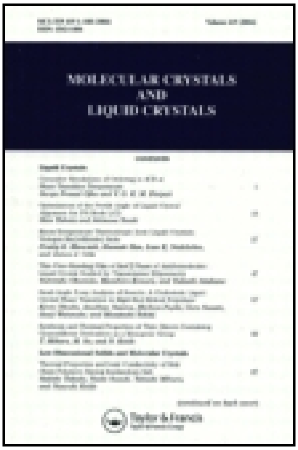

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The harmonics of free electron laser (FEL) were irradiated to the surfaces of compressed C_{60} *and/or mixture of* C_{60} *and* I_2 *in the vacuum. After the irradiation of FEL with the typical wavelength, 450 nm or 345 nm, the Raman peak of Ag(2)-derived vibration mode of* C_{60} *shifted to the lower energy side. This result suggested that polymerization reactions of* C_{60} *proceeded. The largest peak shift,* ca. *10 cm*$^{-1}$ *was obtained in the mixture powder irradiated by 345 nm irradiation. The decrease of the lattice parameter was confirmed by XRD analyses revealed that inter-molecular combinations took places. Furthermore the change of the crystal structure was closely studied by changing the wavelength of FEL in the range of 350–600 nm. The obtained results demonstrated that three-dimensional polymerization of* C_{60} *was effectively promoted by FEL irradiation and/or especially the effect of the photon-assisted hole-doping from iodine atoms to* C_{60} *molecules.*

Keywords: *Ag*(2) mode; C_{60} polymer; Free Electron Laser (FEL); Raman; XRD

1. INTRODUCTION

Since the polymerization of C_{60} films had been done by a phototransformation first [1], many research on polymerization was carried out,

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such as electron beam irradiation, high-pressure, plasma-induced excitation and so on. By adequate chemical or physical excitations a carbon double bond in a hexagon of a C_{60} cage is broken to be transformed into an intermolecular four-fold ring with a neighbor molecule. As the result the two C_{60} molecules are combined and change into the dimmer or polymers. The polymerized fullerite structures based on a "$2+2$ cycloaddition" bonding are observed experimentally and theoretically as one-dimensional (1D) chains namely an orthorhombic phase, and two-dimensional (2D) planes include a tetragonal and a rhombohedral phase [2–6]. Although the possibility of a three-dimensional (3D) polymerized phase was discussed, the polymerizations proceed usually by compressing at the order of GPa or heating above thousand degree [7]. These polymerization processes are not suitable to supply large samples enough for applications.

The purposes of this work are to develop a novel photon-assisted process for C_{60} polymerization and to synthesize 3D C_{60} polymers by irradiating Free Electron Laser (FEL) under not so high pressure. From the absorption spectrum of C_{60} thin film, large absorption peaks in 221 nm, 271 nm and 347 nm, or small absorption peaks in neighborhood 400 ~ 550 nm appearance [8]. The absorption spectrum demonstrates what wavelength of FEL should be irradiated to promote. We choose 450 nm FEL, which the value was evaluated from the difference of the bonding energy of C=C double bond and C−C bond. Since the electron affinity of the C_{60} is high, we have noticed a "hole doping effect" which was demonstrated in the synthesis of a diamond from a graphite [9]. We aimed to promote electron transfers from C_{60} to iodine atoms by the photon-excitation, and we expect that this effect may be applicable to the polymerization of C_{60} molecules because of the resemble structure of carbon networks.

2. EXPERIMENTAL

Since the 1980 mid-infrared (wavelength of few tens μm) FELs have been developed and applied to many researches of the laser-solid interaction [10]. On the other hand we adopted a newly developed FEL system which generated a tunable near-infrared laser and the higher harmonics. The details of the FEL system used appeared in the elsewhere [11]. A few tens microsecond macro-pulse, which included few hundreds picosecond micro-pulses, was the FEL pulse and was repeated in 2 Hz. The power of the fundamental macro-pulse was *ca.* 0.5 mJ/pulse. The irradiation time was typically 60 ~ 180 min. Since the FEL can supply a laser with a tunable wavelength, the fundamental wavelength was changed continuously in this work.

Figure 1 shows the schematic apparatus for the synthesis of C_{60} polymers. The vacuum chamber was evacuated to *ca.* 10^{-4} Pa by a turbo molecular pump. The two kinds of pristine powder were studied. The pure C_{60} (99.95%) was a commercial product. The C_{60} was also mixed with I_2 in the mole ratio, 1:4. Here iodine was adopted for the enhancement of polymerization reactions expected from the hole doping effect. Since the electron affinity of the C_{60} is high, we aimed to promote electron transfers from C_{60} to iodine atoms by the photon-excitation. The powder was set in an anvil which was placed in the vacuum and was pressed via a bellows by a hydraulic press. The pressure, typically *ca.* 600 MPa, was applied to the sample powder by the quartz window.

FEL was introduced to the surfaces of the pressed sample by aluminum cold mirrors which reflect only lights with the wavelength less than *ca.* 700 nm. The irradiated laser was the third harmonics of FEL with the fundamental wavelength, *ca.* 1350 nm, the wavelength mainly noticed was *ca.* 450 nm. Ultraviolet laser (345 nm) was also taken out as the fifth harmonics of *ca.* 1700 nm fundamental FEL. Furthermore 350–600 nm FEL, of which the wavelength was tuned

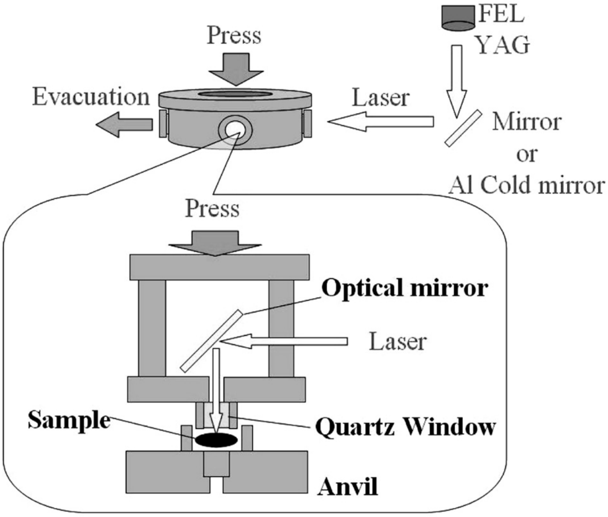

FIGURE 1 The schematic apparatus constructed for the synthesis of C_{60} polymers. The compressed surfaces of the sample were irradiated by laser by the BK7 window. Aluminum cold mirrors were used for a high reflectance of visible laser (the wavelength less than *ca.* 700 nm) and for cutting near infrared lights. The quartz BK7 ensures a high transmittance, above 95% of visible lights.

by changing the fundamental wavelength, was through the band pass filter (BPF) irradiated in the vacuum chamber pre-annealed at *ca.* 400 K for 3 h.

The obtained samples were 5-mm-diameter disks with thickness of less than 0.5 mm. They were brought with a vacuum case in order to prevent contaminations reaction with oxygen.

A Raman microscopic spectroscopy (Renishaw SYSTEM1000) was used to study molecular vibration spectra. The light source was Ar ion laser with the wavelength of 514.5 nm. Crystal structures were studied by a reflective X-ray diffraction (XRD) (Rigaku RAD-C) with CuKα1 X-ray.

3. RESULTS AND DISCUSSION

Figure 2 shows the typical Raman peaks of the *Ag*(2)-derived mode in the case of 450 nm FEL irradiation. The wave number of the peak of the non-irradiated pristine C_{60} was 1463 cm^{-1}, while that of the irradiated C_{60} changed to 1460 cm^{-1} with the increment by *ca.* 3 cm^{-1}. On the other hand, the irradiated mixture of $C_{60} + I_2$ revealed the peak wave number of 1455 cm^{-1}. The amount of the Raman shift attained to *ca.* 8 cm^{-1}. The half width of the Raman peak also increased corresponding to the amount of the peak shift.

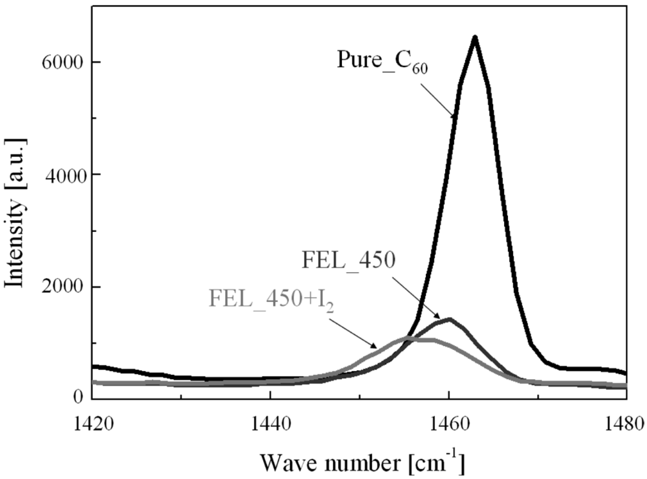

FIGURE 2 The Raman peaks of the *Ag*(2)-derived vibration modes observed in the three samples: non-irradiated pristine C_{60}, C_{60} and $C_{60} + I_2$ irradiated by 450 nm FEL.

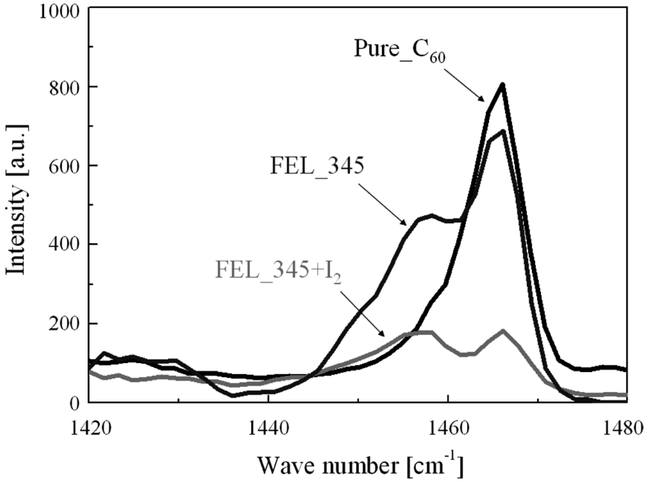

FIGURE 3 The Raman peaks of the *Ag*(2)-derived vibration modes observed in the three samples: non-irradiated pristine C_{60}, C_{60} and $C_{60} + I_2$ irradiated by 345 nm FEL.

The ultraviolet laser resulted in somewhat different changes of the Raman spectrum. Figure 3 shows the Raman peaks of the *Ag*(2)-derived mode in the case of 345 nm FEL irradiation. By the irradiation the double split of the peak was observed probably because the ultraviolet rays were strongly absorbed in C_{60} and only in the vicinity of sample surfaces were changed by the irradiation. The maximum amount of the Raman shift attained up *ca.* 10 cm^{-1} in the $C_{60} + I_2$ sample. Then the large decrease of the pristine peak at 1466 cm^{-1} was also observed. The shape of the shifted peak was rather different to that of the samples irradiated by 450 nm FEL.

The results of these Raman shifts were summarized in Table 1.

TABLE 1 The FEL Irradiation Conditions and the Observed Raman Peak Shift

Pristine powder	Wavelength [nm]	Laser powder [mJ/Pulse]	Irradiation time [min]	*Ag*(2) peak shift [cm^{-1}]
C_{60}	450 (3rd)	0.5	300	3
$C_{60} + I_2$	450 (3rd)	0.5	300	8
C_{60}	345 (5th)	2	120	7.6
$C_{60} + I_2$	345 (5th)	2	120	9.7

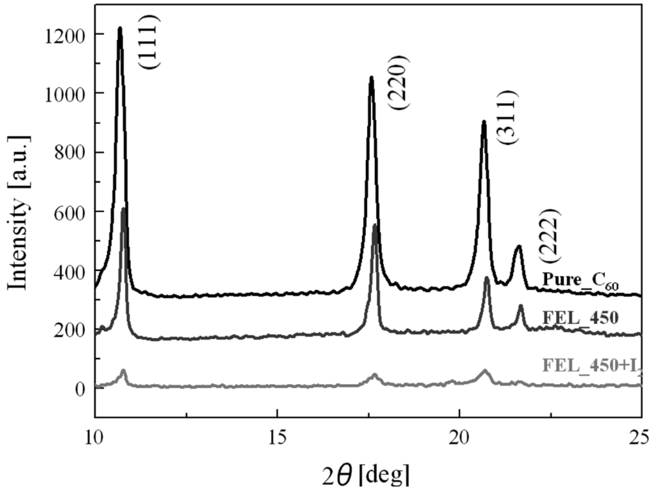

FIGURE 4 XRD patterns of the three samples: non-irradiated pristine C_{60}, C_{60} and $C_{60} + I_2$ irradiated by 450 nm FEL. The inset index corresponds to each the fcc plane of C_{60}. The (111) peak intensity of the irradiated $C_{60} + I_2$ remarkably decreased.

Figure 4 shows the XRD patterns in the case of 450 nm FEL irradiation. After the irradiation diffraction peaks became broad and small. Especially the fcc lattice parameter estimated from the XRD pattern distinctly decreased by irradiation. In the case of irradiated $C_{60} + I_2$ sample the lattice parameter of (111) planes decreased by *ca.* 6×10^{-3} nm. These results revealed that covalent bindings between C_{60} molecules took place and the alignment of C_{60} molecules became irregular to the polymerization reactions induced by FEL irradiation.

Figure 5 shows the change of the lattice parameter of (111) planes by irradiation of 350–600 nm FEL through the BPF under non-pressure. The lattice parameter of C_{60} and $C_{60} + I_2$ sample irradiated by 500 nm FEL decreased by *ca.* 1.1×10^{-2} nm and *ca.* 1.2×10^{-2} nm, respectively. These results revealed that covalent binding between C_{60} molecules took place and the decline of the crystalline structure proceeded according to the polymerization reactions induced by FEL irradiation.

4. CONCLUSION

The FEL with the wavelength of typically 450 nm or 345 nm was irradiated to the surfaces of compressed C_{60} or $C_{60} + I_2$ powder. The Raman peak of the *Ag*(2)-derived mode clearly shifted to the lower

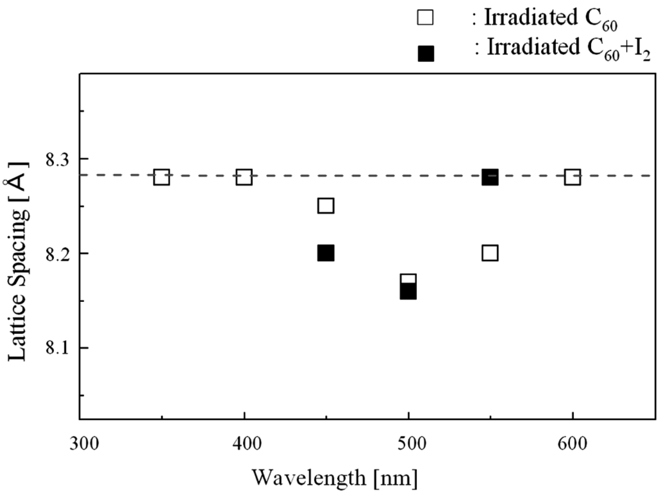

FIGURE 5 Lattice parameter of (111) planes of the sample irradiated by 350–600 nm FEL through the BPF. The dotted line was pressed C60. The open square and closed one show the result of C_{60} and $C_{60} + I_2$ sample, respectively.

energy side and/or the half width of the peak became broad. These characteristic changes were well interpreted as the results of polymerization reaction. Furthermore the lattice parameter of C_{60} decreased by FEL irradiation. The largest decrease of the bond length between C_{60} molecules was observed in the C_{60} sample irradiated 500 nm FEL. These distinct changes of the crystalline structure suggest that various kinds of inter-molecular combinations take place. Conclusively the obtained results suggested that the 3D polymerization of C_{60} was effectively promoted by the laser irradiation and/or the effect of the photon-assisted hole-doping from iodine to C_{60} molecules. The detailed characterization of the obtained samples is a subsequent work.

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