PART I

GENERAL

CHAPTER I

GENERAL INTRODUCTION

The growth of Solid State Physics during the last two decades has been more spectacular than of any other branch of Physics. While this has not necessitated the total abandonment of the basic tenets of the physical theory of solids, this single branch of Physics has brought within its field of influence, various other fields, particularly Electronics, Metallurgy, Crystallography and the Chemistry of solids.

Crystals, being the most ideally perfect form of solids, the study of its properties would be the easiest and the most elucidative, for the appreciation of the physical properties of matter. This fact has led to the development of the field of crystal growth. The progress in this field during the last few decades has resulted in the development of a variety of techniques to grow angle crystals and the study of the factors controlling the purity and perfection of the crystals. Crystal growth as such, has attracted the attention of many investigators, since quite long, but the earlier centre of attraction was the morphology of crystals, and the earlier workers in the field of crystal growth had always attempted to develop a theory as to how the crystals grow and maintain their shape. One of the most important achievements in the field of crystal growth during the last two decades is the screw Dislocation theory, developed by Frank. This theory, known as Frank's theory, explains successfully the observed fact that crystals grow under low supersaturation from vapour and solution. Eventhough a host of experimental evidence has been obtained in support of this theory, this mechanism is valid only for the crystals growing from dilute solutions or vapour and is not directly applicable to the growth from melt. A brief discussion on the growth is given in the next chapter.

The study of crystal imperfections has been in the focus of interest of many workers in recent years. Among the imperfection dislocations are the most common and most important. The dislocation theory has been developed over the past several years to describe satisfactorily, the mechanical behaviour of metals. In fact, the existence of dislocations was first inferred from the facts of plastic deformation of metal. According to classical calculation of Frenkel, an ideal crystal should yield at a critical shear stress of the order of G, the shear modulus, in the direction of slip. But in practice, metals are found to yield at a critical shear stress smaller by a factor of 10^4. Refinements of the calculation reduced the theoretical estimate by a factor of 10; but the glaring discrepancy between the theory and the experiment still remained. The natural way out of this difficulty is to postulate the existence of some structural flaw or weakness within the crystal, which behaves as the active agent in the plastic flow. It must possess three fundamental attributes: it must be mobile under low stress, cause macroscopic changes of the crystal shape by its motion and leave the crystal structure unaltered. After some preliminary attempts at using such a model, all the above requirements were eventually met by the "edge dislocation", introduced into physics by Taylor, Orowan and Polányi independently in 1934. Its equally important companion, the "screw dislocation" was introduced by Burgers. The evidence for the existence of dislocation has been steadily accumulating during the intervening years and they are now universally accepted as the inherent feature of all real crystal. However, the fundamental questions as to the origin of dislocations and their thermodynamical status have not yet been completely solved. The properties of dislocations and interaction among them are being investigated by a large number of workers.

In view of their importance on the properties of materials, the dislocation theory occupies a prominent position in modern technology, and a number of methods have been devised to reveal dislocation. These methods employ Electron Microscopy, X-ray Diffraction analysis, X-ray Diffraction Microscopy and Chemical etching. Among these techniques, the "etch method" offers the unique advantage of studying the bulk material. This method has been successfully applied to various species of crystals, to study the re-distribution of dislocation after deformation and the modifications which this distribution undergoes on subsequent etching. It has been possible to follow the motion of dislocation by successive etching. The successful application of this method has been mainly in the field of semi conductors and ionic crystals. A discussion on the applications of this method to various metals and semi conductors is presented in Chapter 3.

Another important achievement of recent years is the development of the techniques of zone-melting. Introduced about a decade ago by Pfann, the techniques of zone melting have provided the solid state Physicist, with a means of obtaining material of extremely high purity and also of precisely controlled composition. 'zone-melting' is the general term for a varied group of methods for controlling the purity and composition of crystalline substances. In all these methods a small melted region, or zone, travels thro' the solid charge. As the zone move, it takes in at its leading interface impure material which mixes with the contents of the zone by natural or forced convection and by diffusion. At the trailing interface the solid differing in composition from the liquid freezes out. The magnitude of the difference depends on the solutes involved. Because of the difference in composition at the freezing interface, the zone is able to move solute along the solid charge. Depending on the size, the number of zones and the initial make-up of the charge, various useful distribution can be achieved. This technique has been most successful in the field of semi conductors and has been employed in some metals also.

In spite of all these developments, the complete understanding of the growth and etch phenomena in metals still presents various difficulties. In the field of crystal growth, the physicist is far away from his goal of perfection. On the other hand, in the case of semi-conductors the crystal perfection achieved has out-stripped the means of its measurement. The growth of good quality single crystals of metal from melt is still an art as well as a science and it has not yet been possible to generalise the conditions required for successful growth. The behaviour of metals to the external conditions imposed during growth is characteristic of the metal itself. The first condition of high purity of metal has been satisfied only during recent years, after the development of zone melting techniques and hence it is necessary that much of the earlier work is reconsidered.

As regards the etch phenomena, eventhough the work of Vogel and others are quite significant and leave no doubt that dislocations can be revealed by etch method, the fundamental question of one to one correspondence between etchpits and dislocations has not yet been established in many metals. However, it has been proved that dislocations can be revealed by etch method in almost all metals. In a particular metal, etch pit densities can be a function of the etchant and even of how it is used. Hence, for determining the density of dislocations the etch pit technique must be used with care. Only when the etch pits aggregate in a manner clearly attributable to dislocations or produce a distinct orientation effects, as is the case at a low angle boundary, or exhibit motion explanable only by dislocations can they be safely regarded as dislocations.

Referring again to the growth, the preferred orientation of a metal is in general, controlled by the temperature gradient, the anisotropy of thermal conduction, impurities and the rate of growth. Earlier work of Goss and Weintroub and others have shown that even in the case of metals having the same structure, the behaviour was different and each metal behaved in its own way. The general conclusion that could be drawn was that no one factor is responsible for the existence of preferred orientation in metals. It should, therefore, be hoped that a study as to how far these growth parameters of crystals influence this property will be quite worth while.

The discussion presented above forms the basic background for the work reported in this thesis. The object of this investigation is to study in detail, the growth and etch phenomena in metals of different structure having different physical properties and growth under different conditions. The choice of the metal has been guided by three main factors, namely, the availability of the metal in sufficiently pure form, the possibility of growing single crystals by the conventional method and the presence of a good cleavage plane which gives a perfect surface for the optical studies. Zinc and

Antimony have been chosen for this work. The work on zinc is on crystals grown from melt and that on antimony is on crystals grown from vapour phase. The former is typical of the h.c.p. structure and is ~~truely~~ metallic in properties while the latter is rhombohedral and is more a semi-metal. Both these metals possess a perfect cleavage plane which satisfies all the requirements for present study. The interest of the present investigation can be broadly outlined as follows:

a) Detailed study of growth phenomena. This includes the study of the various factors influencing the orientation of the unseeded crystal. The investigation is limited to zinc crystal.

b) Detailed microtopographical studies of the free surfaces and the cleavage surfaces of the crystals.

c) Study of cellular interface structure of zinc using etch method.

d) Study of the etch phenomena using a large number of crystals, and etchants.

e) Microtopographical studies of the plastically deformed crystals and the results of etching them.