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## **HYDROGEN DIFFUSION AND SHALLOW ACCEPTOR PASSIVATION IN p-TYPE InP**

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### ABSTRACT

Hydrogen diffusion in InP:Zn, protected by an undoped GaInAs epilayer, has been performed from a hydrogen plasma exposure. Passivation of shallow acceptors occurs in the hydrogen diffused region of InP:Zn. Secondary ion mass spectrometry, transport measurements and thermal annealing experiments indicate the existence of neutral Zn,H pairs in InP:Zn,H. We find that these pairs have a relatively higher thermal stability than in GaAs:Zn. This is interpreted with the help of the microscopic description of the Zn,H complexes.

### INTRODUCTION

Attention has been recently paid to the problem of hydrogen passivation of shallow impurities in III-V crystalline semiconductors. The first demonstration has been provided after exposure of n-type Si doped GaAs samples to a R.F. hydrogen plasma [1]. The formation of Si-H complexes responsible for the passivation of the Si donors has been readily proved later on by Fourier Transform Infrared Spectroscopy (FTIR) [2, 3]. The passivation of various acceptors in GaAs by hydrogen has been demonstrated in the case of zinc [4], beryllium [5] and silicon (on arsenic site) [6]. Interpretation of this phenomenon is based on the proposal provided by Pantelides [7] for the hydrogen passivation of boron doped silicon where hydrogen should be considered as a deep donor compensating the material. The coulombic interaction between the proton and the negatively charged acceptor species would be responsible for the formation of the hydrogen-acceptor complexes detected in F.T.I.R. [5,6,8]. Until now, nothing has been reported in the literature concerning the hydrogen-shallow acceptor interactions in InP which is a semiconductor of technological importance in optoelectronics and microelectronics. In this paper, we show that hydrogen diffusion in zinc doped InP leads to an efficient passivation effect of shallow acceptors.

### EXPERIMENTAL PROCEDURES

Hydrogen diffusion in Si and GaAs is usually performed by exposure to a hydrogen plasma. This technique can be used because of the relative stability of their surface in this ambient. However, if we directly expose an InP sample to a hydrogen plasma we note a strong decomposition of the surface with the formation of phosphine and the occurrence of metallic indium islands on the surface. For this reason, one has to protect the InP surface with a thin hydrogen permeable

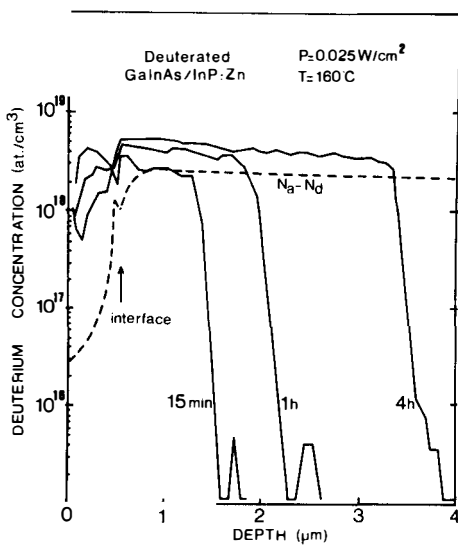
cap layer. In the present study, we show that a correctly lattice matched GaInAs layer epitaxially grown on InP can be used as a cap layer for hydrogen diffusion and passivation studies in p-type InP [9].

The samples have been grown by metal organic vapor phase epitaxy. They have the following structure : 0.55  $\mu\text{m}$  of undoped  $\text{Ga}_x\text{In}_{1-x}\text{As}$ /4.9  $\mu\text{m}$  of InP:Zn/semi-insulating InP:Fe substrate. The detailed experimental set-up and growth conditions are described elsewhere [10]. The ternary layer has a composition  $x$  equal to 0.47 with a good lattice matching to the InP layer (relative lattice mismatch of  $5 \times 10^{-4}$  to  $10^{-3}$ ). The InP:Zn layer has a free hole concentration of  $2.5 \times 10^{18} \text{ cm}^{-3}$  and a hole mobility of  $60 \text{ cm}^2/\text{V.s.}$  at 300K.

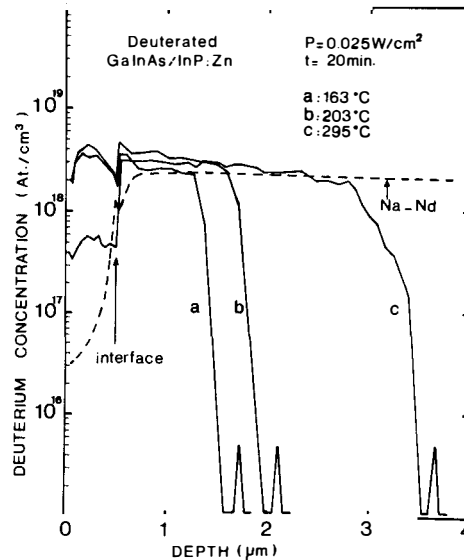
For hydrogen diffusion studies, we have exposed the above structure to a R.F. deuterium plasma for various exposure durations from 20 min. to 6 hours and at various temperatures ranging from 160°C to 300°C. The R.F. power density has been kept constant and equal to  $0.025 \text{ W/cm}^2$ . After hydrogen (or deuterium) plasma exposures, the GaInAs cap layer remains specular in the conditions used and no visible degradation is observable under optical microscope.

The deuterium diffusion profiles have been analyzed by S.I.M.S. experiments (CAMECA IMS 4F system). The deuterium concentration was obtained by using a  $\text{D}^+$  implanted InP sample as a standard. Profiles of the net dopant concentration were obtained from capacitance-voltage measurements on Schottky diodes formed either with mercury or with an electrolyte. In the case of the mercury diode, this profile was measured from successive chemical etching steps followed by C-V measurements. A Polaron Semiconductor Profile Plotter has also been used to get a continuous determination of the net dopant concentration. Hall effect and conductivity measurements have been carried out using the Van der Pauw method after removal of the GaInAs cap layer.

## RESULTS AND DISCUSSION



**Figure 1** : Deuterium concentration profiles in GaInAs/p-InP(Zn) structures exposed to a R.F. deuterium plasma at 160°C for various durations.



**Figure 2** : Deuterium concentration profiles in GaInAs/p-InP(Zn) structures exposed to a R.F. deuterium plasma for 20 min.

Figure 1 shows the deuterium concentration profiles in samples exposed at 160°C for various exposure durations. Since the deuterium penetration depth follows a  $t^{1/2}$  dependence, we conclude that the deuterium distribution is governed by a diffusion-limited process. Figure 2 presents deuterium concentration profiles in samples exposed at different temperatures. We observe an increase of the penetration depth with temperature.

On these two figures, we note the absence of deuterium accumulation at the GaInAs/InP interface. This holds true for structures with good lattice matching ( $5 \times 10^{-4}$  to  $10^{-3}$ ). In order to see the effect of a poor lattice matching on the deuterium diffusion profile, we have exposed structures with relative lattice mismatch of  $13 \times 10^{-3}$ , using the same plasma conditions. In this case, accumulation of deuterium is visible at the interface as a consequence of trapping on defects and impurities. The deuterium concentration at this interface peaks at values 3 to 5 times higher than the deuterium concentration in the InP epilayer. However, in structures with lattice mismatch of  $13 \times 10^{-3}$  we find deuterium penetration depths and hydrogen solubilities in the InP:Zn layer similar to that in structures with good lattice matching.

In figure 2, we notice that the deuterium concentration profile in InP consists of a plateau followed by an abrupt decrease. An important feature is that the deuterium concentration in the plateau region is quite temperature independent for  $T < 300^\circ\text{C}$  and is close to the free hole concentration. The same remark holds true for figure 1. This result suggests the existence of a hydrogen-acceptor pairing effect.

On figure 3 we show the deuterium concentration and the free hole concentration profiles deduced from C-V experiments, for a sample exposed for 20 min. at 163°C. In the region below 1.3  $\mu\text{m}$  the sample contains 2 to  $3 \times 10^{18} \text{cm}^{-3}$  deuterium and is highly resistive. The resistivity of the hydrogen diffused region has been determined by transport experiments on a sample exposed to the hydrogen plasma for 6 hours at 300°C in order to ensure a hydrogen diffusion on the whole thickness of the epilayer. In these conditions, the resistivity of the sample is found to be higher than  $10^5 \Omega \cdot \text{cm}$ . These results show that a strong passivation of zinc acceptors occurs in the hydrogen diffused regions of the InP sample. We note the excellent correspondence in the depths where the hydrogen concentration drops down and the free hole concentration goes up.

Very similar deuterium profiles showing hydrogen-acceptor pairing in the plateau region have been obtained in Si:B [11], in GaAs:Zn for diffusion experiments at 200°C [4] and in p-type GaAs:Si for plasma exposures up to 305°C [6]. Passivation of acceptors occurs similarly in these materials in the hydrogen diffused regions. An explanation of the above phenomena has been given in the case of Si:B,D [7,12] assuming that hydrogen impurities act as deep donors which compensate the acceptors. A rather good description of the hydrogen diffusion profile has been obtained in Si:B,D under this assumption with the proton being accelerated by the built-in electric field which results from the hole concentration gradient [12]. The assumption of hydrogen moving as a positively charged species in p-type silicon is supported by deuterium electrotransport experiments performed in reverse biased p-type deuterated silicon Schottky diode. Similar experiments in GaAs or InP have not been performed yet but hydrogen acting also as a deep donor in III-V compounds is a plausible assumption. The coulombic attraction between the protons and the negatively charged acceptors has been proposed for the formation of pairing in Si:B,H [7]. In InP:Zn, this is evidenced through matching of the hydrogen and the net acceptor concentrations and through the direct observation of Zn,H complexes in F.T.I.R. experiments [13].

In order to get additional information on the electronic properties of the passivated sample and the thermal stability of the complexes, we performed some thermal annealing experiments on the InP:Zn layer passivated on the whole thickness. Partial reactivation of the acceptors in the InP layer has been carried out under annealing at 275°C for 5 min. After such an annealing, the

hole concentration at 300 K is  $1.3 \times 10^{16} \text{cm}^{-3}$  which means that 99% of the acceptors are still passivated.

Figure 4 shows the variation of the hole mobility versus temperature for the as-grown epilayer (curve a) and for the hydrogenated and partially annealed epilayer (curve b). The hole mobility in the hydrogenated layer is significantly higher than in the as-grown layer. This can be interpreted in terms of a decrease of the ionized impurity concentration as hydrogen passivation of acceptors leads to the creation of neutral Zn,H complexes. However, if compared with conventional as-grown InP:Zn containing a similar free hole concentration of  $10^{16} \text{cm}^{-3}$ , we find that the hole mobility in our passivated InP:Zn,H material is relatively low. Our sample probably contains some amount of ionized compensating centers in addition to the ionized de-passivated acceptors. Due to absence of free electrons in the material, we expect that the ionized donors cannot be passivated by hydrogen. Support to this assumption has been provided by F.T.I.R. in p-type GaAs:Si,H [6]. It has been shown that the amount of ionized silicon donors (Si on gallium sites) remains unchanged after hydrogenation. Consequently, unpassivated ionized donors and de-passivated ionized acceptors are probably scattering centers limiting the hole mobility after hydrogenation.

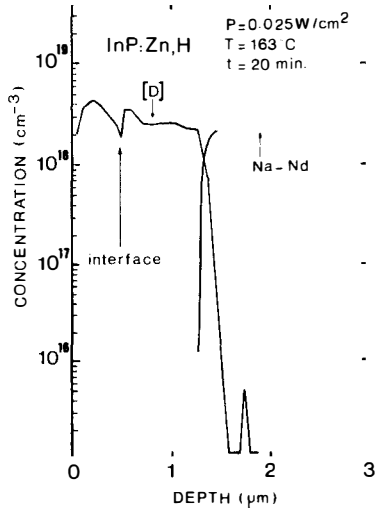


Figure 3 : Comparison of the deuterium and free hole concentration profiles in a GaInAs/p-InP(Zn) structure exposed to a R.F. deuterium plasma at 163°C for 20 min.

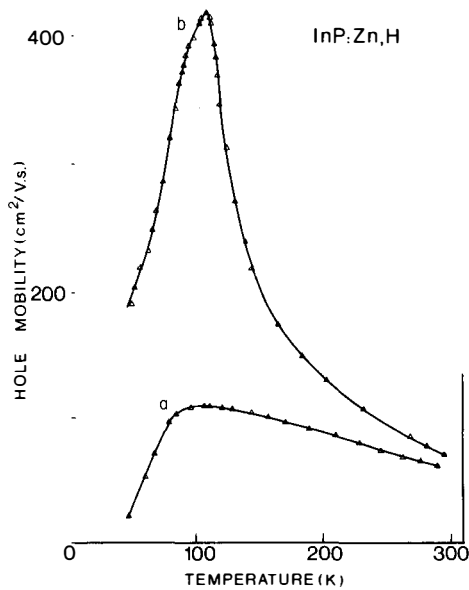


Figure 4 : Hole mobility versus temperature curves for an InP:Zn epilayer before any hydrogenation (a) and after hydrogen plasma for 6 h at 200°C followed by a 275°C, 5 min annealing (b).

From our annealing experiments, it is clear that Zn,H complexes are quite stable up to 275°C in InP. This temperature has to be compared with the temperature of 210°C where Zn,H complexes start to decompose in GaAs [14]. Then Zn,H complexes are more stable in InP:Zn than in GaAs:Zn. Confirmation of this result is provided by the temperature dependence of the global pairing tendency in GaAs:Zn and InP:Zn. In GaAs:Zn, the existence of a pairing effect is reported in diffusion experiments at 200°C. For exposures at 250°C or above, no plateau is observable and the hydrogen concentration is below the acceptor concentration

[4]. This result means that the tendency to pairing decreases in GaAs:Zn,H for temperature of 250°C or above. In InP:Zn, we find that the tendency to pairing is still high at 300°C. A reason of the higher stability of Zn,H complexes in InP if compared with GaAs can be found in their microscopic description. In GaAs:Zn,H, it has been proposed that the complex formation implies the breaking of a Zn-As bond [8]. Zinc becomes threefold-coordinated and thus electrically inactive. The hydrogen is bonded to the arsenic atom giving rise to the  $2147\text{cm}^{-1}$  vibrational line detected in F.T.I.R. Similar investigations in hydrogen passivated InP:Zn prove the existence of Zn,H complexes. The same model proposes the breaking of a Zn-P bond and the formation of a P-H bond observable at  $2287.7\text{cm}^{-1}$  [13]. Then, the higher thermal stability of Zn,H complexes in InP compared to GaAs can be understood since the binding energy of P-H bonds (75 kcal) is known to be higher than that of As-H bonds (56 kcal) [15].

#### CONCLUSION

Hydrogen diffusion occurs in InP using GaInAs as a hydrogen permeable protecting cap layer with reasonable lattice matching at the interface. Zn,H pairing is evidenced in InP:Zn,H by the close correspondence of the hydrogen and the net acceptor concentrations. Hydrogen diffusion in InP:Zn results in an efficient passivation of zinc acceptors leading to a high resistivity material. The increased hole mobility in lightly reactivated epilayers is due to the presence of a large amount of neutral Zn,H complexes. Getting resistive InP using plasma hydrogenation with a relatively sharp hole concentration drop may be very useful in microelectronics or optoelectronics if one wants to make electrical insulation region in devices.

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