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GROWTH OF InP-EPITAXIAL LAYERS : A COMPARISON BETWEEN MOVPE- AND VPE-TECHNIQUES

K.W. Benz, H. Haspeklo and R. Bosch*

Physikalisches Institut, Kristallabor, Universität Stuttgart, D-7000 Stuttgart-80, F.R.G.
*Fraunhofer Institut für Angewandte Festkörperphysik, D-7800 Freiburg, F.R.G.

1. Introduction. - In the past most work on InP-epitaxy has been invested in the PCl₃/In/H₂-VPE process. The main reason for the widespread application of this technique is the possibility of obtaining high purity In- and PCl₃ starting materials. Recently, the metalorganic vapour phase epitaxy (MOVPE) which has been successfully applied to GaAs and GaAlAs has stimulated the growth of InP-epitaxial layers by this technique.

In this paper we would like to give some new results on the MOVPE-growth of InP with a metalorganic adduct, a trimethylindium-trimethylphosphane compound. These results on MOVPE-epitaxial growth will be compared with the PCl₃/In/H₂-process. In the latter case the following points will be emphasized: growth of high purity and doped layers and the reproducible growth of n+/n/n+-structures for TEO-applications. From these structures Gunn-oscillators in the 100 GHz region have been constructed.

2. InP-epitaxial growth with (CH₃)₃P-In(CH₃)₃-adduct. - Metalorganic compounds have received much interest for the epitaxial growth of III-V-semiconductors. GaAs and GaAlAs layers, for instance, have been grown by using (CH₃)₃Ga, (CH₃)₃Al and AsH₃. There are two main advantages of MOVPE over the chlorine process:
i) reproducible pyrolysis reactions in the epitaxial growth system, which allow the production of very thin layers with uniform thickness and of abrupt junction,

ii) normally lower growth temperatures, which may reduce parasitic diffusion effects and the incorporation of unwanted impurities.

We have grown InP-epitaxial layers by taking a trimethylindium-trimethylphosphane-adduct, (CH₃)₃P-In(CH₃)₃. The compound is stable at room temperature and melts at 42°C. By this way the formation of polymer products of the form (CH₃InPH)ₙ, which is typical for the (C₃H₅)₃In/PH₃-MOVPE-process may be avoided. Fig. 1 shows our growth system including a vertical quartz-reactor, an adduct-bubbler as well as an (CH₃)₃P-bubbler as important supply-systems for the growth of InP epitaxial layers. PCl₃ is needed for in situ etching of the substrates prior to growth; the additional use of phosphane (CH₃)₃P is important to control the P/In-ratio. The layers were grown on 2° off (100) oriented InP substrate crystals. Prior to the epitaxial growth the InP-substrates were etched with PCl₃ (e.g. H₂ flow ~ 7⋅10⁻³ min⁻¹, PCl₃ molar fraction α = 1,2⋅10⁻³ at T = 350°C, etching time t = 1 min).

The following growth results have been obtained:

i) After etching the substrate the In-P-adduct was decomposed in the substrate zone with the addition of small amounts of PCl₃ (γ = 1,7⋅10⁻⁴). The growth temperature was kept at 500°C. Epitaxial layers of uniform thickness and a good surface morphology up to 2 µm could be grown. The growth of thicker layers was not possible due to the appearance of In-droplets on the surface of the epitaxial layer. Undoped layers grew n-type with carrier concentrations between 10¹⁴ and 10¹⁶ cm⁻³.

ii) The growth results above indicated, that additional P is necessary for the InP-growth. This has been verified by the use of phosphane (CH₃)₃P. Before entering the reactor, (CH₃)₃P was cracked at 720°C in a separate furnace (Fig. 1). The following reactions could be important:
Fig. 2 : Growth rate of InP-layers as a function of adduct-flux

Fig. 2 depicts a linear dependence between growth rate and the adduct mole fraction, which means, that the epitaxial growth is thermodynamically controlled. The growth temperature was varied between 500 and 600°C, InP-layers have been grown up to 5 μm. The surface of the layers was of excellent quality and mirror-like.

Fig. 3a, b shows the carrier profiles of two epitaxial layers grown on different InP-substrates. The layer in Fig. 3a was grown by the Adduct/PCl₃-System, whereas the layer of Fig. 3b is the result of the Adduct/P(CH₃)₃-Process.

Growth parameters and growth results of both the VPE- and MOVPE-process are summarized in tab. 1 and table 2, respectively.
Fig. 3: Carrier Profile of InP-MOVPE layers grown on InP-substrates
a) Adduct/PCl₃-process    b) Adduct/Phosphane-System

<table>
<thead>
<tr>
<th></th>
<th>Temperatures (°C)</th>
<th>Total H₂ flow (cm³/min)</th>
<th>Growth rate (µm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPE</td>
<td>640-660</td>
<td>750</td>
<td>1-12</td>
</tr>
<tr>
<td>adduct/PCl₃</td>
<td>500</td>
<td>-</td>
<td>0.5-1</td>
</tr>
<tr>
<td>MOVPE adduct/(CH₃)₃P</td>
<td>500-600</td>
<td>-</td>
<td>1-2</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Tab. 1: Growth parameters of InP-MOVPE and VPE-processes
Range of carrier concentration of undoped layers deduced from C-V-measurements (cm$^3$) & Van der Pauw measurements of mobility

<table>
<thead>
<tr>
<th>Process</th>
<th>1x10$^{14}$ - 5x10$^{16}$</th>
<th>n$^{300K}$</th>
<th>n$^{77K}$</th>
<th>$\mu^{300K}$</th>
<th>$\mu^{77K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPE</td>
<td></td>
<td>1,2x10$^{14}$</td>
<td>1,1x10$^{14}$</td>
<td>4930</td>
<td>74090</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3,1x10$^{15}$</td>
<td>2,8x10$^{15}$</td>
<td>4460</td>
<td>42730</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,5x10$^{16}$</td>
<td>1,1x10$^{16}$</td>
<td>4260</td>
<td>17890</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5,2x10$^{16}$</td>
<td>2,3x10$^{16}$</td>
<td>2450</td>
<td>5530</td>
</tr>
<tr>
<td>adduct/PCl$_3$</td>
<td>1x10$^{14}$ - 1x10$^{16}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOVPE</td>
<td></td>
<td>7,6x10$^{18}$</td>
<td>4x10$^{16}$</td>
<td>2820</td>
<td>4790</td>
</tr>
<tr>
<td>adduct/(CH$_3$)$_3$P</td>
<td>&gt; 5x10$^{16}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tab. 2: MOVPE and VPE-processes: properties of grown InP-layers

3. VPE-layer growth and a comparison with MOVPE-results. - The PCl$_3$/In/H$_2$-process has been applied in many laboratories and extensively described in the literature. A carefully controlled concentration of PCl$_3$-vapour, transported by hydrogen as a carrier- and reactant gas is passed over In at 750$^\circ$C. The products InCl, P-vapour and PH$_3$ pass over (100) oriented InP-substrates. InP-epitaxy takes place at the seed wafer (T = 650$^\circ$C) with an impurity content depending on the starting materials In and PCl$_3$ and, more importantly, on the growth conditions employed. Important features for the growth of n+/n/n+-structures by the PCl$_3$/In/H$_2$-process are the following:

i) control of residual impurities between $n = 1 \cdot 10^{14}$ cm$^{-3}$ and $5 \cdot 10^{16}$ cm$^{-3}$ by varying the PCl$_3$ fraction over the seed, (Fig. 4);

ii) intentional doping with S by adding H$_2$S to the H$_2$-flow. Thin n+ contact and buffer layers with $n$ between $1 \cdot 10^{17}$ cm$^{-3}$ and $5 \cdot 10^{18}$ cm$^{-3}$ can be easily grown in this manner (Fig. 5).

Typical growth parameters of the PCl$_3$/In/H$_2$-process are summarized in tab. 1; properties of grown layers are shown in tab. 2.

Fig. 6 shows the profile of a n+/n/n+-structure grown on a Sn-doped InP substrate. The following advantages of the adduct/(CH$_3$)$_3$P-system over the PCl$_3$/In/H$_2$-process may be pointed out:

i) in the case of the adduct epitaxy the growth temperature is lowered by about 50 to 100 degrees, which may lead to a reduction of impurity or dopant-outdiffusion from the substrate into the epitaxial layer,

ii) the low growth rate of 1 - 2 \mu m/h and the low growth temperature enables the fabrication of thin layers (< 1 \mu m) with abrupt junctions.
Fig. 4: PCl₃/In/H₂-process: net electron concentration as a function of PCl₃-mole fraction α over the seed --- after Cardwell et al.⁵)

Fig. 5: PCl₃/In/H₂-process: net electron concentration as a function of H₂S mole fraction

Fig. 6: PCl₃/In/H₂-process: profile of an n+/n/n+-structure

4. Gunn diode fabrication. - The n+/n/n+-structures have been used for the fabrication of InP mm-wave TEO's. The main features of the diode fabrication are:

a) contacts were made using AuGe/W/Au metallization,
b) an integral heat sink is plated directly onto the active layer,
c) the cross section of the diodes are kept very low (30 - 40 μm diameter) to reduce the operating current. Light activated etching is used to obtain well shaped mesa-structures;
d) the substrate is removed almost completely in order to reduce the series resistance. The resulting mesa-height is around 10 μm;
e) after bonding the back contact a further reduction of the diode cross section is attempted by chemically etching the mesa within the package.

Electrical performance data showed a power output from fundamental mode oscillations. At a frequency of 110 GHz diodes with an output power of 50 mW (pulse operation) were obtained.

5. Conclusions. - We have demonstrated that the InP adduct epitaxy with (CH₃)₃In-P(CH₃)₃ and (CH₃)₃P is well suited for the growth of thin InP-layers with abrupt junctions. The growth temperature of the adduct process is about 50 to 100°C lower than the substrate temperature during the Chlorine VPE-process.

6. Literature. -
2. STRINGFELLOW, G.B. and HALL jr., H.T. J. Electron. Mat. 8, 201 (1979)