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Spectral and conductive properties of film heterostructures based on fullerene-containing material and 4-methylphenylhydrazone N-isoamilisatine

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Abstract. The 4-methylphenylhydrazone N-isoamylisatin method consists of 4-methylphenylhydrazone and a diode heterostructure. The best method for producing, synthesizing, microscopy of carbon films and an organic precursor. The results of the successive x-ray phase analysis of the materials used are presented. Also, the optical spectra of isatins having short wavelength (420-500 nm) and long wavelength (850-900 nm) extrema giving absorption peaks at 3-3.1 eV and luminescence at 1.4 eV. The results of studies of IR spectroscopy of primary carbon films and an organic composite are obtained. The current-voltage characteristics of a thin-film heterostructure based on a fullerene-accessible material and an organic precursor with ITO-aluminum strapping are presented. It was shown that the experimental structures have rectifying diode characteristics with hysteresis of the forward branch of the I-V characteristic.

Keywords: organic heterostructure, thin-film structures, current-voltage characteristics, X-ray phase analysis, fullerene-containing material, hydrazone

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1. INTRODUCTION

The future simplification in the construction of electronic circuits is directly related to the printing technologies of flexible microcircuits, in which, to date, carbon materials demonstrate relatively high performance [1, 2]. Such composites are of particular interest when combined with organic and inorganic materials [3, 4]. On the other hand, the

achievements of thin film organic electronics optimistically promise to enable the creation of stable and fully functional devices on organic structures in the near future [5]. The construction of heterostructures based on organics with the addition of fullerenes allows not only to provide an acceptable quantum yield [6], but also makes it possible to construct 3D bulk barrier structures [7]. The use of organic materials as a donor allows us to create a potential barrier similar to diode structures. The simplicity and cheapness of the production of organic functional layers and fullerene-containing materials (FCM) is an indisputable advantage over the more expensive and complex analogues in production [8].

Based on the above assumptions, in this work, an attempt was made to build an organic heterostructure based on FCM and organic material, 4-methylphenylhydrazone N-isoamylisatin (IMPH). We also attempt to draw analogies with classical solid state barrier structures in terms of their optical and electrical properties. The FCM obtained by the low-temperature cracking method [9] was used as an acceptor. The synthesis of the organic precursor was carried out according

to the technique presented in previously published works [10, 11].

2. COMPOSITION OF HETEROSTRUCTURES

To determine the composition of fullerene-containing soot and to confirm the molecular structure of IMPH, methods of X-ray phase analysis and IR spectroscopy were used. The X-ray diffraction patterns of FCM and IMPH were recorded on a DRON-3 general-purpose X-ray diffractometer (Bragg-Brentano focusing scheme using a graphite monochromator) in the angular range - 2θ from 7° to 110° . An X-ray tube with a copper anode λ ($K\alpha$) = 0.154184 nm was used. The primary and secondary beams were limited by slits: horizontal — 0.25 mm, vertical — 6 mm, and Soller slits — 0.5 mm. The detector rotation speed is $0.5^\circ/\text{min}$, the time constant is $1 \cdot 10^3$ imp/s. Sample rotation speed — 120 rpm (axis in the survey plane) (**Fig. 1**).

The proportion of 2.7% C_{60} (Buckminsterfullerene, **Table**) in the total share of 93% in the carbon component of the entire starting material and the corresponding peaks in the X-ray diffraction pattern (**Fig. 1**) allow us to classify the starting carbon powder as a fullerene-containing material

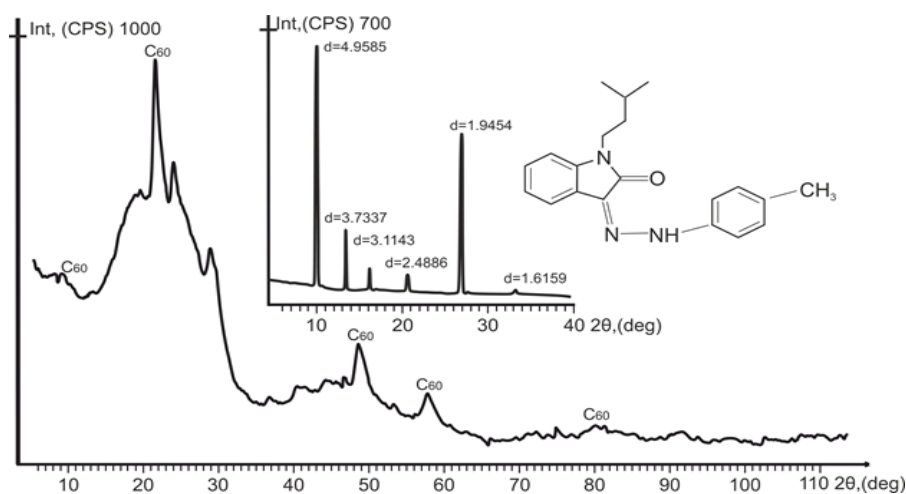


Fig. 1. X-ray diffraction pattern of FCM sample (main graph) and 4-methylphenylhydrazone N-isoamylisatin (inset).

Table

Key FCM components

International name	Mass fraction, %	COD ID	International name	Mass fraction, %	COD ID
Carbon Lonsdaleite	28.9	1100004	Buckminsterfullerene	2.7	9011073
Carbon	13.2	9012588	Supercubane	2.2	9012241
Carbon	12.9	2101499	Carbon	2.0	9012593
Carbon	12.2	9014004	Carbon	0.7	9012592
Carbon Graphite 3R	9.7	1101021	Carbon Graphite 2H	0.4	1011060
Carbon	7.7	9012594	Carbon	0.4	9012590

[9]. An X-ray phase analysis of IMPH in the solid phase showed that the organic precursor has a tetragonal system with sides: $a = 19.27609045 \text{ \AA}$; $b = 19.27609045 \text{ \AA}$; $c = 14.14478333 \text{ \AA}$. In this case, the simplest space group P4 can line up at angles: $\alpha = 90^\circ$; $\beta = 90^\circ$; $\gamma = 90^\circ$ (inset in Fig. 1).

3. HETEROSTRUCTURE SPECTROSCOPY

Spectral analysis in the visible range (400–900 nm) involved using a prismatic monochromator with a halogen lamp, with appropriate filters after normalization to the hydrogen line. Each of the constituent functional layers of the general heterostructure was separately deposited on coverslips with corresponding volume fractions. The dependences of the intensities of the transmitted (T) and reflected (R) signals normalized to the spectra of the initial substrates had at least $1.5 \cdot 10^3$ points

with a prism rotation duration of at least 30 minutes (Fig. 2a).

The relatively even spectra of R and T IMPH films 2.2–2.3 μm thick had short-wave (420–500 nm) and long-wave (850–900 nm) extrema giving absorption peaks at 3–3.1 eV and luminescence in the region of 1.4 eV (insets in Fig. 2a).

An attempt to preliminary estimate the band gap using the Tauc equation, by analogy with [12], showed the presence of an energy barrier of 3.05 eV. FCM films deposited from a benzene solution had practically zero transmission and reflection spectra lying at the noise level of the photomultiplier with an absorption coefficient even lower than that of pure fullerene.

A characteristic feature of the IR spectra of IMPH and FCM (inset in Fig. 2b), in the

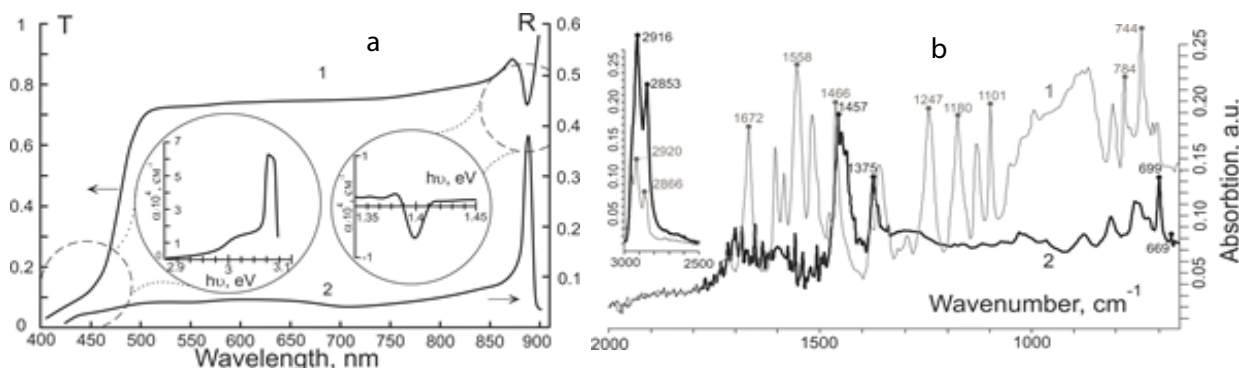


Fig. 2. Optical spectra of IMPH (a) — transmission (1), reflection (2), absorption peaks (insets). IR spectra (b) - IMPH (1) and FCM (2).

region of small wavelengths (3000–2500 cm^{-1}), is the presence of several absorption bands associated with vibrations of the C-H group [11]. The intensity of the FCM peaks in this range is several times higher than the IMPH peaks. In the region of lower frequencies (2000–650 cm^{-1}), the bands of 1375 and 1457 cm^{-1} are inherent for FCM, which can be assigned to the C_{sp^3} -H group, and peaks 669, 699 cm^{-1} to C_{sp^2} -H [13]. In the range (2000–650 cm^{-1}), IMPH is characterized by the presence of peaks of 1672 and 1558 cm^{-1} associated with C = O and C = N groups, the peaks in the region of 1610–1364 cm^{-1} are due to stretching vibrations of C = C of benzene rings. The range of 1295–1054 cm^{-1} is C-N, C-C, C-H oscillations. Deformation vibrations of C-H groups at 1128–744 cm^{-1} are observed in benzene rings and an alkyl substituent.

4. ELECTRICAL PARAMETERS OF THE HETEROJUNCTION

To determine the electrical parameters, the heterojunction was created in the form of a “sandwich” structure (insert in **Fig. 3**). As the contact group, we used aluminum (Al) on a setall, 120 nm thick, with a specific resistance of 40 Ω/sq and indium tin oxide (ITO) with a specific resistance of 16–18 Ω/sq having a transparency of at least 82%. By the method of pouring from a solution, IMPH was applied to ITO, and FCM to aluminum. Volume resistivity measurements were made at least 10 times using the Keysight B1500 Semiconductor Analyzer. Samples were placed in a sealed shielding chamber with a lighting matrix at a temperature of 20–25°C.

The current dependences of the assembly were built according to the averaged eightfold

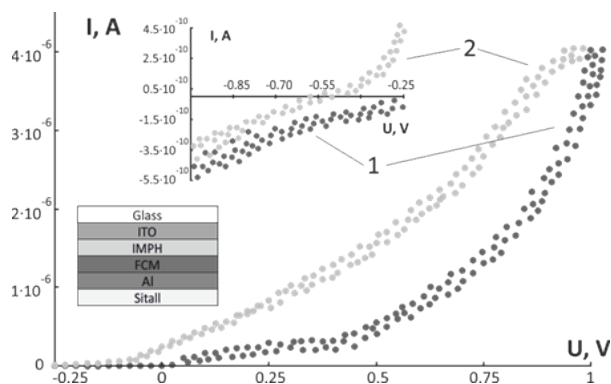


Fig. 3. The current – voltage characteristics of the FCM heterostructure is 4-methylphenylhydrazone of *N*-isoamylisatin (1-straight branch; 2-reverse branch).

point measurement with a voltage scan duration of 5, 10, 15 minutes. The ratio of the forward current to the reverse one in the interval from -1 V to +1 V, averaged over five cycles, amounted to 104 with apparent hysteresis in the positive quarter of the I–V characteristics (Fig. 3). By analogy with classical semiconductor devices, for a carbon-organic heterostructure, it is also possible to derive bias voltages at direct connection of 0.45–0.5 V with access to a linear current section at 4.1 μA (Fig. 3). At the same time, the achievement of reverse currents of 530 pA at a voltage of -1 V may be due to the not ideal construction of the space charge region and the presence of recombination levels, which reduce the photosensitivity of the FCM-IMPH heterostructure to zero, in comparison with C_{60} -4-methylphenylhydrazone of *N*-isoamylisatin [11].

5. CONCLUSION

The key result of the study is a demonstration of the possibility to build a potential barrier on the basis of fullerene-containing material and the organic precursor 4 - methylphenylhydrazone *N*-isoamylisatin.

Determination of the studied materials composition by X-ray phase analysis confirmed the molecular structures of the

samples. Spectral analysis in the visible range yielded the characteristics of reflection, absorption, and transmission, and also made it possible to calculate the energy barrier. The study of IR spectra showed the presence of peaks characteristic of both IMPH and FCM used. The addition of an organic compound made it possible to significantly enhance the conductive properties of the thin film structure of a fullerene-containing material and to achieve a direct and reverse current ratio of 4 orders.

The type of current-voltage characteristic indicates that there is a potential barrier due to different morphologies of basic molecular systems which requires additional studies.

In general, the results confirm the prospects for research into organic quantum electronics, which, together with nanostructured carbon materials, will significantly expand the frontiers of modern instrument engineering.

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