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Synthesis of carbon clusters and thin films by low temperature plasma chemical vapor deposition under atmospheric pressure

Hideomi Koinuma, Takao Horiuchi, Kiyoto Inomata,[a] Hyun-Kwon Ha, Kenji Nakajima, Kaliq. A. Chaudhary [b]

The Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226, Japan

Abstract: We have developed a torch-type plasma generator to make low temperature material processings possible in open air conditions. The cylindrical plasma CVD apparatus is composed of a metal needle acting as the cathode at the center and a grounded cylindrical anode. The inner surface of the anode was lined by a thin insulator nozzle. A low temperature homogenous plasma was generated by applying rf voltage to the needle cathode under a constant flow of atmospheric pressure He or Ar. The plasma generated in the insulator nozzle was released to open air. This cold plasma torch has been verified to be applicable for various plasma processings. Fullerene was found to be formed by the analyses with HPLC and TOF-MS in the soot produced by introducing a vaporized aromatic hydrocarbon into the after-glow region of the plasma with Te and Tg at about 1.9eV and 400℃, respectively. Different from the conventionally employed arc-plasma, which decompose graphite into fullerenes at much higher temperatures, this is a polycondensation reaction that wraps up small molecules into a large molecule. We examined the possibility of using this plasma for encapsulating or incorporating hetero-atom(s) in the fullerene. The plasma was successfully employed for the deposition of such inorganic thin films as glassy carbon, SiO_2, and TiO_2 in open air environment.

1. Introduction

Low temperature plasma is widely used for various material processings such as film deposition, and etching conducted usually in a vacuum chamber. Electrons excited in the plasma have such high energies that they can achieve these processes at temperatures apparently far lower than the temperature estimated to be required from thermodynamics. Glow discharge type cold plasma is usually generated under reduced pressures of 0.01 Torr - 10 Torr. As the pressure increases and approaches atmospheric pressure, cold plasma turns to be thermal plasma with nearly equal high temperatures of ions and electrons. If cold plasma can be generated under atmospheric pressure, such plasma is expected to find wider applicability. Besides the silent discharge[1, 2], a few plasmas of apparent glow discharge type were reported to occur at atmospheric pressure[3-5]. These plasmas were, however, generated in chambers as in the conventional low pressures and by using He gas to sustain the plasmas. Operation of such a plasma in Ar and without using a chamber attracts our interest because not only of economic issue but also of its possible applicability to new plasma processings.

Herein we report successful rf excitation of Ar or He flow to generate a beam type plasma at atmospheric pressure. With admixing of a reactive chemical agent in the plasma, we have investigated the application of this plasma to cluster synthesis as well as to the deposition of thin films in open air environment.

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a) Present address : Tokyo Gas Co., Ltd., Frontier Technology Research Institute, 7-7, Suehiro-cho, 1-chome, Tsurumi-ku, Yokohama 230, Japan

b)Present address : Dept. of Physics, Islamia University, Bahcwalpur, Pakistan

2. Plasma Generation and Characterization

The plasma generator is composed of a needle cathode (1mmϕ) and a grounded cylindrical anode(i.d. 5 mm) of its inner surface covered with an insulator tubing (0.5mm thick). The application of rf (13.56MHz) power in the range of 30-140 W to the cathode ignited a discharge in Ar or He gas which was flowing thorough the space between the cathode and the insulator tubing. The emissive beam length from the nozzle could be controlled in the range of 0.5-10 mm by varying the rf power and/or gas flow rate. By fixing an insulator cap with pinholes at the outlet of insulator nozzle, the plasma could further be split into finer and longer beams.

When quartz was used as the insulating material, Ar plasma with undesired micro discharge was generated under atmospheric pressure. Such arc-like micro discharges turned to be homogenous glow-like discharge either by replacing the insulator to a higher dielectric constant material or by mixing He in the Ar flow. By employing alumina (ε_r= 9.3) instead of quartz (ε_r= 4.3) as an insulator tubing material, for instance, a homogenous Ar plasma without any uncontrollable micro discharges was steadily generated.

The plasma was characterized by using the conventional Langmuir probe method, optical emission spectroscopy, and thermocouple to measure electron temperature (Te), excited temperature (Tex), and gas temperature (Tg), respectively. Tex was evaluated from the emission intensities of five atomic lines of helium (HeI:501.6, 492.2, 471.3, 447.2, and 402.6 nm) mixed in Ar plasma, by the linear least square fitting with the intensities calculated by assuming the Boltzman's law. These measurements showed that our rf excited atmospheric pressure plasma is far from the arc mode, since Te, Tex and Tg were typically 1.1 eV, 0.8 eV, and 600 K (51 meV), respectively, for the Ar (200 sccm)/Al_2O_3 system at a location 2 mm below the gas nozzle outlet, Thermal erosion of electrodes which often occurs in arc was not observed.

3. Applications

The plasma generator was tested for the application to various material processings in open air by admixing reactive gases in Ar and/or He flow and adjusting the reaction conditions. Some details of the syntheses of carbon clusters and carbon films are described below.

3-1 Fullerene synthesis by plasma CVD

An aromatic compound (benzene, naphthalene, or phenanthrene) was vaporized in a glass tube kept at a constant temperature and carried by Ar flow for introduction into an after-glow region of the plasma. Typical reaction conditions were as follows: rf power 75-130W, He and/or Ar 70-230 sccm, an aromatic compound 0.1-1.0 sccm, and reaction time 10-20 min. The soot deposited on a glass substrate was mixed with hexane and the extract was subjected to the separation by high performance liquid chromatography (HPLC) and to spectroscopic analyses. Laser-desorption time of-flight mass spectroscopy (TOF-MS) (Finnigan Laser MAT, Vision2000, Reflection type) was also employed to analyze the soot.

Naphthalene (0.3-0.6 sccm) was introduced in Ar (13 sccm) / He (47 sccm) plasma at an rf power between 70 and 130 W to produce soot. Toluene/ hexane (7/3) extracts of the sooty powders gave HPLC peaks with retention times corresponding well to those of C_{60} and C_{70}. C_{60} production was also verified by the fact that the UV spectrum of hexane solution of an extract of the soot was the same as that of authentic C_{60} powder, as shown in Fig.1 [6]. From the comparison of the absorptions at 403 nm, the yield of C_{60} was evaluated to be 2.2 % in the soot produced from the plasma of a mixture of naphthalene (0.3 sccm), Ar (24 sccm), and He (36 sccm) at 130 W rf power. From benzene and phenanthrene, C_{60} could also be produced in the same way, but their yields were lower under the conditions we employed.

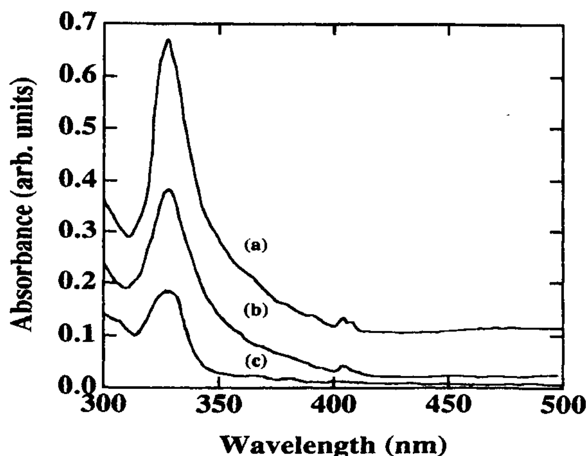

Fig.1. UV-visible spectra of n-hexane solutions (a) pure C_{60}, (b) a fraction by HPLC from the soot produced by the plasma reaction of naphthalene, (c) original soot

3-2 Attempts for producing hetero-atom(s) containing fullerenes

Since fullerene should be produced by a dehydrogenating polycondensation reaction in which aromatic compounds were wrapped up into a spherical giant molecule, we could expect the encapsulation or incorporation of hetero atom(s) into the sphere by the presence of hetero-atom molecules in the plasma. As hetero-atom molecules, we have examined phenylsilane and quinoline. Figures 2 shows the TOF-MS patterns measured on the soots obtained from naphtharene (a) and Phenylsilane (b). A naphthalene/phenylsilane (1/1) mixed gas plasma gave the soot whose TOF-MS pattern was essentially the same as Fig.2(a). Thus, no indication of the formation of Si-encapsulating fullerene ($Si@C_{60}$=748) was observed, but the formation of C_{60} from phenylsilane was verified from Fig.2(b). Soots were obtained from the plasma generated by applying 120 W rf power to a mixture of quinoline (0.4 sccm) in Ar (30 sccm).

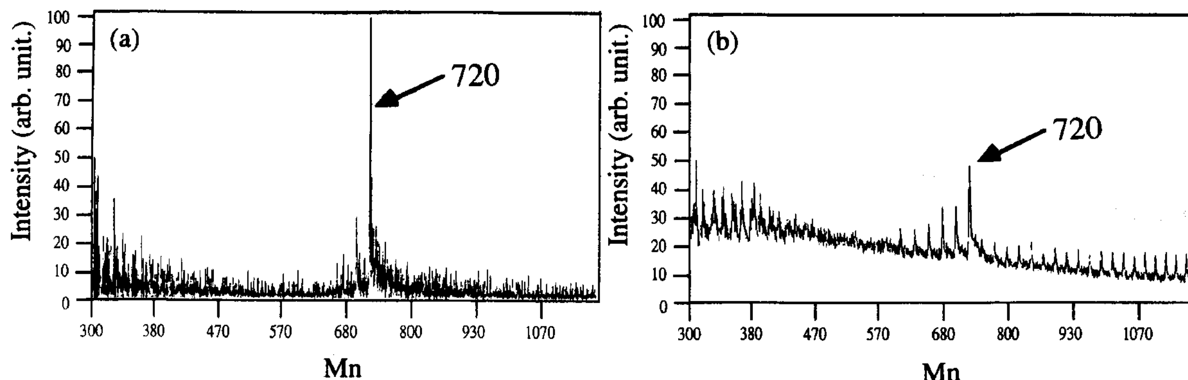

Fig.2. The TOF-MS patterns measured on the soots obtained from the naphthalene(a) and phenylsilane(b) containing plasmas

The soot produced from quinoline containing plasma gave the TOF-MS pattern shown in Fig.3. We could not observe high peaks at Mn corresponding to $C_{60-x}N_x$ (x=1, 2,• • • •), but a clear peak at 720. As in the mass spectra of laser ablated carbon clusters, there was a notable change in the fragment pattern at about Mn=400.

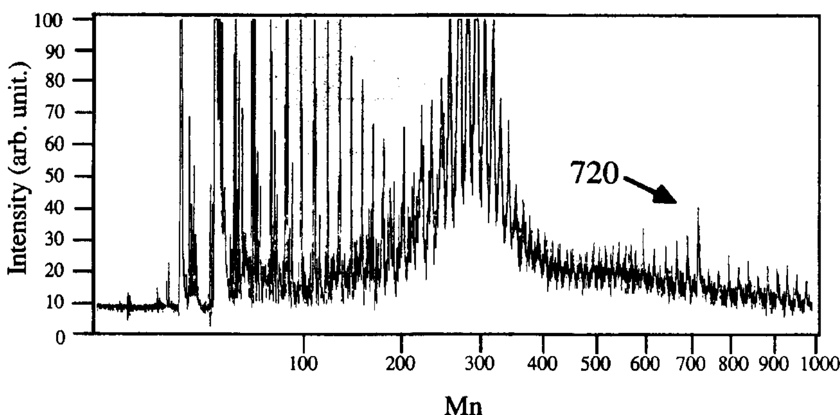

Fig.3. The TOF-MS patterns measured on the plasma containg soot obtained from the qhinoline

3-3 Plasma CVD of carbon films

By feeding mixtures of methane (1-4 sccm) and hydrogen (2 sccm) into rf excited He (120sccm) plasma, carbon films of various forms were deposited at high rates (>10 μm/min) on the substrates placed 2mm below the tip of the insulator nozzle. The product ranged from hydrogen-rich polymer film to amorphous and glassy carbons depending on the applied rf power which was varied from 70 to 140W. Figure 4 shows the Raman spectrum of a 200μm thick film deposited at 120W rf power on Ag-coated glass substrate for 10min plasma CVD[7]. This spectrum (a) is almost identical with the spectrum (b) of commercial glassy carbon (Tokai glassy carbon GC-20) prepared by the heating at 2000℃. This film can be used as an electrode in electrochemical applications. By changing the source gas, various other plasma CVD films could be produced on air-exposed substrates [8, 9].

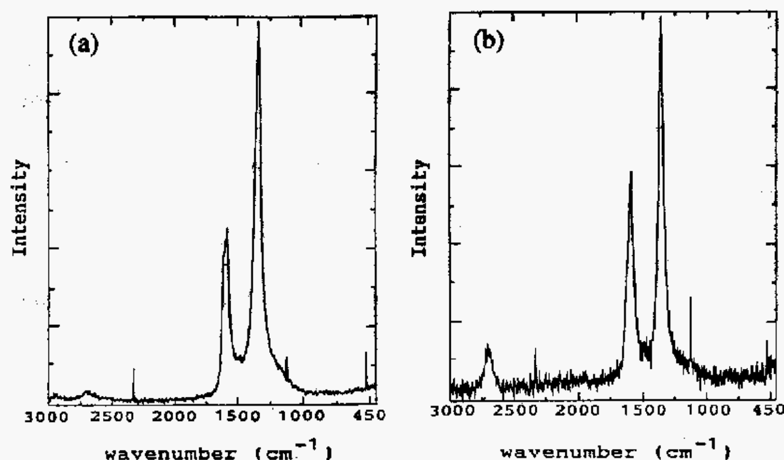

Fig.4 Raman spectra of 200 μm thick amorphous carbon film (a) and typical glassy carbon film (Tokai glassy carbon GC-20) (b).

4. Conclusion

Figure 5 summarizes the results. A cold plasma torch we developed has been verified to be useful for plasma CVD systhesis of fullerene and carbon films from volatile hydrocarbons. Further application of this plasma generator includes oxide (SiO_2, TiO_2, etc.) and other film deposition, photoresist ashing, and semiconductor etching in open air. We are also interested in using this plasma for investigating plasma effect on biomedical materials.

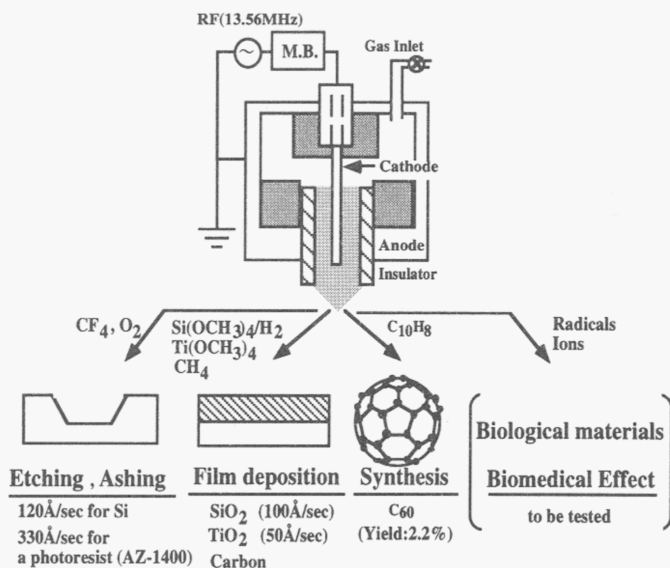

Fig.5. Schematic diagram of the atmospheric pressure cold plasma torch and the application to various material processing.

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