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The composition and the structure of thin films based on metal porphyrin complexes

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Abstract

Thin films based on CuTPP, ZnTPP and FeClTPP (TPP – TetraPhenylPorphyrin) complexes and manufactured by vacuum deposition under quasi-equilibrium conditions have been investigated. The hot-wall epitaxy method was chosen for the preparation of samples. The structure of objects and their composition were examined by scanning electron microscopy (SEM) and energy dispersive microanalysis (EDX). The CuTPP film was established to form whiskers about 20 nm in diameter and 5 µm in length. The structural features and morphology of ZnTPP and FeClTPP films' surface were revealed. The theoretical interpretation of obtained results was proposed that made it possible to relate the film structure with its composition.

Keywords: Organic electronics; Thin film; Metal porphyrin complex.

1. Introduction

Currently, organic materials are increasingly used in micro- and optoelectronics for creating photo- and light-emitting diodes, sensors, RFID tags, and other devices. There is a particular interest in compounds that may have some advantages over classic semiconductors, as the methods for obtaining the structures in mass production are simple and inexpensive, and it is possible to create flexible and transparent devices, modify the properties and the band structure of molecules [1].

Combining organic materials allows to fabricate donor-acceptor complexes, and molecular and bulk heterojunctions required in organic photonics and nanoelectronics [2]. Metalloporphyrins, in particular, are considered to be promising materials for these purposes [3].

Porphyrins are derivatives of the $C_{20}M_{14}N_4$ porphin whose molecules are formed by four pyrrole rings linked together by methine bridges. Porphyrins readily form metal complexes (chelates), with the metal ion incorporated into the core of a tetrapyrrolic macrocycle, replacing two hydrogen atoms. The macrocyclic structure with a high degree of porphyrin π-conjugation leads to a high absorption of light in the ultraviolet and visible regions of the spectrum, as well as imparts good donor properties to porphyrins and their derivatives [4]. Metalloporphyrins obtained via precipitation from solutions are capable of supramolecular self-assembly [5], wherein the self-assembly type of the resulting structure depends on the

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nature of the solvent [5]. Self-assembly can occur due to various intermolecular interactions (Van der Waals forces, (π-π)-stacking, hydrogen bonding), and in the condensed state lead to the formation of molecular assemblies or aggregates. Their luminescent, photochemical and other physical properties are different from those of monomolecular condensates, which must be taken into account when developing device structures.

Obtaining thin films by industrial methods offers appealing opportunities for practical applications of organic materials [6]. Currently, there are several most technologically advanced approaches to fabricating thin films from various organic materials. Such films can be prepared by thermal evaporation of molecules in a technical vacuum by using different evaporators, by applying polymeric films from the centrifuge (centrifugation), by polyionic assembly in solution, by applying the Langmuir–Blodgett technology, and by other methods. However, self-assembly in the films obtained by the Langmuir–Blodgett method can lead to 2D and 3D-aggregates appearing and to a loss of functional properties [7]. This means that one of the unsolved technological problems is developing a reproducible precision method for creating organic thin films with a predetermined structure.

Currently, self-assembly processes and their effect on film structure and the changes in the composition of porphyrin-containing thin films prepared by vacuum deposition remain virtually unstudied. Analyzing these processes is the goal of the present work.

2. Experimental procedure

In order to study the structure and composition of thin metalloporphyrin films of $\mathrm{Me}^{\mathrm{II}}$ meso-tetraphenylporphyrins (MeTPP), these films were obtained via vacuum deposition (a modified hot-wall method) under quasi-equilibrium conditions during an intense exchange interaction between the condensate and the vapor phase. In contrast to molecular beam deposition, these conditions facilitate self-assembly and make it possible for ordered structures of organic complex to form. Among the advantages of this method are the uniformity of the films obtained in one technological cycle and the good reproducibility of the properties of the films obtained under identical technological conditions. It is known that porphyrins are stable up to high temperatures considerably exceeding the sublimation temperature which lies in the 500–700 K range (depending on the type of metal).

We used the commercially available CuTPP and ZnTPP powders (by Sigma-Aldrich) for the initial mixture, along with a coordinated $\mathrm{Fe}^{\mathrm{III}}\mathrm{ClTPP}$ complex (obtained by the Institute of Chemical Physics (ICP) RAS, Moscow). These objects have been selected for the study because copper and zinc tetraphenylporphyrins are already widely used in organic electronics and other fields. The new ferric porphyrin complex with a coordinated chlorine atom, synthesized in the ICP RAS, has been chosen as a poorly studied object with potentially interesting magnetic properties.

Films of 200–600 nm thickness were deposited in vacuum (10^{-6} Torr) onto various substrates:glass with indium-tin oxide (ITO) coating (conducting amorphous);

BDS-10 grade boron-doped (111) silicon with p-type conductivity (crystalline semiconductors);freshly cleaved mica, KBr (dielectric).

The temperature values of the evaporator and the substrate were selected in view of our goal of facilitating the self-assembly processes during film growth. For this purpose, the film condensation temperature was to be as close as possible to the evaporator temperature, making up more than two-thirds of it. Despite the high temperature of the substrate, due to a high density of the gas-dynamic vapor flow, film growth rate was rather high, about 2 nm/s, allowing to obtain pure films in an ultrahigh vacuum instead of a technical one. Table 1 shows the compositions, mass values and basic conditions for obtaining the samples.

A JEOL JSM-6390 scanning electron microscope with the ultimate resolution of 3 nm was used for studying the self-assembly processes and the surface morphology. Transfer processes and film composition in the selected areas were investigated using an Oxford INCA Energy EDS (energy dispersive spectroscopy) microanalysis system for scanning electron microscopes with the ultimate sensitivity of 0.1 wt%. The surface of the films and their composition were investigated using electron beams with the energies of 5 and 8 keV mainly on samples with silicon (Si) substrates, as this provided the optimal ‘drain’ of the accumulated charge and, consequently, the best signal/noise ratio for this method.

To refine the experimental results and confirm the uniformity of the samples studied, spectra were accumulated on several large (about 200 $\mu\mathrm{m}^2$) sites in about 5–7 areas; when confirming the uniformity of the film in discrete points, the experimental data was averaged, generalized and used for further analysis.