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Dedicated to the 90th Anniversary of Academician M.G. Voronkov

Size Effect and Mechanochemical Contraction of the Si(100) Specimens

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Abstract—Variation of thickness of specimens of single crystalline silicon Si(100) prepared by scribing of the water of 100 mm diameter to parts of smaller size under atmospheric conditions is studied. It is shown that the thickness of specimens having small surface (~1 cm^2) decreases after scribing by 0.8–1.0% (with the error of measurements < 0.3%). The observed decrease in the thickness is explained by the effect of sorption of vapors of atmospheric moisture in micropores with the decrease in the external surface of specimens of Si(100) (the sorbostriction phenomenon).

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Development of the technology of nano- and micromechanical systems makes more and more severe requirements to the precision of the size of parts and elements of these devices [1]. Therefore the question of the limits of the part sizes for which possible nanoeffects still can be ignored becomes more and more urgent.

Earlier it was shown that mechanochemical deformation, one of nanoeffects, takes place on compact objects (plates of aluminum, glass, and monocrystalline silicon) [2]. In the present work the precision of measurement of the sizes was increased ca. twice (±0.25 μm) as compared to the data of [2].

The investigation was performed on a standard water of silicon single crystal used in microelectronics, where it undergoes scribing to specimens of different size. Normally, it is assumed that the thickness of the water remains unchanged in the specimens, too, or, at least, changes by no more than several fractions of μm. To check this assumption, specific procedure was elaborated, which allows to perform the measuring of the size in such a way that it would be possible to compare thickness h_w in a fixed point of the water surface with thickness h of a specimen cut at the same point of the water. Normally, it is assumed that $\Delta h = h_w - h = 0$.

The surface of polished plates of monocrystalline silicon, the basic material for microelectronics, is studied in detail [3]. It is known that surfaces of solid objects are conventionally divided into smooth and rough (disperse). To make this classification more definite, IUPAC [4] has introduced subdivision of pores by size, according to which there are three types of pores: (a) micropores[1] with the size less than 2 nm; (b) mesopores (intermediate) with the size from 2 to 50 nm; (c) macropores with the size more than 50 nm. Therefore, the surface of standard silicon plates can be considered to be smooth but containing a number of micropores. Such a relief was often observed in microscopic studies of silicon surface, including the Si (100) used by us [5].

It is known that in the investigation of adsorption a decisive role is played by the value of specific surface of the sorbent S_v.

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[1] The designation “nanopores” often used now in publications is apparently unofficial since its sense is identical to “micropores.”

Geometry of the specimens cut out from the water Si(100)

Specimen	Size of specimen, cm			Volume, V, cm^3	Surface, cm^2			S/V, cm^{-1}	$\Delta h = h_w - h$, μm
	width, a	length, b	thickness, $h \times 10^4$		"upper" S_{ab}	"side" S_{ah}	total S		
I	2.0	9.0	305.9	0.55	36.0	0.67	36.67	66.6	0.35
II	1.0	9.0	305.6	0.28	18.0	0.61	18.61	67.7	0.65
III	2.0	4.0	304.9	0.24	16.0	0.37	16.37	67.1	1.35
IV	2.0	2.5	303.8	0.15	10.0	0.27	10.27	67.6	2.45
V	1.0	4.0	304.9	0.12	8.0	0.30	8.30	68.1	1.35
VI	1.0	4.0	304.0	0.12	8.0	0.30	8.30	68.3	2.25
VII–XI	1.0	2.0	303.8	0.06	4.0	0.18	4.18	68.8	2.45
13–67[a]	1.0	1.0	303.7	0.03	2.0	0.12	2.12	69.9	2.55
6[a,b]–14[a,b]	0.9	0.6	303.2	0.016	1.08	0.09	1.17	71.5	3.05
14[b]–55[c]	0.9	0.4	303.1	0.011	0.72	0.08	0.80	73.2	3.15
48[a]	0.5	0.5	302.3	0.007	0.50	0.06	0.56	74.2	3.95

[a] Mean from 16 specimens, specimens 15, 16, 23, 24, 32, 33 were prepared from specimen I. [b] Mean from 3 specimens, prepared from specimens nos. 6 and 14 by cutting to specimens of smaller size. [c] Mean from 4 specimens prepared by cutting of specimens nos. 14, 53, 54, 55; specimen 48[a] was prepared from specimen 48.

$$S_v = S/V = (S_r + S_i)/V.$$

Here S_r is the external (geometric) surface, cm^2; S_i is the internal surface (cracks, micropores), cm^2; V is the volume of the sorbent, cm^3.

For the specimens studied in the present work the specific surface can be calculated from geometric measurements. The results of calculations are presented in the table.

While the value of S in our case is easily calculated from geometrical measurements of specimens, the value of S_i is difficult for determination, because this surface arises on the end surfaces of the separated specimens after scribing. However, these very newly formed end parts of the juvenile surface of the specimens, apparently, play the main role in the observed deformation of small specimens, since they are ideal "gates" for an adsorbate and contain micropores. The external surface, subject to mechanical treatment (grinding and polishing) is, apparently, "puttied."

As can be seen from Fig. 1, the thickness of the water in the edge zone is substantially smaller than its thickness in the central region. It is reasonable to assume that the reduced (as compared to the center) thickness of these parts is connected with the quality of mechanical treatment of the water. Not excluding the possibility of such a technological defect, note, that in this case, as will be shown below, the decrease of the thickness $\Delta h = h_w - h$ of the edge cells of the water grid has another reason caused by mechanochemical effects [2].

After separation of the water to specimens (scribing), the values of h (h_m for specimens whose surface exceed 1 cm^2) were measured. They are shown in Fig. 2 in the coordinates $h = f(S,\text{No.})$. As follows

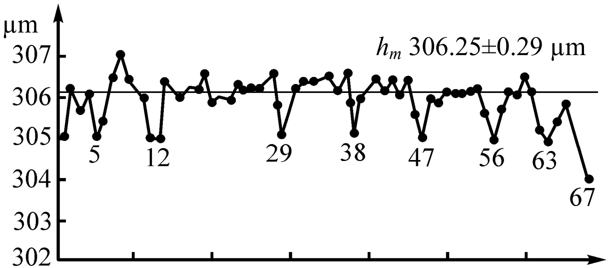

Fig. 1. Dependence of the thickness h_w on the number of the cell on the water.

from these data, the thickness of specimens gradually decreases as compared to the mean thickness of the water with decreasing size (surface) of the specimen. The maximum decrease of the thickness for the smallest specimens is ~3.5 µm (more than 1%) with the error of separate measurement no higher than ±0.3 µm (~0.1%) at the 0.95 level of confidence. It is important to note that the observed decrease of *h* for small specimens does not depend on which part of the water they were cut from (in the center of the water or at its edges). The decreased values of *h* for small specimens, cut from the central part of the water suggest that the observed variations of *h* at the edges of the water cannot be explained by defects of previous technological operations during fabrication of the water. This is indicative, apparently, of a specific role of the end "edge" juvenile surfaces formed after fracture of the water.

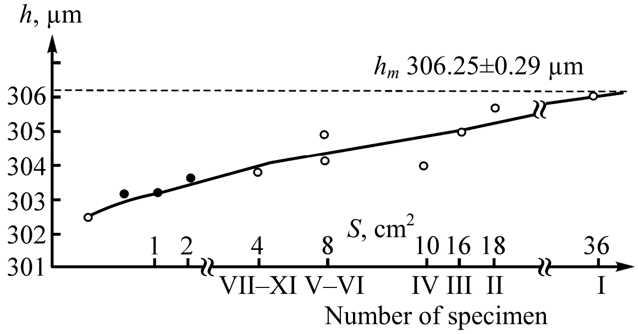

Fig. 2. Dependence of the thickness of specimens *h* on the number of the specimen and its surface *S*. (Light circles) correspond to *h* for separate specimens; (dark circles) correspond to mean value of *h* for the set of identical specimens (see the table).

Apart from the results obtained for the specimens when scribing the water along the grid (Fig. 3), the Table includes additional data for the following specimens: (a) with the size less than 1 cm^2, made by separation of small specimens (nos. $6^{a,b}$ and $14^{a,b}$, 48^{a}); (b) with the size of 1 cm^2, cut from large specimens I and II (nos. 15, 16, 23, 24, 32, 34). As expected, the values of *h* on the additional samples with the surface $S < 1$ cm^2 were even less. Based on the data of the table the dependence $\Delta h = f(S/V)$ (Fig. 4) was plotted.

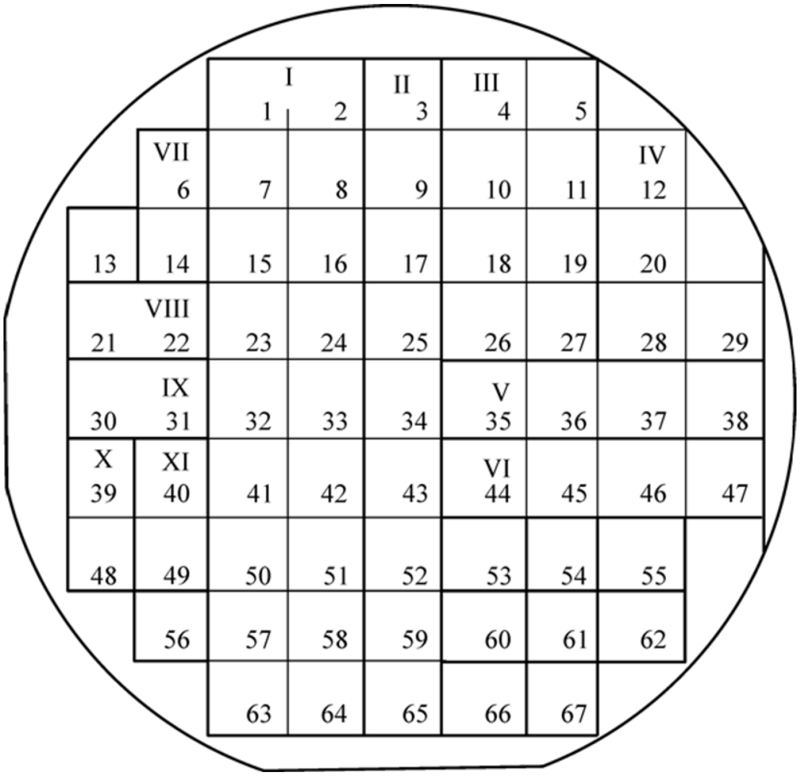

Fig. 3. Scheme of distribution of the points of measurement of thickness h_w on the water. The mean value and standard deviation of thickness refer to the central zone of the water (~70 mm), which includes 49 cells. Arabic numerals denote the numbers of the cells of the measuring grid, Roman numerals, the numbers of specimens after scribing the water.

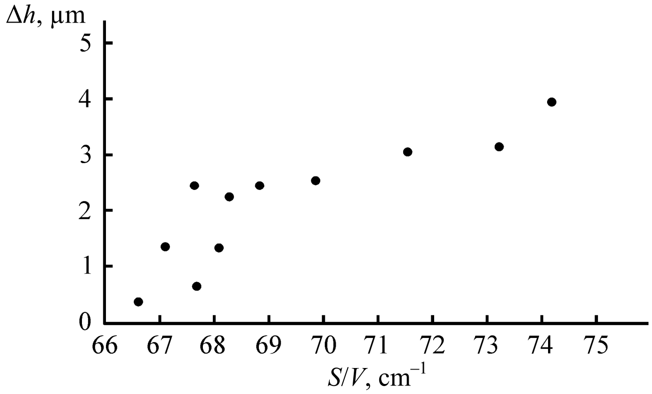

Fig. 4. Dependence of variation of the thickness $\Delta h = h_w - h$ on the specific surface S/V.

Earlier, the isotherms of sorbostriction on the plates of aluminum, glass, and monocrystalline silicon for sorption of water vapors were obtained [2]. The observed deformation (increase in the diameter of the plates by 6.8 μm and decrease in its thickness by 3.5 μm) was explained by superposition of two effects: the influence of the surface tension of the external surface of the specimens upon physical adsorption of water vapors, and effect of the process of chemisorption of H_2O in micropores.

The mechanical state of solids is determined by the mechanical surface tension γ (rather than the free surface energy). The value of γ depends on adsorption.

$$(\partial\gamma/\partial\mu)_S = [\partial(\Gamma S)/\partial S]_\mu.$$

Here, μ is the chemical potential of the adsorbate, S is the surface area, Γ is adsorption. Therefore, as shown in [2], physical adsorption must lead to an increase in the linear sizes of the water. Chemisorption of water vapors in micropores leads to contraction of specimens.

In the present work, the investigations were performed under atmospheric conditions, that is, for approximately constant content of water vapors in atmosphere (humidity ~60%). As shown in [6], under these conditions the surface of Si(100) contains chemisorbed water, whose amount was estimated as ~0.3–0.5 monolayer. Consequently, the deformation of the plates Si(100) we observed upon scribing can be considered from mechanochemical point of view.

Note that the dependence shown in Fig. 4 has a limiting character, that is, provides a possibility to determine a limit of the value of specific surface (S/V), after reaching which the nanochemical (mechanochemical) effects appear. It is seen from Fig. 4, that there is a narrow region of the values of S/V (65–70 cm^{-1}), in which the contraction forces caused by chemisorption in micropores start to predominate and cause a sharp decrease in the thickness of specimens (sorbostriction). Interestingly, the dependence $\Delta h = f(S/V)$ does not show any signs of saturation for the region $S/V > 70\ \text{cm}^{-1}$.

EXPERIMENTAL

The values of thickness were measured on a device based on a standard measuring instrument of the I class with a flat table and a digital measuring head with the smallest scale factor of 1 μm. The measurements were performed on a spherical support of 30 mm radius. The required precision was achieved by the use of special procedure of adjustment of the instrument and repeated measurements. The conditions of the experiment in the laboratory provided the temperature within 22±3°C and relative humidity of 50–70%.

The measuring device was adjusted prior to each measurement (series of measurements) by the use of two gauge blocks chosen so that the correction to the nominal of thickness for one gauge block did not exceed ±0.05 μm, and for another gauge block was 0.2–0.25 μm. The nominals of the gauge blocks differ by 60 μm. The threshold of operation of the digital head was adjusted so that for both gauge blocks the indicator readings would correspond to the nominal. Such an adjustment fixed the threshold of operation of the indicator when the deviation of thickness from an integer value was ~0.5 μm and allowed to provide standard deviation for repeated measurements of ca. 0.25 μm. In this procedure the unaccounted systematic error does not exceed 0.25 μm. The adjustment retained in the absence of notable thermal and air flows and at constant temperature during the process of measurements.

For statistical control of the adjustment of the device and estimation of the accidental error of the thickness measurements in the experiments a control specimen made of monocrystalline silicon of p-type doped with phosphorus having resistivity of 4.5 Ω cm of the size 10×15 mm was used. The control specimen was kept in a closed dessicator and was intermittently measured during 3 months, as well as prior to each series of measurements of the specimens. One measurement included 5 successive readings with the checking of adjustment prior to and after fixing the specimen. The result was averaged from 5 readings. The drift (trend) of the thickness of the control specimen during this period was 0.44±0.38 μm; the confidence limits were calculated for the probability of 0.95 taking into account the *t*-distribution. Standard deviation of the results of measurements from the regression straight line is 0.248 μm, the histogram of distribution of deviations from the mean value is shown in Fig. 5a.

The following sequence of operations was used in the experiments. To measure the thickness of the water h_w in a fixed position and compare it with the analogous value h of the specimen cut at this place, the surface of the original water was marked using marker with the drawing of grid consisting of square cells with the side of 1.0±0.1 cm (Fig. 3). After enumeration of all cells by lines parallel to the basic section of the single crystal, the thickness of the water in the center of each cell was measured using the procedure described above. The results of these measurements as a dependence of thickness h_w on the number of the cell on the water are shown in Fig. 1.

The results of measuring the thickness of the water in the cells (Fig. 3), apart from the main goal of the experiment of determination of h_w, allow to estimate the accidental component of the measurements and to compare it with the value given above for the control sample.

For this, the shape of the water surface in a number of cross-sections was approximated by power polynomials according to the Fisher criterion [7] at the 0.95 level of confidence. Standard deviation of the experimental points calculated from the residual sum of the deviation squares in each cross-section and averaged to all cross-sections is equal to 0.250 μm, which is well consistent with the value obtained for the control specimen. The histogram of deviations of the experimental values from the approximating curves is shown in Fig. 5b for comparison with the histogram of distribution of the accidental error for the measurements of the control sample.

The aforementioned details of the procedure of the thickness measuring and statistical parameters are given to show that the accidental component of the error of the thickness measuring in our experiments estimated by different methods is characterized by standard deviation not exceeding 0.29 μm; for determination of confidence limits normal estimations can be used.

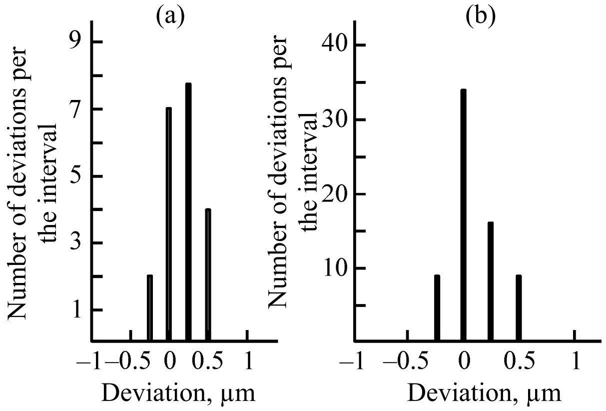

Fig. 5. Histograms of deviations of the results of measurements of thickness from the mean value (0.00), characterizing the accidental component of the error: (a) is the deviation with the time drift of thickness of the specimen taken into account (standard deviation 0.248); (b) is the deviation in a fixed point on the surface of the studied water from the best approximated surface calculated by the least-squares method (standard deviation 0.250).

After measuring the thickness in the center of each cell the water was separated by hand[2] to specimens of different sizes using a corundum bar. Then, thickness h was measured for all specimens obtained after scribing, according to Fig. 3. In the cases, when the area of the specimen exceeded 1 cm^2, the mean value h_m was determined by averaging the values of h measured for each cell forming the surface. Numeration of the specimens consisting of more than one cell is given in Roman numerals (Fig. 3).

Note, that the measurement of h was performed both directly after scribing the water and after its exposure to atmospheric conditions from several hours to several days. The value of h, measured directly after scribing, remained constant in this period.

The results obtained in this work were discussed on the II All-Russia Seminar "Physical chemistry of surfaces and nanosize systems" (Moscow, 2010), and the International Scientific Technological Conference NFM'2010 (St. Petersburg, 2010).

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[2] Apart from hand scribing, cutting with diamond disc and laser were used.

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REFERENCES

1. Peshekhonov, V.G., Nesenyuk, L.P., Gryazin, D.G., Nekrasov, Ya.A., Evstifeev, M.I., Blazhnov, B.A., and Aksenenko, V.D., Abstract of Papers, *Yubileinaya XV Sankt-Peterburgskoi mezhdunarodnaya konferentsiya po integrirovannym navigatsionnym sistemam* (XV Anniversary of St. Petersburg Int. Conf. on Integrated Navigation Systems), St. Petersburg, 2008.
2. Novikov, S.N., Timoshenkov, S.P., and Rusanov, A.I., *Russ. J. Gen. Chem.*, 2007, vol. 77, no. 3, p. 393.
3. Krasnikov, G.Ya. and Zaitsev, N.A., *Sistema kremnii–dioksid kremniya submikronnykh SBIS* (System of a Silicon–Silicon Dioxide Submicron VLSI), Moscow: Tekhnosfera, 2003.
4. Gregg, S.J. and Sing, K.S.W., *Adsorption, Surface Area and Porosity*, London: Academic Press, 1982, 2nd ed, p. 36.
5. Borman, V.D., Lebedinski, Yu.Yu., and Trojan, V.J., *Phys. Low-Dim. Struct.*, 1998, vols. 7–8, p. 167.
6. Novikov, S.N. and Timoshenkov, S.P., *Ross. Nanotekhnologii*, 2006, vol. 1, nos. 1–2, p. 217.
7. Hudson, D., *Statistics for Physicists*, Moscow: Mir, 1970.