presumably have a specific orientation relation with the particle and hence a low σ_{SP}). As a stationary particle is approached by the interface, contact will be made at a random orientation of particle to solid, which in general is different from that which will nucleate. Such particles may then be pushed.

ACKNOWLEDGMENTS

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Study of the Filamentary Growth of Silicon Crystals from the Vapor

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The preparation from vapor and the structure of filamentary crystals of silicon have been studied in detail. It was found by chemical etching, by examination for a twist associated with a screw dislocation, and by observations in the electron microscope, that both ribbons and needles of small dimensions are free of dislocations and imperfections. Certain impurities such as gold, nickel, or platinum, however, are essential for the growth of filamentary crystals.

The growth of micron size and larger whisker crystals from the vapor takes place in two stages. The first is a rapid extension in length of a leader-like crystal of small cross section; the second, a slow thickening of the leader through deposition on lateral faces. Initial growth is associated with impurities and does not require an axial screw dislocation. Subsequent growth may be explained by classical nucleation at a step and lateral translation of the step.

INTRODUCTION

FILAMENTARY crystals (whiskers) can be grown by several processes. Common processes are condensation,[1,2] the reduction of halides,[3–5] and disproportionation.[6–11] Since whisker crystals grow essentially in one direction, their growth usually has been explained[2] by the "Frank mechanism."[12,13] This mechanism is based on the concept of crystal growth with the aid of a structural defect. A screw dislocation, emerging at the growth interface, provides a self-perpetuating step for the addition of new layers. Two-dimensional nucleation is unnecessary and growth can occur at a relatively small supersaturation. Axial screw dislocations have been reported for a few filamentary substances lending support to the Frank mechanism. Lately, however, reservations have arisen regarding its universal application. Webb and co-workers[14] examined whiskers of nine different metals grown from the vapor and found unequivocal evidence for a single axial dislocation in only one, palladium. These considerations have stimulated the present investigation with silicon filamentary crystals.

The investigation was undertaken to study morphology and growth features, structural defects if present, and the role of impurities. Impurities and added substances are noted in many literature references[4] to exert a pronounced effect on the growth of whiskers. A number of theories have been advanced to explain specific observations but the role of the impurity still remains largely unanswered.

Silicon has several advantages for this investigation. Whisker crystals can be grown readily by disproportionation of SiI_2.[8–11] Several independent methods, such as etching, infrared and electron microscopy, and x-ray diffraction, are available to study imperfections. Of particular importance is that silicon does not deform plastically at room temperature, and therefore it is unlikely that dislocations are introduced during experimentation.

[1] G. W. Sears, Acta Met. 1, 457 (1953).
[2] G. W. Sears, Acta Met. 3, 361 (1955).
[3] S. S. Brenner, Acta Met. 4, 62 (1956).
[4] S. S. Brenner, *The Art and Science of Growing Crystals* (John Wiley & Sons, Inc., New York, 1963), p. 30.
[5] E. R. Johnson and J. A. Amick, J. Appl. Phys. 25, 1204 (1954).
[6] W. W. Webb and W. D. Forgeng, J. Appl. Phys. 28, 1449 (1957).
[7] G. R. Antell and D. Effer, J. Electrochem. Soc. 106, 509 (1959).
[8] E. S. Greiner, J. A. Gutowski, and W. C. Ellis, J. Appl. Phys. 32, 2489 (1961).
[9] W. J. McAleer, H. R. Barkemeyer, and P. I. Pollak, J. Electrochem. Soc. 108, 1168 (1961).
[10] R. S. Wagner and W. C. Ellis, J. Metals 15, 76 (1963).
[11] A. V. Sandulova, P. S. Bogoyavlenskii, and M. I. Dronyuk, Fiz. Tverd. Tela 5, 2580 (1963) [English transl.: Soviet Phys.–Solid State 5, 1883 (1964)].
[12] F. C. Frank, Discussions Faraday Soc. 5, 48 (1949).
[13] W. K. Burton, N. Cabrera, and F. C. Frank, Phil. Trans. Roy. Soc. (London) A243, 299 (1951).
[14] W. W. Webb, *Growth and Perfection of Crystals* (John Wiley & Sons, Inc., New York, 1958), p. 230.

PREPARATION OF WHISKERS AND THE THERMOCHEMISTRY OF THE PROCESS

Whiskers were prepared by reaction of silicon and iodine in a closed quartz tube in a temperature gradient, following the procedure described by Greiner, Gutowski, and Ellis.[8] In a typical experiment, a carefully cleaned reaction tube (25 cm long and 140 cm^3 in volume) is charged with approximately 1 g of high-purity silicon (resistivity 2000 Ω-cm) and 0.84 g of high-purity iodine. A known amount of a suitable impurity, for example, 1 mg of nickel, is added. The reaction tube is subsequently evacuated to about 10^{-6} Torr, sealed, and placed in a furnace with a temperature profile ranging from 1100° to 800°C. The silicon source material and the impurity are located at the higher temperature. Crystal growth is observed after about 10 min.

The quantity, character, and size of whiskers and the region of deposition depend on the impurity added, the duration of heating, and upon other factors whose effects are not clearly understood. Whisker crystals have been prepared with cross-sectional dimensions as small as 500 Å and as large as 100 μ or more, with lengths to a few centimeters.

The thermochemistry of the process has been developed by Schäfer and Morcher[15] and by Wajda and Glang.[16] The process uses the disproportionation reaction:

$$2SiI_2(g) \rightleftarrows Si(s) + SiI_4(g).$$

At a high temperature, typically 1050°C, and with pressure of the iodine species above about 80 Torr, the reaction proceeds to the left with the production of SiI_2. The SiI_2 moves to a region of lower temperature, typically 900°–1000°C, where the reaction goes to the right. Silicon is deposited and SiI_4 returns to the higher temperature region to combine with additional source silicon. It can be assumed that the chemistry of the transfer process is not affected significantly by the relatively small concentrations of added impurities.

Since the deposition of silicon is by a chemical reaction there are complexities not encountered with condensation. The reaction could take place either homogeneously in the vapor phase followed by condensation of silicon or heterogeneously at local areas of the substrate or growing crystal. The question of a homogeneous vs a heterogeneous or surface-catalyzed reaction has been considered in detail for the reduction of halides by hydrogen to produce metal whiskers, for example, iron and copper.[17–20] Conclusive experiments show that in these cases a surface-catalyzed reaction is the main source of metal atoms. It seems likely that the disproportionation of SiI_2 is also surface catalyzed.

ROLE OF IMPURITIES

In earlier studies[8] of silicon filamentary crystals, it was found that with arsenic-doped silicon as the source material, the addition of small traces of nickel iodide was essential to promote whisker growth. Hydrogen also was present in the reaction tube. Later, Gutowski and Beaver[21] extended the studies of impurities and found that in addition to nickel iodide, iodides of copper, manganese, silver, and cadmium promoted whisker growth when the source material was arsenic-doped silicon. They did not obtain filaments when the impurities were iron, zinc, or magnesium.

The pronounced impurity effect was emphasized in the studies described here when filamentary crystals were not obtained from high-purity source silicon (2000 Ω-cm resistivity) and high-purity iodine. The product consisted of nodules or was a film. If, however, a trace of gold (about 1 mg) was added to the high-purity materials, a copious crop of filamentary crystals resulted. The ratio of filamentary to nodular deposit increased with increasing addition of gold. Preliminary transport experiments indicate that under effective temperature and pressure conditions, the amount of transported silicon is independent of the presence and concentration of impurities.

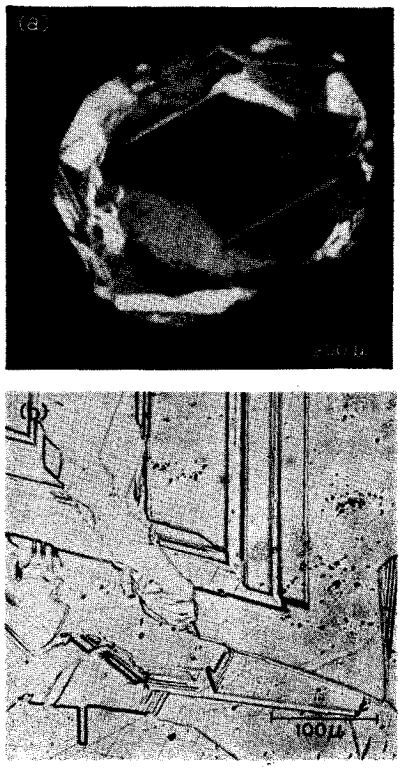


FIG. 1. Silicon nodular crystal formed in the absence of impurities. (a) A typical nodule showing surface twinning features; (b) A section through a nodule etched to show twin plane markings.

[15] H. Schäfer and B. Morcher, Z. Anorg. Allgem. Chem. **290**, 279 (1957).
[16] E. S. Wajda and R. Glang, Met. Soc. Conf. **12**, 229 (1961).
[17] R. V. Coleman and G. W. Sears, Acta Met. **5**, 131 (1957).
[18] W. W. Webb and E. F. Riebling, J. Chem. Phys. **28**, 1242 (1958).
[19] S. S. Brenner, Acta Met. **7**, 519 (1959).
[20] C. R. Morelock and G. W. Sears, J. Chem. Phys. **31**, 926 (1959).
[21] J. A. Gutowski and W. D. Beaver (private communication).

A number of other impurities promoted the growth of filamentary crystals. Those which produced extensive filamentary growth under the conditions of the present study were: Au, Ni, Pd, Cu, Gd, Mg, and Os. The following impurities did not promote growth: Zn, C, Mn, Sn, and Ge; only a film or a nodular deposit was obtained. When a small amount of oxygen was added intentionally, no transfer occurred. The silicon source material became discolored, probably by an oxide film.

MORPHOLOGY OF WHISKERS

Silicon deposits from SiI_2 disproportionation may be of three forms: The first is either a film or nodule-like deposit attached to the walls of the reaction tube. A nodule and a section through a nodule are shown in Fig. 1. Nodules are polycrystalline, containing a large number of twin orientations. The second form, in the micron size range, is a hexagonal needle growing in a ⟨111⟩ direction[10,22] with well-developed {211} lateral faces. Needle crystals prepared from high-purity silicon or

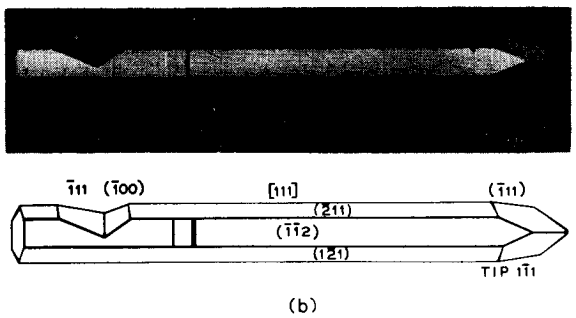


FIG. 2. Silicon needle morphology: (a) A typical silicon needle showing surface and tip morphology; (b) Schematic drawing of the morphology of a ⟨111⟩ needle. The needle is six-sided with a ⟨111⟩ axis. The main lateral surfaces are {211}.

from silicon doped with arsenic or boron, and with nickel as the growth-promoting impurity, had the same morphology. The third form is a twinned ribbon growing in a ⟨211⟩ direction[23] with a {111} twinning plane parallel to the main faces.

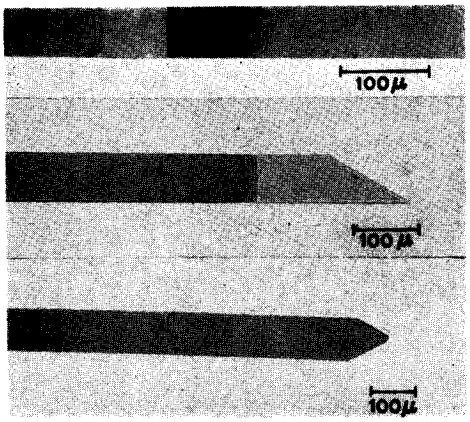
In the present study 15 needle crystals were examined for growth direction, presence of twinning, and external faces using light microscopy and a Weissenberg x-ray diffraction technique.[24] All needles had a hexagonal cross section, as shown in Fig. 2(a), and the larger ones frequently were tapered. The growth direction was ⟨111⟩ and the lateral faces were {211}, as illustrated in Fig. 2(b). Twinning over the length of the needle was not detected. The terminating faces of a needle were established unambiguously to be {111} type. Sometimes

FIG. 3. A branched needle. The branched and main stems have the same orientation.

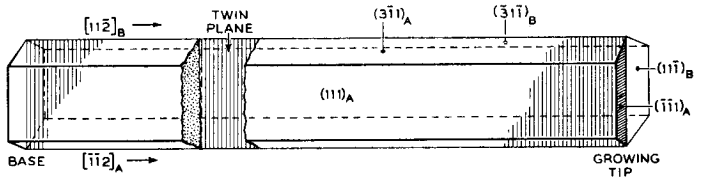
notches were present in the hexagonal column as seen in Fig. 2(a). The surfaces of the notch are {111}- and {100}-type planes. The gradual change of cross section of larger needles probably occurs through small step-planes of these types. A branched needle in Fig. 3, which occurs rarely, was examined and the entire crystal was found to be a single orientation. The branch resulted from simultaneous growth in another [111] direction from the point of branching.

Over 20 ribbons and blades have been examined by x-ray diffraction. Typical ribbons are shown in Fig. 4(a). In all cases, ribbons and blades were twinned crystals, as first reported by Wagner and Treuting,[23] with the {111} twinning plane parallel to {111} main faces as depicted schematically in Fig. 4(b). In thin ribbons the growth direction is ⟨211⟩, but thicker blades obtained after prolonged growth may have other edge directions. The blade shown in Fig. 5(a), which is twinned with {111} main faces and about 5 mm long, has a maximum thickness of 20 μ. Steps exist at a, b, and d having ⟨110⟩ directions. The larger steps a and b slope away from the facet region c, where the crystal is thickest. The slope of the steps is quite small, being about 15° to the (111) plane and does not appear to be crystallographic. It seems likely that the slope is made up of a series of steps which have not quite coalesced into a smooth plane. Silicon ribbons apparently thicken by the lateral movement of these steps. The triangular facet c, approximately 52 μ high, is typical of the early stages of

[22] R. G. Treuting and S. M. Arnold, Acta Met. 5, 598 (1957).
[23] R. S. Wagner and R. G. Treuting, J. Appl. Phys. 32, 2490 (1961).
[24] R. G. Treuting and S. M. Arnold, "Orientation Determinations in Whisker-like Metal Crystals," 13th Annual Diffraction Conference, Pittsburgh, Pennsylvania, November 1955.



(a)



(b)

FIG. 4. Silicon ribbon morphology: (a) Photographs of typical ribbons. The one at the top shows faceting, which frequently occurs. The lower two show growth terminations often observed; (b) schematic drawing of ribbon morphology. The growth direction is ⟨211⟩. The ribbon is twinned with {111} main faces.

the growth of a hexagonal needle on a ribbon or blade substrate.

The blade in Fig. 5(a) has a number of straight edges. Typical directions for the straight edge are $[\bar{2}11]$, $[\bar{4}31]$, and $[\bar{4}13]$ as identified in Fig. 5(b). In addition, noncrystallographic edge directions were observed. Variety in direction appears to be the result of overgrowth as distinguished from the initial extension of the crystal in length.

MACROSCOPIC GROWTH OF CRYSTALS

The growth of crystals was viewed in a furnace fitted with an observation window. The temperature gradient could be varied through control of the current in sections of the furnace while the reaction tube could be translated to observe the source material or the site of crystal growth. By raising the temperature in a region of growth, whisker crystals could be made to evaporate.

When the gradient in the furnace was adjusted so that the source material was at about 1100°C and observations made in a region of lower temperature, where crystal growth could be expected, the first visible occurrence was the development of a number of dark specks on the tube wall. Each small speck rapidly developed into a cluster of fine radiating filamentary crystals (needles and ribbons) which often grew in a few seconds to lengths of 1 cm. A cluster of this type is shown in Fig. 6. The initial growth was rapid and similar to the leader growth reported by Gordon[25] for hydroquinone from water solution, and by Brenner[4] for copper whiskers produced by hydrogen reduction of CuI. With a steep temperature gradient the initial rate of growth was large; lengthening was so rapid, we could not consciously observe the progress. After a short period of rapid growth, increase in length ceased or continued only at a slow rate. Thickening then began. The final product was one of several forms: (1) a very fine clump of wool-like needles or ribbons, (2) a thick cluster of ribbons, (3) a thinly grouped cluster of small needles or ribbons, (4) large needles and blade-like growths. The conditions for the production of the different morphologies are obscure and not presently established.

Experiments were performed in which the temperature of the growth region was raised relative to other parts of the reaction tube. Under these conditions the needles and ribbons evaporated back from the tip. On lowering the temperature evaporation was halted and regrowth began. The new growth was an extension of the parent crystal but with a smaller cross section, as illustrated in Figs. 7(a) and (b).

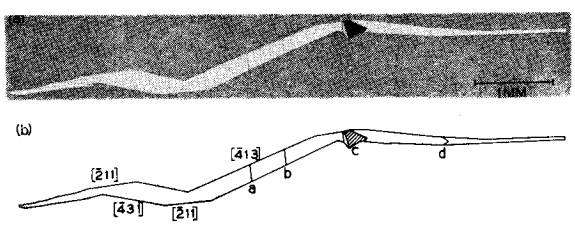


FIG. 5. A thick silicon blade: (a) Twinned blade showing changes in growth direction and faceting; (b) morphology of blade in (a) indicating growth directions and steps active in thickening. The major surfaces are (111). Crystal edge directions are $[\bar{2}11]$, $[\bar{4}31]$, and $[\bar{4}13]$. Growth steps have ⟨110⟩ directions in the {111} surface.

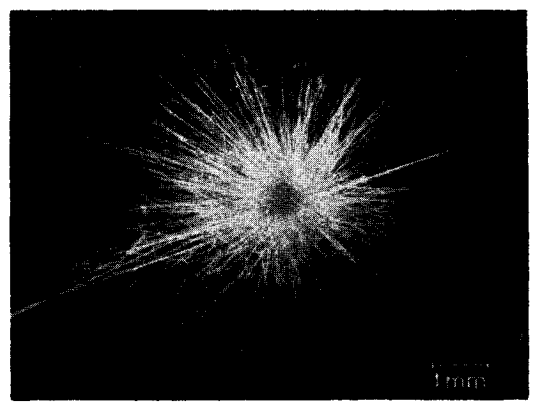


FIG. 6. Silicon filaments extending radially from a nucleation site.

[25] J. E. Gordon, Nature **179**, 1270 (1957); *Growth and Perfection of Crystals* (John Wiley & Sons, Inc., New York, 1958), p. 57.

Orientations of the parent and regrowth regions were determined by x-ray diffraction. Needles regrew in the ⟨111⟩ direction as a continuation of the original orientation; ribbon regrowth was twinned and also was a continuation of the orientation of the parent twinned crystal. No new orientation was observed. One concludes that the condition necessary for regrowth of the same morphology was present in the solid after a substantial end-portion had evaporated. If a dislocation was required for growth, it must have survived the thermal treatment and stresses accompanying the original growth and partial evaporation.

Abrupt changes in growth direction (kinking) were sometimes observed during growth of ⟨111⟩ needles. The extension in length beyond the kink definitely established that these crystals grew by addition of material at the tip. The regrowth experiments discussed above also show that silicon whiskers lengthen by adding on at the tip.

The mechanism of nucleation of the ⟨111⟩ morphology is suggested from observations in which needles grew on ribbons. Twinned blades were grown and then partly evaporated. Subsequently, the temperature conditions were changed to cause deposition of silicon on the blades. An example of such a growth is shown in Fig. 8. Needles grew normal to the {111} surface of the twinned blade. It was demonstrated in a similar specimen that the blade was twinned and that the needles had the orientation of one of the twin components, presumably the one of the side from which the needles grew. Triangular facets have been observed frequently on the surfaces of blades, as seen here and in Fig. 4(a). An example of such a facet after etching is reproduced in Fig. 9. Etching disclosed the straight line marking, evidence of a stacking fault. It is possible that ⟨111⟩ needles originate from such a defect.

The nucleation of a twinned crystal has not been clearly observed. However, the presence of a large number of twin markings on the polished section of a nodule in Fig. 1(b) suggests that a possible site for a ribbon to nucleate is on an exposed edge of a twin interface. Growth from such a site in the ⟨211⟩ direction would produce the observed morphology.

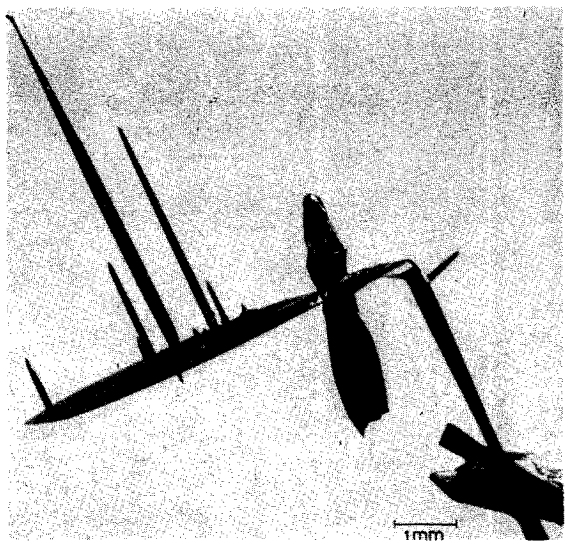


FIG. 8. Nucleation and growth of needles on a blade.

SEARCH FOR IMPERFECTIONS IN SILICON WHISKERS

A search was made for imperfections in both needles and ribbons by chemical etching, by examination of needles for the twist proposed by Eshelby,[26] and by observation of needles and ribbons of about 4000 Å and smaller cross sections with transmission electron microscopy.

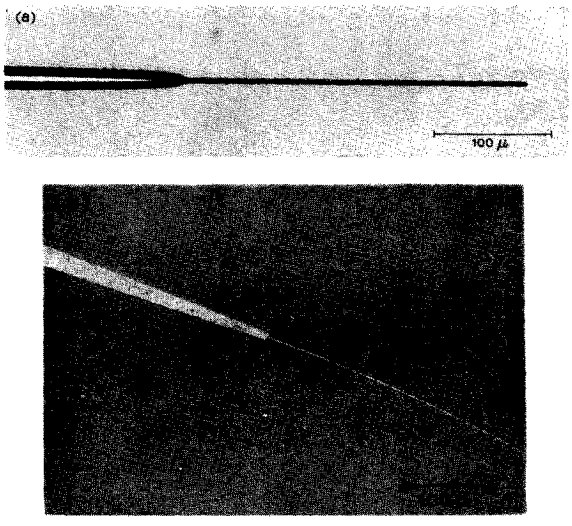


FIG. 7. Regrowths on needles and blades; (a) needle; (b) blade.

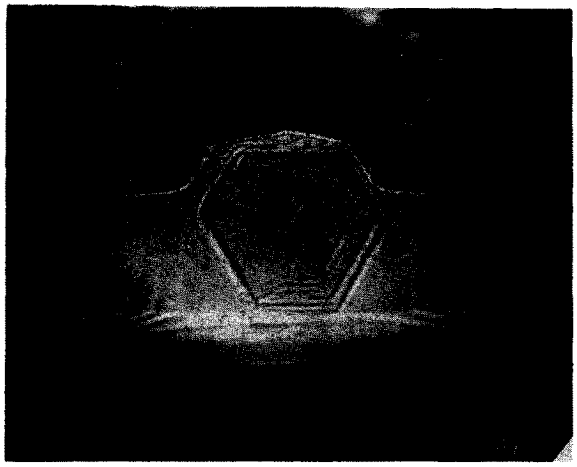


FIG. 9. Facet on the surface of a ribbon etched to reveal a line marking. The marking could be evidence for a stacking fault.

[26] J. D. Eshelby, J. Appl. Phys. 24, 176 (1953); Phil. Mag. 3, 440 (1958).

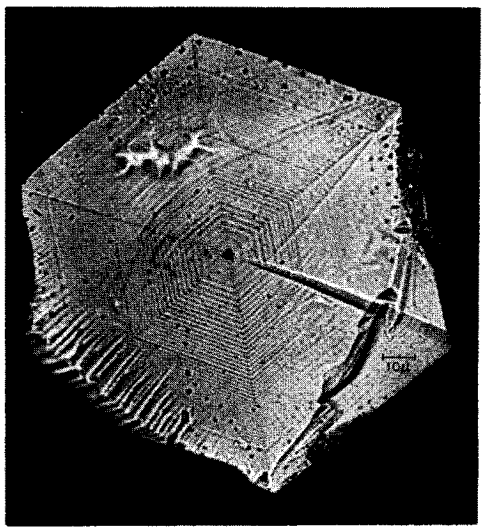


FIG. 10. Etched cleaved cross section of a hexagonal needle showing a central triangular etch pit and concentric hexagonal markings.

Hexagonal needles of about 50-μ section were cleaved to expose a transverse {111} surface and then etched with

CP-4 (120cc HF, 200cc HNO_3, 120cc CH_3COOH, 2cc Br),
Superoxol (H_2O_2:HF:H_2O::1:1:4),
W-Ag (HNO_3:HF:5%$AgNO_3$ sol.::1:1:2), or
Sirtl etch (HF:50g CrO_3 in 100cc H_2O::1:2).

Etching developed a triangular pit in the center of the needle cross section as seen in Fig. 10, suggesting the presence of an axial screw dislocation. The etch pattern surrounding the etch pit consists of closed hexagons and is not a spiral. When such a needle was viewed on its side with transmitted infrared light, a narrow dark band was observed extending longitudinally in the crystal. A similar narrow band was observed in a ribbon when viewed with transmitted light normal to a {111} major surface. However, after annealing in vacuum at 1350°C for 2 h, the central darker band was no longer observed in either needles or ribbons. Likewise, the etching of a cleaved {111} surface of a heat-treated needle did not reveal a pit or the hexagonal pattern of Fig. 10. Rather, a shallow round depression formed in the central region.

It is concluded that the narrow dark bands in needles or ribbons are regions of relatively higher impurity content resulting from the initial rapid growth of the leader which subsequently thickens. The annealing treatment caused a diffusion of the impurities throughout the specimen and the disappearance of the dark band. These observations emphasize the role of impurities in the growth of these crystals and suggest that the initial rapid and predominately unidirectional growth is related to impurities.

A test for Eshelby twist was made on three hexagonal ⟨111⟩ crystals of the sizes set forth in Table I. The twist α in rad/mm for a single axial screw dislocation is given by the equation $\alpha=(b/\pi R^2)$, where b is the Burgers vector for the dislocation and R is the "radius" of the crystal. All dimensions are in millimeters. The crystals were examined by the Weissenberg moving film technique[24] on areas separated by a few millimeters. The calculated total twist for a central screw dislocation for the largest crystal was large enough for easy detection by the method, precise to at least 0.2°. No twist was observed in any of the crystals. Since the whiskers examined were of micron size, it is improbable that a dislocation initially present could migrate out at room temperature due to imposed handling stresses. It is concluded that the crystals did not contain an axial screw dislocation during growth.

TABLE I. Test for Eshelby twist in silicon needles.

Specimen number	Cross-section (μ)	Calculated[a] twist, α (deg/mm)	Separation of irradiated areas (mm)	Calculated total twist (deg)	Observed twist (deg)
Si92C	10	0.23	4.5	1.0	0
Si41A	3.5	1.86	2.0	3.7	0
Si41B	2.0	5.7	2.0	11.4	0

[a] Burgers vector is taken as $\frac{1}{2}d_{111}=3.13$ Å.

Whisker crystals with cross sections from 500–4000 Å, prepared with Ni, Au, and Pd as introduced impurities, were examined in the electron microscope. The most striking feature of the small whisker crystals was the constancy of cross section. A given whisker was seldom observed to change in width along its length, which was hundreds of times greater than the width.

Cross sections of crystals were revealed by extinction contours in photographs of bent crystals. The origin of these extinction contours is given in another paper[27] but is briefly described here. The phenomenon is illustrated schematically in Fig. 11 which shows the intersections of a set of bent crystal planes with the plane of the

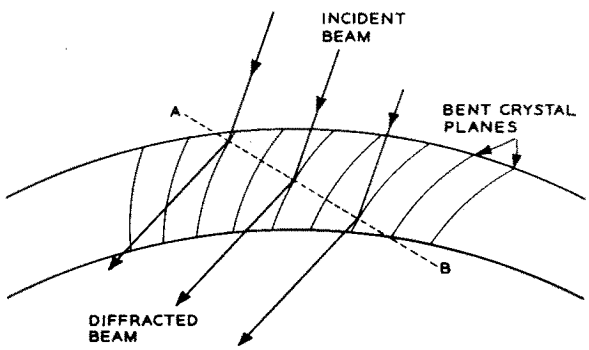


FIG. 11. Schematic drawing illustrating formation of extinction contours in electron transmission microscopy of a bent filamentary crystal.

[27] K. A. Jackson and R. S. Wagner, J. Appl. Phys. (to be published).

paper. The normals to the crystal planes are contained in the plane of the paper. There will be some region in the crystal in which the crystal planes are inclined at a particular angle θ to the incident beam. This region is, in fact, a plane whose normal is in the plane of the paper, and which intersects the paper in the line AB. The incident electron beam, therefore, satisfies Bragg's law for the bent crystal planes only in the plane whose edge is defined by AB. Electrons falling on this plane are diffracted out of the direct beam and the plane AB appears as a dark region with an outline of the cross section of the crystal.

The cross sections of untwinned whisker crystals were either hexagonal or circular. With gold as an added impurity, the cross section was hexagonal as in Fig. 12(a), and the side faces of the whisker were {110} planes. With

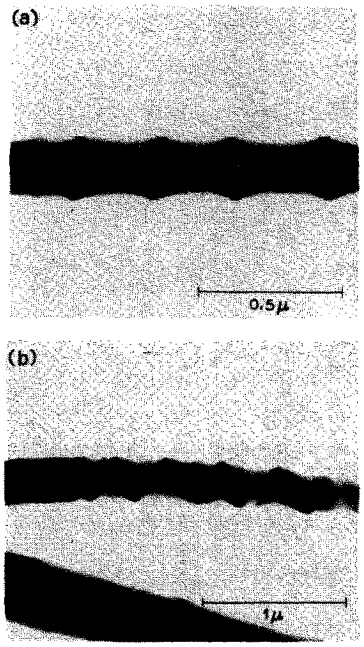


FIG. 12. Extinction contours revealing the shape of silicon needles: (a) a hexagonal needle; (b) a nearly circular needle.

nickel as an added impurity, both hexagonal and circular cross sections were observed, and in some cases the cross section was rounded with flat segments as in Fig. 12(b). The growth axis of untwinned crystals was ⟨111⟩. The twinned crystals in a lot often had larger cross sections than needle crystals; 3000 Å for a twinned specimen compared to 1000 Å for needles. The twin plane usually extended through the narrow dimension of the crystal as shown by the extinction contours in Fig. 13. The growth direction of twinned crystals was ⟨211⟩ and the broad flat faces were {110}. The narrow faces of the twin were irregular and could not be uniquely identified but were approximately {113}. Twinning could be readily detected in a crystal by tilting the specimen stage in the electron microscope to obtain a difference in extinction contrast between the two components, as illustrated in Fig. 14. The twin plane was identified as {111}.

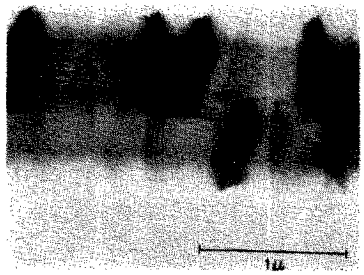


FIG. 13. Extinction contours establishing the morphology of a twinned crystal.

A few crystals were observed to contain many parallel twin boundaries. In general, there were no axial defects in any of the whisker crystals. The two exceptions were one whisker which had dislocations in a local area, and a broad, flat, twinned crystal which had a series of parallel dislocations. A few branched whiskers were found. In these an axial dislocation, if present, would be pinned at the intersection and unable to glide out of the crystal. No dislocation was observed in such specimens.

Differences in morphology were found between submicron and micron or larger whiskers. The long axes of both were ⟨111⟩. In the initial lengthening of the leader, {110} side faces most frequently occur but whiskers with circular cross sections or {211} side faces also are found. Larger macroscopic crystals, produced by thickening of these leaders, have {211} side faces only.

A difference in morphology was observed also for twinned crystals. In this case both small and large crystals had ⟨211⟩ axes. The submicron twinned crystals have large flat {110} faces, normal to the twin plane. The {111} external faces, parallel to the twin plane, were not developed; the lateral surfaces were irregular and on the average were approximately {113}. The large twinned crystals, formed by the thickening of the smaller crystals, had large flat {111} external surfaces parallel to the twin plane.

These differences in morphology support a two-stage growth process. The first stage, in which the whisker lengthens without change in cross section, is very rapid as discussed earlier. It is believed that the lateral faces of the whisker are determined by surface energy relationships and the growth mechanism at the tip. These lateral faces probably have a minimum surface free energy. During subsequent thickening of the whiskers, a much slower process, the exposed side faces are de-

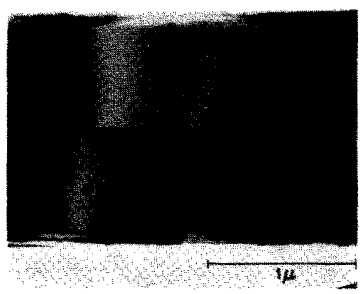


FIG. 14. Components of a twin revealed by extinction induced by tilting the specimen stage.

termined by the relative rates of nucleation and growth of steps on these faces. The exposed faces on the larger crystals need not be equilibrium ones.

An alternate but less likely explanation would attribute the change in morphology with size to a change in relative surface free energy as growth proceeds. After the initial growth in length of the crystals, the composition and supersaturation of the vapor in the neighborhood of the crystal will probably change. This could alter the amount of adsorption of impurities and reaction constituents on the several crystal surfaces, and thereby change the relative values of surface free energy.

DISCUSSION AND CONCLUSIONS

It has been shown in this study that filamentary crystals of silicon do not contain axial screw dislocations or other line defects during growth. It was concluded from observation of growing whiskers that these crystals lengthen by the addition of new material at the tip. The requirement of certain impurities for filamentary growth and the absence of filamentary growth without these impurities are of the highest significance. Without impurities silicon is deposited in the form of nodules or films. With certain impurities, silicon whiskers are formed. Whiskers grow rapidly in the initial stage as leaders that subsequently thicken. It was found that the impurity concentration in the leader is higher than in the subsequent overgrowth.

Whiskers with submicron diameters have extremely uniform cross sections. Thicker whiskers, however, exhibit relatively large steps on their surfaces. This strongly supports the concept that silicon whiskers grow by a two-stage mechanism; a rapid leader-like growth in length followed by a subsequent slower growth in thickness. The effect of impurities on whisker growth appears to be most important during the growth of the leader and of lesser importance during epitaxial deposition on the leader.

It was found that needle crystals always grow in a ⟨111⟩, whereas twinned ribbon crystals initially grow in a ⟨211⟩ direction. The morphology and growth direction of ribbon crystals from the vapor and of "twin dendrites"[28] from a supercooled melt are identical except for the presence of but one twin plane in a ribbon crystal. In twinned dendrites the ⟨211⟩ growth direction is the mean of the ⟨111⟩ growth directions of twin components. It is reasonable to conclude that a ribbon crystal also grows in ⟨111⟩ directions, the two ⟨111⟩ directions of the twin components resulting in the observed ⟨211⟩ direction. The ⟨111⟩ direction, however, is the slowest growing one for silicon crystals from the vapor or from the liquid. Wajda and Glang,[16] using the silicon disproportionation reaction, studied epitaxial deposition rates on silicon substrates of different surface orientations. The measured growth rates were found to be small for {111} and {100} and increasingly larger for {110} and {211} surfaces. The growth rate apparently increases with decreasing atomic density (increase in roughness) of the deposition plane in accordance with the bonding model. The fast ⟨111⟩ growth rate of silicon whiskers therefore cannot be attributed to normal epitaxial growth from the vapor phase.

We conclude that present theories of whisker growth cannot explain the experimental results of this investigation. However, the observations support a new concept of whisker growth, a vapor–liquid–solid mechanism described in a recent paper.[29] In this mechanism certain impurities or agents form a liquid alloy with silicon. The liquid alloy acts as a sink for arriving material from the vapor phase. The whisker grows essentially by crystallization of silicon from supersaturated liquid alloy at the liquid–crystal interface.

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