

## Long-range Interaction between $p_b$ -centers and $\text{NO}_2$ Molecules Adsorbed on the Silicon Surface

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DFT calculations showed that the interaction between adsorbed nitric oxide ( $\text{NO}_2$ ) molecules (or  $\text{N}_2\text{O}_4$  dimers) and distant  $p_b$ -centers (Si atoms with dangling bonds) can occur through a Si or  $\text{SiO}_2$  layer. This interaction is effective only when  $\text{NO}_2$  is fixed on surface OH groups. In this interaction, the  $p_b$ -center charges positively, which causes an additional Coulomb blockade (CB) of the holes and can explain the decrease in the conductivity of low-doped  $p$ -type porous silicon (PS) samples.

**Keywords:** DFT calculations, Porous silicon, Adsorption,  $\text{NO}_2$ .

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### 1. INTRODUCTION

Emission of  $\text{NO}_2$  from on-road vehicle and industrial process exhaust, have a dangerous effect on human health and the environment [1]. Therefore, an important problem is the monitoring of nitrogen oxide emissions and the creation of reliable miniature  $\text{NO}_2$  sensors with a low detection threshold and high sensitivity. Silicon structures of various types have great prospects as  $\text{NO}_2$  sensors. In the review papers [2, 3], data on the creation of  $\text{NO}_2$  sensors based on PS and silicon nanowires (SiNWs) are systematized.  $\text{NO}_2$  sensors were also created on the basis of silicon  $p$ - $n$  junctions [4, 5] and transistors [6] made of crystalline and porous Si. The influence of  $\text{NO}_2$  on silicon structures (especially on the  $p$ -type PS) has been extensively investigated by the authors [7-9] in a series of their experimental and theoretical works. In our paper [10], a brief review of the results of studies of this problem is given. Until recently, the increase in the conductivity of  $p$ -PS in the  $\text{NO}_2$  atmosphere was explained by the theory of reactivation of impurity boron atoms [9]. According to this theory, subsurface B atoms are passivated by neighboring  $p_b$ -centers (B atoms capture electrons from  $p_b$ -centers). The  $\text{NO}_2$  molecules adsorbed to such  $p_b$ -centers again capture electrons from the boron atoms and reactivate them. But, as we noted in [10, 11], this theory does not explain a whole series of experimental facts. For example, a reversible increase in the conductivity of high-doped  $p$ -PS samples and decrease in the conductivity of low-doped  $p$ -PS samples [7, 8] in the  $\text{NO}_2$  atmosphere remained unexplained. This theory also did not explain the mechanism of sensitivity to  $\text{NO}_2$  for  $n$ -PS samples [12, 13],  $p$ - $n$  junctions [5] and the negative influence of humidity on the sensitivity of PS-sensors [7]. Therefore, it became necessary to clarify the microscopic mechanism of the interaction of  $\text{NO}_2$  molecules with the silicon surface. Our previous papers [10, 11] were devoted to the DFT-modeling of such an interaction and explained some of the experimental facts mentioned. It was shown in [5, 10] that when adsorption of  $\text{NO}_2$  molecules on OH groups of silicon or  $\text{SiO}_2$  surfaces, their acceptor properties significantly

increase. This is due to the fact that with such adsorption,  $\text{NO}_2$  molecules interact with positively charged hydrogen atoms of hydroxyl groups. With this, the lowest unoccupied molecular orbital (LUMO) of  $\text{NO}_2$  molecules can fall below the midgap of silicon, that is, generate a deep acceptor level. In [11], we clarified the mechanisms for reducing the conductivity of  $p$ -PS in comparison with bulk silicon and increasing its conductivity in the  $\text{NO}_2$  atmosphere. It was shown that the passivation of impurity boron atoms by  $p_b$ -centers can occur at large distances (up to 25 Å) between the B and  $p_b$ -centers. In this case, the  $p_b$ -center gives a part of the electron density to the boron atom and is charged positively. This positive charge generates an area of increased potential around itself, leading to the appearance of a Coulomb blockade of free holes. When the  $\text{NO}_2$  molecule is adsorbed on the OH group near the positively charged  $p_b$ -center, its LUMO level is significantly lowered and creates a shallow acceptor state. Electrons from the valence band can be trapped at this level, that is, free holes can arise. The  $\text{NO}_2$  molecule, which captured the electron, is charged negatively and creates around itself a region of reduced potential, that is, it removes the CB of free holes. Such a mechanism can only explain the increase in conductivity in the  $\text{NO}_2$  atmosphere of high-doped  $p$ -PS samples, and the decrease in the conductivity of low-doped  $p$ -PS under the influence of  $\text{NO}_2$  remains unclear. This work is devoted to clarifying this problem by DFT-modeling. We will also try to explain the sensitivity of  $p$ - $n$  junctions to  $\text{NO}_2$  and explain the mechanism of dissociation of  $\text{N}_2\text{O}_4$  dimers on the Si or  $\text{SiO}_2$  surface.

### 2. SELECTION OF MODELING OBJECTS AND CALCULATION PROCEDURE

It was established in [8] that the concentration of paramagnetic  $p_b$ -centers  $N_s$  (not participating in B passivation) in  $p$ -PS with different doping levels at low  $\text{NO}_2$  pressures (up to  $10^{-2}$  Torr) is reversibly reduced. Therefore, it is obvious that there is an interaction between  $\text{NO}_2$  molecules and such  $p_b$ -centers, which transfers them into a nonparamagnetic state. The role of

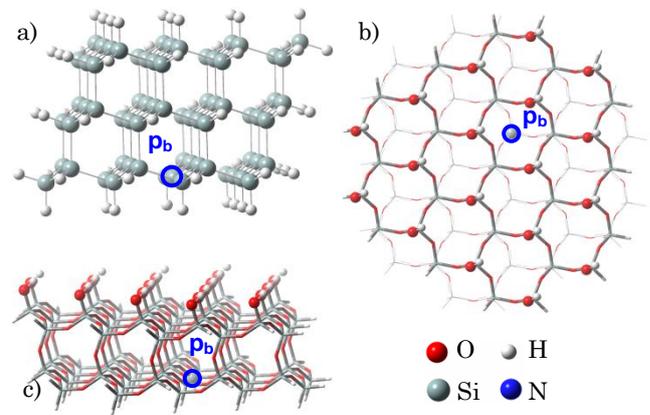
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paramagnetic  $p_b$ -centers in the interaction with  $\text{NO}_2$  should increase with decreasing doping level ( $N_B$ ), as the ratio  $N_S/N_B$  increases. Therefore, we assumed that the decrease in the conductivity of low-doped  $p$ -PS samples in the atmosphere of nitric oxide, described in [7], is due exactly to the interaction of  $\text{NO}_2$  molecules with paramagnetic  $p_b$ -centers. It was shown in [7] that in  $\text{NO}_2$  vapors at a concentration of 10 ppm, conductivity decreased in  $p$ -PS samples made of a substrate with a resistivity of  $0.5 \Omega \text{ cm}$ .  $N_S$  and  $N_B$  for such structures can be estimated from the results of other works, where samples of mesoporous PS with similar parameters were studied. In [8], the IR and EPR spectra were used to calculate the concentration of free holes ( $N_P$ ) and  $N_S$  in  $p$ -PS samples with different levels of doping. For low-doped samples made of substrates with a resistivity of  $10\text{-}15 \Omega \text{ cm}$ , the following parameters were registered:  $N_B \sim 10^{15} \text{ cm}^{-3}$ ,  $N_S = 7.3 \cdot 10^{17} \text{ cm}^{-3}$ , and  $N_P < 10^{16} \text{ cm}^{-3}$  (limit of sensitivity of the experiment). In an atmosphere of  $\text{NO}_2$  at low pressures (up to 0.01 Torr),  $N_S$  decreased somewhat, and there was no change in  $N_P$ . For higher doped samples made of substrates with a resistivity of  $0.01\text{-}0.02 \Omega \text{ cm}$ , ( $N_B \sim 5 \cdot 10^{18} \text{ cm}^{-3}$ ),  $N_S = 9.1 \cdot 10^{16} \text{ cm}^{-3}$  and  $N_P = 2 \cdot 10^{17} \text{ cm}^{-3}$ , which grew in the  $\text{NO}_2$  atmosphere to  $N_P \sim 4 \cdot 10^{18} \text{ cm}^{-3}$ , that is, practically to the value of  $N_B$ . Thus, for the samples described in [7], the estimated values of the parameters will be as follows:  $N_B \sim 2 \cdot 10^{16} \text{ cm}^{-3}$ ,  $N_S > 10^{17} \text{ cm}^{-3}$ . It can be concluded that for  $p$ -PS samples, whose conductivity decreases in the  $\text{NO}_2$  atmosphere, the concentration of paramagnetic  $p_b$ -centers is larger than the dopant concentration,  $N_S > N_B$ .

It is noted in [7, 8] that after removal from the atmosphere of  $\text{NO}_2$  (with low pressures), the conductivity and  $N_S$  take their initial values, that is, they change reversibly. This indicates that the binding energies of adsorbed  $\text{NO}_2$  molecules to the PS surface are small. The adsorption energy, when the  $\text{NO}_2$  molecule is directly attached to the dangling bond of the surface Si atom, is very high (2.62 eV [5]), which makes impossible the reversible change in conductivity. Therefore, we assumed that the interaction of  $\text{NO}_2$  molecules with  $p_b$ -centers should be long-range. If the surface  $p_b$ -center and the  $\text{NO}_2$  molecule are nearby and do not separate anything, the  $\text{NO}_2$  molecule will be attracted to the  $p_b$ -center, a stable silicon nitride compound is formed. Therefore, we assumed that the interaction between  $\text{NO}_2$  and the  $p_b$ -center should occur through a thin layer of  $\text{SiO}_2$  (in oxidized PS) or Si (microroughness of the PS surface).

Based on these considerations, the model structures of silicon and silicon oxide, already used in [10], were chosen. The basis for modeling the interaction of the  $\text{NO}_2$  molecule and the  $p_b$ -center separated by a Si layer was a  $\text{Si}_{68}\text{H}_{55}$  cluster with a completely hydrogenated surface, depicted in Fig. 1 a. The  $p_b$ -center was modeled by the Si atom, which was located in the middle on the lower face of the cluster and was not passivated by the hydrogen atom. As was shown in [10], OH groups significantly affect the acceptor properties of the adsorbed  $\text{NO}_2$  molecule. To investigate this effect on the long-range interaction of the  $p_b$ -center and  $\text{NO}_2$ , some hydrogen atoms were replaced by OH groups (from 1 to

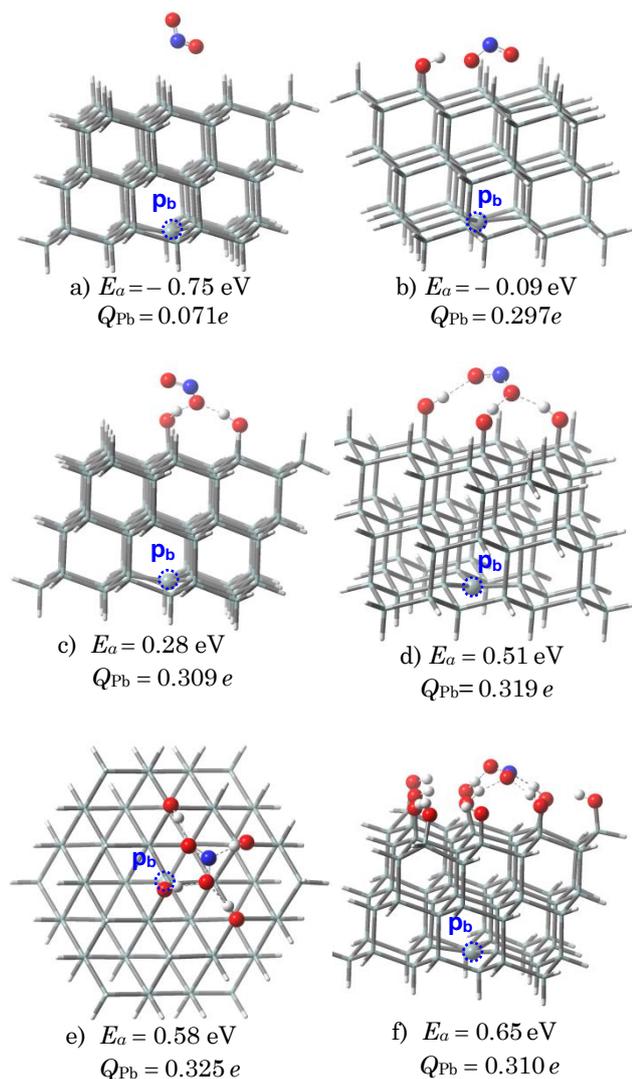
10) on the upper face of the cluster. The corresponding models are shown in Fig. 2. The interaction of  $\text{NO}_2$  and the  $p_b$ -center through a  $\text{SiO}_2$  layer was simulated on a cluster of  $\beta$ -cristobalite  $\text{Si}_{74}\text{O}_{133}\text{H}_{65}$  with a fully hydroxylated upper face (111), Fig. 1 b, c. The choice of this particular modification of  $\text{SiO}_2$  is explained in [10]. The  $p_b$ -center was also modeled by the Si atom, which was located on the lower face of the cluster and was not passivated by the hydrogen atom. Quantum-chemical modeling was carried out in Gaussian 09 package [14] by the DFT-method with exchange-correlation functional B3LYP. For surface OH groups,  $p_b$ -centers, and adsorbed  $\text{NO}_2$  molecules, a 6-311++ $g(d, p)$  basis was chosen with diffuse functions, which are important when modeling long-range interactions and adsorption. To save computation time, other atoms were modeled in a less broad basis, 6-31 $g(d, p)$ , which did not affect the simulation results. The chosen basis and calculation method showed very good reproducibility of the experimental geometric and energy parameters of the investigated objects [10].



**Fig. 1** – Model clusters with  $p_b$ -centers on the lower edge (marked with blue circles). a) – silicon cluster  $\text{Si}_{68}\text{H}_{55}$ ; b) and c) –  $\text{SiO}_2$  cluster ( $\beta$ -cristobalite)  $\text{Si}_{74}\text{O}_{133}\text{H}_{65}$ , top and side views, respectively

### 3. THE ROLE OF SURFACE OH GROUPS IN THE INTERACTION OF DISTANT $\text{NO}_2$ MOLECULES AND $PB$ -CENTERS

The presence and effectiveness of long-range interaction between an  $\text{NO}_2$  molecule and a  $p_b$ -center was checked by the method already used in [11]. We calculated the energy of the model clusters in the singlet state (with zero total electron spin) and the triplet state (with unit spin) and also the adsorption energy of the  $\text{NO}_2$  molecule. In the singlet state, the unpaired electrons of the  $p_b$ -center and  $\text{NO}_2$  molecules combine into one molecular orbital, while in the triplet state they remain unpaired. If the energy of the model cluster in the singlet state ( $E_{\text{SINGL}}$ ) is greater than in the triplet state ( $E_{\text{TRIPL}}$ ), this means that there is an effective attraction between  $\text{NO}_2$  and the  $p_b$ -center. When the triplet state is more favorable, there is no interaction (attraction) between  $\text{NO}_2$  and the  $p_b$ -center. The negative value of the calculated  $\text{NO}_2$  molecule adsorption energy ( $E_a$ ) in the singlet state can also indicate that there is no interaction between  $\text{NO}_2$  and the  $p_b$ -center. The

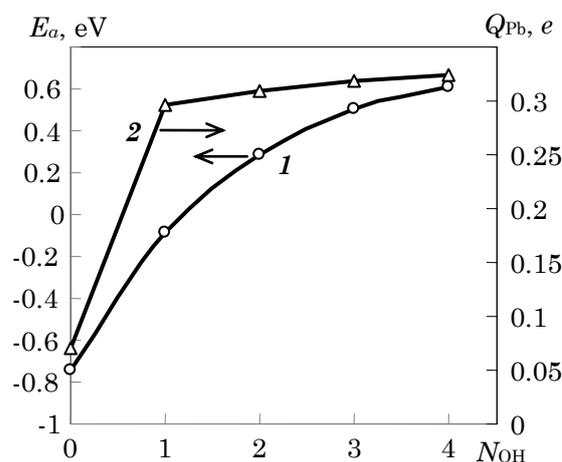


**Fig. 2** – Model silicon clusters in the singlet state with a  $p_b$ -center and a NO<sub>2</sub> molecule fixed to 1-10 OH groups (b-f) and without an OH group (a). The figure also shows the adsorption energy of the NO<sub>2</sub> molecule and the charge of the  $p_b$ -center

singlet state in this case is energetically unfavorable and in reality does not arise.

Calculations show that the efficiency of this interaction is critically affected by the number of surface OH groups on which the NO<sub>2</sub> molecule is fixed. When NO<sub>2</sub> is adsorbed onto a fully hydrogenated silicon surface, Fig. 2a, there is no interaction between NO<sub>2</sub> and the  $p_b$ -center, since  $E_a$  in this case is negative, ( $-0.75$  eV). This can be explained by the fact that the attraction between the  $p_b$ -center and NO<sub>2</sub> in the singlet state leads to a convergence of the NO<sub>2</sub> molecule with the surface hydrogen atoms (the NO<sub>2</sub> molecule is located at  $\sim 0.7$  Å closer to the hydrogen atoms than in the triplet state). The surface hydrogen atoms are negatively charged, like the NO<sub>2</sub> molecule, hence the artificial rapprochement between them is energetically unfavorable. Simplistically we can say that the attraction to the  $p_b$ -center and the repulsion from the surface H atoms act on the NO<sub>2</sub> molecule in opposite directions. A similar situation is observed when the NO<sub>2</sub> molecule is

fixed on a single OH group. But in this case the negative value of the binding energy in the singlet state is much smaller ( $-0.10$  eV). When the NO<sub>2</sub> molecule is attached to two or more OH groups, the singlet state becomes energetically more favorable, and the NO<sub>2</sub> adsorption energy increases to  $0.65$  eV (when fixed on a fully hydroxylated surface), Fig. 3, curve 1. This result can be explained by the fact that positively charged hydrogen atoms in OH groups attract NO<sub>2</sub> molecules to the surface, that is, they act in the same direction as the attraction to the  $p_b$ -center.

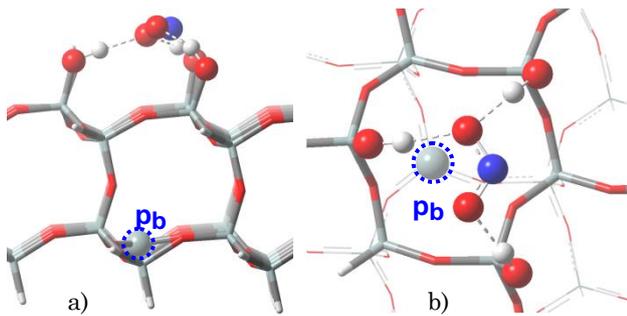


**Fig. 3** – The adsorption energy of the NO<sub>2</sub> molecule (curve 1) and the positive charge of the  $p_b$ -center in units of  $e$  (curve 2), depending on the number of surface OH groups on which the NO<sub>2</sub> molecule is fixed

The charge of the  $p_b$ -center also depends on the presence and number of OH groups on which the NO<sub>2</sub> molecule adsorbs. If there are no adsorbed NO<sub>2</sub> molecules on the surface of the cluster (hydrogenated or hydroxylated), the charge of the  $p_b$ -center is slightly negative (about  $-0.1e$ ). When NO<sub>2</sub> is adsorbed on the hydrogenated surface of a silicon cluster, the charge of the  $p_b$ -center becomes weakly positive,  $0.07e$ , Fig. 3, curve 2. When the NO<sub>2</sub> molecule is adsorbed on hydroxyl groups, the charge of the  $p_b$ -center becomes greater than  $0.3e$  and increases with the increase in the amount of OH groups, since the electron density is more efficiently transferred to the binding region of NO<sub>2</sub>. The NO<sub>2</sub> molecule in all the cases considered is negatively charged (both in the singlet and triplet states), its charge varies within the limits of  $-0.45 \div -0.55e$ . We also calculated the electronic structure of model objects. Simulation showed that there is no shallow acceptor states when NO<sub>2</sub> interacts with the  $p_b$ -center: the LUMO level of all the described clusters in the singlet state was higher  $-4.5$  eV, that is, above the midgap of silicon.

The interaction between  $p_b$ -centers and NO<sub>2</sub> molecules can also occur through a layer of silicon oxide. Fig. 4 shows a fragment of a Si<sub>74</sub>O<sub>133</sub>H<sub>65</sub> cluster with a  $p_b$ -center and an adsorbed NO<sub>2</sub> molecule bound by three OH groups. The singlet state of the cluster shown in the figure is  $0.57$  eV more energetically favorable than the triplet state. Thus, between the NO<sub>2</sub> molecule and the  $p_b$ -center there is an effective attraction

through a layer of SiO<sub>2</sub> with a thickness of  $\sim 8 \text{ \AA}$ . The binding energy of the NO<sub>2</sub> molecule in the singlet state of the cluster is 0.86 eV. This value practically coincides with the adsorption energy estimated in [5] from the kinetics of the reverse current decay in the *p-n* junctions with the oxidized surface, when the sample is taken from NO<sub>2</sub> atmosphere, 0.85 eV. In the singlet state, the charge of the p<sub>b</sub>-center substantially increases, in comparison with the triplet (about 2.05 *e*), and reaches a value of +1.66 *e*. The interaction of NO<sub>2</sub> and the p<sub>b</sub>-center does not give rise to shallow donor or acceptor levels – the LUMO level of the cluster in the singlet state is –2.81 eV.

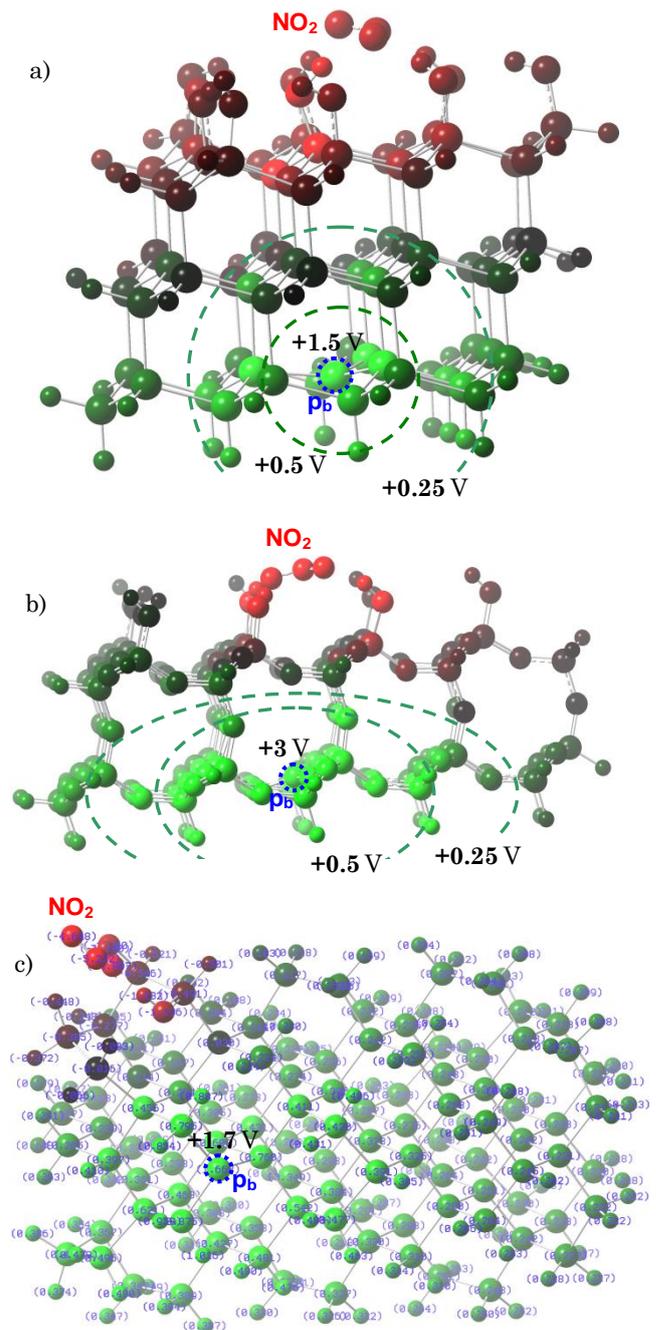


**Fig. 4** – Fragment of model cluster Si<sub>74</sub>O<sub>133</sub>H<sub>65</sub> with p<sub>b</sub>-center and adsorbed NO<sub>2</sub> molecule. a) top view, b) side view

#### 4. INFLUENCE OF THE REGION OF INCREASED POTENTIAL AROUND THE P<sub>B</sub>-CENTER ON THE CONDUCTIVITY OF SILICON STRUCTURES

The appearance of a significant positive charge of p<sub>b</sub>-centers upon interaction with NO<sub>2</sub> molecules (through a Si or SiO<sub>2</sub> layer) leads to an increase in the local potential around the p<sub>b</sub>-centers. Fig. 5 a, b shows the change in the potential on the atoms of Si and SiO<sub>2</sub> clusters in the transition from the triplet state to the singlet state (i.e., when there is an effective interaction between NO<sub>2</sub> and the p<sub>b</sub>-center). The region of potential reduction is shown in red, and the region of increase is shown in green. The potential at the p<sub>b</sub>-center of the silicon cluster Si<sub>68</sub>H<sub>46</sub>(OH)<sub>10</sub> increases by 1.48 V, and at the p<sub>b</sub>-center of the Si<sub>74</sub>O<sub>133</sub>H<sub>65</sub> silicon oxide cluster by 2.93 V. The geometry of the clusters did not allow us to establish the boundaries of the regions of increased potential, since the increase in potential should occur on atoms further away from the negatively charged NO<sub>2</sub> molecule, that is, below the p<sub>b</sub>-center in Fig. 5 a, b.

Therefore, a large cluster of Si<sub>103</sub>H<sub>101</sub>(OH)<sub>2</sub> with a p<sub>b</sub>-center and two OH groups on which the NO<sub>2</sub> molecule was adsorbed was constructed specifically to establish the dimensions of the region of the increased potential. The distance between NO<sub>2</sub> and the p<sub>b</sub>-center was approximately 9 Å. The distribution of the change in the potential after the transition from the triplet state to the singlet state of this cluster is shown in Fig. 5 c. The potential at the Si atom with the dangling bond increased by 1.67 V, and the region of the increased potential was very large. It can be seen from the figure that at almost all cluster atoms, with the exception of a small region around the NO<sub>2</sub> molecule, the potential is increased. Even on atoms distant from the p<sub>b</sub>-center by  $\sim 17 \text{ \AA}$ , the potential rises by more than 0.2 V.



**Fig. 5** – The distribution of the change in the potential on atoms after the transition of clusters with p<sub>b</sub>-centers and adsorbed NO<sub>2</sub> molecules from the triplet state to the singlet state. a) cluster Si<sub>68</sub>H<sub>46</sub>(OH)<sub>10</sub>, b) cluster Si<sub>74</sub>O<sub>133</sub>H<sub>65</sub>, c) cluster Si<sub>103</sub>H<sub>101</sub>(OH)<sub>2</sub>. Green color shows area of increased potential, and red – of reduced

A significant local increase in the potential due to the interaction of NO<sub>2</sub> molecules with paramagnetic p<sub>b</sub>-centers can lead to the appearance of an additional CB of holes in narrow sections of nanowires, of which the PS consists. This process plays a decisive role in the sensitivity to NO<sub>2</sub> of low-doped *p*-PS samples, in which  $N_S > N_B$ . In such samples, an increase in  $N_P$  due to the interaction of NO<sub>2</sub> with the B–p<sub>b</sub>-center pairs has a less significant effect on the conductivity than the ap-

pearance of an additional CB due to the interaction of NO<sub>2</sub> with paramagnetic p<sub>b</sub>-centers. This explains the increase in resistance of low-doped samples of *p*-PS in the NO<sub>2</sub> atmosphere, described in [7].

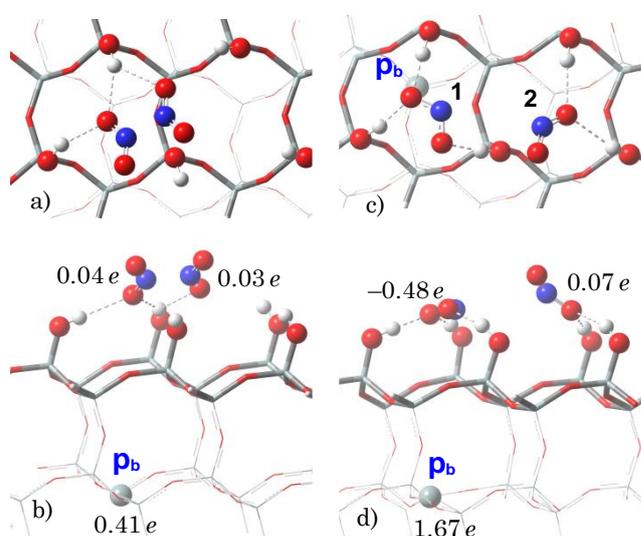
The appearance of an increased potential region around the p<sub>b</sub>-centers can explain the decrease in the resistivity of *p-n* junctions in the NO<sub>2</sub> atmosphere [5]. On the surface of the *p-n* junctions in the *p*- and *n*-regions, there is a depleted layer, where the concentration of free carriers is low. This is caused by the compensation (passivation) of impurity atoms by various surface centers. When adsorbed on the surface of oxidized silicon, NO<sub>2</sub> molecules interact with paramagnetic p<sub>b</sub>-centers located under a SiO<sub>2</sub> layer (their concentration is about 10<sup>12-13</sup> cm<sup>-2</sup>, [15]). Increasing the potential around positively charged p<sub>b</sub>-centers in *p-n* junctions does not lead to the appearance of a CB, as in PS. The layer of positively charged centers p<sub>b</sub> causes bending of the energy bands and an increase in the concentration of free electrons near the surface (an *n*-type surface channel appears). As already mentioned, the NO<sub>2</sub>-p<sub>b</sub>-center pair does not form acceptor states. The calculated energy of the LUMO levels of Si and SiO<sub>2</sub> clusters with a hydroxylated surface, p<sub>b</sub>-center and NO<sub>2</sub> molecule was -4.48 and -2.81 eV, respectively. This means that free electrons entering the surface channel are not captured by positively charged p<sub>b</sub>-centers and freely pass through the *p-n* junction.

## 5. DISSOCIATION OF N<sub>2</sub>O<sub>4</sub> DIMERS ON THE SURFACE OF SI AND SiO<sub>2</sub> UPON INTERACTION WITH DISTANT P<sub>B</sub>-CENTERS

At low partial pressures of NO<sub>2</sub> (up to 0.01 Torr), most of the nitrogen oxide molecules are not dimerized. It is at these pressures that a reversible increase in the PS conductivity in the NO<sub>2</sub> atmosphere is observed experimentally. But some of the NO<sub>2</sub> molecules remain dimerized at low pressures, and at high pressures, the dimers prevail over the monomers. At relatively high partial pressures (>0.01 Torr), the effect of NO<sub>2</sub> on the concentrations of free holes and p<sub>b</sub>-centers in *p-PS* [8] and on the current in *p-n* junctions was investigated [6]. Therefore, the question arose whether N<sub>2</sub>O<sub>4</sub> dimers can influence the conductivity of silicon structures and what is the mechanism of this influence. The experimentally obtained value of the binding energy of NO<sub>2</sub> molecules in the N<sub>2</sub>O<sub>4</sub> dimer is 0.595 eV [16]. DFT calculations performed using the B3LYP functional and the 6-31++*g* (*d*, *p*) basis give a very close value of 0.588 eV. Therefore, spontaneous dissociation of dimers can occur with low probability. As shown in [5], the destruction of dimers is possible with the adsorption of N<sub>2</sub>O<sub>4</sub> directly on the dangling bond of the surface Si atom. But in this case, the adsorbed NO<sub>2</sub> molecule forms a stable chemical bond with the surface, and can not affect the renewable sensitivity of silicon sensors. We assumed that the above-described interaction of one of the NO<sub>2</sub> molecules forming a dimer with a distant p<sub>b</sub>-center could lead to the destruction of N<sub>2</sub>O<sub>4</sub>. The long-range interaction between NO<sub>2</sub> molecules and p<sub>b</sub>-centers is effective only when NO<sub>2</sub> is adsorbed on surface OH groups. Therefore, the modeling of the adsorption and destruction of dimers was carried out on

Si and SiO<sub>2</sub> clusters with a hydroxylated surface.

We first consider the possibility of dissociation of the N<sub>2</sub>O<sub>4</sub> dimer on the hydroxylated surface of SiO<sub>2</sub> (β-cristobalite), Fig. 6. DFT simulation showed that the most energetically favorable is the case of dimer adsorption, when two of its molecules are located above neighboring hexahedral cells, Fig. 6 a. With this type of fixing, one of the NO<sub>2</sub> molecules binds to two OH groups, and the other – to one. Simulation showed that in the absence of a p<sub>b</sub>-center on the lower face of the cluster, the destruction of the dimer is very unlikely. If we placed distant NO<sub>2</sub> molecules in neighboring cells, then during the geometry optimization, the dimer was restored. Disruption of the dimer with fixation of NO<sub>2</sub> molecules in the more distant cells required additional energy of more than 0.45 eV. This value is less than the energy of dimerization of NO<sub>2</sub> in air, but still large for the spontaneous destruction of dimers.

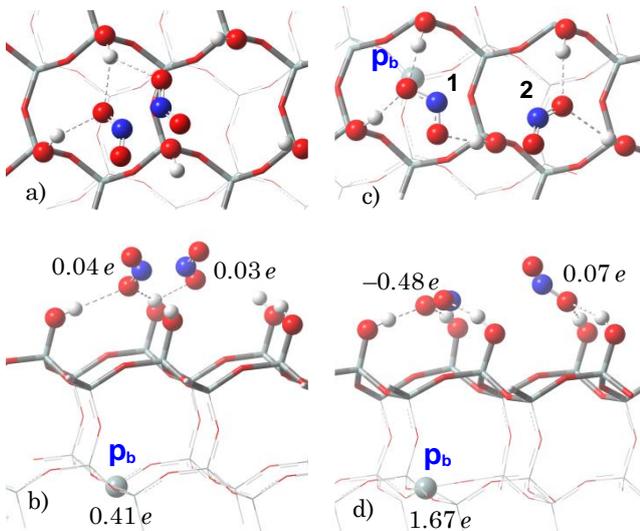


**Fig. 6** – (a) Fragment of the cluster Si<sub>74</sub>O<sub>133</sub>H<sub>66</sub> (without p<sub>b</sub>-center) with adsorbed dimer N<sub>2</sub>O<sub>4</sub>. Fragments of the cluster Si<sub>74</sub>O<sub>133</sub>H<sub>65</sub> with the p<sub>b</sub>-center: (b) – with an adsorbed dimer; (c, d) – with a dissociated dimer (side view and top view)

The addition of a p<sub>b</sub>-center on the lower face of the cluster does not affect the position of the adsorbed unbroken dimer. The geometry of N<sub>2</sub>O<sub>4</sub> and the length of the hydrogen bonds with the OH groups on which the dimer is fixed practically coincide in the absence and presence of the p<sub>b</sub>-center, Fig. 6 a, b. The dimer does not interact with the p<sub>b</sub>-center, the charges of NO<sub>2</sub> molecules are close and small (0.03 and 0.04 e), and the charge of the p<sub>b</sub>-center is 0.41 e. Fig. 6 c, d shows the case when a dimer is dissociated into two molecules (1 and 2), which are located in adjacent cells. In this case, when the geometry is optimized, the dimer is not reconstructed. The binding and charges of separated NO<sub>2</sub> molecules are already significantly different. Molecule 2, which does not interact with the p<sub>b</sub>-center, remains far from the surface of the cluster, and its charge remains insignificant (0.07 e). Molecule 1 interacts with the p<sub>b</sub>-center and pulls the electron density from it. Its charge becomes negative, -0.48 e, and the charge of the p<sub>b</sub>-center, which the electron gave, significantly in-

creases – to  $1.68 e$ . A negatively charged molecule **1** is attracted to a positively charged  $p_b$ -center, so it is much closer to the surface than molecule **2**, and is no longer bound by two but three hydrogen bonds to surface OH groups. The simulation showed that the energy of a cluster with a dissociated dimer is only  $0.03 eV$  greater than the energy of a cluster with dimerized  $NO_2$ . This means that the presence of  $p_b$ -centers (even separated by a  $9 \text{ \AA}$   $SiO_2$  layer) makes the process of dissociation of  $N_2O_4$  dimers on the surface of hydroxylated  $SiO_2$  very probable.

A similar situation is observed when adsorbing  $N_2O_4$  dimer on the hydroxylated surface of silicon. If there is no  $p_b$ -center on the lower face of the cluster, the dissociation of the dimer is again energetically unfavorable. Fig. 7 shows the cases of fixing the dimer (*a, b*) and isolated molecules of  $NO_2$  (*c, d*) on the  $Si_{68}H_{48}(OH)_7$  cluster with the  $p_b$ -center on the lower face. In the case of a dissociated dimer, the charge of the nitrogen oxide molecule **1**, which interacts with the  $p_b$ -center, again becomes negative,  $-0.42 e$ , and it is attracted to the surface of the cluster. The charge of the  $p_b$ -center increases from  $-0.11 e$  (for the case of an unbroken dimer) to  $0.34 e$ . The energy of a cluster with separate  $NO_2$  molecules is only  $0.016 eV$  greater than a cluster with a dimer. Thus, the dissociation of dimers on the hydroxylated surface of silicon can also occur with a high probability.



**Fig. 7** – Fragments of the  $Si_{68}H_{48}(OH)_7$  cluster with a  $p_b$ -center on the lower face. (*a, b*) – with an adsorbed dimer; (*c, d*) – with separated  $NO_2$  molecules (side view and top view)

The positive charge of the  $p_b$ -center, which occurs when interacting with the broken dimer, creates an area of increased potential. This can cause the CB of free holes in the PS and the appearance of a conducting channel on the surface of the  $p-n$  junctions. Thus, an

increase in the resistance of low-doped  $p$ -type PS samples and an increase in the current in  $p-n$  junctions are possible when interacting with both  $NO_2$  monomers and dimers.

The desorption energies of  $NO_2$  molecules that do not interact with the  $p_b$ -center, ( $0.18$  and  $0.30 eV$  for Si and  $SiO_2$ , respectively) are less than the dissociation energy of an isolated dimer,  $0.59 eV$ . Desorption of such molecules leads to an increase in the concentration of  $NO_2$  monomers, which affect the conductivity of silicon structures. Therefore dissociation of dimers on the surface of Si or  $SiO_2$  plays an important role in the mechanism of sensitivity of silicon sensors to  $NO_2$ .

## 6. CONCLUSION

DFT calculations showed that a long-range interaction (attraction) can occur between  $NO_2$  molecules and  $p_b$ -centers separated by a layer of Si or  $SiO_2$ . With this interaction, the  $NO_2$  molecule pulls the electron density from the  $p_b$ -center and charges negatively. Shallow donor or acceptor states do not arise in this case. The interaction between  $NO_2$  and the  $p_b$ -center occurs only when  $NO_2$  is adsorbed on surface OH groups. The more OH groups with which the  $NO_2$  molecule is bound, the more effective this interaction is. This is explained by the fact that the interaction of a negatively charged  $NO_2$  molecule with positively charged hydrogen atoms in OH groups is energetically favorable. When interacting with  $NO_2$ , the  $p_b$ -center charges positively, around it a wide region of increased potential arises (on the atoms in a radius of  $\sim 17 \text{ \AA}$  around the  $p_b$ -center, the potential increases by more than  $0.2 V$ ). This can cause the occurrence of an additional CB of free holes in  $p$ -PS and explains the decrease in the conductivity of low-doped  $p$ -PS samples (in which  $N_S > N_B$ ). Charging of  $p_b$ -centers upon interaction with  $NO_2$  causes a near-surface bending of the energy bands in the  $p-n$  junctions. Due to this, a surface channel with electronic conductivity can appear in both regions of the  $p-n$  junctions. This explains the increase in current in the  $p-n$  junctions in the  $NO_2$  atmosphere. The calculated  $NO_2$  adsorption energy on the hydroxylated  $SiO_2$  surface ( $0.86 eV$ ) coincides with the value experimentally estimated in [5] by the kinetics of the reverse current decay in  $p-n$  junctions with the oxidized surface. Interaction with distant  $p_b$ -centers can lead to the dissociation of  $N_2O_4$  dimers adsorbed on the hydroxylated surface of Si or  $SiO_2$ . In this case, only one of the dimer molecules interacts with the  $p_b$ -center, and the other can relatively easily be desorbed from the surface. The questions of the interaction of  $NO_2$  with  $n$ -PS and the reduction of  $N_P$  in  $p$ -PS at high pressures of  $NO_2$ , which have not been explained yet, will be the subject of our further research.

## Дальнодіюча взаємодія між рb-центрами та молекулами NO<sub>2</sub>, адсорбованими на поверхні кремнію

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DFT-розрахунки показали, що між адсорбованими молекулами або димерами NO<sub>2</sub> та віддаленими рb-центрами (атомами Si з оборваним зв'язком) може виникати взаємодія через шар Si або SiO<sub>2</sub>. Ця взаємодія є ефективною лише при закріпленні NO<sub>2</sub> на поверхневих OH-групах. При такій взаємодії рb-центр заряджається позитивно, що викликає додаткову кулонівську блокаду вільних дірок і може пояснити спад провідності у низьколегованих зразків поруватого кремнію *p*-типу.

**Ключові слова:** DFT-розрахунки, Адсорбція, NO<sub>2</sub>, Поруватий кремній.

## Дальнодействующее взаимодействие между рb-центрами и молекулами NO<sub>2</sub>, адсорбированными на поверхности кремния

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DFT-расчеты показали, что между адсорбированными молекулами или димерами NO<sub>2</sub> и удаленными рb-центрами (атомами Si с оборванной связью) может возникать взаимодействие через слой Si или SiO<sub>2</sub>. Это взаимодействие является эффективным только при закреплении NO<sub>2</sub> на поверхностных OH-группах. При таком взаимодействии рb-центр заряжается положительно, что вызывает дополнительную кулоновскую блокаду свободных дырок и может объяснить спад проводимости низьколегированных образцов пористого кремния *p*-типа.

**Ключевые слова:** DFT-расчеты, адсорбция, NO<sub>2</sub>, пористый кремний.

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