



HAL
open science

LPE GROWTH AND CHARACTERIZATION OF CADMIUM AND BERYLLIUM DOPED InP AND In.7Ga.3As.6P.4

A. Perronnet, J. Magnabal, D. Sigogne, D. Huet, J. Benoit

► **To cite this version:**

A. Perronnet, J. Magnabal, D. Sigogne, D. Huet, J. Benoit. LPE GROWTH AND CHARACTERIZATION OF CADMIUM AND BERYLLIUM DOPED InP AND In.7Ga.3As.6P.4. Journal de Physique Colloques, 1982, 43 (C5), pp.C5-73-C5-83. 10.1051/jphyscol:1982510 . jpa-00222229

HAL Id: jpa-00222229

<https://hal.science/jpa-00222229>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

LPE GROWTH AND CHARACTERIZATION OF CADMIUM AND BERYLLIUM DOPED InP AND $\text{In}_{0.7}\text{Ga}_{0.3}\text{As}_{0.6}\text{P}_{0.4}$

A. Perronnet, J. Magnabal, D. Sigogne, D. Huet and J. Benoit

Laboratoires de Marcoussis, Centre de Recherches de la C.G.E., Route de Nozay, F-91460 Marcoussis, France

Résumé. Cet article traite de l'étude des couches épitaxiales de InP et $\text{In}_{0.7}\text{Ga}_{0.3}\text{As}_{0.6}\text{P}_{0.4}$ réalisées sur substrat de InP par la technique à deux phases et dopées au beryllium et au cadmium.

Après avoir décrit les conditions de croissance propres à l'emploi de ces dopants on analysera les propriétés électriques et optiques de ces couches épitaxiales à la lumière de résultats de mesures de photoluminescence (4,2 K - 300 K) et d'effet Hall (77 K - 300 K). On déterminera les énergies d'ionisation des niveaux accepteurs associés à ces impuretés. On analysera également la variation de la mobilité en fonction du dopage.

Abstract. Properties of cadmium and beryllium doped InP and $\text{In}_{0.7}\text{Ga}_{0.3}\text{As}_{0.6}\text{P}_{0.4}$ layers grown by liquid phase epitaxy by the two phase technique will be studied in this paper.

Growth conditions related to the use of these dopants will be described. Electrical and optical properties of the grown layers will then be studied from photoluminescence (4.2 K - 300 K) and Hall effect measurements (77 K - 300 K). Ionization energies of the acceptor levels associated to these impurities will be determined. Mobility variation versus doping level will also be studied.

1. Introduction

The elaboration of submicronic devices requires not only a precise control of the thickness of very thin epitaxial layers but also of the doping level for n and p type impurities and of the localization of the p-n junctions made with these impurities. The example of buried heterostructure laser [1] in which the p-n junction plane of the blocking regrown layers has to be positioned with a precision of 0.1, 0.2 μm relative to the active region plane is a clear illustration of such a statement. The processing of such devices by liquid phase epitaxy becomes easier when one can use p and n type dopants which fulfill the following requirements : a low diffusivity (good localization), a high effective solubility (wide range of electrically active doping without crystal properties deterioration), a low distribution coefficient together with a high atomic weight (doping level easy to control by weighing) and a low vapor pressure (precluding dopant losses and melt contamination).

For the InP, $\text{In}_{1-x}\text{Ga}_x\text{As}_y\text{P}_{1-y}$ system tin and germanium doping can be considered as good n type dopants. For p type dopants the situation is not so satisfactory, since zinc which is more often used presents many inconvenients such as a high distribution coefficient, a high diffusivity and a relatively high vapor pressure. The other candidates for p type doping are Be, Cd, Mg and Mn. Due to the unusefulness of Mg owing to its strong reactivity with oxygen together with a very high diffusivity ($D \approx 10^8 \text{ cm}^2/\text{s}$ at 600°C) [2] and to the depth ($E_a = 270 \text{ meV}$) [3] of the Mn acceptor levels in InP which precludes high doping levels, we have chosen in this work to study the growth and the properties of LPE layers of indium phosphide and $\text{In}_{0.7}\text{Ga}_{0.3}\text{As}_{0.6}\text{P}_{0.4}$ ($\lambda \approx 1.3 \mu\text{m}$) doped with cadmium and beryllium since from previously published data [3, 4, 5, 6, 7, 8, 9, 10] (Table I) these dopants seem to have better doping properties than zinc if one excepts the high vapor pressure of cadmium.

DOPANT		k	$\frac{\rho \text{ Atomic Weight}}{k}$	$D(\text{cm}^2/\text{s})$ 630°C	Vapor Pressure (torr, 630°C)	E_A (meV)
Zn	InP	1.14 Astles .88 Abrams .86 Kuphal	60	$3 \cdot 10^{11}$	20	50 Astles 27 White 47.8 Burkard
	Q ($\lambda = 1.3 \mu\text{m}$)	1.7				15
Cd	InP	2 10^3 Astles 10 ³ Umabu 10 ³ Kuphal 4 10^3 Kunosuki	56000	$3 \cdot 10^{12}$	140	58 Astles 56.3 White 58 Yamaguchi 56 Chevrre 58 Burkard
	Q	35 10^3 Fujita 410 ³ Kunosuki				4 < < 14 Fujita
Be	InP	.1 Abrams	90	-	10^{-9}	-
	Q	-				-

Table I

2. Epitaxial growth

The doped layers which have been studied were grown in the same conditions (fig. 1) as the active layer, or the p type confinement layer, of classical double hetero-structure on n type substrate made in our laboratory and which are designed to make LED and lasers. The growth temperature of such layers is 635°C . The growth technique is the two-phase one, the height of the solutions was 3.5 mm, the hydrogen flow rate was $4 \text{ l} / \text{min}$. The solutions were entirely covered with an InP single or polycrystal source which was itself covered with a graphite plate limiting so melt contamination due to dopant evaporation. Before growth, the melts were homogenized during 1 h at 675°C . The purity of the doping material was 6 N for Cd and only 4 N for Be.

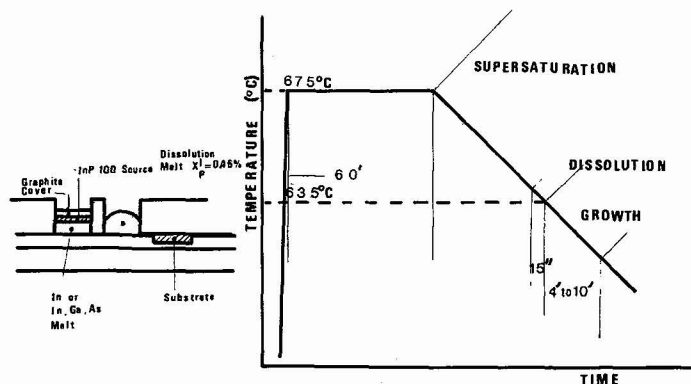


Figure 1

The amount of dopant in the melts has varied from 10^{-3} to 10^{-1} for Cd and from 10^{-4} to 10^{-2} for Be. For this doping range the layers were smooth and uniform and did not exhibit any particular type of defects like precipitates. One cannot say however that the dopant does not affect the growth since it has been observed that any increase in the Cd amount in the melt above a value $\sim 1\%$ gives a corresponding increase of the growth rate of quaternary layers (fig. 2).

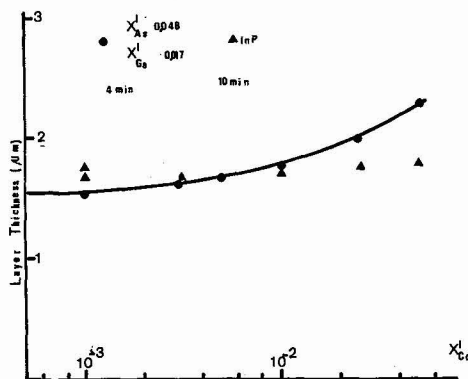


Figure 2

This effect which was not observed with indium phosphide can be ascribed to a modification of the liquidus quaternary composition at the growth and a subsequent temperature variation of the composition of the quaternary grown material [11]. Such a hypothesis may, at least in part, explain the shift of the photoluminescence peak wavelength observed as the Cd content in the solution increases (fig. 3).

For the case of Cd doping it has been verified that, in our growth conditions and presumably due to both effects of a close cover of the melt and of a high hydrogen flow rate, if the evaporation of dopant cannot be avoided, the contamination of other melts by Cd is not effective. This has been verified by evaluating by Hall measurements the electronic concentration of an undoped InP layer which was grown from a two-phase covered melt placed just behind the Cd doped melt. It was found that this layer was of n type with a concentration of $2 \cdot 10^{16} \text{ cm}^{-3}$ which is the background doping value we find in our equipment when two-phase growth is used.

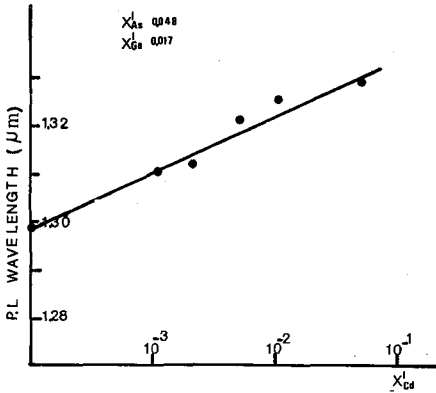
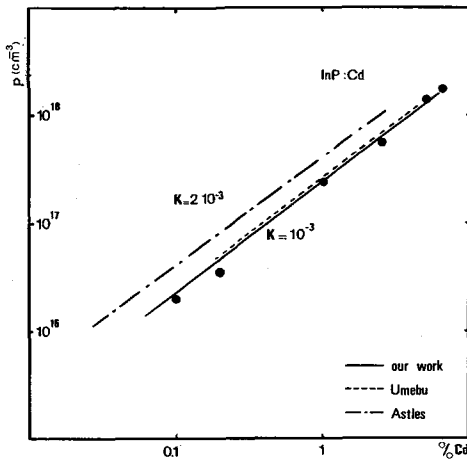


Figure 3

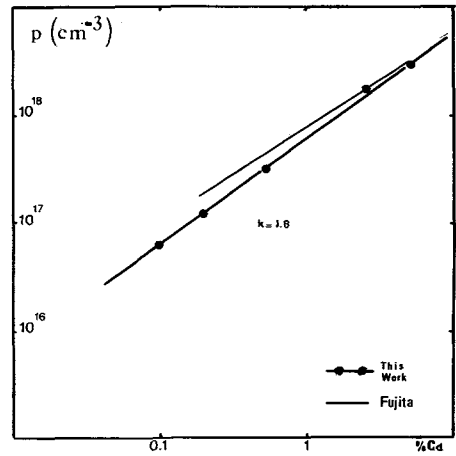
3. Effective distribution coefficient

The effective distribution coefficient for Cd and Be has been determined from Hall measurements. This coefficient was taken equal to the ratio of the hole density at room temperature to the impurity atomic density in the melt.



Hole concentration of Cd doped InP measured at 300K versus Cd atomic fraction in the melt.

Figure 4



Hole concentration of Cd doped $Ga_{0.3}In_{0.7}As_{0.6}P_{0.4}$ measured at 300K versus Cd atomic % in the melt.

Figure 5

From figures 4 and 5 it can be seen that the results obtained in this work agree quite well with previously published data [3, 5, 6]. The apparent discrepancy between FUJITA's results [7] and ours concerning the k value for quaternary material owns to the fact that we have taken into account the variation of the density of the solid with the quaternary composition.

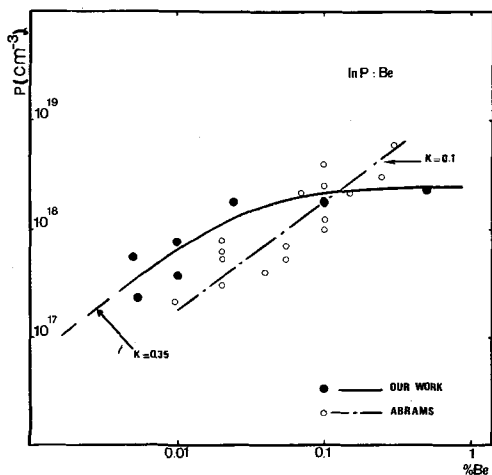


Figure 6 : Hole concentration of Be doped InP measured at 300 K versus Be atomic fraction in the melt

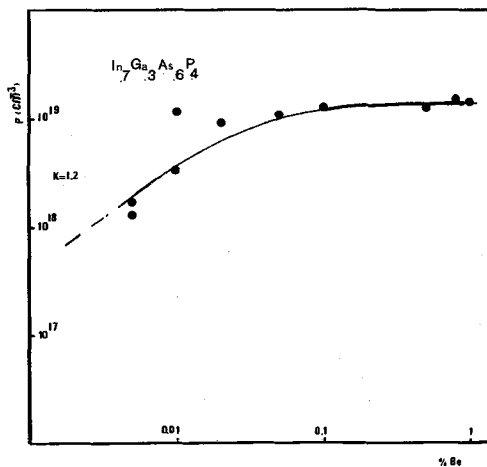


Figure 7 : Hole concentration of Be doped $\text{In}_{0.7}\text{Ga}_{0.3}\text{As}_{0.6}\text{P}_{0.4}$ versus Be atomic fraction in the melt

From figures 6 and 7 concerning Be doping different statements have to be made. First the scattering of the experimental data is more important than for Cd. Second from our results one can observe a strong saturation effect in the effective doping when the beryllium fraction in the melt exceeds 1%. This saturation corresponds to a hole concentration of $2 \cdot 10^{18} \text{ cm}^{-3}$ holes for indium phosphide and to 10^{19} cm^{-3} for quaternary layers. Third that our data are very difficult to fit with an effective value of $k = 1$ previously published by ABRAMS [4], even in the low doping range ($X_{\text{Be}}^1 \approx 10^{-4}$) which however corresponds to unrealistic weighing conditions (1 μg of Be for 4 g of solution). In this low concentration range the value that we can estimate tentatively is a k value of 0.35 for the binary and of 1.2 for the 1,3 μm quaternary.

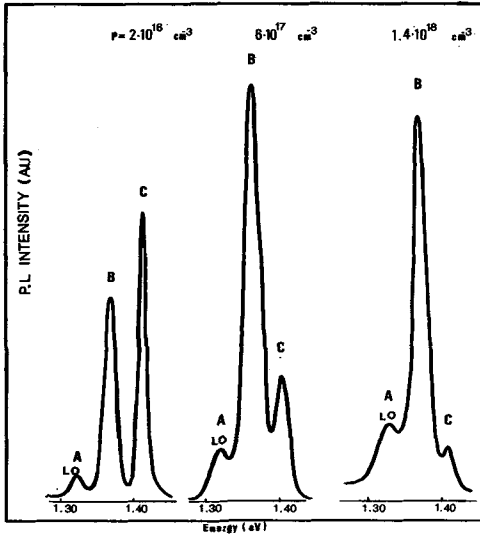
3. Photoluminescence and Hall measurements

1. Photoluminescence

Photoluminescence experiments have been performed between 4.2 K and 300 K using the 5145 Å line of an argon laser. The excitation conditions correspond to a quite high excitation level ($\sim 10 \text{ W/cm}^2$).

The low temperature photoluminescence spectra of Cd doped binary layers exhibit, in the considered range of doping, typically three marked peaks labelled A, B and C on figure 8. The peak C corresponds to near band edge emission presumably involving impurity-bound exciton states. The peak B corresponds to free electron-bound acceptor recombination. The peak C, which lies 40 meV, i.e. the energy of the L.O. phonon, below B is a replica of this later.

Photoluminescence spectrum made at 4.2 K enables to determine the position of the cadmium acceptor level above the valence band, which has been measured as 55 meV (fig. 9) a value very close to most often published value of 56 meV [3, 8, 9].



P.L spectrum at 4.2 K of Cd doped InP

A : $E = 1.33$ eV
 B : $E = 1.37$ eV
 C : $E = 1.41$ eV

Figure 8

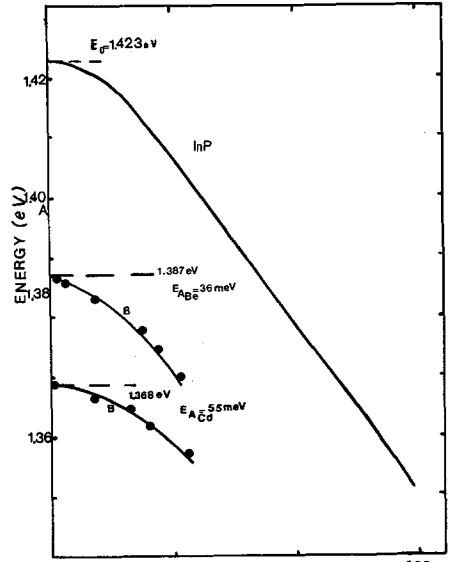
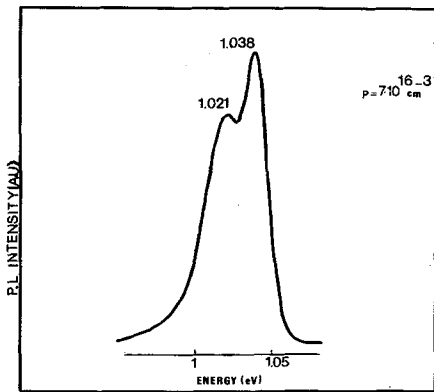


Figure 9

Photoluminescence spectra of Cd doped quaternary alloys exhibit wider peaks. This can be related to the grading of composition that exists in the quaternary layers grown by the two-phase technique. However the low temperature spectrum on figure 10 shows both near band-edge and free electron bound acceptor recombination. Although the energy gap of the quaternary grown layer cannot be determined from these measurements one can estimate from 4.2 K measurements the ionization energy of the Cd acceptor in the material. This energy (fig. 11) is near 20 meV.



PHOTOLUMINESCENCE SPECTRUM AT 60K OF Cd DOPED

$In_7Ga_3As_8P_4$

Figure 10

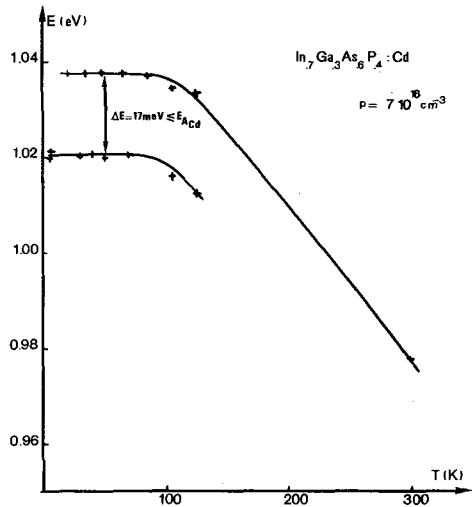


Figure 11

The photoluminescence of beryllium doped indium phosphide layers shows the same features as previously described for cadmium doping. The B peak that corresponds to free electron-neutral acceptor is dominant at low temperature when the doping level is above 10^{18} cm^{-3} . The energy separation between this acceptor level and the valence band can be determined from the 4.2 K photoluminescence spectrum (fig. 12). The measured value is 36 meV (fig. 9).

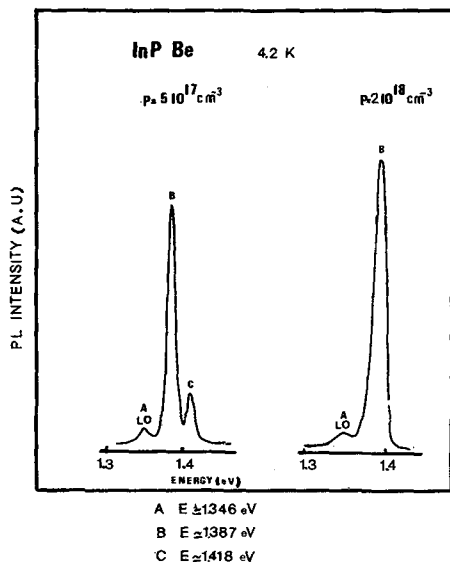


Figure 12

The photoluminescence of Be doped quaternary layers are characterized by a single peak emission whatever the doping level and the temperature are. The peak even at low temperature is quite broad. Since the investigated range of doping levels corresponds to a quite high level ($N_A > 10^{18} \text{ cm}^{-3}$) one can attribute this peak to a transition between conduction band and a quite shallow acceptor level, more precisely an acceptor impurity band resulting of the overlapping of the acceptor orbitals. This hypothesis will be confirmed by the analysis of Hall effect data.

2. Hall effect measurements

From Hall effect measurements and by using the charge neutrality equation, assuming a single acceptor level, we have determined by a best fit method the ionization energy of the Cd and Be acceptor levels in the binary doped layers. This method gives also the compensation ratio which can be evaluated to less than 1.2 for most of the studied samples. The ionization energies determined by this method ($E_a = 46 \text{ meV}$ for Cd and $E_a = 27 \text{ meV}$) are comparable though lower than those determined by photoluminescence. The degeneracy factor of the acceptor level has been taken equal to 4 for this determination (fig. 13, 14, 15).

Hall data for quaternary layers exhibit two main features as soon as the hole concentration exceeds 10^{18} cm^{-3} :

- the hole concentration is independent on the temperature (fig. 15),
- the mobility is maximum near 150 K and decreases at liquid nitrogen temperature (fig. 16).

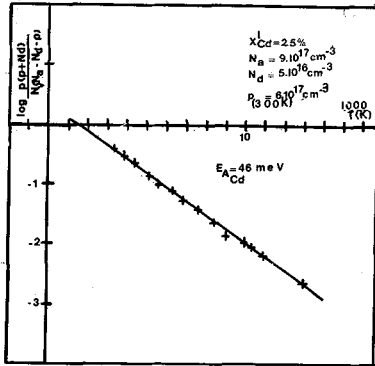


Figure 13

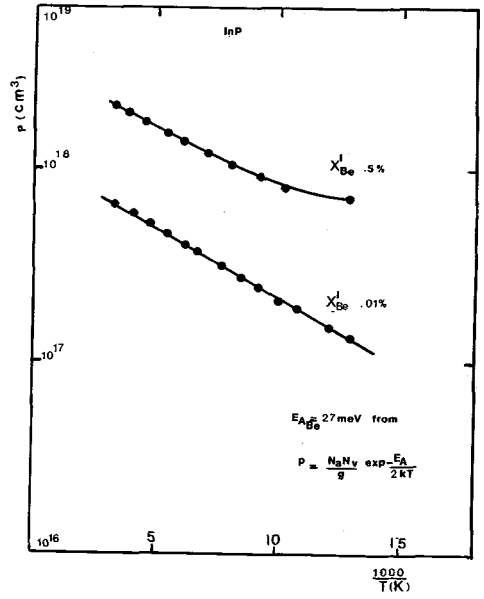


Figure 14

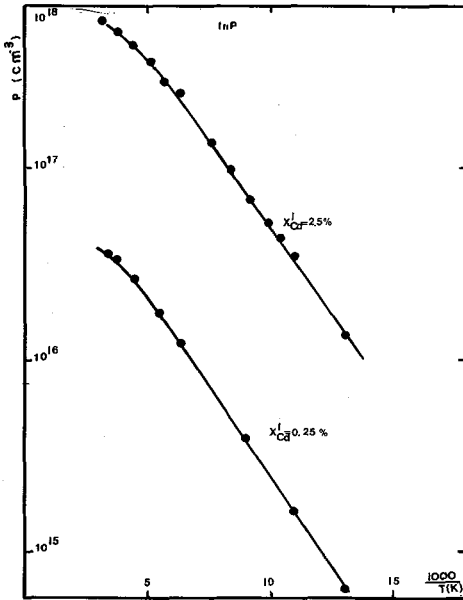


Figure 15

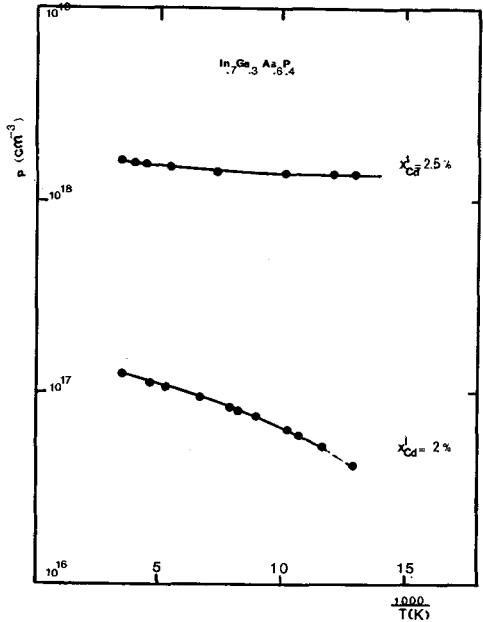


Figure 16

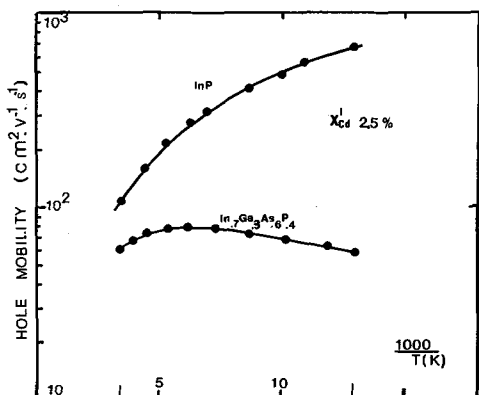


Figure 17

Such a behavior is characteristic of conduction in a low mobility impurity acceptor band [11]. This behavior is always observed in Be doped quaternary layers and in the case of Cd doping when the impurity atomic fraction in the melt is above 1%. For lower Cd doping, the Hall data obtained on quaternary layers can be interpreted on the basis of a single hydrogenoid acceptor level. The ionization energy of this acceptor level has been determined as 16 meV (fig. 17).

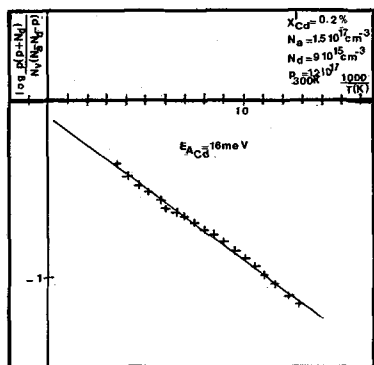


Figure 18

The variation of the Hall mobility at 300 K and 77 K as a function of the hole density at room temperature is represented on figures 19 and 20 in the case of binary doped layers. The liquid nitrogen temperature mobilities are roughly 10 times higher than the room temperature ones. This is constant as well as the numerical values, with ionized impurity scattering as a dominant scattering mechanism for holes in the valence band. On the contrary, in the quaternary doped layers, the liquid nitrogen temperature mobility is comparable, if not lower, to the room temperature mobility. This is another clear evidence of the conduction by holes in an impurity acceptor band.

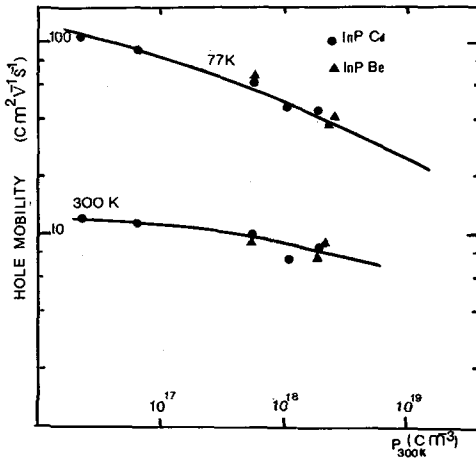


Figure 19

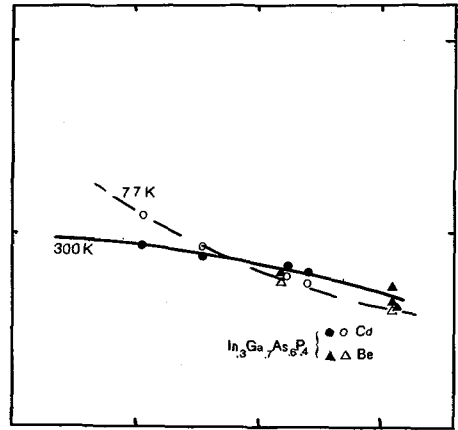


Figure 20

4. Conclusion

The effective distribution coefficients of Be and Cd in InP and $\text{In}_{0.7}\text{Ga}_{0.3}\text{As}_{0.6}\text{P}_{0.4}$ grown by LPE at 635°C have been determined from Hall measurements. Due to a lower distribution coefficient, a higher atomic weight and a lower diffusivity, Cd can be used instead of Zn as a suitable dopant in order to control doping levels lower than 10^{18} cm^{-3} , especially in the $10^{16} - 10^{17}\text{ cm}^{-3}$ range which is the useful range for the doping of the laser active layer [12]. Melt contamination due to the high vapor pressure of Cd can be minimized by a proper design of the crucible and by using high hydrogen flow rates (4 l/min). Due to a high distribution coefficient and a small atomic mass Be appears to be an unuseful dopant in this temperature range for LPE growth of InP and $\text{In}_{0.7}\text{Ga}_{0.3}\text{As}_{0.6}\text{P}_{0.4}$ except for the growth of highly doped thin contact layers for which Be will be preferable to Zn and Cd owing to its low diffusivity.

The activation energy of the acceptor levels for these impurities has been determined by photoluminescence and Hall effect measurements in the case of Cd for InP and $\text{In}_{0.7}\text{Ga}_{0.3}\text{As}_{0.6}\text{P}_{0.4}$ and in the case of Be for InP. Photoluminescence and Hall effect measurements on quaternary materials doped with Cd and Be have also shown the evidence of an impurity band associated to the acceptor level when the hole concentration is above 10^{18} cm^{-3} .

References

- [1] HIRAO M., TSUJI S., MIZUISHI K., DOI A. and NAKAMURA M., J. Opt. Comm (1) 10 (1980).
- [2] KUPHAL E., Proceedings of InP NATO workshop, Harwich port (1980) 443.
- [3] WILLIAM E.W., ELDER W., ASTLES M.G., WEBB M., MULLIN J.B., STRAUGHAM B. and TUFTON P.J., J. Electrochem. Soc. 120 (1973) 1741.
- [4] ABRAMS E.B., SUMSKI S., BONNER W.A. and COLEMAN J.J., J. Appl. Phys. 50 (1979) 4469.
- [5] ASTLES M.G., SMITH F.G.H. and WILLIAM E.W., J. Electrochem. Soc. 120 (1973) 1750.

- [6] UMEBU I. and ROBSON P.H., J. Crystal Growth 53 (1981) 292.
- [7] FUJITA S., MATSUDA K. and SASAKI A., Jap. J. of Appl. Phys. 20 (1981) L 889.
- [8] WHITE A.M., DEAN P.J., FAIRHURST K.M., BARDSLEY W., WILLIAM E.W. and DAY B., Solid state communications 11 (1972) 1099.
- [9] HESS K., STATH N. and BENZ K., J. Electrochem Soc. 121 (1974) 1208.
- [10] CHEVRIER J., HORACE E. and GOLDSTEIN L., J. Appl. Phys. 53 (1982) 3247.
- [11] RENVOISE M., Thèse de 3ème cycle, PARIS VI (1977).
- [12] TAMARI N., Appl. Phys. Letters 39 (1981) 792.