Amorphous nanostructuralization in HOPG by $10^{14}$ W cm$^{-2}$ laser

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Abstract. This reports provide an amorphous nanostructuralization technique on the surface modification in Highly Oriented Pyrolytic Graphite (HOPG) by using a femtosecond laser. We showed, for the first time, that the surface of HOPG is changed to the amorphous nanostructuralization graphite by using a femtosecond laser-driven compression technique. Our results also suggest that the HOPG surface is changed until the deeper area from the surface by the laser-driven shock wave. A single shot of a femtosecond laser beam ($1.27 \times 1.33 \times 10^{14}$ W cm$^{-2}$ in intensity, with 2 mm-diameter, and 110 fs in pulse width) is irradiated under the vacuum ambiance onto a 2 mm-thick of HOPG. The calculated impact pressures on a sample was $8.3 \sim 8.7$ GPa. Crystal structure in the HOPG were analyzed using a Raman spectroscopy and an X-ray diffraction, those analyzing depth from the surface were 50 nm and 350 $\mu$m, respectively.
1. Introduction
The recent study of materials surface modification is performed by using a femtosecond laser-driven compression techniques [1-5]. In this paper, we demonstrate an amorphous nanostructuralization in highly oriented pyrolytic graphite (HOPG) by laser irradiation with $10^{14}$ W cm$^{-2}$.

Tsujino et al., reported that the laser of 130 fs, 5.5 mJ was irradiated to the silicon and they observed the $\beta$-Sn crystal grains of a few tens nm [1]. Cuq-Lelandais et al., reported that the intensity of $0.6 \text{ PW cm}^{-2}$ (300 fs in pulse duration and 30 J in energy with 4 mm-diam. on the sample) laser was irradiated to aluminum and they demonstrated a spallation mechanism and propagation of laser-driven compression in metal [2]. Matsuda et al., reported the nanocrystallization of iron in depth of 2 m from the surface by intense-laser multiple irradiation of 130 fs, 0.2 mJ [3, 4]. Sano et al., also reported that a hexagonal crystal diamond was synthesized in the HOPG by laser-driven compression with $2 \times 10^{15}$ W cm$^{-2}$ [5]. Those reports have described a phase transition, spallation mechanism, propagation of laser-driven compression, nanocrystallization of metal, and synthesis, but they did not describe a nanostructuralization formation in depth direction of graphite in detail.

We are studying the surface modification of ceramics by using the ultra-intense laser-driven compression technique. We revealed the multilayered polycrystallization in single crystal yttria-stabilized zirconia by counter-irradiation with a single shot of ultra-intense laser ($10^{17}$ W cm$^{-2}$) in our previous research [6]. Here, we provide that the HOPG is changed to nanostructuralization in depth direction by using a laser-driven compression technique in a single shot of femtosecond laser irradiation in $10^{14}$ W cm$^{-2}$. We report an amorphous nanostructuralization in depth 350 $\mu$m from the surface by a Raman spectra and an X-ray diffraction (XRD) analysis results.

2. Experimental procedure
This experiments have been performed on the graduate school for the creation of new photonics industries’s "7 TW" facility [7-11]. Its laser beam is focused to 10 $\mu$m-diameter at the focal position by using a off-axial parabolic mirror. In order to give a $10^{14}$ W cm$^{-2}$ of irradiation intensity on the HOPG surface, it was placed at 5 mm away from the focal position along the laser-incidence axis. An irradiation laser beam diameter of the surface was 2 mm in this layout. The irradiation laser beam on the HOPG were 430 ~ 450 mJ, 110 fs in pulse width and 0.82 $\mu$m in wavelength. The shape of HOPG was 10 mm $\times$ 10 mm square of 2 mm-thick (Furuchi Chemical Corp.). The ambient pressure was $10^{-3}$ Pa.

When a laser irradiates on the HOPG surface, the surface is pushed by the high pressure driven by the ponderomotive force of the laser [12, 13]. We can estimate the pressure $P$ by;

$$P = (1 + \eta) \frac{I_L}{c},$$

where $\eta$ is the reflectively of the laser at the surface, which is nearly 1 for the pulse duration. $I_L$ and $c$ are, respectively, the laser intensity and the speed of light. The impact pressure given to the HOPG in this experiment is 8.3 ~ 8.7 GPa, using a Formula (1).

We analyzed the irradiated HOPG surface by using the following techniques. The laser Raman spectrooscope (NRS-5100, JASCO of Aichi Center for Industry and Science Technology) analyzed the structure of the molecular state, and the XRD equipment (BL5S2 beam line of Aichi Synchrotron Radiation Center) analyzed the crystalline. The beam of laser Raman spectrocope (532 nm in wavelength, 1 $\mu$m-diam. in spot size) was illuminated on the HOPG and line-scanned with 10 $\mu$m steps of 2 mm length in irradiated area, and skin depth of laser beam was 50 nm. The X-ray beam of BL5S2 irradiation angle to the HOPG was 5.000 $\pm$ 0.004 $^\circ$ in a grazing incidence, beam size was 0.6 $\times$ 0.5 mm, energy was 12.4 keV, observation angle was separated with 5 step in 30 ~ 70 degrees, irradiation time was 3 minute per step, and the skin depth of the X-ray at this time was 350 $\mu$m.
3. Results and discussions
The laser irradiation trace and laser Raman line scanning image shows in the Figs.1 (a) and (b). The irradiation trace seems to discolored a little bit, and it is formed wavy pattern that is dependent on the influence of the energy distribution in the irradiation laser beam. As shown in Fig.1 (a), the irradiation pattern inside the encircled reflects square beam pattern. The laser Raman image also shows that the distribution of irradiated area peaks are changed to depending on the irradiation trace. And irradiated and nonirradiated area have different peak.

We performed a detailed analysis to selecting three analysis-points from the irradiation trace. Those analysis points are shown in (c), (d), and (e) of Fig.1 (a). We discussed in comparison with the Raman spectra of various carbon materials shown in the Fig.1 (f). Nonirradiated area of Fig.1 (c) agree with a Raman spectra of HOPG, certainly. On the other hand, the irradiation areas of Figs.1 (d) and (e) are appeared D-band peak, and these spectrum are very different with Fig.1 (c). Figures 1 (d) and (e) was similar to the amorphous carbon and the carbon black (nano-powders) having a nanostructure, respectively. Those discussions also suggest that the molecular structure in irradiated area is changed to the amorphous nanostructuralization carbon in depth of 50 nm from the surface by $10^{14}$ W cm$^{-2}$ femtosecond laser irradiation.

![Figure 1. Observation results of the Raman spectrum from the irradiated HOPG. (a) irradiation trace. Inside of dashed black line is an irradiation trace. Green line is a scanning place of (b). (b) laser Raman line scanning image. (c), (d), and (e) are Raman spectrum in analysis point of (a), respectively, those position X are 15446 nm, 16236 nm, and 16906 nm. (f) Raman spectrum from various carbon materials.](image1)

![Figure 2. Observation result of the X-ray diffraction profiles. Black line is a nonirradiated HOPG, and blue line is an irradiated HOPG. The different crystalline is observed in an irradiated HOPG.](image2)

We next analyzed the inside structure of irradiated HOPG by the XRD analysis. The XRD profile from an irradiated and a nonirradiated HOPG area shows in the Fig.2. The strong XRD peak from nonirradiated HOPG (Black line) is disappeared by laser irradiation shown in irradiated HOPG (blue line) of Fig.2, and the two new peaks appear on it. Those phenomenon also are suggested which occurred between with 350 $\mu$m in depth from the surface. Since the shift amount is too large, we considered that the original peak is not shifted or separated by...
the residual stress of laser irradiation like a blue line peaks. Then, we analyzed an identification of these diffraction peaks. The peak on the left side of blue line in the Fig. 2 agreed with a nanotubes (004), and the right side agreed with a graphite-3R (006), respectively.

Here, we hypothesized why our results agreed with the nano-structures peak in Raman and XRD analysis. The HOPG surface is ablated with $10^{14}$ W cm$^{-2}$ femtosecond laser. Its surface is additional heated to the radial direction with radiant heat of generated plasma, and at the same time, to the depth direction with the ablation driven shock wave is propagated, which pressure is $8.3 \sim 8.7$ GPa. The surface is heated with pulse duration and its is quenched. Under the irradiation area, it is presumed to have broken to nanosized in the same as our previous studies [6]. Especially, the HOPG having a sheet structure is torn to pieces in a depth direction by the shock wave. Then, those pieces are changed to amorphous-like nanostructuralization which edge are rounded to individually by residual stress in quenching process.

Accordingly, we considered that the results of Raman and XRD analysis agreed with the nanostructuralization peak of carbon. Although it is possible to explain our results by this hypothesis, we are thinking that only these discussion is insufficient to reveal this mechanism. We now are performing an additional experiment and detailed analysis, and will reveal this mechanism in a next step.

4. Conclusions

We demonstrated a single shot of the irradiation in 2 mm-thick of Highly Oriented Pyrolytic Graphite (HOPG) with the laser intensity in $1.27 \sim 1.33 \times 10^{14}$ W cm$^{-2}$. Crystal structure in the HOPG were analyzed using a Raman spectroscopy and an X-ray diffraction, those analyzing depth from the surface were 50 nm and 350 μm, respectively. We showed, for the first time, that the surface of HOPG is changed to the amorphous nanostructuralization graphite by the femtosecond laser-driven compression technique. Our results also suggested that the HOPG surface is changed until the deeper area from the surface by the laser-driven shock wave.

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