

LP–MOVPE growth for high–speed electronic devices on InP

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Abstract: The subject of this tutorial paper is a detailed analysis of a non–gaseous source MOVPE set–up for the growth of high–speed electronic devices on InP. The layer sequences of heterobipolar transistor (HBT) and resonant tunnelling diode (RTD) are selected in order to discuss the specific requirements of doping capabilities, interface sharpness, group–V exchange, and growth stability.

1 Introduction

The standard Metal–Organic Vapor Phase Epitaxy (MOVPE) uses liquid metal–organics and gaseous hydrides as compound precursors for III/V epitaxial growth. This way an extremely wide epitaxial material scope is provided combining source atoms of both very high and very low vapor pressure. However, the growth temperature is not only used for the surface mobility of ad–atoms but also for the decomposition of the compound precursors. This may result into a smaller parameter window for optimised growth. Initially, the MOVPE use of non–gaseous sources like tertiarybutyl arsine (TBAs) and tertiarybutyl phosphine (TBP) was originally driven by [1–5]: (i) safety aspects, and (ii) lower V/III ratio (lower consumption and service efforts). More recently, a third argument had a distinct impact on their usage in electronic applications [6–7]: the lower decomposition temperature (cf. Table 1). This aspect may relax possible trade–offs and becomes dominantly important for extremely high and abrupt doping. This paper is organized as follows. In section 2 the experimental conditions of the growth using all non–gaseous sources are given in detail. Next, the growth for electronic devices is discussed in terms of growth challenges such as heterointerface and InAlAs for RTD, and p–type doping and stable growth uniformity for HBT.

2 Basic Growth Conditions

The experiments were done on epi–ready semi insulating (001) InP:Fe substrate in an AIX 200 reactor with RF heating. Purified nitrogen (N₂) was used as a carrier gas providing a reactor pressure of $p_{\text{tot}} = 50$ mbar at a total flow of $Q_{\text{tot}} = 3.4$ slm corresponding to a gas velocity of $v_{\text{gas}} = 0.4$ m/s. Hydrogen was exclusively connected to the source gas line. A completely non–gaseous source configuration was used based on TBAs*/TBP*/TMSb**/TMAs as group–V, DitBuSi/CBr₄* as group–IV n–/p–type dopant sources, and the metalorganics TMin/TEGa/TMAI*** (produced by: *MOCHEM, **Akzo Nobel, ***EMF–Limited).

Table 1: Some data of MOVPE source materials

Precursor	chemical formula	vapor pressure	T ₅₀ /°C	LC ₅₀ /ppm
arsine	AsH ₃	14 Bar (20 °C) [1]	600 [1]	5–50
phosphine	PH ₃	24 Bar (20 °C) [1]	700 [3]	11–30
tertiarybutyl arsine (TBAs)	(C ₄ H ₉)AsH ₂	109 mBar (10 °C) [4]	450 [3]	70
tertiarybutyl phosphine (TBP)	(C ₄ H ₉)PH ₂	189 mBar (10 °C) [4]	550 [3]	>1,100
trimethyl arsenic (TMAs)	(CH ₃) ₃ As	317 mBar (20 °C) [1]	530 [1]	20,000

3 N–type doping, InAlAs, and interface sharpness: Resonant Tunnelling Diode

The control of doping in a wide range is a key issue for high–speed device applications. Disilane or silane [8] are commonly used to provide high n–type doping at growth temperatures in the range of T_g = 640 °C – 680 °C. The liquid compound ditertiarybutyl silane DitBuSi [9] is used for n–type doping at T_g = 600 °C / 620 °C. Down to

this growth temperature region the doping concentration is verified for GaAs and InP [10] to depend nearly linearly on the IV/III–ratio.

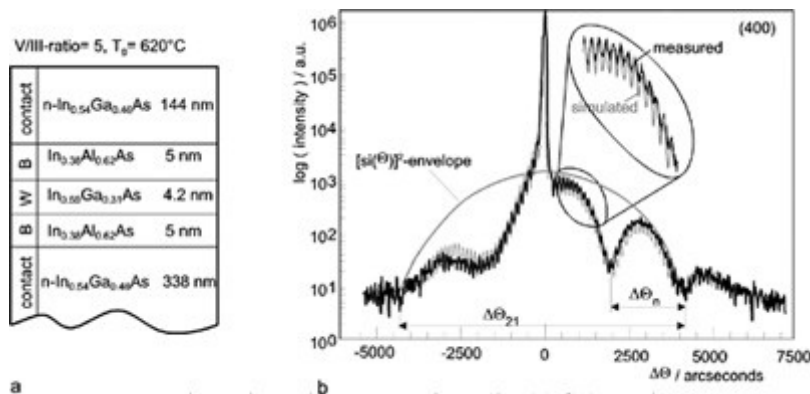


Fig. 1: Layer stack (a) and X-ray characterization of $In_{0.38}Al_{0.62}As/InGaAs$ RTD (b) [12].

Compared to disilane the growth temperature can be reduced by 30 °C to 620 °C in nitrogen carrier gas while keeping a high concentration of $n = 1.8 \times 10^{19} \text{ cm}^{-3}$ ($\mu_n = 1580 \text{ cm}^2/\text{Vs}$). Using the non–gaseous source configuration thick InAlAs bulk layers grown at $T_g = 600^\circ\text{C}$ exhibit a mirror like surface and a FWHM = 26.5 meV of the low temperature photoluminescence peak. An intentional n–type doping is feasible at higher growth temperatures, which suggest that the C–incorporation at higher growth

temperatures sufficiently compensates the constant deep O–donor concentration [11]. I. e. at $T_g = 670^\circ\text{C}$ a high doping level of $n = 1.5 \times 10^{18} \text{ cm}^{-3}$ ($\mu_n = 440 \text{ cm}^2/\text{Vs}$) suitable for HEMT applications is achieved [11]. A background concentration of $n = 1.5 \times 10^{16} \text{ cm}^{-3}$ ($\mu_n = 2185 \text{ cm}^2/\text{Vs}$) is measured by van der Pauw Hall measurements while CV–measurements determine $n = 1.7 \times 10^{17} \text{ cm}^{-3}$. The different donor concentration of CV and Hall is attributed to impurities with different activation energies like silicon/carbon/oxygen.

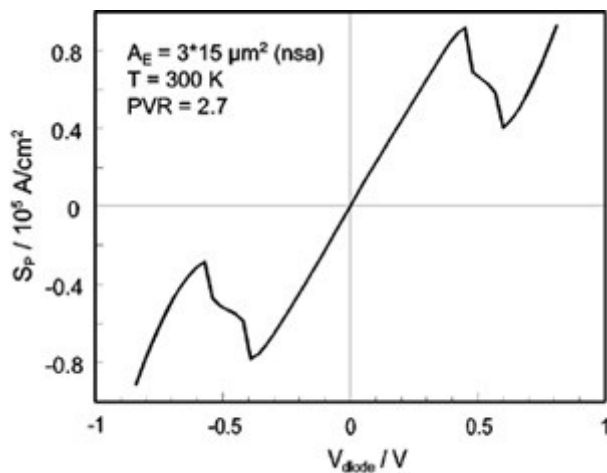


Fig. 2: I - V characteristic of the RTD device grown by MOVPE [12]

A Resonant Tunnelling Diode (RTD) consists of very thin undoped (Al–rich) InAlAs barrier layers and an undoped InGaAs well sandwiched between doped lattice matched InGaAs contact layers (cf. Fig. 1a). This device is very well suited to proof the layer and interface quality of MOVPE grown InAlAs/InGaAs/InP heterostructures using a non–gaseous source configuration [12]. In Figure 1a the RTD layer data are given which were determined from the simulation of the measured rocking curve in the vicinity of the (004)–reflection (c.f. Fig. 2). An excellent agreement of the measured and simulated rocking curve is achieved with the assumption of ideal interfaces. No interface degradation effects were observed while the complete RTD structure is grown at a growth temperature of $T_g = 620^\circ\text{C}$. The RTD devices fabricated from a layer stack like in Figure 1a exhibit

a peak–current density of up to $S_p = 9 \times 10^4 \text{ A/cm}^2$ and a peak–to–valley ratio of $PVR = 2.7$ at room temperature (cf. Fig. 2). The RTD device performance is significantly improved compared to former MOVPE grown structures [13] and comparable to MBE grown devices [e.g. 14 and references therein]. This RTD technology is optimally suited for monolithic integration with HBT and has been used for various high functionality and high–speed logic circuits. [15].

4 Carbon doping and group–V exchange: Heterobipolar transistor

A high–speed npn heterobipolar transistor (HBT) makes use of a large valence band discontinuity forming a hole barrier at the base to emitter interface [16]. This way a higher p–type base layer concentration is allowed which is a key parameter to reduce the base resistance and finally to realize high–speed HBT devices. The demand for a high valence band discontinuity provided by InP–based heterostructures can be fulfilled by (a) InGaAs/InP or (b) GaAsSb/InP heterointerfaces. Both interfaces have in common a group–V exchange which is critical because of the different vapor pressure of antimonides, arsenides, and phosphides inhibiting the realisation of ideal interfaces.

a) InGaAs/InP

On InP–substrate the p–type base layer is made of p– $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ layer doped either with zinc or carbon. Compared to zinc the use of carbon results in a higher dopant density and higher stability and may contribute to a higher device reliability and performance. Carbon p–type doping of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ is difficult because of the weak In–C bond strength ($\text{In–C} < \text{As–C}$) which leads to an amphoteric character [17]. Intrinsic carbon doping with TMAs is not successful [18] and the use of external dopant sources like CCl_4 or CBr_4 is indispensable. Comparative studies show that CBr_4 is more efficient than CCl_4 [6] and also a change to nitrogen carrier gas increases the maximum doping concentration [7]. In order to reduce the etching and to provide carbon incorporation on the arsenic site, both the growth temperature and the V/III–ratio have to be lowered far into the kinetic controlled growth mode. In this regime a high layer quality and especially a high homogeneity is difficult to assure because of the exponential impact of temperature fluctuation on the growth result. Though, substantial effort have been undertaken to realize the necessary base doping $p = 1.5 \times 10^{19} \text{cm}^{-3}$ for HBT at the highest possible growth temperature ($T_g = 500 \text{ }^\circ\text{C}$) [6–7].

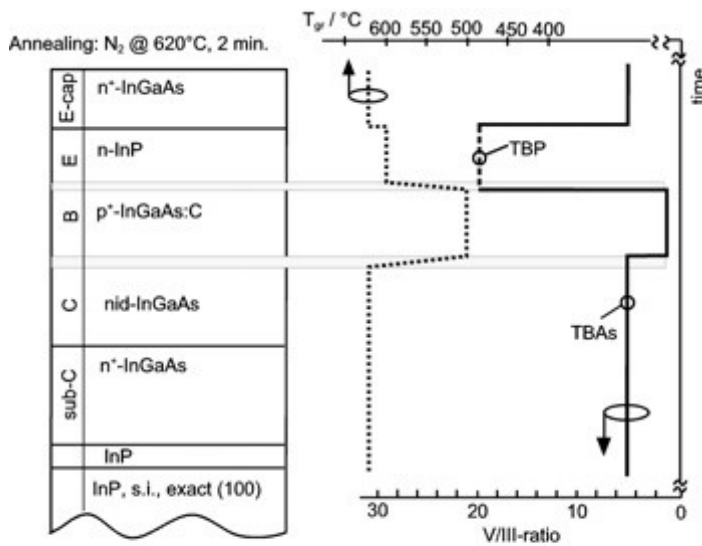


Fig. 3: Layer stack and MOVPE growth parameters of InP/InGaAs single heterojunction bipolar transistor [12].

The growth parameters for the complete HBT layer stack are designed as depicted in Fig. 3. The $n^+ - \text{In}_{0.53}\text{Ga}_{0.47}\text{As}:\text{Si}$ contact layers for collector and emitter are grown at $600/620 \text{ }^\circ\text{C}$ providing a dopant concentration of $n = 2 \cdot 10^{19} \text{cm}^{-3}$. At the collector–to–base and base–to–emitter interface both the growth temperature and V/III ratio have to be ramped. Using the non–gaseous source configuration this temperature ramp is $100 \text{ }^\circ\text{C}$ compared to $200 \text{ }^\circ\text{C}$ in case of hydride sources. This smaller temperature ramp enables shorter growth interruptions and lower interface degradations. The HBT structure is in–situ annealed in a hydrogen radical–free TMAs/ N_2 ambient directly after growth and then cooled down in TMAs/ N_2 ambient. The $n - \text{InP}$ emitter and $n^+ - \text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ emitter cap layer seems not to block the hydrogen removal out of the base layer if the annealing is carried out at sufficiently high temperatures [19]. The InP/InGaAs HBT structure is

analysed by high–resolution x–ray diffraction in the vicinity of the 004 reflection in a coupled $\theta - 2\theta$ mode. The

measured and simulated reflection curves show that interfacial strained quaternary InGaAsP layers with a thickness of 0.16 to 0.22 nm [6] occur at both base layer interfaces.

HBT devices were fabricated by optical lithography and wet chemical etching. The Gummel plots of six HBTs ($A_E = 3 \times 15 \mu\text{m}^2$, non–self aligned) were examined in a line mapping from the center to the edge of 2" –wafer and show excellent homogeneity of epitaxial layers by this novel system (Fig. 4b). It is worth stating that this result proves that an excellent homogeneity is obtained despite the used kinetic controlled growth mode with a wide variety of parameters with an exponential temperature dependence. The MOVPE technique allows a wide range of specialized device optimisations. I. e. graded base HBT, which combine high current gain up to 400 and excellent high frequency performance ($f_T = 149 \text{ GHz}$; $A_E = 20 \mu\text{m}^2$) have been developed [20].

b) GaAsSb/InP

The InGaAs/InP HBT with low band–gap InGaAs collector exhibits a low breakdown voltage ($V_{\text{CE,Br}} \leq 3 \text{ V}$, cf. Fig. 4a). The replacement of the low band–gap collector by InP results in a double heterostructure bipolar transistor

(DHBT) exhibiting a high breakdown voltage but also in substantial efforts in order to avoid the current blocking effect related to the positive conduction band discontinuity at the InGaAs/InP base–collector interface [21]. On the contrary GaAs_{1-x}Sb_x forms a type-II staggered transition to InP [22] resulting in a negative conduction band discontinuity and avoiding any current blocking effect. Hence, the replacement of the p–InGaAs base layer by p–GaAs_{1-x}Sb_x is an attractive alternative. The lack of Indium in GaAs_{1-x}Sb_x enables a very high p–type doping with carbon comparable to p–GaAs:C. A hole concentration of up to $p = 3 \times 10^{20} \text{ cm}^{-3}$ has been demonstrated [24].

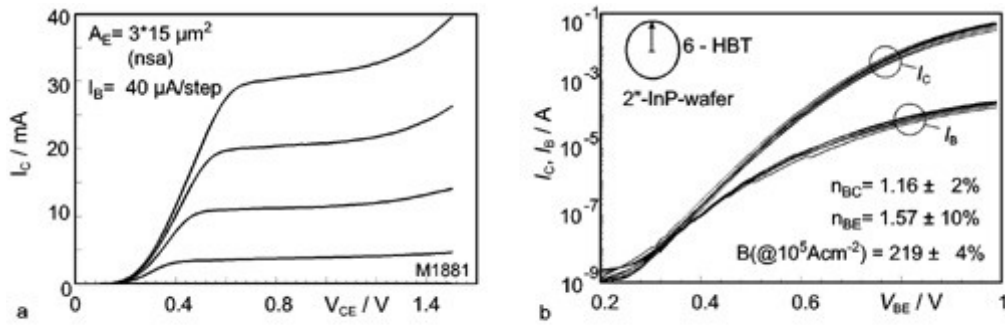


Fig 4: Non self-aligned InP/InGaAs single heterojunction bipolar transistor with an Emitter area of $3 \times 15 \mu\text{m}^2$: (a) Common Emitter output characteristic and (b) Gummel plot of 6 HTB along the wafer diameter

The ternary III/V semiconductor GaAs_{1-x}Sb_x has temperature dependent solid phase miscibility gap. At the growth temperatures required for high p–type doping such as 550 °C this gap is ranging from $x = 0.2$ to 0.8 [25] clearly covering the desired Sb content of 50 % for lattice matched growth on InP. With MOVPE, the metastable growth of GaAsSb lattice matched on InP has been demonstrated at very low V/III ratio <1. The precise adjustment of flows for a desired composition is one of the mayor challenges of GaAsSb growth. The solid composition of the GaAs_{1-x}Sb_x depends on the vapour phase composition $\text{Sb/V} [= p_{\text{TMSb}} / (p_{\text{TMSb}} + p_{\text{TBA}})]$, The IV/III ratio, and additionally on the V/III ratio. In Figure 5a the effect of the V/III ratio on the Sb incorporation is shown [26]. With decreasing V/III ratio the Sb incorporation increases almost linearly. After a reduction of the V/III ratio values lower than 1 the Sb content increases such that lattice matched growth on InP is feasible. Figure 5b shows the carrier concentration dependence with the IV/III ratio. P–type doped GaAsSb layers with carrier concentration up to $p = 4 \times 10^{19}$ were realized with a linear relationship between CBr₄ flow and carrier concentration [26]. The hole mobility is typically around $30 \text{ cm}^2/\text{Vs}$.

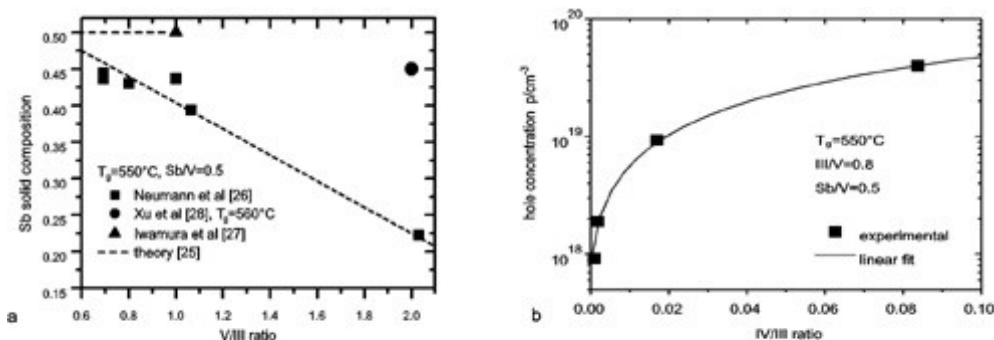


Fig 5: MOVPE growth of GaAsSb at $T_g = 550^\circ\text{C}$ and $\text{Sb/V} = 0.5$ [26]: (a) Sb incorporation as a function of the V/III and (b) hole concentration as a function of the IV/III ratio using CBr₄

However, with increasing IV/III ratio we observe a reduction of the Sb incorporation in the GaAsSb layers. The influence of the CBr₄ flow on the solid composition is a well–known etching effect in general for III/V semiconductors. The increasing CBr₄ flow leads in the GaAsSb–system to a reduction of Ga atoms in the gas phase and consequently to higher V/III ratio, thus, as shown in Figure 5a, causes a lower Sb incorporation in the solid phase. We observe a strong Sb memory effect of up to 8% Sb take up in the following growth processes.

After growing of a single 300 nm thick GaAsSb layer we directly start a second growth run of a single 140 nm thick GaAsSb:C layer grown on a 50 nm InP buffer layer. The composition of the GaAs_{1-x}Sb_x layer is determined to x=44 and of the InP_xSb_{1-x} to x=95. That means, that from the previous growth run 5% Sb was transferred in to the following growth run. Dependent on the history of the liner and susceptor of the MOVPE system and the Sb contamination, the memory effect can be reduced to values lower 1% which have no impact on HBT properties.

The GaAsSb/InP growth has made substantial progress in recent years and state-of-the-art devices proof the high potential of this approach combining (i) high breakdown voltage and high saturation drift velocity of the electrons in the InP collector with a (ii) low base resistance of the p-GaAsSb resulting in a very high f_T and f_{MAX} values up to 300 GHz [23].

5 Conclusions

The use of today's TBAs/TBP/TMAs/TMSb as group-V precursors, DitBuSi/CBr₄ as group-IV dopant sources and conventional metalorganics like TMIIn/TMAI/TEGa in nitrogen carrier gas enables the growth state-of-the-art electronic device structures at a reduced hazard potential. In addition, the optimum growth conditions for different As/P/Sb containing compounds matches close to each other resulting in a more stable MOVPE process control. It is known that nitrogen carrier gas supports this effect by an increased p-type doping efficiency for p-In_xGa_{1-x}As:C and a general improved homogeneity which is essential for a high yield of the interesting application.

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