

Recent progress in micromorph solar cells

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Abstract

Recently, we have demonstrated that intrinsic hydrogenated microcrystalline silicon, as deposited by the very high frequency glow-discharge technique, can be used as the active layers of p-i-n solar cells. Our microcrystalline silicon represents a new form of thin film crystalline silicon that can be deposited (in contrast to any other approach found in literature) at substrate temperatures as low as 200°C. The combination of amorphous and microcrystalline material leads to a 'real' silicon-based tandem structure, which we label 'micromorph' cell. Meanwhile, stabilised efficiencies of 10.7% have been confirmed. In this paper, we present an improved micromorph tandem cell with 12% stabilised efficiency measured under outdoor conditions. Dark conductivity and combined SIMS measurements performed on intrinsic microcrystalline silicon layers reveal a post-oxidation of the film surface. However, a perfect chemical stability of entire microcrystalline cells as well as micromorph cells is presented. Variations of the p/i interface treatment show that an increase of the open circuit voltages from 450 mV up to 568 mV are achievable for microcrystalline cells, but such devices have reduced fill factors.

Keywords: Very high frequency glow-discharge; Thin film crystalline silicon; Solar cells; Micromorph; Hydrogenated microcrystalline silicon

1. Introduction

The micromorph tandem cell concept has been introduced by our group [1] in 1994. It represents a new promising thin film solar cell using thereby the same deposition technology as applied for amorphous silicon based devices. The 'micromorph' cells consist of hydrogenated microcrystalline silicon ($\mu\text{c-Si:H}$) as low band gap and of amorphous silicon (a-Si:H) as high band gap semiconductor.

Microcrystalline silicon can have excellent photovoltaic properties when grown with the very high

frequency glow-discharge (VHF-GD) technique. The properties of microcrystalline silicon indicate that it can be considered as a form of thin film crystalline silicon. In contrast to other approaches, our microcrystalline silicon can be deposited for the first time at temperatures as low as 200°C. Fig. 1 shows the absorption spectra of a $\mu\text{c-Si:H}$ film measured by the photothermal deflection spectroscopy (PDS) method [2] and by the constant photocurrent measurement (CPM) [3] in comparison with amorphous and monocrystalline silicon [4]. Our material shows a smaller defect-connected absorption and an absorption behaviour similar to that of monocrystalline silicon, however, increased by a factor ~ 4 . Very recent modelling studies indicate that the increase of

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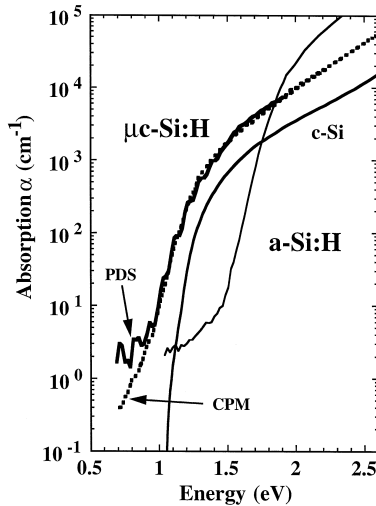


Fig. 1. Absorption spectra of a VHF grown μc -Si:H film characterised by PDS² and by CPM³. The film is deposited on Corning glass. For comparison, the absorption coefficients of amorphous and crystalline silicon [4] are added.

absorption with respect to crystalline silicon is mainly due to light-scattering at internal structures in the film [5]. More insight to this subject will be presented at this conference [6]. The apparent high absorption of μc -Si:H is favourable for its application in thin film solar cells.

A further important condition for photovoltaic active microcrystalline silicon is its 'midgap' character. This can be achieved either by delicate compensation technique using boron [1,2,7] or, by our recently reported silane gas purifier technique [7–10]. The gas purifier reduces oxygen contaminations of the feed gas and thereby also the oxygen content in the deposited films for both amorphous as well as microcrystalline silicon. Microcrystalline silicon with reduced oxygen content, less than 5×10^{18} at./cm³, shows 'midgap' character (Fermi level in the middle of energy gap). The reduction of oxygen (that acts as n-type dopant) is the important condition to obtain intrinsic material. The electronic properties of purified μc -Si:H suggests, at least for VHF grown material, that the influence of internal structure to the midgap character is small. However, especially for intrinsic films (depending on the preparation conditions) the lateral conductivity is sensitive to surface oxidation. This effect is shown here and in another contribution of this conference [11].

The incorporation of such purified i-layers in μc -Si:H cells leads to an efficiency of 7.7% [7]. As predicted from the absorption behaviour, μc -Si:H cells show, indeed, an increased infrared spectral response and thus larger short circuit current densities (J_{sc}) as compared to a-Si:H cells. Different light-soaking experiments, even under intense illumination (10 suns), have shown that the stability of μc -Si:H solar cells is not affected [1,2,7,8]. Based on these properties of μc -Si:H new ways for the thin film solar cell manufacturing are now open, namely realised in the micromorph solar cells. Besides the glass/p-i-n-p-i-n structure, we have recently shown that inverted aluminium/n-i-p-n-i-p micromorph cells [12] are also feasible.

The micromorph concept based on the well-established a-Si:H technology combines both the potential for high efficiencies and the low fabrication costs (low temperatures, low-cost substrates). Different approaches have been demonstrated for thin film crystalline silicon solar cells on low-cost substrates [13–15]. To our knowledge our VHF-GD is, among these approaches, the only technique which allows deposition of thin film crystalline silicon cells at temperatures as low as 200°C. Hence, a large variety of different low-cost substrates (glass, aluminium, plastics, etc.) can be used. A further advantage of the micromorph cells lies in the material aspect: there are no expensive, rare, and toxic materials involved in the production of the cells.

However, still an effort in obtaining higher deposition rates for μc -Si:H is required. Preliminary studies in this field are encouraging [16,17], but not yet completed; a further optimisation with respect to efficiency of micromorph cells has to be accomplished as well.

In this paper, an overview of recently obtained results on single μc -Si:H and micromorph tandem solar cells is given.

2. Experimental

All films and cells, amorphous as well as microcrystalline ones, were deposited in a capacitively-coupled parallel plate single-chamber reactor at plasma excitation frequencies of 70 and 110 MHz. Detailed description of the fabrication of amorphous

silicon cells for the application in the micromorph tandems are given elsewhere [18,19], whereas details for the whole $\mu\text{c-Si:H}$ p-i-n cell fabrication using the purifier method can be found in earlier reports [7,8]. Further information of undoped $\mu\text{c-Si:H}$ growth can be found in Ref. [20].

Films were grown on sodium-free glass substrates. The micromorph tandem and the entirely $\mu\text{c-Si:H}$ p-i-n single cell were deposited on SnO_2 -coated glass substrates (Asahi type U). The TCO (transparent conductive oxide)/Ag back contact was realised either by ITO (indium-tin-oxide) or ZnO [21,22]. To study the open circuit voltage (V_{oc}) dependence in function of the i-layer thickness of $\mu\text{c-Si:H}$ cells a stepwise opening of a shutter during the deposition in front of the substrate was performed.

Light-soaking experiments on micromorph tandem cells were performed under spectral conditions close to AM1.5 (air mass) at 50°C over 1000 h. I - V (current-voltage) measurements using a two-source solar simulator (Wacom WXS-140S-10) and outdoor conditions were measured. The outdoor measurements were executed on a clear cloudless day (9th and 21st of July 1997) at noon in Neuchâtel (northern latitude of 47°). The temperature of the cells was

controlled by a Pt100 sensor glued on the backside of the cells. The micromorph tandem cells were simultaneously measured with respect to a calibrated reference detector (error of $\pm 5\%$). The sun light intensity varied in the range between 93 and 95 mW/cm^2 during the outdoor experiments.

To study chemical stability of $\mu\text{c-Si:H}$ material with respect to long-term exposure, in ambient air, films and cells were investigated either by coplanar dark conductivity (σ_{dark}) or illuminated I - V properties. The σ_{dark} measurements were taken at 25°C in a nitrogen atmosphere after an annealing step at 180°C . The measured σ_{dark} -values are within an experimental error of $\pm 20\%$. The reproducibility of the indoor efficiency measurements (to observe relative changes during time, see Fig. 2) is within an error of $\pm 0.1\%$.

3. Results

3.1. Chemical stability

Obviously a native oxidation of the $\mu\text{c-Si:H}$ surface [23] starts as soon as the films are exposed to ambient air, as observed for crystalline and amorphous silicon as well. Furthermore, variations of atmospheric impurity profiles (O, N, C) near the surface can be attributed to different porosities of the films, as secondary ion mass spectroscopy (SIMS) measurements [7,9,11] indicate. Depending on the sample preparation one observes an increase of the σ_{dark} of the films after air exposure [11]. In other words, does that effect bear the risk of complete deterioration of layers or even $\mu\text{c-Si:H}$ cells? In the following, we tried to give an answer to this question.

To investigate the phenomena of post-oxidation in detail intrinsic films and cells were fabricated with identical deposition conditions of the purified i-layer. Fig. 2 compares the effect of air exposure on the dark conductivity of a film ($2.3 \mu\text{m}$ on glass) and the AM1.5 efficiency of the corresponding p-i-n cell. While for the film an increase of σ_{dark} over three orders of magnitude is observable, the $\mu\text{c-Si:H}$ solar cell is not affected by continuous air exposure. In case of Fig. 2, the initial value of the dark activation energy of 524 meV decreased after 70

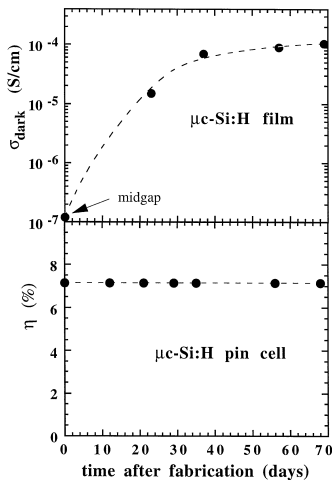


Fig. 2. Comparison of an intrinsic $\mu\text{c-Si:H}$ film and the corresponding p-i-n solar cell in function of air exposure after deposition. The film was characterised by the dark conductivity measurement and the cell by the I - V characteristics under AM1.5. The dashed lines are drawn to guide the eye.

Table 1

Stabilised micromorph tandem cells (1000 h light-soaked) measured at the ISE-FhG Freiburg (Germany) and under outdoor illumination of 93–95 mW/cm² (clear cloudless sky conditions at noon in Neuchâtel at the 9th and 21st of July 1997). The given J_{sc} -values are normalised to 100 mW/cm² for comparison

	Earlier tandem (H2-diluted a-Si:H top)		Recent tandem (undiluted a-Si:H top, not confirmed yet)
	ISE-FhG Freiburg	Outdoor at 25°C	Outdoor at 25°C
J_{sc} [mA/cm ²]	11.9	12.6	13.5
V_{oc} [V]	1.34	1.343	1.284
FF	66.7	66.9	69.2
η [%]	10.7 ± 0.7	11.3 ± 0.6	12.0 ± 0.6

days to 170 meV due to native oxidation. In contrast, the solar cell parameters of entire μc -Si:H p-i-n cells are not affected by air exposure. In the case of micromorph cells, no chemical degradation has been detected even without a special encapsulation of the cells after 18-month air exposure (ISE-FhG confirmed cells in Table 1).

3.2. V_{oc} of μc -Si:H cells: bulk or interface limited?

The most important task for further progress in the micromorph concept is an increase of the presently reduced open circuit voltage of μc -Si:H cells. Hence, further research must be addressed to the following questions: can we obtain higher V_{oc} -values with the μc -Si:H material at all? Is the V_{oc} limiting recombination channel due to bulk or interface properties?

If the presently low $V_{oc} = 450$ mV is affected to bulk recombination, a substantial variation of the i-layer thickness in the cell should indicate the an-

swer. Therefore, two cells with i-layer thicknesses of a ratio of 1/4 were deposited in one run with the help of a shutter in the reactor. Fig. 3 shows that both cells have clearly the same V_{oc} , i.e., the thicker cell does not suffer under a V_{oc} reduction due to increased internal recombination losses as compared with the thinner cell.

3.3. Recently obtained results in open circuit voltage

To achieve larger V_{oc} -values special p/i interface treatments have been carried out. Results of these experiments are summarised in Table 1. Some of these cells reveal that, indeed, V_{oc} as large as 568 mV can be obtained, however, it seems that V_{oc} is related to the fill factor (FF).

3.4. Micromorph tandem cells

Different amorphous silicon top cells were combined with μc -Si:H bottom cells with open circuit voltages of 440 to 450 mV. The complete micromorph tandem cells were light-soaked as described in Section 2. For an older set of stabilised tandems, an efficiency of 10.7% has been confirmed by ISE-FhG (Freiburg, Germany) [24,25]. This older set of tandem cells was provided with strongly H-diluted amorphous top cells (0.21 μm thickness) in order to increase the stability and the V_{oc} of the top cell [18,19]. The spectral response analysis shows, however, that the short circuit current of the whole tandem cell could be higher due to the current potential of the μc -Si:H bottom cell.

Therefore, in a new set of micromorph tandem cells undiluted top cells (0.32 μm thickness) with a

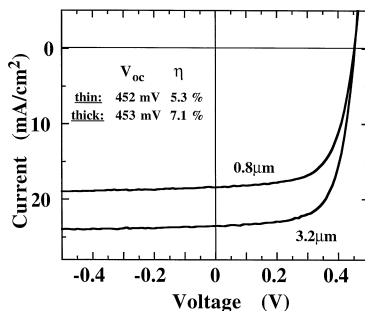


Fig. 3. I - V characteristics of a thin and thick μc -Si:H p-i-n solar cell under AM1.5 conditions. Both cells were deposited in the same run by using a shutter in the reactor. Note that the V_{oc} is not influenced by the i-layer thickness.

Table 2

Different results of $\mu\text{c-Si:H}$ p-i-n solar cells. The error of the measurements is due to variations from the standard AM1.5 spectrum (assumed $\pm 5\%$), whereas the value of J_{sc} , FF and V_{oc} have been measured with an accuracy of less than $\pm 1\%$

η [%]	7.7	7.5	7.7	4.4	3.2
J_{sc} [mA/cm^2]	25.3	24.0	23.5	18.2	18.4
FF [%]	67.9	68.1	68.4	48.0	30.5
V_{oc} [mV]	448	460	478	499	568

lower energy gap (E_{03} of about 1.72 eV) were applied. A further improvement of the junction between top and bottom cells was also applied to this recent generation of micromorph cells. These cells were light-soaked over 1000 h as the former ones.

The value of the short circuit current density (J_{sc}) –especially of stacked cells– depends critically on the used artificial sun light source (AM1.5 conditions can only approximately be obtained in the laboratory); a good alternative are outdoor measurements. Table 2 compares the results of the earlier and the newer generation of tandem cells. The earlier cells show a good agreement with respect to the FF and the V_{oc} between the ISE-FhG and the outdoor measurements. However, under the real sun we observe higher J_{sc} -values and, thus, a higher efficiency of 11.3% (normalised to $100 \text{ mW}/\text{cm}^2$).

As an example in Fig. 4, a scanning electron microscope (SEM) picture of a broken micromorph cell is represented. The different layers can be clearly distinguished and are indicated in the photo.

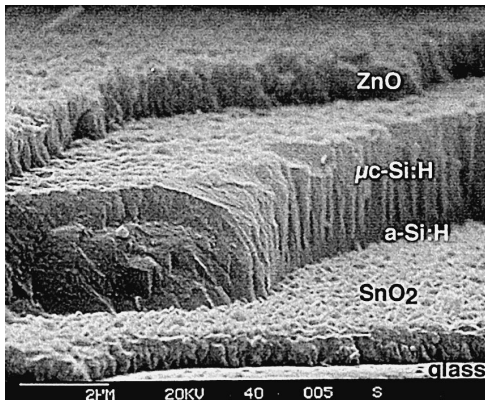


Fig. 4. SEM cross-section of a micromorph tandem cell deposited on SnO_2 coated glass.

4. Discussion

The results have shown that post-oxidation of intrinsic $\mu\text{c-Si:H}$ films leads to an increase of the dark conductivity when measured in a coplanar configuration. In contrast to isolated films entirely $\mu\text{c-Si:H}$ p-i-n solar cells show no chemical degradation effect when exposed to air. The good chemical stability of the cells is attributed to a passivation and protection of the intrinsic absorber layer by the n-type back contact with respect to oxygen. Therefore, we are convinced that $\mu\text{c-Si:H}$ based cells equipped with a state-of-the-art encapsulation have the potential for long lifetimes and stability.

The thickness variation of the intrinsic $\mu\text{c-Si:H}$ layer in the p-i-n device indicates that the present open circuit voltage is not related to bulk recombination but to the p-i interface. Recently obtained cells by the variation of the p-i interface support this. Such cells achieve larger V_{oc} 's values of 568 mV, but so far with reduced fill factors. These results suggest that bulk recombination in the i-layer plays a minor role to the present low V_{oc} of $\mu\text{c-Si:H}$ cells. We think that further optimisation of the p/i interface will lead to larger V_{oc} with good fill factors. Thus, there is hope to increase the efficiencies of the micromorph tandem cells by a larger open circuit voltage of the $\mu\text{c-Si:H}$ bottom cell.

The comparison of the new generation of micromorph tandems with the earlier ones (Table 1) shows, indeed, an improvement of the efficiency to 12% when based on outdoor conditions. The decrease of the V_{oc} and the increase of the J_{sc} with respect to the earlier set of tandem cells is related to the smaller band gap of the amorphous top cells involved. The higher FF, as compared to former undiluted a-Si:H top cells, we attribute to the improved junction between the amorphous top and the $\mu\text{c-Si:H}$ bottom cell. But even assuming equal stabilised fill factors of both generation of micromorph cells, the one with undiluted a-Si:H top cells leads to higher stabilised efficiencies of the entire micromorph cell. This effect is surprising because hydrogen diluted a-Si:H single cells tend to be more stable than undiluted ones under light-soaking. We explain the phenomenon by the fact that the smaller gap a-Si:H material contributes to a better balance of the current density between top and bottom cell. By that the micro-

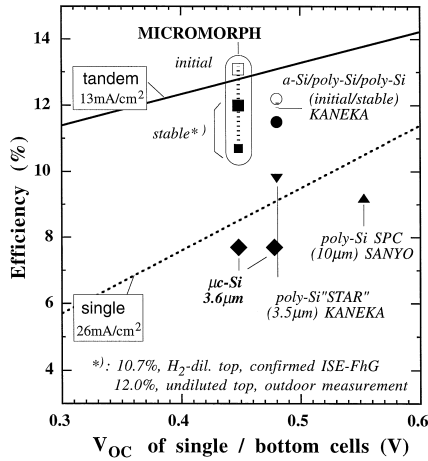


Fig. 5. Projected efficiencies of single-junction $\mu\text{c-Si:H}$ (dashed lines) and micromorph tandem cells (full lines) as a function of the V_{oc} of the $\mu\text{c-Si:H}$ bottom cells, assuming a total current of 26 mA/cm^2 , a fill factor of 73% and a V_{oc} of 900 mV for the a-Si:H cells. Symbols represent experimentally obtained results.

morph cell benefits from the larger current potential of the $\mu\text{c-Si:H}$ bottom cell.

The work on such kind of new devices is not without problems: we have shown that intrinsic $\mu\text{c-Si:H}$ layers on glass substrates may be affected by surface post-oxidation effects, which makes systematic studies of the transport very difficult. Entire $\mu\text{c-Si:H}$ single cells as well as micromorph tandem cells, however, are chemically stable.

The thin film micromorph cells do not only bear the possibility for cost reduction but also the potential for larger efficiencies. In this paper, we present a cell with a stabilised efficiency of 12% measured under outdoor conditions. The future potential for obtaining even higher efficiencies of micromorph cells is presented in Fig. 5. It can be concluded from this diagram that a direct improvement for the efficiency of micromorph tandem cells towards 13 to 14% can be obtained by an increase of the open circuit voltage of the $\mu\text{c-Si:H}$ bottom cell.

The present state of our research shows that it is principally possible to increase the V_{oc} from 450 V up to 568 mV, however, the other solar cell parameters have to be improved in parallel in order to get a net gain in the efficiency.

5. Conclusions

Microcrystalline silicon deposited by the very high frequency glow-discharge (VHF-GD) has been demonstrated to be an active semiconductor for solar cells. Compared to alternative thin film crystalline silicon solar cell concepts, the most striking advantage of VHF-GD consists in the low deposition temperatures of 200°C. The use of such low temperatures allows the use of a large variety of low-cost substrates. By that the herein presented micromorph solar cell concept has, hence, the potential for further cost reduction of photovoltaic devices.

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