THE ADSORPTION KINETICS OF HYDROGEN-LIKE PARTICLES IN POROUS Si

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We have modeled the processes of adsorption of hydrogen-like particles in porous silicon at the initial time moment of the physical adsorption. A model of cylindrical pores in Si is developed with regard for hydrogen admixtures. We have calculated the potential energy of interaction of drifting particles with the wall of a pore and determined the parameters of the adsorption centers. The simulation algorithm which is based on the methods of molecular dynamics and accounts the phenomena of diffusion, drift, adsorption, and desorption is proposed, and the distributions of the concentrations of adsorbed particles at various pressures and temperatures are obtained.

1. Introduction

At present, the studies of the processes of adsorption-desorption of hydrogen molecules in porous materials, in the first turn in porous Si, rise a considerable interest of researchers. First, the hydrogen-based power industry is considered as one of the promising alternative ways to get energy. Its advantages include the energy capacity, ecological safety, and technological pliability, and, as a drawback, the problem of the creation of compact solid-material tanks of hydrogen should be mentioned. The most promising materials from the viewpoint of the accumulation of hydrogen are metal-hydrides, carbon nanotubes, and porous silicon [1–3].

Second, a significant attention is paid to the peculiarities of the behavior of porous Si in the atmosphere of gases and vapors of various compounds [4–13] from the viewpoint of the creation of efficient gas- and biosensors with the use of various electrical, optical, or luminescent transducers. The high-speed response and the sensitivity of such sensors are defined by the phenomena of transport and adsorption of molecules from the environment inside a porous structure [9–13]. Till now, the studies in this field have been focused on the methods and algorithms of porometry [9, 10] and on the experimental and theoretical description of the parameters of an equilibrium state under adsorption interaction [11–13]. At the same time, the description of the dynamics of the processes of adsorption [especially the description of regularities of the deposition of

particles at the initial time moments (the time intervals are of the order of several pico- or nanoseconds and are related to the characteristic time of the process of physical adsorption)] has attracted the insufficient attention, though this information is needed for the prediction of of parameters required to realize the capture of substances from the ambient atmosphere. The simulation of the relevant phenomena for the known geometry of the disordered structure of Si allows one to determine the temporal regularities of both the deposition of molecules of the ambient environment on the walls and the filling of pores by them.

The purpose of this work is the simulation of the processes of adsorption of hydrogen-like particles in porous silicon at the initial time moment of the physical adsorption.

2. Model of Adsorption of a Hydrogen-like Particle in a Pore of Si

2.1. Model of a pore in Si

One of the most spread geometries of pores is a cylindrical one. Moreover, the modern technologies allow one to fabricate specimens with the exact form, depth, and the diameter of holes [4]. In addition, the cylindrical geometry is a good approximation for pores obtained by usual methods of electrochemical etching [4, 5]. Therefore, as the geometric model of a pore in Si, we chose a circular cylinder with diameter d and height (depth) h (Fig. 1). The wall is considered smooth and defectless.

In freshly prepared porous Si, the walls of pores are densely covered by hydrogen groups [3, 5]. Therefore, it is necessary to account their presence, which is realized in the following way. The surface of the wall of a pore contains periodically positioned sites of the Si crystal lattice, whose free bonds are connected with atoms of hydrogen. Each broken surface bond takes one adatom of hydrogen. That is, we accept the model of a one-layer coating. Groups $Si-H_3$ and $Si-H_2$ are not taken into account. Atoms

of hydrogen are positioned along the walls periodically with a step equal to the lattice constant of Si a. Oxygen and the other admixtures were not introduced in the model. On the holding of a specimen under conditions of darkness and superhigh vacuum, its chemical composition is practically invariable [2]. Therefore, we can experimentally verify the results of theoretical calculations on freshly prepared specimens.

The axial symmetry of the problem allows us to pass from the three-dimensional geometry of a cylinder to a two-dimensional rectangle. Along the lateral sides, the one-dimensional chains of hydrogen atoms connected with Si are positioned. In this case, we introduce the Cartesian coordinate system (x, y, and the radius vector r) with the origin on the specimen surface in the middle of the pore.

2.2. Parameters of particles

For the problems of physical adsorption, a widespread model of adsorbate molecules involves spherical Lennard-Jones (LJ) particles [9, 14]. Such an approximation allows one to account exclusively the van der Waals forces of interaction which are described by the Lennard-Jones potential:

$$U_{\mathrm{LJ}}(r) = 4\varepsilon_{\mathrm{LJ}} \left[\left(\frac{\sigma_{\mathrm{LJ}}}{r} \right)^{12} - \left(\frac{\sigma_{\mathrm{LJ}}}{r} \right)^6 \right], \qquad (1)$$

where $\varepsilon_{\mathrm{LJ}}$ is the energy of a minimum of the potential, and σ_{LJ} is the characteristic diameter.

One of the most wide-spread realizations of such an abstraction involves molecules of hydrogen, inert gases, and methane. Therefore, as the adsorbate, we took hydrogen-like spherical Lennard-Jones particles.

Particles go to a pore from the ambient atmosphere. Near the surface of a pore, their concentration C_0 is held to be constant, and the parameters used in calculations are as follows:
– radius (linear size) of a particle r_{H} (or the effective cross-section σ) $r_{\mathrm{H}} = \sigma_{\mathrm{LJ}} = 0.2138$ nm, i.e., it is the the effective radius of overlapping of the electron spheres for the van der Waals interactions;
– m is the particle mass, $m = m_p = 1.672614 \times 10^{-24}$ g, i.e., the proton mass.

2.3. Force field inside a pore

The potential energy and forces acting on a particle depend on its parameters and a periodic field created by hydrogen atoms adsorbed on the walls of a pore. These
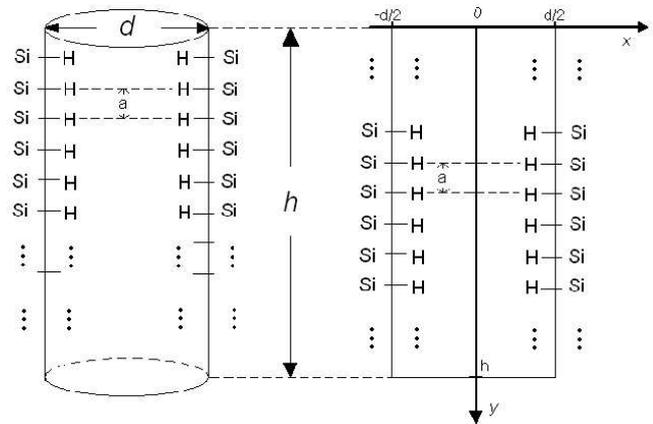

Fig. 1. Geometric model of a pore in Si

atoms screen practically completely the field created directly by a Si wall [15]. In the chosen model of particles, it is sufficient to account only the van der Waals interaction with adatoms of hydrogen which is defined with the help of the Lennard-Jones potential. The potential was calculated directly as a superposition of fields of adsorbed particles which are located at distances not more than the critical radius of the van der Waals interaction. We took it as $r_c = 2.5\sigma_{\mathrm{LJ}}$.

2.4 Simulation of the motion of particles in a pore

The main task of the present simulation is to calculate the dynamics of the processes of adsorption. Therefore, we chose two approaches to its solution: molecular simulation within the method of random walks and the solution of the Dirichlet problem for the diffusion equation [16, 17].

The assumptions valid for all approximations in this work are as follows:
– No interaction between particles is present. Collisions are elastic, and the scattering is isotropic. This is accounted by the simulation with the use of random walks and the diffusion approach,
– We do not consider the phenomena of the generation of drops, condensation, and surface tension (due to the approximation of the absence of any interaction between particles),
– Forces act only between the adsorbent and the adsorbate. That is, the drift appears near the walls of a pore (near the upper absorbed layer),
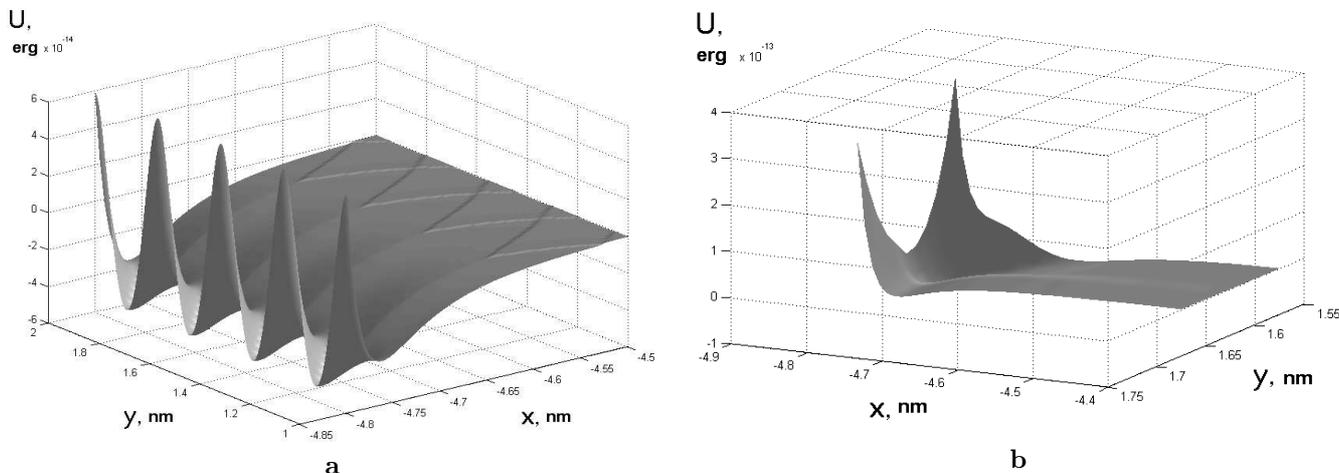– Pressure and temperature are constant, i.e., no flows appear due to the gradients of temperature and pressure.

Fig. 2. Potential energy of particles in a pore: near the wall (*a*) and near the minimum of the Lennard-Jones potential which serves as a center of adsorption (*b*)

The account of the deposition of particles on the wall leads to a considerable change of the calculation of the dynamics of the model. Therefore, as the algorithm of calculations, we took random walks within the methods of molecular dynamics with a fixed duration of steps. On each step, we consider the following processes:

1) A new portion of particles, which is determined by the concentration of a gas in the ambient atmosphere, goes to pores,

2) Such parameters of a step as the free path length λ and the value of a displacement δ are calculated,

3) For all particles which are present in a pore as of the given time moment and are not adsorbed, we calculated:

– Components of a diffusion displacement (due to random collisions),

– Components of a drift displacement (due to the potential in a pore). Moreover, the potential is recalculated in order to account the contribution of earlier adsorbed particles to the field,

– Coordinates of the nearest free center of adsorption and the probability of the capture by it.

4) The condition of desorption is verified. If it is satisfied, one of the surface deposited particles becomes free in the random way.

3. Results of the Simulation

3.1. Field structure in a pore

The distribution of the potential for the initial state of the model is shown in Fig. 2,*a*. The fields of opposite walls do not overlap with each other. Therefore, in order to represent the structure of the potential, we can

restrict ourselves by the scale of several adatoms near one of the walls.

The analysis of plots indicates the presence of stable potential wells in the field. Just they can serve as the centers of adsorption. They are positioned halfway between adatoms of hydrogen and at a fixed distance from the wall of a pore. That is, the adsorption is accompanied by the appearance of a dense packing of particles.

The adsorbed particles induce two main changes. First, they occupy the corresponding center of adsorption, and, second, they become the centers of a field analogous to the input centers (hydrogen adatoms) by their properties. These particles change the properties of adjacent centers of adsorption and create new centers for the deposition of next layers.

In order to create a center of adsorption for the deposition of particles of the next layer, it is necessary that two deposited particles occupy adjacent potential wells. The calculations show that the centers of adsorption, which appear for particles of the next layers, have parameters similar to those of the input state of the model. This is a result of both the screening of the field of particles positioned in subsurface layers and the existence of the critical distance for the action of the Lennard-Jones potential (1) which covers the neighborhood with 2 adatoms. That is, the potential is formed by deposited particles of the surface layer.

The results of calculations are generalized in the following way:

– The depth of a potential well $U_{\min}$, which is the binding energy of an adsorbed particle, is 5.21×10^{-14} erg in the
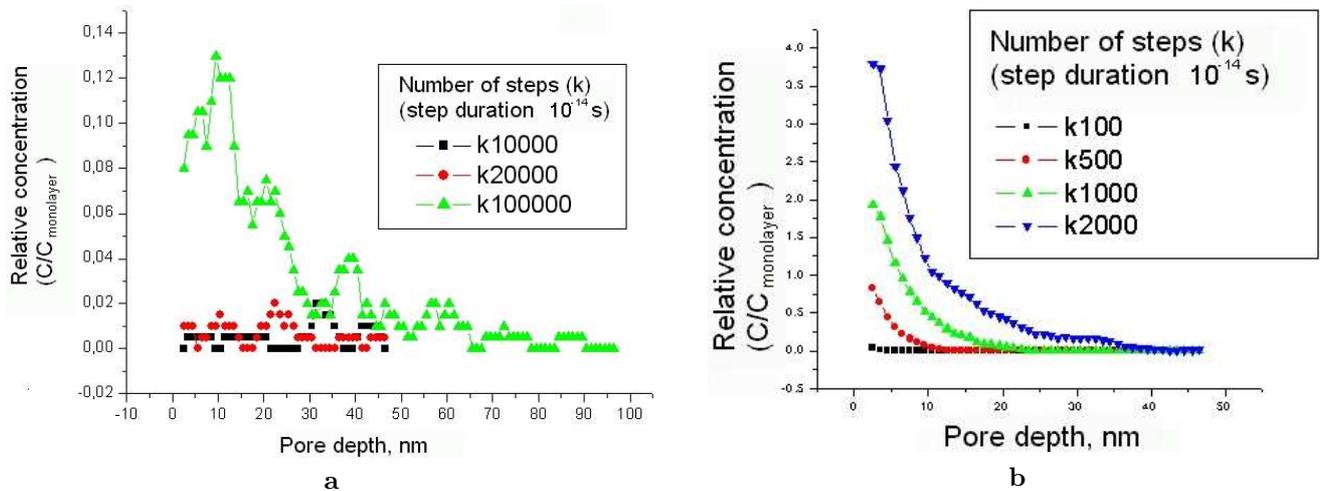
Fig. 3. Relative concentrations of adsorbed particles versus the depth for various numbers of steps for the concentrations of particles in the atmosphere $C_0 = n_0$ (*a*) and $100n_0$ (*b*). Desorption is not taken into account. The pore diameter is equal to 10 nm, and the temperature is equal to 293 K

case of its deposition into the next layer (the neighbors are absent) and 7.4×10^{-14} erg in the presence of adsorbed neighboring particles in the corresponding layer. That is, a particle, which is positioned in a dense packing, is bound more strongly than a particle deposited on the surface.

– The distance between the layers of adatoms, like the distance from the upper layer to the empty center of adsorption, is constant and is $r_{\min} = 0.21$ nm. The distance between particles of a layer is equal to the lattice constant of Si (0.25 nm). Each next layer of particles is shifted relative the previous one by a half of the lattice constant of Si, i.e. the adsorption is accompanied by the formation of a dense packing of particles.

– The potential well of the center of adsorption is narrow with a half-width of about 0.05 nm, which allows one to exactly localize a captured particle.

3.2. Distributions of concentrations in a pore

The main parameters which are set at the beginning of a simulation are the initial value of a step (from which we determine the fixed duration of a step), the concentration of particles near the surface (whence we calculate the number of particles which fall into a pore during a step), and the number of steps (i.e., the duration of the process). By choosing the value of a step, we accept that it cannot be greater than a half-width of the potential well of a center of adsorption. At the same time, too small values of a step cause the significant increase in the time of calculations. Therefore, we took the following numerical values of parameters: $\delta_0 = 0.1a = 0.025$ nm – the initial value of a step, $\tau = \delta / \bar{v} = 1 \times 10^{-14}$ s – the duration of a step (at room temperature).

Below, we give the following limits of variation of the parameters:

– $C_0 = (1 \div 100)n_0 = (2.5 \times 10^{19} \div 2.5 \times 10^{21})$ cm^{-3} – the concentrations of particles near the surface which correspond to the normal and high atmospheric pressures. The simulation in the case of high pressure was performed for the sake of greater clearness of the processes of adsorption (the greater number of particles goes into a pore and is deposited).

– $d = 2$, 10, and 50 nm – the diameters of a pore corresponding to micro-, meso- and macroporous silicon.

– $T = 77$ and 293 K – the temperature corresponding to the cooling by liquid nitrogen and room one.

The number of steps is a variable parameter which determines the duration of the process.

According to the chosen values of parameters, we separate the results into three blocks.

3.2.1. Simulation for different concentrations of particles at a source

The results of simulations for different numbers of steps without regard for the processes of desorption at different concentrations of particles near the surface (all other parameters are the same) are given in Fig. 3.
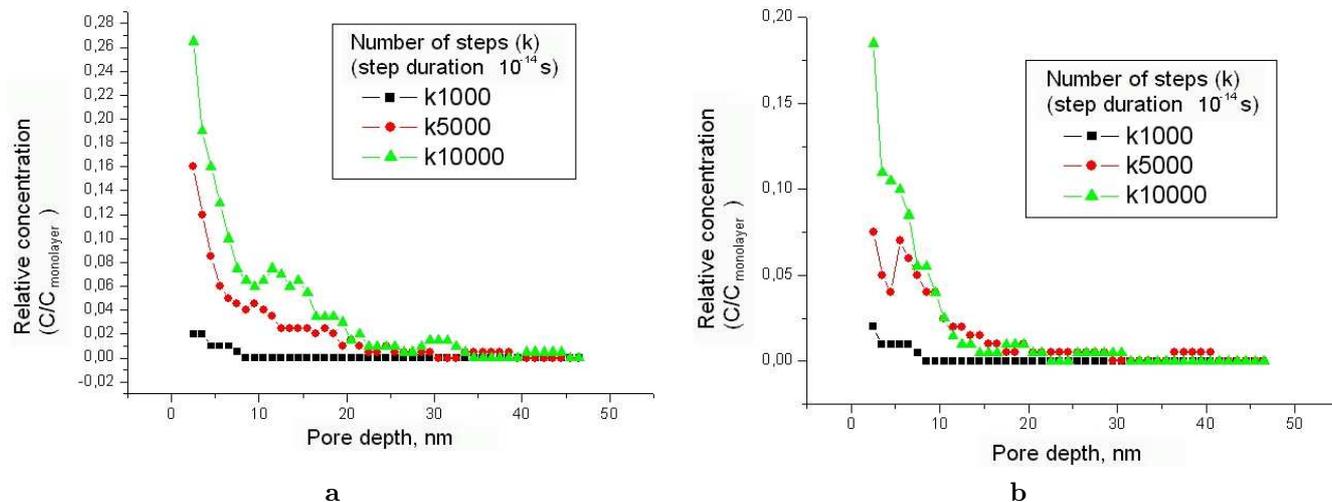
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Fig. 4. Relative concentrations of adsorbed particles at a temperature of 77 K versus the depth for various numbers of steps (the corresponding time range is from 0.01 to 1 ns) without regard for desorption (*a*), and with regard for it (*b*). The concentration of particles in the atmosphere $C_0 = n_0$ (atmospheric pressure), the pore diameter is 10 nm, and the temperature is equal to 77 K

At a smaller pressure, i.e. at a smaller concentration of particles at a source, the processes of filling of a pore are slower, but they require the smaller amount of calculations (see Fig. 3,*a*). The last circumstance appears due to a small number of particles in a pore and allows the simulation for greater time intervals. The high concentrations of particles give a more clear pattern of the processes of adsorption (see Fig. 3,*b*). But the calculations are carried on slower, which restricts the time interval of the process.

The account of desorption at room temperature gives, as a result, that the deposited particles are absent, on the average, on the walls of a pore. That is, there occurs the dynamical exchange between the wall and the medium inside a pore.

That is, the accumulation of particles inside a pore and the adsorption are faster for greater concentrations of particles at a source (for greater pressures). All other regularities are similar.

3.2.2. Simulation for different temperatures

The results of simulations for different numbers of steps without regard for the processes of desorption at different temperatures (all other parameters are the same) are given in Figs. 3,*a* and 4.

At smaller temperatures (77 K), the filling of a pore goes slower, particles penetrate smaller depths, but the processes of adsorption run faster (see Fig. 4). With regard for the desorption, the concentration of particles on the walls of a pore increases, as distinct from the case of room temperature.

3.2.3. Simulation for different diameters of pores

A change of the diameter of a pore leads to the essential change in the results of the simulation (see the Table).

A micropore (with a diameter of 2 nm) does not accumulate particles under normal conditions (the atmospheric pressure and room temperature). That is, those particles which fall in a pore are pushed backward into the ambient atmosphere. In such a way, the average number of particles in a pore is equal to zero. At greater pressures (100 atm), the situation is preserved. At lower temperatures (77 K), there appears the capture on walls, but also in small amounts. However, the account of the desorption indicates the absence, on the average, particles on the walls.

A macropore (with a diameter of 50 nm) accumulates a considerable number of particles, but the adsorption at room temperature does not happen. At a temperature of 77 K, particles are captures on walls, but the processes run slower as compared with a mesopore. This can be explained by other mechanisms of adsorption in pores of great diameters (such as the capillary condensation).

Number of particles in pores with various diameters as of the time moment of 100 ps

Pore diameter, nm	Total number of particles in a pore	Number of adsorbed particles
2	4	0
10	34	9

We note that the proposed model does not account the phenomenon of condensation of particles which can occur at their great concentrations.

4. Conclusions

The proposed model allows one to calculate the parameters and the spatial structure of adsorption centers, as well as the dynamics of the processes of physical molecular adsorption and desorption of hydrogen-like particles in pores of Si for the initial time moments, which was not realized within the well-known models.

The accumulation of particles in a pore increases with its diameter. The characteristic times of adsorption in a mesopore with a 10-nm diameter under normal conditions are of the order of 0.1 ns, which coincides with experimental data. In pores of greater diameters, the processes run more slower. In pores of smaller diameters, particles are not practically accumulated.

The concentration of adsorbed particles increases with the pressure and with decrease in the temperature.

The phenomena of desorption lead to the dynamical exchange by particles between the wall and the medium in a pore. Moreover, the concentration of adsorbed particles at room temperature is zero on the average. The cooling of a system favors the increase in these concentrations.

Thus, porous Si can serve as an accumulator of hydrogen-like particles if the diameter of a pore is greater than 5 nm. The regularities of adsorption, which are obtained on the basis of the van der Waals interaction and the processes of polymolecular growth, require the further development with regard for the phenomena of interaction between particles and condensation. The proposed algorithm can be generalized for the simulation of the adsorption of other, more complicated molecules with the corresponding changes in the parameters of interaction. Therefore, the mentioned questions require the further studies.

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КІНЕТИКА АДСОРБЦІЇ ВОДНЕПОДІБНИХ ЧАСТИНОК У ПОРУВАТОМУ КРЕМНІЇ

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Р е з ю м е

Проведено моделювання процесів адсорбції воднеподібних частинок у поруватому кремнії в початковий момент фізичної адсорбції. Створено модель циліндричної пори кремнію з врахуванням домішок водню. Розраховано потенціальну енергію взаємодії дрейфуючих частинок із стінкою пори. Визначено параметри центрів адсорбції. Розроблено алгоритм моделювання на основі методів молекулярної динаміки, що враховує явища дифузії, дрейфу, адсорбції та десорбції. Отримано розподіли концентрацій адсорбованих частинок при різних тисках та температурах.