REDUCTION OF ITO BY A LOW-COST SPRAYED TIO_X CAPPING LAYER FOR SHJ SOLAR CELLS

Ulrike Heitmann, Leonard Tutsch, Angela De Rose, Dominik Dreja, Leonie Jakob, Radwa Elgazzar, Martin Bivour,

Jonas Bartsch

Fraunhofer Institute for Solar Energy Systems ISE Heidenhofstraße 2, 79110 Freiburg, Germany

ABSTRACT: We demonstrate a spray pyrolysis process for deposition of titanium oxide (TiO_x) on ITO on silicon heterojunction (SHJ) solar cells. Layer stacks of 20 nm ITO + 55 nm TiO_x, 50 nm ITO + 25 nm TiO_x and references with 75 nm ITO were deposited on M2+ ($157 \times 157 \text{ mm}^2$) solar cells. All three layer stacks yield similar cell efficiencies of close to 21 %. Homogeneous sprayed coatings were achieved despite using a small laboratory spray coater. Single cell modules were manufactured from cells of all three groups. Only slight modifications in the soldering process were necessary, even though the screen-printed metallization is covered with TiO_x for two groups. Module efficiencies are also on par for the three cell types. A slightly increased series resistance is measured on both cell and module level for the cells with 20 nm ITO layer, due to higher resistance for lateral current transport in this layer. Consumables costs of <1ct/wafer are estimated based on the laboratory process.

Keywords: Heterojunction, Antireflection Coating, Spray Pyrolysis, Soldering

1 INTRODUCTION

The global photovoltaic production capacity is steadily rising, with currently >200 GW_P production per year and with an estimated capacity of >1TW_P around 2030 [1]. Demand for material resources needed for PV production will increase likewise, unless technical solutions are found to lower the material needed per W_P. For some materials, a five-fold demand as compared with today can be satisfied in principle (though the practical realization of this capacity growth will still be challenging). For other, more scarce materials, high shares would need to be taken for PV production, meaning increasing costs and competition with other uses. Silver, indium and bismuth have been identified as critical materials in this respect [2].

Indium consumption for PV production originates from thin film PV such as CdTe and CIGS, and from silicon heterojunction (SHJ) solar cells in the field of crystalline silicon PV. Indium is part of the transparent conductive oxide (TCO), which is needed for contacting the semiconductor material, for lateral conductance of the extracted charge carriers and for antireflection purposes. Tin-doped indium-oxide (ITO) is mostly used for this layer at present. Indium-based oxides offer the most attractive properties for solar cells, as they combine excellent transparency with high conductivity. They are typically deposited using physical vapor deposition (PVD), namely sputtering. While this process delivers high-quality layers, it is more costly than some alternative processes that do not require vacuum conditions.

Several approaches have been proposed to lower the Indium consumption of SHJ solar cells [3-7]. Using alternative, indium free TCOs such as Aluminum doped zinc oxide (AZO) can mitigate Indium altogether, but comes at the cost of reduced stability and slightly affected performance. AZO can also be used in TCO stacks, covered with thin layers of ITO, which reduces In consumption effectively and relies on known sputtering processes.

In other approaches, a thin ITO layer is capped with a dielectric layer. A thinner ITO layer would have less ideal antireflective properties, so the dielectric layer is selected to compensate or even overcompensate for this loss. In addition, the dielectric layer can improve the stability of SHJ solar cells encapsulated into modules in the field. Different techniques can be used to deposit the dielectric layer, such as APCVD, PECVD [4,7] or Spray Pyrolysis [8]. Some of these techniques are potentially cheaper than sputtering. The dielectric layer is typically applied after the metallization has been printed onto the SHJ solar cell. This brings on challenges for the module interconnection, but can also be exploited, e.g. for a subsequent copper plating process [7] which may additionally lower the consumption of another scarce material, silver.

In this work, we demonstrate the application of a dielectric layer deposited by spray pyrolysis, a potentially cheap and mass-production capable deposition technique. The work is based on our previous work on small-area solar cells [8], where we first demonstrated that this process can work effectively. Here, we show the transition to an industrial wafer format (M2+,157 \times 157mm²) and the fabrication of single-cell-modules.

2 EXPERIMENTAL

SHJ solar cells were manufactured at Fraunhofer ISE from $157 \times 157 \text{ mm}^2$ *n*-type Cz wafers, 1 Ω cm base resistivity. Wet-chemical saw damage etching and texturization were made prior to a cleaning step with ozone. After an HF dip, intrinsic and doped *a*-Si:H layers were deposited by PECVD, followed by sputtering of ITO.



Figure 1: Overview of the experimental groups in the presented experiment.

The TCO deposition process was altered for some of the solar cells (all layer thicknesses refer to texturized surfaces). Besides a reference group with 75 nm ITO for ideal antireflective properties, two groups with thinner ITO (20 nm and 50 nm) were created. An overview of the experimental groups is given in Figure 1.

After screen-printing and curing (200 °C, 5 min) of silver metal contacts (5 busbar layout) on all cells, the latter two solar cell groups were coated with a 55 nm and a 25 nm titanium oxide (TiO_x) layer by spray pyrolysis. A precursor solution containing a titanium alkoxide dissolved in an alcoholic solvent was used. A spray coater from Equisonics was used, which is equipped with an ultrasonic nozzle (40 kHz) and a pneumatic nozzle. The nozzles can be moved by an X-Y-Z robot over the sample surface, which can be heated to up to 500°C. Substrate set temperature in the experiments to fabricate solar cells was 200 °C. Both nozzle types were tested. Better homogeneity of the TiO_x layer was obtained with the pneumatic nozzle, while material consumption is lower with the ultrasonic nozzle (0.8 ml of precursor solution per wafer). The used setup is laboratory scale and requires multiple passes of the nozzle over the surface. Spraying times of one minute (25 nm TiOx layer thickness) and two minutes (55 nm TiOx layer thickness) were required for the deposition of the layer. For better comparison, the cells from both groups were left on the heated substrate platform after spraying for a total duration of 5 minutes.

After performing IV measurements of the SHJ cells, single-cell-modules were fabricated. It has been shown, that infrared (IR) soldering is well suited for the interconnection of SHJ solar cells [9]. For our experiment, a semi-automatic soldering station with IR heating was used. The cells were pre-heated on a hotplate and soldered using Sn60Pb40-coated Cu ribbons and no-clean flux. After cross connection, small-format modules were laminated with glass, POE encapsulant and polymer-based black backsheet. The finished modules were characterized by EL imaging and IV measurements.

For optical investigations, borofloat glass with a thickness of ~0.7 mm was spray coated using different substrate set temperatures (200 °C, 300 °C and 400 °C). Other conditions in these spray processes were as discussed above.

3 RESULTS

3.1 Optical properties of the spayed TiO_x layers

The requirements for the application as a capping layer in SHJ solar cells are high transparency and a refractive index close to that of the underlying ITO. The transparency of the sprayed TiOx was analyzed by coating of a 0.7 mm thin Borofloat glass slide with approx. 50 nm TiO_x. The transparency was evaluated by measuring the reflection (R[%]) and the transmission (T[%]) and calculating the absorption according to A=100-R-T. Different substrate temperatures during spraying were compared. The results are shown in Figure 2. It should be noted that the accuracy of the reflection-transmission measurement is ≈ 2 % absolute, which could explain the calculated negative absorption. However, when comparing the absorption of the TiO_x thin film deposited at 200 °C with the one deposited at 300 °C, it can be seen that the absorption between 400-650 nm decreases with reduced substrate temperature, resulting in a highly transparent thin film when depositing at a substrate





Figure 2: Calculated absorption of spray coated TiO_x at substrate temperatures of 200 °C and 300 °C from transmission/reflection measurements.

The refractive index of the TiO_x thin film was determined by spectroscopic ellipsometry (SE) measurements on TiO_x coated silicon substrates (TiO_x thickness \approx 100nm). The results are shown in Figure 3. The refractive index was analyzed for different substrate set-temperatures during the deposition as well. It decreases with reduced substrate temperature. At 200 °C it is very close to the refractive index of the sputtered ITO.

In conclusion, the optical properties of the thin sprayed TiO_x film deposited at a substrate temperature of 200 °C are ideal for the use as a capping layer on ITO layers and compatible with the low-temperature regime (max. 200 °C) of SHJ solar cells.



Figure 3: Refractive index n of spray coated TiO_x thin films deposited on silicon at substrate temperatures of 200 °C, 300 °C and 400 °C; determined from SE measurements. For reference, the refractive index of a sputtered ITO is also included in the graph.

3.2 Solar cell results

The optically ideal TiO_x layer that can be spray deposited at 200°C substrate set-temperature was used in the fabrication process of the solar cell groups 1 and 2 presented in Figure 1. A schematic representation of the process flow is given in Figure 4, together with a photograph of a finished M2+ wafer.



Figure 4: Top layers of the cells processed in this work (left), photograph of cell (without metallization, right)

Groups 1 and 2 were IV measured before and after spray pyrolysis of the TiO_x layer. In the post spray coating measurement, the reference group 3 was included. All IV results on cell level are given in Table I. The overall efficiency level is poor, as the fabrication process was only ramped up at the time these cells were made. The measurements still allow to assess the proposed process and to compare it to the reference process.

Table I: IV results of groups 1 - 3 on cell level, groups1&2 before and after TiOx spray pyrolysis.

	Voc	$J_{\rm SC}$	FF	η	R _s		
	[mV]	[mA/cm ²]	[%]	[%]	$[\Omega cm^2]$		
20 nm ITO (group 1)							
Before TiO _x	725	34.7	76.7	19.3	1.12		
After TiO _x	725	37.0	77.1	20.7	1.14		
50 nm ITO (group 2)							
Before TiO _x	723	36.3	77.0	20.3	0.87		
After TiO _x	722	37.0	77.2	20.6	0.87		
75 nm ITO (Ref., group 3)							
	727	37.1	77.2	20.8	0.88		

Groups 1 and 2 show a clear disadvantage in short circuit current density before TiO_x spray pyrolysis (marked red in Table I). After the deposition of the TiO_x layer, this disadvantage is fully compensated (marked green and bold). Group 1 also shows a higher series resistance as compared to the other groups, which does not mirror in the cell efficiency. The thinner ITO layer limits the lateral transport of the extracted charge carriers towards the printed metal contacts. This can partly be compensated by the silicon bulk, but for the 20 nm thin ITO layer, a measurable effect results.

3.3 Single cell module results

After the cells were soldered and laminated, the singlecell-modules were measured for their IV parameters. Two modules were built for group 1 and 2 each, and four modules were built for group 3. The soldering process was similar to a standard soldering process as used on an industrial stringer. The IV results of the modules are presented in Table II. A photograph of one of the modules is shown in Figure 5.

 Table II: IV results of single-cell-modules after lamination

	V _{OC}	J _{SC}	FF	η	Rs
	[mV]	[mA/cm ²]	[%]	[%]	$[\Omega cm^2]$
20 nm ITO 55 nm TiO _x (group 1)	724	35.1	74.0	18.8	1.92
50 nm ITO 25 nm TiO _x (group 2)	719	34.9	74.5	18.7	1.69
75 nm ITO (Ref., group 3)	727	34.9	73.5	18.7	1.88

As for the cells, the efficiency level of all three module groups is on the same level. The fill factor drops as compared to the cells for all three groups, as additional resistances are added to the system. The increasing $R_{\rm S}$ confirms this interpretation. The measured values are in the expected range for cell-to-module losses. The $J_{\rm SC}$ drops as well, due to optical losses and the larger reference area.



Figure 5: Photograph of single-cell-module fabricated from a M2+ SHJ solar cell with ITO/TiO_x layer stack.

4 DISCUSSION

We present a simple and potentially cheap process to reduce the indium consumption in SHJ solar cells by as much as 70 %, without sacrificing efficiency. The TiO_x thin film can be sprayed on the full wafer, no masking or subsequent partial etching of the TiO_x is necessary. The spraying process is already quite quick in the lab setup (1-2 minutes), in an industrial multi-nozzle setup, process times should be significantly faster. The spraying process might even be combined with the curing of the screenprinted Ag grid, which is also carried out at a temperature of 200 °C. However, this was not done for the presented results. Standard soldering is feasible and small-scale modules were successfully fabricated..

At the current indium price level, it still remains uncertain if this process will be economically advantageous. Calculations presented at the EU PVSEC 2021 [10] show that additional 55 nm of ITO currently cost around 1.75 \notin ct/wafer. In the same publication, it has been discussed that replacing sputtering of ITO with PECVD of SiN_x does not lower the production cost. In the present work, the material costs for the chemical precursor are $2.5 \notin ct/wafer$ in our labs, where we buy in small volume and in lab quality. We can estimate that the material cost will be below $1 \notin ct/wafer$ for industrial throughput production. The cost for the machine is currently difficult to estimate, but the small cost advantage for avoiding ITO sputtering make it very improbable that an established production line will be altered.

Three factors might change this:

- 1. A demonstration of superior stability of modules with top layer stack of thin sputtered ITO and thick spray coated TiO_x.
- A demonstration of a fully sprayed top layer stack
 Increasing indium prices and/or reduced availability of indium.

5 CONCLUSION AND OUTLOOK

In this paper, a simple and effective spray pyrolysis process of TiO_x to coat a thin layer of ITO is demonstrated on M2+ SHJ solar cells. Small-scale modules are fabricated by IR soldering and laminating these cells. It is shown that the amount of indium per cell can be reduced by as much as 70 % using this approach without sacrificing efficiency. While the advantage in costs and performance may be insufficient to motivate cell manufacturers to change their current or planned production at present, this may change in the future. Besides the perspective of rising indium costs, we plan to demonstrate that this approach can yield superior longterm stability of modules in the field, and that sputtering can be avoided altogether by spraying both TCO and TiOx layer. This may be an attractive option for newly installed SHJ production lines.

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7 REFERENCES

- [1] Goldschmidt, Jan Christoph; Wagner, Lukas; Pietzcker, Robert; Friedrich, Lorenz (2021): Technological learning for resource efficient terawatt scale photovoltaics. In: Energy Environ. Sci. 14 (10), S. 5147–5160. DOI: 10.1039/D1EE02497C.
- [2] Zhang, Yuchao; Kim, Moonyong; Wang, Li; Verlinden, Pierre; Hallam, Brett (2021): Design considerations for multi-terawatt scale manufacturing of existing and future photovoltaic technologies: challenges and opportunities related to silver, indium and bismuth consumption. In: Energy Environ. Sci. 14 (11), S. 5587–5610. DOI: 10.1039/D1EE01814K.
- [3] Han, Can; Santbergen, Rudi; van Duffelen, Max; Procel, Paul; Zhao, Yifeng; Yang, Guangtao et al. (2022): Towards bifacial silicon heterojunction solar cells with reduced TCO use. In: Progress in Photovoltaics 30 (7), S. 750–762. DOI: 10.1002/pip.3550.
- [4] D. L. Bätzner, P. Papet, B. Legradic, D. Lachenal, R. Kramer, T. Kössler, L. Andreetta (2019): 'HJT 2.0'

PERFORMANCE IMPROVEMENTS AND COST BENEFITS FOR SILICON HETEROJUNTION CELL PRODUCTION. In: Proceedings of the 36th European Photovoltaic Solar Energy Conference and Exhibition, Marseille, S. 300–303, zuletzt geprüft am 28.08.2020.

- [5] Morales-Vilches, Anna B.; Cruz, Alexandros; Pingel, Sebastian; Neubert, Sebastian; Mazzarella, Luana; Meza, Daniel et al. (2019): ITO-Free Silicon Heterojunction Solar Cells With ZnO:Al/SiO 2 Front Electrodes Reaching a Conversion Efficiency of 23%. In: IEEE J. Photovoltaics 9 (1), S. 34–39. DOI: 10.1109/JPHOTOV.2018.2873307.
- [6] Wang, Jianqiang; Meng, Chuncai; Liu, Huan; Hu, Yunfei; Zhao, Lei; Wang, Wenjing et al. (2021): Application of Indium Tin Oxide/Aluminum-Doped Zinc Oxide Transparent Conductive Oxide Stack Films in Silicon Heterojunction Solar Cells. In: ACS Appl. Energy Mater. 4 (12), S. 13586–13592. DOI: 10.1021/acsaem.1c02209.
- [7] Adachi, Daisuke; Terashita, Toru; Uto, Toshihiko; Hernández, José Luis; Yamamoto, Kenji (2017): Effects of SiOx barrier layer prepared by plasmaenhanced chemical vapor deposition on improvement of long-term reliability and production cost for Cuplated amorphous Si/crystalline Si heterojunction solar cells. In: Solar Energy Materials and Solar Cells 163, S. 204–209. DOI: 10.1016/j.solmat.2016.12.029.
- [8] Bartsch, J.; Heitmann, U.; Jakob, L.; Mahmoud Algazzar, R.; Tutsch, L.; Hermann, R. et al. (2020): Spray Pyrolysis – A Versatile Technique for Thin Film Deposition in PV. 4 pages / 37th European Photovoltaic Solar Energy Conference and Exhibition; 44-47. DOI: 10.4229/EUPVSEC20202020-1AO.3.6.
- [9] A. De Rose, T. Geipel, D. Eberlein, A. Kraft, and M. Nowottnick, "Interconnection of Silicon Heterojunction Solar Cells by Infrared Soldering -Solder Joint Analysis and Temperature Study," in *Proceedings of the 36th European Photovoltaic Solar Energy Conference and Exhibition (EU PVSEC)*, Marseille, France, 2019, pp. 229–234.
- [10] L. Tutsch, L. Jakob, C. Luderer, T. Hatt, B.S. Goraya, U. Heitmann, J. Bartsch, B. Bläsi, S. Pingel, A. Moldovan, S. Nold, M. Hermle, M. Bivour (2021), Strategies for Minimizing ITO Consumption in SHJ Modules: Combined Consideration of Electro-Optical Performance and Costs, In: Proceedings of the 38th European Photovoltaic Solar Energy Conference and Exhibition, Lisbon