CHAPTER 11

DISSOLUTION KINETICS AT DISLOCATION SITES

11.1 Introduction

The dissolution kinetics at defect centres on crystal surfaces are such that sometimes it may lead to changes in the orientation, morphology and position of the etch pits. Many workers of various laboratories have observed these changes on different crystals and attributed these to the different parameters involved in the etching conditions. These parameters are mainly, the type of etchant, concentration, impurities, time of etching, temperature and finally the structural deformation of the crystal.

The credit of being the first to report change in orientation of etch pits on (001) plane of lithium fluoride goes to Gilman and Johnston (74). During the investigation of etchants to reveal and distinguish between fresh and grown in dislocations, they were successful in preparing two types of etchants namely acidic and neutral etchants. Their published photographs of etch pits on match faces with these two etchants show change in orientation of etch pits on the two surfaces. Since their main interest was to assess the ability of the etchants to distinguish between fresh and grown in dislocations, they did not give due attention to this unusual behaviour of the pits. Ives (87) later simplified the acidic etchant of Gilman and Johnston, by adding the acidic etchant in increasing volumes to the neutral
etchant, and was able to gradually change the morphology of the pits and their orientation. He explained the different etch figures on the basis of little inhibition and greater inhibition of the etchants.

Kostin et al (194) used the concept of microstructures to explain the different etch figures observed on NaCl cleavages, saying that the density of fractures along the $<110>$ and the 100 direction varies with temperature and this variation is responsible for the change in etch pit morphology. Temperature dependence on the etch pit morphology have been studied by Evan et al (195) on diamond, Hughes et al (196) Thomas et al (197) on graphite crystals. Patel et al (198) studied the variations in orientations on barium fluoride cleavages with change of concentration and temperature. It was conjectured that these variations were due to different activation energies along the steps of different directions.

The effect of concentration and impurity on the rotation and morphology of etch pits have been investigated at large in NaCl crystal than any other crystals by different workers (199),(194),(186),(220),(201),(202). Among them, the works of Haribabu et al (200),(201),(202) are noteworthy. On the basis of an ideal etch pit model of Ives (87) consisting of ledge and kink surfaces, Haribabu and co-workers argued that the ultimate shape of the etch pit is defined by the slowly moving ledges followed by etching. The relative
dissolution velocities of the ledges depend upon the complexes present in the stagnant layer of the etchant very close to the surface. Bhagavan Raju et al.\(^{(95),(203)}\) pursued the work on NaCl and an attempt has been made to investigate the nature of the complexes responsible for etching, by measuring the conductivity of the etchant close to the crystal surface. Among the other noted works on the variation of the morphology of etch pits due to change in concentration are due to Katsuhiro Kawabuchi et al.\(^{(204),(205)}\) on silver and Patel et al.\(^{(206)}\) on calcium fluoride crystals. Joshi et al.\(^{(182)}\) studied the rotation of etch pits by changing the concentration of etchants on apophyllite crystal and related this to the growth mechanism. Toshio Suzuki\(^{(207)}\) using a constant etchant, effected the rotation of etch pits on \((110)\) surface of silver by changing the etching time gradually.

In the absence of reported works on these aspects of etching, in this chapter a brief account of the works done on the change of orientation and morphology on \((001)\) and \((111)\) cleavage surface of lead molybdate crystal grown by pulling method, is given.

11.2 Rotation of etch pits

The \((111)\) match cleavage surfaces of lead molybdate crystals were taken and one flake was etched in nitric acid and the other in sodium hydroxide. Figs. (69 a), (69 b) are the etch figures on these match cleavages. Similarly
(001) cleavages were etched in the above mentioned etchants and the etch patterns are shown in (64 a) and (64 b). The square pits were rotated through 22.5° on the (001) face, similar to that observed on the gel grown crystal. The orientations of the triangular pits on (111) face were rotated through 45° in the same etchants and conditions. The activation energies of the etchants are different and therefore their resistivity to attack the edges of the growth layers, parallel to the sides of the prism forms will be different. Accordingly as discussed previously, the orientation of the pits can change. The two dimensional layer spreading process parallel to (001) plane, followed by the truncation mechanism of different prism forms during growth, will produce different edges of growth layers in different crystallographic planes. The edges of the growth layers thus formed on (111) planes can also have different resistivities to the different etchant and hence the observed change in orientation of the pits.

11.3 Effect of concentrations of the etchants on the morphology of etch pits

A set of experiments were conducted to see whether impurities play any role in bringing about the change in orientation of etch pits on these faces. Measured quantities of impurities were added in the etching solutions. While
selecting impurities, the atomic size of the impurity atoms, which makes the inhibition and enhancement of step motion possible, should be comparable to the size of the constituent atoms of the crystal. The impurities tried were nitrates and chlorides of calcium, barium and cadmium. By adding different amount of such impurities, no change in the shape and orientation of pits occured. The same was the case with the change of temperature and time of etching.

Different concentration of etchant were used to see the etching behaviour of the lead molybdate cleavages. No change in orientation of etch pits was observed.

The idea of producing an effective change of morphology of etch pits using various concentrations of nitric acid and sodium hydroxide came from the results of the activation energies of the two etchants for different concentration (Table-12). Change of concentration of the etchants, changed the activation energies of the etchants and it was anticipated that it will produce some changes in the etch pit morphology also. So systematic experiments were conducted by selecting various concentrations of nitric acid for (001) surface and sodium hydroxide for (111) surface. Figs. (71), (72), (73) and (74) show the morphology of the pits on (001) face, when the concentration ratio of the nitric acid (HNO₃:H₂O) was 1:1, 1:3, 1:5 and 1:7 respectively. When the concentration ratio was decreased, the circular pits were changed to square pits with bent sides (Figs. 71 and 72) for the same time of etching. Further reduction of concentration
changed the bend edges of the square pits in to straight edges. (Figs. (73) and (74)). It is to be noted that when the concentration was decreased the linear size of the pits decreases. This may be due to the lesser activation energies of the etchants at lower concentration (Table-12). Figs. (75), (76), (77) show the morphology of the pits on (111) face when etched with 2N, 1.5N and 1N sodium hydroxide solution respectively. Here also the sides of the triangular pits were bending in the beginning and later on straight edges were formed when the concentration was reduced. But the linear sizes of the pits increased as the concentration was decreased for the same time of etching. For sodium hydroxide, since the activation energy decreases when the concentration was increased, there can be the possible smaller size of the pits and vice versa.

11.4 Conclusion

The conclusions that can be drawn from these investigations are: (a) like gel grown crystal, change of orientation of dislocation etch pits can be possible here also by the same two etchants. When the square pits were rotated through 22.5° on (001) face, the triangular pits on (111) face were rotated through 45°. These rotations of pits depend upon the different activation energies of the etchants; and the resistivities of the edges of the growth layers to the etchants. (b) change of concentration alters, the morphology of the pits. The opposite nature of the activation behaviours (Table 12) of the etchants due to
Figs. 71, 72 & 73, 74 Morphology of etch pits on (001) face when etched with different concentrations of nitric acid.

(X 125)

Figs. 75, 76 & 77 Morphology of etch pits on (111) face when etched with different concentrations of sodium hydroxide solution.

(X 125)
change of concentration is also apparent in their mode of etching. When the concentration of the nitric acid was decreased, the pit size also decreased, whereas for sodium hydroxide the pit size increases for the constant time of etching.