

HIGH- T_s AMORPHOUS TOP CELLS FOR INCREASED TOP CELL CURRENTS IN MICROMORPH TANDEM CELLS

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Abstract

In the present paper, the authors discuss the application of amorphous p-i-n solar cells containing i-layers which are deposited at high substrate temperatures as top cells in amorphous/microcrystalline tandem ("micromorph") solar cells. Increasing the substrate temperature for the deposition of intrinsic a-Si:H results in a reduced optical gap. The optical absorption is enhanced and thereby the current generation. A high current generation within a relatively thin amorphous top cell is very interesting in the context of micromorph tandem cells, where the amorphous top cell should contribute a current of at least 13mA/cm² for a total cell current density of 26mA/cm².

A detailed study is presented of the intrinsic material deposited by VHF-GD at 70 MHz at substrate temperatures between 220°C and 360°C, including samples deposited from hydrogen-diluted silane plasmas. The stability of the films against light soaking is investigated employing the $\mu_0\tau_0$ parameter, which has been shown to be directly correlated to the cell performance.

The paper discusses in detail the technological problems arising from the insertion of i-layers deposited at high substrate temperatures into solar cells. These problems are specially pronounced in the case of cells in the p-i-n (superstrate) structure. The authors demonstrate that an appropriate interface layer at the p/i-interface can largely reduce the detrimental effects of i-layer deposition at high temperatures.

Finally, the application of such optimized high-temperature amorphous cells as (a) bottom cells in a-Si:H/a-Si:H stacked cells and (b) as top cells in micromorph tandem cells is discussed. Current densities of 13mA/cm² in the top cell are available with a top cell i-layer thickness of only 250nm. The potential of such top cells for raising the stabilized efficiency of micromorph tandem cells is discussed.

I. Introduction / Motivation

Micromorph cells, i.e. amorphous silicon / microcrystalline silicon (a-Si:H/ μ c-Si:H) tandem cells, are continuously gaining in interest as promising thin-film silicon solar cells. 10.7% stabilized efficiency has been achieved so far [1] (as confirmed by the Fraunhofer Institut für Solare Energiesysteme, Freiburg/Germany). There is a high potential for a further increase of the stabilized efficiency for such micromorph tandem cells. To raise the efficiency, the basic problem of combining a high-current but low-voltage (μ c-Si:H) bottom cell with a low-current but high-voltage amorphous top cell must be resolved.

Table 1 compares different types of a-Si:H based solar cells with respect to the current density in the top cell. The thickness of the top cell is a very decisive parameter for the stability of an a-Si:H based solar cell. Whereas a top cell current density of 7-9mA/cm² is sufficient for an a-Si:H/a-Si:H stacked cell, this current must be raised to 10-11mA/cm² when an a-SiGe:H bottom cell is employed. The total generated current remains on the order of 22mA/cm². Top cell currents of 10-11mA/cm² are easily achievable with relatively thin and therefore highly stable cells. USSC achieves with their a-SiGe:H alloys a total cell current of

27mA/cm². However, in this case, the total cell current is distributed in 3 component cells, again resulting in only 8-9mA/cm² for the top cell. In the case of our micromorph cells, the total current of 26mA/cm² is distributed in only 2 component cells resulting in a need of at least 13mA/cm² for the amorphous top cell. Currents of up to 30mA/cm² seem to be within possibility with microcrystalline bottom cells. In this case, conventional amorphous top cells are unable to match the bottom cell current, and the need for top cells with a higher current level becomes even more urgent.

Type	Laboratory	Efficiency/ %	Top/ mA/cm ²	Middle/ mA/cm ²	Bottom/ mA/cm ²	Sum/ mA/cm ²
a-Si:H/ a-Si:H	IMT Neuchâtel [2]	9 stab.	7.6	--	8.0	15.6
	ISI-PV Jülich (D) [3]	9 stab.	7.7	--	?	15-16
	USSC [4]	10.1 stab.	7.9	--	?	16-17
	Fuji [5]	12 initial	8.97	--	?	~ 18 ?
a-Si:H/ a-SiGe:H	Solarex [6]	11.1 initial	10.3	--	10.5	20.8
	Sanyo [7]	10.6 stab.	10.9	--	?	~ 22 ?
	USSC [4]	11.2 stab.	10.6	--	?	~ 22 ?
a-Si:H/ a-SiGe:H/ a-SiGe:H	USSC [8]	13.0 stab.	8.6	9.0	9.3	26.9
a-Si:H/ μc-Si:H	IMT Neuchâtel [1]	11.2 stab.	~ 13	--	~ 13	~ 26

Table 1.: Subcell currents of several a-Si:H based multi-junction solar cells. A-Si:H top cell currents range from 7-8mA/cm², for the case of a-Si:H bottom cells, to 10-11mA/cm² for a-SiGe:H bottom cells. A top cell current of 13mA/cm² is needed for the micromorph tandem cell.

The difficult task is to combine the required current generation with high stability. We have previously shown [9] that an a-Si:H top cell with an optical gap slightly lower than of standard a-Si:H material will yield micromorph tandem cells with increased stabilized efficiency. In addition, other concepts such as selectively reflecting interface layers between the top and the bottom cell can contribute to higher stabilized efficiencies [10,11].

In the present paper we discuss in detail the use of higher than standard substrate temperatures to obtain a lower optical gap, and therefore a higher current. We describe the application of such amorphous top cells, deposited at high substrate temperatures, in micromorph tandem cells. We also discuss the technological problems which arise from depositing a p-i-n structure at high substrate temperature.

II. Intrinsic material with reduced optical gap as a result of increased deposition temperature

In order to study the influence of the substrate temperature on the optical and electronical properties of intrinsic a-Si:H films, we deposited a series of samples at different substrate temperatures, T_s , and at varying hydrogen dilution ratios (dilution = $[H_2]/[SiH_4]$). We used glass (AF45, Schott) substrates and crystalline silicon for IR measurements. All samples and cells in this study were deposited using the Very High Frequency Glow Discharge (VHF-GD)

technique at 70 MHz. A gas purifier [12] was employed for all films in order to keep the oxygen content of the films low.

2.1. Optical properties

Fig.1 shows the absorption spectra (as determined from transmission/reflection and PDS measurements) for undiluted samples (left) and diluted samples (right) deposited with a H_2 -dilution ratio of 9 at 3 different substrate temperatures, 270°C being our "standard" deposition temperature. For the undiluted samples we find a clear increase of the absorption over the whole spectrum with increasing deposition temperature. The absorption coefficient of the diluted samples increases with increasing substrate temperature. However, the absorption of the diluted samples is strongly reduced compared to the undiluted samples. Fig.2a and Fig.2b show values of the absorption coefficient at characteristic wavelengths (600nm Fig.2a and 700nm Fig.2b) for a larger set of samples in a direct comparison. The sample deposited with a dilution ratio of 9 at a substrate temperature of 360°C shows a partially microcrystalline absorption behavior. At standard (270°C) substrate temperature, the onset of microcrystalline growth appears only for dilution ratios of about 13-15 in the case of VHF-GD [13]. The increase of the absorption (corresponding to a decrease of the optical gap) is correlated to a decrease of the hydrogen content (Fig.3) as determined from the integrated 630cm^{-1} absorption peak in the infrared absorption spectra. On the one hand, the hydrogen content decreases with increasing substrate temperature during deposition, on the other hand an increasing H_2 -dilution ratio of the silane plasma during deposition results in a higher hydrogen content in the film.

2.2. Electrical properties and degradation behavior

A study of material properties of amorphous silicon for solar cell applications implies the question for the electronic properties of this material and especially the behavior under light-soaking. The correlation between material properties and solar cell performance has always been a field of controversy. Recently, it has been shown [14,15], that the material parameter $\mu_0\tau_0$, which contains combined information on the minority and the majority carriers independent of the Fermi level position in the band gap, shows a good correlation with the solar cell performance in the initial and the degraded state. Fig.4 shows this parameter in the degraded state as a function of the substrate temperature T_s and the dilution ratio employed for the deposition of the i-layer. The degradation and measurement procedures are described in more detail in [16]. The measurement confirms the enhanced stability against light-soaking for films deposited with hydrogen dilution [17]. In fact, the H_2 -diluted i-layers at $T_s=220^\circ\text{C}$ have successfully been incorporated into a-Si:H/a-Si:H stacked cells and as top cells in micromorph tandem cells resulting in stabilized efficiencies of 9% [2] and 10.7% [1] respectively. The purpose of this work is to further enhance the efficiency of micromorph tandem cells by increasing the optical absorption in the top cell i-layer. Hydrogen dilution has shown to strongly reduce the optical absorption (Fig.2) and is therefore not desirable in this context. A further increase of the optical absorption has shown to be possible by increasing the deposition temperature of the i-layer (Fig.2). Fig.4 shows that undiluted i-layers show increasing $\mu_0\tau_0$ values with increasing deposition temperature whereas the diluted samples show quite high degraded $\mu_0\tau_0$ values independently of the deposition temperature. Deposition at increased substrate temperatures does therefore not only increase the optical absorption due to a reduced optical gap, but ameliorates also the stability of the material thereby obtained. The persisting loss in stability as compared to optimized diluted i-layers may be compensated by a much thinner top cell for a given top cell current, as will be discussed in section IV of this paper.

2.3. Deposition rate

We observe a slight increase of the deposition rate with increasing substrate temperature T_s as shown in Fig.5. For undiluted samples, we obtain deposition rates of 5-6Å/s, for dilution ratios of 2 and 9, these values decrease to 3.5-4Å/s and 2-2.5Å/s respectively. These values for our VHF deposition technique at 70MHz are much higher than what is generally obtained for device-grade RF (13.56 MHz) deposition [2].

III. p-i-n cells at increased deposition temperatures for the i-layer

Having characterized the intrinsic material for a wide range of deposition temperatures and dilution ratios, we incorporated this material as the absorbing layer in single-junction p-i-n cells. We restricted the study to the case of undiluted films as the optical absorption decreases strongly with dilution (Fig.2) which counteracts our goal of strongly absorbing cells. The doped layers were deposited at the standard (273°C) substrate temperature. Before the deposition of the i-layer, the grounded electrode with the substrate was heated up to the deposition temperature of the i-layer. A gas flux of 20 minutes prior to the deposition assured a homogeneous temperature over the substrate. After the deposition of the i-layer, the substrate was cooled down before n-layer deposition.

Fig.6 shows spectral response (SR) curves (measured under short circuit conditions, i.e. at 0V bias) for two cells deposited at substrate temperatures of 300°C and 330°C normalized to the SR of a "standard" p-i-n cell at 270°C. One clearly observes an increase of the SR in the long wavelength-region due to the increased absorption coefficient (Fig.1 left) of the i-layer material deposited at high temperature. At 700nm the spectral response is increased by 20% for the 330°C cell as compared to the "standard" 270°C cell. This desired increase of the red spectral response with increasing T_s is, however, combined with a decrease of the blue wavelength spectral response. This point will be discussed in the following section.

3.1. Influence of high temperatures on the p/i interface

Fig.6 shows a decrease of the blue SR at 0V bias for increasing i-layer deposition temperature. At a reverse bias voltage of -3V, there is, however, no difference for the three temperatures which excludes a reduced transparency of the p-layer as the reason for the reduced blue response. We attribute this effect of a voltage-dependent blue SR to boron contamination of the i-layer due to diffusion of boron out of the p-layer when heating it up. The internal electric field in the i-layer is reduced due to a slight boron-doping of the first part of the i-layer. Strongly absorbed blue light creates electron-hole pairs close to the p-layer. The collection of these carriers is reduced due to enhanced recombination. Heating up of the p-layer in order to deposit the i-layer at higher T_s has also detrimental effects on the other cell characteristics, i.e. V_{oc} and FF. On the one hand, we observe strongly reduced V_{oc} -values for cells with high- T_s i-layers (Fig.7, left), on the other hand the FF values of those cells also decrease with increasing substrate temperature during i-layer deposition (Fig.7, right). The decrease of the V_{oc} is stronger than what can be explained by the decrease of the optical gap of the i-layer material [18]. Fig.7 (left) shows for comparison $E_{03}/2$ of the i-layer as a function of the substrate temperature. E_{03} is hereby taken as a measure for the optical gap of the i-layer.

An appropriate p/i interface layer (IL) can reduce both these problems to a large amount. Fig.7 shows for $T_s=330^\circ\text{C}$ the influence of an optimized p/i interface layer on V_{oc} and FF in the initial and degraded state (squares). With the IL, the decrease of V_{oc} in both the initial and the degraded state is reduced to the amount that can be attributed to the decrease of the optical gap (Fig.7 left). Furthermore, the p/i interface layer prevents a strong decrease of the FF with increasing deposition temperature (Fig.7 right). The IL, deposited at the same temperature as the p-layer, acts as a diffusion barrier for boron atoms and prevents thereby the diffusion of

boron out of the p-layer into the i-layer during i-layer deposition at high temperature. A slight doping of the p/i interface layer due to boron diffusion into the IL has a positive effect on the performance of the device [19].

3.2. Optimized high- T_s p-i-n cells

Fig.8 shows the characteristic cell data for a thickness series of single-junction p/IL-i-n cells containing an IL as described above with an i-layer deposited at 330°C in the initial and the degraded (1000h) state. For comparison and in order to establish a larger context, we show also the degraded values for "standard" cells deposited at 270°C and cells with low-temperature (220°C) H_2 -diluted i-layer as described in [9].

The gain in current by increasing the deposition temperature from 270°C to 330°C is about 1mA/cm² after degradation for the single cells. Obviously, from the efficiency point of view, these high- T_s cells are only interesting as top cells in the context of micromorph tandem cells where the generation of a sufficient current density at reasonable cell thickness has shown to be more important for the efficiency than the V_{oc} . For the application as single cells, in contrast, the V_{oc} plays a very decisive role which is confirmed by the fact, that the low-temperature H_2 -diluted p-i-n cells with their high V_{oc} values show a higher stabilized efficiency than standard cells in spite of their reduced current level.

A stabilized efficiency of up to 7% for our high- T_s p/IL-i-n cells demonstrates, however, that it is possible to deposit quite good solar cells with reduced optical gap due to high substrate temperature also by employing the "conventional" p-i-n structure.

IV. Tandem cells incorporating high- T_s cells

4.1. a-Si:H/a-Si:H stacked cells with high- T_s bottom cells

Such a high-temperature amorphous cell can contribute to a higher a-Si:H/a-Si:H stacked cell performance [18]. We have previously reported on an a-Si:H/a-Si:H stacked cell with 9% stabilized efficiency [2] in a conventional (superstrate) structure. An amorphous cell with a reduced optical gap would be interesting as a bottom cell in such a stacked structure. In order to avoid damage to the top cell during deposition of the bottom cell at high temperatures, an inverted (substrate) structure (n-i-p-n-i-p) would be more convenient for such a cell. Assuming an increase of the total cell current in the degraded state due to the high deposition temperature of $\approx 1\text{mA/cm}^2$ and a reduction of the V_{oc} for the bottom cell from 840mV to 780mV, one can make the following estimation for a stabilized efficiency of such a cell, based on the 9% stabilized efficiency value:

$$9\%: \quad \begin{array}{llll} V_{oc}=1.71\text{V} & 69\% \text{ FF} & 7.64\text{mA/cm}^2 & \\ V_{oc}=1.65\text{V} & 69\% \text{ FF} & 8.14\text{mA/cm}^2 & \rightarrow 9.3\% \text{ efficiency.} \end{array}$$

Thus, even with the conservative assumption of the same V_{oc} for a p-i-n as for a n-i-p structure, we can expect a net increase of the stabilized efficiency. This increase is potentially even higher due to an increased V_{oc} value for a n-i-p cell, as compared to a p-i-n cell, especially at high deposition temperatures for the i-layer.

4.2. Micromorph tandem cells with high- T_s top cells

Finally, we incorporated these high- T_s p/IL-i-n cells as top cells in micromorph tandem cells. Due to the relatively thick (3-5 μm) bottom cell and the strong absorption of the microcrystalline bottom cell material, incoming light passes the amorphous top cell only once, without an optical enhancement due to a reflection of non-absorbed light at the back contact. The influence of a variation of the optical gap of the top cell i-layer can therefore be expected to be even more pronounced in this case than in the case of single-junction cells. Fig.9

compares measured top cell SR curves for 3 top cells with different optical bandgap energies and the same i-layer thickness of 300 nm. The decrease of the SR curves in the red wavelength region is clearly shifted towards higher wavelengths with decreasing optical gap of the top cell i-layer.

Fig.10 shows currents of such high-temperature micromorph top cells in comparison to "standard" and low-temperature top cells and for different top cell i-layer thicknesses in the initial state. The gain in current for a given i-layer thickness is in the order of $1\text{mA}/\text{cm}^2$ when going from "standard" temperature undiluted top cells to high-temperatures p/IL-i-n top cells as described in section 3.2. of this paper. A top cell current of $13\text{mA}/\text{cm}^2$, as would be necessary to match a total cell current of $26\text{mA}/\text{cm}^2$, is available with a high- T_s top cell of about 250nm thickness, whereas one needs a "standard" temperature top cell of around 400nm thickness in order to obtain this current. By employing the optimized p/IL-i-n top cell and additionally a selectively reflecting intermediate ZnO layer in between the top and bottom cell, we have obtained a top cell current of $13\text{mA}/\text{cm}^2$ with only 150nm top cell thickness [11].

We have previously demonstrated a 10.7% stable micromorph tandem cell [1]. The characteristic data of this cell were $V_{oc}=1.34\text{V}$, $\text{FF}=66.7\%$ and $I_{sc}=11.9\text{mA}/\text{cm}^2$. Based on this experimental and independently confirmed result we may establish the following estimation for micromorph tandem cells with a high- T_s top cell as described above: Fig.10 indicates an increase in current density of about 15% when going from low-temperature H_2 -diluted top cells (as employed for the 10.7% stable cell) to high- T_s top cells for the same cell thickness as the 10.7% stable cell. The V_{oc} of the top cell decreases from about 0.88V to 0.78V resulting in a decrease of the V_{oc} for the tandem cell by 7% to 1.24V. Assuming the same fill factor for the same top cell thickness and a bottom cell that can provide enough current, we may estimate the stabilized efficiency of such a micromorph tandem cell to be 11.4%. This estimation is only justified if the microcrystalline bottom cell can match a total cell current of 27-28 mA/cm^2 .

V. Conclusions

The optical gap of a-Si:H deposited by the VHF-GD at 70 MHz decreases with increasing substrate temperature during deposition. The decrease in the optical gap is correlated to a decrease of the hydrogen content of the films.

Hydrogen dilution of the silane plasma causes an increase of the optical gap of the resulting film for all deposition temperatures. The onset of microcrystalline growth appears for lower hydrogen dilution ratios when increasing the deposition temperature.

The stability against light-soaking of intrinsic films can be improved by hydrogen dilution of the silane plasma. A dilution ratio of 2 results in films showing $\mu_0\tau_0$ values in the light-soaked state of $1\text{-}2\cdot 10^7\text{cm}^2/\text{V}$ independent of the deposition temperature. A further increase of the dilution ratio does not improve the $\mu_0\tau_0$ product in the light-soaked state further. For undiluted films, the $\mu_0\tau_0$ product in the light-soaked state increases with increasing deposition temperature from $5\cdot 10^8\text{cm}^2/\text{V}$ at 220°C to $8\cdot 10^8\text{cm}^2/\text{V}$ at 330°C .

At higher than standard deposition temperatures, efficient solar cells can be made in the p-i-n structure, also, if diffusion is counteracted by an appropriate interface layer (IL) at the p/i-interface. Such an interface layer reduces the boron contamination of the first part of the i-layer and prevents a strong V_{oc} reduction for i-layers deposited at higher than standard temperature. For the same i-layer thickness, optimized p/IL-i-n single-junction cells show I_{sc} values in the degraded state which are 0.8-1 mA/cm^2 higher than for p-i-n cells with an i-layer deposited at "standard" temperature. After 1000h of light-soaking, an optimized p/IL-i-n cell

with an i-layer thickness of 200 nm shows $V_{oc}=0.78V$, $FF=61\%$, $I_{sc}=14.9mA/cm^2$ which results in 7% stabilized efficiency.

Amorphous cells with i-layers deposited at higher than standard temperature are specially appropriate as top cells in micromorph tandem cells due to their high current densities. The gain in current for a given i-layer thickness is on the order of $1mA/cm^2$ for optimized p/iL-i-n cells as compared to "standard" temperature undiluted top cells. With 250nm i-layer thickness, such a high- T_S p/iL-i-n top cell can provide a current of $13mA/cm^2$ in a micromorph tandem. Such high current densities provided by thin and therefore relatively stable amorphous top cells can contribute to a further improvement of the stabilized efficiency of micromorph tandem cells. Stabilized efficiencies of 12% should be achievable with this kind of p/iL-i-n top cells and today's available microcrystalline bottom cells.

Acknowledgements

Financial support by Swiss Federal Department of Energy BEW/OFEN, grant 19431, is gratefully acknowledged. R. Platz thanks the Arthur u. Aenne Feindt Stiftung, Hamburg/D, as well as the Fondation Charles-Edouard Guillaume, Bienne/CH, for financial support during his stay at Princeton University.

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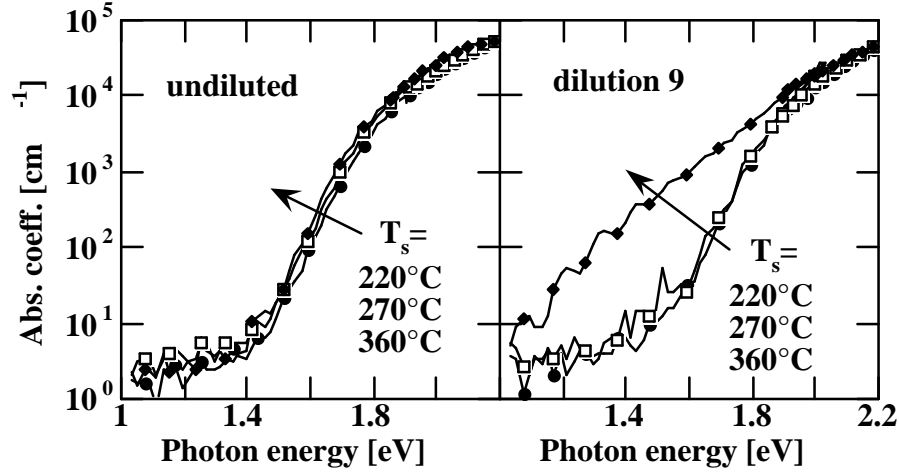


Figure 1a,b: Absorption spectra as measured by transmission/reflection ($h\nu > 1.9\text{eV}$) and PDS ($h\nu < 1.9\text{eV}$) for three substrate setpoint temperatures T_s without hydrogen dilution (left) and with a hydrogen dilution ratio of 9 (right). Note that the sample at dilution 9 and $T_s = 360^\circ\text{C}$ shows partially microcrystalline absorption.

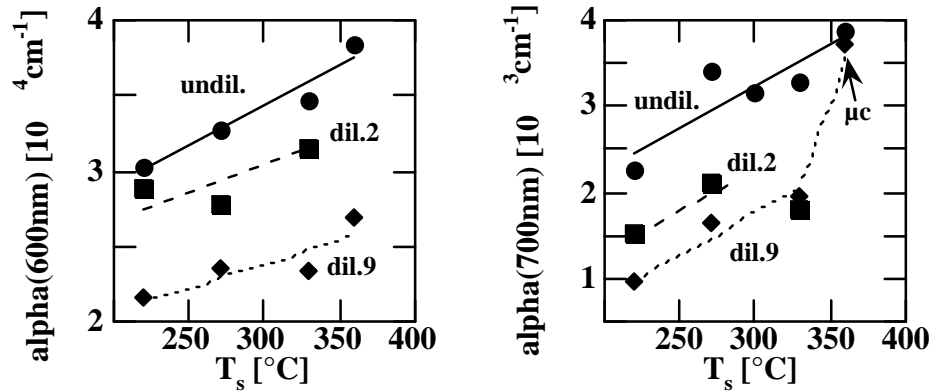


Figure 2a,b: Absorption coefficient at 600nm (a) and 700nm (b) for intrinsic films deposited at different substrate temperatures and hydrogen dilution ratios. The material obtained at $T_s = 360^\circ\text{C}$ and a dilution ratio of 9 is partially microcrystalline (cf. Fig.1, right).

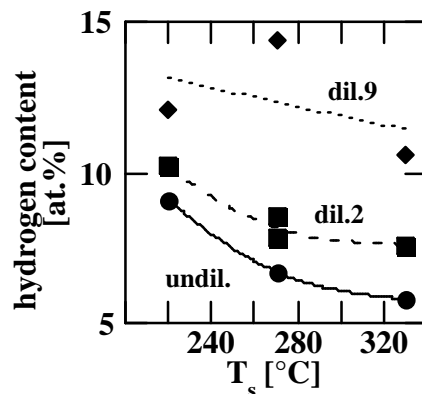


Figure 3: Hydrogen content, as determined from the 630cm^{-1} IR absorption peak, of intrinsic films deposited at three substrate temperatures and three hydrogen dilution ratios.

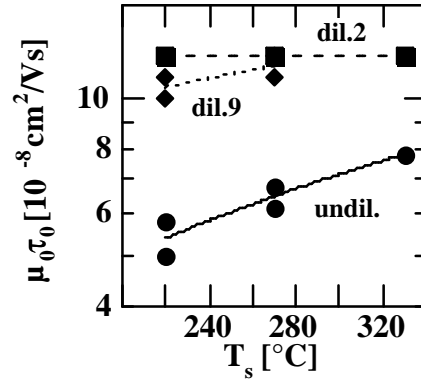


Figure 4: $\mu_0\tau_0$ values in the degraded state for three substrate temperatures and dilution rates. (The sample at $T_s=330^{\circ}\text{C}$ and a dilution rate of 9 is partially microcrystalline and does not appear in the figure.)

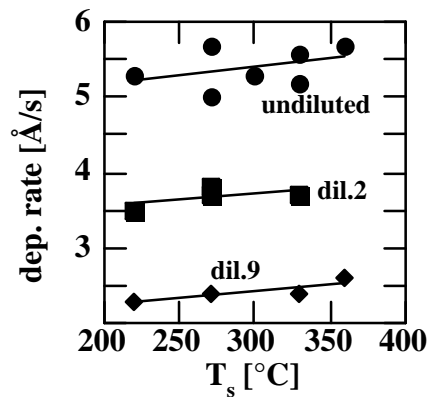


Figure 5: Deposition rates for three dilution ratios in function of the substrate temperature T_s . Input power was $45 \text{ mW}/\text{cm}^2$ for all samples.

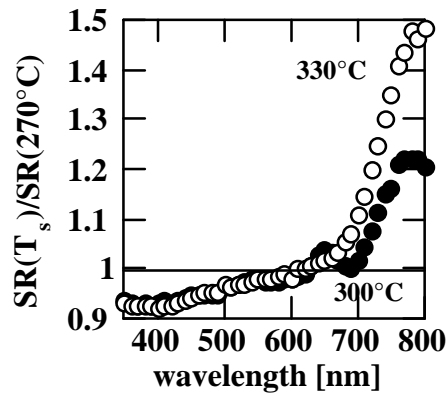


Figure 6: Spectral response curves (at 0V bias) for 300nm thick p-i-n cells with i-layers deposited at 300 and 330°C from undiluted silane normalized to the $\text{SR}(0\text{V})$ of a cell deposited at 270°C . In order to exclude experimental variation due to the reflectivity of the back contact, all 3 samples were contacted in the same run with silver contacts.

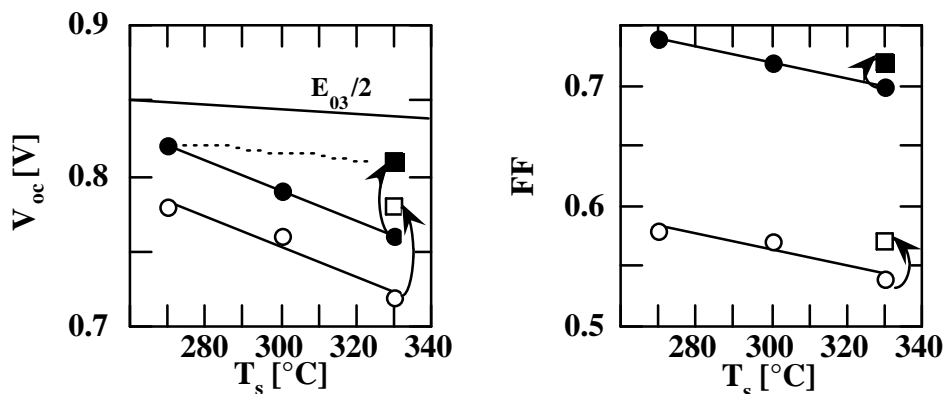


Figure 7a,b: V_{oc} and $E_{03}/2(T_s)$ (left) and FF (right) as functions of the substrate temperature T_s during i-layer deposition in the initial (filled symbols) and degraded (open symbols) state. i-layer thickness is 300nm. The reduction of V_{oc} and FF can be counteracted by an appropriate p/i interface layer (squares).

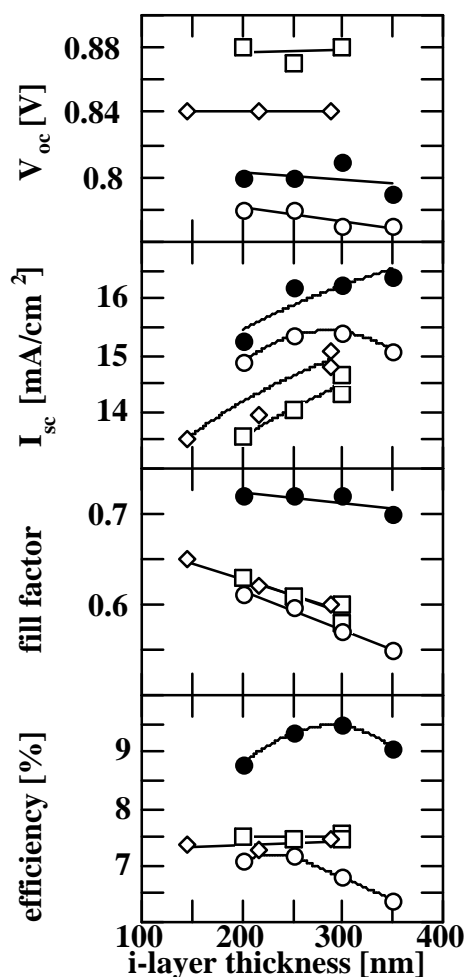


Figure 8: Performance data of optimized high- T_s p/iL-i-n cells in the initial (●) and degraded (○) state, "standard" ($T_s=270^\circ\text{C}$, ◇), and low-temperature H_2 -diluted ($T_s=220^\circ\text{C}$, □) p-i-n cells [9] (all open symbols are for degraded values).

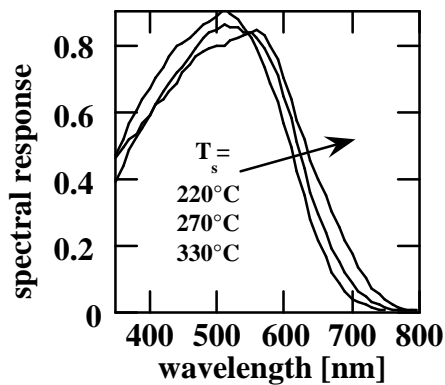


Figure 9: Measured spectral response curves for micromorph top cells deposited at 220°C (with H₂-dilution), 270°C and 330°C ($d_t=300\text{nm}$) setpoint temperature.

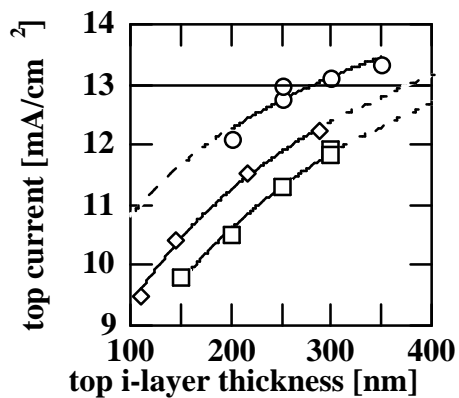


Figure 10: Current densities determined from spectral response measurements in function of the cell thickness for different types of top cells for micromorph tandem cells. High-T_s p/iL-i-n top cells (○) as described in this work, "standard" (◇) and low-temperature H₂-diluted (□) p-i-n top cells (initial values). The target value is 13mA/cm².