# CHAPTER 2

## GROWTH AND DISSOLUTION OF CRYSTALS

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2.1 Introduction

The theories of growth and dissolution have been used to interpret some of the observations presented in this thesis. It is, therefore, reasonable to give briefly the salient points of these theories.

One of the characteristic features of crystals is their ability to grow in predetermined geometrical shapes bound by plane faces. Since the rates of growth of crystals are, in general, functions of the supersaturation of the fluid from which they grew, it may be asked how the surface of the crystal can grow truly plane, when in many cases the conditions of supersaturation may vary from point to point on the surface. When the fluid is undersaturated the crystal dissolves. Depending on the solution undersaturation, the dissolution may proceed on the crystal surface as a whole or at some isolated points on the surface.

2.2 Theories of crystal growth

Crystallization can be regarded as a two-stage process, nucleation and growth. A complete understanding of crystal growth would require the knowledge of many disciplines such as equilibrium thermodynamics,
irreversible thermodynamics, chemistry, surface sciences, heat transfer, mass transfer, crystallography, etc. There is a voluminous literature on the various existing theories of crystal growth. These have been extensively covered by Buckley\(^1\), Verma and Krishna\(^2\), Strickland-Constable\(^3\) and others without going into their mathematical intricacy, we can sum them up as follows:

Essentially, the theories can be divided into parts: the growth of ideally perfect crystal and that of an imperfect one. An ideal crystal is one in which each atom is symmetrically surrounded by neighbouring atoms in a regular geometrical configuration. As against this, an imperfect crystal is one in which the relative positions of the atoms differ from those of an ideal lattice by amount comparable to an interatomic spacing.

2.3 Growth of a perfect crystal

In the first quantitative theory of crystal growth given by Gibbs\(^4\), based on thermodynamic grounds, an analogy is made between the growth of a water droplet in a mist and the growth of a crystal. It is agreed that only those crystals develop which would lead to a minimum surface free energy for a given volume. Curie\(^5\) calculated the shape and end forms of the crystal
in equilibrium with solution or vapour consistent with
the conditions of possessing a minimum sum total of surface
free energies. Wulff\textsuperscript{6}) further extended Curie's theory by
measuring growth velocities of different faces. Marc and
Ritzel\textsuperscript{7}) have modified Curie's theory by considering the
influence of surface tension and solution pressure, i.e.
solubility. When the differences in the solubilities are
small, growth is influenced by surface energy any increase
in the surface of one form is necessarily at the expense
of the other. The idea that different forms might exhibit
difference in solubility was urged as a possibility by
Lecoq de Boisbaudran\textsuperscript{8}).

Berthoud\textsuperscript{9}) and Valeton\textsuperscript{10}) assailed
Curie's theory on the ground that greater supersaturation
would cause rapid growth and consequently, the crystal
habit ought to approximate to the spherical shape, a
contradiction to the commonly observed fact. The more
rapid the growth, the simpler the crystal becomes usually
until one single form predominates with the practical
exclusion of all others.

Between 1920 and 1940, Kossel\textsuperscript{11}),
Stranski\textsuperscript{12}), Volmer\textsuperscript{13}) and others built up a conventional
theory on the mechanism of crystal growth. Fig. 2.1
illustrates the growth of a single cubic crystal. The growth proceeds by the addition of molecules at A, the so-called repeatable steps or kinks as the binding energy is the greatest at this point. This happens because a molecule joining the surface at any other position, viz. B or C will be held by one or two bonds respectively, rather than by three bonds at a repeatable step. When a whole line of molecules has been added to the molecular ledge, the starting of a new line will be a difficult process, for the first molecule to be added will be held by two bonds. Finally, when a whole monomolecular ledge has been completed, the next molecule will be held only by one bond, and launching of a new layer will involve an even longer delay than starting a fresh line. This is so because the process of starting a new layer (surface nucleation) involves the simultaneous arrival of a number of molecules on adjacent sites.

The mechanism described above results in the formation of monomolecular layers similar to that of layer-by-layer growth. Both the theories suggest that growth occurs by spreading of layers of constant thickness across the face and the thickness of the layers must be very small as compared with the distance between the advancing fronts. The repeatable step theory is based on
a particular molecular mechanism for the attachment of molecules whereas the layer-by-layer theory is of a general nature, since nothing is assumed here.

Experiments indicate that in the growth from solution or vapour, the rate of direct arrival of molecules at any particular point on the crystal surface is generally small compared to the rate of indirect arrival through surface migration. Volmer\textsuperscript{13} suggested that adsorbed molecules would be able to migrate freely over the surface and might change sites a large number of times before evaporating. Layer mechanism of growth has been extensively studied by Bunn and Emmet\textsuperscript{14}, Griffin\textsuperscript{15}, Forty\textsuperscript{16}, Williams\textsuperscript{17}, Buckley\textsuperscript{1} and Sunagawa\textsuperscript{18-49}.

2.4 \textbf{Discrepancy in growth theory}

The theory of growth at the kink sites eventhough assisted by surface migration, becomes less satisfactory to account for the observed rate of spreading of layers and still, to explain the rate of surface nucleation. Calculations for the concentration of kink in steps and the rate of diffusion of molecules led Burton et.al\textsuperscript{20} to the conclusion that at normal supersaturation the rate of surface nucleation would be immensely small, and to obtain an observable growth rate,
a large supersaturation of at least 25-50% is required. Above this value of supersaturation, the growth is not limited by nucleation and an ideal crystal will be able to grow layer-by-layer. Real crystals do, however, grow at observable rates at supersaturation of 1% or lower\textsuperscript{21}, indeed the crystal grown at such low supersaturation are almost well faceted and of high quality with respect to normal defects. The theoretical prediction of the rate with which a crystal should grow at this saturation turned out to be too small by a factor of 10\textsuperscript{1200}. Since there is an appreciable disagreement between theoretical and experimental growth rates nucleation theory was rechecked, but found to be correct.

2.5 Growth of real (imperfect) crystals

In an attempt to explain the disparity between theory and experiment, Frank\textsuperscript{22} drew attention to the probable role of screw dislocation in furthering the growth process. He pointed out that the emergence of screw dislocation on a crystal face produces a ledge of height equal to the Burger's vector. If the crystal is pictured as growing by the attachment of molecules to the edge of this ledge, then no surface nucleation is necessary since the ledge is itself perpetuating and
continues to be present on the surface, so long as the dislocation line intersects the surface. As the growth proceeds on the surface, the edge winds itself up to a spiral centered on the dislocation itself. Several stages in the development of the spiral are shown in Fig. 2.2. Further, since the turns of the spiral will be closed together, a large portion of the molecules adsorbed will reach the ledge before re-evaporation.

Direct evidence for the occurrence of spirals on grown faces was obtained by Griffin\(^1\) on beryl and, subsequently by Verma\(^2\), Amelinckx\(^3\), Forty\(^4\) and others in a variety of crystals.

2.6 Criticism of screw dislocation theory

Though the experimental observations in support to the theory of spiral growth increased considerably, there were contrary ideas about several aspects of it. The step heights of growth spiral, e.g. in SiC are often too large to be understood in terms of screw dislocations and Buckley\(^5\) suggested their formation to be connected with macroscopic events occurring in the vapour adjacent to the surface at the moment of solidification. Jagodzinski\(^6,7\) suggested
that the high energy required for the creation of a screw dislocation cannot come from the crystal structure until the crystal has grown to a considerable volume. The screw dislocations will, therefore, play a role only in the later stages of growth, thereby determining the surface structure but not the crystal structure. This was further supported by Knippenberg's\(^2\) observations on SiC crystals.

It appears that screw dislocation theory, despite many setbacks, explains several facts associated with the phenomenon of polytypism in crystals. It may be mentioned that in the VLS mechanism put forth by Wang et al.\(^3\) the atoms dissolve in a molten metal alloy phase from the vapour and condense in turn from the liquid phase into the crystal surface.

2.7 Whisker, needles and platelet growth mechanism

Whiskers or filamentary crystals are of particular interest due to their fast growth along an axis which is often not a unique crystallographic axis. The inference is that whiskers contain axial screw dislocation which determine the fast growth direction. The side faces of whiskers are low energy planes which grow slowly or not at all. Sears\(^3\) has found that there is a critical supersaturation above which whiskers of Cd, Ag, Zn and CdS
do not grow. For whisker growth supersaturation on the side faces must be sufficiently low to prevent two dimensional nucleation which would allow radial growth. If low energy planes are parallel to a unique crystallographic axis, needles are produced. At supersaturation too high for whisker growth, platelets come into being.

2.8 Dendritic growth mechanism

The name "dendrite" comes from the Greek word for "tree" and denotes any tree-like branched structure. A typical dendrite consists of a primary stem onto which grow secondary branches and on these tertiary branches. This frequently occurs in one plane but three-dimensional dendrites are also observed. Dendrites have been found almost invariably in metals and is common in crystals from solution, melt and vapour. Dendrites are normally single crystals and the branches follow definite crystallographic directions. The opposite sides of the dendrite exhibit remarkable symmetry and branches are often spaced out at regular interval. Originally, a dendrite was thought to be the result of a growth protrusion of a crystal surface. It was felt that the protrusion would be in a position to collect more material and hence grow more rapidly than rest of
the crystal surface\textsuperscript{35}). Though a currently believed cause of such an abnormal growth is known to be the large supersaturation (rapid deposition). No definite explanation regarding the regularity of a dendritic branching has been completely accepted so far. At times, dendrites whose limbs are not related to definite crystallographic direction are also observed. Buckley\textsuperscript{1)} gives a detailed account of the theories of dendritic growth.

2.9 Crystal dissolution

Crystal dissolution and evaporation take place by the retreat of monomolecular steps across the crystal surface, a process reverse of growth. In the dissolution of a smooth face, atoms or molecules must be removed from crystal steps, just as they must add to a step during growth. In crystal dissolution new steps may be initiated by two dimensional or at a screw dislocation. In addition to these, during dissolution steps may also be initiated at the edge of a crystal (Fig. 2.3) or at edge dislocation. Therefore, dissolution is often found to be controlled mass transfer, particularly for polycrystalline materials, which have preferential sites for initiation of steps.\textsuperscript{36–39)}

Under a slight undersaturation there is a
a tendency for pits to form at emergent dislocation sites. This tendency is often generally amplified by the presence of impurities, which are thought to adsorb on the steps and greatly retard the removal of atoms.

2.10 Nucleation of etch pits

According to Cabrera and Levine, all structural defects are strained regions and hence have some extra energy localised around them. This decreases the activation energy needed for the nucleation and motion of steps, resulting thereby in rapid formation of etch pits at dislocations. In the case of screw dislocations, the surface cannot sustain stress and hence to relieve the stress the atoms must re-arrange themselves. In doing so, their bonds become strained and this strain causes the nucleation of a pit at screw dislocation. This screw dislocation pit is believed to nucleate due to revolving retreat of a perpetual step it makes with the surface. Gilman questioned this theory and suggested that the very core of dislocation is most important in the nucleation process.

Besides these facts, impurity segregation is necessary in many metals before dislocation can be reliably etched. Addition of poison can
inhibit or enhance the motion of steps from the sites of nucleation centre as shown by Gilman et. al.\(^46\), Haribabu and Bansigir\(^47\), Ives and Hirth\(^48\) and Frank\(^49\) inferred that all etchants that produced well defined pits contain a poison either by chance or by design.

The formation of visible dislocation pits depends on the nucleation rate of unit pit at a dislocation sites, \(V_n\), and on the rate of motion of steps across the crystal surface, \(V_s\). In readily observable pits \(V_n/V_s \gg 0.1\). The ratio \(V_n/V_s\) can be increased by:

(i) increasing \(V_n\) as has been done in the etchants of several metals,

(ii) decreasing \(V_s\) by the addition of an inhibitor, as in LiF and

(iii) by varying the temperature to take the advantage of the difference in the activation energy of \(V_n\) and \(V_s\).

Gilman et.al.\(^46\) have shown that \(V_s\) depend very much on the inhibitor concentration whereas \(V_n\) remains almost independent of it. In case of LiF, Al\(^{3+}\) and Fe\(^{3+}\) were found to be effective ions for slowing down the motion of steps across the surface by forming strong complexes.
with fluorine. The importance of complex forming properties of additive cations has subsequently been stressed by Urusovskaya and Haribabu and Bansigir, but their views widely differ from those of Gilman et al.

2.13 Implications of selective etch

Etch pits essentially reveal the emergence points of dislocations on the surface, and therefore they give a direct measure of dislocation density. Since they have a definite depth, they may also give useful information about the kind, configuration and inclination of dislocations. Etching has, further, been applied to study the following:

a) growth history of crystals,
b) stress velocity of individual dislocation,
c) deformation patterns like pile-ups, polygon walls,
d) dislocation multiplication and movement,
e) origin of dislocations in as-grown crystals,
f) fresh and grown in dislocations,
g) plastic flow around indentation,
h) radiation hardening.
i) fracture and dislocation\textsuperscript{62),}

j) surface orientation determination\textsuperscript{63),}

k) polarity of crystal lattice\textsuperscript{56),}

l) reaction mechanism\textsuperscript{64)},

m) grain boundaries\textsuperscript{65), and}

n) the formation of dislocations with different Burgers vectors\textsuperscript{66), etc.}
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Captions of figures

Fig. 2.1 Growth on (100) faces of a cubic crystal by repeatable step mechanism.

Fig. 2.2 Different stages (α·γδf) of α-formation of spiral at a screw dislocation.

Fig. 2.3 Growth and dissolution of crystals initiating at kink sites.