

Principles of creating the devices that are able to control the current flow in the second class conductors

Yu.Yu. Bacherikov, O.B. Okhrimenko

V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, 41, prospect Nauky, 03680 Kyiv, Ukraine

E-mail: yuyu@isp.kiev.ua

Abstract. From the position of conceptions inherent to semiconductor physics and semiconductor technology, the processes occurring in conductors of the second class, which take place due to the current flow in them, have been considered in this paper. It has been shown that using the several composite materials consisting of a porous matrix filled with an electrolyte enables to obtain multilayer structures, in which potential barriers appear in the electrolyte medium. These barriers are caused by the difference in properties inherent to layers of porous matrix. Considered here has been the prospect of creating the new devices based on the second-class conductors capable to control the direction and magnitude of the current flow in these conductors that are in a liquid state (in electrolytes). In other words, it was considered the possibility to obtain the ionic devices that are closest in their functional properties to basic electronic devices, such as diodes, transistors, etc.

Keywords: second class conductors, current flow control, ionic devices, potential barriers in the electrolyte, multilayer porous composite materials.

<https://doi.org/10.15407/spqeo25.02.137>

PACS 66.10.Ed, 82.45.Gj, 84.32.Ff

Manuscript received 23.03.22; revised version received 19.04.22; accepted for publication 22.06.22; published online 30.06.22.

1. Introduction

It is well known that conductive materials can be separated into three groups: the conductors of the first and second class as well as the mixed class conductors [1]. The study of the features of the properties of materials in which charge carriers are electrons, *i.e.* 1st class conductors, as well as using these materials in the large quantities in a variety of instruments and devices capable to control current parameters in electrical circuits, has been used for several hundred years. During this time, the entire scientific areas were created, namely: vacuum electronics, solid-state electronics, semiconductor physics, micro- and nanoelectronics, and a number of other areas, and independent branches of production appeared in industry. This colossal interest to the 1st class conductors, their high demand and use in production to some extent diverted the attention of both researchers, engineers and designers from the problems that arise when using 2nd class conductors. This led to a strong backlog in the development of the devices capable to control the current flow in 2nd class conductors. It should be noted that a large number of terms have recently appeared in the literature, such as ion-selective field-effect transistors ISFET or the similar ones [2–4]. However, in essence, the ISFET are ordinary MIS field-effect transistors, on the surface of which an ion-selective

membrane is deposited [5, 6], *i.e.* they can be attributed to classical electronic devices. Some exceptions from this situation are the work which related to membranes and corresponding electrochemistry [7–11].

The interest in membrane electrochemistry began in 1950, when the cation-exchange membranes that are selectively penetrable to cations and the anion-exchange membranes selectively penetrable to anions were first synthesized [12–16]. An additional impetus to the emergence of a new generation of membranes was the active development and research of nano-dispersed and porous materials. The unique properties of these materials are increasingly expanding the scope of their practical application. This is caused by high activity of their highly developed surface, which in turn enables to increase the efficiency of membranes created on their basis. Here, it should be also noted the results of a number of studies [17, 18] showing the changes in properties of dispersed materials, including the properties of their surface, which depend on the particle size (D) falling into the range $D \leq 2L$, where L is the Debye screening length, which further expands their scope.

The lag in the use of 2nd class conductors in various electrical, semiconductor and other similar devices is associated with their specificity. Most of them are in a liquid or gaseous state, in addition, the passage of an electric current through them causes the movement of a substance

in the form of a stream of ions and is accompanied by chemical transformations at the points of current entry and exit (electrochemical reactions) [10, 11, 16, 19, 20], which, in turn, strongly complicates their use. This specificity of the 2nd class conductors, on the one hand, can be overcome, if you organize the cyclicity in the movement of ions, which, of course, will require the additional efforts, and on the other hand, it can play a positive role depending on the tasks that should be solved by this electrical circuit. At the same time, the presence of a greater variety of the charge carriers in the 2nd class conductors, both in their sign and in magnitude, suggests that with their help it will be possible to solve more complex problems as compared to the tasks solved using the devices created on the basis of materials with electronic conductivity.

The purpose of the work is to provide the research and the phenomenological analysis of the possibility to apply the concepts used in semiconductor physics and semiconductor technology to conductors of the 2nd kind in order to create new structures that can control the current flow in such conductors being in the liquid state, *i.e.* electrolytes. In addition, we shall consider possible ways to obtain devices based on these structures that are very similar in their functionality to the main electronic devices, such as diodes, transistors, *etc.*, capable to control the current flow in electrolytes. We shall consider the possibility to create ionic devices similar to these electronic devices.

2. The features of potential barrier formation

As it is well known, on the basis of the 1st class conductors the huge number of electrical devices, which receive energy in the form of a stream of electrons and then convert it into another form of energy – most often into light, heat or motion, have been already created. Besides, there designed is also no less amount of electronic devices that are destined not only to transform the electric energy to its alternative forms or, on the contrary, other types of energy into the electrical one, but also to control the current in such a way that this flow of electrons already carries some information in addition to the transferred energy. The leading role in the control of electric current is played by the semiconductor devices, which are created on the basis of materials related to the 1st class conductors.

The functional ability of the semiconductor devices to control the current flow in electrical circuits is due to the non-uniform distribution of the magnitude of the electric potential within their structure. As a rule, it is achieved by creating a series of interfaces in these structures and by bringing into contact the materials that differ in their electronic properties. The contact of such materials leads to formation of a set of space charge regions in them and, as a consequence, the appearance of the potential barriers in the resulting structure. The presence of a potential barrier allows one to control the direction to move for charge carriers in an electrical

circuit and to prevent their motion in the opposite direction. The control of the current flow in electrical circuits by using the transistors or more complex devices is implemented by changing the value of these barriers.

The creation of the interfaces in the liquid electrolytes is also possible, for example, due to the temperature gradients, impurity concentrations in them, insolubility of one electrolyte in another, *etc.* However, the instability of the properties of these interfaces, and most importantly, the changes in their parameters under action of external influences, as a rule, is irreversible, which makes their usage practically one-time and inefficient. At the same time, the use of surface of a solid body as an adjacent medium enables to stabilize the properties of the electrolyte, at least in a certain area, which is affected by the surface of a solid body. The change in the external influences (temperature, *etc.*) will lead to changes in the properties of electrolyte, but these changes, in a number of cases, can be organized as reversible. Of course, the range of changes in external influences for devices that use liquid electrolytes will not be as large as when using semiconductor devices, but this limitation can be overcome due to the design features of such devices. Finely dispersed or porous materials can be used as an adjacent medium for the electrolyte. This is supported by the membranes actively used in electrochemistry, which are, as a rule, porous or dispersed materials.

The electrolyte separation by using ion-exchange membranes is the result of interactions of electrolyte components (ions) with the membrane surface [21, 22]. Therefore, depending on the material properties of membranes used in electrochemical processes, a specific membrane allows only one type of ion to pass through, either cations or anions [12–16]. At the same time, almost all the problems solved within these areas concern separation of a composition (electrolyte) of components (cations and anions), and only partially consider a membrane or a porous structure with conical pores as a device that affects the current flow in a medium [11, 23–28].

An ion-exchange membrane, being placed into an electrolyte and being in the equilibrium state, is electrically neutral. Its current-voltage characteristic has a symmetrical form [28, 29]. In the case of a passing direct electric current, the ion-exchange membranes become the unipolar conductors of electricity of the second class, since the cation-exchange membranes let selectively pass cations, and the anion-exchange membranes let selectively pass anions. This is due to the fact that the fixed positive or negative charges are located on the surface of the membrane material. The high density of these charges inside the membrane creates a space charge that is compensated by an equivalent number of charges of the opposite sign – counterions. The latter, in the ambience of firmly localized (fixed) charges, creates an ionic atmosphere and provide the electrical neutrality of the entire structure.

At the same time, as mentioned above, the membrane filled with electrolyte is a unipolar conductor of the second class, which allows it to be considered as an analog of a semiconductor material. The membrane filled with electrolyte, or more correctly, a composite material, in which cations act as the main charge carriers, is an analog of a material with p -type conductivity. The material with the main charge carriers that are anions is analogous to the material with n -type conductivity. In this case, the combination of several layers obtained from these materials that have different concentrations, mobility, charge and different signs of mobile charge carriers will allow obtaining the different values of electric potential in a structure consisting of a set of such layers, which in turn will lead to formation of potential barriers in the volume of electrolyte filling this structure. Thus, the combination of several layers of these composite materials with different properties enables to design devices with more advanced functionality than the analogous semiconductor devices, such as diodes, transistors, thyristors, *etc.*

Considering the membrane filled with electrolyte as a composite material allows one to apply to its description some of the basic concepts used in the solid state physics, such as pseudopotential, *etc.* It is due to the fact that in this composite material that is in the equilibrium state, *i.e.* in the absence of a voltage applied to it, the charges fixed on the surface of matrix form a space charge, which leads to ordering the localization of mobile ions in the filler (electrolyte in pores), which

ensures the electrical neutrality of the entire bulk of material. Therefore, this material can be considered from the standpoint both of the short-range order and that including the elements of long-range order. However, these questions require separate consideration.

The simplest option to obtain a device, in which the potential barrier takes place at the interface in conductors of the second class, is to use two layers brought into contact, each of which is a composite material (solid-state matrix filled with electrolyte), with different parameters of the main charge carriers in each layer.

Fig. 1a,b schematically shows the contact of these materials with different types of electrical conductivity. When they come into contact, due to the concentration gradient of charge carriers across the interface, ions diffuse from the region with the opposite type of electrical conductivity. Due to the diffusion of charge carriers, the electrical neutrality of the regions adjacent to the interface is disturbed. In a cation-permeable material, after diffusion of positive ions from it, uncompensated negative ions remain near the interface that is localized on the surface of a solid-state matrix. These negative ions are supplemented by mobile anions from the anionic region. In an anion-permeable material, uncompensated positive immobile ions are supplemented by mobile cations from cationic region. Thus, the space charge region consisting of two oppositely charged layers is formed. The diffusion electric field between uncompensated opposite charges of immobile ions, which is directed from the anionic region (analogous to the n -region) to the cationic region (analogous to the p -region) are arises. This emerging diffusion electric field prevents further diffusion of mobile carriers through the interface, and the equilibrium state is established. As a result, the contact potential difference arises between the anionic and cationic regions (see Fig. 1c). Thus, the contact of the materials that are the 2nd class conductors with different types of electrical conductivity is an analog of a p - n junction. However, taking into account a number of differences in the processes occurring in the former and latter cases, it is more correct to interpret the contact of the 2nd class conductors with different types of electrical conductivity as an anion-cation transition.

The use of dispersed and porous materials, when preparing these solid-state matrices, significantly expands the possibilities for choosing the required concentration, mobility, and magnitude of charge carriers in an electrolyte localized in the pores or interparticle space. First of all, it can be applied to porous materials. To create the structure having a potential barrier at the interface of its layers, it is necessary to select porous materials filled with electrolyte in such a manner that the surface states of one layer in this structure, due to the certain localization of ions in them, contribute to the appearance in the electrolyte of only one type of mobile ions with different values of their concentration, mobility or the sign of the charge from ions located in another layer.

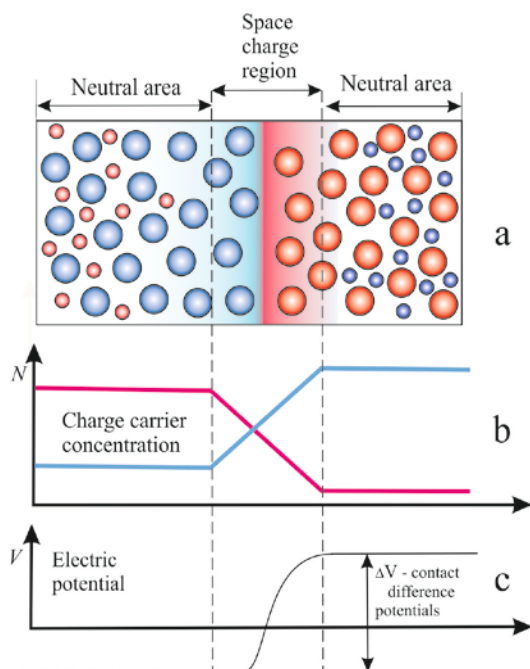


Fig. 1. a) Schematic representation of the contact in composite materials with different types of electrical conductivity; b) charge carrier concentration; c) contact potential difference.

3. Influence of the size factor of corpuscular porous material on the concentration and mobility of ions in the electrolyte

The influence of surface on the structure of the adsorption layer is a well-known fact for highly dispersed materials [30]. Let us consider what opportunities are provided by dispersed and porous materials filled with electrolyte, when they are used as a unipolar conductor of the second class. As a model material, we consider a corpuscular porous layer obtained from a dispersed material after its pressing, sintering, compacting, or in some other way.

There are various ways to classify dispersed materials [31]. Note that the classification of dispersed materials in this work will be carried out from the position of comparability of their sizes with the value of the doubled Debye screening length ($2L$). The first group consists of the massive particles with a classical band structure, which dimensions are much larger than twice the Debye screening length ($D \gg 2L$). The second group includes the particles with sizes comparable or smaller than twice the Debye screening length ($D \leq 2L$).

In the first group, changing the average size of particles, from which the porous layer is obtained, leads to changing the specific surface area of this layer, which in turn leads to the change in the total number of surface states in it. Changing the number of surface states in this layer already makes it possible to influence on the concentration of charge carriers in the electrolyte that fills the interparticle space or pores.

Note that the curvature of the solid-electrolyte interface, *i.e.*, the shape of the particles, will also affect the number and occupancy of the surface states of these particles, which, accordingly, will lead to a distortion of the structure of adsorption films on the surface of particles. And, as is well known, distortion of the structure of adsorption films extends into the bulk of electrolyte that fills the pores, thereby changing the structure of electrolyte and affecting on the behavior of ions in it [32–38].

Fig. 2a schematically shows a porous structure filled with electrolyte, in which a potential barrier appears. This structure consists of two layers of the same material with different particle sizes (D_1 and $D_2 \gg 2L$) in

each layer. The density of surface states for particles in both layers is the same, as it is defined by the type of surface states. The difference in the total surface area of the particles of each layer leads to different concentrations of mobile ions in the layers. Ions from a layer with a higher concentration diffuse into the adjacent layer, which causes appearance of the potential barrier inside the resulting structure.

It should be taken into account that the configuration and size of pores filled with electrolyte also significantly affect behavior of ions in them. First of all, it will affect ion's mobility. As was shown in [39, 40], the movement of ions under conditions of "limited geometry" turns out to be difficult due to a decrease in the number of ions that can move in a given pore volume (see Fig. 2b). This, among other things, can lead to changing the mechanism of the ions movement in the electrolyte. For example, when the drift mechanism cannot be implemented, it can be replaced by a jump mechanism, *etc.* In addition, the mutual overlapping of the potentials from opposite surfaces of the pore will also lead to a change in behavior of ions, similar to the behavior of electrons in particles when their size is $D \leq 2L$ [17, 18]. We should also note one more factor that affects the structure of the electrolyte localized in the pores. This is the wetting of the surface of the pores with electrolyte. Depending on the degree of wetting with the liquid in the capillaries, it will be subject to either tension or compression, which in turn will also affect behavior of ions in the liquid electrolyte.

In addition, in some cases, the pore size will affect the average charge state of ions (\bar{Z}) localized in the pores. Thus, according to [41], in the distilled water, in addition to hydroxyl ions OH^- , protons (H^+) in different charge states are the charge carriers. Therefore, at the certain pore sizes, it can be realized the case when changes in the pore size ($r_1 \neq r_2$) practically does not affect the mobility of ions (μ) in pores ($\mu_1 = \mu_2$), but at the same time affect the average charge state of ions in the adjacent layers of structure, *i.e.*, $\bar{Z}_1 \neq \bar{Z}_2$ at $r_1 \neq r_2$. In this case, even at the same concentration of ions ($N_1 = N_2$) in these layers, the potential barrier will appear in the interface of their contact.

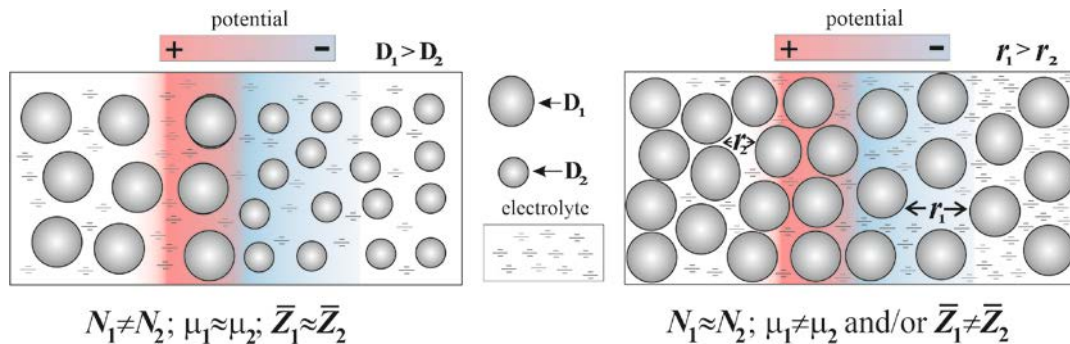


Fig. 2. The model of a two-layer structure with a potential barrier due to: a) different concentrations of mobile ions (N) (in this case, the donor type); b) different values of ion mobility (μ) and/or average charge state (Z) of the mobile ions in each layer.

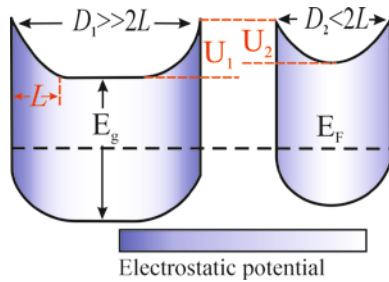


Fig. 3. The energy diagrams for particles with dimensions $D_1 \gg 2L$ and $D_2 < 2L$.

In the second group of dispersed materials, as the particle size decreases, starting from a value of the order of $D = 2L$, the space charge region (SCR) localized along one surface of the particle is superimposed on SCR localized along the opposite surface. Mutual overlapping of SCR leads to decreasing the surface barrier (U), as well as to decreasing the distance between the Fermi level (E_F) and the top of the valence band (E_V) [17] (see Fig. 3). As a result, the concentration of main charge carriers in a particle with a size of $D \leq 2L$ is less than the concentration of carriers in a particle with $D \geq 2L$. This, in turn, affects the number of surface states [17, 18]. Thus, a change in the average particle size in the layer obtained from particles, which size falls into the range $D \leq 2L$ also makes it possible to influence on the concentration of charge carriers in the electrolyte that fills the interparticle space or pores in the compacted material. The modeling of the potential distribution in such structures is considered in [42].

Since the electrical properties of the matrix from the compressed dispersed material and the electrolyte placed in the pores are interrelated, this circumstance enables to change the properties of the material localized in the pores by changing the pore size (l) and the particle size (D), which make up the porous layer. As it was already noted, the subsequent combination of these several layers with different values of l and D will enable to form a potential barrier at the interface between them. The barrier parameters can be varied by changing the ratio of l and D values.

Thus, the presented concept shows how the use of several composite materials, each of which consists of a porous matrix filled with an electrolyte, due to differences in the properties of the matrix, makes it possible to obtain structures, in which a potential barrier is formed in the electrolyte medium that determines the parameters of the movement of ions of a certain sign (anions or cations) through these structures.

4. Ionic devices for current transfer control in electrolytes

Any device, in the structure of which there is a potential barrier for some type of charge carriers, can be used as a diode, *i.e.*, the device with different electrical conductivity depending on the polarity of the voltage applied to it.

Considering this type of devices based on the 2nd class conductors placed in an electrical circuit, it is necessary to take into account the features of these conductors. Because current flow in the 2nd class conductors is accompanied by mass transfer, the operation of a device consisting of two layers brought into contact, in one layer of which the main charge carriers are cations, and in another – anions, will be very short-term. This is due to the depletion of the electrolyte in the region of the interlayer boundary by charge carriers (ions), as a result of which the structure will go into the insulator mode.

It should be noted that the devices, in the structure of which there is a potential barrier due to only dimensional factors (size, shape, *etc.* of particles or pores), can be considered as the analogs of *n-n* and *p-p* structures realized. In other words, the multilayer structures, in which there is only one type of mobile ions with different values of their concentration, mobility, *etc.* in different layers of structures, can perform the functions of a diode only for one type of ions. Ions of the opposite sign cannot pass through this device. This indicates that for the 2nd class conductors the ionic diodes can be of various types: diodes for cations or anions.

Thus, in the paper [29] presented are the results of studying the two-layer structure based on compacted nanodispersed zirconium dioxide with different sizes of nanoparticles in each layer (the average particle size in one layer is 10 nm, in another – 20 nm) the interparticle space of which is filled with electrolyte (water) (see Fig. 2). The current-voltage characteristics (CVC) of this structure has a rectifying character with a maximum rectification factor close to 3 [29]. In [29], the diode type of CVC in this structure was explained by the different specific surface area of zirconium dioxide in each layer, and, as a consequence, by appearance of a potential barrier in the interface between the layers due to the difference in the number of surface states in each layer. In other words, presented in [29] is the structure capable to perform the functions of the diode for cations, in which protons (H^+) act as mobile carriers.

In a number of semiconductor electronic devices, such as transistors, to control the magnitude of potential barrier, the intermediate layer called the base is introduced into their structure. Depending on the magnitude and sign of the charge applied to the base, the magnitude of potential barrier changes, which increases or decreases the current passing through the transistor. Similar introduction of an additional thin layer in the interface into the structure consisting of several corpuscular layers filled with an electrolyte and having a potential barrier will enable to obtain an ionic device (a device for the 2nd class conductors) capable to control the magnitude of current in an electrical circuit, similar to the transistor in semiconductor electronics.

The practical application of the ionic devices designed to control the current flow in the electrical circuits consisting of the 2nd class conductors, of course, requires separate consideration. This is caused by the fact

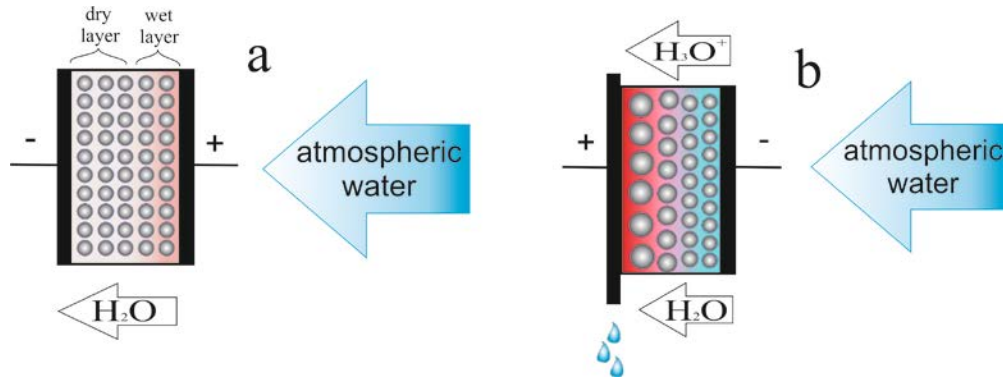


Fig. 4. Appearance of the potential difference between the dry and wet sides: a) in a two-layer structure; b) in a multilayer structure.

that, as already mentioned, they can enable to solve more diverse and complex problems than electronic devices and appliances. However, at least, it can be unequivocally stated that the development of these devices will make it possible to create a new generation of membranes and bring to a new level the capabilities of membrane technologies, which are currently widely used in industry.

Note that separation of the electrolyte by using the ion-exchange membranes is due to the potential formed by ions of the same sign and localized on the surface, as a result of which this potential prevents the passage of ions of this sign through the pores of the membrane. At the same time, transformation of ion-exchange membranes into ionic devices, *i.e.*, using the several layers of material enables to create a potential barrier in the structure of device, which sharply increases the efficiency of electrolyte separation by components. Introduction of another layer, capable to perform the role similar to the base in a transistor, makes the process of separation of substance into components by such a device not only more efficient, but also manageable.

5. Ionic devices that generate electric current

Given the relevance in the development of ecologically clean technologies, let us dwell in more detail on using the ionic devices that are close in their functionality to the electronic ones capable to generate electric current. The simplest way is to develop the ionic devices by analogy with electronic ones. Let us consider two types of ionic devices, one of which can operate in the electrostatic mode (analogous to an electrochemical capacitor), and the second – in the mode of an electric current generator.

Recently, one is trying more and more to use atmospheric moisture to generate electric current [43–47]. The porous materials adsorbing moisture are most actively studied. For example, one can obtain a potential difference between the dry and wet sides by placing a porous panel on the wall of a building that becomes

wet from the outside (see Fig. 4a). The authors [29] considered the effectiveness of such a panel based on the compacted zirconia. This effect can be enhanced, if the panel will consist of a set of layers with different specific surface, which will lead to the migration of ions to the layers with their lower concentration, thereby increasing the efficiency of the panel (see Fig. 4b). Its efficiency can be increased, if its structure is organized in such a way that water condenses on the opposite side, for example, due to the capillary effect, with its subsequent exit from the panel, as shown in Fig. 4b.

The general principle of operation of the electronic devices that are involved in generation of electric current is as follows. The device has three functional regions. In the first region, due to the external influences, generation of electron-hole pairs occurs, which forms the concentration gradient of carriers and leads to their drift deep into the structure of the device. In the second region, the carriers are separated by sign; this is the region of the potential barrier (*p-n* junction). In the third region, recombination of charge carriers takes place. The combination of these three processes leads to the appearance of current in the circuit. The ionic device can be created in accord to the same principle (see Fig. 5b).

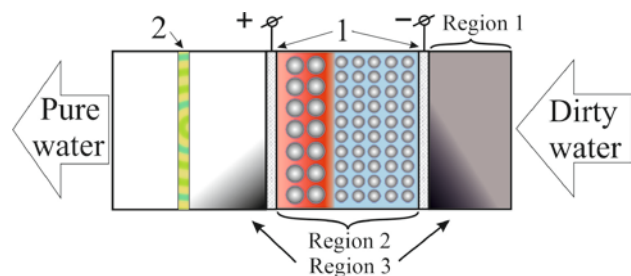


Fig. 5. Schematic diagram of the ionic device that generates the electric current. Region 1 is the region of high ion concentration, region 2 is the region of separation of carriers according to the charge sign, region 3 is the region of recombination of charge carriers. 1 – contacts, 2 – ion-exchange membrane.

In the first region, it is necessary to form the carrier concentration gradient. It can be realized due to the flow (inflow) of an electrolyte with a high concentration of ions from one side of this device. For example, due to the flowing waste water. When ions pass through the structure of this device, they are separated in the second functional area. Ions of the same sign pass through the potential barrier into the second layer of the structure, then entering the next zone of the device (region 2 in Fig. 5b). The additional membrane (3 in Fig. 5b) does not let ions to pass into the third zone, which leads to an increase in their concentration in this region (Fig. 5b, region 2). When the concentration of ions reaches a value corresponding to the solubility limit of a substance in a given medium (solvent), the neutral molecules are formed in it, which falling out in the form of a precipitate (analogous to the recombination of charge carriers in the electronic devices). Ions of the other sign remain in the first zone. When their concentration reaches the value of the solubility limit, they are also restored and precipitated, and the potential difference appears on the contacts of the device.

6. Conclusions

Thus, in the paper it was shown the possibility of applying the concepts on which physics of semiconductors is based and the development of semiconductor technology are implemented to the materials that are the 2nd class conductors. It has been shown how using the several composite materials consisting of a porous matrix filled with an electrolyte, due to differences in the properties of individual structural elements, enables to obtain the structures in which potential barriers are formed in the electrolyte. These structures are able to control the direction and magnitude of the current that flow in the 2nd class conductors, *i.e.*, these are structures on the basis of which the ionic devices with the functionality of classical diodes, transistors, *etc.*, but for the 2nd class conductors can be obtained.

References

- Guth U. Mixed Conductors, Determination of Electronic and Ionic Conductivity (Transport Numbers). In: *Encyclopedia of Applied Electrochemistry*, Editors: G. Kreysa, K. Ota, R.F. Savinell. Springer, New York, NY, 2014. https://doi.org/10.1007/978-1-4419-6996-5_313.
- Covington A.K. and Sibbald A. Ion-selective field-effect transistors (ISFETS). *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences*. 1987. **316**, No 1176. P. 31–46. <http://www.jstor.org/stable/2396492>.
- Fakih I., Durnan O., Mahvash F. *et al.* Selective ion sensing with high resolution large area graphene field effect transistor arrays. *Nat. Commun.* 2020. **11**. P. 3226. <https://doi.org/10.1038/s41467-020-16979-y>.
- Artigas J., Beltran A., Jiménez C. *et al.* Application of ion sensitive field effect transistor based sensors to soil analysis. *Computers and Electronics in Agriculture*. 2001. **31**, No 3. P. 281–293. [https://doi.org/10.1016/S0168-1699\(00\)00187-3](https://doi.org/10.1016/S0168-1699(00)00187-3).
- Hong J.G., Gao H., Lan Gan *et al.* Chapter 13 – Nanocomposite and nanostructured ion-exchange membrane in salinity gradient power generation using reverse electrodialysis. Editors: W.-J. Lau, A.F. Ismail, A. Isloor, A. Al-Ahmed, In: *Micro and Nano Technologies, Advanced Nanomaterials for Membrane Synthesis and its Applications*, Elsevier, 2019. P. 295–316. <https://doi.org/10.1016/B978-0-12-814503-6.00013-6>.
- Maksymiuk K., Stelmach E. and Michalska A. Review. Unintended changes of ion-selective membranes composition – origin and effect on analytical performance. *Membranes*. 2020. **10**. P. 266. <https://doi.org/10.3390/membranes10100266>.
- Tanaka Y. *Ion-exchange Membranes: Fundamentals and Applications*. 2nd ed. Amsterdam: Elsevier, 2015.
- Strathmann H. *Ion-exchange Membrane Separation Process*. Amsterdam: Elsevier, 2004.
- Garcia A.A.R., Leron Rh.B., Soriano A.N., Li M.-H. Thermophysical property characterization of aqueous amino acid salt solutions containing α -aminobutyric acid. *J. Chem. Thermodyn.* 2015. **8**. P. 136–142. <https://doi.org/10.1016/j.jct.2014.05.019>.
- Zabolotsky V.I., Nikonenko V.V. Effect of structural membrane inhomogeneity on transport properties. *J. Membrane Sci.* 1993. **79**. P. 181–198. [https://doi.org/10.1016/0376-7388\(93\)85115-D](https://doi.org/10.1016/0376-7388(93)85115-D).
- Pärnamäe R., Mareev S., Nikonenko V. *et al.* Bipolar membranes: A review on principles, latest developments, and applications. *J. Membrane Sci.* 2021. **617**. P. 118538. <https://doi.org/10.1016/j.memsci.2020.118538>.
- Luo T., Abdu S., Wessling M. Selectivity of ion exchange membranes: A review. *J. Membrane Sci.* 2018. **555**. P. 429–454. <https://doi.org/10.1016/j.memsci.2018.03.051>.
- Alabi A., AlHajaj A., Cseri L. *et al.* Review of nanomaterials-assisted ion exchange membranes for electromembrane desalination. *npj Clean Water*. 2018. **1**. P. 10. <https://doi.org/10.1038/s41545-018-0009-7>.
- Maurya S., Shin S.-H., Kim Y., Moon S.-H. A review on recent developments of anion exchange membranes for fuel cells and redox flow batteries. *RSC Adv.* 2015. **5**. P. 37206–37230. <https://doi.org/10.1039/C5RA04741B>.
- Crothers A.R., Darling R.M., Kusoglu A. *et al.* Theory of multicomponent phenomena in cation-exchange membranes: Part II. Transport model and validation. *J. Electrochem. Soc.* 2020. **167**, No 1. P. 013548. <https://doi.org/10.1149/1945-7111/ab6724>.

16. Ellatar A., Elmidaoui A., Pismenskaia N. *et al.* Comparison of transport properties of monovalent anions through anion-exchange membranes. *J. Membrane Sci.* 1998. **143**. P. 249–261. [https://doi.org/10.1016/S0376-7388\(98\)00013-1](https://doi.org/10.1016/S0376-7388(98)00013-1).
17. Bacherikov Yu.Yu., Gilchuk A.V., Zhuk A.G. *et al.* Nonmonotonic behavior of luminescence characteristics of fine-dispersed self-propagating high-temperature synthesized ZnS:Mn depending on size of its particles. *J. Lumin.* 2018. **194**. P. 8–14. <https://doi.org/10.1016/j.jlumin.2017.09.010>.
18. Bacherikov Yu.Yu., Lytvyn P.M., Okhrimenko O.B. *et al.* Surface potential of meso-dimensional ZnS:Mn particles obtained using SHS method. *J. Nanopart. Res.* 2018. **20**, No 12. Article 316. <https://doi.org/10.1007/s11051-018-4413-1>.
19. Pismenskaya N., Laktionov E., Nikonenko V. *et al.* Dependence of composition of anion-exchange membranes and their electrical conductivity on concentration of sodium salts of carbonic and phosphoric acids. *J. Membrane Sci.* 2001. **181**. P. 185–197. [http://dx.doi.org/10.1016/S0376-7388\(00\)00529-9](http://dx.doi.org/10.1016/S0376-7388(00)00529-9).
20. Martí-Calatayud M.C., García-Gabaldón M., Pérez-Herranz V. Mass transfer phenomena during electro dialysis of multivalent ions: Chemical equilibria and overlimiting currents. *Appl. Sci.* 2018. **8**. P. 1566. <https://doi.org/10.3390/app8091566>.
21. Hosseini S.M., Madaeni S.S., Khodabakhshi A.R. The electrochemical characterization of ion exchange membranes in different electrolytic environments: Investigation of concentration and pH effects. *Separation Science and Technology*. 2012. **47**, No 3. P. 455–462. <https://doi.org/10.1080/01496395.2011.615046>.
22. Stenina I., Golubenko D., Nikonenko V. and Yaroslavtsev A. Review. Selectivity of transport processes in ion-exchange membranes: Relationship with the structure and methods for its improvement. *Int. J. Mol. Sci.* 2020. **21**. P. 5517. <https://doi.org/10.3390/ijms21155517>.
23. Bishop G.W., Lopez M.M., Rajasekaran P.R. *et al.* Electroosmotic flow rectification in membranes with asymmetrically shaped pores: Effects of current and pore density. *J. Phys. Chem. C.* 2015. **119**, No 29. P.16633–16638. <https://doi.org/10.1021/acs.jpcc.5b03510>.
24. Lan W.-J., Edwards M.A., Luo L. *et al.* Voltage-rectified current and fluid flow in conical nanopores. *Acc. Chem. Res.* 2016. **49**, No 11. P. 2605–2613. <https://doi.org/10.1021/acs.accounts.6b00395>.
25. Vlasiouk I. and Siwy Z.S. Nanofluidic diode. *Nano Lett.* 2007. **7**, No 3. P. 552–556. <https://doi.org/10.1021/nl062924b>.
26. Pärnamäe R., Gurreri L., Post J., *et al.* The acid-base flow battery: Sustainable energy storage via reversible water dissociation with bipolar membranes. *Membranes*. 2020. **10**, No 12. P. 409. <https://doi.org/10.3390/membranes10120409>.
27. Tulachan B., Meena S., Rai R. *et al.* Electricity from the silk cocoon membrane. *Sci. Rep.* 2014. **4**. P. 5434. <https://doi.org/10.1038/srep05434>.
28. Kravets L.I., Dmitriev S.N., Satulu V. *et al.* Formation of composite polymer ‘diode-like’ membranes. *Romanian Rep. Phys.* 2014. **66**, No 4. P. 1165–1179.
29. Bacherikov Y.Y., Lytvyn P.M., Mamykin S.V. *et al.* Current transfer processes in a hydrated layer localized in a two-layer porous structure of nanosized ZrO₂. *J. Mater. Sci.: Mater. Electron.* 2022. **33**. P. 2753–2764. <https://doi.org/10.1007/s10854-021-07481-2>.
30. Weyl W.A. Effect of the environment upon the properties of solids. In: *Solid Surfaces and the Gas-Solid Interface*. Eds: L.E. Copeland, R.A. Beebe, D.P. Graham *et al.* *Adv. in Chem.* 1961. **33**. P. 72–85. <https://doi.org/10.1021/ba-1961-0033.ch010>.
31. Meng F., Gala U. & Chauhan H. Classification of solid dispersions: correlation to (i) stability and solubility (ii) preparation and characterization techniques. *Drug Development and Industrial Pharmacy*. 2015. **41**, No 9. P. 1401–1415. <https://doi.org/10.3109/03639045.2015.1018274>.
32. Posada-Pérez S., Hautier G., Rignanese G.-M. Effect of aqueous electrolytes on LiCoO₂ surfaces: Role of proton adsorption on oxygen vacancy formation. *J. Phys. Chem. C.* 2022. **126**, No 1. P. 110–119. <https://doi.org/10.1021/acs.jpcc.1c09348>.
33. Arano K., Begic S., Chen F. *et al.* Tuning the formation and structure of the silicon electrode/ionic liquid electrolyte interphase in superconcentrated ionic liquids. *ACS Applied Materials & Interfaces, Washington, D.C.: Am. Chem. Soc.* 2021. **13**, No 24. P. 28281–28294. <https://doi.org/10.1021/acsami.1c06465>. hal-03287950.
34. Steinrück H.-G., Cao C., Tsao Y. *et al.* The nanoscale structure of the electrolyte–metal oxide interface. *Energy Environ. Sci.* 2018. **11**. P. 996–996. <https://doi.org/10.1039/c7ee02724a>.
35. Xu K. Electrolytes and interphases in Li-ion batteries and beyond. *Chem. Rev.* 2014. **114**, No 23. P. 11503–11618. <https://doi.org/10.1021/cr500003w>.
36. Vatamanu J., Vatamanu M., Borodin O. and Bedrov D. A comparative study of room temperature ionic liquids and their organic solvent mixtures near charged electrodes. *J. Phys.: Condensed Matter*. 2016. **28**. P.464002. <http://dx.doi.org/10.1088/0953-8984/28/46/464002>.
37. Vatamanu J., Borodin O., Olguin M. *et al.* Charge storage at the nanoscale: understanding the trends from the molecular scale perspective. *J. Mater. Chem. A.* 2017. **5**. P. 21049–21076. <https://doi.org/10.1039/C7TA05153K>.
38. Xing L., Vatamanu J., Borodin O. *et al.* Electrode/electrolyte interface in sulfolane-based electrolytes for Li ion batteries: A molecular dynamics simulation study. *J. Phys. Chem. C.* 2012. **116**. P. 23871–23881. <https://doi.org/10.1021/jp3054179>.

39. Bacherikov Yu.Yu., Indutnyi I.Z., Maidanchuk I.Yu. *et al.* Formation of nano-structured CdSe composites in porous SiO_x layers. *Ukr. J. Phys.* 2010. **55**, No 7. P. 817–821.
40. Bacherikov Y.Y., Indutnyi I.Z., Okhrimenko O.B. *et al.* Distribution of CdSe nanoparticles synthesized in porous SiO_x matrix. *Semiconductors.* 2011. **45**. P. 1189.
<https://doi.org/10.1134/S1063782611090028>.
41. Li Vage J., Doi K., Maziers C. Nature and thermal evolution of amorphous hydrated zirconium oxide. *J. Am. Ceram. Soc.* 1968. **51**, No 6. P. 349–353.
<https://doi.org/10.1111/j.1151-2916.1968.tb15952.x>.
42. Bacherikov Yu.Yu., Okhrimenko O.B., Goroneskul V.Yu. *et al.* The model of potential barrier appearing in a hydrolyzed layer localized in a two-layer porous nanostructure. *SPQEO.* 2021. **24**, No 3. P. 288–294. <https://doi.org/10.15407/spqeo24.03.288>.
43. Shen D., Duley W.W., Peng P. *et al.* Moisture-enabled electricity generation: From physics and materials to self-powered applications. *Adv. Mater.* 2020. **32**. P. 52.
<https://doi.org/10.1002/adma.202003722>.
44. Zhang Y., Nandakumar D.K., Tan S.C. Digestion of ambient humidity for energy generation. *Joule.* 2020. **4**, No 12. P. 2532–2536.
<https://doi.org/10.1016/j.joule.2020.10.003>.
45. Liu X., Gao H., Ward J.E. *et al.* Power generation from ambient humidity using protein nanowires. *Nature.* 2020. **578**. P. 550–554.
<https://doi.org/10.1038/s41586-020-2010-9>.
46. Sun Z., Wen X., Wang L. *et al.* Emerging design principles, materials, and applications for moisture-enabled electric generation. *eScience.* 2022. **2**, No 1. P. 32–46. <https://doi.org/10.1016/j.esci.2021.12.009>.
47. Yang L., Nandakumar D.K., Miao L. *et al.* Energy harvesting from atmospheric humidity by a hydrogel-integrated ferroelectric-semiconductor system. *Joule.* 2020. **4**, No 1. P. 176–188.
<https://doi.org/10.1016/j.joule.2019.10.008>.

Authors and CV



Yuriy Yu. Bacherikov defended his Doctoral Dissertation in Physics and Mathematics in 2010. Leading scientific collaborator at the V. Lashkaryov Institute of Semiconductor Physics, NASU. Authored over 300 publications, 6 patents, 1 monograph. The area of his scientific interests includes physics and applications of wide-band semiconductor compounds and devices based on them. <https://orcid.org/0000-0002-9144-4592>



Olga B. Okhrimenko, defended his Doctoral Dissertation in Physics and Mathematics in 2010. Leading scientific collaborator at the V. Lashkaryov Institute of Semiconductor Physics, NASU. Authored over 140 publications, 1 patent, 1 monograph. The area of her scientific interests

includes investigation of the patterns and physical mechanisms of formation and rearrangement of the defect-impurity system of the thin-film dielectric-semiconductor structures, depending on technology of preparation, composition of thin films, additional processing and introduction of buffer layers. <https://orcid.org/0000-0002-7611-4464>; e-mail: olga@isp.kiev.ua

Author's contribution

Bacherikov Yu.Yu.: phenomenological analysis, concept development, investigation, data curation (partially), writing – original draft, writing – review & editing, visualization.

Okhrimenko O.B.: concept refinement, validation, phenomenological concept agreement with literature data, investigation, data curation (partially), writing – original draft, writing – review & editing.

Принципи створення пристроїв, які здатні керувати протіканням струму у провідниках другого роду

Ю.Ю. Бачеріков, О.Б. Охріменко

Анотація. У роботі з позиції уявлень, що використовуються у фізиці напівпровідників та напівпровідникової техніки, розглядаються процеси, які протікають у провідниках 2-го роду та зумовлені струмопроходженням у них. Показано, що використання кількох композитних матеріалів, що складаються з пористої матриці, яку заповнено електролітом, дозволяє отримувати багат шарові структури, в яких у середовищі електроліту з'являються потенціальні бар'єри, поява яких зумовлена відмінностями у властивостях пористої матриці кожного шару. Показано перспективу створення нових пристроїв на базі провідників 2-го роду, які здатні керувати напрямком і величиною струмопроходження у таких провідниках, що знаходяться в рідкому стані (електролітах), тобто перспективу отримання іонних пристроїв, які максимально наближуються за своїми функціональними властивостями до основних електронних пристроїв, таких як діоди, транзистори і т.ін.

Ключові слова: провідники 2-го роду, контроль струмопроходження, іонні пристрої, потенціальні бар'єри в електролітах, багат шарові пористі композитні матеріали.