Comparative study of transparent conductive In$_2$O$_3$:Sn (ITO) coatings made using a sol and a nanoparticle suspension

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Abstract

Transparent conducting In$_2$O$_3$:Sn (ITO) layers have been deposited by spin coating on glass substrates using two different solutions, an ethylene glycol solution of indium and tin salts (sol) and a suspension of crystalline ITO nanoparticles redispersed in ethanol. The coatings have been sintered in air at 550 °C for 30 min. and then post annealed in a reducing atmosphere at 300 °C for 30 min. The electrical, optical, morphological and mechanical properties of both types of coatings are compared. The use of the suspension leads to thick 500 nm single layers with a specific resistivity ρ 1.6 × 10^{-2} Ω cm but only very thin ones, about 12 nm for a single layer, with ρ 1.8 × 10^{-3} Ω cm (a factor of 10 smaller) are obtained using the sol. The resistivity still decreases down to a minimum ρ 6 × 10^{-4} Ω cm for multilayer coatings, a value quite close to that obtained by PVD or CVD processes. These differences originate from the different morphologies of the coatings. The conventional sol gel layers exhibit a columnar structure with a low porosity (28%) while the others have a granular structure with a high porosity (51%). Correspondingly the electron mobility μ is 14 and 1.1 cm^2/V s, respectively. The visible transmission of both types of layers is high ($T > 85$%). The influence of the sintering temperature is also discussed.

1. Introduction

Making glasses electrically conductive by depositing on their surface a conducting layer which at the same time allows to retain a high visible transparency has opened many avenues for their application. Except for a few cases, the production of transparent conducting oxide coatings (TCO) by the sol–gel process has not yet asserted its position along with the established vacuum processes as they usually have a higher resistivity and need a high sintering temperature to bring the crystallites into contact to assure a high mobility of the charge carriers and, consequently, a low resistivity. For In$_2$O$_3$:Sn (ITO) films, which exhibit the lowest resistivity among the TCO family, a post annealing treatment under reducing atmosphere allows to increase the carrier density and therefore decrease the resistivity down to a few 10^{-4} Ω cm [1,2]. It is however practically impossible to produce single sol–gel layers with reasonable thickness to get a low sheet resistance ($R_\square = \rho/t$). This can only be achieved by multiple depositions, a process inadequate for practical application. The production of thick films in a single step is however possible using suspensions of crystalline nanoparticles [3–5] but the achievement of a high conductivity still remains a challenge as the coatings have to be processed at very high temperatures to sinter the particles together. Nevertheless the route is a promising alternative for some forthcoming development because of the lower deposition cost and particularly because of the possibility to process layers at room temperature on plastic substrates [4,7].

This paper is dedicated to a comparative study of the electrical, structural and optical properties of ITO coatings deposited on glass substrates by the spin coating process using two chemical routes, one using a conventional sol and the other a suspension of dispersed crystalline ITO nanoparticles.

2. Experimental

2.1. Coating systems

2.1.1. Conventional sol

An indium tin oxide solution containing 10 mol% Sn was prepared by using indium nitrate anhydrous $In(NO_3)_3$ and tin acetate $Sn(CH_3COO)_4$ as sources for In and Sn. Both salts were dissolved separately in ethylene glycol for 3 h at room temperature. The two solutions were mixed at room temperature and stirred at 70 °C for 2 h until a clear solution was obtained. The indium concentration in the ITO sol with 10 mol % Sn-dopant was 0.3 M. A sol of 0.1 M concentration was then obtained by subsequent addition of ethanol. The coating sol was deposited on borosilicate or fused silica glasses using the spin coating method. The coatings were then sintered in air up to 900 °C during 30 min and further post annealed in forming gas (N_2/H_2: 92/8) at 350 °C during 30 min. Multilayers were made by repeating the whole coating procedure (deposition, sintering and annealing).

2.1.2. Suspension

The solution was prepared by dispersing in ethanol a crystalline conducting ITO powder made of aggregated nanoparticles down to their primary size (<25 nm). The solid content was 25 wt.%, corresponding to 14 vol.%. The detailed preparation of the ITO powder can be found in [3,4,8]. The stable suspension was spin coated on the same substrates and the coatings have been heat treated and post annealed as reported above.

2.2. Characterizations

2.2.1. Morphological properties

The thickness (t) of the coatings was determined using a Tencor P10 profilometer. The surface and cross-section morphology have been analyzed using Scanning Electron Microscopy (SEM-JEOL 6400). The roughness was deter-
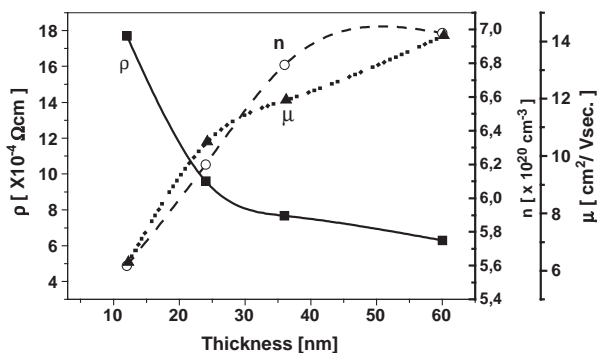

Fig. 1. Electrical parameters ρ, n, μ of spin coated ITO single and multilayers (1, 2, 3, 5) sintered in air at 550 °C, 30 min and further post annealed in forming gas at 300 °C, 30 min versus layer thickness. Each single layer is approximately 12 nm thick.
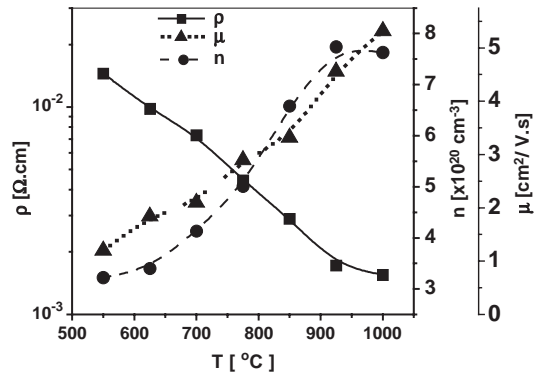

Fig. 2. Electrical parameters of a 500 nm thick single ITO layer made with the nanoparticle suspension versus sintering temperature (after post annealing in forming gas).

mined using a Zygo Newview 5000 white light interferometer. The porosity (P) of the coatings was calculated as P (%)$=100[1-(n_p^2-1)/(n_s^2-1)]$, where n_p is the measured refractive index of the film at the wavelength of 550 nm and $n_s=1.9$ is the theoretical value at the same wavelength of the dense material [6].

2.2.2. Optical properties

The transmittance and reflectance have been determined using a Varian Cary 5 E spectrophotometer in the wavelength range 300 to 3000 nm. The infrared reflection was measured in the range 2.5 to 22 μm using a Bruker IFS 66V Fourier Transform Infrared Spectrometer. The refractive index of the film was determined in the visible range using the Variable Angle Specular Reflectance Accessory (VASRA) of the Cary 5E equipment.

2.2.3. Electrical properties

The sheet resistance ($R_\square$) was measured by a 4-point probe technique using a homemade system and a 34401-A Hewlett-Packard multimeter. The resistivity was calculated from $\rho=R_\square t$. Carrier density (n) and mobility (μ) were determined using a MMR van der Pauw equipment with a 1.4 T magnetic field.

2.2.4. Mechanical properties

The adhesion of the coatings has been evaluated by the tape test procedure according to DIN 58196-6-K2, the abrasion following a cloth and rubber test according to DIN 58196-5 (H 25) and 58196-4 (G10), respectively, and the hardness using the pencil test (ASTM D3363-92a).

3. Results and discussion

3.1. Electrical properties

The use of the conventional sols leads to very thin coatings, typically 12 nm for a single layer. The electrical properties of such single and multilayer ITO coatings

Table 1
Comparative results of the electrical properties and porosity P of ITO layers sintered at 550 °C and post annealed at 300 °C made using a conventional sol and a nanoparticle suspension

Solution	t [nm]	ρ [10^{-4} Ω cm]	$R_\square$ [$\Omega_\square$]	n [10^{20} cm^{-3}]	μ [cm^2/V s]	P [%]
Suspension	500 Single layer	160	320	3.2	1.2	52
Conventional sol	60 Five layers	6.3	105	6.95	14.2	28

sintered at 550 °C with a further forming gas treatment at 300 °C are shown in Fig. 1. A single layer has a resistivity of 1.8×10^{-3} Ω cm, an electron density of 5.6×10^{20} cm^{-3} and a mobility of 6 cm^2/V s. The deposition of multilayers improves all parameters. The resistivity of a 5-layer coating is a factor of 3 lower ($\rho = 6.3 \times 10^{-4}$ Ω cm) because of the slight increase of the electron density (up to 6.9×10^{20} cm^{-3}) but particularly of the large increase of the charge mobility up to 14.2 cm^2/V s. The variation of the resistivity and mobility with the thickness is a known phenomenon observed with all very thin conducting layers which present a high electron surface scattering which restricts the mean free path of the carriers and hence limits their mobility to low values [9].

Sintering of the layers at temperatures higher than 550 °C still improves all the parameters. As an example, a resistivity of 3.3×10^{-4} Ω cm, a mobility of 25.3 cm^2/V s and an electron density of 7.5×10^{20} cm^{-3} have been typically obtained after sintering in air at 900 °C for 30 min and post annealing in forming gas at 300 °C for 30 min. The rise of the sintering temperature leads essentially to an observable increase of the charge mobility so that the improvement of the resistivity is mainly due to a smaller electron grain boundary scattering. Takahashi et al. [10] have also reported a decrease of the resistivity of dip coated ITO films by one order of magnitude by increasing the firing temperature from 400 to 700 °C. This decrease also was due to the remarkable increase of the carrier mobility from 1.3 cm^2/V s at 400 °C to 14 cm^2/V s at 700 °C.

On the other hand, 500 nm (or more) thick single layers are obtained using the nanoparticle suspension. The electrical properties of such coatings determined as a function of the sintering temperature are shown in Fig. 2. The resistivity of the layer sintered at 550 °C is 1.6×10^{-2} Ω cm, i.e. typically a factor of about 25 higher than that of conventional sol–gel ITO coatings and also decreases with the sintering temperature down to 1.4×10^{-3} Ω cm. The figure also shows that the improvement in ρ comes mainly from the remarkable increase of the mobility from 1.1 to 5.4 cm^2/V s and of the electron density from 3.3 to about 8.0×10^{20} cm^{-3}. A similar approach of making ITO coatings has been also recently reported [5]. The annealing step was however different as all coatings have been sintered and annealed in N$_2$ at the same temperature ($300 < T < 800$ °C). The measured resistivity after sintering and annealing at 500 °C was $\rho = 6.3 \times 10^{-2}$ Ω cm, i.e. a factor of 4 higher than our result and was also found to decrease with the temperature. By analyzing the spectral transmittance and reflectance using the Drude theory with a frequency-dependent scattering time characteristic for ionized impurity scattering and then applying an effective medium theory to account for the coating's porosity, the authors found that the electrical resistivity of the individual particles had a resistivity of 9.5×10^{-4} Ω cm (for a sintering at 550 °C), close to that found for ITO coatings made by PVD or CVD processes. A theoretical analysis of the electrical parameters of our sol–gel and the nanoparticulate coatings is reported in [14] and a
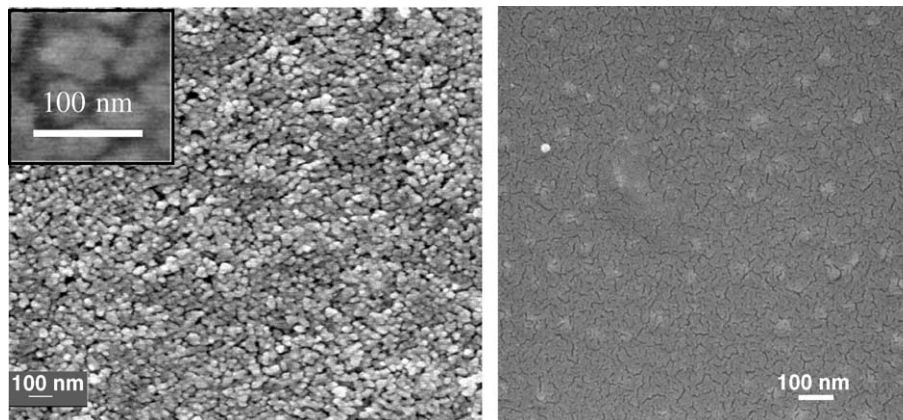

Fig. 3. SEM image of the surface morphology of spin coated ITO layers sintered at 550 °C. Left: made with the suspension; right: made with the conventional sol.

similar conclusion has been reached. As also discussed in Section 3.2, the high macroscopic resistivity of these nanoparticulate coatings is due to their granular morphology which leads to high grain boundary electron scattering.

The comparison between the electrical properties of coatings sintered at 550 °C obtained from both routes and submitted to the same post annealing treatment is listed in Table 1. The coatings made using the conventional route have a remarkable higher mobility and a lower porosity than those obtained using the nanoparticles suspension (calculated with the value $n_p = 1.69$ for the sol−gel coating and $n_p = 1.50$ for the nanoparticulate coating). As shown below this is due to the different morphologies of the coatings. However, the use of the suspension is an interesting issue as thick films (up to more than 500 nm) can be obtained in a single step and because such layers can be deposited on polymeric substrate, a process that is still a real challenge with the conventional sol−gel route [7].

3.2. Structural properties

The surface morphology of both films fired at 550 °C is shown in Fig. 3. The morphology of the coating made with the suspension consists of crystalline nanoparticles having a regular granular shape and the film is highly porous. The surface roughness measured on an area of $1 \times 1 \ \mu m^2$ is $R_a = 19$ nm with maximum peak-to-valley value of 85 nm. The low charge mobility of such films is therefore understandable and results from a high electron scattering process at the grain boundaries. The electrical conductivity can only be improved by increasing the size of nanoparticles and by a better densification which are both achieved with a sintering at higher temperatures (e.g. at 900 °C). Choi et al. [11] reported that the carrier mobility of sputtered films increases with the film density and evidently the same hold for our ITO coatings. The right side shows the surface morphology of the sol−gel film. It is much smoother and its roughness measured on an area of $70 \times 50 \ \mu m^2$ is $R_a = 0.35$ nm with peak-to-valley maximum not exceeding 12.2 nm and no particles can be seen, even using a higher magnification.

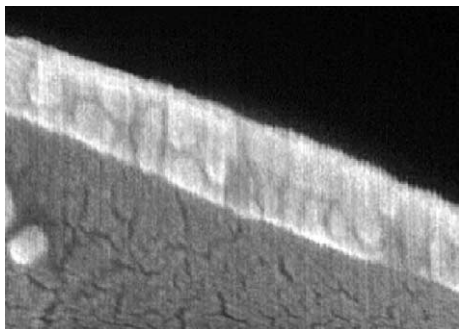Table 2
Typical results of both types of ITO coatings sintered in air at 550 °C and post annealed in forming gas at 300 °C

Coating system	Tape test	Cloth test	Rubber test	Pencil test
Sol	Ok	Class 1*	Class 1*	5 H
Suspension	Ok	Class 2**	Class 4***	6 B

*no visible damage; **slight light scattering; ***partial damage observable.

Therefore, a better insight in this structure was found by studying cross-sections of these coatings.

Fig. 4 shows a SEM cross-section of a 5-layer film 60 nm thick made by the conventional sol−gel route sintered at 550 °C and then post annealed. A columnar microstructure of densely packed crystallites with a base size ranging between 25 and 40 nm is observed. The grains are larger than at least the thickness of 2 layers. This structure does not exhibit intergranular voids as observed in the nanoparticulate films as well as discontinuities between the layers. This explains the low porosity $P = 28\%$ (higher density) and the higher mobility of the carriers, $\mu = 14.2 \ cm^2/V$ s, observed in such films (Table 1). Moreover no cracks have been observed either visually or by SEM at all processing temperatures.

Schuler et al. [12,13] proposed recently a microstructural zone model to explain the different structural morphologies of sol−gel coatings (granular, layered and columnar) as well as their influence on the conducting properties of ZnO:Al layers [13]. A columnar structure, observed essentially for multilayer sol−gel coatings made of very thin layers, leads to a higher conductivity than a layered or a granular structure. Such a structure was found to occur when the structure parameter q defined as the ratio of the intrinsic crystallite size to the single layer thickness [12,13] was $q > 1$. Our result is in a good agreement with this classification as q is larger than 2 for our coatings.

The mechanical properties are summarized in Table 2. The coatings made with the sol show outstanding properties. The ones made with the suspension indicate that the

Fig. 4. SEM cross-section of a 60 nm thick sol gel ITO (5 layers) made with the conventional sol and sintered at 550 °C.
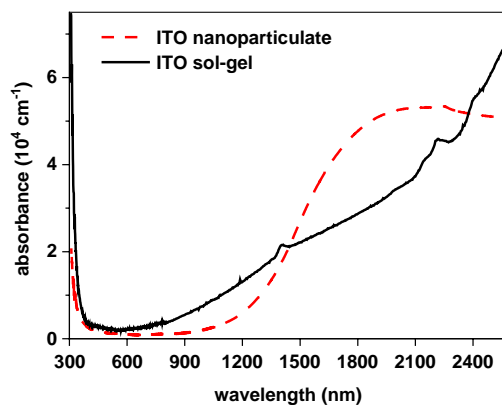

Fig. 5. Absorbance spectrum of spin coated ITO layers sintered at 550 °C and post annealed at 300 °C.
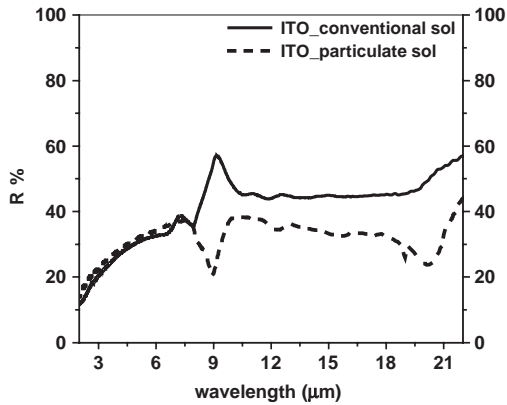
Fig. 6. IR reflection spectrum of the coatings shown in Fig. 5.

particles are not yet fully sintered together. The coatings are rather soft and can be easily scratched and their adhesion is poor and should be improved. This can be done either by sintering them at higher temperatures or by binding the particles together by adding an organic binder to the suspension. However in this case the conductivity slightly decreases [4,7].

3.3. Optical properties

Fig. 5 shows the absorbance α of the 60 nm thick 5-layer ITO film made with the conventional sol and that of a 500 nm thick single ITO layer made with the suspension. It has been calculated using the relation α (cm^{-1})$=2.3/d$ (cm)$\times \log[(1-R)/T]$ where d is the thickness, R is the reflectance and T is the transmittance of the coatings. Both films sintered at 550 °C and post annealed at 300 °C exhibit a low absorbance (<2000 cm^{-1}) in the visible range, corresponding to a transmittance close to 90%. Because of its smaller thickness, the sol–gel coating shows however a slightly larger transmission window which extends up to 2.7 µm in the near IR. Both coatings exhibit in the near IR range an absorbance due to the free carriers. The effect is particularly visible with the nanoparticulate single coating that has a high thickness although the carrier concentration is half of that of the sol–gel film (Table 1). An increase of the carrier concentration shifts the onset of the absorbance to lower wavelength [4]. As discussed in more details in [14], the optical properties of such coatings cannot be described using the simple Drude model because of their granular morphology but those of the sol–gel coatings presenting a columnar morphology are very well described by such a model.

The IR reflection spectrum of both layers is shown in Fig. 6. The influence of the free charge carriers is clearly observed as the increase of the reflection in the far IR range. The conventional sol–gel layer exhibits a slightly higher reflection than that of the particulate coating, as the charge carrier density is higher (Table 1).

4. Conclusion

ITO coatings have been deposited on glass substrates by the spin coating process. Two different chemical routes have been used, one being a conventional sol and the other a suspension of dispersed crystalline nanoparticles. The coatings have been sintered in air at 550 °C and annealed in forming gas at 300 °C. The coatings made with the conventional sol have a very small layer thickness, typically 12 nm per layer, but up to 500 nm thick single layer can be deposited using the suspension. The sol–gel coatings show a lower resistivity, $\rho=6.4\times10^{-4}$ Ω cm, than those made with a nanoparticle suspension, $\rho=1.6\times10^{-2}$ Ω cm. For both types of coatings a lower resistivity can be achieved by sintering them at higher temperature. Typical values are $\rho=3.3\times10^{-4}$ Ω cm and $\rho=1.4\times10^{-3}$ Ω cm at 900 °C. The large difference in the resistivity is due to the different morphology and structural property of the coatings: a 5-layer sol–gel ITO coating exhibits a low porosity ($P=28\%$) and a columnar structure while the other type shows a higher porosity ($P=52\%$) and a granular structure. They all show a high visible transmittance up to 90% and an increase of the reflection in the IR range. The transmittance of the nanoparticulate coatings in the near IR range is however peculiar and decreases strongly while that of the sol–gel coatings remains high ($>70\%$). This behavior is also due to the different structures [13].

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