A TWINNING STUDY OF CUBIC (β) SILICON CARBIDE

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ABSTRACT

The recent emphasis on silicon carbide as a potential high-temperature electronic material has led to improved crystal growth techniques. As one result, well-formed, high-purity, cubic (β) SiC specimens have become available for crystallographic investigations. A study of 25 pure and doped β SiC crystals by the Weissenberg x-ray method showed prolific twinning (normal and high-order), some stacking randomness, and one case of polytypism (15R). Only two crystals were "structurally pure." No clear correlation between these findings and morphology or doping could be established. High-order twinning in β SiC is discussed, with emphasis on the relationship of a multiple-individual, non-parallel, twin complex to its resultant Weissenberg diffractometry.

INTRODUCTION

From a crystallographic point of view, the compound silicon carbide is one of the most intriguing materials in the realm of inorganic chemistry. Silicon carbide and polytypism are practically synonymous, the term having been introduced by Baumhauer (1915) to describe the three forms of the material known at that time. The subsequent work of Thibault (1944) and of Ramsdell (1947) began a quest for additional polytypes, the number of which has now grown to 39, with 25 having known structures. Numerous papers, based on such variables as temperature, supersaturation, geometrical factors, impurities, etc., have been written in an attempt to explain this almost unbelievable variety of structures. The literature on such studies has been summarized by Mitchell (1957). Silicon carbide has been the subject of extensive research on screw dislocations, spiral growth figures and their relationship with internal structure (Mitchell, 1957). It is generally conceded that a screw dislocation mechanism, operating on prototype structures having simply-periodic stacking reversals, plays a major role in establishing a given stacking sequence (*i.e.*, polytype) in the growing crystal. Thereafter, spiral growth perpetuates the sequence throughout the crystal bulk, generating unit cells having hexagonal c dimensions up to at least 1500 Å (Honjo *et al.* 1950).

The various silicon carbide polytypes can be considered as built up of $(00 \cdot l)$ layers stacked in an ordered manner along c. Each structure is described by a stacking sequence, which contains reversals at periodic intervals. A stacking reversal involves a 180°-rotation around c of the structure above a given $(00 \cdot l)$ plane relative to the structure below this plane. Such an operation is identical to the geometry of twinning, and one would expect silicon carbide crystals to show twinning of this type.

In most of the hexagonal polytypes (those having space group $P6_3mc$), single-crystal x-ray patterns show an apparent plane of symmetry in $(00 \cdot l)$ owing to the addition of a symmetry center by the x-ray geometry. Thus a twinning operation which introduces a local mirror plane normal to c would go unnoticed. In rhombohedral polytypes (and rare hexagonal forms of space group $P3m$), on the other hand, an added symmetry center does not introduce an apparent mirror plane in $(00 \cdot l)$, and twinning, if it were present, would be detected. The only truly common rhombohedral polytype is the 15-layer modification, 15R. Thibault's (1944) morphological studies yielded two examples of c axis twinning in 15R, but the authors are not aware of any systematic x-ray study of such crystals to determine frequency of twinning.

Cubic (β) SiC, having the sphalerite structure, can be regarded as a 3-layer rhombohedral (3R) polytype and would serve as an excellent subject for twinning studies. The analogous twin plane becomes (111), and the twinning is after the spinel law. Until recently, however, cubic SiC was known only as a fine-grained powder or as relatively small, generally irregular crystals intergrown with hexagonal or rhombohedral polytypes (Thibault, 1944). The present emphasis on SiC as an electronic material has resulted in new methods of crystal growth and made possible well-formed β SiC specimens for crystallographic studies. This paper presents the results of such an investigation.

Experimental Results

The β SiC crystals, grown by Dr. F. A. Halden, Stanford Research Institute, were prepared by melting silicon or a silicon alloy in a silicon-carbide-coated graphite crucible, holding at temperature to permit carbon saturation, and cooling in a temperature gradient (Halden, 1960). Specimens ranged in morphology from thin (111) plates to laths and needles along [110]. Typical dimensions were $0.1 \times 0.5 \times 1.0$ mm. Pure crystals (colorless to pale yellow-green), as well as some doped with 0.1 at. % gallium (yellow-green) and others with 1 at. % boron (yellow to olive-green), were examined. On the basis of morphology, pure crystals were indistinguishable from those containing boron. Gallium-doped

TABLE 1. EXPERIMENTAL SUMMARY OF β SiC STUDY

Crystal	Doping[1]	Habit	% Normal	% Twinned	% High-order Twinned	Random Stacking
1	—	thin plate	45	40	15	—
2	B	thin plate	70	20	10	v. weak
3	Ga	plate	50	50	—	v. weak
4	—	needle	60	20	20	v. weak
5	B	thin lath	50	50	—	trace
6	Ga	lath	50	50	trace	v. weak
7	—	thin lath	50	50	—	v. weak
8	B	thin lath	90	10	—	—
9	Ga	plate	85—	15—	2	trace
10	—	thin plate	50	50	—	v. weak
11	B	needle	50	50	—	weak
12	Ga	plate	65	35	trace	trace
13	—	thin lath	100	—	—	—
14	—	thin plate	50	50	—	v. weak
15	B	thin lath	100	—	—	—
16	Ga	plate	85—	15—	2	—
17	B	thin lath	50	50	—	—
18	—	thin lath	85	15	—	—
19	—	thin plate	80	20	—	—
20	—	thin plate	50	45	5	trace
21	—	thin lath	75—	25—	—	(2% 15R)
22	—	thin plate	80	20	trace	trace
23	—	thin plate	75—	25—	2	—
24	—	thin plate	65	35	—	—
25	—	needle	50	45	5	—

[1] Boron = 1 at. %; gallium = 0.1 at. %.

specimens, on the other hand, were less well-formed and noticeably thicker along the plate or lath normal, *i.e.* [111].

Twenty-five randomly selected β SiC crystals were studied by the means of the Weissenberg method, specifically with [110]-axis, zero-level patterns in each case. This has been one of the standard methods for distinguishing silicon carbide polytypes and related phenomena. Features sought included polytypism, twinning, high-order twinning, and stacking randomness. To varying degrees, all of these features were noted. Composite data are summarized in Table 1.

The salient experimental result is that all but two of the 25 crystals were found to be twinned, the scattering mass in twin orientation comprising 10 to 50% of the crystal. In addition, eleven specimens showed

high-order twinning, *i.e.*, twinning on at least two different octahedral planes (refer to discussion below); the individual in high-order twin orientation comprised up to 20% of the crystal mass. Stacking randomness, evidenced by streaking along $(10 \cdot l)$ and $(20 \cdot l)$ Weissenberg lattice lines, varied from "trace" to "weak" in 13 of the crystals examined. Polytypism was noted in only one crystal (no. 21); in this case, reflections of the 15-layer type (15R) amounted to approximately 2% of the scattering mass. Only two crystals (nos. 13 and 15) were entirely free of all these features.

Experimental results on the 25 crystals studied show no clear correlation between twinning and either morphology or doping material.

DISCUSSION

The detection of high-order twinning in cubic silicon carbide is a new, though not entirely unexpected, finding. Since high-order twinning involves two or more non-parallel twin operations on the same individual, cubic tetrahedral structures, commonly twinned and having four equally potential (octahedral) twinning directions, are logical possibilities for this phenomenon. It has previously been reported in diamond (Slawson,
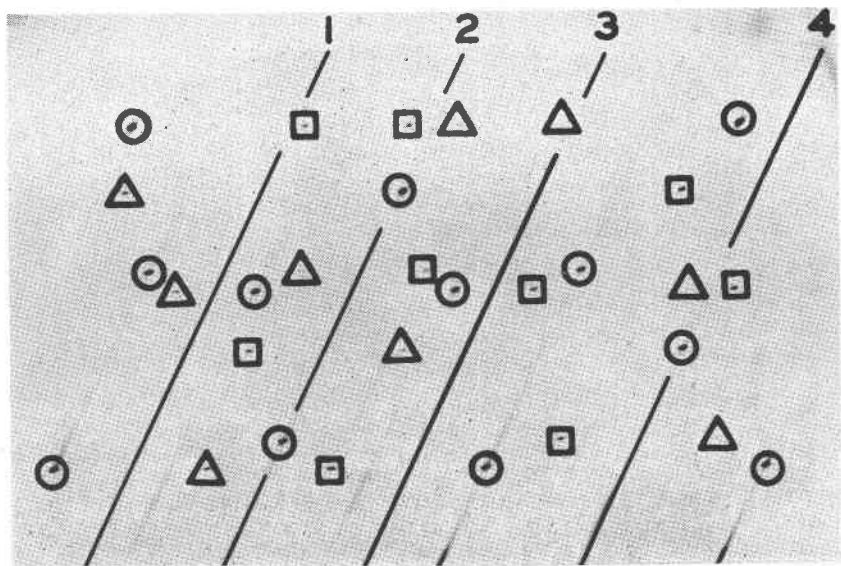

FIG. 1. Zero-level, [110]-axis, Weissenberg pattern of β SiC crystal no. 4. Circles, normal orientation; squares, twinned structure; triangles, high-order twinning. CoKα, 23 hrs. (1.1× relative to normal Weissenberg film).
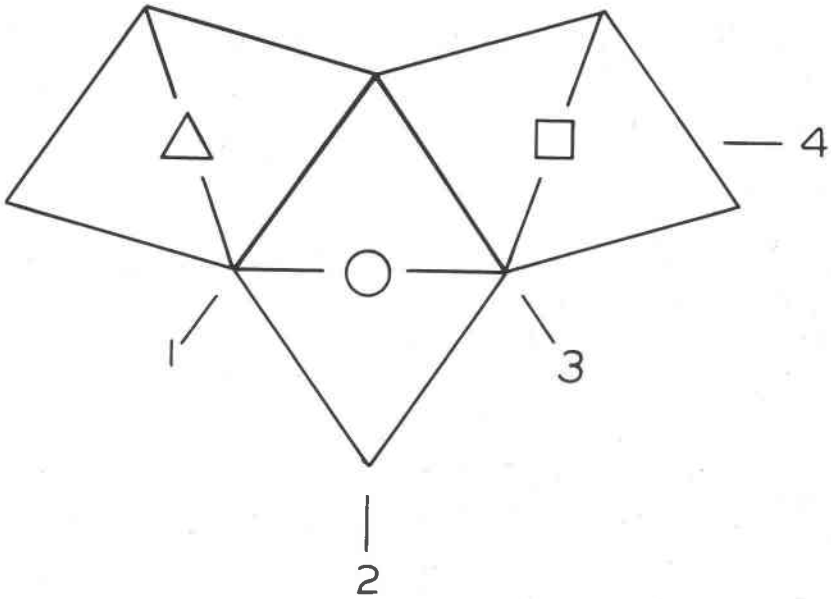
FIG. 2. Three-individual, octahedral twin complex projected on (110). Symbols and directions correspond with those of Fig. 1.

1950; Kohn, 1953) and silicon (Kohn, 1956, 1958), but the authors know of no earlier finding in materials with the sphalerite structure.

Figure 1 shows the [110], zero-level, Weissenberg pattern of β SiC crystal no. 4, the best example of high-order twinning in the group studied. Circles represent reflections deriving from structure in the normal (host) orientation; squares are associated with twinning (and resultant mirroring) across host octahedral direction 3; triangles represent twinning (and mirroring) across host octahedral direction 1. The triangle-square relationship, with positional symmetry across directions 2 and 4, is one of high-order (in this case, second-order) twinning. The corresponding twin complex is shown in Fig. 2, where [110] (rotation axis of Fig. 1) is normal to the diagram and common to all three individuals. The central octahedron is the host individual, with the two flanking octahedra bearing a first-order twin relationship with the host and a second-order relationship with each other. Symmetry directions noted in the Weissenberg pattern are indicated on the (110)-projected twin complex of Fig. 2.

As mentioned earlier herein, the relatively recent exploitation of silicon carbide as a possible high-temperature electronic material has given

added impetus to crystal growth and crystallographic studies. One of the first direct results was discovery of the long-sought zincite-type (2H) SiC (Adamsky & Merz, 1959). Another consequence is a capability to prepare very pure SiC crystals, permitting more controlled studies of the growth mechanism and the polytypism-screw dislocation relationship. It is reasonable to anticipate that further investigation of newly-available crystals will continue to yield interesting results and add to our knowledge of this most intriguing material. Those studying electronic properties of SiC should be aware, however, that such crystallographically interesting features as twinning, polytypism, stacking disorder, etc., may very well have a noticeable effect on the more structurally sensitive electronic properties and should be considered in any studies of this type.

Acknowledgment

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