ZnO:In deposition by spray pyrolysis - influence of the growth conditions on the electrical and optical properties

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Abstract
Indium-doped Zinc Oxide (ZnO:In) has been prepared on glass substrates by spray pyrolysis in air at substrate temperatures of between 350 and 450°C. The spray has been generated by means of an ultrasonic nebulizer from a zinc acetate solution (0.1 M) with varying [In]/[Zn] ratio (1-5 at%). Using the ultrasonic nebulizer 1.3 µm thick ZnO:In layers with a resistivity as low as 3 mΩ cm have been deposited. The XRD spectrum shows a hexagonal zinc oxide structure. Unfortunately, the specular transmittance of a 1.3 µm thick layer in the visible spectrum is only 60 to 80%. In order to improve the optical properties, the effect of underlayers has been investigated. The application of 100 nm intrinsic ZnO (i-ZnO) underneath ZnO:In resulted in a change from a more granular to a dense columnar film structure. The XRD-spectrum still shows the typical diffraction pattern of hexagonal zinc oxide. As a result the specular transmittance and layer homogeneity of ZnO:In have improved without changing the layer conductivity, giving 1.3 µm thick TCO layers with a resistivity of 3 mΩ cm and a transmittance of more than 80% in the visible light range.

Keywords: zinc oxide, ITO, TCO, spray

1. Introduction
Zinc oxide (ZnO) is a multifunctional material, which has widely been used for sensors, light emitters and other electronics. As a wide bandgap material (Eg=3.3 eV) and due to its low material costs ZnO is one of the most attractive Transparent Conductive Oxides (TCO). These ZnO TCO's are mostly applied by sputtering, but also wet-chemical methods like sol-gel deposition or spray pyrolysis have been studied. The spray process makes use of an earlier published approach to influence the ZnO:In layer growth in direction of (002) preferential orientation by using an intrinsic ZnO nucleation layer.

2. Experimental
An ultrasonic spray nebulizer is placed at a distance of 10 cm above the hotplate with a 10x10 cm glass substrate. The ZnO:In precursor solution consists of 0.1 M zinc acetate dissolved in a water/ethanol mixture (ratio 1:3). For the doped layers indium acetate is added to the spray solution in a [In]/[Zn] ratio of 1-5 at%. After heating the substrate to 380°C the precursor is nebulized by ultrasonic agitation and is continuously vortexed with 200 mbar air in direction of the substrate. For the investigation of a controlled ZnO:In layer nucleation a 100 nm thick layer of undoped ZnO (i-ZnO) was sprayed first, before the ZnO:In layer has been deposited on top of it. To keep a better survey over the diverse samples investigated in this work the codes A and B have been introduced. A ZnO:In with [Zn]/[In] =3 at% B i-ZnO (100 nm)+ ZnO:In with [Zn]/[In]=3 at%

Variation of In-doping concentration: The experiment series with [In]/[Zn]=1-5 at% have been carried out under condition B, thus with i-ZnO underlayer. 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 performed on a Bruker AXS 320 R5 apparatus with integrating sphere (Instrument Systems GmbH).

3. Results and discussion
3.1 Morphology
The effect of an initially sprayed 100 nm thick i-ZnO underlayer on the morphology of ZnO:In layers has been investigated by XRD measurements. Fig. 1 represents the XRD spectra of solely i-ZnO and of ZnO:In (3 at% In) without (spectrum A) and with i-ZnO underlayer (spectrum B).¹

¹ Both ZnO:In layers (A and B) have a comparable thickness of 1.3 µm and form compact layers (see Fig. 4), so that changes due to the X-ray penetration depth are not expected.
Fig. 1. X-ray diffraction spectra (coupled scan) of i-ZnO (1\,\mu m thick), ZnO:In (3\,at\%\,In, 1.3\,\mu m thick) without (spectrum A) and with i-ZnO underlayer (spectrum B)

All spectra in Fig. 1 show a hexagonal wurtzite structure, but the crystal orientation of the ZnO layer changes by going from undoped (i-ZnO) to doped material. For doped ZnO (spectrum A) in comparison to the exclusive (002) growth found for i-ZnO other crystal orientations came up and the (101) signal became most prominent, whereas the (002) signal almost disappeared. If the same doped ZnO:In layer is deposited on i-ZnO (Fig. 1, spectrum B) the peak ratios change and the (002) signal appears again. The changes of the signal intensities (100), (101) and especially (112) in spectrum B compared to spectrum A indicate that the i-ZnO layer indeed influences the growth of the ZnO:In layer deposited on top of it. To prove, if the (002) signal in spectrum B is not a (background) signal of the underlying i-ZnO the experiments have been extended by a series of i-ZnO/ZnO:In stacks with different indium doping concentrations (1-5\,at\%\,In). As shown in Fig. 2 with increasing [In]/[Zn] ratio the (002) intensity decreases gradually whereas other signals such as (100), (101) and (110) increase\(^2\). Since the i-ZnO is only a thin nucleation layer (100 nm) and the layer thickness is supposed to be the same for all samples the change of the (002) intensity is explained by a change in the overall properties of the upper ZnO:In layer. As a conclusion, the overall ZnO:In layer property and along with it the intensity of the (002) orientation change by going from 1 to 5\,at\%\,In.

The same samples have been analysed by using a flat X-ray incidence angle of 0.5 degrees in order to get more knowledge about the surface region of the sprayed layer (Fig.3). In comparison to Fig. 2 in the upper layer part again other crystal orientations seem to be preferred than in the bulk. Regarding the (002)/(101) ratio with increasing doping concentrations compared to Fig. 2 the ratio decreases again with increasing [In]/[Zn] ratio but the signal ratio is much lower now; the (002) signal is even not visible anymore for [In]/[Zn]>2\,at\%.

These observations suggest, that the ZnO:In composition changes gradually with increasing layer thickness. Moreover, the prominent (002) signal in the bulk (Fig.2) and the decreased (002) signal intensity in the upper part of the ZnO:In layer let presume, that the i-ZnO nucleation layer influences the ZnO:In growth mainly in the initial deposition phase.

Fig. 2. X-ray diffraction spectra (coupled scan) of i-ZnO/ZnO:In stacks with different [In]/[Zn] ratio (1 to 5\,at\%) (see Fig. 7 for individual layer thickness)

Fig. 3. X-ray diffraction spectra (flat X-ray source angle of 0.5 degrees) of i-ZnO/ZnO:In stacks with different [In]/[Zn] ratio (1 to 5\,at\%) (see Fig. 7 for individual layer thickness) 

The cross section SEM-photographs of ZnO:In without (A) and with underlayer (B) (see Fig. 4) show that the i-ZnO underlayer indeed influences the ZnO:In morphology. In contrast to the more granular morphology of ZnO:In (A) i-ZnO causes a well-ordered dense columnar growth of the ZnO:In layer (B).

Both the SEM observations and the XRD results indicate a change in the ZnO:In morphology respectively in the crystal orientation if i-ZnO has been used as underlayer. In the following we investigate if these results have a consequence for the electrical and optical properties.

\(^2\) Again it is assumed that all layers have a comparable compactness and variations in the layer thickness are negligible (see Fig. 7 for layer thickness values). Therefore no influence on the X-Ray penetration depth is expected.
3.2 Electrical properties

Table 1 and 2 show the electrical parameters of various ZnO:In layers. Regarding the underlayer effect for both, ZnO:In (3 at%In) without (A) and with i-ZnO (B) the resistivity, charge carrier mobility and charge carrier density do not differ significantly (see Table 1). With increasing [In]/[Zn] ratio the charge carrier density increases (excluding ZnO:In with 5 at% In), confirming that indium addition indeed causes a doping effect (see Table 2). The mobility and resistivity pass an optimum at an [In]/[Zn] ratio of 3 at% with values of 2.9 m²V⁻¹cm and 12.5 cm²/Vs.

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

<table>
<thead>
<tr>
<th></th>
<th>ZnO:In</th>
<th>i-ZnO/ZnO:In</th>
</tr>
</thead>
<tbody>
<tr>
<td>R (Ω/square)</td>
<td>23.7</td>
<td>22.4</td>
</tr>
<tr>
<td>ρ (mΩcm)</td>
<td>3.2</td>
<td>2.9</td>
</tr>
<tr>
<td>μ (cm²/Vs)</td>
<td>13.7</td>
<td>12.5</td>
</tr>
<tr>
<td>N (x10²⁰cm⁻³)</td>
<td>1.40</td>
<td>1.71</td>
</tr>
</tbody>
</table>

(R- sheet resistance, ρ- resistivity, μ-charge carrier mobility, N- charge carrier density)

For both layers total transmittances above 80% and approximately 15% reflectance have been measured. But, in the end, a clear difference has been found regarding the specular transmittance spectra.

The specular transmittance of ZnO:In without i-ZnO underlayer (A) is significantly lower, which is in line with its milky appearance and is thus due to internal light scattering. The amount of light scattering has been quantified in Fig. 6 by plotting the Haze factor, defined by (T_total-T_specular)/T_total.

Summarising, the i-ZnO underlayer causes changes in the light passing properties of ZnO:In. The layer transmits the direct light much better than ZnO:In sprayed on glass.

3.3. Optical properties

The transmittance and reflectance spectra of ZnO:In layers again without (A) and with i-ZnO layer (B), both with comparable layer thickness and 3 at% In doping, are summarised in Fig. 5.

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Summarising, the i-ZnO underlayer causes changes in the light passing properties of ZnO:In. The layer transmits the direct light much better than ZnO:In sprayed on glass.
In Fig. 7 the specular transmittance spectra have been collected for layers with different \([\text{In}] / [\text{Zn}]\)-ratio. Except for \(\text{ZnO:In}\) with 1 at% In the doping amount influences the spectra only marginally. However, the highest transmittance has been found with 4 and 5 at% In whereby the latter has even the highest layer thickness. As has already been seen in the XRD spectra (compare i-\(\text{ZnO}\) in Fig. 1 and \(\text{ZnO}\) with 1 at% In in Fig. 2), \(\text{ZnO:In}\) with 1 at% In behaves similar to intrinsic material. Both layers show a hazy appearance and lower spectral transmittance, if thicker layers are grown.

![Graph showing transmittance spectra](image)

Fig. 7. Specular transmittance spectra of i-\(\text{ZnO}/\text{ZnO:In}\) stacks with different \([\text{In}] / [\text{Zn}]\) ratio (1 to 5 at%). (The individual layer thickness is given in the legend)

5. Conclusion

It has been demonstrated that using an intrinsic \(\text{ZnO}\) nucleation layer can indeed influence the \(\text{ZnO:In}\) layer growth. The deposited \(\text{ZnO:In}\) layer shows a dense columnar structure and a changed crystal orientation, whereby mainly the initial growth phase seems to be influenced by the preferential (002) orientation of the underlying i-\(\text{ZnO}\). The electrical properties have not significantly been changed in comparison to \(\text{ZnO:In}\) on glass. But earlier observed light scattering could be reduced if \(\text{ZnO:In}\) has been grown on i-\(\text{ZnO}\). A correlation between the \([\text{In}] / [\text{Zn}]\) ratio in the spray solution and the charge carrier density indicates a real doping effect. The lowest resistivity of 2.9 m\(\Omega\)-cm has been reached with 3 at% In. Moreover, the variation of the \([\text{In}] / [\text{Zn}]\) ratio causes changes in the preferential crystal orientation of \(\text{ZnO:In}\).

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References