

InP Grown by Low-Pressure MOVPE Using Dimethylindium Pyrazole

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Abstract

An unusual liquid organoindium precursor for MOVPE was synthesised, purified and tested for homo- and hetero-epitaxial growth of InP. The good quality of the obtained epilayers was tested by Hall and PL measurements. The measured growth rate is low ($0.2\mu\text{m/h}$), and constant in a wide temperature range ($580\text{--}680\text{ }^\circ\text{C}$). This makes dimethyl indium pyrazole a good candidate for the growth of In-based MQW structures. InP nanostructures on a GaAs substrate were also grown using the same precursor.

Introduction

Epitaxial layers of InP and related ternary and quaternary alloys are commonly deposited, for industrial scale production by LP-MOVPE (Low Pressure Metal Organic Vapour Phase Epitaxy) process using trialkylindium and phosphine [1]. Trimethylindium (TMI) is, at the present, the most common indium precursor in that it may be purified so efficiently as to yield excellent quality epitaxial layers. However TMI is solid at room temperature and the evaporation from a solid source may cause agglomeration from powder into large crystals over few months, thereby continually reducing the surface area available for sublimation. This results in long-term variations of TMI feed rate with consequent poor reproducibility in a production line. Aiming to solve this problem, alternative liquid indium precursors have been proposed such as Et_3In and EtMe_2In that, however, exhibit low thermal stability at room temperature. In any case the trialkyl indium compounds show other drawbacks: they all are highly pyrophoric and moisture-sensitive, i.e. hazardous to prepare, purify and handle, and therefore they result very expensive. Their high reactivity towards dioxygen and water is mainly due to the unsaturation so that the organoindium compounds behave as Lewis acids. An improvement of their stability can be obtained by a coordinative or electronic saturation of the indium atom that can take place through formation of an adduct between the organoindium compound (Lewis acid) and an electron donor molecule (Lewis base) [2]. In this context intense efforts have been devoted to the synthesis of new organometallic indium precursors with a coordinatively saturated metallic atom. In particular our attention has been devoted to organoindium compounds containing a $\text{In-N}\sigma$ bond such as dialkylindium amides [3] or dialkylindium azolides [3c, 4] where the electron lone pair on the N atom of the ligand is shared with the indium atom of another moiety to form dimeric species. In such a way the indium atom, saturated by the bridging ligand, is protected against further reactions with dioxygen and moisture.

Unfortunately the known compounds of this type are solid at room temperature or liquid with low vapour pressure that severely limits the maximum achievable growth rate, so that they cannot represent the ideal alternatives of traditional precursors. On the other hand this drawback turns into an important advantage when the deposition of very thin InP layers is pursued as those required for quantum well heterostructures or for the deposition of quantum dots. In particular dimethylindium pyrazole is a liquid at room temperature and has been already used for the growth of InP in an atmospheric pressure reactor, obtaining rather poor quality material. Here we report that the use of a purer batch of dimethylindium pyrazole (Me_2InPz) in a low pressure regime reactor leads to a significant improvement of the electrical properties and allows the growth of nanostructures of InP on GaAs substrates.

Experimental

Me_2InPz was first synthetised according to the following methods: (a) displacement of chloride ions from Me_2InCl by LiPz or (b) reaction of pyrazole (PzH) with Me_3In . With respect to the reported synthesis [4] we brought an improvement consisting of better yield and higher purity of Me_2InPz . Due to their very high air-sensitivity, organoindium precursor must be handled in a glove box under rigorously purified nitrogen. The solvents have been dried by heating at reflux over potassium benzophenone under purified nitrogen and distilled just prior to use. An equimolar amount of PzH (purified by sublimation) in hexane was slowly added to a vigorously stirred solution of freshly distilled $\text{InMe}_3\text{-Et}_2\text{O}$ in a few ml. of hexane. The solution was stirred for 24 hours, then the solvent was removed under vacuum and the residue purified by distillation.

Growth procedure.

All growth experiments have been performed in a standard LP-MOVPE reactor (AIXTRON AIX 200) with a rectangular reaction chamber and a carbon susceptor heated by IR lamps. The group V source was 100% PH_3 (UCAR electronic grade) and the carrier gas was Pd-purified H_2 . The organoindium source (Me_2InPz) was thermoregulated at 45°C and the distribution lines between source and reactor were heated at 60°C to prevent condensation. Substrate materials for the deposition of InP layers was (100) Fe-doped, semi-insulating InP. The total pressure in the reactor was 20 mbar, the gas velocity 1.3 m/sec (calculated for room temperature conditions) and the growth temperatures were in the range 580-700 °C.

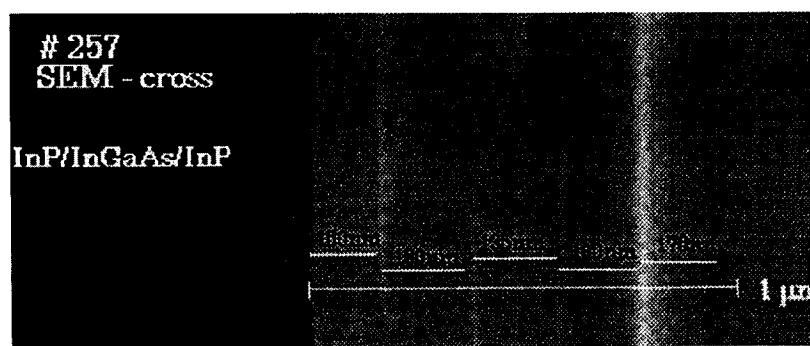


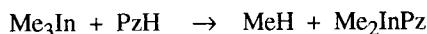
Figure 1 SEM micrograph of the cross section of a 4-layer sample

The electrical properties of the films were evaluated by Van der Paw measurements using alloyed In contacts on square samples (1 cm^2) at room temperature and at 77K. The PL spectra were obtained at 4.2 K by a previously described apparatus [5] using a He-Ne laser.

In order to evaluate the growth rate of InP, some layers of InP, obtained as above described, were grown between InP-matched InGaAs layers obtained with commercial precursor (Me_3In and Me_3Ga). The layer thickness of the multiple epilayers was determined by SEM observation of a sample cross section after selective etching of InGaAs layers with $\text{H}_3\text{PO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (1/1/3) solutions (Figure 1). SEM micrographs were taken using a XL40 model (LaB₆ source) Philips microscope. Nanostructures of InP on GaAs substrates were obtained growing in short time InP using Me_2InPz on semi-insulating Cr-doped (100) GaAs substrates after deposition of a 300 nm of GaAs buffer layer at 700 °C.

Results and discussion

Dimethylindium pyrazole can be easily synthetised according to the following reactions:



in ether or toluene [4]. We have found an improvement of the method, in fact using a less polar solvent as n-hexane we obtained a purer product which is not contaminated with lithium salts. Me_2InPz is liquid at room temperature, it is significantly more air-stable than trimethylindium and triethylindium and its vapour pressure is $1.7 \cdot 10^{-2}$ Torr at 45°C. It was previously used as precursor for the growth of InP in an atmospheric pressure MOCVD reactor, giving layers with good surface morphology but with low mobility values [4]. With the newly prepared sample and the low pressure apparatus a significant improvements of the electrical properties of the InP layer has been obtained. These two conditions lead to InP with lower incorporation of impurities and higher mobility values.

Sample	T_g (°C)	$\mu_{300K}(\text{cm}^2/\text{Vs})$	μ_{77K} (cm ² /Vs)	$n_{300K}(\text{cm}^{-3})$	$n_{77K}(\text{cm}^{-3})$	Reference
	580	3350	5300	6×10^{16}	4×10^{16}	[4]
a	580	3482	11957	2.7×10^{15}	2.8×10^{15}	This work
b	640	3225	12320	2.7×10^{15}	2.9×10^{15}	This work
c	680	3480	13464	8.2×10^{14}	1.6×10^{15}	This work

Table 1

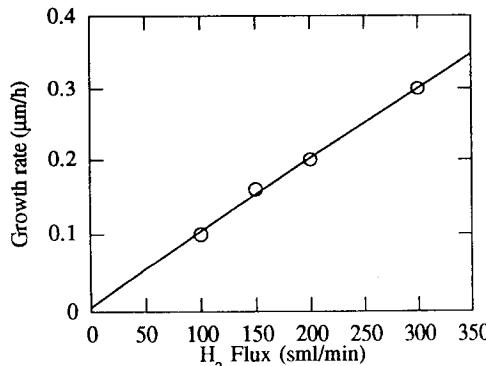


Fig. 2 Dependence of InP growth rate on H_2 flux through Me_2InPz bubbler

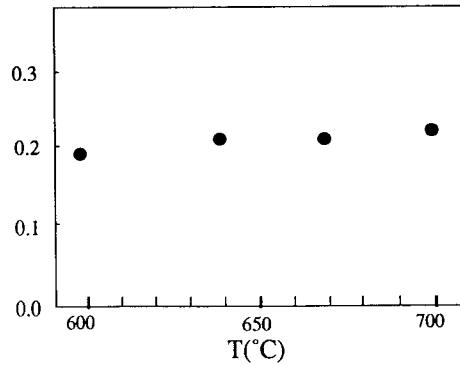


Fig. 3 Dependence of InP growth rate on growth temperature.

Under the described experimental conditions we obtain an average growth rate of about 0.2 $\mu\text{m}/\text{h}$. This is independent of growth temperature in the investigated range (580–680 $^{\circ}\text{C}$), whereas it exhibits a linear dependence on the H_2 flux through the Me_2InPz bubbler (Figures 2 and 3).

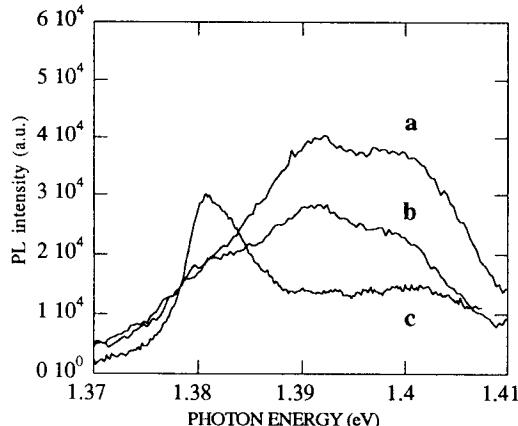


Fig.4: PL spectra (non-excitonic region)

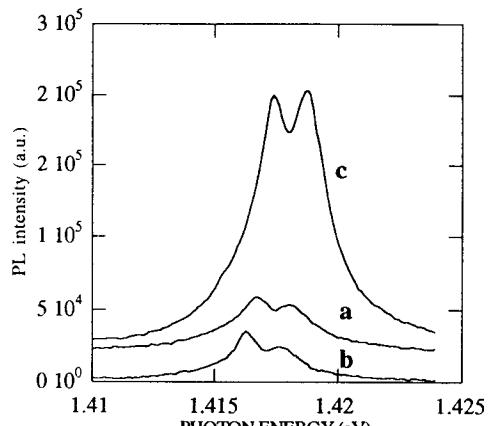


Fig.5: PL spectra (excitonic region)

The PL spectrum at 4.2 K of the sample **c** exhibits an intensity significantly higher than that of both **a** and **b**. The ratio between the peak-intensities in the excitonic and non-excitonic regions [6, 7] is very similar for **a** and **b**, while it is much higher in **c**. The non-excitonic region of the spectra are reported in figure 4: two wide peaks centered at 1.39 and 1.40 eV are present. This interesting feature was previously observed [7] for InP grown using $\text{Et}_2\text{InNMe}_2$ and a high V/III ratio (2000), and it was associated to deep levels [8]. This is consistent with the even higher (>5000) V/III ratio used in the present work. A further shoulder (1.38 eV), suggesting incorporation of a deep acceptor $[(\text{D}^{\circ}, \text{A}^{\circ}) - (\text{e}, \text{A}^{\circ})]$, is evident in sample **b**, and even more intense in **c** grown at the highest T_g . In the excitonic region (Fig. 5) the free exciton peak [FE: 1.419 eV, [9]] is not resolved, in the presence of a strong $(\text{D}^{\circ}, \text{X})$ band, and the $(\text{A}^{\circ}, \text{X})$ band [10] is rather intense in all the samples. However, the intensity ratio between the higher-energy peak and the lower-energy one $[(\text{D}^{\circ}, \text{X}) - (\text{D}^{\circ}, \text{h})]$ is higher in **c**, so indicating a better quality of the latter sample.



(1x2 μm) $T_g=700\text{ C}$



(1x2 μm) $T_g=600\text{ C}$

Figure 6 : SEM micrograph of two InP/GaAs samples (growth time ≈ 1 minute)

In addition to the depositions of InP homoepitaxial layers we have investigate the possibility to use the new precursor in the growth of nanostructures of InP on GaAs substrates. Our aim is to exploit the strong mismatching between the InP and GaAs lattice to grow InP islands of nanometric size. The Me_2InPz precursor should be favoured with respect to TMI because, owing to its low vapor

pressure, it makes easier working at small growth rate. The effect of growth temperature T_g was investigated in the range 600+700 °C, while keeping constant the V/III ratio (≈ 5000). SEM analyses indicate that islands with small and uniform "in plane area" A are obtained at $T_g=700$ °C, where the size distribution s shows a peak around 100 nm ($s=2\sqrt{A/\pi}$). Smaller islands are round-shaped, while the larger ones show faceting (Figure 6). The nanostructure time-evolution exhibits two regimes: at first the number of small islands increases with time, then the larger structures start growing, while the total coverage remains nearly constant. At present the details of the growth mechanism are not clear, and further investigations on samples grown in a broader temperature range and with different values of the V/III ratio are in progress.

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