

Modeling of hydrogen diffusion in *n*- and *p*-type silicon

D. Mathiot

Centre National d'Études des Télécommunications de Grenoble, Chemin du Vieux Chêne,
Boîte Postale No. 98, 38243 Meylan CEDEX, France

(Received 5 April 1989)

A model is proposed to describe the behavior of hydrogen in silicon at moderate temperatures. It is assumed that H has both a donor and an acceptor level in the band gap, and thus it can exist in the three charge states H^0 , H^+ , and H^- . Its motion is slowed down by the formation of H_2 molecules as well as by interactions with the dopant atoms. Good simulations are obtained in both *n*- and *p*-type Si for various doping levels. The fitted diffusivity of neutral hydrogen is in agreement with the extrapolated high-temperature data.

Since it was shown that hydrogen neutralizes the electrical activity of deep impurities and also of shallow acceptors in semiconductors, the understanding of its behavior in silicon has become the subject of numerous experimental and theoretical studies (see Ref. 1 for a recent review). One of the major questions which remains to be solved is the determination of the microscopic mechanisms of hydrogen motion in silicon. The first experimental results were obtained by Van Wieringen and Warmoltz (VWW) using permeation near 1000°C, and lead to a migration enthalpy of about 0.48 eV for hydrogen in Si (Ref. 2). Extrapolation of these high-temperature data in the 100–200°C temperature range leads to values of hydrogen diffusivity of the order of 10^{-9} – 10^{-7} cm²s⁻¹. On the other hand, direct measurements by secondary ion mass spectroscopy (SIMS) of deuterium profiles indicate penetration depths of only a few μm for plasma hydrogenations at 150°C, corresponding to effective diffusivities several orders of magnitude lower than the extrapolated values from VWW data, and which depend on both dopant type and concentration.^{3,4}

As proposed by Pantelides⁵ and by Capizzi and Mittiga (CM) (Ref. 6) most data can be consistently interpreted if one assumed that hydrogen has a deep donor state in the energy gap and is positively charged (H^+) in *p*-type material. On this basis CM were able to obtain good simulations of hydrogen profiles in highly doped *p*-type silicon,⁶ but they did not present any attempt to describe the influence of dopant type and concentration. One of the major problems with the CM model is that they take into account neither the pairing between H^+ and the ionized acceptor, nor the possible formation of H_2 molecules, which is nevertheless necessary to explain hydrogen concentrations well above dopant concentrations in high-resistivity silicon. A more detailed analysis has been performed by Borenstein, Angell, and Corbett (BAC) and leads to satisfactory simulations in *n*- and *p*-type samples of various resistivities.⁷ Although the BAC model allows rather good simulations for various conditions, it seems to the present author that this model suffers from some weaknesses which render the extracted parameter values somewhat doubtful. For example, the BAC analysis does not take into account the influence of the built-in electric field on H^+ diffusion, and totally neglects the dissociation

of the boron-hydrogen (BH) complexes, which is known to occur at temperatures above about 80°C.¹ Moreover, some pairing reactions considered by BAC do not respect the charge conservation condition. Finally, the BAC model does not take into account the possible existence of an acceptor level, leading to the existence of negatively charged hydrogen (H^-) in highly doped *n*-type silicon. This acceptor level has been suggested both from experimental⁸ and theoretical⁹ arguments.

In this analysis it is considered that hydrogen can have both an acceptor (E_a) and a donor (E_d) level in the band gap, and thus can exist in the three charge states H^+ , H^0 , and H^- , the relative concentrations of which depend on the local Fermi-level position:

$$[H^-] = (n/n_a)[H^0], \quad (1a)$$

$$[H^+] = (n_d/n)[H^0], \quad (1b)$$

where n is the local concentration of free electrons, and n_a and n_d reflect the position of the E_a and E_d levels in the gap,

$$n_a = N_c \exp[-(E_c - E_a)/k_B T], \quad (2)$$

and the corresponding relations for n_d .

The isolated charged hydrogen atoms can react with the ionized dopants to form neutral complexes, following the relations



The rate coefficients are given by

$$k_{BH} = 4\pi r_c D_{H^+}, \quad (4a)$$

$$k_{PH} = 4\pi r_c D_{H^-}, \quad (4b)$$

where D_{H^+} and D_{H^-} are the diffusivities of H^+ and H^- , and r_c is a capture radius which can be easily estimated if one assumes a pure Coulombic interaction. In this case r_c is the distance where the Coulombic energy drops to the thermal energy, i.e., $k_B T = (1/4\pi\epsilon)q^2/r_c$. This corresponds to a capture radius of about 30 Å at 150°C. In

addition to these neutralization reactions (dopant passivation), it is considered that H_2 molecules can be formed following the reaction



with

$$k_{H_2} = 8\pi r_{H_2} D_{H^0}. \quad (6)$$

Finally, we also take into account the possibility for H^0 to be trapped by other less clearly identified traps T :



with

$$k_{TH} = 4\pi r_{TH} D_{H^0}. \quad (8)$$

As explained below, such an extra trapping is necessary to accurately simulate the surface region of the hydrogen profiles.

Among these various species, only the free hydrogen atoms, in their three charge states, are assumed to be mobile and actually contribute to H diffusion.

The individual fluxes are given by the first Fick's law, modified by a drift term in order to take into account the influence of the built-in electric field on the charged species:

$$J_{H^0} = -D_{H^0} \frac{\partial [H^0]}{\partial x}, \quad (9a)$$

$$J_{H^+} = -D_{H^+} \frac{\partial [H^+]}{\partial x} - D_{H^+} [H^+] \frac{1}{n} \frac{\partial n}{\partial x}, \quad (9b)$$

$$J_{H^-} = -D_{H^-} \frac{\partial [H^-]}{\partial x} + D_{H^-} [H^-] \frac{1}{n} \frac{\partial n}{\partial x}. \quad (9c)$$

With the help of Eq. (1), the total flux can be easily written in the simple form

$$J_H = - \left(D_{H^0} + \frac{n}{n_a} D_{H^+} + \frac{n_d}{n} D_{H^+} \right) \frac{\partial [H^0]}{\partial x}. \quad (10)$$

The evolution of the various concentrations are then given by the following system of differential equations:

$$\frac{\partial [H]}{\partial t} = - \frac{\partial J_H}{\partial x}, \quad (11a)$$

$$\frac{\partial [H_2]}{\partial t} = k_{H_2} [H^0]^2 - k'_{H_2} [H_2], \quad (11b)$$

$$\frac{\partial [BH]}{\partial t} = k_{BH} [B^-] [H^+] - k'_{BH} [BH], \quad (11c)$$

$$\frac{\partial [PH]}{\partial t} = k_{PH} [P^+] [H^-] - k'_{PH} [PH], \quad (11d)$$

$$\frac{\partial [TH]}{\partial t} = k_{TH} [T] [H^0]. \quad (11e)$$

And finally, the local density of free carriers is obtained by the simultaneous resolution of Poisson's equation.

By using appropriate boundary conditions, simulations of hydrogen profiles can be obtained by the resolution of the system of coupled differential equations presented above. The surface condition is empirically described by a

constant effective surface concentration for H^0 ($[H^0] = [H^0]_s$ at $x=0$), whereas the total flux of hydrogen is zero deep in the bulk. Moreover, instantaneous local charge neutrality is assumed both in the bulk and at the surface.

The unknown parameters can be determined by fitting the calculated hydrogen profiles on experimental results. For this purpose, we used here the published SIMS results of Johnson and co-workers for silicon deuterated at 150°C (Refs. 3, 4, and 10). Since in this case the total bulk hydrogen concentration largely exceeds the dopant concentration, the experimental profile obtained on an n -type sample with $[P]^{tot} = 2 \times 10^{14} \text{ cm}^{-3}$ (deuteration time of 10 min) was used to determine the parameters controlling the H_2 molecule formation. In a first attempt, any extra trapping was neglected ($[T]^{tot} = 0$) and D_{H^0} was extrapolated from VWV data corrected by the $\sqrt{2}$ isotopic effect, i.e., $D_{H^0} = 1.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. As shown in Fig. 1 (solid line), a very good fit is obtained with $r_{H_2} = 2 \text{ \AA}$ and $k'_{H_2} = 0$ (stable molecules), with the exception of the near-surface region. The value obtained for the capture radius r_{H_2} , of the order of the interatomic distance, is quite reasonable and indicates that the kinetics of H^0 dimerization at 150°C can be described with a diffusivity consistent with the high-temperature data.

For this low-doped sample it has been verified that the calculated hydrogen profile is independent of the other parameters (E_a , E_d , D_{H^-} , D_{H^+} , k'_{PH}) as long as H^0 is the dominant species. As a consequence, it is not possible to describe the near-surface region without altering the profile shape in the bulk, and thus we conclude that the high-concentration region is due to extra trapping on hydrogenation-induced defects. This interpretation is in agreement with the observation of Johnson and co-workers who reported the existence of hydrogen-stabilized platelets or microcracks within 0.1 μm of the exposed sur-

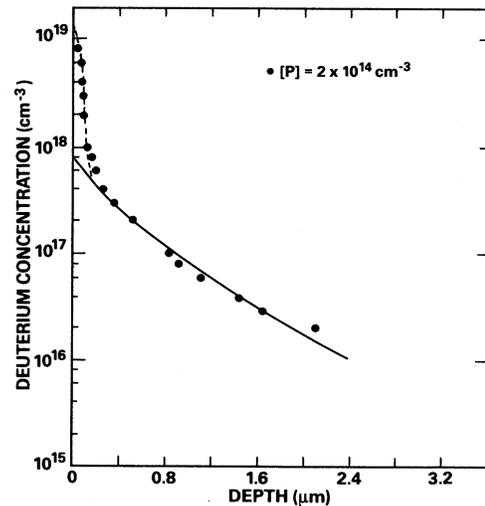


FIG. 1. Comparison between calculated and experimental deuterium profiles in low-doped n -type Si and 150°C (10 min; $n = 2 \times 10^{14} \text{ cm}^{-3}$). Solid line: without trapping on surface defects. Dotted line: with trapping on surface defects.

face, in both *n*- and *p*-type hydrogenated silicon.¹⁰ Here, this perturbed layer is empirically described by an initial trap profile with a Gaussian shape ($[T]_{\text{tot}} = [T]_0 \times \exp[-x^2/L^2]$). As shown by the dotted line of Fig. 1, an excellent fit is then obtained with $[T]_0 = 1 \times 10^{19} \text{ cm}^{-3}$, $L \approx 600 \text{ \AA}$, and a capture radius $r_{\text{TH}} = 5 \text{ \AA}$. This fit is obtained with nearly the same surface concentration $[H^0]_s$, as used previously. This indicates that the surface trapping does not influence the behavior of H^0 in the bulk sample (in fact, with the parameter we used, a total saturation of the traps by hydrogen is achieved in a time negligible with respect to the hydrogenation duration). Moreover, it is likely that the value of the effective surface concentration, which has to be taken into account in the simulation, is the result of a quasiequilibrium between the external phase (plasma) and the highly perturbed surface layer.

Good fits such as those shown in Fig. 1 assuming perfectly stable H_2 molecules ($k'_{H_2} = 0$) can, in fact, be obtained as long as k_{H_2} is lower than about $5 \times 10^{-4} \text{ s}^{-1}$. Assuming an attempt frequency of 10^{13} s^{-1} , this leads to a lower-limit value of 1.4 eV for the dissociation energy of H_2 in agreement with the theoretical predictions.^{1,9}

The fits obtained for the other conditions of dopant type and concentration are shown in Figs. 2 and 3. Depending on the samples, these fits were obtained with maximum trap concentrations $[T]_0$ varying from $1 \times 10^{19} \text{ cm}^{-3}$ to $1.5 \times 10^{20} \text{ cm}^{-3}$, with distribution widths L nearly constant, ranging between 500 and 600 \AA . The fitted surface concentrations of neutral hydrogen exhibit only small variations from sample to sample ($1.5 \times 10^{14} \text{ cm}^{-3} \leq [H^0]_s \leq 8 \times 10^{14} \text{ cm}^{-3}$) which can be easily explained by some small variations of the plasma parameters among the different hydrogenation treatments.

In the case of the most doped samples, good fits such as those shown in Fig. 2 can be obtained with various sets of parameters. For example, starting with a convenient set of parameters, a change of E_d towards the conduction

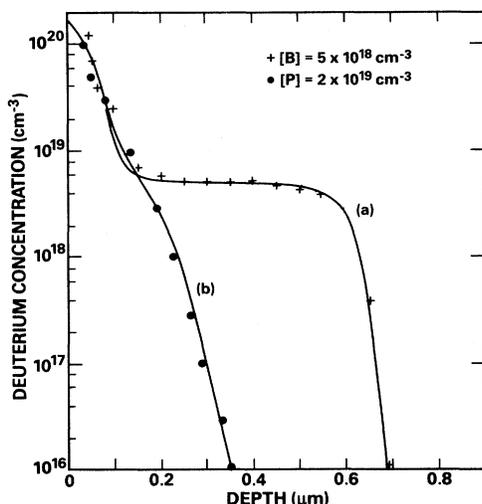


FIG. 2. Comparison between calculated and experimental deuterium profiles in highly doped Si at 150 °C. (a) $p = 5 \times 10^{18} \text{ cm}^{-3}$; 30 min; (b) $n = 2 \times 10^{19} \text{ cm}^{-3}$; 10 min.

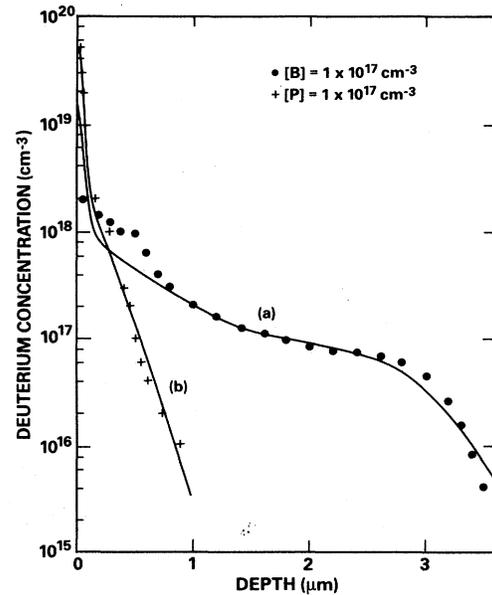


FIG. 3. Comparison between calculated and experimental deuterium profiles in medium-doped Si at 150 °C. (a) $p = 1 \times 10^{17} \text{ cm}^{-3}$; 60 min; (b) $n = 1 \times 10^{17} \text{ cm}^{-3}$; 10 min.

band (of E_d towards the valence band) can be compensated by a decrease of D_{H^+} (D_{H^-}) and a corresponding change of k'_{BH} (k_{PH}) in order to maintain about the same level of dopant passivation, i.e., $k_{BH}[H^+]/k'_{BH}$ ($k_{PH}[H^-]/k_{PH}$) nearly constant. Thus, it is clear that a single fit performed in the highly doped case [as done by CM (Ref. 6)] does not allow an accurate determination of the physical parameters governing the hydrogen behavior in Si. Nevertheless, more information concerning this behavior in *p*-type material can be obtained by simulations of hydrogen profiles in medium doped Si. Indeed, it is found that the shape of the calculated profiles for $[B]_{\text{tot}} = 1 \times 10^{17} \text{ cm}^{-3}$ strongly depends on the position of the donor level. In fact, the strong decrease of the hydrogen concentration in the bulk of the sample (indicative of a rather strong interaction with the dopant atoms) can be simulated only if the donor level is sufficiently far from the valence band, i.e., for high relative concentrations of $[H^+]$. The result presented in Fig. 3 corresponds to the limit case, i.e., to the closest possible position from the valence band (associated with the highest possible values of D_{H^+}) allowing simultaneous fits for $[B]_{\text{tot}} = 1 \times 10^{17} \text{ cm}^{-3}$ and $[B]_{\text{tot}} = 5 \times 10^{18} \text{ cm}^{-3}$. The values used for the calculation are $D_{H^0} = 1.4 \times 10^{-8} \text{ cm}^{-2} \text{ s}^{-1}$ and $r_{H_2} = 2 \text{ \AA}$ (as determined previously in the low-doped samples), and $E_c - E_d = 0.52 \text{ eV}$, $D_{H^+} = 6 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$, and $k'_{BH} = 0.4 \text{ s}^{-1}$. Thus it appears that good fits can be obtained only with the donor level above the intrinsic Fermi-level position, and with a very low H^+ diffusivity.

On the other hand, it was found that good fits of the existing hydrogen profiles in *n*-type Si are possible for any position of the acceptor level, and an unambiguous determination of the parameters in *n*-typed Si is not possible on the basis of these profile simulations alone. The fits presented in Figs. 2 and 3 are obtained with a further as-

sumption. In fact, in hydrogenated samples Johnson *et al.* reported the existence of two deep levels at $E_c - 0.06$ and $E_c - 0.51$ eV, associated with a single-defect center.¹⁰ Due to the similarity with the value of 0.52 eV that we determined for $E_c - E_d$, we make the suggestion that the levels observed by Johnson *et al.* could be the H donor and acceptor levels, and thus the fits presented in Figs. 2-3 are for $E_c - E_a = 0.06$ eV. The values for the other parameters are then $D_{H^-} = 3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and $k_{PH} = 0.3 \text{ s}^{-1}$. If one assumes an attempt frequency of about 10^{13} s^{-1} , the fitted values of k'_{BH} and k'_{PH} correspond to a dissociation energy of about 1.13 eV for the dopant hydrogen pairs, in agreement with the upper limit of 1.2 eV determined by Deicher *et al.* for the BH pair.¹¹

Since the simulations were performed at a unique temperature, it is not possible to extract any direct information on the migration energy barriers of H in its various charge states. Nevertheless, some comments can be made on this subject. First, it is pointed out that, because of the rather low temperature, small changes in the migration energies lead to rather high variations of the absolute diffusivities. For example, the calculated ratio D_{H^-}/D_{H^0} corresponds to an energy difference of only 0.14 eV. Such a low difference between the migration energies of H^- and H^0 turns out to be consistent with the theoretical es-

timations of Ref. 9. On the other hand, the theoretical calculations predict a lower migration energy for H^+ than for H^0 or H^- (Refs. 9 and 12). Thus, the fact that D_{H^+} is found to be significantly lower than both D_{H^0} and D_{H^-} is rather surprising. However, such a result is a common feature of all the simulation models proposed so far.^{6,7} A tentative explanation could be that H^+ encounters some other interactions which are not properly taken into account in the model, so that the extracted value of D_{H^+} is only an effective value. However, much more investigation is needed to elucidate this point.

In conclusion, we have presented a model which allows good simulations of the diffusion of H in Si at 150°C for various dopant types and concentrations. In lightly doped samples a comprehensive description of the behavior of neutral hydrogen is obtained with parameters consistent with the high-temperature data. In more doped samples the situation is more complex; although the model is able to describe quantitatively the diffusion of hydrogen and its interactions with the dopant atoms, the extracted parameters are not unique, and thus more systematic fits on numerous hydrogen profiles obtained with various experimental conditions (doping, temperature) will be necessary to be able to extract the physical values of the parameters.

¹S. J. Pearton, J. W. Corbett, and T. S. Shi, *Appl. Phys. A* **43**, 153 (1987).

²A. Van Wieringen and N. Warmoltz, *Physica* **22**, 849 (1956).

³N. M. Johnson and M. D. Moyer, *Appl. Phys. Lett.* **46**, 787 (1985).

⁴N. M. Johnson, C. Herring, and D. J. Chadi, *Phys. Rev. Lett.* **56**, 769 (1986).

⁵S. T. Pantelides, in *Defects in Semiconductors*, edited by H. J. von Bardeleben, Materials Science Forum Series, Vol. 10-12 (Trans. Tech. Publications, Aedermannsdorf, Switzerland, 1986), p. 573.

⁶M. Capizzi and A. Mittiga, *Appl. Phys. Lett.* **50**, 918 (1987).

⁷J. T. Borenstein, D. Angell, and J. W. Corbett, in *Characterization of the Structure and Chemistry of Defects in Materials, Fall 1988*, edited by B. C. Larson, M. Ruhle, and D. M.

Seidman, Materials Research Symposia Proceedings, Vol. 138 (Materials Research Society, Pittsburgh, in press).

⁸N. M. Johnson and C. Herring, in *Defects in Semiconductors 15*, edited by G. Ferenczi, Materials Science Forum Series, Vol. 38-41 (Trans. Tech. Publications, Aedermannsdorf, Switzerland, 1989), p. 961.

⁹C. G. Van de Walle, Y. Bar-Yam, and S. T. Pantelides, *Phys. Rev. Lett.* **60**, 2761 (1988).

¹⁰N. M. Johnson, F. A. Ponce, R. A. Street, and R. J. Nemanich, *Phys. Rev. B* **35**, 4166 (1987).

¹¹M. Deicher, G. Grübel, R. Keller, E. Recknagel, N. Schulz, H. Skudlik, and Th. Wichert, in Ref. 8, p. 1045.

¹²P. Deak, L. C. Snyder, and J. W. Corbett, *Phys. Rev. B* **37**, 6887 (1988).