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Generation of Quasi-Pair Fullerene Ion Plasma for Purification of Lithium Endohedral C_{60}

リチウム内包C_{60}高純度化のための準ペアフラーレンイオンプラズマ生成

Takatusugu Nagai, Toshiro Kaneko, Hiroyasu Ishida and Rikizo Hatakeyama
永井 貴嗣, 金子 俊郎, 石田 裕康, 畠山 力三

Department of Electronic Engineering, Tohoku Uninversity
6-6-05 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
東北大学 大学院工学研究科 電子工学専攻 〒980-8579 仙台市青葉区荒巻字青葉6-6-05

The plasma consisting of the lithium endohedral fullerene positive ion ($Li@C_{60}^+$) and the fullerene negative ion (C_{60}^-) is generated by an electron beam ionization method for purification of $Li@C_{60}$. The ionization potential of $Li@C_{60}$ is measured for the first time and it is found to be lower than that of C_{60}. In addition, it is implied that argon positive ions (Ar^+) can dissociate the $Li@C_{60}$ - C_{60} cluster more effectively than the high energy electron beam, resulting in generation of high density $Li@C_{60}^+$ - C_{60}^- plasma.

1. Introduction

Alkali metal endohedral fullerenes, such as lithium endohedral fullerene ($Li@C_{60}$), have attracted much attention [1] because they are expected to be used in the field of single molecule electronics, owing to their unique electronic properties which have roots from the lithium off-center position in the C_{60} cage [2].

Although $Li@C_{60}$ has been isolated from C_{60} by a chemical method [3], this method takes a long time and needs to chemically modify the surface of $Li@C_{60}$, which makes it difficult to be used for a practical application. In this sense, a plasma separation method is expected as one effective way to purify the $Li@C_{60}$ sample which is mass-produced by Ideal Star Ink. in collaboration with Tohoku University, because the plasma process is fast and simple, and no chemical modification is needed during the whole process. However, the problem of this method is that both the C_{60} and $Li@C_{60}$ can become positive ions [4], though an ideal $Li@C_{60}^+$ - C_{60}^- plasma is required for the plasma separation. Therefore, the difference in the plasma characteristics, e.g., electron impact ionization cross section, between $Li@C_{60}$ and C_{60} [5] should be found out to selectively generate $Li@C_{60}^+$.

2. Experimental Setup

The fullerene plasma is generated by an electron beam ionization. The plasma source setup is schematically shown in Fig. 1. Thermionic electrons are emitted from a tungsten cathode by applying a DC power P_k and are accelerated by a potential difference between the cathode V_k and a grounded grid located at z = 0 mm. The mixture of C_{60} and $Li@C_{60}$ in a copper furnace is sublimated by heating up to 650 ℃. High energy electrons easily ionize $Li@C_{60}$ molecules into $Li@C_{60}^+$ while low energy electrons produced as a result of positively ionizing $Li@C_{60}$ are attached on C_{60} molecules. The $Li@C_{60}^+$ - C_{60}^- plasma is generated radially outside of the electron beam by a magnetic filter effect. An end plate is located at z = 330 mm, which cuts the electron beam and thus produces a pure $Li@C_{60}^+$ - C_{60}^- plasma behind it. Stainless steel substrates are located at z = 650 mm. The C_{60} and $Li@C_{60}$ ions are deposited on the substrates by applying positive and negative bias voltages to the substrates (V_{sub}). The deposited materials are measured by laser-desorption time-of-flight mass spectrometer (LD TOF-MS).

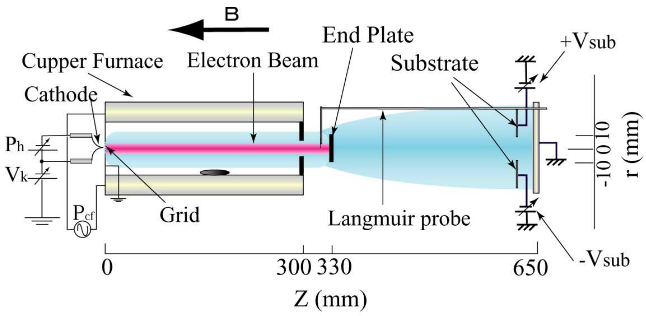

Fig. 1: The schematic illustration of experimental set up.

3. Experimental Results

Figure 2 shows the typical Langmuir probe voltage V_p - probe current I_P characteristics of $Li@C_{60}^+$ - C_{60}^- plasma measured at z = 390 mm. Remarkably, positive and negative saturation currents are almost the same unlike the ordinary electron - ion plasma and both the floating potential

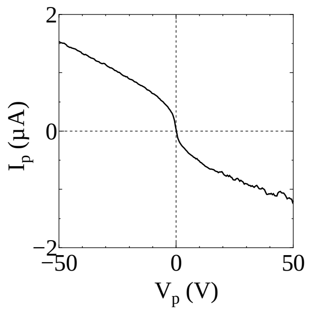

Fig. 2: The typical V_p - I_P characteristics of $Li@C_{60}^+$ - C_{60}^- plasma

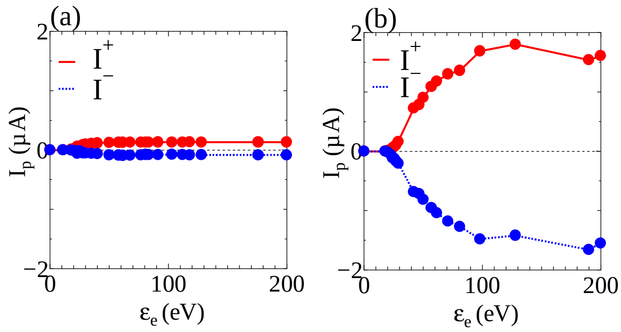

Fig. 4: ε_e - I_p characteristics of $Li@C_{60}$ compound (a) with and (b) without Ar plasma.

and space potential are almost zero because the positive and negative ions weights are the same.

Figure 3 presents positive probe currents (I_p^+) of (a) C_{60} plasma and (b) $Li@C_{60}^+$ - C_{60}^- plasma as a function of electron energy (ε_e) using the probe located at z = 370 mm. Here, the cathode current is constant (the current between the cathode and the grid: I_k = 1 mA) and probe bias voltage for I_p^+ and negative probe current (I_p^-) are -100 V and +100 V, respectively. It is noteworthy that there is a difference of threshold energy (ε_{th}) for second peak between C_{60} and $Li@C_{60}^+$ - C_{60}^- plasmas. The ionization potential of the $Li@C_{60}$ is approximately 3 eV lower than that of C_{60}. This result might be very useful in terms of the selective generation of $Li@C_{60}^+$ and C_{60}^+.

Figure 4 gives the change of I_p^+ and I_p^- as a function of ε_e (a) without and (b) with introduction of the Ar plasma in the furnace area. It is shown that the plasma density in the diffusion area is increased significantly by the Ar plasma introduction, which is considered to dissociate the cluster of $Li@C_{60}$ - C_{60} inside the furnace. The $Li@C_{60}$ - C_{60} cluster consists of one $Li@C_{60}$ molecule and 10 - 12 C_{60} molecules. The cluster can not keep its ion state for a long time because its Larmor radius is much larger than the device as explained in Fig.1. However, when the cluster is dissociated, one cluster is divided into more than 10 molecules and each molecule becomes the ionic state. The formed ions can diffuse behind the end plate. The content described above is the mechanism that the Ar plasma can increase the $Li@C_{60}^+$ - C_{60}^- plasma density.

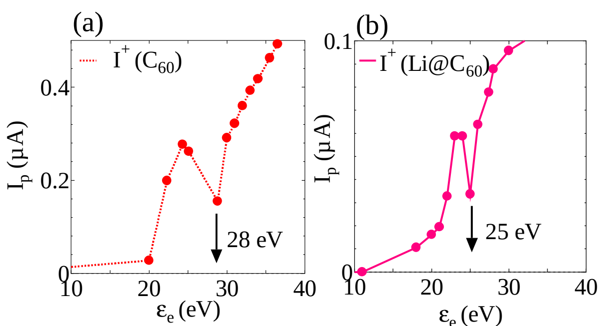

Fig. 3: The ε_e - I_P characteristics of (a) C_{60} plasma (b) $Li@C_{60}^+$ - C_{60}^- plasma

4. Summary

The $Li@C_{60}^+$ - C_{60}^- plasma is successfully generated, which is confirmed by the Langmuir probe. The ionization potential of $Li@C_{60}$ is found to be lower than that of C_{60}. It is the really valuable result in terms of realizing the selective ionization of $Li@C_{60}$ from C_{60} and more efficient purification of $Li@C_{60}$. Furthermore, the Ar plasma is found to be useful to increase the density of $Li@C_{60}$ plasma because the Ar plasma dissociates the $Li@C_{60}$ - C_{60} cluster more effectively than the electron beam. Our current result is very important for realizing the separation of $Li@C_{60}$ and C_{60}. More detailed experiments are required to understand the ionization mechanism of $Li@C_{60}$. The deposited material on the substrate will also be studied as a future work.

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