

## Dopant-type effects on the diffusion of deuterium in GaAs

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The diffusion depth and total amount of deuterium incorporated in GaAs during plasma exposure is found to depend strongly on the conductivity type of the surface. A shallow  $n^+$  layer inhibits the in-diffusion of deuterium, consistent with that species having a level in the upper half of the GaAs band gap. The deactivation of donors and acceptors by deuterium is then the result of different chemical reactions based on its different charge states in  $n$ - and  $p$ -type material. Zn acceptors display a reactivation energy of 1.6 eV, less than the typical value for donors of 2.1 eV.

The passivation of both shallow donor<sup>1-3</sup> and acceptor<sup>4</sup> impurities in GaAs by exposure to a hydrogen plasma has recently been reported. Various models for the passivation process have been proposed,<sup>2,4</sup> but the actual deactivation mechanism will depend on the charge state of hydrogen as it approaches the dopant ion. A similar situation holds for the hydrogen passivation of shallow impurities in Si where some confusion exists as to the exact chemical reaction taking place.<sup>5</sup> Initially it was assumed that hydrogen in Si was in a neutral charge state,<sup>6</sup> but recent biased diffusion experiments provide strong evidence that it exists as a positively charged species in  $p$ -type Si.<sup>7,8</sup> In contrast, some theoretical calculations predict a negative charge state as a possible stable form of hydrogen in  $n$ -type material.<sup>9</sup> A further key observation is that a thin  $n$ -type layer on  $p$ -type Si will impede the incorporation of hydrogen into the bulk of the material.<sup>10,11</sup> It is obviously of benefit to study the chemical doping dependence of hydrogen diffusion in GaAs, to establish whether similar behavior can provide an insight into the passivation mechanism in compound semiconductors.

A variety of  $n$  and  $p$ -type and undoped GaAs was utilized. The  $n$ -type samples were taken from Si-doped  $\langle 100 \rangle$  single-crystal boules grown by the horizontal Bridgman technique, with net carrier concentrations determined by Hg-dot, Schottky-contact capacitance-voltage profiling to be in the range  $5 \times 10^{15}$ – $2 \times 10^{18}$  cm<sup>-3</sup>. The  $p$ -type specimens were obtained from Zn-doped  $\langle 100 \rangle$  Bridgman crystals with net carrier concentrations in the range  $3 \times 10^{16}$ – $5 \times 10^{18}$  cm<sup>-3</sup>. For comparison with this conducting material, we included undoped semi-insulating ( $10^7$   $\Omega$  cm) samples from liquid encapsulated Czochralski crystals in all hydrogenation treatments.

In some samples an  $n^+$  layer was formed by implanting 60-keV <sup>29</sup>Si ions to a dose of  $6 \times 10^{13}$  cm<sup>-2</sup>, followed by rapid annealing at 900 °C for 10 s with the sample of interest face down on another GaAs substrate. This procedure created a 1700-Å thick  $n$ -type layer doped at  $\sim 2.4 \times 10^{18}$  cm<sup>-3</sup> at the surface of the GaAs. Companion sections were implanted with 40-keV <sup>9</sup>Be ions at a dose of  $1 \times 10^{14}$  cm<sup>-2</sup>, and rapidly annealed at 850 °C for 3 s to form a 1500-Å thick  $p$  surface layer doped at

$\sim 1 \times 10^{19}$  cm<sup>-3</sup>. Thus we were able to study the diffusion of hydrogen or deuterium in samples with thin highly doped regions of either similar or opposite conductivity to the bulk material.

In order to facilitate high-sensitivity secondary-ion mass spectrometry (SIMS) measurements, isotopic substitution of deuterium for hydrogen was used. The only difference in the impurity passivation properties of these isotopes is that the diffusion coefficient for D is less by a factor of the square root of the masses (0.71).

Deuterium plasma exposures were performed as described previously by exposing the samples to a 30-kHz, 750-mTorr, 0.08-W cm<sup>-2</sup> plasma within a parallel-plate reactor system.<sup>1,2</sup> This is an efficient and convenient method for deuterating or hydrogenating samples, provided that energetic ion, electron, and photon bombardment of the sample do not cause spurious effects.<sup>12,4</sup> As we have shown previously by comparison with electrolytically hydrogenated GaAs, our plasma conditions induce no significant changes in the incorporation kinetics of hydrogen, nor do they degrade the electrical properties of the material,<sup>1</sup> at least at depths of  $\geq 400$  Å.

Figure 1 shows the deuterium concentration profiles in  $n$ -type GaAs as a function of doping level, for three samples deuterated during the same plasma exposure. Considering that the relative concentrations determined by SIMS are accurate to  $\pm 20\%$  and the depth scales accurate to  $\pm 7\%$ , the data show an  $n^{-1/2}$  dependence of deuterium incorporation depth.<sup>13</sup> This result is consistent with the deuterium diffusion being modulated by trapping at donor impurities. The net electrically active Si donor profiles after deuteration do not always correlate well with the total D profile, indicating that much of the D is inactive due to trapping at other sites, principally other D atoms, forming deuterium molecules. For example, from the data in Fig. 1 one should see passivation of Si donors in the  $n = 5 \times 10^{15}$  cm<sup>-3</sup> material to a depth of  $\sim 12$   $\mu$ m, whereas the carrier concentration profile shows detectable donor passivation to  $\sim 3.5$   $\mu$ m. We emphasize that changes in the plasma parameters and sample exposure temperature can cause significant variations in both the total amount of deuterium incorporated into the GaAs, and in the efficiency of that deuterium in passivating the

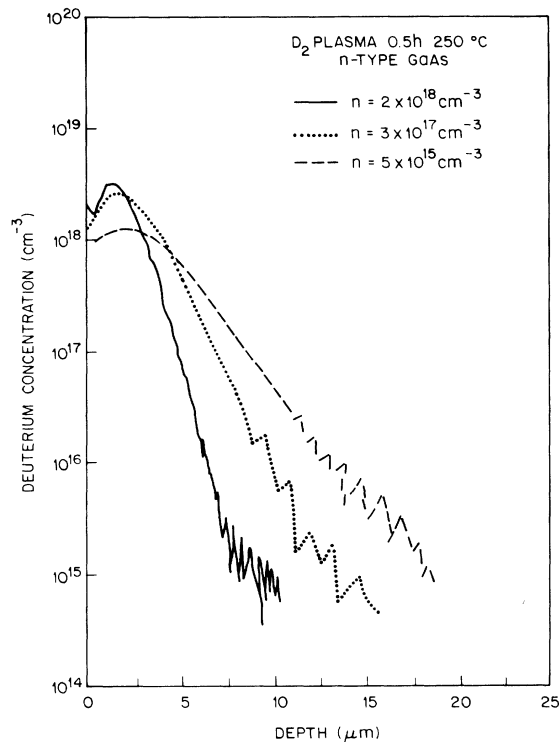


FIG. 1. SIMS depth profiles of deuterium in *n*-type GaAs as a function of donor doping level for a plasma exposure time of 30 min at 250 °C.

shallow dopants, and therefore we used constant conditions throughout the experiment.

For example, at low plasma power densities ( $\sim 0.05 \text{ W cm}^{-2}$ ) there is a relatively small amount of deuterium available for donor or acceptor passivation, and its diffusion is strongly reaction limited. At intermediate power densities ( $\sim 0.13 \text{ W cm}^{-2}$ ) there is a very good correlation of deuterium incorporation depth with the depth of donor passivation. For higher power densities ( $\sim 0.28 \text{ W cm}^{-2}$ ) it is difficult to avoid plasma-induced sample heating, and increases of a factor of 2 in the effective diffusion coefficient of deuterium have been observed for a nominal sample temperature of 250 °C. This would correspond to an increase in the effective near-surface temperature of the sample of 15 °C.<sup>14,15</sup>

Depth profiles of deuterium in Zn-doped GaAs display a very strong dependence of the total D concentration on the initial doping level of the material, in contrast to the behavior in GaAs(Si). Figure 2 compares D profiles in plasma-exposed *p*-type GaAs with that obtained in a semi-insulating sample, for the same plasma exposure conditions employed on the *n*-type samples shown in Fig. 1. It can be observed that both diffusion depths and concentrations are larger in the *p*-type than in the *n*-type material. The semi-insulating sample shows a deuterium profile similar to that in lightly doped *n*-type GaAs. This result is in agreement with Ref. 4, but here we show the full extent of the D incorporation depth. Deuteration for 0.5 h at a higher temperature of 300 °C resulted in D

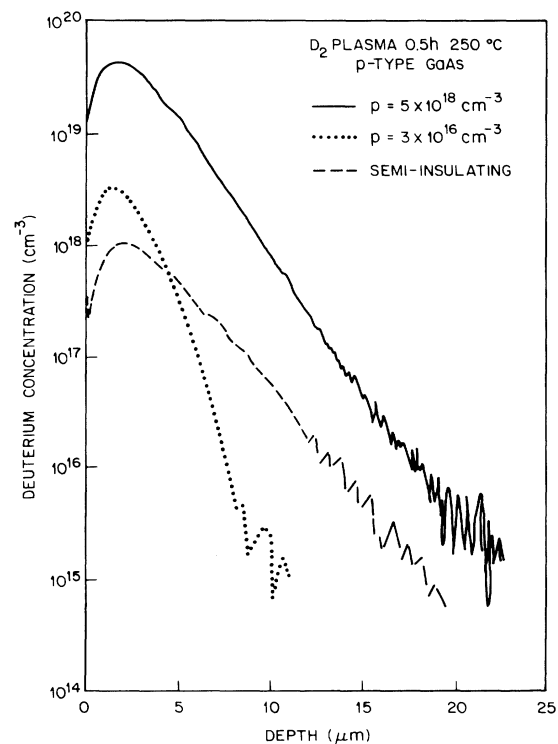


FIG. 2. SIMS depth profiles of deuterium in *p*-type GaAs as a function of acceptor doping level, and in a semi-insulating sample, for a plasma exposure time of 30 min at 250 °C.

profiles extending to  $\sim 35 \mu\text{m}$  in  $p = 3 \times 10^{16} \text{ cm}^{-3}$  Zn-doped material. Once again there was not a good correlation between the total D profile and the passivated acceptor profile under our deuteration conditions. For example, for 250 °C deuterations we see acceptor passivation extending to  $\sim 1.5 \mu\text{m}$  in the  $3 \times 10^{16} \text{ cm}^{-3}$  Zn-doped samples, whereas the SIMS data shows the total D concentration is above this level to  $\sim 6 \mu\text{m}$ . However, in particular it should be noted that increasing *p*-type doping does not impede the D in-diffusion at this temperature in contrast to the case for *n*-type doping as shown in Fig. 1. Indeed, both the total D concentration and diffusion depth are increased for high acceptor concentrations, with the peak D concentration exceeding that attained in the *n*-type samples.

The thermal stability of donor passivation for all donor species has been treated in detail in Ref. 2. We find acceptor passivation in GaAs is less stable than that for donors. As for donors, we can obtain the dissociation energy of deuterium from the ion or complex to which it is attached from

$$E_D = kT \ln \left[ \frac{1}{t\nu} \ln(N_0/N) \right], \quad (1)$$

assuming the dissociation obeys first-order kinetics and is the rate-limiting step. In Eq. (1)  $N/N_0$  is the fraction of acceptor-deuterium complexes remaining after annealing at temperature  $T$  for a time  $t$ , and  $\nu$  is the dissociation at-

tempt frequency (assumed equal to  $10^{14} \text{ s}^{-1}$ ). For Zn we obtain  $E_D \sim 1.6 \text{ eV}$ , compared to  $\sim 2.1 \text{ eV}$  for the Si, Ge, or Se donors in  $n$ -type material.<sup>1,2</sup> The D profiles in separate Zn-doped samples as a function of post-deuteration annealing temperature are shown in Fig. 3. There is significant deuterium redistribution upon heating at  $350^\circ\text{C}$ , and higher, and although the acceptors are reactivated at this temperature, much of the deuterium remains in the GaAs at concentrations high enough to passivate all of the Zn. That it does not again indicates it is present in an inactive form, possibly  $\text{D}_2$  or more extended platelets containing deuterium.<sup>16</sup>

The inhibiting effect of an  $n$ -type layer on deuterium diffusion in  $p$ -type GaAs is shown in the SIMS profiles of Fig. 4. Both the depth and total amount of D incorporation is reduced in the  $n^+-p$  sample compared to either a  $p^+-p$  or a bulk  $p$ -type specimen. The electrical profiles showed a factor of 2 less acceptor removal in the  $n^+-p$  sample, and a shallower deactivation distance compared to either the  $p^+-p$  or  $p$  material. This retardation of D diffusion cannot be explained by differing amounts of residual implant damage in the  $n^+-p$  or  $p^+-p$  samples. Our implant and annealing conditions were chosen to create a highly doped essentially defect-free layer.<sup>17,18</sup> Similar retardation by  $n$ -type doping on deuterium diffusion is seen by comparing the SIMS profiles from  $n^+-n$ ,  $n$ , and  $p^+-n$  samples in Fig. 5. Once again the donor deactivation was less efficient in the  $n^+-n$  sample, in good correlation with the SIMS data.

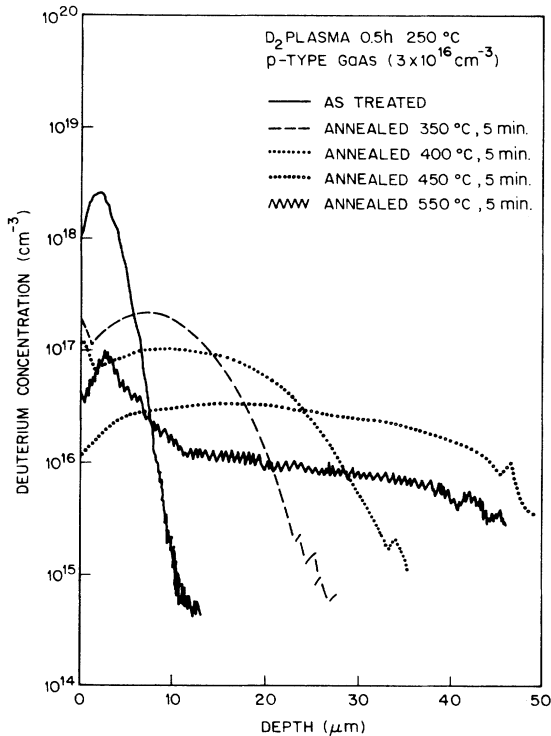


FIG. 3. SIMS depth profiles of deuterium in Zn-doped GaAs ( $p = 3 \times 10^{16} \text{ cm}^{-3}$ ), deuterated at  $250^\circ\text{C}$  for 30 min, as a function of annealing temperature for 5 min treatments.

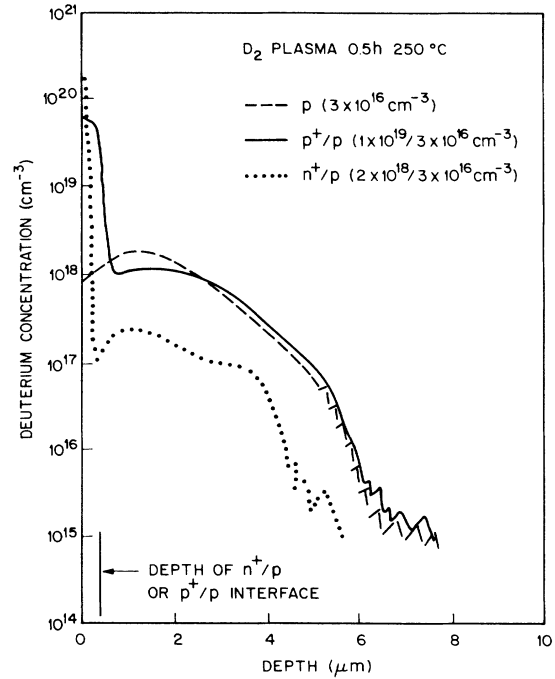


FIG. 4. SIMS depth profiles of deuterium in  $p$ -type GaAs (Zn doped,  $3 \times 10^{16} \text{ cm}^{-3}$ ) with a thin  $p^+$  or  $n^+$  surface layer exposed to a  $\text{D}_2$  plasma for 30 min at  $250^\circ\text{C}$ , and then cooled under molecular deuterium. The near surface features are similar to those in Fig. 5.

We therefore make the following observations.

(1) While deuterium diffuses rapidly in both  $n$ - and  $p$ -type GaAs passivating the electrical activity of both donors and acceptors, the diffusivity at  $250^\circ\text{C}$  is faster by approximately a factor of 3 in  $p$ -GaAs under our experimental conditions.

(2) The diffusion of D under our plasma conditions is enhanced by increased levels of acceptor doping, whilst being retarded for increased donor doping.

(3) D diffusion is inhibited and the degree of acceptor (donor) passivation decreases when a thin  $n^+$  region is present at the surface of  $p$  ( $n$ ) material.

These observations are similar to those seen for hydrogen incorporation in Si, and can be explained by hydrogen having a donor level in the upper half of the GaAs band gap. In analogy with the explanation of the diffusion and passivation behavior of H in Si by Pantelides,<sup>5</sup> in  $n$ -type GaAs the H is neutral and readily forms  $\text{H}_2$ , which is nonreactive and less mobile than the atomic species. The diffusion coefficient of hydrogen for two-species motion can be represented by<sup>19</sup>

$$D_{\text{eff}} = \frac{[\text{H}]}{C_{\text{tot}}(\text{H})} D_{\text{H}}, \quad (2)$$

where

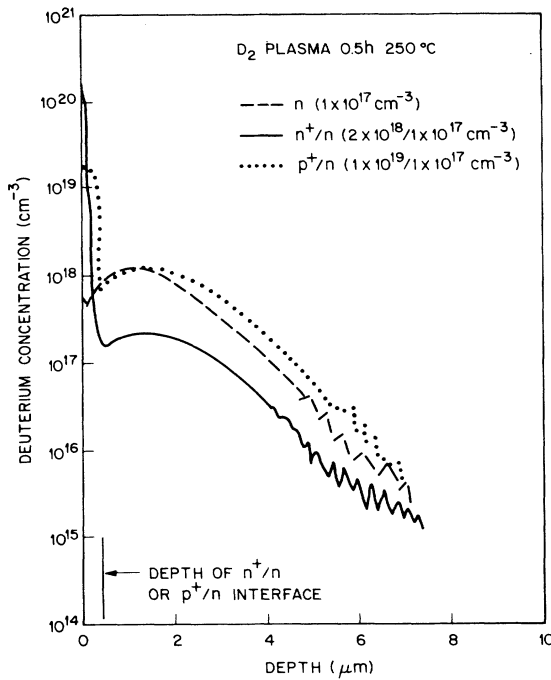
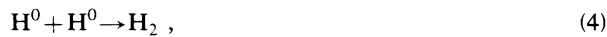


FIG. 5. SIMS depth profiles of deuterium in  $n$ -type GaAs (Si doped,  $1 \times 10^{17} \text{ cm}^{-3}$ ) with a thin  $n^+$  or  $p^+$  surface layer exposed to a  $\text{D}_2$  plasma for 30 min at  $250^\circ\text{C}$ . In these samples the plasma was extinguished after 30 min, and the samples cooled in molecular deuterium. This results in a smaller incorporation depth than in samples cooled in the plasma (Figs. 1 and 2). The near surface features are consistent with acceptor passivation in the  $p^+$ - $n$  sample, and  $\text{D}_2$  molecule formation in the  $n^+$ - $n$  sample.

$$C_{\text{tot}}(\text{H}) = [\text{H}] + 2[\text{H}_2], \quad (3)$$

where  $C_{\text{tot}}(\text{H})$  is the total hydrogen concentration, being the sum of the atomic  $[\text{H}]$  and molecular  $[\text{H}_2]$  concentrations, and  $D_{\text{H}}$  is the diffusivity of atomic hydrogen. Thus an  $n$  layer on  $p$ -type GaAs will lead to a slower effective diffusivity for hydrogen by allowing a relatively greater formation of  $\text{H}_2$ .

In  $n$ -type material the two dominant reactions will then be



This applies equally well for the other donor species.

The exact experimental conditions will determine the relative importance of these reaction pathways, leading to a result varying from near complete donor passivation to a very small degree of passivation, as observed.

By contrast in  $p$ -type GaAs the hydrogen will always be present as  $\text{H}^+$  ( $\text{H}^0 + \text{h}^+ \rightarrow \text{H}^+$ ), inhibiting the formation of molecules because of the Coulombic repulsion involved, and leading to a faster diffusivity than in  $n$ -type

material. At plasma exposure temperatures of  $200^\circ\text{C}$  and lower there is essentially complete compensation of acceptors by an ion pairing reaction



where  $A$  is  $\text{Zn}_{\text{Ga}}$ ,  $\text{Cd}_{\text{Ga}}$ ,  $\text{Be}_{\text{Ga}}$ , or  $\text{Mg}_{\text{Ga}}$ . As pointed out by Pantelides<sup>5</sup> the passivation reaction, with formation of the neutral complex, follows the initial compensation of the acceptor by the hydrogen donor because of the Coulombic attraction of the two species. At temperatures above  $200^\circ\text{C}$  the compensation is unstable,<sup>4</sup> and rapid diffusion of the hydrogen can occur as  $\text{H}^+$ . The higher diffusion depth at  $250^\circ\text{C}$  in samples of higher acceptor doping levels is a result both of this instability and of the inhibition of molecule formation, and the fact that more deuterium was incorporated initially because of the higher number of available bonding sites (acceptors).

More direct evidence for the dopant deactivation mechanisms in GaAs is lacking for a number of reasons. Firstly, identification of infrared absorption or photoluminescence lines related to hydrogen in GaAs is much more difficult than in Si, where a large body of knowledge existed from the  $\alpha$ -Si(H) area. Secondly, the maximum  $n$ -type doping level in GaAs is limited to  $\leq 10^{19} \text{ cm}^{-3}$  so that IR measurements looking for isotope shifts in deuterated and hydrogenated material will suffer from a lack of adequate signal. Thirdly, bias annealing experiments to monitor unidirectional drift of hydrogen in GaAs under the action of an electric field in a Schottky diode structure by measurement of the carrier concentration profile would need to be performed at quite high temperatures ( $\sim 200^\circ\text{C}$ ) in GaAs compared to those in Si ( $\sim 80^\circ\text{C}$ ), because of the considerably greater thermal stability of hydrogenated dopants in GaAs. Variation with time of the Schottky contacts on such samples could be a concern. The present evidence suggests that in  $n$ -type GaAs, hydrogen attaches to the donor ion forming a bond,<sup>1,2</sup> whereas in  $p$ -type GaAs the hydrogen may form an As—H bond.<sup>4</sup>

In summary, we demonstrate a strong dependence of the diffusivity of deuterium at fixed temperature and plasma conditions in GaAs on the doping type and concentration in the material. The results can be explained by hydrogen having a donor level in the upper half of the band gap of GaAs, as is postulated for hydrogen in Si.<sup>5,7</sup> The chemical reaction between deuterium and donors or acceptors is dependent on the charge state of the deuterium (postulated to be neutral in  $n$ -type GaAs and positively charged in  $p$ -type GaAs), leading to donor passivation and acceptor compensation which may also lead to acceptor passivation.

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- <sup>16</sup>It is worth noting that no direct observation has ever been made of hydrogen or deuterium molecules. In fact there is evidence that argues against isolated molecule formation [see B. Bech Nielsen, *Mat. Res. Soc. Symp. Proc.* **59**, 487 (1986)]. The more general form of precipitated or clustered hydrogen or deuterium may be platelets, observed in GaAs [J. H. Neethling and H. C. Snyman, *Radiat. Eff. Lett.* **76**, 163 (1983)] and Si [N. M. Johnson, F. A. Ponce, R. A. Street, and R. J. Nemanich, *Phys. Rev. B* **35**, 4166 (1987)]. We use the representation of molecule formation in this paper as a convenient description of the coalescence of atoms to form stable clusters. In reality, the clusters will be of varying sizes and molecules are their simplest form.
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