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**Polymerized phase and amorphous diamond synthesized from
C₆₀ fullerene by shock compression**

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Abstract

C₆₀ fullerene films were shock compressed to 23 and 52 GPa. Both the recovered samples exhibit fracture into platelets and broad photoluminescence, of which intensity increases with increasing the pressure. At 23 GPa, a characteristic single broad band appears at 1560-1570 cm⁻¹, which is similar to the one found for three-dimensional (3D) polymerized C₆₀ fullerene under high-pressure-high-temperature treatment. At 52 GPa, on the other hand, the single broad band has disappeared and a diamond peak sometimes appears, depending on the platelets.

Keywords: C₆₀ fullerene, Shock compression, Polymerization, Diamond

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1. Introduction

Shock compression and rapid quenching (SCARQ) technique is a unique method to generate new interesting carbon materials [1-3]. Hirai et al. have found a transparent carbon product from C₆₀ fullerene [2]. This product has a characteristic features, exhibiting σ -electron state in sp³ hybridization by electron energy loss spectroscopy (EELS) and a diffuse pattern by electron diffractometry. Then, it was judged as amorphous in the long-range order and diamond in short-range order and labeled as "amorphous diamond". Recently, broadband photoluminescence for the amorphous diamond has been reported [4].

High-pressure-high-temperature (HPHT) treatment for solid C₆₀, on the other hand, also allows us to create a new carbon material such as superhard fullerite materials [5-8]. The superhard fullerites have features similar to the amorphous diamond fabricated by the SCARQ technique in the structure and physical properties, but there exists some essential differences. The superhard samples did not include both diamond and the so-called "collapsed fullerite" carbon state. The molecules in the HPHT samples are suggested to either create 3D polymers with crystalline and amorphous structures or a cellular nanostructure of sp²- and sp³-hybridized carbon atoms under different high pressure, high temperature and shear deformation conditions [5].

The aim of this study is to investigate polymerization of C₆₀ fullerene by SCARQ at a pressure lower than the formation of amorphous diamond.

2. Experimental

We used a commercial grade C₆₀ fullerene purified to 99.9 % as a starting material. Gold disks of 12 mm in diameter and 100 μm in thickness were utilized for rapid quenching after shock compression. C₆₀ films of approximately 4.5 and 4.0 μm in thickness were prepared by vacuum deposition on the gold disks. Nondeposited gold disks were superimposed on the C₆₀ deposited gold disks, making sandwiches. They were inserted into capsules made of stainless steel. Then the capsules were put into a protective assembly and subjected to shock loading from a flyer accelerated by a powder gun. The flyer velocities were estimated to 1.09 and 1.65 km/s, corresponding to a shock pressure of 23 and 52 GPa, respectively. The samples recovered from the capsules were investigated by scanning electron microscopy (SEM) and micro-Raman spectroscopy.

3. Results and discussion

Figures 1(a) and 1(b) show SEM micrographs of a recovered sample shock compressed to 23 GPa. A part of gold foil of the sandwiched sample was stripped and then dark areas corresponding to the C₆₀ deposited area can be seen. In Fig. 1(a), we observe division of the dark areas by bright lines, indicating an occurrence of fracture into platelets due to the shock compression. Similar bright lines can be seen on the surface of gold foil. Figure 1(b) shows a magnified view of the area denoted by a square in Fig. 1(a). One can see the correspondence between platelets stuck to the gold foil and the bright squares in the dark area where the platelets were stripped off. The size of platelets ranged from several μm to several tens of μm . Optically most of the platelets looks dark blue. The recovered sample after shock compression at 52 GPa, on the other hand, was also divided into platelets but mostly transparent, as reported before [1-4]. An oblique view of the platelets on the gold foil for the 23 GPa sample is shown in Fig. 2. There exist breaches in the platelets. The bright lines on the gold foil are seen to be ridges formed between the platelets.

Figure 3 compares Raman spectra for a pristine C₆₀ deposited film, and the two recovered samples shock compressed to 23 and 52 GPa. Raman measurements were done in the same condition for the samples in order to compare the relative intensity. At 23 GPa, photoluminescence can be seen as an increase of the Raman intensity, compared to the background intensity of the pristine C₆₀ fullerene, over a wide range of 500-7000 cm^{-1} . The sharp peaks observed at Raman shift of 1469 cm^{-1} on Ag₂ pentagonal pinching mode of a C₆₀ fullerene crystal disappeared and single intense broad at 1560-1570 cm^{-1} appeared instead, as denoted by an arrow. Other broad peaks at 3000, 4500 and 6300 cm^{-1} can change the peak positions and the intensities, depending on the platelets. Then, we guess the three peaks do not reflect the internal structure but originate in interference between the incident and the reflected laser beams. At 52 GPa, on the other hand, the single broad band observed at 23 GPa had disappeared and the intensity of the photoluminescence at a peak of 3000 cm^{-1} significantly increased over the wide range of 500-7000 cm^{-1} . A broad diamond peak sometimes appeared at around 1320-1330 cm^{-1} , depending on the platelets. The absence of Raman peaks of C₆₀ fullerene and graphite peaks, and the appearance of broad diamond peak and the broad photoluminescence indicate that this sample is in a transient state from amorphous

diamond [2] to nanocrystalline diamond [3].

In HPHT studies, it has been reported that one intense broad band at 1560-1570 cm^{-1} , which was assigned to a characteristic peak of 3D polymerization of C_{60} fullerene [9], appears in conditions 9.5-13 GPa and 300-1560 $^{\circ}\text{C}$, although the conditions are still rather controversial [8]. The 3D polymer can reach a hardness near to, or even greater than, that of diamond [5-8]. One should note that the SCARQ sample at 23 GPa in the present study exhibits a similar single broad band at 1560-1570 cm^{-1} , suggesting 3D polymerization. A fracture into platelets for the SCARQ sample seen in Figs. 1 and 2 also suggests the formation of some hard material. Nevertheless, the highest pressure on the observation of the characteristic Raman band for the 3D polymerization by HPHT treatment reported so far is 13 GPa, which is significantly lower than 23 GPa of SCARQ.

Photoluminescence, on the other hand, is also a characteristic feature on the SCARQ specimens [4]. Probably, the photoluminescence should relate to some defective sites in the samples, because pristine C_{60} fullerene, diamond and graphite do not show such a type of photoluminescence. By utilizing other experimental methods, a variety of defective sites can be induced into carbon materials. High energy particle irradiation will produce point defects or defect clusters in the bulk materials [10-12] and ball milling will also make defective sites mechanically [13]. However, no photoluminescence has been reported so far for such the defective graphite or diamond specimens. Photoluminescence barely appears for chemical vapor deposited (CVD) diamond [14] and ultrafine explosive diamond [15]. Notably, no photoluminescence has been reported for the HPHT samples, suggesting some difference in the defective structures between SCARQ and HPHT samples.

One should remember that the SCARQ technique generates adequately high pressure and temperature for an extremely short duration within a fraction of a microsecond, and also quenches transformed phases with cooling rates of 10^6 to 10^{10} K/s [16]. Then, a transformed phase from single crystals of the initial C_{60} fullerene would be quenched in more defective structure, and (P,T) condition on the products may be different from that of the HPHT treatment due to the short duration.

In conclusion, we have found a characteristic Raman feature which suggests 3D polymerization and photoluminescence for a SCARQ sample. Further experimental investigations at pressures lower than the critical pressure for the synthesis of

amorphous diamond by SCARQ technique are needed to clarify the nature of the polymerized materials and the formation mechanism.

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List of figure captions

Fig.1 SEM micrographs of a sample recovered from a shock compression to 23 GPa. A part of gold foil of the sample was stripped. Dark and bright areas correspond to the areas of C₆₀ fullerene deposition and gold foils, respectively. Photo (b) is a magnified view of area denoted by a square in photo (a).

Fig.2 An oblique view of platelets on a gold foil. The bright lines appeared on the gold foil are ridges formed between the platelets.

Fig. 3 Raman spectra for pristine C₆₀ fullerene, and samples recovered from a shock compression to 23 and 52 GPa. Broad photoluminescence can be seen for both the recovered samples as an increase of the Raman intensity over a wide range of 500-7000 cm⁻¹. At 23 GPa, the sharp peaks observed for pristine C₆₀ fullerene disappeared and single broad band at 1560-1570 cm⁻¹ appeared as denoted by an arrow. At 52 GPa the single broad band has disappeared.

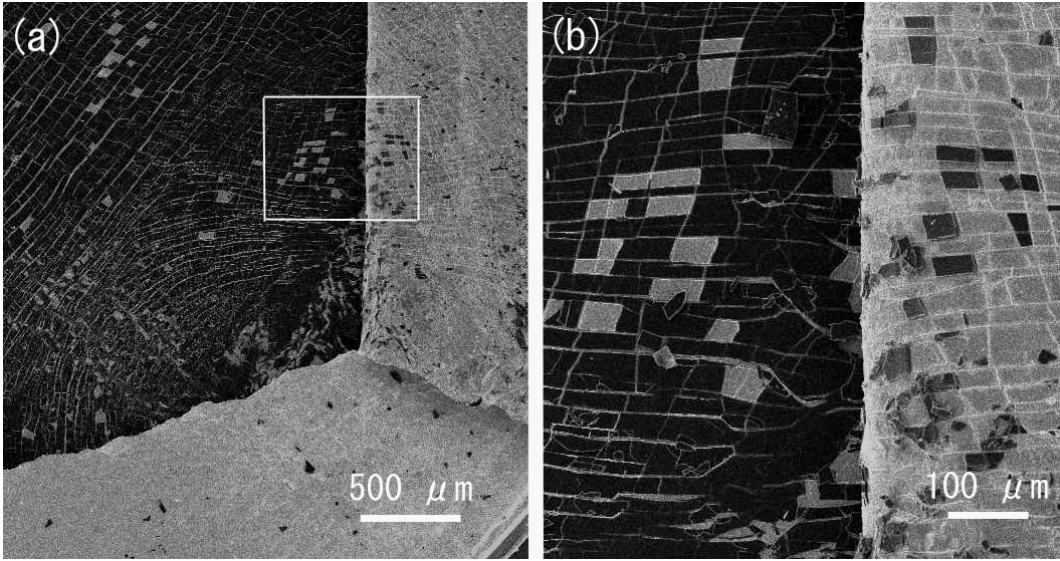


Fig. 1 K. Niwase et al.

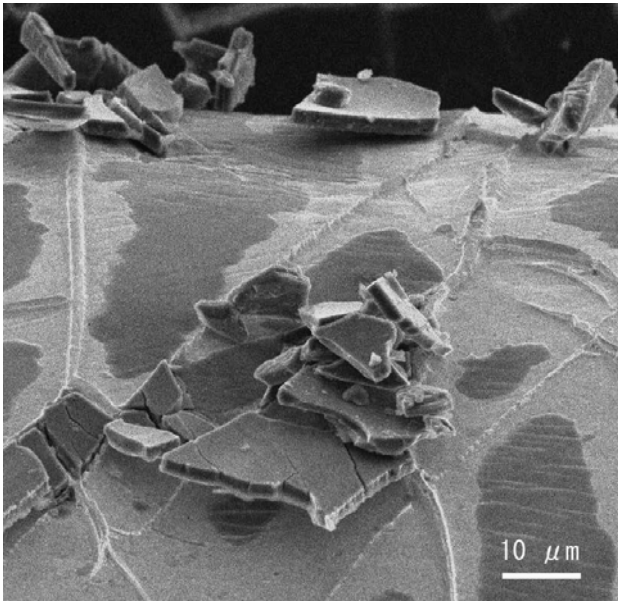


Fig. 2 K. Niwase et al.

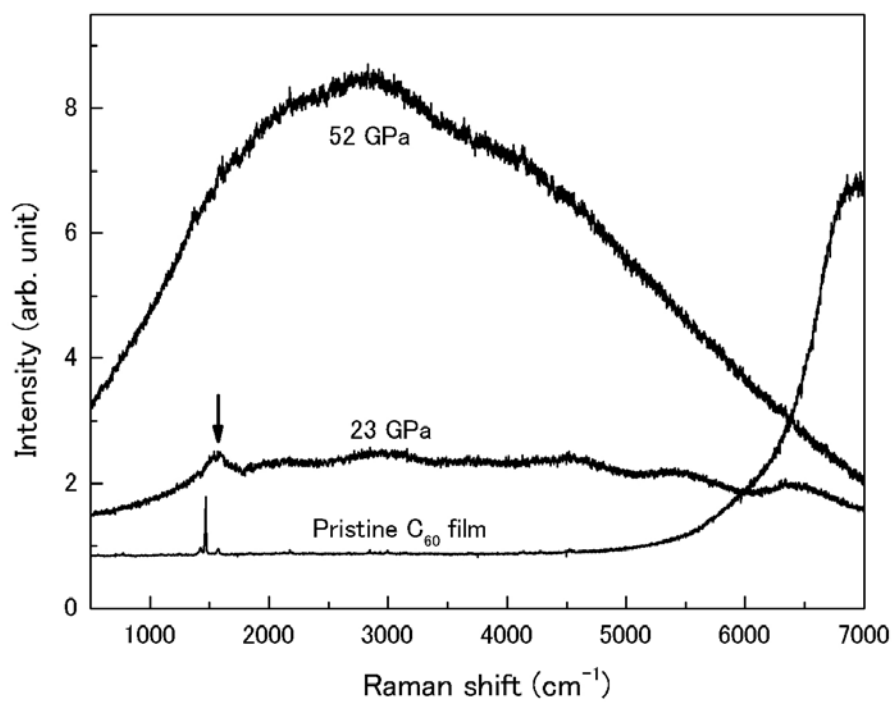


Fig. 3 K. Niwase et al.