Comparison of different ceramic Al-doped ZnO target materials

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ABSTRACT

Highly conductive transparent films are of significant interest in the field of thin-film photovoltaics. ZnO-based films in particular have attracted much interest due to the low cost of materials with good film properties for CIGS and a-Si/µc-Si solar modules. Investigations have been ongoing at Fraunhofer IST into ceramic $ZnO:Al_2O_3$ targets from different manufacturers. This paper presents a comparison of target material, sputter characteristics and film properties of ZnO:Al. Sputter characteristics are in this case determined by voltage and current data showing arcing rates at different power loads and process pressures. ZnO:Al films are deposited by DC magnetron sputtering with various deposition parameters (e.g. oxygen flow, total pressure, sputtering power and substrate temperature) and investigated with respect to optical and electrical properties. A correlation between film properties, sputter characteristics and target material can therefore be determined. As it appears that arcing has the biggest influence on film properties, the ceramic target material can be optimized for minimal arcing.

Introduction

On a global scale, around 30 different companies use $Cu(In,Ga)(Se,S)_2$ as the absorber material for their thin-film solar modules [1]. Reduction of production cost is desirable for future production, either at the deposition process of individual films or by lowering the encapsulation effort. The final film deposited in the module stack is a transparent front contact on top of the absorber and intermediate layers, usually consisting of Al-doped zinc oxide (AZO) and deposited by magnetron sputtering. This process is crucial for overall performance, as high sheet resistance, low transmission or insufficient damp heat stability can severely limit module performance.

In industrial production of chalcopyrite solar modules, magnetron sputtering is the standard deposition technique for transparent front contacts. It is easy to scale up, for example, substrates of up to $18m^2$ in area are coated by sputtering

Process	DC excitation at 0kHz, AE Pinnacle Plus generator, PK 750 cathode		
System parameters	Distance target-substrate	dST	90mm
	Target material		$ZnO:Al_3O_3$ (A-D)
	Argon gas flow	qAr	200, 198, 196 sccm
Process parameters	Mixing gas flow		
90% Ar, 10% O_2	qMG	0, 2, 4 sccm	
	Substrate temperature	TS	150, 200°C
	Discharge power	P	4, 6, 8kW
	Total pressure	ptot	0.2, 0.6, 1Pa
	Substrate		Float glass, AF45 glass, Si

Table 1. Deposition parameters for the Al-doped ZnO films presented in this paper. Deposition was carried out in the A700V vertical in-line coater at Fraunhofer IST.

	Result
Density	95–99% TD
Resistivity	0.8–7.0*$10^{-3}\Omega$cm
Phase composition	96% ZnO (hex.) 4% $ZnAl_2O_4$ (cub.)
Impurity	Purity 3N

Table 2. Result of different target material properties.

with architectural glazings. For the TCO film, the cost is determined by both the film quality that can be obtained and the process involved. If a the conductivity of a TCO film can be doubled by a certain deposition process, in general a film of half the thickness will be sufficient for the solar cell in general. This is not only beneficial for the saved material, but thinner films will also absorb less light.

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In the AZO deposition process, the films can be deposited by sputtering of ceramic $ZnO:Al_2O_3$ targets or by reactive sputtering of metallic Zn:Al targets [2]. In the latter case, oxygen is introduced as reactive gas. Consequently, a metallic target of the same thickness as a ceramic target can reach longer operation times and more absorber area can be coated without the need for changing the target. Coupled with the much lower cost for a metallic target, this means that the cost for the TCO film will be considerably lower for films sputtered from metallic targets as compared to films sputtered from ceramic ones.

Unfortunately in the case of reactively sputtered TCO films it is more difficult to realize homogeneous electrical and optical properties on large-area substrates [3,4]. It is also more difficult to stabilize the operating point at low substrate temperatures (i.e. below 200ºC). Furthermore, the substrate temperature during deposition of AZO on chalcopyrite absorbers is limited to 200ºC. Therefore ceramic targets are still used, preferably as rotatable tube targets.

Experimental

AZO target materials from four different manufacturers have been benchmarked at Fraunhofer IST. This process involved the target materials being evaluated for structural analysis by XRD measurements with a Panalytical MRD Pro using Cu K_α radiation. GDMS (glow discharge mass spectrometry) was used for elemental analysis. Resistivity of the target materials was determined by Hall measurements at room temperature using van der Pauw geometry. The microstructures were investigated using a LEO 1530 field emission scanning electron microscope (SEM).

We operated a PK750 cathode in the Leybold A700V in-line coater with DC excitation by an Advanced Energy Pinnacle Plus power supply operating at pure DC. For evaluation of the sputter behaviour, current-voltage characteristics as well as arc characteristics were determined using the detection system of the power supply.

In order to get a correlation of target material, sputter conditions and the film quality, a screening design of different parameters like pressure, oxygen gas flow and power was carried out at two different temperatures (150°C and 200°C) (see Fig. 1).

The gas flow of argon and oxygen was always kept constant at 200 sccm (standard cubic centimetres per minute). The deposition conditions using ordinary float glass as substrate are summarized in Table 1. In order to determine if there are disturbance variables, the sequence of depositions with different screening parameters were randomized and the series was repeated. This was done for temperatures of 150°C (series 1 and 2) and 200°C (series 3 and 4).

Film thickness was determined by setting optical transmittance and reflection from 250 to 2500nm (Varian Cary-5) and spectroscopic ellipsometry at variable angle (SEVA) from 250 to 850nm (Sentech SE 850). The dielectric function was established using a model for the fundamental absorption proposed by Leng and a model for the IR free carrier absorption as proposed by Sernelius [5]. The visual absorption α_V was determined by convolution of the measured spectral transmission with the spectral sensitivity of the human eye. Sheet resistance was measured with a four-point probe and the resistivity calculated from the obtained thickness and sheet resistance.

Results

Characterization of the target material

The application of AZO in different products, e.g. thin-film solar cells (CIGS or micromorph silicon) or architectural glazing can vary the role of the target material. Therefore the material has to be optimized for its special purpose. It is also important for customers that material from different producers shows film properties that are as comparable and constant as possible. For this reason the target material of the four different target producers was characterized in order to find a correlation between the ceramic materials, the sputter behaviour and the obtained film properties.

Table 2 shows the results of different target material properties. The target density showed no influence on the arcing behaviour of the sputtered target material in the measured range, nor was there any correlation of the varied target resistivity on arcing or on the target voltage.

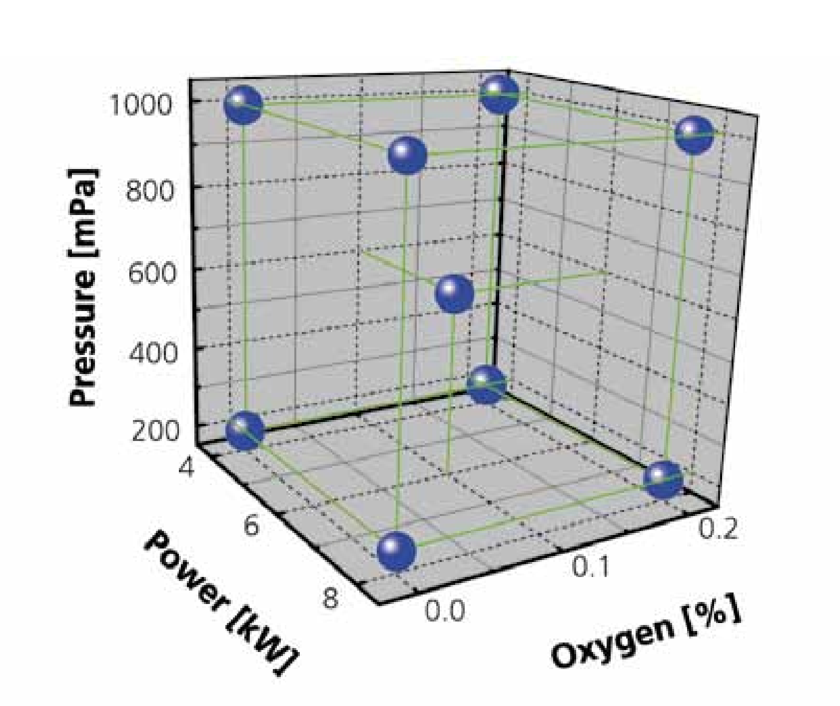

Figure 1. Chosen parameter variation for screening.

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All targets examined by XRD showed an identical phase composition consisting of the same amount of ZnO and gahnite ($ZnAl_2O_4$). The impurity level of the ceramic materials determined by GDMS was 3N or better. The majority of the elements are below 10 ppm. One target showed a slightly higher Fe and Si content, which probably has some influence on arcing. All materials' microstructures (SEM) and element distribution (EDX) were measured, which showed a broad range of variation, thus proving the main influence of the arcing behaviour.

Sputter characteristics

Prior to film deposition, the targets were first pre-sputtered under different power and pressure conditions in order to obtain information on the current-voltage characteristics and their arcing behaviour. All materials were problem-free during the pre-sputtering process; micro-arcing was the only behaviour exhibited, which correlates with the different material characteristics. The micro arcs increased with higher pressure and higher power.

However, the targets showed slightly different current-voltage behaviour (see Fig. 2). Although target A showed a lower voltage, which was not reproducible during the sputtering of the films, it also showed an extremely small micro-arc rate, which was reproducible. Thus all targets demonstrated similar current-voltage behaviour, leading us to conclude that the resistivity of the target material has no influence on arcing.

Film properties

All targets were sputtered under the same conditions using the aforementioned screening. Sputtering was carried out on every target at one temperature and varying pressure, power and oxygen flow within one day to restrict potential troubles from disturbance variables. By default, the deposited films were then evaluated with respect to their optical and electrical

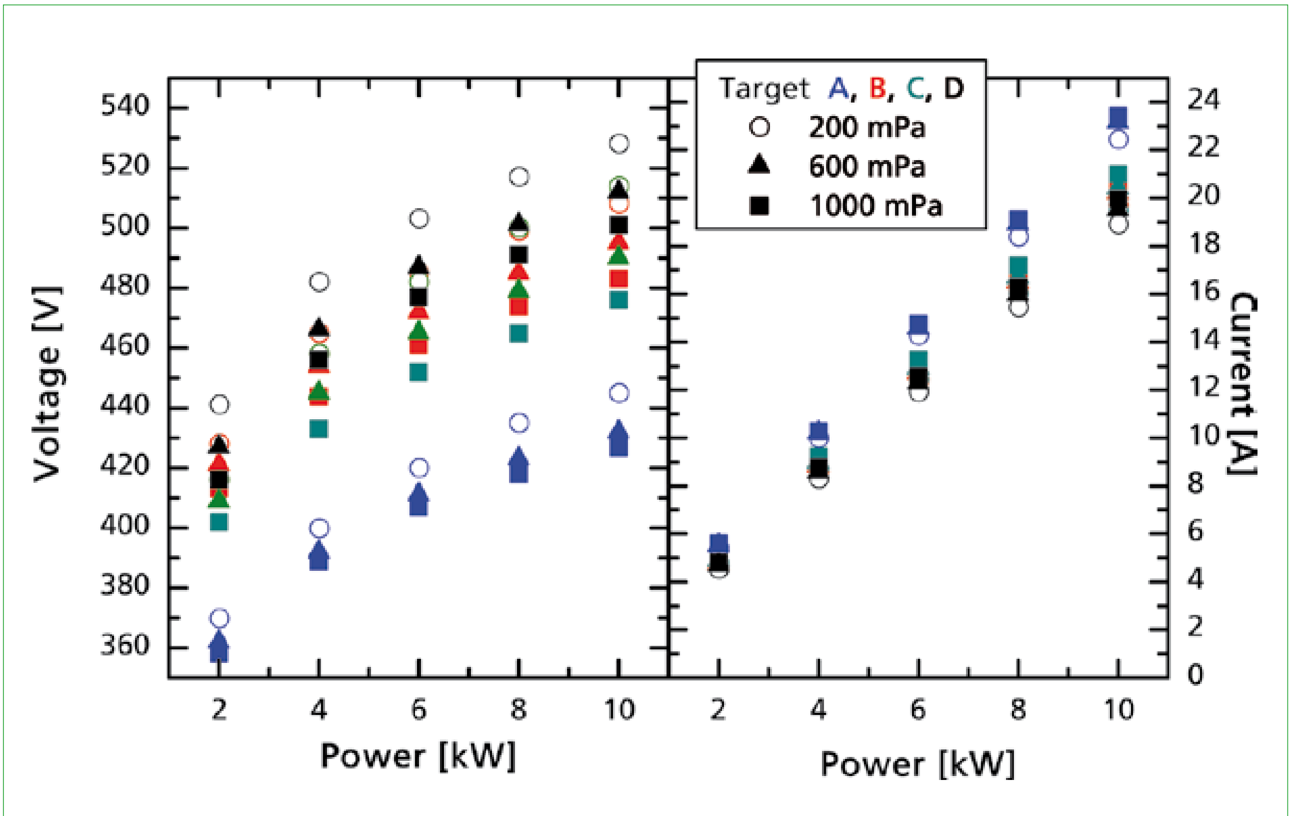

Figure 2. Target voltage and current as a function of power for different total pressure and target material.

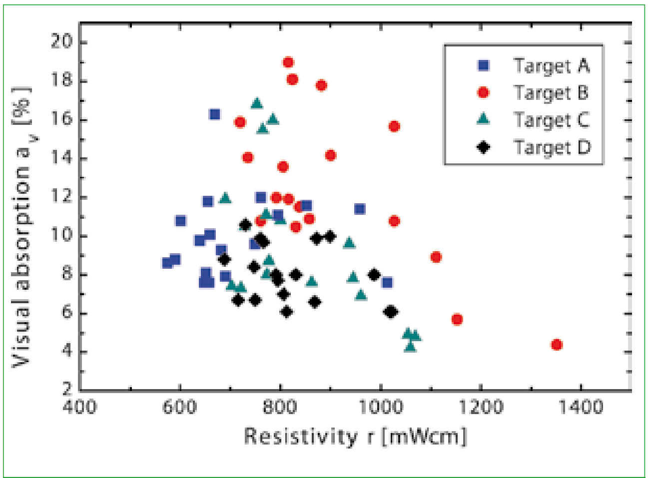

Figure 3. Performance of ZnO:Al films deposited by using various sputtering parameters at a substrate temperature of 150°C for different target material.

properties. All films had a similar thickness of 900nm, which was adjusted by different carrier velocities for the different power levels. For the replicate, a block construction was used to determine the main disturbance variable. It was found that the behaviour of equally deposited films changes rapidly when comparing a new target with the same target in the eroded state with a deeper race track [6]. On examination of the accumulated data, it appears that this change occurs in the middle of the replicate of the first series (not shown here). It can be deduced that properties are quite stable and any change is minimal.

An examination of the films for different target materials was carried out, which provided an overview of the determined variables' resistivity and visual absorption (Figs. 3 & 4). Target erosion was the main influence during the first two series at 150°C.

The behaviour of the varied parameters was also evaluated. In series 3 and 4, the target state was no longer relevant at 200°C. It was found that temperature had the main influence on lowering the visual absorption drastically and reducing resistivity for all targets in all four series. As depicted in Fig. 5, the arcing of the targets had the greatest influence on the film properties. The graph shows the micro-arc behaviour that occurred during the film deposition of series 3 and 4 at 200°C as a result of the applied target voltage. The micro-arc rate is normalized to 1kW for comparability. As mentioned before, the target voltage of target A during deposition is nearly the same compared to the other targets, but the arc rate was drastically lower. The increase of the micro-arc rate was dependent on the material itself.

"All targets have a non-linear behaviour in regards to the amount of oxygen present and thus require individual optimization for each target."

Fig. 3 and Fig. 4 show a strong correlation between micro-arc rate and film properties. Target A with the lowest micro-arc rate shows the lowest resistivity overall.

The optimized sputter conditions for every single material were determined. Fig. 6 and Fig. 7 show the response surface of resistivity and optical absorption for the different parameters (variables) using target A.

A response surface shows extrapolated data. Two variables are free; the other two are fixed to the centre point conditions, and for this reason, no real data point except that of the centre points (q,P,p) can be found in these plots. Nevertheless, the effects of each variable are properly shown.

For all material types, a low pressure is important for low

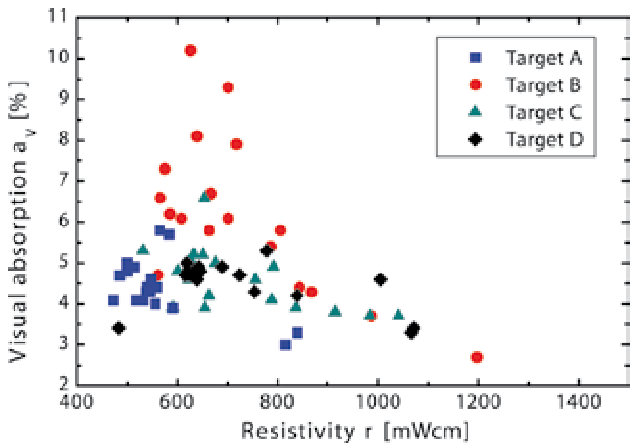

Figure 4. Performance of ZnO:Al films deposited by using various sputtering parameters at a substrate temperature of 200°C for different target material.

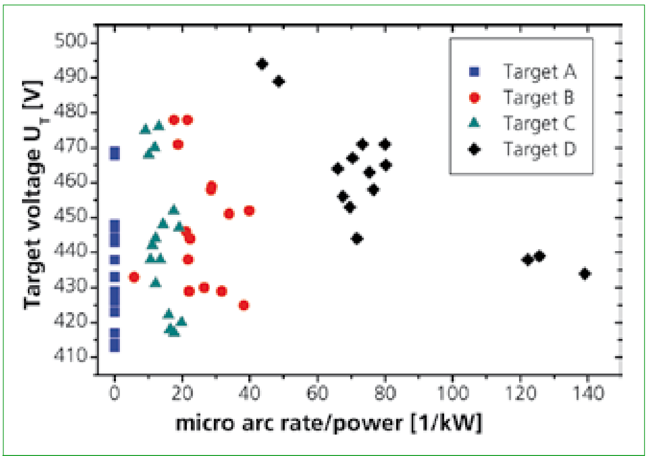

Figure 5. Target voltage as a function of normalized micro arc rate.

resistivity. The oxygen dependence was, however, more complicated. All targets have a non-linear behaviour in regards to the amount of oxygen present and thus require individual optimization for each target. Three out of four targets showed an optimized resistivity at low power, but in an industrial environment high power is necessary for high throughput. In the screening process, resistivities below 480μΩcm were reachable with visual absorption lower than 4% by standard DC sputtering at 200°C.

Conclusion

The main influences on resistivity and absorption are the target material's arcing behaviour, high temperature and low pressure. Power and oxygen amount are highly dependent on the target material. The ceramic target material could be optimized for minimal arcing during this project with the help of the different target producers. If the target material cannot be further improved in relation to arcing, the arc handling of the power supply can also be enhanced. All in all, the higher the temperature, the better the result. Our low temperature process technique for ZnO:AL deposition meet the constraints of CIGS thin-film photovoltaics.

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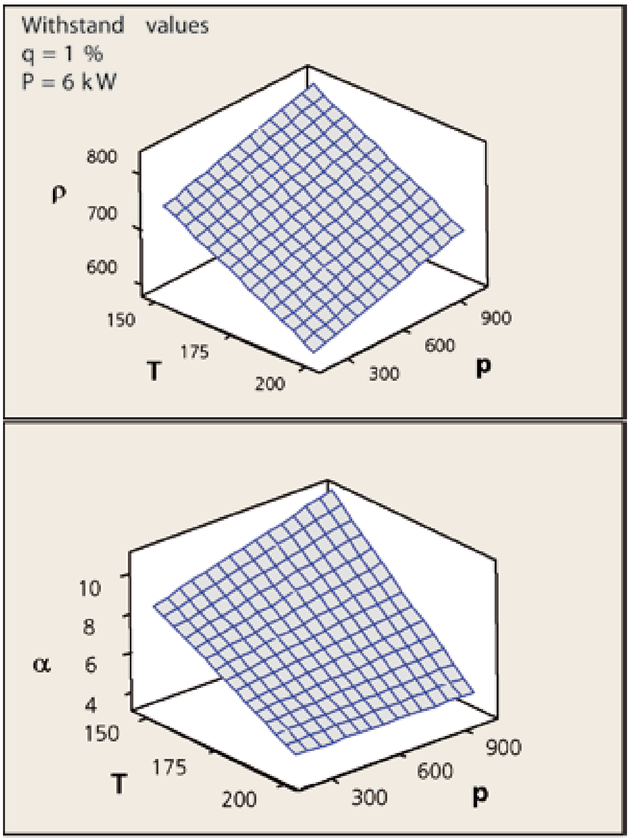

Figure 6. DOE analysis example for target A. Resistivity and visual absorption as function of temperature and pressure at fixed withstand values.

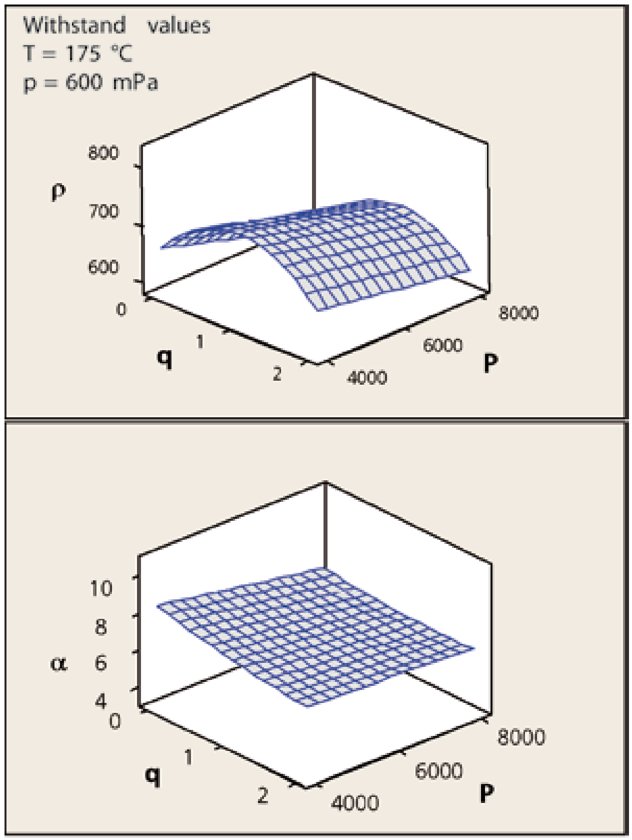

Figure 7. DOE analysis example for target A showing resistivity and visual absorption as a function of oxygen amount and power at fixed withstand values.

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