

# Preparation of ITO films using a spray pyrolysis solution containing an acetylacetonone chelating agent

YUN GAO, GAOYANG ZHAO\*, ZONGFAN DUAN, YANG REN

School of Materials Science and Engineering, Xi'an University of Technology, Xi'an, 710048, China

Indium tin oxide (ITO) films were deposited on soda-lime glass substrates by the spray pyrolysis method using a spray solution of  $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$  as a precursor,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  as a dopant and acetylacetonone (AcAcH) as a chelating agent. The effect of the addition of AcAcH to the spray solution on the surface morphology of the ITO film was investigated. The surface quality of the film prepared from the spray solution with AcAcH was better than that without AcAcH. The ITO film with the thickness of 230 nm, using the spray solution with AcAcH, exhibited the lowest resistivity of  $4.75 \times 10^{-4} \Omega \cdot \text{cm}$  and higher optical transmittance of 85 %, respectively.

Keywords: *spray pyrolysis; ITO; acetylacetonone; chelate*

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## 1. Introduction

Indium tin oxide (ITO) is a kind of the most popular transparent conductor compounds which has attracted intensive interest because of its unique properties of high transmission and low resistivity. ITO films have been widely applied to the manufacture of devices, such as flat panel displays, liquid crystal displays, electroluminescent devices, sensors, organic light-emitting diodes and solar cells [1]. Various physical and chemical methods based on different principles have been introduced to the preparation of ITO thin films, such as spray pyrolysis, magnetron sputtering, pulsed laser deposition (PLD), sol-gel, electron beam evaporation, chemical vapor deposition (CVD), etc. [2–7]. Among these methods, the spray pyrolysis is one of the most commonly used practical techniques owing to its simplicity, non-vacuum processing and inexpensive deposition of large area coatings.

In the spray pyrolysis process, the properties of obtained transparent conductive oxide (TCO) films are strongly dependent on the spray solution, the control of the deposition parameters,

annealing, etc. The ITO spray solution is usually prepared from an alcoholic solution of  $\text{InCl}_3$  and sometimes using  $\text{InNO}_3$ . The solvents are mainly ethanol/methanol mixed with water and rarely butyl-acetate [8]. Acetylacetonone (AcAcH), as chelating agent, can chelate with metal ions in solution and easily form a stable metal-organic compound, which has different decomposition temperatures and physical chemistry properties [9]. In the present work, AcAcH has been added to an alcoholic solution of  $\text{InCl}_3$  to prepare a metal-organic salt of indium solution (In–AcAc). It has been consecutively used as a spray pyrolysis solution to prepare the ITO films with high electrical conductivity and optical transmittance. The structural, optical, and electrical properties were investigated in detail and presented.

## 2. Experimental

The ITO spray solution containing AcAcH chelating agent was prepared as follows: Indium(III) chloride trihydrate ( $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$ , 99.0 %) was firstly dissolved in AcAcH (99.0 %). The mixture ( $\text{AcAcH}/\text{InCl}_3 \cdot 3\text{H}_2\text{O}$ ) was then refluxed at 60 °C for 3 h. For doping, tin (IV) chloride pentahydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , 99 %

\*E-mail: zhaogy@xaut.edu.cn

purity) was dissolved in alcohol (EtOH). After that it was put into the In–AcAc mixture and stirred at room temperature for 2 h. The final ITO spray pyrolysis solution had a molar ratio of  $\text{InCl}_3 \cdot 3\text{H}_2\text{O} : \text{SnCl}_4 \cdot 5\text{H}_2\text{O} : \text{AcAcH} : \text{EtOH} = 1 : 0.1 : 6.0 : 80$ . The ITO spray solution without AcAcH chelating agent was prepared by simply mixing of  $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  and EtOH with the same molar ratio (1:0.1:80) at room temperature.

The ITO films were deposited on the soda-lime glass by the self-made spray pyrolysis system [10]. The system was composed of a heating system, a deposition system and an exhaust system. In all depositions, the solution was sprayed at a rate of 80 ml/min. Compressed  $\text{N}_2$  at a pressure of  $5.0 \text{ kg/cm}^2$  was used and substrate-to-nozzle distance was 25 cm. The substrate temperature was  $520 \text{ }^\circ\text{C}$  and the whole process was conducted in air.

The reaction mechanism of AcAcH and  $\text{InCl}_3$  was studied by IR spectroscopy (Shimadzu Prestige-21, Japan) and UV-Vis spectrophotometer (Jasco V-570, Japan), respectively. ITO film structure was determined with X-Ray diffractometer (Shimadzu 7000, Japan). The thickness of the film was determined by surface roughness measuring instrument (Surfcorder SE3500, Japan). The sheet resistances and optical transmission of ITO films on soda-lime glass were measured with a four-point probe tester (SDY-5, Guang Zhou, China) and UV-Vis spectrophotometer, respectively. The high resolution optical microscope (Olympus BX51M, Japan) was used to study the morphology of the film surface.

### 3. Results and discussion

#### 3.1. The component of ITO spray pyrolysis solution

UV-Vis spectra of AcAcH chelating agent and the solution of AcAcH/ $\text{InCl}_3$  in alcohol are shown in Fig. 1. For AcAcH ligand, only an absorption peak at 274 nm is observed, which can be attributed to the  $\pi-\pi^*$  transition of the conjugated backbone. However, there are two obvious absorption peaks for the AcAcH/ $\text{InCl}_3$

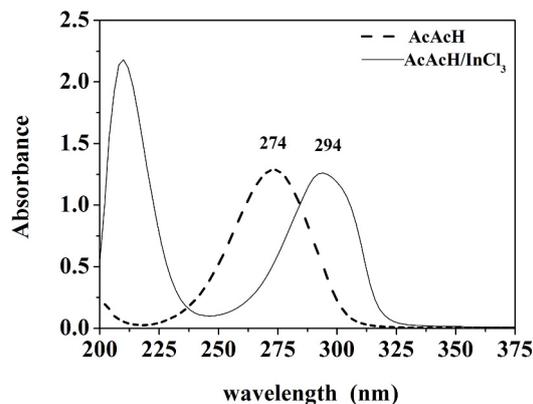
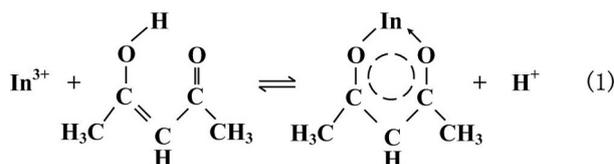


Fig. 1. The UV-Vis spectra of AcAcH and the solution of AcAcH/ $\text{InCl}_3$  mixture.



solution. Compared with maximum absorption ( $\lambda_{\text{max}}$ ) for AcAcH in alcohol, the  $\lambda_{\text{max}}$  for AcAcH/ $\text{InCl}_3$  solution is much higher, at 294 nm. Such a large red-shift in the absorption maxima was due to electron transfer from AcAcH ligand to  $\text{In}^{3+}$  and further indicated the formation of chelate bonds of AcAcH with  $\text{In}^{3+}$  resulting from the following chelate reaction (1). In order to further confirm the occurrence of coordination reaction between AcAcH and  $\text{InCl}_3$ , the AcAcH compound and the AcAcH/ $\text{InCl}_3$  mixture were characterized by IR spectra (Fig. 2). In the spectrum of AcAcH compound, the C=O stretching vibration of keto appears at  $1730 \text{ cm}^{-1}$ , while the C=O stretching vibration of enol appears at  $1622 \text{ cm}^{-1}$  [11]. The deformation vibration bands of  $\text{CH}_3-$  and  $-\text{CH}_2-$  in AcAcH are  $1419 \text{ cm}^{-1}$  and  $1389 \text{ cm}^{-1}$ . The band at  $1309 \text{ cm}^{-1}$  was assigned to the C–C–O stretching vibration [12]. In the spectrum of AcAcH/ $\text{InCl}_3$  mixture, the bands of C=O stretching vibration of keto and enol appeared at  $1724 \text{ cm}^{-1}$  and  $1620 \text{ cm}^{-1}$ . This indicates that the bands of stretching vibrations of keto and enol shift to long-wave after adding the  $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$  into AcAcH. Two bands at  $1620 \text{ cm}^{-1}$  and  $1571 \text{ cm}^{-1}$

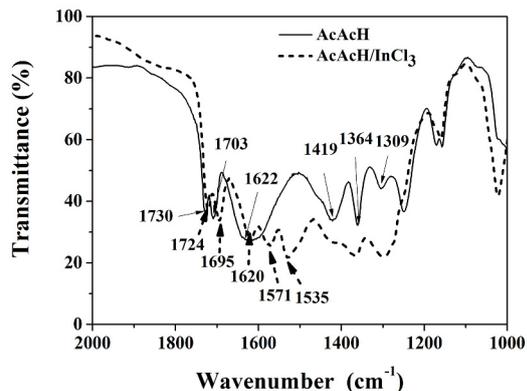


Fig. 2. The IR spectra of AcAcH and the solution AcAcH/InCl<sub>3</sub> mixture.

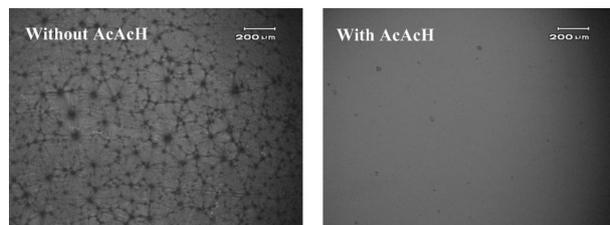


Fig. 3. The microscopic photographs of ITO films fabricated using two different spray solutions.

can be attributed to the stretching vibrations of C=O, and the band at 1535 cm<sup>-1</sup> can be assigned to C=C stretching of the anionic acetylacetonate complex in the spectrum of AcAcH/InCl<sub>3</sub> mixture when the AcAcH was coordinated to In<sup>3+</sup>.

### 3.2. The effect of AcAcH on ITO films

Fig. 3 shows the microscopic photographs of the ITO films deposited on the soda-lime glass by spray pyrolysis using two kinds of spray solutions at the same spray time (150 s) and deposition condition. One was the ITO spray solution with AcAcH chelating agent, the other one was ITO spray solution without AcAcH chelating agent. The surface morphology of the film prepared from the ITO spray solution without AcAcH was powdery and exhibited a great number of voids while the ITO film prepared from the ITO spray solution with AcAcH had a uniform and smooth surface. Table 1 shows the electrical and optical properties of the ITO films deposited on the soda-lime glass by

spray pyrolysis using two different spray solutions. The resistivity and optical transmission of the ITO film prepared from the spray solution with AcAcH are  $4.75 \times 10^{-4} \Omega \cdot \text{cm}$  and 85 %, and are much better than those of the film prepared from the spray solution without AcAcH. It is well-known that the film morphology plays an important role in obtaining low resistance and high optical transmission of ITO films. According to the previous report by Dainius Perednis [7], the powdery surface is not desirable for the fast charge transport between the neighboring grains and the transmission of light in the solid films. The results indicate that the component of spray pyrolysis solution had a great impact on the electrical and optical properties of the ITO films, and the replacement of metal salt as a precursor by the mixture of a metal salt and chelating agent probably was an effective way to avoid powdering and prepare high quality TCO films by the spray pyrolysis.

### 3.3. The effect of thickness on ITO films

In this work, the electrical and optical properties of the ITO film deposited from the spray solution with AcAcH were better than those obtained from the spray solution without AcAcH. To clarify this, it was necessary to investigate the influence of the film thickness on the preferential orientation of ITO film. The ITO films with different thicknesses were prepared using the precursor solution with AcAcH. The thickness of the ITO films was controlled by adjusting the spray time while keeping all the other parameters the same. Four kinds of ITO films with the thicknesses of 50 nm, 110 nm, 170 nm and 230 nm, corresponding to the spray time of 60 s, 90 s, 120 s and 150 s, respectively, were fabricated and characterized by XRD measurement (as shown in Fig. 4), to study the influence of the film thickness on preferential orientation of ITO films. The films exhibited intense peaks at 30.60°, 35.48°, 51.02°, and 60.63°, corresponding to (222), (400), (440), (622) planes, respectively. These peaks correspond to the body centered cubic (bcc) structure of In<sub>2</sub>O<sub>3</sub> films indexed according to the JCPDS standards

Table 1. Electrical and optical properties of ITO films.

ITO spray solution	Temperature (°C)	Thickness (nm)	Resistivity ( $\times 10^{-4} \Omega \cdot \text{cm}$ )	Transmission at 550 nm (%)
Without AcAcH	520	215	10.78	70
With AcAcH	520	230	4.75	85

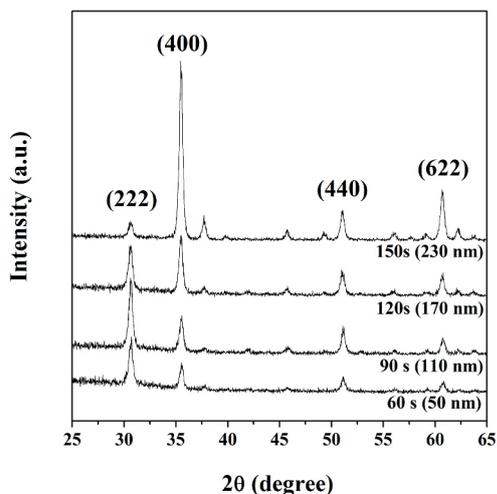


Fig. 4. The XRD patterns of the ITO films obtained at different spray time (or thickness).

(Card No. 06-0416). ITO films had the preferential orientation along (400) crystal plane, which was found to increase with the spray time. These polycrystalline thin films preferred to orientate along (400), due to the extended spray time, which helped to accumulate more oxygen in the structure. The analysis of X-Ray diffraction patterns of ITO films with respect to spray time was concluded under the assumption that the crystallization of  $\text{In}_2\text{O}_3$  along (100) planes required more energy than that required for the crystallization along (111) planes [13]. The resistivity curve of the ITO film with different thicknesses measured at room temperature is shown in Fig. 5. The resistivity of the films decreased with increasing the thickness of ITO film because the carrier concentration in the ITO film could increase with the growth of the thickness of the ITO film. The lowest resistivity was  $4.75 \times 10^{-4} \Omega \cdot \text{cm}$  when the thickness was up

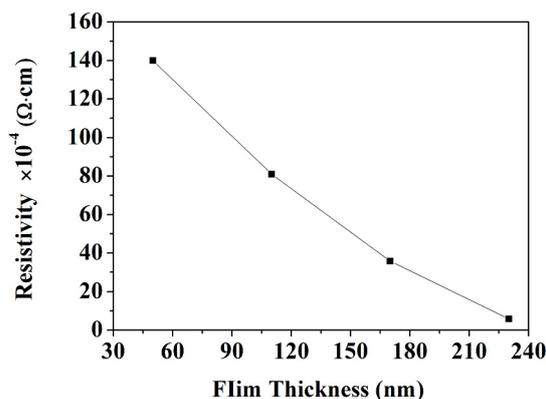


Fig. 5. The resistivity curve of the ITO film with different thicknesses.

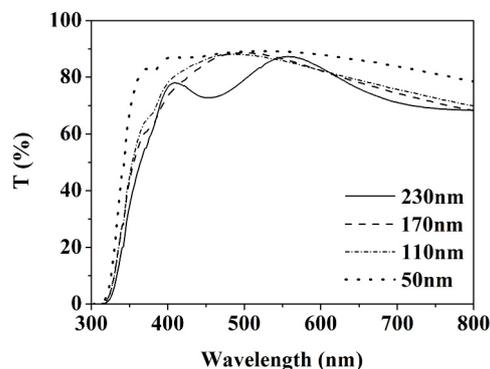


Fig. 6. The curves of transmission of ITO films with different thicknesses.

to 230 nm. Fig. 6 depicts the optical transmission spectra of ITO films with different thicknesses. It was clearly observed that the films were transparent in the region from 400 to 800 nm. The optical transmission of the films was found to decrease with the increase of the thickness of ITO film, and the interference of the films appeared when the thickness of the film reached 230 nm.

## 4. Conclusions

The component of spray pyrolysis solution had a great impact on the surface morphology, electrical and optical properties of the ITO films. The replacement of metal salt as a precursor by the mixture of a metal salt and chelating agent could be an effective way to avoid powdering and prepare high quality TCO films by spray pyrolysis. A 230 nm-thick ITO film with the resistivity of  $4.75 \times 10^{-4} \Omega \cdot \text{cm}$  and the optical transmission of 85 % was obtained by spray pyrolysis at 520 °C using the spray pyrolysis solution containing chelate agent. It was found that ITO films had the preferential orientation along (400) crystal plane, which was found to increase with the spray time or the thickness.

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