Influence of the Layer Morphology on the Electrical Properties of Sol Gel Transparent Conducting Oxide Coatings

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Abstract. Tranparent conducting coatings have been prepared by sol gel methods either by a conventional sol-gel process (Antimony doped Tin Oxide—ATO, Aluminium doped Zinc Oxide—AZO) or a new wet chemical process using fully dispersed crystalline nanoparticles (ATO, Indium Tin Oxide—ITO). The dip coating technique has been used as deposition technique with single coating thickness varying from a few nanometer to ca. 400 nm. The layers have been fired in a furnace. Structural properties have been determined by x-ray diffraction and TEM analysis and the electrical properties by the van der Pauw/Hall measurement. Three different coating procedures have been used to investigate the effect on the structure, morphology and the electrical properties of the coatings. It is shown that the individual layer thickness in multilayer coatings influences dramatically the mentioned properties. Very thin individual layers favour a heterogeneous nucleation with dense columnar growth of the crystallites leading to low electrical resistivity ($\rho \approx 10^{-3}\Omega$ cm), while thick individual layers result in a porous morphology made of small crystallites leading to resistivities in the 10^{-2} Ω cm range.

Keywords: morphology, electrical properties, transparent conductive coatings

Introduction

Transparent conducting coatings like antimony doped tin oxide (ATO), aluminium doped zinc oxide (AZO) and tin doped indium oxide have (ITO) found a wide range of application in opto-electronic devices. They also find applications as gas sensors, catalysts and heat shields [1].

The sol gel technique allows produces thin homogeneous layers with high transmission in the visible, but the resistivity is always found at least one order of magnitude higher than that obtained with coatings prepared by deposition methods such as CVD, sputtering or spray pyrolysis. One of the factors which influences the electrical properties is the morphology of the layers. The influence of the sintering temperature and the heating rate on the morphology of the layers have been already investigated [2, 3].

The aim of this work is to investigate the influence of the single layer thickness on the morphology and electrical properties of ATO, ITO and AZO sol gel multilayer coatings.

Experimental

Single and multilayer coatings have been deposited by dip coating technique on borosilicate (ATO, ITO) and on fused silica (AZO) respectively using an ethanolic solution of the metal salt and dopant (5 mole % Sb for ATO, 1 mole % Al for AZO, 8 mole % Sn for ITO). In order to investigate the influence of already crystalline particles a dispersion of redispersed ATO

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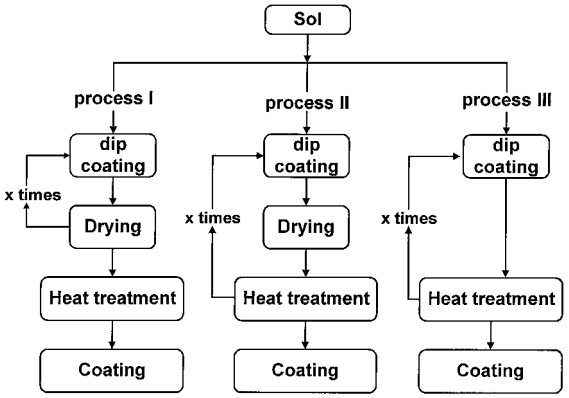


Figure 1. Flow diagram of the various procedures.

nanoparticles was used as well [4]. Three different types of procedures have been used (Fig. 1).

After their deposition the AZO coatings have been tempered in a furnace under forming gas to reduce their resistivity. The thickness of the single layers was determined by a stylus profiler (Tencor P10). The resistivity was determined by the 4-point, van der Pauw and Hall measurements. X-ray diffraction and HRTEM cross sections have been used to investigate the morphology of the samples.

Results and Discussion

AZO Coatings

TEM cross section of a single and a 10 layers coating made by process I with 25 nm thick single layers are shown in Fig. 2(a) and (b) respectively. The single layer coating is made of spherical particles with 15–25 nm in diameter scattered over the surface of the substrate. The 10 times dipped multilayer shows a columnar texture perpendicular to the surface. An increase of the thickness of the single layers to 40 nm drastically changes the morphology of the multilayer. No columnar texture is observed (Fig. 2(c)) but the coating practically consists of elongated crystallites in the direction perpendicular to the surface. From these data the critical single layer thickness for columnar texture of ZnO : Al is approximately 15–20 nm. The film resistivity decreases from 5×10^{-1} Ω cm for the single layer ($d = 25$ nm) to 4×10^{-2} Ω cm for the multilayer made of thin single layers ($d = 17$ nm).

ATO and ITO Coatings

The electrical properties and the morphology of ATO single layers with thickness >10 nm is independent on the densification process. For all three processes the single layers are made of small almost spherical crystallites that are loosely packed. The layer is porous and its top surface is denser than the rest of the layer. With a sintering temperature of 550°C resistivities as low as $\rho = 9 \times 10^{-3}$ Ω cm could be reached.

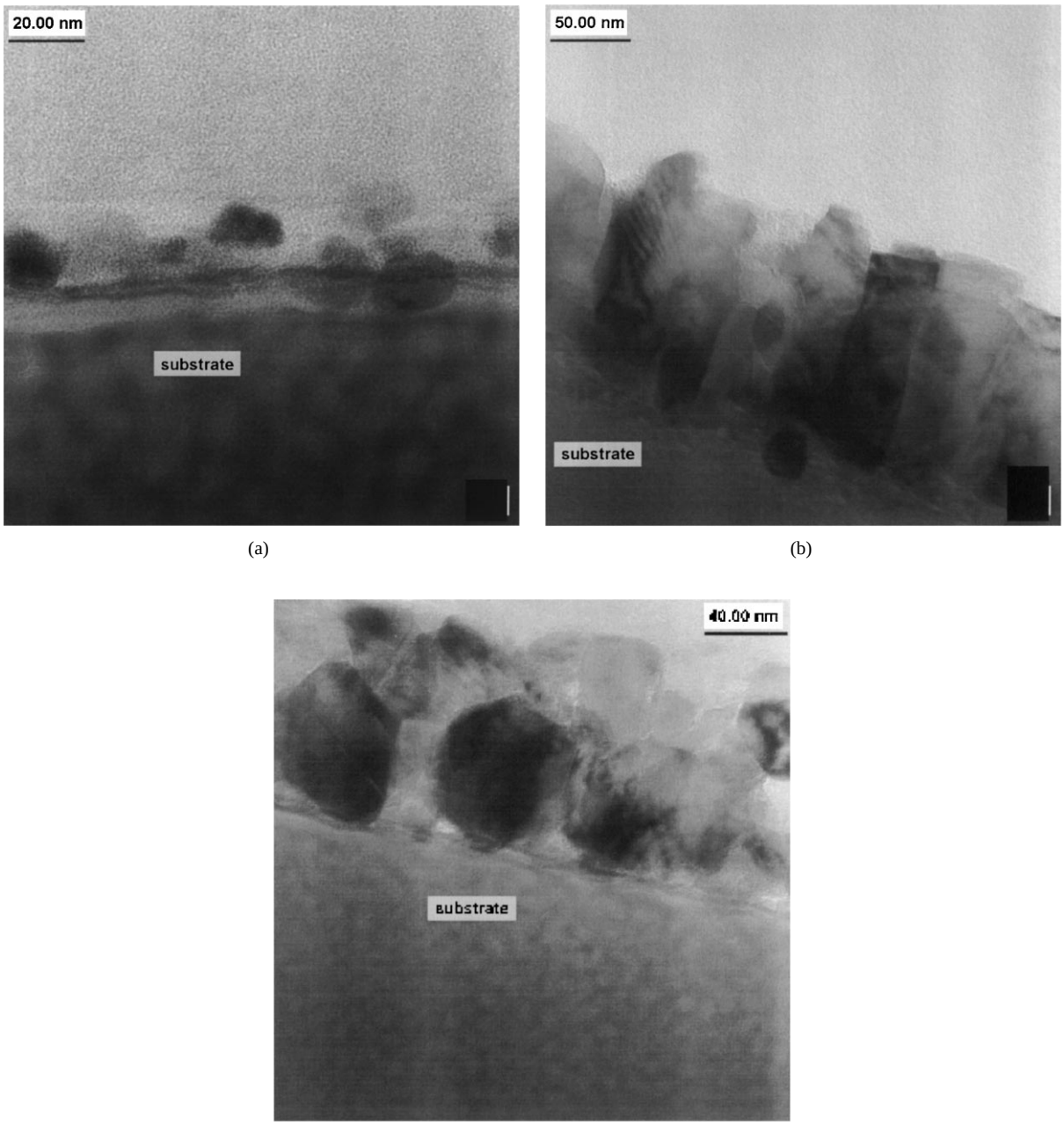
On the hand the sintering conditions and the thickness of the single layers influence the morphology and the electrical properties of the ATO multilayer coatings. Multilayers made with single layer thickness of 20 nm by process I are homogeneous and built with small spherical crystallites that are loosely packed (Fig. 3(a)). The morphology of the multilayers obtained by process II or III reveals that each individual layer consisting of a 10 nm relatively dense interface layer on top of a porous bulk layer (Fig. 3(b)). The resistivity of the 200 nm thick multilayer made by process I and II (or III) is 1.4×10^2 Ω cm and 1.8×10^{-3} respectively. A reducing of the thickness of the single layers in the multilayer system leads to a change in the morphology of the coatings. Multilayers made with single layers having a thickness ≤5 nm and a columnar growth is observed (Fig. 3(c)). The resistivity has a value of 2.9×10^{-3} Ω cm.

The reason for the change in the morphology in the SnO_2 : Sb system might be the same as in the ZnO : Al system. The thickness of the single layer is smaller than the crystallite size in the single layer. The critical thickness can be observed by a 2–4 nm single layer thickness.

The morphology of coatings made from redispersed ATO and ITO nanoparticles using processes I, II and III is identical to that shown for thick ATO sol gel coatings (Fig. 3(a) and (b)). The results on thin coatings could not be confirmed because it was not possible to produce thin layers with the redispersed particles. The electricaal properties are similiar as well, the resistivity for a 150 nm single layer is $\rho = 1.8 \times 10^{-2}$ Ω cm, which decrease to $\rho = 6.8 \times 10^{-3}$ Ω cm for a 10×150 nm multilayer.

Conclusion

The morphology and texture of ATO, ITO and AZO coatings have been related to the coating procedure.

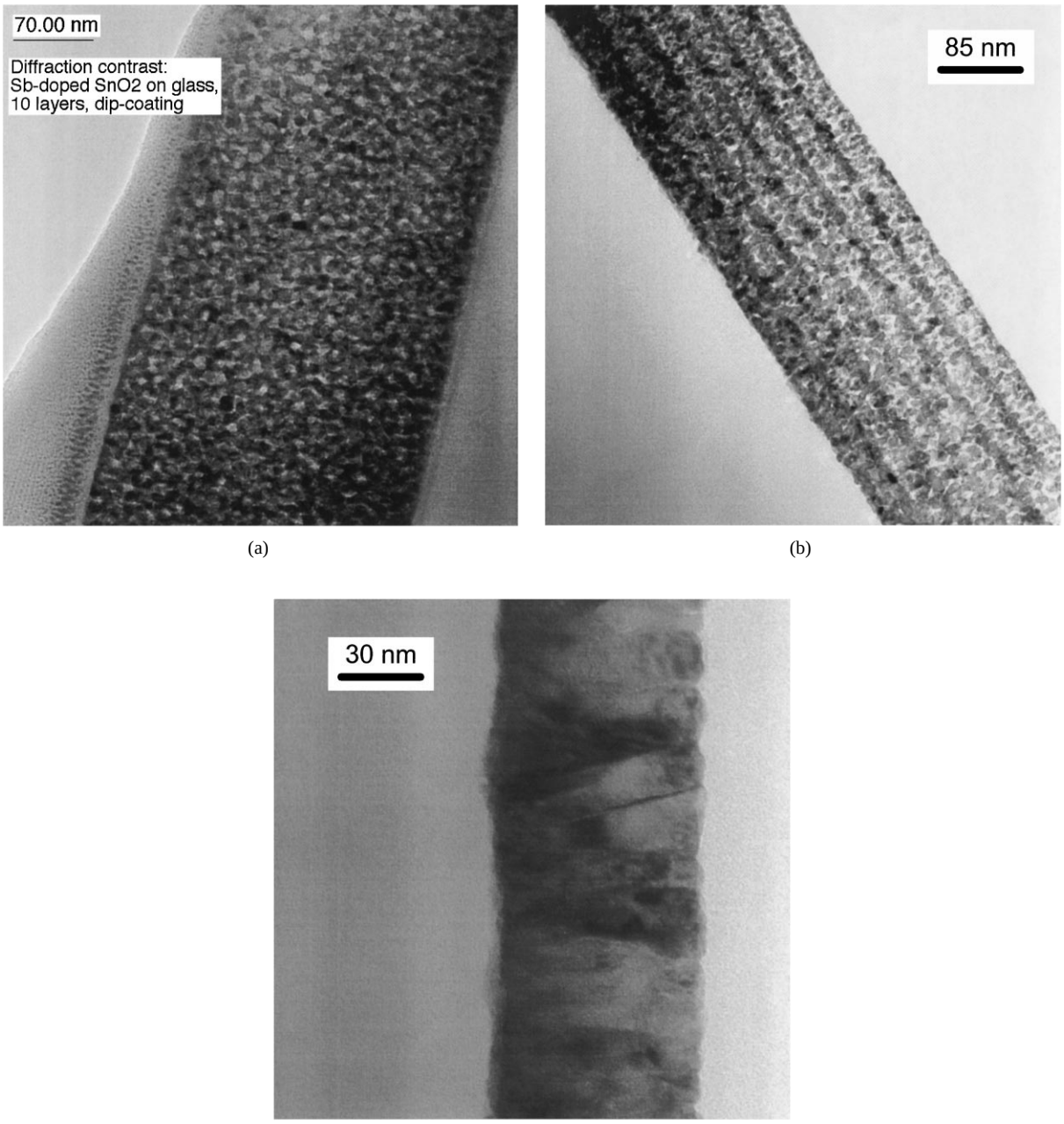


(a) (b)

(c)

Figure 2. AZO HRTEM cross-section of (a) a 25 nm thick single layer, (b) a multilayer made of 10 × 17 nm thin single layers, (c) a multilayer made of 4 × 40 nm thick single layers.

Using conventional sols the morphology of ATO and AZO coatings can be tailored from an agglomeration of spherical particles to a columnar type of arrangement. The morphology of ATO and ITO coatings made of redispersed nanoparticles always consists of loosely packed and not orientated crystallites. These structures have an important influence on the electrical properties of the coatings. Thick



(a) (b)

(c)

Figure 3. HRTEM cross section of ATO multilayers made of (a) 10 × 20 nm thick single layers densified by process I, (b) 6 × 20 nm thick single layer densified by process II, (c) 40 × 2 nm thin single layer densified by process II.

single layers are always made of an agglomeration of spherical particles with a high void fraction and exhibit a low density and high resistivity. In very thin single layers (<20 nm) heterogeneously nucleated crystals predominate and their size is limited by the thickness of the layer. As the single layer thickness increases the formation of homogeneously nucleated crystals becomes more likely.

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