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The Structure of a New SiC Polytype

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A direct method of determining the structure of polytypic crystals has been applied to a new 69*R* polytype of SiC. The lattice constants are $a = 3{\cdot}077 \pm 0{\cdot}002$ and $c = 173{\cdot}75 \pm 0{\cdot}15$ Å; the Zhdanov symbol is $[(43)\,(33)\,(22)\,(33)]_3$. A total of 84 crystals of the same growth run were analysed by Laue and precession techniques and a frequency distribution of polytypes has been tabulated.

Introduction

A new SiC polytype has been found during an investigation of the epitaxic growth of SiC. After removing the epitaxic layer a crystal piece of about 5 mm² and a thickness of 0·1 mm could be isolated. It turned out to be homogeneous and to consist entirely of a 69-layer polytype. A cursory inspection of the precession pictures revealed that its intensity distribution deviated considerably from the polytype 69*R* described by Kuo Chang-lin (1964). Subsequently the growth cavity was unsuccessfully examined for other crystals of the same or a closely related structure in order to recover an unmutilated specimen of 69*R* and to shed some light on the growth mechanism.

Experimental observations

The crystals were grown at 2500°C in a small Lely furnace under an argon pressure of 660 torr. 1 torr of nitrogen was introduced to overcompensate the p-dopants present in the starting material (mainly aluminum with a concentration of 0·02%). The growth cavity had an inside diameter of 4·5 cm and a height of 6 cm. The walls were 1 cm thick. The largest crystals measured 0·3 cm² and ranged in thickness from 0·1 mm to 2 mm. Around the equator of the cavity there was a band approximately 1·5 cm wide which consisted mainly of 6*H*, whereas judging by the color the upper and lower part contained more 15*R* (Biedermann, 1965).

84 crystals varying in thickness and size and coming from different locations in the growth cavity were analysed by Laue and precession techniques. Two thirds of the crystals investigated were composed of two or more polytypes and all but 5 crystals contained the 6*H* polytype. Two of these 5 crystals were pure 15*R*, the remaining 3 contained polytypes with very long stacking sequences and could not be identified. Table 1 lists the polytypes found and the intergrowth observed. This polytype distribution seems to be rather typical for our growth conditions and does not depend significantly on the purity of the SiC. Batches of crystals grown under the same conditions but using high purity starting material (less than 1 ppm p-dopants) and the purest argon available (0·05 ppm N_2, 0·6 ppm O_2, 0·01 ppm H_2), exhibit roughly the same pattern. In this and in other growth runs it was observed that an overwhelming majority of the platelets contain the polytype 6*H*. In most specimens the most intense Laue spots belong to 6*H*. Of some platelets containing several polytypes surface layers of a few 10 μm were re-

Table 1. *Polytype distribution*

Combination	Number	Percentage	
6*H*	22	26·2	28·6% pure polytypes
15*R*	2	2·4	
6*H*+15*R*	29	34·6	57·2% two distinguishable polytypes intergrown
6*H*+ 4*H*	4	4·8	
6*H*+ 3*C*	3	3·6	
6*H*+*X*	9	10·7	
3*C*+*NR*	2	2·4	
8*H*+*NH*	1	1·2	
6*H*+2×15*R*	3	3·6	11·9% three distinguishable polytypes intergrown
6*H*+15*R*+*Y*	7	8·3	
6*H*+2×15*R*+ 3*C*	1	1·2	2·4% four distinguishable polytypes intergrown
6*H*+2×15*R*+21*R*	1	1·2	

N = not identified, large.
X = 21*R*, 27*R*, 39*R*, 48*H* once each, *NR* 5 times observed.
Y = 4*H*, 3*C*, 21*R*, 57*R*, *NH* once each, *NR* twice observed
2×15*R* = two regions of 15*R* rotated against each other by 60°.

moved. This invariably resulted in pure 6*H* crystals of very good perfection. It is therefore quite remarkable that not only two pure 15*R* of several 100 μm thickness but also a 69*R* of 100 μm thickness was found.

On 12 platelets growth spirals were observed. 8 of these platelets contained unusual or unidentified polytypes, 3 consisted of 6*H* and 15*R* and showed some disorder, 1 showed three well developed polytypes (4*H*, 6*H*, 15*R*).

Structure determination

A fragment of 0·02 mm³ of the new polytype $69R_b$ was mounted on a Stoe precession camera and the intensity of the 10.*l* reflexions ($\overline{68} \le l \le 67$) recorded. Four different exposure times were chosen and the films were processed together (Fig. 1).

Additional pieces of information were gathered by measuring the optical absorption at the band edge. It coincides almost with the absorption in 6*H* and suggests strongly that about a third of the layers are hexagonally stacked (Choyke, Hamilton & Patrick, 1964). This implies that the structure should be described by an 8-digit Zhdanov symbol. Raman scattering experiments are in good agreement with predictions for a 69*R* polytype based on the data of Feldman, Parker & Choyke (1968).

In addition to $[(33)_3 32]_3$ there is only one other simple structure with a repeat distance of 69 namely $[(44)_2 43]_3$. Of this series only the end members 21*R* and 8*H* are known (the structure of 93*R* which could belong to this series has not been determined). The calculated intensities for $[(44)_2 43]_3$ disagree completely with our experimental results. Thus we failed to establish the existence of yet another structure series $[(44)_n 43]_3$.

The direct method of obtaining the structure of polytypes described by Tokonami (1966) and Gomes de Mesquita (1968) was chosen because the optical data only implied an 8-digit Zhdanov symbol but could not rule out a higher or lower percentage of hexagonal stacking. The observed intensities were used to compute $\pi(0,p)$, the frequency of occurrence of the stacking vector $[0,0,p/n]$. The redundancy provided by measuring the intensities $|F(10,l)^2$ and $|F(10.\bar{l})|^2$ allowed to estimate the uncertainty $\delta\pi(0,p)$: The data were split into two groups and the summation was carried over $\overline{35} \le l \le 34$ and $37 \le |l| \le 68$. The choice to split the data in this fashion was made because the small errors introduced by neglecting all geometrical corrections were minimized within one set of data.

This procedure lead to the conclusion that the structure belonged to the group of the permutations of the Zhdanov symbol (43333322).

In Table 2 two of the calculated intensity distributions are compared to the observed one. It is evident that our structure is [(43) (33) (22) (33)]$_3$ with the lattice constants $a = 3{\cdot}077 \pm 0{\cdot}002$ and $c = 173{\cdot}75 \pm 0{\cdot}15$ Å.

Table 2. *Comparison of observed and calculated intensities for some of the reflexions* (10.*l*) *of two types of* 69*R*

l	Calculated intensity [(43) (33) (23) (32)]$_3$	Calculated intensity [(43) (33) (22) (33)]$_3$	Observed intensity
1	19	15	5
4	2	25	10
7	20	65	80
10	330	66	78
13	155	460	565
16	160	40	39
19	160	46	46
22	1000	1000	1000
25	200	280	290
28	74	26	18
31	195	41	25
34	610	785	740
37	200	75	70
40	2	7	3
43	125	140	105
46	90	85	85
49	140	120	90
52	4	2	1
55	120	125	75
58	3	6	2
61	83	70	60
64	6	3	1
67	17	19	8

l	Calculated intensities [(43) (33) (23) (32)]$_3$	Calculated intensities [(43) (33) (22) (33)]$_3$	Observed intensities
2	35	37	22
5	14	6	4
8	215	180	200
11	10	17	10
14	420	430	435
17	15	9	6
20	550	475	490
23	325	310	300
26	360	405	330
29	3	15	8
32	285	105	150
35	570	730	615
38	120	25	13
41	31	11	5
44	63	88	100
47	265	265	200
50	40	12	4
53	43	11	4
56	47	140	110
59	115	23	9
62	8	28	12
65	1	12	3
68	10	8	2

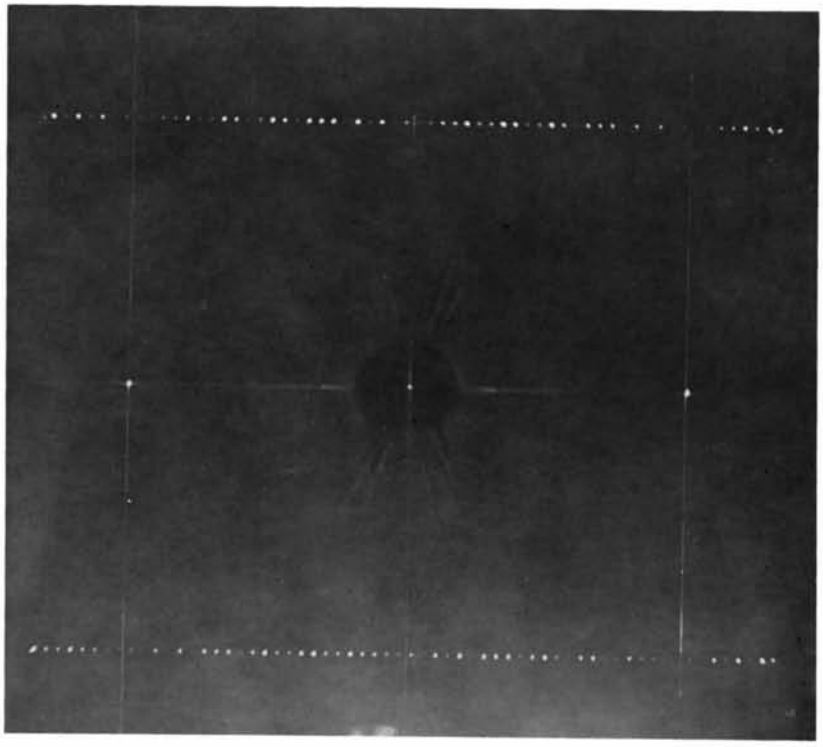

Fig. 1. Buerger precession photograph of SiC-type $69R_b$ (Cu $K\alpha$).

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Discussion

It is interesting to note that the second $69R$ type presently found is not the other simple structure $[(44)_2(43)]_3$ but a structure with a highly irregular stacking sequence. Thus it belongs to the rare groups of SiC polytypes with the three Zhdanov symbols 2,3 and 4 and emphasizes the importance of considering many more possible polytypes.

Unfortunately nothing conclusive can be said about the growth mechanism because we have no idea what the virgin crystal looked like. It is remarkable that a homogeneous core of 100 μm thickness remained after polishing and not a trace of another polytype could be found. Such observations have so far been restricted to $6H$ although there may be some platelets containing a $15R$ core. The extremely frequent occurrence of $6H$ (also in other growth furnaces under similar conditions) has led to the hypothesis (G. S. Kamath, personal communication) that $6H$ is the thermodynamically stable phase. Other polytypes would grow during the cooling period at non-equilibrium conditions. The two massive $15R$ crystals and the 100 μm thick core of $69R_b$ disagree with such a hypothesis since it is very unlikely that crystals of this size can grow in such a short time. Moreover from one of the pure $15R$ platelets two subsidiary crystals extend which obviously grew later.

Two-thirds of the growth spirals found are connected with unusual polytypes whereas less than a quarter of all crystals analysed contained rarer polytypes. This fact tends to support the Frank (1951) mechanism.

It should also be noted that the $69R_b$ polytype contains large building blocks of the $[(33)_n(34)]_3$ series of which the polytypes $21R$, $39R$, and $57R$ could be recovered. This may be an indication that the polymer theory (Ramsdell & Kohn, 1952) has some bearing on the growth of polytypes although a modification of it might bring it closer to reality. Such a modification should include the ideas of Bulakh (1969).

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Crystal Structures of Two 20-Layered CdI_2 Polytypes

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Crystal structures of two newly discovered 20-layered polytypes of cadmium iodide have been determined. One is found to be $(22)_4 1111$, belonging to the $(22)_n 1111$ series of CdI_2, three members of which are already known. The other structure is found to be (22111121122112). Their space group is $P3m1$. Their formation is discussed in terms of partial edge dislocations created at regular intervals during crystal growth.

Introduction

Cadmium iodide is known to be a strongly polytypic substance. Nearly 140 polytypes of CdI_2, grown from solution and vapour, have so far been reported by various workers (Mitchell, 1956; Trigunayat & Verma, 1962; Chadha & Trigunayat, 1967; Jain, Chadha & Trigunayat, 1970). Hitherto, complete crystal structures of only 25 polytypes have been determined. There have been two reasons for this relatively small number. First, the X-ray photographs of CdI_2 crystals frequently show streaking and arcing (Agrawal & Trigunayat, 1969), rendering them unsuitable for structure work, and secondly, the polytypes have the number 1 in their Zhdanov symbols, which enormously increases the number of possible structures to be considered. The structure determination of a polytype becomes

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