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Comparison of ZnO film prepared by spray pyrolysis and screen printing methods

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Abstract

Zinc oxide (ZnO) thin films were prepared and compared between spray pyrolysis and screen-printing techniques. The obtained thin films from both methods were annealed at 400, 450, 500 and 550°C in the air for 30 min, then characterized by x-ray diffraction, ultraviolet-visible spectroscopy and four-point probes techniques. Optical transmittance spectra of ZnO thin films prepared by spray pyrolysis methods and screen printing methods were transmitted through thin film in the range from 300 nm to 800 nm. The lowest of sheet resistance of thin films from both techniques were found to develop at the same annealing temperature of 400°C with the values of 90.64 $\Omega\cdot$square^{-1} and 104.80 $\Omega\cdot$square^{-1} for spray pyrolysis method and screen printing method, respectively.

1. Introduction

Transparent conducting oxides (TCOs) such as indium tin oxide (ITO), tin oxide (SnO_2), zinc oxide (ZnO) is one of the most important extensively studied II– VI semiconducting metal oxides [1]. Numerous papers have been appearing in various journals only for this material every year. TCOs, particularly ZnO which is an n-type conductivity, has a direct wide band gap of around 3.2–3.37 eV at room temperature. It has a large exciton binding energy of 60 meV and high optical gain (320 cm^{-1}) at ambient temperature. Moreover, compared to other metal oxides, it has lower cost and is environmentally friendly. According to these unique properties, thin ZnO films have been widely used in optoelectronic applications such as solar cells, flat panel displays, and light emitting diodes (LEDs) [2]. The thick films of ZnO are used in many applications in the field of optoelectronics, gas sensing, antibacterial and cancer treatment, and so forth. For highly efficient optoelectronic device applications, it is desirable to reduce or tune the band gap in a broad range together with precisely control the conductivity possessed by the films. The band gap energy of ZnO can be varied by doping appropriately with metals. The ZnO thin films could be prepared by either cost consuming technique such as radio frequency (RF) magnetron sputtering [3], co-sputtering, Pulsed Laser Deposition [4], or by the low-cost techniques such as spray pyrolysis and screen printing.

The spray pyrolysis technique is the technique that the reaction takes place from the vapor phase at moderate high temperature [5]. The reaction from the spray pyrolysis technique can be performed in air for oxides. A solution of the dissolved precursor was sprayed by using a vector gas flowed the fine solution droplets onto a heated substrate then the solvent on a hot substrate is evaporated or decomposed into gaseous products. To form a deposition generally based on oxide was occurred by the salt reacts. Two reactive compounds were reacted in the solution, and the activation of the chemical reaction between the two compounds were helped by the temperature of the substrate. The spray pyrolysis technique has been used for deposition of ZnO thin film on the transparent conducting oxide surface. The ZnO compact layer was coated prior to the nanostructured n- type transparent semiconductor. The powerful method for fabricating ZnO semiconducting layers for photovoltaic device applications are screen printing technique [6]. ZnO semiconductor is an important group II–VI metal oxide semiconductor with a wide energy direct band gap. The n-type semiconducting

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properties and occupies a special place among wide band gap were exhibited with ZnO material that have been extensively studied because of increased need for solid state light sources and semiconductor detectors in the blue and ultraviolet (UV) spectral ranges. ZnO semiconductor material can be used in electronics and optoelectronics applications [7] because it is a transparent conductive oxide (TCO) with low electrical resistivity, higher optical gain (320 cm^{-1}) at room temperature, low cost and non-toxic. By virtue of these properties it can find numerous potential applications in many fields such as for solar cell fabrication, light emitting diodes (LED), many types of gas sensors, anti-bacterial and cancer treatment [8,9].

In this work, we compare the basic properties of thin ZnO films between those prepared by spray pyrolysis technique and by using simple and economic screen printing process. Their physical properties were characterized by means of x-ray diffraction (XRD), ultraviolet-visible (UV-Vis) spectroscopy and the standard four-point probes techniques.

2. Experimental

The transparent thin films of ZnO were prepared using two techniques i.e., spray pyrolysis and screen printing techniques. For the spray pyrolysis technique, the zinc acetate $(CH_3COO)_2Zn.2H_2O$ of 0.05 M in 50 ml of ethanol was used to prepare the ZnO thin film. Glass substrate with the thickness of 1.2 mm was cut into equal small rectangular with the dimension of approximately 25 x 25 mm^2. The substrates were cleaned in DI water and ethanol. The precursor solution was transformed into fog solution using ultrasonic transducer which was then injected on to the hot substrate by the air compressor with the flow rate of 3 $l \cdot min^{-1}$. During the preparation process, the substrates were heated using hot plate where the temperature were found to be varied between 323°C and 350°C. The substrates were kept heated on the hot plate throughout the fixed spraying time of 3 min. For the screen printing technique, the ZnO paste with the average particle size of less than 0.1 μm was screened on the glass substrate with the dimension of 8 x 12 mm^2, then the thick films were dried and heated in a box furnace in the air at the temperatures of 400, 450, 500 and 550°C for 30 min. The films obtained from both techniques were then examined to study their physical and electrical properties.

The degree of crystallinity of ZnO thin films was examined by the XRD with copper K_α x-ray line. The sheet resistance of ZnO thin films was determined by the standard four- point probe technique where each probe was approximately 1.5 mm separated along a straight line. The measurements were performed three times on different area throughout the sub strate for statistical average. The optical transmission of thin film was examined by UV-visible spectrophotometer at room temperature.

3. Results and discussion

The crystal structure of ZnO film was examined using XRD. ZnO n-type metal oxide semiconductor has a hexagonal wurtzite crystal structure. In this work, the spray pyrolysis method and the screen printing method were used for preparing of ZnO film which Figure 1 shows the XRD patterns of ZnO film obtained from both methods. The annealing temperature of 550°C was selected for studying the structure. From the XRD patterns, the peaks were not observed from the films prepared by both techniques. The preparation temperature of spray pyrolysis technique has the average value of 350°C which was the low temperature therefore the high annealing temperature could not induce any peak of ZnO structure. The deposition time of this work was fixed at 3 min which may be the reason of the ZnO amorphous structure. For the screen printing method, the amorphous structure was observed in this technique. The reason for the amorphous structure result may occur from the screen printing repetition time that, in this case, was used only for 1 time. It should be noted that the higher repetition time could result in a good crystallinity of the film however the thickness might be substantially increased due to the nature of the thin film preparation technique. The crystallography of ZnO thin films can range from amorphous to polycrystalline and to single crystal. In the spray pyrolysis method, the substrate temperature and deposition time were the key features. The high temperature annealing of ZnO thin films on the substrate can reduce the void by diffusion adatoms. However, for the screen printing method, the screen printing time was the key parameter. The high void of ZnO thin films were found on a single printing time while the high temperature annealing was not observed to affect the structure of the films.

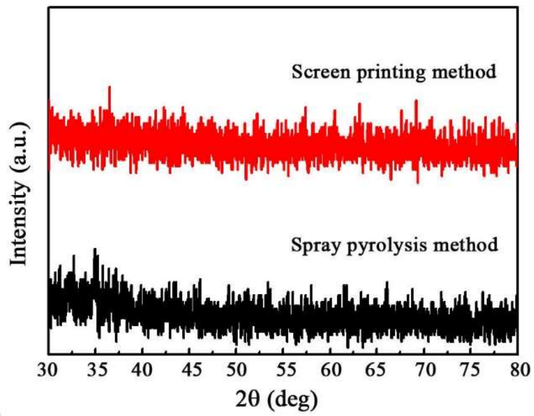

Figure 1. X-ray diffraction patterns of ZnO films prepared by screen printing technique and spray pyrolysis technique with annealing in air at 550°C.

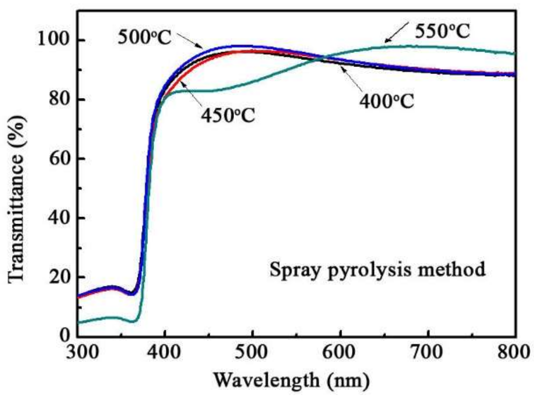

Figure 2. Optical transmittance spectra of ZnO films prepared by spray pyrolysis technique with annealing in air at various temperature.

To investigate the optical properties of ZnO nanostructures, optical transmittance spectrum at room temperature were measured [10]. The optical transmittance spectra of ZnO films that prepared by spray pyrolysis method is shown in Figure 2. The ZnO films were annealed at different temperature in the air for 30 min. The spectra were transmitted through the ZnO thin films in the range of 300 nm to 800 nm. From the graphs, the ZnO films absorbed the electromagnetic wave in the same range of 300 nm to 360 nm. They also transmitted the electromagnetic wave in the same range of 361 nm to 800 nm. The graph lines of the ZnO films almost overlap with the other lines when the annealing temperature were 400, 450 and 500°C where the maximum transmittance occurred at about in the same wavelength of approximately 450 nm. The ZnO thin film that was annealed at 500°C, on the other hand, showed the opposite result that the minimum transmittance was at approximately 450 nm, in visible range.

The optical transmittance spectra of ZnO films prepared by screen printing methods are shown in figure 3. The absorption and the transmission ranges show the same trend with the spray pyrolysis method that the UV range was absorbed and the visible range was transmitted. In the range of transmission, the graph lines showed the same pattern which the percent transmittance increased lineally with the wavelength because of the transparency of ZnO film prepared by screen printing method less than the transparency of ZnO film prepared by spray pyrolysis method. Thus, we have characterized the transmittance of the ZnO thin films grown by spray pyrolysis method and the screen printing method the range of 350–800 nm. The transmittance spectra are reported, we observe for all samples a large absorption in the UV region and a high transparency in the visible region; the absorption edge being around 380 nm for all the films. In the visible range, all the films present a high average transmittance greater than 80% for the spray pyrolysis method. The average transmission ($\%\overline{T}$) can be calculated using equation (1) as follows,

$$\%\overline{T} = \frac{\sum \%T}{n} \tag{1}$$

where $\%T$ is the transmission in visible region, and n is the number of the data collected.

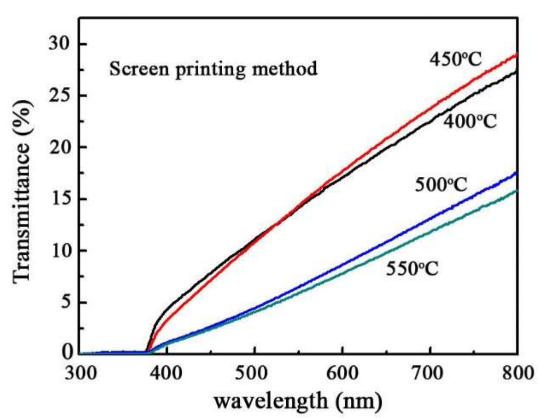

Figure 3. Optical transmittance spectra of ZnO films prepared by screen printing technique with annealing in air at various temperature.

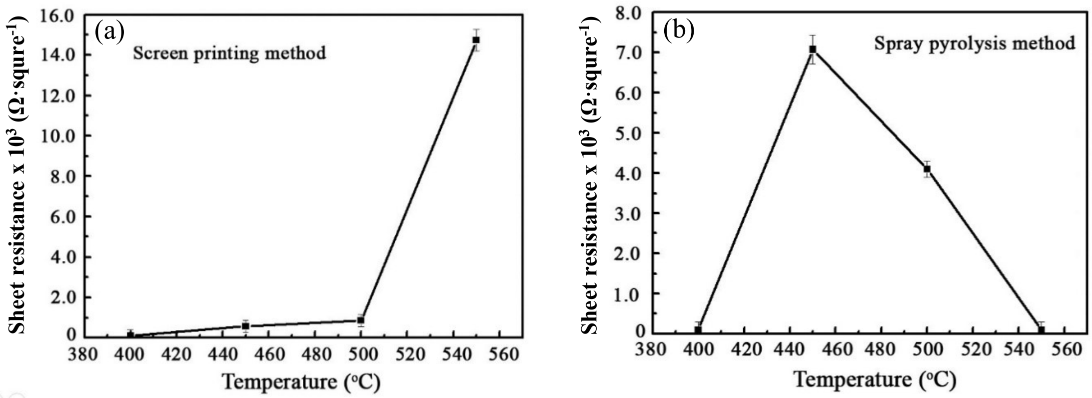

Figure 4. Sheet resistance of ZnO thin film with annealing temperature by (a) screen printing technique and (b) spray pyrolysis technique.

For the electrical property, the ZnO semiconductor has the electrical conduction that ranges in the same order of the insulator materials. The electron conduction, n-type semiconductor of the ZnO film was induced from the defect in atomic scale, oxygen vacancy. For the data (Table 1 and Figure 4), there was the effect between the annealing temperature and the sheet resistance. The lowest of sheet resistance of both methods were at the same annealing temperature as 90.64 $\Omega\cdot square^{-1}$ for spray pyrolysis method and 104.80 $\Omega\cdot square^{-1}$ for screen printing method.

Table 1. Sheet resistance of ZnO films at different preparation technique and at various annealing temperature.

Annealing temperature (°C)	**Sheet resistance ($\Omega\cdot$square^{-1})**	
	Spray pyrolysis method	**Screen printing method**
400	90.64	104.80
450	70.81 x 10^2	566.5
500	40.99 x 10^2	849.75
550	99.14	147.29 x 10^2

4. Conclusions

The ZnO films were prepared by using spray pyrolysis method and by screen printing method. In both techniques, films were annealed at the same temperatures of 400, 450, 500 and 550°C in the air for 30 min. The crystal structure of the films from both techniques showed amorphous structure that came from the preparation process of ZnO film. The optical transmittance of spray pyrolysis ZnO thin films showed high percent transmission in the visible range which was opposite to the screen printing ZnO thin films that showed low percentage of transmittance in the same visible range. The electrical resistivity of thin films prepared by both techniques also showed consistency, the spray pyrolysis ZnO films showed low sheet resistivity as 90.64 $\Omega\cdot$ square^{-1} at annealing temperature of 400°C. However, screen printing is more cost effective and user- friendly compared to the spray pyrolysis or other techniques and can be used to fabricate polycrystalline thick films that having good stability. These films are suitable for solar cells as well as for other gas sensing devices.

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