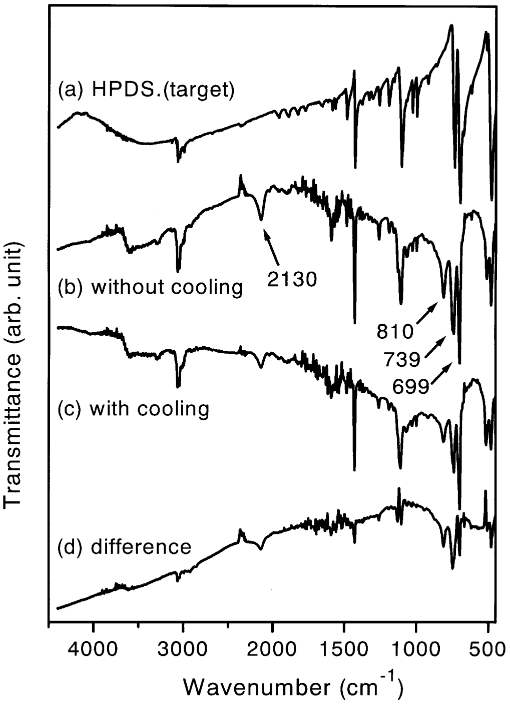

Fig. 2. IR spectra of: (a) HPDS (target); (b) the deposited film at 2 Hz, 135 mJ cm^{-2} without target cooling; (c) the deposited film at 2 Hz, 135 mJ cm^{-2} with target cooling; (d) difference spectrum between (b) and (c).

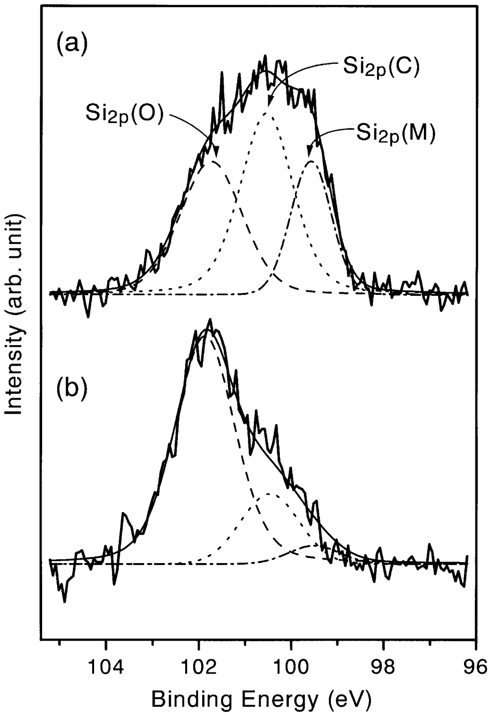

Fig. 3. Results of peak separation of the Si 2p XPS spectra: (a) the film without target cooling; (b) the film with target cooling.

target was very weak, while bluish-white luminescence with a short lifetime and a clear orange plume were observed without target cooling. Figs. 2(a) and (b) show the IR spectrum of the HPDS (target) and that of the deposited film at 2 Hz, 135 mJ cm^{-2} without target cooling. These spectra were similar, but new absorption peaks appeared at around 2130 and 810 cm^{-1}. The absorption at 2130 cm^{-1} could be attributed to Si–H. The absorption at 810 cm^{-1} could be attributed to overlapping by Si–C and 1,4-di-substituted benzene [17]. Figs. 2(c) and (d) show the IR spectra of the deposited film with target cooling and the difference spectrum between Figs. 2(b) and (c). There was no significant disparity in the IR spectra with and without cooling. However, a small difference was observed in the intensity ratios of the 699, 739, and 810 cm^{-1} peaks. Since these peaks are related to substituted benzene and S–C, this difference suggests that the binding structure of the Si and phenyl group differed between films with and without target cooling.

Table 1 lists the composition of the film determined by XPS measurement and deposition rate. The deposition rate decreased significantly by target cooling, and the composition of the film was also changed by target cooling. The C/Si atomic ratio of film without target cooling was 14.4, close to that of HPDS (18). The C/Si atomic ratio of film with cooling was 9.2, much smaller than that of the film without cooling. The Si 2p XPS spectra were separated according to the previous research [17] (Fig. 3). The Si 2p spectrum of the film with target cooling, contained a substantial amount of the Si 2p(O) component, the structure of which is considered to be similar to the siloxane structure. It also contained an Si 2p(C) component, which has a structure similar to the carbosilane structure. It contained a very small amount of the Si 2p(M) component with a structure similar to HPDS. The Si 2p spectrum of the film without cooling exhibited a different shape and contained more of the Si 2p(M) component. These results suggest that target cooling suppresses the thermal effect, and thus evaporation and the thermal decomposition of HPDS decrease. Consequently, the deposition rate of the film without cooling was higher than that with cooling. The film without target cooling was formed with relatively larger fragments, and its composition was close

Table 1
Composition of the film determined by XPS and deposition rate of the film

Condition			Composition (at.%)			Atomic ratio of C/Si	Deposition rate (nm per pulse)
Repetition rate (Hz)	Fluence (mJ cm^{-2})	Target cooling	Si	C	O		
2	135	No	5.8	83.8	10.4	14.4	1.6
2	135	Yes	8.8	81.7	9.5	9.2	0.9

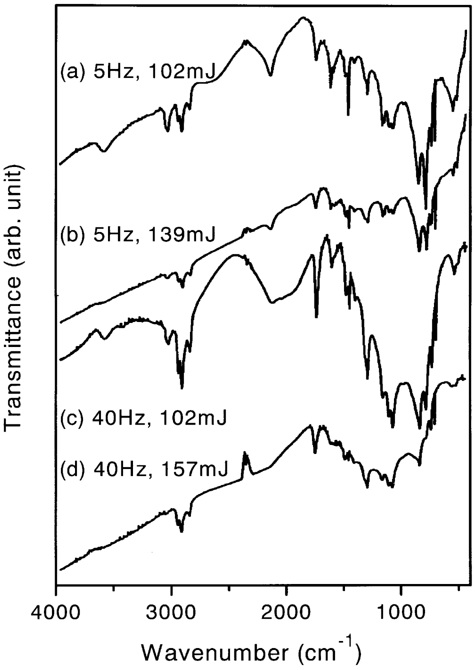

Fig. 4. IR spectra of the deposited films prepared at $T_S = 573$ K: (a) 5 Hz, 102 mJ cm^{-2}; (b) 5 Hz, 139 mJ cm^{-2}; (c) 40 Hz, 102 mJ cm^{-2}; (d) 40 Hz, 157 mJ cm^{-2}.

to that of HPDS. The cooling target is a useful method to control the film structure.

3.2. Effect of heating substrate

The effect of the heating substrate was investigated during laser ablation of HPDS. Fig. 4 shows the IR spectra of the deposited films at a substrate temperature (T_S) of 573 K. These IR spectra exhibited a relatively large aliphatic C–H peak (2990 cm^{-1}), while the films prepared without substrate heating did not display a large aliphatic peak (Fig. 2). In particular, the aromatic C–H (3045 cm^{-1}) became very small when the laser fluence was high, which indicates that many phenyl groups were broken and did not remain in the film.

Fig. 5 shows the effect of substrate temperature on the Vickers microhardness of the deposited films. Without substrate heating, the hardness depends on the repetition rate and laser fluence [15]; the hardness depends on the laser fluence at a repetition rate of 40 Hz. The hardness was 10 kg/mm^2 when the fluence was 70 mJ cm^{-2} and it increased somewhat with the fluence. When the fluence exceeded 150 mJ cm^{-2}, the hardness increased rapidly and it reached 35 kg/mm^2 at a fluence of 170 mJ cm^{-2}. The films prepared at $T_S = 573$ K exhibited much greater hardness than those prepared without heating. They also depended on the repetition rate.

Fig. 6 shows the TG curves of films prepared at $T_S = 573$ K. Although they were heated at 573 K during the deposition, these films exhibited a gradual decrease in weight below 573 K. The film prepared at 40 Hz, 157 mJ cm^{-2} in particular exhibited a remarkable weight decrease below 373 K. They also exhibited a gradual weight decrease up to 773 K and then a rapid decrease above 773 K. The decrease in weight below 573 K may be due to the absorbed water during treatment in air. Substrate heating was very effective for increasing the film hardness, but it was not beneficial for improving the thermal stability of the film under the present conditions. A decrease in the phenyl groups in the film may be part of the reason; further study is required to clarify the relationship between the film structure and the preparation conditions.

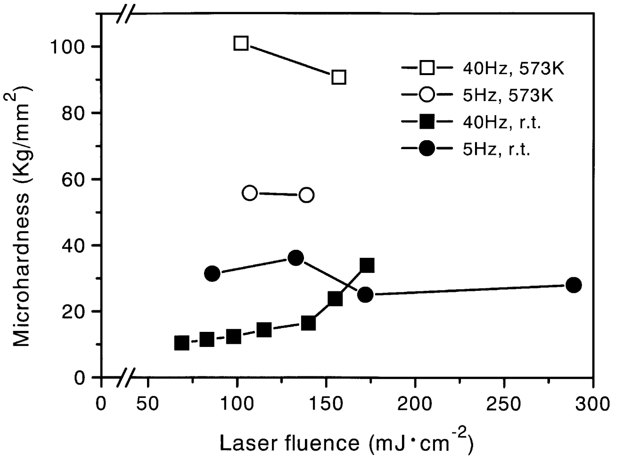

Fig. 5. Effect of substrate temperature on the Vickers microhardness of the deposited film.

3.3. Effect of polymer addition

Polysilanes, with main chains consisting of Si–Si bonds, are very interesting polymers and are expected to become new functional materials [13,14]. The laser ablation deposition of PMPS [16] was studied, and it was found that silicon-based polymer films, which contain a well-developed Si–C network structure, were derived by laser ablation deposition of PMPS. The Si–Si bonds in the main chain are easily broken by laser ablation at 248 nm and converted

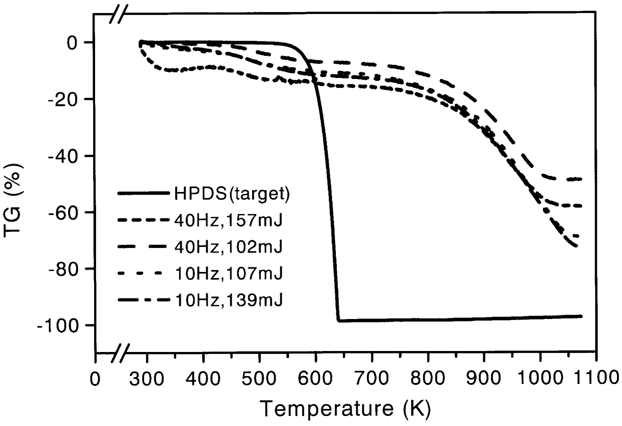

Fig. 6. TG curves of the films prepared at $T_S = 573$ K.

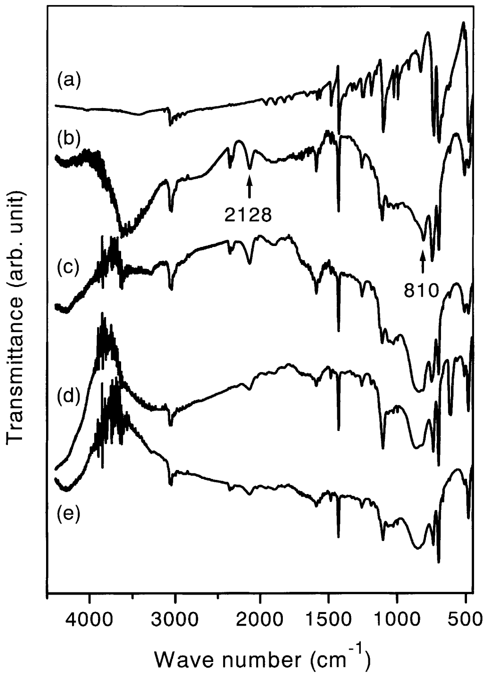

Fig. 7. IR spectra of the films deposited by laser ablation of a mixture with HPDS and PDMS (10%), together with that of the target: (a) HPDS + PDMS (10%) (target); (b) 5 Hz, 119 mJ cm^{-2}; (c) 10 Hz, 120 mJ cm^{-2}; (d) 40 Hz, 120 mJ cm^{-2}; (e) 60 Hz, 119 mJ cm^{-2}.

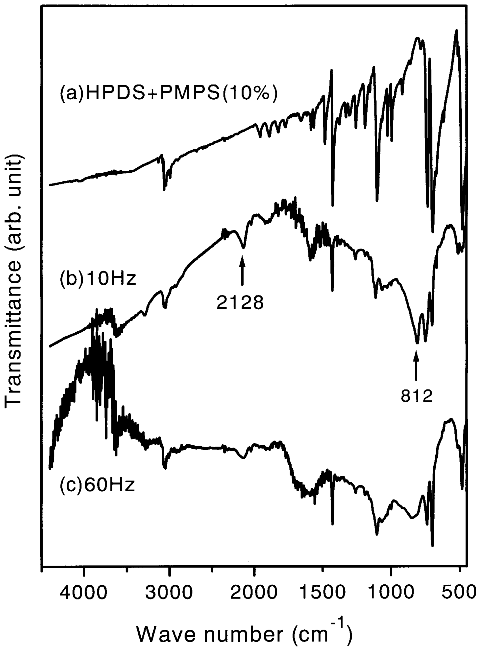

Fig. 8. IR spectra of the films deposited by laser ablation of a mixture with HPDS and PMPS (10%), together with that of the target: (a) HPDS+PMPS (10%) (target); (b) 10 Hz, 99 mJ cm^{-2}; (c) 60 Hz, 100 mJ cm^{-2}.

to Si–C bonds, since the binding energy of a Si–Si bond is much smaller than that of a Si–C bond. Therefore, addition of polysilanes may provide many active fragments during ablation and develop a Si–C network structure in the deposited films. This development of a Si–C network structure could improve the mechanical properties and thermal stability of the deposited films.

Fig. 7 shows the IR spectra of films deposited by laser ablation of a mixture of HPDS and PDMS (10 wt.%), together with that of the target. The IR spectrum of the mixture powder was very similar to that of pure HPDS powder. The IR spectrum of a deposited film prepared at 5 Hz, 119 mJ cm^{-2} displayed new peaks at 2128 cm^{-1} (Si–H) and around 810 cm^{-1}, similar to the case of HPDS. It exhibited an aromatic C–H peak, but almost no aliphatic C–H. The 810 cm^{-1} peak became broader and shifted to a higher wavenumber as the repetition rate increased. These peaks were very broad compared to that of the film prepared by pure HPDS. This finding suggests that the Si–C network structure is well developed in the deposited films by an addition of PDMS, without affecting the phenyl groups. The films prepared at 100 mJ cm^{-2} and 10–60 Hz showed spectra similar to those in Fig. 7.

Fig. 8 shows the IR spectra of the films deposited by laser ablation with a mixture of HPDS and PMPS (10 wt.%), together with that of the target. The IR spectrum of the mixture powder was very similar to that of pure HPDS powder. The IR spectra of the deposited film prepared at 10–60 Hz, 100 mJ cm^{-2} showed new peaks at around 2128 cm^{-1} (Si–H) and 812 cm^{-1}, similar to the case of HPDS. However, the broad peak around 810 cm^{-1} was not as large as in the HPDS and PDMS mixture. Perhaps, the Si–C network structure was not as well developed as in the HPDS and PDMS mixture due to the bulky phenyl group in the PMPS.

Fig. 9 depicts the TG curves of the deposited films prepared with the HPDS and PDMS mixture, together with those of HPDS and PDMS powders. It also provides an example of the TG curve of the deposited film prepared with pure HPDS under a similar condition. The deposited films exhibited greater thermal stability than HPDS and PDMS. However, the addition of PDMS did not seem to have any remarkable effect on the thermal stability.

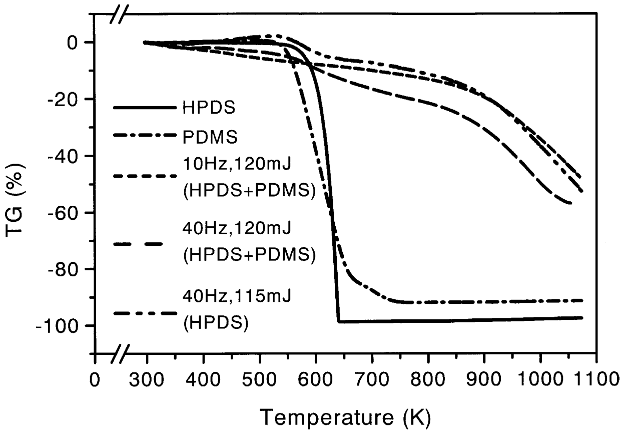

Fig. 9. TG curves of the deposited films prepared with an HPDS and PDMS mixture, together with those of HPDS and PDMS powders.

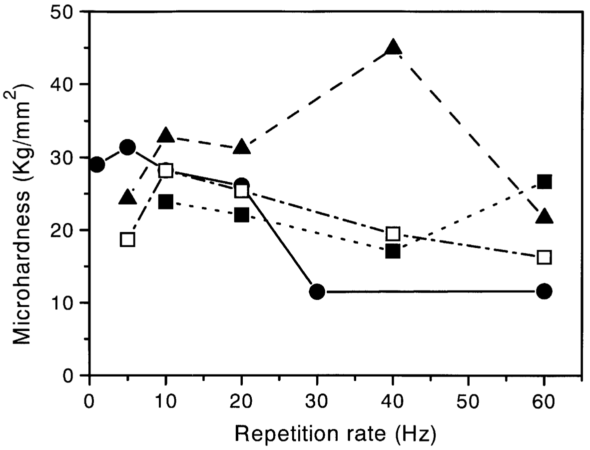

Fig. 10. Effect of polysilane addition on the Vickers microhardness of the deposited films: (●) HPDS, 76–86 mJ cm^{-2}; (▲) HPDS–PDMS (10 wt.%), 120 mJ cm^{-2}; (■) HPDS–PDMS (10 wt.%), 100 mJ cm^{-2}; (□) HPDS–PMPS (10 wt.%), 100 mJ cm^{-2}.

Fig. 10 shows the Vickers microhardness of the deposited films. The hardness of the films prepared with pure HPDS depended on the repetition rate and laser fluence [15]. The hardness depended on the repetition rate at moderate laser fluence ($<$150 mJ cm^{-2}). When the repetition rate was less than 20 Hz, the films exhibited significant hardness around 30 kg/mm^2. The hardness decreased above 30 Hz and became almost constant (10 kg/mm^2). The films prepared with the target mixture exhibited greater hardness at a high repetition rate and did not demonstrate clear dependence on the repetition rate, while the hardness of the film prepared with HPDS did depend on the repetition rate. The addition of polysilane was effective for developing the Si–C network structure, resulting in an increase in hardness of the film.

4. Summary

1. The cooling target reduced the thermal effect during the ablation of organic materials and is a potentially useful method to control the film structure.
2. Many phenyl groups were broken and did not remain in the film following substrate heating. The substrate heating was not beneficial for improving the thermal stability of the film. However, it was very effective in increasing the film hardness.
3. The addition of polysilanes, PDMS in particular, to the HPDS target was very effective for developing the Si–C network structure in the resultant films. It did not have a remarkable effect on the thermal stability, but it improved the film hardness. Further study regarding the ablation conditions and film structure and properties are needed to improve the thermal stability of the films.

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