CHAPTER III

A BRIEF REVIEW OF ETCH PITS AND DISLOCATIONS

A brief review of the experimental results on etching of crystals is presented in this chapter. The discussion of the previous results is limited mainly to the metals and semiconductors, but reference has been made to the results on LiF crystals for the sake of continuity. An attempt has been made to bring into the text, all the recent results on etching for studying the dislocations. Also, the present day understanding of the theory is given in brief.

Dislocations are the regions of lattice defects in the material, giving rise to local strains. It is possible to reveal their presence by means of etchants which attack preferentially at their sites. Depending on the type of etchant and the method used, a few or many etch pits which are bounded by crystallographic planes can be observed on the surfaces of the crystals. Therefore a general conclusion that such pits indicate the sites where these dislocations terminate has been drawn.

In 1940, Burgers[1] proposed a dislocation model for the boundary between two crystals differing in orientation by a small angle θ about an axis in the boundary. This model consists of a series of identical edge dislocations which are equally spaced, lying in the boundary and running parallel to the axis. If the dislocation spacing is 'd' and if the magnitude of the Burgers' vector is 'b' then

$$d = \frac{b}{\theta} \qquad (1)$$

The work of Vogel et al.[2] offered a verification of the equation (1). They were the first to show that pits revealed by etching correspond to dislocations by studying the lineage boundaries on germanium. They observed that the lineage boundary on the (100) plane revealed, on etching with CP-4 reagent which consists of 3 parts HF, 6 parts HNO_3, 3 parts CH_3COOH and 1 part Br_2, a series of regularly spaced conical pits. The implication was strong that these were edge dislocations and the careful X-ray study showed a small rotation about the $\langle 100 \rangle$ direction. The dislocation spacing was calculated from equation (1) using the observed rotation and was compared with the observed spacing. Excellent agreement was obtained demonstrating that Burgers' model is valid and that etch pits are associated with dislocations. This is the first qualitative evidence in support of the theory of the dislocation etch pits.

The work of Vogel et al. evoked considerable interest in many workers and subsequently many significant experiments were conducted. The study of the dislocation etch pits has grown rapidly during the last decade and many laboratories are engaged in this type of work. The basic information regarding the behaviour and the structure of the metals is provided by all these experiments. Though there are other techniques for the study of the dislocations, the etch pit technique facilitates the study of the behaviour of dislocations in the bulk metals. The semiconductor materials, germanium and silicon, being the materials largely required in the form of extremely perfect crystals for their varying applications, have been subjected to a wide range of investigations of this sort.

Successful application of the etch-pit method has been made in studying the dislocations in crystals deformed plastically. Vogel[3] using germanium crystals having a (111) slip plane and a [110] slip direction, has bent them, both at 42° to the longitudinal axis of the specimen around a [112] axis normal. The bending of these crystals were carried out by applying a static load on two knife edges placed one cm. apart, at 550°C. The crystals were, then, sectioned nearly normal to the axis of bending and were etched in CP-4 etchant and examined to verify the Nye formula

$$\rho = \frac{1}{\gamma b \cos\theta} \qquad (2)$$

where ρ is the dislocation density, γ is the radius of curvature, b is the Burgers' vector and θ is the angle of inclination of the neutral plane to the slip plane. There was general agreement between the observed and calculated densities after annealing the specimens at 800°C for 3 days. On the contrary no such agreement could be observed in the crystals which were not annealed. This anomalous behaviour has been explained in terms of work-hardening. This provides excellent illustration of the way in which the etch-pit technique may be used in getting the information regarding the generation of the dislocations and their movement under controlled conditions. Greiner[4] has studied the dislocations resulting from twisting a specimen. The study of the effect of indenting the {100} and {111} faces of germanium has been made by Breidt[5] et.al. On etching these indented faces, he observed that etch-pits were formed along the slip lines and these pits were thought of as due to glissile dislocations. All the above observations give support to the view that the etch-pits correspond to dislocations. However, Ellis[6] could observe a hundred fold increase in the number of pits by using potassium hypochlorite instead of CP-4. Pits produced by CP-4 reagent get over-etched by this etchant. These new pits are small in size and show inner details such as terraces and spirals. If the spirals are attributed to the screw dislocations, their Burgers' vector must be large, of the order of 1000 A°. The significance of this is still not understood completely. Hobstetter[7] has discussed these observations in detail.

The work of Gilman and Johnston[8] yielded detailed information on the dislocation etch-pits in the case of LiF crystals. They have shown that etch-pits do correspond to dislocations and that an etch-pit does not grow but becomes flat bottomed when a dislocation has moved away and that a small point bottomed pit is produced at the point where the migration of dislocation has taken place,on etching the crystal for a second time. This indicated that the etch-pit technique could be utilized in studying the motion of the dislocations. Gilman[9] has given an excellent account on etching of LiF crystals.

The basic question involved in the etch-pit technique is to see whether one-to-one correspondence between etch-pits and dislocations exists. In other words and in more general terms the problem can be written as: (1) Is there some correlation between the etch-pits and dislocations? (2) Are all dislocations etched? (3) Do all etch-pits correspond to dislocations? For the first question, the usual approach is to show that the etch-pits are distributed at dislocations. The second question can be solved directly by introducing the various possible dislocations and examining whether they all produce pits. It has been shown that defects other than dislocations do cause etch-pits to form and hence the third question can never be answered in the affirmative. The fundamental question of one-to-one correspondence of etch-pits and dislocations remained unanswered. In aluminium and silicon-iron Lacombe[15] and others have shown that only those dislocations are revealed by etching which have impurities at the core. On the other hand, it has been shown that impurities are not necessary for the pit formation in the case of germanium. Taking the motion of the dislocations into account, Gilman and Johnston[10] concluded that impurities are not necessary to reveal the dislocations. Similar controversial results have been obtained on metals which indicate that the problem requires reconsideration.

It is known that the strain energy of a dislocation line is small. So a successful etching technique to delineate it must be able to differentiate small differences in energy. The work of Chalmers and King[11] on silver has indicated that a thermal etching might accomplish this purpose. They observed that thermal etching at 300°C revealed grain boundaries and at 600°C started becoming etch grooves. Young[12] observed on copper crystals annealed under hydrogen atmosphere and then heated to a temperature of 1050°C under evacuation, spirals around (111) poles which were attributed to the screw dislocations finishing at the surface around the (111) poles. The work of Machlin[13] on the thermal etching of silver crystals showed that the pits were formed at stationary dislocation grooves. They also showed that the screw oriented dislocations could be distinguished from those of edge oriented ones in that the pits at the former were several times smaller and shallower than that at the edge dislocations. This shows that, besides chemical etching the thermal etching can also be used successfully to reveal dislocations. In thermal etching the removal of the atoms occurs mainly at the exits of dislocation lines on the surface since the binding strength of atoms is weak in a dislocated region. One-to-one correspondence between the thermal etch-pits and dislocations is not yet fully established and a careful study is necessary before any definite conclusions can be drawn.

The investigations of Lacombe and co-workers[14-17] yielded much information on dislocation etch-pits. Forty[18] has studied the dislocation etch-pits in aluminium crystals grown from the melt and carefully annealed. Wycon and Lacombe[15] observed that even after deep etching, etch-pits were not formed in the regions from where impurities have been swept away and that the etch-pit formation is only possible in the case of dislocations which are decorated by impurities.

Without decorating the dislocations, Lovell and Wernick[19] have reported the etching of copper crystals and have obtained the evidence for dislocation climb. The distribution of dislocations in deformed copper crystals by etch method has been studied by Basinski and Basinski[20]. Young[21-27] has described an excellent and systematic study of etch-pits on copper single crystals. Also, etchants have been developed which can reveal dislocations on the (111), (100), and (110) faces, and can distinguish between 'clean' and 'dirty' dislocations with a Cottrell atmosphere. His study included the distribution and density of dislocations under tension before, during and after deformation. It was observed that a large amount of multiplication of dislocations occured prior to yielding in the crystals having low dislocation density. It was also observed that the yield stress did not depend on the initial density and the distribution of dislocations. The crystals with 10^3 to $10^4/cm^2$ dislocation density were annealed and bent in a 4-point jig and etched. The motion and multiplication of the dislocations were studied prior to yielding. They also observed the dislocation interaction and pile-ups at sub-boundaries. The spacing of the etch-pits did not tally with the expected value in the case of pile-ups. This has been attributed to the fact that the plane of etching do not contain the barrier. Young has also studied the effect of various doses of neutron irradiation on the density and the distribution of dislocations. For these crystals dislocation multiplication before yielding was not observed. This result has been suggested to be due to source hardening. These results of Young also suggest that for revealing the dislocations by etch-pit technique, decoration is not necessary. However, the study of Ruff[28] on the single crystal foils of copper using etching as well as transmission electron microscopy techniques, shows that one-to-one correspondence does not exist in these samples. There were grown-in dislocations which were not etched, suggesting atmospheric effects and etch-pits which could not be attributed to dislocations.

On the cleavage of bismuth, Lovell and Wernick[29] were able to obtain triangular etch-pits which were attributed to the dislocations as indicated by the density and the deformation studies. Using 5% aqueous solution of $AgNO_3$, Pandya and Bhatt[30] have also observed the same kind of pits on (111) plane of bismuth. Palatnik et al.[31] have studied the formation of etch-pits on (111) planes of bismuth and antimony and (0001) plane of zinc by subjecting them to spark treatment and etching. They studied the distribution of dislocations in this plane. A three dimensional picture of the dislocation distribution was obtained by them in the vicinity of the point of attack on the crystal by the spark. Kosevich[32] has studied the undulatory relief on bismuth crystals by etching technique. He observed that the dislocation density is a periodic function having maxima coinciding with points of retardation of the movement of crack. Wernick et al.[33] have observed etch-pits on antimony crystals by using CP-4 reagent and spiral and terraced pits by using superoxol. Rows of etch-pits on the (111) plane, probably representing low angle boundaries were observed by them. Shigetta and Hirmastu[34] were able to show that an etchant containing ferric chloride develops etch-pits on the cleavage plane of antimony. Similar results have been obtained by Pandya and Bhatt[35] by using an etchant consisting of 6 parts tartaric acid, 3 parts nitric acid and one part water. Using modified CP-4, Kosevich[36,37] has studied the etch-pits on the (111) plane of antimony. He observed etch grooves connecting large etch-pits whose origin is not yet understood completely. The block boundaries, twin lamella, slip lines, and pile-ups were studied. The motion of the dislocations in antimony crystals has been studied by Sojefer and Startsev[38] by this technique. They observed wedge-shaped tracks which indicated the path of the motion of the dislocations and wedge-shaped tracks having a point bottomed pits at their termination which were interpreted as due to dislocations which were arrested. These traces were thought to be dislocation loops involved in the process of slip. They concluded that impurity decoration was not necessary to reveal the dislocations.

The easy methods of growing single crystals, its availability in sufficiently pure form and the existence of a perfect cleavage offered zinc as a very convenient metal to study the dislocations. Various workers have used the etching technique to study the dislocations in zinc single crystals. Abodu[39] was the first to observe pits along the slip lines using 20% chromic acid solution and he attributed them to dislocations. The first systematic study of the distribution of etch-pits in high purity zinc using 0.1% solution of alcohol was done by Meleka[40]. A satisfactory agreement between the theoretical and experimental values for the spacing of pits was obtained, assuming every pit to be due to a dislocation of unit strength. Pits representing low angle boundaries, polygonization boundaries, pile-up of dislocations, slip bands etc., have been observed by Gilman[41] in high purity zinc crystals and cast polycrystals of zinc containing 0.1 atomic percentage of cadmium as an impurity. For this study he developed an etchant consisting of 160 gms of CrO_3, 50 gms of Na_2SO_4 and 500 c.c. of water. Servi[42] observed etch spiral pattern on a plane which was nearly parallel to the basal plane. He also observed certain complex spirals which were interpreted subsequently by Frank and Vreeland[43] in terms of dislocation theory. Goerge[44] has observed spirals and star-shaped pits on the surfaces of zinc crystals grown from vapour and droplets. On surfaces nearly parallel to the (0001) plane of zinc having purity of 99.998%, 99.997% and that containing 0.07% cadmium, loops and spiral etch patterns were observed by Damiano and Herman[45].

Rosenbaum and Saffren[46,47] concluded that screw dislocations could be revealed on the basal plane of zinc without decorating them by impurities. They used halogens and their acids to reveal dislocations. They have also studied non-basal slip and twin accomodation in zinc crystals by means of the etching method. Kosevich and Soldatov[48] also studied etching of zinc single crystals. Pandya and Shah[49] used acetic acid for the etching of zinc crystals. The existence of a one-to-one correspondence between etch-pits and dislocations has been shown by Brandt et al.[50,51] from their studies on etching of high purity zinc single crystals. Their studies also included the slip on (0001) planes and $\{1\bar{2}12\}$ pyramidal planes and twinning. The comparative study of the reagents developed by Gilman and Meleka has been made by Stepanova and Urusovskaya[52]. They have shown that Gilman's etchant is suitable for revealing the dislocations while Meleka's was not. They were able to reveal various distribution of dislocations including Frank-Read sources by using Gilman's reagent. Damiano et al.[53], using this etch-pit method, studied the arrangement of dislocations in zinc single crystals doped with cadmium. The effect of annealing was evidenced by the arrangement of dislocations into low angle boundaries and hexagonal networks. George[54] has observed spiral etch-pits having a complex structure on cadmium crystals grown from the vapour phase. The study of the distribution of dislocations in cadmium was made by Predvoditlev et al.[55] They observed the presence of dislocation configurations corresponding to Frank-Read sources. Tyapunima et al.[56] have made an analysis of the conditions for anchoring of dislocations in hexagonal metals and the multiplication of dislocations by the Frank-Read mechanism by etching method.

Hiki[57] has studied the electrolytic etching of single crystals of lead having 99.99% purity. He observed an increase in etch-pit density by annealing at 150°C in ethylene glycol and interpreted it in terms of the formation of Cottrell atmospheres. The study of the dislocation etch-pits on silver crystals has been made by Forty and Frank[58]. Levinstein and Robinson[59] were able to show a one-to-one correspondence between etch-pits and dislocations in silver recently. Evidence has been obtained to show that impurities have an effect on the size, shape and density of the pits from the studies on electrolytic and chemical etching of tungsten[60].

The above observations show that one-to-one correspondence between etch-pits and dislocations is not obtained in all cases. However, an excellent agreement between etch-pits and dislocations is obtained in some metals. This proves that the etch-pit method is a powerful tool in the hands of a careful worker to reveal dislocations, as is evidenced in the case of copper. Ellis and Ruff have warned that this technique should be used with care. It has not been confirmed conclusively that the presence of impurities is necessary to reveal dislocations. From the contradictory nature of the above results one can 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.

It was Cabrera[61] who made the first attempt towards the theoretical aspect of the etching of dislocations. The problem bears a close resemblance to the phenomena of preferred evaporation and of crystal growth. The role of dislocation in the process of etching has been explained in terms of the reduction of energy near a dislocation by the removal of an atom or an electron from the surface of the solid near the dislocation. It has been shown that the dislocations having large Burgers' vector have sufficient energy to produce pits, while in the case of elementary dislocations, Cabrera points out that impurities are required to reveal their presence. This is in good agreement with the work of Lacombe and others, but the results of Young, Vogel, etc., are contradictory to this. However, the highest purity metals do contain some impurities which might be sufficient to migrate towards the dislocations. This indicates that before generalising this statement a careful analysis and a lot of experimental evidences are required.

Frank[62] has given a kinematic theory of growth and dissolution which is a new approach to the problem. In his theory, the basic assumption is that the growth or dissolution of a crystal takes place by deposition or dissolution of atoms at a step. The development of the form of the crystal takes place by two processes, the creation of new steps and the motion of the steps away from the surface, which occur simultaneously. Cabrera[63] applied the Frank's theory to the problem of etching and showed that the shape of the pits are very much sensitive to the type of relation existing between the concentration of the steps and the rate at which they migrate over the surface. Two types of flow concentration curves lead to two types of situations. The etching is controlled by the rate of generation of the steps at the source in one type and in the other by the rate of migration of the steps. Pits are formed only when the rate of generation of steps exceeds a certain critical value. It is expected that this theory may be helpful in solving some of the problems of growth and dissolution of the crystals.

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