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Evidence for structural relaxation in measurements of hydrogen diffusion in rf-sputtered boron-doped *a*-Si:H

S. Mitra
Ames Laboratory-U.S. Department of Energy and Physics Department, Iowa State University, Ames, Iowa 50011

R. Shinar
Microelectronics Research Center, Iowa State University, Ames, Iowa 50011

J. Shinar
Ames Laboratory-U.S. Department of Energy and Physics Department, Iowa State University, Ames, Iowa 50011

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H diffusion in boron-doped rf-sputter-deposited hydrogenated amorphous Si (*a*-Si:H) was measured by secondary ion mass spectrometry profiles of deuterium in annealed *a*-Si:H/*a*-Si:(H,D)/*a*-Si:H multilayers. The exponent $\alpha = 0.7 \pm 0.1$ of the diffusion constant $D(t) = D_{00}(\omega t)^{-\alpha}$ strongly decreases after annealing for ~50 h at 180 °C and ~35 h at 225 °C. It then increases to ~0.8–1, i.e., the diffusion is nearly quenched, at longer annealing periods extending up to 1100 h. This behavior is believed to result from modifications in the microvoid system related to structural relaxation of the Si network.

Hydrogen motion in hydrogenated amorphous silicon (*a*-Si:H) is a subject of considerable interest since it is suspected to be linked to the creation and annihilation of intrinsic defects and electronic relaxation processes.[1-5] The diffusion constant $D(t)$ has generally been observed to obey a power-law time dependence[2-9]

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

where ω is an attempt frequency and D_{00} a constant. The nature of this time dependence is, however, contested. Pantelides' fivefold coordinated floating bond model[10] suggests that it results from annihilation of excess mobile defects as the system approaches (quasi)equilibrium. Jackson and co-workers[2-5] have suggested that it is due to a multiple-trapping mechanism. Within this scheme, hydrogen becomes increasingly trapped at the deeper sites which are approximately exponentially distributed in energy, with characteristic energy kT_0. T_0 is then related to α as

$$\alpha(T) = 1 - T/T_0. \tag{2}$$

Extensive electronic measurements on doped and compensated glow-discharge-deposited (gd) films indeed yielded $600\ \text{K} \leq T_0 \leq 650\ \text{K}$ for $T < 400$ K.[2-5] While their results of secondary ion mass spectrometry (SIMS) studies of H diffusion were consistent with this behavior, their scope was too limited to independently confirm it.[2-5] Recent SIMS studies of H diffusion in a variety of rf-sputter-deposited (rf-sp) and gd *a*-Si:H yielded values of α which clearly deviate from Eq. (2).[9]

Other recent studies on both rf-sp (Ref. 7) and gd (Ref. 8) films have clearly shown that α is also affected by the microstructure, generally increasing with increasing microvoid content. When the microvoid content becomes excessive the diffusion is essentially quenched, i.e., $\alpha \sim 1$. Structural relaxation which affects the microvoid system should therefore lead to an exponent α which may depend on time in a complex manner. In this work we present such SIMS results providing indirect evidence for structural network relaxation which modifies the microvoid system in boron-doped rf-sputter-deposited *a*-Si:H.

Boron-doped *a*-Si:H/*a*-Si:(H,D)/*a*-Si:H multilayers 1–2 μm thick were deposited by 550-W rf sputtering of a 6-in.-diameter polycrystalline silicon target held 1.25 in. above the substrate, in a mixture of 10 mTorr Ar, ~1 mTorr H_2, ~0.3 mTorr D_2, and B_2H_6 diluted in Ar. The temperature of the unheated substrates was estimated to be 120–150 °C.[11] Additional details of the deposition process can be found elsewhere.[7,11,12] The films were then annealed at $T = 180$ and 225 °C in evacuated sealed pyrex tubes.

The boron content of the films, about 2 at.%, was determined by comparing its relative SIMS count to that of B implanted Si standards. The total Si-bonded H content $[H_t]$ was determined from the 640 cm^{-1} IR wagging-mode absorption peak using the absorption coefficient given by Cardona.[13] The density N_d of SiH_2 and SiH_3 configurations was determined from the bond-bending scissors mode at 840–890 cm^{-1}.[7,11,13] The Si-H stretch band at 2000–2100 cm^{-1} does not provide a determination of N_d since the mono Si-H frequency shifts from 2000 to 2100 cm^{-1} as the radius of the void around the H atom increases to 2 Å.[13] N_{d0}, the value of N_d in the as-deposited film, provides a rough estimate of the microvoid content.[11] This correlation, however, is qualitative only since the latter may be largely unhydrogenated.[11,14]

Depth profiles of deuterium were obtained using a Perkin-Elmer SIMS model PHI 6300. The depth resolution was typically ~150 Å at the film/c-Si interface. Additional experimental details are given elsewhere.[7,12]

The measured deuterium profiles were fitted to a complementary error function[15]

$$c(x,t)=c''\text{erfc}[x/2\sqrt{\Theta}(t)]\ , \tag{3}$$

where $c(x,t)$ is the concentration at a distance x from the interface after annealing for time t, c'' is an adjustable parameter which is chosen close to the value of the concentration at (0,0), and

$$\Theta(t)=\int_0^t D(\tau)d\tau\equiv\Theta_0 t^{1-\alpha}\ . \tag{4}$$

The agreement between the measured profiles and Eq. (3) was generally excellent for all but the three shortest annealing periods at each temperature. Figures 1 and 2 display $\Theta(t)$ vs t at 180 and 225 °C, respectively, in the top and the bottom layers.

Figures 1 and 2 indicate that the results can be divided into three distinct stages. (i) During the first annealing periods of up to ~50 h at 180 °C and ~30 h at 225 °C, the slope $1-\alpha$ of $\log_{10}\Theta(t)$ vs $\log_{10}t$ is low, indicating a high value of $\alpha=0.7\pm0.1$. These large values are not surprising[7,8] in view of the considerable SiH_2 and SiH_3 configuration density N_d (see Table I and below), indicating a significant microvoid content. (ii) The second stage is characterized by a sharp rise of $\Theta(t)$ with time, i.e., a sharply decreasing α. (iii) Following prolonged annealing, the diffusion of hydrogen drastically slows down beyond ~100 h at 225 °C (α~0.8) and is essentially quenched beyond ~200 h at 180 °C (α~1).

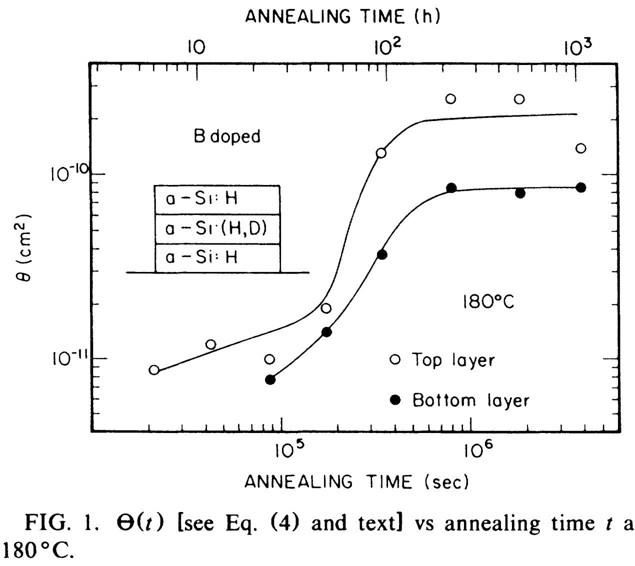

FIG. 1. $\Theta(t)$ [see Eq. (4) and text] vs annealing time t at 180 °C.

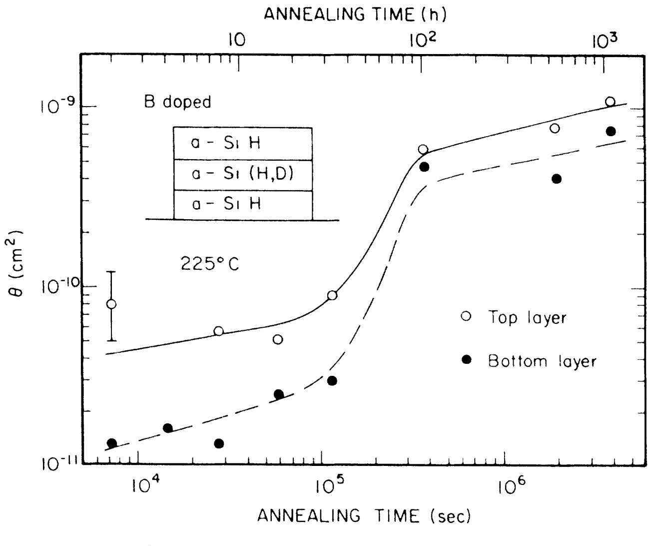

FIG. 2. $\Theta(t)$ [see Eq. (4) and text] vs annealing time t at 225 °C.

Figures 1 and 2 also show that the values of $\Theta(t)$ in the top layer are consistently higher than those in the bottom layer. This observation is not understood at present.

The IR absorption was monitored both before and after annealing of the samples. The results are summarized in Table I. The average value of $[\text{H}_t]$ and N_d in the as-deposited samples were found to be $9.4\pm1\%$ and $1.7\pm0.3\%$, respectively, indicating a significant microvoid content. $[\text{H}_t]$ slightly decreased during the initial annealing step of 2 h at 225 °C and 6 h at 180 °C. N_d decreased significantly during this annealing. $[H_t]$ and N_d then remained almost constant for at least ~100 h at 180 °C and ~30 h at 225 °C. During the prolonged annealing beyond these periods, $[\text{H}_t]$ decreased by evolution of H from SiH_2 and SiH_3 configurations. Note, however, that the ratio $I(2100)/I(2000)$ of the integrated intensity of the 2100 to the 2000 cm^{-1} stretch modes, with the latter being the dominant peak, did not change beyond the 30% margin of error during the entire annealing procedure.

It is interesting to compare these observations with recent IR results of Fritzsche and Deng on various gd films annealed for moderate periods at 220 °C.[16] They noticed that in boron-doped films, some hydrogen irreversibly converts *from* bulk mono-H bonding *to* SiH_2 and SiH_3 configurations during annealing at 220 °C. Although no emergence of a bond bending scissors mode was observed in n-type-doped films, the stretch peak at 2100 cm^{-1} did increase. These processes were faster in p-type-doped (< 20 h) than in the n-type-doped films. Thus, even moderate annealing of these doped gd films resulted in changes in the Si network consistent with a rise in the microvoid-related H content. Since H diffusion is most rapid in p-type-doped, slower in n-type-doped, and slowest in undoped films, it appears to be the process controlling the above changes and consequent evolution of the Si network. We observed a *decrease* in N_d in the boron-doped rf-sp films during the initial annealing step at each temperature. This may be due to the difference between the

TABLE I. Total Si-bonded H concentration $[H_t]$, SiH_2, and SiH_3 bonding configuration density N_d, both in at.% relative to Si, and the ratio $I(2100)/I(2000)$ of the integrated intensity of the 2100 to 2000 cm^{-1} stretch modes, after each annealing step at 180 and 225 °C.

	Annealing at 180 °C			Annealing at 225 °C			
Annealing time (h)	$[H_t]$ (at.%) ($\pm 10\%$)	N_d (at.%) ($\pm 20\%$)	$\frac{I(2100)}{I(2000)}$ ($\pm 30\%$)	Annealing time (h)	$[H_t]$ (at.%) ($\pm 10\%$)	N_d (at.%) ($\pm 20\%$)	$\frac{I(2100)}{I(2000)}$ ($\pm 30\%$)
as deposited:	9.4	1.7	0.54				
6	10.0	1.1	0.62	2	8.9	1.4	0.45
12	8.0	1.0	0.50	4	8.9	1.6	0.57
24	8.0	0.9	0.65	8	9.9	1.2	0.75
48	7.6	0.9		16	8.5	1.3	0.47
96	8.5	1.0	0.49	32	8.5	1.0	0.47
222	8.8	0.7	0.70				
516	8.3	0.6	0.57	552	5.7	0.4	0.52
1080	7.5	0.5	0.62	1100	6.9	trace	0.44

rf-sp and the gd films, or differences between doping levels. The gd films were apparently device quality, containing few microvoids as deposited. In the as-deposited rf-sp films, the intensity of the 840–890 cm^{-1} bond-bending scissors mode, characteristic of microvoids, was significant.

The evolution of hydrogen and the *decrease* in N_d observed in this work on rf-sp films are generally in agreement with thermal desorption spectroscopy (TDS) studies.[17,18] These have clearly shown that H in SiH_2 and SiH_3 configurations evolves out of undoped films at 325–375 °C, whereas the bulk, mono-H evolves at 475–575 °C. The evolution process is apparently similar in doped films, but the absolute temperatures of the TDS peaks are lower.[19] The observation that $I(2100)/I(2000)$ does not change beyond the 30% margin of error is significant. It indicates that most of the contribution to the peak at 2100 cm^{-1} is due to mono-H bonds at the surfaces of large microvoids (radius ≥ 2 Å), rather than to SiH_2 or SiH_3 configurations. It does not, however, mean that the distribution of hydrogen among bulk sites and voids of various sizes is largely unchanged: An H atom moving from a bulk site to the surface of a "compact" microvoid (see below), would still yield a stretch vibration frequency of 2000 cm^{-1}. Even the distribution of hydrogen among bulk and "compact" voids on the one hand, and large microvoids on the other hand, is qualitative only, since the oscillator strength varies with the size of the void around the H atom.[11,13,18] Thus, although the 2000-cm^{-1} peak dominates the stretch band, it only suggests that a significant fraction of the H atoms is either bonded in the bulk or on "compact" microvoid surfaces.

No deviation of $\Theta(t)$ from the power-law time dependence [Eq. (1)] has been previously reported. These previous studies included prolonged annealing of undoped films, extending to 500 h at 275 °C (Ref. 7) and 210 h at 330 °C.[9] The sharp rise in $\Theta(t)$ during annealing beyond ~ 50 h at 180 °C [Fig. (1)] and ~ 30 h at 225 °C [Fig. (2)] is thus unprecedented. Indeed, during some part of this second stage of the annealing process, the slope of $\log_{10}\Theta(t)$ vs $\log_{10}t$ appears to be larger than one. Equation (4) would then imply that $\alpha < 0$, and Eq. (1) that $D(t)$ increases with t. Although such extraordinary behavior cannot be ruled out, the available results are insufficient to firmly establish it. They do, however, clearly show that during this second stage of annealing α is not significantly larger than zero. $D(t)$ is then roughly constant during this period. A constant $D(t)$ may indicate that the H atoms have reached the bottom of the trapping distribution following the initially dispersive motion in the relaxing network. We note, however, that the high value of α in both the first and third stages indicates strong effects of microvoids in both. Thus, the transition between these stages is believed to involve structural relaxation processes which rearrange the microvoid system. During this period, as the structure relaxes, some of the immobile hydrogen trapped in deep microvoid-related sites is released and becomes relatively mobile. This results in a relatively rapid rise of $\Theta(t)$. Following these processes, the system reaches a quasiequilibrium state, i.e., a local minimum in configuration space. The diffusion of hydrogen may then become nearly quenched, if most of the H atoms reoccupy deep microvoid-related sites.

The nature of the deep H-trapping sites induced by microvoids is still not settled. Previous studies,[7,8] and the high initial value of α observed in the present work, linked such sites to the presence of large microvoids (radius > 2 Å). Since the IR peak at 2000 cm^{-1} still dominates the IR stretch band (see Table I), a significant fraction of the hydrogen is not located on the surfaces of such voids. Some of the deep H-trapping sites are consequently located at other sites. At present, we can only speculate on the nature of these other deep sites. Highly "compact," "pancake"-like microvoids, of opposing surfaces only ~ 3 Å apart, would probably be present along with larger microvoids.[14] Such compact microvoids may possibly be identified with the multivacancies discussed by Mahan *et al.*[14] Hydrogen atoms on their surfaces would experience a dielectric screening similar to H atoms in the bulk, and consequently vibrate at ~ 2000 cm^{-1}.[13,14] Preliminary ^{1}H NMR measurements on various as-deposited and annealed undoped rf-sp films[20] suggest that most of the hydrogen migrates to "clustered" sites, i.e., those yielding a broad ^{1}H NMR line, during annealing at 300 °C. The deep H-trapping sites may therefore be such mono-H clustered sites, occurring on the surfaces of both large and "compact" microvoids or multivacancies.

In conclusion, effects of prolonged annealing on hydrogen diffusion at 180° and 225 °C in boron-doped rf sputter deposited a-Si:H were described and discussed. Striking deviations from the power-law time dependence of the diffusion constant $D(t)$ were observed. The exponent α sharply decreases during annealing beyond $\sim$50 h at 180 °C and $\sim$30 h at 225 °C. At 180 °C it subsequently increases to $\sim$1, i.e., the diffusion is quenched, during prolonged annealing beyond $\sim$200 h. At 225 °C it increases to $\sim$0.8, i.e., the diffusion drastically slows down, beyond $\sim$100 h. This behavior was attributed to processes which modify the network of hydrogen sites, as the Si network relaxes to a quasiequilibrium state.

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