CHAPTER - 6

CHEMICAL ETCHING ON BARIUM DOPED CRYSTALS OF SODIUM FLUOROANTIMONATES

6.1 INTRODUCTION

The different methods used by crystal growers to characterize a crystal can be classified as

1) Electrical method
2) X-ray analysis
3) Development of etch figures and dissolution phenomena.

The first two methods are physical means where as the last one is a chemical means. The phenomenon of preferential chemical attack by a suitable solvent on a crystal is called chemical etching. The solvent (etchant) can be week acids, bases, distilled water, alcohol or their mixtures. On examining the surface with a microscope after treating with etchants, small depressions called etch pits are seen.

Chemical etching is a powerful technique to reveal dislocations and other defects in crystals. Etch method is important in revealing the sites of dislocations, dislocation content or density, growth history in crystals and solubility differences in faces. Metallographic results agree quite well with X-ray ones if the dislocation density is less than $10^6 \text{cm}^{-2}$. 
Importance of etching technique towards materials characterisation is realised by many authors recently. Annamalai et al (1991) used the etchants HNO₃ and H₂O to distinguish tetragonal zirconia and monoclinic zirconia. On the basis of the occurrence of rapid etching of the grain boundaries, homoepitaxial films are distinguished from polycrystalline films (Malta et al 1995). The perfection of ADP crystals on the basis of etching is reported by Sen Gupta et al (1992). The switching between ferromagnetic and antiferromagnetic characteristics when given etching treatment with acids in the case of conducting polymer polyaniline is reported by Katsumi Yoshino et al (1994).

KI:1:H₂SO₄ solution is used to reveal lattice defects on (001) GaAs surfaces (Gottschalch and Herrnberger 1990). Anisotropic etching of silicon crystals in KOH solution is revealed by Tellier and Brahimbounab (1994). Sangwal et al (1996) concluded that dislocation density in low temperature solution grown crystals are less than high temperature grown crystals.

The kinetics of etching of dislocations in lead hydrogen phosphate (Desai et al 1990); corrugated structures on Si (110) surfaces treated in ammonium fluoride solutions (Ken Fujita and Norio Hirashita 1994); defect revealing etchant for Bi₁₂SiO₂₀ (Sluss and Doty 1992); Kuntman (1992); chemical topography of polycrystalline silicon (Guinn and Donnelly 1994); etching on gel grown crystals of potassium dihydrogen ortho phosphate (Suparna Sen Gupta et al 1993); characterisation of HF treated Si(111) surfaces (Tomohiro Konishi et al 1993); Annamalai et al (1992) are some of the important recent work in etching on different materials.
6.2 EXPERIMENTAL

The crystals free from damage and inclusion are selected and the etching studies are carried out on the as grown faces. Methyl alcohol of concentration 1.0 and 2.0% in water are used as the etchant. Neither the etchant nor the crystal is shaken during the entire period of etching, to avoid the discrepancy on etch pattern arises due to agitation of the crystals. The etch patterns are obtained for various concentrations of the etchant. After keeping the samples in contact with the etchant for the required period of times, the crystals are removed from the etchant, examined under a metallographic microscope MEF-2 after removing the adhered etchant on the crystal surface. The best results are photographed.

6.3 RESULTS AND DISCUSSION

Studies on different types of pits and their densities give useful information regarding the nature of the defects, impurity content, solubility differences and growth history. The etch pits are formed at the points where dislocations meet the surface. More amount of modifications occurs along a direction of easy solubility (Sangwal 1987). The etch figures are microscopic in nature having definite shape but vary with the nature of the solvent, crystal form, surface characteristics, concentration of the solvent etc. Etch pits are dependent on crystallographic direction of the sample and on the composition. On the line of dislocation bonds between the atoms are distorted. The energy stored around the dislocations is equal to the elastic energy of the bonds broken around the edge of dislocation. The excess energy available makes the region less resistant to the chemical attack.
When the surface of the as-grown surface of barium doped NaSbF₄ crystal is exposed to 1% methyl alcohol for one minute rapid attack is seen. After two minutes of etching, well ordered triangular pits are seen. When the etching time is increased the pits are increased in number. Prolonged etching causes complete disappearance and the re-appearance of etch pits at different sites. Fig 6.1 shows the etch pattern for etching time of two minutes. Similar results are obtained even for the crystals with different doping concentration of barium. Changing the concentration of etchant to 2% yields mixture of triangular and circular pits for 2 minutes of etching. The pits get elongated and is noticed for higher etching time. In both the cases of 1% and 2% methyl alcohol concentration rapid attack is seen initially. The rapid attack at the initial stages of etching and subsequent modification of pits suggest that the crystals have high density of impurities adsorbed on the surfaces. Similar results of rapid attack on gel grown nickel molybdate crystals are reported by Kurien and Ittyachen (1987). The increase in size and depth of the pits confirm that etch pits are formed at sites of dislocation (Sen Gupta et al 1992). In the study on undoped sodium fluoroantimonate crystals (Benet Charles and Gnanam 1990) similar results of disappearance of etch pits and re-appearance at different sites is noticed. The disappearance and re-appearance is due to the presence of point defects.

In the case of barium doped Na₂SbF₅ crystals, a mixture of flat bottomed, circular and elliptical pits (Fig. 6.2) are seen. During successive etching it is observed that an increase of etching time increases the number of pits. The size of pits as well as etch pit density increases. The variation in etch pit density is due to the difference in dissolution rates at different dislocation sites. Re-polishing and re-etching reveals the same effect.
6.4 CONCLUSION

The rapid attack with etchant on both NaSbF$_4$ and Na$_2$SbF$_3$ confirms that the impurities added during growth get adhered to the surface. Increase of etching time yields etch pits of different shape. Dislocation distribution varies in both NaSbF$_4$ and Na$_2$SbF$_3$ crystals. The variation in etch pit density is due to the difference in dissolution rates at the different dislocation sites.