Generation of Electron Cyclotron Resonance Plasmas Including Iron-Atom for Synthesis of Iron Endohedral Fullerenes

Go YOKOKURA, Hiroyasu ISHIDA, Toshiro KANEKO, and Rikizo HATAKEYAMA

Department of Electronic Engineering, Tohoku University, Aoba 6-6-05, Aoba-ku, Sendai 980-8579, Japan

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The synthesis of iron-atom endohedral fullerenes with a plasma irradiation method is investigated. In the case using a ferrocene sublimation method, iron ions are effectively generated in an electron cyclotron resonance (ECR) argon plasma including the ferrocene under a minimum-B mirror configuration. In the case using an iron plate sputter method, on the other hand, the iron ions are generated by high-energy electrons in the ECR argon plasma, similarly. It is found that the iron ions and neutral irons are efficiently generated under the condition of low argon gas pressure. The existence of the iron ions is revealed by optical emission spectra and the iron ions are irradiated to fullerene C_{60} on a substrate immersed in the plasma. According to the time-of-flight mass spectra of the compounds on the substrate, it is found that the iron ions are actually deposited on the substrate. As a result of the plasma irradiation to the fullerene, the electron spin resonance spectrum of the residue of the ion-irradiated compound dissolved in toluene has a unique peak which is derived from the iron atoms. Therefore, it emerges that a material consisting of iron-atom and fullerene is possibly synthesized.

Keywords: electron cyclotron resonance plasma, minimum-B mirror configuration, endohedral fullerene, iron-atom, ferrocene, sputter

1. Introduction

Fullerenes such as C_{60} discovered in 1985 have actively been studied up to now because of their unique structure and electric/magnetic/optical properties. The fullerenes can produce compounds by trapping other atoms inside their cages and by replacing carbon atoms of the cage with other atoms, which are called endohedral- and hetero-fullerenes, respectively. On the other hand, organic semiconductors and quantum computing devices have been investigated as alternative devices to silicon semiconductors. Since the endohedral fullerenes have also attracted considerable interest as candidates for such devices, a lanthanum-atom or nitrogen-atom endohedral fullerene ($La@C_{60}$ or $N@C_{60}$) has been synthesized using laser vaporization, ion implantation, arc discharge plasma, and glow discharge plasma methods [1,2]. Similarly, an iron-atom endohedral fullerene ($Fe@C_{60}$), which is expected as functional materials in the electronic or medical field, has been attempted to be synthesized. However, the approach using a conventional arc discharge or laser vaporization method has not succeeded in synthesizing $Fe@C_{60}$. Recently, it is reported that multiply charged ions of iron are generated in a 2.45 GHz electron cyclotron resonance (ECR) ion source [3]. It is also reported that fullerene plasmas and beams have been produced in the ECR ion sources and mixed iron-fullerene plasmas and Fe related C_{60} molecules are produced in the ECR region [4]. In this system, however, most of the fullerenes are decomposed by the high energy electrons generated in the ECR region. On the other hand, the nitrogen-atom endohedral fullerene has been synthesized by a plasma irradiation method using a highly dissociated plasma which is separated from the ECR region with the high energy electrons [5,6]. Therefore, in this study, the synthesis of the iron-atom endohedral fullerene with the plasma irradiation method is investigated.

2. Experimental Apparatus

It is necessary to generate the iron ion plasma for synthesis of $Fe@C_{60}$ using the plasma irradiation method. Here, iron ions and neutral irons are generated by two methods. One is the method using dissociation and ionization of ferrocene, and the other is the method using sputter of an iron plate. Since the energy of about 20 eV is needed to dissociate and ionize the ferrocene [7], an ECR discharge argon plasma in a minimum-B mirror configuration is adopted, which can contain high-energy electrons more than 20 eV [5,6]. The ferrocene is dissociated and ionized by the high-energy electrons and the iron ion plasma is expected to be generated. In the latter case, the iron plate is sputtered by the energetic electrons and ions in the ECR discharge argon plasma, and the iron ions are generated by collision with the electrons.

author's e-mail:yokokura@plasma.ecei.tohoku.ac.jp

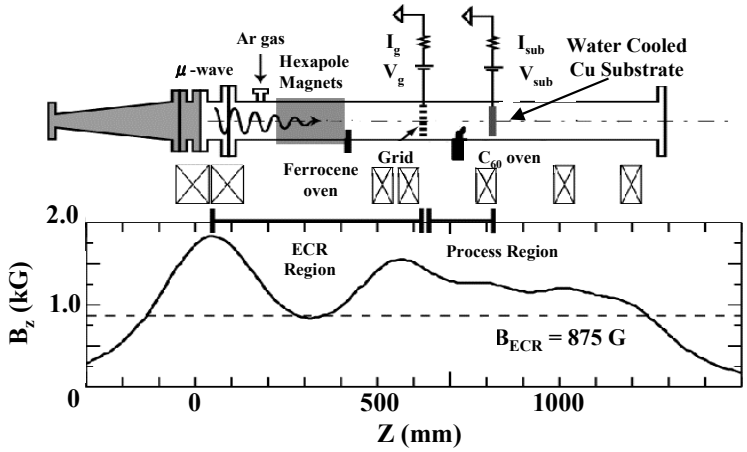

Fig. 1 Schematic of an experimental apparatus for Fe@C_{60} synthesis using ferrocene.

An experimental apparatus for Fe@C_{60} synthesis using the ferrocene is schematically shown in Fig. 1, where a microwave (2.45 GHz, 800 W) is launched into a stainless steel chamber with diameter of 11 cm through a waveguide. Solenoid coils surrounding the chamber generate inhomogeneous magnetic fields, which form mirror configurations. The axial profile of the magnetic field at the radial center is calculated and shown in the bottom of Fig. 1. The hexapole neodymium permanent magnets for radial confinement of the plasma are mounted around the bottom of the axial mirror magnetic field, and the minimum-B mirror configuration is realized [6]. Since electrons are trapped in the mirror magnetic field and accelerated owing to ECR at the bottom of the mirror region (875 G), an argon plasma is generated as a result of the effective ionization of argon gas (2.5×10^{-2} Pa). The plasma is divided into two regions (ECR and process regions) using a separation grid which is supplied with a voltage V_g and can control the plasma density in the process region.

The ferrocene is sublimated toward the ECR region by a ferrocene oven. The iron ions are generated as a result of the effective dissociation and ionization of the ferrocene by the high-energy electrons in the ECR argon plasma. In the sputtering method, a cylinder of the iron plate is set up in the ECR region, and the iron ions are generated as a result of the sputter of the iron plate by the high energy electrons and ions. In this case, the permanent magnets are not installed for the purpose of effective ion and electron irradiation to the iron plate. The argon plasma containing the iron ions diffuses toward the process region through the separation grid.

C_{60} molecules (Frontier Carbon Corp., 99 % purity) sublimated from a fullerene oven are deposited continuously on a copper substrate, to which a DC voltage V_{sub} is applied. The iron ions arriving in front of the substrate are accelerated by the difference between the substrate bias voltage and a plasma space potential ϕ_s, and irradiated to a C_{60} thin film throughout the period of C_{60} deposition. The substrate is maintained at a low temperature during ion irradiation using a water-cooling system. The deposition time is one hour in each experiment. The typical plasma density and electron temperature in the ECR region are 1×10^{10} cm^{-3} and about 10 eV, respectively, which are measured using a couple of Langmuir probes. The plasma is also measured by optical emission spectrometry (OES). Analysis of the compound on the substrate is performed by time-of-flight mass spectrometry (TOF-MS) and electron spin resonance (ESR).

3. Experimental Results

Figure 2 presents optical emission spectra of the plasma in the ECR region. In the case of the argon plasma without the ferrocene, the emission intensity peaks of neutral argon (763.5, 811.5 nm) are observed, while that of the iron is not detected. When the ferrocene is sublimated toward the ECR region, on the other hand, the emission intensity peaks of iron ion (274.9, 275.5 nm) and neutral iron (371.9, 373.4 nm) are observed. The iron ion plasma is obviously generated as a result of the effective dissociation and ionization of the ferrocene by the high-energy electrons in the ECR argon plasma.

The ion irradiation experiment is performed under the following conditions: V_{sub} = –400 V, V_g = 4 V, 1000 mg of ferrocene in the ferrocene oven, and 600 mg of C_{60} in the fullerene oven. About 300 mg of C_{60} is deposited on the substrate for 1 hour. The C_{60} compound after the ion irradiation is analyzed by TOF-MS, as shown in Fig. 3. The mass/charge values yielding spectrum intensity peaks are observed in the range from 720 to 723 m/z corresponding to C_{60}. The peak of ferrocene at the mass number 186 m/z is clearly observed. In addition, the peak at the mass number 56 m/z indicating Fe is observed. It becomes clear that a number of iron ions are irradiated to the C_{60} on the substrate. However, the peak at the mass number 776 indicating Fe@C_{60} is not observed at present.

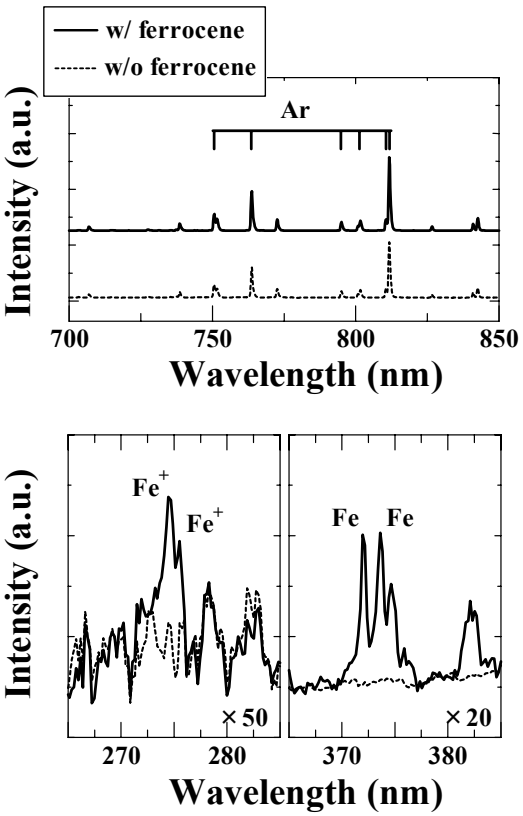

Fig. 2 Optical emission spectra of an Ar/ferrocene plasma.

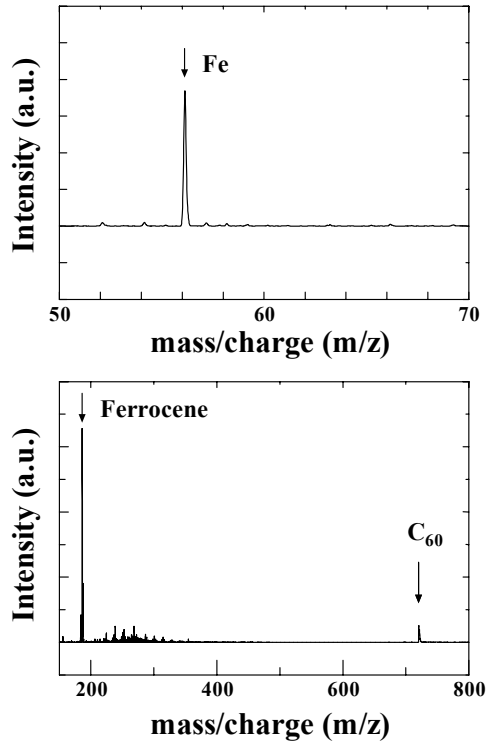

Fig. 3 Mass spectra of the compound by TOF-MS analysis.

Figure 4 presents optical emission spectra of the plasma in the case of the sputter method in the (a) ECR and (b) process regions. The emission intensity peaks of the neutral argons, the neutral irons, and the iron ions are observed both in the ECR and process regions. The iron ion plasma is obviously generated as a result of the iron sputter from the iron plate using the high-energy electrons in the ECR region. The emission intensity peaks of neutral argon decreases greatly under the condition of low argon gas pressure. On the other hand, the emission intensity peaks of neutral irons are not changed with an increase in the argon pressure.

Figure 5 gives intensities of the neutral irons in the optical emission spectra as a function of argon gas pressure P_{Ar}, where the emission intensity of neutral iron (388.6 nm) is normalized by that of neutral argon (811.5 nm). The intensity of neutral iron gradually increases

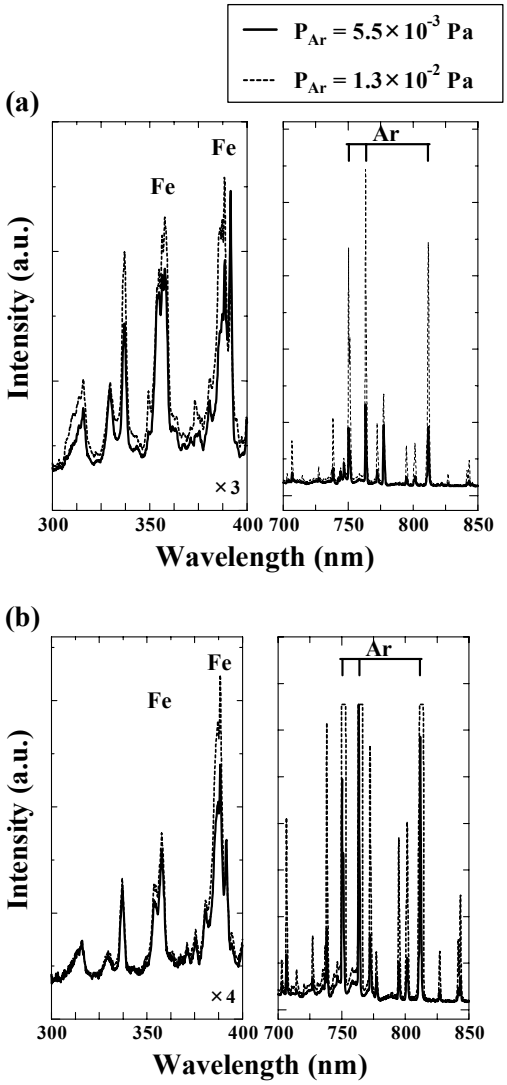

Fig. 4 Optical emission spectra of Ar/Fe plasma. (a)ECR region. (b)Process region.

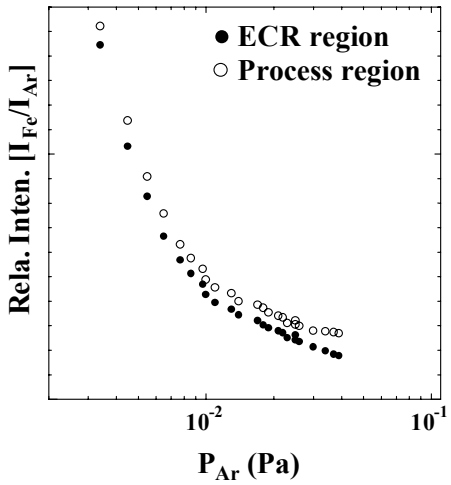

Fig. 5 Intensities of optical emission spectra in the ECR and process regions as a function of argon gas pressure P_{Ar}. The emission intensity of neutral iron (388.6 nm) is normalized by that of neutral argon (811.5 nm).

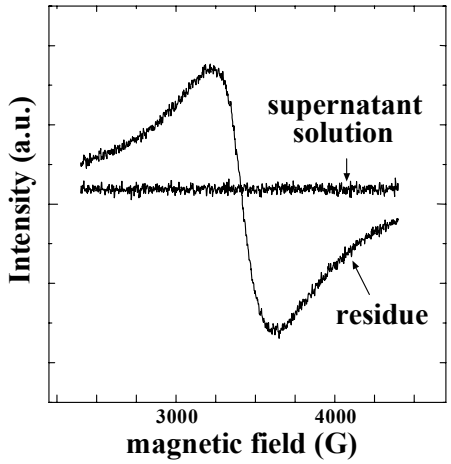

Fig. 6 ESR spectra of the residue and the supernatant solution of the compound at room temperature.

with a decrease in P_{Ar} in the ECR and process regions. Therefore, it is found that the iron ions and neutral irons are efficiently generated under the condition of low argon gas pressure.

The ion irradiation experiment is performed under the following conditions: $P_{Ar} = 5.0 \times 10^{-3}$ Pa, $V_g = -90$ V, $V_{sub} = -70$ V, and 600 mg of C_{60} in the fullerene oven. About 300 mg of the total amount of C_{60} is deposited on the substrate for 1 hour. The compound after ion irradiation is dissolved in toluene and filtered to divide it into a residue and a solution, which are analyzed by ESR. Figure 6 shows ESR spectra of the residue and the solution of the compound. The ESR spectrum of the supernatant solution does not have any peak and that of the residue has a unique peak. Since the ESR spectrum of Fe(III) complexes in the case of g-value g=2 and the low-spin state (S=1/2) is reported in Ref.[8] and is almost the same as that in our sample, it is considered that the unique peak in our sample is derived from the iron atoms and there is a positive possibility that the sample consisting of fullerene and iron-atom is synthesized by our experiment.

4. Conclusion

In the case using a ferrocene sublimation method, iron ions are effectively generated using high-energy electrons in an electron cyclotron resonance argon plasma including the ferrocene under a minimum-B mirror configuration. In the case using an iron plate sputter method, on the other hand, the iron ions are efficiently generated by the irradiation of high-energy electrons and ions to the iron plate in the ECR argon plasma. The existence of the iron ions is revealed by optical emission spectra and the iron ions are irradiated to C_{60} on the substrate. The ESR spectrum of the residue of the ion-irradiated compound dissolved in toluene has a unique peak which is derived from the iron atoms. Therefore, there is a hopeful possibility that a material consisting of iron-atom and fullerene is synthesized. However, the synthesis of the iron-atom endohedral fullerene by the ion irradiation method is not confirmed at present and is under investigations.

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