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Features of obtaining and properties of thin films organic semiconductors

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In recent decades, thin films of organic semiconductors (OS), or, as they are also called, organic molecular crystals, have attracted special attention in connection with a number of proposals for their use in functional units of modern electronics, and therefore in modern technological equipment. At the same time, the optical, electrophysical and photoelectric properties of OS are very important, which are determined both by the structure of organic molecules, that is, the starting material, and by the crystal structure of condensates, that is, by the technological conditions of film production. In this regard, this article presents the results of studies of some properties of OS and the technology of obtaining thin films based on them. OS are characterized by weak intermolecular bonds of the Van der Waals type, which causes the low energy of their crystal lattice. In this regard, the electronic structure of individual molecules during the formation of a crystal does not change significantly, and the properties of the crystals almost completely preserve the individual features of the molecules in combination with new properties caused by their collective interaction. This determines the main features of optical and electrophysical properties of OS, their energy structure of neutral and ionized states. In this article, it is experimentally confirmed that the planar structure of atoms of molecular crystals, in particular, linear acenes, and therefore the number of π -electrons responsible for exciton absorption in the visible region of the spectrum determines the position of the edge of their own optical absorption. It was also confirmed that the long-wavelength shift of the optical absorption edge of thin films of phthalocyanines is observed when atoms of heavy elements, for example, lead, are introduced into the molecule. When atoms of lighter elements are introduced into the phthalocyanine molecule, their planarity is not disturbed, and the long-wavelength shift of the edge is much smaller. An explanation of such changes is presented based on the interaction of foreign atoms with the π -electron system of phthalocyanine rings of neighboring molecules. The significant influence of the technological parameters of production, in particular the temperature of the substrate during thermal sputtering, on the crystal structure and optical properties of thin films of linear polyacenes and metallophthalocyanines has been demonstrated and substantiated. The possibility of controlling and presetting the necessary properties of thin-film condensates of molecular crystals is shown.

Key words: organic semiconductors, molecular crystals, thin films, production methods, linear acenes, phthalocyanines.

Особливості отримання і властивостей тонких плівок органічних напівпровідників

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В останні десятиліття привернули до себе особливу увагу тонкі плівки органічних напівпровідників (ОН), або, як їх це називають, органічних молекулярних кристалів у зв'язку із цілим рядом пропозицій щодо їх використання у функціональних вузлах сучасної електроніки, а отже в сучасному технологічному обладнанні. При цьому дуже важливими є оптичні, електрофізичні та фотоелектричні властивості ОН, які визначаються як будовою органічних молекул, тобто вихідним матеріалом, так і кристалічною структурою конденсатів, тобто технологічними умовами отримання плівок. У зв'язку із цим, в даній статті викладені результати досліджень деяких властивостей ОН і технології отримання тонких плівок на їхній основі. ОН характеризуються слабкими міжмолекулярними зв'язками типу Ван-дер-Ваальсівських, що зумовлює низьку енергію їх кристалічної ґратки. У зв'язку із цим електронна структура окремих молекул при утворенні кристалу суттєво не змінюється, і у властивостях кристалів майже повністю зберігаються індивідуальні особливості молекул у поєднанні з новими властивостями, зумовленими їх колективною взаємодією. Це визначає головні особливості оптичних і електрофізичних властивостей ОН, їхню енергетичну структуру нейтральних та іонізованих станів. В даній статті експериментально підтверджено, що планарна структура атомів молекулярних кристалів, зокрема, лінійних аценів, а отже і кількість π -електронів, які відповідають за екситонне поглинання у видимій області спектру визначає положення краю їх власного оптичного поглинання. Підтверджено також, що довгохвильовий зсув краю оптичного поглинання тонких плівок фталоціанінів спостерігається при введенні в молекулу атомів важких елементів, наприклад, свинцю. При введенні в молекулу фталоціаніну атомів легших елементів їхня планарність не порушується, і довгохвильовий зсув краю значно менший. Представлено пояснення таких змін на основі взаємодії чужорідних атомів з π -електронною системою фталоціанінових кілець сусідніх молекул. Продемонстровано і обґрунтовано суттєвий вплив технологічних параметрів отримання, зокрема, температури підкладки при термічному напilenні на кристалічну структуру і оптичні властивості тонких плівок лінійних поліацинів та металофталоціанінів. Показано можливість керувати і наперед задавати необхідні властивості тонкоплівкових конденсатів молекулярних кристалів.

Ключові слова: органічні напівпровідники, молекулярні кристали, тонкі плівки, технологічні методи отримання, лінійні ацени, фталоціаніни.

Introduction

In previous reviews (Tsizh & Dziamski, 2019; 2020; 2022), we provided an analysis of existing methods of applying thin films of inorganic semiconductor materials. In recent decades, thin films of organic semiconductors (OS), or, as they are also called, organic molecular crystals, have attracted special attention in connection with a number of proposals for their use in functional units of modern electronics, and therefore in modern technological equipment. In a significant part of such devices, the properties of interfaces between organic thin films with metals and inorganic semiconductors are used. At the same time, the optical, electrophysical and photoelectric properties of OS are very important, which are determined both by the structure of organic molecules, that is, the starting material, and by the crystal structure of condensates, that is, by the technological conditions of film production. In this regard, this article presents the results of studies of some properties of OS and the technology of obtaining thin films based on them. OS are characterized by weak intermolecular bonds of the van der Waals type, which causes the low energy of their crystal lattice (Pope & Swenberg, 1999; Corpinot & Bučar, 2019). In this regard, the electronic structure of individual molecules during the formation of a crystal does not change significantly, and the properties of the crystals almost completely preserve the individual features of the molecules in combination with new properties caused by their collective interaction. This determines the main features of optical and electrophysical properties of OS, their energy structure of neutral and ionized states (Simon & Andre, 1985).

As a result of weak intermolecular interaction forces in OS, there is a pronounced localization of free charge carriers on individual molecules, in contrast to typical inorganic semiconductors with delocalized carriers in the entire volume of the crystal (Simon & Andre, 1985). Due to the strong localization, the charge carriers move to OS with the help of separate jumps with a time interval long enough for the occurrence of electronic polarization of the

crystal due to the Coulomb interaction of the carriers with the weakly bound π -electrons of the neighboring molecules of the crystal lattice.

Such electronic crystallization is a significant multi-electron process in OS, therefore, in principle, the band theory traditional for inorganic semiconductors cannot be applied to them within the one-electron approximation (Pope & Swenberg, 1999). The energy scheme of the ionized states of OS is most often built according to the phenomenological model of Lyons, taking into account the energy parameters of the crystal, the effects of electronic polarization and the states associated with charge transfer (Corpinot & Bučar, 2019). The energy position of narrow zones of ionized states of OS is determined by empirical molecular parameters (ionization energy of the molecule, its electron affinity) and parameters of the multi-electron interaction of charge carriers with neighboring molecules of the crystal lattice (electron polarization energy). According to the Lyons model, the following equality of the sum of the parameters of the ionized molecules and the crystal is fulfilled:

$$I_g + A_g = I_c + A_c = E_g + 2A_c = K_c, \quad (1)$$

where I_g , I_c are the ionization energy of the molecule and crystal, respectively; A_g , A_c – electron affinity of molecule and crystal; E_g is the band gap width, which is determined for OS as the energy distance from the conduction level of a localized hole to the conduction level of electrons with the lowest energy; K_c is a characteristic constant of the polarization model of ionized states.

Condition (1) is most precisely fulfilled for linear polyacenes, and in this case the constant $K_c = 7.93 \pm 0.6$ eV (Pope & Swenberg, 1999). A comparison of the parameters of the ionized states of linear acene crystals convincingly shows the influence of the molecular structure on these parameters with an increase in the number of benzene rings and, accordingly, π -electrons. The I_c and E_g parameters monotonically decrease, while

the A_g parameter increases, the quantum efficiency value increases significantly. The significant influence of heteroatoms on the energy structure of the crystal is evidenced by a comparison of the parameters of the isostructural derivatives of tetracene – tetrachlorotetracene and tetrathiotetracene with the parameters of tetracene. In the crystals of these derivatives, the value of the I_s , E_g parameters decreases and the value of the A_c parameter increases.

The chemical composition of OS is determined by the carbon-hydrogen basis of their molecules. For example, for pure linear polyacenes, the chemical formula of the molecule has the form $C_{4n+2}H_{2n+4}$, where n is the number of benzene rings in the molecule. When doping acenes and phthalocyanines, one or more alloying atoms are appropriately included in the composition of the main molecule, without changing the type of crystal lattice, and do not significantly affect the intermolecular bond forces and mechanical properties of OS, although their energy spectrum may undergo significant changes. Under the influence of external fields, primarily during heating, weak intermolecular bonds are quickly destroyed, therefore the sublimation temperatures of OS are relatively low (600...800 K), which allows them to be sprayed in a vacuum without decomposition of molecules. At the same time, high-temperature or high-energy methods of obtaining thin films of complex semiconductors, such as electron beam sputtering, cathode sputtering, sputtering followed by pyrolysis, the method of gas transport reactions, liquid phase epitaxy, and others cannot guarantee the preservation of the integrity of the molecule, and therefore for production of thin OS films is rarely used. Recently, the Langmuir-Blodgett method has been widely used to apply very thin OS layers, including monomolecular ones (Luo et al., 1992; Khalid & Jassem, 1993). Thin films of OS, especially metallophthalocyanines, are obtained by the method of deposition (epitaxy) from molecular beams of organic compounds (Tada et al., 1992; Maruno et al., 1993), but due to the high cost of the equipment, this method was not widely used. A known method of obtaining OS films by polymerization without a solvent (Pankow et al., 1993). Other types of methods of applying thin films are also used.

Material and methods

One of the most used methods of applying OS thin films is thermal vacuum sputtering (Bunshah, 1994; Baumann et al., 1996; Seshan, 2002; Frey & Khan, 2015; Aksimentyeva et al., 2018). As already mentioned, the low sublimation temperature ensures the transition of OS molecules to the gas phase, transfer to the substrate and film growth without dissociative-associative processes at the molecular level. A very important factor in the thermal sputtering of organic molecular crystals is a high degree of vacuum (Pankow et al., 1993; Hosokawa et al., 2008), since foreign atoms, especially residual gases, are effectively captured by OS molecules and significantly affect the entire spectrum of their electrophysical, optical, photoelectric and other properties. In addition, during thermal sputtering of OS, minimum sublimation rates

should be set in order to avoid the transfer of high-molecular fractions to the gas phase and the formation of non-homogeneous areas on the condensation surface.

Substrate temperature is a determining factor for the crystal structure of OS during thermal sputtering (Seshan, 2002; Frey & Khan, 2015; Aksimentyeva et al., 2018). As a rule, thin OS films are characterized by polymorphism with a large number of crystalline phases, starting from a quasi-amorphous structure at room temperature of the substrate, and ending with oriented polycrystalline modifications at $T_s = 350...500$ K. For example, for PbPc films, it is known that at $T_s < 310$ K, films of quasi-amorphous modification are obtained, and at $T_s > 430$ K, films of the most stable triclinic modification are obtained (Pankow et al., 1993). There are no unambiguous data on the conditions for obtaining PbPc films of monoclinic modification by thermal spraying in a vacuum, and we assume that they can be obtained at values of $T_s = 340...380$ K. In our research, thin films of linear polyacenes and metallophthalocyanines were obtained by thermal vacuum sputtering in a URM 3.279.047 unit with an ion-heterogeneous high-vacuum pump at a residual gas pressure of $3...7 \cdot 10^{-5}$ Pa from a molybdenum evaporator. The temperature of the substrates during sputtering was set from room temperature to 403 K. It was experimentally confirmed that high-quality OS films without heterogeneous inclusions, with properties close to single crystals, are deposited at low sputtering speeds. Therefore, the sputtering rate of OS was $0.5...1.0$ nm·s⁻¹. Control of sputtering speed and film thickness was carried out using the KST-1 ionization sensor, the work of which is based on the partial ionization of the material transferred to the substrate by an electron beam, and the measurement of the resulting ion current proportional to the density of the vapor phase, and, accordingly, the speed of film sputtering. For each substance, the sensor was calibrated according to the results of thickness measurements on an interference microscope MII-4.

Optical absorption spectra of polymer films were obtained using a modified two-beam optical spectrometer Specord M-400 with the following measurement parameters: spectral range: 200...900 nm, slit width: 1 nm, integration time: 1 s, scan step: 1 nm, recording speed: 10 nm/s. Optical beam of the spectrometer passed directly through the film and the substrate, was collimated and perpendicular to the surface of the film. Surface reflection when measuring spectra optical absorption was not taken into account because the relative changes. All measurements were performed at temperature 293 ± 1 K. The analysis of the results was performed using a standard correlation program, in which the relative error in the entire measurement range did not exceed 1.5 %.

Results and discussions

Neutral excited states in molecular crystals are associated with the emergence of a set of discrete levels of small radius excitons of the Frenkel exciton type (Pope & Swenberg, 1999). In the absence of intermolecular interaction forces (that is, in the gaseous state or solutions), the energy spectra of organic molecules are characterized by a set of bands formed from individual

atomic levels as a result of intramolecular and thermal interaction. During the formation of molecular crystals, the forces of weak intermolecular interaction are imposed on the energy spectrum of molecules, as a result of which the energy bands of individual molecules are split into narrow zones of the order of 0.1...0.3 eV and shift to the vacuum level towards lower energies. To date, the energy structure of the neutral states of molecular crystals and dyes has mainly been studied. In the process of OS light absorption, photons are converted into Frenkel excitons and phonons and neutral excited states are formed, associated with various transitions from filled π - and σ -states to higher singlet, ionized, and surface states (Simon & Andre, 1985). The energy of σ -states is usually higher than 6 eV and they are responsible for absorption in the far ultraviolet region of the spectrum, and π -states for absorption in the visible and near infrared and ultraviolet regions. In the optical spectra of organic molecular crystals, the spectral properties of individual molecules and their electronic vibrational structure are preserved. At the same time, in the absorption spectra of crystals, in comparison with the spectra of individual molecules, there is a broadening of the bands and a slight shift of their maxima towards lower energies. A characteristic feature of molecular crystals is the Davidiian splitting of spectral bands caused by the geometrically non-equivalent arrangement of identical molecules in the unit cell. In the Table 1 presents the positions of the eigenabsorption edge of thin films deposited by us on some typical OS from a number of linear polyacenes based on the approximation of their optical absorption spectra.

Table 1
Position of the intrinsic optical absorption edge in organic semiconductor thin films

No s/p	Organic semiconductor	The wavelength of the intrinsic optical absorption edge, nm
1.	Anthracene	412
2.	Tetracene	546
3.	Tetrachlorotetracene	617
4.	Pentacene	709
5.	Tetrathiotetracene	824

It can be seen that with an increase in the number of benzene rings (from anthracene to pentacene), a shift of the edge of the own absorption to the long-wavelength region of the spectrum is observed. This is caused by an increase in the number of π -electrons in linear acenes, which are responsible for exciton absorption in the visible region of the spectrum. A similar effect of a long-wavelength shift of the eigenabsorption edge, as well as the appearance of new bands in the absorption spectrum, is observed for tetracene derivatives – tetrachlorotetracene and tetrathiotetracene (see Table 1). These effects are due to the increase in intermolecular interaction forces when chlorine and sulfur atoms, respectively, are introduced into the tetracene molecule.

In the Table 2 presents the position of the edge of the intrinsic absorption of thin films of phthalocyanine deposited by us and a number of its derivatives based on the approximation of their optical absorption spectra.

Table 2
Position of the edge of the intrinsic optical absorption in thin films of phthalocyanines

No s/p	Organic semiconductor	The wavelength of the intrinsic optical absorption edge, nm
1.	H ₂ Pc	412
2.	Cu ₂ Pc	546
3.	ClAlClPc	617
4.	PbPc	709

For phthalocyanines, a long-wavelength shift of the absorption edge is observed when atoms of heavy elements, for example, lead, are introduced into the molecule. This is due to the fact that the heavy lead atom goes beyond the plane of the molecule, and its interaction with the π -electron system of the phthalocyanine ring of the neighboring molecule increases significantly (Davydenko et al., 2016). When atoms of lighter elements are introduced into the phthalocyanine molecule, their planarity is not disturbed, and the long-wavelength shift of the edge is much smaller (see Table 2).

In thin OS films, by varying the technological conditions of production, it is possible to change their crystalline and, therefore, their energy structure. This is confirmed by the optical absorption spectra of pentacene thin films obtained at different substrate temperatures in comparison with the absorption spectrum of a single crystal. In the long-wavelength region of the optical absorption spectra of an oriented crystalline film and a single crystal, *a*- and *b*-components of the David splitting of the 1st singlet transition are observed. In the quasi-amorphous film, instead of the Davidiian doublet, a more intense *b*-component of the 1st transition is observed, which indicates the absence of Davidiian splitting and is related to the chaotic arrangement of molecules (Corpinot & Bučar, 2019).

Already one of the first studies of the optical absorption spectra of phthalocyanine films obtained by vacuum sputtering showed their strong dependence on the crystal structure, which was determined by the temperature of the substrate during vacuum sputtering. Most often, such a dependence is observed in the area of the lowest energy, so-called *Q*-transitions. The absorption caused by these transitions is mainly in the spectral region 1.5...2.5 eV and consists of two intense broad and partially overlapping bands or bands (1.6...1.8 eV), which are denoted by *Q_x*, *Q_y*, and are associated with electronic transitions of Frenkel excitons, and with at least two weaker bands associated with intramolecular vibrations in the region of 2.0...2.5 eV. Common to most phthalocyanines is that the intensity of the *Q_x* band (1.7...1.8 eV) in *a*-form films is greater than the intensity of the *Q_y* band (1.6...1.7 eV), and in *b*-form films – on the contrary, which can be used to identify their crystal structure.

This dependence is characteristic of phthalocyanine films with the most symmetrical molecules, a typical representative of which is CuPc. With decreasing symmetry of Pc molecules, that is, with increasing ionic radius and atomic mass of their central atom, this dependence becomes more complicated. This is due to the

contribution of transitions caused by states (excitons) with charge transfer, which are not present in Pc molecules, as well as the interaction of nearby molecules of the crystal lattice. The intensity of such transitions in CuPc is low and they appear as an inflection on the long-wavelength side of the Q_y band, and their existence can be proven by absorption data.

The intensity of the π -bands, which indicate absorption in the visible and near-ultraviolet and infrared regions, increases, and the energy of the maximum decreases in the range of CuPc, H₂Pc, GaCIPc, VOPc, PbPc. As a result, the intensity of the π -bands in PbPc crystals of triclinic modification is greater than the intensity of the Q -bands, and their maximum is at 1.35 eV, which affects the dependence of the absorption band parameters on the T_S values. In PbPc films, the Q_x - and Q_y -bands strongly overlap, and only the electronic Q_x -band with a maximum at 1.8 eV and a π -band with a maximum at 1.4 eV are clearly visible. With increasing T_S , i.e., when transitioning from a monoclinic to a triclinic modification, the intensity of the Q_x -bands decreases, and the Q_y -band increases. The maximum intensity of the Q_y -bands, and therefore the content of crystals of the triclinic modification, is observed at values of $T_S = 460\text{--}480$ K.

To confirm such data, the reflection spectra of PbPc films obtained at $T_S = 300$ and 480 K, as well as the corresponding single crystals of triclinic modification in unpolarized light, were investigated. Measurements showed that the reflection spectra of single crystals and films at $T_S = 480$ K are very close to each other and differ significantly from the reflection spectra of films at $T_S = 300$ K. Note that the optical density D_K of the films at $h\nu = 2.0 \pm 0.02$ eV is the same (does not depend on the crystal structure of the films with an accuracy of up to 5 %, that is, twice the accuracy of measuring the thickness of thin PbPc films, equal to approximately 10 nm). Since there is a possible scatter of experimental data (weak dependence of film thickness on T_S values), to prove the presence of an isosbestic point at $h\nu = 2.0$ eV, we measured the absorption spectra of films obtained simultaneously at $T_S = 300$ K before and after one-hour annealing at different temperatures from the range of 380–500 K. The spread of D_K values before annealing was 1 %, and after annealing – 3 %. This made it possible to use the D_K value to control the thickness of the films after sputtering, and the ratio of the optical densities in the area of the Q_y -band maximum and the D_K values to qualitatively control the content of triclinic crystallites in the films. The relevant comparisons showed that the ratio $(D_R - D_K)/2D_K$ in the first approximation is proportional to the content of triclinic modification in PbPc films. To qualitatively control the content of this modification, you can also use the ratio of D_R values to the optical density D in the absorption maximum of the obviously monoclinic modification at $h\nu = 1.8$ eV. The possibility of estimating the content of monoclinic modification from the absorption spectra of PbPc films remains debatable, since the absorption and reflection spectra of crystals of monoclinic modification were not measured due to their small size, and a peak at $T_S = 400 \pm 10$ K observed on the dependence of D_R/D_K on T_S , which only allows us to predict at these T_S values, the maximum content of monoclinic modification.

Similar regularities were observed by us for other metallophthalocyanines, while the position of the isosbestic point depends slightly on the nature of the central atom. Polyacene films also have spectral regions in which the optical absorption coefficient does not depend on the crystalline structure of the films. For example, in Pn films, when T_S values increase from 100 to 400 K, a smooth transition from a quasi-amorphous to an oriented polycrystalline film is observed, which is accompanied by a significant decrease in the absorption coefficient in the region of the b -component of the David doublet with a maximum at $h\nu = 1.87$ eV, and in the region of the electron-vibrational transition $h\nu = 2.0\text{--}2.25$ eV, it practically does not change.

Conclusions

In this article, it is experimentally confirmed that the planar structure of atoms of molecular crystals, in particular, linear acenes, and therefore the number of π -electrons responsible for exciton absorption in the visible region of the spectrum determines the position of the edge of their own optical absorption. It was also confirmed that the long-wavelength shift of the optical absorption edge of thin films of phthalocyanines is observed when atoms of heavy elements, for example, lead, are introduced into the molecule. When atoms of lighter elements are introduced into the phthalocyanine molecule, their planarity is not disturbed, and the long-wavelength shift of the edge is much smaller. An explanation of such changes is presented based on the interaction of foreign atoms with the π -electron system of phthalocyanine rings of neighboring molecules.

The significant influence of the technological parameters of production, in particular the temperature of the substrate during thermal sputtering, on the crystal structure and optical properties of thin films of linear polyacenes and metallophthalocyanines has been demonstrated and substantiated. The possibility of controlling and presetting the necessary properties of thin-film condensates of molecular crystals is shown.

Prospects for further research. In further research, the optimization of methods for obtaining thin films of multicomponent organic semiconductors should be continued in order to improve their properties. For this, new designs of devices for the synthesis of thin films should be developed and technological regulations for their production should be improved.

Conflict of interest

The authors declare that there is no conflict of interest.

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