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Strain of Plates of Aluminum, Glass, and Silicon at Sorption of Water Vapor

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Abstract—It has been suggested and realized a kinetic approach to the investigation of sorbostriction isotherms on plates of aluminum, glass, and monocrystalline silicon at the sorption of water from its vapor. It is established increasing the plate area and decreasing the plate thickness with passing the contraction through a minimum in the process of sorption. The strain observed is explained by the interference of two effects: the influence of variation of the surface tension of the outer surface of samples and the role of micropores (with possible chemisorption in them).

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INTRODUCTION

As is known, sorption processes on solid surfaces are subdivided into physical and chemical ones. The criterion of referring a process to one or another group is the value of the energy of binding sorbate molecules to the surface. For this purpose, they often use in practice the desorption temperature that is about 190°C for physically adsorbed water molecules on the oxidized silicon surface [1]. The case of chemisorption is more complex and actually is only the stage of decomposition of water molecules with formation and chemisorption of hydroxyl groups already more firmly bonded with the silicate frame (the temperature of a maximum rate of dehydroxylation of surface is estimated as 600 K [1]). Both the groups of sorption processes at the surface are in action at atmospheric conditions.

In the literature devoted to the gas and vapor sorption, an adsorbent is often assumed to be inert, i.e. not changing its properties at adsorption. However, this assumption is valid only in the first approximation. A wide literature is devoted to the influence of adsorbed particles (molecules and ions) on the properties of solids [2]. In particular, there was investigated the influence of various adsorbates on the geometrical dimensions of an adsorbent. For this, solids of high porosity were usually investigated. The reason for such choice of samples is a relative simplicity of determining the coverage of surface with an adsorbate by traditional methods. According to the literature data, the experimental dependence of the adsorbent dimensions on the specific amount of adsorbed matter (or on the relative pressure of the gas phase of an adsorbate) is a curve of a complex shape, having two (or more) different parts: a decrease of linear dimensions (“contraction”) at a small surface coverage (to 20–30% of a monolayer) and an increase of the size (“expansion”) at a surface coverage more than 30%. Sometimes, one more expansion can be previous to the first stage [3].

The phenomenon of the sorption strain of an adsorbent attracted the attention of researchers for a long time (at least, since 1927). Papers by Yakovlev and Berin [4, 5] are devoted to this problems and contain a circumstantial analysis of the problem. Several attempts of theoretical explanation of the observed experiment dependence of the adsorbent strain on the degree of surface coverage were not crowned with success. Early theories of Bangham and Flood managed to explain only the last part of the adsorbent strain curve (expansion). These theories could not explain the phenomenon of contraction developing at a small surface coverage as well as the primary expansion. The experiment curve of the adsorbent strain was described more successfully with the aid of the “osmotic” theory of adsorption equilibrium [5] that considered for the system gas/adsorbent as two-component (in contrast with the above theories where this system treated as one-component) on the base of the theory of solutions. In [6], a pheno-menological theory was formulated on the mechanochemical

Table 1. Characteristics of the samples investigated

Run no.	Material		Dimensions of the plates, cm			Thickness variation in water vapor	
			Width A	Length L	Thickness H	$\Delta H_{\max}$, μm	$\Delta H/H$, %
1	Aluminum, oxidized foil		1.0	5.0	0.03	–2.4	–0.9
2	Quartz glass	K1	2.0	3.0	0.07	–12.0	–1.7
		K2	2.0	3.0	0.07	–12.0	–1.7
3	Glass slide	C1	1.5	3.8	0.10	–4.0	–0.4
		C2	1.5	6.0	0.10	–8.0	–0.8
4	Glass disk		Diameter 10.0		0.10	–10.0	–1.0
5	Monocrystalline silicon, surface orientation (100), disk		Diameter 10.0		0.05	–4.0	–0.8

ground explaining the areas of both contraction and expansion in the experiment curve of the sorption strain.

However, the above theoretical considerations are phenomenological and do not discover a specific mechanism of the phenomena observed in experiment. Only in [7] at simultaneous using three investigation methods (adsorption, dilatometry, and the IR spectroscopy), an attempt was made to explain the process of contraction of a microporous adsorbent by decreasing the distance between active centers of adsorption on the surface (the oxygen or silicon atoms) due to the development of hydrogen bonds between OH-groups (vicinal silanols) sorbed on these centers. As for the adsorbent expansion at a high surface coverage, it is described by the mechanism still suggested by Bangham who related variations of the bulk modulus to variations of surface free energy at adsorption. It was established that sorbates whose molecules has no dipole or quadrupole moment cause only expansion of an adsorbent at a high coverage, whereas polar molecules lead to its contraction at the surface coverage of 0.2 to 0.3, and passing to expansion is observed at a larger surface coverage. These date confirm the theoretical prediction [6] that the stronger the adsorbate/adsorbent interaction (with approaching chemisorption as a limit), the larger is probability of observing the adsorbent contraction at the earlier stage of sorption.

As was already noted above, the investigation of sorbostriction was carried out for microporous bodies up to the present time. The works where an adsorbent was a compact material with a low specific surface, are unknown for us, although the importance of such studies is evident. First, an adsorbate penetrates much more slowly (by days) in the bulk of such an adsorbent, which makes easier the kinetic investigation. In the course of sorption at the 100% saturation with the adsorbate vapor, the adsorbate passes all the stages of surface coverage that are observed at obtaining the adsorption isotherm, but here the whole picture (including the sorbostriction isotherm) is observed in one experiment. This is a new methodological approach. Second, at the existence of a smooth outer surface, the effect of surface tension of the whole sample arises that, together with the effect of (small in our case) porosity, contributes to sorbostriction. This contribution is small, but interesting in the scientific respect. Similar chemomechanical effects are usually investigated at observing the bending thin console plates whose one side is inaccessible for an adsorbate (see [8–10]). If, however, the complex investigation of the influence of both the porosity and the outer body surface on sorbostriction, one has to deal with the two-sided adsorption on plates.

This work is devoted to investigation of the kinetics of sorbostriction at sorbing water on compact samples of aluminum, glass, and silicon with the aim of testing the novel approach to the study of the phenomenon.

EXPERIMENTAL

The investigations were carried out on plates or disks made out of the materials whose characteristics are shown in Table 1. Besides the geometrical dimensions of initial samples, Table 1 exhibits the values of a maximum change of the size controlled (the plate thickness) at the action of water vapor, and also the average values of the relative contraction of samples.

The most detailed investigations were performed with silicon plates. Before a cycle of measurement, samples of monocrystalline silicon were subjected to

Table 2. Average dimensions of Si (100) plates

Thickness of oxide film on plates h, Å	In “dry” atmosphere			At 100% humidity				
	$\overline{H}$, μm	$\overline{D}$, cm	V, cm^3	$\overline{H}$, μm	$\Delta H/H$, %	$\overline{D}$, cm	V, cm^3,	$\Delta V/V$, %
30	437.8	9.9800	3.423	433.8	–0.91	9.9814	3.393	–0.88
100	443.8	9.9780	3.469	440.8	–0.67	9.9795	3.446	–0.66
300	438.0	9.9852	3.428	434.6	–0.78	9.9848	3.401	–0.79
500	446.5	10.0026	3.508	442.3	–0.94	10.0028	3.473	–0.97
1000	446.0	10.0088	3.507	443.0	–0.67	10.0095	3.484	–0.65
					Av. –0.79			Av. –0.79

the standard operation of cleaning accepted in the microelectronic technology. Then the metering oxidation of the Si (100) surface was made. Given thicknesses of oxide films h were obtained by thermal oxidation in a diffusion furnace. The experimental sample had oxide films of three kinds: natural oxide (h ~3 nm); thermal oxide (h ~10–30 nm, the oxidation temperature 850°C, dry oxygen); thermal oxide ($h \geq 60$ nm, the oxidation temperature 1000°C, humid oxygen). The oxide film thickness was determined with the aid of an ellipsometer LEF-3M.

The plate size under control was mainly determined by mechanical instruments: the plate thickness H by micrometric indicator MIG with the scale factor 1.0 μm. The average thickness $\overline{H}$ was calculated from eight measurements in various points of a plate. The accuracy of the average values of $\Delta\overline{H}$ was estimated as ±0.6 μm. The plate diameter $\overline{D}$ was measured with a micrometer with accuracy ±5 μm. In parallel with mechanical instruments, the scanning microscope “Stereoscan-360” with magnification 200× was used for the size determination. Herewith, the accuracy of average values of $\Delta\overline{H}$ was ±1 μm. The results of measurements ν with the aid of the indicator and the microscope were in a satisfactory agreement, but the accuracy of the first method turned to be higher.

The investigations were carried out according the following program. First, they measured values of $\overline{H}$ and $\overline{D}$ for samples under the atmospheric conditions. Then the samples were placed for 4 days in the dry atmosphere of an exsiccator containing concentrated H_2SO_4 (oleum) or P_2O_5 where the humidity was controlled with a hygrometer and was 0–5%. After that, under the atmospheric conditions, they measured new values of $\overline{H}$ and $\overline{D}$ that were taken for initial for the experiment. After the measurements, the samples were transferred to another exsiccator and kept in the vapor of a distilled water at the 100% humidity for various time τ from 2 to 18 days. Once a day, the samples were extracted from the exsiccator for measuring during 15–30 min, after that were returned to the exsiccator. In this way, kinetic curves were obtained for $\overline{H}$ and $\overline{D}$. Since the time of establishing the dynamic equilibrium in the samples was great (several days), the measurement time (no more than half an hour under the atmospheric conditions) did not insert an essential error.

RESULTS AND DISCUSSIN

The results obtained are presented in Fig. 1 and 2 and in Table 2. The view itself of the curves of changing the thickness increment in Fig.1 shows that the kinetic data reproduce indeed the sorbostriction isotherm. The characteristic transition from contraction to expansion is observed at the growth of adsorption irrespective of the nature of a material. The maximum contraction is observed at the exposition in water vapor for about 3 days. The value of a maximum (in its absolute value) increment ΔH is –12 μm, the major part of the samples having ΔH = –6 to –8 μm. Herewith, the relative value $\Delta H/H$ (the linear strain) is 0.4 to 1.7%. The minimum contraction was registered for samples of the aluminum foil (about –2 μm). The value of $-\Delta H$ decreases as the exposition time τ increases and makes only 1–2 μm at τ = 20 days, which is already close to the accuracy of measurements (±0.6 μm).

Samples of silicon with the surface (100) were studied in more detail in the time range to seven days. The dependence of ΔH on τ is shown in Fig. 2 for disks with various thickness of the oxide film h. It is seen that these samples, depending on the thickness h, have rather different kinetic curves $\Delta H = f(\tau)$. In a special cycle of experiments, it was found that the effects observed are reversible, although the surface relaxation proceeds slowly (about three days) under the atmospheric conditions.

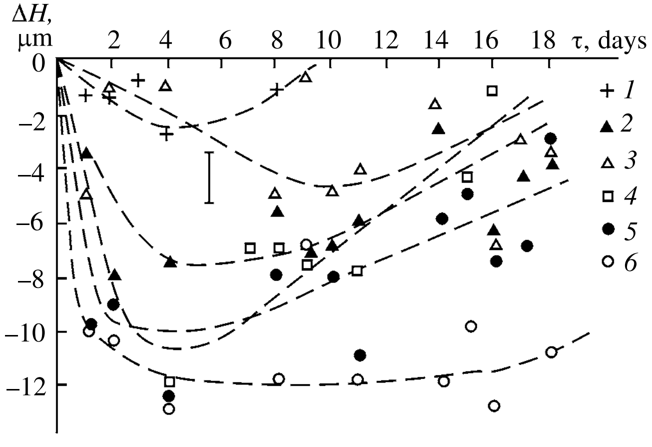

Fig. 1. The dependence of the thickness increment $\Delta\overline{H}$ for plates of aluminum, quartz, and glass on the exposure time τ at 100% humidity: (*1*) aluminum foil, (*2*) glass plate, (*3*) glass plate, (*4*) glass disk, (*5*) quartz plate, and (*6*) quartz plate.

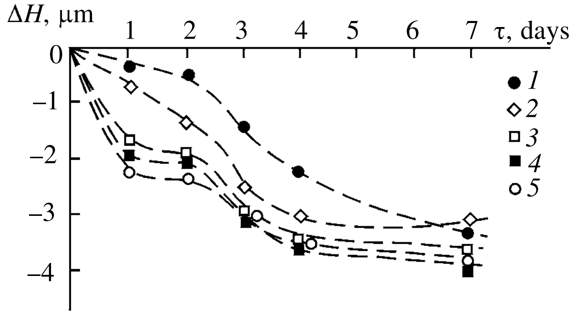

Fig. 2. The dependence of the thickness increment $\Delta\overline{H}$ for plates of monocrystalline silicon with various thickness of the oxide film on the exposure time τ at 100% humidity: (*1*) h = 10 nm, (*2*) h = 100 nm, (*3*) h = 30 nm, (*4*) h = 50 nm, and (*5*) h = 3 nm.

The data obtained for the silicon samples show that the plate diameter D, at exposing in the water vapor, is subjected to a strain of the opposite sign: an increase in $\overline{D}$ is observed in the region of decreasing $\overline{H}$. However, as it follows from Table 2, there is the diameter variation $\Delta\overline{D}$ = 6.8 mcm, that makes only 10^{-3}%, whereas the average decrease of thickness $\Delta\overline{H}$ is –3.5 µm or –0.8%. The corresponding average variation of the plate volume is $\Delta V/V$. The comparison of these data shows that the volume decrease is mainly caused by the thickness change, i.e. by the strain in direction of a normal to the surface.

Passing to the discussion of the data, we begin with the effect of surface tension. To be more exact, we mean the mechanical surface tension γ since just it (but not free surface energy) is responsible for the mechanical state of a solid. Similarly to free surface energy (for which the known Gibbs adsorption equation acts), γ is also dependent on adsorption, but in a more complicated manner. The theory of Eriksson [11]–Halsey [12] leads to the expression

$$\left(\frac{\partial\gamma}{\partial\mu}\right)_A = -\left[\frac{\partial(\Gamma A)}{\partial A}\right]_\mu, \qquad (1)$$

where µ is the chemical potential of an adsorbate, A is the surface area, and Γ is adsorption (the quantities µ and \ always change in the same direction). The product ΓA is the surface excess of a substance sorbed on the whole surface of a solid.

In the case of physical adsorption, increasing the surface area (by stretching) can only increase the total amount of the substance sorbed, and, hence, the whole right-hand side of Eq. (1) is of the negative sign. Then also the surface tension derivative in Eq. (1) will be negative. Let us see what effect can it produce on a sample under investigation. If $\gamma > 0$ (which is characteristic for free solid surfaces), surface tension keeps the surface in a compressed state. But we have $\partial\gamma/\partial\mu < 0$, and this means that surface tension diminishes at adsorption. Then also the degree of compression of the surface lowers, and the surface area increases. If now $\gamma < 0$, the surface is initially in a stretched state. Then, again at a negative value of the derivative $\partial\gamma/\partial\mu$, adsorption will lead to increasing the absolute value of γ, which will cause an additional stretching of the surface (and of the whole sample with it). Thus we arrive at the conclusion that, irrespective of the surface tension sign, physical adsorption should lead to increasing the linear dimension of a sample. As for chemisorption, Halsey [12] excluded its influence with the motivation that the number of active centers does not change at surface stretching (the right-hand side of Eq. (1)).

The above discussion shows that the observed increase of the diameter of silicon disks can be explained by the physical adsorption of water on the outer disk surface. As is known from the theory of elasticity, the longitudinal expansion of a sample is accompanied, as a rule, by its transversal contraction. For this reason, as it can seem, also decreasing the disk thickness in the course of sorption becomes understandable. However, such explanation does not work. Since the Poisson ratio changes within the limits from zero to 0.5, the transversal strain should be much smaller that the longitudinal one. We observe the reverse picture, and, therefore, the transversal contraction is a primary effect and should have an independent explanation.

One can easily relate such explanation to penetrating the matter in pores with subsequent chemisorption that causes the contraction of a sample [6]. However, the theory implies the microporosity of solids as an important condition of their strain. The sample surfaces used in this work are usually referred to as "smooth," although, at preparing them, there were no special measures securing the absence of micropores. The samples were real products used in the laboratory techniques and electronic technology and, therefore, not secured from the presence of micropores on the surface (moreover, the microporosity of the surface of analogous plates Si (100) was discovered in [13]).

On the other side, it is necessary to note that the observed phenomena can also not be explained by the influence of porosity only. The contraction of micropores should act in all directions and, hence, should lead to a decrease in the disk diameter. The observed increase of the diameter can be explained by the superposition of two effects: the surface tension of the outer surface and the porous structure of the bulk phase (or the subsurface layer). As it was shown in the theory [6], the influence of the second factor depends on the porosity value (the volume fraction of pores in a body). At the superposition of the two effects, one can say the influence of pores should dominate for bodies with a high porosity. This leads to the sample contraction, which was multiply observed at working with microporous adsorbents. If, however, porosity is not great, the stretching can be observed along the largest sample size as it occurs in our case.

It is worthy of attention that fact that the effect of change of thickness is great as compared with the sorbostriction values described in the literature. In this connection, we note that usually the variation of the largest size of a sample (a plate, a strip, or a bar) was registered. In our case, the sorbostriction effect was also small for the largest of the dimensions (the disk diameter). As for the transversal dimensions, they were not measured for highly porous bodies, so additional experimental data are needed for making the situation clear.

Thus, the following regularities are established in this work.

(1) The exposition of samples of various nature (a metal, a semiconductor, and glass), preliminary dried in an exsiccator at "zero" humidity, in the water vapor at a room temperature leads to the variation of their geometrical dimensions: decreasing the thickness during 4–5 days and increasing at longer expositions.

(2) The thickness decrease is 3 to 12 μm or, in average, about 0.8%.

(3) The sample volume variation (in the case of silicon plates) is also about 0.8%, which gives evidence of contracting in the direction of the normal to the flat.

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