# PART I

## GENERAL

# CHAPTER I

## GENERAL INTRODUCTION

Crystals have been grown from times immemorial and have always attracted the attention of lapidaries and crystallographers because of their geometrical shapes and other properties. But it started developing as a branch of science only during the last decades of the 19th century. The application of crystals in industries, spectroscopy, piezoelectricity and semiconductor devices, necessitated the growth of large and flawless single crystals. This marked a rapid advancement, both theoretical and experimental, in the field of crystal growth. As a result, crystal growing is a new and expanding technology and provides with a variety of crystals for research and industry. The growth and growth mechanisms of crystals have been reviewed in detail in the literature.

Early in this century Kossel, Stranski, Volmer and Frenkel put forward an atomic theory of growth of an ideally perfect crystal. A great discrepancy was observed between the calculated rate of growth of the perfect crystal and the observed rate of growth of real crystals. The solution to this problem was met by the screw dislocation theory of crystal growth developed by Frank. This explains successfully the growth of crystals from vapour and solutions at low supersaturations. This mechanism is applicable only for crystals growing from vapour and dilute solutions and is not directly applicable to other modes of growth.

The study of crystal imperfections has been in the focus of interest of many workers in recent years. Among the imperfections, 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 crystals. In fact, the existence of dislocations was first inferred from the studies of plastic deformation of metals. The shear stress at which plastic flow begins in a single crystal is amazingly small when compared to the theoretical shear strength of a perfect crystal, computed in terms of cohesive forces between atoms. The ratio of the theoretical stress to start the shear of the crystal to that observed in a real crystal is of the order of $10^4$. Refinements of the calculation reduce the theoretical estimate by a factor of 10, but the glaring discrepancy still remains. The natural way out 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 microscopic changes of crystal shape without altering the crystal structure. After some preliminary attempts at using such a model, all the requirements were finally met by "edge dislocations" introduced into Physics by Taylor, Orowan and Polanyi independently in 1934. The concept of screw dislocation, an equally important companion of edge dislocation, was introduced by Burgers in 1939. The evidence for the existence of dislocations has been accumulating for the past years and they are now universally accepted as the inherent features of all real crystals.

The interest in the study of dislocations 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 effect on the electrical properties of metals, semiconductors and ionic crystals. The effect is more pronounced 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 for studying them have been developed. They are (a) etching methods, (b) decoration techniques, (c) X-ray diffraction methods, (d) transmission electron microscopy and (e) field emission and field ion microscopy. The combined use of all these methods have led to a detailed verification of large chapters of dislocation theory. Moreover, several new and unexpected facts have been discovered which led to a revision of some parts of the existing theory and to the development of new theory.

Investigations, in which etching methods have been used, have furnished a wealth of valuable information on dislocation phenomena. Of all the etching methods, chemical etching offers many advantages. The method is very powerful and rapid. Since etch pits essentially reveal emergence points of dislocations on the surface, the method gives a direct measure of dislocations densities. In some cases, it has been possible to distinguish between dislocations in screw and edge orientations, between fresh and aged dislocations and between positively and negatively charged dislocations. The conditions, under which dislocation loops generate and expand on a glide plane near the surfaces of crystals, have been successfully studied by successive etching.

However, many limitations arise from the fact that whether or not well defined pits are formed at and only at sites of 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 observations.

The study of the role of dislocations in etching process has led to a better understanding of the mechanism of dissolution. A large amount of information, on the formation of pits at clean dislocations and at dislocations with impurities collected about them in metal crystals, ionic crystals and semiconductors has been reported.

Inspite of all these developments, etch phenomenon in crystals still pauses many problems. Even though the work of Vogel and others is quite significant and leaves no doubt that dislocations can be revealed by etch method, the fundamental question of one to one correspondence between etch pits and dislocations has not yet been established in many metals. In a particular metal, etch pit densities depend on the etchant and even on the way it is used. Hence for determining the density of dislocations the etch pit technique must be used with care.

Again, coming back to the problem of growth, the preferred orientation in metals, is in general, controlled by the temperature gradient, anisotropy of thermal conductivity, purity and rate of growth. The earlier work of Goss and Weintroub on the low melting point metals shows that metals having the same structure behave in different manners and each metal behaves in its own way. This leads to the conclusion that no one factor is responsible for the preferred orientation. This leads to the study of how these various factors influence the growth and orientation of the crystals.

This discussion is the basic background of the work reported in this thesis. The work is, in fact, a part of an organised research programme taken up in this laboratory on growth and etch phenomena in metals, alloys and semiconductors. The present study deals with tellurium crystals. The choice of this element was influenced mainly by the availability of the material in fairly pure forms and the presence of an easy cleavage.

The following points give a broad outline of the work presented in the thesis:

(1) Study of the growth of tellurium single crystals from the vapour phase.

(2) Study of etch phenomena on tellurium crystals.

(3) Microhardness studies on Te crystals.

(4) Study of surface features of vapour-grown Zn-Sb platelets.