



# Direct patterning ITO transparent conductive coatings

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## Abstract

A low cost sol–gel process to directly prepare patterned ITO thin films has been developed by Chemat Technology, Inc. This technique eliminates the photolithography process. ITO polymeric precursors were prepared by modification of indium isopropoxide and tin isopropoxide followed by hydrolysis and polycondensation. The polymers were applied onto glass substrates either by dip coating or by spin coating. The ITO polymer films were then patterned by covering with a photomask, exposed to UV irradiation, and developed in an organic solvent. After sintering in air and annealing in an inert atmosphere, the patterned ITO films have a sheet resistance of  $< 25 \Omega/\square$  and a transmittance of  $> 90\%$ . The ITO coatings were also found to have very good chemical and mechanical properties. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Transparent conductive coatings exhibit high transmittance in the visible spectral region, high reflectance in the IR region and nearly metallic conductivity. These coatings include non-stoichiometric and doped oxide films of tin, indium, cadmium, zinc and their various alloys. Transparent conductors are widely used in electronic, opto-electronic and mechanical applications [1]. A variety of processes, including evaporation, sputtering, CVD, and spray pyrolysis, have been employed to deposit transparent conducting oxides. In many device applications, (e.g. flat panel display), transparent conductive coatings must be patterned [2–4]. The films are normally

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patterned via standard photolithography in which the deposition of photoresist is followed by patterning and chemical etching. Fabrication of the patterned transparent conductive films is a multiple step process.

The sol-gel process has been used to apply thin films for decades, especially on glasses with large surface areas. In this technology, the liquid precursor is laid out onto the substrate, followed by drying, and then firing. The process is essentially simple, without the need of expensive equipment, and the operational cost is low. In addition, the sol-gel method is a low-temperature process so that the deposition of metal organic precursor thin films with functional organic groups is permitted. There are many reports on the sol-gel processing of cadmium stannate [5], indium tin oxide (ITO) [6–9] and antimony doped tin oxide [10–14] thin films.

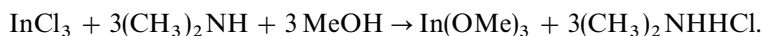
In this work, a novel one-step sol-gel-based process to make patterned and homogeneous transparent conductive coatings was developed. In this process, an UV curable ITO polymeric precursor, was synthesized. This precursor itself is patternable, therefore, no need of using photoresist-based photolithography process. Unexposed part of the green coating can be easily washed out with commonly used solvents, such as alcohols. UV light intrigued photolysis leads to amorphous oxide and forms the pattern. This process advances the current state-of-the-art patterned ITO thin films fabrication process, which involves the deposition of ITO films and patterns the films using a regular photolithography process.

## 2. Experimental

### 2.1. Preparation of precursors

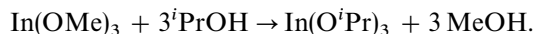
Conductivity of the ITO film is very sensitive with dopings. Low valence ion doping, such as  $\text{Na}^+$ ,  $\text{K}^+$ , will decrease greatly the conductivity of the film. Therefore, a synthesis procedure for a high-purity tin isopropoxide precursor had been developed by reaction of tin chloride to isopropanol.

A high-purity indium isopropoxide precursor is not commercially available. The conventional method of synthesis of indium alkoxide is to react sodium alkoxide with indium chloride. Complete removal of sodium ions from indium alkoxides after this reaction has been proven to be extremely difficult. Since alkali metal ions will poison the ITO thin film to increase sheet resistance, elimination of alkali ions in the ITO films is essential. In this work, we developed a novel process to make alkali metal free from indium alkoxides. In this process, vacuum-dried indium chloride (from American Indium Co.) was dissolved in excess distilled methanol first, then dimethyl amine flowed into the reaction solution. This exothermic reaction finished when the temperature of the solution started going down. The reaction is assumed to proceed as follows:



Indium methoxide is insoluble in most common solvents. After reaction, it precipitates in a crystalline form which can be separated from dimethylamine hydrochloride

(which is soluble in methanol) either by filtration or by centrifuge. The crystalline indium methoxide was added to isopropanol and toluene and moderately heated. Methanol and toluene were easily distilled off by forming an azeotrope while the indium methoxide was converted into indium isopropoxide, as shown in the following:

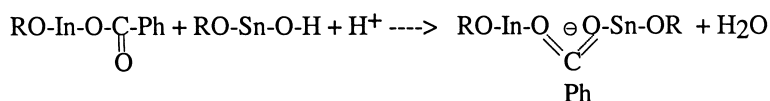
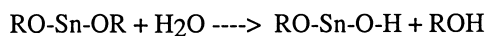
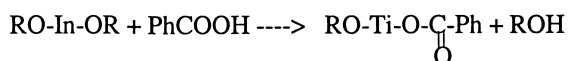


A complete conversion from indium chloride into isopropoxide was confirmed by chemical analysis (Pat-Chem Laboratories). The chlorine content was less than the detection limit (0.05 mg/l). The high purity of indium isopropoxide precursor was synthesized and the processing procedure was successfully developed.

## 2.2. Preparation of UV sensitive ITO polymeric solutions

The key part of this work is to synthesize a photosensitive ITO polymer that can be directly patterned. Some ligands of organic acids, such as 2-ethylhexanoic acid, phthalic acid, acrylic acid, maleic acid and benzoic acid, have been proved that it can react with oxygen under UV exposure [15].

To obtain a stable photosensitive precursor solution for an ITO coating, indium isopropoxide was modified with organic acids followed by a reaction with tin isopropoxide. The mixture was then hydrolyzed and polymerized to form a polymeric precursor. Following is an example of the reactions and polymer structure:



The water content was controlled and the isopropoxide was partially hydrolyzed. The presence of  $\text{OPr}^i$  groups in the polymerized solution promotes the bonding of the polymer to the hydroxyl-covered glass surface, while the extensive indium–tin oxide bonding that formed in the solution reduces the reaction temperature required to densify the oxide. ITO crystalline forms at as low as  $450^\circ\text{C}$  by using sol–gel method, which are at least  $500^\circ\text{C}$  lower than conventional ceramic process.

To facilitate photolysis of ITO polymeric precursor, 2–5 wt% Daracur ( $\text{C}_6\text{H}_5\text{-COC}(\text{CH}_3)_2\text{OH}$ ) was added as a photoinitiator.

## 2.3. Deposition of the ITO films

Before the deposition of ITO films, all of the glass substrates were cleaned with detergents, then washed in vaporized isopropanol, followed by drying with compressed air. All the coating solutions were filtered with  $0.2\ \mu\text{m}$  syringe filters before

use. Two methods have been used to apply ITO films: (1) dip coating and (2) spin coating by using commercially available dip-coater Chemat DipMaster™ Model 200 and spin-coater Chemat Model KW-4A, respectively. In the process of spin coating, disposable droppers were used to puddle the polymer solution onto stationary glass substrates, the polymer was then spun at a speed of 1000 rpm for 20 s. This resulted in thin, uniform coatings as evidenced by the uniform interference colors. The solvents were evaporated under the influence of the rapid air flow over the specimens. All the films made were later sintered in a tubular atmosphere furnace (Lindberg). Three atmospheres were used to sinter ITO coatings: air only, air then nitrogen, and vacuum. The coating process was conducted in our Class 1000 clean room.

#### 2.4. Characterization of coatings

The UV photolysis behavior of the ITO polymeric coating was studied by FTIR (Perkin-Elmer 1600). The effect of process parameters on transmittance of the coating was tested by Milton Roy spectronic 20D spectrometer. Microstructure of the ITO coating was examined by using scanning electronic microscope (SEM, which is conducted at PHOTOMETRICS INC). Sheet resistance was measured using four-probe method at UCLA. The thermal reaction of the polymeric precursor and thermal stability of the coating were determined by thermogravimetric analyzer, TGA (Shimadzu TGA-50). The powder samples were used for TGA analysis by drying the precursor in the furnace to remove the solvent.

### 3. Results and discussion

#### 3.1. Characteristics of films

Films of different thickness were obtained by varying the concentration of precursor solution. The dependence of film thickness (by dip coating and spin coating) on concentration of ITO polymer solutions is shown in Fig. 1. The crystallization of green ITO film started at 450°C. High annealing temperature, up to 550°C is needed to obtain high conductivity. Common glasses contain alkali metals ions such as Li<sup>+</sup> or Na<sup>+</sup> which easily diffuse into substitutional sites of ITO and thus cause lower electrical conductivity. In this work, we have deposited ITO films on three different substrates: regular sodalime glass, glass and quartz glass. The results indicated that resistivity of ITO coatings on SiO<sub>2</sub>-coated glass or quartz glass was more than an order of magnitude lower than the films on the sodalime glass. The ITO films were smooth, highly uniform (see Fig. 2).

The electrical conductivity of the ITO coatings stems from the oxygen vacancy in indium tin oxide. The conductivity of ITO films is 20 times higher by annealing in nitrogen than in air. The sheet resistance of 25 Ω/□ of sol-gel derived ITO film has been obtained with thickness of 100 nm and annealed at 550°C in the nitrogen.

It is known that the sol-gel derived ceramic film has fine crystallites. As shown in Fig. 2, the ITO film has uniform crystallites with size of 20 nm. The surface of the ITO

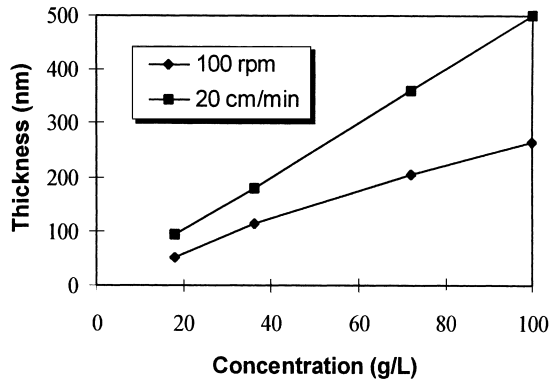


Fig. 1. Film thickness vs. concentration of ITO polymer. Films heat treated at 450°C.

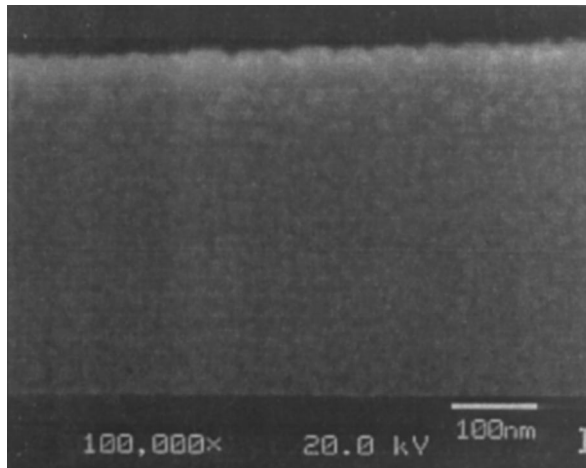


Fig. 2. The microstructure of ITO fine grain film which was annealed at 500°C.

thin film is smooth as the result of nanosize of ITO crystallites. This fine microstructure of the ITO film yields high transparency. Excellent transmission was observed beyond 400 nm. The transmission was measured up to 1200 nm (Fig. 3). The transmittance is measured through the substrate. This sol-gel ITO coating has high transparency and compatible sheet resistance with commercial available sputtered ITO coatings.

### 3.2. Direct patterning of gel or green ITO films

The key of direct patterning is to cure or cross-link the desired part of polymeric coating (gel coating or green coating). The cured part (exposed to UV irradiation) is not soluble in most solvents and will be sustained. A pattern is left on the substrate by

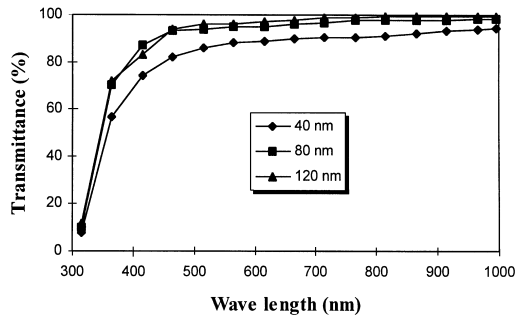


Fig. 3. Transmission spectrum for ITO coatings with three different thickness.

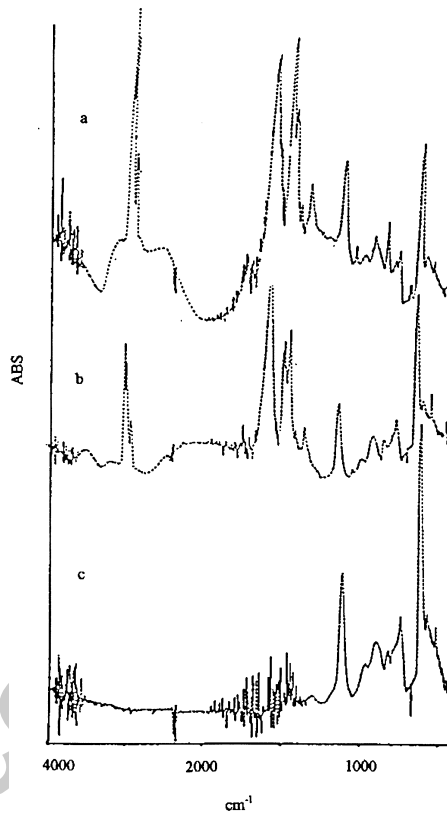


Fig. 4. FTIR of ITO polymer made of 2-EHA before (a) and after exposure for 20 min. (b) and 1 h (c). The peaks in the wavelength range of  $1400\text{--}1700\text{ cm}^{-1}$  are due to phenyl ligand and COO vibration modes.

washing off the uncured part (protected by the mask without exposing to UV light) by using alcohols or other organic solvents.

A UV irradiation source, with a wavelength of 365 nm and average intensity of  $2\text{ mW/cm}^2$  at 1" distance, was used to pattern the polymeric ITO gel films. The gel film

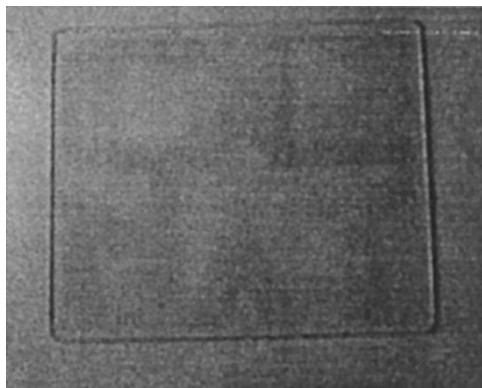


Fig. 5. ITO patterns on glass substrate.

becomes insoluble upon exposure to UV radiation at certain time. The unexposed area remains in the original state and can be simply washed off by using organic solvents (such as isopropanol). The preliminary results showed that patterning a 0.1  $\mu\text{m}$  thick ITO gel film using the UV source described above needed 20 min using an organic acid modified precursor, while 10 min if using 2 wt% of Daracur photoinitiator-doped organic acid modified precursor.

The photolysis process of the ITO gel films was examined by using FTIR. Fig. 4 shows the FTIR spectra of UV exposed and unexposed ITO green films. After exposure to UV light, the intensity of the COO-, CH<sub>2</sub>-, CH<sub>3</sub>- and OC<sub>3</sub>H<sub>7</sub>- peaks decreased. In addition, the intensity of the In–O peak ( $\sim 550\text{nm}$ ) continuously increased. This is probably due to photolysis of the organic group and formation of oxide amorphous film. This photolysis process induced by UV light converted soluble polymeric coating to insoluble amorphous oxide coating. Thus, direct patterning of ITO was realized. Fig. 5 shows two ITO patterns on a glass slide by using home made photomasks. The bright areas are the remaining patterns after washing away the uncured portion in isopropanol.

#### 4. Conclusions

High-purity (alkali metal free) polymeric precursors for ITO were successfully synthesized by reacting chloride with dimethyl amine. The organic acid modified polymeric precursor has been proven to be UV curable and has successfully direct-patterned. The resultant ITO coatings showed very good chemical and mechanical properties with electrical sheet resistance  $< 25\ \Omega/\square$  and transmittance of higher than 90% beyond 400 nm. The ITO coating prepared via sol–gel technology has a fine grain structure and very smooth surface.

Based on FTIR analysis, the direct patterning process is due to a photolysis process. The photoinitiator was found to accelerate the photolysis process. The exposure time can be cut up to 50%. In this work, using our UV source, UV exposure time for

high-resolution patterning was 20 min without photoinitiator and 10 min with photoinitiator. The exposure time can be expected to be cut further by using a high power UV source and by optimizing initiator doping process.

### Acknowledgements

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