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Evidence for the hydrogen-glass model of metastability annealing in phosphorus-doped amorphous silicon

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We present qualitative and quantitative evidence that the H-glass model is applicable to metastability annealing in P-doped hydrogenated amorphous silicon and measure the principal parameter of the model. We study the effect of H content on the annealing of quenched-in, metastable, excess dark conductivity in amorphous silicon. The annealing temperature (T^*) is 355±20 °C in sputtered P-implanted amorphous silicon (*a*-Si) containing 0.1 at. % of H. After hydrogenation with about 10 at. % of H, T^* falls to 175±20 °C, much closer to the 130 °C observed in glow-discharge hydrogenated *a*-Si. We derive a quantitative prediction of the H-glass model: the H-diffusion coefficient at T^* is inversely proportional to the H content in *a*-Si samples. Our measurements of H-diffusion coefficient at T^* are in agreement with this prediction.

I. INTRODUCTION

Hydrogenated amorphous silicon (*a*-Si:H) is used in a variety of electronic devices, including photovoltaic cells and thin-film transistors. However, widely studied, reversible, metastable changes induced by light, carrier injection, and thermal quenching limit the use of *a*-Si:H.[1] Since the discovery of metastable effects in *a*-Si:H,[2] many workers have proposed that H plays a central role in the microscopic mechanism of the changes.[3–6] In particular, Street *et al.*[6] postulate a "hydrogen glass" model of metastability in which H diffusion mediates defect creation and annealing.

The principal quantitative evidence given for the H-glass model is a relation between the stretched exponential kinetics of metastability annealing and the dispersive diffusion of H in *a*-Si:H.[7] However, stretched exponential decays are widely observed in disordered systems, and Crandall[8] and Redfield[9] are able to explain the metastability annealing kinetics in *a*-Si:H without reference to H diffusion. There are also many qualitative correlations between the defect equilibration temperature (T^*) and the H-diffusion coefficient (D_H) in glow-discharge P-doped, B-doped, and undoped *a*-Si:H samples.[6,10] However, the change of T^* with doping type could be related to the different defects now known to undergo the metastability.[11,12]

In this paper, we describe evidence that the H-glass model of metastability is applicable to quenched-in metastability in P-doped *a*-Si:H. We observe quenched-in metastability of the dark conductivity in P-doped *a*-Si containing only 0.1 at. % of H, with a value of $T^*=355°\pm20$ °C. This is more than 200 °C higher than T^* found in P-doped glow-discharge (GD) *a*-Si:H containing 10 at. % H. After we hydrogenated this *a*-Si sample with 10 at. % of H, T^* fell to 175±20 °C, closer to the glow-discharge value.

We develop a quantitative prediction of the H-glass model: the H-diffusion coefficient at $T^*,D_H(T^*)$, should be inversely proportional to the H concentration. Our measurements and published data for P-doped GD *a*-Si:H agree with this prediction. Finally, we discuss the physical implications of the proportionality constant that we measure.

The H-glass model describes our data for P-doped films. However, previously published data for metastability annealing and H diffusion in *undoped* *a*-Si:H suggest there may be no connection between H diffusion and metastability annealing in undoped *a*-Si:H.

II. HYDROGEN-DIFFUSION-LIMITED ANNEALING

Street *et al.*[6] propose that the submatrix of bonded H in *a*-Si:H undergoes a glass transition at T^*, and that H above this temperature is sufficiently mobile to permit thermal equilibration of the defect structure. This is the H-glass model. To estimate T^*, Street *et al.*[6] assume that H diffusion mediates the diffusion of dangling-bond defects and use measured H-diffusion coefficients (D_H) to calculate the temperature at which dangling-bond mobility is high enough to anneal out metastable defects.

We reinterpret the H-glass model slightly and derive a relationship between the film H content (C_H) and the H-diffusion coefficient at $T^*,D_H(T^*)$. We assume that a H atom must mediate thermal creation or annealing of a defect and that the arrival of a diffusing H atom is the rate-limiting step in the annealing process. We believe that hydrogen-diffusion-limited annealing is a direct consequence of the H-glass model. Of course, H could be involved in the annealing process even if H diffusion is not the rate-limiting step, but in this case the existence of the H glass would be irrelevant to *a*-Si:H metastability kinetics.

T^* is the temperature at which thermal equilibration of the defect sites is accomplished within the experimental time. (Because T^* depends logarithmically on the experimental time, one must hold heating rates and anneal-

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ing times roughly constant for a standard definition of T^*.) For H-diffusion-mediated defect equilibration, we expect T^* to be the temperature at which H can visit each atomic site some definite number of times during the anneal.

To calculate the time required for H to visit each atomic site for a given H-diffusion constant, we first oversimplify the H-diffusion process and assume that $D_H = a^2 \nu/6$. Here, the hydrogen hop distance is the interatomic spacing a. Each H atom then visits sites at the H hopping rate ν and reaches all atomic sites during a time $t = (\nu C_H)^{-1} = a^2/6 D_H C_H$.

Branz, Asher, and Nelson[13] recently observed that H diffusion in a-Si:H is actually trap controlled. They found that $D_H = \lambda^2 f$, where $\lambda \approx 100-300$ Å is the mean distance between H trapping events, and f is the detrapping rate. Assuming the H makes a random walk between trapping events, each H visits sites at the rate $f(\lambda^2/a^2)$. H reaches all atomic sites in the time $a^2/f\lambda^2 C_H = a^2/D_H C_H$.

The time it takes H to visit all atomic sites once is proportional to $(D_H C_H)^{-1}$ in either H-diffusion model. The time to visit a fixed fraction of the sites or to visit each site a fixed number of times is also proportional to $(D_H C_H)^{-1}$. If defect thermal equilibration is H diffusion limited, the quantity $D_H(T^*)C_H$ will remain constant as we vary C_H in a-Si:H samples.

III. EXPERIMENT

Samples were grown by magnetron sputtering in a 3–5-mtorr Ar atmosphere at North Carolina State University. The fused silica (conductivity) and crystalline Si substrates coated in each sputtering run were unheated, and the chamber base pressure was below 10^{-8} torr. The sample thickness is about 1 μm.

Films on both substrates were ion implanted with 2 at. % P to a depth of 0.28 μm by Ion Implantation Corp. of Santa Clara, Calif. We then divided each film and hydrogenated half at 250 °C with 1-keV H^+ ions from a Kaufmann ion source.[14] We refer to the sputtered low-H-content films as "sample LH" and the hydrogenated high-H-content films as "sample HH." Cs^+ secondary-ion-mass spectrometry (SIMS) profiling shows H concentration of 0.1 at. % in the doped region of sample LH, and 8–10 at. % in the doped region of sample HH. The O concentration is 5×10^{19} cm^{-3} (0.1 at. %), and the C concentration is 10^{19} cm^{-3}.

We evaporated Ag coplanar contacts 5 mm (3 mm) long and 1 mm apart onto sample LH (HH) on the glass substrate after all the implantations were complete. We preannealed sample LH for 24 h at 450 °C, and sample HH for 1 h at 300 °C and 24 h at 230 °C before electrical measurement. Preannealing minimized the irreversible effects observed during our quenching studies.

Slow-cooling and quenching procedures were as follows. For each anneal, we placed the sample under test in an oven for 30 min at an elevated temperature. To slow cool, we simply shut the oven off and the sample cooled at about 1 °C-min^{-1}. To quench, we pushed the sample from the oven into a beaker of liquid nitrogen (LN). We quenched sample LH from 250 °C at a slightly lower rate by flowing LN-cooled nitrogen through the hollow heater stage. We estimate that the quench rate in all cases was 10–100 °C-s^{-1}.

After cooling, we transferred the samples to a measurement chamber, pumped to below 10^{-6} torr, and then measured conductivity (σ) in 1 torr of flowing N_2. We increased the temperature (T) from room temperature at ~5 °C-min^{-1} and measured σ at intervals of about 5 °C. After each measurement, we cooled the sample to room temperature and transferred it to the oven for another annealing and cooling treatment.

Room-temperature current-voltage characteristics were linear to above 100 V, with a contact voltage drop that was negligible compared to the σ measurement voltage of 50 V. Because sample conductance increases by more than three orders of magnitude after P implantation, we use the implantation depth as the sample thickness when calculating σ from the measured conductance.

We determined conductivity activation energy (E_{act}) from the slope of the linear best fit to $\ln(\sigma)$ versus $1/T$ up to 250 and 150 °C for samples LH and HH, respectively. We derived error bars from the probable uncertainty in the slope of the fit. Occasionally, there is a sudden jump in conductivity 25% or less during measurement (e.g., the first slow cool of sample LH in Fig. 1). We believe the jumps are caused by a shifting of the contact probes during heating or some other experimental artifact. Because we observed anomalously high values of chi squared for the linear fit during runs with conductivity jumps that affect E_{act} most, we systematically reject data with the highest values of chi squared. We exclude 21 of 111 scans by this procedure.

We made quench and slow-cool conductivity measurements on sample LH after annealing at seven different temperatures. To reduce the importance of irreversible changes in the sample, we used the following sequence of temperatures: 250, 400, 370, 340, 310, 410, and 300 °C. We measured the conductivity of sample HH for quench and slow-cool series at five different temperatures: 230, 170, 185, 200, 170, and 180 °C. Except for a few control scans, we alternately quenched and slow cooled each

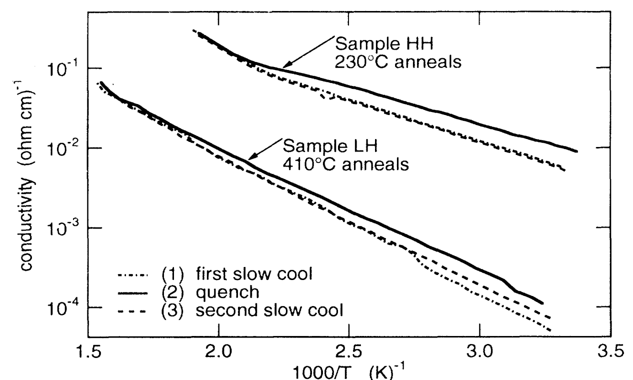

FIG. 1. Log σ vs inverse temperature of samples LH and HH after annealings at 410 and 230 °C, respectively. The legend indicates the experimental sequence.

sample. We made 4–15 measurements of $\sigma(T)$ at each temperature.

We studied the hydrogen diffusion in samples LH and HH by deuterating the surface of the films on crystalline Si substrates with about 10^{14} cm^{-2} of 200-eV D^+ ions from the Kaufmann ion source. The surface-deuterated samples were then annealed in the oven and the D diffused into the film. Deuterium profiles measured by Cs^+ SIMS were normalized point by point to the Si matrix profile to compensate for the ion yield transient near the surface. The as-implanted D concentration decayed roughly exponentially with a characteristic length of 60–80 Å.

IV. CONDUCTIVITY DATA

Figure 1 shows $\sigma(T)$ curves for each sample after consecutive slow-cool, quench, and slow-cool treatments. Hydrogenation increases σ by more than two orders of magnitude and reduces E_{act} from about 0.3 to about 0.2 eV. Qualitatively similar reversible changes in $\sigma(T)$ and E_{act} are clearly observed in each sample. The quench treatment increases the low-temperature conductivity of each sample by about 50%, and reduces E_{act} by 20–30 meV. We anneal sample LH at 410 °C and sample HH at 230 °C before cooling. The conductivity of sample HH is independent of pretreatment above about 200 °C, while the $\sigma(T)$ curves for sample LH seem to converge above about 350 °C. This gives a rough estimate of T^* for these samples.

However, in some scans, we find that the annealing itself causes an irreversible drift of σ and E_{act} that obscures reversible changes and prevents a precise determination of T^* from the convergence of $\sigma(T)$ curves. Instead, we determine T^* for the metastabilities with an alternate technique that reduces the importance of irreversible drift effects.

Figure 2 shows the relative magnitude of the reversible and irreversible changes in conductivity. The figure shows E_{act} for sample LH after annealing and cooling from 250 [Fig. 2(a)] and 400 °C [Fig. 2(b)]. We alternate slow-cool and quench treatments. Both series show the irreversible drift of E_{act} mentioned above. Reversible changes are not evident in Fig. 2(a). However, Fig. 2(b) shows clear, reversible, quench-induced changes in the conductivity activation energy of the 400 °C series. This reversible metastability is superimposed on the irreversible increase of E_{act}. Taken together, Figs. 2(a) and 2(b) imply that $250 < T^* < 400$ °C in sample LH.

A more exact value of T^* is best determined by computing the difference of activation energy between quenching and slow cooling for consecutive runs. We calculate the differences and plot them in Fig. 3 as a function of the annealing temperature of the runs. In Fig. 3, Δ_q is the change in E_{act} for a quench that follows a slow cool, and Δ_{sc} is the change for a slow cool that follows a quench. We define these as follows:

$$\Delta_q = (E_{act})_{quench} - (E_{act})_{slow\ cool}$$

and

$$\Delta_{sc} = (E_{act})_{slow\ cool} - (E_{act\ quench}) \ .$$

Figure 3(a) shows the results for sample HH, and Fig. 3(b) shows the results for sample LH.

V. DETERMINATION OF T^*

In doped GD-deposited *a*-Si:H, quenching after annealing above T^* reduces E_{act}.[15] Consequently, Δ_q is negative and Δ_{sc} is positive. Below T^*, variations in quench rate and unpredictable irreversible drifts yield small values of Δ_q and Δ_{sc} that should average to zero. This behavior is shown for both samples LH and HH in Fig. 3.

Quenched-in metastability of sample HH is observed for anneals at $T \geq 180$ °C, as shown in Fig. 3(a). Quenching reduces E_{act} by 20±10 meV. Quenching from $T = 170$ °C causes no systematic changes in the conductivity. Apart from an estimated error of ±5 °C in determining the oven temperature, T^* must lie between 170 and 180 °C. Because of the long oven anneals, this is slightly lower than $T^* \sim 200$ °C determined from the joining of conductivity curves in Fig. 1; during $\sigma(T)$ mea-

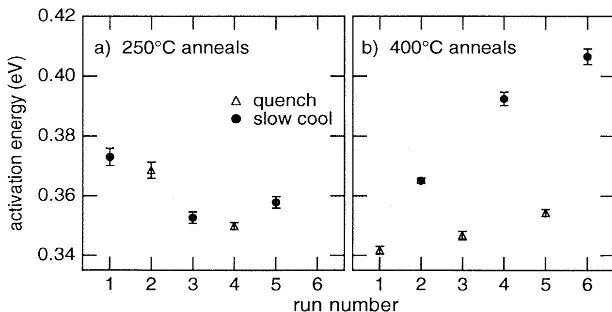

FIG. 2. Activation energy of dark conductivity of sample LH after alternate slow-cool and quench treatments from (a) 250 and (b) 400 °C.

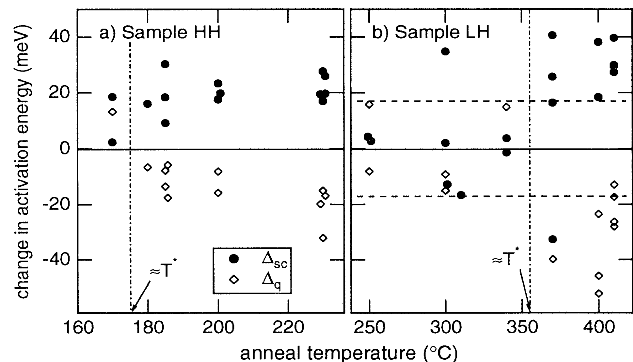

FIG. 3. Changes in activation energy caused by quenching after slow cooling (Δ_q) and by slow cooling after quenching (Δ_{sc}) of (a) sample HH and (b) sample LH. Samples were slow cooled or quenched after annealing at the temperatures indicated on the abscissa. Vertical dot-dash lines show the approximate positions of T^*.

surements, we scan quickly from 170 to 200 °C in about 6 min, and the structure does not have time to fully equilibrate. We conclude that $T^*=175\pm20$ °C in sample HH.

Quenched-in metastability of sample LH is observed for anneals at $T\geq370$ °C, as shown in Fig. 3(b). Quenching reduces E_{act} by 30 ± 10 meV. For $T\leq340$ °C, we observe no systematic trend in either Δ_q or Δ_{sc} [see also Fig. 2(a)]. Irreversible effects and measurement noise are about 17 meV in the difference between consecutive runs, as indicated by the horizontal dashed lines in Fig. 3(b). We conclude that $T^*=355\pm20$ °C in sample LH.

VI. H DIFFUSION

We annealed the surface-deuterated samples for varying lengths of time at T^* to determine $D_H(T^*)$. Anneals ranging from a few hours to a few days yielded no measurable change in the as-deposited exponentially decaying profile in either sample, and this suggests rather low diffusion coefficients ($<10^{-17}$ cm^2 s^{-1}). Longer anneals did enable us to observe D diffusion at T^*.

Figure 4 shows a typical D depth profile taken after annealing sample LH for $t_a=841$ h (about 35 days) at $T^*=355$ °C. The high concentration spike near the surface suggests that some of the implanted D was deep trapped and did not participate in the diffusion. The near-Gaussian profile from 200 to 1500 Å in depth corresponds to the ideal solution[16] of the diffusion equation for a planar source, $C(x)=C_0\exp(-x^2/4D_Ht_a)$. The inset to Fig. 1 shows that there is a linear relation between the $\log_{10}D$ concentration and the square of the depth. The slope of the best-fit line corresponds to $D_H=4\times10^{-18}$ cm^2 s^{-1}. Several other SIMS craters in sample LH yielded D_H within a factor of 2 of this value.

The D profile of sample HH after $t_a=1962$ h (about 82 days) at $T^*=175$ °C was not Gaussian. Instead, it decayed exponentially from 150 to 500 Å with a characteristic length of about $d=140$ Å. Jackson and Tsai[17] also observed exponential tails for diffusion from the surface in dehydrogenated glow-discharge a-Si:H. An exponential tail indicates that the anneal time was insufficient to obtain a dynamic equilibrium between free and trapped D and that most D atoms were detrapped once or less during the anneal.[18] Thus d^2/t_a is an upper bound to D_H. The amplitude of the tail suggests that at least 10% of the implanted D is participating in the diffusion and $d^2/10t_a\leq D_H$. We conclude that $3\times10^{-20}\leq D_H\leq3\times10^{-19}$ cm^2 s^{-1} at 175 °C in sample HH.

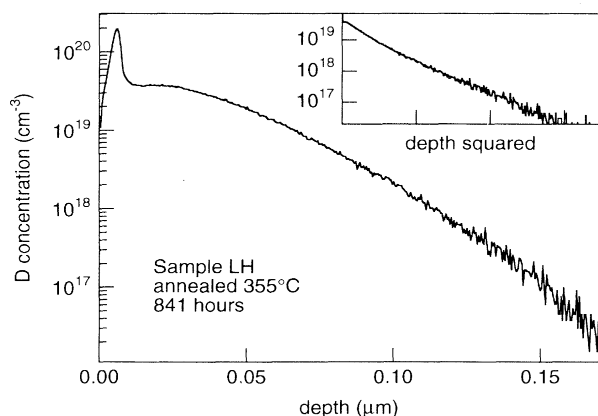

FIG. 4. Deuterium concentration vs depth in sample LH after an 841-h anneal at $T^*=355$ °C. Inset shows logarithmic D concentration vs the square of the depth. This should be linear for a Gaussian diffusion profile.

VII. DISCUSSION

A. H involvement in the metastability

We measure $T^*=355$ °C for quenched-in metastability in the P-doped sample LH with 0.1 at. % of H. The value of T^* in sample LH is more than 200 °C higher than the 130 °C observed in 10 at. % H, P-doped, a-Si:H prepared by GD.[15] This subsequent hydrogenation of sample LH with 10 at. % of H reduces T^* from 355 to 175 °C.

Matsuo *et al.*[19] previously studied P-doped a-Si:H and saw an increase of T^* by 50 °C in a series of samples grown with decreasing H contents from 16 to 3 at. %. Recently, Fritzsche[20] measured an 85 °C increase in T^* for P-doped GD a-Si:H as they reduced C_H by progressive annealing. Our result is obviously consistent with the trend observed at higher C_H and this suggests that the dramatic changes in T^* we observe are not an artifact of our film preparation or hydrogenation techniques. H appears to play a crucial role in determining T^* in P-doped a-Si:H, independent of sample preparation technique.

The magnitude of the quenching effect in a-Si with only 0.1 at. % H is comparable to that observed in a-Si:H. The Fermi-level decrease in sample LH after quenching is 30 ± 10 meV, slightly larger than 20 ± 10 meV observed after hydrogenation in sample HH. These values are roughly equal to the 30 meV measured in P-doped a-Si:H deposited by glow discharge,[15,21] and to the 20 meV measured in P-doped a-Si:H deposited by laser-induced chemical vapor deposition.[22]

Despite the low H content of sample LH, we cannot rule out direct H involvement in the metastable defect annealing reaction. In GD-deposited a-Si:H, it was shown[11,12] that the increase in conductivity after quenching is due primarily to an increase of P-dopant activation.[23] We estimate the number of dopants activated by the quench to be about 10^{16} cm^{-3}, the product of the Fermi-level (E_F) shift (30 meV) and the density of electronic states at E_F (more than 10^{17} cm^{-3}-eV^{-1} at 0.3 eV below the conduction-band edge). Consequently, even in sample LH, with only 5×10^{19} cm^{-3} of H, the density of H atoms is at least three orders of magnitude greater than the density of P atoms activated by the quench.

The change in T^* with H content in our samples is qualitatively consistent with the H-glass model for a-Si:H metastability.[6] Because there is less H in sample LH, that H must visit sites more frequently to equilibrate the defects in a given time. This requires a higher H-diffusion coefficient for sample LH than for sample HH. The value of T^* is therefore high in sample LH.

B. Quantitative agreement with H-glass model

In Table I, we show measured values of $D_H(T^*)$ in our samples and in standard GD material. We determined T^* of samples LH and HH by studies of equilibration after anneals of $t_a=30$ min. Street, Kakalios, and Hayes[15] found $T^*=130\,^\circ$C for P-doped GD material by studies of equilibration during heating of films they had previously quenched. Their heating rate of 3 °C-min^{-1} corresponds to about 7-min annealing within $\pm10\,^\circ$C of any given temperature, compared to our 30-min oven anneals. These techniques of determining T^* yield only slightly different results, because T^* is inversely proportional to the *logarithm* of the product of t_a and the annealing prefactor. For an annealing prefactor of 10^{12} s^{-1}, the heating rate of Street, Kakalios, and Hayes[15] will give a value of T^* about 4% (15 °C) higher than our oven anneals. In Table I, we have therefore indicated a T^* of 130–145 °C for P-doped GD a-Si:H.

Early-time hydrogen diffusion studies suggest that one can accurately extrapolate D_H to lower temperatures than the ordinary measurement range.[13] Extrapolation to 130 or 145 °C of H-diffusion data[24] in GD P-doped (10^{-3} P in the gas phase) a-Si:H yields $D_H(T^*)\sim10^{-19}$ cm^2 s^{-1}. The measured diffusion coefficient in sample LH at 355 °C is five to six orders of magnitude lower than D_H in GD a-Si:H at the same temperature,[24] because the unhydrogenated material has a high density of H-trapping sites.

Table I demonstrates rough quantitative agreement with the prediction of the H-glass model that $D_H(T^*)C_H$ is a constant (see Sec. II). Sample LH contains roughly two orders of magnitude less H than does GD a-Si:H, and $D_H(T^*)$ is two orders of magnitude higher than in the GD material. $D_H(T^*)C_H$ in sample HH is also consistent with the $D_H(T^*)C_H$ in sample LH. By measuring D_H at T^* for the first time in P-doped amorphous silicon, we have demonstrated that the principal parameter of the H-glass model, $D_H(T^*)C_H$, is 4×10^{-21} cm^2 s^{-1}.

The difficulty of measuring both T^* and the low values of D_H (T^*) introduces some scatter into the data of Table I. However, the H-glass model provides a good framework for understanding both the remarkably high value $T^*=355\,^\circ$C in sample LH, and the dramatic reduction of T^* upon hydrogenation. Studies of $D_H(T^*)$ across a wider range of H contents will be required to develop more confidence in the model.

Our measured H-glass constant $D_H(T^*)C_H$ suggests features of the equilibration process in P-doped a-Si:H. For our anneal time of 30 min, the sample must equilibrate in about $t_{eq}=10^3$ s at T^*. Extending the arguments of Sec. II, we find that H visits a fraction $6D_H(T^*)C_H t_{eq}/a^2$ of atomic sites in this time. The H thus visits only 10^{-2} of atomic sites, and we conclude that H does not mediate equilibration by visiting all the P sites. The H also visits only 10^{-2} of the P sites that were activated by the anneal/quench procedure and therefore cannot deactivate all the quenched-in defects. However, in our samples (2 at. % P), H does visit about 10^{19} cm^{-3} of P sites. We expect that roughly 1% of this P visited by H will be activated;[25] therefore, H visits about 10^{17}-cm^{-3} activated P in the time t_{eq}. This is about ten times the number of P atoms metastably activated by the quench, and can account for the equilibration.

It appears that the H can enable equilibration by deactivating *any* of the activated P atoms, *not* precisely the same P sites that were activated during the anneal/quench procedure.[26] Electronic transfers between P and the Fermi energy govern the thermal equilibrium density of activated P atoms at a given temperature. The H diffusion establishes only the rate of equilibration.

C. Microscopic model

Liu and Spear[27] propose a microscopic mechanism for the H-glass model of defect equilibration in a-Si:H. These authors suggest that the Zhang-Chadi model[28] of P-Si-H complexes in crystalline Si also describes H-diffusion-limited deactivation of the P in a-Si:H. Basically, H diffuses to the activated fourfold-coordinated dopant site and bonds to a Si atom that is bonded to P. The Si-P bond is soon broken, and the P becomes an inactive threefold-coordinated P. Mechanistically, this proposal is particularly appealing in a-Si:H; the intermediate state involves a short-lived, fivefold-coordinated Si "floating bond" state.[29] Our data for metastability annealing is consistent with the proposal of Liu and Spear.[27]

For each of our samples, the P-activation (anneal/quench) process has roughly the same value of T^* as the deactivation (anneal) process. This suggests that dopant activation is also rate limited by H diffusion to the defect. However, Liu and Spear[27] conclude from the pure exponential kinetics of the dopant activation that the activation rate is determined by a simple H release from the P-Si-H complex. These results appear to be mutually inconsistent. More work is needed to clarify the issue of whether the dopant activation rate is H diffusion limited.

TABLE I. Measured values of H-glass model parameters in P-doped amorphous silicon.

Sample	C_H (at. %)	T^* (°C)	$D_H(T^*)$ (cm^{2}s^{-1})	$C_H D_H(T^*)$ (cm^{2}s^{-1})
LH	0.1	355	4×10^{-18}	4×10^{-21}
HH	8–10	175	3×10^{-20}–3×10^{-19}	2×10^{-21}–3×10^{-20}
GD	~10	130–145[a]	$\sim10^{-19}$[b]	$\sim10^{-20}$

[a]Reference 15, corrected to 30-min anneals.
[b]Extrapolated from Ref. 24 data.

D. B-doped and undoped *a*-Si:H

After we presented preliminary results of our quenching studies,[30] Pietruszko[31] measured T^* by conductivity quenching experiments in a series of B-doped *a*-Si films with varying H contents. As the H content decreased from more than 10 to 0.08 at. %, T^* increased monotonically from 170 to 380 °C. Migrating atomic H is known[32] to deactivate acceptor dopants in crystalline Si. Pietruszko's results[31] suggest that there is a similar connection between T^* and C_H in both P- and B-doped *a*-Si:H, and that the H-glass model for dopant deactivation is applicable to both. Of course H-diffusion measurements on the samples would be required to confirm its applicability.

Despite the success of the H-glass model in describing our doped *a*-Si:H metastability data, previously published evidence suggests that the model is not applicable to undoped *a*-Si:H. Some of this evidence is described below. However, we cannot exclude the possibility that annealing of metastable defects involves a subset of mobile H that does not also determine the measured H-diffusion coefficient. For example, local H motion might cause metastability annealing even if the H-glass model does not apply. We interpret the H-glass model as requiring that the diffusion of most of the H is relevant to metastability annealing, and that the measured D_H determines anneal kinetics.

Xu *et al.*[33] quenched undoped GD *a*-Si:H and saw almost no change of the value of T^* (211±20 °C) for deep-defect-density equilibration as C_H increased from 7 to 31 at. %. However, as Shinar *et al.*[34] increased C_H from 7 to 16 at. % H in undoped GD *a*-Si:H, they found that D_H increased by about two orders of magnitude, presumably because the density of H traps was reduced. Taken together, these studies are inconsistent with the H-glass model.

The wide variety of defect annealing temperatures that have been observed in undoped *a*-Si:H also appear inconsistent with the H-glass model. For example, Stradins and Fritzsche[35] found that 40% of defects created by 4.2-K light soaking anneal out in only 5 min at 300 K. Annealing at such a low temperature is obviously not H-diffusion-limited annealing involving most of the H. Also, McMahon and Tsu observed that the equilibration temperature is 150 °C for dangling bonds created by light soaking of undoped *a*-Si:H, but $T^*=200$ °C for dangling bonds created by quenching in the same sample.[36] We do not see how the H-glass model can apply to all metastable defect annealing processes in undoped *a*-Si:H when $D_H(T^*)$ varies by about two orders of magnitude for different types of defects in a single sample.

VIII. CONCLUSION

We observe a reversible metastable effect by quenching P-doped *a*-Si containing 0.1 at. % of H. The equilibration temperature of this effect is 355±20 °C, more than 200 °C higher than in P-doped GD *a*-Si:H containing 10 at. % of H. However, the product $D_C(T^*)C_H$ is about 4×10^{-21} cm^2 s^{-1} in both types of films. Hydrogenation with 8–10 at. % of H reduces the equilibration temperature to 175±20 °C, but $D_H(T^*)C_H$ is unchanged within the accuracy of the measurements. Our results support the applicability of the H-glass model[6] to quenched-in metastability annealing in P-doped *a*-Si:H.

Note added in proof. M. Vanecek, J. Fric, R. S. Crandall, and A. H. Magan [J. Non-Cryst. Solids (to be published)] recently presented evidence that the H-glass model is not applicable to quenched-in metastability annealing in undoped *a*-Si:H. They measured $T^*=220\pm8$ °C, independent of H concentration, for undoped hot-wire *a*-Si:H films in which C_H varied from 0.3 to 12.6 at.%. Their experimental result is distinctly different from the present result for *P*-doped a-Si:H films.

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[1]See, for example, *Amorphous Silicon Materials and Solar Cells,* AIP Conf. Proc. No. 234, edited by B. L. Stafford (AIP, New York, 1991).

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