Structural Characterization of Mg-doped C₆₀ Thin Films

N Kojima, M Natori, H Suzuki and M Yamaguchi
Toyota Technological Institute, 2-12-1 Hisakata Tenpaku, Nagoya 468-8511, Japan
E-mail: nkojima@toyota-ti.ac.jp

Abstract. The epitaxial growth of Mg-doped C₆₀ films has been investigated. It is found that the epitaxial growth of Mg-doped C₆₀ film is enabled by using mica (001) substrate in the low Mg concentration region (Mg/C₆₀ molar ratio < 1). The crystal quality of the epitaxial Mg-doped C₆₀ film is improved drastically in compared with micro-crystalline film on glass substrate. Such drastic improvement of crystal quality in the epitaxial films results significant increase in conductivity. This result may indicate the significant increase of carrier mobility. In addition, the crystal structure change is observed in high Mg concentration region (Mg/C₆₀ molar ratio > 2). The C₆₀ polymer sheet formation is suggested.

1. Introduction
C₆₀ solids have been known as high resistive semiconductor materials. For organic solar cell applications, such high resistivity is one of the reasons of low charge transport efficiency in a C₆₀ accepter layer. Impurity doping in organic semiconductor can increase conductivity, and control band profile at the interface between organic/metal or organic/organic materials. Previously, metal-doped C₆₀ has been studied extensively with regard to the superconducting compounds. Alkali and alkaline earth metals, such as Li, Na, K, Rb and Ba have been used mostly as guest metals in the previous study. The valence electron level of most alkali and alkaline earth metals lies at higher energy than LUMO-derived band of C₆₀, and the valence electrons of guest metals transfer to the C₆₀ LUMO-derived band. Thus, these compounds show the metallic behavior. For the semiconductor device application, the search for new guest materials is necessary. Mg is one of the promising materials for guest metal showing semiconductor property. R. P. Gupta et al. reported the energy band calculation of Mg₂C₆₀ solids, and indicated that Mg₂C₆₀ was semiconductor, since Mg 3s-derived occupied band was formed between C₆₀ HOMO-LOMO levels [1]. In experimentally, it was reported that the conversion efficiency of C₆₀/MEH-PPV organic cells was significantly improved by the automatic Mg-doping in a C₆₀ layer during the Mg electrode deposition [2, 3]. However, the detailed discussion of semiconductor properties of Mg-doped C₆₀ films has not been reported yet.

The electric conduction of organic materials is also affected by the crystal quality. The band conduction mechanism has been observed in organic single-crystal materials, while the amorphous one shows the hopping conduction mechanism. Therefore, to investigate the essential electric conductivity behaviors, the well-crystalline film is required.

In this paper, we investigate the epitaxial growth of Mg-doped C₆₀ films to obtain the well-crystalline films, and electric properties of the epitaxial Mg-doped C₆₀ films.
2. Experimental

$C_{60}$ and Mg-doped $C_{60}$ films were grown on mica (001) or quartz glass substrates by molecular beam epitaxy (MBE). The base pressure of the MBE chamber was $3 \times 10^{-7}$ Pa. The pure (99.98%) $C_{60}$ powder and Mg (99.9%) were evaporated from a Knudsen cell. The beam flux of each source was monitored by a nude ion gauge at the substrate position, and was controlled by the source temperature. The $C_{60}$ beam flux was fixed at around $6.7 \times 10^{-6}$ Pa. The film composition of Mg/$C_{60}$ was changed by the changing the Mg beam flux from 0 to $2.7 \times 10^{-6}$ Pa. The resulted film composition of Mg/$C_{60}$, estimated by X-ray Photoelectron Spectroscopy (XPS), was proportional to the beam flux ratio of Mg/$C_{60}$. The growth rate of Mg-doped $C_{60}$ was around 5 nm/min, and the total film thickness was around 1 μm.

In our previous work, we have already established the growth conditions for epitaxial growth of pure $C_{60}$ films on mica (001) substrate. (111)-oriented crystalline $C_{60}$ can be grown on mica (001) at the growth temperature of 165°C. Therefore, we selected the same growth temperature for achieving the epitaxial growth of Mg-doped $C_{60}$ films. Figure 1 shows the schematic model of molecular arrangement of $C_{60}$ on mica (001) surface.

For the conductivity measurements, bottom electrode structure was used. MgAg or Al metal was evaporated through a metal mask on the substrate to form a pair of electrodes with 0.5 mm spacing, before Mg-doped $C_{60}$ was grown. The conductivity was estimated from I-V characteristics between the adjacent bottom electrodes under the vacuum condition.

The crystal structure was analyzed by X-ray diffraction (XRD) measurements with two configurations. One is 2θ-ω goniio scan, and the other is pole figure configuration, i.e. rotating on the axis normal to the substrate surface (azimuthal angle φ) and rotating on the intersecting axis between the substrate surface and the X-ray path plane (azimuthal angle ψ), and fixing 2θ and ω at the specific crystal plane, as shown in Figure 2. In pole figure configuration, the orientation of the specific crystal planes can be determined.

![Figure 1. Schematic model of molecular arrangement of $C_{60}$ on mica (001) surface.](image1)

![Figure 2. Pole figure configuration in XRD measurement.](image2)

3. Results and Discussion

Figure 3 shows the XRD patterns of undoped $C_{60}$ films on glass and mica (001) substrates. For undoped $C_{60}$ films on glass, the observed diffraction peaks correspond with polycrystalline $C_{60}$ phase with fcc lattice, though these diffraction peaks are rather broad. In contrast, undoped $C_{60}$ films on mica (001) shows only sharp (111)-related diffraction peaks, suggesting good crystal quality.
Figure 4 shows the XRD patterns of Mg-doped C$_{60}$ (Mg/C$_{60}$ molar ratio = 0~2.9) grown on mica (001). In Mg-doped C$_{60}$ with Mg/C$_{60}$ molar ratio of 0~0.7, fcc (111)-related sharp diffraction peaks are observed and the lattice parameter is expanded from $a=14.14\text{Å}$ for undoped C$_{60}$ to 14.29Å by Mg incorporation, though these peaks become a little broader with increasing Mg concentration. While in Mg-doped C$_{60}$ with Mg/C$_{60}$ molar ratio of 2.9, these peaks considerably weakened, suggesting less crystal quality, and fcc (111) diffraction peak splits into two peaks. This result suggests the possibility of phase separation or anisotropic lattice parameter change. Recently, formation of rhombohedral 2-dimensional polymer of Mg$_x$C$_{60}$ ($x=4,5$) is reported [4, 5]. If we attribute these peaks to rhombohedral, the lattice parameters are $a=b=9.44\text{Å}$, $c=24.61\text{Å}$. From the calculated $a$ value, it is indicated that the distance between adjacent C$_{60}$ molecules of Mg-doped layer is shorter than that of pure C$_{60}$ film. It is suggested that C$_{60}$ polymer sheets are possibly formed in high Mg concentration region (Mg/C$_{60}$ molar ratio > 2).

In the low Mg concentration region (Mg/C$_{60}$ molar ratio < 1), the relation of crystal orientation between the mica substrate and Mg-doped C$_{60}$ film was investigated by the XRD with pole figure configuration. Figure 5 shows the pole figure mapping of C$_{60}$ {111} planes and mica {112} planes of Mg-doped C$_{60}$ film with Mg/C$_{60}$=0.8. The center of the circle corresponds to $\phi=0$ and $\psi=0$, and means the normal direction of the sample surface. From this figure, it is clearly seen that C$_{60}$ {111} planes have same symmetry with mica {112} planes. Thus, we can conclude that Mg-doped C$_{60}$ film is grown epitaxially on mica (001) substrate in the low Mg concentration region (Mg/C$_{60}$ molar ratio < 1).

Figure 6 shows Mg concentration dependence of the conductivity in comparison between glass and mica substrates. For the mica substrate, the conductivity was measured in the low Mg concentration region where the epitaxial growth was obtained. The conductivity increases with increasing Mg concentration.
concentration in both substrates. Furthermore, significant increase in conductivity can be seen in Mg-doped C_{60} film on mica substrate. It is considered that such significant increase is caused by the drastic improvement of crystal quality realized by epitaxial growth, as shown in Figure 3. This result may indicate the significant increase of carrier mobility. The difference in conductivity between mica and glass substrates decreases with increasing Mg concentration. This tendency may be caused by the crystal quality degradation with Mg-doping in the films on mica substrate, as seen in fig. 4.

Figure 5. Pole figure mapping of (a) mica \{112\} planes and (b) C_{60} \{111\} planes of Mg-doped C_{60} film with Mg/C_{60}=0.8.

Figure 6. Mg concentration dependence of the conductivity in comparison between glass and mica substrates.

4. Conclusion
The epitaxial growth of Mg-doped C_{60} films was investigated. It was found that the epitaxial growth of Mg-doped C_{60} film was enabled by using mica (001) substrate in the low Mg concentration region (Mg/C_{60} molar ratio < 1). The crystal quality of the epitaxial Mg-doped C_{60} film was improved drastically in compared with micro-crystalline film on glass substrate. Such drastic improvement of
crystal quality in the epitaxial films resulted significant increase in conductivity. This result may indicate the significant increase of carrier mobility. In addition, the crystal structure change was observed in high Mg concentration region (Mg/C_{60} molar ratio > 2). The C_{60} polymer sheet formation was suggested.

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