PART I

G E N E R A L

CHAPTER I

GENERAL INTRODUCTION

The past two decades have witnessed an expanded activity in the field of Solid State Physics in the nature of refinements of the basic theory and applications. Man's achievements in space research and equally significant advances in industrial automation and communication would not have been possible, but for the availability of an amazingly large varieties of solid state devices, such as transistors, diodes, photo cells, photoemissive cathodes and laser - to name only a few of them. The rapid growth of the solid state electronic device industry is in itself a direct reflection of the progress being made in the field of solid state research. The impetus for the accelerated activity has been, among other things, an increased availability of good single crystals and the development of a number of new and powerful tools of research and of new materials.

Crystals have long been objects of curiosity for man. As precious stones and curios they have found their way to Royal museums and jeweler's show-cases, where they have remained as precious possessions. Their well developed faces have attracted the attention of early crystallographers who have attempted to gather information about their symmetry and structure using optical methods. Later on

X-ray crystallography emerged as a new field of active research. Some methods of growing crystals, mainly from aqueous solutions were developed out of curiosity and theoretical attempts were made to explain the rate of growth of the facets. The activity in the field of crystal growth however remained insignificant in those days.

The situation has completely changed in present times. Crystals are no longer passive curios, but are active elements of immense importance in science, technology and industry. Modern solid state physics, which includes piezoelectricity, ferroelectricity, ferromagnetism, luminiscence, photoelectricity and semiconduction, is closely bound up by the study and use of large single crystals. The requirements of solid state devices in the field have put much importance on crystal perfection, while the industry demands large scale manufacture of crystals. This has stimulated much theoretical and experimental work on crystal growth. As a result crystal growing is a new and expanding technology and provides with a variety of crystals for research and industry. Even crystals such as quartz and diamond, which a few years ago could be obtained only in nature, can now be grown in a laboratory.

There are at present two main theories of crystal growth - the Kossel-Stranski molecular theory of crystal growth which applies to ideal and perfect crystals and the dislocation theory of imperfect crystal growth. The two supplement each other, although the rapidly developing dislocation theory relies somewhat on Kossel-Stranski theory for its complex physico-mathematical and structural geometry.

Another important achievement of modern times is the development and increased application of the technique of zone melting. Introduced just over a decade ago by Pfan, this technique has provided the solid state physicist, metallurgist and the electronic industry, a valuable and indispensable method of obtaining purity or controlled impurity concentration. With the application of this technique to refining of material, especially in the field of semiconductors, a purity level outpassing the methods of determining their impurity level has been achieved. Zone melting is a general term used for controlling the impurities and composition of crystalline substances. In all these methods a small melted region or zone passes through the solid charge. As the zone moves, it takes at its leading interface impure material which mixes with the contents of the zone material by forced convection and by diffusion. At the trailing interface solid differing in composition from the liquid freezes out. The magnitude of the differences in composition depends on the solutes involved. Because of the differences in composition at the freezing interface the zone is able to move the solute along the solid charge. Depending on the size, number of zones and the initial make-up of the charge, various useful distributions can be achieved. This technique has been most successful in the field of semiconductors and has been employed in many metals also.

Dislocations have an important effect in the physical properties of solids. The dislocation theory has been developed over the past several years to describe satisfactorily the mechanical behaviour of metals. Infact, the existance of dislocations was first inferred from the studies on plastic deformation of metals. 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 much smaller by a factor 10^4. Refinements of the calculation reduced the theoretical estimate by a factor of 10, but the glaring discrepancy still persisted. The natural way out of this difficulty is to postulate the existence of some structural flaw or weakness within the crystal, which behaves as an active agent in plastic flow. It must be mobile under stress thereby causing macroscopic changes of crystal shape and leave the crystal structure unaltered. After some preliminary attempts at using such a model all the requirements were finally met by 'edge dislocation' introduced into physics by Taylor, Orowan and Polyanyi independently in 1934. Its equally important companion, the 'screw dislocation' was introduced by Burgers. The evidence for the existence of dislocation in crystals has steadily accumulated during the intervening years and more, they are universally accepted as an inherent feature of all real crystals. However the fundamental question as to the origin of dislocations and their thermodynamical status have not yet been completely established. The properties of dislocations and their interaction have been investigated by a large number of workers.

The interest in the study of dislocation has increased steadily in recent years, in view of its profound effect on the properties of solids. In addition to its effect on mechanical properties of crystals, they have a high influence on the electrical properties of metals, semiconductors and ionic crystals. The effect is more profound in semiconductors, where they act as recombination centres, introduce additional acceptor levels and reduce the life time of minority carriers. As a result several methods of studying them have been developed. They are: (a) etching methods, (b) internal decoration,(c) direct observation using electron microscope and (d) X-ray diffraction. There have been a number of attempts in growing crystals of controlled dislocation density and also instances where crystals with no observable dislocations have been grown.

Investigations in which etching methods have been used, have furnished a wealth of valuable information on dislocation phenomena. Etching methods have many advantages over all other methods, the method is very powerful and rapid. The density of dislocations can be determined for surfaces with certain crystallographic orientation with reasonable reliability. In some cases screw and edge dislocations can be distinguished. The conditions under which dislocation loops are generated and expanded on a glide plane near the surfaces of the crystals can be studied by successive etching and pile up of dislocations against barriers observed.

However, many limitations arise from the fact that whether or not well defined pits are formed at and only at dislocations depends critically on the precise composition of the etchant. The information that can be obtained is confined to a plane section through a system of dislocations. This is quite a serious limitation from the point of view of interpretation of observation. Etching methods give satisfactory results only when they are applied to single crystals of low dislocation density.

Surface topography studies have been used to study many growth and etch phenomena in crystals. Existence of growth spirals provided the first direct evidence for the screw dislocation theory of Frank. Considerable work was done by Forty, Frank, Verma and others in this field. Use of multiple beam interferometric techniques to evaluate Burgers vector of the screw dislocation by measuring the step height of the microscopic spiral has been attempted by Verma and Tolansky. Many of the early observations were made on the naturally occurring habit faces of diamond, topaz and other crystals. Contribution by Tolansky and his group to this study is praiseworthy. Cleavage faces of alkali halides, zinc, calcite, mica, quartz, etc. have been studied.

However, growth and etch phenomena in crystals, still pose as many questions as there are answers. Theory of Frank which is the only one successful in explaining the observed growth rates of crystals from vapour and solution under low supersaturation runs into difficulties in explaining growth of crystals from melt. Recent experimental evidences, of which special tributes should be paid to the achievements of Dash, rule out the necessity of a screw dislocation for promoting growth from melt. Alternative mechanism capable of forming spiral and loop pattern usually attributed to screw dislocations has been proposed recently. A brief review of these will be made in the next chapter.

The fundamental question of one-to-one correspondence between etch pits and dislocations is still not conclusively established. The experimental investigation of dislocations using etch method cannot be considered as complete until studies help to establish whether all the dislocations are made visible by etching and whether all etch pits represent dislocations. In this matter any additional contribution to the available information should be considered as welcome. It is particularly desirable to use more than one method to observe distribution of dislocations to establish correlation between results. Thermal etching studies in some metals have indicated the formation of pits at dislocation sites. A systematic study of thermal and chemical etching may give some useful information.

Many crystals exhibit preferred orientation during growth. Earlier investigations have revealed that growth rate, temperature gradient and impurities are the main factors responsible for the existence of preferred orientation in crystals. However, the data available is incomplete. An investigation into this phenomenon is likely to be very informative and may have practical significance. In many cases it is required to grow a crystal of a desired orientation and the normal practice is to grow crystals using seeds of the desired orientation. Once the normal preferred orientation for a given growth rate and temperature gradient is established, it will be possible to stimulate these conditions so that the growing interface has least strain and crystal perfection may be increased. Often it may be possible to grow single crystals without seed, yet in the desired orientation.

Studies on growth and etch phenomena in metals is an organised programme of research in this laboratory. The work to be reported in this thesis is a part of this programme and deals with antimony crystals. The choice of this metal is influenced mainly by the availability of the metal from indigenous resources in sufficiently high purity, an easy method of growing large single crystals due to low melting point and easy cleavage. The study covers broadly the following points:

(1) Growth of crystals from vapour phase and study of the surface topography and preferred orientation.

(2) Study of preferred orientation under varying conditions of growth from melt.

(3) Detailed investigation of etch pits.

(4) Systematic study of thermal etching.