

## Effect of Long-Range Passivation of Impurity Atoms by Surface Dangling Bonds on the Conductivity of Porous Silicon

F. Ptashchenko\*

National University "Odesa Maritime Academy", 8, Didrikhson St., 65029 Odesa, Ukraine

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In the introductory part of the work, experimental data on the influence of various factors on the conductivity of porous silicon (PS), in particular, the surface structure, doping level, temperature, electric field, and the atmosphere of active molecules, are analyzed. Analysis of the theoretical models of PS conductivity, proposed to date, shows that none of them can simultaneously explain all experimentally established results. In particular, the models do not explain the energy range of thermal activation of PS conductivity  $E_a$ , the presence of two  $E_a$  values in different temperature ranges, the dependence of  $E_a$  on the size of PS nanocrystallites, the mechanism of influence on the PS conductivity of  $\text{NO}_2$  molecules.

In this paper, a model of PS conductivity is proposed, according to which the main factor that causes low conductivity of PS is the presence of charged  $p_b$ -centers (Si atoms with dangling bonds) that remotely passivate the impurity atoms of boron or phosphorus. Barriers for free carriers appear around charged  $p_b$ -centers, which prevent them from passing through thin sections of nanowires in PS. To test this hypothesis, 3D modeling of the passage of free carriers through a thin (2-5 nm) cylindrical nanowire with a surface barrier was performed. For this, the finite-element method was used to solve the single-particle Schrödinger equation with "transparent boundary conditions" on the bases of the cylinder. The potential in the barrier was taken from previous papers on DFT modeling of long-range passivation. The transparency  $Tr$  of such a barrier structure was calculated depending on the energy  $E$  of the free carrier. According to the obtained dependences  $Tr(E)$ , the values of the energy  $E_{th}$  for overcoming these barriers in nanowires of different diameters were found. The obtained values  $E_{th} = 0.1-1$  eV are in good agreement with the range of experimental values of the thermal activation energy of PS conductivity. The energy  $E_{th}$  increases with decreasing diameter of silicon nanowires, which also agrees with the experimental results. The presence of two values of the activation energy can be explained by the dominance of the processes of impurity depassivation at low temperatures and thermal overcoming of barriers near  $p_b$ -centers at high temperatures.

**Keywords:** Conductivity, Porous silicon,  $p_b$ -centers, Doping passivation.

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### 1. INTRODUCTION

Porous silicon (PS), due to its huge specific surface, has been widely used in recent years as a material for creating gas sensors, biomedical applications, etc. [1]. Although over the past 30 years, PS has been studied extensively enough, some of its properties have not yet found a generally accepted explanation. In particular, the reasons for the high PS resistance and the mechanism of its conductivity were explained differently by the authors of various papers [1]. The absence of an exhaustive theory of the conductivity of PS is associated not only with a large variety of sizes and pore morphology in different types of PS. The difference in the conductivity of PS samples manufactured under nominally identical conditions prevents the comparison of the results of studies of various scientific groups [2]. Even within a single PS sample, inhomogeneity of the microstructure can lead to inhomogeneity of the electrical properties [3]. The electrical properties of PS depend not only on its microstructure, but also on many other factors [1]. In particular, this is the type of silicon substrate from which PS is made (crystallographic direction, type and doping level), the etching method, the formation method and the geometry of the metal contacts, the presence of an un-etched substrate in the structure, the annealing process, and the electrical measurement method. In addition, external factors such as the chemical structure of the surface, the aging

process, the presence of electrolyte residues, the composition of the surrounding atmosphere, and temperature greatly influence the electrical conductivity of PS. Thus, the explanation of the transport properties of PS is a difficult task due to the disordered structure of the PS and a large number of factors affecting conductivity.

By DFT modeling of the effect of active  $\text{NH}_3$  and  $\text{NO}_2$  molecules on the conductivity of PS and other silicon structures, we established the possibility of passivation of impurity boron [4] and phosphorus [5] atoms by distant  $p_b$ -centers. When a boron atom is passivated, the electron density from the  $p_b$ -center is transferred to B, and an increased potential region appears near the  $p_b$ -center, that is, a barrier for free holes (which is removed by adsorption of  $\text{NO}_2$  molecules). This work is devoted to the explanation of the experimentally observed behavior of the PS conductivity by the presence of these barriers near  $p_b$ -centers.

### 2. RESULTS OF EXPERIMENTAL RESEARCHES AND THEORETICAL MODELS OF PS CONDUCTIVITY

The study of the influence of internal and external factors on the conductivity of microporous and mesoporous silicon and the creation of carrier transport models in PS has been the subject of many publications. Various research groups studied and tried to explain the effect of temperature [6-17], constant [9] and variable

\* [fed.ptas@gmail.com](mailto:fed.ptas@gmail.com)

[6] electric displacement, doping level [9, 11], porosity [10, 14], preparation conditions [11], NO<sub>2</sub> atmosphere [15] on the conductivity of the PS, and also investigated the current-voltage characteristics (*I-V*) of PS-based structures [13, 15, 16]. Analyzing these works, it is possible to establish the following peculiarities of PS conduction behavior under the influence of various factors.

1. At sufficiently low temperatures (up to  $\sim 200$  K), in PS there are conduction mechanisms characteristic of substances in which the concentration of free charge carriers is very low and there are no extended (delocalized) states or unblocked percolation paths:

– this is the Berthelot-type conductivity (tunneling between thermally vibrating barriers) at  $180 < T < 280$  K [17];

– Mott's hopping conductivity over states near the Fermi level with variable hopping length at  $T < 200$  K [14],  $140 < T < 180$  K [17]; the average hopping length ( $\sim 27$  Å) was estimated in [14];

– Efros-Shklovskii conductivity with hopping between states near the Fermi level through Coulomb barriers at  $50 < T < 120$  K [17];

– the resistance does not depend on temperature at  $T < 200$  K [6], and at  $T < 40$  K [17].

2. At higher temperatures, activation conductivity is observed in PS, which is subject to the Arrhenius law [6-11, 17]

$$\sigma(T) = \sigma_0 \exp[-E_a / (k_B T)], \quad (1)$$

where  $E_a$  is the thermal activation energy of conductivity,  $\sigma_0$  is a constant, which is a parameter of the material PS,  $k_B$  is the Boltzmann constant,  $T$  is the temperature. Such a law of the temperature dependence of conductivity is characteristic of carrier transfer over extended (delocalized) states.

3. Although it is generally accepted that the activation energy of conductivity  $E_a$  lies in the range of 0.3-0.7 eV [1], significant deviations from these values were observed both in the direction of decrease and increase. For example, for various nano-PS samples studied in [10, 11], the value of  $E_a$  varied within 0.1-1.0 eV.

4. The thermal activation energy of conductivity increases with decreasing size of PS nanocrystallites, which indicates the presence of quantum effects:

– when the substrate resistance decreases (with an increase in the doping level) from 15 to 0.3 Ω cm,  $E_a$  increases from 0.37 to 0.67 eV [9];

– with an increase in porosity from 40 to 80 % (with a decrease in the size of nanocrystallites from 6 to 3 nm),  $E_a$  increases from 0.3 to 1.0 eV, and the transmission spectrum shows a blue shift (the band gap increases), [10];

– the value of  $E_a$  increases with an increase in porosity [24];

– with an increase in the intensity of illumination and anodization current during etching of *n*-type PS (with a decrease in crystallite size), the  $E_a$  increases from 0.1 to 0.44 eV [11].

5. In a number of works [12, 13, 17], two linear regions of the temperature dependence of PS conductivity were observed in Arrhenius coordinates: with low values of  $E_a$  at low temperatures and large  $E_a$  at high  $T$ .

For example, at  $170 < T < 280$ ,  $E_a \approx 0.05$  eV, and at  $T > 300$  K,  $E_a \approx 0.51$  eV [17].

6. The conductivity of PS at relatively high temperatures depended exponentially on the square root of the applied voltage [10] (obeyed the Poole-Frenkel law) and increased with increasing frequency [6]. This indicated the presence of conductivity over partially localized states.

7. The *I-V* of the meso-PS with the tree structure of the pores described in [15] had a threshold character and obeyed the power law

$$I = I_0 \left( \frac{V}{V_{th}} - 1 \right)^\zeta, \quad (2)$$

where  $V_{th}$  is the threshold voltage, and the exponent  $\zeta$  lies in the range between 1.7 and 3. Such a law is characteristic of matrices of metal or semiconductor nanoparticles and is explained by the appearance of a Coulomb blockade (CB) for free carriers [18]. An increase in temperature linearly decreased the value of  $V_{th}$  without changing the shape of the *I-V*.

8. The *p*-type PS conductivity grows in NO<sub>2</sub> atmosphere [15]. The value of  $V_{th}$  in expression (2) logarithmically decreased with increasing NO<sub>2</sub> pressure.

Summing up, it can be said that at low temperatures, micro- and meso-porous silicon behaves as a blocked network of nanocrystallites (with quantum properties), which unblocks as  $T$  grows and in the presence of NO<sub>2</sub> molecules.

During 1990-2010, many PS conductivity models were proposed that had some degree of explanatory and predictive ability. The low PS conductivity and its growth with temperature were first explained by the effects of quantum confinement and carrier depletion (reduction of their thermal generation) due to expansion of the band gap [10], impurity depletion (increase in its activation energy), narrowing of conductive channels due to repulsion from surface traps [7] or by capturing on them [8] and the occurrence of CB [11, 12, 15]. Percolation models were also created that took into account the PS disordered or fractal structure [6, 12, 15]. Other models described PS as a combination of several phases: two (amorphous and crystalline silicon) or three (vacuum, SiO<sub>2</sub>, and Si nanocrystallites) – a model of an effective medium [16].

In various works, the authors also interpreted the activation energy of conduction  $E_a$  in different ways:

– as the energy distance between the Fermi level and extended states in the conduction band [8, 13, 17].

– as the barrier height between neighboring localized states [9, 13];

– as the activation energy of surface traps [7] or impurities [11, 13];

– as the energy of quantum confinement of carriers [10];

– as the charging energy of nanocrystallites (or overcoming CB) [15].

So, at present, there is no generally accepted model of PS conductivity, and the existing models cannot simultaneously explain all the experimental facts described above.

### 3. DISCUSSION OF POSSIBLE MECHANISMS OF INFLUENCE OF BARRIERS NEAR THE P<sub>B</sub>-CENTERS ON THE PS CONDUCTIVITY

Since the increase in *p*-PS conductivity under the action of NO<sub>2</sub> molecules was explained by the removal of barriers near charged p<sub>b</sub>-centers [4], it can be assumed that these barriers play a significant role in the PS conductivity mechanism. The task arose to clarify this role, to explain the experimental facts about the behavior of the PS conductivity, in particular, to clarify the origin and variation of the values of  $E_a$ .

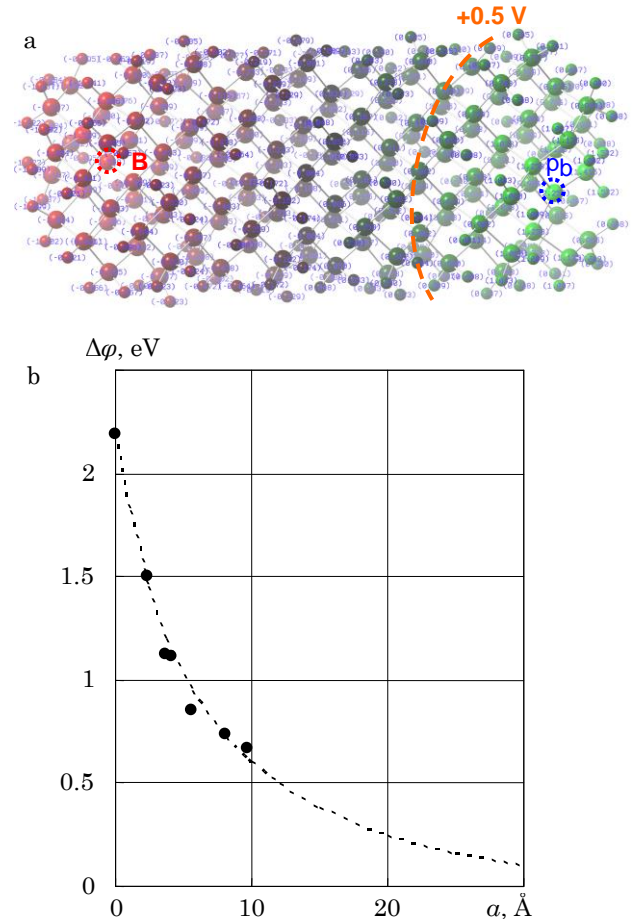
The first was the assumption of thermally stimulated reactivation of impurity atoms remotely passivated by p<sub>b</sub>-centers (modified model [7, 11, 13]). In this process, free carriers should appear and barriers near p<sub>b</sub>-centers should disappear. At first glance, the results of our calculations show the validity of such a hypothesis [4, 59]. The simulation showed that the reactivation energy of the impurity atoms B and P increases from 0.03 to 0.8 eV as the distance  $l$  between the impurity atom and the p<sub>b</sub>-center decreases from 23 to 6 Å, that is, lies in the range of experimental values of  $E_a$ . The increase in the impurity reactivation energy with decreasing  $l$  (or decreasing size of nanocrystallites in PS) also does not contradict the experimental results. But the hypothesis of thermal reactivation of impurity atoms has several disadvantages. DFT calculations [4, 5] also show that when approaching impurity atoms with p<sub>b</sub>-centers, the magnitude of the increased potential and the region of its propagation around the p<sub>b</sub>-centers decreases. For example, for the reactivation energy of a boron atom to be 0.8 eV, the distance  $l$  must be  $\sim 6$  Å. In this case, the region of increased potential near the p<sub>b</sub>-center narrows, for example, the barrier for holes at a distance of  $a=5$  Å from the p<sub>b</sub>-center is only 0.25 V. So, closely spaced pairs of impurity atom – p<sub>b</sub>-center do not create significant barriers for free carriers, that is, they do not affect the PS conductivity. The described process of reactivation of the impurity can only increase the concentration of free carriers, and does not affect the number of percolation paths blocked by barriers in the PS network. The fact that boron atoms must be far from p<sub>b</sub>-centers and, therefore, have a low reactivation energy ( $\sim 0.05$  eV) is also suggested by the hypothesis put forward in [4]. According to this hypothesis, the *p*-type electrochemical etching of silicon should stop when the B atoms are at a distance of  $\sim 25$  Å from the Si/electrolyte interface. Then the p<sub>b</sub>-centers that are formed at this interface begin to remotely passivate the boron atoms and charge positively. With their electric field, they block the movement to the surface of free holes, which is necessary for further etching [32].

The following assumption was to explain the behavior of the conductivity by the action of several pairs of an impurity atom – p<sub>b</sub>-center, which could cause the appearance of a CB for free carriers. This was indicated by the characteristic *I-V* behavior of the PS samples described in [25]. To pass a current through the PS network, it is necessary that a free electron (hole) fall into each nanocrystallite, that is, charge it with an elementary charge  $e$  [12]. For a crystallite of small diameter (and small electric capacity  $C$ ) the charge energy  $\Delta E = e^2/(2C)$  can be quite significant. This means that

the percolation path for free carriers is blocked by the  $\Delta E$  barrier, which creates the CB. In the work [15], it was hypothesized that in some thin sections of the *p*-PS nanowires (on both sides of the nanocrystallites) some positive charge can be accumulated, which causes the CB. In the NO<sub>2</sub> atmosphere, this charge is screened and CB is removed. In [4], we showed that it is the p<sub>b</sub>-centers that passivate boron atoms that can cause CB in *p*-PS, and also explained the mechanism for removing barriers for holes by NO<sub>2</sub> molecules. But the hypothesis of the occurrence of CB also has a significant drawback. The charge energy  $\Delta E$  of a spherical nanocrystallite with a minimum diameter of  $d=2$  nm, at which quantum confinement is not very significant, is only

$$\Delta E = \frac{e^2}{2 \cdot 2\pi\epsilon\epsilon_0 d} \approx 0.06 \text{ eV},$$

where  $\epsilon=12$  is the dielectric constant of silicon,  $\epsilon_0 = 8.85 \cdot 10^{-12} \text{ F/m}$  is the vacuum permittivity. So, the CB phenomenon also cannot correctly explain the experimentally obtained values of  $E_a \sim 0.5 \text{ eV}$ .



**Fig. 1** – (a) The distribution of the potential change on the Si<sub>140</sub>H<sub>136</sub>B cluster atoms (with a distance of  $l \sim 23$  Å between the B atom and the p<sub>b</sub>-center) after an electron transitions from the B atom to the p<sub>b</sub>-center (the green and red colors correspond to the areas of increase and decrease of the potential); (b) dependence of the potential change on atoms on their distance  $a$  to p<sub>b</sub>-center. The dotted curve reflects the hyperbolic law of potential reduction with distance

Finally, the region of high (low) potential near  $p_b$ -centers, which passivate impurity atoms, can affect the conductivity through narrow sections of PS nanowires (modified model [7]). However, the assessment of such an impact is not a trivial task. The DFT simulation carried out in [4, 5] made it possible to calculate the potential change on atoms, which occurs during the transition from the non-passive (triplet) state to the passivated (singlet) state, Fig. 1a. Fig. 1b shows the values of the variation of the potential  $\Delta\varphi$  calculated on the atoms of the  $\text{Si}_{140}\text{H}_{136}\text{B}$  cluster (with  $l \approx 23 \text{ \AA}$ ) depending on their distance from the  $p_b$ -center. The  $\Delta\varphi$  values are calculated for atoms lying in a plane perpendicular to the B- $p_b$ -center line. From Fig. 1b it can be seen that the barrier height for holes can reach large values, for example, at a distance of  $\approx 10 \text{ \AA}$  from the  $p_b$ -center, the change in potential is  $\Delta\varphi \approx 0.65 \text{ eV}$ . Therefore, the value of  $E_a$  correlates with the values of  $\Delta\varphi$  for small  $a$ . However, nanocrystallites (or nanowires) in meso-PS have minimum sizes (diameters) of about 20-30  $\text{\AA}$  [1]. At such sizes of nanocrystallites, the barriers for carriers moving far from  $p_b$ -centers are significantly reduced. For example, at  $a \approx 20 \text{ \AA}$ ,  $\Delta\varphi$  decreases to a value of  $\sim 0.25 \text{ eV}$ , and at  $a \approx 30 \text{ \AA}$ ,  $\Delta\varphi$  tends to zero, Fig. 2b. Thus, free carriers that pass along the part of the nanowire distant from the  $p_b$ -center must overcome minor barriers or move without barriers. Therefore, at first glance, the direct influence of areas of high (low) potential near  $p_b$ -centers cannot explain the decrease in the PS conductivity and the experimental values of  $E_a \sim 0.5 \text{ eV}$ . But this conclusion does not take into account the quantum effects that arise when carriers move near the barriers in thin sections of the PS nanowires.

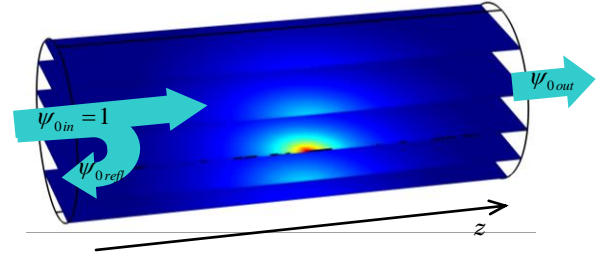
#### 4. MODELING THE PASSAGE OF CHARGE CARRIERS THROUGH NANOWIRES WITH SURFACE BARRIERS

In order to evaluate the influence of areas of high (low) potential near  $p_b$ -centers on the conductivity of PS, one can consider the passage of free carriers through a thin section of a cylindrical silicon nanowire with a charged  $p_b$ -center on the side surface. Such a quantum-mechanical problem reduces to solving the single-particle Schrödinger equation for a free particle in a field with an effective potential in the envelope function approximation [19]. The problem was solved by the finite element method in the Comsol Multiphysics software environment.

For a cylinder 20 nm long and  $d = 2\text{-}5 \text{ nm}$  in diameter, the stationary Schrödinger equation was solved in a three-dimensional formulation:

$$\left( -\frac{\hbar^2}{2m} \hat{\Delta} + U(x, y, z) \right) \psi(x, y, z) = E\psi(x, y, z), \quad (3)$$

where  $\hbar$  is the Planck constant,  $m = 0.56 m_e$  is the effective mass of a free hole in silicon (or  $m = 1.08 m_e$  for free electrons),  $U(r)$  is the potential energy distribution approximated from DFT calculations of the electrostatic potential near the  $p_b$ -center (Fig. 2); the energy  $E$  of a free hole was set by the boundary conditions, and as a result of solving equation (3), the distribution of the wave function  $\Psi(r)$  was determined.



**Fig. 2** – Distribution of the electrostatic potential on the model cylinder

The conductivity of the structure under consideration can be characterized by the transmission coefficient of carriers  $Tr$  (ratio of the fluxes of particles passing through a cylinder with a barrier and entering the cylinder). The transmission coefficient characterizes the probability of tunneling and is defined as

$$Tr = \frac{|J_{out}|}{|J_{in}|}. \quad (4)$$

In (4),  $J_{in}$  is the probability flow entering the left base of the cylinder, and  $J_{out}$  is the flow leaving the right base (Fig. 2). In the general case, the probability flow is determined by the expression [19]:

$$\vec{J} = \frac{\hbar}{2mi} (\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^*) = \frac{\hbar}{m} \text{Im}(\psi^* \vec{\nabla} \psi). \quad (5)$$

For this problem with the geometry of a long cylinder, the wave functions on its basis can be considered as plane waves:

$$\psi_{in} = \psi_{0in} \exp(ikz), \quad (6)$$

$$\psi_{refl} = \psi_{0refl} \exp(ikz), \quad (7)$$

$$\psi_{out} = \psi_{0out} \exp(ikz), \quad (8)$$

where equation (6) describes a wave that enters the left base, (7) – which comes out of it, reflected from the barrier, and (8) corresponds to a wave that leaves the right base, Fig. 2. The modulus of the wave vector  $k$  will be the same for all three waves, provided  $U = 0$  on the faces of the cylinder, and depends on the energy  $E$ , which can be set when solving the problem [19]:

$$k = \sqrt{2m(E - U)} / \hbar = \sqrt{2mE} / \hbar. \quad (9)$$

In the case of a plane wave, the probability flow will be equal to

$$\begin{aligned} \vec{J} &= \frac{\hbar}{m} \text{Im}(\psi^* \vec{\nabla} \psi) = \\ &= \frac{\hbar}{m} \text{Im}(\psi_0 e^{-ikz} \cdot (ik\psi_0 e^{ikz})) = \frac{\hbar k}{m} |\psi_0|^2. \end{aligned} \quad (10)$$

Then the transmission coefficient will be

$$Tr = \frac{|J_{out}|}{|J_{in}|} = \frac{|\psi_{0out}|^2}{|\psi_{0in}|^2}. \quad (11)$$

If introduce the normalization

$$\psi_{0in} = 1, \quad (12)$$

into the boundary conditions and take into account the existence of the spatial dependence of  $\psi_{0out}(x,y)$ , we obtain the final expression for calculating the transmission coefficient of the model cylinder:

$$Tr = \frac{1}{S_{base} S_{base}} \int |\psi_{0out}(x,y)|^2 dS. \quad (13)$$

In accordance with the formulated problem of finding  $Tr$ , the following boundary conditions were chosen. On the right (emitting) base of the cylinder, on which the  $\psi_{0out}(x,y)$  distribution is calculated to find  $Tr$  from the expression (13), the "transparent boundary conditions" were used. Such boundary conditions should allow the wave function of a particle with energy  $E$  to leave the modeling region without reflection from the specified face. The "transparent boundary condition" can be obtained from equation (8), taking the derivative with respect to  $\partial z$  from its left and right sides:

$$\left. \frac{\partial \psi}{\partial z} \right|_{S_{out}} = ik\psi. \quad (14)$$

The particle (probability wave), which is described by equation (6), must enter the left base of the cylinder without reflection. The part of the wave that is reflected from the barrier and described by equation (7) must also go out through the left base of the cylinder without reflection. Therefore, on the left base of the cylinder, the "transparent boundary conditions" were also used for the waves entering and reflected from the barrier. These conditions can be obtained after adding derivatives of expressions (6) and (7) and taking into account the normalization condition (12):

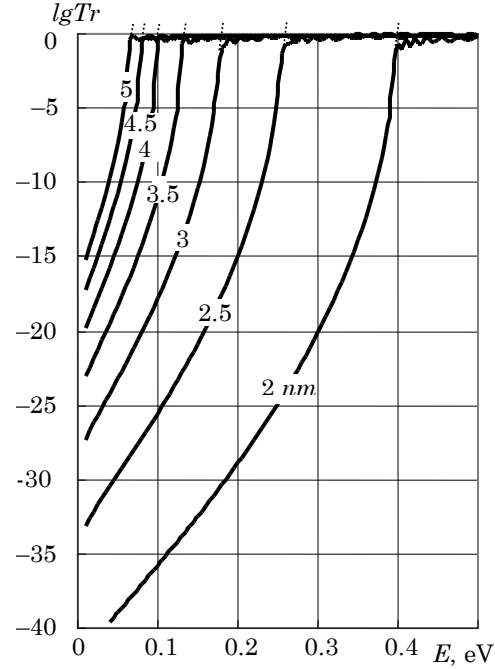
$$\left. \frac{\partial \psi}{\partial z} \right|_{S_{in}} = -ik\psi + \frac{\partial \psi_{in}}{\partial z} + ik\psi_{in} = -ik\psi + i2k \exp^{ikz}. \quad (15)$$

On the side of the cylinder we took

$$\psi|_S = 0. \quad (16)$$

This condition, although somewhat narrows the region of localization of a free hole (electron), but corresponds to the actual behavior of the wave function outside the silicon nanowire.

First, the problem was solved for the case  $U = 0$ , that is, for a free electron or a hole in the cylinder without the influence of the field of  $p_b$ -centers. This was done to assess the contribution of the quantum confinement effect to the overall transmission coefficient and test the adequacy of the model. Fig. 3 shows the dependence of the logarithm of the transmittance on the energy  $E$  of a free hole for cylinders with different diameters  $d$ . Extrapolation of curves to the intersection with the line  $Tr = 1$  gives the value of the decrease in the depth of the valence band  $\Delta E_V$ , that is, describes the quantum confinement effect of a hole in a thin nanowire. Similarly,  $\Delta E_C$  values were calculated for the case of free electrons, and the total increase in the band gap



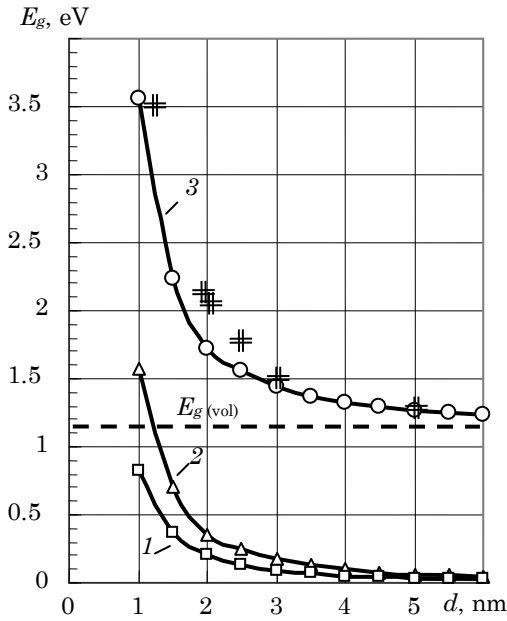
**Fig. 3** – Dependences of the logarithm of the transmittance  $Tr$  on the free hole energy  $E$  for cylinders with diameters  $d = 2\div 5$  nm (indicated on the corresponding curves)

$$E_g = E_{g(vol)} + \Delta E_C + \Delta E_V, \quad (17)$$

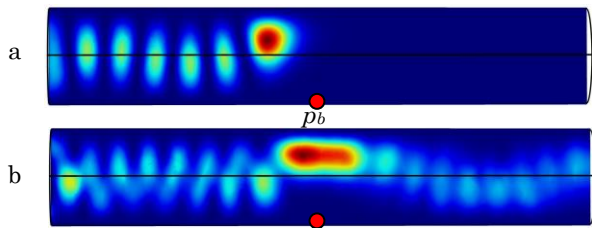
where  $E_{g(vol)}$  is the band gap in bulk silicon, Fig. 4. The values of  $E_g$  calculated in this way (curve 3 in Fig. 4) are in fairly good agreement with the results of experimental work [20], where the  $E_g$  of silicon nanowires of various thickness (marks # in the figure) were studied by scanning tunneling spectroscopy. Although the envelope method (or effective mass method) usually gives overestimated values of  $E_g$  for small  $d$ , calculations show even a slight underreporting compared with experimental results [20]. This can be explained by the effective narrowing of real silicon nanowires due to the influence of the hydrogenated surface. Fig. 4 also shows that at  $d \geq 3$  nm, the quantum confinement effect becomes insignificant.

After the preliminary calculations described above, we studied the effect of the field of positively charged  $p_b$ -centers on the transmission coefficient of nanowires of different diameters for free holes. A centrally symmetric potential energy distribution was used, obtained and approximated by DFT calculations of the potential change near the charged  $p_b$ -center [4]. Fig. 5 shows the distributions of  $|\psi|^2$  for cases  $Tr \ll 1$  (a) and  $Tr \approx 1$  (b).

In the first case, a hole is reflected from the barrier, the probability of its being on the right side of the cylinder is zero. In the second case, a hole with a nonzero probability passes through the barrier and exits through the right base of the cylinder. Note that the increased probability density of finding a hole near the  $p_b$ -center is associated with an increase in its potential energy in this region, therefore, a decrease in velocity and an increase in the residence time near the  $p_b$ -center.



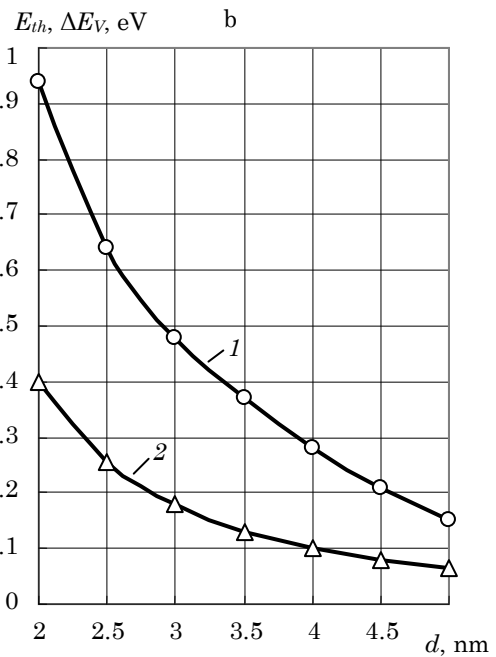
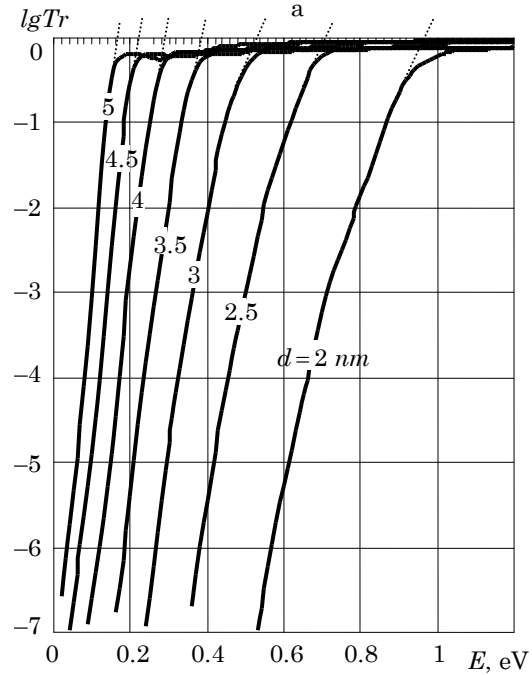
**Fig. 4** – The calculated dependences of the change in the position of the valence band (1), conduction band (2) and the band gap (3) depending on the nanowire diameter  $d$ . The # marks show the experimental values of  $E_g$  according to [20]



**Fig. 5** – The distribution of  $|\psi|^2$  for a free hole in a cylinder with a barrier created by a positively charged  $p_b$ -center: a – when reflected from the barrier, b – when passes through the barrier

Fig. 6a shows the calculated values of the dependence of the logarithm of the transmittance  $Tr$  on the free hole energy  $E$  for cylinders of diameters  $d = 2 \div 5$  nm with barriers. According to the obtained dependences  $\lg Tr(E)$ , the threshold energy values  $E_{th}$  were found, at which a hole begins to pass through the barrier structure with probability  $Tr \approx 1$  (Fig. 6b, curve 1). In the same figure (curve 2), the energies  $\Delta E_C$  are shown, which correspond to the barriers for holes arising from quantum confinement in thin nanowires. From a comparison of the curves, it is clear that the influence of barriers near the  $p_b$ -centers is more significant than the quantum confinement effect. These barriers affect the movement of holes and in relatively thick nanowires (with  $d > 3$  nm), in which the region of increased potential does not cover the entire cross section. This is due to the reflection of a quantum particle from a barrier lower than the particle energy.

The calculated values of  $E_{th}$  lie in the range of  $0.1 \div 1$  eV, which correlates with the experimentally obtained values of the thermal activation energy  $E_a$  of PS conductivity. The increase in  $E_{th}$  with decreasing  $d$  also agrees with the experimentally observed increase in



**Fig. 6** – (a) Dependences of  $\lg Tr$  on the free hole energy  $E$  for cylinders with diameters of  $d = 2 \div 5$  nm; (b) – dependence of the threshold energy  $E_{th}$  (1) and the quantum confinement energy of holes  $\Delta E_V$  (2) on the cylinder diameter  $d$

$E_a$  with decreasing sizes of PS nanocrystallites. The diameters of the thinnest nanowires in the PS network are determined by the substrate doping level and PS preparation conditions (electrolyte composition, etching current density, etc.). This means that for a particular PS sample, the diameters of the thinnest nanowires are about the same. Therefore, the values of  $E_{th}$  will be approximately the same for the entire percolation network of this PS sample. Therefore, the value of  $E_{th}$  can be interpreted precisely as the energy necessary for

thermally overcoming barriers near charged  $p_b$ -centers in thin sections of the nanowires of which PS is composed. Similarly, calculated  $E_{th}$  values for electrons were about half as much (which is due to their higher effective mass). This also agrees with the experimental data [11], according to which in n-type PS the values of the energy  $E_a$  are lower than in  $p$ -PS.

The presence of two linear sections in the temperature dependence of conductivity in Arrhenius coordinates (with  $E_a \sim 0.05$  eV at low temperatures and  $E_a \sim 0.5$  eV at high  $T$ ), which was observed in [12, 13, 17], can be explained as follows. At low  $T$ , the main mechanism of the increase in conductivity is the depassivation of impurity atoms, which requires energies of just about 0.05 eV. This process is accompanied by the simultaneous removal of barriers near the  $p_b$ -centers (unblocking of some percolation paths in the PS network) and a slight increase in the concentration of free carriers. Note that after depassivation, passivation of the impurity by distant  $p_b$ -centers occurs very quickly, since the passivated state is more energetically favorable. Therefore, the number of percolation paths that are unblocked (due to the depassivation of the impurity) depends insignificantly on  $T$  and has little effect on the PS conductivity. Higher values of  $E_a \sim 0.5$  eV at high  $T$ , as already noted can be attributed to thermal overcoming of barriers near charged  $p_b$ -centers. More significant values of  $E_a > 1$  eV can be explained by the presence of several charged  $p_b$ -centers located nearby. The

mechanisms of collective action of  $p_b$ -centers on conductivity (in particular, the effect of resonant tunneling) will be the subject of our subsequent research.

## 5. CONCLUSIONS

The PS conductivity models created to date cannot explain all the experimental results (in particular, the effect of  $\text{NO}_2$  molecules and the range of values of the thermal activation energy of PS conductivity). The previous DFT calculations showed [4] that the increase in the conductivity of PS in an  $\text{NO}_2$  atmosphere most likely occurs due to the removal of barriers near charged  $p_b$ -centers passivating the impurity boron atoms. The simulation by the finite element method showed that these barriers significantly affect the conductivity in thin sections of silicon nanowires. The range of calculated energies required to overcome these barriers is  $E_{th} = 0.1-1$  eV, which correlates with the spread of experimental values of  $E_a$ . The effect of barriers and the energy  $E_{th}$  increase with decreasing diameter of silicon nanowires, which also corresponds to the experimental results. The presence of two values of  $E_a$  can be explained by the predominance of impurity depassivation at low  $T$  and thermal overcoming of barriers near the  $p_b$ -centers at high  $T$ . So, the main factor that causes the low conductivity of PS is the presence of barriers near the surface charged  $p_b$ -centers, which passivate impurity atoms.

## REFERENCES

1. *Handbook of Porous Silicon* (Ed. L. Canham) (Switzerland: Springer International Publishing: 2014).
2. H. Föll, M. Christophersen, J. Carstensen, G. Hasse, *Mater. Sci. Eng. R* **280**, 1 (2002).
3. S.K. Dutta, S.M. Hossain, S. Chakraborty, H. Saha, *Phys. Status Solidi A* **191**, 535 (2002).
4. F. Ptashchenko, *phys. status solidi b* **255**, 1700654 (2018).
5. F. Ptashchenko, *J. Nano-Electron. Phys.* **10**, 05017 (2018).
6. M. Ben-Chorin, F. Möller, F. Koch, W. Schirmacher, M. Eberhard, *Phys. Rev. B* **51**, 2199 (1995).
7. V. Lehmann, F. Hoffmann, F. Möller, U. Grüning, *Thin Solid Films* **225**, 20 (1995).
8. R. Schwarz, F. Wang, M. Ben-Chorin, S. Grebner, A. Nikolov, F. Koch, *Thin Solid Films* **255**, 23 (1995).
9. J. Kocka, J. Oswald, A. Fejfar, R. Sedlacik, V. Zelezny, H. The-Ha, K. Luterowa, I. Pelant, *Thin Solid Films* **276**, 187 (1996).
10. W.H. Lee, C. Lee, J. Jang, *J. Non-Cryst. Solids*, **198-200**, Part 2, 911 (1996).
11. A. Diligenti, A. Nannini, G. Pennelli, F. Pieri, *Appl. Phys. Lett.* **68**, 687 (1996).
12. B. Hamilton, J. Jacobs, D.A. Hill, R.F. Pettifer, D. Teehan, L.T. Canham, *Nature* **393**, 443 (1998).
13. P. A. Forsh, L. A. Osminkina, V. Y. Timoshenko, P. K. Kashkarov, *Semiconductors* **38**, 603 (2004).
14. S.P. Zimin, *Semiconductors* **40**, 1350 (2006).
15. S. Borini, L. Boarino, G. Amato, *Adv. Mater.* **18**, 2422 (2006).
16. M. Bouaïcha, M. Khardani, B. Bessais, *Mater. Sci. Eng. B* **147**, 235 (2008).
17. M.N. Islam, S. K. Ram, S. Kumar, *Physica E* **41**, 1025 (2009).
18. A.A. Middleton, N.S. Wingreen, *Phys. Rev. Lett.* **71**, 3198 (1993).
19. P. Harrison, A. Valavanis, *Quantum Wells, Wires and Dots: Theoretical and Computational Physics of Semiconductor Nanostructures, 4th Edition* (Chichester, United Kingdom: John Wiley & Sons Ltd.: 2016).
20. D.D.D. Ma, C.S. Lee, F.C.K. Au, S.Y. Tong, S.T. Lee, *Science* **299**, 1874 (2003).

## Вплив далекодіючої пасивації домішкових атомів поверхневими обірваними зв'язками на провідність поруватого кремнію

Ф.О. Птащенко

Національний університет «Одеська морська академія», вул. Дідріхсона, 8, 65029 Одеса, Україна

У вступній частині роботи проаналізовані експериментальні данні про вплив на провідність поруватого кремнію (PS) різних чинників, зокрема, структури поверхні, рівня легування, температури, електричного поля, атмосфери активних молекул. Аналіз теоретичних моделей провідності PS, які запропоновані на даний час, показує, що жодна модель не може одночасно пояснити всі експериментально встановлені закономірності поведінки провідності. Зокрема, не поясненими є розбіг значень енергії термічної активації провідності  $E_a$ , наявність двох значень  $E_a$  в різних температурних діапазонах, зале-

жність  $E_a$  від розмірів нанокристалітів PS, механізм впливу на провідність молекул  $\text{NO}_2$ .

В роботі запропонована модель провідності PS, згідно з якою, основним чинником, що обумовлює низьку провідність PS, є наявність заряджених  $\text{r}^{\bullet}$ -центрів (атомів кремнію з обірваними зв'язками), які віддалено пасивують домішкові атоми бору або фосфору. Навколо заряджених  $\text{r}^{\bullet}$ -центрів виникають бар'єри для вільних носіїв, які перешкоджають їх руху через тонкі ділянки нанодротів у PS. Для перевірки цієї гіпотези було проведено 3D-моделювання проходження вільного носія через ділянку тонкого (2-5 нм) циліндричного нанодрота з поверхневим бар'єром. Для цього методом кінцевих елементів розв'язувалося одночастинкове рівняння Шредінгера з «прозорими граничними умовами» на основі циліндру. Потенціал на бар'єрі був узятий із попередніх робіт, присвячених DFT-моделюванню далекодіючої пасивації. Розраховувалася прозорість  $Tr$  такої бар'єрної структури в залежності від енергії  $E$  вільного носія. По отриманим залежностям  $Tr(E)$  були знайдені значення енергії  $E_{th}$  долання вказаних бар'єрів у нанодротах різного діаметру. Отримані значення  $E_{th} = 0.1-1$  еВ добре узгоджуються з енергіями термічної активації провідності PS. Енергія  $E_{th}$  зростає при зменшенні діаметрів кремнієвих нанодротів, що також відповідає експериментальним результатам. Наявність двох значень енергії активації провідності можна пояснити домінуванням процесів депасивації домішки при низьких температурах та термічного долання бар'єрів поблизу  $\text{r}^{\bullet}$ -центрів при високих температурах.

**Ключові слова:** Провідність, Поруватий кремній, Кремнієві нанодроти,  $\text{r}^{\bullet}$ -центри.