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# Study of the Formation and Properties of In–CuPcF<sub>4</sub> Nanocomposite Materials in the Mode of the Millisecond Recording of Photoelectron Spectra

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**Abstract**—A study of the formation processes and properties of nanocomposite materials consisting of indium nanoparticles in a thin film of the organic semiconductor copper tetrafluorophthalocyanine (CuPcF<sub>4</sub>) is presented. The results are obtained by the new setup for dynamic photoelectron spectroscopy, which allows the recording of spectra in a millisecond interval using the ARGUS photoelectron spectrometer and synchrotron radiation (PETRA III/DESY, Germany). The evolution of the core level (CL) spectra: C 1s, N 1s, and In 3d<sub>5/2</sub> recorded directly during the deposition of indium onto the CuPcF<sub>4</sub> surface under ultrahigh vacuum conditions is traced. The thickness of the indium coating during deposition increased from 0 to 5 nm. In this range of coatings, more than 150 spectra are recorded for each CL with a recording rate of 0.1 s/spectrum. The following is established: the significant diffusion of indium atoms deep into the organic matrix is observed; in fact, no chemical interaction of indium with carbon atoms is found; indium atoms are located in places close to pyrrole nitrogen of the CuPcF<sub>4</sub> molecule. Apparently, during the interaction of In atoms and pyrrole nitrogen atoms, a negative charge is transferred from indium to the CuPcF<sub>4</sub> molecule. Thus, data on the fast-flowing processes of the formation of organometallic In–CuPcF<sub>4</sub> interfaces are obtained.

**Keywords:** electron spectrometer, dynamic photoelectron station, snapshot, high vacuum, thin organic film, indium, fluorine-substituted copper phthalocyanine CuPcF<sub>4</sub>

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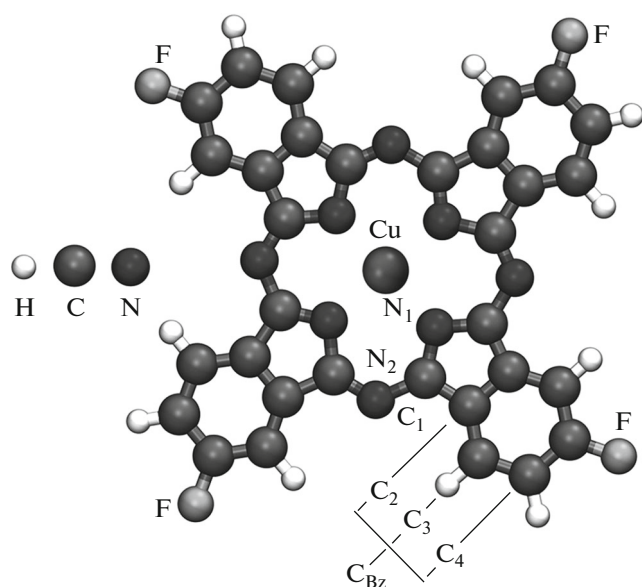
## INTRODUCTION

The emergence and development of molecular electronics has drawn particular attention to molecular semiconductors, e.g., metal phthalocyanines (MePc). They have unique properties and are technologically advanced in the production of films. Using ultrathin films as a matrix, organometallic composites can be created containing metal nanoparticles self-assembled in the MePc matrix. The technologies for creating the described nanocomposites are quite simple and relatively cheap; therefore, such materials can take a prominent place in practical use in various electronic devices. However, despite growing interest in hybrid systems, numerous questions about their properties and the processes occurring during their formation still remain unanswered. For example, interfacial

phenomena can radically change the electronic properties of organic wide-gap matrices. It should also be noted that the processes of the formation of organometallic interfaces in the manufacture of hybrid organic-inorganic systems are fast flowing. Therefore, recording experimental data in the dynamic mode could reveal the additional properties of these materials important for electronics.

## EXPERIMENTAL

This work describes the creation of model organometallic nanocomposite materials consisting of an organic semiconductor matrix of CuPcF<sub>4</sub> and indium atoms, as well as the study of their characteristics. The uniqueness of the properties of fluorine-substituted



**Fig. 1.** Flat  $\text{CuPcF}_4$  molecule consisting of a central copper atom surrounded by four nitrogen atoms (pyrrole ones,  $\text{N}_1$ ), four other nitrogen atoms (connecting bridge,  $\text{N}_2$ ), 32 carbon atoms (pyrrole ones  $\text{C}_1$  and benzene ones  $\text{C}_2$ ,  $\text{C}_3$  and  $\text{C}_4$ ). Unlike  $\text{CuPc}$ , four hydrogen atoms are replaced with fluorine atoms.

metal phthalocyanines, to which  $\text{CuPcF}_4$  belongs, is that they noticeably change the physical and chemical properties of a substance due to a change in the band gap and the relative position of the Fermi level in it. The Fermi level in the band gap is shifted towards the bottom of the conduction band (LUMO), which is a prerequisite for a change in the hole conductivity of copper phthalocyanine  $\text{CuPc}$  to electron conductivity for  $\text{CuPcF}_4$  [1, 2]. The choice of indium as the metal component is due to its low melting point, low work function, and the fact that this metal is an important material for the semiconductor industry [3–7].

X-ray photoelectron spectroscopy (XPS) is a universally recognized and widely used method for obtaining information about the electronic structure of the surface and near-surface layers of different materials. The observed progress in the development and construction of synchrotron X-ray sources, as well as in the production of electronic spectrometers and detectors, opens up the opportunity to explore more complex modern materials, as well as fast-flow processes. Such processes can be monitored and studied using dynamic photoelectron spectroscopy with a recording rate of each spectrum within a few milliseconds. One of the ways to record photoemission spectra with a sufficiently fast temporal resolution is to combine a high-brilliance synchrotron photon source PETRA III (DESY/Hamburg) with a new hemispherical ARGUS analyzer (Scienta Omicron GmbH, Germany). ARGUS has a 128-channel multi-anode detector that can record photoelectron spectra in two

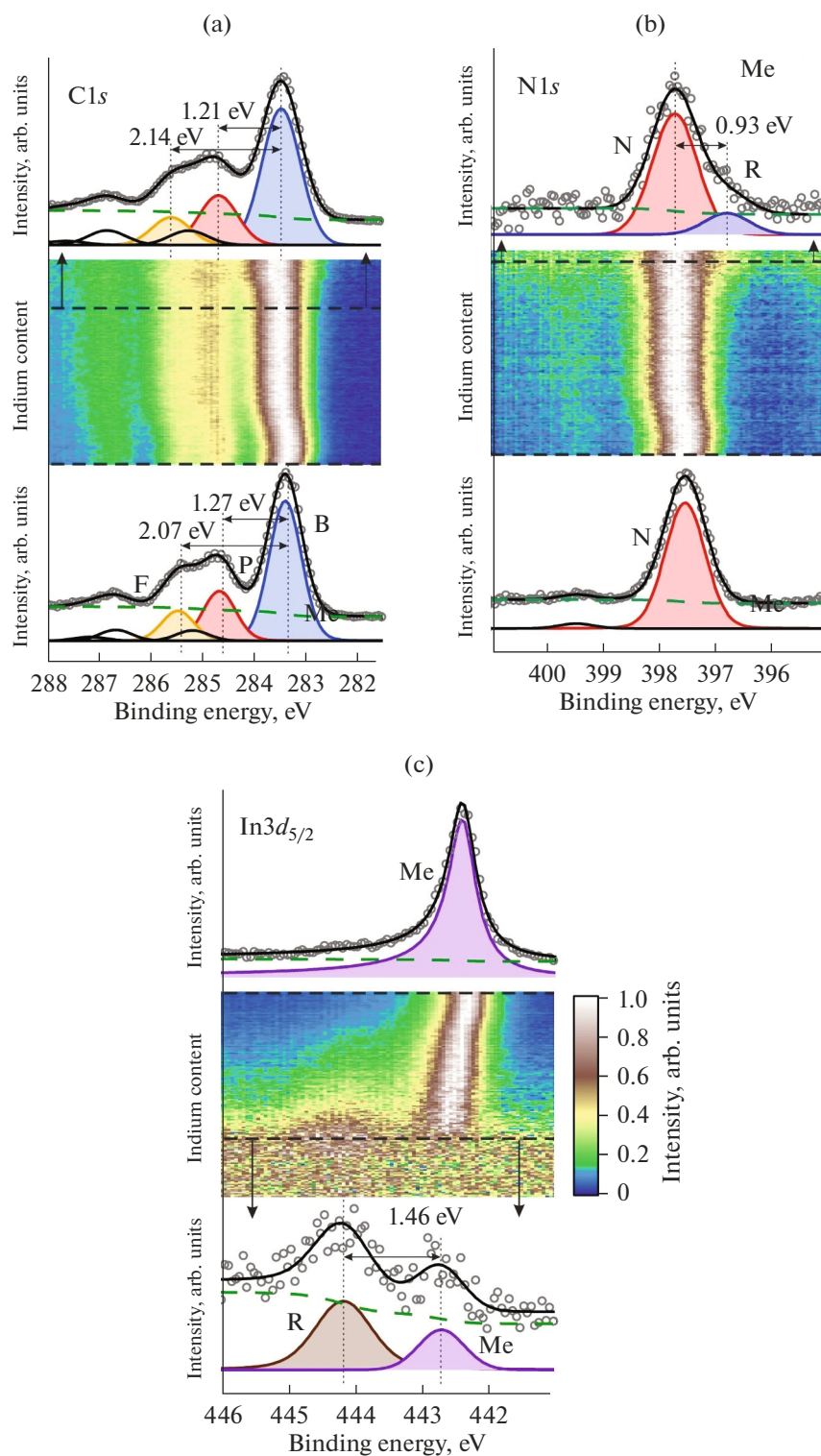
modes: the first mode is traditional energy scanning with subsequent unfolding of the spectrum in the given energy range, and the second one is the so-called snapshot mode (128 channels of the electron detector cover simultaneously the entire spectral range of energies). In addition to the two recording modes, the design of the spectrometer allows scanning of the probed micron-sized area along the sample surface with simultaneous recording of the XPS spectra without mechanical displacement of the sample under study. This mode makes it possible to examine complex local chemical reactions and obtain local XPS spectra along the surface of the analyzed sample with a spatial resolution better than several micrometers [8]. The successful use of dynamic photoelectron spectroscopy for the real-time investigation of fast-flow processes of the formation of nanostructured two-dimensional systems was demonstrated in [9–11].

## RESULTS AND DISCUSSION

Detailed schematic description of the structure of the  $\text{CuPcF}_4$  organic molecule shown in Fig. 1 can be found, for example, in [12, 13].

In this study, the evolution of the spectra of core levels (CL)  $\text{C}1s$ ,  $\text{N}1s$ , and  $\text{In}3d_{5/2}$  recorded directly during the deposition of indium on the  $\text{CuPcF}_4$  surface under ultrahigh vacuum conditions was traced (Fig. 2). All data were obtained in the dynamic mode in the form of sequentially recorded cycles. More than 150 spectra were obtained with a recording rate of 0.1 s/spectrum for each of the CLs. The thickness of the indium coating during deposition increased from 0 to 5 nm. The initial spectra of the core levels  $\text{C}1s$  and  $\text{N}1s$  before indium deposition are shown in the lower part of Figs. 2a and 2b. The position of the peaks and their spectral shape correspond to the spectra from a pure  $\text{CuPcF}_4$  film measured earlier using conventional photoelectron spectroscopy. The fact that the position of the  $\text{C}1s$  spectra on the energy scale does not change depending on the deposition of indium indicates the absence of chemical interaction of the metal with carbon atoms of the  $\text{CuPcF}_4$  molecule. An increase in the coverage leads to some broadening of the  $\text{C}1s$  and  $\text{N}1s$  spectra, which gives reason to assume the diffusion of indium atoms deep into the organic film and the formation of In clusters. The appearance of the reactive component in the  $\text{N}1s$  spectra shifted by 0.93 eV towards lower binding energies with respect to the main nitrogen peak (R in the upper part of Fig. 2b) is explained by the interaction of In and N atoms and the transfer of a negative charge from indium to nitrogen. This also indicates that indium atoms, apparently, are located in places close to the pyrrole nitrogen of the  $\text{CuPcF}_4$  molecule, which is in good agreement with the data obtained earlier for a similar In/ $\text{CuPc}$  system [14].

Due to the possibility of recording spectra in the millisecond interval, the reactive component was



**Fig. 2.** Evolution of the spectra of core levels (a) C1s, (b) N1s, and (c) In3d<sub>5/2</sub> recorded in the millisecond interval directly during the deposition of indium on the CuPcF<sub>4</sub> surface under ultrahigh vacuum conditions.

found in the first fifty spectra of In3d<sub>5/2</sub> (R in the lower part of Fig. 2c). This indicates the diffusion of indium atoms into the volume of the organic film already at

the very initial stages of the deposition of metal and the chemical interaction of In with an organic molecule. Thus, the significant chemical interaction of

indium atoms with nitrogen atoms of the CuPcF<sub>4</sub> molecule was found. In addition, a metallic component appears almost simultaneously (Me in the lower part of Fig. 2c), which indicates the formation of indium metal clusters already at the earliest stage of the deposition of In atoms on CuPcF<sub>4</sub>. Upon increasing coverage, the metal component becomes dominant (Me in the upper part of Fig. 2c). These conclusions are also confirmed by the data obtained in the study of the structure of model nanocomposite materials using transmission electron microscopy.

## CONCLUSIONS

When creating a nanocomposite material by indium deposition on a thin film of CuPcF<sub>4</sub> organic semiconductor, the recording of photoelectron spectra in the millisecond interval allowed convincing data on the fast-flowing processes of the formation of organometallic In–CuPcF<sub>4</sub> interfaces to be obtained. Herewith, the following was established: (i) strong diffusion of indium atoms deep into the organic film was observed; (ii) no chemical interaction of In with carbon atoms of the CuPcF<sub>4</sub> molecule was found; (iii) some of the indium atoms, apparently, are located in places close to the pyrrole nitrogen of the CuPcF<sub>4</sub> molecule; (iv) during the process of the strong interaction of In atoms and pyrrole nitrogen atoms, a negative charge is transferred from indium to the CuPcF<sub>4</sub> molecule; (v) indium atoms self-organize into metal nanoparticles and clusters.

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## CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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