

## Passivation and thermal reactivation of Mg acceptors in *p*-type GaAs

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This paper reports on the efficient passivation of Mg-doped GaAs. The extent of the passivation was demonstrated to be highly temperature dependent, with the passivation being even more efficient than that of Zn-doped GaAs at temperatures below 140 °C. By performing reverse bias annealing measurements between 60 and 130 °C, we observed the reactivation of the Mg acceptors within the high-field region of the Schottky diode. This reactivation was found to obey first-order kinetics, with a dissociation energy  $E_{\text{MgH}} = (0.90 \pm 0.03)$  eV and an attempt frequency  $\nu_0 = (3_{-2}^{+5}) \times 10^8$  s<sup>-1</sup>. These results suggest that the Mg-H configuration is not bond centered, as also suggested by previous infrared absorption studies.

It has been demonstrated in the past that the exposure of GaAs to a hydrogen plasma results in the neutralization of both shallow acceptors (e.g., Zn, Be, and Cd) and shallow donors (e.g., Si and Se). In the case of *p*-type material, passivation of the acceptor atoms results from the capture of free holes by the hydrogen atoms, followed by the formation of neutral acceptor-hydrogen complexes. Compared to other group-II acceptors, magnesium has received significantly less attention. This is partly attributed to the notion that GaAs:Mg is only mildly passivated by hydrogen.<sup>1,2</sup> The main contributions to understanding the properties of the Mg-hydrogen complex have come from infrared absorption spectroscopy.<sup>2,3</sup> The absorption line observed at 2 144.01 cm<sup>-1</sup> in hydrogenated GaAs:Mg was initially ascribed to the presence of interstitial As-hydrogen entities.<sup>2</sup> From a comparative study with hydrogenated InP:Mg and GaAs:Mg, however, it was subsequently suggested that the absorption line is related to Mg passivation by the formation of a Mg-H center.<sup>3</sup> Although the experimental evidence ruled out a bond-centered (BC) configuration, the exact configuration could not be resolved.

Although Mg is generally not used as a dopant in bulk grown GaAs, it is a widely used implantation source for device manufacturing. Since hydrogen is incorporated during many of the processing procedures, the effect it has on the electrical properties of Mg needs to be well understood. Infrared absorption measurements of acceptor-hydrogen complexes also require the passivation of a high concentration of the acceptors in the material. The effectiveness by which Mg is passivated, as well as the stability of the Mg-H complex, are therefore important considerations. An important parameter describing its stability is the dissociation energy of the complex. As a result of the perception that Mg passivation is only very moderate, this parameter has not yet been obtained. This paper addresses these issues by demonstrating the efficient passivation of Mg under the appropriate conditions, and by extracting the dissociation energy using thermal reactivation measurements.

Mg-doped ( $p = 5.3 \times 10^{16}$  cm<sup>-3</sup>) epilayers were grown by metalorganic vapor phase epitaxy on *p*<sup>+</sup>-type GaAs, orientated 2° off the (100). Since very little is known of the passivation behavior of Mg, the passivation study was simultaneously performed on both Mg-doped, as well as on the

better understood Zn-doped ( $p = 6.3 \times 10^{16}$  cm<sup>-3</sup>) GaAs. Epilayers in which *no* dopants were intentionally introduced had a donor concentration of  $4 \times 10^{14}$  cm<sup>-3</sup>, with little *p*-type impurity compensation. The Mg precursor used, bis-(cyclopentadienyl)magnesium, has also been established to decompose cleanly, with hardly any impurity compensation.<sup>4,5</sup> Any carbon incorporation is therefore considered to be negligible. Schottky diodes (50 nm thick) were formed by electron beam evaporation of ruthenium onto the surface of the material. These contacts were simultaneously fabricated on both Mg- and Zn-doped materials and displayed identical electrical characteristics. Details of the Ru contact characteristics and thermal stability have been reported elsewhere.<sup>6</sup>

The GaAs layers were hydrogenated by exposing the Schottky diodes to a dc hydrogen plasma,<sup>6,7</sup> with a plate voltage of 600 V. This alternative approach of hydrogenating the material through the Ru contacts, instead of exposing the GaAs surface directly to the plasma, has several advantages: first, the metal film reduces near-surface damage that could impede the reactivation of Mg-H complexes, and second, the built-in field of the Schottky diode reduces the accumulation of near-surface hydrogen by causing field-assisted drift of positively charged hydrogen species away from the surface during hydrogenation. The samples were placed on a heater block 10 cm downstream from the plasma for 2–4 h, and were biased –100 V relative to the plasma. The hydrogen pressure was maintained at 0.5 mbar and the sample temperatures ranged between 60–140 °C. The hole concentrations in the epilayers were profiled at room temperature using a standard 1-MHz capacitance-voltage measuring technique. All anneals were performed in the dark at a temperature  $T_a$ , with a reverse bias applied to the Schottky diode. After an annealing period  $t_a$ , the samples were rapidly cooled by immersing the sample holder into liquid nitrogen, while still maintaining the reverse bias.

Figure 1 shows the active acceptor concentration profiles following the exposure of the layers to the hydrogen plasma at 60, 100, and 140 °C. A clear decrease in the carrier concentration is observed for both doping types. This reduction is attributed to the passivation of the shallow acceptors by the formation of neutral Mg-H and Zn-H complexes. The extent of the passivation differs between the two materials:

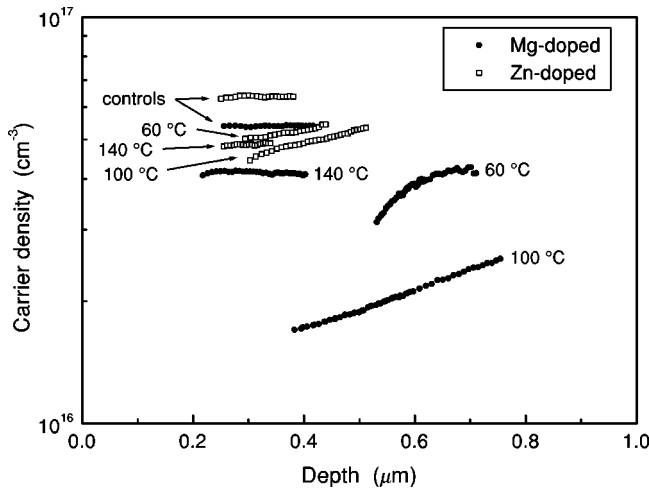


FIG. 1. Active acceptor concentrations in hydrogenated Mg and Zn-doped GaAs after exposure to a dc plasma for 2 h at different temperatures.

When hydrogenated at 100 °C, the carrier density of GaAs:Mg reduced by roughly 70%, as compared to 20% for GaAs:Zn. The overall degree of passivation also decreased with increasing temperature. This is believed to result from an increase in the hydrogen diffusion length, which causes the distribution of hydrogen over a larger volume. The relative extent of passivation between the two dopants also became less prominent with an increase in temperature, with the layers hydrogenated at 140 °C showing a similar reduction in carrier density.

The effect of annealing a passivated GaAs:Mg epilayer, while a reverse bias is applied to the Schottky diode, is illustrated in Fig. 2. After hydrogenation, the shallow acceptor concentration was reduced to roughly  $1.3 \times 10^{16} \text{ cm}^{-3}$  at a depth of 0.4  $\mu\text{m}$ . The acceptor distributions following a series of isothermal anneals at 115 °C, with a reverse bias of 4 V applied to the Schottky diode, are shown in Fig. 2. In the region  $x < 0.43 \mu\text{m}$  of the space-charge region, the Mg acceptors became progressively more reactivated. This was accompanied by a simultaneous deactivation of Mg acceptors

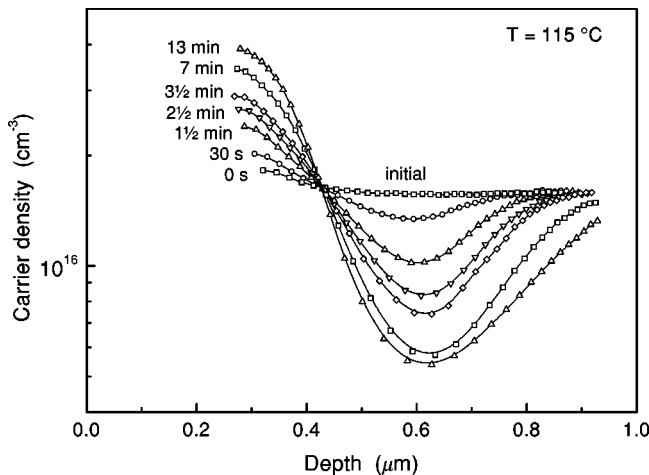


FIG. 2. Active magnesium concentration profiles after 4-V reverse bias anneals of a hydrogenated GaAs sample at 115 °C for different annealing times  $t_a$ .

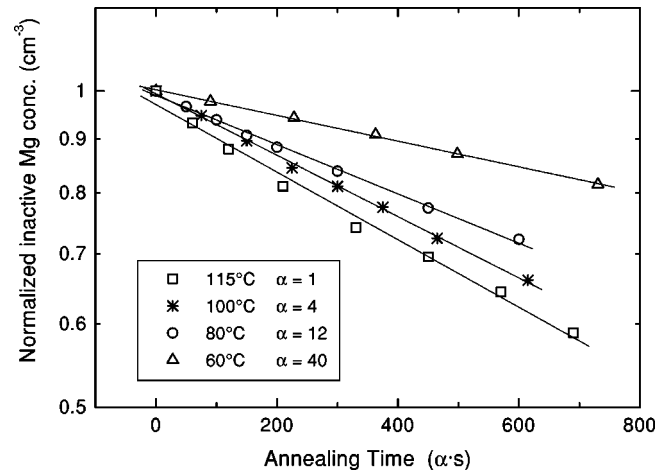


FIG. 3. Inactive Mg concentration in the high-field region versus annealing time. The annealing times are adjusted by a factor  $\alpha$  to accommodate for the large time differences.

deeper into the material ( $0.43 \mu\text{m} < x < 1 \mu\text{m}$ ). This result is similar to what has been reported for other acceptor dopants and can be explained as follows: annealing hydrogenated GaAs:Mg at elevated temperatures results in the dissociation of Mg-H complexes according to the equation  $(\text{MgH})^0 \rightleftharpoons \text{Mg}^- + \text{H}^+$ . The released hydrogen is positively charged and hence undergoes field-assisted drift deeper into the material, where it recombines to form new Mg-H complexes, thereby reducing the carrier concentration. The atomic H concentration is consequently low within the high-field region due to this drift. The above reaction therefore predominantly occurs to the right.

Assuming the room-temperature concentration of  $\text{H}^+$  is negligible compared to the Mg-H concentration, the electrically active Mg distribution, following an annealing period  $t_a$ , can be approximated by the measured hole concentration  $N_A(t_a)$  in the GaAs. The rate of hydrogen capture by electrically active Mg acceptors and the dissociation of the Mg-H complexes is described by

$$\frac{\partial[\text{MgH}]}{\partial t} = \sigma_{\text{MgH}}(p - [\text{MgH}])[\text{H}^+] - \nu_{\text{MgH}}[\text{MgH}], \quad (1)$$

where  $\sigma_{\text{MgH}}$  is the capture rate of  $\text{H}^+$  by  $\text{Mg}^-$  and  $\nu_{\text{MgH}}$  is the dissociation frequency of the Mg-H complexes.  $[\text{H}^+]$  and  $[\text{MgH}]$  denote the concentration of free-atomic hydrogen and Mg-H complexes, respectively. If the electric field is sufficiently high to suppress the recapture of hydrogen within the space-charge region, then the term  $\nu_{\text{MgH}}[\text{MgH}]$  will dominate in Eq. (1). As a result, the dissociation of the Mg-H complexes is predicted to obey first-order kinetics. An expression for such a first-order reactivation process is described by  $I(t_a) = I(t_a = 0) \exp[-\nu_{\text{MgH}}(T_a)t_a]$ , where  $I(t_a)$  is the concentration of electrically inactive Mg acceptors (at a specified depth) after an anneal period. In order to verify this prediction, the inactive Mg concentration  $I(t_a) = p - N_A(t_a)$  is plotted versus the isothermal annealing time. Since the linear fit shown in Fig. 3, obtained for  $T_a = 115 \text{ °C}$  at a depth of 0.34  $\mu\text{m}$ , corroborates the first-order reactivation of the Mg-H complexes, a dissociation frequency  $\nu_{\text{MgH}}(115 \text{ °C}) = (7.5 \pm 0.9) \times 10^{-4} \text{ s}^{-1}$  can be obtained. The reactivation

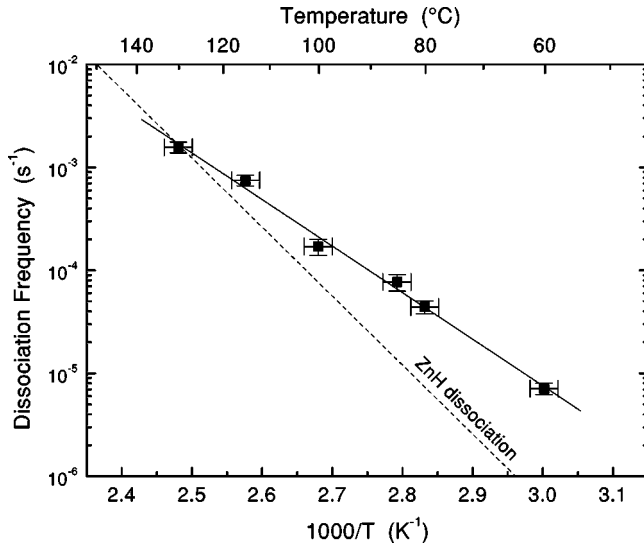


FIG. 4. Arrhenius plot of the measured dissociation frequencies of the Mg-H complex. The solid line represents the fit of the equation  $\nu_{\text{MgH}} = \nu_0 \exp(-E_{\text{MgH}}/kT)$  to the data, with  $\nu_0 = (3_{-2}^{+5}) \times 10^8 \text{ s}^{-1}$  and  $E_{\text{MgH}} = (0.90 \pm 0.03) \text{ eV}$ . The broken line, which represents the dissociation frequencies for the Zn-H complex (Ref. 10), has been included for comparison.

measurements were performed in a similar manner for various temperatures in the range 60–130 °C. For the sake of clarity, only the time dependencies of the reactivation experiments corresponding to  $T_a = 60, 80, 100,$  and  $115 \text{ °C}$  are illustrated in Fig. 3. The plots have been normalized relative to the initial inactive Mg concentration of each of the reactivation experiments. The annealing times have also been adjusted by a factor  $\alpha$  to accommodate for the large time differences.

The reactivation kinetics was seen to deviate from first order after long anneal times (not shown in Fig. 3). This has previously been attributed by Zundel and Weber<sup>8</sup> to the build-up of hydrogen at the edge of the space-charge region. The saturation of available acceptor trapping centers then impedes the drift of hydrogen away from the high-field region. The resulting increase in  $[\text{H}^+]$ , together with the increased availability of electrically active Mg acceptors within the space-charge region, consequently causes the capture term in Eq. (1) to become significant. The study by Zundel and Weber also revealed that the annealing time available for first-order reactivation was higher for acceptors with a larger dissociation energy. This was attributed to the slower release of hydrogen, accompanied with an unchanged hydrogen drift. Reactivation measurements were consequently obtained for limited anneal periods ( $\sim 1/\nu_{\text{MgH}}$ ). The Arrhenius plot of the dissociation frequencies  $\nu_{\text{MgH}}(T_a)$  is shown in Fig. 4. The Arrhenius plot representing the dissociation of the Zn-H complex,<sup>10</sup> with its dissociation energy of 1.33 eV and attempt frequency of  $7 \times 10^{13} \text{ s}^{-1}$ , has been included for comparison. The horizontal and vertical error bars represent a 3 °C and  $5 \times 10^{15} \text{ cm}^{-3}$  uncertainty in  $T_a$  and  $N_{A0}$ , respectively. The values satisfy the equation  $\nu_{\text{MgH}}(T_a) = \nu_0 \exp(-E_{\text{MgH}}/kT_a)$ , with a dissociation energy  $E_{\text{MgH}} = (0.90 \pm 0.03) \text{ eV}$  and an attempt frequency  $\nu_0 = (3_{-2}^{+5}) \times 10^8 \text{ s}^{-1}$ .

Table I lists the known dissociation energies and attempt

TABLE I. Dissociation energies  $E_D$  and attempt frequencies  $\nu_0$  of the different group-II acceptors in GaAs.

Dopant	$E_D$ (eV)	$\nu_0$ ( $\text{s}^{-1}$ )	Reference
$\text{Mg}_{\text{Ga}}$	$(0.90 \pm 0.03)$	$3 \times 10^8$	This work
$\text{Be}_{\text{Ga}}$	$(1.15 \pm 0.10)$	$1.5 \times 10^{13}$	Ref. 11
$\text{Cd}_{\text{Ga}}$	$(1.35 \pm 0.10)$	$10^{13}$	Ref. 12
$\text{Zn}_{\text{Ga}}$	$(1.33 \pm 0.03)$	$7 \times 10^{13}$	Ref. 10

frequencies of Mg and other group-II acceptor-H complexes in GaAs. The dissociation energy of the Mg-H complex is significantly lower than what has been reported for any of the other acceptors. The measured dissociation energy is composed of the binding energy of the acceptor-H complex, plus the migration energy required to remove the H atom beyond the capture radius of the acceptor atom. If it is assumed that the diffusion path of H is independent of the acceptor properties, then the 0.58-eV migration energy obtained by Rahbi *et al.*<sup>9</sup> should have the same contribution to the different group-II acceptor-H dissociation energies. The binding energy of the Mg-H complex is therefore determined to be roughly half that of the other acceptor-H complexes where H resides in the BC position.

The Mg-H dissociation frequency is also seen to exceed that of Zn-H for temperatures below 130 °C, and to be a lower value for higher temperatures. This convergence of the dissociation frequencies of Mg-H and Zn-H can therefore explain the observed passivation results: the larger passivation depth of GaAs:Mg hydrogenated at 60 °C, as compared to that of hydrogenated GaAs:Zn, is possibly due to a larger  $\text{H}^+$  diffusion length. If the  $\text{H}^+$  diffusion is purely controlled by the association and dissociation processes, then a larger dissociation frequency would result in an increase in the diffusion length.<sup>7</sup> The similar passivation of Mg- and Zn-doped GaAs at 140 °C can then be attributed to the similarity of their dissociation frequencies at the same temperature. A study of GaAs:Mg by Rahbi *et al.*<sup>2</sup> showed negligible interaction between deuterium atoms and Mg acceptors when hydrogenated at 150 and 170 °C. Although the thermal reactivation results from this present study give no clear indication of the capture efficiency of the Mg atoms, the passivation results suggest a lowering in interaction between H and Mg with increasing temperatures.

The lower stability of the Mg-H complex was also observed in a photoluminescence study by Szafranek and Stillman,<sup>13</sup> which showed that the susceptibility of the Mg-H complex to light-induced reactivation far exceeded that of other acceptor-hydrogen pairs.

The dissociation attempt frequency  $\nu_0$  is also seen to be five orders of magnitude lower than what is typically observed for other group-II acceptor-hydrogen pairs (Table I), which have prefactors in the order of the lattice-phonon vibration frequencies ( $\sim 10^{13} \text{ s}^{-1}$ ). This, together with the low dissociation energy (binding energy), suggest that the bonding configuration of the Mg-H complex differs from the conventional configuration, where the H atom is bond-centered between the acceptor and the group-V atom. First-principles calculations of the Mg-H center predicted the BC and antibonding site to have similar stabilities.<sup>3</sup> Although the bond-centered configuration has been ruled out experimen-

tally on the basis of its local vibrational mode,<sup>3</sup> the Mg-H centers could exist where H is antibonded.

In conclusion, we have shown that Mg-doped GaAs can be passivated by the introduction of hydrogen with a dc plasma system. The efficiency by which the Mg acceptors are neutralized was also shown to be highly temperature dependent, with the efficiency decreasing with increasing passivation temperatures. For temperatures below 140 °C, the extent of Mg passivation was in fact found to be greater than that of GaAs:Zn. Thermal reactivation measurements also

confirmed the positive charge state of hydrogen in GaAs:Mg, with the dissociation energy and dissociation attempt frequency of the Mg-H complex found to be  $(0.90 \pm 0.03)$  eV and  $(3_{-2}^{+5}) \times 10^8$  s<sup>-1</sup>, respectively. The contrast between these values and that of other group-II acceptors suggests that the Mg-H configuration is not bond centered, as is the case for other group-II acceptor-H complexes in GaAs.

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