Optimisation of chemical solution deposition of indium tin oxide thin films

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ABSTRACT

An environmentally friendly aqueous sol–gel process has been optimised to deposit indium tin oxide (ITO) thin films, aiming to improve the film properties and reduce the deposition costs. It was demonstrated how parameters such as cation concentration and viscosity could be applied to modify the physical properties of the sol and thereby reduce the need for multiple coatings to yield films with sufficient conductivity. The conductivity of the thin films was enhanced by adjusting the heat treatment temperature and atmosphere. Both increasing the heat treatment temperature of the films from 530 to 800 °C and annealing in reducing atmosphere significantly improved the electrical conductivity, and conductivities close to the state of the art sputtered ITO films were obtained. A pronounced decreased conductivity was observed after exposing the thin films to air and the thermal reduction and ageing of the film was studied by in situ conductivity measurements.

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1. Introduction

Transparent conducting oxides (TCOs) demonstrate the unique combination of having a near-metallic electrical conductivity and being transparent in the visible region of the electromagnetic spectrum. TCOs have therefore found numerous technological applications, such as flat panel displays, photovoltaic devices, light emitting diodes and gas sensors [1–4]. Indium oxide doped with tin oxide, referred to as indium tin oxide (ITO) is often recognised as the TCO with the superior combination of properties and is therefore widely used for many of these applications [5–8]. ITO thin films can be deposited by a variety of techniques, such as sputtering, pulsed laser deposition, chemical vapour deposition and vacuum evaporation, with sputtering being the most widely used industrially [1–8]. On the other hand, wet chemical methods offer many advantages compared to the physical deposition techniques, such as cost, simplicity and readily control of homogeneity and composition, combined with no need for vacuum in the deposition chamber [9–11]. Water and organic liquids can both be used as solvents for wet chemical synthesis, but the organic solvents are often flammable, expensive or harmful to the environment, and aqueous solution processing is therefore potentially more suitable for industrial processes [12]. The majority of the reported wet chemical methods for depositing ITO are based on organic solvents like ethylene glycol, ethanol or acetylacetone [13–16], although some water based processes have

been reported [12,17–19]. In several of these cases chlorides are used as the chemical precursor, where the removal of residual chlorides can complicate the process.

We have recently developed an environmentally friendly aqueous sol–gel route to ITO thin films [20]. The method is a modified Pechini process [21] using simple and inexpensive precursors, which also circumvents the challenges related to the use of chlorides. The specific resistance of these films was demonstrated to be about $4.6 \cdot 10^{-3}$ Ωcm which show the potential of the method, but calls for further optimisation in order to match the conductivity of sputtered ITO thin films [6]. Here we report on the optimisation of the chemical solution deposition process. The synthesis was modified in order to control the thickness of the deposited layer, the viscosity of the sol was characterised and the thermal decomposition/crystallisation of the prepared gel was further analysed. Deposition on single crystalline substrates is also reported. Finally, the annealing temperature and atmosphere was further optimised in order to enhance the electrical conductivity. In situ characterisation of the electrical conductivity of the films was performed during the thermal annealing.

2. Experimental

2.1. Sample preparation

The deposition of the thin films from the sol–gel process is described in detail elsewhere [20]. Indium (III) nitrate hydrate ($In(NO_3)_3 \cdot xH_2O$, 99.9%, Aldrich) and tin (II) acetate ($Sn(CH_3CO_2)_2$, 99.9%, Aldrich) were used as precursors, with a tin doping amount of 10 cation% (cat%). Acetic acid (p.a. Acros Organics) and ethylene glycol ($C_2H_4(OH)_2$,

VWR) were used as complexing agents, with a molar ratio between the cations in the solution and each of the organic additives of 1:1.5. Stoichiometric amounts of the cation precursors and organic complexing agents were dissolved in deionised water, and solutions with cation concentrations of 0.4 or 1.0 M were prepared. These solutions were mixed in a 1:1 volume ratio with a solution of de-ionised water with either 3 or 5 wt.% polyvinyl alcohol (PVA, VWR, average $M_w \approx 88{,}000$ g/mol), utilised as a wetting agent, giving a final cation concentration in the solutions used for spin coating of 0.2 or 0.5 M. Four different solutions were used, with different cation concentrations and PVA content as labelled in Table 1. The cation concentration is the final concentration after mixing of the solutions, while the PVA content is the content in the PVA solution before mixing. The films that were used to optimise the conductivity were all prepared from Solution 1, in order to be comparable with the previous work.

The thin films were deposited by spin coating on polished square single-crystalline <100> YSZ, <0001> Al_2O_3 and <100> MgO substrates (MolTech GmbH) of 15×15 mm and on glass substrates (Menzel-Gläser, microscope slides) of 25×25 mm. After the solution was applied to the substrates they were spun at 3000 rpm for 45 s (Laurell WS-400B-6NPP-Lite Spinner). The films were calcined under vacuum (1 Pa) in a rapid thermal process furnace (RTP, Jipelec JetFirst 200 Processor) at 530 or 600 °C for 1 h or at 700 or 800 °C for 30 min. This procedure was repeated two times in order to make films with three deposited layers. After about two weeks of storage in ambient conditions some of the films were annealed in 5% hydrogen in argon for 10 h at 400 °C.

Corresponding gels were prepared by dissolving stoichiometric amounts of the precursors and complexing agents and evaporating the solvent. For the gels, tartaric acid (ReagentPlus ≥99%, Sigma-Aldrich) and ethylene glycol were used as complexing agents, and the amount of tin was 5 cation%.

2.2. Characterisation

The electrical properties of the thin films were measured using an in-house built van der Pauw apparatus with platinum contacts. The sheet resistance at ambient conditions was obtained by performing eight different measurements on each film, where the current and voltage drop was measured along different sides of the films and in different directions. The sheet resistance, R_s, was calculated by Eq. (1) [22]:

$$R_s = \frac{\pi}{\ln 2} * \frac{R_{horizontal} + R_{vertical}}{2} * f \qquad (1)$$

where the resistances, $R_{horizontal}$ and $R_{vertical}$, were determined as the average of the first and last four measurements respectively and f is a correction factor obtained from Eq. (2) [22]:

$$\frac{R_{horizontal} - R_{vertical}}{R_{horizontal} + R_{vertical}} = \frac{f}{\ln 2} * \operatorname{arccosh} \frac{e^{\frac{\ln 2}{f}}}{2}. \qquad (2)$$

The sheet resistance is the specific resistance of the material, ρ, divided by the thickness of the film, t, as shown in Eq. (3):

$$R_s = \frac{\rho}{t}. \qquad (3)$$

Table 1
Label, PVA content and cation concentration of different solutions used for spin coating.

Solution label	PVA content [wt %]	Cation concentration [M]
Solution 1	3	0.2
Solution 2	3	0.5
Solution 3	5	0.2
Solution 4	5	0.5

In situ conductivity during and after annealing in 5% H_2 in Ar was measured by placing the sample inside a quartz tube in a furnace. A gas flow of about 50 mL/min was applied. The heating and cooling rates were 200 K/h. The sheet conductivity in the in situ measurements was calculated from the current and voltage drop in the van der Pauw set-up, which corresponds to the inverse of either $R_{horizontal}$ or $R_{vertical}$ in Eq. (1). This value should not be mistaken for the real sheet conductivity of the film, which generally would be about a factor of $\pi/\ln(2)$ lower.

X-ray diffraction (XRD) was performed on the thin films with a Siemens D5005 with a gracing incidence angle set-up, Cu-radiation source (CuKα$_{1,2}$), Göbel mirror, equatorial soller slits on the detector side and a Scintillation detector. The incident angle was 2°, and the films were analysed from 20 to 70°, with an incremental step of 0.08° and a counting time of 7.3 s per step. Rietveld refinements of the diffractograms were carried out using the Topas software, v4.2 and the space group $Ia\overline{3}$ [23] in order to obtain the lattice parameter and the crystallite size by the line broadening.

Scanning electron microscopy (FEG-SEM, Zeiss Ultra 55 Limited Edition) was performed on the top view of the film surfaces.

The viscosity of prepared solutions was measured with a Thermo Scientific HAAKE Mars III rheometer using the RheoWin 4 software. The experiments were performed at 25 °C. The reported values for the viscosity were obtained at a shear rate of 500 s^{-1}.

The thermal behaviour of the prepared gels was analysed by a thermogravimetrical analysis (TGA, Netzsch, STA 449 C) up to 800 °C in air, with a heating rate of 2 K/min. Differential scanning calorimetry (DSC) was also performed in the same experiment. A Netzsch, QMS 403 Aëolos mass spectrometer (MS) was attached to analyse the evolved gases.

3. Results

3.1. Effect of different substrates and modifying the spin coating solution

The thickness of each deposited layer from Solution 1 was ~17 nm as previously reported [20], which means that multiple depositions is required to achieve sufficient conductivity. An optimisation of the process was performed in order to control the thickness of the deposited layers. An important parameter during spin coating is the viscosity of the solution [24,25], and the measured viscosity of selected solutions is summarised in Table 2. The amount of PVA clearly had a dramatic effect on the viscosity. Increasing the cation concentration in the solution was also observed to increase the viscosity as the ratio between cations and complexing agents was kept constant for all solutions. The solutions demonstrated Newtonian behaviour, as illustrated in Fig. 1(a), except for the 10 wt.% PVA solution which exhibited shear thinning properties, as shown in Fig. 1(b). In the first case the viscosity quickly reached a stable value as the shear rate was increased, whereas the viscosity was observed to be reduced as the shear rate increased in the latter.

Table 2
The viscosity of selected solutions with varying PVA content and cation concentration and the sheet resistance of ITO thin films prepared from the different solutions. The estimated uncertainty is ±2% for the viscosity and ±1% for the sheet resistance.

Solution	PVA content	Cation concentration	Viscosity	Sheet resistance
	[wt%]	[M]	[Pa · s]	[Ω/□]
Distilled water	–	–	$9.06 \cdot 10^{-4}$	
Solution 1	3	0.2	$2.50 \cdot 10^{-3}$	1191
Solution 2	3	0.5	$3.65 \cdot 10^{-3}$	221
Solution 3	5	0.2	$7.92 \cdot 10^{-3}$	248
Solution 4	5	0.5	$9.49 \cdot 10^{-3}$	131
3 wt.% PVA	3	–	$1.23 \cdot 10^{-2}$	
5 wt.% PVA	5	–	$4.93 \cdot 10^{-2}$	
10 wt.% PVA	10	–	1.01	