

## REVIEW OF TECHNIQUES ON GROWTH OF GaAs AND RELATED COMPOUNDS

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GaAs is a technologically important material owing to its interesting properties. Several applications like high speed switching, VLSI, solar cells, lasers, LED's etc. warrant the use of different fabrication techniques. This paper deals with a concise review about the various techniques used for growth of GaAs thin films. The review discusses the principles underlying each technique and reports the work done till date.

**Key words:** Gallium arsenide, film growth, electrodeposition

## INTRODUCTION

GaAs is a III - V compound semiconductor possessing a zinc blende structure with high electron mobilities of the order of  $10^4 \text{ cm}^2/\text{V} \cdot \text{sec}$  at room temperature. It also has a direct optical band gap of  $\sim 1.5 \text{ eV}$  which makes it suitable for solar photovoltaic devices and light emitting diodes. Further the bandgap energy of GaAs is a good match to the solar spectrum and lies close to the value which will produce the 23 - 26 percent efficiency predicted for p-n junction devices.

The thickness of the solar cell required to absorb the photons in the solar spectrum is decided by the absorption coefficient of the material used. In the case of GaAs the absorption coefficient is very high ( $\sim 10^5 \text{ cm}^{-1}$ ) at the band edge, hence thin films ( $\sim 5$  to  $8 \mu\text{m}$  thick) of GaAs would suffice for photovoltaic devices and hence the requirement for thin layers of GaAs of high purity and perfection. This can be achieved by epitaxial growth technique. This technique has more advantages over other techniques to deposit thin layers of GaAs, since it gives better uniformity in thickness and distribution of impurities in deposited films. The major fields of application of GaAs are given in Table - I.

Table - I: Major fields of application of GaAs

IR emitting diodes	- GaAs, GaInAs
LED's	- GaAsP, GaAs
Fiber-optic sources	- AlGaAs
Optical detectors	- GaAs, GaInAs
Optical - isolators	- GaAs, GaAsP
Injection lasers	- GaAs, AlGaAs
Integrated-optics	- GaAs, AlGaAs
Negative electron affinity devices	- GaAs, GaInAs
Photovoltaic cells	- GaAs, GaAlAs
Transferred electron devices	- GaAs, GaInAs
Field effect transistors	- GaAs, GaInAs
IMPATT diode	- GaAs
Integrated circuits	- GaAs

Device quality GaAs and related compounds have been grown by several techniques like chemical vapour deposition (CVD), molecular beam epitaxy (MBE), vapour phase epitaxy (VPE), liquid phase epitaxy (LPE), hot wall epitaxy (HWE) and electrodeposition. However, specific device fabrication warrants the

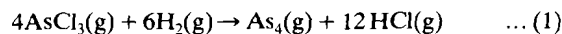
selection of a particular technique. Hence, an analysis of all the available techniques would provide a clear insight. Amongst the various techniques cited, use of electrodeposition for the growth of GaAs is very scanty and in our laboratory we have successfully electrodeposited GaAs layers on conducting indium tin oxide substrates using aqueous baths of sodium gallate and sodium arsenite. The purpose of this paper is to describe the basic principle of each technique and review the work done till date.

## Chemical vapour deposition (CVD)

CVD is a process in which gases or vapours are chemically reacted which leads to formation of solid phase reaction products on substrate surface. The fundamental process steps in CVD are:

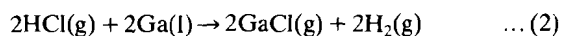
- (i) Transport of reactants to reaction chamber
- (ii) Chemical reaction on the substrate surface
- (iii) Adsorption of product on heated surface of substrate
- (iv) Desorption of product gases from the surface
- (v) Transportation of product gases away from surface and system.

The metal organic CVD (MOCVD) technique has been exhaustively used for the growth of gallium arsenide and related compounds. The first CVD reactor used metal halides as transport agents for GaAs crystal growth employing a closed tube system. In this arsenic trichloride ( $\text{AsCl}_3$ ), metallic gallium (Ga) were used as sources and  $\text{H}_2$  as the transporting agent to carry  $\text{AsCl}_3$  from a bubbler into the Ga source zone. The first step in this process is thermal decomposition of  $\text{AsCl}_3$  by the reaction:



The epitaxial growth of GaAs using halides was reviewed by Heyen and Balk [1].

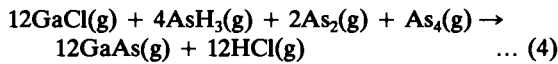
A modified form of the halide process is the use of arsenic hydride ( $\text{AsH}_3$ ) instead of  $\text{AsCl}_3$ . The basic hydride process employs  $\text{HCl}$ , Ga metal and  $\text{AsH}_3$ . A flow of  $\text{H}_2$  is used to transport the reaction products from the source zone to substrate. The source reaction is:



while  $\text{AsH}_3$  is pyrolysed as below:



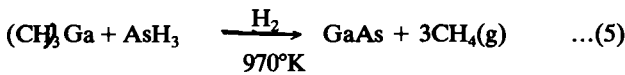
to provide arsenic. The reaction occurs in the substrate zone according to the equation:



Owing to the ability to independently control the As<sub>4</sub> and GaCl partial pressures, the hydride system is more flexible than the halide process.

In the MOCVD technique metal-organic compounds like trimethyl gallium, triethyl gallium etc are employed along with the hydrides. The process involves the pyrolysis of vapour phase mixtures of two or more metalorganic vapor sources or vapor phase mixtures of one or more hydrides and one or more metalorganic compounds. In the pioneering work, vapor-phase mixtures of the metalorganic compound trimethyl gallium (CH<sub>3</sub>)<sub>3</sub> Ga and AsH<sub>3</sub> were used. The mixture was pyrolysed at 970°K in a H<sub>2</sub> atmosphere [2].

The metalorganic compounds are typically liquids at room temperature with relatively high vapour pressures and can be readily transported into the reaction zone by bubbling a carrier gas, such as H<sub>2</sub>, through the liquid source. The hydrides used are gases at room temperature and are generally used as dilute mixtures in a H<sub>2</sub> mixture that are contained in high pressure cylinders. The pyrolysis of these source compounds is usually carried out in a flowing H<sub>2</sub> atmosphere in an open tube reactor. Deposition temperatures in the range 870 to 1100°K are typically employed. The net chemical reaction for the case of GaAs employing trimethyl-gallium is,



These chemical reactions are generally carried out in a cold wall quartz reactor and radio frequency (RF) induction heating is used to heat a graphite susceptor upon which substrate is placed. A schematic of the system is shown in Fig. 1. An

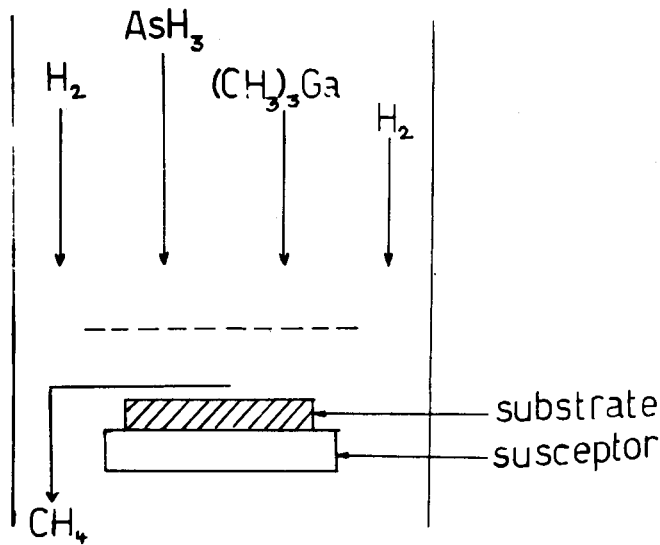


Fig. 1: Schematic of MOCVD process

interesting development in the MOCVD growth of III-V semiconductors is the pyrolysis of metalorganic and hydride sources at low pressures to grow GaAs epitaxial layers [3].

Undoped GaAs films were grown on GaAs substrates using arsine and trimethylgallium [4,7], they could be made n-type or p-type depending on initial partial pressures of arsine and trimethyl gallium. Mobilities of the order of 7000 cm<sup>2</sup>/V-sec with a carrier concentration of ~10<sup>16</sup>/cm<sup>3</sup> were obtained. A comparison of purity of MOCVD GaAs layers using triethyl gallium and trimethylgallium was studied [8] and it was observed that both produced layers of the same purity but trimethyl gallium is preferred in large area devices.

The main features which make MOCVD attractive for the growth of thin semiconductor structures are: (i) the process is scalable to high volume (ii) multilayer, multicomponent growths can be accomplished in a single run and (iii) process control is inherent.

**MOLECULAR BEAM EPITAXY (MBE)**

MBE has now become a versatile technique for growing epitaxial thin films of semiconductors and metals by impinging thermal energy beams of atoms or molecules onto a heated substrate under ultrahigh vacuum (UHV) conditions.

In this method the substrate is held in a high vacuum while molecular or atomic beams of the constituents impinge upon its surface (Fig. 2). For example, in the growth of GaAs layers

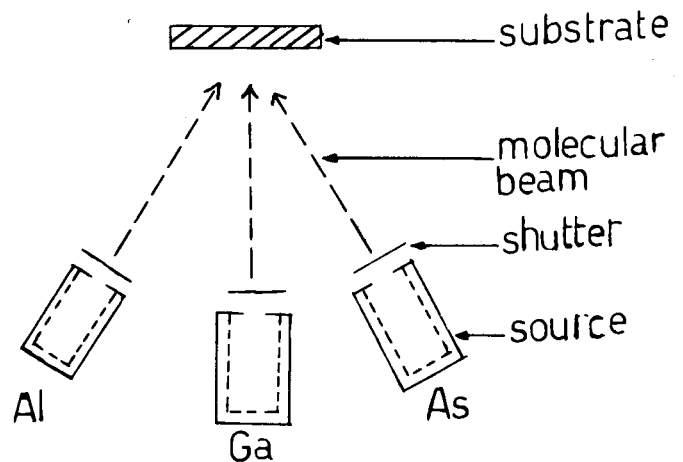


Fig. 2: Growth of GaAs and GaAlAs by MBE

on GaAs substrates, the gallium and arsenic components, along with the dopants are heated in separate cylindrical cells. Collimated beams of these constituents escape into the vacuum (~10<sup>-10</sup>torr) and are directed onto the surface of the substrate. The rates at which these atomic beams strike the surface can be closely controlled, and growth of very high quality crystalline layer results. The substrate is held at a relatively low temperature (820°K for GaAs) in this growth procedure. Abrupt changes in doping or in crystal composition can be obtained by controlling shutters in front of the individual beams. Using slow growth rates

( $\sim 1\mu\text{m/hr}$ ), it is possible to control the shutters to make composition changes on the scale of the lattice constant. Both n and p-type GaAs layers have been prepared by several workers [9-12] with mobilities for n-layers around  $10^4\text{cm}^2/\text{Vsec}$  at 77K. The possibility of growing GaAs layers from trimethyl gallium and arsine or from triethyl gallium and arsine was also investigated [13]. Unintentionally doped layers exhibited p-type conductivity and a mobility of  $6000\text{cm}^2/\text{V-sec}$  at 40K [14].

The salient features of MBE are (a) the slow growth rate ( $0.1 - 2.0\mu\text{m/hr}$ ) that permits very precise control of layer thickness in the submicron range (b) the reduced growth temperature ( $820^\circ\text{K}$  for GaAs), which is low enough not to disturb abrupt compositional or doping profiles because of negligible bulk diffusion (c) the specific non-equilibrium growth mechanism that is responsible for progressive smoothing of the surface for most substrate orientation (d) the ability to abruptly cease or initiate molecular beams that produce hyper abrupt material interfaces and dopant profiles and (e) the facility for in situ analysis to assure that the desired surface and reaction conditions are reached before commencement of growth and are maintained during growth.

#### VAPOR PHASE EPITAXY (VPE)

In VPE solid epitaxial layers are deposited by passing chemical vapors over a substrate. The two methods for VPE growth of III -V compounds are the chloride method and the hydride method. In the chloride method, arsenic in chloride passes over gallium metal to form  $\text{GaCl}_3$ . In the hydride process the substrates are held at about  $1100^\circ\text{K}$  on a rotating wafer holder while arsine ( $\text{AsH}_3$ ) and gallium chloride gases are mixed and passed over the substrate. The  $\text{GaCl}$  is obtained by reacting anhydrous  $\text{HCl}$  with molten Ga within the reactor. Epitaxial layers of GaAs have been grown by this technique using  $\text{AsCl}_3/\text{Ga}/\text{H}_2$  system [15],  $\text{AsCl}_3 - \text{Ga}$  using nitrogen as carrier gas [16],  $\text{Ga-HCl-AsH}_3\text{-H}_2$  system at various partial pressures at  $970\text{-}1070^\circ\text{K}$  [17]. GaAs can be grown with better purity and crystal perfection by VPE than by other methods. Furthermore, this technique offers a great flexibility in actual fabrication of devices. When an epitaxial layer is grown on a substrate, it is relatively simple to obtain a sharp demarcation between the type of impurity doping in the substrate and in the grown layer.

#### LIQUID PHASE EPITAXY (LPE)

LPE involves the precipitation of material from a cooling solution onto an underlying substrate. The solution and substrate are kept apart in the growth apparatus and the solution is saturated with the growth material until the desired growth temperature is reached. The solution is then brought into contact with the substrate surface and allowed to cool at a rate and during a time interval which is appropriate for the generation of the desired layer. When the substrate is single crystalline and the lattice constant of the precipitation material is the same or nearly the same as that of the substrate, the precipitating material forms a layer on the substrate surface which is an extension of the single crystal body of the substrate.

Since a solvent for the material to be deposited is needed in LPE, the usefulness of the process is limited to applications where the solvent does not adversely affect the epitaxially deposited layer. LPE has the following major advantages over VPE: (i) simplicity of equipment (ii) generally higher deposition rates (iii) elimination of hazards due to use of reactive gases and their products, which are often toxic and corrosive and (iv) larger selection of dopants that can be easily incorporated into the layer.

LPE technique has been employed for the growth of GaAs epitaxial layers by tipping method or sliding boat method [18]. Nearly perfect crystalline layers of GaAs have also been obtained by a temperature difference method [19]. Mobilities of around  $10^5\text{cm}^2/\text{V-sec}$  at  $77^\circ\text{K}$  [20] was reported for GaAs layers grown at  $970^\circ\text{K}$ .

#### HOT WALL EPITAXY (HWE)

In HWE technique, growth of epitaxial films under conditions as near as possible to thermodynamic equilibrium is achieved with a minimum loss of material. Also, since this is a closed system, the vapour pressures of the constituents are maintained and stoichiometry of the films can be controlled with ease. Epitaxial layers of GaAs have been grown on mica, GaAs, Ge substrates [21-23] by this technique.

#### FLASH EVAPORATION

In this technique polycrystalline GaAs powder is fed from a vibrating hopper to a red hot filament. The powder vaporises instantaneously and the vapour deposit on a substrate. GaAs layers have been grown on glass substrates under a vacuum of  $10^{-5}\text{torr}$  [24,25].

#### SPUTTERING

Vapor species may be created by kinetic injection from the surface of a material (called target or cathode) by bombardment with energetic and nonreactive ions. The ejection process, known as sputtering, takes place as a result of momentum transfer between the impinging ions and the atoms of the target surface. Sputtering has been employed for the growth of GaAs films [26].

#### VACUUM EVAPORATION

In this technique either presynthesized GaAs powder is used as source or two sources containing gallium and arsenic are used. The vapors of the material condense on a substrate in vacuum ( $10^{-5}\text{torr}$ ). The two-source evaporation method has been successfully employed [27] for growth of GaAs on glass substrates.

#### ELECTRODEPOSITION

Electrodeposition has been used for the preparation of epitaxial layers. It has the advantages that the growth rate is controlled by electrical parameters and is relatively insensitive to temperature. Electrochemical purification also occurs in addition to normal impurity segregation. In the pioneering work on growth of GaAs by electrodeposition at about  $1025^\circ\text{K}$  [28] a melt

composition containing  $B_2O_3/NaF/Ga_2O_3/NaAsO_2$  (6.4 : 20.3 : 4.2 : 8.1 wt %) was used. A cell used for this purpose is shown in Fig. 3. Later GaAs was deposited from  $AsI_3$  and  $KGaCl_4$

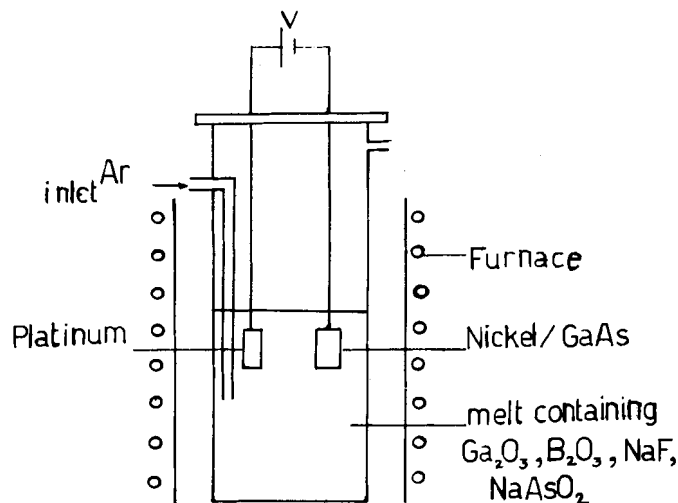


Fig. 3: Electrochemical reactor for preparation of GaAs

at a relatively low temperature of around 570°K [29]. However the layers were arsenic-rich [29]. Recently GaAs has been electrodeposited from a room temperature  $AlCl_3$  - butylpyridinium chloride melt [30]. The behaviours of gallium and arsenic species have been studied by voltammetry and coulometry. Potentiostatically controlled reduction of mixtures of Ga(III) and As(III) halides in the melt lead to films containing both gallium and arsenic. In our laboratory attempts are being made to electrodeposit GaAs from aqueous and nonaqueous baths. In the first instance Ga has been electrodeposited on Cu foil from sodium gallate solution under galvanostatic conditions. Over this gallium layer arsenic has been electrodeposited from arsenite solution. These layers were annealed in high vacuum ( $\sim 10^{-5}$  torr) at different temperatures in the range 520 - 800°K. Work on the characterisation of these films is in progress.

### CONCLUSION

Fabrication techniques such as LPE, MBE, MOCVD etc have reached a point where proposed device structures may be routinely investigated. MBE and MOCVD are capable of growing epitaxial films whose crystalline quality is comparable to that obtainable with LPE and halide CVD. A distinct advantage of MBE and MOCVD over LPE and halide CVD is their ability to yield high level, highly controllable changes in the doping without interrupting the growth. Also, because of the comparatively low growth temperatures, diffusion effects during film growth are extremely limited and it is possible to grow not only precisely graded doping profiles, but nearly abrupt ones as well. Both MOCVD and MBE processes have demonstrated a capability to achieve thickness less than 10 Å. LPE offers the creative possibilities of nonequilibrium growth over nonplanar surfaces which helps to produce unique device configurations.

In this context, electrodeposition is in the very initial stages of development and there is much scope for this technique to occupy a prominent position in the field of device fabrication. The salient features are the possibility of precise control over the layer thickness and the economical usage of materials.

Each technique has advantages that are best exploited by selective uses. Therefore, a single epitaxial technology does not meet all of the present or foreseeable device requirements. Table II indicates the devices fabricated using different techniques.

Table - II: Application of different techniques for device applications

Device	Active layer growth method
Laser, Field Effect Transistors Avalanche photo diode	VPE, LPE and MBE
Charge coupled devices	MOCVD
Laser	LPE
Photodiode (eg. PIN)	MBE
Photocathode	MOCVD
Light emitting diode	LPE and VPE
Solar cell	MOCVD and MBE

Amongst the various techniques, MOCVD is rapidly becoming a maturely developed growth process with proved capabilities for the growth of GaAs based ternary and quaternary compounds. Large scale production oriented MOCVD reactors are now commercially available.

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Murali et al – Review of techniques of growth of GaAs and related compounds

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