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SPRAY PYROLYSIS – A VERSATILE TECHNIQUE FOR THIN FILM DEPOSITION IN PV

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ABSTRACT: Different applications of spray coating and spray pyrolysis processes in photovoltaics are presented in this paper. These include the deposition of thin dielectric layers (AlOx, TiOx, ZnO) and layer stacks, the deposition of TCOs and spray coating of organic solutions. The applications range from optically active layers to absorber layers and transparent conductive adhesives in tandem solar cells. Sprayed layers and layer stacks have been shown to be suitable for coating of thin ITO in silicon heterojunction solar cells, for MorphoColor® coating of glass panes and for double layer ARCs in standard solar cells. A sprayed IZO interconnect has been demonstrated in III-V on silicon tandem solar cells.

Keywords: Spray coating, Spray pyrolysis, dielectric layers, tandem solar cells

1 INTRODUCTION

The deposition of thin layers (10-1000 nm) has always been a key factor in solar cell processing. Starting with anti-reflection coating layers (ARCs) even in very early and simple solar cell concepts, the range of applications for such layers has been growing with the increase in cell concepts that are commercialized.

The choice of deposition technique is often a compromise between performance and cost. High quality deposition methods like atomic layer deposition (ALD) are often slow and costly. Even PVD and CVD processes add considerably to the total cell processing cost due to complex machine concepts and process pressure requirements.

Low-cost and high-throughput fabrication processes for PV production are gaining interest [1] as a means to further lower levelized cost of electricity from solar cells. Spray coating features both properties, but has so far not been considered extensively in PV manufacturing application, even though there is much research in the field [2]. The method can deposit thin films of organic materials or inorganic materials (mostly oxides).

The present work gives an overview of the capabilities of spray coating and of spray pyrolysis (heated substrate decomposing the chemical precursor) and its potential uses in photovoltaics, illustrating these with examples from our labs such as thin dielectric deposition for optical applications (cell / module glass), spray coating of perovskite materials, spray pyrolysis of Cu_2SnS_3 absorbers or spray deposition of TCOs for TOPCon solar cells or transparent connecting material for III-V on Si solar cells.

Spray pyrolysis has been used in many different applications in a renewable energy context, such as photovoltaics, batteries and supercapacitors [2]. As a thin film deposition technique, it can in principle be employed in all applications where thin films play a role. The class of materials to be deposited most simply with spray pyrolysis is oxides, which form readily in ambient atmosphere. This allows the deposition of layers and layer stacks, for instance for optical purposes (double layer ARCs, bragg reflectors etc.).

At Fraunhofer ISE, early activities were towards connecting III-V with Silicon solar cells with a sprayed transparent conductive adhesive (TCO) to create monolithic tandem solar cells [3]. This has been achieved with sprayed IZO, which has shown high carrier mobility and low resistivity through the layer from top to bottom due to a directed growth mode. Sprayed IZO has also been tested as contacting layer to both III-V semiconductors and poly silicon with moderate contact resistivity of so far around 200 mΩcm². Apart from tandem solar cells, the layer is currently studied for potential applications in TOPCon solar cells and also in CdTe solar cells.

In an earlier work, spray coating has also been used to complete a perovskite absorber in a hybrid process by spraying methylammonium iodide onto evaporated PbI on pyramid texture [4].

Spray coating has also been used at Fraunhofer ISE to create absorber layers. Spraying of Cu_2SnS_3 layers was successfully accomplished on glass substrates, but no solar cells were created from this material.

2 EXPERIMENTAL APPROACH

On a lab type spray coating setup (Equisonics, Figure 1), deposition processes for different materials have been developed by varying the metal salts in chemical precursor solutions, deposition temperature, nozzle and geometry settings etc. Spray coating can be realized in this setup by moving either an ultrasonic (US) nozzle or a pressure air (PA) nozzle by means of a three axis robot over a substrate, which can be heated with a hotplate (up to 500°C).

A variety of chemical solutions (aqueous and organic) can be sprayed conformally at high rate onto any substrate (currently mostly glass and textiles in industrial application). These can form a film on the surface themselves, or react with the substrate to form a new material. The substrate is typically heated, to drive out solvents, or to induce a reaction. Under atmospheric conditions, different kinds of oxides (e.g., transition metal oxides) can be formed as thin films.

We have deposited materials such as TCOs (ITO, IZO and AZO, Aluminumoxide and Titaniumoxide with such methods. In addition, we have deposited photovoltaic absorber materials.

Figure 1: Laboratory **s**pray coating / pyrolysis tool at Fraunhofer ISE

3 RESULTS AND DISCUSSION

3.1 Deposition of Thin Dielectric Films

Titaniumoxide, Aluminiumoxide and undoped Zincoxide were deposited by spray pyrolysis at different process conditions from methanol or ethanol solutions of titanium-, aluminum- and zinc salts. Focus was on obtaining dense layers at high deposition rate and with good homogeneity over the wafer surface. Figure 2 shows a cross sectional view in SEM of a TiOx layer deposited by spray pyrolysis, which is dense and homogenous. ZnO layers and AlOx layers of similar quality were obtained. Figure 3 shows an ellipsometer map and a photograph of a 4" silicon wafer sprayed with an AlOx layer, the homogeneity is as desired with deviations of few nanometers, with the biggest effect towards the wafer rim.

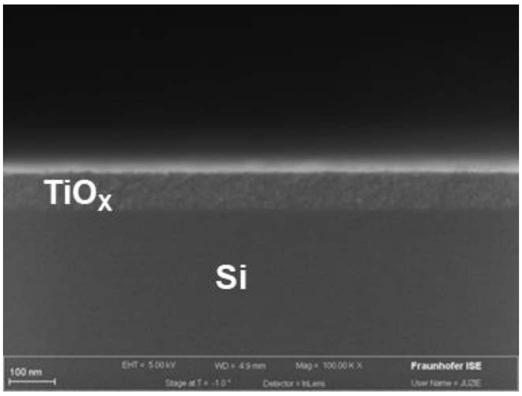

Figure 2: Laboratory **s**pray coating / pyrolysis tool at Fraunhofer ISE

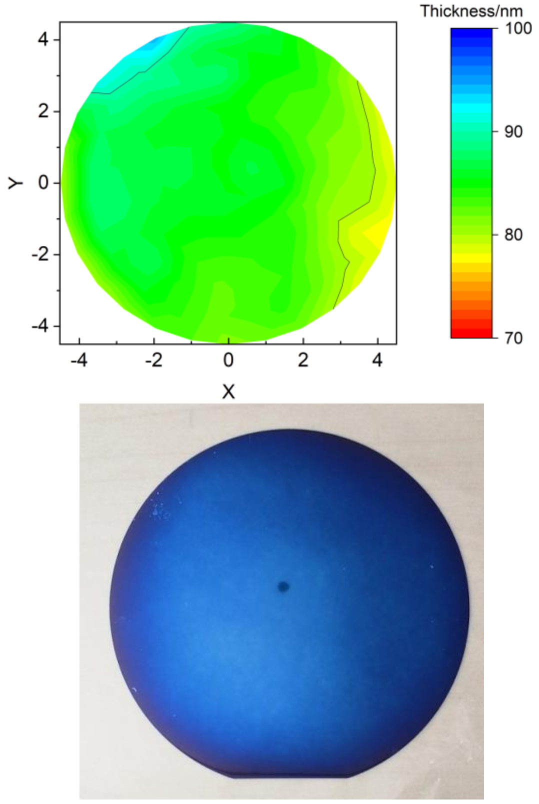

Figure 3: Ellipsometer map (upper image) and photograph of Si wafer spray coated with AlOx. The black dot in the center of the photograph is the reflection of the camera lens.

The deposition rate of these layers ranged from 10 nm/pass to 50 nm/pass at a nozzle speed of 400 mm/s. A simple calculation, assuming an array of several nozzle rows in transport direction of the substrate, yields a potential throughput of 20.000 – 50.000 wafers/hour (M2) depending on application (layer thickness). This is even beyond the goals described in the ITRPV roadmap [1].

The sprayed layers showed refractive indices at 589 nm wavelength of 1.88 (AlOx), 1.96 (ZnO) and between 2-2.4 (TiOx) where the latter refractive index could be influenced by the substrate temperature during deposition (see Figure 4**)**. Aluminiumoxide was originally intended as passivation layer for PERC solar cells, but proved to exhibit only poor passivation properties on lifetime samples (best measured lifetime was ~70 µs, while ALD reference showed >1 ms). As the layer features very high transmission, it is in any case well suited for optical applications.

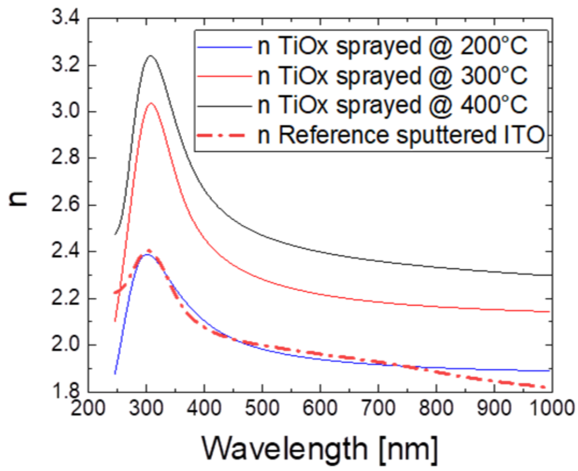

Figure 4: Refractive index of sprayed TiOx in dependence of the substrate temperature during the spray process.

3.2 Sprayed TiOx as capping layer in SHJ solar cells

Layers of Titaniumoxide and layer stacks of TiOx/ZnO were tested as optical layers on solar cells and on glass. TiOx may serve as optical and capping layer in silicon heterojunction (SHJ) solar cells combined with efforts to reduce the layer thickness of the ITO layer [5], yielding both improved stability under module conditions and reduced material cost at similar cell efficiency. In a first experiment, SHJ solar cells with only 21 nm ITO (instead of 75 nm that are typically used) were capped with ~50 nm of sprayed TiOx (deposited at 200°C substrate temperature). As can be seen in Figure 4, when comparing the refractive index to that of sputtered ITO, both refractive indices match very well.

Figure 5 shows the solar cell efficiency of the resulting SHJ solar cells. The cell efficiency of the cells with sprayed TiOx is almost on the same level as the reference group, with the optical properties (mirrored in the short circuit current density J_{SC}) being the same and only the FF (slightly higher series resistance due to thinner ITO layer) suffers to a small extent. The gain in J_{SC} after spray deposition is about 2 mA/cm², V_{OC} is not compromised by the spray process at 200°C (see table 1).

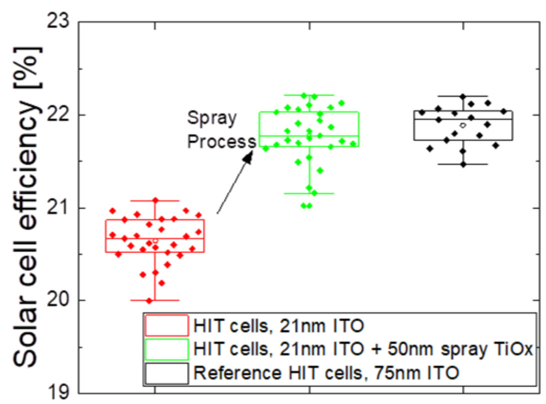

Figure 5: Solar cell results of SHJ solar cells with standard ITO layer (Group 1) and with 30nm ITO layer + sprayed TiOx (Groups 2 und 3).

Table 1: IV Results of SHJ solar cells

2x2 cm² lab cells (avg. values)	**V_{OC} [mV]**	**J_{SC} [mA/cm²]**	**FF [%]**	**Eta [%]**	**R_S [Ωcm²]**
Before TiOx spray	732	34.7	81.3	20.6	0.84
After TiOx spray	**733**	**36.6**	81.1	**21.8**	0.85
Reference 75nm ITO	733	**36.5**	**81.7**	**21.9**	**0.73**

More applications as optically active layers result from the combination of sprayed TiOx with sprayed ZnO or AlOx as layer stack.
Another application that was tested is the combination of TiOx with ZnO. The refractive indices of these two materials match the requirements to create a MorphoColor® [6] coating on a glass pane. In a first experiment, a simple four-layer stack was created to yield the morpho effect. The colour intensity and the transmission are not yet as excellent as reported in literature, but this can be overcome by spraying a layer stack with a higher number of alternating layers. The four layer stack is basically the easiest one that is functional. Optical measurements of the sprayed layer stack confirm the morpho effect and match well with simulations (Figure 6). Figure 7 shows a photograph impression on a glass pane and an SEM cross section of the sprayed layers.

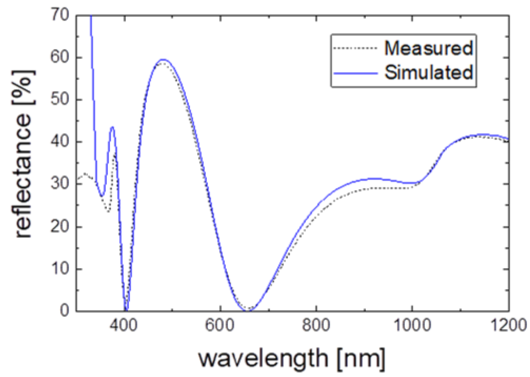

Figure 6: Reflectance measurements and corresponding simulation of the four layer stack of TiOx and ZnO.

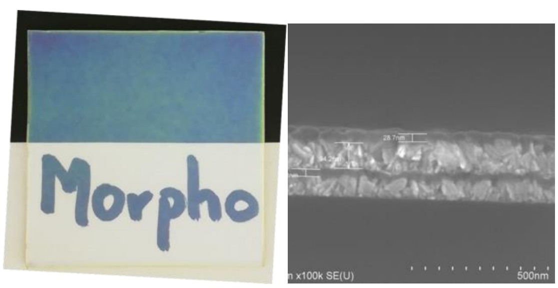

Figure 7: Left image: Photograph of glass coated with morpho layer stack before black background (upper half) / white background with black writing „Morpho“ (lower half). Right image: SEM cross section view of sprayed MorphoColor® layer stack

4 SUMMARY, CONCLUSION AND OUTLOOK

In this study, spray pyrolysis of thin dielectric layer for PV production was introduced in general and with a focus on two specific applications, namely as optical layer for SHJ solar cells with thinned ITO layers and for creating MorphoColor® layer stacks for colored module glass. Both applications were successfully demonstrated, the former with a similar cell efficiency at >70% reduced ITO consumption, the latter with a first coated glass showing the morpho effect, which was not yet optimized but showed the desired function.

The coating of SHJ solar cells with an atmospheric pressure process offers the advantage that after the screen printing step at ambient conditions, the cell does not need to be transferred into vacuum once more, as was proposed by Meyer&Burger [5] who used PECVD to apply the SiNx as optical layer. The sprayed TiOx layer may also improve SHJ cell stability in modules under moisture ingress, which will be tested in the future.

Regarding the glass coating, spray coating is already known in this application, which may be an advantage for its adoption. Also, the coating process can potentially be done right after the float process, which reduces the energy consumption for heating up the substrate. Such a coating is generally referred to as a hard coat, which is particularly stable as chemical bonds are formed between glass and layer. In replacing a sputtering process, spray coating may in addition lower the costs of MorphoColor® glasses for PV module production.

As an outlook, many more applications can be thought of, as there are many applications for thin layers in PV. Next steps will comprise testing sprayed TiOx layers as firing barriers in PERC solar cells on top of ALD AlOx layers.

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