CHAPTER - 2
DISLOCATIONS AND CHEMICAL ETCHING
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All real crystals contain defects. Various important properties like conductivity and hardness of a crystal depend on these defects. The various types of static defects in crystals are as follow:

1. Point defect
2. Line defect
3. Surface defect and
4. Volume defect

The line defect is of two types known as edge and the screw dislocations. They are the most dominating ones since they affect many of the physical properties of a crystal to a significant extent according to Orowan\(^{(1)}\), Polanyi\(^{(2)}\) and Taylor\(^{(3)}\).

Dislocations in an as-grown crystal may originate, according to Brice\(^{(4)}\), by

(i) propagation from seed crystal
(ii) shear strains due to mechanical and thermal stresses or due to change in composition
(iii) dendritic growth and
(iv) collapse of vacancies

Weertman et al\(^{(5)}\), Cottrell\(^{(6)}\) and Bueren\(^{(7)}\) have discussed the properties of dislocations with their various geometrical features in detail. The theory of dislocations formed by condensation of vacancies which results due to
thermal gradients present during crystal growth from melt, in particular, has been discussed by Teghtsoonian et al.(8) and Frank(9). Kuhlman-Wilsdorf et al.(10) have proposed the theory of vacancy condensation mechanism for dislocation formation in plastic deformation. Billig(11) showed, for germanium, that the thermal stresses set up by non-uniform cooling of the crystal during crystal growth are responsible for giving rise to dislocations. The perfection of a crystal can be judged in terms of its dislocation content though many other lattice imperfections exist in a crystal. The dislocation density is a measure of the dislocation content and is defined as the dislocation line length per unit volume. The other equivalent definition used to measure dislocation density is, the number of dislocations intersecting a unit area of a surface of the crystal. Though this is not truly equivalent to the former definition, since dislocations may exist in the form of closed loops inside the crystal and hence do not intersect any surface of the crystal, it has been used as a fairly good measure of dislocation density.

Dislocations occur in various geometrical configurations ranging from straight lines, jogs and helices to complex spatial networks, irregular three-dimensional tangles etc. Regarding different types of dislocations, Orowan(1), Polanyi(2) and Taylor(3) have developed the concept of dislocations as line imperfections in crystals and postulated edge type of dislocations. Burger(12) discovered screw type of dislocations. Later, Mott et al.(13) and Frank(14) proposed that the dislocation lines can be curved and assume any orientation.

Many reliable techniques were developed for direct observation of dislocations. These techniques have helped to get various informations regarding dislocation motion, their interactions with grain boundaries and with other defects (Read, Shockley and Fisher(15-17)). Three-dimensional
dislocation structures can be made visible by the method known as decoration. In this method of decoration, a suitably chosen impurity is allowed to precipitate on dislocation lines which makes the dislocations visible under the microscope in optically or infra-red transparent crystals. By this method, dislocations were observed in silicon crystals (Dash\(^\text{18}\)), silver halides (Hedges et al\(^\text{19}\)), in alkali halides (Amelinckx\(^\text{20}\)) and in CdTe crystals (Wada et al\(^\text{21}\)). For the direct observations and study of dislocations, highly sophisticated techniques of Electron microscopy and X-ray topography have been successfully introduced by Hirsch et al\(^\text{22}\) and Lang\(^\text{23}\), respectively.

It has been experimentally proved that the dislocations can be revealed in the form of etch pits (Horn\(^\text{24}\), Gevers et al\(^\text{25}\), Vogel et al\(^\text{26}\) and Burgers\(^\text{27}\)). Gilman et al\(^\text{28,29}\) suggested that in the case of LiF single crystals, an etch pit formed at 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.

Among the different techniques of revealing dislocations, the simplest and easily accessible technique is the chemical etching technique, first used and reported by Horn\(^\text{24}\), Gevers et al\(^\text{25}\) and Vogel et al\(^\text{26}\). This technique is given below in detail with the discussion limited to metals and semiconductors and where ever it is necessary, some references to non-metals are given.

When a crystal is attacked by appropriate solvent which chemically or physically dissolves it, the initial dissolution begins only at certain preferential sites on the crystal surface. This phenomenon is known as chemical etching and the appropriate solvent used for dissolution is known as the etchant. The chemical etching gives rise to various types
of geometrical features on a crystal surface. Due to anisotropy of the crystal, the dissolution rates are different in different directions giving rise to the production of conical depressions, with regular geometrical outlines at the preferential sites of attack on the crystal surface, known as etch pits, etch marks or etch figures. The form and symmetry of such etch pits were used by mineralogists to determine crystal planes and their orientations. Dissolution of a crystal surface is effected by the retreat of monomolecular steps, being reverse to that of growth which takes place due to the addition of steps on the surface. It is believed that when a single crystal face is exposed to a solvent, dissolution begins by the nucleation of unit pits of one molecular depth and these unit pits grow as steps retreat across the crystal surface through the action of kinks. In the case of metals, the etching process can be regarded as the dissolution by controlled oxidation of the surface where the dislocation sites act as catalysts. The chemical etching of a crystal surface involves the following sequence:

The reactant/s

(i) Approach the surface
(ii) Interact with the surface and
(iii) React chemically

The products

(iv) Disengage themselves from the surface and
(v) Move away from the surface.

Gatos and Gatos et al. reported that the overall etching process may be electrochemically controlled or diffusion controlled or controlled by the combination of both. The factors affecting the process of dissolution of a crystal surface are as follows:

(i) Crystallographic orientation of the surface
(ii) Impurity concentration on the surface
(iii) Crystal defects present in the surface and
(iv) Surface damage and cleanliness.

The above said factors affecting the etching process are discussed in detail by Irving\(^{(32)}\). Regarding the formation of etch pits at dislocation sites, explanations have been given by various workers. For the initiation of etch pits, the presence of impurities preferentially segregated at dislocations was considered essential for a long time. Gilman\(^{(33)}\) and Young\(^{(34)}\) considered impurity segregation to be responsible for the formation of dislocation pits in zinc and copper crystals. But Coleman\(^{(35)}\) had grown single crystals of pure iron practically free from dislocations. He further reported that the impurities were not essential for the formation of dislocation etch pits. This was supported by the reports of Lovell et al\(^{(36)}\), Livingston\(^{(37)}\) and Young\(^{(38)}\).

Cabrera\(^{(39)}\) and Cabrera et al\(^{(40)}\) reported the etch pit formation as a nucleation process analogous to crystal growth and attributed the nucleation of etch pits at dislocations to the elastic energy associated with dislocations. Gilman\(^{(41)}\) suggested that etch pit formation is due to dislocation core energy on the basis of the following arguments:

(i) The core energy in metals is indeed very small, still it is much more difficult to get etch pits on them.

(ii) When dislocations form a tilt boundary, the stress fields of dislocations close to each other tend to cancel out and hence the isolated dislocations should etch much more than those close together if their elastic energies were significantly effective in etching process. But actually, all dislocations in a given crystal are etched at approximately the same etching rate.
In compounds with zinc blende structure, the positive and negative dislocations are etched differently even though their strain fields are identical.

Schaarwachter\(^{(42)}\) modified Cabrera's treatment according to the suggestions given by Gilman\(^{(41)}\) and derived the conditions under which dislocation core energy, strain energy and both together, become essentially important for the formation of dislocation etch pits. Gatos et al.\(^{(31)}\) explained the formation of dislocation etch pits for diamond type structure on the basis of chemical bonding of atoms along the dislocation lines. Frank\(^{(43)}\) suggested a new approach to the problem of the formation of dislocation etch pits by giving a kinetic theory of growth and dissolution. His theory was based on the assumption that the growth and dissolution of a crystal proceed by way of diposition and dissociation of atomic steps. The theory was later applied to the etching process by Cabrera\(^{(44)}\) with the sufficient conditions for the creation of etch pits at dislocation sites as modified by Gilman\(^{(41)}\) and Schaarwachter\(^{(42)}\). Hence the production of a visible etch pit is governed by the kinetic considerations of dissolution process as used in Frank's theory. According to this the visibility of an etch pit depends on,

(i) the dissolution velocity "\(V_d\)" along dislocation line,
(ii) the ledge dissolution velocity "\(V_I\)" and
(iii) the average vertical dissolution velocity "\(V_s\)" at a dislocation free region of the crystal surface.

For the formation of visible etch pits, according to Frank,

\[
\frac{V_d}{V_I} \geq 0.1 \text{ and } V_d > V_s
\]
The formation of etch pits during chemical etching, does not necessarily correspond to dislocations. Precipitates or impurity inclusions, clusters of point defects etc. may also be responsible for etch pit formation.

The study of dislocation motion by etch pit technique has also been reported by Vyas, Trivedi, and Bhatt et al. Also a crystal can be etched electrolytically as reported by Pandya and Berlec. This technique has also been successfully applied to the study of dislocations in plastically deformed crystals (Vogel, Greiner, Breidt et al, and Ellis). An excellent review of etching of LiF crystals has been given in detail by Gilman. Trivedi et al. and Iwanaga et al. used etching technique to study dislocations in Cd$_{0.96}$Zn$_{0.04}$Te and CdTe single crystals, respectively. Imashimizu et al. studied the formation of slip pattern in copper crystals and its dilute alloy crystals.

In order to study etching mechanism with various parameters affecting etching process, a systematic study has been carried out by several workers (Forty, Young et al, Popkova et al, Sagar et al, Grabmaier et al and Williams). Recently in 1989, Lin et al. has reported anisotropic etching on different crystallographic surfaces of AlSb single crystals.

The reliability of an etchant as a dislocation etchant can be judged by one or more of the following tests:

1. Etch pits associated with individual dislocations reappear after each successive polishing and etching, since a dislocation line cannot terminate inside a crystal.
(2) The etch pattern produced by the etchant on two oppositely cleaved surfaces, should appear as mirror images of each other, if cleavage of a grown crystal is possible. Sagar et al\(^{(65)}\) and Bhatt et al\(^{(66)}\) have shown branching and bending of dislocations at the cleavage which may result in deviations from one to one correspondence of etch pits on the oppositely matched cleavage surfaces.

(3) The etch pit density should show a reasonable agreement with the theoretically estimated dislocation density.

(4) Plastic deformation always involves the creation and motion of dislocations which result in increase of etch pit density at least in the vicinity of the region of deformation.

For the development of a dislocation etchant for a given material, still a trial and error method is used. Faust\(^{(67)}\) has suggested that the minimum ingredients for an etchant are an oxidizing agent to place the elements in a suitable form for being taken into solution and a complexing agent to put the oxidized species into a soluble state. Well established dislocation etchants for a large number of materials have been reported by various workers (Johnston, Faust, Warekois et al, Holmes, Amelinckx, Robinson and Kane et al\(^{(68-74)}\)).

The chemical etching technique can be used,

(1) to decide whether a given solid is a single crystal or not.
(2) to distinguish between different faces of a crystal.
(3) to reveal the growth history of a crystal.
(4) to determine the dislocation density.
(5) to assess the impurity distribution in crystals.
(6) to study deformation patterns like pile-up and polygonization.
(7) to study dislocation motion and multiplication.
(8) to study plastic flow around indentations.
(9) to study fracture mechanisms.
(10) to study slip and twin systems.
(11) to study interactions of dislocations under stress.
(12) to study configuration and inclination of dislocations.
(13) to distinguish between fresh and as-grown dislocations.
(14) to delineate grain boundary and
(15) to study polarity of crystal lattice.

An account of dislocation etching study in InBi:Te single crystals carried out by the present author is given in detail in chapter 7.
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