PART III

STUDIES ON ANTIMONY CRYSTALS

CHAPTER X

GROWTH AND GROWTH FEATURES OF ANTIMONY SINGLE CRYSTALS

The work reported in this chapter refers to the growth of Antimony crystals from vapour and the interpretation of the various growth features observed on the surface of these crystals. The work was taken up mainly with an idea of the comparision with the results presented in chapters V to IX on zinc and is limited to this aspect. Hence the observations and their interpretation, in the present chapter and the next, are discussed in brief.

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 ... are very similar so far as the atomic stacking is concerned. In fact, the rhombohedral structure of antimony can be considered as two interpenetrating hcp structure. The lattice parameters of antimony are $a = 4.497\ A^{\circ}, \alpha = 57^{\circ}\ 65'$. It has a perfect cleavage along the (111) plane at temperature of liquid nitrogen. The vapour pressure is high enough, though less than that of zinc, to enable the growth of crystals from the vapour. Vapour grown crystals have an advantage of higher purity and perfection over melt grown crystals. The metal has poor thermal and

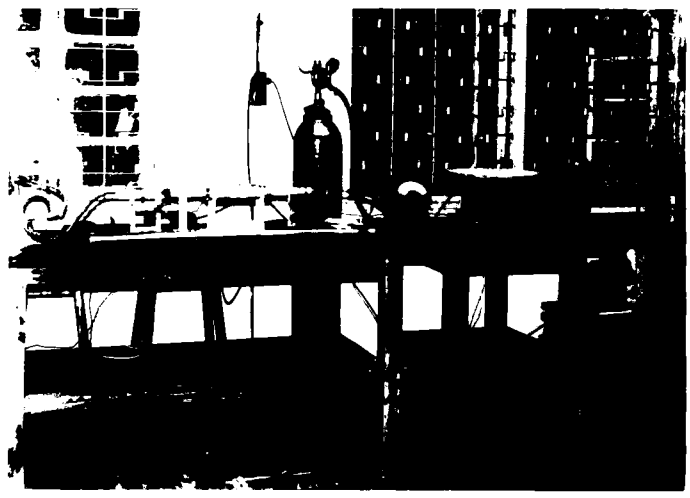

Fig. X -1(a)

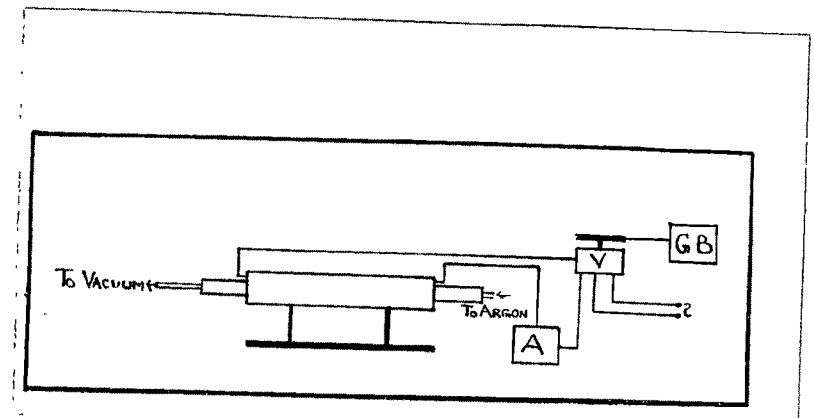

Fig X-1(b)

electrical conductivity and is more non-metallic. These properties and others such as elasticity are strongly anisotropic in the crystals.

There has been no report of the vapour grown crystals of antimony so far. Nor has any spiral growth observed on this metal. However, Wernick[1] et.al. have observed etch spirals on melt grown crystals. There has been very few reports of successful growth of antimony single crystals and the etch phenomena of these crystals. Wernick et.al. have obtained large single crystals of antimony in a zone refining apparatus at the last pass without seeding. Melt grown crystals have been studied by Kosevich[2], Shigetta[3], Pandya and Bhatt[4] and others. Because of the high melting point of this metal (630°C) the glass containers cannot be used in the growth of these crystals. Bridgman[5] in the original work has used graphite crucible for the growth of the metal crystals.

The arrangement used for the growth of the crystals, in the present studies is shown in fig.X-1. A fused silica tube 30" long and 1.5" in diameter is used for the purpose. The central portion of the tube forms the core of the furnace. The tube is connected to a vacuum system with all usual accessories. The other end of the tube can be either closed or connected to a source of dry argon as shown in fig.X-1. The temperature inside the furnace is measured with

the help of a thermocouple. The metal is contained in graphite crucible with a point bottom. This special shape of the crugible enables one to get melt grown single crystals also accasionally. High purity metal has been used in the present studies. The crucible filled with the metal is covered with a graphite plate. The arrangement is such that the plate is kept at the centre of the tube diametrically. The system is evacuated with a cenco hyvac pump to a pressure less than 0.1 m.m of Hg. At this stage a stream of argon gas is sent through the tube to displace the air remaining in the tube. The system is evacuated again and the furnace is switched on. The steady temperature is attained within 3 hours. The temperature of the furnace is kept between 650°-700°C. The furnace is cooled down gradually by reducing the current. A steady reduction of current is possible with an arrangement shown in the right hand side of the fig.X-1. A large wheel, 18" in diameter, is attached to the variac and this is pulled by a motor and a worm gear arrangement. This mechanism enables a gradual reduction of the temperature at the rate of 15°C/hr, which can be also adjusted to any desired value by controlling the speed of the gear mechanism. The furnace is cooled to room temperature gradually, the tube opened and the crystals are removed carefully.

Crystals are obtained from 3 different sections: (1) At the cooler ends of the quartz tube (2) At the bottom

of the graphite cover and (3) occasionally, the molten metal in the crucible solidifies as a single crystal. The former two are the results of vapour phase growth while the last one is the case of growth from melt. The vapour grown crystals are micro-crystals and bear triangular faces of 1 mm. sides. In certain cases large crystals of 3 m.m. sides are also obtained. The crystal in the crucible in the form of a tablet and in certain cases large single crystals 0.8 x 0.4 x 0.4 cm size could be cleaved out of this. Such crystals are seldom obtained and the solid in the crucible is generally polycrystalline in nature.

Microcrystals offer various advantages. Firstly, they are more perfect and contain less dislocations. This is extremely useful to the study of individual dislocations, the nature of which can be followed up throughout the crystal. Secondly, because of their small size the whole crystal surface can be kept in the field of view of the microscope, using higher magnification. The triangular nature of the surface enables us to determine the orientations of the growth and etch features without any difficulty. The surface of these crystals are very bright and hence interferograms could be taken over these very easily. Further, these can be cleaved carefully.

The nature and appearance of these faces suggest that they are the (111) faces. This has been confirmed from

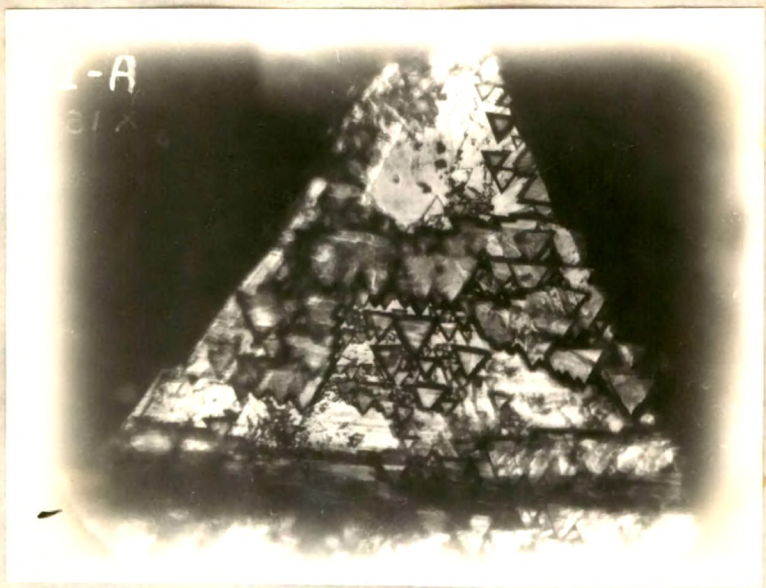

Fig. X -2 X 55

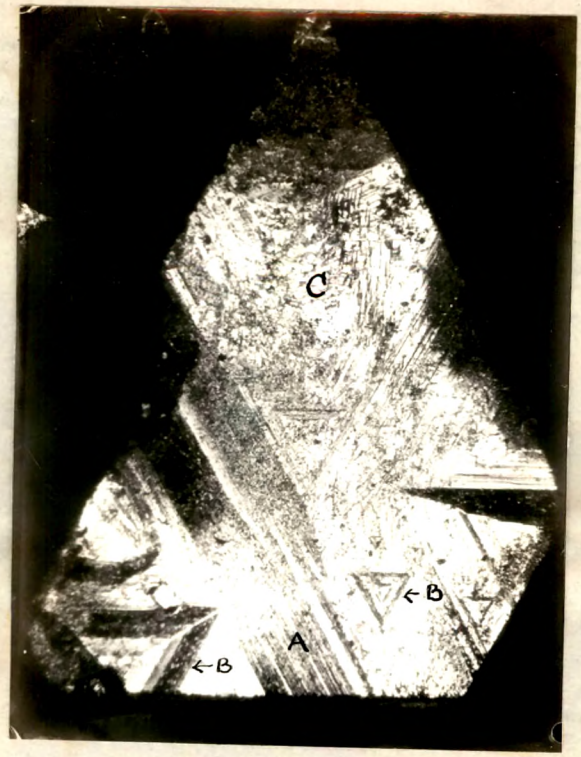

Fig. X -3 X 35

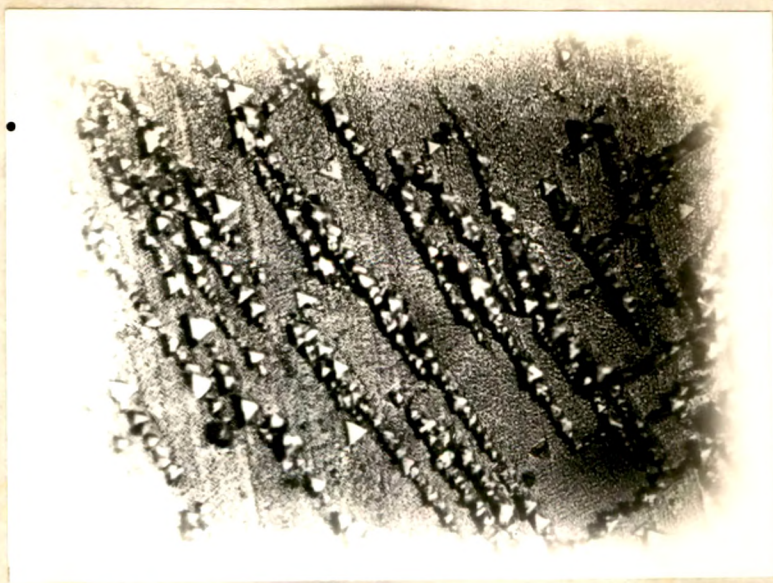

Fig. X -4 X 170

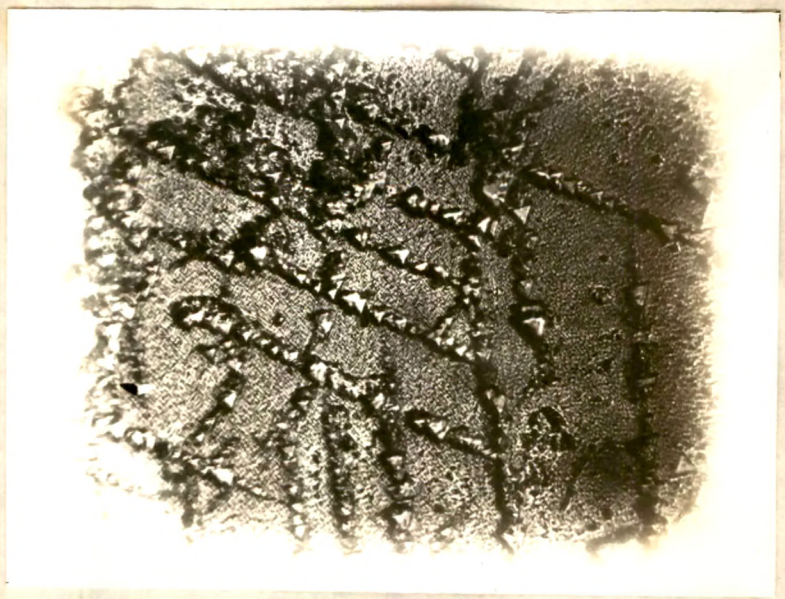

Fig. X -5 X 170

the etch studies as well as X-ray studies. The growth therefore, proceeds along $\langle 111 \rangle$ direction. This preferred orientation arises naturally, out of the strong anisotropy in the properties of the metal. The crystals are very brittle and extreme care is to be taken in mounting them.

The various growth features are shown in fig.X-2 to X-8, fig.X-2 is a phase contrast photomicrograph of the as-grown crystal showing a large number of growth triangles. These triangular features are elevated pyramids. The most striking feature of these growth pyramids is that they are all oriented opposite to the edges of crystal itself. Fig.X-3 shows another crystal surface, under low magnification. A large number of straight lines shown by A, rows forming a triangular pattern, B, and a series of irregular lines,C, are seen in the surface. Under higher magnification each of these markings could be resolved into rows of growth triangles, small in size, all oriented along the same line. These are shown in fig.X-4 and X-5. Fig.X-4 shows linear rows of triangles running parallel to each other while fig.X-5 is the intersecting rows forming a cross-grid of growth pyramids. In addition to these 'Y' shaped rows and randomly distributed triangles also could be observed. From the consideration of the directions individual straight lines shown in figs.X-4 and X-5 could be proved to be traces of the various $\{111\}$ planes of close packing existing inside the crystal. In addition to

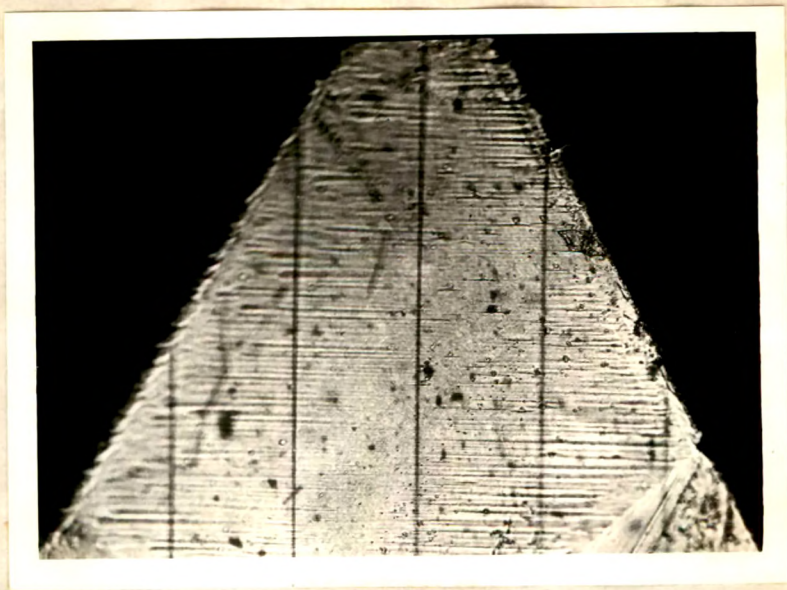

Fig. X -6 X 55

Fig X-7 x55

these features, other features are also prominent. Fig.X-6 shows a crystal surface containing a large number of parallel striations, suggestive of a mosaic boundaries. Along these straiations a number of triangles could also be observed. The profiles indicate that the surface is quite smooth and plane, but for these striations. In addition to the single crystals, sometimes crystals containing a number of (111) planes oriented at small angles from each other are also observed under phase - contrast microscope. Fig.X-7 shows a unique observation of a crystal containing a number of planes. This complex surface contains growth triangles different from all others in orientation. Furthermore the size of these growth pyramids are larger than those seen in other cases. The case X-3 to X-7 are observed when the rate of cooling is large while in crystals grown at slow rates of cooling the features correspond to those observed in fig.X-1.

A number of crystals grown under different conditions have been examined. The results can be summarised as follows: (1) The crystals grown from vapour grow along the [111] direction. (2) The as-grown faces of these crystals are triangular in shape and have been confirmed to be {111} planes of the crystal by X-ray studies. (3) These faces bear many growth features which are triangles oriented opposite to the faces themselves. (4) The growth triangles are

distributed in linear arrays, 'Y' shaped rows, intersecting rows etc. (5) The growth triangles are elevations and not depressions. (6) The size of the growth triangles is inversely proportional to their density of distribution and the rate of cooling. (7) They are seen to develop along the inter crystal boundaries and the intersections of the $\{111\}$ slip planes on the surface. (8) In some special cases parallel striations are also observed on the surface. (9) No growth spiral or closed-loop suggestive of a growth mechanism analogous to the Frank-Read source could be observed. (10) The density of the growth triangles were seen to vary between 10^4 to 10^5 cm^{-2}.

The nature and origin of these growth features has been investigated. The fundamental questions to be ansered are whether these feature are surface phenomena or body phenomena and what are the factors responsible for their observed distribution. David et.al.[6] have observed triangular growth of pyramids from the vapour phase growth of Germanium. These authors have studied the epitaxial deposition of Germanium vapours produced by the decomposition of Germane (GeH_4) by passing it through a hot tube and allowing the resultant vapour to deposit on the (111) face of a Germanium single crystal. The resultant pattern on the surface consists of a number of triangular pyramids which the authors have suggested to be the epitaxial growth of the (111) facet on

the (111) substrate. These features are similar to the present results and therefore suggest that the triangles observed in the present case also are the (111) facets grown on the (111) plane. If this be so, the next problem is the source nucleating such a growth and the factor responsible for the orientation of these features.

The regular distribution of these growth features suggest that they may be connected with dislocations. According to Burger's model a low angle boundary consists of a row of dislocations arranged regularly. This model has already been confirmed. Wernick et.al[1] have derived a mathematical relation connecting the spacing of dislocations along intersecting low angle boundaries. It can be shown from Frank's boundary equation that the model having a minimum free energy, for the dislocation tilt boundary must consist of an array of two kinks of parallel edge dislocations which utilize two of the three a/2 [110] Burger's vectors lying in the (111) plane. Thus if the boundary trace makes an angle ϕ with the nearest Burger's vector, then the other two Burger's vectors are used and the number of dislocations per unit length of the boundary is given by

$$n = \frac{\theta}{\sqrt{3}\,b} \cos\phi \quad - - - (1)$$

where θ is the angle of the tilt boundary. Considering the intersection of three tilt boundaries, in order that the sum of the three tilt angles may be zero, one boundary, say A, must have an opposite sense of tilt from the other two, say B & C, so that

$$\theta_A = \theta_B + \theta_C \quad \ldots \quad \ldots \quad (2)$$

combining equations (1) and (2)

$$\frac{n_A}{\cos\phi_A} = \frac{n_B}{\cos\phi_B} + \frac{n_C}{\cos\phi_C} \quad \ldots \quad (3)$$

The angle ϕ is defined as that between the boundary trace and the nearest Burger's vector, and hence cannot be greater than 30°, so that $\cos\phi$ is not very different from unity. Therefore,

$$n_A = n_B + n_C \quad \ldots \quad \ldots \quad (4)$$

i.e. the dislocation density is the sum of the other two. When two boundaries meet at a point $n_C = 0$ and hence,

$$n_A = n_B \quad \ldots \quad \ldots \quad (5)$$

i.e. the dislocation density along two intersecting boundaries are equal. If the growth triangles observed on the faces of these crystals are formed at dislocations as has been anticipated, then the intersecting rows such as shown in fig.X-8 etc. should satisfy the above equation. A number

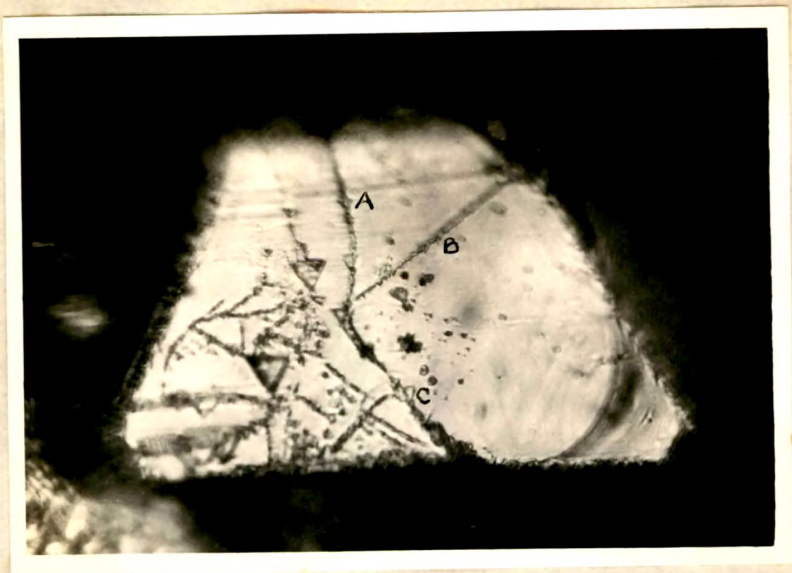

Fig. X -8 X 360

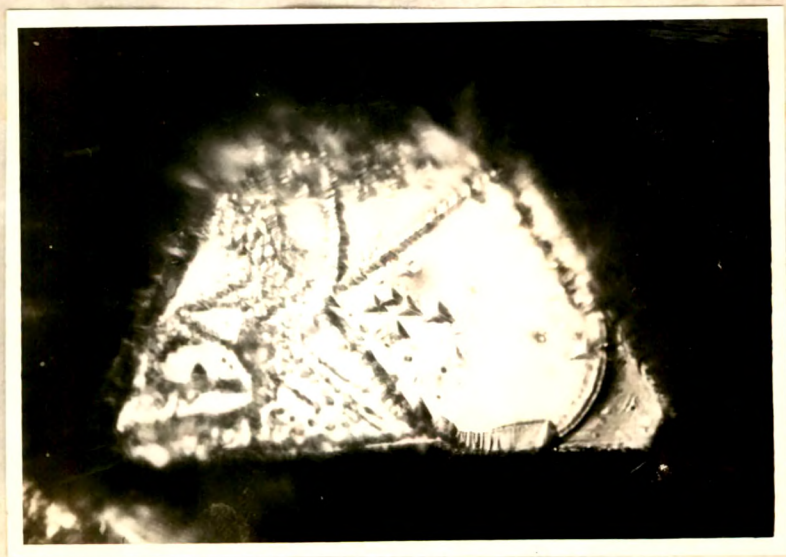

Fig. X -9 X360

of crystals examined were seen to agree well with these relations suggesting that these are formed at sites of dislocations. To confirm the results the crystals have been etched with reagents known to produce dislocation etch pits. A number of reagents have been tried for this purpose. A reagent consisting of 3 parts HNO_3, 9 parts tartaric acid and 1 part water was used for the purpose. The etch pits are formed at places where the triangles are seen. This is shown in fig.X-8 and 9. The linear rows A,B,C marked in fig.X-8 could be seen under high magnification to consist of rows of growth triangles as shown in fig.X-4. It can clearly be seen that after etching etch pits have been produced along these lines. These observations go far in supporting the idea that the growth triangles are formed at dislocation sites. It is interesting to note that the orientation of the growth and etch figures are also opposite.

To study whether these features are surface or body phenomena, the crystals were examined after short periods of etching and it was observed that the growth triangles were gradually dissolved away before pits are produced. It has been possible in a few cases, such as shown in fig.X-10, to show the beginning of the etch pit formation at the centre of the growth pyramid. No such growth triangles were observed on the cleavage surfaces.

The results, therefore, conclusively prove that the growth triangles are the (111) facets developed on the (111)

Fig. X -10 X 1900

planes, at regions of dislocations and that they are formed at the last stage of growth. The dislocations identified this way are of edge orientation. There is no evidence to show the presence of screw dislocations. On comparision with the results of David et.al. it seems possible that these might have also been formed in the same way from the vapour at the last stage of growth. Cottrell has suggested that even edge dislocations obliquely inclined to the surface can provide a step on the surface of a crystal and hence the evidence presented here confirm that the linear rows are tilt boundaries consisting of edge dislocations and the oriented growth of the (111) facets occur at these sites. While the presence of screw dislocations cannot be ruled out, the absence of the expected spirals at these can only explained as due to the fact that these spirals if present are small and hence cannot be resolved under an optical microscope because of the low step heights between the ledges.

The cause of the change in the orientation of these growth triangles is not yet known. Also it is not known whether impurities play any part in the development of these growth features.

Subsequent to the publication[7] of these results presented above, similar growth features have been observed on many other crystals. Crocker[8] has observed triangular

Fig. X -11 X 360

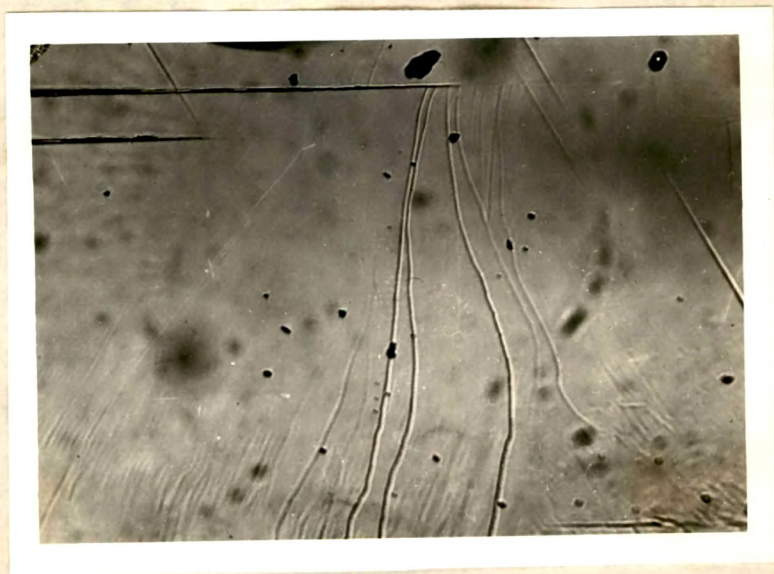

Fig. X -12 X 360

features on Gallium Arsenide crystals. These crystals were grown in quartz apparatus. Crystals formed at the cold end of the tube and were found to form $\{110\}$ dodecahedron modified by $\{111\}$ octahedra. The (111) face showed pyramidal growth protuberences whereas $(1\bar{1}1)$ face had triangular protuberences. No explanation has been offered by these authors.

Arizumi and Akaski[9] have studied the structural properties of the vapour deposited Germanium layers. They have made use of the reaction

$$2\ GeI_2 \rightleftharpoons GeI_4 + Ge$$

and have observed three fold symmetrical pyramids. The features have been explained in terms of dislocations and lend support to the views presented by the author. Yamanaka[10] et.al. also have observed triangular pattern on the (111) planes plate-like crystals of zinc selenide prepared by sublimation.

The high degree of perfection of the crystals were observed on the cleavage surface also. The crystals are easily cleaved parallel to the triangular faces with the help of sharp razor blade. The cleavage surface show good matching also as shown in figs. X-11 and 12. Except for the scratch shown in fig.X-12, the matching is nearly perfect. Interferometric studies yield results similar to these of Holden[11] and others and need not be discussed at length here.

SUMMARY AND CONCLUSIONS:

(1) The as-grown faces of the crystals have in general, a triangular shape and are the (111) planes.

(2) The faces bear many growth features, consisting of triangular pyramids oriented opposite to the surface itself.

(3) From the nature and distribution of these growth triangles and from studies of etch pits they have been identified as the (111) facets grown at dislocation sites.

(4) The factor responsible for the orientation of these (111) facets is not known.

(5) No growth spirals or closed-loops suggestive of spiral growth mechanism has been recorded.

(6) Recent observation on other crystals lend support to the views expressed by the author.

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