2. EXPERIMENTS

2.1 Sample preparations

2.1.1 C_{60} single crystal

Solid C_{60} is obtained efficiently by arc-method [3]. C_{60} can be extracted from the carbon soot containing other fullerenes and graphite nanoparticles by high-performance liquidcolumn chromatography. Because C_{60} molecule is soluble in aromatic solvent, such as benzene, toluene, hexane, and carbon disulphide, the C_{60} single crystal can be easily obtained from the solutions. However, it is known that the solvent molecules either physically fill the interstitials of C_{60} crystal or chemically bind a C_{60} molecule. These solvent molecules lead deterioration of the crystallinity to which the electronic and vibrational properties of C_{60} crystal are very sensitive. Therefore, it is necessary to fabricate highly purified C_{60} single crystals in order to investigate the photo-induced structural transformation of C_{60} crystals through spectroscopic investigations. A sublimation method [54] can eliminate the undesirable mixing of solvent molecules, and can improve the crystallinity of the C_{60} single crystals. Millimeter sized C_{60} single crystals grow through the condensing of C_{60} vapor.

In this study, C_{60} single crystals were prepared by the sublimation method in a quartz tube evacuated to 1.0×10^{-3} Pa. About 15 mg of C_{60} powder (Tokyo Kasei Kogyo Co., Ltd. 99.9 %) was pre-heated at 200 °C in dynamical vacuum for 24 hours to remove residual solvent molecules. After the heat treatment, the quartz tube was sealed in vacuum and was placed in an electric furnace having a temperature gradient from 520 to 550 °C, as shown in Fig. 2-1. The C_{60} vapor crystallized at the low temperature end of the tube during the heat treatment for 10 days.

2.1.2 Iodine doped C_{60} crystals

Iodine doped C_{60} (I_xC_{60}) crystals were obtained by the saturation doping of iodine to the C_{60} powder which was heated in vacuum preliminary to the doping. Two crystalline structures of I_xC_{60}, FCC and hexagonal structures, have been reported to

depend on the reaction temperature, rather than the amount of iodine molecule [31]. In the present study, I_xC_{60} was synthesized from the mixture of 20 mg of the well purified C_{60} powder and 200 ~ 400 mg of iodine flakes, which were encapsulated in a quartz tube in vacuum below 1.0×10^{-2} Pa. The mixtures were heated at $T_1 \approx 350$ °C, $T_2 \approx 150$ °C or $T_1 \approx 250$ °C, $T_2 \approx 120$ °C for 20 hours. Here, T_1 and T_2 denote the temperature at the hot and cold ends of the quartz tube as shown in Fig. 2-1. After the reactions at high temperature, the samples were subjected to additional heat treatment at 100 °C for several hours to remove residual iodine molecules which were weakly bonded to the surface of the I_xC_{60}. During the additional heat treatment, another end of the tube was kept at room temperature to condense the residual iodine. After the additional heat treatment, I_xC_{60} was brought out from the quartz tube and handled in the atmosphere.

2.1.3 Alkali metal doping to C_{60} crystal

Alkali metals and C_{60} polycrystalline powder can form compounds of A_xC_{60} with x=1, 3, 4, and 6. In this study, the compounds of A_1C_{60}, A_3C_{60} and A_6C_{60} were prepared with potassium (K) and rubidium (Rb). Because alkali metals sensitively react with oxygen and water vapor, it is undesirable to weigh them in the air. As described in Fig. 2-2, the capillary tubes of 1.0 and 0.5 micro liters were used in order to obtain the precise amount of alkali metals. Alkali metals which were dipped in paraffin oil were heated above melting points (K=64 °C, Rb=39 °C) [55] and then the alkali metals were drawn into the capillary tubes. The capillary tubes were kept in benzene to prevent alkalis at both ends of the tube from contact with O_2 or H_2O, and to remove the paraffin oil which smeared on the outer wall of the capillary tube. The stoichiometric amount of the C_{60} powder and the alkali containing capillary tube were sealed in a quartz tube, evacuated to 1.0×10^{-3} Pa. Then, the quartz tube was heated by electric furnace at 350 °C for 24 hours to complete the intercalation of alkali metals into C_{60} polycrystalline powder.

2.2 Spectroscopic investigations of C_{60} single crystals and related materials

2.2.1 Optical transmittance measurements

Information of electronic structure of materials can be obtained through the measurement of optical transmittance. The optical transmittance of thin film is given by

$$T = \left\langle \bar{t} \cdot \bar{t}^* \right\rangle = \frac{(1-R)^2}{\exp(\alpha d) - R^2 \exp(-\alpha d)}$$

where $\bar{t}$ and $\bar{t}^*$ denote the complex amplitude of the transmitting light and its complex conjugate, respectively. R, α and d correspond to reflectance, absorption coefficient of material, and width of the film, respectively. The second term in the denominator arises from the multi reflection in the film. When multi reflection is negligible in the film which has strong absorption, the equation can be reduced to $T = (1-R)^2 \exp(-\alpha d)$. In the present study, optical transmittance spectra of C_{60} single crystals in the sample chamber of the diamond anvil cell were obtained using a 0.3 m polychromator system (Acton Reserch Corporation, Spectra Pro-300i) with liquid nitrogen cooled CCD detector. A halogen lamp was used for the incident illuminant for optical transmittance measurements. The block diagram for optical transmittance measurements is shown in Fig. 2-3.

2.2.2 Photoluminescence measurements

Information of electronic properties of materials can also be obtained from photoluminescence spectra. Photoluminescence and absorption spectra are in a complemental relationship each other. Following absorption of incident light, material emits the light of photon energy which corresponds to the energy difference between the ground state and the excited state to which the electron finally reached after relaxation in a conduction band. In the present study, photoluminescence spectra of C_{60} single crystals were excited by the 514.5 nm line of an Ar^+ laser and recorded by the same optical apparatus employed in the optical transmittance measurements. The block diagram for photoluminescence measurements is shown in Fig. 2-4.

2.2.3 Raman scattering measurements

Raman scattering spectroscopy is one of the most powerful tools for detection of the structural transformation of solid C_{60} and C_{60} related materials. In general, Raman scattering is generated through interactions between incident light and elementary excitations in material. The frequency shift between scattered light (ω_s) and the incident light (ω_i) is detected as Raman scattering. The conservation law of the energy and the crystal momentum require that $\omega_i-\omega_s=\pm\omega$ and $\mathbf{k}_i-\mathbf{k}_s=\pm\mathbf{k}$ for the phonon with the frequency of ω and the wavenumber of $\mathbf{k}$, where the minus sign corresponds to the annihilation of a phonon (anti-Stokes Raman) and the plus sign to the creation of a phonon (Stokes Raman). Raman Scattering intensity, I_R, is governed by the Raman tensor R which is closely related to the fluctuation of the polarizability due to the molecular vibrations, expressed as

$$I_R \propto \left| e_I\, R\, e_s \right|^2$$

where e_I and e_s are the polarization of incident and scattered light, respectively. The isolated C_{60} molecule with an I_h point symmetry exhibits 46 vibrational modes in spite of $3\times60-6=174$ internal degrees of freedom of the C_{60} molecule. The vibrational modes are classified into the following symmetries,

$$\Gamma(C_{60})=2A_g+3F_{1g}+4F_{2g}+6G_g+8H_g+A_u+4F_{1u}+5F_{2u}+6G_u+7H_u.$$

The two A_g and eight H_g modes are Raman active, and four F_{1u} modes are infrared active according to the selection rules. The remaining 32 eigen-modes correspond to silent modes and can not be detected experimentally. The Raman scattering spectra of solid state C_{60} can be explained on the basis of the molecular vibrations of C_{60}, because the interactions among C_{60} molecules in the solid state are weak van der Waals interaction. Each Raman active mode is denoted as $A_g(1)$, $A_g(2)$, $H_g(1)$, $H_g(2)$ and so forth. The number in parentheses denotes an order counted from the vibrational mode of the lowest frequency within the same point symmetry. The Raman scattering spectra were measured using a triple spectrometer system (Jasco TRS-600) equipped with a liquid nitrogen cooled CCD detector (Photometrics TK512CB, and Roper Scientific Inc. Spec-10: 100B). The block diagram for Raman scattering measurements is shown in Fig. 2-5.

2.3   Pressure generation

2.3.1   Diamond anvil cell

In the present study, diamond anvil cell (referred to as DAC) of the Mao-Bell type was used for the pressure generation. The assembly of the Mao-Bell type DAC was shown in Fig. 2-6. As illustrated in Fig. 2-7, pressure is generated at the culet surfaces of two opposed brilliant-cut diamonds separated by the stainless steel gasket. The gasket was drilled a hole of 150 ~ 200 μm in diameter which worked as a sample chamber. The two diamond anvils were mounted on just above an optical path of semi-conical rockers made from tungsten carbide. The diamond anvils were glued on the rockers with epoxy resin. One rocker with diamond anvil was placed onto the top of a piston, and the other was placed at the base of a cylinder. Though the pressure generation with a DAC in the range of several tens of GPa is routine work, the failure in the alignment of the parallelism of diamond culet faces makes the diamonds unexpectedly fragile. Horizontal adjustment was achieved by two sets of 4 screws which change the positions of diamonds in X and Y directions of the plane perpendicular to the axis of the piston-cylinder. Angular orientation between two culet surfaces of the diamonds was achieved by tapping the corners of the rockers. The adjustment was carried out continuously until the optical interference fringes seen on close approach of the two diamond culets are eliminated. The interference fringes can be detected with a microscope which focused on the culet surface of the cylinder diamond along the axis of the piston-cylinder. Finally, the monochromatic interference can be detected under the white light illumination with the perfect alignment. Through the alignment procedure, accidental contact of diamonds must be avoided by giving a certain device, such as a safety spacer or safety screws. Unnecessary contact of diamonds degrades the performance of diamond and shortens the life. The maximum pressure is empirically determined by the diameter of the culet surface of the diamond, excluding the inaccuracy of the alignment. In the present study, diamonds with the culets of 800 and 500 μm in diameter were used for pressure generation up to 10 and 35 GPa, respectively.

2.3.2 Pressure transmitting medium

Pressure transmitting media suitable for experimental conditions were chosen from three kinds of liquid medium, the methanol-ethanol 4:1 mixture, inert liquid Fluorinart FC-75 (Sumitomo 3M), and paraffin oil. The limit of hydrostatic pressure of the alcohol mixture is known to be 11 GPa. The limit for Fluorinart and paraffin oil is around up to ~ 2 GPa. Non-hydrostatic pressure can be observed as peak broadenings of ruby fluorescence lines which are used for pressure calibrations. As an example of the non-hydrostatic pressure generation with paraffin oil, the peak broadening of the ruby fluorescence lines under pressure are shown in Fig. 2-8.

The alcohol mixture was used in the experiments with C_{60} single crystals. Fluorinart and paraffin oil were used in the experiments with iodine doped C_{60} and alkali metal doped C_{60}, respectively, in order to prevent undesirable deterioration of samples.

2.3.3 Pressure calibrations by ruby fluorescence methods

The pressure applied on the sample was calculated using shifts of R_1 (694.2 nm) and R_2 (692.8 nm) ruby fluorescence lines. The relation between pressure and shift of the R_1 line [56] is given by

$$P[\text{GPa}] = 3.808 \times 10^{-2} \left\{ \left(\frac{\Delta\lambda}{694.2} + 1 \right)^5 - 1 \right\} \quad (2.1)$$

here, $\Delta\lambda$ denotes the difference in wavelength of R_1 lines between at ambient (λ_0) and at high pressure (λ). This relation can be used up to 19.5 GPa for the compression using the alcohol mixture.

In non-hydrostatic condition in the range from 6 to 100 GPa, the relation between pressure and the wavelength of R_1 line [57] is given by

$$P[\text{GPa}] = 1904 \times \left\{ \left(\frac{\lambda}{\lambda_0} \right)^5 - 1 \right\} \Big/ 5 \quad (2.2)$$

For the pressure calibration in the temperature range from 15 to 600 K, the temperature dependence of the shifts of the ruby fluorescence lines were taken into

consideration using the cubic equation in temperature [58].

$$R_1(T) = 14423 + 4.49 \times 10^{-2}T - 4.81 \times 10^{-4}T^2 + 3.71 \times 10^{-7}T^3 \,(cm^{-1})$$
$$R_2(T) = 14452 + 3.00 \times 10^{-2}T - 3.88 \times 10^{-4}T^2 + 2.55 \times 10^{-7}T^3 \,(cm^{-1})$$

$$(2.3)$$

Especially, in the range of 300 ~ 600 K, the cubic equations are reduced to liner equations as follows.

$$R_1(T) = 14450 - 0.158 \times T \,(cm^{-1})$$
$$R_2(T) = 14483 - 0.162 \times T \,(cm^{-1})$$

$$(2.4)$$

2.3.4 Photo-irradiation to C_{60} single crystals under high pressure

The experimental procedure of photo-irradiation to C_{60} single crystals under high pressure is described in the following:

(i) C_{60} single crystals were loaded in the sample chamber of the DAC with the alcohol mixture and ruby chips for the pressure calibration.

(ii) The C_{60} samples were compressed in the range from ambient to 30 GPa, and left for an hour to ease non-hydrostatic stress in the sample chamber due to the solidification of the alcohol mixture.

(iii) Photo-irradiation to the C_{60} single crystals was performed under high pressure for 90 minutes with the 488.0 nm line of an Ar^+ laser of 1.5 kW/cm^2.

(iv) After the photo-irradiation under pressure, the pressure was reduced to ambient pressure, and the DAC was left for an hour in order to eliminate residual pressure.

(v) Raman scattering, PL and optical transmittance spectra were **measured at ambient pressure**. The 514.5 nm line of an Ar^+ laser at 100 W/cm^2 was used for the probe light for Raman and PL measurements, and a halogen lamp was used for optical transmittance measurements. All PL spectra were calibrated using a sensitivity curve with a halogen standard illuminant (Ushio electric, Inc. JPD-100-500CS).

To investigate the structural transformation induced only by pressure, the series

of experiments of (i) ~ (v) were performed without photo-irradiation in the step (iii).

In situ PL spectra of the C_{60} single crystal were also measured under pressure up to 5 GPa with the excitation of the 514.5 nm line of 100 W/cm^2.

In situ PL and Raman spectra of C_{60} photopolymer which was subjected to the photo-irradiation at ambient pressure were measured with the excitation of the 514.5 nm line of 100 W/cm^2.

2.3.5 Photo-irradiation to C_{60} single crystals under high pressure and high temperature condition

C_{60} single crystals were loaded in the sample chamber of the DAC with Fluorinart FC-75 (inert liquid) and ruby chips for the pressure calibration. Fluorinart was used for the prevention of unexpected chemical reaction between pressure transmitting media and C_{60} molecule under HPHT condition. The temperature and the photo-irradiation time dependences under HPHT conditions were investigated in the following step:

(i) C_{60} single crystals were compressed at 3 GPa.

(ii)   The sample temperature was stabilized in an hour at room temperature, 50, 75, and 100 °C by the cylindrical shaped heater attached on the cylinder part of the DAC. Precise sample temperatures were monitored by chromel-alumel thermocouples equipped on a gasket very close to a sample chamber. The pressures in the sample chamber were calculated from the R_1 line of ruby chips using the equation 2.1 and 2.4.

(iii)   Photo-irradiation to the C_{60} single crystals was performed under the HPHT condition for 90 minutes with the 488.0 nm line of an Ar$^+$ laser of 1.5 kW/cm^2.

(iv)   After the photo-irradiation under pressure, the pressure was released to ambient pressure after the samples were cooled to room temperature in an hour.

(v)   Raman scattering and PL spectra were **measured at ambient pressure and room temperature** with the excitation of the 514.5 nm line of an Ar$^+$ laser at 100 W/cm^2. PL spectra were calibrated using a sensitivity curve with a halogen standard illuminant.

2.3.6 Photo-irradiation to iodine doped C_{60} under high pressure

The experimental procedure is basically the same as described in subsection 2.3.4. Fluorinart FC-75 was used for the pressure transmitting medium. In addition to the photo-irradiation with the 488.0 nm line, the 457.9 nm and the 514.5 nm line of an Ar^+ laser and the 647.1 nm line of a Kr^+ laser were used for the investigation of the photon energy dependence of the photo-induced structural transformation of the I_xC_{60}.

2.3.7 Photo-irradiation to alkali metal doped C_{60} under high pressure

Because the alkali metal doped C_{60}, A_xC_{60} (A = K, Rb, x = 3, 6), is very sensitive to the air, the sample loading acquires some devices for not making A_xC_{60} exposed to the air. A_xC_{60} samples in quartz tubes were transferred quickly into the pre-desiccated paraffin oil in a glove box filled with high-purity Ar gas. The sample loading to the DAC was performed in the atmosphere. The A_xC_{60} polycrystalline powder which was drawn up in the glass capillary tube with paraffin oil was dropped in the sample chamber which was preliminary filled up with paraffin oil with a ruby chip. The paraffin oil works as the shielding from the air and as the pressure transmitting medium. The photo-irradiation to the A_xC_{60} under pressure and high temperature was performed in the same way as described in subsections 2.3.4 and 2.3.5.