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# Glassy carbon layer formed in diamond-like carbon films with femtosecond laser pulses

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**ABSTRACT** We report the first observation, to our knowledge, of a glassy carbon (GC) layer modified from diamond-like carbon (DLC) films with femtosecond (fs) laser pulses. The GC layer, which is confirmed by Raman spectroscopy, is produced most efficiently at low laser fluence near the ablation threshold of the DLC films. This surface modification depends little on the laser polarization and wavelength used. The fs laser-induced GC layer should be a new thin-film material useful for a variety of engineering applications due to its characteristics similar to those of DLC and the additional properties inherent in GC.

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## 1 Introduction

Amorphous diamond-like carbon (DLC), consisting of a mixture of tetrahedral ( $sp^3$ ) diamond structure and trigonal ( $sp^2$ ) graphite structure, is extensively used as protective films for hard disks and magnetic heads, because of its hardness, chemical inertness and insulation properties close to those of diamond [1]. Furthermore, applications of DLC films to tribological technologies are growing rapidly due to their excellent surface smoothness and low frictional coefficient. Compared with a diamond film, however, a DLC film is inferior in heat resistance and does not fully exhibit its excellent properties at temperatures higher than about 400 °C. In addition, since the DLC film is an insulating material, some metal ions have to be doped to improve the conductivity.

On the other hand, glassy carbon (GC) is known as a carbonaceous material having physical and chemical properties similar to those of DLC [2]. This material is a kind of graphite having a small crystallite size of about 3 nm

that leads to the high hardness. The bulk GC material is commercially available and applied, for example, to fine electrodes and melting pots for reactive materials, based on its abrasion resistance, corrosion resistance, durability and low reactivity. In contrast to DLC, however, few technologies for growing a thin GC film have been developed so far, although GC films are expected to have a variety of potential applications due to the characteristics similar to those of DLC films and additional properties of higher conductivity and thermal resistance than DLC.

In this communication we report for the first time, to our knowledge, that a thin GC layer can be produced from DLC films by intense femtosecond (fs) laser pulses. In a recent paper [3], we have shown that DLC and TiN film surfaces are structured on a nanometer level by irradiation with the fs laser pulses. With laser Raman spectroscopy of these nanostructured film surfaces, we have found that the thin DLC film is modified into a GC layer by the fs laser pulses. We present the experimental results and dis-

cuss the experimental conditions for the novel surface modification.

## 2 Experimental

The experimental apparatus and procedure are almost the same as those described in our recent paper [3]. Briefly, the DLC film was coated on a stainless steel plate of 1-mm thickness, using an unbalanced magnetron sputtering system in a mixed gas of 95% Ar and 5% CH<sub>4</sub>. The coated DLC film was 1.4 μm in thickness, Hv 3000 in hardness and 9 nm in surface roughness. This DLC film was irradiated by intense fs laser pulses from a Ti:sapphire chirped-pulse amplification system operated at a repetition frequency of 10 Hz. The fundamental 800-nm, 40-fs pulses and the frequency-tripled 267-nm, 150-fs pulses were used to ablate the DLC film. A half-wave plate was employed for rotating the linear polarization direction, and a quarter-wave plate for producing circular polarization. The fs laser beam with the pulse energy of 40–200 μJ was focused on the DLC film in air with a 100-cm focal-length lens. The focal spot size on the target film was about 200 μm in diameter, and the fluence on the target was 0.1–0.5 J/cm<sup>2</sup>. Depending on the fluence, 1–300 shots of the fs pulse were superimposed on the target.

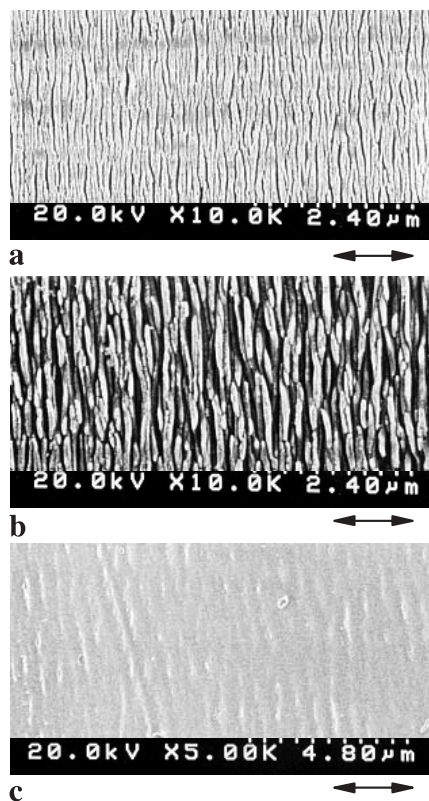
With a field-emission scanning electron microscope (SEM) and an atomic force microscope (AFM), we carefully examined the morphology change of the DLC film surface that was ablated by the fs laser pulses. The bonding structure of the ablated DLC films was analyzed by Raman spectroscopy using the

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514.5-nm line of an argon-ion laser at a focused spot size of about 1  $\mu\text{m}$ .

### 3 Results and discussion

Figure 1 shows the SEM images around the center of DLC film surfaces ablated by the 800-nm pulses at three different fluences of  $F = 0.13$  (Fig. 1a), 0.15 (Fig. 1b) and 0.17 J/cm<sup>2</sup> (Fig. 1c), where 100 pulses are superimposed for Fig. 1a and b, and 10 pulses for Fig. 1c. The different pulse numbers used for the ablation are due to the fact that the ablation rate increases with an increase in the fluence  $F$ , so that 100 pulses at  $F = 0.17$  J/cm<sup>2</sup> were observed to completely remove a part of the thin DLC film on the substrate. As seen in Fig. 1a and b, the periodic fine structures almost oriented to the direction perpendicular to the laser polarization are formed at such small fluences of  $F = 0.13$  and 0.15 J/cm<sup>2</sup>, just above the observed ablation threshold of  $F \sim 0.11$  J/cm<sup>2</sup>. The mean spacing  $D$  of these fine structures is measured



**FIGURE 1** SEM images of the DLC surfaces ablated by the linearly polarized, fs laser pulses at the fluences of  $F = 0.13$  (a), 0.15 (b) and 0.17 J/cm<sup>2</sup> (c). The arrows indicate the fs laser polarization direction

to be 100 nm in Fig. 1a and 140 nm in Fig. 1b, which are much smaller than the laser wavelength  $\lambda$ :  $D/\lambda = 1/8$  in Fig. 1a and  $1/6$  in Fig. 1b, as in our recent observations [3]. For a higher value of  $F = 0.17$  J/cm<sup>2</sup> in Fig. 1c,  $D$  is increased to 430 nm. This increase in  $D$  with an increase in  $F$  has also been observed for other hard thin films such as TiN. On the other hand, however, the higher fluence is observed to smooth the DLC film surface to make the periodic structure unclear, as seen in Fig. 1c. With a further increase in  $F$  to 0.4 J/cm<sup>2</sup>, the surface was observed to become much flatter.

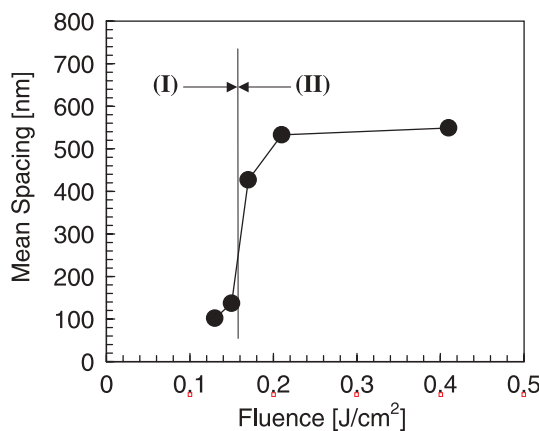
To see the detailed experimental conditions for producing the fine periodic structures on the DLC surface, we measured  $D$  as a function of  $F$ , and the result is shown in Fig. 2. As indicated in the figure,  $D$  may be divided into two regions depending on  $F$  for convenience of discussion, i.e. the region I where  $D$  increases rapidly with increasing  $F$  near the ablation threshold, and the region II where  $D$  increases slowly and almost saturates. The ratio  $D/\lambda$  is 0.13–0.18 in the region I, while  $D/\lambda$  is 0.5–0.7 in the region II. The ratio in the region II almost corresponds to that of the so-called ripple patterns that have often been observed on the laser-ablated material surfaces [4, 5].

We have focused our attention on a possible change in intrinsic bonding structures of the DLC films that may accompany the formation of the fs laser-induced surface nanostructures. Raman spectra were observed on the DLC films irradiated by the fs laser pulses at different fluences near the ablation threshold. The results of four Raman spectra are shown in (b) to (e) of

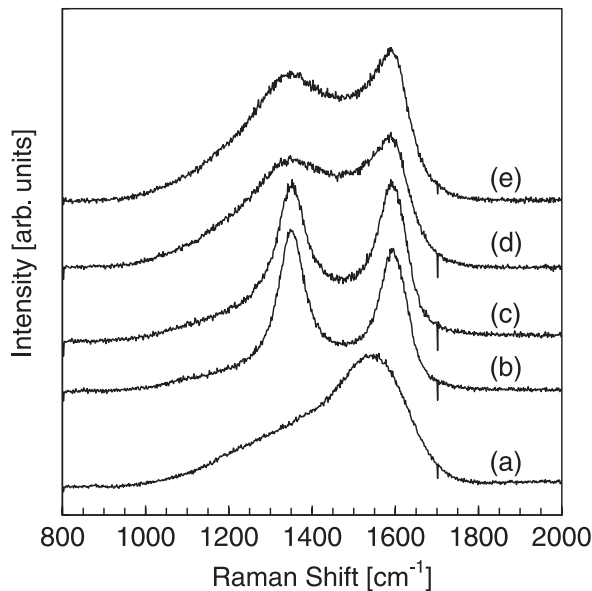
Fig. 3, together with a spectrum (a) of a non-ablated DLC film for comparison. Raman spectra of such carbonaceous materials have been studied in detail and are well known, as given in the literature [1, 6–9]. For the argon-ion laser line at 514.5 nm, diamond having the sp<sup>3</sup> bonding structure shows a sharp spectral peak at 1333 cm<sup>-1</sup>. In contrast, Raman spectra of DLC usually consist of an asymmetric broad structure having a relatively sharp peak around 1530 cm<sup>-1</sup> and a broad shoulder band around 1400 cm<sup>-1</sup>, as seen in (a). This specific Raman spectrum of DLC is due to a mixture of the sp<sup>3</sup> and sp<sup>2</sup> bonding structures.

It should be noted in Fig. 3 that the Raman spectra for  $F = 0.13$  (b) and 0.15 J/cm<sup>2</sup> (c) represent those of GC that have two spectral peaks at 1355 and 1590 cm<sup>-1</sup> [6–9]. In particular, the spectrum shown in (b) of Fig. 3 is a typical one of GC, where the spectral peak at 1355 cm<sup>-1</sup> is much larger than that at 1590 cm<sup>-1</sup>. With an increase in  $F$  to  $F = 0.17$  and 0.41 J/cm<sup>2</sup>, as shown in (d) and (e), the dip between two spectral peaks increases to make the peaks shallow, and the peak at 1355 cm<sup>-1</sup> becomes smaller than that at 1590 cm<sup>-1</sup>. In addition, the side-band structure is broadened toward to the low-wavenumber region, suggesting some superposed spectra consisting of those for GC, DLC and/or other carbonaceous materials.

GC is usually manufactured as a bulk material by means of carefully controlled heating of polymeric resin [2]. The intense fs laser pulses enable very local injection of high-density energy into the material surface, keeping the thermal influences on the environment extremely small. Thus, it is reasonable



**FIGURE 2** Mean spacing of the periodic fine structures formed on the DLC film as a function of the laser fluence



**FIGURE 3** Raman spectra of non-irradiated DLC film (a) and those irradiated by the fs laser pulses at the fluences of  $F = 0.13$  (b),  $0.15$  (c),  $0.17$  (d) and  $0.41 \text{ J/cm}^2$  (e)

to consider that the fs laser pulses would induce a direct modification of DLC to produce the GC layer. The results shown in Figs. 2 and 3 demonstrate that the surface modification of DLC to GC is induced most efficiently at the laser fluence near the ablation threshold, suggesting that the excess fs laser energy injected into the DLC surface should bring about an undesirable structure change for the purpose of the GC layer formation.

We note that the experimental condition for the modification to GC almost coincides with that for producing periodic nanostructures on the DLC surface. Referring to the experimental conditions in our previous work [3], we carried out the same experiment using circularly polarized fs laser pulses at  $\lambda = 800 \text{ nm}$ . The fine dot structures of

$D/\lambda \sim 1/10$  were formed on the DLC surface at the fluence near the ablation threshold [3], and the Raman spectrum of this DLC surface was almost the same as those for the linear polarization in (b) of Fig. 3. Furthermore, the experiment was also carried out with linearly polarized, ultraviolet fs laser pulses at  $267 \text{ nm}$  [3]. At the fluence of  $F = 0.12 \text{ J/cm}^2$  near the ablation threshold, the ultraviolet fs pulses have been observed to certainly induce the modification of DLC to GC, representing almost the same Raman spectrum as shown in (b) of Fig. 3. These results strongly suggest that the fs laser-induced surface modification does not depend on the laser polarization and wavelength.

In summary, we have demonstrated, for the first time to our knowledge, that

a DLC film can be modified into a GC layer by intense fs laser pulses. The GC layer is formed most efficiently at low laser fluence near the ablation threshold of DLC films. The experimental condition for this novel surface modification is almost the same as that for the formation of periodic fine structures on the DLC surface, depending little on the laser polarization and wavelength used. The GC layer is expected to have excellent physical and chemical properties similar to those of the bulk GC and to provide a new functional thin film for a variety of engineering applications.

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