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Hydrogen diffusion in crystalline semiconductors

S.J. Pearton[a], J.W. Corbett[b] and J.T. Borenstein[c]
[a] *AT&T Bell Laboratories, Murray Hill, NJ 07974, USA*
[b] *State University of New York, Albany, NY 12222, USA*
[c] *Mobil Solar Energy Corporation, Billerica, MA 01821, USA*

The diffusion of hydrogen in semiconductors is complicated by the existence of several charge states (notably H^+ in p-type material and H^- or H^0 in n-type material, at least for Si) and also that hydrogen is present in a number of different forms, namely atomic, molecular or bound to a defect or impurity. Since the probability of formation of these different states is dependent on the defect or impurity type and concentration in the material and on the hydrogen concentration itself, then the apparent hydrogen diffusivity is a function of the sample conductivity and type and of the method of hydrogen insertion. Under conditions of low H^+ concentration in p-type Si, for example, the diffusivity is of the order of $10^{-10}\,cm^2\cdot s^{-1}$ at 300 K and is consistent with the value expected from an extrapolation of the Van Wieringen and Warmoltz expression $D_H = 9.4\times10^{-3}\exp[-0.48\,eV/kT]\,cm^2\cdot s^{-1}$. The characteristics of hydrogen diffusion in n- and p-type Si and GaAs are reviewed in this paper, and the retardation of hydrogen permeation by molecular formation and impurity trapping is discussed. The measurement of several key parameters, including the energy levels for the hydrogen donor and acceptor in Si and the diffusivity of the H^0 and H^- species, would allow a more quantitative treatment of hydrogen diffusion in semiconductors.

1. Introduction

While there has been a tremendous amount of experimental and analytical work on the formalism of hydrogen diffusion in metals [1], and particularly on the trapping, diffusion and release of hydrogen (tritium) from fusion reactor containment walls [2], there has been much less effort on hydrogen diffusion in semiconductors. There are many similarities between hydrogen motion in metals and semiconductors, with the hydrogen diffusing rapidly between interstitial sites. As an example, hydrogen in vanadium has a diffusion coefficient greater than $10^{-5}\,cm^2\cdot s^{-1}$ for temperatures above 200 K, a value typical of atomic diffusion in liquids. The activation energy for diffusion of H in V is very low (~45 meV), whereas in semiconductors it is more usually in the 0.5–1 eV range. In metals, the dependence of the diffusivity on hydrogen isotope mass is much different from that expected from thermally activated processes, and requires a quantum mechanical treatment at low temperatures. In this regime hydrogen atoms migrate by coherent tunnelling, whereas at higher temperatures phonon interactions promote a range of other migration paths ranging from thermally activated tunneling to excited state transitions to thermally excited over-the-barrier jumps and finally to fluid-like motion [1]. Usually, therefore, a number of different slopes are observed in the Arrhenius plot of the diffusion coefficient of hydrogen in a metal.

A further similarity between hydrogen diffusion in metals and semiconductors is the fact that the presence of traps for hydrogen will reduce the apparent diffusivity leading to an effective diffusion coefficient [1]:

$$D_{EFF} = D_H\left[\frac{T_F}{T_B + T_F}\right], \qquad (1)$$

where T_F and T_B are the average time the hydrogen spends in a free or bound state, respectively. Since these are proportional to the concentration of hydrogen atoms in free and bound states

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($[H_F]$ and $[H_B]$), then

$$\frac{T_B}{T_F}=\frac{[H_B]}{[H_F]}=\left(\frac{[H_B]}{[H_F]}\right)_0\exp\left(\frac{E_B}{kT}\right), \tag{2}$$

where E_B is the binding energy of the hydrogen traps. We then obtain

$$D_H=D_{EFF}\left(\frac{[H_B]}{[H_F]}\right)_0\exp\left[\frac{E_B-E_a}{kT}\right], \tag{3}$$

where E_a is the activation energy for hydrogen diffusion. Wert and Frank [3] have shown that the apparent diffusion coefficient falls off rapidly, with a sub-linear dependence at low temperatures, as a function of either trap concentration or trap binding energy.

There are a variety of conditions under which one can define an effective diffusion coefficient, but it may be a misleading concept in that it implies that the diffusion profile will be described by the appropriate solution of the normal diffusion equation with the diffusion coefficient replaced by D_{EFF}. That conclusion is not correct and in many cases important in semiconductors the diffusion profile is not the normal solution. In this paper we will review the experimental results for hydrogen diffusion in n- and p-type Si and GaAs.

2. Diffusion profiles

Normal diffusion of hydrogen in a material satisfies Fick's equation

$$\frac{\delta}{\delta t}[H]=\nabla(D\cdot\nabla)[H]. \tag{4}$$

If the diffusion coefficient is independent of position, the one-dimensional equation is

$$\frac{\delta}{\delta t}[H]=D\frac{\delta^2}{\delta x^2}[H], \tag{5}$$

with solution

$$[H]=[H_0]\operatorname{erfc}\left[\left(\frac{x^2}{4Dt}\right)^{1/2}\right]. \tag{6}$$

The mean diffusion distance x is given by $(4Dt)^{1/2}$. Hydrogen in a semiconductor may be charged and may diffuse in the presence of an electrostatic potential or an electric field, giving use to an additional force term in the diffusion equation.

For the case of trapping hydrogen by the formation of molecules

$$[H]+[H]\xleftrightarrow{B_2\ K_2}[H\cdot H], \tag{7}$$

with

$$K_2=4\pi D\ R(H\cdot H), \tag{8}$$

and

$$B_2=\nu_2\exp\left(\frac{-E_2}{kT}\right). \tag{9}$$

In these equations $R(H\cdot H)$ is the capture radius for molecule formation, ν_2 is the vibrational frequency for dissociation of H_2 and E_2 is the binding energy of H_2. Now the total hydrogen concentration $[H_T]$ is given by

$$[H_T]=[H]+2[H\cdot H], \tag{10}$$

and for negligible dissociation of H_2 we obtain

$$D_{EFF}=\left(\frac{[H]}{[H_T]}\right)D. \tag{11}$$

In this regime the diffusion of free hydrogen is again Fickian and has an erfc solution provided one uses D_{EFF}. The profile of the molecules will be related to be square of the erfc profile. In the steady state regime with $\delta/\delta t\,[H]\simeq 0$,

$$[H]=\frac{[H_0]}{(1+\beta x)^2}, \tag{12}$$

where

$$\beta=\left(\frac{K_2[H_0]}{6D}\right)^{1/2}. \tag{13}$$

A similar result to eq. (11) is obtained for trapping of hydrogen at an impurity assuming local equilibrium. Where there is no dissociation of the resulting complex, once all the traps are saturated the diffusion is Fickian with D the appropriate diffusion coefficient, rather than D_{EFF}. Further, in the steady state regime

$$[\mathrm{H}] = [\mathrm{H}_0] \exp\left[\frac{\pi R(\mathrm{X},\mathrm{H})[\mathrm{X}] \cdot x}{Dt}\right]^{1/2} . \qquad (14)$$

It has been suggested by Corbett and co-workers that many experimental profiles for hydrogen in Si are suggestive that more than one hydrogen can interact with an impurity. Two approaches have been considered:

(i) multiple trapping of hydrogen,

(ii) a pick-off process in which a second hydrogen removes a trapped hydrogen, forming a molecule. For the multiple trapping case at steady state, a similar solution to eq. (14) is obtained if all of the capture radii are assumed equal. Borenstein et al. [4] found a capture radius of 40 Å for the process

$$\mathrm{H}^+ + \mathrm{B}^- \rightarrow (\mathrm{H} \cdot \mathrm{B}) , \qquad (15)$$

and capture radii of 4 Å for the reactions

$$\mathrm{H} + (\mathrm{H} \cdot \mathrm{B}) \rightarrow (\mathrm{B} \cdot \mathrm{H} \cdot \mathrm{H}) , \qquad (16)$$

and

$$(n-2)\mathrm{H} + (\mathrm{B} \cdot \mathrm{H} \cdot \mathrm{H}) \rightarrow (\mathrm{B} \cdot \mathrm{H}_n) . \qquad (17)$$

3. Diffusion of hydrogen in Si

The earliest quantitative measurements on hydrogen diffusion in Si were performed by Van Wieringen and Warmoltz [5]. They used two types of cylindrical Si diffusion cells and mass spectroscopic detection of the hydrogen diffused through the cell walls, and were able to determine both the diffusion coefficient and solubility of H over the temperature range 970–1200°C. Basically, a known volume of hydrogen was contained within a Si cylinder and then the apparatus was baked to remove background gases. The mass spectrometer records the permeation (F) of the H through the Si as

$$F = -AD_{\mathrm{H}} \frac{\delta[\mathrm{H}]}{\delta r} \text{ molecules s}^{-1} , \qquad (18)$$

where A is the cell area and $\delta[\mathrm{H}]/\delta r$ is the concentration gradient in molecules per cm^3 per cm thickness of the is cylinder wall. This can be obtained from a solution of Fick's equation for this geometry and hence D_{H} can be inferred. Over the temperature range 970–1200°C the diffusion coefficient for hydrogen was found to be given by [5]:

$$D_{\mathrm{H}} = 9.4 \times 10^{-3} \exp\left[\frac{-0.48 \text{ eV}}{kT}\right] \text{cm}^2 \text{ s}^{-1} . \qquad (19)$$

Based on the small deviations of the hydrogen permeation from a strict square root dependence, it was concluded that hydrogen might be present in at least two forms, as atoms or protons, and bound to another impurity, presumably forming hydrogen molecules.

The only other experiment of comparable quality measuring the diffusivity of hydrogen was reported by Ichimiya and Furuichi [6]. They prepared 150 Ω cm FZ, p-type Si samples in the form of $5 \times 10 \times 2$ mm^3 slabs and heated them in a tritium ambient at 900–1200°C for 1 h. After quenching to room temperature within 3–4 min, the samples were transferred to another ampoule connected to an ionization chamber for detecting tritium evolved from the Si. The ampoule was then heated at various temperatures to measure the diffusivity and solubility of the tritium in Si. The amount of tritium remaining in the slab can be obtained by solving the equation for out diffusion from a slab into a large ambient volume [7]. They found the ^{3}H diffusivity to be given by

$$D_{\mathrm{T}} = 4.2 \times 10^{-5} \exp\left[\frac{0.56 \text{ eV}}{kT}\right] \text{cm}^2 \text{ s}^{-1} . \qquad (20)$$

The frequency factor for hydrogen would be expected to be a factor of $\sqrt{3}$ larger because of the effective mass dependence, not the factor of

230 observed here. Ichimiya and Furuichi postulated that the presence of a thin oxide on the sample during the out-diffusion experiments may have been responsible for the rather puzzling pre-exponential factor.

Plasma hydrogenation experiments are typically performed at temperatures ≤300°C, where the VWW relation would predict very large mean diffusion depths – approximately 11 μm h^{-1} at 300 K and ~1000 μm h^{-1} at 600 K. Direct measurement of the hydrogen (or deuterium) incorporation depths in Si for such exposure temperatures usually show that the hydrogen is present at depths up to two orders of magnitude less than the predicted values, corresponding to diffusion coefficients approximately four orders of magnitude lower than expected from an extrapolation of the high temperature data. Figure 1 shows a compilation of experimentally determined effective diffusivities for hydrogen, together with the values expected using either the VWW or the Ichimiya and Furuichi data.

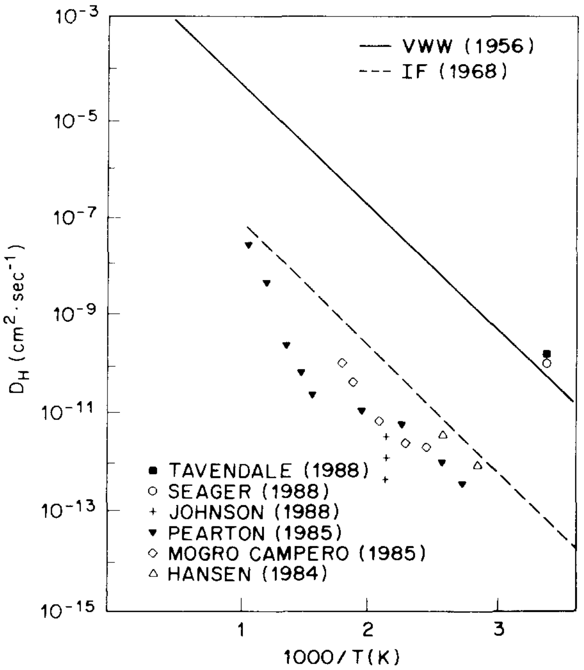

Fig. 1. Compilation of experimental data for effective diffusivities of hydrogen in Si, together with lines representing the Van Wieringen and Warmoltz and Ichimiya and Furuichi data. (After ref. [19].)

The experimental data can be grouped into two types:

(i) under conditions of high hydrogen concentration (plasma injection) the effective diffusivities are considerably lower than would be expected,

(ii) under conditions of dilute hydrogen concentration and where the hydrogen is predominantly in the positive charge state, much higher apparent diffusivities are obtained. Tavendale et al. [8] obtained estimates of D_H between 2×10^{-9}–4×10^{-10} cm^2 s^{-1} for injection at 25°C into p-type Si samples etched in various acid solutions and rapidly contacted in order to perform *C–V* measurements to obtain the boron passivation depth. This is comparable to the values expected from an extrapolation of the VWW relation. Seager and co-workers [9–11] have reported very high hydrogen diffusivities in p-type Si Schottky diodes injected with low energy H$^+$ ions through the contact metallization. This facilitated real time observations of the boron acceptor passivation depth by *C–V* measurements. These data found a significant fraction of the hydrogen to be in a positive charge state after entering the Si, and as a result the negatively charged B acceptors had a high cross-section for hydrogen capture (~10^{-12} cm^2 at 300 K). They obtained a 300 K diffusivity of ~10^{-10} cm^2 s^{-1} for hydrogen injected by implantation through the metal contact, while for insertion by etching in a Bright or Sirtl solution the lower limit was estimated to be ~2×10^{-11} cm^2 s^{-1} (300 K). The key point in all of this is that the H$^+$ state is the one which migrates rapidly in Si.

In the case of injection of hydrogen from a plasma or when the Si is heavily doped, the apparent hydrogen diffusivity is much lower than expected from an extrapolation of eq. (19). This is due to a substantial fraction of the hydrogen being in a bound state (B–H, H$_2$, P–H, depending on the conductivity type). This trapping is clearly observed in highly doped p-type Si, where increasing acceptor concentrations lead to decrease in passivation depth for fixed hydrogenation time. For lower resistivity material this is shown in fig. 2, there the B–H complex concentration in plasma exposed p-type Si was de-

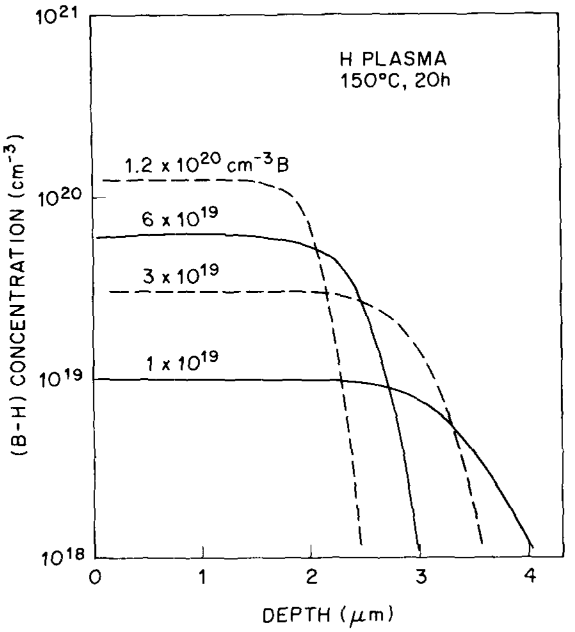

Fig. 2. [B–H] concentration profile as a function of B doping concentration for a fixed H plasma exposure of 20 h at 150°C (from ref. [12]).

termined from an analysis of the infrared reflectance spectra from the samples [12]. It is obvious from this data that the hydrogen diffusion process is trap-limited at these high B concentrations. Moreover, the amount of hydrogen incorporated is determined by the number of available bonding sites, i.e. the B doping level.

Typically the atomic profiles of hydrogen in p-type Si show three regions. first, there is a very shallow, high concentration region ($\geqslant 10^{18}$ cm^{-3}) near the surface of a plasma-exposed sample. This appears to be correlated with the presence of platelets caused by the coalescence of hydrogen or deuterium, with each platelet estimated to contain roughly 400 Si–H bonds [13]. Extending beyond this depth is a region where the deuterium exceeds the doping density of the Si and it has generally been accepted that the deuterium is bonded both to the acceptors (perhaps multiply) and to itself in the form of molecules. These molecules have never been observed directly, but this is the simplest explanation for the optically and electrically inactive,

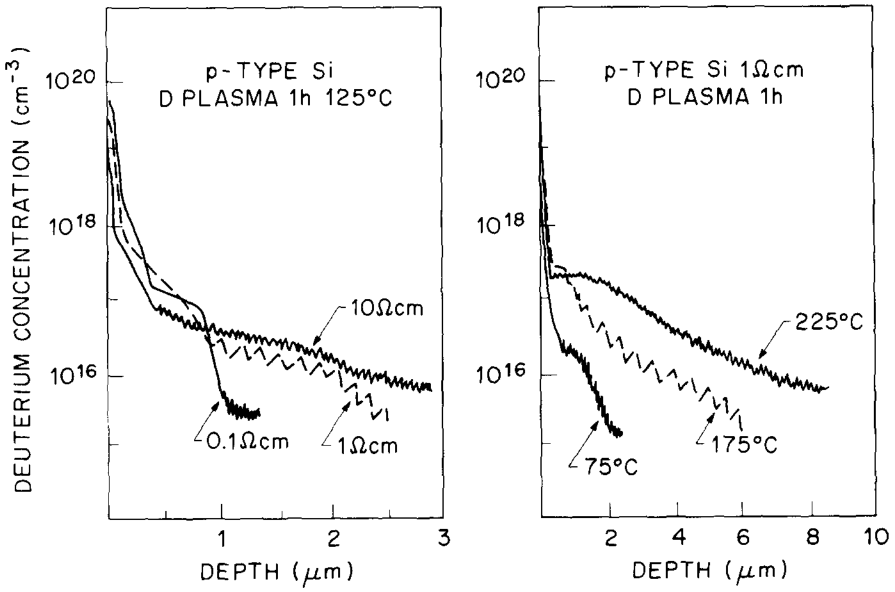

Fig. 3. Atomic profiles of deuterium in p-type Si of different resistivities exposed to a deuterium plasma for 1 h at 125°C (at left), and in 1 Ω cm p-Si as a function of plasma exposure temperature (at right).

relatively immobile hydrogen species present after plasma injection. Channeling data shows two populations of deuterium in plasma-exposed, boron-doped Si in which the near-surface, deuterium rich region has been removed [14]. The majority of the deuterium occupies near bond centered sites, assumed to be boron–deuterium pairs, and the remainder sits close to a tetrahedral interstitial position consistent with the predicted position for deuterium molecules [15, 16]. The third region observed in the deuterium profiles is a relatively flat section in which the deuterium concentration matches that of the acceptor dopant concentration if the latter is high. It is assumed that in this region all of the deuterium is bonded to the acceptor. In highly doped Si the deuterium profile falls sharply beyond this region, whereas in more lightly doped material it shows a more gentle slope. These types of profile are shown for different resistivity boron-doped Si samples in fig. 3, together with profiles in 1 Ω cm material as a function of the temperature of the sample during plasma exposure. In these cases the hydrogen content of the Si is well above the boron concentration and presumably much of it is present in precipitated form (molecules beyond a depth of ~0.5 μm, and platelets in the near-surface region).

Qualitatively similar data are obtained in n-type Si. Figure 4 shows SIMS profiles of deuterium in n-type Si of various resistivities after exposure to a plasma for 1 h at 125°C. At least for resistivities less than 10 Ω cm the diffusion of deuterium is slower than in p-type Si. Since donor passivation is less thermally stable than acceptor passivation (i.e. the hydrogen is less strongly bound to donors than to acceptors), this implies that the predominant hydrogen species in n-type material diffuses slower than the H^+ species in p-type Si. The temperature dependence of the deuterium incorporation depth in 1 Ω cm n-type Si is also shown in fig. 4.

4. Charge states of hydrogen in Si

The question of the charge state of hydrogen in n- and p-type Si has been addressed in a number of studies. It was first established by

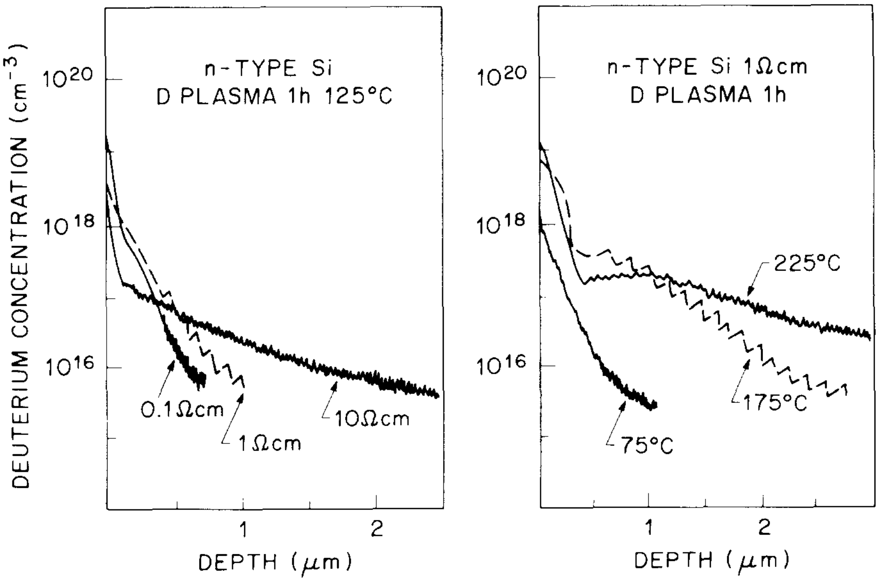

Fig. 4. Atomic profiles of deuterium in n-type Si of different resistivities exposed to a deuterium plasma for 1 h at 125°C (at left), and in 1 Ω cm p-Si as a function of plasma exposure temperature (at right).

Tavendale et al. [17, 18] that hydrogen would drift as a positively charged species under the action of an electric field in the depletion region of a reverse-biased p-Si diode. The redistribution is exactly that expected for the undirectional drift of a positively charged species, with field-dependent trapping. The drift of hydrogen as a positively charged species indicates that it has a donor state (E_D) somewhere near the middle of the band gap. The relative concentration of H^+ and H^0 states will be given by [19]:

$$\frac{[H^+]}{[H^0]} = \tfrac{1}{2} \exp\left(\frac{E_D - E_F}{kT}\right) . \tag{21}$$

An example of changes in the net hole concentration in a hydrogenated p-type Si diode sequentially reverse-bias annealed at 80°C for 6 h at biases of 5 V, 10 V and 20 V is shown in fig. 5.

Johnson and Herring [20] have interpreted the bias-drift experiments to show that the reaction $H^0 + H \rightarrow H_2$ is not as dominant as $H^0 + H^+ \rightarrow H_2 + h^+$, and estimated an upper limit for H_2 diffusion of $\sim 10^{-14}$ cm^2 s^{-1} at 350°C in p-type material with the removal of these molecules occurring primarily by dissociation and subsequent diffusion of H^0 and H^+ rather than by molecular hydrogen motion itself.

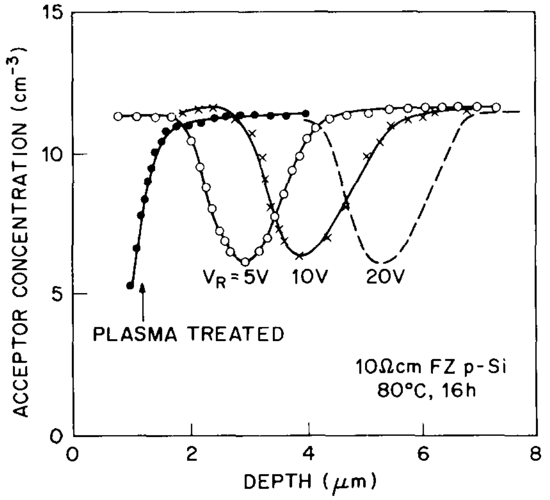

Fig. 5. Net hole concentration profiles in a hydrogenated p-Si diode annealed at 80°C for 16 h at reverse biases of 5, 10 and 20 V (from ref. [8]).

Seager et al. [11] have shown that as a result of this positive charge state for hydrogen in p-type Si, one has to include a drift term to the diffusion equation. For conventional diffusion, the flux of hydrogen is equal to the trapping rate at acceptors,

$$J_H = D_H \frac{[H_s]}{d} = N_A \frac{\delta d}{\delta t} \tag{22}$$

where $[H_s]$ is the surface concentration, N_A is the acceptor concentration and d is the diffusion depth. Then

$$d(t) = \left[\frac{2[H_s]}{N_A} \cdot D_H t\right]^{1/2} . \tag{23}$$

In the case of diffusion and drift in an electric field,

$$J_H = \frac{eD_H E[H^+]}{kT} \tag{24}$$

where the electric field is $E(=(V + V_b)/d$, where V is the applied bias and V_b is the built-in bias). Then

$$d(t) = \left[\frac{2[H_s]}{N_A} \cdot \left[\frac{V + V_b}{kT}\right] \cdot eD_H t\right]^{1/2} . \tag{25}$$

As Seager has pointed out, experimentally it is often observed that the passivation depth proceeds as log(t), rather than $t^{1/2}$ [11].

The question of an acceptor state (H^-) for hydrogen in Si is less firmly established, although two recent publications have provided evidence for such a species based on field-drift experiments similar to those described above for H^+ in p-type Si [21, 22]. Theoretically most groups find an H^- state would occupy a tetrahedral interstitial site, passivating donor impurities. The passivation reaction could then be written as $P^+ + H^- \rightarrow (PH)^0$ in the case of P donors. Figure 6 shows net donor profiles in reverse-bias annealed (V_R = 25 V, 60°C, duration of 14–25 h) Schottky diodes from plasma-deuterated n-type Si. Transport of the donor passivating species across the depletion region and into the bulk is clearly seen as a function of the duration with the reverse

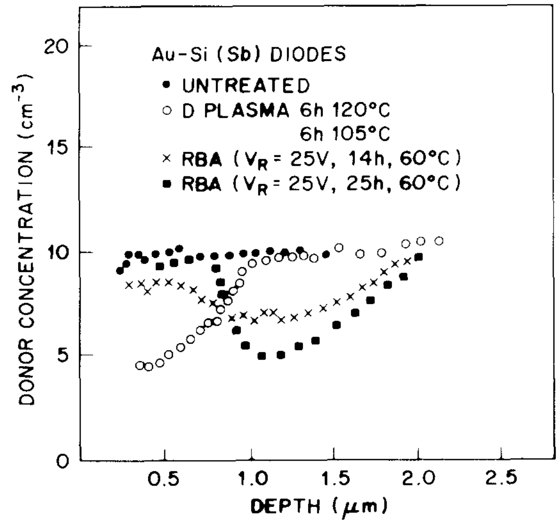

Fig. 6. Net donor profiles in reverse bias annealed (V_R = 25 V, 60°C, duration of 14–25 h) Schottky diodes from plasma deuterated n-type Si.

bias applied. This is in the direction expected for a negatively charged hydrogen species. This species is transported to the low field region of the diode depletion layer opposite the Au Schottky contact. The depletion layer contracts toward this contact as the concentration of the passivating species falls in the near-surface zone with time and the unneutralized donor concentration returns to its original value. As with the results for H^+ drift in p-type Si, it was observed that the mobility of the deuterium passivating species was less than that of the corresponding hydrogen species. This is consistent with both being in a monatomic state. Chemical confirmation of the transport of deuterium was obtained by SIMS measurements. The position of the acceptor level hydrogen in Si is not known, but would be expected to be near the middle of the gap. We should also mention at this point that a competing explanation for the bias-drift experiments has been forwarded by Seager and Anderson [23], involving debonding of the PH pairs in the depletion region, diffusion of the hydrogen as a neutral species, with rebonding to a P ion at greater depths where the debonding rate is suppressed by the lower hole-to-electron ratio. However, the existence of a H^- species seems to be the most plausible explanation for all of the experimental data.

5. Diffusion path for hydrogen

There have been a large number of theoretical investigations on the diffusion path of hydrogen in Si [24–35]. Deák et al. found in agreement with other calculations, that the most stable configuration for hydrogen in undoped or p-type Si is at the bond-centered site, with a calculated heat of solution of 1.98 eV, which is in reasonable agreement with the experimental value of 1.88 eV [24]. The two Si neighbours of the hydrogen are pushed back symmetrically along the ⟨1 1 1⟩ direction line by 0.42 Å, and a three-center bond is formed with the hydrogen located at 1.64 Å from each of the two silicons. The other potential well is centered at 0.42 Å from the T_d site in the ⟨1 1 1⟩ direction, opposite to a Si–Si bond. This is the antibonding site, which is a local minimum about 0.92 eV above the energy of the BC site. In this case, the nearest Si relaxes toward the hydrogen (to a Si–H distance of 1.51 Å) and becomes almost coplanar with its three Si neighbours. There is a strong bonding between the hydrogen and the nearest Si, while the bond between the two silicons along ⟨1 1 1⟩ is greatly weakened.

The study of the diffusion path of atomic hydrogen suggests that at low temperatures when practically all of the hydrogen atoms occupy a BC site, the activation energy for diffusion is 0.84 eV and the hydrogens are essentially trapped. At high temperatures, some part of the total hydrogen concentration may occupy AB-sites, and diffusion may occur with an activation energy of about 0.4 eV via AB-sites. This is comparable with the high temperature experimental value of 0.48 eV.

It is important to note that the bond center of H_2 molecules was found to be stable on the T_d site, with the ⟨1 1 1⟩ and ⟨0 0 1⟩ orientations almost degenerate in energy. The energy per one hydrogen atom in the molecule in 0.12 eV higher than for a single atom at the BC site, implying that the BC site is at least competing with the molecule formation in trapping the hydrogens. Other calculations have predicted the existence of a barrier to molecule formation, even further favoring the BC site over molecule formation.

Amore-Bonapasta et al. [25] have argued that a hydrogen atom at a T_d site sees a high energy barrier toward the BC site and is therefore in a metastable state. At low temperatures the T-hexagonal interstitial site-T path ($E_a = 0.63$ eV in their calculation) appears to play a major role. At higher temperatures there is an increasing population in the BC site, and BC–BC diffusion ($E_a = 1.6$ eV in the calculation of ref. [25]) is dominant. Pennetta [27] found also that a variety of migration paths were possible, with quite different energy barriers. Van der Walle et al. [28, 35] found from density functional calculations that the lowest energy migration path is from BC to C (or M) site to BC site. For the case of hydrogen in a negative charge state in n-type material the migration path is from the AB site to the AB site through the hexagonal site. Deák et al. [33] found that the H^+ species in p-type material is essentially neutralized by the Si lattice, and the diffusion process is then the same for both H^+ and H^0. It is clear that atomic hydrogen is much more mobile than molecular hydrogen. Early calculations by Shi et al. [36] found that H_2 migrates from one T_d site to another via a hexagonal interstitial site with a potential barrier of 2.7 eV. This is much higher than for migration of atomic hydrogen.

All of the calculations on hydrogen molecules predict that the stable site is the T_d position, with the molecule oriented along the $\langle 1\,1\,1 \rangle$ or $\langle 1\,0\,0 \rangle$ axis. Deák et al. [33] found atomic hydrogen to be more stable than H_2 by 0.24 eV per molecule, while Van der Walle et al. [28] and Chang and Chadi [37] found the reverse was true. These latter calculations found H–H separations of 0.86–0.88 Å and binding energies relative to the atomic species at BC sites of 2–3.8 eV per molecule. Doyle and Brice [2] solved general equations for steady state permeation of hydrogen into a substrate material containing N_T traps (which could be impurities or other hydrogen atoms) and obtained an expression for D_{EFF}:

$$D_{EFF} = \frac{D_0}{(1 + N_T \exp(E_b/kT))/\mu N_s}, \tag{26}$$

where E_b is the trap binding energy, μ a constant of order unity, required in order that the local thermodynamic equilibrium between trapped and mobile hydrogen be reached in steady state conditions and N_s is the density of hydrogen solution sites. A complete model for hydrogen diffusion in Si needs not only to consider the immobilization of hydrogen as molecules, but also the trapping at impurity and defect sites. These can be a dominant factor in the permeation of hydrogen in, for example, highly doped p-type Si (acceptor trapping) or amorphous Si (defect trapping). Several experimental studies have shown that the boron passivation depth in p-type Si varies as the square root of the initial boron concentration [38, 39].

The Albany group have calculated the steady state solution for molecule formation (eqs. (7)–(13) and impurity trapping (eq. (14)). In most experimental situations several processes are taking place simultaneously. In no place we know of the features of the diffusion profile have been studied systematically, but the type of diffusion profile described above for the molecule formation regions has been observed in the diffusion of hydrogen in amorphous Si, [40, 41] but it is also true that the nature of such diffusion is more complex in a-Si.

The Albany group has also studied the diffusion profiles generated numerically for the simultaneous diffusion of atomic hydrogen and the formation of immobile trapped hydrogen and of immobile molecular hydrogen. They showed that the trapping case is much as discussed above; the equations can indeed be manipulated to yield the effective diffusion coefficient which for this case is independent of the hydrogen concentration. The profile has an exponential fall-off with distance as long as the hydrogen concentration is less than the trap concentration. When the hydrogen concentration exceeds the trap concentration, a normal erfc profile occurs until the hydrogen concentration falls below the trap density at which point the profile reverts to an exponential fall-off. They also showed that for the molecule formation regime, a normal D_{EFF} does not obtain because the dissociation of the molecules into two hydrogen atoms yields an extra power of the hydrogen concentration, i.e. D_{EFF} is not independent of the hydrogen concentration as would be expected in a normal diffusion equation. The equation can be integrated numerically, however, when the hydrogen concentration is high and the profile discussed above for the molecule regime occurs, and as the concentration of atomic hydrogen falls to the point that molecule formation is negligible, the profile reverts to an erfc.

Capizzi and Mittiga modelled hydrogen diffusion in p-Si assuming a two-flow process of neutral hydrogen diffusion and electric field drift of positively charged hydrogen [26, 32]. The latter is analogous to the drift of Li in Si, and in p-type material the concentration of the hydrogen will be self-regulated by the field to be equal to the acceptor concentration. An activation energy for neutral hydrogen diffusion of 1.2 eV was obtained, while a value of 0.8 eV was calculated for motion of H^+. Mathiot [42] introduced a model for diffusion of hydrogen in n- and p-type Si which explicitly assumes the existence of three charge states H^0, H^+ and H^- and of the formation of H_2. The ionized hydrogen atoms were assumed to form neutral complexes with acceptors and donors, and to form molecules. A term was introduced to account for the trapping of hydrogen at unidentified traps, which was generally necessary only in the near-surface region where platelet formation was significant. The total hydrogen flux was given by Fick's law modified by a drift term to account for the influence of electric fields on the charged species [42]:

$$J_H = -\left[D_{H^0} + \frac{n}{n_a} D_{H^-} + \frac{n_d}{n} D_{H^+} \right] \frac{\delta[H^0]}{\delta x} , \tag{27}$$

where n is the free carrier concentration and n_a and n_d are a function of the acceptor (E_a) and donor (E_d) levels of hydrogen in the gap, i.e.

$$N_a = N_c \exp\left[\frac{-(E_c - E_a)}{kT} \right] , \tag{28}$$

$$N_d = N_v \exp\left[\frac{-(E_v + E_d)}{kT} \right] . \tag{29}$$

The time rate of change of each hydrogen species was solved with the boundary conditions of a constant surface hydrogen concentration, zero hydrogen in the bulk and total instantaneous charge neutrality.

Mathiot [42] was able to fit a variety of experimental hydrogen SIMS profiles in both n- and p-type Si. However, it appears that the fitting may have been in the wrong region of the possible parameter space, because it was found that H^0 diffused faster than H^+, which we have seen earlier to be incorrect.

Buda et al. [43] reported an ab initio molecular dynamics simulation of high temperature proton diffusion in crystalline Si. They found that the diffusion proceeded via a jump-like mechanism, with the most likely path calculated to be from bond-centered to bond-centered sites, passing through an M-site and a hexagonal site. The protons spends most of its time in the high density BC regions and makes forays out into the low density Hex sites many times before actually transferring to another BC site. Another path for motion was from one antibonding site to another via T_d or Hex sites.

6. Summary of diffusion behavior in Si

(i) In p-type Si hydrogen is predominantly present as H^+. The H^+ will passivate the ionized acceptors by Coulombic attraction to form a neutral complex. The H^+ diffuses rapidly ($\sim 10^{-10}\,\mathrm{cm}^2 \cdot \mathrm{s}^{-1}$ at room temperature) and drifts in the electric field set up in the near-surface region of the Si. Depending on the sample temperature and doping conditions, the diffusion of the H^+ may be either strongly or weakly impeded by trapping at acceptor ions. At high temperatures ($\geq 500°C$) most of the diffusion is by rapid interstitial motion that is unimpeded by either acceptor trapping or molecule formation.

(ii) In n-type Si the mobile species (a mixture of H^- and H^0 depending on the doping density) moves much more slowly than the H^+ species in p-type Si. At low temperatures (<150°C) donor-Si–hydrogen bonds can form impeding the hydrogen motion and passivating the donor electrical activity. Even at relatively high donor concentrations, a large excess of hydrogen over the donors can be present.

(iii) Molecule formation occurs through hydrogen association reactions such as $H^0 + H^0 \rightarrow H_2$, $H^0 + H^+ \rightarrow H_2 + h^+$, $H^0 + H^- \rightarrow H_2 + e^-$. The molecules are much less mobile than the atomic species, and generally break up rather than diffuse. The H_2 species in n-type Si appears to move faster than the related species in p-type material, suggesting a different microstructure for the former [19].

7. Diffusion in GaAs

Very little quantitative data exists for the diffusion and solubility of hydrogen in GaAs and other compound semiconductors. Zavada et al. [44] from SIMS profiling of proton implanted n-GaAs as a function of heat treatment in the range 200–600°C determined the diffusivity to be

$$D_H = 1.5 \times 10^{-5} \exp\left[\frac{-0.62\ \text{eV}}{kT}\right] \text{cm}^2\,\text{s}^{-1}\,. \quad (30)$$

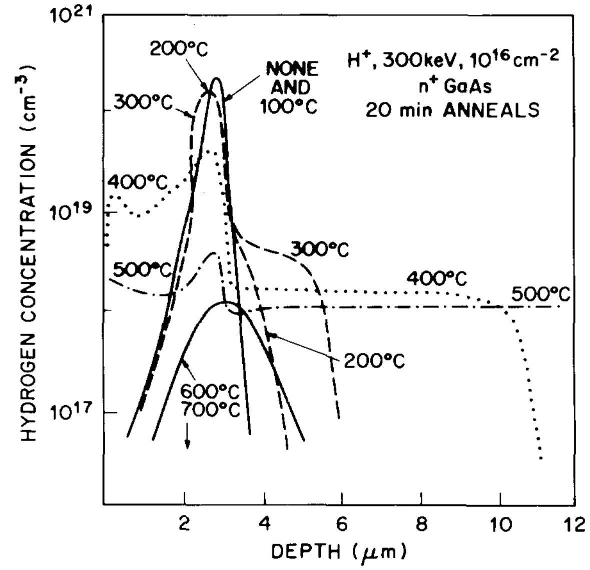

Fig. 7. Hydrogen profiles in implanted (^{1}H, 300 keV, 1×10^{16} cm^{-2}) n^+ GaAs as a function of 20 min anneals up to 700°C (from ref. [44]).

These results were obtained in material with a donor concentration of 3×10^{18} cm^{-3} in which hydrogen trapping would be significant. Omeljanovsky et al. [45] found in semi-insulating GaAs that

$$D_H = 2 \times 10^{-2} \exp\left[\frac{-0.83\ \text{eV}}{kT}\right] \text{cm}^2\,\text{s}^{-1}\,, \quad (31)$$

with little difference in slightly n- or p-type material.

The substantial differences in effective diffusivity of hydrogen reported by various authors is undoubtedly a result of the sensitivity of this parameter to the experimental conditions. Specifically Dautremont-Smith [46] has given an extensive review of the properties of hydrogen in III–V semiconductors, especially the effect of dopant concentration, conductivity type and the type of plasma exposure on the diffusion depth of hydrogen. For similar doping levels diffusion is always greater in p-type GaAs, and low frequency H_2 plasmas directly exposed to the sample produce the greatest permeation depth.

Tavendalé et al. have reported bias-drift experiments showing the presence of H^+ in p-type GaAs [47]. Comparable experiments to detect the presence of H^- in n-type GaAs have not yet been reported. There are very few data on hydrogen diffusion in other materials [48, 49] and the only report of a diffusion coefficient for hydrogen in a III–V compound other than GaAs is for GaP [50]:

$$D_H = 2.3 \times 10^{-2} \exp\left[\frac{-1.11\ \text{eV}}{kT}\right] \text{cm}^2\,\text{s}^{-1}\,, \quad (32)$$

in the range 200–500°C.

8. Summary

The diffusion of hydrogen in semiconductors bears many similarities to its diffusion in metals, with rapid interstitial migration of the atomic species and the concept of an effective diffusivity because of the presence of trapping sites for hydrogen. These can include crystalline defects, other hydrogen atoms or agglomerates of hydrogen, and impurity atoms, whether they be dopant ions or contaminating impurities. There is considerable complexity associated with the diffusion of hydrogen because of these factors, although reliable experimental data now exist for many cases in Si and GaAs. The presence of several possible charge states for hydrogen gives an explanation for its more rapid migration in p-type semiconductors than in n-type material.

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