CHAPTER - 7

CHEMICAL ETCHING OF ALKALI HALIDES

7.1 INTRODUCTION :

When a crystal is attacked by an appropriate solvent which chemically or physically dissolves it, the initial dissolution begins at certain preferential points. This phenomenon is known as etching, which is as old as the art and science of metallography. It gives rise to various types of geometrical features on a crystal surface. The production of conical depressions with regular geometrical outlines on crystal surfaces are usually known as etch pits, etch figures or etch marks. The form and symmetry of etch pits were used by mineralogists to determine crystal planes and their orientation with one another. At that time the production of etch pits on a crystal surface was not understood satisfactorily. Dissolution on a crystal surface is now thought to occur by retreat of mono molecular steps, being reverse to that of growth, which takes place due to the motion of steps on a surface; It is believed that when a crystal is exposed to a solvent, the dissolution usually begins by a nucleation of unit pit of one molecular depth at relatively weak spot on the surface. The unit pit grows as steps retreat across the crystal surfaces through the action of kinks.

The understanding of etch phenomenon was enhanced by the recognition of various types of imperfections in a crystal. The defect points are relatively weakly bound with the crystal surface. They used less energy to dissociate than that required by points (atoms) in regular structure. If chemical or physical change gives sufficient energy to dissociate imperfections from the exposed surface, etch pits or etch figures are observed on it. It is not necessary that the solvent should be present at the time of etching, other appropriate physical conditions such as ionic bombardment, temperature, etc., also help to form etch pits at preferential points on a crystal surface. Following are the ways of obtaining preferential dissolution on a crystal surface : i) Chemical Etching ii) Thermal Etching iii) Ionic Etching iv) Electrolytic Etching and v) Etching by dehydration.

The chemical etching usually gives a few or all features on a crystal surface mentioned below : i) Etch pits, terraced, flat-bottomed and point-bottomed. ii) Shallow pits, pits with beaks. iii) Linear etch rows and intersecting etch rows. iv) Tunnels and dendritic etch figures. v) Etch hillocks, vi) Etch spirals and vii) Irregular Etching.

7.2 DISLOCATION DELINEATION BY ETCHING :

The study of topographical features on crystal surfaces has assumed increasing importance due to the information it provides for defect structure and under favourable circumstances the history of the growth of crystals. There are several methods of studying surface for revealing dislocations ending on the surface. They are i) Etching technique, ii) Decoration method, iii) X-rays, and iv) Electron microscopy.

Important experimental studies on microtopographical features were made by utilizing the above techniques.

The number of papers published on observations of dislocations under controlled dissolutions of the above types is so large that it is impossible to do justice to each one of them in a few pages. It should be emphasised that all methods mentioned above have contributed and are still contributing valuable information on dislocations in crystals.

7.3 FORMATION OF VISIBLE ETCH PITS :

The formation of visible etch pits on a crystal surface depends on the kinetics of dissolution ledges as they move across the surface during dissolution. For formation and better quality of etch pits, the conditions are as follows :

$$10 \geqslant \frac{v_1}{v_n} \quad \text{and} \quad v_{nd} > v_{ndf} \;, \quad \frac{E_t}{E_s} > 1$$

where v_1 is lateral or ledge dissolution velocity parallel to surface and v_n is normal dissolution velocity ; v_{nd} is normal dissolution velocity at a dislocation and v_{ndf} the average vertical dissolution velocity of a dislocation free portion of the surface; E_t is the active energy for tangential movement of steps away from dislocation and E_s is activation energy for surface dissolution.

7.4 APPLICATION OF ETCH TECHNIQUE :

Etch technique is a simple and powerful method and under favourable circumstances gives information on kind, configuration inclination and density of dislocations and various properties controlled by them. Thus it is used to study 1) Stress velocity for individual dislocations,

2) deformation patterns like pile ups, polygonal wells, 3) configuration of dislocations in as-grown crystals, 4) dislocation multiplications and movements, 5) fresh and grown-in dislocations, 6) plastic flow around dislocations, 7) radiation hardening, 8) fracture and dislocations, 9) polarity of crystal lattice, 10) reaction mechanism, 11) grain boundaries. Besides review articles on etching, excellent accounts of the technique are given by Robinson (1968) and Sangwal (1978)/1,2/.

7.5 CHEMICAL ETCHING OF CLEAVAGE FACES OF NaCl, KCl & KBr : Etching of NaCl cleavage faces.

The present work is taken with the purpose of delineation of dislocation etch pits, their characteristics, study of rosette pattern and correlation with the hardness studies of the cleavage faces of NaCl, KCl and KBr. Quite a sizeable amount of work on etching of the ionic crystals in general and of cleavage faces of NaCl, KCl and KBr in particular is now available. The etchants employed by various researchers are given in Table-I. After several trials, etchants are developed. A saturated solution of lead chloride in Methanol for NaCl cleavages and a mixture of 95 % Isopropyl Alcohol and 5 % doubly distilled water/ 14/ saturated with $PbCl_2$ for cleavage faces of KCl & KBr were used for controlled etching of crystal cleavages. The etched samples were rinsed by ethyl ether and then dried by hot air blower.

Freshly cleaved surface of NaCl etched in the above etchant for 30 sec. was subsequently rinsed and dried. A typical photomicrograph (fig. 7.1) exhibits the characteristic features of the etched cleavage surface. It consists of symmetrical pyramidal etch pits which are dark, thereby indicating that the pits have considerable depth. They are of identical sizes and the amount of micropitting is very much less. Etching also reveals grain boundaries of different types. The boundary AB as shown on the left side is formed by etch pits stacked in a row in such a manner that their depth points are joined in forming a line. The boundary BC on the right side consists of a channel with the clustering of etch pits on and near the channel walls. The boundary BD in the upward direction is not smooth. It consists of broken segments formed by etch pits. The background of the figure consists of a series of fine slightly blackish parallel lines, (e.g. PQ) running almost diagonally in the figure. These are likely to be slip lines revealed by etching. Further increase of etching by the 30 sec. of the same area shows (fig. 7.2) the increase in size of the etch features of fig. 7.1. All boundaries are heavily etched and the fine lines are disclosed better with the tips of pits on them. Fig. 7.3 and 7.4 are the photomicrographs of the same area successively etched for a further period of 30 secs. each. Thus the photomicrographs (figs. 7.1, 2, 3, and 4) represent a typical area on a cleavage face successively etched four times with the etching time 30 secs. each. All photomicrographs revealed the following :

1) The deep pyramidal black etch pits with boundaries along [100] and [010] directions enlarge on multiple etching.
2) No new pits are formed on successive etching i.e., the pit density is constant.
3) Micropitting is almost absent.
4) The size, shape, location, number and orientation of etch pits remain unchanged on successive etching.

5) The boundaries which are likely to be grain boundaries increase their sizes on multiple etching.

6) The scars of fine lines become thicker on etching. The tips of etch pits are on same lines. The lines appear to be slip lines revealed by etching.

Figs. 7.5 and 7.6 are the typical photomicrographs of oppositely matched cleavage counter parts of NaCl etched in the above etchant for 1½ minutes. A close examination of these figures revealed the following :

i) Perfect matching of etched cleavage cracks.

ii) Matching of dark etch pits is almost perfect as compared to light pits.

iii) Etching time is so short that during the act of rinsing and drying small pits are formed on both the counter parts.

iv) There are certain irregular features, likely to be due to post-etching treatment.

v) Micropitting is almost absent.

From the qualitative study of successive etching of a cleavage surface and matching of cleavage counter parts, it can be said that the etch pits are at the emergent sites of dislocations on the surface under observation. Fig. 7.7 is a photomicrograph of a freshly cleaved surface of NaCl etched for 15 secs. and indented along the direction $\langle 110 \rangle$ under a load of 80 gm. The etched and indented surface was reetched in the above etchant for a further period of 10 secs. The photomicrograph reveals bigger and smaller dark etch pits with indentation mark etched accompanied by a cluster of small light etch pits. The diagonal of etch pits are along $\langle 110 \rangle$ directions, along with the primary slip lines.

The photomicrograph (fig. 7.8) represents a cleavage surface etched by the above etchant for 15 secs., indented and reetched for 10 secs. The diagonal of the indentation mark produced by 40 gm load is along $\langle 100 \rangle$ direction. The figure depicts a perfect rosette pattern consisting of dark etch pits with diagonals making an angle of 45° (or 135°) with the major diagonal of the indentation mark. Further there are four etch wings along directions $\langle 110 \rangle$ and containing a very large number of small light etch pits. It is apparent that a very large number of slip lines, giving rise to slip bands are etched with tips of etch pits along these bands, giving rise to a fairly trimmed etch pit forest. It is also interesting to observe that in these trimmed clusters of etch pits, big dark pits are not observed, except near the boundaries. Further at the sharp narrow ends and also along broad ends of the indenter along directions $\langle 100 \rangle$, the short ends of wings form a v-shape. In the absence of linear arrays of pits along directions $\langle 100 \rangle$, it can be concluded that the onset of secondary slips is not realised. The photographic comparison of figs. 7.8 and 7.7 suggests the photomicrograph (fig. 7.7) to be of poor quality.

Etching of KBr cleavage faces

Freshly cleaved surface of KBr was subjected to multiple etching (figs. 7.9, 10,11 and 12) by a composite etchant containing 95% isopropyl alcohol and 5% of distilled water saturated with lead chloride for 30 secs. 60 secs., 90 secs. and 120 secs. at room temperature. The boundaries of square pits on the surface are along $\langle 100 \rangle$ directions and diagonal along $\langle 111 \rangle$ directions. The photomicrograph (fig. 7.9) reveals a series of cleavage lines, a grain boundary and large number of etch pits of assorted sizes, likely to be due to small error in adjusting etching times. Successive etching increases the sizes of etchs pits without a change of their shape, number, location, orientation and dissolves the cleavage ledges with their gradual disappearance and the conversion of grain bounary into a channel with small etch pits at the channel walls. Figs. 7.13 and 7.14 are the oppositely matched cleavage counter parts simultaneously etched for 2 minutes in the composite etchant mentioned above. There is a perfect correspondence of etch features, viz. i) grain boundaries ii) dark etch pits iii) light etch pits of small and smaller sizes iv) a series of parallel slip lines along $\langle 110 \rangle$ directions. In addition to the etch features revealed by multiple etching, the correspondence of features on oppositely matched cleavage faces clearly indicate that the etch pits are at dislocations ending on the surface. The etching of cleavage faces of KCl had also unfold more or less the same types of etch features.

The above sets of observations on etching of NaCl and KBr cleavage faces by different etchants (wide Table-7.1) have been made by a number of workers. The present work is done with the purpose of obtaining evidence (1) to support for the degree of plasticity of NaCl, KCl and KBr cleavage faces for different orientations and for different quenching temperatures and room temperature (2) to determine quantitative relations between lengths of etch wings, applied loads, orientations and temperature (3) to determine new slip systems, if any (4) to correlate quantitatively anisotropic hardness with density of etch pits, wing lengths etc. However these objectives could not be qualitatively and quantitatively fully realised. The present study simply confirms the existence of primary and secondary slip systems along directions $\langle 110 \rangle$ and $\langle 100 \rangle$ and supports the conclusion obtained in Chapter IV for considering directions $\langle 110 \rangle$ to be reference directions and not $\langle 100 \rangle$. It also suggests in a qualitative manner the role played by old dislocations in the as-grown crystals and new dislocations created by indentations. It also reveals the limitations of optical and also of etch techniques.

TABLE - 7.1

CHEMICAL ETCHING OF NaCl, KCl and KBr

No.	Crystal and plane	Composition of etchant	Etching time	Temp. of etching	Shape of eatch pit	Remarks and references
1.	NaCl(100)	Methanol containing NH_4Cl	-	Room temp.	-	Etch pits displaying oriented overgrowths./3/.
2.	NaCl(100)	Ethyl alcohol+$CdCl_2$	-	-	-	The effects of under saturation, temp.and stirring were studied. The results are not consistant with the theoretical predictions. /4/.
3.	NaCl(100)	Ethyl alcohol+$HgCl_2$	-	-	-	A detailed study by varying the poison ratio is reported /5/.
4.	NaCl(100)	Methanol (& ethanol) + $HgCl_2$,$PbCl_2$ & $CaCl_2$	-	Room temp.	-	Terraced etch pits are produced /6/.
5.	NaCl(100)	Methanol+$CdCl_2$	-	Room temp.	-	Produces beaks at aged dislocation sites /7/.
6.	NaCl(100)	Glacial acetic acid + $FeCl_3$	-	-	-	Small traces of water in the etching solution shortens the etching time and produces more shallow pits /8/.

Cont.....

Cont......

7.	NaCl(100) KCl(100) KBr(100)	Ethyl alcohol containing .5% of water + lead acetate	30 mins.	Room temp.	Square pits	The poison concentration has no effect in the orientation of etch pits for NaCl & KCl whereas for KBr it changes from ⟨100⟩ to ⟨110⟩ with change in concentration of the inhibitor/9/.
8.	NaCl(100) doped with $CaCl_2$	Methyl alcohol (saturated with NaCl) with $CdCl_2$ 2.5 mg/cm^3	-	Room temp.	Pyramidal pits of ⟨110⟩ orientation	/10/.
9.	KCl(100)	Glacial acetic acid with methanol in the volume ratio 1:1.	5 mins.	Room temp.	Octagonal & circular etch hillocks	Hillocks nucleate due to the dissolution process and have nothing to do with- dislocations /11/.
10.	KCl and KBr(100)	Freshly distilled methanol+$PbCl_2$	1-5 min.	Room temp.	Octagonal etch pits	/12/.
11.	KCl(100)	Freshly distilled methanol +.01 mg/cc of $CdCl_2$.	3 and 5 sec.	Room temp.	-	/13/.
12.	KBr(100)	95% isopropanol +5% water by volume + $PbCl_2$.	½ min. to 2 min.	Room temp.	Pyramidal	/14/.

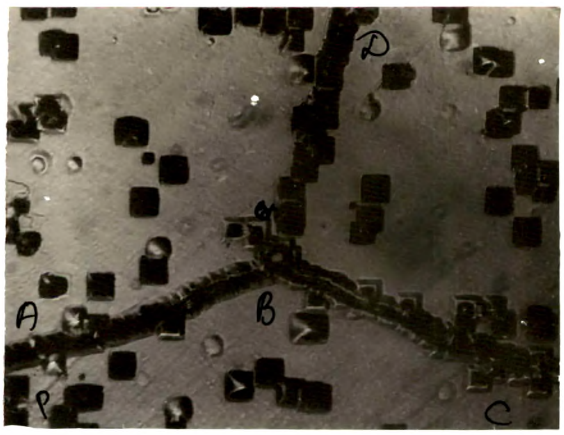

FIG. 7.1

FIG. 7.2

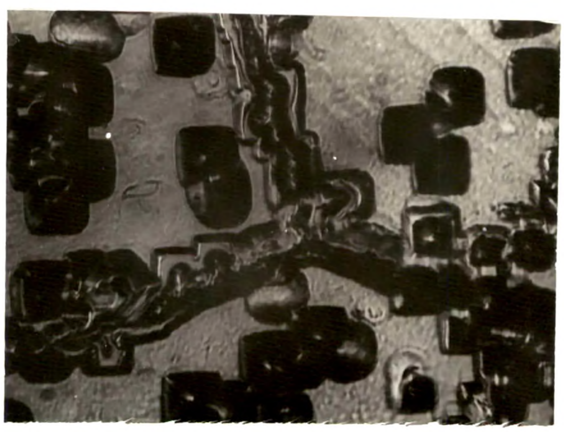

FIG. 7.3

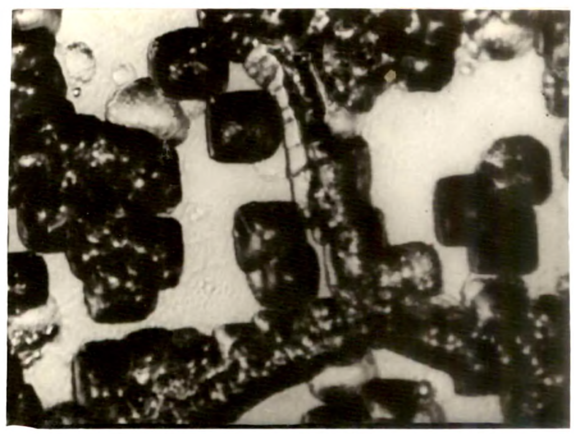

FIG. 7.4

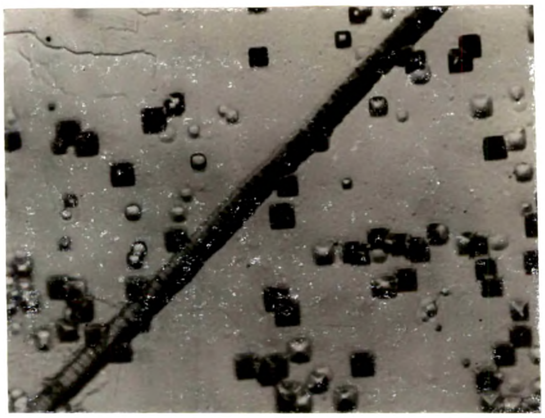

FIG. 7.5

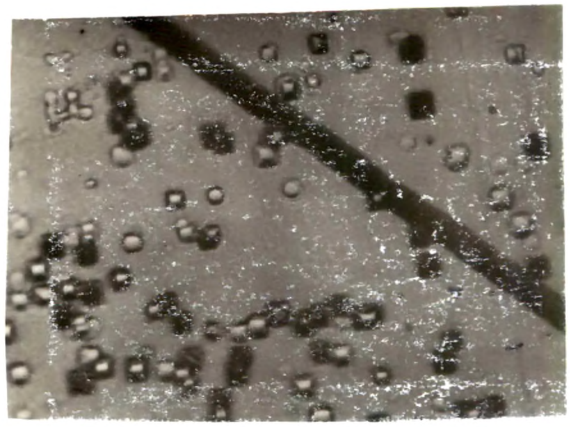

FIG. 7.6

FIG. 7.7

FIG. 7.8

FIG. 7.9

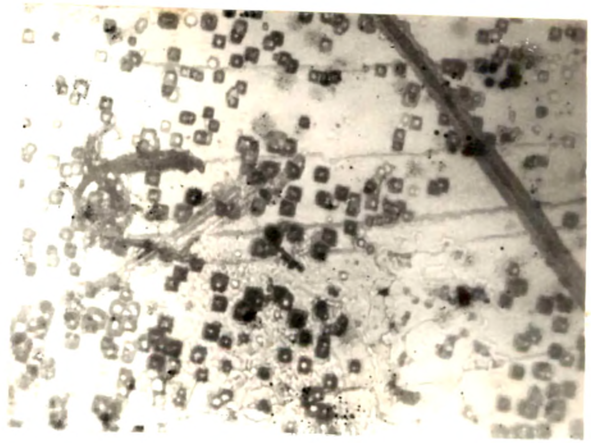

FIG. 7.10

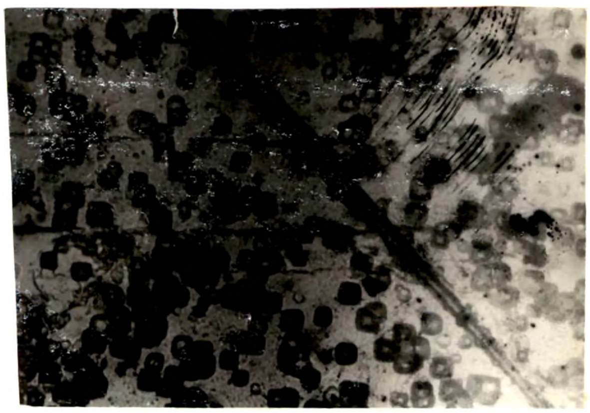

FIG. 7.11

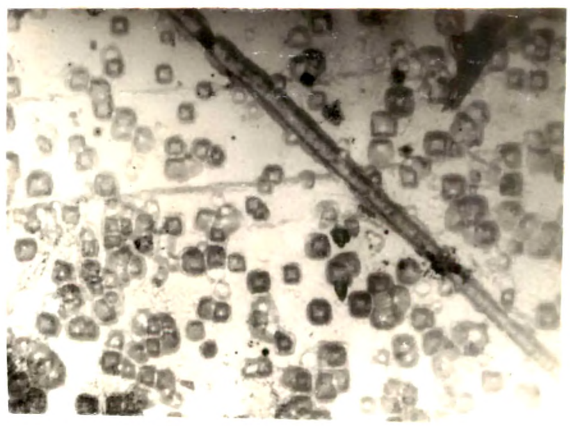

FIG. 7.12

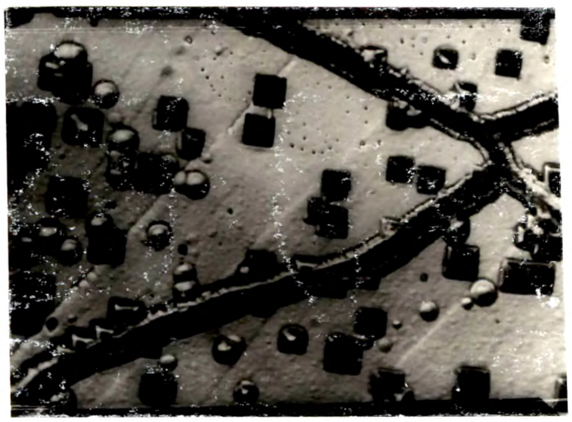

FIG. 7.13

FIG. 7.14

CAPTION TO FIGURES

1. Fig. 7.1, 7.2, 7.3 & 7.4 (x240) Successive etching of NaCl, 30, 60, 90, & 120 Sec.

2. Fig. 7.5 and 7.6 (x240) Matched cleavage planes of NaCl simultaneously etched for 30 Sec.

3. Fig. 7.7 (x240) Etched (15 sec.) surface indented with a load of 80 gm along <110> and reetched for further 10 Sec.

4. Fig. 7.8 (x240) Etched surface (15 sec.) indented with a load of 40 gm along <100> direction and reetched for further 10 sec.

5. Fig. 7.9, 7.10, 7.11 & 7.12 (x140) Successive etching of KBr 30, 60, 90 & 120 Sec.

6. Fig. 7.13 and 7.14 (x240) Matched cleavage planes of KBr simultaneously etched for 120 Sec.

REFERENCES

1. Robinson, W. H., "Tech. for the Direct Observation of structure and imperfections" (John Wiley & Sons, Inc., N.Y.)(1968).

2. Sangwal, K. and Patel, T.C., Kristall and Technik, 13, 281 (1978).

3. Lingschit, J. and Gethardt, M., Semicond. and Insul. (G. B.), 2, 209-219 (1977).

4. Shrivastava, A. K. and Bansigir, K. G., Surf. Tech. (Switzerland) 26, 153-63 (1983).

5. Bhagavan Raju, I. V. K. and Bhimasankaran, T., Cry. Res. and Tech.(Germany) 21, 33-37 (1986).

6. Koziijowska, A. and Sangwal, K., Cryst. Res. and Tech. (Germany), 21, 641-6 (1986).

7. Bhagvan Raju, I. V. K., Haribabu,V. and Bansigir, K.G., J. Phys. D. Appl. Phys., 5, 774-776 (1972).

8. Bhagavan Raju, I. V. K., J. of Cry. Growth, 35, 318-20 (1976).

9. Haribabu, V. and Bansigir, K. G., J. of Appl. Phys., 40 (1969).

10. Bhimasankaran, T. and Bhagvan Raju, I. V. K., J. of Cry. Growth, 43, 267-269 (1978).

11. Patel, A. R. and Chaudhari, R. M., Ind. J. Pure and Appl. Phys., 14, 494-6 (1976).

12. Haribabu, V., Subha Rao, U. V. and Venkata Ramia, K., Phys. Stat. Sol. (a), 28, 269 (1975).

13. Lakshmipathi Rao and Haribabu, V., Ind. J. Pure and Appl. Phys., 14, 769-771 (1976).

14. Acharya, C. T., Ph. D. Thesis, M.S. University of Baroda, Baroda (1978).