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The NO_2 sensing ITO thin films prepared by ultrasonic spray pyrolysis

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Abstract: In this paper ITO thin films were deposited on alumina substrates by ultrasonic spray pyrolysis. The NO_2 sensing properties of ITO thin films were investigated. The results show ITO thin films have good sensitivity to nitrogen dioxide.

Keywords: Thin film, spray pyrolysis, Gas sensor, ITO

Introduction

Indium tin oxide (ITO) thin films have been extensively used as transparent conducting electrodes in flat-panel displays (FPDs), solar cells [1,2], and organic light-emitting diodes (OLEDs)[3,4] because they have high electrical conductivity, high optical transparency, and smooth surface morphology. ITO thin film can also be used as gas sensor, to detect NO_x gases and carbon tetrachloride [5-8].

ITO thin films have been prepared by various deposition techniques including chemical vapor deposition (CVD)[9], vacuum evaporation [10], reaction evaporation [11], pulsed laser deposition [12,13] and magnetron sputtering [14]. In this paper, we present a study of the NO_2 sensing properties of the ITO films deposited by ultrasonic spray pyrolysis on alumina substrates.

Experimental

A 0.01M aqueous ethanol solution of a mixture of indium nitrate (Analytical reactant, provided by Shanghai Second Chemical Reagent Co. Ltd.) and $SnCl_4 \cdot 5H_2O$ (Analytical reactant, provided by Shanghai Second Chemical Reagent Co. Ltd.), Sn:In=1:9 mole ratio, was chosen as the precursor for the preparation of ITO thin films. Air was employed as the carrier gas, and the substrate temperature was varied between 200^{o}C and 500^{o}C. The solution was ultrasonically pre-treated in an ultrasonicator for about 30 minutes at 50^{o}C before spraying. The alumina substrates were ultrasonically pretreated in acetone and ethanol, followed by ultrasonic cleaning in distilled water prior to deposition.

The schematic diagram of the ultrasonic spray pyrolysis reactor is shown in figure 1. The solution was nebulized by a commercial ultrasonic humidifier and the resulting mist was swept into the reactor by compressed air at a flow rate of 7-9 l/min. The nebulized solution was delivered to the substrate in 5s pulses with 5s intervals between pulses. The deposition time was 15-30 min, and the nozzle-substrate distance was 6.0-8.0cm.

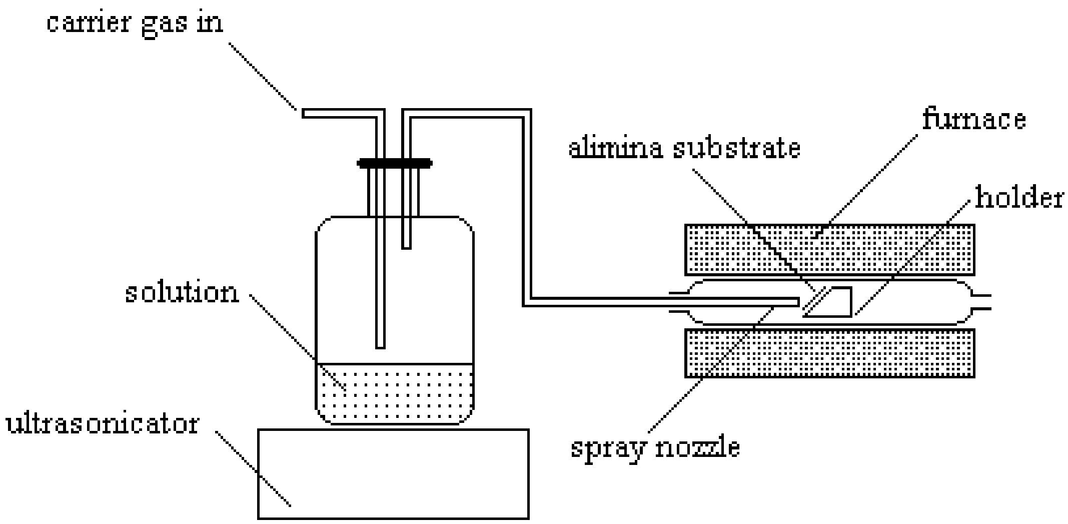

Figure 1. Schematic diagram of ultrasonic spray pyrolysis reactor.

The phase and crystallinity of as -prepared films were characterized by a RICOH Geigerf/ex X-ray diffractometer. The surface structures were observed on a HITACHI X-650 scanning electron microscope SEM operating at 25kV.

Gas sensors were fabricated in a conventional way from ITO thin films. The gas sensitivity S is denoted by Rg/Ra, where Ra and Rg stand for the resistances of the samples in air and oxidative NO_2 gas respectively. The resistance of the sample was measured in a gas chamber with an inside stirring fan. The sample was heated and a thermoregulator controlled its temperature.

Results and discussion

Structure analysis

The surface morphology of thin films was analyzed by HITACHI X-650 scanning electron microscopy, shown in figure 2. The shape of particles is like filament, 30nm in diameter and 200 nm in length.

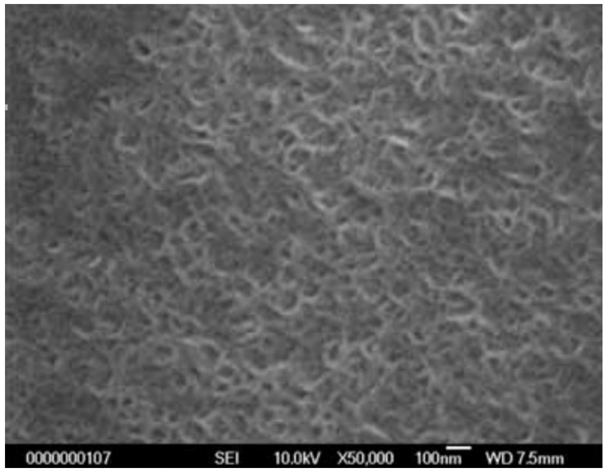

Figure 2. SEM photograph of ITO thin film prepared by spray sprolysis method.

Gas sensing properties

The resistance of prepared ITO thin films is 1MΩ at room temperature, but decreased to several hundreds kΩ at working temperature (around 300°C). The Sn amount in ITO thin film is an important factor to increase the resistance of prepared ITO film. T.Sako's group prepared ITO thin film by DC magnetron sputtering has a 60 kΩ resistance when Sn:In=1:9 [5]. Another reason of the high resistance is ultrasonic spay pyrolysis preparation. The thin film prepared by sol-gel method generally has more defects than by CVD or magnetron sputtering, which makes a higher resistance.

Figure 3 shows sensitivity-temperature curves of ITO sensor. The best sensitivity was obtained at 300°C.

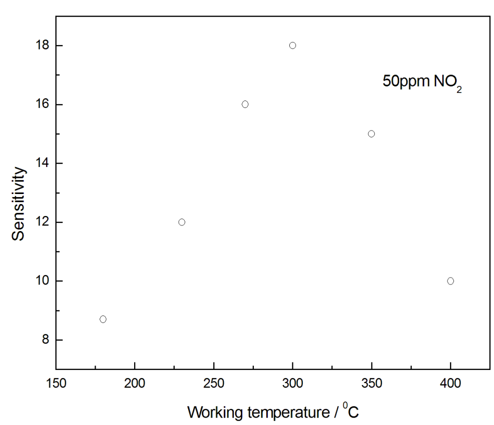

Figure 3. The temperature-sensitivity curves of ITO thin films.

Figure 4 shows the effects of adulterant to sensitivity of ITO gas sensors. The adulteration ratio is 1 mol%. La adulterant increases the sensitivity to NO_2. The reason is that La element can active the surface adsorption sites, increase the NO_2 adsorption on ITO thin film, Thus promote the sensitivity of ITO sensor to NO_2.

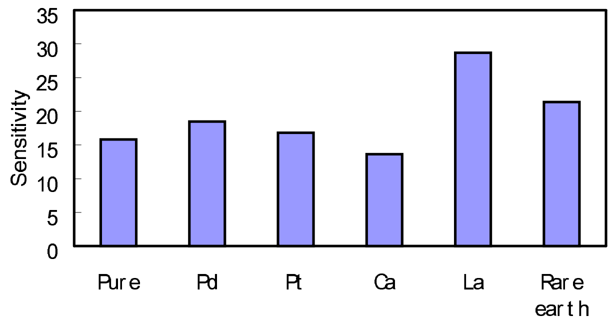

Figure 4. The sensitivities of ITO thin film gas sensors with different adulterant (*Rare earth is the mixture of La, Ce, Sm, Eu and Er).

The sensitivity of ITO thin film sensors to NO_2 at different working temperature was shown in figure 5. The NO_2 sensitivity of ITO thin film sensors at different working temperature was investigated. At 300°C, ITO sensors have best response to NO_2, especially to concentration lower than 100ppm. At 100ppm, the sensitivity to NO_2 reach 19. But at higher concentration, the sensitivity increase slightly. At 180°C working temperature, ITO gas sensor has good response to NO_2 at a wider range, We got a nearly linear response from 10ppm to 500 ppm.

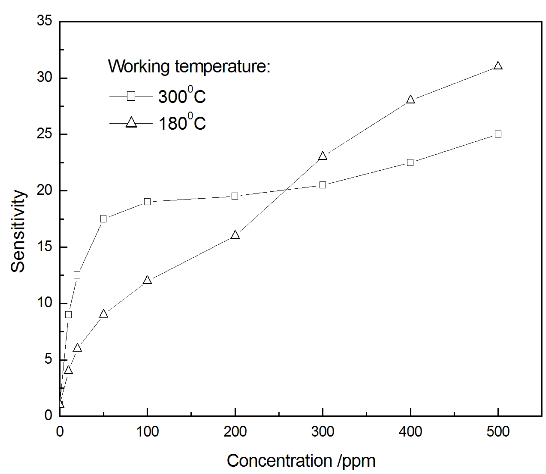

Figure 5. Sensing properties of ITO thin films.

NO_2 molecules are very active and may decompose into other materials on adsorption sites. If there are no stable adsorption sites for NO_2 on the ITO thin film sensor, some NO_2 molecules will decomposed and desorb from the sensor, which inhibits the net adsorptipn of NO_2. Therefore, higher working temperature will accelerate decomposeing and desorbing of NO_2, and get a higher sensitivity at low concentration. By adjusting working temperature, the ITO NO_2 gas sensor can adapt applications in both low and high NO_2 concentration.

Conclusion

The ITO thin films prepared by spray pyrolysis method are good gas sensing materials. It has high sensitivity NO_2. The sensitivity of ITO thin films were slightly affected by adulterant. La and rare earth adulteration will increase the sensitivity to NO_2 of ITO thin films. Because under different working temperature the ITO sensor show different sensing characteristics to NO_2, By adjusting working temperature, the ITO sensor can adapt applications in different NO_2 concentration.

Acknowledgements

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Sample Availability: Available from the authors.