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The Influence of PCl 3 on Planarisation and Selectivity of InP Regrowth by Atmospheric Pressure MOVPE

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Abstract

The introduction of phosphorus trichloride into the AP-MOVPE growth of InP has been found to dramatically improve the regrowth adjacent to mesa structures. By suppressing growth in the [100] direction and enhancing growth in the [311] directions planar regrowth is achieved. Polycrystalline deposits on dielectric masks can also be completely suppressed.

Introduction

Re-growth of InP onto lithographically defined non-planar structures, selective area epitaxy (SAE), is often a fundamental part of device fabrication. The morphology of this growth step influences both device performance and the ease with which subsequent processing steps can be carried out and in some cases dictates device architectures. In conventional atmospheric pressure MOVPE, growth adjacent to areas of dielectric is enhanced by migration of material from the vicinity of the dielectric to the semiconductor[1] giving rise to growth rate enhancement and 'ear' formation[2] . If the dielectric is wider than ~20μm then polycrystalline deposition is likely. Both 'ears' and polycrystalline deposits can seriously degrade subsequent lithographic and re-growth steps.

Considerable effort is being made world-wide, using a wide range of techniques, to develop routes to planar regrowth. Growth at reduced pressure can significantly improve selectivity and reduce growth rate enhancement[3]. Low pressure MOVPE at <10 Torr greatly reduces 'ear' growth. Further improvement is possible by going to still lower pressures and growing by Chemical Beam Epitaxy, CBE. By CBE, when conditions are optimised, growth on the dielectric can be eliminated. By Molecular Beam Epitaxy, MBE, growth occurs equally on semiconductor and dielectric unless impractically high temperatures are used.

An alternative approach to lowering the pressure is to modify growth chemistry at atmospheric pressure. There has been a revival in one of the original epitaxy techniques, Vapour Phase Epitaxy, VPE, and in particular Hydride VPE[4-7] . In this technique, hydrides are used to transport the group V elements but chlorides are used for the group III's. Selectivity of InP growth by HVPE is excellent with planar overgrowth of 14μm high dry etched mesas having been reported[8] . A modification of the VPE technique using group III alkyls and group V chlorides has recently been reported[9] .

The potentially more versatile technique is a modification to the MOVPE process by the addition of a chlorine containing compound. Using this method the growth chemistry can be modified to mimic HVPE while retaining the rapid switching, excellent compositional control, range of materials and uniformity of MOVPE in the same system. The simplest chlorine containing compound that could be added to the MOVPE reactor is hydrogen chloride, HCl, but it is known that HCl reacts with trimethylindium, TMIn, to form a low volatility white solid. The use of carbon tertrachloride, CCl_4, has been reported[11] as has the use of 1, 1, 1 trichloroethane[12]. The use of group V chlorides have also been investigated, i.e. $AsCl_3$ in the growth of GaAs from TMGa and arsine, and PCl_3 in the growth of InP from TMIn and phosphine[13].

The use of group V chlorides in the MOVPE process has been questioned because of parasitic reactions on mixing with group III alkyls[14], however in our work, using PCl_3 in the growth of InP has not shown any problems.

Experimental

All growths were carried out in an atmospheric pressure MOVPE kit using TMIn in a stainless steel bubbler held at 40.0°C and 100% PH_3 in a high pressure cylinder. The PCl_3 was held in a borosilicate glass bubbler in a temperature controlled bath between 0°C and -30°C. Growth was in a horizontal, rectangular section , water cooled reactor with IR heating and three zone temperature control. Total gas flow was held near 7 l/min and all growth was on (100) substrates unless otherwise noted.

Four batches of reactive ion etched, RIE, vertical walled mesa stripes were prepared on (100) substrate or planar

material for use during the work. The initial batch of mesas were in both [011] and $[0\bar{1}1]$ directions but all subsequent mesas were in the [011] direction only. The test samples each contained four different mesa widths, i.e. 2µm, 4µm, 6µm and 15µm wide and broad areas of dielectric mask 500µm wide. The mesas were 5.4µm high. One batch of mesas were prepared consisting of 5µm, 10µm, 15µm and 20µm wide square and circular pillars to investigate growth in both directions simultaneously. All mesas had silica dielectric masks on top during growth.
Analysis of growth was carried out using optical Nomarski microscopy, to show surface morphology and cleaved cross sections, and by Scanning Electron Microscopy, SEM. Cleaved sections were stained in a solution of potassium ferricyanide and potassium hydroxide, 1:2 by weight, under white light illumination. Atomic Force Microscopy, AFM, was carried out by AEA Technology.

Results

General Features of Growth with PCl_3

The use of PCl_3 in the growth of InP on (100) surfaces has two significant effects. Firstly, the growth rate is reduced in proportion to the concentration of PCl_3 as illustrated in Figure 1.

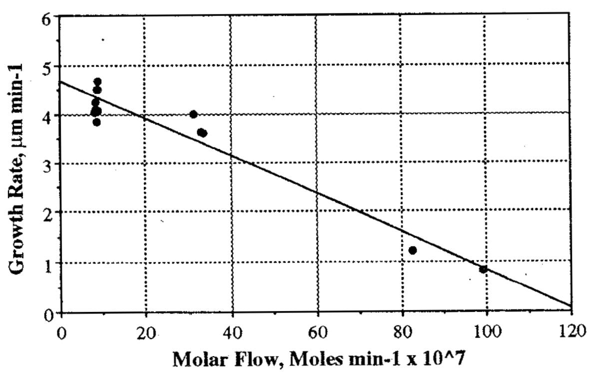

Figure 1. InP growth rate in the (100) direction with the addition of PCl_3.

The second effect is the degradation of the surface morphology illustrated in Figure 2. Surface relief is approximately 30nm with slope angles of between 2° and 3° with the long axis of the features aligned with the [011] direction. Atomic Force Microscopy (AFM) images show that the features are terraced on the atomic scale with each step being of the order of 3Å. It was found that the surface morphology could be improved by growing on mis-

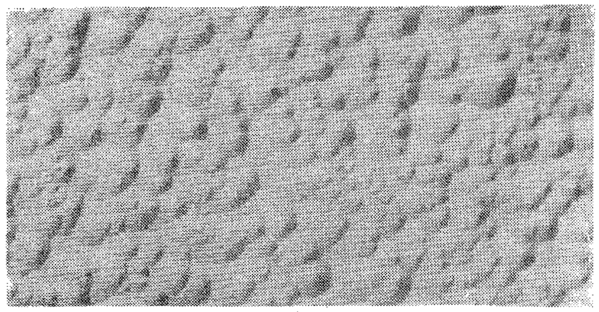

Figure 2. (100) surface morphology of InP grown with PCl_3. White bar is 500µm long

oriented substrates. Growth on $(100)\xrightarrow{2^\circ}(110)$ resulted in smooth, specular morphology.

Mesa Regrowth

The improvement of growth adjacent to mesas is illustrated in Figure 3. Growth at 600°C without PCl_3 results in

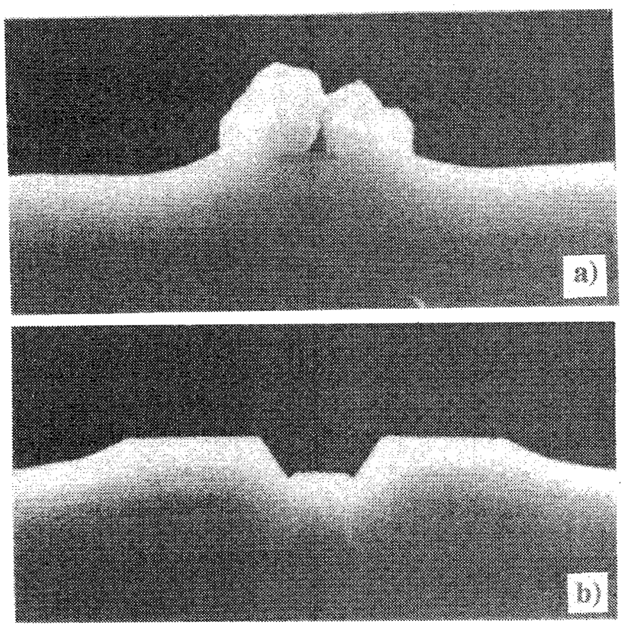

Figure 3. Effect of adding PCl_3 during regrowth of InP adjacent to RIE mesas. a) without PCl_3, b) with PCl_3

irregular overgrowth of the silica mask whereas with PCl_3 growth is pinned to (111) planes at the mesa edge and terminates at the (100) surface. A range of growth temperatures were investigated and found to significantly affect the shape of the regrowth. At higher growth temperatures (700°C) the region of enhanced growth adjacent to the mesa became narrower but more pointed whereas at lower growth temperature (500°C) depressions

appeared at the mesa edges. In both cases the surface morphology was seen to be smoother than at 600°C.
The influence of V/III ratio on growth was studied but found to be less important than growth temperature. As the V/III ratio was increased over the range 15 to 200 the regrowth features were seen to become more angular although the general form of the growth remained the same. The greatest effect of V/III ratio was seen at the lower growth temperature where the depressions at the mesa edge became much more pronounced.
Increasing the concentration of PCl_3 during growth further reduces the growth rate enhancement near the mesa as illustrated in Figure 4, where the flow has been increased by a factor of 3.

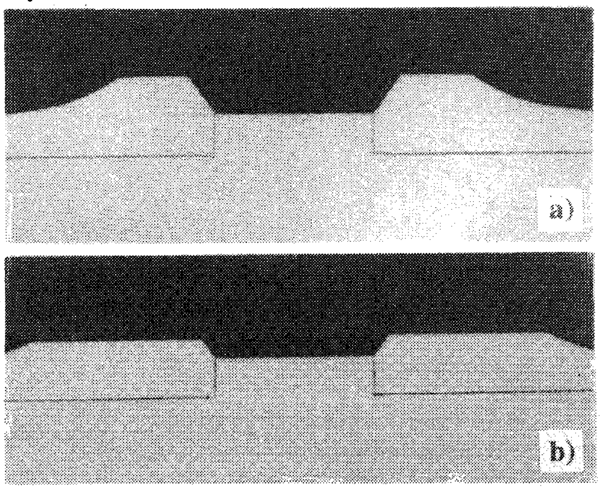

Figure 4. Effect of increasing flow of PCl_3 on mesa regrowth at 600°C. a) 9×10^{-7} moles min^{-1} PCl_3, b) 2.5×10^{-6} mole min^{-1} PCl_3.

Complete suppression of growth in the [100] direction can be achieved by increasing the PCl_3 concentration to 6×10^{-6} moles min^{-1}. Figure 5 shows one side of a 15μm wide 5.4μm high RIE mesa, regrown with the above PCl_3 concentration, with six alternating layers of p-type and n-type InP.

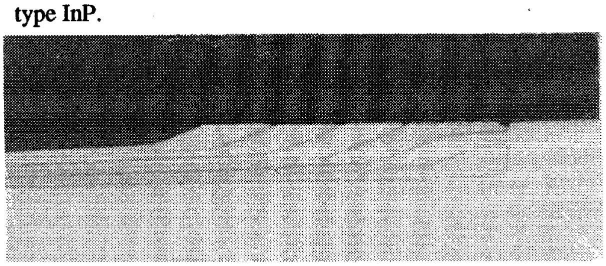

Figure 5. Regrowth of alternating p- and n-type InP around 5.4μm high mesas with 6×10^{-6} moles min^{-1} PCl_3.

The growth from the sides of the mesa is seen to proceed on the (311) planes with a growth rate of 11.5μm $hour^{-1}$. This form of growth is very similar to that seen in HVPE[14] and it is the presence of the fast growing (311) planes which is responsible for the complete suppression of growth in the [100] direction[15].
Dopant incorporation during PCl_3 assisted regrowth is expected to differ from conventional regrowth as growth proceeds on (311) in preference to (100) surfaces and because of the higher growth rate[16-17]. As a result dopant precursor flows will have to be modified for regrowth using PCl_3.
The PCl_3 assisted planarisation seen above has also been observed on mesas formed by wet etching and on in-situ etched mesas formed using PCl_3 etching before regrowth. In both cases growth stopped at the top of the mesa demonstrating that the planarisation is independent of the initial mesa shape.
The planarity of the regrowth is however found to depend on the mesa width and as the mesa width is increased beyond 15μm, growth in the [100] direction again becomes significant. Increasing the concentration of PCl_3 does not improve the growth but starts to degrade the surface by introducing etch pits. Improved growth on wide mesas can however be achieved by reducing the growth temperature and growth adjacent to 500μm wide 5.4μm high stripes has been observed with as little as 1.25μm excess growth above the top of the mesa. Thus the technique may also be applicable to butt-coupling in active-passive waveguide devices.
Regrowth of InP around pillars is illustrated in Figure 6.

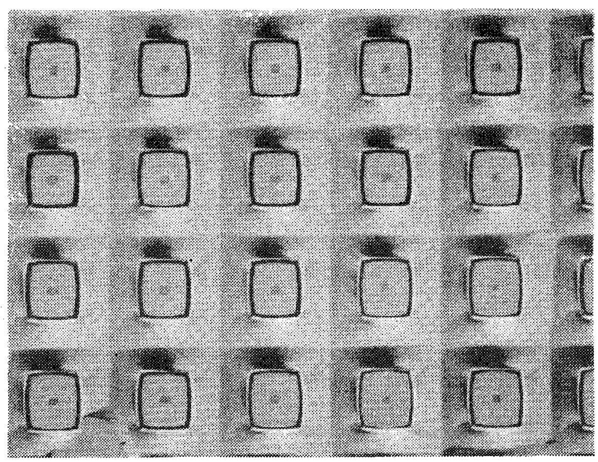

Figure 6. An array of pillars after planarising regrowth with Fe-doped InP. The separation between centres of the devices is 125μm.

It can be seen that a square, planar region is formed adjacent to the pillar and that the extent of growth is similar in both [011] and $[0\bar{1}1]$ directions. This behaviour is different to that seen in HVPE in which growth in the [011] direction is significantly faster than in the $[0\bar{1}1]$ direction[14].

Conclusions

The incorporation of PCl_3 into the AP-MOVPE process has been demonstrated to planarise regrowth adjacent to mesa structures up to 15μm wide and completely suppress polycrystalline growth on dielectric masks over 500μm wide. The planar regrowth around pillars demonstrates that the vertical extent of the growth is the same in both [011] and $[0\bar{1}1]$ directions. By modifying the growth conditions, near planar regrowth can be achieved adjacent to tall mesa stripes up to 500μm wide.

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