Effect of light-soaking on the hydrogen effusion mechanisms in polymorphous silicon thin film structures

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HIGHLIGHTS

- We study hydrogen effusion due to light-soaking in pm-Si:H PIN and NIP structures.
- Hydrogen diffuses from the bottom layer to the top layer and effuses.
- Hydrogen diffusion process depends on the device structure (PIN or NIP).
- A hydrogen diffusion barrier is generated by defects while trying to effuse on PIN.
- Light-soaking increases the effused hydrogen and is more pronounced on the NIP.

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ABSTRACT

This work describes a study performed on hydrogenated polymorphous silicon PIN and NIP structures, deposited by plasma enhanced chemical vapor deposition (PECVD). We study hydrogen stability and its evolution during exodiffusion experiments in these structures, trying to determine the effect of light-soaking pre-treatments on the hydrogen effusion mechanisms. We examined the structural and optical properties of PIN and NIP structures after exodiffusion experiments. These were analyzed in terms of the different hydrogen diffusion processes comparing light-soaked samples and samples without light-soaking. Also, an analysis of both structures was done in order to determine which one is less affected by light-soaking. From the simultaneous measurement of temperature and hydrogen desorption, we propose a model for long range diffusion of hydrogen. We show that long range motion of hydrogen during light-soaking and annealing causes a hydrogen rearrangement on the film and microstructure changes which result in a shift on the exodiffusion peaks. Both structures were compared and are discussed in terms of the hydrogen bonding configurations and environment. We determined that for the PIN structure a hydrogen diffusion barrier is generated by light-induced defects, which is expected to cause less degradation of its optoelectronic properties under illumination, and a more stable device during operation along with an enhanced functional performance of this type of structure.

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1. Introduction

Hydrogenated polymorphous silicon (pm-Si:H), which consists of silicon nanocrystals embedded in an amorphous silicon (a-Si:H) matrix, is a material suitable for solar cell devices. The latter is because it exhibits better electronic transport and stability properties compared to those of the conventional a-Si:H [1–3]. Most of the improved properties related to these materials are a consequence of the hydrogen ability to passivate defects and impurities in the Si network, removing or reducing the intra-bandgap levels [4]. Reversible Staebler–Wronski effect is one of the most significant phenomena that affects the stability and performance of amorphous silicon thin films solar cells [5]. This light induced degradation causes changes in structural and electronic properties of the material [5–9]. Bonded hydrogen atoms may break during light exposure and diffuse through the amorphous network generating an increase of the dangling bonds. On the other hand, diffusing hydrogen atoms may be trapped by the dangling bonds generated previously or may exodiffuse leading to a film richer in

defects [10]. The trapping probability of free hydrogen atoms increases with temperature due to a higher dangling bonds formation and it is more pronounced closer to the film surface, which shortens the diffusion length [10]. Hydrogen diffusion is considered a key process in this kind of materials [6–8,10,11]. In general, the proposed models in literature for explaining the Stabler–Wronski effect are: weak bond breaking without hydrogen involvement, Si–Si breaking with involvement of hydrogen, charge transfer between charged states and bridge bonded hydrogen in interstitial site [12]. Hydrogen is also known to passivate Si–SiO$_2$ interfaces and grain boundaries [4]. As a consequence H passivation has become a crucial point of study in microelectronics and photovoltaic materials. A good passivation of the solar cell structure is necessary to improve the cell performance. An important technique to study the hydrogen diffusion is exodiffusion measurements where hydrogen diffusion occurs due to an external energy excitation. Hydrogen moves through all the film generating several reactions during its motion and when it reaches the films surface it exodiffuses. The hydrogen exodiffusion depends on the film structure, hydrogen bonding environment and hydrogen concentration. Recently, studies determined that pm-Si:H thin films and devices present better stability under illumination than conventional a-Si:H [13]. However, an excessive incorporation of weak Si–H bonds into the pm-Si:H film could affect the degradation rate of the device for photovoltaic applications and, moreover, the device conversion efficiency [3,13]. During annealing, exodiffusion of hydrogen takes place and it activates the defects and impurities as recombination centers [4]. At moderate temperatures (100–300 °C), a slow diffusion was observed while at higher temperatures (400–800 °C) fast hydrogen interstitial diffusion is present [14,15]. During diffusion, hydrogen interacts with defects, dangling bonds and electrically active dopant atoms [7,14,18], which in turn could improve the device performance via defects passivation. Hydrogen diffusion is more complex than the diffusion of electrically active dopants [15] but the activation energy is lower. Diffusion in this material is thought to be similar to that of a-Si:H, mediated by the dangling bonds and thermally activated [16–18]. In the low concentration region H diffusion has an activation energy of 2.7 eV and is independent of the H concentration [16], whereas for the higher hydrogen concentration region the diffusion process becomes more complex, decreasing the diffusivity [16,19]. Hydrogen diffusion activation energies for a-Si:H range from 0.5 to 2.7 eV [8], so the incident photon energy of a halogen lamp would be sufficient to enhance (generate) atomic or molecular hydrogen diffusion by breaking atomic bonds and also creating electron-hole pairs [8]. It has been determined that for a-Si:H with diffusion activation energies of 1.8 eV, diffusion coefficients of 9.5×10^{-2} and 9.6×10^{-1} cm^2/s are observed, while for energies of 2.7 eV the values are between 2.2×10^4 and 5.4×10^4 cm^2/s [16,20,21]. The activation energy of free-H diffusion was estimated to be less than 0.5 eV. Therefore, several models related to hydrogen motion have been proposed to explain the light degradation effect in a-Si:H [7,10]. It is considered that hydrogen moves through bond switching between a Si–H bond and a Si dangling bond and/or H exchange between Si–H bonds [10]. Since the H diffusion process depends mostly on the dangling bond density [17], this suggests that hydrogen movement involves the process of bond switching between a Si–H bond and a dangling bond.

During hydrogen diffusion pm-Si:H can be crystallized due to subsurface reactions of bond breaking taking place as part of the exodiffusion process [22–24]. For annealing temperatures greater than 300–400 °C hydrogen in a-Si:H becomes unstable and exodiffuses, which is expected on pm-Si:H as well [1,11]. Thus, it is crucial to understand the hydrogen diffusion process in pm-Si:H and its effects on the structural and optoelectronic properties of this material. In previous works, hydrogen profiles on silicon have shown that p-type and n-type materials have different hydrogen concentration regions. For p-type high, intermediate and low concentration regions are present while for n-type a high concentration near the surface and a low concentration region are present [15,25]. In a PIN type substrate solar cell structure the incident light enters through the p-type layer. Here the absorption of the glass-transmitted UV part of the solar spectrum is expected along with a larger chance of generating dangling bond defects which reduce the cell performance as well [5]. Trying to determine the effect of previous light-soaking on the hydrogen effusion mechanisms in pm-Si:H thin film structures, in this work we examined the optical properties of PIN and NIP structures after exodiffusion experiments. Their structural and optical properties were analyzed in terms of the different hydrogen diffusion processes for samples exposed previously to light-soaking and samples without light-soaking. A comparison of both structures was done in order to determine which one is less affected by light-soaking. Also, we propose a model for long range diffusion of hydrogen in both structures which explains the effects of the light-soaking treatment and the differences between both structures.

2. Material and methods

Pm-Si:H thin films structures were grown in a conventional PECVD system with parallel plates, activated by a RF signal of 13.56 MHz [13,26,27]. The depositions were done with a chamber pressure of 3.3 Torr, substrate temperature of 275 °C and a RF power of 30 W. Hydrogen (H$_2$) and silane (SiH$_4$) were used as precursor gases with mass flow rates of 200 and 40 sccm, respectively. Doped layers were grown using conditions similar to previous works [22]. Doping is obtained by adding 5 sccm of a doping gas (trimethylboron for p-doping and phosphine for n-doping) diluted at 2% in hydrogen. To avoid any oxidation effect, the films were grown in a single process without breaking vacuum. The p and n type layers were around 20–30 nm of thickness, while the intrinsic layer was ~200 nm thick. The parameters for both structures were maintained constant and only the order of deposition of the layers was varied. Thus, the structures were deposited on corning glass #7059 in both substrate and superstrate configurations. Analyzed samples description is summarized in Table 1. The light-soaking treatment was performed during 1 h in a homemade equipment under AM1.5 spectrum and the temperature was controlled at 25 °C by heat dissipation and exposition was through the glass side. Thermal annealing during exodiffusion experiments was done with an incremental ramp of 10 °C/min starting at room temperature and up to 650 °C for hydrogen evolution studies in all the pm-Si:H structures. These experiments were performed in a vacuum chamber with a controlled heating system which increases the temperature and the effusing hydrogen was detected with a mass spectrometer. Table 1 shows the NIP and PIN structures studied in this work and their thicknesses. The different states described in Table 1 are as follows: the "exodiffusion" state refers to a structure after the exodiffusion experiment, and the "exodiffusion after light-soaking" state refers to a structure that was exposed to light-soaking and immediately after an exodiffusion experiment was

Table 1
Description and thickness of the PIN and NIP structures used in this work.

Sample	Name	Total thickness (nm)	Description
D04086	PIN	243.7	Exodiffusion
D04086-LS	PIN-LS		Exodiffusion after light-soaking
D04087	NIP	248.3	Exodiffusion
D04087-LS	NIP-LS		Exodiffusion after light-soaking