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Preparation of ITO Thin Films by Injection Ultrasound Spray Pyrolysis and its Physical Properties

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Indium tin oxide (ITO) films were deposited on glass substrates by using the homemade injection ultrasound spray pyrolysis system. Orthogonal test was designed to examine the optimal conditions for preparation of the ITO films. The results showed that the ITO thin films can be prepared by the homemade injection ultrasound spray pyrolysis device successfully. The device is simple in structure and easy to use. The substrate temperature is the main factor on the photoelectric properties of the ITO films. The optimal conditions for preparing the ITO thin films were as following: the substrate temperature was 400°C, the carrier gas was argon, the injection speed was 0.4 ml.min^{-1}, the annealing temperature was 500°C, the distance between substrate and nozzle was 5.5 cm, and the spray volume was 2 ml. The average optical transmittance in the visible range and sheet resistance of the ITO film were 93.5°C and 210Ω/□, respectively

Keywords Injection ultrasound spray pyrolysis; ITO thin film; photoelectric properties

1. Introduction

Tin-doped indium oxide (ITO) is a kind of n-type semiconductor material and has attracted significant interest because of its excellent photoelectric properties, such as high conductivity, wide band gap and high electron mobility [1]. Its visible light transmittance can be as high as 85°C and has high absorption rate of ultraviolet. The ITO thin films are high hardness with good wear resistance and chemical resistance [2].

ITO thin films have been widely applied in different field, such as anti-static coating, heat-reflective, solar cells, flat panel displays, liquid crystal displays, electroluminescent diodes, transparent electrodes and other fields [3]. In addition, ITO thin films can be used for electromagnetic shielding glass [4] and heat mirror [5] because of its strong attenuation of microwave.

ITO thin films have been prepared by any methods, such as spraying [6], vacuum spraying [7], magnetron sputtering [8], sol-gel [9], and pulse laser deposition [10]. Generally, these methods require expensive and sophisticated equipments, such as vacuum and preparation of target materials. Therefore, it is important to develop new processing material methods with low costs and simple technology to prepare ITO thin films.

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In this paper, ITO thin films were deposited on glass substrates by homemade Injection ultrasound spray pyrolysis (IUSP) device. The crystal structure, microstructure and photoelectric properties of the films were respectively analyzed by X-ray Diffraction (XRD), atomic force microscope(AFM), ultraviolet-visible spectrophotometer(UV-Vis) and four-point probe impedance analyzer. Then, the influences of the substrate temperature, speed injection and gas source on the performance of the ITO thin films were studied detailed.

2. Experiments

2.1. Experimental Device

The injection ultrasound spray pyrolysis device to prepare ITO thin films was shown in Fig. 1. In the middle of the device there is the main spray device, with resistance heater under it. A piece of mica is placed on the resistance heater to ensure the uniform heating of the substrate. The substrate temperature can be controlled by temperature controller through control system. Solutions can be injected by syringe to the nozzle and then be sprayed by ultrasonic effect. The use of pumping system is pumping from the tube to prevent combustion caused by high alcohol concentration.

2.2. Preparation of ITO Precursor Solutions

Appropriate amount of $InCl_3 \cdot 4H_2O$ and $SnCl_4 \cdot 5H_2O$ were dissolved in ethanol. Proper deionized water (the molar ratio between deionized water and the mixture of indium and tin is 25:1) was added into the solution for stirring about 7–8 hours at room temperature to become homogeneous solution. Solution will be shallow tawny after aging for 48 hours.

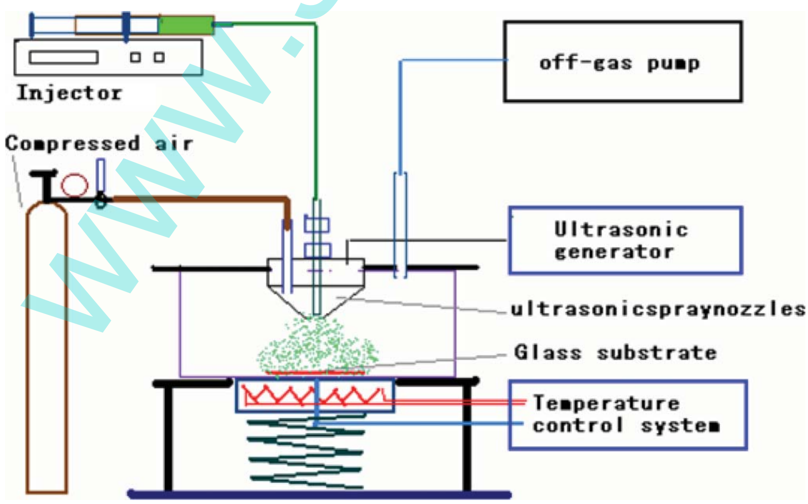

Figure 1. Schematic diagram of the homemade injection ultrasound spray pyrolysis device. (Figure available in color online)

2.3. Design of Orthogonal Experiment Table

There are many factors influencing ITO thin films prepared by injection ultrasound spray pyrolysis. We choose three factors: the substrate temperature, speed injection and gas source. It is difficult to form a transparent film when the temperature is below 300°C so we design the substrate temperature higher than 300°C. We design the factors as follows: the substrate temperature (300°C, 350°C, 400°C), speed injection (0.3 ml.min^{-1}, 0.4 ml.min^{-1}, 0.5 ml.min^{-1}), gas source (N_2, Ar, air). The orthogonal Table was shown in Table 1. The spray volume is 2 ml, the annealing temperature is 500 ºC, the distance between nozzle and substrate is 5.5 cm.

2.4. Preparation of ITO Thin Films

ITO thin films were prepared with the homemade spray pyrolysis system as shown in fig. 1. First, a certain amount of ITO precursor solutions were transported into the atomizer and atomized by ultrasonic. The amount and the injection speed of the solutions are controlled

Table 1
Orthogonal table of ITO thin films

		Factors		Sheet resistance	Average transmittance
Sample number	Substrate Temperature/°C	Injection Speed/(ml.min^{-1})	Carrier gas	Ω/□	°C
1	400	0.3	N_2	340	84.7
2	400	0.4	Argon	491	85.9
3	400	0.5	Air	372	94.0
4	300	0.3	Argon	10526	91.5
5	300	0.4	air	16438	97.6
6	300	0.5	N_2	17021	84.4
7	350	0.3	air	4377	81.3
8	350	0.4	N_2	1029	88.5
9	350	0.5	Argon	1742	89.0
I	1203	15243	18390		
II	43985	17958	12759		
III	7148	19135	21187	Sheet	
K_1	401	5081	6130	resistance	
K_2	14662	5986	4253		
K_3	2383	6378	7062		
S	14261	1297	2809		
I	264.6	257.5	257.6		
II	273.5	272	266.4		
III	258.8	267.4	272.9	Average	
K_1	88.2	85.8	85.9	Trans-	
K_2	91.2	90.7	88.8	mittance	
K_3	86.3	89.1	91.0		
S	4.9	4.9	5.1		

by the injection system. The atomized liquid was deposited on glass substrates with high temperature and the solvent was continuously decomposed in the reactor. Then, ITO thin films were synthesized on glass substrates. Finally, the crystallization of the ITO thin films was made through high temperature annealing.

2.5. Characterization

The crystal structure of the films was determined by XRD (SHIMAZU XRD-7000, Cu target, Kα radiation). The surface morphology was observed by atomic force microscope (CSPM5500, Benyuan nanometer instrument). The sheet resistance was measured by four-point probe impedance analyzer (Guangzhou four-point probe technology Co., LTD). Optical properties of the films were measured by ultraviolet-visible spectrophotometer (UV-3501S, Tianjin port east technology development Co., LTD).

3. Results and Discussion

3.1. DSC-TGA Tese

Fig. 2 shows the DSC-TGA curves of the viscous liquid which was left by the evaporation of solvent. It is shown from the curve that there is a decomposition process at 200°C which leads to the loss of quality and formation of wet films. Therefore, the substrate temperature was designed between 200°C to 350°C. There is the second decomposition process between 420°C and 500°C, which maybe the formation process of the films. Therefore, the annealing temperature was designed between 400°C to 540°C. According to the results of previous experiments, the ITO thin films which the annealing temperature was 500°C has excellent photoelectric properties, so the annealing temperature was designed at 500°C.

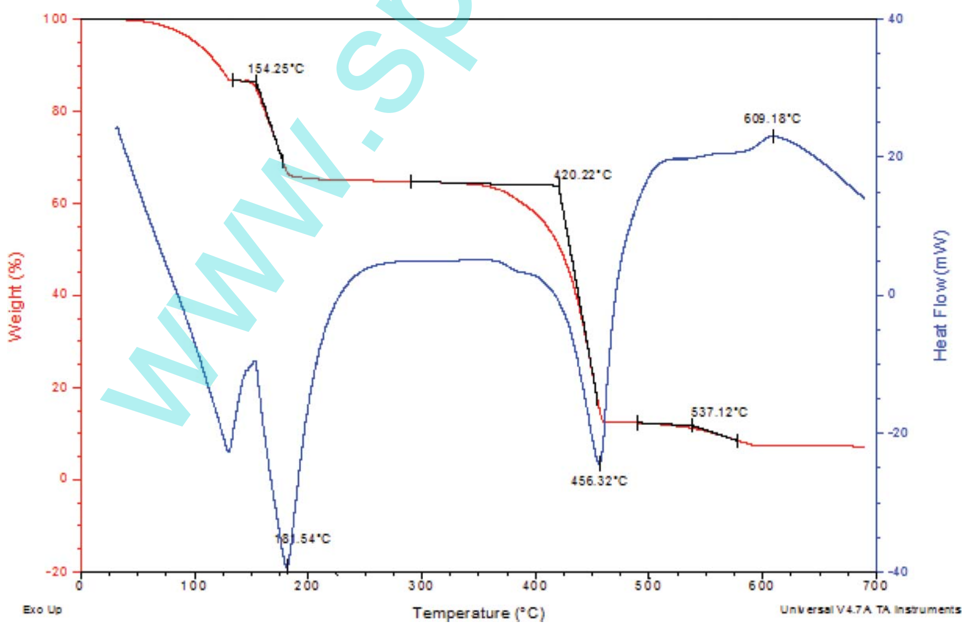

Figure 2. DSC-TGA curves of ITO precursor solutions. (Figure available in color online)

3.2. The Photoelectric Properties Test Results of the ITO Thin Films

3.3. Electrical Properties of the ITO Thin Films

According to sheet resistance results shown in Table 1, the order of the factors affecting resistance of ITO thin films was: the substrate temperature, the carrier gas and the injection speed. The resistance of the ITO thin films decreased with the increased of the substrate temperature. High substrate temperature can be useful to accelerate thermal decomposition so that the amount of vacancy can be added by the deposition of the particles. In addition, the high substrate temperature is useful for the density of the films because it can aggravate the thermal motion of the molecular. When at slow injection speed, the reaction that the droplet deposition on the substrate can slow down so that the In, Sn atoms can react with oxygen fully.

3.4. Optical Properties of the ITO Thin Films

According to average transmittance in Table 1, the order of the factors affecting transmittance of ITO thin films was: the carrier gas, the substrate temperature and the injection speed. However, the influence of three factors to the average transmittance is not very different from each other. The transmittance of the ITO thin films is high when at a low substrate temperature. The transmittance is higher than others when use air as the carrier gas which because that the In, Sn atoms can sufficient reaction with oxygen.

In summary, the substrate temperature is the most influential factor for the photoelectric properties of ITO thin films. If we emphatically considered the electrical properties of the films, the optimal conditions should be as following: the substrate temperature was 400°C, the carrier gas was argon, the injection speed was 0.3 $ml.min^{-1}$. If we emphatically considered the optical properties of the films, the optimal conditions should be as following: the substrate temperature was 300°C, the carrier gas was air, the injection speed was 0.4 $ml.min^{-1}$. As the substrate temperature has little influence to the average transmittance, we suggested the optimal conditions for preparing the ITO thin films as follow: the substrate temperature was 400°C and the injection speed was 0.4 $ml.min^{-1}$. Then we designed some additional experiments to study on the influence of the carrier gas on the ITO thin films.

3.5. Additional Experiments

According to the test results shown in Table 2, compared A with C which use air as the carrier gas, the photoelectric properties of the ITO thin films used argon as the annealing protection

Table 2
Additional experiments of ITO thin films

		Factors	Sheet resistance	average transmittance
Sample number	Carrier gas	Annealing gas	Ω/□	°C
A	air	argon	363	89.9
B	argon	argon	212	92.1
C	air	air	782	81.5
D	argon	air	210	93.5

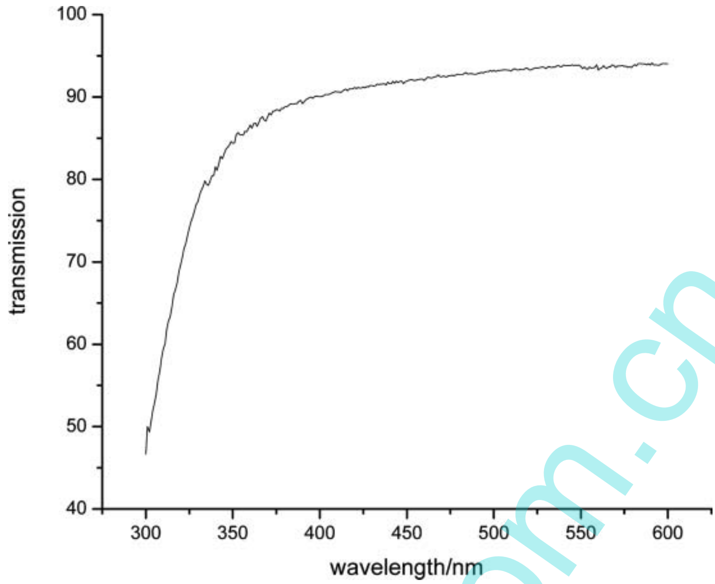

Figure 3. Ultraviolet-visible spectropscopy of optimum conditions.

gas was much better than those used air as the annealing protection gas. Compared C with D which has the same annealing protection gas, there are minor differences between them. Therefore, the carrier gas has greater influence on the photoelectric properties ITO thin films than the annealing protection gas. Sample D has the best photoelectric properties of all the four samples. This is because that although the oxidation degree of the ITO thin films enhanced and the oxygen vacancy increased when use air as the carrier gas, the microstructure of the ITO thin films becomes more disordered which has the scattering process to the carrier. So the sheet resistance became larger. In addition, using air as the carrier gas can lead to the concentration increasing of the impurity oxygen atomic which has the scattering process to the light. So the average transmittance decreased.

Therefore, we suggested the optimal conditions for preparing the ITO thin films as follow: the substrate temperature was 400°C, the carrier gas was argon, injection speed was 0.4 ml.min^{-1}, the annealing protection gas was air, The spray volume is 2 ml, the annealing temperature is 500°C, the distance between nozzle and substrate is 5.5 cm. The corresponding transmittance is 93.5°C, the sheet resistance is 210 Ω/□. Fig. 3 is the Ultraviolet-visible spectropscopy of the ITO thin film prepared in optimum conditions.

3.6. Crystal Structure of ITO Thin Films

Figure 4 is the XRD patterns of ITO thin films prepared in additional experiments.

There has been formed In_2O_3 cubic structure when the substrate temperature was 300°C. In addition, there were not SnO_2 and other phase which showed that Sn has replaced In in structure. The ITO thin films was well-crystallized when use argon as the carrier gas. The thin films along the (400) preferred orientation when the substrate temperature was 400°C.

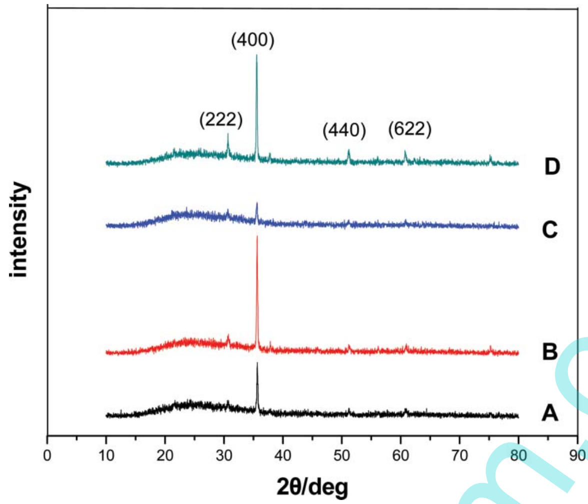

Figure 4. XRD patterns of ITO thin films in additional experiments, (The substrate temperature was 400°C, injection speed was 0.4 $ml.min^{-1}$), (A: The carrier gas was air, the annealing protection gas was argon, B: The carrier gas was argon, the annealing protection gas was argon, C: The carrier gas was air, the annealing protection gas was air, D: The carrier gas was argon, the annealing protection gas was air). (Figure available in color online)

3.7. Surface Morphology of ITO Thin Films

Figure 5 is the AFM patterns of ITO thin films prepared in optimum conditions. The substrate temperature was 400°C, the carrier gas was argon, injection speed was 0.4 $ml.min^{-1}$,

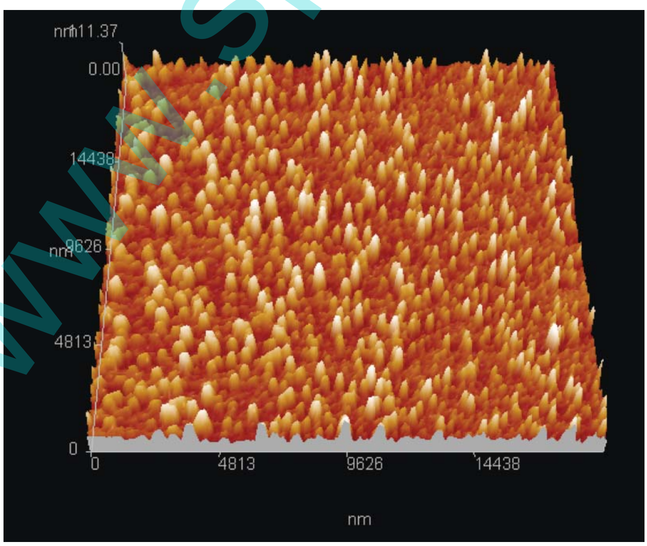

Figure 5. AFM patterns of ITO thin films in optimum conditions(20 μm × 20 μm). (Figure available in color online)

the annealing protection gas was air, The spray volume is 2 ml, the annealing temperature is 500°C, the distance between nozzle and substrate is 5.5 cm.

The distribution of the particle on the film surface is uniform because that high substrate temperature is beneficial to the growth of the grains. But the grains are large when in high substrate temperature which can also be seen from the patterns.

4. Conclusions

The ITO thin films have been prepared successfully with the homemade injection ultrasound spray pyrolysis device. The device is simple in structure and easy to use. The substrate temperature is the main factor on the photoelectric properties of the ITO films. The optimal conditions for preparing the ITO thin films were as following: the substrate temperature was 400°C, the carrier gas was argon, the injection speed was 0.4 ml.min^{-1}, the annealing temperature was 500°C, the distance between substrate and nozzle was 5.5 cm, and the spray volume was 2 ml. The average optical transmittance in the visible range and sheet resistance of the ITO film were 93.5°C and 210 Ω/□, respectively.

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