Nanocrystalline zinc oxide for surface morphology control in thin-film silicon solar cells

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1. Introduction

A good transparent conductive oxide (TCO) layer fulfils two main functions in thin film (silicon) solar cells in superstrate configuration: (1) as front and back electrode it collects the generated current by the absorber layers and carries it to the external terminals of the device (2) as front window layer it transmits and scatters light into the photovoltaic cell. A third and equally important criterion that makes a good TCO superstrate for thin film solar cells is the surface morphology and the effect on subsequent thin film silicon material growth as highlighted in literature [1–7]. Thin film silicon a-Si:H/μc-Si:H tandem and μc-Si:H single junction solar cells deposited on high haze self-structured low pressure chemical vapor deposition (LPCVD) ZnO are known from literature to suffer from so-called “cracks”, that are regions of less dense Si material. Cracks are regarded as defective regions in the μc-Si:H material and they act as conduction channels, thus reducing diode quality and causing open-circuit voltage ($V_{oc}$) and fill factor (FF) losses in the device [2,3,8,9]. The steeper the ZnO surface features become and the abrupter its morphology changes, the more the μc-Si:H absorber material suffers [3]. Variations in process parameters for μc-Si:H deposition may also influence the formation of these less dense material zones [1]. As an example, optimized microcrystalline silicon absorber layers deposited by TEL solar at high pressures (typically 20 mbar) in new generation narrow gap (7 mm inter-electrode separation) plasma enhanced chemical vapor deposition (PECVD) reactors are more tolerant to a rough superstrate morphology as shown elsewhere [8,9].

Reducing the surface roughness, smoothening the surface and influencing the shape of surface features usually leads to a reduction of cracks. Some approaches to smoothen LPCVD ZnO surface and thus favor μc-Si:H material growth were presented in the literature. These include ex-situ argon plasma etching of the ZnO surface after deposition [5,10] and in-situ methods among them the LPCVD ZnO surface is covered by (a) a capping layer grown with high DEZ precursor flows and (b) capping layers grown with adding ethanol into the gas mixture [11–14].

An alternative in-situ approach for modifying the ZnO surface morphology is introduced in this publication. A surface treatment based only on diborane and water is shown to be able to influence the growth of ZnO crystallites: a regular repetition of such treatment during the growth of a ZnO layer allows to prepare a nominally flat LPCVD ZnO material later referred as nanocrystalline ZnO (NC-ZnO). Additionally, the influence on the surface morphology of gradually covering a LPCVD ZnO surface with NC-ZnO will be described together with the effect on solar cell performance. Especially the effect on fill factor and open circuit voltage of the solar cells will be used as measure for μc-Si:H material quality.

**Keywords:** ZnO film, Surface morphology, Light scattering, Micromorph, Thin-film silicon solar cells

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Abstract

Zinc oxide (ZnO) is a widely used transparent conductive material for thin-film solar cells. Naturally textured ZnO deposited by low pressure chemical vapor deposition (LPCVD) is currently used to prepare high efficiency thin film silicon solar cells. However it is known that a strong roughness can disturb the growth of microcrystalline silicon and induce performance losses. An alternative approach denominated “nanocrystalline ZnO” is presented which allows to control surface roughness and haze during growth independently of other layer properties such as thickness, doping or conductivity for layers thicker than approximately 80 nm. Surface morphologies, optical properties and material properties of the nanocrystalline ZnO layers together with solar cells results are presented.

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2. Material and methods

Large area (Gen5, 1.4 m²) LPCVD systems were used for depositing boron-doped ZnO front and back electrodes. a-Si:H and µc-Si:H doped and intrinsic silicon based layers for thin film solar cell fabrication were deposited in conventional wide gap (28 nm inter-electrode separation) large area (Gen5, 1.4 m²) KAI™ PECDV reactors [15–17]. ZnO was deposited by using diethyl-zinc (DEZ), diborane (B₂H₆) and water (H₂O) as precursor gases. If not mentioned differently, the LPCVD hot plate temperature was set to 180 °C, the H₂O/DEZ precursor ratio was set to 1:22; and the process pressure to 0.5 mbar (50 Pa) for layer deposition [17]. Reference ZnO layers for the two separate blocks of experiments for this study had a thickness of 1.65 μm and 1.8 μm, an average sheet resistance of 23 Ω/sq and 35 Ω/sq, and an haze at 600 nm of 27% and 35%, where B₂H₆/DEZ ratio was set to 1.1 · 10⁻³ and 4.2 · 10⁻⁴, respectively. The absolute doping ratio is reported although in the process 2% B₂H₆ diluted in hydrogen was used. If not mentioned differently, the surface treatment was performed using a B₂H₆/H₂O precursor ratio of 6.1 · 10⁻³; H₂O flow, pressure and hotplate temperature were kept constant as during deposition. The sputtered and etched ZnO sample was provided by Forschungszentrum Jülich and prepared by sputtering at 0.1 Pa pressure and 300 °C substrate temperature, further information can be found elsewhere [18]. Typical MICRO-MORPH™ solar cells had an a-Si:H top cell i-layer thickness of 200 nm, 40 nm intermediate reflector layer and a µc-Si:H bottom cell i-layer thickness of 1100 nm. Alternatively, µc-Si:H single junction solar cells were deposited on top of an n-doped a-Si:H layer having a thickness suitable to roughly match the optical absorption of the real top cell. This configuration denoted filtered bottom cell allows to study the bottom cell close to conditions existing in tandem cell, although the relatively low conductivity of a thick n-doped a-Si:H layer entails an increase of Rₛ and to a systematic decrease of fill factor. ZnO layer thickness, sheet resistance and haze data from 143 evenly distributed positions over GEN5 superstrate was accessed via SENTECH Sensol-H combined mapping tool equipped with a thin film reflectometry setup, a four point resistivity probe and an integrating sphere. Haze was determined from the ratio of diffuse transmitted light to total transmitted light at the wavelength of 600 nm if not otherwise specified. Thickness measurements by reflectometry were separately validated by profilometry measurements. The reported thickness of thin layers below a few 100 nm is based on the product of deposition rate (obtained from reflectometry measurements of thicker layers) and deposition time. This approach was verified by profilometry and cross section analysis in separate experiments. Information on surface morphology was accessed by Atomic Force Microscope (AFM) using a Digital Instruments Dimension 3100 System in tapping mode. Processing of AFM data and root mean square (RMS) roughness measurements were done using the open source software Gwyddion [19,20]. X-ray diffraction (XRD) measurements were done using a PANalytical X-Pert Pro MRD-XL diffractometer equipped by a CuKα source and operated in Bragg–Brentano configuration. Solar cells (both a-Si:H/µc-Si:H tandem and µc-Si:H p-i-n devices) were produced to investigate the influence of variations in the front TCO morphology on performance. A combination of sub-modules (100 cm² total area, 37.87 cm² active area, 10 series interconnected cells) and 1 cm² solar cells were used to study the applications of NC-ZnO. Current–voltage characterization at AM1.5 conditions was performed using a Wacom two lamp WXS Solar Simulator. External quantum efficiency (EQE) measurements were done using a PV measurement QEX-10 setup, bias light was used to measure tandem cells and all measurements were done in reverse bias conditions. Optical transmittance, reflectance and absorbance were measured by a PerkinElmer LAMBDA 950 UV/vis/NIR Spectrophotometer equipped with a 15 cm diameter integrating sphere to collect diffuse light. Absorbance was determined by subtracting the measured total transmittance and reflectance from 1.

3. Results

3.1. Nanocrystalline ZnO

The preparation and the properties of NC-ZnO can be at best described by using a sequence of growing nominally 165 nm of ZnO by LPCVD (B₂H₆/DEZ=1.1 · 10⁻³) and then performing a diborane–water treatment. A complete stack of approximately 1.65 μm thickness is composed of 10 deposition steps separated by 9 treatment steps.

To study the influence of a diborane–water (d–w) treatment on ZnO growth and morphology a treatment with varying time was applied. Fig. 1 shows the ZnO haze together with the sheet resistance as a function of d–w treatment length. The longer the in-situ treatment between subsequent zinc oxide depositions the lower is the haze. Between 0 and 30 s treatment there is a nearly linear relationship between the decrease in haze and treatment length. From 30 s to 45 s the effect starts to saturate and after 45 s the haze value is nearly constant reaching a value below 2%. At the same time the sheet resistance only slightly decreases considering the measurement scattering. It is important to note that the total layer thickness and nominal doping are constant. The d–w treatment acts as a lever to control LPCVD ZnO morphology and enables decoupling of TCO haze from layer thickness and doping.

The surface morphology of ZnO layer stacks prepared using selected treatment times and measured by AFM are shown in Fig. 2. The reference sample (Fig. 2(a)) prepared without d–w treatment has surface RMS roughness of 68 nm and the surface shows the typical pyramidal structures observed in LPCVD ZnO [21,22]. Using an intermediate treatment time of 20 s (Fig. 2(b)) reduces the surface RMS roughness to 54 nm and the surface shows qualitatively more rounded pyramidal structures. Finally, using 80 s treatment time (Fig. 2(c)) further reduces the surface RMS roughness to 18 nm and the surface shows qualitatively very small structures and pyramids. The qualitative AFM observations were repeatedly verified by SEM observations to exclude measurement artefacts.

An additional qualitative impression of the changes in surface morphology can be gained observing profiles as shown in Fig. 3(a). Again a smoothening of the pyramidal structures can be observed when introducing a 20 s treatment compared to the reference sample. A longer treatment of 80 s leads to a profile with few nm
height variations. A more quantitative analysis can be done by calculating the height distribution as shown in Fig. 3(b). With increasing d–w treatment time the height distribution function becomes narrower and its mean shifts towards lower values indicating a smoothening of the layers and a reduction of the peak to valley roughness.

The major changes of surface morphology suggest a possible modification of the preferential crystalline orientation during layer growth. XRD measurements confirmed this hypothesis as shown in Fig. 4 comparing a reference layer without d–w treatment with a layer stack prepared using 80 s d–w treatment. In the reference layer the (110) orientation is dominating corresponding to an a-axis preferential orientation as known from literature [21,22]. However, in the case of a layer stack grown using 80 s d–w treatment the peak intensity of the (110) orientation is smaller and comparable with other orientations. Similar observations were reported for LPCVD ZnO layers below 500 nm thickness were a-axis oriented crystallites could not yet overgrow the other crystallites. This development is attributed to a disturbance or possibly even an interruption in the crystalline growth introduced by the d–w treatment followed by a new nucleation. Possibly the high boron concentration induces a change in surface chemistry or the growth of a very thin strongly doped ZnO layer disturbs the subsequent layer growth. Repeated treatments seem to suppress the change of surface preferential orientation from mainly c- to mainly a-axis with increasing LPCVD ZnO thickness as normally described in literature. The more frequent the d–w treatments are for a given layer thickness, c-axis related peaks become more intense in the XRD data. Considering the crystalline nature of the layers produced with 80 s treatment time combined with few nm surface roughness the material will be denominated nanocrystalline ZnO (NC-ZnO).

The exact mechanism of the d–w treatment is not understood. However, both diborane and water are necessary to cause the observed effects. Control experiments replacing the d–w treatment by: hydrogen, vacuum, H₂O vapor treatment, air exposure and water rinsing were not successful in reproducing the surface variations.
smoothening. Highly doped ZnO layers were tested too and the resulting surface structure was different resembling untreated ZnO with smaller pyramids as documented in literature. Dipping of ZnO layers in boric acid diluted in water allowed to reproduce the observed effects. Further experiments showed a water/diborane ratio of 6 to be optimal hinting at a possible formation of boric acid in the chamber or on the surface. From these observations it may be possible to speculate on surface etching to be responsible for the smoothening effect, however very long treatment times of ZnO layers did not show a measurable etching of the surface. In the presence of DEZ the treatment time necessary to obtain the layer properties described earlier increases, and introducing additional evacuation steps does not improve the treatment effectiveness. Later experiments aimed at reducing the d–w treatment time indicated that increasing the treatment pressure to 2 mbar (200 Pa) and increasing the total diborane flow reduce the treatment time necessary to obtain a nominally flat layer. Combining these optimizations the treatment time to obtain nominally flat layers was reduced below 10 s making the process suitable for industrial applications.

Several experiments investigated the surface morphology and light scattering properties of NC-ZnO and related layer stacks. Reporting all results is beyond the scope of this publication, however the main aspects can be easily summarized. By using d–w treatments to split a ZnO layer of a given thickness it is possible to reach any haze value between nominally no haze and the reference haze value of the ZnO layer without treatments. The surface morphology can be tuned in a similar way from very small features of a few nanometers RMS roughness to the full pyramids present on a single layer. This is a consequence of the d–w treatment influencing only the nucleation and not the growth. Increasing the number of treatments will decrease the haze for a given total layer thickness, modifying the treatment effectiveness as shown in Fig. 1 will allow to carefully control the final haze value. As a result, haze can be completely decoupled from conductivity, from total layer thickness and from layer doping. Applications of NC-ZnO can stretch from thin film solar cells based on different technologies to OLED, smart windows and other applications where sputtered flat TCO layers such as ZnO or ITO are used.

Fig. 5. RMS roughness (triangles, right axis); relative ZnO:B haze at 600 nm (diamonds, left axis) and relative haze at 800 nm (squares) as a function of NC-ZnO filling layer thickness on a 1.8 µm thick base ZnO layer (B₂H₆/DEZ = 4.2 \times 10^{-4}). Haze values are normalized to the values of the base layer: 34.5% and 16.1% for 600 nm and 800 nm, respectively. All haze data points depict averages from 143 equidistant measurement points on Gen5 superstrate. RMS data were obtained from 10 \times 10 \mu m² AFM scans from samples at the center of Gen5 superstrates. Plotted lines are guides to the eye.

Fig. 6. ZnO:B morphology as a function of NC-ZnO filling layer thickness on a 1.8 µm thick base layer measured by AFM. (a) Base layer reference ZnO without filling, B₂H₆/DEZ = 4.2 \times 10^{-4}, (b)–(f) Base layer and NC-ZnO filling with a thickness of 85 nm, 170 nm, 340 nm, 680 nm and 1020 nm, respectively. All AFM scans are 2 \times 2 \mu m², the scale bar is 500 nm, and the vertical scale is the same for all scans.
3.2. Filling ZnO with nanocrystalline ZnO

Toward the application to solar cells, NC-ZnO was investigated as a possible filling material to be deposited on top of an high haze, high roughness ZnO layer (called base layer, B$_2$H$_6$/DEZ=4.2·10$^{-4}$). The filling layer is based on sublayers of nominally 85 nm thickness with the same doping and separated by a d–w treatment. Depositing only a stack of such sublayers on glass would produce a NC-ZnO coating with haze at 600 nm below 2% as described in the previous section.

The effect on haze and on RMS roughness of gradually increasing the number of filling layers from 0 to 14 on top of a base ZnO with 35% Haze at 600 nm is shown Fig. 5. Three stages can be identified. Stage 1: for the first 85 to 340 nm NC-ZnO filling (e.g. 1 to 3 layers) the resulting haze increases at both 600 nm and 800 nm. RMS roughness makes a step down and remains roughly constant. Stage 2: for a NC-ZnO filling layer thickness from 340 nm to 680 nm, haze at 600 nm and RMS roughness decreases linearly whereas haze at 800 nm remains roughly constant. Stage 3: from 850 nm filling layer onwards, both haze at 600 nm and 800 nm and also RMS roughness decrease linearly with increasing filling layer thickness. The sheet resistance (data not shown) decreases linearly from 35 Ωsq in the reference layer to 15 Ωsq when using 14 filling layers due to the increase of the total layer thickness.

AFM scans of selected samples are shown in Fig. 6 and the corresponding RMS roughness values are shown in Fig. 5. The reference layer without any additional NC-ZnO filling is depicted in Fig. 6a. For the samples at the beginning of morphology evolution (stage 1; Fig. 6(b) and (c)), the thin NC-ZnO layer (85 or 170 nm) is visible as finely grained features covering the underlying pyramids. The valleys are deep and increasing the filling layer thickness the pyramidal features become laterally bigger in size. Such a development could explain, why the TCO haze is increasing both for 600 and 800 nm filling thicknesses ranging from 340 to 680 nm (stage 2, Fig. 6(d) and (e)), the pyramids start merging into bigger rounded features and the filling of valleys is more effective. As a result, RMS roughness and haze at 600 nm decreases with decreasing aspect ratio, haze at 800 nm is nearly constant since the increase in feature size is compensating for the structure depth loss. Finally, for NC-ZnO filling layer thickness larger than 850 nm (stage 3, Fig. 6(f)), the surface morphology is rounded and narrow valleys are completely filled. Both haze value at 600 nm and at 800 nm start to decrease. For 1190 nm NC-ZnO thickness, the RMS roughness is only 30% of the reference value.

A similar qualitative impression of the changes in morphology can be obtained from the cross sections shown in Fig. 7(a). Increasing the NC-ZnO filling layer thickness turns the pyramid surface features into hemispheres: valleys become filled, smaller pyramids merge, larger pyramid apexes become round, aspect ratio decreases due to concurring expansion in lateral size. A more quantitative analysis based on height distributions is shown in Fig. 7(b). For stage 1, the height distribution is very similar to that of the reference layer without NC-ZnO filling supporting the qualitative statement of steep deep valleys above. With increasing NC-ZnO filling thickness, the distribution becomes narrower and moves towards lower height values, indicating a reduction in peak-to-valley and an effective smoothening of the ZnO surface as shown in Fig. 5.

Angular resolved scattering (ARS) measurements allow to study the light scattering properties of ZnO surface in depth and enable access to information on diffusion angle which is as important as haze itself [23]. The three stages in morphology evolution with increasing NC-ZnO filling thickness are visible in angular resolved scattering (ARS) measurements at 500 nm of wavelength as shown in Fig. 8. For NC-ZnO filling layer thickness until about 170 nm, the ARS behavior is very similar to the reference ZnO base layer without filling, and light diffusion is quite uniform throughout the angle range from 10° to 70°. With increasing NC-ZnO filling thickness, the angle of maximum diffusion shifts towards lower angles and diffusion into wider angles decreases continuously. Two groups can be distinguished: for filling layer thicknesses from 340 to 680 nm a transition in scattering behavior occurs (corresponding to stage 2) and for higher thicknesses (corresponding to stage 3) the diffusion is mainly into narrower angles. The ARS curve is then similar in shape with a sputtered and etched ZnO sample added for comparison.

Finally the XRD patterns of layer stacks combining a base layer and a NC-ZnO filling layer were compared as shown in Fig. 9. For all the samples a–axis preferential orientation (110) is the dominating peak where its intensity also remains approximately the same. With the introduction of the NC-ZnO on the base layer, the intensity of additional orientations increases similarly to the NC-ZnO diffraction pattern showed earlier in Fig. 4. This observation suggests again that a d–w treatment enhances the growth at additional orientations beside the already existing preferential orientation on the layer surface.

3.3. Applications to thin film silicon solar cells

In a final step, smoothed ZnO layers deposited as described above were used as front contacts for a-Si:H/µc-Si:H tandem and µc-Si:H p–i–n PV devices. A series of otherwise identical solar cells was prepared on ZnO front contacts with gradually increasing NC-
ZnO filling thickness to study the influence of NC-ZnO filling on cell performance. Results of the relevant solar cells parameters are shown in Fig. 10. Increasing the thickness of the NC-ZnO filling layer has a clear benefit for both $V_{oc}$ and FF. In the case of tandem modules, a maximum improvement of 60 mV was reached when the filling layer had a thickness of 1020 nm and the maximum gain in FF of 1.8% was already reached for 340 nm filling layer thickness and further increasing the filling layer had little influence on FF. A negative consequence of increasing the filling layer thickness is a constant loss of $J_{sc}$. Filtered bottom cells gained up to 44 mV and 8.2% FF at 1020 nm filling layer thickness. Again, $J_{sc}$ decreases with increasing filling layer thickness. Finally, the maximum gain in conversion efficiency for tandem cells of 0.3% was achieved using 340 nm filling layer thickness. Preliminary light induced degradation (LID) experiments did not indicate a significant difference in LID between cells deposited on ZnO base layer and on layers filled with NC-ZnO.

Increasing the filling layer corresponds to reducing the surface roughness and the observed improvements of $V_{oc}$ and FF are similar to results achieved by other methods for smoothening the TCO surface [5,12,13] and are probably related to a better growth of the microcrystalline Si material [2,3,5]. Comparing the filtered bottom cells with tandem cells reveals larger $V_{oc}$ gains in tandem cells suggesting that rough TCO has a detrimental effect on the a-Si:H material quality too [6,7]. It is to be noted that the μc-Si:H bottom cells are in both case nominally the same and the systematic difference in $J_{sc}$ is related to the thickness of the filter layer not perfectly matching the top cell absorption. The FF in tandem

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**Fig. 8.** Angular resolved scattering measured at 500 nm for a series of layer with increasing NC-ZnO filling layer thickness on a 1.8 μm thick base layer ($B_2H_6/DEZ = 4.2 \times 10^{-4}$). Thick solid line: base layer. Dashed line with no marking: sputtered ZnO:Al textured by HCl wet chemical etching.

**Fig. 9.** XRD measurements of ZnO layers with increasing NC-ZnO filling thickness. Base layer of 1.8 μm thickness, $B_2H_6/DEZ = 4.2 \times 10^{-4}$. Dashed line: base layer only. Continuous line: 510 nm NC-ZnO filling. Dotted line: 1020 nm NC-ZnO filling layer.

**Fig. 10.** Initial JV parameters for filtered μc-Si:H bottom cells (diamonds, primary axis) and a-Si:H/μc-Si:H tandem cells (squares, secondary axis) as a function of NC-ZnO filling layer thickness on a 1.8 μm thick base layer ($B_2H_6/DEZ = 4.2 \times 10^{-4}$). (a) open circuit voltage ($V_{oc}$), (b) fill factor (FF), (c) short circuit current density ($J_{sc}$) and (d) conversion efficiency ($\eta$). All data points show average values obtained from 8 submodules per experiment. Error bars show the standard deviation for each experiment. Dashed lines are guides to the eyes.
cells does not continuously increase with increasing filling layer thickness as for the filtered bottom cells, however this evolution is not fully understood. Increasing the filling layer thickness does not lead to poorer ZnO sheet resistance thus excluding an increase of not fully understood. Increasing the thicknesses on a 1.8 μm base layer (B:16/DEZ=4.2·10−6). The absorptance of cells without filling layer and with 1020 nm NC-ZnO filling are shown for reference. Lines are guide to the eyes.

To better understand the losses in Jsc, EQE was measured in selected tandem modules on selected NC-ZnO thickness are shown in Fig. 11. As expected from surface AFM scans and ARS measurements, the current generated in a-Si:H top and μc-Si:H bottom cells is not significantly affected for the first 170 nm of NC-ZnO cover layer (stage 1). The first significant change in EQE curve occurs with 340 nm NC-ZnO thickness: both the top and bottom cell EQE response decreases in the wavelength range from 370 nm to 800 nm. Increasing the filling layer thickness increases the losses in EQE response, especially for the bottom cell in the wavelength range from 650 nm to 950 nm.

The EQE losses in the top cell from 350 nm to 550 nm were attributed to an increased reflection due to a smoother ZnO/a-Si:H interface as confirmed by reflection measurements on the entire cell shown in Fig. 11. The EQE losses at wavelengths above 550 nm were attributed to an increasingly poorer light scattering as shown in Fig. 8. As a consequence of poorer light scattering, a part of the top cell current is transferred to the bottom cell in the range 550 nm to 650 nm, thus partially compensating for losses in the bottom cell at longer wavelengths. Two cell absorbance curves (1-T-R) for no filling and for 1020 nm NC-ZnO filling confirm poorer light trapping with increasing reflection from the cell. Additionally, smoothing the TCO surfaces lead to interference effects which require further study. Parasitic absorption by the thicker ZnO layers plays a minor role.

The losses in EQE by increasing NC-ZnO layer thickness are stronger for longer wavelengths were light scattering and light trapping is more critical confirming that smoothing the ZnO surface has a detrimental effect on light scattering.

4. Conclusions

In conclusion diborane–water treatments and NC-ZnO were introduced as a simple and industrially applicable method for controlling the haze of LPCVD ZnO layers during deposition independently of layer thickness and conductivity for layers thicker than approximately 80 nm. Industrial production of NC-ZnO can be done using conventional ZnO LPCVD equipment at high speed and maintaining optimal DEZ utilization. Furthermore, neither additional treatment systems nor additional precursor gases are necessary. On the contrary, solutions presented in literature do not seem to fulfill all these criteria. NC-ZnO can be used to gradually smooth the surface of a LPCVD ZnO layer improving the material quality of μc-Si:H bottom cells resulting in improved Voc and FF in μc-Si:H cells. However, smoothing the ZnO surface leads to a poorer light trapping and lower Jsc.

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