Mechanisms of Changing the Conductivity of Porous Silicon in an Ammonia Atmosphere – DFT Modeling

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Based on quantum-chemical calculations by the density functional theory (DFT) method, four possible mechanisms of the influence of ammonia vapors on the conductivity of silicon nanostructures, in particular, porous silicon (PS), were examined. The first mechanism involves the emergence of donor states in the interaction of NH_3 molecules with p_b-centers (surface Si atoms with dangling bonds). The change in conductivity by the second and third mechanisms can occur in p-type silicon structures. The second mechanism involves the protonation of an ammonia molecule with the subsequent passivation of subsurface impurity boron atoms by NH_4^+ ions. The third mechanism combines the first two. At the first stage, it involves the interaction of NH_3 molecules with passivated B-p_b-center pairs. After protonation of the NH_3 molecule, the boron impurity atom is already passivated by the NH_4^+ ion, and the paramagnetic state of the p_b-center is restored. At the second stage, the formation of donor states occurs during the interaction of NH_3 molecules with already paramagnetic p_b-centers. The processes according to the fourth mechanism can occur in n-type silicon structures. It provides for the restoration of donor properties of surface phosphorus atoms passivated by two hydrogen atoms. Such a restoration occurs after protonation of the NH_3 molecule, when the proton (the ion of the surface hydrogen atom) is separated from the phosphorus atom. The last three models involve the protonation of NH_3 molecules with the necessary participation of water molecules and surface OH-groups, the important role of which has been demonstrated in most experimental studies.

Keywords: Porous silicon, Ammonia, Conductivity, p_b-centers.

1. INTRODUCTION

The creation and study of silicon nanostructures as ammonia sensors remains an urgent research topic. Over the past few years, many experimental and theoretical works have been published on the effect of ammonia on the conductivity of porous silicon (PS) [1, 2], silicon nanowires (SiNW) [3], silicon with a microstructured and oxidized surface [4-6]. This interest is primarily due to the environmental aspect, since ammonia emissions from industrial production and agriculture significantly pollute the environment. The European Commission regularly monitors NH_3 emissions and their reduction is part of the long-term A Clean Air Program for Europe. Secondly, NH_3 molecules have the most pronounced donor properties, that is, they cause an increase in the electronic conductivity of semiconductors. These molecules are also typical representatives of Bronsted bases, because they have a very high proton affinity. Therefore, an explanation of the effect of NH_3 adsorption on the conductivity of silicon will also explain the effect of other basic molecules, amino compounds, and molecules with high proton affinities.

The effect of NH_3 vapors on p-type PS (p-PS) has been most widely studied experimentally, since its manufacture is the simplest. The study of the current-voltage characteristics, IR and electron paramagnetic resonance (EPR) spectra showed that with increasing NH_3 pressure in p-PS, the concentration of free holes first decreases (resistance increases), then the type of conductivity changes and the concentration of free electrons begins to increase [7-11]. In n-type PS (n-PS), the concentration of free electrons monotonically increases with increasing ammonia pressure. The process of changing the concentration of free carriers (or conductivity) is reversible, and conduction is restored in tens of seconds [12, 13]. Most authors claim that a significant change in conductivity occurs only in wet ammonia vapors [10, 11]. It was also shown that at high pressures of NH_3 on the surface of PS, the concentration of p_b-centers increases irreversibly [11].

Many authors tried to explain the mechanism of changes in the conductivity of PS and SiNW in an ammonia atmosphere, but the proposed explanations were imperfect, a critical review of theoretical models of the conductivity change can be found in our work [6]. The most common model at present is the appearance of donor states in silicon upon adsorption of ammonia molecules on surface p_b-centers [14, 15]. But this model has significant drawbacks, for example, it does not explain the important role of water molecules. In addition, the measured concentration of free electrons in p-PS at high pressures of NH_3 turns out to be higher than the concentration of paramagnetic p_b-centers [10, 16]. In previous studies, we showed that a change in the conductivity of oxidized silicon can be associated with protonation of the NH_3 molecule in the presence of water molecules [5, 6]. But such an explanation was also imperfect: protonation could occur only with the simultaneous migration of three protons and required the participation of at least four H_2O molecules (that is, it was a weakly probable process). So, the microscopic mechanism of the effect of ammonia on the conductivity of silicon structures is still considered incompletely clarified [15]. In our recent work [17], it was shown that long-range passivation of boron impurity atoms by

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p_b-centers exists. This allowed us to propose a model of the change in the conductivity of *p*-type silicon structures upon passivation of a boron impurity by NH_4^+ ions [18]. In this paper, we will revise existing and propose new models of changing the conductivity of silicon in an ammonia atmosphere, which explain most of the experimentally obtained results.

2. A MODIFIED MODEL OF THE INTERACTION OF p_b-CENTERS WITH AMMONIA MOLECULES (1)

In the most recognized calculation works, it was shown that the adsorption of NH_3 molecules over the p_b-centers in SiNW leads to a rise in the Fermi level to the bottom of the conduction band [14, 15]. But, as the authors themselves claimed, the imperfection of the calculation method (calculation of the exchange correlation energy within the GGA method in the PBE parametrization) led to a significant (0.6-0.8 eV) decrease in the calculated band gap, which allowed only qualitative conclusions about the change in the electronic state of the system [15]. In addition, the imperfection of the basis set without diffuse functions (pseudopotentials for the core electrons and double-ζ plus polarization functions for the valence electrons) could lead to a distortion of the geometric and energy parameters of the adsorption system.

We tried to make such calculations by the DFT method using the more adequate B3LYP hybrid functional in the Gaussian 09 environment [19]. The simulation was based on small $Si_{68}H_{55}$ and large $Si_{286}H_{143}$ (Fig. 1) silicon clusters with diameters of approximately 10 and 20 Å. This made it possible to investigate and subsequently take into account the effect of cluster sizes on their electronic structure. The faces of the clusters were crystallographic planes (111) passivated by hydrogen, since these surfaces are the most stable and common in PS crystallites [20]. The fairly wide 6-311++g(d,p) basis set used for cluster atoms near the adsorption site and NH_3 molecules, included diffuse functions that are important for describing long-range interactions. Other cluster atoms were modeled in the 6-31g(d,p) basis, which did not affect the geometric and energy parameters of the calculations. For example, the average value of interatomic distances in the model cluster was 2.37 Å, which almost coincides with the known experimental value of 2.35 Å.

Modeling showed that the adsorption energy of the NH_3 molecule over the p_b-center is $E_{ADS} = 0.04$ eV (coincides for large and small clusters). Such a low value of E_{ADS} is physically justified: the ammonia molecule has a negative electron affinity and a very large electron work function (more than 10 eV). This means that it is energetically disadvantageous for the NH_3 molecule to either take an unpaired electron from the p_b-center or give up its own. The bond is formed due to the weak correlation interaction between the lone electron pair of the nitrogen atom and the unpaired electron of the p_b-center. Therefore, the value of $E_{ADS} = 0.21$ eV, obtained in a similar case [14, 15], is overestimated and once again indicates the imperfection of the basis set and the calculation method chosen in the mentioned works.
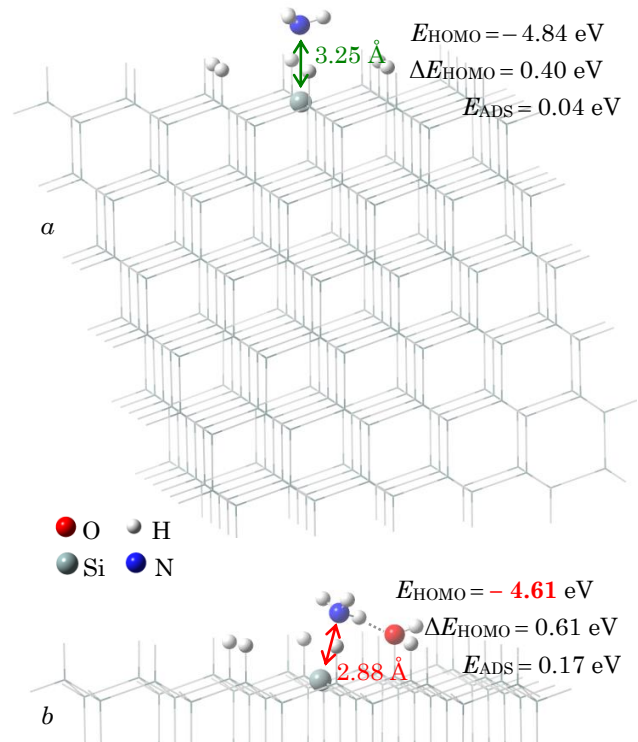
Fig. 1 – a) Model cluster $Si_{286}H_{143}$ with a p_b-center and an NH_3 molecule adsorbed above it; b) a fragment of the $Si_{286}H_{143}OH$ model cluster with a p_b-center and an NH_3 molecule adsorbed on an OH-group near the p_b-center

The simulation also showed that when the NH_3 molecule is adsorbed above the p_b-center, the energy of the highest occupied molecular orbital (HOMO) localized near the p_b-center increases. The corresponding increase for the small cluster is $\Delta E_{HOMO} = 0.44$ eV (to $E_{HOMO} = -4.89$ eV) and $\Delta E_{HOMO} = 0.40$ eV (to $E_{HOMO} = -4.84$ eV) for the large cluster. So, the increase in the HOMO recorded in our calculations is in qualitative agreement with the results of Rurali et al. [14, 15]. But it should be noted that the calculated E_{HOMO} value does not reach the middle of the silicon band gap (approximately − 4.5 eV). This can be explained by the relatively small size of the model clusters, therefore, the increased band gap. On the one hand, it can be expected that for silicon nanocrystallites with real diameters greater than 4 nm, the E_{HOMO} value will exceed the middle of the band gap, i.e. the corresponding level will have certain donor properties (although it will not be a shallow donor). On the other hand, as intermediate calculations showed, the closer the NH_3 molecule is to the p_b-center, the higher the HOMO rises. Therefore, the absence of delocalized diffuse functions in the basis set in calculations [14, 15] (neglecting long-range repulsion) could artificially reduce the distance of the adsorbed NH_3 molecule to the p_b-center. This, in turn, could lead to an artificial overestimation of E_{HOMO} (to the bottom of the conduction band). The neglect of long-range repulsion is indirectly indicated by the overestimated value of E_{ADS} obtained in [14, 15]. So, modeling showed that although the adsorption of the NH_3 molecule over the p_b-center increases the HOMO energy, it can only lead to the appearance of deep donor states.

Since the concentration of surface OH-groups even in freshly prepared PS is significant [1], we suggested that the adsorption of NH_3 molecules on OH-groups near p_b-centers (Fig. 1b) can cause a more substantial increase in the HOMO level. This assumption is due to the fact that the hydrogen bond formed by the NH_3 molecule with a silanol group is stronger than the bond with the p_b-center. Therefore, the NH_3 molecule should be fixed closer to the cluster surface and interact more strongly with the unpaired electron of the p_b-center (i.e. increase its energy). Modeling confirmed these assumptions. When attached to the OH-group, the NH_3 molecule approached the p_b-center at a distance of 2.88 Å (versus 3.25 Å without the OH-group). The adsorption energy of the NH_3 molecule was already $E_{ADS} = 0.17$ eV (this value coincided in calculations for large and small clusters). The HOMO energy for a small cluster rises by 0.64 eV (to $E_{HOMO} = -4.65$ eV) and by 0.61 eV (to $E_{HOMO} = -4.61$ eV) for a large cluster. It can be expected that in larger silicon nanocrystallites, E_{HOMO} will increase more significantly and correspond to shallow donor states.

Due to the relatively low concentration of paramagnetic p_b-centers in PS and other silicon structures, the mechanism of the effect of ammonia on conductivity described above is not the main one. But it can play a significant role at low NH_3 pressures and in the absence of water vapor.

3. THE MODEL OF PASSIVATION OF IMPURITY BORON ATOMS BY NH_4^+ IONS (2)

The second model of changes in the conductivity of silicon in an ammonia atmosphere is applicable only for *p*-type structures and is based on the results of our previous work [18]. It describes the passivation of subsurface impurity boron atoms by NH_4^+ ions, which are formed after protonation of an ammonia molecule. According to this model, protonation occurs upon the simultaneous transition of two protons: from the surface silane group to the H_2O molecule and from H_2O to NH_3 (the corresponding transitions are shown by green arrows in Fig. 2a). Such a proton transition leads to the formation of a positively charged NH_4^+ ion and a negatively charged p_b-center. But the subsequent transition of the electron from the p_b-center to the distant boron atom (that is, its long-range passivation) is energetically favorable [17]. This is evidenced by a change in the localization and energy of the lowest unoccupied molecular orbital (LUMO). Before protonation, the LUMO (like HOMO filled with a single electron) was localized near the boron atom (Fig. 2a). The LUMO energy was about -5.06 eV, that is, it corresponded to the acceptor level located near the top of the valence band. After protonation (Fig. 2b), the LUMO is already localized near the neutral (paramagnetic) p_b-center, and its energy rises by ~ 1 eV to $E_{LUMO} = -4.14$ eV, i.e. the acceptor properties of LUMO are completely lost. The HOMO, already filled with two electrons, does not change its localization near the boron atom, and the corresponding energy level rises somewhat. Note that the energy level of the unpaired electron at the p_b-center is lower than HOMO. Thus, in this case, long-range passivation of the acceptor impurity occurs not by the dis-

tant p_b-center, but by the NH_4^+ ion. This passivation is manifested in the fact that a passivated boron atom cannot generate a free hole (its negative charge is compensated not by a free hole, but by the NH_4^+ ion).
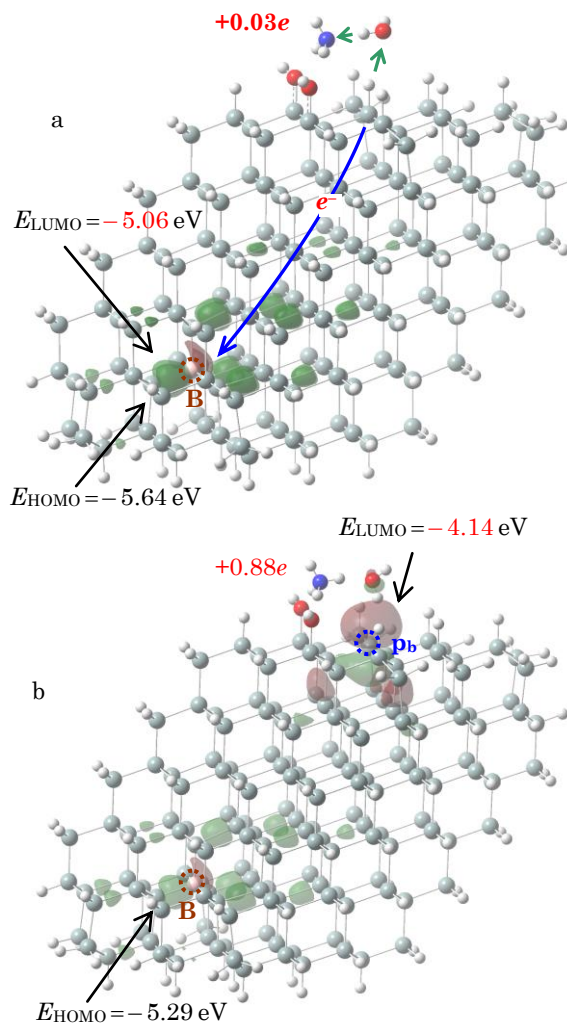
Fig. 2 – Model cluster $Si_{173}BH_{116}(OH)_2$ with adsorbed NH_3 and H_2O molecules a) before protonation, b) after protonation. The figure also shows the localization and energy of the HOMO and LUMO and the Mulliken charge of the NH_3 and NH_4^+ molecules

The described model can explain the reversibility of the change in the conductivity of *p*-type silicon structures at low ammonia pressures. When *p*-Si is removed from the atmosphere of wet ammonia, deprotonation of the NH_4^+ ion (which requires an energy of $E_{PROT} = 0.01$ eV) and subsequent desorption of the neutral NH_3 molecule ($E_{DESORB} = 0.21$ eV) can occur. These processes are accompanied by the depassivation of boron impurities, therefore, the restoration (growth) of conductivity. The desorption of a positively charged NH_4^+ ion from a cluster with a negatively charged boron atom is very unlikely, since $E_{DESORB} = 3.67$ eV. After protonation-deprotonation processes, the formed p_b-centers disappear and no changes remain on the silicon surface; therefore, a decrease in the conductivity in the atmosphere of wet ammonia is reversible.

Summing up, we can say that model (2) explains the reversible change in the conductivity of *p*-type silicon structures in an ammonia atmosphere and the important role of water molecules and surface OH-groups in this process. But it is also not the main one, since the concentration of non-passivated boron impurity atoms (or free holes) in *p*-PS is only ~ 10 % of the total acceptor impurity concentration [8, 10]. Moreover, the proposed model explains only the initial decrease in the concentration of free holes, and does not explain the increase in the concentration of free electrons at higher ammonia pressures.

4. THE MODEL OF THE INTERACTION OF AMMONIA MOLECULES WITH p_b-CENTERS THAT PASSIVATE BORON ATOMS (3)

As already noted, in *p*-PS, the concentration of free holes (or non-passivated boron atoms) and paramagnetic p_b-centers is tens of times lower than the initial concentration of the acceptor impurity. So, most boron atoms are in a passivated state (they are passivated by distant p_b-centers) [17]. Therefore, it seems logical that the interaction of NH_3 molecules with B–p_b-center pairs should be the main factor in the formation of free electrons in *p*-PS. But the adsorption of an ammonia molecule over the p_b-center, near which there is a boron atom, does not lead to the formation of a donor state [6, 14]. In this case, the NH_3 molecule with its lone electron pair forms a fairly strong bond with the positively charged p_b-center, which, on the contrary, leads to a decrease in the HOMO energy [6]. Therefore, we hypothesized that protonation of NH_3 molecules (model 2) can transform positively charged p_b-centers (passivating boron atoms) into the paramagnetic (uncharged) state. Then adsorption on such p_b-centers of other NH_3 molecules can create donor complexes (model 1). So, the third model under consideration is a combination of the first two. The task of modeling was to establish the fundamental possibility of the described processes and their conditions.

In the simulation, we used the $Si_{173}BH_{114}(OH)_3$ cluster described above. On the upper face of the cluster, protonation of the ammonia molecule could occur according to the model 2, and on the lower face there was a p_b-center (p_b-1), which passivates the boron atom inside the cluster, Fig. 3. In the configuration with the unprotonated NH_3 molecule (Fig. 3a), the p_b-1 center transferred its unpaired electron to the boron atom and charged positively ($Q_{Pb} = + 0.27e$). After passivation, the HOMO (filled with two electrons) is localized near the boron atom ($E_{HOMO} = -5.42$ eV). The LUMO is localized near the p_b-1 center and has an energy $E_{LUMO} = -4.68$ eV, i.e. the corresponding center does not exhibit acceptor properties. Note that the configuration described above with a passivated boron atom corresponds to the singlet state of the cluster (with zero total spin). The triplet state (with a total spin equal to unity), when unpaired electrons are localized on p_b-1 and the boron atom, has 0.17 eV higher energy than the singlet state, therefore it is not realized.

The cluster with an ammonia molecule after protonation is shown in Fig. 3b. Protonation occurs according
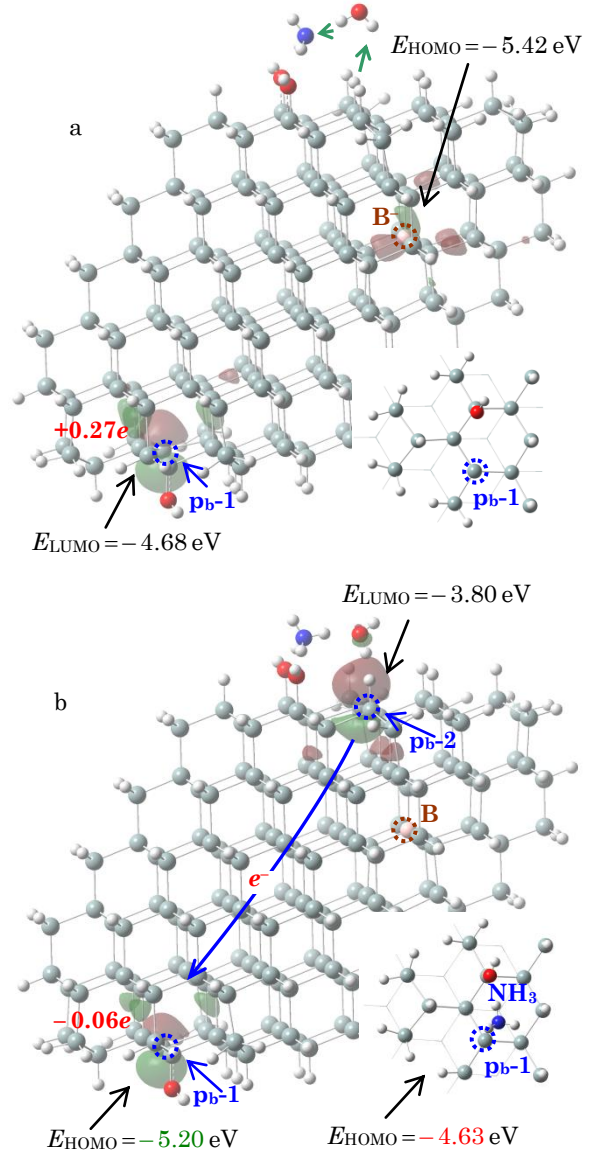
Fig. 3 – Model cluster $Si_{173}BH_{114}(OH)_3$ with adsorbed NH_3 and H_2O molecules a) before protonation, b) after protonation. The insets show fragments of the lower face of the cluster with the OH-group and the p_b-center (p_b-1) before (a) and after (b) the adsorption of the second NH_3 molecule. The figure also shows the localization and energy of the HOMO and LUMO and the Mulliken charge of the p_b-1 center

to the scheme described above: protons simultaneously pass from the hydrogen atom of the surface ≡Si–H group to the H_2O molecule and from H_2O to NH_3. In this case, a positively charged NH_4^+ ion and a negatively charged p_b-center (p_b-2) are formed. But the subsequent transition of the electron from the newly formed p_b-2 to p_b-1 is energetically favorable. This corresponds to the transition of the cluster to the triplet state, which has 0.65 eV lower energy than the singlet state. In this case, the boron atom remains in the passivated state, but it is already passivated by the NH_4^+ ion. Thus, protonation with the subsequent transition of an electron leads to the restoration of the paramagnetic state of the p_b-1 center, near which the HOMO is already localized.

The HOMO energy in this case rises by 0.22 eV to the value of $E_{HOMO} = -5.20$ eV.

Modeling showed that for the energetically favorable processes of protonation and the transition of the cluster to the triplet state, it is necessary that the distance between the boron atom and the p_b-1 center be greater than the distance between the boron atom and the NH_3 molecule (the probability of protonation increases with decreasing this distance). The role of water molecules and OH-groups in protonation is as important as in the model 2 described above.

After the transition of the p_b-1 center to the paramagnetic state, the adsorption of the NH_3 molecule on this center (or on the nearest OH-group, inset in Fig. 3b) leads to the appearance of a donor state (model 1). Calculations showed that in the model cluster, the HOMO level rises by 0.57 eV to the value of $E_{HOMO} = -4.63$ eV. For a larger cluster, this level should rise even more significantly, therefore, acquire donor properties. The binding energy of the NH_3 molecule with the OH-group near the p_b-1 center is 0.18 eV, i.e. the adsorption process is reversible. Thus, the transition of charged p_b-centers passivating boron atoms to the paramagnetic state and further adsorption of other NH_3 molecules on them can be the main mechanism for the reversible increase in the electron concentration in p-PS.

## 5. THE MODEL OF REACTIVATION OF SURFACE IMPURITY PHOSPHORUS ATOMS BY NH_4^+ IONS IN n-PS (4)

As already noted [10, 11], in n-type PS samples, the concentration of free electrons monotonically increases with increasing vapor pressure of wet ammonia. Drained ammonia vapors have little effect on the electron concentration in n-PS. Model 1 of the appearance of donor states in the interaction of NH_3 molecules with p_b-centers is universal (it does not depend on the type of doping). But due to the relatively low concentration of p_b-centers in n-PS, this model can describe only a slight increase in the concentration of free electrons under the influence of dry ammonia vapors. Model 2 of the passivation of subsurface phosphorus atoms by NH_4^+ ions cannot explain the increase in the concentration of free electrons in n-PS. This process can only lead to a decrease in the electron concentration, and, as shown by quantum chemical modeling, is energetically disadvantageous. The interaction of NH_3 molecules with a passivated pair P–p_b-center (according to model 3) is also not suitable for the case of n-type PS. DFT modeling showed that the processes of the ammonia molecule protonation and the transition of the cluster to the triplet state (depassivation of the subsurface impurity of phosphorus) are significantly energetically disadvantageous (require energies of the order of 0.85 eV). Therefore, a need arose for a new explanation of the mechanism of origin (or reduction) of donor centers in n-PS under the influence of ammonia molecules and in the interaction with water molecules.

We hypothesized that, unlike p-PS, in n-type PS a significant number of impurity phosphorus atoms are in the surface layer. This is due to the need for photo-generation of free holes in the n-PS surface layer during etching. Surface phosphorus atoms (to which the etching process has reached), absorbing free holes, block the etching of silicon in the nearest region. Therefore, such phosphorus atoms are not etched and must remain on the surface of p-PS. They lose their donor properties because they are passivated by two hydrogen atoms (and have bonds with five neighboring atoms). It is the interaction of NH_3 molecules with surface phosphorus atoms that was considered in quantum-chemical modeling.

The simulation was carried out on the basis of the already described $Si_{173}PH_{117}(OH)$ cluster with a surface phosphorus atom and a nearby OH-surface group (a fragment of this cluster is shown in Fig. 4). The HOMO level of the model cluster without adsorbed water and ammonia molecules is located at a depth of -5.16 eV, i.e. significantly lower than the middle of the silicon band gap. This means that the phosphorus atom, passivated by two hydrogen atoms, does not have donor properties. The HOMO level rises somewhat with increasing size of the model cluster. Adsorption of NH_3 and H_2O molecules also slightly increases the indicated level: before protonation of the NH_3 molecule, the E_{HOMO} value was -5.01 eV (Fig. 4a).
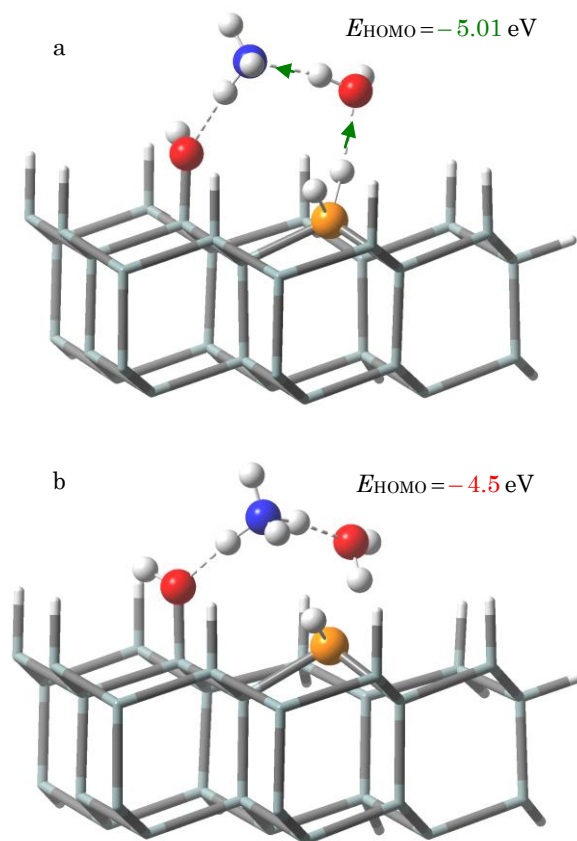
Fig. 4 – A fragment of a model cluster $Si_{173}PH_{117}(OH)$ with an ammonia and water molecule: a) before protonation of NH_3, b) after the formation of the NH_4^+ ion. The green arrows in the figure indicate the direction of transition of the protons

The protonation of the NH_3 molecule occurs by simultaneous proton transfer from the hydrogen atom to the H_2O molecule and from H_2O to NH_3 (the corresponding transitions are shown in green arrows in Fig. 4a). This process is energetically favorable: the

energy of the unprotonated system (Fig. 4a) is 0.09 eV higher than that of the system with the NH_4^+ ion (shown in Fig. 4b). Protonation without the participation of water molecules and surface OH-groups is energetically disadvantageous. After protonation, the phosphorus atom remains bound to only four neighboring atoms, therefore it must restore its donor properties. Modeling showed that protonation leads to a significant (~ 0.5 eV) increase in the HOMO level. Depending on the configuration of the adsorption system (the number of surface OH-groups and adsorbed water molecules), the HOMO level can rise to a depth of $E_{HOMO} = -4.5$ eV. With an increase in the size of the model cluster, the HOMO level can turn out to be significantly higher than the middle of the silicon band gap, i.e. the phosphorus atom can restore its donor properties. Due to the high concentration of surface passivated phosphorus atoms in n-PS, their depassivation by NH_4^+ ions can be the main mechanism for increasing the concentration of free electrons in wet ammonia vapors.

6. CONCLUSIONS

DFT calculations showed that four mechanisms of interaction of NH_3 molecules with the PS surface are possible, which lead to an increase in the concentration of free electrons or a decrease in the concentration of free holes.

The first model involves the interaction of an NH_3 molecule with a surface paramagnetic p_b-center. Adsorption of the NH_3 molecule at such a center leads to an increase in the HOMO level to a value of -4.84 eV. Adsorption of NH_3 on the OH-group near the p_b-center leads to an even more significant increase in HOMO, to -4.61 eV. An increase in the size of the model cluster also leads to an increase in the HOMO energy. Thus, in PS nanocrystallites with a diameter of more than 40 Å, adsorption of ammonia molecules near p_b-centers can lead to the appearance of donor states and the generation of free electrons. The described mechanism is not the main one, since the concentration of paramagnetic p_b-centers is relatively small.

The second model provides for long-range passivation of boron impurities by NH_4^+ ions, which occurs after protonation of ammonia molecules. After the for-

mation of the NH_4^+ ion, the acceptor level of the boron atom (-5.06 eV) rises to -4.14 eV, that is, it loses the acceptor properties. But this process is also not critical in changing the conductivity of p-Si. Firstly, the concentration of non-passivated boron atoms in p-PS is low, and secondly, the model explains only the initial decrease in the concentration of free holes and does not explain the increase in the concentration of free electrons at high ammonia pressures.

The third model involves the interaction of NH_3 molecules with B–p_b-center pairs. The protonation of ammonia molecules near such pairs transfers positively charged p_b-centers (passivating boron atoms) to the paramagnetic (uncharged) state. Subsequent adsorption on such p_b-centers of other NH_3 molecules creates donor states (the HOMO level raises to -4.63 eV). Since p-PS contains tens of times more B–p_b-center pairs than non-passivated boron atoms and paramagnetic p_b-centers, the third model can describe the main mechanism of the formation of free electrons, although processes according to the first two models can occur in parallel.

The fourth model is applicable to n-PS and describes the restoration of donor properties of surface phosphorus atoms passivated by two hydrogen atoms. The HOMO level of such atoms is at a depth of -5.16 eV, so it does not have donor properties. During protonation of the NH_3 molecule, a proton (surface ion of a hydrogen atom) detaches from the phosphorus atom. This leads to an increase in the HOMO level to a value of -4.5 eV, i.e. to a restoration of the donor properties of the phosphorus impurity. Since the concentration of passivated phosphorus atoms is high, model 4 may be the main one for n-PS.

The last three models include the protonation of NH_3 molecules with the necessary participation of water molecules, an important role of which in the change in PS conductivity was noted in most experimental studies. Water molecules serve as a "transfer link" for proton transfer, due to the large dipole moment they shield the electric field of the NH_4^+ ion and create energetically favorable hydrogen bonds with it. DFT modeling also demonstrated the role of impurity atoms as catalysts for the protonation of ammonia molecules and changes in the conductivity of PS.

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Механізми зміни провідності поруватого кремнію в атмосфері аміаку – DFT моделювання

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На основі квантовохімічних розрахунків методом теорії функціоналу густини (DFT) розглянуті чотири можливі механізми впливу парів аміаку на провідність кремнієвих наноструктур, зокрема, поруватого кремнію (PS). Перший механізм передбачає виникнення донорних станів при взаємодії молекул NH_3 з p_b-центрами (поверхневими атомами Si з обірваними зв'язками). Зміна провідності по другому і третьому механізмам може відбуватися в кремнієвих структурах p-типу. Другий механізм передбачає протонування молекули аміаку з наступною пасивацією підповерхневих домішкових атомів бору іонами NH_4^+. Третій механізм поєднує перші два. На першому етапі відбувається взаємодія молекул NH_3 з пасивованими парами B–p_b-центр. Після протонування молекули NH_3, домішку бора пасивує вже іон NH_4^+, а парамагнітний стан p_b-центра відновлюється. На другому етапі відбувається утворення донорних станів при взаємодії молекул NH_3 вже з парамагнітними p_b-центрами. Процеси за четвертим механізмом можуть відбуватися в кремнієвих структурах n-типу. Цей механізм передбачає відновлення донорних властивостей поверхневих атомів фосфору, пасивованих двома атомами водню. Таке відновлення відбувається після протонування молекули NH_3, при відриві від атома фосфору протона (іона поверхневого атома водню). Останні три моделі включають в себе процес протонування молекул NH_3, в якому важливу роль відіграють молекули води і поверхневі OH-групи, важлива роль яких зафіксована в більшості експериментальних робіт.

Ключові слова: Поруватий кремній, Аміак, Провідність, p_b-центри.