Dendritic Growth of Germanium Crystals

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Controlled dendritic growth of germanium from the melt yields long thin strips whose principal surfaces are optically flat {111} crystallographic planes except for the occasional presence of small steps. The crystals grow rapidly in the ⟨211⟩ direction, have twin planes parallel to the flat surfaces, and can withstand an elastic strain exceeding 10^{-3}. The distribution coefficients of impurities are close to unity compared to quasi-equilibrium values.

A mechanism for dendritic growth is proposed, in which the presence of at least one properly oriented twin plane is fundamental and necessary. This mechanism explains most of the observed growth features in germanium dendrites, and is expected to apply generally to materials with the zincblende structure.

The presence of the twin plane makes growth in opposite directions in the twin plane dissimilar, not only in the zincblende lattice but generally. The effect of this asymmetrization on the growth of α-SiC is considered. A crystal growth mechanism based on this asymmetrization is proposed, which should be of general validity.

I. INTRODUCTION

WHEN the usual methods of single crystal growth are employed the maximum growth rate possible is usually determined by the onset of dendritic growth in an uncontrolled manner. The mechanism has been described by Chalmers[1] and involves growth into a supercooled region of the melt. By utilizing supercooled melts initially we believe we have synthesized this process in a controlled way. The resultant crystals are unique in structure and in their anisotropic growth features.

A theory is presented which explains these growth features and was able to predict the observed anisotropy. The theory has certain very general aspects which are applicable in explaining some features of crystals grown from supersaturated vapors.

II. DENDRITIC GROWTH

In this section we will describe a technique for controlled dendritic growth of germanium. Although controlled dendritic growth in itself is not new, having been described by Billig[2-4] in germanium, we shall present a manner of growth, and a theory of the growth process, which have not been previously reported. The process has the following characteristics:

(a) The linear growth rate is high, typically 15 centimeters per minute.

(b) The melt from which the crystal grows is supercooled.

(c) The grown specimen is in the form of a thin sheet, typically 0.025 centimeter thick, with {111} crystallographic faces. The growth direction is ⟨211⟩. No other growth direction or crystal orientation occurs.

(d) The seed and the grown specimen are not single crystals but bicrystals, containing a single twin plane (or sometimes, as later described, several) parallel to the faces.

A. Description of Experimental Growth Technique

For reasons which will become clear, it is generally desirable to use as a seed a section of a previously grown dendrite, although other seeds have occasionally been successfully used. Our seeds have typically been 25 mm long, 0.25 mm thick, and 1.5 mm wide. This seed is held with long dimension vertical in a suitable chuck and is lowered, just as in the Czochralski method, until its tip makes contact with a pool of molten germanium whose temperature is everywhere above the melting point. The melt temperature adjacent to the seed should be
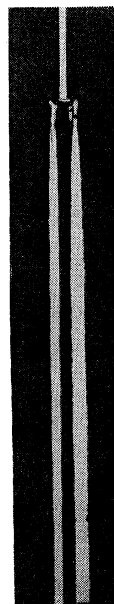

FIG. 1. Typical pair of grown dendrites.

[1] B. Chalmers, Trans. Am. Inst. Mining Met. Engrs. **200**, 519 (1954).
[2] E. Billig, Proc. Roy. Soc. (London) **A229**, 346 (1955).
[3] E. Billig and P. J. Holmes, Acta Cryst. **8**, 353 (1955).
[4] E. Billig and P. J. Holmes, Acta Met. **5**, 53 (1957) and following Letter by E. Billig, Acta Met. **5**, 54 (1957).
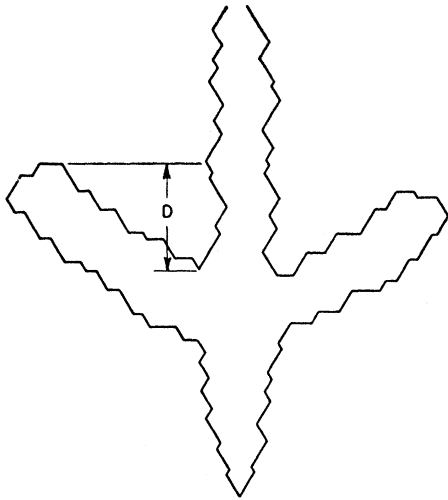
FIG. 2. Anchor-shaped growth.

Length has been limited by our pulling apparatus to 12 cm.

The wide faces of these crystals are (111) crystallographic planes; a twin plane occurs midway between them, extending the entire length of the dendrite. The growth appears to take place by extension of (111) layers in the $[2\bar{1}\bar{1}]$ direction, growth in other directions either in the (111) plane or inclined thereto not being preferred. The growth direction and long dimension of the dendrite is accordingly a $[2\bar{1}\bar{1}]$ direction, and the crystallographic geometry is as indicated in Fig. 3. The edges of the dendrites are not straight but are serrated; the serrations themselves are straight, except at the corners, and are inclined 30° to either side of the $[2\bar{1}\bar{1}]$ growth direction, as shown in Fig. 4. The length of the individual serrations is variable; infrequently the serrations on opposite edges of a face are correlated, but no correlation has been observed between serrations on opposite faces of a dendrite.

high enough to wet and melt a small portion of the seed tip; about 2°C above the melting point is suitable. After wetting, the power input to the crucible is suddenly reduced, in an amount corresponding to a temperature reduction of about 10°C, thus supercooling the melt about 8°C. Crystallization then commences on the seed, but not elsewhere, since no other nucleation centers are available. After a short time, of the order of 15 seconds, upward pull of the seed at a rate of about 10 to 15 cm per minute is begun. As the seed is raised, a pair of dendrites grows downward. Such a pair of grown dendrites is shown in Fig. 1, still attached to the seed. The occasional presence, in earlier poorly-controlled work, of anchor-shaped growths such as sketched in Fig. 2 shows that the actual growth takes place at least a distance D below the melt surface; this distance has been observed as roughly 6 mm.

B. Description of Grown Crystals

The grown crystals, as exemplified in Fig. 1, are thin flat strips or sheets. Thicknesses between 0.08 and 0.5 mm have been obtained, and the width of those so far grown has usually been two or three millimeters.
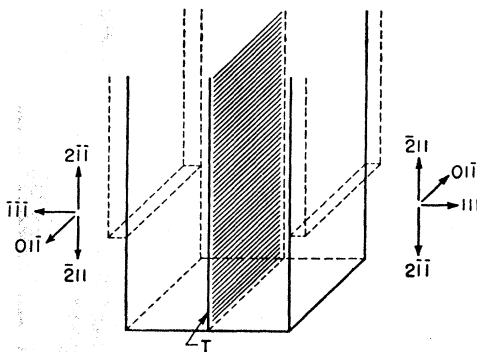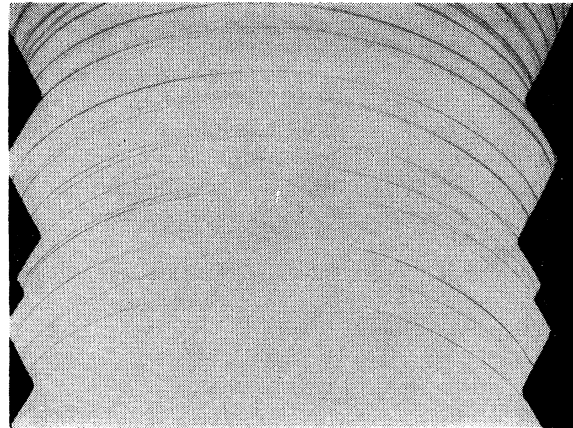

FIG. 3. Crystallography of dendrite.

FIG. 4. Dendrite surface as grown.

C. Surface of Dendrites

The wide faces of the dendrites appear to the eye to be very shiny and absolutely mirror-smooth, except for the presence of a series of more or less pronounced curved lines, which can be seen in Fig. 4. These lines are always concave downwards, i.e., in the growth direction, and furnish a convenient permanent indication of this direction. The shape of these lines appears identical with the shape of the intersection of the melt surface with the dendrite face as the crystal emerges during growth; surface tension raises the liquid more in the middle than at the ends. It is observed that as the growing dendrite is pulled upward, this intersection does not remain stationary but moves upward a fraction of a millimeter with the dendrite, then drops suddenly back, repeating this action irregularly as the dendrite grows. It appears reasonable that the formation of the lines is correlated with this stick-slip process.

Interference microscopy shows these lines to be the edges of steps. Figure 5 is an interference photo-

micrograph of a dendrite surface exactly as grown; the entire width of the picture corresponds to about one millimeter. The surface is seen to be composed of areas of extreme flatness, separated by steps whose height is measured by the displacement of fringes on crossing the step. A displacement equal to the fringe spacing would correspond to a step height of half a wavelength; these photographs were taken in monochromatic green light of $\lambda = 5350$ A. The large step in the figure is thus about 600 A high, all others being considerably smaller. Much better surfaces, showing no discernible steps whatever, have also been grown.

Small hills are occasionally found along the center of the dendrite surfaces; those shown in Fig. 6 range from five to twenty thousand angstroms in height. Some of these hills show faults which may have been caused by slip on {111} planes during cooling after growth. Three

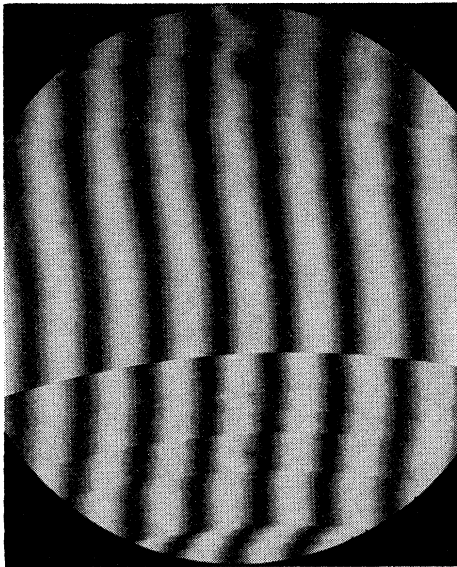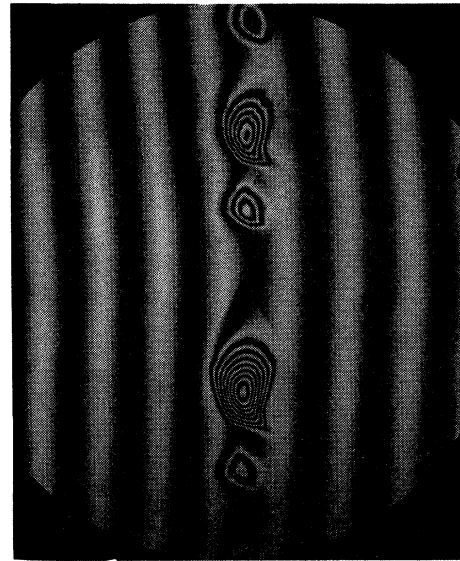Fig. 6. Dendrite surface showing hills.

Fig. 5. Dendrite surface showing several steps.

triangles lying in $\langle 110 \rangle$ directions, parallel to the edge serrations.

It will be observed, by comparing the pits to the curved steps, that for the faces shown the etch pits point opposite to the growth direction. This is characteristic of both faces of properly grown dendrites; this important point will be fully discussed later in this paper.

Figure 9 shows a cluster of etch pits which suggest the presence of a central inclusion of foreign matter. Each of the six radiating arrays of pits can be seen to comprise two adjacent parallel rows. It seems reasonable that differential expansion of dendrite and inclusion,

very small steps are also visible. It may be remarked in passing that although these monochromatic photographs do not rule out the possibility of fringe displacements exceeding by an integral number of fringe spacings the specified values, white light photographs, in which individual fringes are identified by different colors, show that such large displacements do not occur.

Figures 7 and 8 show two views of dendrite surfaces which have been given a WAg [5] etch. This etch reveals {111} planes. The presence of a characteristic narrow band of etch pits along the center of the dendrite face is evident; this appears to correspond to a well-defined region of high dislocation density. Such rows of pits are also infrequently found near the edges of the faces. The etch pits are seen to be triangular, the sides of the

Fig. 7. Dendrite surface, etched.

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[5] R. H. Wynne and C. Goldberg, Trans. Am. Inst. Mining Met. Engrs. **197**, 436 (1953).
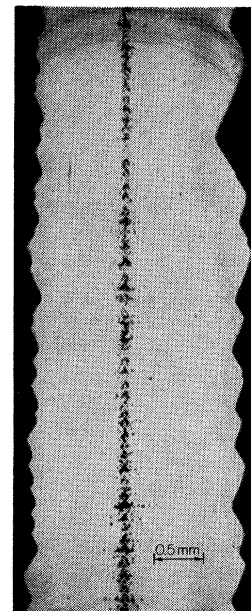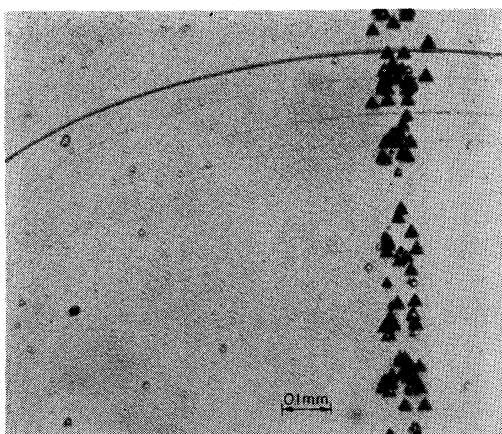
FIG. 8. Dendrite surface, etched.

during the cooling following growth, may have caused the material between the rows to slip.

D. Cross Sections of Dendrites

It is apparent from symmetry considerations that, if a dendrite were a single crystal, etch pits on opposite faces would point in opposite directions. The observation of dendrites on both faces of which the etch pits point in the same direction implies the presence of a twin plane (or, in general, any odd number of twins) between the faces. Several of our dendrites were accordingly sectioned and etched. All dendrites thus observed have been found to contain at least one twin; occasionally more have been present, in one instance eight. The total number may be odd, in which case, as stated, etch pits on opposite faces will point in the same direction, or it may be even, in which case the pits point in opposite directions. The method of growth as earlier described, using a properly oriented seed with a single twin plane, has invariably resulted in dendrites containing one twin, situated essentially midway between the faces.

E. Mechanical Properties

Although germanium is normally considered a brittle material, dendrites grown as described are remarkably flexible. A dendrite held by hand was bent into a circle of roughly three inches radius before breaking. From the thickness and curvature a surface strain, at fracture, of about 1.5×10^{-3} was calculated. A somewhat more refined experiment in which couples were applied to the ends of the dendrite yielded similar results, but the breakage occurred at the points of constraint where it seemed reasonable that unknown stress concentrations might have existed, making the estimated strain too low. Accordingly, a sample was broken by applying axial compressive forces to both ends, thus bowing the dendrite. In this case maximum bending occurs at the center, far from the constraints, so that fracture occurs

in a region where the stress is well known. An analysis of the experimental results yields a maximum surface strain of 1.5×10^{-3}, in excellent agreement with the first results. It was noted that the sample broke within one-sixteenth inch of the center. The effect of any variations in cross section, or stress concentrations at the bottoms of the serrations along the sides of the faces, would only serve to make the actual strain still greater than the computed strain. It should be added that these experiments were performed at room temperature, and that the strains appeared completely elastic, the samples recovering their original shape if the stress were removed before breakage.

This strain is considerably higher than is commonly observed in germanium samples whose faces have been cut or otherwise worked. It seems likely that the high strength of these samples results from the freedom of the surface from minute cracks, which would inevitably be present in worked surfaces; stress concentrations at the bottoms of these cracks would presumably cause crack propagation and fracture at relatively low over-all stresses. Results in support of this hypothesis have been obtained by Dr. R. W. Keyes of this laboratory, who pulled dendrites apart under a known tensile load. From the observed tensile stress and cross section and known elastic constants he calculated the fracture strain as 1.5×10^{-3} in agreement with the results of bending. He then lightly lapped one surface of the specimen, enough to cause surface working but insufficient to cause an appreciable change in cross section, and on breaking the lapped specimen in tension observed a reduction in breaking stress of about a factor of five as compared to the unlapped specimen. It must, however, be added that other samples used in repetitions of this experiment failed to show the same high initial tensile strength.

Both the dendrites fractured in tension and those broken by bending broke along {111} planes, leaving a wedge- or groove-shaped end, with the central twin
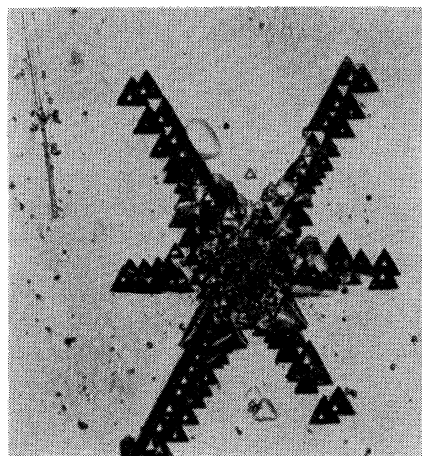

FIG. 9. Etch pit array suggesting inclusion.

plane clearly visible. Figure 10 is a sketch of the geometry of this fracture.

F. Behavior of Impurities

Dendrites were grown from melts containing Al, As, In, or Sb, each at two different concentration levels. In view of the rapid growth it was expected that the effective segregation coefficient, defined as the ratio of the impurity concentration in the solid to that in the liquid, would be unity, and the melt impurity concentrations were chosen to yield dendrites of resistivity of either 2.5 or 20 ohm-cm. The resistivity of the grown crystals was measured at room temperature by passing a known current through the dendrite, parallel to the growth direction, and measuring with a potentiometer the variation of voltage along the sample.

The results are summarized in Table I. It will be noted that the measured resistivities were not at all the expected values, but were greater or less by factors of five or more. Interpretation of these resistivities as a measure of the impurity content suggests effective segregation coefficients exceeding unity in those cases where the measured resistivity is less than the expected value. In view of the known segregation coefficients of these impurities at low growth rates, such an interpretation does not seem reasonable, especially since it is not consistent for a given impurity at the two concentration levels given. It seems apparent that further research on this matter is necessary.

It does seem likely, however, that the effective segregation coefficients do not differ from unity by a factor exceeding ten. In view of the known segregation coefficients for In and Sb of the order of 10^{-3} for normal crystal growth, it thus appears that these crystals contain over one hundred times the amount of impurity which would result in a crystal grown by conventional methods from the same melt.

III. THEORY OF DENDRITIC GROWTH

A. Comments on Early Theory of Dendritic Growth

In an attempt to account for dendritic growth in germanium, Billig[2] has proposed a mechanism for ex-

TABLE I. Resistivities of dendrites with different impurities in ohm-cm.

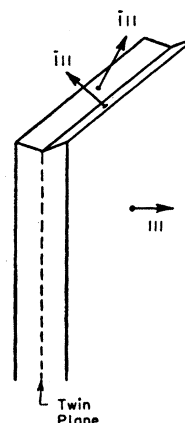| Impurity	Impurity type	Expected resistivity for no segregation	Observed resistivity	Apparent distribution coefficient	Quasi-equilibrium distribution coefficient
In	p	20	4	5	0.001
In	p	2.5	7	0.4	0.001
Al	p	20	11	2	0.1
Al	p	2.5	27	0.1	0.1
Sb	n	20	15	1.3	0.005
Sb	n	2.5	12	0.2	0.005
As	n	20	11	2	0.06
As	n	2.5	0.7	4	0.06

FIG. 10. Geometry of broken end.

tension of {111} atomic layers on an existing substrate, which predicts three "good" $\langle 211 \rangle$ directions lying in the layer plane 120° apart, and opposite "bad" directions. Clearly such a process cannot be the rate-determining factor, for two reasons: (a) dendrites can readily be grown in which both surfaces, only one surface, or neither surface grows in a "good" direction, and (b) such a mechanism cannot describe the growth of those layers which extend to the tip of the growing dendrite, as such layers must grow in the absence of any pre-existent surface on which they could be deposited. Perhaps Billig realized this situation as he later suggested[4] that a dendrite core might be extended by means of a double screw mechanism. Once the dendrite core has extended into the melt, outer layers can readily be added.

B. Propagation of Dendrite Core

In the following it is shown that if the two central layers are twinned with respect to each other, the core can be propagated more easily in one direction, and less easily in the opposite direction, than in the case where no twin plane exists. In accord with these ideas, the observed dendrites all have twin planes, and have highly anisotropic growth characteristics.

In Fig. 11 we show four adjacent (111) atomic planes of the diamond lattice, except that the lower two planes, B and D, are twinned with respect to the upper two, A and C; the twin plane is the perpendicular bisecting plane of all the AB bonds shown in the figure. Consider now the propagation of this structure from left to right, assuming that only the leftmost rows of A and B atoms are initially present. The leftmost row of C atoms can now be added, one at a time, to the A row, each C atom making on addition two bonds to A atoms. Symmetrically, the leftmost D row can be added to the B row. The next step would be the addition of, say, an A atom, making one bond to the corresponding C atom; as soon as this occurs, a single B atom can evidently be added, bonding to the new A atom as well as to a previously-added D atom. It makes no
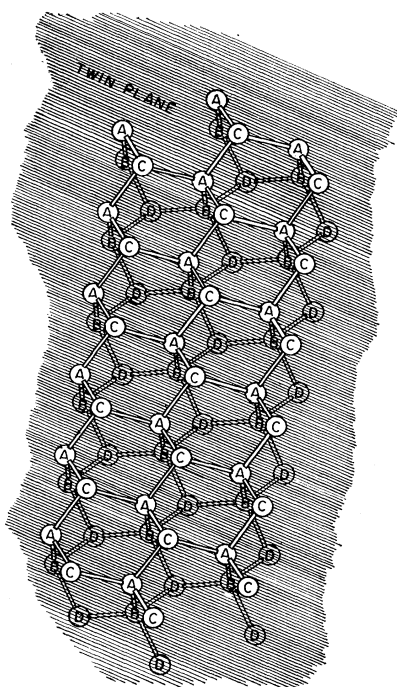
FIG. 11. Twinned dendritic core.

difference to our discussion whether the latter two additions occur simultaneously or successively, and we shall consider the former to occur, speaking of the addition of an AB dumbbell, or atomic chain two atoms long. The remainder of the central A and B rows can be filled by further additions of such dumbbells, the order in which these are added being immaterial. This entire process is now repeated, continuing this atomic sandwich to the right. There is no need to complete the AB rows before beginning the subsequent CD rows.

We next discuss the growth of this structure in the opposite direction, assuming that only the rightmost A, B, C, and D rows are present and that the structure is to grow toward the left. The smallest atomic structure which can be added to the lattice, making at least two bonds, is a chain of three atoms, C-A-C or D-B-D (herein we assume that no structure consisting of more than one atom is to be considered part of the lattice unless bonded at least twice). After the addition of one such chain, it is then possible to complete the central rows of A, B, C, and D by the addition only of dumbbells, each bonding twice, only if the filling proceeds sequentially along the rows in either direction from the initial triatomic chain. If the filling is not sequential, triatomic chains are required instead of dumbbells. Repetition of this process would propagate the entire structure to the left. If no further triatomic chains after the first are added in any row, it is clear that the propagation of growth is essentially normal to the nominal growth direction.

It is thus evident that growth to the right in the

structure of Fig. 11 is easier than growth to the left. The threefold symmetry of Fig. 11 results in three easy directions, separated by 120°, and three opposite difficult directions.

Examination of the case of a monocrystalline structure, similar to that of Fig. 11 but without a twin plane, shows that growth in each of the six $\langle 211 \rangle$ directions is of equal difficulty, intermediate between the easy and difficult directions for the twinned structure. Specifically, this growth can proceed by the addition of a mixture of doubly-bonding single atoms and doubly-bonding triatomic chains.

The presence of the twin plane thus has the effect of creating an easy direction of propagation for the central core of the dendrite, a direction in which growth is easier than for any direction of growth in an untwinned structure. We have also seen that opposite to this direction there is a direction in which growth is more difficult than for any growth direction in an untwinned structure. The effect of the twin plane can thus be considered one of asymmetrizing the growth process in opposite directions in the twin plane, a point to which we shall later return.

The fundamental reason for the presence of a twin plane in a dendrite thus appears to be that it furnishes an easy direction for growth of the central dendritic core. We thus conclude that a single, properly-oriented twin plane is an essential feature of the fundamental mode of dendritic growth. The desirability of using dendrites as seeds for further dendritic growth is clearly due to the need for a twin plane. Experimentally it is found that occasionally single crystal seeds can be successfully used, but dendritic growth will proceed only after a twin has been nucleated.

The layer-propagation process of Billig was proposed[2] to apply to the extension of surface layers in germanium dendrites. The "good" directions are distinguished therein from the opposite "bad" directions in that propagation of a layer in a "good" direction can occur through the addition of atoms each of which, on addition, bonds twice to the lattice, while in the "bad" direction propagation requires the addition of equal numbers of singly-bonding and triply-bonding atoms. We shall refer to the foregoing theoretically-defined "good" directions as G-directions. Billig states[2,3] that each of his dendrites had one "good" and one "bad" face, with x-ray reflection photographs showing greater asterism for the "bad" face than for the "good" face. However, he identified his "good" face as that face on which etch pits point in the growth direction, while consideration will readily show that his G-directions of layer propagation are opposite to the directions in which the etch pits point. If indeed this asterism is evidence of preferred growth directions, these preferred directions must be opposite to Billig's G-directions; the asterism, however, may be the result of dislocations produced after solidification by thermal stresses due to aniso-

tropic cooling. The asymmetric cross section of Billig's dendrites makes it probable that such stresses can arise.

In Fig. 6 the largest hill appears to sit on a triangular base, which is shown interferometrically to be an elevation rather than a depression. If Billig's mechanism had been effective in propagation of this layer, the preferred directions of propagation would necessarily again be opposite to his G-directions. It seems possible, however, that this elevation may have been formed after solidification by thermal stresses resulting in slip on the three {111} planes whose intersections with the surface bound the base.

We see no experimental evidence that Billig's mechanism is operative. We point out that in a properly-grown dendrite, with one twin plane, the layers on both sides of the core propagate in a G-direction, i.e., the etch pits on both faces point opposite the growth direction.

C. Reversal of Seed

If a dendrite were a single crystal, the lattice symmetry would require that either end of the dendrite would be the same if used as a seed. We have seen, however, that for a dendrite containing a single twin plane, one direction along its length is the easy direction

FIG. 12. Growth from opposite ends of dendritic seed.

for propagation of the dendrite core, while the opposite direction is the difficult growth direction. We therefore expect that growth from opposite ends of such a dendrite seed would differ, there being three good growth directions 120° apart.

The growth shown in Fig. 12 provides striking confirmation of the foregoing ideas. The same dendrite was used as a seed for both specimens. The left-hand specimen was grown first, from end 1 of the seed; the seed was then removed, turned upside down in its holder, and the right-hand specimen grown from end 2, to which it is still attached. In the first specimen, growth was stopped at A; after a few seconds, pulling was resumed, resulting in a characteristic pair of vertical stems. Growth was similarly interrupted at B and C and the resulting four dendrites were then allowed to grow to a total length of about four inches. Note that in every case growth has proceeded vertically downward. In the right-hand specimen, growth refuses to propagate downward; instead, it proceeds along the two sloping good directions 60° away from the vertical. At E the edge of the crucible is reached; growth is now initiated in the other good direction, and finally downward propagation commences. Growth was again interrupted at F, and resumed a few seconds later, resulting in both vertical and diagonal growth at G.

Several sections of these specimens were detached and etched. The four left-hand dendrites all showed etch pits pointing upward on both sides, just as expected; cross sections of these samples showed a single twin. In both diagonal growths from D, etch pits on both sides again point opposite the growth direction. Both vertical dendrites at F, however, show that etch pits on one side point upward and on the other side point downward, necessitating the existence of an *even* number of internal twin planes. Examination of the etched cross section of these dendrites indeed shows the presence of two twin planes, the second twin having been initiated just below E. Consideration will show that in such a dendrite the good directions for the growth of the structure of Fig. 11, centered on one of these twins, are opposite the good directions for growth centered on the other twin. Thus although the downward direction is difficult for the original twin, it is the easy direction for the second twin. This second twin plane then becomes the core of a downward-growing dendrite, and propagates ahead of the rest of the structure; planes are added to both sides of this core. No difficulty now occurs in the downward propagation of the original twin, because it need not be propagated alone; layers deposited on the advancing second twin furnish a substrate on which the original twin can be laid down without requiring polyatomic chains.*

* *Note added in proof.*—Improved observational techniques developed by H. F. John and J. W. Faust of these laboratories (work to be published) have shown that an odd number of very closely spaced twins appears as a single twin by techniques used in this paper. An odd number of closely spaced twins results in threefold growth preference symmetry.
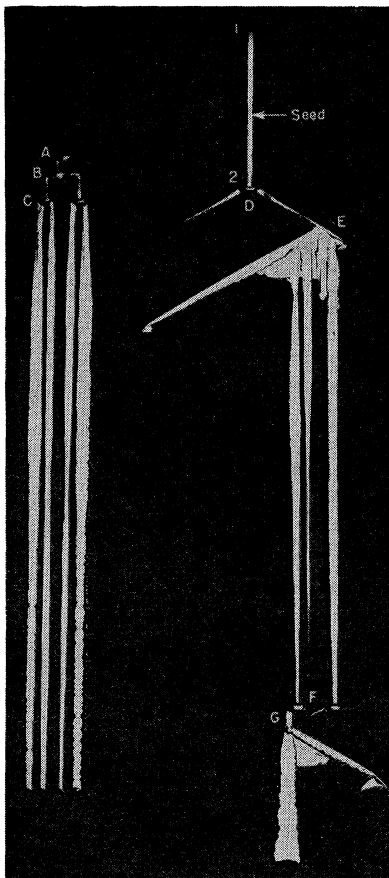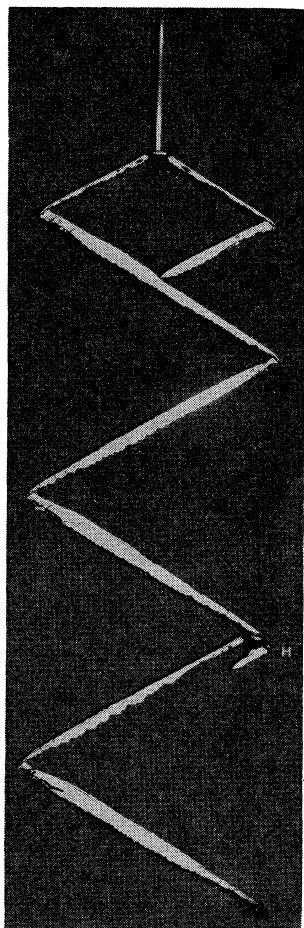
FIG. 13. Another growth
from an inverted seed.

By suitable alteration of the pulling program it is possible to carry out the inverted-seed experiment without initiating a second twin. Under these circumstances the growth shown in Fig. 13 results. Beginning at the seed, growth proceeds in the two sloping good directions until the edges of the crucible are reached; in both cases, growth in the other good direction follows. Because of thermal asymmetry, one of these reaches the center first, and thereafter grows alone, alternating from side to side in the good directions. The branches are widest in the center, probably because the melt is coolest there. At *H*, the pull rate was fast enough that the dendrite was pulled free of the melt. Its tip was then reinserted as a seed, resulting in the two characteristic parallel stems shown.

IV. APPLICATION TO OTHER GROWTH SYSTEMS

A. Dendrites of Silicon and III-V Compounds

It seems probable that the proposed growth process should be applicable to growth of dendrites of silicon, as well as of III-V or other compounds with the zinc-blende lattice. The III-V dendrites should have the interesting property that, regardless of the number of twins present, all surface atoms on one face will be

type III while all on the other face will be type V. There should thus be differences between wetting, etching, and other characteristics, of opposite faces. This property is not unique to the dendrite structure.

B. General Mechanism of Crystal Growth from the Vapor

Burton, Cabrera, and Frank[6] (BCF) have suggested a now generally accepted model of crystal growth by means of the termination of a screw dislocation at the crystal surface. Crystal growth should most readily occur through the propagation of steps on the crystal faces, for added atoms can more easily be bound there than elsewhere. In a perfect crystal these steps are eliminated as each atomic plane is completed, and the growth rate is limited by the difficulty of nucleating new steps. BCF show how the presence of a screw dislocation permits a step to be propagated indefinitely without ever being lost through completion of an atomic layer. By the BCF mechanism a crystal grows as a helical ramp, each turn around the central screw dislocation increasing the crystal thickness by the Burgers vector of the dislocation.

We wish to point out that the foregoing process describes only the addition of layers to an already existing layer or substrate, and can operate only after this initial layer has been formed. As a growth theory, therefore, this description is incomplete in that it accounts only for growth in a direction parallel to the screw axis, and does not explain the lateral growth necessary for the formation of the initial layers of the crystal. When crystals grow in platelets, as e.g., in silicon carbide, the screw dislocation process is observed to act toward increasing the thickness of these platelets. Growth must actually be more rapid, however, in directions lying in the plane of these platelets than in the direction of the screw axis, normal to the platelet faces, otherwise platelet growth would not be observed. It seems reasonable to conclude that some growth mechanism other than the screw dislocation process is active in extending the initial crystal layer in directions lying in the layer plane.

The α-silicon carbide structure can be described as a zincblende lattice with twins every two or three double layers. The planes of these twins are parallel to the platelet faces. It is thus clear that the boundaries of these twin planes are precisely the same as those encountered in germanium dendrites. We suggest that the twin propagation mechanism described in connection with Fig. 11 is responsible for the lateral growth of platelets in silicon carbide. Since the easy growth directions are opposite for adjacent twins, all six $\langle 211 \rangle$ directions will be equally favored, resulting in hexagonal platelets. The magnitude of the Burgers vector is presumably such as to repeat the entire twin complex

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[6] Burton, Cabrera, and Frank, Nature **163**, 398 (1949); Phil. Trans. Roy. Soc. (London) **A243**, 299 (1951).

on each turn around the dislocation. Each resulting twin can act as a growth center so that the edges of the platelet can grow uniformly.

This mechanism should be applicable to many other structures besides that of silicon carbide. It seems clear that, in all cases in which the screw dislocation process is presumed to account for growth through addition of layers, the problem of lateral propagation of the substrate or initial layers will arise. In many structures, although not all, it will be found that, just as in the discussion of Fig. 11, the presence of a twin plane will make propagation in some specific direction, or set of directions, easier than for any possible direction in the untwinned structure. The growth system would then combine lateral extension of an initial layer array containing one or more twins, with the addition of further layers by the screw mechanism.

It has been pointed out to us by Hamilton that Frank[7] and Amelinckx[8] have explained interlacing spiral patterns observed on SiC as being due to directional dependence of growth velocity. The detailed bonding mechanism proposed by Billig[2] for adding layers in the diamond structure may be operative in α-SiC; the directions of best growth would rotate 60° with each twin, resulting in the observed interlacing. It is thus apparent that all mechanisms proposed for dendritic growth may be operative in the vapor growth of α-SiC as well.

Some effects of twinning on enhanced crystal growth have been reported by Frank[9], and by Dawson.[10]

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Switching Mechanism in Triglycine Sulfate and Other Ferroelectrics

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The reversal of the spontaneous polarization in a ferroelectric crystal is governed by two mechanisms: the nucleation of new domains and the growth of these domains by domain wall motion. We have investigated the switching properties of triglycine sulfate (TGS) as a function of applied electric field, temperature, and thickness of the samples.

It is proposed that at low fields nucleation is the slower mechanism and hence dominates the switching process while at high fields domain wall motion determines the rate of switching. The former process leads to an exponential dependence of switching time on applied electric field and the latter to a linear dependence.

A model for the nucleation and domain wall motion is treated mathematically and is compared with experimental observations. The shape of the switching current pulse was found to yield much information. The shape depends strongly on the applied electric field and is correlated with the nucleation time as well as the domain wall motion time. The asymmetry of the pulse increases with decreasing field and can be associated with the interaction between domains and domain nuclei. This interaction in various ferroelectrics is discussed and its relation to the switching is considered.

1. INTRODUCTION

A NUMBER of investigators have dealt with the problem of determining the mechanism by which the spontaneous polarization in a ferroelectric material is reversed. Merz,[1,2] Little,[3] Wieder,[4] Landauer-Young-Drougard,[5,6] Chynoweth,[7] Miller,[8] and Burfoot[9] have examined this process in BaTiO$_3$ while similar studies have been conducted on Rochelle salt (RS) by Wieder[10]

on guanidine aluminum sulfate hexahydrate (GASH) by Prutton[11] and Wieder[12] and on triglycine sulfate (TGS) by Pulvari and Kuebler.[13] From these studies it is generally concluded that two steps are involved in the switching process: nucleation of ferroelectric domains at the surface of the sample followed by growth of these domains through the crystal by domain wall motion.

It is assumed, on the basis of phenomenological arguments, that nucleation of domains is a statistical process while the domain wall motion is assumed to be controlled by a kind of viscous drag.

In this paper we shall discuss the switching properties of triglycine sulfate (TGS), a ferroelectric discovered

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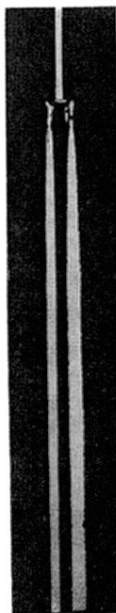[9] J. C. Burfoot, Proc. Phys. Soc. (London) 73, 641 (1959).
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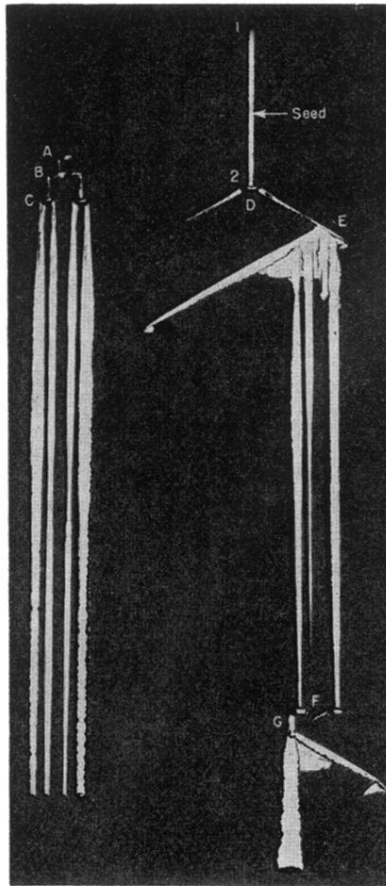
FIG. 1. Typical pair of grown dendrites.

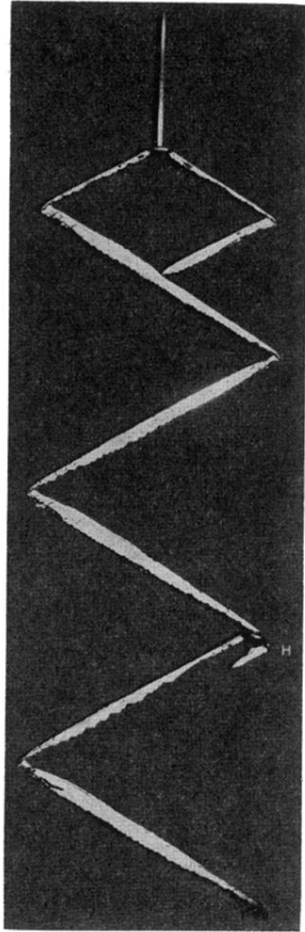FIG. 12. Growth from opposite ends of dendritic seed.

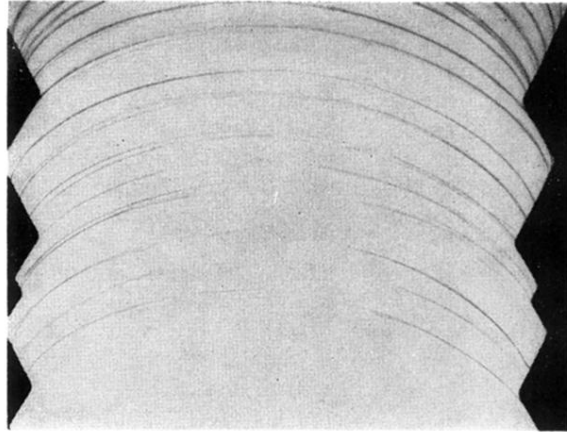FIG. 13. Another growth from an inverted seed.

FIG. 4. Dendrite surface as grown.

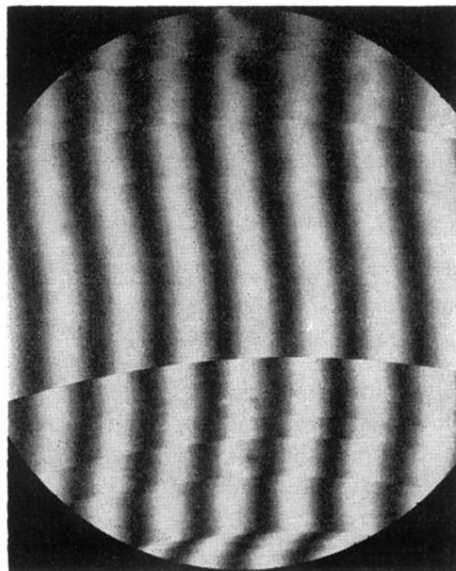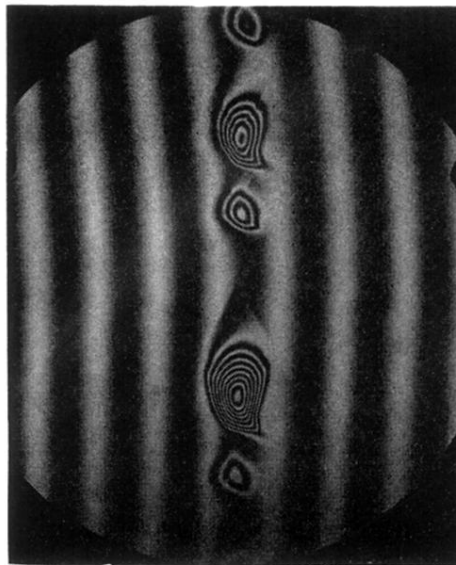Fig. 5. Dendrite surface showing several steps.

FIG. 6. Dendrite surface showing hills.
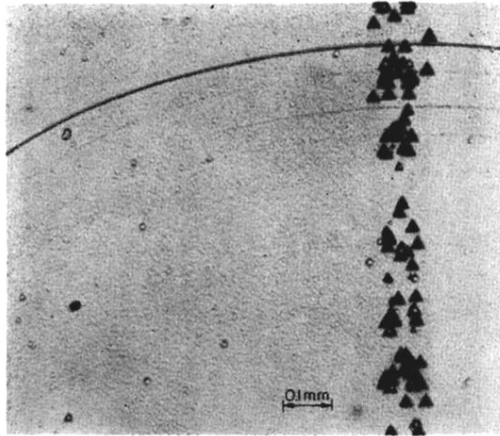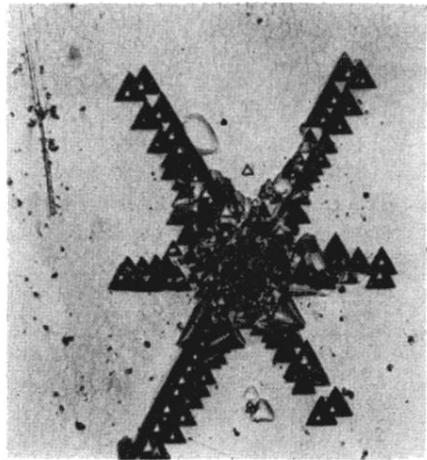
Fig. 7. Dendrite surface, etched.

0.5 mm

FIG. 8. Dendrite surface, etched.

FIG. 9. Etch pit array suggesting inclusion.