Thin-film electronic devices based on conjugated structures

E G Shubenkova
Omsk State Technical University, 11, Mira Ave., Omsk, 644050, Russian Federation

Abstract. In this research, the annealing method in solvent vapor was adapted to produce single-crystal thin films of oligomers based on thiophene and benzene. Monocrystalline silicon substrates with a layer of silicon oxide deposited on it were used. Monocrystals grew from the solutions directly on substrates at a room temperature. Variable parameters for crystal growth were: solvent type (toluene, dichlorobenzene), solution concentration (from 1 g l⁻¹ to 0.03 g l⁻¹), method of application (spin-coating, drop-casting). The crystallinity and geometry of the synthesized single crystals were determined on a Carl Zeiss AXIO LAB.A1 microscope by microscopy and polarization microscopy. The substrates are already a complete part of the OTFT architecture (gate and dielectric layer). After plotting contacts of PEDOT:PSS organic field-effect transistors were obtained and they electrophysical characteristics were measured. It is established that in the obtained OTFT semiconductor crystals has hole conductivity with a hole mobility \(\mu = 0.03 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}\) in a linear mode.

1. Introduction
Both inorganic and organic substances can possess semiconductor properties, but their electrical conductivity is usually small (\(s \sim 10^{-10} \text{ohm}\cdot\text{cm}\)) and strongly increases under the influence of light [1]. For the crystals and polymers based on perylene, violanthrene, and some other organic semiconductors at room temperature, conductivity comparable to the conductivity of good inorganic semiconductors was observed [2-3]. Organic compounds with semiconductor properties and their derivatives can form the basis of such electronic elements and devices as field effect transistors, electroluminescent diodes, sensors, memory devices, photocells, emitting diodes (OLEDs), OLED displays and solar cells. That is opens the prospect of cheaper production and expands the field of application of electronic devices [5-8]. The combination of semiconductor properties with the elasticity of some organic semiconductors makes it possible to fabricate on their basis working elements in the form of flexible tapes and fibers [2] and use simple manufacturing techniques with a low final cost of the product. Organic light-emitting diodes have already entered industrial production, devices based on them can be bought in any supermarket of equipment. OLED-TVs have a high degree of color rendition and low power consumption, but the control matrix in them is still made on silicon transistors.

Field-effect transistor (FET) – the basis of modern electronics and is the main element of microprocessors underlying almost any electronic device. FET is a semiconductor device in which the output orderly motion of charged electrical particles is controlled by an electric field. The most common material for the production of FET is monocrystalline silicon. Because of its cost, it is not suitable for applications where it is required to cover a large area, for example, in the manufacture of LCD displays with active matrices. To reduce the cost of production can use amorphous silicon, polycrystalline silicon or organic semiconductors [11]. It is possible to create devices that combine the functions of control and image transmission. Such devices are organic light-emitting field-effect
transistors or light-transistors. For their creation you need materials that have both good electrical and luminescent properties. Materials that can solve this problem are crystals of organic semiconductors. In order to make organic electronics devices competitive with inorganic devices, a fast, efficient and accurate production technology have to be developed. The determining factor for obtaining an effective transistor and light-transistor is the quality of the organic layer deposited on the substrate [9-11]. This makes us think about improving the technology of applying organic layers with a controlled thickness and a given morphology, with the required electrophysical properties for different types of substrates.

2. Formulation of the problem
This work is devoted to the development and optimization of growth conditions of high-efficiency monocrystal structures from solutions on the substrate surface for devices of organic electronics.

The purpose of this work is to create monocrystal layers of organic semiconductors from solutions on substrates for organic field-effect transistors (OFETs). The tasks to be accomplished to achieve this aim include:

– development and optimization of organic semiconductors thin crystals growth conditions from solutions;
– study of the their crystallization processes;
– characterization of the obtained crystals properties by microscopy;
– manufacturing OFET and other devices using the piezoelectric printing technology and measuring the electrical characteristics of the resulting devices.

3. Theoretical basis
For the manufacture of semiconductor devices, both monocrystals and polycrystalline materials are used. Monocrystals are simpler systems, with a more perfect structure than polycrystalline materials. They are most thoroughly studied, physical phenomena in them are more amenable to calculations, and they provide greater reliability and identity of semiconductor devices parameters. The best characteristics of thin-film devices were obtained on monocrystals. In order to reduce the cost and simplify the production of organic electronics devices, monocrystals should be obtained from solutions directly on the substrate for the final device. This opens the possibility of using flexible polymer substrates and, as a result, the creation of portable electronic devices. In addition, it is necessary to improve the technology of depositing semiconductor layers with a controlled thickness and morphology, with the required electrophysical properties for various types of substrates. In this case, monocrystallinity is a necessary requirement for ensuring high mobility of carriers in the final device.

It is believed, that in organic field transistors (OFETs), charge transport occurs mainly in several molecular layers of the semiconductor adjacent to the shutter layer, which corresponds to the conducting channel thickness of 3–5 nm [10]. Therefore, the resulting monocrystal structures should have a thickness of several molecular layers to achieve low currents in the switched-off state.

On the other hand, the methods commonly used for making OFETs give a conductive channel thickness of 30 to 100 nm, which increases the material consumption, and also increases the current in the closed state of the OFET. In this regard, it is important to understand how many molecular layers of an organic semiconductor are required for the efficient operation of the OFET. Therefore, it is relevant to search for a technique for manufacturing OFET with a small number of molecular layers (1, 2, etc.) without compromising their electrical properties [11-12].

To date, among the organic semiconductors, the best electrical characteristics have been obtained on conjugated oligomers [13]. The mobility values in them exceeded the mobility in amorphous
silicon. At the same time, organic molecules make it possible to create flexible, lightweight and cheaper devices, since they allow replacing expensive processes used in the production of conventional electronics (lithography) with cheaper solution and printing technologies (inkjet, offset or gravure printing) [14].

4. Experimental

Oligomers with conjugated bonds consist of a chain of carbon atoms, bound by strong $\sigma$-bonds and weak $\pi$-bonds. The $\pi$-bonds form an electron cloud along the polymer chain. This is an explanation of the fact that polymers have semiconducting properties: strong absorption in the visible range, high mobility of charge carriers, etc. [9].

Materials based on the chemistry of benzene and thiophene are very various, have a different molecular design, and usually have a high mobility of charge carriers, ease of obtaining from solutions, oxidative and thermal stability, and else an effective luminescence at certain molecular structure. In this paper we used organic semiconductors, which are molecules of oligomers based on thiophene and benzene, the interest in which is due to the fact that they have good conductivity values, as well as good solubility.

Silicon substrates for the growth of crystals were used with a layer of silicon dioxide 200 nm to 850 nm thick serving as a dielectric with a permittivity $\varepsilon = 3$, the specific capacitance of the dielectric was $C_i = 13.2 \, \text{nF/cm}^2$. Substrates of monocrystalline silicon with a layer of silicon oxide deposited on it are a complete part of the OFET architecture, namely, they act as a gate and a dielectric layer on which a conducting layer of an organic compounds are deposited from the solutions and piezoelectric printing contacts are made from a conductive material.

To create a thin single-crystal film on the substrate, spin-coating method and the method of applying a large drop of solution onto a substrate (drop casting) were used [14-15]. The methods make it possible to obtain thin films of a given thickness, which can be controlled by the solution concentration and the rotation speed of the substrate. In the experiment the device of the company Specialty Coating Systems was used. The parameters at which the semiconductor was deposited are shown in table 1.

| Parameter                  | Value        |
|----------------------------|--------------|
| Time $t$ (min)             | 0.5          |
| Acceleration time $t_a$ (min) | 0.5         |
| Temperature $T$ ($^\circ$C) | 25-50        |
| Angular velocity $\omega$ (turn min$^{-1}$) | 400-800      |

Oligomers were applied from solutions in dichlorobenzene and toluene at concentrations of 1000 to 30 mg / l.

The resulting films were analyzed by microscopy and polarization microscopy using a Carl Zeiss AXIO LAB.A1 microscope.

A highly conductive polymeric dispersion of poly (3,4-ethylenedioxy-thiophene) -polysulfonic acid (PEDOT: PSS) (Heraeus Clevios grades) for the application of contacts in the manufacture of OFET
was used. Polyoxyethylene (20) sorbitan monolaurate surfactant (polysorbate 20) to change the surface tension of PEDOT: PSS was used.

Measurements of the I-V characteristic of the OFET samples were made on a laboratory experimental setup based on a precision source – the Keithley 2400 meter at room temperature. The device is equipped with two coordinate microchips for connecting the source and drain electrodes and a video microscope.

5. Results and considerations
The results of microscopy showed that under conditions of annealing in a solvent dichlorobenzene, by spin-coating from a solution with an oligomer concentration of 120 mg / l, thin single-crystal films of an organic semiconductor with a thickness in the range from 2.5 nm to 4 nm were obtained (figure 1).

![Microscopy of monocrystals.](image)

On the basis of organic conjugated structures obtained on silicon substrates the PEDOT: PSS contacts were applied. As a result OTFTs were obtained and the electrophysical characteristics of the obtained devices were measured. Dependences of $I_d$ on $V_d$ for various $V_g$ (output characteristics) and $I_d$ on $V_g$ (transfer characteristics) for various $V_d$ were obtained. The source electrode was grounded and all the voltages were counted out from it. For the sample of an organic thin-film-field-effect transistor (OTFT) obtained in the laboratory by spin coating, the following output and transfer characteristics were obtained (figures 2-3).
Figure 2. Output characteristics of a monocrystal oligomer films.

Figure 3. Transfer characteristics of a monocrystal oligomer films.

In the framework of the model described in [9], the mobility does not depend on the gate voltage. The equations for calculating $\mu$ obtained for inorganic field-effect transistors both in the linear regime and in the current saturation regime can be successfully applied to the OTFT [9].

From the volt-ampere characteristics of the OTFT, the mobility of the charge carriers $\mu$ was calculated for various $V_g$ in the linear regime by the formula:

$$I_D = \frac{W}{L} \cdot \mu \cdot C \cdot (V_g - V_f) \cdot V_g,$$

and in saturation mode:
$I_D = \frac{W}{2L} \cdot \mu \cdot C \cdot (V_G - V_T)^2,$

where $I_D$ and $V_D$ are the current and voltage between the source and drain, $V_G$ stands for the gate voltage, $V_T$ is the threshold voltage at which the current starts to rise, $C$ is the capacitance of the unit area of the dielectric, $W$ and $L$ are the width and length of the conductor channel, $\mu$ is the mobility of the main charge carriers [14-15].

As a result of the processing of the experimental data, it was established that in the thin-film organic field-effect transistor obtained in a linear mode, semiconductor crystals have a hole conductivity with mobility up to $\mu = 0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

6. Summary
As a result of the studies, the following conclusions were drawn:

1. The effect of the solvent type and the concentration of an organic semiconductor on the parameters of synthesized monocrystals has been established.
2. Obtained thin-film organic field-effect transistor (OTFT) on the basis of a monocrystal.
3. Volt-ampere characteristics of the thin-film organic field-effect transistor were measured.
4. It was established that in the thin-film organic field-effect transistor obtained in a linear regime, semiconductor crystals have hole conductivity with mobility up to $\mu = 0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Acknowledgments
The work was carried out within the framework of an individual internship program at ILC M.V. Lomonosov Moscow State University. The author is grateful to Prof. D.Y. Parashchuk and A.V. Glushkova for scientific advice and assistance in the formulation of the experiment, as well as materials provided for the study.

References
[1] Smits E C P and Mathijssen S G J 2000 Nature 455 pp 956–959
[2] Ranke P et. all 1997 Appl. Phys. Lett. 71 pp 1332–1334
[3] Haskal E I, Buchel M and Duineveld P C 2002 MRS Bull. 27 p 864
[4] Brown T M, Friend R H , Millard I S et. all 2001 Appl. Phys. Lett. 79 p 174
[5] Ohmori M and Azároff V Leonid 1993 J. Appl. Phys. 32 pp 1663–1666
[6] Kido J, Ohtaki C, Hongawa K, Okuyama K and Nagai K 1993 J. Appl. Phys. 32 p 917920
[7] Murata N, Malliaras G G, Uchida M, Shen Y and Kafafi Z H 2001 Chem. Phys. Lett. 339 pp 161–166
[8] Baldo M A, Lamansky S, Burrows P E, Thompson M E and Forrest S R 1999 Appl. Phys. Lett. 75 p 4–6
[9] Horowitz G 1999 Physics of organic field-effect transistors In: Semiconducting polymer: chemistry, physics and engineering (Weinheim: WileyVCH)
[10] Dodabalapur A, Torsi L and Katz H E 1995 Science 268 pp 270–271
[11] Mathijssen S G J, Smits E C P et. all 2009 Nature Nanotechnology 4 pp 674–680
[12] Higashi H, Hosokawa C, Nakamura H and Kusumoto T 1995 Appl. Phys. Lett. 67 pp 3853–3855
[13] Dimitrakopoulos C D and Malenfant P R L 2002 Adv. Materials 14 p 99
[14] Tanase C, Meijer E J, Blom P W M and D.M. de Leeuw 2003 Organic Electronics 4 pp 33–37
[15] Lim J, Lee W, Kwak D and Cho K 2009 Langmuir 25 pp 5404–5410