Planarised selective regrowth of semi−insulating InP by LP−MOVPE using Tertiarybutylchloride

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Abstract

Selective regrowth of Fe−doped InP by tertiarybutylchloride (TBCl) assisted low pressure MOVPE on tall and narrow ridges has been investigated regarding the chloride addition, the surface morphology, and the mesa shape. Planarisation experiments have been carried out on ridges orientated in the [110] direction on (100) InP:Sn substrate. An excess growth ratio as low as 6 % was achieved on 1.5 µm wide – 3 µm high mesas. The planarisation effect was found to depend mainly on the chloride concentration during the selective growth. Thus, we were able to demonstrate the establishment of a successful planarisation process by means of TBCl addition, essential to the fabrication of high speed optoelectronic devices
Key words: planarisation, InP, TBCl, MOVPE

1. Introduction

Selective regrowth of current blocking InP layers by low pressure MOVPE has proved to be a promising technique for e.g. the regrowth of current confining layers in buried heterostructures (BH) laser diodes [1,2]. However, in such a process epitaxial difficulties are encountered when regrowing mesa structures, because of the excess growth effect at the ridge edges or polycrystalline deposition on the mask. Thus, historically, growth at high temperature and low pressure [3], pulsed metalorganic epitaxy [4] or processes using low cracking temperature precursors [5] have first been investigated to overcome these planarisation difficulties.
However, to this aim, chloride assisted processes were found to be much more effective than chloride−free epitaxy. HCl [6], PCl_3 [7], CCl_4 [8] or CH_3 Cl and other chlorocarbons [9] have already been applied, and planarised regrown tall and narrow InP ridges were obtained. Among the available chloride compounds, the recently developed precursor tertiarybutylchloride (TBCl) shows significant advantages as excellent purity, compatibility with stainless−steal systems and a side−product−free pyrolysis during epitaxy. TBCl has initially been used for in−situ etching [10−12]. Our group has already published results on TBCl in−situ etching of InP and related materials [11,13,14] and, recently, a study on the interaction with Fe−doping in InP [15]. However, to our knowledge, there has been no investigation of the planarisation effect of this compound.
In the work presented here, we investigated the epitaxial conditions required for the planarised regrowth of 3 µm thick Fe−doped InP at 1.5 µm wide mesas with TBCl addition. After a brief description of the experimental conditions, we will analyse the observed dependence of the regrowth morphology on the TBCl/TMIn molar fraction ration (MFR). Finally, we will describe the influence of TBCl addition on the surface state.

2. Experimental procedure

In this study, an Aixtron−200 MOVPE system equipped with a gas foil rotation substrate holder was used. Highly concentrated phosphine (PH_3) and trimethylindium (TMIn) were employed as group (V) and (III) precursors, respectively. Tertiarybutylchloride (TBCl) was utilized as additive chloride compound in the range of 0 % − 40 % TBCl/TMIn MFR. The reactor pressure was adjusted between 20 mbar and 100 mbar. The temperature was monitored in the body of the graphite susceptor and varied between 635°C and 700°C. Due to the gas foil rotation the actual wafer temperature is slightly lower, the assessed wafer temperature at 670°C was c. 635°C. The morphology and the dimensions of the grown wafers were observed and measured via secondary electron microscope. The samples used in this study were etched in InP:Sn substrates by means of reactive ion etching (RIE), or chemical etch solutions to form 1.5 µm wide – 3 µm high ridges in the [110] direction, spaced by 250 µm and covered with a 250 nm thick SiNx mask.

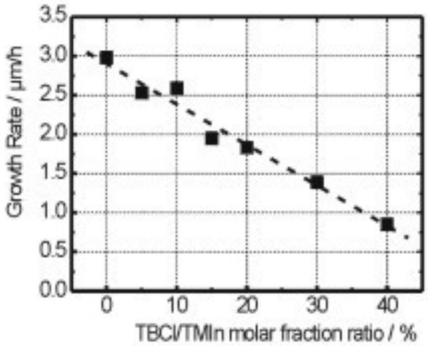

Fig. 1 *Measured dependence of the growth rate on the TBCl/TMIn molar fraction ratio during growth at 635°C-100 mbar. A linear decrease at higher TBCl flow rates is observed.*

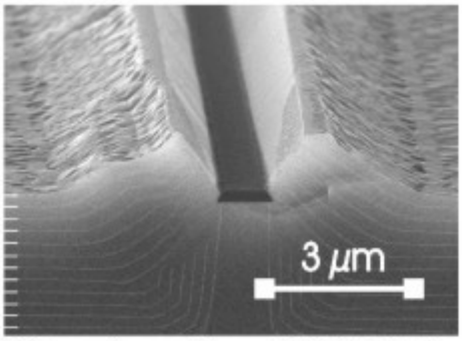

Fig. 2 *Regrowth morphology at 635°C-100 mbar on a 1.5 µm wide 3 µm high mesa without TBCl addition. Surface roughness and excess growth at the ridge ridge edges is observed. The excess ratio is 40 %.*

3. Results and discussion

If we assume that the TBCl and TMIn are almost fully cracked in the gas phase and that they react to form In−Clx complexes, which are very volatile and so do not contribute to the growth, then TBCl addition should reduce the In−molar flow on the growth surface, i.e. reduce the growth rate. Fig. 1 shows the dependence of InP growth rate on TBCl addition at 635°C – 100 mbar, for a TBCl/TMIn MFR varying from 0 % to 40 %. The growth rate was found to decrease linearly with increasing the TBCl flow. This tendency is common for temperature and pressure varying from 635°C to 700°C, and 20 mbar to 100 mbar, respectively.

The main purpose for adding TBCl is to improve the regrowth form at the mesa edges. Fig. 2 shows a selectively regrown mesa, after a regrowth process at 635°C−100 mbar under PH_3 and TMIn, without TBCl addition. In this case, surface roughness and a strong excess growth are visible. However, no overhang or polycrystalline depositions on the 250 nm thick SiNx mask are present, indicating an acceptable selectivity. The amount of excess growth can be evaluated via the excess growth ratio, which is defined as the ratio between the mesa height and the excess growth height above the regrowth surface. In the case presented on Fig. 2 this ratio reaches 40%.

In Fig. 3, the result of a selective growth with TBCl addition is presented for a TBCl/TMIn MFR of 10 % , demonstrating that TBCl addition produces a substantial planarisation effect. Due to this effect, better selectivity and improved surface roughness are observed. A significantly lower excess growth ratio of 26 % is now obtained.

Table 1 shows the evaluation of the excess growth ratio in dependence on the epitaxial conditions and the TBCl/TMIn MFR. According to these results, the possibilities to reduce the excess growth ratio and to obtain a better planarisation effect are either to increase the temperature or to reduce the reactor pressure or to increase the TBCl/TMIn MFR. However, a small increase of the TBCl/TMIn MFR, e.g. from 0 to 10 %, leads to a much stronger reduction of the excess growth ratio as compared to the effect of a temperature rise (635°C to 670°C) or a pressure decrease (100 mbar to 20 mbar). This confirms that TBCl addition is the determining factor for planarisation. However, as TBCl is an etchant for InP and related materials [10−12,14], its addition should be limited to a level where planarisation can be obtained and deterioration of the sample surface be avoided. Above this limit, a strong etch of the mesas and surface roughness are generated during epitaxy. Fig. 4 shows this effect for TBCl/TMIn MFR = 40 %, on a sample grown at 635°C – 100 mbar.

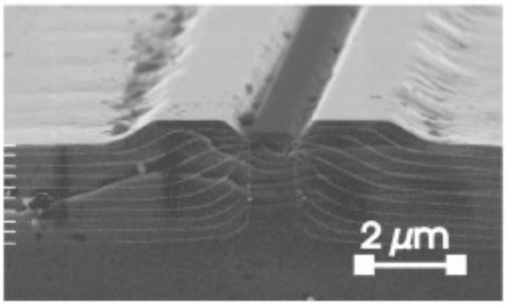

***Fig.3** Regrowth morphology at 635°C-100 mbar on 1.5 µm wide - 3 µm high mesas without TBCl addition. A reduced surface roughness and excess growth at the ridge edges is observed. The corresponding excess growth ratio is 26 %.*

***Table 1.** Dependence of the excess growth ratio on the epitaxial conditions on 1.5 µm wide - 3 µm high mesas.*

Temp.	Pressure (mbar)	TBCl/TMIn MFR	Overgrowth Ratio
635°C	100	0 %	40 %
635°C	100	10 %	26 %
670°C	100	0 %	35 %
670°C	100	10 %	12 %
670°C	20	0 %	31 %
670°C	20	10 %	6 %

Due to the etch effect of TBCl, a modification of the surface quality has also been observed in dependence on the chloride addition during epitaxy. Table 2 shows the dependence of size and density of growth defects for different epitaxial conditions with and without TBCl addition. The defect density diminishes with rising reactor temperature or pressure. At a growth temperature of 635°C TBCl addition led to an increase of the defect size. In case of TBCl/TMIn higher than 10 %, the defect density increased as well. Above 670°C the defects were round shaped with a diameter below 10 µm, and TBCl addition did not show any influence on their size or density. Defect densities below 20 defects·cm^{-2} were routinely achieved.

In order to investigate a possible dependence of the regrowth morphology on the mesa shape, a comparison was carried out between two different mesa etch techniques, RIE and HCl:H_3PO_4, respectively. Selectively regrown mesas at 700°C – 100 mbar, with TBCl/TMIn MFR = 10 %, showed that the excess growth ratio was similar for both etch techniques, measured between 6 % (RIE) and 15 % (HCl:H_3PO_4). The growth rate was about 2.6 µm/h in both cases. Thus, the flexibility of the TBCl planarisation process concerning the required mesa shape could be demonstrated.

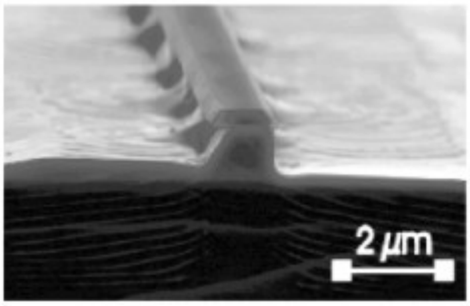

***Fig. 4** Regrowth morphology at 635°C-100 mbar on a 1.5 µm wide - 3 µm high mesa with TBCl/TMIn = 40 %. A strong etch of the ridge due to the high TBCl/TMIn MFR is observed.*

***Table 2.** Dependence of the surface defects size and density on the epitaxial conditions.*

Temp.	Pressure (mbar)	TBCl/TMIn MFR	Defect density (d/cm^2)	Typical defect diameter (µm)
635°C	100	0 %	194	10
635°C	100	10 %	45	40
635°C	100	20 %	89	60
670°C	100	0 %	24	< 10
670°C	100	10%	15	< 10
670°C	20	10%	35	< 10
700°C	100	10%	18	< 10

Finally, following the previous observations, 700°C – 100 mbar with TBCl/TMIn MFR = 10 %, were chosen as optimised growth conditions for planarisation. Fig. 5 shows regrowth experiments at these conditions, demonstrating an excellent selectivity and practically nonexistent excess growth (excess growth ratio < 6 %). Further more, planarisation is obtained consistently over the whole sample surface, indicating the possibility of a smooth consecutive device fabrication.

4. Conclusion

In conclusion, we have comparatively investigated the selective InP:Fe regrowth at tall and narrow mesas with TBCl−assisted LP−MOVPE. An excellent selectivity and high quality surface morphology were achieved at 700°C – 100 mbar with TBCl/TMIn MFR = 10 %. Under these conditions, excess growth ratios as low as 6 % on 1.5 µm wide – 3 µm high mesas were assessed. The planarisation effect is independent of the mesa shape. An excellent and reproducible planarisation was obtained over the whole space (250 µm) between the mesas over the entire wafer.

The growth defect size and density were found to increase for temperatures below 670°C when TBCl was added. For all other epitaxy conditions, growth defects with diameters below 10 µm and densities below 20 defects·cm^{-2} were routinely obtained. As TBCl is an etchant of InP and related materials, its addition was maintained below 20 %, in order to obtain a planarisation effect without affecting the regrown surface quality.

Own results, published elsewhere [15], demonstrate that TBCl addition to the growth of Fe−doped InP does not alter the high semi−insulating quality of the layer, with resistivity values remaining in the 10^8 Ohm·cm range. In compliance with this requirement, we were able to demonstrate the establishment of a successful planarisation process by means of TBCl addition as a powerful technique for the fabrication of high speed optoelectronic devices.

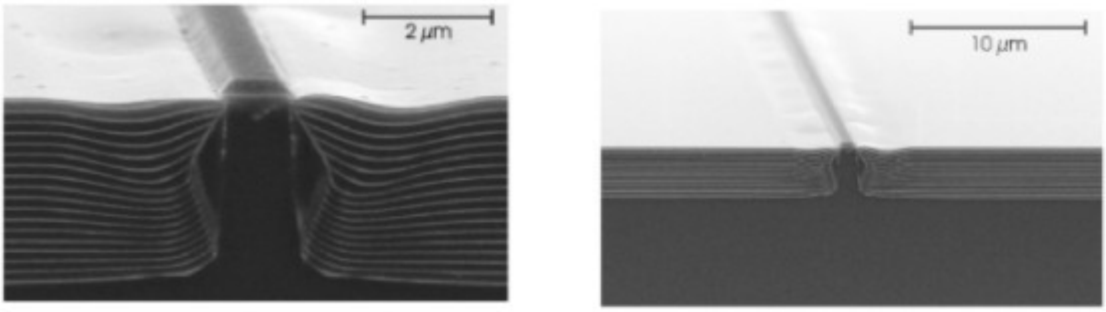

Fig. 5 Regrowth morphology at 670°C-100 mbar, TBCl/TMIn MFR = 10 %. Full planarisation is obtained in the mask vicinity (a), as well as in the space between adjacent ridges (b).

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