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A new precursor for epitaxial growth of indium based semiconductors

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Abstract

Epitaxial layers of n-type InP have been grown via metalorganic vapour phase epitaxy (MOVPE) using the new precursor Et_2InNMe_2 and studied mainly by photoluminescence and Hall measurements. The results point to encouraging electrical and optical properties, although they are not as good as those of InP grown with conventional precursors. Samples grown at different growth temperatures and V/III ratios exhibit quite different properties. In particular, incorporation of Mg at higher and Zn at lower growth temperature is shown by photoluminescence at liquid-helium temperature.

1. Introduction

The deposition of epitaxial InP via MOVPE (metalorganic vapour phase epitaxy) is usually carried out by using $InMe_3$ and $InEt_3$ as indium precursors [1]. However, due to several drawbacks of these "conventional" precursors – mainly high pyrophoricity and high reactivity towards nucleophilic agents, low long-term thermal stability of $InEt_3$ and poor growth rate reproducibility of $InMe_3$ – we recently undertook a research activity aimed at synthetizing new indium organoderivatives [2] more stable than conventional sources. Since the stability of organometal compounds of this series is related to coordinative saturation of the central atom, we turned our attention to heteroleptic indium compounds, such as Et_2InNMe_2 (dimeric in the solid state) bearing atoms with lone pairs that are available for dative bonding, so forming an intermolecular adduct [3]. Its high stability and thermal properties (cracking temperature) render this compounds suitable for MOVPE applications.

2. Experimental procedure

Et_2InNMe_2 was synthetized as previously reported [3,4] and purified by sublimation at 310 K ($P \approx 10^{-2}$ mbar). Its vapour pressure curve was measured in the range 298–314 K: a Pyrex cell containing Et_2InNMe_2 was thermoregulated by a water bath and the pressure was measured with a

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capacitance pressure gauge (Datametrics Barocel Type 621, 10 Torr f.s.). The InP growth was performed in a standard low pressure, (LP) MOVPE reactor (Aixtron AIX-200) equipped with a rectangular quartz reaction chamber and a carbon susceptor heated by an IR lamp. The group V source was 100% PH_3 (Ucar electronic grade), and the carrier gas was Pd-purified H_2. The organometal source was thermoregulated at 41°C and the distribution lines, between source and reactor, were heated at 45°C to prevent condensation. The substrate material was (100) Fe-doped, semi-insulating InP. The total pressure in the reactor was 20 mbar, the gas velocity 1.06 m/s (calculated for standard temperature and pressure), and the growth temperatures were in the range 580–640°C.

The electrical properties of the films were evaluated by Hall measurements using the Van der Pauw method at room temperature and at 77 K. The thickness of the epitaxial films was determined optically and, in some cases, verified by transmission electron microscopy (TEM) at the edge of a cleaved 90° wedge specimen according to Ref. [5]. For this purpose different InP layers were grown with thin GaInAs spacer layers between them. The PL spectra were measured [6] using a He–Ne laser (NEC), a grating spectrometer with reciprocal dispersion of 24 Å/mm (Jobin Yvon HR640), a LN_2 cooled germanium detector (North Coast EO817L) and a helium-flux cryostat (TBT-Alphagaz).

3. Results and discussion

The vapour pressure P of the new indium precursor Et_2InNMe_2 follows, in the range 298–314 K, the curve $\log P\ (\text{mbar}) = -1460/T + 2.978$ (Fig. 1). At room temperature P is much lower than that of the usual In sources, therefore it was necessary to heat the bubbler at 41°C (thus raising the metalorganic partial pressure), in order to achieve growth rate greater than 0.1 μm/h. The total pressure in the bubbler was always kept at low values ($\sim$ 70 mbar). The growth rate is independent of growth temperature (T_g) in the investigated range, whereas it exhibits a linear

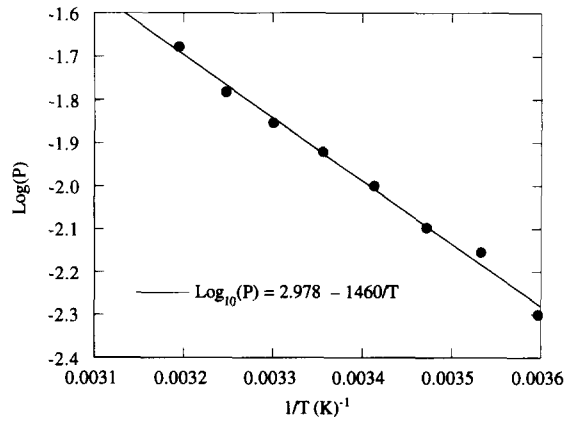

Fig. 1. Saturated vapour pressure curve of Et_2InNMe_2.

dependence (Fig. 2) on the Et_2InNMe_2 molar ratio (a signature of diffusion controlled growth).

The growth efficiency η (defined as the ratio of the growth rate to the metalorganic molar flow) does not depend on T_g, and we obtain $\eta = 4.8 \times 10^4$ μm/mol. If we take into account the η values achieved in our reactor with $InMe_3$ ($\eta = 3.7 \times 10^4$ μm/mol), it may be suggested that the stability towards parasitic homogeneous gas-phase reactions of the new precursor is comparable with that of $InMe_3$.

The epilayers described in Table 1, obtained at different growth T_g and V/III ratios, result mirror-like and n-type. Preliminary Hall and room-temperature PL measurements provide evidence

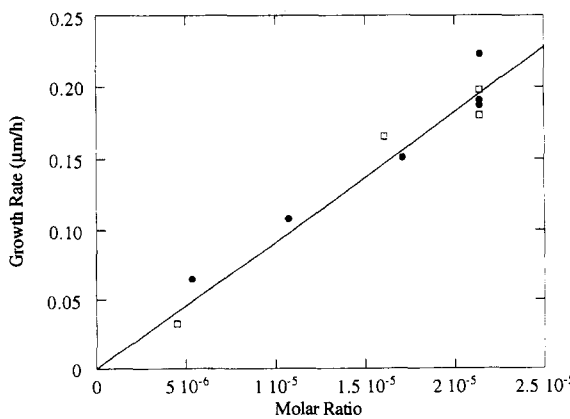

Fig. 2. Growth rate of InP versus molar ratio of Et_2InNMe_2. Squares: thickness measured by an optical microscope, circles: thickness measured by the TEM edge.

Table 1
Growth parameters and electrical properties at 77 K

Sample	Thickness (μm)	T_g (°C)	V/III ratio	μ (cm^2/V·s)	n (10^{15} cm^{-3})
a	4.7	640	325	97000	1.5
b	1.1	640	1300	17000	8.4
c	1.0	580	1300	20000	5.7
d	1.2	610	1000	10000	15.5
e	1.1	610	2000	18000	8.3
f	1.5	610	1300	22000	8.9

of good quality, although not as good as that of InP grown in our laboratory [4] by the conventional precursor $InMe_3$ (sample a).

The chemical nature of impurities in the epilayers may be inferred from the analysis of the PL spectra measured at liquid-helium temperature. The 4.2 K PL spectra of the samples listed in Table 1 are reported in Figs. 3–5.

640°C: The excitonic region of the 4.2 K spectrum (Fig. 3) of sample b (grown at the same temperature $T_g = 640$°C as sample a) suggests a comparatively high concentration of both donor and acceptors, the sample grown by the new precursor being more compensated with respect to the "conventional" one. Support to this view is given by the non-excitonic region of the spectrum where an intense (D°, A°)–(e, A°) band is present. According to the literature [7,8] we associate this unresolved bump (1.382 eV) and the less intense one (1.337 eV), with the same temperature dependence in the range 4.2–20 K, to a significant concentration of acceptor Mg, possibly

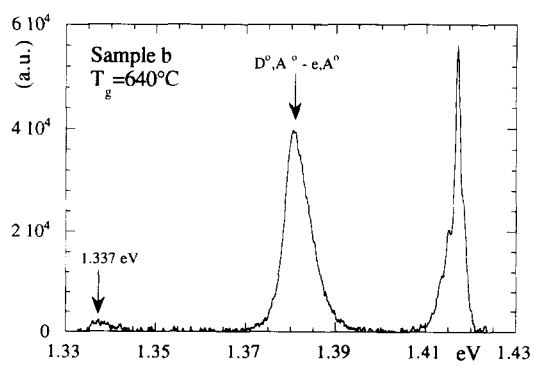

Fig. 3. PL spectrum of sample b, measured at 4.2 K.

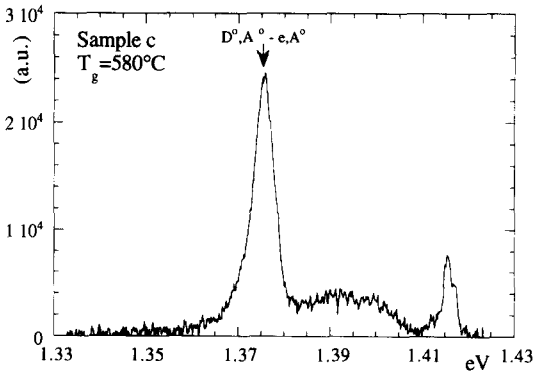

Fig. 4. PL spectrum of sample c, measured at 4.2 K.

arising from the precursor synthesis. In fact, recent secondary ion mass spectroscopy (SIMS) measurements give support to the presence of Mg in the epilayer [9]. On the other hand, the presence of a "tail" on the high-energy side could be ascribed to incorporation of Si, in line with energy values reported for acceptor Si in Ref. [7], namely (D°, A°) = 1.3833 eV, (e, A°) = 1.3865 eV.

580°C: The excitonic region of the 4.2 K spectrum of sample c is less intense with respect to b, and it does not exhibit the free-exciton peak (Fig. 4). The non-excitonic region is dominated by the band at 1.375 eV, that we associate to the well-known incorporation of Zn at lower T_g [10]. The same band might be also consistent with a contribution from acceptor C (D°, A°), but lack of other evidences, such as the related C (e, A°) [7], forces us to rule out this hypothesis.

$T_g = 610$°C: At this intermediate temperature,

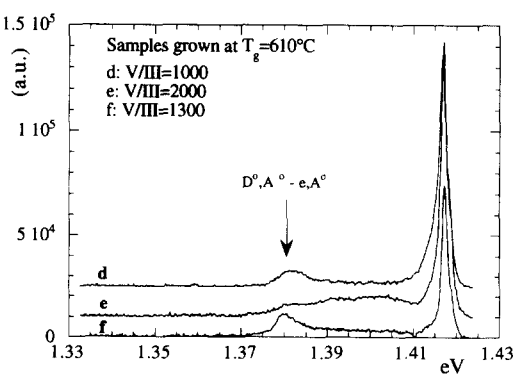

Fig. 5. PL spectra of samples d,e,f, measured at 4.2 K.

the growth was carried out at three different values of the V/III ratio.

V/III ratio = 1000: The excitonic PL spectral region (Fig. 5) of sample d exhibits an intense band, whose broadness is related to the remarkable incorporation of donor Si, responsible of the poor electrical properties (Table 1). The (D°, A°)–(e, A°) region of d has the same position and shape of b, so suggesting incorporation of Mg and acceptor Si.

V/III ratio = 2000: In the spectrum of sample e the more interesting feature is the region 1.39–1.41 eV, probably associated to deep levels, such as interstitial donors or donor–vacancy complexes [11] presently under more specific investigation.

V/III ratio = 1300: Sample f is the less compensated sample. The position and the shape of the (D°, A°)–(e, A°) band point to incorporation of acceptor Mg.

4. Conclusions

The above results prove that Et_2InNMe_2 may be successfully used as indium precursor for LP MOVPE. Its main limit is the small value of the maximum allowed growth rate due to the low vapour pressure of the precursor: this feature, however, may become an advantage when a good control of the epilayer thickness is an important parameter, for instance when very thin (tens of Å) layers for multiple quantum well (MQW) structures have to be grown.

The best electrical properties and lower acceptor concentration are exhibited by the sample f, grown at lower T_g with respect to the "conventional" a. No evidence of C incorporation was found, the major identified impurity being the acceptor Mg at higher T_g and Zn at lower T_g. As a matter of fact, in the present work we used for the precursor synthesis and purification only standard laboratory techniques, but it is our aim to use a more efficient purification method based on the adsorption of impurities such as Mg or Li, deriving from the precursor synthetic route, on sorbents based on titanium and zirconium phosphates [12].

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