CHAPTER III
GROWTH AND DISSOLUTION OF CRYSTALS

3.1 Introduction

Since the observations reported in the thesis are interpreted using the theories of the phenomena of growth and dissolution of crystals, a brief description of the salient points of the two phenomena is given in this chapter.

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 most characteristic features of crystals is their ability to grow in predetermined geometrical shapes bounded by plane faces. Since rates of growth of crystal faces are, in general, functions of the supersaturation of the fluid phase from which they are growing, it is pertinent to ask how the face of a crystal can grow truly plane when in many cases the conditions of supersaturation may vary from point to point on the face.

3.3 Growth by Surface Nucleation and the Repeatable Step Mechanism

Between 1920 and 1940 Kossel, (1927), Stranski (1928), Volmer (1939) and others had built up a
conventional theory of the mechanism of growth of crystals. One of its principal ideas can be illustrated in Fig. 13 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 greatest at this point; a molecule joining the surface at any other position, B, C or D will be held by a smaller number of bonds. The binding energy at the repeatable step or kink is equal to the energy of evaporation of the crystal as a whole. 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 only be held by one bond and launching of a new layer will involve an even longer delay than the starting of a fresh line. 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 described above results in the formation of a succession 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 height of the
layers must be very small 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 (loc. cit.) suggested that face-adsorbed molecules would be able to migrate freely over the surface and might change sites a very large number of times before evaporating.

Growth by layer deposition has been extensively studied by many workers (Bunn and Emmet 1949, Griffin 1950, Forty 1961, Williams 1954, Buckley 1951).

3.4 The Discrepancy with the Observations

The theory of growth at the kink sites, even when assisted by surface diffusion becomes less satisfactory to account for the observed rate of spreading of layers, and still less to explain the rate of surface nucleation. The calculations of the concentration of kinks in a step and the rate of diffusion of molecules, by Burton et. al. (1951) led to the conclusion that at normal supersaturation the rate of surface nucleation would be prohibitively slow and for an observable growth rate it required a
supersaturation of at least 25 - 50 %. 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. But Volmer and Schultze (1931) found the growth rate proportional to the supersaturation down to a value of 1 %.

3.5 Screw Dislocation Theory of Growth

The nucleation theory was reexamined and found to be correct. At this stage Frank (1949) in an attempt to explain this big disparity between the theory and experiment drew the attention to the probable role of screw dislocation in furthering the growth process, retaining many features of the older theory. He pointed out that the emergence of a screw dislocation on a face of a crystal produces on the 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 needed since the ledge in question is self-perpetuating and continues to be present on the surface so long as the dislocation line intersects the surface. The ledge winds itself up into a close spiral centred on the dislocation and as growth proceeds the spiral apparently resolves as shown in Fig. 14a, b, c, d and e. 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 published experimental observation supporting the theory of growth of crystal by the spiral mechanism was by Griffin (1950) on beryl. Verma (1951 a) and Amelinckx (1951a), simultaneously observed spirals on SiC crystals. A definite correlation between the lattice parameter c and the step height of growth spirals was made by Verma (1951 b) in his measurement of a step height of $(15 \pm 1) \text{Å}$ on the 6H type of SiC. However, as early as 1907 Tone (1907) reported the presence of different spiral markings typical of large numbers of SiC crystals. A number of other investigators observed these figures on SiC but without explanation of their origin (Lemmlein 1945, 1947; Kalt and Wittborg 1951; Gliki 1953, 1954; Lemmlein and Gliki 1954; Mellor 1924, Menzies and Sloat 1929).

3.6 Screw Dislocation Theory of Polytypism

Lemmlein (1947) suggested that the step heights might be equal to multiples of the c distances in the various unit cells. He later found step heights of the order $10 \text{Å}$ for 4H SiC and concluded that growth steps of $2.5 \text{Å}$ probably exist corresponding to a single layer in the SiC structure. Verma (1951 a, b) confirmed Lemmlein's work when he found step heights of 15.1 and 15.2 Å on 6H crystals. Amelinckx (1951 a, b, c) reported the
existence of step heights equal to unimolecular layers. These results led Frank (1951), Amelinckx (1951 c) and Vand (1951 a, b) almost simultaneously to give a relationship between growth spirals, screw dislocations and polytypism in SiC. Mitchell (1957) attempted to explain the absence of possible structure series by investigating the actual atomic configurations resulting from screw dislocations of different magnitude.

Other mechanisms of polytype formation have been suggested but not generally accepted. Krishna and Verma (1963) cite much evidence for the non-universality of the screw dislocation mechanism.

3.7 Criticism of Dislocation Theory

The volume of experimental observations in support of the various theory of spiral growth of crystals has increased considerably. A collected account of these observations can be got from Buckley (1951), Verma (1953), Forty (1954) and Amelinckx (1954). However, there were workers who expressed doubts about several aspects of it. The step-heights of growth spirals are often too large to be understood in terms of screw dislocations and Buckley (1952) suggested that the formation of spirals is connected with macroscopic events occurring in the vapour adjacent to the surface, at the moment of solidification. Jagodzinski (1954) 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 dislocation, hence, will play a role only in the later stages of growth of a crystal thereby determining its surface structure but not its crystal structure. This was supported by Knippenberg (1963) who observed that the growth of SiC largely occurred not on the well-developed (0001) face of the crystal which showed growth spirals, but on the opposite face, which was usually stepped or undeveloped.

3.8 Vapour-Liquid-Solid Mechanism

Another mechanism of importance is the vapour-liquid-solid (VLS) mechanism. It differs from the layer nucleation mechanism in that a molten metal alloy phase is present. Atoms are dissolved in the metal from the vapour and condense in turn from the liquid phase onto the crystal surface. This mechanism was suggested by Wagner et. al. (1964 a, b; 1965).

3.9 Dissolution of Crystal Surfaces

The heterogeneous nature of the reactivity of crystal surfaces has been known for very long time. However, the existence of an interrelation between these heterogeneities and the dislocations in the crystal was suggested by Shockley and Read (1950) particularly in the case of etch pits.
Since dissolution and evaporation are phenomena which are the reverse of growth, the same concepts of crystal growth can be considered in these phenomena also. Dissolution presumably takes place under conditions of low supersaturation by the retreat of surface steps which have kinks as the active sites. Normal surface steps will disappear in the process. Similarly, when a perfect crystal face is exposed to a solvent dissolution probably begins by the nucleation of unit pits of one molecular depth. These unit pits grow as steps retreat across the crystal face, through the action of kinks.

3.10 Nucleation of Etch Pits

According to Cabrera and Levine (1956) all structural defects are strained regions and hence have some extra energy localized around these regions. This will decrease the activation energy required for a nucleation of steps and motion of the steps. Therefore, a repeated and rapid nucleation process at the sites of dislocations which are line defects will occur, as a result of which etch pits will be formed. In the case of a screw dislocation, the surface cannot sustain the stress; however, to relieve the stress the atoms must rearrange themselves. In doing so their bonds become strained and it is this strain which may cause nucleation of a pit at a screw dislocation. An etch pit at a screw dislocation can be nucleated due to the
revolving retreat of a perpetual step it makes with the surface. Gilman (1959) has questioned this theory and has suggested that the very core of a dislocation is the most important in nucleating process.

Besides these facts there are many controlling factors in the etch pit formation. In many metals some impurity segregation is necessary before dislocation can be reliably etched (Wyon and Lacombe 1955). Addition of poison can inhibit or enhance the motion of steps from the site of the nucleation centre as shown by Gilman (1957) and Ives and Herth (1960). Frank (1958) inferred that all etchants that produce well-defined pits contain a poison 'either by chance or by design'.

The reason why emergence points of dislocations are attacked preferentially is not well understood yet. But that pits are produced at the dislocation sites is verified by many workers. The first direct proof was given independently by Gevers et al. (1952) and Horn (1952) who showed that etch pits are developed at the centres of growth spirals of SiC. Later on many workers have employed this technique to study the dislocation contents and these works have been reviewed several times by Forty (1954) Faust (1959) Johnston (1962) and Amelinckx (1964).

3.11 Information Obtainable from Etch Pits

Etch pits essentially reveal emergence points
of dislocations in the surface and they, therefore, give a
direct measure of dislocation densities. Since they are
having a certain depth, they may also give some indication
concerning the general direction. The etching technique has
been used to study: (a) the stress-velocity relation for
individual dislocations (Gilman and Johnston, 1959), (b)
deformation patterns like pile-ups and polygon walls
(Amelinckx 1960) (c) multiplication and movement of
dislocations (Young and Noggle 1960) (d) fresh and as grown
dislocations (Gilman and Johnston 1957), (e) radiation
hardening (Aerts et. al. 1959), and (f) fracture and dis-
locations. (Stokes et. al. 1959).

The (111) and (111) planes of zincblende
structure and (0001) and (0001) planes of wurtzite structure
respectively behave quite differently with respect to the
same etching solution. Silicon carbide crystals show this
behaviour in a pronounced way.