10.1 Introduction

The microtopographical study of crystal faces enables one to understand some of their growth history. This is because the habit faces exhibit growth features and possibly dissolution features in their final forms. Since imperfections affect the growth and dissolution pattern, one can also obtain information regarding these. Microtopographical study of crystal faces also enables one to trace the changes, which the crystal has undergone in the time interval lapsed after the cessation of growth. It gives an opportunity to view the dynamical nature of the crystals. Various investigators,
like Verma$^{1}$, Augustine and Hale$^{2}$, Sunagawa$^{3}$, Desai$^{4}$, etc. have made attempt to unfold the growth mechanism of different crystals by studying their growth patterns.

The preceding chapters (5 to 9) described the growth and characterization of SnI$_2$ and SnI$_4$. The present chapter deals with a detailed, yet precise, investigation of microstructures on the habit faces of gel grown crystal of SnI$_2$, with the specific aim of understanding the mechanism of its growth.

10.2 Experimental Procedure

The two different phases, single crystals of SnI$_2$ and SnI$_4$ together in the same experimental setup were grown at ambient temperature, under a controlled reaction between SnCl$_2$ and KI in gel media as described in previous chapter 5. The SnI$_2$ needles and platelets were thoroughly cleaned and were coated with silver film in a vacuum coating unit to enhance the contrast. These faces were then examined under a metallurgical microscope.

10.3 Observations

So far as the mechanism by which these crystals have grown is concerned, it is to be noted that
the layer mechanism seems applicable where the growth take place by the two dimensional piling and spreading of growth layers. This is evidenced by fig. 10.1, in which the layers are clearly seen to have initiated at the edges and then spreading over the surface.

The growth layers or striations as they are called, are always parallel to the b-axis i.e. \langle 010 \rangle. Narrowly spaced and very fine striations with wider bands (fig. 10.2(a)) or less well defined and widely separated striation (fig. 10.2(b)) usually appear on the both sides of the platelets. Sometimes the growth striations do not extend along the length of platelet, but terminate on the platelet surface. This is illustrated in fig. 10.3(a), while sometimes the entire layer terminate and spread on the surface as shown in fig. 10.3(b). Figure 10.4 shows along with the striations, the dendritic growth features at the edges of the crystals.

The (001) faces of the crystals were rather rough and consisted of several misaligned micro crystals. It appears that these micro crystals influence considerably the growth and development of the faces on which they were observed. The attached
micro crystal may cause a kink on growing face, the adsorption of atoms at which leads to the spreading up of layers two-dimensionally or spiral mechanism, depending upon the nature of kink and condition of growth. Figure 10.5 illustrates the initiation of growth layers which has taken place at the edge of a micro crystal attached to (001) face. The growth layers are spreading out over the entire face.

The faces are also characterised by striations parallel to c-axis of the crystal i.e. perpendicular to those reported above may be called as vertical striations. These striations are of two types (i) widely spaced and (ii) narrowly spaced on the surface. One such case is illustrated in fig. 10.6. These striations are assumed to be corresponding to growth steps. Figure 10.7, shows, how the growth steps are running one over the other. The kinking of these steps is attributed to the interaction of growth fronts. Figure 10.8 illustrates the lamellar growth of the platelet with vertical striations. The composite growth of the needles with growth steps (fig. 10.9) is also observed.

Sometimes the secondary nucleation growth occurs on the (010) face of the primary (host) crystals.
Figure 10.10 illustrates a case in which (010) faces of secondary nucleated crystals are attached to the host face.

Crystallization of SnI₂ crystals in gel medium require about 2-3 weeks' period. {010} faces of SnI₂ crystal showed the presence of the rectangular pits (fig. 10.11), which are oriented in <010> direction. These pits are due to dissolution of crystals in acid set gels.

10.4 Discussion

Most SnI₂ crystals exhibit striations parallel to [010] on their {010} faces (horizontal striations) but a small percentage of them show striations perpendicular to this direction (vertical striations). Sunagawa⁵ described striations parallel to [001] on {210} faces of pyrite crystals as positive and perpendicular to it as negative striations. Positive and negative striations have different origin. The positive striations are associated with the pile up of edge growth layers developed on {100} face. The specific conditions required for the formation of negative striations are not yet clear. However, the most responsible explanation may be impurity adsorption.
White and Brightwell\(^6\) in ruby crystals grown by doping varying chromium concentration believed that striations arose because of preferred adsorption on different faces. In present case, during the initial stage of growth, needle grew at the gel solution interface by spontaneous nucleation. When the supersaturation exceeds the value necessary for two dimensional nucleation to occur on the close packed prismatic plane, a platelet nucleated and grew laterally. Therefore, the striations on thin or thick platelets of SnI\(_2\) crystals are formed by two dimensional nucleation and growth of bands of coherent needles along the b-axis. The various types of striations (very fine striations with wider bands, less well defined striations, etc.) could be readily correlated with the mode of growth as rapid growth following nucleation and bands are presumably related to the period between the passage of successive layers\(^7\). Some of striations terminate before they reach the end of the platelet, because they do not have enough time to grow out at the end. Striations usually appeared on both the sides of platelets, suggest that both the faces of the platelet are equally exposed to the nutrients. Vertical striations, or growth steps on the surfaces are interpreted here as the traces of growth fronts of the needle arrays. By
the deposition of ions, the steps tend to become parallel to the c-axis. The dendritic growth at the edges of the crystals is due to rapid growth at high supersaturation.

During the long period of growth in gels, the fresh nuclei may form nearer to the already grown crystals. Sometimes new nuclei may grow at the expense of already grown crystal. The secondary growth of nuclei reported here is thus accounted for.

The rectangular pyramidal shaped etch pits observed on the as grown faces of SnI$_2$ crystal are attributed to the dissolution of crystals in acid set gels.

10.5 Conclusions

1. The horizontal striations parallel to growth axis on as grown faces of crystals are associated with the pile-up of two dimensional nucleation of growth layers, while vertical striations are related to growth fronts by the adsorption of molecules.

2. Absence of growth spirals on these faces
rules out their growth by screw dislocations, at least for the crystals examined here.

3. The natural etch pits on (010) faces of the crystals may be due to the dissolution of the crystal in acid set gel.
References

1. Verma, A. R.
   Phil. Mag. 42 (1951) 1005.

2. Augustine and Hale, D. R.

3. Sunagawa, I.

4. Desai, C. C.
   Kristall und Technik 14 (1979) 289.

5. Sunagawa, I.

6. White, E. A. D. and Brightwell, J. W.
   Chem. and Ind. (1965) 1162.

7. Chase, A. B.
Captions of the figures

Fig. 10.1 Crystals demonstrating layer mechanism of growth.

Fig. 10.2(a) Narrowly spaced horizontal striations.

Fig. 10.2(b) Widely spaced horizontal striations.

Fig. 10.3(a) Striations terminating on the platelet.

Fig. 10.3(b) Entire layers terminate and spread on \{100\} face.

Fig. 10.4 Dendritic growth features at the edge of crystal.

Fig. 10.5 Growth layers from edge of micro crystal attached to (001) face.

Fig. 10.6 Narrowly and widely spaced vertical striations.

Fig. 10.7 Kinking of vertical striations.

Fig. 10.8 Lamellar growth on \{010\} face.

Fig. 10.9 Composite growth of needles with growth steps.

Fig. 10.10 Occurrence of some secondary nucleation.

Fig. 10.11 Etch pattern on natural (010) face of the as grown crystal.