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Light-enhanced deep deuterium emission and the diffusion mechanism in amorphous silicon

Howard M. Branz, Sally E. Asher, and Brent P. Nelson
National Renewable Energy Laboratory, Golden, Colorado 80401
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We demonstrate that hydrogen diffusion in hydrogenated amorphous silicon (*a*-Si:H) is trap controlled and measure a 1.4-eV barrier for deep deuterium emission to a transport level in D-doped *a*-Si:H. We show that light-enhanced diffusion in *a*-Si:H is caused by light-enhanced detrapping of H and not by heating of the sample. From our experiments, we obtain estimates of the free-H-diffusion coefficient (3×10^{-8} cm^2 s^{-1}), the mean H displacement between deep trapping events (250 Å), and the other parameters that determine the measured H-diffusion coefficient in *a*-Si:H.

I. INTRODUCTION

Amorphous silicon is a technologically important semiconductor only in its hydrogenated form, *a*-Si:H. Hydrogen dramatically improves material quality by reducing the density of gap-state electronic defect levels. However, many workers suspect H of enabling the deleterious metastable effects caused by illumination and carrier injection[1] that limit commercial applications of the material. A connection between illumination and H motion is suggested by two recent experiments. Weil, Busso, and Beyer[2] report that illumination reduces the D effusion temperature in *a*-Si:D:F and Santos, Johnson, and Street[3] observe light-enhanced D diffusion in *a*-Si:H between 175 and 300 °C. However, neither of these experiments directly addresses the mechanism for light enhancement of H motion. The mechanism of dark H diffusion in *a*-Si:H is also poorly understood.

In this paper, we report detailed studies of light-enhanced and dark D diffusion using high-depth-resolution secondary-ion-mass spectrometry (SIMS). D tracer profiles after annealing of *a*-Si:H containing a D-doped layer normally follow the complementary error function (erfc) solution of the ideal diffusion equation. However, we find extremely poor fits to the erfc after dark diffusion below 300 °C. This is because a significant fraction of the D is deep trapped as annealing begins and must overcome a 1.4-eV barrier to begin moving. Our results show that diffusion of H in *a*-Si:H is described by a trap-controlled model whose analytic solution is presented in a companion paper by Kemp and Branz.[4] From our data, we develop a detailed quantitative model of the diffusion process.

Illumination within a narrow temperature range above 200 °C increases the detrapping rate of the deep D and the diffusion profiles become more ideal. This light-enhanced detrapping is the origin of light-enhanced D diffusion in *a*-Si:H. We confirm definitively that the effect is not caused by heating of the sample and discuss the origin of the light-enhanced detrapping.

II. EXPERIMENT

For this study, we grow *a*-Si:H (0.2 μm)/*a*-Si:H:D (0.2 μm)/*a*-Si:H (0.5 μm)/*c*-Si sandwich structures under H (and D) dilution at 230 °C in a conventional rf-glow-discharge deposition system. To ensure that the layers are as similar as possible, they are deposited without breaking plasma or changing substrate temperature. The resulting sandwich is device quality: Its Air Mass 1.5 photoconductivity is 5×10^{-5} $(\Omega\,\mathrm{cm})^{-1}$. The Si-$H_2$ scissors-mode infrared (IR) absorption at 860 cm^{-1} is barely detectable in the sandwich and in a companion *a*-Si:H:D layer.

We anneal and illuminate the samples on a heated stage in flowing nitrogen. We measure the anneal temperature (T) with a calibrated thermocouple attached to a nearby piece of crystalline Si. One sample was dark annealed in air at 180 °C in a separate calibrated oven. Table I lists the anneal conditions.

We illuminate the sandwiches with a focused tungsten-halogen lamp. During white-light soaks, the intensity absorbed by the sample (i.e., below 820 nm) is about 2.5 W cm^{-2}. We also light-soak in 380 mW cm^{-2} of red light by inserting a 650±50-nm bandpass filter in the beam. From absorption measurements, we estimate that the sample absorbs 10^{22} photons cm^{-3} s^{-1} of red light nearly uniformly. Red-light soaking for one hour at room temperature causes an order of magnitude metastable decrease in the sandwich photoconductivity. During each light soak, we shadow a portion of the sample with Al foil or black graphite paint to produce dark- and light-annealed portions with identical thermal histories. We heat-sink the entire sample to the copper heater block with thermally conducting paste.

TABLE I. Anneal conditions and qualitative descriptions of observed D profiles.

Temperature (time)	Dark profile	Red-light profile	White-light profile
25 °C (30 days)	unchanged	unchanged	
130 °C (10 days)	unchanged	unchanged	
180 °C (30 days)	low C wings		
210 °C (5 days)	squared erfc	erfc[a]	erfc[a]
240 °C (2 days)	squared erfc	squared erfc	erfc[a]
270 °C (2 h)	squared erfc	squared erfc	
300 °C (2 h)	nearly erfc	nearly erfc	

[a]Light-induced broadening of D profile observed.

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To measure D and O concentrations using SIMS, we monitor D^- and O^- secondary ions produced by Cs^+ bombardment. We select the SIMS parameters to optimize depth resolution. We sputter slowly (about 7 Å s^{-1}) and measure only O and D to minimize the cycle time and collect a data point for each element every 30 Å. As-grown D profiles have upper edges that decay with the inverse logarithmic slope of 35 Å. This sets an upper limit of 35 Å to the SIMS depth resolution per factor of e of concentration. Absolute D concentrations, accurate to within a factor of 2, are obtained from a crystalline Si standard implanted with a dose of 1×10^{14} cm^{-2} D ions.

The a-Si:H:D layer contains 1.5×10^{-20} cm^{-3} of oxygen contamination compared to about 3×10^{19} cm^{-3} O in the a-Si:H. The oxygen does not diffuse during the anneals, so we match the edges of the corresponding O profiles to set precisely matched depth scales for comparing D profiles. We adjust slightly the relative D sensitivities between profiles in order to match the D concentrations in the center of the D layer (which loses no D during annealing) and in the background region (which gains no D). We measure the profiles of many craters in each region and find that we can easily resolve a 30-Å difference between profiles. Absolute depth measurements, accurate to $\pm5\%$, are calibrated by profilometry of the SIMS craters.

We fit the logarithm of the upper (left) edge of the measured D profile, $C(x)$, to the logarithm of the ideal concentration profile,[5]

$$C(x)=A/2\,\mathrm{erfc}\{(x_0-x)/\sqrt{D_H t}\}\ , \qquad (1)$$

for diffusion from a semi-infinite region of initial concentration A. Here x is the depth, x_0 is the initial step depth, D_H is the deuterium diffusion coefficient, and t is the anneal time. Taking the logarithm gives nearly equal weight to all points in a profile.

III. RESULTS

Figure 1(a) shows a typical as-grown D profile together with profiles measured after a dark and red-light 5-day anneal at 210 °C. Illumination broadens the D profile by 100 Å; this is more than three times the normal scatter among craters in identically treated regions. Figure 1(b) shows the quality of the erfc fits to the same 210 °C dark and illuminated profiles. We fit both data sets from the center of the a-Si:H:D layer to a point at which $C(x)$ is about three times the background level. Equation (1) fits the light profile very well, but the dark profile is extremely nonideal. When we fit logarithmic dark data, as in Fig. 1(b), the fit follows the low-concentration portion of the profile but the fit to the high-concentration portion is poor. When we fit linear dark data, the fit of the high-concentration portion of $C(x)$ is better, but we obtain an extremely low value of D_H and the fit to the wings is very bad. After 210 °C dark annealing, $C(x)$ is more square than an erfc function and follows the as-grown deuterium profile at high concentration.

Figure 2 shows the $C(x)$ after a 30-day dark anneal at 180 °C. This profile shows even more clearly the tendency to follow the as-grown profile, rather than the erfc. The profile is indistinguishable from the as-grown profile except for exponential wings at low concentration. Because the concentration is displayed on a logarithmic scale, the wings contain very little D compared with the main portion of the profile.

Table I qualitatively summarizes our diffusion data. Within the sensitivity of our measurement, anneals at 25 and 130 °C for the indicated times leave the as-grown D profile unchanged. The fit to Eq. (1) improves as the light intensity increases at fixed temperature or as the dark-anneal temperature increases. The "squaring" of ideal erfc profiles that we observe after dark annealing at temperatures below 300 °C also characterizes some previously published D diffusion data.[6] We observe light-induced broadening of the D profile at 210 °C with red or white light and at 240 °C only with white light.

Figure 3 shows D profiles taken after two days at 240 °C. The results are from three different regions of a single unbroken sample. As indicated in the figure legend, these regions were Al-foil shadowed, black-graphite-paint shadowed, and white-light illuminated. Our optical measurements show that the Al foil reflects 60–66 % of incident light from 400 to 800 nm, the unshadowed portion reflects 35–40 %, and the black paint reflects only about 15%. The Al-foil and black-

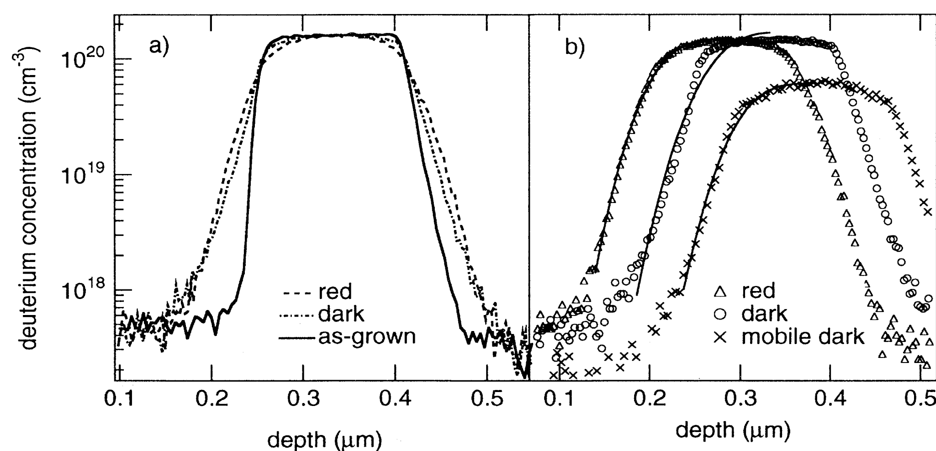

FIG. 1. D profiles after five days dark and red-light annealing at 210 °C, together with (a) the as-grown profile and (b) the results of the subtraction procedure described in text. In (b), the solid curves are fits to Eq. (1) and the data is offset for clarity.

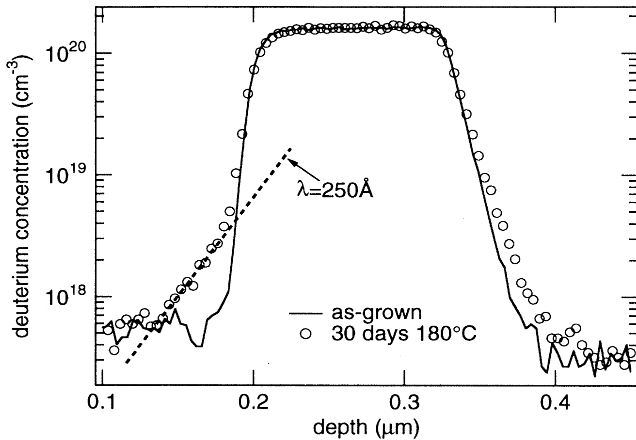

FIG. 2. D profiles as-grown and after 30 days dark annealing at 180 °C. An exponential fit to the wing is shown.

paint shadowing yield identical profiles, but the light enhancement of diffusion is easily observed in the unshadowed portion. We find similar results when we perform this experiment at 210 °C with white-light illumination.

IV. DISCUSSION

A. Trap-controlled diffusion in the dark

1. *Early-, intermediate-, and long-time regimes*

The non-erfc dark-anneal profiles we measure are compelling evidence for a trap-controlled H diffusion mechanism in *a*-Si:H. We propose that normal H diffusion in *a*-Si:H proceeds though a minority of the H in a transport level (either interstitial or bond-centered sites) which permits rapid diffusion. The observed H diffusion rate is five to ten orders of magnitude lower than the free H diffusion coefficient (in the transport level), because diffusion is limited by deep trapping. The trap is a deep Si-H level that contains nearly all of the H. The model is described in more detail below and in the companion

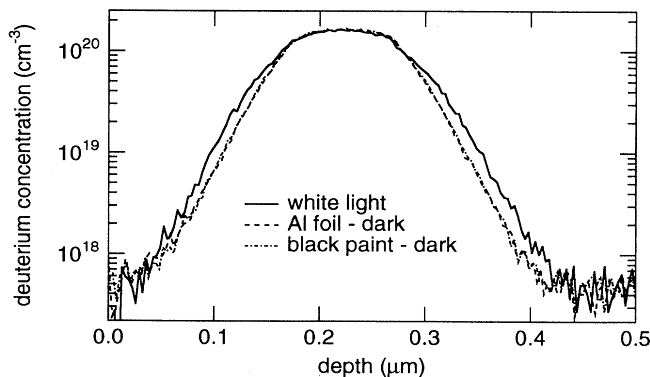

FIG. 3. D profiles from a single sample after a two-day anneal at 240 °C. Illumination and shadowing methods are indicated in the legend.

theory paper.[4] Street and Winer[7] originally proposed many qualitative elements of this model of H diffusion. However, we note that only a single H-trap level is required to describe our data quite accurately.

To begin each anneal, we suddenly raise the film temperature from room temperature to T. Nearly all the D atoms begin the annealing period deep-trapped in the Si-D bonds. As the annealing progresses, they are released into a transport level at a rate $R(T)$. The D in the traps does not reach thermal equilibrium with the transport level until several release times $\tau = 1/R(T)$ have passed. Halpern[8] previously discussed the importance of the equilibration process. We propose that the early-time nonequilibrium D distribution gives rise to the nonideal profiles we observe. In their companion paper, Kemp and Branz[4] derive the analytic solutions of our model for the evolution of the D tracer profiles in a trap-controlled diffusion model after a sudden increase in temperature. We next compare our data to their solutions.

The 180 °C data of Fig. 2 is an excellent example of the early-time regime ($t < \tau/3$) of trap-controlled tracer diffusion. Figure 2 illustrates the predicted exponential decay of the wings.[4] The wing width is λ, the mean D displacement between deep trapping events, because almost no D atoms have been released more than once. In this regime, the amplitude of the exponential wings grows linearly, roughly as $tR(T)/2$. We fit the upper (left) wing to an exponential according to the procedure of Kemp and Branz[4] and find $\lambda = 250 \pm 30$ Å and $\tau = 170 \pm 40$ days. The lower (right) wing has a similar exponential decay of comparable slope, but it is difficult to distinguish from the background because the as-grown edge broadened significantly during growth. It may be considered surprising, but at 180 °C even 30 days of annealing is still the early-time regime.

The 300 °C dark anneal profiles are examples of the long-time ($t > 3\tau$) regime of trap-controlled diffusion. The D profiles approach the erfc solutions to the ideal diffusion equation, with $D_H = \lambda^2/\tau$ as the effective diffusion coefficient.[4] This is the time regime in which D_H can properly be measured.

The dark anneal profiles taken between 210 and 270 °C are examples of the intermediate-time regime ($\tau/3 < t < 3\tau$) of trap-controlled tracer diffusion. In this regime, the analytic solution is complicated, but its graphical representation[4] clearly shows squared erfc profiles similar to the results we obtain. For example, the dark-anneal profile of Fig. 1 shows that the 5-day anneal time at 210 °C is approximately equal to τ.

2. *Deep D release rate*

Much of our data lies in the intermediate-time regime and we can approximate $\tau \approx t$. To obtain better estimates of τ, we use an approximate subtraction technique. We begin with the assumption that a fraction f of the D remains fixed during annealing. This approach is suggested by the dark-annealing profiles, which follow the as-grown profile at high concentration [e.g., Figs. 1(a) and 2]. By subtracting the fixed fraction of the as-grown profile from the dark profile, we recover a near-ideal

diffusion profile for the mobile fraction, $1-f$, of the deposited D. We vary f to find the value which yields a mobile-D profile with the minimum χ^2 for the fit to Eq. (1). Figure (1b) shows the profile of mobile D that results from subtracting 0.58 of the as-grown profile from the 210 °C dark-annealing profile. Equation (1) clearly fits this mobile fraction far better than it fits the dark profile. Finally, we assume $f(t)=\exp(-t/\tau)$ to estimate τ at each T.

The values of $R(T)=1/\tau$ obtained by the subtraction technique appear with error bars in Fig. 4. We also plot the more exact value of $R(180\,°\mathrm{C})=(170\ \mathrm{days})^{-1}$ obtained above from early-time data and the value $R\approx 1/t$ for profiles clearly in the intermediate-time regime. The agreement among the various estimates of $R(T)$ supports our use of the subtraction technique. The best Arrhenius fit to the data obtained by the subtraction technique is $R(T)=10^{8\pm1}\exp(-1.4\pm0.1\ \mathrm{eV/kT})\mathrm{s}^{-1}$.

From our measurements of R, we know that the immobile fraction of D in these experiments ranges from about 20% to 80%. Because nearly all H in a-Si:H is normally in Si-H bonds, we conclude that the fixed D is located in Si-D bonds. Assuming kinetic barriers are insignificant, our value of 1.4 eV is the first direct measurement of the energy difference between the Si-H level and the H transport level in the H density of states proposed by Street and Winer.[7] Although many of our observations are similar to those of earlier workers,[3,6] we cannot exclude the possibility that the D is incorporated and deep trapped as O-D from D_2O contaminants.

3. *Quantitative model*

We estimate the effective diffusion coefficient D_H by fitting profiles in the intermediate- or long-time regime to Eq. (1). Figure 4 shows these values and the best Arrhenius fit, $D_H=2\times10^{-3}\exp(-1.4\pm0.1\ \mathrm{eV/\ kT})$ $\mathrm{cm^2\,s^{-1}}$, together with the diffusion coefficients measured by Carlson and Magee.[6] The activation energies for R and D_H are roughly the same. This confirms that the rate-limiting step for H diffusion is emission from deep Si-H traps. In other words, the reason that the activation energy of H diffusion is roughly 1.4 eV is that the H population equilibrates between a transport level and a Si-H level 1.4 eV below it.

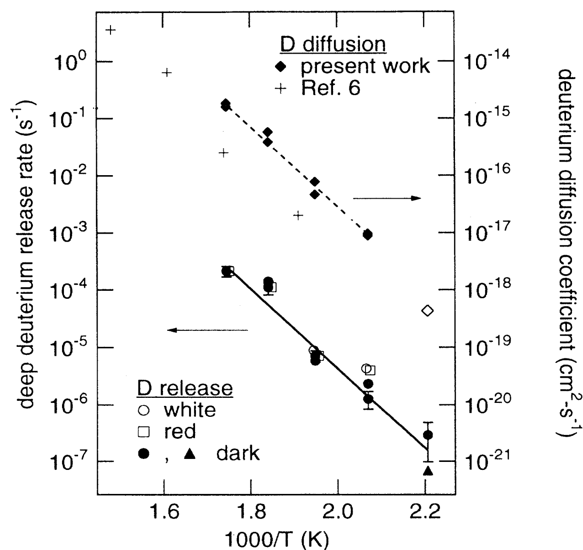

FIG. 4. Arrhenius plots of D_H and of the release rate (R) of deep-trapped D. At 180 °C, we show the exact value of R (solid triangle) measured in the early-time regime and the value of D_H (open diamond) calculated from R. The lines are best fits to our diffusion coefficients and to the dark rates determined by the subtraction method.

The width of the exponential wings at early times yields directly a value of $\lambda\approx250$ Å at 180 °C. From our separate measurements of R and D_H, we estimate $\lambda=\sqrt{D_H/R}\approx400$ Å. The wing-width measurement is far more accurate than this alternate approach. However, the reasonable agreement between the two measurements of λ supports the applicability of the trap-controlled model.

From the values of λ and R measured in the early-time regime at 180 °C, we estimate that $D_H(180\,°\mathrm{C})=\lambda^2R\approx4\times10^{-19}\ \mathrm{cm^2\,s^{-1}}$. This value is plotted (open diamond) in Fig. 4. It agrees well with an extrapolation of the higher temperature diffusion measurements. To reach the long-time regime and measure D at 180 °C directly would require about two years annealing.

Between deep-trapping events, the "free" H moves rapidly with a diffusion coefficient D_f either through interstitial sites or three-center Si-H-Si bonds about 3 Å apart. Diffusion-limited capture and release kinetics[9] determine the deep D emission rate R. The prefactor of $R(T)$ is $4\pi D_f r_c N_i$. Here r_c is the 3-Å capture radius and N_i is the $5\times10^{22}\ \mathrm{cm^{-3}}$ density of transport sites. Substituting, we find $D_f\approx3\times10^{-8\pm1}\ \mathrm{cm^2\,s^{-1}}$, far higher than D_H, but comparable to the diffusion coefficient in crystalline Si at these temperatures. D_f must be nearly temperature independent since the temperature dependences of D_H and R are similar. The ratio of free to trapped H is $D_H/D_f\approx10^{5\pm1}\exp(-1.4\ \mathrm{eV/kT})$. At 210 °C, about 10^{12} $\mathrm{cm^{-3}}$ of the $5\times10^{21}\ \mathrm{cm^{-3}}$ H in a-Si:H are free. At room temperature only $10^3\ \mathrm{cm^{-3}}$ H are free, less than one in a typical 1-μm film.

In its random walk between trapping events separated by a mean distance of 250 Å, the H makes $(250\ \text{Å}/3\ \text{Å})^2\approx10^4$ hops. If the probability of trapping is unity, the trap-site density is about $5\times10^{18}\ \mathrm{cm^{-3}}$. It is also possible that any of $5\times10^{22}\ \mathrm{cm^{-3}}$ sites can trap H, but because of a capture barrier the capture probability per encounter is only 10^{-4}.

The hopping time for free H between transport sites $a\approx3$ Å apart is $a^2/3D_f\approx10$ ns. The deep-trapping time of a free H is thus about 100 μs.

B. Effect of illumination on diffusion

After five days annealing at 210 °C, the erfc fits the red-light-illuminated profile far better than it fits the dark-annealed profile. Five days dark annealing leaves the sample in the intermediate-time regime, but five days red-light annealing takes the sample to the long-time regime. Illumination reduces the equilibration time and

improves the ideality of the $C(x)$ profile. We conclude that the light has increased the emission rate of D from Si-D bonds. This is the mechanism for the light enhancement of diffusion.[3] Values of $R(T)$ estimated by the subtraction technique for red and white illumination are plotted in Fig. 4. At 210 °C red and white illumination increase R by factors of 3.1 and 3.4, respectively, while at 240 °C white light increases R by a factor of 1.25.

A different perspective on the data is that the release rate of D from Si-D bonds under red-light illumination at 210 °C is roughly equal to the dark release rate at 230 °C. This 20 °C increase in the effective temperature for D release corresponds well to the 20–30 °C reduction in D-effusion temperature observed by Weil, Busso, and Beyer[2] under 100 $\mathrm{mW\,cm^{-2}}$ of IR-filtered white light. In their effusion experiments, Weil, Busso, and Beyer[2] were most likely observing a consequence of this same light enhancement of D release from Si-D bonds. The puzzling aspect of their result is that the reduced effusion temperatures were observed between 400 and 500 °C. We are not able to observe red-light-enhanced D diffusion effects above 210 °C despite an illumination intensity four times higher than that used by Weil, Busso, and Beyer.[2] It may be that illumination enhances effusion by increasing the release rate of H from the *a*-Si:H surface at 400–500 °C.

The shadowing experiment (see Fig. 3) demonstrates that the light-enhanced diffusion is not a thermal effect. Although the film under the black paint is heated more than the illuminated portion, light enhancement is observed only where light enters the *a*-Si:H. The Al-foil and black-paint regions yield indistinguishable profiles despite their different values of reflectance. Evidently, the thermal conductance of the substrate and stage is high enough so that significant temperature differences cannot be maintained between different regions of this unbroken film. We conclude that the light-enhancement effect is caused either by the light itself or by light-generated carriers. The intensity and temperature dependence of the light enhancement give further clues to its origin.

We observe an effect of red-light illumination on the diffusion profile only at 210 °C. By increasing the illumination intensity, we also observe a light-enhancement at 240 °C. Santos, Johnson, and Street[3] use far higher illumination intensity and observe the effect between 175 and 300 °C, with a maximum effect at 250 °C. Because the quasi-Fermi-level splitting is proportional to both temperature and the logarithm of illumination intensity, these results suggest that the increase in Si-D bond breaking is related to the changing occupation of the electronic states under illumination.

At 240 °C, we measure photo-to-dark conductivity ratios of 6 and 12 for red and white light, respectively. These correspond to electron quasi-Fermi-level shifts of 75 and 110 meV, respectively. This difference may explain why we see light-enhanced Si-D bond breaking only with the white light at this temperature.

If the hole quasi-Fermi level also shifts 100 meV under illumination, the occupation of valence-band states, including the Si-H level, is increased an order of magnitude and may reduce the barrier to Si-H bond breaking. However, Si-H bonds are located deep in the valence band and their occupation by holes is vanishingly small, with or without light. We prefer the proposal of Muller[10] that bandtail carriers in Si-Si bonds produce local distortions that lead to Si-H bond breaking.

The relationship between light-enhanced Si-H bond breaking and light-induced metastability at room temperature remains uncertain. We do not observe any light-enhanced diffusion effects below 210 °C. However, D_H extrapolates to such a low value at room temperature that we would not expect to observe either light-induced bond breaking or diffusion. We describe elsewhere[11] the constraints our experiment places on Si-H bond-breaking models of light-induced metastable effects.

V. CONCLUSIONS

We observe D diffusion profiles characteristic of the early-, intermediate-, and late-time regimes of trap-controlled diffusion. From the early-time profile at 180 °C, we find the mean D displacement between deep-trapping events is 250±30 Å. We also measure the rate constant for initial release of D from Si-D deep traps. The activation energy for the emission is 1.4±0.1 eV, comparable to the activation energy of H diffusion. We obtain the first estimates of the free-H-diffusion coefficient ($3\times10^{-8\pm1}$ $\mathrm{cm^2\,s^{-1}}$), the free H hopping time (10 ns), and the deep-trapping time of free H (100 μs).

Under illumination at 210 and 240 °C, the release rate of D from the deep traps increases measurably. This is the cause of the light enhancement of the diffusion coefficient in this temperature range. We show that this increase is not an effect of sample heating and attribute the light enhancement to the changing occupation of electronic levels.

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