Hydrogen Motion and Light-Induced Defects in Hydrogenated Amorphous Silicon

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Hydrogen diffusioii experiments in hydrogenated amorphous silicon (a-Si:H) demonstrate that hydrogen migration is enhanced under illumination. Tlie enhancement is suppressed when tlie photo-generated carriers are extracted from the diffusion region by an electric field. Tlie dependence of liydrogen diffusion on illuinination suggests a close connection between hydrogen diffusion aiid metastability in a-Si:H.

I. Introduction

Hydrogenated amorphous silicon (a-Si:H) is a promising maierial for application in large area electronics and iii photovoltaic energy conversion. a-Si:H films of good e ectronic properties can be deposited over large areas by standard thin-film depositioii processes such as sputtering of a silicon target and plasma enhanced decomposition of silane gas (SiH_4). The material has a large light absorption coefficient in the visible range and has been used as active layers in field-effect transistors, phsto-detectors, and solar cells.

Unfortunately, tlie electronic properties of a-Si:H degrade when extra electronic carriers (i.e., electrons and/or l oles) are introduced in tlie material by illumination[1], current[2] or tlie application of an electric field[3]. T1e degradation is reversible and can be eliminated by annealing the material above $\sim$ 180°C. Tlie degradation is associated with the creation of defects with electronic states near tlie center of tlie energy gap. Tlie defects have been identified as uiisaturated silicon bonds (dangling-bonds) which act as effective recombination centers for minority carriers and considerably decrease tlie doping efficiency of tlie material. A considerable effort lias been devoted in the recent years to obtain films of high stability against defect formation[4].

Two classes of models have been proposed to explain tlie origin of metastable dangling-bonds in a-Si:H. In the first class ("extrinsic models") dangling-bond formation is attributed to tlie aweakening of silicon bonds in tlie neighborhood of an extrinsic impurity atom[5]. Many impurities atoms (sucli as, for instance, oxygen and carbon) are present in a-Si:H films in concentrations well exceediiig tlie density of metastable defects ($\sim 10^{17}$ cm^{-3}). In addition, it is well-established that the incorporation of dopant atoins in a-Si:H is accompanied by an increase in the defect density[6].

In tlie secoiid class of models ("intrinsic models"), on the other hand, metastability is viewed as an intrinsic property of tlie a-Si:H network. It has been proposed tliat tlie presence of excess carriers weakens silicon-hydrogen[7] or neighboring silicon-silicon bonds[8] and increases tlie emission probability of a hydrogen atom from a silicon-hydrogen bond, leading to tlie formation of a dangling bond. If tlie emitted atom migrates away, a silicon dangling-bond remains when tlie carrier population is reduced to tlie thermal equilibriuin value after the removal of the external excitation[9]. The metastable cliaracter of dangling-bonds arise from tlie small liydrogen inigration rate around rooin temperature. At higher temperatures (i.e, above - 180°C) liydrogen diffuses relatively fast through the networlt so that tlie defect can be quicltly annihilated. In this regime tlie amorplious network respoiids quicltly to changes is the carrier concentration and there is a thermal equilibrium between carriers and defects.

A natural consequeiice of tlie intrinsic model for inetastability is tliat liydrogen diffusion should be enhanced when extra carriers are introduced in a-Si:H. In this paper we review tlie experimental results on hydrogen diffusion and its dependence on carrier concentration in a-Si:H. As will be described in Sec. II, the ex-

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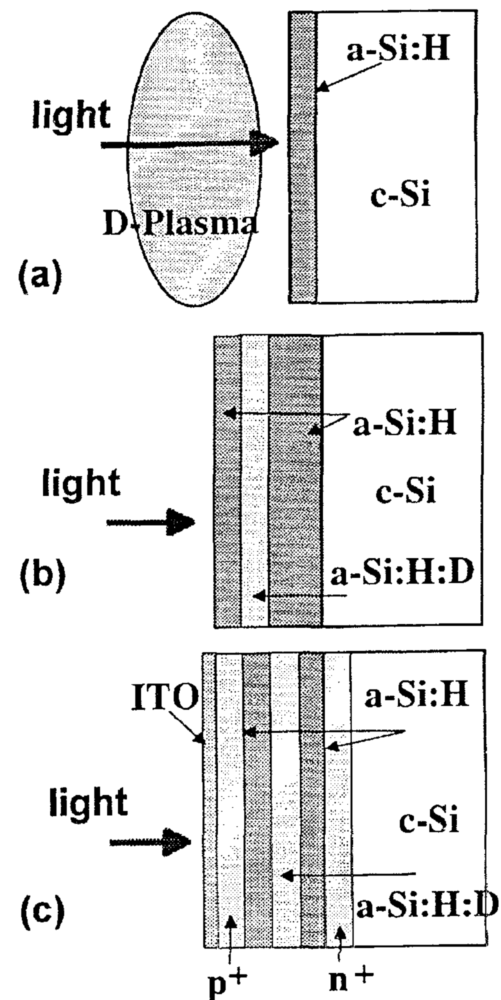
periments were performed by diffusing deuterium from a plasma or from a deuterated a-Si:H:D layer into an intrinsic a-Si:H film. The deuterium profiles after diffusion were determined by Secondary lon Mass Spectrometry (SIMS). In Sec. III we present experimental results demonstrating that hyclrogen migration in a-Si:H is controlled by an elcctronic mechanism and (i) is enhanced wlien the carrier populationis increased by illumination and (ii) is suppressed when the photogenerated carriers are extracted from the diffusion region by an electric field. Microscopic models for hydrogen migration and its connection to metastability are discussed in Sec. IV.

II. Experimental

Light-enhanced hydrogen diffusion was investigated by diffusing deuterium (^{2}H) into an a-Si:H film during illumination and measuring the resulting deuterium profile by secondary ion mass spectrometry (SlMS)[10]. The deuterium diffusion source was either a plasma or a deuterated amorphous silicon layer (a-Si:H:D). In the first case (see Fig. 1a), single glow-discharge a-Si:H layers were exposed to a remote microwave plasma in the dark or under illumination from an Ar-laser ($\sim$ 15 W/cm^2). In tlie second case, the experimcnts were performed in the a-Si:H/a- Si:H:D/a-Si:H multilayer structures shown in Fig. 1b. These structtires have layer thicknesses of 100nm, 200nm, and 500 nm, respectively. The bottom a-Si:H film was grown by glow discharge decomposition of pure silane at 230°C. The two capping layers were deposited at a lower temperature (130°C) in order to reduce deuterium diffusion during growth, and deuterium incorporation in the a-Si:H layer was achieved by diluting silane with a 20% volume fraction of deuterium. The samples in this case were illuminated with water-filtered light from a xenon arc lamp (15 to 20 W/cm^2).

Diffusion experiments were also performed in p-i-n a-Si:H photodiodes (Fig.1c). The deuterium source in this case is an a-Si:H:D layer inserted in the middle of the intrinsic layer. Al! layers were deposited at 200°C. The diodes have transparent indium-tin oxide top contact to allow illumination of the intrinsic layer during the thermal treatment. The main advantage of using these photodiodes in diffusion studies is that the carrier concentration in the diffusion region can be controlled either by illumination or by an external bias[11].



Fignre 1: Deuterium diffusion from (a) a deuterium plasma and (b) from a cleuterated in a-Si:H. In (c) tlie deuterated layer was inserted into tlie intrinsic region of a p-i-n solar cell. All a-Si:H layers were deposited by tlie glow discliarge decompositicn of silane. Tlie solar cell is covered witli a transparent indium-tin-oxide (ITO) film and a cliromium grid (not shown in the diagram). In all cases tlie samples were grown on crystalline silicon substrates (c-Si).

In all experiments the samples were mounted on a temperature-controlled heating stage and special care was taken to reduce sample heating due to the strong light intensity (15 - 20 W/cm^2) on the sample surface. The samples were grown on crystalline silicon substrate, and a heat conductive paste was used to minimize temperature gradients between the substrates and the temperature-controlled sample liolders. By using the thermal paste the temperature increase (for samples measured in vacuum) due to liglit absorption was reduced from $\sim$ 20°C (without paste) to less than 5°C (i.e., with paste the thermal component was negligible). As an additional precaution, the diffusion experiments

in multilayer structures were always performed by irradiating simultaneously two sâmples: one facing tlie lamp and tlie other ("dark") illuminated from the back side of the silicon substrate. The temperature difference between tlie illuminated and the non-illuminated samples is thereby reduced to the thermal gradient across the silicon wafer (< 3°C).

III. Results

Light-enhanced deuterium diffusion[12] is illustrated in Figs. 2a tc 2c, where deuterium concentration profiles in multilayer structures annealed in the dark (thin lines) and under illumination (thick lines) at different temperatures are compared. The diffusion times 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 drops from 7 x 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 6 x 10^{17} cm^3 in the a- Si:H layer. The latter concentration corresponds to the natural deuterium abundance in a-Si:H with 8% hydrogen. At 200°C and below (Fig. 2a), diffusion in the dark is negligible in comparison with tlie depth resolution of tlie SIMS profiles of —8.0 nm for each factor of e decay in concentration. Under illumination, diffusion is strongly enhanced and can be noticed in the SIMS profiles for temperatures above ~ 175°C. Diffusion in the dark and under illurnination are temperature-activated, and the largest difference between the two profiles occur, at 250°C, for the illumination intensity used here.

The deuterium concentration profiles in the a-Si:H layers in Fig. 2a to 2c are well described by a complementary error function[10], $erfc[x/2(D_{\text{eff}}t_d)^{1/2}]$. Here, x is the depth in the layer, and D_{eff} and t_d are, respectively, the effective diffusion coefficient and the diffusion time. The effective diffusion coefficient in the dark is thermally activated with an activation energy of 1.2-1.5 eV. Under illumination, the diffusion coefficient at 250°C increases by an order of magnitude, and the enhancement is even larger for lower temperatures.

Deuterium incorporation from the plasma in the dark (thin lines) and under illumination (thick lines) is illustrated in Fig. 2d. Enhanced deuterium diffusion is also observed in this case, but the diffusion coefficient increases by a factor of only 1.5 to 2, as compared to an order cf magnitude enhancement observed in diffusion from a deuterated layer. In diffusion experiments from the plasma the atorns are directly injected from the gas phase into weakly bonded interstitial sites. In çontrast, when the deuterium atoms proceed from an a-Si:H:D layer, they first have to be emitted from Si-D bonds to the interstitial migration path. The diffusion kinetics is then determined by the deuterium emission rate from Si-D bonds[13]. Tlie larger diffusion enhancement in the latter case indicates that light-enhancement is associated with an increase in the deuterium emission rate in the presence of photo-generated carriers[12,14].

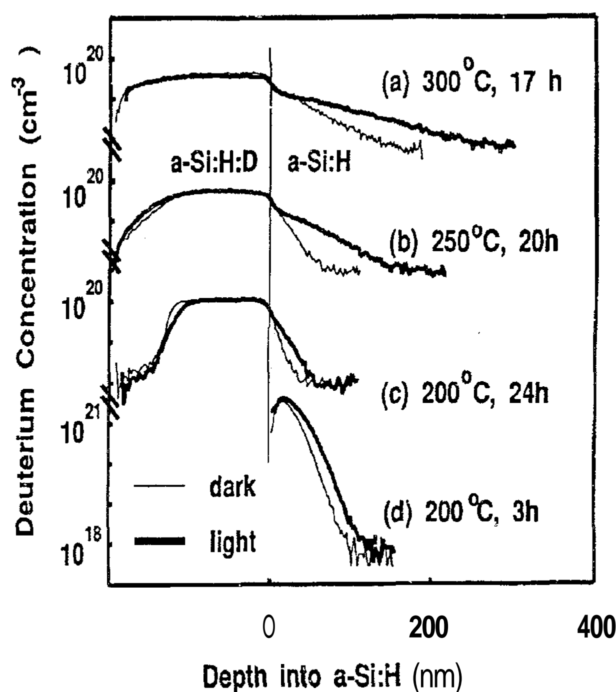


Figure 2: Deuterium depth profiles after diffusion in the dark (thin lines) and under illumination with 17 W/cm^2 from a xenon lamp (thick lines) in (a)-(c) a-Si:H/a-Si:H:D/a-Si:H multilayer. Curve (d) shows corresponding results for a-Si:H layers exposed to a remote deuterium plasma. In this case the samples were illuminated with the λ = 514.5 nm line of an argon laser. The diffusion time and temperature are indicated in each case. The vertical line marks tlie beginning of the bottom a-Si:H layers, were deuterium diffusion was studied.

Hydrogen diffusion under illumination was also investigated in doped and in compensated amorphous silicon films. In this study, the bottom a-Si:H layer in tlie multilayer structures (see Fig. 1 b) was replaced by a doped film. Figure **3** compares deuterium concentration profiles after annealing at 250°C in the dark (dashed lines) and under illumination (thick lines) for boron doped, phosphorus doped, and for a compensated film. The corresponding diffusion profiles for an undoped sample at the same temperature are shown

in Fig. 2b. Tlie phosphorus (boron) doped layer was grown with a phosphine (diborane) to silane gas phase molar ratio of $10^{-4}(10^{-2})$. For tlie compensated sample, equal molar ratios of 10^{-3} of phosphine and diborane were used. When compared to undoped material, the diffusion coefficient in the dark is approximately a. factor of $\sim 5 - 10$ larger iii tlie coinpensated and iii tlic pliospliorus doped samples, and a. factor of 100 larger in the boron doped film. Under illumination, tlie diffusion coefficient increases by less than 20%, as compared to an order of magnitude increase in undoped samples. Since any temperature increase due to light absorption is expected to be tlie same in doped aiid undoped samples, these results clearly demonstrate that tlie large light-induced enhancement of tlie hydrogen diffusion coefficient in undoped a-Si:H is not due to sample heating during illumination.

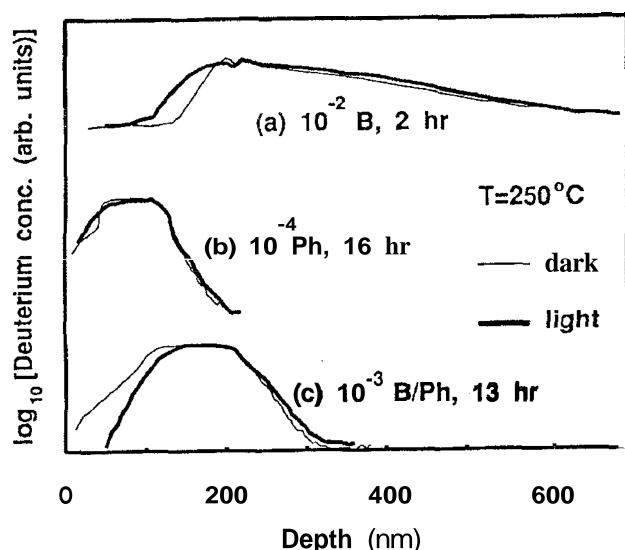


Figure 3: Diffusion profiles in tlie dark (tliin lines) and under illumination with 17 W/cm^2 from a xenon lamp (tliick lines) iri (a) boron-doped (1% volume ratio of diborane in silane), (b) phosphorus-doped (0.01% volume ratio of phosphine in silane), and in (c) compensated a-Si:H layers (0.1% phosphine plus 0.1% diborane in silane). Tlie diffusion experiments were performed at 250°C for tlie times indicated in tlie figure.

The interaction between hydrogen migration aiid electronic carriers was furtlier investigated by performing diffusion experiments where the a-Si:H/a-Si:H:D/a-Si:H multilayers were inserted in tlie intrinsic region (i-layer) of a p-i-n solar cell (see Fig. 1c). The carrier concentration in tlie diffusion region in tliis case can be controlled by varying either the external bias or the illumination intensity. An example is shown in Fig. 4. The dashed line in tliis figure is tlie deuterium profile in a control sample annealed at 225°C in tlie dark. The thin solid line reproduces tlie profile obtained when the solar cell is illuminated during tlie thermal treatment. As in Fig. 2, tlie profiles are broadened at the interfaces due to light-induced diffusion. Tlie tliick line in Fig. 4 sliows tlie combined effects of illumination aiid of an average reverse field of 9.2 x 10^4 Wcm in tlie intrinsic lnycr during annealing obtained by applying a reverse bias of 5V. The diffusion profiles are asymmetric with respcct to tlie center of tlie a-Si:H:D layer due to an inhomogeneous carrier density in tlie intrinsic layer, and small changes are observed on tlie right-hand side of the deutcrated layer[15]. On tlie left-hand side. on tlie otlier hand. light-enhancement of hydrogen diffusion is completely suppressed when the photogenerated carrieis are extracted from tlie diffusion region by the reverse electric field.

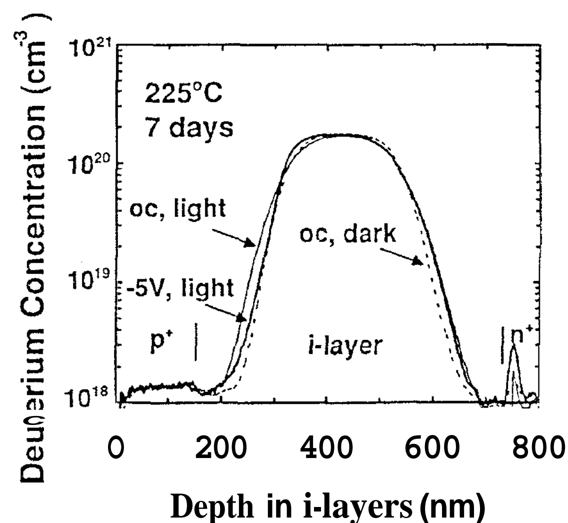


Figure 4: Deuterium profiles in p-i-n photodiodes annealed at 225°C for 7 days under open circnit (oc) conditions (daslied line), under oc and illumination (thin solid line), and under illumination and a reverse bias of 5V (tliick line). Tlie top cliromium grid and the indium-tin-oxide layers were cliemically etched before tlie SIMS analysis. p$^+$ and n$^+$ indicate the position of tlie corresponding doped layers.

IV. Discussion and Conclusions

The results presented in tlie previous section indicate that hydrogen diffusion aiid metastable defect formation in a-Si:H have inany aspects in common. Tlie most important is tlie fact that both processes are mediated by electronic carriers (i.e., electrons and/or holes)

and are accelerated when tlie carrier density is increased by illumination. From tlie comparison between diffusion experiments from a plasma and from a deuterated layer (see Fig. 2) we concluded tliat the main effect of tlie carriers is to increase tlie release rate of liydrogen atoms from Si-H bonds[12]. If dangling-bonds are created following liydrogen release, a clirect connection is established between liydrogen motion and metastable defect formation.

Two mechanisms can account for tlie interaction between carrier, liydrogen atoms, and defects. In tlie first tlie recombination of electron-liole pairs provide tlie energy necessary for liydrogen emission from a Si-I1 bonds and consequent defect formation[16]. Tlie second possibility is tliat tlie presence of carriers aweaken Si-Si or a Si-H bonds, thereby decreasing tlie effective energy for hydrogen emission[7].

Diffusion experiments in doped layers give additional support for a hydrogen-related metastability model. Tlie relative changes in the defect density due to illumination are considerably smaller in doped and in compensated materials than in undoped a-Si:H.[17,18] Similar observations apply to hydrogen diffusion in doped films. Finally, light-degradation experiments in solar cells indicate tliat tlie defect formation rate is suppressed under reversed biased solar cells[19]. As is shown in Fig. 4, tlie hydrogen migration is also strongly suppressed under reverse bias.

These experimental results strongly support a close connection between liydrogen diffusioii and liglit-induced defect generation and, tlierefore, an intrinsic, hydrogen-related mechanism for metastability in a-Si:H. Metastable defect forination under illumination is attributed to tlie increased rate of release of hydrogen from Si-H bonds iii the preseiice of pliotogenerated carriers. According to this model, tlie efforts to improve material stability against defect formatiori should concentrate in obtaining a-Si:H films with more stahle Si-I1 bonds.

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