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OPTICS,  
QUANTUM ELECTRONICS

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## Spectral Characteristics of an Atmospheric-Pressure Arc Discharge during the Synthesis of Fullerene Derivatives

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Received February 27, 2007; in final form, August 28, 2007

**Abstract**—The electron concentration and temperature are measured when elements having various ionization potentials are introduced into the carbon–helium plasma that forms in a high-frequency atmospheric-pressure arc discharge. The effect of the introduced elements on the relative fullerene content in a carbon condensate is also studied. The plasma parameters are determined by in situ emission spectral analysis during the synthesis of fullerene derivatives with scandium, sodium, and silicon. The variation of the atomic and molecular line intensities of the plasma radiation with the distance from the carbon-arc axis is investigated upon the introduction of various doping substances. The optimal temperature conditions for the synthesis of fullerene derivatives with Sc, Na, and Si are found.

PACS numbers: 81.05.Tp

DOI: 10.1134/S1063784208060133

### INTRODUCTION

Fullerene derivatives have a large variety of optical, mechanical, physical, and chemical properties. These are used to solve the problems of microelectronics, high-temperature superconductivity, and medicine [1–4]. To solve these problems, researchers need new substances with new unique properties. Medicine requires precursor substances that can dissolve in water and contain metals killing viruses and microbes. Electronics requires materials exhibiting a metal–insulator transition under a relatively weak external action.

The conditions for fullerene synthesis at a helium pressure of 100–200 Torr were discovered more than 16 years ago [5, 6], and those at atmospheric pressure, more than 11 years ago [7]. The production of metallofullerenes at a low pressure is known to be more effective than that at a high pressure. Although substantial results are achieved in the field of fullerenes, a complete theory of fullerene and metallofullerene formation is still undeveloped [8, 9]. To clearly understand the formation of fullerene and fullerene derivatives, researchers need information on the main plasma parameters that affect the growth rate and, hence, yield of these products.

On the other hand, laser sputtering, ion implantation, and electric discharge produce metallofullerenes in small amounts [10–12]. Numerous experimental results indicate that fullerenes and metallofullerenes form most effectively under electric-arc conditions [10, 13]. The carbon that is present an arc discharge channel in the form of atoms and ions sequentially forms chains, rings, and more complex objects that are

considered as fullerene precursors [14]. The temperature ranges where the carbon chains and rings begin to form fullerenes have been detected [15]. In this work, we search for ways for optimizing the synthesis of fullerene derivatives.

### EXPERIMENTAL

Fullerene derivatives were synthesized at atmospheric pressure in a plasmachemical reactor [7]. The arc discharge was simultaneously powered by direct and high-frequency currents. The chamber was complemented by quartz windows to detect plasma radiation, which was projected onto a spectrograph slit with a system of lenses. Sc, Na, and Si were introduced through an axial hole in a graphite electrode using a sample feeding device [16]. This device can introduce a sputtered substance into the discharge zone with the maximum temperature and can increase the time of residence in plasma, which increases the number of collisions with clusters, i.e., fullerene precursors.

The spectral characteristics of the plasma were studied using the technique described in [17]. The spectra were recorded on a film, scanned, and digitized. The studies were carried out in the wavelength range of the most intense lines of the substances given above.

Introducing a various amount of an MgO powder, we changed the plasma parameters (the absolute values of the electron concentration and temperature), which were calculated from the relative intensities of spectral lines. For the calculation, we used both the atomic (278.0, 285.2 nm) and ionic (279.6 nm) magnesium lines.

Variation of the plasma parameters with the type and amount of introduced substance

Introduced substance	$T$ , K	$n_e$ , $\text{cm}^{-3}$	Dopant content in the fullerene benzene-assisted extract, %	Yield of fullerenes, %
No	7250	$3 \times 10^{17}$	–	10
Sc	–	–	0.002	–
Sc <sub>2</sub> O <sub>3</sub> + 5% MgO	4900	$5.17 \times 10^{12}$	0.002	–
Sc <sub>2</sub> O <sub>3</sub> + 20% MgO	4650	$1.67 \times 10^{12}$	0	–
Sc <sub>2</sub> O <sub>3</sub> + 50% MgO	4150	$3.83 \times 10^{11}$	0	–
NaCl	–	–	0.003	5.2
NaCl + 17% MgO	6650	$1.26 \times 10^{17}$	<0.003	8.2
NaCl + 50% MgO	5300	$1 \times 10^{16}$	<0.003	7.2
NaCl + 83% MgO	4650	$1.58 \times 10^{15}$	<0.003	5.3
Si	–	–	0.006	4.4
Si + 17% MgO	7250	$3.16 \times 10^{17}$	>0.01	10.2
Si + 50% MgO	5950	$3.98 \times 10^{16}$	0.01	8.1
Si + 83% MgO	5000	$5.03 \times 10^{15}$	0.003	7.7

To separate fullerene derivatives, the carbon condensate forming on the chamber walls was collected, flooded with benzene, and filtered through an FS-III paper filter. The solvent was then evaporated under normal conditions to yield a powder.

## RESULTS AND DISCUSSION

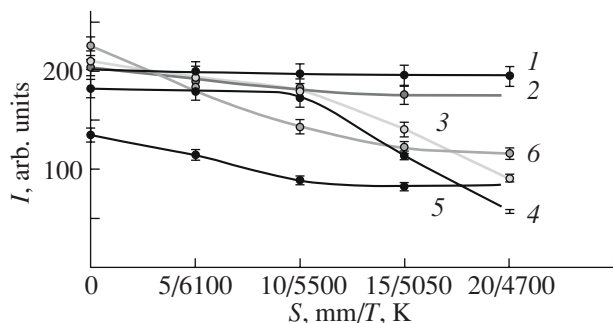
The table lists the results of studying the effect of the temperature and electron concentration ( $n_e$ ) on the synthesis of fullerenes with scandium, silicon, and sodium. The introduction of Sc<sub>2</sub>O<sub>3</sub>, NaCl, or Si strongly decreases the yield of fullerenes, and the addition of up to 17% MgO compensates for this change. As the MgO content increases in an introduced substance, the yield of fullerenes and the concentration of doped fullerenes in the fullerene-containing soot decrease. Thus, the

experimental results demonstrate that the decrease in the yield of fullerene derivatives with Sc, Na, and Si is related to a decrease in the electron concentration.

In all cases, the emission spectra of the fullerene plasma radiation contain the atomic lines of the introduced substances, which indicates the presence of Sc, Na, and Si atoms that can form fullerene derivatives. The X-ray diffraction studies of the fullerene-containing soot show that the reflections of a doping substance are present only in the case of Sc<sub>2</sub>O<sub>3</sub>. In other cases, introduced substances are fully sputtered; that is, only Sc<sub>2</sub>O<sub>3</sub> is incompletely atomized.

We also investigated the variation in the atomic and molecular line intensities of the plasma radiation with the distance from the arc discharge axis upon the introduction of doping substances (see figure). The plasma radiation was analyzed at various distances  $S$  from the arc axis. The spectral lines of carbon atoms and molecules are present over the entire range under study. The lines of metallic atoms virtually disappear at a distance of 20 nm from the arc axis, which is related to cluster formation; therefore, the atomic state of the metal is not observed beginning from 4700 K (see figure). Fullerenes are known to form at temperatures below 3000 K [13]. Thus, the temperature ranges of the atomic state of the metal and fullerene formation do not coincide for the arc at atmospheric pressure. For fullerene derivatives to be effectively synthesized, the low-temperature part of the carbon plasma should be brought into coincidence with the high-temperature plasma flow of the doping substance.

When analyzing the fabricated substances by X-ray diffraction, laser ablation mass spectroscopy, and electron absorption spectroscopy, we failed to detect any differences in the compositions of the synthesized sub-



Spectral line intensities and temperature as functions of the distance from the arc axis: (1) atomic line of C (247.85 nm), (2) sequence band of the Swan system of the C<sub>2</sub> molecule (438.25 nm), (3) atomic line of Na (330.23 nm), (4) atomic line of Si (250.68 nm), (5) atomic line of Sc (301.93 nm), and (6) ionic line of Sc (255.23 nm).

stances from an ordinary fullerene mixture within the limits of experimental error.

### CONCLUSIONS

We are the first to experimentally find that the low yield of metallofullerenes in an atmospheric-pressure arc discharge is caused by the fact that metals are virtually absent in ionic and atomic states in the temperature range of fullerene formation. The temperature range of metal coalescence into clusters is well above the temperature range of effective fullerene formation.

Therefore, for fullerene derivatives to be effectively synthesized, the low-temperature part of the carbon plasma should be brought into coincidence with the high-temperature plasma flow of the doping substance. To this end, the doping substance should be sputtered by an independent plasma source, and the temperature zone with the atomized substance should be brought into coincidence with the temperature range of fullerene formation in a carbon–helium plasma.

### ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 06-08-00331.

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*Translated by K. Shakhlevich*