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ELECTROSTATIC FIELD TENSITIES NEAR IRREGULARITIES OF POROUS SILICON SURFACE

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*Equilibrium spatial structure of the $Si_{89}(OH)_{43}H^*_{36}$ cluster model simulated for a pyramid-like formation on porous silicon surface has been calculated within the frameworks of density functional theory method with 6-31G** basis set. The electron charge and electrostatic field distribution have been evaluated in the vicinity of such a formation. The electrostatic field tensity has been found to be great enough to ionize adsorbed organic molecules.*

Nowadays porous silicon is widely used not only in scientific studies but also finds practical applications. Creation of isolating support should be noticed among them for the structures "silicon over insulator", of thick isolating films, light guides, and growing of quantum dots and fibers of various fractal dimensions. The method of matrix-free laser desorption ionization on porous silicon surface occupies none the worse position among them. The most weak spot of this method consists in the absence of an adequate theory explaining the mechanism of soft ionization of analyte molecules and following selective formation of fragment ions what somewhat complicates the interpretation of the data obtained [1, 2].

When using polished crystalline silicon as a support, this method gives no opportunity to achieve an ionization of the most of organic molecules even in the high intensity laser field. This allows us to suggest that just silicon porosity (i.e. the presence of surface nanostructure objects containing relatively small quantity of silicon atoms or pores of various diameters and forms) causes its capability to ionize adsorbed molecules. Electrostatic fields with a tensity enough to ionize molecules due to mechanism of field ionization should be generated just near such irregularities of surface structure. The aim of this paper is a theoretical estimation of electrostatic field tensities on porous silicon surface.

All the calculations have been carried out within the frameworks of density functional theory method [3, 4] with exchange-correlation functional B3LYP [5] and basis set 6-31 G**.

Fig. 1 shows the equilibrium spatial structure of the cluster model $Si_{89}(OH)_{43}H^*_{39}$ simulated for a pyramid formation (PF) on porous silicon surface. The H* symbol depicts hydrogen-type pseudoatoms inserted at the cluster periphery adjacent to the bulk phase in order to take its effect into account. Free valences of silicon atoms stationed at the side faces of the pyramid were saturated with one or two hydroxyl groups.

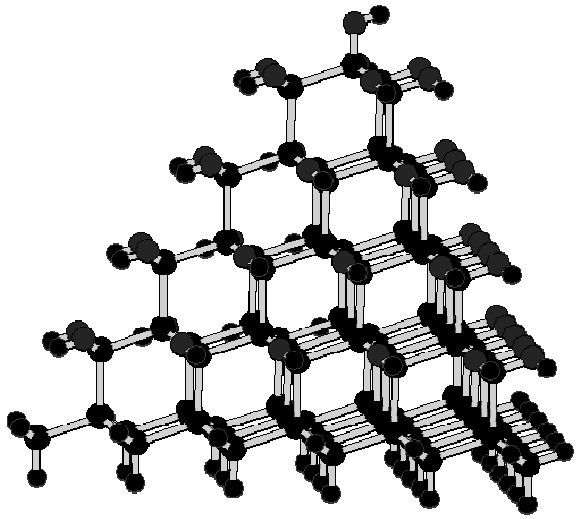

Fig. 1. Equilibrium structure of the cluster simulated for a pyramid nanostructure object on porous silicon surface

Such a choice of a model relates to the experimental data: silicon of the electron type of conductivity (n-Si) or high alloyed hole one (p-Si) have pores as perpendicular to surface channels with diameter of some nanometers and more small branches. An adsorption of organic molecules followed by their ionization occurs just in the vicinity of these pores. When designing

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the model, silicon atoms positions in porous silicon were taken into account remaining typical of silicon support.

When crystalline silicon contacts with aqueous solution of hydrofluoric acid, its surface is saturated with hydrogen atoms adding to superficial silicon atoms so compensating their dangling valences. After keeping the samples in air to mature for a few days, separate areas of their surfaces covered with ≡Si–H and >SiH_2 groups undergo a transformation when hydrogen is desorbed, surface is oxidized so resulting in siloxane groups detecting by IR-spectroscopy.

Analysis of the charge distribution in PF shows that silicon atoms inside the pyramid bear almost zero charge on average what testifies covalent bonds between them whereas silicon atoms of side faces have rather essential positive charges (Q). Their values depend on the number of silanol groups bound with silicon atom (~0.50 e in case of isolated silanol groups and ~0.52 e in case of silanediol ones).This fact along with large negative charge (from ~0.58 to ~0.62 e) results in appearance of a system of altering charge densities generating long-range electrostatic interactions.

Such an altering of charge results in generation of an electrostatic potential (ρ) in the vicinity of a pyramid, its maxima and minima being distant one from another for approximately for an interatomic distance (Fig. 2). As a result, when adsorbed, organic molecule on the PF under consideration are oriented and polarized considerably by the surface.

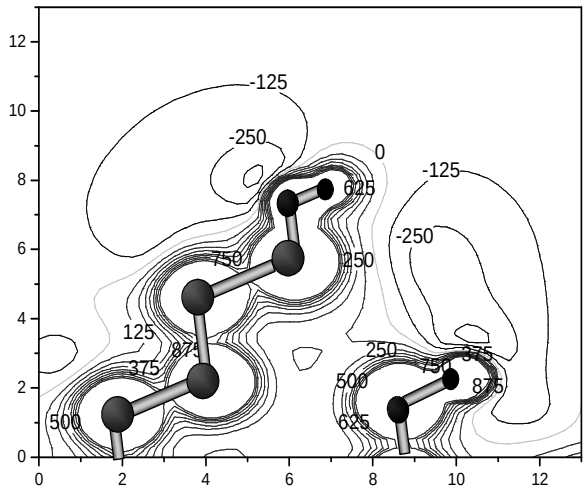

Fig. 2. Electrostatic potential distribution in the vicinity of the pyramid formation. The potential values are given in kJ/mol

The level of this effect can be estimated due to the difference in the molecule energy with the equilibrium geometry as infinitely far from the surface as compared with that in the adsorption complex (ΔE_{str}). The results of calculations for pyridoxine (PD) molecule show this difference to be of 5.3 kJ/mol.

Fig. 3 shows the HOMO structure of the pyramid formation examined. It is seen from it that when the electromagnetic irradiation acts on porous silicon surface with such a PF followed by ionization, the positive charge should be localized mainly on the top of pyramid.

As a result, electrostatic fields of high tensity should be generated in the vicinity of the regions where positive charge is localized what promote the interaction with nucleophilic functional groups of adsorbed molecules. Such fields are also formed near PF's on porous silicon surface in absence of charge on them as it is testified by Fig. 4 where a distribution is shown of the absolute tensity values of the electrostatic field found from the electrostatic potential distribution due to relation $|\vec{E}| = |grad\rho|$.

An additional evidence of the suggestion made on the role of near-surface electrostatic fields can be the calculated data on electrostatic field tensities near the surface of unrelaxed crystalline silicon face (111) and near the latter completed with OH–groups. In sites of probable localization of the atoms of adsorbed molecule they are of ~ (3–5) 10^8 V/m.

It is seen from Fig. 4 that the tension of electrostatic field near uncharged PF is large enough to ionize an adsorbed molecule due to mechanism of field ionization.

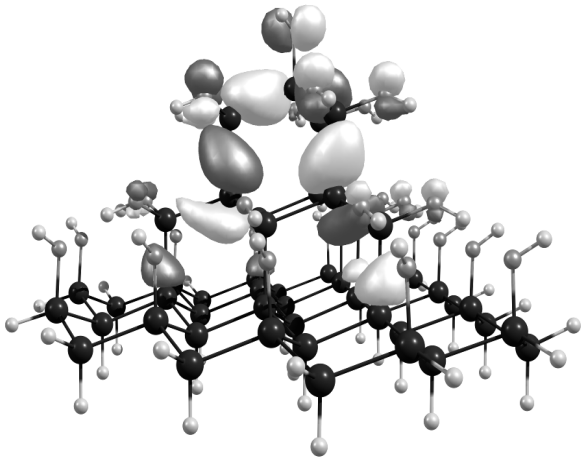

Fig. 3. Spatial distribution of the electron density related to HOMO of the pyramid formation on porous silicon surface

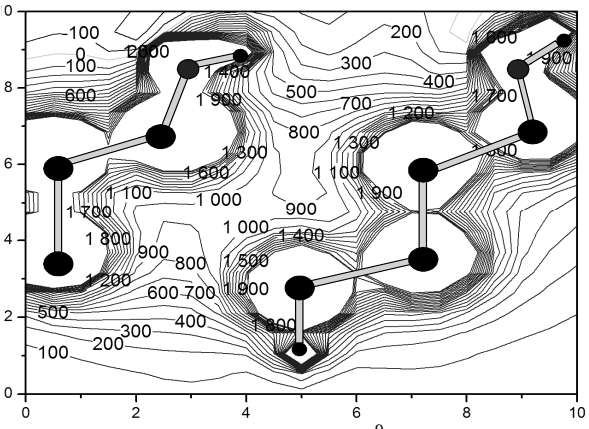

Fig. **4**. Electrostatic field tension (10^9 V/m) in the vicinity of pyramidal formation on porous silicon surface

It is important that, according to the data obtained, the forbidden zone contains some one-electron levels with negative energies at the lower bound of conductivity zone (~ - 0.04 eV). This testifies the spontaneous electron transition from adsorbed molecule to the pyramid nanoformation with generation of a positively charged molecular ion. Such a transition is not connected with accumulation of the energy of electron excitation on the molecular ion but only that of vibrational one appearing as a result of disagreement between the equilibrium structure of adsorbed molecule and that of related ion. Examination of the problem on the distribution of this energy among internal vibrational states of molecular ion and on the possibility of its localization at definite chemical bonds needs additional information about the spatial structure of analyte molecule.

Thus, one can claim that large enough electrostatic field tensity near nanoobjects on porous silicon surface along with presence of unoccupied one-electron levels near the bottom of conductivity zone let it possible to explain general features of the method of matrix-free laser desorption ionization.

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Напруженість електростатичного поля в околі неоднорідностей на поверхні поруватого силіцію

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*Методом функціоналу електронної густини з використанням базисного набору 6-31 G** розраховано рівноважну просторову будову кластерної моделі складу $Si_{89}(OH)_{43}H^*_{36}$ для пірамідального утворення на поверхні поруватого силіцію. Одержано розподіл електронного заряду та електростатичного поля в околі такого утворення. Виявлено, що напруженість електростатичного поля достатня для іонізації адсорбованих органічних молекул.*

Напряженность электростатического поля вблизи неоднородностей на поверхности пористого кремния

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*Методом функционала электронной плотности с использованием базисного набора 6-31 G** рассчитано равновесное пространственное строение кластерной модели состава $Si_{89}(OH)_{43}H^*_{36}$ для пирамидального образования на поверхности пористого кремния. Получено распределение электронного заряда и электростатического поля вблизи такого образования. Обнаружено, что напряженность электростатического поля достаточна для ионизации адсорбированных органических молекул.*