PART II
3.1 **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.

3.2 **Growth of crystals**

Interest in crystal growth has, of recent years, been greatly enhanced by the need for the industrial production of single crystals for electronic and optical purposes. One of the important characteristic features of the crystals is their ability to grow in predetermined geometrical shapes bounded by plane faces.
Since rates of growth of crystal faces, in general, are functions of supersaturation of the fluid (phase from which they are growing), it is pertinent to ask how the crystal face can grow truly plane, when in many cases the conditions of supersaturation may vary from point to point on the face.

3.2.1 Earlier theories of crystal growth

The first quantitative theory of crystal growth was given by Gibbs\(^1\) on thermodynamic grounds. He made use of the analogy between the growth of a liquid droplet in the mist and that of a crystal, and argued that only those faces would develop in the crystal which lead to a minimum total surface energy for a given volume. However, Gibbs\(^1\) realized the essential difference between the random arrangement of molecules or atoms in a liquid drop and regular arrangement of them in a crystal. Curie\(^2\) calculated the shape and end forms of the crystal in equilibrium with solution or vapour, consistent with the conditions of possessing a minimum total surface free energy. Wulff\(^3\) further extended Curie's theory and deduced a simple relation between the velocities of growth of different faces in the directions of their normals and the appropriate specific surface free energies. Marc and
Ritzel\textsuperscript{4) modified Curie's theory by considering the influence of surface tension and solution pressure (solubility) and proposed that the crystal will assume an equilibrium form which takes into account both these tendencies.

3.2.2 Growth by surface nucleation and the repeatable step mechanism

Between 1920 and 1940 Kossel\textsuperscript{5)}, Stranski\textsuperscript{6)}, Volmer\textsuperscript{7)} and others had built up a conventional theory for the mechanism of growth of crystals. One of its principal ideas is illustrated in Fig. 3.1 which represents the surface of a simple cubic crystal. The crystal will grow by the addition of molecules at A, the so-called repeatable step because the binding energy is the greatest at this point; the molecule joining the surface at any other position B, C or D will be held by a smaller number of bonds. When a whole line of molecules has been added to the monomolecular ledge, starting of a new line will be a difficult process, since the first molecule to be added, will be held by only two bonds. Finally, when a whole monomolecular layer has been completed, the next molecule will be held by only one bond and launching of a new layer will involve an even longer delay than the
The process of starting a new layer is known as surface nucleation and involves the simultaneous arrival of a number of molecules on a small group of adjacent sites.

The mechanism of growth described above results in the successive formation of monomolecular layers similar to the principle of layer-by-layer growth. In this mechanism the crystal grows by the spreading of layers of constant thickness across the face and the thickness of the layers must be very small as compared to the distance between the advancing fronts. This argument does not depend on assumptions about the detailed mechanism by which the molecules are built into the crystal.

Experiments indicate that in growth from 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 by surface migration. So Volmer\(^7\) suggested that face adsorbed molecules would be able to migrate freely over the surface and might take on an average a very large number of steps on the surface before re-evaporating and this enormously facilitates the rate of growth of the crystal by the repeatable step mechanism.
Growth by layer deposition has been extensively studied by many workers such as Bunn and Emmett, Griffin, Forty, Williams, Buckley, Seager, and Sunagawa.

3.2.3 Discrepancy with the observations

The theory of growth at kink sites even when assisted by surface migration becomes less satisfactory to account for the observed rate of spreading of layers, and still less to explain the rate of surface nucleation. Calculations for the concentration of kinks in steps and the rate of diffusion of molecules led Burton et al. to the conclusion that at normal supersaturation the rate of surface nucleation would be prohibitively slow and for an observable growth rate a supersaturation of at least 25 - 50% is required. Above this saturation the growth process is not limited by nucleation and an ideally perfect crystal will therefore be able to grow layer-by-layer. However, Volmer and Schultze found that crystals do grow at observable rates at supersaturations down to a value of 1% or lower, indeed most regular and well faceted crystals are observed at lower supersaturations. The nucleation theory was re-checked and found to be essentially correct.
The reason for the incapability of the theory to account for the large disparity between the theoretically calculated and the experimentally determined growth rates was yet to be traced out.

3.2.4 Screw dislocation theory of growth by Frank

This big disparity between theory and experiment was attributed by Frank\textsuperscript{18}, to the probable role of screw dislocations in furthering the growth process. He pointed out that the emergence of a screw dislocation on the face of a crystal produces on that face a ledge of height equal to the Burgers 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 in question is self-perpetuating and continues to be present on the crystal surface so long as the dislocation line emerges on the surface. The ledge winds itself up to a close spiral centered on the dislocation and as growth proceeds the spiral apparently revolves as shown in Fig. 3.2. Further, since the turns of the spiral will be close together a large proportion of the molecules adsorbed in the surface will reach the ledge before re-evaporating.
The first experimental observation published in support of the spiral growth mechanism of crystals was by Griffin\textsuperscript{9)} on beryl. The steps in this case were measured to be a unit cell high and thus the observed spiral was interpreted as a 'growth spiral'. Verma\textsuperscript{19)} and Amelinckx\textsuperscript{20)} also observed spiral growth steps on silicon carbide, simultaneously.

3.2.5 Criticism of screw dislocation theory

The volume of experimental observations in support to the theory of spiral growth has increased considerably. A collected account of these observations can be obtained from Buckley\textsuperscript{12)}, Verma\textsuperscript{21)}, Forty\textsuperscript{22)} and Amelinckx\textsuperscript{23)}. However, there were workers who expressed their doubts about its several aspects. The step heights of growth spirals (e.g. in SiC) are often too large to be understood in terms of screw dislocations and Buckley\textsuperscript{24,25)} suggested their formation to be connected with macroscopic events occurring in the vapour adjacent to the surface, at the moment of solidification. Jagodzinski\textsuperscript{26,27)} suggested that the high energy needed for the creation of a screw dislocation cannot come from the crystal structure until the crystal has grown to a considerable volume. The screw dislocation will,
therefore, play a role only in the later stages of growth thereby determining the surface structure, but not its crystal structure. This was further supported by Knippenberg's observations on SiC. The observations on the microstructures of MoSe2 presented in this thesis also support this view.

It appears that the screw dislocation mechanism, despite many setbacks, explains well several facts associated with polytypism in crystals.

3.2.6 Vapour-liquid-solid mechanism

In this mechanism, put forth by Wagner et al., atoms are dissolved in a molten metal alloy free from the vapour and condense in turn from the liquid phase onto the crystal face.

3.3. Crystal dissolution

Crystal dissolution and evaporation take place by the retreat of monomolecular steps across the crystal surface, a process reverse of growth. In dissolution of a smooth face, atoms or molecules must be removed from crystal steps just as they must add to steps in growth. In crystal growth, new steps may be started by two dimensional nucleation or at a screw dislocation. In addition to these methods, during dissolution steps may
also be initiated at the edges of a crystal (Fig. 3.3) or at edge dislocations. Therefore dissolution is often found to be controlled by mass transfer, particularly for polycrystalline materials which have plentiful sites for initiation of steps.^{32-35}

Under slight undersaturations there is a tendency for pits to form at dissolution sites. This tendency is often greatly simplified by the presence of impurities, which are thought to adsorb on the steps and greatly retard the removal of atoms.^{36-38}

3.3.1 Nucleation of etch pits

According to Cabrera and Levine^{39}, all structural defects are strained regions and hence have some extra energy localised around them. This decreases the activation energy needed for nucleation and motion of steps, resulting thereby into rapid formation of etch pits at dislocations. In the case of screw dislocations, the surface cannot sustain stress, however, to relieve the stress the atoms must rearrange themselves. In doing so, their bonds become strained and it is this strain that causes nucleation of a pit at a screw dislocation. This screw dislocation pit is believed to be nucleated due to revolving retreat of a perpetual step it makes.
with the surface. Gilman\textsuperscript{40}, questioned this theory and suggested that the very core of a dislocation is most important in nucleation process.

Besides these facts, impurity segregation is necessary in many metals before dislocation can be reliably etched\textsuperscript{41}. Addition of poison can inhibit or enhance the motion of steps from the site of nucleation centre as shown by Gilman et al.\textsuperscript{42} and Ives and Hirth\textsuperscript{43}. Frank\textsuperscript{44} inferred that all etchants that produce well defined pits contain a poison 'either by chance or by design'.

3.3.2 Mechanism of etching

The formation of visible dislocation pits depends on the nucleation rate of unit pit at a dislocation site, $V_n$, and on the rate of motion of steps across the crystal surface $V_s$. In readily observable pits $V_n/V_s \geq 0.1$. 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 activation energy of $V_n$ and $V_s$. Gilman et al.\textsuperscript{42} have shown that $V_s$ depends very much on the inhibitor.
concentration whereas $V_n$ remains almost independent of it. In the case of LiF, $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ were found to be effective ions for slowing down the motion of pits across the surface by forming strong complexes with fluorine. The importance of complex forming properties of additive cations has subsequently been stressed by Urusovskaya\textsuperscript{45}, Gutumanas and Nadgorny\textsuperscript{46}, Hari Babu and Bansigir\textsuperscript{47}, but their views widely differ from those of Gilman et al.\textsuperscript{42}. Hence, it can be said that, by and large, the reason why the emergence points of dislocations are preferentially attacked is not yet well understood. Nonetheless, the fact that the pits are produced at dislocation sites is verified by a large number of workers. The first direct proof was independently given by Gevers et al.\textsuperscript{48} and Hom\textsuperscript{49} who showed that etch pits are developed at the centres of growth spirals in SiC. Later many workers employed this technique to study dislocations and their work have been reviewed several times by Forty\textsuperscript{52}, Faust\textsuperscript{50}, Johnston\textsuperscript{51} and Amelinckx\textsuperscript{52}.

3.3.3 Kinetics of etching

In addition to the behaviour of impurities added to the crystal or to the solvent in altering $V_n$
and $V_s$, it is seen\(^{43,53}\) that their values also depend on external conditions such as undersaturation, temperature, stirring, etc. Hence quantitative parameters, e.g. activation energy for the process can be evaluated. The time dependence of $V_s$ and $V_n$ throws light on the adsorption processes occurring on the surface\(^{54}\). The study of activation energy for normal and lateral etching with etchants composed of different concentrations of the components permits one to relate the activation energy with the energy of dislocations, with undersaturation, and so a limited extent with the nature of activated complex.

3.3.4 **Information obtainable from etch pits**

Etch pits essentially reveal the emergence points of dislocations on the surface; and they, therefore, give a direct measure of dislocation density\(^{55}\). Since they have a definite depth, they may also give useful information about the kind, configuration and inclination of dislocations.\(^{42}\) Etching has, further been applied to study: (a) the growth history of crystals,\(^{56,57}\) (b) stress velocity for individual dislocations,\(^{58}\) (c) deformation patterns like pile-ups, polygonal walls,\(^{59,60}\) (d) dislocation multiplication and movement,\(^{58}\) (e) the
origin of dislocations in as-grown crystals, (f) the fresh and as-grown dislocations, (g) plastic flow around indentation, (h) radiation hardening, (i) fracture and dislocations, (j) surface orientation determination, (k) polarity of crystal lattice, (l) reaction mechanism, (m) grain boundaries, and (n) the formation of dislocations with different Burgers vector.

3.4 References


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