Femtosecond-pulsed laser deposition of diamond-like carbon films onto silicone rubber

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Abstract. Low frictional, textured diamond-like carbon (DLC) films were deposited onto silicone \([\text{SiO} (\text{CH}_3)_2]_n\) rubber by femtosecond laser ablation of frozen pentanal \((\text{C}_5\text{H}_{11}\text{OH})\). Deposition rate of the films for silicone rubber was higher than that for Si wafer. A broad Raman peak centred at 1530 cm\(^{-1}\) was measured from the films deposited on silicone, showing a DLC film. The Raman spectra of the DLC films on silicone and Si wafer, a textured DLC films were also formed on silicone rubber. A coarse texture of the films was obtained by increasing the deposition time. The textured DLC films could improve frictional property of a sticky silicone rubber.

1. Introduction
Pulsed laser deposition (PLD), which is based on ablation of target materials by intense laser pulses, has been widely used for thin film deposition of any material [1]. Among the materials, diamond-like carbon (DLC) has been widely investigated in even PLD technique because DLC shows superior properties such as low friction, hardness, optical transparency and so on [2]. The DLC film is, thus, one of the promising materials for thin-film coating applications [2].

In the PLD of DLC films, UV-, nanosecond (ns)-pulse lasers, excimer or Nd:YAG lasers, were conventionally employed with a laser target of solid carbon, graphite, for instance [3,4]. However, a solid carbon target produced large fragments mixed in the deposited films. Hanabusa et al. succeeded to prevent the ejection of fragments from a target by using a frozen hydrocarbon gas target, instead of conventional solid carbons [5]. At high laser fluence, however, a few fragments were produced because isolated carbons were formed even on the frozen hydrocarbons during the UV-ablation. Therefore, we have applied a near-IR femtosecond (fs) laser to the PLD of DLC films with frozen hydrocarbon targets, which resulted in the successful deposition of fragment-free DLC films [6,7].

In this paper, DLC films were deposited onto silicone \([\text{SiO} (\text{CH}_3)_2]_n\) rubber by the fs-PLD with a frozen hydrocarbon of pentanal \((\text{C}_5\text{H}_{11}\text{OH})\), for the purpose of improving frictional property of silicone rubber. Such DLC/silicone structures are useful for industries in electrical-, chemical-, mechanical- and medical-engineering fields. In addition, the DLC-coating is also required for the other polymers recently [8]. In the present work, we compared DLC films on silicone rubber with that on Si wafer in the fs-PLD with a frozen pentanol. High deposition rate-, high sp\(^3\) content- and coarse textured-DLC films were successfully obtained for fabricating a low frictional DLC/silicone structure.
2. Experimental
The experimental arrangement used in the present work is shown schematically in Fig. 1. The 790-nm, 130-fs Ti:sapphire laser pulses were operated at the pulse energy of 0.8 mJ with 500-Hz pulse repetition rate. The laser beam was introduced into the deposition chamber through a fused silica window and focused on the target by a 170 mm focal length lens. The single pulse laser fluence on the target was estimated to be approximately ~10 J/cm². Pentanol (98 %) was frozen on a bottom surface of a liquid nitrogen reservoir made of stainless steel. A rotary pump evacuated the chamber at 0.4 Pa during the target preparation. After the preparation, the gas supply was stopped, and a turbo molecular pump was turned to improve the pressure of the chamber to 3 x 10⁻³ Pa. The target was separated from 2-mm-thick silicone rubber substrate (10mm x 10mm) by 20 mm. For comparison, 0.3-mm-thick Si(100) wafer was also used as a substrate. The deposition time was varied from 1 to 60 min. The films were deposited at room temperature.

![Figure 1. A side view of the arrangement used in the present PLD experiment](image)

3. Results and discussion
Figure 2 shows the film thickness as a function of the deposition time on silicone rubber substrate. For comparison, Si wafer substrate was employed. Thickness of the deposited films was measured by an atomic force microscope (AFM, SII, Nanopics-1000). When the deposition time increased from 1 to 60 min., the thickness linearly increased on both silicone and Si substrates. The deposition rate in silicone was ~ 30 nm/min, which is two fold increase over the ~ 15 nm/min. deposition rate for Si substrate. This might be due to a high sticking coefficient of silicone rubber substrate. To identify the deposited films as a DLC, Raman spectroscopy (Jasco, NR-1800) was conducted as shown in Fig. 3. A 0.02 W Ar⁺ laser of 514.5-nm line was used for the excitation. A broad Raman peak centred at 1530 cm⁻¹ was measured from the film deposited on silicone, showing a DLC film. The deposited film on Si was estimated to be a DLC as well. Therefore, the fs-PLD can produce DLC films on both silicone and Si substrates. However, the two Raman spectra were slightly different in shape.

To understand the slight difference in the Raman spectra, a wave-form separation was carried out by assuming two Gaussian peaks. The results were shown in Fig. 4. The ratios of I(D)/I(G) [9] in Si were higher than those in silicone. Thus, sp³ content in the films deposited on silicone was higher [9]. In addition, sp³ content, the I(D)/I(G) ratios, do not depend on the film thickness, compared to Fig. 2.
Figure 2. Film thickness as a function of the deposition time on two different substrates

Figure 3. Raman spectra of the deposited films on silicone and Si substrates

We compared surface morphology of the films deposited on silicone and Si by the AFM, as shown in Fig. 5. On silicone rubber substrate, a textured-DLC film was formed for 30-min. irradiation. A coarse texture of the DLC was obtained with increasing the deposition time. Such texture structure was not seen in the film deposited on Si. Figure 6 shows the roughness of the textured-DLC as a function of the deposition time. As shown in Fig. 5, the roughness of the textured-DLC increased with increasing the deposition time, meanwhile the DLC films on Si were still flat. Mechanism of the texture formation is not clear, but we should assume a large difference of thermal expansion coefficients between silicone \((4.0 \times 10^{-3})\) and Si \((2.4 \times 10^{-6})\) would be related.

Figure 4. I(D)/I(G) Raman peak area ratio as a function of the deposition time

Figure 5. AFM image of the DLC films deposited on silicone and Si at two different deposition time

The textured-DLC films on silicone are suitable for improving frictional property of DLC/silicone structures. We evaluated the improvement of frictional property of the fabricated DLC/silicone samples. In this measurement, a DLC surface of the DLC/silicone structure was contacted with a silica glass plate, and the plate was gradually tilted, then stopped when the sample starts to slide. The angle of silica plate to the ground is defined as the angle of friction. Figure 7
presents the angle of friction as a function of the deposition time. Lower frictional samples were obtained with increasing the deposition time, which originates in the coarse textured-DLC films deposited on silicone rubber. Therefore, a low frictional, hard silicone rubber was successfully fabricated with the coarse textured-DLC films deposited by the fs-PLD with frozen pentanol.

![Figure 6. Surface roughness of deposited films obtained by result of AFM](image1)

![Figure 7. Angle of friction with DLC/silicone for slide glass plate](image2)

4. Conclusions

Low frictional-, textured-DLC films were successfully deposited onto silicone rubber by the fs-PLD with frozen pentanol. The deposition rate for silicone was higher than that for Si. Quality of the deposited DLC films on silicone and Si was slightly different; sp³ content in the films was higher. The coarse textured-DLC films were obtained on silicone rubber with increasing the deposition time. The textured-DLC films could improve friction property of the fabricated DLC/silicone structures. This result will open up the micromachining technique for developing DLC-based micro devices.

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