GROWTH OF ZINC OXIDE CRYSTALS FROM VAPOUR AND LIQUID PHASE TECHNIQUES

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PREFACE

II-VI compounds, in their broadest sense, include compounds formed from elements of group II and group VI of periodic table; such a definition encompasses the oxides, sulphides, selenides and tellurides of Zn, Cd, Be, Mg and Hg. These compounds have been and still are a subject of intense investigation because of the variety in their usefulness. Earlier studies were conducted almost exclusively on powdered samples in doped and undoped states. 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 single crystals. Besides, single crystals are preferred over polycrystalline or powdered samples for fabrication of certain devices.

The essential requirement of these materials in the form of single crystals has led to an extensive work in the field of crystal growth. The crystals required for various studies often vary in size, ranging from big crystals to platelets and whiskers. It is, therefore, important, both from scientific and technological points of view, to understand and establish the growth conditions for growing crystals in different morphologies. In the work reported in this thesis, the author has studied these aspects in the case of ZnO. Zinc oxide was chosen as a material for investigations because of a need for understanding the mechanisms involved in the growth of crystals of various morphologies and because of non-availability of ZnO single crystals in the country. In addition, the material has a great apppli-cation potential; ZnO crystals are especially suited for general application areas where strength, high electrome-chanical coupling coefficient and low dielectric constant are important.

The work reported in the thesis has been divided into six chapters. Chapter 1 reviews ZnO crystallization, origin of dislocations and techniques for their detection.

Chapter 2 describes the growth of ZnO hollow crys-tals. Prior to the present work, there was no report avail-able on the growth of ZnO hollow crystals. A modification of the usual vapour phase technique has resulted in the growth of hollow needles of typical dimensions - 10 mm in length and 1 mm in diameter - at $\sim 970^{o}C$. The conditions necessary for obtaining such crystals have been established.

Growth of ZnO crystals of various morphologies has been included in the third chapter. Zinc oxide whiskers, platelets and dendrites have been grown by the modified va-pour phase method. The whiskers thus grown are up to a few mm in length and a fraction of a mm in diameter. The con-ditions of growth of various morphologies and the observed change in growth habit - from whisker to platelet - have been discussed. It has been pointed out that the growth of whiskers took place by the operation of a volume diffusion field at supersaturations higher than those usually required for whisker growth; that the growth is rather dendritic has been supported by the actual observation of dendrites and fourlings.

Chapter 4 deals with the reinvestigation of the growth of crystals from molten PbF_2-ZnO system. Zinc oxide crystals, mainly in the form of plates and hexagonal prismatic needles, have been grown in a temperature range of 1070-1200°C. In addition to various stages of crystallization - heterogeneous nucleation, dendritic growth and layer growth, thermal and supersaturation effects on the morphologies of the grown crystals have been discussed. Segregation of impurities has been found to result in the formation of cellular structure and growth striations. These structures have been explained on the bases of constitutional supercooling and thermal fluctuations existing in the solution.

Growth of ZnO needles from molten hydrous KOH solvent, at comparatively low temperatures ($\sim$480°C), has been detailed in Chapter 5. To understand the growth mechanism involved, laser Raman investigation of molten hydrous KOH-ZnO system has been carried out; this has revealed the presence of ZnO_2^{2-} as the most prominent species in the system.

It has been established that, unlike other molten salt solutions, in this case the supersaturation is induced by the dissociation of ZnO_2^{2-} species; this subsequently leads to heterogeneous nucleation and growth of ZnO crystals.

The last and final chapter of the thesis includes thermal etching of the crystals grown from PbF_2 flux. To the best knowledge of the author no report has, so far, appeared on thermal etching of ZnO crystals. It has been shown that thermal etching is capable of revealing dislocations in ZnO crystals; this has been done by way of evidence presented in terms of geometrical etch pits at individual dislocation sites, at low-angle tilt boundaries, and along polygonisation walls. The origin of dislocations has also been discussed; it appears that the impurity segregation is the main cause of dislocations in ZnO crystals grown from flux technique.

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