

Long-range Interaction between p_b -centers and NO_2 Molecules Adsorbed on the Silicon Surface

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DFT calculations showed that the interaction between adsorbed nitric oxide (NO_2) molecules (or N_2O_4 dimers) and distant p_b -centers (Si atoms with dangling bonds) can occur through a Si or SiO_2 layer. This interaction is effective only when 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, NO_2 .

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1. INTRODUCTION

Emission of 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 NO_2 sensors with a low detection threshold and high sensitivity. Silicon structures of various types have great prospects as NO_2 sensors. In the review papers [2, 3], data on the creation of NO_2 sensors based on PS and silicon nanowires (SiNWs) are systematized. 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 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 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 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 NO_2 atmosphere remained unexplained. This theory also did not explain the mechanism of sensitivity to 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 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 NO_2 molecules on OH groups of silicon or SiO_2 surfaces, their acceptor properties significantly

increase. This is due to the fact that with such adsorption, NO_2 molecules interact with positively charged hydrogen atoms of hydroxyl groups. With this, the lowest unoccupied molecular orbital (LUMO) of 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 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 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 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 NO_2 atmosphere of high-doped p -PS samples, and the decrease in the conductivity of low-doped p -PS under the influence of 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 NO_2 and explain the mechanism of dissociation of N_2O_4 dimers on the Si or 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 NO_2 pressures (up to 10^{-2} Torr) is reversibly reduced. Therefore, it is obvious that there is an interaction between 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 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 NO_2 molecules with paramagnetic p_b -centers. It was shown in [7] that in 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 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 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 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 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 NO_2 molecules to the PS surface are small. The adsorption energy, when the 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 NO_2 molecules with p_b -centers should be long-range. If the surface p_b -center and the NO_2 molecule are nearby and do not separate anything, the 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 NO_2 and the p_b -center should occur through a thin layer of 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 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 NO_2 molecule. To investigate this effect on the long-range interaction of the p_b -center and 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 NO_2 and the p_b -center through a SiO_2 layer was simulated on a cluster of β -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 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 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].

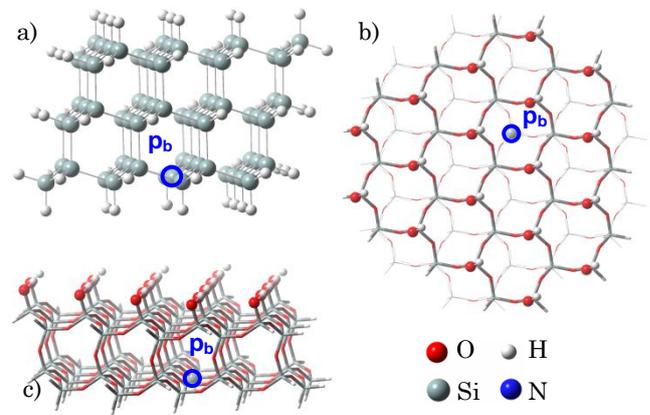


Fig. 1 – Model clusters with p_b -centers on the lower edge (marked with blue circles). a) – silicon cluster $\text{Si}_{68}\text{H}_{55}$; b) and c) – SiO_2 cluster (β -cristobalite) $\text{Si}_{74}\text{O}_{133}\text{H}_{65}$, top and side views, respectively

3. THE ROLE OF SURFACE OH GROUPS IN THE INTERACTION OF DISTANT NO_2 MOLECULES AND PB -CENTERS

The presence and effectiveness of long-range interaction between an 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 NO_2 molecule. In the singlet state, the unpaired electrons of the p_b -center and 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_{SINGL}) is greater than in the triplet state (E_{TRIPL}), this means that there is an effective attraction between NO_2 and the p_b -center. When the triplet state is more favorable, there is no interaction (attraction) between NO_2 and the p_b -center. The negative value of the calculated NO_2 molecule adsorption energy (E_a) in the singlet state can also indicate that there is no interaction between NO_2 and the p_b -center. The

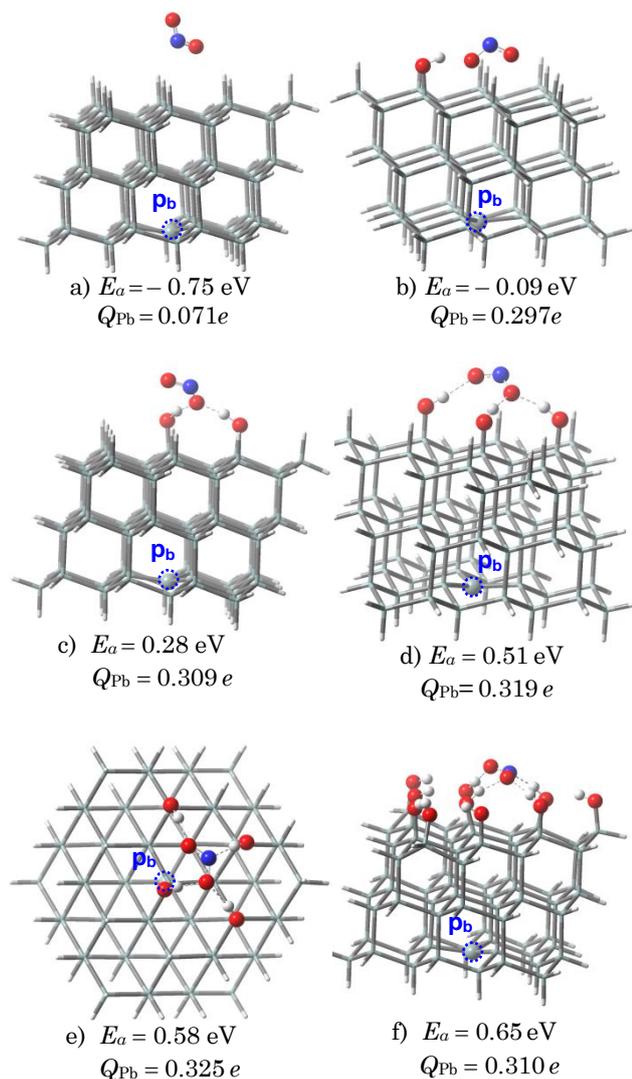


Fig. 2 – Model silicon clusters in the singlet state with a p_b -center and a NO₂ molecule fixed to 1-10 OH groups (b-f) and without an OH group (a). The figure also shows the adsorption energy of the NO₂ molecule and the charge of the p_b -center

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 NO₂ molecule is fixed. When NO₂ is adsorbed onto a fully hydrogenated silicon surface, Fig. 2a, there is no interaction between NO₂ 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 NO₂ in the singlet state leads to a convergence of the NO₂ molecule with the surface hydrogen atoms (the NO₂ molecule is located at ~ 0.7 Å closer to the hydrogen atoms than in the triplet state). The surface hydrogen atoms are negatively charged, like the NO₂ 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 NO₂ molecule in opposite directions. A similar situation is observed when the NO₂ 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 NO₂ molecule is attached to two or more OH groups, the singlet state becomes energetically more favorable, and the NO₂ 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 NO₂ molecules to the surface, that is, they act in the same direction as the attraction to the p_b -center.

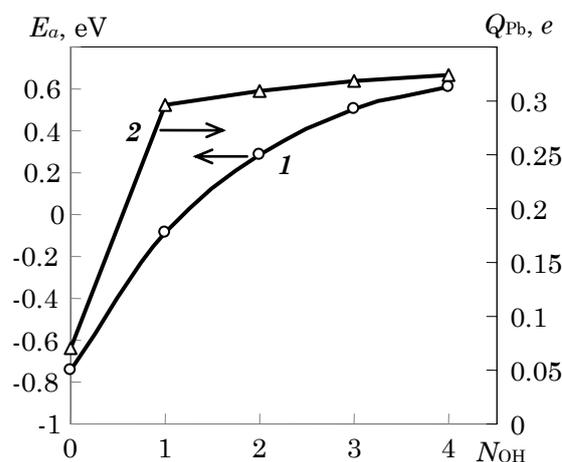


Fig. 3 – The adsorption energy of the NO₂ molecule (curve 1) and the positive charge of the p_b -center in units of e (curve 2), depending on the number of surface OH groups on which the NO₂ molecule is fixed

The charge of the p_b -center also depends on the presence and number of OH groups on which the NO₂ molecule adsorbs. If there are no adsorbed NO₂ molecules on the surface of the cluster (hydrogenated or hydroxylated), the charge of the p_b -center is slightly negative (about $-0.1e$). When NO₂ 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 NO₂ 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 NO₂. The NO₂ 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 NO₂ 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 NO₂ molecules can also occur through a layer of silicon oxide. Fig. 4 shows a fragment of a Si₇₄O₁₃₃H₆₅ cluster with a p_b -center and an adsorbed NO₂ 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 NO₂ molecule and the p_b -center there is an effective attraction

through a layer of SiO₂ with a thickness of $\sim 8 \text{ \AA}$. The binding energy of the NO₂ 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 NO₂ atmosphere, 0.85 eV. In the singlet state, the charge of the p_b-center substantially increases, in comparison with the triplet (about 2.05 *e*), and reaches a value of +1.66 *e*. The interaction of NO₂ and the p_b-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.

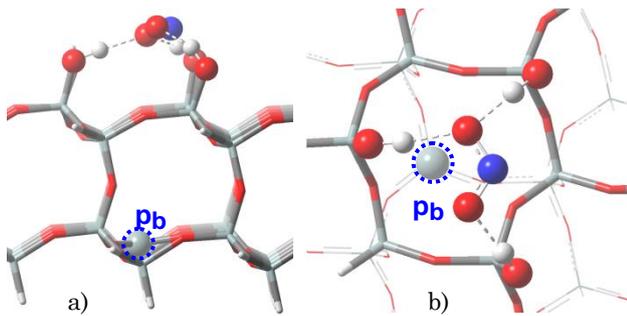


Fig. 4 – Fragment of model cluster Si₇₄O₁₃₃H₆₅ with p_b-center and adsorbed NO₂ molecule. a) top view, b) side view

4. INFLUENCE OF THE REGION OF INCREASED POTENTIAL AROUND THE P_B-CENTER ON THE CONDUCTIVITY OF SILICON STRUCTURES

The appearance of a significant positive charge of p_b-centers upon interaction with NO₂ molecules (through a Si or SiO₂ layer) leads to an increase in the local potential around the p_b-centers. Fig. 5 a, b shows the change in the potential on the atoms of Si and SiO₂ clusters in the transition from the triplet state to the singlet state (i.e., when there is an effective interaction between NO₂ and the p_b-center). The region of potential reduction is shown in red, and the region of increase is shown in green. The potential at the p_b-center of the silicon cluster Si₆₈H₄₆(OH)₁₀ increases by 1.48 V, and at the p_b-center of the Si₇₄O₁₃₃H₆₅ 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 NO₂ molecule, that is, below the p_b-center in Fig. 5 a, b.

Therefore, a large cluster of Si₁₀₃H₁₀₁(OH)₂ with a p_b-center and two OH groups on which the NO₂ molecule was adsorbed was constructed specifically to establish the dimensions of the region of the increased potential. The distance between NO₂ and the p_b-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 NO₂ molecule, the potential is increased. Even on atoms distant from the p_b-center by $\sim 17 \text{ \AA}$, the potential rises by more than 0.2 V.

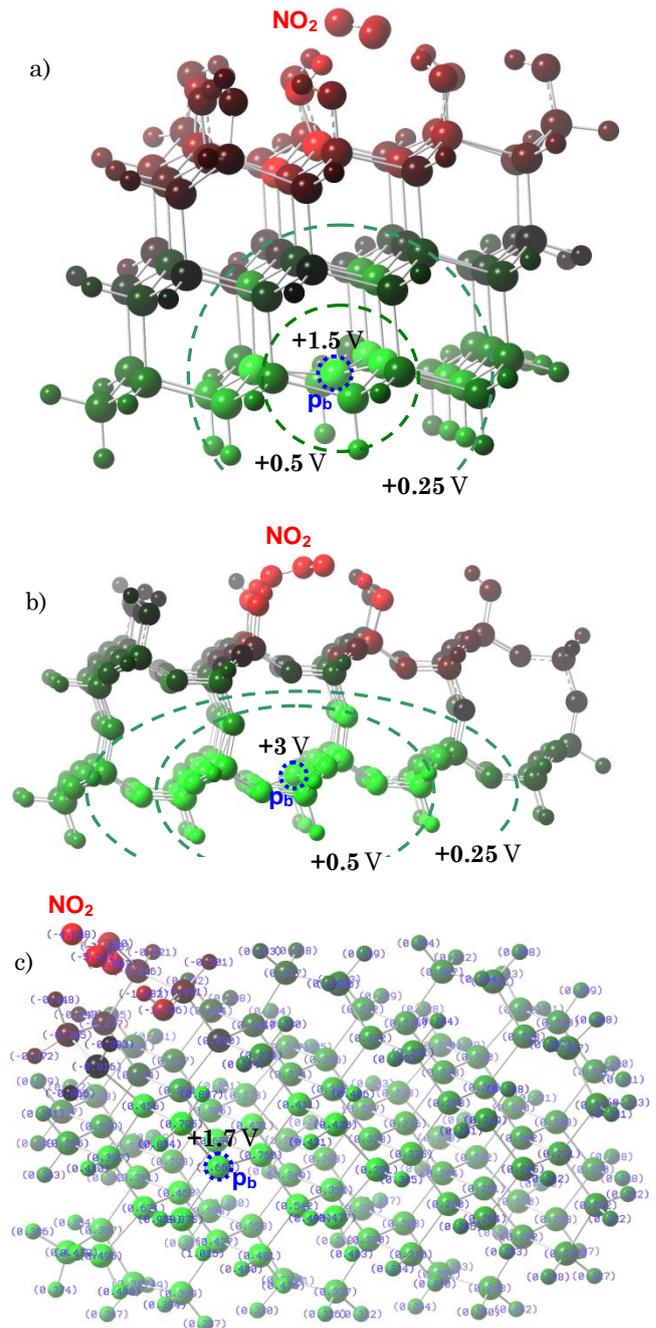


Fig. 5 – The distribution of the change in the potential on atoms after the transition of clusters with p_b-centers and adsorbed NO₂ molecules from the triplet state to the singlet state. a) cluster Si₆₈H₄₆(OH)₁₀, b) cluster Si₇₄O₁₃₃H₆₅, c) cluster Si₁₀₃H₁₀₁(OH)₂. Green color shows area of increased potential, and red – of reduced

A significant local increase in the potential due to the interaction of NO₂ molecules with paramagnetic p_b-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 NO₂ 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 NO₂ with the B-p_b-center pairs has a less significant effect on the conductivity than the ap-

pearance of an additional CB due to the interaction of NO₂ with paramagnetic p_b-centers. This explains the increase in resistance of low-doped samples of *p*-PS in the NO₂ atmosphere, described in [7].

The appearance of an increased potential region around the p_b-centers can explain the decrease in the resistivity of *p-n* junctions in the NO₂ 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, NO₂ molecules interact with paramagnetic p_b-centers located under a SiO₂ layer (their concentration is about 10¹²⁻¹³ cm⁻², [15]). Increasing the potential around positively charged p_b-centers in *p-n* junctions does not lead to the appearance of a CB, as in PS. The layer of positively charged centers p_b 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 NO₂-p_b-center pair does not form acceptor states. The calculated energy of the LUMO levels of Si and SiO₂ clusters with a hydroxylated surface, p_b-center and NO₂ 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_b-centers and freely pass through the *p-n* junction.

5. DISSOCIATION OF N₂O₄ DIMERS ON THE SURFACE OF SI AND SiO₂ UPON INTERACTION WITH DISTANT P_B-CENTERS

At low partial pressures of NO₂ (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 NO₂ atmosphere is observed experimentally. But some of the NO₂ 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 NO₂ on the concentrations of free holes and p_b-centers in *p-PS* [8] and on the current in *p-n* junctions was investigated [6]. Therefore, the question arose whether N₂O₄ 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 NO₂ molecules in the N₂O₄ 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 N₂O₄ directly on the dangling bond of the surface Si atom. But in this case, the adsorbed NO₂ 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 NO₂ molecules forming a dimer with a distant p_b-center could lead to the destruction of N₂O₄. The long-range interaction between NO₂ molecules and p_b-centers is effective only when NO₂ is adsorbed on surface OH groups. Therefore, the modeling of the adsorption and destruction of dimers was carried out on

Si and SiO₂ clusters with a hydroxylated surface.

We first consider the possibility of dissociation of the N₂O₄ dimer on the hydroxylated surface of SiO₂ (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 NO₂ molecules binds to two OH groups, and the other – to one. Simulation showed that in the absence of a p_b-center on the lower face of the cluster, the destruction of the dimer is very unlikely. If we placed distant NO₂ molecules in neighboring cells, then during the geometry optimization, the dimer was restored. Disruption of the dimer with fixation of NO₂ 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 NO₂ in air, but still large for the spontaneous destruction of dimers.

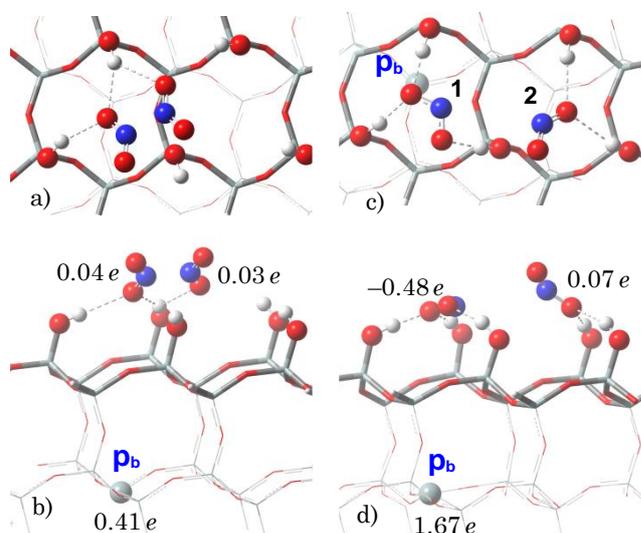


Fig. 6 – (a) Fragment of the cluster Si₇₄O₁₃₃H₆₆ (without p_b-center) with adsorbed dimer N₂O₄. Fragments of the cluster Si₇₄O₁₃₃H₆₅ with the p_b-center: (b) – with an adsorbed dimer; (c, d) – with a dissociated dimer (side view and top view)

The addition of a p_b-center on the lower face of the cluster does not affect the position of the adsorbed unbroken dimer. The geometry of N₂O₄ 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_b-center, Fig. 6 a, b. The dimer does not interact with the p_b-center, the charges of NO₂ molecules are close and small (0.03 and 0.04 e), and the charge of the p_b-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 NO₂ molecules are already significantly different. Molecule 2, which does not interact with the p_b-center, remains far from the surface of the cluster, and its charge remains insignificant (0.07 e). Molecule 1 interacts with the p_b-center and pulls the electron density from it. Its charge becomes negative, -0.48 e, and the charge of the p_b-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 \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.

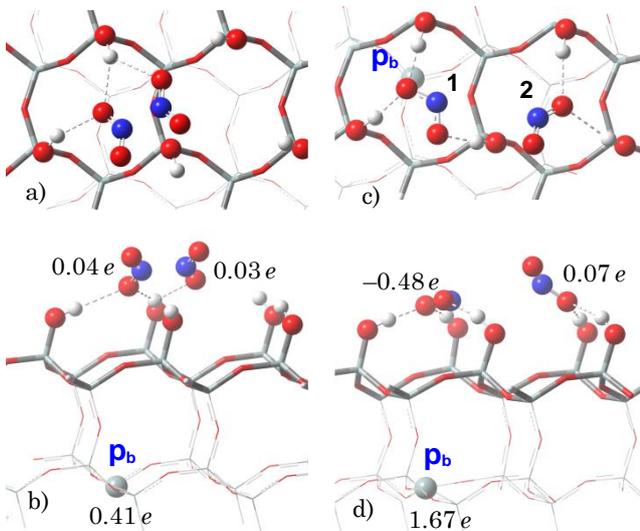


Fig. 7 – Fragments of the $Si_{68}H_{48}(OH)_7$ cluster with a p_b -center on the lower face. (*a, b*) – with an adsorbed dimer; (*c, d*) – with separated NO_2 molecules (side view and top view)

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 NO₂, адсорбованими на поверхні кремнію

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DFT-розрахунки показали, що між адсорбованими молекулами або димерами NO₂ та віддаленими рb-центрами (атомами Si з оборваним зв'язком) може виникати взаємодія через шар Si або SiO₂. Ця взаємодія є ефективною лише при закріпленні NO₂ 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, NO₂, Поруватий кремній.

Дальнодействующее взаимодействие между рb-центрами и молекулами NO₂, адсорбированными на поверхности кремния

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DFT-расчеты показали, что между адсорбированными молекулами или димерами NO₂ и удаленными рb-центрами (атомами Si с оборванной связью) может возникать взаимодействие через слой Si или SiO₂. Это взаимодействие является эффективным только при закреплении NO₂ 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, NO₂, пористый кремний.

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