CHAPTER III

RESEARCH METHODOLOGY

3.1 General

Upon completion of this master's degree project, thorough planning and scheduling have been organized on the methodology and research sequence to ensure a smooth running of the research program from literature review, experimental data collection, discussion and validation of result and conclusion.

3.2 Literature Review

Literature review involves a thorough search and investigation of solar cells related issues through many different sources such as text books, articles, journals, international conference papers. Additionally, there is also searching and browsing through internet web pages, internet websites, online library, online articles and journals to seek complementary information. The aim of literature review is to gather important information related to the topic and to deepen the proper understanding of the knowledge and competencies of heterojunction solar cells characterization.

3.3 Experimental Data Correction

Not only literature review on the solar cell basic theory but also the experimental study on heterojunction solar cells is needed to gain practical information.

The technologies and equipment utilized to gather the useful practical information are Liquid Phase Epitaxy (LPE), Molecular Beam Epitaxy (MBE), Photoluminescence Measurement, Vacuum Evaporation, I-V curve Measurement, and Spectral Response Measurement Machine, etc. The description of LPE and MBE technologies, and also photoluminescence will be provided.

3.3.1 Liquid Phase Epitaxy (LPE)

Since its invention by Nelson in 1963 **[13]** Liquid Phase Epitaxy (LPE) has proved to be a versatile, flexible method to grow thin layer of III-V, II-VI and IV-VI compound for material investigations and device application. Many"first" of electronic devices were based on LPE structure. One important example was the GaAs/AlGaAs double-heterostructure (DH) laser diode continuous-wave (CW) lasing at the room temperature **[14, 15]**. The LPE technique has many advantages, there are

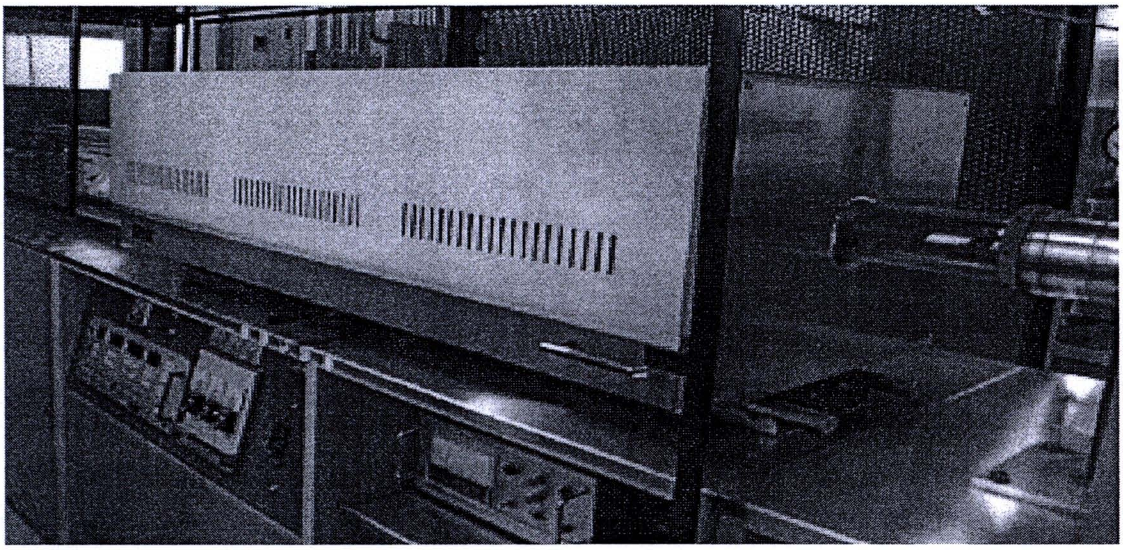
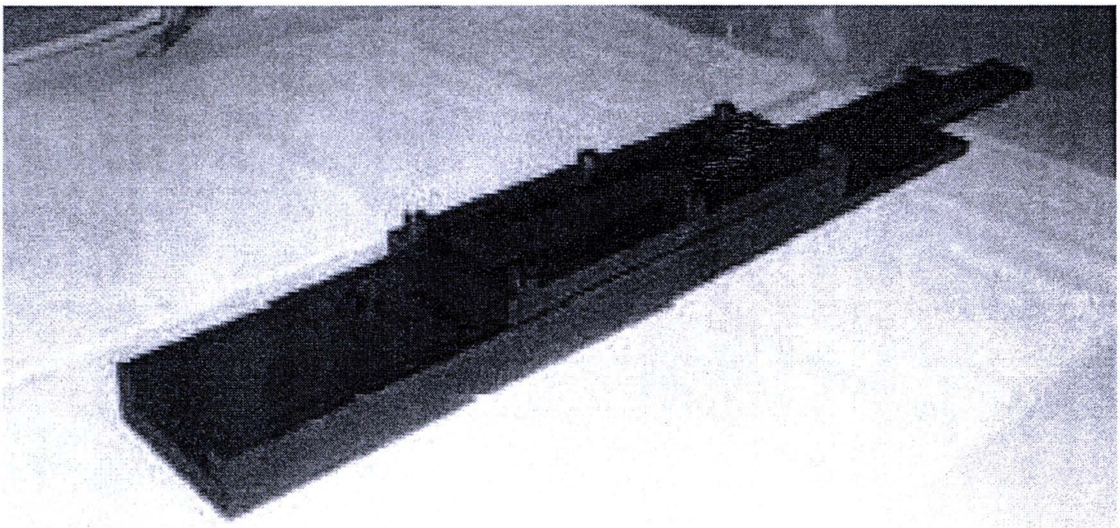


Figure 3.1 Horizontal LPE systems **[16]**



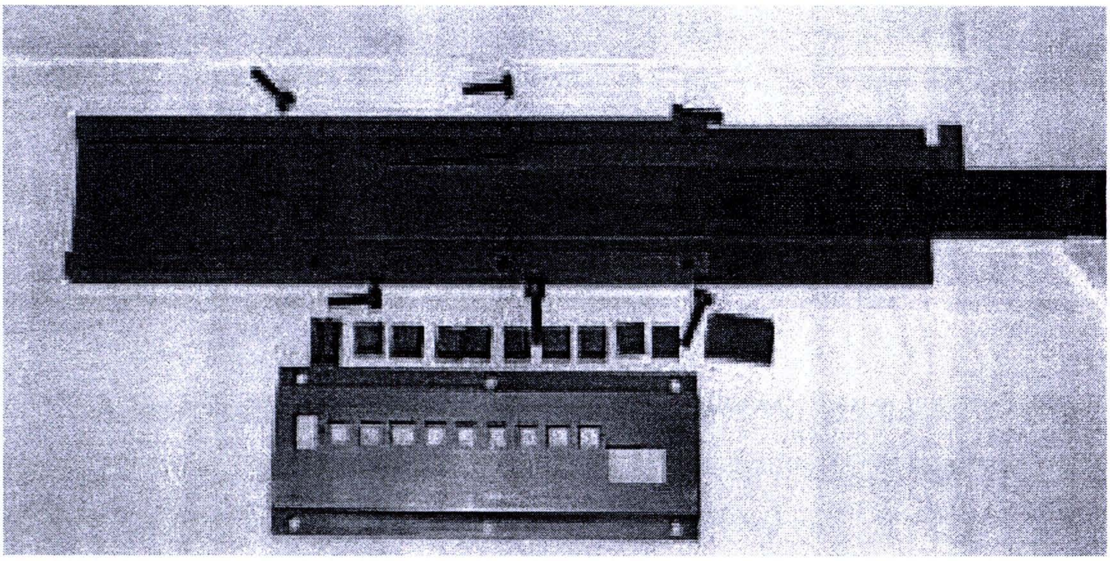


Figure 3.2 Multi-bin graphite boats **[16]**

(1) Experimental setup is simple and inexpensive.

(2) Growth temperature is low (approximately 350 to 900°C).

(3) Relatively height growth rate of 0.1 mm/min is possible.

(4) Elimination of hazards due to use of reactive gasses and their reactive products.

(5) Non-requirement of vacuum equipment.

The limitations of LPE technique is the difficulty of growing layers that differ in lattice constant by more than ~1% from substrate and its inability to produce ultra-thin layer whose thickness is less than 0.1μm. Furthermore, LPE layers generally do not have a good surface morphology as layers grown by Vapor Phase Epitaxy (VPE), as well as Molecular Beam Epitaxy (MBE). However, because of simplicity and flexibility, LPE has been attractive for growing complex layered structure required for optoelectronic devices.

The horizontal LPE system, which is installed at Chulalongkorn University, Semiconductor Device Research Laboratory (SDRL) is shown on **figure 3.1.** The apparatuses use for LPE systems are

(1) Programmable temperature controller.

(2) Movable resistance furnace.

(3) Quartz tube.
(4) Pd-purified H_2 as well as gas system.
(5) Hygrometer.
(6) Nitrogen hood.
(7) Thermocouple as well as gas system.
(8) Multi-bin graphite boat (see on **figure 3.2**).
(9) Quartz rode (use for sliding).

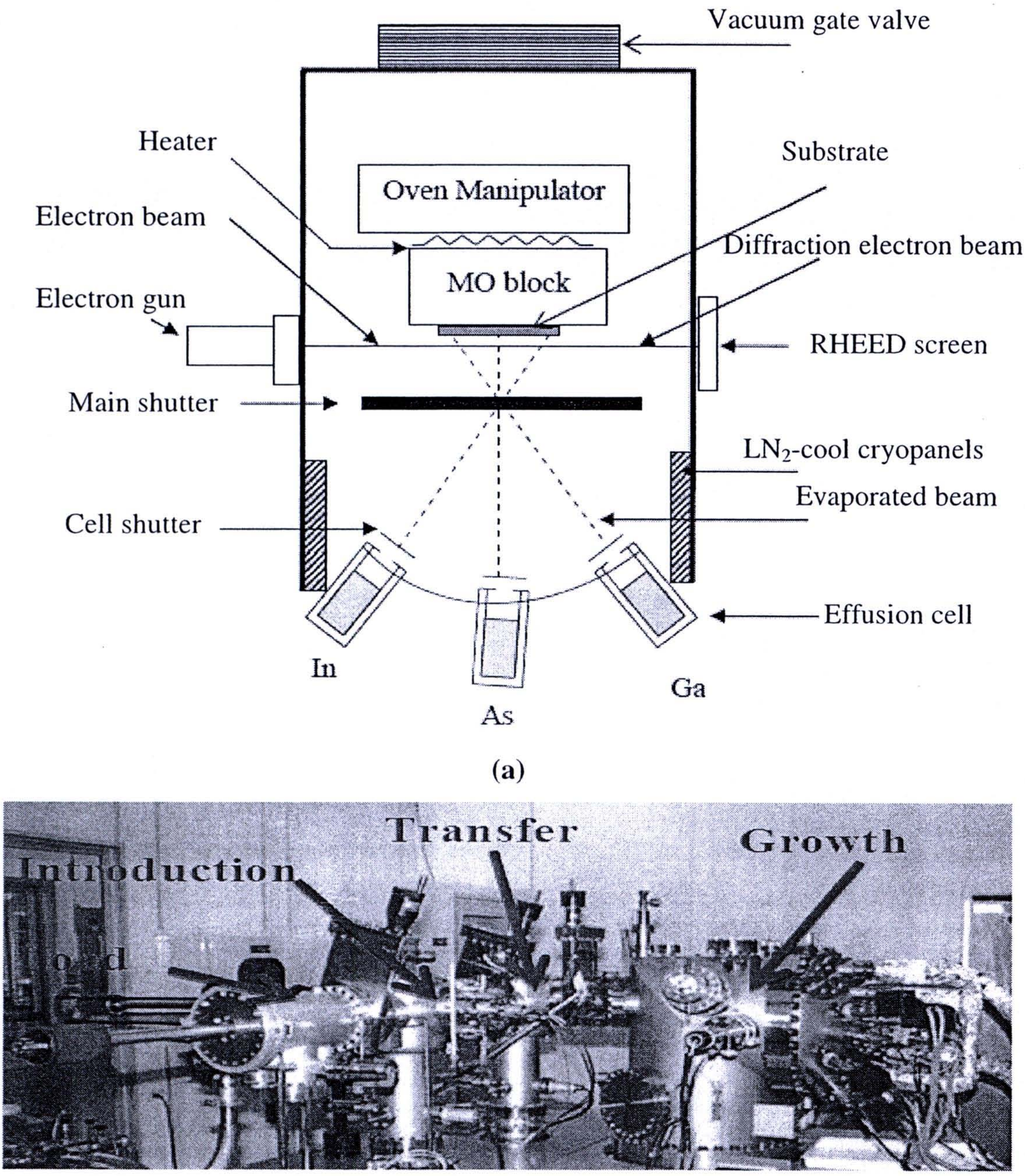
Actually, LPE is suitable for growing thick epitaxial layers quickly because the growth rate is high and it is also suitable for forming multi-layers structures, such as heterostructures because it has multi-bins graphite boats **[16]**.

3.3.2 Molecular Beam Epitaxy (MBE)

Molecular beam epitaxy (MBE) is a process for growing thin, epitaxial films of a wide variety of materials, ranging from oxides to semiconductors to metals. It was first applied to the growth of compound semiconductors. That is still the most common usage, in large part because of the high technological value of such materials to the electronics industry. In this process beams of atoms or molecules in an ultra-high vacuum environment are incident upon a heated crystal that has previously been processed to produce a nearly atomically clean surface. The arriving constituent atoms form a crystalline layer in registry with the substrate, i.e., an epitaxial film. These films are remarkable because the composition can be rapidly changed, producing crystalline interfaces that are almost atomically abrupt. Thus, it has been possible to produce a large range of unique structures, including quantum well devices, superlattices, lasers, etc., all of which benefit from the precise control of composition during growth. Because of the cleanliness of the growth environment and because of the precise control over composition, MBE structures closely approximate the idealized models used in solid state theory **[17]**.

3.3.2.1 The MBE system

The Molecular Beam Epitaxy (MBE) is consisting of four chambers: load chamber, introduction chamber, transfer chamber, and growth chamber. Each chamber is separated by isolated gate valves and the substrate is transferred from load chamber to each other chamber. The introduction and growth chambers are heater for a heat the substrate. The ultra-high vacuum is obtained via the pumping systems are consisting of sorption pump, ion pump, titanium sublimation pump.



(a)

(b)

Figure 3.3 **(a)** diagram of growth chamber and **(b)** schematic illustration of a RIBER 32P MBE system **[16]**

The diagram of a typical MBE growth chamber shows in **figure 3.3 (a)**. Inside the growth chamber of the MBE are material source cells, substrate heater, monitoring equipment, and pumping system. The solid source of materials is separately contained different effusion cells. During the MBE working, the chamber wall and effusion cells are cooling by liquid N_2 to protect contamination as result of outgases from heated part. There are two type of monitoring equipments such as mass spectroscopy and reflection high-energy electron diffraction (RHEED). The mass spectroscopy is used for particle analysis, and RHEED is used to observe the surface of crystallization during the MBE grows. And there are two ionization gauges which measures the beam flux and background pressure (BP). And one of the ionization gauges is measured for BEP is located at the level of manipulator behind the substrate, and the other gate is situated in front of ion pump for measuring background pressure. The temperature measures by W-Re thermocouple and the temperature is controlled by computer via a controller card (EUROTHERM). In order to get a uniforms flux profile on the surface of the substrate during epitaxy. All of the samples are grown on semi-insulating (001)-GaAs substrates in the solid source MBE system (RIBER 32P) shows in **figure 3.3(b)**. The substrate is attached to molybdenum block (MO in the figure). The prior to crystal growth, the contamination is removed from substrate surface for 3 hour pre-heat process in the introduction chamber before being transferred to the growth chamber. The pre-heat process has done when the pressure in the introduction chamber is $1X10^{-8}$ Torr or lower than. The temperature profile of pre-heat process shows on the **figure 3.4**.

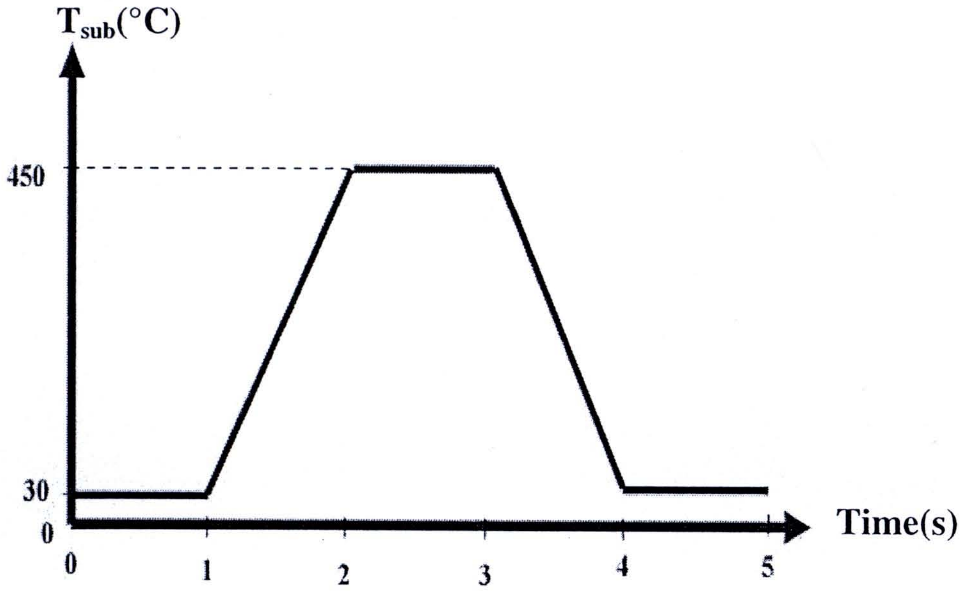


Figure 3.4 Temperature profile of the pre-heat process **[17].**

In the pre-heat process, the sample is heat by increasing the temperature of the substrate (T_{sub}) from 30°C to 450°C at the rate of 7°C/min, to take one hour for ramp up. During ramp up, the contaminations from the substrate surface is removed and purges, at that time the pressure also increases. Then the T_{sub} is ramp down from 450°C to 30°C. The pre-heat process, this takes three hours and almost of the samples are subject to this process without exception.

When we finish pre-heat process, the substrate is transferred to growth chamber and de-gas is carrier out. The temperatures of effusion cells are increased from standby temperature (T_{std}) to require temperature in order to remove contaminations from each effusion cells. The profile of de-gas process for the temperature is ramp up for Ga and In effusion cells are shown on the **figure 3.5**, and As effusion cell and substrate are shown on the **figure 3.6**.

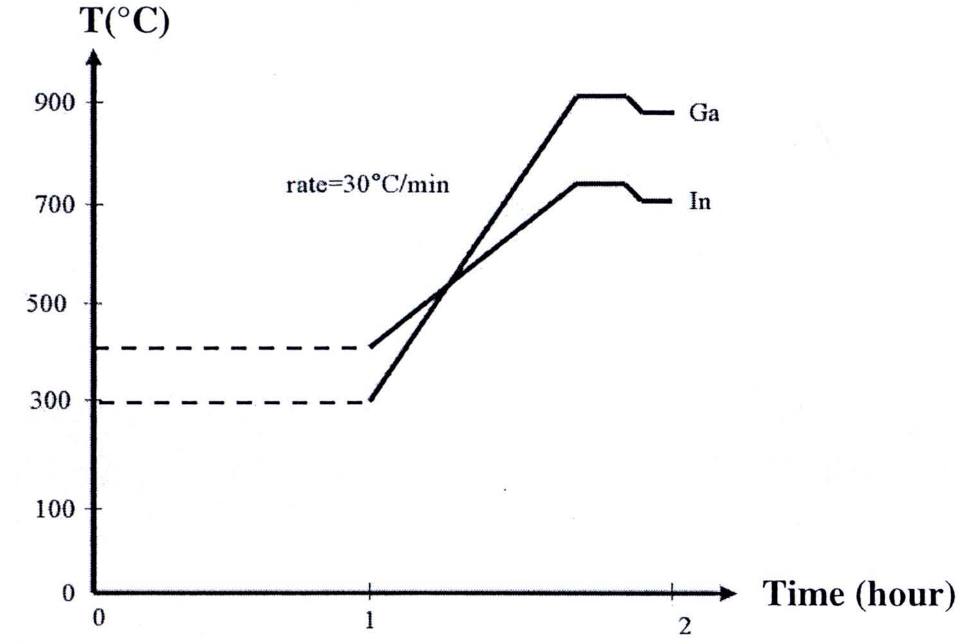


Figure 3.5 Temperature of Ga and In effusion cells. The effusion cell is closed in the dotted line range and opened in solid line range during respective temperature ranges **[17]**.

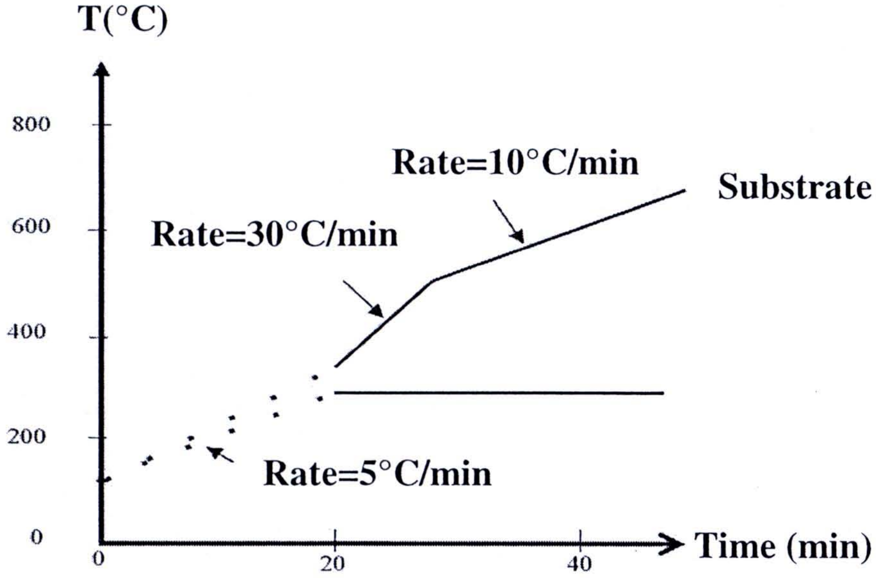
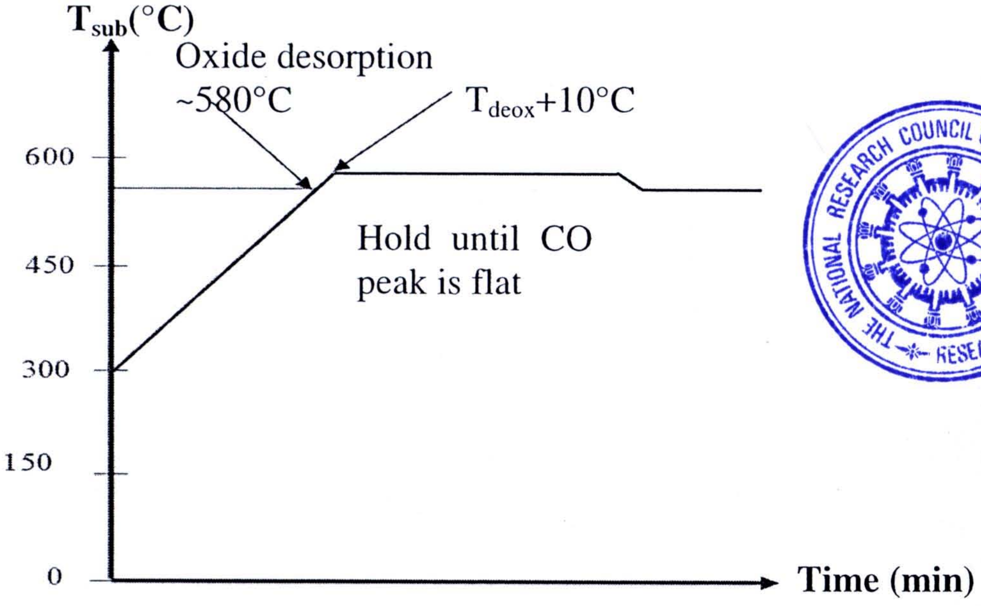
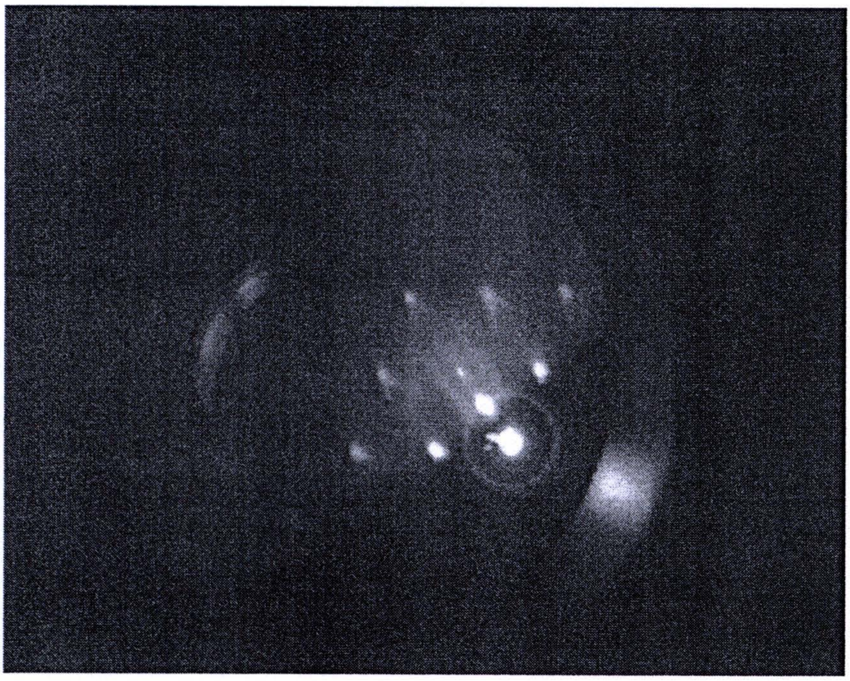


Figure 3.6 Temperature profile of As effusion cell and substrate. The effusion is closed in the dotted line range and opened in solid line range during respective temperature ranges **[17]**.

The **figure 3.5**, the temperatures of Ga and In effusion cells are increased from their standby temperature (T_{std}) to the set point temperature at the same rate of 30°C/min. After ramp up the temperature of the effusion cell, then the each effusion cell is measured by opening corresponding cell. Typically, BEP of In, Ga and As effusion cells are ~10^{-8}, 10^{-7} and 10^{-6} Torr respectively. The de-gas process of effusion cell has done last because the BEP of As effusion cell is significantly higher than other effusion cells. So the temperature of the de-gas of As effusion cell and substrate are ramp up in he same time from T_{std} 100°C to 300°C in the same rate of 5°C/min in order to suppress the As atoms out gassing from the substrate surface. When the T_{sub} increases higher than 300°C, out gassing As atoms from the substrate result in the surface roughness. Between 300°C to 500°C, rate of 30°C/min. Between 500°C to 650°C, the rate of 10°C/min. After de-gas process which prepares the effusion cells for growing, then the substrate has to de-oxide process in order to prepare the surface for subsequent epilayer growth. The de-oxide process and RHEED pattern for substrate, the temperature increases in this process is shown in **figure 3.7(a)**. When T_{sub} is arrived 580°C, the spotty pattern shows in **figure 3.7(b)** start to occur because the native oxide goes out from the GaAs substrate. To ensure complete oxide removal and thus a clean GaAs surface, the temperature is kept at slightly above the de-oxide temperature. Usually, T_{deox}=580°C, the temperature would be kept at 590°C until the CO peak is almost flat.



(a)



(b)

Figure 3.7 **(a)** temperature profile of the oxide desorption process and RHEED pattern when the temperature increases and **(b)** photo took from view port showing RHEED spotty pattern at de-oxide temperature at 580°C **[17]**

3.3.2.2 In-situ characterization tools

There are two important in-situ characterization tools such as mass spectroscopy and RHEED. The mass spectroscopy is used to investigate the chemical constitutes inside the growth chamber. And the RHEED is used to calibrate the growth rate and indicate the 2D and 3D growth mode transition point.

★ **Mass Spectroscopy (An introduction to Mass Spectroscopy, Ashcroft)**

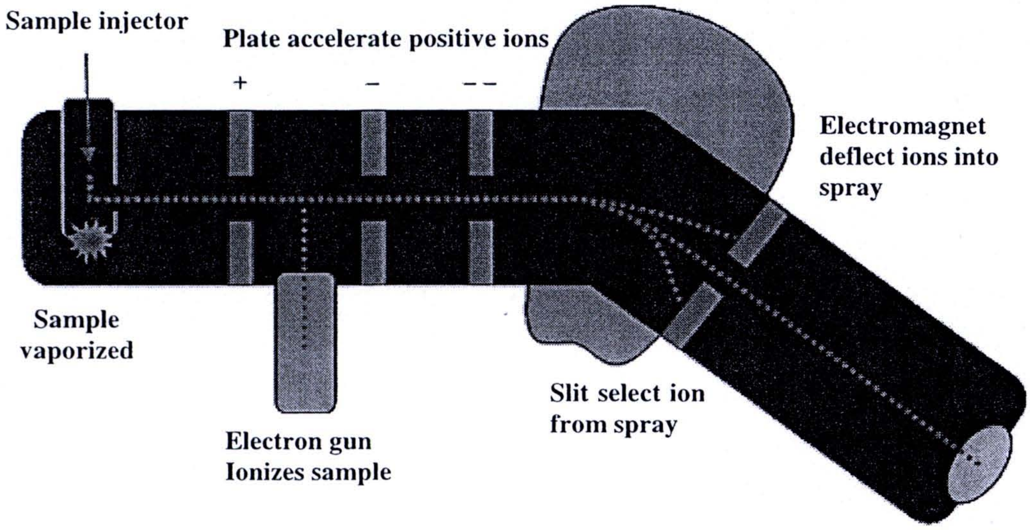


Figure 3.8 Schematic diagram of mass spectrometer
(From: www.stev.gb.com/science/spectroscopy.html)

The mass spectroscopy is an analytical technique uses to measure mass-to-charge (m/z) ratio of ions. The composition of a sample is determined from the mass spectrum representing the masses. A typical mass spectrometer is comprised three parts such as ion source, a mass analyzer, and detector system. The **figure3.8** is shown the schematic diagram of spectrometer. The sample is introduced into ionization source of the instrument. Inside the ionization source, the sample molecules are ionized, because ion is easier to manipulate than neutral molecules. These ions are extracted into analyzer region of mass spectrometer where they separate according to their mass-to-charge ratios. The separated ions have been detected and this signal is sent to a data system where the m/z ratios to store together with their relative abundance for presentation in the format of m/z spectrum. In experiment, masses of particle such as hydrogen, helium, argon, water, oxygen, carbon dioxide, and monoxide have been checked by mass spectrometer. Especially, the complete removal of native oxide from the substrate surface is investigated by mass spectrometer. In de-oxide process, when the signal 28 peak (carbon monoxide) is flat, further growth process is continued.

★ Reflection High-Energy Electron Diffraction (RHEED)

Undoubtedly the single most important analytical tool for layer grower has been the RHEED system for real time observation of the crystal structure of the growth. Most MBE systems today either include an electron gun and phosphor screen for displaying RHEED pattern while the layer is growing, the photo of the film pattern is shown on **figure 3.7 (b) [16]**. And the RHEED system provides a tool for monitoring growth rate, for a qualitative measure of surface topography and for monitoring surface structure that, in certain instances, can provide a measure of the surface composition. Also important to the user is that the RHEED system is relatively insensitive to the ambient in the growth chamber, that is, RHEED images can be obtained with equal clarity either while beams are incident on the substrate or when the growth has been terminated and the substrate is cooled; furthermore the geometry is such that there is no part of the RHEED system positioned in front of the sample to block access to the surface since the RHEED arrives at a glancing angle **[19]**. The **figure 3.9** is shown the schematic diagram presentation of RHEED geometry shows the incident electron beam at an angle Θ to the surface plane.

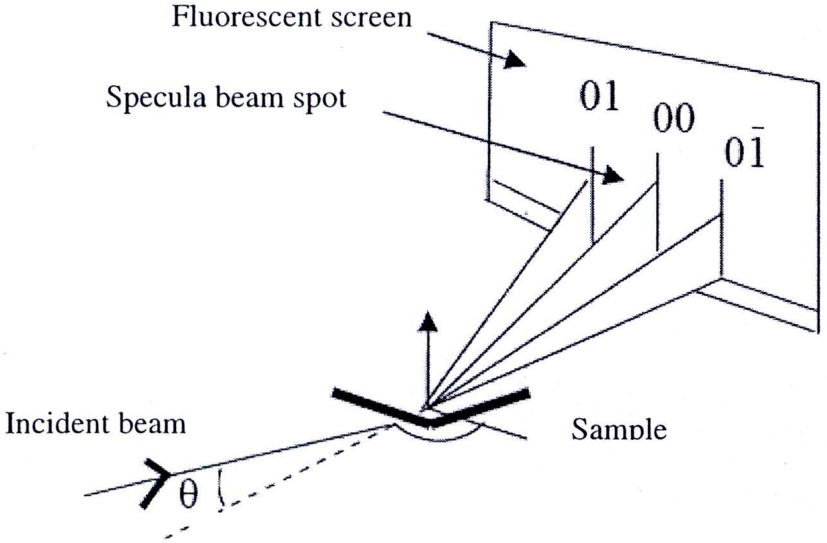


Figure 3.9 Schematic diagram presentation of RHEED geometry shows incident electron beam at an angle Θ to the surface plane **[18].**

3.3.3 Photoluminescence (PL)

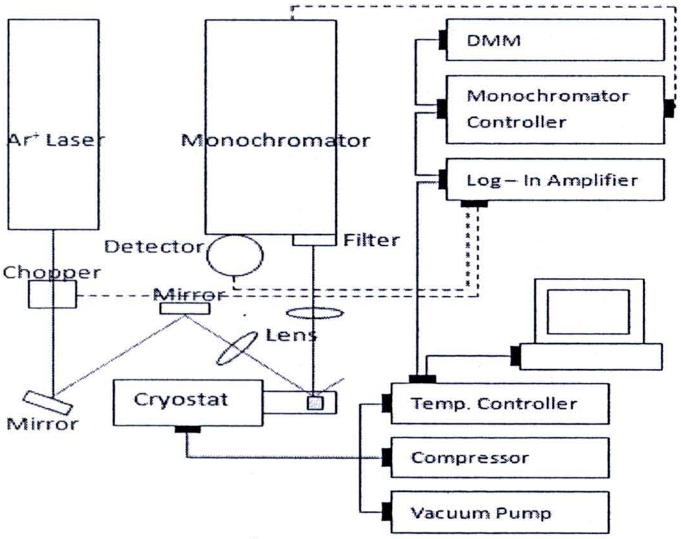


Figure 3.10 Schematic diagram of PL experiment set up.

The photoluminescence is a light emission properties of semiconductor when excited by photon energy. While the semiconductor is excited, electron-hole pair is generated and recombined. The resulting radiation from the recombination of carriers is called Photoluminescence (PL) **[19]**.

The photoluminescence (PL) spectroscopy is a useful technique for the study and characterization of material and dynamical processes occurring in materials. However, PL spectroscopy, like all other experimental technique, does not give a universal, all-encompassing view of energy aspect of the properties of a particular material, or even more specifically of the optical properties of materials.

Photoluminescence from semiconductor is most commonly characterized via spectroscopic techniques. These techniques involve measuring the energy distribution of emitted photons after optical excitation. This energy distribution is then analyzed in order to determine properties of the material, including defect species, defect concentration, possible stimulated emission, etc. This technique for material characterization has achieved significant success and popularity in this regard at least party due to the simplicity of the technique and absence of sample process requirements **[20]**.

3.4 GaAs and AlGaAs for LPE

The GaAs and AlGaAs are the basic materials for solar cell structure. The understanding of these materials preparation and weight calculation are very important and will be provided by this section.

3.4.1 Material preparation

The material which it can be used to fabricate GaAs or $Al_xGa_{1-x}As$ epilayer should be commonly prepared in the Ga solvent and as other materials such as As, and dopant is also prepared as solute. The commonly n-type dopant is Sn or Te, and for the p-type dopant is Ge or Zn. These materials are prepared in solid form and can calculate by the formula below.

$$X_{Ga} + X_{As} + X_{Al} + X_{im} = 1 \qquad \textbf{(3.1)}$$

X is the m ole fraction of each other element in $Al_xGa_{1-x}As$ alloy. The Ga weight (W_{Ga}) to As weight (W_{As}) can be writing as

$$W_{As} = (X_{As}/X_{Ga})(M_{Al}/M_{Ga})W_{Ga} \tag{3.2}$$

M is the atomic weight of each element. Then other element can be writing

$$W_{Al} = (X_{Al}/X_{Ga})(M_{As}/M_{Ga})W_{Ga} \tag{3.3}$$

$$W_{im} = (X_{im}/X_{Ga})(M_{im}/M_{Ga})W_{Ga} \tag{3.4}$$

The weight of GaAs is given by

$$W_{GaAs} = (X_{GaAs}/X_{Ga})(M_{GaAs}/M_{Ga})W_{Ga} \tag{3.5}$$

Where $M_{Ga}=69.72$ $M_{As}=74.92$

$M_{Al}=26.98$ $M_{Ge}=72.59$

$M_{Sn}=118.69$ $M_{Te}=127.60$

$M_{GaAs}=M_{Ga}+M_{As}=144.64$

The value of each element can be approximated from graphs as shown in **figure 3.11, 3.12, 3.13 and 3.14**

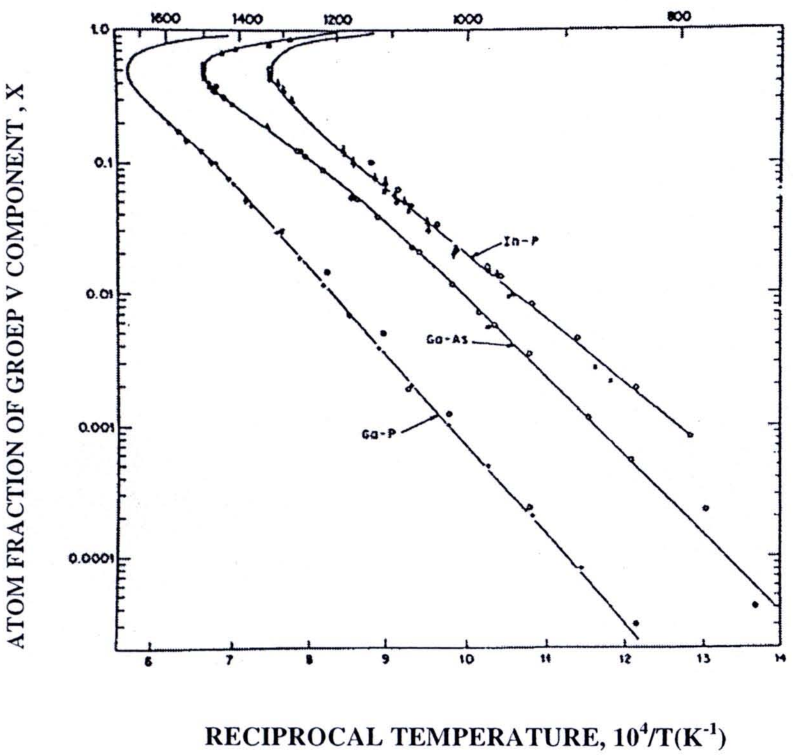


Figure 3.11 Liquidus composition versus reciprocal temperature for GaAs, GaP and InP [21].

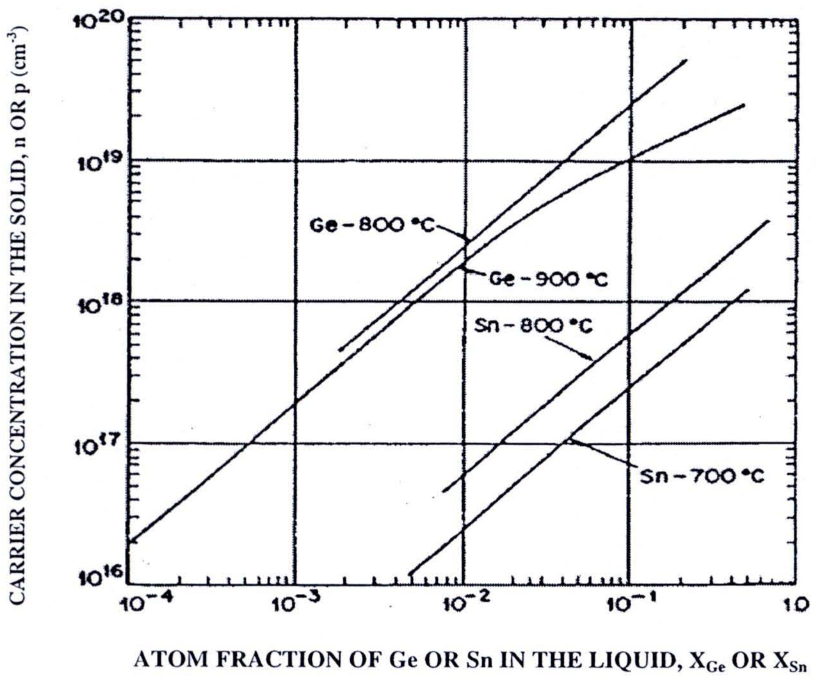


Figure 3.12 Room temperature hole concentration in GaAs versus the atom fraction of Ge in the liquid along the 800 and 900°C and the lower curves are the

room temperature electron concentration in GaAs versus the atom fraction of Sn in the liquid along the 700 and 800°C **[21]**.

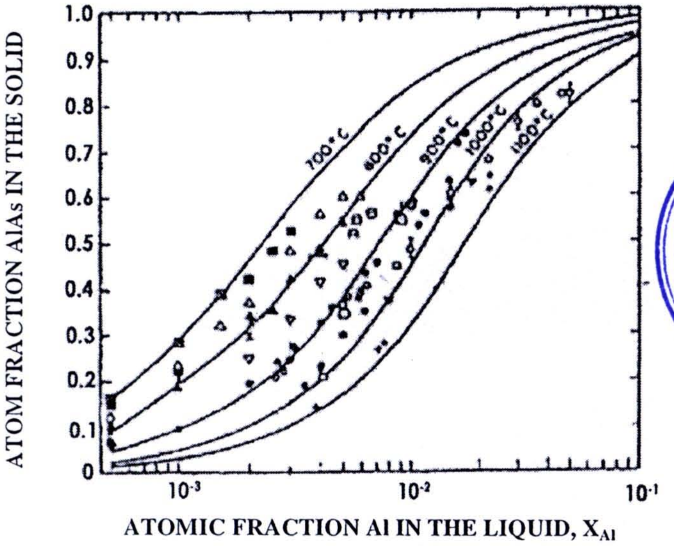


Figure 3.13 Solidus compositions in $Al_xGa_{1-x}As$ as a function of liquidus composition **[21]**.

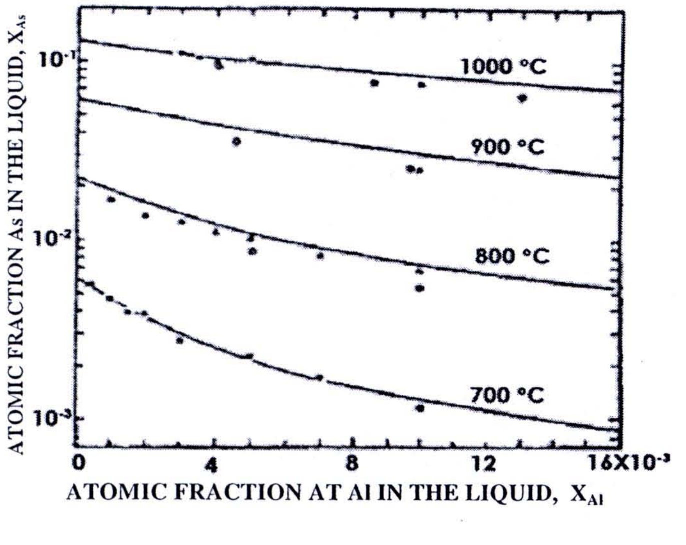


Figure 3.14 Liquidus isotherms in the AlGaAs system **[21]**.

3.4.2 Material weight calculation

The weight of materials are calculated by the following

- **$Al_{0.35}Ga_{0.65}As$ (p) $10^{18}cm^{-3}$, Ge-doped**

$X_{Al}=0.0025$

$X_{Ge}=0.04$

$X_{As}=0.015$

Then $X_{Ga}=1-X_{Al}-X_{As}-X_{Ge}=0.9425$

We use 3g of Ga, therefore we get

$W_{Al} = (X_{Al}/X_{Ga}).(M_{Al}/M_{Ga}).W_{Ga}$

$= (0.0025/0.9425).(26.98/69.72).3g$

$= 3.079mg$

$W_{GaAs}= (X_{GaAs}/X_{Ga}).(M_{GaAs}/M_{Ga}).W_{Ga}$

$\approx (X_{As}/X_{Ga}).(M_{GaAs}/M_{Ga}).W_{Ga}$

$= (0.015/0.9425).(144.64/69.72).3g$

$= 99.05mg$

$W_{Ge}= (X_{Ge}/X_{Ga}).(M_{Ge}/M_{Ga}).W_{Ga}$

$= (0.04/0.9425).(72.59/69.72).3g$

$= 120mg$

- **$Al_{0.35}Ga_{0.65}As$ (p^+) $5x10^{18}cm^{-3}$, Ge-doped**

$X_{Ge}=0.025$

$X_{Al}=0.0025$

$X_{As}=0.015$

Then we get $X_{Ga}=1-X_{Al}-X_{As}-X_{Ge}=0.97$

We use 3g of Ga, therefore we get

$W_{Al} = (X_{Al}/X_{Ga}).(M_{Al}/M_{Ga}).W_{Ga}$

$= (0.0025/0.97).(26.98/69.72).3g$

$= 3mg$

$W_{GaAs}= (X_{GaAs}/X_{Ga}).(M_{GaAs}/M_{Ga}).W_{Ga}$

$\approx (X_{As}/X_{Ga}).(M_{GaAs}/M_{Ga}).W_{Ga}$

$= (0.0015/0.97).(144.64/69.72).3g$

$=96.66\text{mg}$

$W_{Ge}= (X_{Ge}/X_{Ga}).(M_{Ge}/M_{Ga}).W_{Ga}$

$= (0.025/0.97).(72.59/69.72).3\text{g}$

$= 80.70\text{mg}$

- **GaAs (n^-)**

$X_{As}=0.022$

Then we get $X_{Ga}=1-X_{As}=0.978$

We use 3g of Ga, therefore we get

$W_{GaAs}= (X_{GaAs}/X_{Ga}).(M_{GaAs}/M_{Ga}).W_{Ga}$

$\approx (X_{As}/X_{Ga}).(M_{GaAs}/M_{Ga}).W_{Ga}$

$= (0.022/0.978).(144.64/69.72).3\text{g}$

$= 140.01\text{mg}$

- **GaAs (p^+) $5\text{x}10^{18}$ m^{-3}**

$X_{As}=0.022$

$X_{Ge}=0.02$

Then we get $X_{Ga}=1-X_{As}-X_{Ge}$

$= 1-0.022-0.02$

$= 0.96$

$W_{GaAs}= (X_{GaAs}/X_{Ga}).(M_{GaAs}/M_{Ga}).W_{Ga}$

$\approx (X_{As}/X_{Ga}).(M_{GaAs}/M_{Ga}).W_{Ga}$

$= (0.022/0.96).(144.64/69.72).3\text{g}$

$= 142.2\text{mg}$

$W_{Ge} = (X_{Ge}/X_{Ga}).(M_{Ge}/M_{Ga}).W_{Ga}$

$= (0.02/0.958).(72.59/69.72).3\text{g}$

$=60\text{mg}$

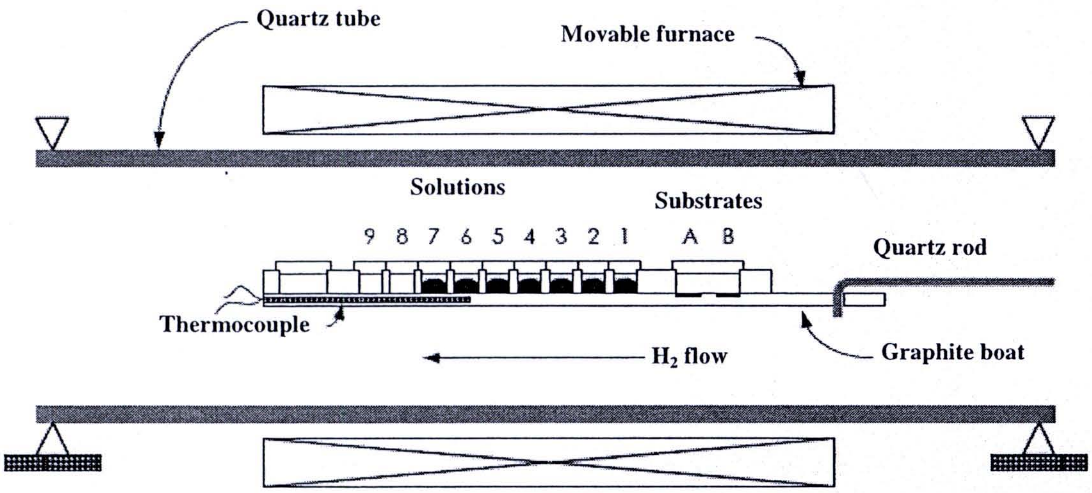
Table 3.1 Material weight

Material Solution	Ga(g)	GaAs(mg)	Al(mg)	Ge(mg)
$Al_{0.35}Ga_{0.65}As(p^+)$	3	96.66	3	80.70
$Al_{0.35}Ga_{0.65}As(p)$	3	99.05	3.079	120
$GaAs(p^+)$	3	142.2	-	60
$GaAs(n^-)$	3	140.01	-	-

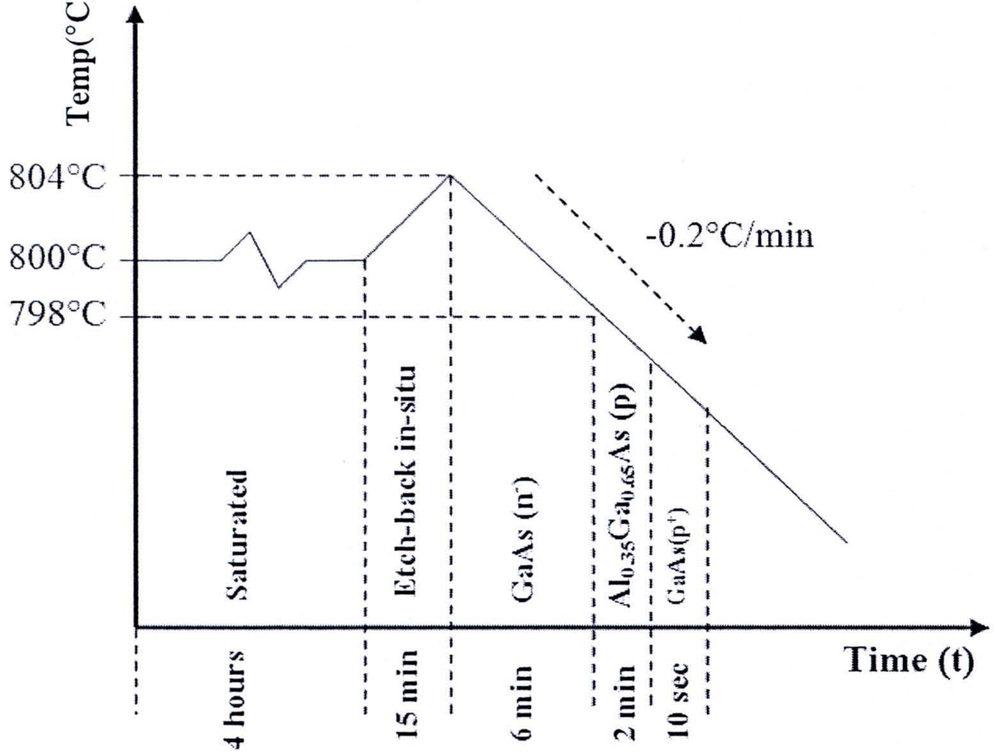
3.5 Growth process

3.5.1 Liquid phase epitaxy

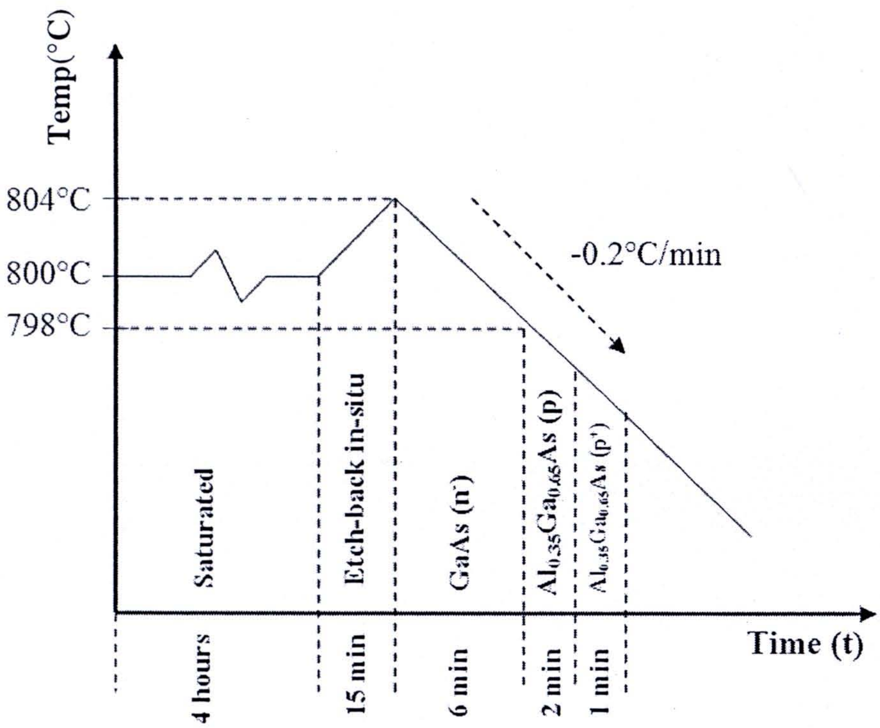
The growth process is run after the boat is loaded with substrate and the material solution is already preparation, and it is placed in the quartz tube, but initially remains outside the furnace. First, it is flushed with flowing N_2, evaluated and checked for leaks about 1 hour, and then flowing Pd-purified H_2 (prevents oxidation of solution and substrate). The furnace is moved into the position for heating the boat **figure 3.15 (a)** shows the basic set up of LPE system, **figure 3.15 (b)** and **(c)** illustrate schematic profile of the furnace temperature versus the growing time duration, samples **G** and **H**.


Quartz tube
Movable furnace
Solutions
Substrates
9 8 7 6 5 4 3 2 1
A B
Quartz rod
Thermocouple
H_2 flow
Graphite boat

(a)


Temp(°C)
804°C
800°C
798°C
-0.2°C/min
Saturated
Etch-back in-situ
GaAs (n⁻)
$Al_{0.35}Ga_{0.65}As$ (p)
GaAs(p⁺)
Time (t)
4 hours
15 min
6 min
2 min
10 sec

(b)



(c)

Figure 3.15 **(a)** Basic set up of LPE system, **(b)** and **(c)** schematic profile of the furnace temperature versus the growing time duration, samples **G** and **H**.

The temperature is kept constant at 800°C at least for 4 hours to substrate, material and solution, then step up to 804°C for in-situ etching. When the temperature reaches peak of 804°C, and then it decreases at the rate of 0.2°C/min to saturate the material solution, then the temperature of the solution is below the saturation condition, and the epitaxial layer started growth. In the other hand, the temperature is more decreasing, the solution is oversaturated, then the oversaturated comes into contact with the substrate, the oversaturated temperature, ΔT will, therefore, force the solution GaAs to precipitate. The growth layer is terminated by sliding the substrate out from under solution. The thickness of growth layer can be determined by the oversaturated temperature and the range of time which the substrate and solution are contact and can calculate by equation of **3.6**.

$$d = K\left(\Delta T^{\frac{1}{2}} + \frac{2}{3}\alpha t^{\frac{3}{2}}\right) \qquad \textbf{(3.6)}$$

K : The constant which is a function concentration of As in the liquid

ΔT : The over saturation temperature of solution

α : The cooling rate

3.5.2 Molecular Beam Epitaxy

The growth process of MBE briefly discusses below

- The GaAs substrate (100) is loaded into the MBE, and is cleaned by chemical; it is the case that the substrate is epi-ready type and kept in a dust-free condition. After mounting on the molybdenum block with indium, the substrate is preheated at 450°C for one hour in the preparation chamber, then the substrate transferred to the growth chamber, this chamber is cooling by liquid nitrogen, and the titanium sublimator of the growth chamber is switched off.

- Increase the substrate temperature (OM= oven manipulator) as well as the Al, Ga and Si containing cell.

OM 100°C ⟶ 250°C
Al 300°C ⟶ Calibrate from the flux pressure
Ga 300°C ⟶ 910°C
Si 300°C ⟶ depend on the carrier concentration

- Rotate the manipulator up of 224 degree to obtain the "optimum" flux pressure measurement position. First, the Ga flux will be measured. The Ga containing cell and the main shutter are then opened, while the other shutter is closed. Adjust the Ga cell temperature to get the flux pressure of 4.3×10^{-7}Torr (wait until the pressure is stabilized). The growth rate of GaAs is gotten 0.8μm/hour. Close the individual cell shutter as well as the main shutter. To get the ternary compound $Al_{0.1}Ga_{0.9}As$, we have to adjust the Al cell temperature by reading on the gauge.

$$\text{Al flux} = (\text{Ga flux})\ \text{x}\ \frac{10}{90}\ (\text{mole fraction})\ \text{x}\ \frac{0.92}{1.68}\ (\text{gauge sensitivity})$$

$$= 2.6164\text{x}10^{-8}\text{Torr}$$

And the $Al_{0.2}Ga_{0.8}As$, $Al_{0.3}Ga_{0.7}As$

★ $Al_{0.2}Ga_{0.8}As$

$$\text{Al flux} = 4.3\text{x}10^{-7}\text{x}\frac{20}{80}\text{x}\frac{0.92}{1.68}$$

$$= 5.8869\text{x}10^{-8}\text{Torr}$$

★ $Al_{0.3}Ga_{0.7}As$

$$\text{Al flux} = 4.3\text{x}10^{-7}\text{x}\frac{30}{70}\text{x}\frac{0.92}{1.68}$$

$$= 1.0092\text{x}10^{-7}\text{Torr}$$

Gradually increase the As cell temperature up to 190°C. To make small steps (5°C/min each). The individual shutter of the As containing cell is opened, as well as the main shutter. All other individual shutters are closed. The partial pressure of As_4 is about 20 times grater than Ga, so it might reach about $8.6\text{x}10^{-6}$Torr. During the time, the substrate temperature is adjusted to be 300°C.

- Rotate up the manipulator to obtain 320 degree (still remain opened the main shutter as well as As cell). Increase the substrate temperature to 550°C. The electron gun of RHEED system is powered on and the shutter that protects the RHEED screen is opened. By using the deflectors, position the electron beam so that it strike the substrate. A diffused light must be observed on the screen, and possibly circles due to the surface oxide. Gradually increase the substrate temperature (10°C each step) until spotty pattern is clearly observed. To set the substrate temperature cools down by 20°C less than that of the temperature. Deoxidation is processed for approximately 10-15 minutes. The streaky pattern will slowly appear. They gradually become less and less diffuse as the oxide evaporates.

- Open the Ga individual shutter to begin the GaAs deposited on the substrate. To store at this condition until the designed thickness (2 minutes and 30 second to obtain 2μm of GaAs epitaxy for the growth rate 8.8μm/hour). Other cell shutter such as Al and Si are also opened if either the AlGaAs epitaxial layer or dopant is required **[21].**