Basic Structures of Organic and Biologic Electrochemical Transistors

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Abstract: Electrical current control in organic electrochemical transistors (OECT) and bioelectrochemical transistors (PCC-OECT) is carried out by changing the speed and direction of red-ox reactions. Unlike other types of transistors, this allows them to be used at a very low initial voltages and creates other functional and technological advantages. The significance of these benefits depends on the structure of transistors. This article briefly describes the most relevant structures of electrochemical and bioelectrochemical transistors which are based on the semiconductor PEDOT: PSS with the aim of comparative assessment of their effectiveness.
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1. Introduction

Organic polymers are now widely applied in electronic equipment. Various types of transistors are developed on the basis of organic semiconductors: organic field effect transistors (OFET) [1], organic electrochemical transistors (OECT) [2], electrolyte-gated organic field effect transistors (EGOFET) [3], organic light-emitting field-effect transistors (OLEFET) [4], and ion bipolar junction transistors (IBJT) [5].

One important feature of OECT transistors when compared to organic field-effect and bipolar transistors is their ability to function at very low voltages. This is caused by the fact that the current control in OECTs is defined by the speed of the electrochemical red-ox reaction. On the other hand, in inorganic field-effect and bipolar transistors, current control is achieved by changing the electric field or resistance of the electron-hole transition, which due to its innate structure demands higher initial voltage than an electrochemical reaction.

In addition, OECTs have also other advantages over the aforementioned types of organic transistors and over traditional solid-state transistors (MOSFET, etc.), which allow simple and the cheap manufacturing. Due to many promising qualities, OECTs have good prospects of application in the manufacture of highly sensitive chemical and biological sensors, fabric fibers, RFID tags, contrast screens, large-scale integrated circuits and other electronic products. The aim of the article is to review the basic structures of OECTs and to compare their effectiveness in various applications.

There are two equivalent terms for designation of composition and arrangement of the basic elements within a transistor: architecture and structure (see, e.g., references [2] and [10]). In this article we use the term "structure."

2. Structures of the Primary OECT Models

The experimental structure of the first OECT model was described in articles by H.S. White et al [6] and in more detail by J.W. Thackeray et al [7]. The plate of a monocrystalline silicon with a diameter of 2 inches was used as a substrate. This plate was covered by insulating layers of silicon oxide 1 μm and nitride silicon 0.43 μm thick. Upon the insulation layers were deposited gold or platinum microelectrodes, which had dimensions of: length 50 μm, width 2.4 μm, thickness of 0.1 μm. One substrate housed eight microelectrodes, three of which were chosen as a source, gate and drain. The gaps between the microelectrodes were only 0.12 microns. According to the authors, reducing overall dimensions can allow for faster switching of the transistor.

The microelectrode wires were insulated by an epoxy lacquer. Above the microelectrodes was deposited a layer of organic semiconductor which was polypyrrole at first, and later poly(3-methylthiophene), in subsequent experiments. The thickness of the layer was adjusted to the minimum amount necessary for creation of reliable contact between the source and drain: it ranged from 0.5 μm to several microns. After manufacturing, the substrate produced in this process was immersed into an electrolyte solution of 0.1M $NaClO_4$ / 0.05M NaH_2PO_4 at pH=5.3 for measurements.

Fig. 1 shows a vertical section of the structure of the transistor according to the authors' description. The gate potential was measured by a potentiostat relative to a calomel electrode.

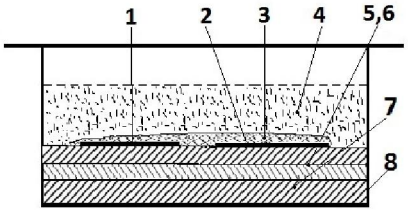

Fig.1. Sketch of the structure of the first invented OECT (The gate is outside the of the vertical section. The sketch is made on the basis of descriptions and drawings by the authors [6,7]).
1. Source, Au or Pt.
2. Drain, Au or Pt.
3. Semiconductor, polypyrrole or poly(3-methylthiophene).
4. Electrolyte, aqueous solution of $NaClO_4$ / NaH_2PO_4.
5,6. Insulating layer, Si_3N_4+SiO_2.
7. Substrate, Si (crystalline).
8. Container of electrolyte and submerged structure.

As a result of the measurements, the following parameters were received:

1.Transconductance, $g_m=dI_D/dV_G$, divided by millimeters of channel width (W), i.e. g_m/W, was 120 mS/mm, corresponding to the best MOSFET transistors of that time period (1985).

2. A power amplification factor of about 1,000 was possible at the frequencies of 10 Hz.

3. The ratio of change in channel resistance to change of gate potential was $>10^5$.

The next prototype OECT structure was created by a group of authors at Linkoping University [8]. The basic conductive elements of these transistors had a layer structure similar to Fig.1. The main difference was that the source, gate and drain together with the electrolyte were enclosed in a waterproof protective encapsulation. This made possible to use transistors not only in the form of experimental models, but also as separate electronic devices. The encapsulation was made of a polymeric film or foil that allowed functioning of the transistors for several months.

In addition, essential changes were made in the application of the conductive materials. The material of the source, gate and drain was PEDOT: PSS, manufactured by the firm Bayer, which had significantly better conductivity and stability than the previously applied polymeric semiconductors. The contacts adjacent to the electrodes were created with silver paste. As a substrate, silicon was substituted for a polyester or other thin-film material. This allows various configurations of transistors by simultaneous printing onto large surface areas, and thereby achieves almost unlimited flexibility of printed boards.

The electrolyte was an aqueous solution containing calcium chloride (2%), isopropanol (35%), and gelatin mixed with an antifoaming agent (12%). The thickness of the electrolyte layer was 20-100 μm. The channel width was 210 μm, the size of the active area of the channel under electrolyte was 0.053 cm^2. The surface channel dimensions were more than two orders of magnitude larger than in the previous model. As a result, these structural differences allowed simplification and cost reduction of OECT manufacturing techniques. The main parameters of transistors reported by authors were:

1. The transconductance, g_m, expressed as a relation of the current increment to the increment of the voltage on the gate at the constant V_{DS}, was between -0.10 and -1.2 mA/V for various types of transistors.

2. The interval of the voltage on the gate was 0 to 5 V.

3. The ratio of currents of I_{DS} max / I_{DS} min was up to 1,000.

4. The relation of currents I(ON) /I(OF) reached 10^5.

5. Regulation of current remained possible until 200 Hz.

The structures of the first OECTs were further enhanced for performance improvement. One such structure [10] is shown in Fig. 2. A silver wire coated with silver chloride was used as the gate electrode. The electrolyte was an aqueous solution of 100 mM NaCl. Contacts to the source and drain electrodes were made of gold and insulated from the silicon substrate by a film of parylene 2 microns thick. The length of the conductive channel was fixed by the boundaries of parylene layer.

The semiconductor, similar to the previous model, was PEDOT:PSS, but in this case possessed of a larger conductivity (according to the authors, up to 1,000 S /cm, at least one order higher than the previous model). The channel length was 5-10 μm, width 10 μm. Hence, the working surface was 50-100 μm^2, five orders of magnitude less than the previous model. The thickness of the channel was only 10 nanometers. Another important feature of the considered transistor is that the gate, which was made from a thin silver wire, reduced the ratio of the gate surface area to the surface area of the channel. Earlier research by participants of the same group [9] demonstrated that reduction of this ratio increases the sensitivity of the signal received from the transistor. As a result, the transistor developed [10] also had high ratio of signal to noise. Such qualities of transistors are necessary for creation of highly sensitive elements which are capable of integrating with biological systems. The structure of the described transistor is shown in Fig. 2.

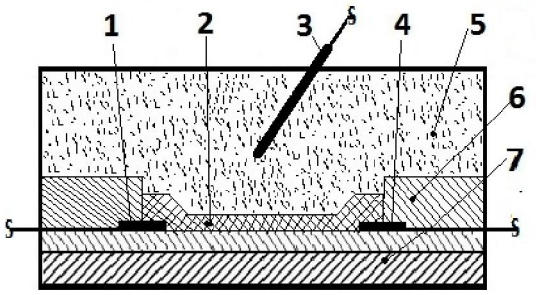

Fig 2. Sketch of the OECT structure of the transistor with high transconductance and improved sensitivity (The sketch is made on the basis of the drawing in [10]).

1. Source, Au.
2. Channel, PEDOT:PSS.
3. Gate, Ag/AgCl.
4. Drain, Au.
5. Electrolyte, aqueous solution of NaCl.
6. Insulation layer, parylene–C.
7. Substrate, Si (fused).

The basic parameters of transistors reported by the authors were:

1. The transconductance of the output characteristic (g_m) was in the range of 2.7 to 4.02 m**S** depending on the quality of PEDOT:PSS - by comparison approximately 10 times higher than in the previous example of the structure.

2. The maximum transconductance was observed at the gate voltage Vg = 0.275 V.

3. The greatest frequency at which this high value of the transconductance remained was 1,000 Hz.

Features of developed OECTs depend on their application. When such transistors are designed for use in large-scale integrated circuits, their most essential values are: the switching time from the ON to the OFF state, the time vice versa, and the temporal symmetry of these two processes.

In 2013 a new vertical transistor structure was described[11], whose distinguishing feature was the presence of a hole in the substrate. In this structure, the source and drain were located on the different sides of the substrate. The substrate material was a 50 μm thick film of polyethylene terephthalate. The hole in the film was made by a laser and filled with a carbon paste. PEDOT:PSS was applied as the semiconductor. The gate electrode was placed above the hole and separated from the source and drain by the layer of electrolyte. The offered vertical structure made it possible to reduce the length of the conductive channel, which in turn allowed accelerating switching of the transistor.

The time of switching OFF to a non-conducting state was 5 ms, and the time ON to switch back approached 20 ms. As the authors noted, the switching was more than ten times faster in comparison to a transistor with a lateral structure, where the length of the channel can't be reduced by means of a hole. The disadvantage of the proposed structure was the asymmetry of the ON and OFF switching time. The reason for this was the slow migration of the reducing PEDOT: PSS border after turning OFF the transistor.

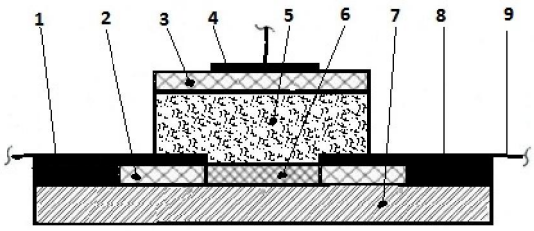

Fig 3. Sketch of the OECT structure with a partial carbon layer between the channel and electrolyte (The sketch is made on the base of the drawing in [12], C-C design).

1. Source contact, C.
2. Semiconductor, PEDOT: PSS, oxidized.
3. Gate, PEDOT: PSS, oxidized.
4. Gate contact, C.
5. Electrolyte (PSSNa / D-sorbitol / glycerol / water 40/10/10/40).
6. Semiconductor, PEDOT: PSS, reduced.
7. Substrate, polyiethylene terephtalate.
8. Drain contact, C.
9. Wire.

An enhanced structure (Fig. 3), which eliminated the asymmetry, was later described by the same group of authors [12]. Improved switching characteristics were achieved by means of an additional carbon layer. This layer forms the contact surface of source and drain electrodes, and then continues over a layer of PEDOT:PSS, partially closing the active surface of contact between the channel and electrolyte.

The carbon layer has a higher electrical conductivity than the semiconductor. Therefore, its existence at the ends of the channel accelerates the transition from the OFF to the ON state. The authors have shown that this method can effectively be used not only for vertical but also for lateral structures, the use of which reduces the number of operations in the fabrication of transistors.

The OECT developed by them has a symmetrical switching time of approximately 5 ms. Another important difference of this structure is the use of hardened electrolyte based on sorbitol and glycerol instead of electrolytes based on aqueous solutions.

This upgrade allows for expanding the scope of the OECTs as full-fledged elements of integrated circuits and matrix displays.

3. Features of Bioelectrochemical Transistors

The examples of the structures of OECTs reviewed above are currently thoroughly investigated and developed. Transistors based on these structures have characteristics which allow them to successfully compete with more widely applied solid-state elements presently available on the market.

In addition to established OECT models, there are propositions for new, promising, fundamentally different OECT structures, which would allow completely new areas of application. First and foremost, these include the models in which biological materials are used as structural elements. Compatibility of biological components with organic semiconductors has been established in studies carried out in sensors for analysis of enzymes, molecules of DNA, cancer cells and other substances found in living organisms [13, 14].

Simultaneously, a number of other works have been carried out which demonstrate the possibility of applying certain biological materials for unconventional computing. Notably, the greatest results were achieved by using the properties of the *Physarum polycephalum* cell (abbreviated PPC). This fungus is able to remember its distribution in the process of searching for food and then finds the shortest routes by repeated searches, i.e. actually carrying out the process of self-training [15, 16].

V. Yerokhin and coauthors [17,18] established the possibility of a combination of fungus (PPC) and polyaniline (PANI - which possesses the properties of an organic semiconductor). Moreover, significant progress in this direction was made in subsequent research [19, 20]. In these articles, the authors presented results of their studies combining PCC with the organic semiconductor, achieving the most comprehensive set of properties necessary for creation of an OECT. Currently, this distinction is held by the semiconductor PEDOT: PSS. The studied hybrid electrochemical element is named by its authors PPC-OECT.

The experimental sample of the proposed item had the following structure. On a 2x2 cm glass substrate a layer of PEDOT: PSS was deposited which was pre-doped with 20% diethylene glycol and contained a surfactant of sodium dodecyl benzene sulfonilic acid. The channel of the transistor was formed by the photolithography method. The thickness of the channel was 100 nm, the width 2 mm. Above the surface of the channel was housed a porous membrane of polydimethylsiloxane in the shape of a rectangular parallelepiped. In experimental practice, this membrane is known as "PDMS well", and its key property is harmlessness to living species [28].

The channel length was set by the corresponding size of the contact between membrane area and the PEDOT:PSS, measuring at approximately 10 mm. The PPC solution drop with a volume of about 500μL was applied on a membrane. The basic purpose of the membrane was to keep the PPC solution over the surface of the semiconductor. The PPC solution served as the electrolyte which was carrying out electrical connection between the gate and the channel. Electrodes of the source and drain were formed on the ends of the semiconductor channel.

The gate electrode was located directly on the top surface of the membrane. Several gate materials were investigated, including Ag, Au and Pt. The structure of the described transistor is shown in Fig. 4.

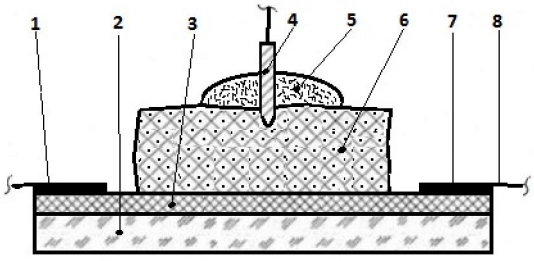

Fig 4. Sketch of the experimental PPC-OECT structure (The sketch is made on the basis of descriptions and pictures in [19,20]).

1. Source contact, C paste.
2. Substrate, glass.
3. Semiconductor, PEDOT:PSS.
4. Gate, Ag.
5. Drop of PPC solution.
6. Membrane, PDMS.
7. Drain contact, C paste.
8. Wire.

The studies showed the following characteristics of PPC-OECT.

1. This element can operate at very low input voltages (beginning at zero).

2. In case of connection to all three electrodes, the element operates as a transistor. In case of shutdown of the drain electrode and creation of a chain "source-gate," PPC-OECT can work as a memory element.

3. The main functional parameters of the PCC-OECT are similar to those obtained previously in cases the of gelled electrolytes. Therefore, PPC can be characterized as a quasisolid electrolyte.

4. Relative change of regulated current depends on the material of the gate electrode. When applying

gates Au and Pt, the possible regulation limits are reduced as compared with gate Ag. This results from the fact that (in case of Ag) the electrode dissolves and the dedoping reaction occurs by a red-ox (Faraday) mechanism. Therefore, transfer of charges happens in the whole volume of the channel. In the case of insoluble gates Au and Pt, the dedoping reaction occurs by field mechanism and transfer of charges is carried out only in the surface layer.

5. PCC-OECT has good reproducibility of transient characteristics and no conduction losses during its operation.

Based on the carried out studies, the authors concluded that on the basis of PCC-OECT it is possible to create sensors that are able to work directly in the neural networks and other tissues of living organisms. This conclusion follows from the fact that PCC-OECT can serve not only as a transistor, i.e. a transducer of current-voltage characteristics, but also as a memristor, i.e. the element which memorizes the actions produced earlier. It is known that such properties are possessed by living, as well as by artificial neurons [21].

The first application of electrochemical elements of memory for creation of artificial self-training was introduced in 1960 [22]. The theory of memristors was developed in 1971 [23], and the possibility of their practical realization in 2008 [24]. Advantages of electrochemical transducers (including transistors, memristors, and artificial electrochemical organs of taste) when creating self-training systems was considered in our last article [25]. In this regard, creation of new bioelectrochemical transducers allows additional benefits in comparison with solid-state devices existing presently.

In the above-mentioned work [19], it was established that the PCC served as a reservoir of cations which can enter into exchange reaction with PEDOT:PSS. Consequently, a question arises as to how PCC improves characteristics of electrochemical transistors. It can be assumed that this desirable effect is caused by increasing of conductivity of the semiconductor layer.

Earlier, [26, 27] it was shown that in the process of drying, PEDOT:PSS solution formed solid films of semiconductor which had an anisotropic structure: their electrical conductivity along length was different from height. In addition, the electrical conductivity of semiconductor films also significantly depends on the sizes of PEDOT micelles which are formed in the original colloidal solution and remain in the form of separate monocrystals after drying of the layer.

The final conductivity of a dry semiconductor film also depends on the composition of additional components of the initial solution and of the conditions during drying. Under optimum conditions of film preparation, its electrical conductivity along the length can reach > 1,000 S/cm. The sizes of PEDOT monocrystals are usually 5-10 nm.

The current flow in a semiconductor is carried out by means of movement of the electric charges from each separate monocrystal to the next. In such a mechanism, the conductivity of a semiconductor layer depends on the integrated length of particular trajectories on which electric charges are moving. In a structure where PPC is a major component of the electrolyte, its ability to find and remember the shortest ways of propagation allows the reduction of the total size of the trajectories of charge advancement, and thus allows optimization of the conductivity of a semiconductor layer. In turn, this allows improvement of overall transistor characteristics.

4. Conclusion

Structural models of organic electrochemical transistors in development now differ in their components depending on the requirements of their functional characteristics. They also differ widely depending on their application.

Models characterized by reduced gate surface versus the channel surface [9, 10] have improved performance signal to noise ratio, which allows their use in transistors designed to create highly sensitive sensor elements.

Transistor models containing an additional carbon layer [12] have a symmetry of switching time that allows the application of OECTs as full-fledged elements of integrated circuits and matrix displays.

Structural models of bioelectrochemical transistors such as PPC-OECT combine the transistor and the memristor into one element with several functions [19]. Based on these elements, it is possible to create sensors that are able to work directly in neural networks and other tissues of living organisms.

On the basis of the considered mechanism of the current flow in PEDOT:PSS, it is proposed that PCC optimizes the total length of trajectories of charge advancement between PEDOT monocrystals.

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