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Transparent conducting oxide deposition techniques for thin-film photovoltaics

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ABSTRACT

Highly conductive transparent films are of significant interest in the field of thin-film photovoltaics. The solar cell type defines the necessary properties of the TCO used. Besides the obvious qualities of transparency and conductivity, stability and morphology are important. The most significant properties of these aspects for front contacts in amorphous/microcrystalline silicon tandem, CIGS and CdTe solar cells are presented in this paper. Commonly used deposition techniques like CVD and sputter technology are described herein, focusing on particular techniques for SnO_2:F and ZnO:B (CVD) and ZnO:Al (sputtering) fabrication. New developments of deposition methods are also discussed.

Introduction

Transparent conductive oxides (TCOs) are a special class of materials, combining the two contradicting physical properties of transparency and electrical conductivity. Electrical conductivity is limited in this application because a high electron density leads to absorption in the near infrared, a result of the interaction between electrons and incoming light. To avoid pronounced absorption, there has to be a trade-off between conductivity and optical transmittance.

Conductivity is often optimized for high transmittance in the spectral range corresponding to the sensitivity of the human eye. In this case, conductivities below $10^{-4}\mu\Omega$cm can be reached, which are close to the theoretical limit of conductivity in current research materials [1,2].

Nevertheless, there are many applications for which the characteristics of high transparency and low resistivity alone do not suffice. Therefore, optimization of the deposition processes has to be adapted to the final application of the TCO films. For photovoltaic applications, the desired properties of the TCO are as follows:

- Minimal optical absorption
- High electrical conductivity
- Durability against environmental impact
- Suitable light trapping due to structured rough surfaces
- High transparency in the near infrared (absorption range of the absorber).

The necessary material properties as set out above are only one aspect of the necessary TCO optimization. The film also has to survive several processing steps that can damage the material, such as the high temperatures used during the production of electronic devices like solar cells, or reactive plasmas (e.g. hydrogen) used for depositing silicon absorbers.

Finally, the whole process of TCO deposition has to be chosen and approached carefully in order to ensure a good integration into the production line and the desired material properties. Temperature-limited processes include the deposition of TCOs on photovoltaic absorbers or the usage of sensitive substrates as foils – it is of utmost importance that the substrate is not affected in any way.

Therefore, the selection of a suitable TCO material for a certain application should involve the consideration of further material properties as well as optical and electrical properties and cost. Some material characteristics can be adjusted with the proper deposition parameters, ensuring that the deposition process is cost effective, below the maximum substrate temperature and capable of being industrially integrated.

The most widely used TCOs are tin-doped indium oxide (ITO), fluorine-doped tin oxide (FTO) and aluminium-doped zinc oxide (AZO). Photovoltaics comprise one of the main application fields of large-area coating with TCOs, while silver-based multilayers that display similar properties to TCOs are employed by default as low emitting films in architectural glass applications. A silver film has to be as thin as 10nm in order to achieve the required transparency. As a result of this and the low chemical stability of silver, these films were applied only on the protected interior glass sides. Recent developments show the thin silver multilayers being implemented more and more often as front electrodes in organic photovoltaics, mainly because of better encapsulation methods being available nowadays.

The development of TCOs needs to heed the advances in thin-film solar technology. In particular, the optical properties and the deposition parameters

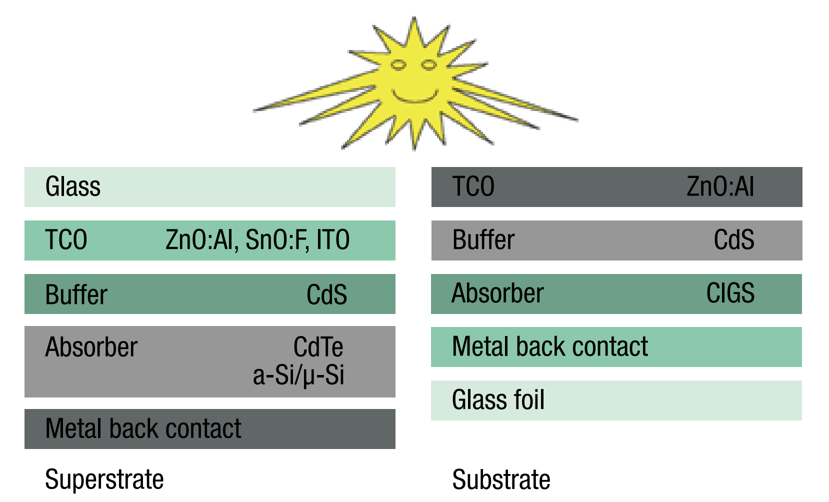

Figure 1. Superstrate and substrate configurations of a solar cell.

have to be adapted to the specific cell type and production process, such as whether the cells are fabricated in the so-called superstrate or substrate (Fig. 1).

Optical transmittance of the TCO film

In both cell configurations (superstrate and substrate), the conversion of incoming light to electron-hole-pair and therefore electrical current takes place in the absorber film. In order to achieve a high conversion efficiency, any loss due to reflectance at and absorption in the TCO has to be minimized. The optical properties have to be adjusted with reference to the absorber properties and not, contrary to some reference literature, to the sensitivity of the human eye. The all-important absorption rate of the absorber is illustrated via the example of amorphous (a-Si:H) and microcrystalline silicon (μc-Si:H), as shown in Fig. 2. As μc-Si:H absorbs up to a wavelength of 1100nm, the TCO should be expected to have a high transmittance in that range.

> "In order to achieve a high conversion efficiency, any loss due to reflectance at and absorption in the TCO has to be minimized."

The free charge carriers in TCO films show a metallic optical behaviour in the infrared and have a high reflectance [3]. The transition frequency, where high transmittance changes to high reflectance, is known here as plasma frequency ω_p and is connected to the carrier concentration n_e in the film as shown in Equation 1.

$$\omega_p^{\ 2} = \frac{n_e \cdot e^2}{m^* \cdot \varepsilon} \qquad (1)$$

where *e* is the electrical charge of an electron, m* is its effective mass and *ε* is the dielectrical constant. The higher the free carrier concentration, the higher the frequency at which TCO films become transparent.

The TCO film can be optimized only with a low carrier concentration, brought about by a low doping or by applying specific deposition techniques. In addition, the conductivity of the TCO, which is proportional to n_e, must be maintained at a high enough level if the sheet resistance of the films is to be kept constant. Alternatively, thicker films are required.

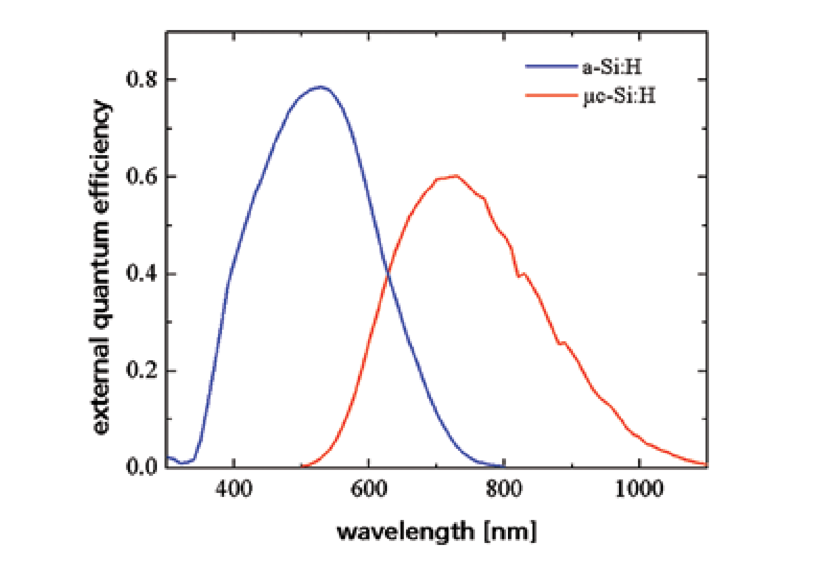

Figure 2. Quantum efficiency of a-Si:H (red)/μc-Si:H (blue) solar cells. Cell deposition and EQE measurements were performed at IEF5 Forschungszentrum Jülich.

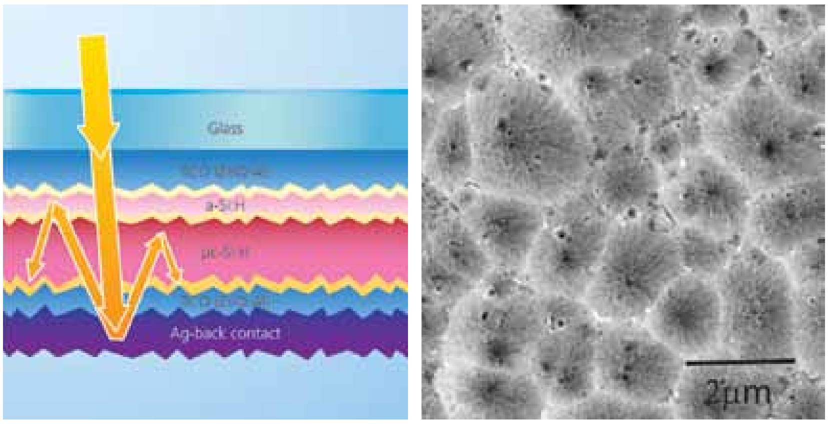

Figure 3. Sketch of light trapping in a thin-film silicon solar cell (left); optimized and etched AZO film from Fraunhofer IST (right).

Light trapping

A low absorber thickness in thin-film silicon solar cells leads to an incomplete light absorption. In order to overcome this

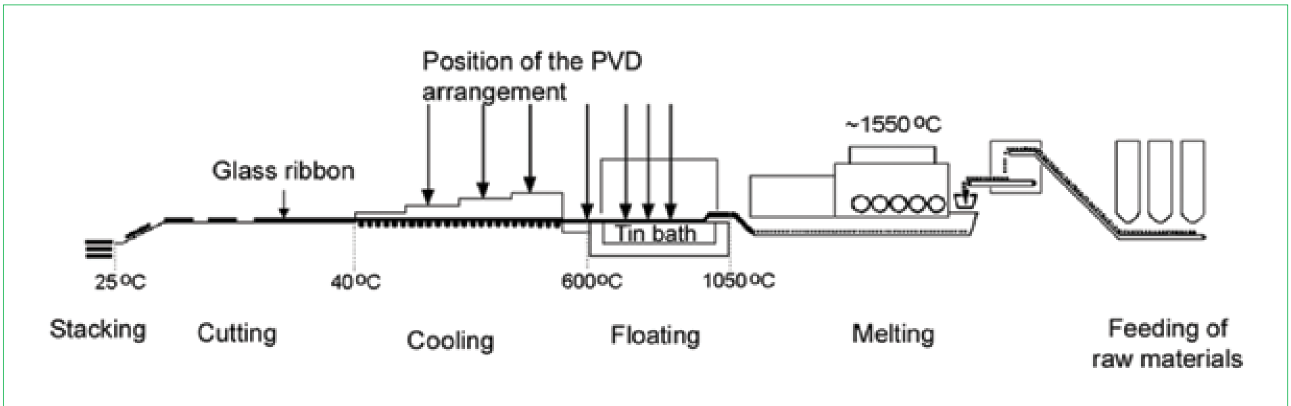

Figure 4. Sketch of a float line with an inline CVD coating and its position in relation to the required temperature [8].

drawback, either the absorber films can be thicker, which means longer deposition times, or the internal light pass of the incoming light has to be increased. In a-Si:H-based solar cells, it is necessary to avoid thick absorbers, as this will increase cell degradation as a result of the Staebler-Wronski effect. Therefore, efficient light-trapping schemes should be used in these cells. As light falls onto a cell's surface, the light rays are scattered and pass through the cell at different angles. The light then undergoes reflection at the back reflector. If this angle of reflection is bigger than a critical angle, total reflection occurs at the TCO/glass interface. Multiple internal reflections occur in this way until the major part of the light has been absorbed. This process is similar in principle to an optical fibre.

Literature on the subject has informed us of approaches such as the roughening of TCO films like AZO in a post-deposition etch step in diluted HCl in order to effect a strong light scattering behaviour at the TCO surface [4]. This scattering is strongly dependent on the deposition parameters of the film. Using this method effectively scatters the light into the cell, increasing the short-circuit current and the conversion efficiency of the solar cell.

Stability of TCO

The stability of the TCO is crucial. Depending on the chosen configuration (substrate or superstrate) and the deposition process, the quality of TCOs can suffer under certain conditions. In the superstrate configuration for thin-film silicon, the silicon process takes place in hydrogenated plasma. Hydrogen can reduce the TCO, which leads to a loss in transmittance. Zinc oxide (ZnO) shows the highest stability against activated hydrogen [5].

Whereas the deposition takes place at temperatures of 200°C for thin-film silicon, the CdTe and CIGS process needs a considerably higher temperature of over 500°C, which poses a high risk for degradation of the TCO. In response to this, TCOs with a higher temperature stability are used, such as SnO_2:F and ITO for CdTe, and ZnO:Al for CIGS solar cells' substrate configuration. These encapsulated solar modules show good stability, withstanding the typical damp heat test conditions of 85% relative humidity at 85°C for 1000 hours to gain EN/IEC 61646 certification. Nevertheless, non-encapsulated modules tend to exhibit a severe degradation in this test [6], caused by an increase in resistivity of the ZnO:Al [7]. This topic is subject of ongoing research, as discussed in the following sections.

Manufacturing technology for TCOs

There are various different technologies available for the production of TCO coatings. The more commonly used approaches are outlined in the following.

Chemical vapour deposition technologies

Using the online APCVD (atmospheric pressure CVD) technique, electrically conductive layers based on SnO_2:F can be produced on a large area at a float glass drawing velocity of 9m/min. In this process, precursors are dissolved in an organic or inorganic solvent and dispersed in a carrier gas like nitrogen, and then supplied to the float glass at temperatures between 500 to 700°C [8]. A schematic sketch

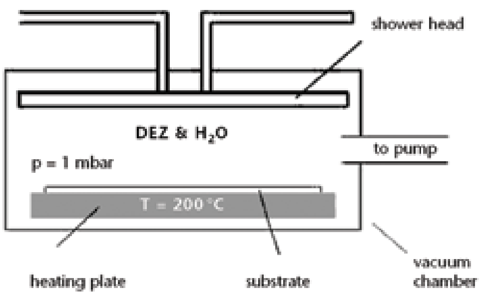

Figure 5. Typical assembly of an LPCVD reactor [10].

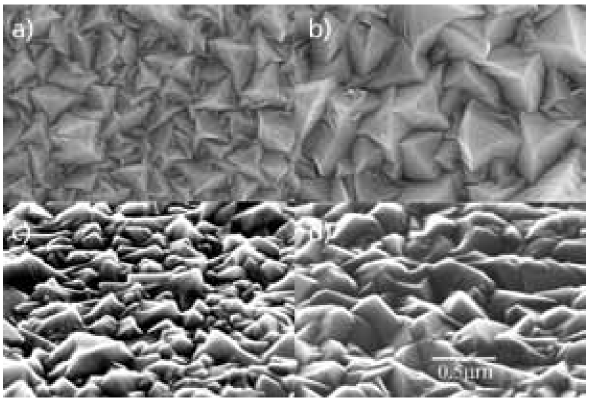

Figure 6. Examples of difference in morphology of CVD-deposited TCOs: a) and b) ZnO:B from LPCVD deposited under different conditions (topview); c) SnO_2:F from NSG; d) SnO_2:F from Asahi (60° tilted).

	Horizontal	Vertical
Carrier	No	Yes
Carrier return	No	Necessary
Large substrate size	Yes	Complex
Problem with back-side deposition	Yes	No
Deposition to edge	Yes	Problematic
Particle contamination	Problematic	Low

Table 1. Comparison of horizontal and vertical sputter coater geometry.

of such a line is shown in Fig. 4. The main advantage of this process is that it is carried out at atmospheric pressure and therefore offers lower production costs than vacuum-based deposition technologies. This kind of concept is widely used by companies such as Nippon Sheet Glass, Pilkington, AFG Industries or Saint Gobain.

SnO_2:F coatings produced in this way are commonly used in CdTe and amorphous silicon solar cells. For application in amorphous microcrystalline silicon tandem solar cells, attaining higher efficiency requires a more sophisticated film morphology regarding the light-trapping issue. Offline CVD is used by the Asahi Company to reach larger and more homogenous feature sizes, such as the Ashai U type.

Another possibility for producing optimized light scattering for so-called 'micromorph' cells was introduced by Oerlikon by applying the LPCVD (low pressure CVD) technique. Typically, boron-doped ZnO is deposited at low pressure with diethylzinc and water vapour and diboran as doping gas [9]. The deposition takes place at ~ 50Pa at substrate temperatures of approximately 200°C. A sketch of the process can be seen in Fig. 5 [10].

A similar process entitled MOCVD (metal organic CVD) is used at Solar Frontier for the deposition of ZnO:B on CIGS solar cells. Research is also being carried out for plasma-enhanced MOCVD [11]. Variable morphologies can be reached using the different CVD techniques, as shown in the SEM picture in Fig. 6.

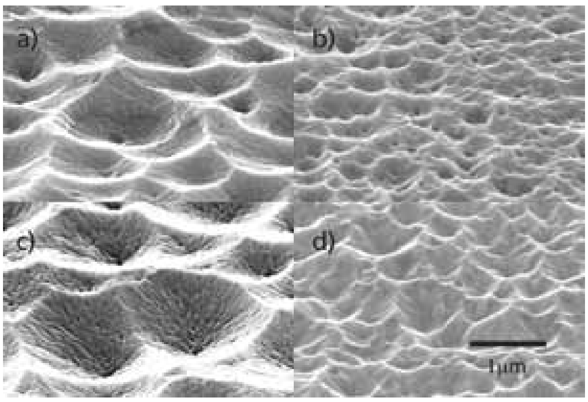

Figure 7. Examples of difference in morphology between sputtered ZnO:Al samples at Fraunhofer IST: a) RF; b) DC; c) DC with seed layer; d) reactive MF.

State-of-the-art sputter technology

Magnetron sputtering is the standard deposition technique for transparent front contacts in industrial production of chalcopyrite solar modules. It is easy to scale up, and substrates up to $18m^2$ can be coated in coaters designed for deposition of architectural glazings. For aluminium-doped zinc oxide (AZO), sputtering of ceramic ZnO:Al_2O_3-targets or reactive sputtering of metallic Zn:Al-targets can be carried out. Because of the sophisticated control that is needed for reactive sputtering, ceramic targets are normally used. Intensive work has been carried out on the optimization of target materials [12]. Nowadays, more and more production lines use rotatable targets for their higher material utilization and therefore higher throughput than planar targets. Benefits and drawbacks of horizontal and vertical coaters, two different concepts for magnetron sputtering coaters, are shown in Table 1.

Both types of coaters are available from a variety of companies; a good overview of TCO equipment for sputter and CVD coaters can be found in [13].

Because the absorber buffer interface is not stable above substrate temperatures of 200°C, the AZO deposition for CIGS solar cells takes place at this temperature. For the amorphous/microcrystalline tandem solar cell, higher deposition temperatures are possible because of the superstrate technology used in these cell types. As mentioned, an effective light trapping is crucial for a good performance of these cell types.

In order to prevent shunts, the particle density on the substrates also has to be lowered significantly. Magnetron cathodes are themselves a potential particle source, as oxide material is re-deposited at the edges of the racetracks and forms dust. Moving magnets [14] or rotatable targets offer a possible solution as the target surface is kept clean during the process.

Recently, Applied Materials deposited highly-conductive ZnO:Al films by magnetron sputtering from a rotatable ceramic target and post-etched the films in diluted hydrochloric acid. The crater-like etching morphology is responsible for a good light-trapping behaviour and an stable efficiency of 10.5% was reached for a micromorph silicon module (a-Si:H/μc-Si:H) on the $1.43m^2$ size [15]. Applied Materials used a horizontal ATON coater for TCO deposition for $5.7m^2$ substrates. Rotatable targets offer a very good

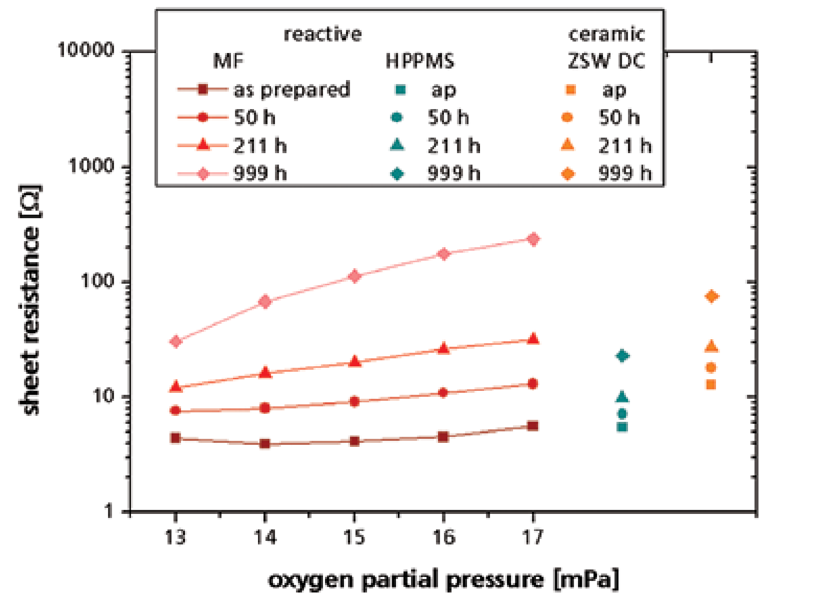

Figure 8. Damp heat stability of ZnO:Al films on CIGS substrates deposited by reactive sputtering MF at 180°C and reactive HPPMS sputtering at 190°C versus a DC process from ZSW Stuttgart.

utilization of target material and stable deposition conditions over the target lifetime and during deposition.

Sontor built up a vertical in-line facility, the 'New Aristo 1200L', as supplied by Applied Films, now Applied Materials. In production, the company uses SnO_2:F as TCO, but research is now focusing on ZnO:Al planar ceramic ZnO:Al_2O_3 targets, which are DC sputtered. A planar Movemag is used to improve the target utilization. The glass substrate has a dimension of 1.78m^2 and the substrate temperature during deposition is selected at below 300°C. As the process is currently being upscaled, efficiencies reached were higher than for conventional SnO_2:F [16].

For further cost reduction, the reactive sputtering from metallic targets will likely be established over the next few years. Many efforts are ongoing to come to a stable process control [17,18].

Different morphologies are reached using different sputtering conditions. Typical structure size is shown in the SEM examples in Fig. 7. An optimized morphology is typically deposited with RF sputtering [19]. With pure DC from ceramic targets, slightly smaller feature sizes can be reached [20]. The morphology of etched reactively sputtered ZnO:Al is dependent on the operating point during sputtering [21]. Reactive mid-frequency magnetron sputtering (RMFMS) from metallic zinc targets is also an interesting option for CIGS solar cells. This approach with reactive MF sputtering is described in [22,23].

Sputter technology development

A further option in the quest for higher damp heat stability in CIGS solar cells is the use of high power pulse magnetron sputtering (HPPMS), also known as high power impulse magnetron sputtering (HiPIMS) technology [24].

The sheet resistance of an AZO film on a CIGS substrate was measured before and several times during damp heat testing at ZSW Stuttgart, the results of which

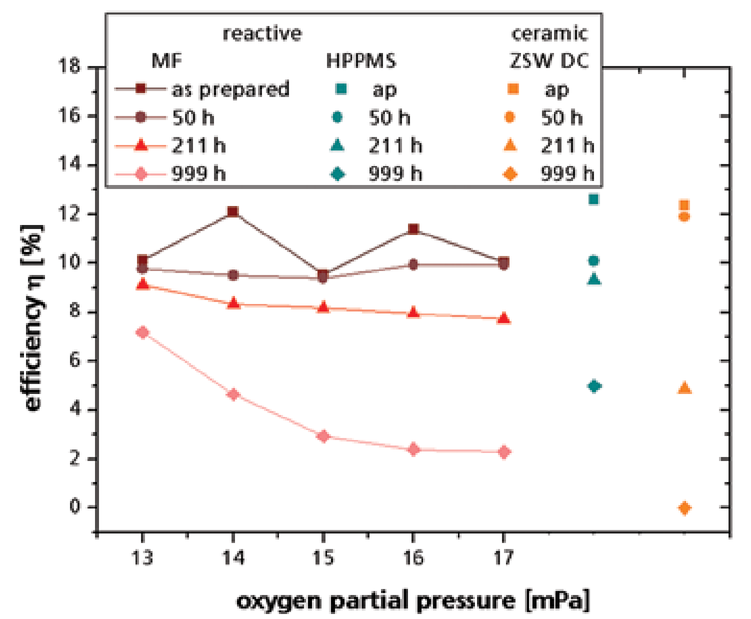

Figure 9. Damp heat stability of mini-module efficiency deposited by reactive sputtering MF at 180°C and reactive HPPMS sputtering at 190°C in comparison with a DC process from ZSW Stuttgart. All module characterization and manufacturing were performed at ZSW Stuttgart.

are visible in Fig. 8. A film deposited by DC sputtering from a ceramic target and from the reactive MF process is included for the purposes of comparison. The reactively sputtered HPPMS films on CIGS substrates show the lowest degradation compared to the conventional reactively sputtered MF films and the reference film coated with DC process, as performed at ZSW Stuttgart.

Fig. 9 shows the efficiency of the mini modules made at ZSW Stuttgart. Aside from the good damp heat stability, the efficiency for the HPPMS-sputtered ZnO:Al shows the best performance compared to the other deposition techniques.

Fig. 10 shows SEM pictures of cross-sections of the mini-modules. A more dense columnar structure of the AZO layer is observed for HPPMS compared to an MF-deposited film at 180°C as well as a DC-sputtered film at 150°C substrate temperature.

This is attributed to higher ad-atom mobility on the growing film. The increased mobility can also explain a better coverage of the CIGS grain boundaries that form macro grain boundaries in the AZO layers, which are known to limit damp heat stability severely [25].

It should be taken into account that this investigation's remit was restricted to one set of process parameters for AZO on CIGS. Therefore, research on partial pressure variation as well as charge voltage variation is an optional field for further improvements.

Further research

Another possible deposition technique for ZnO:Al is the so-called expanding thermal plasma CVD process. The method was tested in a-Si solar cells with a comparable efficiency to Asahi's U type [26]. Many other options exist for developments in producing TCOs with vacuumless techniques. For example, sol gel technology shows the feasibility for TCO deposition of n-type materials (such as ZnO:Al and ITO) and p-type materials (such as $CuCrO_2$), more details of which can be found in [27]. The electrodeposition technique has the ability to deposit a ZnO film on electrical conducting substrates [28]. Both of these processes would be attractive for a reel-to-reel process, which has a high cost reduction potential.

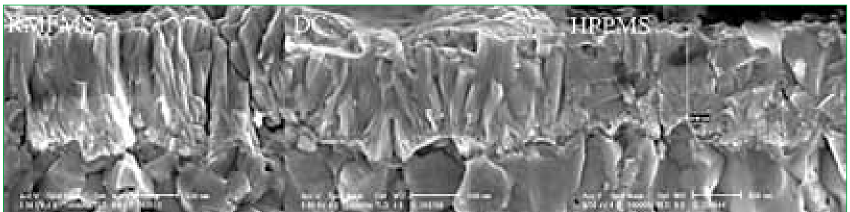

Figure 10. SEM pictures of cross-sections of CIGS mini modules measured at ZSW Stuttgart. The pictures show the top part of the module structure with the ZnO:Al layer. The samples show (left to right): reactive MF sputtering at 180°C; DC sputtering of ceramic target at 150°C; and reactive HPPMS sputtering at 190°C.

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Florian Ruske is a senior scientist at the Institute for Silicon Photovoltaics of the Helmholtz-Zentrum Berlin (HZB). He works on transparent conducting oxides and functional layers for silicon-based photovoltaic devices. He studied physics at the University of Bonn and afterwards worked at the Fraunhofer IST in the Large Area Coating department as a Ph.D. student. He received his doctoral degree from the University of Gießen in 2008 for a thesis on reactive sputtering of Al-doped ZnO for photovoltaic applications.

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