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ScienceDirect
Thin Solid Films 516 (2008) 4102–4106
www.elsevier.com/locate/tsf

Effects of annealing temperature and heat-treatment duration on electrical properties of sol–gel derived indium-tin-oxide thin films

A. Beaurain [a], D. Luxembourg [a], C. Dufour [a], V. Koncar [b], B. Capoen [c], M. Bouazaoui [c,]*

[a] IEMN (CNRS, UMR 8520), Université des Sciences et Technologies de Lille, Avenue Poincaré BP 69 F59652 Villeneuve d'Ascq, France
[b] GEMTEX, 9 rue de l'Ermitage – BP 30329, 59056 ROUBAIX cedex 1, France
[c] PhLAM (CNRS, UMR 8523), Bât. P-5, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France

Received 12 January 2007; received in revised form 28 August 2007; accepted 1 October 2007
Available online 13 October 2007

Abstract

Transparent indium tin oxide (ITO) thin films have been deposited by the dip-coating process on silica substrates using solutions of 2,4-pentanedione, ethanol, indium and tin salts. The films have been first dried in air at 260 °C for 10 min and then annealed in a reducing atmosphere at different temperatures for various durations. The resistivity of ITO layers was found to decrease with increasing the metal concentration of the starting solution or the annealing temperature. Hence, by adjusting both metal concentration in the coating solution and heat-treatment, resistivities lower than 5×10^{-3} Ω cm for an annealing temperature of 550 °C and lower than 2×10^{-2} Ω cm for an annealing temperature of 300 °C, were obtained. These results are correlated with the density and the size of ITO grains in the films.

Keywords: ITO nanoparticles; Sol–gel; Morphology; Dip-coating

1. Introduction

Indium tin oxide (ITO) thin films combine high optical transparency, high infrared reflectance, good electrical conductivity, excellent substrate adhesion, hardness and chemical inertness. This inorganic material has been elaborated by a variety of methods such as sputtering [1], evaporation [2], spray pyrolysis [3], screen printing [4], and sol–gel method [5–10]. Recently, Daoudi et al. [11] reported hybrid synthesis of ITO matrices. They showed that a resistivity down to 9.5 10^{-2} Ω cm can be achieved.

ITO thin films have a number of applications such as transparent electrodes in liquid-crystal display (LCD), solar cells and protective coatings. The sol–gel method presents interesting advantages such as the possibility of deposition on complex shaped substrates, the easy control of the final materials properties, and the low-cost equipment for their fabrication. These advantages are very attractive for smart textile applications because the ITO properties (transparency, infrared reflectance, electrical conductivity …) can be adequate to make high-tech clothes. However, in the case of inorganic ITO matrices some previous works [5–8] showed that the best performances, can only be obtained for an annealing temperature around 550 °C. The lowering of this high sintering temperature still remains a challenge as regards the use of the sol–gel process for the coatings on plastic substrates or smart textile. The aim of our study is to investigate the electrical properties of the sol–gel derived ITO films as a function of annealing temperature, heat-treatment duration and metal concentration of the sol. We established a correlation between the conductivity and the size of ITO grains, which was measured by atomic force microscopy (AFM) and scanning electron microscopy (SEM). We showed that good conductivities can be obtained for annealing temperatures lower than 350 °C. We performed an ITO coating on a Kevlar fibre and we evaluated its electrical properties.

2. Experimental details

2.1. Sol preparation

ITO sol was prepared using anhydrous indium trichloride ($InCl_3$), dihydrated tin(II) chloride ($SnCl_2{\cdot}2H_2O$) as sources of

* Corresponding author. Tel.: +33 3 20 43 68 26; fax: +33 3 20 33 64 63.
E-mail address: mohamed.bouazaoui@univ-lille1.fr (M. Bouazaoui).

0040-6090/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2007.10.021

In and Sn, 2,4-pentanedione and absolute ethanol as solvents (all products were purchased from Sigma-Aldrich). $InCl_3$ was dissolved in 2,4-pentanedione (i.e. for solution with 0.1 mol/l: 1.1075 g of $InCl_3$ for 45 ml of 2,4-pentanedione) and the solution was refluxed at 85 °C for 3 h. $SnCl_2{\cdot}2H_2O$ was dissolved in absolute ethanol at room temperature (i.e. for solution with 0.1 mol/l: 0.1256 g of $SnCl_2{\cdot}2H_2O$ for 5 ml of ethanol). These solutions were then mixed and refluxed at 85 °C for 3 h. Solutions with metal (In+Sn) concentrations of 0.1 and 0.2 mol/l were prepared. Both solutions contain an atomic percentage of Sn (i.e. atoms Sn/(atoms Sn+atoms In)) of 10%. All solutions were synthesized in a gloves-box under an anhydrous nitrogen atmosphere.

2.2. Coating process

Synthetic fused silica (HOQ310 from "Applications Couches Minces" company, Villiers St Frédéric, France) substrates (75×25 mm^2) were carefully cleaned with a detergent and washed with distilled water and ethanol. The RMS roughness of these substrates is lower than 1 nm. The substrates were then dipped in the starting solution for 30 s and withdrawn at a rate of 10 cm/min. The coated substrates were heated at 260 °C for 10 min under ambient atmosphere after each dipping in order to dry the ITO layers. After the last dipping and heating, the ITO films were brought to different temperatures ranging from 300 °C to 550 °C, with a heating rate of 12 °C/min in N_2/H_2 atmosphere. This annealing temperature was maintained for durations varying from 30 min to 24 h until the ITO films became optically transparent. Each sample was taken out from the oven when the temperature was lower than 150 °C. Dip-coating process, drying and annealing were performed in a clean room. Fig. 1 shows the overall flow-chart for ITO thin films preparation. The film thickness measurements were performed using the surface profilometry technique (a Tencor P10 profilometer). The ITO

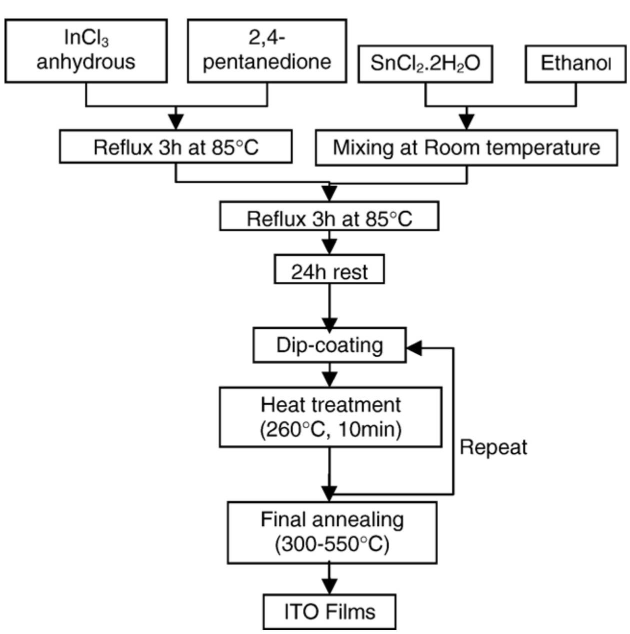

Fig. 1. A flow-chart for ITO thin films preparation.

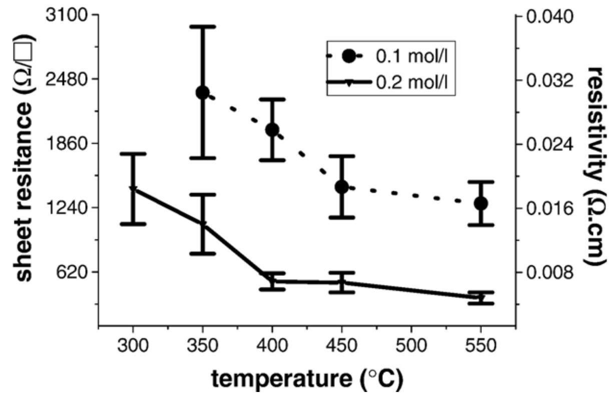

Fig. 2. Room temperature resistivity and sheet resistance versus the annealing temperature for 0.1 and 0.2 mol/l metal concentrations. Error bars represent the root mean square (RMS).

films prepared using the heating rate (12 °C/min) were reproducible and free of cracks. However, when a Rapid Thermal Annealing (RTA) is employed (heating rate: 2000 °C/min) the films cracks. Hence, All the films investigated in this study were prepared with the above heat-treatment procedure (heating rate=12 °C/min).

2.3. Electrical and texture properties

Sheet resistance and resistivity were measured by using the resistance scale method. This technique consists in the measurement of the I/V feature for different distances between two electrodes. Hence, after the measurement of the film thickness and the resistance between different electrodes, we determined a sheet resistance (Ω/□) and the resistivity (ρ) of the ITO film by using the following formula: $R=\Omega/\Box\cdot\frac{L}{W}+2R_C=\frac{\rho}{t}\frac{L}{W}+2R_{\mathrm{C}}$, where R is the measured resistance, L the distance between electrodes, W the electrode width, t the film thickness and R_{C} the contact resistance between the ITO cell and the electrode. Gold resistance scales were deposited on the ITO film by PECVD process. The texture of the ITO films surfaces were then investigated by Scanning Electron Microscopy (model "Ultra 55" from Zeiss and operating at 10 kV) and Atom Force Microscopy using an apparatus from Digital instruments (Dimension 3100) and operating in the tapping mode (tip with a curvature radius of 20 nm).

3. Results and discussion

In order to compare our process with previous works [5,7–9], the evolution of the sheet resistance (and the resistivity) as a function of the annealing temperature for films prepared with a solution containing 0.1 mol/l of metal (sol 1) are shown in Fig. 2. The films were obtained after 10 layer coating with a typical thickness of 10 nm for a single layer. We obtained sheet resistance values between 2350 Ω/□ and 1280 Ω/□. The resistivity decreased continuously with increasing the annealing temperature. The lowest values were measured for an annealing temperature of 550 °C. This behaviour is in good agreement with works reported previously on sol–gel derived ITO films