Optical and electrical properties of zinc oxide based TCO layers on polymer films

Matthias Fahland, John Fahlteich, Steffen Günther, Tobias Vogt

Fraunhofer Institute of Electron Beam and Plasma Technology,

Dresden, Winterbergstrasse 28, Germany

Contact: matthias.fahland@fep.fraunhofer.de

Abstract:

TCO (transparent conducting oxide) layers on polymer films have a high importance for emerging applications like flexible solar cells and large area lighting. The restriction for substrate temperatures to be below 150°C results into a different process compared to the well investigated coating on glass. The new results will be focused on zinc oxide based materials. The effect of the type of doping as well as the doping level will be investigated. The electrical and optical properties of the layers are presented, including an evaluation of application in the above mentioned areas.

Introduction

Transparent conductive layers on polymer films have gained a considerable interest over the last decades. This is mainly driven by some major applications. First of all the touch screens are one of the popular devices which require a bendable transparent electrode that can be made by a special polymer film with a thin transparent conductive layer on it.

However, there are still some other striking applications which may become important markets in future. Flexible solar cells are one of these opportunities. They offer some advantages over their counterparts on glass substrates. They can easily be applied on various surfaces which makes them interesting for building integrated photovoltaics. Additionally they are light weight and shatter proof opening the market of mobile devices and energy supply from flat roofs. Another fascinating opportunity are flexible lamps based on organic light emitting devices. All these applications require electrodes which have a high optical transmittance and a low sheet resistance at the same time. Very often the requirements are far beyond that what is needed for contemporary applications like touch screens e-books or EL lamps.

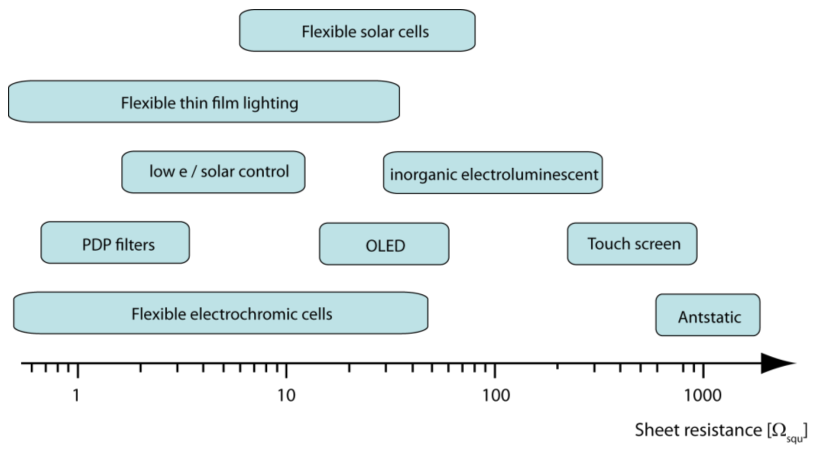

Figure 1: Overview of the sheet resistance requirements of different applications of flexible transparent electrodes

The major material for transparent electrodes is indium tin oxide (ITO). This is a transparent conducting oxide with has s specific resistance in the range of $5x10^{-4}$ Ohm cm on ordinary plastic substrates. Layers made on glass can be better by a factor 3-4 due to the increased substrate temperature during deposition.

Transparent electrodes for future applications need to fulfill a whole bunch of requirements. A major one is the low cost for the transparent electrode. This is a precondition for becoming a real mass product. The indium content in the ITO material is a serious obstacle for that. This rare metal had experienced a considerable price race with the increased popularity of flat screen TV. It can be expected hat another large scale application would boost the price again. Therefore several research groups are looking for alternative materials. Zinc oxide based transparent conductors are the most promising candidate. Doping this material with a trivalent ion like Al^{3+} results into a conductor with excellent properties and a conductivity only slightly above that of ITO. However, the best values can only be reached for heated substrates. The loss of performance in case of room temperature deposition is more pronounced compared to ITO. This fact prevented the industrial usage of ZnO-based materials on polymer films up to now.

The material ZnO:Ga

It was suggested by several authors that the substitution of Al by Ga would result into a good alternative material. [1-3]. This assumption can be made on the basis of the data given in table 1.

Table 1: Typical dopants of ZnO, the heat of formation oft he oxide and the radius oft he cation

Dopant	ΔH [kJ mol^{-1}]	Ion radius Cation [nm]	Technology
B_2O_3	1271	0.020	CVD
Al_2O_3	1676	0.050	Sputtering (ceramic, reactiv)
Ga_2O_3	1104	0.062	Sputtering (ceramic)
In_2O_3	924	0.081	Sputtering (ceramic)
ZnO	*347*	*0.074*	

The very close relation of the ion radius of gallium to that of zinc provides a possibility of a low internal stress in the material. Additionally the lower enthalpy of formation of Ga_2O_3 compared to Al_2O_3 suppresses the tendency to insulating layers at internal boundaries. The latter fact is especially interesting for low temperature deposition.

Experiments

Three different materials were used for the experiments: ZnO:Al_2O_3 (2wt%) , ZnO:Ga_2O_3 (5wt%), ZnO:Ga_2O_3 (6.5wt%) . All targets were manufactured by GfE with the measures of 12x35 cm² and a thickness of 8 mm. The experiments were carried out in the DC sputtering chamber of the sputter roll coater labFlex® 200 (Fig 2).

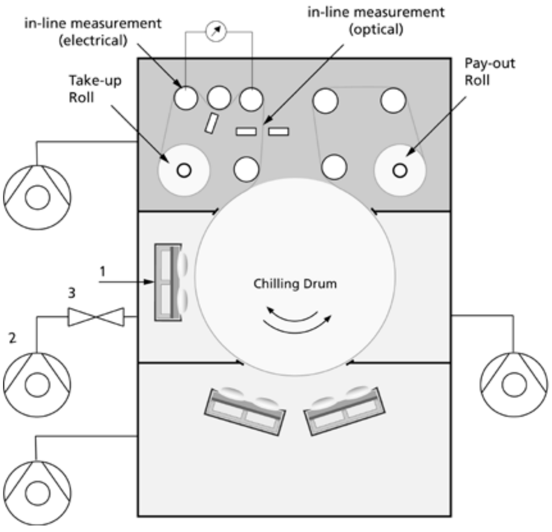

Figure 2: Schematic drawing of the laboratory roll coater labFlex® 200, (1) magnetron used for the deposition, (2) turbomolecular pump TMP 1000 (Leybold), (3) throttle valve (MKS instruments)

The transmittance and reflectance spectra of all samples were measured by a spectrophotometer (Perkin Elmer Lambda 900). The sheet resistance was measured by a 4-point probe (Veeco).

The substrate was polyethylenterephtalate (PET, Melinex 400, Duponteijinfilms). The substrate was kept at room temperature during the deposition be the chilling drum.

Results

A very important feature of each TCO material is the R-Φ- characteristic, the dependence of the specific resistance of the material on the oxygen flow into the process. In Figure 3 this characteristic is shown for different ZnO based materials and for ITO as a reference.

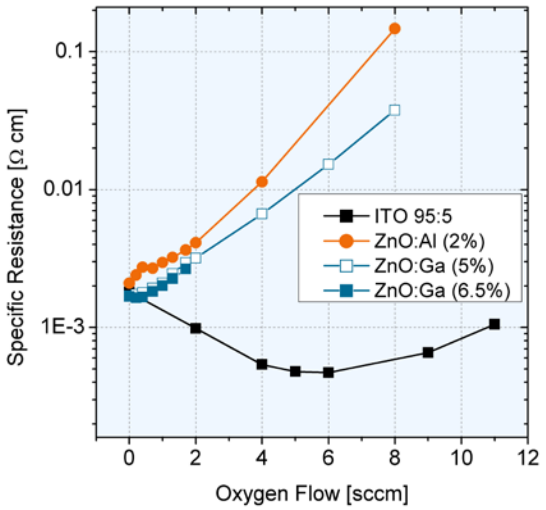

Figure 3: Resistance-Flow (R-Φ) characteristic for different TCO materials

In contrast to ITO the zinc oxide based samples show no optimum for the sheet resistance (or a very shallow one for the Ga-doped samples. The samples with the lowest resistance (near zero oxygen) have a certain absorption. The higher the oxygen flow the better gets the transmittance of the sample. The choice of the oxygen flow finally depends on the special requirement of the application. The relation between transmittance and sheet resistance for different TCO materials is shown in Figure 4.

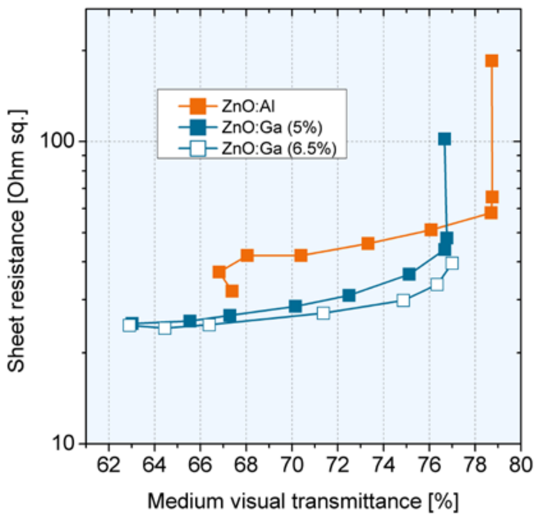

Figure 4: Relation between sheet resistance and visual transmittance for different zinc oxide based materials.

All layers evaluated for Figure 4 have a thickness of approximately 600 nm. The parameter of the curves is the oxygen flow. Similar to Figure 3 the flow is varies from zero to 8 sccm. The Al- doped samples have a higher transmittance for the oxygen saturated samples. However, these samples are worse in sheet resistance. The most interesting samples are at some point in the plateau region of the curves in Figure 4. However, in the plateau region the Ga-doped samples have a clear advantage over the Al-doping.

The specific resistance can be a function of the layer thickness. This is due to different effects. In case of ZnO-based samples the degree of crystallinity plays an important role and can lead to a continuous reduction of the specific resistance with the layer thickness. This can be seen in Figure 5.

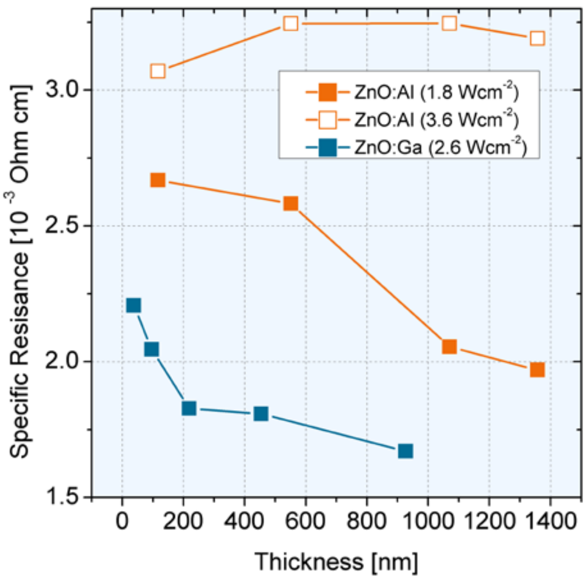

Figure 5: Dependence of the specific resistance with the layer thickness for zinc oxide based samples at different power levels.

In Figure 5 one can see that also with respect to the thickness dependence the Ga- doped samples have an advantage over the Al-doped ones.

Outlook:

Based on the presented results an optimum sample of single layer ZnO was deposited onto a heat stabilized PET film. The obtained transmission spectrum is shown in Figure 6.

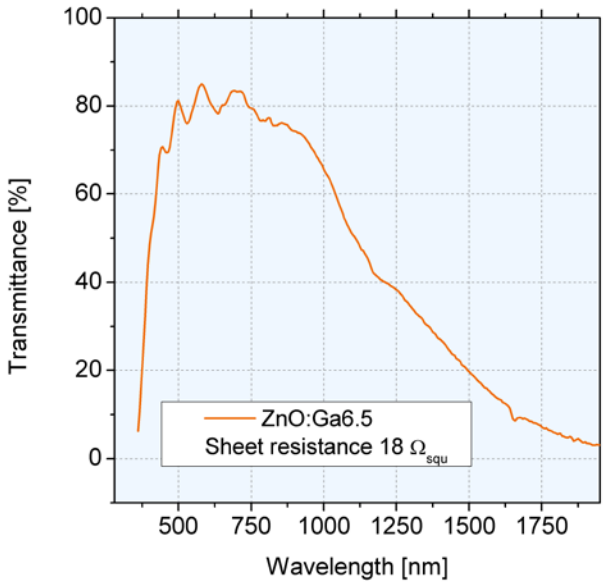

Figure 6: Optimum ZnO-based sample with the following parameters: HC-coated PET substrate, thickness 770 nm, sheet resistance 18 Ω_{sq}

The high thickness of 770 nm makes it difficult to find a low cost deposition. However, the layers can be combined with either metal networks or embedded Ag-layers [4]. These approaches reduce the required thickness and open the way for low cost samples.

Acknowledgement

Nicole Pager and Frank Naumann are acknowledged for the preparation of the samples and the detailed measurements.

Literature

[1] Fortunato et al. Thin Solid Films 451-452 (2004) 443-337

[2] Tseng et al Thin Solid Films 517 (2009) 6310-6314

[3] Song et al. Thin Solid Films 411 (2002) 82-86

[4] Fahland et al. Conference Proceedings of CIMTEC meeting (2010)