VAPOUR PHASE GROWTH OF VARIOUS FORMS OF CADMIUM SULPHIDE CRYSTALS

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PREFACE

II-VI compounds as a collective group of materials have been and still are the subject of much investigations because of the variety in their usefulness. Attention was first focussed on some of the large band gap II-VI compounds, like CdS and ZnS, due to their photoconductive and luminescent properties. Much effort was expended to prepare powders of such materials in doped and undoped states and the early studies were conducted almost exclusively on these powder samples. Although these investigations did set forth a basis for understanding this group of materials, much of our present knowledge has been gained through studies on crystals. The essential requirement of crystalline materials, for the fabrication of some devices and for making definite measurements of certain properties, has led to extensive work in the field of crystal growth. One may, however, use a polycrystalline sample rather than a single crystal for certain studies but often a single crystal is required. For example, much better frequency stability and lower acoustic losses can be achieved in single crystals than in polycrystalline aggregates. Thus, single crystal piezoelectric samples are used for frequency control elements.

Conductivity and mobility experiments also dictate the use of single crystals of semiconductors.

For some studies and applications, reasonably large single crystals are required. However, in certain cases like fluorescence studies where one would like to work with undamaged surfaces, it is advantageous to grow crystals of definite form and size as this eliminates the need of any further mechanical or chemical treatment which is necessary with large crystals. It is thus important, both from the scientific as well as from technological point of view, to understand and establish the conditions of growth of various forms of crystals. In the work reported here, the author has studied this aspect in the case of cadmium sulphide crystals. Cadmium sulphide was chosen because of the non-availability of its single crystals in the country and also because of its great application potential. CdS crystals are employed in photoconducting cells to detect radiation in a spectral region which extends from near infrared to gamma radiation. Piezoelectric effect and laser emission have both been observed in high quality cadmium sulphide crystals. The combination of electric field and phonon sensitive properties has permitted the application of cadmium sulphide in image intensification, image processing, logic networks and shift registers. Photovoltaic effect has also been observed both in electrochemical and p-n heterojunction arrangements. Finally, single crystal platelets of cadmium sulphide have been successfully used to fabricate SCL devices.

The work reported in this thesis has been divided into five chapters. Chapter I reviews the different methods of growing CdS crystals and studying their dislocation structure. Chapter II is concerned with the growth of large single crystals in vacuum. Prior to this work, large single crystals of CdS have been grown in ambient atmospheres at temperatures in the range 1100^{o}-1200^{o}C. At these temperatures, there is a slight softening and collapse of the quartz which causes the sticking of the crystal to the ampoule and consequent surface slip and surface cracking due to the difference in the thermal coefficients of the crystal and the ampoule. Higher temperatures may also cause greater contamination of the crystal by quartz. It is, therefore, desirable that the growth should be carried out at lower temperatures. This is possible if the growth is performed under vacuum where higher flux rate can be available as material transport is not limited by gaseous diffusion. Earlier attempts on growth in vacuum, however, have not been very successful. In the present case, large single crystals about 3 cm long and 1 cm diameter have been successfully grown in vacuum at comparatively lower temperatures. of the order of 1025°-1060°C. The conditions necessary for obtaining such crystals have been discussed.

A study of the free growing surface under varying growth conditions has also been made. At normal growth rates, the free growing surface of the crystal is confined by curved-non-singular surfaces. When the rate of growth is small, a number of flat, well defined and mainly prismatic facets develop. The growth mechanisms have been discussed in both the cases.

The presence of voids in the grown crystals is known to cause scattering of light and this affects the performance of optical devices. The causes and mechanism of formation of voids in CdS crystals have been discussed. Conditions have been established in which voids can be eliminated.

The growth of hollow crystals is discussed in Chapter III. There are a few earlier reports on this growth habit which has been attributed to the presence of impurities or of nucleation centres and it has been mentioned that hollow crystals cannot be grown by starting from pure material. The author has grown hollow centered CdS crystals, both in the presence and absence of impurities, in dynamic as well as static systems, with stoichiometric composition and with excess of cadmium or sulphur. The results indicate that polygermination of platelets is a probable mechanism for the formation of this habit. However, in the case of impurities, it has been suggested that the mechanism may be impurity modified hopper growth.

Chapter IV deals with the growth of whiskers, needles and platelets. Needles and platelets have been grown inside the quartz ampoules whereas whiskers grow on the walls of the mullite tube. Whiskers contain a few or no dislocations and are relatively perfect single crystals. Evidence has been presented to support the dislocation mechanism operating in the growth of platelets. It has been shown that the contamination, of the growing interface of a crystal, by impurities can lead to the formation of platelets, needles and hollow crystals.

Thermal etching can be advantageously employed to reveal the dislocation structure of as grown crystals. To the author's best knowledge, no report has appeared so far on the thermal etching of dislocations in cadmium sulphide. In the present case, this technique has been successfully used to study etch patterns in different grains, dislocation motion and polygonisation. The role of impurities in the formation of thermal etch pits has also been investigated. A comparison of thermal etching and chemical etching has been made. This forms the fifth and the last chapter of the thesis.