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Journal of Physics: Conference Series **165** (2009) 012019 doi:10.1088/1742-6596/165/1/012019

Femtosecond laser-driven shock synthesis of hexagonal diamond from highly oriented pyrolytic graphite

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Abstract. We synthesized hexagonal diamond directly from highly oriented pyrolytic graphite (HOPG) using a femtosecond laser pulse without catalyst. A femtosecond laser pulse with wavelength of 800 nm, pulse width of 130 fs, the intensity of 2×10^{15} W/cm^2 was irradiated onto the HOPG surface in air. Crystalline structures of the fs laser-affected region in the HOPG were analyzed using grazing-incidence XRD method. We found that the hexagonal diamond which is the metastable high-pressure phase of carbon appeared in the HOPG which was irradiated by the femtosecond laser normal to the basal plane. We suggest that the femtosecond laser-driven shock wave induces the graphite - hexagonal diamond transformation and that the hexagonal diamond is synthesized due to the rapidly cooling in the shock heated region.

1. Introduction

A stable phase of carbon is graphite in the lower pressure regime and cubic diamond in the higher pressure regime [1]. The cubic diamond is one of the most important materials in the field of the manufacturing industry due to its high hardness and thermal conductivity. Hexagonal diamond was discovered in the Canyon Diablo iron meteorite [2] and is considered the metastable high-pressure phase of carbon. The hexagonal diamond is synthesized artificially using the shock compression method from graphite with catalyst [3] and from cubic diamond without catalyst [4], the static compression method [5], and the chemical vapor deposition method [6]. There still exist many unresolved subjects on the synthesis mechanism of cubic and hexagonal diamonds. Metallization of carbon is predicted theoretically under more than 1.1 TPa [7]. The metallic carbon is the lightest metal on earth if we can synthesize and retain it under the atmospheric pressure. Therefore, exploration of the high-pressure polymorphic carbon is significantly important for not only the industry but the materials and planetary sciences.

A solid material transits directly to the plasma, which expands to the vacuum explosively, after an intense femtosecond laser pulse is irradiated to the solid. The shock wave is driven by the recoil pressure during the plasma expansion and propagates into the solid. There is no interaction of the

femtosecond laser pulse with the expanding plasma because the plasma expansion occurs after the whole femtosecond laser pulse injection, which is the definitively different point from the nanosecond laser pulse irradiation. The expansion velocity of the plasma is faster than that of the nanosecond laser induced plasma. Therefore, the disturbance due to heating by the radiation from the plasma is negligible. The femtosecond laser-driven shock wave is used for the investigation of the materials dynamics under pressure [8]. A high pressure ε phase of iron, which has not been synthesized using conventional compression methods, was synthesized using the femtosecond laser-driven shock wave [9,10]. The femtosecond laser-driven shock wave is the potential tool to synthesize high-pressure materials.

The purpose of this study is to investigate synthesized structures of carbon after the femtosecond laser irradiation to the graphite. We expect that diamond will be synthesized if the strong shock wave is driven. But we do not expect whether the structure of the diamond is cubic or hexagonal because the rapidly cooling effect is significant for the femtosecond laser-driven shock wave compression compared to the conventional compression methods such as the flyer impact method and the nanosecond laser shock method.

2. Experimental method

The target used in this study was the highly oriented pyrolytic graphite (HOPG, NT-MDT Co., Russia, 10 mm × 10 mm × *t* 1.5 mm) with the ZYA quality, the mosaic spread of 0.4 – 0.7 deg, and the mass density of 2.267 g/cm^3. A femtosecond laser pulse (Spitfire, Spectra-Physics Inc.) with wavelength of 800 nm, pulse width of 130 fs, and spatial energy distribution of the near Gaussian firstly passed through an aperture of 6 mm diameter, and secondly was focused onto a target surface in air using a plano-convex lens with the focal length of 70 mm. The femtosecond laser pulse was irradiated normally to the basal plane of the HOPG target. A single pulse was shot at a point, and the shot to shot interval was 100 μm on the surface. Two kinds of the laser pulse energy, 0.7 and 5.5 mJ, was used. The spatially averaged laser intensity was approximately 3×10^{14} and 2×10^{15} W/cm^2 for the laser pulse energy of 0.7 and 5.5mJ, respectively, because the laser spot size was approximately 50 μm. Crystalline structures were analyzed using the grazing incident XRD method at the BL13XU in the SPring-8 [11]. The synchrotron X-ray with the wavelength of 1.000 Å passed through a slit with the horizontal width of 410 μm and the vertical width of 50 μm, and was irradiated to the sample. The incident angle α was fixed and the detector angle δ was varied. A solar slit was located in front of the detector, which is the YAP scintillation counter.

3. Results and discussion

The laser irradiated area was explosively removed and the deep crater was created for the laser pulse energy of 5.5 mJ, while the significant crater was not created for the laser pulse energy of 0.7 mJ. The deep crater created explosively indicates that the explosive ablation occurs and that the strong shock wave was driven.

Grazing incidence XRD patterns are shown in Fig. 1 for the laser pulse energy of (a) 0.7 and (b) 5.5 mJ. The incident angle of the X-ray to the sample surface was 0.1 deg, the angular resolution of the detector was 0.02 deg/step, and the exposure time was 5.0 s/step. The critical angle of carbon for the light wavelength of 1.000 Å is 0.13 deg. Therefore, there is no scattered X-ray if the HOPG surface is perfectly planar. However, the laser irradiated region is roughened so that the X-ray is scattered at the region. Peaks of (100) and (101) planes of the graphite appear after the 0.7 mJ laser pulse irradiation as shown in Fig. 2 (a). This means that the plastic deformation induced by the femtosecond laser-driven shock wave collapsed the orientation in the laser irradiated region. We found peaks of not only (100), (101), and (102) planes of graphite but (002) and (101) planes of hexagonal diamond appeared after the 5.5 mJ laser pulse irradiation. This means that the laser pulse of 5.5 mJ induced the shock wave, which is strong enough to induce the graphite - diamond transition.

Grazing incidence XRD patterns of the HOPG which was irradiated by the laser pulse of 5.5 mJ are shown in Fig. 2 for the incident angle 0.1, 0.2, and 0.3 deg. The X-ray penetration depth is 10 and 18

μm for the incident angle of 0.2 and 0.3 deg, respectively. The smaller incident angle shows the larger peak of the hexagonal diamond. This means that the induced hexagonal diamond is distributed mainly near the surface.

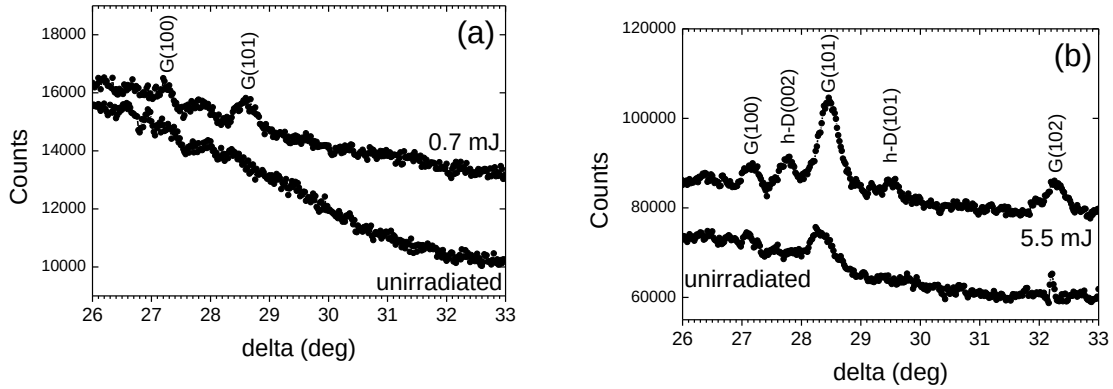

Figure 1. Grazing incidence XRD patterns of the femtosecond laser irradiated HOPG. The laser pulse energy: (a) 0.7 and (b) 5.5 mJ. G: Graphite, h-D: hexagonal diamond.

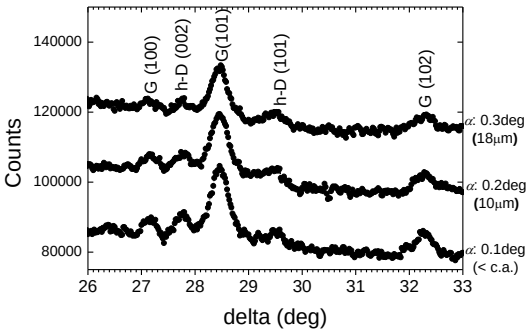

Figure 2. Grazing incidence XRD patterns for the incident angles of 0.1, 0.2, and 0.3 deg.

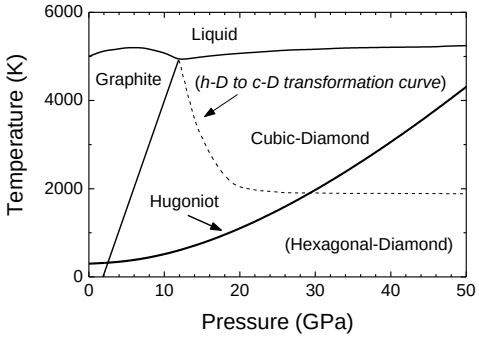

Figure 3. Calculated temperature-Hugoniot described on the carbon phase diagram.

We calculated the pressure-temperature curve under shock compression (temperature-Hugoniot) using the thermodynamic equation expressed below [12,13] in order to investigate the synthesis mechanism of hexagonal diamond;

$$C_{V\mathrm{H}}\frac{dT_{\mathrm{H}}}{dV_{\mathrm{H}}}+\frac{\gamma_0}{V_0}C_{V\mathrm{H}}T_{\mathrm{H}}=\frac{1}{2}\frac{dp_{\mathrm{H}}}{dV_{\mathrm{H}}}(V_0-V_{\mathrm{H}})+\frac{1}{2}(p_{\mathrm{H}}-p_0), \quad (1)$$

where T is the temperature, p is the pressure, V is the specific volume, C_V is the constant-volume specific heat, γ is the Grüneisen parameter, subscript 0 is an ambient state, and subscript H is a shocked state. Constant values such as C_V and γ are referred to Nellis's data [14]. The calculated result is shown on the phase diagram of carbon [1] in Fig. 3. The Hugoniot curve passes through the hexagonal diamond to cubic diamond transformation curve at approximately 30 GPa. The femtosecond laser-driven shock pressure, which was estimated 100 - 300 GPa for the pulse intensity of around 10^{14} W/cm^2 [8], is strong enough to induce the graphite - hexagonal diamond - cubic diamond transformation. Mechanism of the transformation from graphite to hexagonal diamond is diffusionless and from hexagonal diamond to cubic diamond is diffusive. More than microseconds is required to induce the diffusive hexagonal to cubic diamond transformation in contrast to the relaxation time of picoseconds in case of the diffusionless graphite - hexagonal diamond transformation. Therefore, the

femtosecond laser-driven shock compression with the duration of sub-nanoseconds [15] can only induce the graphite → hexagonal diamond transformation. We suggest that the recovery of the hexagonal diamond induced by the femtosecond laser shot is due to the rapidly cooling in the shock heated region [16].

4. Conclusions

We found that the hexagonal diamond which is the metastable high-pressure phase of carbon is synthesized in the HOPG, which was irradiated by the femtosecond laser normal to the basal plane, due to the shock induced graphite - hexagonal transformation. Measurements of both shock and particle velocities to estimate the shock pressure and duration are necessary to solve the detail mechanism.

Acknowledgements

This study was supported by Priority Assistance for the Formation of Worldwide Renowned Centers of Research - The Global COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design). The synchrotron radiation experiments were performed at the BL13XU in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (Proposal Nos. 2006A1613, 2006B1553, and 2008B1160).

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