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REGULAR ARTICLE

DFT Modeling of Chemical Reactions Occurring Under the Influence of Positive Ionic Complexes of Aqueous HF Solutions During Electrochemical Etching of Silicon

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Based on quantum chemical calculations, the restoration of the hydrogen coating occurring during the first stages of silicon etching in HF solutions under the influence of positive ionic complexes of the electrolyte have been studied. It has been shown that in aqueous solutions of HF, restoration of the hydrogen coating can occur both with and without current flowing through the silicon/electrolyte system. It is shown that the parallel occurrence of mutually inverse reactions of removal of surface hydrogen atoms and restoration of the hydrogen coating explains the low rate of purely chemical etching of silicon in aqueous solutions of HF. A method has been created for reliable assessment of the energy parameters of chemical reactions with a variable charge state of a cluster that occur on the surface of bulk silicon based on the results of calculations carried out on clusters of finite sizes. The energy yields of the restoration of the hydrogen coating under the influence of ionic complexes H3O+ and 3(H2O)(H3O)+ are calculated when current flows and without injection of free holes into silicon.

Keywords: Porous Silicon, Electrochemical Etching, DFT-Calculations, Nanomaterials.

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1. INTRODUCTION

Porous silicon (PS) is a fairly promising nanomaterial and is widely used in modern systems for storing and converting energy, sensors, medicine, etc. [1-5]. Although the properties of PS have been fairly well studied, the microscopic mechanism of its production is still poorly understood [3-5]. Almost all authors of works devoted to the study of PS rely on the model of electrochemical etching of Si in HF solutions, proposed by Lehmann and Gösele back in 1991 [6]. Although this model is in qualitative agreement with experimental results, it contains many assumptions and leaves many questions. In particular, questions about the role of free holes during electrochemical etching of Si and the mechanism of replacement of surface hydrogen atoms with fluorine have still remained controversial. More modern works [7, 8], devoted to the theoretical study of electrochemical etching of PS, indicate the need for quantum chemical modeling of these processes. The results of such modeling were presented by us in [9], in which, based on quantum chemical calculations, a new model of electrochemical etching of PS was proposed, which made it possible to explain most of the characteristic features and peculiarities of this process. Despite this, some comments arose regarding the calculation results [9] related to the estimated nature of the obtained energy parameters of the considered chemical reactions. For most cases, simulation results were presented that indicated only the fundamental possibility or low probability of certain reactions occurring. We tried to eliminate this drawback in [10], where a method was proposed for a refined assessment of the energy parameters of chemical reactions with a changing charge state (including reactions involving electrolyte ions). This technique was applied to the reactions of removal of surface hydrogen atoms that occur during the first stages of electrochemical etching of silicon.

This work is a logical continuation of the studies described in [9, 10]. The application of a technique for refined calculation of the energy parameters of reactions involving positive electrolyte ions, which (as demonstrated in [9]) play a very important role in the electrochemical etching of silicon, will be considered.

2. MODELING DETAILS

Quantum chemical modeling used the density functional method (DFT method) in the cluster approximation. The main disadvantage of this method when studying chemical reactions on a silicon surface under the influence of electrolyte ions was the fact that the calculated values of the energy yields of the chemical reactions under consideration depended on the size of the model clusters. This effect is due to the fact that the chemical interaction of clusters with electrolyte ions is accompanied by electron transitions to the conduction band or valence band of silicon. But the position of these bands depends on the size of the clusters: the band gap increases with decreasing sizes of both model silicon clusters and real silicon nanocrystallites, which is associated with the effect of quantum confinement of charge carriers. To determine the degree of influence of cluster size on the energy yield of chemical reactions,

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two main types of clusters of similar shape were used – $Si_{35}H_{36}$ and $Si_{84}H_{64}$, Fig. 1 *a*, *b*. These clusters were hexagonal pyramids formed by (111) faces covered with hydrogen atoms. Calculations were performed in the TeraChem 1.93P software environment [11] using the B3LYP exchange-correlation functional. Most of the cluster atoms were modeled in a fairly broad 6-31g(d,p) basis. To achieve the set objectives, only chemical reactions near the corner silicon atom located at the intersection of the (111) planes were considered (it is outlined in blue dotted line in Fig. 1). Quantum chemical calculations carried out on clusters of other shapes 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 Si atoms on the (100) faces. Therefore, for the corner Si atom, hydrogen atoms, ions and electrolyte molecules attached to it, the 6-311++g(d,p) basis with diffuse functions was chosen. Taking into account diffuse basis functions is important when modeling long-range interactions of atoms observed during chemical reactions. The selected basis set and calculation method showed good reproducibility of the geometric parameters of the model objects under consideration. For example, the average value of interatomic distances in a model silicon cluster was 0.237 nm and practically coincided with the known experimental value of 0.235 nm.

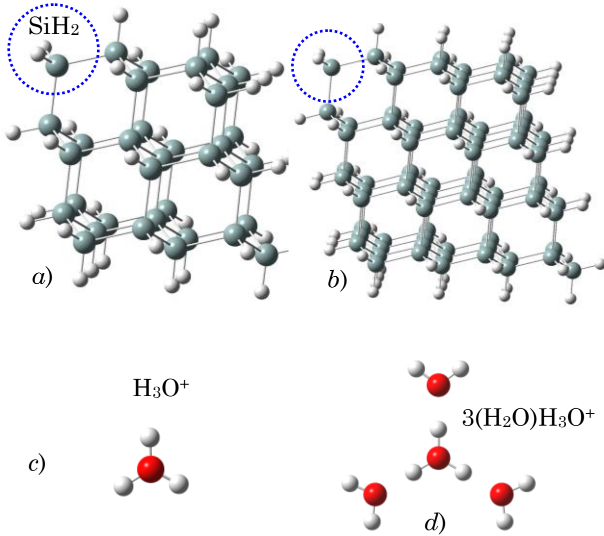


Fig. 1 – View of model clusters $Si_{35}H_{36}$ (*a*) and $Si_{84}H_{64}$ (*b*); positive ionic complexes of the electrolyte H_3O^+ (*c*) and $3(H_2O)H_3O^+$ (*d*). The blue dotted line indicates the positions of the corner SiH_2 groups involved in the chemical reactions under consideration.

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

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

where E_{reag} is the sum of the energies of the reactants in states with optimized geometry, and E_{prod} is the energy of the reaction products in the optimized state (all indicated energies have negative values). The binding energies of individual molecules or molecules with Si clusters were calculated using expression

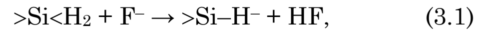
$$E_{bind} = E_{reag} - E_{reakt}, \quad (2.2)$$

where E_{reag} is the sum of the energies of individual molecules and clusters, and E_{reakt} is the energy of the system after the formation of the corresponding bond.

Although well-known literature sources have not considered the participation of positive electrolyte ions in the processes of electrochemical etching of silicon, modeling has shown that they also play an important role. Free protons practically never occur in aqueous solutions of HF, and positive ions of the electrolyte exist mainly in the form of hydronium ions H_3O^+ (Fig. 1 *c*) and its aqueous complexes $3(H_2O)H_3O^+$ (in Fig. 1 *d*), [12]. The formation of complexes of protons with HF molecules is unlikely, since the binding energy of a proton with a water molecule (7.37 eV) is much higher than with a HF molecule (4.46 eV).

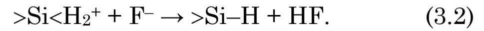
3. REACTIONS ON SILICON SURFACES THAT CAN OCCUR UNDER THE INFLUENCE OF POSITIVE ELECTROLYTE IONS

As was shown in [9], in aqueous solutions of HF on the silicon surface, under the influence of negatively charged fluoride complexes (F^-), reactions that remove surface hydrogen atoms can occur. These reactions occur both during purely chemical etching (without the participation of free holes) and during the flow of current (with the injection of free holes into the near-surface region of Si)



$$>Si<H_2 + F^- \rightarrow >Si{-}H^- + HF, \quad (3.1)$$

and during the flow of current (with the injection of free holes into the near-surface region of Si)



$$>Si<H_2^+ + F^- \rightarrow >Si{-}H + HF. \quad (3.2)$$

After these reactions occur, a negatively charged (or neutral) p_b-center (>Si–H group, silicon atom with a dangling bond) appears on the cluster and an HF molecule is formed (Fig. 2).

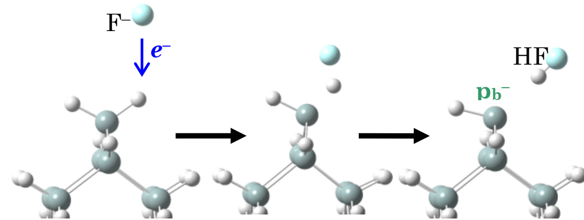
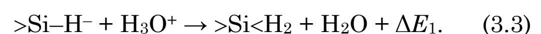


Fig. 2 – Fragments of a model cluster illustrating the reaction of the removal of a surface hydrogen atom by an F^- ion with the formation of a p_b-center and an HF molecule.

Since after reaction (3.1) a negatively charged p_b-center is formed, fluoride complexes are repelled from it by Coulomb forces, and hydronium ions H_3O^+ are attracted. In this case, the extra electron from the p_b-center goes into the hydronium ion, which is reduced and disintegrates into a water molecule and a hydrogen atom, Fig. 3. After this, the H atom attaches to the already neutral p_b-center, i.e. the process of restoration of the hydrogen coating of the silicon surface occurs, inverse to (3.1):



$$>Si{-}H^- + H_3O^+ \rightarrow >Si<H_2 + H_2O + \Delta E_1. \quad (3.3)$$

Reaction (3.3) turned out to be barrier-free, and its energy yield depended on the size of the model, namely, it decreased as the model cluster increased. For the $Si_{35}H_{36}$ and $Si_{84}H_{64}$ clusters, the ΔE_1 value was 7.26 and 7.06 eV, respectively. Note that reaction (3.3) of restoration of hydrogen coating can occur not only on the (100) silicon faces, but also on the (111) and (110) faces.

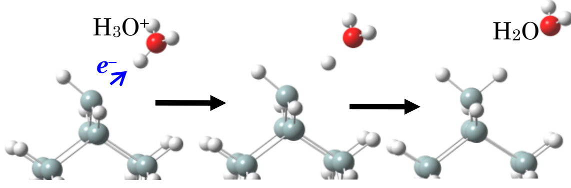
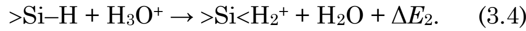


Fig. 3 – Fragments of a model cluster illustrating the process of restoration of the hydrogen coating of the silicon surface under the influence of hydronium ion.

Hydrogen coating restoration reactions can occur during the interaction of positive ions with neutral p_b-centers, which are formed after reaction (3.2) under the influence of free holes:



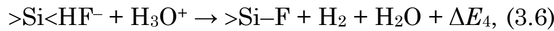
$$>Si–H + H_3O^+ \rightarrow >Si<H_2^+ + H_2O + \Delta E_2. \quad (3.4)$$

Although the value of ΔE_2 decreased compared to ΔE_1, it remained positive (2.92 and 3.25 eV for $Si_{35}H_{36}$ and $Si_{84}H_{64}$ clusters, respectively). Therefore, when interacting with hydronium ions, p_b-centers will disappear regardless of their charge state, and the hydrogen coating of silicon will be restored.

The remaining reactions we simulated under the influence of positive ions of the electrolyte did not lead to modification of the silicon surface. In the Si etching process, the hydronium reduction reaction plays a certain role with the formation of a water molecule and a hydrogen atom:

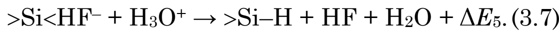
$$>Si<HF^- + H_3O^+ \rightarrow >Si<HF + H_2O + H + \Delta E_3. \quad (3.5)$$

This reaction removes the negative charge of silicon obtained after the addition of the F^- ion to the neutral p_b-center. Its energy yield turned out to be positive and amounted to 4.84 eV for the $Si_{84}H_{64}$ cluster. Under the influence of hydronium ion, instead of reaction (3.5), reactions of removal of surface hydrogen atoms can potentially occur:



$$>Si<HF^- + H_3O^+ \rightarrow >Si–F + H_2 + H_2O + \Delta E_4, \quad (3.6)$$

or the reaction of removing surface fluorine atoms:



$$>Si<HF^- + H_3O^+ \rightarrow >Si–H + HF + H_2O + \Delta E_5. \quad (3.7)$$

Although the values of ΔE_4 and ΔE_5 calculated for the $Si_{84}H_{64}$ cluster turned out to be positive and even higher than ΔE_3 (5.81 and 5.32 eV, respectively), reactions (3.6) and (3.7) are practically not realized. When approaching a silicon cluster, positive ions are immediately reduced (reaction (3.5) occurs), and the hydrogen atom becomes neutral and begins to be repelled from the hydrogenated silicon surface by exchange interaction forces. Despite this, it can be assumed that due to the barrier reaction (3.7), fluorine atoms are slowly removed, which explains their almost complete absence on the PS surface [7].

The presented results indicate that positive ions of the HF electrolyte play an important role in the electrochemical etching of silicon. The simulation also showed that the calculated energy yields of most of the reactions under consideration depended on the size of the model clusters. Therefore, it became 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. The procedure for such extrapolation will be described below and applied to hydrogen coating restoration reactions.

4. CALCULATION OF ENERGY YIELD OF REACTIONS OF HYDROGEN COATING RESTORATION

Analysis of the hydrogen coating restoration reactions (3.3) and (3.4) is necessary to establish the exact values of the energy yield of these reactions on the surface of bulk silicon and to assess the possibility of their occurrence under the influence of $3(H_2O)(H_3O)^+$ ionic complexes. To find the energy yields of these reactions on the surface of bulk silicon, the reactions under consideration should be formally divided into certain stages and the energies released or absorbed at these stages should be calculated [10]. Using this procedure, it is easier to estimate and control the errors introduced by the assumptions and approximations applied at each stage.

Let us first consider reaction (3.3), which involves the hydronium ion and the negatively charged p_b-center formed after reaction (3.1). The energy yield of reaction (3.3), calculated on a cluster of finite sizes, is equal to

$$\Delta E_1 = E(>Si–H^-) + E(H_3O^+) – E(>Si<H_2 + H_2O), \quad (4.1)$$

where $E(>Si–H^-)$ is the energy of a cluster with a negatively charged p_b-center, $E(H_3O^+)$ is the energy of the hydronium ion, $E(>Si<H_2 + H_2O)$ is the energy of a cluster with an adsorbed water molecule, formed after the reaction of the hydrogen coating restoration. Expression (4.1) includes the energies of clusters in different charge states, which entails the dependence of ΔE_1 on the size of the model. To find the value of ΔE_{1bulk} corresponding to reaction (3.3) on the surface of bulk silicon, we formally divide it into five stages.

At the first stage, an extra electron is removed from the negatively charged silicon cluster, which will subsequently participate in the reduction of the hydronium ion. This process formally represents the transition of an electron from the level of a negatively charged p_b-center to the zero vacuum level, after which the p_b-center becomes neutral. For such a transition you need to spend energy

$$– E_{pb} = E(>Si–H^-) – E(>Si–H) < 0, \quad (4.2)$$

where E_{pb} is the energy level of the p_b-center on the surface of bulk silicon (its position does not change when the charge state changes); $E(>Si–H)$ and $E(>Si–H^-)$ 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 energy zones and

individual levels, their relative position is reproduced correctly. Our calculations showed that the level of the uncharged p_b-center is localized approximately in the middle of the band gap. The same estimate is given by calculations [13] performed by the plane wave method, which more reliably describes the electronic structure of crystals. Therefore, for bulk silicon we can write

$$-E_{pb\ bulk} = E_{Vbulk} + E_g/2, \quad (4.2a)$$

where $E_g = 1.11$ eV is the band gap of silicon, and $E_{Vbulk} = -5.16$ eV is the level of the valence band top of silicon, therefore $-E_{pb\ bulk} = -4.61$ eV.

At the second stage, the hydronium ion is reduced (captures an electron) from the vacuum level, which is accompanied by the release of energy

$$E_{red} = E(H{+}H_2O) - E(H_3O{+}) > 0. \quad (4.3)$$

For the hydronium ion and the ionic complex $3(H_2O)(H_3O)^+$, the calculated E_{red} values were 6.25 and 3.66 eV, respectively.

At the third stage, in reduced H_3O, the bond between the neutral hydrogen atom and the water molecule is broken, which requires energy

$$E_{(H-H2O)} = E(H_2O) + E(H) - E(H_2O + H). \quad (4.4)$$

Note that the binding energy of H and H_2O is very low, < 0.01 eV.

At the fourth stage, the hydrogen atom joins the neutral p_b-center and energy is released

$$E_{(Si-H)} = E(>Si-H) + E(H) - E(>Si<H_2) > 0, \quad (4.5)$$

where $E(>Si–H)$ and $E(>Si<H_2)$ are the energies of clusters before and after the addition of a corner 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 from expression (4.5), does not depend on the cluster size and is 3.77 eV.

At the last stage, energy is released during the adsorption of a water molecule onto a neutral silicon cluster:

$$E_{a(Si-H2O)} = E(>Si<H_2) + E(H_2O) - E(>Si<H_2 + H_2O). \quad (4.6)$$

Hydrogenated silicon surface is hydrophobic, so the value $E_{a(Si-H2O)}$ is very small, < 0.01 eB, and doesn't depend on the size of the model.

As a result, the total energy yield of reaction (3.3) is equal to

$$\Delta E_1 = -E_{pb} + E_{red} - E_{(H-H2O)} + E_{(Si-H)} + E_{a(Si-H2O)}. \quad (4.7)$$

After substituting expressions (4.2)-(4.6) into (4.7), we exactly obtain expression (4.1). For bulk silicon in (4.7), you only need to replace the term E_{pb} with its estimated value from expression (4.2a):

$$\Delta E_{3bulk} = E_{Vbulk} + E_g/2 + E_{red} - E_{(H-H2O)} + E_{(Si-H)} + E_{a(Si-H2O)}. \quad (4.8)$$

In this relation, none of the terms depends on the size of the model cluster. An equivalent expression can be obtained by substituting expressions (4.2a)-(4.6) into (4.8):

$$\Delta E_{1bulk} = E_{Vbulk} + E_g/2 + E(H_3O^+) + E(>SiH) - E(>Si<H_2 + H_2O). \quad (4.9)$$

This relationship can also be extended to the ionic complex $3(H_2O)(H_3O)^+$:

$$\Delta E_{3bulk} = E_{Vbulk} + E_g/2 + E(3(H_2O)(H_3O)^+) + E(>Si-H) - E(>Si<H_2 + 4H_2O). \quad (4.9a)$$

The E1bulk values calculated using expressions (4.9) and (4.9a) were 5.41 and 3.01 eV for the ionic complexes H_3O^+ and $3(H_2O)(H_3O)^+$, respectively. Therefore, the reaction of restoration of the hydrogen coating under their influence will proceed very efficiently in the case when free holes are not injected into the silicon.

Let us now analyze reaction (3.4), in which the neutral p_b-center formed after reaction (3.2) participates. The energy yield of reaction (3.4) is equal to

$$\Delta E_2 = E(>Si-H) + E(H_3O^+) - E(>Si<H_2^+ + H_2O), \quad (4.10)$$

where $E(>Si–H)$ is the energy of a cluster with a neutral pb center, and $E(>Si<H_2^+ + H_2O)$ is the energy of a positively charged cluster with an adsorbed water molecule. When analyzing reaction (3.4), we again divide it into five stages, but change their order.

We will assume that at the first stage of the reaction the hydronium ion is reduced by an electron "temporarily borrowed" from the zero vacuum level (at the penultimate stage this electron will need to be returned to the zero level). When H_3O^+ is reduced, energy is released, which can be found using expression (4.3). The second stage of breaking the $H–H_2O$ bond requires energy, which can be found from expression (4.4). At the third stage, the hydrogen atom attaches to the neutral p_b-center, so expression (4.5) can be used for the corresponding energy.

As already noted, at the fourth stage it is necessary to return the "borrowed" electron to the zero vacuum level. This means that an electron is removed from the valence band of silicon, and the cluster receives a $+e$ charge. This process requires energy

$$E_V = E(>Si<H_2^+) - E(>Si<H_2) < 0, \quad (4.11)$$

where $E(>Si<H_2)$ and $E(>Si<H_2^+)$ are the energies of neutral and positively charged clusters, respectively. For bulk silicon, the exact energy position of the valence band top can be used

$$E_{Vbulk} = -5.16 \text{ eV}. \quad (4.11a)$$

At the last stage, a water molecule is adsorbed onto a positively charged silicon cluster:

$$E_{a(Si+-H2O)} = E(>Si<H_2^+) + E(H_2O) - E(>Si<H_2^+ + H_2O). \quad (4.12)$$

Modeling showed that the silicon surface remains hydrophobic even in the presence of a positive cluster charge +e, that is, the delocalized unit charge of bulk silicon will not affect the adsorption energy of a water molecule. Therefore, for bulk silicon, we can replace $E_{a(Si+-H2O)}$ with the value $E_{a(Si-H2O)}$, determined by expression (4.6).

As a result, the total energy yield of reaction (3.4) is equal to

$$\Delta E_2 = E_{red} - E_{(H-H2O)} + E_{(Si-H)} + E_V + E_{a(Si+-H2O)}. \quad (4.13)$$

After substituting expressions (4.3)-(4.5), (4.11), (4.12) into (4.13), we exactly obtain expression (4.10). For bulk silicon in (4.13), you need to replace the last two terms with expressions for E_{Vbulk} and $E_{a(Si-H2O)}$:

$$\Delta E_2 = E_{red} - E_{(H-H2O)} + E_{(Si-H)} + E_{Vbulk} + E_{a(Si-H2O)}. \quad (4.13a)$$

Analyzing expressions (4.8) and (4.13a) for the energy yields of reactions (3.3) and (3.4), one can see that their difference is equal to

$$\Delta = \Delta E_{2bulk} - \Delta E_{1bulk} = - E_g / 2. \quad (4.14)$$

Thus, the injection of free holes into silicon reduces the energy yield of the hydrogen coating restoration reaction by ~0.55 eV. Calculated using the expression

$$\Delta E_{2bulk} = \Delta E_{1bulk} - E_g / 2 \quad (4.15)$$

the ΔE_{2bulk} values were 4.86 and 2.46 eV for the ionic complexes H_3O^+ and $3(H_2O)(H_3O)^+$, respectively. Therefore, the reaction of restoration of the hydrogen coating remains very probable even when free holes are injected to the silicon surface. The parallel course of the reactions of removal of surface hydrogen atoms and restoration of the hydrogen coating explains the low rate of purely chemical etching of silicon in aqueous solutions of HF.

5. CONCLUSIONS

Using the DFT method, quantum chemical modeling of reactions on the silicon surface that occur under the influence of positive ionic complexes of aqueous solutions of hydrofluoric acid was carried out. Simulations have shown that the hydrogen coating restoration reactions can occur both with and without current flowing through the electrolyte. The parallel course of the reactions of removal of surface hydrogen atoms and restoration of the hydrogen coating explains the low rate of purely chemical etching of silicon in aqueous solutions of HF. To accurately estimate the energy parameters of the reactions under consideration, an original technique was used, applicable for reactions with a change in the charge state of the cluster. The calculated energy yields for the reactions of reduction of the hydrogen coating under the action of ionic complexes H_3O^+ and $3(H_2O)(H_3O)^+$ were 5.41 and 3.01 eV, respectively. Therefore, the reaction of restoration of the hydrogen coating under their influence will proceed very efficiently in the case when there is no injection of free holes to the silicon surface. Injection of free holes into silicon reduces the energy yield of these reactions by ~ 0.55 eV.

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DFT-моделювання хімічних реакцій, які протікають під дією позитивних іонних комплексів водних розчинів HF при електрохімічному травленні кремнію

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На основі квантово-хімічних розрахунків досліджено реакції відновлення водного покриття, які проходять на перших етапах травлення кремнію у розчинах HF під дією позитивних іонних комплексів електроліту. Показало, що у водних розчинах HF реакції відновлення водневого покриття можуть проходити як при протіканні струму через систему кремній/електроліт, так і без нього. Показано, що паралельний перебіг взаємно обернених реакцій видалення поверхневих атомів водню та відновлення водневого покриття пояснює низьку швидкість суто хімічного травлення кремнію у водних розчинах HF. Створена методика достовірної оцінки енергетичних параметрів хімічних реакцій зі змінним зарядовим станом кластера, які відбуваються на поверхні об'ємного кремнію по результатам розрахунків, проведених на кластерах конечних розмірів. Розраховані енергетичні виходи реакції відновлення водневого покриття під впливом іонних комплексів H_3O^+ і $3(H_2O)(H_3O)^+$ при протіканні струму та без інжекції у кремній вільних дірок.

Ключові слова: Поруватий кремній, Електрохімічне травлення, DFT-Розрахунки, Наноматеріали.