Spray deposition of oxides at ambient atmosphere
Part 1:Transparent Conductive oxides

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1 Introduction

The spraying process is a low cost and easy up-scalable technique and its applicability for the deposition of Transparent Conductive Oxide layers (TCO) has already been published [1-5]. However, despite of the required high-cost equipment, physical deposition of TCO's is still favored. This work describes the spray deposition of TCO's with the purpose to get a deeper understanding about the parameters impacting the layer growth and properties. The materials of choice are ITO and ZnO:In. ITO has already widely been used in the flat panel and optoelectronics industry and is known to have excellent optical and electrical properties [6]. ZnO is beside of its special properties [7-9], the today's low cost alternative to ITO, which is currently under discussion due to indium supply and costs concerns. The spraying process is rather complicated, as it combines chemical and physical processes. The nebulisation and decomposition of the precursor material is one of the most crucial steps. In this work ultrasonic agitation of the precursor has been chosen to create a fine mist. In addition to the ITO and ZnO:In deposition on sodalime glass, the effect of a nucleation layer on the ZnO:In layer growth has been studied

2 Experimental

The ultrasonic spray nebulizer is placed at a distance of 10 cm above the hotplate with a 5x5 cm sodalime glass substrate. After heating the substrate to 380°C for ZnO respectively 450°C for ITO the precursor is nebulized by ultrasonic agitation and is continuously vortexed with air in direction of the substrate.
The zinc oxide precursor solution consists of 0.2 M zinc acetate dissolved in a water/propanol mixture (ratio 1:3). The 100 nm thick intrinsic ZnO layer has directly sprayed with this precursor. For the doped layers indium acetate is added to the spray solution in a [In]/[Zn] ratio of 3 at%. ITO has been deposited from a 0.1 M $InCl_3$ solution with 5 at% $SnCl_4*H_2O$ in water/propanol (ratio 2:3).

The morphology of the samples has been studied by using a JEOL JSM-6330F Field Emission Scanning Electron Microscope (SEM) (cold-cathode field emission) with a resolution of 2 nm at 15kV. The X-ray diffraction (XRD) measurements have been perfomed on a Bruker AXS (type D8 Advance) using the Bragg Brentano method. The UV-VIS transmittance and reflectance spectra have been taken with a Spectro 320 R5 apparatus with integrating sphere (Instrument Systems GmbH). The electrical properties are determined by four-point probe sheet resistance meter and Hall measurements.

3 Results and discussion

3.1 ITO deposition by spray pyrolysis

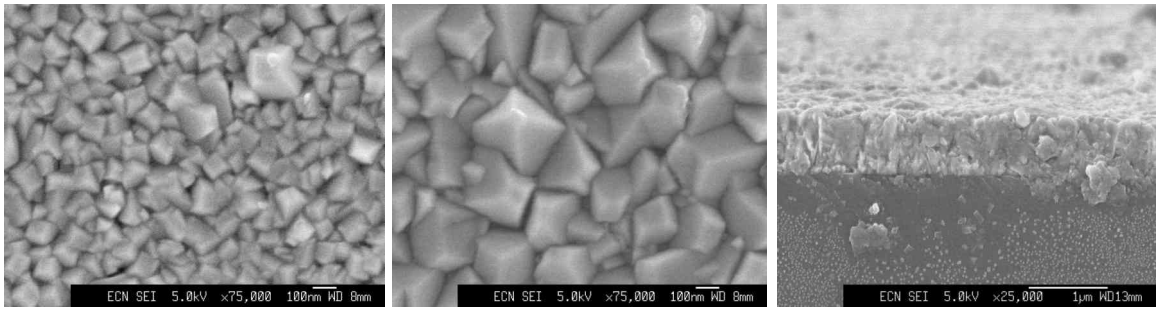

Figure 1 From left to right: SEM top view of a 300 nm thick ITO layer (x75.000) and SEM-top view (x75.000) and cross section (x50.000) of a 800 nm thick ITO layer

ITO layers with 300 and 800 nm thickness have been spray deposited at 450°C. The SEM photographs in figure 1 show that the layers are crystalline and the crystallite size increases with layer thickness. The cross section shows a compact layer.
The XRD results in figure 2 cover nicely with the SEM observations. The layers are indeed crystalline. They show the typical cubic lattice of indium oxide. Going from 300 to 800 nm the spectra show a higher crystallisation degree and a preferential (400) orientation at 800 nm. This observation has also been made by Lee et al [6] for magnetron sputtered ITO layers. The electrical resistivity values measured for the as grown ITO layers are 840 µΩ.cm (300nm) and 460. µΩ.cm (800 nm). A forming gas anneal at 400°C leads to a further reduction to 590 µΩ.cm respectively 310 µΩ.cm, the latter being only twice the value of high-quality sputtered ITO layers [6].
The transmittance of a 300 nm thick film is in average 85% over the visible light range (Fig.3).

As can be seen in the figure, annealing in forming gas results in a spectrum shift, called Burstein Moss shift. This shift is caused by a charge carrier density increase, which is presumably the reason for the measured conductivity increase.

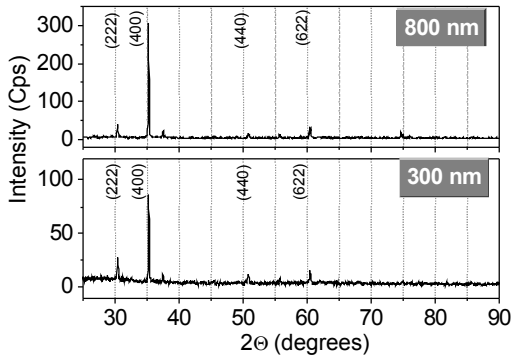

Fig.2. X-ray diffraction spectra of a 300 nm and 800 nm thick ITO layer

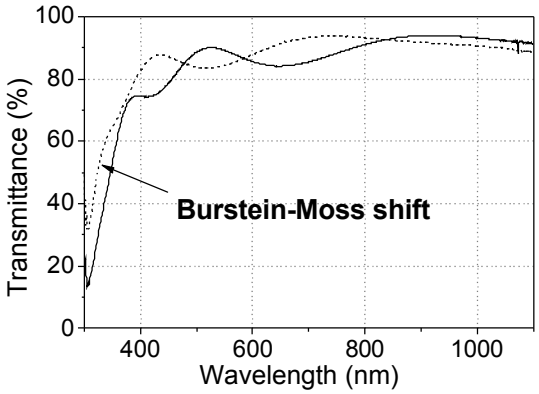

Fig.3 UV-VIS transmittance spectrum of an as-deposited (solid line) and forming gas annealed (dotted line) ITO layer (layer thickness: 300 nm)

3.2 ZnO deposition by spray pyrolysis

Spray deposition of doped ZnO usually leads to a polycrystalline layer [2]. Therefore in this work it will be attempted to aid the crystal growth by a likewise sprayed but undoped ZnO nucleation layer, which is known to crystallize in the same crystal pattern as sputtered ZnO layers [2, 7-9]. The properties of ZnO:In directly sprayed on glass (structure A) will be compared to ZnO:In deposited on a 100 nm thick intrinsic ZnO layer (structure B). As is shown in the cross section SEM-photographs of 1300 nm thick ZnO:In with structure A and B (Fig. 4) the i-ZnO buffer indeed influences the ZnO:In morphology. In contrast to the more granular morphology of ZnO:In on glass (A) i-ZnO causes a well-ordered dense columnar growth of the ZnO:In layer (B). The SEM top view shows a compact layer of grains with a diameter of 500-800nm, which are covered with a film of smaller particles. Unfortunately the sharp crystals found for ITO could not be reproduced with ZnO.

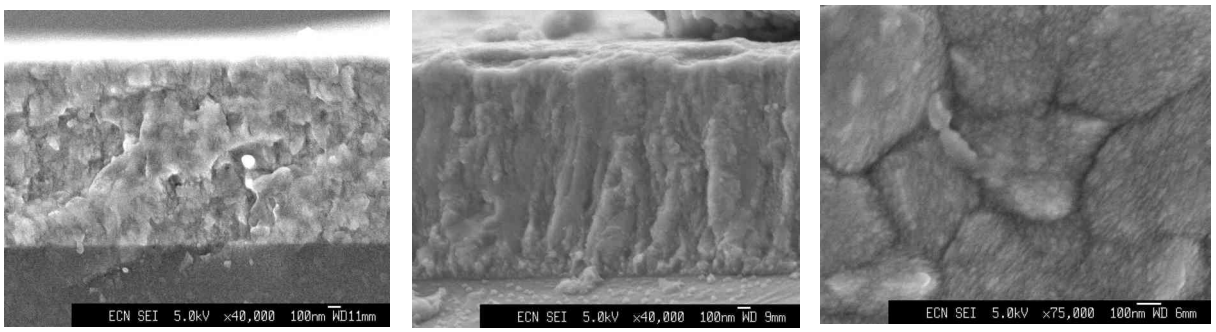

Fig. 4. From left to right: SEM cross section of ZnO:In (A**)** (x40.000) and cross section (x40.000) and top view (x75.000) of (i-ZnO)/ZnO:In (B)

To get deeper insights into layer growth and structure XRD measurements have been performed on solely i-ZnO, ZnO:In and (i-ZnO)/ZnO:In (Fig.5). All spectra show a hexagonal wurtzite structure, but the crystal orientation of the ZnO layer changes. By going from undoped (i-ZnO) to doped material (A) the preferential growth in (002) direction found for i-ZnO has almost been quenched and other signals appear with (101) as most prominent crystal orientation. If the same doped ZnO:In layer is deposited on the i-ZnO nucleation layer (B) the peak ratios change again. However, the presumption that the (002) orientation of the i-ZnO nucleation layer would dominate the orientation of ZnO:In does not hold, but the (002) signal appears again. Also the optical properties of ZnO:In are influenced by the nucleation layer. Although structure A and B show similar spectra for the total transmittance and reflectance, the specular transmittance spectra are different. The lower specular transmittance of the ZnO:In layer (A) is in line with its milky appearance. The reason for that is internal light scattering, which points toward a granular structure. The better light transmittance of structure B is in agreement with the more columnar morphology as shown in Fig.4.

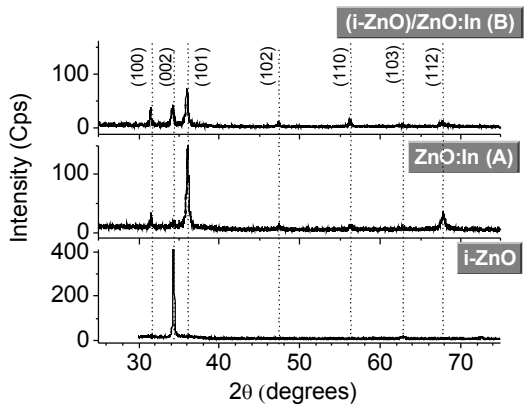

Fig. 5. X-ray diffraction spectra (coupled scan) of i-ZnO, ZnO:In (A) and (i-ZnO)/ZnO:In (B)

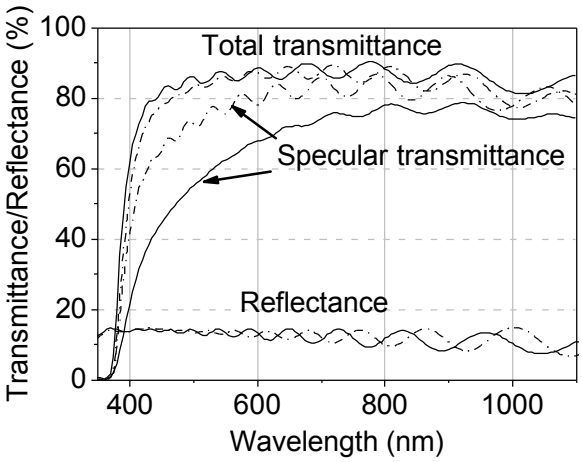

Fig. 6. UV-VIS spectra of ZnO:In (A) (solid lines) and (i-ZnO)/ZnO:In (B) (dash-dotted lines) (The layer thickness is 1300 nm).

In contrast to the above-described findings, the i-ZnO buffer layer does not affect the electrical parameters of ZnO:In significantly (see Table 1). The charge carrier concentration is in the range of the introduced indium amount implying that the indium ions are acting as active dopant.

Table 1 Electrical properties of ZnO:In (3 at% In) without (A) and with (B) i-ZnO buffer layer (the layer thickness is 1300 nm)

	ZnO:In (A)	i-ZnO/ZnO:In (B)
R (Ω/square)	23.7	22.4
ρ (mΩcm)	3.2	2.9
μ (cm^2/Vs)	13.7	12.5
N (x$10^{20}$$cm^{-3}$)	1.40	1.71

But the charge carrier mobility is a factor 3 to 4 if lower compared to sputtered material [7-10], most likely limited by small grains and impurity (indium) segregation at the grain boundaries. In contrast to the findings for ITO, a forming gas anneal does not influence the electrical properties of ZnO:In.

4 Conclusion

It has been demonstrated, that it is possible to deposit TCO layers by spray pyrolysis in ambient atmosphere. Crystalline ITO layers with resisitivities down to 310 μΩ.cm have been applied on glass. Indium doped ZnO layers have been grown with a dense columnar structure, if deposited on a thin i-ZnO nucleation layer. The changed layer structure leads to a significant reduction of the internal light scattering. The electrical properties, namely the mobility, could not be affected.

References

1. H.Gomez, A.Maldonado, M.D.L.L.Olvera, D.R.Acosta, Sol. Energ. Mat. Sol. Cells 87 (2005) 107.
2. M.Krunks, E.Mellikov, Thin Solid Films 270 (1995) 33.
3. P.Nunes, E.Fortunato, P.Tonello, F.B.Fernandes, P.Vilarinho, R.Martins, Vacuum 64 (2002) 281.
4. Kawashima,T., T.Ezure, K.Okada, H.Matsui, K.Goto and N.Tanabe Journal of Photochemistry and Photobiology A: Chemistry 164 (1-3) (2004) 199.
5. H. Bisht, H.-T.Eun, A.Mehrtens and M.A.Aegerter (1999), Thin Solid Films 351 (1999) 109.
6. H.C. Lee, O.O.Park, Vacuum 80(8) (2006), 880-887
7. T.Nakada, M.Mizutani, Jpn. J. Appl. Phys. 241 (2002) L165.
8. J.Müller, B.Rech, J.Springer, M.Vanecek, Thin Solid Films 392 (2001) 327.
9. C.Agashe, O.Kluth, J.Hüpkes, U.Zastrow, B.Rech, M.Wuttig, J. Appl. Phys. 95 (2004) 1911

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