MULTILAYER SnO$_2$:Sb TRANSPARENT ELECTRONIC CONDUCTING COATINGS MADE BY THE SOL-GEL PROCESS

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ABSTRACT

Transparent conducting thin sol-gel SnO$_2$:Sb multilayer coatings having the same total thickness, but different numbers of layers have been deposited on borosilicate glass by the dip-coating method using an ethanolic solution of SnCl$_2$(OAc)$_2$ doped with 5 mol% SbCl$_5$. The densification of the multilayers was done by 3 different processes. In process I each layer was dried at 200°C and the coating process repeated to obtain a thick dry coating which was then sintered as a whole at 550°C. In process II every single layer was dried at 120°C and then directly sintered at 550°C before repeating the coating process. In process III every single layer was directly sintered at 550°C without a drying step. The electrical properties and the morphologies of the coatings depend highly on the sintering and drying conditions. With process I all layers are homogeneous and have a high resistivity (1.4×10$^{-2}$Ωcm) whatever their thickness. The multilayers produced by process II and III show a sandwich structure with alternated dense and porous layers. The resistivity of a 10 times dipped multilayers obtained by these processes is about 3.2×10$^{-3}$Ωcm. Moreover the electrical properties vary with the number of layers whereas in process I no such correlation can be found. A model was developed which allows to calculate the electrical properties of the dense and porous layers. The chemical composition of the homogeneous coating and of the multilayers with the alternated structure is also reported.

INTRODUCTION

Thin transparent conducting oxide coatings such as tin doped indium oxide (ITO), fluor or antimony doped tin dioxide (FTO, ATO) are of broad interest because of their high optical transmission, high conductivity and numerous of application fields [1]. They are used as electrodes in solar cells [2], LCD’s, optical electrical devices [3], catalysts or as heat shields [4]. Commercial coatings are essentially made by physical or chemical deposition techniques like sputtering [5], spray pyrolysis [2] or chemical vapour deposition (CVD) [6]. The vacuum techniques give coatings with good electrical and optical quality but bear the disadvantage of high production costs. The spray techniques are cheaper and give also highly conductive coatings but with lower homogeneity.

The sol-gel technique [7-15] allows to produce layers with high transmission in the visible part but their resistivity was always found at least one order of magnitude higher than those obtained for coatings prepared by the other methods. Therefore numerous investigations are underway to understand the reasons of this high resistivity and to improve the electrical properties of sol-gel coatings. The morphology of the sol-gel layer is one of the main factors influencing the conductivity of the layer. They are porous and consist of small crystalline particles whereas spray coated films show a densely packed columnar
structure [14]. Recent studies indicated that it is possible to improve the structure of sol-gel coatings by increasing the sintering temperature and the heating rate of the sintering process [15] using for example CO₂ laser densification [16, 17]. The resistivity of the coatings depends also on the layer thickness. It sharply decreases with increasing total thickness up to a value of 200-300 nm. Therefore one way to improve the sheet resistance is to increase the total layer thickness by repeating the coating cycles [18].

In this paper we investigate the influence of the sintering conditions on the electrical and structural properties and on the chemical composition of SnO₂:Sb multilayers made by the sol-gel process.

EXPERIMENTAL

Multilayer sol-gel coatings have been deposited on borosilicate glass by dip coating using a 0.2 molar ethanolic solution of SnCl₂(OAc)₂ containing 5 mol% SbCl₃ in a controlled atmosphere (T=20°C, RH=40 %). The densification of the coatings was performed by three different processes (Fig. 1) where each coating consisted of a different number of layers having the same total thickness about 250 nm in dry state. The thickness of the individual layers was adjusted by changing the withdrawal speed. It is worthwhile to note that for process I a drying stage at a temperature lower than 200°C (e.g. 120°C) leads to cracked layers. The final heat treatment was always realised by introducing the layers directly into a preheated furnace at 550°C.

![Flow diagram of the various procedures](flow_diagram.png)

Fig. 1: Flow diagram of the various procedures

The layer thickness was determined by a surface profiler (Tencor P10). The electrical properties of the coatings were measured by the 4 probe method and the Van der Pauw/Hall technique (MMR Technology with a 1.5 T magnetic field). The texture has been observed by high resolution transmission microscopy and the crystallite size was determined from XRD spectra (Siemens D500). The chemical composition was investigated by Secondary Neutral Mass Spectrometry (SNMS) using a Leybold INA 3-equipment connected to a quadropole-mass spectrometer. The SNMS measurement were performed with a different batch of samples than the electrical measurements.

RESULTS AND DISCUSSION

The drying and sintering temperature influence the thickness of the multilayer. For example a multilayer coating prepared with 10 coating cycles with the same withdrawal speed and sintered according to process II or III has a total thickness of 180 nm while the same coating prepared according to process I has a total thickness of 232 nm. The total thickness for all multilayer coatings made according to process I
was always found about 25% higher than the thickness of those obtained by the other processes, which hardly differ from each other. This can be explained by differences in the layer morphology as shown by the HRTEM cross sections. (Fig. 2 and Fig. 3). The multilayer coating made by process I is porous but homogeneous and built with small (6-8 nm) almost spherical crystallites that are loosely packed (Fig. 2). On the contrary, the morphology of the multilayers obtained according to process III reveals that each individual layer consists of a two layer structure: a thin 10 nm relatively dense interface lying on top of a more porous bulk layer (Fig. 3). The crystallite's size is about 6 nm. Because the multilayers made by processes II and III are equally thick it is assumed that the structure of the coating prepared by process II is also built of consecutive porous and dense layers. The morphologies of the multilayers is similar to that found for single layers sintered and heated in the same conditions [10].

These different morphologies have a dramatic effect on the electrical parameters of the coatings. For multilayer coatings obtained by process I the resistivity is practically independent of the number of layers i.e. the resistivity is the same $1.4 \times 10^{-2}$ Ω cm for a coating made of 4 x 58 nm or a 10 x 23.2 nm thick layers (Fig. 5). The electron mobility $\mu = 1.7$ cm$^2$/V s and the carrier density (electron) $N = 2.5 \times 10^{20}$ cm$^3$ are also practically constant for each coating. A different behaviour has been found for coatings made by process II and III. In both cases the electrical properties are strongly dependent on the number of layers (Fig. 5). An increasing number of layers leads to a decrease of the resistivity from $\rho = 3.6 \times 10^{-3}$ Ω cm for a 4 x 45 nm thick coating to $\rho = 1.8 \times 10^{-3}$ Ω cm for a 10 x 18 nm thick coating. The electron mobility increases from $\mu = 2.93$ cm$^2$/V s for the 4 layers coating to $\mu = 4.5$ cm$^2$/V s for a 10 layers coating. However the carrier density remains constant $N = (4 \times 10^{20}$ cm$^3)$. A higher conductivity is therefore observed when the number of the dense interfaces increases. The thin layers should have consequently a lower resistivity than the internal part of each layers.

The resistivity $\rho_e$ of the dense interfaces and the resistivity $\rho_i (\rho_i > \rho_e)$ of the porous bulk can be determined by assuming that the sequence of the single layers is connected electrically in parallel (Fig. 4). In this case the macroscopic sheet resistance is given by the sum of the single layer sheet resistance. For a given multilayer built with n layers with alternating porous and dense regions, the macroscopic resistivity is given by:
A plot of the measured resistivity of the multilayers made by the three processes versus the number of layers is shown in Fig. 5. For each process a straight line is obtained with almost equal intercept ~ 50 (Ωcm)$^{-1}$. For process II and III the slope has nearly the same value of 22 (Ωcm)$^{-1}$, while for process I the reciprocal resistivity is practically constant.

\[
\frac{1}{\rho_n} = \frac{1}{\rho_i} + \frac{d_e}{d} \left( \frac{1}{\rho_e} - \frac{1}{\rho_i} \right) \cdot n \tag{1}
\]

The resistivity $\rho_e$ of the dense interface of each layer was calculated assuming that the thickness of the dense interfaces measured from the HRTEM pictures was 10 nm (Table 1).

Table 1: Values of $\rho_i$ and $\rho_e$ calculated from (1) and Fig. 5 for coatings made according to process I, II, III.

<table>
<thead>
<tr>
<th>Process</th>
<th>I</th>
<th>II</th>
<th>III</th>
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<tbody>
<tr>
<td>$\rho_i$ (Ωcm)</td>
<td>0,014</td>
<td>0,014</td>
<td>0,014</td>
</tr>
<tr>
<td>$\rho_e$ (Ωcm)</td>
<td>-</td>
<td>0,0018</td>
<td>0,0022</td>
</tr>
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The chemical composition of the coatings (C, O, Si, Sn, Sb) and the ratio Sn:Sb was examined by SNMS for two 4 times dipped multilayers made by process I and process III respectively (Fig. 6 and Fig. 7). In both samples no carbon was detected and the surface shows an excess of O probably due to atmospheric water and OH-group absorbed after the obtention of the coatings.

For the multilayer coating produced by process I the depth profile of the ratio Sn:Sb is practically constant and corresponds to the composition of the sol. The Sn concentration slightly increases continuously toward the substrate while the O concentration has an opposite behaviour. Near the
substrate the ratio Sn:O corresponds practically to the SnO$_2$ composition. In this process the 4 layers where first dried at 200°C and at this stage considerable amount of organic materials are still included in the coating. During the sintering process at 550°C the organic material lying at the air/coating interface will react more strongly with the oxygen from air than the organic material lying deeper in the layer, which will mostly react with oxygen inside the coating.

When each layer is sintered at 550°C without a predrying step (process III) the shape of the concentration profile of Sn, O, Sb is totally different (Fig. 7). The oxygen concentration does not decrease in the direction to the substrate and the 4 sequential structures of the coating are clearly observed by the alternating maxima and minima for O, Sn and the ratio Sb:Sn. As the first minimum of this ratio lies at the layer's surface it is assumed that their minima correspond to the dense part of the multilayer and their maxima to the porous part of the layer. At the minima, the Sn:Sb ratio agrees with the value of the sol composition. The Sb and Sn concentration proceeds according to the Sn:Sb curve while the O concentration has an opposite behaviour. The composition of the dense and porous part is therefore different. As the amount of Sb is small compared to the amount of Sn the difference in the composition of the dense vs. bulk part of the layers is essentially related to change in Sn. In the dense interface the ratio Sn:O corresponds almost perfectly to the SnO$_2$ composition whereas in the porous structures the ratio Sn:O corresponds to a composition SnO$_{2-x}$, with x > 0.5. In the porous part of the layer the Sb concentration is higher than in the dense part. More Sb seems necessary to keep the electrical neutrality of the layer, due probably to the higher surface of the particles (lower density).

![SNMS of a 4 layers coating 187 nm thick prepared by process I](image1)

![SNMS of a 4 layers coating 230 nm thick prepared by process III](image2)

**CONCLUSION**

The influence of drying and sintering conditions on the electrical and morphological properties and the chemical composition profiles of sol gel SnO$_2$:Sb multilayers has been reported. Multilayers coating made of layers of same thickness, individually sintered in air at 550°C are composed of alternated layers consisting of a dense external layer on top of a porous bulk structure. A model was proposed to calculate the resistivity of the dense layer $\rho_d = 2.2 \times 10^{3}$ $\Omega$cm and the porous layer $\rho_p = 1.4 \times 10^{-2}$ $\Omega$cm. The chemical composition of both layers is different. In the dense part the composition is nearly SnO$_2$ with a ratio Sb:Sn = 5 %. In the porous layer the composition corresponds to SnO$_{2-x}$, with x >0.5 and a ratio Sb:Sn = 7 %. For coating made with single layers all dried at 200°C and where the whole coating was then sintered at 550°C, the resistivity is independent of the number of layers and the final total thickness. The value is $\rho_z = 1.4 \times 10^{-2}$ $\Omega$cm. The morphology of the coating is homogenous as well as their chemical composition. It corresponds to SnO$_2$ with a ratio Sb:Sn = 5 %.
ACKNOWLEDGEMENTS

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REFERENCES