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RESUME - On étudie l'influence de l'incorporation d'indium (0 - 6,5x10^{19} cm^{-3}) dans
des couches OMVPE de GaAs, sur les propriétés optiques en bord de gap et les centres
profonds. En photoluminescence (PL), les bandes d'excitons liés et de recombinaisons
donneur-accepteur glissent vers les basses énergies: il y a formation d'un alliage
ternaire GaInAs très dilué. Les intensités de PL augmentent d'un facteur 10. Cette
amélioration de la qualité optique des couches est en corrélation avec une réduction
de la photoémission impliquant le chrome, dans le même rapport. Par contre, la
concentration et le profil de EL2 déterminés par DLTS ne sont pas affectés. Nos
résultats, conjointement à ceux de la littérature, semblent indiquer une réduction par
l'indium des distorsions de réseau autour des défauts, limitant ainsi la formation de
dislocations.

ABSTRACT - The influence of indium incorporation (0 - 6.5x10^{19}cm^{-3}) in GaAs OMVPE
layers, on near-band-edge optical properties and deep trap content has been
investigated. The bound exciton and donor-acceptor recombination lines in
photoluminescence (PL) spectra shift toward lower energies versus indium content. This
indicates the formation of a very dilute GaInAs ternary compound. The corresponding PL
intensities increase by a factor of 10. This improvement in the optical quality of the
layers correlates with a decrease in a ratio 10 for chromium-related PL intensities.
On the opposite, the EL2 concentration and depth profile determined by DLTS are not
affected. We suggest that indium relaxes lattice distorsions arround residual defects
and limits the formation of dislocations.

In bulk GaAs technology, a large reduction of dislocation density has been noticed by
incorporating indium /1/. This resulted in significant improvements of the electrical
substrate properties /2/ and the same technics was soon extended to GaAs epitaxial layers.
Again a significant improvement in devices properties has been claimed /3/ and, to help
clarifying the mechanism of indium incorporation in GaAs, we have investigated a series of
samples grown by OMVPE, with calibrated indium concentrations ranging from 0 to
6.5x10^{19} cm^{-3}. This corresponds to about 0.3% in standard notations. We report in this work
the results of a cross investigation of both the near band edge optical properties and the
deep trap content. All experimental details have been given in separated papers /4,
J.P. LAURENTI et al., unpublished/.

In Fig. 1, we show typical luminescence spectra, collected at 2K on a reference sample
(indium-free GaAs layer) with different experimental arrangements. At high energy, we used an
optical multichannel analyzer with 500 silicon targets and an experimental resolution of 0.1
meV. We resolved, first, a series of excitonic lines, associated with the recombinations of
standard bound exciton complexes. Next come two lines, labelled L$_1$ and L$_2$, associated with
the radiative decay of well identified donor-acceptor pairs. Line L$_1$ corresponds with both Zn
and/or Mg substituted onto the Ga sites and was associated with accidental contamination
processes; on the opposite L$_2$, which is associated with C substituting on the anion sites,
was mostly dependent on the growth process; in both cases, weak LO replica have been found.

At lower energy, we have used a Ge-detector, cooled down to liquid nitrogen
temperature, and an experimental resolution of typically 0.5 meV. We notice, first, a large
luminescence band around 1.23 eV, which corresponds with the reported range of energy for the
series of gallium vacancy-substitutional donor complexes first investigated by Williams /5/.
Depending on the donor species and the lattice sites where they substitute, the top position
varies. However, whatever are the donor atoms, the net concentration (N$_d$-N$_a$) must be larger
than 10^{16} cm^{-3} in order to get a clear PL signal. This is, at least, one order of magnitude
above the residual donor concentration achieved in our samples and makes the residual amount
of electrically active impurities hardly involved in the strong luminescent features

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experimentally found. As a matter of fact, we could establish a 1 to 1 correspondence between the magnitude of the donor-vacancy related band and the magnitude of the chromium-related zero phonon line (ZPL). This is shown in Fig. 2 where the intensity of the $(D-V_{Ga})$ complex is plotted against the intensity of the Cr-ZPL line for all samples and pieces of substrates investigated in this work. Clearly a strong correlation exists, which suggests to identify the previously unknown donor with Cr^{4+}. The sharp luminescence bands, observed at lower energy, correspond with standard features of the Cr^{2+} trigonal center. Their energy positions (ZPL at 0.839 eV) are in excellent agreement with the data of the litterature /6,7/.

Versus indium content, all high energy features shift toward lower energy, in a linear way as illustrated in Fig. 3. The slope parameters are listed in Table I. This indicates that, even at these extremely dilute indium concentrations ($\sim 6 \times 10^{18}$ to 6×10^{19} atoms cm^{-3}), the formation of a ternary compound GaInAs happens and no effet of isoelectronic impurity can be evidenced. This is clear from the slope of the D*X feature obtained in this work (- 16.22 meV per percent). Within experimental uncertainty it is in perfect agreement with the value (- 15.84 meV per percent) reported in Ref. 8 for the free exciton transition. Slightly different values have been obtained for the acceptor-related features and come from microscopic effects /4/ associated with a change in binding energy of the bound holes. These linear relations between the energy shifts and the indium concentration make low temperature PL measurements the most precise and non-destructive tool for quantitative determinations of indium-doping levels. Finally, we display in Fig. 3 the energy position of the Cr-ZPL line versus indium content. Within experimental uncertainty, no finite shift could be evidenced. This small sensitivity to indium content depart from the results of Ref. 9 where bulk (In,Cr)-codoped LEC-grown GaAs samples were investigated. However, in this previous work, higher indium concentrations (4×10^{18} to 1.2×10^{21} cm^{-3}) have been used and a shift, towards the low-energy side, of all chromium related features had been noticed versus indium
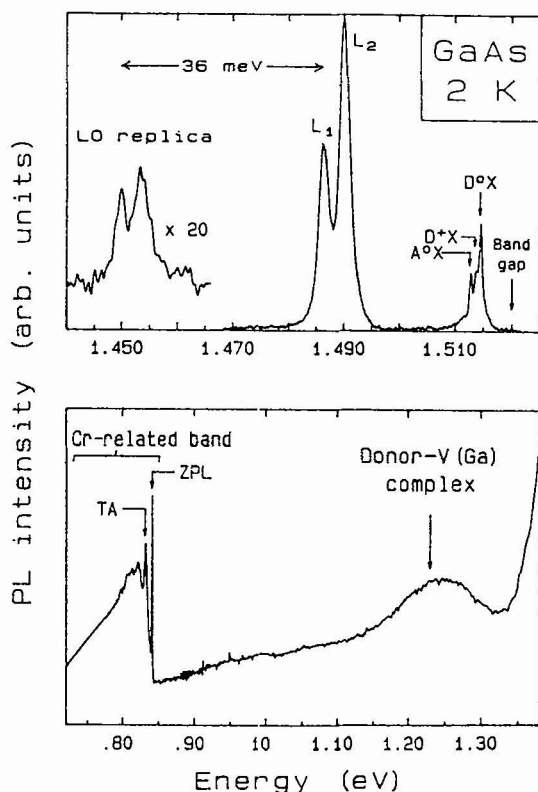

Fig. 1 - Photoluminescence (PL) spectra recorded for a GaAs OMVPE layer at 2K; (i) in the near-band-edge energy range (upper part); (ii) in the range 0.7 - 1.4 eV (lower part). All labelled features are described in the text.
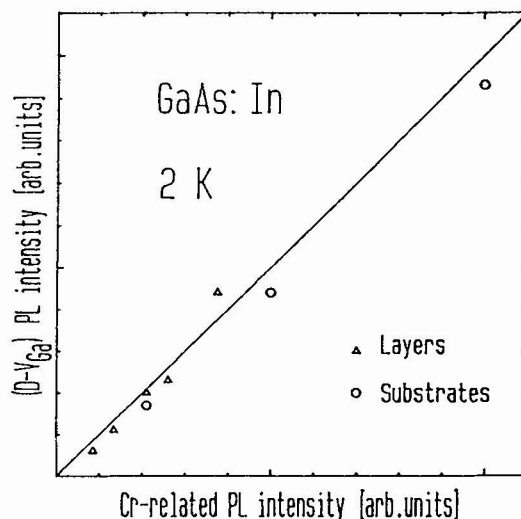

Fig. 2 - Comparison between the PL intensities of the $(D-V_{Ga})$ complex (1.23 eV), and the chromium-related zero-phonon line (0.839 eV), respectively. A 1 to 1 correspondance between these two PL features is evidenced for all GaAs:In layers and GaAs corresponding substrates.

concentration. Owing to the internal character of the transition, and based on general crystal-field theory, the change in magnitude of the crystal-field splitting was estimated from an inverse fifth power of the lattice constant of the host material /10/:

$$\Delta E = E_o \ [\ (a_{GaAs}/a_{GaAs:In})^5 - 1 \ ] \tag{1}$$

With usual values of the crystal parameters /11/, the computed shift is far above our experimental uncertainty. We have found a better agreement using only the Ga-As nearest neighbour distancy in $Ga_{1-x}In_xAs$ /11/. This is shown in Fig. 3.

Concerning now the absolute luminescence intensities, we find the following : (i) all near-band-edge PL intensities increase by a factor of 10 when incorporating indium (Fig. 4); (ii) all defect (chromium) -related transitions decrease by a factor of 10 when incorporating indium (Fig. 5); (iii) there is a one to one correspondance between the changes in the near band edge (NBE) and the chromium related transitions (Fig. 6). On the opposite, the EL2 concentration and depth profile determined by capacitance spectroscopy (DLTS) are not affected.

We believe that most of the improvements concerning bulk and epitaxial materials rely on similar features: there is an interplay of indium and chromium incorporation. Both our results and the work of Ref. 9 show that the concentration of trigonal Cr^{2+} centers decreases; in addition, we show that the concentration of (Cr^{4+}-V_{Ga}) complexes also decreases. The simplest explanation would be that the overall concentration of chromium in the material decreases. However, there are also evidences for a complexation of chromium with indium /9/. This suggests that indium fills in natural cluster surrounding the residual impurities and/or structural defects, and relaxes the lattice distorsions. Lowering the crystal total energy, this would limit the amount of dislocations which can be formed.
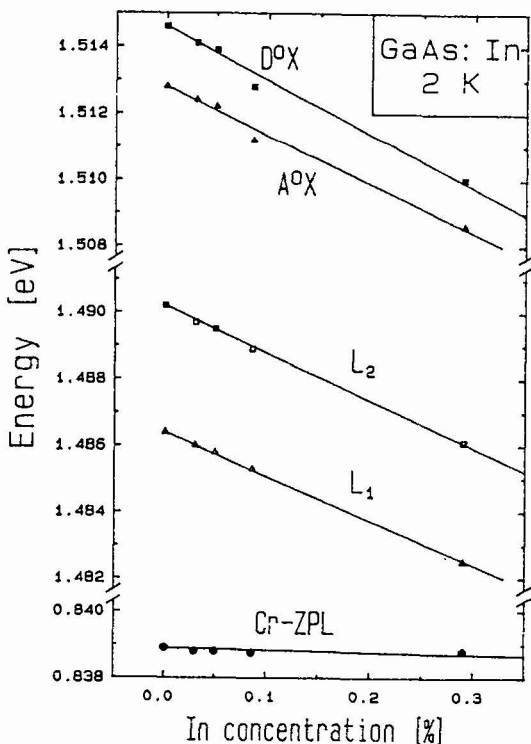

Fig. 3 - Energy positions of the near-gap and Cr-related PL lines, plotted as a function of indium concentration. For the near-gap transitions, the staight lines are drawn with the slope parameters listed in Table I and obtained from a least-mean-square fit. For the Cr-related transition, the line is drawn from Eq. (1) (see text).
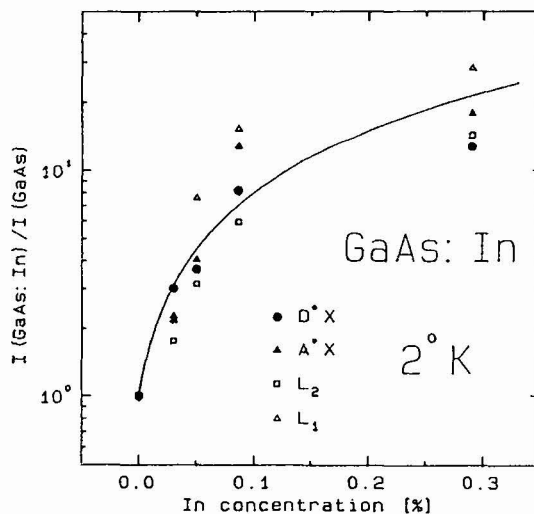

Fig. 4 - Changes in PL intensities as a function of indium concentration for the near-band-edge transitions. All values have been normalized to the In-free reference layer.
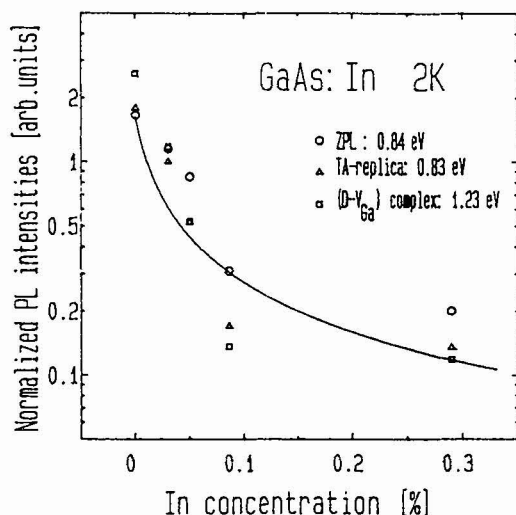
Fig. 5 - Changes in PL intensities as a function of indium concentration for the defect (chromium) -related transitions. For every layer and every transition, all values have been normalized to the PL intensities from the corresponding piece of substrate.
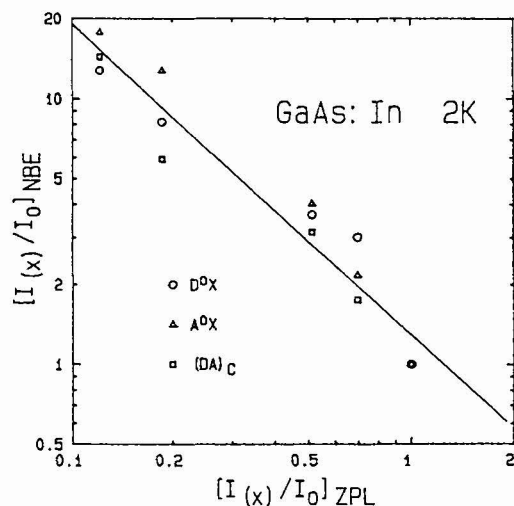
Fig. 6 - Relative intensities of the near-band-edge transitions versus Cr-related zero-phonon line (ZPL). The straight line is a least-mean-square fit on the log-log scale.

Table I : Slope parameters (meV/%) obtained at 2K in this work for the near band edge optical features and comparison with (i) the change in band gap obtained in Ref. 8, and (ii) the initial slope parameters obtained from Eq.(1) for Cr-related ZPL energy (see text).

Transitions	E_g	D°X	A°X	L_2	L_1	Cr^{2+}(ZPL)
This work		- 16.22	- 14.73	- 14.235	- 13.36	- 0.69
Ref.8	- 15.84					
Refs.10,11						- 2.96

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