CHAPTER – 2

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The concept of dislocations as line imperfections in crystals was developed by Orowan(1), Polanyi(2) and Taylor(3) for the purpose of resolving the large discrepancy in the observed value of yield strength of a real crystal from that theoretically derived on the basis of an ideally perfect crystal. All real crystals contain defects. Various important properties of a crystal, from electrical conductivity to hardness, depend to more or less extent on these defects also. There are various types of defects in a crystal :

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

The line defect is of two types, edge and screw dislocations(4). Dislocations in an as – grown crystal may originate, according to Brice(5), by

I. propagation from seed crystal
II. Shear strains due to mechanical and thermal stresses or due to change in composition
III. dendrite growth and
IV. collapse of vacancies

Properties of dislocations and their various geometrical features have been discussed in detail by Weertman and Weertrman(6), Cottrell(7) and Bueren(8).

While much is known about motion of dislocations, their various interactions, their multiplication and the way in which they affect various properties of crystals ranging from plastic deformation to electrical conductivity, the nature of their origin is not exactly known. Since dislocations do not appreciably lower the configurational entropy of a crystal through their presence and their energy of formation is very large, they are not thermodynamically stable lattice imperfections. Several theories giving the possible causes of their origin have been proposed. Teghtsoonian and Chalmers(9) and Frank(10) showed in their theory that the dislocations are formed by condensation of vacancies as a result of thermal gradient present at the time of crystal growth from melt. Kuhlman – Wilsdorf et al(11) proposed a vacancy condensation mechanism for dislocation formation in plastic deformation. Billig(12) showed for germanium that thermal stresses set up by non-uniform cooling of the crystal during crystal growth are responsible for giving rise to dislocations.

Though there are other lattice imperfections, which can exist in a crystal, perfection of a crystal is usually assessed in terms of its dislocation content. 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. This 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 thus do not intersect any surface of the crystal), it has been used as a fairly good measure of dislocation density.

The simplest and easily accessible technique employed to observe dislocations is the "etch – pit" technique(13-15). The etch pits at the sites of dislocation can be formed either by chemical reaction or by physical dissolution of a crystal in a suitable solution known as an etchant. Some times, etching is also done by other methods like ion bombardment and by thermal treatment. The etching process is in general almost opposite to that of growth(16-18).

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(4) discovered screw type of dislocations. Later, Mott et al(19) 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(20-22)). 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 percipitate 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)(23), Silver halides (Hedges et al(24)), in alkali halides (Amelinckx(25)) and in CdTe crystals (Wada et al(26)). For the direct observations and study of dislocations, highly sophisticated techniques of Electron microscopy and X-ray topography (Lang(27)) have been successfully introduced.

The chemical dislocation etching technique is discussed below in detail with the discussion limited to metals and semiconductors and wherever it is necessary, some references to non-metals are given. The chemical etching gives rise to various types of geometrical features on a crystal surface. Due to anisotropy of a crystal, the dissolution rates are different in different directions giving rise to the production of depressions, with regular geometrical out lines 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 minerologists to determine crystal planes and their orientations. Dissolution of a crystal surface is effected by the re-treat of monomolecular steps, the process being reverse to that of growth which takes place due to the addition of steps on the surface. It is believed that when a crystal face is exposed to a solvent, dissolution begins by nucleation of unit pits of one molecule depth and these unit pits grow as steps re-treat across the crystal surface through the action of kinks. The chemical etching of a crystal surface involves the following sequences :

Reactants :

1. Approach the surface
2. Interact with the surface and react chemically.
3. React chemically.

Product :

1. Disengage themselves from the surface
2. Move away from the surface

Gatos(28) and Gatos et al(29) reported that 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 :

a. Crystallographic orientation of the surface
b. Impurity concentration on the surface
c. Crystal defects present in the surface

d. Surface Damage and cleanliness

The way in which these factors affect the etching process is discussed in detail by Irving(30). 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 etch pits. For example, Gilman(31) and Young(32), considered impurity segregation to be responsible for formation of dislocation pits in zinc and copper crystals. However, Coleman(33) had grown single crystals of pure iron practically free of dislocations. His study showed that impurities were not essential for formation of dislocation etch pits. This was further supported by Lovell and Wernick(34), Livingston(35) and Young(36) in the case of etchants that can produce etch-pits on {111} surfaces of high purity copper crystals.

The problem of etch pit formation was treated altogether in a different way by Cabrera and Lavine(17) and Cabrera(18). 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(37), on the basis of the 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 dislocations 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 the zinc blende structure, the positive and negative dislocations are etched differently, although their strain fields are identical.

For the formation of visible etch pits, according to Frank

$V_d / V_l \geq 0.1$ and $V_d > V_s$, where,

V_d = The dissolution velocity along the dislocation line,

V_l = The ledge dissolution velocity and

V_s = The average vertical dissolution velocity at a dislocation free region of the crystal surface.

The formation of etch pits during chemical etching does not necessarily correspond to dislocation. 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(38), Trivedi(39) and Bhatt et al(40). Also a crystal can be etched electrolytically as reported by Pandya(41) and Berlec(42). This technique has also been successfully applied to the study of dislocations in plastically deformed crystals (Vogel, Greiner, Breidt et al and Ellis)(43-46). An excellent review of etching of LiF crystals has been given in detail by Gilman(47). Trivedi et al(48) and Iwanaga et al(49), used etching technique to study dislocations in $Cd_{0.96}Zn_{0.04}Te$ and CdTe single crystals, respectively. Imashimizu et al(50) studied the formation of slip pattern in copper crystals and its dilute alloy crystals.

In order to study etching mechanism with various parameters affecting the 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)(51-56). Recently in 1989, Lin et al(57) have 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 can

not terminate inside a crystal.

2. The etch pattern produced by the etchant on two oppositely matched cleaved surfaces should appear as mirror images of each other, if cleavage of a grown crystal is possible. Sagar et al(58) and Bhatt et al(59) have shown that branching and bending of dislocation at the cleavage may result in deviations from the one to one correspondence of etch pits on the oppositely matched cleavage surfaces.

3. The etch pit density should have 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, a trial and error method has usually to be used. Etching can be efficiently used to characterize the crystal and(60-67).

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 dislocation density of a crystal.
5. To assess the impurity distribution.
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 dislocation.
13. To study origin of dislocations in as – grown crystals.
14. To distinguish between fresh and as – grown dislocations.
15. To delineate grain boundary and
16. To study polarity of crystal lattice.

Chemical etching, though an old technique, is quite useful even in modern days in variety of crystals(68-70). The results of dislocation etching of $InBi_{1-x}Sb_x$ and $InBi_{1-x}Se_x$ (where x = 0.2,0.3,0.4) crystals on their cleavage faces carried out by the author are reported in chapter 7.

REFERENCES

1. Orowan,E.Z., Physik 89 (1934) 634
2. Polanyi, M.Z., Physik 89 (1934) 660
3. Taylor, G.I., Proc. Roy. Soc., A145 (1934) 362
4. Burgers, J.M., Proc. Acad. Sci., Amsterdam, 42 (1939) 293
5. Brice, J.C., Growth of Crystals from the Melt, North Holland Publishing Co., (1965) 13
6. Weertman, J. and Weertman, J.R., Elementary Dislocation Theory (Macmillan), (1964)
7. Cottrell, A.H., Dislocations and Plastic Flow in Crystals (Oxford Univ.) (1953)
8. Van Bueren, H.G., Imperfections in Crystals (North Holland), (1960)
9. Teghtsoonian, E. and Chalmers, B., Can. J. Phys., 29 (1951) 390
10. Frank, F.C., Deformation and Flow of Solids (Springer, Berlin), (1956) 73
11. Kuhlman – Wilsdorf, D., Madin, R. And Kimura, H., Z. Metallk., 49 (1958) 584
12. Billig, E., Proc. Phys. Soc., A235 (1956) 37
13. Horn F.H., Phil Mag., 43 (1952) 1210
14. Vogel F.L., Pfann, W.G., Correy, H.E. and Thomas, E.E., Phys. Rev., 90 (1953) 489

15. Gevers, W., Amelinckx, S. and Dekeyser, W., Naturwise, 33 (1952) 448

16. Frank F.C., Growth and Perfection of Crystals (Wiley), (1958) 411

17. Cabrera, N. and Lavine, M.C., Phil. Mag., 1 (1956) 450

18. Cabrera, N., Semiconductor Surface Physics, ed. R.H. Kingston (Univ. Pennsylvania), (1957) 327

19. Mott, N.F. and Nabarro, F.R.N., The Stregth of Solids (Physical Soc., London), (1948) 1

20. Read, W.T., Dislocations in Crystals (Mcgraw Hill), (1953)

21. Shockley, W., Imperfections in nearly Perfect Crystals (Wiley) (1952)

22. Fisher, J.C., Dislocations and Mechanical Properties of Crystals (Wiley), (1957)

23. Dash, W.C., J. Appl. Phys., 27 (1956) 1153

24. Hedges, J.M. and Mitchell, J.W., Phil. Mag., 44 (1953) 223

25. Amelinckx, S., Dislocations and Mechanical Properties of Crystals, eds. J.C. Fisher et al (Wiley), (1957) 3

26. Wada, M. and Suzuki, J., Jpn. J. Appl. Phys. Lett (Japan), 27 6 (1988) 972-5

27. Lang, A.R., J. Phys. Soc. Jap., Suppl. II, 18 (1963)

28. Gatos, H.C., Crystal Growth and Characterization, eds.

R.Ueda and J.B. Mullin (North Holland), (1957)

29. Gatos, H.C. and Lavine, M.C., Progress in Semiconductors, eds. A. Gibson and R. Burgess [Temple] , 9 (1965) 3

30. Irving, B.A., Electrochemistry of Semiconductors, ed. P.J. Holmes (Academic), (1962) 256

31. Gilman, J.J., Trans. AIME, 206 (1956) 998

32. Young, F.W., J. Appl. Phys., 29 (1958) 760

33. Coleman, R.V., J. Appl. Phys., 29 (1958) 1487

34. Lovell, L.C. and Wernick, J.H., J. Appl. Phys. 30 (1959) 590

35. Livingston, J.D., J. Appl. Phys., 31 (1960) 107

36. Young, F.W., J. Appl. Phys., 32 (1956) 192

37. Gilman, J.J., The Surface Chemistry of Metals and Semiconductors, ed. H.C.Gatos (Wiley), (1960) p.136

38. Vyas, D.D., Private Communication, (1983)

39. Trivedi M.D., Ph.D. Thesis, M.S.Uni. Baroda., (1977) 137

40. Bhatt, V.P., Vyas, A.R. and Pandya, G.R., J. Appl. Cryst., 9 (1976) 48

41. Pandya, G.R., Ph.D. Thesis, M.S. Uni. Baroda, (1973) 168

42. Berlec, I., J. Appl. Phys., 33 (1962) 197

43. Vogel, F., J. Metals, 8 (1956) 946

44. Greiner, E.S., J. Metals, 7 (1955) 203

45. Breidt, D., Greiner, E.S. and Ellis, N.C., Acta. Met., 5 (1957) 60

46. Ellis, S.G., J. Appl. Phys., 26 (1955) 1140

47. Gilman, J.J., Solid State Physics (Academic Press), 10 (1962)

48. Trivedi, S.B., and Wiedemeier, H., J. Electrochem. Soc.(USA), 134 12 (1987) 3199 – 201

49. Iwanaga, H., Shibata, N., Tanaka, A. and Masa, Y., J. Cryst. Growth (Netherlands), 84 3 (1987) 345 – 8

50. Imashimizu, Y. and Watanabe, J., J. Cryst. Growth (Netherlands), 99 1 – 4 (1990) 2, 979 – 82

51. Forty, A.J., Advance in Phys., 3 (1954) 1

52. Young, F.W. and Noogle, T.S., Appl. Phys., 31 (1960) 604

53. Popkova, R.G. and Predvoditelev, A.A., Kristallogrphiya, 15 (1970) 91

54. Sagar, A., Lehmann, W. and Faust, J.W., J. Appl. Phys., 39 (1968) 437

55. Grabmaier, B.G. and Watson, C.B., Phy. Status Solidi (Germany), 32 (1969) 13

56. Williams, R.H., J. Materials Sci. (G.B), 5 (1970) 566

57. Lin, C.T., Schonherr, E., Bender, H. and Busch, C., J. Cryst. Growth (Netherlands), 94 4 (1989) 955 – 8

58. Sagar A. and Faust J.W., J. Appl. Phys. 38 (1967) 482

59. Bhatt V.P. and Pandya G.R., J. Phys., 'C' 6 (1973) 36

60. Faust, J.W., Jr., Reactivity of Solids, ed. J.W. Mitchell John

Wiley and Sons. Inc. N.Y., (1969) 337

61. Johnston, W.G., Prog. Ceram. Sci., 2 (1962) 1

62. Faust, J.W., Compound Semiconductors, eds. R.K. Willardson and H.L.Goering, 1 (1962)

63. Warekois E.P., Lavine, M.C., Mariano, A.N. and Gatos, H.C., J. Appl. Phys., 33 (1962) 690

64. Holmes, P.J., Electrochemistry of Semiconductors, ed. P.J. Holmes (Academic Press), (1962)

65. Amelinckx, S., Solid State Phys. (Academic Press) Suppl., VI (1964)

66. Robinson, W.H., Techniques of Metals Research, ed. R.F. Bunshah, II (1968) 1, 291

67. Kane, P.F., Larrabe, G.B., Characterization of Semiconductor Materials (McGrow Hill), (1970)

68. Chand, R.F. Karlicek Jr., J. Electrochem. Soc. (USA), 140 3 (1993) 705

69. Tellier, A. Brahun-Bounab, J.Mat. Sci. (UK), 29 (1995) 5953

70. Lai – Cheng Chen, Minsan Chen, Chenhsin Lien Chi-Chao Wan, J. Electrochem. Soc. (USA), 142 1 (1995) 170