Hydrogen Bonding and Transport in Disordered Silicon [and Discussion]

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Hydrogen bonding and transport in disordered silicon

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This paper reviews recent measurements of trap dominated hydrogen diffusion in disordered silicon. H transport can be described by a model with three levels: a transport level, shallow traps and deep traps. At low concentrations the diffusion is dominated by deep traps well separated in energy from shallow traps. At high H concentrations, the trap density ranges from 8×10^{19} to 10^{21} traps per cubic centimetre and increases roughly as the square root of the H concentration. Moreover, H diffusion depends on carrier concentration and doping levels as well as the H concentration. Muon spectroscopy should be able to provide previously inaccessible information about the transport levels, shallow traps and the effects of carriers on H motion in the shallow traps.

1. Introduction

Hydrogen bonding and diffusion are important for understanding the growth, stability and structure of amorphous materials, particularly hydrogenated amorphous silicon (a-Si:H). Hydrogenation is critical for enhanced performance of polycrystalline Si (poly-Si) devices. Despite the importance of H in semiconductors, details concerning H bonding and transport remain poorly understood even in crystalline Si (c-Si).

The primary difficulty is that H has a complex interaction with Si. Interstitial H interacts with carriers and can diffuse in various charge states (Van de Walle *et al.* 1989). H also forms complexes: molecular, Si–H pairs and multi-H complexes (see, for example, articles in Stutzmann & Chevallier 1990). Furthermore, because H_2 molecules in the gas are lower in free energy at standard temperature and pressure than if bonded within crystalline Si (Herring & Johnson 1991), the hydrogen configurations depend strongly on the previous temperature and hydrogenation conditions. In a-Si:H there is the additional complexity that the number of possible bonding configurations are greater because vacancies, voids and strained and dangling bonds are all possible bonding sites for H.

In this work, recent findings for hydrogen in amorphous and poly-Si are reviewed with a special emphasis on those aspects most relevant to muon spectroscopy. The basic trap dominated H transport is compared with experimental results. Diffusion in hydrogenated amorphous, poly-Si, and crystalline silicon are compared and discussed in the context of multi-H complexes. Finally, the effect of light and carriers is reviewed.

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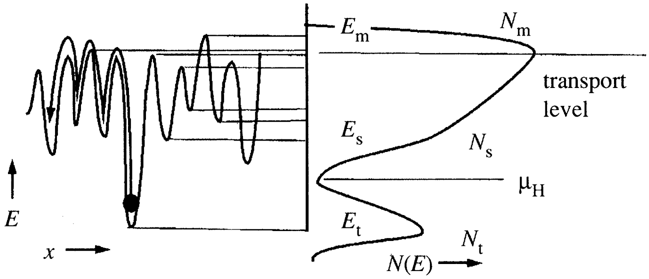

Figure 1. Energy of H versus position in the sample (left) and density of sites (right). The various states are divided into barrier, shallow, and deep states of average energies $E_{\rm m}$, $E_{\rm s}$, and $E_{\rm t}$ and concentration $N_{\rm m}$, $N_{\rm s}$, and $N_{\rm t}$, respectively. The barriers form the transport level and merge with the shallow states. The deep states are separated in energy from the shallow states at the approximate position of $\mu_{\rm H}$.

2. Trap dominated diffusion

A description of H bonding and transport in amorphous silicon is generally quite complex. The bonding and transport processes consist of H hopping from site to site. The H remains in some sites for long periods of time, while in others the H lingers only briefly (figure 1). The probability of hopping to neighbouring sites depends on the barriers and site energies. For further progress, a number of simplifications must be made (Jackson & Tsai 1992; Santos *et al.* 1992). First, the barriers between states, of density $N_{\rm m}$, are assumed to be more or less at the same energy, $E_{\rm m}$, independent of position. A second assumption is that the highest energy states connected by these barriers can communicate rapidly with each other and consequently can be regarded approximately as one single transport level approximately at energy $E_{\rm m}$. The microscopic diffusion coefficient for H in these states is D_0. A third assumption is that for most experimental times, the effect of shallow energy traps of density $N_{\rm s}$ at $E_{\rm s}$ on transport can be lumped together with the microscopic transport into an effective diffusion coefficient, $D_{\rm s}^{\rm eff}$. This effective diffusion coefficient can be written as $D_{\rm s}^{\rm eff} = D_0(N_{\rm m}/N_{\rm s})\exp[-(E_{\rm m}-E_{\rm s})/kT]$ assuming that both the mobile states and the shallow states are primarily empty. There is a continuum of states between the transport and shallow traps (figure 1). Lastly, the deep traps, of concentration $N_{\rm t}$ at an energy $E_{\rm t}$, are separated from the shallow traps by a minimum in the density of traps (figure 1), an assumption is supported by experiment. Deep traps are those traps whose emission time is equal to or longer than the experimental time scales while shallow traps have emission times short than the experiment.

With these assumptions, the trapping and diffusion of H can be greatly simplified and described approximately by the following simple equations,

$$\frac{\partial H_{\rm s}}{\partial t} = D_{\rm s}^{\rm eff}\frac{\partial^2 H_{\rm s}}{\partial x^2} - \frac{\partial H_{\rm t}}{\partial t}, \tag{2.1}$$

$$\frac{\partial H_{\rm t}}{\partial t} = 4\pi R_{\rm c} D_{\rm s}^{\rm eff} H_{\rm s} N_{\rm t}^{\rm unocc} - \nu H N_{\rm s}^{\rm unocc}, \tag{2.2}$$

where $\nu = 4\pi R_{\rm c} D_{\rm s}^{\rm eff} N_{\rm s}\exp[-(E_{\rm s}-E_{\rm t})/kT]$, $N_{\rm t}^{\rm unocc} = N_{\rm t} - H_{\rm t}$ is the number of unoccupied deep traps, $N_{\rm s}^{\rm unocc} = N_{\rm s} - H_{\rm s}$ and $R_{\rm c}$ is the trap capture radius. The solution to these equations depends on the boundary conditions. If the sample is

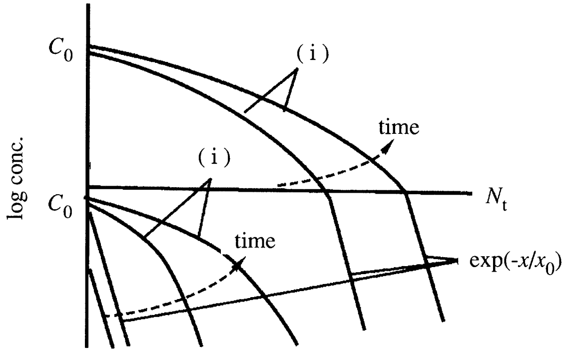

Figure 2. The log of the H concentration as a function of distance for diffusion under high ($C_0 > N_T$) and low concentrations ($C_0 < N_T$) for various times according to (2.1)–(2.5). The exponential behaviour (2.4) is observed for concentrations less than the number of traps N_t and for diffusion times less than the release times for deep traps. Otherwise, an erfc behaviour is observed characterized by either D_s or D_t for C_0 less than or greater than N_t respectively.

exposed to a constant source of atomic H surface concentration, C_0, with $C_0 \gg N_t$, then the second term in (2.1) can be ignored and the approximate solution is given by

$$H_s = C_0 \operatorname{erfc}(x/2\sqrt{D_s^{\text{eff}} t}), \tag{2.3}$$

where erfc is the complementary error function. Thus, the activation energy $E_m - E_s$ can be determined by measuring D_s^{eff} as a function of time and temperature by fitting the secondary ion mass spectroscopy (SIMS) spatial concentration profiles (figure 2). For concentrations less than N_t^{unocc} when $C_0 > N_t^{\text{unocc}}$ or when $C_0 < N_t^{\text{unocc}}$ but before the H has had any chance to be emitted from a trap (figure 2), the profile is an exponential given by (Branz *et al.* 1993)

$$H_s \propto \exp(-x/x_0), \tag{2.4}$$

where $x_0 = (4\pi R_c N_t^{\text{unocc}})^{-1/2}$. Finally, for low concentrations $C_0 \ll N_t^{\text{unocc}}$ and for long times when each H has had a chance to be remitted several times from the traps, the solution again has an erfc profile given by (2.3) but with D_s^{eff} replaced by

$$\begin{aligned} D_t^{\text{eff}} &= D_s^{\text{eff}}(N_s/N_t^{\text{unocc}}) \exp[-(E_s - E_t)/kT] \\ &\approx D_0(N_m/N_t) \exp[-(E_m - E_t)/kT] \quad \text{if } \mu_H < E_t, \\ &\approx D_0(N_m/N_t) \exp[-(E_m - \mu_H)/kT] \quad \text{if } \mu_H > E_t, \end{aligned} \tag{2.5}$$

where μ_H is the H chemical potential dividing occupied states from unoccupied. Thus, the activation energy of D^{eff} is either the deep trap energy or the shallow trap energy depending on the H concentration (figure 2). Therefore, if a-Si contains deep traps associated with the disorder such as Si dangling or weak bonds, the diffusion activation energy should increase particularly for low H concentrations. The transition between exponential and erfc behaviour takes place when the H concentration equals the trap concentration N_t^{unocc}. This relatively simple model is consistent with experimental observations presented next.

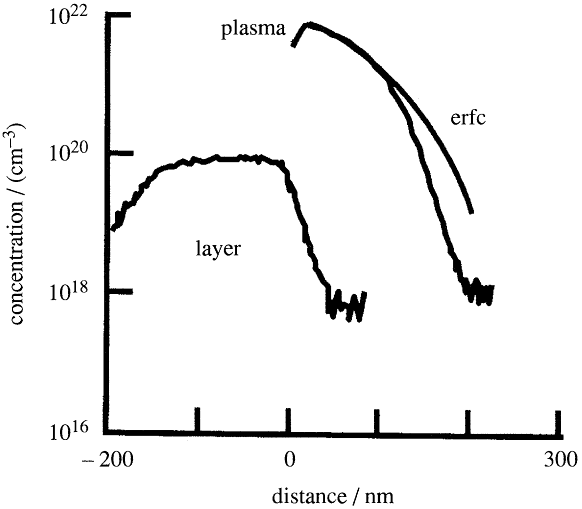

Figure 3. Comparison of diffusion from an atomic plasma and layer diffusion for standard good quality a-Si:H with a erfc shown for comparison. The estimated trap density is roughly 8×10^{20} cm^{-3}.

3. Results

The relations developed above for diffusion in the presence of traps provide a useful interpretation for the results of diffusion experiments in various forms of Si. The results are consistent with trapping-dominated diffusion although H–H interactions and H–carrier interactions complicate the situation.

The standard experiment consists of exposing a sample to a deuterium (D) plasma for various times while the sample is held at various temperatures. Amorphous silicon, thermally recrystallized poly-Si, and c-Si are exposed to the plasma in order to compare diffusion in the various forms of silicon. Alternatively, a deuterated layer of a-Si:D can be deposited over a layer of a-Si:H. The sandwich structure can be annealed for various times and temperatures and then profiled using SIMS. The spatial distribution of D is determined by SIMS profiling with a resolution of about 8–10 nm. For further details see Jackson & Tsai (1992). H and D diffusion are observed to be nearly identical. Hence, in the subsequent discussion, the terms deuteration and hydrogenation will be used interchangeably.

In figure 3, D profiles of amorphous Si exposed to an atomic D plasma and a deuterated overlayer are presented (from Santos & Jackson 1992). For the plasma case, C_0 exceeds the apparent trap density (about 5×10^{20} traps per cubic centimetre), and the profiles display an erfc profile. When D decreases below the trap density, the profile becomes exponential consistent with (2.4). The exponential slope is independent of layer or plasma deuteration depending only on the trap concentration and capture radius. The trapping radius is estimated to be greater than 0.01 nm. Concordant with the trap dominated behaviour described by (2.3)–(2.5), layer diffusion exhibits an erfc again at longer times. From the profiles for different hydrogenation temperatures, the activation energy of the effective diffusion has been obtained (figure 4). As expected for trap dominated transport, the high concentration diffusion from an atomic plasma exhibits a considerably smaller activation energy (0.5 eV) than the low concentration layer diffusion (1.2–1.5 eV) (Santos & Jackson 1992). Thus, in a two-level model for H

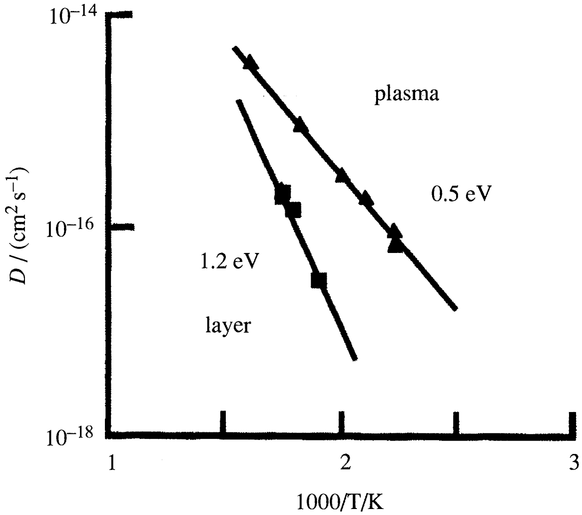

Figure 4. Diffusion coefficient versus $10^3/T$ for layer diffusion and diffusion from a plasma. The solid lines represent the solution to (2.1)–(2.2) for shallow traps at about 0.5 eV below E_{m} and deep traps at 1.2 eV below E_{m}.

trapping, the results indicate that the shallow states have a trapping energy of about 0.5 eV while the deeper states an energy of about 1.2–1.5 eV. The observation of a sharp transition between an erfc and an exponential profile indicates that there is an energy range of reduced trap density between the deep and shallow traps as shown in figure 1. Otherwise, the profiles would display a gradual shift from a slowly decreasing erfc to a steeper profile. The large change in activation energy from layer to plasma diffusion is caused by only a 10–20% change in the H concentration. This observation further supports the assumption made earlier that there is a region of considerably reduced density of traps for energies between the shallow and deep states. The generally good agreement between the observed diffusion profiles and those expected from trap dominated diffusion suggest that the assumptions used to derive (2.1)–(2.5) are valid. Moreover, one can determine the effect of sample parameters on the trap densities and depths using the trap dominated diffusion results discussed above.

In particular, the effect of Si network disorder can be investigated. Figure 5 depicts D profiles in c-Si, poly-Si and H-depleted a-Si exposed to an atomic D plasma at temperatures in the range of 250–275 °C. Over long distance scales at low concentrations, the H diffusion in c-Si is substantially larger (4×10^{-11} cm^2 s^{-1}) than diffusion in poly-Si or a-Si. In the case of c-Si, the absence of deep traps such as dangling bonds leads to rapid diffusion. In disordered forms of silicon, the traps greatly suppress diffusion. According to (2.5), the trap dominated diffusion should display a stronger temperature dependence in a-Si than in c-Si. The activation of H diffusion in different forms of silicon verifies this result (figure 6) (from Jackson & Tsai 1992). The activation energy for very low concentrations of H is about 0.48 eV in undoped c-Si, 0.7 eV in n-type c-Si, and 1.2 eV for p-type. The various dopants act as traps for H. A-Si and poly-Si have diffusion activation energies exceeding 1.5 eV at high concentrations. At very low H concentrations, less than the dangling bond concentration, only lower bounds have been placed on the diffusion activation energy. The diffusion activation energy is larger than

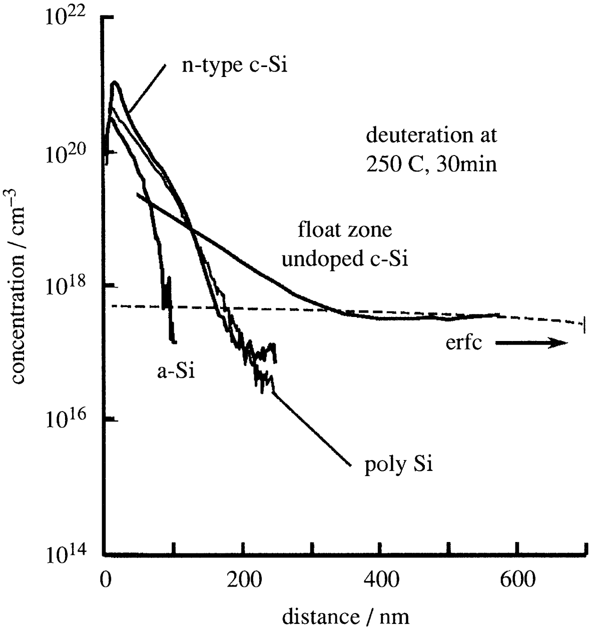

Figure 5. High concentration diffusion due to exposure of an atomic plasma at the designated temperature and time for c-Si, a-Si:H, and poly Si along with an erfc fit to the c-Si data. The c-Si has a rapid diffusing component while none is observed for the poly-Si. The arrow denotes the poly-Si/oxide interface that does not show any build-up of D eliminating the possibility of any fast diffusing component in the poly.

1.8 eV and could be as large as 2.2–2.7 eV (Jackson & Tsai 1992). The trap density estimated from the concentration where the profile deviates from an erfc, is found to be about 10^{20} cm^{-3} in poly-Si and H depleted a-Si. In summary, the shape and activation energy are consistent with trapping-dominated diffusion.

Unfortunately, the diffusion of H in Si is considerably more complex than just simple trapping within a static distribution of traps. The dependence of diffusion on H concentration for example indicates that the simple model must be refined. Returning to the comparison of diffusion between various forms of silicon at high concentrations (figure 5), a striking result is observed. In the near surface region extending about 30 nm into the sample, D_{eff} is the same within a factor of two in a-Si, poly-Si, and c-Si. Hence, in c-Si the diffusion for high concentrations is slower than the low concentration diffusion whereas the opposite holds for disordered silicon. The slower diffusion for high concentrations is characteristic of complex formation and H–H interactions. The probability of H complex formation increases nonlinearly as the H concentration rises causing a reduction in the effective diffusion. In the case of disordered Si, the higher concentrations fill up deep traps such as dangling bonds causing the diffusion to be dominated by other trapping mechanisms. The fact that diffusion is the same in the various forms of Si suggests that complex formation in the three forms of silicon is quite similar. This result is perhaps not surprising because the energetics of H bonding depend primarily on the nearest neighbour configurations of Si. In the high concentration limit, the average Si configuration determines the H bonding energetics rather the extremes of the Si configuration distribution. The average nearest neighbour Si configurations are nearly identical for the various forms of silicon. Therefore,

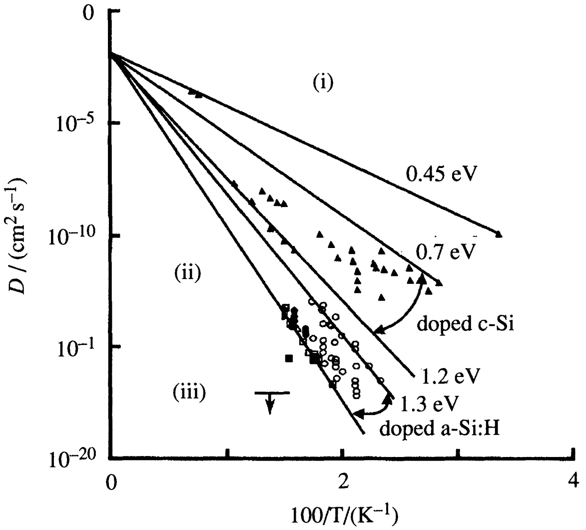

Figure 6. Compilation of a number of different diffusion measurements in c-Si, poly-Si, and a-Si:H. The low concentration high T diffusion in c-Si is quite rapid. Doping reduces the diffusion by introducing traps between 0.7–1.2 eV. A-Si has a diffusion activation energy of 1.3 eV for doped and 1.5 eV for undoped. At low concentrations the activation energy is above 1.8 eV and could be as high as 2.7 eV (Herring & Johnson 1992).

similar high concentration H bonding configurations are apt to be present in the various forms of Si as will be discussed further.

A related result is the observation that the trap density apparently increases as the H concentration in a-Si. By rehydrogenating H-depleted a-Si, the effect of H concentration on D diffusion could be determined. In particular, the trap density displays a significant *increase* with H concentration. If simple trap filling were controlling diffusion, trapping should decrease with increasing H. The results can be only explained if the trap density is proportional to the H concentration, i.e. H atoms must interact. A possible source of these traps is the multi-H complexes as suggested above. Studies on annealed samples have shown that the trap distribution moves to deeper energies if the sample is annealed at 350 °C for 5–65 hours. The increased binding energy reflects changes in the multi-H complexes favouring tighter H binding configurations.

Another important aspect of H diffusion in a-Si is the effect of carriers on H diffusion. If a sample is strongly illuminated during annealing, the D diffuses significantly more rapid than if the sample is held in the dark (figure 7) (from Santos & Johnson 1993). The effects of heating could be eliminated by also incorporating a deuterated layer with a p–i–n structure and applying various biases during diffusion. If the p–i–n structure was reverse biased, sweeping out both electrons and holes, the diffusion was suppressed even if the sample was illuminated. The diffusion profiles were found to be affected by illumination (Santos *et al.* 1993). Both the emission and trapping rates increase roughly linearly with illumination intensity, and because both increase roughly by the save amount, the net increase in the diffusion constant is small. This effect of carriers is consistent with results observed in c-Si. Carriers introduced by doping, particularly holes, enhance the diffusion rate of H in c-Si (Santos & Johnson 1993; Pearton *et al.* 1992).

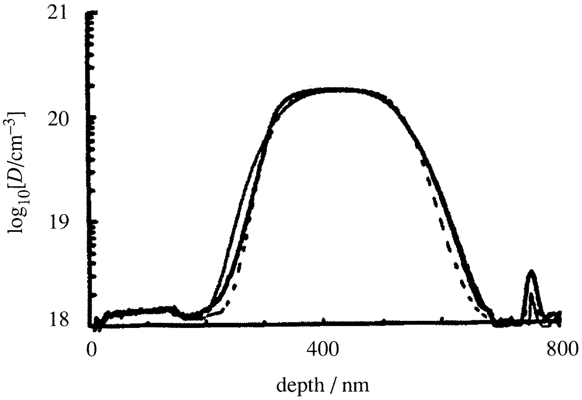

Figure 7. The effect of illumination on diffusion from (Santos *et al.* 1992) in a p–i–n diode at 225 °C for 7 days. The dashed line depicts diffusion under open circuit in the dark, the thin line open circuit under illumination, and the thick line diffusion under illumination and reverse bias that sweeps the photogenerated carriers away.

4. Model for H bonding in amorphous silicon

The preceding sections discussed aspects of H diffusion and bonding determined by analysis of diffusion profiles as a function of time, temperature, H concentration, and sample. An important question is what is the overall picture for H diffusion in amorphous silicon?

The current picture for H diffusion in amorphous silicon is the following. As H is introduced into unhydrogenated material, the first H binds primarily to Si dangling bonds. These are low energy sites for H and are estimated to be about 3.5 eV relative to atomic H in a vacuum (Van de Walle & Street 1994). Once these states are occupied, subsequent H must break existing Si–Si bonds. Initially one would expect H to break weak Si–Si bonds because of the lower energy cost. As the H concentration increases, however, the H must break strong Si–Si bonds to form Si–H bonds. When a Si–Si bond is broken, two Si dangling bonds are created which eventually form Si–H bonds. After one H breaks an Si–Si bond, the remaining dangling bond will be hydrogenated either immediately or after diffusing a small distance. The result is that H atoms essentially bind in pairs; a singly occupied Si–Si bond is energetically unfavourable (Zafar & Schiff 1989). When two H atoms break an Si–Si bond, the surrounding network is strained. The strain energy is reduced if the pairs coalesce into larger complexes. In c-Si, these larger complexes can be directly viewed using lattice imaging. The complexes are two-dimensional (1 1 1) oriented platelet structures that can be as large as 100 nm in diameter (Johnson *et al.* 1992). The same sorts of structures are likely to exist in amorphous and polycrystalline Si (figure 8).

The H-rich platelets act as a distinct phase from the low-H Si. In thermal equilibrium, the chemical potential of H outside the platelets is equal to the platelet chemical potential. As H is added or removed from the sample, the platelets grow or shrink but the chemical potential remains nearly fixed. Near the surface where the concentration of H is high, the platelets are large while deeper in the sample the platelets are smaller (figure 8). The concentration gradient due to atomic H exposure moves by H trapping and release from the platelet perimeter. The sites at the edges of the platelets act as traps for H. The number of perimeter sites

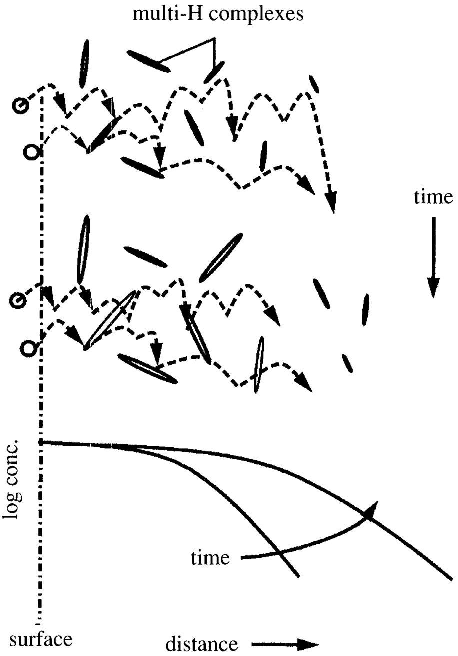

Figure 8. A proposed model for H diffusion dominated by multi-H complex formation. The complexes are largest near the interface creating a concentration gradient. Mobile H detraps from the complexes, diffuses, and retraps further into the sample. The complexes grow in size giving rise to the observed concentration profiles. The measured diffusion rate characterizes multi-H complex dominated diffusion.

grow as the platelets grow either as the square root of the H concentration if the number of platelets remains constant or linearly if the platelets remain at a constant size and the number increases accounting for the observed increase in the trap density as the H concentration increases.

5. Future role of muon studies

Most studies have concentrated on the deep and shallow traps since the measurement time scales are only compatible with these deeper states. Properties of the transport states and barriers and even the shallow states are not accessible using SIMS. Muonium studies could contribute significantly to the understanding of H transport in disordered silicon for these high energy states. The fast time scales and high sensitivity make muon spectroscopy a good probe of these states. Variations in the muon linewidths due to motional narrowing could measure the rate of muon diffusion during hopping between the shallow states. The change in the diamagnetic fraction in poly-Si observed by (Singh *et al.* 1993) may be related to sudden changes in conduction in hydrogenated poly-Si (Nickel *et al.* 1994). Also hyperfine interactions with nearby H could yield structural information about the local environment of the high energy states. In particular the role of clustering and H–H interactions could be investigated through such studies. A final area of interest is the effect of carriers on muon diffusion. It is expected that the charge state of muonium should change depending on the position of the Fermi level. Muon studies may be able to answer questions such as the charge state of diffusion and how carriers affect microscopic motion particularly under illumination. The ratio of diamagnetic to paramagnetic fractions should change under illumination and doping. Because light-induced motion of H is the leading candidate for causing metastability in Si–H alloys, the effect of light on muon studies is of great interest. Thus, muon studies in disordered semiconductors could provide a number of new insights into the physics of H in the shallow states and its interaction with other H atoms and carriers.

6. Summary

A brief introduction to H diffusion in disordered Si has been presented. The complexities of diffusion, trapping, and release can be simplified into trap dominated diffusion. The shallow traps are about 0.5 eV below the transport barriers and the deep traps about 1.3–1.5 eV below. Very deep traps associated with dangling bonds are at least 1.8 eV or more below the transport level. The 1.3–1.5 eV traps increase with H concentration and are associated with multi-H complexes such as platelets. The diffusion in the high concentration limit appears to be quite similar in c-Si, poly-Si, and a-Si suggesting that the multi-H complexes are similar in the three cases. Muon spectroscopy could shed light on the nature of the shallow traps, H complexes and capture of carriers.

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Discussion

M. SYMONS (*Department of Chemistry and Biological Chemistry, University of Essex, U.K.*). I want to call attention to your suggestion that, following the 'loss' of an electron from the bond-centre $Mu^{\cdot}$ unit, the muon is released in some way. As I stressed earlier, H^+ (Mu^+) cannot be free, i.e. the following reaction is impossible:

$$X\text{–}H + B \rightarrow X^- + H^+.$$

It is absolutely necessary to have a proton-acceptor (B, say) so that the reaction is:

$$X\text{–}H + B \rightarrow X^- + HB^+.$$

So, if the unit $Si\text{–}Mu^+\text{–}Si$ is to eject Mu^+ there has to be some acceptor close enough to form a bond to Mu^+ as it leaves the Si–Si bond:

$$Si\text{–}Mu^+\text{–}Si + B \rightarrow Si\text{–}Si + Mu^+\text{–}B.$$

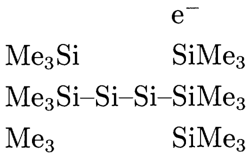
What is the nature of B? It seems to me to be far more probable that the centre is lost when it is in the unionized form, with migration of $Mu^{\cdot}$. Is this reasonable?

W. JACKSON. In the context of a solid, a $Si\text{–}Mu^0\text{–}Si$ can emit an electron or capture a hole making a $Si\text{–}Mu^+\text{–}Si$ configuration. The electron or hole is interchanged with the electron reservoir formed by the rest of the solid. The energy cost and therefore probability is determined by the position of the Fermi level. The Mu^+ can then migrate from one Si–Si bond to another. If the Mu^+ arrives at a Si dangling bond it can form $Si\text{–}Mu^+$ which could capture an electron (or emit a hole) to form $Si\text{–}Mu^0$ depending on the position of the gap state relative to the Fermi level. The Mu^+ could also break a weak Si–Si bond forming $Si\text{–}Mu^0$/Si dangling bond ($^+$). The dangling bond state may or may not capture an electron depending on its energy level relative to the Fermi level. Another possibility is suggested from the fact that we believe that the H interstitial in Si is a negative U defect. Hence the reaction

$$2[Si\text{–}Mu^0\text{–}Si] \rightarrow Si\text{–}Mu^+\text{–}Si + Si\text{–}Mu^-\text{–}Si$$

is likely to be exothermic, i.e. most Si–Mu–Si would be ionized and very few would be neutral. Depending on the doping level, there would be more + or − charge Mu.

M. SYMONS. Doctor Roduner has asked if there are 'chemical' examples of the bond chemical muonium concept. I think that the answer is 'no', and that, of course, is one reason why the results are so interesting. However, I think that some recent work that we have done using compound I suggests a way forward. Exposure of this compound in suitable solvents to ionizing radiation at 77 K gave a species whose EPR spectrum is consistent with a radical-anion in which the



$$\begin{array}{lcl} & & \mathrm{e^-} \\ \mathrm{Me_3Si} & & \mathrm{SiMe_3} \\ & \mathrm{Me_3Si{-}Si{-}Si{-}SiMe_3} & \\ \mathrm{Me_3} & & \mathrm{SiMe_3} \end{array}$$

Compound I.

added electron is in an anti-bonding σ^*-orbital involving only the central Si–Si bond, making this a so-called 3-electron band (Mishra, S. P. & Symons, M. C. R., unpublished results). We hope that by using a more acidic solvent these anions may protonate, but these experiments have not yet been tested.