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DFT-modeling of Ammonia Molecules Protonation on a p-type Silicon Surface

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In this work, DFT modeling was carried out in order to establish the conditions necessary for the protonation of ammonia molecules on the silicon surface. Simulations have shown that for an energetically favorable protonation, three conditions are necessary: the fixing of NH_3 molecules on at least two OH-groups, the participation of one water molecule, and the presence of a distant boron atom. In this case, the protonation energy (decrease in the cluster energy after protonation) is $E_{prot} = 0.01$ eV. Protonation occurs with the simultaneous transition of two protons: one from the surface silane group to the H_2O molecule and the other from H_2O to NH_3. Such a transition leads to the formation of a positively charged NH_4^+ ion and a negatively charged p_b-center (Si atom with a dangling bond). After that, the electron is transferred from the p_b-center to the distant boron atom, and passivates it. Such passivation of acceptors by NH_4^+ ions can lead to a decrease in the concentration of free holes (and a decrease in conductivity) in *p*-type silicon. The proposed model of NH_3 molecules protonation can also explain the processes of surface-assisted laser desorption/ionization (SALDI) of amino compounds. Free holes formed by laser radiation can recombine with electrons localized on passivated boron atoms, i.e., remove their negative charge. After this, the desorption energy of NH_4^+ decreases from 3.67 to 1.05 eV, which is close to the experimental values for amino ions. The simulation also showed that the absence of a distant boron atom significantly reduces the protonation efficiency, $E_{prot} = -0.50$ eV, since the negative charge is localized not at the distant boron atom, but at the p_b-center located near NH_4^+. Significant Coulomb attraction between the NH_4^+ ion and the charged p_b-center leads to a substantial displacement of the silicon atom, which is energetically unfavorable. The fixation of NH_3 molecules on only one OH-group or the absence of water molecules also reduces the protonation probability: the value of E_{prot} in these cases is – 0.37 and – 0.08 eV, respectively. This can be explained by the fact that H_2O molecules and OH-groups create energetically favorable hydrogen bonds with the NH_4^+ ion and shield its electric field.

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

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1. INTRODUCTION

The creation and study of silicon structures as ammonia sensors is an actual topic. In recent years, there have been published experimental and theoretical works on the effect of ammonia on the conductivity of porous silicon (PS) [1-2], silicon nanowires (SiNW) [3], silicon with microstructured [4] and oxidized surface [5-7]. In all the works devoted to this issue, it is mentioned that the resistance of *p*-type silicon structures increases in the NH_3 atmosphere. At the same time, in the majority of works it is directly indicated that a change in the *p*-Si resistance occurs only in the presence of water vapor [8, 9]. Many authors tried to explain the mechanism of PS and SiNW conductivity changes in the ammonia atmosphere and the role of water molecules in this process, but the proposed explanations were imperfect (a detailed review of experimental data and theoretical models of conductivity change can be found in [7]). In [6, 7], we attempted to explain the above phenomena for silicon structures with a substantially oxidized and hydroxylated surface. It was shown that a change in the conductivity of oxidized silicon can be associated with the protonation of the NH_3 molecule in the presence of several water molecules. The proposed hypothesis also made it possible to explain the mechanism of the SALDI process for ammonia and molecules with terminal amino groups, which also occurs only with the participation of H_2O molecules and surface OH-groups [10, 11]. But the explanation of the NH_3 protonation mechanism proposed in [6, 7] had certain disadvantages. In [6, 7], NH_3 protonation was simulated only on the fully oxidized and hydroxylated silicon surface, it could occur only with simultaneous migration of three protons and was energetically favorable only with the participation of five H_2O molecules. In addition, the mechanism for changing the silicon conductivity after NH_3 protonation in [7] was explained not too thoroughly. So, at present, the mentioned issues are not fully elucidated in the literature [9]. In [12, 13], it was shown that there is a long-range passivation of impurity boron atoms by surface p_b-centers. This allowed us to re-explain the process of ammonia molecules protonation and changes in the conductivity of *p*-type silicon structures in an NH_3 atmosphere.

2. RESULTS OF CALCULATIONS AND DISCUSSION

A large rhombic cluster $Si_{174}H_{118}$ with a hydrogenated surface was chosen as the basis for the simulation, Fig. 1. The faces of the cluster were crystallographic planes (111), which are the most stable and common in PS crystallites [14]. Large cluster sizes (with the largest diagonal of ~ 28 Å) made it possible to simulate the interaction between NH_3 and H_2O molecules and p_b-centers located on the upper cluster face with an impurity boron atom distant by ~ 20 Å. Some hydrogen atoms of the upper face could be replaced by OH-groups,

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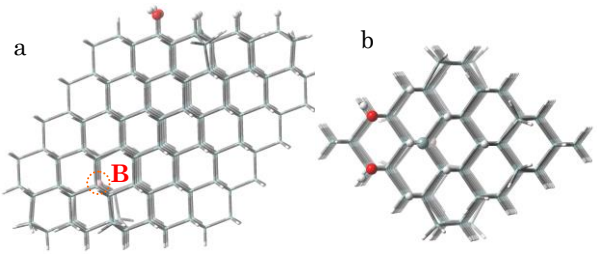

Fig. 1 – Model cluster $Si_{173}BH_{116}(OH)_2$ with a boron atom and two OH-groups on the upper face: side view (a), top view (b)

a high concentration of which on the PS surface was recorded, for example, in [15].

The calculations were carried out in Gaussian 09 package [11] in a cluster approximation by DFT-method with the exchange-correlation functional B3LYP. For surface hydrogen atoms, OH-groups, adsorbed NH_3, H_2O molecules, Si atoms with dangling bonds (p_b-centers) and boron atoms inside the cluster, a basis 6-311++g (d, p) with diffuse functions was chosen to simulate long-range interaction and adsorption. To save computer time, other atoms (shown in Fig. 1 with sticks) were modeled in the 6-31g (d, p) basis. The selected basis set and the calculation method showed good agreement with the experiment for the geometric parameters of the cluster and the adsorbed molecules. For example, the average value of interatomic distances in a model silicon cluster was 0.237 nm and almost coincided with the known experimental value of 0.235 nm.

The task of modeling was to ascertain the conditions for the energetically favorable protonation of the NH_3 molecule. In contrast to [6, 7], the source of the proton in this model was a hydrogen atom, which did not belong to the distant silanol group, but to the nearest silane group. Simulations have shown that for efficient protonation, the fixation of the ammonia molecule on at least two OH-groups, the participation of one water molecule and the presence of a distant boron atom are necessary. Fig. 2 shows a cluster with an NH_3 molecule before protonation (a) and after protonation (b). The energy of a cluster with an unprotonated NH_3 molecule was ~ 0.01 eV higher than with an NH_4^+ ion (i.e., protonation is energetically favorable). Protonation occurs with 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 in Fig. 2a with blue arrows). Such a transition leads to the formation of a positively charged NH_4^+ ion and a negatively charged p_b-center. But the transition of an electron from a p_b-center to a distant boron atom (that is, its passivation) is energetically favorable. This is evidenced by a change in the localization and energy of the lowest unoccupied molecular orbitals (LUMOs). Before protonation, the LUMO (like the highest occupied orbital HOMO) was localized near the boron atom (Fig. 2a). The LUMO energy was about – 5.06 eV, that is, it corresponded to the acceptor level near the valence band top. After protonation, the LUMO is already localized near the neutral p_b-center, and its energy rises by ~ 1 eV to the value $E_{LUMO} = -4.09$ eV, that is, the acceptor properties of LUMO are lost. The HOMO does not change its localization near the boron atom, the corresponding energy level also rises somewhat, and two electrons are located on it. The energy level of an electron localized at the p_b-center is lower than HOMO. Consequently, in this case, long-range passivation of the acceptor impurities occurs not by the distant p_b-center, but by the NH_4^+ ion. This passivation is manifested in the fact that the passivated boron atom no longer generates a free hole (its negative charge is compensated not by a free hole but by the NH_4^+ ion).

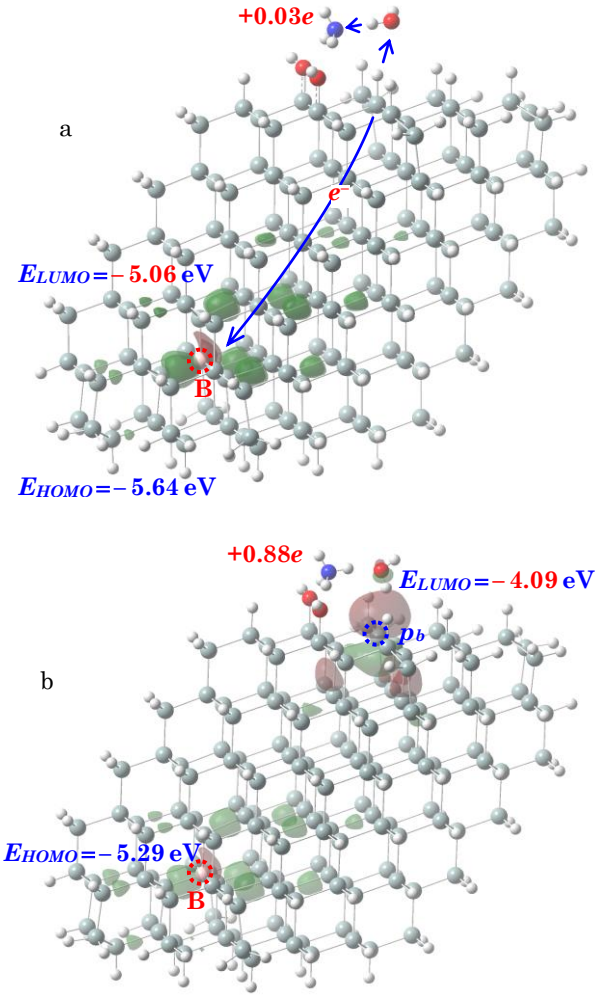

Fig. 2 – Model cluster $Si_{173}BH_{116}(OH)_2$ with adsorbed NH_3 and H_2O molecules: before protonation (a), after protonation (b). The figure also shows the form and energies of the molecular orbitals of HOMO and LUMO and the Mulliken charge on the NH_3 and NH_4^+

Long-range passivation of impurity boron atoms may be responsible for a reversible change in the conductivity of p-type silicon structures. After protonation of the adsorbed NH_3 molecules and passivation of the impurity, the conductivity of these structures decreases. It was established experimentally that after p-PS is removed from the atmosphere of humid ammonia, its conductivity is restored [8, 9]. This can be explained by the processes of deprotonation of the NH_4^+ ion and desorption of the neutral NH_3 molecule, which is accompanied by depassivation of boron and the restoration of conductivity. The neutral NH_3 molecule can be easily desorbed, the calculated energy of its desorption is ~ 0.17 eV. Desorption of

NH_4^+ ions is very unlikely, since the energy required for the separation of NH_4^+ from a cluster with a negatively charged boron atom is ~ 3.67 eV. Therefore, after protonation-deprotonation processes, the formed p_b-centers disappear and no changes remain on the silicon surface, hence the decrease in conductivity is reversible.

Another, irreversible process of ammonium ions desorption is possible. In the SALDI process, a significant amount of non-equilibrium charge carriers is formed by laser radiation near the silicon surface. The resulting free holes can recombine with electrons localized on boron atoms, that is, remove their negative charge. After this, the desorption energy of NH_4^+ ions decreases from 3.67 to 1.05 eV, which is close to the experimentally obtained values of the laser desorption energy for amino ions [10, 11]. In [10], in addition to the need for SALDI surface OH-groups and water molecules, a significant amount of surface dangling bonds after SALDI is also indicated. This also indirectly confirms the proposed NH_3 protonation model.

Fig. 3 illustrates the effect of various factors (the presence of distant boron atoms, OH-groups, and H_2O molecules) on the probability of ammonia molecule protonation. The figure shows fragments of a model cluster with the NH_4^+ ion (after NH_3 protonation) and shows the values of the protonation energy E_{prot} (the difference between the cluster energies in the unprotonated and protonated states). All the simulated cases can be compared with the configuration considered above (two OH-groups, one H_2O molecule and a distant boron atom), Fig. 3a. The absence of a distant boron atom (Fig. 3b) makes protonation in such a configuration essentially energetically unfavorable ($E_{prot} = -0.50$ eV). In this case, the negative charge is localized not at the distant boron atom, but at the p_b-center located close to NH_4^+. A significant Coulomb attraction between the NH_4^+ ion and the charged p_b-center leads to a deformation of the crystal lattice and a significant displacement of the silicon atom, which is energetically unfavorable. Therefore, the presence of a distant boron atom is crucial for the ammonia protonation process. Therefore, the other considered configurations of model clusters included such a boron atom.

The configurations shown in Fig. 3c and Fig. 3d differ from Fig. 3a by the different number of water molecules adsorbed near NH_4^+. Without a water molecule (Fig. 3c), protonation becomes energetically unfavorable ($E_{prot} = -0.08$ eV), and the presence of two H_2O molecules (Fig. 3d) makes protonation even more energetically favorable ($E_{prot} = 0.07$ eV). Therefore, the presence of water molecules is also a significant factor for the efficient ammonia protonation. They serve as a "transfer link" for the proton, due to the large dipole moment they shield the electric field of the NH_4^+ ion and create energy-efficient hydrogen bonds with it.

Fig. 3e and Fig. 3f show the cases of fixation of NH_4^+ ions on one OH-group and generally without OH-groups. It can be seen that in these cases the probability of protonation decreases again, the corresponding protonation energies are – 0.37 eV and – 0.74 eV. In the absence of water molecules and without fixation on the OH-groups, stable states with the NH_4^+ ion are not formed at all. So, the importance of OH-groups is manifested in the fact that they fix the NH_4^+ ion with energetically favorable hydrogen bonds and somewhat shield its electric field.

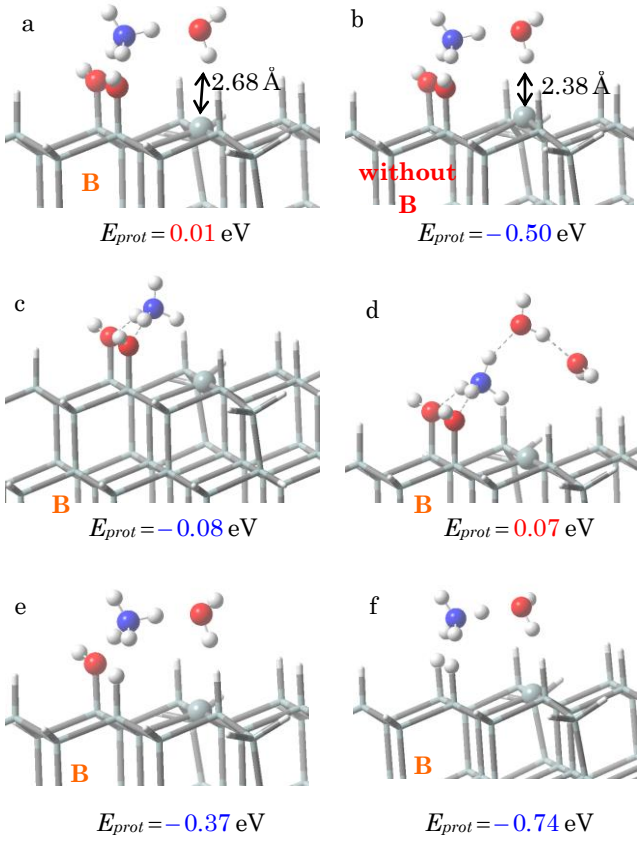

Fig. 3 – Fragments of model clusters with a protonated ammonia molecule and different amounts of surface OH-groups, H_2O molecules and a boron atom present (a, c, d, e, f) or absent (b). The figure also shows protonation energies in appropriate cases (positive values of E_{prot} indicate that protonation is energetically favorable)

Preliminary calculations have shown that the protonation of ammonia molecules in the presence of an already existing passivated pair of p_b-center/boron atom is also energetically beneficial. Subsequent studies will be devoted to modeling such processes.

3. CONCLUSIONS

DFT modeling showed that protonation of ammonia molecules can occur spontaneously on the silicon surface. In order for protonation to be energetically favorable, the following conditions are necessary: fixing of NH_3 molecules on at least two OH-groups, participation of one water molecule, and the presence of a distant boron atom. After protonation of the ammonia molecule, the boron atom goes into a passivated state (its acceptor properties are lost). This process may explain the reduction in p-PS conductivity in a humid ammonia atmosphere. The proposed model of NH_3 protonation can also explain the processes of laser desorption/ionization for amino compounds. Free holes formed by laser radiation recombine with an electron localized on a boron atom. After this, the desorption energy of NH_4^+ decreases significantly (from 3.67 to 1.05 eV). The water molecules involved in protonation serve as the "transfer link" for the proton;

due to the large dipole moment, they shield the electric field of the NH_4^+ ion and create energetically favorable hydrogen bonds with it. The importance of OH groups during protonation is manifested in the fact that they fix the NH_4^+ ion with energetically favorable hydrogen bonds and somewhat shield its electric field.

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DFT-моделювання протонування молекул аміаку на поверхні кремнію p-типу

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У роботі проводилося DFT-моделювання з метою встановлення умов, необхідних для протонування молекул аміаку на поверхні кремнію. Моделювання показало, що для того, щоб протонування було енергетично вигідним, необхідно виконання трьох умов: закріплення молекул NH_3 хоча б на двох OH-групах, участь одної молекули води та наявність віддаленого атома бору. В цьому випадку енергія протонування (різниця між енергіями модельного кластера в непротонованому і протонованому станах) $E_{prot} = 0{,}01$ еВ. Протонування відбувається при одночасному переході двох протонів: від поверхневої силанової групи до молекули H_2O та від H_2O до NH_3. Такий перехід веде до утворення позитивно зарядженого іона NH_4^+ та негативно зарядженого p_b-центра. Після цього відбувається перехід електрона від p_b-центра до віддаленого атому бору, тобто його пасивація. Саме пасивація акцепторної домішки іонами NH_4^+ може призводити до зниження концентрації вільних дірок та провідності кремнієвих структур p-типу. Запропонована модель протонування молекул NH_3 також може пояснити процеси поверхнево стимульованої лазерній десорбції-іонізації (SALDI). Вільні дірки, утворені під дією лазерного випромінювання, можуть рекомбінувати з електроном, локалізованим на атомі бору, тобто знімати його негативний заряд. Після цього енергія десорбції NH_4^+ знижується від 3,75 до 1,05 еВ, що є близьким до експериментально отриманих значень енергій лазерної десорбції іонів аміносполук. Моделювання також показало, що відсутність віддаленого атома бору суттєво знижує ефективність протонування, $E_{prot} = -0{,}50$ еВ, оскільки негативний заряд зосереджується не на віддаленому атомі бору, а на p_b-центрі, розміщеному поруч з NH_4^+. Значне кулонівське притягання між іоном NH_4^+ та зарядженим p_b-центром веде до суттєвого зміщення атома кремнію, що є енергетично невигідним. Закріплення молекул NH_3 лише на одній OH-групі та відсутність проміжної молекули води також роблять протонування малоймовірним: значення E_{prot} в цих випадках становлять $-0{,}37$ і $-0{,}08$ еВ, відповідно. Це можна пояснити тим, що молекули H_2O і OH-групи створюють енергетично вигідні водневі зв'язки з іоном NH_4^+ та екранують його електричне поле.

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