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INFLUENCE OF SPRAY RATE ON STRUCTURAL AND OPTICAL PROPERTIES OF SPRAYED ZnO FILMS

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Abstract. *In this report, the ZnO nanostructure films have been deposited by ultrasonic spray pyrolysis technique (USP) on fluorine doped tinoxide (FTO) substrate using zinc acetate and aqueous 2-propanol as reactants. The effects of solution spray rate on structural, morphological and optical properties of ZnO nanostructure films were investigated by X-ray diffraction (XRD), atomic force microscopy (AFM) and UV-Vis measurements. ZnO films were crystallized in the hexagonal wurtzite phase and preferential orientation changed with changing of spray rate. Grain size and roughness of films depended on spray rate. Increasing spray rate made the films grown with bigger grain size and higher roughness. Band gap energy was determined from the UV-Vis. Its value was found to be of 3.25 eV and was almost independent on the spray rate.*

Keywords: ZnO, Ultrasonic Spray Pyrolysis, thin film, Solution Spray Rate.

I. INTRODUCTION

Zinc oxide (ZnO) has attracted much attention recently for potential applications due to its wide band gap (∼3.4 eV) and large exciton binding energy (∼60 meV) at room temperature [1]. ZnO is one of the typical II-VI semiconductor materials which have various applications such as light-emitting diodes, electroluminescent devices, electrooptic modulators and window layers in photovoltaic cells and gas sensors [2–9]. ZnO thin film have been fabricated by various methods such as electrochemical deposition [10], sol-gel method [11], chemical bath deposition [12], RF magnetron sputtering [13], and chemical spray pyrolysis [14,15]. Among these methods, the spray pyrolysis is a simple but efficient method for the rapid production of large-area metal oxide thin films.

Many technological parameters affect on the properties of deposited ZnO films in spray pyrolysis method such as zinc source and concentration, dopant type and concentration, solvent, growth temperature, etc. [8–10, 16–18]. Among these parameters, the solution spray rate and its effect on properties of sprayed ZnO thin films have been studied not much. The report of [19]

is consider as a first research dealing with the spray rate effect of solution. Besides, the solution spray rate also affects the surface morphology and roughness of undoped ZnO thin films produced by spray pyropysis on glass substrate [20]. The effect of solution srpay rate on the properties of undoped ZnO thin films fabricated by spray pyrolysis onto fluorine doped tinoxide (FTO) have not been studied yet. Therefore in this work we investigated the effect of the solution spray rate on the structural, morphological, optical properties of undoped ZnO thin films deposited by chemical spray pyropysis.

II. EXPERIMENTAL

ZnO thin films were grown from 30 ml of spray solution that was sprayed onto preheated FTO substrate ($10 \times 25 \times 2.2$ mm^3). The spray pyrolysis system is reported elsewhere [15]. The zinc oxide precursor solution consisted of 0.1 M zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$ (Merck, analytical grade, 99.5%)) in a ratio of water and isopropanol mixture about 2:3 volume. A few drops of acetic acid were added to the spray solution to avoid the precipitation of zinc hydroxide. The starting solution was atomized at a frequency of 130 kHz by an ultrasonic nebulizer. Deposition temperature was kept at 420^oC. The solution spray rate was changed at 0.5 ml/min, 1 ml/min and 4 ml/min to investigate its effect on properties of fabricated ZnO thin films.

The structure of the films was characterised by X-ray diffraction (XRD) with monochromatic Cu Kα radiation (λ= 0.15406 nm). The FTO substrates were washed with soapy water, rinsed with deionised water, and cleaned ultrasonically in ethanol. The morphology of the ZnO nanostructures was investigated by using atomic force microscope. The optical transmission and reflectance spectra of the ZnO thin films were measured at room temperature with a HP Agilent 8453 spectrometer, operated in air in the range of $300 \div 900$ nm.

III. RESULTS AND DISCUSSION

III.1. The structure and morphology of ZnO films

Fig. 1 presents the XRD patterns of ZnO film prepared by spray pyrolysis at different solution spray rates. All ZnO films were indexed to the hexagonal wurtzite structure. It can be seen that in the XRD patterns, there are peaks at 2θ = 31.71, 34.36, 36.196, 47.52, 56.58, 62.82 and 68.02 corresponding to (100), (002), (101), (102), (110), (103) and (201) diffraction planes of ZnO, respectively (PDF 36-1451). Peaks presented at 2θ = 26.42, 37.733 and 51.5 which correspond to SnO_2 (substrates). When spray rate was low (0.5 ml/min), the film had the highest peak intensity at 2θ = 36.25^o, indicating that film was crystallized with preferably oriented (101) plane.

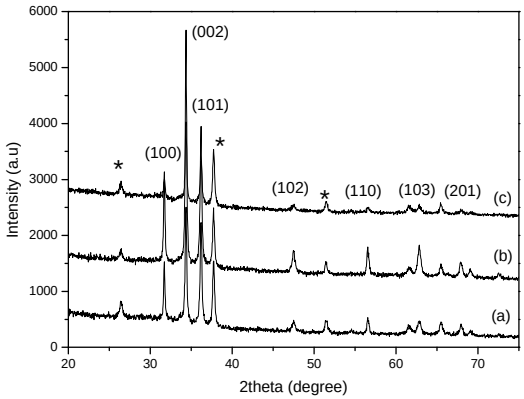

Fig. 1. XRD patterns of ZnO thin films prepared by spray pyrolysis at different spraying rate: (a) 0.5 ml/min, (b) 1 ml/min and (c) 4 ml/min.

When spray rate increased to 1 ml/min, the intensity of this peak decreased and peak at 34.42° became the strongest intensity, and the film preferred orientation in the (002). When the (002) dominated the XRD diagram, axis mainly found perpendicular to the membrane surface. However, when the (101) dominated, *c* axis will tilt away from substrate. Spray rate increased to 4 ml/min, XRD pattern was similar to case of spray rate 1 ml/min. The high peak intensity of (002) of these thin films exhibited the preferential orientation of the [001] axis.

The microstructure of ZnO films was studied using AFM. As can be seen in AFM images (Fig. 2), all sprayed ZnO films fabricated at different spray rate exhibited a dense structure without either cracks or pinholes. The grain size, surface topology and roughness of the film were dramatically affected by solution spray rate. The surface of the film grown with the spray rate of 0.5 ml/min consists of grains that vary in size from 100 nm to 200 nm (Fig. 2a). Besides, many small grains gathered and formed mountains with size of ∼1.2 μm. These mountains size decreased to ∼900 nm and to 500 nm in case of spray rate of 1 ml/min and 4 ml/min, respectively. Using 4 ml/min spray rate, the film surface had the fine grain size and homogeneous structure. The formation of a big mountain at solution spray rate 0.5 ml/min and 1 ml/min resulted in a high surface roughness. For the film obtained at a solution rate of 0.5 ml/min, mean roughness value estimated from AFM images was of 67 nm. This value decreased to 40 nm and 24 nm for the film obtained at a solution rate of 1 ml/min and 4 ml/min, respectively.

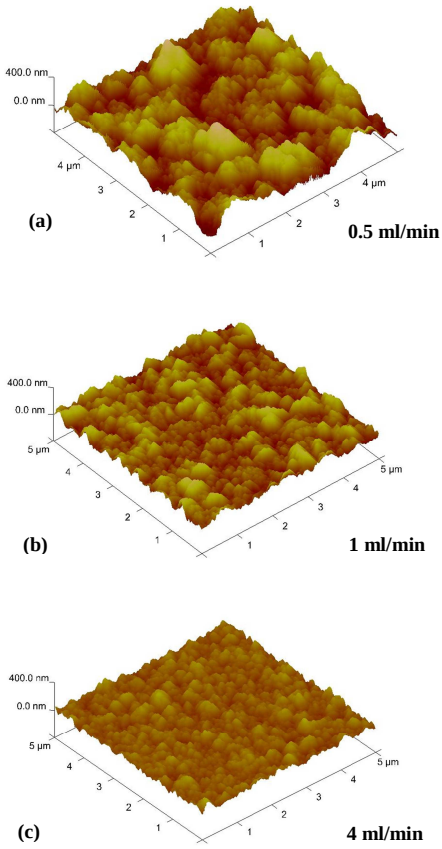

Fig. 2. AFM 3D images of ZnO films deposited on FTO substrate with different solution spray rates: (a) 0.5 ml/min, (b) 1 ml/min and (c) 4 ml/min.

III.2. The optical properties of ZnO films

Fig. 3 shows the optical transmission spectra of ZnO films prepared at different solution spray rate. The obtained results show that spray rate had affected on the transmission properties of the films. Transmitance decreased drastically in the visible region when spray rate was 0.5 ml/min. The absorption edge of the sample was not clearly seen on the spectra. Transmission behavior of the film fabricated at 1 ml/min had the transmission spectrum increased rapidly and had a sharp edge of absorption around 370 nm. When the spray rate increased to 4 ml/min, the transmittance spectra of the film had a similar feature of one of the film fabricated at 1 ml/min. The transmittance value reached over 80 % in visible region. The small transmitances of films at 0.5

ml/min can be affected by high roughness of film surface. As seen above, the surface roughness of films fabricated at low spray rate was higher than that of the film fabricated at high spray rate.

To determine the band gap of the ZnO film, one can use UV-Vis data. The absorption coefficient (α) is calculated from the transmittance spectra using the relation [21]:

$$\alpha = \frac{\ln(1/T)}{d} \tag{1}$$

where d is the film thickness and T is the transmittance. It is now well established that ZnO is a direct band gap semiconductor. The absorption coefficient is related to the band gap E_g according to the equation [21]:

$$(\alpha h\nu)^2 = A\,(h\nu - E_g) \tag{2}$$

where A is a constant and h is the Planck constant. Band gap of the films is estimated from plots of $(\alpha h\nu)^2$ vs. $h\nu$ by extrapolating the straight line from height absorption region as shown in Fig. 3.

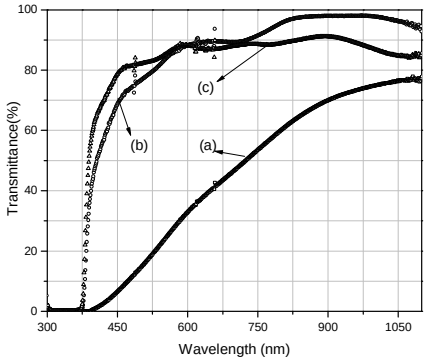

Fig. 3. The optical transmission spectra of ZnO films deposited at different solution spray rate: (a) 0.5 ml/min, (b) 1 ml/min and (c) 4 ml/min.

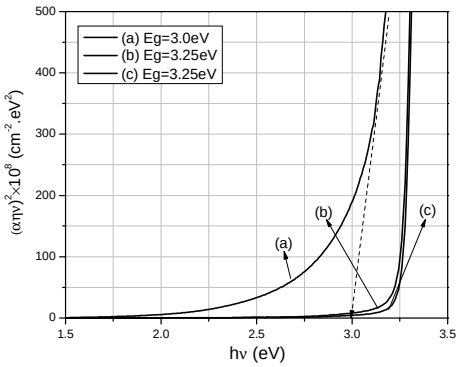

Fig. 4. The plots of $(\alpha h\nu)^2$ versus $h\nu$ for the calculation of band gap E_g: (a) 0.5 ml/min, (b) 1 ml/min and (c) 4 ml/min.

The results of the determination of E_g from $(\alpha h\nu)^2$ versus the $h\nu$ plot is shown in Fig. 4. One can see that the both ZnO films fabricated with spray rate of 0.5 ml/min has a band gap of about 3.0 eV. The band gap slightly increased 3.25 eV with increase of spray rate to 1 ml/min and the same bandgap for spray rate of 4 ml/min. This is similar to results reported in [22] for ZnO:In films.

IV. CONCLUSION

ZnO thin films on FTO subtrate have been prepared by using chemical spray pyrolysis from the solutions of $Zn(CH_3COO)_2$ 0.1M with spray changing rates from 0.5 ml/min to 4 ml/min. All ZnO films have a hexagonal wurtzite structure. ZnO films have prefered orientation in the (101) plane at spray rate of 0.5 ml/min and in the (200) plane at spray rate of 1 ml/min. Spray rate had drammatically affected on the roughness of film's surface. Roughness of films increased with decrease of spray rate. ZnO thin film prepared at spray rate of 4 ml/min has a highest transmittance, namely 80 $\div$ 90% in visible range. The optical band gap energy of ZnO films was found about of 3.0 $\div$ 3.25eV depends on the spray rate.

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