Light-Enhanced Hydrogen Motion in *a*-Si:H

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We report the first direct observation of light-enhanced hydrogen motion in hydrogenated amorphous silicon. Diffusion enhancement increases with illumination intensity in undoped material and is suppressed in doped and in compensated material. The enhancement is attributed to an increased release rate of hydrogen from silicon-hydrogen bonds in the presence of photogenerated carriers. The implications of the effect for metastable defect formation are discussed.

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Hydrogenated amorphous silicon (*a*-Si:H) owes its technologically useful electronic properties to the efficient role of hydrogen in passivating unsaturated silicon orbitals (dangling bonds). Hydrogen, however, diffuses relatively rapidly through the amorphous network at low temperatures [1], and modifications of the hydrogen bonding configuration due to hydrogen migration have been proposed as a mechanism defect generation in *a*-Si:H [2,3]. Metastable defects are created by illumination (the Staebler-Wronski effect [4]) or electric fields and currents. Identification of the physical mechanism underlying metastability is one of the important fundamental problems in these materials.

Light-enhanced hydrogen diffusion is a direct consequence of the proposed link between metastability and hydrogen motion. A correlation between hydrogen diffusion and defect generation has so far been demonstrated only indirectly, by comparing the kinetics of defect generation and annealing with that expected from hydrogen diffusion [5] and by hydrogen-evolution experiments [6]. This paper presents the first experimental evidence of light-induced hydrogen motion in undoped *a*-Si:H, obtained from diffusion experiments under strong illumination. We attribute the enhanced diffusion to an increase in the release rate of hydrogen from silicon-hydrogen bonds, when photogenerated electron-hole pairs are present. The results strongly suggest a direct connection between hydrogen motion and light-induced defect generation in *a*-Si:H.

Light-enhanced hydrogen diffusion was investigated by using secondary-ion mass spectroscopy (SIMS) to measure depth profiles of H and D in deuterated films. Two deuteron techniques were used. In the first case, multilayered films were deposited with a buried deuterated layer. These *a*-Si:H/*a*-Si:H:D/*a*-Si:H structures had layer thicknesses of 100, 200, and 500 nm, respectively (from the top surface) and were grown by glow discharge decomposition of pure silane. The bottom layer was grown at 230 °C, and the two capping layers were deposited at 130 °C to reduce deuterium diffusion during growth. Deuterium incorporation was achieved by diluting silane with a 20% volume fraction of deuterium. In the diffusion experiments, the multilayers were illuminated with water-filtered light from a xenon arc lamp. For the second deuteron technique, homogeneous layers of *a*-Si:H were exposed to monatomic deuterium in a remote microwave plasma system. In this case, the specimen was optically isolated from the deuterium plasma [7], and illumination was provided by an argon laser at 514.5 nm.

Special care was taken to minimize and evaluate sample heating from light absorption. The samples were grown on crystalline silicon substrates and a thermal conductive paste was used to minimize temperature gradients between the substrates and the sample holders. Diffusion experiments in multilayer structures were performed by irradiating two samples simultaneously: one facing the lamp and the other ("dark") with the back side of the silicon substrate illuminated. The temperature difference between the illuminated and the nonilluminated samples is thereby reduced to the thermal gradient across the silicon wafer (<3 °C).

Light-enhanced deuterium diffusion in the multilayer structures is illustrated in Figs. 1(a) to 1(c), by comparing deuterium concentration profiles annealed in the dark (thin lines) and under illumination (thick lines). An illumination intensity of 17 ± 2 W/cm^2 was used and the annealing times and temperatures are indicated in each case. The vertical line in the figure marks the interface between the *a*-Si:H:D and the bottom *a*-Si:H layers. The deuterium concentration decreases from 7×10^{19} cm^{-3} in the *a*-Si:H:D layer, corresponding to an atomic concentration of 1.5% relative to the silicon atoms, to the natural deuterium abundance of 6×10^{17} cm^{-3} in the *a*-Si:H layer. Diffusion in the dark is negligible at 200 °C and below [Fig. 1(a)], in comparison with the depth resolution of the SIMS profiles. Diffusion is strongly enhanced under illumination at temperatures above $\sim$175 °C, as can be seen in the SIMS profiles. Diffusion in the dark and under illumination is thermally activated and the largest difference between the profiles occurs at 250 °C, for the illumination intensity used.

The deuterium concentration profiles in the *a*-Si:H layers fit a complementary error function, $\mathrm{erfc}[x/2\sqrt{(Dt)}]$, where x is the depth in the layer, and D and t are, respectively, the effective diffusion coefficient and the time. Diffusion coefficients are plotted as a function of the in-

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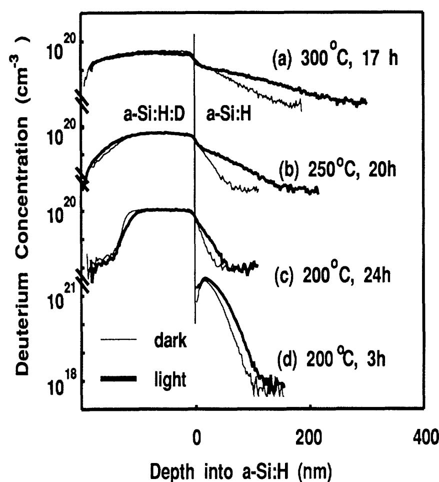


FIG. 1. (a)-(c) Deuterium concentration profiles for diffusion from a deuterated layer in the dark (thin lines) and under an illumination intensity of 17 ± 2 W/cm^2 (thick lines). The diffusion temperature and time are indicated in each case, and the vertical line indicates the interface between the *a*-Si:H:D and the *a*-Si:H layers. In (d) the corresponding profiles for diffusion from a deuterium plasma are displayed. The illumination intensity in this case was 20 ± 2 W/cm^2.

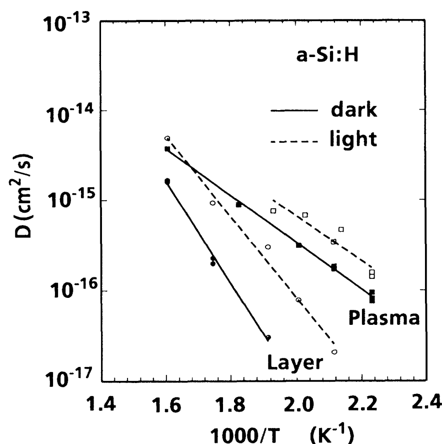


FIG. 2. Temperature dependence of the deuterium diffusion coefficient in the dark (solid symbols) and under illumination (open symbols) for diffusion from a deuterated layer (dots) and from a deuterium plasma (squares).

verse temperature in Fig. 2 (solid and open dots). In the temperature range from 200 to 350 °C, diffusion in the dark is consistent with previous measurements [1] which find an activation energy of about 1.3–1.5 eV. Illumination reduces the activation energy to 0.9 ± 0.1 eV. At 250 °C the diffusion coefficient under illumination is enhanced by an order of magnitude, and the enhancement is even larger for lower temperatures.

Deuterium incorporation from the remote plasma also exhibits light-enhanced diffusion. Concentration profiles in *a*-Si:H layers exposed to deuterium in the dark (thin line) and under argon laser irradiation of 20 W/cm^2 (thick line) are shown in Fig. 1(d). The 200 °C deuterium diffusion from the plasma is substantially faster than from the multilayer structures, as can be verified by comparing with Fig. 1(c). The temperature dependence of the diffusion coefficients for diffusion from the plasma is shown by the squares in Fig. 2 and has an activation energy of only 0.5 eV. Under illumination, the diffusion coefficient increases by a factor of 1.5 to 2, as compared with an order-of-magnitude enhancement observed in diffusion from a deuterated layer.

Hydrogen diffusion under illumination was also investigated in doped and in compensated amorphous silicon films. The dark diffusion coefficient of phosphorus-doped (doping gas volume fraction $[PH_3]/[SiH_4]=10^{-4}$) and of compensated ($[PH_3]/[SiH_4]=[B_2H_6]/[SiH_4]=10^{-3}$) samples is approximately a factor of 10 larger than undoped material, and the boron-doped material ($[B_2H_6]/[SiH_4]=10^{-2}$) is a factor of 100 larger. In the doped specimens, the small increase in deuterium penetration depth under illumination (< 15%) can be accounted for by purely thermal effects, and no diffusion enhancement is observed. Since any temperature increase due to light absorption is expected to be the same in doped and undoped samples, these results clearly demonstrate that the large light-induced enhancement of the hydrogen diffusion coefficient in undoped *a*-Si:H is not due to sample heating during illumination.

The illumination-intensity dependence of the diffusion coefficient and the photogenerated carrier density were also investigated in undoped samples. The diffusion coefficient varies with illumination intensity F, as $D\sim F^{\varepsilon}$ with $\varepsilon=0.9\pm0.1$, as shown in Fig. 3 for measurements performed at 250 °C. At this temperature, the diffusion

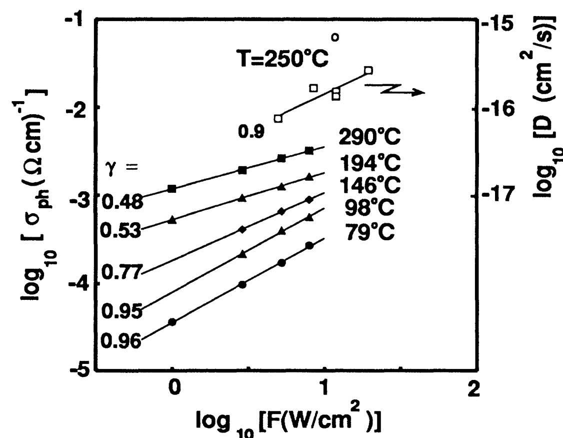


FIG. 3. Deuterium diffusion coefficient D and photoconductivity σ_{ph} as functions of the illumination intensity F. The measurement temperatures and the exponent γ in the relationship, $\sigma_{ph}\propto F^{\gamma}$, are indicated in each case.

coefficient in the dark $[(1-1.5)\times10^{17}\ \mathrm{cm^2/s}]$ is negligible in comparison with its value under illumination. The photoconductivity was measured under the illumination conditions of the diffusion experiments and is shown in Fig. 3 as a function of illumination intensity for temperatures between 75 and 300 °C. At each temperature, the sample was initially irradiated with the largest illumination intensity for a time sufficiently long for the light-induced defect density to achieve a steady-state value. The intensity dependence of the photoconductivity, $\sigma_{\mathrm{ph}}(F)$, is described by

$$\sigma_{\mathrm{ph}} \propto F^{\gamma}, \tag{1}$$

where γ is a temperature-dependent exponent. Below 150 °C, $\gamma=0.8-1$ and the photoconductivity, because of the photogenerated electronic density, increases approximately linearly with the carrier generation rate. The exponent decreases with increasing temperature and reaches a value of $\gamma=0.4-0.5$ between 200 and 300 °C.

The diffusion coefficient is

$$D=\nu\lambda^2/6, \tag{2}$$

where ν is the excitation rate and λ the mean free path. Normal diffusion in a-Si:H is controlled by hydrogen trapping and release from silicon-hydrogen bonds [8]. The excited hydrogen migrates through shallower traps, so that an alternative description of the diffusion is

$$D=N_{\mathrm{HS}}D_{\mathrm{HS}}/N_{\mathrm{H}}, \tag{3}$$

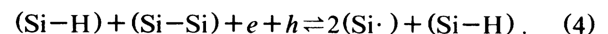
where N_{HS} and D_{HS} are the density and diffusion coefficient of H in the shallow sites, respectively, and N_{H} is the total H concentration. Possible mechanisms of light-enhanced diffusion are the increase of the excitation rate ν, a change in the mean free path λ, or an increase in the diffusion coefficient for hydrogen through shallow states.

The photon energies involved in the diffusion experiments are too small to directly ionize a silicon-hydrogen bond. The interaction between light and the silicon-hydrogen configuration controlling diffusion is expected to be mediated by photogenerated carriers. Two mechanisms suggest themselves, both related to models of metastable defects. First, the recombination of electron-hole pairs releases energy and may induce the excitation of hydrogen from an Si–H bond. This mechanism of defect creation has been discussed before in the context of light-induced defect creation [3]. Second, the presence of excess electrons and holes may change the hydrogen diffusion coefficient, perhaps by modifying its charge state. Different charged states of migrating hydrogen have been identified in crystalline silicon [9], and the increased dark diffusion coefficient of doped a-Si:H is attributed to an electronic effect [8].

In the plasma diffusion experiments, the extra deuterium atoms saturate the deep silicon-hydrogen traps, and hydrogen diffuses faster through the shallow states [10]. The relatively small changes induced by illumination, as compared to diffusion in the multilayer sample, indicate that hydrogen transport through shallow states is less affected by illumination. Thus we suggest that the light enhancement is mainly due to an increase in the release rate of hydrogen from Si–H bonds. A release rate of $\nu=0.12\ \mathrm{s^{-1}}$ is obtained from Eq. (2) for an illumination intensity of 17 W/cm^2 at 250 °C, with the assumption that $\lambda\approx10$ Å. These values yield an estimated lower limit of ~500 absorbed photons per released hydrogen atom.

Models of hydrogen-induced metastable defects are based on the hypothesis that the energy released by electron-hole recombination causes hydrogen motion, resulting in the formation of dangling bonds. Our observation of light-enhanced hydrogen diffusion demonstrates that such a mechanism definitely exists. The results are therefore the strongest evidence to date for the hydrogen mechanism of metastability. The relative changes in the defect density in doped and in compensated a-Si:H induced by illumination are significantly smaller than in undoped samples [11], consistent with the lower light enhancement of the diffusion coefficient in doped and compensated samples.

The relationship between hydrogen diffusion and defect generation can be described by the following chemical reaction [12]:



$$(\mathrm{Si-H})+(\mathrm{Si-Si})+e+h \rightleftharpoons 2(\mathrm{Si}\cdot)+(\mathrm{Si-H}). \tag{4}$$

A silicon-hydrogen complex (Si–H) dissociates in the presence of photogenerated electrons (e) and holes (h). In the dissociation process, hydrogen is released and a silicon dangling bond (Si·) is created. The released hydrogen atom diffuses through the amorphous network until it is trapped in a dangling bond, annihilating a defect. Alternatively, the diffusing hydrogen can be inserted into a weak silicon-silicon bond (Si–Si), resulting in the formation of a second dangling bond in the right-hand side of the reaction.

In the above model of light-induced defects, the generation rate is proportional to the product np of the densities of photogenerated electrons (n) and holes (p) [3]. The diffusion temperatures are above the defect equilibration temperature of ~200 °C in undoped a-Si:H [13], so that defect creation and annealing times are small compared to the diffusion times. The concentrations of the different species in Eq. (3) are then expected to have their chemical equilibrium values during diffusion. From the law of mass action, the dangling-bond concentration, $N_s=[(\mathrm{Si}\cdot)]$, is related to the carrier densities by $N_s^2=K_1np$, where K_1 is a temperature-dependent factor. This expression neglects the small changes in the concentration of silicon-silicon and silicon-hydrogen bonds during defect generation. The defect density under illumination is expected to be sufficiently high for the photogenerated carrier density to be determined by monomolecular recombination, i.e., $n\sim p\sim F/N_s$. As a conse-

quence, $N_s \sim F^{1/2}$ and $\sigma_{\rm ph} \sim n \sim F^{1/2}$, in agreement with the photoconductivity results for temperatures above 150 °C.

According to Eq. (4), the hydrogen release rate is proportional to the np product. The diffusion coefficient also depends on how the mean free path in shallow traps λ varies with illumination intensity. If λ does not depend on illumination, then $D \sim np \sim F$, in agreement with the results in Fig. 3. However, λ may depend in an intricate way on the defect density and on illumination, and further investigations are needed to clarify this interesting issue.

In conclusion, we have presented experimental evidence for a photoelectric enhancement of hydrogen diffusion in a-Si:H during illumination. The diffusion enhancement is attributed to an increased rate of release of hydrogen from Si—H bonds, mediated by photogenerated carriers. The overall process involves silicon dangling-bond formation, and the results presented here provide evidence for a direct connection between hydrogen motion and metastability in a-Si:H.

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