CHAPTER 9

Etching (Experimental)

9.1 Introduction :

Applications of selective etching as a tool in the study of dislocation behaviour are well demonstrated (1). However the basic mechanism of the process is not yet fully understood. Since the classical work of Gilman et al (2), much work in this direction has been appeared in the literature on alkali halides (3-9) as well as on metals (10-12) in which attempts have been made to understand it. Excellent account on etching of crystals is now available (13-15).

The shape of an etch pit is dependent on the nature, concentration and temperature of an etchant. Occurrence of different shapes of etch pits on calcite cleavage faces due to various types of etchants and their different concentrations are reported (16-22). It is clear that with the same etchant, either concentrated or diluted, the chemical reaction is not materially changed.

The present author has carried out a detailed systematic study of controlled chemical dissolution on as-grown and cleavage faces of d-AHT single crystals employing various etchants.

9.2 Experimental:

Crystals of d-AHT grown by the gel method (chapter IV) were used for etching purposes. The cleavage faces were obtained by giving a sharp blow with a hammer on a razor blade kept in contact with the crystal along the cleavage direction. The surfaces were fully immersed in a still etchant of known concentration for a desired time of etching at constant temperature. After etching the crystal for the given period, it was kept in amyl acetate for some time. It was then dried by hot air blower. The samples were optically studied by Vicker's microscope described in chapter II.

9.3 Observations and Results :

Etching can be studied in different ways. eg. chemical etching, thermal etching etc. A study of the effect of different etchants for the different faces of d-AHT has been carried out. Chemical etching depends on a number of factors.

1. The texture of the surface to be etched.
2. The etching time.
3. The etchant concentration and composition.
4. The etching temperature.
5. Still or dynamic etching.

Etching experiments were carried out for all the above variants, keeping any one factor from 1 to 5 constant. The etchant acts differently on different surfaces. The author reports here a detailed account of these etchants on different surfaces of d-AHT. The different types of etchants for the as grown a-face are hereby discussed. It is to be noted that controlled chemical dissolution is very difficult on the as grown faces of crystals.

1. Because due to the simultaneous growth and dissolution of the gel grown d-AHT crystals, it is rarely possible to get a clear face.

2. Because of the different surface features and microstructures, the etching is not uniform which therefore results in pits of assorted dimensions. Keeping in view these difficulties and overcoming them to the extent possible, the present etching work was carried out.

a. **Etching on as grown a-face of d-AHT crystals.**

The following is a list of chemical etchants used to etch d-AHT faces.

Alkaline etchants.

a. Ammonia solution.
b. Sodium hydroxide solutions.

Acidic etchants.

a. Formic acid
b. Glacial acetic acid (GAA) and saturated aqueous solution of trichloro acetic acid, TCl_3 (CCl_3-COOH, T = COOH)

A quantitative study of the etch rate on the as-grown a-face was difficult because of the inconsistent sizes of the etch pits, but it is rather very interesting to study the effect of various etchants on the as-grown a-face; which is likely to provide wealth of information on growth and dissolution characteristics of d-AHT. Both alkalies and acids etch the surface to different degrees.

Alkaline etchants:

a. **Aqueous solution of ammonia (sp/ gr. 0.91).**

d-AHT crystal exhibiting several a- and m- prism faces (100) and (110) respectively was put in ammonia solution (sp. gr. 0.91) for three seconds at room temperature. Depending upon the nature of features at different points - areas - on the a-face, several dissolution patterns are observed. Fig. 9.1(a) (x140) shows a large number of flat bottomed elongated rectangular etch pits with the long and short sides along the directions [001] and [100] respectively. At certain places the pits coalesce to form bigger elongated rectangular pits. Fig. 9.1(b) (x 140).

It is interesting to observe that with increase in etching time short side of the rectangle does not change and that coalition takes place with extension along direction [001] only. Some times the coalition produces terracing and the dark sides of pits indicate higher amounts of dissolution. The background pitting is not quite noticeable. At some places on the a-face elongated rectangular etch pits with dark square cross section and also long rectangular pits with dark outlines on right hand side (fig 9.1c(x 140)) are observed. This suggests that the as-grown surface features interact heavily with the etchant and that the surface features are having varying amounts of surface energy.

Fig. 9.2 (a) (x 140) exhibits etch features produced by an etchant containing 1 cc of ammonia solution (sp. gr. 0.91) and 300 cc distilled water for three seconds. There is a significant increase in the lateral etching along direction [001] with practically no increase along direction [100]. The background etching is very less. A small crack on the

CAPTION TO FIGURES

Fig 9.1(a),(b)& (c)	Face	:-	As grown a - face {100}
	Etchant	:-	Ammonia solution (sp.gr. 0.91)
	Time	:-	3 seconds
	Temp	:-	30° C

Fig 9.2 (a) & (b)	Face	:-	As grown a - face {100}
	Etchant	:-	Ammonia solution (sp.gr. 0.99)
	Time	:-	3 seconds
	Temp	:-	30° C

FIG.9.1a

FIG.9.1b

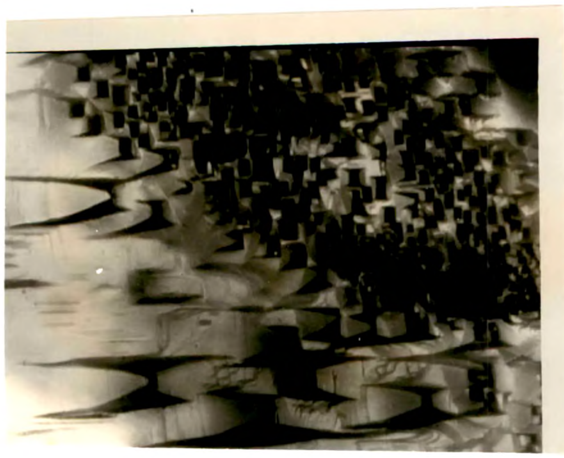


FIG.9.1c

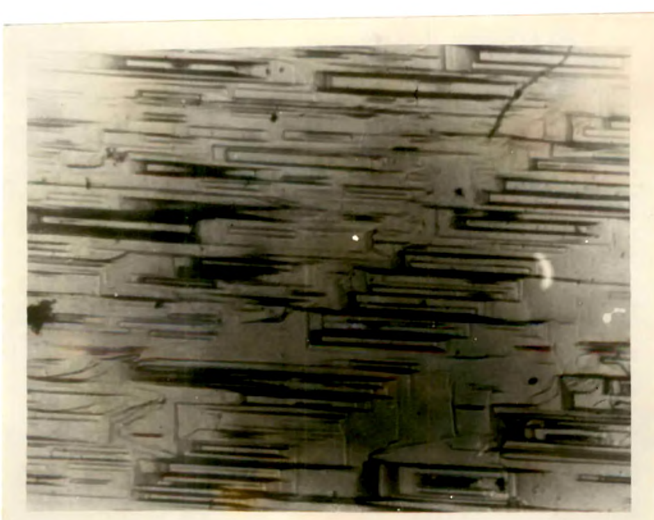


FIG.9.2a

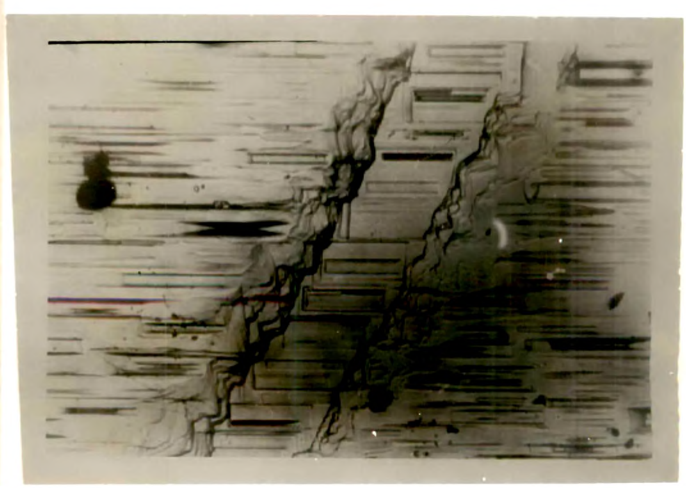


FIG.9.2b

a-façe can create interesting and useful feature of etching with the above solution . Fig 9.1 (b) (x 140) shows such a feature. The etchant had produced etch pits with rectangular outlines. Because the propagation of crack was uneven, the pattern gives rise to the formation of stair case with unequal spacing between different steps. Since the strain energy along the sides of the crack is more as compared to those on steps, the stair case sides are more etched. It is thus clear that increase of distilled water, say from 100 cc, 200 cc to 300 cc and so on, in a fixed quantity of the above referred ammonia solution, produces elongation of the rectangular etch pit along direction [001].

d-AHT is insoluble in amyl acetate liquid. It therefore provides ideal environment to study the effect of a small quantity of ammonia solution (sp. gr. 0.91). One drop (~ 0.016 cc) of this solution was added to 10 cc of amyl acetate liquid. d-AHT was put in this solution for one minute. Photo-micro-graph of a-face etched by the above solution is shown in fig. 9.3 (x 140). It exhibits well defined flat bottomed rectangular pits. A close examination indicates that even in the flat bottomed bigger pits are formed smaller rectangular pits. The direction of the sides of the bigger pits are same as those of the smaller pits inside them but the broadening of big rectangular pit is at right angles to the one for smaller etch pits. This means that the orientation of smaller pit is at right angles with respect to that of larger pits. Along with these features there is a large amount of pitting all over the surface. If the ammonia solution is still diluted as mentioned above and one drop of this distilled solution was added to 10 cc of amyl-acetate and the etching of d-AHT was carried out for a minute, the shorter side is reduced with a large increase of the long side of the rectangular etch pit. This means that aqueous solution of ammonia of specific concentration range is responsible for the movement of step along [100] and [001] giving rise to etch pits with rectangular outline on the surface under observation.

In addition to the above experiments on etching, it is quite useful to assess the effect of dry ammonia gas on a-face. d-AHT crystal was put in dry ammonia gas for three seconds. Fig 9.4 (x 140) shows the etching effect of dry gas. The figure reveals large amount of line etching along [001] accompanied by a white patch ABCDE. This patch should be a reaction product because it could be removed by water (fig. 9.5 (x 140)). Immersion of the specimen in distilled water for a second, removes the particles, etches other areas free from reaction product and delineates bunches of large number of etch patterns, which consist of thin rectangular etch pits (fig. 9.5 (x 140)). This also shows that when water was added to ammonia gas in the reaction product, rectangular etch pits are formed. It also indicates incomplete chemical reaction between ammonia gas and a-face of d-AHT. Pure distilled water dissolves d-AHT (3.24 gms in 100 ml distilled water at 25° C). The etching of a-face of d-AHT in

CAPTION TO FIGURES

Fig 9.3	Face :-	As grown a - face {100}
	Etchant :-	1 drop ammonia solution in 10 cc amyl acetate liquid.
	Time :-	1 minute
	Temp :-	30° C
Fig 9.4	Face :-	As grown a - face {100}
	Etchant :-	Dry ammonia gas
	Time :-	3 seconds
	Temp :-	30° C
Fig 9.5	Face :-	As grown a - face {100}
	Etchant :-	Distilled water
	Time :-	1 second
	Temp :-	30° C
Fig 9.6	Face :-	As grown a - face {100}
	Etchant :-	Distilled water
	Time :-	3 seconds
	Temp :-	30° C

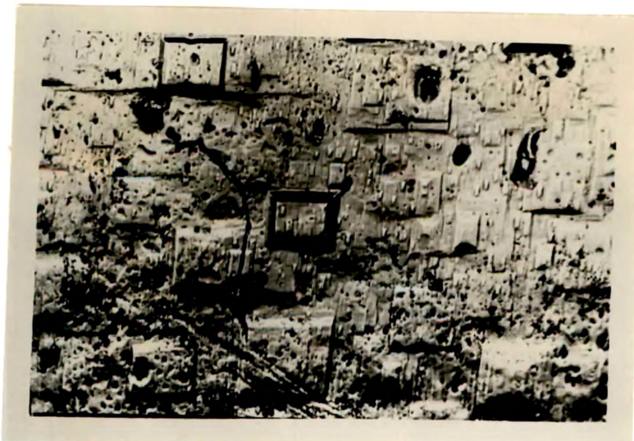


FIG.9.3

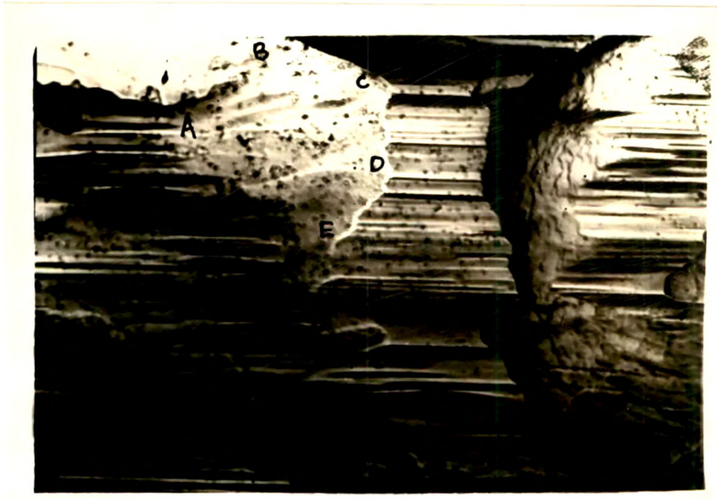


FIG.9.4

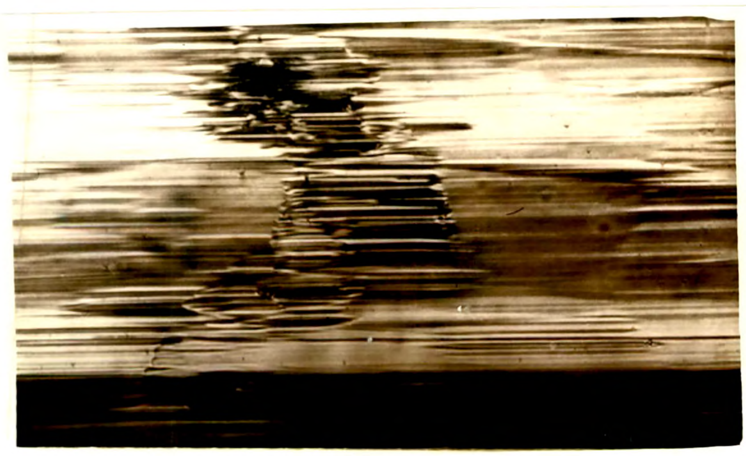


FIG.9.5

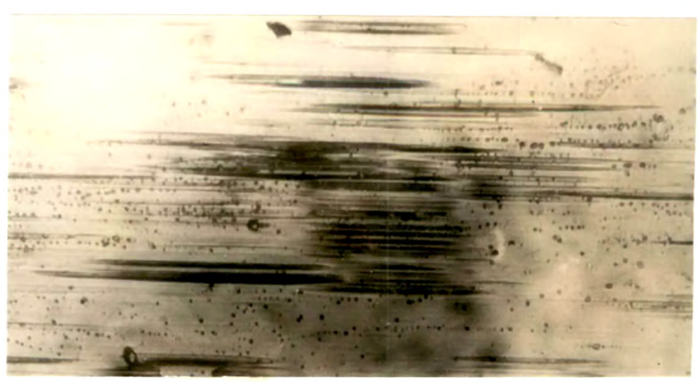


FIG.9.6

distilled water for three seconds has disclosed (fig. 9.6 (x 140)) a large number of striations parallel to [001] and small dot like features. The striations form the base of rectangular etch pits. The effect of pure water is to delineate striations. This is also true for the action of pure dry ammonia gas. However the combination of ammonia gas and water giving rise to weak ammonium hydroxide solution for a specific range of concentration produces rectangular etch pits. In other words, aqueous solution of ammonia forces steps or ledges along [001] and [100] at preferential points to move, thereby producing a geometrically well defined etch figure with a rectangular outline. Further etching time is also increased from three seconds to a minute. The etch pit formation is in accordance with the binary symmetry axes coinciding with the crystallographic axes [100] and [001] of d-AHT.

b. <u>Aqueous solution of sodium hydroxide:</u>

It is clear from the above studies on etching of a-face of d-AHT that ammonium hydroxide solution chemically reacts with d-AHT. Hence the obvious conclusion is that any base (weak or strong) should react with d-AHT. The author has therefore tried sodium hydroxide solution and Potassium hydroxide as etchants. It was observed that basically the effect of each one of them, is almost the same. Hence only the etching work carried out with aqueous solution of sodium hydroxide is reported here. Pure NaOH pellets (4 gms) were dissolved in 200 cc of distilled water giving rise to a solution of 0.5N. Fig. 9.7 (a) (x 140) exhibits a photo-micro-graph of a-face etched by 0.5N solution of NaOH for five seconds at room temperature. The various as-grown features are differently etched. In addition to irregular etching of several growths features such as PQR, there are striations, flat bottomed and point bottomed etch pits with rectangular outlines. A careful study of etch pits indicates that the centre is not a point but a line and that the pits are quite deep. Three bunches of pits can be very well marked out (S,T,U). Successive etching of this surface for a further increase of five seconds each (Figs. 9.7(b), 9.7(c), 9.8(d) (x 140)) exhibit the increased etching along with constancy in shape, number, orientation and position of etch pits at S,T and U. The irregular growth patterns P,Q,R which are elevations as can be seen by considering Figs 9.7 a,b and c wash out with progressive reduction of features, giving rise to lines in the direction [001] (fig 9.7 (d) (x 140)).

The multiple etching simply enlarges the etch pits. This suggests that the pits are formed at specific weak points, likely to be dislocations ending on the surface. The enlarged pits join with a tendency to form bigger etch pits. It is useful to note that the background pitting decreases with increase of etching. Sodium hydroxide solutions of different normalities were also tried. It is found that up to certain strength of solution (0.22N) there is not any

CAPTION TO FIGURES

Fig 9.7 (a),(b), (c) & (d)	Photomicrographs of successive etching of as grown a-face by 0.5N sodium hydroxide solution at 30° C for 5,10,15 & 20 seconds respectively

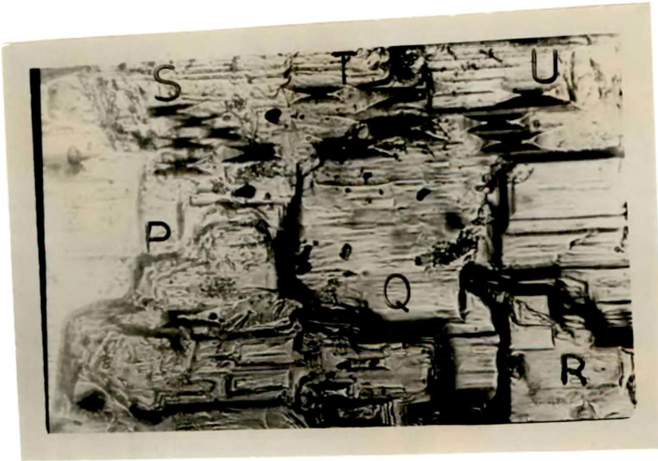


FIG 9.7a

FIG 9.7b →



FIG 9.7c

FIG 9.7d →


significant change in the shape, position, number and orientation of etch pits. Further the increased etching does not produce pits within the bigger pits. This is in sharp contrast with the etching by ammonium hydroxide solution. Small quantity of aqueous solution (0.5 N) of NaOH (fig 9.3) namely two drops (~ 0.032 cc) is kept in 10 cc amyl acetate liquid and a-face of d-AHT crystal was etched for a minute at room temperature (fig 9.8 (x 140)). This produced increased etching. The photo-micro-graph is quite remarkable from the point of view of a large number of flat bottomed and terraced etch pits and practically no pits with centre. The flat bottomed and terraced pits are bound by sides with directions [100] and [001].

ACIDIC ETCHANTS

c. Formic acid

Controlled chemical dissolution with formic acid (85 %) as an etchant yields different results. Rhombic etch pits were observed on etching as-grown a-face for five minutes in formic acid. The photo-micro-graph (fig 9.9 (x 140)) reveals the curvilinear character of rhombic etch pits which are mostly flat bottomed. There is also a large number of curvilinear lines resembling a river pattern. The diagonals of rhombic pits are having directions [001] and [100]. Addition of a few drops of water, to the above etchant (pure formic acid) produces a significant change in the shape and size of etch pits. Fig 9.10 (x 140) is a photo-micro-graph of a typical a-face etched by an etchant containing 5 ml formic acid and two drops of distilled water (~ 0.032 ml) for one minute. The plane rhombic shape turns into a hexagonal shape with a centre and having the inherent crystallographic symmetry. Pits are of bigger sizes with many of them having terraced structure and smaller flat bottomed pits.

Increasing the amount of distilled water chemically dilutes the formic acid and produces etch pits with rectangular outlines. Fig 9.11 (x 140) is a typical photo-micro-graph of etch pits produced by keeping a-face for a minute in an etchant containing 5 ml formic acid and 1 ml distilled water at room temperature. There are a large number of flat bottomed rectangular etch pits with a few point bottomed pits. The directions of the pit sides are [001] and [100]. When the a-face was etched by an etchant containing equal quantity of distilled water and formic acid, it exhibits large flat bottomed rectangular etch pits showing merger of various small flat bottomed pits and a reduction in the number of point bottomed pits (fig. 9.12 (x 140)). It is thus clear from a close study of the above figs. 9.9 to 9.12 that variation in the quantity of water present in the fixed quantity of formic acid noticeably affects the surface structure and etch pit shape and orientation. This is shown by the line diagram of etch-pits. (fig. 9.12(b)).

The diagram clearly reveals the change in the orientation of

CAPTION TO FIGURES

Photomicrographs of etched as-grown a - face at 30° C

Fig 9.8	Etchant :-	2 drops 0.5 N NaOH in 10 cc amyl acetate liquid.
	Time :-	1 minute
Fig 9.9	Etchant :-	Formic acid 85%
	Time :-	5 minutes
Fig 9.10	Etchant :-	1 drop distilled water in 5 ml formic acid
	Time :-	1 minute
Fig 9.11	Etchant :-	1 part distilled water and 5 parts formic acid
	Time :-	1 minute
Fig 9.12	Etchant :-	Equal parts of water and formic acid
	Time :-	1 minute

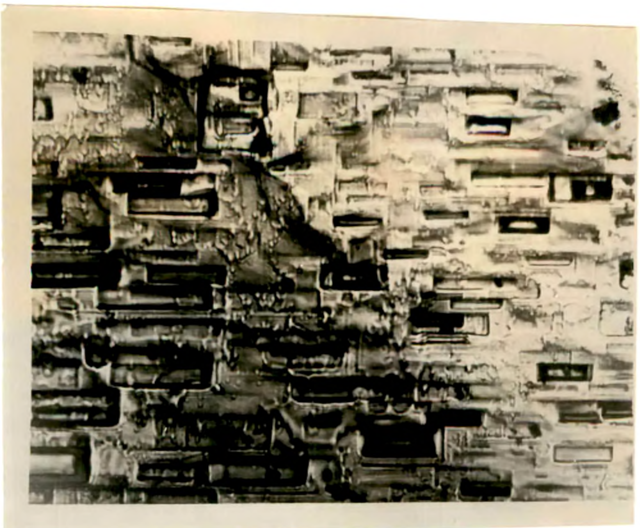


FIG.9.8

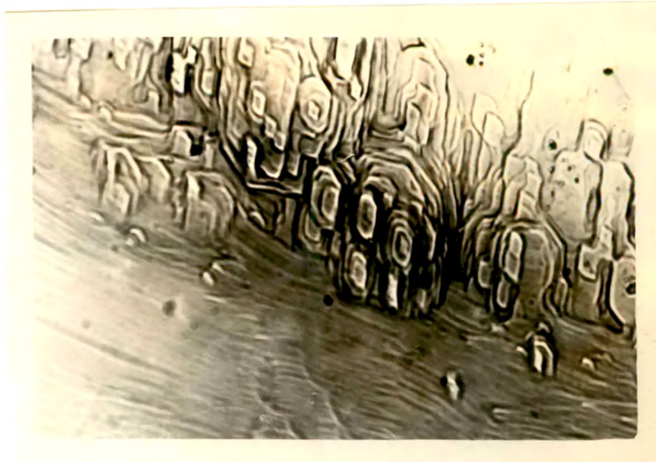


FIG.9.9

FIG.9.10

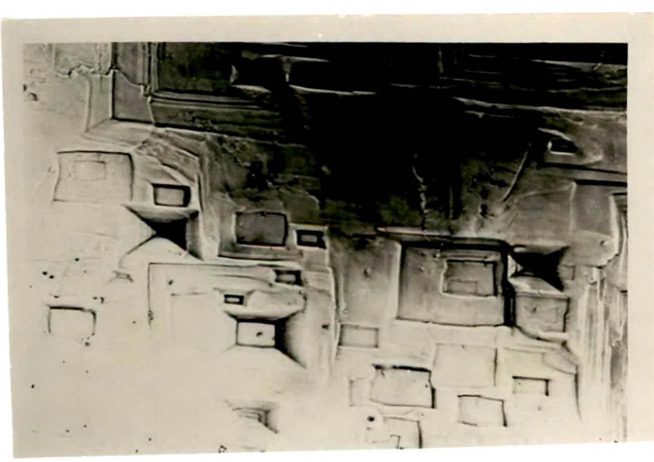


FIG.9.11

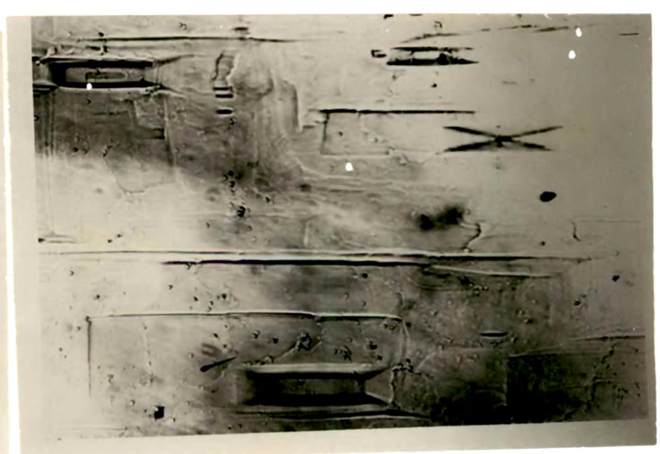
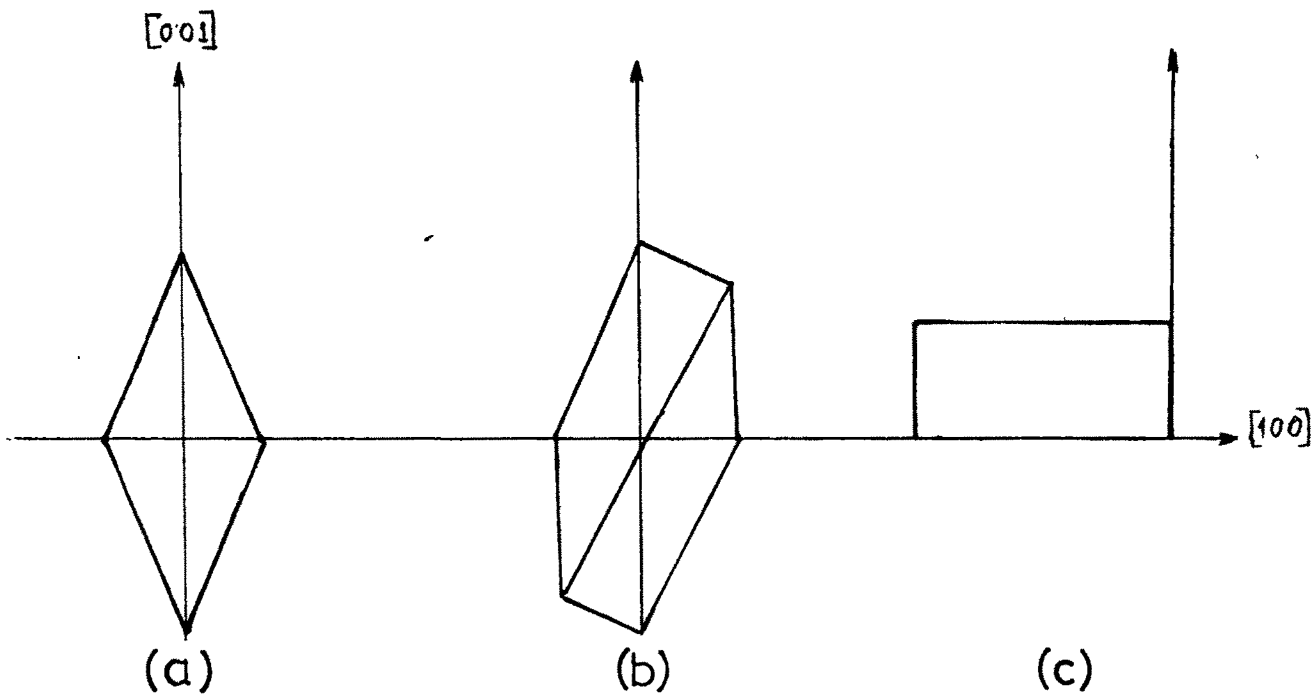


FIG.9.12

Fig 9.12 (b)

Line diagram of the different shapes of etch pits produced by varying quantities of formic acid in water.



etch pit on a-face. The gradual change in orientation is associated with the increase of distilled water in a fixed quantity of formic acid. It suggests the tendency for greater lateral dissolution. This change in orientation of an etch pit with a change in concentration and/or composition or both was observed for cleavage faces of LiF (23), NaCl (24) and Calcite (19) crystals. The explanations observed were offered on the basis of the anisotropic rate of chemical reactions. This is true in the present case also. The interesting point is the conversion of flat bottomed pits into point bottomed and conversely with the dilution of formic acid by water. This clearly indicates the existence of dislocation lines and loops of varying strength and angles termination on a-face.

(d) Glacial acid (Ch_3COOH) and saturated aqueous solution trichloro acetic acid, TCl_3 (T = C-COOH)

It is found form the individual use of the above acids that they react heavily with a-face. Eg glacial acetic acid produces striations with direction [001] on a-face whereas saturated aqueous solution of trichloro acetic acid corrodes the face and produces reaction product which remains on the face. The effect of pure water on a-face is already mentioned. This action will be highly accelerated, with the addition of TCl_3 in pure water etching of an cleavage face [010] of d-AHT crystals.

Etching on cleavage face (010) of d-AHT crystals:

The as grown faces of d-AHT exhibit surface features which are due to the two active processes viz. growth and dissolution, being in progress during the growth of these crystals in silica gel. Hence study of such faces could not differentiate in general the characteristic features, since growth and initial dissolution are reciprocal processes. It is therefore desirable to carry out micro topographical studies on surfaces which are free from inherent etch features forming a part on the as-grown faces. d-AHT has a perfect cleavage (010). Hence the topographical study of the controlled chemical dissolution of d-AHT cleavages by alkaline and acidic etchants is useful and reported here. The following etchants were used.

1. Alkaline etchants.
2. Acidic etchants.

Alkaline etchants.

Alkaline etchants namely ammonia solution of different specific gravities (0.91 to 0.99) (ii) ammonia solution in amyl acetate (iii) ammonia gas (iv) sodium hydroxide in (a) water and (b) amyl acetate were used to delineate features on a-face of d-AHT. The same set of etchants grouped under alkaline etchants were used in the present investigation.

It is observed that ammonia solution of specific gravity

0.91 diluted by the addition of varying quantity of distilled water produced striations on the cleavage surfaces within a few seconds. Fig. 9.13 (x 140) is a photo-micro-graph of a fresh cleavage face etched by etchant ammonia solution of specific gravity 0.99. The entire area is covered by striations almost parallel to each other and having direction [001]. The spacing between consecutive striations is varying; even the depth of valleys between striations is not constant. This was verified by light profile microscopy. The etching of cleavage face by dry ammonia gas made to pass over the surface at a constant rate for a few seconds, has produced heavy etching creating deep striations. This is expected in view of the accelerated chemical reaction between ammonia/ammonium hydroxide (Sp. Gr. 0.99) and cleavage surface. The above observations suggest that dry ammonia gas and ammonium hydroxide (greater than 0.99 sp. gr.) produces striations. Hence the quantity of water has noticeable effect on cleavage face. The photo-micro-graph (fig. 9.14 (x 140)) represents typical surface structure of a fresh cleavage face etched by ammonia solution of sp. gr. 0.91. Alongwith the striations etch pits are found scattered over the surface. The pits are having rectangular outlines bounded by sides with directions [001] and [100]. This is also found to be the case when a small quantity of ammonia solution was taken in amyl acetate. Fig. 9.15 (x 140) is photo-micro-graph of cleavage face etched by a solution containing 3 drops (1 drop ~ 0.016 ml) ammonia solution of sp. gr. 0.91 and 5 cc of amyl acetate for 15 seconds at room temperature. It is covered by a large number of rectangular flat bottomed and point bottomed etch pits of assorted sizes. There is a large amount of back ground micro pitting. It can be concluded from the above observations that ammonia solution (sp. gr. 0.91) produced pits whereas with increase in specific gravity of the solution these pits rapidly merge with each other and produce striations. The merging of the pits suggests that large amount of strain energy at the defect structure is released rapidly.

Acidic Etchants

This group consists of the following etchants:-

(i) Formic acid

(ii) Glacial acetic acid and saturated solution of trichloro acetic acid

Formic acid

Figures 9.16 (x 140) and 9.17 (x 140) are photo-micro-graphs of cleavage face etched by formic acid (85 %) at room temperature for 30 seconds and one minute respectively. Fig. 9.16 shows a large number of point bottomed rectangular etch pits, a deeply etched channel and a certain amount of micro pitting, whereas fig 9.17 exhibits a large number of rectangular etch pits with terraced structures. Compared to the rectangular etch pits produced by alkaline etchants, the present one produces rectangular etch pits which are mostly

CAPTION TO FIGURES

Photomicrographs of freshly cleaved surface (010)

etched at 30° C

Fig 9.13	Etchant :-	Ammonia solution (sp.gr. 0.91)
	Time :-	3 seconds
Fig 9.14	Etchant :-	Ammonia solution (sp.gr. 0.99)
	Time :-	3 seconds
Fig 9.15	Etchant :-	3 drops ammonia soln (sp.gr 0.91) in 5 cc amyl acetate liquid
	Time :-	15 seconds
Fig 9.16	Etchant :-	Formic acid
	Time :-	30 seconds
Fig 9.17	Etchant :-	Formic acid
	Time :-	1 minute

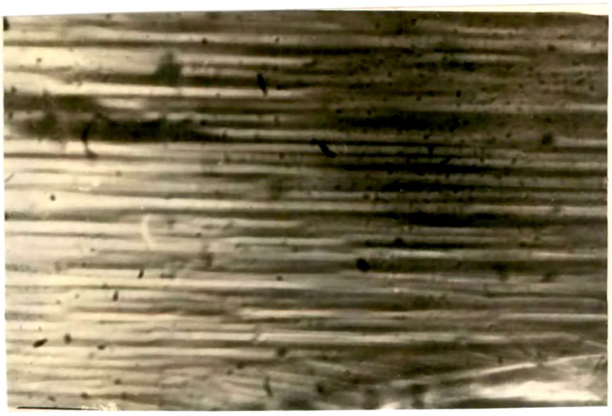


FIG 9.13

FIG 9.14

FIG.9.15

FIG.9.16

FIG.9.17

point bottomed and shortened along [001] and there is almost absence of striations. These observations indicate that with advanced etching by formic acid for more than a minute formation of striations should take place. Further with diluted acid, the formation of striations should be quicker. This is indeed found to be the case.

(ii) <u>Glacial acetic acid & trichloro acetic acid</u>

Saturated solution of trichloro acetic acid TCl_3 (CCl_3-COOH) was prepared in distilled water. This was used in conjunction with glacial acetic acid (CH_3COOH) as an etchant. TCl_3 solution acts on d-AHT cleavage surface and produces white precipitate which cannot be removed easily from the surface. Hence it could not be used alone. Further, the action of glacial acetic acid on d-AHT is poorer on cleavage face than that on a-face. Hence a suitable combination of glacial acetic acid (GAA) and TCl_3 should be able to produce useful etching. It was found from etching experiments that when the quantity of TCl_3 solution was less as compared to that of GAA in an etching solution, preferential attack at strained area/points is poor.

The ratios of TCl_3 solution to GAA tried for these observations are 1:0.5, 1:2 and 1:2.5. These do produce leaf-shaped etch pits (fig 9.18 (x 560)) on cleavage surface with the longer vein of leaf shape in the direction [201] (Table 9.1). For a constant temperature and time of etching, the lengths in the above direction are in the ratios

1:1:0.5. This indicates that with increasing quantity of GAA, there is a reduction of length in the direction [201]. It also suggests that the movement of ledge in this direction is influenced by the quantity of GAA present in the etchant.

When the quantity of TCl_3 solution and GAA are in the ratio as mentioned in the table 9.2 it is observed that rhombic etch pits are produced more at preferential points and less at other places; further the pit boundaries are comparatively sharper. These ratios of TCl_3 solution to GAA are as follows: 0.024:1, 0.032:1, 0.048:1, 0.096:1, 0.16:1. It is interesting to observe that

i) the longer diagonal of the rhombic pit (fig. 9.19, x560) has the same direction, viz. [201] as the one for the longer vein of leaf shaped pits (fig. 9.18 x 560)

ii) the etching solution with components in the above ratios produces pits at the same location. This is found by studying the oppositely matched cleavage counterparts.

iii) the shape of the etch pits remain unchanged for all the ratios mentioned above.

iv) the density of leaf-shaped etch pits produced by etching solution with ratios of components mentioned in Table 9.1 indicating more but fixed quantity of GAA solution in TCl_3 is less than those produced by etching solution with ratios of components mentioned in table 9.2. The sides of these pits are curved whereas the sides of rhombic pits produced by the etchant having proportion of components in the ratio mentioned in Table 9.2 are rectilinear.

v) curvilinear etch pits are due to irregular movement of ledges involved in the etch-pit formation, and the miller indices for direction of the curved sides will change from point to point along the curvature.

vi) the rhombic pits are due to systematic movement of ledges taking part in the formation of etch-pits.

vii) in the above cases, a cleavage surface is covered by large number of etch pits and certain amount of micropitting. The number of rhombic etch pits per unit area is on an average more than the number of leaf-shaped pits per unit area. This is found from the comparison of identical areas on cleavage counterparts, one etched by a solution with TCl_3 more, and the other with TCl_3 less in a fixed quantity of GAA.

viii) the increase of one component in the above etching solution produces either elongated leaf-shaped or elongated rhombic etch-pits along [201]. Further this elongation is accompanied by a lateral reduction along [102] in thecase of rhombic pits and a lateral increase for leaf-shaped etch pits both along [201] and [102]. This indicates that Tcl_3 solution has a dominant effect on the movement of the step along the directions, one parallel to and other perpendicular to [201], whereas GAA solution allows less movement of the steps in a direction perpendicular to [201].

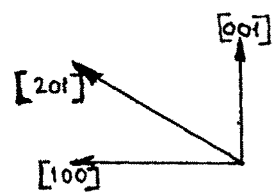
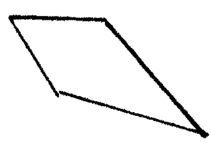
ix) A careful study of oppositely matched cleavage counterparts discloses that although for the above etchants, the matching is excellent, a reasonably geometrically well-defined etch pit is preferable to the unusually elongated pits. Keeping this main point in view, it is found that the etchants with ratios of TCl_3 to GAA as 0.032:1 and 0.08:1 are preferable. The successive etching of the same area of a cleavage face has produced etch pits at the same location and the shape, orientation and number of pits remain unchanged (figs. 9.20 a,b,c). In these photomicrographs the number density of bigger etch pits is constant and they are all point-bottomed pits.

x) The density of rhombic pits on an average taken from a study of large number of specimans is $7 \times 10^4/cm^2$ whereas the number density of leaf shaped etch pits is about $10^4/cm^2$. This indicates that the etchant containing more TCl_3 and less GAA in the ratios mentioned in Table 9.2 is superior in disclosing greater number of dislocations ending on the cleavage surface than the one having less $T\ l_3$ and more GAA (Table 9.1).

xi) A large number of specimens of oppositely matched cleavage counterparts were studied under normal and oblique illuminations attached with incident light microscope (cf.

Table 9.1

Different shapes of etch pits produced by varying quantities of GAA* in a fixed quantity of TCl_3** at 30° C on a cleavage surface of d-AHT for a fixed time(1 minute)

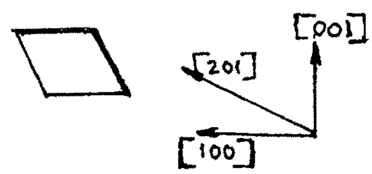
Quantity of GAA* in fixed qty(2ml) of TCl_3**	Ratio of the components of etchant (TCl_3**/GAA*)	Shape of etch pit	Diagonal length (microns)
1 ml	1 : 0.5	 	113
4 ml	1 : 2		89
5 ml	1 : 2.5		46

GAA* _ glacial acetic acid

TCl_3** _ trichloro_ acetic acid

Table 9.2

Different shapes of etch pits produced by varying quantities of TCl_3** in a fixed quantity of GAA* at 30°C on a cleavage surface of d-AHT for a fixed time(1 minute)

Quantity of TCl_3** in fixed qty of GAA*	Ratio of the components of etchants (TCl_3/GAA)	Shape of etch pit	Diagonal length (microns)
3 drops***	0.024:1		32
4 drops	0.032:1		76
6 drops	0.048:1		82
12 drops	0.096:1		121
20 drops	0.16:1		147

GAA* _ glacial acetic acid

TCl_3** _ trichloro_ acetic acid

Drops*** - (1 drop 0.016 ml)

CAPTION TO FIGURES

Photomicrographs of freshly cleaved surface (010)

etched at 30° C

Fig 9.18 — Etchant :- TCl_3 and GAA in the ratio 1 : 0.5

Time :- 1 minute

Fig 9.19 — Etchant :- TCl_3 and GAA in the ratio 0.032 : 1

Time :- 1 minute

Fig 9.20 (a,b,c) — Successive etching

Etchant :- TCl_3 and GAA in the ratio 0.08 : 1

Time :- 1,2 & 3 minutes respectively

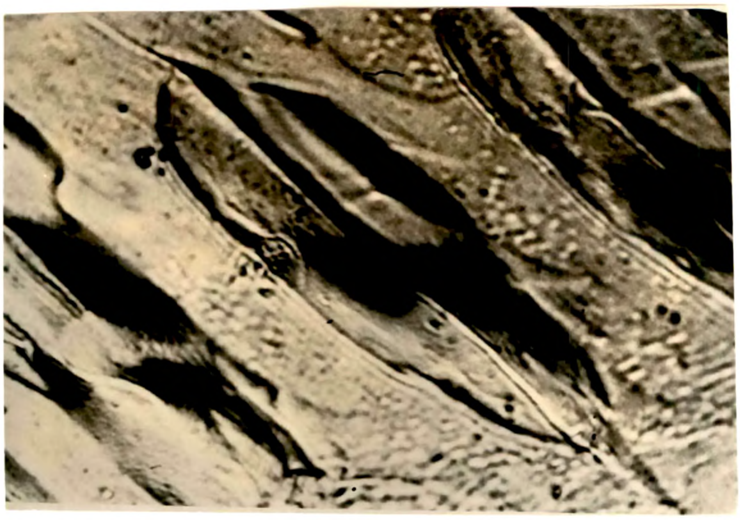


FIG.9.18

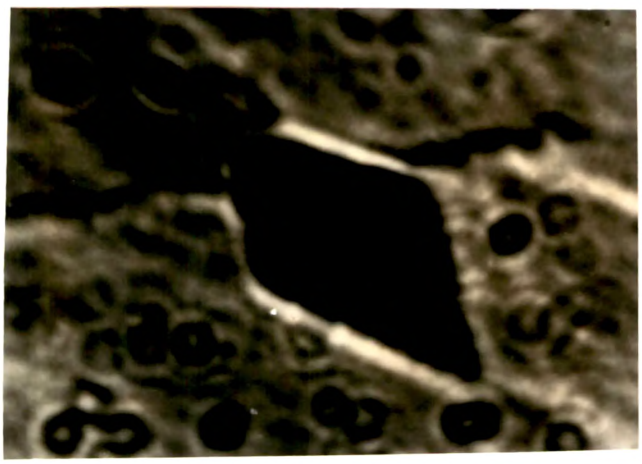


FIG.9.19

FIG.9.20a

FIG.9.20b

FIG.9.20c

Vickers Microscope, Chapter 2). It was found that the matching in all cases was excellent. A typical pair of oppositely matched cleavage faces with identical areas on the counterparts is shown in fig. 9.21 (b) (x140) and fig. 9.21 (a) (x140) exhibiting point-bottomed etch pits, matching in number, position and orientation. Fig. 9.21 (a) is a photomicrograph taken under normal incidence and fig. 9.21 (b) under oblique illumination. Under oblique illumination one side of the etch pit is fully exposed whereas under normal illuminations, all sides of the pits are equally exposed. It should be noted that the eccentricity of pits on opposite faces are almost equal. Further it is clear from the figures that the etchant reveals dislocations prominently and attacks very little other areas free from line defects.

xii) Etching of a-face and cleavage face by the above etchants and also distilled water produces striations on these faces. From a detailed study of such striations on prism and cleavage faces and also from a study of habit faces of d-AHT (cf. Chapter 4) it is crystal clear that the growth of a full-fledged orthorhombic disphenoidal crystal from a silica gel medium should consist of a large number of needles with their cross-sectional edges arranged in a particular manner to form the prism faces and sphenoidal faces. Accordingly a model is prepared (fig.9.24) showing the crystallographic directions, prism faces and sphenoidal faces.

xiii) Due to constraints in the laboratory facilities, the optical study of etched surfaces of d-AHT could not differentiate between the nature of dislocation etch pits.

Etching of z faces:

z-faces are enantiomorphous with one another. A fully grown orthorhombic disphenoidal crystal exhibits eight z-faces and eight prism faces (cf. fig. 4.6, Chapter 4). Out of eight z-faces there are two pairs of enantiomorphous faces - faces on top and four at the bottom. Since the faces are enantiomorphous, their etching and hardness characteristics are different. The d-AHT crystal faces, during their growth, were etched because of the presence of the acidic reaction product in the gel-solution and the z-faces are more etched than prism faces. Since the growth is faster as compared to the inherent etching, in the growth process, the d-AHT crystal grows. The reaction product depends upon the feed solution (cf. fig. 4.11, Chapter 4). For feed solutions, NH_4Cl, NH_4Br and NH_4I, the reaction products in gel-solution are HCl, HBr and HI respectively. HCl is the strongest amongst all in the acidic reaction. Photomicrographs [figs. 4.11 (a) and 4.11 (b)] strikingly reveal the etching effect on z-face (111). There are a large number of etch-pits, triangular in nature produced by HCl whereas HBr has not affected the growing z-face significantly. The growing d-AHT was taken out from the gel-solution after about a month. This also indicates the inherent competition between the growth and dissolution process going on simultaneously in the gel solution.

In this case, growth process is more dominant than etch process. However, due to dissolution, the size of z-face is comparatively smaller than prism faces. The data on knoop hardness numbers of different faces mentioned below can be correlated with etch rate. Harder is a face, smaller is the etch rate.

9.4 Indented Etched Surfaces of d-AHT:

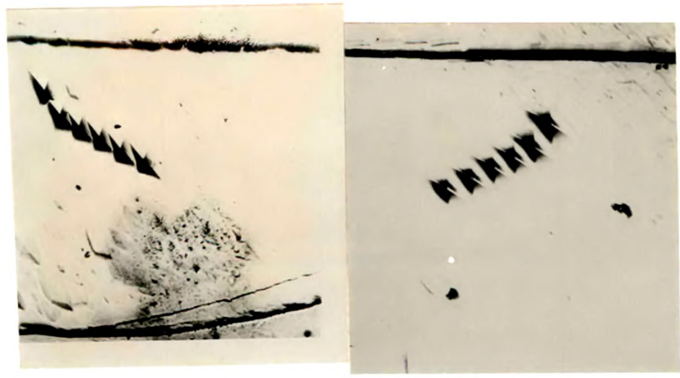
It is clear from a study of hardness of, a-face, cleavage face and z-face, that for a given applied load, the knoop hardness number has the largest value. Thus for a load of 80 gm in the high load region, the hardness numbers for different faces are as under:

Load	Knoop hardness number in Kg/mm^2		
(gm)	a-face	c-face	z-faces
	(100)	(010)	(111)/(TIT)
80	24.91	33.77	39.52/81.88

Thus the Z-face (TIT) face is the hardest among all faces of d-AHT. Figs. 9.22 (x140) and fig. 9.23 (140) exhibit photomicrographs of indented z-face and cleavage face etched by an etchant containing TCl_3 and GAA in the ratio of 0.08:1 for a minute respectively. The knoop indentation marks were heavily etched in both cases along with formation of a few etch pits which are triangular and elongated rhombic pits. The etch pits on indented z-faces are having the same outlines as those on natural as-grown z-faces.

CAPTION TO FIGURES

Fig 9.21(a,b)	Typical pair of oppositely matched cleavage faces with identical areas on counterparts
Fig 9.22 , 9.23	Photomicrographs of indented z -face and cleavage face respectively, Etchant :- TCl_3 and GAA in the ratio 0.08 : 1 Time :- 1 minute



(a) (b)

FIG.9.21

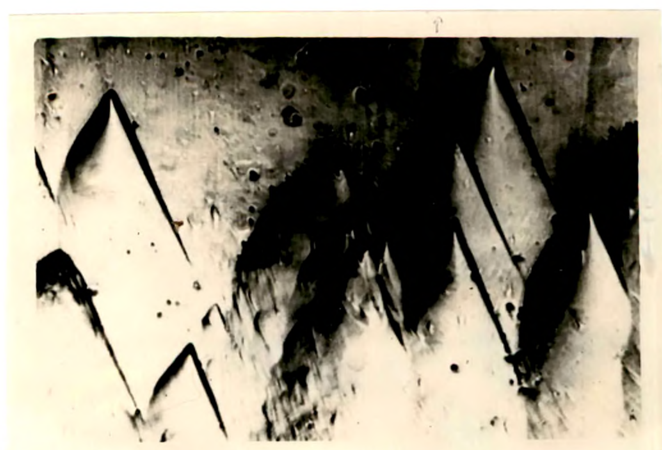


FIG.9.22

FIG.9.23

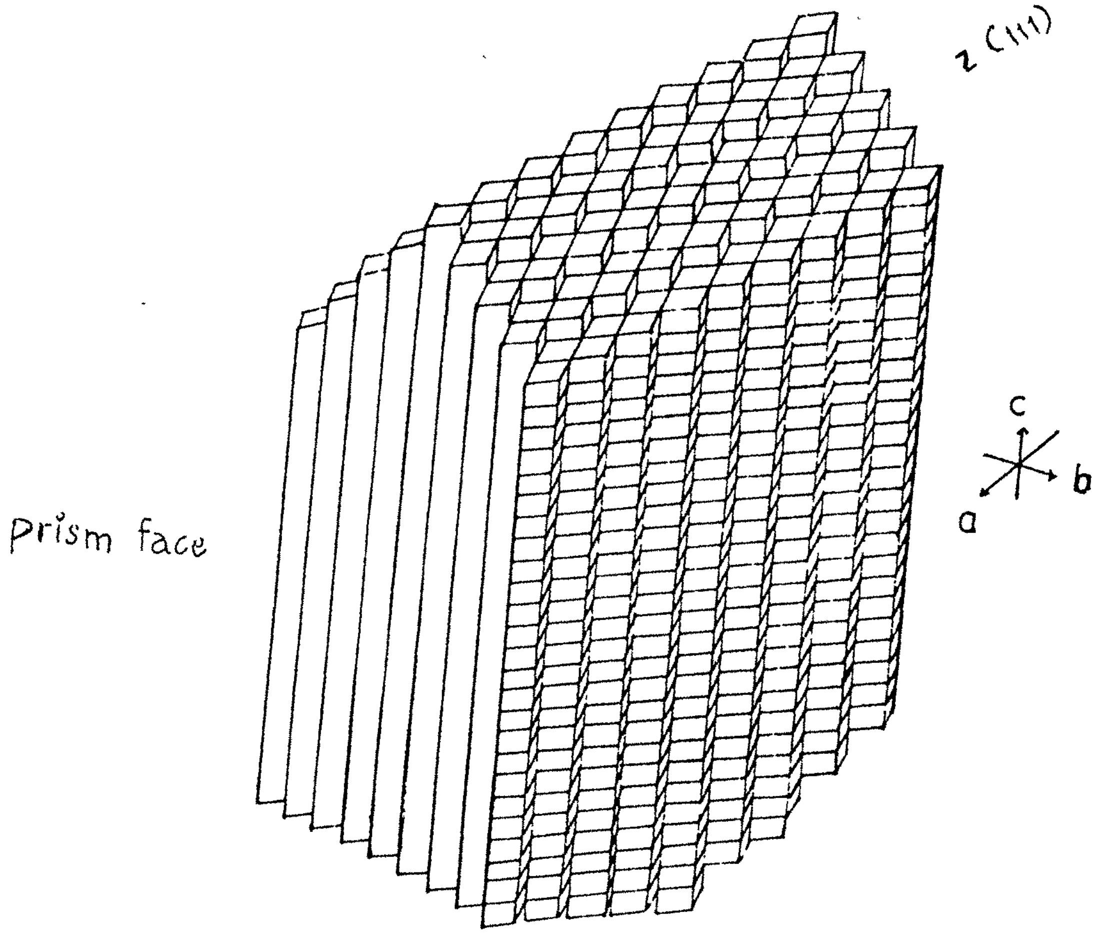


Fig. 9.24

9.5 Conclusions

It is clear from a close study of acidic and alkaline etchants used for different faces of d-AHT crystal that,

1. a) for as-grown a-face aqueous solution of sodium hydroxide (0.5N) is the best etchant for revealing characteristic etch features and

   b) for a cleavage face as well as as-grown z-face, the combination of trichloroacetic acid solution and glocial acetic acid, (so that trichloroacetic acid is less than glacial acetic acid) produces etch pits which retain their geometrically well-defined shape on prolonged etching.

2. The above etchants produce etch-pits which are at the sites of dislocations ending on the surface. The strengths of inclinations of dislocation lines are different not only on different faces, but also on the same face. Hence point bottomed etch pits which are formed at preferential points during the initial stage of etching becomes flat bottomed when the energy is reduced, indicating removal of dislocations from these points.

3. The dislocation density on a cleavage face is $7x10^4/cm^2$.

4. With acidic etchants, the pit shape on different faces, namely, a-face, cleavage face and z-face, changes with concentration of acid, whereas the etch pits produced by alkaline etchants on different faces retain their shape irrespective of the etchant concentration.

5. Glacial acetic acid acts differently on different faces, heaviest on a-face and poorest on z-face indicating that z-face is the hardest among all faces.

This conclusion supports the hardness studies of d-AHT faces. (cf. Chapter 7).

List of Tables

Captions to Figures

9.1 (a)Photomicrograph of Rectangular etch-pits on as-grown a face with sides along [001] and [100] with ammonia solution (Sp.Gr.0.91) as etchant for 3 Secs. at room temperature.

9.1 (b)Coalition of etch-pits on as-grown a-face (100) using ammonia solution (sp.gr.0.91) for 3 secs. at room temperature.

9.1 (c)Dark rectangular pits with square outlines formed with ammonia solution (sp.gr.0.91) for 3 secs. at room temperature, on as grown a-face.

9.2 (a)Etch-pits formed with ammonia solution (sp.gr.0.99) as etchant for 3 secs. at room temperature, on as grown a-face.

9.2 (b)Photomicrograph of etching of a crack on as-grown a-face ammonia solution (sp.gr.0.99) for 3 secs. at room temperature.

9.3 Photomicrograph of a-face etched by one drop (0.016 c.c) of ammonia solution in 10 c.c. of amyl accetate liquid for one minute at room temperature.

9.4 Line etching of as-grown a-face by dry ammonia gas for 3 secs. at room temperature.

9.5 Thin rectangular etch pits formed during removal of the reaction product in fig. 9.4 by distilled water for a second at room temperature.

9.6 Etching of as-grown a-face of d-AHT in distilled water for 3 seconds.

9.7 Successive etching of as-grown a-face by 0.5 N Sodium hydroxide solution for 5, 10, 15, 20 secs. respectively at room temperature.

9.8 As-grown a-face etched for a minute at room temperature by an etchant containing 2 drops (one drop = 0.016 cc) of 0.5 N NaoH solution in 10 c.c. amyl acetate liquid.

9.9 Rhombic pits on as-grown a-face with 85% formic acid as etchant for 5 mins. at room temperature.

9.10 A typical photomicrograph of as-grown a-face etched by an etchant containing 2 drops (one drop = 0.016 c.c) of distilled water in 5 ml formic acid (85%) for a minute at room temperature.

9.11 The as-grown a-face etched by an etchant containing 5 parts of formic acid with 1 part of water, for 1 minute at room temperature.

9.12 Flat bottomed rectangular etch-pits formed on as-grown a-face with an etchant containing equal parts of formic acid and water, for a minute at room temperature.

9.12 (b)A line diagram of the different shapes of etch pits produced by varying quantities of formic acid and water on as-grown a-face.

9.13 A freshly cleaved face of d-AHT etched by ammonia solution (sp.gr.0.99) for 3 secs, at room temperature.

References

1. Johnston, W.G. :
J. Appl. Phys. 27, 1018, 1952

2. Gilman, J.J. :
Trans. AIME 212, 781, 1958

3. Ives, M.B. and Hirth, J.P. :
J. Chem. Phys. 33, 817, 1960

4. Ives, M.B. and Mcaushand, D.D :
Surface Science, 13, 189, 1963

5. Urusovskaya, A.A. :
Sov. Phys. Cryst., 10, 437, 1963

6. Haribabu, V and Bansigir, K.G. :
Physica, 30, 2003, 1969

7. Raju, I.V.K. Bhagvan and Bansigir, K.G. :
J. Cryst. Growth, 11 (2), 171, 1971

8. Raju, I.V.K. Bhagvan, Sankaram, T, Bhima :
J. Phys. D. 3(12), 1796, 1970

9. Sangwal, K and Patel, T.C :
Kristall and Technik, 13, 281, 1978

10. Popkova, E.G., Predvoditelev, A.A :
Kristallografiya, 15(1), 97 (Russ) 1970

11. Popkova, E.G. Matveeva, G.S.
and Predvoditelev, A.A. :
Kristallografiya, 53 (Russ) 1969

12. Bhatt, V.P. Vyas, A.R. and Pandya,
G.R. Ind. J. Pure Appl. Phys. 12, 807, 1974.

13. Johnston, W.G. Prog. in Ceramic
Sci. 33, 21, edt. by J.E. Purke (Pergamon Press) 1962.

14. Robinson, W.H. :
Techniques for the Direct Observation of Structure
and Imperfections, John Wiley & Sons, Inc. NY 1968

15. Sangwal, K :
Etching of Crystals, Theory Experiment and Application
(Defects in Solids, Vol.15), Elsevier Science, Publishers
1987

16. Watt, H.
Nature (London), 163, 314, 1959

17. Stanley, R.C. :
Nature (London), 182, 1958

18. Pandya, N.S. and Pandya, J.R.:
Journal of M.S. University of Baroda, 10, 21, 1961

19. Mehta, B.J. :
Ph.D. Thesis, M.S. University of Baroda, Baroda, 1972

20. Shah, R.T. :
Ph.D. Thesis, M.S. University of Baroda, Baroda 1976

21. Bhagia, L.J,:
Ph.D. Thesis, M.S. University of Baroda, Baroda 1983

22. Shah, A.J.:
Ph.D. Thesis, M.S. University of Baroda, Baroda 1984

23. Ramachandran, T.R.; Ives. M.B.,:
J. Appl.Phys., 38, 3675, 1967

24. Haribabu, V; Bansigir:
J. Phy. Soc. Japan, 23, 860, 1967