ABSTRACT

In the last few decades or so the growth of crystals has assumed enormous importance for both academic research and technology (particularly in the field of 'electronics'). The range of fields involved is great: from electro-optics to metal corrosion, from semiconductors to magnetic bubble materials - one can add to the list almost indefinitely. However, while the general principles of crystal growth can be applied almost right across the board, it turns out that the precise way in which one can grow a particular crystal best varies considerably, from material to material. Chemical Vapour Transport (CVT) is one of the most prominent techniques of crystal growth and virtually any material can be crystallized by this technique.

The present thesis consists of four major parts. The first part deals with the nucleation, thermodynamical aspects and growth of some I-III-VI₂ compound semiconductors by chemical vapour transport. The second part deals with the growth rate calculation by evaluating productivity function and growth of pure and doped crystals of CdS, ZnS and ZnSe. The third part deals with the growth of a transition metal dichalcogenide: MoTe₂ by physical vapour transport and chemical vapour transport techniques. The
fourth part deals with the characterization of the grown single crystals.

Single crystals of some ternary and quaternary chalcopyrite semiconductors CuInS$_2$, CuInSe$_2$, CuInTe$_2$, CuGaS$_2$, AgGaS$_2$, CuInSSe, CuGaSSe and AgGaSSe have been grown by chemical vapour transport technique using iodine as the transporting agent. The grown crystals have been analysed with X-ray diffractogram and the lattice parameters have been determined. SEM, ESCA and EDSA studies have been made to assess the quality of the crystals.

Classical nucleation theory has been extended to chemical vapour transport. Homogeneous and heterogeneous nucleation of ternary compounds have been discussed. Values of critical free energy, critical radius of the nucleus and gas-solid interfacial surface tension for CuGaS$_2$ system have been computed theoretically. Theoretical investigation is found to be in good agreement with the experimental observations.

A thermodynamical model for predicting source and deposition temperatures for the growth of ternary compound semiconductors by chemical vapour transport technique has been discussed. Minimum source and growth temperatures have been predicted for the growth of single crystals CuGaS$_2$ and
AgGaS$_2$ by chemical vapour transport, using the thermodynamical model.

The productivity function $F$, as defined by Klosse, has been reformulated in terms of Lever Mandel theory of diffusive closed tube chemical vapour transport (CT-CVT), in which the efficiency of reaction process has been given by a function involving the mole function of the gaseous species and the stoichiometric coefficients. The main advantage in using the productivity function $F$ for predicting the maximum efficiency of diffusion CT-CVT process is that only thermodynamic parameters, and no fluid dynamic quantity, are involved in its calculation. The features of such productivity function in the case of ZnS are discussed. Single crystals of pure and doped CdS, ZnS and ZnSe have been grown by chemical vapour transport technique using iodine as the transporting agent.

Growth aspects of a transition metal dichalcogenide, molybdenum ditelluride (MoTe$_2$) have been discussed. Single crystals of MoTe$_2$ have been grown by two different techniques: physical vapour transport and chemical vapour transport. Crystals grown by physical vapour transport were found to be bulk and it is due to mass transport mechanism involved. By chemical vapour transport, the crystals were grown by using two different transporting agents, iodine and TeCl$_4$. In CVT grown crystals, growth has taken place by two
dimensional precipitation of molecules or atoms around a nucleus.

The electrical conductivity and Raman studies have been carried out for the grown single crystals. Unlike II-VI compounds, their ternary analogues I-III-VI₂ compounds can be readily made into both p-type and n-type conducting. Most of the single crystals of I-III-VI₂ compounds grown in the present investigation were found to be p-type, as grown. Upon giving proper annealing treatment in the chalcogen atmosphere they were made to n-type conducting. The Raman spectra for the crystals were recorded using different geometries such as back scattering (180°), right angle (90°) and approximately forward (≈ 0°). Different lattice vibration modes were characterized by Raman Scattering and the results have been discussed.

Vickers microhardness studies on selected smooth surfaces of the grown crystals were carried out by subjecting them to static indentation test in air at room temperature. For all the single crystals grown, Vickers hardness number decreases with increase of applied load and varies non-linearly before attaining a saturated value. For some of the crystals radial crack patterns were developed and so toughness and brittleness index value have been calculated. Hardness anisotropy has been observed in the crystals of MoTe₂ and CdS doped with zinc and the results have been discussed. Finally a summary of the results and suggestions for the future work have been presented.