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# Trap-limited diffusion of hydrogen in Zn-doped GaAs

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An effective diffusion coefficient $D_{\rm eff}$ for hydrogen in zinc-doped GaAs is accurately determined within the temperature range 90–150 °C and for doping levels of $N_A = 3.4\times10^{16}\ \mathrm{cm}^{-3}$ and $N_A = 2.6\times10^{17}\ \mathrm{cm}^{-3}$. The effective diffusion coefficients are measured directly from the profiles and satisfy the Arrhenius equation $N_A D_{\rm eff} = P_o \exp(-E_P/kT)$, where $E_P = (1.36\pm0.04)$ eV and $P_o = (8^{+24}_{-2})\times10^{20}\ \mathrm{cm}^{-1}/\mathrm{s}$. The measured activation energy $E_P = (1.36\pm0.04)$ eV is found to be closely matched to previously determined values for the dissociation energy of the zinc-hydrogen complex, while $D_{\rm eff}$ is inversely proportional to the acceptor concentration. The values of $D_{\rm eff}$ consequently display the same temperature dependence as the zinc-hydrogen dissociation kinetics. The diffusion process, under the experimental conditions of this study ($T < 150\,^\circ\mathrm{C}$, $N_A > 2\times10^{15}\ \mathrm{cm}^{-3}$), is found to be controlled entirely by the association and dissociation processes of hydrogen with the zinc atoms and to be independent of the intrinsic diffusivity of hydrogen in the GaAs layers. [S0163-1829(99)11627-8]

## I. INTRODUCTION

An understanding of the migration of hydrogen in crystalline semiconductors is a challenging problem. Atomic hydrogen is affected by various effects during its motion through the lattice, such as interconversion between the monatomic charge states[1] $\mathrm{H}^+$, $\mathrm{H}^o$, and $\mathrm{H}^-$, trapping by immobile impurities and lattice defects,[1,2] and hydrogen-hydrogen interaction,[2] such as molecular hydrogen ($\mathrm{H}_2$) and dimer ($\mathrm{H}_2^*$) formation.[3]

The most commonly used technique for investigating the diffusion behavior of hydrogen has been secondary ion mass spectrometry (SIMS). This technique yields the hydrogen distribution directly and has the advantage of providing the total hydrogen concentration. However, due to the large background signal, SIMS is only feasible for relatively large hydrogen concentrations. The indirect technique of capacitance-voltage ($C$-$V$) measurements provides the charge density of the ionized dopants within the depletion region of a reverse biased Schottky barrier diode. The reduction in charge density is then related to the amount of dopants neutralized by the formation of dopant-hydrogen complexes.[4–6] Diffusion profiles are generally obtained by exposing the samples to a hydrogen/deuterium plasma (or a proton beam) and monitoring the introduction (or redistribution) as a function of time and temperature.[7,8]

An important parameter used to describe the migration of hydrogen (or any impurity) in a semiconductor, in the absence of trapping centers, is the intrinsic diffusion coefficient $D_i$. High-temperature diffusion experiments[9] and computer simulation studies[10,11] have shown $D_i$ to display an Arrhenius temperature dependence

$$D_i = D_{io} \exp\left[\frac{-E_m}{kT}\right], \tag{1}$$

where $E_m$ is the migration activation energy required for the hydrogen atom to leave its equilibrium lattice site. The prefactor $D_{io}$, also called the diffusion constant, depends on entropy effects. A review of available diffusion studies on silicon and GaAs suggests that the values reported for $D_i$ are only ''apparent'' values, instead of the true intrinsic value. This deviation from $D_i$ stems from a diffusion model used to extract $D_i$ not fully incorporating all aspects of the diffusion process. Excluding experimental factors that influence diffusion will therefore result in $D_i$ showing a dependence on these factors, which in turn could vary from one diffusion study to the next. The reliability of a reported diffusion coefficient should therefore be rated by the number of factors influencing the diffusion process and how well the diffusion model takes them into account.

In many cases, however, an effective diffusion coefficient $D_{\rm eff}$ is produced by applying the standard (Fickian) diffusion model to the hydrogen profiles. The profiles, which are usually hydrogen passivation[12] or redistribution[13,14] profiles, are fitted either by an error function or the measured diffusion depth $L$ inserted into the expression $D_{\rm eff} = L^2/t$. Since the standard diffusion model excludes hydrogen interaction effects, the resulting values are expected to have a dependence on the density of trapping sites within the material and the dissociation energies of the defect-hydrogen complexes. This appears to be the case when studying the redistribution profiles of post-implanted deuterium in $n$-GaAs:Si,[13] which provided an effective diffusion coefficient expressed by an Arrhenius equation with an activation energy $E_{m\ \rm eff} = 1.43$ eV and a prefactor $D_{o\ \rm eff} = 90\ \mathrm{cm}^2/\mathrm{s}$. The similarity of the activation energy and the silicon-hydrogen dissociation energy of (1.25±0.05) eV (Ref. 4) suggests that dopant-hydrogen interaction could be involved in the diffusion process. The same is noticed for diffusion studies on deuterium plasma exposed $n$-GaAs:Si,[12] which yielded an activation energy of 1.38 eV by fitting the complementary error function to the deuterium profiles. Although the measured activation energies are explained by the dissociation energy of the Si-H complex, no clear relationship has been established for the prefactor $D_{o\ \rm eff}$ in GaAs.

To extract the intrinsic diffusion coefficient from the class of diffusion studies in which the hydrogen profiles are dependent on the conditions by which the hydrogen is introduced requires complex diffusion models to take factors such as the interaction of hydrogen with itself and defects introduced during hydrogenation, variations in the surface hydrogen concentration, as well as the built-in electric field, into account. Although the hydrogen distribution profiles are usually simulated well by the model used, the large number of parameters required could prevent the solution from being unique.

The majority of diffusion studies on GaAs used SIMS to profile the migration of hydrogen. This is, however, the first diffusion study to our knowledge on *p*-type GaAs that utilizes the neutralizing property of hydrogen to obtain diffusion profiles. In this work, the effective diffusion coefficient is accurately determined for zinc-doped GaAs by performing the diffusion study independently from the passivation procedure. This is achieved by employing the ability of the charged hydrogen species to undergo field-assisted drift, in order to produce a hydrogen gradient within the bulk of the samples. This is then used as a starting position from which to initiate the diffusion of hydrogen back towards the surface. The ability of hydrogen to neutralize acceptors is used to determine the hydrogen distribution from $C$-$V$ measurements of the free-carrier distribution. This technique has the advantage of using a relatively small hydrogen concentration, as compared to that required by SIMS. The formation of molecular hydrogen is hence minimized and the built-in field at the passivation edge reduced. The influence of defect centers formed during hydrogenation is also eliminated by obtaining the diffusion profiles within the bulk of the layers. The diffusion model used describes the diffusion process fully using only three parameters. The initial conditions of the model are also simple and well defined.

A previous study by Zundel and Weber,[6] which applied this technique to boron-doped silicon, revealed the diffusion process to be independent of the intrinsic diffusion coefficient $D_i$ and entirely controlled by the trapping and detrapping of hydrogen by the boron atoms. This technique has recently been used to demonstrate the trap-limit diffusion of lithium in *p*-type GaAs.[15] The present study is, however, believed to be the first report of the technique being used to study the diffusion of hydrogen in GaAs.

In Sec. II the sample preparation and experimental procedures are discussed. In Sec. III the measurement of the hydrogen profiles is described and $D_{\mathrm{eff}}$ is extracted in Sec. IV. The dependence of the diffusion process on temperature and zinc concentration is illustrated in Sec. V and discussed in Sec. VI.

## II. EXPERIMENTAL DETAILS

Zinc-doped GaAs ($N_A = 3.4\times10^{16}$ cm$^{-3}$ and $N_A = 2.6\times10^{17}$ cm$^{-3}$) was grown by metalorganic vapor phase epitaxy (MOVPE) on $p^+$-GaAs, orientated 2° off the (100).

Initially the GaAs layers were hydrogenated by exposing the as-grown samples to a dc hydrogen plasma at a temperature of 60 °C for 1 h. Note that this passivation temperature is significantly lower than previously reported values.[7,16] Schottky diodes were then formed by electron beam evaporation of ruthenium onto the hydrogenated surface. The direct exposure of the samples to the H plasma resulted in a large hydrogen concentration up to a depth of ~0.5 μm, followed by a sudden decrease. This high concentration of hydrogen, together with the possible defects introduced during the exposure to the plasma,[17] impeded the reactivation of the zinc-hydrogen complexes within the near-surface region. This problem was overcome by hydrogenating the layers *after* fabricating the ruthenium contacts (400–450 Å thick). This approach resulted in an even distribution of neutralized acceptors, with the passivated region stretching deep into the layer. The electric field produced by the Schottky diode resulted in the positively charged hydrogen species undergoing field-assisted drift away from the surface during hydrogenation, thereby leaving the near-surface region less passivated. The efficient reactivation of these layers, compared to layers exposed directly to the plasma, suggested that the ruthenium overlayer minimized both surface damage and the accumulation of near-surface hydrogen observed for directly exposed layers.

Due to the annealing procedure utilized in this work, the Schottky diodes were required to remain functional after extended periods of reverse-bias annealing. Annealing experiments on ruthenium/$p$-GaAs Schottky barrier diodes revealed superior annealing properties and an improvement in barrier height upon hydrogenation.

The distribution of active acceptors $N_{\mathrm{act}}$ was measured using a standard capacitance-voltage ($C$-$V$) measuring technique. The total hydrogen concentration $[\mathrm{H}_T]$ was extracted from $N_{\mathrm{act}}$ using the approximation: $[\mathrm{H}_T]=[\mathrm{ZnH}]+[\mathrm{H}^+] = N_A - N_{\mathrm{act}} \simeq [\mathrm{ZnH}]$, where $[\mathrm{H}^+]$ and $[\mathrm{ZnH}]$ denote the concentration of free hydrogen and zinc-hydrogen complexes, respectively. The assumption that $[\mathrm{H}^+]$ is negligible compared to $[\mathrm{ZnH}]$ will be validated in Sec. VI.

All anneals were performed in the dark in air using a filament-heated quartz tube. The initial hydrogen distribution, from which the diffusion experiment is to be initiated, was produced by reverse-bias annealing the Schottky diode in two stages:[6] for the $N_A = 3.4\times10^{16}$ cm$^{-3}$ material, the first anneal was at ~150 °C for a period of 30 min, with the Schottky diode reverse-biased at 4 V. The initial step profile for the $N_A = 2.6\times10^{17}$ cm$^{-3}$ material was produced by 2.3 V reverse-bias annealing at 125 °C for 40 min. The lower required voltage is due to the smaller space-charge region of the higher doped material. This first anneal ensured the fast reactivation of the near-surface region, as well as an even distribution of neutralized acceptors that stretched deep into the bulk of the material. This was followed by a second anneal at the diffusion temperature $T_{\mathrm{diff}}$ for approximately 1 h. The second anneal at $T_{\mathrm{diff}}$ ensured that the temperature stabilized before the diffusion anneal was initiated. The diffusion experiment was initiated directly after the second anneal by terminating the bias to the Schottky diode. The sample was then annealed for a duration $t_{\mathrm{diff}}$, after which it was cooled rapidly to room temperature for the $C$-$V$ measurements, using liquid nitrogen. Before obtaining a diffusion profile for a different $t_{\mathrm{diff}}$, the sample was again two-step reverse-bias annealed to obtain another initial hydrogen distribution (The initial profiles were all closely matched.)

## III. DIFFUSION RESULTS

As a typical example, the diffusion of hydrogen at $T_{\mathrm{diff}} = 114$ °C in a $N_A = 3.4\times10^{16}$ cm$^{-3}$ sample is illustrated.

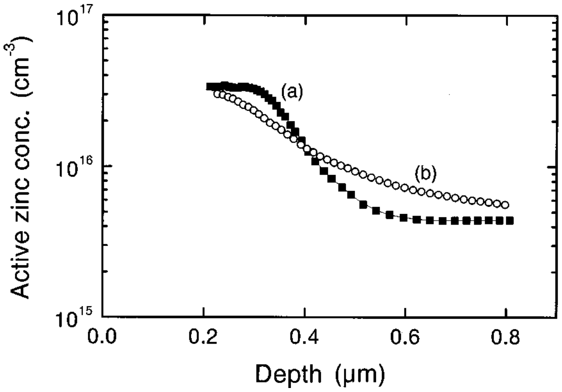

FIG. 1. Active zinc concentration $N_{\mathrm{act}}$ in hydrogenated Zn-doped GaAs, after (a) a two-step 4 V reverse-bias anneal and (b) a subsequent 40-min zero-bias anneal at 114 °C.

The *C-V* measurements on the hydrogenated layer showed a 98% neutralization of acceptors, stretching at least 3 $\mu$m into the layer. Figure 1(a) shows $N_{\mathrm{act}}$ following the reverse-bias anneals. The acceptors in the near-surface region ($x < 0.3$ $\mu$m) of the layer have been completely reactivated. This is followed by a sharp decrease in $N_{\mathrm{act}}$, which reaches an even distribution after 0.6 $\mu$m. This distribution is explained in the following way: positively charged hydrogen atoms resulting from the dissociation of zinc-hydrogen complexes undergo field-assisted drift from the high-field near-surface region of the Schottky diodes to the low-field region, where it recombines with zinc atoms at the edge of the space-charge region.

The acceptor distribution following the zero-bias anneal is shown in Fig. 1(b). The sharp initial acceptor profile has become smoothed, with $N_{\mathrm{act}}$ having decreased for $x < 0.4$ $\mu$m and increased for $x > 0.4$ $\mu$m.

Figure 2 shows the hydrogen distribution extracted from the active acceptor profiles for $t_{\mathrm{diff}} = 22$, 40, and 80 min. Note that the curves are only intended to show the general trends of the hydrogen profiles. The hydrogen concentration $[\mathrm{H}_T]$ progressively decreases for increasing anneal times in the region $x > 0.4$ $\mu$m, while a corresponding increase is evident in the region $x < 0.4$ $\mu$m.

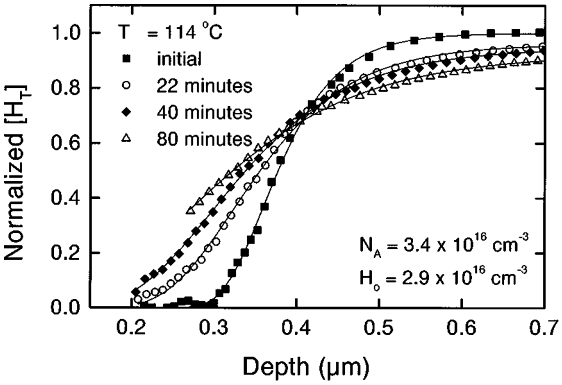

FIG. 2. Normalized hydrogen distribution in Zn-doped GaAs ($N_A = 3.4 \times 10^{16}$ cm$^{-3}$), after zero-bias annealing for various times at 114 °C. $H_o$ denotes the total hydrogen concentration for $x > 0.6$ $\mu$m. The curves are drawn as an aid to the eye for determining the trends of the data.

## IV. ANALYSIS

The redistribution of hydrogen shown in Fig. 2 is interpreted as follows: hydrogen atoms that have dissociated from the zinc atoms undergo random motion in the absence of an electric field. The concentration gradient, however, causes a net flux of hydrogen from the high concentration region to the low concentration region. The hydrogen impurity shows an amphoteric behavior by taking on three possible charge states,[3] $\mathrm{H}^+$, $\mathrm{H}^-$, and $\mathrm{H}^o$, with their relative concentrations dependent on the positions of the energy levels induced by the hydrogen impurity within the band gap. The efficient passivation and reactivation of acceptors, together with the existing uncertainty in the positions of the energy levels,[7,18] has led to the assumption that, within the Fermi-level range of this study, hydrogen predominantly exists in the positive charge state $\mathrm{H}^+$. This results in the dissociation-association reaction $\mathrm{H}^+ + \mathrm{Zn}^- \rightleftarrows (\mathrm{ZnH})^\circ$ being the dominant process influencing diffusion, while the formation of molecular hydrogen may be neglected. The free hydrogen concentration $[\mathrm{H}^+]$ is then described by the modified diffusion equation

$$\frac{\partial[\mathrm{H}^+]}{\partial t} = D_i^+ \frac{\partial^2[\mathrm{H}^+]}{\partial x^2} - \frac{\partial[\mathrm{ZnH}]}{\partial t}, \tag{2}$$

where $D_i^+$ is the intrinsic diffusion coefficient of $\mathrm{H}^+$ in GaAs. The term $\partial[\mathrm{ZnH}]/\partial t$ accounts for the association and dissociation of H atoms with the zinc acceptors and is represented by

$$\frac{\partial[\mathrm{ZnH}]}{\partial t} = \sigma_{\mathrm{ZnH}}(N_A - [\mathrm{ZnH}])[\mathrm{H}^+] - \nu_{\mathrm{ZnH}}[\mathrm{ZnH}], \tag{3}$$

where $\sigma_{\mathrm{ZnH}}$ is the capture rate of $\mathrm{H}^+$ by the acceptors and $\nu_{\mathrm{ZnH}}$ is the dissociation rate of the acceptor-hydrogen complex. The parameter $\sigma_{\mathrm{ZnH}}$ can be expressed in terms of the hydrogen diffusivity and the capture radius of the ionized zinc atom *R*, according to the relation $\sigma_{\mathrm{ZnH}} = 4\pi R D_i^+$. The dissociation frequency of the zinc-hydrogen complex is described by the Arrhenius equation

$$\nu_{\mathrm{ZnH}} = \nu_o \exp\left[\frac{-E_D}{kT}\right], \tag{4}$$

with the values $\nu_o = 7 \times 10^{13}$ s$^{-1}$ and $E_D = (1.33 \pm 0.03)$ eV having been determined previously by thermal reactivation studies.[19]

An analytical solution to Eqs. (2) and (3) provides an effective diffusion coefficient $D_{\mathrm{eff}}$, which is measured directly from the experimental diffusion profiles. Following the arguments of Zundel and Weber,[6] $D_{\mathrm{eff}}$ is represented by

$$D_{\mathrm{eff}} = \frac{\nu_{\mathrm{ZnH}}}{4\pi R N_A}, \tag{5}$$

which has *no* dependence on $D_i^+$, thus implying that the diffusion process is entirely controlled by the association-dissociation reactions.

The derivation of Eq. (5) is based on the assumptions that (i) the dissociation-association processes are in dynamic

TABLE I. The effective H diffusion coefficient $D_{\rm eff}$ calculated using Eq. (6). Total zinc concentration is $N_A = 3.4\times10^{16}$ cm$^{-3}$.

| $T_{\rm diff}$ (°C) | $D_{\rm eff}$ (cm$^2$/s) |
|---|---|
| 89 | $2.17\times10^{-15}$ |
| 114 | $(3.72\pm0.55)\times10^{-14}$ |
| 130 | $(2.01\pm0.71)\times10^{-13}$ |
| 148 | $(1.18\pm0.12)\times10^{-12}$ |

equilibrium throughout the diffusion process (i.e., $\partial[\mathrm{ZnH}]/\partial t \simeq 0$), that (ii) $\nu_{\rm ZnH} \gg \sigma_{\rm ZnH}[\mathrm{H}^+]$, and that (iii) $\sigma_{\rm ZnH} N_A/\nu_{\rm ZnH} \gg 1$. These assumptions are discussed in Sec. VI.

If the initial hydrogen distribution is approximated by a steplike distribution ($[\mathrm{H}_T]=0$ for $x<0.4$ $\mu$m and $[\mathrm{H}_T]=\mathrm{H}_o$ for $x>0.4$ $\mu$m), then the effective diffusion coefficient is given by[6]

$$D_{\rm eff} = \frac{1}{4\pi t}\,\frac{1}{[s(t)]^2}, \tag{6}$$

where $s(t)$ is the gradient of the normalized hydrogen profiles at $[\mathrm{H}_T] = \frac{1}{2}\mathrm{H}_o$. The measured profiles depicted in Fig. 2 are, however, asymmetric, with the curves crossing at $[\mathrm{H}_T] \sim 0.70$ $\mathrm{H}_o$. Measurement of $s(t)$ at the $\frac{1}{2}\mathrm{H}_o$ concentration will therefore be at smaller depths with respect to the initial hydrogen profile. The nearly linear dependence of $[\mathrm{H}_T]$ on $x$ in the range 0.3–0.45 $\mu$m will, however, result in $s(t)$ being insensitive to this change in position. By measuring the slope in this region for the different annealing times, a mean value for the effective diffusion coefficient of $D_{\rm eff} = (3.72\pm0.55)\times10^{-14}$ cm$^2$/s is determined. The displacement of the inflection point from $\frac{1}{2}\mathrm{H}_o$ is discussed in Sec. VI.

## V. DEPENDENCE OF THE DIFFUSION PROCESS ON THE TEMPERATURE AND ZINC CONCENTRATION

TABLE II. The effective H diffusion coefficient $D_{\rm eff}$ calculated using Eq. (6). Total zinc concentration is $N_A = 2.6\times10^{17}$ cm$^{-3}$.

| $T_{\rm diff}$ (°C) | $D_{\rm eff}$ (cm$^2$/s) |
|---|---|
| 100 | $(1.59\pm0.36)\times10^{-15}$ |
| 123 | $1.43\times10^{-14}$ |

Equation (5) predicts that $D_{\rm eff}$ is inversely proportional to the acceptor concentration $N_A$ and that the diffusion process obeys the same kinetics as the zinc-hydrogen complex. To obtain an activation energy, the diffusion experiment described above was repeated at 89 °C, 130 °C, and 148 °C. The resulting diffusion profiles were similar in shape, with the point of intersection remaining relatively unchanged. The values obtained for $D_{\rm eff}$ are given in Table I.

In order to ascertain whether the inverse dependence on $N_A$ is satisfied, the diffusion experiments were also performed on $N_A = 2.6\times10^{17}$ cm$^{-3}$ doped material. Exposing these samples to the H plasma resulted in an even neutralization of zinc acceptors which stretched $\sim1.5$ $\mu$m into the layer. The normalized diffusion profiles obtained by zero-bias annealing at 100 °C for 30 and 60 min are shown in Fig. 3. Although the profiles are also asymmetric, an approximately linear region exists for $x<0.12$ $\mu$m. From the slope, an effective diffusion coefficient of $D_{\rm eff} = (1.59\pm0.36)\times10^{-15}$ cm$^2$/s was calculated. A diffusion profile was also obtained at 123 °C by zero-bias annealing for 5 min. The results are summarized in Table II.

To show the inverse dependence of $D_{\rm eff}$ on $N_A$, the product $P = N_A D_{\rm eff}$ is plotted in Fig. 4 as a function of $1/T$ for $N_A = 3.4\times10^{16}$ cm$^{-3}$ (solid circles) and $N_A = 2.6\times10^{17}$ cm$^{-3}$ (open squares). It is evident that the values for $N_A D_{\rm eff}$ are well fitted by the Arrhenius equation $P = P_o \exp(-E_P/kT)$, with $P_o = (8^{+24}_{-2})\times10^{20}$ cm$^{-1}$/s and an activation energy $E_P = (1.36\pm0.04)$ eV. By substituting Eq. (4) into Eq. (5), $P$ is instead given by

$$P = \frac{\nu_o}{4\pi R}\exp\left[\frac{-E_D}{kT}\right]. \tag{7}$$

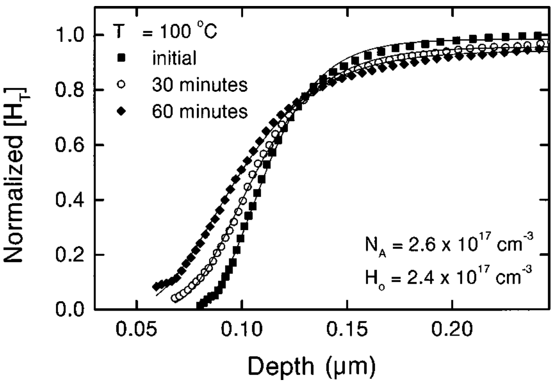

FIG. 3. Normalized hydrogen distribution in Zn-doped GaAs ($N_A = 2.6\times10^{17}$ cm$^{-3}$), after zero-bias annealing for various times at 100 °C. $H_o$ denotes the total hydrogen concentration for $x>0.2$ $\mu$m. The curves are drawn as an aid to the eye for determining the trends of the data.

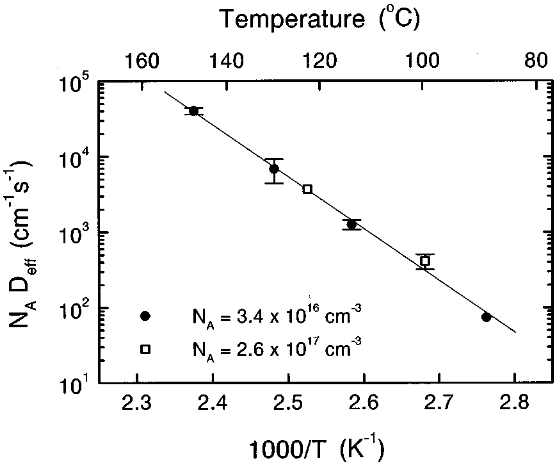

FIG. 4. Arrhenius plot of $P = N_A D_{\rm eff}$. The solid line represents the fit of the equation $P = P_o\exp(-E_P/kT)$ to the data, with $P_o = (8^{+24}_{-2})\times10^{20}$ cm$^{-1}$/s and $E_P = (1.36\pm0.04)$ eV.

Excellent agreement exists between the activation energy $E_P = (1.36 \pm 0.04)$ eV and the zinc-hydrogen dissociation energy of $E_D = (1.33 \pm 0.03)$ eV. Taking $R = 30$ Å (from the approximation $kT \simeq e^2/[4\pi\varepsilon_s R]$) and $\nu_o = 7\times10^{13}\ \mathrm{s}^{-1}$, the prefactor $\nu_o/(4\pi R) \simeq 2\times10^{19}\ \mathrm{cm}^{-1}/\mathrm{s}$ is calculated and found to compare reasonably well to the measured value $P_o = (8^{+24}_{-2})\times10^{20}\ \mathrm{cm}^{-1}/\mathrm{s}$.

## VI. DISCUSSION

The results have shown the effective diffusion coefficient $D_{\mathrm{eff}}$ to be accurately represented by Eq. (5). The inverse dependence on the acceptor concentration, together with the knowledge that the diffusion activation energy $E_P$ equals the zinc-hydrogen dissociation energy, strongly suggests that the diffusion process is entirely controlled by the dissociation and association of hydrogen with the zinc atoms. This is further supported by Eq. (5) being independent of the intrinsic diffusion coefficient. This independence on $D_i^+$ will be the case if the time that hydrogen is captured at a zinc atom significantly exceeds the time spent diffusing between nearest-neighboring zinc atoms.[6] The intrinsic diffusion coefficient will therefore only affect the solution to the diffusion equations [Eqs. (2) and (3)] if a significantly small value is substituted when attempting to solve the equations numerically, thereby implying a longer diffusion time between zinc atoms. Thus, if the diffusion process is entirely trap-limited, only a lower limit can be assigned to the intrinsic diffusion coefficient when trying to find a numerical solution. This is the case for the hydrogen diffusion study by Zundel and Weber[6] on boron-doped silicon.

The deviation of the measured inflection point from $\frac{1}{2}\mathrm{H}_o$ is believed to be a consequence of the asymmetry of the initial hydrogen profiles. This is thought to result from an increase in diffusion length as the hydrogen undergoes field-assisted drift (during reverse-bias anneal) towards the accumulation region. A larger step in the active zinc concentration will therefore produce a more notable change in the diffusion length, and hence a more asymmetric initial distribution. The $N_A = 3.4\times10^{16}\ \mathrm{cm}^{-3}$ material, which has a step in concentration of $2.9\times10^{16}\ \mathrm{cm}^{-3}$, has an inflection point of roughly 0.70 $\mathrm{H}_o$, whereas the $N_A = 2.6\times10^{17}\ \mathrm{cm}^{-3}$ material, which has a $2.4\times10^{17}\ \mathrm{cm}^{-3}$ step, has an inflection point at about 0.80 $\mathrm{H}_o$. The slightly smaller step of $2.1\times10^{16}\ \mathrm{cm}^{-3}$, reported by Zundel and Weber,[6] would therefore explain their measured inflection point of 0.57 $\mathrm{H}_o$. The relative change in the diffusion length ($\triangle L/L$) across the step in hydrogen concentration can be estimated, since the diffusion coefficient has been shown to be inversely proportional to the active zinc concentration. Hence, $L \propto N_A^{-1/2}$, which yields $\triangle L/L = [(N_A - \mathrm{H}_o)/N_A]^{-1/2} - 1$. The relationship between $\triangle L/L$ and the inflection point of this work, and that of Zundel and Weber,[6] is illustrated in Fig. 5. It is evident that smaller changes in hydrogen concentration are preferable in this kind of experiment, since it will result in a more symmetric initial profile, which will be approximated better by a perfect steplike distribution.

In order to find an analytical solution to the diffusion equations [Eqs. (2) and (3)], a few assumptions had to be made in Sec. IV. Assumption (i) has been verified by using Eqs. (2) and (3) to monitor the change in [ZnH] and [$\mathrm{H}^+$] over short time intervals. This numerical analysis revealed that the rate at which the acceptor-hydrogen concentration reached equilibrium significantly exceeded that of the diffusion process. This was observed for a large range of diffusivity and capture radius values. The association and dissociation processes, therefore, maintain the acceptor-hydrogen complex concentration at a dynamic equilibrium.

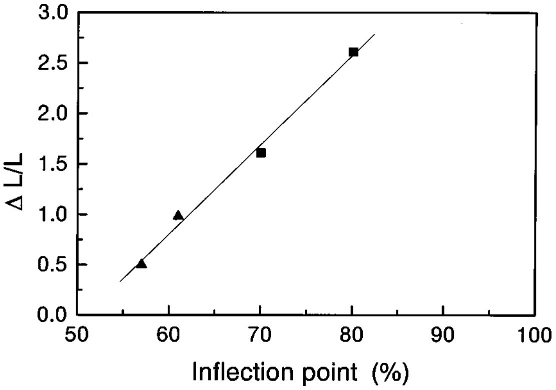

FIG. 5. The relative change in diffusion length across the step in hydrogen concentration versus the measured inflection points. The data are from this work (solid squares) and from Ref. 6 (solid triangles).

From assumptions (i) and (ii), the effective diffusion coefficient is represented by

$$D_{\mathrm{eff}} = \frac{D_i^+}{1 + \dfrac{4\pi R D_i^+ N_A}{\nu_{\mathrm{ZnH}}}}. \tag{8}$$

The fact that the data in Fig. 4 rigorously satisfy the Arrhenius Eq. (7) implies that

$$\beta = \frac{4\pi R D_i^+ N_A}{\nu_{\mathrm{ZnH}}} = \frac{\sigma_{\mathrm{ZnH}} N_A}{\nu_{\mathrm{ZnH}}} \tag{9}$$

is much larger than unity for the range of diffusion temperatures and acceptor concentrations studied, which supports assumption (iii). A lower limit to the acceptor concentration of $\sim 2\times10^{15}\ \mathrm{cm}^{-3}$ is calculated at $T_{\mathrm{diff}} = 148\,^\circ\mathrm{C}$ by setting $\beta = 1$. This implies that a trap density below $\sim 2\times10^{15}\ \mathrm{cm}^{-3}$ will result in the diffusion process becoming increasingly affected by intrinsic diffusion and consequently leading to $D_{\mathrm{eff}}$ deviating from the Arrhenius relation.

Assumption (ii) ($\nu_{\mathrm{ZnH}} \gg \sigma_{\mathrm{ZnH}}[\mathrm{H}^+]$) was previously validated[6] by suggesting it to be equivalent to $[\mathrm{H}^+] \ll [\mathrm{ZnH}]$. It is, however, believed that these assumptions are not equivalent. Due to the fact that [$\mathrm{H}^+$] is unknown at the diffusion temperatures, and due to the uncertainty expected in the previously reported values for $\nu_o$ (Ref. 19) and $D_i^+$,[7] it is not possible to directly verify assumption (ii). However, the agreement between the measured activation energy and the dissociation energy, together with the reasonably good agreement between the measured $y$ intercept and calculated prefactor in the present work and in other studies,[6,15] suggest that Eq. (5) is essentially correct.

Finally, in order to extract the hydrogen concentration from the measured free-carrier density profiles, it was assumed that $[\mathrm{H}^+]\ll[\mathrm{ZnH}]$. To show this, Eq. (3) is rewritten as follows by taking $\partial[\mathrm{ZnH}]/\partial t=0$, and using Eq. (4) and $\sigma_{\mathrm{ZnH}}=4\pi R D_i^+$,

$$\frac{[\mathrm{H}^+]}{[\mathrm{ZnH}]}=\frac{\nu_o\triangle^{-1}}{4\pi R D_{io}^{+}\exp\left(\frac{E_D-E_m}{kT}\right)}. \tag{10}$$

Here $\triangle=N_A-[\mathrm{ZnH}]=[\mathrm{Zn}^-]$. A maximum $[\mathrm{H}^+]$ to $[\mathrm{ZnH}]$ ratio of $\sim 0.4$ is calculated using the parameters $T_{\mathrm{diff}}=148\,^\circ\mathrm{C}$, $E_D=1.36$ eV, $\triangle=(N_A-\mathrm{H}_o)=5\times10^{15}$ $\mathrm{cm}^{-3}$, $\nu_o=7\times10^{13}$ $\mathrm{s}^{-1}$, and the values $D_{io}^{+}=4.21\times10^{-6}$ $\mathrm{cm}^2/\mathrm{s}$ and $E_m=0.58$ eV determined by Rahbi *et al.*[7]

This ratio quickly decreases with decreasing temperature and with increasing carrier concentrations. The condition that $[\mathrm{H}^+]\ll[\mathrm{ZnH}]$ will therefore also be satisfied at the measuring temperature ($T=300$ K), thereby ensuring that the relation, $[\mathrm{H}_T]=[\mathrm{ZnH}]+[\mathrm{H}^+]\simeq[\mathrm{ZnH}]$ holds true.

The independence of $D_{\mathrm{eff}}$ on the intrinsic diffusion coefficient also suggests that the diffusion process is unaffected by the diffusion path and corresponding potential barriers. The diffusion process is consequently expected to be similar for different semiconductor materials with a sufficient impurity density. This is indeed the case, with the same trap dependence having been demonstrated in a similar diffusion study on boron-doped silicon.[6] The only significant difference between Fig. 4 and their reported values is a slight difference in gradient due to the smaller dissociation energy of the boron-hydrogen complex in silicon. The activation energies obtained from the diffusion studies performed by Zavada *et al.*[13] and Chevallier *et al.*[12] on *n*-type GaAs also suggest that the diffusion process is trap limited within the ranges of their experimental conditions.

The insensitivity of the diffusion process to $D_i^+$ resulted in the numerical analysis of hydrogen diffusion in boron-doped silicon[6] only providing a lower limit to the diffusivity $D_i$. In order to accurately extract an intrinsic diffusion coefficient from the diffusion data, a reduction in hydrogen trapping during the diffusion process, or quantitatively, a reduction in $\beta$, would be required. In the present case, this could be achieved by performing the diffusion experiment at temperatures well in excess of 200 °C or by reducing the zinc concentration in the GaAs. Both modifications would make diffusion measurements difficult due to the restrictions imposed by the Schottky diode stability and *C-V* depth resolution. An alternative could be to use magnesium-doped GaAs instead. Until now, passivation of Mg-doped GaAs has been unsuccessful due to a possible small capture radius.[20] If it could, however, be successfully passivated, diffusion results with a sensitivity to $D_i^+$ could be achieved, while at the same time retaining a sufficiently high doping density to allow *C-V* profiling.

## VII. CONCLUSIONS

It has been shown how the ability of hydrogen to undergo field-assisted drift can be utilized to produce a hydrogen gradient from which to initiate the diffusion of hydrogen from the bulk of the material towards the surface. The results illustrate how the resulting diffusion profiles are used to obtain an effective diffusion coefficient $D_{\mathrm{eff}}$. The experimental values of $D_{\mathrm{eff}}$, which were determined within the temperature range 89–148 °C and for the zinc concentrations $N_A=3.4\times10^{16}$ $\mathrm{cm}^{-3}$ and $N_A=2.6\times10^{17}$ $\mathrm{cm}^{-3}$, satisfy the Arrhenius equation $N_A D_{\mathrm{eff}}=P_o\exp(-E_P/kT)$, with $E_P=(1.36\pm0.04)$ eV and $P_o=(8^{+24}_{-2})\times10^{20}$ $\mathrm{cm}^{-1}/\mathrm{s}$. This suggests that $D_{\mathrm{eff}}$ has an inverse dependence on the density of zinc acceptors and that the diffusion process obeys the same kinetics as the dissociation of the zinc-hydrogen complex. It is concluded that, within the experimental conditions of this study, the diffusion of hydrogen within the GaAs lattice is entirely controlled by the association and dissociation processes of hydrogen with the zinc acceptors and that the diffusion process is independent of the intrinsic diffusion coefficient of hydrogen $D_i^+$ in the GaAs.

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