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Hydrogen passivation of shallow acceptors in p-type InP

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Abstract. Undoped GaInAs/zinc-doped InP structures grown by metal–organic chemical vapour deposition have been exposed to a RF hydrogen or deuterium plasma. Secondary ion mass spectrometry experiments show deuterium diffusion in both materials and the existence of a hydrogen–acceptor pairing effect in the p-type InP layer. After hydrogenation, the InP layer becomes highly resistive as a result of a strong passivation of acceptors by hydrogen. Hall effect and conductivity measurements performed on a lightly thermally reactivated InP layer indicate that the hole mobility is significantly higher than in the non-hydrogenated InP layer. This increase is attributed to a decrease of the ionised acceptor concentration under hydrogenation and is consistent with the existence of a pairing between the proton and the ionised acceptor giving rise to neutral Zn–H complexes. The relative thermal stability of Zn–H complexes in InP:Zn if compared to GaAs:Zn can be interpreted with the help of the microscopic model of these complexes, hydrogen being more tightly bonded to a phosphorus than to an arsenic atom.

There is currently considerable interest in the hydrogen passivation of shallow dopants and deep levels in crystalline semiconductors [1, 2]. Most of the studies on the interactions between hydrogen and acceptors or donors have been performed in Si, Ge, GaAs, GaAlAs and more recently in CdTe and ZnTe. However, until now, nothing has been reported in the literature on the hydrogen–shallow acceptor interactions in InP.

One of the most common methods of hydrogen introduction in semiconductors is by exposure to hydrogen plasma. The plasma offers a source of chemically active hydrogen species which permits hydrogen diffusion into the sample. This holds true for materials which are relatively stable in presence of such an ambient. In some cases however, strong surface decomposition can occur. For example, etching of the CdTe crystal surface has been reported when such a material is exposed to a hydrogen plasma [3]. Consequently, molecular hydrogen or low-energy implantation have to be used for hydrogen introduction in CdTe. Hydrogenation of InP encounters the same difficulty. Exposure of InP to a hydrogen plasma leads to a rapid degradation of the surface due to the reaction of phosphorus with hydrogen and the subsequent formation of PH_3 . Indium droplets are observed in this

case [4, 5]. In order to ensure hydrogen diffusion into InP it is necessary to find a surface protection for this material.

In the present work, we show that hydrogen diffusion in p-type InP can be achieved by protecting the InP surface with a thin layer of undoped lattice-matched GaInAs and that this diffusion leads to efficient passivation of shallow acceptors.

For this study, we have used samples grown by metal–organic vapour phase epitaxy. The detailed experimental set-up and growth conditions are described elsewhere [6]. The samples consist of a $0.55\text{ }\mu\text{m}$ layer of undoped $\text{Ga}_x\text{In}_{1-x}\text{As}$ and a $4.9\text{ }\mu\text{m}$ layer of zinc-doped InP epitaxially grown on a InP:Fe semi-insulating substrate. The ternary layer has a composition x equal to 0.47 with good lattice matching to the InP layer ($|\Delta a/a| = 5 \times 10^{-4}$ to 10^{-3}). The zinc-doped InP layer has a free hole concentration of $2.5 \times 10^{18}\text{ cm}^{-3}$ and a hole mobility of $60\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ at 300 K.

For hydrogen diffusion studies, we have exposed these samples to a RF deuterium plasma for 20 min. The RF power density was 0.025 W cm^{-2} . The deuterium diffusion profiles have been analysed by SIMS experiments using a CAMECA IMS 3 f system. The deuterium concentration was obtained by the use of a D^+ -implanted InP sample as a standard. After hydrogen (or deuterium) plasma exposures, the GaInAs cap

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layer remains specular in the conditions used and no visible degradation is observable under optical microscopes.

Figure 1 presents deuterium concentration profiles in samples exposed at different temperatures. Deuterium diffuses through the undoped GaInAs and the p-type InP layers. We note the absence of deuterium accumulation at the GaInAs/InP interface. This holds true for structures with good lattice matching. In structures with poor lattice matching, deuterium accumulation occurs at the interface. For example, in structures with $|\Delta a/a| = 13 \times 10^{-3}$, the deuterium peak concentration at the interface is 3 to 5 times higher than the deuterium concentration in the InP epilayer. However, the deuterium penetration depth and the hydrogen solubility in the p-type InP layer are quite similar in structures having good lattice matching and in structures with poor lattice matching of 13×10^{-3} .

In figure 1, we notice that the deuterium concentration profile in InP consists of a plateau followed by an abrupt decrease. Besides the fact that the penetration depth increases with temperature, an important feature of this set of diffusion curves is that the deuterium concentration in the plateau region is quite independent of temperature for $T < 300^\circ\text{C}$ and is equal to the free hole concentration. Similarly, we find that the deuterium concentration is not dependent on the exposure duration [7]. It is clear from these results that we are observing a diffusion process in which the hydrogen

concentration follows the net acceptor concentration. This effect is a first indication that pairing occurs between hydrogen and zinc acceptors in p-type InP at diffusion temperatures 300°C or below.

Very similar deuterium profiles have been obtained by Johnson *et al* [8] in deuterated Si:B. Studies of the interaction between hydrogen and silicon acceptors in p-type GaAs:Si show a similar pairing effect in SIMS experiments for plasma exposures up to 305°C [9]. In zinc-doped GaAs, Johnson *et al* reported the existence of a pairing effect in diffusion experiments at 200°C . For exposures at 250°C or above, no plateau is observable and the hydrogen concentration is significantly below the acceptor concentration [10]. This result means that the tendency to pairing decreases in hydrogen diffused GaAs:Zn for temperatures of 250°C or above. From the comparison between the pairing effect in GaAs:Zn and InP:Zn, we can readily deduce that hydrogen interacts more strongly with zinc in InP:Zn than in GaAs:Zn. This stronger interaction of hydrogen in InP:Zn will be confirmed further in this work. Modelling of the deuterium diffusion profile has been made for Si:B, D [11]. A rather good description of the profile has been given in this case: assuming that hydrogen acts as a deep donor, the proton is accelerated by the built-in electric field which results from the free carrier concentration gradient. The assumption of hydrogen moving as positively charged species in p-type silicon is supported by deuterium electrotransport experiments performed in reverse-biased p-type deuterated silicon Schottky diodes [12, 13]. Similar experiments in GaAs or InP have not yet been performed, but hydrogen acting also as a deep donor in III-V compounds is a plausible assumption. Then, acceleration of protons in p-type InP by the built-in electric field has to be taken into account in the modelling of the hydrogen diffusion profile. The coulombic attraction between the protons and the negatively charged acceptors has been proposed for the formation of pairing in p-type silicon [14]. In p-type InP:Zn, as already mentioned, this is evidenced through matching of the hydrogen and acceptor concentrations and through the direct observation of Zn-H complexes by infrared absorption spectroscopy [15]. Moreover, these Zn-H complexes are relatively stable at the diffusion temperatures. Consequently, hydrogen trapping on zinc acceptors has to be included in the modelling of the hydrogen diffusion profile in InP:Zn, H.

Passivation of zinc acceptors by hydrogen in InP is clearly demonstrated by transport experiments. For this investigation, we have exposed the samples to a hydrogen plasma for 6 h at 200°C . From SIMS experiments, we know that under these exposure conditions hydrogen diffuses through the whole thickness of the epilayer. Hall and resistivity measurements have been performed after removal of the GaInAs cap layer. The resistivity of the hydrogenated InP layer increases by more than six orders of magnitude as a result of a strong hydrogen passivation of zinc acceptors. Due to the high resistivity of the sample, reliable Hall effect

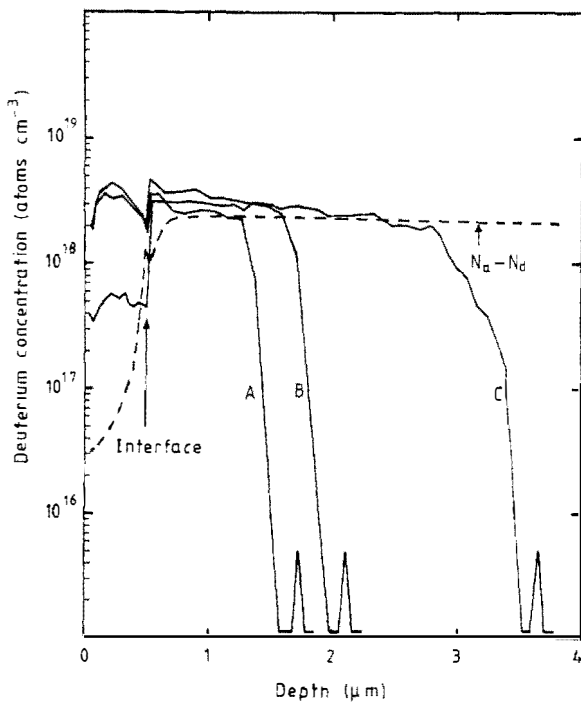


Figure 1. Deuterium concentration profiles in p-type InP:Zn covered with an undoped GaInAs cap layer and exposed to a RF deuterium plasma at different temperatures for 20 min. The $N_a - N_d$ profile has been obtained with a Polaron semiconductor profiler. The plasma power density is 0.08 W cm^{-2} . Curve A, 163°C ; curve B, 203°C ; curve C, 295°C .

measurements could not be obtained after passivation. For this reason thermal annealing experiments were carried out in order to partially reactivate the acceptors and to get measurable transport properties. After annealing the sample at 275 °C for 5 min, the hole concentration at 300 K is $1.3 \times 10^{16} \text{ cm}^{-3}$ indicating that 99% of the acceptors are still passivated.

Figure 2 shows the variation of the hole mobility versus temperature for the epilayer before hydrogenation (curve A) and for the hydrogenated and partially annealed epilayer (curve B). Both curves peak at a temperature close to 120 K. The effect of the passivation is clearly seen at low temperatures. At 50 K, where scattering by ionised impurities is the limiting mechanism, the hole mobility in the hydrogenated layer is one order of magnitude higher than in the as-grown layer. This can be interpreted in terms of a decrease of the ionised impurity concentration, as hydrogen passivation of acceptors leads to the creation of neutral complexes. At higher temperatures, where scattering by phonons is the limiting mechanism, mobilities are nearly equal in the two samples. Such a behaviour is similar to the one which has been observed in Si doped n-GaAs [16]. In our p-InP samples, the effect of hydrogenation upon the mobility is still more pronounced. Indeed, we note a maximum increase of the mobility by a factor of 10, whereas in n-GaAs the electron mobility is only enhanced by a factor of 2.

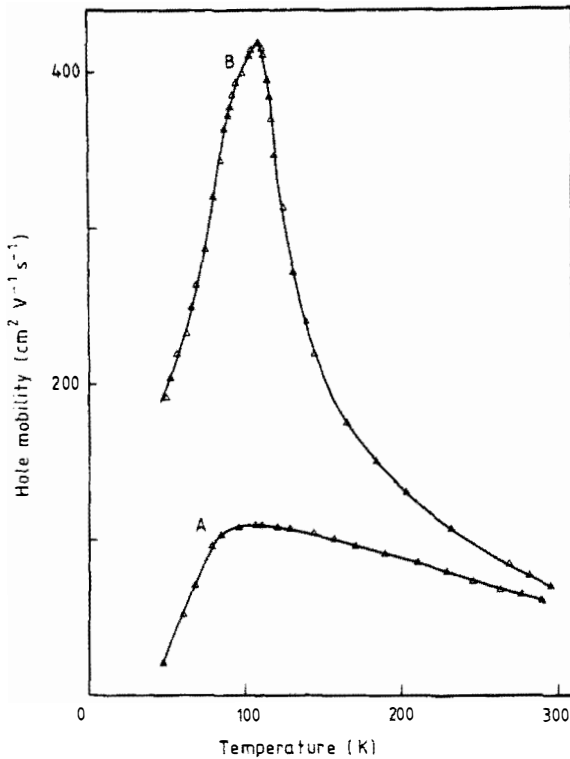


Figure 2. Hole mobility versus temperature curves for a zinc-doped InP epilayer before any hydrogenation (curve A) and after hydrogen plasma exposure for 6 h at 200 °C followed by annealing at 275 °C for 5 min (curve B).

The curves on figure 2 have been compared with the results obtained by Galavanov *et al* [17] concerning the hole mobility in Zn doped InP samples. From the behaviour of the mobility of our as-grown sample (figure 2, curve A), it appears that the ionised impurity concentration is smaller than in the crystals used by Galavanov *et al* [17]: the hole mobility we have measured is larger and its maximum is obtained for a lower temperature (120 K instead of 200 K). On the other hand, after hydrogenation and partial annealing (figure 2, curve B) which restores a hole concentration of about 10^{16} cm^{-3} , the comparison with [17] shows that, in our samples, the hole mobility is smaller and its maximum value is obtained at a higher temperature. This result means that in our samples, the hole mobility is limited by additional and/or remaining scattering centres. Due to the repulsive effect between protons and ionised donors, we might expect that the remaining ionised donors are unpassivated. Support for this assumption has been provided by infrared optical spectroscopy in p-type GaAs:Si, H [9]. It has been shown that the number of ionised silicon donors (Si_{Ga}) remains unchanged before and after hydrogenation. Consequently, unpassivated ionised donors and acceptors are probably scattering centres limiting the hole mobility after hydrogenation.

From these annealing experiments, one can make some other comments. 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 at which Zn-H complexes start to decompose in GaAs [18]. This comparison proves that Zn-H complexes are more stable in InP:Zn than in GaAs:Zn. A reason for this can be found if we consider the microscopic description of Zn-H complexes in these materials. In GaAs:Zn, H, it has been proposed that the complex formation implies the breaking of a Zn-As bond [19]. Zinc becomes threefold coordinated and thus electrically inactive. The hydrogen is bonded to the arsenic atom giving rise to the 2147 cm^{-1} vibrational line detected in infrared absorption spectroscopy. Similar investigations in hydrogen passivated InP:Zn prove the existence of Zn-H complexes [15]. The microscopic model of these complexes similarly proposes the breaking of a Zn-P bond and the formation of a P-H bond observable through its stretching vibrational mode at 2287.7 cm^{-1} [15]. The higher thermal stability of Zn-H complexes in InP compared with GaAs can thus be explained since the P-H bonds are known to have higher thermal stability than the As-H bonds.

As a conclusion, hydrogen diffusion occurs in InP by using GaInAs as a hydrogen permeable protecting cap layer which has reasonable lattice matching at the interface. Zn-H pairing is evidenced in InP:Zn by the close correspondence of the hydrogen and the acceptor concentrations. Passivation of zinc acceptors by hydrogen in InP:Zn produces a semi-insulating material or a lightly doped p-type material with a high hole mobility after appropriate thermal annealing. Getting highly resistive InP using plasma hydrogenation may be very

useful in microelectronics or optoelectronics if one wants to make electrically isolated regions in devices. For example, this method may advantageously replace proton implantation in InP/GaInAs laser technology and could then avoid the presence of a high damage region close to the active region of the laser.

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