HIGHLY EFFICIENT SILICON THIN FILM SOLAR CELLS WITH ADVANCED LIGHT TRAPPING

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1. ABSTRACT

This paper addresses the development of silicon thin film solar cells by plasma-enhanced chemical vapour deposition (PECVD) at 13.56 MHz excitation frequency. For an efficient light trapping we focus on textured ZnO:Al films prepared by sputtering and post deposition wet chemical etching. These films were optimised with respect to conductivity, transparency and film structure, the latter one controlling the surface texture obtained after etching. A-Si:H/µc-Si:H tandem cells yielded stable efficiencies up to 11.2 % for a cell area of 1 cm². Initial module efficiencies of 10.8 % and 10.1 % were achieved for aperture areas of 64 cm² and 676 cm², respectively.

2. 1. Introduction and Approach

Silicon thin film modules based on a-Si:H and µc-Si:H tandem cells are one of the most promising future thin film PV technologies. Necessary prerequisites for a cost-effective mass production of solar cells incorporating µc-Si:H films are the demonstration of high deposition rates and scalability to large areas. Moreover, effective light trapping is essential to obtain high cell efficiencies at small absorber layer thickness. The a-Si:H/µc-Si:H tandem cell concept was pioneered at the University of Neuchâtel [1] using the VH-PECVD technique. Since then several research groups have demonstrated high efficiencies by applying different deposition techniques, light trapping concepts and substrates [1-5]. First commercial solar modules were demonstrated by Kaneka Co. [5]. However, these modules are only available on the Japanese market so far.

This contribution addresses scientific and technological efforts to develop highly efficient silicon thin film solar modules. The first part describes the development of textured zinc oxide films prepared by sputtering and post deposition etching as TCO material which provides excellent light trapping properties. The second part treats the development of µc-Si:H solar cells at high deposition rates using 13.56 MHz plasma excitation frequency. Both techniques were developed on laboratory scale and are now implemented in solar modules with sizes of up to 30x30 cm². We will present the current status of our tandem cell and module technology and discuss efforts to further enhance the module efficiency.

3. 2. Experimental Details

All cells and modules presented in this study were prepared in the superstrate configuration starting from bare glass substrates. The substrate size for all films, solar cells and modules was either 10x10 cm² or 30x30 cm².

Textured ZnO coated glass substrates prepared by magnetron sputtering and post deposition chemical etching were applied as front TCO. These films are smooth in the as-deposited state. A textured surface is realized by a wet chemical etching step in diluted hydrochloric acid, which is either done manually in a chemical bath or by using an etching apparatus, especially designed for this purpose. The ZnO films were either prepared in a small area sputtering system in static mode or in a recently installed in-line system in dynamic mode. This system is capable of RF-, DC- and MF- (mid frequency) sputtering and is described in more detail in [6].

The silicon layers of a-Si:H, µc-Si:H and a-Si:H/µc-Si:H solar cells were prepared either in a multi-chamber PECVD system for 10x10 cm² substrate size or in a large area (30x30 cm²) PECVD reactor [7]. All silicon layers were deposited using 13.56 MHz plasma excitation frequency at substrate temperatures below 250 °C. The back contact of all cells and modules is a ZnO/metal double layer, also prepared by sputtering. All patterning steps for the module fabrication were performed using high speed laser scribing. The solar cells and modules with areas up to 10x10 cm² were characterised by current-voltage (J-V) measurements under standard test condition (AM1.5, 100 mW/cm², 25 °C) using a class A double light source solar simulator (Wacom-WXS-140S-Super). For light soaking tests, cells and modules were exposed for several 100 hours to AM1.5 illumination (100 mW/cm²) at open-circuit condition and a constant temperature of 50 °C.

4. 3. TCO and light trapping

For silicon thin film solar cells in the p-i-n (superstrate) structure the transparent conductive oxide (TCO) films are required as front contact material and have to combine low series resistance, high transparency and an adequate surface texture. Fluorine doped tin oxide films (SnO₂:F), which fulfill these requirements to a large extent, have been developed by Asahi Glass (Asahi Type U) [8]. Doped ZnO has been established as a successful alternative on laboratory scale. Examples are boron-doped ZnO prepared by low pressure chemical vapour deposition (LPCVD) [9] or intrinsic and aluminium-doped films deposited by expanding thermal plasma CVD [10]. The promising approach followed at the IPV is the use of magnetron sputtering together with a post-deposition chemical etching step. The sputtering process leads to highly conductive and transparent but smooth ZnO films. A simple chemical etching step in diluted acid yields a textured surface which can be adjusted to give optimal light scattering over a wide wavelength range [3,11,12].

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3.1 ZnO material properties and surface texture

In the following, we focus on results obtained for ZnO:Al films which have been prepared by RF sputtering from ceramic targets. In this case, the deposition parameters working pressure and substrate temperature control the structural film properties which lead to distinctly different surface morphologies after the etching step. We applied atomic force microscopy (AFM) as one technique to describe different surface morphologies in a quantitative way. As an example, Fig. 1 shows the root mean square roughness and typical opening angles of a series of texture-etched ZnO:Al films prepared at different working pressures. The opening angles are characteristic for the different surface morphologies observed, while the surface roughness shows some scattering between 30 and 80 nm in this series. Opening angles of 135° are typical for structures with a crater-like appearance (see also the SEM micrographs in Fig. 2) usually obtained at low pressures. At higher pressures, pyramid-like surfaces develop which show opening angles of ~70° down to 47°.

The analysis of the surface morphology by AFM and the interpretation of the results in terms of a “modified Thornton Model” are described in detail in [13].

Note that almost all changes of the applied deposition parameters or deposition technique result in different structural film properties which are often not reflected in changes of the optical and electrical film properties, but appear as distinctly different surface morphologies after the etching step. In further experiments we optimised the ZnO:Al films with respect to conductivity and also long wavelength transparency by optimising the Al-concentration [14] and transferred the results to our large area in-line sputtering system for 30x30 cm² substrate size.

After prolonged etching the crater formation proceeds until a homogenously textured surface is obtained (see Fig. 2b). The root mean square roughness of the latter texture-etched ZnO:Al film is 150 nm, as determined by AFM.

The sheet resistance $R_{\text{sheet}}$ of the film shown in Fig. 2b was only 7.2 Ω, which demonstrates the good electrical properties even after the etching step. The optical properties of the latter film were measured with a dual beam spectrometer attaching the textured film to another thin glass substrate with CH₂I₂ as index-matching fluid. This method avoids systematic measurement errors due to light scattering of the rough TCO (see e.g. [15] for a description of the method). The corresponding transmission and reflection curves, shown in Fig. 3, demonstrate the high optical transparency over a wide wavelength range. These texture etched ZnO films show high optical haze for a wide wavelength range, indicating good light scattering properties also for µc-Si:H based solar cells, which will be demonstrated in the next section.

3.2 Solar cell results

The textured ZnO films shown in Figs. 2a) and 2b) together with a smooth (as deposited) reference film were applied as substrates for µc-Si:H p-i-n solar cells. The i-layer thickness was 1.1 µm. The external quantum efficiency (e.q.e.) curves (see Fig. 4) illustrate how the spectral response increases over the whole wavelength range by introducing an optimised surface texture.

![Fig. 1 Root mean square roughness (open circles) and opening angles (closed squares) of ZnO:Al films prepared at different sputter pressures (see [13] for more details).](image-url)

![Fig. 2 SEM micrograph of an etched ZnO:Al film a) shortly dipped in diluted hydrochloric acid and b) after prolonged etching.](image-url)
In the blue and green part of the spectrum the increased e.q.e. is due to a reduction of solar cell reflection, which is shown in Fig. 5. The textured ZnO surface provides an effective index grading layer between the ZnO and the silicon films. The increase in the red and infrared part of the spectrum can partly be attributed to this AR-effect, but the main gain in current must be attributed to light trapping. This becomes also obvious from Fig. 4 by looking at the spectral absorbance of a µc-Si:H film with 1 µm thickness, which was calculated from the absorption coefficient, as determined by photothermal deflection measurements [16]. By comparing the e.q.e.- and µc-Si:H absorbance values at 900 nm one can estimate that the effective light path through the i-layer must be more than 10 µm for the optimised substrate (solid line). ZnO coated glass substrates similar to those presented in this section were applied for the development of µc-Si:H single junction and a-Si:H/µc-Si:H stacked solar cells which will be described later.

3.3 Up-scaling issues

Further progress towards an application of textured ZnO for industrial a-Si:H solar module production requires large area high quality uniform ZnO films to be manufactured at high deposition rates and reasonable costs. This challenge of up-scaling small area ZnO films to substrate areas of the order of one square-meter was taken up in an R&D project [17], which focuses on a high rate reactive mid-frequency (mf) sputtering process for ZnO:Al [18]. Using the mf-technique, ZnO films can be manufactured at high deposition rates with good homogeneity and with excellent optical and electrical properties on a substrate area of 0.6 m² [17].

To further support this project and to show the viability of the ZnO sputtering technique for a-Si:H/µc-Si:H tandem cells and modules, sputtering processes developed on small areas in static mode are now being up-scaled using dynamic sputtering techniques on 30x30 cm² substrate area in our institute [6].

4. MICROCRYSTALLINE SILICON SOLAR CELLS

First efficient µc-Si:H p-i-n solar cells were developed at the University of Neuchâtel using the very high frequency (VHF) PECVD technique [1].

The VHF-technique is still widely used as a standard technique on laboratory level to achieve excellent µc-Si:H material quality and solar cell properties at high deposition rates [1-3]. However, these high frequencies (typically above 50 MHz) make an up-scaling to production scale (module sizes ~ 1 m²) more difficult. For this reason we favour conventional RF (13.56 MHz) excitation frequency which is also compatible with existing deposition equipment. High rate deposition of µc-Si:H films in a high pressure regime at 13.56 MHz has been reported by Guo et al. [19]. Early results on µc-Si:H solar cells in this regime were achieved in our group revealing the key role of a “high pressure deposition regime” to achieve high quality solar cells at high growth rates [20,21].

In the first step, the development of µc-Si:H solar cells was performed in a small area PECVD reactor. Later on, the cell process was up-scaled to 30x30 cm² substrate size. The influence of the i-layer deposition parameters was investigated by the characterisation of p-i-n cells directly.

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**Fig. 3** Transmission T and Reflection R of the texture-etched ZnO film shown in Fig. 2b). T and R were measured using CH₂I₂ as index-matching fluid.

**Fig. 4** External quantum efficiency of µc-Si:H solar cells co-deposited on smooth and texture-etched ZnO coated glass substrates. Additionally included are the external quantum efficiency of a p-i-n cell with an i-layer thickness of 2.7 µm and the absorbance of a µc-Si:H film with a thickness of 1 µm (both as dashed-dotted line).

**Fig. 5** Reflection of the µc-Si:H solar cells shown in Fig. 4.
4.1 Role of deposition parameters

Purpose of this work was to investigate and understand the influence of different deposition parameters applied for µc-Si:H i-layer deposition on device performance. In general, a transition between a-Si:H and µc-Si:H growth can be achieved by almost any deposition parameter. The most convenient way is to reduce the silane to hydrogen flow ratio [SiH₄]/[H₂]. For each variation of deposition parameters the highest µc-Si:H solar cell efficiencies were achieved in the µc-Si:H growth regime close to the transition to amorphous Si growth [3,21]. In ref. [22] this is illustrated by a series of solar cells where the transition between µc-Si:H and a-Si:H growth is either achieved by increasing [SiH₄]/[H₂] or by increasing the deposition pressure $p_{dep}$. In both cases the increase in efficiency observed in the µc-Si:H growth regime when approaching the transition to a-Si:H growth is due to an increase of $V_{OC}$ and FF, while the short-circuit current density $J_{SC}$ stays almost constant. Passing the transition to a-Si:H growth causes a sudden drop in $J_{SC}$.

To separate the role of deposition pressure from the shift between the amorphous and microcrystalline growth regime, we prepared solar cells at different $p_{dep}$ and optimised the [SiH₄]/[H₂] ratio to obtain optimal cell performance for each $p_{dep}$. Additionally, we adapted the plasma power to maintain similar growth rates ($±1 \text{ Å/s}$) over the whole $p_{dep}$ region. Fill factor FF and open-circuit voltage $V_{OC}$ served as a measure for the quality of the µc-Si:H i-layer material. Only the µc-Si:H solar cells exhibiting the highest efficiency for a given $p_{dep}$ are used for the following discussion. The results are plotted in Fig. 6. For both FF and $V_{OC}$ there is an increase with rising deposition pressure from ~50 % FF and $V_{OC}$< 400 mV at 1.5 Torr to ~70 % and 520 mV at 10 Torr respectively. A further increase of the deposition pressure did not lead to further improved cell performance in this series. Only at deposition pressures above 10 Torr we achieved both high efficiencies of above 8 % and high growth rates of 5 - 6 Å/s. At $V_{OC}$-values above 500 mV these cells exhibit FFs of more than 70 % indicating good interface quality and electrical transport properties of the corresponding µc-Si:H i-layer material.

In further experiments we investigated the influence of the electrode distance and the effect of using pulsed plasma instead of continuous wave (CW) plasma excitation in the small area PECVD reactor. The studies are described in [22,23] and here we just summarise the key results. Highly efficient solar cells were achieved in cw (continuous wave) mode at electrode distances of 5 and 20 mm. For small electrode distances (5 and 10 mm) high solar cell performance is maintained for deposition rates up to 9 Å/s, while for 20 mm cell performances worsen significantly for rates above 3 Å/s. Pulsed plasma deposition yielded good results for deposition rates up to ~5 Å/s, for higher rates a strong decrease of efficiency was observed. Although no advantage of a pulsed plasma for µc-Si:H growth was found in our work, pulsed plasma excitation can still be a method to reduce powder formation.

4.2 Discussion and up-scaling to 30x30 cm²

Conventional 13.56 MHz PECVD is capable of producing device quality µc-Si:H films at high growth rates in a deposition regime of high plasma powers and deposition pressures. Comparing plasma properties and solar cell performance, it is evident that “soft” deposition parameters (i.e. low ion energy) are essential to obtain device quality µc-Si:H i-layers. Note that these “soft” conditions are also fulfilled for high efficiency µc-Si:H cells prepared by very high frequency (VHF)-deposition (e.g. [1-3]) or by Hot-Wire CVD. Using the latter technique Klein et al. recently achieved a µc-Si:H cell efficiency of 9.4 % [24]. In case of 13.56 MHz PECVD homogenous plasma properties can be achieved at very high pressures with high plasma densities. These conditions yield high growth rates (~5 Å/s), but still provide sufficiently “soft” deposition for high material quality. If these boundary conditions are fulfilled, usually the silane concentration has to be adjusted to grow the µc-Si:H i-layer in a deposition regime close to a-Si:H growth. This means that the best µc-Si:H solar cells are generally prepared in a narrow deposition regime. Subsequent up-scaling to large areas requires carefully designed PECVD reactors with respect to power feeding (and substrate grounding), homogeneity of the gas supply and pumping.

These criteria were taken into account for the design of our 30x30 cm² PECVD reactor. We succeeded in preparing µc-Si:H i-layers with good homogeneity over the inner 27x27 cm² of the 30x30 cm² substrate. Only boundary effects caused by the substrate carrier limit the area of homogeneous deposition. More details are discussed in [7,25,26].

5. HIGHLY EFFICIENT SOLAR CELLS AND MODULES

The µc-Si:H p-i-n cells described above were applied as bottom cells in a-Si:H/µc-Si:H tandem cells. We optimised the tandem cell design with respect to the stabilised cell efficiency. Top and bottom cell i-layer thickness were prepared as thin as possible to maintain high fill factors after light soaking. The influence of the current matching behaviour on the initial and stabilised cell performance is discussed in an accompanying paper [27].

In Fig. 7 we compare the light soaking behaviour of an a-Si:H/µc-Si:H tandem cell, an a-Si:H top cell and a µc-Si:H bottom cell. The a-Si:H top cell has a simple Ag back contact while the two other cells ZnO/Ag back contacts were applied. The best stabilised cell efficiencies obtained in the 30x30 cm² PECVD reactor (on small area ZnO substrates) were 8.9 % and 11.2 % for a µc-Si:H pin cell and an a-Si:H/µc-Si:H tandem cell, respectively (see...
Fig. 8 for the J-V curves). The deposition rate for the µc-
Si:H i-layers was 5 Å/s for both cells.

By the end of 2002 the 30x30 cm² process
technology at the IPV had started operation and first
a-Si:H/µc-Si:H modules could be realised on texture-
etched ZnO coated glass substrates. All patterning steps
were performed using high speed laser scribing. So far, the
best aperture area initial efficiencies were 10.1 % and
10.8 % on substrate areas of 30x30 cm² and 10x10 cm²,
respectively (see [7]). Light soaking of the small area
module has started and the efficiency of this mini-modules
stabilises near 10 % after several hundred hours (see Fig.
9). A 10x10 cm² a-Si:H/a-Si:H tandem module cut from
an industrially produced large area (0.6 m²) module was
included for comparison. The stabilised aperture
efficiency is slightly above 6.5 %, which is the specified
efficiency for this module type. The comparison
demonstrates the potential of the a-Si:H/µc-Si:H tandem
cell technology on textured ZnO coated glass substrates
for highly efficient large area thin film solar modules.
However, the transfer of the technology to a cost-effective
module production still requires strong efforts in research
and technology development.

![Fig. 7](image_url)

**Fig. 7** Efficiency of silicon thin film solar cells as
function of light exposure time.

![Fig. 8](image_url)

**Fig. 8** Illuminated J-V curve of a µc-Si:H and an
a-Si:H/µc-Si:H solar cell measured after 900 h and more
than 1000 h hours of light soaking, respectively.

![Fig. 9](image_url)

**Fig. 9** Aperture area module efficiency of Si thin film
10x10 cm² modules as a function of light exposure time.

5. 6. toward 14 % module efficiency

The long term goal of the silicon thin film approach
is to reach module efficiencies comparable to those of the
silicon wafer technology. For the further discussion we
address possible improvements of the 10x10 cm² mini
module with 10 % stable efficiency described above.

The quantum efficiency of a µc-Si:H p-i-n cell with
an i-layer thickness of 2.7 µm is shown in Fig. 4. Applied
as bottom cell in a-Si:H/µc-Si:H tandem cells Jsc-values
above 13 mA/cm² can be achieved. However, the
 electrical properties of both the thick µc-Si:H cell and the
required rather thick a-Si:H top cell deteriorate with
increasing i-layer thickness, especially for the stabilised
state in case of the a-Si:H top cell. An optimal absorption
scheme consisting of anti-reflective coatings, intermediate
reflectors, further improved front TCO films and perfect
mirrors as back reflectors can boost the efficiency by
improving Jsc at small i-layer thickness, thus maintaining
high Voc and FF. See also [28] for further discussions.

The limits of µc-Si:H p-i-n cells with regard to Voc
are still under discussion. Compared to mono- or multi
crystalline silicon cells the Voc is still rather low, typically
520–550 mV for PECVD cells. Note that Klein et al.
achieved Voc-values close to 600 mV [24] using Hot-Wire
CVD. In general, Voc can be limited by tail states [29], by
recombination losses in the bulk of the i-layer or at
interfaces. To reduce the latter recombination losses we
propose to transfer the point contact approach to silicon
thin film cells [30].

Finally it should be mentioned that every
improvement of the a-Si:H top cell e.g. by more stable
i-layer material would strongly contribute to an
improvement of the tandem cell discussed here.

7. CONCLUSIONS

ZnO:Al films prepared by magnetron sputtering and
post deposition wet chemical etching were applied as front
contact TCO-material with excellent light scattering
properties for silicon thin film solar cells and modules.
These substrates introduce an effective light trapping and
the textured surface reduces reflection losses at the
ZnO/Si-interface. Moreover, low sheet resistances
can be achieved while high optical transparency for visible and near-infrared light is maintained.

We developed μc-Si:H i-layers by plasma-enhanced chemical vapour deposition (PECVD) using 13.56 MHz excitation frequency, very high deposition pressures and high RF-powders. These conditions provide sufficiently "soft" deposition for the growth of high quality μc-Si:H material and yield high deposition rates. Subsequent up-scaling to 30x30 cm² substrate area was performed in a carefully designed PECVD reactor.

Finally, highly efficient silicon thin film solar cells and modules were realised starting from bare glass substrates. A-Si:H/µc-Si:H tandem cells yielded stable efficiencies up to 11.2 % for a cell area of 1 cm². First solar modules were prepared in our recently installed process technology showing initial module efficiencies of 10.8 % and 10.1 % for aperture areas of 64 cm² and 676 cm², respectively.

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