PHYSICAL REVIEW B VOLUME 46, NUMBER 4 15 JULY 1992-II

Trap-limited hydrogen diffusion in boron-doped silicon

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(Received 10 February 1992)

The hydrogen diffusion process in boron-doped silicon for temperatures T in the range from 60 °C to 140 °C is entirely trap limited and shows no dependence on the diffusivity of the free hydrogen. The effective hydrogen diffusion coefficient D_{eff} is determined at two values of the boron concentration $N_A = 1.4 \times 10^{15}$ cm^{-3} and $N_A = 3.8 \times 10^{16}$ cm^{-3}. The values of D_{eff} satisfy the Arrhenius equation $N_A D_{\text{eff}} = P_0 \exp(-E_p/kT)$ with $E_P = 1.28$ eV and $P_0 = 1 \times 10^{20}$ cm^{-1} s^{-1}. We present a model which predicts that $N_A D_{\text{eff}} = \nu/(4\pi R)$, where ν is the dissociation frequency of the BH complex and $R \simeq 3.5$ nm the collision radius which describes the trapping of H at the boron atom.

I. INTRODUCTION

The electronic properties of isolated atomic hydrogen were only recently observed in silicon.[1,2] The reason is that this species spontaneously forms immobile, molecular hydrogen, or is trapped at defects.[3,4] The various defect reactions have a strong influence on the H-atom motion, and the diffusion profiles show anomalous features which makes it very difficult or even impossible to determine the "intrinsic" diffusivity D_i of free atomic hydrogen.[3,4]

The values of Van Wieringen and Warmoltz for the diffusivity, derived from H-permeation measurements are considered to be the most reliable ones.[5] Their diffusivities were determined in the temperature range from 1090 °C to 1200 °C and satisfy the Arrhenius equation

$$D = D_0 \exp\left[\frac{-E_m}{kT}\right], \tag{1}$$

with a prefactor $D_0 = 9.4 \times 10^{-3}$cm^2/s and a migration energy $E_m = 0.48$ eV. All H-related defects are fully dissociated in the investigated temperature range. It is therefore reasonable to state that D equals the intrinsic diffusivity D_i. However, D is derived in a quite narrow temperature interval and one should be cautious to use Eq. (1) at low temperatures $T < 300$ °C. There is no other report of diffusion data at high temperatures ($T > 900$ °C). The measurements of Van Wieringen and Warmoltz,[5] however, are supported by recent theoretical investigations.[6,7]

In contrast, a considerable amount of work has been performed below 400 °C.[3,4,8-17] In typical experiments the samples are exposed to a hydrogen plasma,[10,11,18] or a low-energy (1-keV) proton beam,[9,11,13] and the hydrogen incorporation is monitored as a function of the hydrogenation time t and temperature T.[9,10,12,13]

In one kind of study the hydrogen profile is determined indirectly using the ability of H to passivate an electrically active defect X (X represents boron[17,16,13,10,12,11,9] or gold[14,15]). The depth $L(T,t)$ to which the boron or the gold is passivated is determined by electrical[17,16,13,11,14,15,9] or reflectance[10,12] measurements. An effective diffusion coefficient $D_{\text{eff}}(T)$ is derived using the equation $L(T,t) = \sqrt{D_{\text{eff}}(T)t}$.

Systematic measurements of L vs t in H-implanted B-doped samples ($[\text{B}] = 2 \times 10^{15}$ cm^{-2}) show that L is proportional to $\sqrt{t}$ only for intermediate times.[13] The corresponding values of D_{eff} satisfy the Arrhenius Eq. (1) with a prefactor $D_{0\,\text{eff}} = 2$ cm^2/s and an activation energy $E_{m\,\text{eff}} = 0.83$ eV. No deeper H migration is observed for times longer than $\simeq 30$ min. At short times ($t < 2$ min) a very fast and weakly temperature-dependent increase of L is observed in agreement with other studies.[11,16] The slowdown of the diffusion process is tentatively explained[16,13] by the formation of a thin subsurface layer with a very high concentration of molecular hydrogen. This layer would act as a barrier to H in-diffusion. Herrero *et al.*[10,12] performed similar experiments on highly doped ($[\text{B}] = (10^{19}-10^{20})$ cm^{-3}) samples treated in a H plasma. They give evidence of a strong dependence of L on the sample bias and the surface oxide thickness.[12] Keeping these parameters fixed, they determine D_{eff} as a function of T and [B]. A trap-limited diffusion model is used to derive both the binding energy of the BH-complex $E_{\text{B}} = (0.6 \pm 0.1)$ eV and the intrinsic diffusivity D_i. They assume D_i to satisfy Eq. (1) and determine $D_0 = 2.4 \times 10^{-7}$ cm^2 s^{-1}, $E_m = 0.43$ eV.

In the other class of studies the *total* hydrogen concentration is measured by secondary-ion mass spectroscopy (SIMS).[8,18,19] The deuterium isotope is generally substituted for H in order to reach a detection limit of 10^{15}cm^{-3}. The H profiles do not only depend on temperature and time but show complex features which strongly depend on the conductivity type of the sample and the dopant concentration.[10,12,18,20] All profiles show a very high H concentration in a layer near the surface. In boron-doped samples, the H profiles show a plateaulike region where the H concentration is pinned to the dopant level, provided T is lower than the dissociation temperature of the hydrogen-dopant complexes.[13,8,19]

Several different models have been developed which take into account the formation of molecular hydrogen[8,9,18,21,22] and/or the trapping and detrapping of H at boron[9,10,12,23,18,22] or phosphorus[21] atoms. In some studies, these reactions and the intrinsic diffusivity are assumed to depend on the charge state of H.[18,21,20,22] A model derived by Cappizi and Mittiga[20] and Cappizi, Mitiga, and Frova[22] favors as the driving force the drift of charged hydrogen in the electrical field induced by the dopant gradient. Unfortunately, the kinetic parameters which control the formation of H_2 and H-dopant complexes as well as the H-energy levels, which determine the relative concentration of the various charge states, are unknown. Therefore the fit of the calculated profiles to the experimental SIMS curves requires an adjustment of many free parameters. Apparently the fits are very good, provided the number of parameters is large enough. The reliability of the parameters and especially that of D_i decreases as their number increases. The choice of appropriate boundary conditions makes the excellent fits even more suspect. As was discussed above, the real boundary conditions depend on the sample surface, on the hydrogenation method, and probably vary with time t. In most studies[8,23,28,21] a constant surface H concentration H_S is assumed. It is recognized that good fits can be obtained with various sets of parameters, e.g., the solution is not unique.[8,23,21] Due to these experimental and modeling problems the spread in the diffusivities reported by different authors is very large, and no agreement has been obtained on which data are the most reliable. A critical, recent compilation of the hydrogen diffusion data is given in Ref. 24.

In this work we try to determine D_i from a simple diffusion experiment. A sharp H-concentration gradient in the *bulk* is generated by using the drift property[25,26] of hydrogen in B-doped silicon. This gradient defines a well-defined initial state for subsequent diffusion from the bulk towards the surface. The boundary conditions are simple and well defined. Our results fully agree with a model that requires only *two* free parameters. However, it is clearly shown that the intrinsic diffusivity D_i cannot be determined in a sample with a boron concentration larger than 10^{15} cm^{-3}, due to the ambiguity of the fitting process.

Section II provides the experimental details. In Sec. III we describe the method used to measure diffusion profiles, which are modeled in Sec. IV. Further diffusion data which confirm the model are presented in Sec. V and are discussed in Sec. VI.

II. EXPERIMENTAL DETAILS

Boron-doped, (100) float-zone silicon samples with a resistivity of 0.47 Ω cm or 10 Ω cm are exposed to a radio-frequency- (13.6 MHz) driven hydrogen plasma at a temperature of 130 °C for 2 h. After the plasma treatment at least 1 μm was chemically etched off from the surface to reduce the near surface damage. Titanium Schottky contacts (1 mm in diameter) are evaporated onto the hydrogenated surface, and an indium-gallium alloy scratched onto the back surface gives the Ohmic contact. The annealing experiments are performed in the dark and under ambient atmosphere. Capacitance versus voltage $[C(V)]$ measurements at room temperature provide the profile N_I of the net electrically active boron concentration, i.e., $N_I = N_A - [\mathrm{BH}] - [\mathrm{H}^+]$, where N_A is the boron concentration in the nonhydrogenated control samples, and [BH] and $[\mathrm{H}^+]$ are the concentrations of electrically inactive BH complexes and untrapped positively charged atomic hydrogen, respectively. We will show in Sec. VI that the atomic hydrogen concentration [H] is negligible compared to [BH]. Hence, the profile of the BH complexes is easily derived from the $C(V)$ profile N_I, using $R = N_A - N_I = [\mathrm{BH}] + [\mathrm{H}^+] \approx [\mathrm{BH}]$.

III. DESCRIPTION OF A TYPICAL DIFFUSION EXPERIMENT

We investigate the H diffusion at a temperature $T_D = 100\,^\circ\mathrm{C}$ in a sample with $N_A = 3.8 \times 10^{16}$ cm^{-3}. The $C(V)$ profile just after the H plasma treatment shows a complete passivation of the boron acceptor up to a depth of $\simeq 2$ μm. The starting conditions for the diffusion experiment are generated by a two-step annealing process with a reverse-bias $V_R = 9$ V applied to the Schottky diode. The corresponding thickness of the space-charge layer is $W = 0.57$ μm. The first annealing is performed at $T_{R_1} = 140\,^\circ\mathrm{C}$ for a time $t_{R_1} = 10$ h and is followed by a treatment at $T_{R_2} = T_D = 100\,^\circ\mathrm{C}$ for 24 h. The resulting profile of the BH complexes (Fig. 1, curve labeled "initial") is characterized by a layer ($x < 0.5$ μm) free of BH complexes and a uniform BH-complex concentration ($N_0 = 2.1 \times 10^{16}$ cm^{-3}) in the region $x > 0.7$ μm. The BH concentration strongly increases in the transition region 0.5 μm $< x < 0.7$ μm, which coincides with the edge of the space-charge region in the biased diode. The observed profile is well known from literature[25,26] and has been explained in the following way: Due to the electric field, the positively charged hydrogen, which is released by the thermal dissociation of the BH-complex drifts out of the space-charge region and spreads over about one effective diffusion length L_D in the neutral bulk where new complexes are formed.[25,26] The boron-concentration increases again at a depth x_0 located deeply in the bulk, out of the range of the $C(V)$ profiling. A crude estimate of x_0 is given by $x_0 \simeq W + L_D$. The anneal at the higher temperature T_{R1} gives a value of $L_D = \sqrt{D_{\mathrm{eff}} t_{R1}} \simeq 2$ μm ($D_{\mathrm{eff}} \simeq 8 \times 10^{-13}$ cm^2/s, see Sec. V) which is much larger than W. The long annealing step at the diffusion temperature ($T_{R2} = T_D$) ensures that the BH concentration is in thermal equilibrium at the beginning of the diffusion experiment. Indeed, only a negligible change is observed in the initial profile of Fig. 1 after an additional annealing of the reversed bias diode for 10 h at $T = 100\,^\circ\mathrm{C}$.

The diffusion experiment starts when the bias is switched off at time $t_D = 0$ at temperature $T_D = 100\,^\circ\mathrm{C}$; the sample remains at this temperature for a duration t_D and is rapidly cooled to $T = 300$ K for the $C(V)$ measurement. The profiles of the BH complexes are shown in Fig. 1 for different values of t_D. As t_D increases, the BH concentration progressively decreases in the region $x > 0.57$ μm. In the region $x < 0.57$ μm an increase of

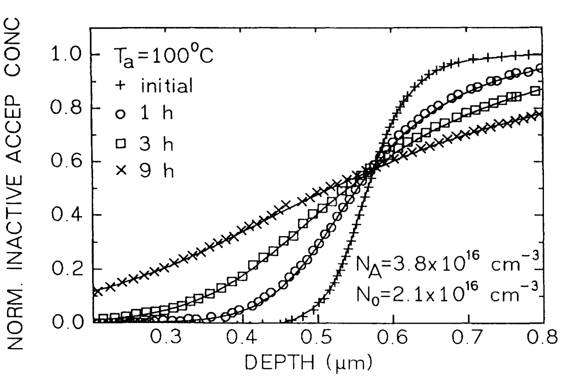

FIG. 1. Normalized inactive boron profile $\Delta N/N_0$ after a two-step reverse-bias annealing ($V_R=9$ V) at $T_{R1}=140\,^\circ\mathrm{C}$, $t_{R1}=10$ h, and $T_{R2}=100\,^\circ\mathrm{C}$, $t_{R2}=24$ h (initial) and subsequent zero bias annealing for various times at $T_a=T_D=100\,^\circ\mathrm{C}$. The symbols N_A and N_0 denote the total boron concentration and the normalization factor. The solid lines represent the fit to Eqs. (1) and (2) with $D_i=1\times10^{-12}$ cm^2/s, $R=3.5$ nm.

[BH] occurs; the sharp initial profile is thus smoothed out. All profiles cross at the point defined by $x=0.57$ μm and $[\mathrm{BH}]/N_0=0.57$.

IV. ANALYSIS OF THE DIFFUSION PROFILES

The profiles in Fig. 1 are explained in the following way. The BH complexes partially dissociate, and the hydrogen diffuses towards the defect-free surface layer where it is trapped by the boron atoms. The free H concentration satisfies the modified diffusion equation

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

where D_i is the H-diffusion coefficient in the absence of a trap (intrinsic diffusivity). In our experiments the ratios of the concentrations $[N_I(x<W)/N_I(x>W)]$ are in the order of 2 to 4 and we can neglect in Eq. (2) the small internal field produced by the step in the active acceptor concentration. The term $\partial[\mathrm{BH}]/\partial t$ accounts for the trapping and detrapping of the H atom at the boron acceptor and is given by equation

$$\frac{\partial[\mathrm{BH}]}{\partial t}=\sigma(N_A-[\mathrm{BH}])[\mathrm{H}]-\nu[\mathrm{BH}]\ , \tag{3}$$

where σ is the capture rate of H at the B atom and ν the dissociation frequency of the BH complex. The parameter σ is related to the collision radius R and the diffusion coefficient D_i according to

$$\sigma=4\pi R D_i\ . \tag{4}$$

The dissociation frequency ν has been determined in Ref. 25 and is given by the Arrhenius equation

$$\nu=\nu_0\exp\left[\frac{-E_D}{kT}\right] \tag{5}$$

with $\nu_0=2.8\times10^{14}$ s^{-1} and the dissociation energy of the BH complex $E_D=(1.28\pm0.03)$ eV.

A. Numerical solution

The profiles [H] vs x and [BH] vs x are calculated by solving numerically Eqs. (2) and (3). For boundary conditions, we assume that the medium is impermeable to diffusion at the planes $x=W(0\mathrm{V})\simeq0.15$ μm and $x=x_0$ with $x_0=2.5$ μm. The positively charged diffusing H species are excluded from the zero-bias space-charge layer of thickness $W(0\mathrm{V})$. The room-temperature $C(V)$ measurement provides $\Delta N=[\mathrm{BH}]+[\mathrm{H}^+]$. We will demonstrate in Sec. V that the free hydrogen concentration is negligible at 300 K. Therefore the following approximations hold at 300 K for the total hydrogen concentration $\mathrm{H}_T=[\mathrm{BH}]+[\mathrm{H}]:\mathrm{H}_T\approx[\mathrm{BH}]\approx[\mathrm{BH}]+[\mathrm{H}^+]=\Delta N$. There is only negligible H diffusion during the rapid cooling from the diffusion temperature to the measurement temperature, therefore $\mathrm{H}_T(T_D)=\mathrm{H}_T(300\ \mathrm{K})=\Delta N$. We fit the total hydrogen concentration $\mathrm{H}_T(T)=[\mathrm{BH}]+[\mathrm{H}]$ calculated from Eqs. (2) and (3) to the experimental profiles ΔN of Fig. 1 by adjusting the *two* parameters D_i and R. The profiles H_T calculated for $D_i=1\times10^{-12}$ cm^2/s and $R=(3.5\pm0.5)$ nm (Fig. 1, solid lines) are in very good agreement with the experimental curves. The two parameters are varied over wide ranges and we find that it is impossible to obtain a good fit for D_i lower than about 4×10^{-13} cm^2/s. For D_i larger than 1×10^{-12} cm^2/s the calculated profiles show a negligible dependence on D_i but are very sensitive to R. Therefore, the fit provides only a *lower limit* D_l of the diffusivity D_i which is in the range from 7×10^{-13} cm^2/s to 1×10^{-12}cm^2/s. The fit provides a constant value of R [$R=(3.5\pm0.5)$ nm] for any value of D_i larger than D_l.

B. Analytical solution

We derive an analytical solution of Eqs. (2), (3), and (4) which allows us to define an effective diffusion coefficient D_{eff} which can be accurately determined from the experimental profiles. We make the following assumptions: (i) dynamical equilibrium is achieved for the reaction $\mathrm{B}+\mathrm{H}\rightleftharpoons\mathrm{BH}$, i.e., $\partial[\mathrm{BH}]/\partial t\simeq0$ in Eq. (3), (ii) $\nu\gg\sigma[\mathrm{H}]$, (iii) $\sigma N_A/\nu\gg1$. The validity of the assumptions will be discussed in Sec. VI.

Taking into account assumptions (i) and (ii), we calculate [BH] from Eq. (3),

$$[\mathrm{BH}]\approx\frac{\sigma N_A[\mathrm{H}]}{\nu+\sigma[\mathrm{H}]}\approx\frac{\sigma N_A}{\nu}[\mathrm{H}]\ . \tag{6}$$

Substituting in Eq. (2), we obtain

$$\frac{\partial[\mathrm{H}]}{\partial t}=D_{\mathrm{eff}}\frac{\partial^2[\mathrm{H}]}{\partial x^2}\ , \tag{7}$$

where D_{eff} is an effective diffusion coefficient given by

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

If assumption (iii) is satisfied, (8) writes

$$D_{\mathrm{eff}} \approx \frac{\nu}{4\pi R N_A} , \tag{9}$$

which does *not* depend on the diffusivity D_i, e.g., the diffusion process is entirely controlled by trapping and detrapping of the H atom at the boron acceptor.

Using Eq. (6), it is easy to show that $\mathrm{H}_T = [\mathrm{BH}] + [\mathrm{H}]$ also satisfies Eq. (7),

$$\frac{\partial \mathrm{H}_T}{\partial t} = D_{\mathrm{eff}} \frac{\partial^2 \mathrm{H}_T}{\partial x^2} . \tag{10}$$

Assuming that the critical H_T (or ΔN) profile has a steplike shape ($\mathrm{H}_T = 0$ for $x < w$ and $\mathrm{H}_T = N_0$ for $x > w$), the solution of Eq. (10) is given by

$$\mathrm{H}_T(x,t) = \frac{N_0}{2} \operatorname{erfc}\left[\frac{w - x}{2\sqrt{D_{\mathrm{eff}} t}} \right] . \tag{11}$$

It is clear from Eq. (11) that the profiles corresponding to different values of t concur at the point $x = w$, $\mathrm{H}_T = 0.5 N_0$ which is a center of symmetry. The effective diffusivity D_{eff} can be calculated from the slope $s(t) = d\mathrm{H}_T(x,t)/dx|_{x=w}$ of the straight line which is tangent to $\mathrm{H}_T(x,t)$ at $x = w$,

$$D_{\mathrm{eff}} = \frac{N_0^2}{4\pi t} \frac{1}{s^2(t)} . \tag{12}$$

The profiles in Fig. 1 cross at $x_0 = 0.57$ μm ($\mathrm{H}_T \approx \Delta N = 0.57 N_0$) and are slightly asymmetric with respect to this point. However, ΔN shows a nearly linear dependence on x for x varying from ≈ 0.45 to 0.57 μm. From the slopes we determine the mean value $D_{\mathrm{eff}}(100\,^\circ\mathrm{C}) = (1.4 \pm 0.5) \times 10^{-14}$ cm^2/s.

V. INFLUENCE OF TEMPERATURE AND BORON-CONCENTRATION ON THE DIFFUSION PROFILES

In Eq. (9) it is predicted that D_{eff} is inversely proportional to N_A and is thermally activated with the activation energy $E_D = 1.28$ eV. To confirm this dependence, we performed the diffusion experiments described in Sec. III on the same material at $T = 120\,^\circ\mathrm{C}$ and $T = 140\,^\circ\mathrm{C}$. The changes in the diffusion profile are qualitatively similar to those in Fig. 1. At any temperature the profiles are well fitted by Eq. (1) and (2). The adjusted values of R and the lower limit of D_l are shown in Table I as well as the effective diffusivity D_{eff} calculated from the slope of the profiles.

Similar diffusion experiments are also performed on a sample with $N_A = 1.4 \times 10^{15}$ cm^{-3}. Just after the plasma exposure 90% of the boron acceptors are passivated up to a depth of ≈ 8 μm. The initial step profile is generated by annealing the sample with the following parameters: $\mathrm{V}_R = 60$ V, $T_{R1} = 140\,^\circ\mathrm{C}$, $t_{R1} = 2$ h, $T_{R2} = T_D$, $t_{R2} = 10$ h. The thickness of the space-charge layer is $W = 7.6$ μm for $\mathrm{V}_R = 60$ V. The total H concentration in the region $x > 9.0$ μm is $N_0 = 1.08 \times 10^{15}$ cm^{-3}. The diffusion profiles at $T_D = 100\,^\circ\mathrm{C}$ are shown in Fig. 2 for $t = 2$, 10, and 33 h as well as the profiles calculated from Eqs. (1) and (2) with $D = 8 \times 10^{-12}$ cm^2/s and $R = 3.5$ nm. A negligible change in the profiles occurs for $D > 8 \times 10^{-12}$ cm^2/s. Therefore, only a lower limit of D_l which is in the range from 4×10^{-12} cm^2/s to 8×10^{-12} cm^2/s can be determined. However, D_l is about one order of magnitude larger than the corresponding value in the sample with $N_A = 3.8 \times 10^{16}$ cm^{-3}. All the profiles except the one recorded at $t = 33$ h cross at $x_0 = 8.05$ μm and $\Delta N = 0.61 \times N_0$ cm^{-3}. The discrepancy at $t = 33$ h (Fig. 2) is probably due to the fact that the uniform part ($x > 9.0$ μm) of the initial profile does not extend deeply enough into the bulk and cannot be considered as infinite for the longest diffusion time (33 h). Even though the profiles are not symmetrical to the point of convergence, they show a nearly linear part for $x < 7.8$ μm, of which the slope can be substituted in Eq. (12) to calculate the effective diffusion coefficient $D_{\mathrm{eff}} = (3.7 \pm 0.6) \times 10^{-13}$ cm^2/s. Similar experiments are performed at $T_D = 120\,^\circ\mathrm{C}$, 80 °C, and 60 °C. The results are summarized in Table II.

TABLE I. Lower limit of the H diffusivity and collision radius R obtained from the fit of the experimental profiles to the numerical solution of Eqs. (2) and (3) and effective H diffusivity D_{eff} calculated from the slopes of the diffusion profiles using Eq. (12). The total boron concentration is $N_A = 3.8 \times 10^{16}$cm^{-3}; T denotes the diffusion temperature.

T (°C)	D_l (cm^2/s)	R (nm)	D_{eff} (cm^2/s)	D_l/D_{eff}
100	$(7 \pm 3) \times 10^{-13}$	3.5 ± 0.5	$(1.4 \pm 0.5) \times 10^{-14}$	50
120	$(3 \pm 2) \times 10^{-12}$	3.3 ± 0.5	$(9 \pm 1) \times 10^{-14}$	33
140	$(3 \pm 2) \times 10^{-11}$	3.6 ± 0.5	$(7.5 \pm 1) \times 10^{-13}$	40

In order to verify Eq. (9), we plot the product $P = N_A D_{\mathrm{eff}}$ as a function of $1/T$ for $N_A = 3.8 \times 10^{16}$ cm^{-3} (Fig. 3, squares) and $N_A = 1.4 \times 10^{15}$ cm^{-3} (Fig. 3, crosses). The values of P are well fitted to the Arrhenius

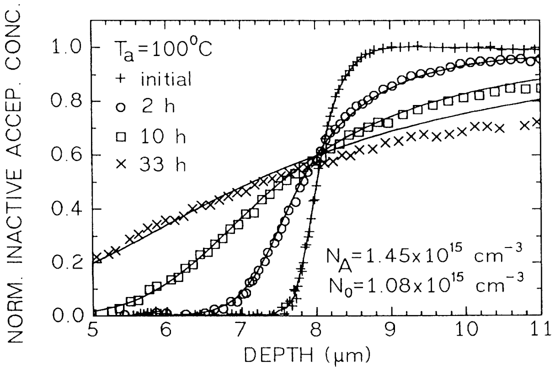

FIG. 2. Normalized inactive boron profile $\Delta N / N_0$ after a two-step reverse-bias annealing ($V_R = 60$ V) at $T_{R1} = 140\,^\circ\mathrm{C}$, $t_{R1} = 2$ h, and $T_{R2} = 100\,^\circ\mathrm{C}$, $t_{R2} = 10$ h (initial) and subsequent zero bias annealing for various times at $T_a = T_D = 100\,^\circ$ C. The symbols N_A and N_0 denote the total boron concentration and the normalization factor. The solid lines represent the fit to Eqs. (1) and (2) with $D_i = 8 \times 10^{-12}$ cm^2/s, $R = 3.5$ nm.

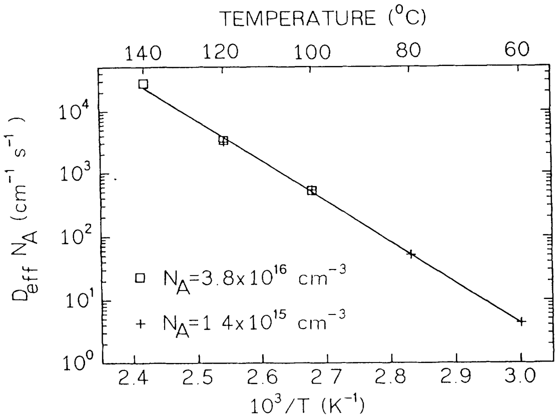

FIG. 3. Arrhenius plot of $P=N_A D_{\text{eff}}$. The solid line represents the fit to equation $P=P_0\exp(-E_P/R_T)$ with $P_0=1\times10^{20}\ \text{cm}^{-1}\,\text{s}^{-1}$ and $E_P=1.28$ eV.

equation $P=P_0\exp(-E_P/kT)$ with a prefactor $P_0=(1^{+0.9}_{-0.5})\times10^{20}\ \text{cm}^{-1}\,\text{s}^{-1}$ and an activation energy $E_P=(1.28\pm0.03)$ eV. (See Fig. 3, solid line.)

From Eqs. (5) and (9) we derive the following expression for P:

$$P=\frac{\nu_0}{4\pi R}\exp\left[-\frac{E_D}{kT}\right]. \tag{13}$$

The experimental activation energy $E_P=(1.28\pm0.03)$ eV is in excellent agreement with the dissociation energy of the BH complex ($E_D=1.28\pm0.03$ eV) which has been determined from the thermal reactivation kinetics of the BH complex after annealing under reverse bias.[25] Taking $R\simeq3.5$ nm (Tables I and II) and $\nu_0=2.8\times10^{14}\ \text{s}^{-1}$ as determined in Ref. 25, we are able to calculate $P_0=\nu_0/(4\pi R)\simeq6\times10^{19}\ \text{cm}^{-1}\,\text{s}^{-1}$ which agrees remarkably well with the experimental value $P_0=(1^{+0.9}_{-0.5})\times10^{20}$ cm^{-1}s^{-1}.

VI. DISCUSSION

The values calculated for D_{eff} according to Eq. (13) with the parameters ν_0 and E_D determined in Ref. 25 and $R=3.5$ nm, derived from the fit described above, agree fully with the experimental effective diffusivities D_{eff} measured in the temperature range $T=(60-140)\,^{\circ}\text{C}$. Equation (13) is, however, valid only if assumptions (i), (ii), and (iii) of Sec. IV B are satisfied.

TABLE II. Lower limit of the H diffusivity and collision radius R obtained from the fit of the experimental profiles to the numerical solution of Eqs. (2) and (3) and effective H diffusivity D_{eff} calculated from the slopes of the diffusion profiles using Eq. (12). The total boron concentration is $N_A=1.45\times10^{15}\ \text{cm}^{-3}$; T denotes the diffusion temperature.

T (°C)	D_l (cm^2/s)	R (nm)	D_{eff} (cm^2/s)	D_l/D_{eff}
60	$(8\pm4)\times10^{-14}$	4.8 ± 0.4	$(3.0\pm0.5)\times10^{-15}$	26
80	$(8\pm3)\times10^{-13}$	3.9 ± 0.4	$(3.5\pm0.5)\times10^{-14}$	22
100	$(6\pm3)\times10^{-12}$	3.5 ± 0.5	$(3.7\pm0.6)\times10^{-13}$	16
120	$(3\pm3)\times10^{-11}$	3.9 ± 0.5	$(2.2\pm0.5)\times10^{-12}$	13

In order to check assumption (i), we neglect diffusion; e.g., we take a constant value of H_T, and we solve analytically Eq. (3) to calculate [BH] as a function of time for $[\text{BH}](t=0)=N_A$, $H_T=N_A$, and $D_i>D_l$. Under all investigated experimental conditions (T,N_A) the [BH]-complex concentration reaches an equilibrium value within a time which is negligible compared to the typical diffusion times. Therefore a dynamical equilibrium is always achieved for reaction $\text{B}+\text{H}\rightleftarrows\text{BH}$.

Taking $\partial[\text{BH}]/\partial t=0$ in Eq. (3), we have $[\text{H}]/[\text{BH}]=\nu\sigma^{-1}\Delta N^{-1}$. The maximum of the ratio [H]/[BH] is 0.2 which is obtained for the experimental condition $T_D=120\,^{\circ}\text{C}$, $N_A=1.4\times10^{15}\ \text{cm}^{-3}$, and the following corresponding parameters $\Delta N=N_A-N_0=3.7\times10^{14}\ \text{cm}^{-3}$, $D=D_l=3\times10^{-11}\ \text{cm}^2/\text{s}$, $R=3.5$ nm, $\nu=1\times10^{-2}\ \text{s}^{-1}$. Of course, this lower limit strongly decreases with temperature and increasing values of N_A. We conclude that assumption (ii), e.g., $[\text{H}]\ll[\text{BH}]$ is also satisfied for all investigated annealing conditions and in particular at the measurement temperature (300 K). Therefore the relation $\Delta N=N_A-N_I=[\text{BH}]+[\text{H}^+]\approx[\text{BH}]$ used to determine the BH profile (see Sec. II) is valid. The inequality $[\text{H}]\ll[\text{HB}]$ has also been established[27] from a careful analysis of the thermal reactivation kinetics of the H-passivated boron for annealing temperatures below 220 °C.

Under assumptions (i) and (ii), D_{eff} is given by Eq. (8), which also writes

$$D_{\text{eff}}=\frac{D_0\exp\left[-\dfrac{E_M}{kT}\right]}{1+\dfrac{4\pi N_A R D_0}{\nu_0}\exp\left[\dfrac{E_D-E_M}{kT}\right]}. \tag{14}$$

The fact that the experimental values of $N_A D_{\text{eff}}$ rigorously satisfies Arrhenius Eq. (13) implies that

$$\alpha=\frac{4\pi N_A R D_0}{\nu_0}\exp\left[\frac{E_D-E_M}{kT}\right] \tag{15}$$

is much larger than unity [condition (iii)] for any investigated experimental condition (N_A and T_D). This defines an upper limit of the H-migration energy $(E_M)_{\max}=E_D-kT_D l_n(\alpha\nu_0/4\pi N_A R D_0)$ with $N_A=1.4\times10^{15}\ \text{cm}^{-3}$ and $T_D=120\,^{\circ}\text{C}$. Taking $\alpha=5$, $E_D=1.28$ eV, $\nu_0=2.8\times10^{14}\ \text{s}^{-1}$, $R=3.5$ nm, and the prefactor $D_0=9.4\times10^{-3}\ \text{cm}^2/\text{s}$ determined by Van Wieringen and Warmholtz,[5] we find $(E_M)_{\max}=0.7$ eV which is consistent with $E_M=0.48$ eV derived from the high-temperature measurements.[5]

Herrero *et al.*[10,12] determine the temperature dependence of the effective H diffusivity from the boron passivation depth L in highly doped samples ($N_A\geq1.5\times10^{19}$ cm^{-3}). The Arrhenius plots of D_{eff} strongly deviate from linearity, and the temperature and the N_A dependence of D_{eff} is in agreement with an equation which is equivalent to Eq. (14). At $N_A = 1.5 \times 10^{19} \text{cm}^{-3}$, D_{eff} equals D_i for $T \geq 200\,°\text{C}$ (e.g., $\alpha < 1$) and becomes much less than D_i for $T < 200\,°\text{C}$ (e.g., $\alpha > 1$) (see Fig. 4 in Ref. 10). Therefore the value of α should be close to unity for $T = 200\,°\text{C}$ and $N_A = 1.5 \times 10^{19}\ \text{cm}^{-3}$. The lower limit of α given by Eq. (15) for this condition is $\alpha = 3 \times 10^3$ (we take $E_M = 0.7$ eV). Therefore Eq. (13) should hold for the whole temperature and N_A range investigated by Herrero *et al.*,[10,12] and the Arrhenius plots of D_{eff} should be linear in contrast to what is observed in Refs. 10 and 12. It should also be underlined that our values of $P = N_A D_{\text{eff}}$ are several orders of magnitude lower than the corresponding values from Ref. 10. (At $T = 100\,°\text{C}$, $P = 5 \times 10^2\ \text{cm}^{-1}\,\text{s}^{-1}$ and $P = 1 \times 10^6\ \text{cm}^{-1}\,\text{s}^{-1}$ from Fig. 3 and Ref. 10, respectively.)

In Ref. 13 the effective H diffusivity is derived from the boron passivation depth L in moderately doped samples ($N_A = 2 \times 10^{15}\ \text{cm}^{-3}$) after low-energy H implantation. The values of $\ln D_{\text{eff}}$ show a linear dependence on $1/T_D$ in the investigated temperature range ($T = 80\,°\text{C}$–$140\,°\text{C}$), but the activation energy $E_A = (0.83 \pm 0.05)$ eV is much lower than $E_P = E_D = 1.28$ eV determined in the present work. The values of P calculated from Ref. 13 ($P = 3 \times 10^4\ \text{cm}^{-1}\,\text{s}^{-1}$ at $100\,°\text{C}$) also largely exceed the corresponding values of the present work.

In the studies by Herrero *et al.*[10,12] and Zundel *et al.*,[13] D_{eff} is determined *during* the hydrogenation treatment. The method used in the present work allows us to separate the hydrogenation treatment from the diffusion experiment. Thermal equilibrium prevails, the free-electron concentration is negligible, and H is predominantly in the positive charge state.[27] Due to the Coulomb interaction between H^+ and B^-, the trapping of H at the boron atom is very effective, in agreement with the large collision radius $R = 3.5$ nm. The very large values of P from Refs. 13, 10, and 12 might be explained by a strong increase of the electron concentration n during the hydrogenation treatment. For large values of n, a significant part of the hydrogen donor converts from the positive to the neutral charge state.[27] The trapping at the boron becomes less effective; α decreases, and D_{eff} or P increases in qualitative agreement with the results in Refs. 13, 10, and 12.

The excellent agreement between the experimental and the calculated diffusion profiles ensures that Eqs. (2), (3), (4) and the boundary conditions specified in Sec. IV A fully account for the diffusion process. We have assumed that H is in the positive charge state in agreement with the large collision radius and previous experimental[27,25,26] and theoretical investigations.[28] We have implicitly neglected the formation of molecular hydrogen H_2. Some molecular hydrogen probably forms during the hydrogenation treatment and the reverse-bias annealing at 140 C, but this species is stable and immobile at least up to $200\,°\text{C}$ (see Ref. 27) and does not contribute to the diffusion process.

A remarkable result is the fact that the calculated profiles are insensitive to the diffusion coefficient D, provided D exceeds a lower limit D_l and $\sigma = 4\pi R D$ with a constant value of R. From the analysis of the diffusion profiles it is therefore impossible to determine the intrinsic diffusion coefficient D_i. This behavior has not been recognized by several authors[8,9,18,21,22] who used models based on Eqs. (2) and (3) in order to determine D from fits of the H profiles in samples exposed to an H plasma. Of course this basic problem remains if the present model is complemented by an additional process such as H_2 formation[8,9,18,21] or the drift of H^+ in an electric field.[9,25] The same ambiguity of the fitting process was encountered in Ref. 29. From the diffusion experiments only an effective diffusion coefficient D_{eff} can be derived, contrary to the conclusion drawn in Ref. 29.

The lower limit D_l is well correlated with the effective diffusivity D_{eff}, and the ratio D_l/D_{eff} is in the range from 10 to 50. (See Tables I and II.) From Eqs. (8), (9), and (15) we derive $\alpha \approx D/D_{\text{eff}}$. Therefore the condition $D > D_l$ is equivalent to the condition $\alpha \gg 1$ derived from the analytical analysis. If this condition is satisfied, the diffusion process is entirely controlled by the trapping and detrapping of the hydrogen at the boron atom. On a microscopic scale the interpretation is as follows. At large values of the diffusivity D the transit time of a free H atom between two next-nearest-neighbor traps is negligible compared to the mean time t_t the H atom stays at a trap. The H-atom motion is then determined by the trapping and does not depend on D_i.

In order to derive the intrinsic diffusivity D_i from such experiments, one should increase the temperature and/or decrease the boron concentration N_A. Taking $E_m = 0.48$ eV, $D_0 = 9.4 \times 10^{-3}\ \text{cm}^2/\text{s}$ from Ref. 5, Eq. (15) gives $\alpha / N_A \approx 3 \times 10^{-12}$. The condition $\alpha < 1$ would be satisfied for N_A lower than $3 \times 10^{11}\ \text{cm}^{-3}$. Such experiments require very pure material and have not been performed at the present time.

VII. SUMMARY

Using the drift property of positively charged hydrogen, we generate a H concentration gradient *in the bulk* which allows us to study the hydrogen motion in B-doped silicon. The boundary conditions are well defined, and the diffusion experiment is completely separated from the hydrogenation procedure, in contrast to previous studies. We present a model based on a modified diffusion equation which takes into account the trapping and detrapping of H at the boron atom [Eqs. (2) and (3)]. The numerical solution of Eqs. (2) and (3) fully agrees with the experimental profiles provided the diffusivity D exceeds a lower limit D_l, and the collision radius R equals 3.5 nm. The analytical treatment shows that the diffusion process can be described by an effective diffusion coefficient $D_{\text{eff}} = \nu/(4\pi R N_A)$ [Eq. (9)]. The experimental values of D_{eff} are accurately determined from the slope of the diffusion profiles and agree quantitatively with Eq. (9). In particular D_{eff} is inversely proportional to N_A ($N_A = 1.4 \times 10^{15} \text{cm}^{-3}$ and $N_A = 3.8 \times 10^{16}\ \text{cm}^{-3}$) and shows the same temperature dependence as the BH-complex dissociation frequency ν. Under the experimental conditions of this work ($T \leq 140\,^{\circ}\mathrm{C}$, $N_A \geq 1 \times 10^{15}$ cm^{-3}), the diffusion process is entirely controlled by the trapping and detrapping of H at the boron atom, and it is basically impossible to determine the intrinsic diffusivity of H due to the ambiguity of the fitting process. We can, however, estimate an upper limit of the H migration energy $(E_m)_{\max} = 0.7$ eV.

ACKNOWLEDGMENTS

We thank H. J. Queisser for his interest and support throughout this work. We acknowledge stimulating discussions with M. Stutzmann, J. T. Borenstein, and Th. Prescha. We appreciate the technical assistance of W. Heinz and W. Krause.

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