Encapsulation of Nickel Atom inside Fullerene by Energetic Ion Irradiation

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Nickel ions generated by sputtering with argon plasma are irradiated to fullerene C_{60}, and the possibility of synthesizing nickel atom endohedral fullerene is demonstrated. The mass spectra of the samples analyzed by laser desorption/ionization mass spectrometry are similar to a calculated isotope distribution ratio of the nickel atom endohedral fullerene. The optimum ion irradiation energy is approximately 35 eV, which corresponds to the energy expected by the molecular dynamics simulations.

Keywords: plasma ion irradiation, nickel endohedral fullerene, sputtering, electron cyclotron resonance discharge, optical emission spectrometry

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Fullerenes such as C_{60} have been actively studied for their unique structures. Fullerenes can produce compounds by trapping other atoms inside their cages. Such fullerenes, called endohedral fullerenes, have attracted considerable interest as candidates for electric and magnetic devices. In particular, nickel atom endohedral fullerene (Ni@C_{60}) is expected to produce a single molecular magnetic device focusing on its magnetic moment [1]. However, the synthesis approach, which uses a conventional arc discharge method to create a lanthanoid atom endohedral fullerene, appears to be ineffective for synthesizing Ni@C_{60}, because the binding energy of nickel–carbon is weaker than that of lanthanoid–carbon [2]. On the other hand, a nitrogen atom endohedral fullerene has recently been synthesized by plasma ion irradiation method in which a plasma ion is irradiated to the previously formed fullerene [3]. The possibility of synthesizing Ni@C_{60} by ion irradiation method was theoretically suggested by using classical molecular dynamics simulations [4]. Therefore, Ni@C_{60} synthesis by using the plasma ion irradiation method is investigated in this paper.

Figure 1 shows a schematic of the experimental apparatus in which a microwave (2.45 GHz, 800 W) is launched in a stainless steel chamber. Solenoid coils surrounding the chamber generate magnetic fields with mirror configurations, as shown in the bottom illustration of the figure. Argon plasma is generated by an electron cyclotron resonance (ECR) discharge near the bottom of the mirror region (875 G). Using a separation grid, the device is divided into the ECR and process regions. A nickel plate is set in the ECR region, to which a negative voltage V_{pl} can be applied. Because the high-energy argon ions sputter the negatively biased nickel plate, nickel atoms and ions are effectively generated. The nickel grid is also negatively biased (V_g) for generating the nickel ions by sputtering, which are effectively flow to the process region. C_{60} (99% purity) molecules are sublimated from an oven to a substrate to which a negative voltage V_{sub} is applied. Thus, nickel ions are irradiated to C_{60} on the substrate.

The plasma parameters are measured using Langmuir probes and optical emission spectrometry (OES) at $z = 35$ cm and 75 cm ($z = 0$: left mirror throat), which correspond to the ECR and process regions, respectively. An analysis of the samples is performed by laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF-MS).

Because the argon pressure and microwave power are fixed at 1.7×10^{-2} Pa and 800 W, respectively, in this experiment, the electron density ($n_e \sim 7 \times 10^{11}$ cm^{-3}) and electron temperature ($T_e \sim 5$ eV) are almost constant in the ECR region.

Figure 2 shows emission intensities of the nickel ion (227.1 nm) as a function of V_{pl} in the ECR region. Here

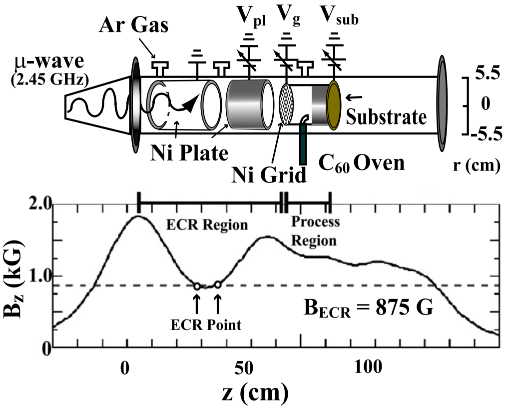

Fig. 1 Experimental apparatus.

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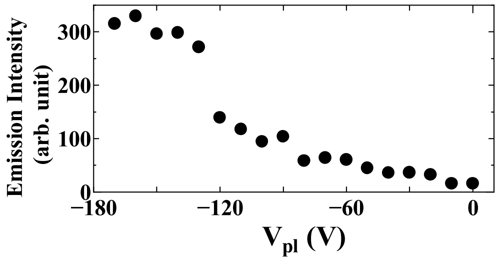

Fig. 2 Emission intensity of nickel ion (227.1 nm) as a function of V_{pl} in the ECR region.

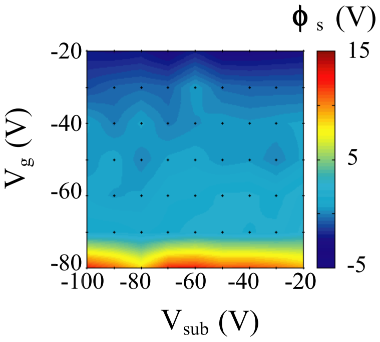

Fig. 3 Space potential as functions of V_g and V_{sub} in the process region.

V_g is −60 V, and the plasma parameters are confirmed to be independent of V_{pl}. The intensity of the nickel ion remarkably increases with decrease in V_{pl}. Therefore, it is revealed that the nickel ions are efficiently generated by argon-ion sputtering under conditions of highly negative voltages of V_{pl}.

Figure 3 shows space potential ϕ_s in the process region as functions of V_g and V_{sub}, where $V_{pl} = -150$ V. ϕ_s is almost constant with changing V_{sub}. Therefore, by varying V_{sub}, we can control the irradiation energy (E_i) of the ions that are accelerated by the potential difference between ϕ_s and V_{sub}. The sample deposited on the substrate after 2 h of plasma ion irradiation is collected by peeling off the surface of the substrate, and is analyzed by LDI-TOF-MS.

Figure 4 presents mass spectra of the samples deposited on the substrate under the following conditions: (a) $V_{pl} = -150$ and $V_{sub} = -30$, and (b) $V_{pl} = 0$ V and $V_{sub} = -10$ V, where $V_g = -60$ V. The peaks of mass numbers 778 and 766, which are indicated by red colors, are observed only when numerous nickel ions are generated for $V_{pl} = -150$ V. An expected isotope distribution ratio of Ni@C_{60}, calculated using the natural isotope ratio of carbon and nickel, is presented in Fig. 4 (c). The experimental peak intensities of mass numbers 778 to 782 coincide with the calculated isotope distribution ratio of Ni@C_{60}.

Because the samples are sonicated in dilute nitric acid and the nickel attached to the outside of C_{60} is considered to be almost removed, it is difficult to detect Ni exohedral C_{60} by LDI-TOF-MS. Furthermore, it has been reported that Ni exohedral C_{60}, which consists of one C_{60} and one Ni—specifically, Ni–C_{60}—cannot be synthesized because of its unstable condition [5]. Therefore, the possibility of Ni exohedral C_{60} is considerably low for our samples, and the experimentally obtained mass peaks at 778 to 782 are believed to be Ni@C_{60}. In addition, mass numbers 766 and 767 corresponding to Ni–C_{59} are observed under some conditions of V_{pl} and V_g that are generated by replacing C with Ni.

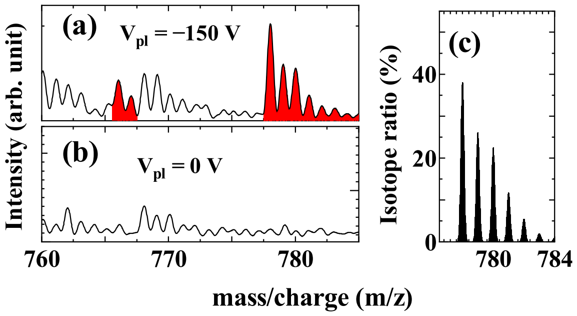

Fig. 4 Mass spectra of samples deposited on the substrate for (a) $V_{pl} = -150$, $V_{sub} = -30$, and (b) $V_{pl} = 0$ V, $V_{sub} = -10$ V. (c) Expected isotope distribution ratio of Ni@C_{60}.

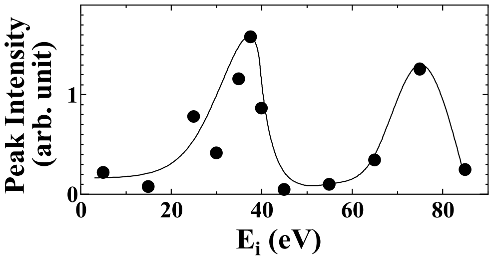

Fig. 5 Dependence of peak intensity of mass number 778 (Ni@C_{60}) on E_i with changing V_{sub}.

Figure 5 shows the dependence of the peak intensity of mass number 778 (Ni@C_{60}) on E_i with changing V_{sub}, where $V_{pl} = -150$ V and $V_g = -60$ V. It is discovered that plasma ion irradiation energy influences the Ni@C_{60} synthesis, and the maximum peak intensity occurs near $E_i \sim 35$ eV. The E_i yielding the maximum peak intensity corresponds to the simulation result, which affords a peak at $E_i \sim 40$ eV [4], suggesting optimum synthesis efficiency.

In conclusion, we demonstrated the possibility of synthesizing a novel endohedral fullerene, Ni@C_{60}, for the first time, by using the plasma ion irradiation method in an argon–nickel mixture plasma. Furthermore, we present the possibility of increasing the amount of produced Ni@C_{60} by controlling the plasma ion irradiation energy.

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