TWINNING IN DIAMOND-TYPE STRUCTURES: HIGH-ORDER TWINNING IN SILICON*

J. A. KOHN, *Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey.*

ABSTRACT

Diamond-type structures are predisposed to twinning, owing to the relatively slight energy difference between the normal and twinned configurations. A non-parallel set of twinning operations produces high-order twinning. Previously known in diamond, this structural defect is extended to silicon. The method of analysis by x-ray means, applicable to the study of intergrowths in general, is given.

High-order twinning in diamond-type structures introduces substantial structure discontinuities. The geometrical aspects of such "high-order twin joins" are discussed.

INTRODUCTION

High-order twinning derives from a set of non-parallel twinning operations. In a diamond-type structure, for example, an initial twininng operation generates a twin, I, on (111) of a host crystal. A second operation generates a twin, II, on $(1\bar{1}1)$ of the same host crystal. The relationship between the host and each of twins I and II is that of simple, or first-order twinning; that between individuals I and II is high-order (in this case, second-order) twinning.

Twinning in diamond-type structures introduces deviations from normal bonding commencing with the tertiary coordinations. Since the primary and secondary coordinations remain unaffected by the twinning operation, there obviously exists only a very slight energy difference between the normal and twinned configurations. It is to be expected, then, that the frequency of twinning in such materials would be high. Also, since there are four structurally equivalent, potential twinning directions available, examination of these substances should reveal the type of multiple operations involved in high-order twinning.

A study of diamond crystals, even those of gem variety, almost invariably reveals the presence of at least microscopic twinning. High-order twinning in diamond has been described on the basis of both morphological (1) and x-ray (2) evidence. Nevertheless, owing to the limited availability of diamonds and to the fact that one cannot perform a simple synthesis and thus easily vary experimental conditions, the study of such structural defects is considerably handicapped. Fortunately, however, recent emphasis on solid state research in silicon and germanium has made available many excellent crystals for such studies. Since these materials are isomorphous with diamond, the information

* Presented at the Thirteenth Annual Pittsburgh Diffraction Conference, Pittsburgh, Pa., Nov. 3, 1955.

thus gleaned can easily be extrapolated to the latter. The present study demonstrates high-order twinning in silicon and discusses some general geometrical aspects of this phenomenon in diamond-type structures.

Procedure and Results

The particular crystal with which this paper is mostly concerned was grown by the Czochralski technique, i.e., by pulling an oriented seed from a melt. The seed, in this case, was oriented and pulled along [001]. A surface portion of the resultant silicon crystal showed a scallop-like structural outcrop, with cusps at 90°-intervals around the circumference of the crystal. One such cusp became the subject of detailed x-ray study. An enlargement of the area of interest is reproduced in Fig. 1, in

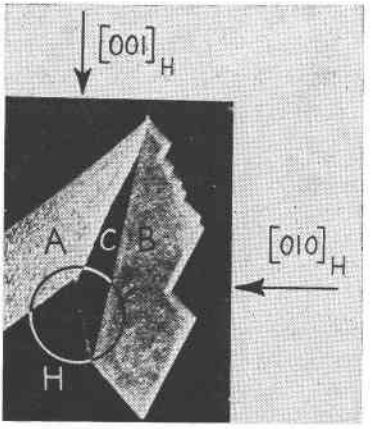

Fig. 1. Localized surface structure on silicon, viewed along [100] of the host (H) crystal. Circle shows position of incident x-ray beam (20×).

which the host crystal is viewed along [100]. In addition to the host (H), three other individuals, A, B, and C, are noted in the figure. Their mutual orientations were determined by the back-reflection Laue technique.

The area circled in Fig. 1 denotes that which was bathed by the x-ray beam. The resultant back-reflection Laue pattern, centered on (100) of the host crystal, is reproduced in Fig. 2*a*. The different profiles of the reflections on the pattern can be correlated with the shapes of the surface areas exposed to the beam by the different crystal orientations. Thus, it is easily possible to locate symmetry centers due to each of the individuals noted in Fig. 1. Three octahedral centers were located, which could be correlated with orientations A, B, and C. The schematic drawing in Fig. 2*b* shows clearly the threefold symmetry about $(11\bar{1})_A$ and

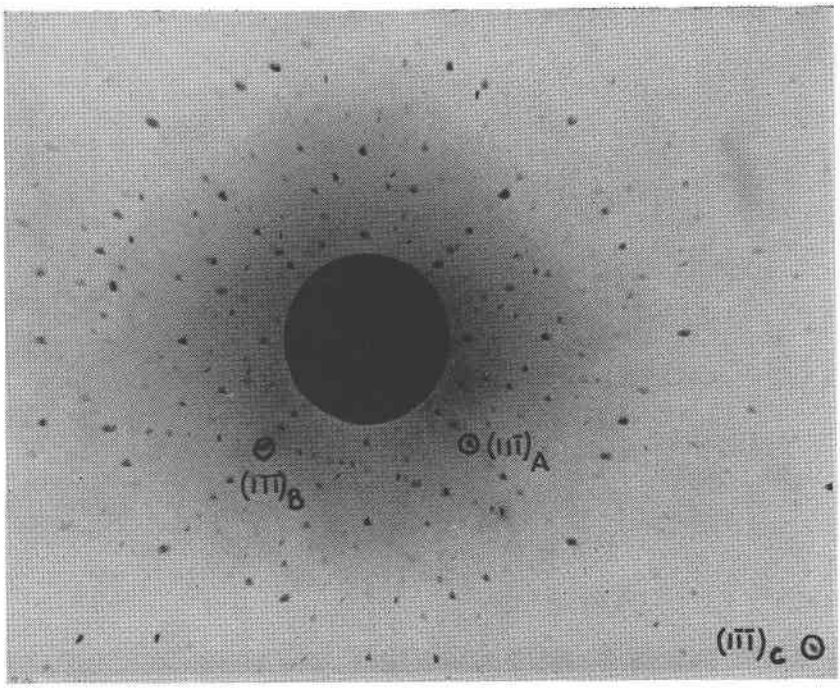

FIG. 2*a*. Back-reflection Laue pattern centered on (100) of the host crystal: CuK, 24 hrs., crystal to film = 2.78 cm. (1.1×).

$(1\bar{1}\bar{1})_B$. The threefold center due to individual *C* is not immediately evident, however the symmetrical distribution of reflections along the $(1\bar{1}\bar{1})_B$–$(1\bar{1}\bar{1})_C$ zone line bears out the positioning of $(1\bar{1}\bar{1})_C$. This symmetrical distribution can be traced in either direction from the $(1\bar{1}\bar{2})$ reflection (Fig. 2*b*), which is common to individuals *B* and *C*.

The model depicted in Fig. 3 demonstrates the mutual orientations of the four individuals, host, *A*, *B*, and *C*. The faces labelled on the model correspond with the symmetry centers noted in the Laue pattern. This postulated twin complex was confirmed by a comparison of calculated interfacial angles with those measured on the Laue pattern. The following table presents these data.

Angle between $[100]_H$ *and*	*Calculated*	*Observed*
$[11\bar{1}]_A$	15° 48′	15.8°
$[1\bar{1}\bar{1}]_B$	15° 48′	15.8°
$[1\bar{1}\bar{1}]_C$	33° 30′	33.4°

Thus, the localized silicon section under consideration is actually a twin complex in which the individuals are related as follows: *A* and *B*

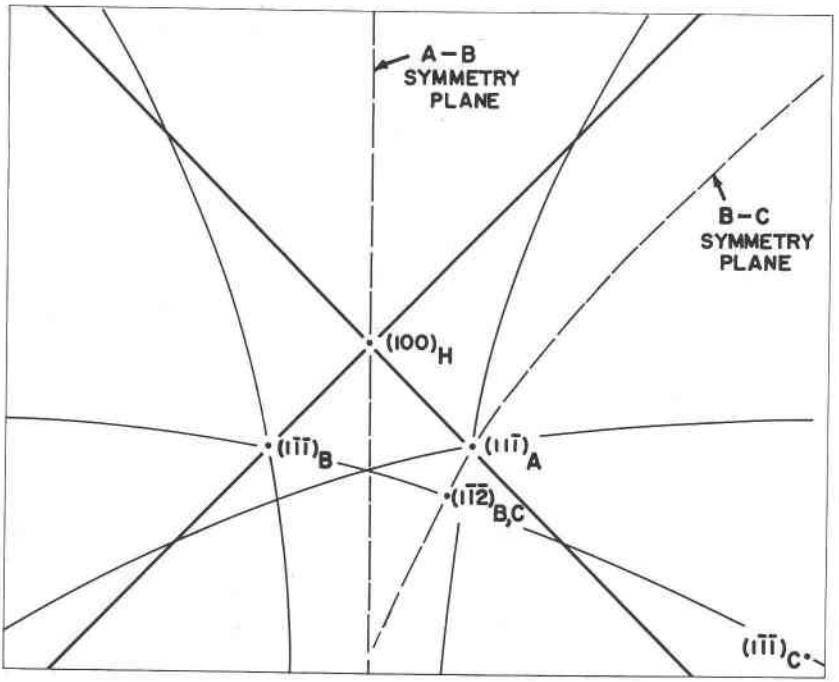

FIG. 2*b*. Schematic drawing of the symmetry relationships in Fig. 2*a*.

each bear a first-order twinning relationship with the host; *C* is a first-order twin with respect to *B*; *C* has a high-order (second-order) twin relationship with the host and a high-order relationship (third-order) with *A*.

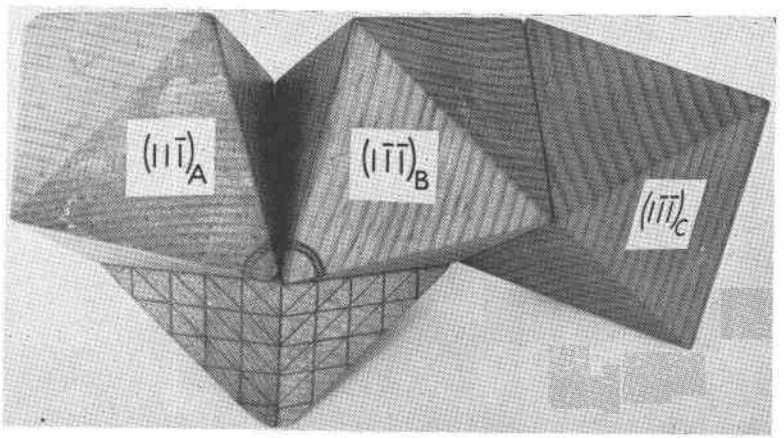

FIG. 3. Twinned complex, showing the orientations of the individuals noted in Fig. 1. View is along [100] (double arc) of the host crystal (ruled; only lower half visible).

In addition to the first-order twinning on (111) and ($1\bar{1}1$), as depicted in the model (Fig. 3), the host crystal also showed first-order twinning on the remaining two upper octahedral planes, i.e., ($\bar{1}11$) and ($\bar{1}\bar{1}1$). Upon sectioning for further investigation of the internal structure, it was disclosed that all twinning could be traced back to a common point within the crystal and that this point was coincident with a spherical cavity (gas bubble), approximately 0.7 mm. in diameter. Subsequent examination with an infrared image tube (3) revealed strong stress fields concentrated at the cavity. It seems probable that in this particular case the twinnings were simultaneously generated by the inclusion of a gas bubble within the structure.

Discussion

Twinning on all four upper (or, in some cases, lower) octahedral planes is limited to, and fairly common in, crystals grown by pulling along a cubic (fourfold) axis. The particular crystal described above is a special case for two reasons: (1) additional twinning has developed (individual *C*, Fig. 3) and (2) the twinning derived from a gas bubble inclusion. In other crystals examined, the twinnings were simultaneously generated by a sudden change in either the pulling rate or temperature gradient. The restriction of this twinning pattern to crystals pulled along a fourfold axis is explained by the fact that only in such a case do all four octahedral planes make the same angle with the direction of the temperature gradient (pulling direction).

Figure 4 presents a view along the gradient direction of a crystal pulled along [001] and twinned on all four upper octahedral planes. Such a drawing need not be considered idealized, since crystals have been observed in which the boundary traces have actually attained the pictured geometrical perfection. The dashed lines in the pattern are first-order twin boundaries. The vertical dashed line to the right, for example is the trace of the boundary between the host crystal and an individual developed by twinning on ($\bar{1}11$) of the host. Such boundaries represent minor structure discontinuities, since the initial deviation from normal bonding lies in the tertiary coordinations. The cross-hatched lines are traces of boundaries between high-order (second-order) twins and represent substantial structure discontinuities, since even the primary coordinations are disturbed. These are common in diamond crystals and are usually the loci of inclusions. From a geometrical point of view, boundaries of this type could be termed "high-order twin boundaries." Such terminology, however, implies that the discontinuity is a composition plane across which there has been a twinning operation, and this is not the case. It is merely the plane (or planes) along which two individ-

uals related by high-order twin geometry are joined. In this respect, it might more properly be termed a "high-order twin *join*." Considerations such as these emphasize the importance of regarding twinning as a physical rather than a geometrical phenomenon.

Owing to the sensitive structural dependence of electrical properties in the diamond-type semiconductors silicon and germanium (4), the presence of substantial structure discontinuities in these materials is

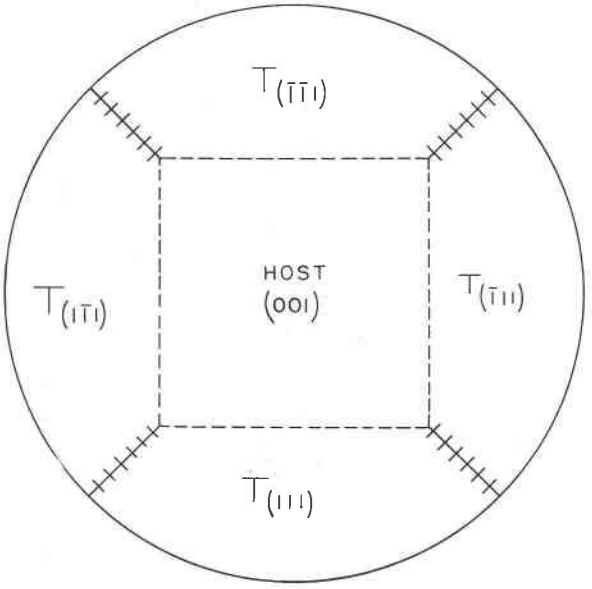

FIG. 4. Schematic drawing of the twinning pattern on (001) of a silicon crystal pulled along [001].

significant. Knowing that such discontinuities can be introduced by high-order twinning of a diamond-type material, it remains to describe their nature and variety.

A general grain boundary has five degrees of freedom, three deriving from the mutual orientation of the two individuals, and two introduced by the orientation of the join itself (5). The twinning operations establish the first three degrees of freedom. The join, however, will seek a minimum energy position, which in turn is influenced by environmental factors. Geometrical analysis of second- and third-order twinning has revealed a surprisingly small number of possible grain boundaries, as regards the first three degrees of freedom, i.e., the mutual orientation of the two individuals. Second-order twinning, as typified in Fig. 4, can develop but *one* such grain boundary. Specifically, this is a pure tilt boundary (6),

having a tilt angle of 38°57′ about [110]. Third-order twinning (cf. *A–C* relationship, Fig. 1) can introduce only *two* additional grain boundaries. One is a pure tilt operation of 31°35′ around [110]. This is the case with the *A–C* relationship in Figs. 1 and 3. The other third-order twin join is of the more general tilt-twist variety (7). The mutual orientation of the two individuals is defined as follows: $[111]_1 \wedge [111]_2 = 77°53'$; $[111]_1 \wedge [\bar{1}\bar{1}1]_2 = 22°11'$. It must be remembered, however, that the orientation of the join itself is not uniquely established by the twinning operations.

Summary

A unique, localized, structural outcrop on a silicon crystal pulled from a melt is actually a four-individual twin complex. This is a special case of a more general twinning pattern, typical of crystals pulled along a four-fold axis, wherein twinning develops on all four upper (or lower) octahedral planes. Such non-parallel, multiple twinning in diamond-type materials results in high-order twin joins, which represent substantial structure discontinuities.

Acknowledgments

The writer is indebted to Dr. W. Kaiser, of this laboratory, for the infrared observations and for periodic helpful discussions, to Mr. W. Pharo, Evans Signal Laboratory, who grew the crystal and kindly donated it for study, and to Dr. H. Kedesdy, also of this laboratory, for his critical review of the manuscript.

References

(1) Slawson, C. B., *Am. Mineral.*, **35,** 193 (1950).
(2) Kohn, J. A., *Ind. Diamond Rev.*, **13,** 56 (1953).
(3) Bailly, René, *Bull. Geol. Soc. Am.*, **60,** 1871 (1949).
(4) Taylor, W. E., Odell, N. H., and Fan, H. Y., *Phys. Rev.*, **88,** 867 (1952).
(5) Read, W. T., Jr., Dislocations in Crystals, McGraw-Hill, New York, 173, 183 (1953).
(6) *Ibid.*, 156, 178.
(7) *Ibid.*, 182.

Manuscript received Jan 18, 1956.