

Mechanical and optical characteristics of Al-doped C₆₀ films

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Abstract

Al-doped C₆₀ films are grown on GaAs and quartz glass substrates by solid source molecular beam epitaxy. Mechanical and optical properties of the films are investigated by Vickers hardness test, absorption and reflectance spectra, and photoluminescence measurements. Vickers hardness of 250HV is confirmed for the Al-doped C₆₀ films with the molecular ratio of Al to C₆₀ of 30, and the Al-doped C₆₀ films are found to be undissolved in organic solvents. The absorption spectra of pure C₆₀ films show some peaks caused by the electron transition among the C₆₀ molecular orbitals. These absorption peaks become less pronounced in Al-doped C₆₀ films, probably due to the Al incorporation in C₆₀ matrix. In addition, new photoluminescence peaks appear around 1.75eV, 1.85eV and 1.95eV. The energy of 1.95eV coincides well with the energy difference between HOMO and LUMO states. These results suggest that the parity forbidden transition is relieved by the molecular distortion due to the Al-C₆₀ bonding.

PACS codes: 62.20.Qp; 78.40.Ri; 78.55.Kz

Keywords: B1. Fullerenes; B1. Organic compounds; A3. Molecular Beam Epitaxy; A1.

1. Introduction

Feasibility of C_{60} films as a practical electronic material has been investigated by using solid source molecular beam epitaxy (MBE). Early works on the growth of C_{60} films have proved that C_{60} molecules crystallize in the face-centered cubic crystal on the crystalline substrates such as Si and GaAs [1-6]. Indeed, we have successfully grown high quality single crystalline (111) oriented C_{60} films on GaAs (001) and GaAs (111)B substrates [7]. However, the grown C_{60} films are very fragile and chemically unstable, probably because C_{60} crystals are formed by the van der Waals force, which is very weak at room temperature [8]. Thus, the films are not suitable for practical device applications. To investigate the feasibility of C_{60} layers, it is inevitable to obtain stronger and more stable C_{60} films, keeping the original characteristics of C_{60} films. It has been reported that the metal- C_{60} interaction is stronger than the C_{60} - C_{60} van der Waals interaction [9-11]. Therefore, metal doping in C_{60} films may produce much harder and chemically stable materials.

In this paper, in order to enhance the binding energy while keeping the original nature of C_{60} films, we investigate the effect of Al doping into C_{60} films grown on GaAs substrates and quartz glass substrates. The mechanical and optical properties of the films are investigated by Vickers hardness test, absorption and reflectance spectra, and

photoluminescence (PL) measurements. The Al-doped C₆₀ films are found to be much harder and more chemically stable than pure C₆₀ films. A new PL peak appears around 1.95eV, which coincides well with the energy difference between HOMO and LUMO states.

2. Experimental procedure

Al-doped C₆₀ films are grown on GaAs (001) and quartz glass substrates by solid source MBE with background pressure of 10⁻¹⁰ Torr. The crystalline characteristics of the films grown on GaAs substrates are compared with those of pure C₆₀ films also grown on GaAs substrates. Vickers hardness test, optical transmittance and reflectance measurements are performed on the layers grown on quartz glass substrates. GaAs substrates are first etched in an alkaline etchant, and loaded in the growth chamber. The surface oxide layer is removed by thermal anneal at 580°C. After growing a 50-nm-thick GaAs buffer layer at 580°C, Al-doped C₆₀ film growth is performed at a substrate temperature of 100°C. Purity 99.5% C₆₀ powder is used as the C₆₀ source. The beam equivalent pressure of C₆₀ is fixed at 1.0x10⁻⁷ Torr with the deposition rate of 0.23Å/sec. Al cell temperature is varied between 985°C and 1120°C. The flux ratios of Al atoms to C₆₀ molecules are estimated to be 3, 6 and 30 for Al cell temperatures of 985°C, 1020°C and 1120°C, respectively. The sticking coefficient of C₆₀ at 100°C should be unity because the growth rate of C₆₀ layers at substrate temperatures below 150°C remains

constant, and decreases gradually with temperatures above 200°C. Therefore, the resulting composition of the grown layer is equal to the flux ratio.

Quartz glass substrates are degreased by organic solvent, and the surface contaminations are evaporated by thermal anneal at 600°C for 30 minutes in the growth chamber before deposition. Al-doped C₆₀ films are grown on the same manner as those grown on GaAs substrates.

The crystalline properties are investigated by reflection high energy electron diffraction (RHEED) and X-ray diffraction (XRD) $2\theta/\omega$ scan. The Al distributions in the films are estimated by secondary ion mass spectroscopy (SIMS) measurement using Cs ions. Vickers hardness test is applied to investigate the mechanical properties. Absorption and reflectance spectra of the films grown on quartz glass substrates are measured at the wavelength range between 220 and 800 nm at room temperature. Photoluminescence (PL) measurement is performed at 4.2 K and room temperature by using the 488 nm line of Ar ion laser as an excitation source.

3. Results and discussions

The RHEED patterns of pure C₆₀ films grown on GaAs (001) and GaAs (111)B substrates exhibit well characterized (1x1) structure and indicate that the epitaxial orientation is (111) direction on both substrates [7]. On the other hand, the RHEED patterns of the Al-doped C₆₀ films on both GaAs and quartz glass substrates are halo patterns from the beginning of the growth, and the films show no peak in XRD $2\theta/\omega$

scan, indicating that Al-doped C₆₀ films are amorphous structure.

Figure 1 shows the depth profiles of aluminum and carbon measured by SIMS. The thickness of this sample is 350nm, and the ratio of Al to C₆₀ is 6. It is confirmed that there is no segregation of aluminum atom in the films. Figure 2 compares the profiles of aluminum and carbon distributions in the films grown at different Al cell temperatures. The growth time is fixed at 3 hours, and the molecular ratios of Al to C₆₀ are 3, 6 and 30. As shown in the figure, Al concentration in the film increases with Al cell temperature.

The Vickers hardness of pure C₆₀ crystals is reported to be around 20HV [12, 13]. To investigate the effect of Al incorporation on the hardness, we performed Vickers hardness test for the 6.0- μ m-thick Al-doped C₆₀ film grown with the molecular ratio of 30. The obtained Vickers hardness is as high as 250HV, which is approximately the same as that of plated copper surfaces.

Pure C₆₀ crystals are quickly dissolved in organic solvents due to the nonpolarity and the weak interaction among C₆₀ molecules. However, the Al-doped C₆₀ films are found to be undissolved in organic solvents. The dramatic structural changes and the observed improvements in hardness and chemical stability mentioned above suggest that C₆₀ molecules react with aluminum, forming stable bonds between them.

Figure 3 shows the absorption and reflectance spectra of a 25-nm-thick pure C₆₀ film grown on quartz glass substrate. Since the interaction among C₆₀ molecules is very weak, the absorption profiles are governed by the electron structure of C₆₀ molecule.

The four absorption peaks are observed at 2.7eV, 3.6eV, 4.6eV and 5.6eV. These absorption profiles are in agreement with reported experimental results [14, 15] and the calculated spectra [8, 16]. The absorption peaks correspond to the transitions among the C₆₀ molecular orbitals. The simplified electron energy levels of the C₆₀ molecular orbitals are shown in the inset of Fig. 3. The h_u is the energy level of the highest occupied molecular orbital (HOMO) and the t_{1u} is that of the lowest unoccupied molecular orbital (LUMO). The electron transition between HOMO and LUMO is not observed due to dipole forbidden [8].

Figure 4 shows absorption coefficient spectra of the pure C₆₀ film and the Al-doped C₆₀ films grown at several Al cell temperatures on quartz glass substrates. It is confirmed that the absorption peaks in the Al-doped C₆₀ films become less pronounced as a result of the Al-C₆₀ interaction.

The PL spectra of both pure and Al-doped C₆₀ films are shown in Figs. 5 (a) and (b). The measurement is performed at 4.2K and at room temperature. The PL spectra of the pure C₆₀ are in good agreement with previous results [15, 17, 18]. The spectral positions of the PL peaks shift only slightly when measurement temperature varies. This is due to the weak intermolecular bonds of C₆₀ solids [8]. The most dominant emission line lies around 1.69eV (peak 2), which is attributed to the radiative recombination of a self-trapped polaron exciton. Such an exciton complex occurs due to the strong electron-vibration coupling on C₆₀ clusters. This excitation is localized, and

can be a Frenkel exciton trapped by a lattice dislocation. The peak around 1.50eV (peak 1) is considered to be a phonon replica of peak 2. The energetic difference between peak 1 and peak 2 is about 180meV. The phonon mode involved in the peak 1 corresponds to the strongest phonon peak in Raman spectrum [19] at 1469cm^{-1} (182meV). This is a total-symmetric A_g mode, corresponding to the double bond stretching pentagonal pinch mode of the C_{60} molecules.

In pure C_{60} films, the electron transition between HOMO and LUMO is parity forbidden [16]. In the Al-doped C_{60} films, however, new PL emission peaks appear around 1.75eV (peak 3), 1.85eV (peak 4) and 1.95eV (peak 5). The energies of the new PL peaks remain when measurement temperature varies, indicating that the new peaks also may be attributed to the C_{60} molecules. The energy of the peak 5 coincides well with the energy difference between HOMO and LUMO states [20], suggesting that the parity forbidden transition is relieved by the molecular distortion due to Al- C_{60} bonding. The peaks around 1.75eV (peak 3) and 1.85eV (peak 4) are considered to the phonon replicas of peak 5. The energetic difference between peak 4 and peak 5 is about 90meV. This phonon mode corresponds to the phonon peak in Raman spectrum at 709cm^{-1} (88meV). The energetic difference between peak 3 and peak 5 is about 200meV. This phonon mode corresponds to the phonon peak in Raman spectrum at 1575cm^{-1} (196meV).

4. Conclusions

Al-doped C_{60} films are grown on GaAs and quartz glass substrates by solid

source MBE. The RHEED exhibits halo patterns from the beginning of the Al-doped C₆₀ films growth, and the films show no peak in XRD 2 θ / ω scan, indicating that Al-doped C₆₀ films are amorphous structure. SIMS measurements show that there is no segregation of aluminum atoms in the films. The Vickers hardness of 250HV is confirmed for the Al-doped C₆₀ films with the molecular ratio of Al to C₆₀ of 30, and the films are found to be stable against organic solvents. For pure C₆₀ films, the absorption peaks caused by the electron transition among the C₆₀ molecular orbitals are observed. However, the absorption peaks of the Al-doped C₆₀ films become less pronounced due to the Al-C₆₀ interaction. New PL peaks appear around 1.75eV, 1.85eV and 1.95eV in addition to the original excitonic emissions at 1.5eV and 1.7eV in pure C₆₀ films. The energy of 1.95eV coincides well with the energy difference between HOMO and LUMO states, suggesting that the parity forbidden transition is relieved by the molecular distortion due to the Al-C₆₀ bonding.

Acknowledgements

This work is partly supported by Grant-in-Aid for Scientific Research on Priority Areas program Photonics Based on Wavelength Integration and Manipulation, by the COE Program “Molecular Nano-Engineering”, and by 21 COE “Practical Nano-Chemistry” from the Ministry of Education, Science, Sports and Culture, Japan.

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Figure Captions

Fig. 1. Depth profiles of aluminum and carbon of the Al-doped C₆₀ film on GaAs substrate measured by SIMS. The growth time of this sample is 3 hours, and the molecular ratio of Al to C₆₀ is 6.

Fig. 2. Profiles of aluminum and carbon distributions in the films grown at different Al cell temperatures. The growth time is fixed at 3 hours, and the molecular ratios of Al to C₆₀ are 3, 6 and 30.

Fig. 3. Absorption and reflectance spectra at room temperature of a 25-nm-thick pure C₆₀ film deposited on quartz substrate. The inset shows the simplified electron energy levels of the C₆₀ molecular orbitals.

Fig. 4. Absorption coefficient spectra at room temperature of the pure C₆₀ film and the Al-doped C₆₀ films grown at several Al cell temperatures on quartz glass substrates.

Fig. 5. PL spectra of the pure C₆₀ film and the Al-doped C₆₀ film with the molecular ratio of Al to C₆₀ of 30 grown on quartz glass substrates measured at 4.2K (a) and room temperatures (b). The samples are excited by the 488nm line of an Ar ion laser.

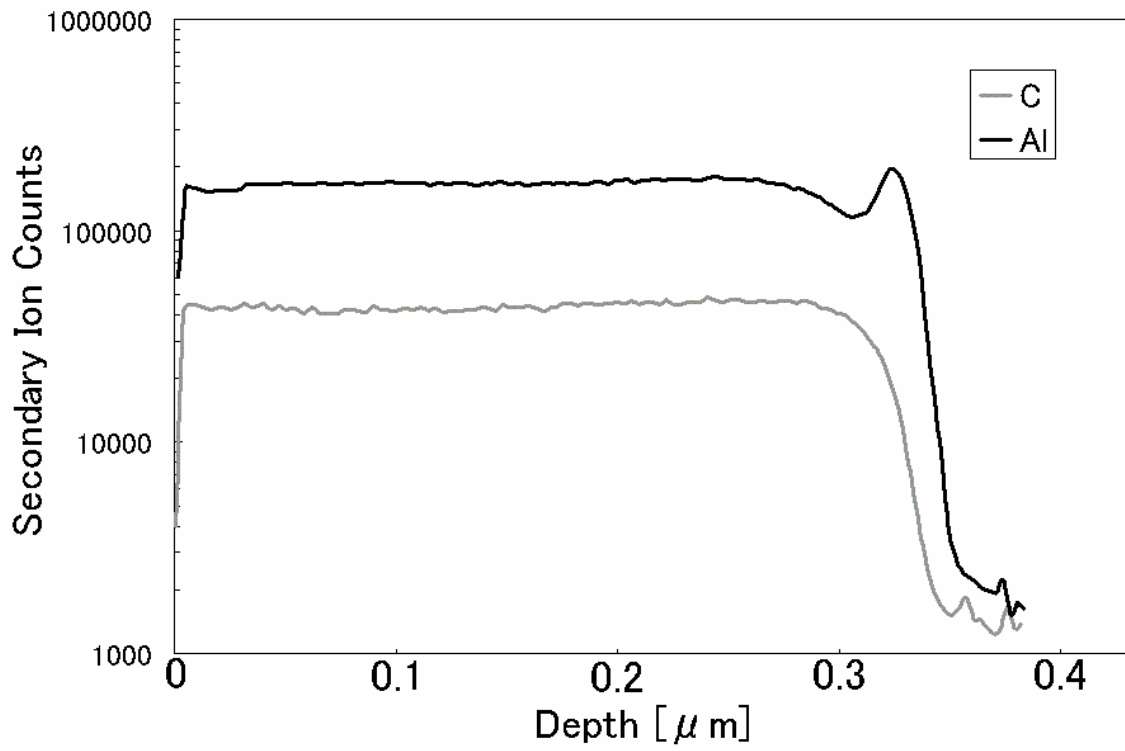


Fig. 1

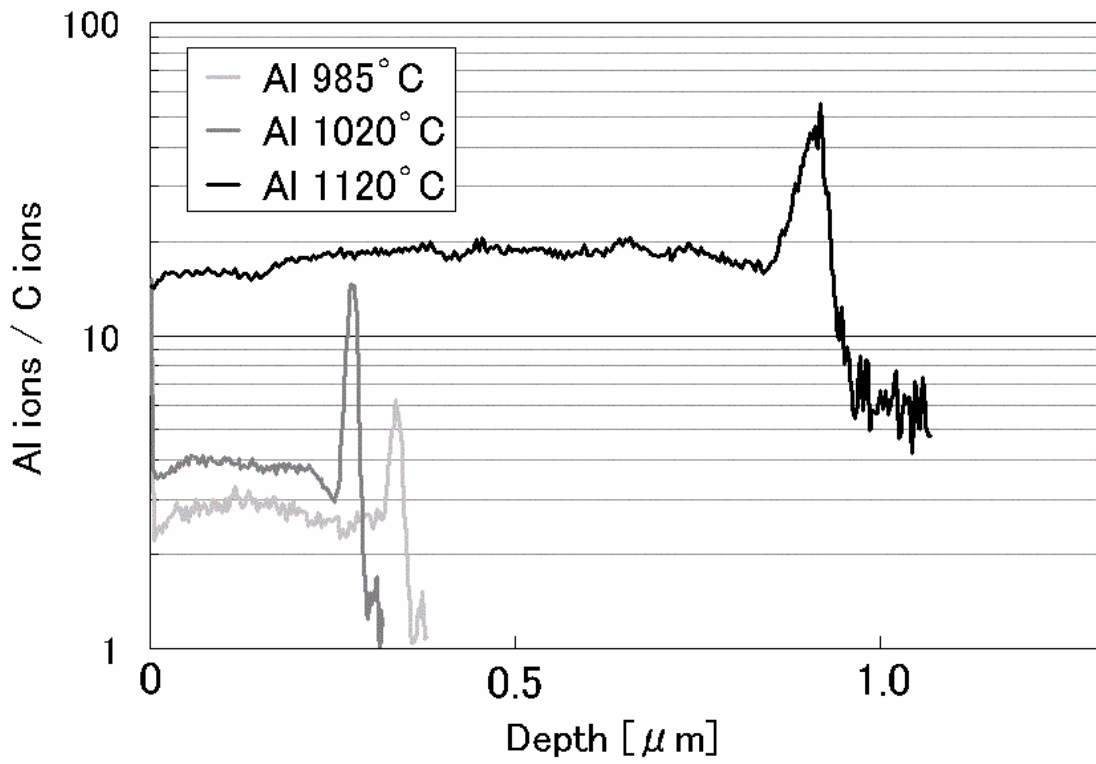


Fig. 2

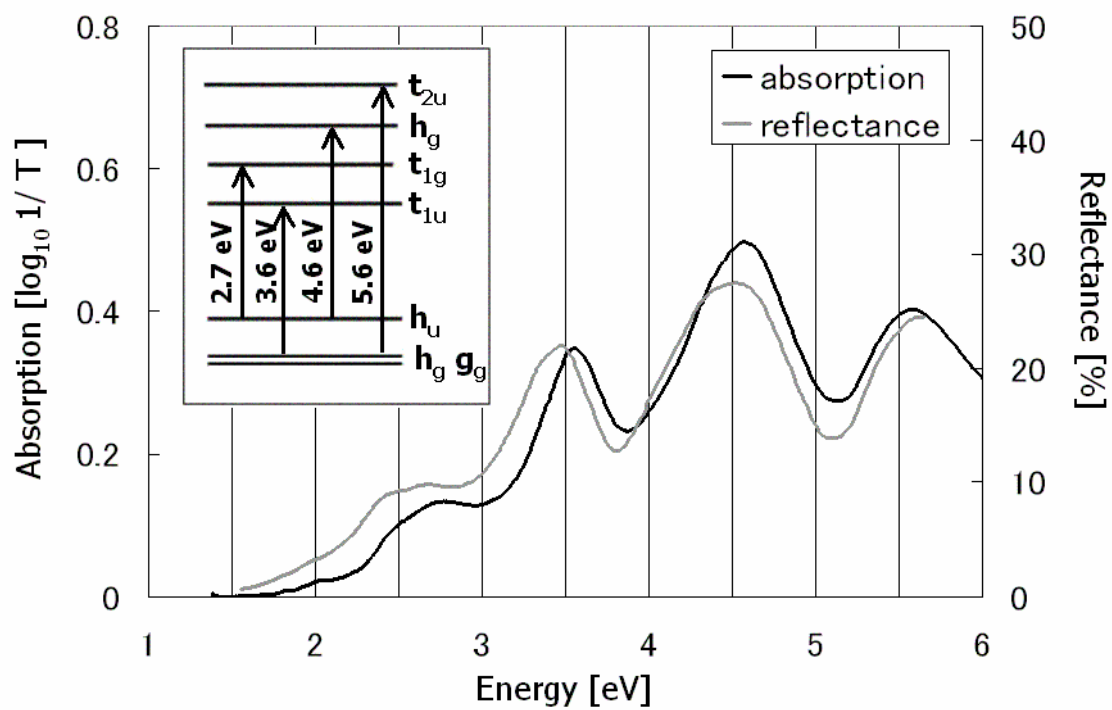


Fig. 3

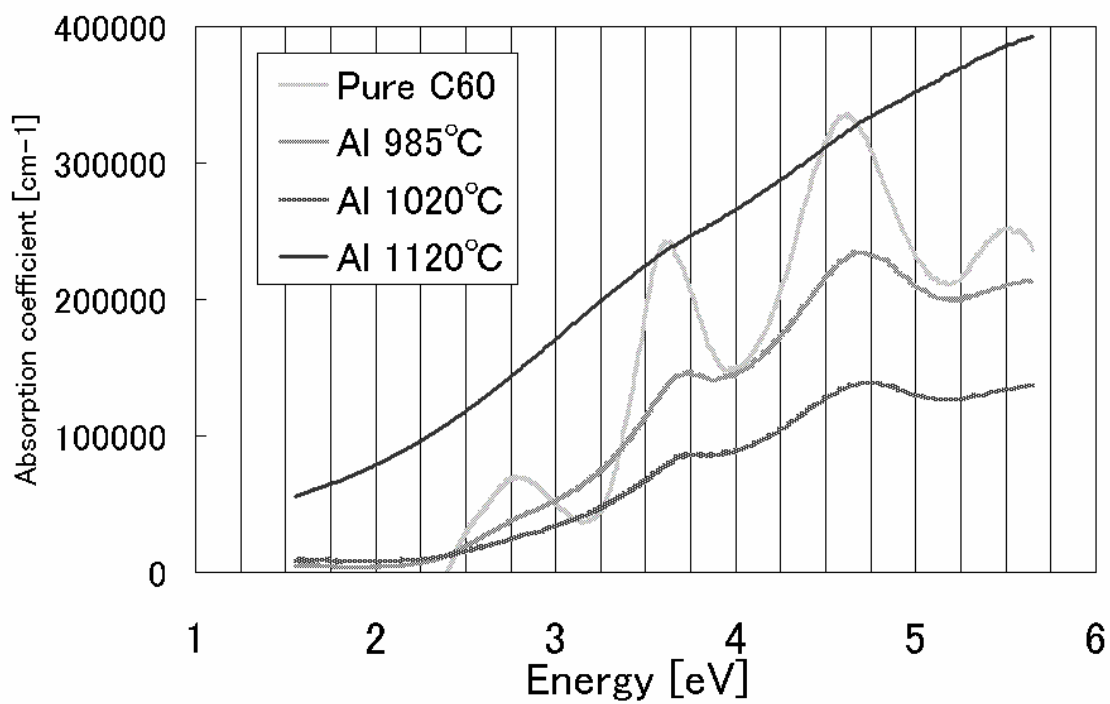


Fig. 4

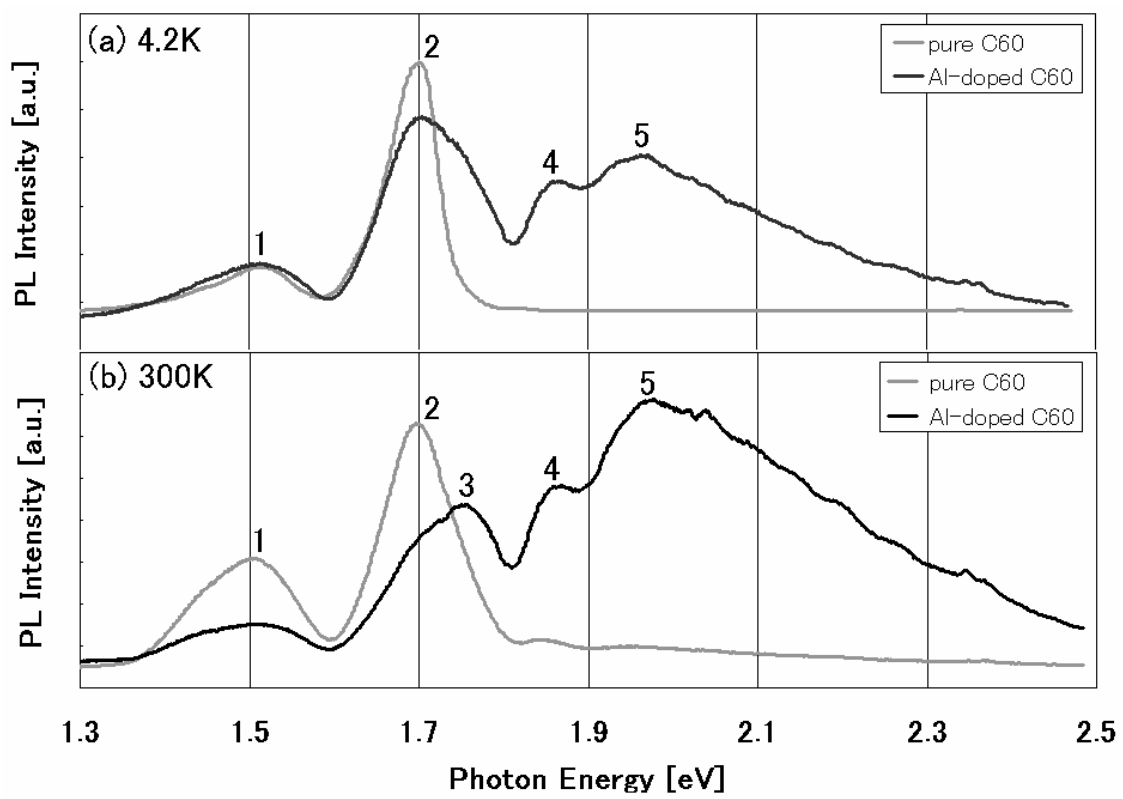


Fig. 5