DEPOSITION OF C_{60} IN MICROWAVE PLASMAS

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In the hydrocarbons-He microwave plasmas, a deposition of fullerenes has been investigated. Although polycyclic aromatic hydrocarbons were identified, C_{60} was not identified in the deposits from C_2H_2-He and C_6H_6-He plasmas. C_{60} was identified in the deposit from $C_{10}H_8$-He plasma. The relative peak head intensity of optical emission ratio of C_2 and H, I_{C2}/I_H, in the plasma corresponded to the formation of C_{60}.

INTRODUCTION

Fullerenes (C_{60}, C_{70} etc.) were obtained by means of laser irradiation on graphite at first [1] and a vaporization of graphite with resistive heating and contact arc method in a helium atmosphere at reduced pressure [2, 3] followed the laser irradiation. We reported the formation of fullerenes by the vaporization of graphite in an argon-helium plasma arc [4]. Equilibrium concentration of C_{60} and C_{70} in the products by thermal dissociation or combustion of hydrocarbons in different C/H ratios were calculated. The yield reached to the maximum value of 50 % at C/H=2 [5]. Fullerenes were identified in sooting flames and the yield of fullerenes from flames change with changing amounts of polycyclic aromatic hydrocarbons prepared in the flame [6].

By the analogy of results obtained in the vaporization of graphite in the argon-helium plasma arc [4], the deposition of C_{60} was expected from helium-hydrocarbons plasmas. When methane, ethylene, and acetylene were selected as carbon source in the plasmas, a deposition of graphite including little amount of C_{60} in the center of the cavity and plasma polymerized hydrocarbons, polyethylene and polyacetylene, upstream the gas flow were observed at low pressure [7]. The deposits depended on the kind of hydrocarbons and the electron energy distribution in the plasma.

Recently, the deposition of C_{60} was observed by a pyrolysis of naphthalene at 1000 ℃ in an argon stream along with condenced polycyclic aromatic hydrocarbons (PAH) [8]. Intermediate products of the pyrolysis were identified as PAH. C_{10} fragments was condenced with elimination of hydrogen to give PAH. In this process, the intentional poisoning of fullerene production by the addition of hydrogen to quenching atmosphere was observed by adding hydrogen in varrying amounts [9]. Therefore, we have investigated the formation process of fullerenes from helium-hydrocarbons microwave plasmas by both the characterization of deposits and diagnostics of plasmas.

In the present paper, the depositon of C_{60} and PAH from plasmas, in which several hydrocarbons were diluted with helium, are investigated by means of several characterization methods with plasma diagnostics to develop the deposition scheme of C_{60} from hydrocarbons.

EXPERIMENTAL

Methane, ethylene, acetylene, and helium were used as plasma gases. Each hydrocarbon was diluted with helium and a concentration of hydrocarbon in the mixture was 2.5 vol.% in every case. As benzene and naphthalene were liquid and solid, respectively, at ordinary temperature and pressure, they were introduced into the helium plasma by vaporization of condenced phase by heating and gas composition was determined by the heating temperature. A fused silica plate (10x10x0.5 mm) or a silicon wafer (10x10x0.4 mm) was used as a substrate.

The apparatus with microwave discharge and deposition procedures were approximately the same with those in the diamond deposotion as well as fullerenes deposition reported previously [7]. The fused silica plate or silicon wafer was placed in the cavity or upstream the gas flow in the fused silica discharge tube. After the evacuation in the discharge tube, the gas mixture was introduced into the discharge tube. A gas flow rate and a pressure was maintained at suitable values to deposit desired materials. Both benzene and naphthalene were introduced into helium by keeping at estimated temperature. The microwave power was introduced into the discharge tube and the discharge was continued for the period of 2 h. A power input was 140 W in CH_4-He, C_2H_4-He, and C_2H_2-He plasmas and 20W in C_6H_6-He and $C_{10}H_8$-He plasmas, respectively. During the discharge, the distributions of electron energy and ion density in the plasmas were estimated by means of double probe technique and the species in the plasmas were identified with optical emission spectroscopy. After the exposure of the substrates in the plasmas, the deposits on the substrates and on the wall of the discharge tube were characterized by means of UV-VIS, IR and mass (FAB or EI) spectroscopies as deposit or as extract in benzene.

RESULTS

Deposition from CH_4-He and C_2H_4-He plasmas

Black films were observed on the fused silica substrates placed in the center of the cavity from CH_4-He and C_2H_4-He plasmas. On the other hand, yellowish brown films were deposited on fused silica and silicon substrates placed upstream the gas flow in the same dischargre. These deposits were characterized by means of several types of characterization methods. In this case, the electron energy in the plasma was higher than 10 eV in the center of the cavity.

Gaphite was observed in the deposits on the substrates placed in the center of the cavity from both plasmas. In the deposits from CH_4-He plasma, no product except graphite was identified. Although weak peak at m/z = 721 was observed in the mass spectrum of the deposit from C_2H_4-He plasma, it could not be identified due to C_{60} because the other peaks due to isotopic effect were not observed. In IR and UV/VIS spectra of benzene extract, neither fullerenes nor PAH could be observed. On the other hand, deposits on the substrates placed upstream the gas flow of CH_4-He and C_2H_4-He plasmas were attributed to polyethylene-like polymer and a mixture of polyethylene and polyacetylene-like polymers, respectively.

Deposition from C_2H_2-He plasma

No black film was observed on the fused silica substrate placed in the center of the cavity from the C_2H_2-He plasma at 650 Pa. Moreover, yellowish brown film was deposited on the fused silica and silicon substrates placed upstream the gas flow in the same discharge. On the other hand, black powdery deposit was observed on an inner

wall of the discharge tube near the center of the cavity at higher pressure than 1.3 kPa. In this case, the electron energy in the plasma was higher than 10 eV in the center of the cavity.

In the mass spectra of the deposit in the center of the cavity at low pressure, weak peak at m/z=720 was observed, but it could not be identified due to C_{60} by the same reason mentioned in the deposit from C_2H_4-He plasma. From IR spectra of the deposit upstream the gas flow at low pressure, the deposit was attributed to polyacetylene-like polymer. IR spectra of benzene extract of the deposits on the wall of the discharge tube near the center of the cavity with varying pressure are shown in Fig. 1. The deposits included PAH in addition to polyacetylene-like polymer. Moreover, the existence of PAH are suggested from UV/VIS spectra of benzene extract of the deposits as shown in Fig. 2.

Deposits from C_6H_6-He plasma

Small amount of powdery deposit was only identified on the wall of the discharge tube near the cavity. IR spectra of benzene extracts from the deposits obtained varying pressure are shown in Fig. 3. In every sample, peaks due to polycyclic aromatic hydrocarbons were identified. There were weak absorption peaks due to PAH in UV/VIS absorption spectra as shown in Fig. 4. The deposition of C_{60} was not identified in mass spectra, though the electron energy was about 5 eV in the plasma in the center of the cavity.

Deposits from $C_{10}H_8$-He plasma

Small amounts of black film on the fused silica substrate and powdery deposit on the wall of the discharge tube near center of the cavity were obtained. IR absorption due to PAH were clearly identified in the spectra of benzene extracts from the deposits obtained varying pressure as shown in Fig. 5. Weak peaks due to PAH were also identified in UV/VIS spectra (Fig.6). Mass spectra (FAB) shows the existence of C_{60} of m/z=720 in the benzene extract from the deposit at 1.5 kPa of pressure (Fig.7). Moreover, a peak at m/z= 254 was observed in the mass spectra (EI) as shown in Fig. 8. This mass number corresponded to that of $C_{20}H_{14}$ which was an intermediate of formation of C_{60} from $C_{10}H_8$. In this case, the electron energy in the plasma was about 5 eV in the center of the cavity.

DISCUSSION

From several hydrocarbons-He plasmas, the formation of C_{60} has been carried out. C_{60} was obtained only from $C_{10}H_8$-He plasma at low pressure. An intermediate species of C_{60} formation from $C_{10}H_8$ was identified as $C_{20}H_{14}$ which was one of PAH. By the condensation of naphthalene and elimination of hydrogen, C_{60} would be formed through PAH. PAH was also identified in the deposits from C_2H_2-He and C_6H_6-He plasmas. Because PAH is the precursor of fullerenes from hydrocarbons, C_2H_2 and C_6H_6 are candidates of starting materials of formation of fullerenes. In the formation of fullerenes from hydrocarbons, a composition ratio of C/H is considered to select hydrocarbons as candidates of starting materials. In this case, product amounts of fullerens increased with increasing C/H ratio. In the formation process of fullerenes, C_2 molecules are considered as precursors and poisoning of fullerenes production by the addition of hydrogen is observed. Therefore, the species formed in the plasma would contribute to form fullerenes.

Relative peak head intensities of bands and lines observed in the emission spectra from several plasmas are given in Table 1. Since C_2 molecules are considered as precursors of fullerenes and H atoms would be poison in the fullerenes production as mentioned above, an increase of C_2 molecules and a decrease of H atoms in the plasma may promote the fullerenes production reaction. Thus the relative peak head intensity of emission of C_2 molecules and H atoms, I_{C_2}/I_H, was selected as one of the parameters to search possibility of the fullerenes production from hydrocarbons. A correlation between products and I_{C_2}/I_H is given in Table 2. In Table 2, the values of I_{C_2}/I_H corresponded to starting materials and products in the deposition process of fullerenes from hydrocarbons. In the case of small amounts of I_{C_2}/I_H, neither fullerenes nor PAH were observed in the deposits. With increasing value of I_{C_2}/I_H, PAH appeared. When the value of I_{C_2}/I_H reached to larger values, both C_{60} an polycyclic aromatic hydrocarbons were identified.

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Table 1 Relative peak head intensity in spectra of helium-hydrocarbons plasmas

Plasma	Relative intensity			
	C_2 Swan (0-0)	CH 4300 (0-0)	H_β	C 2749
CH_4-He	100	83	86	14
C_2H_4-He	40	67	90	17
C_2H_2-He	209	48	66	32
C_6H_6-He	93	26	21	23
$C_{10}H_8$-He	27	11	4	12

Table 2 Products from helium-hydrocarbons plasmas and I_{C_2}/I_H

Hydrocarbons	C/H	Product	I_{C_2}/I_H
CH_4	0.25	Polyethylene, Graphite	1.2
C_2H_4	0.50	Polyenes, Polyethylene, Graphite	0.4
C_2H_2	1.00	Polycyclic aromatic hydrocarbons, Polyenes, Graphite	3.2
C_6H_6	1.00	Polycyclic aromatic hydrocarbons, Polyenes	4.4
$C_{10}H_8$	1.25	C_{60}, Polycyclic aromatic hydrocarbons	6.8

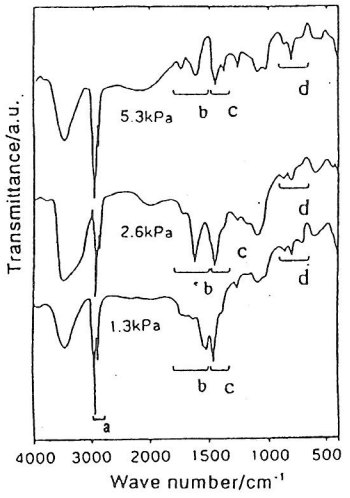

Fig.1 IR spectra of benzene extracts of deposits from C_2H_2-He plasma : b and d correspond to the absorption due to PAH.

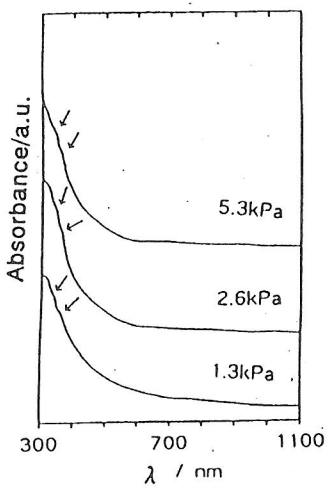

Fig.2 UV/Vis absorption spectra of benzene extracts of deposits from C_2H_2-He plasma: ← correspond to the absorption due to PAH.

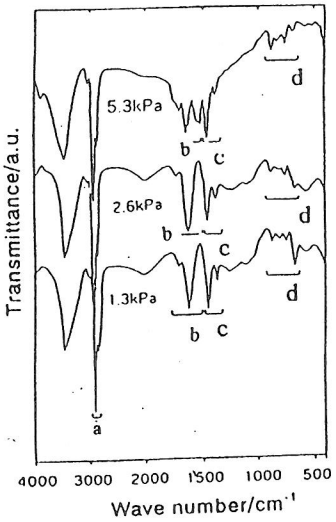

Fig.3 IR spectra of benzene extracts of deposits from C_6H_6-He plasma b and d correspond to the absorption due to PAH.

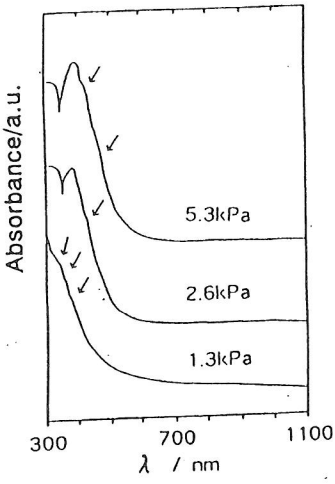

Fig. 4 UV/vis absorption spectra of extracts of deposits from C_6H_6-He plasma: ← corresponds to the absorption due to PAH.

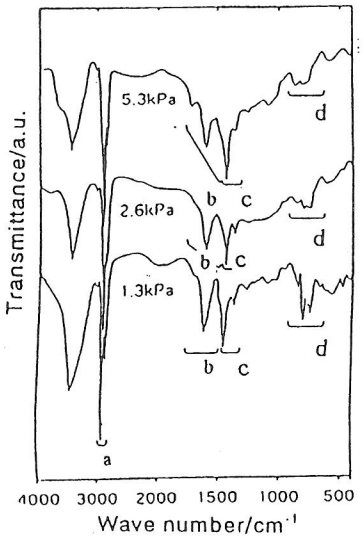

Fig. 5 IR spectra of benzene extracts of deposits from C10H8-He plasmas: b and d correspond to the absorption due to PAH.

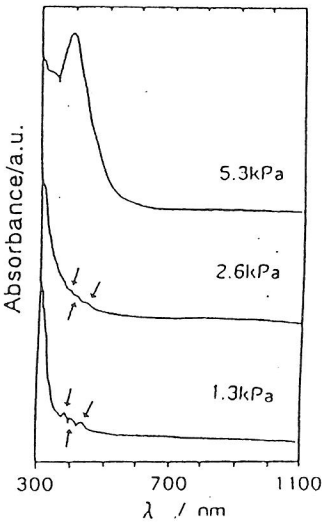

Fig. 6 UV/Vis absorption spectra of benzene extracts of deposits from C10H8 -He plasmas: ← corresponds to the absorption due to PAH.

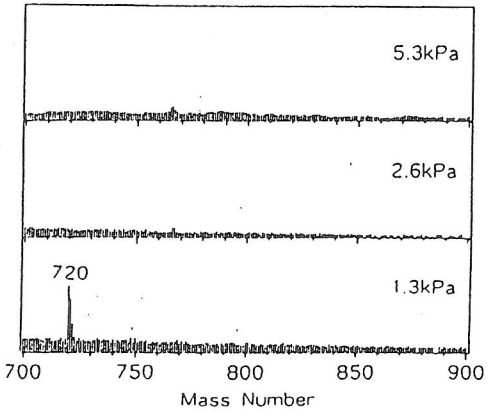

Fig. 7 FAB mass spectra of benzene extracts of deposits from C10H8-He plasma.

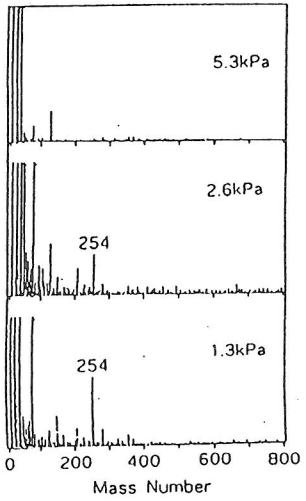

Fig. 8 IE mass spectra of benzene extracts of deposits from C10H8-plasma.