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Impurities in InP grown by MOVPE using a new precursor Et₂InNMe₂: photoluminescence and Hall study

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Abstract

Epitaxial layers of n-type InP have been grown by metal organic vapor phase epitaxy at different growth temperatures and V/III ratios using a new indium precursor and characterized mainly by photoluminescence and Hall measurements. Their electrical and optical properties are encouraging, although they are not as good as those of the layers grown with conventional precursors. Samples grown in different conditions exhibit quite different properties. In particular, incorporation of Mg and Zn at higher and lower growth temperature, respectively, is shown by photoluminescence spectra recorded at liquid-helium temperature.

Keywords: Indium phosphide; Photoluminescence; MOVPE; New precursor

1. Introduction

The deposition of epitaxial InP by metal organic vapor phase epitaxy (MOVPE) is usually carried out by using trimethylindium (InMe₃) or triethylindium (InEt₃) as indium precursors [1]. However, owing to several drawbacks of these "conventional" precursors, i.e. mainly pyrophoricity and poor growth rate reproducibility, we recently undertook a research activity aimed at synthetizing new indium organo derivatives which are more stable than InMe3 and InEt3 while having comparable vapor pressure. The volatility depends on the actual molecular weight in the condensed phase and the stability is related to coordinative saturation of the central atom. Therefore, we turned our attention to heteroleptic indium compounds, such as diethyldimethylaminoindium (Et₂InNMe₂), dimeric in the solid state (see Fig.1), bearing atoms with lone pairs which are available for dative bonding [2].

2. Experimental details

InP was grown on (100)Fe-doped InP wafers by using Et₂InNMe₂ (see Refs. [2,3] for synthesis and puri-

fication) and PH $_3$ as precursors, and H $_2$ as the carrier gas. The reactor was a conventional low pressure MOVPE (Aixtron AIX 200) system operating at 20 mbar. The photoluminescence (PL) spectra were measured by a custom-made apparatus (Laser Point) [4] using a He–Ne laser (NEC), a grating spectrometer with a reciprocal dispersion of 24 Å mm $^{-1}$ (Jobin Yvon HR640), an LN $_2$ -cooled germanium detector (North Coast EO817L) and a helium-flux cryostat (TBT-Alphagaz).

3. Results and discussion

Epilayers described in Table 1, obtained at different growth temperatures ($T_{\rm g}$) and V/III ratios, were mirror-like and of n-type. Preliminary Hall (Table 1) and room-temperature PL (Fig. 2) measurements evidenced appreciable quality of layers, although they are not as good as that of InP grown in our laboratory [3] using the conventional precursor InMe₃ (sample a).

Deeper insight into the dependence of layer properties, in particular the chemical nature of impurities, was given by an accurate study of the PL spectra measured at liquid-helium temperature. The lateral homogeneity of the grown layers was confirmed both at room temperature and at 4.2 K. The PL spectra at 4.2 K of the samples listed in Table 1 are shown in Figs. 3–5.

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3.1. $T_g = 640 \,^{\circ}C$

In the excitonic region (Fig. 3(b)) of the spectrum at 4.2 K, the sample **b** (grown at 640 °C, i.e. the same T_g value as **a**) clearly shows the free exciton (FE) peak (where FE = 1.4186 eV; [5]) and an intense (D°,X) one, while (D⁺,X) and (D°,h) lines are supposed to be embedded in the quite intense (A°,X) band [6]. These results, together with the Hall ones, show a comparatively high concentration of both donors and acceptors, suggesting that the sample grown by the new precursor is more highly compensated [7] than the "conventional" one (**a**). This view is supported by the non-excitonic

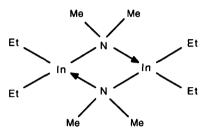


Fig. 1. Schematic view of [Et₂InNMe₂]₂.

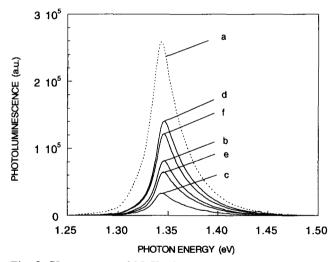


Fig. 2. PL spectra at 295 K of InP grown by InMe₃ and by Et₂InNMe₂.

region of the spectrum where an intense (D°, A°) – (e, A°) band is present. According to the literature [5,8], we associate this unresolved bump (i.e. 1.382 eV) and the less intense one (i.e. 1.337 eV) (the position of which is identically affected by the temperature of the measurements taken between 4.2 and 20 K) with a significant concentration of Mg acceptors possibly resulting from the precursor synthesis. In fact, recent secondary ion mass spectroscopy (SIMS) measurements give support to the presence of Mg in the epilayer [9]. However, a contribution of acceptor Si is suggested by the "tail" on the high-energy side $((D^{\circ}, A^{\circ}) = 1.3833 \text{ eV}, (e, A^{\circ}) = 1.3865 \text{ eV},$ according to Ref. [5]).

3.2.
$$T_g = 580 \, ^{\circ}C$$

The excitonic region for sample \mathbf{c} (Fig. 4(b)) is less intense than that for sample \mathbf{b} , and it does not exhibit the FE peak. The higher energy peak is attributed to (D°,X) , and the more intense one to (D^+,X) and (D°,h) [6]. The non-excitonic region (Fig. 4(a)) is dominated by the band at 1.375 eV, which we associate with the well-known incorporation of Zn at a lower T_g value [10]. The same band might also be consistent with a contribution from acceptor $C(D^\circ,A^\circ)$, but lack of other evidences, such as the related $C(e,A^\circ)$ (i.e. 1.3796 eV, according to Ref. [5]), forces us to rule out this hypothesis.

3.3.
$$T_g = 610 \,^{\circ}C$$

At this intermediate T_g value, layers were grown at three different V/III ratios.

3.3.1. V/III ratio = 1000

The excitonic spectral region (Fig. 5(b)) for sample **d** exhibits an intense band, the broadness of which is related to the remarkable incorporation of donor Si, responsible for the comparatively poor electrical properties (Table 1). Nevertheless, the high-energy shoulder allows us to identify the FE peak. The (D°,A°-e,A°) region (Fig. 5(a)) of **d** has the same

Table 1 Growth parameters and electrical (Hall) properties at 77 K

Sample	Thickness (μm)	$T_{\mathrm{g}}(^{\circ}\mathbf{C})$	V/III ratio	$\mu (\text{cm}^2 \text{V}^{-1} \text{s}^{-1})$	$n(10^{15}\mathrm{cm}^{-3})$
b c d e f	1.1 1.0 1.2 1.1 1.5	640 580 610 610	1300 1300 1000 2000 1300	17000 20000 10000 18000 22000	8.4 5.7 15.5 8.3 8.9

 $[\]mu$, Hall mobility; n, carrier concentration.

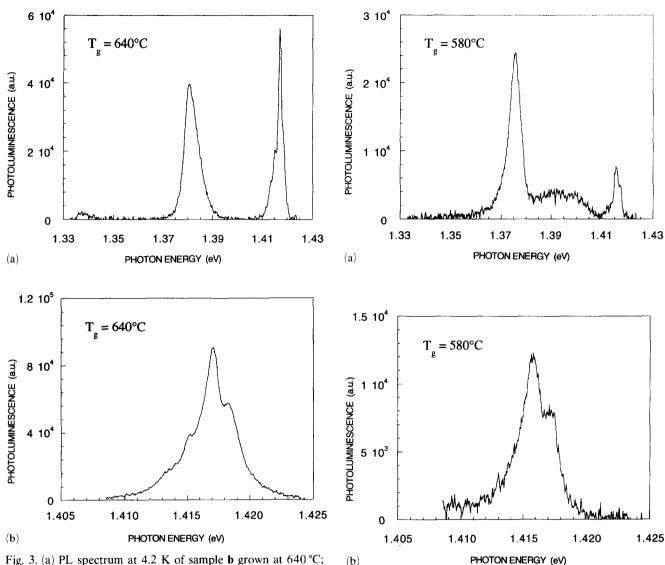


Fig. 3. (a) PL spectrum at 4.2 K of sample **b** grown at $640\,^{\circ}$ C; (b) PL spectrum of sample **b**: excitonic region.

Fig. 4. (a) PL spectrum at 4.2 K of sample c, grown at 580 °C; (b) PL spectrum of sample c: excitonic region.

position and shape of **b**, so suggesting the incorporation of Mg and acceptor Si.

3.3.2. V/III ratio = 2000

In the spectrum of sample e (Fig. 5(a)), the most interesting feature is the region 1.39–1.41 eV, probably associated with deep levels such as interstitial donors or donor-vacancy complexes [11] presently under more specific investigation. In the excitonic region (Fig. 5(b)) the FE peak is well resolved.

3.3.3. V/III ratio = 1300

Sample f is the less compensated of all the samples. The excitonic region (Fig. 5(b)) exhibits an FE peak less resolved than in the spectrum of e. The position and the shape of the $(D^{\circ},A^{\circ})-(e,A^{\circ})$ band (Fig. 5(a)) point to incorporation of Mg acceptors.

4. Conclusions

The PL analysis of both the excitonic and non-excitonic spectral regions of samples grown in different conditions provides several pieces of information, in particular regarding incorporation of impurities as a function of $T_{\rm g}$, so proving to be a useful tool in optimizing the growth procedure. The best electrical properties and lower acceptor concentration are exhibited by the sample ${\bf f}$, grown at a lower $T_{\rm g}$ than the "conventional" ${\bf a}$. The major identified impurities are the Mg and Zn acceptors at higher and lower $T_{\rm g}$ respectively. No evidence of C incorporation was found. Further SIMS studies parallel to the PL ones are in progress.

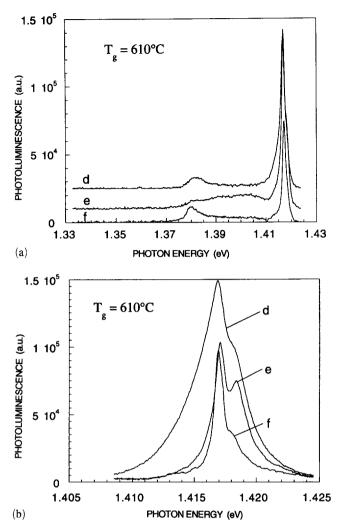


Fig. 5. (a) PL spectra at 4.2 K of samples **d,e** and **f** grown at 610 °C; (b) PL spectrum of samples **d,e** and **f**: excitonic region.

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References

- [1] P. Zanella, G. Rossetto, N. Brianese, F. Ossola, M. Porchia and J.O. Williams, *Chem. Mater.*, 3 (1991) 225.
- [2] M. Porchia, F. Benetollo, N. Brianese, G. Rossetto, P. Zanella and G. Bombieri, J. Organomet. Chem., 424 (1992)

 1.
- [3] G. Rossetto, A. Camporese, M.L. Favaro, D. Ajò, G. Torzo, P. Zanella, V. Corrado, F. De Zuane, M. Porchia, B. Ballarin and R. Franzheld, in S. Daolio, E. Tondello and P.A. Vigato (eds.), Syntheses and Methodologies in Inorganic Chemistry: New Compounds and Materials, 1994, p.349.
- [4] D. Ajò, G. Torzo, G. Rossetto, P. Zanella, F. De Zuane, M.L. Favaro, A. Camporese and M. Mazzer, *Vuoto—Scienza e Tecnologia*, 22 (1994) 128.
- [5] Properties of Indium Phosphide, EMIS Data Reviews No. 6, Inspec, Institute of Electron. Eng., Exeter, 1991, pp. 199-201.
- [6] L. Pavesi, F. Piazza, A. Rudra, J.F. Carlin and M. Ilegems, Phys. Rev. B, 44 (1991) 9052.
- [7] Y. Takeda, S. Araki, S. Noda and A. Sasaki, *Jpn. J. Appl. Phys.*, 29 (1990) 11.
- [8] S.S. Bose, I. Szanfranek, M.H. Kim and G.E. Stillman, Appl. Phys. Lett., 56 (1990) 752.
- [9] A. Carnera, personal communication, 1994.
- [10] N.D. Gerrard, F.J. Nicholas, J.O. Williams and A.C. Jones, Chemtronics, 3 (1988) 17.
- [11] O. Aina, M. Mattingly, S. Steinhauser, R. Mariella, Jr. and A. Melas, J. Cryst. Growth, 92 (1988) 215.