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Hydrogen diffusion in *a*-Si:H: Solution of the tracer equations including capture by exchange

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We propose a model of trap-controlled diffusion in which diffusing atoms can be captured either by trapping at an empty trap or by exchange with chemically identical trapped atoms of different isotope number. We solve the model's equations describing tracer diffusion experiments, and compare the predictions in the cases of dominant exchange and of dominant trapping. Comparison with experiments in *a*-Si:H shows that exchange is the dominant capture mechanism in D tracer diffusion measurements. This allows us to understand the relatively short distance (~200 Å) D travels before trapping. It also reconciles the smoothness of the D tracer diffusion profiles at long times with the existance of deeply bound (> 2.0 eV) H in *a*-Si:H.

I. INTRODUCTION

Hydrogen is crucial in determining the electronic density of states and the growth mechanism in hydrogenated amorphous silicon (*a*-Si:H). Many researchers have also proposed that H motion is connected with metastability effects in *a*-Si:H.[1] Direct tests of the metastability proposal are only possible if the mechanism of H diffusion is well understood.

Short-time tracer diffusion experiments[2,3] suggest that the motion of H proceeds rapidly through transport states, and that diffusion is limited by trapping and thermal emission due to a single-trapping level. We previously analyzed[4] this trap-controlled diffusion model for a D tracer experiment, and have shown that it is consistent with the observed exponential wings of the tracer concentration profile at short times, and with the ideality of the long-time profiles.[2,3] However, studies of the evolution of H from *a*-Si:H during thermal annealing cast doubts on this interpretation. Evolution experiments suggest that *a*-Si:H has two principal H-trap energy levels (Fig. 1), and not one.[5,6] The first level is located at 1.4 eV below the transport level (shallow trap), and the second at about 2.1 eV (deep trap[5]). This division into two species of trapped H appears even more clearly in the nuclear-magnetic-resonance (NMR) experiments.[7] A broad line associated with "clustered" H, containing about 70% of the H, begins to evolve at 450 °C and disappears after 6 h annealing at 530 °C. The remaining 30% of "isolated" H has a narrow NMR line. Most of this narrow NMR component remains in the film even after the 530 °C anneal. Apparently, the isolated H component corresponds to the deep H level observed by Mahan *et al.*[5]

In tracer diffusion experiments,[3,8,9] a thin, interior, sandwich layer is doped with small quantities of D tracer. After annealing, secondary-ion-mass-spectrometry (SIMS) concentration profiles of the D tracer are analyzed to determine the mechanism of H diffusion and bonding. Because the emission time from a 2.1-eV trap is much longer than typical experimental time scales, deep-trapped tracer atoms cannot be released during these diffusion experiments. This should result in (i) a discontinuity in the long-time D tracer profile due to deeply trapped tracer D atoms, and (ii) saturation of the D density in the deuterated layer at about 30% of the initial D concentration due to deep-trapped D. These predictions are not observed:[10] the long-time profiles are continuous, and the tracer density decreases continuously, without any apparent plateau.[8-10]

The apparent contradiction between the evolution and tracer diffusion data forces us to reexamine the assumptions underlying the simple trap-limited diffusion model. In Sec. II, we present a model of tracer diffusion including H-D exchange.[2,6,11,12] We solve the equations of the

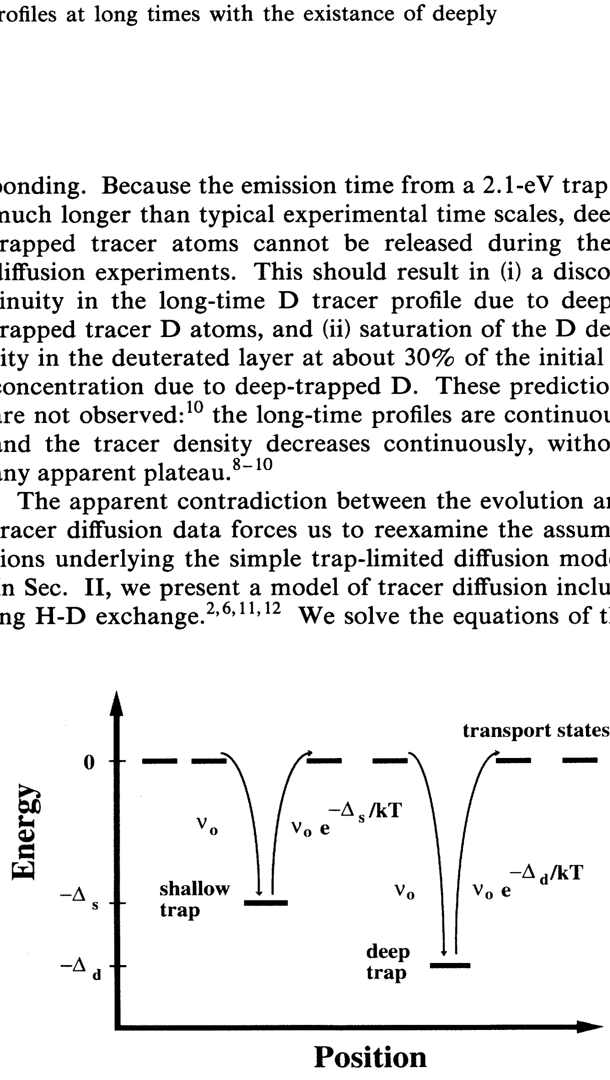

FIG. 1. Schematic diagram of the H density of states for the two-level trap-controlled diffusion model, without exchange. Transitions between transport states occur at a rate ν_0. Trapping can either take a free H to a shallow level located at Δ_s below the transport level, or to a deeper one located at Δ_d. Emission from either traps is an activated process.

exchange model for tracer diffusion in Sec. III, and discuss the solutions in Sec. IV. Comparison of the solutions with experiment shows that the exchange model is consistent with both the D tracer diffusion and with the H evolution data.

II. EXCHANGE MODEL

The trap-controlled diffusion model[4] rests on the assumptions that a diffusing H or D moves freely along a manifold of transport states (interstitials or bond-centered sites) until it encounters an empty trap, and escapes the trap by thermal emission back to this transport level.

As described in the Introduction, the single-trapping model is inconsistent with H evolution data.[5,6] Also, the measured decay length of the early-time exponential wings is only for order 200 Å, which implies an empty-trap density of order 10^{18} cm^{-3}. This is inconsistent with the interpretation that the trapping center is a dangling bond, since there are only about 10^{16}-cm^{-3} neutral dangling bonds in *a*-Si:H at 200 °C.[13]

H evolution data suggests the presence of deeper H levels. If we add deeper-trapping levels to the model, we must also add exchange capture/escape mechanisms to be consistent with the continuous tracer diffusion profiles observed in the long-time regime. Exchange of D for H was first proposed by Abeles *et al.*[11,12] to explain rapid plasma deuteration of *a*-Si:H films. Exchange occurs when a free atom of one species trades places with an atom of another species. Of particular interest to us is that exchange is a substitution mechanism, and because of this, it does not discriminate whether the trapped atom comes from a deep or a shallow level.

In agreement with the H evolution data, we therefore postulate the existence of two types of H traps in *a*-Si:H, shallow and deep (Fig. 1). In reality, these peaks are undoubtedly broadened into a continuous, though not monotomic, density of states. We denote the energies of the shallow and deep traps by Δ_s and Δ_d, respectively. Second, we assume that in addition to H or D capture to an empty trap and thermal emission from the trap, exchange also can also take place between H and D.[14] The various capture and escape processes are all illustrated schematically in Fig. 2. Here, single arrows indicate the movement of H between levels, double arrows indicate the movement of the D tracer atoms. Processes 1 and 2 of Fig. 2(a) correspond to shallow trapping and thermal emission of H. Processes 3 and 4 correspond to deep trapping and thermal emission of H. The corresponding processes for D are shown in Fig. 2(b). Figure 2(c) shows the exchange processes: Process 9 represents D tracer capture by exchange into a shallow level, process 10 represents shallow tracer escape by exchange, process 11 represents D tracer capture into a deep level, and process 12 represents deep D escape by exchange.

We now formulate the equations describing the exchange model. In our notation, subscripts *f*, *s*, and *d* refer to the free, shallow, and deep states, respectively. We define ρ_f, ρ_s, and ρ_d to be the free, shallow, and deep H densities, and θ_f, θ_s, and θ_d to be the free, shallow, and deep D tracer densities. The rate of exchange[11,12] is

$$C\rho_f\theta_t \tag{1a}$$

when a free H atom exchanges with a trapped tracer atom, and is

$$C\theta_f\rho_t \tag{1b}$$

when a free tracer atoms exchanges with a trapped H atom. We call the constant *C* in Eq. (1) the *exchange constant.* For simplicity, we assume that the exchange constant is the same for exchange involving a deep-trapped atom or a shallow-trapped one.

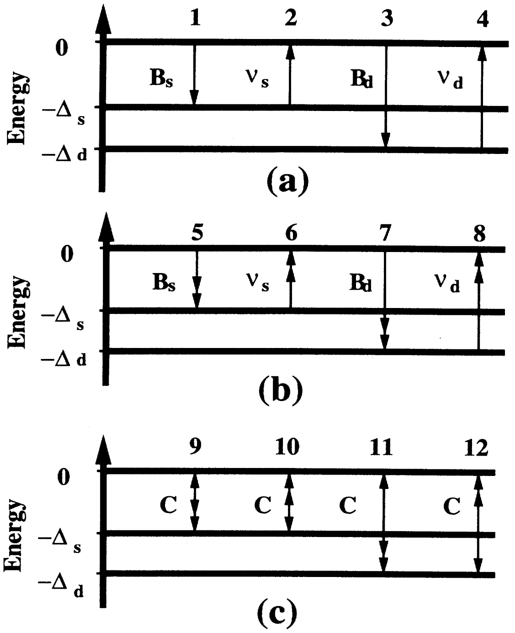

FIG. 2. Capture and escape processes included in the exchange model. Single arrows point in the direction taken by H atoms, and double arrows to that taken by D atoms. (a) and (b) include trapping processes (1, 3, 5, and 7) and thermal-emission processes (2, 4, 6, and 8). (c) includes only exchange processes (9–12). Rates for each process are indicated beside the relevant arrow.

The H concentration evolves according to

$$\begin{aligned}\frac{\partial\rho_f}{\partial t}&=D_f\frac{\partial^2\rho_f}{\partial x^2}-B_s\rho_f+\nu_s\rho_s-B_d\rho_f+\nu_d\rho_d\\&\quad-C\rho_f\theta_s+C\rho_s\theta_f-C\rho_f\theta_d+C\rho_d\theta_f\ ,\\\frac{\partial\rho_s}{\partial t}&=B_s\rho_f-\nu_s\rho_s+C\rho_f\theta_s-C\rho_s\theta_f\ ,\\\frac{\partial\rho_d}{\partial t}&=B_d\rho_f-\nu_d\rho_d+C\rho_f\theta_d-C\rho_d\theta_f\ ,\end{aligned}\tag{2}$$

and the D tracer concentration according to

$$\begin{aligned}\frac{\partial\theta_f}{\partial t}&=D_f\frac{\partial^2\theta_f}{\partial x^2}-B_s\theta_f+\nu_s\theta_s-B_d\theta_f+\nu_d\theta_d\\&\quad-C\theta_f\rho_s+C\theta_s\rho_f-C\theta_f\rho_d+C\theta_d\rho_f\ ,\\\frac{\partial\theta_s}{\partial t}&=B_s\theta_f-\nu_s\theta_s+C\theta_f\rho_s-C\theta_s\rho_f\ ,\\\frac{\partial\theta_d}{\partial t}&=B_d\theta_f-\nu_d\theta_d+C\theta_f\rho_d-C\theta_d\rho_f\ .\end{aligned}\tag{3}$$

Here, D_f is the free H and D diffusion constant, ν_s and ν_d the shallow- and deep-trap emission rates, and B_s and B_d the shallow- and deep-trap capture rates.

Comparison with the single-level trapping model of Kemp and Branz[4] is in order. First, the exchange model has two trap levels, not one. Second, a free D tracer atom can be captured either by trapping to an empty trap (processes 5 and 7 of Fig. 2), or by exchange with either a shallow- (process 9) or with a deep-trapped H atom (process 11). Finally, D tracer can escape from a trap either by thermal emission to the transport level (processes 6 and 8), or by exchange with a free H atom (processes 10 and 12).

III. SOLUTION

A. Reduction of the equations

The situation of experimental interest is this. We consider a sample of *a*-Si:H where H is nearly spatially homogeneous but with a D tracer inhomogeneously introduced into an interior layer. Ideally there are steps in the D tracer concentration, as in the "as-grown" curves of Fig. 3. The sample is then brought rapidly to the annealing temperature T, causing H and D atoms to begin diffusing in the sample.

Five observations can be made that greatly simplify Eqs. (2) and (3). First, we note that the D tracer density is normally much smaller than the H density, even in the deuterated layer. Second, for good samples, one normally finds that the initial H density is spatially constant. Third, deep traps are fully occupied for the duration of the experiment, because the H chemical potential (near the shallow-trap level) is much shallower than Δ_d. Fourth, the energy difference between the shallow level and the transport level, Δ_s, is large compared with kT. Fifth and last, we note that the time for a hop between two transport states is much smaller than the time for emission from either a shallow or a deep trap.

We can now simplify Eq. (2). The first consequence of these observations is that all three H densities are essentially constant: The first observation implies that in Eq. (2), any term that involves the D tracer density can be neglected [processes 9–12 of Fig. 2(c)]. The second observation means that since the free, shallow, and deep H densities are initially spatially constant, they will remain spatially constant for the duration of the experiment. The third observation implies that the deep H density is also time independent, and that processes 3, 4, 7, and 8 of Fig. 2 can be neglected (formally, by setting $B_d=\nu_d=0$). Equation (2) is simplified to

$$\begin{aligned}\frac{\partial\rho_f}{\partial t}&\approx-B_s\rho_f+\nu_s\rho_s\ ,\\\frac{\partial\rho_s}{\partial t}&\approx B_s\rho_f-\nu_s\rho_s\ ,\\\rho_d(t)&\approx\rho_d(t=0)\ .\end{aligned}\tag{4}$$

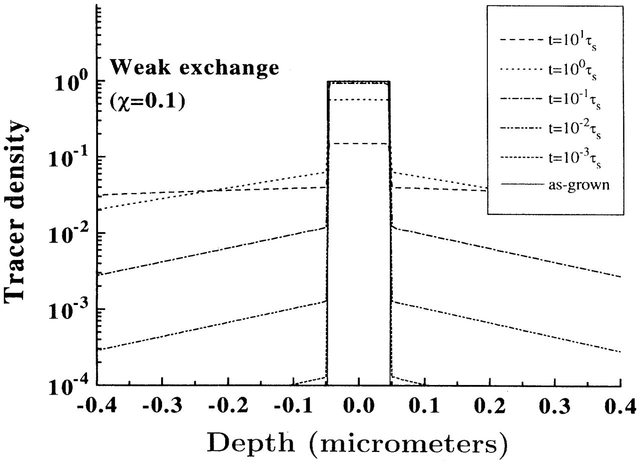

FIG. 3. Time development of the D tracer density for weak exchange. The as-grown tracer profile here is a layer of unit height and 1000 Å width centered around $x=0$ [a symmetric analog of the Eq. (15) profile.] Parameters are $\gamma=\frac{3}{7}$, $\lambda_t=2500$ Å, $\Delta_s=1.4$ eV, and $\Delta_d=2.1$ eV, and time is in units of $\tau_s=1/\nu_s$. At long times, the profiles outside the deuterated layer are ideal, but the tracer density in the step saturates at about 0.3. At short times, the tracer profiles develop exponential tails whose height increases linearly with time.

The first two equations in (4) can be solved fairly simply because of the fourth observation, $B_s\gg\nu_s$. This means that ρ_f and ρ_s reach their steady-state values much faster than the shallow emission time $1/\nu_s$. We therefore replace ρ_f and ρ_s by their steady-state values:

$$\begin{aligned}\rho_f(t)&\approx\frac{\nu_s}{B_s}\rho_s(t=0)\ ,\\\rho_s(t)&\approx\rho_s(t=0)\ .\end{aligned}\tag{5}$$

Having established that ρ_f, ρ_s, and ρ_d are constants, we find from Eq. (3) that the motion of the D tracer can still be described by an effective trapping model *even with exchange processes included.* Using the fact that all three H densities are constant and neglecting all deep trapping and thermal-emission processes, Eq. (3) is reduced to

$$\begin{aligned}\frac{\partial\theta_f}{\partial t}&=D_f\frac{\partial^2\theta_f}{\partial x^2}-(B_s+C\rho_s)\theta_f+(\nu_s+C\rho_f)\theta_s\\&\quad-(C\rho_d)\theta_f+(C\rho_f)\theta_d\ ,\\\frac{\partial\theta_s}{\partial t}&=(B_s+C\rho_s)\theta_f-(\nu_s+C\rho_f)\theta_s\ ,\\\frac{\partial\theta_d}{\partial t}&=(C\rho_d)\theta_f-(C\rho_f)\theta_d\ .\end{aligned}\tag{6}$$

This equation describes an effective trap-controlled diffusion model. Note that all terms that involve H are now constant. Through exchange, H has the crucial effect of changing the values of the effective trap parameters seen by D tracer atoms:

$$\begin{aligned} B_s^{\text{eff}} &= B_s + C\rho_s \ , \\ \nu_s^{\text{eff}} &= \nu_s + C\rho_f \ , \\ B_d^{\text{eff}} &= C\rho_s \ , \\ \nu_d^{\text{eff}} &= C\rho_f \ . \end{aligned} \tag{7}$$

Note in particular that even though deep trapping and thermal emission of D by processes 9 and 12 are negligible, exchange has the effect of making capture and emission from all states nearly equally likely, independent of their energy depth.

A final simplification of Eq. (3) comes from our fifth observation, that the time for a hop between two transport states is much smaller than the time for emission from either a shallow or deep trap. We therefore apply an adiabatic approximation to simplify the first equation in (7) to

$$\left[D_f \frac{\partial^2}{\partial x^2} - B_s^{\text{eff}} - B_d^{\text{eff}} \right] \theta_f = -[\nu_s^{\text{eff}}\theta_s + \nu_d^{\text{eff}}\theta_d] \ . \tag{8}$$

The formal solution of this equation is

$$\theta_f(\theta_s,\theta_d) = \left[B_s^{\text{eff}} + B_d^{\text{eff}} - D_f \frac{\partial^2}{\partial x^2} \right]^{-1} [\nu_s^{\text{eff}}\theta_s + \nu_d^{\text{eff}}\theta_d] \ , \tag{9}$$

(where $[\ ]^{-1}$ denotes the inverse of the operator between the brackets), which expresses the fact that the free tracer density follows the trapped D densities at all times.

Using these observations, the diffusion model embodied by Eq. (2) and (3) now simplifies to

$$\begin{aligned} \frac{\partial\theta_s}{\partial t} &= B_s^{\text{eff}}\theta_f(\theta_s,\theta_d) - \nu_s^{\text{eff}}\theta_s \ , \\ \frac{\partial\theta_d}{\partial t} &= B_d^{\text{eff}}\theta_f(\theta_s,\theta_d) - \nu_d^{\text{eff}}\theta_d \ , \end{aligned} \tag{10}$$

where the effective trap parameters are given in Eq. (7), and the dependence of θ_f on θ_s and θ_d is formally given by Eq. (9).

B. Analytic solution

In order to eliminate the differential operator in Eq. (9), we perform a Fourier transform. The free tracer density θ_f is now explicitly expressed in terms of the trapped tracer densities. Substituting the resulting expression for θ_f in Eq. (10), using $\sqrt{D_f/B_s}$ for the spatial scale and $1/\nu_s$ for the time scale, we obtain

$$\begin{aligned} \frac{\partial\theta_s}{\partial t} &= \left[\frac{1+\chi}{k^2+1+\chi+\gamma\chi} \right] [\chi\theta_d - (k^2+\gamma\chi)\theta_s] \ , \\ \frac{\partial\theta_d}{\partial t} &= \left[\frac{1+\chi}{k^2+1+\chi+\gamma\chi} \right] \chi \left[\gamma\theta_s - \left[\frac{k^2}{1+\chi} + 1 \right] \theta_d \right] \ , \end{aligned} \tag{11}$$

Here, k is the variable of the Fourier transform, and the constants γ and χ are defined by

$$\begin{aligned} \gamma &= \rho_d/\rho_s \ , \\ \chi &= C\rho_s/B_s \ . \end{aligned} \tag{12}$$

γ measures the ratio of deep-to-shallow H densities (and is about $\frac{3}{7}$ in device quality *a*-Si:H). The quantity χ is a measure of the relative importance of exchange and trapping: when $\chi \ll 1$, trapping is more important than exchange but when $\chi \gg 1$, exchange dominates over trapping; for this reason, we call χ the *strength of exchange.*

Equation (11) is now the focus of attention. It is equivalent to Eqs. (2) and (3), modulo the approximations discussed in Sec. III A. Equation (11) consists of two linear equations, and can therefore be solved exactly. The solution is obtained by (i) defining the Green's functions G_s and G_d, as the shallow and deep tracer densities for δ-functions initial tracer profiles, (ii) solving for G_s and G_d in Fourier space, (iii) computing the real-space Green's function

$$G(x,t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk\, e^{ikx} [G_s(k,t) + G_d(k,t)] \ , \tag{13}$$

and (iv) solving for an arbitrary initial D tracer profile $\theta(x,0)$

$$\theta(x,t) = \int_{-\infty}^{\infty} dx'\theta(x',0)G(x-x',t) \ . \tag{14}$$

Note that the free D tracer contribution has been neglected in Eq. (13) because it makes a negligible contribution to the total D tracer profile.

This procedure is general. In what follows, we will assume that the initial tracer profile is a step function:

$$\theta(x,0) = \theta_0 \begin{cases} 1, & x<0 \\ 0, & x>0 \ , \end{cases} \tag{15}$$

where θ_0 is the initial tracer density in the deuterated region.

In the general case, Eq. (11) can be solved exactly. The general solution, however, is complicated enough as to render the inversion of the Fourier transform impossible to perform analytically. A numerical solution is always possible, but is of little use in extracting meaningful conclusions from the model. Despite this, there are two situations where good approximate solutions can be obtained, with the added bonus that they correspond to the situations of physical relevance. The first case is that of times short compared with the shallow emission time. The second case is that of long times, in the limits of small ($\chi \ll 1$) and large ($\chi \gg 1$) exchange.

1. *Early-time profiles*

In the early-time limit ($\nu_s t \ll 1$), the solution to Eq. (13) is

$$\begin{aligned} G(x,t) = {} & \left[\frac{\gamma}{1+\gamma} e^{-\nu_x t} + \frac{1}{1+\gamma} e^{-(\nu_x+\nu_s)t} \right] \delta(x) \\ & + \nu \frac{t}{2\lambda} e^{-|x|/\lambda} \ . \end{aligned} \tag{16}$$

Here, we have defined the decay length

$$\lambda=\frac{\lambda_t}{\sqrt{1+\chi+\gamma\chi}}\ , \tag{17}$$

where $\lambda_t=\sqrt{D_f/B_s}$ is the decay length of the single-level trapping model. We also have defined the effective emission rate

$$\nu=\frac{\nu_s}{1+\gamma}+\nu_x\ , \tag{18}$$

where $\nu_x=\chi\nu_s$ is called the *exchange emission rate.*

The first situation of interest is the case where the D-H exchange can be neglected, $\chi \ll 1$. In this case, λ is equal to the decay length of the single-level trapping model λ_t and ν is equal to the shallow emission rate multiplied by the shallow trap function. Assuming an initial step-function tracer profile [Eq. (15)], the early-time profile without exchange is

$$\theta(x,t)=\theta_0\begin{cases}\left[\dfrac{\gamma}{1+\gamma}+\dfrac{1}{1+\gamma}[e^{-\nu_s t}+\nu_s t(1-e^{-|x|/\lambda_t}/2)]\right] & \text{(inside step)}\\[2ex] \dfrac{\nu_s t}{2(1+\gamma)}e^{-x/\lambda_t} & \text{(outside step)}\ .\end{cases} \tag{19}$$

This solution will be discussed at length in Sec. IV A.

The second situation of interest is where the D-H exchange is more important than trapping, $\chi \gg 1$. For dominant exchange, the decay length is inversely proportional to the square root of the exchange strength: $\lambda\equiv\lambda_x=\lambda_t/\sqrt{\chi(1+\gamma)}$, and the emission rate ν is approximately equal to the exchange emission rate $\nu=\nu_x$. The early-time profile for dominant exchange is

$$\theta(x,t)=\theta_0\begin{cases}e^{-\nu_x t}+\nu_x t[1-e^{-|x|/\lambda_x}/2] & \text{(inside step)}\\ [\nu_x t/2]e^{-x/\lambda_x} & \text{(outside step)}\ .\end{cases} \tag{20}$$

This solution will also be discussed at length in Sec. IV A.

2. *Long-time profiles*

In the long-time limit, explicit results can only be derived in the limits of no exchange and strong exchange. In the absence of exchange ($\chi \ll 1$), we get

$$\theta(x,t)=\frac{\gamma}{1+\gamma}\theta(x,0)+\frac{1}{1+\gamma}\frac{\theta_0}{2}\operatorname{erfc}(x/\sqrt{4\pi\lambda_t^2\nu_s t}\ )\ , \tag{21}$$

and in the limit of dominant exchange ($\chi \gg 1$)

$$\theta(x,t)=\frac{\theta_0}{2}\operatorname{erfc}(x/\sqrt{4\pi\lambda_x^2\nu_x t}\ )\ . \tag{22}$$

The significance of these solutions will be discussed in Sec. IV B.

IV. DISCUSSION

A. Early-time profiles

We first discuss the early-time solution. The early-time Green's function, Eq. (16), is made up of two contributions. The first corresponds to the decay of the tracer density inside the deuterated region, and the second to the development of exponential tails outside. The expression for decay length of the exponential tail λ is given by Eq. (17).

For an initial tracer step profile, the evolution of the tracer concentration in the early-time regime is easily described [Eqs. (19) and (20)]. The height of the initial profile decreases, but its shape is maintained and exponential wings develop outside the initial profile with a decay length λ (Figs. 3 and 4). Such exponential wings

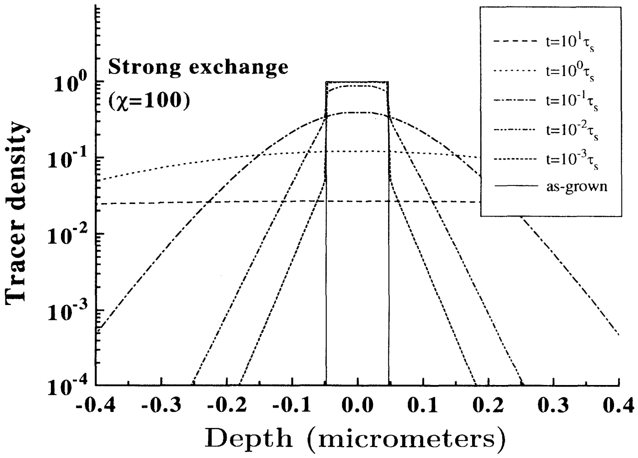

FIG. 4. Time development of the D tracer density of strong exchange. All parameters except χ are the same as for Fig. 3. The step profiles initially develop exponential tails, but their decay length is much smaller here than for weak exchange (Fig. 3). The long-time profiles are ideal, and show no memory of the initial profile. At short times, the tracer density in the deuterated layer decreases continuously, without saturation.

were observed by Branz *et al.*[2,3] In Figs. 3 and 4, we plot the solutions for the case of a sandwich layer of D, 1000 Å thick. This result holds for any well-localized D profile, not only for ideal step profiles.

In the absence of exchange [Eq. (19) and Fig. 3)], the D tracer profile within the step is made up of a time-independent component from the deep-trapped tracer atoms and of a second component that decays with a rate equal to the shallow emission rate. The decay length of the exponential wing is precisely that of the single-level trapping model λ_t. This wing agrees with the trap-controlled result of Kemp and Branz,[4] since in the absence of exchange, only capture to an empty shallow trap and thermal emission from a shallow trap contribute to the wing formation.

In the limit of strong exchange [Eq. (18) and Fig. 4], the deep and the shallow D tracer components of the step decay at the same rate. The decay rate within the step is equal to the exchange emission rate $\nu_x = \chi \nu_s$. The decay length of the exponential tails λ_x is proportional to $\sqrt{1/\chi}$. These results can be understood as follows: since exchange is the dominant capture/release mechanism, and since it does not discriminate shallow from deep traps, then all traps are effectively equivalent. The release rate must then be ν_x, much faster than the shallow emission rate ν_s. The decay length λ_x is inversely proportional to the square root of the capture rate, and is therefore much shorter than λ_t.

Comparison of Figs. 3 and 4 shows that the decay length of the exponential wing is reduced when exchange dominates, but that the wing magnitude (at equal times) is increased. This arises because exchange increases the rates of both D emission and recapture, a result consistent with the principle of detailed balance.

B. Effective diffusion constant

We now discuss the long-time tracer profiles given by Eq. (21) and (22). In the absence of exchange, there are two contributions to the profile (Fig. 3). The first part is associated with the D frozen in deep traps. The second part describes an ideal profile, with effective diffusion constant

$$D_{\text{eff}} = D_t = D_f \nu_s / B_s \ , \tag{23}$$

where D_t is the long-time diffusion constant of the single-level trapping model.[4] As Eq. (21) shows, the frozen fraction that does not diffuse, $\gamma/(1+\gamma)$, is the deeply trapped, frozen, fraction of the tracer. The fraction that diffuses, $1/(1+\gamma)$, is the shallow-trapped fraction.

In the limit of strong exchange, Eq. (22), the long-time profile is ideal (Fig. 4). The effective diffusion constant is

$$D_{\text{eff}} = \frac{1}{1+\gamma} D_t \ . \tag{24}$$

Note that within a factor of order 1, the effective diffusion constant is the same with or without strong exchange, and the activation energy of diffusion is unchanged. This result may be somewhat surprising. Although exchange increases the D emission rate, it also increases the trapping rate. The independence of the diffusion constant on exchange expresses the fact that these two effects cancel each other out. We recall that for the single-level trap-controlled diffusion model, the effective diffusion constant obeys the relation $D_{\text{eff}} = \nu_s \lambda_t^2$. By comparison of Eqs. (17) and (24), we also see that $D_{\text{eff}} = \nu_x \lambda_x^2$ for strong exchange. As we showed above, $\nu_x \propto C$, and $\lambda_x \propto C^{-1/2}$. Thus, by cancellation, D_{eff} is independent of C. This cancellation is a result of the principle of detailed balance.

Another way of explaining the independence of the diffusion constant and the strength of exchange is to note that D_{eff} equals D_f times the ratio of free to trapped H atoms. Here, D_f is the free H diffusion constant. Since the energy gap between shallow trap and transport states is the same in both cases, the density of free H are the same within a factor of order unity. The effective diffusion constants differ only by the ratio of the numbers of trapped H that are able to equilibrate with the transport level.

C. Extraction of diffusion length and of emission rate from experiment

We previously showed[4] how to extract the shallow emission rate from experimental D tracer profiles, assuming the validity of the single-level trap-controlled diffusion model. This method rests on the prediction that in the early-time regime, the height of the exponential tail at the point where the tail meets with the tracer step increases as $\theta_h = \theta_0 \nu_s t/2$. Here, ν_s is the shallow emission rate, θ_0 the step height, and t the measurement time. Hence, the shallow emission rate ν_s is easily obtained from the amplitude of the exponential tail.

Equation (15) shows that a similar procedure also obtains for the exchange model (Figs. 3 and 4). Now, $\theta_h = \theta_0 \nu t/2$, where

$$\nu = \nu_x + \frac{\nu_s}{1+\gamma} \ . \tag{25}$$

One important difference, as we see, is that the presence of exchange implies contributions to the wing amplitude from both the shallow emission rate and from the exchange rate. In the absence of exchange, this use of Eq. (25) yields $\nu = \nu_s/(1+\gamma)$, the shallow emission rate multiplied by the shallow fraction. The denominator arises because the deep-trapped D is frozen in the step region. For dominant exchange, the procedure gives directly the exchange emission rate ν_x.

D. Comparison with experiment

It was previously argued by several authors[6,11,12,15] that exchange must be important in plasma deuteration experiments. In view of our analysis, we now assess the role of exchange in a-Si:H tracer diffusion experiments.

In our model, a free D tracer atom can be captured either by trapping to an empty trap, or by exchange with a trapped H atom. The relative importance of these processes is determined by the ratio of their respective rates. We have defined a quantity χ, called the strength of exchange [Eq. (12)], whose value is given by the ratio of the rate of capture by exchange to the rate of capture by trapping to an empty trap. Our analysis in Sec. III B 1 shows that the measured decay length of the exponential tracer wings depends upon χ. If we call the empty shallow trap density N_e, then using Eq. (17) and the microscopic relations.[4]

$$D_f = 2/3 \nu_0 a^2 \,, \qquad B_s = 4\nu_0 N_e a^3 \,, \tag{26}$$

we get

$$\chi = \frac{1/(6aN_e\lambda^2) - 1}{1+\gamma} \,. \tag{27}$$

Here, a is the Si-Si bond length, ν_0 is the rate of hopping between two transport states, γ is the ratio of deep over shallow trap densities, and λ is the measured decay length of the exponential tracer wings. If we assume that empty shallow traps are dangling bonds, $N_e = 10^{16}$ cm^{-3},[13] and using $a = 3$ Å, $\gamma = 3/7$,[4] and the measured value $\lambda \sim 200$ Å (Branz *et al.*[12,13] $T = 180$ C), we get $\chi \sim 100$.

This value of $\chi \sim 100$ implies that a free D tracer atom is 100 times more likely to exchange with a trapped H atom than it is to be captured to an empty trap (dangling bond). We conclude that exchange, and not trapping, is the dominant capture mechanism in *a*-Si:H tracer experiments.

A test of consistency of this conclusion is provided by comparison of the measured shapes of the early and long-time profiles with the predictions of the exchange model. Our analysis of Sec. III shows that without exchange ($\chi = 0$), the long-time D tracer profiles are discontinuous (Fig. 3). The tracer density within the step initially decreases down to about 30% of the initial value, and then saturates. This leaves a residual step even at long times. However, with dominant exchange ($\chi \gg 1$), the long-time tracer profiles are continuous (Fig. 4). The tracer density within the step decreases continuously, without saturation, and no step is observed at long times.

Experimentally,[2,3,8-10] the long-time profiles are continuous, showing no memory of the initial profile. The early-time decay of the tracer concentration in the central layer is continuous, and shows no indication of plateau formation. These observations are consistent with our conclusion above that exchange is the dominant free-H and -D capture mechanism in *a*-Si:H.

There are important consequences to exchange being the dominant capture mechanism in *a*-Si:H tracer experiments. The first is that tracer and nontracer experiments do not probe the same processes. In a nontracer experiment, exchange processes are irrelevant because a H-H exchange conserves the free H density. Assuming that deep traps are inactive (because they are filled and deep) and that empty shallow traps are dangling bonds, H diffusion is described by the single-level trapping model. In consequence, the mean distance for recapture of a free H atom is $\lambda_t = 1/\sqrt{6aN_e} \sim 2500$ Å, and the emission rate from a trap is given by the shallow emission rate ν_s. In a tracer experiment, the mean distance between capture events is not the single-level trapping length λ_t, but the exchange length $\lambda_x = \lambda_t/\sqrt{\chi(1+\gamma)} \sim 200$ Å, and the relevant emission rate from traps is not the shallow emission rate ν_s, but the exchange emission rate $\nu_x = \chi\nu_s$. The mean distance traveled before capture is about 10 times smaller in the tracer experiment, and the emission in a tracer experiment is 100 times faster than in a nontracer experiment.

A second important consequence of exchange being the dominant capture mechanism, is that it clears up one of the difficulties of the single-level trapping model. Based on the measured decay length of the exponential wings, the single-level trapping model requires an empty-trap density of order 10^{18} cm^{-3}.[2] Since the neutral dangling-bond density is of order 10^{15} cm^{-3} even at 200 °C,[13] this precludes the identification of the empty trapping states with neutral dangling bonds. With strong exchange, this difficulty is avoided, since every H atom can act as a trap for free D through the exchange process.

A third consequence comes from the fact that the measured decay length of 200 Å implies D makes $\sim 10^4$ jumps between two capture events. Since the H density in *a*-Si:H is about 10%, this implies that D visits about 1000 H centers before exchanging with one. This indicates that the probability for exchange when D and H are in contact is of order 10^{-3}.

Finally, we note that the diffusion constant measured by D tracer experiments is comparable with that measured in hydrogen effusion experiments where no tracer is present.[16] In view of our conclusion that exchange dominates tracer experiments, and trapping dominates the nontracer ones, this may seem odd. Clearly, the exchange mechanism is irrelevant to the effusion experiment, because a single atomic species is present. (Only trapping to an empty shallow trap will change the free H density.) However, Eq. (23) shows that, in fact, the diffusion constants for weak and strong exchange are the same (up to a constant of order one). As we discussed in Sec. IV B, the effective diffusion constant depends only on the density of free H, which in the long-time limit is the same in both cases.

E. Temperature dependence of experimental quantities

Several authors have measured the temperature dependence of the effective diffusion constant, and Branz *et al.*[2,3] applied the procedure described in Sec. IV C to the extraction of the temperature dependence of the emission rate. From measurements of this type, one can extract information about the free-carrier diffusion lengths, trap depths, and any barrier to the exchange process.

In this section, we make the assumptions that (i) exchange is the dominant tracer capture mechanism, (ii) that the shallow trapping level is located an energy Δ_s below the transport level, (iii) that exchange requires activation over a barrier Δ_x, and (iv) that the empty shallow-trap density is activated (above the equilibration temperature of 200 °C) with activation energy Δ_e:

$$\begin{aligned} \nu_s(T) &= 4\nu_0 e^{-\Delta_s/kT}\,, \\ C(T) &= C_0 e^{-\Delta_x/kT}\,, \\ N_e(T) &= N_0 e^{-\Delta_e/kT}\,. \end{aligned} \tag{28}$$

Using the microscopic relations Eq. (26), the exchange model predicts that

$$\begin{aligned} \nu &= \frac{C_0 H}{(1+\gamma)N_0 a^3} e^{-(\Delta_s+\Delta_x-\Delta_e)/kT}\,, \\ \lambda &= \left[\frac{2\nu_0 a^2}{3C_0 H}\right]^{1/2} e^{\Delta_x/2kT}\,, \\ D_{\text{eff}} &= \frac{2\nu_0}{3(1+\gamma)aN_0} e^{-(\Delta_s-\Delta_e)/kT}\,. \end{aligned} \tag{29}$$

Here, H is the total hydrogen density, a is the Si-Si bond length, and ν_0 is the rate of hopping between two transport states.

The physical origin of these temperature dependences can be understood from three principles: (i) Exchange dominates the motion of D. (ii) By detailed balance, the free H density is $\rho_f = \nu_s(\rho_s + \rho_d)/B_s$. This density is not affected by the presence of D. (iii) B_s is proportional to the empty shallow-trap density.

1. Emission rate

Since exchange dominates, the rate of release of a free D is equal to the exchange constant C times the free H density. Using (ii) and (iii), the free H density is proportional to the shallow emission rate ν_s and it is inversely proportional to the empty shallow-trap density. Thus, the activation energy of the emission rate is $\Delta_x + \Delta_s - \Delta_e$. Note that unlike emission in the trap-controlled diffusion model, the exchange emission rate is inversely proportional to the empty-trap density.

2. Diffusion length

Regardless of the trapping mechanism, the diffusion length is always inversely proportional to the square root of the capture rate. Since here exchange dominates, the free D capture rate is equal to the exchange constant C times the trapped H density. Assuming the H density is temperature independent, the temperature dependence of λ is determined by that of C only, and has an activation energy of $-\Delta_x/2$. In contrast to the trap-controlled diffusion model, the diffusion length is independent of the empty trap density.

3. Diffusion constant

Regardless of the trapping and emission mechanisms, the diffusion length is always $\nu\lambda^2$. Using the arguments above, the activation energy of the diffusion constant is therefore $\Delta_s - \Delta_e$. Notice that the diffusion constant is independent of the exchange mechanism, and that just like with the trap-controlled diffusion model, it is inversely proportional to the empty-trap density.

Equation (29) suggests that the activation energy of the diffusion constant is $\Delta_s - \Delta_e$. If we assume that empty shallow traps states are dangling bonds, then the measured diffusion activation energy of 1.4 eV and $\Delta_e \sim 0.3$ eV (Ref. 13) imply a shallow H trapping level located at 1.7 eV (not 1.4 eV) below the transport level. Unfortunately, not enough is known about the relation between dangling-bond density and the occupation of the H energy levels to draw a firm conclusion about this consequence of the model.

Equation (29) also shows that the activation energy of the emission rate is larger by Δ_x that of the diffusion constant. It also shows that the diffusion length λ increases with temperature, and the activation energy of this increase is half the barrier to exchange, $\Delta_x/2$. This provides two methods of directly measuring the barrier to exchange. We will carry out a complete analysis of the data in a future publication. Preliminary analysis suggests that $\Delta_x < 0.2$ eV.

Finally, we note that the measured activation energy of D_{eff} in D tracer experiments does not yield information about the density of H trap levels below the shallowest level. As pointed out by Jackson,[6] the thermal emission rate of D from the shallowest level will determine the activation of D_{eff}. D emission from deep H levels proceeds by an exchange of free H for deep D. The deep D depth does not significantly influence measured D tracer profiles in any time regime.

F. Mechanism of exchange

Branz *et al.*[2] proposed that the D-H exchange process proceeds via a fivefold-coordinated Si "floating bond"[17] intermediate state. As shown in Fig. 5, an initially free D atom forms a temporary fifth bond to one of the 5×10^{21} cm^{-3} Si-H centers. If the H atom (rather than the D that was trapped) is released to the transport level, exchange has occurred: the final state then consists of one trapped D atom and one H atom at the transport level. The H level associated with five-bonded Si must be nearly degenerate with the H transport level, since the barrier to exchange experimentally appears to be small.

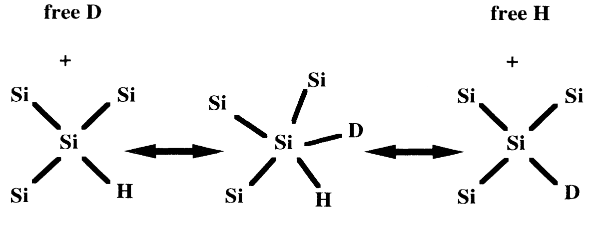

FIG. 5. Schematic diagram of the proposed microscopic origin of the exchange processes. From left to right we see process 9 or 11 (of Fig. 2): an initially free D atom forms a temporary fifth bond to the Si-H center and the H is then released to the transport level. From right to left, we see the inverse processes (10 or 12).

V. SUMMARY

The trap-controlled model of tracer diffusion *without exchange* cannot be reconciled with the second H trapping level observed in H evolution experiments. We have included capture and emission by exchange in a tracer diffusion model that includes a second deeply trapped H level. Comparison of this model's predictions with tracer diffusion data shows that in *a*-Si:H, capture by exchange is 100 times more likely to occur than trapping to an empty trap. This conclusion enables us to understand the small value of the mean distance before D retrapping (~200 Å). It also reconciles the measured smooth H tracer diffusion profiles at long times with the existence of about 30% of deeply bound H in *a*-Si:H.

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