This paper first appeared in the thirteenth print edition of the *Photovoltaics International* journal, published in August 2011.

Reactive magnetron sputtering of ZnO:Al

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ABSTRACT

Transparent conductive oxides (TCOs), such as aluminium-doped zinc oxide (ZnO:Al), play an important role in thin-film photovoltaics. As a material for front contacts, ZnO:Al is standard in industrial-scale production, especially in the field of Cu(In,Ga)Se_2 solar cells. Over the last few years, there has been a strong push to use ZnO:Al films on glass as substrates for amorphous or amorphous/microcrystalline silicon solar cells, and these films have now been introduced as an alternative to the typically used fluorine-doped tin oxide (SnO_2:F) films in production. Sputtering coaters for large area deposition of ZnO:Al are widely available, and ZnO:Al films are produced in these coaters by sputtering of ceramic targets. This technology offers high process stability and is therefore favoured over reactive sputtering of metallic targets. With respect to cost and quality, however, the reactive process is an interesting alternative. In this paper we will give an overview of the process of reactive sputtering of ZnO:Al and discuss the most important insights.

Introduction

Despite the advantages of reactive sputtering, the process of sputtering of ceramic targets has taken the lead in industrialization, due to the simplicity of process operation. Once suitable deposition conditions have been established, the process is easy to control and promises high yields. In contrast, the reactive sputtering process has to be thoroughly controlled. Nevertheless, reactive deposition via magnetron sputtering is a well-known technique for the deposition of oxides and nitrides. During this process a metallic target is sputtered, with oxygen or nitrogen acting as a reactive gas. Stoichiometric films are typically reached under excess of the reactive gas.

In general the operation can be conducted in two stable modes. If oxygen is fed into the discharge zone in abundance, the metallic target will form an oxidized surface and the process is characterized by low deposition rates and films with high transmission. This mode is referred to as 'oxide mode'. On the other hand, in 'metallic mode', oxygen partial pressures are low and the target will essentially be sputtered as clean metal. The resulting films are deposited at high rates but usually suffer from sub-stoichiometry and hence high optical absorption. Fig. 1 shows the typical hysteresis behaviour that often occurs during the process of reactive sputtering of ZnO:Al. Such curves are predicted from the Larson model [1]. An accurate description of the reactive process can be found in Berg & Nyberg [2] and Depla & Stijn [3]. In order to obtain both highly transparent and highly conductive films that are necessary for transparent conductive oxides (TCOs), the reactive process has to be controlled in the normally unstable transition mode. Different control mechanisms are possible to stabilize such a process. Mass spectrometry or a lambda sensor would be a direct method for the measurement of the partial pressure. An indirect method would be the use of the target voltage (impedance) [4] or the optical emission spectroscopy (OES) of the sputtered atoms of the reactive gas [5] to determine the partial pressure. To stabilize the partial pressure with this signal, it is necessary to adjust, for example, the power as shown in Fig. 1 or adjust the gas flow. Nevertheless, in either case a high-speed control is necessary. Dependent on the material and reactive flow rates, sometimes a very fast control of a few milliseconds is essential, especially for TCOs.

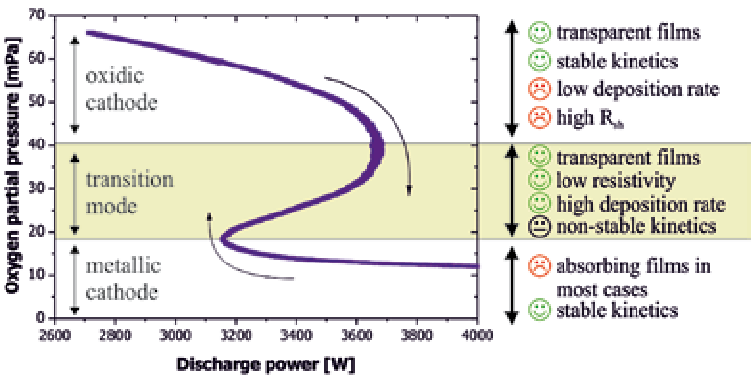

Figure 1. Process curve of a reactive magnetron sputtering process. In this example, the discharge power was varied in order to stabilize oxygen partial pressure at a constant oxygen flow rate.

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At Fraunhofer IST, a stable oxygen partial pressure is maintained by a closed-loop process control system that constantly adjusts the discharge power of the targets [6]. Films can be deposited at different oxygen partial pressures and film properties will differ significantly. For example, the resistivity of ZnO:Al films will usually reach a minimum at an intermediate oxygen partial pressure, with a steep increase to higher values towards the oxide mode.

Transmission of deposited films is normally constant for higher values and will steeply decrease for low oxygen partial pressures. In order to fully exploit the potential of the reactive sputtering process, the optimum operating point has to be stabilized during deposition and adjusted throughout the lifetime of the targets: therefore closed-loop feedback control systems are necessary. In addition, stabilization along the target is required, as well as the detection of process drifts to adjust operating-point settings in long-term operation.

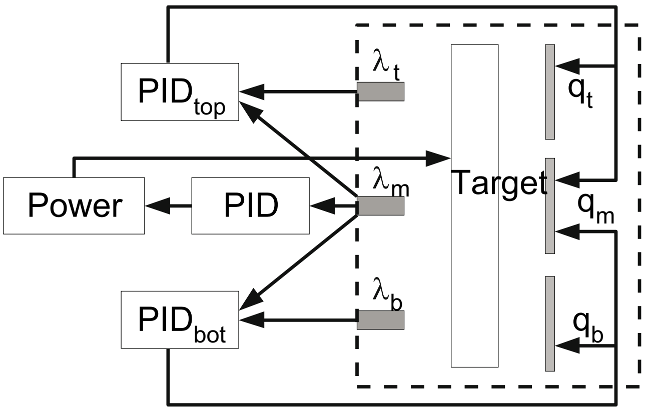

Figure 2. Principal setup of the symmetry control system used at Fraunhofer IST. Three λ-sensors are used to monitor oxygen partial pressure at different positions along the target. The measured values are used as input to a control loop for adjusting the flow of the threefold oxygen inlet.

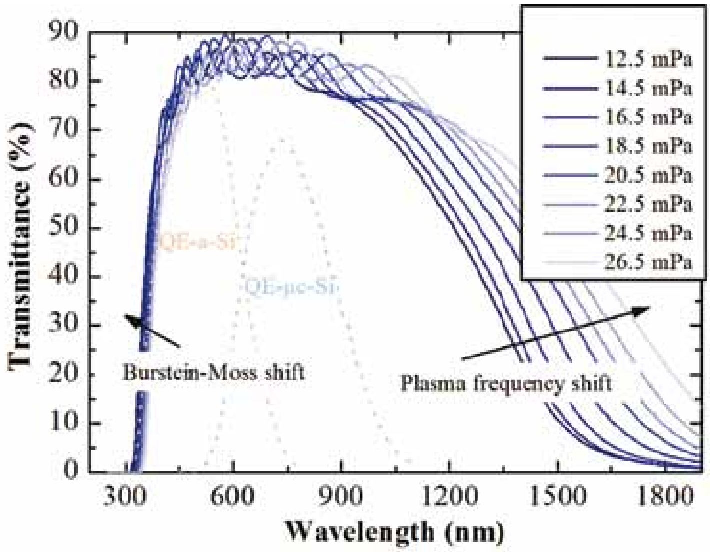

Figure 3. Transmittance of reactively sputtered ZnO:Al films at different operating points. The Burstein-Moss shift and also the shift in plasma frequency can be observed.

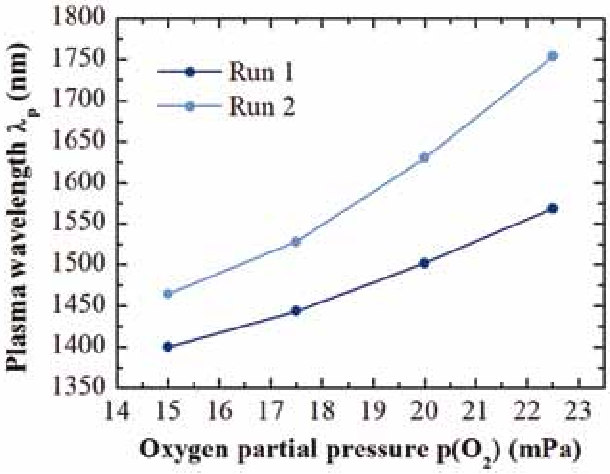

Figure 4. Drift of plasma wavelength of films deposited at the same operating points but in different runs. The film properties are highly dependent on the history of the target.

In the last few years reactive sputtering has been tested for different solar cell applications [7-11]. Every application has its own needs. Besides the requirements of optimal conductivity and lowest possible absorption for CIGS and HIT solar cells, the deposition temperature has to be less than or equal to 200°C due to the sensitive heterojunction. For a-Si/μSi solar cells, because of the superstrate structure and the need for an optimized light-trapping texture, a higher deposition temperature can be used.

Long-term stabilization

A. Target symmetry control

At Fraunhofer IST, ZnO:Al films are deposited in the in-line coater Leybold A700V using two PK750 cathodes run as a dual magnetron and fed by MF power generators. A constant oxygen flow is introduced into the chamber in a separate, threefold gas-inlet system and a lambda sensor monitors oxygen partial pressure in the centre of the discharge. MF power is then controlled by a proportional-integral-derivative (PID) control so that the oxygen partial pressure is kept constant at a desired operating point. With this control, it is possible to operate the discharge in the transition mode between oxide and metallic modes.

We coat the glass substrates of 100 × 60cm^2 with Al-doped zinc oxide. These films are meant to act as front contacts in solar cells [12]. So far, deposition at higher pressures on large-scale substrates has led to strong inhomogeneity of film thickness, sheet resistance and optical transmittance. It has been observed repeatedly that, in the vertical direction, one side of the film is insulating while the other side shows strong absorption. Moreover reproducibility of results obtained using the same deposition parameters was poor.

This behaviour is also known to occur with industrial-size cathodes for architectural glazing, where cathode lengths can exceed 3.75m. As the operating point is only stabilized at the target centre, the outer parts can operate in different discharge states, and fall into either the metallic or the oxide state. The effect has been explained by the decrease of the mean free path of the electrons running along the racetrack at higher pressures [13]. If this mean free path becomes too small with respect to cathode length, the coupling of different target regions is impaired and the process becomes unstable. In order to overcome these difficulties, symmetry control systems are used.

For the additional symmetry control, two more λ-sensors have been added to the setup, at the upper and lower sides of the target. These sensors can be used to monitor the distribution of oxygen partial pressure along the cathode. If symmetry

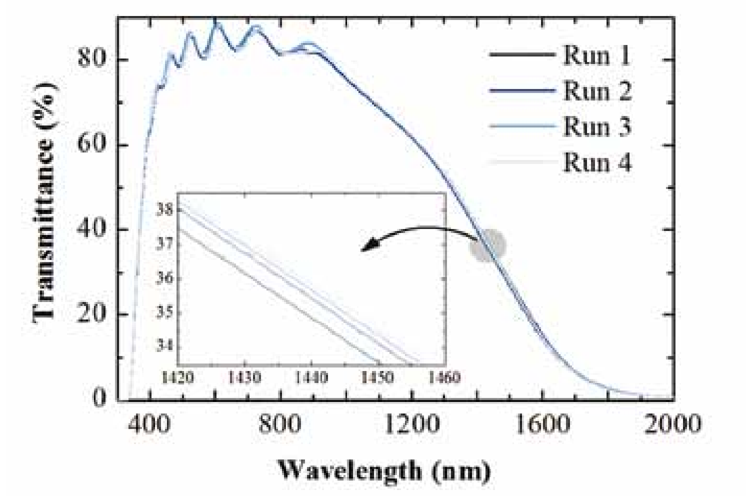

Figure 5. Transmittance of reactively sputtered ZnO:Al films at the same operating points in four different runs. A slight shift of the spectra can be seen in the inset.

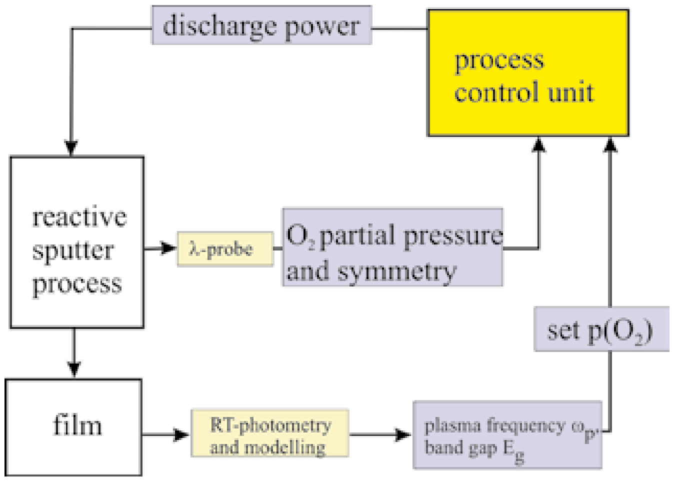

Figure 6. Schematic of the closed loop of the online control. The first cycle (top loop) controls oxygen partial pressure during deposition by adjusting power, and the symmetry by adjusting the flow. The second cycle (bottom loop) controls the deposited film properties by adjusting the set point for $p(O_2)$ via taking optical measurements and curve fitting.

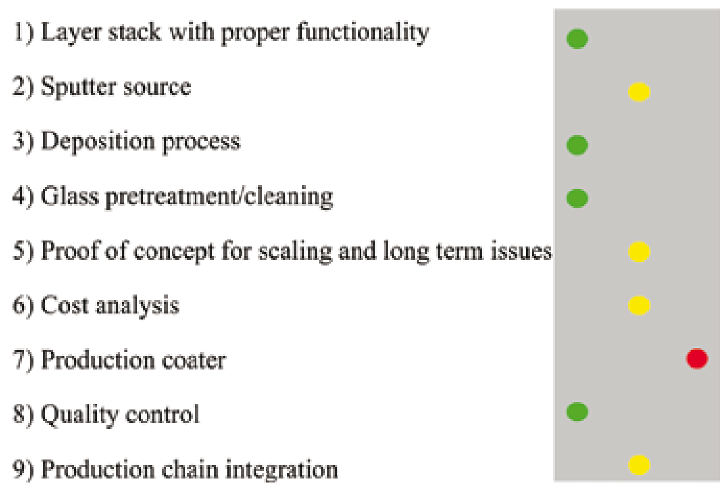

Figure 7. Estimation of the readiness for production of the reactive large area ZnO:Al process.

control is activated, an additional closed-loop control system continuously adjusts the oxygen flow distribution of the threefold gas inlet in order to maintain a suitable oxygen partial pressure distribution (Fig. 2). This type of symmetry control has described in detail elsewhere [14].

All three λ-sensors are calibrated by measuring the pressure increase in the vacuum chamber on increasing the oxygen flow, and recording the sensor signals. Set points for the oxygen partial pressures $p(O_2)_t$, $p(O_2)_m$ and $p(O_2)_b$, monitored by the sensors λ_t, λ_m and λ_b, respectively, were obtained by experiment. First the optimum value of $p(O_2)_m$ is determined by deposition onto small substrates until a highly transparent film with high conductivity is obtained in the middle of the discharge. An oxygen flow distribution known to lead to good homogeneity at lower total pressures is chosen, and partial pressures λ_t and λ_b are monitored throughout the coating process. These values are taken as the starting point for a series of coatings deposited with activated symmetry control. The pressures $p(O_2)_t$ and $p(O_2)_b$ are then tuned to achieve optimal homogeneity.

Generally a fast response and high repetition rate of the PID cycle controlling the gas flow distribution is important to keep the discharge balanced. The control has been shown to be capable of stabilizing homogeneous partial-pressure distributions, even at high total pressures. A more detailed description can be found in [15]. Another example of a partial-pressure distribution control with plasma-emission monitoring is given in [16].

B. Long-term drift control

An online control method that is able to detect process drifts and offers the possibility of adjusting operating-point settings in long-term operation is necessary. This type of control system is based on the evaluation of spectroscopic photometry measurements in the visible and near-infrared wavelength regime. The measured spectra are analyzed with respect to their band-gap and free-carrier absorption.

Fig. 3 shows that the band gap and plasma frequency shift as a function of the oxygen partial pressure. One explanation for this is the mechanism of zinc desorption that occurs at the substrate at low oxygen partial pressures [17,18].

By this mechanism, the relative aluminium content and accordingly the free-carrier density are increased compared to films deposited at high oxygen partial pressure. In contrast, a high oxygen flow causes a better infrared (IR) transmittance and a lower band gap, while a low oxygen flow decreases the IR transmittance and increases the band gap, due to the Burstein-Moss shift. (A more detailed description can be found in [19].) Nevertheless, all fabricated

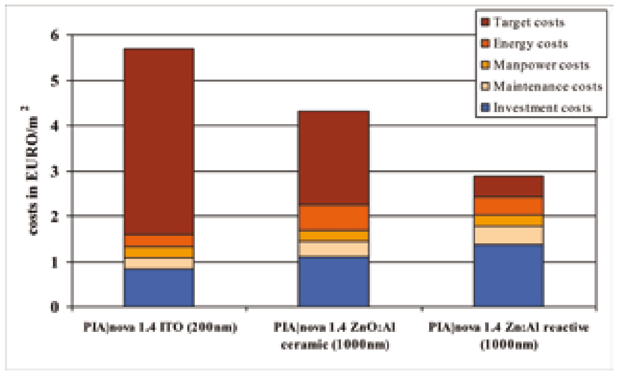

Figure 8. Comparison of typical cost-of-ownership calculations for ITO, ZnO:Al (ceramic process), and ZnO:Al (reactive process)[21].

films show a sufficient transmittance for applications in a-Si/µc-Si tandem solar cells, which is demonstrated by the quantum efficiencies (QE) plotted in Fig. 3. In experimental practice, however, samples prepared under the same process parameters can show very different properties. As an example, Fig. 4 gives the plasma wavelength of such films for two runs in succession.

Besides the long-term target change due to target erosion, the recent target operation history also seems to be important. There are significant differences when starting from a poisoned target or from the metallic mode. In this regard, it might even be necessary to control the oxygen flow in situ during deposition instead of film-by-film control. Fig. 5 shows four consecutive runs carried out at the same operating points. There is only a slight change in the optical transmission spectra.

At least for normal production processes with constant parameters, an online control (substrate by substrate) is sufficient. The closed-loop diagram of the online control is shown in Fig. 6.

There are three loops necessary:

1. Closed-loop control of the oxygen partial pressure during deposition, by adjusting the power with a cycle time smaller than 20ms for high oxygen consumption.

2. Symmetry control, by adjusting the flow with a cycle time of a few seconds.

3. Closed-loop control for adjusting a new set point for oxygen partial pressure, regarding the optical analysis and shifting of the optical spectra (plasma frequency) as shown in Fig. 5 on a large timescale (substrate by substrate).

Besides these, a further important control will be the interconnection of the different cathodes in a typical in-line coater, which has not been addressed so far. However, taking into account our successful experiments for homogeneous large area deposition and the modelling and simulation capabilities available today, we feel that process control is a delicate issue, but a resolvable one.

We have estimated the readiness for production as shown in Fig. 7 [20]. Our next step is the transfer to rotatable cathodes using an environment for closed-loop control that is fully programmable logic controller (PLC) integrated.

Cost aspects

For a discussion of costs, it is instructive to proceed with the analysis shown in Fig. 8 for large area ceramic rotatable target sputtering of either 200nm ITO or 1000nm ZnO:Al at $T_S = 200°C$, using Gen 5-size coaters, compared with a reactively sputtered 1000nm ZnO:Al. This is done for a CIGS-based front contact, and therefore

a linear depreciation is foreseen for seven years, as noted by Linss et al. at VON ARDENNE Anlagentechnik (VAAT) [21]. The main cost is driven by the target material. Changing from ceramic target sputtering to reactive magnetron sputtering allows the target costs to be reduced by a factor of three, since casting of Zn:Al alloy is a very robust and cost-effective technique compared to more complex sintering or plasma-spraying processes necessary for $ZnO{:}Al_2O_3$ tube targets. Furthermore, a reduction in energy costs by roughly a factor of two can be expected by taking into account the difference in sputter yield for ceramic and metal targets. As a consequence of this preliminary analysis, a potential cost reduction of the order of 65% for a Gen 5 can be envisaged.

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About the Authors

Volker Sittinger is a senior scientist at the Fraunhofer IST in the Large Area Coating Department and is currently working on magnetron sputtering for photovoltaic applications. He previously held the role of scientific assistant at the Institute of Solar Energy Research GmbH (ISFH). Volker received his doctoral degree in optical and electrical characterization of electrodeposited $CuInSe_2$ solar cells from the University of Oldenburg in 2003 and studied physics at the University of Karlsruhe.

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Bernd Szyszka is head of the Large Area Coating Department at the Fraunhofer IST, which he founded in 2003. After studying physics at the TU Brunswick, he started his scientific work at the Fraunhofer IST in 1995, and received his doctorate degree Dr. rer. nat. in 1999 on the topic of reactive magnetron sputtering of transparent conductive oxides.

Florian Ruske is a senior scientist at the Institute for Silicon Photovoltaics at Helmholtz-Zentrum Berlin (HZB). He works on transparent conducting oxides and functional layers for silicon-based photovoltaic devices. Florian 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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