

**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 cm²/V·sec at room temperature. It also has a direct band gap of -1.5 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 last 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 (-10⁶ cm⁻¹) at the band edge, hence thin films (<5 µm 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 1.

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 (AsCl₃) and metallic gallium (Ga) were used as sources and H₂ as the transporting agent to carry AsCl₃ from a bubbler into the Ga source zone. The first step in this process is the thermal decomposition of AsCl₃ by the reaction:

\[ 4 \text{AsCl}_3(g) + 6 \text{H}_2(g) \rightarrow 3 \text{As}_4(g) + 12 \text{HCl}(g) \quad (1) \]

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 (AsH₃) instead of AsCl₃. The basic hydride process employs H₂, Ga metal and AsH₃. A flow of H₂ is used to transport the reaction products from the source zone to substrate. The source reaction is:

\[ 2\text{HCl}(g) + 2\text{Ga}(l) \rightarrow 2\text{GaCl}_3(g) + 2\text{H}_2(g) \quad (2) \]

while AsH₃ is pyrolysed as below:

\[ 4\text{AsH}_3 \rightarrow \text{As}_4 + 6\text{H}_2 \quad (3) \]

Table 1: Major fields of application of GaAs

<table>
<thead>
<tr>
<th>Technique</th>
<th>GaAs, GaAlAs, AlGaAs</th>
<th>GaAs, GaInAs, InP, InGaAs</th>
<th>GaAs, GaInAs, InGaAs</th>
<th>GaAs, GaInAs, InGaAs</th>
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<tr>
<td>Electrochemical deposition</td>
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**Key words:** Gallium arsenide, film growth, electrodeposition
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Molecular Beam Epitaxy (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.

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 interesting development in the MOCVD growth of III-V semiconductors is the pyrolysis of metallicorganic 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 cm²/V-sec with a carrier concentration of ~10¹⁸cm⁻³ were obtained. A comparison of purity of MOCVD GaAs layers using trimethylgallium 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 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 (~10⁻¹⁰torr) 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.
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\textbf{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 1000000 cm²/V·sec at 77 K [20] were reported for GaAs layers grown at 970 K.

\textbf{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.

\textbf{FLASH EVAPORATION}

In this technique polycrystalline GaAs powder is fed from a vibrating hopper to a hot filament. The powder vapourizes instantaneously and the vapour deposit on a substrate. GaAs layers have been grown on glass substrates under a vacuum of 10⁻¹⁰ Torr [24-25].

\textbf{SPUTTERING}

Vapour 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].

\textbf{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 (10⁻¹⁰ Torr). The two-source evaporation method has been successfully employed [27] for growth of GaAs on glass substrates.

\textbf{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 77 K [28] a melt...
composition containing B2O3/Naf/Ga2O3/NaAsO3 (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 AsI3 and KGaCl4 at a relatively low temperature of around 579°K [29]. However the layers were arsenic-rich [29]. Recently GaAs has been electro-deposited from a room temperature AICI3 - betylpyridinium 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 elec trodeposit 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 (~10−6 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 commercially available. Large scale production oriented MOCVD reactors are now commercially available. 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.

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