PART II

CHEMICAL ETCHING OF CALCITE CLEAVAGES.

CHAPTER 3

CHEMICAL ETCHING (GENERAL)

3.1 Introduction:

When a crystal is attcked by an appropriate solvent which chemically or physically dissolves it, the initial dissolution begins ~~of~~ at certain preferential points. This phenomenon is known as etching. It gives rise to various types of geometrical features on a crystal surface. It is well known that single crystals are anisotropic. The rate of attack on the crystal surface is also anisotropic, being different along different directions. This anisotropy usually gives rise to the production of conical depressions with regular geometrical outlines on crystal surfaces. They are usually known as etch pits, etch marks or etch figures. The form and symmetry of etch pits were used by mineralogist to determine crystal planes and their orientation with one another. At that time, production of etch pits on a crystal surface was not understood satisfactorily. 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 perfect 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 understanding of etch phenomenon was enhanced by the recognization of various types of imperfections in a crystal. The defect points are not bound with the surface as strongly as the other points of the crystal. They need less energy to dissociate than that required by points (atoms) in the regular structure. If chemical or physical change gives energy to dissociate imperfections from the exposed surface substantially, etch pits or etch features may be observed on it. It is not necessary that solvent should be present at the time of etching; other appropriate physical conditions such as ionic bombardment, temperature etc. also help to form preferential etch pits at defect points on a crystal surface. Following are the ways of obtaining preferential dissolution on a crystal surface (i) Chemical etching, (ii) Thermal etching, (iii) Ionic etching, (iv) Electrolytic etching and (v) Etching by dehydration. The etch patterns obtained by any one of the above methods are studied by high resolution optical techniques, or by X-ray microscopy or by electron microscopy. The behaviour of materials towards a given method of etch depends upon the nature of the material. For example, etching of metallic crystals usually initiate at preferential points with the formation of oxide layers, subsequently followed by their dissolution. In this chapter a brief review of various methods of etch is given with special reference to etching of ionic crystals.

Chemical etching includes major portion of research work in etching and substantial work on different crystals is now available in literature (Regel et al, 1960; Johnston, 1962). It is difficult to give a full account of chemical etching here. Some of its important salient features will be given in the present chapter.

3.2 Etch Features on a Crystal Surface:

Chemical etching produces usually a few or all of following etch features on a crystal surface: (1) Etch spirals, (2) Etch pits, terraced, flatbottomed and point-bottomed, (3) Linear etch rows, (4) Polygonized etch figures, (5) Tunnels and dendritic etch features and (6) Shallow pits, pits with beaks, etch hillocks etc.

3.21 Etch Spirals:

Frank, (1949), has considered the effect of screw dislocations on crystal growth and suggested that if a crystal grows by screw dislocation mechanism, a growth spiral should be obtained on the surface. He concluded that the conditions that could cause it to grow would also make it imperfect. Spiral etch pits were observed to form on surfaces of many crystals including metals and semi-conductors. In the earlier work, spiral pits were correlated with the emergent point of screw dislocations. The condition which produces spiral etch pits is opposite to that by which a growth spiral is created. Amelinckx et al, (1957), Ellis, (1957) etc. gave explanations of spiral etch pits with large step heights on the basis of helical dislocations. Lang, (1957), has shown that there is no need of a screw dislocation in a crystal for the formation of spiral etch pits. The correspondence of growth spirals with etch pits was first observed by

Horn, (1952), on the silicon carbide crystals. He was first to delineate dislocations by chemical etching. Gevers et al, (1952), also independently observed etch pits on growth spiral in silicon carbide crystals. They observed deep polygonized etch pits at the emergence of the screw dislocations on the surface, in contrast to the shallow rounded pits formed elsewhere.

3.22 Etch pits:

The most noticeable feature on a chemically etched surface consists of etch pits. They represent the early stages of crystal dissolution and subsequent information concerning the origin, distribution and other important aspects of pits has been sought by many workers. Etch pits are used to locate dislocations terminating on a crystal surface. Density of dislocation etch pits usually remains constant for different periods of etching. Generally it is higher in metal crystals (10^5 to 10^7 /cm^2), than in ionic crystals (10^3 to 10^5 /cm^2). Crystals with low dislocation density are desirable for study of individual dislocations by etch pit technique. Whether all etch pits reveal dislocations or all dislocations give rise to etch pits is a question which is not yet fully answered. The different types of dislocation etch pits (symmetric and asymmetric) were produced on cleavage surfaces of

NaCl and LiF by Amelinckx, (1954) and Gilman and Johnston, (1956), respectively. This is found to be due to different inclinations of edge and screw dislocations. Gilman and Johnston have shown that edge dislocation lines lie normal to the plane of observation in LiF crystals, so symmetric pits arise after heavy etch by CP-4 etchant, while screw dislocations lie 45° to the plane of observation and etching of the screw dislocations gives rise to asymmetric etch pits though symmetrical etchant was used in both cases. They could also distinguish between aged and fresh dislocations. Etch pits formed at aged dislocations are shallower than those formed at fresh dislocations. The different types of etch pits (edge and screw) terminating on grain boundaries were distinguished by their varying depths on surfaces of NaCl crystals by Amelinckx, (1956). Livingston, (1962), developed etching technique to distinguish between positive and negative edge dislocations in copper. He found two different types of pits (light and dark) on the (111) surface of copper single crystals. He has further shown that 95% of the dislocations were of the majority sign. Marukuwa, (1967), also observed dark and light pits on Cu{111} surface. He concluded that pits at screw dislocations had dark appearence.

The visibility of an etch pit depends on the combination of the rate at which the steps move on the surface, i.e. function of normal and lateral rates of dissolution of a given site (Gilman et al, 1958). If V_n and V_s represent the normal and the lateral rates of dissolution respectively, the visibility of a pit depends upon the ratio V_n/V_s. If $V_n << V_s$, very shallow pits will be formed which would not be visible under optical microscope. It is found that readily visible pits can be obtained when $V_n/V_s \geq 0.1$. If pits are produced at line defects the factor V_n/V_s appears to be related with the slope of etch pits. For a symmetric pit, all the planes forming a pit are equally inclined; while slopes of these planes are different for asymmetric pits. A detailed study of slopes of etch pits was systematically done by Ives and Mcausland, (1968). They had classified pits into three categories, depending upon the various ranges of slopes of pits on $\{0001\}$ surface of Zinc crystals. They reported that planes of the etch pits were vicinal faces. Benabraham, (1965), reported that the planes of pits are low index planes in ZnS crystals. It is now known that shapes of etch pits are functions of concentration of etchant, etching time, temperature and condition of etching. The shapes of pits produced by various etchants of different concentrations on calcite cleavage surfaces were studied by Honess and Jones, (1937), Keith and Gilman, (1960), Patel and Goswami, (1962a), Pandya and Pandya, (1961). The bounding side of a pit may be rectilinear or curvilinear depending upon the energy of an etchant. Tolansky and Patel, (1957b), observed rectilinear etch pits when etching was carried out on octahedral faces of diamond by fused potassium nitrate at temperatures below 475°C, while at 525°C, etching was much faster and the sides of pits became rounded. Pandya, (1969) had also studied the aspect of curvilinearity of etch pits for various crystals, such as calcite and mica.

The effect of stirring of etching solution on KBr and NaCl crystals was studied by Kostin et al, (1961) and Toropov and Udalov, (1965) respectively. Kostin et al, observed conical etch figures instead of pyramidal etch pits due to vigorous stirring while Toropov and Udalov observed octahedral etch pits on NaCl instead of circular etch pits due to vigorous stirring. It was well known that widening rate (that is V_s) of an etch pit also increased due to vigorous stirring though shape remained unchanged.

The present author has made a detailed

systematic study of different shapes of pits produced by different concentrations of various etchants on cleavage faces of calcite. Further the effect of the time of etching and condition of etching on the shape of etch pits is also studied. This will be discussed in the relevent chapters.

The necessary condition for revealing dislocations by etch pits is exact matching of cleavage counterparts of a single crystal having cleavage planes. The other condition is constant etch pit density for successive etching, if all etch pits reveal dislocations only. Amelinckx, (1956) observed slight imperfect matching on etched cleavage counterparts of sodium chloride crystals. He concluded that it was due to branching of dislocations on the crystal surface. Sagar and Faust, (1967) have made a detailed study of bending and branching of dislocations on the cleavage faces of $Bi_2 Te_3$. Pits which are formed at the point defects become too shallow to be visible after prolonged etching. Successive etching and polishing of crystals may help to understand three dimensional behavior of dislocations. Polishing is usually an advance stage of etching where all regions of a given surface are equally attacked. In other words, V_n is same for all points. Further it should be noted that polishing is not possible for all crystals. The reasons are not very clear.

Etch pits are usually of three types i.e. (i) Flat-bottomed, (ii) Point-bottomed and (iii) Terraced etch pits. The third type may further be subdivided into (1) Flat-bottomed with terrace structure (2) Point-bottomed and terraced with closed layers or with spiral formation. Flat-bottomed pits occur on etched surfaces at the sites of point defects. This is due to formation of chemically highly resistant layers after certain dissolution at point defects, where V_n has extremely small value, nearing zero. However rate of surface dissolution V_s, does not become zero thereby increasing shallowness of flat-bottomed pits. Point-bottomed pits are observed at line defects intersecting the plane of observation. Depth of a point bottomed etch pit usually increases with etching time. There is also variation of normal velocity of dissolution V_n with etching time. Hanke, (1961)observed different slopes of the same etch pits for different periods of etching by the same etchant. Terraced etch pits are formed at the dislocations associated with the impurities (Gilman, 1960). Sometimes the distance, between any two successive layers of terraces are unequal. This was explained on the basis of unequal distribution of impurities around dislocations. Hanke (loc. cit) has also observed stepped structure of etch pits on cleavage faces of calcite crystals etched by low concentration of glacial acetic acid. He explained that dissociation constant of the etchant at low concentration was more, while reaction product was considerably less. This gave rise to a stepped structure of etch pits.

3.23 Eccentricity of Etch Pits:

When a pit is projected on the observation plane, depth point is the projection of the point of maximum depth. The normal rate of etching is maximum at depth point of an etch pit. Lines of intersection of planes forming a pit pass through the point of maximum depth. The eccentricity of pit arises due to the non-coincidence of geometrical centre with the depth point, in the plane figure of etch pit. It is reported in many cases (e.g. on NaCl by Amelinckx, (1956), on diamond by Patel (1961) on calcium fluoride by Patel & Desai, (1965), on gypsum by Patel and Raju, (1967). They had explained the formation of the eccentric pits at the seat of inclined dislocations ending on the surface. They found practically no effect of concentration of an etchant on the eccentricity of an etch pit. The study made by the present author on eccentricity of etch pits on calcite cleavages produced by etchants of various concentrations has shown very clearly that besides other factors concentration of an etchant does affect the eccentricity of an etch pit.

3.24 Orientation of Etch Pits:

The change in the orientation of etch pit produced by various etchants on crystal surfaces has been observed by many workers. Gilman and others, (1958) noticed orientation difference between etch pits produced by etchants containing water with poison (such as FeF_3) and CP-4 (acid mixture) which were named by them as etch W and etch A, on LiF crystals. Evans and Sauter, (1961) were first to observe change in etch pit orientation on (111) face of diamond by changing temperature of the etchant. They explained this to be due to formation and motion of different steps at different reaction energies due to different etching temperatures. Joshi and Ittiaychan, (1967), observed change in etch pit orientation on the basal cleavage of apophyllite crystals by the change of concentration of an etchant. The rotation is attributed to the difference in resistivity offered by the edges of growth layers on different planes. Recently Haribabu and Bansigir, (1970) observed change in etch pit orientation on sodium chloride cleavage faces etched by ethyl alcohol containing different concentrations of a poison. They explained it to be due to formation of different types of complexes at defect points. The crystals studied above have either isometric or tetragonal structure. The change in orientation of etch pits in a rhombohedral crystal surface is of a different type. In the above cases, etch pit shape was preserved because all boundaries of pits rotated for the same angle, say 45° or 90°. For example orientation change of 45° of a square pyramidal etch pits having boundaries parallel to ⟨100⟩ and diagonals parallel to ⟨110⟩ produces same pit, having boundaries parallel to ⟨110⟩ and diagonals parallel to ⟨100⟩. Here directions of diagonals and boundaries of etch pits are interchanged. This is not true for a crystal having rhombohedral and other structures. If directions of diagonals and boundaries are interchanged for etch pits produced on a rhombohedral cleavage of a crystal, shapes of etch pits do not remain unchanged. As a matter of fact rhombohedral pyramidal etch pits turn into rectangular pyramidal etch pits on interchanging directions of diagonals and boundaries of pits.

As far as the author is aware, such changes in the orientation of pits on rhombohedral cleavages of single crystals, and in particular calcite are not reported in the literature. In the present work a systematic study of changes in orientation of etch pits on calcite cleavages etched by glacial acetic acid of varying concentrations is reported. The above mentioned change in orientation of pits was pertaining to the whole etch pit shape with reference to various directions on surface under observation. There is also a distinct type of orientation change within the structure of an etch pit. In this case the shape and orientation of etch pit with reference to a given direction on a crystal surface remain unchanged. However, it is found from the present studies that the position of a depth point with respect to the geometrical centre of the plane figure of a pit is a function of concentration of an etchant. The concentration of an etchant may be chosen in such a manner so as to produce pits of almost identical sizes with 180° change in the position of depth point from the [illegible] geometrical centre. This can be treated as a change in orientation of etch pits by 180° although shapes and sides of etch pits remained nearly same. The present work reports a systematic study of these two types of change in orientation of etch pits.

Some etchants are optically active such as dextro--, levo -- tartaric acid etc. Etch pits of different characteristics are produced on a crystal surface etched by etchants of different optical activities. Blackmore and Nomura, (1961) observed that cleavage planes of tellurium crystals could not be made congruent. When matched counterparts were etched, the etch pits formed on them can be made congruent by the rotation of one with respect to the other.

3.25 Dislocation Etch Pits:

Dislocation etch pits are usually of same size and shape but may be of different depth. The difference in depth may be due to inclination of dislocation line or energy of a dislocation. Patel and Ramnathan,(1964) observed oppositely oriented triangular etch pits as well as hexagonal etch pits on octahedral cleavages of diamond. They explained these observations by assuming different energies of various dislocations inside the crystal. It is well known that dislocation line never ends within a crystal. However, if it remains inside the crystal it must form a closed loop. The distance between the positions of depth points of a pair of point bottomed etch pits produced on a dislocation loop are ~~ranging~~ varying with etching time and when the loop is exhausted pits coalesce with each other and form a single pit. Due to non-existence of dislocation line it becomes shallower on further etching. It is possible to observe the movement of dislocation line by the application of an external stress between the process of etching and reetching. When a dislocation line moves, a point bottomed pit becomes flat-bottomed. Gilman and Johnston, (1956) were first to observe dislocation motion in Lithium fluoride crystals. They concluded that it was difficult to control the motion of dislocation in a simple tension or compression test. Even without the application of a stress to a crystal, large rapid motion of a dislocation was observed on etching (Pariskii et al, 1963). This was explained by assuming the presence of local arresters which prior to etching locked dislocations in the crystal. The etching of this crystal removed the local arresters by dissolving them, thereby enabling them to move in the crystal. Tyagrazdzhan and Urusovskaya, (1965) also observed dislocation movement in Caesium Iodide by double etching technique. They established that dislocations moved at a stress less than that required to multiply them.

The above characteristics of etch pits are common for all crystals. Impurity segregati~~g~~on was believed to be necessary for the etch pit formation in metal crystals. Vermilyea, (1958) observed that very large undersaturation required for produc~~t~~ing etch pits in metal crystals, could not be maintained due to diffusion of dissolved material away from the surface. Hence prior segregation of impurity around defect points is required for producing etch pits in metal crystals. Lovell and Wernick, (1959) found an etchant for metal crystals which required no impurity segregation around dislocation sites for producing etch pits. Prekel and Lawley, (1966) observed that impurity was not necessary for dislocation etch pit formation in molybdenum crystals.

3.26 Etch Rows:

Sometimes etch pit raws are observed on many crystals. They reveal surface defects. Burgers, (1940) proposed a dislocation model for the boundary betweenn two crystals differing in orientation by a small rotation θ about an axis in the boundary. It consisted of a set of edge dislocations parallel to the axis, with regular separation $D = {}^{b}/_{\theta}$ where b is the appropriate transofrmation vector. Vogel et al, (1953) confirmed the identity of the disorientation measured at a sub-boundary by X-ray diffraction and inferred from the spacing D of dislocations revealed by etch pits. This was the first proof giving correlation between etch pits and dislocations in a lineage boundary as well as for isolated edge dislocations. Earlier Shockley and Read, (1950) investigated theoretically the energies and motion of grain boundaries between two crystallites by use of a dislocation model of a grain boundary. They also described various types of arrays of dislocations. If etch rate V_n along the normal to the plane is much more than the lateral rate V_s, etch tunnel may be observed. While etch grooves may be obtained if the dislocations are lying just parallel or just below the surface. Dendritic etch features are also observed on a crystal surface, when irregular etching or etching with simultaneous growth of a crystal surface takes place. Dendritic etch features on barite surfaces were observed when single crystals of barite were grown by the flux method in the laboratory (Saraf, 1971). This is found to be due to irregular etching of growing crystals of barite by sodium chloride present in flux at high temperatures.

Alongwith point-bottomed and flat-bottomed pits shallow background pits are observed on etched surfaces. It is believed that these pits are formed at point defects on a surface. Because of more etching these pits become too shallow to be observed and their density is usually very high and does not appear constant. Pits with beaks are occasionally observed when etch rate V_n is higher than the rate of surface dissolution. Recently Haribabu and Bansigir, (1969a) had observed etch pits with beaks on cleavage faces of Sodium Chloride. They observed that beaks were formed at low undersaturation or high poison content. Vigorous stirring of the etchant at the time of etching suppressed the formation of beaks. They conjectured that beaks were associated with the segregation of impurity at dislocations. Instead of etch pits, etch hillocks were also observed in some cases. The formation of etch hillocks is opposite to that of etch pit formation. Sometimes defect points offer high resistance to the etchant than the defect-free areas on the surface. Hence the defect-free surface is dissolved without affecting the defect points very much. It results in the formation of etch hillocks. Sometimes they are also formed due to growth of the crystal at defect points in the process of etching. Usually this occurs during the thermal etching of a crystal.

3.3 Thermal etching:

It is known that surface atoms are bound with one another and with the crystal by a comparatively large force of attraction. If a crystal is provided enough energy, against the force of attraction, many of the atoms will leave the surface. One way to provide energy to a crystal surface is by heating it to a certain temperature. If the amount of heat required to raise the temperature of a crystal surface is properly controlled, those surface atoms having higher energy than others will be the first to fly away from the surface. As a result etch marks will be produced at these points. These are known as thermal etch figures and the process is called thermal etching. This type of etching is considered to be the reverse of growth of crystals from vapour. Thermal etching is done usually in the desired atmosphere or in vacuum. Various etch features such as spirals, closed loops, etch pits etc., are observed on a thermally etched crystal surface. If thermal etch figures are formed on the dislocations, the movement of dislocations may be observed. It is thought that thermal etching is much similar to chemical etching. However there are some differences in both types of etching. The detailed study of thermal etch figures is reported in the relevent chapter.

3.4 Ionic etching:

Initial dissolution of surface at defect points due to ionic bombardment is called ionic etching.

Etching by ionic bombardment can be carried out in a wide temperature range. Different types of ions such as Krypton, Argon etc. can be used. The ionic etching is generally used for revealing defect structures in semi conductors. Details of ionic etching is given in chapter 7.

3.5 Electrolytic etching:

Electroplating is a process where two electrodes of similar or dissimilar materials are placed in an electrolyte through which is passed a constant current for some time. Hence deposition of material takes place on one electrode with a corresponding loss of material on the other electrode. As a result of this loss, the electrodes get etched or dissolved. When the surface of this electrode was examined, it was found to be covered with etch patterns. This process is called electrolytic etching. Very little work on this type of etching appears to have been reported in the literature. Berlac, (1961) observed variation of density of electrolytic etch pits with change in current density. Demkin, (1964) found that small variation in the condition of electrolytic etching induced a movement of dislocations in molybdenum in the absence of external stress.

3.6 Dehydration etching:

Dehydration etching is less understood phenomenon and very less work on microtopographical study of dehydrated crystal surfaces is available in literature. Some crystals contain water of crystallization. Water usually evaporates at all temperatures. However, in the crystal, water of crystallization is normally intimately connected with the crystal structure. Hence it cannot be removed easily at room temperature. In order to remove it, the crystal should be given an additional amount of heat energy. This is done by keeping crystal at temperatures higher than the room temperature and usually less than the boiling point of water. Dehydration was then obtained either below or above $100^{\circ}C$ in many crystals. Evaporation of water of crystallization gave rise to dehydration figures on a crystal surface. Change of structure of crystals is also observed in many cases in the process of dehydration. When a crystal possesses more than one molecule of water of crystallization, dehydration occurs in steps for different temperatures. A large amount of literature is available on the chemical study of complete dehydration of materials. Initial stage of dehydration is thought to be a physical phenomenon. Whether dehydration figures occur at the site of dislocations in a crystal is not yet fully resolved. It is known that dehydration process is a reversible one while chemical etching is irreversible. Insufficient experimental evidence is available for the reversibility of dehydration figures. Detailed study about dehydration will be given in chapter 9.

3.7 Theoretical Development:

In the earlier section of the present chapter, different types of etch features produced by various types of etching were referred to and the correlation between etch pits and dislocations or other types of defects were also observed. The study of formation of etch figures may be divided into two stages

(a) nucleation of pits (b) formation of visible pits. The first is a sufficient condition for etch pit formation while other is a necessary condition of etching. Detailed understanding about the formation of dislocation etch pits is of vital importance for developing new etchants with specific characteristics which in turn is likely to promote better understanding of the mechanism of chemical etch pitting process.

Daniell, (1816) who was a pioneer in etching work tried to correlate the nature of etch figures with the molecular structure of the crystalline solids. Increasing interest in the phenomenon of etching is attributed mainly to the efforts of German scientists, in the later half of nineteenth century. The first attempt to explain, several aspects of chemical process of etching is due to Goldschmidt, (1904). According to him the chemical action between the corrosive and surfaces gives rise to currents, some of which are directed towards, and some are away from the surfaces, the interference of the ascending with the descending currents tends to form eddies, each of which is a starting point of a pit. He reported the occurrence of preferential etching along fine scratches, impurities, inclusions, dust particles etc. Further interest was created in the etching method with the discovery of

X-rays and the development of the X-ray analysis of the crystal structure. The importance of chemical etching was increasingly felt when it was used for revealing dislocations and other kinds of structural defects. A detailed synthesis of the imperfections, primary & secondary is given by Seitz, (1952).

The first extensive theoretical treatment of the nucleation of etch pits at dislocations were given by Cabrera and Lavine, (1956). They postulated that the strain energy localized in the vicinity of a dislocation, lowered the free energy required for the nucleation of a cavity of unit depth at the site of intersection of the dislocation with the cleavage surface. This leads to ~~proper~~ preferred dissolution of the surface at dislocation sites. Gilman, (1960a) has criticized the above model because elastic strain energy of a pure screw dislocation is zero at the surface and both types of dislocations (having some finite energy at a surface) seem to be etched in almost identical fashion. He has suggested that the dislocation core energy is more important than the elastic strain energy for the nucleation of etch pits. This is supported by the observations that dislocations in metals are more difficult to etch than those in ionic or covalent crystals. The core energies of dislocations in metals are less than in other types of materials while the elastic strain energies of dislocations are about the same for all materials. Schaarwachter, (1965) has modified Cabrera's treatment taking due care of core energy suggested by Gilman. He distinguished three cases depending on the relative importance of the contributions of the dislocation core and elastic strain energy respectively.

The necessary condition for the formation of visible etch pits is governed by the kinetics of dissolution ledges as they move across the crystal surface during dissolution. Successive monomolecular ledges usually sweep across close-packed surfaces. In order for an etch pit to be visible under an optical microscope, the slope of the etch planes should be at least about 3° with respect to a close-packed surface. It should be remembered that vertical dissolution velocity at a dislocation should be greater than its average value at a dislocation free portion of the surface. Yamamoto, (1958) considered that etch pits on a crystal surface might originate from a microscopic pit or from an easily soluble, minute portion or inclusions or from a dislocation existing or terminating on a surface. Both the depth and diameter of an etch pit originating from a dislocation increases with etching time. Frank (1958) developed kinematic theory of crystal ~~forwth~~ growth and dissolution. He has given equations to describe crystal growth and dissolution based on the consideration that it takes place as a progression of unit step with similar heights across an approximate reference face of a crystal.

Impurity may segregate around dislocations in impure crystals. Impurity may enhance greater chemical reactivity, giving rise to preferential two-dimensional nucleations in metal crystals. It is normally observed that etch pitting solutions for most of the metals and semiconductors studied so far are strong oxidizing agents. It is presumed that the first step in the dissolution process is an oxidation of crystal surface. This is followed by the removal of oxide layer. It was observed that oxide nuclei were formed on pure Cu crystals (Young, 1960) and on Ge crystals (Faust, 1963). However, these oxide nuclei were not related to dislocations. The influence exerted by impurities on and around dislocations has been discussed in detail by Gilman et al (1958) on LiF crystal which was etched by water with the addition of impurities such as FeF_3, AlF_3 etc. They found that nature of etch pits was dependent on the concentration of FeF_3 in solution. The function of FeF_3 is to inhibit the ledge motion. It means that V_s depends upon Fe^{+++} concentration. The Fe^{+++} ion (and such other [illegible] in about 30 compounds) retards the step motion, apparently by adsorption on the steps, but does not seem to effect V_n. Cations (Fe^{+++}, Al^{+++} etc) are believed to have strong tendency to form (FeF_6) , (AlF_6) complexes and that is why they play a major role and anions donot effect the pit formation.

Burton - Cabrera and Frank, (1956) developed a theory of crystal growth with the help of unimolecular steps. The equilibrium structure of steps, the activation energy of nucleations, the statistics of kinks in steps as well as effect of dislocations were discussed. Cabrera, (1956) examined theoretically the conditions for the formation of etch pits and oxide nuclei at dislocations. He observed that the energy associated with the dislocations having large Burger Vector, is sufficient to cause etch pit or oxide nuclei. Sears, (1960) reviewed theory of Cabrera and modified it by including the effect of solution poison. Step poison increases the rate of ~~3~~2-dimensional nucleation at fixed supersaturations but markedly decreases the rate of step motion or of spreading of the newly formed layers. Ives and Hirth, (1960) studied the etch pit profile as a function of concentration of LiF and FeF_3 in the etching solution. The results were consistent with a mechanistic theory involving dissociation of LiF from unimolecular steps on it and subsequent diffusion into solution if a time-dependent adsorption of FeF_3 poison at the receding unimolecular steps was invoked. The above theory deals with 'Part diffusion part inhibitor control of ledge kinetics'. It explains very well other results except slope of etch pits. According to this theory, the slope of a dislocation pit should decrease with decreasing undersaturation of Lithium fluoride. Experiment showed the pit slope to be essentialy independent of LiF concentration. The explanation given for this discrepancy was that the accumulation of an inhibitor on a given ledge increased as the distance between ledge and surface increased i.e. it is a time - dependent process. Westwood et al, (1961) used aqueous solutions of long chain fatty acids to reveal the point of emergence of dislocations in LiF. This shows that fatty acid may provide a ready source of potential inhibitors for a variety of crystal-etchant systems. Chemisorption and complex formation in this process is likely to affect the core energy available for the nucleation of kinks. Ives and Ramchandran, (1967) studied the morphology of etched LiF surface with an electronmicroscope. It reveals complex structure of surface ledges on $\{100\}$ cleavage face of this crystal. The ledge structure is complex due to irregular inhibition by the Ferric ions. Haribabu and Bansigir, (1969b) studied the role of poison and undersaturation of the solvent in the etching mechanism, concluded that the stability of the complexes formed at the kink site and those formed in the solvent layer very close to the crystal surface played a very important role in the formation of etch pit.

It is known that optical resolution of a microscope is inadequate to observe the atomic steps or the small bunches of steps in the pit nucleation and early stages of growth. How do steps move during the etching of a crystal? Where does it (Poison) act? How does it act for inhibiting the nature of steps? What is the exact role of poison? The present theory is not yet developed to the extent of answering convincingly these questions.