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C_{60} fullerene under high pressure; a transition to diamond and to an amorphous diamond under shock-compression

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Phase transition studies of C_{60} fullerenen under extremely high pressure by shock-compression and hydrostatic compression were summarized. And, two shock-compression experiments applying a rapid cooling technique were described: Amorphous diamond was successfully quenched from C_{60} fullerene purified to 99.9 %. X-ray and electron diffractometry of this material showed amorphous pattern, and electron energy loss spectroscopy represented σ-electron state in sp^3 hybridization completely equivalent to that of a typical diamond. While, diamond crystallite 20 to 30 nm in size were obtained from C_{60} fullerene which contained impurities and disordered structure. The implication of these results are discussed.

1. INTRODUCTION

1.1. A brief review of pressure effect

Pressure is an important factor in the characterization and understanding of fullerenes and their phenomena. The effect of pressure on superconducting transition temperature, Tc, of alkali and alkali earth doped C_{60} superconductors has been intensively investigated, and dTc/dP=-7.8 K/GPa were already shown in A_3C_{60} compounds [e.g.1,2]. On orientational ordering and phase transition to simple cubic structure from fcc one, pressure dependence is influenced by the presence of ambient species in the interstitial lattice sites; He appears to diffuse readily into the lattice whereas N_2 and O_2 diffuse less rapidly and occupy octahedral sites [3]. From these properties, a feasibility of using C_{60} as "lattice sieves" for separation of gases under pressure was considered [4]. In addition, the role of pressure on orthorhombic structure and its transition was also examined [5].

Under much higher pressure more than 10 GPa, which is diamond-stable region [6], C_{60} fullerene behavior including transition to diamond has been a hot issue these days. C_{60} cluster itself is very hard hollow cage, while these clusters are joined by very weak van der Waals interaction. This structural characteristics is reflected in the compression property and transition feature. The fcc structure of C_{60} fullerene is maintained stable up to at least 20 GPa under hydrostatic compression in spite of its large compressibility of bulk modulus of B_0=18.1 GPa [7]. On the contrary, nonhydrostatic, but static, compression allows a transition to diamond at 20 GPa [8] and also a transition to a lower symmetry structure at 16 GPa [7].

Tabl. 1 Experimental conditions and phases identified

Run	Assembly Capsule	heat sink	Impact Velocity Km/s	Peak Pressure GPa	Shock Temp. K	Phases Identified
Using 99.9% C_{60} fulleren						
1.	W	Au	0.56	23	600	$C_{60}{}^{a}$
2.	W	Au	1.17	54	2000	tr.>90%, $C_{60}{}^{b}$
3.	W	Au	1.21	55	2000	tr.>90%, $C_{60}{}^{b}$
4.	SUS	Ag	1.61	50	2150	tr.>90%, $C_{60}{}^{b}$
Using 87.0% C_{60} fullerenee						
5.	W	Au	1.17	54	815*	dia
6.	W	Au	0.59	25	450*	dia, $C_{60}{}^{b}$
7.	W	Au	0.39	16	380*	dia
8.	W	Au	0.39	16	380*	$C_{60}{}^{b}$
9.	W	Au	0.23	9	340*	C_{60}

tr:transparent phase, a:slightly altered, b:seriously damaged
* Calculated as Au heat sink

Shock compression generates unique environment with strong shear stresses, thus this is effective to make such "soft" C_{60} structure squeeze. Several shock-compression studies recovered various carbon forms such as diamond, graphite, amorphous carbon, and transparent phase [9-12]. The first study in the range of 10 to 110 GPa, described that the onset of reconstructive transition to graphite occurred near 17 GPa, and a continuous transformation to an amorphous state was observed above 50 GPa [9]. The second one at 62 GPa using thin film produced a diamondlike transparent metastable phase [10]. The third one, 12 to 37 GPa, using the mixedpowder of C_{60} fullerene and copper showed a transition to diamond above 20 GPa, which was accompanied by graphite and unknown metastable phases [11]. Non-agreement in the product and transition path among these previous studies is probably depend on different kinetics due to experimental condition and initial state of starting material. Thus, it is still required to examine exact behavior of pure C_{60} fullerene under shock-compression.

1.2. Potential for new material, amorphous diamond

Amorphous diamond is a metastable state of carbon with great potentialities for new material and also with great interest in carbon behavior. It will partly be produced as once-molten carbon atoms or randomly-arranged carbon atoms brought in diamond stable region form diamond embryos, and are quenched rapidly without crystal growth as diamond. A transparent diamondlike phase was obtained from C_{60} fullerene by a shock-compression [10] and by a non-hydrostatic compression [8], respectively.

The former one was so unstable that it turned into black and disordered amorphous carbon in a few days [10]. The reasoning for "diamondlike" was only transparency. Any direct measurement on hybridization state (sp^2 or sp^3) and electron state (π- or σ-electron) was not carried out using such as electron energy loss spectroscopy (EELS), Auger electron spectroscopy or Raman spectroscopy. These analyses are indispensable for identifying carbon phases, especially for characterizing amorphous carbon. Therefore, well-assured amorphous diamond has neither been synthesized, nor been characterized yet.

Shock-compression and rapid quenching (SCARQ) technique has the great advantage of freezing a transient state of material such as amorphous diamond, because this technique generates adequately high pressure at extremely short duration of nanosecond order [13] and also quenches a transformed phase with cooling rate of more than 10^{10} K/s [14]. Making effective use of the potential of C_{60} fullerene to transform to diamond, it is expected to obtain amorphous diamond by applying SCARQ technique. This paper summarized our SCARQ studies on C_{60} fullerene using different initial materials. One quenched amorphous diamond, and the other showed complete transition to diamond. The difference is discussed in term of a behavior of C_{60} fullerene under shock-compression.

2.EXPERIMENTAL

A commercial grade C_{60} fullerene purified to 99.9 % and another one containing 87 % C_{60}, C_{70} and extract solvent were used as starting materials. X-ray diffraction (XRD) and electron diffraction (ED) showed only C_{60} fcc structure with high crystallinity for the former one. The other hand, the latter contained fcc C_{60} having five times larger peak-width as well as minor hcp C_{60} and C_{70}. Micro-Raman spectroscopy showed a sharp and broad C_{60} fullerene peak at -1469 cm^{-1} for the former and latter one, respectively.

In order to quench a transient phase, C_{60} fullerene crystals were sandwiched by heat sink material, gold and silver disks. The detailed experimental procedure was

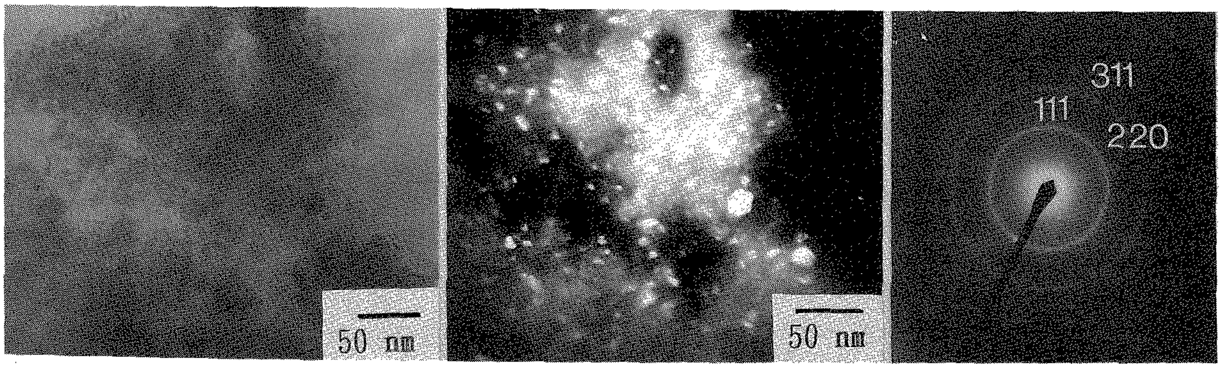

Fig.1 TEM micrograph and EDP of diamond crystallites.

described elsewhere [12]. The capsule was impacted by a tungsten flyer accelerated using a powder gun. Impact velocity of the flyer were 0.56, 1.17, 1.21 and 1.61 km/s for the former one, and were 0.23, 0.39, 0.59, 1.17 km/s for the latter one (Table 1). Peak pressure was obtained by the impact velocities to be 23, 54, 55 and 50 GPa for the former, and 8, 16, 25 and 53 GPa for the latter. Peak bulk temperature was approximately estimated to be 600 K and 2000-3000 K at peak pressure of 23 GPa and 55 GPa, respectively. Cooling rate were estimated to be 10^{10} K/s within a distance of 5 μm from the heat sink by one-dimensional thermal diffusion analysis.

3.RESULTS

For using the latter fullerene, at a shock pressure of 53 GPa, a numerous diamond crystallite 20 to 30 nm in average size were obtained (Fig.1). At 25 and 16 GPa, diamond crystallite and altered C_{60} fullerene recovered. At 8 GPa, almost unchanged C_{60} fullerene remained. The ED pattern from some parts of the altered C_{60} showed a halo, indicating an amorphous. A trace of graphite was not found. This result demonstrate that C_{60} fullerene transformed to diamond not through graphite but through an amorphous state.

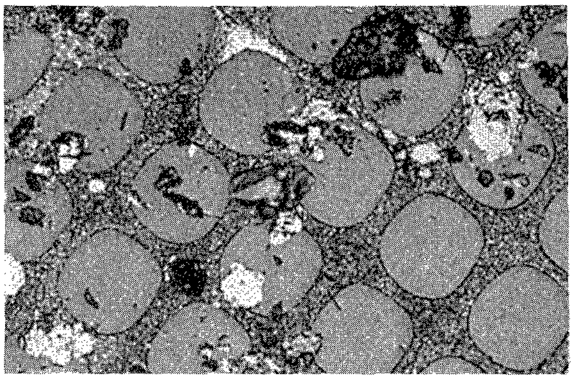

Fig.2 Optical micrograph of transparent material.

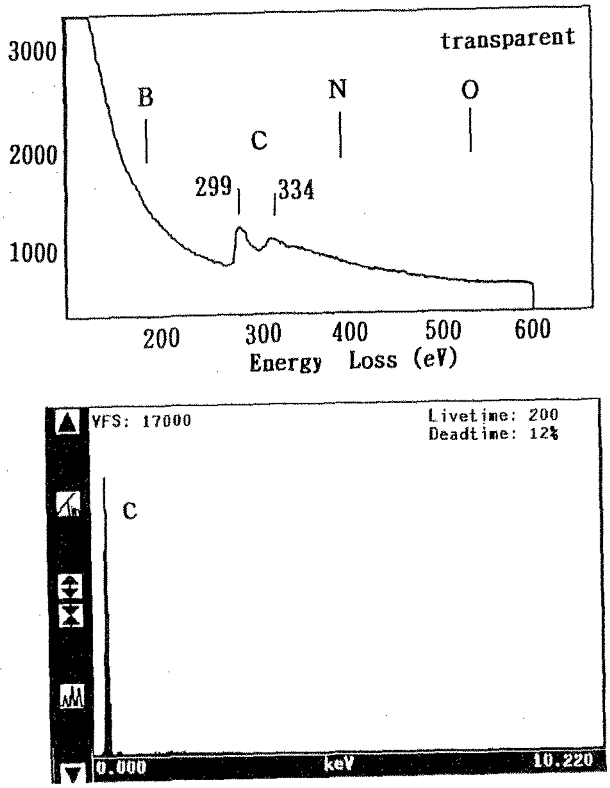

Fig.3 Elemental analyses by EELS (upper) and EDX (lower).

For the former one, in the sample of 23 GPa, altered C_{60} fullerene remained. At 54 GPa, transparent material resembling glassy chips was recovered (Fig.2). The transparent phase was obtained in good reproducibility from 55 and 50 GPa compression. The transparent phase was confirmed at first to consist only of carbon using EDX which can detect light element and also using EELS which measures K-absorption edge at higher energy (Fig.3). Single crystal XRD provided no reflection but halo. The micro-Raman spectroscopy

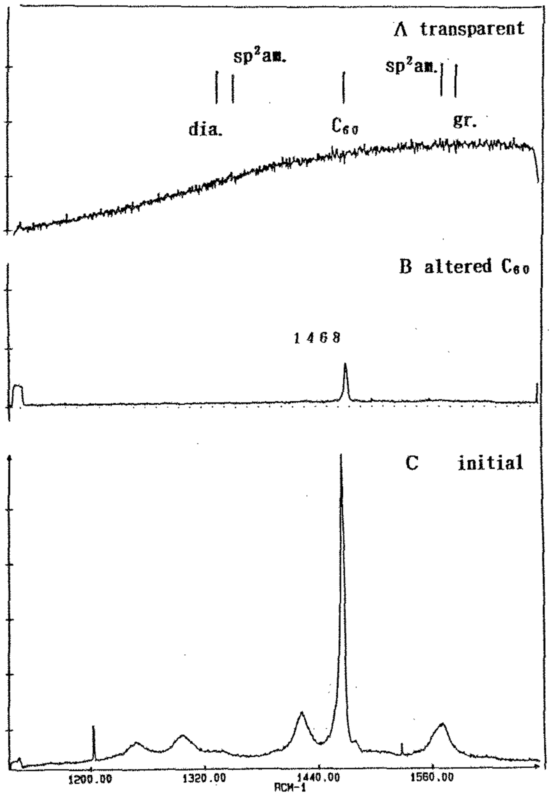

Fig.4 Raman spectra. (A) the transparent phase, (B) altered C_{60} fullerene at 23 GPa, (C) the initial 99.9% C_{60} fullerene.

represented simple base line (Fig.4). Any peak assigned to C_{60} fullerene and diamond, as well as, any slight sign of sp^2 bond, regardless crystalline or noncrystalline, did not appear. TEM image of the specimens was very homogeneous and dense mass (Fig.5). ED pattern showed two quite broad and diffuse bands which is common for amorphous carbon material. EELS measurement showed that π-electron plasmon loss peak observed in the initial C_{60} fullerene was lost. Instead of this, bulk and surface plasmon peaks of σ-electron in sp^3 bond were distinguished (Fig.6), of which energy values were completely coincident with those of a typical cubic diamond synthesized by GE Co. Ltd.

EELS and Raman spectroscopy provide an information of short range order comparable to range of a few to several neighboring atoms. While, XRD and ED give an information of long range order. All characterization proved that the transparent phase in short range order is diamond and in long range order is amorphous. Therefore, the transparent phase can be determined as amorphous diamond at least in a wide sense.

4. DISCUSSION

An elemental consideration why the amorphous diamond was produced from C_{60} fullerene is shown below. The present P-T conditions were 50 to 55 GPa and 2000 to 3000 K which is diamond-stable region [6]. C_{60} fullerene essentially has an isotropic structure consisting of spherical units stacked in fcc sequence. And, each C_{60} cluster involves highly modified sp^2 hybridization close to sp^3 one, because the bond angle 108° in the pentagon is close to

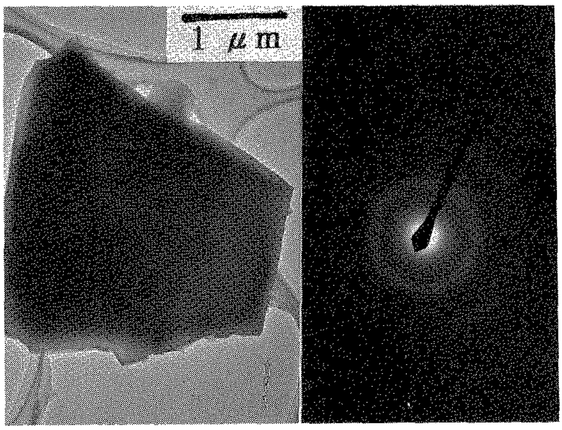

Fig.5 TEM micrograph and EDP of the the transparent phase

the angle 109°28' in the ideal sp^3 hybridization [15]. Under compression of C_{60} fullerene, each sphere is brought closer without deformation, until an inter-sphere atom distance is near to the intra-sphere distance [7,9]. All these situations, at breaking down of C_{60} fullerene, favor consistently tetrahedrally-coordinated sp^3 bond, rather than sp^2 bond. A vast number of sp^3 bonds or diamond embryos less than critical size simultaneously and homogeneously form throughout a C_{60} fullerene crystal. And, the rapid quenching did not allow these embryos to achieve crystal growth.

For the use of the latter material, the C_{60} fullerene transformed to diamond 20 to 30 nm in size. The diamond crystallite represented distinct morphology, wide size distribution and random orientation. The impurities such as C_{70} and solvent and poor crystallinity might make nucleation and subsequent crystal growth easy even under almost same condition. C_{60} fullerene which is not so pure is suggested to have possibility as raw material for diamond synthesis, and pure C_{60} fullerene is expected to have a high potential for new material, amorphous diamond.

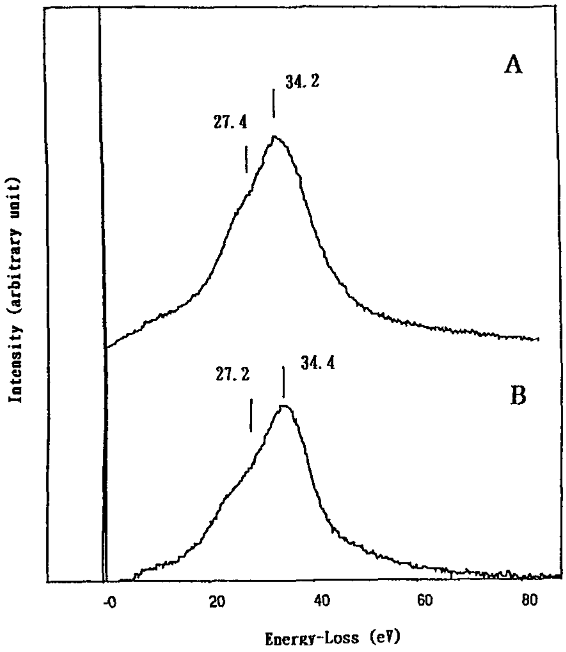

Fig.6 EELS from (A) the transparent phase, (B) from a typical diamond

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