

## Energy Parameters of the Simplest Chemical Reactions Occurring at the First Stages of Silicon Electrochemical Etching – DFT-Modeling

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Based on quantum chemical calculations, the reactions of removal of surface hydrogen atoms, which occur at the first stages of silicon etching in HF solutions under the action of various fluoride ionic complexes, are studied. To do this, a method has been developed for reliable estimation of the energy parameters of chemical reactions with a changing charge state of a cluster that occur on the surface of bulk silicon based on the results of calculations performed on clusters of finite sizes. It is shown that in aqueous HF solutions the reactions of removal of surface hydrogen atoms can occur both with current flowing through the silicon/electrolyte system and without it. The reactions of removing the hydrogen coating of the silicon surface occur only under the influence of "light" ionic fluoride complexes containing no more than one HF molecule. Based on simulations, the reasons for the slowdown in purely chemical etching of silicon in high concentration HF are explained.

**Keywords:** Porous silicon, Electrochemical etching, DFT-calculations.

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### 1. INTRODUCTION

Porous silicon (PS) is a promising material and is widely used in energy storage and conversion systems, sensors, medicine, etc. [12]. Although the properties of PS have been widely studied, the microscopic mechanism of its electrochemical etching has not been sufficiently studied [3-6]. The literature mentions many macroscopic models describing different stages of pore formation in silicon, but these models have limited predictive ability [5, 6]. At present, only paper [7] presents the results of quantum-chemical studies of the process of electrochemical etching of silicon in aqueous solutions of hydrofluoric acid. The simulation performed in [7] made it possible to explain a number of characteristic features and features of PS etching. Among them is an explanation of the mechanism of transition between different regimes of silicon etching, the dependence of the electrochemical etching rate and pore size in PS on the HF concentration in the electrolyte, and the difficulty of electrochemical etching of silicon on (111) faces and near impurity boron atoms. At the same time, certain comments arose on the results of the calculations presented in [7]. The main remark to this work is that the authors provide only a qualitative estimate of the energy yields of chemical reactions that occur during PS etching. For most cases, the results of DFT modeling were presented, indicating only the fundamental possibility or low probability of certain reactions occurring. This shortcoming stems from the properties of the cluster method of quantum chemical calculations used in [7]. When using this method, the calculated energy yield of reactions occurring with a change in the cluster charge (including reactions involving electrolyte ions) depends on the size of the model clusters. In this work, which is a logical continuation of [7], we proposed a technique that allows us to get rid of this shortcoming. Using this technique, reliable quantitative estimates of the energy yields of several simplest chemical reactions occurring at the first stages

of PS electrochemical etching, independent of the size of the model clusters, were obtained.

### 2. MODELING DETAILS

To determine the degree of influence of the size of the model cluster on the energy yield of the considered chemical reactions, four main types of clusters of a similar shape were used in the simulation:  $\text{Si}_{35}\text{H}_{36}$ ,  $\text{Si}_{84}\text{H}_{64}$ ,  $\text{Si}_{165}\text{H}_{100}$  (Fig. 1) and  $\text{Si}_{286}\text{H}_{144}$ . These clusters were hexahedral pyramids with the largest diagonal up to 28 Å formed by (111) faces coated with hydrogen atoms. The calculations were performed in the TeraChem 1.93P software [8] using the density functional method with the B3LYP exchange-correlation functional. Most of the Si and H atoms were modeled in a fairly wide 6 – 31  $g(d,p)$  basis set. To achieve the goals set, only chemical reactions near the corner dihydral silicon atom located at the intersection of the (111) planes (circled in blue dotted line in Fig. 1) were considered. Quantum-chemical calculations performed on clusters of a different shape showed that such a choice of the target atom does not affect the simulation results, and chemical reactions occur in the same way near other dihydral atoms of the (100) face. Therefore, for the corner Si atom, attached hydrogen atoms, ions, and electrolyte molecules, we chose the 6-311++ $g(d,p)$  basis with diffuse functions, which are important to take into account when modeling the long-range interaction. The selected basis set and calculation method showed good reproducibility of geometric parameters. For example, the average value of interatomic distances in a model silicon cluster was 0.237 nm, which practically coincided with the known experimental value of 0.235 nm. During the simulation, the energy parameters were also well reproduced. For example, according to the experimental data [9] obtained by the electron impact method, the  $\text{SiH}_3\text{-H}$  binding energy in the  $\text{SiH}_4$  silane molecule is  $94 \pm 2$  kcal/mol (4.08 eV), while our calculations gave a very close value of 4.10 eV.

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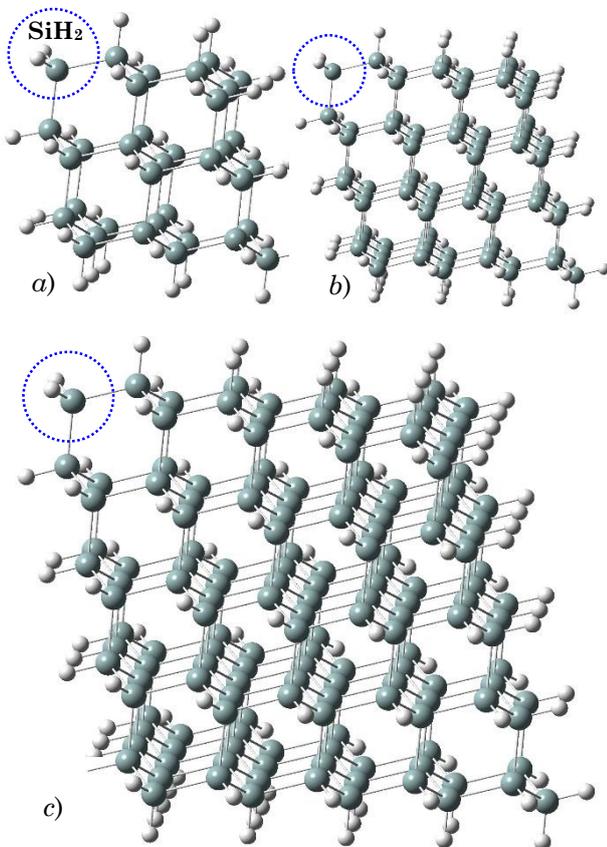
The energy yields of the reactions considered in the work were calculated by the expression

$$\Delta E = E_{reag} - E_{prod}, \quad (2.1)$$

where  $E_{reag}$  is the sum of the energies of the reactants (in the states with optimized geometry), and  $E_{prod}$  is the energy of the reaction products in the optimized state (all of these energies are negative). The binding energies of individual molecules or molecules with silicon clusters were calculated from the expression

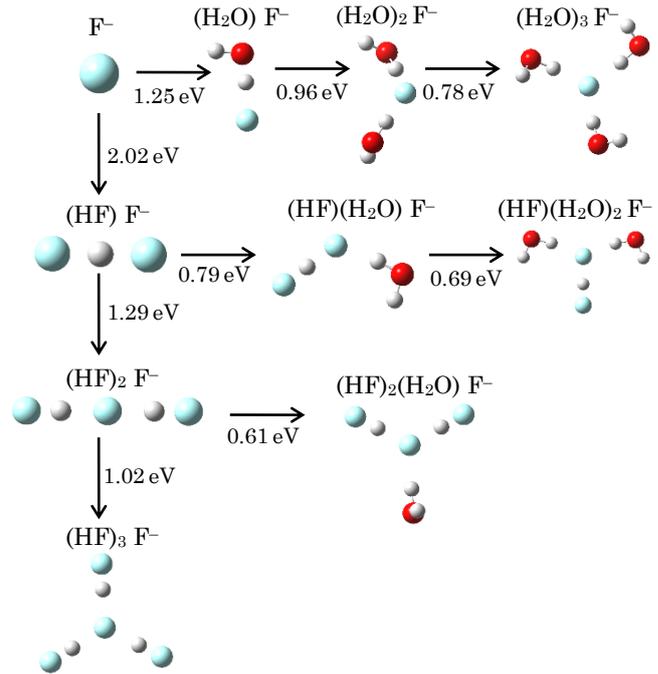
$$E_{bind} = E_{reag} - E_{reakt}, \quad (2.2)$$

where  $E_{reag}$  is the sum of the energies of non-interacting reagents (individual molecules or a molecule and a cluster), and  $E_{reakt}$  is the energy of a system with an optimized geometry after the formation of the corresponding bond.



**Fig. 1** – Model clusters  $\text{Si}_{35}\text{H}_{36}$ ,  $\text{Si}_{84}\text{H}_{64}$ ,  $\text{Si}_{165}\text{H}_{100}$ . The blue dotted line indicates the positions of the angular  $\text{SiH}_2$  groups involved in the considered chemical reactions

When modeling the electrolyte, the presence in it of a wide range of solvation complexes of  $\text{F}^-$  and  $\text{H}^+$  was taken into account. The interaction of silicon clusters with ionic complexes of fluoride with different amounts (up to three) of HF and  $\text{H}_2\text{O}$  molecules was studied, Fig. 2. For these complexes, the attachment energies of additional HF and  $\text{H}_2\text{O}$  molecules were calculated (they are indicated next to the arrows in Fig. 2). All considered ionic complexes are quite stable, and their concentration depends on the concentration of HF in the solution and its temperature [10].



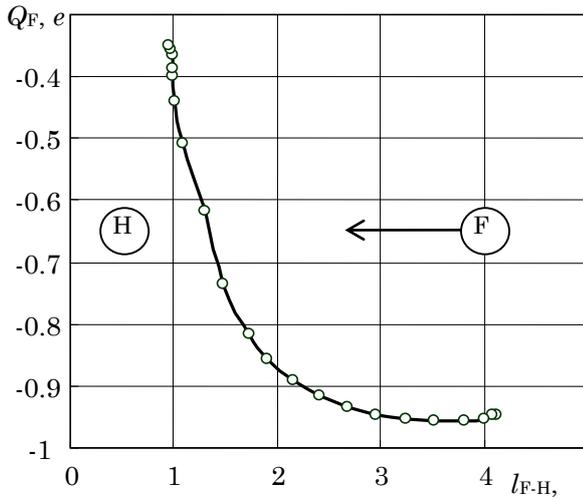
**Fig. 2** – Types of fluoride ionic complexes, which were considered in the simulation of the electrolyte. In the figure, next to the arrows, the energy values are indicated that are released after the addition of HF and  $\text{H}_2\text{O}$  molecules and the formation of new ionic complexes

### 3. REACTIONS OF THE REMOVAL OF A HYDROGEN ATOM FROM THE SILICON SURFACE IN HF SOLUTIONS

As was shown in [7], in aqueous solutions of HF, reactions of removal of surface hydrogen atoms under the action of negative ionic fluoride complexes can occur on the silicon surface. These reactions occur both during electrochemical etching of silicon (in the modes of pore formation and electropolishing) and during purely chemical etching (without current flow and without the participation of free holes). Since these reactions occur under the action of negatively charged ionic complexes of fluoride, the charge state of model clusters changes during simulation. Therefore, for the correct description of these most common and simple reactions, a method was created and tested for a reliable estimate of the energy yields of chemical reactions with a variable cluster charge. Below, a detailed description of these reactions and the results of calculating their energy yields using model clusters of different sizes will be given.

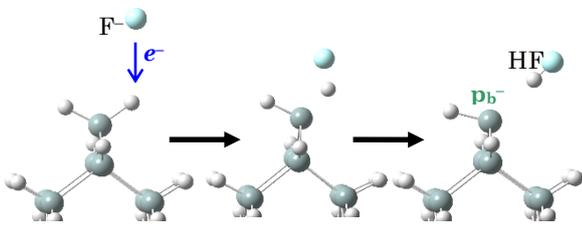
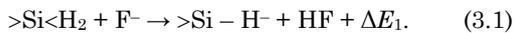
When modeling the reaction of removing a hydrogen atom under the action of the  $\text{F}^-$  ion without the participation of free holes, we considered a system consisting of a neutral cluster and an  $\text{F}^-$  ion distant by  $\sim 7 \text{ \AA}$ , i.e., the total charge of the system was equal to  $-1$  (in units of  $e$ ). When optimizing the geometry, the fluoride ion approached the cluster (under the influence of the exchange-correlation interaction), and its Mulliken charge remained close to  $-1e$ . At a distance of  $\sim 2.5 \text{ \AA}$  from the corner hydrogen atom, the negative charge of fluoride began to decrease, i.e., the  $\text{F}^-$  ion began to oxidize, Fig. 3. Gradual oxidation of the fluoride ion occurred when it approached the silicon cluster, which

was gradually charged negatively (the electron passed into the conduction band of silicon).



**Fig. 3** – The value of the Mulliken charge of the fluoride ion as it approaches the surface H atom as a function of the F–H distance

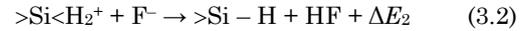
After oxidation, the neutral fluorine atom interacted with its unpaired electron with the surface hydrogen atom, attracted it, and detached it from the cluster. As a result of the reaction, a negatively charged  $p_b$ -center (silicon atom with a dangling bond) appeared on the cluster and a neutral HF molecule was formed (Fig. 4), i.e., the reaction proceeded according to the scheme



**Fig. 4** – Fragments of a model cluster illustrating the removal of a surface hydrogen atom by the  $F^-$  ion followed by the formation of an HF molecule

Modeling showed that the reaction described above was energetically favorable, but its energy yield depended on the size of the model cluster. The value of  $\Delta E_1$  was 2.11, 2.25, and 2.33 eV for the  $Si_{32}H_{40}$ ,  $Si_{84}H_{64}$ , and  $Si_{165}H_{100}$  clusters, respectively. Such a change in  $\Delta E_1$  is due to quantum effects: with an increase in the size of clusters, the level of the negatively charged  $p_b$ -center, where an electron fell after  $F^-$  oxidation, rose. An increase in  $\Delta E_1$  with an increase in the size of the model indicates that, on the surface of bulk silicon, reaction (3.1) of the removal of hydrogen atoms under the influence of the non-solvated  $F^-$  ion is also energetically favorable. Modeling also showed that such a reaction can proceed without a barrier under the action of "light" fluoride complexes containing no more than one HF molecule. "Heavy" complexes of fluoride, containing two or three HF molecules, in most cases were adsorbed near the silicon surface without oxidation.

Simulation also showed that, when free holes are injected into silicon, the reactions of removing hydrogen atoms will be more energy efficient. The energy yield of the hydrogen atom removal reaction in the interaction with the  $F^-$  ion with the participation of a free hole



increased to 6.06 and 5.66 eV for the  $Si_{32}H_{40}$  and  $Si_{84}H_{64}$  clusters, respectively. In this case, the energy yield of the reaction decreased with an increase in the model size, which is associated with an underestimation of the valence band top for small clusters.

The results presented illustrate the fact that the energy yield of all considered reactions depends on the size of the model clusters. Modeling only shows that the energy yield of reaction (3.1) increases under the influence of free holes, but the absence of reliable quantitative estimates of these changes does not allow one to explain the role of holes in the process of silicon etching. Therefore, it becomes necessary to extrapolate the energy parameters of reactions calculated for clusters of finite sizes to the corresponding values for an infinitely large cluster or bulk silicon. Below, the procedure for such extrapolation will be described and applied to the considered reactions, and the possibility of their occurrence under the influence of various ionic complexes will be analyzed.

#### 4. A METHOD FOR EVALUATION OF THE ENERGY YIELD OF CHEMICAL REACTIONS ACCOMPANIED BY A CHANGE IN THE CLUSTER CHARGE

To find the energy yields of the considered reactions on the surface of bulk silicon, we formally divided them into certain stages and calculated the energies released or absorbed at these stages. Using such a procedure, it is easier to evaluate and control the errors introduced by the assumptions and approximations used at each stage.

Let us first analyze the course of reaction (3.2), for which the application of the proposed technique requires a minimum number of approximations. According to the reaction equation, its energy yield is

$$\Delta E_2 = E(>Si<H_2^+) + E(F^-) - E(>Si<H + HF), \quad (4.1)$$

where  $E(>Si<H_2^+)$  is the energy of a positively charged cluster,  $E(F^-)$  is the energy of the  $F^-$  ion (before the reaction, the silicon cluster and the fluorine ion do not interact),  $E(>Si<H + HF)$  is the energy of a cluster with a  $p_b$ -center on which an adsorbed HF molecule (it is taken into account in (4.1) that all energies are negative). Expression (4.1) includes the energies of clusters in different charge states, which leads to the dependence of  $\Delta E_2$  on the model size. To find the value of  $\Delta E_{2bulk}$  corresponding to bulk silicon, we formally divide reaction (3.2) into five stages.

At the first stage, the fluoride ion is oxidized. To remove an electron from  $F^-$  (its transition to a vacuum level with zero energy), it is necessary to spend the oxidation energy  $E_{ox}$ . Its modulus is equal to the electron affinity  $E_a$  for the fluorine atom, and its experimental

value is 3.40 eV [11]. The DFT calculation using expression

$$-E_{oxF} = E_{eaF} = E(F^-) - E(F) < 0 \quad (4.2)$$

in the selected basis yields a close value, 3.49 eV.

The effect of free hole injection is that, in the second stage, an electron from the zero level enters an empty level in the valence band, and not into the conduction band of silicon. This process releases energy

$$-E_V = E(> Si < H_2^+) - E(> Si < H_2) > 0, \quad (4.3)$$

where  $E(> SiH_2)$  and  $E(> SiH_2^+)$  are the energies of neutral and positively charged clusters, respectively. In bulk silicon, an electron passes to the top of the valence band with exactly known energy

$$-E_{Vbulk} = 5.16 \text{ eV}. \quad (4.3a)$$

At the third stage, under the influence of a fluorine atom, the surface hydrogen atom is detached and a neutral  $p_b$ -center is formed. This requires energy

$$E_{(Si-H)} = E(> Si - H) + E(H) - E(> Si < H_2) > 0, \quad (4.4)$$

where  $E(> Si < H_2)$  and  $E(> Si - H)$  are the energies of clusters before and after the detachment of a hydrogen atom,  $E(H)$  is the energy of a single hydrogen atom. The simulation showed that the binding energy of a hydrogen atom with a neutral cluster, calculated by expression (4.4), does not depend on the cluster size and is 3.77 eV.

At the fourth stage, a hydrogen atom combines with a fluorine atom and forms an HF molecule, with the release of energy

$$E_{(H-F)} = E(H) + E(F) - E(HF) > 0. \quad (4.5)$$

The value of  $E_{(H-F)}$  calculated using the chosen basis was 5.97 eV.

At the last stage, the HF molecule is adsorbed on a cluster with a  $p_b$ -center, with the release of energy

$$E_{apb0} = E(> Si - H) + E(HF) - E(> Si - H + HF) > 0. \quad (4.6)$$

The calculated adsorption energy of the HF molecule on the neutral  $p_b$ -center was independent of the model cluster size and amounted to 0.12 eV.

As a result, the total energy yield of reaction (3.2) for a cluster of finite sizes is

$$\Delta E_2 = -E_{oxF} - E_V - E_{(Si-H)} + E_{(H-F)} + E_{apb0}. \quad (4.7)$$

If expressions (4.2) – (4.6) are substituted into (4.7), after reduction, expression (4.1) will be exactly obtained. For bulk silicon in expression (4.7), the second term must be replaced by the value  $E_{Vbulk}$ :

$$\Delta E_{h1bulk} = -E_{oxF} - E_{Vbulk} - E_{(Si-H)} + E_{(H-F)} + E_{apb0}. \quad (4.8)$$

Note that none of the terms in (4.8) depends on the size of the model cluster, so that  $\Delta E_{2bulk}$  can be calculated exactly. Substituting the expressions for the corresponding terms in (4.8), we can obtain a simplified equivalent expression

$$\Delta E_{h1bulk} = -E_{Vbulk} + E(F^-) + E(> Si < H_2) - E(> Si - H + HF), \quad (4.9)$$

which is easy to calculate using a cluster of arbitrary

sizes. The obtained value of  $\Delta E_{2bulk}$  for the non-solvated  $F^-$  ion was 4.04 eV, which is 1.27 eV less than the value of  $\Delta E_2$  calculated for the  $Si_{84}H_{64}$  cluster.

Relation (4.9) can be applied to any ionic complex of fluoride ( $F^- + n(HF) + m(H_2O)$ ) with  $n$  HF molecules and  $m$  water molecules, replacing the second and fourth terms in it:

$$\Delta E_{2bulk} = -E_{Vbulk} + E(F^- + n(HF) + m(H_2O)) + E(> Si < H_2) - E(> Si - H + HF + n(HF) + m(H_2O)), \quad (4.10)$$

The correctness of such a replacement can be checked using in (4.8) instead of expressions (4.2), (4.5), and (4.6) for the first, fourth, and fifth terms, the following relations:

$$E_{oxFnm} = E(F + n(HF) + m(H_2O)) - E(F^- + n(HF) + m(H_2O)), \quad (4.11)$$

$$E_{(H-Fnm)} = E(H) + E(F + n(HF) + m(H_2O)) - E((n+1)HF + m(H_2O)), \quad (4.12)$$

$$E_{apb0} = E(> SiH) + E((n+1)HF + m(H_2O)) - E(> SiH + (n+1)HF + m(H_2O)). \quad (4.13)$$

Using expressions (4.11) and (4.10), the values of  $E_{oxFnm}$  and  $\Delta E_{2bulk}$  were calculated for the ten simplest fluoride ionic complexes (the first two columns in Table 1).

**Table 1** – The value of the oxidation energy of ionic complexes of fluoride and the parameters of the reaction of the removal of a hydrogen atom, which occurs with their participation.

Ionic complexes	$E_{oxFnm}$ , eB	$\Delta E_{2bulk}$ , eB	$\Delta_h$ , eB	$\Delta E_{1bulk}$ , eB
$F^-$	3.49	4.04	0.11	3.93
$H_2O F^-$	4.18	2.97	-0.01	2.98
$2(H_2O) F^-$	4.23	2.59	0.18	2.41
$3(H_2O) F^-$	5.61	1.98	-0.03	2.01
$HF F^-$	5.44	2.32	-0.12	2.44
$HF H_2O F^-$	4.91	1.77	-0.18	1.95
$HF 2(H_2O) F^-$	4.94	1.99	0.13	1.86
$2(HF) F^-$	6.73	1.24	-	-
$2(HF)H_2O F^-$	5.80	1.27	-	-
$3(HF) F^-$	7.13	0.33	-	-

An analysis of the obtained results shows that the oxidation energy of the fluoride complex mainly increases with the addition of HF and  $H_2O$  molecules. Deviations from this trend are explained by a significant change in geometry and the formation of new bonds during the oxidation of some complexes. The energy yield of reaction (3.2) decreases with increasing  $E_{oxFnm}$ , and HF molecules in the solvation layer around  $F^-$  reduce  $\Delta E_{2bulk}$  more significantly than water molecules. The values of  $\Delta E_{2bulk}$  turned out to be positive for all considered ionic complexes, i.e. the reaction of removal of a hydrogen atom with their participation is energetically favorable. Note that with the participation of the last three "heavy" complexes (with two or three HF molecules) a barrier appeared in reaction (3.2). When optimizing the geometry, these complexes were not oxidized when approaching the silicon cluster, but were only adsorbed near its surface

(this behavior was also observed for the fluoride complex surrounded by four water molecules). As shown in [7], under the action of precisely such “heavy” fluoride complexes, direct silicon fluorination reactions occur, which are responsible for its electrochemical dissolution.

Now, let's analyze the course of the reaction of removing a surface hydrogen atom, which occurs without the involvement of a free hole. The energy output of the reaction (3.1) is equal to

$$\Delta E_1 = E(>\text{Si}<\text{H}_2) + E(\text{F}^-) - E(>\text{Si}-\text{H}^- + \text{HF}), \quad (4.14)$$

where  $E(>\text{Si}<\text{H}_2)$  is the energy of the neutral cluster,  $E(\text{F}^-)$  is the energy of the  $\text{F}^-$  ion, and  $E(>\text{Si}-\text{H}^- + \text{HF})$  is the energy of the cluster with a negatively charged  $p_b$ -center on which the HF molecule is adsorbed. At the first stage of the reaction, the  $\text{F}^-$  ion is also oxidized with the transition of the electron to the zero level. For this, the oxidation energy  $E_{\text{oxF}}$  is spent, the value of which is given by expression (4.2).

To avoid unnecessary complications, we will formally change the sequence of the second and third stages of the reaction, which will not affect the overall energy balance. We assume that at the second stage, the surface hydrogen atom is detached from the neutral cluster (as in reaction (3.2)), while the extra electron from  $\text{F}^-$  continues to be at the vacuum level. This process consumes energy  $E_{(\text{Si}-\text{H})}$ , the value of which is given by expression (4.4).

At the third stage, the electron from the zero level no longer enters the valence band (which is completely occupied without hole injection), but to the level of the  $p_b$ -center. This releases energy

$$E_{p_b} = E(>\text{Si}-\text{H}) - E(>\text{Si}-\text{H}^-) > 0, \quad (4.15)$$

where  $E(>\text{Si}-\text{H})$  and  $E(>\text{Si}-\text{H}^-)$  are the energies of clusters with neutral and negatively charged  $p_b$ -centers. Although the cluster method introduces significant errors in the quantitative assessment of the position of the energy bands and individual levels, their relative position is reproduced correctly. Our calculations showed that the level of the uncharged  $p_b$ -center falls approximately in the middle of the band gap. The same estimate is given by calculations [12] performed by the plane wave method, which more reliably describes the electronic structure of crystals. Therefore, for bulk silicon, we can write

$$E_{p_b \text{ bulk}} = -E_{V \text{ bulk}} - E_g / 2, \quad (4.15a)$$

where  $E_g = 1.11 \text{ eV}$  is the silicon band gap, hence  $E_{p_b \text{ bulk}} \approx 4.61 \text{ eV}$ .

As in reaction (3.2), at the fourth stage, a hydrogen atom is attached to a fluorine atom and forms an HF molecule. In this case, energy  $E_{(\text{H}-\text{F})}$  is released, the value of which is given by expression (4.5).

In contrast to reaction (3.2), at the fifth stage, the HF molecule is already adsorbed on the negatively charged  $p_b$ -center, which is accompanied by the release of energy

$$E_{\text{apb}^-} = E(>\text{Si}-\text{H}^-) + E(\text{HF}) - E(>\text{Si}-\text{H}^- + \text{HF}). \quad (4.16)$$

Although, for the case of negatively charged  $p_b$ -centers, the value of  $E_{\text{apb}^-}$  somewhat decreased with an

increase in the size of the model, such a decrease was insignificant. The calculated adsorption energies were 0.610, 0.576, 0.561, and 0.558 eV for the  $\text{Si}_{32}\text{H}_{40}$ ,  $\text{Si}_{84}\text{H}_{64}$ ,  $\text{Si}_{165}\text{H}_{100}$ , and  $\text{Si}_{286}\text{H}_{144}$  clusters, respectively. This decrease is no longer associated with a change in the band gap of the cluster, but is caused by a weaker effect of “compression” of the electron wave function at the negatively charged  $p_b$ -center as the cluster size decreases. Therefore, for bulk silicon, the asymptotic value  $E_{\text{apb}^-} \approx 0.55 \text{ eV}$  is a fairly reliable estimate. Note that the significant difference between the adsorption energies of the HF molecule on the neutral and negatively charged  $p_b$ -centers (0.12 versus 0.55 eV) has a clear explanation. The hydrogen atom of the HF molecule has a partial positive charge, therefore, it forms a stronger bond with a negatively charged  $p_b$ -center than with a neutral one.

As a result, the total energy yield of reaction (3.1) for a cluster of finite sizes is

$$\Delta E_1 = -E_{\text{oxF}} + E_{p_b} - E_{(\text{Si}-\text{H})} + E_{(\text{H}-\text{F})} + E_{\text{apb}^-}. \quad (4.17)$$

If expressions (4.2), (4.4), (4.15), (4.5), and (4.16) are substituted into (4.17), expression (4.14) will be exactly obtained after reduction. For bulk silicon in expression (4.17), the second term must be replaced by the value of  $E_{p_b \text{ bulk}}$ :

$$\Delta E_{1 \text{ bulk}} = -E_{\text{oxF}} + E_{p_b \text{ bulk}} - E_{(\text{Si}-\text{H})} + E_{(\text{H}-\text{F})} + E_{\text{apb}^-}. \quad (4.18)$$

It is easy to see that relations (4.8) and (4.18) for the energy yields of reactions (3.3) and (3.1) differ only in the second and fifth terms. Therefore, the expression for the difference in the energy yields of the above reactions has a rather simple form:

$$\Delta_h = \Delta E_{2 \text{ bulk}} - \Delta E_{1 \text{ bulk}} = E_g / 2 - (E_{\text{apb}^-} - E_{\text{apb}^0}), \quad (4.19)$$

Thus, the participation of free holes in the reaction of removal of a hydrogen atom manifests itself in two ways. On the one hand, the energy yield should increase by  $\sim E_g / 2$  due to the transition of an electron to the valence band, and not to the  $p_b$ -center. On the other hand, the energy yield decreases due to the difference between the adsorption energies of the HF molecule on the negatively charged and neutral  $p_b$ -centers. The value of  $\Delta_h$  calculated from expression (4.19) was 0.11 eV, hence the energy yield of reaction (3.1)

$$\Delta E_{1 \text{ bulk}} = \Delta E_{2 \text{ bulk}} - \Delta_h, \quad (4.20)$$

amounted to 3.93 eV.

Relations (4.19) and (4.20) we extended to other fluoride complexes, using expression (4.13) for  $E_{\text{apb}^0}$ , and expression

$$E_{\text{apb}^-} = E(>\text{Si}-\text{H}^-) + E((n+1)\text{HF} + m(\text{H}_2\text{O})) - E(>\text{Si}-\text{H}^- + (n+1)\text{HF} + m(\text{H}_2\text{O})). \quad (4.21)$$

for  $E_{\text{apb}^-}$ . Calculations of  $E_{\text{apb}^-}$  using expression (4.21), as well as for non-solvated  $\text{F}^-$  ions, were carried out on the largest  $\text{Si}_{286}\text{H}_{144}$  cluster. For the last three “heavy” fluoride complexes, it was not possible to establish the value of  $E_{\text{apb}^-}$ . When optimizing the geometry of reaction products (3.1) (from the third configuration in Fig. 3), the HF molecule was destroyed, and the de-

tached hydrogen atom returned to its place on the surface. From the obtained values of  $E_{apb0}$  and  $E_{apb^-}$ , using expressions (4.19) and (4.20), the values of  $\Delta_h$  and  $\Delta E_{1bulk}$  were calculated, provided in the third and fourth columns of Table 1. Since the obtained values of  $\Delta E_{1bulk}$  turned out to be positive for all "light" fluoride complexes, the detachment of hydrogen atoms from silicon surface under their action can occur without the participation of free holes. The injection of free holes does not significantly affect the energy yield of the hydrogen atom removal reaction, and for some fluoride complexes it even reduces it. The reaction of removal of hydrogen atoms under the action of "heavy" fluoride complexes is a barrier reaction both with the participation of free holes and without them. It was shown in [13] that the purely chemical dissolution of silicon slows down in highly concentrated HF solutions. This can be explained by the fact that in such solutions the relative fraction of "light" fluoride complexes is smaller than in weak HF solutions [10].

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## 5. CONCLUSIONS

Using DFT calculations, we studied the reaction of removal of surface hydrogen atoms, which can occur on the silicon surface under the action of fluoride complexes of an aqueous solution of HF. A technique was created and used for estimating the energy parameters of reactions with a change in the charge state of the surface of bulk silicon based on the results of calculations performed on clusters of finite sizes. Modeling has shown that in aqueous HF solutions, reactions of removal of surface hydrogen atoms can occur both with and without current flow. Such reactions can take place only under the influence of "light" fluoride complexes containing no more than one HF molecule. This explains the fact that the chemical etching of silicon occurs more intensively in more dilute aqueous HF solutions, where the concentration of "light" fluoride complexes is high.

## Енергетичні параметри найпростіших хімічних реакцій, які протікають на перших стадіях електрохімічного травлення кремнію – DFT-моделювання

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На основі квантово-хімічних розрахунків досліджено реакції видалення поверхневих атомів водню, які проходять на перших етапах травлення кремнію у розчинах HF під дією різних іонних комплексів фтору. Для цього створена методика достовірної оцінки енергетичних параметрів хімічних реакцій зі змінним зарядовим станом, які відбуваються на поверхні об'ємного кремнію по результатам розрахунків, проведених на кластерах кінцевих розмірів. Показало, що у водних розчинах HF реакції видалення поверхневих атомів водню можуть проходити як при протіканні струму через систему кремній/електроліт, так і без нього. Реакції видалення водного покриття поверхні кремнію відбуваються лише під впливом «легких» іонних комплексів фтору, які містять не більше однієї молекули HF. На основі моделювання пояснено причини уповільнення суто хімічного травлення кремнію у розчинах HF високої концентрації.

**Ключові слова:** Поруватий кремній, Електрохімічне травлення, DFT-розрахунки.