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Compound Semiconductor Epitaxial Growth Techniques

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Abstract: The aim of this paper is to review the different growth techniques used for compound semiconductor epitaxial layer growth, including LPE, HVPE, MOVPE, MOCVD, MBE & their reasonable comparison. As the compound semiconductor have elegant characteristics, so recently different semiconductor and its alloys becoming great importance in many applications due to its variable band gap properties. We can change its properties by changing temperature, doping & carrier concentration, & most importantly the performance of semiconductor devices strongly dependent on precious control of growth techniques. So, the choice of efficient growth techniques by accumulating with the proper doping we can get high quality semiconductor device, as well high power and high temperature electronics devices.

Keywords: Growth techniques, Deposition, Film growth, Epitaxy.

1 Introduction

Now a day's semiconductor materials attain great attraction due to its elegant properties, e.g. GaAs, GaN, InGaN etc. The GaAs is a group III -V compound semiconductor with a direct optical band gap of around 1.5eV which makes it suitable for thin film solar cell and light emitting diodes. GaAs devices also generate less noise than other types of semiconductor. This is very important in weak-signal amplification application [2]. The absorption coefficient of GaAs is very high at the band edge, hence high purity and perfection of thin layers of GaAs is required [2]. It can be achieved by choosing a right epitaxial growth technique. Major fields of application of GaAs are e.g. Integrated-optics-GaAs, AlGaAs; Optical detectors-GaAs, GaInAs; Injection lasers-GaAs, AlGaAs; Photovoltaic cells-GaAs, GaAlAs; Optical isolators- GaAs, GaAsP [2]. Currently, GaN is the most important member of this material class III-IV [4]. Therefore, it is typically needed as substrate for the respective epitaxy of device structures. The synthesis of GaN bulk material is very difficult. Hence, the conventional growth of bulk crystals can only be done under some extreme conditions. Many current investigations focus on various methods of growth out of solutions [4]. So we need growth of fairly thick epitaxial layers (several 100μm) on foreign substrates which then can be used as quasi-substrates [12]. GaAs is also a potential substrate having the advantages such as the iso-electronic structure [3]. Moreover, nowadays, it is mostly used as substrate for the growth of thick GaN layers by HVPE which then act as quasi-substrates. In fact, this thick GaN can easily be removed from GaAs simply by wet chemical etching [4].

GaN has attracted much more attention as an efficient material for optoelectronic devices in the blue and near UV region [2]. Hydride vapor phase epitaxy (HVPE) [14-16], Metal organic vapor deposition (MOVPE) [17, 18] and Molecular beam epitaxy (MBE) [19] are the most popular and accurate methods used for GaN epitaxial growth. HVPE is one of the premature techniques that are used for GaN growth; it offers high growth rate. MOVPE has become the main technique for the growth of GaN and its alloys. It has produced the highest quality of GaN based devices, light emitting diodes (LED) [18] and laser diodes (LD) [15]. MOVPE and MBE can produce a variety of interesting structures such as quantum well [20], quantum wire and quantum dots [21], which need abrupt changes in composition and doping during growth. In this paper we review the various techniques used for GaAs & GaN heteroepitaxial growth including recent modifications that have been done on each technique.

2 Epitaxial Growth Techniques

2.1 Liquid Phase Epitaxy (LPE)

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The growth in LPE is controlled by moving the metallic solution mechanically onto the sample substrate & this sample substrate is brought into contact with a saturated solution of the film material at an appropriate temperature(shown in fig:1). The substrate is then cooled at a suitable rate to lead to film growth) .This is normally done by using tilting crucible or sliding boat technique [13].In a sliding boat technique multi chamber susceptor are used which being filled with saturated solutions. That can be moved over the substrates one after the other by this way & enabling desired multi hetero structure growth. We can control our desired epitaxial layer thickness by temperature variation [4].

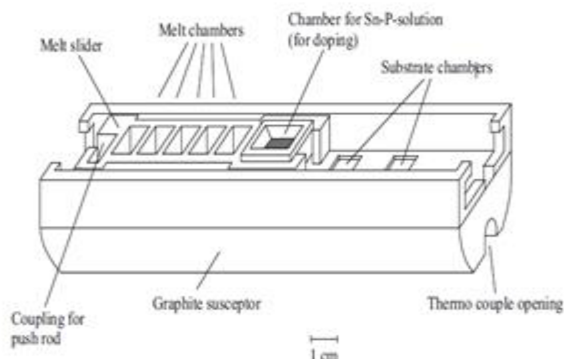

Fig 1: Sliding boat susceptor of a LPE system [5].

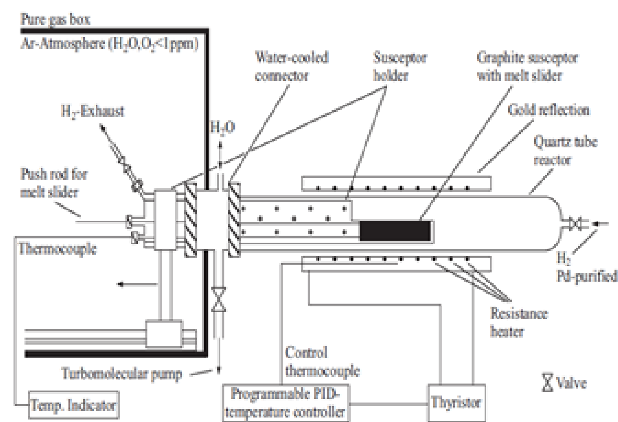

Fig 2: The resistance heater can be shifted to the right to allow fast cooling of the susceptor (LPE system.) [5].

By using a sliding a boat, steeper motor, effective & fast process time can be achieved (shown in fig: 2). With a high amount of care, thicknesses down to 10 - 20 nm could be achieved [4]. The largest challenge in LPE in the case of heteroepitaxy is the misfit between substrate and epilayer at the growth temperature and the difference of the thermal expansion coefficients [10].

2.2 Vapor Phase Epitaxy (VPE)

The elements which are needed (Ga, Al, In, As, P) in VPE are not gases. However, metals typically do not form gaseous compounds at all. We can synthesis of a volatile compound at high temperatures *in-situ* in the epitaxial reactor [11]. This can be done by reacting the metal with HCl gas at temperatures above 600^oC.In VPE solid epitaxial layers are deposited by passing chemical vapors over a substrate. Two types of reactor are used in VPEE ,one is horizontal type; here the growth temperature is usually kept between 950 and 1050°C. Sapphire is the most important substrate used for HVPE GaN growth. In order to improve the nucleation density of GaN layer on (0001) sapphire, GaCl pretreatment or RF sputtered ZnO buffer layer techniques are used [11]. Wheres Vertical reactor can also be used to grow GaN, facilitates substrate rotation during growth that improves the uniformity of the film [11].The two methods for VPE growth of III -V compounds are the chloride method and the hydride method [2].

For the group V elements, two main methods have been discussed in the flowing subsection:

1) *Hydride Vapor Phase Epitaxy:* The HVPE Growth with its high growth rate up to 100 mm/h appear to be a very attractive technique for production of high quality, large diameter and thick GaN layers (>200mm in thickness) which eventually used as free-standing substrates. So far freestanding GaN layers with thickness of 230mm and area up to $10mm^2$ has been achieved [1]. HVPE regarded as quasi bulk technique for GaN growth. In the hydride process the substrates are held at about 1100°K on a rotating wafer holder while arsine and gallium chloride gases are mixed and passed over the substrate (shown in fig. 3). HCI and the group V hydride gas are provided by separate gas precursor lines. Hence, the control of group III and group V is independent from each other. The HCI gas reacts *in-situ* in the reaction chamber with the hot metal forming MeClGas which further flows to the substrate thus transporting the metal component to the growth zone. At the substrate surface (heated typically 600 to 800^oC) the growth reaction takes place:

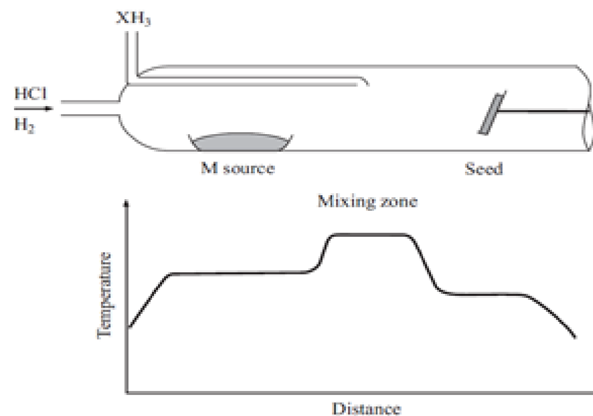

Fig 3: Hydride VPE system [6].

2) *Chloride Vapor Phase Epitaxy:* Arsenic in chloride passes over gallium metal to form GaCl. Here, the HCl

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gas is generated *in-situ* from the chlorides XCl_3 ($AsCl_3$, PCl_3), which simultaneously are used as group V precursor. These liquid compounds are stored in so called bubblers at a stabilized temperature which defines their vapour pressure $pXCl_3$. Through these bubblers, the carrier gas is flown which gets saturated with the material according to its vapour pressure [14].

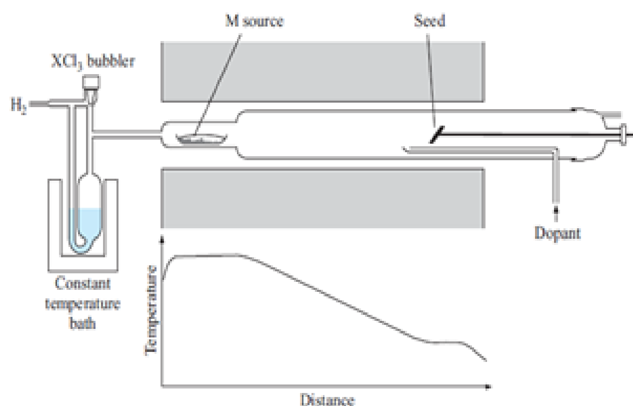

Fig 4: Chloride VPE system [6].

The XCl3 enters the hot reactor where it chemically reacts. The products are XH3, HCl, X2, X4, XCl3. All these arrive at the liquid metal source, where the elemental products are solved up to saturation .This requires a good temperature control of the metal source. In some cases, they form a solid crust on top limiting the useability of the source. As in the Tietjen process, the *in-situ* generated HCl reacts with the metal to form MeCl which then is transported to the substrate.

2.3 Metal Organic Vapour Phase Epitaxy (MOVPE)

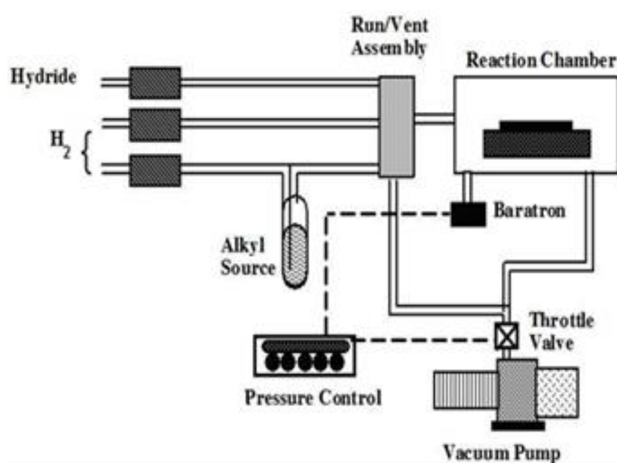

Fig 5: Schematic diagram of simple MOVPE reactor [7]

The epitaxial structure is the heart of the semiconductor device and metal organic vapour phase epitaxy (MOVPE) or synonymously metal organic chemical vapour deposition (MOCVD) is considered the dominant technique. In MOVPE metal organic compounds are used as the group-III precursors [12]. A typical example for these metal organic compounds is tri-methyl-gallium TMGa (Ga (CH3)3), while ammonia NH_3 is used as nitrogen source. These precursors are brought into the reactor using a carrier gas. In MOVPE growth technique, the chemical reactions take place only near the substrate or on the substrate surface and then the products are deposited on the substrate.

$$Ga\,(CH_3)_3 + NH_3 = GaN + 3CH_4$$

The bubbler technology is used for transporting the gas precursors. By doing adjustments of the parameters, the alloy composition and impurity doping, abruptness of layers can be controlled quite precisely. In the reactor chamber a RF coil is used to increase the susceptor temperature while the reactor walls remain at a rather lower temperature. The substrate is kept on the susceptor and in order to enhance the homogeneity over the surface of the epilayer, the susceptor rotates during the growth. The carrier gas which is generally high purity hydrogen gas is fed to the system and is saturated with the precursor material in the bubbler. However, recondensation due to oversaturation should be avoided by keeping the bubbler temperature below at room temperature. After transportation of the materials, the epitaxial growth takes place on the substrate [16].

The temperature of the substrate plays a vital rule for chemical reactions and cracking of the precursors. Depending on susceptor temperature three distinct growths rate regimes exist during growth in MOVPE, such as low temperature regime (roughly 700 K), medium temperature regime (roughly between 700 K to 1200 K depending on the materials) and high temperature regime (roughly above 1200 K). The medium temperature regime is the normal temperature range for MOVPE because in this range the growth rate is limited by the group III precursor supply but does not depend on temperature [12] .

2.4 Molecular Beam Epitaxy (MBE)

This is the most precious method for deposition. The idea is very simple like develop the “Gas phase epitaxy” by using the needed elements and nothing else. The elements are not gaseous, but (nearly all) are solids. *For that* Vaporization is necessary which requires high temperatures (some 100°C). But, a transport in gas lines is not possible (or the gas lines must be hotter than the vaporization temperature). Hence, vaporized material transported as molecular beam in an ultrahigh vacuum (UHV) environment.

Then, there is no problem with particle-particle interaction. Basic construction is quite simple. Just use an ultrahigh vacuum chamber. On the one side introduces molecular beam; place the substrate where the epitaxial growth should take place. Every needed element is heated for evaporation [12].The respective molecular beams hit the substrate.

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Heating of the substrate is needed so that the atoms can find their correct site on the surface.

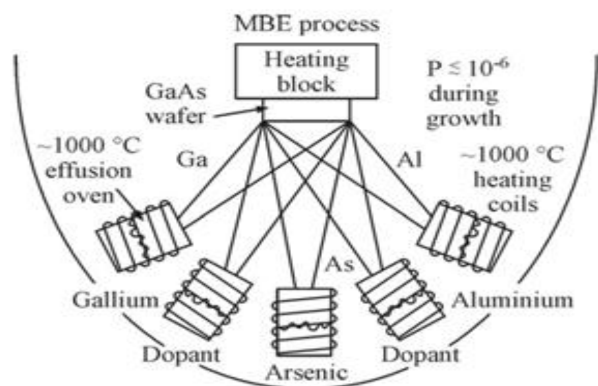

Fig 6: Basic principle of a MBE system [8].

Table 1: Application of different techniques for devicee

Device	Growth techniques
Laser, Field Effect Transistors Avalanche photo diode	VPE, LPE &MBE
Charge coupled devices, Photocathode	MOVPE
Photodiode (eg. PIN)	MBE
Light emitting diode	VPE,LPE
Solar cell	MOVPE,MBE

Table 2: Effective comparison of different techniques

Epitaxial Growth	Pros	Cons
LPE	Simplicity of equipment Higher deposition rates	Scale economics, inflexible
VPE	Very high growth rate Well developed	Hazardous precursors Extreme tempera
MOVPE	Potentially flexible uniform growth Selective growth In-situ monitoring High throughput	Expensive reactants hazardous precursors Lack of in-situ characterization hazardous precursors
MBE	Sharp interfaces In-situ characterization Hydrogen free environment Precise control of doping No chemical reaction Quality of layer is excellent	Oval defects low throughput Very Expensive Ultra-high vacuum Low growth rate Maintenance
	No boundary layer problem	difficult

3 Conclusion

The LPE, VPE, MOVPE, MBE etc has different advantages where proposed device structures could be strongly depends proper choice of techniques. Mainly LPE is done at lower temperature. This process is relatively fast but very difficult to grow thin layers. Thus, LPE is most important when ultimate performance of optoelectronic, optical, magnetic, magneto-optic and superconducting devices is envisioned. The thermodynamic limitation can be overcome by introducing VPE techniques. In Chloride VPE no toxic gas is necessary & cheap also compare to HVPE. We have flexibility problem in VPE techniques. We can have great flexibility in MOVPE techniques, only problem is no gases for group III elements are available. We can use metal organic compound, such compounds are at least liquid or solid with fairly high vapor pressure.

By utilizing Bubbler technology the parasitic reaction can be minimized by lowering the gas pressure. In this technique we can have even laminar flow, so by using low gas pressure we can suppress parasitic gas phase reaction between different precursor's molecules. In HVPE no saturation of metal source is necessary; therefore temperature control is not critical. But the problem is using toxic gases. In VPE we have boundary layers problem also, we can reduce it by increasing gas velocity but it cost much but HVPE the control of group-III & V is independent from each other, in Chloride VPE uses bubbler, through these bubblers, the carrier gas is flown which gets saturated with the material according to its vapour pressure. In MBE the Quality of layer is as good or better compare to other methods, because surfaces & interfaces can be growth with excellent flatness (1 atomic layer or less). The growth rate is in the range of 0.1 to 1 μm/h, important no boundary problem. Amongst the various techniques, MOVPE is becoming a popular technique due to flexibility & cost effectiveness to develop growth process with proven capabilities for the growth of GaAs & GaN based ternary and quaternary compounds.

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