

# Wet Chemical Deposition of Crystalline, Redispersable ATO and ITO Nanoparticles

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**Abstract.** A new wet chemical concept to produce coatings by dip, spin or spray processes is presented. It is based on the preparation of solutions made of crystalline nanoparticles fully redispersable in a solvent. It is exemplified for the preparation of  $\text{SnO}_2 : \text{Sb}$  (ATO) and  $\text{In}_2\text{O}_3 : \text{Sn}$  (ITO) transparent conducting coatings. The process combines the advantages of using particles having already a low resistivity and the possibility to sinter the coatings at low temperature. The particles are prepared using an in-situ monitoring of the surface energy to control the growth of the particles and to avoid their agglomeration. The dried powders can be fully redispersed in alcohol (ITO) or water (ATO). Single layers with thickness up to 200 nm (ATO) and 400 nm (ITO) have been fabricated. The sheet resistance of the coatings decreases with the sintering temperature. Typical values are  $430 \Omega_{\square}$  for ATO ( $550^{\circ}\text{C}$ ) and  $380 \Omega_{\square}$  for ITO ( $550^{\circ}\text{C}$ ). Sols made by redispersing the powders in organosilanes allow to produce coatings at low temperature with antistatic ( $R_{\square} > 100 \text{ k}\Omega_{\square}$ ) and anti-glare properties ( $R_{\square} > 100 \text{ k}\Omega_{\square}$ , 60 to 80 gloss units).

**Keywords:** ATO, ITO, redispersed particles, transparent conductive coatings

## Introduction

Transparent conducting oxides deposited on glass and plastic are widely used as transparent electrodes in the field of optoelectronic devices such as electrochromic windows, solar cells, electroluminescence and liquid

crystal displays [1]. Typically, the compounds are n-type semiconductors such as indium tin oxide (ITO), fluorine or antimony doped tin dioxide (FTO, ATO) or aluminium or gallium doped zinc oxide (AZO, GZO). Practically all known coating processes have been used for their preparation [1, 2].

The coatings obtained by the sol-gel route present a resistivity,  $\rho$ , higher than those obtained by other

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processes. Typical reported values are  $3 \cdot 10^{-3} \Omega\text{cm}$  [3, 4] for  $\text{SnO}_2:\text{Sb}$  coatings and  $8 \cdot 10^{-4} \Omega\text{cm}$  for  $\text{In}_2\text{O}_3:\text{Sn}$  coatings [5]. The reason for their low conductivity is their high porosity (low density) even after sintering at high temperature [6]. A morphology with large and densely packed crystallites obtained by spray pyrolysis, sputtering and CVD processes leads to higher electron mobility and carrier density and consequently lower resistivity [1].

The preparation of transparent coatings by wet chemical processes using crystalline powders is possible if stable suspensions of particles with sufficiently small size ( $<100 \text{ nm}$ ) can be obtained. In conventional ceramics synthesis, particulate systems minimize their surface free energy by growing into larger particles and forming larger agglomerates which are then difficult to redisperse. These reactions can be avoided by controlling the growth of the particles during the precipitation process and by adjusting the particle's surface free energy by in-situ surface modification. The basic principle of this concept has been applied to many oxide materials [7–9].

The paper reports on the preparation of ATO and ITO coatings on glass and plastic substrates based on this concept. The influence of the densification temperature and sintering time on the resistivity of the coatings are examined.

## Experimental

The preparation of ATO and ITO powders was carried out as already reported [8, 9]. Colloidal suspensions were prepared by redispersing the dried ITO and ATO powders in water or ethanol. The ATO solutions are clear with a yellowish orange colour and no evidence of precipitation was found after several months with a solid content up to 8.8 vol.%. The ITO suspensions showed a blue colour and are stable (no precipitation) during several month with solid content up to 6.2 vol.%.

ATO coatings were deposited on clean borofloat substrates by spin coating process (2000 rpm, 15 s). ITO films were prepared by dip coating clean silica or borosilicate substrates at a withdrawal speed of 3 mm/s. The thermal densification of the films was carried out in a furnace in air up to 900°C. ITO coatings were also annealed afterwards in a  $\text{N}_2$  atmosphere at a temperature of 300°C in order to decrease their resistivity.

To deposit coatings on substrates which do not withstand heat treatment at high temperature, the ITO suspension was modified by adding up to 40 wt.%

organofunctionalized silanes and a photostarter. These additives allow to polymerise and harden the layer by UV irradiation at room temperature.

ITO sols modified by addition of alkoxysilanes were also used to coat glass substrates at room temperature by spraying process.

## Results and Discussion

The dried particles of all materials are already crystalline and have a cassiterite structure for  $\text{SnO}_2$ ,  $\text{SnO}_2:\text{Sb}$  and a cubic  $\text{In}_2\text{O}_3$  phase for the ITO powder. The TO, ATO and ITO crystallites are not oriented. The crystallite size calculated from the (110) peak is 7 nm for  $\text{SnO}_2$  and 3 nm for  $\text{SnO}_2:\text{Sb}$  (5 mole% Sb). A systematic decrease of the crystallite size was observed with increasing antimony content. The crystallite size of  $\text{In}_2\text{O}_3:\text{Sn}$  calculated with the (222) peak is 15 nm [10].

The water based ATO suspensions are stable at  $\text{pH} > 8$  ( $\text{pH}_{\text{iep}} = 3.7$ ) and the mean hydrodynamic particle size is 4 nm. ITO suspensions are stable at  $\text{pH} < 6$  ( $\text{pH}_{\text{iep}} = 8.5$ ) and the mean hydrodynamic particle size is 11 nm. The average values are identical to the values of the crystallite size determined from the TEM picture and indicate that the particles are fully dispersed down to the primary particle size and that each particle appears to be formed by a single crystallite. The particle size distribution is monomodal and their width is narrow (Fig. 1).

The film thickness of ATO and ITO increases with the solid content in the dispersion. Crack free 200 nm thick single layer coatings can be prepared using a ATO suspension with a solid content of 25 wt.%. For 400 nm thick ITO coatings a suspension with 21 wt.% solid content was used. With solid content higher than 28 wt.% (ATO) and 32 wt.% (ITO) the coatings are too thick and cracks are observed. Their resistivity and sheet resistance decrease with the sintering temperature. Typical lowest values are  $\rho = 1.2 \times 10^{-2} \Omega\text{cm}$  ( $R_{\square} = 430 \Omega_{\square}$ ) for ATO (550°C) and  $\rho = 7 \times 10^{-3} \Omega\text{cm}$  ( $R_{\square} = 90 \Omega_{\square}$ ) for reduced ITO (900°C) (Fig. 2).

The decrease of the resistivity with increasing sintering temperature is due to the growth of the particles which reduces the scattering of the electrons at the grain boundaries (higher mobility) (Figs. 3, 4). The increase of the sheet resistance of ATO at  $T > 600^\circ\text{C}$  is due to the diffusion of  $\text{Sb}^{3+}$  towards the particle surface which increases the electron scattering [11].

The UV cured ITO coatings deposited at low temperature and then UV cured exhibit a sheet resistance

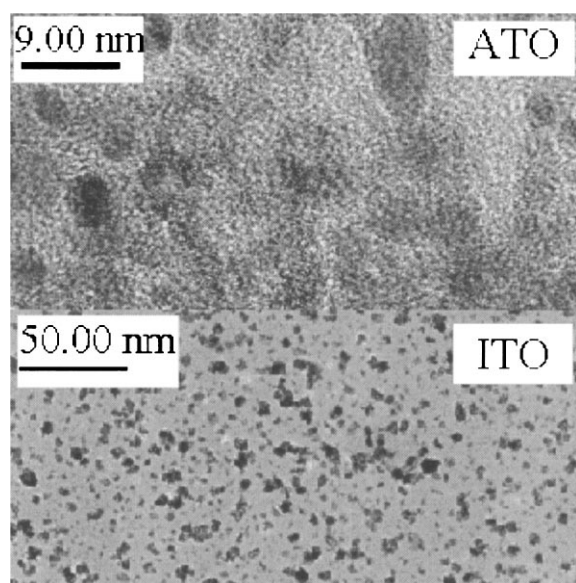


Figure 1. HRTEM picture of crystalline  $\text{SnO}_2:\text{Sb}$  nanopowder redispersed in water with TMAH as dispersion agent ( $\text{pH} = 10$ ) and  $\text{In}_2\text{O}_3:\text{Sn}$  nanopowder after annealing and redispersion in ethanol ( $\text{pH} = 4$ ).

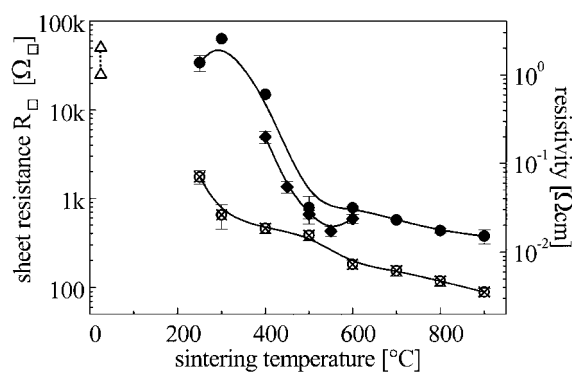


Figure 2. Sheet resistance (left) and resistivity (right) of 400 nm thick ATO and ITO coatings vs. sintering temperature (30 min): as deposited ATO ( $\blacklozenge$ ), as deposited ITO ( $\bullet$ ), ITO annealed in a nitrogen atmosphere at  $300^\circ\text{C}$  ( $\boxtimes$ ), ITO deposited at room temperature and cured under UV radiation ( $\triangle$ ).

in the range of  $20\text{--}50\text{ k}\Omega_{\square}$ , depending on the amount of added organosilanes, conferring antistatic properties to the system.

### Conclusion

Crystalline  $\text{SnO}_2$ ,  $\text{SnO}_2:\text{Sb}$  (ATO) and  $\text{In}_2\text{O}_3:\text{Sn}$  (ITO) nanoparticles fully redispersible in water or ethanol have been prepared. Transparent conducting coatings with thickness up to 400 nm/layer for ITO and 200 nm/layer for ATO have been obtained by spin

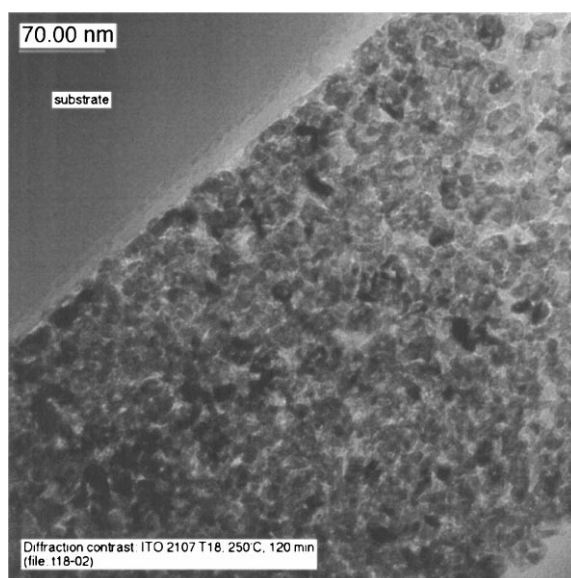


Figure 3. Cross section HRTEM picture of ITO coatings made of  $\text{In}_2\text{O}_3:\text{Sn}$  nanopowder redispersed in ethanol; annealed at  $250^\circ\text{C}$ , 2 h.

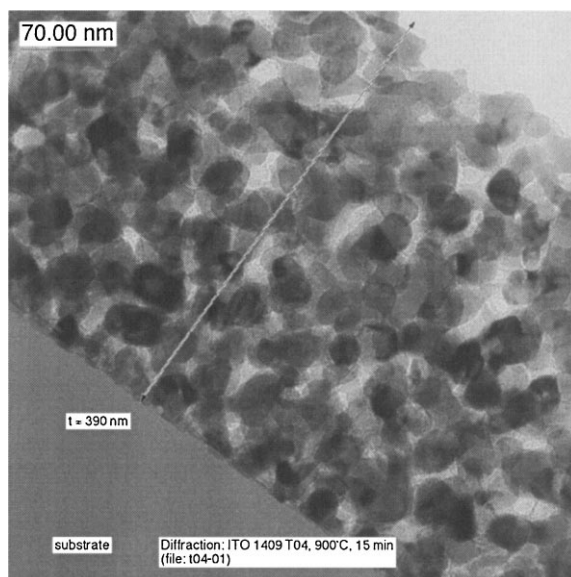


Figure 4. Cross section HRTEM picture of ITO coatings made of  $\text{In}_2\text{O}_3:\text{Sn}$  nanopowder redispersed in ethanol; annealed at  $900^\circ\text{C}$ , 15 min.

coating (ATO, ITO) and dip coating (ITO) process. For ATO the lowest resistivity value,  $\rho = 1.7 \cdot 10^{-2}\ \Omega\text{cm}$ , was obtained at a sintering temperature of  $550^\circ\text{C}$  while for ITO layers the lowest resistivity  $\rho = 2 \cdot 10^{-2}\ \Omega\text{cm}$  was obtained after sintering at  $900^\circ\text{C}$ . This value was reduced to  $\rho = 3.4 \cdot 10^{-3}\ \Omega\text{cm}$  after annealing at  $300^\circ\text{C}$  in nitrogen atmosphere. All resistivity values

are higher than those obtained by sputtering, spray pyrolysis and CVD process. This is due to the porous, particulate morphology of the the layers. The electrical properties of as sintered ATO and ITO coatings are stable under normal conditions (20°C, 40% RH, tested up to 80 days) and also under high temperature continuous use. The resistivity of reduced ITO coatings, however, slightly increases with time at 20°C.

The use of crystalline ATO and ITO nanopowders offers a new way to produce large transparent conducting coatings on low  $T_g$  substrates for antistatic application and on glass substrates for devices requiring transparent, conductive or antiglare coatings.

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