Nature of Long-Range Atomic H Motion in *a*-Si:H

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An infrared and secondary ion mass spectrometry study of H diffusion in undoped, rf-sputtered, multilayered, hydrogenated and deuterated amorphous silicon is reported. The results indicate that the long-range motion of atomic H is suppressed when the microvoid content exceeds a critical value associated with an initial SiH_2 and SiH_3 density $N_{d0} \simeq 7 \pm 1$ at.%. The strong power-law time dependence of the diffusion constant (exponent $\alpha \simeq 0.75 \pm 0.15$) somewhat below this value of N_{d0} is discussed in relation to H migration mediated by mobile intrinsic defects, and the presence of an exponential distribution of traps for these defects and/or hydrogen.

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Thin-film hydrogenated amorphous silicon (*a*-Si:H) based alloys and multilayers have matured in various technological areas in recent years,[1] and novel applications are being presently considered.[2] Yet fundamental issues such as the nature of the dominant defect[3] and the motion of hydrogen remain undecided.[4] This work offers new results addressing both issues.

The motion of hydrogen in *a*-Si:H deposited by glow-discharge decomposition of silane (GD films) was initially studied by Carlson and Magee (CM).[5] Using secondary ion mass spectrometry (SIMS), they determined the activation energy $E_a = 1.53$ eV and prefactor $A_0 = 0.012$ cm^2/s by profiling the smeared interfaces of *a*-Si:H/*a*-Si:D/*a*-Si:H multilayers annealed over widely varying periods in the temperature range $250 \leq T \leq 400$ °C. Subsequent detailed SIMS studies by Street *et al.*[4] and Kakalios *et al.*[6] on mostly *p*-doped, some *n*-doped, and compensated GD films annealed at temperatures $T < 275$ °C indicated, among other results, that the diffusion constant decreases with time, in a power-law dependence given by

$$D(t) = D_{00}(\omega t)^{-\alpha}, \qquad (1)$$

where ω is the H attempt frequency. Kakalios *et al.*[6] initially assumed that D_{00} is temperature dependent. The value of α ($\simeq 0.2$ at 480 K) was suggested to explicitly depend on the temperature in the following manner:

$$\alpha = 1 - T/T_0, \qquad (2)$$

where $T_0 = 600$ K is the characteristic energy width of the exponential hopping distribution in the dispersive transport of hydrogen. This exponential distribution is an important element in the "hydrogen glass" model developed by the Xerox group.[7] Recent analysis of the previous results by Jackson[8] suggested that D_{00} is actually temperature independent. He shows that the diffusion constant following annealing at times necessary to diffuse a constant distance L, $D(t_L)$, is thermally activated due to the dependence of α and t_L on T.

All of the previous studies involved device-quality films, essentially devoid of SiH_2 and SiH_3 bonds which are associated with microvoids. This work involves rf-sputter-deposited films[9,10] and it indicates that when the microvoid content corresponds to an initial di- and tri-H density N_{d0} exceeding 7 ± 1 at.% (relative to the Si atom density), the long-range motion of atomic H and D is suppressed. In films of as-deposited N_{d0} values somewhat below this critical value, the diffusion is highly anomalous, with the diffusion constant exhibiting a strong power-law time dependence. These new observations are discussed in relation to H motion mediated by the migration and annihilation of bulk intrinsic defects,[3] and the presence of an exponential distribution of hydrogen site energies. While neither is ruled out, some problems associated with both scenarios are pointed out.

a-Si:H/D/H and *a*-Si:H/(H,D)/H multilayers 1-2 μm thick were deposited by rf sputtering (see Table I). Detailed descriptions of the deposition processes may be found elsewhere.[10,11] The films were annealed at temperatures $270 \leq T \leq 355$ °C in evacuated sealed Pyrex tubes. The total Si-bonded H content of the films $[H_t]$ was determined from the 640-cm^{-1} ir wagging-mode absorption peak using the absorption coefficient given by Cardona.[12] Since the frequency of the mono-H stretch mode increases from 2000 to 2100 cm^{-1} as the radius of the void around the H atom increases to 2 Å,[12-14] that band was considered unreliable in determining the bonding configuration. The density of the di-H and tri-H bonds N_d, generally associated with microvoids which are larger than those around the mono-H, was then determined from the intensity of the bending modes at 840 and 890 cm^{-1}.[12,13] The structure of the stretch peak and the initial values of $[H_t]$ and N_d, $[H_t]_0$ and N_{d0}, are also summarized in Table I. The ir spectrum of each sample was obtained following its annealing. During the shortest annealing period at each temperature, $[H_t]$ and N_d decreased to final values denoted by $[H_t]_a$ and N_{da}, respectively, and are also listed in Table I.

Depth profiles of Si, H, D, O, and other species present in the films were obtained using a Perkin-Elmer SIMS model PHI 6300.[1] The depth resolution was typically ~150 Å at the *a*-Si:H/*c*-Si substrate interface of a

TABLE I. Deposition parameters,[a] total Si-bonded H[b] and di-H[c] content of as-deposited ($[H_t]_0$ and N_{d0}, respectively) and all annealed ($[H_t]_a$ and N_{da}, respectively) films, primary (ν_1) and secondary (ν_2) ir stretch frequencies, and presence (+) or absence (−) of long-range H diffusion in some films studied in this work.

Sample number	Type	rf power (W)	$[H_t]_0$ (at.%)	$[H_t]_a$ (at.%)	N_{d0} (at.%)	N_{da} (at.%)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	Diffusion
11	H/D/H	50	22		11		2093	···	−
13	H/D/H	500	14		3.5		2000	···	+
21[d]	H/(H,D)/H	200	19	13	9	3[g]	2045	2100	−
22	H/(H,D)/H	550	13		2.5		2000	···	+
23	H/(H,D)/H	50	33	20	11	5.5[g]	2080	···	−
27[e]	H/(H,D)/H	550	17	11.5	4	3.5	2080	2000	+
29[f]	H/(H,D)/H	550	19	13.2	5	2.9[g]	2022	···	+

[a] Generally, the H content is higher and plasma-film interactions responsible for the destruction of microvoids and incipient columnar morphology are weaker at low rf power (see Ref. 10).

[b] Determined from the 640-cm^{-1} wagging mode. See Refs. 10, 12, and 13.

[c] Determined from the 840–890-cm^{-1} bending modes (Refs. 10, 12, and 13).

[d] After initial annealing primary stretch shifted to ~2073 cm^{-1} and a shoulder remained at ~2000 cm^{-1}.

[e] The target to substrate separation was 2 in., and thus the plasma-film interactions weaker (see Ref. 9), during deposition of this sample.

[f] Primary stretch peak split into two components at ~2020 and ~2075 cm^{-1} during initial stages of annealing.

[g] Although N_d decreases upon initial annealing, the overall microvoid content is probably little changed from the pristine value (see Refs. 1 and 9).

~1-μm-thick film. The oxygen content was concluded to be insignificant in all cases.[15] The deuterium content at the surfaces was usually lower than in the middle layer by at least 2 orders of magnitude, except in the cases of the most extensive diffusion, where the ratio was ~20. In these latter cases, the contribution of reflection (but not evolution, since the total H and D content did not change following the initial annealing) was also included.[16]

Figure 1 shows the SIMS deuterium profiles of one sample before and after annealing, and two other annealed samples. As clearly seen, the interfaces in film 29 became smeared following annealing, whereas those in films 11 and 23 remained very sharp. The evolution of the ir spectra upon annealing is treated in detail elsewhere,[11] but two observations are noteworthy: (i) As expected,[17] $[H_t]$ and N_d are somewhat reduced ($[H_t]$ from ~14%-19% to ~10%-14%) upon initial annealing (Table I). (ii) In sample 27, with stretch band components at 2000 and 2080 ± 10 cm^{-1}, the latter peak slightly increased relative to the former, during the initial annealing process. In sample 29, the stretch band initially peaking at 2020 cm^{-1} evolved into two components of equal intensity at 2020 and 2090 cm^{-1}. All the observable changes in H content and bonding configuration occurred only during the shortest annealing period at each temperature. Note that even though N_d is reduced upon annealing, the overall microvoid content probably remains unchanged.[1,9]

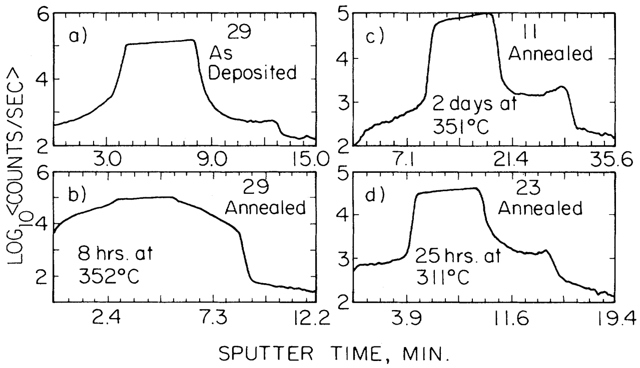

FIG. 1. Deuterium SIMS profiles of (a) film 29, as deposited, (b) film 29, annealed for 8 h at 352 °C, (c) film 11, annealed for 2 d at 351 °C, and (d) film 23, annealed for 25 h at 311 °C. See also Table I.

A clear correlation between N_{d0} and the occurrence of long-range diffusion is immediately apparent from Table I and Fig. 1. This as-deposited value of N_d is generally believed[1,9,10] to be directly related to the microvoid content of the film. One of the most striking observations is that for any given film, either a significant smearing of the interfaces was observed, or none at all. In multilayers that displayed smeared interfaces, the diffusion constant D was determined by fitting the deuterium profiles at the H/D/H and H/(H,D)/H interfaces by a complementary error function (see below).[16] The agreement with such a function was usually excellent. We thus conclude that a critical content of microvoids, corresponding to an initial di- and tri-H configuration density of ~7 ± 1 at.%, critically suppresses the long-range motion of atomic hydrogen and deuterium in *a*-Si:H. This phenomenon occurs even when a significant fraction of the hydrogen in the film remains in a bulk mono-H configuration, i.e., not on an internal surface.

SIMS profiles of the deuterium content in samples 27 and 29 were measured following annealing for several periods of time in the temperature range $275 \leq T \leq 355$ °C. The results clearly indicated that D decreases strongly with time. Yet in spite of this time dependence, the profiles are still describable by a complementary error function,[16]

$$c(x,t)=n_0\{1-\mathrm{erf}[x/2\sqrt{\Theta(t)}]\}\,, \qquad (3)$$

where

$$\Theta(t)=\int_0^t D(\tau)d\tau\,. \qquad (4)$$

The experimental values of Θ versus annealing time t are shown in Fig. 2, as are, for rough comparison, the values of Dt measured by CM.[5] As clearly seen, in all cases $\Theta \propto t^{1-\alpha}$, so $D \propto t^{-\alpha}$, where $\alpha \simeq 0.75 \pm 0.1$. This value is much higher than those reported by Street *et al.*[4] and Kakalios *et al.*[6] ($\simeq 0.2$) and does not exhibit any clear temperature dependence.

Since the diffusion constant decreases with time as a power law, and a threshold condition for H motion exists, one may initially be tempted to picture the diffusion as occurring on a percolating fractal network, presumably composed of the intrinsic dangling- and floating-bond defects, weak Si—Si bonds, and sites already occupied by hydrogen. While the microvoid-induced disruption of such a network below the percolation threshold cannot be ruled out, and probably warrants further consideration and theoretical study, its fractal nature is improbable. This follows from the observation that the fractal nature is retained over a long range only very near the percolation threshold.[18]

A close examination of Fig. 2 offers another striking observation: The diffusion constant at constant annealing time appears to be only weakly temperature dependent at $270 \leq T \leq 355$ °C. If the recent approach of Jackson,[8] which successfully accounts for the time dependence of the diffusion constant, is adopted, and it is assumed that $D(t_L)=D_0\exp(-E_{\mathrm{diff}}/kT)$ for constant L instead of constant annealing time, then the activation energy E_{diff} for $L \simeq 700$ Å is estimated to be ~ 1.3 eV. This value is in good agreement with the accepted value of ~ 1.4–1.5 eV. In that case, however, $T_0 \simeq 2300$ K. This value of the characteristic energy width is almost 4 times greater than that obtained by Jackson and coworkers.[6-8] In addition, $D_0 \simeq 2\times 10^{-5}$ cm^2/s, 3 orders of magnitude lower than that in the p-doped GD samples studied by Jackson and co-workers.[4,6-8] This difference may be due to either microstructural differences between the GD films studied by Jackson and co-workers and the rf-sputtered ones,[9,10] and/or to differences between doped and undoped films studied at different temperatures.[4,6] Yet the discrepancy in the resulting values of ω and D_{00}, with the latter expected to be independent of film deposition conditions,[8] are even greater. The dispersive diffusion model discussed by the Xerox group can account for the suppression of the diffusion in microvoid rich films if the exponential distribution energy width is even wider and renders $\alpha \simeq 1$ in these cases. Further study is obviously required before this picture can be adopted.

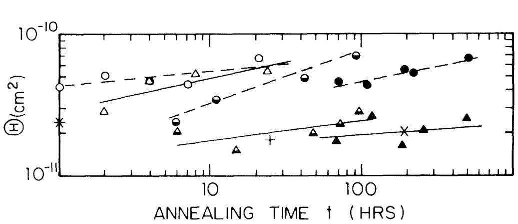

FIG. 2. The values of $\Theta(t)=\int_0^t D(\tau)d\tau$ obtained by fitting the observed SIMS profiles of samples 27 (circles) and 29 (triangles) by a complementary error function [see Eqs. (3) and (4)]. Open symbols are values at 350–355 °C; half open, at 310 °C; the solid, at 275 °C. ✱, +, and × are the values of Dt measured by Carlson and Magee (Ref. 5) at 350, 300, and 250 °C, respectively.

If it is assumed that D_{00} is thermally activated, plotting the average of $\ln D(t)+\alpha \ln t$ vs $1/T$ [see also Eq. (1)] and ignoring any temperature dependence of α in each sample separately, the apparent activation energy is estimated to be $\sim 0.55 \pm 0.2$ eV. This value is much smaller than the values previously reported,[4-6] but in (possibly fortuitous) agreement with the recently calculated wide distribution of floating- (dangling-) bond formation energies averaging 0.3 (0.6) eV.[19] An attractive explanation of our results then involves a mechanism suggested by Pantelides[3] and the results of recent calculations by Biswas *et al.*[20] In this approach the diffusion is mediated by bulk intrinsic defect migration.[3] The diffusion constant then decreases with time as the excess density of floating and dangling bonds decreases. However, in a typical film, $[\mathrm{H}_t] \sim 4\times 10^{21}$ cm^{-3}, whereas the dangling-bond density is $\sim 10^{15}$–10^{17} cm^{-3}. Thermally generated defects would thus also be involved in the diffusion process.[21] As the network relaxes in its quasiequilibrium state, the generation rate and mobility of the defects may decrease, as they increasingly occupy deeper sites in the broad distribution of their formation (equivalent to their switching or migration activation) energy.[19] This, together with a possible exponential energy distribution of Si—H bonds that need to be broken by a migrating defect in order to create the interstitial H, might account for the power-law-like decay of the hydrogen diffusion constant. These suggestions obviously require a study of the diffusion following very prolonged annealing.

The experimental results show that microvoids are also involved in suppressing the diffusion. Biswas *et al.*[20] indeed find that microvoids in a-Si quench the floating bonds and trap the dangling ones at their surfaces. The density of microvoids may thus affect the value of α, through its effect on annihilation and/or various structural relaxation processes. In particular, an increasing content of microvoids would increasingly trap newly generated defects before they can mediate the diffusion process. In this picture α approaches unity, and the diffusion is quenched, as the critical microvoid content is approached. This scenario would explain the low value of α observed by Street *et al.*[4] and Kakalios *et al.*[6] If indeed microvoids are dominant in determining α, then it would be only weakly temperature dependent as the microvoid content is (essentially) temperature independent.[1,9,10] This temperature dependence of α would then be unobservable above the experimental scatter existing within the relatively narrow temperature range employed in this work. Current studies are under way to enable a judgement of these various suggestions.

Street *et al.*[4] also showed that the prefactor of the diffusion constant is directly proportional to the bulk dangling- and floating-bond density. Yet since a significant (even dominant) fraction of these and weak Si—Si bonds indeed reside at internal surfaces in rf-sputtered films of significant microvoid content,[9,10] such a relation could not be observed in this work.

In summary, it is shown that the long-range motion of atomic H is suppressed when the microvoid content exceeds a critical value associated with an initial SiH_2 and SiH_3 density $N_{d0} \simeq 7 \pm 1$ at.%. When the initial density of these di- and tri-H configurations is somewhat below the critical value, the diffusion constant is strongly power-law time dependent, with exponent $\alpha = 0.75 \pm 0.15$. The results are discussed in relation to the multiple-hydrogen-trapping model of the Xerox group,[7,8] and a combination of the bulk-intrinsic-defect-mediated diffusion model suggested by Pantelides[3] together with an exponential distribution of either dangling- and floating-bond migration and Si—H bond energies. While these comparisons do not yield a clear verdict on either of these models, the dependence of the diffusion on the presence of microvoids is clearer within the framework of the latter.

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