CHAPTER VII

CHEMICAL ETCHING OF DOME FACES OF Te CRYSTALS

The work reported in this chapter refers to the etching studies carried out on the as-grown dome faces of the vapour-grown tellurium whiskers.

Purified tellurium is an intrinsic semiconductor at room temperature with a forbidden gap Ei = 0.32 ev. It is to be expected that the electrical properties of tellurium will be sensitive to departures from crystalline perfection. The very marked adverse effect of dislocations on carrier lifetime in tellurium[1,2],

justifies the interest taken by previous workers to develop chemical etchants to reveal dislocations in tellurium.

A variety of chemical reagents had been used to develop pits on $(10\bar{1}0)$ faces of tellurium. Lovell et al.[3] used a hydrofluoric-nitric-acetic acid mixture to reveal randomely distributed etch pits, low angle boundaries and pits around mechanically worked regions. This etchant removes tellurium very rapidly at room temperature.

Blum[4], employing the etchant developed by Lovell et al. failed to produce etch pits on a plane parallel to C-axis. Blum developed an etchant consisting of 49 gm H_3PO_4(d = 1.55 gm/cc), 1 ml conc. H_2SO_4 and 5 gm crystalline CrO_3, which produced isolated pits and pits in pairs on the plane of the skull, parallel to C-axis.

Using concentrated sulphuric acid at 150°C well designed pits were produced on the $(10\bar{1}0)$ faces of melt grown tellurium single crystals by Blakemore et al.[5]. The pits had a very characteristic shape and were

assymetric about the c-axis. By optical reflection methods, the authors had shown that the planes constituting the pits were $(1\bar{1}00)$, $(10\bar{1}3)$, $(01\bar{1}1)$ and $(0\bar{1}1\bar{1})$.

Blakemore and Nomura[6] and Herrman[7], independently observed two types of etch pits which were mirror-images of each other, on etching with hot concentrated sulphuric acid. These were attributed to the dextro- and laevo-rotary forms of tellurium.

Shukla[8] used chromic acid to produce pits on the prism faces of tellurium and found that the addition of potasium dichromate to H_2SO_4 increases the rate of dissolution of tellurium.

Etching of Te has been done till now only on the $(10\bar{1}0)$ prism faces. No work on the etching of $(10\bar{1}1)$ rhombhohedron faces has been reported so far.

The present work was taken up with a view to study in detail the etching of $(10\bar{1}1)$ rhombohedron faces of the vapour-grown tellurium crystals, using the reagents reported for the prism planes of tellurium crystals. No attempt is made to develop any new etchant. Table I gives a list of the etchants used in the present work.

TABLE 1

Etchants

Reagent symbol	Authors	Composition	Ref. in Text
A	Blakemore, Schultz, and Nomura	Concentrated H_2SO_4 at elevated temperatures	5
B	Shukla	Concentrated H_2SO_4 - 9 parts by volume and 1 part saturated aqueous solution of Pot. dichromate.	8
C	Lovell, Wernick, and Benson	3 parts HF 5 parts HNO_3 6 parts CH_3COOH	3
D	Blum	49 gm H_3PO_4, (1.55 gm/cc) 1 ml conc. H_2SO_4, 5 gm crystalline CrO_3	4

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The dome faces, like the prism faces, are free of any growth features. It is of about 0·14 to 0·25 cm^2 in area and sometimes contain a crater at the centre or on the side where the hollow core of the crystal ends. Fig.VII-1 is such a micrograph showing a cavity, on a dome face. The cavity is not at the centre.

A. Etching with hot Sulphuric Acid

A dome face was etched in hot sulphuric acid, which was maintained at a temperature of 100°C. No pits are formed even after etching for about 5 minutes.

Slip lines were produced on a dome face by indenting a nearby prism plane. Fig.VII-2 shows such a micrograph. The same face was etched in H_2SO_4 at 110°C for two minutes. Randomely distributed , small pits are produced. The surface after etching is shown in Fig.VII-3. Note that the pits are not along the slip lines. Rate of attack is much slower than that on the prism face at the same temperature. The etchant is not good in revealing fresh dislocations.

Fig.VII-1 X110

Fig.VII-2 X135

Fig.VII-3 X210

Fig.VII-4 is another dome face with the slip lines. The surface was etched in H_2SO_4 at 130°C for 1.5 minutes. Small pits are produced along the slip lines as seen from photograph VII-5. Fig.VII-6 is the same surface as in VII-5 at a higher magnification. It can be noted that the pits are not exactly along the slip lines. It seems that the dislocations have moved out of slip planes. Or it may be that the etchant does not reveal all the fresh dislocations.

Fig.VII-7 is the dome face on another crystal. The surface consists of slightly misoriented planes. Sliplines are also visible. Fig.VII-8 is the same face etched in H_2SO_4 at 150°C for two minutes. Small etch pits somewhat triangular in shape are seen. The planes forming the pits are not well-defined. The density of pits increases towards the edges and is a minimum at the centre. The pit density was determined. The density at the centre was of the order of $1.5 \times 10^6/cm^2$ and that at the edges was of the order of $3.5 \times 10^6/cm^2$.

Fig.VII-9 is a region of another dome face etched in H_2SO_4 at 150°C for 30 secs. Pits are small and the density is low. Pits are seen along lines, which may

Fig.VII-4 X70

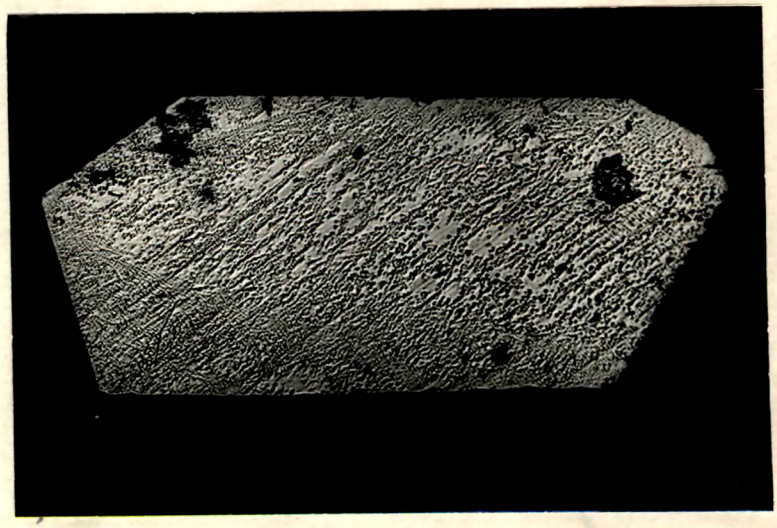

Fig.VII-5 X70

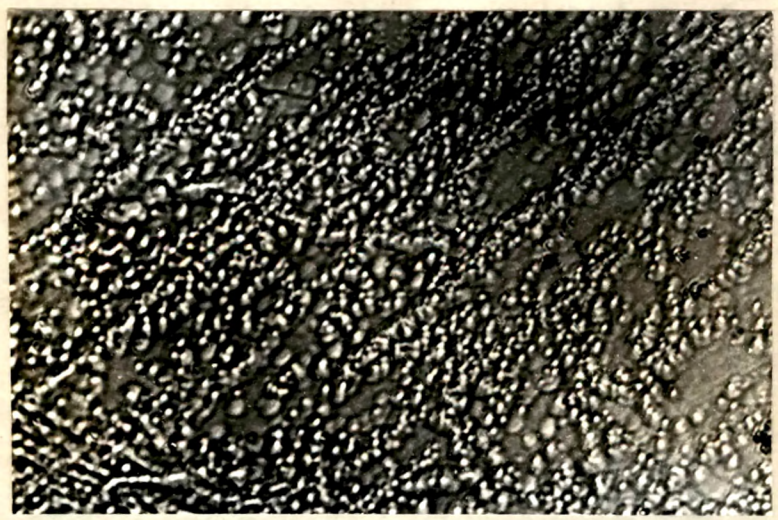

Fig.VII-6 X450

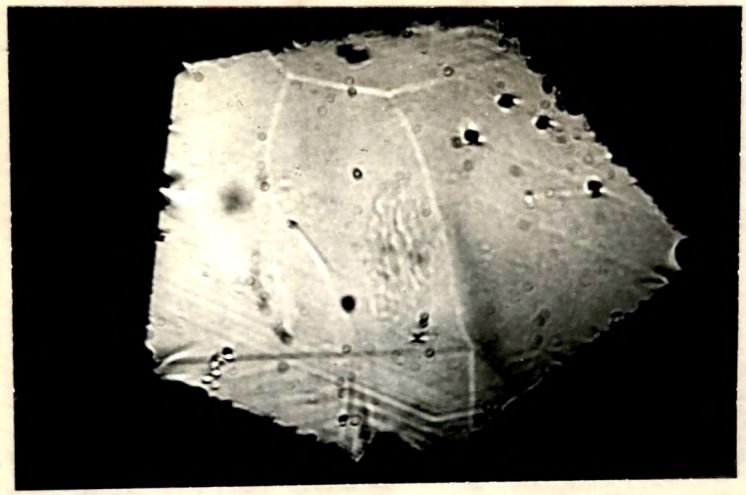

Fig.VII-7 X90

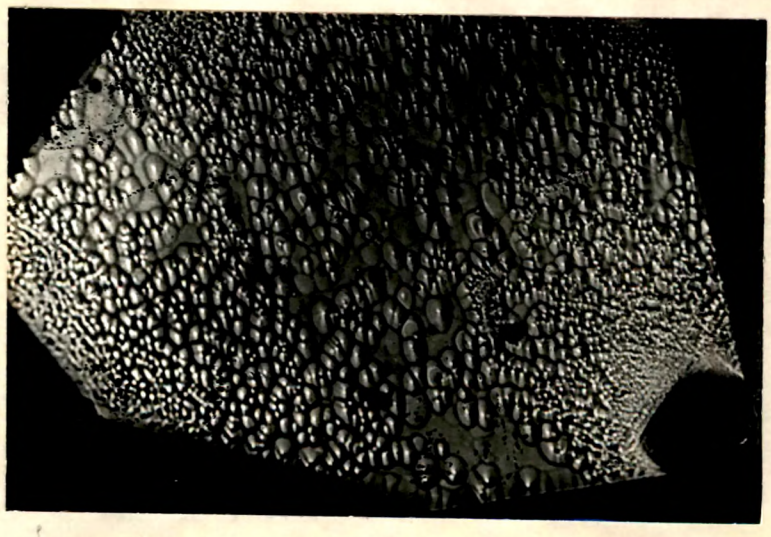

Fig.VII-8 X170

be at low-angle grain boundaries. Pit density was found to be of the order of 1.6 x $10^6/cm^2$. The pits along the big row are not constant. If the pits are at the emergence points of dislocations, then the row represents a twin boundary. Fig.VII-10 is another region of the same face. Short grain boundaries are seen distributed at random.

The same dome face had been etched further for 30 secs in H_2SO_4 at the same temperature. That is for a total time of one minute. Pit-size increased, but the density of pits remained practically the same as seen from Fig.VII-11. The pit-size is so large that they have encroached each other.

Fig.VII-12 is the same region as in VII-9,etched for a total time of 1.5 minutes. On comparing the micrographs VII-9,11 & 12 it is found that the spacing between the pits along the row AB is not changed by successive etching, whereas row CD has become a groove in Fig.VII-12. The spacing between pits along EF has changed considerably. The row AB is along a twin boundary, the pits marked 'X' and 'Y' being sessile dislocations and the others twinning dislocations. The sessile dislocations may be formed as a result of

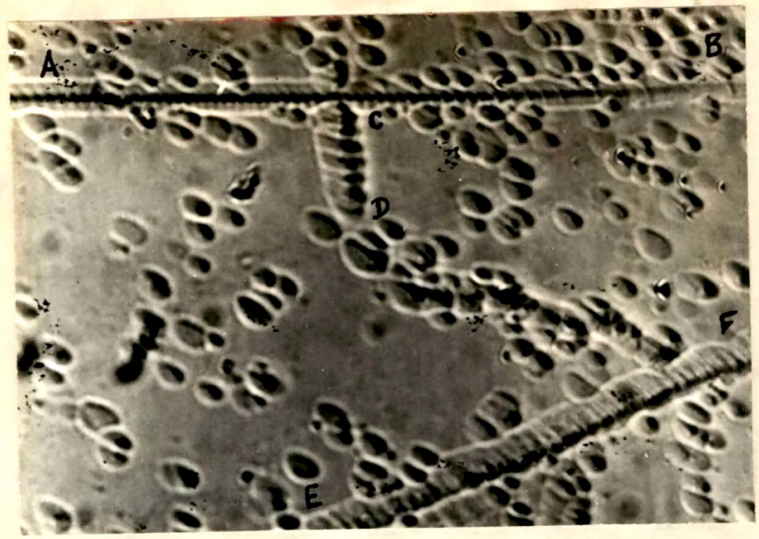

Fig.VII-9 X810

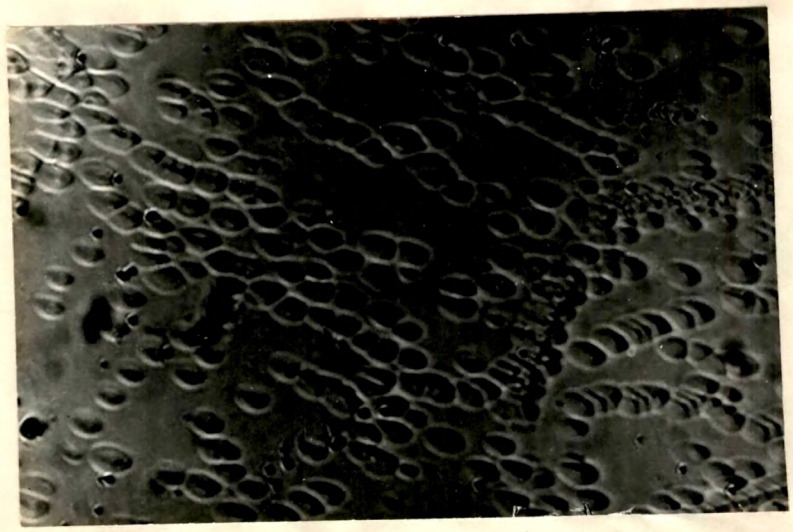

Fig.VII-10 X810

Fig.VII-11 X810

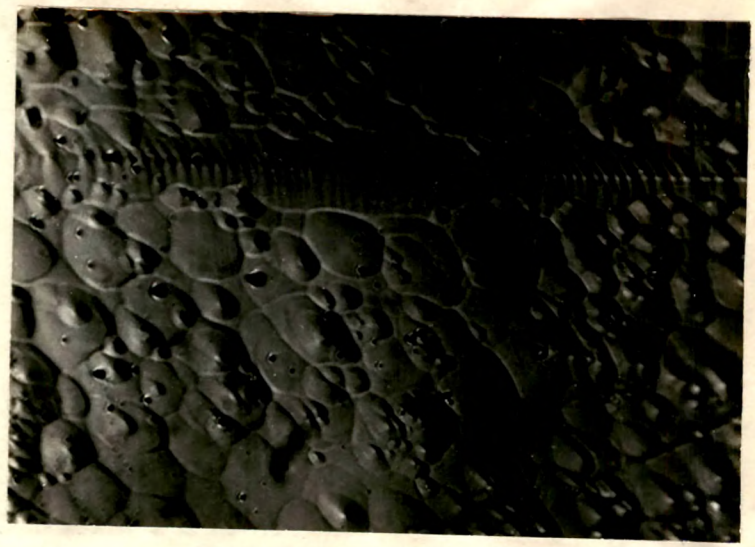

Fig.VII-12 X810

interaction between twinning dislocations and perfect dislocations. The clusters of pits seen in the photographs may be at the sites of point defects introduced during the growth of the crystal. A number of pits in Fig.VII-9 have become flat bottomed on further etching as seen from the other photographs. They are mostly at the sites of intersection of shallow dislocation loops with the surface.

Fig. VII-13 shows another dome face which had been etched in H_2SO_4 at 150°C for 1.5 minutes. A grain boundary is seen. The etch pits on the two grains are of different shapes and therefore the row of pits represents a large angle grain-boundary. The pit density on the two grains are of the same order, from which it is quite clear that the etchant is not orientation sensitive.

The rate of etching increases considerably with the rise in temperature of the etchant. The etching is slow on the dome faces compared to that on the $(10\bar{1}0)$ faces.

The pit density on the dome faces are more than that on the prism faces. This may be due to the fact that there are more dislocations running parallel to the prism faces and emerging on the dome faces, than those which are emerging on the prism faces.

B. Etching with Chromic Acid

This work was undertaken with a view to study the effect of addition of potassium dichromate to sulphuric acid and the effect of temperature of the etching reagent on the etching characteristics of tellurium.

Chromic acid used in the present case was prepared by taking 9 parts by volume of concentrated H_2SO_4 and 1 part saturated aqueous solution of potassium dichromate.

The effect of temperature of the acid on the etching characteristics was studied. It was found that the size of the pits increased and they developed well-contrasted and sharp etch planes with increase in temperature.

At about 100°C no pits are produced in the case of H_2SO_4, whereas big pits are formed when the dome face is etched with solution B for one minute. Fig.VII-14 is that of a region of a dome face etched in solution B at 100°C for one minute. The pits produced are different in shape and bigger in size than those produced by H_2SO_4 at the same temperature. Narrow boat-shaped pits are obtained. The pit density is also slightly higher than that in the case of etching with H_2SO_4. Fig.VII-15 is a photomicrograph of another dome face etched at 120°C in solution B for one minute. The size has increased and the pits are more well-defined. Pits in the background are due to general dissolution.

Another dome face has been etched in solution B at 140°C for one minute. Fig.VII-16 shows the surface after etching. Well-defined point-bottomed pits are produced. The shape of the pits is slightly different from that in Fig.VII-14. Fig.VII-17 is the same dome face at a lower magnification. At the side, a differently oriented grain is seen. The pits are having sharp planes and are well-defined. Fig.VII-18

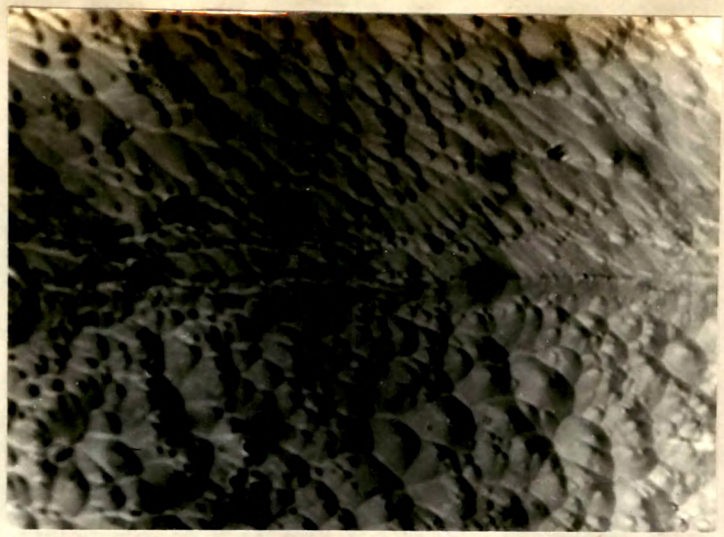

Fig.VII-13 X560

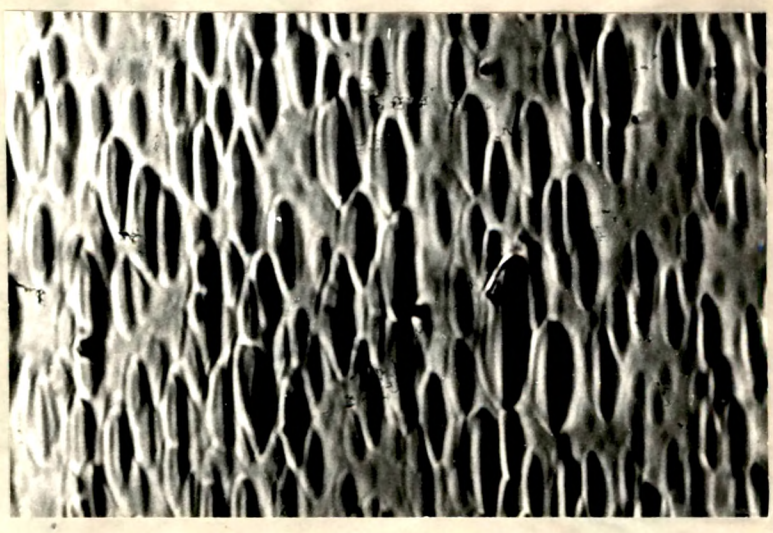

Fig.VII-14 X560

Fig.VII-15 X560

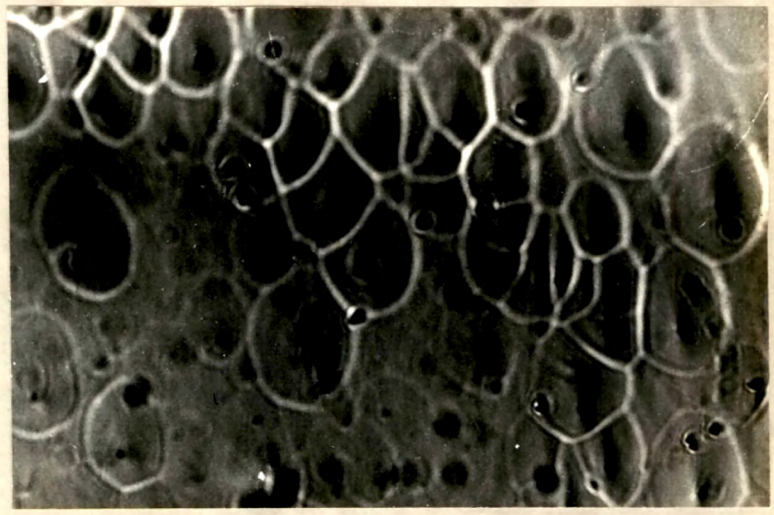

Fig.VII-16 X560

Fig.VII-17 X120

Fig.VII-18 X420

Is the grain boundary at a higher magnification. The shape of the pits in both the grains are different, which shows that the boundary must be a large angle grain boundary. It is also clear from the photograph that the etching with solution B is not selective to orientation.

As can be inferred from the large size and depth of the pits and also from the absence of flat-bottomed pits, the addition of $K_2Cr_2O_7$ to H_2SO_4 increases the rate of dissolution of tellurium. This may be due to the fact that chromic acid is a strong oxidising agent, though it is not possible to say about the exact role of $K_2Cr_2O_7$ in etching. The planes constituting the pits are not well-defined.

C. Etching with Hydrofluoric-Nitric-Acetic acid mixture

A dome face was etched with the solution developed by Lovell et al.[3], at room temperature. A thin film was formed on the surface. To avoid this the composition was slightly changed. It consisted of 3 parts HF, 4 parts HNO_3 and 6 parts CH_3COOH.

The etching rate was found to be very fast. Even etching for only two seconds gave a corroded look to the surface. This is much faster than the etching rate on prism faces. In the case of all other etchants, the etching rate on the dome face was found to be comparatively slower than that on the prism face. No attempt was made to modify the etchant so as to obtain a desirable etching rate.

D. Etching with Blum's Solution

The etchant developed by Blum for revealing the dislocations that intersect the prism faces, consisted of 49 gm H_3PO_4, 1 cc conc. H_2SO_4 and 5 gm crystalline CrO_3. The etching was carried out at 110 to 120°C.

A crystal was etched at 90° for 5 minutes. No etch pit was produced on the surface. At 100°C after etching for 10 to 12 minutes very small pits of no definite shapes are formed.

Fig.VII-19 is a dome face etched at 110°C for 3 minutes. Large pits are formed and the pit density

is very low. As seen from Fig.VII-20 the pits are square in general, but have irregular edges, giving a plygonal appearance. In the case of prism faces the same etchant forms rectangular pits. Small etch grooves are seen along the edge of the cavity. Fig.VII-21 is a region on the same surface at a higher magnification. The planes constituting the pit are not smooth but have a dendritic appearance. The diffused appearance on one side is due to film formation. When etched in Blum's reagent, it always forms an yellow film on the surface which may be hindering the dissolution of the surface. The low pit density and the slow etching rate may be due to this factor.

Fig.VII-22 is of a dome face etched at 120°C for 2 minutes. The etching rate has increased considerably and the surface is over etched. The pit shape is the same as that in the previous case. Another thing that can be noted from the above photograph is that the steps inside the cavity are also etched. This confirms the earlier observation that the steps inside the cavity are constituted by the same plane as $(10\bar{1}1)$.

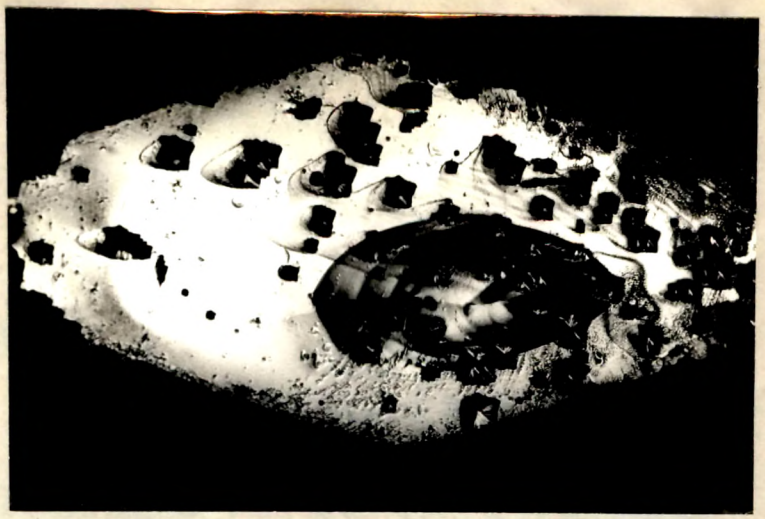

Fig.VII-19 X115

Fig.VII-20 X225

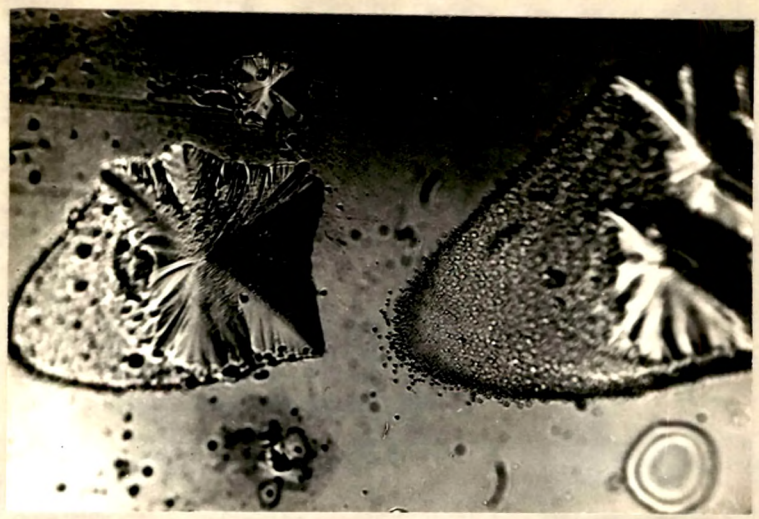

Fig.VII-21 X450

Fig.VII-22 X360

The film formation on the face hinders the dissolution. The few pits which are produced on the dome faces cannot be said to be at dislocation sites. The varied and large size of the pit infers that they may be at the sites of adsorbed impurities.

The etching rate increases with temperature. The pit size increases considerably as the temperature of the etchant is raised. Above 120°C the surface acquires a corroded look and this does not help to reveal the sites of dislocations.

Conclusions

Comparing the different etchants, mentioned above, it is found that the etchants developed by Lovell and the one developed by Blum are not helpful in revealing dislocations on the dome faces of as-grown tellurium crystals.

The H_2SO_4 etchant reveals most of the sites of dislocations on the dome faces when etched at temperatures between 100 to 150°C. The rate of etching is much slower on the dome face than that on the prism face. Also the etching commences at a higher temperature than in the

case of prism faces.

When $K_2Cr_2O_7$ is added to H_2SO_4 it enhances the etching rate. The pit density on the dome faces is found to be higher by an order than that on the prism faces. This may be due to the fact that in the vapour grown, hexagonal, rod-like crystals there are more dislocation lines running parallel to the crystal axis and intersecting the dome faces than those intersecting the prism faces. Small angle grain boundaries and short grain boundaries are observed on the dome faces.

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