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On the Identification of the Polar Surfaces of SiC Crystals

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The identification of the polar surfaces of silicon carbide with an alkaline solution was investigated by phase-contrast microscopy and two-beam interferometry. It is found that the alkaline solution produces growth patterns on the (000$\bar{1}$) carbon surface, while the opposite (0001) silicon surface remains essentially unaffected. The merit of polarity determination by a growth method combined with phase-microscopy was proposed.

1. Introduction

The polar surface identification in non-centrosymmetric crystals is fundamentally important in producing and fabricating compound semiconductor crystals or epitaxial films. In the case of II-VI or III-V compounds, the anomalous X-ray dispersion effect [1, 2] can be used for this purpose since the reflected intensities differ markedly between the polar faces. Silicon carbide is a IV-IV compound and the polarity determination by an X-ray method is very critical and one needs great care in the experiment.

Brack [3] has attempted the X-ray examination and determined the polarity of α-SiC as shown in fig. 1. He also established the connection between polarity and etch figures by molten salt etching. Recently Bartlett and Barlow [4] also applied the same method to β-SiC.

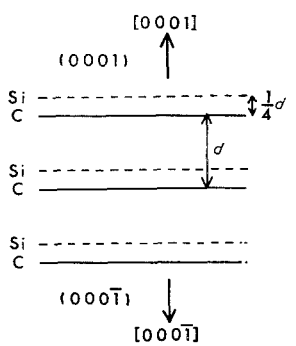


Figure 1 Schematic representation of polar surfaces.

Once the absolute structure is established by an X-ray method one can make use of chemical etching with great ease since the activities of two kinds of polar surfaces in a crystal are strikingly different. Harris *et al* [5] have found that alkaline solution etching is more efficient and rapid in polarity determination than the molten salt etching which had been extensively used on silicon carbide. These authors, however, did not clearly establish the relation between molten salt etching and solution etching so that no confirmation was made with respect to the result of X-ray determination.

We have carried out etching experiments and investigated the surfaces with the aid of a sensitive phase-contrast microscope and interferometer. It was found that the patterns produced in the alkaline solution are due to growth on the (000$\bar{1}$) carbon surface and implication of this result has been considered.

2. Experimental

Three batches of semiconductor grade α-SiC crystals grown at temperatures of 2400, 2550, and 2620°C by Lely's sublimation method [6] were used for this study. They are transparent pale green hexagonal platelets having specular basal polar faces of 1 to 5 mm in size. More than thirty single crystals were hand picked from each batch and treated in etchants shown in table I. The solution etching was carried out at boiling temperatures between 104 and 115°C within 15 min in a 200 cc beaker kept in a hot oil bath. Some of the crystals were cleaned in

TABLE I Compositions of working reagents

Alkaline solutions	Reagents (weight ratio) $K_3Fe(CN)_6$	NaOH	H_2O	Temperatures (°C)	Time (max.) (min)	Patterns obtained
S-1	1	1	4	105 to 114	15	Ground glass
S-2	3	3	11			Network
S-3	1	1	3			Dendritic
Molten salts	Na_2O_2	$NaNO_2$	KNO_3			
M-1	1	1		600	30	Rough
M-2			1	500	30	Rough

HF and HNO_3 solution before the test to eliminate the effect of surface films which may mask the innate surfaces.

The basal surfaces of the specimens were carefully observed before and after etching under a phase-contrast microscope and a differential interference microscope (both of the reflection type), which are capable of detecting the step height down to a few Å in the vertical direction. The patterns which appeared in etching were also measured by a two-beam inteferometer of the Michelson type. It must be stressed that the absolute surface microtopography, (i.e. the identification of a three dimensional pattern as being protrusion or depression) can be explicitly determined by phase-contrast microscopy. An ordinary light microscope or a differential interference microscope is unable to provide the information as to which side is higher, though the latter is as sensitive as a phase-contrast microscope in revealing small level differences.

3. Results and Discussion

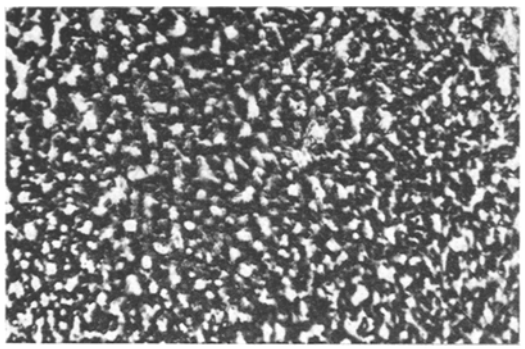
It was found that only one of the two basal surfaces of every silicon carbide crystal, regardless of cleaning in HF and HNO_3 solution prior to etching, showed a contrasting change to the opposite basal surface in the alkaline solutions. As there was not a single exception in characteristic over more than a hundred crystals examined, it is possible to conclude that the alkaline solutions discriminate one polar surface from another.

While Harris *et al* [5] obtained only dendritic patterns and observed no change in the general features of the patterns in the various solution concentrations, we observed two additional distinct patterns. It was found that the surface features acquired on one of the basal surfaces differ depending on the concentration of the alkaline solution. The typical patterns which appeared on increasing the concentration may be classified into three types of patterns such as ground glass, network and dendritic shown in the positive phase-contrast micrographs of figs. 2a, b and c. In these photographs, protrusions or hills should be seen as bright figures in the dark background. For instance, in a positive phase-contrast image, a growth layer having step height of some 10 Å is clearly seen with a bright halo appearing along the higher side of the step, as can be seen in a thin growth layer in fig. 4. Judging from the contrast effect of phase-contrast microscopy, it is apparent that all the patterns shown in fig. 2 are protrusions on the surface.

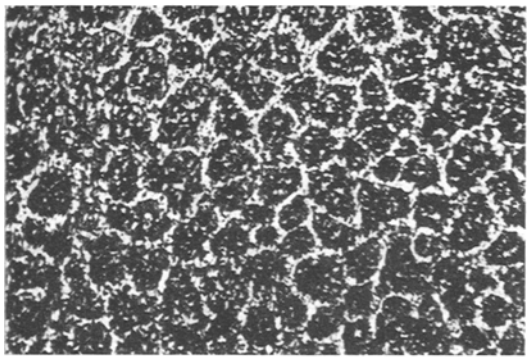
This was further demonstrated in a two-beam interferogram (fig. 3) taken on a growth spiral which was covered by dendritic patterns formed in the alkaline solution S-3. As the interferogram was photographed by white light without a filter, the relation between interference fringes is so clear that no ambiguity remains in estimating the order of interference. Starting from the lower left to the centre of fig. 3, the fringes kink to higher level at the spiral ledge. The same kind of kinks are also observed in the fringes which run across the dendrites. From the interferometric measurement it is established that the dendritic patterns are protrusions of less than 1000 Å in height. The spiral step height is estimated to be about 2500 Å.

From these results, it is possible to conclude that the patterns obtained in the alkaline solution were due to growth and not due to etching, contrary to our expectation. The thickness of the growth layers tend to increase with etching time, but the typical patterns such as shown in fig. 2 were generally unchanged provided that the concentration of the solution was kept constant.

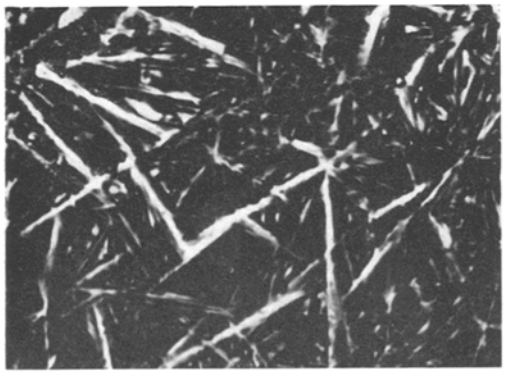
The growth layers thus obtained were subjected to washing in an ultrasonic cleaner with distilled water or HF and HNO_3 solution but were



(a)



(b)



(c)

Figure 2 Positive phase-contrast micrographs on polar surfaces after treatment in the alkaline solutions. (a) ground glass pattern (× 650) (S-1 solution), (b) network pattern (× 400) (S-2 solution), (c) dendritic pattern (× 550) (S-3 solution).

not observed to change at all. The growth patterns could be mechanically removed using a needle-point or knife edge.

It should be indicated that in addition to the growth patterns produced, the alkaline solution attacked the starting point of growth spirals (emergent sites of screw dislocations) as well as mechanically scratched parts, forming pits and grooves, respectively. This real etching action took place in any of the surfaces irrespective of polarity. A positive phase-contrast micrograph shown in fig. 4 is taken on the opposite polar surface of fig. 3. No dendritic patterns were formed on this polar surface but only the starting point of composite spirals were etched.

Figure 3 Two-beam interferogram of dendritic patterns formed using an alkaline solution on a polar surface containing a growth spiral. The scale marking corresponds to 0.1 mm.

Figure 4 Positive phase-contrast micrograph of the centre of growth spirals. Etch pits were formed at the screw dislocation sites. Thin layers are also seen. (× 450).

In order to correlate the result of the anomalous X-ray dispersion effect in polar surface identification with that using alkaline solutions, about thirty SiC crystals were etched in molten salts M-1 and M-2 after treating in an alkaline solution. For confirmation, we also etched the crystals in a molten salt prior to an alkaline solution. It was found in either process of

chemical treatment that only one side of the polar face was severely changed and it turned out that the rough basal surface acquired in molten salt etching of M-1 corresponds to that of forming the dendritic growth layer in an alkaline solution.

Following the result of Brack [3] it is found that the polar surface covered by growth layers in alkaline solution is the $(000\bar{1})$ carbon surface. Gabor and Jennings [7] have also reported that the attack by molten salts is chiefly on the $(000\bar{1})$ carbon face.

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