

1. INTRODUCTION

A C_{60} molecule was discovered in 1985 by H. Kroto, R. Smally, and co-workers [1]. The truncated icosahedral structure (soccer ball) of the C_{60} molecule is very attractive because of its symmetrical beauty as described in Fig. 1-1 [2]. The C_{60} molecule belongs to “Fullerene” family. Fullerene is a general term which represents several kinds of hollow cage structures of carbon clusters. The fullerenes include the C_{60} and the other fullerene clusters, such as C_{70} , C_{82} , and carbon nanotubes and so on. Experimental studies of solid C_{60} were ignited by the pioneering work by Krätschmer *et al.* which laid the foundation of the production method of solid C_{60} in macroscopic quantity in 1990 [3]. They synthesized C_{60} contained soot by evaporation of pure graphite rods, and extracted C_{60} from the soot using several organic solvents. The C_{60} molecules crystallizes in the face centered cubic (FCC) structure as shown in Fig. 1-2 [2]. Weak van der Waals interaction binds fullerene clusters together in solid-state fullerenes.

Interesting physical phenomena, for example, superconductivity and polymerization are derived from solidification of C_{60} molecules. In the solid C_{60} , there are large interstitial spaces which can accommodate several foreign atoms. The FCC structure of C_{60} single crystal has two kinds of regular interstitials as shown in Fig. 1-3. One is named a “tetrahedral site (T-site)” which is surrounded by four C_{60} molecules, and another is named an “octahedral site (O-site)” which is surrounded by six molecules. There are eight T-sites and four O-sites in the FCC unit cell of C_{60} single crystal. The radii of T-site and O-sites are 1.12 Å and 2.06 Å, respectively. Because the two kinds of interstitials can accommodate guest ions, several kinds of C_{60} compounds have been fabricated. In particular, the intercalations of alkali metals have attracted considerable attentions for the superconductivity with the stoichiometry of A_3C_{60} or $A_1A'_2C_{60}$. Here, A and A' denote alkali metals. K_3C_{60} shows superconductivity with superconducting critical temperature $T_c = 19$ K [4]. The highest $T_c = 33$ K has been achieved by Tanigaki *et al.* with $RbCs_2C_{60}$ [5] in this system. The discovery of superconductivity accelerated the studies of solid state physics of C_{60} .

Polymerization of C_{60} is another interesting phenomenon which arises from the solidification of C_{60} molecules. Hitherto known C_{60} polymers can be categorized in

three groups. One- and two-dimensional C_{60} polymers were synthesized by (1) UV-visible photo-irradiation [6], (2) structural transformation of alkali metal doped C_{60} [7,8,9], and (3) high pressure treatments at high temperature (HPHT) [10,11]. Rao *et al.* reported firstly the occurrence of C_{60} polymerization by photo-irradiation [6]. They observed laser desorption mass spectra which indicated the formation of $(C_{60})_n$ clusters in the oxygen-free C_{60} film irradiated by UV-visible light. Besides, they found the drastic reduction in solubility of the photo-irradiated C_{60} film to organic solvents, which also indicated the structural transformation of C_{60} molecule. They suggested a [2+2] cycloaddition mechanism as the formation mechanism of photo-induced polymeric phases of C_{60} . In the [2+2] cycloaddition mechanism, C_{60} molecules are bound to each other via a four-membered ring to which the parallel C=C double bonds on each adjacent C_{60} molecule transform through photochemical reaction. The cycloaddition mechanism is schematically described as follows:



Several theoretical studies [12,13,14,15] have confirmed that the four-membered ring is the most stable structure among intermolecular bonding models, such as single bond formation or coalescence of C_{60} molecules. (In contrast, the polymer structures of the alkali metal doped C_{60} tend to be achieved by single intermolecular bonds [13,15].) Further intensive studies on the photo-induced structural transformation of C_{60} have been performed from theoretical [16,17,18] and experimental [6,19,20,21,22,23] approaches. Wang *et al.* showed that the photo-induced polymerization of C_{60} molecules is photochemical reaction initiated by a single photon absorption by C_{60} molecules [19]. The schematic explanation of photo-polymerization process given by Wang *et al.* is presented in Fig. 1-4. The photo-excited singlet states (S_n) of C_{60} decay very rapidly to S_1 state. However, the singlet exciton recombination ($S_1 \rightarrow S_0$) has a low quantum yield [24], and the system decays to T_1 state with a nearly 100 % efficiency. The highly reactive triplet T_1 state with a long lifetime ($\sim 40 \mu s$ [25]) reacts with the C_{60} molecule in a ground state (S_0) to form the intermolecular bond. This representation is consistent with the results of other spectroscopic investigations. However, the real structure of photo-polymerized C_{60} has not been fully understood. Spectroscopic investigations have showed that the photo-polymerization does not occur neither with

the irradiation of light of photon energy lower than ~ 1.8 eV nor in low temperature below 260 K [26]. The photo-polymerization requires the electronic transition because the [2+2] cycloadditional four-membered ring is created between C_{60} in the ground state and highly reactive C_{60} in the triplet state [19]. The threshold of the photon energy corresponds to the energy gap of the C_{60} single crystal. In low temperature below 260 K, suppression of the photo-polymerization relates to first order phase transition of the C_{60} single crystal [26]. The phase transition arises from the anisotropy of the electronic distribution on the C_{60} molecule. At the temperature above 260 K, C_{60} molecules are rotating freely on each lattice point of FCC structure. When the C_{60} single crystal is cooled to below 260 K, the rotational axes of C_{60} molecules are restricted into two energetically stable orientations, and the lattice structure of C_{60} crystal changes from FCC to SC (simple cubic) structure due to the absence of isotropic rotation of C_{60} molecules. Because the double bond of a C_{60} molecule (high electron density) faces the center of the hexagon or pentagon (low electron density) of adjacent C_{60} molecule in [110] direction of the FCC lattice, the crystal structure stabilizes by gaining the electrostatic energy in the SC structure. Accordingly, the photo-polymerization among C_{60} molecules in the SC structure cannot proceed with the [2+2] cycloaddition mechanism because of the absence of parallel configurations of C=C double bonds between adjacent molecules.

Secondly, alkali metals doping to solid C_{60} (A_1C_{60} ; A=K, Rb, Cs) derives charge transferred one-dimensional C_{60} polymers which have interconnections into [110] directions by the [2+2] cycloadditional four-membered ring or C-C single bonds. The $(K_1C_{60})_n$ polymer chain reportedly could be greater than $n=100000$ for the single crystalline phase [9]. These charge transferred C_{60} polymers transform into monomeric NaCl structure above *ca.* 400 K. In the A_1C_{60} system, the polymer-monomer structural transformation is reversible with temperature. The NaCl structure of A_1C_{60} is described in Fig. 1-5. In addition to the one-dimensional structure, recently the charge transferred two-dimensional polymer structure in which C_{60} molecules were bound by C-C single bond was discovered in Na_4C_{60} [27]. In contrast to the electron transfer to C_{60} from alkalis, acceptor doping to C_{60} has been investigated by halogen doping. Fluorine (F), chlorine (Cl) and bromine (Br) have been reported to covalently bind a C atom in the composition F_xC_{60} ($x=30\sim 52$) [28], Br_xC_{60} ($x=6, 8$ and/or 24) [29]. On the other hand,

iodine molecules are accommodated in the interstitials of solid C_{60} without any chemical bonding to C_{60} molecule nor charge transfer [30]. It has been reported that the iodine doped C_{60} compounds crystallize into FCC and hexagonal structures in the composition of I_xC_{60} with $x=0.2-1.2$ and $x=0.9-1.5$, respectively [31]. The polymerization of C_{60} lattice has been proposed because the lattice constant 14.14 Å of the I_xC_{60} with a FCC structure was slightly smaller than that of the pristine C_{60} single crystal, 14.17 Å. Contrary to the proposal, no evidence for the formation of C_{60} polymer and charge transfer were observed in low temperature Raman investigations [32].

Thirdly, high pressure treatment at high temperature (HPHT) forms one-, and two-dimensional crystalline polymer structures [33,34]. Intermolecular connections of HPHT polymers are also constructed by the [2+2] cycloaddition four-membered ring structure. One-, and two-dimensional structures of C_{60} polymers have been identified to orthorhombic (O) for one-dimensional, and tetragonal (T) and rhombohedral (R) for two-dimensional structures. The structural models of the C_{60} polymers are described in Fig. 1-6. The HPHT techniques go so far as synthesizing C_{60} -derived hard materials [35,36,37] whose hardness exceeds that of diamond. The hardness has been reported to owe to the three-dimensional connections of C_{60} intermolecular bonds [38,39]. However, several kinds of spectroscopic investigations of the hard materials show the destruction and coalescence of C_{60} molecules into an amorphous structure. Three-dimensional C_{60} polymer structure (Fig. 1-7) with a metallic electronic state has been predicted by Okada *et al.* [40]. This three-dimensional C_{60} polymer was reported to be attainable using uniaxial compression along to the c axis of the T polymer. In recent years, highly crystallized HPHT polymers have been fabricated [33,41]. A three-dimensional C_{60} polymer has been attempted to construct from the two-dimensional tetragonal HPHT polymer [42,43,44,45,46]. However, the structural transformation of T polymer has not been fully understood due to variance in experimental results.

While intensive studies of C_{60} polymers have been performed, effects of the photo-irradiation under high pressure have been reported only under relatively low pressure region [47,48]. Negrii *et al.* [47] have reported that the photo-induced transformations of X-traps [49] proceed under high pressure. They observed that the PL spectra which consist of the PL bands related to the X-traps radically changed by the photo-irradiation under pressure up to 2.3 GPa in the temperature range from 160 to 240

K. They also reported that the different specimens which were photo-irradiated under different pressures exhibited an identical PL spectrum after releasing pressure. Sakai *et al.* [48] have performed the rate equation analysis of the photo-polymerization process under pressures up to 1.1 GPa. They found that the contraction of the cell parameter of C_{60} single crystal drastically reduces the potential barrier of the photo-polymerization.

In addition, combination of photo-irradiation and alkali metal doping has been investigated by Onoe *et al.* [50]. They observed *in situ* IR spectra of K_3C_{60} film under light irradiation and observed IR spectra which indicate the occurrence of the photo-induced structural changes of C_{60}^{3-} molecules. They proposed several kinds of C_{120} models which include coalescent C_{120} like peanuts structure. As combination of alkali metal doping and HPHT treatments, HPHT-treated K_xC_{60} [51] and Li_xC_{60} polymers [52,53] have been reported. In Raman measurements, the A_g and H_g modes of the K_xC_{60} polymer exhibited shifts to lower frequencies due to charge transfer and the large broadening indicating the strong electron-phonon interaction of K_3C_{60} [51]. However, the XRD and Raman measurements of the K_xC_{60} polymer were inconclusive. In the case of Li_xC_{60} , XRD, infrared [52], and NMR [53] measurements revealed the formation of the two-dimensional polymers in which the C_{60} molecules are linked through the [2+2] cycloaddition four-membered rings. The polymeric structures have been determined to rhombohedral for LiC_{60} and tetragonal for Li_4C_{60} . Despite of the incorporation of Li atoms, the electronic properties of Li_xC_{60} ($x=1$ and 4) were semiconductor.

The cooperative effect of the external pressure and photo-excitation on the structural transformation of C_{60} is of great interest. Electronic transition followed by strong electron-lattice interaction is expected to induce many intermolecular connections into solid C_{60} where the intermolecular distance is contracted by pressure. However, it is obvious that further systematic studies are necessary to elucidate photo-induced structural transformation of C_{60} single crystals under pressure. Hence, the photo-induced structural transformation of C_{60} single crystals is investigated up to 30 GPa in this study by means of Raman scattering, photoluminescence, and optical transmittance measurements. Furthermore, the effects of temperature and impurity doping on the photo-induced transformation under pressure are investigated. The doping of guest species to C_{60} single crystals would give C_{60} compounds a capability which

changes the structure of intermolecular bonds and/or electronic state of C_{60} polymers. The doping effects have been investigated with halogen- (iodine) and alkali metals- (potassium and rubidium) intercalated C_{60} compounds by means of Raman scattering spectroscopy.

In this thesis, we demonstrate experimentally that the photo-induced structural transformation of C_{60} single crystals and its compounds depends on the pressure applied during the photo-irradiation. It will be pointed out that the combination of pressure and irradiation plays a primary role on the formation mechanism of C_{60} intermolecular bonds.