J. of Korean Oil Chemists' Soc.,
Vol. 33, No. 4. December, 2016. 734~740
ISSN 1225-9098 (Print)
ISSN 2288-1069 (Online)
http://dx.doi.org/10.12925/jkocs.2016.33.4.734

Synthesis of IZTO(Indium Zinc Tin Oxide) particle by spray pyrolysis and post-heat treatment and characterization of deposited IZTO film

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(Received November 18, 2016; Revised December 7, 2016; Accepted December 23, 2016)

Abstract : The micron-sized indium zinc tin oxide (IZTO) particles were prepared by spray pyrolysis from aqueous precursor solution for indium, zinc, and tin and organic additives such as citric acid (CA) and ethylene glycol (EG) were added to aqueous precursor solution for indium, zinc, and tin. The obtained IZTO particles prepared by spray pyrolysis from the aqueous solution without organic additives had spherical and filled morphologies, whereas the IZTO particles obtained with organic additives had more hollow and porous morphologies. The micron-sized IZTO particles with organic additives were changed fully to nano-sized IZTO particles, whereas the micron-sized IZTO particles without organic additives were not changed fully to nano-sized IZTO particle after post-treatment at 700 °C for 2 hours and wet-ball milling for 24 hours. Surface resistances of micron-sized IZTO's before post-heat treatment and wet-ball milling were much higher than those of nano-sized IZTO's after post-heat treatment and wet-ball milling. From IZTO with composition of 80 wt. % In_2O_3, 10 wt. % ZnO, and 10 wt. % SnO_2 which showed a smallest surface resistance IZTO after post-heat treatment and wet-ball milling, thin films were deposited on glass substrates by pulsed DC magnetron sputtering, and the electrical and optical properties were investigated.

Keywords : IZTO(Indium Zinc Tin Oxide), spray pyrolysis, post-heat treatment, organic additives, transmittance, Transparent Conducting Oxide(TCO)

1. Introduction

Indium tin oxide (ITO) as a transparent conducting oxide (TCO) has been widely used in transparent electrode applications, such as, touch screen panels and thin film solar cells [1-3]. However, depletion of ITO may become the main hindrance for the growth of those transparent electrode applications in the near future. In order to solve these problems, many efforts have been focused on reducing the indium content in TCO. Such efforts include the preparation of IZTO (Indium Zinc Tin Oxide) materials [4-16]. The need to reduce

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the high dependence on ITO in TCO applications has encouraged many researchers to develop alternative materials. IZTO as a multi-component oxide is considered possible alternative materials, with the advantages of high electrical conductivity and optical transparency, good chemical stability, and low temperature deposition capability [11,12]. In this study micron-sized IZTO particles were obtained by spray pyrolysis with organic additives such as citric acid (CA) and ethylene glycol (EG), were heated at 750°C and ball-milled under wet condition. After post-heat treatment and wet-ball milling nano-sized IZTO was obtained. By using nano-sized IZTO, IZTO films were deposited on glass substrates by pulsed DC magnetron sputtering. The electrical and optical properties of IZTO films were investigated.

2. Experimental

2.1. Materials

Indium nitrate (24 wt. % aqueous solution) was supplied from ANP Co., Ltd.. Tin(IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, 98 %), and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99 %) and citric acid (CA, 99.5 %), and ethylene glycol (EG, extra pure) were purchased from Sigma Aldrich. Distilled water was used in all our experiments.

Characterization Size and shape of the IZTO synthesized in the present work were studied using SEM. SEM images were obtained with JEOL JSM 6300 instrument. For structural analysis XRD patterns were recorded in the range from 20° to 80° with a scanning step of 0.01° using the Rigaku-D/max-2500/PC with Cu-Ka radiation. Surface resistances of IZTO were measured by 4-point probe analyzer (Mitsubishi, Loresta-GP MCP-T610). The transmittance was investigated at the wavelength 550 nm using a UV-visible spectrometer(Varian, UV-VIS-NIR Spectro-photometer Cary 5000). The film thickness was measured by surface profile inspector (KMAC, ST-4000).

2.2. Spray Pyrolysis

A 1.7 MHz ultrasonic spray generator with six vibrators was used to generate a large amount of droplets, which are carried into the high-temperature tubular reactor by a carrier gas. The liquid droplets were evaporated, decomposed, and/or crystallized in the quartz reactor. The length and diameter of the quartz reactor are 1200 and 50 mm, respectively. The reactor temperature was maintained at 900°C. The flow rate of the air used as the carrier gas was fixed to 20 L/min. The precursor solution was prepared by dissolving indium nitrate, tin(IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$,), and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) salts in distilled water. The overall solution concentration of indium, zinc and tin components was 0.5 M. Organic additives such as CA and EG were introduced to control the spherical morphology, porosity, and hollowness of micron sized precursor particles in spray pyrolysis. The concentrations of CA and EG were both 0.1 M.

2.3. IZTO synthesis by spray pyrolysis and post-heat treatment

The IZTO's compositions for each spray pyrolysis are tabulated in Table 1. Post-heat treatment at 700 °C for 2 hours was done to the obtained IZTO from spray pyrolysis. After post-heat treatment the obtained IZTO was ball-milled in the methanol for 24 hours using zirconia ball and dried.

2.4. Fabrication of IZTO film

IZTO thin films with a thickness of 1600, and 2400Å were deposited on Corning 1737 glass substrate at room temperature by pulsed DC magnetron sputtering with a sintered target of IZTO (80 wt. % In_2O_3, 10 wt. % ZnO, and 10 wt. % SnO_2) using DC sputter(VTS, DaON-100S). The plasma power and working pressure were 150 W and 6

Table 1. IZTO's compositions for each spray pyrolysis

Ingredients / Sample No.	In_2O_3 (wt. %)	SnO_2 (wt. %)	ZnO (wt. %)	CA (M)	EG (M)
# 1	85	10	5	-	-
# 2	80	10	10	-	-
# 3	80	15	5	-	-
# 4	85	10	5	0.1	0.1
# 5	80	10	10	0.1	0.1
# 6	80	15	5	0.1	0.1

mTorr, respectively. During film deposition, the sputtering gas was a mixture of argon and oxygen, and the oxygen partial pressure ($O_2/(Ar+O_2)$) was fixed at 2 %.

3. Results and Discussion

The SEM image of IZTO without organic additives such as EG and CA was shown Fig. 1. IZTO without organic additives had spherical in shape, micron-sized particles with filled morphologies. IZTO had undergone post-heat treatment at 700°C for 2 hours from spray pyrolysis and ball-milling in the methanol for 24 hours using zirconia ball and dried. Fig. 2 showed that effective wet-ball milling did not occur because most ball-milled IZTO had maintained micron size. This indicated that IZTO's from spray pyrolysis without organic additives were micron-sized particles with filled morphologies. The SEM images of IZTO's with organic additives such as EG and CA were shown Fig. 3. Compared with SEM images for IZTO's without organic additives, the IZTO's with organic additives were non-spherical in shape, micro-sized particles with more porosity and hollow morphologies. Fig. 4 showed that effective wet-ball milling occurred because most micron-sized IZTO's had changed fully to nano-sized IZTO particles. This indicated that IZTO's from spray pyrolysis with organic additives were non-spherical in shape,

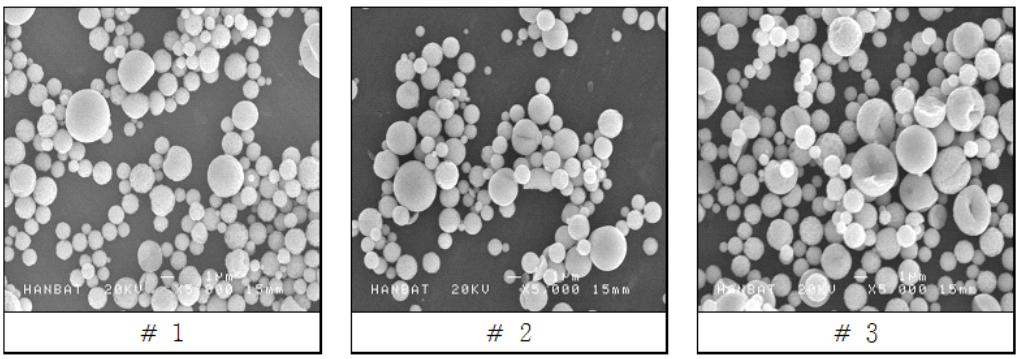

Fig. 1. SEM images of IZTO without organic additives such as EG and CA.

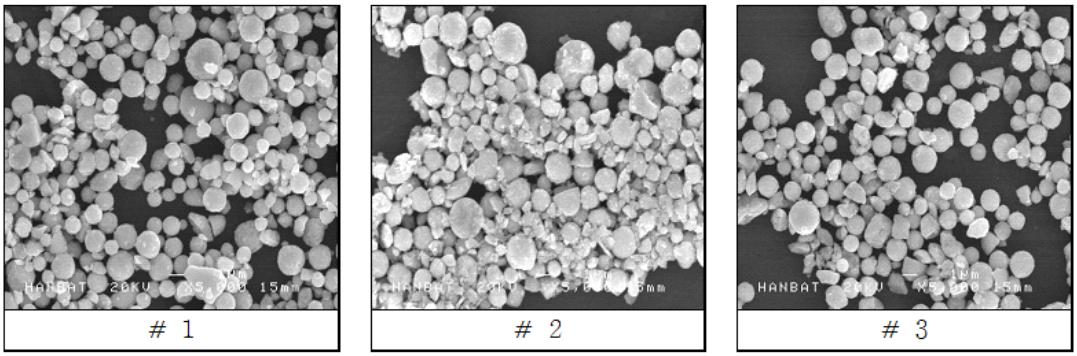

Fig. 2. SEM images of IZTO without organic additives such as EG and CA after heat treatment at 700 °C for 2 hours and wet-ball milling.

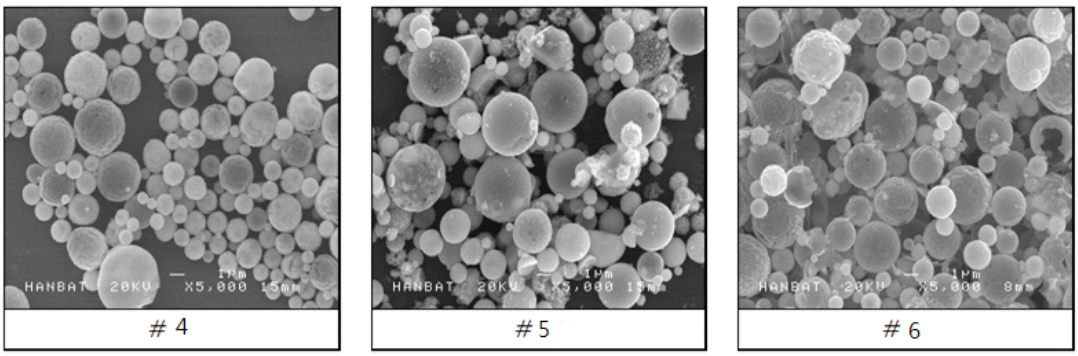

Fig. 3. SEM images of IZTO with organic additives such as EG and CA.(The concentrations of CA and EG were both 0.1 M.)

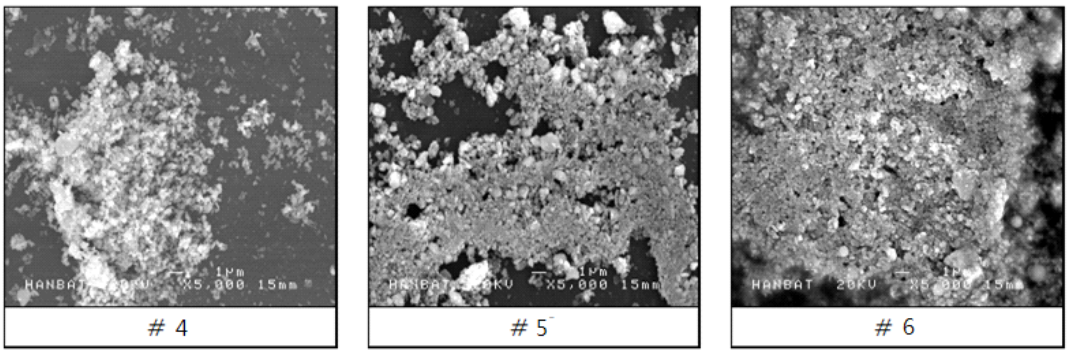

Fig. 4. SEM images of IZTO with organic additives such as EG and CA after heat treatment at 700 °C for 2 hours and wet-ball milling. (The concentrations of CA and EG were both 0.1 M.)

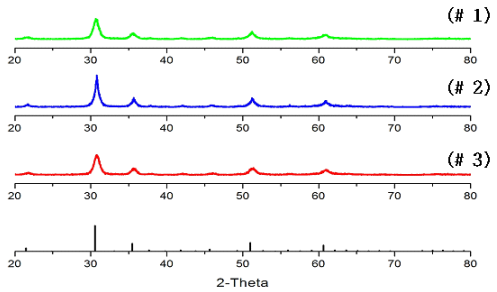

Fig. 5. X-ray diffraction patterns of IZTO without organic additives such as EG and CA after heat treatment at 700 °C for 2 hours and wet-ball milling.

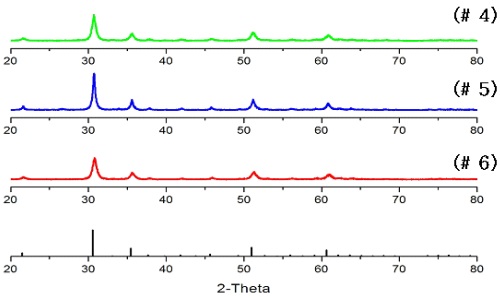

Fig. 6. X-ray diffraction patterns of IZTO with organic additives such as EG and CA after heat treatment at 700 °C for 2 hours and wet-ball milling. (The concentrations of CA and EG were both 0.1 M.)

micro-sized particles with more porosity and hollow morphologies so that micron-sized IZTO's had changed easily to the nano-sized IZTO's after the post-heat treatment and wet-ball milling. The powder X-ray diffraction (XRD) patterns of IZTO particles without organic additives (Fig. 5) and with organic additives (Fig. 6) did not have any difference compared with standard XRD patterns for ITZO particle.

Surface resistances for IZTO before and after post-heat treatment and wet-ball milling were tabulated in Table 2. Surface resistances of micron-sized IZTO's before post-heat treatment and wet-ball milling were much higher than those of nano-sized IZTO's after post-heat treatment and wet-ball milling.

Among the nano-sized IZTO's after post-heat treatment and wet-ball milling, #5 IZTO (80 wt. % In_2O_3, 10 wt. % ZnO, and 10 wt. % SnO_2) was adopted as targeted material because it showed a smallest surface resistance after post-heat treatment and wet-ball milling.

IZTO films were deposited by pulsed DC magnetron sputter at room temperature onto glass substrate and the electrical and optical properties of deposited IZTO film were investigated. Sputtering conditions for IZTO film from IZTO target with composition of # 5 were summarized in Table 3.

The IZTO films deposited at optimal oxygen partial pressure of 2.0 % in sputtering process showed the best properties, such as low surface resistance and high optical transmittance of 〈103.5 Ω/□ and 〉84.8 % in the visible wavelength at 550 nm, respectively (Table 4).

Table 2. Surface resistances of IZTO before and post-heat treatment and wet-ball milling

Sample Condition and No. / Property	Before post-heat treatment and wet-ball milling			After post-heat treatment and wet-ball milling		
	# 4	# 5	# 6	# 4	# 5	# 6
Surface Resistance (Ω/□)	82.7	40.9	25.3	7.10	4.06	5.13

Table 3. Sputtering conditions for IZTO film from IZTO target with composition of # 5

Sputtering Conditions / Sample #	DC power (W)	Sputtering Rate (sec)	Film Sintering Condition (hours at 250°C)
Film A	150	200	1 hour
Film B	150	200	-
Film C	150	300	1 hour
Film D	150	300	-

Table 4. Sputtering conditions for IZTO film from IZTO target with composition of # 5

Properties / Sample #	Transmittance at 550nm (%)	Surface Resistance (Ω/□)	Thickness of Sputtered IZTO Film (Å)
Film A	93.0	73.84	1600
Film B	90.1	103.5	1600
Film C	85.2	64.75	2400
Film D	84.8	86.06	2400

Film A and C which were sintered for 1 hour at 250℃ showed much higher transmittance and lower surface resistance than film B and D without sintering. As the film thickness increased, film C and D showed lower transmittance and surface resistance than film A and B.

4. Conclusions

The obtained IZTO particles prepared by spray pyrolysis from the aqueous solution without organic additives had spherical and filled morphologies whereas the obtained IZTO particles with organic additives had more hollow and porous morphologies. The micron-sized IZTO particle with organic additives was changed fully to nano-sized IZTO particle whereas the micron-sized IZTO particle without organic additives was not changed fully to nano-sized IZTO particle after post-treatment at 700 °C for 2 hours and wet-ball milling for 24 hours. Surface resistances of micron-sized IZTO's before post-heat treatment and wet-ball milling were much higher than those of nano-sized IZTO's after post-heat treatment and wet-ball milling. From IZTO with composition of 80 wt. % In_2O_3, 10 wt. % ZnO, and 10 wt. % SnO_2 which showed a smallest surface resistance, IZTO thin films were deposited on glass substrates by pulsed DC magnetron sputtering. The IZTO film deposited at optimal oxygen partial pressure of 2.0 % in sputtering process showed the best properties, such as low surface resistance and high optical transmittance of 〈103.5 Ω/□ and 〉84.8 % in the visible wavelength at 550 nm, respectively.

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