A grain boundary of α-SiC bicrystals

There are reports [1, 2] that bicrystals of α-SiC combining at the (0 0 0 1) face in a certain rotation angle around the *c*-axis have been discovered in highly pure α-SiC single crystals which had been prepared by sublimation at 2500° C [3, 4]. It is well known that SiC crystals have a covalent character and that Si or C atoms take up a 6-fold rotational symmetry on the (0 0 0 1) face of α-SiC; the same as the (1 1 1) face of diamond or silicon crystals. Every atom of these surfaces has a dangling bond perpendicular to the surface. In the case of α-SiC bicrystals combining at the surface, it could be considered that some of the atoms on the surfaces of both crystals combine using their dangling bonds. The number of combined atoms is varied by rotation of the adjacent crystals around their *c*-axis in opposite directions. The stability of the bicrystals will increase with increasing number of combining atoms. When the rotation angle is $n \times 60°$ ($n = 0$ and positive integers), all dangling bonds contribute to the combination. Examples of such combinations are often observed as stacking faults or twins. Here, however, bicrystals combining with unusual rotation angles different from the values mentioned above will be discussed. The reason why bicrystals with unusual rotation angles appear may be because the movement of the crystals on combining is restricted by their weights. Two crystals might be settled in a state with a maximum proportion of combined atoms in the neighbourhood of the initial contact position. Examples of experimentally-observed α-SiC bicrystals are presented in Table I. Many of them have a relatively high proportion of combined atoms, as pointed out by Sueno *et al.* [1] and Inomata *et al.* [2]. In the case of the sample combining at 23.75°, however, the proportion is very low. This was noticed and a model calculation was carried out as follows.

(1) The calculation was restricted to inside a circle which included 3259 lattice points of hexagonal symmetry.

(2) The distance between the nearest neighbour lattice points on the sheet was taken as unity. The *d* value was a diameter of the sphere placed at each lattice point and might be corresponded to the spread of electron cloud at the middle point between Si and C atoms [6, 7].

TABLE I Examples of α-SiC bicrystals

θ_e°*	θ_c°*	DOC	$c_1 \Lambda c_2$*
21.47 (21°28′) (= 38°22′)†	21.79	0.1429	–
27.80 (27°48′)†	27.80	0.0769	–
10.90 (10°54′)†	10.99	0.0092	–
22.12 (22°07′)‡	21.79	0.1429	6°
18.05 (18°03′)‡	17.90	0.0323	3°
11.12 (11°08′)‡	10.99	0.0092	0°
19.75 (19°45′)§	19.65	0.0097	0°
17.08 (17°05′)§	16.43	0.0204	7°
23.75 (23°45′)§	23.72	0.0031	0°

* θ_e: Rotation angle of bicrystals in experiments.
θ_c: Theoretical value for maximum DOC near by the θ_e.
DOC: The degree of coincidence.
$c_1 \Lambda c_2$: The angle deviated from the parallelism of *c*-axis obtained experimentally.
† Sueno *et al.* [1].
‡ Inomata *et al.* [2].
§ Inoue *et al.* [5].

(3) The two circular sheets were superposed as mentioned above, and were rotated in opposite directions around the axis perpendicular to the plane and passing the centre of the circle.

(4) The overlap volume of the sphere as a function of rotation angle in the vicinity at 23.75° was calculated.

(5) The ratio of the overlap volume summed over the circle to the total volume of sphere within the circle was termed the degree of coincidence (DOC) and the ratio of the number of overlapping spheres to the total number of spheres within the circle was termed the degree of pseudo-coincidence.

The degree of coincidence and the degree of pseudo-coincidence against the rotation angles are shown with values of *d* in Figs 1 and 2, respectively. In order that the values show maxima at 23.72°, which is the theoretical maximum point of DOC, the *d* values should be smaller than 0.06 in Fig. 1 or smaller than 0.03 in Fig. 2.

The boundary energy of the α-SiC bicrystals combining at the (0 0 0 1) face can be evaluated using the values of $d = 0.06$ and 0.03. The calculation was performed in the same manner as the above one except that the number of lattice points included in the circle was 1459 and the range of rotation angle was 0° to 30° with a 0.1° step. It results in an average boundary energy for α-SiC bicrystals of 1.980 and 1.975 times the surface energy of α-SiC in the case of coincidence

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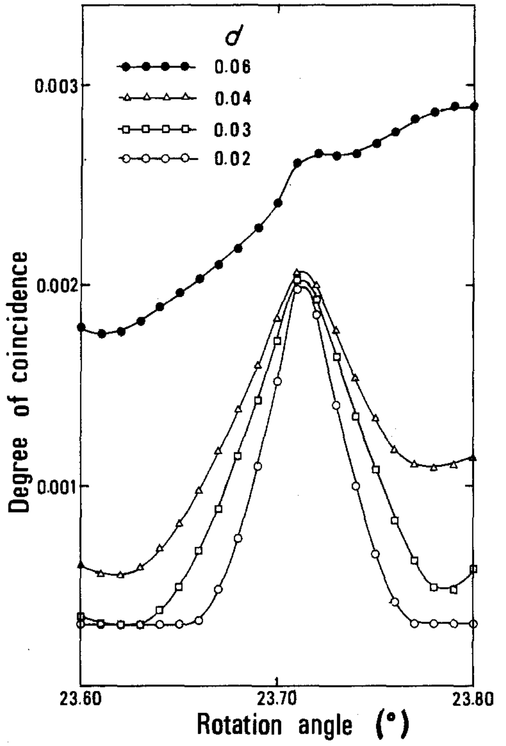

Figure 1 The computed relation between the degree of coincidence and the rotation angle.

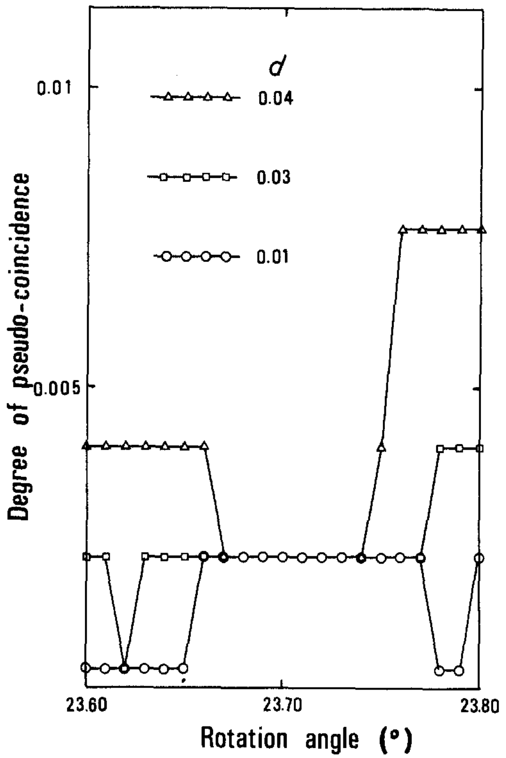

Figure 2 The computed relation between the degree of pseudo-coincidence and the rotation angle.

and pseudo-coincidence, respectively. It can be concluded that the relaxation of energy on forming such bicrystals will be relatively small in the case of SiC.

The angle of distortion of the tetrahedral structure could be deduced to be 5.62° and 2.80° from 0.06 and 0.03 of *d*, respectively. These values were obtained from the assumption that the combination of the two crystals should be settled in the maximum condition of the DOC. Snyder and Wasserman [8] calculated the co-ordinate of the carbon atom on the diamond (1 1 1) surface with SCF–MO (self-consistent field–molecular orbital) method. According to their result, the surface carbon atom with a dangling bond shifts 0.1 Å toward the bulk from its initial unrelaxed lattice site. The angle of bond distortion deduced from this value is 3.83°. On the other hand, the Si (1 1 1) surface structure has been extensively studied by many authors in theoretical calculations [9–11] and experiments [12, 13]. The treatment of the Si (1 1 1) surface which exhibits superlattice structures 7 × 7 or 2 × 1 seemed to be rather complicated. In the simplest case, 1 × 1, the displacement of the surface atom was calculated to be 0.33 Å towards the crystal [9]. This corresponds to an angular distortion of about 8°. The α-SiC (0 0 0 1) surface may not be compared directly with diamond (1 1 1) or Si (1 1 1) surfaces. The result obtained in the case of coincidence, however, seemed to be plausible and might represent the upper limit of the distortion in α-SiC.

In the present calculations, there are simplifications in the model and assumptions to simplify the calculations. Above all, the effect of impurities possibly existing at the boundary, the deviation from the parallelism of the *c*-axis of the two crystals and the ionic character of SiC crystal are completely neglected. Even though the model calculation is based on these simplifications and assumptions, it could be concluded from the existence of the bicrystals with unusual rotation angles that the tetrahedron of SiC is rigid and the relaxation of energy in combination of SiC crystals is very small.

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