

## Deep Silicon Barrier Structure as Chemical Sensor for Detection of Hydrochloric Acid Salt Solutions

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The possibility of the detection of hydrochloric acid salts by silicon sensory structures with photovoltaic principle of transformation has been considered in this work. The proposed structures realize transducer principle that differs from the well-known conventional LAPS (light-addressable potentiometric sensors). The basis of such devices is a “deep” barrier silicon structure. In the proposed scheme, the sensor signal is the photocurrent through the barrier structure induced by light in the range of high absorption. It allows receiving maximum changes of photocurrent due to changes of recombination rate on working surface. It should be noted that the proposed structure allows simpler technical realization than conventional LAPS. Several analytes (chlorides), containing different metals with various relative electronegativity (Fe, Zn and Al), were experimentally investigated. It has been experimentally shown that dependences of photocurrent on polarization voltage (the voltage that changes the surface band bending) is very informative for the detection of such analytes. Within the framework of the Stevenson-Keyes model, the obtained results can be explained qualitatively. The principal reason allowing the detection is the influence of the local electrostatic field of adsorbed ions on the recombination parameters of the silicon surface.

**Keywords:** Chemical sensor, Photocurrent, Surface recombination, Deep silicon barrier structure.

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### 1. INTRODUCTION

Chemical sensors are considered as important practical advances in the semiconductor physics. As well known, each type of semiconductor transducer has specific scope of practice application and sometimes they can complement each other for obtaining more information about the analyte. That is why new mechanisms of sensory transformation should be proposed and investigated.

The detection of polar molecules can be realized, for example, by different ways. In particular, well-known light addressing potentiometric sensor (so-called LAPS) is a principal structure that can be utilized for detection and recognition of a wide range of analytes [1, 2]. During the last decades, the physical principles of LAPS operation have been investigated and the high-effective industrial designs were developed [3-8]. The operation principle is based on a variation of the thickness of the space charge region in the electrolyte – insulator – semiconductor structure, whereas the sensor signal is associated with the process of photo-induced barrier capacitance charging. On the other hand, the search and use of photoelectric sensory structures with other transducer principles (allowing “conversion” of adsorption into a useful signal) can provide additional information about the analyte, especially in the complex sensory systems such as electronic nose or electronic tongue [9]. It can be important also in sensory systems that combine different elements [3, 9].

It was proposed to use the deep barrier silicon structures for effective sensory devices [10-12]. This

structure is similar in some aspects to LAPS, but the transformation mechanism is different. The sensor signal is the photocurrent through the barrier in that case. The parameters of a deep silicon structure should be carefully optimized to obtain maximum changes of photocurrent as a result of adsorption on the working surface [4]. The principal conditions of high efficiency are: 1) close values of the length of minority carriers diffusion and the junction depth, 2) the light used for illumination is characterized by short wavelength and strong absorption in silicon. The general principle of the operation in such case is the change of the recombination characteristics on the silicon surface due to the chemical (or physical) adsorption of the molecules via electrostatic influence. They can be easily registered due to the change of surface recombination rate and corresponding change of the photocurrent. The proposed structure allows simpler technical realization than conventional LAPS.

The suitability of recombination sensors for the detection of various molecular structures (water, alcohols, carbon nanoparticles, etc.) was earlier demonstrated experimentally [11, 12]. The peculiarities of the adsorption processes on the silicon surface as well as mechanisms of their transformation into a useful signal are not completely clear. For model approach developed in the proposed work, the analytes with a well pronounced polar structure were chosen. The aqueous solutions of salts of HCl were experimentally investigated. All these salts contain the same Cl ion and metal ions with different relative electronegativity (Fe, Zn, Al). This approach

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allows studying the device operation taking into account the structural features of the analytes at the same time. The feasibility of such approach is obvious, since it allows completing the model representations and provides some practical recommendations.

The problems of the physical properties of silicon interface should also be considered. It is well known that treatment in solution of  $\text{FeCl}_3$  salt provides some passivation properties on the surface of  $n$ -Si [13]. It is interesting to know if  $\text{ZnCl}_2$  or  $\text{AlCl}_3$  salts offer the similar passivation effect. This is another motivation for the presented research.

## 2. EXPERIMENTAL PROCEDURE

To study the features of adsorption processes the "deep" barrier silicon structures with photoelectric conversion principle were created on the base of metal-silicon contact. Silicon wafers (100) had  $n$ -type conductivity and specific resistance of 30-50  $\Omega\cdot\text{cm}$ .

It was shown [10] that photocurrent significantly depends on the recombination properties of the surface  $S$  in case when region with generation of non-equilibrium holes ( $1/\alpha(\lambda) \sim 1 \mu\text{m}$ ) and the region, where these carriers are collected by electric field, were separated in space. The value of photocurrent via barrier structure (or measured signal in Fig. 1) can be expressed as:

$$i(S) \cong \frac{1 + \frac{S}{\alpha(\lambda)D}}{S \frac{l}{D} \text{sh}\left(\frac{d}{l}\right) + ch\left(\frac{d}{l}\right)}, \quad (1)$$

where  $D$  is the hole diffusion coefficient,  $\alpha(\lambda) \sim 10^5 \text{ cm}^{-1}$ . In our case, the thickness of  $n$ -Si wafer  $d$  is about 300  $\mu\text{m}$ , the hole diffusion length  $l$  is about 150  $\mu\text{m}$ .

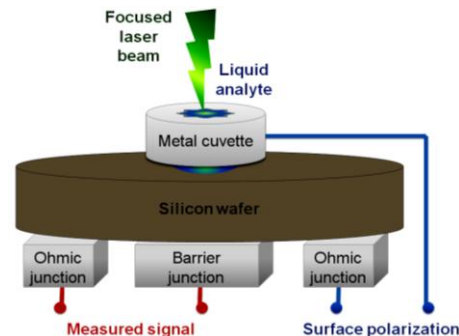
Surface of the structure was scanned by green laser with wavelength  $\lambda = 535 \text{ nm}$ . In order to realize the scanning of silicon surface, the system of laser beam deviation was applied. Such deviation of the laser beam was obtained with the help of acoustic-optical crystals [14]. The contact of liquid analyte with surface of the sensory structure was realized with the aid of metal cuvette (volume of the cuvette is 0.1 ml) that served as an electrode, Fig. 1.

Thus, it was possible to observe and compare the surface distributions of induced photocurrent through the barrier junction received for the area of silicon surface that contact with analyte in the cuvette. In our studies, silicon barrier structures based on the metal-semiconductor contact were used.

In general, there are the possibilities to perform two types of measurements for the proposed experimental scheme: 1) in the case of illumination of a fixed point on the surface, it is possible to obtain the polarization curves i.e. the dependences of photocurrent versus polarization voltage  $U$  (voltage applied to metal cuvette, which changes the surface band bending in the region of silicon which contacts with analyte); 2) in the case of silicon surface scanning by a laser beam, the maps of the distribution of the photocurrent can be obtained.

The water solutions of  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$  and  $\text{AlCl}_3$  used

as the analytes were characterized by the same value of molar concentration (1 mole per liter). As known, salt molecules are dissociated in aqueous solutions, for example,  $\text{FeCl}_3$  solution represents an electroneutral mixture of positive  $\text{Fe}^{3+}$  ions, negative  $\text{Cl}^-$  ions and dipole  $\text{H}_2\text{O}$  molecules. The same effect exists in water solutions of  $\text{ZnCl}_2$  and  $\text{AlCl}_3$  salts.

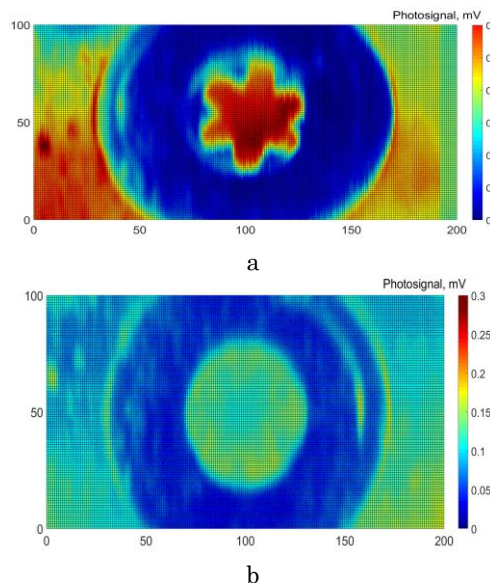


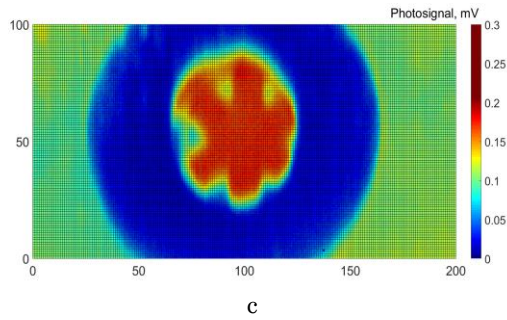
**Fig. 1** – Schematic representation of the sensory structure and cuvettes with an analyte

## 3. RESULTS AND DISCUSSION

Generally speaking, physical and/or chemical adsorption of molecules on the working surface of the sensor is possible. In the case of physical adsorption, the main factor determining changes of the recombination properties (and the surface band bending) is electric field that forms dipole structures near the surface. In the case of chemical adsorption, chemical bonds between metal atoms and with unsaturated bonds of silicon atoms are formed. In addition, certain chemical reactions are possible on the surface of the silicon structure. These processes are usually accompanied by the injection/extraction of electrons into a semiconductor that effects the change in the surface band bending additionally. In the real situation, the adsorption processes on the surface of the silicon structure are more complex and combine the main features of all mechanisms.

In Fig. 2, the surface distributions of the photocurrent are shown for three analytes at zero external bias.





**Fig. 2** – The surface distribution of photocurrent for analytes in the case of zero external bias: a)  $\text{FeCl}_3$ , b)  $\text{AlCl}_3$ , c)  $\text{ZnCl}_2$

The surface distributions of photocurrent as well as the average value of photocurrent are different for each salt. So, as follows from the analysis of the surface distributions of the photocurrent in Fig. 2, there is a fundamental possibility of the detection, since in each case (a)-(c) the rate of effective recombination  $S$  changes differently for the investigated samples. The change in the surface band bending  $Y_s$  (for a zero external voltage  $U = 0$ ) is supposed to be the main factor that causes the changes in recombination characteristics.

For a more detailed analysis of physical mechanisms that determine the influence of adsorption processes, it is necessary to compare the polarization curves. Fig. 3 and Fig. 4 show the typical dependences of the photocurrent  $I$  on the polarization voltage  $U$ , which is applied between the electrode and the illuminated surface. A fixed point on the silicon surface is illuminated. The applied voltage changes the surface band bending  $Y_s$  of the silicon structure in a wide range. Thus, the minimum photocurrent value (corresponding to the maximum of  $S$ ) can be reached when surface concentrations of electrons and holes near the surface obey the condition  $c_n n_s = c_p p_s$  [14], where  $c_n$ ,  $c_p$  are the capture cross sections,  $n_s$ ,  $p_s$  are the surface concentrations of electrons and holes, respectively.

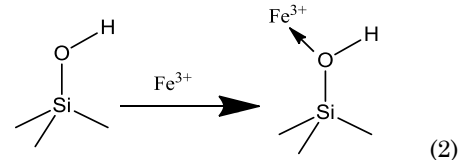
In the case of simple recombination level at the surface, recombination  $S$  can be given by the expression:

$$S(Y_s) = \frac{c_p c_n N_t (p_0 + n_0)}{c_n (n_s(Y_s) + n_1) + c_p (p_s(Y_s) + p_1)}, \quad (2)$$

where  $n_0$  and  $p_0$  are the equilibrium carrier concentrations;  $n_1$  and  $p_1$  are the carrier concentrations when Fermi level at the surface is equal to the energy of recombination at the surface,  $N_t$  is the concentration of recombination centers (the relationships between the surface and volume concentrations are  $n_s = n_0 \exp(-Y_s)$ ,  $p_s = p_0 \exp(Y_s)$ ). As well known, the dependences  $S(Y_s)$  calculated according to (2) are bell-shaped in this approach [14]. The increase of photocurrent (1) corresponds to a decrease of  $S$  due to the lack of carriers of a certain charge sign. We can say that there is some conformity between the dependences  $S(Y_s)$  and  $I(U)$ .

Note, that in all cases, the minimum of the curves  $I(U)$  corresponds to the polarization voltages, which form the region of depletion near the working surface. This may indicate small values of the initial band bending  $Y_{s0}$  in the  $n$ -silicon wafer before the contact with analytes (in other words, the deep inversion does

not occur and the condition  $n_s > p_s$  is satisfied). As can be seen, the shape of the curves  $I(U)$  has the specific features (see Fig. 3b, Fig. 4a, Fig. 4b) that allows to distinguish the analytes with nice accuracy. Let us analyze the possible process on the silicon surface contacting with chlorides from our set. All metal ions ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Zn}^{2+}$ ) possess the properties of Lewis acid, able to interact with Lewis bases, such as surface hydroxyls, forming coordination bonds. A charged complex is formed on the silicon surface as a result. For example, we can give the possible reaction at the silicon surface for  $\text{FeCl}_3$  solution (containing ion  $\text{Fe}^{3+}$ ):

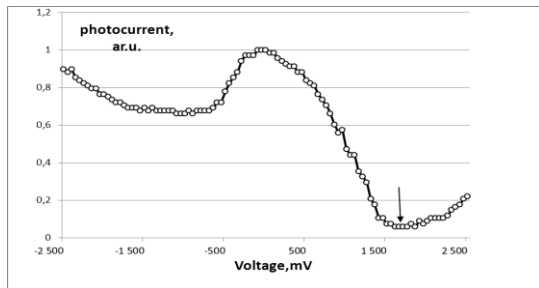


In principle, this reaction describes the process of chemical absorption on the silicon surface. As it was mentioned after contact with solution, these processes can lead to the formation of an additional positive charge at the silicon surface via coordination bond (donor-acceptor interaction). In turn, the electrostatic influence of charged structures in the solution on the parameters of recombination centers of the Si/SiO<sub>2</sub> interface can be described in terms of physical absorption. It seems that these two reasons should be principal. Let us suppose that the cross sections remain stable due to contact with  $\text{FeCl}_3$  solution and, moreover, their values are close  $c_n \sim c_p$ . The activity of  $\text{Fe}^{3+}$  ions on the surface of the sensory structure, as already noted, may be manifested in the appearance of a positive charge at the interface. As a result (in comparison with the case when the surface is in contact with water), the minimum photocurrent should be shifted to the region of lower positive voltage. This shifting of  $I(U)$  is 0.3-0.5 V due to the change of the initial band bending. In other words, since the additional positive charge on the surface decreases the hole concentration  $p_s$  near the surface, the minimum photocurrent can be achieved for lower positive voltages. This effect is very similar to that which can be experimentally observed for measurements of high-frequency capacitance-voltage characteristics of MIS structures [15]. Indeed, in the case when an electric charge is embedded in a dielectric layer, it is well known that the shifting of flat band voltage can be observed. It is due to the influence of the electric field of embedded charge.

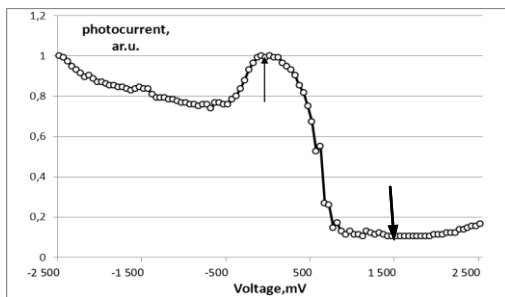
The contact with an aqueous solution of  $\text{FeCl}_3$  also causes significant changes of the shape of  $I(U)$  curves in comparison with water, Fig. 3. It can be observed that there is a significant "widening" of the curves in comparison with the "water curves". In the frame of Stevenson-Keyes theory [14], this fact may indicate the change of the energy of main recombination level at the silicon interface (the level is "removed" from the middle of the silicon band gap). An additional reason for the shape of recombination curves is the electrostatic effect of an effective electric field, which is formed due to a certain spatial orientation of the dipole near the silicon surface. An interesting result to note is the presence of specific features that arise in the

non-monotony of polarization curves  $I(U)$ . It should be noted that the non-monotonic features correspond to voltages from the accumulation range ( $\sim -1.0$  V). Such features indicate that the photocurrent is determined not only by recombination via the main energy level [14] (corresponding to the middle of silicon band gap). The presence of such features proves the contribution of additional channel of recombination at the surface of sensory structure. It can be provided either by the additional level in the band gap or by the system of levels distributed in some energy range  $dN/dE$ . The case cannot be fully described by the model of surface recombination that assumes expression like (3).

It is interesting to note that zero external voltage corresponds to the maximum value of the photocurrent. This means, in a certain sense, that  $\text{FeCl}_3$  solution exhibits passivation properties. In other words, the surface recombination has a minimum (the photocurrent has the maximum value) when the surface of  $n$ -silicon wafer is treated with  $\text{FeCl}_3$  and external bias is not applied.

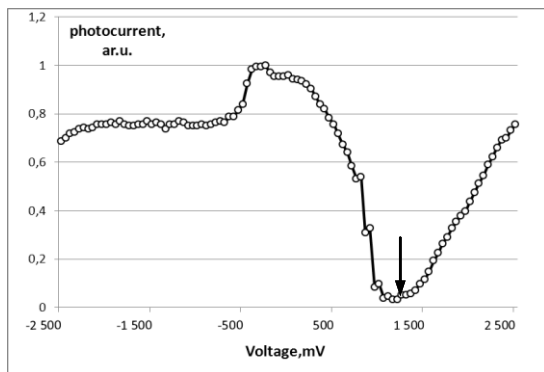


a

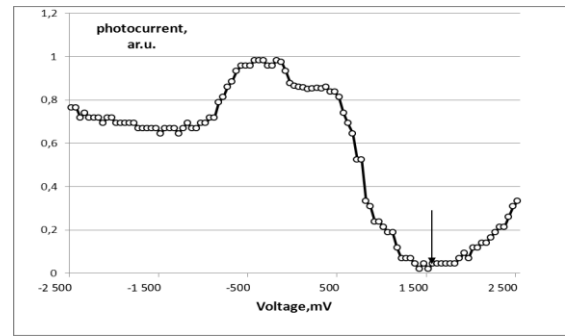


b

**Fig. 3** – Dependence of the photocurrent on the polarization voltage  $I(U)$  for the contact of the silicon structure surface with water (a) and  $\text{FeCl}_3$  (b)



a



b

**Fig. 4** – Dependence of the photocurrent on the polarization voltage  $I(U)$  for the contact of the silicon surface with water solution of  $\text{ZnCl}_2$  (a) and  $\text{AlCl}_3$  (b) salts

As follows from the analysis of the results in Fig. 4, the shape of the curve changes when the silicon surface contacts with solutions  $\text{ZnCl}_2$  or  $\text{AlCl}_3$ . In other words, the activity of  $\text{Zn}^+$  and  $\text{Al}^{3+}$  ions on the surface of the sensory structure appears rather different from the case discussed above. Let us compare the corresponding  $I(U)$  curves with the case when the surface  $s$  is in contact with  $\text{FeCl}_3$  (Fig. 3b). First, in both cases, the non-uniformity in the voltage region ( $U \sim -1$  V) is more pronounced. Secondly, the "widening" of the curves is practically not observed. The position of the minimum for solutions  $\text{ZnCl}_2$  and  $\text{AlCl}_3$  corresponds to the voltages  $U \sim 1.4-1.5$  V and  $U \sim 1.5$  V, respectively. As can be concluded, the solutions  $\text{ZnCl}_2$  and  $\text{AlCl}_3$  also provide effective passivation of  $n$ -silicon if external bias is not applied. The effect is about the same.

Note that the shifting of the minimum of  $I(U)$  (in comparison with the case of the surface with water) can also be related to changes in the capture cross sections  $c_n, c_p$ . This is due to the electrostatic effect of the charged structures in the solution. Since the quasi-equilibrium spatial configuration of such structures near silicon surface may be different for each solution, it seems quite probable. Consequently, an effective electric charge (i.e. the charge existed due to a certain configuration of charged elements near the recombination centers) changes the recombination parameters at Si/SiO<sub>2</sub> interface. That can cause the additional deformation of  $I(U)$  curves (in other words, the condition of the photocurrent minimum can be fulfilled for other band bending due to changes in the capture cross-sections).

Thus, measurements of the current dependences on the polarization voltage  $I(U)$  allow distinguish the analytes with similar chemical structure. It can be assumed that the formation of thin nanostructured or organic films can stabilize the surface properties and increase the absorption efficiency of such sensory structures [10, 16, 17].

#### 4. CONCLUSIONS

The possibility of detection of hydrochloric acid salts ( $\text{FeCl}_3$ ,  $\text{ZnCl}_2$  and  $\text{AlCl}_3$ ) with sensory structures based on new photovoltaic transducer has been demonstrated. To detect the analytes with the specified chemical structure, it is proposed to analyze the surface distribution of the photocurrent and the dependence of the photocurrent on



polarization voltage applied between the analyte and the silicon substrate. It is shown that each curve has a very specific character. The obtained results can be qualitatively explained within the framework of the Stevenson-Keys model. In particular, the change of the shape of polarization curves can be related to the electrostatic effect of charged structures that are present in the solution (their specific spatial configuration near defects on the surface). It has been shown that the electrostatic effect influences the parameters of the recombination centers on the silicon surface differently for each analyte. It is important to take into account not only the influence of the

recombination level near the middle of the band gap, but also the additional levels or system of levels in the silicon band gap. It was proved in an independent way [13] that FeCl<sub>3</sub> solution demonstrates the passivation properties on the surface of silicon *n*-Si. For ZnCl<sub>2</sub> and AlCl<sub>3</sub> solutions the passivation effect is about the same order.

#### ACKNOWLEDGEMENTS

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#### Застосування кремнієвої структури з глибоким бар'єром для виявлення солей хлорної кислоти

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У роботі розглянуто можливість виявлення солей соляної кислоти за допомогою кремнієвих сенсорних структур з фотоелектричним принципом перетворення. Запропоновані структури реалізують принцип перетворення, що відрізняється від принципу, який застосовано у відомих структурах типу LAPS (потенціометричний сенсор із світловою адресацією). Основою таких пристроїв є «глибока» кремнієва бар'єрна структура. У запропонованій схемі сигналом датчика є фотострум через бар'єрну структуру, індукований світлом із області сильного поглинання кремнію. Це дозволяє отримувати максимальні зміни фотоструму внаслідок зміни швидкості рекомбінації на робочій поверхні. Слід зазначити, що запропонована структура дозволяє більш просту технічну реалізацію, ніж структури LAPS. Експериментально досліджено декілька аналітів (хлоридів), які містять метали з різною відносною електронегативністю (Fe, Zn та Al). Експериментально показано, що залежність фотоструму від напруги поляризації (напруга, яка змінює приповерхневий вигин зон) є інформативною для виявлення таких аналітів. В рамках моделі Стівенсона-Кейса отримані результати можна пояснити якісно. Основною причиною, яка дозволяє виявлення таких аналітів, є вплив локального електростатичного поля адсорбованих іонів на параметри рекомбінації поверхні кремнію.

**Ключові слова:** Хімічний сенсор, Фотострум, Поверхнева рекомбінація, Кремнієва бар'єрна структура.