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GALLIUM ARSENIDE, INDIUM PHOSPHIDE.

CHEMICAL VAPOR DEPOSITION AND PHOTOLUMINESCENCE PROPERTIES OF Zn-DOPED GaAs

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Résumé. — L'étude expérimentale de l'accroissement du GaAs obtenu à partir de l'épitaxie en phase gazeuse à 1 023 K montre que la concentration des trous dépend des paramètres technologiques selon :

$$p \, (300 \text{ K}) \sim p_{\text{HCl}} \cdot p_{\text{GaCl}}^{-1} \cdot p_{\text{AsH}_3}^{1/2} \cdot p_{\text{Zn}} \,.$$

Nous concluons après cette étude que le processus se déroule de manière déséquilibrée. L'intensité de la photo-luminescence dépend distinctement des paramètres technologiques, mais cette dépendance ne s'explique pas par un modèle simple.

Abstract. — An experimental study of the VPE growth of GaAs at 1 023 K from the AsH_3-HCl-Ga-H_2 system yields for the dependence of the hole concentration on the technological parameters :

$$p \, (300 \text{ K}) \sim p_{\text{HCl}} \cdot p_{\text{GaCl}}^{-1} \cdot p_{\text{AsH}_3}^{1/2} \cdot p_{\text{Zn}} \,.$$

It is concluded that the process takes place under non equilibrium conditions. The PL intensity depends distinctly on the preparation conditions but does not fit a simple model.

1. **Introduction.** — Concentrated technological efforts during the past decade have led to considerable improvement in the performance of epitaxial III-V optoelectronic structures. Because of its adaptability to large scale production and its good control of growth and impurity incorporation, vapor phase epitaxy seems to be more attractive than the commonly used LPE technique for GaAs devices. However, to compete with LPE material the near band gap photoluminescence (PL) of vapor grown layers needs to be improved. Since the luminescence of GaAs light emitting diodes originates predominately from the p-side of the device structure it is important to control the properties of p-type vapor grown GaAs. It is commonly accepted that the different stoichiometries of liquid and vapor grown materials are responsible for the divergent PL properties. Therefore we have investigated the properties of Zn-doped vapor grown GaAs layers obtained for different gas phase compositions which were varied in order to affect the stoichiometry of the films.

2. **Experimental.** — The depositions were carried out in an AsH_3-HCl-Ga-H_2 system [1]. A schematic is shown in figure 1. In brief, the metal was transported as GaCl by passing HCl (HCl_{Input}) over a 40 g Ga source (99,999 9 %, MCP). AsH_3 (99.995 %, Matheson) and also additional HCl (HCl_{By}) were introduced into the deposition system downstream of the Ga source. Carrier gas was palladium diffused hydrogen. The flow rate in the deposition zone was 800 ml/min
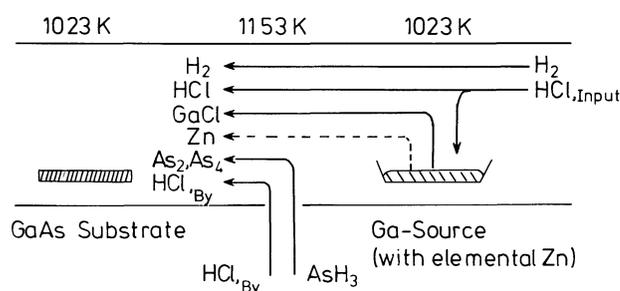

FIG. 1. — Schematic of deposition system.

(inner diameter of tube : 50 mm). Source and deposition temperature were 1 023 K, the temperature in the gas mixing zone was 1 153 K. For substrates we used semiinsultating GaAs wafers (Wacker) oriented 2° off $\langle 100 \rangle$ towards $\langle 110 \rangle$. As the dopant elemental Zn solved in the Ga source was chosen. The stability of this source system with regard to the loss of Ga and Zn from run to run was measured (this loss amounts to 0.5 % and 3 % respectively) and the dependence of the hole concentration on the Zn pressure was obtained using data corrected for this effect. The samples were electrically characterized by measuring hole concentrations with the van der Pauw method [2]. PL measurements were carried out by exciting the samples with a He-Ne laser and analysing the luminescence using a photomultiplier with S 1 response.

3. Results.

3. **Results.** — The dependence of the hole concentration measured at 300 K on the partial pressure of Zn was found to remain linear up to 6×10^{19} cm^{-3} and saturate at this value. These data were obtained by varying the amount of Zn in the Ga source. In figure 2 our experimental results on the maximum near band gap PL intensity (in arbitrary units) as a function of the hole concentration are plotted. The intensity increases up to a maximum at a hole concentration of 1×10^{19} cm^{-3} and then decreases for larger values.
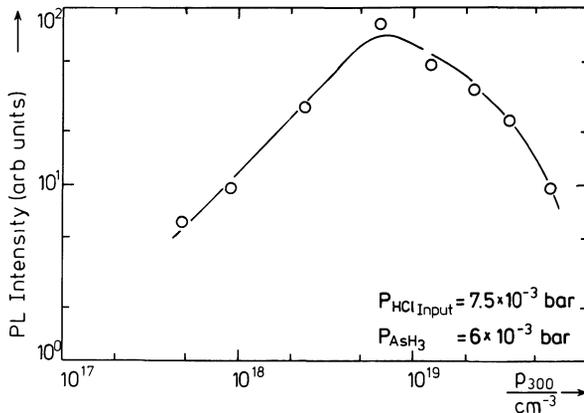

FIG. 2. — PL intensity vs. hole concentration.

Figure 3 shows the dependence of the hole concentration (top) and PL intensity (bottom) on $p_{HCl_{Input}}$ and $p_{HCl_{By}}$. The calculated partial pressure of Zn in the gas phase was 3×10^{-5} bar and 2×10^{-5} bar respectively for the first runs of the two sets of experi-

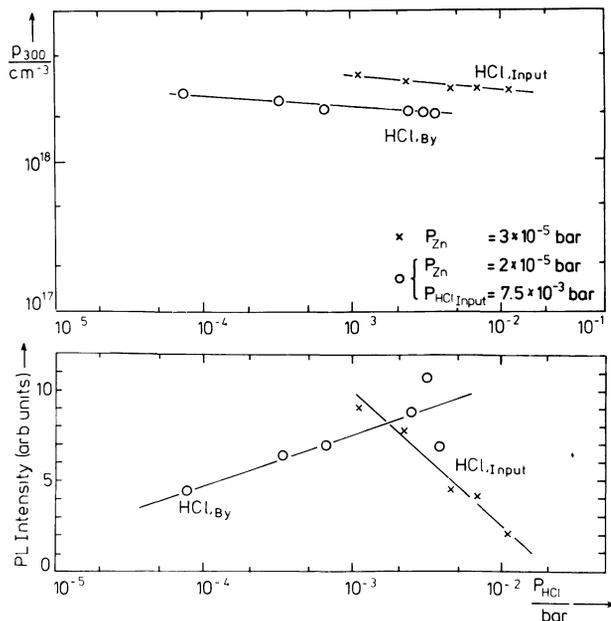
FIG. 3. — Hole concentration (top) and PL intensity (bottom) vs. HCl input pressure ($p_{HCl_{By}} = 0$) and HCl bypass pressure; $p_{AsH_3} = 6 \times 10^{-3}$ bar (all partial pressures given by their value in deposition zone).

ments; the Zn pressures in the following runs were corrected for the Ga and Zn loss of the source. The dependence of the hole concentration on the HCl input pressure is very weak whereas the PL intensity shows a pronounced effect. Namely, the intensity decreases by a factor of 5 when increasing the HCl input pressure by an order of magnitude (from 10^{-3} bar to 10^{-2} bar).

The dependence of the hole concentration on the HCl bypass pressure is again very weak. The PL intensity increases by a factor of 2.5 with increasing bypass pressure in the investigated pressure range.

In figure 4 the dependence of the hole concentration (top) and PL intensity (bottom) on the AsH$_3$ input pressure is plotted. The calculated partial pressure of zinc in the gas phase was 3×10^{-5} bar for the first run of these experiments. The hole concentration shows a positive half order dependence on the AsH$_3$ input pressure. The PL intensity also increases with increasing AsH$_3$ pressure : by a factor of 4 in the investigated range.

FIG. 4. — Hole concentration (top) and PL intensity (bottom) vs. AsH$_3$ pressure in deposition zone.

4. Discussion.

4. **Discussion.** — Incorporation of Zn on Ga sites at the growing surface can be described by

$$Zn(g) + V_{GA} \rightleftharpoons Zn_{Ga}^{-} + h .\qquad(1)$$

For Zn uptake under near equilibrium conditions one has

$$[Zn_{Ga}^{-}] \sim [V_{Ga}] \cdot p_{Zn}[h]^{-1} .\qquad(2)$$

However, the growth of GaAs itself is kinetically limited [3, 4, 5]. Thus one would expect that the incorporation of Zn is also affected by the growth conditions and that the Ga vacancy concentration beneath the growing surface might deviate from the equilibrium concentration. Since the concentration of interstitial Zn is always small compared to that of $[Zn_{Ga}]$ [6, 7, 8] we assumed that its role can be neglected in the present discussion.

We next turn to our results on the dependence of the hole concentration on the partial pressures of the gas phase species (Figs. 3 and 4). Equating the hole concentration measured at 300 K to $[Zn_{Ga}^-]$ our experimental data can be described by
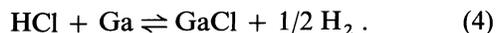
$$[Zn_{Ga}^-] \sim p_{HCl} \cdot p_{GaCl}^{-1} \cdot p_{AsH_3}^{1/2} \cdot p_{Zn} . \qquad (3)$$

The finding that a linear dependence of $[Zn_{Ga}^-]$ on p_{Zn} was observed, even for values beyond the intrinsic hole concentration (5×10^{16} cm^{-3} at 1 023 K), points to a kinetic limitation. It could imply that during the doping process only local thermodynamic equilibrium pertains with constant hole concentration at the surface, the Fermi level being pinned by surface states at some energy in the forbidden gap. A similar behavior was found for the incorporation of sulfur during VPE [9] and Sn in LPE growth [10].

When increasing the HCl input pressure the HCl and GaCl pressures in the deposition zone increase proportionally, the ratio p_{HCl}/p_{GaCl} remaining constant. Injecting additional HCl at the downstream side of the source does not affect $[Zn_{Ga}^-]$, since the Zn pressure will decrease at approximately the same rate as the HCl pressure increases in the range investigated. Here we assume that the Zn incorporation is determined by the pressure of elemental Zn and not by that of the Zn chlorides.

In the investigated AsH_3 pressure range arsenic occurs at 1 023 K as As_4 and As_2 at comparable concentrations [11]. The As_4 pressure increases nearly linearly, the As_2 pressure with the square root of the AsH_3 input pressure. If the growth process is controlled by only one of the two arsenic species it

follows from our findings that $[Zn_{Ga}^-]$ increases linearly with the As_2 pressure or with the square root of the As_4 pressure. Comparing eq. (3), which describes our experimental findings, with eq. (2) certain similarities become obvious. According to eq. (3) the Zn uptake increases with increasing AsH_3 pressure and decreases with increasing Ga activity, the latter being defined by the process.

$$HCl + Ga \rightleftharpoons GaCl + 1/2 H_2 . \qquad (4)$$

The same behaviour would be expected for the Ga vacancy concentration under equilibrium conditions. Therefore we speculate that the pressure dependent factor relating the Zn_{Ga}^- concentration to the Zn pressure in eq. (3) is the same as that governing the Ga vacancy concentrations for our growth conditions.

The PL spectrum in the range 1.0 to 1.5 eV is dominated by the band to acceptor transition in all cases; its intensity is distinctly affected by the preparation parameters. The increase with increasing AsH_3 partial pressure (Fig. 4) is related to that of the hole concentration (Fig. 2). An effect specifically caused by the As pressure on the PL intensity can therefore be excluded. Contrary to this we have found a direct influence of the HCl input and bypass pressures on the intensity. On the other hand both HCl pressures affect the hole concentration only to a minor extent.

Reviewing these pressure dependencies of the PL intensity with regard to the stoichiometry of the deposited films it may be concluded that a simple relationship between growth conditions (which should affect the stoichiometry of the films) and the PL intensity does not exist. Also, moving from the typical As-rich VPE conditions toward the typical Ga-rich LPE conditions reduces the PL intensity against common expectations. Our experiments have demonstrated that the PL intensity of p-type VPE films is strongly dependent on the growth conditions. Therefore the expectation appears justified that further investigation will result in better optical performance of optoelectronic devices fabricated by the VPE growth technique.

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