A Brief Review of Growth Techniques for Obtaining of III-V Semiconductor Compounds


Abstract—Electronic devices have essential importance in our quality of life. Our species has multiple comforts and benefits obtained by current technology, such as microelectronics, optoelectronics, and nanotechnology. However, few are interested in the different physical phenomena that are behind our technology. This paper presents a brief review of four growth techniques for the obtaining of III-V semiconductors compounds. Techniques such as metalorganic chemical vapor deposition, hot filament chemical vapor deposition, liquid phase epitaxy, and molecular beam epitaxy are described in a simple way to motivate the understanding of the theoretical concepts that make operated our technology.

Index Terms—Growth, Layers, Epitaxy, Semiconductor Compound.

I. INTRODUCTION

The development of quantum mechanics during the first three decades of the XX century contributed to the consolidation of solid-state electronics, which nowadays has produced a technological revolution [1]. The study of electronic band structure has also allowed the understanding of conductors, insulators and semiconductor materials. The semiconductor materials have had a significant participation in our quality of life, productivity; moreover, they project a bright future for our species. In these days, the microprocessors, LED technology lamps, blue laser, microwave devices, solar cells, ultra-high power devices, computers, intelligent phones, smart TV’s, and communication technologies, would not be possible, without the semiconductor materials. The constant advance of the semiconductor technology as silicon, germanium and semiconductor compounds (GaAs, GaN AlGaN, etc), continues attracting the interest of the researchers to the obtaining of new semiconductor materials that allow the high complexity of the current devices.

On the other hand, the III-V semiconductor compounds have found applications in optoelectronic devices due to its direct band gap [2]. Generally, III-V semiconductor materials are synthesized by epitaxial growth, which consists in the obtaining a layer of solid material of a few micrometers or nanometers. The growth is made on a substrate (monocrystalline), where the layer grows with the same crystalline orientation of the substrate and its composition determines the band gap, refractive index and other important properties [3, 4].

The epitaxial techniques more commonly used in the obtaining of III-V semiconductor compounds are generally, metalorganic chemical vapor deposition (MOCVD), hot filament chemical vapor deposition (HFCVD), liquid phase epitaxy (LPE), and molecular beam epitaxy (MBE) [5]. This work presents a brief review of the techniques more used for the synthesis of III-V semiconductors compounds. It presents the MOCVD, and HFCVD techniques. Also, it is reviews the growth method by LPE, which use the solid-liquid equilibrium of a liquid metallic solution for the obtaining of a semiconductor layer. Finally, it is presents the MBE technique as a form of obtaining semiconductor layers with the greater crystalline quality.

II. DEVELOPMENT

A. Metalorganic chemical vapor deposition (MOCVD)

The manufacture of wafers from bulk material for some semiconductor compounds as GaN, continues be a weak point in the development of new devices. Thus, the heteroepitaxial growth on non-native substrates such as sapphire, SiC, ZnO, AlN and GaAs, is still a solution for the obtaining of semiconductor compound layers [3,6]. There are two important techniques for the epitaxial growth of structures based on III-V semiconductor compounds, metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). H.M. Manasevit [7], was pioneer in MOCVD, which demonstrated that the triethylgallium (TEGa) and the arsine deposited GaAs crystals. MOCVD is a technique used to deposit layers of atoms on a substrate. This technique consists basically in the introduced of metalorganic precursors in vapor phase with an open flow system, in which a carrier gas (usually H2, N2, He, Ar), transports the reactive species toward a hot substrate for obtain a crystalline layer [8, 9]. There are different gases that are used in MOCVD processes, which are classified according to their operation in precursors and carriers. The precursors have in their molecules the elements that will be incorporated into the layer.

The metalorganic compounds more important are showed

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in the Table I.

The growth mechanism during a MOCVD process can be classified in seven stages, which is shows in Fig. 1: 1) Transport of precursors to the growth region, 2) Transfer of the reagents to the substrate surface, 3) Rupture of the bonds of the metalorganic molecules and adsorption of one, or more radicals on the substrate surface, 4) Surface processes that include diffusion reactions and nucleation, 5) Desorption of subproducts, 6) Transfer of the subproducts to the main gas flow, and 7) Transport of the subproducts outside the growth region [8].

MOCVD process is highly complex due to the presence of different reagents, and multiphase chemical reactions. Generally, the fundamental process of MOCVD is divided into thermodynamic and kinetic [10]. The thermodynamic determines the control of forces during the growth process, while kinetic determines the form in which the different steps can occur. The kinetics of a reaction can be divided into mass transport and surface kinetics.

On the other hand, in the thermodynamics of the epitaxy is important to define the equilibrium of the different phases (solid, liquid, gaseous), and composition (constant temperature and pressure). The equilibrium is definite as the state in which the Gibbs energy per mole (G) is minimal. Gibbs free energy is definite in terms of the enthalpy (H) and entropy (S) (equation 1).

\[ G = H - TS \] (1)

TABLE I: TYPICAL METALORGANIC COMPOUNDS FOR THE GROWTH BY MOCVD

<table>
<thead>
<tr>
<th>Metalorganic Compound</th>
<th>(C(_2)H(_5))(_3)Al</th>
<th>(C(_2)H(_5))(_3)Ga</th>
<th>(C(_2)H(_5))(_3)In</th>
<th>(C(_3)H(_5))(_2)Mg</th>
<th>NH(_3 )</th>
<th>SiH(_4)</th>
<th>Si(_2)H(_6)</th>
<th>(C(_2)H(_3))(_2)Zn</th>
<th>(CH(_3))(_2)Zn</th>
</tr>
</thead>
</table>

Some advantages of MOCVD technique are its high versatility for growth different III-V materials, and growth of abrupt junction for devices. On the other hand, some inconvenient of MOCVD are the use of expensive precursors, besides highly dangerous [11-13].

B. Hot filament chemical vapor deposition (HFCVD)

Another technique used in the synthesis of III-V semiconductor compounds, which is related to the chemical deposition in vapor phase, is HFCVD. This technique is widely used due to easy configuration of deposit system. In HFCVD a molecules source in gaseous form are decomposed on a filament, which acts as a hot catalyst surface to produce free radicals. These radicals can directly deposit on the surface substrates to grow a layer. Also, radical species can initiate chemical reactions in gas phase to produce other radicals [14].

The quality and properties of the layers depend on the deposition parameters, such as substrate temperature, filament temperature, distance between filament and substrate, vacuum pressure, and composition of the filament [14]. The deposition process of HFCVD technique consists basically in three main processes: 1) Dissociation of the gas molecule on the surface of the filament, 2) Secondary reactions between filament and substrate, 3) Nucleation and growth of the layer over the surface substrate.
a temperature control, a line gasses, a bubbler flask, a variable transformer, and exhaust line with connection toward to a vacuum pump, and output to the atmosphere. Some of the advantages of HFCVD technique is its easily scalable method, so that, the scaling to large areas requires an increase in catalytic surface, besides of a greater supply of gas. Another advantage is that the substrates can be rigid or flexible, and these can be moved during deposition.

C. Liquid phase epitaxy (LPE)

The liquid phase epitaxy (LPE), consists in growth of monocrystalline layers on a substrate by direct precipitation, from a saturated liquid solution. The solution can be formed of two components, one of which acts as a solvent and the other as a solute. When the temperature of the saturated solution decrease slightly, is supersaturated, causing the precipitation of compound matter on the surface of the substrate [15]. The solvents most commonly used in III-V semiconductor compounds are gallium, and indium, this due to its low melting temperature [16]. Another element that can be used as solvent is the antimony with a melting temperature greater at 590 °C.

In general, liquid phase epitaxy method requires a furnace with a chamber in vacuum, which should be free of leaks, besides have a reducing atmosphere. The furnace also should have a thermal zone sufficiently flat, in which the solution will be located. The system should have a good control device for the cooling rate. Finally, it should be considered that the material to grow has a lower melting point than the substrate. In liquid phase epitaxy there are two different growth techniques, which could affect the type of layer obtained, its thickness, and surface morphology. The first is the steady-state growth, and the second is the transient growth. Transient growth is divided into; equilibrium cooling, step cooling, supercooling, and two-phase solution cooling.

Equilibrium cooling: In this technique, the liquid temperature coincides with the selected for growth. Then, at this temperature are put in contact the solution and substrate, starting the cooling. The growth time starts there, keeping the cooling rate constant (figure 4a).

Step cooling: In this technique, the substrate and the solution are at the same temperature, but separated. Then, the system is abruptly cooled, without causing a spontaneous precipitation of the solution. After this cooling, the temperature is conserve constant, and are put in contact the solution and substrate, starting the growth time (figure 4b).

Supercooling: In this technique, also the substrate and the solution are separated at the same temperature. In this moment, a constant cooling rate of the system begins. This should not be abrupt, and when the temperature chosen for growth is reached, the substrate and the solution are put in contact, starting the growth time without changing the initial cooling rate (figure 4c).

There are two kinetic phenomena, which take place when the solution is equilibrium state, and when is imbalance state, this is due to a decrease in the saturation temperature. These phenomena are the matter transport from the liquid phase and the coupling kinetics. The kinetic at the liquid-solid interface is very fast with respect to the matter transport, so that growth is limited by diffusion from the solution to the substrate surface. The deposition rate of the material depends on the elapsed time, since that the solution and the substrate are in contact, besides of saturation degree that has the solution.

The systems for the growth in liquid phase epitaxy are of three types [17]; tipping, dipping, and sliding. All uses a furnace as heater, whose temperature can be controlled. The difference between them is the accessory that is introduced in the furnace, in which the growth takes place. This accessory for growth is called a boat; the most important boats are described below:

Tipping: This boat was used by Nelson [17], for first time. To use this boat, the system should allow the inclination in both extremes, where initially the substrate is placed on top part of boat, while the solution is placed on lower part. When the solution has reached the saturation, and growth temperature, the boat is tipping until the solution into contacts with the substrate. Finished the growth time, the boat is returned to its original position, breaking the contact solution - substrate, ending the growth.

Dipping: This boat was used by Woodall for first time in 1969. In the system the furnace, and reactor are vertical, in which a crucible was placed in the lower part of the reactor. This crucible contains the solution, and the substrate is upon the solution. The process begins when the substrate descends and is submerged in the solution, where once the solution covers the substrate, the temperature is decreases. The process ends when the substrate is extracted from the solution.

These types of boats are designed to grow a single layer by process. Then are not convenient for growing multilayer structures in the same process, which is necessary for current devices.

Sliding: This boat was also developed by Nelson in 1971 [17]. The furnace and reactor have a horizontal shape, where the reactor is fixed at both extremes, while the heater rests on rails to be able to move horizontally and facilitate the heating or cooling of the boat. The boat can contain different solutions, which allows deposit several layers on a substrate during a one process. The material most used for this type of boat is graphite. A sliding boat is showed in Fig. 5 [18].

Figure 6a) shows a liquid phase epitaxy system, which consists of a quartz tube that functions as a reactor. Inside, the boat with the solution and substrate is placed. The boat and support are showed in figure 6b).
In Fig. 6a), the reactor passes through another quartz tube coated internally with a gold layer to concentrate the heat from the heater. The extremes of reactor rest on stainless steel supports. The caps and cap-passages were welded in argon atmosphere to reduce impurities. Other components of LPE system are a thermocouple, a temperature control, a line gasses, and exhaust line with connection toward to a vacuum pump, and output to the atmosphere.

A particular characteristic of growth by liquid phase epitaxy are the meniscus lines on the superficial morphology of layers obtained from III-V semiconductor compounds [15, 19]. Fig. 7a), shows the superficial morphology of a layer of AlGaAsSb on GaSb obtained by LPE at 350 °C, while Fig. 7b) shows the transversal section of layer. In these figures are shown the meniscus lines and the layer thickness of 1.25 µm.

Some LPE advantages is the simplicity of technique, besides that can be obtained samples of high-purity. On the other hand, an inconvenient of LPE is the little versatility to obtain abrupt junctions, besides of use limited of materials in which the nitrogen is incorporated (III-Nitride). Another inconvenient, is the difficult control of the growth rate of layers obtained by LPE.

D. Molecular beam epitaxy (MBE)

MBE is the deposit method technologically most important for the obtaining of ultra-thin layers on a monocrystalline substrate. MBE growth is characterized by its geometric precision and controlled composition, which highlights of other techniques such as MOCVD and LPE [20-23].

MBE is the dream of every semiconductor device designer. MBE has a careful regulation of the co-evaporation of the component elements in ultrahigh-vacuum conditions (UHV, 10⁻¹⁰ torr) (Fig. 8a). This implies a precise control of the chemical composition, crystalline quality, and doping levels, using an atom beams finely focused. Also, MBE is an important method due to the growing demand for nanotechnology. One of the main applications in MBE is the development of MEM devices, as well as the obtaining of microelectronic devices of high-quality, and purity (Fig. 8b).

Some MBE advantages are the obtaining of uniform layers, possibility of obtains abrupt junctions, in addition to high-purity devices and monitoring at the growth site. Some MBE inconvenient are slow production of electronic devices, high economic cost of system, in addition to difficulty in the growth of materials that incorporate As, S, and P.
III. CONCLUSIONS

This work presented a brief review of four growth techniques, which are widely used for the obtaining of III-V semiconductors compounds. MOCVD consists in the introduced of metalorganic precursors in vapor phase inside an open flow system, where a carrier gas, transports the reactive species toward a hot substrate to obtain the crystalline growth. Another technique related to the chemical deposition in vapor phase, is HFCVD. In this method, a molecules source in gaseous form is decomposed in a hot filament, which trough of high temperatures to produce free radicals. These radicals can directly deposit on substrate surface and this way grow a semiconductor layer. LPE consists in growth of monocrystalline layers on a substrate by direct precipitation, from a saturated liquid metallic solution. This solution generally can be formed of two components (solvent and solute). When the temperature of the saturated solution decreases slightly, the solution will be supersaturated, precipitating the excess of compound material on substrate surface, growing a semiconductor layer. Finally, MBE has a precise control of the chemical composition, and doping levels. This is achieved using an atom beams finely focused, growing a semiconductor layer with the greater crystalline quality.

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REFERENCES