

## SURFACE MODIFICATION OF LPCVD ZNO-FILMS FOR SILICON THIN FILM SOLAR CELLS

F. Lükermann<sup>1</sup>, V. Mönkemöller<sup>1</sup>, H. Kurz<sup>2</sup>, M. Sacher<sup>1</sup>, F. Hamelmann<sup>2</sup>, H. Stiebig<sup>2</sup>, U. Heinzmann<sup>1</sup>

<sup>1</sup>Molecular and Surface Physics, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld, Germany,  
Phone: +49(521)106-5471, Fax: +49(521)106-6001, email: [fluekermann@physik.uni-bielefeld.de](mailto:fluekermann@physik.uni-bielefeld.de)

<sup>2</sup>Malibu GmbH & Co. KG, Böttcherstraße 7, 33609 Bielefeld, Germany,  
Phone: +49(521)9892880, Fax: +49(521)98928813, email: [fhamelmann@malibu-solar.de](mailto:fhamelmann@malibu-solar.de)

**ABSTRACT:** The influence of the surface morphology of the front contact layer on the properties of amorphous silicon based solar cells is presented. Based on a textured LPCVD substrate, which consists of pyramidal grains emerging out of the surface plane, the surface topology is modified by plasma etching. By varying the gas composition in the plasma at a fixed total flow, we were able to create surface morphologies whose features show deviations from the pyramidal shape, without significantly changing the surface roughness. For the plasma etched samples  $J_{SC}$  decreases in comparison to the as-deposited ZnO. The decrease in current is not exclusively caused by a degraded red response but also due to a lowered quantum efficiency in the whole visible spectral range. This is attributed to a degraded light incoupling at the ZnO/ a-Si interface due to the altered pyramidal shape. It could be shown experimentally that the shape of the surface morphology is important for light incoupling as well as light trapping.

**Keywords:** TCO Transparent Conducting Oxides, Light Trapping, Plasma Etching

### 1 INTRODUCTION

Transparent conductive oxides (TCO) with a nanotextured surface topology are used as front electrode in thin-film silicon solar cells. Theoretical studies by Haase et al. [1] indicate that not only the surface roughness and haze are important for good light incoupling and light scattering. The shape and especially a pyramidal shape of the surface features is of great importance, for light scattering and light incoupling.

Especially ZnO deposited by Low Pressure Chemical Vapor Deposition (LPCVD) provides useful features in this context. Along with a high conductivity and high transmittance for visible light it provides a rough surface consisting of pyramidal grains with the crystallographic c-axis in the substrate plane. This morphology leads to an efficient light incoupling and good light scattering capability. The latter effect results in an enhanced absorption path in the thin film silicon absorber and consequently in an improved spectral response for the red and near infrared light [2].

LPCVD provides some advantages compared to other established methods of depositing TCO films such as sputtering [3] and APCVD [4]. A relatively low deposition temperature under 200 °C is sufficient for high growth rates and good material quality [5]. In agreement with corresponding studies [6,7], optical and electrical properties of the TCO films can be controlled by variation of deposition parameters such as deposition time, deposition temperature and boron doping concentration.

This study is focused on the influence of the ZnO surface morphology on the optical properties and the consequences on a-Si:H solar cell parameters. In particular we tried to modify the shape of the pyramidal surface features to investigate the influence of shape on light incoupling and scattering in a-Si solar cell devices.

Therefore we applied an ion sputtering procedure with argon (Ar) and oxygen (O<sub>2</sub>) in a parallel plate RF plasma reactor on the ZnO surface. This procedure

significantly changed the surface morphology, in dependence of the used plasma conditions.

### 2 EXPERIMENTAL

#### 2.1 ZnO deposition

The ZnO layers were deposited on 3 mm thick float glass substrates in an Oerlikon LPCVD 1200 reactor suitable for substrates of 1.4 m<sup>2</sup>. In the reaction chamber diethylzinc (DEZ) and water react to ZnO at temperatures below 200 °C. The layers were doped by adding diboran (B<sub>2</sub>H<sub>6</sub>) to the gas mixture which leads to sheet resistances of less than 10 Ω<sub>□</sub>. The samples show a transmission of more than 80% in the visible spectral range. We used ZnO layers of different thickness (1700 nm and 3300 nm) which possess a surface roughness between  $\delta_{rms}=50$  nm corresponding to the thinnest layer and 80 nm to the thickest layer. This difference involves a variation of the haze factor (at a wavelength of 600 nm) between 15% and 40%.

The samples were cut into pieces of 5x5 cm<sup>2</sup> for further handling. They were then cleaned by ultrasonification in isopropanol and de-ionized water successive for 10 min each and dried by blowing the water off with nitrogen.

#### 2.2 Plasma etching of ZnO films

Plasma treatment on the ZnO films was carried out in an Oxford Plasmalab 80plus RIE. The setup consists of an evacuated chamber which is equipped with two circular electrodes with a diameter of 20 cm in a parallel plate arrangement. The lower electrode is coupled inductively via a matching network to a radio frequency generator which creates a frequency of 13.56 MHz, the upper electrode is grounded. If gas is injected into the chamber at pressures around 1 mbar and RF-power is applied to the system, a plasma is generated and a DC-voltage is built up between the electrodes [8]. This so called self-bias voltage results from the fact, that the

electrons created in the plasma are able to follow the RF-field and can reach the electrodes. The plasma ions in contrast can not follow the RF-field because of their large mass. The upper electrode is grounded, so the electrons can only accumulate at the lower electrode. The self-bias then accelerates the positive ions towards the lower electrode and leads to an ion-bombardment. If the ZnO samples are placed on the lower electrode the surface will be modified by these ions.

The experiments were carried out at a fixed pressure of 0.1 torr, and a total gas flow of 30 sccm. We used Ar as well as O<sub>2</sub> and varied the content from pure Ar over a mixture of both to pure O<sub>2</sub>. In the following the mixture will be characterized by the ratio of Ar flow [Ar] to the total flow [Ar+O<sub>2</sub>] ranging from [Ar]/[Ar+O<sub>2</sub>]=0 (pure O<sub>2</sub> plasma) to 1 (pure Ar plasma).

### 2.3 a-Si:H deposition

To study the influence of the surface modification on the properties of amorphous silicon solar cells, a-Si:H was deposited in pin configuration on the ZnO films followed by the LPCVD deposition of a boron doped ZnO back contact. The a-Si:H layers were deposited in a PECVD (Plasma Enhanced CVD) reactor suitable for the deposition of 1.4 m<sup>2</sup> substrates by placing the previously cut 5x5 cm<sup>2</sup> samples on top of a large glass substrate. The deposited sheet configuration was p: 15 nm/ i: 270 nm/ n: 20 nm.

The 5x5 cm<sup>2</sup> layer stacks were afterwards separated by laser scribing to 8 cells each of 1 cm<sup>2</sup> active area.

### 2.4 Experimental methods

The as-deposited and plasma-treated ZnO samples were analyzed with regard to their surface morphology using atomic force microscopy (AFM) with a self-built set up and scanning electron microscopy (SEM) in a Zeiss Gemini DSM 982.

To check whether the chemical surface composition is changed especially by the plasma treatment, auger electron spectroscopy (AES) was performed on selected samples. AES is well suited for this purpose because of its high surface sensitivity [9].

UV-VIS spectroscopy in a Perkin Elmer-Lambda 950 UV/VIS spectrometer was used to evaluate the optical properties of the ZnO films and a-Si solar cells.

Solar cell characteristics were measured under AM 1.5 illumination with a class A solar simulator in addition to external quantum efficiency (EQE) measurements. It has to be noted that these measurements, in contrast to the optical measurements, were carried out with a white reflector foil on the back side of the samples.

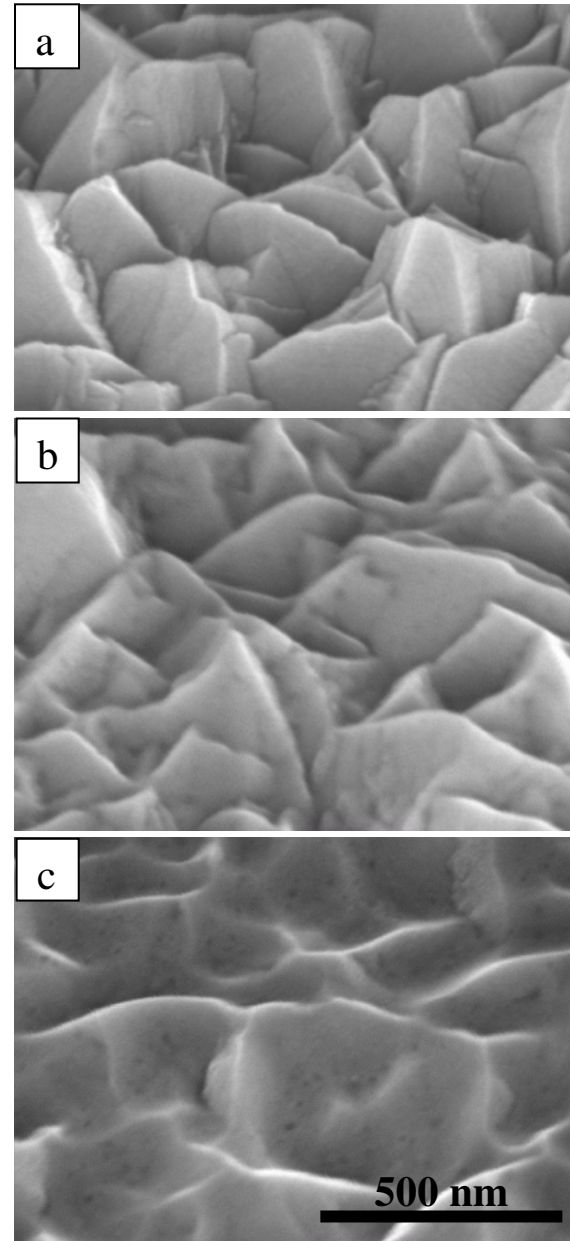
## 3 RESULTS AND DISCUSSION

Figure 1 shows SEM measurements of as-deposited 1700 nm thick ZnO as well as ZnO samples exposed to plasmas of different gas compositions. The SEM measurements are made under an angle of view of 50 degree, to get an insight into the surface morphology.

The as-deposited ZnO surface shows pyramidal features with plane faces as well as clear-cut edges and vertices. In between the large pyramids small grains are evident.

The influence of plasma etching on the surface morphology strongly depends on the gas composition as can be seen in Figure 1 images b-c.

Pure oxygen plasma almost does not change the surface topology. The pyramidal shape is preserved except for the rounded edges and vertices on top of the pyramids.

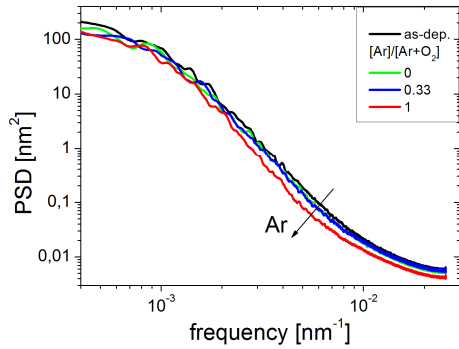


**Figure 1:** SEM images under a tilted view angle of 50 deg of 1700 nm thick ZnO surfaces exposed to plasmas of different gas mixtures: a) as-deposited, b) [Ar]/[Ar+O<sub>2</sub>]=0, c) [Ar]/[Ar+O<sub>2</sub>]=1, by fixed conditions: time 30 min, pressure 0.1 torr, total flow 30 sccm, rf-power 70 W.

Pure argon plasma in contrast changes the surface strongly. The pyramid shape has changed, only the ridges are preserved. The small features in between are vanished and the valleys exhibit an U-shaped morphology. The surface features do not show a continuous slope, they rather exhibit a peak-like morphology with a smooth

slope in the valleys and a steep slope towards the preserved ridges. The ridges seem to be rounded on top compared to as-deposited ZnO. The surface exposed to pure argon plasma shows the strongest deviation from a pure pyramidal shaped surface.

Figure 2 shows power spectral density (PSD) curves derived from AFM scans of the ZnO samples exposed to argon/ oxygen plasmas. PSD curves provide information about the distribution of surface roughness over all spatial frequency (detailed information can be found in [10]).



**Figure 2:** Power spectral density (PSD) derived by AFM measurements of 1700 nm thick ZnO samples exposed to different kinds of argon and oxygen plasmas for 30 min at 70 W, 0.1 torr and a total flow of 30 sccm.

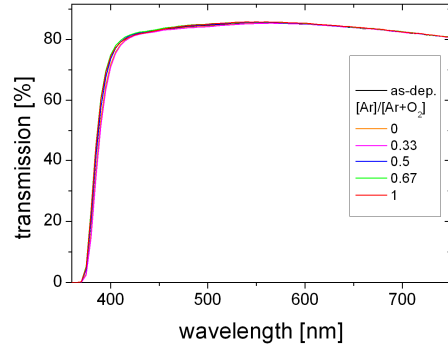
Plasmas with a large amount of oxygen nearly show no difference to the as-deposited sample. For increasing Ar content a decrease in PSD in the frequency range between  $2 \cdot 10^{-3} \text{ nm}^{-1}$  to higher frequencies can be observed. This range corresponds to lateral feature dimensions of 500 nm to about 50 nm. This is in agreement with the SEM image for the pure Ar plasma, where the small features are gone and the large grains have lost substance due to a smoothing of the valleys. The root mean square roughness  $\delta_{\text{rms}}$  shows only a small change, as it can be derived by the square root of the integrated PSD(f) over all frequencies. It decreases from  $\delta_{\text{rms}}=48 \text{ nm}$  to 44 nm for the sample treated with pure argon plasma.

The dependence of the argon content on the impact on surface morphology might be addressed to the fact that argon plasma mainly consists of electrons and  $\text{Ar}^+$  ions. These positive ions are accelerated in the electrostatic field created by the self-bias towards the lower electrode. The sample is placed on that electrode and consequently the surface is sputtered by the positive ions. In contrast oxygen plasma contains beside positive ions and electrons also negative  $\text{O}_2^-$  and  $\text{O}^-$  ions due to the strong electronegativity of oxygen [11]. These negative ions cannot sputter the lower electrode because of the direction of electrostatic field inside the chamber. Thus less ion impact occurs on the ZnO surface for oxygen rich plasmas.

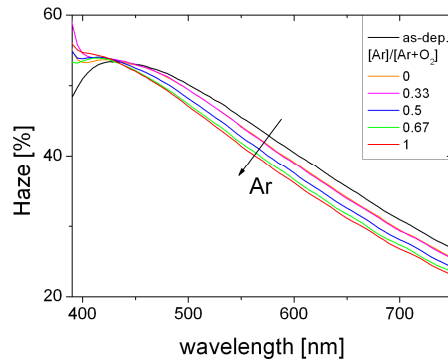
The plasma process provides the ability to change the shape of the ZnO surface features from a nearly pyramidal shape to a smoothed and flattened surface morphology. Thus the influence of the shape on the optical properties as well as the consequences on a-Si solar cell devices can be investigated.

The plasma etching does not affect the total transmission of the ZnO films, as shown in Figure 3.

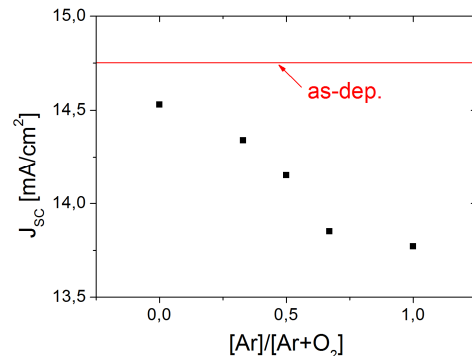
The light scattering behavior denoted by the haze in contrast is affected by the plasma treatment, as shown in Figure 4. Increasing the argon content leads to a slight decrease in haze. This is consistent to the SEM images as well as the AFM measurements, which show a slight decrease in surface roughness at least for pure argon plasma.



**Figure 3:** Total transmission of plasma-etched 3300 nm thick ZnO samples. A difference between plasma-treated samples and as-grown ZnO can not be observed.



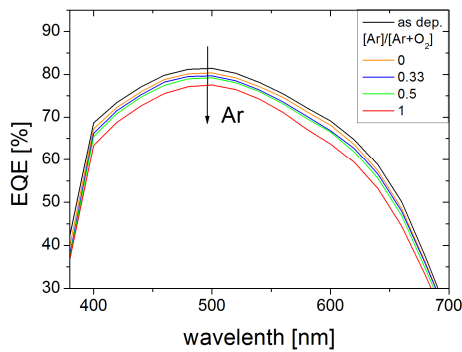
**Figure 4:** Haze of 3300 nm thick ZnO films treated with different kinds of argon and oxygen plasmas for 30 min at 70 W, 0.1 torr and a total flow of 30 sccm.



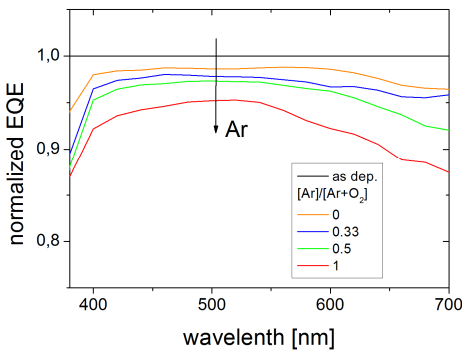
**Figure 5:**  $J_{\text{sc}}$  of a-Si cells deposited on 3300 nm ZnO samples previously treated with different Ar/O<sub>2</sub> plasmas.

The short circuit current density  $J_{\text{sc}}$  of the a-Si:H solar cells deposited on the ZnO substrates is correspondingly decreased with increasing argon content (Figure 5). To investigate whether this loss is attributed to a loss in the red region of the spectrum due to a worse light trapping caused by flattened TCO/a-Si interface, external quantum efficiency measurements are performed.

The measurements are shown in Figure 6. The EQE decreases in agreement with the haze and  $J_{SC}$  for increasing argon content, but remarkably over the whole visible spectrum. For a decrease in light scattering due to a smoothed surface one would only expect a deviation from the as-deposited cell in the long wavelength range above 550 nm. To clarify the differences, Figure 7 shows the EQE measurements normalized to the as-deposited cell. Indeed the deviation is largest for long wavelength which is addressed to a loss in light trapping and associated decrease in red response caused by the smoothed surface features. This statement is also supported by the total transmission of the completed solar cell, measured without white back reflector (Figure 8). For wavelengths above 500 nm, where the a-Si absorption is less pronounced a noticeable increase of the total transmission with increasing argon content can be observed.



**Figure 6:** EQE of a-Si cells deposited on plasma-etched ZnO front contacts

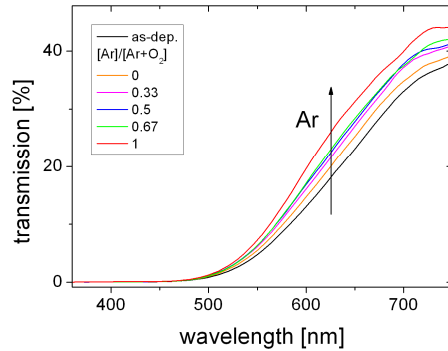


**Figure 7:** Normalized EQE of the a-Si cells deposited on plasma-etched ZnO front contacts. The curves are normalized to the quantum efficiency of the as-deposited reference cell.

This is attributed to the smoothing of the ZnO surface features, especially the smoothed slope in the valleys (Figure 1 c), which goes along with a larger specular part of the transmitted light. Consequently the reflection at the a-Si/ back ZnO interface is lowered and more light is coupled out of the device in the long wavelength regime.

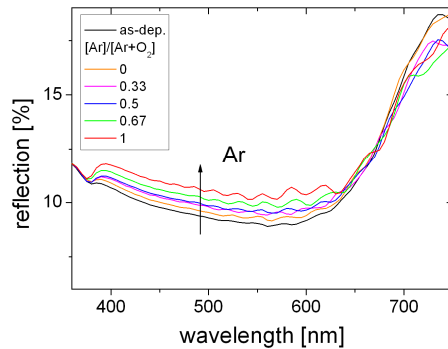
Nevertheless a reduced light scattering can not explain the lowered EQE of plasma etched cells for wavelengths below 500 nm, because light trapping effects are negligible due to the short penetration depth for amorphous silicon in this wavelength range. It must

be related to light incoupling at the front ZnO/ a-Si interface.



**Figure 8:** Total transmission of a-Si cells deposited on plasma-etched ZnO front contact including a ZnO back contact, without white reflector.

Figure 9 shows the total reflection of the completed solar cells, again measured without white back reflector. A clear increase in reflection with increasing Ar content is observed in the visible range from 400 nm to 650 nm. This can only be caused by reflections at the TCO/ a-Si interface, due to the depicted small penetration depth which does not allow light to travel twice through the a-Si absorber.



**Figure 9:** Reflection of a-Si cells deposited on plasma-etched ZnO front contacts including a ZnO back contact, measured without white reflector.

This increased reflection could result from a metallic film of zinc produced by the plasma-treatment at the ZnO surface, which would act as reflector. Investigations on total transmission of the ZnO films after the plasma-process (Figure 3) along with auger measurements reveal no evidence of decreased transmission nor changed surface composition due to the plasma-treatment.

The increased reflection is rather related to the change in shape of the pyramidal surface features and the corresponding change in effective gradient of refraction between the ZnO ( $n \approx 2$ ) and Si ( $n \approx 4$ ). A continuous change in refractive index between two media in general reduces the reflection at that interface [1]. For a modified surface morphology this change is more abrupt and the antireflection effect is less pronounced at that interface. Accounting for the fact that the ZnO surface roughness only slightly decreases with increasing Ar content, the shape of the surface features must be the dominant quantity which affects the light incoupling. The larger the deviation from a pyramidal shape the worse the light

incoupling. This in turn leads to a lower photocurrent as mentioned above.

#### 4 CONCLUSION

Ion sputtering with argon and oxygen is capable of modifying the shape of LPCVD-grown ZnO surface features and allows the investigation of the influence of shape on the optical as well as the solar cell device properties.

Corresponding with theoretical studies by Haase et al. [1] it turns out that a rough surface structure consisting of pyramidal features is essential for good light incoupling, in particular the shape is important. We could show that the light incoupling decreases with ongoing deviation from the pyramidal shape.

The haze of the ZnO films as well as the red response of the solar cells reveals a clear decrease with increasing Ar content, while the rms-roughness of the ZnO surface almost remains unchanged. Consequently the shape of the surface features might also play the most important role in light trapping. The pyramids exhibit the best properties needed for light scattering.

#### 5 REFERENCES

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