

90 YEARS



## INVESTIGATIONS OF A BARRIER LAYER BY THE THERMOPROBE METHOD

Translated and reprinted from *Izv. Akad. Nauk SSSR, Ser. Fiz.* 5, No. 4–5, pp. 442–446 (1941)

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The method of thermoprobe, developed by the present author, was applied to the investigation of the barrier layer of cuprous oxide and silver sulphide photocells and of selenium rectifiers. These experiments enabled the author to show that the barrier layer is on both sides bordered by semi-conductors, the current carriers in these semi-conductors having opposite signs. A new mechanism of formation of the barrier layer is proposed and theoretically investigated.

The question whether the barrier layer in rectifiers and photocells borders directly on a metal electrode or there is the intermediate layer of a well conducting semiconductor between the electrode and the barrier layer has been open up to date. Only in separate cases, the theoretical conceptions concerning this matter are available. For example, Rother and Bomke have shown [1] that, in cuprous oxide rectifiers, the presence of a cuprous oxide layer with a copper excess between the matrix copper and the barrier layer should be expected. In this case, the barrier layer was interpreted by the authors in the common manner as the layer of a semiconductor without any impurities. As to front-wall  $\text{Cu}_2\text{O}$ -photocells, the question about a layer between the top electrode and the barrier layer was not raised at all.

Investigations of the influence of donor-type impurities on the valve photoeffect in cuprous oxide made in our laboratory resulted in the almost doubtless conclusion that, in some cases, there is a well conducting semiconductor layer between the top electrode and the barrier layer, and donor impurities can penetrate through this barrier layer and deepen into the main semiconductor as well [2].

In this paper, it is shown which direct experiment can prove the presence of a semiconductor between the barrier layer and the adjacent electrode and determine the character of its conduction. The most simple way to ascertain the character of the conduction of a semiconductor is to determine the sign of the thermo-electromotive force: the cold electrode acquires a positive

charge in the case of hole conduction and a negative one in the case of electron conduction.

The possibility to measure the thermo-e.m.f. in the thinnest semiconductor layer deposited onto a massive semiconductor is closely related to what measure this thin semiconductor layer is isolated from the massive one. To solve the task posed by us, the conditions were favorable: between the thin surface layer and the rest semiconductor, there is the barrier layer, i.e., a layer with high resistance.

It remains to remove the top electrode and to measure the thermo-e.m.f. by using miniature electrodes touching the surface (thermoprobes). As for the front-wall cuprous oxide photocells, we used three ways to obtain an element without top electrode: 1) washing out the top electrode with mercury; 2) etching the photocell by a wedge with nitric acid; 3) breaking the technological process that results in the creation of a barrier layer and a top electrode (for instance, cathode sputtering) at that stage when the top electrode possesses no noticeable conduction.

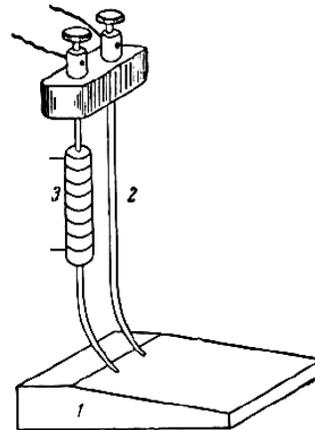


Fig. 1. Experimental setup with a front-wall cuprous oxide photocell etched by a wedge: 1 – photocell, 2 – thermoprobe, 3 – electric oven

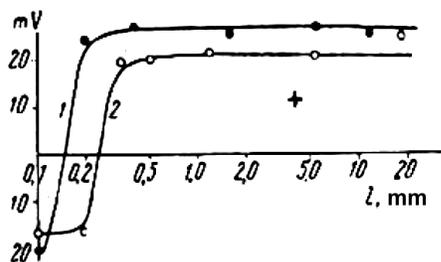


Fig. 2. Change of the thermo-e.m.f. as a function of the distance of a thermoprobe from the wedge edge. Curve 1 was obtained for a photocell prepared by reduction with the quenching in water containing glycerol, curve 2 – by reduction in a  $ZnSO_4$  solution with glycerol

The construction of a thermoprobe and the method of its use in the case of etching by a wedge are apparent from Fig. 1.

The studied surface is touched by two copper wires rounded at their ends  $\varnothing$  (of 1 mm in diameter), one of them being heated with electric oven 3. The sample was mounted at the table taken off a microscope and provided with a facility to shift it along two mutually orthogonal directions. A compensation scheme allowed us to measure both the arising thermo-e.m.f. and the sample resistance between the thermoprobe electrodes.

Heating the electrode was controlled in such a manner that the thermo-e.m.f. arising from the main semiconductor was of the order of 20 to 30 mV, which corresponds to the temperature difference of several tens of  $^{\circ}C$ . As the sign of the fact that the thermoprobe electrodes touch just the semiconductor and not the metallic non-etched electrode, we consider the presence of a high electrode-to-electrode resistance (of the order of several hundred thousand Ohms) as well as the value of the arising thermo-e.m.f. itself.

In Fig. 2, we show the result of using the thermoprobe method in the case of etching by a wedge (curves were measured by V.A. Yurkov in our laboratory). Plotted along the abscissa on the logarithmical scale are the distances from the non-etched electrode along the photocell surface. The measured values of the thermo-e.m.f. are plotted along the ordinate axis. The sign “plus” corresponds to the hole conduction, the sign “minus” – to the electron one. Curve 1 was measured on the photocell prepared by reduction after the quenching in water with glycerol, curve 2 – by reduction in a  $ZnSO_4$  water solution with glycerol. Let us assume that the etching by a wedge proceeded uniformly. Then the thermoprobe shift by 0.1 mm corresponds to the depth change of  $4 \times 10^5$  cm in these experiments.

The magnitude and sign of the thermo-e.m.f. near the electrode clearly indicate the presence of a cuprous oxide layer with electron conduction in this place.

Referring for details to [2], we will limit ourselves by the enumeration of results obtained by us with the thermoprobe method. It was ascertained that, in the front-wall  $Cu_2O$  photocells prepared in any way, there is a semiconductor with electron conduction between the top semi-transparent electrode and the barrier layer (main semiconductor possesses the hole conduction). A similar result was obtained for selenium rectifiers (selenium possesses the hole conduction, while the layer under the top electrode has the electron one). For silver sulfide valve photocells, the effect with opposite sign was obtained (main semiconductor has the electron conduction, while the layer under the top electrode has the hole one).

The common feature for all the photocells and rectifiers studied with the thermoprobe method is the presence of semiconductors with conduction of opposite signs on both sides of the barrier layer.

Probably, this fact is observed in many cases; therefore, it seems interesting to consider the question how the nature of the barrier layer should be represented. The assumption that the barrier layer consists of a practically pure semiconductor bordering with layers that contain acceptors on one side of the barrier layer and donors on the other side is not obligatory. This statement can be clarified with the following example. Let us consider a well conducting  $p$ -semiconductor with a high acceptor concentration of about  $10^{16} \text{ cm}^{-3}$ , for example, which gives the specific resistance close to  $10^4 \text{ Ohm}\cdot\text{cm}$  with regard for the dissociation work of 0.3 eV and the mobility of  $50 \text{ cm}^2/\text{Vs}$ . Let us introduce donor impurities<sup>1</sup> into a semiconductor containing acceptor levels. At some concentration of the donor impurity, the chemical potential of the semiconductor reaches the middle of the forbidden gap, and the semiconductor will possess the resistance inherent to its basic lattice, i.e., that corresponding to the absence of impurities et all. This

<sup>1</sup>Donor impurities are those, which are capable, after their introduction into a semiconductor, to donate their electrons to the conduction band or to other unfilled levels, while the acceptor impurities are those capable to capture electrons.

The levels of a donor impurity can lie both above and below the level of the chemical potential. In the first case, the donor impurity levels lose partially or fully their electrons and play the role of an acceptor, in the second case – the role of a donor in the usual mean of this word. The levels of the acceptor impurity can be considered in a similar way.

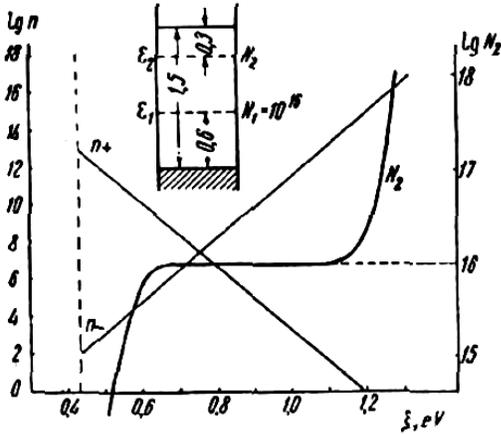


Fig. 3. Concentrations of holes and electrons versus the chemical potential

effect will take place at a less concentration of the donor impurity, if its local levels will lie higher.

This estimation can be easily performed starting from the known equations describing the thermodynamic equilibrium of electrons in a semiconductor. The concentration of holes in the filled band ( $n_+$ ) and that of electrons in the conduction band ( $n_-$ ) are unambiguously determined by the position of the chemical potential  $\chi$  (measured, as usual, from the top of the filled band):

$$n_+ = Q_+ e^{-\frac{\chi}{kT}}, \quad n_- = Q_- e^{\frac{\chi-u}{kT}},$$

where  $u$  is the forbidden gap width, and

$$Q_{\pm} = \frac{2(2\pi m_{\pm} kT)^{3/2}}{h^3}$$

( $m_+$  is the effective mass of a hole, and  $m_-$  is that of an electron).

If all the acceptor levels lie at the height  $\varepsilon_1$ , and donor levels at the height  $\varepsilon_2$ , then  $n_+$  is determined from the relation

$$n_+ + \frac{N_2}{1 + a/n_+} = \frac{c}{n_+} + \frac{N_1}{1 + bn_+},$$

where  $N_1$  and  $N_2$  are the concentrations of acceptor and donor impurities, respectively,

$$a = Q_+ e^{-\frac{\varepsilon_2}{kT}}; \quad b = \frac{1}{Q_+} e^{\frac{\varepsilon_1}{kT}}; \quad c = Q_+ + Q_- e^{-\frac{u}{kT}}.$$

There is a relation between  $n_+$  and  $n_-$ :  $n_+ n_- = c$ .

The results following from the expression for  $n_+$  are shown in Fig. 3 for one special case ( $u = 1.5$  eV,  $\varepsilon_1 =$

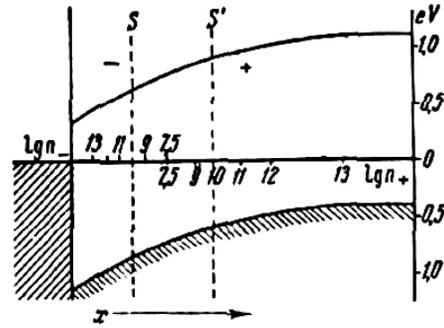


Fig. 4. Energy scheme of a photocell or a rectifier

0.6 eV,  $\varepsilon_2 = 1.2$  eV,  $N_1 = 10^{16}$  cm $^{-3}$ ,  $T = 300$  K).  $Q_+$  and  $Q_-$  are accepted to have the value of  $3 \times 10^{19}$ . Plotted along the abscissa is the value of chemical potential  $\zeta$  depending on  $N_2$  at a constant temperature. When  $T = 300$  K and  $N_2 = 0$ ,  $\zeta = 0.42$  eV. Plotted along the ordinate axis are the logarithms of the concentrations of holes ( $n_+$ ), electrons ( $n_-$ ) and the donor impurity ( $N_2$ ). It is seen from Fig. 3 that when  $N_2$  grows from zero up to  $10^{16}$  cm $^{-3}$ , the hole concentration decreases approximately by  $3 \times 10^5$  times and becomes equal to the concentration of conduction electrons. With the further growth of  $N_2$ , conduction electrons begin to dominate. The conduction of the semiconductor changes from the  $p$ - to  $n$ -type. When  $N_2 = N_1 + 1\% N_1$ , the electron concentration becomes equal to the hole concentration that was intrinsic to this semiconductor before the introduction of a donor impurity.

In the light of this consideration, the obtained facts can be treated in the following way: the concentration of a donor impurity introduced through the surface into the  $p$ -semiconductor in the course of the creation of a barrier layer diminishes with increase in the depth. At the surface, we obtain a well conducting layer with electron conduction. The conduction decreases with increase in the depth, reaches its minimum, and then begins to grow becoming the hole one. Thus, we obtain the barrier layer at a definite depth in the semiconductor.

The energy band diagram for a photocell or a rectifier based on this principle (the main semiconductor is a  $p$ -one) is shown in Fig. 4. There is a metal on the left. Bands in the semiconductor are "curved" as a consequence of the continuous change in the donor impurity concentration with depth  $x$ . The level of the chemical potential is depicted with a horizontal line. The bottom row of numbers gives  $\lg n_+$  at the respective depth  $x$ , the top set does the values of  $\lg n_-$ . Some part

of the band distortion in this figure can be caused by the action of the metal - semiconductor contact. The signs “+” and “-” indicate the domination of the hole or electron conduction in the respective semiconductor areas. If we accept that the creation of a barrier layer is provided with the specific resistance of a semiconductor higher than  $10^7$  Ohm·cm (that is,  $n < 10^{10}$  cm<sup>-3</sup>), then the barrier layer in Fig. 4 will be confined between dashed lines  $SS'$ .

In most cases, the acceptor concentration is not constant but decreases in the direction to the metal electrode. However, this fact does not change the general character of the phenomenon.

For our treatment of the barrier layer, it is essential that if the donor impurity decreases with increase in the depth (the amount of acceptors being constant or increasing) and  $N_2(\text{max}) > N_1$ , then the barrier layer is automatically formed. The sharper the concentration of donor impurities drops or the greater the acceptor impurity concentration with increase in the depth, the less the total resistance of this layer.

The barrier layer obtained by the way described above will be distinguished by its high thermal resistance and stability. Indeed, the diffusion of the acceptor impurity from the semiconductor depth to the metal (and reversely for the donor impurity) will result at the first stages only in a spatial shift of the barrier layer. Only after the time moment when the acceptor impurity concentration exceeds the donor one all over the semiconductor, the barrier layer will fully vanish. These conclusions can be generalized to the case of the electron conduction inherent to the main semiconductor.

The above conceptions are directly applied to the case where the barrier layer is created after the introduction of acceptor and donor impurities into the same semiconductor, which takes place, for instance, in cuprous oxide photocells and rectifiers. The situation is complicated if the barrier layer is formed from a

semiconductor of another chemical composition as, for example, in silver sulfide photocells.

The influence of donor impurities on the thermal stability of front-wall cuprous oxide photocells has been considered in [2].

1. F. Rother and H. Bomke, *Zs. f. Phys.*, **81**, 771 (1938).
2. V.E. Lashkaryov and K.M. Kosonogova, *Izv. AN SSSR., Ser. Fiz.*, **5**, 478 (1941). on

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(07.10.1903–01.12.1974)

V.E. Lashkaryov was born on October 7, 1903 in Kyiv. In 1924, he graduated from Kyiv Institute of People Education (now Taras Shevchenko Kyiv National University). His scientific activity began during the postgraduate course at the Chair of Physics in Kyiv Polytechnical Institute, where he was also teaching. On the invitation of Academician A.F. Ioffe in 1930, he relocated to Leningrad, where he headed the Department of X-rays during five years and then the Department of Electron Diffraction at Leningrad Physico-Technical Institute (now A.F. Ioffe Physico-Technical Institute of the RAS). In the period from 1935 to 1939, he was Head of the Chair of Physics of Arkhangelsk Medical Institute. In 1939 on the invitation of the AS of Ukrainian SSR, he returned in Kyiv, where he took a position of Head of the Department of Semiconductors at the Institute of Physics of the AS of Ukrainian SSR and Head of the Chair of Physics at Taras Shevchenko Kyiv State University. In the years of the Great Patriotic War, he worked in Ufa and Moscow, where was relocated Institute of Physics of the AS of Ukrainian USSR. In 1944 on the invitation of O.O. Bogomolets, President of the AS of Ukrainian SSR, he again returned to Kyiv, where he was elected Academician of the AS of Ukrainian SSR in 1945. In 1960 on his initiative, the Institute of Semiconductors of the AS of Ukrainian SSR was organized (now V.E. Lashkaryov Institute of Semiconductor Physics of the NAS of Ukraine) and was headed by V.E. Lashkaryov till 1970.