CHAPTER II

GROWTH OF CRYSTALS FROM THE VAPOUR PHASE

The recent developments in the growth of crystals from the vapour phase are discussed in this chapter. Stress is given to the growth of filamentary crystals. The theory of growth from the vapour, the different mechanisms proposed to explain the growth of filamentary crystals and the observed morphologies of the crystals are discussed. The results obtained by different workers on metal crystals are reviewed and some results on non-metallic crystals are also discussed for the sake of continuity.

Theory of Crystal Growth

The classical theories for the growth of perfect crystals predicted that they should be bounded by atomically smooth surfaces. Low index crystallographic planes exhibit a much lower surface energy than the other planes because of the dense atomic packing of these planes. These faces should then grow by the spread of successive layers created by a two-dimensional nucleation process on the face. At absolute zero the crystal tends to be bounded by planes of low indices which are as smooth as possible so as to keep the surface energy the lowest. As the temperature is raised atoms arrive at the surface and also leave the surface including those which diffuse out of the bulk of the crystal creating vacancies. The crystal will exhibit all kinds of planes. If now the vapour pressure is increased above the equilibrium vapour pressure at that temperature, on an average more atoms will arrive at the surface than those leaving the surface and the crystal will start growing. An atom or a molecule arriving at the surface passes through three stages before it is incorporated into a crystal lattice, viz. (1) its diffusion on the surface towards a step, (2) diffusion over the steps towards a kink and (3) the incorporation of the atom or the molecule at the kink. However, the addition of an atom or a molecule to the surface where there is no kink or step is a very unfavourable process, because of the energy considerations. Only an atom, which can reach a step or a kink by migration over the surface, before it is evaporated, can be incorporated into the crystal lattice. When all the kinks and steps are filled by such a process, the growing surface becomes smooth. Further growth can proceed only by the accidental formation of an island of atoms, providing kinks and steps where the adsorbed atoms can be attached. The critical size of such a nucleus is found to be dependent on the vapour pressure 'p' as

$$R_c = \frac{\gamma a^3}{KT\log P/P_0} \qquad (1)$$

where γ is the surface tension, 'a' is the lattice parameter and P_0 the equilibrium vapour pressure. The formation of a critical nucleus increases the surface free energy by a factor $(2\pi\gamma aR_c/KT)$ and by the action of thermal fluctuations can be expected to occur at a rate proportional to $-\mathrm{exp.}(2\pi\gamma aR_c/KT)$ which is a very small factor. The growth rate then will be controlled by the probability of nucleation and usually will not be appreciable until the supersaturation reached the order of a few tens of percent. Under this condition, the subsequent growth of a layer after nucleation will be extremely fast and would not be a limiting factor in controlling the rate.

It is observed, however, that most real crystals grow at very low supersaturations, leading to the conclusion that sources of steps are always present which make the nucleation process unnecessary.

The problem of the continous presence of steps on the crystal surface was resolved by Frank's screw dislocation mechanism[1] of crystal growth. A screw dislocation emergent at a point on the crystal surface provides a step on the surface equal in height to the projection of the Burgers vector of the dislocation on the normal to the surface. This provides a self-perpetuating step. During growth the step will not remain straight, because this requires its speed of motion to be proportional to the distance from dislocation, whereas this is more or less uniform. Because of this the step lags behind at the edges and winds itself into a spiral hill. Under a given condition of supersaturation, the crystal surface rapidly winds itself into a spiral, centred on the dislocation, until the curvature at the centre reaches the critical value. At this point for the section of the step near the centre, because of the higher curvature, there will be a higher equilibrium vapour pressure and therefore a lower supersaturation. Hence its rate of advance is slower. As a result the angular velocity at all the turns of a spiral hill becomes the same. The spiral reaches a steady state and the whole spiral starts rotating with a stationary shape. The number of turns the spiral makes decides the characteristic growth rate of the crystal, which is proportional to the square of the supersaturation. This has been confirmed by many authors.

Owing to the change in growth-rate with crystallographic direction, the spiral many-a-times assumes a polygonal shape. The shape of the spiral depends on the type and structure of the growing crystal. The emergence of two or more dislocations at the same point, or very near to each other, gives rise to complex spirals if they are of the same sign and closed loops if there is an even number of dislocations of opposite signs and equal magnitudes.

Heck[2] has observed spiral patterns on paraffin crystals and Menzes and Sloat[3] and others have observed spiral patterns on SiC, much earlier than the dislocation theory was put forward by Frank. But none of these authors could offer a satisfactory theory to explain these patterns. It was Griffin[4] who presented the first experimental proof in support of Frank's theory. On the $(10\bar{1}0)$ faces of beryl crystals he observed line markings, which, there are reasons to believe, were edges of growth layers. He also observed patterns originating from single and double screw dislocations, in agreement with the shape predicted by the theory.

Since then, a large number of experimental evidences, in support of the growth of crystals by the screw dislocation mechanism has been reported by many workers. Verma[5] has given a detailed account of various types of spirals and their significances. Forty[6] in a review article gives an account of the growth spirals observed on various crystal surfaces.

Amelinckx[7] and others[8] have obtained direct evidences of screw dislocations in metal crystals. They observed growth spirals on chemically deposited gold. Due to the large step height they are thought to be anomolous, because there is no evidence for expecting such large dislocations in metals. Forty[9] has observed growth spirals on the vapour deposited facets of the hexagonal metals Mg, Cd and Zn. Mg and Cd showed faint growth spirals which from their low visibility could be infered as being monomolecular in height. In each of these crystals no evidence was available of the presence of two or more dislocations. No growth spirals on Zn were observed, but a large number of loops with a speck at the centre could be observed. Forty says that this could be due to the growth by two dimensional nucleation, catalysed by the crystalline overgrowth of ZnO. If this were the case the Mg crystals also should have grown by the same process and hence this cannot be considered conclusive. Dawson[10] explains this as due to two dislocations of opposite sign which have moved together to form a closed inner loop. According to Frank's theory such a mechanism is possible.

Forty and Frank[11] were the first to observe growth spirals on cubic crystals. They observed screw dislocations of unit Burgers vector on the cubic and octahedral faces of silver grown from the vapour. Before this a major criticism of the dislocation theory was that spirals were observed only on thin plates with layered structure and crystals of complex structure such as beryl. Dash[12], using a microscope fitted with an infrared tube has shown closed loop patterns not only on the surface, but also inside the silicon crystals. Williams[13,14] has studied the growth of Lead nitrate crystals from the solution and also the effect of local deformation during the process of growth. She has shown that growth centres can be initiated at the sites of deformation and these can also overtake the existing ones if they are strong enough.

Henshke[15] has observed closed loops, partly centric and partly eccentric, on microblisters of copper films grown on glass substrate. The large step height, of the order of a micron is explained by a double alternative active growth mechanism analogous to the Frank-Read source, without assuming dislocations of large Burgers vector.

Dukova[16] has studied the effect of supersaturation on the form of spirals using paratoluine and other organic crystals. As the supersaturation was increased slowly polygonal spiral layers, rounded spiral layers, disintegration of the spiral layer to concentric loops and layers of dendritic form at the highest supersaturation.

Testuya et al.[17] observed threefold symmetrical pyramids developed on the (111) surface of germanium crystals, due to the vapour deposition of Ge produced by decomposition of GeI_2. They argued that these were formed at the dislocation sites due to the rapid growth as suggested by Frank's theory. Their further suggestion was that an obliquely inclined edge dislocation can also give rise to a self-perpetuating step. Similarly Dekeyser and Amelinckx[18] observed growth terraces on the surface of SiC crystals which contained a single spiral or a complex spiral at the tip of the terrace. They concluded that when growth was slowed down by poisons on the edges of the step, near a dislocation site, the centre continued to grow at the original rate giving rise to the terrace.

Lang has tried, in one of his papers, to give an explanation to the large step heights observed in many cases. He has shown that a periodic bunching of the monomolecular steps occurs on a crystal surface inclined at a small angle to the densely packed atomic plane and causes observable steps to appear. Generally they form concentric rings. But a simple mistake in the step formation in the early stage of growth can give rise to a spiral. Thus, in such cases, it is not necessary to have a dislocation to form a spiral.

Pandya and Balasubramanian[19] have observed spirals and loop patterns on the facets of Zn crystals grown from the melt. The spirals showed a low step height, while the loops had a step height of about one micron. The large step heights were explained by assuming a double spiral mechanism. They have shown that these patterns are due to deposition from the vapourphase and not due to growth from the melt. Pandya and Thattey[20] have reported the growth spirals of large step heights on cadmium crystals. They suggested that these large step heights are due to the formation of multiple dislocations during nucleation or due to the bunching of steps of different rates of advance. These spirals are shown to develop during growth from the vapourphase. Thakkar[21] has observed spirals of large step heights on the (111) faces of Antimony crystals grown from the vapourphase. The large step height is due to the coalescence of a number of dislocations of the same sign.

The above discussion gives a clear idea of the different experimental results in support of the dislocation theory of growth. In brief it can be stated that a screw dislocation provides a suitable nucleation centre for growth of crystals from the vapourphase at low supersaturations. Impurities can also provide suitable steps for the growth of the crystals as observed by Forty in Zn.

Theory of Whisker Growth

A good amount of information has been obtained on the growth of whisker crystals during the past two decades. Many theories have been put forward to explain their growth and behaviour. Generally the whisker crystals are nearly perfect and their strength comes very near to the theoretically predicted value. This leads one to believe that they are free of dislocations and other crystal imperfections.

The whiskers can be classified into three groups, depending on their growth: (1) proper whiskers, (2) whiskers grown from solution and (3) whiskers grown from the vapour. Proper whiskers are those growing from a solid bulk material and they grow from the base. Whiskers grown from the solution and vapourphase are considered to grow by addition of material at the tip and the theories are applicable to both in general.

The earliest theory of growth of proper whiskers has been presented by Peach[22] based on the dislocation mechanism. The theory was discarded because later observations have shown that the proper whiskers grow from the base and not from the tip and that proper whiskers usually do not have axial screw dislocations. The next theories to be proposed were those of Frank[23] and Eshelby[24]. The two are very similar in principle.

Eshelby assumes that a small hump already exists on the surface and that as a result of oxidation the surface free energy has a -ve value. The surface tractions are such as to pull out a whisker while providing a constraining collar at the ~~root~~ which keeps the diameter constant. The specific mechanism considered is that a Frank-Read source, in a plane some distance below the surface, has its Burgers vector normal to its plane. Under the influence of tensile stress in the whisker, the source climbs in its own plane to form loops which are sheets of interstitial atoms. Under the influence of the shearing stress around the root, these loops climb towards the surface, each one adding a single atomic layer to the root of the whisker. It is assumed that stresses produced by surface tension are appreciably larger than those required to operate the Frank-Read source. In fact they will be usually of the same order of magnitude $\mu b/R$ for a whisker of radius R in a medium of shear modulus μ. In the case of very fine whiskers for R of the order of 0.05 microns this is about $\mu/200$, and it is difficult to imagine any other source of such large stresses. Accepting that the driving stress is of this order of magnitude and is adequate to operate the Frank-Read source, Eshelby shows that the rate of whisker growth is controlled by the rate of migration of vacant sites from the climbing dislocation to the surface and that the rate of elongation is a numerical multiple of $\gamma Db^3/R^2KT$ where D is the coefficient of self-diffusion and KT is the thermal energy.

Frank also assumes a -ve surface energy caused by oxidation and remarks that a dislocation meeting a free surface will never be in stable equilibrium since a screw dislocation can increase the exposed surface by gliding and an edge dislocation can increase the surface by climbing. If there is a hump on the surface, the dislocation is anchored, by its line tension to the concave base of the hump and moves round and round the base. Frank considers only the case of ordinary diffusion of vacancies from a curved segment of dislocation line to the surface. His model consists of a spiral of dislocation at the base of the whisker, one end of the spiral meeting the free surface and the other running as a screw into the main mass. He arrives at a formula for the rate of growth which is essentially the same as Eshelby's. Frank finds that the rate of growth is independent of the number of turns in the spiral, since the rate of rotation is inversely proportional to the number of turns.

Franks[25] has developed a theory of whisker growth which is very similar to that of Frank and Eshelby. He takes loops from a source of Eshelby's type, but supposes that instead of gliding to the surface without meeting any obstructions they intersect another dislocation of the same Burgers vector. The portion of this second dislocation, which has been carried towards the surface by the Eshelby loops, is joined to the stationary portions outside the loops by the screw segments. These screw segments can glide under the same shearing stresses as those which cause the Eshelby loops to glide. If they reach the free surface, they become anchored to the base of the whisker and migrate around it; if they do not reach the surface they trace out spiral edge dislocations of Frank's type. This is essentially a mechanism of prismatic punching and has the merits of explaining the irregular heads which are found on regular whiskers. It also explains the zig-zag boundaries which are presumably the easy glide planes of dislocations. But the theories of Frank and Eshelby can explain this equally well as the directions of low energy for edge dislocations. Franks attributes the cessation of whisker growth to the formation of stacking fault in the lattice.

That proper whiskers grow from arreys of dislocation loops which form spirals, helices or processions does not seem to be in doubt. The details of the dislocation mechanism will be difficult to establish and may well vary from case to case. The need for a -ve surface energy is not well established. Experiment indicates that it is not required while the theory provides no other source powerful enough to drive Frank-Read or similar sources of the small size required. The rapid growth rate obtained under pressure are greater than the random flux of vacancies will allow and cannot be explained on ordinary diffusion theory. There is no satisfactory theory of the cessation of whisker growth, especially in view of Frank's observation that fresh growth can be stimulated by wiping off the completed whisker. The growth of whiskers with diameters large compared to the grain size of the substrate is unexplained.

It is accepted by most workers that growth from the vapourphase and solutions is by layer growth. In layer growth, two simultaneous and interdependent processes are going on: (1) creation of steps at a source and (2) the motion of the steps away from the source. The layer growth should be divided into two types according to whether or not every singular surface of the growing crystal has active sources. In the first case the crystal will develop into a more or less regular polyhedron. A perfectly regular polyhedron will develop only if the rates of all sources are exactly equal, which is not likely. In the second case particularly if only one of the singular surfaces possesses an active source the crystal will have an assymmetrical shape. This type of growth is denoted as whisker growth since it corresponds to many of the conditions of growth of whiskers. Such crystals have a lengthwise dimension, orders of magnitude larger than that of cross-section. For most filamentary crystals both the fast growth direction and the directions of lateral growth have small Miller indices. The special growth form of a whisker crystal implies that the tip of the crystal must be a preferred growth site. Taking into consideration the fast rate at which a crystal grows, even at a supersaturation below the critical value for two dimensional nucleation, it is not possible to say that the tip is advancing by two dimensional nucleation. This made the necessity to look for other mechanisms for the growth of whiskers.

If the crystal lattice is perfect, any projection on the surface grows into a complete lattice plane, so that the crystal reaches an equilibrium form in which it is bounded by low index planes of high atomic density meeting in slightly rounded edges. Further growth can occur only by two-dimensional nucleation on the surface of those low-index faces. Burton and Cabrera[26] have shown that this two-dimensional nucleation will occur only at very high supersaturations.

If this result is neglected temporarily, an approach to the theory of whisker growth may be made as follows. The sides of the whisker on which the nucleation is difficult should be faces of high density and low surface energy. The axis which is the direction of easy growth should be a direction of high density. These conditions are adequate to explain the growth of highly anisotropic substances. They are obviously important in determining the habits of mercury platelet, silver needles and mercury whiskers observed by different authors. However, they do not explain why a silver whisker growing in the $[110]$ direction and bounded by the close-packed planes $(1\bar{1}1)$ and $(1\bar{1}\bar{1})$ should not terminate in a close-packed plane (111), on which nucleation will be as difficult as it is on the sides of the whisker. Brenner and Sears[27] offered a partial answer to this by considering the rate of diffusion from the vapour to the crystal. The crystal faces are in a part of the vapour which is impoverished by the previous growth of the whisker. The tip is in a region of the original concentration and diffusion towards the tip can take place three-dimensionally instead of two-dimensionally. The equilibrium concentration of the vapour will be recovered at the root of the whisker sooner than at any other point, and the re-entrant angle at the root allows easy nucleation. Thickening of the whisker will therefore be initiated at the root.

The theory has so far omitted the important factor of surface-diffusion. Volmer and Estermann had shown that the rate of growth of mercury plate was 1000 times the rate of impingement of mercury atoms on the edges of the platelets and found it necessary to assume that every mercury atom striking a face of the platelet was adsorbed on the surface, migrated until it came to the edge and was there incorporated into the growing crystal. The observations of Hock and Neumann on potassium whiskers and of Sears and Gomer on mercury whiskers led to similar conclusions.

An adsorbed atom[28] on a perfect crystal face has a definite mean free path 'λ' for diffusion before it evaporates. Rough theoretical estimates of this diffusion length can be made which leads to results of the order required to explain the experimental observations. When the major linear dimension of the whisker or platelet is smaller than the diffusion length, the whole surface of the crystal makes an effective catchment area. The ratio of the catchment area to the area of growth is proportional to the major linear dimension of the crystal and this linear dimension increases exponentially with time. When the major linear dimension is greater than 'λ', atoms incorporated within the unit diffusion length of the area of growth are incorporated into the crystal lattice while atoms adsorbed at greater distances are evaporated. The major linear dimension increases at a constant rate which exceeds the rate corresponding to direct impingement on the growing area by a factor 'λ/l' where l is the minor linear dimension of the whisker or platelet. If the whisker tip or platelet edge is an effective trap for adsorbed atoms the theory explains the growth kinetics quantitatively. It also explains the observations of Coleman and Sears[29] that whiskers nucleated on glass soon begin to thicken. In the case of whiskers growing from a substrate of their own material the substrate forms a sink for adsorbed atoms. In the case of whiskers growing on glass there is no such sink and the tendency to nucleate new layers is increased.

Coleman and Sears have attempted to estimate the maximum rate of whisker growth in terms of the coefficient of self-diffusion of the vapour. They have found that after time 't' the whisker has been able to draw matter from a sphere of radius proportional to $(t^{\frac{1}{2}})$ and limited only by the size of the container. The maximum rate of whisker growth is proportional to this rate. The calculation is erroneous because the rate of adsorption of matter by the sink is proportional to the concentration gradient close to the sink, which is clearly a decreasing function of time, when the time is large. Since the observed growth rates are satisfactorily accounted for by the rate of impingement calculated without allowance for diffusion, it is necessary to assume that the concentration of the vapour near the catchment area is equal to that in the bulk of the vapour. This concentration must be maintained by a turbulent motion of the vapour which is almost certain to be produced by the large temperature gradient in a distillation vessel or the container in which the crystals will be growing. The presence of an inert gas will hinder diffusion and inhibit whisker growth if diffusion is a limiting factor, but will aid whisker growth by converting latent heat from the whisker tip if there is turbulent flow.

As soon as Burton and Cabrera[26] haveshown that the rate of two-dimensional nucleation, under moderate supersaturations of the vapour was far too small for the observed rates of crystal growth, Frank[1] pointed out that when a screw dislocation meets a surface normally, a ridge runs from the point of emergence to the edge of the crystal. If growth is allowed to continue by the same mechanism, the faces parallel to the axis of the dislocation remains perfect and adsorbed atoms either evaporate again or get incorporated on the ridged surface. The screw dislocation introduces the anisotropy required to give one growth direction preference over another in a cubic crystal. Growth ceases if the screw dislocation ceases to emerge at the tip and reaches a surface parallel to its Burgers vector. The presence of the screw dislocation explains the axial twist observed by Gomer.

The effect of a dislocation on the growth properties of a crystal face, on which it terminates, depends only on the height of the step it creates on that surface apart from minor effects close to the dislocation core. The height of the step is given by the scalar product ($\underline{b}.\underline{f}$) where $\underline{b}$ is the Burgers vector and $\underline{f}$ is the unit vector normal to that surface. If $\underline{b}$ is a lattice translation then ($\underline{b}.\underline{f}$) can be only an integral multiple of interplanar spacing for the face concerned. A dislocation can control the direction of growth if the dislocation line adheres to a particular crystallographic direction. In that case, instead of ending normally on the growth face, it can bring about growth on an oblique-terminating face or alternate growth on a pair of oblique faces.

In many cases, such as silver and copper, helical whiskers have been observed. If a partial dislocation is present in a whisker, the edge component of the dislocation will climb, and in order to keep the strain energy minimum, shifts from one face to the other emerging alternately on either sides of the direction of the screw component. As a result the helices and twisted whiskers are formed. Price, Vermilyea and Webb[30] extended this theory still implying the presence of a screw dislocation at the tip of the whisker. They postulated that impurities, arriving at the fast growing tip face, become burried while those arriving at the surface of slow growing lateral faces accumulate and hinder growth.

Sears[31] has discussed the growth of mercury platelets. During growth the attachment of a crystal continues to be at a point and does not broaden into a line. Sears deduces that growth is confined to the rhombohedral planes (010) and (001) of high density. Growth may occur either through the presence of a crossed grid of screw dislocations or through the presence of a single screw dislocation. In the former case all the planes (010) and (001) should contain growth pyramids and all the four faces must grow contrary to the observation of continued attachment to a single point. Therefore Sears rejects the crossed grid and accepts only the single screw dislocation mechanism.

Roth[32] has explained the formation of spirals of zinc sulphide in the following manner. The habit of these curved zinc sulphide whiskers has the basal plate (0001) parallel to the whisker axis which is $[10\bar{1}0]$. Since ZnS does not possess a centre of symmetry, but has $[0001]$ as a polar axis edge dislocations with Bargers vectors $[10\bar{1}0]$ and lines $[1\bar{2}10]$ may occur more frequently than similar dislocations of opposite sign. This excess of dislocations of one sign curves the crystal in the observed manner. At the high temperature of whisker growth the dislocations form polygon boundaries. The growth of graphite whiskers as tubes or scrolls is unexplained.

Because of their high vapour pressures Zn, Cd and Mg have been studied most frequently. Straumannis[33] has studied the growth process of each of these metals. The Zn and Cd metals first formed as hexagonal plates with their c-axis perpendicular to the walls of the container. New layers grow out from the centres of the platelets with the edges of each succeeding layer remaining some distance from the edges of the underlying layer. For Cd he found the height of each layer to be 0.8 ± 0.1 μ or multiples of that. On the other hand McNutt and Mehl[34] found no characteristic step height, but only a range of step heights from 300 to 3000 A° were observed. The Mg crystals were more regular in shape and considerably larger than the Cd or Zn crystals. They were bounded by fewer and better developed surfaces, primarily of (0001), $(10\bar{1}0)$ and $(10\bar{1}1)$ types. As the condensation temperature was decreased and supersaturation increased dendritic crystals and polycrystalline aggregates were observed. Keepin[35] made use of an inert gas atmosphere to grow large crystals of Zn and Cd. The metal was heated in an Mo crucible and was collected on independently heated metal plates suspended above the crucible. Everything was kept inside a bell-jar containing N_2. Dendritic crystals were obtained when either the collector temperature or the N_2 pressure was decreased from its optimum value.

Sears[36] has grown platelets and whiskers of mercury in a growth cell similar to that used by Volmer and Estermann. He studied the kinetics of whisker and platelet growth and proposed that the edges of platelets and the tips of whiskers are prefered growth sites because they contain one or more emerging screw dislocations whereas the basal surfaces of platelets and the lateral sides of the whiskers are free of dislocations. Sears[37] has found that Zn and Cd whiskers can be grown in large numbers in vacuum of 10^{-6} Torr. Coleman and Sears[38] found that Zn whiskers grew in greater abundance and to a much greater length in the presence of pure inert gases than in vacuum. Cabrera and Price[39] grew a profusion of Zn whiskers in an atmosphere of helium. The impurities in the whiskers were estimated to be less than 10^{-2} atomic percent. In addition to whiskers, platelets, rhomboids and ribbons were observed. The axial twists of the whiskers were determined. Although larger than zero, the twist was never large enough to be accounted for, on the basis of a single screw dislocation. This implies the existence of several dislocations along the axis of the whisker.

Price[40] studied the growth of Cd crystals from the vapour and concluded that whisker growth for metals is not a unique phenomenon, but is a transition stage during crystal growth at moderate supersaturations. He imposed a supersaturation gradient in the growth region and found that the crystal habit varied largely with supersaturation. For $\sigma < 2$ whiskers and thin platelets formed predominantly. For $\sigma > 2$ the density of the crystals increased and the whiskers and thin platelets thickened rapidly to give thick hexagonal plates. At a supersaturation less than 0.4 Price did not observe any nucleation. This is in contrast with the observations of Parker and Kushner[41] who found that zinc crystals, under carefully controlled temperature and vacuum conditions, nucleate at supersaturations as low as 0.009. The discrepancy may result either from the much longer periods used by Parker and Kushner or from the difference in substrate.

Dittmar and Neumann[42] and Parker and Kushner[43] have studied the growth of potassium whiskers. The whiskers were hexagonal in cross-section with the

[111] direction parallel to their axes and were bounded by the six (110) planes. Evidences were found for axial screw dislocations in many of the crystals by Parker and Kushner. But there were some crystals which did not show any evidence for an axial twist.

Relatively large whiskers of metals can be grown by reduction of their halides. In addition to their perfection these whiskers have better defined orientations and are often bounded by extremely smooth, low index crystallographic planes. Their main disadvantage is their small size, necessitating careful handling and manipulation. Brenner[44] and Wayman[45] have grown whiskers of copper and iron as long as 10 to 20 cms long and 1 mm or more wide by increasing the scale of operation. These large whiskers are not as perfect as the thinner ones.

The mechanism of whisker growth is not well understood. In some cases it is even difficult to determine whether it occurs by vapourphase transport or by diffusion through the substrate or by capillary flow of the liquid halide along the whisker surfaces.

Observations suggest that whiskers are nucleated on small metal or oxide crystals. For the more noble metals such as Cu and Ag small crystals form directly from the halide and the whiskers grow from these. For the more reactive metals such as Ni and Co whiskers are believed to form on metal particles formed by reduction of oxide crystals. For Ni whiskers, from NiBr in an atmosphere containing water vapour, Cech[46] has shown clearly the oxide-metal-whisker sequence. Gorsuch[47] has shown that for Fe the whiskers can nucleate both on metal and oxide particles. The orientation depends on the nucleating particle. The growth forms of whiskers imply that their tips are prefered growth sites, especially when the whiskers are bounded by equivalent crystallographic planes.

Ruth *et al.*[48] have discussed the problem of crystal growth cessation. It is not yet clearly understood why the crystal cease to grow after a certain length. The rapid exponential growth may terminate i) when the spiral dislocation responsible for the whisker growth may slip[49] or climb[50] out of the whisker. The likelihood of the former mechanism is enhanced if the whisker tip is exposed to a lower supersaturation or if the impurity adsorption slows down the ratio. Another chance is that the impurity adsorption may poison the tip decreasing or stopping rapid growth.

The VLS mechanism of Whisker Growth

In whiskers of many materials axial screw dislocations have been observed. In these cases, growth is attributed to the inexhaustible steps at the tip of the whiskers where the screw dislocation emerges. Webb and co-workers[51] have studied a variety of whiskers of metals using an X-ray technique and have observed evidence of screw dislocations in some of them. Truiting[52], Hirsch[53] and Shlichta[54] have made attempts to detect screw dislocations in whiskers using X-ray diffraction, exploiting a calculation made by Eshelby[55] showing that a screw dislocation parallel to the whisker axis produces a lattice twist about the axis given by $\mathcal{L} = (b/\pi R^2)/(1-\xi^2/R^2)$, where b is the Burgers vector of dislocation, R is the whisker radius and ξ is the displacement of dislocation from the whisker axis. The most common observation made by Webb and others is the absence of any detectable lattice twist. Any twist more than 0.01, that expected of a prime axial screw dislocation would have been observed. This does not eliminate the dislocation mechanism for the growth of these whiskers, because there may be an even number of parallel dislocations of equal Burgers vector but of opposite signs or a dislocation that climbs or is forced out of the whisker through the lateral surfaces.

But there is increasing evidence that a good many of the whisker crystals grown from the vapour are free of dislocations. Webb and co-workers have studied the whiskers of nine metals and found unequivocal evidence of axial screw dislocations in only one element, palladium. However, not every palladium whisker examined did contain a dislocation. Observations with the electron-microscope have been made by Price[56] in zinc whiskers and by Wagner[57] _et al_. in silicon whiskers. They have failed in observing any dislocations. Since many whiskers are completely free of dislocations an axial screw dislocation does not appear to be a necessary factor for whisker growth of many substances.

A significant advance in understanding whisker growth has been the recognition of the need for impurities. This requirement has been clearly demonstrated for copper, iron and silicon whiskers by different authors. For silicon Wagner et al.[57] and Ellis and co-workers[58] have proved conclusively that certain impurity, for example nickel or gold, is essential for whisker growth.

Another phenomenon that occurs during whisker growth is the presence of a liquid layer or droplet on the top surface of some crystals growing from the vapour. The liquid layers or globules were considered to originate from metastable phases, molecular complexes or intermediate polymers originating from condensation of the vapour.

In the case of many whiskers rounded terminations have been observed at the tip of the crystals. Barber[59] has observed ribbon-like crystals of Aluminium with a globule at the tip of each crystal. Barber[60] and Webb and Forgeng[61] have observed independently Al_2O_3 whiskers with rounded terminations. Edwards and Happel[62] could observe BeO whiskers with a hemispherical globule at the tip of each whisker. They suggested that during the growth of the whisker the globule consisted of molten beryllium enclosed in a solid shell of BeO. The preparation of silicon whiskers from the vapour and their structure has been studied by Wagner et al.[57]. It was found by chemical etching, by examination for an Eshelby-twist and by observations in the electron microscope that silicon whiskers and ribbons are free of dislocations and imperfections. They concluded that the filamentary crystals of silicon do not require an axial screw dislocation to initiate the growth. Certain impurities like platinum, gold and nickel are essential for the growth of silicon whiskers. Whisker growth is a two-stage process; a fast initial extension in length followed by a slow increase in thickness. The rapid initial growth occurs by addition of material at the tip. During the observations made by these authors whisker crystals of micron thickness were observed occasionally, to exhibit during regrowth, a small liquid-like globule at the tip.

To account for such observations, which could not be explained on the basis of screw dislocation mechanism of growth, Wagner and Ellis[63] put forward a new concept of whisker growth; a vapour-liquid-solid mechanism. In this mechanism, a layer of liquid, in which the crystal material is soluble, is situated between the vapour and the growing crystal. The presence of a liquid layer, in contact with the growing crystal has important consequences. The surface of the liquid has a large accomodation coefficient and will, therefore, be a prefered site for deposition. The liquid becomes supersaturated with material received from the vapour and crystal growth occurs by precipitation at the solid-liquid interface. Unidirectional growth is the consequence of an anisotropy in solid-liquid-solution interfacial energy.

The VLS mechanism[64] occurs in two steps as has been described. First, there is deposition from the vapour directly on a liquid solution in the vapour-liquid system. The second and the subsequent step, occuring in a liquid-solid system,is precipitation from the supersaturated liquid solution at the liquid-solid interface.

If we consider the surface of a perfect crystal, the surface of an imperfect crystal and a surface of unit accomodation coefficient (clean liquid), in the first two cases the growth rate becomes zero below a particular value of supersaturation, and increases to the ideal value with increasing supersaturation. Nucleation of new layers, within the respective ranges of supersaturation, occurs either by two-dimensional nucleation on the perfect surface or by the screw dislocation mechanism on the imperfect surface. The surface of unit accomodation coefficient, that is a clean liquid surface is distinctly different from that of a perfect or imperfect crystal surface. It can be considered as ideally rough, that is composed of ledges and steps, only interatomic distances apart[65]. Accomodation sites exist over its entire area. Deposition on a liquid surface, therefore, follows the ideal growth rate even at extremely small supersaturations.

The stability of the liquid solution is a must for the VLS mechanism to operate. This condition, imposes a limitation on the minimum diameter of a VLS grown crystal. The stability of a liquid droplet, of curvature 'r' in its own vapour, depends on the supersaturation σ. The minimum critical radius is given by

$$r_{min} = \frac{2\gamma_{LV}V_L}{RT\log\sigma} \qquad (2)$$

where γ_{LV} is the liquid-vapour interfacial energy, V_L is the liquid molar volume and R and T have the usual meanings. For most materials r_{min} is about 10^{-5} cm for $\sigma = 1.02$. For whiskers with submicron dimensions stability of the liquid droplet can be obtained by an appropriate increase in supersaturation of all components of the liquid.

The next point to be considered is the deposition from the vapour on a perfect crystal, with a local area covered by a liquid solution. Such a solution can be readily formed by alloying a suitable solvent agent (impurity) with the crystal substrate.

The liquid solution in contact with the crystalline substrate seeks to maintain equilibrium composition at a given deposition temperature. However, the liquid solution receives a flux of material from the surface. The resulting concentration gradient in the solution provides the driving force for the diffusion from the surface to the liquid-interface. The material transport in the liquid is diffusion controlled and occurs under essentially isothermal conditions.

Wagner and Ellis[64] have grown silicon crystals by VLS mechanism. Gold was the solution forming agent. Etching of these crystals have shown that most of them are completely free of dislocations and stacking faults. In the part of the crystal close to the substrate and at the original liquid-alloy-substrate interface there are sometimes small islands of eutectic surrounded by a dislocation net work.

Barns and Ellis[66] have grown GaAs and GaP whisker crystals by VLS mechanism. Au, Pd and Ga have been used to produce the required liquid layer. Three morphologies of crystals have been observed; (1) a twinned ribbon with a $\langle 112 \rangle$ growth direction and $\{111\}$, $\{110\}$ and $\{113\}$ lateral faces, (2) a hexagonal needle with a $\langle 111 \rangle$ growth direction and $\{110\}$ lateral faces; and (3) a newly found habit, a single crystal blade which grows in a $\langle 001 \rangle$

direction with $\{110\}$ lateral faces. The most frequently occuring habit was the thin rectangular blade or ribbon with a tapered end surmounted by a spherical termination. The thickening of the ribbon is by the motion of the series of steps visible on the broad faces.

Wagner and Doherty[67] have grown silicon whiskers by VLS mechanism under controlled conditions. They have shown that the location of growth, the diameter of the crystal and its ultimate length can be controlled.

It has been shown by Wagner[68] that the mechanism of kinking and branching during growth is a straightforward consequence of the VLS concept. Defects such as dislocations or twin planes are not necessary for these processes. Both branching and kinking are mainly caused by a lateral temperature gradient during VLS growth. Such a gradient may result in a breakdown of the solid-liquid interface. A new interface will be formed which will be as parallel as possible to the temperature isotherm. Growth perpendicular to the new interface will be slower than that on the old one, which finally disappears. Further growth proceeds perpendicular to the new interface.

In most cases, the process of branching is a consequence of incomplete kinking. The liquid alloy droplet may break up during the kinking process due to surface tension and the individual droplet may give rise to VLS growth on their respective interfaces.

Whisker growth by re-entrant twin mechanism

Silicon whiskers have been grown from the vapour phase by Mendelson[69]. The tips of the whiskers generally taper with low index planes and sometimes contain a small crater rather than the rounded caps typical of the VLS mechanism. He suggests that the growth in these cases occurs by a re-entrant twin-mechanism as has been observed by previous authors.

Melmed and Holyward[70] and Melmed[71] have found that a significant number of whiskers and whisker stems of many metals contain symmetrical twins parallel to the whisker axis. One might then suppose that the whisker growth in these cases is by a re-entrant twin mechanism similar to that found in ribbon dendritic growth in semiconductor materials[72].

The model would predict a ribbon if the nuclei contain only closely spaced parallel twins. Those whiskers which show a crater at the tip might grow by the re-entrant twin mechanism.

Furuta[73] has studied the growth of Se crystals grown from the vapour phase with the supersaturation ratio maintained constant. The crystals can be classified into five groups depending on the shape and crystal structure. The growth mechanism of these crystals relates to the twinning. The difference in shape of these crystals come from the number of twin boundaries contained therein and the mutual relations between them. The growth of dendritic crystals containing twin boundaries mainly starts at the steps and kinks formed by overlapping of two twin films originating from each boundary.

The re-entrant twin mechanism, has been suggested by many authors to play an equally important role as screw dislocations or partial dislocations in the growth of whisker crystals and platelike crystals from the vapourphase. The high thermal stresses that accompany growth at low supersaturations can cause the production of twins in many substances.

Hollow Whiskers

Hollow needles have been observed in the case of many substances, mostly in compounds like CdS and ZnS. Whiskers with a crater at the tip or with a hollow funnel shaped channel running through the entire length or part of the crystal are reported by many workers.

Frank[74] has shown that for a dislocation, whose Burgers vector exceeds a critical value, of the order of magnitude of 10 A°, there exists a state of equilibrium in which the core of the dislocation is an empty tube. For simplicity, considering a material with isotropic elastic constants, Frank has examined the conditions that a dislocation should have less energy when its core is hollow than when it is filled with strained material. Let there be a cylinder of material of radius 'R' with the dislocation of Burgers vector 'b' lying along its axis. Then the elastic energy of unit length is of the form

$$E_1 = (b^2\mu/4\pi)\ln(R/\theta b) \qquad (3)$$

where 'μ' is the rigidity modulus and θ is of the order of unity, depending on the law of force in the core of the dislocation. If the dislocation is hollow with radius 'r' so large that Hooke's law applies accurately beyond this radius, there is an elastic energy $(\mu b^2/4\pi)\ln(R/r)$. In addition there is surface energy $2\pi\gamma r$, where 'γ' is the specific surface free energy of the substance, so that the total energy is

$$E_2 = (\mu b^2/4\pi)\ln(R/r) + 2\pi\gamma r \qquad (4)$$

As r varies E_2 passes through a minimum for

$$r = r_0 = \mu b^2/(8\pi^2\gamma) \qquad (5)$$

Now emperically (γ/μ), which is a measure of intermolecular forces is very roughly a constant length for different substances and is about 1/4 A°. In consequence 'r' is less than 1 A° unless b exceeds 4 to 5 A° and it is only when $b > 20$ A° that $r_0 > b$. For values of b greater than this, the dislocation will be hollow, only if the minimum value of E_2 given by equations (4) and (5) is less than E_1. This requires $b > 8\pi^2\theta\gamma/\mu$ which will be satisfied if $r_0 > b$, since θ is usually less than unity. Therefore the dislocation will be hollow only if $b > 20$ A°.

Frank has estimated this to be 10 A° as a more reliable value. For b as large as 100 A°, a hollow core of the order of 1000 A° in diameter can be expected. The same causes will generally give rise to a dimple or a crater at the point where such a dislocation will meet a free surface. If the surface energy is independent of orientation, the dimple will be shallow in form, but of infinite volume and depth except at a natural habit face of a crystal where it is of finite depth and may even be totally absent.

Hollow dislocations were first observed by Verma[75] on SiC crystals with a Burgers vector b = 15 A°. The point of emergence of the spiral has been visibly hollow at the centre of the spiral. In many cases a hollow, much large in size has been observed for spirals originating from dislocations of multiple strength.

For the general case of a group of like dislocations Burton, Cabrera and Frank[76] predicted that a deep pit may be developed on the crystal face if the growth-front has a difficulty in penetrating the group itself.

Webb[77] has observed hollow whiskers of NaCl with a square cross-section and thin walls. These whiskers did not show any of the axial twist associated with a screw dislocation. He tried to explain this to be because of the release of elastic strain associated with screw dislocation due to its tendency to fracture longitudinally. He agrees with Amelinckx[78] that the growth of these whiskers is by the screw dislocation mechanism.

Mason[79] could grow hollow hexagonal prisms of ice under conditions of high supersaturations. The crystals usually contained pronounced funnel-shaped cavities. If the crystal.is practically stationary, relative to the surrounding vapour layers,will usually be nucleated near the edge of the crystal where the supersaturation is highest and will then spread more slowly as they approach the centre of the face where the supersaturation is lower. This gradient of supersaturation together with the onset of bunching allows new growth layers, to form at the edge before the earlier ones have completed their travel towards the face centre. This leads to a preferential thickening at the periphery and a more pronounced starvation of the face centre and thus to the formation of hollow prisms or shallow hexagonal dishes.

Vadilo[80] observed that $(NH_4)_2SO_4$ crystalizes as a large cluster of hollow needles from a solution saturated at 20°C, when seeded with a fibrous crystal of the same material and cooled to 15°C. It is suggested that molecules are deposited at the edges of the growing tip because,during the rapid process of growth the latent heat of crystallization is most rapidly removed from the edge.

Park and Reynolds using ZnSe as the starting material could obtain hollow whiskers of ZnO. The morphology of these crystals resembled that of the ice crystals reported by Mason[79]. He explained that the growth mechanism of these crystals is the same as that of ice crystals, described by Mason.

Hollow crystals of CsCl grown from the solution has been reported by Webb[82]. The growth is attributed to capillary rise of saturated solution to the tips and the subsequent evaporation of water from the solution. The driving force for crystal growth is local supersaturation due to evaporation of water from the solution. Screw dislocation provide the lattice step on the whisker tip.

The growth of hollow whiskers of ZnS has been described by Soxman[83]. Hexagonal hollow prisms were obtained upto nearly 1 mm length and about 0.4 mm width. In a single run the thickness of the walls was found to be a constant independent of the size of the crystal. All of the crystals flare out from some nucleation point from which the hexagonal prism faces commences. In hexagonal cross-section the perimeters of these hollow crystals is characterised by sharply defined corners. However, the interior angles, each show a fillet. In terms of the known modifying role that impurity plays in crystal growth, it may be that the atmospheric oxygen was influential in the development of the ZnS hollow crystals.

Mash and Firth[84] studied the growth of CdS crystals adding sodium salts as impurity. They observed that this encourages the growth of hollow crystals, and they could not obtain any hollow crystals from ultrahigh purity material.

Dreeben[85] has shown that the hollow centre growth habit of CdS crystals does not depend on the presence of less than 3 ppm of sodium or potasium salts as shown by Mash and Firth. They concluded that the availability of many suitable nucleation centres, such as those provided by the quartz wool, is one of the requirements for the formation of this particular habit.

Two types of hollow ZnS single crystals have been observed by Lendvay and Kovacs[86], viz. the large hollow crystals with dendritic morphology and the needle-like crystals. Growth spirals were observed on the basal plane of needle crystals and no dendritic growth was observed inside the hollow. Therefore it is believed that these crystals grow by the simple screw dislocation mechanism. It is found that the doping do not affect the morphology of the crystals under the same growth conditions and it is determined by the temperature distribution of the growth system.

Paorici[87] has obtained hollow hexagonal pyramids of CdS doped with sodium. The high concentration of Na impurity makes it easily workable.

Paorici[88] changed the dopant to iodine and he could obtain hollow rods of CdS in a colder zone of the growth system. Solid hexagonal rods and platelets were obtained in the hotter regions.

No work has been reported so far on the growth of hollow crystals of pure elements, by sublimation. Mostly the observations of hollow crystals are in ZnS and CdS, crystals. Nor could the growth of these crystals be explained on the basis of any one of the proposed mechanisms of whisker growth. They cannot be explained on the basis of growth by two-dimensional nucleation, or by VLS mechanism. The general explanation given is that they grow by the re-entrant twin mechanism or the screw dislocation mechanism depending on the growth conditions.

REFERENCES

1. Frank, F.C. (1949) Disc. Farad Soc, 5, 67.
2. Heck, C.M. (1957) Phys. Rev., 51, 686.
3. Menzes, A.W.C. and Sloat, C.A. (1929) Nature, 123, 348.
4. Griffin, L.J. (1950) Phil Mag., 41, 196.
5. Verma, A.R. (1953) Crystal growth and dislocations, Butterworth Publications.
6. Forty, A.J. (1954) Adv. Phys., 3, 1.
7. Amelinckx, S. (1952) Phil Mag., 43, 562.
8. Amelinckx, S. Grosjean, C.C. and Dekeyser, W. (1952) Comples. Randus Acad. Sci. Paris, 234, 113.
9. Forty, A.J. (1952) Phil Mag., 43, 949.
10. Dawson, T.M. and Anderson, N.G. (1953) Proc.Roy.Soc., A218, 255.
11. Forty, A.J. and Frank, F.C. (1953) Proc.Roy.Soc., A217, 262.
12. Dash, W.C. (1956) J.Appl.Phys., 27, 1193.
13. Williams, A.P. (1957) Phil Mag., 2, 317.
14. Williams, A.P. (1957) Phil Mag., 2, 635.
15. Henschke, E.B. (1958) J.Appl.Phys., 29, 1495.
16. Dukova, E.D. (1960) Kristallografia, 5, 813.
17. Testuya, A., Arisumi, J. and Akasaki, I. (1962) J.Phys.Soc.Japan, 17, 714.

18. Dekeyser,W. and Amelinckx, S. (1955) Les dislocations et la croissance des cristaux, ed. Masson et Cie, Paris (Cited from Growth and perfection of crystals, ed. Doremus *et al*.)

19. Pandya,N.S. and Balasubramanyan,A.P. (1963) Curr.Sci., 32, 542.

20. Pandya,N.S. and Thattey,A.S. (1964) Ind.J. Pure & Appl.Phys., 2, 233.

21. Thakkar,B.B. (1967) Ph.D. Thesis,M.S.University of Baroda.

22. Peach, M.O. (1952) J.Appl.Phys., 23, 1401.

23. Frank, F.C. (1953) Phil Mag., 44, 854.

24. Eshelby, J.D. (1953) Phys.Rev., 91, 755.

25. Franks, J. (1958) Acta Met., 6, 103.

26. Burton,W.K. and Cabrera, N. (1949) Disc. Farad. Soc.,5,33,40.

27. Brenner,S. and Sears, G.W. (1956) Acta Met., 4, 268.

28. Nabarro, F.R.N. and Jackson, P.J. (1958) Growth and perfection of crystals, Doremus, Roberts and Turnbull, ed. John Wiley & Sons,pp. 14.

29. Coleman,R.V. and Sears, G.W. (1957) Acta Met., 5, 31.

30. Price,P.B., Vermilyea,D.A. and Webb,M.B. (1958) J.Appl.Phys.,23, 1401.

31. Sears, G.W. (1956) J.Chem.Phys., 25, 637.

32. Roth, W.L. (1954) Nature, 173, 38.

33. Straumanis, M. (1931) Z. f. Physik Chem., B13, 316.

34. McNutt, J.E. and Mehl, R.F. (1958) Trans. ASM, 50, 1006.

35. Keepin, G.R. Jr. (1950) J. Appl. Phys., 21, 260.

36. Sears, G.W. (1955) Acta Met., 3, 361.

37. Sears, G.W. (1955) Acta Met., 3, 367.

38. Coleman, R.V. and Sears, G.W. (1957) Acta Met., 5, 31.

39. Cabrera, N. and Price, P.B. (1958) Growth and perfection of crystals, Edt. Doremus *et al.*, John Wiley & Sons, New York, pp.204.

40. Price, P.B. (1960) Phil Mag., 5, 473.

41. Parker, R.L. and Kushner, L.M. (1961) J.Chem.Phys., 35, 1345.

42. Dittmar, W. and Neumann, K. (1958) Growth and perfection of crystals, pp.253.

43. Parker, R.L. and Kushner, L.M. (1961) J. Chem. Phys., 35, 1345.

44. Brenner, S.S. (1956) Acta Met., 4, 62.

45. Wayman, C.M. (1961) J.Appl.Phys., 32, 1844.

46. Cech, R.E. (1959) Acta Met., 7, 787.

47. Gorsuch, P.D. (1961) Int. Symp. Phys. Chem. Proc. Metallurgy, 2, ed. G. St. Pierre, Inter Science, 771.

48. Ruth,V. and Hirth,J.P. (1964) J.Chem.Phys.,41, 3139.

49. Hirth,J.P. and Frank, F.C. (1958) Phil Mag., 3, 1110.

50. Webb, W.W. (1962) J.Appl.Phys., 33, 1962.

51. Webb, W.W., Drysdorf, R.D. and Forgeng, W.D. (1957) Phys. Rev., 108, 498.

52. Treuiting, R.G. (1957) Acta Met., 5, 173.

53. Hirsch, P.B. (1957) Dislocations amd Mech. properties of crystals, pp.545, ed. Fisher et al.

54. Shlichta, P.J. (1957) Bull.Amer.Phys.Soc.,2,263.

55. Eshelby, J.D. (1953) J. Appl.Phys.,24, 176.

56. Price, P.B. (1960) Phil Mag., 5, 873.

57. Wagner,R.S., Ellis,W.C., Jackson,K.A. and Arnold, S.M. (1964) J.Appl.Phys., 35, 2993.

58. Greiner,E.S., Gutowski,J.A. and Ellis, W.C. (1961) J.Appl.Phys., 32, 2489.

59. Barber, D.J. (1962) Nature, 144, 272.

60. Barber, D.J. (1964) Phil Mag., 10, 75.

61. Webb, W.W. and Forgeng, W.D. (1957) J.Appl.Phys.,28,1449.

62. Edwards,P.L. and Happel, R.J. (1962) J.Appl.Phys, 33, 943.

63. Wagner, R.S. and Ellis, W.C. (1964) Appl. Phys. Letters, 4, 89.

64. Wagner, R.S. and Ellis, W.C. (1965) Trans. Met. Soc., AIME, 233, 1053.

65. Hirth, J.P. and Pound, G.M. (1963) Progr. Mater. Sci., 11, 107.

66. Barns, R.L. and Ellis, W.C. (1965) J. Appl. Phys., 36, 2296.

67. Wagner, R.S. and Doherty, C.J. (1966) J. Electro. Chem. Soc., 113, 1300.

68. Wagner, R.S. (1967) Crystal Growth, Suppl. J. Phys. Chem. Solids, Pergamon Press.

69. Mendelson, S. (1965) J. Appl. Phys., 36, 2525.

70. Melmed, A.J. and Hayward, D.O. (1959) J. Chem. Phys., 31, 545.

71. Melmed, A.J. (1963) J. Appl. Phys., 34, 3325.

72. Bennet, A.I. (1959) Phys. Rev., 116, 53.

73. Furuta, N. (1964) Jap. J. Appl. Phys., 3, 237.

74. Frank, F.C. (1951) Acta Cryst., 4, 497.

75. Verma, A.R. (1961) Phil Mag., 42, 1005.

76. Burton, W.K., Cabrera, N. and Frank, F.C. (1951) Phil. Trans. Roy. Soc., A243, 299.

77. Webb, W.W. (1958) Growth and perfection of crystals, pp. 230.

78. Amelinckx,S. (1958) Physica, 24, 390.

79. Mason, B.J. (1963) Art & Science of Growing Crystals, Ed. Gilman,J.J., John Wiley & Sons,pp.119.

80. Vadilo, P.S. (1962) New York Consultant Bureau, 3, 114.

81. Park, Y.S. and Reynolds,D.C. (1967) J.Appl.Phys.,38,756.

82. Webb, W.W. (1960) J.Appl.Phys.,31, 207.

83. Soxman, E.J. (1963) J.Appl.Phys.,34,948.

84. Mash,D.H. and Firth, F. (1963) J.Appl.Phys.,34,3636.

85. Dreeben, A. (1964) J.Appl.Phys.,35,2549.

86. Lendvey,E. and Kovacs, P. (1970) J.Cryst.Growth, 7,61.

87. Paorici, C. (1968) J.Cryst.Growth,2,324.

88. Paorici, C. (1969) J.Cryst.Growth,5,315.