CHAPTER 4

DEFECT STUDY

A perfect crystal is an idealized concept. Real crystals in nature are always imperfect to more or less extent. The various kinds of imperfections that may exist in a crystal are:

1) phonons
2) free electrons and holes
3) excitons
4) vacant lattice sites, interstitial atoms and surface vacancies
5) foreign atoms in either interstitial or substitutional positions and surface impurities
6) dislocations
7) stacking faults, twin boundaries and small angle boundaries -- two dimensional
8) a long range strain -- three dimensional

While 2) – 5) are point imperfections, 6) are one dimensional. Phonons must be treated as similar to 8) but are transient.

Single crystals grown from melt show structural defects such as twinning, slip or glide bands, dislocations, low angle boundaries and stacking faults, macroscopic features like morphological faceting and striations, and chemical effects like constitutional supercooling, normal freeze segregation and precipitation phenomena.

The imperfections 2) and 3) are electronic. They are revealed by the measurements of electric conductivity, Hall effect, spectroscopic and ESR experiments, etc. Various techniques in diffraction crystallography can be utilized to reveal structural imperfections. They are non-destructive and almost direct in principle. Unfortunately the diffraction techniques are insensitive to surface defects although a potential use of LEED may be expected. In special cases, ion emission microscopy is the most direct and informative and SEM can reveal the surface structure on a 100Å scale whereas, for macroscopic defect characterization, optical observations combined with etching techniques are better than any other methods. Etching techniques can be tailored to reveal a variety of physical imperfections. Such knowledge is easily susceptible to feed back for improving growth.

DISLOCATIONS AND THEIR OBSERVATION

The perfection of a crystal is usually assessed in terms of its dislocation content though there are other lattice imperfections as mentioned above. The measure of dislocation content is dislocation density which can be defined as dislocation line length per unit volume. Since this cannot be directly measured, the other equivalent definition is used. It is defined as 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 thus do not intersect any surface of the crystal, it has been used as a fairly good measure of dislocation density.

Dislocations can exist in various geometrical configurations ranging from straight lines, jogs and helices to complex spatial networks, irregular three – dimensional tangles, etc. Such three – dimensional dislocation structures can be made visible by the method known as decoration, in which a suitably chosen impurity is allowed to precipitate on dislocation lines. These opaque precipitates make the dislocations visible under the microscope in optically or infra-red transparent crystals. Dislocations were most vividly observed in silicon crystals[1], in silver halides[2] and in alkali halides[3] by the precipitation method. Electron microscopy has proved to be the most powerful technique in direct observation of dislocations. Here the lattice strains around dislocations reduce the transmittance of the specimen foil and produce the contrast in the image. This technique was first used by Hirsch et al.[4] who observed arrangement and motion of dislocations in aluminium. The method of X-ray topography first used by Lang[5] is also a fairly powerful technique used for studying dislocations. In this technique, point - by – point differences in X-ray reflecting power of the specimen surface are utilized to detect local strain fields due to lattice defects.

DISLOCATION ETCHING

Compared to the techniques mentioned above, the technique of chemical etching is quite simple, applicable to almost any crystal and efficient for many purposes. Although only one surface at a time is exposed for observation and the structural detail of dislocations cannot be observed by this technique, the reliability of the technique has been vividly illustrated by Dash[6] in the case of silicon crystals.

Etching is the result of variation in surface reaction or dissolution rates, brought about by crystallographic orientation effect, lattice imperfections, and chemical composition. The terms preferential and non-preferential etchings are often used to designate the presence and absence of crystallographic orientation effects, respectively. In conjunction with light microscopy, etching continues to be a powerful tool in the study of defects. Identification, origin and characteristics of defects such as grain boundaries, slip lines, dislocations, stacking faults, vacancies, and others may rely heavily on etching.

The etching process involving spontaneous chemical reactions between the solid and the etchant is referred to as chemical etching. Although etching by solvents involves no chemical reaction, no distinction usually is made between these two types of etching. Liquid etchants are most commonly employed, however, gaseous media can also be successfully used. Etching is often achieved at elevated temperatures (in the absence of a liquid etchant) when various parts of a surface exhibit differences in sublimation rates, this type of etching being referred to as thermal etching. Other means of etching such as anodic dissolution (electrolytic etching) and sputtering (or ion bombardment) are less commonly used.

Etching processes are generally very complex and their detailed mechanisms are not quantitatively understood. Although a number of generalizations and guidelines have been formulated over years, etching techniques are still based on qualitative concepts. Developing an etchant or an etching procedure for a specific material or purpose is still a " trial and error" process.

When a crystal is attacked by an appropriate solvent which chemically or physically dissloves it, the initial dissolution begins at certain preferential points. This phenomenon gives rise to various types of geometrical features on a crystal surface. Crystals being anisotropic, the rate of attack by an etchant on the crystal surface is also anisotropic in general. This anisotropy usually gives rise to production of conical depressions with regular geometrical outlines. They are known as etch pits, etch marks or etch figures. The sites where dislocations emerge on the surface may become such preferential sites with appropriate choice of the solvent or reactant. Of course, probably the only other preferential sites may be those provided by impurities on the surface. The presence of dislocations was first experimentally confirmed by Horn[7] and Vogel[8] et al with the help of the etching technique. Thereafter, many workers have experimentally proved that dislocations can be revealed in the form of etch – pits. The form and symmetry of etch pits were often used by mineralogists to determine crystal planes and their orientations.

Gilman and Johnston [9,10] have shown in the most striking way the use of etching for studying dislocation kinematics in the case of LiF single crystals. They have studied the etch phenomenon with respect to various aspects including the distinction between grown in and freshly introduced dislocations and the movement of dislocations under the action of applied stress. Lists of dislocation etchants for a large number of materials have been given by many investigators[11-17].

Chemical etching of a crystal surface involves the following sequence:

The reactant (a) Approaches the surface
(b) Interacts with the surface and
(c) Reacts chemically
The products (d) Disengage themselves from the surface
(e) Move away from the surface.

The overall etching process may be electrochemically controlled or diffusion controlled or controlled by a combination of both. The electrochemical concepts involved are discussed by Gatos and Lavine[18] and Gatos[19].

Dissolution of a crystal surface is now thought to occur by the retreat of monomolecular steps, being reverse to that of growth, which takes place due to the motion of steps on a surface. It is believed that when a single crystal face is exposed to a solvent, dissolution usually begins by the nucleation of unit pits of one molecular depth. These unit pits grow as steps retreat across the crystal surface through the action of kinks. The process of dissolution of a crystal surface is affected by a number of factors like

(1) Crystallographic orientation of the surface
(2) Impurity concentration on the surface
(3) Crystal defects present in the surface.
(4) Surface damage and cleanliness.

The way in which these factors affect the etching process is discussed in detail by Irving[20]. Various explanations for the formation of etch pits at dislocation sites have been proposed by different investigators. For a long time, the presence of impurities preferentially segregated at dislocations was considered essential for the formation of etch pits. For example, Gilman[21] and Young[22] considered impurity segregation to be responsible for formation of dislocation pits in zinc and copper crystals. However, Coleman[23] had grown single crystals of pure iron and showed that impurities were not essential for formation of dislocation etch pits.

The problem of etch-pit formation was treated altogether in a different way by Cabrera and Lavine[24] and Cabrera[25]. They treated the initiation of etch-pits as a nucleation process analogous to crystal growth and attributed the nucleation of etch-pits at dislocations to the elastic energy associated with dislocations. While on the other hand, Gilman[26], on the basis of following arguments, proposed that dislocation core energy is primarily responsible for the formation of dislocation etch pits:

1) It is much more difficult to produce dislocation etch pits in metals than in covalent and ionic crystals. The core energy of dislocation in metals is indeed less than that in other types of materials while the elastic strain energy associated with dislocations is about the same in all materials.
2) The stress fields of dislocations close to each other tend to cancel out, particularly when dislocations form a tilt boundary. Thus isolated dislocations should etch more readily than those close together if their elastic energies were significantly effective in etching process. However, all dislocations in a given crystal are etched at approximately the same rate.
3) In compounds with zinc blende structure, the positive and negative dislocations are etched differently, although their strain fields are identical.

Schaarwachter[27] modified Cabrera's treatment as suggested by Gilman and derived the conditions under which dislocation core energy, strain energy and both of these together can be important for the formation of dislocation etch pits.

Gatos and Lavine[18] explained the formation of dislocation etch pits for diamond-type structure on the basis of chemical bonding of atoms along the dislocation lines.

A new approach to the problem was made by Frank[28] giving a kinematic theory of growth and dissolution. The theory assumes that growth or dissolution of a crystal proceeds by way of disposition or dissolution of atomic steps. The theory was later applied to the etching process by Cabrera[29]. While sufficient condition for the creation of etch pits at dislocation sites can be given by Cabrera's theory as modified by Gilman and Schaarwachter, the necessary condition for the production of a visible etch-pit is governed by the kinematic considerations of the dissolution process used in Frank's theory, according to which for an etch pit to be visible, the following two conditions should be satisfied:

1) The ratio of the dissolution velocity along the dislocation line, v_d, to the edge dissolution velocity, v_l, must be greater than a certain value, m, so that the etch pit can have sufficiently steep slope. Thus $v_d/ v_l \geq m$, where $m \sim 0.1$.
2) The dissolution velocity, v_d, at the dislocation site be greater than the average vertical dissolution velocity, v_s, of a dislocation free region of the surface. Thus at dislocation sites, $v_d > v_s$.

Etch pits formed during etching do not necessarily correspond to dislocations. Precipitates or impurity inclusions, clusters of point defects etc. may also lead to etch pit formation.

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

(1) Alternate application of the etchant followed by mechanical or chemical polishing. Etch pits associated with individual dislocations reappear after

each successive polishing and etching, since a dislocation line cannot terminate inside a crystal.

(2) When cleavage is possible, etch patterns produced by the etchant on the two oppositely cleaved surfaces should appear as mirror images of each other. However, Sagar and Faust[30] and Bhatt and Pandya[31] have shown that branching and bending of dislocations at the cleavage may result in deviations from one-to-one correspondence of etch pits on oppositely matched cleavage surfaces. Thus, deviation from one-to-one correspondence of etch pits on oppositely cleaved surfaces does not always indicate unreliability of the etchant as a dislocation etchant.

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

(4) The comparison of measured distances between pits on a lineage line with those calculated from X-ray orientation differences across the boundary may also help in judging the reliability of the etchant as a dislocation etchant.

(5) Any plastic deformation of the crystal should result in increase of etch pit density at least in the vicinity of the region of deformation, since plastic deformation always involves creation and motion of dislocations.

Thus chemical etching is usually an assured way of revealing dislocations and has been widely used with good success. Etching processes are generally very complex and developing a dislocation etchant for a given material still remains a trial and error process. Etching can be effectively used to characterize the crystal and

(1) to decide whether a given solid is a single crystal, a polycrystal or an amorphous body.

(2) to distinguish between different faces of a crystal.

(3) to reveal the history of growth of crystal.

(4) to determine density of dislocations

(5) to determine impurity distribution in crystalline bodies.

(6) to study stress-velocity relation for individual dislocation motion.

(7) to study deformation patterns like pile-up and polygonization.

(8) to study dislocation multiplication.

(9) to study plastic flow around indentation.

(10) to study fracture mechanism.

(11) to study slip and twin systems and interaction of dislocations under stress

(12) to study kink configuration and inclination of dislocations.

(13) to study origin of dislocations in as-grown crystals.

(14) to distinguish between fresh and as-grown dislocations.

(15) to delineatc grain boundary and

(16) to study polarity of crystal lattice.

Chemical etching, though an old technique is quite useful even in modern days in a variety of crystals. A detailed account on chemical etching of $Bi_xSb_{2-x}Te_3$ (x = 0, 0.2, 0.5, 1) and $In_{0.2}Sb_{1.8}Te_3$ crystals carried out by the author is given in Chapter 8.

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