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Perfection of the Lattice of Dislocation-Free Silicon, Studied by the Lattice-Constant and Density Method

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The lattice-constant and density method revealed that a high-purity silicon crystal free of dislocations has a perfect lattice without an excess of vacant sites or interstitials ($n'=8.0000_4$) within the limits of error, in agreement with the results obtained with the decoration method. The lattice constant of vacuum heated silicon powder of semiconductor purity was 5.43070±0.00004 A; that of the nonheat-treated powder was 5.43081 A at 25°C. The constants determined from crystal chips by the rotating crystal method were lower: between 5.43028–5.43048 A at 25°C. As the constants of each series of measurements could be reproduced very well ($s=\pm 0.00004$ A), the lower values suggested the presence of some unknown systematic errors, the magnitude of which is outside the scope of errors due to absorption. The thermal expansion coefficients of all samples between 10°–60°C were $(2.6\pm 0.4)\times 10^{-6}$/°C. The average density of etched crystal chips was 2.3289±0.0001 g/cm³. The lower density of the nonetched chips indicated the presence of microcracks, removable by etching, within the distorted surface layers. There was no significant difference in density of bars sawed, or of chips broken from the crystal and etched.

INTRODUCTION

SILICON of high (semiconductor) purity, free of dislocations,[1] can be used to check the exactitude of the method of n' determination[2] from the expression

$$n'=vdN_0/A, \qquad (1)$$

where v is the volume of the unit cell, N_0 is Avogadro's number, d the density, and A the atomic weight of Si. n', the actual number of atoms per unit cell, should then approach the ideal value of $n=8.0000$, meaning that the lattice of the Si mentioned is perfect,[3,4] free of an excess of vacant sites, interstitials, and other imperfections within the limits of error.

Further objectives of the present work were to find the expansion coefficients of Si, in the form of small crystal fragments and of a powder; the experimental densities of the unetched and etched fragments; the lattice parameters of crystal chips and of powder, and to draw conclusions concerning the applicability of the absorption correction for lattice constants determined from rotation patterns of tiny crystal fragments.

MATERIALS USED, SAMPLES, AND MEASUREMENTS

High-purity single silicon crystals, obtained from Dr. W. C. Dash of the General Electric Company, were used for the study.[1] The major impurities were probably carbon and oxygen, present to no greater extent than 10^{-7} (in atom fraction). Because of the high purity of the crystals, no chemical analysis was available nor could one be made. Etching and copper decoration techniques[5] revealed that the crystals grown by the method of Dash in an argon atmosphere do not contain observable dislocations.[1]

Samples for x-ray single-crystal rotation photographs and powder patterns were made of this material. A multitude of small crystal fragments was obtained by breaking an end of a crystal with pliers. Needle-shaped fragments with the appropriate crystallographic directions along the needle axis were chosen for the studies. However, since the fragments probably contained dislocations and microcracks on their surface as a result of deformation, the distorted layers were removed by etching (one part of concentrated pure HF in three parts of concentrated HNO_3).

To exclude, as much as possible, distortion in the interior of the crystal fragments, further samples were prepared as follows. Several leaflets about 0.5 mm thick were cut approximately parallel to the (111) plane from a crystal by means of a diamond saw blade. They were again cut perpendicularly to the surface into roughly rectangular 0.5×0.5×4-mm bars, then were etched down to needles about 2 mm long and 0.07 mm in diam. For powder mounts, fragments of the fairly brittle crystal were ground and the powder passed through a 350-mesh screen. To detect the influence of cold work on the lattice constant, one part of the powder was heated in vacuum (about 10^{-5} mm) at 600°C for 1 hr. It was assumed that by this treatment stresses were released and a part of the dislocations and other imperfections was annealed out.

For the determination of lattice parameters, asymmetric rotation crystal and powder photographs at a constant temperature of the sample (±0.1°) were made.[6,7] The constants were calculated from the density peaks of back-reflection lines, $444_{\alpha 1}$, which appeared under a Bragg angle of about 80° on the films.[8] Copper radiation was used ($\lambda_{\alpha 1}=1.537395\times 1.00202$ A). The time of exposure in 64-mm precision cameras was 15–30 min for the single-crystal patterns, and 120–150

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min for the powder photographs. As the diameter of the powder mounts was less than 0.2 mm, no corrections, except for refraction, were applied.[9] An amount of 0.00040 kX was added to all constants to allow for refraction. Although the crystal fragments for rotation photographs had diameters between 0.07–0.2 mm, the necessity of an absorption correction was considered.

The thermal expansion coefficients were calculated from constants obtained at sample temperatures between +10 and 60° in increments of 10°.

The density (reduced to vacuum) of the etched and nonetched fragments was determined by the improved suspension method,[10] using tetrabromethane as a heavy liquid. To adjust the density of this liquid to that of the crystals, bromobenzene was used as a diluting agent and finally temperature changes were made.

In order to establish the significance of a measured difference, the standard deviation s was calculated from each series of experimental determinations.[2,10] The least-squares method[11] was used for computation of the lattice parameter at 25°C (a_{25}) from the values a_t obtained between 10 and 60°, and for the determination of the thermal expansion coefficient.

EXPERIMENTAL RESULTS

Lattice Constants

Table I shows the reproducibility of the lattice constant of a nonetched fragment (split from the silicon crystal), adjusted and centered by the goniometer head of the camera. From the mean values at each temperature, the expansion coefficient was calculated and then used to reduce all the lattice constants to 25°C. Using the deviations of these constants from the average value, the standard deviation corresponding to a 50% confidence limit was calculated.

Table II lists the lattice parameters and expansion coefficients of two other Si crystal fragments (one cut from the crystals) both deeply etched.

Although sharp, narrow, and hence easily measurable, spots were obtained on the films, there is still some doubt concerning the reliability of lattice constants calculated from rotation crystal patterns, especially if the axis of rotation of the crystal is not the simplest (like 001). The authors observed that the lattice constants in some cases appeared smaller than calculated from powder photographs. Powder methods are regarded as being more reliable. Because of this reason fragments of single Si crystals were pulverized and powder patterns were made. For the latter, lattice measurements at various temperatures resulted in the expansion coefficient and the lattice constant of the powder (at 25°C) (see Table II). The increased value of the lattice constant, as compared with those obtained from rotation photographs, was not unexpected because of strains (or interstitials) introduced into the lattice by the severe deformation process (crushing). The expansion coefficient of the material was approximately the same.

It was expected that the increased lattice constant could be reduced by the heat treatment mentioned above; the constant indeed decreased (see Table II), but did not reach as low a value obtained from rotation photographs. There was still a possibility that the low value from rotation patterns could be explained by the shift of the spots due to absorption (which was disregarded). However, calculations gave for a completely opaque sample (0.1–0.2 mm in diam) an absorption correction of only 0.00004–0.00007 A. If the absorption shift is interpreted according to Warren, then the correction is larger but still insufficient to explain the low value of constants obtained from rotation crystal photographs.[9,12] Thus this question has

TABLE I. Lattice constants of a nonetched Si crystal fragment at various temperatures. Rotation axis 110, thermal expansion coefficient calculated from the a_t constants,

$$\alpha = (2.8 \pm 0.4) \times 10^{-6}/°C.$$

Temp. (°C)	a_t (A)	a_{25} (A)
11.0	5.42993	5.43014
11.0	5.43001	22
21.0	29	35
21.0	12	18
31.0	41	32
31.0	47	38
41.0	52	28
41.0	33	09
51.0	64	24
51.0	57	17
61.0	77	22
61.0	85	29
	Average	5.43024
	Refraction corr.	0.00004
	a_{25}=	5.43028 ±0.00004 A

TABLE II. Lattice constants, expansion coefficients α, densities d, and perfection of the lattice n', of silicon free of dislocations.

Sample	a_{25} (A)	α ($\times 10^6$/°C)	d_{25} (g/cm³)	n' (atoms/unit cell)
Crystal fragments, unetched	5.43028[a]	2.8±0.2	2.3287[b]	7.9975±0.0009
Crystal fragments, unetched	5.43030	3.4	2.3291	7.9989
Crystal bar, sawed, etched	5.43048	2.5	2.3289	7.9990
Powder (2 samples)	5.43081	2.5	...	...
Powder heated (2 samples)	5.43070	2.0	...	8.00004[c]
	Averages	2.6±0.4	2.3289±0.0001	

[a] ±0.00004
[b] ±0.00004
[c] Using the average density.

[9] M. E. Straumanis, J. Appl. Phys. **30**, 1965 (1959); Acta Cryst. **13**, 818 (1960).
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[12] B. E. Warren, J. Appl. Phys. **16**, 614 (1945).

yet to be answered, and the lattice constant from powder photographs has to be regarded as the most reliable value.

Density Measurements

Four determinations of density were made for each of nine crystal fragments. For example, the densities found for one etched fragment were: 2.32915, 2.32916, 2.32908, and 2.32903 g/cm³ at 25°C. An average $d=2.32910\pm0.00003$ was obtained. The pieces cut from the single crystal and etched exhibited a slightly lower density; still lighter were the unetched fragments broken from the crystal (see Table II). The differences may be explained by the formation of dislocations, vacant sites, and even of microcracks[13] on the surface layers during deformation. By etching, the layers are removed and the core shows a higher density then the fragments as a whole. Because only small amounts of Si powder were available, no density determinations were made with it but preliminary measurements showed a lower value.

Calculation of n' and Discussion

The actual number of atoms n' per unit cell can now be computed from Eq. (1), substituting for N_0 the value[2,4] of $(6.02403\pm0.00030)10^{23}$ and for A (28.0875 ±0.0005).[14] The results are summarized in Table II. To decide whether a deviation of n' from the theoretical value $n=8$ is significant or not, an estimation of the propagated error was made. The latter was calculated as previously described[2,10] assuming that the standard deviation of the lattice constant is ±0.00004 A and that of the density measurements is ±0.0001 g/cm³. To take care of the systematic errors which possibly were made in these measurements, the error in the lattice constant was increased by a factor of 3, the density error by a factor of 2, and the factor 1 was used for A and N_0, thus assuming that all errors were covered by the deviations given. For the lowest value of N_0 $(=6.0237\times10^{23})$,[14] n' diminishes by 0.00044.

Table II clearly shows that for all three groups of single crystals, n' is significantly lower than 8. On comparing the respective lattice parameters, it can be seen that the low value of n' is explained mainly by the low value of the a constant, which because of unknown reasons deviates from that calculated from patterns of heated silicon powder. On the other hand, using for n' calculations the most reliable values, e.g., the a constant from heated powders and densities as determined from etched chips of silicon suspended in a heavy liquid, an n' is obtained which is very close to the theoretical value and completely within the limits of error, ±0.0009, calculated. The n' value obtained with the etched crystal bar is also very close to 8. Therefore, the conclusion drawn is that the dislocation-free silicon crystal has a perfect lattice without a measurable excess of interstitials or vacant sites. This agrees with the results obtained by the decoration method.[1]

CONCLUSIONS

The lattice-constant and density method can be used to determine the excess of one kind of imperfections in a crystalline substance.

For lattice-constant determination, the powder method is more reliable than the rotation-crystal method.

Crushed silicon powder has a slightly larger lattice constant than that heated in vacuum. The thermal expansion coefficients do not change appreciably from sample to sample near room temperature.

Breaking of the brittle silicon introduces vacancies and probably microcracks into the surface of the chips. This layer of lower density can be removed by etching. The core has a higher density. The densities of the cores of various chips differed by amounts outside the limits of error which suggested incomplete removal of the deformed surface layer by etching in some cases.

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