APPENDIX

GROWTH AND GROWTH FEATURES OF Zn-Sb WITH SMALL CONCENTRATIONS OF Sb

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GROWTH AND GROWTH FEATURES OF Zn-Sb SINGLE CRYSTALS WITH SMALL CONCENTRATIONS OF Sb

The work reported in this chapter refers to the growth of Zinc-Antimony crystals from the vapour phase and the interpretations of the various features observed on the surface of these crystals. The work was taken up with a view to see the effect of impurity concentration on the crystal-form morphology. Hence the observations and their interpretations are discussed briefly in this chapter.

Most of the published work assumes that growth, from the vapour phase occurs by the lateral motion of steps which may be generated either by a two dimensional nucleation process, by spiral dislocations, or by the inclination of the surfaces to a singular or stable one. Revesz and Evans[1] observed fine striations along [110] directions with wave ridges along [211] directions, and suggested that their observations could be explained by step motion, the steps being either present originally or formed by nucleation and regenerated by bunching.

They stressed the importance of impurities causing local perturbations in step movement, but considered that the basic phenomenon was not impurity controlled.

In a review article Filby et al.[2] state that, there is abundant evidence that growth from the vapour phase occurs by the lateral motion of steps, particularly at low temperatures. Experimental results show no evidence of step motion at very high temperatures. At lower temperatures the grown surfaces were very rough and this had been suggested as evidence for step motion, the large step height arising from bunching due to the presence of a mobile impurity. The ridged and terraced surface features which represent the evidence that growth is by step motion have been observed in contaminated systems only. The influence, of an impurity deliberately added to the surface, on growth morphology has been well established by the work of Wagner and Ellis[3] on VLS growth and by Filby et al.[4] on the ultra thin alloy zone crystallization process of silicon.

The two metals zinc and antimony have much in common though their properties differ widely. In the first instance, the basal plane of the hexagonal

close packed system stacked in the ab, ab, ab..... sequence and the (111) plane of rhombohedral structure stacked in the abc, abc, abc....are very similar so far as the atomic stacking is concerned. The vapour grown crystals of Zinc[5] and Antimony[6] exhibit these faces; i.e. the basal plane for zinc and the (111) plane for Antimony. Hence Antimony was selected to be the impurity in zinc.

The crystals were grown as explained below. The two metals, in the required composition, were taken in a quartz tube of 1 cm diameter and 15 cm long. One end of the tube was sealed and the other end was connected to a vacuum pump. The tube was evacuated to a pressure of 10^{-4} mm of Hg and then heated to 650°C and was kept at that temperature for 3 to 5 hours. Then the mixture was cut and filled in a pyrex glass tube of 1.5 cm diameter and 6 cm long, and was vacuum sealed. It was then lowered into a vertical gradient furnace with the metal at the hottest region of the furnace. The temperature of the furnace in the hottest region was 450°C and the furnace had a gradient of 30°C/cm. The tube was kept in the

furnace for 18 to 20 hours and then the current was reduced slowly to bring the furnace to room temperature. Hexagonal plates were formed at the cooler end of the tube. No other forms of crystals was found except for a few faceted droplets.

Crystals were grown with three different compositions of Sb to see the effect of impurity concentration on the morphology of the crystals. More precisely, it was the aim of the author to see whether the crystal morphology can be changed from platelet to whisker or vice-versa by changing the impurity concentration and temperature gradient. The three different compositions used were of 1.5, 2.5 and 3.5 of weight per cent Sb in zinc.

For all the three compositions the source temperature was varied from 400 to 470°C, and consequently the gradient also changed. In any of the cases whiskers were not observed. Only platelets were obtained. From 400 to 430°C of source temperature no platelet was observed. Only a few faceted droplets nearer to the source were obtained. Above this temperature, upto 470°C, the change in the source temperature did not

make any difference in the morphology of the crystals. At lower temperatures the number of crystals were less and the platelets were bigger in size. But the as-grown faces were not very smooth. At higher temperatures the as-grown faces were smooth, but the number of crystals were more so that they clustered together making it difficult to study the individual crystals. Therefore the source temperature was kept at 450°C in all the cases. The as-grown top face of the crystals was identified as the (0001) basal plane by X-ray techniques.

The growth features on the top free surfaces of the platelets have been studied in brief.

Zn-1.5% Sb

Thin platelets of a few microns thickness and 4 mm^2 cross-sectional area were obtained. The crystals were more circular in shape than being hexagonal. Fig.1 shows the picture of such a crystal surface. Growth terraces and a few hexagonal patterns are observed. Figs. 2 and 3 show two of these growth hillocks at a higher magnification. It is seen that they are constituted of hexagonal closed loops. In

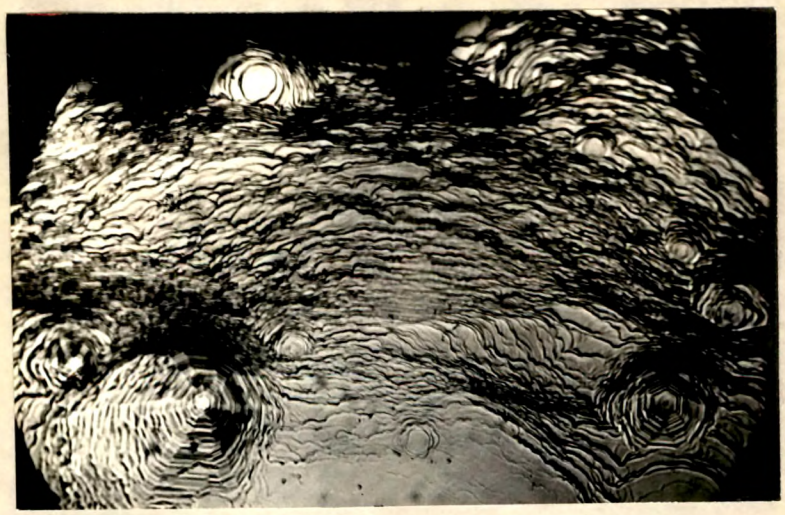

Fig.1 X90

Fig.2 X940

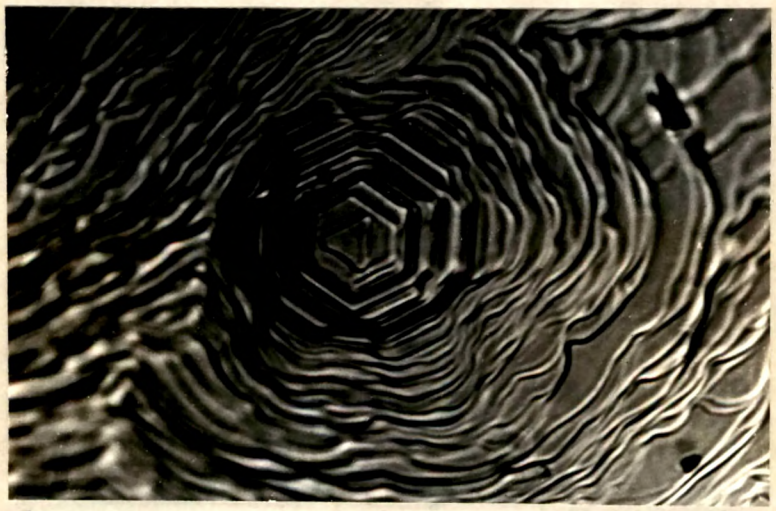

Fig.3 X940

Fig.3 the central loop is trigonal in shape. Bala Subramanian[7] and George[5] have observed spirals and closed loops in vapour deposited zinc crystals. But in all cases the centre was either a spiral or a hexagonal closed loop. Therefore in the present case it is considered that the hillock started growing at a dislocation or Frank-Read source around a segregation of antimony atoms and hence the triangular shape.

In Fig.2, on close observation there can be observed a depression at the centre, and two spirals of the same orientation originate from it. It is due to the over lapping of steps that the hillock appears to be consisted of closed loops. The steps after a stage takes a trunkated shape due to the difference in velocity of step motion for the two spirals.

Fig.4 is an electron micrograph of the top surface of a hexagonal pyramid on another crystal. Two small depressions are observed towards a side of the face. It was thermally etched in the electron microscope itself and the surface after etching is shown in Fig.5. Two spiral arms of opposite orientations can be seen to originate from each depression. So here the closed

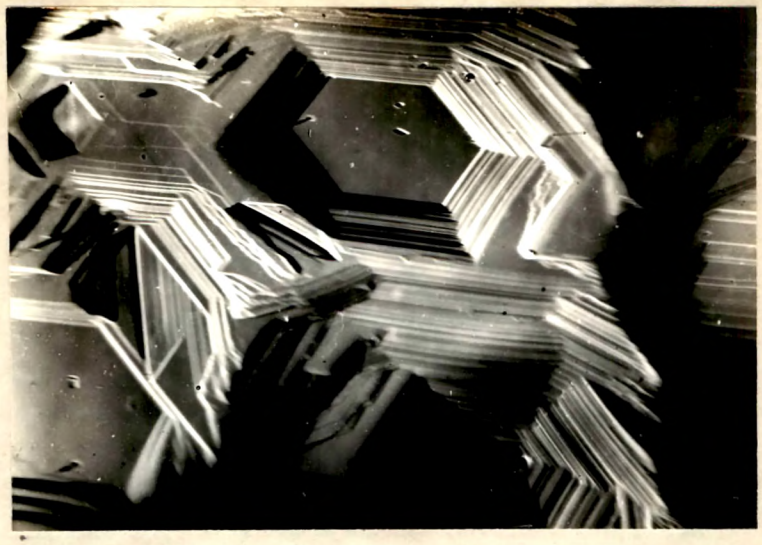

Fig.4 X2500

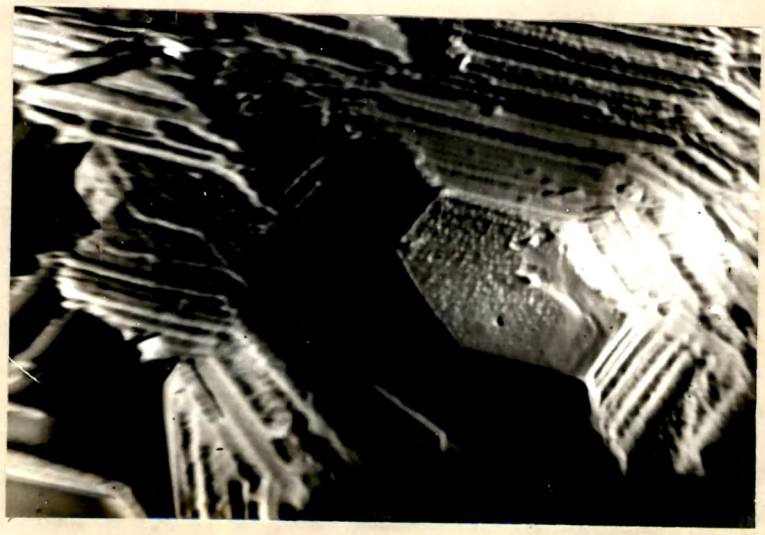

Fig.5 X2500

loops are formed due to the interaction of two oppositely oriented dislocations.

In this case of the platelets the growth takes place by the motion of layers and wherever impurity segregation is there, the growth hillocks originate at those points.

Zn - 2.5% Sb

Crystals, of about 1 mm thick and 5 to 6 mm^2 in cross-sectional , were obtained in this case. The faces were comparatively rough. Only a few complex spirals and closed loops were observed in this case. Fig. 6 shows such a crystal surface. The rough appearance may be due to the adhesion of impurity atoms on the surface. A number of spirals of both orientations are seen to start from the centre. On etching, a deep crater is observed at the centre. Impurity segregation takes place at the edges as revealed by the irregular pits along the steps in Fig. 7. Fig.8 is another complex feature observed on one of the platelets. Grain boundaries as well as impurity rich regions can be observed. Fig. 9 gives

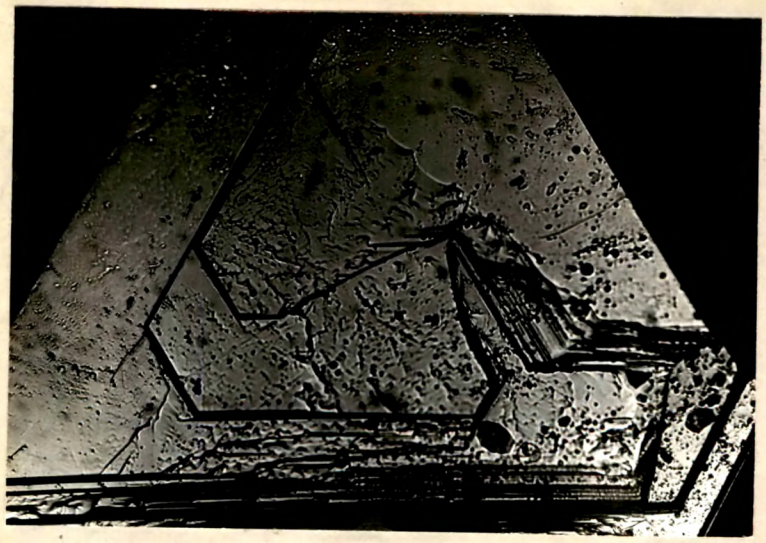

Fig.6 X170

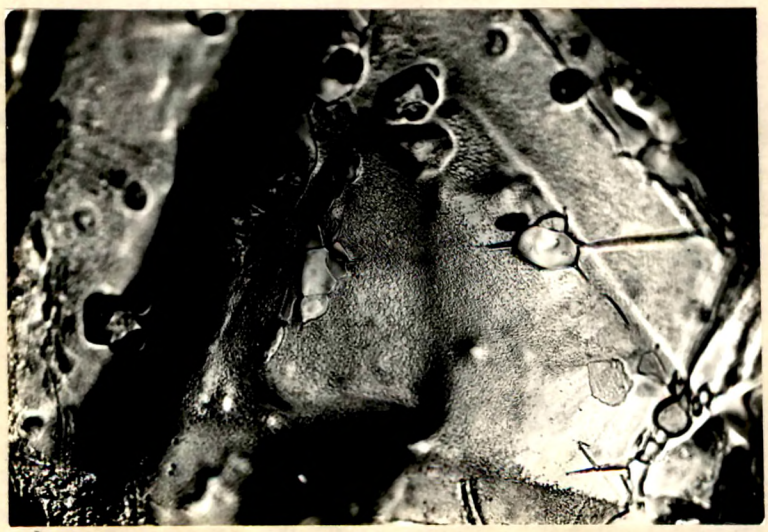

Fig.7 X170

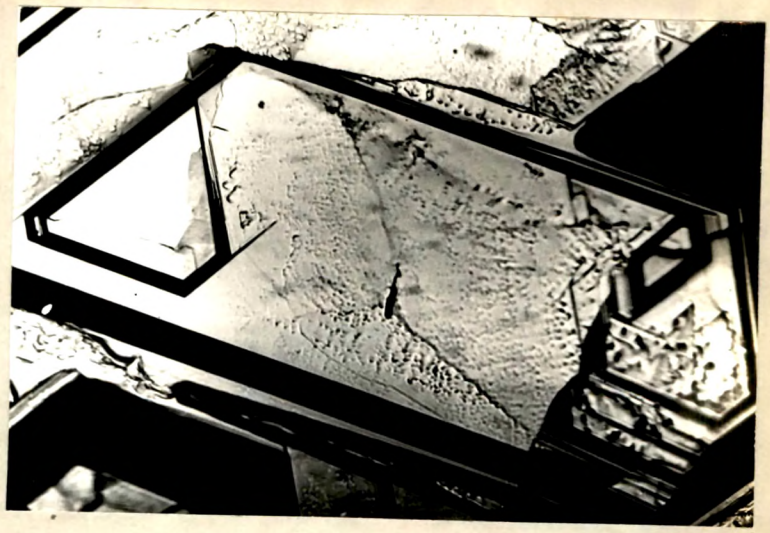

Fig.8 X215

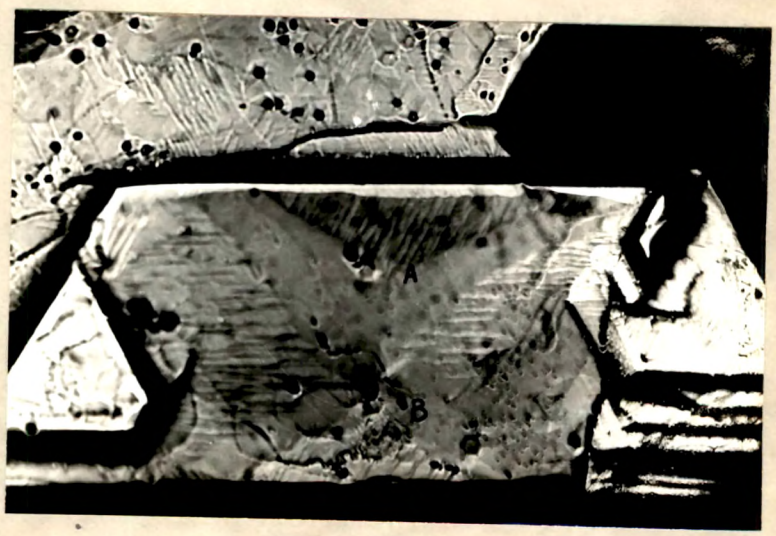

Fig.9 X240

the same surface after etching. Two deep pits (A & B) are observed towards the centre of the growth feature. The irregular shape of the pits indicates that they are due to impurities. Grain boundaries are seen to originate from these points. Another thing that can be concluded from these observations is that the distribution of impurity is not uniform. From Figs.10 and 11 it can be noted that the steps move towards the edge of the crystal. Near these edges where the steps terminate facets are observed. Another feature observed towards the edge of the crystals is the striated platelet structure of growth as seen from Fig.12. These observations show that the platelet structure and the facet effect are active not only in growth from melt but in vapour growth also.

Zn - 3.5% Sb

Hexagonal pyramids, of about 10 to 12 mm^2 area of cross-section and non-uniform thickness, are obtained. It appears like a number of hexagonal platelets stacked over one another and then pushed to a side. The top surface often ends in one or two closed loops as seen in Fig.13. It is a complex feature, a combination of

Fig.10 X170

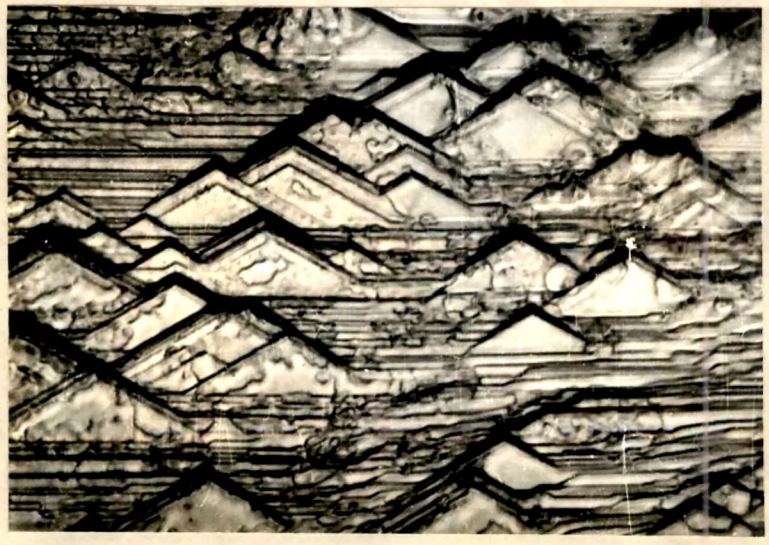

Fig.11 X560

Fig.12 X340

a spiral and a closed loop. As observed earlier the triangular nature of the spiral may be due to the segregation of Antimony atoms over there. The surface was etched and is represented by the micrograph in Fig. 14. A triangular pit is observed at the point where the triangular feature existed, and a very small pit at the origin of the spiral. Deep circular pits are observed near the steps.

In vapour growth, it is known that both impurities and vacancies will move towards steps and will get incorporated over there. In the present problem the impurities do not appear to be completely mobile. They build up towards the steps and the motion of the steps is slowed down considerably. As a result bunching takes place, which accounts for the large step heights observed. It may be due to the same reason that new crystals originate from the edges of the crystals giving the stacked appearance to them.

On examining the back side of the crystal, that is the side away from the vapour source, at the edges of the steps deep hexagonal pits are observed as seen

Fig.13 X360

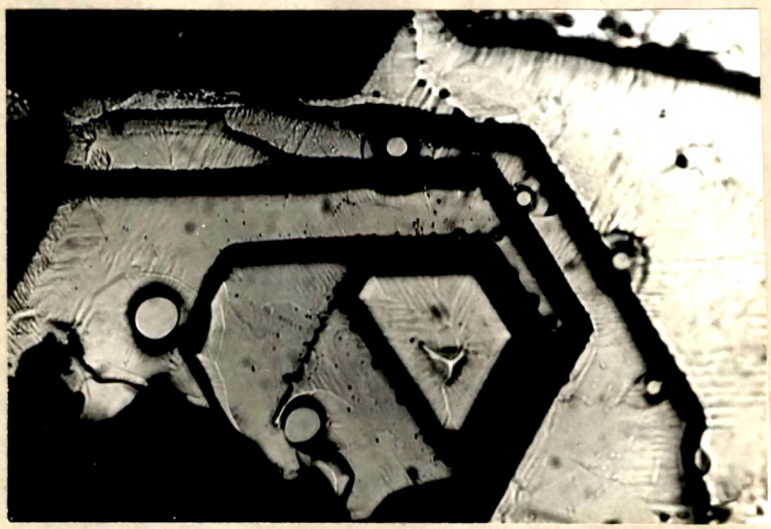

Fig.14 X360

from Fig.15. These may be vacancy condensation pits formed due to the migration of vacancies towards the steps.

The platelet structure and the faceting effects are visible in these crystals also towards the edges. Fig. 16 is the photomicrograph of these features. It is seen that the platelet structure is disappearing slowly giving rise to small facets.

Zinc has been studied most frequently, because of its high vapour pressure and comparatively low melting point. Straumanis[8] obtained thin platelets in an evacuated pyrex glass tube. It can be estimated from his data that the larger crystals formed at a supersaturation of about 3 to 4. Individual crystals could be obtained at supersaturations of about 10. But above this the metal condensed in powder form.

Cabrera and co-workers[9,10] grew a profusion of zinc whiskers in an atmosphere of helium containing 10^{-3} mole per cent nitrogen as the major impurity. The impurities in the whiskers were estimated from the residual resistivity measurements to be less than 10^{-2} atomic per cent.

Fig.15 X340

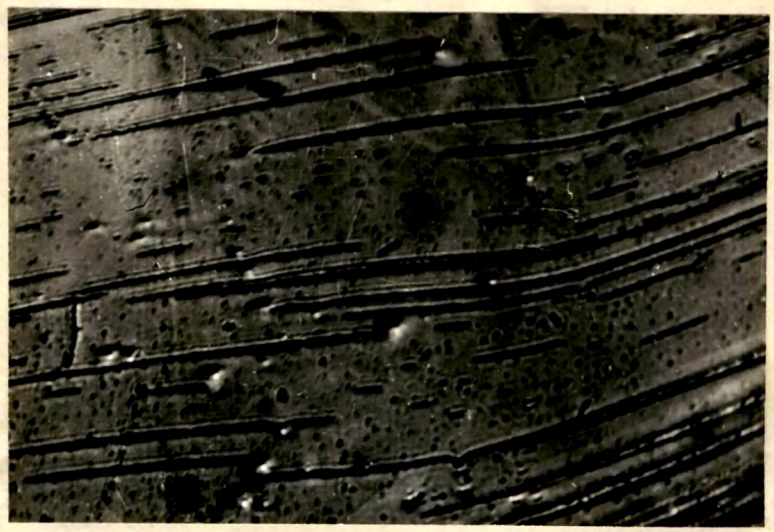

Fig.16 X420

In the present case, whiskers could not be observed either by changing the supersaturation or by varying the impurity concentration. This may be due to the difference in substrate, and the comparatively higher supersaturation.

Conclusions

(1) The morphology of the Zn crystals cannot be changed by varying the impurity concentration.

(2) The platelet structure of growth and facet effect are active in growth from the vapour phase also and not only in growth from the melt.

(3) The distribution of Antimony in the zinc crystals grown is not uniform.

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