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Preparation and Physical Properties of ITO Thin Films by Spray Pyrolysis Method

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Abstract: Indium tin oxide (ITO) films were deposited on glass substrates by using the homemade 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 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 is 300^{o}C, the carrier gas flow of the air was 1.5 L·min^{-1}, the annealing temperature was 500^{o}C, the proportion of the indium and tin was 10:1, the distance between substrate and nozzle was 8 cm, and the deposition time was 3.5 min. The average optical transmittance in the visible range and sheet resistance of the ITO film were 93% and 2786Ω/□, respectively.

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, high visible light transmission, infrared reflectivity, excellent mechanical strength and chemical stability [1]. ITO thin films have been widely applied in different field, such as electronics, information, optical engineering and other fields. In addition, ITO thin films can be used for manufacturing silicon solar cell [3] and electromagnetic shielding glass [4] because of its strong attenuation of microwave.

Centering on conductive films which are similar to ITO thin film, the research are mainly around the following three aspects at home and abroad. Firstly, Study the result of transparent conductive films, conductive mechanism and doping mechanism, and improve the photoelectric properties. Secondly, study the new type of transparent conductive films which can reach the special requirements of photoelectric device development. Thirdly, for reducing the production cost of films, study new preparation process of manufacturing transparent conductive films [5].

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.

In this paper, ITO thin films were deposited on glass substrates by homemade spray pyrolysis 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 solution ratio, substrate temperature, gas flow and annealing temperature on the performance of the ITO thin films were studied detailed.

2. Experimental

2.1 Experimental device

The spray pyrolysis device to prepare ITO thin films was shown in figure 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 transported into the quartz tube through the pipeline by the carrier gas of gas and then be sprayed. The use of pumping system is pumping from the tube to prevent combustion caused by high alcohol concentration.

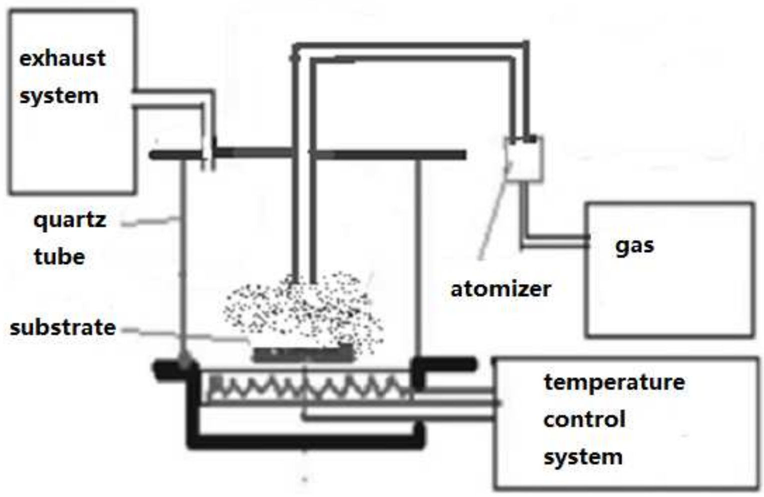

Fig.1 Schematic diagram of the homemade spray pyrolysis device

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.

2.3 Design of orthogonal experiment table

There are many factors influencing ITO thin films prepared by spray pyrolysis. We choose four factors: the substrate temperature (200^{o}C, 250^{o}C, 300^{o}C, 350^{o}C), the gas flow of the N_2 gas (0.5L·min^{-1}, 1L·min^{-1}, 1.5L·min^{-1}, 2L·min^{-1}), the annealing temperature (400^{o}C, 460^{o}C, 500^{o}C, 540^{o}C), the ratio of indium to tin (8:1, 9:1, 10:1, 11:1). The orthogonal table was shown in table 1. N_2 gas was used as the carrier gas, the deposition time is 3.5 min, the distance between nozzle and substrate is 8 cm.

2.4 Preparation of ITO thin films

ITO thin films were prepared with the homemade spray pyrolysis system as shown in figure 1. First, a certain amount of ITO precursor solutions were transported into the atomizer and atomized. 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, K_α 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 test

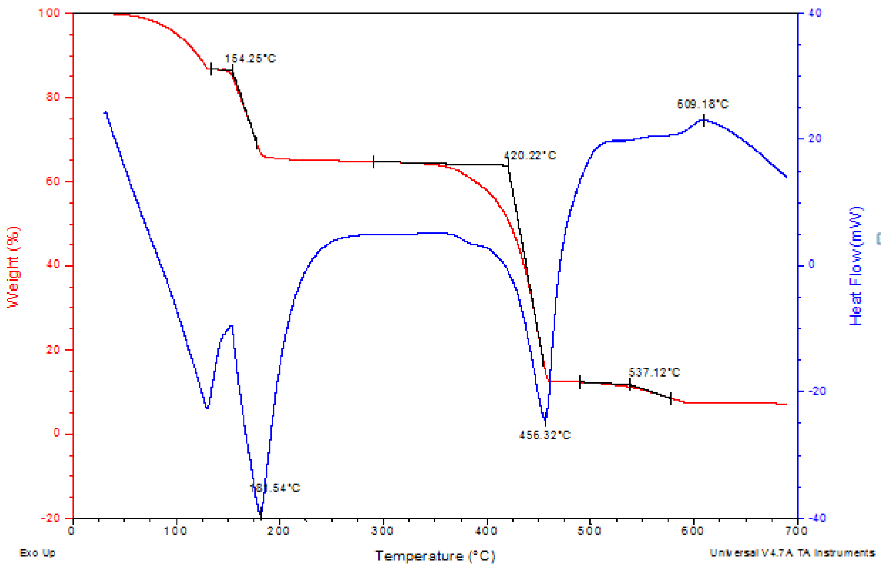

Fig.2 DSC-TGA curves of ITO precursor solutions

Figure 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.

Table 1 Orthogonal experiment table of photoelectric properties of ITO thin films

Sample number	Factors				Sheet resistance	Average transmittance
	Substrate temperature [°C]	Gas flow [L.min^{-1}]	Annealing temperature [°C]	Ratio [In/Sn]	[Ω/□]	[%]
1	200	0.5	400	8:1	14109	93
2	200	1	460	9:1	8437	95
3	200	1.5	500	10:1	7683	97
4	200	2.0	540	11:1	13695	91
5	250	0.5	460	10:1	10222	87
6	250	1	400	11:1	10020	94
7	250	1.5	540	8:1	4936	88
8	250	2.0	500	9:1	4662	94

9	300	0.5	500	11:1	8650	94
10	300	1	540	10:1	3875	97
11	300	1.5	400	9:1	5026	73
12	300	2.0	460	8:1	4057	86
13	350	0.5	540	9:1	7943	87
14	350	1	500	8:1	1781	84
15	350	1.5	460	11:	979	74
16	350	2.0	400	10:1	825	76
I	43924	40924	29980	24883		
II	29840	24113	23695	26068		
III	21608	18624	22776	22605	sheet	
IV	11528	23239	30449	33344	Resista-	
K_1	10981	10231	7495	6220	ance	
K_2	7460	6028	5923	6517		
K_3	5402	4656	5694	5651		
K_4	2882	5809	7612	8336		
S	8099	5575	1918	2685		
I	376	361	336	351		
II	363	370	342	349		
III	350	332	369	357	average	
IV	321	347	363	353		
K_1	94	90	84	87	Trans-	
K_2	90	92	85	87	mittance	
K_3	87	83	92	89		
K_4	80	86	90	88		
S	14	6	8	2		

3.2 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 flow, the annealing temperature and the proportion of the indium and tin. The resistance of the ITO thin films decreased with the increased of the substrate temperature. In addition, the resistivity of ITO thin films prepared by spray pyrolysis is larger than that of other method, which was same with other reports. The main reason for this phenomenon maybe there are many vacancy in the films which caused by thermal decomposition. The vacancy can lead to the density of films decreased and affect the migration rate of charge. When preparing films, 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. High flow rate is benefit to the density of the films for the greater depth of the particles into the films. While with the same substrate temperature of 350^{o}C, the resistance becomes smaller with the gas speed increasing.

3.3 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 substrate temperature, the annealing temperature, the carrier gas flow of the air, and the proportion of the indium and tin. The transmittance of the ITO thin films decreased with the increasing of the substrate temperature. The transmittance is better than others when the substrate temperature is 200°C, which can be higher than 90%. The increase of the annealing temperature is useful to improve the transmittance. The transmittance of ITO thin films can be 97% It is also can be seen that high temperature is useful to form the stable ITO structure from Figure 2.

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 350°C, the carrier gas flow of the air was 1.5 $L \cdot min^{-1}$, the annealing temperature was 500°C, the proportion of the indium and tin was 10:1. If we emphatically considered the optical properties of the films, the optimal conditions should be as following: the substrate temperature was 200°C, the carrier gas flow of the air was 1 $L \cdot min^{-1}$, the annealing temperature was 500°C, the proportion of the indium and tin was 10:1. If considering both conditions, we suggested the optimal conditions for preparing the ITO thin films as follow: the substrate temperature was 300°C, the carrier gas flow of the air was 1.5 $L \cdot min^{-1}$, the annealing temperature was 500°C, the proportion of the indium and tin was 10:1. The corresponding transmittance is 93%, the sheet resistance is 2786 Ω /□. Figure 3 is the Ultraviolet-visible spectropscopy of the ITO thin film prepared in optimum conditions.

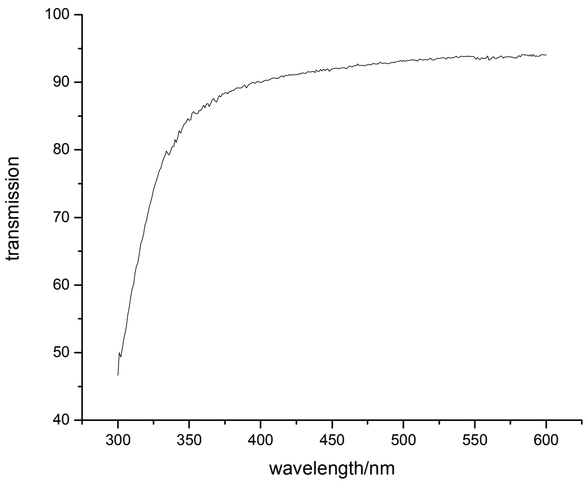

Fig. 3 Ultraviolet-visible spectropscopy of optimum conditions

3.4 Surface morphology of ITO thin films

Figure 4 shows the surface morphology of ITO thin films prepared in different substrate temperature (200°C, 250°C, 300°C, 350°C) which in the same other conditions (the carrier gas flow of the air was 1.5 $L \cdot min^{-1}$, the annealing temperature was 500°C, the proportion of the indium and tin was 10:1). The distribution of the particle on the film surface becomes more and more uniform with the increased of the substrate temperature. This is because low temperature goes against the growth of the grains. Then, the grains become too large and not uniform with the increased of the substrate temperature after reaches a certain temperature. Therefore, there is the most excellent surface morphology of the ITO thin films prepared at 300°C.

Figure 5 is the further study image of the ITO thin films prepared at 300°C.

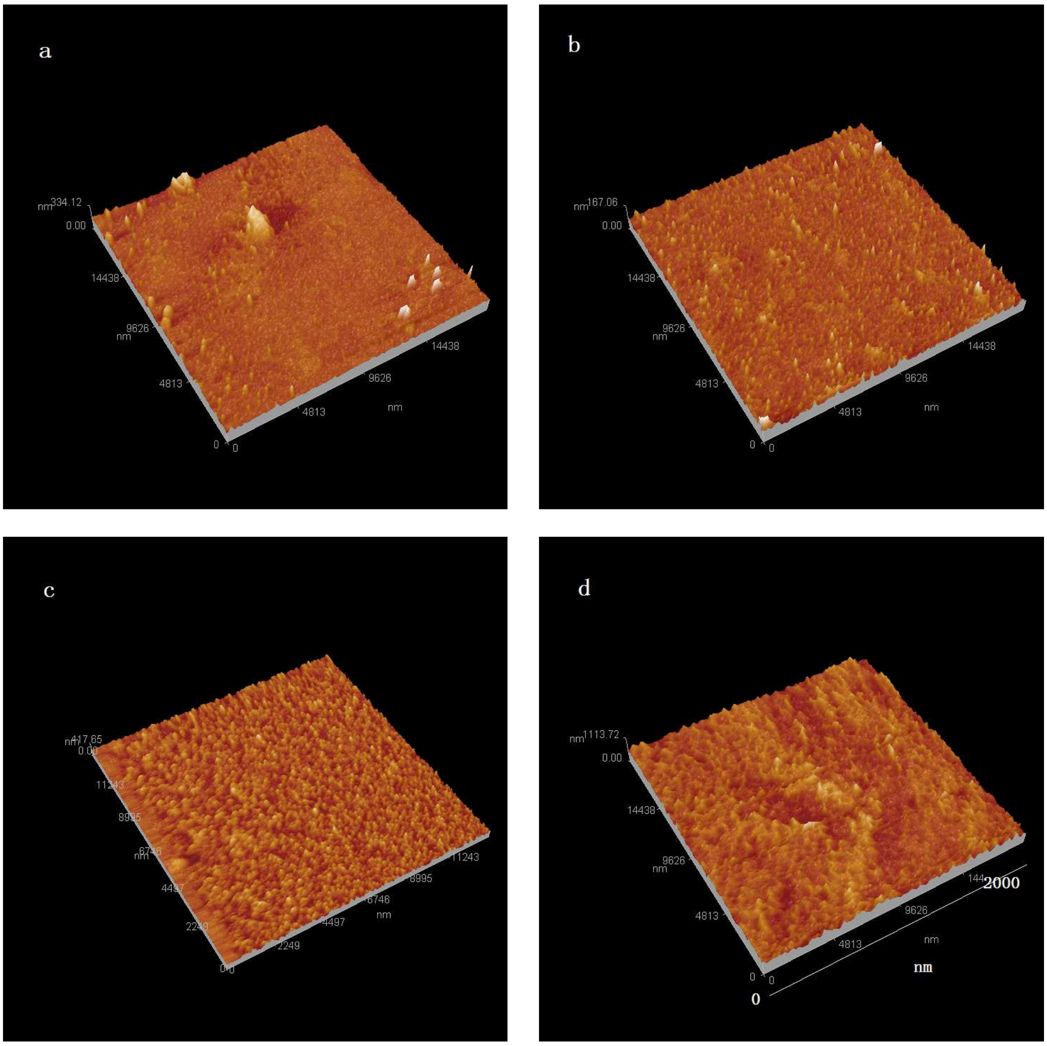

Fig. 4 AFM images of ITO thin films prepared with different conditions
(20μm×20μm)
(a) 200^{o}C, (b) 250^{o}C, (c) 300^{o}C, (d) 350^{o}C

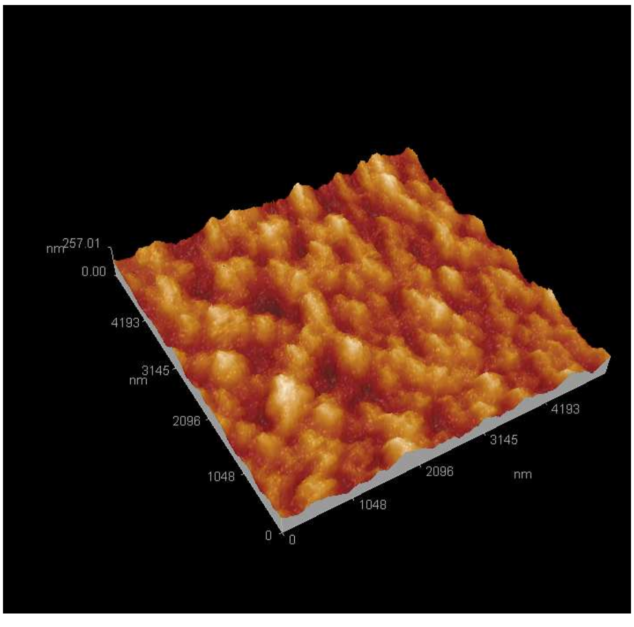

Fig. 5 AFM images of ITO thin films prepared at 300^{o}C
(5000nm×5000nm)

3.5 Crystal structure of ITO thin films

Figure 6 is the XRD patterns of ITO thin films prepared in optimum conditions. the substrate temperature was 300°C, the carrier gas flow of the air was 1.5 $L \cdot min^{-1}$, the annealing temperature was 500°C, the proportion of the indium and tin was 10:1. 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.

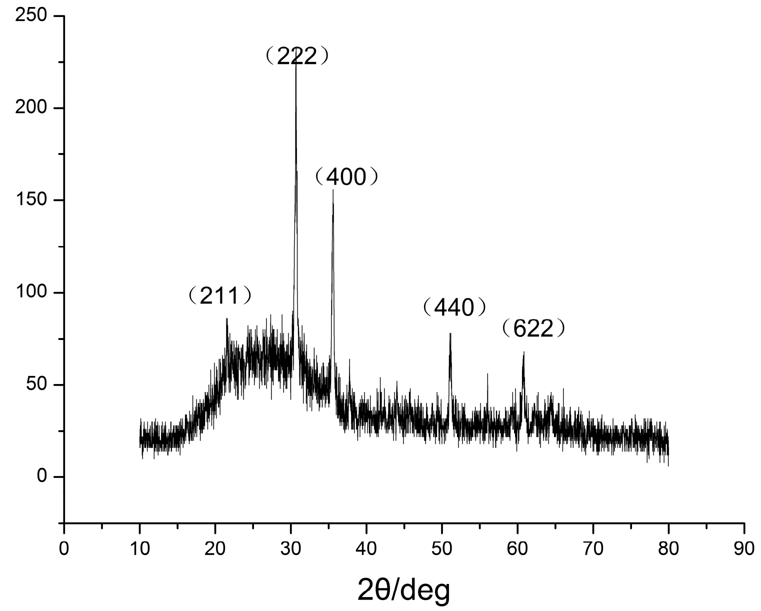

Fig. 6 XRD patterns of ITO thin films in optimum conditions

4. Conclusions

The ITO thin films have been prepared successfully with the homemade 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 is 300°C, the carrier gas flow of the air was $1.5L \cdot min^{-1}$, the annealing temperature was 500°C, the proportion of the indium and tin was 10:1, the distance between substrate and nozzle was 8 cm, and the deposition time was 3.5 min. The average optical transmittance in the visible range and sheet resistance of the ITO film were 93% and 2786Ω/□, respectively.

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