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Thin Solid Films

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# Indium tin oxide thin films elaborated by sol-gel routes: The effect of oxalic acid addition on optoelectronic properties

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## ARTICLE INFO

## Article history:

Received 28 September 2012

Received in revised form 11 July 2013

Accepted 12 July 2013

Available online xxxx

## Keywords:

Sol-gel deposition

Indium tin oxide

Transparent conducting oxide

Optoelectronics

Thin films

## ABSTRACT

Single layer indium tin oxide (ITO) thin films were deposited on glass using modified sol-gel formulations. The coating sols were prepared using indium ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ ) and tin salts ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ). The stable sols were obtained using ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) and acetylacetone ( $\text{C}_5\text{H}_8\text{O}_2$ ) as solvents and by the addition of oxalic acid dihydrate ( $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) in different amounts. The effect of oxalic acid content in the sol formulation and post-coating calcination treatment (in air at 300–600 °C) on electrical/optical properties of ITO films have been reported. It was shown that film formation efficiency, surface coverage and homogeneity were all enhanced with oxalic acid addition. Oxalic acid modification also leads to a significant improvement in electrical conductivity without affecting the film thickness ( $45 \pm 3$  nm). ITO films exhibiting high transparency ( $\approx 93\%$ , visible region) with a sheet resistance as low as  $3.8 \pm 0.4$  k $\Omega$ /sq have been formed by employing coating sols with optimized oxalic acid amount. The mechanisms and factors affecting the functional performance of oxalic acid-modified films have been thoroughly discussed and related to the microstructural and chemical characteristic of the films achieved by oxalic acid addition.

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## 1. Introduction

Transparent conductive oxide (TCO) thin films have been extensively used as electrode layers on glass or silicon for a variety of technological applications including solar cells, electrochromic devices, smart windows, and electromagnetic shielding systems [1,2]. Among a variety of possible TCO coatings, tin-doped indium oxide (ITO) with intrinsically low electrical resistivity and high optical transparency, is the choice material; given its high IR reflectance, good substrate wetting and compatibility, hardness and chemical inertness. Vacuum-based coating methods are typically employed in producing commercial grade ITO films on various substrates. Alternatively, solution based aqueous routes such as sol-gel offer several advantages such as low-cost processing, feasibility in coating large area and complex-shaped substrates and manipulation of sol chemistry at the atomic scale by use of different precursors, solvents, and additives. The latter advantages also enable refining the functional properties of ITO thin films by controlling microstructure, crystallization behavior, chemical homogeneity and film thickness.

The ongoing research and related literature on preparation of ITO films by sol-gel method is vast, yet a number of problems and challenges remain unresolved in obtaining ITO sol-gel coatings with high performance properties. The electrical properties of sol-gel coatings are typically poor compared with ITO coatings produced by sputtering. Another major problem for the ITO coatings obtained by conventional

sol-gel approaches is related with the limitations in obtaining an acceptable coating thickness by a single coating operation. Multiple, subsequent coating and drying cycles are usually required to obtain acceptable film thicknesses, which limits adaptation of sol-gel routes for large scale manufacturing [3–5].

One of the approaches in preparing relatively thick ITO film by wet techniques is employing nanoparticle dispersions or particle-added hybrid sols. By spin or dip coating of suspensions of crystalline ITO nanoparticles with proper size, 500–600 nm thick films exhibiting resistivity values in the order of  $0.1\text{--}0.003 \Omega \cdot \text{cm}$  can be prepared [6–9]. It is worth mentioning that such low resistivity values can be obtained only by annealing in a controlled environment either in vacuum or in reducing atmosphere. In addition, colloidal or particulate-based ITO films inherently possess a significant degree of porosity and poor interparticle contact due to limited packing and sintering, degrading both electrical and optical performance [6].

The optoelectronic quality of wet-processed ITO films can be further enhanced by microstructural control, as shown in this study. This can be achieved to a certain extent with the help of organic modifiers that can be added into the ITO sols or ITO nanoparticle suspensions. Several studies report that organic additives such as polyethylene glycol [10], monoethanol amine [11] and mercapto propyl trimethoxy silane [12] can result in several improvements in crystallization, microstructure/morphology and adhesion of sol-gel derived ITO. Similarly, oxalic acid dihydrate (OAD), a simple carboxylic acid, has been also suggested as a drying/microstructural control agent in various sol-gel derived tungsten oxide ( $\text{WO}_3$ ) coatings [13–16]. In the current study we investigated the effect of oxalic acid modification on physical

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properties of ITO films. Preparation of single-layered, oxalic acid-modified ITO sol-gel thin films on float glass substrates under ambient processing conditions has been described. The specific objective was to investigate the effects of oxalic acid modification and post coating calcination treatment (in air at 300–600 °C) on microstructural/morphological, optical and electrical properties of ITO thin films. The optoelectronic and microstructural properties of plain (*un-modified*) and *oxalic acid-modified ITO* thin films were determined with the help of various, complementary analytical characterization techniques.

## 2. Materials and methods

### 2.1. Materials

In preparation of ITO coating sols, indium trichloride tetrahydrate ( $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ , 97%, Sigma) and tin tetrachloride pentahydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , 98%, Sigma) were utilized as indium and tin sources, respectively. The solvents were acetylacetone ( $\text{C}_5\text{H}_8\text{O}_2$  or AcAc, >99%, Sigma) and ethanol ( $\text{C}_2\text{H}_5\text{OH}$  or EtOH, Sigma). For modified ITO coating solutions, oxalic acid dihydrate ( $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  or OAD, >99.5%, Riedel-de Haën) was used as an additive. Sodium hydroxide (NaOH,  $\geq 97\%$ , Merck), hydrochloric acid (HCl, 37 wt.%, Sigma), acetone (>99.5%, Sigma), EtOH and distilled water (DI) were used for cleaning the glass substrates prior to coating. All the chemicals were used as received without any further purification treatment.

### 2.2. Preparation of plain and oxalic acid-modified ITO coating sols

First, 5.16 g of  $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$  was dissolved in 40 mL of AcAc. After complete dissolution of indium chloride, the solution was further stirred for 15 min and refluxed at 80 °C for 3 h. Meanwhile, 0.62 g of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  was dissolved in 4 mL EtOH in a glass beaker at  $25 \pm 1$  °C and the solution was stirred for 1.5 h. Then, tin-containing solution was added dropwise into the indium solution cooled to  $25 \pm 1$  °C. The final concentration of the indium in the ITO coating sol was 0.4 M, corresponding to an In:Sn atomic ratio of 10.

The oxalic acid-modified ITO solutions were obtained by dissolving oxalic acid in the ITO sol prepared by the above mentioned protocol. The parent ITO sol was mixed for 20 min before addition of oxalic acid powder. Then, 4.16 g of oxalic acid was added into the parent ITO sol (a total volume of 44 mL). This corresponds to an oxalic acid concentration of 0.75 M in the final coating sol formulation. This specific amount of oxalic acid incorporation can be considered as *standard* compositional modification. However, compositionally-modified ITO sols with various amounts of oxalic acid (0.28, 0.56, 1.66, 2.77, 5.55 g) addition were also prepared to enable a parametric analysis based on composition. The other formulations of the modified gels correspond to an oxalic acid molarity of 0.05, 0.1, 0.3, 0.5 or 1.0 M. Oxalic acid addition of more than 5.55 g (corresponding more than 1 M oxalic acid) could not be achieved, because oxalic acid did not dissolve completely in the ITO sol. It was observed that the color of ITO sols was controlled by the amount of oxalic acid. The plain ITO sols were dark orange/brown which turned to orange upon addition of oxalic acid. The color change was more distinct and intensified for sols containing higher amount oxalic acid. Both plain ITO and oxalic acid-modified ITO coating sols were stirred magnetically for 24 h in closed containers and were further aged at rest at 25 °C for 48 h prior to coating.

### 2.3. Preparation of substrates

The substrates were soda-lime-silica (precleaned microscope slides, Gold Seal,  $25 \times 25$  mm) glass. The glass substrates were first treated ultrasonically for 20 min in acetone, in EtOH and then in DI-water. The substrates were washed thoroughly with DI-water in between the

subsequent cleaning operations and finally rinsed with DI-water and dried at 100 °C for 10 min in air after cleaning.

### 2.4. Coating plain and oxalic acid-modified ITO films

The plain and oxalic acid-modified ITO sols were spin-coated (using Laurell, WS-400B-6NPP/LITE) onto the substrates at a spin rate of 3000 rpm for 30 s. For a typical coating operation, approximately 0.2 mL of coating sol was deposited on a pre-cleaned glass substrate by a micropipette. The films were then dried in air at 100 °C for 10 min, and calcined in air at 550 °C for 1 h. Additionally, 1 h post-coating calcination treatments (in air) were also performed at 300, 400, 500 and 600 °C.

### 2.5. Characterization

The phase evaluation for the films was performed by X-ray diffraction (XRD) analyses using a D/Max-2000 PC model (Rigaku) diffractometer. The diffraction tests were performed in diffraction angle ( $2\theta$ ) range of 20°–65°, at a scanning rate of 2°/min using Cu K $\alpha$  radiation and an operation voltage of 40 kV and a current of 30 mA.

In order to investigate the chemical nature of the films, fourier transform infrared spectroscopy (FTIR) analyses were performed. The spectral measurements were carried out using a Mid-IR spectrometer (Frontier, Perkin Elmer) with an attenuated total reflection attachment (GladiATR Single Reflection, PIKE). Transmittance spectra of films were acquired in the range 4000–400  $\text{cm}^{-1}$ .

The microstructure and the thicknesses of the thin films were examined using a Quanta 400 F (FEI) model field emission scanning electron microscope. Prior to scanning electron microscopy (SEM) analyses the samples were coated with a conductive gold layer by sputtering.

The sheet resistance (in  $\text{k}\Omega/\text{sqr}$ ) of the films was measured using a four-point probe conductivity measurement set-up (Jandel) at ten different locations on the same sample and the average and standard deviation values were reported. Standard deviation values in resistance were evaluated as a qualitative indication of the physical homogeneity of the films.

The optical properties of the films were investigated by UV–Vis spectrophotometer (Cary100 Bio, Varian). Double beam scanning was used for the measurement of transmittance values for the thin films in wavelength range of 300–800 nm. The uncoated glass substrate was used as blank reference for baseline measurements.

The coating surfaces of selected samples were imaged using Nanoscope V (Veeco) atomic force microscope (AFM) in Tapping Mode using a silicon sharpened tip (nominal tip radius of 5–10 nm) at a scan rate of 1 Hz. Multiple scans of  $1 \times 1 \mu\text{m}$  or  $2 \times 2 \mu\text{m}$  size were captured at multiple locations on the same film surface in order to ensure representative images.

## 3. Results

### 3.1. Phase analyses and chemical structure

Fig. 1a and b show the XRD diffractograms of plain and oxalic acid-modified ITO films calcined at different temperatures. Oxalic acid-modified films were formed using the *standard* sol formulation corresponding to 0.75 M oxalic acid addition. For both sets of the diffractograms the broad and low intensity humps, expanding in the  $2\theta$  range of 20–36°, are from the underlying glass substrate. The films calcined at 300 °C were amorphous, while higher temperature calcination leads to formation of a crystalline phase. For both cases, the diffraction peaks of this phase match with those for the cubic  $\text{In}_2\text{O}_3$  (JCPDS card no. 06-0416). For both sets of samples, the crystallization starts somewhere in the range of 300–400 °C with higher calcination temperatures resulting in films with higher

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