ANNEALING BEHAVIOUR AND NATURE OF DEFECTS OF LIGHT-SOAKED MICROCRYSTALLINE SILICON SOLAR CELLS

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ABSTRACT: In this paper, we show that the kinetics of annealing of light-induced defects in microcrystalline silicon is similar to that of amorphous silicon. Dilution series of pin and nip single-junction microcrystalline silicon (µc-Si:H) solar cells were light-soaked (AM 1.5, 1000h at 50°C). Their relative efficiency loss between initial and degraded states depends on the i-layer crystallinity. Subsequent annealing steps at 373°K and 403°K exhibit a continuous decrease of the defect-related absorption as a function of time. This annealing kinetics follows a stretched exponential behavior, characterized by a relaxation time and a dispersive parameter. The defect relaxation time is thermally activated, with a characteristic energy that is independent of the intrinsic layer crystallinity, and that is lower than the value observed for thermal recovery of degraded a-Si:H.

Keywords: Thin Film, Micro Crystalline Si, Stability

1 INTRODUCTION

Light-induced degradation is a well-known issue for hydrogenated amorphous silicon (a-Si:H) thin film solar cells, which suffer from the Staebler-Wronski effect [1]. Hydrogenated microcrystalline silicon (µc-Si:H) solar cells, deposited by VHF-PECVD, have, at first, been considered to be quite unaffected by light-induced degradation [2]. Nevertheless it was later on reported that µc-Si:H solar cells deposited with the i-layer close to the amorphous transition do suffer from a mild form of light-induced degradation: Klein et al first suggested a Staebler-Wronski-like degradation of the amorphous phase [3]. Later on, Guha et al. stated that only the amorphous phase degrades by observing that µc-Si:H solar cells show no degradation when exposed to red light [4]. However, recently, Yan et al. suggested that the amorphous phase in µc-Si:H intrinsic layers is not necessarily the determining factor for the stability of nip solar cells under light-soaking. Small grains and/or intermediate-range order may play an important role in improving the stability [5].

In the present work, stability under light-soaking of two dilution series of pin and nip single-junction µc-Si:H cells is investigated by means of sub-bandgap absorption measurements, performed with Fourier transform photocurrent spectroscopy (FTPS). Defect-related absorption, which is defined as the measured absorption coefficient at 0.8 eV, is used to assess the defect density in the (micro)crystalline phase of the intrinsic layer.

After 1000h of light-soaking at AM 1.5 and 50°C, the pin and nip cells studied here present relative efficiency losses between 3 and 15%, according to their Raman crystallinity factor, together with a relative increase of the defect-related absorption of a factor 1.5 to 5, resp. Thereby, the strongest degradation is observed for cells with a low value of Raman crystallinity factor (i.e. for cells deposited near the amorphous transition). Subsequent annealing kinetics at 373°K and 403°K were monitored by FTPS measurements.

2 EXPERIMENTAL

2.1 Samples

The samples consist of two dilution series of µc-Si:H cells that were deposited by Very-High Frequency (VHF) PECVD in both pin and nip configurations. The TCO employed is a 600 nm thick sputtered-etched ZnO (Zinc Oxide), deposited at the Forschungszentrum in Jülich, Germany [6]. The doped layers have thicknesses in the order of 20-30 nm, whereas the i-layer thickness is about 2 µm. Each series was deposited in a double-chamber system, in order to avoid any contamination of the intrinsic layer from the gases used for the doped layers. The doped layers were kept constant within each series, whereas the intrinsic layer crystallinity varied with silane dilution.

2.2 Characterization techniques

Electrical parameters were obtained from current-voltage measurements under AM 1.5 solar simulator at 25°C (V_{oc}, FF), and, by integration, from external quantum efficiency measurements (J_{sc}).

The FTPS technique was used to measure the absorption spectrum of the cells over several orders of magnitude. The setup is described in detail in [7]. The FTPS spectra measured in this study were calibrated at 1.35 eV, by fixing the absorption coefficient of the µc-Si:H cells to the value of the absorption coefficient of crystalline silicon ($\alpha(1.35$ eV) ~ $2 \cdot 10^2$ cm^{-1}, see Fig. 2). Indeed, at 1.35 eV the absorption of amorphous silicon is around 100 times lower than that of microcrystalline silicon, and we may therefore consider that the amorphous part of the material contributes only in a negligible amount to the total absorption. The implicit assumption of this simple calibration procedure is that defect-related absorption $\alpha(0.8$ eV) originates from the (micro)crystalline phase only [8, 9]. Bulk defects (dangling bonds) as present in amorphous silicon possess an optical signature which is a flat region around 1.2 eV.

Raman spectroscopy, with a HeNe laser excitation beam (633 nm), was used to evaluate the average Raman crystallinity factor ϕ_c of the intrinsic layer, calculated as the arithmetical average of the Raman crystallinity factor as measured from the top and bottom of the samples [10]. Thereafter, the crystalline volume fraction X_c could be directly calculated from ϕ_c, see [11] for the detailed calculation procedure.

3 RESULTS

3.1 Electrical parameters

It must first be mentioned that the Raman

crystallinity factors of the samples do not vary with light-soaking: the degradation and annealing phenomena observed here are, thus, clearly not due to structural or microstructural modifications (such as recrystallization).

The effect of light-soaking on the conversion efficiency of the nip and pin solar cells series is shown in Fig. 1, where the relative efficiency loss $\Delta\eta$ is presented as a function of the intrinsic layer Raman crystallinity factor ϕ_c. $\Delta\eta$ is defined as

$$\Delta\eta = \left(\eta_{initial} - \eta_{degraded}\right)/\eta_{initial} \qquad (1)$$

Nip and pin series present very comparable relative losses of efficiency as a function of the Raman crystallinity factor:
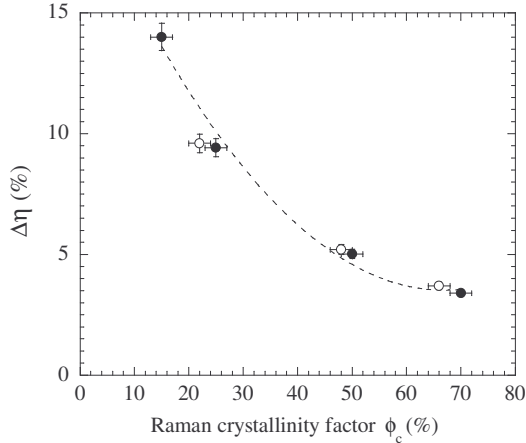

Figure 1: Relative light-induced loss of efficiency versus Raman crystallinity factor ϕ_c for both dilution series of cells (black dots: nip series, empty dots: pin series).

We observe that $\Delta\eta$ decreases when ϕ_c increases: this result is in agreement with the previous observations that highly μc-Si:H solar cells are not subject to noticeable light-induced degradation and agrees as well with the assumption that the amorphous phase may be responsible for the degradation. μc-Si:H solar cells with medium and high crystallinity factors are confirmed to be fairly stable with relative efficiency losses $\Delta\eta \leq 5\%$. Even μc-Si:H cells with a high amorphous fraction present relative losses lower than 15%, a value which is well below those that are obtained for light-soaking of thick a-Si:H cells.

Furthermore, we wonder to which extent the stability of μc-Si:H under light-soaking may be related to contamination of the intrinsic layer. Indeed, previous light-soaking studies that were done on two other series of pin and nip cells, deposited on LP-CVD ZnO [9,12], showed that the pin series degraded much more than the nip one. We attributed this difference in behaviour to a contamination of the pin devices during their deposition process that had been carried out in a single chamber [9]. Here, on the contrary, pin and nip samples present a very similar behaviour under light-soaking, which suggests that contamination of the intrinsic layer may play a significant role with respect to the device stability (see also [13]).

Similarly as for a-Si:H, the fill factor is the electrical parameter that shows the largest decrease with relative losses up to 10%. Open-circuit voltage and short-circuit current density are observed to be rather stable under light-soaking with variations inferior to 2.5%.

3.2 FTPS spectra and defect-related absorption

FTPS spectra of the nip cell with a low crystallinity (i.e. with ϕ_c = 15%) are presented in initial and degraded states in Fig. 2. The defect-related absorption α(0.8 eV) is increased by a factor 5, whereas the slope of the exponential decay of α(hυ), i.e. the Urbach parameter E_0, is not modified by light-soaking:
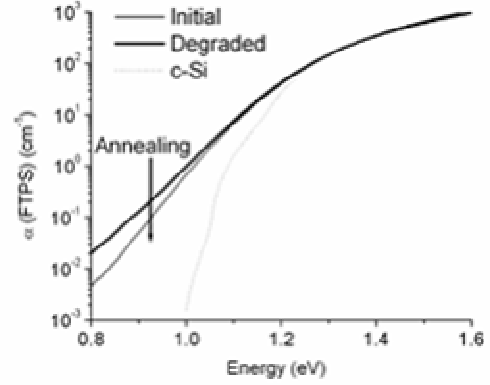

Figure 2. FTPS spectra in initial and degraded states for the nip cell with ϕ_c = 15 %.

Let us now define the relative light-induced defect-related absorption:

$$\Delta\alpha = \left(\alpha_{degraded} - \alpha_{initial}\right)/\alpha_{initial} \qquad (2)$$

Fig. 3 presents $\Delta\alpha$ as a function of the crystalline volume fraction X_c of the intrinsic layer:
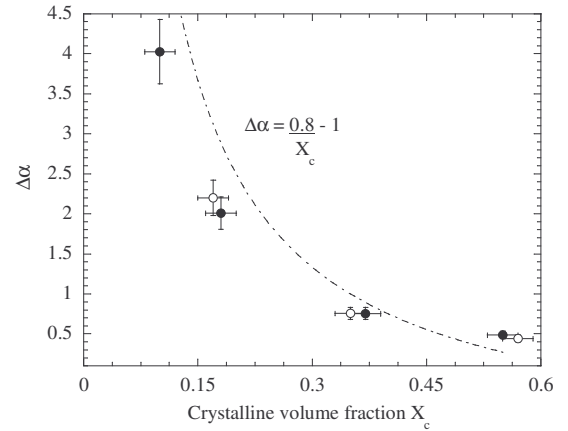

Figure 3. Relative light-induced defect-related absorption, as measured for the nip (black dots) and pin (empty dots) dilution series, as a function of i-layer crystalline volume fraction X_c.

The crystalline volume fraction is defined as:

$$X_c = \frac{V_c}{V_{tot}} \qquad (3),$$

where V_c and V_{tot} are the crystalline volume and the total volume of the sample, respectively. The observed trend (dotted line) is described by the expression:

$$\Delta\alpha(0.8\,eV) \approx \frac{1}{X_c} - 1 \qquad (4)$$

And, therefore, $\Delta\alpha$(0.8 eV) decreases experimentally according to the equation:

$$\Delta\alpha(0.8\,eV) \approx \frac{V_{tot} - V_c}{V_c} = \frac{V_a}{V_c} \qquad (5)$$

Equ. (5), thus, indicates that light-induced degradation is not related to the amorphous volume (V_a)

only, as suggested by [3, 4], but to the ratio of the amorphous to crystalline volume.

However, the kinetics of creation (not given here) and annealing of light-induced defects in µc-Si:H is observed to be very similar to that in a-Si:H: in both cases, the kinetics can be fitted with a stretched exponential function, typically used to model the dispersive diffusion of hydrogen in a-Si:H [14]. Such a stretched exponential function is given, for defect annealing kinetics, by:

$$\Delta\alpha(0.8eV)(t) = \left(\frac{\alpha_{ss}}{\alpha_{in}}\right)\left[\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right]\right] - 1 \quad (6),$$

where α_{ss} is the steady-state value (after light-soaking) of defect-related absorption, α_{in} is the initial state of defect-related absorption, β the dispersive parameter, τ the relaxation time of the defects and t the annealing time.

FTPS measurements of two nip solar cells with ϕ_c = 15% and ϕ_c = 50% were sequentially performed after 20 minutes, 1h, 2h, 5h, and 10 hours, of annealing at T_a = 373 °K (100°C). The sample with ϕ_c = 15% was also measured during annealing at T_a = 403 °K (130°C). All cells fully recover from degradation after sequential annealing up to 180°C and the defect-related absorption α(0.8 eV) returns to its initial value.

Fig. 4 shows the relative light-induced defect-related absorption $\Delta\alpha$ (0.8 eV) as a function of annealing time and temperature:
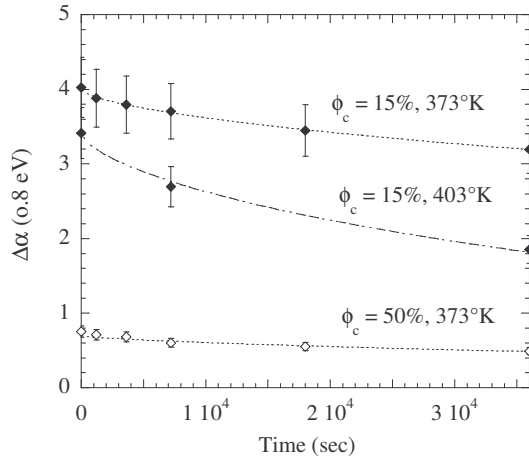

Figure 4. Relative light-induced defect-related absorption as a function of annealing time for two nip cells, with Raman crystallinity factor ϕ_c = 15% (black squares) and 50% (empty squares): at 373°K for both cells and, additionally, at 403°K for the sample with ϕ_c = 15%. The dotted lines are fits according to Equ. (6)

By fitting the results presented in Fig. 4 with Equ. (6), we obtain a value for the dispersive parameter β which does not depend on ϕ_c: β ~ 0.69 for 373°K. Conversely, the value of the relaxation time τ increases with increasing crystallinity. Furthermore, τ is confirmed to be thermally activated, as can be seen in Fig. 5.

τ may, thus, be expressed as a function of the annealing temperature, through the expression:

$$\tau = \tau_0 \cdot \exp\left(\frac{E_a}{kT_a}\right) \quad (7),$$

with E_a the activation energy and T_a the annealing temperature. The value of the activation energy, as given by the slope of the fit in Fig. 5, is equal to E_a = 0.5 eV.
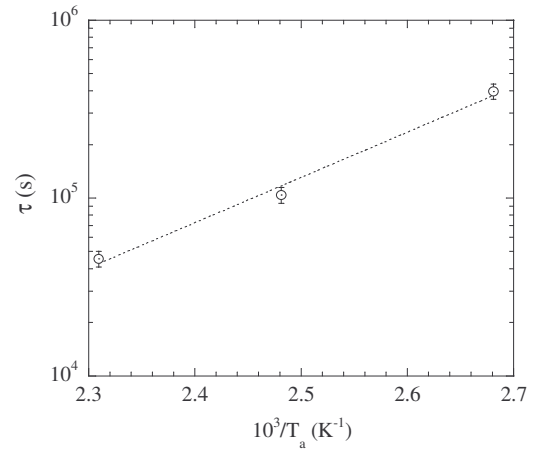

Figure 5. Defect relaxation time τ, in logarithmic scale, as a function of the reciprocal of the annealing temperature, for the nip sample with ϕ_c = 15%. The dotted line is a fit according to equ. (7).

The value of the activation energy established is independent of the crystallinity, as can be seen in Fig. 6. Indeed, from the fits of Fig 4, we know that β varies from 0.69 to approximately 0.74 for annealing temperatures T_a ranging from 373 °K to 433 °K. Nevertheless, if we consider, as a simplification, that β is almost constant, β ~ 0.7, over the range of temperatures used here, the activation energy can then simply be derived from Equs. (6) and (7):

$$\left(\log\left[\frac{\alpha_0(0.8eV)}{\alpha_{10h}(0.8eV)}\right]\right)^{1/\beta} = C(\tau_0) \cdot \exp(-\frac{E_a}{kT_a}) \quad (8)$$

In Fig. 6, we plot this logarithmic ratio (as given in Equ. (8)) as a function of $1/T_a$:
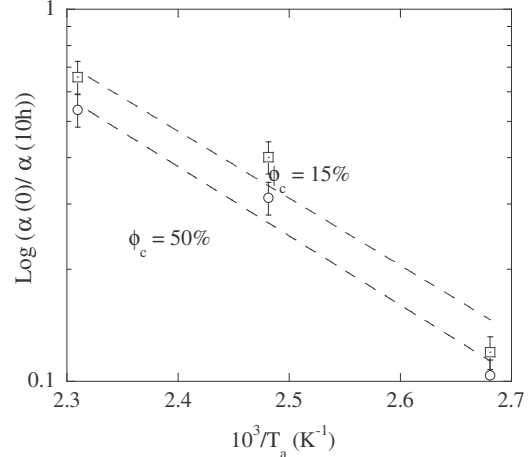

Figure 6. Logarithmic value of the ratio of defect-related absorption before and after 10h annealing, in logarithmic scale, as a function of the reciprocal of the annealing temperature for 2 nip solar cells of different crystallinity. The dotted lines are fits to Equ. (8)

4   DISCUSSION

The study of light-soaking, and subsequent thermal annealing presented in this paper, is based on the basic assumption that in µc-Si.H solar cells, the defect density can be directly related to the absorption α as measured at 0.8 eV. Moreover, by calibrating the whole absorption spectra at 1.35 eV, we assumed that the overall

absorption (at this photon energy) is dominantly given by the (micro)crystalline phase. If one assumes that it is only the amorphous phase that degrades with light-soaking and that defects present in this phase do not contribute to α(0.8 eV), no variation of this value should be observed when light-soaking μc-Si:H. It seems to us, therefore, that the variation in α(0.8 eV) observed here can only be attributed to defects situated at the interface between amorphous and crystalline phases.

Furtheremore, we have shown that there are striking similarities between μc-Si:H and a-Si:H, regarding the kinetics of annealing of light-induced defects. In both cases the kinetics can be fitted with a stretched exponential function, such as typically used when modelling diffusion mechanisms taking place in disordered systems. However, in μc-Si:H, the kinetics of annealing is somewhat slower than in a-Si:H, with larger relaxation times and a lower activation energy $E_a = 0.5$ eV instead of around 1 eV [14].

We propose that, microscopically, defect-related absorption, as measured at 0.8 eV, should be attributed to passivation defects at the amorphous/crystalline interface. The dependence of the relaxation times τ with crystallinity could tentatively be explained by considering that the light-induced defects at the amorphous/crystalline interface are passivated by hydrogen diffusion from the amorphous phase. For a given hydrogen diffusion constant (which depends on the temperature) the largest the amorphous fraction, the longer the time needed for hydrogen to diffuse at the degraded interface.

In a coarse approximation using a value for the hydrogen diffusion constant equal to 10^{-20} cm^{2}s^{-1} and a hopping length of 5 Å, relaxation times observed in the mostly amorphous nip sample ($\phi_c = 15\%$, $\tau \sim 10^5$ s) correspond to a hydrogen diffusion length of the order of 2 nm. Such diffusion length value is in the order of magnitude of the grain boundary thickness in μc-Si:H [10]. Nevertheless, F. Kail et al. reported values for the hydrogen diffusion coefficient in light-soaked amorphous and polymorphous silicon thin films of the order of 10^{-12}-10^{-14} cm^{2}s^{-1}, leading to hydrogen diffusion lengths of the order of the micrometer [15].

5 CONCLUSIONS

Nip and pin type microcrystalline silicon solar cells with intrinsic layers deposited close to the amorphous transition were shown to suffer from slight to mild light-induced degradation. Total recovery of the defect-related absorption is observed in all devices after annealing at 160°C. We find an activation energy for light-induced defect annealing lower than that reported for amorphous silicon, whereas relaxation times are larger in the case of μc-Si:H. The annealing of μc-Si:H solar cells is, thus, slower than that of a-Si:H solar cells (the initial value are not yet reached after 10 hours, as would have been the case for a-Si:H).

From our observations, we conclude that light-induced defects are most likely to be situated at the crystalline/amorphous interface. However, despite striking similarities between the annealing kinetics observed here for μc-Si:H solar and those reported for a-Si:H, a definitive microscopic identification of the light-induced defects optically detected at 0.8 eV is still lacking and hinders the interpretation of the degradation and annealing behaviours observed in this work.

Thus, further measurements should be performed to elucidate the exact microscopic nature of light-induced metastable defects created in the mixed-phase amorphous/microcrystalline material.

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