Deformation-stimulated phase transitions in silicon single crystals

I. M. Shmyt'ko, A. N. Izotov, É. A. Shteĭnman, and N. S. Afonikova
Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russia

(Submitted 5 April 1995)
Pis'ma Zh. Éksp. Teor. Fiz. **61**, No. 11, 906–910 (10 June 1995)

Experiments reveal the formation of polytype modifications in dislocation-free silicon single crystals subjected to directed plastic deformation. The structure of the phases which form depends on the deformation rate. © *1995 American Institute of Physics.*

Occupying a special place among the ten known phases of silicon[1] is the hexagonal form which has come to be known as "lonsdaleite."[1)] The first reports of the existence of lonsdaleite in silicon were published by Wentorf and Kasper[5] in 1963. They observed the formation of the hexagonal form after a prolonged annealing at 200–600 °C of polycrystalline silicon blocks subjected to high pressure. A study by the Debye–Scherrer method revealed a simple wurzite lattice with the constants $\mathbf{a}=0.38$ nm and $\mathbf{c}=0.628$ nm.

In 1972, Eremenko and Nikitenko[6] reported the formation of interlayers of a hexagonal phase in a cubic matrix after silicon single crystals were punctured by an indentor at sample temperatures of 400–700 °C. Examination by electron microscopy revealed an orientational relation between the regions of cubic and hexagonal phases: $(011)_{\text{cub}}\|(\bar{1}2\bar{1}0)_{\text{hex}}$, $[011]_{\text{cub}}\|[0001]_{\text{hex}}$. Lattice constants $\mathbf{a}=0.368$ nm and $\mathbf{c}=0.631$ nm were found.

That a hexagonal phase forms after puncture by an indentor was subsequently confirmed by Tan *et al.*[7] and Pearose *et al.*[8] A distinctive feature of the Eremenko–Tan–Pearose experiments was that the indentation was carried out at elevated temperatures (>400 °C), at which silicon single crystals undergo plastic deformation. Levitan *et al.*[1] showed that a phase analogous to that observed by Eremenko, Tan, and Pearose forms during indentation at room temperature, at which silicon is not plastic. Levitan *et al.* suggested some different orientational relations between the phases $(011)_{\text{cub}}\|(\bar{1}2\bar{1}0)_{\text{hex}}$ and $[111]_{\text{cub}}\|[0001]_{\text{hex}}$. They also proposed a new mechanism for the transition from the diamond structure to the wurzite modification. This new mechanism was based on a layer-by-layer shear of the {111} diamond planes through a motion of partial dislocation.

Some points required clarification here. The hexagonal phase has been produced only in microscopic volumes during the indentation of silicon single crystals. The orientational relations between the cubic and hexagonal modifications reported by different research groups contradict each other. Because of these problems, and in light of our results on the mutual transformations of the wurzite and sphalerite phases by means of plastic deformation in zinc sulfide crystals,[9,10] we undertook the study which we are

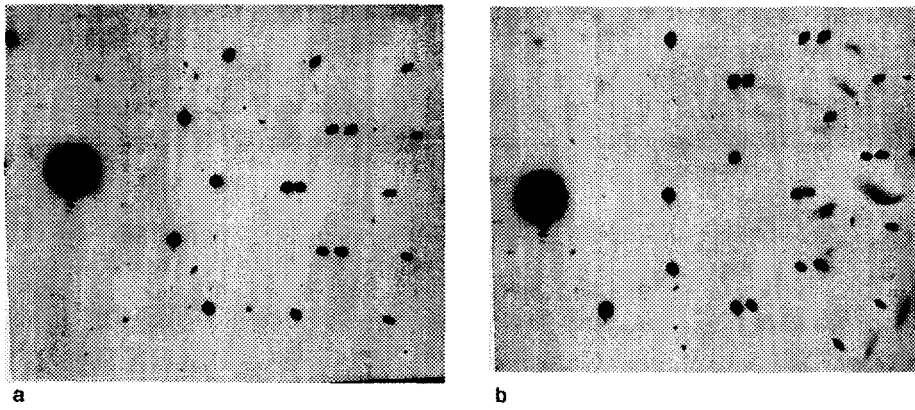

FIG. 1. Rocking x-ray patterns of silicon single crystals deformed along the [123] axis at a rate of 5 μm/min. a—The [110] rocking axis; b—the [112] rocking axis.

reporting in this letter. The intention was to induce bulk structural transitions in silicon single crystals by ordinary plastic deformation.

We studied dislocation-free silicon single crystals in the form of rectangular bars with dimensions of 2.5×3.0×10.0 mm, with $(\bar{5}41)$, (111), and $(\bar{1}\bar{2}3)$ faces, respectively. This orientation of the samples was selected because only one glide plane of the {111} type is active during the deformation. This deformation was carried out at a temperature ~900 °C. In one series of experiments the deformation rate was 5 μm/min, and in another it was 20 μm/min. The total deformation did not exceed 2%.

To study the structural state of the deformed crystals we assembled a rocking chamber on the basis of a DRON-2.0 diffractometer. We used monochromitized Ag Kα radiation from the first monochromator of a GUR-5 goniometer. The tube voltage did not exceed 40 kV; the current was 30 mA. An upper limit was imposed on the accelerating voltage by the need to remove radiation with wavelengths which are multiples of (Ag Kα) /n from the diffraction.

Two series of rocking patterns were recorded for [110] and [112] sample rotation axes. These axes lead to either symmetric (in the case of the [110] axis) or asymmetric (the [112] axis) arrangements of the reflections of the cubic matrix with respect to the zeroth layer line. For the wurzite modification, the choice of the "asymmetric" [112] rotation axis presupposes an asymmetric arrangement of the reflections with respect to the zeroth layer line, for both the relationship indices found by Eremenko, Tan, and Pearose and those obtained by Levitan. For the [110] rotation axis, we expected a symmetric arrangement of diffraction spots of the wurzite modification on the x-ray diffraction patterns, while for the indices proposed by Levitan we expected an asymmetric arrangement.

Figure 1 shows x-ray diffraction patterns recorded in the case of deformation at a rate of 5 μm/min. Part a of Fig. 1 corresponds to the case in which the sample is rocked around the [110] axis, while part b corresponds to the [112] rocking axis. On each of the

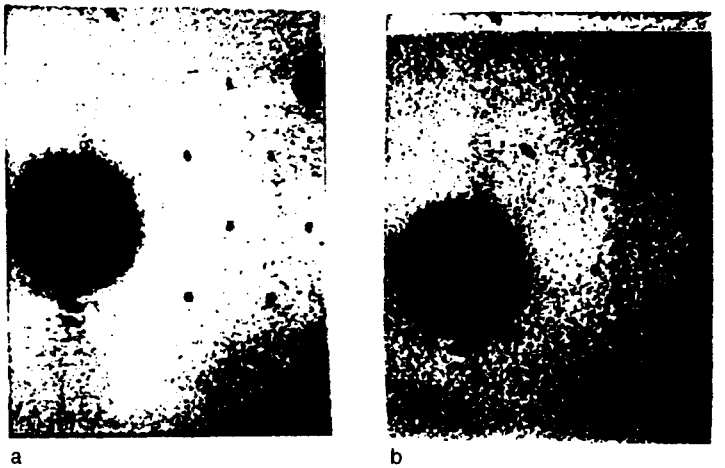

FIG. 2. Enlarged regions of the patterns in Fig. 1 containing additional reflections. a—The [110] rocking axis; b—the [112] axis.

diffraction patterns we see a series of additional weak reflections in addition to the intense reflections from the cubic matrix. Parts of the patterns containing these reflections are shown in large scale in Fig. 2. The presence of regularly positioned additional reflections on the rocking patterns, against the background of reflections of the diamond matrix structure, is clear evidence of the formation of a new phase in the silicon. The "point" nature of the reflections of this phase indicates that the latter has fairly large dimensions (>1000 Å) in the sample. Analysis of diffraction patterns recorded from various parts of a crystal shows that the new phase forms at the surface of the sample, in a zone of active deformation.

We turn now to the arrangement of the additional reflections with respect to the zeroth layer line. This arrangement is symmetric in both Fig. 1a (2a) and Fig. 1b (2b). It follows from the symmetric arrangement of the satellite reflections in the case of rocking around the [112] axis that neither the relation indices proposed by Eremenko, Tan, and Pearose nor those proposed by Levitan are valid for the phase produced by plastic deformation. In addition, the structure observed here is not wurzite: Between the zeroth and first layer lines of the original diamond modification there is a layer line of additional reflections on all the x-ray patterns. This result indicates that the lattice constant of the new phase is twice as large as that of the matrix along the rocking axis (for the Eremenko–Tan–Pearose relation index given above, this situation corresponds to a doubling of the period along the direction **a** of the proposed hexagonal form). At the same time, the lattice constants of the new phase are doubled in the planes perpendicular to the rotation direction, causing additional reflections along the layer lines. The doubling of the lattice constants along the rotation axis and in the perpendicular planes contradicts a lonsdaleite structure. Consequently, the phase induced by the plastic deformation differs from the wurzite modification of silicon which was found in Refs. 1 and 5–8.

To determine the kinetics of the formation of the new phase, we studied crystals

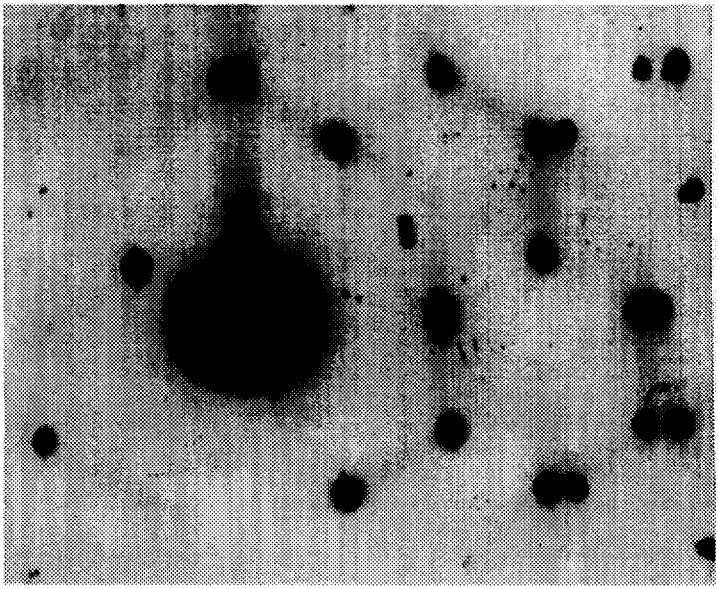

FIG. 3. A rocking pattern of a silicon single crystal deformed at a rate of 20 μm/min ([112] rotation axis).

subjected to deformation at higher rates. Figure 3 shows a rocking x-ray pattern (with a [112] rocking axis) for a crystal deformed at a rate of 20 μm/min. In contrast with Figs. 1 and 2, there are no individual point reflections here, and the intense reflections of the diamond modification are connected by broad-diffuse cords. The blurred reflections are "perceived" only in regions where these cords intersect. The positions of only some of these blurred reflections coincide with positions of the additional reflections in Fig. 1, implying the formation of a structure different from that described above. The broad, diffuse cords indicate that the new phase forms as thin interlayers. Analysis of the diffraction patterns recorded from various faces of a sample shows that the layers of the new phase have large dimensions along the surface at which the dislocations emerge, while they have a small thickness (a small dimension in the direction into the test sample).

In summary, these results demonstrate unambiguously that various polytype modifications arise in silicon subjected to plastic deformation, as in zinc sulfide. In order to decipher these modifications and to determine the kinetics of their formation, it will be necessary to carry out some further research, including the use of various deformation conditions (the level, rate, and temperature of the deformation), various orientations of the active glide planes with respect to the deformation direction, and samples differing in the concentration of point defects.

This study was carried out in accordance with Project 94-02-03277 of the Russian Fund for Fundamental Research.

[1)]The lonsdaleite structure was first observed in some research carried out to produce synthetic diamonds by shock compression of graphite.[2-4] Some x-ray experiments showed that lonsdaleite is related to the cubic diamond lattice in the same way that wurzite is related to the zinc blende structure.

---

[1] S. F. Levitan, A. V. Prikhod'ko, and Yu. V. Sokolov, Ukr. Fiz. Zh. **35**, 1537 (1990).
[2] E. I. du Pont de Nemours and Company, Netherlands Patent Release No. 6506395, 1965.
[3] F. P. Bundy and J. S. Kasper, J. Chem Phys. **46**, 3437 (1967).
[4] K. Lonsdale, Am. Mineral. **56**, 333 (1971).
[5] R. H. Wentorf and J. S. Kasper, Science **139**, 338 (1963).
[6] V. G. Eremenko and V. I. Nikitenko, Phys. Status Solidi (a) **14**, 317 (1972).
[7] T. Y. Tan, H. Foll, and S. M. Hu, Philos. Mag. A **44**, 127 (1981).
[8] P. Pearose, R. Chain, and J. Samuels, Izv. Akad. Nauk SSSR, Ser. Fiz. **51**, 753 (1987).
[9] V. Sh. Shekhtman, I. M. Shmyt'ko, V. V. Aristov, and B. A. Abdikamalov, Fiz. Tverd. Tela (Leningrad) **18**, 1358 (1976) [Sov. Phys. Solid State **18**, 781 (1976)].
[10] I. M. Shmyt'ko, L. A. Matveeva, S. I. Bredikhin *et al.*, Fiz. Tverd. Tela (Leningrad) **26**, 2033 (1984) [Sov. Phys. Solid State **26**, 1233 (1984)].

Translated by D. Parsons