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Diffusion and electronic states of hydrogen in *n*-type GaAs and *n*-type $Ga_{1-x}Al_xAs$

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Deuterium diffusion experiments have been performed in silicon-doped GaAs and $Ga_{1-x}Al_xAs$ ($x \leq 0.30$). In GaAs, the hydrogen diffusion profile closely fits a complementary error function. In $Ga_{1-x}Al_xAs$ alloys with $x \geq 0.055$, the profiles present a plateau followed by a sharp decrease. To interpret this difference we propose that in *n*-type GaAs:Si and $Ga_{1-x}Al_xAs$:Si, hydrogen behaves as a deep acceptor with a level $H^{-/0}$ slightly resonant in the conduction band of GaAs and emerging as a localized state for $x > 0.07$ as the band-gap energy increases. Then, for $x > 0.07$, the H^- species become dominant and are trapped on the positively charged donors during diffusion.

Among the different problems raised by the behavior of monatomic hydrogen in crystalline semiconductors, one is related to its charge states and its interactions with impurities as it migrates in the lattice.

It is now accepted that protons are the main diffusing species in *p*-type silicon and *p*-type GaAs.[1,2] Using infrared local vibrational mode (LVM) spectroscopy, Clerjaud *et al.*[3] have been able to directly locate the hydrogen-donor level $H^{0/+}$ in GaAs. They found that this level is 1 eV below the conduction band. By modeling hydrogen diffusion profiles in GaAs:Zn, Rahbi *et al.*[4] concluded that the hydrogen-donor level is located 1.1 eV below the conduction band,[4] in close agreement with the value of Clerjaud *et al.*. The Coulombic attraction of protons by negatively charged acceptors is at the origin of the formation of neutral hydrogen-acceptor complexes observed by LVM spectroscopy.[5-8] This trapping effect plays an important role in the diffusion process of hydrogen in GaAs:Zn (Ref. 4) and Si:B (Ref. 9) as well.

In *n*-type silicon, the formation of neutral hydrogen-donor complexes has been established a few years ago[10] and there are some indications that hydrogen migrates as H^- in this material.[11,12]

In *n*-type GaAs and *n*-type $Ga_{1-x}Al_xAs$ ($x \leq 0.37$), neutralization of donors by hydrogen has been reported.[13-16] LVM's of hydrogen-donor complexes have been detected only in the case of silicon and tin donors for GaAs (Refs. 17 and 18) and in the case of silicon for $Ga_{1-x}Al_xAs$.[19] It was concluded that hydrogen binds directly to the donor and lies in an antibonding position. Theoretical work supports the antibonding site for an H^- compensating donor.[20] More recently, several groups concluded, from reverse-bias-annealing experiments on Schottky diodes, that H^- is a diffusing species in *n*-type GaAs and *n*-type $Ga_{1-x}Al_xAs$.[21-24]

This paper reports deuterium diffusion experiments in a series of silicon-doped $Ga_{1-x}Al_xAs$ alloys with x ranging from 0 to 0.30. In order to interpret the evolution of the diffusion profile with the alloy composition, we shall propose a model based on hydrogen introducing a deep acceptor level $H^{-/0}$ in these materials. The relative position of this level with respect to the Fermi level will provide different dominant species in the deuterium diffusion profile.

For this study, we have used two series of $Ga_{1-x}Al_xAs$ samples: (i) a highly silicon-doped series consisting of Bridgman grown wafers of GaAs:Si ($[Si]=1.5\times10^{18}$ cm^{-3}), several molecular-beam-epitaxy (MBE) -grown $Ga_{1-x}Al_xAs$:Si epilayers with x ranging from 0.035 to 0.15 ($[Si]=1.5\times10^{18}$ cm^{-3}, $e=3$ μm), a 8-μm-thick silicon-doped $Ga_{0.70}Al_{0.30}As$ epilayer grown by organometallic vapor phase epitaxy ($[Si]=10^{18}$ cm^{-3}) and (ii) a lightly silicon-doped series consisting of MBE-grown $Ga_{1-x}Al_xAs$:Si epilayers with $x=0$, 0.17, and 0.29 ($[Si]=2\times10^{17}$ cm^{-3}, $e\approx2$ μm). The composition of the alloys was deduced from electron microprobe analysis.

All these samples have been exposed to a deuterium radio frequency plasma in the following conditions: rf power is 0.02–0.04 W/cm^2, $T=215$–$240\,°C$, and $t=30$ min. The deuterium diffusion profiles have been carried out on a CAMECA IMS 4f system using deuterium-implanted GaAs standard for the quantification.

Figures 1 and 2 present the deuterium diffusion profiles in the first series of highly silicon-doped samples with different aluminum compositions. In GaAs doped with silicon at a level of 1.5×10^{18} cm^{-3}, we find a hydrogen distribution very close to a complementary error function (erfc) with an effective diffusion coefficient of deuterium of 4×10^{-12} cm^2/s at 240 °C. In undoped GaAs, the deu-

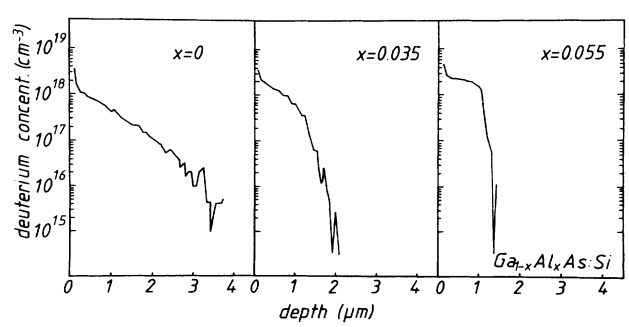

FIG. 1. Deuterium diffusion profiles in highly doped *n*-type GaAs:Si and $Ga_{1-x}Al_xAs$:Si alloys with low amounts of aluminum. The silicon doping level is 1.5×10^{18} cm^{-3}. The plasma conditions are $T=240\,°C$, $t=30$ min, and $P=0.04$ W/cm^2.

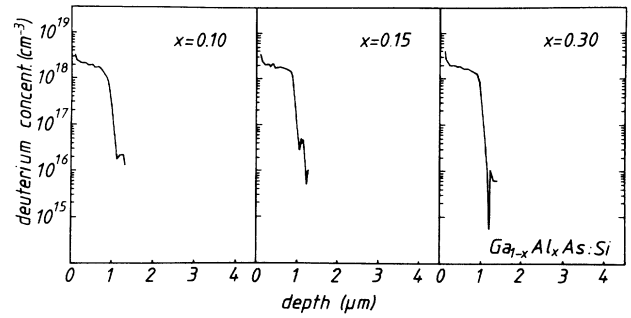

FIG. 2. Deuterium diffusion profiles in a series of highly doped n-type $Ga_{1-x}Al_xAs$:Si alloys with different values of x. Same plasma conditions as in Fig. 1.

terium profile remains an erfc function with an increase of the corresponding diffusion coefficient (1.2×10^{-11} cm^2/s at 240 °C).[4] As the aluminum content increases, the erfc function is progressively replaced by a diffusion profile characterized by a plateau followed by an abrupt decrease of the deuterium concentration. This situation occurs above $x \approx 0.06$. For all studied compositions above this critical value, the diffusion profile is very similar with the same diffusion depth. For $x=0.035$, the situation is somewhat intermediate and the plateau starts showing its signature. We have performed diffusion experiments in undoped alloys ($x=0.37$): The deuterium diffusion profile is again an erfc function with a diffusion coefficient of 3×10^{-12} cm^2/s close to that found in undoped GaAs (6×10^{-12} cm^2/s) for a given temperature of 225 °C.

The solubility of deuterium in the plateau region of alloys with $0.035 < x < 0.15$ is markedly close to the active dopant concentration. For $x=0.30$, this solubility is well above the free-electron concentration measured at 300 K but very close to the silicon dopant concentration. It is well known that the electrical properties of n-type $Ga_{1-x}Al_xAs$ alloys doped with silicon are governed by shallow or deep silicon-donor states depending on the alloy composition. For $x < 0.22$, shallow levels related to substitutional silicon donors (silicon on gallium sites) play a major role. For $x > 0.22$, the electrical properties are governed by deep silicon donors, called DX centers, related to another atomic configuration of silicon implying some lattice relaxation around it. These deep donors have several key features such as a repulsive barrier for both electron emission and capture leading to persistent photoconductivity and also a large binding energy which increases from zero to 160 meV as x varies from 0.22 to about 0.4.[25] At 300 K, the free-electron concentration of alloys with $x=0.30$ is smaller than the deep silicon-donor concentration because the binding energy of DX centers at this composition is high enough (≈ 60 meV) to freeze-out a fraction of the electrons on the deep donor level.[26] However, at 513 K, which is the hydrogen diffusion temperature, or above, most of the DX centers are thermally ionized and the exhaustion regime occurs.[27] Then, the solubility of deuterium in $Ga_{0.70}Al_{0.30}As$ alloys is still equal to the active dopant concentration at the diffusion temperature and deuterium species interact with the positively charged silicon donors. This interaction is at the origin of the neutralization of these donors observed in deuterated $Ga_{1-x}Al_xAs$:Si alloys with $0 < x < 0.37$.

Figure 3 presents the deuterium diffusion profiles in the second series of lightly silicon-doped samples. In GaAs, we again have an erfc diffusion profile, as in undoped and highly doped samples. In alloys with $x=0.17$, the diffusion profile slightly differs from that found in GaAs. However, for alloys with $x=0.29$, the profile shape totally changes: A near plateau region appears with a solubility close to the active silicon concentration at the diffusion temperature followed by a steep decrease.

A first explanation of the modifications of the deuterium profiles as the aluminum composition increases consists of assuming a stronger dissociation energy of the Si-H complexes in the alloys with $x > 0.06$ compared to GaAs. A decrease of the thermal dissociation probability of hydrogen dopant complexes is known to provide similar modifications in p-type GaAs.[4,28] In the present case, we say that this assumption is not valid for the following two reasons.

(i) The dissociation energy of Si-H complexes has been measured in GaAs:Si and $Ga_{1-x}Al_xAs$:Si alloys.[23,24] From the reactivation kinetics of silicon shallow donors, a dissociation energy of ≈ 1.18 eV has been found for Si-H complexes, independent on the alloy composition. Moreover, the same dissociation energy is found for the complexes involved in the DX center neutralization. Following the Chadi and Chang model,[29] silicon donors act as a bistable defect: The most stable configuration is the substitutional position for $x < 0.22$ and the displaced position for $x > 0.22$. Within this model, the above result is not surprising since the Si-H complexes arising from shallow donors or DX centers are basically not different from each other.

(ii) In GaAs:Si, the Si-H complexes are well observable through the presence of vibrational absorption bands located at 896.82 and 1717.25 cm^{-1} at 7 K. These bands, respectively, are attributed to the wagging mode and the stretching mode of Si-H bonds with hydrogen located in an antibonding site.[17] In $Ga_{0.8}Al_{0.2}As$:Si alloys, the wagging related mode of Si-H complexes is characterized by a series of lines:[19] a strong line at 896.4 cm^{-1}, i.e., near the position of the line in GaAs, and other weaker components

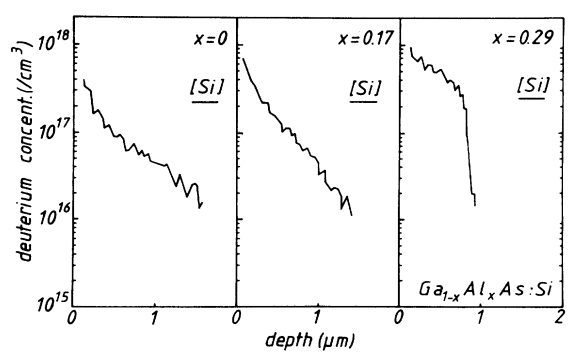

FIG. 3. Deuterium diffusion profiles in a series of lightly doped n-type GaAs:Si and $Ga_{1-x}Al_xAs$:Si alloys. The silicon doping level is 2×10^{17} cm^{-3} in all the samples. The plasma conditions are $T=215$ °C, $t=30$ min, and $P=0.02$ W/cm^2.

spreading from 878 to 912 cm^{-1}. These components are attributed to the splitting of the degenerate wagging mode related to some configurations of Al atoms next-nearest neighbors of the silicon atoms. The small sensitivity of the Si-H wagging mode frequency to the alloy composition is evidence that the Si-H bond characteristics are essentially the same in GaAs and alloys containing up to 20% of AlAs.

We also rule out the possibility that the above changes of deuterium profiles with alloy composition are related to the presence of an oxide layer covering the $Ga_{1-x}Al_xAs$ surface. The presence of an oxide layer might reduce the rate of introduction of deuterium, then decreasing the penetration depth, but should not significantly modify the shape of the deuterium diffusion profile.[30]

An explanation of our results can be provided in terms of hydrogen diffusing with different charge states. In other words, we assume that hydrogen behaves as a deep acceptor in n-type GaAs and $Ga_{1-x}Al_xAs$ alloys doped with silicon with the acceptor level located slightly above or below the conduction-band minimum depending on the band-gap energy, i.e., on the alloy composition. The concentrations of H^0 and H^- depend on the relative position, at the diffusion temperature, of the Fermi level and the hydrogen-acceptor level. Within this model, two situations must be considered.

(i) For compositions where the Fermi level is above the acceptor level, H^- is the dominant diffusing species. Then, the hydrogen diffusion profile is the result of a diffusion of H^- trapped on the positively charged donors by a long-range interaction. This situation is symmetrical of that occurring in p-type GaAs and p-type silicon where hydrogen behaves as a deep donor and where H^+ interacts with negatively charged acceptors leading to the formation of neutral hydrogen-acceptor complexes. This trapping effect is well observable in the hydrogen diffusion profiles of these materials.[8,31] In the present study, the diffusion profiles of alloys with $x \geq 0.05$ in the highly doped sample series and with $x = 0.29$ in the lightly doped one are characteristic of a trapping effect of H^- on the positively charged donors.

(ii) For compositions where the Fermi level is close to the acceptor level, hydrogen diffuses in two different charge states H^0 and H^- with a significant fraction of neutral hydrogen. This is the case for the highly and the lightly doped GaAs:Si and also for the lightly doped alloy with $x = 0.17$. Long-range interactions of the existing H^- with the positively charged donors lead to complex formation. However, neutral hydrogen governs the experimental diffusion profile because of its much higher effective diffusivity compared to that of H^-. The existence of these two forms of hydrogen is consistent with recent results establishing that, in n-type GaAs:Si, at the diffusion temperature, hydrogen is present as a mobile species (involving neutral hydrogen) and as a trapped form known to be Si-H complexes from LVM studies.[32]

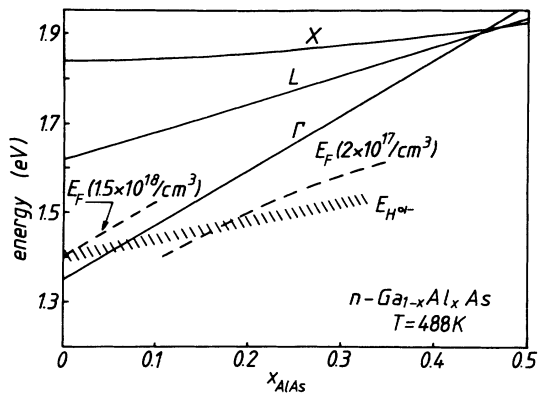

FIG. 4. Alloy composition dependence of the hydrogen acceptor level and the conduction bands of $Ga_{1-x}Al_xAs$. The Fermi level in the lightly silicon-doped sample series has been calculated assuming that DX centers are fully ionized at the diffusion temperature of 488 K. Electronic band parameters are from Ref. 33.

Comparison of the deuterium profiles in the highly doped and the lightly doped series shows that lowering of the Fermi level has lead to a displacement towards aluminum-rich alloys of the crossing composition between the Fermi level and the hydrogen-acceptor level.

Since in GaAs doped at a level of 1.5×10^{18} cm^{-3}, the Fermi level is 50 meV above the conduction-band minimum, we conclude that the hydrogen-acceptor level is lightly resonant in the conduction band of GaAs and alloys with compositions below a critical composition x_c of a few percent of AlAs.

Figure 4 shows the dependence of the hydrogen-acceptor level versus the alloy composition deduced from the above results. From this, we can provide a value of $x_c = 0.07 \pm 0.02$ for the critical composition corresponding to crossing between the hydrogen-acceptor level and the Γ conduction band. Above x_c, the acceptor level becomes localized in the band gap of the alloys.

In conclusion, from a qualitative analysis of hydrogen diffusion profiles in n-type GaAs:Si and n-type $Ga_{1-x}Al_xAs$:Si alloys, we have proposed that hydrogen behaves as a deep acceptor in these materials with a level slightly above the conduction-band minimum or localized in the band gap depending on the alloy composition. The critical composition is around $x \approx 0.07$.

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