DEVELOPMENT OF MORE STABLE AMORPHOUS SILICON THIN FILM SOLAR CELLS DEPOSITED AT "MODERATELY HIGH" TEMPERATURE

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ABSTRACT: The present study aims at obtaining thin film amorphous silicon n-i-p solar cells with improved stability against light-soaking and high electrical performances. First, intrinsic amorphous silicon (a-Si:H) layers deposited by Very High Frequency Plasma Enhanced Chemical Vapour Deposition (VHF-PECVD) have been studied. Higher stable quality and more absorbing a-Si:H thin films have been produced by using the hydrogen dilution technique at moderately high temperature (~350°C). The stabilised material quality was quantified by measuring the quality parameter $\mu^0 \tau^0$ in the degraded state. Second, these improved intrinsic layers have been incorporated into solar cells. Although the parameters used for solar cells deposited at 350°C were optimised for 200°C deposited cells, promising results have already been obtained. The increase in the deposition temperature leads to higher stabilised short circuit current and stabilised fill factor, to a slightly reduced stabilised open circuit voltage and therefore to an increased efficiency.

Key words: a-Si:H-1: Stability-2: Current-3.

1 INTRODUCTION

Amorphous silicon (a-Si:H) material produced by PECVD presents for solar cell applications numerous advantages. Among them, its high absorption coefficient, which allows one to minimise the cell thickness, and its moderately high deposition rate are interesting for the reduction of the production cost. However, the most important problem of the a-Si:H layers and cells is the well-known light-induced degradation phenomenon, which leads to a strong reduction of the stabilised solar cell performances compared to their initial values.

Up to now, the only technological progress that has improved both material and cell stability is the use of the hydrogen (H₂) dilution technique [1,2]. However, this technique results also in an increase in the material's optical band gap (E_g) and thus, in a decrease of its absorption capability [3]. Consequently, thicker intrinsic films must be used to obtain sufficient current. As thick cells are less stable than thinner ones, the cell stability improvement obtained by incorporating H₂-diluted films is partially lost by the increase of the intrinsic layer thickness, particularly for single-junction cells and for amorphous top cell in amorphous/microcrystalline (called "micromorph") tandem cells.

In the present paper, we first study the behaviour of intrinsic a-Si:H material in order to obtain layers with both an improved stable quality and a relatively high absorption coefficient in the red. For this purpose, two dilution series deposited at 300°C and 350°C are compared. Second, intrinsic layers deposited at 350°C have been incorporated in solar cells in a n-i-p configuration. The performances have been compared in the degraded state.

Furthermore, cells performances were compared with the properties of the corresponding intrinsic layer: the relevance of using $\mu^0\tau^0$ as quality parameter (determined from σ_{photo} and SSPG) and a rapid degradation procedure for optimising intrinsic a-Si:H layers for new types of solar cells has been confirmed.

2 EXPERIMENTS

In order to study the effects of the deposition temperature and H_2 dilution on a-Si:H intrinsic layers, two hydrogen dilution series have been produced at 300°C and 350°C by VHF-PECVD [4]. Depositions were made in a single chamber reactor, by using the VHF excitation technique at 70MHz. The pressure, power, and total flow were set at identical values for each deposition. Dilution ratios (H₂/SiH₄) and displayed deposition temperatures (20-30°C higher than the effective substrate temperature) have been varied from 0 to 9 and from 300°C to 350°C, respectively. Schott AF45 glass was used as substrate and the thickness of each layer was set at 1 μ m, within the experimental error.

In the range of wavelengths between 600 and 700 nm, the absorption coefficient has been calculated taking into account the transmission coefficient of the sample, the reflection coefficient on the first interface air/a-Si:H, and the reflection coefficient on the second interface a-Si:H/substrate [5]. E_g has been determined using Tauc's plots.

The stabilised quality of the layers has been quantified by the quality parameter $\mu^0 \tau^0$ [6] in the degraded state. $\mu^0 \tau^0$ was determined, after accelerated degradation, by means of photoconductivity (σ_{photo}) and of steady-state photocarrier grating (SSPG). Accelerated degradation [7] consists of a two-phase procedure: first, an overdegradation of the sample is obtained by exposition to a combination of pulsed and continuous laser illumination during approximately two and half hours, followed by a relaxation of the sample under a red filtered light illumination for 3 days. The temperature and the illumination were set at about 50°C and 50 mW/cm², respectively.

In order to test the feasibility of fabricating reasonable n-i-p cells containing intrinsic layers deposited at 350° C, and to compare their performances with those of their counterparts deposited at lower temperatures (200° C, 250° C), four cells have been produced (table 1).

 Table I: Temperatures used for the deposition of doped and intrinsic layers in the test cells

	2		
Series	n-type layer	i-type layer	p-type layer
1	350°C	250°C	170°C
	350°C	350°C	170°C
2	350°C	200°C	170°C, thicker
	350°C	350°C	170°C, thicker

All cells were deposited on flat unpolished stainless steel substrates, their thickness was 300 nm and only the deposition temperature of the intrinsic layers and the p-doped layer thickness have been varied. Cells deposited at 350°C of the first and second series differ only by the p-doped layer thickness. Indium Tin Oxide (ITO) and a metallic grid were used as top contact for the first series, while Zinc Oxide (ZnO) was used for the second series. Concerning ZnO top contacts, a mechanical problem has been observed. The metallic tips used for contacting the cells cause, after the large number of measurements performed, an irreversible damage of the ZnO contacts. This resulted in a loss of FF during the degradation of the cells.

Degraded cells have been exposed to a continuous white illumination during 1000 hours for the first series and 500 hours for the second one. The temperature and illumination values were set at 50°C and 1/3AM1.5, respectively. Intensity-Voltage (IV) and Spectral Response (SR) measurements before, during and after light soaking have been performed at AM1.5.

3 RESULTS AND DISCUSSION

3.1 LAYER STABILITY AND OPTICAL GAP

The H_2 dilution technique is generally used to improve the stabilised quality $(\mu^0 \tau^0)$ of the a-Si:H layers against light soaking [1].

As predicted, one can see in fig. 1 that $\mu^0 \tau^0$ in the degraded state reaches a maximum for a relatively low dilution value (<4 for deposition temperature between 300°C and 350°C) and for each deposition temperature (300°C and 350°C).



Fig. 1: $\mu^0 \tau^0$ product in the degraded state for layers deposited at 300°C and 350°C as a function of the H₂/SiH₄ ratio.

However, higher temperatures increase the stabilised $\mu^0 \tau^0$ optimum (by a factor 2) and shift the optimum position to even lower dilution ratios (from around 4 at 300°C to around 2 at 350°C).



Fig. 2: Optical band gap (2a) and deposition rate (2b) for layers deposited at 300°C and 350°C as a function of H_2 dilution (H_2 /SiH₄)

Furthermore, between dilution 0 and the optimum dilution (resulting in the highest stable quality), H_2 dilution leads to an increase in the value of E_g (see Fig. 2a) and to a decrease in the deposition rate (see Fig. 2b).

On the other hand, for every H_2 dilution value except for 0 dilution, an increase in the temperature results in a decrease in E_g (i.e. in an increase in the absorption) (cf. figure 2a) and has no influence on the deposition rate (figure 2b).

Because of the decrease in the deposition rate and the increase in the E_g value induced by the H_2 dilution, the use of higher deposition temperatures becomes doubly attractive. Indeed, high stable quality layers deposited at 350°C require lower H_2 dilution compared to layers deposited at lower temperature and have therefore reduced E_g at higher deposition rates.

3.2 CELLS PERFORMANCES

Through this work, the authors were interested only in comparative results. Absolute performances of cells remain low because of the use of smooth back contacts (I_{sc} is approximately 35% lower than on optimised textured back contacts) and because of the lack of back reflectors.

3.2.1 Short circuit current I_{sc}

SR measurements have been performed after light soaking during 1000 hours on the first series and during 500 hours on the second one.

 $I_{\rm sc}$ was calculated by multiplying the measured SR curve with the solar spectrum (number of photons per wavelength) and integrating over all wavelengths.

By plotting the SR of both cells deposited at 200°C and 350°C (Fig. 3), a gain in the range of long wavelengths is obvious. This results in an increase of 4.5% in the stabilised value of I_{sc} .



Fig. 3: Spectral responses measured after 500 hours of light soaking on cells deposited at 350° C and 200° C (second series) - I_{sc} is 10.8 and 10.3 mA/cm² respectively.

The gain is the consequence of the difference between the E_g values of the incorporated intrinsic layers; Indeed, E_g decreases from 1.75eV to 1.72eV for layers deposited at 200°C and 350°C, respectively.

The resulting low gain is probably the consequence of the non optimised H_2 dilution used for the intrinsic layer deposited at 350°C. However, it should be possible to improve it still further.

3.2.2 Open circuit voltage V_{oc}

I-V measurements have been performed on all cells during light soaking.

For the first series of cells, the difference in V_{oc} between cell deposited at 250°C and those deposited at 350°C (Fig. 4a) is attributed to a shortcoming in the built-in voltage, due to a non-adapted p-doped layer.



Fig. 4: V_{oc} as a function of degradation time obtained from the first series (4a) having a p-doped layer optimised around 200°C, and from the second series (4b) fabricated with a thicker p-doped layer.

Indeed, even if p-doped layers of all cells were fabricated with the same parameters (as shown on our instrument display), we suspect that the initial growth on the intrinsic layer deposited at 350°C is different than that on the intrinsic layer deposited at 250°C. Therefore, p-doped layers may be too thin to create a sufficient electrical field in the intrinsic layer deposited at 350°C.

In the case of the second series, the p-doped layer is better adapted (~ 10% thicker) for cell deposition at 350°C and the full V_{oc} is recovered, i.e. it is no more affected by the doped layers (Fig. 4b). Indeed, V_{oc} of cell deposited at 350°C is only slightly lower (1% in the degraded state) than that of cells deposited at 200°C. However, more absorbent intrinsic layers (i.e. with lower E_g) will result in a decreased V_{oc} because of the dependence of V_{oc} on E_g [3].

3.2.3 Fill factor FF

Fig. 5 illustrates the change in FF during light



Fig. 5: FF of cells of first series deposited at 250° C and 350° C (5a) and of the second series deposited at 200° C and 350° C (5b), as a function of the degradation time.

soaking of cells deposited at 200°C, 250°C and 350°C. Although cells of the first series (Fig. 5a) have been deposited at 250°C and 350°C, respectively, their FF exhibit nevertheless the same values. Indeed, FF of both cells decrease of 10% during light soaking and have the same stabilised value (see table II).

Table II: FF in the initial and degraded state and $\mu^0 \tau^0$ in the degraded state of the corresponding intrinsic layer.

-		-	-	-
Series	i layer (300nm)	FF initial	FF final	$\mu^0\tau^0(cm^2/V)$
1*	250°C	69%	62%	1.76 10 ⁻⁷
	350°C	68.5%	62%	$1.76 \ 10^{-7}$
2	200°C	74%	62%	$1.62 \ 10^{-7}$
	350°C	71.2%	64.8%	1.74 10 ⁻⁷

* p doped layer non adapted for deposition at 350°C

This result has been confirmed by measuring the same values for the stabilised quality $(\mu^0 \tau^0)$ of the corresponding intrinsic layers (see table II).

However, the cell of the second series deposited at 350° C is less affected by light soaking than the one deposited at 200° C (Fig 5b). Indeed, FF decreases of 9.4% for cell deposited at 350° C and of 17.6% for that deposited at 200° C (see table II). Moreover, the stabilised FF of the 350° C deposited cell is higher than that of the 200° C deposited one (64.8% compared with 62%). This tendency is found again by determining the corresponding layer stabilised qualities (table II).

Table II shows that in addition to affect the V_{oc} (see part 3.2.2), the non-adapted p-doped layer of the cell deposited at 350°C in the first series influences also the stabilised FF. Indeed, even if the intrinsic layers incorporated in both cells deposited at 350°C have the same $\mu^0 \tau^0$, the stabilised FF of the cell with the adapted p-doped layer is higher (table II). The drop of built-in voltage, i.e. the reduced electrical field through the intrinsic layer, limits the collection of generated carriers.

These observations mean that when increasing the deposition temperature of intrinsic layer (in order to improve its stabilised quality and its absorption capability), the deposition technology for doped layers must be consequently adapted.

3.2.4 Efficiency of cells

Cell efficiencies have been compared in the degraded state (table III).

Table III: Comparative performance of cells incorporating intrinsic layers deposited at 200°C, 250°C and 350°C after light soaking; all cells were deposited on smooth substrate and without back reflector.

Series	i layer	FF (%)	V _{oc} (V)	I _{sc} (mA/c m ²)	Effi- -ciency
1	250°C	61.8	0.882	10.91	5.94%
	350°C	62.5	0.845	11.34	6%
2	200°C	62	0.889	10.28	5.66%
	350°C	64.8	0.888	10.77	6.19%

The absolute performances of cells studied here remain low because of the use of smooth back contacts and the lack of back reflectors. However, one can see that the cell deposited at 350°C of the second series has already a higher stabilised efficiency than the cell deposited at 200°C. In spite of the loss of V_{oc} , the cell deposited at 350°C of the first series has the same efficiency as the one deposited at 250°C. These promising results are due to the increase in the stabilised values of Isc and FF that can and should be further improved by fine-tuning the H₂ dilution ratio of the intrinsic layer deposited at 350°C. Indeed, Fig. 1 shows that around the maximum, the curve of the stabilised quality vs. H₂ dilution obtained from layers deposited at 300°C is much more flat than the curve obtained from layers deposited at 350°C; that mean that H₂ dilution allowing to obtain improved stabilised quality and absorption must be set much more accurately at high temperatures. As, up to now, this fine-tuning has not been performed for cells deposited at 350°C, we suspect that the dilution used for both series is closer to the optimised value at standard temperature than to the optimised value at higher temperature.

4 CONCLUSIONS

This work has shown that deposition at "moderately high" temperatures (350°C) combined with the H₂ dilution technique present many advantages for n-i-p a-Si:H solar cells. Indeed, higher deposition temperatures lead to an enhanced absorption of the a-Si:H layers and furthermore to an improved collection performance of cells in the degraded state. The optimum value of $\mu^0 \tau^0$ is higher and shifted to lower dilution ratios (H₂/SiH₄) for increasing temperature. As a consequence, more absorbing and more stable intrinsic layers are produced at 350°C than at lower temperatures, and the deposition rate, which is generally reduced by H₂ dilution, is also higher.

n-i-p cells incorporating such more stable and absorbent layers have been fabricated and already exhibit promising comparative results. When the doped layers are adapted to higher deposition temperature, cells deposited at 350°C have already a stabilised efficiency that is in relative term 5% higher than those deposited at 200°C. This improved efficiency comes from the increase in the stabilised values of I_{sc} and FF values, that compensate largely the observed slight reduction of V_{oc} due to the lower value of E_g.

In addition, the effect of higher deposition temperature on FF and I_{sc} of the solar cells could be correlated with the values of stabilised $\mu^0 \tau^0$ and of E_g measured on the corresponding incorporated intrinsic layers after accelerated degradation. The usefulness and reliability of the rapid degradation procedure and of the $\mu^0 \tau^0$ tool (as introduced by IMT Neuchâtel) for optimising intrinsic a-Si:H layers for new types of solar cells have thus been confirmed. This is in accordance with results obtain in [3] for p-i-n solar cells.

For future experiments, the H_2 dilution ratio of the intrinsic layer incorporated into the solar cells will be "fine-tuned" at 350°C. This step should lead to a further increase in $I_{\rm sc}$ and FF.

ACKNOWLEDGEMENT

This work was founded by the Japanese New Energy and Industrial Technology Development Organisation (NEDO).

REFERENCES

- S. Guha, K.L. Narasimhan, S.M. Pietruszko, J. Appl. Phys. 52 (1981) 859
- [2] J. Yang, X. Xu, S. Guha, MRS Symp. Proc. 336 (1994) 687
- [3] R. Platz, PhD thesis, Université de Neuchâtel 1999, ISBN 3-930803-61-5
- [4] Y. Ziegler, V. Daudrix, C. Droz, R. Platz, N. Wyrsch, A. Shah, Proceedings of PVSEC-11, Hokkaido, Japan, (1999), to be published in Sol. Energy Mat. & Sol. Cells
- [5] M. Vanecek, private communication
- [6] N.Beck, N. Wyrsch, C. Hof, A. Shah, J. Appl. Phys. 79 (1996) 9361
- [7] C. Hof, Y. Ziegler, R. Platz, N. Wyrsch, A. Shah, J. Non-Cryst. Solids 227-230 (1998) 287