Structure and conductive properties of C_{60} films and fullerene-containing materials deposited using aromatic and non-aromatic solvents

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Abstract. Films of fullerenes and fullerene-containing materials have been synthesized from their solutions of various volumes in aromatic and non-aromatic solvents. The photographs and the sizes of the resulting microstructures have been presented. The comparison of IR spectra has been given. Specific conductivity values have been considered.

1 Introduction

It is indisputable that the electronic industry of the 21st century is marked by a rapid increase in the use of new materials that differ from the elements of traditional solid-state electronics not only in their chemical composition, but also in the phase component of the functional layers. Carbon materials are one of the most remarkable examples of such materials. Flexible screens, scanners, and even functional chips are already widely used today [1, 2]. One of the unique features of carbon systems is that they allow the formation of 2D and 3D nanoscale objects (graphenes, nanotubes, fullerenes, etc.), which can be used as functional elements of integrated microcircuits and are also capable of changing the macro properties of microstructures significantly [1, 3, 4].

Under the influence of various solvents, fullerene forms microstructures of different shapes [5-7]. At present, a detailed description of the causes and the process of their formation is a very complex task requiring multilateral studies [5].

In this paper, we consider the influence of aromatic solvents and chlorinated methanes on the formation of fullerene C_{60} films. Along with fullerene, a fullerene-containing material (FCM) was studied [8]. In this study, we also tried to determine in what way the amount of starting material and the use of various kinds of solvents affect the resistive properties of the studied carbon films.

2 Synthesis and microscopy of thin films

Having been accurately weighed, the starting materials, C_{60} fullerene and FCM, were dissolved in five different substances: aromatic (benzene, toluene) and non-aromatic (dichloromethane, chloroform and carbon tetrachloride). After thorough mixing and settling

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for 48 hours, the carbon materials were deposited by pouring them out from solution onto glass substrates [9, 10].

The analysis of surface morphology and volumatic inhomogeneities of the obtained films was carried out by the microscopy in transmitted and reflected light with the help of the LOMO MII-4M microinterferometer. Microphotographs of the surfaces of fullerene and FCM films deposited using various solvents are shown in Fig. 1 with the indication of the chemical formula of the solvent and the volume of solution deposited on the substrate.

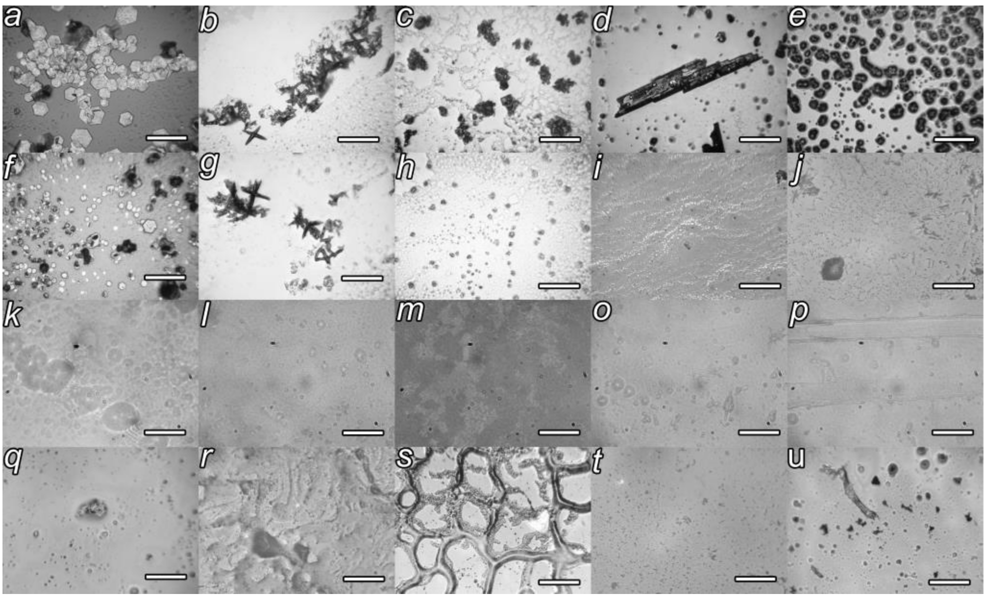

Fig. 1. Microphotographs of fullerene (a - CCl_4 1 ml; b - CH_2Cl_2 1 ml; c - $CHCl_3$ 1 ml; d - C_6H_6 1 ml; e - $C_6H_5CH_3$ 1 ml; f - CCl_4 0.15 ml; g - CH_2Cl_2 0.15 ml; h - $CHCl_3$ 0.15 ml; I - C_6H_6 0.15 ml; j - $C_6H_5CH_3$ 0.15 ml) and FCM (k - CCl_4 1 ml; l - CH_2Cl_2 1 ml; m - $CHCl_3$ 1 ml; o - C_6H_6 1 ml; p - $C_6H_5CH_3$ 1 ml; q - CCl_4 0.15 ml; r - CH_2Cl_2 0.15 ml; s - $CHCl_3$ 0.15 ml; t - C_6H_6 0.15 ml; u - $C_6H_5CH_3$ 0.15 ml) films, obtained using various solvents and the volume of the solution, and microobjects. The line length is 50 μm.

Table 1. Geometry of thin-film structures based on C_{60} and obtained with the use of various solvents.

Material	**Solvent / V, ml**	**CCl_4**		**CH_2Cl_2**		**$CHCl_3$**		**C_6H_6**		**$C_6H_5CH_3$**	
		0.15	**1**	**0.15**	**1**	**0.15**	**1**	**0.15**	**1**	**0.15**	**1**
C_{60}	Object size, μm	6	34	16	58	4	14	5	20	4	10
	Film thickness, nm	309	437	154	199	203	290	70	81	43	63
FCM	Object size, μm	4	36	15	59	3	89	15	20	12	11
	Film thickness, nm	270	308	1115	1246	795	1171	55	341	150	998

The use of a range of different solvents resulted in a wide variety of forms of fullerene microstructures which were observed. Among them there can be distinguished tubular, star-shaped, hexagonal, various agglomerations of spherical particles (Fig. 1, a-j) [11]. At the same time, for fullerene-containing materials, the use of a range of solvents did not lead to the production of various structures with such clear edges (Fig. 1, k-u) [12]. However, there were still differences in the structure of the FCM films. This effect was especially clearly noticeable at low concentrations of the material (Fig. 1, q-u). The surface of the fullerene and fullerene-containing films obtained using aromatic solvents was generally more homogeneous. Average object dimensions and thicknesses for the samples presented are shown in Table 1.

3 IR characteristics

Infrared spectroscopy provides data on the composition of materials. The presented IR absorption spectra of the studied C_{60} and FCM films were obtained using Agilent Cary 630 FTIR Spectrometer.

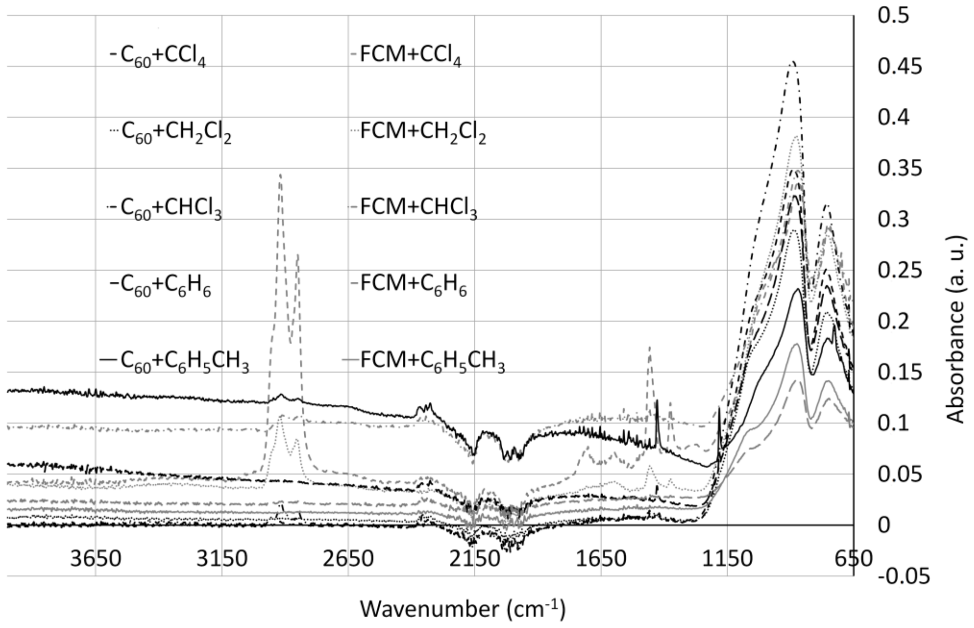

Fig. 2. IR absorption spectra of FCM films (gray lines) and C_{60} (black) on glass substrates using aromatic and non-aromatic solvents (solution volume - 0.15 ml).

With a small amount of the applied solution (0.15 ml) for fullerene films, the absorption coefficient is higher in the case of using aromatic solvents (Fig. 2). This is due to the better solubility of fullerene in them. For film FCM structures, the absorption coefficient is greater for chlorinated methanes due to their greater thickness.

The increase in the amount of solution reveals the following results (Fig. 3). Fullerene films have the highest absorption when chloroform is used, and the lowest absorption is observed when benzene is used. For other types of solvents, the absorption coefficient of the resulting films is approximately the same. Films based on fullerene-containing material are capable of significant absorption when carbon tetrachloride is used.

For fullerene films in the case of using aromatic solvents, the increase in the volume of the solution leads to the decrease in the absorption coefficient, which may be due to the "smearing" of C_{60} on the surface of the substrate with a larger amount of solution. When using chlorinated methanes, due to the growth in the thickness of the films with the increase in the volume of the solution, the absorption coefficient rises. For FCM films, such obvious regularities are not observed.

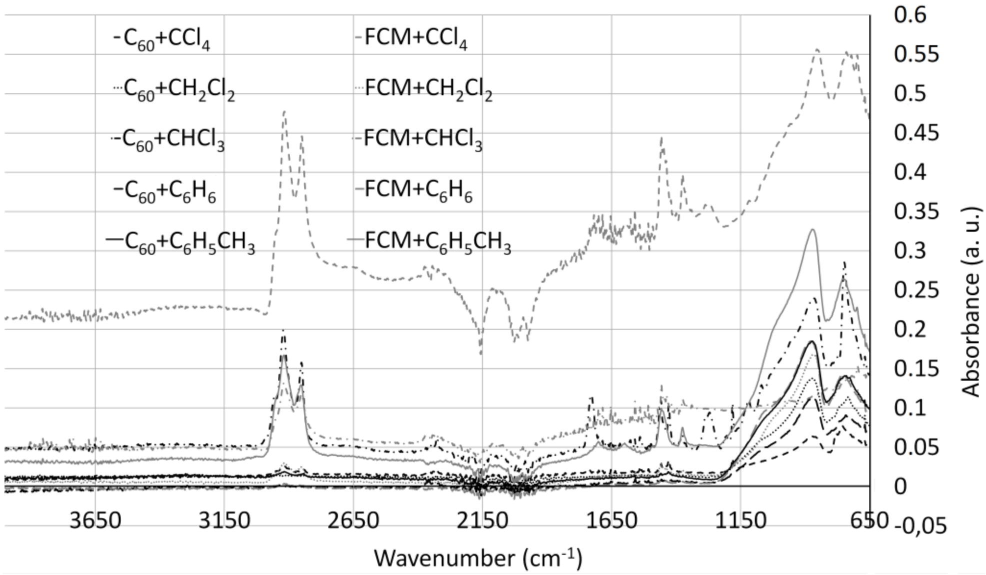

Fig. 3. IR absorption spectra of FCM films (gray lines) and C_{60} (black) on glass substrates when using aromatic and non-aromatic solvents (solution volume - 1 ml).

Peaks of fullerene and impurities, higher hydrocarbons, were found for fullerene films with a small amount of the applied solution. The analysis of the absorption spectra of the group of 1 ml samples revealed peaks of fullerene and the corresponding solvent, as well as peaks of higher hydrocarbons [11].

On the basis of the analysis of the absorption coefficient dependence on the wave number within the studied range for fullerene-containing materials, the volume of the deposited solution being equal to 0.15 ml, we can conclude that there are absorption peaks for only higher hydrocarbons - the components of FCM [12]. The intensities of the observed fullerene absorption peaks are negligible. Also, solvents peaks are not detected, and the increase in the amount of solution up to 1 ml results in occasional absorption bands, characteristic of the solvents used.

4 Conducting properties of the films

The study of the electrical parameters of film modifications of fullerene and fullerene-containing material was carried out on the B1500A Semiconductor Device Parameter Analyzer. The structural diagram of the samples studied was a planar (inset in Fig. 4), where h is the thickness of the active layer, c1, c2 are the contact group, b is the distance between the contacts, d is the dimensions of the contact area.

The use of solvents belonging to the halogen derivatives of alkanes and to the group of benzene derivatives, led to obtaining a variety of the geometric patterns of the films, as well as a variety of the conductive properties of the studied carbon thin-film structures (Fig. 4).

The increase in the volume of the applied substance from 0.15 to 1 ml significantly reduces the resistance. Specifically, the maximum increase in the conductivity of fullerene C_{60} films is observed in dichloromethane - an increase of approximately 60 times, from $5 \cdot 10^{-13}$ S to $2.76 \cdot 10^{-11}$ S. The minimum change in the conductive properties of C_{60} is observed in chloroform - an increase of 40%, from $7 \cdot 10^{-12}$ S to $2.73 \cdot 10^{-12}$ S.

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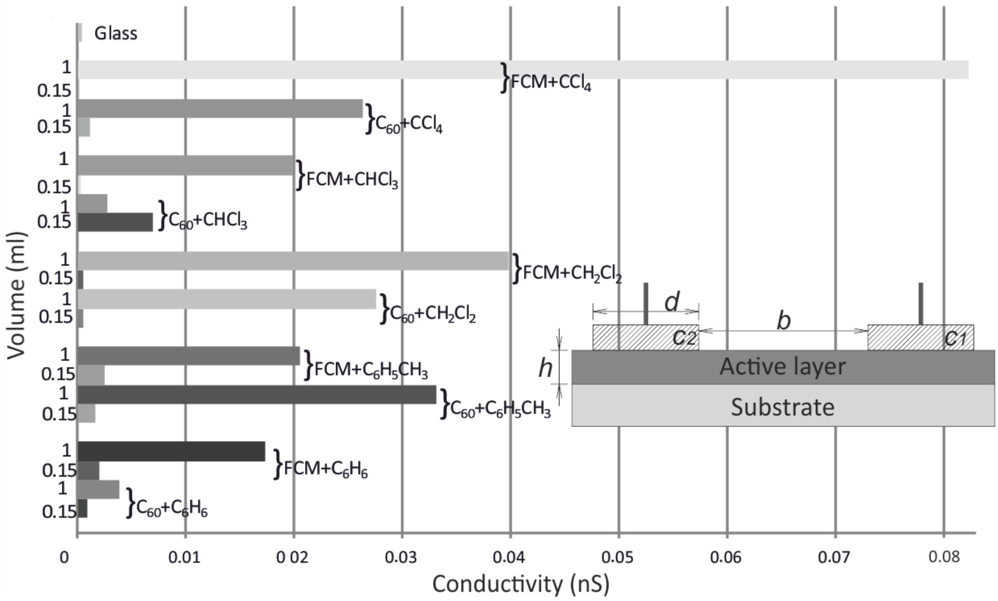

Fig. 4. The comparison of conductivity for FCM and C_{60} films deposited from various solvent groups.

The morphology of the FCM films is significantly different from the C_{60} films. The variety of forms of objects does not occur in fullerene-containing material, while a more uniform distribution of matter is observed there. In this regard, thin-film FCM samples have lower resistance. Thus, the maximum increase in the conductive properties of FCM is observed in carbon tetrachloride - more than 400 times, from $2.07 \cdot 10^{-12}$ S to $1.74 \cdot 10^{-11}$ S. The minimum change in the conductive properties of FCM is in benzene - an increase of 8.5 times, from $2.07 \cdot 10^{-12}$ S to $1.74 \cdot 10^{-11}$ S.

5 Conclusion

Thus, with the use of various solvents, it is possible to obtain microstructures, based on fullerene, that have different geometric shapes. Film samples of fullerene-containing materials are more homogeneous. In our opinion, the diversity of sample architectural patterns is explained, among other things, by the versatility of carbon as an element whose atoms make it possible to construct both dielectric materials like diamond and conductors based on graphite, graphene and nanotubes.

On the basis of the analysis of the IR spectra for the solvents absorption peaks, it becomes clear that the formation of more stable solvates is observed in fullerenes than in FCM.

From the research results analysis of the carbon films conductivity, the following conclusion can be drawn: the conductivity rises with the increase in the quantity of C_{60} and FCM (along with the increase in the amount of the deposited solution from 0.15 to 1 ml), which is accounted for by the growth in the thickness and in the density of particle distribution. The maximum increment in conductivity, observed in the structures, is as follows: for C_{60} - about 60 times in the case of using dichloromethane, and for FCM it is more than 400 times in the case of using carbon tetrachloride.

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References

1. L. Du, X. Luo, F. Zhao, W. Lv, J. Zhang, Y. Peng, Y. Tang, Y. Wang, Carbon **96**, 685 (2016)
2. A.L. Silva, M.M. Correa, G.C. de Oliveira, P.P. Florez-Rodriguez, C.A. Rodrigues Costa, F.S. Semaan, E.A. Ponzio, J. Alloy. Compd. **691**, 220 (2017)
3. F. Torrisi, T. Carey, Nano Today. **23**, 73 (2018)
4. L.K. Shrestha, R.G. Shrestha, J.P. Hill, K. Ariga, J. Oleo Sci. **62(8)**, 541 (2013)
5. X. Zhang, X.-D. Li, Chinese Chem. Lett. **25**, 912 (2014)
6. L. Zhang, S. Zhou, M. Chen, K. Yin, H. Li, New Carbon Mater. **34(3)**, 238 (2019)
7. L.K. Shrestha, Q. Ji, T. Mori, K. Miyazawa, Y. Yamauchi, J.P. Hill, K. Ariga, Chem. Asian J. **8(8)**, 1662 (2013)
8. K.V. Rabotyagov, E.V. Say, E.M. Maksimova, I.A. Nauhatsky, N.I. Karpenko, A.I. Shevchenko, A.S. Mazinov, Scientific Notes of V.I. Vernadsky Crimean Federal University. Biology. Chemistry **1(3)**, 125 (2015)
9. A.S. Mazinov, V.S. Gurchenko, A.S. Tyutyunik, A.I. Shevchenko, Ecological Bulletin of the BSEC Research Centers **15(4)**, 85 (2018)
10. A.S. Mazinov, V.S. Gurchenko, A.S. Tyutyunik, N.I. Karpenko, CriMiCo'2018 28th International Crimean Conference Microwave and Telecommunication Technology. Conference Proceedings. Sevastopol, 1022 (2018)
11. A.S. Mazinov, V.S. Gurchenko, A.I. Shevchenko, N.E. Arutinov, A.S. Tyutyunik, Ecological Bulletin of the BSEC Research Centers **16(2)**, 48 (2019)
12. K.V. Rabotyagov, A.S. Mazinov, V.S. Gurchenko, A.S. Tyutyunik, A.I. Shevchenko, I.O. Ivanchenko, N.E. Arutinov, Scientific Notes of V.I. Vernadsky Crimean Federal University. Biology. Chemistry **5(2)**, 210 (2019)