MODELING OF LIQUID PHASE EPITAXIAL GROWTH OF *GaSb* and *GaP* CRYSTALS

A Dissertation submitted to the Department of Physics,
Bangladesh University of Engineering and Technology, Dhaka
in partial fulfillment of the requirements for the
degree of Master of Philosophy in Physics

MOHAMMAD MOSTOFA KAMAL
Student No : 040014010P
Session : April 2000

Department of Physics
Bangladesh University of Engineering and Technology (BUET)

November 2002

ACKNOWLEDGEMENTS

First of all I would like to express my deep sense of gratitude to my thesis supervisor ***Dr. Md. Mostak Hossain,*** Assistant Professor, Department of Physics, Bangladesh University of Engineering and Technology (BUET) for his indispensable guidance, valuable suggestions, generous help, care and constant encouragement throughout the progress of my research work.

I would like to thank the authority of the ***Independent University, Bangladesh (IUB)*** for permitting me to do M.Phil in BUET. My special thanks to the Director of the School of Communication, Independent University, Bangladesh (IUB) for his continuous support and inspiration to complete the degree.

I am thankful to the Head and my teachers in the Department of Physics, Bangladesh University of Engineering and Technology (BUET), for their keen interest and encouragement during the work. Thanks are also due to all the employees of the Department of Physics for their nice cooperation.

I wish to express my indebtedness to my wife Sharmeen Akhter Jharna for keeping me free from family affairs during the work. Last but not at the least, I would like to thank all of my family members for giving a huge support in carrying out my study.

ABSTRACT

A one dimensional numerical method has been employed to construct the concentration profiles in front of growing crystal interface under the normal conditions and the growth rate, thickness, and dimensionless concentration profiles of Gallium Phosphide (GaP) and Gallium Antimonide (GaSb) in Ga-rich solution are computed by Liquid Phase Epitaxy (LPE). The LPE technique is particularly useful for the growth of III-V compound semiconductors, such as GaP and GaSb, where the metals, e.g. Gallium (Ga) in the group III elements serves as a solvent element and can make the solutions at equilibrium temperature. One-dimensional solute diffusion model equation has been solved numerically by the Laplacian centered difference approximation. Then the concentration profiles of solute atoms (i.e., Phosphorus and Antimony) in the melt, in front of a growing crystal interface during the liquid phase epitaxial growth at different cooling rates have been simulated by the help of the computer simulation technique. The data obtained from the simulation study has been used to calcnlate the growth rate, the thickness of the grown layer and the dimensionless concentration parameter of GaSb and GaP for different growth parameters, such as time and temperature. Our model has been applied to calculate the average thickness of the grown solid as a function of time and these theoretical findings have been compared with the reported experimental values. A good agreement has been found between our findings with the reported experimental values.

CONTENTS

LIST OF FIGURES

CANDIDATE'S DECLARATION

It is hereby declared that this thesis or any part of it has not submitted elsewhere for the award of any degree or diploma.

17/11/02
Mohammad Mostofa Kamal
Candidate

BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY
DHAKA

DEPARTMENT OF PHYSICS

Certification of Thesis work

*The thesis titled "**Modeling Of Liquid Phase Epitaxial Growth Of GaSb And GaP Crystals**",* submitted by ***Mohammad Mostofa Kamal*** *Roll No: 040014010P, Session April-2000 has been accepted as satisfactory in partial fulfillment of the requirement for the degree of Master of Philosophy in Physics on 2 December, 2002.*

BOARD OF EXAMINERS

1 (Hossain 2/12/02)
Dr. Md. Mostak Hossain (Supervisor) — *Chairman*
Assistant Professor
Department of Physics, BUET, Dhaka

2 (2/12)
Dr. Md. Abu Hashan Bhuiyan — *Member*
Professor
Department of Physics, BUET, Dhaka

3 (Jiban Podder 2/12/2002)
Dr. Jiban Podder — *Member*
Professor
Department of Physics, BUET, Dhaka

4. (2/12)
Head — *Member*
Department of Physics, BUET, Dhaka

5. (G.M. Bhuiyan 2.12.02)
Dr. Golam Mohammad Bhuiyan — *Member (External)*
Professor
Department of Physics
University of Dhaka, Dhaka

DEDICATED

TO

MY MOTHER

Mrs. Meherunnessa Ahmed

CHAPTER 1

INTRODUCTION

CHAPTER 1
INTRODUCTION

1.1 INTRODUCTION

Every new solid state device needs a single crystal and the exploration in development of those devices requires much new crystals, which have to be grown and fabricated in order to assess their device properties. The ever increasing application of semiconductor based electronics creates an enormous demand for high quality crystals, and that's why the task for the science and technology of crystal growth has been developed now a days.

In the last two decades a drastic change in the performance of electronic and photonic devices has been occurred based on heterostructure, quantum well superlattice and other similar low dimensional structures *(Haug 1988; Koning and Jorke 1985; Greene et al 1987)*. Such kind of structure can be grown only by means of epitaxial growth. The term 'Epitaxy' refers to the ordered arrangement of some material, oriented growth of epilayers on a single crystalline substrate, so that the atomic planes in contact have unit cells that match each other in shape and size. If the epilayer is grown epitaxially on a substrate of the same material, it is called homoepitaxy, e.g., Gallium Arsenide can be grown on a Gallium Arsenide substrate. When the epilayer is grown on a foreign substrate then it is called heteroepitaxy, as Gallium Arsenide is grown on a Silicon substrate.

In recent years the epitaxial growth techniques have superseded the bulk growth for the fabrication of electronic circuits because the electronic circuits need only few micron dimensions*(Kuphal 1994)*. By using the epitaxial growth the growth time can be reduced, cost can be wafered, and also the wastages of materials can be saved during growth, cutting, polishing etc. The uniformity in the composition, controlled growth parameters and better analysis of the growth itself is the main advantage of the epitaxy.

Among different types of epitaxial growth techniques such as Vapour Phase Epitaxy (VPE), Metalorganic Vapour Phase Epitaxy (MOVPE), Molecular Beam Epitaxy (MBE), Chemical Beam Epitaxy (CBE), Atomic Layer Epitaxy (ALE), Liquid Phase Electro-Epitaxy (LPEE) and Liquid Phase Epitaxy (LPE), the LPE is the subject of our interest. The present investigation deals with the one-dimensional numerical analysis of liquid phase epitaxial growth of III-V binary semiconductors and heat transport in the melt during the LPE growth.

1.2 DIFFERENT TYPES OF EPITAXIAL TECHNIQUES

1.2.1 Vapour Phase Epitaxy (VPE)

Vapour Phase Epitaxy (VPE) is the condensation process of the material from its own vapours, where the group III-V chemical compounds (organic or inorganic) react with the other materials to form the compound semiconductor on the suitable substrate surface by transporting the chemical compound from the gas phase state to solid-vapour interface. In the Vapour Phase Epitaxy the growth is controlled by the partial pressure of each of the components of the source material.

The major advantages of VPE are

(i) High purity and less defect wafer can be grown from high purity charges,

(ii) The epitaxial growth on large wafers and on multiple wafers is possible simultaneously.

1.2.2 Metalorganic Vapour Phase Epitaxy (MOVPE)

Metalorganic Vapour Phase Epitaxy (MOVPE) is an important epitaxial crystal growth technique. The term 'metalorganic' refers to any compound containing metal atoms in combination with organic radicals, whereas the term 'organometalic' refers to those compounds in which the carbon atom is directly bound to the metal atom. Vapours of organometalic compounds are used to transport at least one of the primary film constituents *(Ludowise 1985, Stringfellow 1989).*

The major disadvantages of MOVPE technique are its high cost, the use of highly hazardous starting materials and toxicity of the waste materials. MOVPE technique has been used to grow variety of compound semiconductors such as GaP *(Li et al 1989)*, $GaAs_{1-x}P_x$ *(Cao et al 1989)*.

1.2.3 Molecular Beam Epitaxy (MBE)

Molecular Beam Epitaxy (MBE) can be defined as a process of depositing epitaxial thin films which involves the reaction of one or more thermal beams of atoms or molecules under high vacuum conditions with a crystalline surface. The beams are thermally produced in Knudsen type effusion cells. The cells are accurately controlled. A sophisticated set-up is required for MBE growth process due to high vacuum and close controls involved.

By using MBE growth, it is possible to grow high quality GaAs and AlAs layers at very low substrate temperature (200° C) by enhancing the migration of the materials evaporated on the growing surface *(Horikoshi 1986)*. It is also possible to produce multilayered structures including super-lattices with layer thickness as low as 10Å for double heterostructure lasers and waveguide applications *(Vaya 1989)*.

The disadvantage of MBE growth is the difficulty in growing phosphorus-containing materials. Phosphorus is found to bounce around in the system, ultimately collecting in the vacuum pumps. In addition, the growth of alloy containing As and P is particularly difficult.

1.2.4 Chemical Beam Epitaxy (CBE)

Chemical beam epitaxy (CBE) is a technique for the growth of InP based materials with MBE. In other words it is a technology for doing in-situ characterization with MOVPE. In CBE growth process, beams of compound chemicals directly impinge onto a heated substrate surface. To produce the epitaxial film on single crystalline substrate with the incorporation of the desired elements is the result of decomposition of the arriving chemicals under properly controlled conditions.

The CBE technique has been used to grow a wide range of device structures including optoelectronic devices such as InGaAsP lasers. Bragg refractors and InP based channel high electron mobility transistor. For the growth of InGaAs / InP quantum well structures *(Antolini et al 1992)* and the growth of InGaAs(P) / InP heterostructures *(Gotoda et al 1994)* CBE technique has been used.

The advantage of CBE are :

i) The capability to grow high-quality InP-based materials.

ii) Fewer amounts of decomposition source materials (AsH_3 and PH_3) is required for the growth of GaAs and InP based materials compared to MOVPE.

iii) More homogeneity and good uniformity . and

iv) Vacuum in-situ diagnostics.

1.2.5 Atomic Layer Epitaxy (ALE)

Atomic Layer Epitaxy (ALE) is a well known technique for the fabrication of compound semiconductors film. The technique utilizes either in MBE or Chemical Vapour Deposition approach. In this method, a monolayer of each constituent atoms or molecule is laid down separately in place of having mixed flux at the substrate. Conditions are established when the bonds are stable. For example, in the growth of GaAs by ALE, first layer of As is deposited on the substrate and excess arsenic is swept out of the system. This layer is followed by a flux of gallium that reacts with arsenic layer, filling up sites to complete a layer of gallium and the compound GaAs. Again excess gallium is removed from the system.

1.2.6 Liquid Phase Electro-Epitaxy (LPEE)

Liquid Phase Electro-Epitaxy (LPEE) is a constant temperature growth method which is initiated and sustained by passing an electric current through the solution and the substrate. The growth takes place at a constant furnace temperature and the direct current is the sole externally applied driving forces. One of the principal advantages of liquid phase electroepitaxy (LPEE) is the possibility of controlling the composition of the solid phase by changing the electric current *(Zhovnir and Zakhlenyuk 1985).* Liquid phase electro-epitaxy (LPEE) is one of the noble techniques for the growth of compositionally uniform, controlled thickness and low dislocation ingots of III-V compounds semiconductors.

1.2.7 Liquid Phase Epitaxy (LPE)

Liquid Phase Epitaxy (LPE) has proved to be a versatile technique to grow semiconductor layers for material investigations and device applications. Today, in spite of the availability of highly sophisticated epitaxial techniques like MBE, CBE and MOVPE, the exploration and development of many devices are still carried out using LPE *(Kuphal 1994).* This is essentially due to the simplicity of the technique, high crystalline quality of the grown thin films and inherently less harmful to the environment because the raw materials and the waste products are less toxic and not pyrophoric than that of the other techniques. Our present work is based upon the Liquid Phase Epitaxy and the process is discussed in Chapter Two in detail.

In our present work we have developed a one-dimensional diffusion equation and solved it numerically. We have also constructed the concentration profiles of Sb and P atoms in the Ga-rich solution in front of the growing crystal interface, calculated the thickness of the layer as a function of time and as function of temperature, the dimensionless concentration parameter is also calculated. Finally Our theoretical result has been compared with the reported experimental values.

CHAPTER 2

THE PROCESS OF LIQUID PHASE EPITAXY

CHAPTER 2

THE PROCESS OF LIQUID PHASE EPITAXY

2.1 INTRODUCTION

Liquid Phase Epitaxy (LPE) means the growth of thin films from supersaturated metallic solutions on a crystalline oriented substrate *(Kuphal 1994)*. This technique is convenient for the growth of III-V compound semiconductors. In this process the solvent element of the constituent of the growing solid (e.g. In or Ga) is incorporated in to the solid only as a dopant. The solvent contains a small quantity of a solute (e.g. As in Ga) for epitaxial growth of GaAs layers which are transported towards the liquid-solid interface. The process is controlled best if this transport occurs only by diffusion i.e. the driving force in the solution is a concentration gradient of the solute. The growth boats are commonly designed such that, essentially, only diffusion perpendicular to the interface occurs; convection and surface tension related to the transport are suppressed. The temperature gradient is minimized by utilizing larger dimension of the substrate compared to the height and radius of curvature of substrate. Applying these constraints, the LPE process can be treated as one dimensional and two dimensional diffusion process in which the growth rate is found to be diffusion limited. In LPE growth process, the relationship between the temperature and the solubility as predicted by the phase diagram has to be utilized for the analyzing of the growth process.

There are four steps involved in LPE technique:

i) preparation of the saturated solution containing a quantity of solute at the saturation temperature,

ii) supersaturated solution is obtained by cooling the saturated solution to the growth temperature,

iii) contact is kept between the solution and the substrate for a particular time appropriate to the required layer thickness, and

iv) removing the substrate from the solution which terminates the growth.

2.2 CLASSIFICATION OF LPE

The LPE growth is generally classified into four techniques as follows :

a) Tipping technique
b) Dipping technique
c) Sliding technique, and
d) Sandwich technique

a) *Tipping technique*

Tipping technique was first introduced by *Nelson (1963)*. In this technique the substrate is held tightly bound at the upper end of a graphite boat and the growth solution is placed at the other end. The solution is brought in to contact with the substrate by tipping the furnace. Then the furnace is slowly cooled and an epitaxial layer is grown on the substrate. The growth is terminated by tipping the furnace back to its original position after growing a desired thickness of epitaxial layer on the substrate. Figure (2.1) shows a schematic diagram of the tipping technique of LPE system. *Bauser et al (1974)* modified the Nelson's tipping LPE technique as shown in figure (2.2a), where the quartz tube including the crucible is tipped around the longitudinal axis. This technique produces excellent layer purity. This is due to the fact that the boat design is very simple and the graphite walls are rather thin. Since no sliding of graphite parts occurs so that no dust

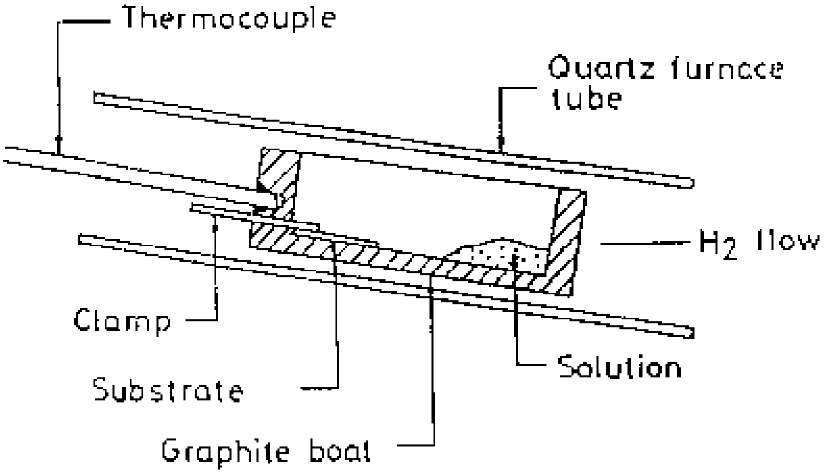

Figure (2.1) Schematic diagram of the tipping technique of LPE growth system

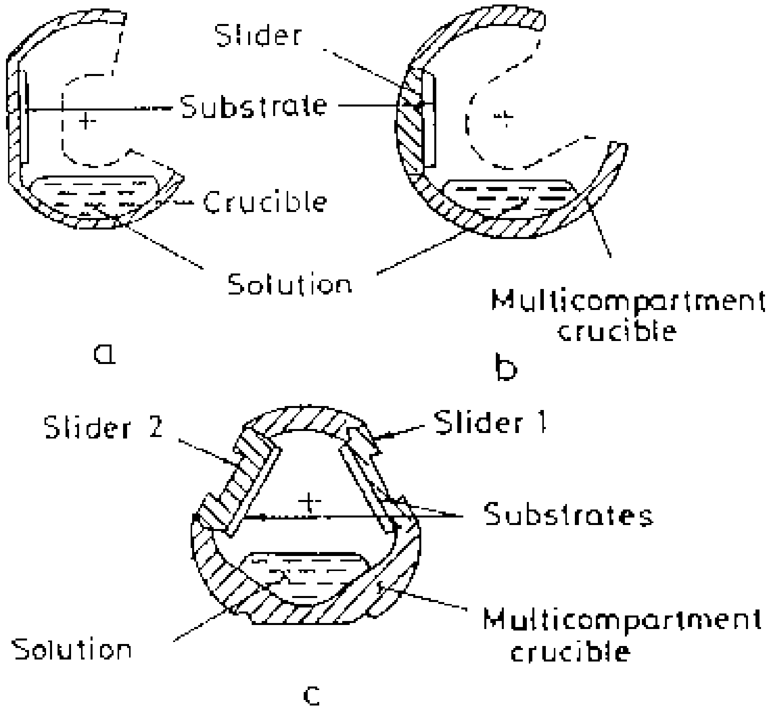

Figure (2.2) Different designs of tipping boat : a) a simple tipping boat, b) a combination between a tipping and a slider boat, c) a tipping slider boat with the ability to be rotated by 360°

can be introduced by abrasion. The disadvantage of this technique are : (i) the thickness homogeneity is only moderate due to two dimensional diffusion in the solution,
(ii)only single epitaxial layer can be grown, and (iii) the solution can not be protected against evaporation of the volatile elements. To overcome the problem of growing multilayer in Bauser technique, *Kaufmann and Heime (1977)* developed a new technique which is capable to produce multilayer. In fact, it is a combination of tipping and slider boat as shown in figure (2.2b). In this case the solution is brought in to the substrate by tipping. the substrate is transported by a slider from one compartment in to the next when the solution is not in contact with the substrate. To start and stop the deposition. the constructions have to be rotated forward and backward in these techniques As a consequence. thin layers are tapered, because the solution rests for a longer time on one side of the substrate than that on the other. This disadvantage was later overcome by an improved version of the tipping slider boat *(Kuphal 1994)* which can be rotated by 360° as shown in figure (2.2c).

b) ***Dipping technique***

The Dipping technique consists of a vertical furnace and growth tube with the graphite crucible which contains the solution at the lower end as shown in figure (2.3) The substrate fixed in a movable holder is initially positioned above the solution. Growth is initiated by immersing the substrate in the solution at the desired growth temperature and it is terminated by withdrawal of the substrate from the solution. The main disadvantage of this technique is that, the thickness is not homogeneous.

The dipping technique has been improved by two German manufacturers for multilayer growth. In this case, a horizontal furnace and two large-volume horizontal solution containers are used. One hundred parallel-positioned 2 inch wafers are simultaneously dipped into one solution. The solutions are used only once, but can be recycled. This technique allows the growth of double layers and it is extremely well suited for the mass production of LED wafers, where thickness homogeneity is not so important *(Kuphal 1994)*.

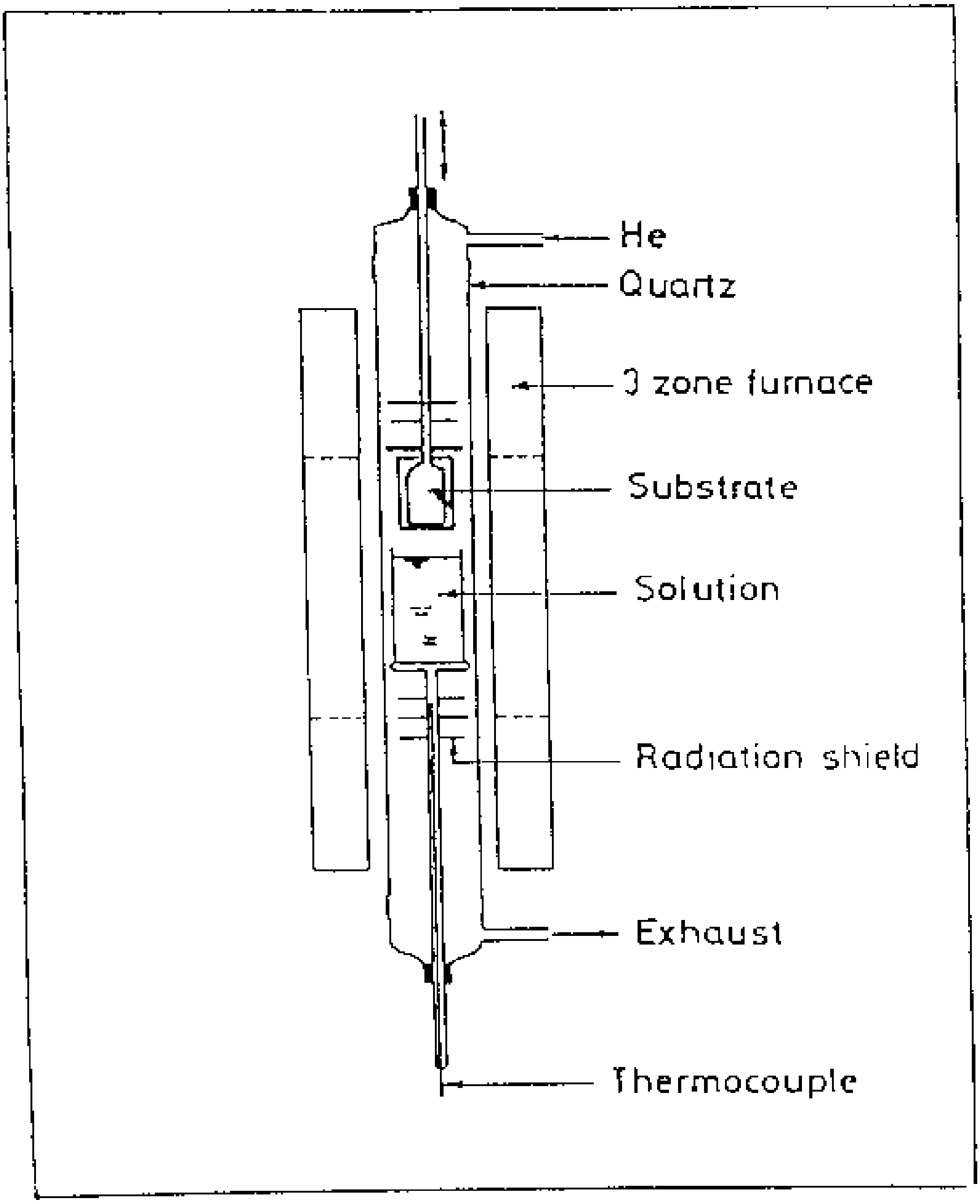

Figure (2.3) : LPE growth apparatus employing the dipping technique

c) Sliding technique

The sliding technique is the horizontal multibin-slider system, which is useful for the growth of multilayered structure *(Panish et al 1970)*. This technique is almost generally used for the growth of heterostructure, for example as in laser diode. In the most simple case the boat consists of a substrate holder with the substrate in a recess and the slider containing the differently composed solutions in its bins as shown in figure (2.4) *(Kuphal 1994)*. As the solution generally does not stick to purified graphite, they can be wiped off the substrate by the graphite walls of the slider to terminate the growth. The slider is moved by a horizontal fused silica push rod, which is actuated by hand or, in modern versions, by a computer-controlled stepper motor.

The pushing direction is forward and backward, also allowing the growth of multilayer from neighboring solution. The minimum growth time required for a single layer is about tenth of a second. To prevent the evaporation and contamination, each solution is usually protected by a graphite cover. Mostly in the slider boat designs, it causes the wetting problems to grow at lower temperatures. Piston boat design is used to overcome this problem. The piston boat design is shown in figure (2.5). The solution used for the growth of one layer is pushed out by the solution used for the growth of next layer and is controlled in a disposal bin, which is the advantage of the piston boat LPE system.

d) Sandwich technique

This system was investigated by *Sukegawa et al (1988)*. Figure (2.6) shows the view of sandwich growth cell configuration, which consists of two horizontal substrates set face and kept 4mm apart in a graphite boat. This growth proceeds by gradually lowering the temperature to maintain the super-saturation after introducing a saturated solution between the substrates. The solution is gradually depleted of solute in the vicinity of a

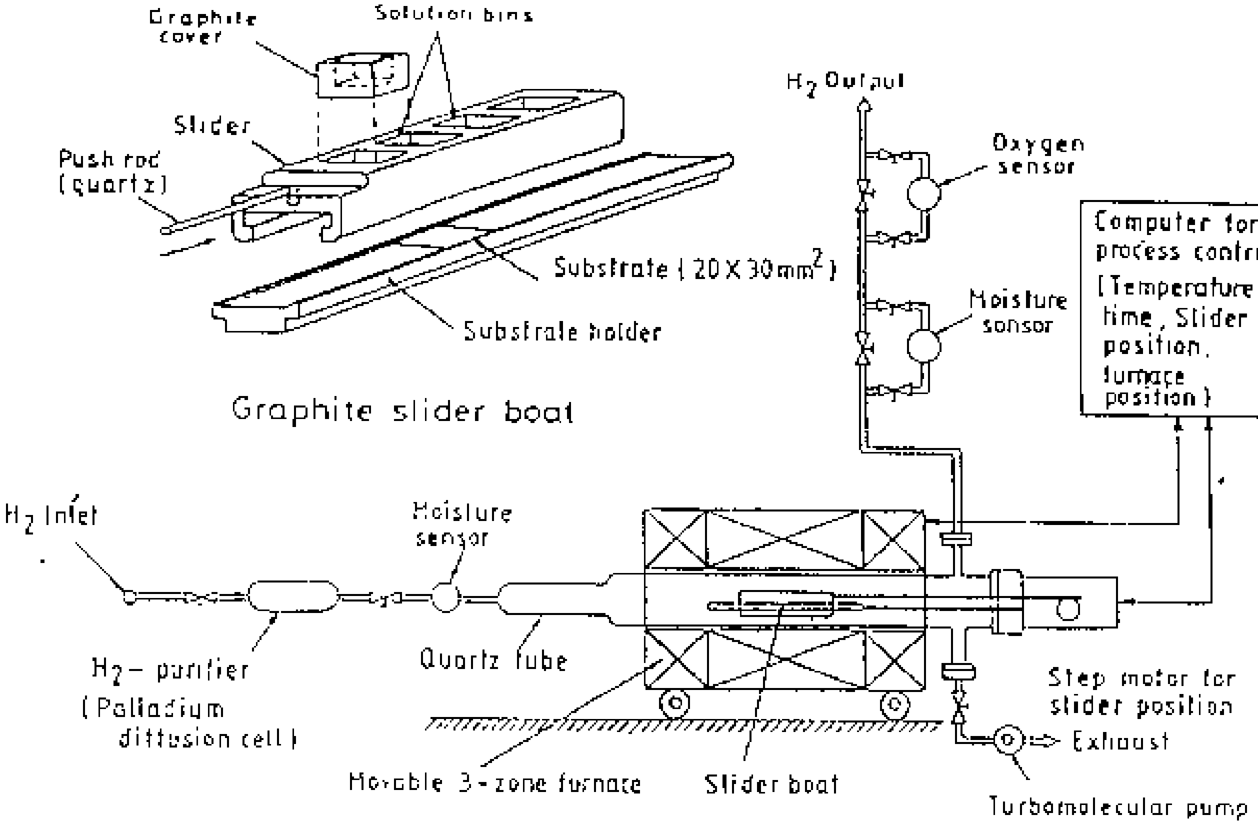

Figure (2.4) Schematic view of a horizontal multibin-slider LPE system

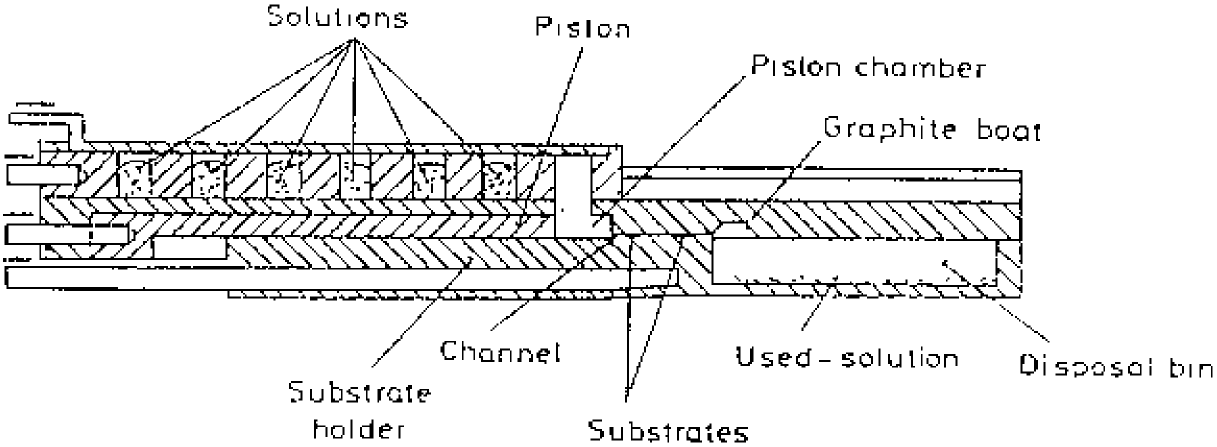

Figure (2.5) Schematic diagram of a piston type slider boat

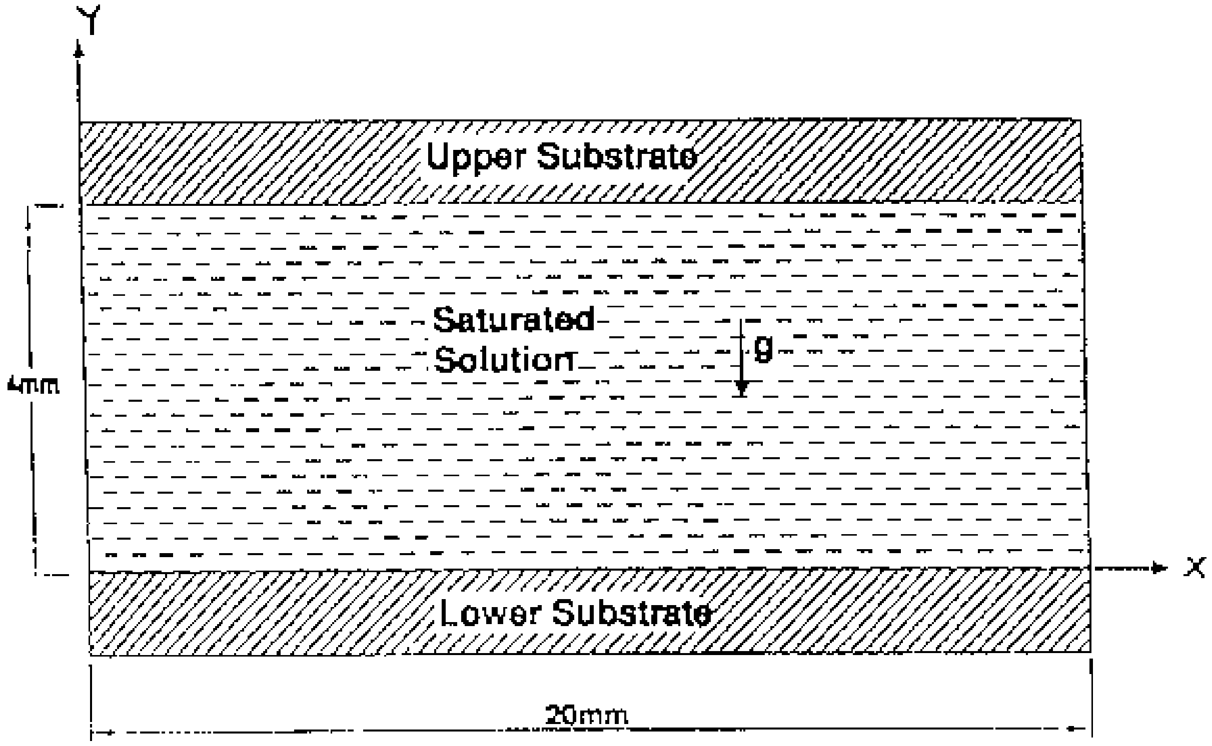

Figure (2.6) LPE growth cell configuration for sandwich technique growing substrate. The solute-depletion convection is, in general, a spatially non-uniform time dependent macroscopic phenomenon The macroscopic phenomena along with the LPE growth which is to be governed by the conservation of mass, balance of linear and angular momentum and conservation of energy. Moreover the principle of conservation of mass of solute species must also be invoked, since the solution is assumed to be a binary fluid mixture *(Kimura et al 1994)* *Kanai et al (1997)* described the experimental results, where numerical simulation was performed in a sandwich cell. The result of the simulation has shown that the higher dissolution rate on the lower substrate and higher growth rate on the upper substrate are a consequence of solute convection.

2.3 ADVANTAGES OF LPE

1) A basic LPE growth system can be built at a very low cost. Almost all kinds of possible semiconductors can be grown with the little modifications of LPE system.
2) In this system grown-in defects are minimum, since it is an equilibrium growth process. Thick layers can be grown very easily due to very higher growth rate.
3) The LPE process is inherently less harmful to the environment than the other techniques due to its high deposition efficiency and also the growth materials are relatively safe to handle.
4) LPE is well suited as an industrial process, especially for the production of green GaP LEDs, red AlGaAs LEDs and GaAs IREDs because of low cost and device performance.
5) The LPE growth technique is much more sensitive to the substrate orientation than the other epitaxial techniques, since it is being a near-equilibrium process.

6) LPE-grown materials are best suited for the fabrication of high quantum efficiency optoelectronic devices.
7) The grown materials have good reproducibility and uniformity.

2.4 *DISADVANTAGES OF LPE*

1) LPE is considered to be applicable only for the production of single device but not for integrated circuits.
2) A miscibility gap occurs in certain alloy systems when produced by LPE but not by other epitaxial methods.
3) LPE technique is not suitable for producing devices based on strained layers.
4) Controlling the growth of each monolayer by a periodical; interruption of the group III and group V fluxes as in ALE is not possible with LPE technique
5) The growing LPE epilayer surface is hidden by the metallic solution hence an in-situ characterization of growing layer is not possible.
6) For the production of the device structures involving thin layers, super-lattice or quantum wells, LPE appear to be not suited. This is essentially due to the moderate thickness control of thin layers.

2.5 *REVIEW OF LITERATURE ON LPE*

The LPE technique was first demonstrated by *H.Nelson* of Bell laboratories in 1963 by fabricating Ge tunnel diodes and GaAs lasers. Today the use of LPE has been mainly concentrated on the growth of III-V compound semiconductors and its ternary and quaternary alloys. III-V compound semiconductors have received much attention due to their use in fabricating microwave and optical devices. Many `first' of electronic and optoelectronic devices were based on LPE structures such as LEDs, lasers, photodetectors and solar cells. Later this technique was successfully used to make high speed electronic devices like Gunn diodes, Field-effect transistors and heterojuction bipolar transistors.

The visible LEDs are the earliest applications from the growth materials by LPE. These devices exhibit efficient infrared methane gas sensors for the cost effective detection and monitoring of methane gas in various applications.

Chen and Wu (1995) from the research institute of Electrical Engineering Tsing Hua University, China have grown InGaAsP epitaxial layers by LPE using a horizontal sliding boat system and fabricated orange light-emitting diodes. From the same institute, *Sun et al (1996)* have obtained high quality GaSb layer grown from Sb-rich solution by LPE and fabricated GaSb photodiodes which exhibits a low dark current of 2μA at -5V. Also it shows a high break down voltage of 28.7V at 20μA.

The advantages of using III-V materials for photo-detector applications compared to Si ands Ge, are that, the band gap of the material can be suitably chosen for a particular wavelength region. Many III-V materials are direct bands gap type, offering high quantum efficiency and their high motilities give the possibility of high speeds applications. Major kinds of photo-detectors are of photodiode type. Some examples of photo-detectors for longer wavelengths made for the first time by LPE are the pin-photodiodes from the systems of InGaAsP/InP *(Wieder et al 1977)*, InGaAs/InP *(Leheny et al 1979)* and GaAlSb/GaSb *(Sukegawa et al 1978)*.

Panish et al (1970) at Bell laboratories have developed double-hetero-structure AlGaAs/GaAs laser diode continuous-wave (CW) lasing at room temperature. Also the continuous-wave (CW) operation of double-heterostructure (DH) lasers emitting at wavelength beyond 1μm, realized in the systems of InGaAsP/InP *(Hsieh et al 1976)* and

AlGaAsSb/GaAsSb *(Nahory et al 1976)* were first successfully achieved with LPE material.

One of the most challenging problems in heteroepitaxcy is the growth of layers with thickness smaller than the electron free path, i.e., of around 10nm.Compared to bulk layers lasers, improved characteristics are expected from such multiple quantum well active layers *(Haug 1988)*. Some of the examples of grown thin layers by LPE are found *(Ohki et al 1987; Cser et al 1987)*, including doping super-lattices *(Koning and Jorke 1985; Greene et al 1987)*.

Bolkhovityanove (1995) had grown pseudomorphic InGaAsP films with elastic strains up to 1% on GaAs substrate of (111) orientation by LPE with a band gaps varies from 1.8 to 1.4 eV. *Zhuralev et al (1998)* have grown P-GaAs:Zn(100) epitaxial layers by LPE from gallium and bismuth melts.

Some excellent reviews on the LPE technique have already been written by several authors *(Kressel and Nelson 1973; Benz and Bauser 1980; Stringfellow 1982; Astles 1990; Kuphal 1994)*. In the past few years there have been many new developments in LPE which makes the technique attractive for the future as well. These includes automation of the growth process for the better layer thickness control, melt casting systems to facilitate the work of weighing the source materials, larger wafer areas up to 510nm in diameter, multiple-wafer boat, refined boat constructions, better control of the layer morphology and a deeper theoretical understanding.

CHAPTER 3

GROWTH KINETICS OF III-V COMPOUND SEMICONDUCTORS IN LIQUID PHASE EPITAXY

CHAPTER 3

GROWTH KINETICS OF III-V COMPOUND SEMICONDUCTORS IN LIQUID PHASE EPITAXY

In epitaxial growth, nucleation is considered to be the initial and important stage. Nucleation can often be induced by external influences like agitation, mechanical shock, friction, extreme pressures, electric and magnetic fields, spark discharge, ultraviolet, x-rays, γ-rays, sonic and ultrasonic irradiation and so on. Recently it has become possible in favorable cases to measure the actual nucleation rates and their variation with super-saturation and temperature *(Adams et al 1984).* In this chapter a brief study of the nucleation kinetics, modeling of one dimensional solute diffusion growth theory and the LPE growth process are given.

3.1 NUCLEATION KINETICS

Nucleation is the process of generating within a metastable mother phase, the initial fragments of a new and more stable phase capable of developing spontaneously into gross fragments of the stable phase. Nucleation is consequently a study of initial stages of the kinetics of such transformations. To occur the LPE growth, the nucleation sites must exist on the substrate surface. The nucleation is initiated at the interface between the melt and the substrate, a composition gradient is established within the melt, driving more materials to the interface. At every point of the interface, the composition gradient within the melt must have the same value and must be perpendicular to the substrate. Nucleation, like ordinary chemical kinetics, involves an activation process leading to the formation of unstable intermediate stages of embryo. If the embryo grows to a particular size (critical size) known as 'critical nucleus', then there is greater probability for the nucleus to grow. Thus the birth of the critical nucleus is an important event in the crystal growth and nucleation is the precursor of crystal growth and of the overall crystallization process *(Michael 1965)*. The critical nucleus process results from the excess of surface energy which is sufficient to produce the aggregate as a new phase in the presence of mother phase *(Chernov 1984)*.

Nucleation may occur spontaneously or it may be induced artificially. These two cases are frequently referred to homogeneous nucleation and heterogeneous nucleation respectively. If the nucleus is formed homogeneously in the interior of the parent phase, it is called homogeneous nucleation. On the other hand if the nuclei are formed homogeneously around ions, impurity molecules or on dust particles, on the surface or at structural singularities such as dislocations or other imperfections, is called heterogeneous nucleation.

3.1.1 Free Energy of formation of a spherical nucleus

In the nucleation process, super-saturation plays an important role and is the main factor controlling the rate of nucleation. The formation of a liquid micro-cluster from the supersaturated vapour or a solid microcrystal from the liquid demands a certain quantity of energy to be spent in the creation of the new phase. Once the embryo of the new phase is created, it will have energies associated with its volume and surface. Let ΔG be the overall excess free energy of the embryo, then the free energy of formation of a nucleus can be written as

$$\Delta G - \Delta G_S + \Delta G_V \tag{3.1}$$

where ΔG_S is the surface excess free energy (positive quantity), and ΔG_V is the volume excess free energy (negative quantity).

The free energy of formation for a spherical shape of nucleus of radius r, can be expressed as *(Hossain et al 1999a)*.

$$\Delta G = 4\pi r^2\sigma + \frac{3}{4}\pi r^3 \Delta G_V \tag{3.2}$$

Where σ is the crystal solution interfacial tension and ΔG_V □ which is related to supersaturating or super-cooling □ is the free energy change of the transformation per unit volume. Since the surface energy term increases with r^2 and the volume energy term decreases with r^3, the total free energy increases with the increase in the size of the nucleus, attains the maximum and decreases for the further increase in the size of the nucleus as shown in figure (3.1)

The size corresponding to which the free energy change is maximum, is known as the critical radius and can be obtained by maximizing equation (3.2)

$$\frac{d(\Delta G)}{dr} = 0 \tag{3.3}$$

According to the classical theory of capillarity approximation, the surface tension is assumed to be independent of the size of the nucleus. Hence the size of the critical nucleus is,

$$r^* = -\frac{2\sigma}{\Delta G_V} \tag{3.4}$$

Substituting the value of r* from equation (3.4) in equation (3.2), the free energy change associated with the formation of a critical nucleus is obtained as,

$$\Delta G^* = \frac{16\pi\sigma^3}{3(\Delta G_V)^2} = \frac{4}{3}\pi(r^*)^2 \tag{3.5}$$

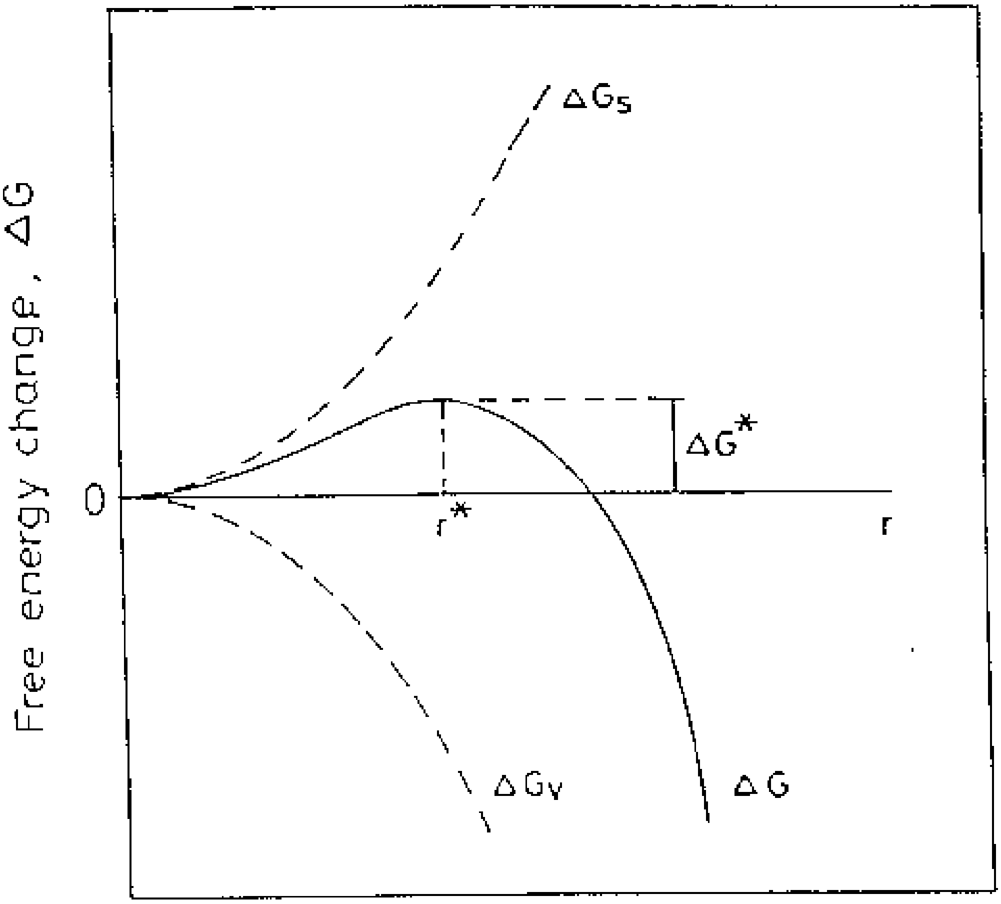

Figure (3.1) Dependence of surface free energy change, ΔG_S, volume free energy change, ΔG_V and the net free energy change, ΔG for the size, r of the nucleus

If there are n molecules per unit volume and if they obey the Maxwell-Boltzmann statistics, then the concentration of nuclei of critical size can be expressed as,

$$n^* = n \exp\left(-\frac{\Delta G^*}{kT}\right) \tag{3.6}$$

where ΔG^* is the total Gibbs free energy change for the formation of the critical nucleus, k is the Boltzmaan constant and T is the Kelvin temperature.

According to the classical nucleation theory the number of critical nuclei formed per unit time per unit volume is known as the rate of nucleation, and is given by,

$$I = A \exp\left(-\frac{\Delta G^*}{kT}\right) \tag{3.7}$$

where I is the nucleation rate and A is a pre-exponential factor.

3.2 DIFFUSION LIMITED GROWTH THEORY

During the growth in liquid phase epitaxy, solute elements are transported towards the growth interface mainly by diffusion. To realize the growth kinetics of the epilayers, the information of concentration gradient of the solute atoms in front of the growing crystal solution interface is very essential. Theoretical modeling and computational methods plays a key role in analyzing the kinetics of growth process and are aimed to make the experimental research more reliable, accurate and efficient. For the design of experimental apparatus and to understand the growth process, preliminary computation are often helpful

3.2.1 One dimensional diffusion limited growth

One dimensional diffusion limited growth theory has been widely used to explain the LPE growth kinetics for a wide range of temperature and different growth techniques *(Crossley and Small 1971; Crossley and Small 1972; Pan et al 1986; Traeger et al 1988; Dobosz and Zytkiewicz 1991, Dizaji and Dhanasekaran 1996)*. Based on this theory, the LPE growth of some binaries (InAs. GaAs, InP etc) and ternaries (InGaP, AlGaAs, GaAsP etc) of III-V compounds semiconductor materials have already been numerically simulated. Details of the one dimensional diffusion limited growth theory are given as follows.

3.2.2 One dimensional mathematical modeling

The diffusion limited growth is possible only when the interface kinetics is extremely fast. For the growth of binary III-V compound, one dimensional solute diffusion equations are given *(Astles 1990)* as,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} + R_V\frac{\partial C(x,t)}{\partial x} \tag{3.8}$$

where C(x,t) is the solute concentration in the binary solution., x is the distance in the solution from the solid-liquid interface and perpendicular to the substrate, t is the growth time, D is the diffusion coefficient of solute atoms in the solvent, and R_v is the interface velocity (by which the interface moves in to the solution). The interface velocity, R_v, is low enough that the term [$R_V\frac{\partial C}{\partial x}$] in the equation (3.8) is negligible. This assumption has been reported *(Moon 1974)* for LPE growth.

Therefore the equation (3.8) can be expressed for the binaries LPE growth as

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \tag{3.9}$$

3.3 LPE GROWTH PROCESS

There are three important LPE growth techniques, namely : the equilibrium-cooling technique, step-cooling technique and super-cooling technique. The typical temperature-time profile during the different LPE growth process is shown in figure (3.2). In these techniques, the system is initially heated above the saturation temperature, T_S, in order to obtain a homogeneous mixture of the solution constituents. Then it is cooled down, and the substrate is brought into contact with the solution at the starting temperature T_A. The growth is then terminated at the end temperature, T_{END}, by removal of the substrate, and the furnace is subsequently cooled down quickly to avoid any thermal degradation of the grown layer *(Kuphal 1994)*.

To find out the equations of epitaxial layer thickness as a function of growth time for different growth techniques from the solution of the solute diffusion equation, we have considered the following principal assumptions:

1) There is no solute diffusion in the solid phase.
2) During the growth, at any given instant the solute concentration in the solution at the growth interface is given by the liquids curve – i.e., the liquid and solid are in equilibrium at the interface.
3) The solute concentration at the free surface of the solution does not change during a growth run – i.e., the solution is semi-infinite.
4) The diffusion coefficient and the slope of the liquids curve are constant during each growth run for the binary compounds.

Some authors *(Moon 1974; Hsieh 1974, Hossain Md. Mostak 1999)* developed different equations for layer thickness as a function of time for binary compounds by solving one dimensional solute diffusion equation with appropriate boundary conditions. *Kuphal (1994)* derived the equation of layer thickness as a function of time for many component systems. The equations for epitaxial layer

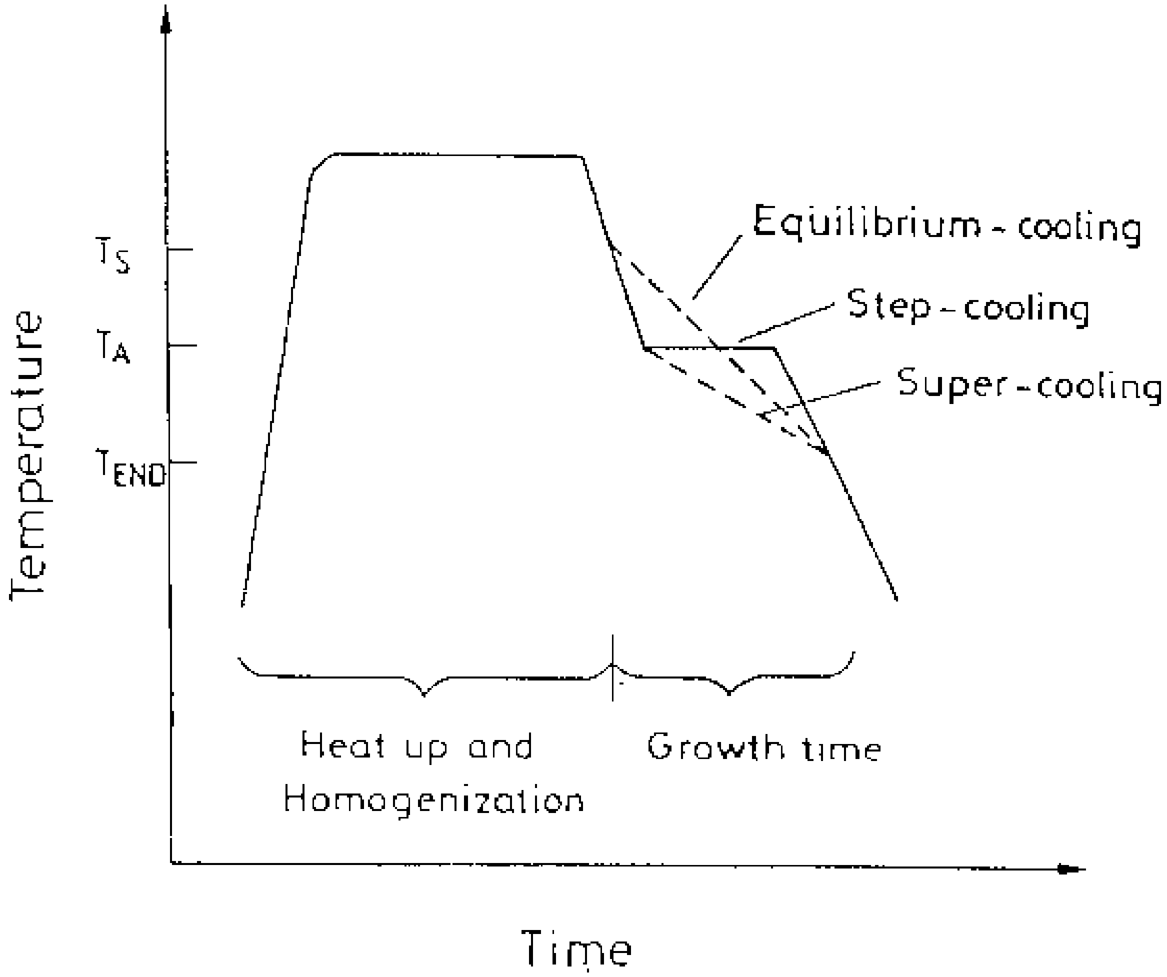

Figure (3.2) Typical temperature-time profile during epitaxy thickness as a function of time for binary compounds are derived here for the different LPE techniques by using the solution of one dimensional solute diffusion equation for the case of semi-infinite growth solution and finite growth solution.

3.3.1 Equilibrium-cooling technique

In equilibrium-cooling technique, the solution is brought in to contact with the substrate at the saturation temperature and solution becomes in equilibrium at the moment of the contact. At the saturation temperature, T_S, the solution having uniform concentration C_0 i.e., $C(x,0) = C_0$ for all positions of x. This solution is then cooled at a constant cooling rate, α, such that

$$T = T_S - \alpha t \tag{3.10}$$

At the time of growth, for small cooling intervals, the equilibrium solute concentration is a linear function of temperature, i.e., $m = dT_E / dC_E$, where m is the slope of liquid curve equal to $\Delta T / (C_0 - C_1)$. Here C_0 is the initial concentration given by the liquids curve at temperature T_S and C_1 is the concentration given by the liquids curve at the temperature of $(T_S - \Delta T)$ where ΔT is the degree of super-cooling.

For equilibrium cooling technique the boundary conditions are

$$C(x,0) = C_0 \qquad \text{and } C(0,t) = C_0 - \frac{\alpha t}{m} \tag{3.11}$$

Using those boundary conditions the equation for the thickness of the epitaxial layer as a function of time for equilibrium cooling technique can be derived as*(Moon 1974 , Hsieh 1974)*,

$$d_a(t) = \frac{4}{3}\left(\frac{\alpha}{C_S m}\right)(D/\pi)^{1/2} t^{3/2} \tag{3.12}$$

where d is the layer thickness, D is diffusion coefficient of solute atoms in the solvent, and C_S is the solute concentration in the grown layer (solid)

3.3.2 Step-cooling technique

In the step-cooling technique, the substrate and the solution is cooled separately at a constant rate from saturation temperature, T_S , till spontaneous precipitation formed in the solution. When precipitation starts to form in the solution at a particular temperature T_A, the temperature is kept constant and the solution is brought into contact with the substrate until the desired layer thickness is grown over the substrate.

For the step-cooling technique the boundary conditions are

$$C(x,0) = C_0 \qquad \text{and } C(0,t) = C_l \tag{3.13}$$

where C_l is the solute concentration given by the liquid curve at (T_S - ΔT) and ΔT is the amount of super-cooling and it is small enough to avoid the occurrence of homogeneous nucleation in the solution. Hence the boundary condition can be expressed as,

$$C(0,t) = C_l = C_{ll} - (C_0 - C_l) = C_{ll} - (\Delta T / m) \tag{3.14}$$

Then the equation for the thickness of epitaxial layer as a function of time for step-cooling technique can be found as *(Moon 1974 ; Hsieh 1974)*,

$$d_{\Delta}(t) = 2\Delta T(\frac{1}{C_S m})(D/\pi)^{1/2} t^{1/2} \tag{3.15}$$

3.3.3 Super-cooling technique

The initial condition for technique are same as step-cooling technique, where both the substrate and the solution are cooled separately at a constant rate α from the saturation temperature T_S to T_A and then the contact is made between them. The system is then further cooled at the same rate until the growth is terminated, as in equilibrium-cooling technique. Therefore super-cooling technique can be considered as a combination of step-cooling technique and the equilibrium-cooling technique.

For the super-cooling technique the boundary conditions are

$$C(x,0) = C_0 \quad \text{and} \quad C(0,t) = C_1 - (\alpha t/m) = C_0 - (\Delta T/m) - (\alpha t/m) \qquad (3.16)$$

where C_0 is the initial concentration of the solute in the solution, α is the constant cooling rate, m is the slope of the liquid curve. ΔT is the amount of super cooling and t is the growth time.

Using these boundary conditions the equation for the thickness of epitaxial layer as a function of time for super-cooling technique can be given by *(Feng et al 1980)*

$$d(t) = \left(\frac{1}{C_S m}\right)\left(\frac{D}{\pi}\right)^{1/2}\left[(2\Delta T t^{1/2}) + (\frac{4}{3}\alpha t^{3/2})\right] \qquad (3.17)$$

or

$$d(t) = d_\Delta(t) + d_\alpha(t) \qquad (3.18)$$

As stated earlier the super-cooling technique is a combination of step-cooling technique and the equilibrium-cooling technique. it was experimentally proved by

Hsieh (1974) for GaAs (Gallium Arsenide) and *Kao and Eknoyan (1983)* for GaP (Gallium Phosphide). Figure (3.3) represents the thickness as a function of growth time for GaP grown for different cooling techniques. It can be observed from the figure that at lower units of time the experimental results are very close to the theoretical line for step cooling growth, whereas the higher units of time, they come closer to that of equlibrium cooling growth.

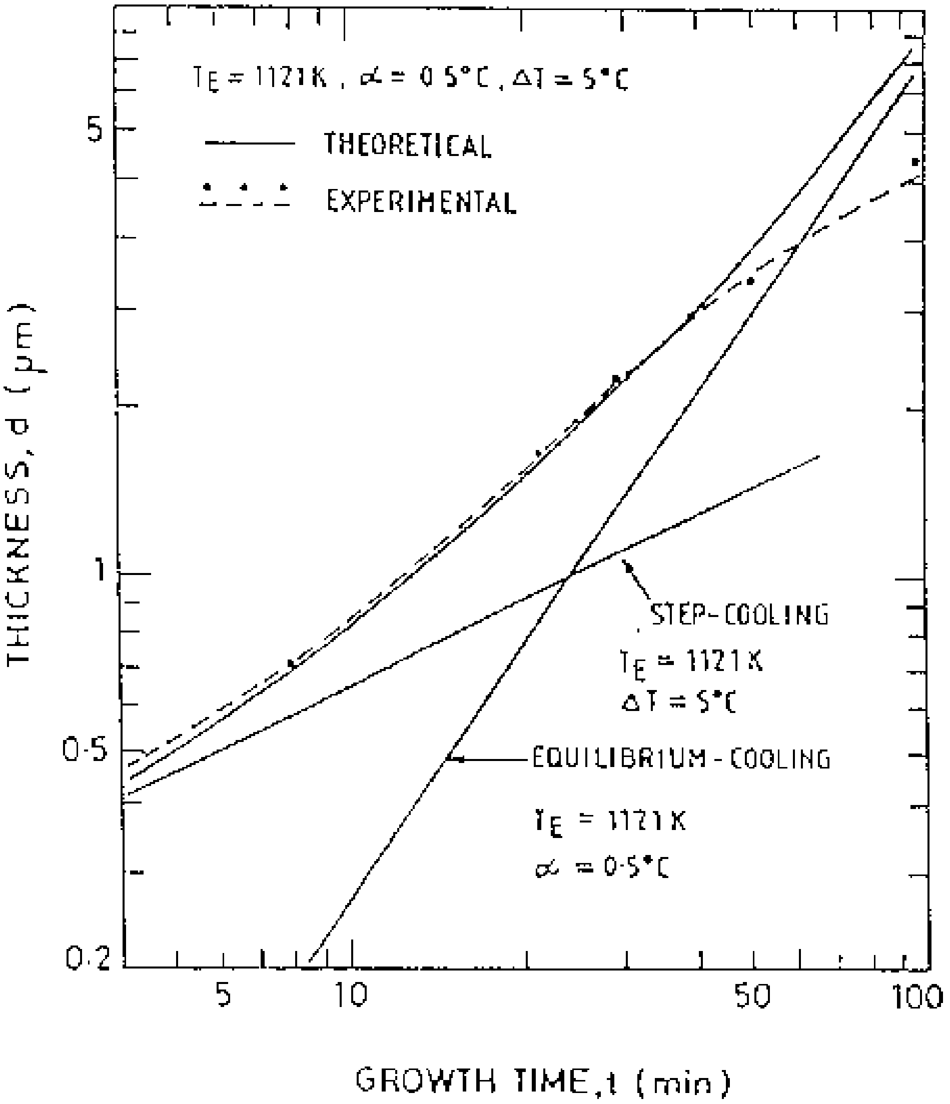

Figure (3.3) Thickness of the GaP LPE layer grown at 1121K as a function of time with different cooling techniques (Kao and Eknoyan 1983)

CHAPTER 4

GROWTH KINETICS OF III-V BINARIES FROM LIQUID PHASE EPITAXY

CHAPTER 4

GROWTH KINETICS OF III-V BINARIES FROM LIQUID PHASE EPITAXY

4.1 INTRODUCTION

During the liquid phase epitaxial growth process, the solute concentration is declined in front of the growing crystal solution interface. The behavior of the solute concentration at the interface can be determined from the concentration profiles. One dimensional simulation of concentration profiles of solute atoms near the interface gives the information about the rearrangement of the solute atoms inside the solution Experimentalists can employ the theoretical predictions for simulating the experimental parameters numerically and using this, they can grow a device quality crystal.

In the present work, a physical model based on the one dimensional diffusion of the solute atoms have been applied to binary III-V compound semiconductors to analyze the epitaxial growth mechanism. The two important III-V binary materials GaSb (Gallium Antimonide) and GaP (Gallium Phosphide) have been considered for our simulation studies. Gallium antimonide (GaSb) based compound semiconductors have received increasing attention recently because the corresponding wavelengths of their alloys cover a wide spectral range from 1.24μm (AlGaSb or AlGaAsSb) to 4.3μm (InGaAsSb) *(Yuh-Maoh et al 1996)*. Consequently, they have turn out to be promising candidates for the application in long wavelength lasers and photo detectors for fibre optic communication system *(Mao and Krier 1993)*. Gallium phosphide (GaP) is an attractive material for its applications in red and green emitting electroluminescent diodes *(Kressel and Nelson 1973)* and in detectors *(Huges et al 1991)*

4.2 KINETIC MODEL

In the case of fast growth, a kinetic model has been developed to understand the epitaxial growth mechanism of GaSb and GaP based on the mass transport limited (diffusion) model *(Crossley and Small 1971, Dizaji and Dhanasekaran 1996)* in which the diffusion of solute atoms in the solution occurs towards the growing crystal interface

The following equation can be used to calculate the initial concentration of solute atoms by using the binary liquids curve provided by *Panish and Ilegems (1972), Hall(1963)* which has been given in figure (4.1)

$$C_u = \frac{C_{Ga} X_u}{1 - X_u} \qquad (4.1)$$

where C_u and x_u are concentration and the atomic fraction of solute atoms (u = Sb or P) respectively, and C_{Ga} is the concentration of solvent atoms (Gallium) in the solution. An expression for equilibrium concentration C_E, at equilibrium temperature can be developed as a function of equilibrium temperature dependent on exponential form *(Astles 1990)*

$$C_E = a \exp\left(b - \frac{c}{T}\right) \qquad (4.2)$$

where a, b and c are the constants (which can be found by using curve fitting method) and T is the temperature in Kelvin.

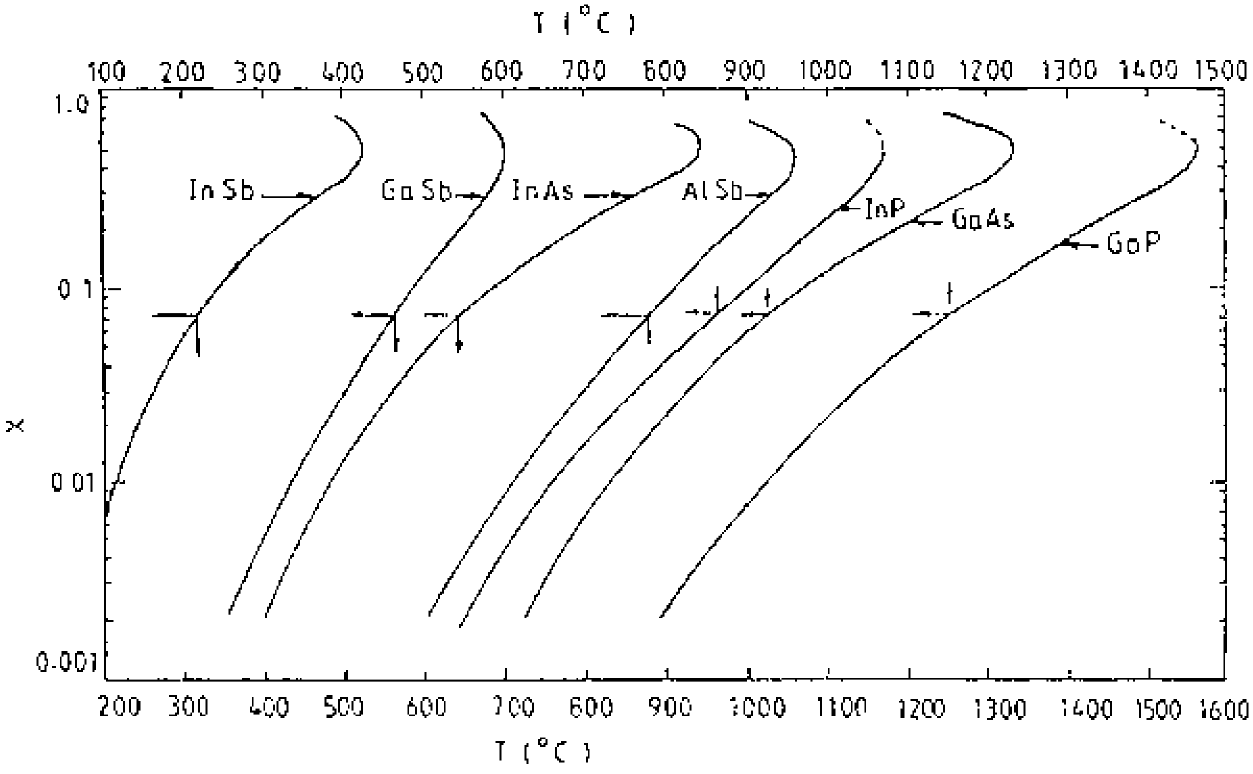

Figure (4.1): Atom fracrion of P, As or Sb required to saturate liquid Ga or In (Panish and Ilegems 1972)

For our simulation study the following assumptions have been considered :

1) When the solution and substrate are placed in contact, the solute concentration in the solution at the growing interface follow the liquids curve, i.e., the liquid and solid are in equilibrium at the interface
2) The slope of the liquids curve is constant during the growth process, and
3) The diffusion coefficient is constant in all directions (along the substrate and perpendicular to the substrate) during the growth process.

4.2.1 Numerical solution of one dimensional diffusion equation

A one dimensional model has been developed by assuming a solution with the thickness 2.5 mm in front of the substrate The solution is divided into 50 equally spaced segment of width ε along the x-axis as shown in figure (4.2). The segment numbers are 1, 2, 3 ....,i..............,50 with corresponding concentrations C_1, C_2, C_3, ... C_i ....C_{50} respectively. These concentrations represent the concentrations of solute atoms (i e., Sb or P) in the solvent (i e., Ga). In this case, the solid composition is assumed to be uniform and stoichiometric.

Initially the solution is perfectly homogeneous and the concentrations of solute atoms in the solution is C_E, that is $C(x, t = 0) = C_E$ for all the position along x axis, and to calculate successive concentration profiles after successive time increments τ, one can write

$$C(x,t) = C(i,n) \; ; \; \text{where,} \quad x = i\varepsilon \quad \text{and} \quad t = n\tau \qquad (4.3)$$

where i is the segment number and n is the number of time cycles.

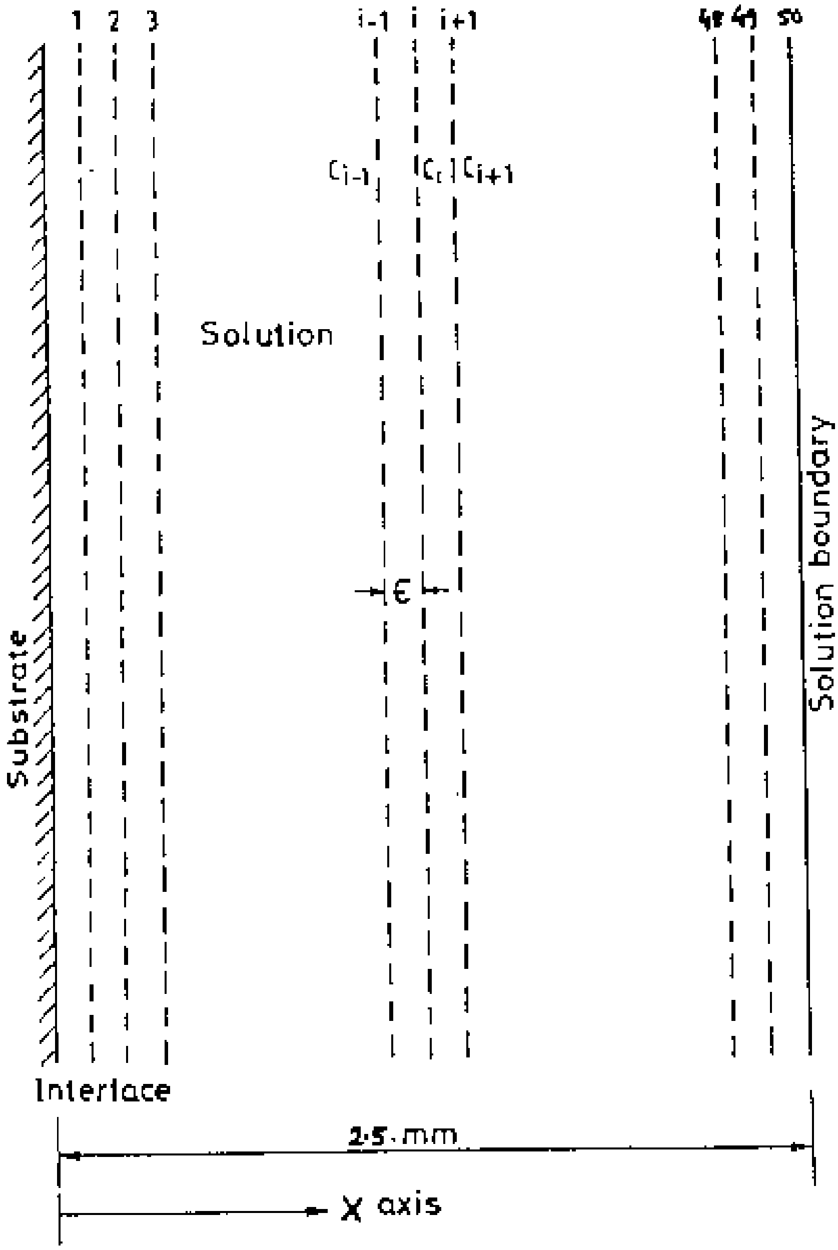

Figure (4.2) Segmented solution in front of growing crystal interface along the axis

The concentration of the solute atoms at the first segment is C_1 and the last segment C_{50} , have been decided by the boundary conditions. The concentration of solute atoms at the remaining segments during the growth can be calculated by using forward difference in time and the formula for the Laplacian based on a centred difference approximation for the second derivative in x axis *(Richard Haberman 1987)*

Let the concentrations at the points $(i + 1)\varepsilon$, $i\varepsilon$ and $(i - 1)\varepsilon$ be denoted by C(i+1, n), C(i,n) and C(i-1, n) at the time $t = n\tau$ respectively and the concentration at the point $i\varepsilon$ at the time $t = (n+1)\tau$ is denoted by C(i, n+1), then by applying the Laplacian approximation *(Richard Haberman 1987)*, we obtain,

$$\frac{\partial C(x,t)}{\partial x} = \frac{[C(i+1,n) - C(i-1,n)]}{2\varepsilon} \tag{4.4}$$

$$\frac{\partial^2 C(x,t)}{\partial x^2} = \frac{[C(i+1,n) - 2C(i,n) + C(i-1,n)]}{\varepsilon^2} \tag{4.5}$$

and

$$\frac{\partial C(x,t)}{\partial t} = \frac{[C(i,n+1) - C(i,n)]}{\tau} \tag{4.6}$$

Substituting equation (4.5) and (4.6) in equation (3.9), we get

$$\frac{[C(i,n+1) - C(i,n)]}{\tau} = D\frac{[C(i+1,n) - 2C(i,n) + C(i-1,n)]}{\varepsilon^2} \tag{4.7}$$

Rearranging the above equation (4.7) we get the numerical solution for one dimensional solute diffusion equation as,

$$C(i,n+1) = C(i,n) + \frac{D\tau}{\varepsilon^2}\left[C(i+1,n) - 2C(i,n) + C(i-1,n)\right] \qquad (4.8)$$

4.3 BOUNDARY CONDITIONS

The following boundary conditions were applied to simulate the concentration profiles for liquid phase epitaxial growth of binary III-V compound semiconductors.

a) When time t = 0, then C(i, 0) = C_E for all x values $(0 \le i \le 50)$

b) When time $t \ge 0, then \frac{\partial C}{\partial x}\Big|_{x=50} = 0$ for x = 50ε

c) When time t > 0, then C(0. n) = C_E for x = 0 (i = 0)
(growth follows the liquids line)

d)When time $t \ge 1$. then the concentration of other segments are given by the equation (4.8) for $(1 \le i \le 49)$.

where C_E is the equilibrium concentration (initial concentration) of solute atoms at the initial temperature of the solution, C(0,n) is the concentration of solute atoms at the interface and x is the distance for the advancing growth interface.

4.3 DETERMINATION OF SOME PARAMETERS

The concentration profiles of the solute atoms in front of growing crystal interface can be constructed during liquid phase epitaxy of III-V binary compound semiconductors by using the equation (4.8) with appropriate boundary conditions. Applying the concentration profiles we can obtain dimensionless concentration parameter, growth rate, average thickness of the epitaxial layers etc.

4.4.1 Determination of dimensionless concentration parameter

A more powerful method of exhibiting concentration profiles was found *(Wilcox 1982)* to make use of the dimensionless concentration parameter, L_u , (where u is the solute atoms), defined as the difference between the original concentration, C_0, at infinity (C_0 = initial concentration of the solute atoms at the initial temperature) and the concentration C at any point during the growth process, divided by the difference between C_0 and the concentration C_E at the growing crystal interface (which is a function of time or growth temperature), i.e.,

$$L_u = \frac{C_0 - C}{C_0 - C_E} \tag{4.9}$$

The dimensionless concentration parameter, L_u, was found to scale very nearly as $(Dt)^{1/2}$ especially for moderate times up to 19.5 minutes i.e.,

$$\frac{C_0 - C}{C_0 - C_E} = f\left(\frac{x}{(Dt)^{1/2}}\right) \tag{4.10}$$

The dimensionless concentration parameter does not depend on diffusion coefficient and cooling rate but it depends on solubility on temperature or interface kinetics coefficient. This parameter varies from one to zero.

4.4.2 Determination of growth rate and thickness for one dimensional simulation

The growth rate of the grown solid layer is determined by the rate at which solute atoms diffuse towards the interface and incorporate into the growing crystal. The following equations have been used for the determination of growth rate and thickness.

An equation for the growth rate. R, can be obtained at the growing crystal interface in terms of a segmented solution *(Crossley and Small 1971)* at the end of each time step in the computation of the equation (4.8) as well as updated the equation of equilibrium concentration C_E as,

$$R = \frac{D[C(1,n) - C(0,n+1)]}{\varepsilon[C_s - C(0,n+1)]} \tag{4.11}$$

where C(0,n+1), C(1,n) and C_S are the concentrations of the solute atoms at the interface of (n+1)th time, first layer of nth time and in the solid binary compound semiconductors respectively. The average thickness of the growth crystal at any given time is obtained by the summation of the growth rate as, *(Hossain et al 1999)*

$$d = \sum_{n+1} R\tau = \sum_{n+1} \frac{D\tau[C(1,n) - C(0,n+1)]}{\varepsilon[C_S - C(0,n+1)]} \tag{4.12}$$

CHAPTER 5

RESULTS AND DISCUSSIONS

CHAPTER 5

RESULTS AND DISCUSSION

To calculate the successive concentration profiles, layer thickness, dimensionless concentration and average thickness of the solute (Sb or P) atoms in the Ga-rich solution, we have applied the proposed model to GaSb *(Hossain et al 1999)* and GaP *(Hossain et al 1999a)* for binary compounds grown by liquid phase epitaxy and the results are presented as follows.

5.1 Gallium Antimonide (GaSb)

The equation for the equilibrium (initial) concentration of antimony (Sb) in Gallium (Ga) rich solution has been developed by using the solubility data reported by *Hall (1963)* and by using the equation 4.2 *(Astles 1990)*, as,

$$C_F = 4.7197467\times10^{22}\exp\left[7.7908844-\frac{8.6538405\times10^{3}}{T}\right] \tag{5.1}$$

where T is the temperature in Kelvin of the substrate at any given instant of time. This equation is a fairly good representation of the Ga-Sb liquids line on the Ga-rich side for the temperature range between 673K and 873K. In the simulation studies of GaSb LPE, the value of the diffusion coefficient of Sb atoms in Ga-rich melt is assumed to be in order of 2×10^{-5} cm^2/sec. The equilibrium temperature T_F = 823K *(Dutta et al 1995)* has been used in our simulation study.

In our present work we have constructed the concentration profiles of Sb atoms in the Ga-rich solution in front of the growing crystal interface, calculated the thickness of the layer as a function of time and as function of temperature, the dimensionless concentration parameter is also calculated. Also our theoretical result has been compared with the reported experimental values. Our results are represented in the figures as shown below.

5.1.1 RESULTS AND DISCUSSION

Figure 5.1 represents the dimensionless concentration profiles of the antimony atoms at different growth temperatures in the Ga-rich solution at the cooling rate 3K/min. From the figure, it is seen that the dimensionless concentration parameter can have the values which vary from 0 to 1. It is calculated that the dimensionless concentration parameter were fitted by, *(Wilcox 1982)*,

$$\frac{C_0 - C}{C_0 - C_A} = \exp\left[-1.332306 - 1.4513239\frac{x}{(Dt)^{1/2}} + 1.6371913\frac{x^2}{Dt}\right] \qquad (5.2)$$

for times up to 19.5 minutes.

Figures 5.2, 5.3 and 5.4 show the concentration profiles of Sb atoms in GaSb solution for different cooling rates 0.3K/min, 1K/min and 3K/min respectively. It is seen from these figures that the concentration of Sb atoms decreases almost linearly. It is important to note that, more linear the concentration profiles curve, the melt is more homogeneous, i.e., the linearity of the concentration profiles curves are the representation of the homogeneity of the melt. The comparison of the concentration profiles for different cooling rates will lead us to a remarkable result. Figure 5.5 shows the comparison between the concentration profiles of Sb atoms in GaSb solution for different cooling rates 3K/min (——) and 0.3K/min (........) respectively. From the figure it can be concluded that the concentration profile is more linear for the lower cooling rate — which means that the melt becomes more homogeneous at lower cooling rates. At higher cooling rates the concentration of solution decreases more rapidly near the growing interface, which means that the melt is not homogeneous. Homogeneous melt is necessary for growing a perfect crystal, because if the melt is inhomogeneous, defects may be occurred in the crystals. And that's why lower cooling rate is preferable for growing such a layer thickness.

Figure 5.6 shows plots of thickness of the GaSb layer grown versus time for different cooling rates of 0.3 K/min, 1 K/min and 3 K/min. From the figure, we can see that the growth is more for higher cooling rate for a particular growth time. On the other hand, figure 5.7 is the representation of thickness of the GaSb layer grown versus temperature for different cooling rates of 0.3 K/min, 1K/min and 3 K/min. It can be concluded from the figure that the growth is more for lower cooling rate for a particular temperature. It happens because the lower cooling rate will take a longer time to be cooled to a particular temperature.

Figure 5.8 compares our theoretical calculations on the average thickness of GaSb grown with reported experimental values when the cooling rate is 0.3 K/min and at the equilibrium temperature T_E = 823K. It is observed from these figures that our theoretical findings have shown good agreements with the values.

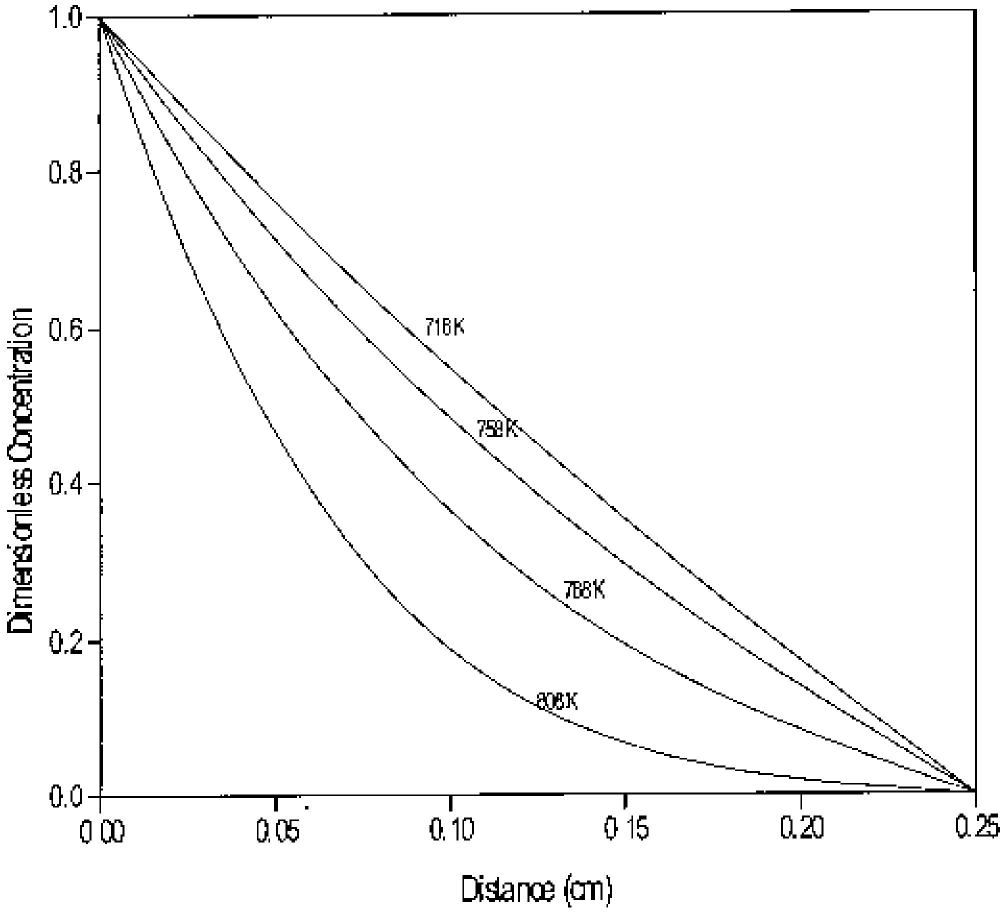

Figure (5.1) : Dimensionless concentration of antimony in front of the growing crystal interface as a function of distance at different growth temperatures for TE = 823K and at a cooling rate of 3K/min

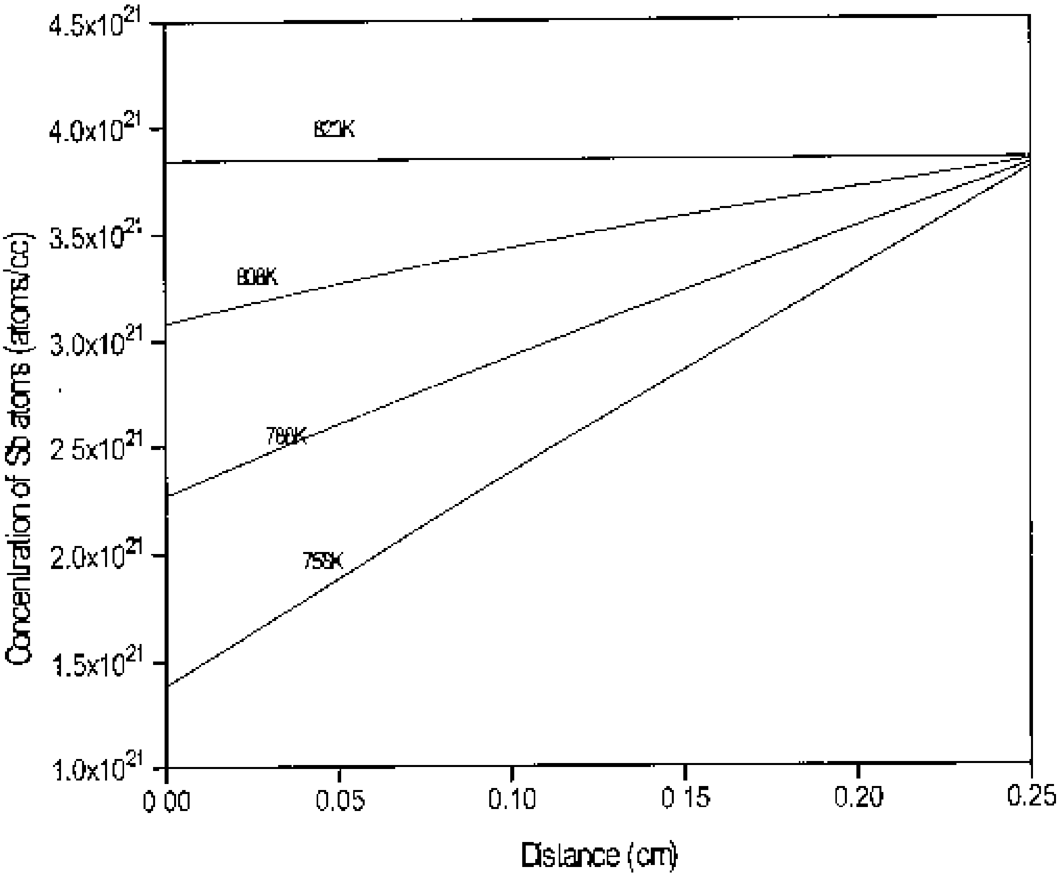

Figure (5.2) : Simulated concentration profiles of antimony (Sb) atoms in front of growing crystal interface for T_L = 823K and cooling rate 0.3 K/min

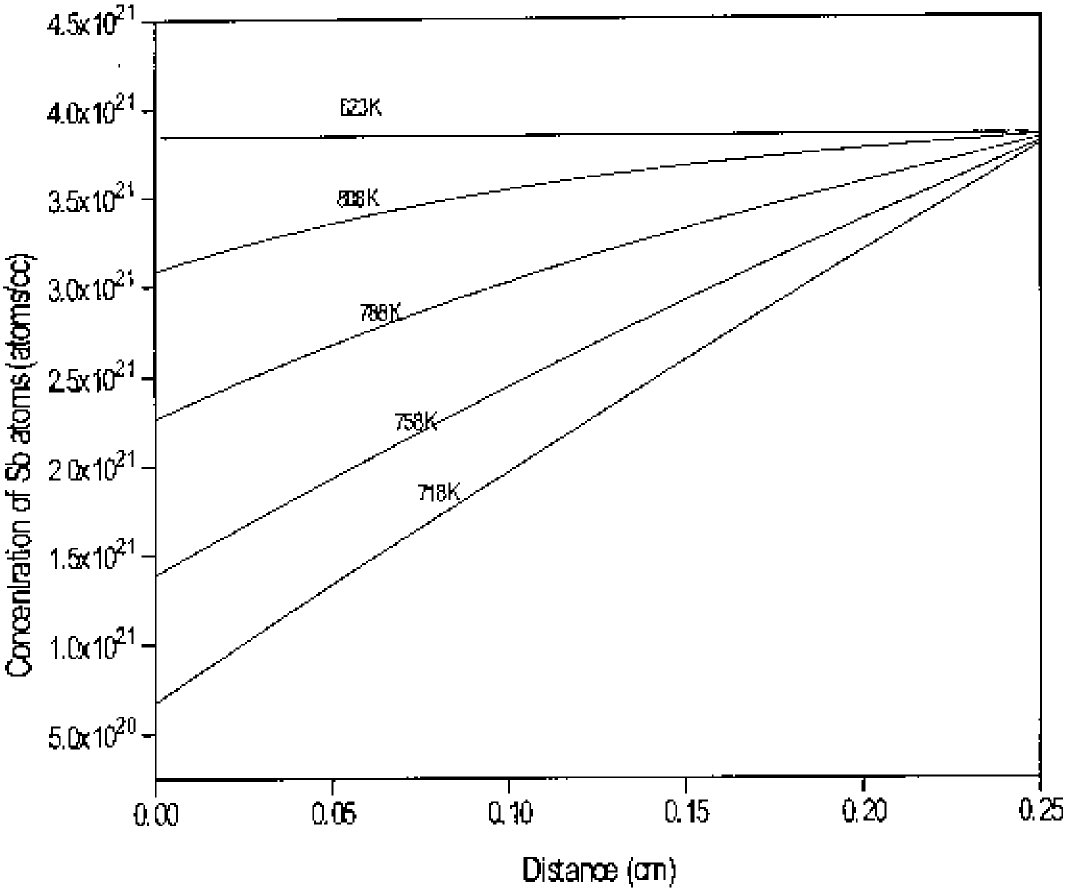

Figure (5.3) : Simulated concentration profiles of antimony (Sb) atoms in front of growing crystal interface for $T_L = 823K$ and cooling rate 1 K/min

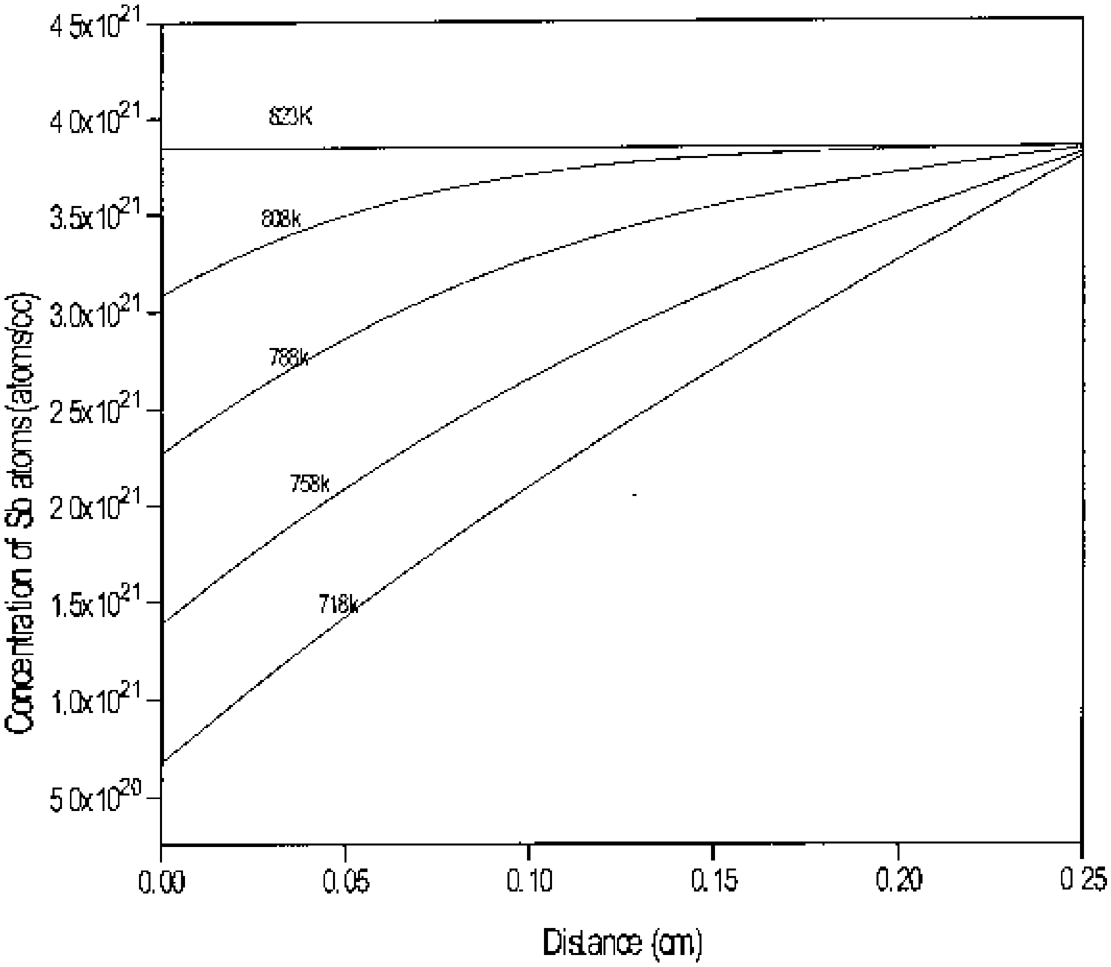

Figure (5.4) : Simulated concentration profiles of antimony (Sb) atoms in front of growing crystal interface for $T_L = 823K$ and cooling rate 3 K/min

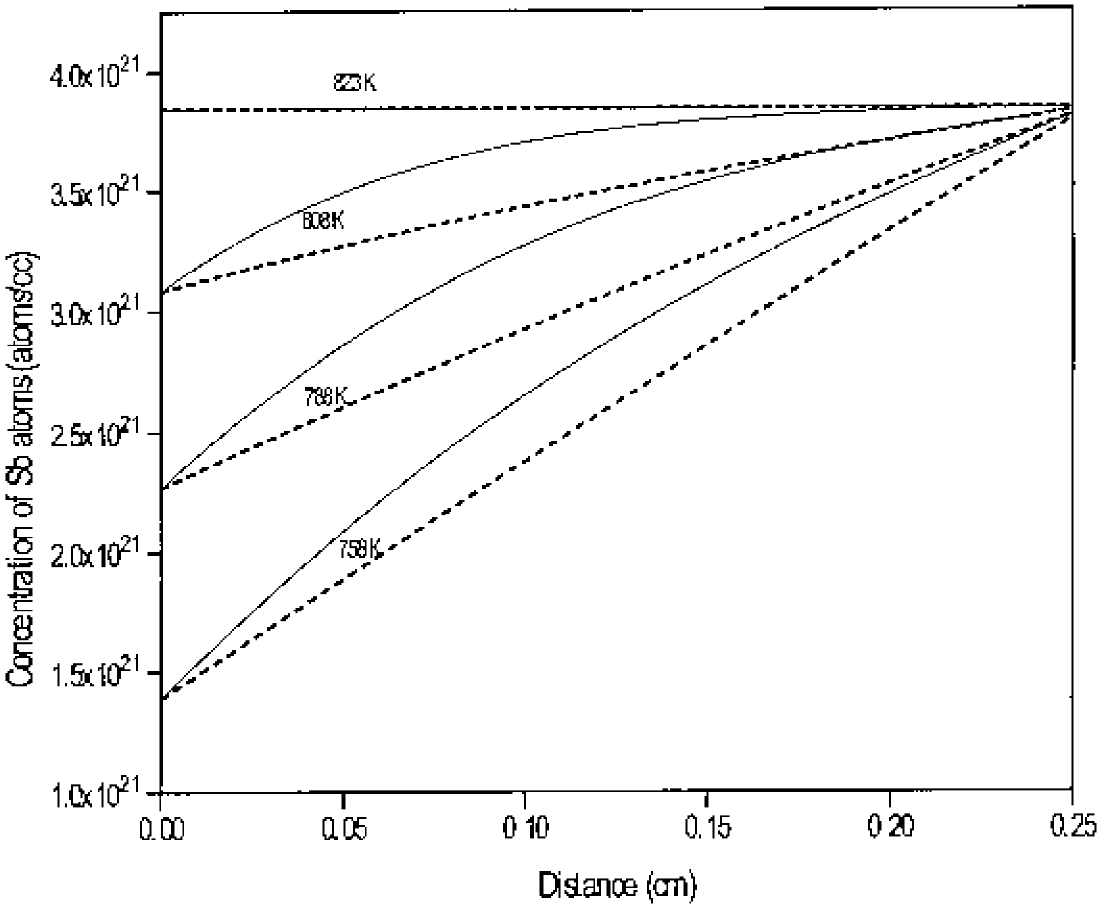

Figure (5.5) : Simulated concentration profiles of antimony (Sb) atoms in front of growing crystal interface for T_E = 823K and at the cooling rate (a) 3 K/min (—) and (b) 0.3 K/min (........)

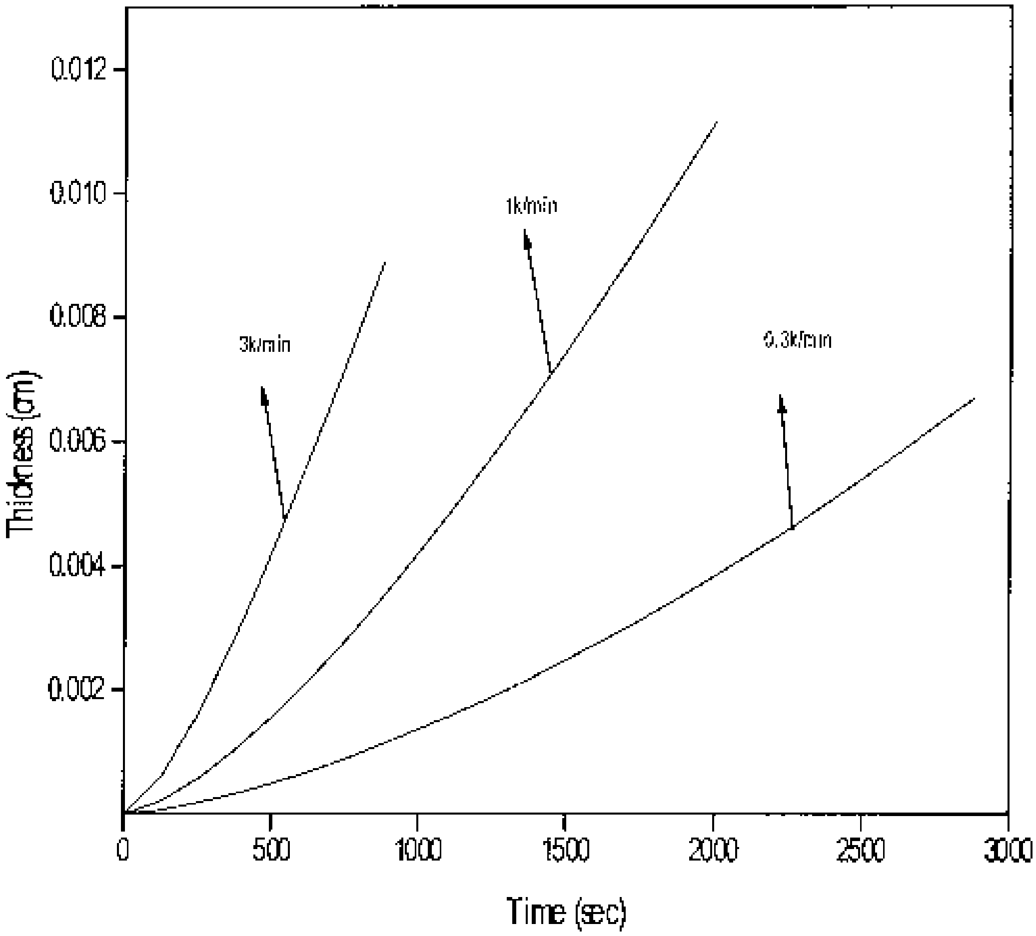

Figure (5.6) : Calculated values of GaSb average layers thickness grown as a function of time for different cooling rates of (a) 3 K/min (b)1.0 K/min (c)0.3 K/min for equilibrium temperature T_E = 823 K

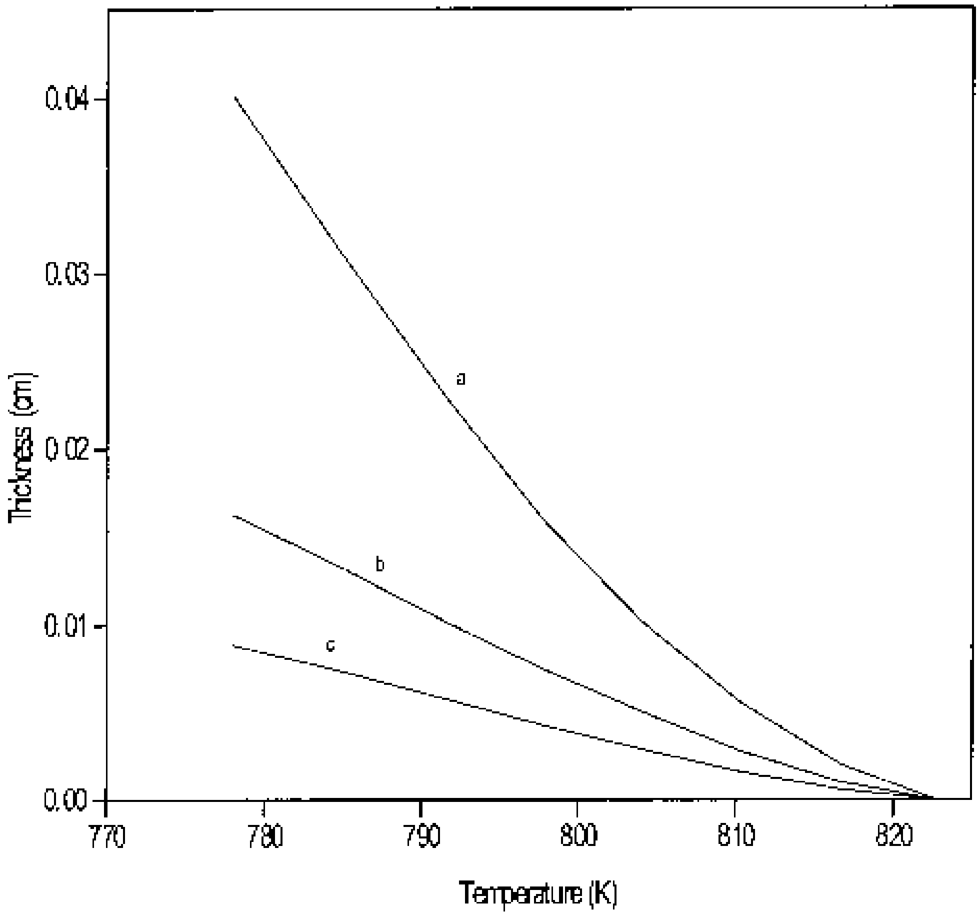

Figure (5.7) : Calculated values of GaSb average layers thickness grown as a function of temperature for different cooling rates of (a) 0.3 K/min (b)1.0 K/min (c) 3 K/min with initial temperature 773 K for equilibrium temperature T_E = 823 K

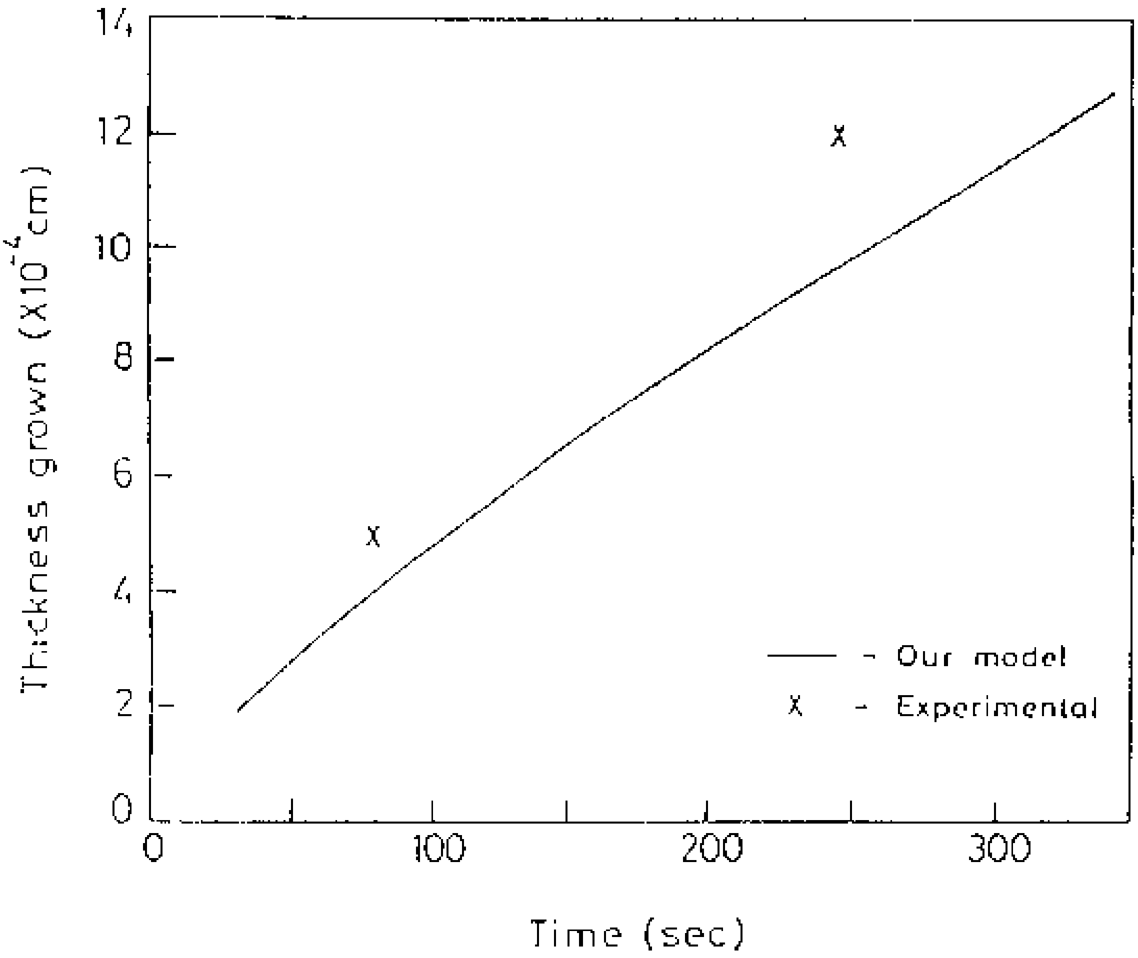

Figure (5.8): Comparison of our theoretical findings with reported experimental results for equilibrium temperature T_L = 823K and at a cooling rate of 0.3 K/min. (——) our model; (×---×) experimental results (Dutta et al 1995)

5.2 Gallium Phosphide (GaP)

In the numerical studies of gallium phosphide (GaP) by liquid phase epitaxy, the value of diffusion coefficient of phosphorus (P) atoms in Ga-rich solution has been used as 2.12×10^{-5} cm^2/sec *(Kao and Eknoyan 1983)* and the equilibrium temperature has been taken as T_l = 1118K. An equation for the equilibrium concentration of phosphorus atoms has been developed by using the solubility data reported in the literature *(Hall 1963)* and by using the equation 4.2 *(Astles 1990)*, as,

$$C_s = 4.58\times10^{22}\exp\left[8.705 - \frac{1.58\times10^4}{T}\right] \qquad (5.3)$$

where T is the substrate temperature in Kelvin at any given instant of time. This equation represents Ga-P liquids line on the Ga-rich side at the temperature range 1000K to 1150K.

In our present work we have constructed the concentration profiles of Phosphorus atoms in the Ga-rich solution in front of the growing crystal interface, calculated the thickness of the layer as a function of time and as function of temperature, the dimensionless concentration parameter is also calculated. Also our theoretical result has been compared with the reported experimental values. Our results are represented in the figures as shown below

The phosphorus dimensionless concentration in the Ga-rich melt at different growth times and a cooling rate of 5 K/min has been shown in Figure 5.13 It has been observed that the dimensionless concentration profiles have been fitted almost perfectly by *(Wilcox 1982)*,

$$\frac{C_0 - C}{C_0 - C_E} = \exp\left[-2.3270647 + 2.1793578\frac{x}{(Dt)^{1/2}} - 1.605883\frac{x^2}{Dt}\right] \tag{5.4}$$

for times up to 20 minutes.

5.2.1 RESULTS AND DISCUSSION

Figures 5.9, 5.10 and 5.11 show the concentration profiles of P atoms in GaP solution for different cooling rates 0.5K/min, 1K/min and 5K/min respectively. It is seen from these figures that the concentration of the P atoms decreases almost linearly. Figure 5.12 shows the comparison between the concentration profiles of P atoms in GaP solution for different cooling rates 5K/min(——) and 0.5K/min(………) respectively. From the figure it can be concluded that the concentration profile is more linear for the lower cooling rate — which means that the melt becomes more homogeneous at lower cooling rates. At higher cooling rates the concentration of P atoms decreases more rapidly near the growing interface, which means that the melt is not homogeneous and that's why lower cooling rate is preferable for growing such a layer thickness.

Figure 5.13 is the representation of the dimensionless concentration profiles of phosphorus atoms at different growth temperatures in the GaP solution at the cooling rate 5 K/min. From the figure, it is seen that the dimensionless concentration parameter can have the values which vary from 0 to 1. From the figures the dimensionless concentration parameter are calculated which are given by the equation 5.4

Figure 5.14 is the plots of thickness of the GaP layer grown versus time for different cooling rates of 0.5K/min, and 1 K/min. From the figure, we can see that the growth is more when the cooling rate is more for a particular growth time.

Figure 5.15 is the plots of thickness of the GaP layer grown versus temperature for different cooling rates of 0.5 K/min, and 1K/min. It can be concluded from these figures that the growth is more when the cooling rate is less for a particular temperature.

Figure 5.16 compares our theoretical calculations on the average thickness of GaP grown with reported experimental and theoretical values when the cooling rate is 1K/min and at the equilibrium temperature $T_E = 1118$. It is observed from the figure that our theoretical findings have shown good agreements with the values.

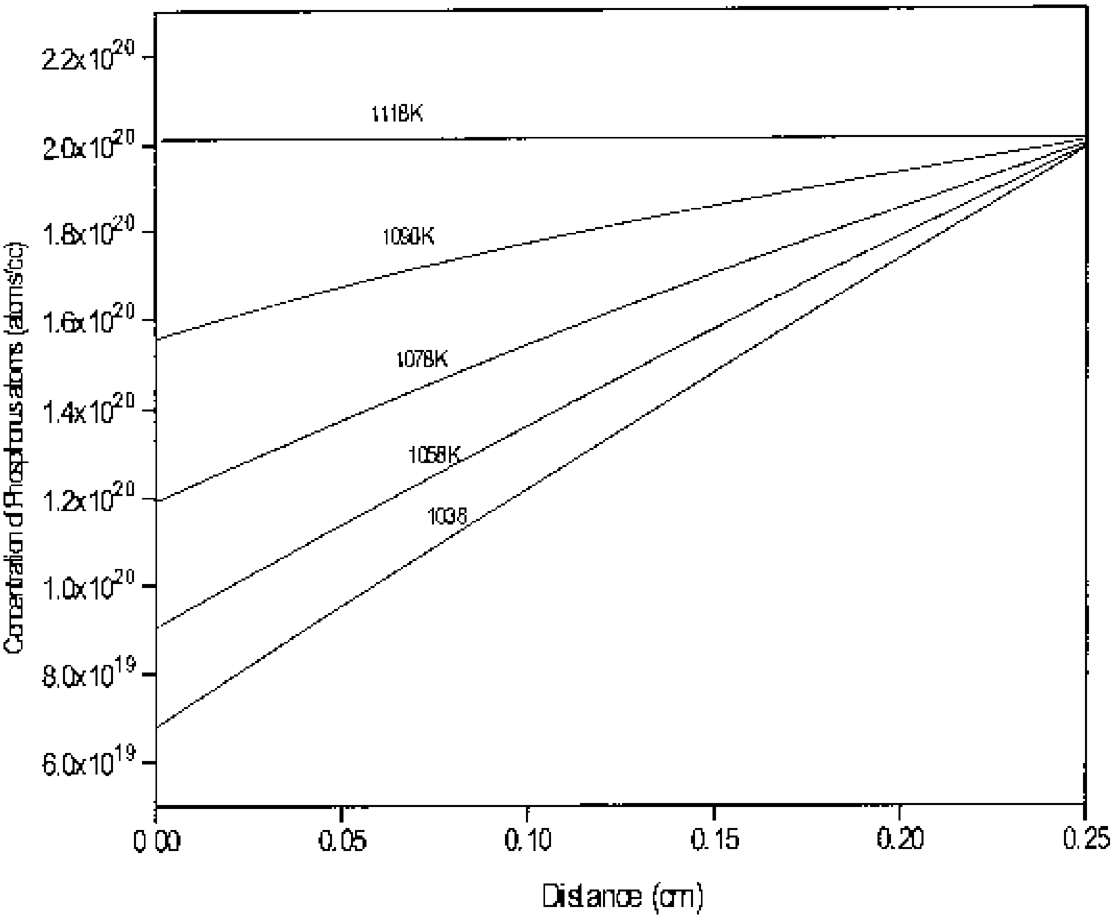

Figure (5.9) : Simulated concentration profiles of phosphorus (P) atoms in front of growing crystal interface for T_E = 1118 K and cooling rate 0.5 K/min

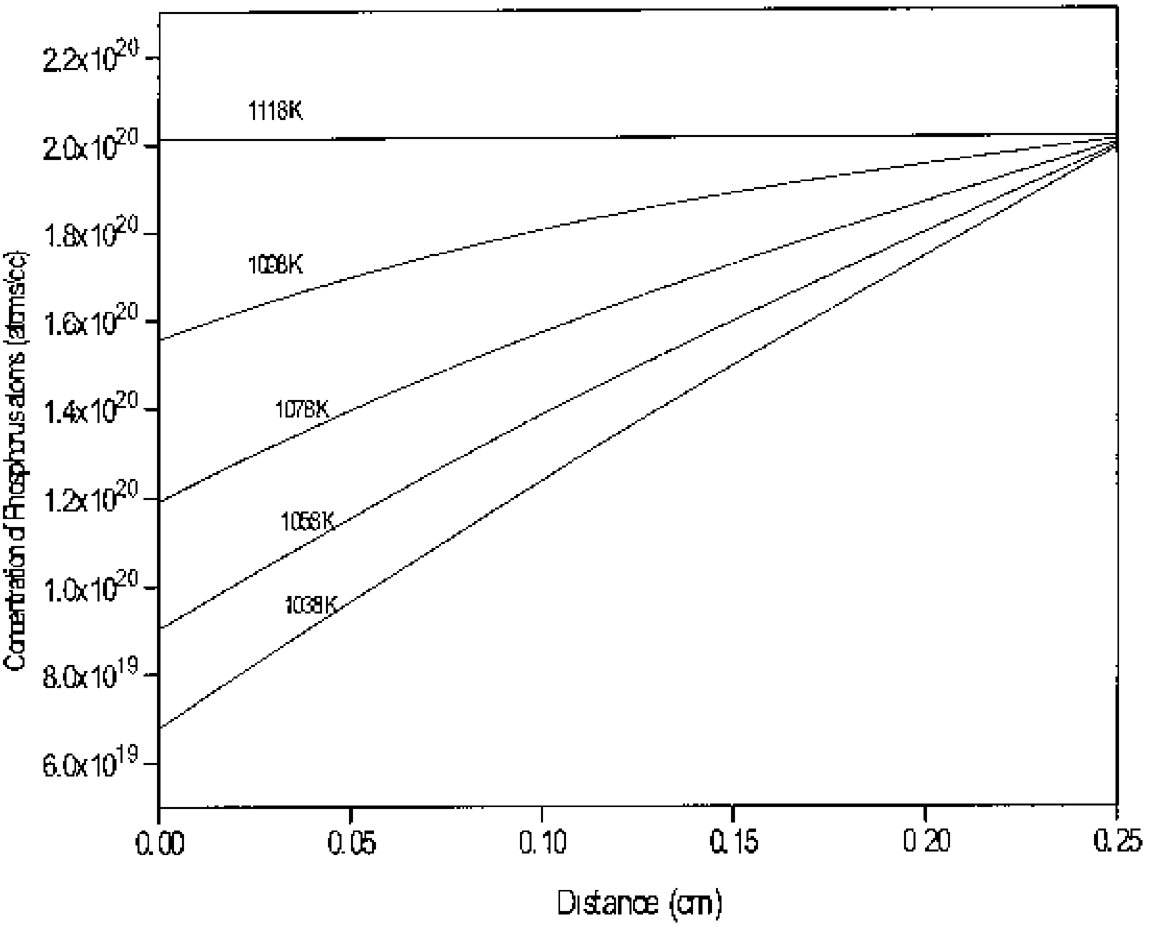

Figure (5.10) : Simulated concentration profiles of phosphorus (P) atoms in front of growing crystal interface for $T_F = 1118$ K and cooling rate 1 K/min

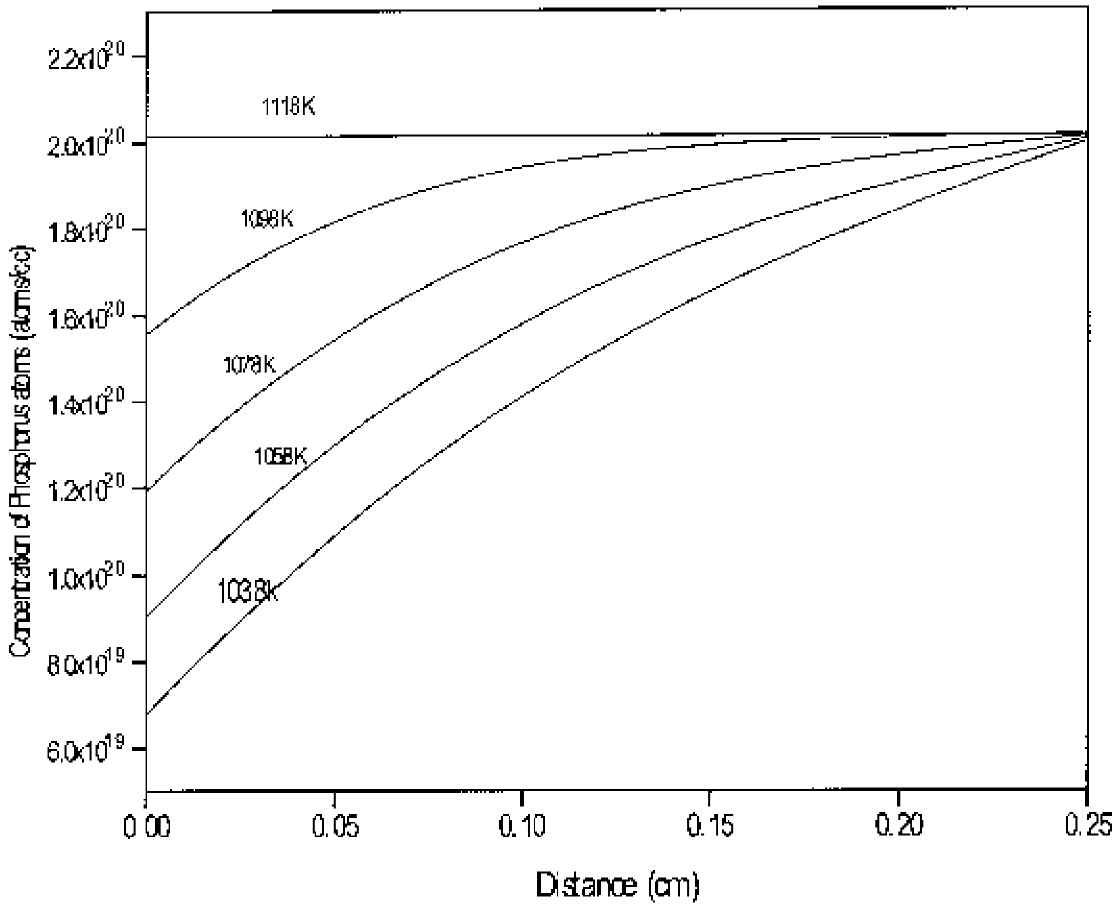

Figure (5.11) : Simulated concentration profiles of phosphorus (P) atoms in front of growing crystal interface for T_E = 1118 K and cooling rate 5 K/min.

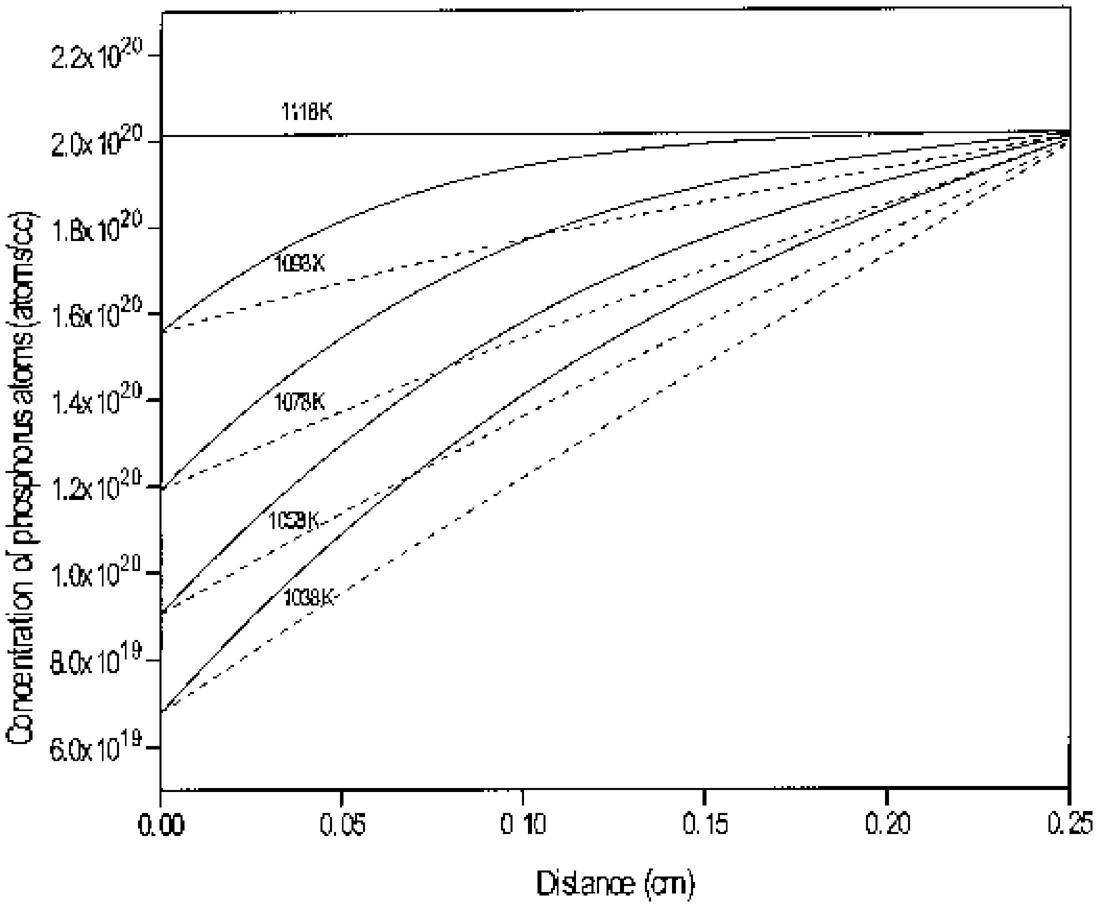

Figure (5.12) : Simulated concentration profiles of phosphorus (P) atoms in front of growing crystal interface for T_E = 1118K and at the cooling rate (a) 5 K/min (—) and (b) 0.5 K/min (.....)

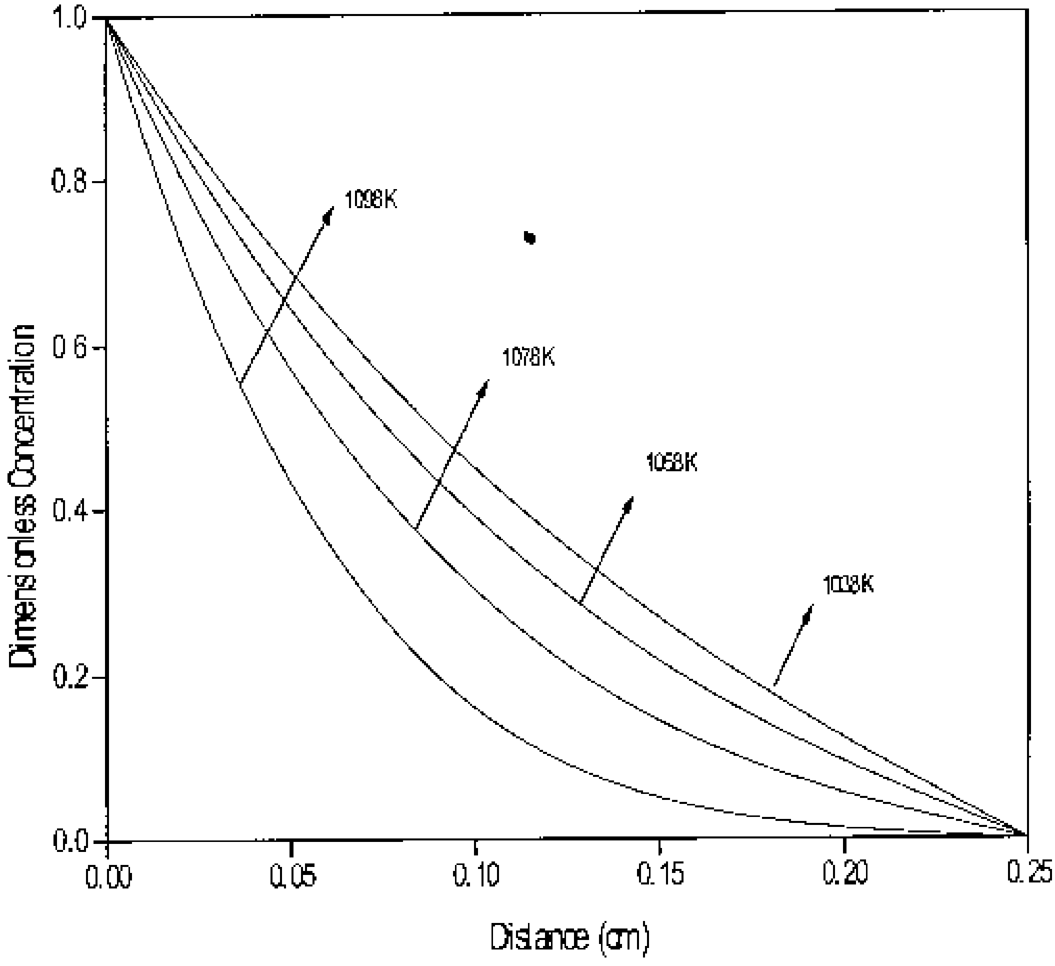

Figure (5.13) :Dimensionless concentration of phosphorus in front of the growing crystal interface as a function of distance at different growth temperatures for TE = 823K and at a cooling rate of 3K/min

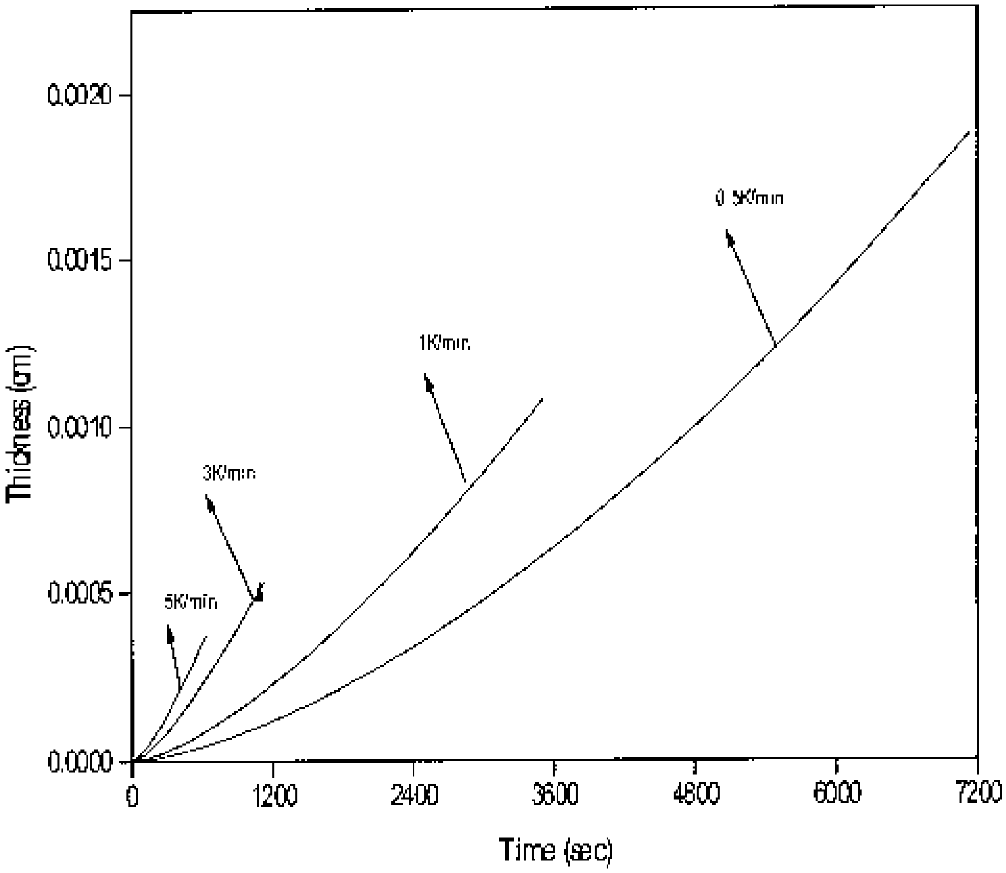

Figure: (5.14) Calculated values of GaP average layers thickness grown as a function of time for different cooling rates of (a) 5 K/min and (b) 3 K/min (c) 1 K/min and (d)0.5 K/min with for equilibrium temperature
T_E = 1118 K

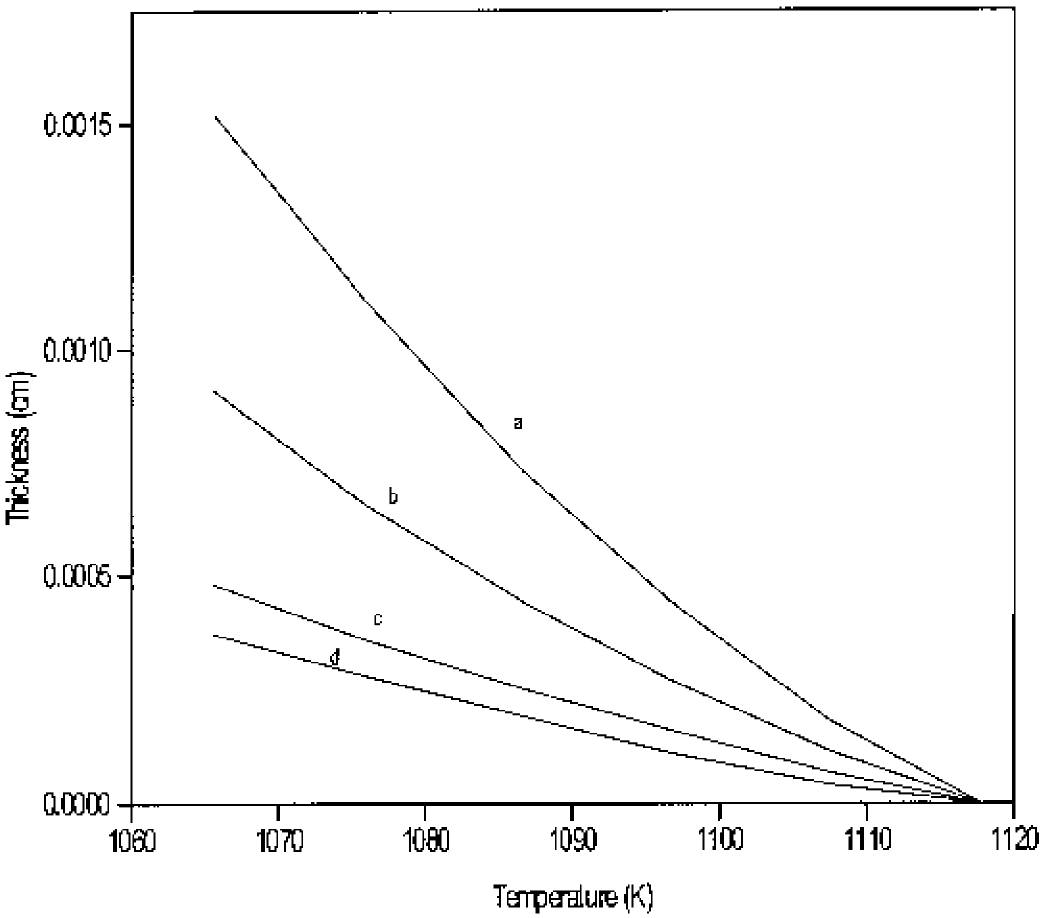

Figure (5.15): Calculated values of GaP average layers thickness grown as a function of temperature for different cooling rates of (a) 0.5 K/min (b)1.0K/min (c) 3 K/min ansd (d) 5 K/min for equilibrium temperature $T_E = 1118$ K

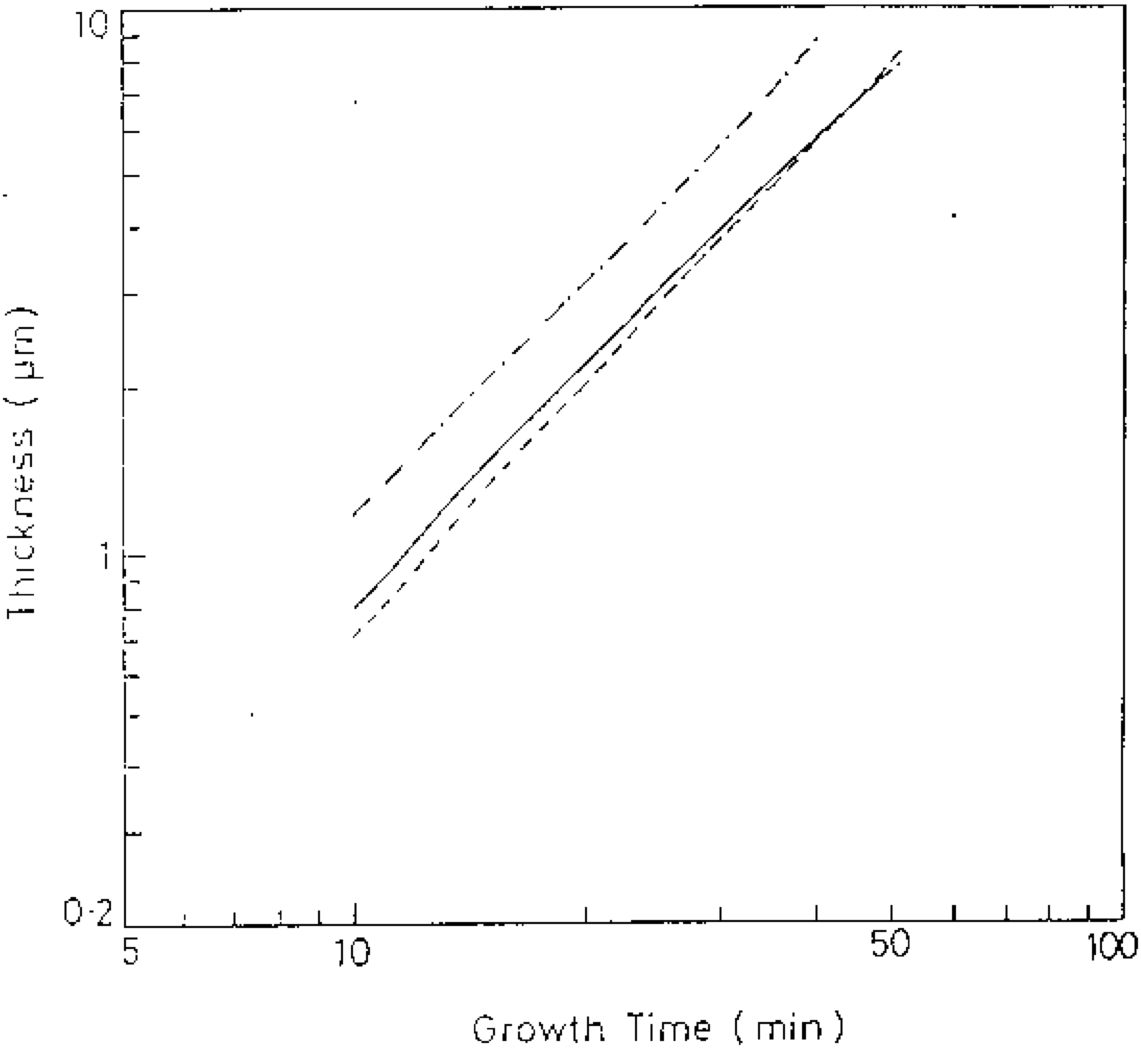

Figure (5.16): Comparison of our theoretical findings with reported experimentally reported values (for equilibrium temperature T_E = 1118K and at a cooling rate of 1 K/min. (----) calculated values with a model equation for equilibrium cooling (Kao and Eknoyan 1983); (- . . - . -) experimentally reported values (Kao and Eknoyan 1983); and (——) the present work.

5.3 CONCLUSIONS

One dimensional numerical simulation technique has been employed for the study of liquid phase epitaxial growth of binary III-V compound semiconductors (GaSb and GaP). The concentration profiles have been constructed along the distance perpendicular to the substrate in front of the growing crystal interface. The concentration profiles studies have shown that concentrations of the Sb and P atoms decreases almost linearly and the concentration profile is more linear for the lower cooling rate — which means that the melt becomes more homogeneous at lower cooling rates. At higher cooling rates the concentration of Sb and P atoms decrease more rapidly near the growing interface, which means that the melt is not homogeneous; and that's why lower cooling rate is preferable for growing such a layer thickness. The thickness of the layer grown have been determined as a function of time and temperature respectively and it is concluded that the growth is more when the cooling rate is more for a particular growth time, whereas the growth is more when the cooling rate is less for a particular temperature. Our theoretical calculations on the average thickness of GaSb and GaP grown have been compared with the reported experimental and theoretical values and it is observed that our theoretical findings have shown good agreements with the values.

REFERENCES

Adams G.W, Schmitt J.L and Zalabsky R.A (1984), 'The homogeneous nucleation of nonane' , J. Chem. Phys., Vol.81, pp 5074-5078.

Antolini A, Bradley P.J., Cacciatore, Campi D., Gastaldi L.,. Genova F., Iori M., Lamberti C., and Rigo C. (1992), 'Investigations on the interface abruptness in CBE grown InGaAs/InP QW structures', J Electron matter., Vol.21, pp 233-238.

Astles M.G (1990) ' Liquid Phase Epitaxial Growth of III-V Compound Semiconductor Materials and their Device Applications', Adam Hilger, England.

Bauser E., Frik M., Loechner K.S., Schmidt L. and Ulrich R (1974), 'Substrate orientation and surface morphology of GaAs liquid phase epitaxial layers', J. Cryst. Growth, Vol 27, pp 148-153.

Benz K.W. and Bauser E. (1980), 'Growth of binary III-V semiconductors from metallic solutions', Crystals, Vol. 3, Berlin, Heidelberg, pp. 1-48.

Bolkhovityanove Yu. B. (1995), 'Elastically strained InGaAsP films grown by LPE and conception of stress-induced supercooling' Phys. Stat. soli. (a), Vol. 151, pp. 363-370.

Cao D.C., Chen C.H., Fry K.L., Reihlen E.H., and Stringfellow G.B. (1989) ' Strained layer super-lattices for reduction of dislocation density in $GaAs_{1-x}P_x$ on

GaAs by organometalic vapour phase epitaxy' , J. Appl. Phys., Vol 65, pp 2451-2456.

Casey, Jr. H.C. and Panish M.B. (1978), 'Heterostructure Lasers, Part B, Academic Press, New York, pp 71-155.

Chen C.W. and Wu M.C (1995) 'Liquid Phase Epitaxial Growth and Characterization of InGaAsP layers grown on GaAsP substrates for applications to orange light-emitting diodes', J. Appl. Phys. Vol. 77, pp 905-909.

Chernov A.A (1984), 'Modern crystallography III', Springer Verlag, Berlin, Germany, pp 48-103.

Crossley I. and Small M.B. (1971), ' Computer Simulation of Liquid Phase Epitaxy of GaAs in Ga solution', J. Cryst. Growth, Vol. 11, pp. 157-165.

Crossley I. and Small M.B. (1972), ' The application of numerical method to stimulate the Liquid Phase Epitaxial Growth of $Ga_{1-x}Al_xAs$ from an unstirred solution,' J. Cryst. Growth, Vol.15, pp 268-274.

Cser J., Katz J. and Hwang D.M. (1987), 'Liquid phase Epitaxy growth of GaAs/GaAlAs multi-quantum well structures', J. Cryst. Growth. Vol.85, pp 341-344.

Dizaji H.R and Dhanasekaran R. (1996) 'A theoretical approach to the $In_{1-x}Ga_xP$ LPE growth by computer simulation technique', Phys. Stat. Soli. (a) Vol. 156, pp 71-79.

Dizaji H.R and Dhanasekaran R. (1996) 'Studies on the concentration profiles and growth rate of GaP by liquid phase epitaxy', J. Matter. .in Electron., Vol. 7, pp. 107-110

Dobosz D. and Zytkiewicz Z.R (1991), ' Diffusion limited LPE growth of $Ga_xIn_{1-x}P$ on (100) GaAs', Phys. Stat. Soli. (a) Vol. 128, pp 123-127.

Dutta N.K., Wessel T., Olsson N.A., Logan R.A., Koszi L.A and Yen R. (1985), 'Fabrication and performance characteristics of 1.55μm InGaAsdP on (100)-InP for 1.1 5-1.31 μm spectral region', Appl. Phys. Lwett., Vol. 46, pp. 525-527.

Dutta P.S., Koteswara Rao K.S.R., Bhat H.L., Gopalakrishna Naik K., and Kumar V. (1995), 'Surface morphology, electrical and optical properties of Gallium Antimonide layer grown by liquid phase epitaxy', J.Cryst. Growth, Vol.152, pp 14-20

Feng M., Cook L.W., Tashima M.M and Stillman G.E (1980), 'Lattice constant, bands gap, thickness and surface morphology of InGaAsP-InP layers grown by step-cooling, equilibrium-cooling, super-cooling and two-phase cooling growth technique', J Electron. Mater., Vol. 9, pp. 241-281.

Godota M., Sugimoto H., Nomura Y., Isu T., Nunoshita M. and Maruno S. (1994), 'Selectivity embedded growth by chemical beam Epitaxy for the fabrication of InGaAs/InP double-heterostructure lasers', J.Cryst. Growth, Vol.140, pp 277-281.

Greene P.D., Prins A.D., Dunstan D.J. and Adams A.R. (1987), 'Indium phosphide and quaternary doping superlattices grown by liquid phase epitaxy', Electron. Lett. Vol.23, pp 324-325.

Hall R.N. (1963), 'Solubility of III-V Compound Semiconductors in column III Liquids', J. Electrochem. Soc., Vol. 110, pp., 385-388.

Haung A. (1988), 'Comparison of T_0-values of bulk and quantum-well semiconductors lasers', Electron. Lett. Vol 24, pp 1442-1443.

Horikoshi L (1986), 'The Physics and fabrication of Micro-structures', Les Houches.

Hossain MD. M., Dhanasekaran R. and Ramasamy P. (1999) 'Concentration profile surfaces and Contour Studies of GaSb by LPE using Simulation Technique', Mater. Sci. and Engg. B., Vol. 64, pp 161.

Hossain Md. Mostak (1999a), 'Theoretical Investigations on the Growth Kinetics of Compound Semiconductors' Ph.D.Thesis, Alagappa University, Karaikudi, India.

Hsieh J.J (1974), 'Thickness and surface morphology of GaAs LPE layers grown by super-cooling, step-cooling, equilibrium-cooling, and two phase solution techniques', J. Cryst. Growth, Vol. 27, pp. 49-61.

Hsieh J.J., Rossi J.A and Donnelly J.P (1976), 'Room temperature cw operation of GaInAsP/InP double hetero-structure diode lasers emitting at 1.1μm', Appl. Phys.Lett., Vol. 28, pp. 709-711.

Hugesd R.C., Zipperian T.E., Dawson L.R., Biefeld R.M , Walko R.J. and Dvorack M.A (1991), 'Gallium phosphide junctions with low leakage for energy conversion and near ultraviolet detectors', J. Appl. Phys., Vol. 69, pp. 6500-6505.

Kanal H., Kimura M., Dost. S., Tanaka A. and Sukegawa T. (1997), 'Gravity effect on dissolution and growth of GaSb by liquid phase epitaxy', J.Cryst. Growth, Vol. 174, pp. 226-229.

Kao Y.C. and Eknoyan O. (1983), 'Thickness of GaP liquid phase epitaxial layers grown by step-cooling, equilibrium-cooling, ramp-cooling methods', J. Appl. Phys., Vol. 54, pp. 1865-1867.

Kimura M., Djilali N and Dost. S (1994), 'Convective transport and interface kinetics in liquid phase epitaxial', J.Cryst. Growth, Vol. 143, pp. 334-348.

Konig U. and Jorke H. (1985), 'Periodic doping and heterostructure multilayers of $Ga_xIn_{1-x}As_yP_{1-y}$: LPE growth and characterization', J.Cryst. Growth, Vol. 73, pp. 515-522.

Kressel H. and Nelson H.(1973), 'Properties and applications on III-V compound films deposited by Liquid Phase Epitaxy', Eds By Hass G., Francombe M.H. and Holfman R.W., Physics of Thin films , Academic press, , New York, Vol.7, pp. 115-256

Kuphal E. (1994), 'Liquid Phase Epitaxy of III-V compounds', Current Topics in Cryst. Growth Res., Vol. 1, pp. 47-82.

Leheny R.F., Nahony R.E. and Pollack M.A. (1979), ' $In_{0.53}Ga_{0.47}As$ pin photodiodes for long wavelength fibre optic systems', Electron. Lett. Vol.15, pp 713-715.

Li S.H., Buchan N.I., Larson C.A., and Stringfellow G.B.(1989) 'MOVPE growth mechanism for GaP using tertiarybutylphosphine and trimethylgallium', J.Cryst. Growth, Vol. 96, pp. 906-914.

Ludowise M.J (1985) 'Metalorganic chemical vapour phase deposition of III-V semiconductors', J. Appl. Phys., Vol. 58, pp. R31-R55.

Mao Y. and Krier A. (1993), 'Liquid phase epitaxial growth and photoluminescence of InAsSb grown on GaSb substrates from antimony solution', J.Cryst. Growth, Vol. 133, pp. 108-116.

Michael B.B (1965), 'Nucleation process' in 'Energetic in Metallurgical phenomena', Vol. 1, pp. 111-160.

Moon R.L (1974), 'The influence of growth solution thickness on the LPE layer thickness and constitutional super-cooling requirement for diffusion limited growth', J.Cryst. Growth, Vol. 27, pp. 62-69.

Nahony R.E. and Pollack M.A., Beebe E.D, DeWinter J.C and Dixon R.W (1976), ' Continous operation of 1.0μm wavelength $GaAs_{1-x}Sb_x/Al_yGa_{1-y}As_{1-x}Sb_x$ double heterostructure injection lasers at room temperature', Appl. Phys. Lett, Vol. 28, pp. 19-21.

Nelson H. (1963), 'Epitaxial growth from the liquid state and its application to the fabrication of tunnel and laser diodes', RCA Rev., Vol.24, pp. 603-615.

Ohki Y., Shimumura K., Kikugawa T., Ravikumar K.G., Izumi A., Arai S. and Suemastu Y. (1987), 'Electric field-induced absorption in GaInAsP/InP MQW structures grown by LPE', Jpn. J. Appl. Phys., Vol. 26, pp. L579-L581.

Pan N., Tabatabaie N. ansd Stillman G.E (1986), 'LPE diffusion limited growth of InGaAs', J.Cryst. Growth, Vol. 78, pp. 97-104

Panish M.B., and Ilegems M. (1972), 'Phase equilibria in ternary III-V systems', Ed. Reiss H. and Mc Caldin J.O., Progr. In Solid-State Chem Pergamon, Oxford, Vol.7, pp 39-83.

Panish M.B., Hayashi I. and Sumski S. (1970), 'Double heterostructure injection lasers with room temperature thresholds as low as 2300 A/cm^2', Appl. Phys.Lett, Vol. 16, pp. 326-328.

Richard Haberman (1987), 'Elementary Applied Partial Differential Equations' 2nd Edition, New Jersey, pp. 478-518.

Sukegawa T., Kimura M.. Tanaka A. (1988), 'Gravity effect on dissolution and growth of silicon in the In-Si system' J.Cryst. Growth, Vol. 92, pp. 46-52.

Sukegawa T., Hiraguchi T , Tanaka A., and Hagina M. (1978), 'Highly efficient p-GaSb/n-$Ga_{1-x}Al_xSb$ photodiodes', Appl. Phys.Lett, Vol. 32, pp. 376-378.

Stringfellow G.B. (1982), 'Epitaxy', Rep. Prog. Phys., Vol. 45, pp. 469-525.

Stringfellow G.B (1989), 'Organometalic vapour phase Epitaxy : Theory and practice', Academic press, London.

Sun Y.M., Jiang W.J. and Wu M.C. (1996), 'Optical properties of GaSb alloys and photodiodes grown by liquid phase epitaxy', J. Appl. Phys., Vol. 80, pp. 1731-1734.

Traeger G., Kuphal E. Zschauer K.H (1988), 'Diffusion limited LPE growth of mixed crystals : Application to $In_{1-x}Ga_xAs$ on InP', J.Cryst. Growth, Vol. 88, pp. 205-214.

Vaya P.R. (1989), 'Introduction to Semiconductor Lasers', I.I.T., Madras, India, pp. 46-56.

Wieder H.H., Clawson A.R. and McWilliams G.E (1977) $In_xGa_{1-x}As_yP_{1-y}/InP$ heterojunction photodiodes', Appl. Phys.Lett, Vol. 31, pp. 468-470.

Wilcox W.R. (1982), 'Computer simulation of growth of thick layers from solution of finite solute concentration without convection', J.Cryst. Growth, Vol. 56, pp. 690-698.

Yuh-Maoh Sun, Meng-Chyi Wu, Yuan-Tzu Ting (1996), 'Low concentration GaSb grown from Sb-rich solution by liquid phase epitaxy in the presence of erbium', J.Cryst. Growth, Vol. 158, pp. 449-454.

Zhovnir G.I. and Zakhlenyuk N.A. (1985), 'Theory of equilibrium liquid phase electro-epitaxy of $A_{1-x}B_xC$ solid solutions', Sov. Phys. Tech. Phys., Vol.30, pp. 538-539.

Zhuravlev K.S., Shamirzaev T.S., Yakusheva N.A. and Petrenko I.P. (1998), ' A new recombination center in heavily doped GaAs : Zn grown by liqnid phase epitaxy'Semiconductors, Vol. 32. pp. 1057-1061.