CHAPTER 4
Fabrication of GaAs/GaAlAs Staircase Band Gap Photodiodes

4.1 Introduction

In this chapter we shall discuss the fabrication technologies and processes of GaAs/GaAlAs staircase band gap photodiodes. The essentials cover: epitaxial growth technique, substrate preparation and cleaning technique, material preparation and calculation, growth process, Zn diffusion and device structure formation. Understanding the fabrication technologies is quite important step to realize the high quality device.

4.2 Epitaxial growth technique

The growth of single-crystal semiconductor layers upon a semiconductor substrate is called "epitaxy". Epitaxy can be broadly classified into two categories: (1) Homoepitaxy and (2) Heteroepitaxy. In homoepitaxy, the composition of the layer is essentially the same as the underlying substrate such as Si/Si and GaAs/GaAs, while the composition of the layer differ from that of the substrate, the epitaxy is termed heteroepitaxy such as GaAlAs/GaAs, GaAs/Si and GaInAsP/InP. In this research, there are two epitaxial growth techniques have been used: one is Liquid Phase Epitaxy (LPE) and another is Molecular Beam Epitaxy (MBE). Each technique will basically report on the following sub-sections.

4.2.1 Liquid Phase Epitaxy (LPE)

LPE is a technique of growing an epitaxial layer on a single-crystal substrate by deposition from a molten saturated under controlled temperature condition at the growth interface. This technique is particularly useful for growing GaAs and related III-V compounds. The supersaturation solution, which is necessary for deposition, is generally achieved by decreasing the solubility of a dilute constituent in a liquid solvent with reducing the temperature. The LPE technique has many advantages, there are:

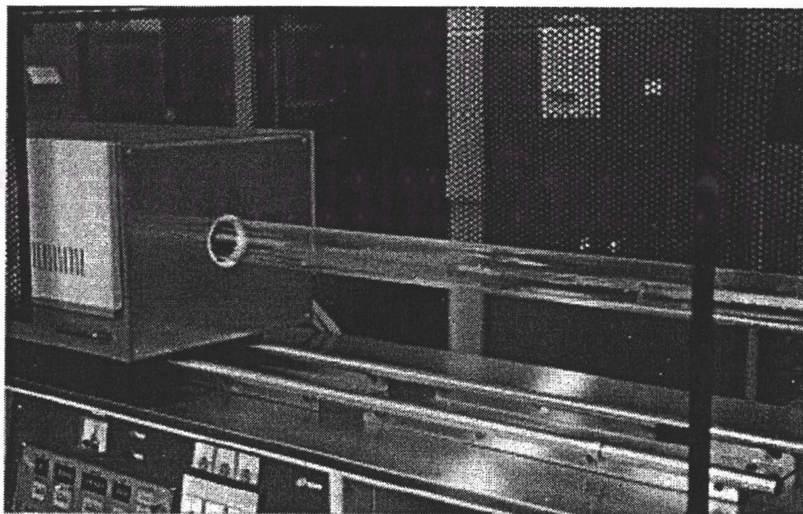

Fig. 4.1 A horizontal LPE system

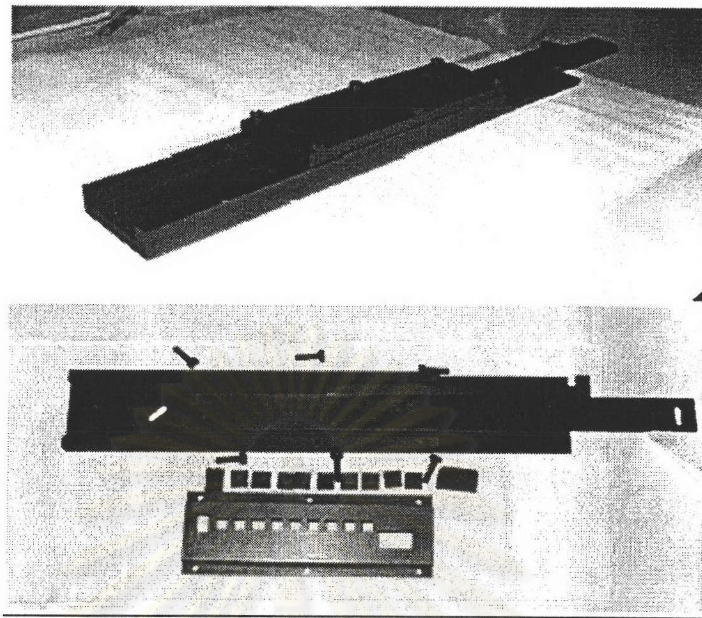

Fig. 4.2 A multi-bin graphite boat

(1) Experimental setup is simple and inexpensive
(2) Growth temperatures are low (approximately 350 to 900 °C)
(3) Relatively height growth rate, 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 are 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 0.1 μm. Furthermore, LPE layers generally do not have as good surface morphology as layers grown by Vapor Phase Epitaxy (VPE), as well as Molecular Beam Epitaxy (MBE). However, because of its simplicity and flexibility, LPE has been attractive for growing complex layered structures required for optoelectronic devices.

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The horizontal LPE system, which is installed at Semiconductor Device Research Laboratory (SDRL), Chulalongkorn University is depicted in Fig. 4.1. The apparatuses used for LPE system are

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(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 temperature recorder
(8) Multi-bin graphite boat (see Fig. 4.2)
(9) Quartz rod (used 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-layer structures, such as heterostructures because it has a multi-bins graphite boat.

4.2.2 Molecular Beam Epitaxy (MBE)

Although MBE is considered a newcomer technique for semiconductor epitaxial growth, it is basically a technique of vacuum evaporation, one of the oldest and the most widely used in depositing solid films. MBE is also considered to be the most promising future growth technique because it allows for precise thickness control and dopant control. Growth is performed under an ultra-high vacuum chamber with a low growth rate (1 μm per hour to 10 μm per hour are typical). The system has multiple sources that allow accurate stoichiometric growth.

The RIBER MBE system (see Fig. 4.3) may combine chambers for loading and preparation of substrates, epitaxy, metallization, and surface analysis. A loading module, a heat treatment module, a transfer module and their related pumping systems are also consisted in the system, which is detail, therefore, given hereunder.

4.2.2.1 Pumping system

- **Rough pumping**

Rough pumping consists of a dry diagram pump to pump down to about 100-50 Torr and three sorption pumps utilized sequentially and allowing to pump down to pressures ranging from $5x10^{-3}$ to $5x10^{-4}$ Torr. A Bourdon-type manometer and a thermocouple gauge permit pressure readings. A flexible metal fitting connects the rough pumping to the rest of the system. Using manual valves operates epitaxy and module rough pumping.

- **Secondary pumping**

Epitaxy chamber, loading, heat treatment and transfer module secondary pumping is made by using ion pumps and titanium sublimators liquid nitrogen cooled. Gate valves allow to isolate the ion pumps from the chamber and the modules. Bayard-Alpert triode gauges permit pressure readings in each section.

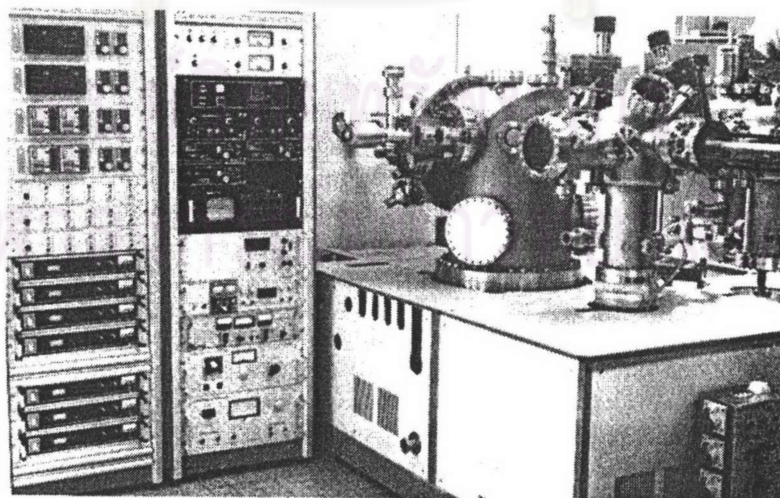

Fig. 4.3 The RIBER MBE system

4.2.2.2 Modules

In order to keep as good as possible the growth environmental conditions, the substrates go through several modules before being introduced into the epitaxy chamber. These modules, namely the loading, heat treatment and transfer modules for the system described here, permit to perform operations such as substrate-holder loading, handing, outgassing and heat treatment. The substrate, mounted on a substrate holder, is inserted into a cassette carrier, which is moved from one module to another by using rotary motion handles. Magnetic motion transfer rods allow substrate holder manipulation. Gate valve isolate the different modules.

4.2.2.3 Epitaxy chamber

The epitaxy chamber, where the growth is elaborated, consists of three main parts: the evaporation flange, the manipulator and the analysis equipments.

- **Evaporation flange**

The evaporation flange bears the various cells containing the materials to be evaporated, and is equipped with two panels liquid nitrogen cooled (main and cell). Each cell – effusion cell, load-lock cell, cracker cell, mercury cell, gas cell- has its own heating power supply (temperature) computer controlled regulation. The cell shutter motors can also be computer-controlled. A viewport allows pyrometric sights to calibrate the substrate holder temperature.

- **Manipulator**

The manipulator that houses the substrate permits its orientation (epitaxy, flux measurement or transfer) and continuously rotates during epitaxy to improve uniformity. It features an inner fixed furnace and a Bayard-Alpert triode gauge to measure fluxes. Using micrometer screws makes the position adjustment.

- **Analysis equipment**

The system features a quadrupole probe to analyze the residual atmosphere and a RHEED electron gun to verify onto a fluorescent screen the crystal-lographic correctness when starting the growth.

4.3 Substrate preparation and cleaning techniques

Substrate: The (100) n-type GaAs wafer dope with Si 3-5 x 10^{18} cm-3 is used to prepare as substrate. For our horizontal LPE system we need to use two pieces of 10x10 cm^2 substrates.

Dummy: The (100) non-doped GaAs wafer is used to prepare as dummy for compensating the solution in each bin of the graphite boat. Consequently, a piece of 5 x 10 cm^2 dummy is needed for each layer growth.

Before loading into LPE system, we need to clean both substrate and also dummy by chemical etching as the following steps:

Step	Solution	Time (min)
1	DI-Water	5
2	Boiled acetone	5
3	Methyl Alcohol + Ultrasonic	5

Step	Solution	Time (min)
4	Boiled acetone	5
5	DI-Water	-
6	HCl (50%)	5
7	DI-Water	-
8	N_2 Gas	-
9	H_2SO_4+H_2O_2+ DI-Water	$\frac{1}{2}$ (Substrate) 6 (Dummy)
10	DI-Water	-
11	HCl (50%)	5
12	DI-Water	-
13	N_2 Gas	-

Precaution: The substrate and dummy should not prepare before use for long time. In case of necessary, they are recommended to store in the HCl solution, but not exceed 10 hours.

4.4 Material preparation and calculation

4.4.1 Material preparation

For material systems where it can be used in the growth of GaAs, or $Ga_{1-x}Al_xAs$ epilayer should be commonly prepared in the Ga-solvent and so other materials such as As, Al and also dopants are prepared as the solute. The commonly n-type dopant is Sn or Te, and as for p-type is Ge or Zn. These materials are prepared in the form of solid, and can be calculated by the mass conservation.

$$X_{Ga}+X_{As}+X_{Al}+X_{im} = 1 \quad (4.1)$$

Where X is the mole fraction of each element in the $Ga_{1-x}Al_xAs$ alloy. The proportion of Ga weight (W_{Ga}) to As weight (W_{As}) can be written as

$$W_{As} = (X_{As}/X_{Ga}).(M_{As}/M_{Ga}).W_{Ga} \quad (4.2)$$

Where M is the atomic weight of each element. Therefore another element can be also written as

$$W_{Al} = (X_{Al}/X_{Ga}).(M_{Al}/M_{Ga}).W_{Ga} \quad (4.3)$$
$$W_{im} = (X_{im}/X_{Ga}).(M_{im}/M_{Ga}).W_{Ga} \quad (4.4)$$

The weight of GaAs compound(W_{GaAs}) is the given by

$$W_{GaAs} = (X_{GaAs}/X_{Ga}).(M_{GaAs}/M_{Ga}).W_{Ga} \quad (4.5)$$

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 mole fraction of each element can be approximated from graphs as shown in Fig. 4.4, 4.6, 4.6 and 4.7

4.4.2 Material weight calculations

The calculations of the weight of materials such as $Ga_{0.6}Al_{0.4}As$ (P^+) and GaAs (n^-) are shown, for example, below[1] whereas the weight of every grown layer are all reported in table 4.1.

- **$Ga_{0.6}Al_{0.4}As$ (P^+) 10^{19} cm^{-3} Ge-doped**

$X_{Al} = 0.003$
$X_{As} = 0.015$
$X_{Ge} = 0.04$

Then, we get $X_{Ga} = 1 - X_{As} - X_{Al} - X_{Ge} = 0.942$

As we use 3 g of Ga, therefore we get

$$W_{Al} = (X_{Al}/X_{Ga}).(M_{Al}/M_{Ga}).W_{Ga} = (0.003/0.942).(26.98/69.72).\ 3\ g = 3.7\ mg$$

$$W_{Ge} = (X_{Ge}/X_{Ga}).(M_{Ge}/M_{Ga}).W_{Ga} = (0.04/0.942).(72.59/69.72).\ 3\ g = 132.63\ mg$$

$$W_{GaAs} = (X_{GaAs}/X_{Ga}).(M_{GaAs}/M_{Ga}).W_{Ga} \approx (X_{As}/X_{Ga}).(M_{GaAs}/M_{Ga}).W_{Ga} = (0.015/0.942).(144.64/69.72).\ 3\ g = 99.1\ mg$$

- **GaAs (n^-)**

$X_{As} = 0.022$

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

As we use 3 g of Ga, therefore we get

$$W_{GaAs} = (X_{GaAs}/X_{Ga}).(M_{GaAs}/M_{Ga}).W_{Ga} \approx (X_{As}/X_{Ga}).(M_{GaAs}/M_{Ga}).W_{Ga} = (0.022/0.978).(144.64/69.72).\ 3\ g = 140.01\ mg$$

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[1] X_{Al} can be approximated from graphs as shown in Fig. 4.4[for $Ga_{1-x}Al_xAs$ (P^+)] and Fig. 4.6[for GaAs (n^-)], whereas, X_{As} and X_{Ge} of $Ga_{1-x}Al_xAs$ can be approximated from graphs as show in Fig. 4.7 and 4.5 respectively

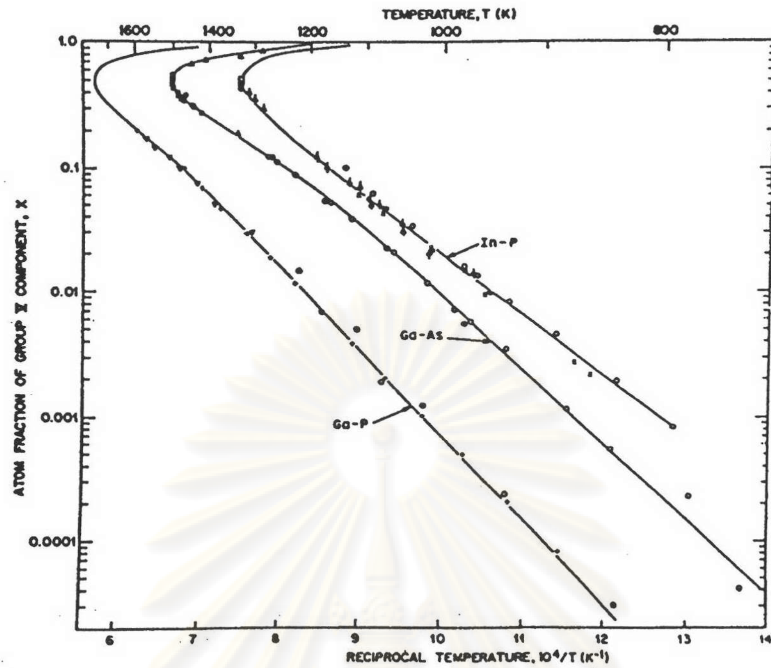

Fig. 4.4 Liquidus composition versus reciprocal temperature for GaAs, GaP and InP

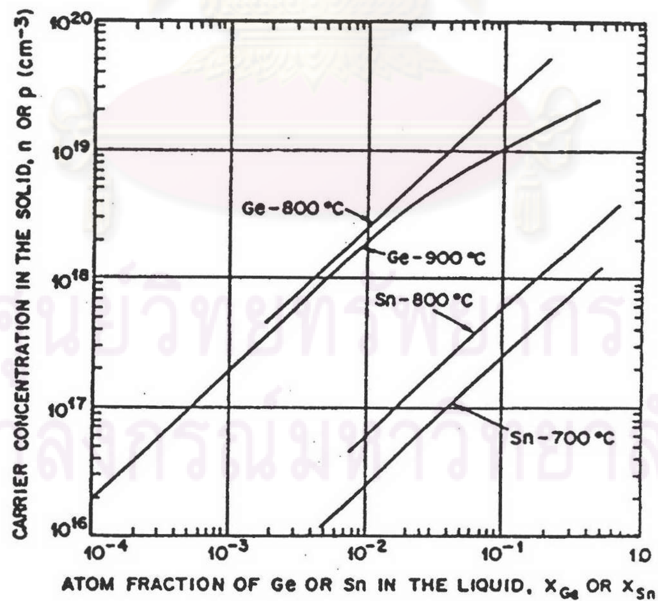

Fig. 4.5 The upper curves are the room temperature hole concentration in GaAs versus the atom fraction of Ge in the liquid along the 800 and 900 °C and the lower curves are the room temperature electron concentration in GaAs versus the atom fraction of Sn in the liquid along the 700 and 800 °C

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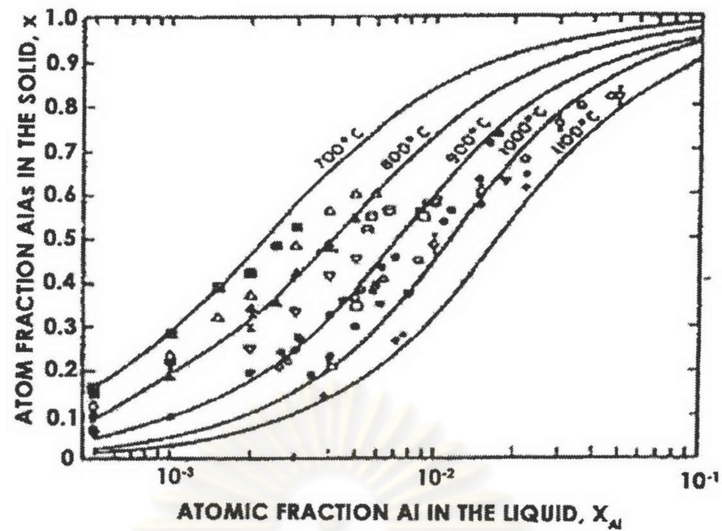

Fig. 4.6 Solidus compositions in $Ga_{1-x}Al_xAs$ as a function of liquidus composition

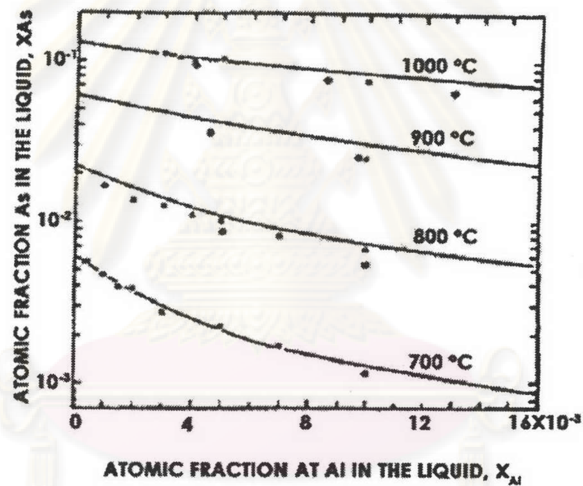

Fig.4.7 Liquidus isotherms in the GaAlAs system

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Material / Solution	Ga(g)	GaAs(mg)	Al(mg)	Ge(mg)
$Ga_{0.6}Al_{0.4}As$ (P^+)	3	99.1	3.7	132.63
$Ga_{0.7}Al_{0.3}As$ (P^+)	3	112.42	2.28	132.75
$Ga_{0.8}Al_{0.2}As$ (P^+)	3	119.064	1.3572	132.7875
$Ga_{0.9}Al_{0.1}As$ (P^+)	3	132.46	0.5001	132.948
$Ga_{0.7}Al_{0.3}As$ (N^-)	3	75.75	2.35	-
$Ga_{0.8}Al_{0.2}As$ (N^-)	3	140.75	1.19	-
$Ga_{0.9}Al_{0.1}As$ (N^-)	3	140.1	0.6	-
GaAs (n^-)	3	140.01	-	-

Table 4.1 Material weight

4.5 Growth process

4.5.1 Liquid phase epitaxy

In a normal growth run, after the boat is loaded with the substrates and the material solutions according to table 4.1, it is placed in the quartz tube, but initially remains outside the furnace. At first, it is flushed with flowing N_2, evacuated and checked for leaks (approximately 1 hr.), then flowing with Pd-purified H_2 (prevents oxidation of the solutions and the substrate). The furnace is then moved into the position for heating the boat as illustrated in Fig. 4.8. Temperature control is very important in LPE and is related to the growth rate, crystal quality, and so forth.

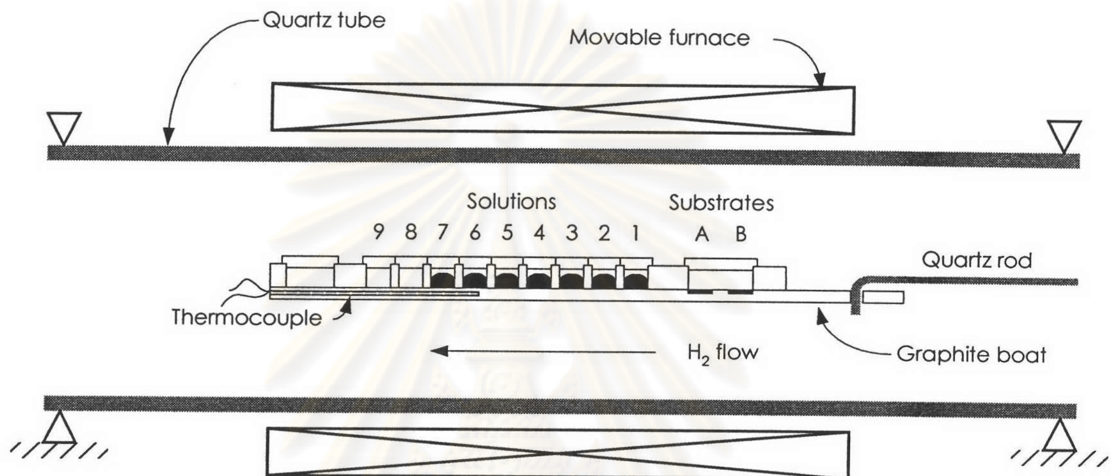

Fig. 4.8 Basic setup for LPE system

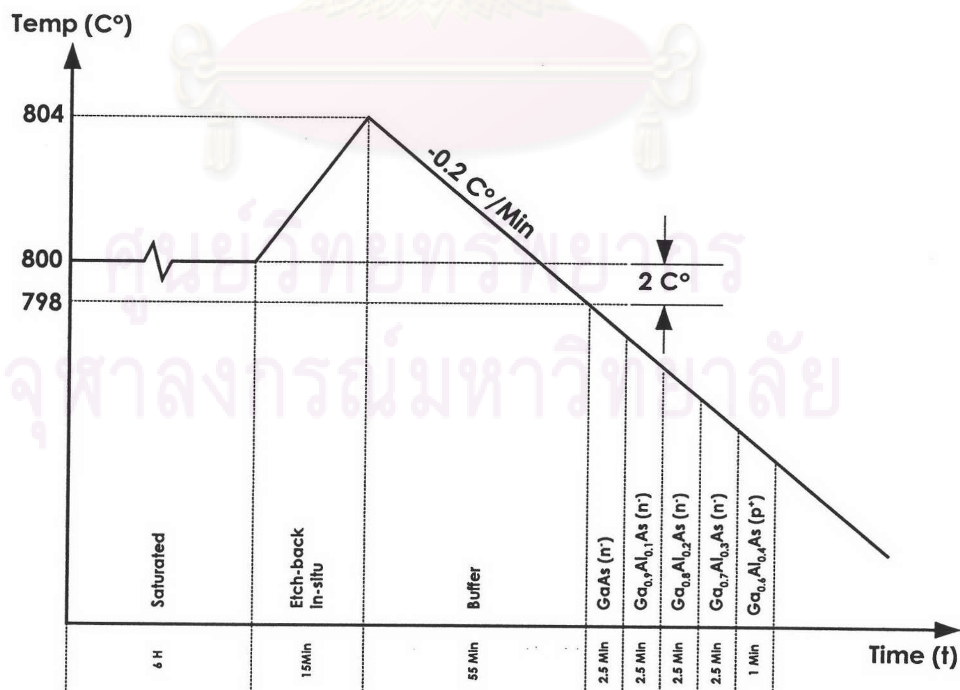

Fig. 4.9 The schematic profile of the furnace temperature versus the growing time duration

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The schematic profile of the furnace temperature versus the growing time duration is shown in Fig. 4.9. Firstly, the temperature is kept constant at 800 °C at least 4 hours to saturate the material solutions and then steps up to 804 °C for the in-situ etching. After the temperature reaches the peak of 804 °C, it is adjusted steadily decreasing at the rate of 0.2° C/min to oversaturate (supersaturate) the material solutions. Just then the temperature of the solution is below the saturation condition, the epitaxial layer naturally starts growing. In other words, the more the temperature of solution is below, the more the solution is oversaturated. At the moment, an oversaturated solution comes into contact with a 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 the solution. The thickness of a grown layer can be determined by the oversaturation temperature and the length of time in which the substrate and solution are in contact. The layer thickness is can then be expressed as

$$d = K\left(\Delta T^{\frac{1}{2}} + \frac{2}{3}\alpha t^{\frac{3}{2}} \right) \tag{4.6}$$

where K is the constant which is a function of concentration of As in the liquid
ΔT is the oversaturation temperature of solution
α is the cooling rate

After the epitaxial growth, the substrates need to check the surface morphology and the thickness of the designed layers by Optical Microscope and Scanning Electron Microscope (SEM) respectively.

4.5.2 Molecular beam epitaxy

The procedures of epitaxial growth can be briefly described hereunder:

1. Generally, the (100) GaAs substrate, before loading into MBE system, is chemically cleaned following the steps described in section 4.3. It is the case that the substrate is epi-ready type and kept in a dust-free condition so the chemical cleaning process is not necessary. After mounting on the molybdenum block with indium glue, the GaAs substrate is preheated at 450 °C for an hour in the preparation chamber. The substrate is then transferred to the growth chamber and the chamber has been liquid nitrogen cooled. The titanium sublimator of the growth chamber is switched off.

2. 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 (see item 3)

   Ga 300 °C → 910 °C

   Si 300 °C → depend on the carrier concentration designed

3. Rotate the manipulator up by 224 degrees to obtain the "optimum" flux pressure measurement position. The gallium flux will first be measured. The Ga-containing cell and the main shutter are then opened, while the others are closed. Adjust the Ga cell temperature to get the flux pressure of 4.3x10^{-7} Torr

(wait until the pressure is stabilized). The growth rate of GaAs is then get 0.8 μm/hour. Close the individual cell shutter as well as the main shutter. To get the ternary compound $Ga_{0.9}Al_{0.1}As$, we have to adjust the Al cell temperature by reading on the gauge:

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

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

The Al flux of $Ga_{0.8}Al_{0.2}As$, $Ga_{0.7}Al_{0.3}As$ and $Ga_{0.6}Al_{0.4}As$ are, therefore, obtained:

$Ga_{0.8}Al_{0.2}As$

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

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

$Ga_{0.7}Al_{0.3}As$

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

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

$Ga_{0.6}Al_{0.4}As$

$$\text{Al flux} = 4.3 \times 10^{-7} \times \frac{40}{60} \times \frac{0.92}{1.68}$$

$$= 1.5698 \times 10^{-7}\ \text{Torr}$$

Gradually increase the As cell temperature up to 190 °C. 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 that of Ga, so that it may reach about 8.6×10^{-6} Torr. During this time, the substrate temperature is adjusted to be 300 °C.

4. Rotate up the manipulator to obtain 320 degrees (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 then opened. By using the deflectors, position the electron beam so that it strikes 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 the spotty pattern is clearly observed. Set the substrate temperature cool down by 20 °C less than that of the temperature. Deoxidation is then processed for approximately 10-15 min. The streaky pattern will slowly appear. They gradually become less and less diffuse as the oxide evaporates.

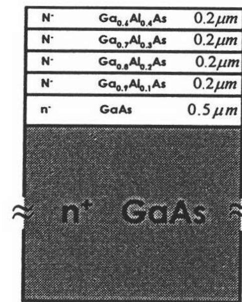

Fig. 4.10 The MBE growth device structure

5. Open the Ga individual shutter to begin the GaAs deposited on the substrate. Store at this condition until the designed thickness is obtained (e.g. 2 hour 30 min to obtain 2 μm of GaAs epitaxy for the growth rate 0.8 μm/hour). Another cell shutter (such as Al and Si) is also opened if either the GaAlAs epitaxial layer or the dopant is required.

Remark that the device structure, for example, as illustrated in Fig. 4.10 is not yet the p-n junction since our MBE cannot grow the p-type epitaxial layer. To form the p-n junction on the epitaxial substrate, it needs to be diffused by p-type dopant. The way to achieve this purpose is realized by Zn-diffusion, described in the following section.

4.6 Zn Diffusion

The experimental technique utilizes a confined chamber in LPE graphite boat modified to hold the diffusion source and wafer in close proximity as illustrated in Fig. 4.11. The Zn is dissolved in a solvent melt such as Ga or Sn as a diffusion charge. In this research, the diffusion charge contains 0.04 g Zn and 0.25 g Sn for the doping carrier concentration of 10^{18} cm^{-3}. The diffusion boat is loaded with the wafer and diffusion charge, then it is placed in a growth tube of LPE system, but initially remains outside the furnace. Until the temperature reach 600 °C, the furnace center is moved to the position of the boat to heat for the desired time under an ambient of flowing hydrogen gas.

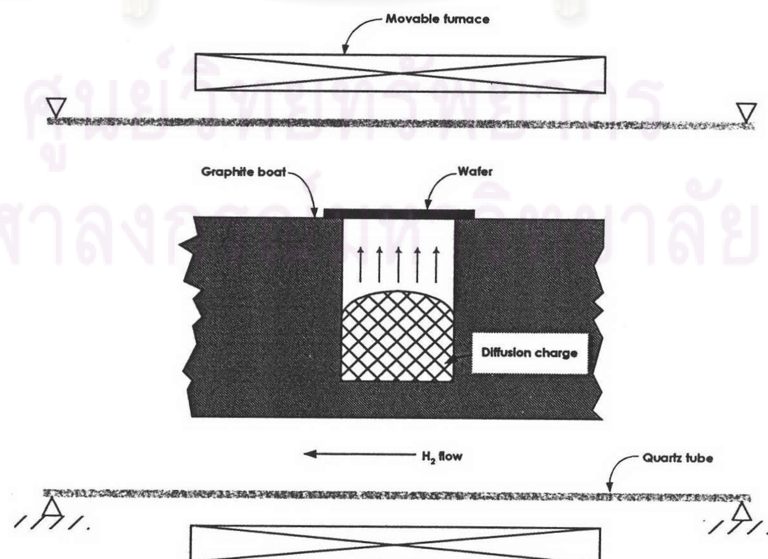

Fig. 4.11 Crossectional view of a modified graphite boat showing diffusion charge and confined vapor chamber between the charge and wafer

In our experiment we found that the heating temperature of 600 °C with the hold time 30 minutes allows the Zn diffuses into the GaAs (n^+) substrate 1.09 μm depth as seen in Fig. 4.12. Its IV characteristic shows the cut-in voltage ~1 V and the breakdown voltage ~ 2 V, as shown in Fig. 4.13.

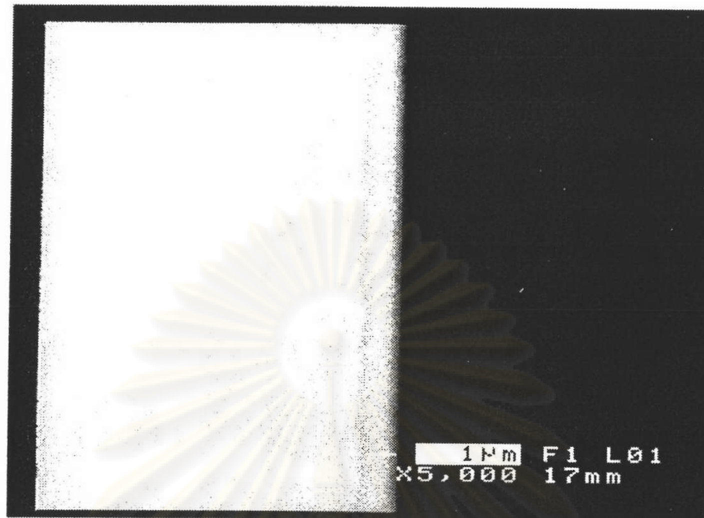

Fig. 4.12 The Zn diffusion depth of 600 °C for 30 minutes

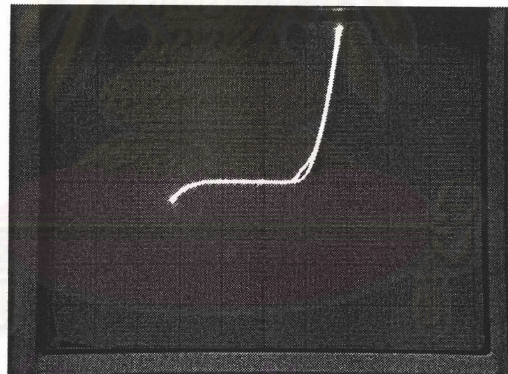

Fig. 4.13 The IV characteristic of Zn diffusion pn junction under 600 °C for 30 minutes

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4.7 Device structure formation

After all epitaxial layers are satisfied, the substrates are then cleaned by HCl (50%) solution to remove the residual oxide layer and also the sticking Ga from the surface. Next, the substrates are ultrasonic cleaned and thoroughly washed by DI-water and then dried by blowing N_2 gas. Up to this point, the device can be processed as follows:

4.7.1 Metallization

After cleaning, the device needs to be made the contact by metal films, which are allowing as electrical signal to enter in and come out of the device. In this research metal films can be formed by the method of filament evaporation. More often the alloyed contacts in GaAs devices are based upon Au or Ag, and these alloys usually contain Zn as the dopant for contacting p-type material and Ge or Sn for contacting n-type. Therefore, the Au-Ge-Ni system was used for n-type GaAs and the AuZn alloy was used for the p-type. During alloying above the Au-Ge eutectic temperature (360 °C), the Ge apparently formed an n^+ layer sufficiently heavily doped to produce a linear current voltage characteristic as a result of field emission at the contact interface. The Au-Ge alone did not wet the GaAs surface well during alloying, but the presence of a small amount of Ni is greatly improved surface uniformity of the alloyed Au-Ge contact and decreases the incorporation of the Ge in GaAs. The thickness of 2500 A° and 500 A° of AuGe and Ni respectively were deposited in our work and then the contact was annealed at 475 °C for 2 minutes in a forming gas 10% H_2 + 90% N_2. Whereas, a 2500 A° thick AuZn alloy is depositing onto the p-type contact.

4.7.2 Photolithography and mesa etching

Lithography is the process of transferring the geometric patterns on a mask to a thin layer of radiation-sensitive material called resist covering onto the surface of a semiconductor wafer. These patterns define the regions of the contact, windows and also the bonding pad areas. The resist film is then subjected to a development process that selectively removes either the exposed or unexposed resist depending upon the photoresit type. Basically, photoresists can be classified as positive or negative, depending on how they respond to radiation. The positive type removes the exposed resist. The net result is that the patterns formed in the positive resist are the same as those on the mask. The negative type forms patterns that are the reverse of the mask patterns because the exposed regions are made less soluble. The photolithography and mesa etching are carried out as follows (See Fig. 4.14);

1. Prebake the device at 90° C, 5 min. Apply a layer of positive photoresist film onto the AuZn film on the p-type contact. Then softbake the device at 90° C 7 min. (Fig. 4.14 (a))

2. Exposure of the photoresist through a patterned contact mask (see Fig. 4.15) by photoexpose. (Fig. 4.14 (b))

3. Developing of the photoresist, then postbake at 120° C, 17 min. Coating another side of substrate with positive photoresist and replicated postbake at 120° C, 3 min. (Fig. 4.14 (c))

4. Etching metal film patterns and rinsing of the patterned photoresist. Anealling the device again at 450° C, 30 sec. in a forming gas 10% H_2 + 90% N_2. (Fig. 4.14 (d))

5. Repeating step 1 to 4 by using mesa mask.

6. Mesa etching by H_2SO_4:H_2O_2:H_2O (3:1:15) etchant (etched rate~ 1.5μm/min). (Fig. 4.14 (e))

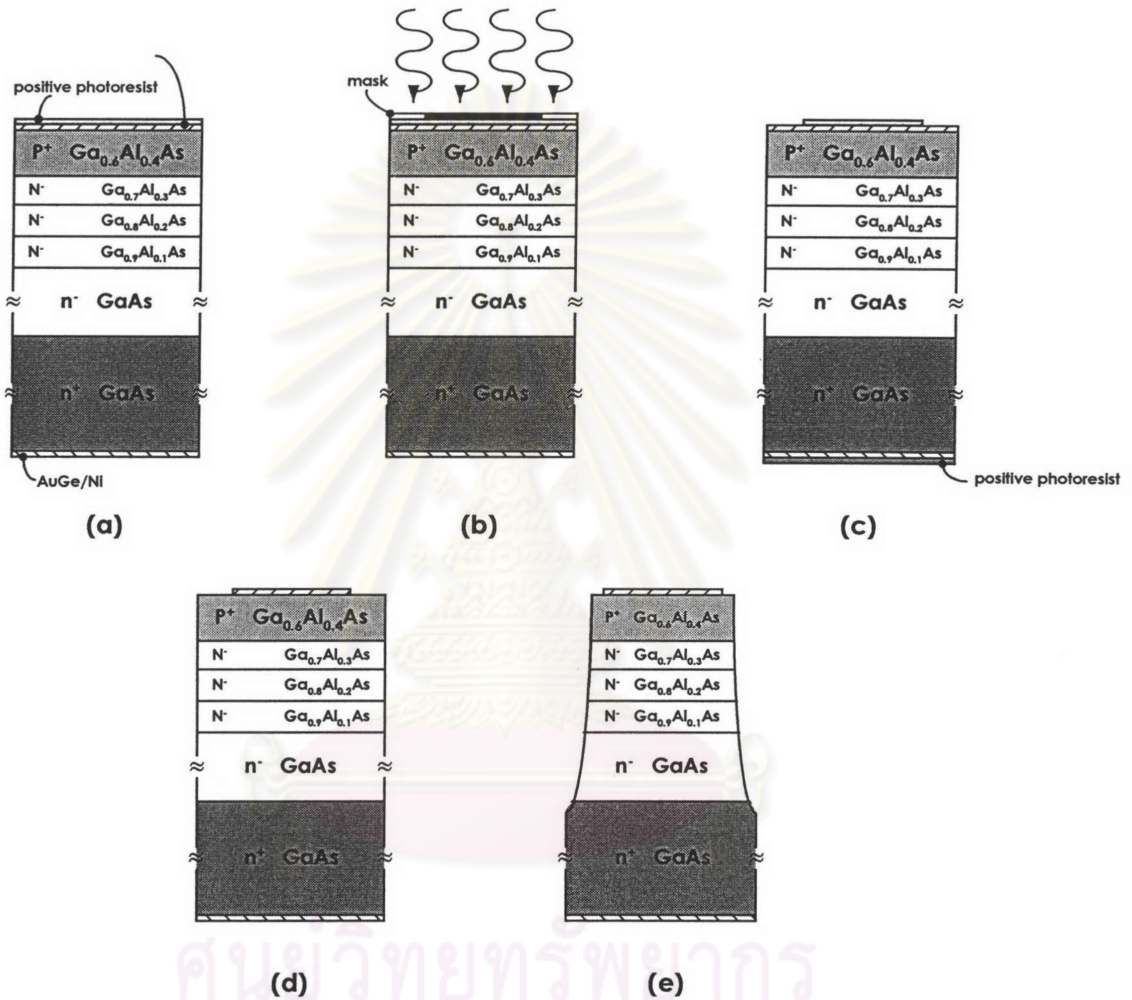

Fig. 4.14 The phtolithograpy process
(a) Photoresist coating
(b) Photoexpose
(c) Developing of the photoresist
(d) Etching metal film patterns
(e) Mesa etching

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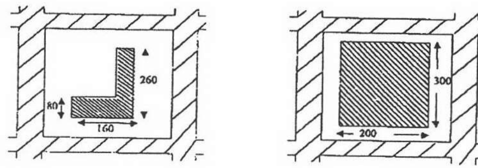

"Contact mask" "Mesa mask"

Fig. 4.15 Contact and mesa mask

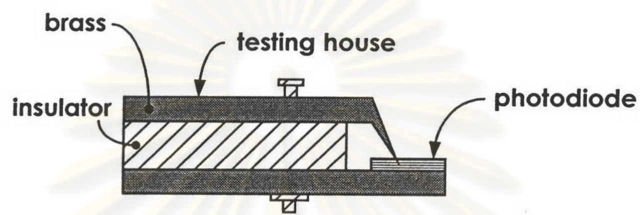

Fig. 4.16 Testing house

The realized photodiodes are then separated by cleaving and afterwards each chip is mounted on the testing house for characterization. (see Fig. 4.16)

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