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A SEMIEMPIRICAL POTENTIAL MODEL FOR H-TERMINATED FUNCTIONALIZED SURFACE OF POROUS SILICON

A. IOANID, M. DIEACONU, S. ANTOHE

Faculty of Physics, University of Bucharest, Bucharest-Magurele, Romania

A semiempirical potential model for functionalized surface of porous silicon has been devised. Considering both the Lennard-Jones and electrostatic contributions for the silicon surface-water and water-water interactions, we have shown that it is probable a Si-H...H-O dihydrogen bond between silicon surface and the interfacial water molecule. Due to their strong reducing character the (Si_3)-H^- silyl anion behaves as an acceptor of proton. This non-conventional dihydrogen bond between silicon surface and interfacial water is competitive with the classical hydrogen bond of between interfacial water-water molecules so that reduces hydrophobicity of surface.

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1. Introduction

Porous Silicon (PS) is a redutable biomaterial for devices with potential impact in biological and medical applications concerning detection, transport and interactions of the macromolecules, due to the great ratio surface/volume and to the amphoter (hydrophobic/ hidrophylic) properties of their functionalizated surface.

Biocompatibility is the ability of a material to interface by adsorption of a layer of protein, with a biological environment without provoking a defence response.

PS can be either a bioactive, a bioinert or a resorbable material, depending on the morphological, chemical and electrical characteristics of the surface layer and those of the biological environment in which it is inserted [1].

Devices based on silicon chip are interesting in the other than microelectronic applications, where control is required over the interfacial characteristics such as microarray technology moving to the forefront of genomics, proteomics and sensing lab on chip [2] , TAS (Total Automated Systems) [3], and also MEMS and NEMS (Micro- and Nano- Electro-Mechanical Systems) [4]. For these potential molecular biological applications, the atomic level surface control by organic functionalization of semiconductor, is crucial. Surface functionalization or organic modification is the process of depositing layers of organic molecules (i.e. those that contain carbon) at semiconductor surfaces. In vivo, these devices have an intimatelly contact with a preponderent aqueous fluid.

Adsorbtion of foreign atoms on a surface can significantly modify its physical and chemical properties. These adsorbates play an important role in thin-film growth by affecting specific processes that adatom diffusion or nucleation, but act as surfactant that saturates the dangling bonds and thus lower the surface free energy, leading to a floating layer segregated from the incorporated growing species. On bare semiconductor surface, the surface energy is correlated with the number of dangling bonds on the ideal surface and the extent to which a reconstruction can reduce them. The morphology and surface-energy anizotropy can be considerable changed by the presence of foreign species if they form chemical bonds with surface atoms.

The surfaces of silicon have several different chemical handles through which functionalization may be carried out. It is well known behaviour of the Si/SiO_2 interface [5]. In contrast, the Si-H and Si-X (X=Fl, Cl,Br,I) terminated surface behaviour is relative poorly known.

In this work we analyze the H-terminated Si(100)-2×1 surface behaviour using an semiempirical treatment of the porous silicon/water interface processes.

2. Hydrogen-covered surface of silicon

The reactivity of the silicon surface is controlled in part by the unsatisfied bonding orbitals, called dangling bonds, which remain upon truncating the bulk. Dangling bonds contain single electrons, whereas normal covalent bonds contain two spin-paired electrons. At the surface, atoms can readjust to minimize the total free energy of the system and eliminate the dangling bonds. This process, associated with the loss of coordination of the silicon atoms, is referred to as surface ‘‘reconstruction’’.

The Si(100) surface reconstructs into a (2×1) structure, where (2×1) designates the new periodicity of the surface atoms. The Si(100)- 2×1 surface consists of pairs of silicon atoms (dimers) in adjacent rows that have bonded to each other, thereby reducing to two the number of dangling bonds, Fig.1.

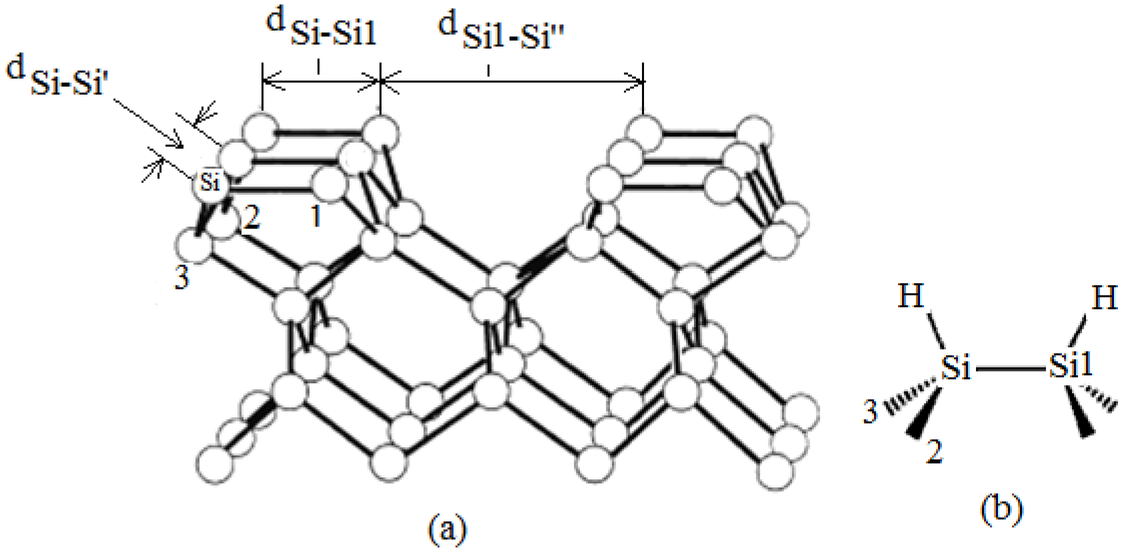


Fig.1: (a) Symmetric Si-Si dimer surface, d_{Si-Si1}*=2.52 Å,* $d_{Si-Si'}$*=3.87 Å,* $d_{Si-Si''}$*=5.15 Å; (b) monohydrides on Si(100)- 2x1 surface (adapted from Fig.1 from [6]*

The resulting surfaces are not stable in air, as they quickly oxidize to form a silicon dioxide layer. On the other hand, silicon surfaces can be rendered relatively stable in air (i.e. relatively resistant to oxidation) by coating the surface with hydrogen. In this case, the outermost layer of Si active surface sites, with one or two dangling bonds, consists of H-terminated Si atoms, named hydrides, Fig.1b, and the newly silicon surface has strongly hydrophobic properties [7]. The fresh sample surface with silicon dioxide layer is more hydrophilic.

Both by hydrides and silicon dioxide surface coverages reduce the activity of surface and the process is known as passivation.

While the devices for filtration and sieving of macromolecules require hydrophobic surfaces, to fill the pores with water solution it is advantageous a more hydrophilic surface. It is therefore desirable to stabilise and to functionalise the surface by the adequate manipulating processes.

It is known that the silicium surface may be functionalized from hydrophobic to hydrophylic properties both by thermal treatements and chemical processes.

The H-terminated surface properties of PS is very similar to same surface of Si(100)-2x1. Thus, the observed values of the desorption activation barrier both for dihydride SiH_2 and for monohydride SiH on PS are very similar to these for Si(100)-2x1 [8]. The hydride-terminated surfaces are reasonably stable and can be prepared and manipulated in air as well as in a number of organic solvents. Thus, high quality materials are available without the need of expensive vacuum systems. Other advantages offered by this surface are their excellent chemical homogeneity (>99% H termination) and strong FTIR vibrational modes (Si-H stretching, ν =2100 cm-1 [9]), which can provide information as to surface flatness.

Despite the Si-H-terminated surface for many applications is precluded due to its propensity to oxidize, it can be easily handled in air for tens of minutes without measurable degradation.

Hydrogen forms more compounds than any other element by one from the three electronic possible processes: 1) loss a valence electron to give H^+ (proton acid); 2) acquisition of an electron to give H^- (hydride); 3) formation of a covalent bond as in CH_4.

The H atoms saturing a Si atom dangling bond named *siligens*, that is, the hydrogen atoms with modified properties (position, charge), so that the central silicon atom is neutral. Because a hydrogen atom is more electronegative (electronegativity 2.1) than a Si atom (electronegativity 1.8), is favorable the transfer of an electron from Si atom to H atom, so that the surface Si-H groups are covalent hydrides. Hydride H^- is known as hydridic hydrogen; it is an anion consisting by one proton and two electrons, is a donor of electrons and reducing agent. The surface-bound Si-H is also known as silyl anion. The polarization induced between the hydrogen and silicon atoms is low because the electron affinity of hydrogen is about that of silicon, Fig.2.

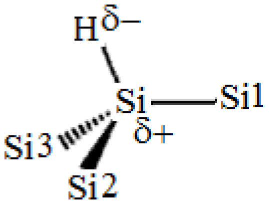


Fig.2.Si-H covalent hydride; $H^{\delta-}$ is hydridic hydrogen (addapted after www.wikipedia)

Hydride group acts as proton acceptor, so that plys a main role in solid surface-water interaction controlling by hydrogen bonds network in the interfacial molecular layer.

3. Dihydrogen bond

Dihydrogen bond is a non-conventional hydrogen bond involving H centers as both the acceptor and donor. This bond has form X-H...H-M and describes the intermolecular interaction between an electronegative atom X (as donor of proton) and a metal- hydride M (as acceptor of proton). Crabtree and coworkers [10] have identified O-H...H-Ir weak interaction in the iridium complexes, with particularities: d(O-Ir)=2.40 Å, d(H...H)=1.8 Å and $\measuredangle$(Ir-O-H)=104.4^0.

The main characteristics of the X-H...H-M systems are: the d(H-H) distances are typically 1.7-2.2 Å, significantly less than the sum of the van der Waals radii for two hydrogen atoms, 2.4 Å; interaction energies are in the range of weak conventional hydrogen bond, 3-7 Kcal/mol.

The best-studied example is the short intermolecular [N-H...H-B] dihydrogen bond (d(H-H)=1.82 Å in length) between an electronegative N atom (as donor of proton) and hydridic- borane B-H (as acceptor of donor) in [NH_3 –BH_3] [11].

A well-defined intermolecular interaction occurs through by dihydrogen bond [C-H...H-B] between the alkenic C-H (as donor of proton) and the hydridic-borane B-H (as donor of proton) having d(H-H)= 2.24 Å, with ca. 0.4 Å shorter than 2.65 Å , the sum of the van der Waals radius [12].

In the XeH$_2$-H$_2$O complex, has identified a dihydrogen bond [O-H...H-Xe] with 4.55 Å

in length and ∡(O-H-Xe)= 165.7^0 [13].

4. Model

Our considerations refer to monohydride terminated ((Si$_3$)Si-H) Si(100)- 2x1 surface /water interface. Si(100)- 2x1 surface geometry is shown in Fig.3. Distances and the angle are from [14].

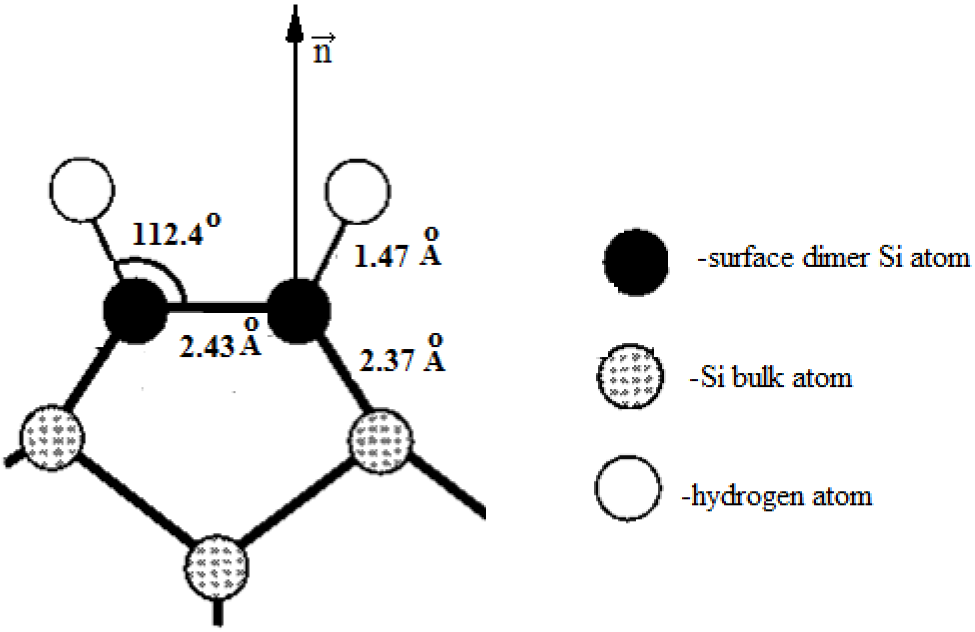


Fig.3. Geometry of Si(100)-2x1 monohydride surface; $\vec{n}$ *is the surface normal versor*

4.1.Water molecule model

The cohesive nature of water is responsable for many of its unusual properties, such as very high surface tension of 72 mN/m at room temperature. Our evaluations are based on the water simple point charge (SPC) model. Interaction parameters are from [15] for water and from [16] for Lennard-Jones parameters of Si.

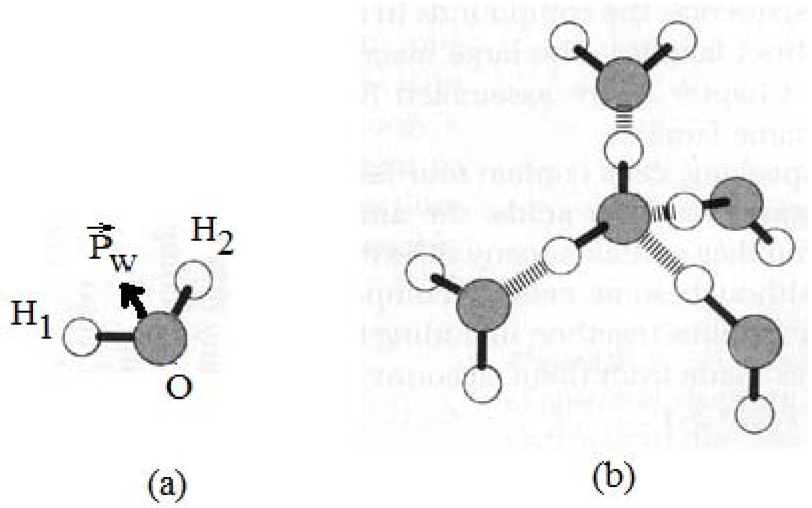


Fig.4 a) Water molecule geometry; $\vec{P}_w$ *is molecular dipole moment; b) the cohesive nature of liquid water via tetrahedral hydrogen bond network ((addapted after* *www.wikipedia)*

Table 1 Force field parameters of the SPC water model and the Si-H group

Force Field Parameter[SI]			
SPC water [15]		Si-H [16]	
ε_O(KJ/mol)	0.6502	ε_{Si}(KJ/mol)	0.6487
σ_O(Å)	3.166	σ_{Si}(Å)	0.3154
q_O(e)	-0.82	q_{Si}(e)	+1
q_H(e)	0.41	q_H(e)	-1
b_0(Å)	1.0		
θ_0(deg)	109.47		

To characterize the solid surface behaviour, hydrophobic or hydriphilic, regarding their contact with a solvent, must be made an analysis of the competitive solid/solvent and solvent/solvent interactions. Because the water molecule has permanent dipole moment, for interfaces of water with a solid phase, interactions are more complex. Besides the exact chemical nature of the substrat, which governs the detailed water/surface interactions, a general characterization of the substrat is given by the affinity of water to contact the surface. Hydrophobicity is observed for nonpolar surface, where the water-water molecules interactions exceed the water-surface interactions, while hydrophilicity characterizes a polar surface for which the water-surface interactions surpass those water-water molecules themselves.

4.2. (Si_3)Si-H)/water interface interactions

a) Hydrophobic interactions are considered by Lennard-Jones (12-6) potential energy corresponding to the associative adsorption of water:

$$U_{LJ}(r) = \left[\left(\frac{\sigma_{Si-O_w}}{r} \right)^{12} - \left(\frac{\sigma_{Si-O_w}}{r} \right)^{6} \right]$$

Where ε_{Si-O_w} and σ_{Si-O_w} are the silicon-oxygen cross-interaction parameters calculated from the Lorentz-Berthelot mixing rules, $\varepsilon_{Si-O_w} = (\varepsilon_{Si}.\varepsilon_O)^{\frac{1}{2}}; \sigma_{Si-O_w} = \frac{1}{2}(\sigma_{Si} + \sigma_O)$.

b). Hydrophylic interactions are considered that the electrostatic interactions between charged atoms Si, H of Si-H group and O,H_1,H_2 atoms of water molecule, corresponding to the dissociative adsorption of water and by addition of the electrostatic (Coulomb) forces:

$$U_{elec}(r) = K\sum_j^2 \sum_i^3 \frac{q_i q_j}{r_{ij}}$$

where $K = 331.2Kcal.\frac{A}{mol}; j = Si,H; i = O,H_1,H_2; q_i, q_j$ are charges of i, j atoms in [C]; r_{ij} is interatomic distance in [Å].

4.3. Water/water interactions

The water-water molecules interaction consists from one Lennard-Jones interaction (between oxygen atoms only) and nine Coulomb interactions between each pair of water molecules,

$$U(r) = 4\varepsilon_{OO}\left[\left(\frac{\sigma_{OO}}{r_{OO}}\right)^{12} - \left(\frac{\sigma_{OO}}{r_{OO}}\right)^{6}\right] + K\sum_j^3 \sum_i^3 \frac{q_i q_j}{r_{ij}}$$

where

$K = 331.2Kcal.\frac{A}{mol}; j = O,H_1,H_2;$ for molecule 1; $i = O,H_1,H_2;$ for molecule 2; q_i, q_j are charges of i, j atoms in [C]; r_{OO}, r_{ij} is oxygen's interatomic distance and interatomic $i, j's$ distances in [Å.].

Electrostatic water-surface interactions intensity mainly depend on the average orientation of the interfacial water molecule. The orientation of a water molecule at solid surface can be specified by two angles: θ_{OH} defined as the angle between an "dangling" OH bond vector of interfacial water molecule and the unit vector normal to silicon surface, and θ_{Pw} defined as the angle between the water molecule dipole moment and the same surface normale. The surface normal vector is defined as pointing toward the water phase. In either rotation plan of the water molecule, $\theta_{Pw} = \theta_{OH} + \frac{\theta_0}{2}$, and for every water molecule, one value for θ_{Pw} two values of θ_{OH} are obtained. Thus, for full orientational water molecule information both the angles must be considered.

Whole range of values for the water molecule angles is shown in Fig.5. Several corresponding typical orientations of water molecule are depicted also.

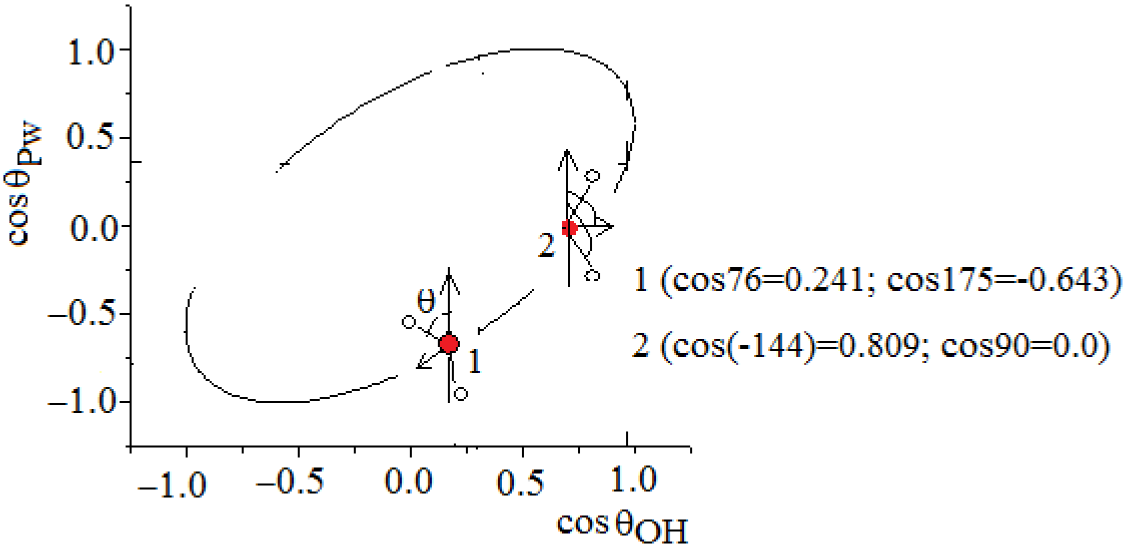


Fig.5. The joint distributions of the possible water molecule θ_{OH} *and* θ_{Pw} *angles values in* $cos(\theta_{Pw}) - cos(\theta_{OH}))$ *plane. It is an ellipse.*

Hydrophobic interactions water-silicon surface stabilizes the oxygen atom of water molecule with the energy $\varepsilon_{Si-O_w} = -0.14 Kcal/mol$, at distance $d_{Si-O_w} = 3.8908 A$ (measured from Si surface atom).

Electrostatic interaction energies depend on the water molecule orientation. In Fig.6 is shown the dependence of the total water-silicon surface interaction potential energy on θ_{OH}.

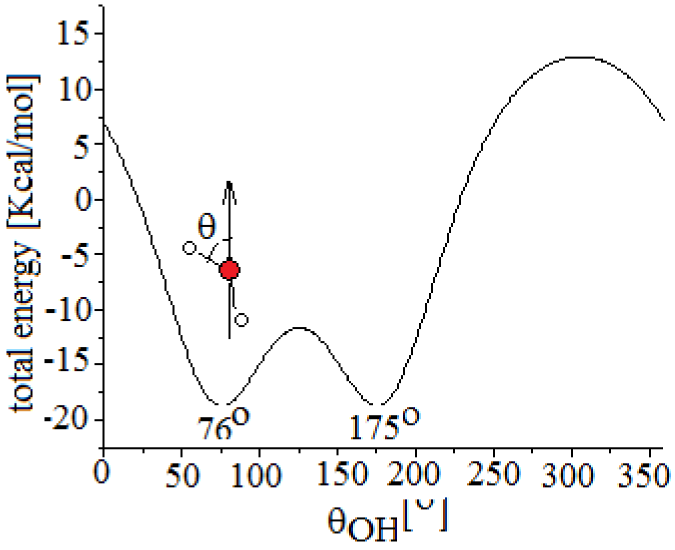
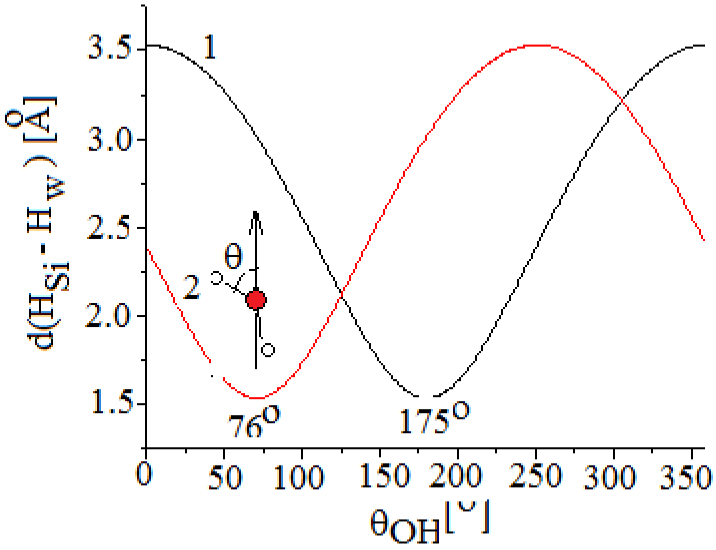


Fig. 6. Dependence of total water-silicon surface interaction potential energy on θ_{OH} *. The equilibrium state (minimal potential energy* $\approx -18 Kcal/mol$ *) of the system is possible for the water molecule orientation identified by* $\theta_{Pw} \approx 127^0$ *and* $\theta_{OH} \approx 76^0$ *and* $\theta_{OH} \approx 175^0$ *it is marked in Fig.5 as position 1.*

Our following considerations needs both the orientation of the ”dangling” OH bond and the distance between H atom of Si-H and H atom of OH, denoted $d_{H_{Si}-H_w}$. In Fig.7 is shown the dependence of $d_{H_{Si}-H_w}$ on the water molecule orientation specified by θ_{OH}.



In Fig.7. Dependence of the $d_{H_{Si}-H_w}$ *on the water molecule angle* θ_{OH}. *The* $d_{H_{Si}-H_w}$ *is minim for the equilibrium state marked in Fig.6.*

On the other hand, the cohesion energy of the water liquid molecules, is $\varepsilon_{w-w} \approx 10kcal / mol$ [17]. This value is in agreement with the formation energy of two hydrogen bonds of each water molecule in liquid phase, i.e., $2 \cdot (8k_BT) = 2 \cdot 4.768Kcal / mol \approx 10Kcal / mol$. According an usual geometric definition of the hydrogen bond, two water molecules are hydrogen-bonded if $r_{O-O} < 0.35nm$ and $\angle O...O - H < 30^0$ [18].

The ”dangling” OH of the interfacial water molecules are a key factor of silicon surface behaviour. What hydrogen bond, classical O-H bond between water molecules or non-conventional dihydrogen bond Si-H...H-O between hydridic hidrogen of monohydride Si-H and H-O group of water molecule is possible?

From the above results, the following geometry of the interface partners configuration is attended, Fig.8.

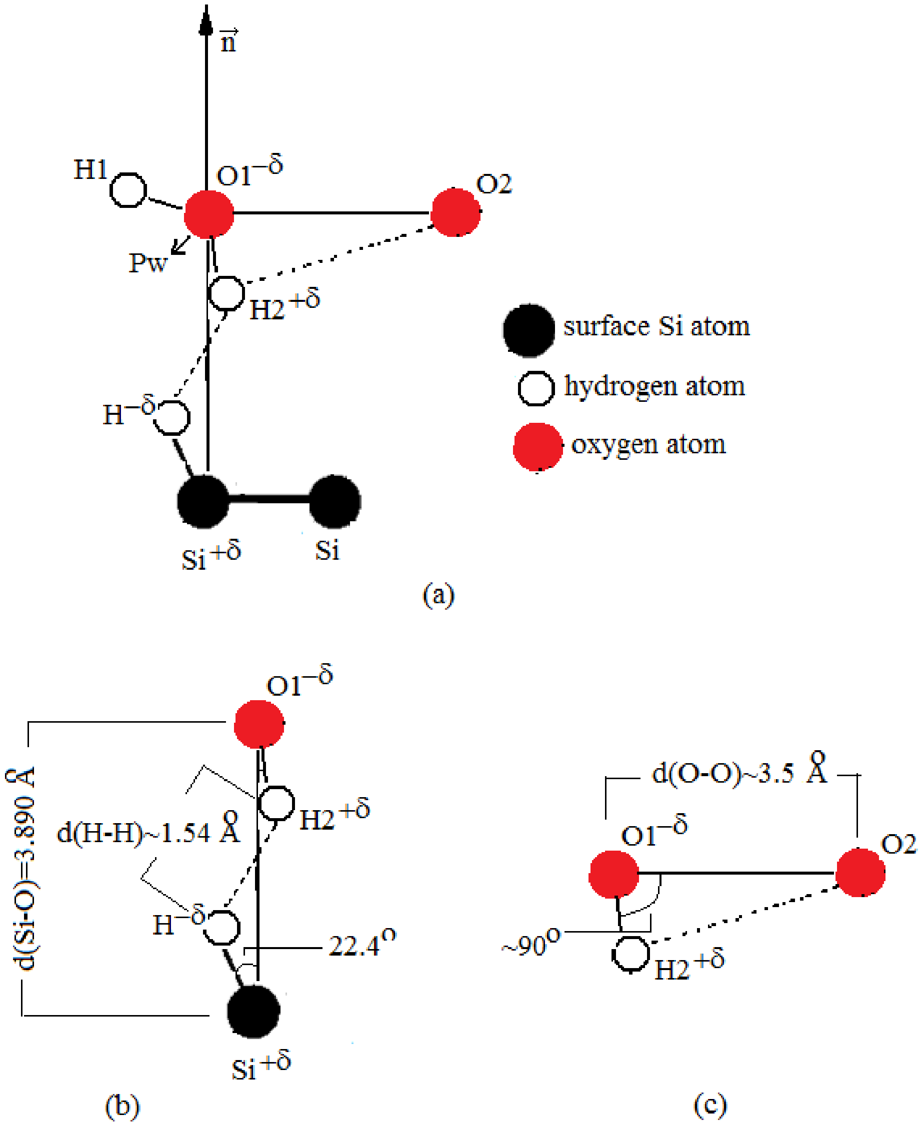


Fig.8.(a) Geometric characteristics of the interface equilibrium configuration. $d(O_1 - O_2) \approx 3.51A$ is the adsorbed water pair separation: (b) geometrical details of dihydrogen bond Si-H....H-O; (c) geometrical details of classical hydrogen bond O-H....O.

5. Results and discussions

Equilibrium orientation of the water molecule at silicon surface given by $\theta_{OH} \approx 76^0$ and $\theta_{OH} \approx 175^0$ and $\theta_{Pw} \approx 127^0$ angles is consistent with the water concentration profile for the first water layer for smooth surfaces of silicon nanotubes obtained using molecular dynamics simulations; it has a peak for $d \approx 3A$, Fig.1 from Ref.17. The orientation $\theta_{OH} \approx 175^0$ reduces the hydrogen bonds water-water number because the constraints of the hydrogen bond are not satisfied; the $\angle O...O - H \approx 90^0$ is too large for classical hydrogen bond. Instead the dihydrogen bond Si-H...H-O is more favorized: $d_{H_{Si}-H_w} \cong 1.5A, \angle O...Si - H < 30^0$. This dihydrogen bond grows the hydrogen bonds umber between the interfacial water molecule and silicon surface, so that this surface has hydrophilic behaviour.

On the other hand, a feature of the compounds containing dyhidrogen bonds is that they release H_2 quite easily [19]. For silicon, the reaction

$$H + (Si_3)Si - H \rightarrow H_2(g) + (Si_3)Si -$$

is energetically favorable since the energy of a H-H bond is higher than the energy a Si-H bond (4.5 eV compared to ~3.2 eV), so that any very efficient desorption processes compete with the hydrogen adsorption [20]. This process ends with a silicon dangling bond so that is enhanced passivation process by hydrogen adsorption and the newly silicon surface has strongly hydrophobic properties [6].

Molecular dynamics simulations predict atomic hydrogen adsorption to be the dominant process over other interfacial processes that reflection and molecular hydrogen desorption, with a probability of 60% even on an already fully passivated surface. Thus the hydrogenated surface of silicon mentains the hydrophobic properties. A macroscopic measure of the surface hydrophobicity is the water contact angle θ_C. Molecular dynamics simulations concerning the effect of surface polarity (defined as the surface total dipol moment) and the interfacial water orientation [21] find that each of three properties, contact angle, surface polarity, and water molecule orientation at the interface quantifies the hydrophobicity/ hydrophilicity of the surfaces.

A hydrophobic Si(100) surface condition is observed after alkaline treatments, like CMP (Chemomechanical polishing) at a pH of about 11 or after etching in alkaline solutions [22], i.e., $\theta_C > 50^0$. This behaviour is an experimental proof of the our above considered mechanisms.

6. Conclusions

To summarize, we have analysed the local intermolecular interactions at the hydrogen-terminated Si(100)-2×1 – water interface, known as a hydrophobic surface. Considerring both the Lennard-Jones and electrostatic contributions for the silicon surface-water and water-water interactions, we have shown that it is probable a Si-H...H-O dihydrogen bond between silicon surface and the interfacial water molecule. Due to their strong reducing character the (Si_3)-H^- siylil anion behaves as an acceptor of proton. This non-conventional dihydrogen bond between silicon surface and interfacial water is competitive with the classical hydrogen bond of between interfacial water-water molecules so that reduces hydrophobicity of surface. We suggest that the presence of any dihydrogen bonds Si-H...H-M, where M is a metal normal or transition metal ion at silicon/biological environment interface, recommands the PS for biomedical applications as biomimetic selective transport of ions, drug delivery, etc.

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