5.1 Introduction

It is well known that a large proportion of even the best-formed silicon carbide crystals exhibit notable growth spirals on the basal pinacoid. These have been studied by many investigators, notably Verma (1951), Amelinckx (1951). Growth steps on layer-structured crystals grown from solution have been observed by several investigators (see, for example, the work of Forty (1952) on CdI₂ crystals). These steps, because of their growth from solution, are typically polygonal spirals. According to Frank (1952) this can be attributed to a reduced rate of advancement of steps (as compared with growth from the vapour phase at a similar supersaturation) resulting from the existence of an unstirred boundary layer of solution whose thickness is less than the average spacing of exchange sites in the step. In growth from the vapour, the surface diffusion distance is expected to exceed the mean distance between exchange sites in a growth step, and the step will advance independently of its orientation forming a circularly symmetric spiral. Not only have spiral growths been established, but in addition a variety of step heights have been evaluated by using the precision techniques of multiple beam interferometry. It is now well known that
these spiral growths afford a most comprehensive confirmation of the dislocation theory of growth put forward by Burton, Cabrera and Frank (1949) and later more extensively developed especially by Frank (1951).

One of the approaches for a better understanding of the history, mechanism and process of crystal growth and dissolution is the microtopographical studies of crystal faces. Since it is the face (crystal plane) through which a crystal grows and develops, all phenomena regarding growth and dissolution are almost perfectly pictured on them. Admittedly though the habit faces of a crystal are due to growth in its final stage and hence they tell more about the conditions and mechanism of growth in the final stage, a good deal of information about the almost entire history of growth and its mechanism can, many a times, be also obtained from a detailed study of such faces. It is also possible to ascertain the presence of imperfections, stacking faults etc., because their behaviour play a significant role in the shaping of surface structures which result either from growth or dissolution. Microtopographical study of crystal faces also enables one to trace the changes, which the crystal has undergone, in time interval lapsed after cessation of growth. It gives an opportunity to view dynamical nature of the crystals.
A microtopographical study of over four hundred prism faces of cultured quartz crystals was carried out, as a result of which a wide variety of interesting features were observed. One of the more outstanding observations was the presence of spiral patterns on prism faces of cultured quartz. Growth spirals on prism faces of a cultured quartz crystal are very rare and this is the first clear evidence of growth spirals on (10\bar10) faces of cultured quartz.

In the present chapter different types of spirals and their interactions on (10\bar10) faces of cultured quartz are presented. A mechanism of growth of such faces is proposed and it is shown that all the observations reported support the proposed mechanism.

5.2 Observation

The specimens examined were grown on C\bar2-cut seeds. The other details about the growth conditions are not known. The crystals were fairly transparent and the prism faces were highly striated. Figure 31(a) shows inclined striations on a prism face of a cultured quartz crystal. It will be of interest to note that these striations make an angle of 45° with the edge between (10\bar10) and (10\bar11) faces. It was further observed that the regions between consecutive striations are widely spaced.
A detailed examination, at a higher magnification, of such widely spaced flat regions reveals rectangular growth pyramids surrounded by thick growth layers, as illustrated in a positive phase contrast photomicrograph in figure 31(b). It may be noted that the longer edges of the growth layers composing all such pyramids are strictly parallel to the inclined striations. The structure of rectangular hillocks (pyramids) were subsequently examined at still higher magnifications with an oil-immersion objective. In doing so a good deal of information about such pyramids was gained.

5.3 Elementary Spirals

The rate of growth of a crystal, once in the range of conditions at which growth proceeds steadily, is very largely independent of the density of dislocations. To see why this is so, we must consider first the effect of a single dislocation. If groups of dislocations in the same crystal face are equally active in emitting growth fronts, the number of growth fronts passing any point in the face is the same as if either were active alone. Thus a group of dislocations is as active as its most active member and the growth rate of the whole face is determined by its most active dislocation group. All other groups yield within a short while to the domination of this most active group, and merely on the growth fronts received from
it with a slight delay and in a slightly modified form. Sometimes amongst the dislocations emerging on a crystal face, one may dominate the rest. This will happen if the supersaturation at one centre is slightly greater than at other centres. The growth pattern originating from the weaker sources will continually shrink and if conditions remain constant, ultimately only one growth pyramid will be seen. This is illustrated in figure 32, observed on a prism face of cultured quartz, where the central screw dislocation is dominant. The weaker screw dislocations play a little part in the growth, and nearly pass on the growth fronts received from the dominating screw dislocation with a slight delay and in a slightly modified form. In figure 32 the central screw dislocation has developed some few turns before reaching the other small screw dislocations on the right. The growth fronts generated by the central screw dislocation travel past this dominated screw dislocation and are slightly bent from their usual shapes. However, in the last phase of growth when the autoclave is switched off, the growth fronts would stop arriving from the dominant centre, and the growth steps attached to the weaker screw dislocations may be able to develop one or two turns of their own.
5.4 Growth forms due to two screw dislocations of the same sign

In figure 33(a) growth patterns due to two screw dislocations A and B of the same sign are drawn schematically for a simple case of circular spirals. The step height and the structure of the step wall originating from these dislocations are assumed to be identical. The layers starting from A goes on rotating and generating the spiral until it meets \( p_1 \), the layer originating from B, where it terminates. The two layers will fuse with one another at \( p_1 \) according to the properties of growth fronts. As the two spirals unfold themselves the layers meet at \( p_1 \), \( p_3 \), \( p_5 \), \( p_7 \), \( p_9 \), \( p_{11} \) in the right half and at \( p_2 \), \( p_4 \), \( p_6 \), \( p_8 \), \( p_{10} \), \( p_{12} \) in the left half of the figure. Over the common portion, between \( p_1 \) and \( p_2 \), \( p_3 \) and \( p_4 \), etc., the two layers annihilate and the missing parts of the two spirals are shown by the dotted line. The resultant figure is the solid line curve. Figure 33(b) shows a three-dimensional growth pattern corresponding to figure 33(a). The schematic diagrams have been drawn for circular spirals, the case for spirals with straight edges can be drawn similarly, where the behaviour will be the same. At times the outer growth fronts of two spirals of the same sense also join each other and give rise to growth patterns which almost resemble closed loops. One such case for two anticlockwise spirals is illustrated in a built-up picture in figure 34 (a positive phase contrast photomicrograph).
A similar case for two clockwise spirals is shown in a positive phase contrast picture of figure 35.

5.5 Growth forms due to two screw dislocations of opposite sign

When two screw dislocations of opposite sign emerge on the face of a crystal a ledge will be formed and will run between them (figure 36). Growth will start if the supersaturation is raised to such a value that the diameter of the critical nucleus (2σc) is less than the distance between them. In the more general case when the critical nucleus is not circular this will be equivalent to a correctly oriented nucleus passing between the two dislocation points. As long as the supersaturation is kept above this value adsorbed atoms will join the step and therefore the step tends to spiral around both dislocations. This is shown in figure 37a looking down from the above. However, as the step doubles back on itself (fourth stage shown in figure 37a) the two points A and B which are at the same level can join up by atoms filling in the lower level C to form a bridge. This stage is shown in figure 37b. The parts D and E of the step grow very rapidly since the curvature is negative; that is to say the length of the step decreases as the step advances. Thus a closed loop is generated and in the final stage, the step returns to its original position and is ready to start again to go through
the above cycle. This mechanism is similar to the Frank-Read source. Therefore, as successive loops are developed the surface of the crystal becomes a pyramid, which will be composed of sheets or molecular layers as shown in figure 37c. Figure 38, a built up picture, illustrates an interesting case of closed loops of growth fronts due to two growth spirals of opposite sense. Figure 39 represents two spirals with unlike signs which fit in without forming any loop. No such case has been put on record until now. Figure 40 shows hexagonal loops from two screw dislocations of opposite sign close to each other and equally developed. The resultant growth pattern consists of closed sheets. Figure 41 illustrates a growth pyramid. Its inner growth layers are rectangular, while the outer ones are pentagonal. It is believed that this pyramid is formed due to growth round closely spaced screw dislocations of equal strength but of opposite sense, which might have annihilated leaving no sign at the centre.

5.6 Growth pattern from three and more dislocations

Occasionally growth fronts of more than one spiral of one sense join those of more than one spiral of the same or opposite sense, and finally result in co-operating spirals or complex growth forms. Such cases are illustrated as follows:-
(1) Figure 42 represents growth fronts from two left-handed co-operating spirals joining with those from one right-handed spiral.

(2) In figure 43 three clockwise spirals co-operate, their initiation centres being closely spaced.

(3) Figure 44 illustrates co-operation of four clockwise spirals. Growth centres of three of them are closely spaced, while that of the fourth one is a bit further away.

(4) In figure 45 four spirals are seen (No. 1, 2, 3 and 4). Arms of a pair of clockwise and anticlockwise spirals (No. 1 and 2) just join up, and this pair is entrapped within growth layers from a right-handed spiral (No. 3). Growth fronts from another somewhat remote left-handed spiral (No. 4) join with those from the third one. It is interesting to note that some region between these spirals is devoid of any structure.

Figure 46 illustrates a case of several spirals. Here in the region marked 'A' two anti-clockwise co-operating spirals have their outermost growth fronts fused after about four turns, while in the region marked 'B', there are two more anti-clockwise spirals, wherein the outermost growth fronts of one branches off, while that of the other fuses
with those of spirals from the region marked 'A'. In the region marked 'C' co-operation and fusing of four right-handed spirals are seen.

5.7 Density of dislocations

The growth patterns on habit surfaces can be used to locate dislocations which need not be pure screw dislocations but may be dislocations with screw components normal to the surface or may be pure edge dislocations which do not meet the surface normally. For a very large number of dislocations emerging on the surface of the crystal, in addition to the study of the individual behaviour of the dislocations, certain statistical properties of the whole population can be studied, the chief amongst them being the density of dislocations, their type and strength. As far as the mechanical properties are concerned the density of dislocations in a crystal is an important parameter of the degree of perfection. Studies of the crystal growth, which have necessarily been made on good crystals grown slowly from solution or from the vapour phase or by hydrothermal process, which reveal only those dislocations which meet the free surface, indicate a consistently low density varying between $10^4$ and $10^6$ dislocations threading every square cm. of the surface.
The density of dislocations varies widely on different faces of the same crystal. The large density of dislocations observed for rectangular spirals on prism faces of cultured quartz is calculated from figure 45. Here the density of dislocations is $\sim 10^4$ screw dislocations per cm.$^2$ of the crystal face.

5.8 Discussion

In the present investigation prism faces of crystals grown on Z-cut, Y-cut, AT-cut, BT-cut etc. seeds show a variety of growth forms on them. The spirals reported here were observed on prism faces of cultured quartz only. From the detailed study of surface structures of all the habit faces of over a thousand natural and about eighty synthetic quartz crystals, it may be suggested that spirals seldom occur on natural quartz, and they are not frequent on cultured ones. Their rarity on (10\overline{1}0) faces of cultured quartz crystals is striking.

In the initial stage, growth takes place mainly on the seed plate by two-dimensional nucleation process by the spreading and piling up of growth layers parallel to the plane of the seed plate. Hence in the early stage of growth, a prism face should be expected to develop as the edges of growth layers which spread on and reach the...
boundary of the seed plate. As growth proceeds prism faces attain appreciable sizes and independent growth on them may then be expected. Growth on such a prism face is, in the beginning, principally by two-dimensional nucleation process due to spreading of layers parallel to the seed plate. However, at a later stage of growth, at higher supersaturations of screw ledges are formed on such faces, growth on them by spiral mechanism is possible. It is believed that such may be the case at least for the prism faces of CT-cut quartz crystals reported here.

It is suggested that as the growth proceeds, internal stresses develop. The abundance and the nature of the spirals observed in the present study suggest that such internal stresses are great in number though not much in magnitude. Such a process is likely to give rise to slip steps, thereby producing screw-ledges on the prism faces, and growth round such ledges will result into spiral patterns. If the crystal is losing heat from its surface by say radiation then the centre of the crystal in any plane normal to the axis will be hotter than the periphery. Because of the thermal contraction, the cooler periphery will be in tension and the core in compression. For such conditions the resolved stress in the slip direction may be sufficient to cause slip in the crystal. It may be noted
that spirals and related features observed are on such micro-scales that it was almost impossible to view them without the use of an oil-immersion objective and a phase-contrast microscope. Consequently multiple beam interferometry techniques were not used for a further detailed study of such features. Thus it may be safely concluded that all the spirals have very small step heights. From the width and the position of the white diffraction bands in the phase contrast micrographs of the spirals it may be concluded that these spirals are growth spirals. That the spirals are true hillocks will be further evidenced in chapter No. 9.

The spacing of the growth layers of spirals on the two sides of the rectangular hillocks is closer than the remaining two. Spacing between successive growth fronts depends on the rate of advance of the growth fronts, the faster it is, the smaller is the spacing. The rate of advance of growth fronts in turn depends on the number of molecules adsorbed at the steps, the greater it is, the faster will be rate of advance of growth fronts. Thus the steepness of the two planes composed of growth layers with smaller spacing of the rectangular growth pyramid is greater than that for the other two.

The shape of all the spirals observed here is
rectangular. The longer sides of growth layers are remarkably parallel to the inclined striations. All the spiral-hillocks were observed on the plateau between two striations. The longer arms of the spirals are inclined at 45° to the C-axis. Out of the four planes (faces) of the rectangular spiral pyramid, one pair is steeper than the other. This may be due to the differential growth rate at 45° and 135° to the C-axis. The growth fronts composing the steeper planes of the spiral pyramids are thus responsible for the formation of the inclined striations. Thus screw dislocations seem to have played an important role in the development of the prism faces in the later stage of growth.