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Observation of secondary particles grown on crystal surfaces of silicon carbide

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Pressureless sintering of ultrafine SiC powder containing a large amount of free Si was carried out with the aid of boron. Epitaxial growth of secondary particles was observed by scanning electron microscopy (SEM) on some hexagonal-shaped surfaces of β-SiC cube-octahedra. The other hexagonal-shaped surfaces were seen to be entirely smooth. The two-fold symmetry of the [1 0 0] axes for the appearance of secondary particles certainly reflects the polarity of β-SiC. When the sintering was repeated again, coalescence growth of secondary particles was remarkable on the former surfaces and layered growth was predominant on the latter surfaces.

1. Introduction

The crystal structure of β-SiC is well-known to be of the zinc blende type and it has no center of symmetry. The trigonal axes [1 1 1] of β-SiC are polar, and the {1 1 1} surfaces of the hexagonal shape are bounded by either Si or C atoms. These polar surfaces {1 1 1} exhibit remarkably different features for etching [1], thermal oxidation [2] and epitaxial growth [3] by the dipping method [4].

In this paper we show another typical example observed by SEM of the morphology of hexagonal polar surfaces {1 1 1} of β-SiC polyhedra. The growth features of secondary particles (hereafter called SP) on hexagonal-shaped surfaces of cube-octahedra reflects the polarity of β-SiC. The original β-SiC polyhedra were obtained by sintering of ultrafine SiC powder containing a large amount of free Si [5]. Adding 1% boron as the sintering agent, the sintering [6, 7] was carried out at a relatively low sintering temperature, less than 2050 °C.

2. Experimental procedure

The raw powder of β-SiC containing a large amount of free Si was the same as those used in a previous paper [7]. After adding 1% amorphous boron, the powder was ball-milled and moulded into the form of a pellet of 8 mm diameter. The pellets were sintered using a furnace described previously, with the heating diagram D_2 shown in Fig. 2 of [7]. In the present case, the primary sintering was carried out at temperature $T_1 = 1400$ °C for 1 h in vacuum, and the secondary sintering at $T_2 = 1750$–2000 °C for 1 h, usually in Ar gas of 6.66–26.66×10^3 Pa. After natural cooling specimens were observed by SEM and X-ray powder diffraction. In some cases observed specimens were sintered repeatedly.

3. Results

An example of an SEM image obtained from the surface of a sintered body (sintering temperature $T_2 = 1960$ °C) is shown in Fig. 1. A lot of polyhedral crystals of β-SiC can be observed and SP are seen on the hexagonal surfaces designated by the symbol A. Other hexagonal surfaces having no such SP are shown by the symbol B. Very few SP which start from the boundary of the surfaces A can be observed on the square and rectangular surfaces designated by the symbol C.

The shape of the SP is mainly rod-like and is a truncated trigonal pyramid. The long edges of each SP are parallel to three directions of the side of the hexagonal basal surface, i.e. SP grow epitaxially. The size of the SP is of the order of 1 μm, and the density of SP is of the order of 0.1 μm^{-2}. When the sintering temperature is higher or the sintering time is longer than in the case of Fig. 1, the SP grow at high density, and coalescence growth becomes predominant.

A typical example of an SEM image in which three types of surfaces are recognized in a single polyhedron is shown in Fig. 2. The square surface C is surrounded by four hexagonal surfaces A and B arranged alternately. Many epitaxially grown SP are observed on the surfaces A, and no SP on the surfaces B. Two sets of hexagonal planes placed in opposite positions are identical with each other. In other words, the normal axis to the surface C shows two-fold symmetry, not four-fold.

The crystal structure of the SP was confirmed to be β-SiC by taking electron diffraction patterns in TEM. The growth of SP was recognized only on the outer surfaces of the sintered pellet-like specimens. No SP could be found on any surface of SiC polyhedra in SEM images taken from the fractured surface of sintered specimens.

When the sintering temperature is slightly lower than in the case of Fig. 1 ($T_2 = 1790$ °C), the growth of SP is not so remarkable. However, if the same specimen was sintered repeatedly under the same sintering

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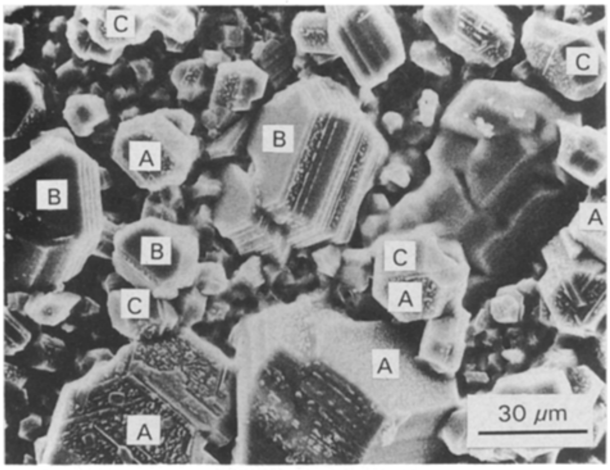

Figure 1 SEM image obtained from the top surface of sintered SiC. Sintering conditions: temperature $T_2 = 1960\,°C$, Ar gas pressure $H = 1.866 \times 10^4$ Pa.

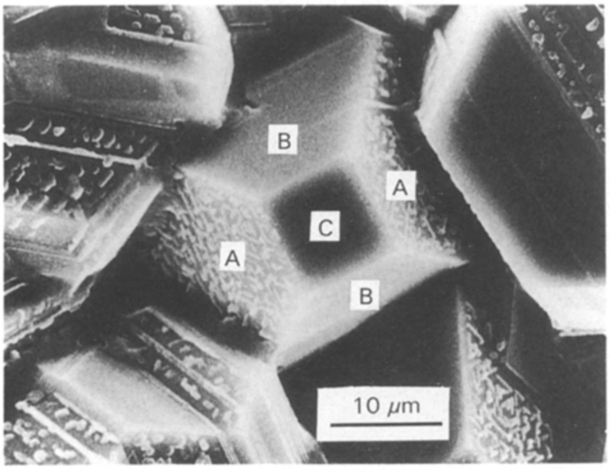

Figure 2 Typical SEM image showing a simple polyhedron covered with secondary particles. The specimen is the same as that of Fig. 1.

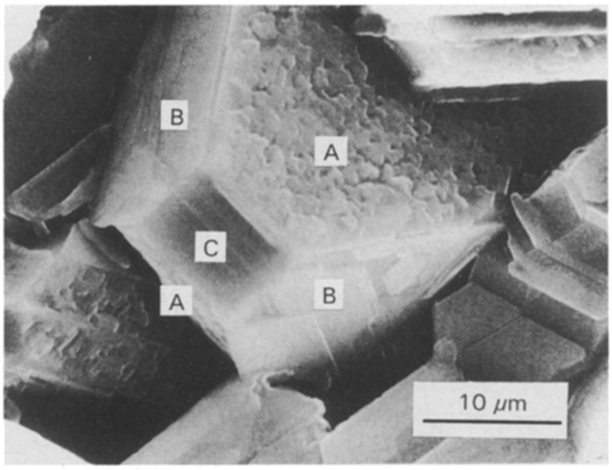

Figure 3 SEM image of twice sintered SiC. Sintering conditions: first, $T_2 = 1790\,°C$, $H = 1.333 \times 10^4$ Pa; second, $T_2 = 1790\,°C$, $H = 1.333 \times 10^4$ Pa.

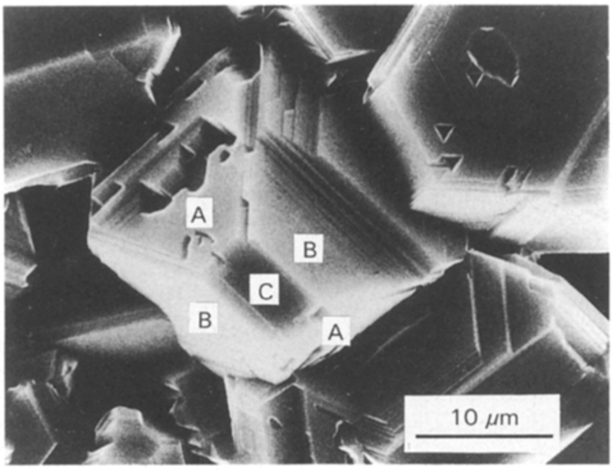

Figure 4 SEM image of twice sintered SiC. Sintering conditions: first, $T_2 = 1820\,°C$, $H = 1.466 \times 10^4$ Pa; second, $T_2 = 2050\,°C$, $H = 1.466 \times 10^4$ Pa.

conditions, remarkable growth of SP could be observed, as seen in Fig. 3. Not only is coalescence growth of SP on surfaces A predominant, but also layered growth on surfaces B can be clearly observed.

When the repeated sintering was carried out at higher temperature ($T_2 = 2050\,°C$), the grain growth observed on surfaces A and B becomes heavier, as seen in Fig. 4. The surfaces A are covered with a thick layer, but have many remains of a filling with crystallographic orientation. The surfaces B are covered by homogeneous thick layers, and sometimes their layers are multiply folded.

After each sintering, the crystal structure of specimens was examined by X-ray powder diffraction. The structure of β-SiC, which is the same structure as the raw powder, was recognized in every case in Figs 1–4, and no existence of α-SiC was recognized. The remaining amount of free Si, which was included in the raw powder at a concentration of about 35%, became less with increasing sintering temperature T_2. Still, a few percent of free Si was recognized as remaining even at the highest sintering temperature, in Fig. 4.

4. Discussion

From the consideration of angular relationships of the crystal surfaces, it is anticipated that the habit of β-SiC shown in Figs 2–4 must be a part of the cube-octahedron. The shape of the cube-octahedron is geometrically formed by truncation with six $\{1\,0\,0\}$ surfaces from a regular octahedron having $\{1\,1\,1\}$ surfaces. Because the β-SiC crystal has a zinc blende structure, the trigonal axes $[1\,1\,1]$ are polar and the $\{1\,1\,1\}$ surfaces consist of either Si or C atoms. We shall distinguish them by calling them the A and B surfaces [8]. Two projections of the cube-octahedron of zinc blende structure onto the $(1\,0\,0)$ and $(1\,1\,1)$ planes are shown in Fig. 5(a) and (b). The $\langle 1\,0\,0 \rangle$ axis normal to the surface C_1 has two-fold symmetry. As shown in Fig. 5(a), the surface C_1 is surrounded by A and B surfaces alternately. The back hexagonal surface of Fig. 5(b) is a B surface. Of course, the interchange between A and B surfaces in these figures is identical geometrically.

Morphological observations of the basal planes of an α-SiC single crystal have been done for the case of

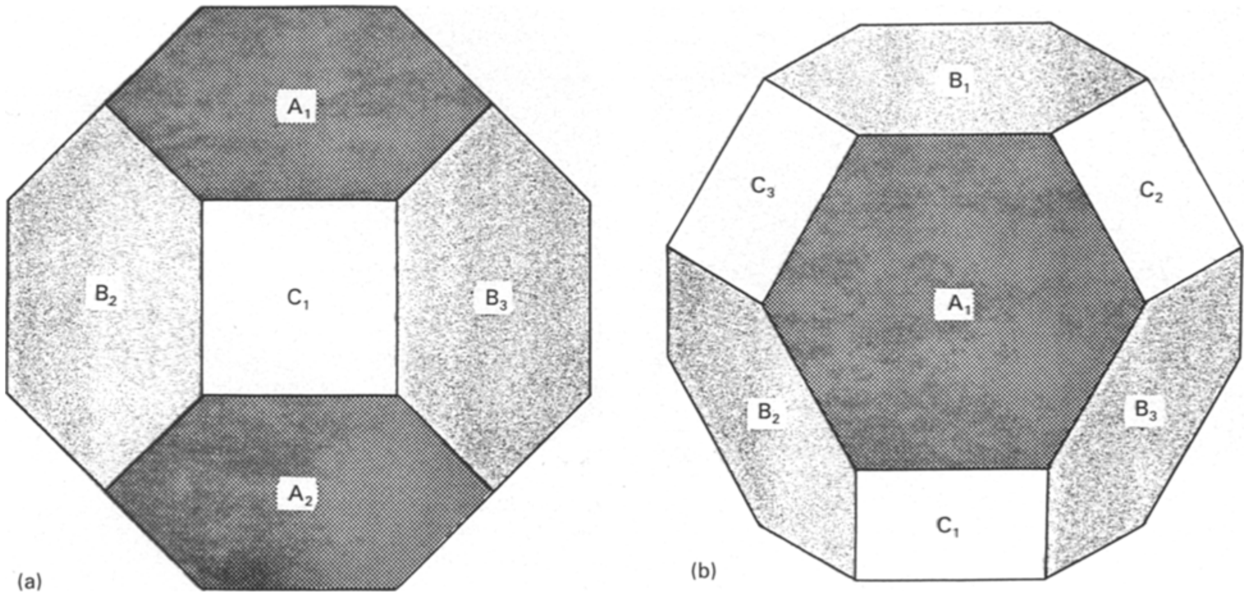

Figure 5 Schematic diagrams of cube-octahedron having zinc blende structure projected on the (a) (1 0 0) and (b) (1 1 1) planes.

etching [1] and epitaxial growth [3]. As a result, it is known that the Si atoms surface (A surface) is rough and the C atoms surface (B surface) is smooth. On the other hand, typical spiral growth steps have been observed with the optical microscope on the Si atoms surface of α-SiC [9], which corresponds to a smooth surface. An alkaline solution produces growth patterns [10] only on the C atoms surface of α-SiC. In the latter two cases, the Si atoms surface is smooth and the C atoms surface is rough, a reversal of the former cases. The surface roughness of the polar surface of α-SiC depends strongly on the growth conditions.

In the present case of β-SiC, it is experimentally confirmed that the A surface grown SP is the rough surface and the B surface grown thin layer is the smooth surface. The determination of the absolute polarity of $\{1\,1\,1\}$ surfaces and whether the A surface is the Si or the C atoms surface is very important in order to clarify the growth mechanism of SP and layers. However, the size of each β-SiC polyhedra is so small that the usual determination method of polarity is hard to apply and the absolute polarity has not yet been determined experimentally.

The necessary conditions for the growth of SP are similar to those for the growth of polyhedral β-SiC crystals [6, 7]. The existence of free Si in the raw powder and boron addition as the sintering agent is essential. The sintering temperature is not as high as that at which plate-like α-SiC crystal growth is predominant. When the Ar gas pressure is lower than 26.66 Pa, the SP appeared on the outer surfaces of the sintered bodies. Once SP grows, its evidence is confirmed in repeated sintering, as seen in Figs 3 and 4. The growth rate of layered growth of β-SiC is estimated to be of the order of $10\,\mathrm{nm\,min^{-1}}$ at $T_2 = 1790\,^{\circ}\mathrm{C}$ from the B surface of Fig. 3.

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