CHAPTER III

ETCH PITS AND DISLOCATIONS IN METALS

This chapter presents a brief review of the experimental results on etching of dislocations. The discussion is limited to metals and semi conductors, though some reference has been made to the work on Li F crystal. Attempt has been made to mention all the recent results on etching. The present theoretical position has also been reviewed briefly.

Dislocations being regions of lattice defects giving rise to local strains, it is possible to reveal their presence by means of etchants which attack their sites preferentially. Depending on the nature of the etchant and the method used, few or many etch pits, bounded by crystallographic planes, could often be observed on the surface of the crystals which are indicated by glide lines before etching. It was therefore generally concluded that such pits indicate sites where dislocations terminate.

The first substantial proof that the presence of dislocations can be revealed in the form of etch pits was made by Vogel[1] et al thro' their study on the lineage boundaries on Germanium. Previously Burgers[2] had proposed a dislocation model for the boundary between two crystals differing in orientation by a small angle θ about an axis in the boundary. The model consists of a series of equally spaced identical edge dislocations lying in the boundary and running parallel to the axis. If d is the dislocation spacing and b the magnitude of their burger's vector then

$$d = b/\theta \qquad \ldots \qquad \ldots \qquad (1)$$

It was the verification of this equation which presented the first quantitative evidence in support of the theory of dislocation etch pits. Vogel[1] et al observed that the lineage boundary on the (100) plane revealed, on etching with CP-4, consisting of 3 parts HF, 6 parts HNO_3, 3 parts CH_3COOH,& 1 part Br_2, a series of regularly spaced conical pits. The implication was strong that these denoted edge dislocations. Accordingly, careful X-ray studies were undertaken which showed small rotation about the [100] direction. The dislocation spacing was calculated from the observed orientation difference using equation (1) and were compared with the observed spacings. Excellent agreement was obtained demonstrating that Burgers model is valid and that etch pits are associated with dislocations.

This discovery triggered the interest of many workers and several significant experiments have been conducted subsequently. The study of dislocation etch pits has grown rapidly during the last ten years and work of this type is being carried out in many laboratories. All these experiments are providing the basic information on the behaviour and structure of metals. The advantage of the etch pit technique is that it offers the facility for examination of the bulk material for the behaviour of dislocation. Semi conducting materials-Silicon and Germanium - are still the most widely investigated substances for dislocation etch pits, for they are the materials which have provided the most perfect crystals todate.

Etch pit technique has been successfully applied to the study of dislocations in plastically deformed crystals. Vogel[3] has bent crystals of germanium, having a (111) slip plane and a [110] slip direction, both at 42° to the longitudanal axis of the specimen around a [112] axis normal. The bending was carried out at 550° C by applying a static load on two knife edges 1 cm. apart. The crystals were sectioned to reveal the (111) plane most nearly normal to the axis of bending and were etched in CP-4 and examined to verify the Nye formula

$$P = \frac{1}{rb} \cos \Theta \qquad \ldots \qquad \ldots \qquad (2)$$

where P is the density of dislocations, r = radius of curvature of the neutral plane, b= appropriate Burgers' vector and Θ is the inclination of the neutral plane to use slip plane. The calculated and observed densities were same in specimens which were annealed at 800°C for 3 days. There was no agreement for the crystals which were not annealed. The anomaly has been expâained in terms of work hardening.

This work is an excellent illustration of the way in which etch pit technique may be used to obtain information on how dislocations are generated and how they move under controlled conditions. Greiner[4] et al have studied dislocations resulting from twisting a specimen. Breidt[5] indented the {100} and {111} faces of Germanium and on etching it was found that pits were formed along the slip lines. These pits are thought to be due to glissile edge dislocations produced by complex stress-system. All these observations offer concrete support to the theory that etch pits correspond to dislocations. However, Ellis[6] observed that a slow etchant based on potassium hypochlorite reveals about hundred fold more pits than CP-4. Pits revealed by CP-4 became highly over etched with this reagent. The new pits are small and show inner details such as terraces and spirals. If spirals denote screw dislocations, their Burgers vector must be large ($\approx 1000A^{o}$). The significance of these is still not completely understood. These observations have been discussed in detail by Hobstetter[7].

Detailed studies of the dislo-cation etch pits have been made on Li F crystals. It has been shown by Gilman and Johnston[8] that an etch pit formed at a dislocation ceases to grow and becomes flat bottomed if the dislocation moves away and a new pit is formed at the site where it has migrated to. This demonstrates how the dislocation motion can be followed up using etch pit technique. An excellent review on etching of Li F crystals is given by Gilman[9].

The fundamental question to be answered on the etching technique is the one-to-one correspondence between etch pits and dislocation. The work of Lacombe and other indicate that in aluminium and silicon-iron, only those dislocations are etched that certain impurities at the core. On the other hand, the results on Germanium indicate that impurities are not necessary for the pit formation. Gilman and Johnston[10], considering the case with which the dislocations move conclude that impurity is not necessary. Similar controversial results have been obtained on many metals and the results indicate that the problem requires careful analysis.

The information on dislocation etch pits on Aluminium has been obtained mainly as a result of the investigation of Lacombe and co-workers[11-14]. Forty[15] has studied the dislocation etch pits in Aluminium crystals grown from melt and carefully annealed. Wycon and Lacombe[12] observed that in regions of the crystals where the impurities had been swept away no etch pit could be observed even after deep etching. This suggests, according to the authors, that only those dislocations which are decorated by impurities develop etch pits on etching.

Lovell and Wernick[23] have reported etching of dislocations in copper without decoration. The authors have obtained evidence for dislocation climb. In a series of publications[16-22] Young describes an excellent systematic study of etch pits on copper single crystals. Etchants have been developed to reveal the dislocations on the (111), (100) and (110) faces. 'Clean' and dislocations with a Cottrell atmosphere can be distinguished by these etchants. Crystals were deformed under tension[19], in a tensile tester and the density and distribution of the etch pits have been studied, before, during and after deformation. For crystals of low dislocation density it was found that a large amount of multiplication occurred prior to yielding. The yield stress is found not to be dependent on the initial density and distribution of the dislocations. Annealed crystals with a density of dislocations 10^3-$10^4/cm^2$ were bent in a 4-point jig and etched. Dislocation motion and multiplication prior to yield were observed. There was evidence for dislocation interaction and pile-up at sub-boundaries. The spacing of the pits do not correlate with the expected value in case of pile up. This has been attributed to the fact that the plane of etching do not contain the barrier. Young has also irradiated the crystals with fast neutrons from a reactor at various doses and subsequently etched. For neutron irradiated crystals there was no dislocation multiplication before yielding. This has been attributed to source hardening. The results are indicative of the fact that no decoration is required for revealing the dislocations by etch pits. The results obtained by Ruff[24] on single crystals foils of copper using etching as well as transmission electron microscopy, however, show that one to one correspondance do not exist in these samples. There were grown in dislocations which were not etched, suggesting atmospheric effects and etch pit which were not belonging to dislocations.

Lovell and Wernick[25] have observed triangular etch pits on the cleavage plane of Bismuth, which by density counts and deformation were shown to be due to dislocations. Pandya and Bhatt[26] have observed similar pits using 5% silver nitrate solution. On Antimony crystals Wernick[27] et at, using, CP-4 observed etch pits on the (111) plane. Rows of etch pits probably representing low angle boundaries were observed. Etching with superoyal produced spiral and terraced pits. Shigetta and Hirmastu[28] observe that an etchant containing ferric chloride also develops etch pits. Similar results have been obtained by Pandya and Bhatt[29] using a solution consisting of 6 parts tartaric acid, 3 parts HNO_3 and one part water. Kosevich[30] also has used CP-4 reagent and studied the etch features on Antimony crystals. He has also observed etch grooves connecting large pits[31], the origin of which is not completely understood.

Etch features of zinc have been investigated by various workers. A number of etchants have been developed. Abodu[32] was the first to observe pits along the slip lines using 20% chromic acid solution and attributes them to dislocation. Meleka[33] using 0.1% solution of alcohol made the first systematic investigation involving the distribution of dislocations. The agreement between the theoretical values and experimental observations of the spacing of pits was satisfactory. Gilman[34] using a reagent consiting of 160 grms CrO_3, 50 grms Na_2SO_4 and 500 c.c. water, has studied the etching of zinc single crystals and has cast polycrystals of zinc decorated with 0.1% (atomic) of Cd. Pits representing low angle boundaries, pile up of dislocations, polygonization boundaries slip bands etc have been observed. Servi[35] observed etch spiral pattern on a plane nearly parallel to the basal plane. Certain complex spirals observed by him were subsequently interpreted by Frank and Vreeland[36] in terms of dislocation theory. Star-shaped pits, spirals and closed loops have been observed by George[37] on the surface of zinc crystals grown from vapour and droplets. Loops and spiral etch pattern were observed on surfaces nearly parallel to basal plane by Damiano and Hermon[38] on zinc of purity 99.998%, 99.997% and metal containing 0.07% Cadmium. Rosenbaum and Saffren[39] conclude from their studies on the basal plane of zinc crystals using Halogens and their acids that at least screw dislocation can be revealed without decoration. Non basal glide and polygonization pattern have been studied by these authors. Kosevich and Soldatov[40] have also studied the etching on zinc single crystals. Pandya and Shah[48] have used acetic acid for etching zinc crystals.

Complex spiral etch pits have been observed by George[41] on cadmium crystal grown from vapour. Dislocation etch pits have been observed on silver by Forty and Frank[42]. Recently Levinstein and Robinson[43] have obtained one-to-one correspondence between pits and dislocations. Evidence on the electrolytic and chemical etching of tungsten[44] indicate that impurities affect the size, shape and density of etch pits. Thermal etching has also been used to study dislocations in some metals.

The observations presented above indicate that one-to-one correspondence between etch pits and dislocations is not obtained in all cases. But excellent agreement is indeed obtained in certain metals. The etch pit technique has proved to be a powerful technique in the hands of a careful investigator as is the case with copper[17-22]. Results of Ellis[6] and Ruff seems to warn us that this technique should be used with care. Whether an impurity is necessary to reveal dislocation has not been conclusively proved. In view of the contradictory nature of the results one has to conclude that only when the pits aggregate in a manner clearly attributable to dislocations or produce distinct orientation effects can they be safely regarded as dislocations.

The first theoretical assessment of the etching of dislocations was done by Cabrera[45]. The problem bears close resemblence to the phenomena of preferred evaporation and of crystal growth. The effect of dislocations on the etching process is explained by the decrease of energy, near a dislocation required to remove an atom or electron from the surface of the solid near dislocation. It has been shown that free energy at the dislocation having large Burgers' vectors is sufficient to produce pits, while in case of elementary dislocations, Cabrera advocates, a really efficient etch pit formation requires the presence of impurity atoms. While this is in agreement of the work of Lacombe and others[11-14], the results of the investigations of Young, Vogel etc. are contradictory to this. However, it has been suggested that even the metal of highest purity available do contain small amounts of impurities which might be sufficient to migrate to dislocation. This statement requires careful analysis and a lot more of experimental evidence will have to be gathered before it is generalised.

A new approach to the problem has been made by Frank[46], which is being called as kinematic theory of growth and dissolution. The basic assumption of this theory is that growth or dissolution of a crystal occurs by deposition or dissolution of atomic steps. The development of the crystal form then results from two simultaneous processes namely, the creation of new steps and the motion of steps away from the surface. The application of the theory to the problem of etching has been attempted by Cabrera[47] who has shown that the shape of pits are very sensitive to the type of relation existing between the concentration of steps and the rate at which they migrate over the surface. Two types of flow concentration curve leads to two different situations. In one, etching is controlled by rate of the generation of steps at the source and in the other the rate of migration of the steps. In this second case it is shown that pits can be formed only if the rate of generation of steps exceeds a certain critical value. It is expected that this new theory may help to solve some of the problems of growth and dissolution of crystals.

R E F E R E N C E S

1.	Vogel F.,Pfann W. Correy H. & Thomas E.	(1953)	Phy.Rev.90,489
2.	Burgers J.M.	(1940)	Proc.Roy.Soc. 52,23
3.	F.Vogel	(1956)	J.Metals 8,946
4.	Greiner E.S.	(1955)	J.Metals 7,203
5.	Breidt D, Greiner E.S. & Ellis N.C.	(1957)	Acta Met. 5,60
6.	Ellis S.G.	(1955)	J.Appl.Phy.26,1140
7.	Hobstetter J.N.		Progress in metal Physis 7,
8.	Gilman J.J. & Johnston W.P.	(1957)	Dislocations and mechanical properties of crystals-P 116
9.	Gilman J.J.	(1962)	Solid State Physics 10,(Academic Press)
10.	Gilman J.J. & Johnston W.P.	(1956)	J.Appl.Phy.27,1018
11.	Lacombe P.	(1948)	Report on Conf. defect in cryst.solids
12.	Lacombe P. & Wycon G.	(1954)	" P.187
13.	Lacombe P. & Berghezan A.	(1954)	Comptes Rendus 238,2420
14.	"	(1949)	Physica 15,161
15.	Forty A.J.	(1954)	Advance in Phys. 3, 1
16.	Young F.W. & Noogle T.S.	(1960)	J.Appl.Phy. 31, 604
17.	Young F.W.	(1961)	J.Appl.Phy. 32,192

18. Young F.W. (1961) J.Appl.Phy.32,1815

19. " (1962) " 33,963

20. " (1958) " 29,760

21. " (1962) " 33,3553

22. " (1962) Proc.Int.Conf.Lattice defects (Japan) P. 1

23. Lovell L.C. & Wernick J.H. (1959) J.Appl.Phy.30,590

24. Ruff A.W. (1962) J.Appl.Phy.33,3392

25. Lovell L.C. & Wernick J.H. (1959) J.Appl.Phy.30,234

26. Pandya N.S. & Bhatt V.P. (1960) J.Sci.Ind.Res.19B,363

27. Wernick J.H., Hobstetter J.N., Lovell L.C. & Dorsi J. (1958) J.Appl.Phy. 29,1013

28. Shigetta J. & Harmastu M. (1958) J.Phy.Soc.(Japan) 13,1404

29. Pandya N.S. & Bhatt V.P. (1960) Current Science 30,293

30. Kosevich V.M. (1961) Soviet Physics Crystallography 5,715

31. " (1961) Soviet Physics Crystallography 6,379

32. Abodu A.H. (1954) Phil.Mag. 45,105

33. Meleka A.H.A. (1956) Phil.Mag.47,803

34. Gilman J.J. (1956) J.Metals P.1

35. Servi I.S. (1958) Phil.Mag.3,63

36. Frank F.C. & Vreeland J. (1958) Phil.Mag.3,419

37. George J.	(1959)	Phil.Mag.4,1142
38. Damiano V. & Hermon M.	(1959)	J.Franklin Inst. 267, 303
39. Rosenbaum H.S. & Saffren M.M.	(1961)	J.Appl.Phy.32,1866
40. Kosevich V.M. & Soldatov V.P.	(1961)	Soviet Physics Crystallography 6,347
41. George J.	(1961)	Nature 189,743
42. Forty A.J. & Frank F.C.	(1953)	Proc.Roy.Soc.A217,262
43. Levinstein H.J. & Robinson W.H.	(1962)	J.Appl.Phy.33,3749
44. Ivan Berlec	(1962)	J.Appl.Phy.33,197
45. Cabrera N.	(1956)	J.Chemi.Phys.3,675
46. Frank F.C.	(1958)	Growth and perfection of crystals p.411
47. Cabrera N.	(1960)	Reactivity of solids (Elsovier Publishing House) p.351
48. Pandya N.S. & Shah C.J.	(1959)	J.Sci.Ind.Res.18B,85