Chapter 3

Liquid Phase Epitaxy (LPE) Growth of GaAlAs/GaAs

3.1 Introduction

Liquid phase epitaxy is the growth technique of an oriented crystalline layer of material from a saturated or supersaturated liquid solution onto a crystalline substrate. This technique is extensively used to grow single crystal layers of semiconductor such as GaAs, GaAlAs, InP and InGaAsP for numerous applications. A variety of optoelectronic and microwave devices have been successfully fabricated by this method.

For material systems where it can be used, LPE has the advantage of yielding accurately controlled composition and thickness by varying only a few growth parameters, i.e. substrate orientation, solution composition, temperature, cooling rate, and growth time. When each of these paremeters is precisely controlled, highly reproducible layers can be obtained. LPE may produce epitaxy with lower dislocation densities than the substrate on which it is grown. Most of the reliable laser diodes and ligth-emitting diode with high quantum efficiency have been produced by LPE.

The purpose of this chapter is to present a general principle of LPE technique for GaAlAs/GaAs, the growth kinetic according to the four technological processes such as uniform cooling, step cooling, supercooling, and two-phase solution cooling.

3.2 Experimental apparatus and procedure

Growing LPE layers of controlled thickness and composition requires the use of experimental apparatus that permits a growth solution of the desired composition to be placed in contact with the substrate for a well-defined period under controlled temperature conditions. The solution supersaturation necessary for deposition is generally achieved by reducing the temperature, since the solubility of the solute in the solution decreases with decreasing temperature [19].

A system for multilayer LPE growth of GaAs or GaAlAs and the alloys by the sliding technique is shown schematically in Fig.3.1. The principal components are a graphite multibin slider boat, a fused silica growth tube to provide a protective atmosphere, and a horizontal resistance furnace that can be kept hot at all times and is mounted on the rails so that it can be moved to facilitate rapid heating and cooling of the boat [20].

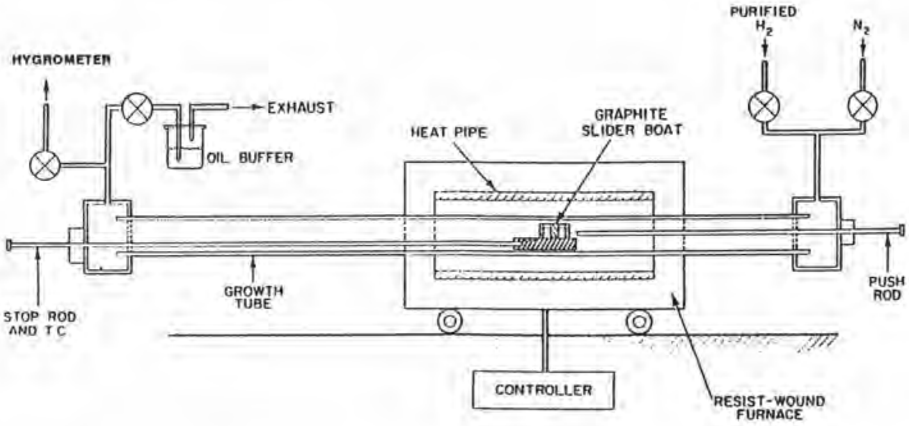

Fig.3.1 Horizontal LPE system for multilayer growth by the sliding technique.

The boat consists of a fixed upper member with bins containing the various growth solutions and a sliding lower member containing the substrate in the shallow depression with the lower member in its initial position, as shown in Fig.3.1. The solutions are in contact with the surface of the substrate holder. A fused silica push rod is used to slide the lower member to position where the appropriate bin is located above the substrate. Contact is terminated by pushing to a position where the bin is no longer above the substrate. The process is repeated for each layer.

In a practical growth run, after the boat is loaded with the substrate and the growth solutions, it is placed in the tube. It initially remains outside the furnace. With the boat at room temperature, the tube is flushed with flowing N_2. Checking for leaks is done by monitoring the humidity in the tube by a moisture detector. In this system the moisture in the tube is less than 0.1 ppm. The tube is then backfilled with Pd-purified H_2. The preheated furnace is moved into position for heating the boat. It is ready for heating. After the boat reaches the operating temperature, the desired LPE layers are grown, using procedures discussed in the section 3.3. The furnace is then moved away. The boat is cooled to the room temperature. The H_2 flow is replaced with N_2 flow, and finally the boat is removed from the tube and unloaded.

The furnace temperature profile for growth by sliding technique must be as flat as possible. In order to simplify the control of the growth conditions and to obtain flat profile, three-zone furnace are used. Such furnace requires three separate temperature controllers.

Fig.3.2 is a photograph of a multibin slider boat used for GaAs and GaAlAs growth [21]. The separate parts are shown in Fig.3.2 a) as well as the assembled unit in Fig.3.2 b). The substrate holder slider has two depressions for substrate and nine depressions for GaAs wafer source. The tapper slider is used for removing the saturation wafer source after equilibrium by means of a lateral slider and setting substrate to growth position. The main base consists of two parts that are held together by six screws. Lower part is base supporter. Upper part has 11 bins. The biggest bin on the right side is the space for GaAs cover and graphite cover. The 9 small bins in the middle part are solution containers for growth solution, and the left side bin is a bin for graphite wiper to insure that the substrate surface is wiped completely free of growth solution when growth is terminated by moving the slider assembly. The graphite cover is for protecting the solution from the diffusion problem of Te and/or Zn vapor that evaporated from the other solutions during growth run and smoothing out the motion of the melts.

a)

b)

Fig.3.2 a) The disassembled graphite boat apparatus
b) The assembled graphite boat.

3.3 Principle of LPE Growth

The basis for the LPE growth process is the fact that the solubility of a dilute constituent in a liquid solvent decrease with decreasing temperature. Hence the cooling of an initially saturated solution in contact with a single-crystal substrate can cause epitaxial deposition of a thin solid layer on the substrate. The growth thickness depends on growth parameters for four different techniques, which they were described as the equilibrium-cooling, step-cooling, supercooling and two-phase solution techniques. Fig.3.3 is refered to describe the procedures of these techniques. A schematic plots shows the temperature during LPE growth as a function of time. At the beginning of each run, with the substrate and solution not in contact, the system is heated to a temperature higher than the liquidus temperature (T_1) that corresponds to the initial composition of the solution, and is then cooled down gradually. For each technique, an arrow indicates the time and temperature at which the substrate and solution are in contact [20].

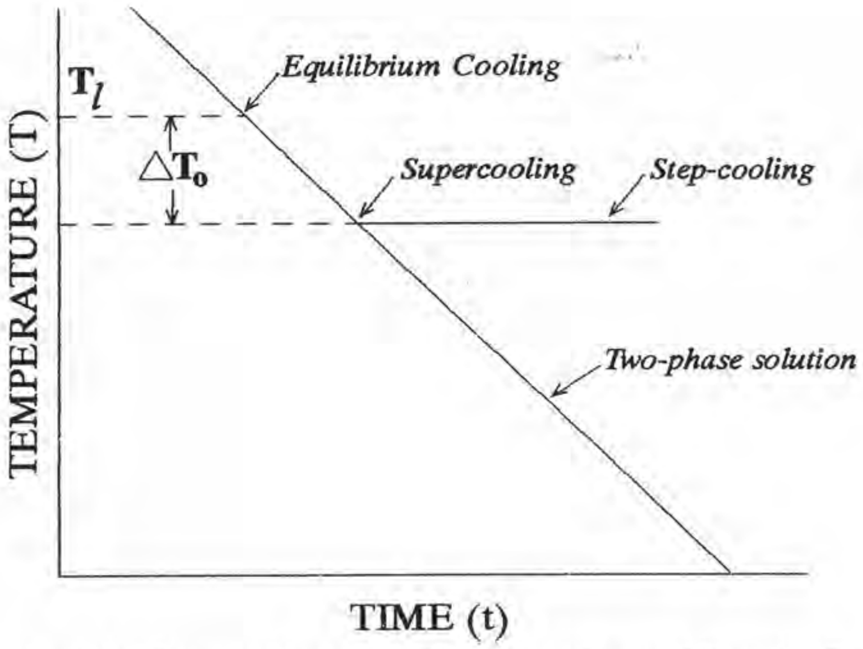

Fig.3.3 Solution cooling procedure for four differnt LPE growth techniques. The arrows indicate the times at which the growth solution is initially placed in contact with the substrate.

3.3.1 The Equilibrium-Cooling Technique

The equilibrium-cooling technique uses a constant rate throughtout the run. The substrate and solution are placed in contact when the temperature reaches T_1 (saturation temperature), so that they are in equilibrium at the moment of contact. At the beginning of the run the temperature is kept constant and the solution is placed in contact with source wafer. After the solution reaches equilibrium, the source is replaced by the substrate and cooling begins.

The growth of the equilibrium-cooling technique for GaAs follows the following expression

$$d = (2/C_s m)(D_{As}/\pi)(2/3)Rt^{3/2} \quad (1)$$

where d is the growth layer thickness, C_s is expressed as atoms of solute per unit volume of growth solid, m is given in degrees per atom of solute per unit volume of solution, D_{As} is the diffusivity of As in Ga-rich solution, R is the cooling rate, and t is the growth time.

3.3.2 The Step-Cooling Technique

In the step-cooling technique, the substrate and solution are initially cooled at a constant rate to a temperature that is below T_1, but not low enough for spontaneous precipitation, and held at this temperature. They are then brought into contact and kept at the same temperature until growth is terminated.

The growth of the step-cooling technique gives the following expression

$$d = (2/C_s m)(D_{As}/\pi)^{1/2}\Delta Tt^{1/2} \quad (2)$$

where T is the degree of supersaturation of the melt, $\Delta T = T_1 - T_o$, T_1 is melt equilibrium temperature, and T_o is the temperature at the beginning of the growth.

3.3.3 The Supercooling Technique

The supercooling technique, like the step-cooling technique, the substrate and solution are cooled at a constant rate to a temperture below T_1 without spontaneous precipitation, then brought into contact. In this case, however, cooling is continued without interruption at the same rate until growth is terminated.

The growth of the supercooling technique gives the following expression

$$d = (2/C_s m)(D_{As}/\pi)^{1/2}(\Delta T t^{1/2} + (2/3)R t^{3/2}) \qquad (3)$$

The supercooling technique is regarded as the combination of equilibrium-cooling technique and step-cooling technique, eq. (3) was obtained from eqs. (1) and (2) by applying the theorem that for a linear differential equation, the sum of two solution is itself a solution.

The advantage of this technique is that layers grown by this method tend to have improved surface morphology, since supercooling of the solution at the time of contact with the substrate provides a driving force that makes nucleation less sensitive to inhomogeneities in the condition of the the substrate surface and therefore insures simultaneous nucleation over the entire surface [19].

3.3.4 The Two-Phase-Solution Technique

The two-phase-solution technique was introduced in the expection that the presence of the precipitates in the growth solution would insure that the soltuion was saturated with solute at the time of its initial contact with substrate. In this case the method could be regarded as a variation of the equilibrium-cooling technique, but with the thickness of the layer grown on the substrate reduced by simultaneous deposition on the precipitates. Therefore no theoretical expression could be derived for the layer thickness, but the equation of equilibrium cooling placing an upper limit on the thickness as a function of the growth time. In a modified technique called the two-phase-solution technique, which has been applied to the growth, a source crytal is placed on the surface of the growth solution. The layers of reproducible thickness can be grown by this technique.

3.4 Phase Diagram of GaAs and GaAlAs

In this section, the liquidus data relevant to the LPE growth of GaAs, as well as both liquidus and solidus data for GaAlAs alloys are described. A single composition-temperature of GaAs is shown in Fig.3.4. For ternary solution system of GaAlAs, the liquidus relationship is represented by a series of isotherms. Each of which gives the concentration of the two minor constituents in the saturated solution at a particular temperature. The liquidus isotherms for Ga-rich solutions of GaAlAs sysytem are shown in Fig.3.5. The solidus isotherms of GaAlAs system are shown in Fig.3.6.

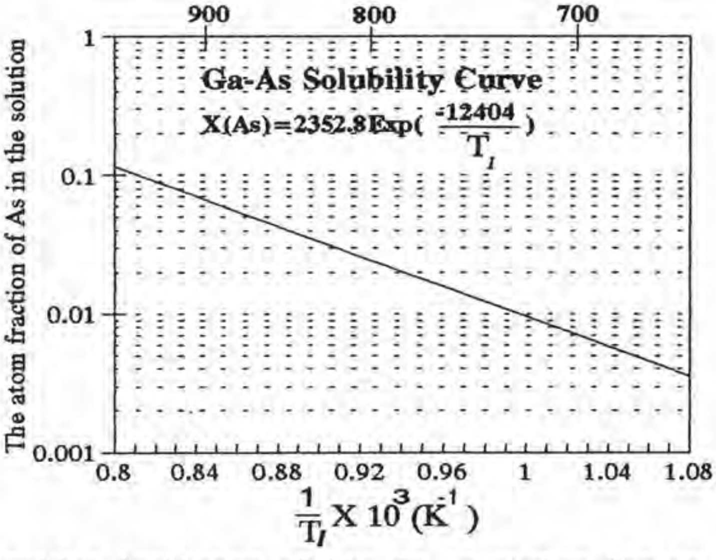

Fig.3.4 Liquidus isotherms of the Ga-As system for Ga-rich solution.

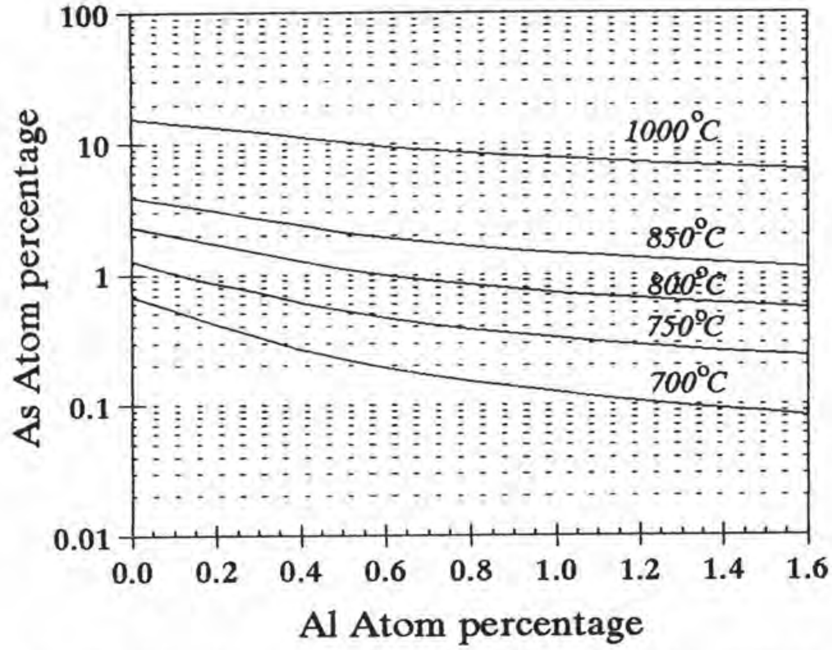

Fig.3.5 Liquidus isotherms of the Ga-Al-As system for Ga-rich solution.

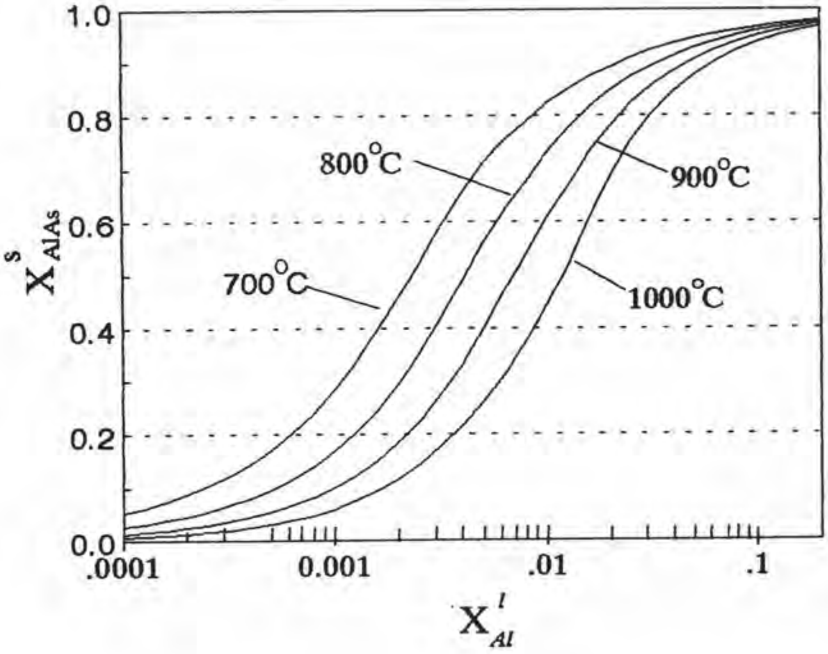

Fig.3.6 Solidus isotherms of the Ga-Al-As system for Ga-rich solution.

The growth of GaAlAs system gives the following expressions

The equilibrium-cooling technique

$$d=(2/3)KRt^{3/2} \tag{4}$$

The step-cooling technique

$$d=K\Delta Tt^{1/2} \tag{5}$$

The supercooling technique

$$d=K(\Delta Tt^{1/2}+(2/3)Rt^{3/2}) \tag{6}$$

For all three cases [22]

$$K = \frac{2C^{l}}{\sqrt{\pi}}\left[\sum_{i}\frac{m_{i}}{\sqrt{D_{i}}}\left(C_{i}^{s}-C_{i}^{l}\frac{C^{s}}{C^{l}}\right)\right]^{-1} \tag{7}$$

where

$$m = \left(\frac{\delta T}{\delta X_{j}}\right)_{X_{j}=C^{l}} \tag{8}$$

corresponds to the slope of the liquidus curve, obtained by solving the system of the graph in Fig. 3.4. Index i corresponds to Al and As.

3.5 Summary

This chapter has distinguished four methods of LPE growth, i.e. the equilibrium-cooling, the step-cooling, the supercooling, and two-phase solution. For the the first three methods, simple equations relating layer thickness to growth time have been described for semi-infinite growth solutions by assuming that the growth rate is diffusion-limited. The solution and substrate are in equilibrium at the interface, and the diffusion coefficient and the slope of the liquidus curve remain constant during a particular growth run.

The supercooling and two-phase solution technique in which a single crystal source is placed on the surface of the growth solution should be of considerable practical value for the growth of GaAs-GaAlAs lasers because it yields very smooth, flat layers of reproducible thickness.